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Six- and Eightfold Palladium-Catalyzed Cross-Coupling Reactions of Hexa- and Octabromoarenes

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Dedicated to Professor Josef Michl on the occasion of his 65th birthday

Abstract: Palladium-catalyzed sixfold coupling of hexabromobenzene (**20**) with a variety of alkenylboronates and alkenylstannanes provided hexaalkenylbenzenes **1** in up to 73% and 16 to 41% yields, respectively. In some cases pentaalkenylbenzenes **21** were isolated as the main products (up to 75%). Some functionally substituted hexaalkenylbenzene derivatives containing oxygen or sulfur atoms in each of their six arms have also been prepared (16 to 24% yield). The sixfold coupling of the less sterically encumbered 2,3,6,7,10,11-hexabromotriphenylene (**24**) gave the desired hexakis(3,3-dimethyl-1-butenyl)triphenylene (**25**) in 93% yield. The first successful cross-coupling reaction of octabromonaphthalene (**26**) gave octakis-(3,3-dimethyl-1-butenyl)naphthalene (**27**) in 21% yield. Crystal structure analyses disclose that, depending on the nature of the substituents, the six arms are positioned either all on the same side of the central benzene ring as in **1a** and **1i**, making them nicely cup-shaped molecules, or alternatingly above and below the central plane as in **1h** and **23**. In **27**, the four arms at C-1,4,6,7 are down, while the others are up, or vice versa. Upon catalytic hydrogenation, **1a** yielded 89% of hexakis(*tert*-butylethyl)benzene (**23**). Some efficient accesses to alkynes with sterically demanding substituents are also described. Elimination of phosphoric acid from the enol phosphate derived from the corresponding methyl ketones gave 1-ethynyladamantane (**3b**, 62% yield), 1-ethynyl-1-methylcyclohexane (**3c**, 85%) and 3,3-dimethylpentyne (**3e**, 65%). 1-(Trimethylsilyl)ethynylcyclopropane (**7**) was used to prepare 1-ethynyl-1-methylcyclopropane (**3d**) (two steps, 64% overall yield). The functionally substituted alkynes **3f–h** were synthesized in multistep sequences starting from the propargyl chloride **11**, which was prepared in high yields from the dimethylpropargyl alcohol **10** (94%). The alkenylstannanes **19** were prepared by hydrostannation of the corresponding alkynes in moderate to high yields (42–97%), and the alkenylboronates **2** and **4** by hydroboration with catecholborane (27–96% yield) or pinacolborane (26–69% yield).

Keywords: alkynes · bromoarenes · cross-coupling · palladium

Introduction

Disk- and star-shaped molecules like hexasubstituted benzene derivatives with six functional side chains have received considerable attention over the last two decades due to their interesting properties such as being discotic liquid crystals,[1] nonlinear optical materials,[2] core structures for dendritic[3] as well as light-harvesting materials.[4] Suitably hexasubstituted benzene derivatives have been designed as hosts and complex-forming ligands with considerable potential.[5] An elegant route to hexaalkylbenzenes is by sixfold alkylation of hexamethylbenzene activated as a cationic cyclopentadienyliron complex under basic conditions as developed by Astruc et al.[6] The sixfold coupling of hexahalobenzenes with alkynes and alkenes under palladium catalysis

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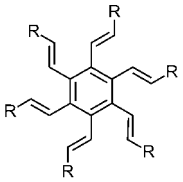
offers another interesting access to a group of aesthetically appealing molecules. Vollhardt et al.[7] reported the first successful sixfold Sonogashira–Hagihara coupling[8] of hexabromobenzene with terminal alkynes to yield hexakis(trimethylsilylethynyl)- and hexakis(trimethylsilylbutadiynyl)benzene. Sixfold Heck coupling[9] of hexabromobenzene with styrene and substituted styrenes under conditions of the Jeffery protocol[10] readily occurred, and gave very good yields of products showing the correct relative molecular masses, but NMR spectroscopy disclosed that these products were multi-component mixtures of different isomers, apparently formed by additional intramolecular 5-*exo*-*trig*-cyclizations during the consecutive palladium-catalyzed alkenylation of an intermediate *o*-bromostilbene unit[11] on the central benzene ring.[9b,c,12] Since pure hexastyrylbenzene derivatives **1** (R = Ar) could never be isolated from these mixtures, and since such side reactions cannot occur in Suzuki[13] and Stille[14] couplings, we turned our attention to the latter coupling protocols to access C_6-symmetric hexaalkenylbenzene derivatives **1**. Herein we report convenient syntheses of several of these molecules and an extension of this approach to compounds with larger aromatic cores.



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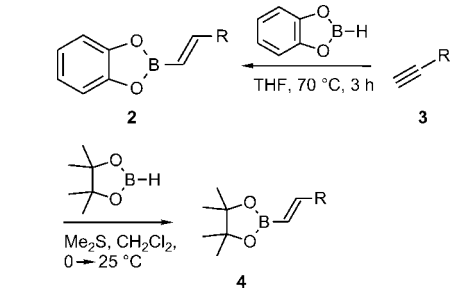
Results and Discussion

Preparation of various alkenylboronates and alkenylstannanes: In order to be able to test the possibilities of carrying out sixfold Suzuki- and Stille-type couplings with hexabromobenzene (**20**), a number of 2-substituted ethenylboronates **2** and **4** and trialkylethenylstannanes **19** were prepared by hydroboration and hydrostannylation, respectively, of the corresponding terminal alkynes **3**.

The hydroborations were performed with catecholborane, described by Brown et al.,[15] and pinacolborane introduced by Knochel et al.[16] One advantage of the pinacol boronates **4** over the catechol boronates **2** is their stability towards water. In addition, the hydroborations of terminal alkynes **3** with pinacolborane occur under milder conditions than those with catecholborane (Scheme 1). The low yields of the pinacol (2-*tert*-butylethenyl)boronate **4a** and the (2-*tert*-pentylethenyl)boronate **4e** are due to losses upon purification by chromatography on silica gel. Flash chromatography, as applied to the hydroboration products **4g** and **4h**, provided higher yields (Table 1).[17]

For the synthesis of adamantylethyne (**3b**), a much more efficient route than the published one[18] was developed. Commercially available adamantanecarboxylic acid (**5b**) was converted to the methyl ketone **6b**, and this was transformed via the enol phosphate into the alkyne **3b** (overall yield for the two operations 60%, Scheme 2).[19] The same sequence was applied to prepare (1′-methylcyclohexyl)-ethyne (**3c**) from 1-methylcyclohexanecarboxylic acid (**5c**) in 76% overall yield.

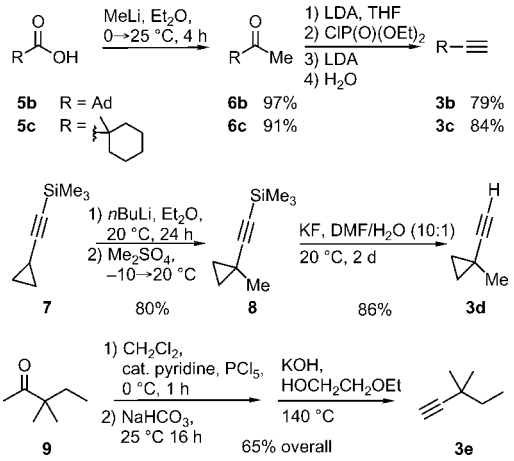


2 **3** **4**

Scheme 1. Hydroboration of terminal alkynes **3**. For details see Table 1.

Table 1. Hydroboration of terminal alkynes **3** to catechol boronates **2** and pinacol boronates **4** (see Scheme 1).

3	R	**2** [%]	**4** [%]
a	*tert*-butyl	91	37
b	1-adamantyl	96	–
c	1-methylcyclohexyl	61	–
d	1-methylcyclopropyl	31	–
e	*tert*-pentyl	29	26
f	1,1-dimethyl-4-methoxybutyl	–	36
g	1,1-dimethyl-3-thiomethylpropyl	–	69
h	1,1-dimethyl-3-methoxypropyl	27	68



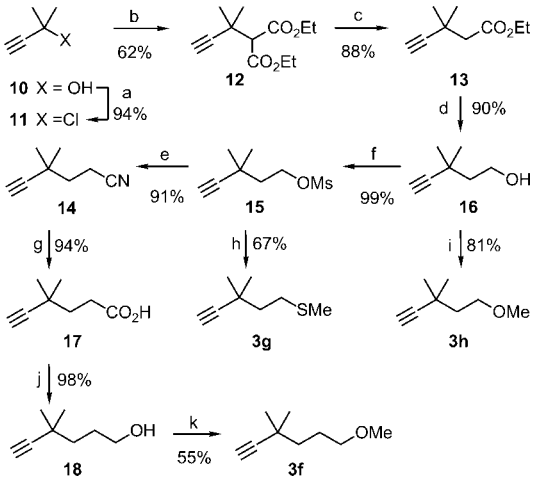
7 **8** **3d** **9** **3e**

Scheme 2. Syntheses of sterically encumbered alkynes **3** from corresponding carboxylic acids **5** via methyl ketone enol phosphates, from silyl-protected cyclopropylacetylene **7** and from 3,3-dimethylpentanone (**9**).

(1′-Methylcyclopropyl)ethyne (**3d**) was prepared by treatment of the lithiated species of (2′-trimethylsilylethynyl)cyclopropane (**7**)[20] with dimethyl sulfate followed by hydrodesilylation in 64% overall yield.[21]

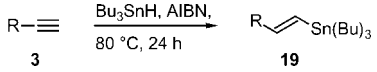
Due to the low boiling point of *tert*-pentylethyne (**3e**), it is difficult to obtain a pure product by the method presented above for **3b** and **c**. A significantly improved method compared to that reported by Meshcheryakov et al.,[22] was used. The direct dehydrochlorination with KOH in 2-ethoxyethanol of the crude product obtained by the chlorination of 3,3-dimethylpentanone with PCl_5 gave **3e** in 65% yield (Scheme 2).

The functionally substituted alkynes **3f–h** were prepared from dimethylpropargylic alcohol **10** (Scheme 3), following in part literature procedures.[23,24] Thus, the tertiary alcohol **10** was transformed in high yield (94%) into the chloride **11**.[25] Treatment of **11** with diethyl sodiomalonate gave the substituted malonate **12** (62%) which,[26] upon heating with sodium bromide in moist dimethyl sulfoxide, underwent clean desethoxycarbonylation to give the monoester **13** (88%). The latter was reduced with $LiAlH_4$ to the primary alcohol **16** (90%), part of which was methylated to yield the methoxypropyl-substituted alkyne **3h** (81%). Another aliquot of the alcohol **16** was converted in almost quantitative yield to the corresponding mesylate **15** (99%), which upon treatment with methylmercaptane in the presence of sodium methoxide provided the methylthiopropyl-substituted alkyne **3g** (67%). A fraction of the mesylate **15** was also transformed with sodium cyanide to the nitrile **14** (91%) which was saponified to the hexynoic acid **17** (94%). Reduction to the corresponding alcohol **18** (98%) followed by methylation, provided the methoxybutyl-substituted alkyne **3f** (55%).



Scheme 3. Syntheses of functionally substituted alkynes **3f–h**. a) $CaCl_2$, $CuCl_2$, Cu, conc. HCl, 0°C, 1 h; b) $NaCH(COOEt)_2$, EtOH; c) NaBr, DMSO (wet), 180°C, 20 h; d) $LiAlH_4$, Et_2O; e) NaCN, DMSO, r.t., 19 h; f) $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0°C, 30 min; g) NaOH, EtOH, H_2O, 100°C, 17 h; h) HSMe, NaOMe, MeOH, r.t., 18 h; i) NaH, Et_2O, MeI; j) $LiAlH_4$, Et_2O, 36°C, 1 h; k) NaH, Et_2O, MeI.

