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Tetrahedron 63 (2007) 10778–10787
Tetrahedron

# Photoswitchable calix[4]arenes bearing dihydroacridine substituents at the upper rim

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Received 26 April 2007; revised 30 May 2007; accepted 4 June 2007
Available online 20 July 2007

**Abstract**—Eight new calix[4]arene host molecules bearing acridinium or the corresponding dihydroacridine substituents have been prepared. $^1$H NMR and electrochemical studies reveal that the acridinium substituents block the host cavity. Both photochemical and chemical switching between acridinium and dihydroacridine hosts are demonstrated.


## 1. Introduction

Calixarenes[1] are an important class of building blocks for supramolecular assemblies[2] and molecular recognition, and are widely used as receptors for inorganic cations[3] and anions,[4] as well as organic cations[5] and neutral compounds.[6] Molecular recognition arises from different forces acting upon complementary faces of the calixarene host and the guest inside the cavity. Endo-cavity inclusion complexes with organic cations such as quaternary ammonium ions and the iminium and tropylium ions may be favored by cation–π-interaction and π-stacking.[7] Switchable hosts such as calixarenes and resorcarenes, which are able to change their structures in response to an external stimulus, are of particular interest.[8–10] A photoswitchable resorc[4]arene based on [4+4] cycloaddition of anthracene has been studied recently by means of single-molecule force spectroscopy.[11] As illustrated by this system, inputs in the form of photons have at least two advantages. (1) Waste products are not formed. (2) Molecules immobilized on a surface are addressable.

We became interested in introducing a photoswitch into calix[4]arenas, which could reversibly alternate between a partially closed and an open cavity. Concomitantly, as the structure interchanges between electron donor and acceptor character, the electronic properties at the upper rim should change drastically. The system 9-alkoxy acridane (dihydroacridine) of the type I, which undergoes photoheterolysis in the photoexcited state to give an acridinium salt II (Fig. 1),[11] was expected to match these requirements. In protic solvents (alcohols), the system is reset by attack of the alkoxide on the acridinium ion. The rate constant of this thermal back reaction is strongly dependent on the properties of the solvent.[12,13] It may be noted that I ($\lambda_{max}$ 320, 285 nm) and II ($\lambda_{max}$ 425 nm) represent a photochromic system (Fig. 1).

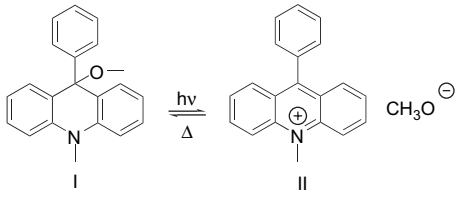


**Figure 1**. The photoswitch acridane/acridiniummethoxide.

Due to the planarity of the acridinium ion formed from the acridane compound, we anticipated that strong interactions would occur between two acridinium units bound to the upper rim of a cone calix[4]arene. Examination of CPK space filling models in addition to model calculations indicated that the acridinium ring should be strongly twisted relative to the aryl group of the calixarene, so that one part should be oriented into the cavity.

Here we report the synthesis and conformation of calix[4]-arenes substituted at the upper rim with acridane and acridinium units.

Photochemical experiments have been performed in order to explore the reversibility of the switching process.

## 2. Results and discussion

### 2.1. Synthesis

**2.1.1. Acridinium calix[4]arenes.** Both calix[4]arenes with a cone conformation and a fixed 1,3-alternate conformation were converted into acridinium substituted compounds. The syntheses are outlined in Schemes 1 and 2.

*Keywords*: Calixarene; Acridinium salts; Acridanes; Photoswitch.
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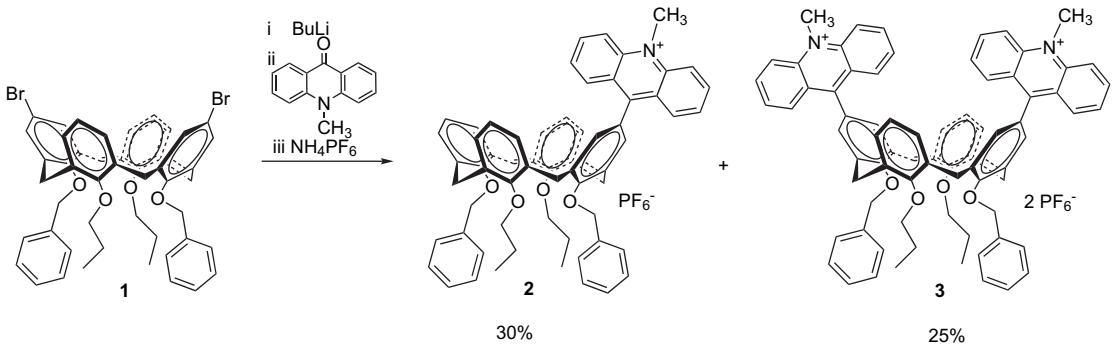
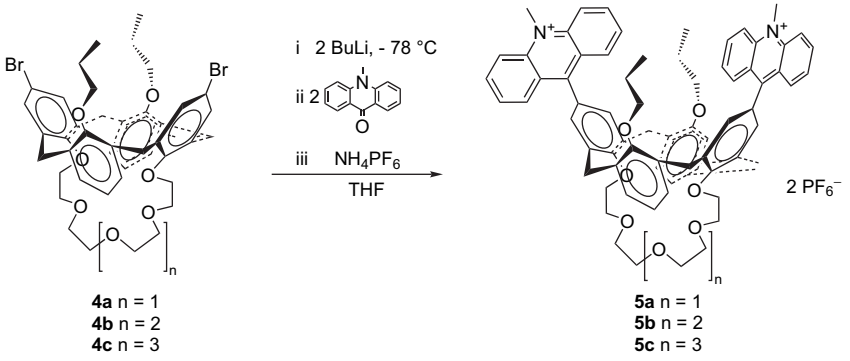
doi:10.1016/j.tet.2007.06.126



