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Synthesis and Structural Characterization of a Series of Mono-*O*-(diphenylphosphinobenzyl)calix[6]arenes with and without *tert*-Butyl Moieties at the Upper Rim

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Synthesis and characterization of a series of mono-*O*-(diphenylphosphinobenzyl)calix[6]arenes are presented. The two types of calix[6]arene moieties were prepared: **1** (with *tert*-butyl groups at the upper rim) and **2** (without the *tert*-butyl groups). With regard to the position of a phosphorus atom, the diphenylphosphino group was introduced onto the ortho, meta, or para positions with the benzyl ether moiety. These phosphines as well as their oxides were fully characterized by elemental analysis, NMR measurements, and HR-ESI-MS. The NMR study indicated that **1** had a cone conformation whereas **2** was very flexible in solution. These phosphines were found to be effective ligands in Rh-catalyzed hydroformylation.

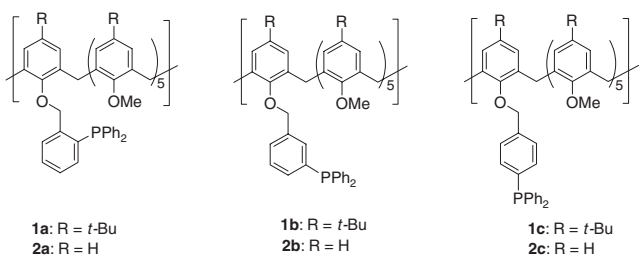
Calix[6]arene is a cyclic compound consisting of six phenol units connected by methylene bridges in the ortho position.[1] The molecules can be functionalized to provide a wide range of unique molecular architectures.[2] Recently, calix[6]arenes bearing various coordination sites and their metal complexes have been developed.[3] Among them, combination of calixarenes with phosphine functionalities, namely phosphinocalixarenes, have received considerable attention, since phosphine ligands generally play an important role in transition-metal-catalyzed reactions.[4] However, examples of phosphinocalix[6]arenes are very limited[5–7] because of lengthy multi-step syntheses. Therefore, major attention has been paid to phosphinocalix[4]arenes[8] due to their rigid conformation and rather simple preparation methods.

We have developed several phosphinocalixarenes bearing calix[4]arene[9] and calix[6]arene[5,6] functionalities. As for the calix[6]arene, a triphosphinocalix[6]arene which functioned as a tripodal phosphine ligand afforded capsule-shaped Ir(I) and Rh(I) complexes.[5] The X-ray crystal structure analysis, $^{31}P\{^{1}H\}$ NMR spectroscopy, and theoretical calculations indicated that the complexes encapsulated a variety of molecules size-selectively. Recently, we have also reported synthesis and characterization of the first example of mono-phosphinocalix[6]arenes.[6]

In the present study, a series of mono-*O*-(diphenylphosphinobenzyl)calix[6]arenes have been designed and synthesized (Scheme 1). We focus our attention on flexibility of the calix[6]arene moiety. Therefore, the two types of calix[6]arene moieties were prepared: i.e., **1** (with the *tert*-butyl groups at the upper rim: R = *t*-Bu) and **2** (without the *tert*-butyl groups: R = H). Furthermore, location of the coordinating diphosphino moiety may be crucial in catalytic reactions as described in a previous study.[10] Therefore, the diphenylphosphino group was introduced onto the ortho (**1a** and **2a**), meta (**1b** and **2b**), or para (**1c** and **2c**) positions, respectively, of the benzyl ether moiety (Scheme 1). To the best of our knowledge, **2a**–**2c** are the first examples of phosphinocalix[6]arenes without *tert*-butyl groups on the upper rim which can realize very flexible ring structure. We synthesized analytically pure **1a** and **1b** (preparation of **1c** has been reported in a previous paper[6]) and **2a**–**2c**, and fully characterized them. In solution, **1a**–**1c** adapt cone conformation, while **2a**–**2c** have flexible structures.

Results and Discussion

Synthesis and Crystal Structure. A series of mono-*O*-(diphenylphosphinobenzyl)calix[6]arenes were synthesized straightforwardly as shown in Scheme 2, where penta-*O*-methylcalix[6]arene compounds (**3**[11] and **4**[12]) were used as the starting materials. The reaction of **3** with $Ph_2P(O)$-$C_6H_4CH_2Br$ bearing the $Ph_2P(O)$ moiety at the ortho (**5a**[13]), meta (**5b**[13]), or para (**5c**[6,13]) position gave the corresponding calix[6]arenes bearing the phosphine oxide functionality



1a: R = *t*-Bu
2a: R = H

1b: R = *t*-Bu
2b: R = H

1c: R = *t*-Bu
2c: R = H

Scheme 1. A series of mono-*O*-(diphenylphosphinobenzyl)-calix[6]arene.

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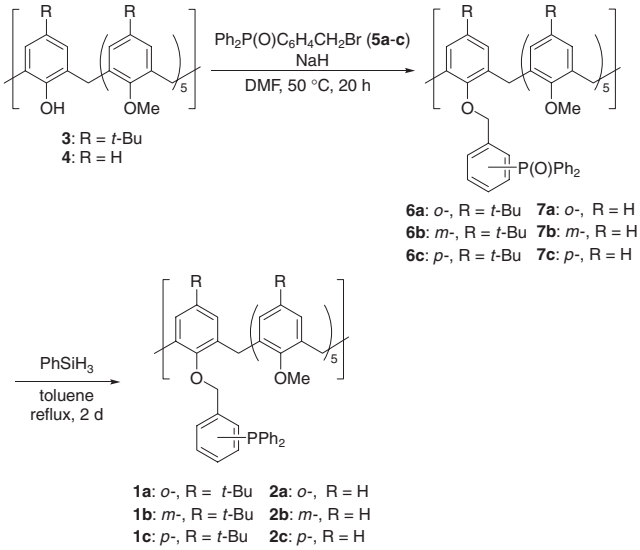


Scheme 2. Synthetic route of **1a**–**1c** and **2a**–**2c**.

