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Narrow-Rim Functionalization of Calix[4]arenes via Sonogashira Coupling Reactions

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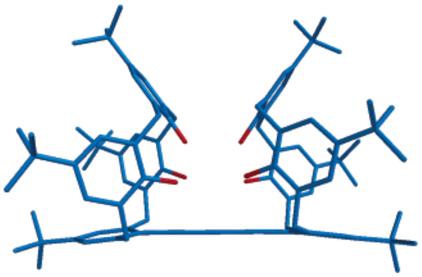
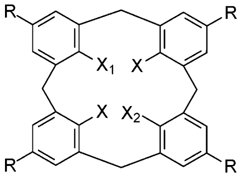


The narrow (or "lower")-rim hydroxyl groups of calixarenes are known to be resistant to substitution/displacement. The Sonogashira coupling reaction with TMSA and phenylacetylene, however, has now been extended to the bistriflate of *p-tert*-butylcalix[4]arene, previously known to be resistant to Stille, Neigishi, or Suzuki–Miyaura reactions. Under some of the reaction conditions investigated, the previously unknown narrow-rim mono- and diiodo-*p-tert*-butylcalix[4]arene products were also produced, in addition to the narrow-rim mono- and dialkynyl products. Homocoupling of the narrow-rim monoethynyl-*p-tert*-butyl-calix[4]arene produced a new narrow-rim rigid butadiyne-linked bis-*p-tert*-butylcalix[4]arene.

Introduction

Many other research groups have demonstrated that structural modifications of calix[4]arenes[1] can lead to significant changes in their chemical and physical properties, and this has resulted in much synthetic effort being directed toward producing analogues and derivatives of these versatile molecules. The great majority of the modifications have involved narrow (or "lower")-rim functionalization of the phenolic hydroxy groups or, to a lesser extent, wide (or "upper")-rim modifications. The latter have generally involved de-*p-tert*-butylation[2] of the readily accessible tetra-*p-tert*-butylcalix[4]arene (**1**) to form **2**, followed, for example, by either halogenation or nitration at the positions *para* to the hydroxy groups, and subsequent functional group interconversions via a broad range of reaction types.[3]



1: R = *t*-Bu; X = X_1 = X_2 = OH
2: R = H; X = X_1 = X_2 = OH
3: R = *t*-Bu; X = OH, X_1 = X_2 = OTf
4: R = *t*-Bu; X = OH, X_1 = X_2 = OMs
5: R = *t*-Bu; X = X_1 = OH, X_2 = OTf

Modifications of the narrow rim of calixarenes have primarily involved aliphatic mono- to tetra-*O*-alkylation

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10.1021/jo050488s CCC: \$30.25

TABLE 1. Some Typical Reaction Conditions Employed and Products (7−10) Obtained for the Pd-Catalyzed Reactions of Bistriflate 3 with Trimethylsilylacetylene (6a) in Refluxing Toluene Solution

entry	**6a** molar equiv	base/molar equiv	CuI mol %	catalyst/mol %	time (h)	**7**	**8**	**9**	**10**
1	1.4	DBU/4	500	$Pd(PPh_3)_2Cl_2$/10	1.5	19	12	8	25
2	1.4	DBU/2	240	$Pd(PPh_3)_2Cl_2$/10	4.0	8	tr	17	64
3	2.0	DBU/4	1	$Pd(PPh_3)_2Cl_2$/1	1.0	tr	51	0	tr
4	2.5	DBU/2	200	$Pd(PPh_3)_2Cl_2$/1	1.0	43	44	tr	tr
5		DBU/2	600	$Pd(PPh_3)_2Cl_2$/10	4.0			14	64

(e.g., with groups such as Me, Et, Bn, -$CH_2CO_2CH_2CH_3$, etc.) or mono- to tetra-*O*-esterification (e.g., using CH_3COCl, PhCOCl, etc.) and *O*-arylation.[4] There are far fewer reported instances of hydroxy group substitution reactions on calix[4]arenes such as **1** by, for example, hydrogen atoms,[5] amino,[6] or sulfhydryl groups.[7]

We have been interested for some time in the potential for functionalizing the narrow rim of calix[4]arenes using metal-assisted coupling reactions such as the Stille[8] and Suzuki−Miyaura[9] reactions on the corresponding calix[4]arene triflates or mesylates. González et al.[10] reported that an attempted Pd-catalyzed Stille reaction with 1,3-bistriflate **3** or 1,3-bismesylate **4** resulted instead in intermolecular migration of the sulfonyl groups and that no narrow-rim substitution occurred with these substances. In our own hands,[11] the following reactions, using the mono- to tetrakistriflates of **1**, failed to afford any of the desired products, affording only unexpected products. For example, a Pd-catalyzed carbonylative Suzuki−Miyaura-type reaction[12] with the 1,3-bistriflate **3** and phenylboronic acid resulted only in the formation of an unprecedented stable 1:1 supramolecular complex of benzophenone and the monotriflate **5**,[11] with no evidence of triflate displacement. Also an attempted deoxygenation of **3** using Snieckus Pd-catalyzed conditions[13] with **3** also failed, affording instead a different 1:1 supramolecular complex between triethylamine and **5**.[11]

We have now found, however, that Pd-catalyzed reactions of **3** under Sonogashira coupling[14] conditions, using trimethylsilylacetylene (TMSA, **6a**) and a few other representative terminal acetylenes to demonstrate the generality of the reaction conditions, produces the desired narrow-rim substitution and coupling products. The aliphatic terminal alkynes 3-butyn-1-ol (**6b**), 5-hexyn-1-ol (**6c**), and the phenyl-containing terminal alkyne phenylacetylene (**6d**) were used in this study. Under certain conditions, an unusual aromatic substitution of the narrow-rim triflates by iodide was also observed. This paper therefore reports the first successful Sonogashira reaction mediated *narrow-rim* functionalizations of a calix[4]arene.

