DOI: 10.1002/ejoc.200700639

Towards A,D-(1,10-Phenanthroline)-Bridged Calix[6]arene Dendrimers[‡]

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Keywords: Calixarenes / Dendrimers / Heterocycles / Macrocycles / 1,10-Phenanthrolines / Supramolecular chemistry

5-Bromo-2,9-bis(bromomethyl)-1,10-phenanthroline (**5**) has been synthesized starting from 5-bromo-2,9-dimethyl-1,10-phenanthroline (**1**) in overall yields of up to 53 % by two approaches. Next, calix[6]arene (**7**) was bridged with **5**, giving the A,D-bridged bimacrocyle **9** in 42 % yield. Under application of Sonogashira reaction conditions, trimethylsilyl-protected ethyne was first coupled to the 5-position of the 1,10-phenanthroline, and the ethyne unit was then deprotected and connected with 1,3,5-triiodobenzene (**12**) as a trivalent core. A trimeric first-generation dendrimer **13** was formed, together with a Glaser dimer sideproduct, and could be isolated in 36 % yield.

Introduction

Steric shielding of reactive centers is crucial for the selectivity of many reagents and catalysts. In nature, the active sites of enzymes are usually embedded in clefts or cavities,[1] and synthetic chemists have therefore tried to copy such concave geometries. For rapid synthesis, a start from some preformed macrocyclic structure is popular, and the calixarenes in particular have gained much attention because of their easy syntheses.[2–6] Calix[6]arene **7**[7] (Figure 1) has thus also been bridged,[8,9] and the A,D-(1,10-phenanthroline)-bridged calixarene **8**[10,11] has proven to be an interesting ligand for copper(I). In contrast with other concave 1,10-phenanthrolines,[12] this ligand promotes *syn* selectivity in the cyclopropanation of alkenes such as styrene or indene.[13,14]

For an efficient catalytic process, the provision of a selective catalyst is inevitable, but its synthesis is often tedious. Therefore, recycling of catalysts is profitable. The separation of a catalyst from a reaction mixture is facilitated if it is bound to a polymer, allowing easy recycling by filtration,[15,16] but a polymeric support of a catalyst is not always inert and may influence the outcome of a reaction, especially if the diffusion of substrates into the polymeric compound is uneven along the polymer.

Identical environments for groups attached to polymeric materials are only found in dendrimers. These are a special class of polymers, which combine two properties from polymer and from non-polymer chemistry: they possess high molecular weights but they are monodisperse, well-defined molecules.[17–20] By combination of a multivalent core with branching units, dendrimers are built up generation by generation. The number of reactive groups of the core is multiplied by each generation of branching units, but the environment of the reactive groups in each generation is always identical. Therefore, catalytic groups bound to the surface of a dendrimer all possess the same environment, and so they should all exhibit the same reactivity and selectivity. Because the catalytic moieties are bound on the surface of the dendrimer, their reactivity and selectivity should be very similar to those of the non-polymeric analogue. With an increasing number of generations, the size and molecular weight of the dendrimer increases drastically, ultimately allowing a separation from the reaction mixture by ultrafiltration.[21]

Results and Discussion

The first step of an envisaged synthesis towards 1,10-phenanthroline-bridged calixarene dendrimers would therefore be the bridging of calix[6]arene **7** with a 1,10-phenanthroline unit containing an additional functionality in, for instance, the 5-position. As in the case of the neocuproine dendrimers,[22] a 5-ethynyl-2,9-bis(methylene)-1,10-phenanthroline bridge was chosen.

To obtain a suitably functionalized bimacrocyclic calix[6]arene **11**, two synthetic pathways are conceivable: (i) bridging of the calixarene **7** with a 1,10-phenanthroline building block already containing the ethynyl group in its 5-position, or (ii) bridging of the calixarene **7** with 5-bromo-2,9-bis(bromomethyl)-1,10-phenanthroline (**5**) as a precursor for the introduction of an ethynyl unit. Because of the basic reaction conditions required for the bridging, the use of a reagent with a free acetylenic functionality in the 5-position was not advisable, and furthermore, a trimethylsilyl-protected acetylene precursor would not be very

[‡] Concave Reagents, 54. Part 53: O. Winkelmann, D. Lindner, J. Lacour, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2007**, 3687–3697.

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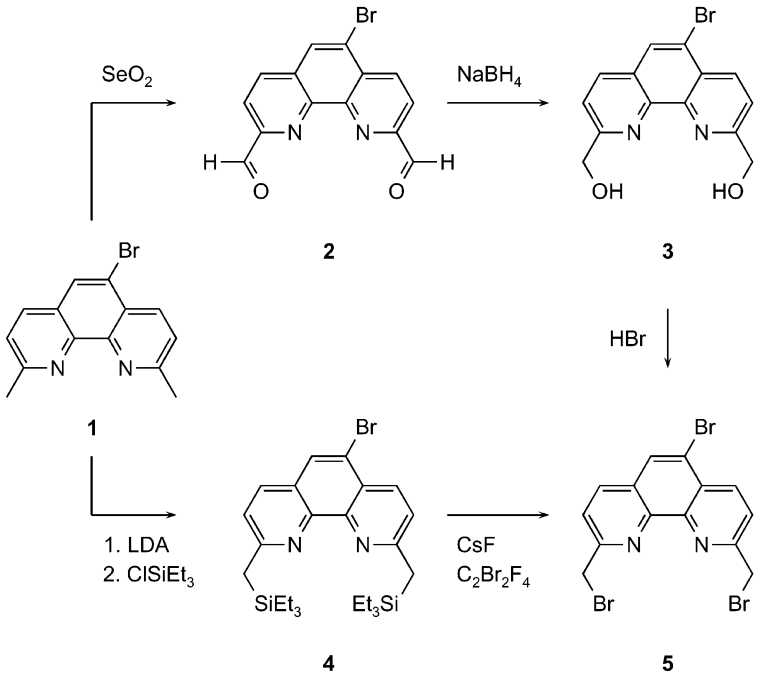


stable. The route via the 5-bromide was therefore chosen, so 5-bromo-2,9-bis(bromomethyl)-1,10-phenanthroline (**5**) had to be synthesized as the bridging reagent.