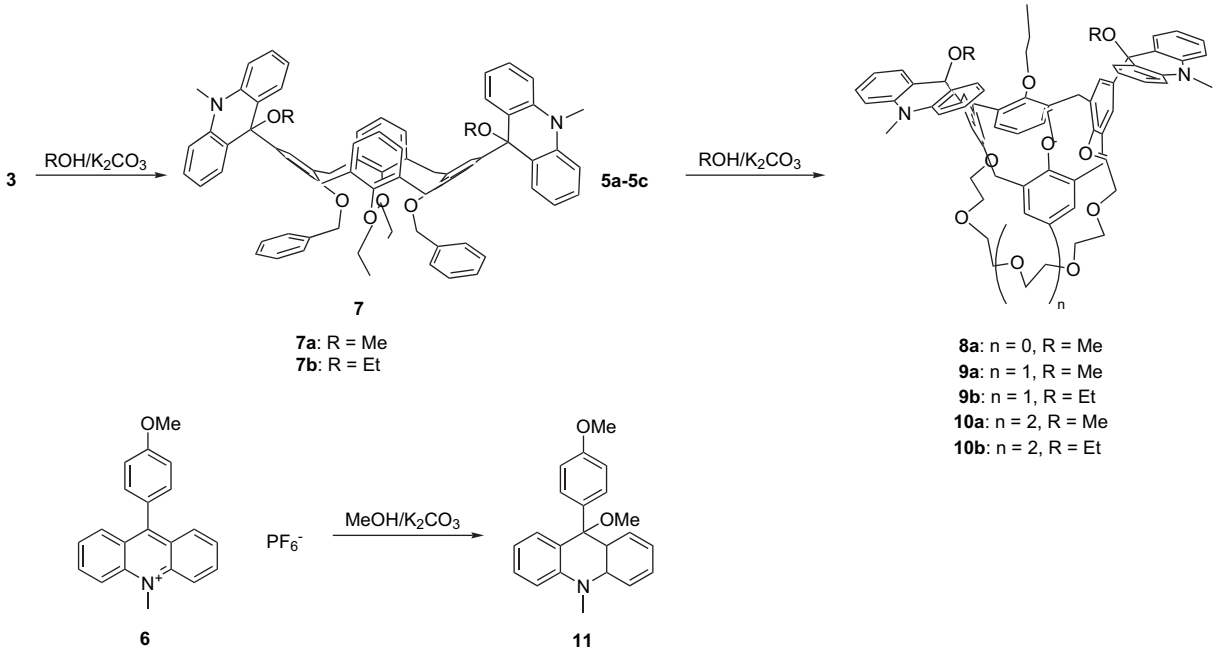

**Scheme 1**. Synthesis of calixarenes **2** and **3** having a cone conformation.



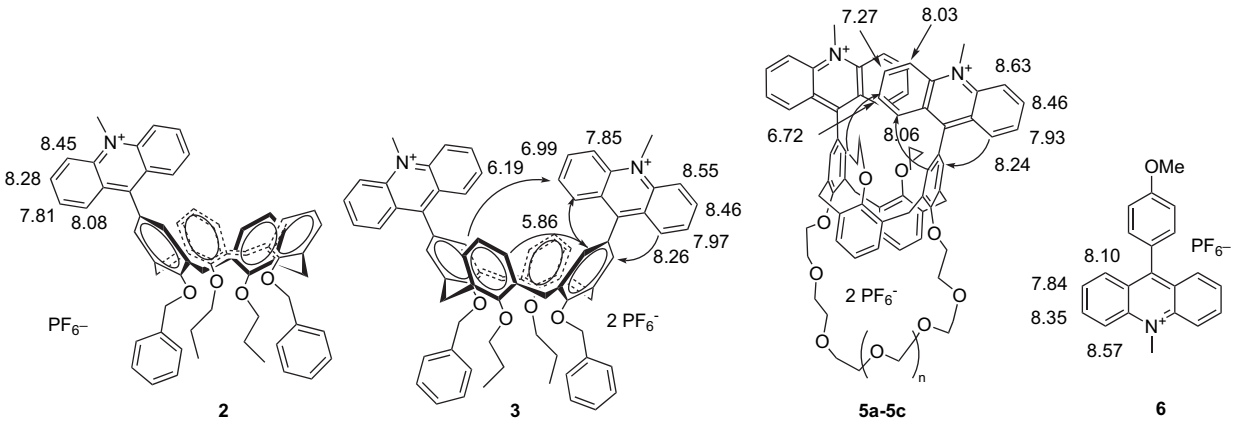

**Scheme 2**. Synthesis 1,3-alternate calixcrowns **5**.

The initial acridane compounds were converted to the acridinium compounds due to the acidic conditions that prevailed during the column chromatography. The yield of the disubstituted compound **3** can be increased with longer reaction times. To create hosts with two binding sites and a nearly square cavity, the 1,3-alternate calixcrowns **5** were synthesized (Scheme 2). For purpose of comparison, compound **6** (Scheme 3) was also studied.

**2.1.2. Acridane calix[4]arenes.** In the presence of $K_2CO_3$, nucleophiles such as methanol and ethanol converted the acridinium calixarenes to the corresponding acridane




**Scheme 3**. Syntheses of acridane calix[4]arenes and of a model acridane.




**Scheme 4**. Proton resonances of acridinium compounds (curved arrows mark NOE's).

compounds **7**–**9** (Scheme 3). The model compound **6** was similarly converted into **11**.

## 2.2. Conformation

**2.2.1. Acridinium calix[4]arenes.** The $^1$H NMR spectrum of the monofunctionalised calixarene **2** showed four resonances typical of the flanking phenyl group protons of the acridinium unit. However, in the spectra of the calix[4]-arenes **3** and **5** with two substituents at the upper rim, two such sets were observed, one set closely matching that of the model compound **6** but the other showing distinct upfield shifts (Scheme 4), though these were smaller for the 1,3-alternate calixarenes **5** than for the cone **3**. ROESY measurements showed that a given acridinium ring was associated with both sets of resonances. This finding clearly demonstrated that one part of the acridinium unit points to the inner π-basic sphere of the calixarene cavity, which shields the acridinium protons of the inserted phenyl ring. The protons of the outer ring showed slight downfield shifts due to their location at the edge of the aromatic core. Even in the relatively open cone conformation of **3**, it appears that rotation about the bond from the acridinium unit to the calixarene phenyl ring is slow on the NMR time scale and thus, in both **3** and **5**, the acridinium units block the calixarene cavity. In **5**, there is little evidence that the crown binding site is significantly influenced by any effects of the acridinium substituents.