Results and Discussion

To the best of our knowledge, there are only six published reports in which the Sonogashira reaction has been employed with calixarenes, and five of these involve functionalization of the *wide* rim.[15−19] The other involves conversion of *tetrakis-p*-iodobenzyloxycalix[4]arene to form the corresponding *tetrakis-p*-(mannopyranosyl)-benzyloxycalix[4]arene,[20] but the reactions described do not involve displacement of the phenolic oxygen atoms on the narrow rim. Our initial experiments with the Sonogashira reaction conditions and 1,3-bistriflate calix[4[arene (**3**)[14,21] were conducted with TMSA since we were also interested in the synthesis of rigid, alkynyl-bridged biscalixarenes (see below). During these experiments, several different bases, for example, triethylamine, 2,6-lutidine, ammonium hydroxide, and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), and different solvents, for example, benzene, THF, dioxane, DMF, and toluene, were evaluated. DBU and toluene were found to be the best base and solvent combination to use (e.g., see Table 1). It was also found to be necessary to use refluxing temperatures for any reaction to occur between **3** and TMSA. In one of these experiments, four new calix[4]arene products **7**−**10** were formed (Scheme 1, reaction conditions *a*; Table 1, entries 1 and 2) in addition to the formation of some of the homocoupling product of TMSA itself, namely, 1,4-bis(trimethylsilyl)-1,3-butadiyne (which was also formed in all of the reactions evaluated).

The structures of **7** and **8** were established by NMR and single-crystal X-ray crystallography to be the narrow-rim functionalized iodo- and trimethylsilylethynyl-substituted calix[4]arene (**7**) and the monotrimethylsilylethynyl-substituted monotriflate, **8**. The X-ray structure of **7** (Figure 1) reveals it to be in a *pinched-cone* conformation in which the two distal aryl rings containing the iodo and the trimethylsilylethynyl groups are parallel to each other. The X-ray structure of **8** (not shown), which has two molecules in the asymmetric unit,

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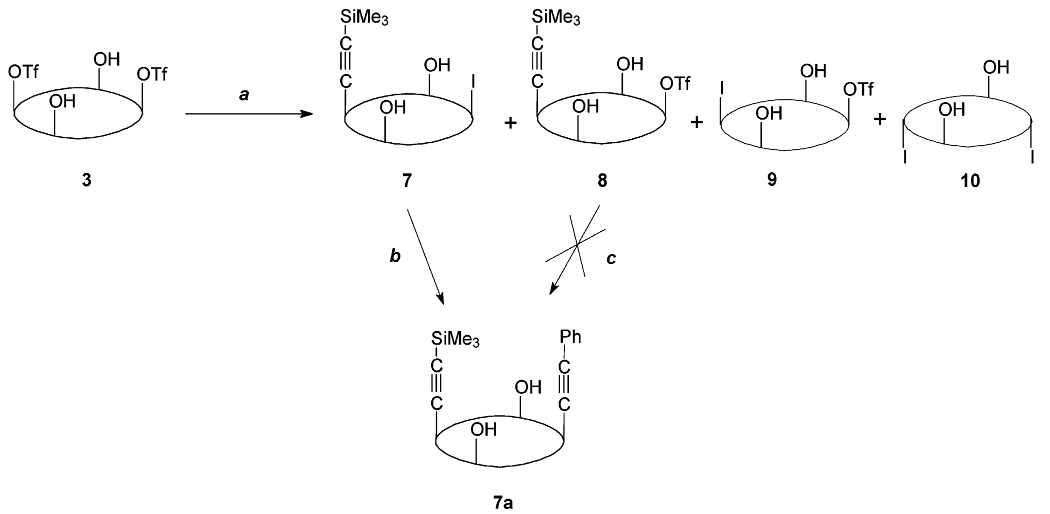
SCHEME 1^a



^{a} Conditions: (*a*) see Table 1; (*b* and *c*) PdCl$_2$(PPh$_3$)$_2$ (5 mol %), CuI (5 mol %), toluene, DBU (2 equiv), reflux, **6d**, 3 h.

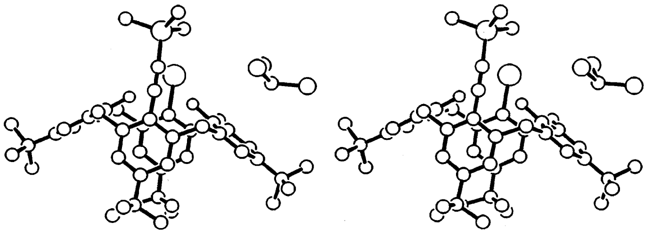


FIGURE 1. X-ray single-crystal PLUTO stereoview of **7** in a *pinched-cone* conformation and a molecule of CHCl$_3$ (all of the H atoms have been removed for clarity).

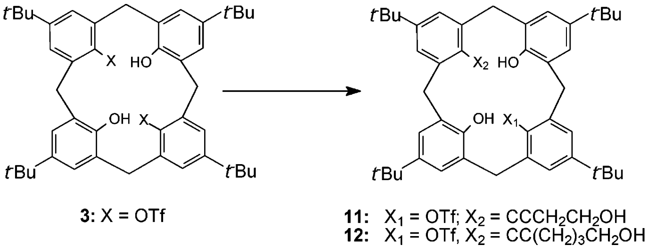
also reveals it to be in a similar *pinched-cone* conformation, in which the two distal aryl rings bearing the triflate and trimethylsilylethynyl groups are parallel to each other, by analogy with the structure of **7**.

Although crystals of **9** or **10** suitable for X-ray analysis were not forthcoming, their NMR and mass spectra were in agreement with the structures depicted. In solution, as ascertained by the NMR spectra, their conformations are *pinched-cone* and 1,3-*alternate,* respectively, as predicted using deMendoza's criteria.[22]

The incorporation of the trimethylsilylethynyl groups onto the narrow rim of calix[4]arene in **7** and **8** are the first examples to be reported of a *metal-assisted* direct coupling of an alkyne moiety, by displacement of the phenolic functionality on the narrow rim of a calixarene. The presence of the iodine atoms in **7**, **9**, and **10**, however, was unexpected. These compounds are also the first examples to be reported in which a direct metal-assisted substitution by a halide has occurred on the narrow rim of a calix[4]arene.

To determine whether the iodo compounds were formed as intermediates or byproducts of the reaction, conditions were evaluated in order to optimize the yields of these iodo products. Using similar Pd-catalyzed conditions as were used above but excluding the terminal acetylenes, the monoiodo- and diiodocalixarenes **9** and **10**, respectively, could be formed in reproducible and synthetically useful yields of 14% and 64%, respectively (Table 1, entry 5). However, with synthetically useful yields of both **9** and **10** in hand, attempts to effect the coupling reaction of TMSA directly on either of these compounds, under the same Sonogashira reaction conditions used previously, failed to produce any TMSA-coupled products. Only 1,4-bis(trimethylsilyl)-1,3-butadiyne and unreacted starting material were recovered. These results suggest that the iodo compounds were therefore not formed as intermediates in the reactions of **3** with TMSA that produced **7** and/or **8** but that they were formed as byproducts instead.

