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Photochemical Cycloisomerizations via 7-*exo-dig* Reactions on a Calix[4]arene Scaffold

Hassan Al-Saraierh, David O. Miller, and
Paris E. Georghiou*

*Department of Chemistry, Memorial University of
Newfoundland, St. John's, Newfoundland and Labrador,
Canada A1B 3X7*

parisg@mun.ca

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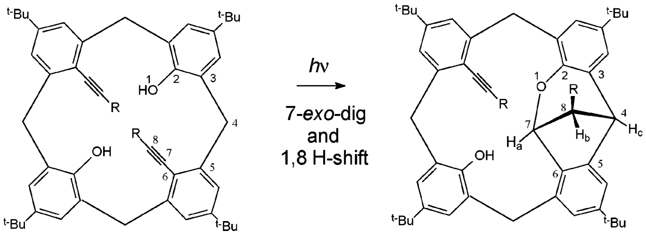
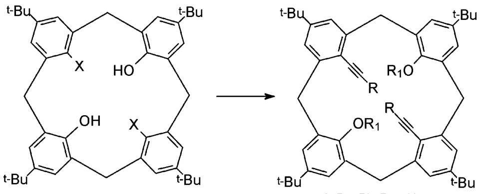


Narrow-rim 1,3-bis(phenylethynyl)-*p-tert*-butylcalix[4]arenes were found to be photolabile, producing unprecedented seven-membered oxacyclic systems formed via 7-*exo-dig* cyclizations and a new [3.2.1]bicyclic system via subsequent 1,8-H shifts. The calixarene provided a scaffold for these unprecedented photochemical reactions to occur.

The chemistry of calixarenes[1] and their derivatives continues to be very extensively studied as a result of the many potential applications[2] of these versatile building blocks. However, there are surprisingly few reports involving their photochemical reactions. Nishikubo et al.[3] summarized the photochemistry of calixarenes, in particular, for their potential application to the field of photoresist technology and UV-curable coatings. Sukwattanasinitt[4] produced a stilbene-bridged *p-tert*-butylcalix[4]-arene (**1**) which could act as a "photoswitchable molecular receptor" for various small electron-deficient molecules. A similar photoswitchable molecular receptor involving a photochemical [4 + 4] cycloaddition with a related resorc[4]arene/anthracene was reported by Schafer and Mattay,[5] and Dyker described the photochemistry of styrylcalix[4]arenes.[6] Varma[7] recently described a novel photochemical rearrangement of calix[4]arene-derived bis(spirodienones).

We have previously reported the application of the Sonogashira reaction to effect the first metal-assisted narrow-rim substitution/functionalization[8] of **1** via its 1,3-bistriflate,[9] **2** (Scheme 1). In order to investigate their potential nonlinear optical[10] properties, the bis(phenylethynyl)calix[4]arenes **3** and **4** were synthesized using this methodology. In the course of this work, we noticed, as the fluorescence spectra of **3** and **4** in CH_2Cl_2 solution were being measured, that the respective emission intensities (at $\lambda_{max} = 330$ nm) and the corresponding absorbance intensities (at $\lambda_{max} \sim 230$ for both **3** and **4**, at $\lambda_{max} \sim 286$ and 311 nm for **2**, and at $\lambda_{max} \sim 295$ and 329 nm for **3**) decreased between successive replicate measurements with the same samples (spectra shown in Supporting Information). Thin layer chromatographic analysis in each case indicated the formation of new products. As will be described below, the observed photolability of **3** and also of **4** was a result of a series of some unprecedented photochemically-induced cycloisomerizations.