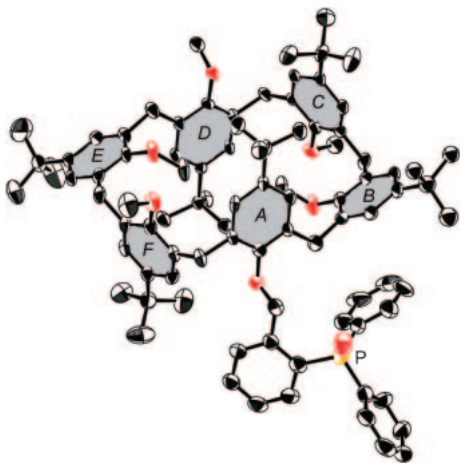


Figure 1. ORTEP drawing of **6a**. Hydrogen atoms were omitted for clarity.

(**6a**–**6c**). The reduction of **6a**–**6c** with $PhSiH_3$ in toluene under reflux afforded the desired phosphines **1a**–**1c** in good yields. The phosphinocalix[6]arenes without the *tert*-butyl groups (**2a**–**2c**) were also synthesized by the same procedure using **4**[12] and **5a**–**5c** via the corresponding phosphine oxides (**7a**–**7c**). These new compounds (**6a** and **6b**, **7a**–**7c**, **1a** and **1b**, and **2a**–**2c**) were fully characterized by elemental analysis, HR-ESI-MS, and NMR spectra.

Single crystals of **6a** suitable for X-ray diffraction study were obtained. The crystal structure shows that **6a** adopts a 1,2,3-alternate conformation in which three pairs of diametrically opposite phenyl rings (**A**–**D**, **B**–**E**, and **C**–**F**) orient in anti position to each other (Figure 1). In the crystal structure, four aromatic rings (**A**, **C**, **D**, and **F**) stand up as the pinched positions whereas the other two aromatic rings (**B** and **E**) splay outwards as the flattened positions. The dihedral angles between the aromatic ring (**A**–**F**) and the calixarene reference plane (an average plane defined by the six bridging methylene carbon atoms: the maximum deviation is 0.172 Å) are 66.7, 40.1, 83.3, 108.2, 38.6, and 82.1° for **A**–**F**, respectively.

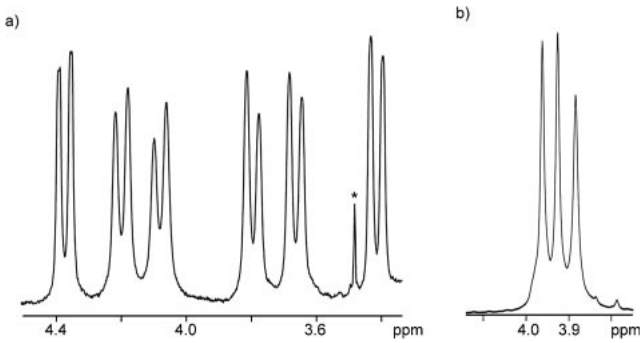


Figure 2. ^{1}H NMR spectra of **1b** (a) and **2b** (b) in $CDCl_3$ at room temperature. * indicates a signal for an impurity.

Similar 1,2,3-alternate conformations in crystalline state were also reported for some calix[6]arene derivatives.[6,14]

Structure in Solution. To elucidate the structure of **1** and **2** in solution, ^{1}H and ^{13}C{^{1}H} NMR spectra of **1a** and **1b** and **2a**–**2c** were measured in $CDCl_3$. As shown in Figure 2a, the ^{1}H NMR spectrum of **1b** exhibited axial bridging methylene proton resonances as three doublets at 4.08, 4.20, and 4.38 ppm in a 1:1:1 ratio, and the corresponding equatorial proton resonances as three doublets at 3.42, 3.67, and 3.80 ppm in a 1:1:1 ratio with geminal coupling ($^2J_{H-H} = 15$ Hz). It is well-known that the difference of chemical shift ($\Delta\delta$) between axial and equatorial proton resonances of the bridging methylenes is dependent on the orientation of the adjacent aromatic rings.[15] For **1b**, the $\Delta\delta$ values (0.96, 0.47, and 0.28 ppm) are quite comparable to values reported for mono-*O*-benzyl-substituted calix[6]arenes,[6,16] which take cone conformation in solution. Furthermore, in the ^{1}H NMR spectrum of **1b**, *tert*-butyl protons appear as four singlet peaks in a ratio of 1:1:2:2 at 0.93, 1.25, 1.01, and 1.27 ppm, and methoxy protons as three singlet peaks in a ratio of 1:2:2 at 2.75, 2.46, and 3.27 ppm. It is also well-known that bridging methylene carbon (Ar–CH_2–Ar) resonances appear at ca. 31 ppm when two adjacent aryl rings are in the syn orientation, and ca. 37 ppm in the anti orientation.[16,17] Actually, the bridging methylene carbon resonances of **1b** appeared around 31 ppm (30.45, 30.64, and 30.70 ppm) not around 37 ppm, indicating the cone conformation with all the adjacent aryl rings in syn orientation. The phosphine **1a** as well as oxides **6a** and **6b** showed the same characteristic ^{1}H and ^{13}C NMR spectra. Thus, these NMR data clearly indicated that **1a** and **1b** and **6a** and **6b** adopt the cone conformation[6,16–18] in solution.