SCHEME 2^a



^{a} Conditions: PdCl$_2$(PPh$_3$)$_2$ (2 mol %), CuI (5 mol %), toluene, DBU (2 equiv), reflux, 3 h. For **11** (32% yield), compound **6b** was used; for **12** (20% yield), compound **6c** was used.

The optimal conditions that were found for synthesizing **8** (in 51% isolated yields) required 1 mol % of both the Pd catalyst and the CuI cocatalyst and 4 molar equiv of DBU, in refluxing toluene (Table 1, entry 3). However, when a higher molar ratio of the CuI was used, together with a more concentrated solution of reactants (Table 1, entry 4), a mixture containing both **7** and **8** in 43% and 44% yields, respectively, was obtained. To test the generality of these reaction conditions for other potential narrow-rim substitutions, **3** was reacted with some other readily available terminal alkynes. The reactions of **3** with, for example, 3-butyn-1-ol (**6b**) or 5-hexyn-1-ol (**6c**), under the optimal conditions found for TMSA, gave the corresponding monosubstituted products **11** and **12**, respectively (Scheme 2). However, as was also found with

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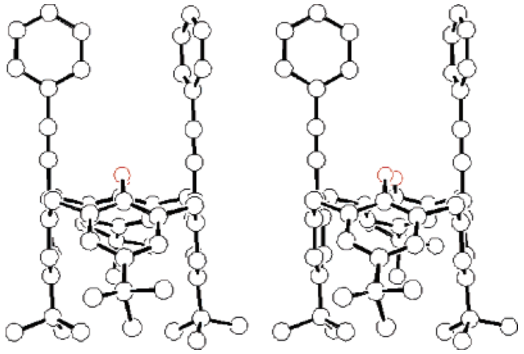


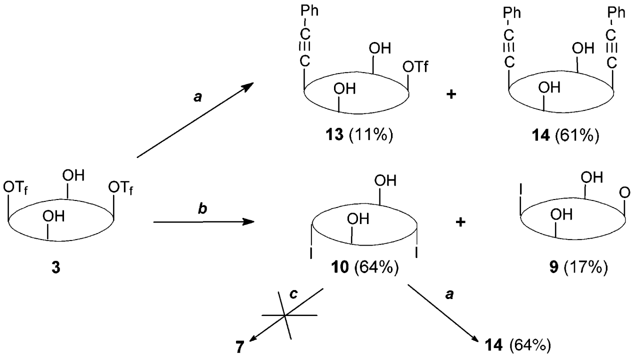
FIGURE 2. X-ray single-crystal PLUTO stereoview of 1,3-bis(phenylethynyl)calix[4]arenes, **14** (all of the H atoms have been removed for clarity).

the reactions of **3** with TMSA, none of the corresponding disubstituted products were obtained.

With phenylacetylene (**6d**), on the other hand, Pd-catalyzed coupling with **3** afforded both the expected mono- *and* 1,3-bis(phenylethynyl)calix[4]arenes **13** and **14**, respectively. A single-crystal X-ray determination of **14** (Figure 2) showed the two aryl groups that bear the phenylethynyl groups to be parallel to each other, in a *pinched-cone* conformation, analogous to those observed for **7** and **8**. The conformation of **14** is similar to that of the *wide-rim*-substituted tetrakis-*p*-nitrophenylethynyl-calix[4]arene compound recently described by Hennrich and co-workers.[20] As determined by X-ray crystallography, the two pendant-type *p*-nitrophenylethynyl groups in their compound and in our narrow-rim-substituted **14** are similarly oriented, having approximate "edge-to-face" types of interactions, in which the twist angles in **14** are 80.8° as compared with the approximately 60° angle in their compound.

The best yields of **13** and **14** (11% and 64%, respectively) that we obtained required the use of 5 mol % of both the Pd catalyst and the cocatalyst CuI, with 3 molar equiv of DBU, in refluxing toluene. When several other reaction condition modifications recently described by others[23] were tried with bistriflate **3** and **6d**, they all failed to produce any of the desired calixarene coupling products, affording instead only 1,4-diphenyl-1,3-butadiyne and recovered unreacted **3**. However, in contrast to the reactions of TMSA or **6b** or **6c** with **10**, phenylacetylene did produce **14** as the major product with 1,3-diiodo calix[4]arene **10** under the coupling conditions (Scheme 3).

SCHEME 3[a]



[a] Conditions: (*a*) $PdCl_2(PPh_3)_2$ (10 mol %), CuI (5 mol %), DBU (4 equiv), **6d**, toluene, reflux, 4 h; (*b*) $PdCl_2(PPh_3)_2$ (10 mol %), CuI (5.7 mol equiv), DBU (2 equiv), toluene, reflux, rt, 3 h; (*c*) $PdCl_2(PPh_3)_2$ (10 mol %), CuI (5 mol %), DBU (4 equiv), **6a**, toluene, reflux, 4 h.

Pd−CuI-catalyzed coupling reaction of **7** with phenylacetylene (**6d**) (Scheme 1, reaction *b*) produced the corresponding mixed bisethynyl product **7a** in 54% yield. When the same conditions were used with **8** and **6d** (Scheme 1, reaction *c*), product **7a** was not formed, affording only 1,4-diphenyl-1,3-butadiyne and unreacted **8**. The reasons for this result can only be conjectured upon at this stage, but a possible explanation is that the steric hindrance due to the presence of both the bulky TMS *with* the triflate groups on the same substrate inhbits the formation of an intermediate in Sonogahira catalytic cycle,[14b] leading to the formation of **7a** in this case.

When the monotriflate **5** instead was employed to effect the same Pd-assisted Sonogashira coupling with TMSA, none of the desired monocoupling product **17** was obtained, producing only 1,4-bis(trimethylsilyl)-1,3-butadiyne and **1**. With **5** and phenylacetylene only 1,4-diphenyl-1,3-butadiyne and **1** was formed. As a result of these findings, subsequent narrow-rim transformations were carried out via the synthetically more accessible bistriflate **3**.