SCHEME 1. Sonogashira Narrow-Rim Functionalization



1 X= OH
2 X= OTf

3 R = Ph; R$_1$ = H
4 R = *p*-$C_6H_4CF_3$; R$_1$ = H
13 R = Ph; R$_1$ = Pr
14 R = *p*-$C_6H_4CF_3$; R$_1$ = Pr

In order to adequately characterize the product(s) formed, relatively larger scale reactions than those which were used for the UV fluorescence spectroscopic determinations were conducted in a photoreactor using solutions of **3** or **4** in CH_2Cl_2 which were irradiated for 0.5−3 h periods. These conditions resulted in the formation of **5** or **6**, respectively. After workup and purification, mass spectrometry indicated that these products were isomers of their respective starting compounds. Their NMR spectra, which were similar, were nonetheless equivocal even after 2-D experiments. The ^{1}H NMR spectrum of **5**, for example, revealed (a) four nonequivalent *tert*-butyl groups; (b) that only one D_2O-exchangeable hydroxyl proton was present, at δ ~7.28 ppm; (c) a new one-proton doublet of doublets at δ ~6.26 ppm (J = 2.0 and 1.5 Hz) which is assigned to a vinyl proton (see below); (d) three pairs of AB-type signals due to three methylene bridge protons having coupling constants of 13.5, 13.0, and 14.0 Hz, and two new, one-proton signals at δ ~3.73 (J = 4.0 and 2.0 Hz) and at δ ~4.06 ppm (J = 4.0 and 1.5 Hz), which were clearly coupled with the proton at 6.26 ppm. The presence of this proton and the fact that only

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(1) For recent monographs, see: (a) Gutsche, C. D. In *Calixarenes Revisited*, Monographs in Supramolecular Chemistry; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1998. (b) *Calixarenes2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.

(2) *Calixarenes in Action*; Mandolini, L., Ungaro, R., Eds.; Imperial College Press: London, England, 2000.

(3) Nishikubo, T.; Kameyama, A.; Kudo. H.; Tsutsui, K. *J. Polym. Sci. (A)* **2002**, *40*, 1293−1302.

(4) Rojanathanes, R.; Tuntulani, T.; Bhanthumnavin, W.; Sukwattanasinitt, M. *Org. Lett.* **2005**, *7*, 3401−3404.

(5) Schäfer, C.; Mattay, J. *J. Photochem. Photobiol. Sci.* **2004**, *3*, 331−333.

(6) Mastalerz, M.; Hüggenberg, W.; Dyker, G. *Eur. J. Org. Chem.* **2006**, 3977−3987.

(7) Varma, R. L.; Ganga, V. B.; Sureshi, E. *J. Org. Chem.* **2007**, *72*, 1017−1019.

(8) Al-Saraierh, H.; Miller, D. O.; Georghiou, P. E. *J. Org. Chem.* **2005**, *70*, 8273−8280.

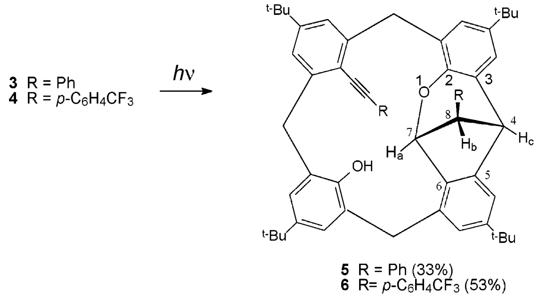
(9) (a) Csok, Z.; Szalontai, G.; Czira, G.; Kollar, L. *Supramolecular Chem.* **1998**, *10*, 69−77. (b) Chowdhury, S.; Bridson, J. N.; Georghiou, P. E. *J. Org. Chem.* **2000**, *65*, 3299−3302.

(10) See, for example: Hennrich, G.; Murillo, M. T.; Prados, P.; Song, K; Asselberghs, I.; Clays, K.; Persoons, A.; Benet-Buchholz, J.; de Mendoza, J. *Chem. Commun.* **2005**, 2747−2749.

