From a Calix[4]arene to a Hexameric Supracycle

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We investigated a simple and economic method for the selective *O*-arylation of calix[4]arenes with N-heteroarenes with temperature control under neat conditions. The resulting multidentate ligands are potential building blocks for transition metal complexes or supramolecular aggregates: dipyridoxycalixarene **3b**, together with palladium(II) chloride, produced a complex with a fascinating crystal structure, six molecules self-assembling into hexameric supracycles with an outer diameter of roughly 30 Å and an inner diameter of roughly 7 Å, containing six dichloromethane molecules. The supracycles themselves are organised into hexagonal assembled tubes along the *c* axis.

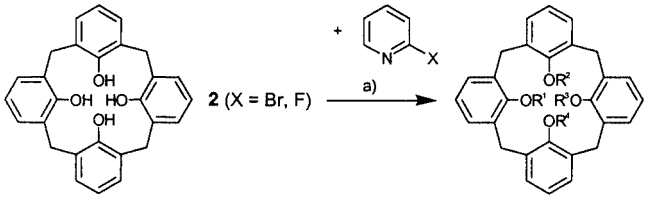
Introduction

Functionalized calixarenes are fascinating objects for study of various aspects of their supramolecular chemistry, from simple host-guest interactions[1] to applications as artificial sensors,[2] synthetic receptors for biological agents,[3] as antibody mimetics[4] or as building blocks for molecular boxes.[5] We set out to introduce pyridyl substituents at the lower rim selectively for the *cone* conformation[6] with the aim of obtaining transition metal complexes at the bottom of a molecular cavity.

The functionalization of the lower rim, including with heterocyclic groups such as pyridylmethyl ethers,[7] has frequently been used to create calixarenes that selectively bind metal cations, but mainly with the focus on the binding properties to alkali metals.[8] We examined the introduction of 2-pyridyl substituents by nucleophilic aromatic substitution: calixarene **1** was treated with an excess of 2-halopyridines **2**, in the presence of an excess of sodium carbonate or sodium hydride as base, under neat conditions at elevated temperatures.

Results and Discussion

For the selective pyridylation of calixarene **1** (Scheme 1) we tested various conditions, especially the influence of the base and the temperature. An excess of the 2-bromopyridine **2** (X = Br) with sodium carbonate at 130 °C under neat conditions gave the monopyridoxy product **3a** in 45% yield as the main product (Table 1, Entry 1). If the fluoropyridine **2** (X = F) was used instead of bromopyridine the selectivity for **3a** increased to a final yield of 70%. With an increase in the reaction temperature to 160 °C − again with



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	R^1	R^2	R^3	R^4
3a	H	H	H	2-Py
3b	H	2-Py	H	2-Py
3c	H	2-Py	2-Py	2-Py
3d	2-Py	2-Py	2-Py	2-Py

Scheme 1. *O*-Arylation of calixarene **1** and halopyridines **2**. a: excess of base, heating for 3 days

Table 1. Selective pyridylation of calixarene **1**

Conditions[a] Entry	**2**	Solvent	Base	Temp.	Yield in %[b] **3a**	**3b**	**3c**	**3d**
1	X = Br	−	Na_2CO_3	130 °C	45	16	−	−
2	X = F	−	Na_2CO_3	130 °C	70	4	−	−
3	X = Br	−	Na_2CO_3	160 °C	11	49	7	−
4	X = Br	−	Na_2CO_3	180 °C	−	17	46	5[c]
5	X = Br	−	Cs_2CO_3	160 °C	−	−	−	45[d]
6	X = Br	−	NaH	100 °C	−	−	−	−
7[e]	X = Br	−	NaH	130 °C	−	25	−	−
8	X = Br	DMF	NaH	reflux temp.	−	−	17	39[c]
9	X = F	pyridine	NaH	reflux temp.	−	−	−	−

[a] 4−8 equiv. base, 10 equiv. 2-halopyridine **2**, neat, 3 days. [b] Yield after flash chromatography; according to ^{1}H NMR the compounds **3a**, **3b** and **3c** each prefer exclusively the *cone* conformation in $CDCl_3$ solution. [c] Exclusively *cone* conformation. [d] 35% in the *1,3-alternate*, 10% in the *1,2-alternate* conformation. [e] 7 h reaction time.

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sodium carbonate as base and 2-bromopyridine as reagent − the dipyridoxy-calixarene **3b** became the dominant product in 49% yield, compounds **3a** and **3c** being minor by-products in this case. At a reaction temperature of 180 °C the tripyridoxy-calixarene **3c** was favoured, being isolated in a 46% yield, while a small amount (5%) of calixarene **3d** could also be isolated.

In relation to the reported monopyridylation of phenols,[9] the yields achieved at the lower rim of **1** are indeed satisfactory. With sodium carbonate as base, products with *cone* conformations were detected and isolated exclusively in all these cases, even at the rather high reaction temperature of 180 °C. These findings confirm the template effect of the sodium cation during lower rim functionalization.[10] If caesium carbonate was used instead of sodium carbonate, again under neat conditions, only *1,3-alternate* and *1,2-alternate* conformations were isolated in an overall yield of 45%. This nicely complements the reported selectivity for *alternate* conformations induced by caesium carbonate at 269 °C in diphenyl ether.[6] However, we prefer the advantageous neat conditions, which obviously give higher yields and enable the simple recovery of unchanged bromopyridine.