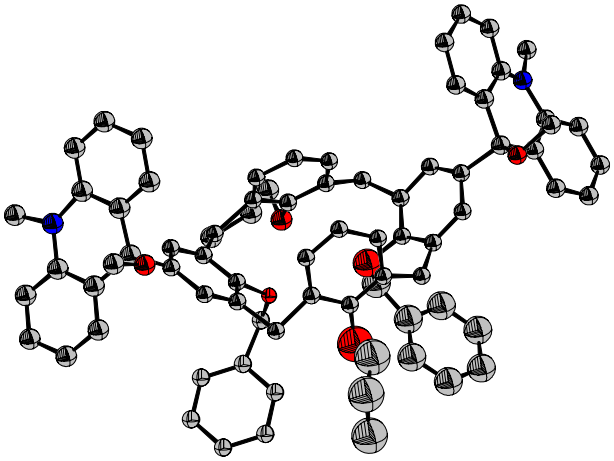
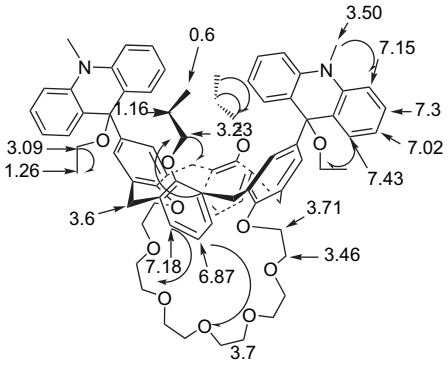


**Figure 2**. Molecular structure for calixarene **7** in the solid state.

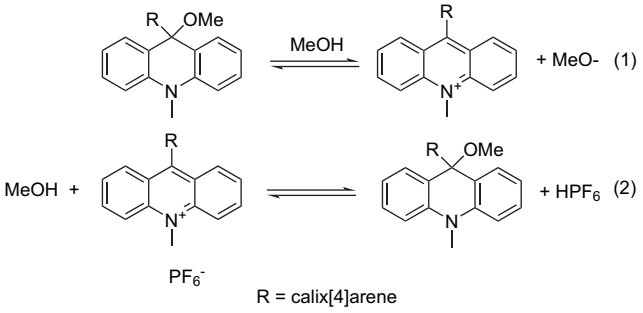
**2.2.2. Acridane calix[4]arenes.** The molecular structure of **7** (Fig. 2) revealed by a crystal structure determination[14] shows that an open cavity results when the acridinium substituents are converted to acridanes. Only one set of four signals was observed for the proton resonances of the acridane units (Scheme 5).




**Scheme 5**. Proton resonances ($CD_3CN$, $\delta$, ppm) of the acridane calix[4]-arene **5c** and NOE's (curved arrows) observed in its ROESY spectrum.

## 2.3. Equilibrium in methanol solution

Acridanes are ionogenic compounds in protic solvents (Scheme 6) although the equilibrium involved has not been studied previously.




**Scheme 6**. Equilibria observed in methanol solution.

The first equation describes the dissociation of acridanes in methanol solution. The higher stability of the acridinium

**Table 1**. UV–vis absorption maxima and the acridane concentration at the equilibrium in methanol solution

| Compound | $\lambda_{max}$ of the acridinium [nm] | % Acridane at equilibrium |
|---|---|---|
| **7a** | 449 | 26 |
| **8a** | 430 | 84 |
| **9a** | 449 | 49 |
| **10a** | 451 | 17 |
| **5a** | 436 | 35 |
| **5b** | 449 | 7 |
| **5c** | 451 | 3 |

compounds leads to their formation according to equilibrium (1) in Scheme 6. The concentrations of the acridane compounds in methanol solution at equilibrium with the corresponding acridinium species are given in Table 1. Ethanol produces quite different equilibria, while **10b** gives 83% acridinium at equilibrium in methanol, it gives only 8% in ethanol.

The acridinium calixarenes react only to a small extent with methanol to give the corresponding acridane (Eq. 2 in Scheme 6). Therefore the equilibrium has to be displaced by adding $K_2CO_3$ in the synthesis of acridane calixarenes.

The steric strain present in the acridinium calix[4]arenes **3** and **5a**–**5c** is manifested in the different concentrations of the acridane compounds obtained from **7**–**9** at equilibrium (1) in methanol solution (Table 1).

The shorter chain at the lower rim results in more steric strain at the upper rim and, therefore, more acridane is present at equilibrium (**8a** in Table 1). Also the acridinium calixarene **5a** forms in methanol solution more acridane at equilibrium than **5b** and **5c** because the steric strain is reduced due to the conversion into the acridane.

## 2.4. Electrochemistry

**2.4.1. Acridinium calix[4]arenes.** 9-Arylacridinium ions combine donor and acceptor units within one entity. Thus, in the excited state, long-lived charge separated states can be formed by intramolecular electron transfer.[15] Since acridinium species usually undergo reversible reduction processes, cyclic voltammetry was used to explore the electron acceptor properties of the acridinium calixarenes, in particular to see if the proximity of the two acridinium substituents at the upper rim influenced the redox properties. Comparison of the peak potentials of compounds **2** and **6** indicated only a slight influence of the calixarene scaffold on the reduction properties. The acridinium unit within the calixarene **2** was shifted by −50 mV (−0.74 V vs −0.69 V) relative to that in **6**. However, in calixarenes **3** and **5** the first acridinium substituent was reduced at a similar potential as measured for **2**, but the reduction of the second acridinium unit could only be accomplished at a potential 0.2 V more negative (Scheme 7). This indicates that the acridinium radical formed in the first reduction step interacts with the remaining acridinium unit.

**2.4.2. Acridane calix[4]arenes.** The cyclic voltammogram of the model compound **11** exhibited an oxidation wave at 0.92 V, which showed a peak separation consistent with reversibility only at scan rates above 10 V $s^{-1}$. This we attribute to the initial one-electron oxidation being followed by loss of methoxy radical and the formation of an acridinium ion. To support this assumption the electrochemical reaction was performed at a constant anode potential slightly more positive than the oxidation peak potential. The total charge consumption of 1 F $mol^{-1}$ resulted in the conversion of the acridane into the corresponding acridinium salt.