In analogy to the synthesis of 2,9-bis(bromomethyl)-1,10-phenanthroline (**6**) from 2,9-dimethyl-1,10-phenanthroline (neocuproine),[23] 5-bromo-2,9-dimethyl-1,10-phenanthroline (**1**) could also be transformed into the corresponding brominated neocuproine derivative **5**. Oxidation of **1** with selenium dioxide gave the dialdehyde **2** in 62% yield, and this was followed by reduction with sodium borohydride (72% yield of **3**) and bromination with 48% hydrobromic acid (76% yield of **5**). Because of the moderate

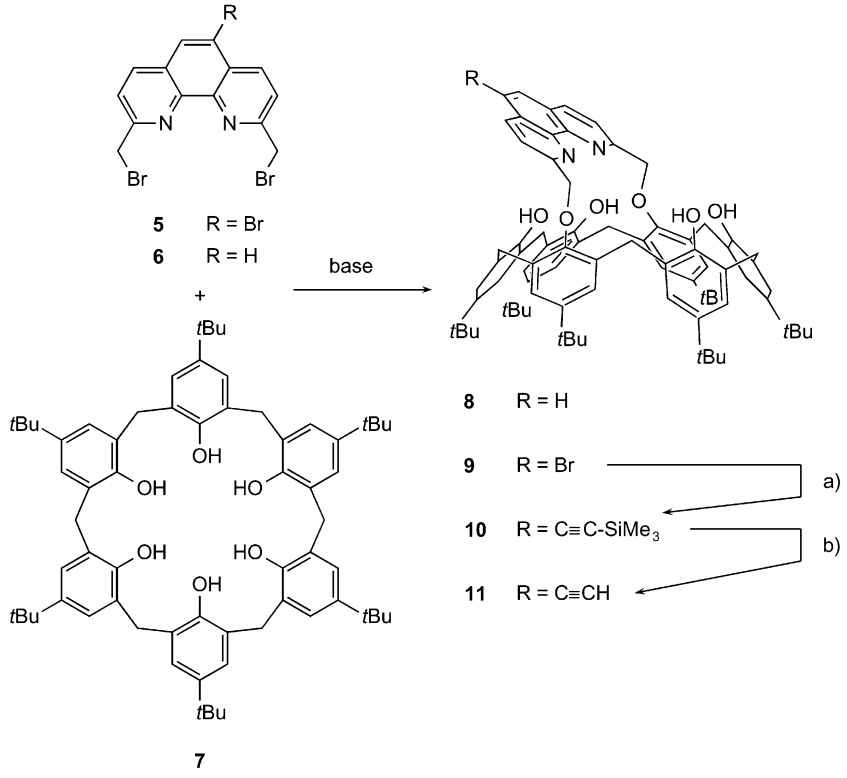


Figure 1. Synthesis of 5′-substituted 1,10-phenanthroline-bridged calix[6]arenes **9**–**11**. (a) $Me_3Si–C{\equiv}C–H$, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3. (b) n-Bu_4NF. Due to the perspective, not all double bonds and substituents are visible in the projection of **8**–**11**.

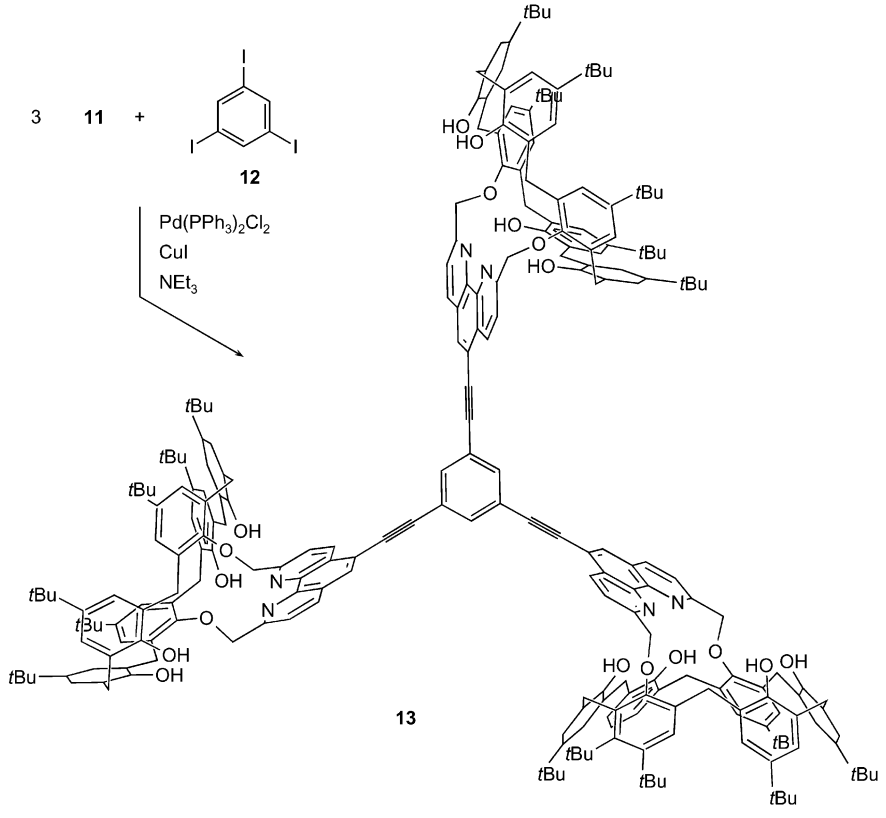
overall yield of 34%, a second route to **5** was established, taking advantage of the easy accessibility of bis(silylated) 5-bromo-1,10-phenanthrolines.[24] 5-Bromo-2,9-bis[(*tert*-butyldimethylsilyl)methyl]-1,10-phenanthroline had already been synthesized,[24] but the *tert*-butyldimethylsilyl groups could not be replaced by bromine. Optimization by variation of the silyl group led to the triethylsilyl derivatives as a compromise between stability of the C–Si bond and reactivity towards substitution by bromine. Deprotonation of 5-bromo-1,10-phenanthroline with lithium diisopropylamide and treatment with chlorotriethylsilane gave the bis(silylated) bromo-1,10-phenanthroline **4** in 72% yield. The two silyl groups could then be replaced by bromine in 74% yield when a mixture of cesium fluoride and 1,2-dibromo-1,1,2,2-tetrafluoroethane was used. The silylation route gives a better overall yield (53%) than the first synthetic access of **5** described above, is quicker, and produces **5** in sufficient purity for the subsequent reaction with calix[6]arene (**7**).

Analogously to the synthesis of the parent 1,10-phenanthroline-bridged calix[6]arene **8**, the bridging of calix[6]-arene **7** with 5-bromo-substituted 1,10-phenanthroline **5** was successful, and the resulting bimacrocycle **9** could be isolated in 42% yield. The pleasing yield of this reaction ensures that enough material is accessible for the following steps of the reaction sequence.

Next, bromo derivative **9** was used as starting material in a Sonogashira coupling with (trimethylsilyl)acetylene, followed by removal of the trimethylsilyl group from **10**. The coupling yielded the protected acetylene **10** in 54% yield. For the deprotection, tetra-*n*-butylammonium fluoride was the reagent of choice, and the resulting acetylene **11** could be isolated in 91% yield (Figure 1).