The remaining preparative problem was to increase the yield of the quadruply and hence fully pyridylated calixarene **3d**. Sodium hydride was tested as a stronger base under neat conditions: at a temperature of 100 °C calixarene **1** was recovered completely. At 130 °C only 25% of **3b** were separated, most interestingly as *syn-distal*-dipyridoxycalixarene: this is in contrast to the general assumption that sodium hydride should favour the formation of *syn-proximal* calixarenes.[7b,11] At the reflux temperature of 2-bromopyridine the reaction mixture became a solid, black mass, indicating decomposition. The use of a catalytic amount of copper(II) oxide with sodium hydride and 2-bromopyridine at 160 °C gave **3d** in roughly 20% yield besides a large amount of 2,2′-dipyridyl. At the reflux temperature of pyridine as solvent − again with NaH as base, but with the more reactive 2-fluoropyridine as the reagent − surprisingly no reaction occurred. Finally, dry DMF turned out to be the solvent of choice: at the reflux temperature calixarene **3d** was indeed the main product, isolated in 39% yield.

All products were identified by their ^{1}H NMR spectra (Table 2), with the methylene protons and the pyridyl protons providing the diagnostic signals. The signals of the methylene carbon atoms in the ^{13}C NMR spectra were also used for identification of the conformation.[12] For all calixarenes in the *cone* conformation (**3a**−**3d**) the shifts of the methylene carbons appear at roughly δ = 32 ppm. For *1,3-alternate*-**3d** the signal at δ = 37.2 ppm is significant. For the calixarene **3a**, the signals of the methylene protons give four doublets at δ = 3.43, 3.52, 4.97 and 4.27 ppm. In addition, it is typical for calixarenes with *cone* conformations that the Δδ values of the *geminal* methylene protons are in the range of ≈ 0.6−0.7 ppm.[13] The relatively broad signals for the pyridyl-6-H at δ = 8.28 ppm and the pyridyl-4-H at δ = 7.77 ppm are a hint for dynamic NMR effects in connection with the rotation of the pyridyl moiety along the py−C−O axis in solution. Calixarene **3b** showed typical fine coupling constants (^4J and ^5J) for the pyridyl protons − for py-6-H at δ = 8.23 ppm and for py-3-H at δ = 7.18 ppm, for instance − and in conclusion we assume a relatively rigid conformation in this case. The nitrogen atoms should be *exo*-orientated because of the repulsion of the lone electron pairs (in the solid state they are *exo*-orientated and nearly orthogonal to the aryl cores of the calixarene; see X-ray crystal structure). The methylene protons of **3b** exhibit a resonance at δ = 3.38 and 4.04 ppm with a Δδ of 0.66 ppm, which is regarded as clear evidence for the cone conformation (see above).[13] The tris-pyridylated compound **3c** exhibits four methylene proton doublets at 3.15, 3.55, 3.68 and 3.83 ppm, which is in agreement with the C_s symmetry. An upfield shift of about Δδ = 0.6 ppm of two py-3-H (δ = 6.38 ppm) orthogonal to the σ_v plane, in comparison with the one py-3-H (δ =6.98 ppm) in the σ_v plane, is remarkable: presumably all nitrogen atoms are *exo*-orientated with the calixarene in a flattened *cone* conformation, resulting in symmetric positions of two py-3-H protons in the anisotropic shielding region of the third pyridine ring on a time-averaged scale.

The fully pyridylated calixarene **3d** in the *cone* conformation with C_{4v} symmetry gives two characteristic signals for the methylene protons, at δ = 3.19 and 3.99 ppm, and also significant signals for py-3-H at δ = 7.46 ppm and for

Table 2. Diagnostic ^{1}H and ^{13}C NMR signals for the calixarenes **3a**−**3d**

Calixarene	^{1}H NMR shifts (δ in ppm) with coupling constants (J in Hz) of the methylene protons				^{13}C NMR shifts of the methylene carbons (ppm)	^{1}H NMR shifts (δ in ppm) of characteristic pyridyl protons			
						Py-6-H	Py′-6-H	Py-3-H	Py-3′-H
3a	3.43 (d, 13.1)	3.52 (d, 13.9)	4.07 (d, 13.5)	4.27 (d, 14.0)	31.9	8.28 (“s”)	−	7.07 (“d”)	−
3b	3.38 (d, 13.7)		4.04 (d, 13.8)		32.1	8.23 (“d”)	−	7.18 (d)	−
3c[a]	3.15 (d, 13.7)	3.55 (d, 14.3)	3.68 (d, 13.7)	3.83 (d, 14.3)	31.2	7.97 (“d”)	8.02 (“d”)	6.98 (d)	6.38 (d)
***cone*-3d**	3.19 (d, 13.1)		3.99 (d, 13.1)		31.0	8.09 (“d”)	−	7.46 (d)	−
1,2-*alt*-3d	3.28 (d, 13.1)	3.58 (s)		3.84 (d, 13.1)	−[b]	7.93 (“d”)	−	6.18 (d)	−
1,3-*alt*-3d	3.42(s)				37.2	8.10 (“s”)	−	5.67 (d)	−

[a] For calixarene **3c** the pyridyl moieties are differentiated into Py and Py′ (with Py being the pyridyl moiety in the σ_v-plane). [b] No ^{13}C NMR spectrum measured.

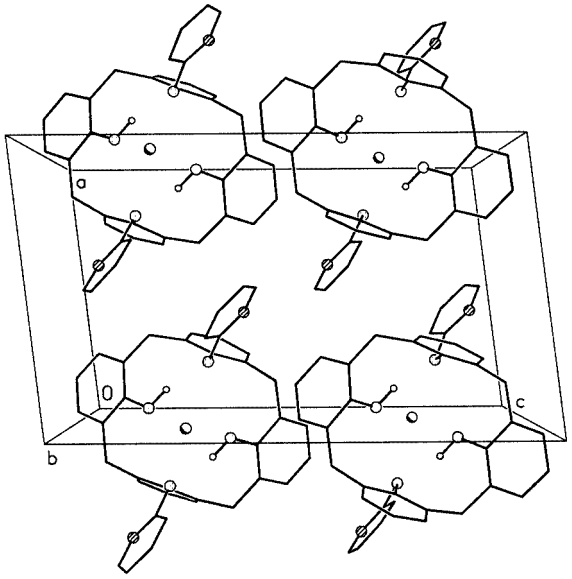
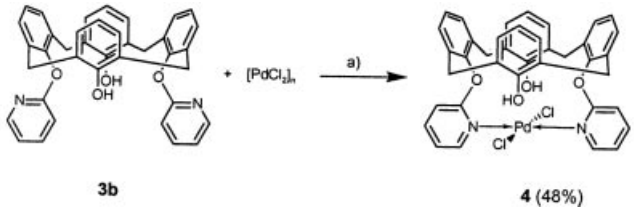