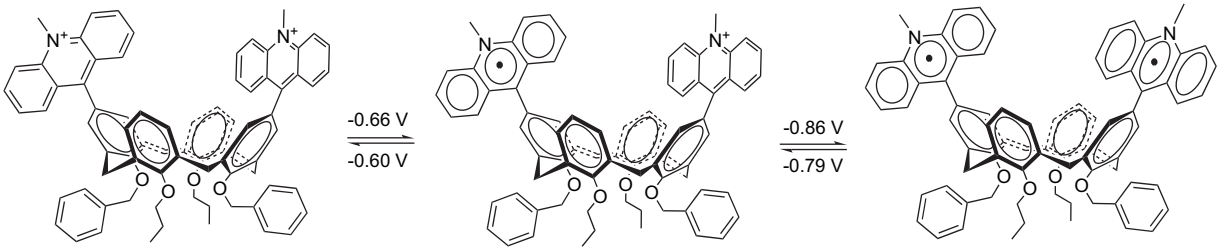
The redox behavior of the calixarene **10a** was similar to that of **11** but the peak observed at 0.87 V remained irreversible in character even at a scan rate of 100 V $s^{-1}$. Current measurements showed the peak to correspond to a two-electron process, with both acridane sites being oxidized at the same potential to give the acridinium calixarene **5**. Thus, unlike calixarene **3**, **10a** undergoes essentially independent reactions at the two sites (Scheme 8).

## 2.5. Switching cycle

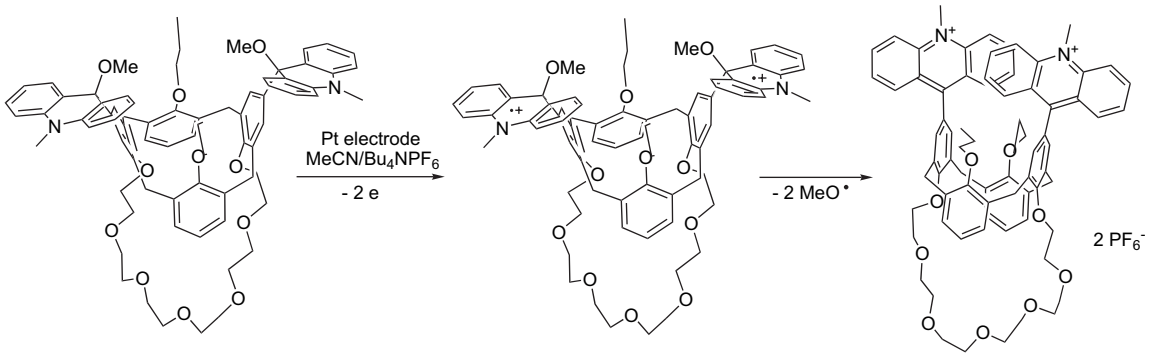
**2.5.1. Photoreaction.** All the acridane compounds investigated undergo photoheterolysis in protic solvents by excitation with 313 nm light, giving the corresponding acridinium compounds. Spectra recorded after consecutive irradiations showed two or three isosbestic points indicating a single-step reaction (Fig. 3).

The lifetime of the generated acridinium alcoholate depends strongly on the solvent. For example, the lifetime of the acridinium ethanolate **5c** $EtO^-$ is 123 s in methanol, 13 min in ethanol, and 50 min in a mixture of acetonitrile and ethanol 1:1. The acridane calixarenes are completely recovered in the thermal reaction (see Scheme 9).

**2.5.2. Chemical switching.** The acridane calixarenes can also be converted into acridinium ions by addition of acids such as trifluoroacetic acid. The back reaction reverting to the acridane compounds can be performed upon addition of a base such as di-*iso*-propylethylamine or $NaHCO_3$ (Scheme 9) or $K_2CO_3$ as in the syntheses. Complexation studies of the acridane and acridinium hosts are currently in progress.




**Scheme 7**. Two different reduction steps in compound **3**.




**Scheme 8**. Electrochemical oxidation of **10a**.

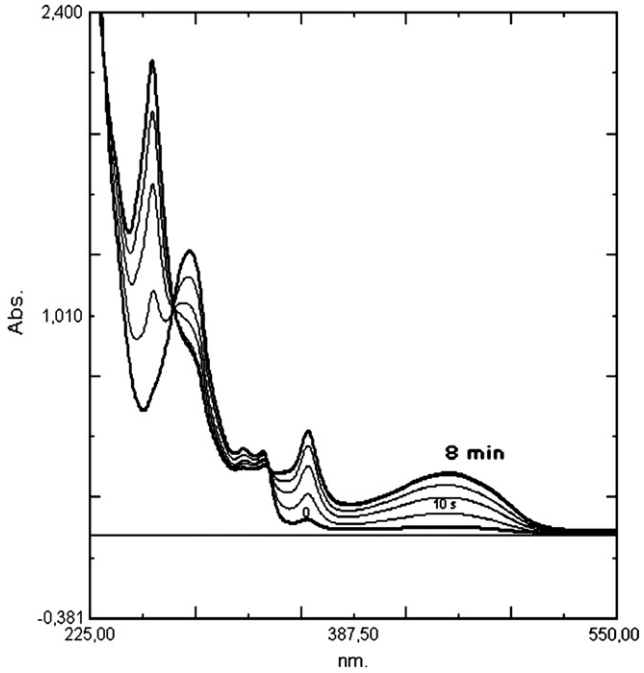



**Figure 3**. UV–vis spectra recorded after consecutive irradiation periods (10 s to 8 min) of calixarene **10b** in 1-propanol solution ($3.7\times10^{-5}$ M).

## 3. Conclusions

Calix[4]arenes bearing two acridane units at the upper rim can be switched reversibly to the corresponding acridinium compounds by photochemical followed by thermal reactions and by thermal reactions alone. The acridinium units are positioned in close proximity and are twisted relative to the calixarene phenyl group to which they are attached, thus blocking the cavity. In contrast, the acridane units are bound with an $sp^3$ carbon at the calixarene scaffold, and accordingly, the cavity is more open. Photochemical and thermal reactions thus provide a means of switching between a closed and an open conformation.