Calix[6]arenes without the *tert*-butyl groups at the upper rim are more flexible due to easy ring inversions[19] than analogs with the *tert*-butyl moiety.[20] Actually, in the ^{1}H NMR spectrum of **2b** the bridging methylene proton resonances appeared as three singlet peaks at 3.89, 3.92, and 3.97 ppm in a 1:1:1 ratio (Figure 2b). In addition, the methoxy protons also appeared as three singlet peaks at 3.16, 2.89, and 3.22 ppm in a ratio of 1:2:2. All these singlet resonances remained singlets over the temperature range from room temperature to −60 °C, although some signals slightly broadened at the low temperature. These results suggest that **2b** has very flexible structure in solution. The phosphines **2a** and **2c** as well as their phosphine oxides **7a**–**7c** also show similar spectra, indicating they also have flexible structures.

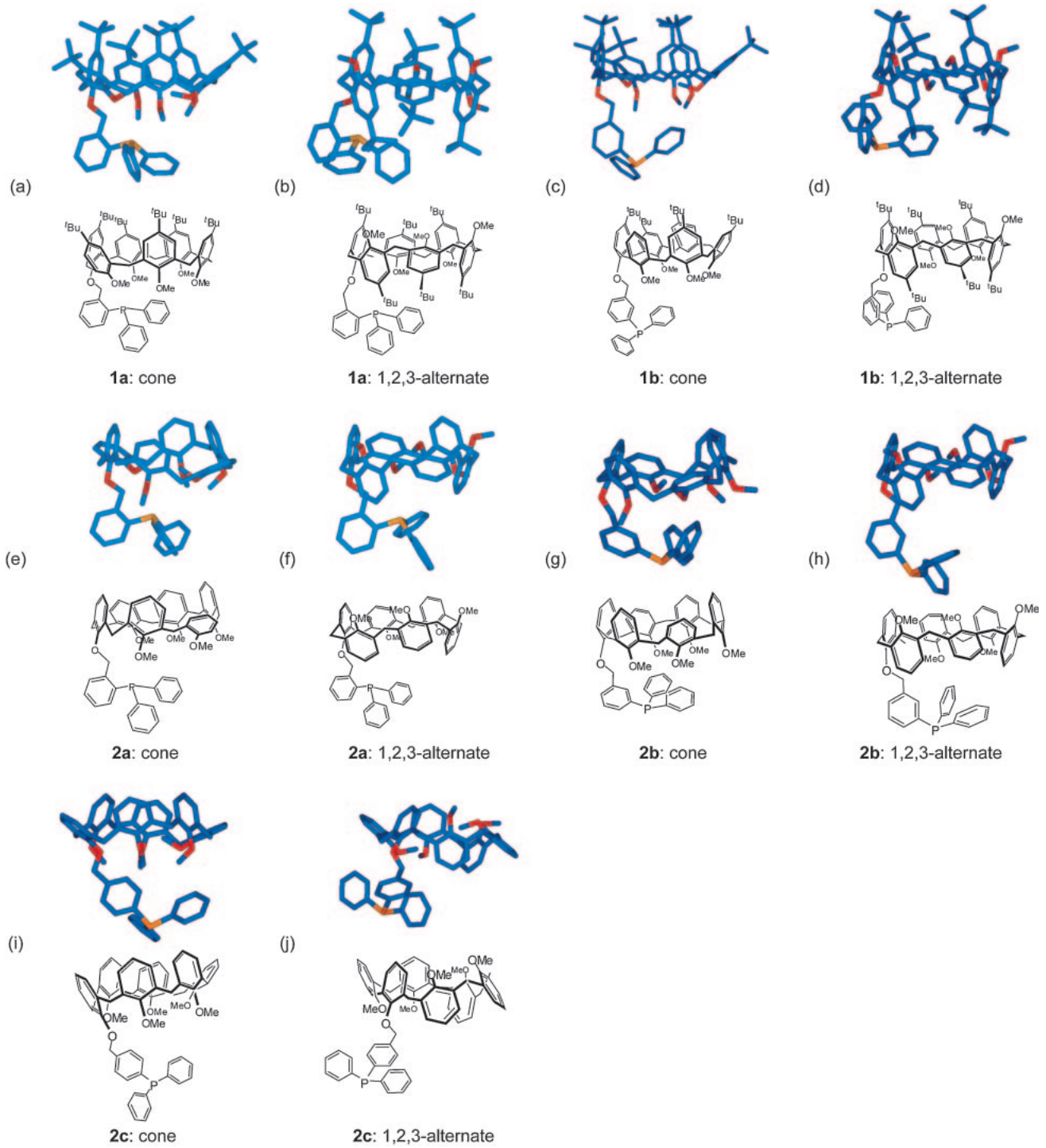


Figure 3. Conformers and optimized structures (B3LYP/LANL2DZ-CONFLEX5/MMFF94s) of **1a** and **1b** and **2a**–**2c**.