With synthetically useful amounts of **8** available, removal of the TMS group was easily achieved using 1 equiv of tetrabutylammonium fluoride (TBAF) followed by mild acid workup, to afford **15** (Scheme 4). Its ^1H NMR spectrum revealed, in addition to other signals due to a minor component (see discussion below), two sets of AB quartets centered at δ 3.87 and 4.02 ppm due to the bridging methylene groups and three singlets at δ 0.90, 0.98 and 1.35 in a ratio of 1:1:2, respectively, due to the *tert*-butyl groups. This is consistent for a structure that is in a *pinched-cone* conformation similar to those observed for **7**, **8**, and **14**. A single-crystal X-ray structure, however, showed a distinct unusual *partial-cone* (*paco*) conformation (Figure 3). The ^1H NMR spectrum of this compound would be expected to have revealed four singlets for the *tert*-butyl groups, which is not the case. It is therefore possible that **15** crystallizes out in a different conformation (i.e., *paco*-**15**) than that which predominantly exists in solution, since the difference in computed (MMFF) free energies between the *paco* and *pinched-cone* conformations is only 1.2 kcal mol^{-1}. The mass and NMR spectra of a trace minor component formed along with **15** is consistent with the 1,3-*alternate* conformational isomer, **16**.

Treatment of **8** with 2 equiv of TBAF, followed by mild acid workup, resulted in both the removal of the TMS group and cleavage of the triflate group to afford the trihydroxy-ethynyl compound **17**. The ^1H NMR spectra of **17** showed similarities to those of all of the other major products formed in this study; however, no crystals suitable for X-ray analysis could be obtained. This compound was next subjected to Glaser homocoupling

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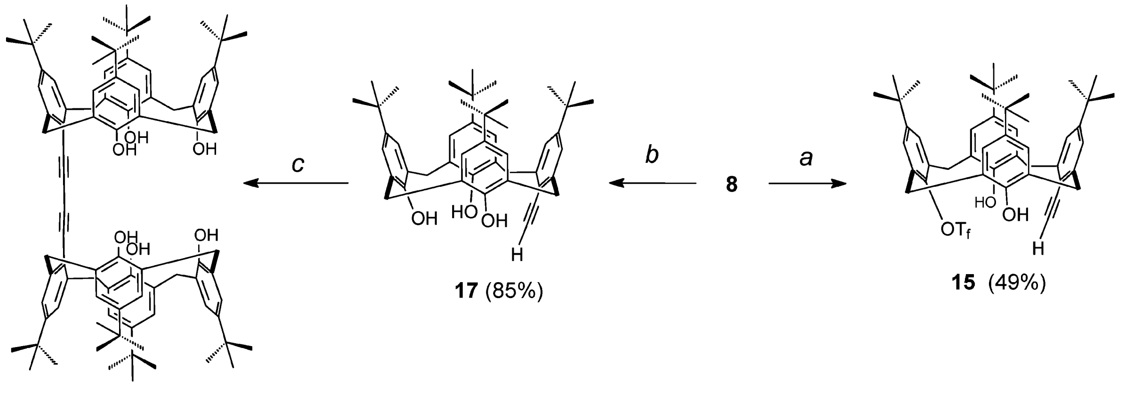
SCHEME 4[a]



[a] Conditions: (*a*) 1 equiv TBAF, THF, rt, 15 min; (*b*) 2 equiv TBAF, THF, rt, 15 min; (*c*) CuI (5 equiv), DBU (2.4 equiv), toluene, rt, 15 min.

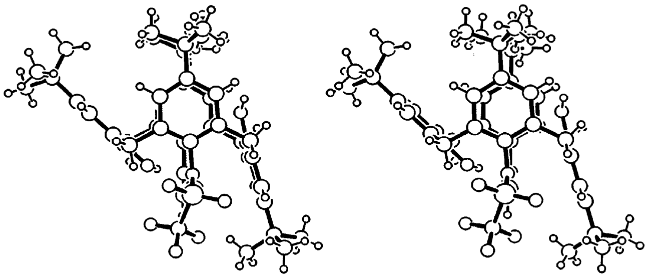


FIGURE 3. X-ray single-crystal PLUTO stereoview of *paco*-**15** in a partial cone conformation in which one pair of distal phenolic groups are anti to each other

conditions[24] to produce the desired narrow-rim mono-butadiyne-bridged biscalix[4]arene **18**. The spectroscopic and mass properties of **18** are consistent with the proposed structure (Scheme 3). In particular, the ^{1}H NMR reveals signals that are consistent for each calixarene unit being in a *cone*-like conformation. The lowest energy conformation predicted by MMFF molecular modeling calculations[25] is one in which the two calixarenes, each of which is in a *pinched-cone* conformation, are situated directly above (eclipse) each other, most likely as a result of hydrogen-bonding that can occur between the hydroxy groups of each calixarene unit. The *intra*calixarene O···H bond distances are 1.67 and 1.73 Å, with the closest O···H and O···O bond distances between the two calixarene units being 2.53 and 2.84 Å, respectively. The rigid butadiyne linkage provides a near-linear "spine" connecting the two calixarene units (Figure 4).

Complexation Studies

Preliminary complexation tests with **18** were conducted individually with NaI, KI, RbI, and $HgCl_2$ in 1:1 methanol-d_4/$CDCl_3$; with tetramethylammonium chloride or CF_3CO_2Ag in neat $CDCl_3$; with $AgBF_4$ or $AgClO_4$ in $CDCl_3$/acetone-d_6; with CH_3CN or hexamethylbenzene in $CDCl_3$; or with C_{60} in CS_2 or toluene-d_8 solutions. As determined by ^{1}H NMR spectroscopy, no significant complexation have yet been discerned with any of these cationic or neutral guests.

Conclusions

We have shown for the first time that the Pd-catalyzed Sonogashira reaction can now be extended to the direct functionalization of the narrow rim of calix[4]arene. While undoubtedly modifications in the future might lead to better synthetic yields, the reactions demonstrated in this paper show that reasonably useful synthetic yields of the narrow-rim alkynyl derivatives can be obtained. Phenylacetylene is the most reactive of the terminal alkynes examined in this study and also appears to be the most robust toward the reaction conditions. Despite the fact that preliminary studies have thus far failed to reveal any significant complexation properties for this biscalix[4]arene, this compound represents the first example of a biscalixarene that has been formed by directly linking two calixarenes at their narrow rims via potentially modifiable hydrocarbon groups. Thus, the molecular architectures of calixarenes can now be further elaborated using the synthetic route that has been opened up and described in this paper. Experiments are currently underway to develop and extend the Sonogashira coupling conditions to these and other calix[*n*]arenes for further applications and studies, especially in the context of the nonlinear optical (NLO) properties of similar but wide-rim-substituted calix[4]arene compounds recently demonstated by Hennrich and coworkers.[20]

Experimental Section

General Methods. For general experimental methods, see ref 11. All of the ^{1}H and ^{13}C NMR spectra reported herein and presented in Supporting Information were recorded at 500 and 125 MHz and in $CDCl_3$.