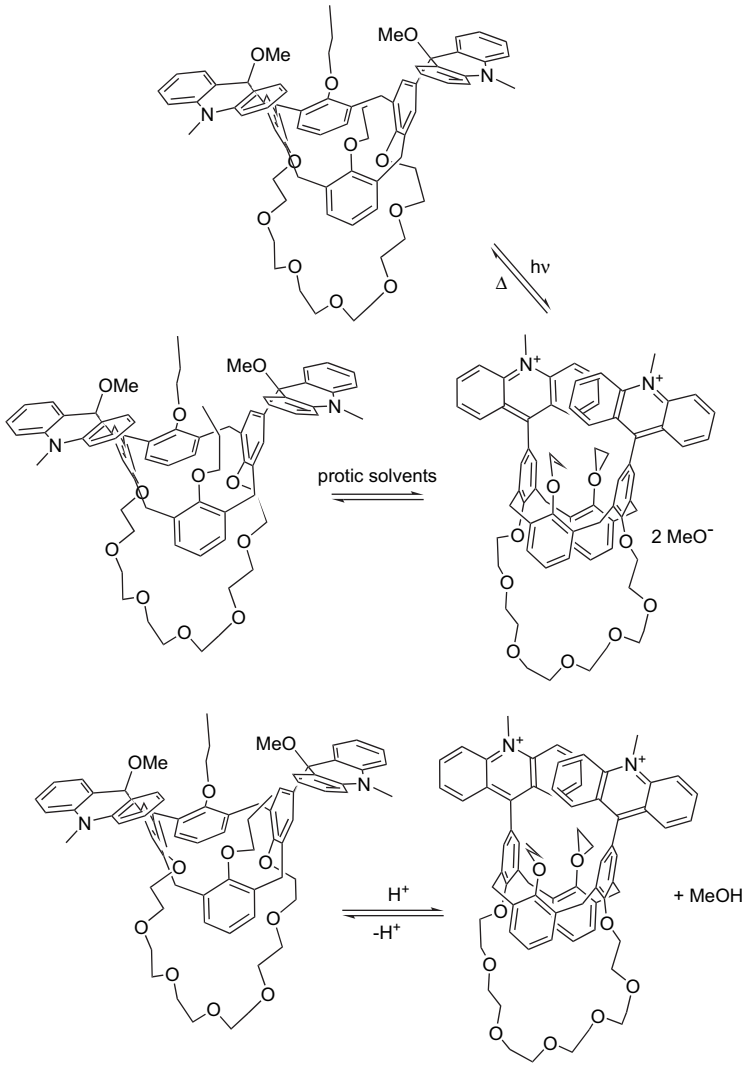
## 4. Experimental

### 4.1. General

Commercially available chemicals and solvents (UVASOL, Merck) were used as received unless otherwise noted; solvents were dried according to standard procedures. Compound **4b** was synthesized according to the literature.[16] Column chromatographies (CC) were carried out on 200 mesh silica gel (Merck). Melting points (mp) were determined with a Boetius heating microscope. ESI mass spectroscopy was carried out on LTQ FT, Finnigan MAT (Bremen, Germany) equipped with an electrospray ion source (Thermo Electron). NMR spectra were recorded on a Bruker DPX 300 (300 MHz), a Bruker Advance 400 (400 MHz), and a Bruker AMX 600 (600 MHz) instruments. The proton signals were attributed to the different subunits with the aid of two-dimensional NMR spectroscopy, such as C–H COSY, H–H COSY, and ROESY. UV–vis measurements were performed with a Shimadzu UV 2101 PC spectrometer. Irradiation of the calixarene solutions were carried out with a conventional mercury arc (HBO 500 or HBO 200) combined with a cut-off filter of 300 nm or metal interference filters. The thermal reactions were followed by UV–vis spectroscopy using the kinetics-program of the spectrometer. The absorption decay curves at the wavelength of 360 nm were analysed by nonlinear regression fits (Origin 6.0, Microcal Software, Inc.). The relative concentrations of the acridane calixarenes and the acridinium calixarenes at equilibrium in methanol solution were determined by the absorbance at 450 nm (only the acridinium compound absorbs light) before and after addition of trifluoroacetic acid.

### 4.2. Synthesis

**4.2.1. 11,23-Dibromo-25,27-dibenzyloxy-26,28-bis-(propyloxy)calix[4]arene (1).** NaH (1.6 g, 60% in paraffin wax, 40 mmol) was added to 11,23-dibromo-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene[17] (6.66 g, 10 mmol) dissolved in a mixture of THF (200 mL) and DMF (30 mL). After stirring at room temperature for 1 h, benzylbromide (8.5 g, 40 mmol) in THF (15 mL) was added dropwise. The mixture was stirred for 2 h at room temperature and for 1 h at reflux. After cooling, HCl (1 M, 50 mL) was added. The separated organic phase was washed with water (50 mL), dried, and evaporated in vacuo. The remaining residue was treated with methanol to provide **1** (7.1 g, 84%), mp 162–165 °C. Anal. Calcd for $C_{48}H_{46}Br_2O_4$ (846.69): C, 68.09; H, 5.48; Br, 18.87. Found: C, 68.32; H, 5.69; Br, 18.60. $^1$H NMR (400 MHz, $CDCl_3$, TMS): $\delta$=7.42 (m, 4H, –$OCH_2$–$C_6H_5$), 7.34 (m, 6H, –$OCH_2$–$C_6H_5$), 6.85 (d, $J$=7.0 Hz, 4H, H-4, 6, 16, 18), 6.78 (t, $J$=7 Hz, 2H, H-5, 17), 6.55 (s, 4H, H-10, 12, 22, 24), 4.82




**Scheme 9**. Switching between an acridane calix[4]arene and the corresponding acridinium calix[4]arene.

(s, 4H, O$CH_2$–$C_6H_5$), 4.34 (d, $J$=13 Hz, 4H, H-2, 8, 14, 20), 3.74 (m, 4H, –O$CH_2CH_2CH_3$), 3.05 (d, $J$=13 Hz, 4H, H-2, 8, 14, 20), 1.66 (m, 4H, –$OCH_2CH_2CH_3$), 0.64 (t, $J$=7 Hz, 6H, –$OCH_2CH_2CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): $\delta$=157.0 (C-25, C-27), 154.1 (C-26, C-28), 137.2, 136.6 (C-1, 9, 13, 21), 135.2, 130.6, 129.3, 128.8, 128.2, 128.1, 122.6, 115.4 (C-11, 23), 76.7 (–O$CH_2CH_2CH_3$), 31.0 (C-2, 8, 14, 20), 22.9 (–$OCH_2CH_2CH_3$), 9.7 (–$OCH_2CH_2CH_3$).