Figure 1. Packing of calixarene **3b** in the elemental cell

the py-6-H at δ = 8.09 ppm. The calixarenes **3d** in the *1,2*- and the *1,3-alternate* conformations could easily be identified by their coupling patterns of the methylene protons. The *1,3-alt*-**3d** gives only one singlet at δ = 3.42 ppm, whereas the *1,2-alt*-**3d** shows two doublets at δ = 3.28 and 3.84 ppm and one singlet at δ = 3.58 ppm.

Diffraction-quality single crystals of **3b** were obtained from dichloromethane/methanol.[14a] The monoclinic elemental cell of **3b** is shown in Figure 1. The molecules are packed nearly lower-rim to lower-rim and upper-rim to upper-rim along the *b* axis. In each molecule of **3b** the pyridyl moieties are positioned almost orthogonal to the phenyl groups with *exo*-orientated nitrogen atoms, caused by the repulsion of the lone pair electrons. This is in agreement with the discussed signals of the ^{1}H NMR spectrum. Each molecule has a flattened *cone* conformation, in which the substituted phenyl rings are the almost parallel ones. Also interesting is a moderate hydrogen bonding between the hydroxy groups and the oxygen atoms of the pyridoxy moieties;[15,16] the bond lengths are d(O−H) = 0.855 Å, d(H···O_{Py}) = 2.011 Å and d(O···O_{Py}) = 2.863 Å. The angle (OHO_{Py}) is 173.6°. Disordered water is detected in the lattice voids, corresponding to clathrated water in the molar ratio **3b**/H_2O = 1:0.5 (additionally confirmed by elemental analysis).

Calixarene **3b** was tested as a ligand for palladium complexes, being heated at reflux for 5 h with a stoichiometric amount of palladium(II) chloride in a mixture of dichloromethane and methanol (4:1) (Scheme 2). Orange crystals were grown from the yellow solution by dilution with ethanol.



Scheme 2. Synthesis of the Pd complex **4**; a: heating at reflux in CH_2Cl_2/MeOH (4:1) for 5 h, then slow dilution with EtOH (3−5 d)

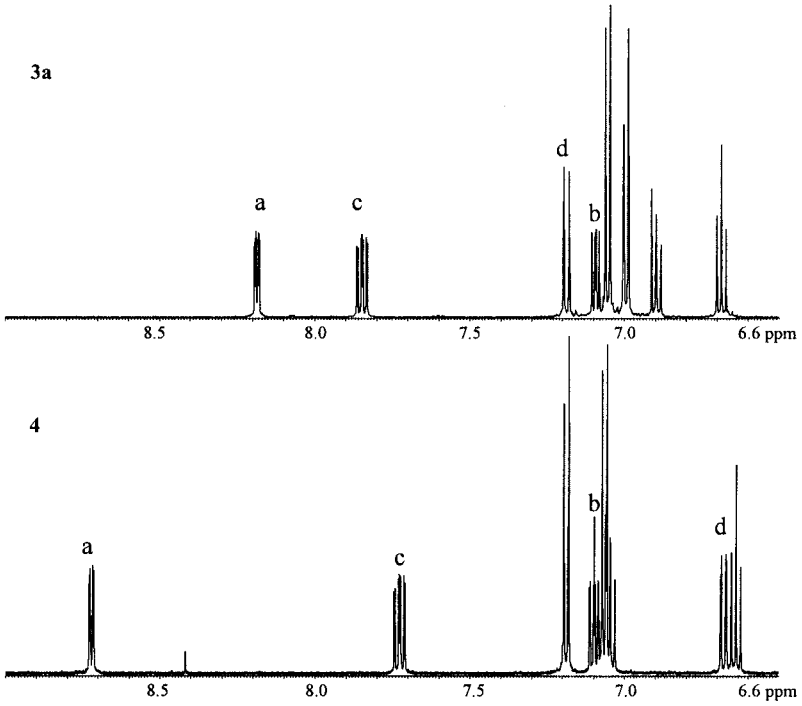


Figure 2. 500.1 MHz ^{1}H NMR spectra of calixarene **3b** and complex **4** in CD_2Cl_2: [D_4]MeOH, 8:1; a = Py-6-H, b = Py-5-H, c = Py-4-H, d = Py-3-H

The ^{1}H NMR spectrum of complex **4** shows that the pyridyl moieties are fixed orthogonal to the aryl rings. The methylene protons give two doublets at δ = 3.39 ppm and 3.90 ppm, with coupling constants of J = 13.6 Hz. Comparison of the pyridyl signals with that of calixarene **3b** (Figure 2) is interesting; py-3-H exhibits resonance at δ = 6.68 ppm, implying an upfield shift of $\Delta\delta = -0.51$ ppm in relation to the py-3-H signal of compound **3b**. This reveals an orthogonal orientation of the pyridyl moieties to the aryl rings, in which the py-3-H atoms are influenced by the ring-current effects in a diamagnetic manner. The py-5-H gives a signal at δ = 7.09 ppm. The py-6-H shows resonance at δ = 8.18 ppm implying a relative downfield shift of $\Delta\delta = +0.54$ ppm in relation to calixarene **3b**, explained by the electron-withdrawing palladium centre. The py-4-H exhibits its resonance at δ = 7.85 ppm with a relative upfield shift of $\Delta\delta = -0.12$ ppm, this being in agreement with a slight anisotropic effect from dynamic host-guest interaction. Unlike in the crystalline state, however, there is no hint of permanent supracycles in solution.