Tri-*n*-butylstannylethene derivatives **19** as reagents to be applied in Stille cross-couplings of **20** were prepared by hydrostannylation[27] of the corresponding alkynes **3** with tri-*n*-butyltin hydride at 80°C without any solvent (Scheme 4). Compounds **19** were obtained as mixtures of (*E*)- and (*Z*)-diastereomers in moderate to very high yields (42–97%). The particularly low yield of **19k** was due to partial decomposition of the product upon distillation at a rather high temperature. The *E*/*Z*-isomer ratios (Table 2) were determined after distillation from the ^1H NMR spectra. *E*/*Z*-diastereomeric mixtures of **19** were used without separation, because the Stille cross-coupling always yields the thermodynamically more stable (*E*)-isomers.[28,29]



Scheme 4. Hydrostannylation of terminal alkynes **3**. For details see Table 2.

Table 2. Hydrostannylation of terminal alkynes **3** with tri-*n*-butyltin hydride (see Scheme 4).

3	R	Yield of **19** [%]	*E*:*Z*
a	*tert*-butyl	72	9:1
b	1-adamantyl	91	9:1
i	trimethylsilyl	97	9:1
j	phenyl	86	9:1
k	3,5-di-*tert*-butylphenyl	42	5:1

Sixfold cross-couplings with hexabromobenzene: An initial attempt to perform a sixfold coupling of hexabromobenzene (**20**) with *tert*-butylethenylboronate **2a**, applying $[PdCl_2(PPh_3)_2]$ as a catalyst and sodium ethoxide in ethanol as a base, only led to partial dehalogenation of **20**. This kind of reductive dehalogenation has frequently been observed in Suzuki couplings,[13a] and found to be suppressed upon use of sodium hydroxide as a base. Under optimized conditions {$[PdCl_2(PPh_3)_2]$, NaOH, toluene/THF (1:1), 100°C, 24 h} the cross-coupling of **20** with **2a** gave hexakis-(*tert*-butylethenyl)benzene (**1a**) in 73% yield.[30] This corresponds to an average yield of 95% for each cross-coupling step.

In an attempt to further optimize this coupling, cesium fluoride[31] and barium hydroxide,[32] which have been reported to be particularly efficient bases for the Suzuki reaction, were also tested. However, the yield of **1a** was significantly lower in both cases (5 and 22%, respectively), and with barium hydroxide a small amount (9%) of the partially reduced fivefold coupling product pentakis(3,3-dimethyl-1-butenyl)benzene (**21a**) was obtained. With the pinacol ethenylboronate **4a** and sodium hydroxide under the conditions optimized for catechol (3,3-dimethyl-1-butenyl)boronate (**2a**), **1a** was obtained in 45% yield along with 38% of **21a**. The formation of such reduction products must be a consequence of the steric shielding of the palladium residue on the benzene ring after oxidative addition of the vicinally dialkenyl-substituted bromoarene by which the rate of transmetallation will be reduced, so that the transfer of hydride from a different source to palladium can compete with the transfer of the alkenyl residue. It has been reported that such dehalogenation products can also be derived from re-

duction of arylpalladium hydroxide intermediates with triphenylphosphine.[33]

Even under the optimized conditions, attempted analogous cross-coupling reactions of hexabromobenzene (**20**) with styryl- and *n*-nonenylboronates did not yield any of the sixfold coupling products,[29] but only octadecadiene **22** as the homocoupling product of the corresponding boronate, when dichloro[1,1-bis(diphenylphosphano)ferrocene]palladium in THF/DMF was applied. With $[PdCl_2(PPh_3)_2]$, only a mixture of reduction products derived from hexabromobenzene (**20**) was obtained. Apparently, the *tert*-butyl groups in **2a** are essential for the success of the sixfold coupling, and indeed catechol (alkenyl)boronates with other *tert*-alkyl groups gave the corresponding sixfold coupling products **1c–h** reasonably well in yields ranging from 10 to 44% (Table 3).

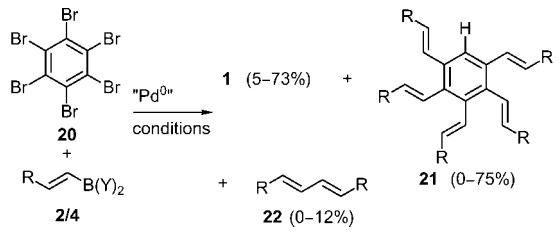
Table 3. Sixfold Suzuki coupling of hexabromobenzene (**20**) with a variety of alkenylboronates in THF/toluene (1:1) at 100°C (Scheme 5).

Boronate	Conditions[a]	*t* [h]	Product (Yield/%)
2a	**A**, NaOH	24	**1a** (73)
2a	**A**, CsF	24	**1a** (5)
2a	**A**, $Ba(OH)_2$	24	**1a** (22), **21a** (9)
2a	**B**, NaOH[b]	48	**1a** (24)
4a	**A**, NaOH	24	**1a** (45), **21a** (38)
2b	**B**, NaOH[c]	48	**1b** (6), **21b** (6)
2c	**A**, NaOH	18	**1c** (44), **21c** (54), **22c** (3)
2d	**A**, NaOH	24	**1d** (16), **21d** (40)[d], **22d** (3)
2e	**A**, NaOH	43	**1e** (10), **21e** (55)
4e	**A**, NaOH	24	**1e** (16), **21e** (74)
4f	**A**, NaOH	24	**1f** (18), **21f** (34), **22f** (6)
4g	**A**, NaOH	24	**1g** (22), **21g** (38), **22g** (4)
2h	**A**, NaOH	24	**1h** (16), **21h** (75), **22h** (8)
4h	**A**, NaOH	24	**1h** (24), **21h** (25), **22h** (24)

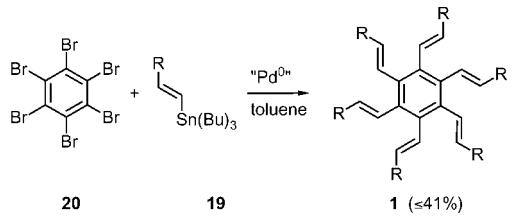
[a] **A**: $[PdCl_2(PPh_3)_2]$; **B**: *trans*-di(μ-acetato)bis[2-(di-*o*-tolylphosphino)-benzyl]dipalladium(II). [b] Toluene, 90°C. [c] Toluene, 110°C. [d] Yield determined from the NMR spectrum.

The coupling of the sterically most encumbered (2-adamantylethenyl)boronate **2b** yielded only a small amount (6%) of the corresponding hexakisadamantylethenyl derivative **1b**. To achieve this, the palladacycle from palladium acetate and tris(*o*-tolyl)phosphine first reported by Herrmann and Beller,[34] had to be used, while for all other alkenylboronates with mimics of the *tert*-butyl group bis(triphenylphosphine)palladium dichloride could be applied. In most cases the pentakis(*tert*-alkylethenyl)benzene derivatives **21** (Scheme 5) resulting from reductive removal of one of the six bromine substituents was isolated as the major product (up to 75%). In addition, small amounts of the 1,4-disubstituted butadienes **22c**,**d**,**f–h**, arising from homocoupling of the corresponding alkenylboronates **2**/**4**, were obtained.[13f,32b,35]

To test the accessibility of hexaalkenylbenzenes **1** by the Stille cross-coupling reaction, sixfold alkenylations of hexabromobenzene (**20**) with various 2-substituted (tri-*n*-butylstannyl)ethenes **19** were carried out in refluxing toluene with the palladacycle catalyst developed by Beller and Herrmann.[34] For each bromine substituent on the arene approximately 1 mol% of the catalyst was used, and the reaction time was increased to up to 5 d (Scheme 6, Table 4). The coupling of the *tert*-butylethenylstannane **19a** gave **1a** in a moderate yield of 35%. The sixfold Stille coupling was also successful with the trimethylsilyl(ethenyl)stannane **19i** and gave **1i** in an acceptable yield of 41%.[30] However, the attempted coupling of **20** with the sterically encumbered (adamantylethenyl)stannane **19b** gave only an inseparable mixture of **1b** and pentakis[2-(1′-adamantyl)ethenyl]benzene. The attempted sixfold Stille coupling of **20** with the (arylethenyl)tributylstannane **19k** produced only an oil which exhibited a strong fluorescence under UV light. NMR and mass spectra indicated the presence of the sixfold coupling product **1k** in this oil, but it could not be purified any further.



Scheme 5. Sixfold Suzuki coupling of hexabromobenzene (**20**) with various alkenylboronates and side reactions. For details see Table 3.



Scheme 6. Sixfold Stille coupling of hexabromobenzene (**20**) with alkenylstannanes **19**. For details see Table 4.

Table 4. Yields for the coupling of hexabromobenzene (**20**) with alkenylstannanes **19** under various conditions (Scheme 6).

19	R	Conditions[a]	Yield of **1** [%]
a	*tert*-butyl	**A**, 120°C, 4 d	35
b	1-adamantyl	**A**, 110°C, 3 d	–[b]
i	trimethylsilyl	**A**, 100°C, 1 d	41
j	phenyl	**B**, 110°C, 4 d	16
k	3,5-di-*tert*-butylphenyl	**A**, 110°C, 5 d	–[c]

[a] **A**: *trans*-Di(μ-acetato)bis[2-(di-*o*-tolylphosphino)benzyl]dipalladium(II); **B**: $[Pd(PPh_3)_4]$, CuI. [b] According to the ^{1}H NMR spectrum, the crude product contained **1b** and pentakis[2-(1′-adamantylethenyl]benzene (**21b**); an attempted purification failed. [c] The product **1k** was formed according to the ^{1}H NMR and mass spectrum, but could not be separated from by-products.

Szeimies et al. recently reported the sixfold cross-coupling of **20** with 1-(tri-*n*-butylstannyl)cyclobutene applying $[Pd(PPh_3)_4]$ as a precatalyst leading to an air-sensitive hexa-

alkenylbenzene derivative.[36] When hexabromobenzene (**20**) was treated with tri-*n*-butyl(phenylethenyl)stannane (**19j**) in the presence of [Pd(PPh_3)$_4$] and copper iodide as a co-catalyst, which is well known to accelerate Stille-type couplings,[37] the sparely soluble hexakis(phenylethenyl)benzene (**1j**) was obtained in 16% yield which is lower than those of the previously reported alternative approaches to **1j**.[2b]

Any of the attempted Suzuki- and Stille-type couplings of hexabromobenzene (**20**) with alkenylboronates and -stannanes without a *tert*-butyl group or a mimic thereof did not furnish the corresponding sixfold coupling product at all or at best in very low yield. Apparently, the steric demand of the *tert*-butyl groups or its mimics is indispensible for these sixfold couplings to occur with moderate to high yields, and this may have to do with attractive van der Waals interactions during the self-assembly in the consecutive coupling steps. This leads to interestingly cup-shaped molecules with all six arms on the same side of the central ring in the case of **1a** and **1i** (Figures 1 and 2).