With application of Sonogashira conditions once again,[25] this acetylene **11** was then treated with 1,3,5-triiodobenzene (**12**)[26] to provide a calix[6]arene trimer **13**, which can be regarded as the first generation of the corresponding dendrimers. Bis(triphenylphosphane)palladium(II) dichloride and copper(I) iodide in a benzene/triethylamine mixture at 50 °C were also successful reagents in the case of 5-bromoneocuproine (**1**) and of **9**, so these reactions conditions were applied in the coupling of 1,3,5-triiodobenzene (**12**) with 3.3 equiv. of the acetylene-substituted bridged calixarene **11**. After 18 h of reaction time, MS analysis revealed a mixture of products. Besides the desired trimer **13**, a number of other products had been produced, including larger quantities of two components, each containing two bridged calix[6]arenes. One of these calixarene dimers was the incompletely coupled intermediate, in which only two of the three iodo functions of the core had reacted, while the other dimer was the Glaser coupling product of **11**, a diyne. These homodimeric side products are frequently found in Sonogashira couplings (Figure 2).[25]

When 5 equiv. of **11** was used, however, the number of products was reduced: only the desired trimer **13** and the Glaser coupling homodimer were identified in a MALDI-MS. The trimer **13** could be separated by chromatography on silica gel with use of a chromatotron, and a 40% yield of **13** was isolated (Figure 3). In addition to the matching



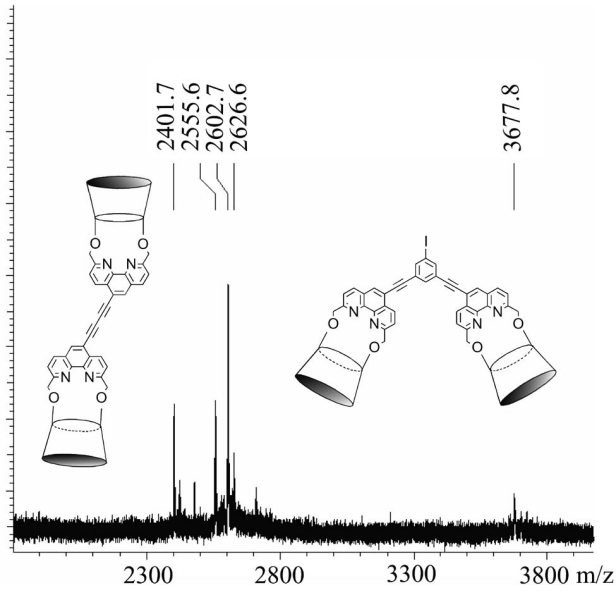


Figure 2. Part of a MALDI-TOF mass spectrum of the reaction mixture obtained from a Sonogashira coupling between the triiodide **12** and the acetylenic calix[6]arene **11**. Besides a smaller amount of the desired trimer **13** (*m*/*z* = 3677.8, protonated), a product of incomplete coupling (*m*/*z* = 2602.7, protonated) and a homodimer from a Glaser coupling (*m*/*z* = 2401.7, protonated) are evident. The sideproducts are drawn with truncated cones representing the calixarene parts.

mass in the MALDI-MS, the identity of **13** was confirmed by its NMR spectrum. Only one signal was found for the hydrogen atoms of the benzene core, and the intensities match those of single hydrogen atoms of the 1,10-phenanthroline bridge [for instance: δ = 8.00 (s, 3 H, Ar-*H*), 8.89 (d, *J* = 8.5 Hz, 3 H, phen-H^4) ppm].

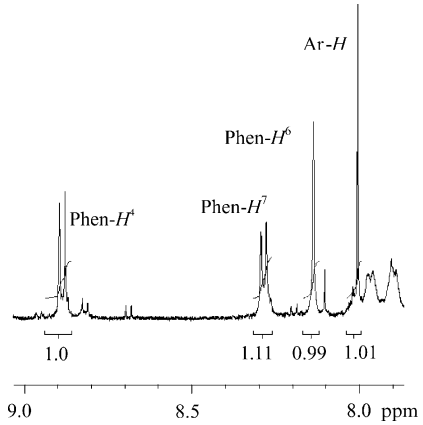


Figure 3. Part of the ^{1}H NMR spectrum of the calixarene trimer **13** confirming the 3:1 ratio of 1,10-phenanthroline-bridged calix[6]arenes and the core (3 × phen-H^4 and 3 H from the core).

Conclusions

Concave calix[6]arenes can be incorporated into dendritic structures by use of a 5-bromo-substituted 1,10-phenanthroline bridge. This synthesis of the trimeric calix[6]arene **13** and experience[22] in the synthesis of related neocuproine dendrimers of higher generation have now opened up the route to further generations of dendrimers covered with catalytic sites based on bridged calix[6]arenes.

Experimental Section

General Remarks: All reactions requiring dry solvents were carried out by standard Schlenk techniques under argon. Dry solvents were purchased or obtained with suitable desiccants: dioxane and benzene were distilled from sodium (benzophenone as indicator). Dry benzene was stored over molecular sieves (4 Å). The following compounds were commercially available and used without further purification: selenium dioxide (Fluka), sodium borohydride (Fluka), THF (> 99.8%, < 0.005% water, Merck), lithium diisopropylamide (2 M solution in THF/heptane/ethylbenzene, Fluka), chlorotriethylsilane (Acros), hydrobromic acid (48%, Fluka), cesium fluoride (Fluka), 1,2-dibromo-1,1,2,2-tetrafluoroethane (ABCR), DMF (> 99.5%, < 0.01% water, Fluka), triethylamine (Fluka), potassium trimethylsilanolate (Aldrich), (trimethylsilyl)acetylene (Fluka), copper(I) iodide (Merck), bis(triphenylphosphane)palladium(II) dichloride (Fluka), tetra-*n*-butylammonium fluoride trihydrate (Fluka), potassium cyanide (Aldrich). 5-Bromo-2,9-dimethyl-1,10-phenanthroline (**1**),[24] *tert*-butylcalix[6]arene (**7**),[27] and 1,3,5-triiodobenzene (**12**)[26] were synthesized according to literature procedures. (Flash) chromatography was carried out on silica (Macherey–Nagel, 0.04–0.063 mesh) or aluminium oxide (0.05–0.15 mm, pH = 9.5 ± 0.5). NMR spectra were recorded with Bruker AM 300 (300 MHz) or Bruker DRX 500 (500 MHz) spectrometers with tetramethylsilane as internal standard. Assignments are supported by HMBC, HSQC, and COSY experiments. IR spectra were obtained with a Perkin–Elmer 1600 Series Fourier Transform spectrometer. Mass spectra were recorded with Finnigan MAT 8200 or 8230 instruments and with a Biflex III MALDI-TOF mass spectrometer (Bruker-Daltonics, with 2,5-dihydroxybenzoic acid as matrix). The elemental analyses were carried out with a HEKAtech GmbH EA3000CHNS instrument.