The X-ray crystal structure (Figure 3−5)[14b] reveals a surprising metal-mediated self-organisation of complex **4** in the crystalline state: six units of **4** assemble in a mutually included arrangement to form a hexameric supracycle (Figure 3).[17]

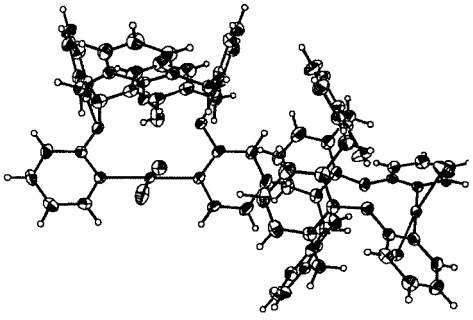


Figure 3. Section of the X-ray structure of **4** (a coloured version is deposited as Supporting Information; see also the footnote on the first page of this article)

We assume that the electrophilic palladium(II) promotes tight accommodation of the pyridyl groups into the π-based calixarene cavity by influencing their orientation and by diminishing the electron density in the pyridyl rings. It is known that pyridinium ions act as suitable guests for the cavities of calix[4]arenes because of π-cation interactions.[18,19] In conclusion, the palladium centres electronically influence the self-organisation, and do not function as linkers between the parts of the supramolecular aggregates as usual.[19,20]

In order to visualise the intrinsic geometry of the supracycle it is interesting to note that from the positions of the palladium atoms one can construct a six-membered ring with a chair conformation, a Pd−Pd distance of about 11 Å and a Pd−Pd−Pd angle of 103.5°. The "Pd-chairs" are packed eclipsed along the *c* axis.

The hexameric supracycles each have a maximum outer diameter of ca. 30 Å, a minimum inner diameter of ≈ 7 Å

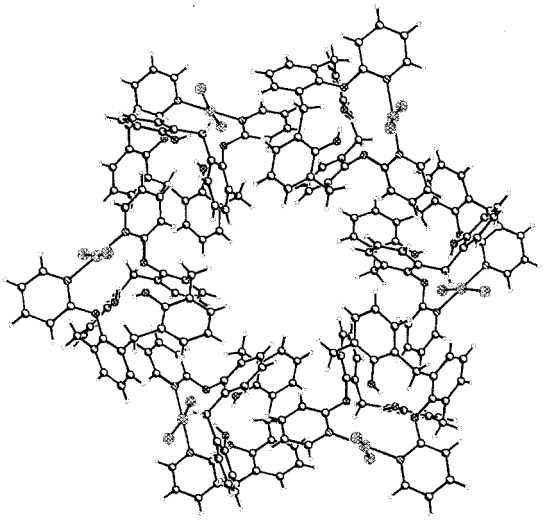


Figure 4. Crystal structure of the hexameric supracycle (view along the *c* axis); dichloromethane molecules are omitted (a coloured version is deposited as Supporting Information)

and a deepness of ca. 10 Å. The tubular voids have a volume of ca. 366 Å^3 for one cyclic unit. The supracycles themselves are organised in hexagonal arrayed tubes along the *c* axis, as can be seen in the elemental cell of the X-ray structure (Figure 5). The hydrophobic tubular lattice voids contain six dichloromethane molecules per supracycle. The solvent molecules are loosely fitting and disordered.

It is also worth mentioning that in the crystalline state the hydrogen bonds between the hydroxy protons and the oxygen atoms of the pyridoxy moieties are somewhat stronger in the Pd complex than in calixarene **3c**. The bond lengths are d(O−H) = 0.755 Å as compared with 0.678 Å, d(H···O$_{Py}$) = 1.998 Å as compared with 2.216 Å, and d(O···O$_{Py}$) = 2.671 Å as compared with 2.815 Å. The angle (OHO$_{Py}$) is 148.5° as compared with 148.2°, and the Cl−Pd−Cl angle is 171.82°. The smaller angle relative to the *trans*-dipyridine palladium(II) dichloride (178.3°) is caused by the repulsion of the hydroxy moieties.[21]

Conclusion

The new calixarenes **3a**−**3d** are easily accessible through nucleophilic aromatic substitution with 2-halopyridines, in yields of the main products of roughly 45−50%. They are interesting multidentate *N*-ligands for the formation of new transition metal complexes or supramolecular aggregates. In structure **4** we have found an interesting calixarene palladium complex that is organised into hexameric supracycles in the solid state. These supracycles themselves are stacked into hexagonal tubes "filled" with dichloromethane. In addition to preorientating the pyridyl moieties the palladium centres promote the self-assembly through electronic effects. Other examples of calixarene-type molecules organised into tubular lattices are rare,[22,23,24] but have some importance for the storage of additional guest molecules such as methane.[25] We are currently investigating