(Trimethylsilyl)ethynyl-*p-tert*-butylcalix[4]arene Iodide 7 and (Trimethylsilyl)ethynyl-*p-tert*-butylcalix[4]arene Triflate 8. To a mixture of $PdCl_2(PPh_3)_2$ (0.77 mg, 0.0011 mmol), CuI (42 mg, 0.22 mmol), and **3** (100 mg, 0.11 mmol) heated at reflux in toluene (10 mL) and with stirring was added a solution of DBU (30 mg, 0.20 mmol) and **6a** (26 mg, 0.26 mmol) in toluene (5 mL). The reaction mixture was

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[24] (a) Glaser, C. *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422. (b) Glaser, C. *Ann. Chem. Pharm.* **1870**, *154*, 137.

[25] Molecular modeling calculations were performed using Spartan '04 for Windows.

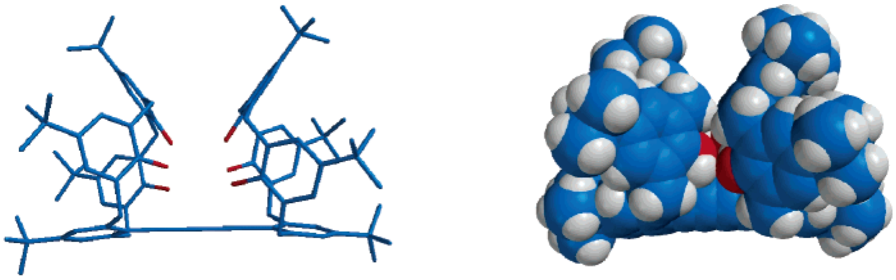

FIGURE 4. Computer-generated (MMFF-minimized) structure of butadiyne-bridged biscalix[4]arene **18** showing the relative orientation of the two calixarene units which are joined by the butadiyne backbone. Left: H atoms have been omitted from the structure for clarity. Right: space-filling representation of the same minimized structure.

stirred for a further 0.5 h at the reflux temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (20 mL) and washed with aqueous saturated NH_4Cl (10 mL) and with H_2O (10 mL). The CH_2Cl_2 extracts was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give the crude product, which was purified by PLC (1:9 acetonitrile/hexanes) to give the following compounds in order of increasing polarity. **7** (40 mg, 43%): ^{1}H NMR δ 0.37 (s, 9H), 0.74 (s, 9H), 0.94 (s, 9H),1.34 (s, 18H), 3.54 (d, J = 13.5 Hz, 2H), 3.65 (d, J = 13.5 Hz, 2H), 4.49 (dd, J = 14.5, 14.5 Hz, 4H), 5.18 (s, 2H, OH), 6.51 (s, 2H), 6.76 (s, 2H), 7.12 (s, 4H); ^{13}C NMR δ 0.41, 30.85, 30.89, 31.99, 33.79, 34.18, 34.51, 36.95, 44.52, 60.61, 103.47, 104.51, 105.87, 118.32, 124.14, 125.51, 125.60, 125.82, 128.10, 129.95, 141.60, 142.47, 143.25, 149.44, 151.60; MS (APCI$^+$) *m/z* 839.3 (M+), calcd for $C_{49}H_{63}O_2ISi$ 839.03. **8** (41 mg, 44%): ^{1}H NMR δ 0.39 (s, 9H), 0.78 (s, 9H), 0.93 (s, 9H),1.34 (s, 18H), 3.38 (d, J = 13.5 Hz, 2H), 3.61 (d, J = 14.0 Hz, 2H), 4.34 (d, J = 13.5 Hz, 2H), 4.40 (d, J = 14.0 Hz, 2H), 5.41 (s, 2H, OH), 6.61 (s, 2H), 6.80 (s, 2H), 7.13 (s, 2H), 7.15 (s, 2H); ^{13}C NMR δ −0.11, 30.80, 30.93, 31.94, 32.07, 34.07, 34.18, 34.56, 36.72, 60.61, 103.15, 106.08, 117.13, 124.44, 125.57, 125.61, 126.51, 127.10, 129.10, 132.92, 141.44, 142.54, 142.73, 149.31, 150.78, 152.35; MS (APCI$^+$) *m/z* 861.3 (M+), calcd for $C_{50}H_{63}O_5SiF_3S$ 861.18.

X-ray Crystal Data for 7. Colorless crystal (MeOH/$CHCl_3$), mp 274−276 °C, $C_{50}H_{64}O_{2I}SiCl_3$, triclinic, space group P-1 (No. 2), Z = 2, a = 13.1511(9) Å, b = 14.402(1) Å, c = 15.419(1) Å, α = 87.811(1)°, β = 76.823(1)°, γ = 62.993(1)°. V = 2526.3(3) Å^3, D_{calc} = 1.26 g cm ^{3}, crystal size = 0.60 × 0.28 × 0.05 mm^3. Intensity data were measured at 193 ± 1 K on a Bruker P4/CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation 2θ_{max} = 52.8°; 17987 reflections converged to a final R_{int} of 0.035 for 10245 unique reflections and 514 variable parameters and converged with unweighted and weighted factors of R1 and wR2. Final R1 and wR2 values were 0.064 and 0.180, respectively, and GOF = 1.04.

X-ray Crystal Data for 8. Colorless crystal (MeOH/$CHCl_3$), mp 285−287 °C, $C_{50}H_{63}O_5SiF_3S$, triclinic space group P-1 (No. 2), Z = 4, a = 13.218(1) Å, b = 18.086(1) Å, c = 22.432(2) Å, α = 106.191(1)°, β = 90.743(1)°, γ = 101.502(2)°. V = 5033.1(6) Å^3. D_{calc} = 1.147 g cm^{-3}, crystal size = 0.42 × 0.21 × 0.19 mm^3. Intensity data were measured at 193 ± 1 K on a Bruker P4/CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation 2θ_{max} = 52.8°; 39051 reflections converged to a final R_{int} of 0.048 for 20502 unique reflections and 1108 variable parameters and converged with unweighted and weighted factors of R1 and wR2. Final R1 and wR2 values were 0.070 and 0.221, respectively, and GOF = 1.03.