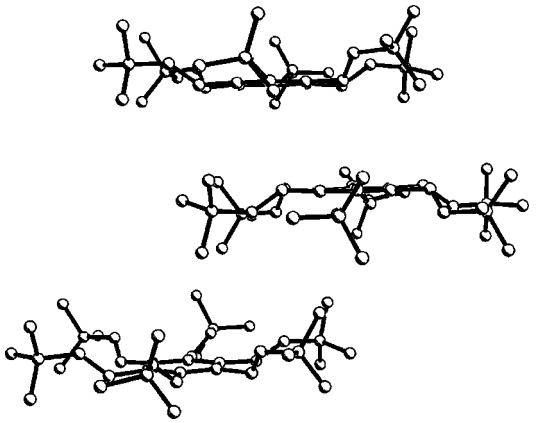


Figure 1. Stacking of the cup-shaped molecules of hexakis(*tert*-butylethenyl)benzene (**1a**) in the crystal.[30,38]

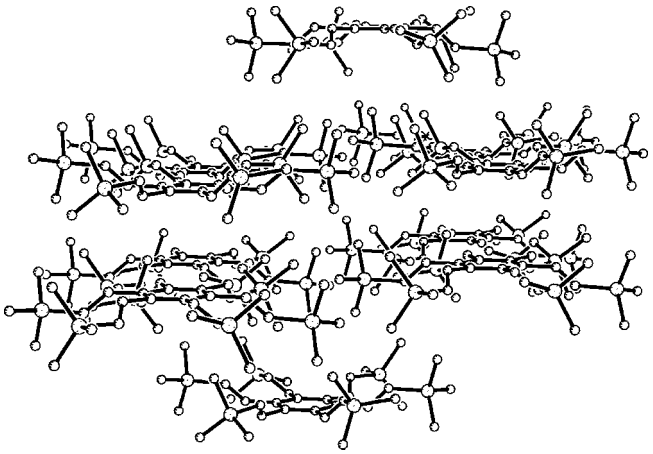


Figure 2. Stacking of the cup-shaped molecules of hexakis(trimethylsilylethenyl)benzene (**1i**) in the crystal.[30,38]

Such molecules with six heteroatom-containing arms, stretching out from a rigid central structure, do bind simple cations.[5,39] In view of this, attempts were made to prepare hexakisalkenylbenzene derivatives with six functionally substituted arms by sixfold cross-coupling of hexabromobenzene (**20**). In fact, the sixfold Suzuki coupling of **20** with catechol **2h** and pinacol (1,1-dimethyl-3-methoxypropyl)ethenylboronate (**4h**), respectively, worked out to give the correspondingly substituted hexakis[(1,1-dimethyl-3-methoxypropyl)ethenyl]benzene (**1h**), albeit only in poor to moderate yield of 16 and 24%, respectively. The corresponding methylthio-substituted analogue **1g** was obtained from **20** with **4g** in 22% yield (Table 3).

Surprisingly, the six functionally substituted arms of **1h** in the crystal do not point to the same side of the central ring, but alternatingly up and down (Figure 3). This must be due to weak intermolecular—possibly dipole–dipole—interactions between the methoxypropyl groups in the crystal of **1h**. Anyhow, intramolecular attractive van der Waals interactions between *tert*-butyl groups as in **1a** are not essential for the six arms of a hexaalkenylbenzene to point to the same side, since the parent hexaethenylbenzene has been shown to have the same orientation in the crystal.[40]

The closest intermolecular contacts in **1h** are those between β-vinylic hydrogen and oxygen atoms which, with 2.67 Å are shorter than the sum of their van der Waals radii.[41] In addition, the distance between a hydrogen atom of the methoxy groups and a carbon atom of a neighboring benzene ring with 2.88 Å is also shorter than the sum of their van der Waals radii.

It is noteworthy that hexakis-(*tert*-butylethyl)benzene (**23**), which was obtained by catalytic hydrogenation of **1a** over palladium on charcoal in hexane at room temperature in 89% yield (Scheme 7), in the crystal also assumes a conformation in which its six arms are rotated alternatingly up and down out of the central plane with a torsional angle of 89.2°. This same conformation has also been found for hexaethylbenzene,[42] and must be attributed to intramolecular repulsion between neighboring benzylic hydrogen atoms. In addition, at least for **23**, there is a contribution from intermolecular attractive van der Waals interactions between methyl groups, as the molecules of **23** are stacked in columns along the axis of the central rings with interlocking *tert*-butyl groups of nearest neighbors within the stacks (Figure 4).

Multifold couplings with other perbromoarenes: The successful sixfold coupling of hexabromobenzene (**20**) with a variety of sterically encumbered alkenylboronates inspired attempts to perform multiple coupling reactions of other perbromoarenes. Indeed, six- and even eightfold Suzuki coupling reactions could be brought about between catechol (*tert*-butylethenyl)boronate **2a** and hexabromotriphenylene (**24**) as well as octabromonaphthalene (**26**), respectively. The sixfold coupling of **2a** with the less sterically congested **24** was particularly efficient and furnished hexakis-(*tert*-butylethenyl)triphenylene (**25**) in a yield of 93% (Scheme 8).

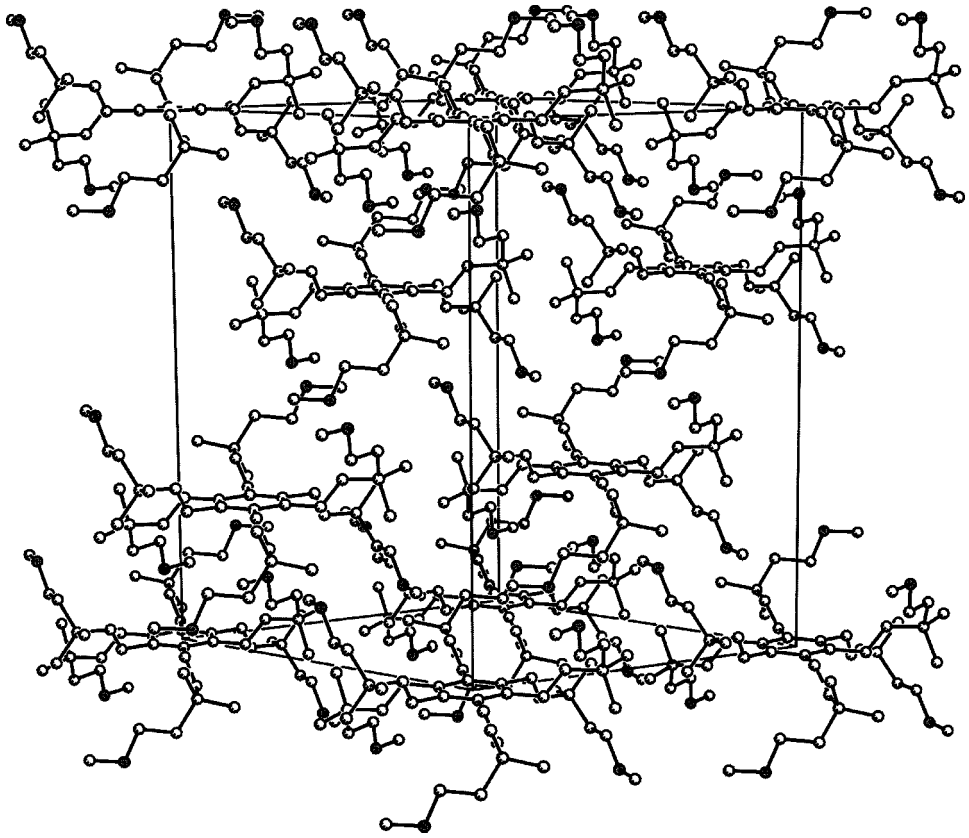
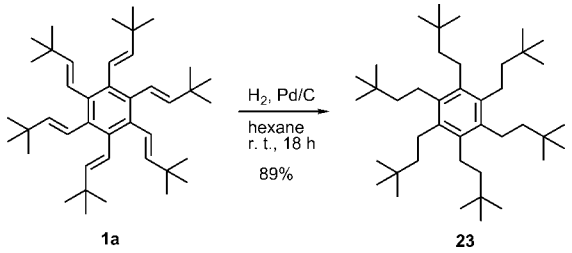


Figure 3. Structure and packing of hexakis[(1,1-dimethyl-3-methoxypropyl)ethenyl]benzene (**1h**) in the crystal.[38]



Scheme 7. Catalytic hydrogenation of hexakis-(*tert*-butylethenyl)benzene (**1a**).

This corresponds to a nearly quantitative yield (~99%) for each newly generated C–C bond. According to an X-ray structure analysis the six arms of **25** in the crystal are irregularly rotated out of the plane of the central core, with two neighboring arms up, the two next down, and the last two almost in the plane (Figure 5).[43]

Under the same conditions, **2a** and octabromonaphthalene (**26**) gave only complex mixtures, which according to mass spectra contained the eightfold coupling product as the minor component along with heptakis(3,3-dimethyl-1-butenyl)naphthalene and other partially reduced oligofold coupling products. This must be attributed to the severe steric congestion of twofold substitution in the *peri*-positions. Nevertheless, the octaalkenylnaphthalene **27** was obtained in 21% yield, when the reaction was carried out in an ultrasonic bath with a large excess of the alkenylboronate **2a** (Scheme 9). An eightfold Suzuki coupling of a porphyrine derivative in which the bromine subtituents are not as close to each other as in **26**, has previously been reported.[44]

After a long series of unsuccessful attempts, good-quality light-yellow crystals of **27** were eventually grown from ethanol/pentane and subjected to an X-ray crystal structure analysis.[38] It disclosed (Figure 6) that the four arms on C-1,4,6,7 are rotated upward with respect to the central plane while the four others are downward, or vice versa.

Some physical properties of the new peralkenylarenes: Arnett et al., who first synthesized the parent hexavinylbenzene in 1966, already discovered that the colorless crystals of this

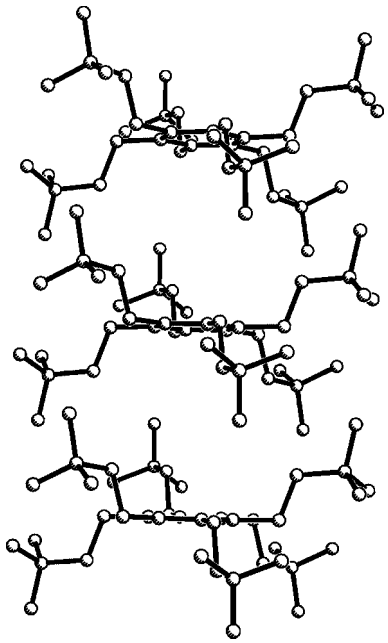
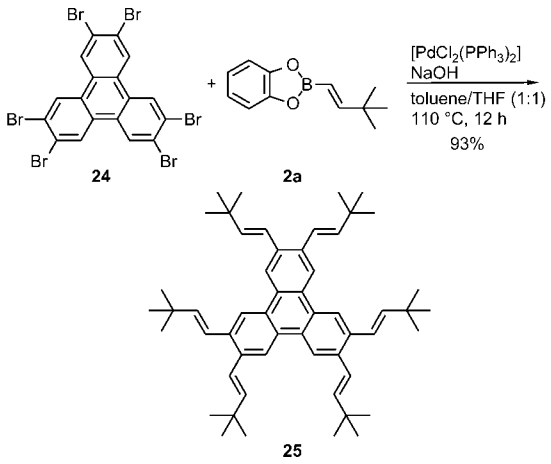


Figure 4. Packing of hexakis-(*tert*-butylethyl)benzene (**23**) in the crystal.[30,38]

compound changed to yellow upon exposure to daylight.[45a] This same effect was observed for hexakis-(*tert*-butylethe-



Scheme 8. Sixfold Suzuki coupling of hexabromotriphenylene (**24**) with catechol (2-*tert*-butylethenyl)boronate (**2a**).