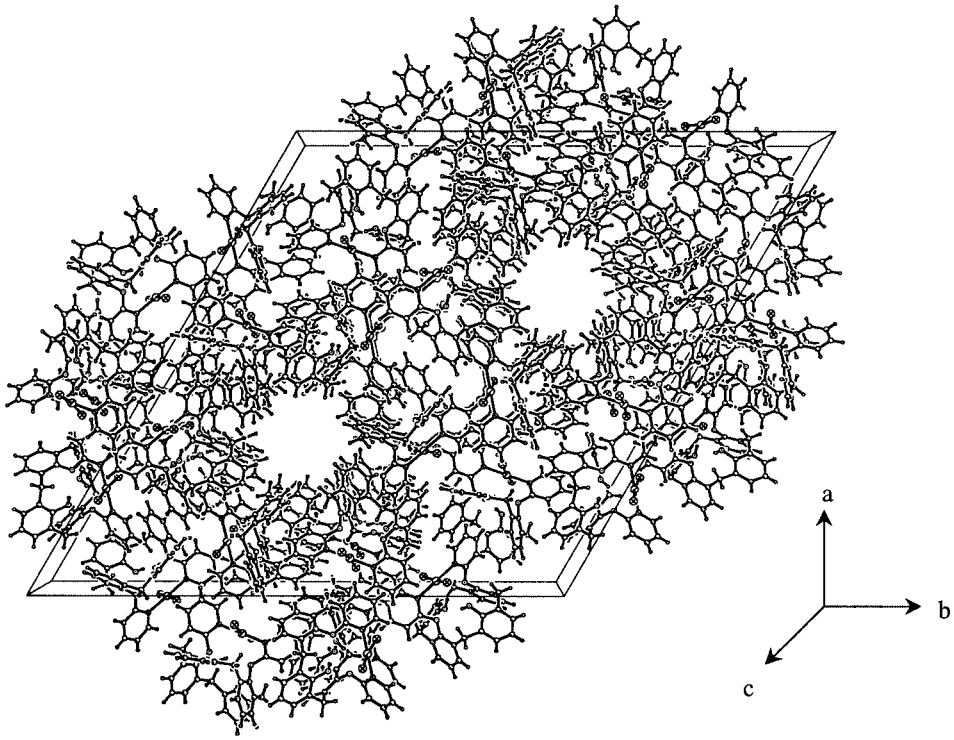


Figure 5. View of the elemental cell of calixarene **4** along the *c* axis

the stability of the supracyclic structure and the tubular lattice of crystalline **4** in contact with other loosely fitting guests, such as various hydrocarbons and alkyl halides, as well as iodine.

Experimental Section

General Remarks: Melting points (°C, uncorrected values) were determined with a Kofler-Heizmikroskop, Modell Reichert Thermovar. Elemental analysis were determined with a Carli Erba Elemental Analyser 1106. Infrared spectroscopy was performed with a Bruker Vector 22 instrument (KBr, $\tilde{\nu}$ in cm^{-1}). UV/Vis spectra were recorded with a Perkin−Elmer Lambda 40 apparatus ($\lambda_{max.}$ in nm, ε in $cm^2 \cdot mmol^{-1}$). ^1H and ^{13}C NMR spectra were recorded with Bruker WM 300 or Bruker DRX 500 machines. Mass spectroscopy was performed with a Varian MAT 311 A or AMD 604 spectrometer. SiO_2 plates (Polygram SIL G/UV 254) from Macherey & Nagel were used for TLC. All compounds were purified by flash chromatography on Kieselgel 60 (Merck, 0.030−0.60 mm). All commercially available products were used without further purification.

General Procedure (GP): Calix[4]arene **1** (300 mg, 0.708 mmol), sodium carbonate (1.260−1.480 g, 11.90−13.98 mmol) and 2-bromopyridine (**2a**, 3.95−7.11 g, 25.0−45.0 mmol) were suspended in a screw-capped vessel, flushed with argon, and heated for 3 days. After the mixture had cooled to room temperature, inorganic salts were filtered off and washed twice with 5 mL portions of dichloromethane. Dichloromethane was removed (900 mbar, 50 °C) and 2-bromopyridine (**2a**) was recovered by distillation in vacuo (0.5 mbar, 100−110 °C). The brown residue was purified by flash chromatography with petroleum ether/ethyl acetate (2:1 or 3:1). The separated compounds were dried at 100−110 °C and 0.5 mbar.

26,27,28-Trihydroxy-25-(2-pyridoxy)calix[4]arene (3a). Method A (with 2-Bromopyridine): Calixarene **1** (498 mg, 1.17 mmol), sodium carbonate (2.40 g, 22.6 mmol) and 2-bromopyridine (**2a**, 5.0 mL, 52 mmol) were suspended and heated for 3 days at 130 °C. TLC (PE/EA 3:1): R_f = 0.19, 0.31 (**3b**), 0.47 (**3a**), 0.66 (**2a**), 0.78 (**1**), 0.88. **1st Fraction (R_f = 0.47):** 261 mg (45%) of calixarene **3a** as a colourless solid with m.p. 201−203 °C. IR (KBr): $\tilde{\nu}$ = 3331 cm^{-1}, 3080, 3044, 3014, 2928, 2868, 1590, 1573, 1466, 1427, 1382, 1232, 1144, 1084, 991, 913, 876, 813, 753, 562. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 273 nm (3.9). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.43 (d, J = 13.1 Hz, 2 H, Ar-CH_2-Ar), 3.52 (d, J = 13.9 Hz, 2 H, Ar-CH_2-Ar), 4.07 (d, J = 13.5 Hz, 2 H, Ar-CH_2-Ar), 4.27 (d, J = 14.0 Hz, 2 H, Ar-CH_2-Ar), 6.68 (t, J = 7.5 Hz, 2 H, Ar′-4-H), 6.70 (t, J = 7.5 Hz, 1 H, Ar′′-4-H), 7.03 (m, 8 H, Py-3-H, Ar′′-3/5-H, Ar′-3/5-H, Ar-4-H), 7.07 (br. d, 1 H, Py-5-H), 7.16 (d, J = 7.6 Hz, 2 H, Ar-3/5-H), 7.77 ("s", br., 1 H, Py-4-H), 8.28 ("s", br., 1 H, Py-6-H), 8.88 (br. s, 2 H, Ar′-O*H*), 9.54 (br. s, 1 H, Ar-O*H*) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 31.9 (t, Ar-*C*H_2-Ar), 110.1 (d, Py-C-3), 119.3 (d, Py-C-5), 121.1 (d, Ar′′-C-4), 122.0 (d, Ar′-C-4), 125.3 (s, Ar′′*C*-CH_2-Ar′), 127.3 (d, Ar-C-4), 128.1 (s, Ar′*C*-CH_2-Ar′′), 128.6 (s, Ar′*C*-CH_2-Ar), 128.7 (d, Ar′′-C-3/5), 128.9 (d, Ar′-C-5), 129.0 (d, Ar′-C-3), 129.5 (d, Ar-C-3/5), 134.5 (s, Ar*C*-CH_2-Ar′), 140.1 (d, Py-C-4), 146.3 (s, Ar′′*C*-OH), 148.2 (d, Py-C-6), 149.2 (s, Ar′*C*-OH), 150.8 (s, Ar*C*-O-Py), 162.8 (s, Py-C-2) ppm. MS (EI, 70 eV, 210 °C): *m*/*z* (%) = 503 (7) [M^+ + 2], 502 (34) [M^+ + 1], 501 (100) [M^+], 485 (5), 484 (17), 483 (5), 197 (7), 196 (9), 195 (7). $C_{33}H_{27}NO_4$ (501.58): calcd. C 79.02, H 5.43, N 2.79; found C 79.13, H 5.45, N 2.79. **2nd Fraction (R_f = 0.31):** 110 mg (16%) of calixarene **3b** as a colourless solid with m.p. 294−296 °C.