(Trimethylsilyl)ethynyl-phenylethynyl-*p*-*tert*-butylcalix[4]arene 7a. To a mixture of $PdCl_2(PPh_3)_2$ (1.68 mg, 0.0024 mmol), CuI (0.45 mg, 0.0024 mmol), and **7** (40 mg, 0.048 mmol) heated at reflux in toluene (3.0 mL) and with stirring was added a solution of DBU (14.6 mL, 0.096 mmol) and **6d** (6.0 mL, 0.055 mmol) in toluene (2.0 mL). The reaction mixture was stirred for a further 3.0 h at the reflux temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (5.0 mL) and washed with aqueous saturated NH_4Cl (5.0 mL) and with H_2O (5.0 mL). The CH_2Cl_2 extracts were dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give the crude product was purified by PLC (CH_2Cl_2/petroleum ether 3:7) to give **7a** (21 mg, 54%): ^{1}H NMR δ 0.035 (s, 9H), 0.84 (s, 9H), 0.86 (s, 9H), 1.35 (s, 18H), 3.49 (d, J = 14.5 Hz, 2H), 3.57 (d, J = 14.0 Hz, 2H), 4.55 (d, J = 14.0, 2H), 4.72 (d, J = 13.0, 2H), 5.46 (s, 2H, OH), 6.65 (s, 2H), 6.66 (s, 2H), 7.13 (s, 2H), 7.16 (s, 2H), 7.31 (m, 3H), 7.61 (dd, 2H); ^{13}C NMR δ 0.22, 30.85, 31.99, 34.16, 34.34, 34.37, 36.71, 87.49, 97.41, 103.28, 119.03, 119.12, 123.99, 124.06, 124.23, 125.52, 128.20, 128.52, 128.64, 128.94, 131.83, 139.81, 141.43, 141.60, 142.29, 150.76, 150.99, 151.43 (one carbon is missing); MS (APCI$^+$) *m/z* 813.6 (M+), calcd for $C_{57}H_{68}O_2Si$ 813.25.

Iodo-*p*-*tert*-butylcalix[4]arene Triflate 9 and Diiodo-*p*-*tert*-butylcalix[4]arene 10. To a stirred mixture of $PdCl_2(PPh_3)$ (8.0 mg, 0.011 mmol), CuI (120 mg, 0.63 mmol), and DBU (30 mg, 0.20 mmol) in toluene (25 mL) was added a solution of **3** (100 mg, 0.11 mmol) in toluene (15 mL) over a period of 1.0 h. The reaction mixture was then stirred for a further 3.0 h at room temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (40 mL) and washed with aqueous saturated NH_4Cl (15 mL) and with H_2O (20 mL). The CH_2Cl_2 extracts was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give the crude product which was purified by PLC (1:9 acetonitrile/hexane) to give the following compounds in order of increasing polarity. **10** (60 mg, 64%): mp 235−238 °C; ^{1}H NMR δ 1.05 (s, 18H), 1.33 (s, 18H), 3.87 (d, J = 14.0 Hz, 4H), 4.02 (s, 2H, OH), 4.10 (d, J = 14.0 Hz, 4H), 6.92 (s, 4H), 7.20 (s, 4H); ^{13}C NMR δ31.14, 31.85, 34.15, 45.64, 103.09, 126.37, 127.42, 128.61, 141.98, 143.87, 150.43, 151.85; MS (APCI$^+$) *m/z* 868.0 (M+), calcd for $C_{44}H_{54}O_2I_2$ 868.72. **9** (14 mg, 14%): mp 298−300 °C; ^{1}H NMR δ 0.91 (s, 9H), 0.98 (s, 9H), 1.35(s, 18H), 3.49 (d, J = 14.0 Hz, 2H), 3.82 (d, J = 14.5 Hz, 2H), 4.06 (s, 2H, OH), 4.19(d, J = 14.0 Hz, 2H), 4.29 (d, J = 14.5 Hz, 2H), 6.76 (s, 2H), 6.85 (s, 2H), 7.18 (s, 2H), 7.19 (s, 2H); ^{13}C NMR δ 30.93, 31.10, 31.85, 33.43, 34.06, 34.21, 34.35, 45.08, 104.07, 125.91, 126.16, 127.16, 127.50, 127.89, 128.17132.15, 133.26, 142.15, 142.99, 143.31, 150.59, 150.73, 151.00; MS (APCI$^+$) *m/z* 890.3 (M+), calcd for $C_{44}H_{54}F_3IO_5S$ 890.88.

4-Hydroxybutynyl-*p*-*tert*-butylcalix[4]arene Triflate 11. To a stirred mixture of **3** (50 mg, 0.055 mmol), CuI (0.52 mg, 0.003 mmol), and $PdCl_2(PPh_3)_2$ (0.77 mg, 0.0011 mmol) in toluene (5 mL) was added a solution of 3-butyn-1-ol (**6b**) (8.4 mg, 0.12 mmol) and DBU (30 mg, 0.20 mmol) in toluene (5 mL) at reflux temperature in toluene (5 mL). The reaction mixture was stirred for a further 2 h at the reflux temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (10 mL) and washed with aqueous saturated NH_4Cl (5 mL) and with H_2O (5 mL). The CH_2Cl_2 extracts was dried ($MgSO_4$) and the solvent was removed under vacuum to give the crude product which was purified by PLC (6:1 petroleum ether/THF) to give **11** (14.5 mg, 32%): mp 206−209 °C; ^{1}H NMR δ 0.82 (s, 9H), 0.95 (s, 9H), 1.35 (s, 18H), 2.82(t, 2H), 3.00 (t, 1H, OH), 3.44 (d, J = 13.5 Hz, 2H), 3.62 (d, J = 14.5 Hz, 2H), 3.94 (q, 2H), 4.29 (d, J = 13.5 Hz, 2H), 3.43 (d, J = 14.5 Hz, 2H), 5.10 (s, 2H, OH), 6.68 (s, 2H), 6.82 (s, 2H), 7.15 (s, 2H), 7.17 (s, 2H); ^{13}C NMR δ24.59, 30.87, 30.94, 31.90, 31.94, 32.54, 34.24, 37.09, 34.50, 61.26, 98.93, 117.75, 124.45, 124.58, 125.65, 125.84, 125.92, 126.86, 128.34, 129.31, 132.96, 141.37, 142.55, 143.54, 150.30, 151.69; MS (APCI$^+$) *m/z* 833.2 (M+), calcd for $C_{49}H_{59}O_6F_3S$ 833.06.