10.1021/jo070236m CCC: $37.00

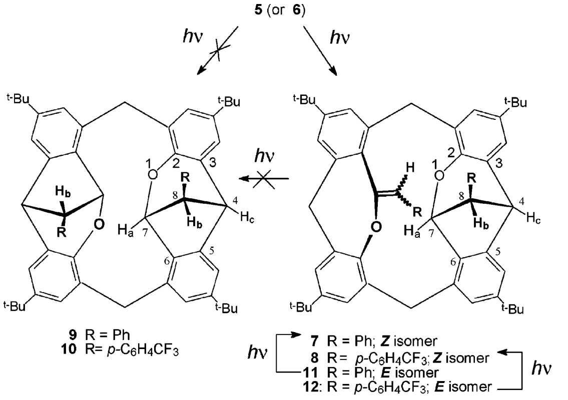
one D_2O-exchangeable hydroxyl proton remained suggested that a reaction had occurred between an ethynyl group with a hydroxyl group. However, the evidence that one of the methylene bridges had undergone a significant change was at first puzzling. Similar observations were made with **6**. Furthermore, although it was apparent that an oxacycle had formed in **5** (and also in **6**) by an intramolecular addition reaction suggested above, it was not immediately obvious as to whether its formation proceeded via an initial "favored" 7-*exo-dig* or 8-*endo-dig* cyclization.[11] Although single crystals of both **4** and **5** were obtained, their X-ray crystallographic determinations failed to provide suitable data due to their low-angle diffractions. The structures of **5** and **6**, depicted in Scheme 2, were deduced subsequently after further experiments yielded the critical X-ray structure of **7**.[12]

SCHEME 2. Photochemical Cycloisomerization of 3 and 4



In order to ascertain whether the remaining ethynyl and hydroxyl groups could undergo a second photochemically induced addition/cyclization, CH_2Cl_2 solutions of either **5** or **6** alone were irradiated under the same reaction conditions as before but this time until all of the starting material appeared to have been consumed. Two new isomeric products were isolated: **7** which was formed from **5**, and **8** which was formed from **6** (Scheme 3).

SCHEME 3. Cycloisomerization Reactions of 5 and 6



Although their NMR spectra showed similarities with those of their precursor compounds in both cases, they were once again ambiguous. The targeted bis-oxacyclic ring containing compounds **9** and **10**, respectively, were expected to be symmetrical, but no such evidence could be seen in their spectra.

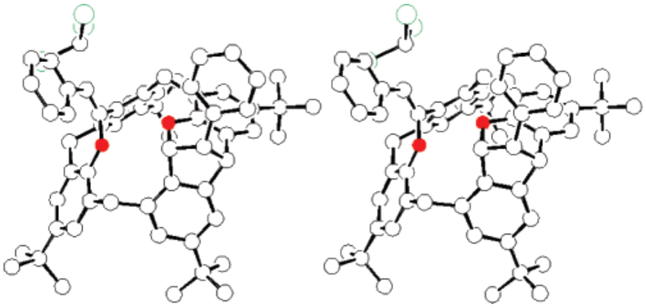


FIGURE 1. X-ray PLUTO stereoview of **7** in which all of the protons have been removed for clarity. A molecule of $CHCl_3$ can be seen at the top left. The oxygen atoms of the oxacycle are highlighted in red.

An unambiguous structure of **7** was derived from X-ray crystallography (Figure 1). This structure revealed not only the seven-membered oxacycle having *Z* configuration at the exocyclic double bond but also the presence of the unprecedented (in the case of calixarenes) [3.2.1] oxabicyclic system. This bicyclic system bridges a pair of proximal calixarene phenyl rings.[12] The structures of **5**−**8** could consequently be assigned as depicted, on the basis of the X-ray structure of **7**, which was also consistent with its ^1H NMR spectra and with those obtained from **5** and **6**.