Method B (with 2-Fluoropyridine): Calixarene **1** (404 mg, 0.95 mmol), sodium carbonate (1.79 g, 16.9 mmol) and 2-fluoropyridine (**2b**, 4.000 g, 41.20 mmol) were suspended and heated for 3 days at 130 °C. TLC (PE/EA, 3:1): R_f = 0.18, 0.25 (**3b**), 0.38 (**3a**), 0.55 (**2b**), 0.65 (**1**). **1st Fraction (R_f = 0.38):** 333 mg (70%) of

calixarene **3a** as a colourless solid with m.p. 201−203 °C. **2nd Fraction (R_f = 0.25):** 21 mg (4%) of calixarene **3b** as a colourless solid with m.p. 294−296 °C.

***syn-distal*-26,28-Dihydroxy-25,27-bis(2-pyridoxy)calix[4]arene (3b):** Calixarene **1** (390 mg, 0.92 mmol), sodium carbonate (1.87 g, 17.7 mmol) and 2-bromopyridine (**2a**, 7.058 g, 44.7 mmol) were suspended and heated for 3 days at 160 °C. TLC (PE/EA, 2:1): R_f = 0.02, 0.29 (**3c**), 0.37 (**3b**), 0.49 (**3a**). **1st Fraction (R_f = 0.49):** 50 mg (11%) of calixarene **3a** as a colourless solid with m.p. 201−203 °C. **2nd Fraction (R_f = 0.37):** 260 mg (49%) of calixarene **3b** as a colourless solid with m.p. 294−296 °C. IR (KBr): $\tilde{\nu}$ = 3447 cm^{-1}, 3044, 3019, 2925, 2853, 1589, 1572, 1466, 1465, 1456, 1427, 1285, 1264, 1236, 1186, 1143, 1087, 990, 912, 881, 806, 776, 762. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 205 nm (4.9), 273 (3.9). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.38 (d, *J* = 13.7 Hz, 4 H, Ar-C*H*$_2$-Ar), 4.04 (d, *J* = 13.8 Hz, 4 H, Ar-C*H*$_2$-Ar), 6.70 (t, *J* = 7.4 Hz, 2 H, Ar′-4-H), 6.85 ("t", *J* = 7.5, *J* = 1.1 Hz, 2 H, Ar-4-H), 6.94 (br. s, 2 H, Ar′C-O*H*), 6.95 (d, *J* = 7.5 Hz, 4 H, Ar −3/5-H), 7.02 ("t", ^3J = 5.0, ^4J = 2.2, ^5J = 0.9 Hz, 2 H, Py-5-H), 7.04 (d, *J* = 7.5 Hz, 4 H, Ar′-3/5-H), 7.18 (d, *J* = 8.3 Hz, 2 H, Py-3-H), 7.77 ("t", ^3J = 7.8, ^4J = 2.0 Hz, 2 H, Py-4-H), 8.23 ("d", ^3J = 5.0, ^4J = 2.0, ^5J = 0.7 Hz, 2 H, Py-6-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 32.1 (t, Ar-*C*H$_2$-Ar), 110.6 (d, Py-C-3), 118.6 (d, Py-C-5), 119.5 (d, Ar′-C-4), 126.5 (d, Ar-C-4), 128.3 (s, Ar′*C*-CH$_2$-Ar), 128.8 (d, Ar′-C-3/5), 129.2 (d, Ar-C-3/5), 133.4 (s, Ar*C*-CH$_2$-Ar′), 139.8 (d, Py-C-4), 146.9 (s, Ar′*C*-OH), 148.0 (d, Py-C-6), 152.9 (s, Ar*C*-O-Py), 163.4 (s, Py-C-2) ppm. MS (EI, 70 eV, 210 °C): *m*/*z* (%) = 634 (7) [M^+ + 56], 580 (10) [M^+ + 2], 579 (42) [M^+ + 1], 578 (100) [M^+], 562 (5), 561 (12), 560 (8), 501 (8), 484 (6), 289 (11), 287 (6), 195 (6), 183 (6), 44 (6). $C_{38}H_{30}N_2O_4$·1/2 H_2O (587.67): calcd. C 77.67, H 5.32, N 4.77; found C 77.56, H 5.15, N 4.77. **3. Fraction (R_f = 0.29):** 41 mg (7%) of calixarene **3c** as a colourless solid with m.p. > 300 °C.