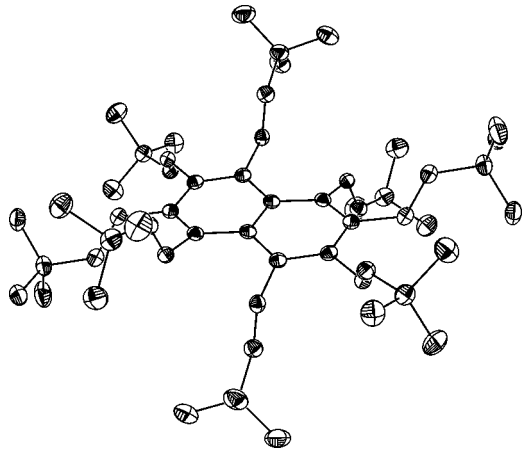


Figure 6. Structure of octakis-(*tert*-butylethenyl)naphthalene (**27**) in the crystal.[38]

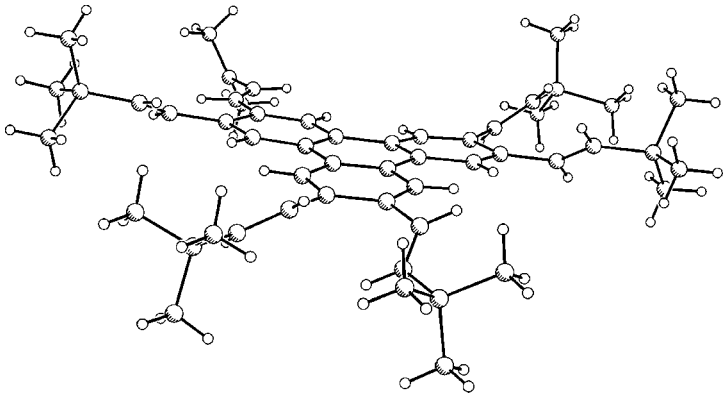
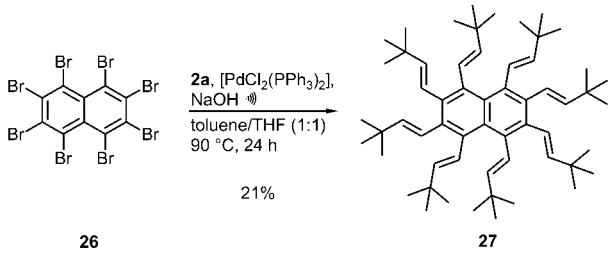


Figure 5. Structure of hexakis-(*tert*-butylethenyl)triphenylene (**25**) in the crystal.[43]



Scheme 9. Eightfold Suzuki coupling of octabromonaphthalene (**26**).

nyl)benzene (**1a**) and its analogues during this work. The freshly recrystallized, colorless crystals turned intensively yellow upon storage in open daylight on the bench, while no such change took place in the dark. Furthermore, when stored for at least 24 h in the dark, the yellow crystals returned to a completely colorless appearance. The same reversible discoloration also occurs in solution. However, the reverse process, the loss of the yellow color, in solution requires much longer than in the solid state of **1a**.

The major absorption band in the UV spectrum of **1a** at $\lambda_{max}=262$ nm ($\varepsilon_{max}=53\,600$) is very close to that of the parent hexavinylbenzene ($\lambda_{max}=258$ nm). Thus, the six additional *tert*-butyl substituents on the vinyl groups in **1a** have almost no apparent effect on the absorption maximum. However, Arnett et al.[45b] report a hypsochromic shift of the absorption maximum of hexaisopropenylbenzene compared with that of α-methylstyrene which they attribute to an out of plane rotation of the alkenyl substituents leading to decreased conjugation. Although such a conformation is also indicated for **1a** and **1i**, respectively—at least in the crystals according to X-ray structure analyses—the major absorptions of the hydrocarbons **1a** and **1c** around 262 nm are at slightly longer wavelengths than that of β-methylstyrene ($\lambda_{max}=248$ nm) and β-*tert*-butylstyrene ($\lambda_{max}=250$ nm).[46] Presumably, the topomerization of **1a** is less hindered in solution than it is in the case of hexaisopropenylbenzene.

The band of octakis-(*tert*-butylethenyl)naphthalene (**27**) at $\lambda=290$ nm with a shoulder at $\lambda=341$ nm, is significantly red-shifted in comparison to that of the absorption of the analogous benzene derivative **1a** (see Table 5). However, the bathochromic shift for this pair of arene derivatives is not as large as for the related hexaphenylbenzene ($\lambda=247$ nm) and octaphenylnaphthalene ($\lambda=329$ nm), respectively.

Monitoring the change of color of a solution of **1a** in cyclohexane upon irradiation with a 250 Watt xenon high-pressure lamp at a wavelength of $\lambda=262$ nm showed that the original maximum disappeared, and new maxima at $\lambda=444$, 278 nm slowly emerged. When the irradiation was continued for more than 30 min, all maxima started to decrease, apparently because the compound was decomposing. When a sample of **1a** in solution was irradiated for 7 min and then stored in the dark for 24 h, the extinction at 262 nm was restored to approximately the same value as before the irradiation (Figure 7), and the new absorption at 444 nm had almost completely disappeared again. It is an open question, what is really happening during the initial phase of the irradiation. As indicated by the observation of isosbestic points,

Table 5. Absorption maxima of selected benzene and naphthalene derivatives.

Compound	Absorption maximum (λ_{max}/nm)	Extinction coefficient ($\varepsilon_{max}/10^4$)
α-methylstyrene[a]	243	1.02
(*E*)-β-methylstyrene[b]	248	–[c]
(*E*)-β-*tert*-butylstyrene[d]	250	18.29
hexaisopropenylbenzene[e]	225	2.55
hexavinylbenzene[f]	258	4
1a	262	5.36
1c	263	4.91
27	290, 341	6.61, 0.78
hexaphenylbenzene[g]	247, 266	5.68, 3.47
octaphenylnaphthalene[h]	329	1.42

[a] Ref. [45b]. [b] Ref. [47]. [c] Not reported. [d] Ref. [46]. [e] Ref. [45b]. [f] Ref. [40,45]. [g] Ref. [48]. [h] Ref. [49].

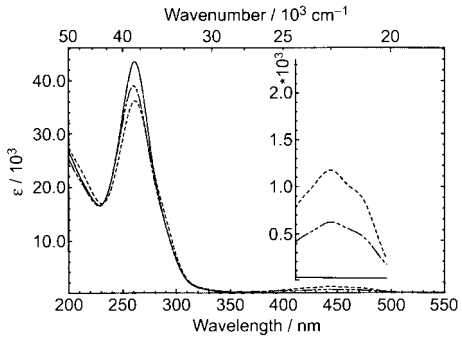


Figure 7. Absorption spectra of **1a** in cyclohexane: without irradiation (——), after irradiation for 7 min at $\lambda = 262$ nm (-----), after 24 h in darkness (··–).

a distinct, long-lived intermediate must be formed upon irradiation. However, there is absolutely no clue to what the structure of this intermediate might be. Both IR and ^{1}H NMR spectra of the yellow modification disclosed no significant differences as compared to the ones of the initial colorless compound.

It is noteworthy that the development of the yellow color in solution can be almost completely suppressed by flushing the solution of **1a** with argon for 5 min before irradiation. This observation would make one suspect that the yellow compound is a photooxygenation product[50] formed by addition of photochemically generated singlet oxygen molecules to one or more of the double bonds of **1a**. However, such an assumed dioxetane[51] would have to have the unlikely feature of not undergoing retro-[2+2] cycloaddition to two carbonyl fragments, but cleavage back to the hexaalkenylbenzene **1a** and oxygen in the dark.

Upon prolonged irradiation, the compound **1a** probably undergoes polymerization such as Meier et al. interpret the complete disappearance of the main absorption band of hexastyrylbenzenes during irradiation as a "statistical C–C bond formation of the olefinic centers (cross-linking) which yields oligomers".[52] In an attempt to monitor the discoloration of a single crystal of hexavinylbenzene, Krüger et al. only observed a progressive disappearance of the diffraction pattern without significant change of the crystal structure.[40]

Conclusion

Six- and eightfold Suzuki and Stille couplings of hexa- and octabromoarenes lead to interestingly shaped molecules with extraordinary efficiency. Some of the functionally substituted hexaalkenylbenzene derivatives thus accessible may have applications as hosts or ligands for supramolecular aggregates and metal complexes, respectively.

Experimental Section

General: ^{1}H NMR spectra were recorded with a Bruker AM 250 spectrometer (250 MHz) at ambient temperature in $CDCl_3$, using $CHCl_3$ ($\delta = 7.26$) or tetramethylsilane ($\delta = 0.00$) as internal standard. Chemical shifts (δ) are quoted in ppm and coupling constants (J) are given in absolute values in Hz to the nearest 0.1 Hz. The following abbreviations are used for the signal multiplicities and shapes: s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). ^{13}C NMR spectra were recorded with a Bruker AM250 spectrometer (62.9 MHz) or a Varian VXR 500S (125.7 MHz) at ambient temperature in $CDCl_3$, using $CDCl_3$ ($\delta = 77.0$) as internal standard. Multiplicities were determined by the DEPT pulse sequence and are described as follows: + = CH or CH_3, – = CH_2 and C_{quat} = C. Signals which could not be assigned unambiguously are marked with an asterisk (*). Under the routine conditions employed, ^{13}C signals of carbon atoms directly attached to boron could not be detected. Infrared spectra were recorded with a Bruker IFS 66 FT-IR spectrometer. Low and high-resolution mass spectra were recorded with a Finnigan MAT 95 instrument using electron impact ionization at 70 eV or direct chemical ionization with NH_3 as reactant gas. High-resolution mass spectra (HRMS) were obtained using preselected ion peak matching at $R \approx 10000$ to be within ±2 ppm. Elemental analyses were performed by the Mikroanalytisches Labor des Instituts für Organische Chemie der Universität Göttingen, Germany. For routine chromatography Merck silica gel 60 (230–400 mesh, 0.063–0.200 mm) and for flash chromatography Macherey–Nagel silica gel 60 (70–230 mesh, 0.040–0.063 mm) was used. TLC plates: Macherey–Nagel foils: Alugram Sil G/UV, detection under UV light at 254 or 366 nm. If the substances were not UV active, the plates were developed with anisaldehyde solution. All solvents were distilled before use. Anhydrous solvents were prepared according to standard laboratory techniques. All reactions with organometallic reagents were performed under nitrogen and anhydrous conditions. In these cases the glassware used was heated in vacuo to remove all of the residual moisture. Unless specified otherwise, solutions of NH_4Cl, $NaHCO_3$ and NaCl were saturated aqueous solutions.

Starting materials: All chemicals were used as commercially available, unless otherwise noted. The compounds **2a**,[15] **3a**,[53] **3i**,[54] **3k**,[55] **7**,[20] **9**,[56] **19i**,[57] **19j**,[28] **24**[58] and **26**[59] were prepared according to literature procedures. For further starting materials and intermediates see Supporting Information.

General procedure for the multifold Suzuki couplings (GP 6): To a solution of the hexabromoarene (2 mmol) in a mixture of anhydrous toluene and THF (50 mL each), which had been flushed with argon for 5 min, was added the palladium catalyst (30 mol%), the respective alkenylboronate **2** or **4** (13 mmol) as well as powdered NaOH (36 mmol), and the mixture was heated under an argon atmosphere at 100 °C for the stated time. After the mixture had been cooled down to ambient temperature, it was treated with 3 M NaOH (18 mL) and 30% hydrogen peroxide (2 mL) and the mixture stirred at ambient temperature for 1 h. The organic layer was then separated, washed with 3 M NaOH (5×12 mL),

and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue purified by chromatography on silica gel.