**4.2.2. 11,23-Di-(*N*-methylacridinium-9-yl)-25,27-dibenzyloxy-26,28-bis(propyloxy)calix[4]arene bishexafluorophosphate (2) and 11-(*N*-methylacridinium-9-yl)-25,27-dibenzyloxy-26,28-bis(propyloxy)calix[4]arene hexafluorophosphate (3).** A solution of **1** (2.1 g, 2.5 mmol) in dry THF (150 mL) was cooled to −78 °C. A solution of butyllithium (BuLi) (3.8 mL, 1.6 M in hexane, 5.7 mmol) in THF (6 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 0.5 h. *N*-Methylacridone (1.1 g, 5.25 mmol) was added. The reaction mixture was slowly warmed to room temperature under argon. After stirring for 8 h at room temperature water (10 mL) was added. The mixture was filtered and the solvent removed in vacuo. The crude product was washed with water until the wash water was neutral. The yellow solid was dissolved in methanol and treated with $NH_4PF_6$. The resulting solid was isolated, and washed with chloroform in order to dissolve compound **2**. The insoluble solid was purified by CC (acetonitrile, aqueous solution of $NH_4PF_6$ (5%) 20:1) to provide **3** (1.36 g, 40%), mp 245–250 °C. Anal. $C_{76}H_{68}F_{12}N_2O_4P_2$ (1363.33); HRMS (ESI): [M−$PF_6^-$]+ calcd for $C_{76}H_{68}F_6N_2O_4P$: 1217.4821, found: 1217.4843; [M−2$PF_6^-$]2+ calcd for $C_{76}H_{68}N_2O_4$: 536.2589, found: 536.2586. $^1$H NMR (600 MHz, $CD_3CN$, TMS): $\delta$=*acridinium*: 8.55 (d, $J$= 9 Hz, 2H, H-5), 8.46 (ddd, $^3J$=9 Hz, $^3J$=8 Hz, $^4J$=1 Hz, 2H, H-6), 8.26 (dd, $^3J$=9 Hz, $^4J$=1 Hz, 2H, H-8), 7.97 (ddd, $^3J$=9 Hz, $^3J$=8 Hz, $^4J$=1 Hz, 2H, H-7), 7.85 (d, $J$=9 Hz, 2H, H-4), 6.99 (dt, $^3J$=9 Hz, $^4J$=1 Hz, 2H, H-3), 6.19 (t, $J$=8 Hz, 2H, H-2), 5.86 (dd, $^3J$=8 Hz, $^4J$=1 Hz, 2H, H-1); *calixarene*: 7.68 (d, $J$=7 Hz, 4H, bzl-*ortho*), 7.51 (t, $J$=7 Hz, 4H, bzl-*meta*), 7.47 (t, $J$=7 Hz, 2H, bzl-*para*), 7.22 (d, $J$=8 Hz, 4H, H-4, 5, 16, 18), 6.80 (t, $J$=8 Hz, 2H, H-5, 17), 6.75 (s, 4H, H-10, 12, 22, 24), 4.98 (s, 4H, bzl-$CH_2$), 4.75 (d, $J$=13 Hz, 4H, H-2, 8, 14, 20 *axial*), 3.98 (m, 4H, –O$CH_2CH_2CH_3$), 3.47 (d, $J$=13 Hz, 4H, H-2, 8, 14, 20 *equatorial*), 1.81 (m, 4H, –$OCH_2CH_2CH_3$), 0.63 (t, $J$=7.5 Hz, 6H, –$OCH_2CH_2CH_3$). $^{13}$C NMR (100 MHz,

$CDCl_3$, TMS) $\delta$=160.3 (*C*, 2C), 157.1 (*C*, 2C), 156.9 (*C*, 2C), 140.9 (*C*, 2C), 139.7 (*C*, 2C), 140.9 (*CH*, 2C), 136.5 (*C*, 2C), 136.3 (*C*, 4C), 135.4 (*CH*, 2C), 135.0 (*C*, 4C), 132.4 (*CH*, 2C), 130.7 (*CH*, 2C), 129.6 (*CH*, 4C), 129.3 (*CH*, 2C), 128.8 (*CH*, 2C), 128.2 (*CH*, 4C), 127.7 (*CH*, 2C), 125.3 (*CH*, 2C), 125.2 (*C*, 2C), 124.6 (*C*, 2C), 123.2 (*C*, 2C), 122.8 (*CH*, 2C), 117.9 (*CH*, 2C), 116.5 (*CH*, 2C), 78.0 (2C, $-OCH_2CH_2CH_3$), 76.6 (2C, $-OCH_2C_6H_5$), 38.2 ($N^+-CH_3$), 30.3 ($CH_2$, 4C, C-2, 8, 14, 20), 22.5 ($-OCH_2CH_2CH_3$), 8.6 ($-OCH_2CH_2CH_3$). The chloroform solution containing the calixarene **2** was evaporated. The remaining solid was purified by CC (acetonitrile, aqueous solution of $NH_4PF_6$ (5%) 20:1) to provide more **3** (0.31 g, 9%) and **2** (0.65 g, 25%) as orange crystals, mp 240–242 °C. Anal. $C_{62}H_{58}F_6NO_4P$ (1026.12); HRMS (ESI): $[M-PF_6^-]^+$ calcd for $C_{62}H_{58}NO_4$: 880.4366, found: 880.4343. $^1H$ NMR (400 MHz, $CDCl_3$, TMS): $\delta$=*acridinium*: 8.45 (m, 2H, H-4, 5), 8.28 (m, 2H, H-3, 6), 8.06 (m, 2H, H-1, 8), 7.81 (m, 2H, H-2, 7); *calixarene*: 7.58 (m, 6H), 7.41 (m, 12H), 7.17 (d, *J*=7.5 Hz, 2H, H-4, 18), 7.00 (d, *J*=7.5 Hz, 2H, H-6, 16), 6.75 (t, *J*=7.5 Hz, 2H, H-5, 17), 6.63 (s, 2H, H-10, 12), 6.47 (d, *J*=7.5 Hz, 2H, H-22, 24), 6.13 (t, *J*=7.5 Hz, 1H, H-23), 4.90 (s, 2H, $-OCH_2C_6H_5$), 4.70 (s, 2H, $-OCH_2C_6H_5$), 4.66 (s, 3H, $N^+-CH_3$), 4.62 (d, *J*=12.8 Hz, 2H, H-8, 14), 4.53 (d, *J*=7.5 Hz, 2H, H-2, 20), 3.85 (m, 4H, $-OCH_2CH_2CH_3$), 3.30 (d, *J*=12.8 Hz, 2H, H-8, 14), 3.24 (d, *J*=7.5 Hz, 2H, H-2, 20), 1.68 (m, 4H, $-OCH_2CH_2CH_3$), 0.53 (t, 6H, $-OCH_2CH_2CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): $\delta$=157.4 (C), 150.4 (CH), 141.3 (C), 137.9 (CH), 137.8 (CH), 136.6 (C), 135.6 (C), 134.8 (C), 133.6 (C), 130.9 (CH), 129.6 (CH), 129.4 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.2 (CH), 126.0 (C), 122.2 (CH), 122.0 (CH), 117.9 (CH), 77.7 ($-OCH_2C_6H_5$), 77.5 ($-OCH_2C_6H_5$), 76.3 ($-OCH_2CH_2CH_3$), 38.2 ($N^+-CH_3$), 30.3 ($-OCH_2CH_2CH_3$), 22.4 ($CH_2$), 8.6 ($-OCH_2CH_2CH_3$).