The reactions of **5** or **6** were slower when more dilute CH_2Cl_2 solutions (~0.1 vs ~0.5 M) were photoirradiated, and this permitted the observation of the formation of additional isomeric products, **11** (in the case of **5**) and **12** (in the case of **6**). The ^1H NMR spectra of these new products have patterns similar to those seen with **7** and **8**. The main difference between the two products was the obvious changes in the chemical shifts of one of the geminal protons and the benzylic proton (which is equivalent to H_a in **7** or **8**). For example, in the ^1H NMR spectra of compound **11**, one of the geminal protons has become more shielded by a neighboring calixarene phenyl ring and has shifted to the high-field region at δ 2.66 ppm, while the benzylic proton (H_a) has become more deshielded and has shifted to the low-field region at ~6.7 ppm. These new compounds were subsequently found to be the immediate precursor intermediates of **7** and **8** since they are rapidly converted with further photoirradiation, directly into **7** and **8**, respectively. Attempts to form **9** or **10** by controlled additional photoirradiation of solutions of these compounds, however, resulted only in degradation of the respective starting compounds.

We have concluded that **11** and **12** are likely the more labile *E* isomers which would be the expected first-formed products from a presumed 7-*exo-dig* cyclization,[13] and that subsequently, a rapid photoassisted isomerization occurs to form their respective *Z* isomers, **7** and **8**. All of the spectral data are consistent with the assigned structures. Examination of molecular models suggests that the bis-bicyclic compounds **9** and **10** are highly strained, which could account for their photoinstability. This was confirmed by molecular mechanics modeling calculations.[14]

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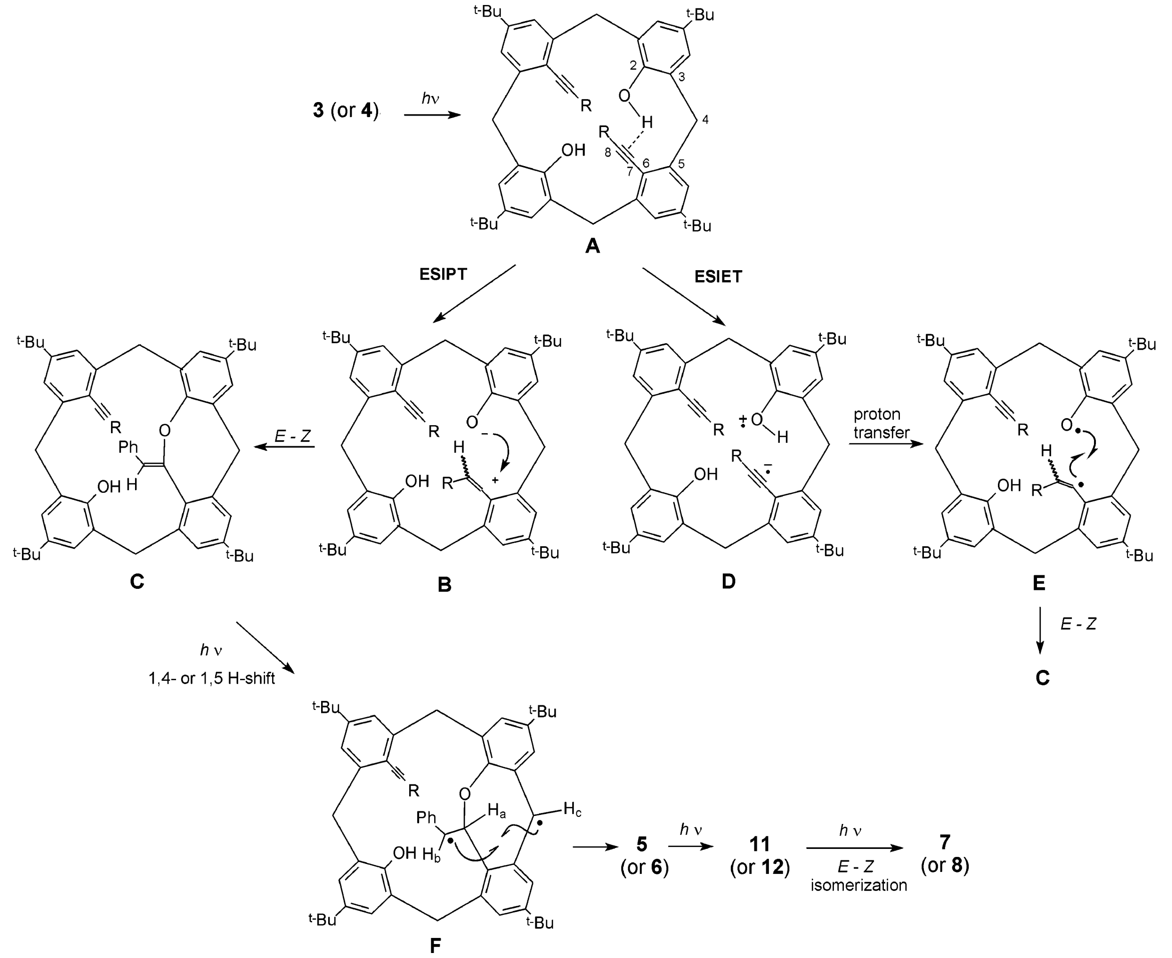
[11] Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734−736.