General procedure for sixfold Stille couplings (GP 7): A solution of hexabromobenzene (1 mmol) in toluene (20 mL) was flushed with argon for 5 min. Then palladium catalyst (30 mol%) and the respective alkenylstannane **19** (6.6 mmol) were added, and the mixture heated at 110 °C for the stated time. The reaction mixture was diluted with diethyl ether (20 mL), mixed with a saturated aqueous solution of KF (20 mL), and after 15 min filtered through a bed of Celite. The organic layer was separated, and the treatment with the KF solution was repeated until no colorless solid was observed.[60] Then the organic layer was dried ($MgSO_4$), the solvent was removed under reduced pressure, and the residue purified by chromatography on silica gel.

Hexakis-[(*E*)-(3,3-dimethyl-1-butenyl)]benzene (1a)—Variant 1: According to **GP 6**, hexabromobenzene (1.001 g, 1.815 mmol) was treated with **2a** (2.453 g, 12.08 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (363 mg, 0.517 mmol) and powdered sodium hydroxide (1.302 g, 32.55 mmol) in THF/toluene (1:1, 100 mL) at 100 °C for 24 h. Column chromatography on silica gel (100 g, pentane, column 5×50 cm), R_f=0.64, and subsequent recrystallization from hexane yielded **1a** (761 mg, 73%) as colorless crystals. M.p. 202 °C; IR (KBr): $\tilde{\nu}$=2947, 2863, 1473, 1385, 1361, 1282, 1259, 1200, 965, 911, 826 cm^{-1}; UV (cyclohexane): λ_{max} (log ε)=262 nm (4.72); ^1H NMR (250 MHz, $CDCl_3$): δ= 1.09 [s, 54H, $C(CH_3)_3$], 5.57 (d, J=16.5 Hz, 6H, 2′-H), 6.24 ppm (d, J= 16.5 Hz, 6H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ= 29.7 [+, $C(CH_3)_3$], 33.8 [C_{quat}, $C(CH_3)_3$], 124.7 (+, C-2′), 134.8 (C_{quat}, Ph-C), 145.5 ppm (+, C-1′); MS (70 eV): m/z (%): 570 (55) $[M]^+$, 513 (5) $[M-C_4H_9]^+$, 457 (60) $[M-C_4H_9-C_4H_8]^+$, 401 (10), 345 (10), 230 (10), 111 (15), 97 (25), 69 (30), 57 (100) $[C_4H_9]^+$; elemental analysis calcd (%) for $C_{42}H_{66}$ (571.0): C 88.35, H 11.65; found C 88.57, H 11.71.

Hexakis-[2-(1-adamantyl)ethenyl]benzene (1b)—Variant 1: According to **GP 6**, hexabromobenzene (149 mg, 0.270 mmol) was treated with **2b** (770 mg, 2.75 mmol) in the presence of *trans*-di(μ-acetato)bis[2-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (75 mg, 0.080 mmol) and powdered sodium hydroxide (160 mg, 4.00 mmol) in toluene (10 mL) at 110 °C for 2 d. Column chromatography on silica gel (80 g, pentane, column 5× 50 cm) yielded fraction I: **1b** (18 mg, 6%) (R_f=0.44). Recrystallization from $CHCl_3$/ethanol yielded a colorless solid. M.p. >320 °C; IR (KBr): $\tilde{\nu}$=2963, 2905, 2848 (C–H), 1751, 1450, 1413, 1260, 1013, 865, 793, 701 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=1.70 (br s, 72H, 2″-H, 4″-H), 2.01 (br s, 18H, 3″-H), 5.45 (d, J=16.6 Hz, 6H, 2′-H), 6.13 ppm (d, J= 16.6 Hz, 6H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=28.6 (C-3″), 35.9 (C-1″), 37.1 (C-4″*), 42.3 (C-2″*), 124.8 (C-2′), 134.6 (Ph-C), 145.8 ppm (C-1′); MS (70 eV): m/z (%): 1039/1038 (25/30) $[M]^+$, 903 (100) $[M-C_{10}H_{15}]^+$, 768 (80) $[M-2C_{10}H_{15}]^+$, 619 (50), 135 (100) $[C_{10}H_{15}]^+$. $C_{78}H_{102}$ (1039.7): calcd 1038.7981 (Without an authentic standard with approximately this value an accurate relative molecular mass could not be obtained by HRMS). Fraction II: 15 mg (6%) of pentakis[2-(1-adamantyl)-ethenyl]benzene (**21b**) (R_f=0.35), colorless solid. M.p. >320 °C; ^1H NMR (250 MHz, $CDCl_3$): δ=1.72 (br s, 60H, 2-$H_{adam.}$, 4-$H_{adam.}$), 2.05 (br s, 15H, 3-$H_{adam.}$), 5.50 (d, J=16.5 Hz, 2H, 2′-H), 5.53 (d, J=16.5 Hz, 1H, 2″-H), 5.89 (d, J=16.5 Hz, 2H, 2″-H), 6.10 (d, J=16.5 Hz, 1H, 1‴-H), 6.15 (d, J=16.5 Hz, 2H, 1′-H), 6.50 (d, J=16.5 Hz, 2H, 1″-H), 7.39 ppm (s, 1H, Ph-H); MS (70 eV): m/z (%): 832 (20), 718 (20) $[M-C_{12}H_{16}]^+$, 342 (60), 264 (40), 203 (35) $[M-5C_{10}H_{15}]^+$, 135 (100) $[C_{10}H_{15}]^+$; $C_{66}H_{86}$ (879.4).

Variant 2: According to **GP 7**, hexabromobenzene (136 mg, 0.247 mmol) was treated with **19b** (1.013 g, 2.245) in the presence of *trans*-di(μ-acetato)bis[2-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (30 mg, 32 μmol) in toluene (15 mL) at 110 °C for 68 h. Column chromatography (50 g, petroleum ether, column 3×30 cm), and subsequent recrystallization from pentane/CH_2Cl_2 yielded 36 mg of a pale yellow solid which, according to its ^1H NMR spectrum, contained mainly **1b** and a small amount of **21b**.

Hexakis-[2-(1′-methylcyclohexyl)ethenyl]benzene (1c): According to **GP 6**, hexabromobenzene (441 mg, 800 μmol) was treated with **2c** (1.28 g, 5.29 mmol) in the presence of dichlorobis(triphenylphosphine)-palladium (168 mg, 240 μmol) and powdered sodium hydroxide (576 mg, 14.4 mmol) in THF/toluene (1:1, 40 mL) at 100 °C for 18 h. Column chromatography on silica gel (60 g, hexane, column 3×50 cm) yielded fraction I: 21 mg (3%) of 1,4-bis(1′-methylcyclohexyl)buta-1,3-diene (**22c**) as a colorless solid, R_f=0.64. M.p. 98 °C; IR (KBr): $\tilde{\nu}$=2983 (C–H), 2854, 1611, 1475, 1384, 1321, 1259, 821 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ= 0.99 (s, 6H, CH_3), 1.26–1.51 (m, 20H, CH_2), 5.55–5.61 [AA′ part of an AA′BB′ system, 2H, 3(6)-H], 5.94–6.01 ppm [BB′ part of an AA′BB′ system, 2H, 4(5)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=22.4 (–, CH_2), 26.3 (–, CH_2), 27.3 (+, CH_3), 35.8 (C_{quat}, C-2), 38.0 (–, CH_2), 127.1 [+, C-3(6)], 142.5 ppm [+, C-4(5)]; MS (70 eV): m/z (%): 246 (35) $[M]^+$, 149 (30) $[M-cHexMe]^+$, 97 (100) $[cHexMe]^+$, 55 (20); elemental analysis calcd (%) for $C_{18}H_{30}$ (246.4): C 87.73, H 12.27; found C 87.48, H 12.11. Fraction II: 285 mg (44%) of **1c** (R_f=0.55). Recrystallization from ethanol/pentane yielded colorless crystals. M.p. 261 °C; IR (KBr): $\tilde{\nu}$=2951 (C–H), 2900, 1475, 1452, 1311, 1256, 1215, 963, 820 cm^{-1}; UV (isooctane): λ_{max} (log ε)=263 nm (4.69); ^1H NMR (250 MHz, $CDCl_3$): δ=1.06 (s, 18H, CH_3), 1.34–1.56 (m, 60H, CH_2), 5.55 (d, ^3J= 16.6 Hz, 6H, 2′-H), 6.27 ppm (d, ^3J=16.6 Hz, 6H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=22.4 (–, CH_2), 26.1 (+, CH_3), 26.3 (–, CH_2), 36.4 (C_{quat}, C-3′), 37.7 (–, CH_2), 125.7 (+, C-2′), 135.3 (C_{quat}, Ph-C), 144.8 ppm (+, C-1′); MS (70 eV): m/z (%): 811/810 (58/90) $[M]^+$, 713 (10) $[M-cHexMe]^+$, 618/617 (90/45), 97 (100) $[cHexMe]^+$, 55 (20); elemental analysis calcd (%) for $C_{60}H_{90}$ (811.4): C 88.82, H 11.18; found C 88.94, H 10.91. Fraction III: 298 mg (54%) of a colorless solid which, according to its ^1H NMR spectrum was pentakis[2-(1′-methylcyclohexyl)ethenyl]benzene (**21c**). M.p. 107 °C; ^1H NMR (250 MHz, $CDCl_3$): δ=1.08 (br s, 15H, CH_3), 1.31–1.69 (m, 50H, CH_2), 5.61 (d, ^3J= 16.4 Hz, 2H, 2′-H), 5.63 (d, ^3J=16.4 Hz, 1H, 2′-H), 6.04 (d, ^3J=16.5 Hz, 2H, 2′-H), 6.22 (d, ^3J=16.4 Hz, 1H, 1′-H), 6.70 (d, ^3J=16.4 Hz, 2H, 1′-H), 6.62 (d, ^3J=16.4 Hz, 2H, 1′-H), 7.46 ppm (s, 1H, Ph-H); $C_{51}H_{76}$ (689.2).