Conformation Analysis of Calix[6]arene Ring. The NMR study suggested that **1a**–**1c** and **6a**–**6c** have cone conformations in solution. In contrast, **2a**–**2c** and **7a**–**7c** have very flexible structures in solution due to ring inversion. In order to obtain further insight into the structures of calix[6]-arene moieties, conformation analysis of **1** and **2** by theoretical calculations were carried out for the cone and the 1,2,3-alternate conformers. In each conformation, the lowest energy structures were found with CONFLEX5[21] using a MMFF94s force field.[22] These structures thus obtained were further optimized by DFT calculation at B3LYP[23]/LANL2DZ[24] level.

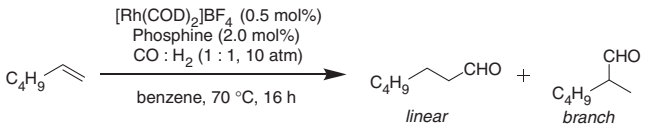
Figure 3 shows the optimized structures of the cone and the 1,2,3-alternate conformations for **1a** and **1b** and **2a**–**2c**. For **1a**, **1b**, and **1c**[6] bearing the *tert*-butyl groups (R = *t*-Bu), the cone conformations are more stable than the 1,2,3-alternate by 0.93, 1.39, and 0.96 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}), respectively (Table 1, Entries 1–3). These calculation data are consistent with the ^{1}H NMR spectra which indicate the cone

Table 1. Energy Difference (ΔE) between 1,2,3-Alternate and Cone Conformations[a)]

Entry	Phosphine	Stable conformation	ΔE/kcal mol^{-1} [a),b)]
1	**1a**	Cone	0.93
2	**1b**	Cone	1.39
3	**1c**	Cone	0.96[c)]
4	**2a**	Cone	2.19
5	**2b**	1,2,3-Alternate	−2.16
6	**2c**	1,2,3-Alternate	−0.65

a) Energy difference (ΔE) = E(1,2,3-alternate) − E(cone). b) DFT calculation (B3LYP/LANL2DZ). c) See Ref. 6.

Table 2. Rh-Catalyzed Hydroformylation of 1-Hexene[a)]



Entry	Ligand	Yield/%[b)] (linear:branch)
1	**1a**	94 (63:37)
2	**1b**	70 (72:28)
3	**1c**	85 (71:29)
4	**2a**	81 (67:33)
5	**2b**	89 (70:30)
6	**2c**	82 (60:40)
7	PPh_3	46 (73:27)

a) 1-Hexene (1.0 mmol), $[Rh(COD)_2](BF_4)$ (0.005 mmol), phosphine (0.02 mmol), CO/H_2 (1:1, 10 atom), benzene (1.0 mL), 70 °C, 16 h. b) Yield based on the GC internal standard technique.

conformations are dominant in solution. On the other hand, **2a**–**2c** have very flexible structures due to the fast ring inversion.[19] For these flexible **2a**–**2c**, the cone conformer is more stable for **2a** by 2.19 kcal mol^{-1} (Entry 4), while the 1,2,3-alternate conformers are more stable for **2b** and **2c** (Entries 5 and 6). Since these conformers were not observed by the ^{1}H NMR spectra of **2** measured at low temperature, the energy barrier of the ring inversion would be very small. As for the orientation of diphenylphosphino groups, it is interesting that the lone pair on the phosphorus atoms of the ortho derivatives (**1a** and **2a**) point to the calix[6]arene moieties in the lowest energy cone conformation (Figures 3a and 3e).

Catalysis. In order to investigate the efficacy of **1a**–**1c** and **2a**–**2c** as a ligand in catalysis, the Rh-catalyzed hydroformylation[25,26] of 1-hexene was carried out. The reaction was performed with a 1:1 mixture of CO/H_2 gas (10 atm) in the presence of a catalytic amount of $[Rh(COD)_2]BF_4$ combined with **1a**–**1c** or **2a**–**2c** (P/Rh = 4) in benzene at 70 °C (Table 2). Among the phosphine employed, **1a** was found to be the most effective ligand to afford a mixture of 1-heptanal (linear) and 2-methylhexanal (branch) in 94% total yield (Entry 1). The phosphinocalix[6]arenes **1b** and **1c** provided the products in 70 and 85% yields, respectively (Entries 2 and 3). The phosphine without the *tert*-butyl group **2a**–**2c** also gave the products in 81%, 89%, and 82% yields, respectively (Entries 4–6). Under the present conditions, PPh_3 as the ligand was less effective (46% yield, Entry 7). These results indicate that the calix[6]-arene moiety on the phosphine core may affect the activity due to its bulkiness. On the other hand, the regioselectivity of the linear and branch products was not affected by the phosphine ligands as listed in Table 2, suggesting the bulkiness and rigidity of calix[6]arene is not be enough to control the selectivity under the present reaction conditions.

Conclusion

Novel mono-*O*-(diphenylphosphinobenzyl)calix[6]arenes with *tert*-butyl groups at the upper rim (**1**) and without the *tert*-butyl moieties (**2**) were synthesized and fully characterized. The X-ray crystal structure analysis of **6a** showed that the phosphine oxide analog of **1a** with *tert*-butyl moieties adapted the 1,2,3-alternate conformation. The NMR study indicated that, in solution, **1** and the corresponding phosphine oxides with the *tert*-butyl groups at the upper rim (**6**) had the cone conformation, whereas **2** and the corresponding phosphine oxide (**7**) without the *tert*-butyl moieties were very flexible. Studies of application to transition-metal-catalyzed reactions are in progress.