[12] X-ray crystallographic data of **7** are included with the Supporting Information and in cif format.

[13] A seven-membered oxacycle formed by radical-initiated 7-*exo-dig* cyclization has been reported by Grigg et al., in which the exocyclic alkene formed has the *E* configuration and is analogous to the structure of the putative labile isomers **11** and **12** proposed herein. See: Grigg, R.; Loganathan, V.; Sridharan, V.; Stevenson, P.; Sukirthalingam, S.; Worakun, T. *Tetrahedron* **1996**, *52*, 11479−11502.

[14] Molecular mechanics calculations with *Spartan06* (MMFF94 using X-ray data from **7** as the basis for generating the structure of **9**) support this hypothesis. The difference in energy between **9** and **7**, for example, is approximately 59 kJ mol^{-1} in favor of **7**.

SCHEME 4. Proposed Mechanism for the Photochemical Cyclization/Isomerization of Phenylethynyl Calixarenes 3 and 4



The actual mechanism can only be conjectured upon, but a mechanism which is consistent with the observed reactions is depicted in Scheme 4. A first step could involve an intramolecular hydrogen bond interaction between one of the hydroxyl groups and one of the triple bonds, in **3** (or **4**), as depicted in complex "**A**". By analogy with some intramolecular phenol−olefin reactions, which have been reported by others,[15] there could be two possible mechanisms for the reactive excited state. The first is an "exited state intramolecular proton transfer" (ESIPT)[16] to form the zwitterionic-type intermediate "**B**". In this case, an intramolecular proton transfer has undergone a 1,8-hydrogen shift.[17] Covalent bond formation in **B** produces intermediate "**C**" presumably formed via a rapid *E*/*Z* isomerization. A second possible mechanism leading to this same putative intermediate **C** involves an "excited state intramolecular electron transfer" (ESIET)[18] between a phenolic hydroxy group and the triple bond (as an electron acceptor) to produce the ionic diradicals as depicted in structure "**D**". Subsequent proton transfer forms the 1,7-diradical intermediate "**E**", which could then lead directly to the formation of **C**. The transformation from **C** to **5** (or **6**) could be achieved via a diradical species "**F**", formed by a 1,5-hydrogen shift[19] (or via a less common 1,4-hydrogen shift). The second seven-membered oxacycle is generated when **5** (or **6**) is photoirradiated to give **11** (or **12**) which undergoes a rapid *E* to *Z* isomerization to form **7** (or **8**).[20] Irradiation of **11** (or **12**) itself under the same conditions formed the corresponding *Z* isomers **7** (or **8**). Furthermore, the observation that the photoreactions which were observed to be faster in the more concentrated solutions suggests that *inter*-molecular proton transfer may compete with intramolecular proton transfer in either the ESIPT or ESIET. This would not necessarily affect the final product outcomes.