Hexakis-[2-(1′-methylcyclopropyl)ethenyl]benzene (1d): According to **GP 6**, hexabromobenzene (276 mg, 500 μmol) was treated with **2d** (1.00 g, 5.00 mmol) in the presence of dichlorobis(triphenylphosphine)-palladium (105 mg, 150 μmol) and powdered sodium hydroxide (520 mg, 13.0 mmol) in THF/toluene (1:1, 40 mL) at 100 °C for 24 h. Column chromatography on silica gel (40 g, pentane, column 3×50 cm) yielded fraction I: 10 mg (2.5%) of 1,4-bis(1′-methylcyclopropyl)buta-1,3-diene (**22d**) (R_f=0.48), colorless solid. M.p. 58 °C; IR (KBr): $\tilde{\nu}$=3053, 2951, 2844 (C–H), 1635, 1478, 1320, 912, 852 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.57 (s, 8H, cPr-H), 1.17 (s, 6H, CH_3), 5.17–5.28 [AA′ part of an AA′BB′ system, 2H, 3(6)-H], 5.92–6.04 ppm [BB′ part of an AA′BB′ system, 2H, 4(5)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=15.47 (–, cPr-C), 17.31 (C_{quat}, cPr-C), 21.47 (+, CH_3), 126.01 [+, C-3(6)], 139.14 ppm [+, C-4(5)]; MS (70 eV): m/z (%): 162 (55) $[M]^+$, 147 (30) $[M-CH_3]^+$, 105 (40), 91 (75), 81 (40) $[CH{\equiv}CHC(ethano)CH_3]^+$, 79 (60), 77 (40), 41 (100); HRMS: m/z: calcd for $C_{12}H_{18}$ (162.3): 162.1408, found 162.1408. Fraction II: 45 mg (16%) of **1d** (R_f=0.25). Recrystallization from pentane/ethanol (2:1) yielded a colorless solid. M.p. 185 °C; IR (KBr): $\tilde{\nu}$=3059, 2951, 2842 (C–H), 1633, 1475, 1382, 1242, 961 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.57 (s, 24H, cPr-H), 1.24 (s, 18H, CH_3), 5.21 (d, ^3J=16.3 Hz, 6H, 2′-H), 6.18 ppm (d, ^3J=16.3 Hz, 6H, 1′-H); ^{13}C NMR (125.7 MHz, $CDCl_3$, additional DEPT): δ=14.6 (–, cPr-C), 17.9 (C_{quat}, cPr-C), 21.6 (+, CH_3), 125.1 (+, C-2′), 134.1 (C_{quat}, Ph-C), 143.1 ppm (+, C-1′); MS (70 eV): m/z (%): 559/558 (44/100) $[M]^+$, 503 (30), 484 (40), 91 (35), 81 (100) $[CH{\equiv}CHC(ethano)CH_3]^+$, 44 (80); HRMS: m/z: calcd for $C_{42}H_{54}$ (558.9): 558.4225, found 558.4225. Fraction III: 121 mg of a pale yellow solid (R_f=0.21) which, according to its ^1H NMR spectrum was a 2:9 mixture of **1d** and pentakis[2-(1′-methylcyclopropyl)ethenyl]benzene (**21d**). ^1H NMR (250 MHz, $CDCl_3$): δ=0.63 (br s, 20H, cPr-H), 1.31 (br s, 15H, CH_3), 5.32 (d, ^3J=16.3 Hz, 2H, 2′-H), 5.36 (d, ^3J=16.2 Hz, 1H, 2′-H), 5.61 (d, ^3J=16.4 Hz, 2H, 2′-H), 6.21 (d, ^3J=16.2 Hz, 1H, 1′-H), 6.27 (d, ^3J=16.4 Hz, 2H, 1′-H), 6.58 (d, ^3J= 16.3 Hz, 2H, 1′-H), 7.35 ppm (s, 1H, Ph-H); $C_{36}H_{46}$ (478.8).

Hexakis-(2-*tert*-pentylethenyl)benzene (1e)—Variant 1: According to **GP 6**, hexabromobenzene (149 mg, 270 μmol) was treated with **2e** (585 mg, 2.71 mmol) in the presence of dichlorobis(triphenylphosphine)-palladium (10 mg, 14 μmol) and powdered sodium hydroxide (271 mg, 6.77 mmol) in THF/toluene (1:1, 20 mL) at 100 °C for 43 h. Column chromatography on silica gel (40 g, hexane, column 3×50 cm, R_f=0.46) yield-

ed a colorless solid. Recrystallization from hexane gave fraction I: 83 mg (55%) of pentakis(2-*tert*-pentylethenyl)benzene (**21e**) as colorless crystals. M.p. 187°C; IR (KBr): $\tilde{\nu}$=3029 (C–H), 2953, 2861 (C–H), 1472, 1425, 1282, 1254, 973, 851 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.81–0.88 (m, 15H, 5′-H), 1.05 [brs, 30H, C(CH_3)$_2$], 1.37–1.43 (m, 10H, CH_2), 5.58 (d, ^3J=16.6 Hz, 2H, 2′-H*), 5.60 (d, ^3J=16.4 Hz, 1H, 2′-H), 5.96 (d, ^3J=16.1 Hz, 2H, 2′-H*), 6.18 (d, ^3J=16.4 Hz, 1H, 1′-H), 6.24 (d, ^3J=16.6 Hz, 2H, 1′-H*), 6.54 (d, ^3J=16.1 Hz, 2H, 1′-H*), 7.42 ppm (s, 1H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=9.2 (+, 2C, C-5′*), 9.3 (+, 1C, C-5′*), 9.3 (+, 2C, C-5′*), 26.7 [+, 4 C, C(CH_3)$_2$], 26.8 [+, 2C, C(CH_3)$_2$], 26.8 [+, 4C, C(CH_3)$_2$], 35.3 (–, 1C, C-4′*), 35.3 (–, 2C, C-4′*), 35.8 (–, 2C, C-4′*), 36.7 (C_{quat}, 2C, C-3′*), 36.9 (C_{quat}, 1C, C-3′*), 37.1 (C_{quat}, 2C, C-3′*), 123.1 (+, 1C, C-2′*), 124.0 (+, 2C, C-2′*), 124.7 (+, 1C, Ph-C), 126.8 (+, 2C, C-2′*), 134.1 (C_{quat}, 2C, Ph-C), 134.9 (C_{quat}, 2C, Ph-C), 136.4 (C_{quat}, 1C, Ph-C), 139.7 (+, 2C, C-1′*), 145.6 (+, 1C, C-1′*), 145.8 ppm (+, 2C, C-1′*); MS (70 eV): *m*/*z* (%): 559/558 (26/60) [*M*]$^+$, 462 (100), 417 (100), 363 (80), 321 (85), 71 (90); HRMS: *m*/*z*: calcd for $C_{41}H_{66}$ (559.0): 558.5164, found 558.5164. Fraction II: 18 mg (10%) of **1e** as colorless crystals. M.p. 263°C; IR (KBr): $\tilde{\nu}$=2945 (C–H), 2867 (C–H), 1762, 1461, 1412, 1364, 1209, 965, 911 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.84 (t, ^3J=7.5 Hz, 18H, 5′-H), 1.04 [s, 36H, C(CH_3)$_2$], 1.36 (q, ^3J=7.5 Hz, 12H, 4′-H), 5.50 (d, ^3J=16.5 Hz, 6H, 2′-H), 6.22 ppm (d, ^3J=16.5 Hz, 6H, 1′-H); ^{13}C NMR (125.7 MHz, $CDCl_3$, additional DEPT): δ=9.2 (+, C-5′), 26.6 [+, C(CH_3)$_2$], 35.4 (–, C-4′), 36.7 (C_{quat}, C-3′), 125.9 (+, C-2′), 135.2 (C_{quat}, Ph-C), 144.1 ppm (+, C-1′); MS (70 eV): *m*/*z* (%): 655/654 (10/20) [*M*]$^+$, 618 (30), 560 (10), 321 (100), 71 (90); elemental analysis calcd (%) for $C_{48}H_{78}$ (655.1): C 88.00, H 12.00; found C 90.02, H 11.92.

Variant 2: According to **GP 6**, hexabromobenzene (275 mg, 500 μmol) was treated with **4e** (1.05 g, 4.68 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (105 mg, 150 μmol) and powdered sodium hydroxide (530 mg, 13.3 mmol) in THF/toluene (1:1, 40 mL) at 100°C for 24 h. Column chromatography on silica gel (40 g, hexane, column 3×50 cm, R_f=0.48) yielded 225 mg of a colorless solid. Recrystallization from hexane gave fraction I: 207 mg (74%) of **21e**. Fraction II: 52 mg (16%) of **1e** as colorless crystals.

Hexakis-[(*E*)-6′-methoxy-3′,3′-dimethyl-1′-hexenyl]benzene (1f): According to **GP 6**, hexabromobenzene (165 mg, 300 μmol) was treated with **4f** (805 mg, 3.00 mmol) in the presence of dichlorobis(triphenylphosphine)-palladium (63 mg, 90 μmol) and powdered sodium hydroxide (324 mg, 8.10 mmol) in THF/toluene (1:1, 40 mL) at 100°C for 24 h. Column chromatography on silica gel [100 g, pentane/diethyl ether (2:1), column 2.5×45 cm] gave fraction I: 26 mg (3%) of 1,12-dimethoxy-4,4,9,9-tetramethyldodeca-5,7-diene (**22f**) as a colorless solid. R_f=0.62; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.01 [s, 12H, C(CH_3)$_2$], 1.26 [m, 4H, 3(10)-H], 1.51 [m, 4H, 2(11)-H], 3.34 (s, 6H, OCH_3), 3.36 [t, ^3J=7.2 Hz, 4H, 1(12)-H], 5.54 [AA′ part of an AA′BB′ system, 2H, 5(8)-H], 5.91 ppm [BB′ part of an AA′BB′ system, 2H, 6(7)-H]. Fraction II: 23 mg of a pale yellow oil (R_f=0.38) which, according to its ^{1}H NMR spectrum was a mixture of reduction products. Fraction III: 80 mg (34%) of pentakis[(*E*)-5′-methoxy-3′,3′-dimethyl-1′-hexenyl]benzene (**21f**) as a colorless solid. R_f=0.26; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.11 [brs, 30H, C(CH_3)$_2$], 1.33–1.61 [m, 20H, 4′(5′)-H], 3.31 (brs, 15H, OCH_3), 3.30–3.41 (m, 10H, 6′-H), 5.59 (d, ^3J=18.3 Hz, 2H, 2′-H), 5.62 (d, ^3J=18.4 Hz, 1H, 2′-H), 5.98 (d, ^3J=18.3 Hz, 2H, 2′-H), 6.18 (d, ^3J=18.4 Hz, 1H, 1′-H), 6.25 (d, ^3J=18.3 Hz, 2H, 1′-H), 6.56 (d, ^3J=18.3 Hz, 2H, 1′-H), 7.39 ppm (s, 1H, Ph-H). Fraction IV: 49 mg (18%) of **1f** as a colorless solid. R_f=0.16; IR (KBr): $\tilde{\nu}$=2989, 2936, 2599, 1654, 1447, 1435, 1379, 1345, 1222, 1045, 977 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.05 [s, 36H, C(CH_3)$_2$], 1.31–1.59 [m, 24H, 4′(5′)-H], 3.30 (s, 18H, OCH_3), 3.35 (t, ^3J=6.9 Hz, 12H, 6′-H), 5.51 (d, ^3J=18.4 Hz, 6H, 2′-H), 6.22 ppm (d, ^3J=18.4 Hz, 6H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=25.1 (–, C-4′), 27.0 [+, C(CH_3)$_2$], 36.3 (–, C-5′), 39.6 (C_{quat}, C-3′), 58.5 (–, C-6′), 125.9 (+, C-2′), 135.0 (C_{quat}, Ph-C), 144.1 ppm (+, C1′).