5-Bromo-1,10-phenanthroline-2,9-dicarbaldehyde (2): A suspension of 5-bromo-2,9-dimethyl-1,10-phenanthroline (**1**, 1.43 g, 5.00 mmol) in dioxane/water (96:4, 30 mL) was added dropwise over 30 min to a solution of selenium dioxide (2.22 g, 20.0 mmol) in dioxane/water (96:4, 50 mL) with warming to 40 °C. After heating of the mixture at reflux for 1.5 h, the hot mixture was filtered through several layers of kieselguhr, separated by filtration papers. The absorbing material was washed with hot dioxane (100 mL). After evaporation of the solvent, the residue was purified by chromatography (aluminium oxide neutral; dioxane/ethanol, 4:1) to yield **2** (975 mg, 62%), m.p. 227 °C (decomp.). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 10.33 (d, *J* = 0.9 Hz, 1 H, PhenC^2-C*H*O), 10.29 (d, *J* = 0.9 Hz, 1 H, PhenC^9-C*H*O), 8.83 (dd, *J* = 8.5, *J* = 0.9 Hz, 1 H, Phen-H^4), 8.71 (s, 1 H, Phen-H^6), 8.69 (dd, *J* = 8.3, *J* = 0.9 Hz, 1 H, Phen-H^7), 8.35 (d, *J* = 8.5 Hz, 1 H, Phen-H^3), 8.27 (d, *J* = 8.3 Hz, 1 H, Phen-H^8) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 193.40 (PhenC^9-*C*HO), 193.13 (PhenC^2-*C*HO), 152.39 (Phen-C^9), 152.35 (Phen-C^2), 145.54 (Phen-C^{10b}), 144.52 (Phen-C^{10a}), 137.67 (Phen-C^7), 137.65 (Phen-C^4), 132.38 (Phen-C^6), 131.37 (Phen-C^{6a}), 129.92 (Phen-C^{4a}), 122.41 (Phen-C^5), 121.00 (Phen-C^3), 120.68 (Phen-C^8) ppm. IR (KBr): $\tilde{\nu}$ = 1704 (C=O), 1594 (arom. C=C), 826, 784 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 316 (100), 314 (99) [M]$^+$, 288 (76), 486 (77) [M – CHO]$^+$, 260 (86), 258 (91) [M – 2 CHO]$^+$, 177 (34) [M – Br – 2 CHO]$^+$. HR-MS:

calcd. for $C_{14}H_7{}^{79}BrN_2O_2$ 313.96909, found 313.96900 (0.3 ppm); calcd. for $C_{14}H_7{}^{81}BrN_2O_2$ 315.96704, found 315.96690 (0.4 ppm).

5-Bromo-2,9-bis(hydroxymethyl)-1,10-phenanthroline (3): Sodium borohydride (181 mg, 4.78 mmol) was added in portions under argon and with ice cooling to a suspension of 5-bromo-1,10-phenanthroline-2,9-dicarbaldehyde (**2**, 965 mg, 3.06 mmol) in dry ethanol (30 mL). After the system had been heated at reflux for 3 h, acetone (10 mL) was added and heating was continued for 15 min. The solvent was evaporated in vacuo, and the residue was heated with water (30 mL) at reflux for 10 min. After filtration at room temperature, the precipitate was dried in vacuo (< 0.1 mbar), to yield **3** (706 mg, 72%), m.p. 205 °C (decomp.). ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 8.65 (d, J = 8.5 Hz, 1 H, Phen-H^4), 8.47 (d, J = 8.3 Hz, 1 H, Phen-H^7), 8.42 (s, 1 H, Phen-H^6), 8.02 (d, J = 8.5 Hz, 1 H, Phen-H^3), 7.90 (d, J = 8.3 Hz, 1 H, Phen-H^8), 5.77 (s, 2 H, CH_2OH), 4.92 (s, 2 H, PhenC^2-CH_2OH), 4.87 (s, 2 H, PhenC^9-CH_2OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 163.35 (Phen-C^9), 163.03 (Phen-C^2), 144.92 (Phen-C^{10b}), 143.75 (Phen-C^{10a}), 136.21 (Phen-C^7), 136.00 (Phen-C^4), 129.30 (Phen-C^6), 127.80 (Phen-C^{6a}), 126.15 (Phen-C^{4a}), 121.27 (Phen-C^3), 120.98 (Phen-C^8), 119.00 (Phen-C^5), 64.89 (PhenC^9-CH$_2$OH), 64.59 (PhenC^2-CH$_2$OH) ppm. IR (KBr): $\tilde{\nu}$ = 3332 (O–H), 1604 (arom. C=C), 1497 (aliph. C–H), 1067 (C–H), 820 (arom. C–H) cm^{-1}. MS (EI, 70 eV): m/z (%) = 319 (95), 317 (100) [M – H]$^+$, 239 (14) [M – Br]$^+$, 192 (86) [M – Br – $C_2H_3O_2$]$^+$. HR-MS: calcd for $C_{14}H_{11}{}^{79}BrN_2O_2$ 318.00400, found 318.00200 (0.6 ppm); calcd. for $C_{14}H_{11}{}^{81}BrN_2O_2$ 319.99835, found 319.99820 (0.5 ppm). $C_{14}H_{11}BrN_2O_2$ (319.16): calcd. C 52.69, H 3.47, N 8.78; $C_{14}H_{11}BrN_2O_2\cdot0.6\,H_2O\cdot0.5\,EtOH$ (319.16 + 10.81 + 23.04): calcd. C 51.03, H 4.34, N 7.94; found C 50.96, H 4.06, N 7.63.