Photoirradiation of **13** and **14**, the corresponding di-*O*-propyl derivatives of **3** and **4** (Scheme 1), did not result in any new product formation, and only unreacted starting material was recovered. It is obvious, therefore, that the presence of a hydroxyl group is essential for the observed photocyclization/rearrangement reactions. However, it is not necessary unequivocal that the calixarene scaffold provides any role in assisting the intramolecular reactions. In order to ascertain this role, experiments were conducted to determine whether or not the same types of reactions could occur intermolecularly between **1** and a tolane such as **15**−**17**. Thus, solutions of **1** with each

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[15] Jiménez, M. C.; Miranda, M. A.; Tormos, R. *Chem. Soc. Rev.* **2005**, *34*, 783−796 and references cited therein.

[16] Chow, Y. L.; Zhou, X.-M.; Gaitan, T. J.; Wu, Z.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 3813−3818.

[17] McNab, H.; Reed, D.; Tipping, I. D.; Tyas, R. G. *ARKIVOC* **2007**, *6*, 85−95.

[18] Morrison, H. *Org. Photochem.* **1979**, *4*, 143−189.

[19] Cummins, J. M.; Dolling, U.-H.; Douglas, A. W.; Karady, S.; Leonard, W. R.; Marcune, B. F. *Tetrahedron Lett.* **1999**, *40*, 6153−6156.

[20] As in ref 14, *Spartan06* MMFF94 calculations, using X-ray data from **7** as the basis for generating the structure of **11**, reveal a difference in energy of approximately 10 kJ mol^{-1} in favor of **7**.

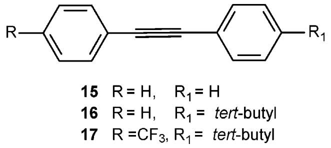

FIGURE 2. Tolanes used in attempted intermolecular photoaddition with **1**.

of the tolanes **15**−**17** (Figure 2) were irradiated under the same reaction conditions in CH_2Cl_2. In all cases, only unreacted starting materials were recovered. Additional experiments were also conducted in which the mole ratios between **1** and **16**, for example, were increased from 1:1 (in which both reactants were 0.1 M) to 1:100 (in which the concentration of **1** was 0.1 M and that of **16** was 9.7 M). Again, only unchanged starting compounds were recovered, with no signs of any new product formation.

In conclusion, we have shown that narrow-rim 1,3-bis-(arylethynyl)-*p*-*tert*-butylcalix[4]arenes, which have free hydroxyl groups on the remaining two calixarene positions, are photolabile. Upon photoirradiation, these compounds undergo facile cyclization/rearrangement reactions which are assisted by the templating effect provided by the calixarene scaffold. A mechanism is proposed to account for the observed results. These findings further expand the versatility of functionalized calixarenes, especially, with respect to their photochemical behavior. Furthermore, to the best of our knowledge the 7-*exo*-*dig* photochemically mediated cyclizations obtained in this study are the first examples of intramolecular cyclizations of such alkynyl-substituted calixarenes to be reported.