Hexakis-[(*E*)-3′,3′-dimethyl-5′-methylthio-1′-pentenyl]benzene (1g): According to **GP 6**, hexabromobenzene (276 mg, 500 μmol) was treated with **4g** (1.35 g, 5.00 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (105 mg, 150 μmol) and powdered sodium hydroxide (540 mg, 13.5 mmol) in THF/toluene (1:1, 36 mL) at 100°C for 24 h. Column chromatography on silica gel [100 g, pentane/diethyl ether (20:1), column 2.5×35 cm] gave fraction I: 1,10-dimethylthio-3,3,8,8-tetramethyldeca-4,6-diene (**22g**) as a colorless solid (61 mg, 4.3%). R_f=0.65; IR (KBr): $\tilde{\nu}$=3025 (C–H), 2960, 2913, 2851 (C–H), 1457, 1380, 1363, 1314, 1261, 1240, 1001, 802 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.02 [s, 12H, C(CH_3)$_2$], 1.59 [m, 4H, 2(9)-H], 2.09 (s, 6H, SCH_3), 2.39 [m, 4H, 1(10)-H], 5.53 [AA′ part of an AA′BB′ system, 2H, 4(7)-H], 5.92 ppm [BB′ part of an AA′BB′ system, 2H, 5(6)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=15.6 (+, SCH_3), 27.1 [+, C(CH_3)$_2$], 29.8 [–, C-1(10)], 36.2 [C_{quat}, C-3(8)], 42.7 [–, C-2(9)], 127.2 [+, C-4(7)], 141.4 ppm [+, C-5(6)]; MS (70 eV): *m*/*z* (%): 288/287/286 (10/16/100) [*M*]$^+$, 271 (14) [*M*–CH_3]$^+$, 211 (30), 107 (18), 75 (70), 61 (28) [C_2H_5S]$^+$; elemental analysis calcd (%) for $C_{16}H_{30}S_2$ (286.6): C 67.07, H 10.55; found C 67.01, H 10.39. Fraction II: 50 mg of a pale yellow oil (R_f=0.41) which, according to its ^{1}H NMR spectrum was a mixture of reduction products. Fraction III: pentakis[(*E*)-3′,3′-dimethyl-5′-methylthio-1′-pentenyl]benzene (**21g**) as a colorless solid (148 mg, 38%). R_f=0.30; IR (KBr): $\tilde{\nu}$=3024, 2958, 2914, 2865, 1652, 1472, 1437, 1383, 1361, 1253, 972 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.13 [brs, 30H, C(CH_3)$_2$], 1.63–1.73 (m, 10H, 4′-H), 2.09 (brs, 15H, SCH_3), 2.41–2.56 (m, 10H, 5′-H), 5.57 (d, ^3J=16.5 Hz, 2H, 2′*-H), 5.59 (d, ^3J=16.5 Hz, 1H, 2′-H), 5.98 (d, ^3J=16.2 Hz, 2H, 2′*-H), 6.17 (d, ^3J=16.5 Hz, 1H, 1′-H), 6.24 (d, ^3J=16.5 Hz, 2H, 2′**-H), 6.51 (d, ^3J=16.2 Hz, 2H, 2′**-H), 7.42 ppm (s, 1H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=15.6 (+, SCH_3), 15.7 (+, SCH_3), 27.2 [+, C(CH_3)$_2$], 27.2 [+, C(CH_3)$_2$], 30.0 (–, C-5′), 30.1 (–, C-5′), 36.9 (C_{quat}, C-3′), 37.1 (C_{quat}, C-3′), 37.2 (C_{quat}, C-3′), 42.6 (–, C-4′), 42.9 (–, C-4′), 123.4 (+, C-2′*), 124.3 (+, C2′*), 125.1 (+, Ph-C*), 126.9 (+, C2′*), 133.9 (C_{quat}, Ph-C), 134.8 (C_{quat}, Ph-C), 136.2 (C_{quat}, Ph-C), 139.2 (+, C-1′), 145.0 (+, C-1′), 145.3 ppm (+, C-1′); MS (70 eV): *m*/*z* (%): 790/789/788 (5/11/22) [*M*]$^+$, 673/672/671 (10/18/36) [*M*–$C_6H_{13}S$]$^+$, 117 (78) [$C_6H_{13}S$]$^+$, 61 (100) [C_2H_5S]$^+$; elemental analysis calcd (%) for $C_{46}H_{76}S_5$ (789.4): C 69.99, H 9.70; found C 70.08, H 9.80. Fraction IV: 102 mg (22%) of **1g** as a waxy solid. IR (KBr): $\tilde{\nu}$=2959, 2916, 2677, 1652, 1472, 1437, 1383, 1363, 1261, 1036, 971, 804 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 [s, 36H, C(CH_3)$_2$], 1.61–1.67 (m, 12H, 4′-H), 2.08 (s, 18H, SCH_3), 2.41–2.48 (m, 12H, 5′-H), 5.49 (d, ^3J=16.5 Hz, 6H, 2′-H), 6.22 ppm (d, ^3J=16.5 Hz, 6H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=15.6 (+, SCH_3), 26.9 [+, C(CH_3)$_2$], 29.9 (–, C-5′), 36.9 (C_{quat}, C-3′), 42.7 (–, C-4′), 126.1 (+, C-2′), 135.1 (C_{quat}, Ph-C), 143.6 ppm (+, C-1′); MS (70 eV): *m*/*z* (%): 934/933/932/931 (5/11/12/20) [*M*]$^+$, 816/815/814/813 (6/12/15/25), 118/117 (28/100) [$C_6H_{13}S$]$^+$, 61 (57) [C_2H_5S]$^+$; elemental analysis calcd (%) for $C_{54}H_{90}S_6$ (931.7): C 69.61, H 9.74; found C 69.69, H 9.53.

Hexakis-[(*E*)-5′-methoxy-3′,3′-dimethyl-1′-pentenyl]benzene (1h)—Variant 1: According to **GP 6**, hexabromobenzene (276 mg, 500 μmol) was treated with **2h** (1.23 g, 5.00 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (53 mg, 75 μmol) and powdered sodium hydroxide (540 mg, 13.5 mmol) in THF/toluene (1:1, 36 mL) at 100°C for 24 h. Column chromatography on silica gel [60 g, pentane/diethyl ether (1:1), column 2.5×30 cm]: Fraction I: 53 mg (8.3%) of 1,10-dimethoxy-3,3,8,8-tetramethyldeca-4,6-diene (**22h**). R_f=0.65; M.p. 49°C; IR (KBr): $\tilde{\nu}$=3027 (C–H), 2977, 2922, 2867 (C–H), 1434, 1376, 1353, 1311, 1257, 1235, 1014 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.02 [s, 12H, C(CH_3)$_2$], 1.61 [t, ^3J=7.2 Hz, 4H, 2(9)-H], 3.28 (s, 6H, OCH_3), 3.31 [t, ^3J=7.2 Hz, 4H, 1(10)-H], 5.54 [AA′ part of an AA′BB′ system, 2H, 4(7)-H], 5.94 ppm [BB′ part of an AA′BB′ system, 2H, 5(6)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=27.6 [+, C(CH_3)$_2$], 35.0 [C_{quat}, C-3(8)], 42.0 [–, C-2(9)], 58.5 (+, OCH_3), 70.0 [–, C-1(10)], 126.7 [+, C-4(7)], 141.8 ppm [+, C-5(6)]. Fraction II: 51 mg of a pale yellow oil (R_f=0.45), according to ^{1}H NMR spectrum a mixture of reduction products. Fraction III: 270 mg (75%) of pentakis[(*E*)-5′-methoxy-3′,3′-dimethyl-1′-pentenyl]-benzene (**21h**). R_f=0,22; IR (KBr): $\tilde{\nu}$=3029, 2981, 2921, 2877, 1661, 1472, 1424, 1368, 1224, 972 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.15 [brs, 30H, C(CH_3)$_2$], 1.68–1.76 (m, 10H, 4′-H), 3.31 (brs, 15H, OCH_3), 3.38–3.47 (m, 10H, 5′-H), 5.60 (d, ^3J=18.3 Hz, 2H, 2′-H), 5.62 (d, ^3J=18.4 Hz, 1H, 2′-H), 6.03 (d, ^3J=18.3 Hz, 2H, 2′-H), 6.18 (d, ^3J=18.4 Hz, 1H, 1′-H), 6.27 (d, ^3J=18.3 Hz, 2H, 1′-H), 6.55 (d, ^3J=18.3 Hz, 2 h, 1′-H), 7.46 ppm (s, 1H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional

DEPT): δ=27.6 [+, C(CH_3)$_2$], 27.6 [+, C(CH_3)$_2$], 27.7 [+, C(CH_3)$_2$], 35.6 (C_{quat}, C-3′), 35.8 (C_{quat}, C-3′), 35.9 (C_{quat}, C-3′), 41.9 (−, C-4′), 42.4 (−, C-4′), 58.5 (+, OCH_3), 70.1 (−, C-5′), 70.1 (−, C-5′), 70.2 (−, C-5′), 123.4 (+, C-2′*), 123.9 (+, C-2′), 124.6 (+, Ph-C*), 126.4 (+, C2′), 133.9 (C_{quat}, Ph-C), 134.9 (C_{quat}, Ph-C), 136.1 (C_{quat}, Ph-C), 139.6 (+, C-1′), 145.4 (+, C-1′), 145.7 ppm (+, C-1′). Fraction IV: 67 mg (16%) of **1h**, R_f=0.20. IR (KBr): $\tilde{\nu}$=2962, 2921, 2687, 1654, 1456, 1441, 1383, 1345, 1225, 1031, 980 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.12 [s, 36H, C(CH_3)$_2$], 1.67 (t, ^3J=6.9 Hz, 12H, 4′-H), 3.30 (s, 18H, OCH_3), 3.41 (t, ^3J=6.9 Hz, 12H, 5′-H), 5.52 (d, ^3J=18.4 Hz, 6H, 2′-H), 6.22 ppm (d, ^3J=18.4 Hz, 6H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=27.4 [+, C(CH_3)$_2$], 35.6 (C_{quat}, C-3′), 41.9 (−, C-4′), 58.5 (+, OCH_3), 70.1 (−, C-5′), 125.7 (+, C-2′), 135.0 (C_{quat}, Ph-C), 143.9 ppm (+, C-1′); MS (70 eV): *m*/*z* (%): 836/835 (54/100) $[M]^+$, 69 (28); elemental analysis calcd (%) for $C_{54}H_{90}O_6$ (835.3): C 77.65, H 10.85; found C 77.48, H 10.45.

Variant 2: According to **GP 6**, hexabromobenzene (276 mg, 500 μmol) was treated with **4h** (1.27 g, 5.00 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (105 mg, 150 μmol) and powdered sodium hydroxide (540 mg, 13.5 mmol) in THF/toluene (1:1, 36 mL) at 100°C for 24 h. Column chromatography on silica gel [100 g, pentane/diethyl ether (1:1, column 2.5×40 cm] gave: Fraction I: 155 mg (24%) of **22h**, R_f=0.65. Fraction II: 98 mg of a pale yellow oil, R_f=0.40, see above. Fraction III: 88 mg (25%) of **21h**, R_f=0.22. Fraction IV: 101 mg (24%) **1h**, R_f=0.12.

Hexakis-(2-trimethylsilylethenyl)benzene (1i): According to **GP 7**, hexabromobenzene (108 mg, 0.196 mmol) was treated with **19i** (770 mg, 1.98 mmol) in the presence of *trans*-di(μ-acetato)bis[2-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (10 mg, 0.011 mmol) at 100°C for 20 h. Column chromatography on silica gel (50 g, pentane, column 3×30 cm, R_f=0.69), and subsequent recrystallization from ethanol/hexane yielded **1i** (53 mg, 41%) as colorless crystals. M.p. 227–230°C; IR (KBr): $\tilde{\nu}$=2955, 2897, 1595, 1247, 1205, 986, 864 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.12 [s, 54H, Si(CH_3)$_3$], 5.93 (d, J=19.6 Hz, 6H, 2′-H), 6.86 ppm (d, J=19.6 Hz, 6H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=−1.10 [+, Si(CH_3)$_3$], 135.8 (C_{quat}, Ph-C), 137.1 (+, C-2′), 143.9 ppm (+, C-1′); MS (70 eV): *m*/*z* (%): 666 (40) $[M]^+$, 593 (90) $[M-Si(CH_3)_3]^+$, 568 (100) $[M-C{=}CHSi(CH_3)_3]^+$, 495 (90), 73 (100) $[Si(CH_3)_3]^+$; HRMS: *m*/*z*: calcd for $C_{36}H_{66}Si_6$ (667.4): 666.3780; found: 666.3780.