6-Hydroxybutynyl-*p*-*tert*-butylcalix[4]arene Triflate 12. To a stirred mixture of **3** (50 mg, 0.055 mmol), CuI (0.52 mg, 0.003 mmol), and $PdCl_2(PPh_3)_2$ (0.77 mg, 0.001 mmol) in toluene (5 mL) was added a solution of hexyn-1-ol (**6c**) (11.8 mg, 0.12 mmol) and DBU (30 mg, 0.20 mmol) in toluene (5 mL) at reflux temperature in toluene (5 mL). The reaction mixture was stirred for a further 2 h at the reflux temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (10 mL) and washed with aqueous saturated NH_4Cl (5 mL) and with H_2O (5 mL). The CH_2Cl_2 extracts was dried ($MgSO_4$) and the solvent was removed under vacuum to give the crude product which was purified by PLC (9:1 petroleum ether/THF) to give **12** (9.5 mg, 20%): mp 193−195 °C; ^{1}H NMR δ 0.78 (s, 9H), 1.04 (s, 9H), 1.31 (s, 18H), 1.90(m, 2H), 2.21(m, 2H), 2.39 (m, 2H), 3.36 (d, J = 13.0 Hz, 2H), 3.47 (d, J = 14.0 Hz, 2H), 3.94 (d, J = 14.0 Hz, 2H), 4.16 (t, 2H), 4.39 (d, J = 13 Hz, 2H), 6.64 (s, 2H), 6.66 (s, 2H), 6.92 (s, 2H, OH), 7.05 (s, 2H), 7.15 (s, 2H); ^{13}C NMR δ 18.37, 24.86, 28.95, 30.89, 31.20, 31.92, 32.23, 32.32, 34.08, 34.38, 69.40, 83.62, 99.81, 117.84, 120.48, 124.99, 125.68, 125.92, 126.35, 126.54, 129.03, 132.24, 132.30, 133.29, 142.33, 142.43, 149.09, 149.10, 150.70; MS (APCI$^+$) *m/z* 861.3 (M+), calcd for $C_{51}H_{63}F_3O_6S$ 886.11.

Phenylethynyl-*p*-*tert*-butylcalix[4]arene Triflate 13 and Bis(phenylethynyl)-*p*-*tert*-butylcalix[4]arene 14. To a stirred mixture of $PdCl_2(PPh_3)_2$ (8.0 mg, 0.011 mmol), CuI (100 mg, 0.53 mmol), DBU (70 mg, 0.46 mmol), and phenylacetylene (**6d**) (26 mg, 0.26 mmol) in toluene (30 mL) was added a solution of **3** (100 mg, 0.11 mmol) in toluene (10 mL) at reflux temperature. The reaction mixture was stirred for a further 4 h at the reflux temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (40 mL) and washed with aqueous saturated NH_4Cl (15 mL) and with H_2O (20 mL). The CH_2Cl_2 extracts was dried ($MgSO_4$) and the solvent was removed under vacuum to give the crude product which was purified by PLC (3:7 CH_2Cl_2/petroleum ether) to give the following compounds. **14** (55.0 mg, 61%): mp 241−244 °C; ^{1}H NMR δ 0.90 (s, 18H), 1.32 (s, 18H), 3.58(d, J = 13.5 Hz, 4H), 4.61 (d, J = 13.5 Hz, 4H), 5.50 (s, 2H, OH), 6.75 (s, 4H), 7.09 (t, 4H), 7.14 (s, 4H), 7.23 (t, 2H), 7.45 (d, J = 8.00 Hz, 4H); ^{13}C NMR δ 30.92, 31.95, 34.15, 34.41, 37.06, 87.31, 97.55, 118.99, 123.51, 124.34, 125.64, 128.17, 128.43, 128.63, 131.74, 141.67, 142.35, 150.95, 151.37; MS (APCI$^+$) *m/z* 817.5 (M+), calcd for $C_{60}H_{64}O_2$ 817.16. **13** (10.1 mg, 11%): mp >310 °C; ^{1}H NMR δ 0.91 (s, 9H), 1.01(s, 9H), 1.27(s, 18H), 3.55 (d, J = 14.0 Hz, 2H), 3.65 (d, J = 14.5 Hz, 2H), 4.36 (d, J = 14.0 Hz, 2H), 4.45 (d, J = 14.5 Hz, 2H), 4.91 (s, 2H, OH), 6.78 (s, 2H), 6.88 (s, 2H), 7.12(s, 2H), 7.13 (s, 2H), 7.33 (m, 3H), 7.54 (t, 2H), ^{13}C NMR δ 31.01, 31.06, 31.68, 31.84, 34.07, 34.09, 34.54, 36.55, 37.73, 86.76,118.65, 120.04, 122.31, 123.30, 124.61, 125.98, 126.39, 126.44, 12.85, 128.35, 128.57, 130.68, 131.91, 137.83, 141.99, 142.36, 148.53, 151.18, 151.38; MS (APCI$^+$) *m/z* 865.4 (M+), calcd for $C_{53}H_{59}F_3O_5S$ 865.10.

X-ray Crystal Data for 14. Colorless prism crystal (MeOH/$CHCl_3$), $C_{60}H_{64}O_2$, I-centered monoclinic, space group *Ia* (No. 9), $Z = 4$, $a = 11.757(4)$ Å, $b = 46.19(1)$ Å, $c = 9.611(3)$ Å, $\beta = 106.585(5)°$. $V = 5002(2)$ Å^3, $D_{calc} = 1.08$ g cm^{-3}, crystal size = 0.56 × 0.52 × 0.17 mm^3. Intensity data were measured at 193 ± 1 K on a Bruker P4/CCD diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation $2\theta_{max} = 53.5°$; 19123 reflections converged to a final R_{int} of 0.062 for 10209 unique reflections and 613 variable parameters and converged with unweighted and weighted factors of R1 and wR2. Final R1 and wR2 values were 0.070 and 0.205, respectively, and GOF = 1.01.