5-Bromo-2,9-bis[(triethylsilyl)methyl]-1,10-phenanthroline (4): A solution of lithium diisopropylamide in THF/heptane/ethylbenzene (2 M, 3.00 mL, 6.00 mmol) was added under argon and with ice cooling to a solution of 5-bromo-2,9-dimethyl-1,10-phenanthroline (**1**, 287 mg, 1.00 mmol) in dry THF (10 mL). After removal of the cooling, the mixture was stirred at room temp. for 1 h. Chlorotriethylsilane (309 mg, 2.05 mmol) was added quickly, and stirring was continued for 30 min. With cooling with ice, the reaction was quenched by addition of water (20 mL), and the layers were separated. The aqueous layer was extracted with THF (2 × 20 mL), and the combined organic layers were washed with brine and dried with sodium sulfate. After removal of the solvent, the residue was purified by flash chromatography (silica gel; deactivated with cyclohexane/triethylamine, 5:1; eluent: cyclohexane/ethyl acetate/triethylamine, 100:10:1; R_f = 0.57). After removal of the solvent and drying at < 0.1 mbar for 24 h, **4** was obtained as a yellow oil (370 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (d, J = 8.5 Hz, 1 H, Phen-H^4), 7.93 (s, 1 H, Phen-H^6), 7.91 (d, J = 8.3 Hz, 1 H, Phen-H^7), 7.36 (d, J = 8.5 Hz, 1 H, Phen-H^3), 7.28 (d, J = 8.3 Hz, 1 H, Phen-H^8), 2.79 (s, 2 H, PhenC^2-CH_2), 2.75 (s, 2 H, PhenC^9-CH_2), 0.91 (t, J = 7.9 Hz, 9 H, PhenC^{2}CH$_2$Si-CH$_2$CH_3), 0.89 (t, J = 7.9 Hz, 9 H, PhenC^{9}CH$_2$Si-CH$_2$CH_3), 0.01 (s, 6 H, PhenC^{2}CH$_2$-SiCH_2), –0.02 (s, 6 H, PhenC^{9}CH$_2$SiCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.99 (Phen-C^2), 162.66 (Phen-C^9), 146.12 (Phen-C^{10b}), 145.06 (Phen-C^{10a}), 135.14 (Phen-C^4), 134.51 (Phen-C^7), 127.75 (Phen-C^6), 126.11 (Phen-C^{6a}), 124.94 (Phen-C^{4a}), 123.66 (Phen-C^3), 123.32 (Phen-C^8), 118.74 (Phen-C^5), 26.99 (PhenC^9-CH$_2$), 26.76 (PhenC^2-CH$_2$), 7.31 (PhenC^{2,9}CH$_2$Si-CH$_2$CH_3), 3.32 (PhenC^{2,9}CH$_2$Si-CH$_2$CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2951 (aliph. C–H), 1603 (arom. C=C), 1492 (aliph. C–H), 776, 734 (arom. C–H) cm^{-1}. MS (EI, 70 eV): m/z (%) = 516 (31), 514 (28) [M]$^+$, 487 (92), 485 (78) [M – Et]$^+$. HR-MS: calcd. for $C_{26}H_{39}{}^{79}BrN_2Si_2$ 514.18358, found 514.18378 (–0.2 ppm); calcd. for $C_{26}H_{39}{}^{81}BrN_2Si_2$ 516.18146, found 516.18144 (0.0 ppm).

5-Bromo-2,9-bis(bromomethyl)-1,10-phenanthroline (5). Method A: A solution of 5-bromo-2,9-bis(hydroxymethyl)-1,10-phenanthroline (**3**, 319 mg, 1.00 mmol) in hydrobromic acid (48%, 20 mL) was heated at reflux for 2.5 h. After neutralization of the mixture with sodium carbonate, the precipitate was filtered off and washed intensively with water. The crude product was dried at < 0.1 mbar and used for further reactions without any additional purification. Yield: 339 mg (76%). **Method B:** Cesium fluoride (3.45 mg, 22.7 mmol, previously dried at < 0.1 mbar and 100 °C for 2 h) was added under argon to a solution of 5-bromo-2,9-bis[(triethylsilyl)-methyl]-1,10-phenanthroline (**4**, 2.93 g, 5.68 mmol) and 1,2-dibromo-1,1,2,2-tetrafluoroethane (14.8 g, 56.8 mmol) in dry DMF (30 mL). The mixture was stirred for 24 h, after which water (20 mL) was added while cooling with ice. The precipitate was filtered off, washed with water, and dried at < 0.1 mbar. Yield: 1.87 g (74%). For characterization, product **5** was purified by flash chromatography (silica gel; dichloromethane/ethanol, 40:1; R_f = 0.35), but this resulted in a considerable loss of product. The product was sensitive to basic conditions. M.p. 165 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, J = 8.6 Hz, 1 H, Phen-H^4), 8.21 (d, J = 8.3 Hz, 1 H, Phen-H^7), 8.16 (s, 1 H, Phen-H^6), 8.00 (d, J = 8.6 Hz, 1 H, Phen-H^3), 7.92 (d, J = 8.3 Hz, 1 H, Phen-H^8), 4.98 (s, 2 H, PhenC^2-CH_2Br), 4.94 (s, 2 H, PhenC^9-CH_2Br) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.36 (Phen-C^9), 158.30 (Phen-C^2), 145.20 (Phen-C^{10b}), 144.19 (Phen-C^{10a}), 137.45 (Phen-C^7), 136.54 (Phen-C^4), 129.80 (Phen-C^6), 128.36 (Phen-C^{6a}), 127.46 (Phen-C^{4a}), 124.41 (Phen-C^3), 124.30 (Phen-C^8), 121.12 (Phen-C^5), 34.82 (PhenC^9-CH$_2$Br), 34.10 (PhenC^2-CH$_2$Br) ppm. IR (KBr): $\tilde{\nu}$ = 2949 (aliph. C–H), 1602 (arom. C=C), 1449 (aliph. C–H), 747, 692 (arom. C–H) cm^{-1}. MS (EI, 70 eV): m/z (%) = 448 (8), 446 (26), 444 (26), 442 (8) [M]$^+$, 367 (52), 365 (100), 363 (52) [M – Br]$^+$, 286 (42), 284 (42) [M – 2 Br]$^+$, 205 (59) [M – 3 Br]$^+$. HR-MS: calcd. for $C_{14}H_9{}^{79}Br^{81}Br_2N_2$ 445.82748, found 445.82775 (–0.6 ppm); calcd. for $C_{13}{}^{13}CH_9{}^{79}Br^{81}Br_2N_2$ 446.83084, found 446.83065 (0.4 ppm).