Experimental Section

Calixarene (5): A solution of **3** (18 mg) in anhydrous CH_2Cl_2 (35 mL) was irradiated for 3 h in a photoreactor using two 21 W 3000 Å lamps. The solvent was evaporated in vacuo and the residue purified by PLC (20% CH_2Cl_2 in petroleum ether) to give **5** (6 mg, 33%): mp 253−255 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.20 (s, 9H), 1.24 (s, 9H), 1.29 (s, 9H), 3.59 (d, J = 13.5 Hz, 1H), 3.40 (d, J = 13.0 Hz, 1H), 3.73 (dd, J_1 = 4.0 Hz, J_2 = 2.0 Hz, 1H), 3.87 (d, J = 14.0 Hz, 1H), 4.06 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 4.46 (d, J = 13.5 Hz, 1H), 4.67 (d, J = 13.5 Hz, 1H), 4.70 (d, J = 14.0 Hz, 1H), 6.26 (dd, J_1 = 2.0 Hz, J_2 = 1.5 Hz, 1H), 6.83 (d, J = 2.5 Hz, 1H), 6.91 (m, 1H), 7.07−7.00 (m, 6H), 7.14 (d, J = 2.5 Hz, 1H), 7.16 (d, J = 2.5 Hz, 1H), 7.20 (d, J = 2.5 Hz, 1H), 7.27 (dd, J_1 = 8.0 Hz, J_2 = 2.5 Hz, 2H), 7.28 (s, D_2O exch, 1H), 7.49−7.42 (m, 3H), 7.77 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 2H); MS (APCI+) *m*/*z* calcd for $C_{60}H_{64}O_2$ 817.16, found 817.30 (M^+).

Calixarene (6): A solution of **4** (10 mg) in anhydrous CH_2Cl_2 (20 mL) was irradiated for 0.5 h in a photoreactor using two 21 W 3000 Å lamps. The solvent was evaporated in vacuo and the residue purified by PLC (CH_2Cl_2/petroleum ether 3:7) afforded **5** (5.3 mg, 53%): mp 147−148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.23 (s, 9H), 1.25 (s, 9H), 1.28 (s, 9H), 3.42 (d, J = 13.5 Hz, 1H), 3.44 (d, J = 13.0 Hz, 1H), 3.73 (m, 1H), 3.81 (d, J = 12.5 Hz, 1H), 4.07 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 4.43 (d, J = 13.5 Hz, 1H), 4.60 (d, J = 13.0 Hz, 1H), 4.65 (d, J = 12.5 Hz, 1H), 6.18 (m, 1H), 6.59 (s, 1H, OH), 6.86 (d, J = 2.5 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 7.00 (d, J = 2.5 Hz, 1H), 7.09 (d, J = 2.5 Hz, 1H), 7.14 (d, J = 2.5 Hz, 1H), 7.18 (m, 1H), 7.19 (br s, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H); MS (APCI+) *m*/*z* calcd for $C_{62}H_{62}F_6O_2$ 953.16, found 953.40 (M^+).

Calixarene (7): A solution of **5** (16.0 mg) in anhydrous CH_2Cl_2 (130 mL) was irradiated for 1.0 h in a photoreactor using two 21 W 3000 Å lamps. The solvent was evaporated in vacuo and the residue purified by PLC (20% CH_2Cl_2 in petroleum ether) to give **7** (3.0 mg, 18.3%): mp 260−263 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (s, 9H), 1.25 (s, 9H), 1.26 (s, 9H), 1.30 (s, 9H), 3.11 (d, J = 13.0 Hz, 1H), 3.28 (d, J = 14.0 Hz, 1H), 3.61 (m, 1H), 3.62 (d, J = 12.5 Hz, 1H), 4.08 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 4.73 (d, J = 12.5 Hz, 1H), 4.81 (d, J = 12.5 Hz, 1H), 4.90 (d, J = 13.0 Hz, 1H), 5.83 (s, 1H), 5.86 (br s, 1H), 6.76 (d, J = 2.5 Hz, 1H), 6.80 (d, J = 12.5 Hz, 1H), 7.09−6.98 (m, 8H), 7.28−7.33 (m, 2H), 7.37 (d, J = 2.5 Hz, 1H), 7.44 (d, J = 2.5 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.0 Hz, 2H); MS (APCI+) *m*/*z* calcd for $C_{60}H_{64}O_2$ 817.16, found 817.50 (M^+).