**4.2.3. 11,23-Dibromo-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene crown-7, 1,3-alternate (4a).** 11,23-Dibromo-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene (3.33 g, 5 mmol) and $Cs_2CO_3$ (6 g, 18.5 mmol) suspended in MeCN (800 mL) were reacted under Ar with hexaethylene glycol ditosylate (2.75 g, 5.5 mmol). The violet suspension was stirred for 12 h at reflux and 12 h at room temperature. The solvent was evaporated in vacuo. The remaining residue was treated with HCl (10%, 150 mL) and dichloromethane (150 mL). The organic phase was separated, washed with water, and dried ($MgSO_4$). After removal of the solvent in vacuo, the solid residue was treated two times with methanol (75 mL) to give **4a**, 2.4 g (58%), mp 212–228 °C. Anal. Calcd for $C_{42}H_{48}Br_2O_7$ (824.65): C, 61.17; H, 5.87. Found: C, 60.62; H, 5.84. $^1H$ NMR (400 MHz, $CDCl_3$, TMS): $\delta$= 7.15 (s, 4H, H-10, 12, 22, 24), 7.05 (d, *J*=7.3 Hz, 4H, H-4, 6, 16, 18), 6.84 (t, *J*=7.3 Hz, 2H, H-5, H-17), 3.82–3.75 (m, 8H, 4×$CH_2$-crown), 3.51 (m, 8H, 4×$CH_2$-crown), 3.43 (t, 4H, $-OCH_2CH_2CH_3$), 3.20 (m, 4H, $CH_2$-calixarene), 3.13 (m, 4H, $CH_2$-calixarene), 1.28 (m, 4H, $-OCH_2CH_2CH_3$), 0.76 (t, 6H, $-OCH_2CH_2CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): $\delta$=156.9 (C-25, C-27), 155.1 (C-26, C-27), 136.2 (C-1, 9, 13, 21), 133.7 (C-3, 7, 15, 19), 132.1 (C-10, 12, 22, 24), 129.6 (C-4, 6, 16, 18), 122.7 (C-5, C-17), 115.0 (C-11, C-23), 72.5 ($-OCH_2CH_2CH_3$), 72.0, 70.4, 70.0, 68.9 (each 2C, $CH_2$-crown-7), 37.8 (C-2, 8, 14, 20), 22.4 ($-OCH_2CH_2CH_3$), 10.1 ($-OCH_2CH_2CH_3$).

**4.2.4. 11,23-Dibromo-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene crown-5, 1,3-alternate (4c).** 11,23-Dibromo-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene (3.33 g, 5 mmol) and $Cs_2CO_3$ (6 g, 18.5 mmol) suspended in MeCN (800 mL) were reacted under Ar with tetraethylene glycol ditosylate (3.25 g, 5.5 mmol). The violet suspension was stirred for 12 h at reflux and 12 h at room temperature. The solvent was evaporated in vacuo. The remaining residue was treated with HCl (10%, 150 mL) and dichloromethane (150 mL). The organic phase was separated, washed with water, and dried ($MgSO_4$). After removal of the solvent in vacuo, the solid residue was treated two times with methanol (75 mL) to give **4c**, 3.75 g (82%), mp 153–158 °C. Anal. Calcd for $C_{46}H_{56}Br_2O_9$ (912.76): C, 60.53; H, 6.18. Found: C, 60.92; H, 6.06. $^1H$ NMR (400 MHz, $CDCl_3$, TMS): $\delta$=7.11 (s, 4H, H-10, 12, 22, 24), 7.10 (d, 4H, H-4, 6, 16, 18), 6.76 (t, 2H, H-5, 17), 3.71–3.55 (m, 36H, H-2, 8, 14, 20, $CH_2$-crown and $-OCH_2CH_2CH_3$), 1.65 (m, 4H, $-OCH_2CH_2CH_3$), 0.98 (t, 6H, $-OCH_2CH_2CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): $\delta$=156.4 (C-25, C-27), 155.1 (C-26, C-27), 135.6 (C-1, 9, 13, 21), 132.8 (C-3, 7, 15, 19), 132.6 (C-10, 12, 22, 24), 130.5 (C-4, 6, 16, 18), 122.1 (C-5, C-17), 114.7 (C-11, C-23), 73.2 ($-OCH_2CH_2CH_3$), 71.2, 71.1, 71.0, 70.9, 70.8, 70.5 (each 2C, $CH_2$-crown), 36.4 (C-2, 8, 14, 20), 23.4 ($-OCH_2CH_2CH_3$), 10.6 ($-OCH_2CH_2CH_3$).

### 4.3. Calix[4]arenes 5a–5c: general procedure

Compound **4** (2.5 mmol) was dissolved in dry THF (150 mL). *n*-BuLi (1.6 M in *n*-hexane, 3.75 mL, 6 mmol) was added dropwise at −78 °C under an argon atmosphere. After stirring for 0.5 h *N*-methylacridone (1.09 g) in THF (50 mL) was added dropwise. After warming the solution to room temperature, stirring was continued for 3 h. The reaction was quenched with water (1 mL). The solvent was evaporated in vacuo and the residue was dissolved in methanol (150 mL). The solution was then treated with $NH_4PF_6$ (2 g). After stirring for 0.5 h, the solvent was removed in vacuo. The resulting solid was three times washed with water and then three times with methyl-*tert*-butylether (MTBE, 150 mL). The crude products were purified by CC (acetonitrile, aqueous $NH_4PF_6$ solution). In order to remove complexed $NH_4PF_6$, the acridinium calixarenes were converted to the corresponding acridanes. Therefore the solid obtained after chromatography was dissolved in acetonitrile (50 mL) and ethanol (4 mL) and $K_2CO_3$ (0.3 g) was added. The suspension was stirred overnight. The solid was filtered and the solvent was evaporated in vacuo. The remaining solid was treated with dry chloroform (20 mL). The suspension was filtered and the solvent was removed in vacuo. The remaining solid was dissolved in acetonitrile (50 mL). The acridinium salt was precipitated by addition of $HPF_6$ (0.2 mL).