Method B (with Sodium Hydride): Calixarene **1** (296 mg, 0.70 mmol), sodium hydride (60%, 550 mg, 13.8 mmol) and 2-bromopyridine (**2a**, 7.07, 45.3 mmol) were suspended and heated for 3 days at 130 °C. TLC (PE/EA, 3:1): R_f = 0.25 (**3b**), 0.54 (**2a**). After workup (GP): yield: 100 mg (25%) of calixarene **3b** as a colourless solid with m.p. 294−296 °C.

***syn*,*syn*-28-Hydroxy-25,26,27-tris(2-pyridoxy)calix[4]arene (3c):** Calixarene **1** (700 mg, 1.65 mmol), sodium carbonate (2.75 g, 25.9 mmol) and 2-bromopyridine (**2a**, 9.42 g, 59.6 mmol) were suspended and heated for 3 days at 180−200 °C. TLC (PE/EA, 2:1): R_f = 0.08 (**3d**), 0.28 (**3c**), 0.37 (**3b**). **1st Fraction (R_f = 0.37):** 158 mg (17%) of calixarene **3b** as a colourless solid with m.p. 294−296 °C. **2nd Fraction (R_f = 0.28):** 492 mg (46%) of calixarene **3c** as a colourless solid with m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3522 cm^{-1}, 3456, 3059, 3015, 2922, 2838, 2824, 1597, 1570, 1455, 1427, 1268, 1187, 1143, 1084, 990, 879, 808, 781, 764, 740, 606, 414. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 204 nm (5.1), 269 (4.2). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.15 (d, *J* = 13.7 Hz, 2 H, Ar-C*H*$_2$-Ar), 3.55 (d, *J* = 14.3 Hz, 2 H, Ar-C*H*$_2$-Ar), 3.68 (d, *J* = 13.7 Hz, 2 H, Ar-C*H*$_2$-Ar), 3.83 (d, *J* = 14.3 Hz, 2 H, Ar-C*H*$_2$-Ar), 4.90 (br. s, 1 H, Ar′′-O*H*), 6.38 (d, *J* = 8.4 Hz, 2 H, Py′-3-H), 6.73 ("d", *J* = 8.3, *J* = 1.9 Hz, 2 H, Ar′-5-H), 6.77 (t, *J* = 7.5 Hz, 2 H, Ar′-4-H), 6.83 ("t", *J* = 5.7, *J* = 2.1, *J* = 0.9 Hz, 2 H, Py′-5-H), 6.94 (m, 3 H, Ar′-3-H, Ar′′-4-H), 6.98 ("t", *J* = 5.6, *J* = 0.9 Hz, 1 H, Py-5-H), 7.01 (br. s, 1 H, Py-3-H), 7.08 (d, *J* = 7.5 Hz, 2 H, Ar′′-3/5-H), 7.15 (t, *J* = 7.5 Hz, 1 H, Ar-4-H), 7.26 (d, *J* = 7.5 Hz, 2 H, Ar′-3/5-H), 7.51 ("t", *J* = 8.3, *J* = 2.0 Hz, 2 H, Py′-4-H), 7.88 ("t", *J* = 8.3, *J* = 1.9 Hz, 1 H, Py-4-H), 7.97 ("d", *J* = 5.0, *J* = 1.4 Hz, 1 H, Py-6-H), 8.02 ("d", *J* = 5.0, *J* = 1.9, *J* = 0.7 Hz, 2 H, Py′-6-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 31.2 (t, Ar-*C*H$_2$-Ar), 110.4 (d, Py′-C-3), 115.9 (d, Py-C-3), 117.1 (d, Py-C-5), 117.6 (d, Py′-C-5), 119.4 (d, Ar′′-C-4), 125.0 (d, Ar′-C-4), 125.4 (d, Ar-C-4), 128.7 (d, Ar′-C-3), 128.9 (d, Ar′-C-5), 129.2 (d, Ar′-C-5), 129.2 (d, Ar-C-3/5), 129.9 (s, Ar′′*C*-CH$_2$-Ar′), 132.8 (s, Ar′*C*-CH$_2$-Ar′′), 133.9 (s, Ar′*C*-CH$_2$-Ar), 136.6 (s, Ar*C*-CH$_2$-Ar′), 137.5 (d, Py-C-4), 139.1 (d, Py′-C-4), 146.3 (d, Py-C-6), 147.6 (d, Py′-C-6), 148.5 (s, Ar′′*C*-OH), 150.1 (s, Ar′*C*-O-Py′), 153.9 (s, Ar*C*-O-Py), 163.5 (s, Py-C-2), 163.8 (s, Py′-C-2) ppm. MS (EI, 70 eV, 210 °C): *m*/*z* (%) = 657 (12) [M^+ + 2], 656 (48) [M^+ + 1], 655 (100) [M^+], 654 (6), 638 (11), 637 (8), 578 (6), 562 (7), 561 (13), 559 (5), 347 (5), 328 (18) [$M^{+ +1}$], 280 (7), 275 (9), 274 (6), 271 (6), 270 (5), 184 (6), 183 (8), 44 (15). $C_{43}H_{33}N_3O_4$ (655.75): calcd. C 78.76, H 5.07, N 6.41; found C 78.68, H 5.01, N 6.40. **3. Fraction (R_f = 0.08):** 70 mg (4%) of calixarene **3d** as a colourless solid with m.p. > 300 °C.