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,40,41-tetrahydroxy-39,42-[5-bromo-2,9-(1,10-phenanthroline)diylbis(methylenoxy)]calix[6]-arene (9): *tert*-Butylcalix[6]arene (**7**, 675 mg, 693 μmol) was suspended in dry THF (40 mL) under argon, and potassium trimethylsilanolate (533 mg, 4.16 mmol) was added, the solid dissolving. After 15 min of stirring, the solution had turned red. After an additional 15 min, a suspension of 5-bromo-2,9-bis(bromomethyl)-1,10-phenanthroline (**5**, 339 mg, 762 μmol) in dry THF (50 mL) was added dropwise, and the mixture was stirred at room temp. for 20 h. HCl (0.1 N, 20 mL) was added, and the THF was evaporated in vacuo. The residue was extracted with dichloromethane (100 mL), the layers were separated, and the organic layer was washed with brine and dried with sodium sulfate, and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography (silica gel; cyclohexane/ethyl acetate, 3:1, for TLC 2:1; R_f = 0.58) giving **9** (356 mg, 42%) as a yellow solid, m.p. 265 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (d, J = 8.6 Hz, 1 H, phen-H^4), 8.14 (d, J = 8.4 Hz, 1 H, phen-H^7), 8.05 (s, 1 H, phen-H^6), 7.90 (d, J = 8.6 Hz, 1 H, phen-H^3), 7.82 (d, J = 8.2 Hz, 1 H, phen-H^8), 7.64 (s, 4 H, OH), 6.93–6.98 (m, 8 H, Ar^{B,C,E,F}-H), 6.87 (m$_c$, 4 H, Ar^{A,B}-H), 5.55 (s, 2 H, phenC^2-CH$_2$), 5.49 (s, 2 H, phenC^9-CH$_2$), 4.49 (d, J = 15.4 Hz, 2 H, Ar-CH$_2$-Ar), 4.48 (d, J = 15.4 Hz, 2 H, Ar-CH$_2$-Ar), 3.79 (d, J = 14.6 Hz, 2 H, Ar-CH$_2$-Ar), 3.61 (d, J = 14.6 Hz, 2 H, Ar-CH$_2$-Ar), 3.53 (d, J = 15.4 Hz, 4 H, Ar-CH$_2$-Ar), 1.16 [s, 9 H, C(CH$_3$)$_3$], 1.16 [s, 9 H, C(CH$_3$)$_3$], 1.12 [s, 18 H, C(CH$_3$)$_3$], 1.12 [s, 18 H, C(CH$_3$)$_3$] ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.99 (phen-C^2), 158.76 (phen-C^9), 151.00 ($Ar^{A,D}$-C^1), 149.70 ($Ar^{B,C,E,F}$-C^1), 147.12, 147.07 ($Ar^{A,D}$-C^4), 145.62 (phen-C^{10b}), 144.59 (phen-C^{10a}), 142.18 ($Ar^{B,C,E,F}$-C^4), 136.76 (phen-C^4), 135.97 (phen-C^7), 132.98 ($Ar^{B,C,E,F}$-$C^{2,6}$), 129.06 (phen-C^6), 128.07 (phen-C^{6a}), 127.10 (phen-C^{4a}), 126.51, 126.49 ($Ar^{A,D}$-$C^{2,6}$), 125.57, 125.52 ($Ar^{A,D}$-$C^{3,5}$), 125.14 ($Ar^{B,C,E,F}$-$C^{3,5}$), 120.58 (phen-C^3), 120.44 (phen-C^8), 120.16 (phen-C^5), 73.59 (phenC^9-CH_2), 73.46 (phenC^2-CH_2), 34.25 [$Ar^{A,D}$-$C(CH_3)_3$], 33.80 [$Ar^{B,C,E,F}$-$C(CH_3)_3$], 32.20 (Ar-CH_2), 31.79 (Ar-CH_2), 31.46 [$Ar^{B,C,E,F}$-$C(CH_3)_3$], 31.36 [$Ar^{A,D}$-$C(CH_3)_3$] ppm. The proper assignment of the signals was achieved by using 2D-NMR techniques, i.e. HMBC, HSQC, COSY. IR (KBr): $\tilde{\nu}$ = 3421 (O–H), 2960 (aliph. C–H), 1605 (arom. C=C), 1482 (aliph. C–H), 1199 (O–H), 875 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 1257 (100), 1255 (70) [M]$^+$. $C_{80}H_{91}BrN_2O_6$ (1256.56): calcd. C 76.47, H 7.30, N 2.23; $C_{80}H_{91}BrN_2O_6 \cdot 1.5\,H_2O \cdot 0.7\,C_6H_{12}$ (1256.56 + 27.02 + 58.91): calcd. C 75.33, H 7.69, N 2.09; found C 75.28, H 7.68, N 1.91.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,40,41-tetrahydroxy-39,42-{5-[(trimethylsilyl)ethynyl]-2,9-phenanthroline-1,10-diylbis(methylenoxy)}calix[6]arene (10): A solution of 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,40,41-tetrahydroxy-39,42-[5-bromo-2,9-phenanthroline-1,10-diylbis(methylenoxy)]calix[6]arene (**9**, 101 mg, 80.0 μmol) in dry benzene (5 mL) and dry triethylamine (1 mL) was degassed with ultrasound under argon for ca. 30 min. Under Schlenk conditions, first (trimethylsilyl)acetylene (111 μL, 800 μmol) and then copper(I) iodide (1.52 mg, 4.00 μmol) and bis(triphenylphosphane)palladium(II) dichloride (2.81 mg, 8.00 μmol) were added, and the mixture was treated in an ultrasound bath for up to 18 h (TLC monitoring), which caused a warming to 50 °C. The solvents were removed in vacuo, and the residue was dissolved in dichloromethane. To avoid potential complex formation between the 1,10-phenanthroline moiety and copper ions, the mixture was washed once with an equal volume of a solution of aqueous potassium cyanide (2 M), and twice with brine. After drying with sodium sulfate, the solvent was removed and the crude product purified by chromatography (chromatotron; silica gel; cyclohexane/ethyl acetate, 5:1; R_f = 0.29) to give **10** (55 mg, 54%), m.p. 169 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 8.5 Hz, 1 H, phen-*H*^{4}), 8.21 (d, *J* = 8.3 Hz, 1 H, phen-*H*^{7}), 8.01 (s, 1 H, phen-*H*^{6}), 7.89 (d, *J* = 8.5 Hz, 1 H, phen-*H*^{3}), 7.86 (d, *J* = 8.3 Hz, 1 H, phen-*H*^{8}), 7.71 (s, 2 H, O*H*), 7.60 (s, 2 H, O*H*), 6.97–6.99 (m, 8 H, $Ar^{B,C,E,F}$-*H*), 6.90, (m_c, 2 H, $Ar^{A,B}$-*H*), 6.87, (m_c, 2 H, $Ar^{A,B}$-*H*), 5.56 (s, 2 H, phenC^2-CH_2), 5.52 (s, 2 H, phenC^9-CH_2), 4.51 (d, *J* = 15.3 Hz, 2 H, Ar-CH_2-Ar), 4.50 (d, *J* = 15.3 Hz, 2 H, Ar-CH_2-Ar), 3.82 (d, *J* = 14.7 Hz, 2 H, Ar-CH_2-Ar), 3.61 (d, *J* = 14.7 Hz, 2 H, Ar-CH_2-Ar), 3.55 (d, *J* = 