Experimental

General. All reactions were performed under argon using standard Schlenk techniques. Solvents were dried and purified before use by usual methods. 5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,40,41,42-pentamethoxycalix[6]arene-37-ol (**3**),[11] 38,39,40,41,42-pentamethoxycalix[6]arene-37-ol (**4**),[12] 5,11,17,-23,29,35-hexa-*tert*-butyl-37-(4-diphenylphosphinoylbenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (**6c**),[6] and 5,11,17,23,-29,35-hexa-*tert*-butyl-37-(4-diphenylphosphinobenzyloxy)-38,39,-40,41,42-pentamethoxycalix[6]arene (**1c**)[6] were also prepared according to literature procedures. Medium-pressure column chromatography (Yamazen YFLC-540) was performed on silica gel (Wakogel C-400HG; particle size 20–40 μm) with a UV detector (Yamazen UV-10V). Preparative-scale GPC was carried out with a Japan Analytical Industry LC-9104 instrument. ^{1}H (400 MHz), ^{13}C{^{1}H} (100 MHz), and ^{31}P{^{1}H} NMR (162 MHz) spectra were recorded with a JEOL ECX-400 instrument. The ^{1}H NMR spectroscopic data are referenced relative to residual protonated solvent (7.26 ppm in $CDCl_3$). ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). The ^{31}P NMR spectroscopic data are given relative to external 85% H_3PO_4. ESI mass spectra were recorded with a JEOL JMS-SX102A instrument at the GC-MS & NMR Laboratory of the Faculty of Agriculture at Hokkaido University. Elemental analysis and HR-ESI-MS were performed at the Center for Instrumental Analysis of Hokkaido University.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-(2-diphenylphosphinoylbenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (6a). 2-Diphenylphosphinoylbenzyl bromide (**5a**: 1.90 g, 5.1 mmol) was added to a suspension of **3** (1.40 g, 1.3 mmol) and NaH (106 mg, 2.7 mmol) in DMF (30 mL). The reaction mixture was stirred at 50 °C for 20 h. After cooling to room temperature, the unreacted NaH was slowly quenched by adding MeOH and H_2O. The crude product was extracted with Et_2O/toluene (3:1) and the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. Purification was performed with preparative GPC. Remove of volatiles gave an analytically pure product as pale-yellow solids (1.75 g, 97%). Anal. Calcd for $C_{90}H_{109}O_7P\cdot CHCl_3$: C, 75.21; H, 7.63%. Found: C, 74.83; H, 7.90%. HR-ESI-MS m/z calcd for $[M + Na]^+$: 1355.7809; found: 1355.7812.