***cone*-25,26,27,28-Tetrakis(2-pyridoxy)calix[4]arene (3d):** Sodium hydride (216 mg, 9.00 mmol) was diluted in dimethylformamide (5 mL), calixarene **1** (300 mg, 0.71 mmol) was added in small portions, and the reaction mixture was heated at reflux for 30 min. After the mixture had cooled to room temperature, 2-bromopyridine (**2a**, 2 mL, 20.8 mmol) was added and the mixture was heated at reflux for 3 days. The solvents were removed in vacuo and the residue was extracted three times with 5 mL portions of dichloromethane. The solvent was removed and the residue was separated by column chromatography (light petroleum ether/ethyl acetate, 2:1) to give calixarene **3c** (80 mg, 17%) with m.p. > 300 °C and calixarene **3d** (200 mg, 39%) as a colourless solid with m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3074 cm^{-1}, 3044, 3007, 2978, 2912, 2853, 1595, 1570, 1470, 1451, 1425, 1286, 1263, 1240, 1186, 1140, 774, 7634. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 209 nm (4.9), 270 (4.1), 277 (4.0). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.19 ppm (d, *J* = 13.2 Hz, 4 H, Ar-C*H*$_2$-Ar), 3.99 (d, *J* = 13.2 Hz, 4 H, Ar-C*H*$_2$-Ar), 6.87 (t, *J* = 6.0 Hz, 4 H, Py-5-H), 6.91 (t, *J* = 7.6 Hz, 4 H, Ar-H), 7.04 (d, *J* = 7.2 Hz, 8 H, Ar-H), 7.46 (d, *J* = 8.4 Hz, 4 H, Py-3-H), 7.61 ("t", *J* = 7.7, *J* = 1.9 Hz, 4 H, Py-4-H), 8.10 ("d", "*J*′′ = 3.5 Hz, 4 H, Py-6-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 31.0 ppm (t, Ar-*C*H$_2$-Ar), 112.5 (d, Py-C-3), 117.4 (d, Py-C-4), 125.0 (d, Ar*C*-H), 128.6 (d, Ar*C*-H), 135.3 (s, Ar*C*-CH$_2$-), 138.4 (d, Py-C-5), 147.3 (d, Py-C-6), 148.8 (s, Py*C*-O), 164.8 (s, Ar*C*-O-) ppm. MS (EI, 70 eV, 300 °C): *m*/*z* (%) = 734 (14) [M^+ +2], 733 (50) [M^+ +1], 732 (100) [M^+], 731 (18), 716 (9), 715 (16), 655 (12), 654 (6), 640 (12), 639 (42), 638 (91), 367 (11), 366 (27) [$M^{+ +1}$], 365 (6), 319 (7), 274 (7), 272 (5), 271 (7), 270 (6), 260 (5), 258 (5), 257 (8), 183 (8), 176 (6), 84 (5), 49 (6), 44 (13), 40 (6). $C_{48}H_{36}N_4O_4$ (732.84): calcd. C 78.67, H 4.95, N 7.65; found C 78.55, H 4.88, N 7.58.

{*syn-distal*-26,28-Dihydroxy-25,27-bis(2-pyridoxy)calix[4]arene}-palladium(II) Chloride (4): Calixarene **3b** (40 mg, 0.069 mmol) and $PdCl_2$ (12 mg, 0.067 mmol) were heated at reflux for 5 h in dichloromethane (10 mL) and methanol (2.5 mL). The yellow solution was cooled to room temperature, the insoluble solids were filtered off, and the solution was slowly diluted with ethanol (10 mL). After 3 to 5 days, orange brown crystals precipitated. The crystals were filtered, washed three times with dichloromethane (1 mL) and dried for 2 h in vacuo (50 °C, 5.0·10^{-1} mbar); yield: 25 mg (48%) orange brown crystals with m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1}, 3073, 3044, 3015, 2923, 2956, 2853, 1608, 1571, 1476, 1438, 1295, 1190, 1155, 1112, 1084, 952, 910, 804, 760. UV/Vis (CH_2Cl_2/MeOH, 4:1): $\lambda_{max.}$ (lg ε) = 278 nm (4.2), 403 (2.4). ^1H NMR (500.1 MHz, CD_2Cl_2/[D_4]MeOH, 8:1): δ = 3.39 (d, *J* = 13.6 Hz, 4 H, Ar-C*H*$_2$-Ar), 3.90 (d, *J* = 13.5 Hz, 4 H, Ar-C*H*$_2$-Ar), 6.64 (t, *J* = 7.5 Hz, 2 H, Ar′-4-H), 6.68 ("t", ^3J = 8.5, ^4J = 1.3, ^5J =

0.6 Hz, 2 H, Py-3-H), 7.04 (t, J = 7.3 Hz, 2 H, Ar-4-H), 7.07 (d, J = 7.6 Hz, 4 H, Ar′-3/5-H), 7.10 ("t", ^3J = 7.3, ^4J = 5.9, ^5J = 1.3 Hz, 2 H, Py-5-H), 7.18 (d, J = 7.5 Hz, 4 H, Ar-3/5-H), 7.73 ("t", ^3J = 8.6, ^3J = 7.3, ^4J = 1.9 Hz, 2 H, Py-4-H), 8.72 ("d", ^3J = 5.9, ^4J = 1.9, ^5J = 0.6 Hz, 2 H, Py-6-H) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2/[D$_4$]MeOH, 8:1): δ = 33.3 (t, Ar-*C*H$_2$-Ar), 110.8 (d, Py-C-3), 119.9 (two superimposed signals: d, Py-C-5; d, Ar-C′-4), 127.4 (d, Ar-C-4), 128.0 (s, Ar′*C*-CH$_2$-Ar), 128.8 (d, Ar′-C-3/5), 131.4 (d, Ar-C-3/5), 133.2 (s, Ar*C*-CH$_2$-Ar′), 142.6 (d, Py-C-4), 147.9 (s, Ar′*C*-OH), 152.6 (d, Py-C-6), 154.4 (s, Ar*C*-O-Py), 164.5 (s, Py-C-2) ppm. $C_{38}H_{30}Cl_2N_2O_4Pd$ (755.96): calcd. C 60.37, H 4.00, N 3.71; found C 60.44, H 3.98, N 3.79.

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