15.4 Hz, 2 H, Ar-CH_2-Ar), 3.54 (d, *J* = 15.4 Hz, 2 H, Ar-CH_2-Ar), 1.18 [s, 9 H, C(CH_3)$_3$], 1.17 [s, 9 H, C(CH_3)$_3$], 1.14 [s, 18 H, C(CH_3)$_3$], 1.12 [s, 18 H, C(CH_3)$_3$], 0.38 [s, 9 H, C≡C-Si(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.27 (phen-*C*^{9}), 158.44 (phen-*C*^{2}), 151.11 ($Ar^{A,D}$-*C*^{1}), 149.75, 149.73 ($Ar^{B,C,E,F}$-*C*^{1}), 147.06, 146.99 ($Ar^{A,D}$-*C*^{4}), 145.15 (phen-*C*^{10a}), 144.80 (phen-*C*^{10b}), 142.16, 142.13 ($Ar^{B,C,E,F}$-*C*^{4}), 136.71 (phen-*C*^{7}), 135.65 (phen-*C*^{4}), 133.08, 133.00 ($Ar^{B,C,E,F}$-*C*^{2,6}), 130.74 (phen-*C*^{6}), 127.58 (phen-*C*^{4a}), 127.15 (phen-*C*^{6a}), 126.54, 126.51 ($Ar^{A,D}$-*C*^{2,6}), 125.60, 125.46 ($Ar^{A,D}$-*C*^{3,5}), 125.14, 125.06 ($Ar^{B,C,E,F}$-*C*^{3,5}), 120.18 (phen-*C*^{8}), 120.06 (phen-*C*^{3}), 119.19 (phen-*C*^{5}), 101.41 (phen-*C*≡C), 100.88 (phen-C≡*C*), 73.60 (phenC^9-*C*H_2), 73.56 (phenC^2-*C*H_2), 34.27 [$Ar^{A,D}$-*C*$(CH_3)_3$], 33.82 [$Ar^{B,C,E,F}$-*C*$(CH_3)_3$], 32.30 (Ar-CH_2), 31.61 (Ar-CH_2), 31.47 [$Ar^{B,C,E,F}$-C(*C*H_3)$_3$], 31.38 [$Ar^{A,D}$-C(*C*H_3)$_3$], 0.02 [Si(*C*H_3)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3372 (O–H), 2957 (aliph. C–H), 2066 (C=C), 1603 (arom. C=C), 1482 (aliph. C–H), 1198 (O–H), 843 (arom. C–H) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 1313 (91) [M + K]$^+$, 1297 (100) [M + Na]$^+$. HR-MS: calcd. for $C_{85}H_{101}N_2O_6Si$ 1273.7429, found 1273.7384 (3.5 ppm); calcd. for $C_{84}{}^{13}CH_{101}N_2O_6Si$ 1274.7462, found 1274.7452 (0.8 ppm). $C_{85}H_{100}N_2O_6Si$ (1273.87): calcd. C 80.15, H 7.91, N 2.20; $C_{85}H_{100}N_2O_6Si \cdot 2\,H_2O \cdot 0.6\,C_6H_{12}$ (1273.87 + 36.02 + 50.50): calcd. C 78.23, H 8.24, N 2.06; found C 78.20, H 8.09, N 1.71.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,40,41-tetrahydroxy-39,42-[5-ethynyl-2,9-phenanthroline-1,10-diylbis(methylenoxy)]calix[6]-arene (11): A solution of 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,40,41-tetrahydroxy-39,42-{5-[(trimethylsilyl)ethynyl]-2,9-phenanthroline-1,10-diylbis(methylenoxy)}calix[6]arene (**10**, 220 mg, 173 μmol) in THF (15 mL, HPLC grade) was cooled to –78 °C, and TBAF·3 H_2O (59.9 mg, 190 μmol) in THF (4 mL, HPLC grade) was added. After the mixture had been stirred at –78 °C for 1 h, an equal volume of water was added [TLC monitoring (silica gel; cyclohexane/ethyl acetate, 5:1; R_f = 0.15) showed complete conversion after 20 min]. After the mixture had warmed to room temp., the same volume of dichloromethane was added, and the layers were separated. The aqueous layer was extracted with the same volume of water, and the combined organic layers were washed with brine and dried with sodium sulfate. After evaporation to dryness, pure **11** (190 mg, 91%) remained, m.p. 302 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 8.5 Hz, 1 H, phen-*H*^{4}), 8.21 (d, *J* = 8.3 Hz, 1 H, phen-*H*^{7}), 8.03 (s, 1 H, phen-*H*^{6}), 7.87 (d, *J* = 8.5 Hz, 1 H, phen-*H*^{3}), 7.86 (d, *J* = 8.3 Hz, 1 H, phen-*H*^{8}), 7.67 (s, 2 H, O*H*), 7.54 (s, 2 H, O*H*), 6.95–6.97 (m, 8 H, $Ar^{B,C,E,F}$-*H*), 6.88 (m_c, 2 H, $Ar^{A,B}$-*H*), 6.85 (m_c, 2 H, $Ar^{A,B}$-*H*), 5.53 (s, 2 H, phenC^2-CH_2), 5.51 (s, 2 H, phenC^9-CH_2), 4.50 (d, *J* = 15.3 Hz, 2 H, Ar-CH_2-Ar), 4.48 (d, *J* = 15.3 Hz, 2 H, Ar-CH_2-Ar), 3.80 (d, *J* = 14.7 Hz, 2 H, Ar-CH_2-Ar), 3.60 (d, *J* = 14.7 Hz, 2 H, Ar-CH_2-Ar), 3.53 (d, *J* = 14.6 Hz, 4 H, Ar-CH_2-Ar), 3.52 (s, 1 H, C≡C*H*), 1.16 [s, 9 H, C(CH_3)$_3$], 1.15 [s, 9 H, C(CH_3)$_3$], 1.12 [s, 18 H, C(CH_3)$_3$], 1.11 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.59 (phen-*C*^{9}), 158.53 (phen-*C*^{2}), 151.15 ($Ar^{A,D}$-*C*^{1}), 149.78, 149.73 ($Ar^{B,C,E,F}$-*C*^{1}), 147.15, 147.01 ($Ar^{A,D}$-*C*^{4}), 145.31 (phen-*C*^{10a}), 144.88 (phen-*C*^{10b}), 142.20, 142.15 ($Ar^{B,C,E,F}$-*C*^{4}), 136.74 (phen-*C*^{7}), 135.45 (phen-*C*^{4}), 133.09, 133.00 ($Ar^{B,C,E,F}$-*C*^{2,6}), 131.35 (phen-*C*^{6}), 127.64 (phen-*C*^{4a}), 127.04 (phen-*C*^{6a}), 126.56, 126.33 ($Ar^{A,D}$-*C*^{2,6}), 125.63, 125.50 ($Ar^{A,D}$-*C*^{3,5}), 125.17, 125.11 ($Ar^{B,C,E,F}$-*C*^{3,5}), 120.26 (phen-*C*^{8}), 120.20 (phen-*C*^{3}), 118.21 (phen-*C*^{5}), 82.92 (phen-C≡*C*H), 80.36 (phen-*C*≡CH), 73.66 (phen$C^{2,9}$-*C*H_2), 34.27 [$Ar^{A,D}$-*C*$(CH_3)_3$], 33.82 [$Ar^{B,C,E,F}$-*C*$(CH_3)_3$], 32.32 (Ar-CH_2), 31.69 (Ar-CH_2), 31.47 [$Ar^{B,C,E,F}$-C(*C*H_3)$_3$], 31.39, 31.37 [$Ar^{A,D}$-C(*C*H_3)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3307 (O–H), 2957 (aliph. C–H), 1604 (arom. C=C), 1482 (aliph. C–H), 1197 (O–H), 873, 818 (arom. C–H) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 1225 (56) [M + Na]$^+$, 1203 (100) [M + H]$^+$. $C_{82}H_{92}N_2O_6$ (1201.69): calcd. C 81.96, H 7.72, N 2.33; $C_{82}H_{92}N_2O_6 \cdot 3.5\,H_2O \cdot 0.7\,C_6H_{12}$ (1201.69 + 63.04 + 58.91); calcd. C 78.22, H 8.18, N 2.12; found C 78.20, H 8.24, N 2.11.