^{1}H NMR ($CDCl_3$): δ 0.98 (s, 18H), 1.14 (s, 9H), 1.28 (s, 9H), 1.30 (s, 18H), 2.34 (s, 6H, OCH_3), 2.71 (s, 3H, OCH_3), 3.03 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.34 (s, 6H, OCH_3), 3.65 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.80 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.95 (br.s, 2H, $ArCH_2Ar$), 4.08 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.20 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 5.10 (s, 2H), 6.71 (s, 2H), 6.78 (s, 2H), 6.85 (s, 2H), 7.00 (s, 3H), 7.10 (br.s, 3H), 7.16 (s, 1H), 7.45 (br.s, 6H), 7.62 (br.s, 6H), 8.27 (br.s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.92, 30.56, 30.65, 31.26, 31.37, 31.50, 31.65, 34.14, 34.21, 34.26, 59.96, 60.04, 60.18, 71.30, 124.09, 124.89, 126.05, 126.56, 126.92, 127.15, 127.81, 128.73 (d, $^3J_{P,C} = 11$ Hz), 132.02 (d, $^3J_{P,C} = 12$ Hz), 132.17, 132.71, 132.84, 132.99, 133.24, 133.27, 133.60 (d, $^2J_{P,C} = 13$ Hz), 133.79 (d, $^2J_{P,C} = 12$ Hz), 143.80, 143.86, 145.64, 145.72, 145.76, 146.00, 151.37, 153.52, 153.95, 154.40; ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.9.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-(2-diphenylphosphinobenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (1a). A solution of **6a** (1.70 g, 1.3 mmol) in toluene (25 mL) was refluxed in the presence of $PhSiH_3$ (4.7 mL, 38 mmol) for 2 d. The solvent was then removed under reduced pressure and the residue dissolved in CH_2Cl_2 (ca. 2 mL). Reprecipitation with MeOH afforded the product as white solids. An analytically pure product was obtained by recrystallization from CH_2Cl_2/MeOH (2:5). White solids were obtained (1.04 g, 62%). Anal. Calcd for $C_{90}H_{109}O_6P\cdot CH_3OH$: C, 80.97; H, 8.44%. Found: C, 80.99; H, 8.48%. HR-ESI-MS m/z calcd for $[M + Na]^+$: 1339.7860; found: 1339.7833. ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 18H), 1.13 (s, 9H), 1.26 (s, 9H), 1.27 (s, 18H), 2.40 (s, 6H, OCH_3), 2.73 (s, 3H, OCH_3), 3.27 (s, 6H, OCH_3), 3.35 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.67 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.83 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.03 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.16 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.32 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 5.14 (s, 2H), 6.79 (s, 2H), 6.81 (s, 2H), 6.88 (s, 2H), 7.00 (s, 2H), 7.09–7.31 (m, 13H), 7.41 (t, 2H, $J = 8$ Hz), 7.62 (t, 1H, $J = 8$ Hz), 8.00 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.50, 31.29, 31.39, 31.48, 31.62, 34.14, 34.20, 34.25, 59.90, 59.94, 126.87, 128.59 (d, $^2J_{P,C} = 8$ Hz), 128.79, 133.20, 133.26, 133.43, 133.56, 133.71, 133.82, 133.92, 134.01, 136.03, 145.58, 154.50; ^{31}P{^{1}H} NMR ($CDCl_3$): δ −15.6.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-(3-diphenylphosphinoylbenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (6b). The compound was synthesized with **3** (1.0 g, 1.0 mmol) and 3-diphenylphosphinoylbenzyl bromide (**5b**, 0.35 g, 1.4 mmol) by a method similar to that used for **6a**. Pale-yellow solids were obtained (1.1 g, 88%). Anal. Calcd for $C_{90}H_{109}O_7P\cdot CHCl_3$: C, 75.21; H, 7.63%. Found: C, 75.00; H, 7.85%. HR-ESI-MS m/z calcd for $[M + Na]^+$: 1355.7809; found: 1355.7806. ^{1}H NMR ($CDCl_3$): δ 0.92 (s, 9H), 0.98 (s, 18H), 1.25 (s, 9H), 1.26 (s, 18H), 2.42 (s, 6H, OCH_3), 2.71 (s, 3H, OCH_3), 3.30 (s, 6H, OCH_3), 3.39 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.62 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.75 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.13 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.21 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.37 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.90 (s, 2H), 6.80 (br.s, 2H), 6.81 (s, 2H), 6.86 (br.s, 3H), 7.10 (br.s, 2H), 7.13 (s, 2H), 7.18 (br.s, 2H), 7.39 (br.t, 4H, $J = 7.8$ Hz), 7.48 (br.t, 3H, $J = 6.0$ Hz), 7.64–7.70 (m, 4H), 7.78 (d, 1H, $J = 5.0$ Hz), 7.80 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.32, 30.43, 30.53, 31.27, 31.36, 31.62, 34.14, 34.25, 59.97, 60.13, 73.86, 124.50, 124.85, 124.98, 126.95, 127.12, 127.42, 128.53, 128.65, 131.98 (d, $^2J_{P,C} = 11$ Hz), 132.12, 132.23, 133.10 (d, $^2J_{P,C} = 11$ Hz), 133.28, 133.38, 133.65, 133.78, 145.73, 145.79, 153.52, 154.37; ^{31}P{^{1}H} NMR ($CDCl_3$): δ 29.6.

5,11,17,23,29,35-Hexa-*tert*-butyl-37-(3-diphenylphosphinobenzyloxy-38,39,40,41,42-pentamethoxycalix[6]arene (1b). The compound was synthesized with **6b** (0.65 g, 0.49 mmol) and $PhSiH_3$ (1.8 mL, 15 mmol) by a method similar to that used for **1a**. White solids were obtained (0.59 g, 90%). HR-ESI-MS m/z calcd for $[C_{90}H_{109}O_6P + Na]^+$: 1339.7860; found: 1339.7844. ^{1}H NMR ($CDCl_3$): δ 0.93 (s, 9H), 1.01 (s, 18H), 1.25 (s, 9H), 1.27 (s, 18H), 2.46 (s, 6H, OCH_3), 2.75 (s, 3H, OCH_3), 3.27 (s, 6H, OCH_3), 3.42 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.67 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 3.80 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.08 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.20 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.38 (d, 2H, $ArCH_2Ar$, $^2J_{H,H} = 15$ Hz), 4.84 (s, 2H), 6.82 (s, 2H), 6.83 (s, 2H), 6.89 (s, 2H), 7.11 (s, 2H), 7.13 (s, 2H), 7.20 (s, 2H), 7.25–7.34 (m, 11H), 7.37 (t, 1H, $J = 10$ Hz), 7.42 (d, 1H, $J = 8$ Hz), 7.58 (d, 1H, $J = 8$ Hz); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.45, 30.64, 30.70, 31.31, 31.40, 31.59, 31.63, 34.15, 34.25, 59.94, 60.00, 60.13, 74.44, 124.48, 124.95, 125.14, 126.92, 127.01, 127.48, 128.58 (d, $^2J_{P,C} = 7$ Hz), 128.78, 133.20, 133.26, 133.31, 133.43, 133.69 (d, $^2J_{P,C} = 8$ Hz), 133.93, 137.10, 137.22, 138.10, 138.18, 145.72, 145.74, 145.96; ^{31}P{^{1}H} NMR ($CDCl_3$): δ −4.79.

37-(2-Diphenylphosphinoylbenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (7a). The compound was synthesized with **5a** (1.18 g, 3.2 mmol) and **4** (1.87 g, 2.7 mmol) by a method similar to that used for **6a**. Pale-yellow solids were obtained (1.37 g, 52%). HR-ESI-MS m/z calcd for $[C_{66}H_{61}O_7P + Na]^+$: 1020.1499; found: 1019.4050. ^{1}H NMR ($CDCl_3$): δ 2.75 (s, 6H, OCH_3), 3.24 (s, 9H, OCH_3), 3.59 (s, 4H, $ArCH_2Ar$), 3.89 (s, 4H, $ArCH_2Ar$), 3.96 (s, 4H, $ArCH_2Ar$), 5.22 (s, 2H), 6.68–6.73 (m, 3H), 6.80–6.83 (m, 4H), 6.89 (t, 2H, $J = 8$ Hz), 6.94–7.02 (m, 10H), 7.44 (br.t, 4H, $J = 8$ Hz), 7.51 (t, 2H, $J = 7$ Hz), 7.57–7.64 (m, 6H), 8.11 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.86, 30.30, 30.39, 60.08, 60.15, 60.48, 71.86, 123.30, 123.48, 123.54, 123.90, 127.72, 128.61, 128.75 (d, $^3J_{P,C} = 11$ Hz), 128.88, 129.26, 129.52, 130.26, 132.09, 132.14, 132.18, 132.67, 134.39, 134.45, 134.59, 134.74, 153.83, 156.17, 156.43, 156.70; ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.9.

37-(2-Diphenylphosphinobenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (2a). The compound was synthesized with **7a** (1.37 g, 1.4 mmol) and $PhSiH_3$ (5.0 mL, 41 mmol) by a method similar to that used for **1a**. White solids were obtained (0.89 g, 66%). HR-ESI-MS m/z calcd for $[C_{66}H_{61}O_6P + Na]^+$: 1003.4103; found: 1003.4113. ^{1}H NMR ($CDCl_3$): δ 2.82 (s, 6H, OCH_3), 3.20 (s, 6H, OCH_3), 3.24 (s, 3H, OCH_3), 3.85 (s, 4H, $ArCH_2Ar$), 3.91 (s, 4H, $ArCH_2Ar$), 3.97 (s, 4H, $ArCH_2Ar$), 5.13 (s, 2H), 6.72 (t, 1H, $J = 8$ Hz), 6.78–7.31 (m, 29H), 7.39 (t, 1H, $J = 7$ Hz), 7.84 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.30, 30.38, 60.11, 60.45, 72.40, 123.35, 123.51, 123.82, 127.21, 127.67, 127.84, 128.69 (d, $^2J_{P,C} = 6$ Hz), 128.91, 128.98, 129.16, 129.31, 129.54, 130.14, 133.02, 133.91, 134.05, 134.46, 134.56 (d, $^2J_{P,C} = 9$ Hz), 134.77, 134.84, 136.19, 154.37, 156.24, 156.42, 156.72; ^{31}P{^{1}H} NMR ($CDCl_3$): δ −15.8.

37-(3-Diphenylphosphinoylbenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (7b). The compound was synthesized with **5b** (0.13 g, 0.35 mmol) and **4** (0.21 g, 0.29 mmol) by a method similar to that used for **6a**. Pale-yellow solids were obtained (0.33 g, 95%). Anal. Calcd for $C_{66}H_{61}O_7P\cdot CHCl_3\cdot MeOH$: C, 71.11; H, 5.79%. Found: C, 71.03; H, 5.64%. HR-ESI-MS m/z calcd for $[M + Na]^+$: 1020.1499; found: 1019.4043. ^{1}H NMR ($CDCl_3$): δ 2.89 (s, 6H, OCH_3), 3.16 (s, 3H, OCH_3), 3.22 (s, 6H, OCH_3), 3.89 (s, 4H, $ArCH_2Ar$), 3.92 (s, 4H, $ArCH_2Ar$), 3.97 (s, 4H, $ArCH_2Ar$), 4.79 (s, 2H), 6.76–7.05 (m, 20H), 7.37 (br.t, 4H $J = 4$ Hz), 7.43–7.49 (m, 2H), 7.54 (d, 1H, $J = 8$ Hz), 7.66–7.79

(m, 4H), 7.77 (d, 1H, $J = 12$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.26, 30.47, 30.67, 60.11, 60.17, 60.38, 74.17, 128.38, 128.57, 128.69, 128.86, 128.93, 129.34, 129.68, 129.86, 131.19 (d, $^3J_{P,C} = 11$ Hz), 131.65 (d, $^3J_{P,C} = 11$ Hz), 132.15 (d, $^2J_{P,C} = 11$ Hz), 133.12, 133.25, 134.36, 134.48, 134.61, 134.77, 138.29 (d, $^3J_{P,C} = 12$ Hz), 154.22, 156.21, 156.54, 156.64; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.5.

37-(3-Diphenylphosphinobenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (2b). The compound was synthesized with **7b** (0.12 g, 0.12 mmol) and $PhSiH_3$ (0.43 mL, 3.5 mmol) by a method similar to that used for **1a**. White solids were obtained (0.06 g, 52%). Anal. Calcd for $C_{66}H_{61}O_6P \cdot CH_2Cl_2 \cdot$MeOH: C, 74.37; H, 6.15%. Found: C, 74.43; H, 6.24%. HR-ESI-MS m/z calcd for $[M + Na]^+$: 1003.4103; found: 1003.4120. ^1H NMR ($CDCl_3$): δ 2.90 (s, 6H, OCH_3), 3.17 (s, 3H, OCH_3), 3.24 (s, 6H, OCH_3), 3.91 (s, 4H, $ArCH_2Ar$), 3.95 (s, 4H, $ArCH_2Ar$), 3.98 (s, 4H, $ArCH_2Ar$), 4.76 (s, 2H), 6.79–7.43 (m, 32H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.31, 30.45, 30.67, 60.11, 60.17, 60.39, 74.82, 123.48, 123.56, 123.85, 128.16, 128.63 (d, $^2J_{P,C} = 7$ Hz), 128.88 (d, $^2J_{P,C} = 8$ Hz), 129.31, 129.70, 130.02, 133.35, 133.55, 133.73, 133.92, 134.50, 134.64, 134.75, 134.85, 137.09, 137.19, 137.41, 137.53, 137.92, 137.99, 154.30, 156.21, 156.53, 156.72; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −4.73.

37-(4-Diphenylphosphinoylbenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (7c). The compound was synthesized with 4-diphenylphosphinoylbenzyl bromide (**5c**: 0.61 g, 1.64 mmol) and **4** (0.97 g, 1.37 mmol) by a method similar to that used for **6a**. A light-yellow solid was obtained. Yield: 0.9 g (66%). HR-ESI-MS m/z calcd for $[C_{66}H_{61}O_7P + Na]^+$: 1020.1499; found: 1019.4055. ^1H NMR ($CDCl_3$): δ 2.87 (s, 3H, OCH_3), 3.05 (s, 6H, OCH_3), 3.24 (s, 6H, OCH_3), 3.88 (s, 4H, $ArCH_2Ar$), 3.89 (s, 4H, $ArCH_2Ar$), 3.96 (s, 4H, $ArCH_2Ar$), 4.50 (s, 2H), 6.68 (t, 2H, $J = 8$ Hz), 6.80 (d, 2H, $J = 8$ Hz), 6.85–6.88 (m, 6H), 6.94–7.01 (m, 8H), 7.33 (br.d, 2H, $J = 7$ Hz), 7.43 (br.t, 4H, $J = 8$ Hz), 7.53 (t, 2H, $J = 7$ Hz), 7.57–7.60 (m, 2H), 7.64–7.67 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.33, 30.48, 60.11, 60.14, 60.20, 73.78, 123.39, 123.51, 123.60, 124.00, 127.61, 127.69, 128.57 (d, $^3J_{P,C} = 11$ Hz), 128.80, 129.40, 129.46, 129.63, 131.94, 132.14, 132.20, 134.29, 134.45 (d, $^2J_{P,C} = 11$ Hz), 134.58, 134.70, 134.77, 154.42, 156.15, 156.44, 156.60; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.5.

37-(4-Diphenylphosphinobenzyloxy)-38,39,40,41,42-pentamethoxycalix[6]arene (2c). The compound was synthesized with **7c** (0.9 g, 0.9 mmol) and $PhSiH_3$ (3.4 mL, 27 mmol) by a method similar to that used for **1a**. White solids were obtained (0.73 g, 82%). Anal. Calcd for $C_{66}H_{61}O_6P \cdot 0.5CH_2Cl_2 \cdot 0.5$MeOH: C, 77.40; H, 6.20%. Found: C, 77.58; H, 6.31%. HR-ESI-MS m/z calcd for $[M + Na]^+$: 1003.4103; found: 1003.4132. ^1H NMR ($CDCl_3$): δ 3.00 (s, 3H, OCH_3), 3.08 (s, 6H, OCH_3), 3.32 (s, 6H, OCH_3), 3.99 (s, 8H, $ArCH_2Ar$), 4.04 (s, 4H, $ArCH_2Ar$), 4.64 (s, 2H), 6.78 (t, 2H, $J = 8$ Hz), 6.90–7.38 (m, 30H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.44, 30.54, 30.59, 60.21, 60.25, 60.28, 74.43, 123.50, 123.57, 123.69, 123.94, 128.15 (d, $^2J_{P,C} = 7$ Hz), 128.67 (d, $^2J_{P,C} = 7$ Hz), 128.76, 128.85, 129.51, 129.70, 129.74, 133.81, 133.94, 134.04, 134.41, 134.61, 134.72, 134.78, 134.91, 136.51, 136.58, 137.36, 137.43, 138.51, 154.60, 156.23, 156.64, 156.69; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.20.

X-ray Diffraction Study. Data of **6a** were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at 153 K, and processed using CrystalClear (Rigaku). The structures were solved by a direct method (SIR92[27]) and refined by full-matrix least-square refinement on F^2. The non-hydrogen atoms, except one disordered *t*-butyl group and solvated molecules, were refined anisotropically. All hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the CrystalStructure software package. Crystal data for **6a**$\cdot 0.5C_2H_4Cl_2 \cdot 0.5CH_3OH \cdot 0.5H_2O$: $C_{94.5}H_{114}ClO_7P$, $M_r = 1428.36$, $T = 153$ K, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.569(2)$, $b = 14.136(14)$, $c = 26.665(18)$ Å, $\alpha = 81.21(1)°$, $\beta = 89.21(9)°$, $\gamma = 83.26(13)°$, $U = 4280(5)$ Å^3, $Z = 2$, μ(Mo Kα) = 1.15 cm^{-1}, observed reflections 8888 ($I > 3\sigma(I)$), R, $Rw = 0.101$, 0.231 ($I > 3\sigma(I)$). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-697714 for compound **6a**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax:+44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Theoretical Calculation. Molecular-orbital calculations were performed with the Gaussian 03 program[28] on a HIT HPC-IA642/SS 1.3/3D-4G. Conformation analysis of each conformer was performed with CONFLEX5[21] program using MMFF94s[22] as a force field. DFT calculation was carried out at B3LYP[23]/LANL2DZ[24] level.

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