Ethynyl-*p*-*tert*-butylcalix[4]arene Triflates 15 and 16. To a stirred solution of **8** (20 mg, 0.023 mmol) in THF (2.0 mL) was added Bu_4NF (6.1 mg, 0.023 mmol), and the reaction mixture stirred, in a flask open to the air, for a further 15 min at room temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (10 mL) and washed with aqueous 10% HCl (5 mL). The CH_2Cl_2 extracts were dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give the crude product which was purified by PLC (3:7 CH_2Cl_2 /petroleum ether) to give the following compounds. **15** (9.0 mg, 49%): mp 156−157 °C; ^{1}H NMR δ 0.88 (s, 9H), 0.97 (s, 9H), 1.34 (s, 18H), 3.45 (d, J = 13.5 Hz, 2H), 3.65 (d, J = 14.5 Hz, 2H), 3.68 (s, 1H), 4.24 (d, J = 14.0 Hz, 2H), 4.35 (d, J = 14.0 Hz, 2H), 4.65 (s, 2H, OH), 6.75 (s, 2H), 6.85 (s, 2H), 7.16 (s, 2H), 7.17 (s, 2H); ^{13}C NMR δ 30.90, 31.04, 31.88, 31.93, 33.11, 34.18, 37.31, 34.59, 81.24, 87.30, 116.96, 120.14, 124.72, 125.85, 126.68, 126.96, 127.44, 128.28, 133.19, 142.29, 142.61, 142.80, 149.96, 150.70, 152.29; MS (APCI$^+$) *m/z* 789.3 (M+), calcd for $C_{47}H_{55}F_3O_5S$ 789.01. **16** (traces): ^{1}H NMR δ 0.89 (s, 9H), 1.02 (s, 9H), 1.35 (s, 18H), 3.56 (s, 1H), 3.63 (d, J = 14.5 Hz, 2H), 3.76 (d, J = 14 Hz, 2H), 4.33(m, 4H), 4.59 (s, 2H, OH), 6.72 (s, 2H), 6.87 (s, 2H), 7.14 (s, 2H), 7.19 (s, 2H); ^{13}C NMR δ 30.98, 31.00, 31.92, 33.98, 34.15, 34.56, 37.69, 44.79, 57.55, 81.36, 86.76, 104.94, 117.13, 124.71, 125.88, 126.64, 127.21, 128.65, 142.23, 142.54,143.58, 149.95, 151.45, 151.70; MS (APCI$^+$) *m/z* 789.5 (M+), calcd for $C_{47}H_{55}F_3O_5S$ 789.01.

X-ray Crystal Data for 16. Colorless crystal (MeOH/$CHCl_3$), $C_{47}H_{55}O_5F_3S$, monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, $a = 14.056(1)$ Å, $b = 24.827(2)$ Å, $c = 12.300(1)$ Å, $\beta = 92.362(2)°$. $V = 4288.6(6)$ Å^3, $D_{calc} = 1.22$ g cm^{-3}, crystal size = 0.34 × 0.34 × 0.16 mm^3. Intensity data were measured at 193 ± 1 K on a Bruker P4/CCD diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation $2\theta_{max} = 52.9°$; 30523 reflections converged to a final R_{int} of 0.058 for 8789 unique reflections and 509 variable parameters and converged with unweighted and weighted factors of R1 and wR2. Final R1 and wR2 values were 0.106 and 0.294, respectively, and GOF = 1.13.

Ethynyl-*p*-*tert*-butylcalix[4]arene 17. To a stirred solution of **8** (20 mg, 0.023 mmol) in THF (5 mL) was added Bu_4NF (12.2 mg, 0.047 mmol) and the reaction stirred for a further 15 min at room temperature in a flask open to the air. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (10 mL) and washed with 10% HCl (5 mL). The CH_2Cl_2 extract was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give the crude product which was purified by PLC (3:7 CH_2Cl_2/petroleum ether) to give **17** (13 mg, 85%): mp 215−217 °C; ^{1}H NMR δ 1.07 (s, 9H), 1.18 (s, 9H), 1.25 (s, 18H), 3.46 (d, J = 14.0 Hz, 2H), 3.64 (d, J = 13.5 Hz, 2H), 3.78 (s, 1H, OH), 4.16 (d, J = 14.0 Hz, 2H), 4.58 (d, J = 13.5 Hz, 2H), 6.99 (s, 2H), 7.01 (s, 4H), 7.13 (s, 2H), 7.83 (s, 2H, OH); ^{13}C NMR δ 30.93, 31.59, 31.78, 32.79, 34.15, 34.21, 34.70, 36.62, 83.17, 85.15, 116.21, 125.13, 125.78, 125.91, 126.17, 126.91, 127.92, 128.19, 143.21, 143.36; MS (APCI$^+$) *m/z* 657.3 (M+), calcd for $C_{46}H_{56}O_3$ 656.95

Biscalix[4]arene 18. To a stirred solution of **17** (25 mg, 0.038 mmol) and CuI (30 mg, 0.16 mmol) in toluene (10 mL) was added a solution of DBU (14 mg, 0.091 mmol) in toluene (2 mL) at room temperature. The reaction mixture was stirred for a further 15 min at room temperature temperature. The solvent was evaporated on a rotary evaporator and the resulting crude product was dissolved in CH_2Cl_2 (15 mL) and washed with aqueous 10% HCl (5 mL). The CH_2Cl_2 extracts was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give the crude product which was purified by PLC (1:1 CH_2Cl_2/petroleum ether) to give **18** (17 mg, 68%): mp 161−164 °C. ^1H NMR δ 1.09(s, 9H), 1.18 (s, 9H), 1.24(s, 18H), 3.38 (d, $J = 13.0$ Hz, 2H), 3.69 (d, $J = 14.0$ Hz, 2H), 4.26 (d, $J = 14.0$ Hz, 2H), 4.74 (d, $J = 14.0$ Hz, 2H), 6.99 (s, 4H), 7.03 (s, 2H), 7.14, 8.11(s, 2H, OH), 9.55 (s, 2H, OH); ^{13}C NMR δ 30.95, 31.62, 31.00, 32.89, 34.17, 34.19, 34.85, 36.66, 81.06, 116.25, 125.18, 125.78, 125.95, 125.99, 127.19, 128.10, 128.12, 133.85, 143.36, 143.61, 144.45, 147.61, 149.32, 152.77; MS (APCI$^+$) *m/z* 1312.7 (M+), calcd for $C_{92}H_{110}O_6$ 1311.88.

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Supporting Information Available: Spectral data for all new compounds and X-ray crystallographic data in CIF format for **7**, **8**, **14**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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