1,3,5-Tris(5′-{5′′,11′′,17′′,23′′,29′′,35′′-hexa-*tert*-butyl-37′′,38′′,40′′,41′′-tetrahydroxy-39′′,42′′-[2′,9′-phenanthroline-1,10-diylbis(methylenoxy)]calix[6]arene}ethynyl)benzene (13): A solution of 1,3,5-triiodobenzene (**12**, 6.14 mg, 13.5 μmol) in dry benzene (5 mL) and dry triethylamine (1 mL) was degassed with ultrasound under argon for 30 min. Under Schlenk conditions, first **11** (81.0 mg, 67.4 μmol) and then copper(I) iodide (1.54 mg, 4.05 μmol) and bis(triphenylphosphane)palladium(II) dichloride (2.84 mg, 8.10 μmol) were added, and the mixture was treated in an ultrasound bath for 18 h (TLC monitoring), which caused a warming to 50 °C. The solvents were removed in vacuo, and the residue was dissolved in dichloromethane. To avoid potential com-

plex formation between the 1,10-phenanthroline moiety and copper ions, the mixture was washed once with an equal volume of a solution of aqueous potassium cyanide (2 M) and twice with brine. After drying with sodium sulfate, the solvent was removed, and the crude product was purified by chromatography (chromatotron; silica gel; cyclohexane/ethyl acetate, first 10:1, then 5:1; R_f = 0.05) to give **13** (20.0 mg, 36%) as a yellow solid, m.p. 277 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.89 (d, J = 8.5 Hz, 3 H, phen-H^4), 8.29 (d, J = 8.3 Hz, 3 H, phen-H^7), 8.14 (s, 3 H, phen-H^6), 8.00 (s, 3 H, Ar-H), 7.97 (d, J = 8.5 Hz, 3 H, phen-H^3), 7.89 (d, J = 8.3 Hz, 3 H, phen-H^8), 7.83–7.51 (s, 12 H, OH), 6.97 (m_c, 24 H, $Ar^{B,C,E,F}$-H), 6.87 (m_c, 12 H, $Ar^{A,B}$-H), 5.58 (s, 6 H, phenC^2-CH_2), 5.54 (s, 6 H, phenC^9-CH_2), 4.52 (d, J = 15.3 Hz, 6 H, Ar-CH_2-Ar), 4.50 (d, J = 15.3 Hz, 6 H, Ar-CH_2-Ar), 3.81 (d, J = 14.5 Hz, 2 H, Ar-CH_2-Ar), 3.62 (d, J = 14.7 Hz, 6 H, Ar-CH_2-Ar), 3.55 (d, J = 15.3 Hz, 12 H, Ar-CH_2-Ar), 1.17 [s, 27 H, C(CH_3)$_3$], 1.16 [s, 27 H, C(CH_3)$_3$], 1.12 [s, 108 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.54 (phen-C^9), 158.79 (phen-C^2), 151.04 ($Ar^{A,D}$-C^1), 149.70 ($Ar^{B,C,E,F}$-C^1), 147.12, 147.04 ($Ar^{A,D}$-C^4), 145.28 (phen-C^{10a}), 144.97 (phen-C^{10b}), 142.18 ($Ar^{B,C,E,F}$-C^4), 136.80 (phen-C^7), 135.45 (phen-C^4), 132.99 ($Ar^{B,C,E,F}$-$C^{2,6}$), 130.86 (phen-C^6), 127.44 (phen-C^{4a}), 127.22 (phen-C^{6a}), 126.50, 126.25 ($Ar^{A,D}$-$C^{2,6}$), 126.12 (Ar-$C^{2,4,6}$), 125.58, 125.49 ($Ar^{A,D}$-$C^{3,5}$), 125.13 ($Ar^{B,C,E,F}$-$C^{3,5}$), 124.10 (Ar-$C^{1,3,5}$), 120.35 (phen-C^8), 120.23 (phen-C^3), 118.63 (phen-C^5), 93.12 (phen-C≡C), 87.86 (phen-C≡C), 73.61 (phen$C^{2,9}$-CH$_2$), 34.25 [$Ar^{A,D}$-C(CH$_3$)$_3$], 33.80 [$Ar^{B,C,E,F}$-C(CH$_3$)$_3$], 32.24 (Ar-CH$_2$), 31.65 (Ar-CH$_2$), 31.45 [$Ar^{B,C,E,F}$-C(CH$_3$)$_3$], 31.35 [$Ar^{A,D}$-C(CH$_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3422 (O–H), 2960 (aliph. C–H), 1604 (arom. C=C), 1482 (aliph. C–H), 1198 (O–H), 875, 801 (arom. C–H) cm^{-1}. MS (MALDI-TOF): m/z (%) = 3700 (50) [M + Na]$^+$, 3679 (57) [M + H]$^+$, 2732 (57) [M + Na – *tert*-butylcalix[6]-arene]$^+$, 2710 (71) [M + H – *tert*-butylcalix[6]arene]$^+$, 1760 (53) [M + Na – 2 *tert*-butylcalix[6]arene]$^+$, 1738 (100) [M + H – 2 *tert*-butylcalix[6]arene]$^+$. $C_{252}H_{276}N_6O_{18}$ (3677.13): calcd. C 82.32, H 7.57, N 2.29; $C_{252}H_{276}N_6O_{18}$·12 H_2O·2 C_6H_{12}·1.8 $CDCl_3$ (3677.13 + 168.32 + 218.51 + 216.70): calcd. C 74.62, H 7.63, N 1.96; found C 74.50, H 7.80, N 1.94. Even with drying at < 0.1 mbar for days, the included solvents could not be removed. The water and cyclohexane molecules were found in the NMR spectra. The sample for analysis was taken from the NMR examination, explaining the $CDCl_3$ contents.

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Received: July 11, 2007
Published Online: November 2, 2007