Hexastyrylbenzene (1j): According to **GP 7**, hexabromobenzene (200 mg, 0.363 mmol) was treated with **19j** (1.396 g, 3.550 mmol) in the presence of tetrakis(triphenylphosphine)palladium (126 mg, 0.109 mmol) and additional copper iodide (15 mg, 0.079 mmol) in 20 mL of toluene at 110°C for 4 d. Column chromatography on silica gel [50 g, petroleum ether/CH_2Cl_2 (3:1), column 3×30 cm], yielded **1j** (40 mg, 16%) as a pale yellow oil. R_f=0.25; IR (film): $\tilde{\nu}$=3026, 2923, 2853, 1699, 1599, 1494, 1449, 1261, 1075, 1030, 966, 754, 697 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=6.61–7.40 (m, 30H), 7.08 ppm (s, 12H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=126.2 [C-2″(6″)], 127.5 (C-4″), 128.0 (C-1′*), 128.4 [C-3″(5″)], 128.7 (C-2′*), 134.9 (C-1*), 137.7 ppm (C-1″*); MS (70 eV): *m*/*z* (%): 690 (10) $[M]^+$, 599 (5) $[M-C_7H_7]^+$, 542 (5), 378 (10), 250 (30), 154 (20), 105 (40), 91 (100) $[C_7H_7]^+$; HRMS: *m*/*z*: calcd for $C_{54}H_{42}$ (690.9): 690.3286, found 690.3286.

Hexakis-[2-(3,5-di-*tert*-butylphenyl)ethenyl]benzene (1k): According to **GP 7**, hexabromobenzene (233 mg, 0.422 mmol) was treated with **19k** (1.500 g, 2.968 mmol) in the presence of *trans*-di(μ-acetato)bis[2-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (58 mg, 0.062 mmol) in toluene (30 mL) at 110°C for 5 d. Column chromatography on silica gel (100 g, petroleum ether, column 3×30 cm) yielded **19k** (30 mg, 5%) as a pale yellow oil. R_f=0.23; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.38–1.42 [m, 108H, C(CH_3)$_3$], 6.39–7.06 [m, 12H, 1′-H, 2′-H], 7.29–7.43 ppm (m, 18H, Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=31.4 [+, C(CH_3)$_3$], 34.8 [C_{quat}, C(CH_3)$_3$], 120.6 [+, C-2″(6″)], 122.0 (+, C-4″), 128.9 (+, C-2′), 133.4 (+, C-1′), 135.7 (C_{quat}, C-1), 136.6 (C_{quat}, C-1″), 150.9 ppm [C_{quat}, C-3″(5″)]; MS (70 eV): *m*/*z* (%): 1365/1364/1363 (14/20/18) $[M]^+$, 1248 (1), 1229 (5), 1162 (10), 1149 (5), 960 (5), 430 (15), 203 (20), 57 (100) $[C(CH_3)_3]^+$; $C_{102}H_{138}$ (1364.2): Without an authentic calibration standard for this relative molecular mass region, the HRMS is not reliable. Nevertheless the isotope ratio for the molecular peak is identical to the one calculated for $C_{102}H_{138}$.

Hexakis-(3,3-dimethylbutyl)benzene (23): A solution of hexakis(3,3-dimethyl-1-butenyl)benzene (**1a**) (52 mg, 91 μmol) in hexane (5 mL) with added palladium on charcoal (10%, 21 mg) was stirred under an atmosphere of hydrogen for 18 h. After removal of the catalyst by filtration, the solvent was distilled off under reduced pressure. Recrystallization from hexane yielded **23** (47 mg, 89%) as colorless crystals. M.p. 187°C; IR (KBr): $\tilde{\nu}$=2961, 2896, 2865, 1477, 1459, 1391, 1363, 1247 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.99 [s, 54H, C(CH_3)$_3$], 1.36–1.43 (m, 12H, 2′-H), 2.43–2.50 ppm (m, 12H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=24.1 (−, C-2′), 29.5 [+, C(CH_3)$_3$], 30.9 [C_{quat}, C(CH_3)$_3$], 46.2 (−, C-1′), 135.6 ppm (C_{quat}, Ph-C); MS (70 eV): *m*/*z* (%): 582 (100) $[M]^+$, 511 (5) $[M-C_5H_{11}]^+$, 333 (10), 231 (10), 161 (10), 57 (15) $[C_4H_9]^+$; elemental analysis calcd (%) for $C_{42}H_{78}$ (583.1): C 86.52, H 13.48; found C 86.48, H 13.38.

2,3,6,7,10,11-Hexakis-[(*E*)-3′,3′-dimethyl-1′-butenyl]triphenylene (25): According to **GP 6**, a solution of hexabromotriphenylene (**24**) (351 mg, 500 μmol) and 2-[(*E*)-3′,3′-dimethylbutenyl]-1,3,2-benzodioxaborol (**2a**) (1.01 g, 5.00 mmol) in THF/toluene (1:1, 40 mL) was treated with powdered NaOH (600 mg, 15.0 mmol) and $[PdCl_2(PPh_3)_2]$ (105 mg, 150 μmol) at 100°C for 12 h. Recrystallization of the crude product from pentane and CH_2Cl_2 yielded **25** (335 mg, 93%) as colorless needles. M.p. 275°C (decomp); IR (KBr): $\tilde{\nu}$=3040 (C−H), 2957, 2900 (C−H), 2864, 1474, 1463, 1362, 1265, 966, 888 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.24 (s, 54H, CH_3), 6.31 (d, ^3J=16.0 Hz, 6H, 2′-H), 6.75 (d, ^3J=16.0 Hz, 6H, 1′-H), 8.51 ppm (s, 6H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=29.7 [+, C(CH_3)$_3$], 33.9 [C_{quat}, C(CH_3)$_3$], 121.3 (+, Ar-C*), 123.7 (+, C-1′*), 128.5 (C_{quat}, Ar-C), 135.5 (C_{quat}, Ar-C), 144.7 ppm (+, C-2′); MS (70 eV): *m*/*z* (%): 722/721/720 (15/59/100) $[M]^+$, 315 (9), 300 (15); elemental analysis calcd (%) for $C_{54}H_{72}$ (721.2): C 89.94, H 10.06; found C 89.78, H 9.88.

Octakis-(3,3-dimethyl-1-butenyl)naphthalene (27): According to **GP 6**, octabromonaphthalene (550 mg, 0.725 mmol) was treated with **2a** (6.30 g, 31.2 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (204 mg, 0.290 mmol) and powdered sodium hydroxide (2.02 g, 50.6 mmol) in THF/toluene (1:1, 35 mL) in an ultrasonic bath for 24 h. Column chromatography on silica gel (80 g, hexane, column 3×30 cm), R_f=0.45 and subsequent recrystallization from CH_2Cl_2/ethanol yielded **27** (120 mg, 21%) as light-yellow crystals. M.p. 172°C (decomp); IR (KBr): $\tilde{\nu}$=2958, 2901, 2864, 1475, 1461, 1390, 1361, 1262, 1201, 964, 945 cm^{-1}; UV (hexane): λ_{max} (log ε)=290 nm (4.82); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.07 [s, 36H, C(CH_3)$_3$], 1.11 [s, 36H, C(CH_3)$_3$], 4.91 (d, J=16.3 Hz, 4H, 2′-H), 5.75 (d, J=16.3 Hz, 4H, 2′-H), 6.24 (d, J=16.3 Hz, 4H, 1′-H), 6.65 ppm (d, J=16.3 Hz, 4H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): δ=29.2 [+, C(CH_3)$_3$], 29.8 [+, C(CH_3)$_3$], 33.6 [C_{quat}, C(CH_3)$_3$], 33.9 [C_{quat}, C(CH_3)$_3$], 124.3 (+, C-2′), 129.9 (+, C-2′), 133.0 (C_{quat}, Ph-C), 133.8 (C_{quat}, Ph-C), 133.9 (C_{quat}, Ph-C), 141.2 (+, C-1′), 145.9 ppm (+, C-1′); MS (70 eV): *m*/*z* (%): 788/787/786/785 (5/22/66/100) $[M]^+$, 715/714 (10/22), 658 (8), 57 (14) $[C_4H_9]^+$; elemental analysis calcd (%) for $C_{58}H_{88}$ (785.3): C 88.71, H 11.29; found C 88.73, H 11.10.

Crystallography: Information concerning the crystallographic data and structure determinations of the five compounds is summarized in Table 6. Intensities were collected with a Nicolet R3m V^{-1} four-circle diffractometer for **1a**, with a STOE-AED2 diffractometer for **1i** and **23**, with a STOE-IPDS II diffractometer for **1h** using in all cases graphite-monochromated $Mo_{K\alpha}$ radiation. Compound **27** was measured with a Bruker SMART 6000 area detector using monochromated $Cu_{K\alpha}$ radiation. All calculations were performed with the SHELXTL-Plus program package.[61] All non-hydrogen atoms were refined anisotropically.

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Table 6. Summary of structure determination data for new arene derivatives.[38]

	1a	**1h**	**1i**	**23**	**27**
F_w	$C_{42}H_{66}$	$C_{54}H_{90}O_6$	$C_{36}H_{66}Si_6$	$C_{42}H_{78}$	$C_{58}H_{88}$
M_w	571.0	835.3	667.4	583.1	785.28
color	colorless	colorless	colorless	colorless	light yellow
crystal size [10 mm]	$5.2\times3.1\times4.5$	$4.0\times0.3\times0.5$	$4.0\times2.0\times2.0$	$6.0\times6.0\times5.0$	$5.0\times4.0\times4.0$
crystal system	triclinic	rhombohedral	triclinic	rhombohedral	monoclinic
space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$	$R\bar{3}$	$P2_1/c$
unit cell					
a [Å]	10.691(3)	14.5509(14)	13.288(6)	23.819(3)	13.904(2)
b [Å]	14.697(3)	14.5509(14)	14.039(6)	23.819(3)	18.781(2)
c [Å]	14.714(4)	21.846(3)	14.760(6)	61.908(12)	10.547(2)
α [°]	60.29(2)	90	66.44(3)	90	90
β [°]	77.78(2)	90	67.88(3)	90	103.28(2)
γ [°]	73.35(2)	120	68.95(3)	120	90
V [Å^3]	1917.2(8)	4005.7(7)	2266 (17)	3041.8(9)	2680.5(7)
Z	2	3	2	3	2
$F(000)$	636	1386	732	990	872
ρ_{calcd} [g cm^{-3}]	0.989	1.039	1.467	0.955	0.973
λ [Å]	0.71069	0.71073	0.71073	0.71073	1.54178
T [K]	125	133	153	153	100
μ [mm^{-1}]	0.05	0.061	0.306	0.052	0.393
θ_{max} [°]	25.00	24.69	25.00	22.54	59.01
reflections measured	5015	5579	10334	2142	12970
$F_{abs}>4\sigma(F_{abs})$	3872	1330	7955	890	3502
unique reflections	5015	1519	7959	894	3758
R_{int}	0.0573	0.0774	0.0365	0.0367	0.0211
$wR_2(F^2)$	-	0.1117	0.1436	0.1040	0.0864
$R(F)$	0.0491	0.0404	0.0616	0.0450	0.0358
parameters refined	380	91	397	67	276
GOF	–	1.036	1.031	1.110	1.027

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