Calixarene (8): A solution of **4** (10.0 mg) in anhydrous CH_2Cl_2 (40 mL) was irradiated for 7 h in a photoreactor using two 21 W 3000 Å lamps. The solvent was evaporated in vacuo and the residue purified by PLC (25% CH_2Cl_2 in petroleum ether) to give **7** (2.8 mg, 28%): mp 185−186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.25 (s, 9H), 1.27 (s, 9H), 1.31 (s, 9H), 3.15 (d, J = 12.5 Hz, 1H), 3.30 (d, J = 14.0 Hz, 1H), 3.63 (m, 1H), 3.67 (d, J = 13.0 Hz, 1H), 4.10 (m, 1H), 4.66 (d, J = 13.0 Hz, 1H), 4.74 (d, J = 13.0 Hz, 1H), 4.85 (d, J = 12.5 Hz, 1H), 5.82 (m, 1H), 5.85 (m, s, 1H), 6.79 (d, J = 2.5 Hz, 1H), 6.92 (d, J = 2.5 Hz, 1H), 6.99 (d, J = 2.5 Hz, 1H), 7.07−7.06 (m, 4H), 7.31 (s, 1H, OH), 7.33 (m, 2H), 7.39 (d, J = 2.5 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 2H); MS (APCI+) *m*/*z* calcd for $C_{62}H_{62}F_6O_2$ 953.16, found 953.30 (M^+).

Calixarene (11): A solution of **3** (18.4 mg) in anhydrous CH_2Cl_2 (40 mL) was irradiated for 4 h in a photoreactor using two 21 W 3000 Å lamps. The solvent was evaporated in vacuo and the residue purified by PLC (30% CH_2Cl_2 in petroleum ether) to give **11** (5.9 mg, 32%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (s, 9H), 1.24 (s, 9H), 1.26 (s, 9H), 1.30 (s, 9H), 2.60 (d, J = 13.0 Hz, 1H), 3.29 (d, J = 14.0 Hz, 1H), 3.58 (d, J = 13.0 Hz, 1H), 3.77 (m, 1H), 4.09−4.07 (d, J = 13.0 Hz, 1H; and m, 1H), 4.73 (d, J = 14.0 Hz, 1H), 4.78 (d, J = 13.0 Hz, 1H), 6.26 (m, 1H), 6.71 (d, J = 2.5 Hz, 1H), 6.93−6.82 (m, 12H), 7.23−7.20 (m, 2H), 7.28−7.43 (m, 4H); MS (APCI+) *m*/*z* calcd for $C_{60}H_{64}O_2$ 817.16, found 817.50 (M^+).

Calixarene (12): A solution of **4** (18.3 mg) in anhydrous CH_2Cl_2 (40 mL) was irradiated for 5 h in a photoreactor using two 21 W 3000 Å lamps. The solvent was evaporated in vacuo and the residue purified by PLC (20% CH_2Cl_2 in petroleum ether) to give **12**(8.2 mg, 45%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (s, 9H), 1.25 (s, 9H), 1.28 (s, 9H), 1.30 (s, 9H), 2.67 (d, J = 12.5 Hz, 1H), 3.32 (d, J = 14.0 Hz, 1H), 3.61 (d, J = 13.0 Hz, 1H), 3.79 (m, 1H), 4.03 (d, J = 13.0 Hz, 1H), 4.10 (d, J = 1.5 Hz, 1H), 4.68 (d, J = 14.0 Hz, 1H), 4.76 (d, J = 12.5 Hz, 1H), 6.25 (m, 1H), 6.75 (d, J = 2.5 Hz, 1H), 6.83 (s, 1H), 6.89 (d, J = 2.5 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 2.5 Hz, 1H), 7.10−7.89 (m, 2H), 7.30 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 2.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H); MS (APCI+) *m*/*z* calcd for $C_{62}H_{62}F_6O_2$ 953.16, found 953.50 (M^+).

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Supporting Information Available: General procedures, including ^{1}H and ^{13}C NMR spectra of all new compounds, and crystallographic data including cif data for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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