**4.3.1. 11,23-Di-(*N*-methylacridinium-9-yl)-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene-crown-5, 1,3-alternate bishexafluorophosphate (5a).** Compound **5a** was purified by CC (acetonitrile, aqueous solution of $NH_4PF_6$ (2.5%) 20:1); yellow crystals, 0.215 g (8%), mp 204–205 °C. Anal. $C_{70}H_{70}F_{12}N_2O_7P_2$ (1341.28); HRMS (ESI): $[M-PF_6^-]^+$ calcd for $C_{70}H_{70}F_6N_2O_7P$: 1195.4824, found: 1195.4822; $[M-2PF_6^-]^{2+}$ calcd for $C_{70}H_{70}N_2O_7$: 525.2592, found: 525.2593. $^1H$ NMR (600 MHz, $CD_3CN$,

TMS): δ=*acridinium*: 8.70 (d, *J*=9.3 Hz, 2H, H-5), 8.48 (t, *J*=9.3 Hz, 2H, H-6), 8.30 (d, *J*=9.3 Hz, 2H, H-4), 8.27 (d, *J*=7.8 Hz, 2H, H-8), 7.96 (t, *J*=7.8 Hz, 2H, H-7), 7.87 (d, *J*=7.6 Hz, 2H, H-1), 7.50 (m, 2H, H-3), 6.54 (t, *J*=7.6 Hz, 2H, H-2), 4.89 (s, 6H, $N^+$–$CH_3$); *calixarene*: 7.58 (s, 4H, H-10, 12, 22, 24), 7.51 (d, *J*=7.4 Hz, 4H, H-4, 6, 16, 18), 7.12 (t, *J*=7.4 Hz, 2H, H-5, 17), 4.08 (d, $^2J$=15.7 Hz, 4H, H-2, 8, 14, 20), 4.04 (d, $^2J$=15.7 Hz, 4H, H-2, 8, 14, 20), 3.78 (m, 4H, –O*CH*$_2$CH$_2$CH$_3$), 1.51 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 0.48 (t, 6H, –OCH$_2$CH$_2$*CH*$_3$); *crown*: 4.36 (m, 4H), 3.96 (m, 4H), 3.85 (m, 4H), 3.82 (m, 4H). $^{13}$C NMR (100 MHz, $CD_3CN$, TMS): δ=161.0 (C, 2C), 158.8 (C, 2C), 156.6 (C, 2C), 142.2 (C, 2C), 141.5 (C, 2C), 139.0 (CH, 2C), 137.7 (CH, 2C), 135.9 (C, 4C), 135.5 (C, 4C), 134.6 (CH, 4C), 131.8 (CH, 4C), 131.0 (CH, 2C), 130.9 (CH, 2C), 128.2 (C, 2C), 128.0 (CH, 2C), 127.0 (CH, 2C), 126.4 (C, 2C), 125.3 (C, 2C), 123.4 (CH, 2C), 118.8 (CH, 2C), 118.4 (CH, 2C), 75.7 (–O*CH*$_2$CH$_2$CH$_3$), 71.3 ($CH_2$, 2C), 70.9 ($CH_2$, 2C), 70.7 ($CH_2$, 2C), 70.1 ($CH_2$, 2C), 39.1 ($N^+$–$CH_3$), 36.8 (C-2, 8, 14, 20), 23.4 (–OCH$_2$*CH*$_2$CH$_3$), 8.6 (–OCH$_2$CH$_2$*CH*$_3$).

**4.3.2. 11,23-Di-(*N*-methylacridinium-9-yl)-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene-crown-6, 1,3-alternate bishexafluorophosphate (5b).** Compound **5b** was purified by CC (acetonitrile, aqueous solution of $NH_4PF_6$ (2.5%) 20:1); orange crystals, 0.245 g (10%), mp 216–218 °C. Anal. $C_{72}H_{74}F_{12}N_2O_8P_2$ (1385.33); HRMS (ESI): $[M-PF_6^-]^+$ calcd for $C_{72}H_{74}F_6N_2O_8P$: 1239.5087, found: 1239.5012; $[M-2PF_6^-]^{2+}$ calcd for $C_{72}H_{74}N_2O_8$: 547.2722, found: 547.2711. $^1$H NMR (600 MHz, $CD_3CN$, TMS): δ=*acridinium*: 8.64 (d, *J*=9.3 Hz, 2H, H-5), 8.45 (dd, *J*=9.3, 9.0 Hz, 2H, H-6), 8.25 (d, *J*=8.8 Hz, 2H, H-8), 8.12 (d, *J*=9.3 Hz, 2H, H-4), 7.93 (d, *J*=8.0 Hz, 2H, H-1), 7.90 (t, *J*=8.8, 9.0 Hz, 2H, H-7), 7.35 (t, *J*=9.3, 8.3 Hz, 2H, H-3), 6.60 (t, *J*=8.0, 8.3 Hz, 2H, H-2), 4.78 (s, 6H, $N^+$–$CH_3$); *calixarene*: 7.44 (s, 4H, H-10, 12, 22, 24), 7.39 (d, 4H, H-4, 6, 16, 18), 7.02 (t, 2H, H-5, 17), 4.15 (m, 4H, H-2, 8, 14, 20), 3.95 (m, 4H, H-2, 8, 14, 20); *crown*: 3.88–3.83 (m, 16H, 8×$CH_2$), 3.80 (m, 4H, 4×$CH_2$), 3.73 (m, 4H, –O*CH*$_2$CH$_2$CH$_3$), 1.51 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 0.50 (t, 6H, –OCH$_2$CH$_2$*CH*$_3$). $^{13}$C NMR (100 MHz, $CD_3CN$, TMS): δ=158.9 (C), 156.9 (C), 141.4 (C), 140.6 (C), 138.4 (CH), 136.2 (CH), 134.9 (C), 133.9 (CH), 131.2 (CH), 131.1 (CH), 130.9 (CH), 127.4 (CH), 126.0 (CH), 125.6 (C), 124.6 (C), 122.1 (CH), 118.1 (CH), 117.4 (CH), 75.5 (–O*CH*$_2$CH$_2$CH$_3$), 72.1, 70.6, 70.4, 70.1, 69.9 ($CH_2$-crown), 38.4 ($N^+$–$CH_3$), 35.9 (C-2, 8, 14, 20), 23.0 (–OCH$_2$*CH*$_2$CH$_3$), 8.4 (–OCH$_2$CH$_2$*CH*$_3$).

**4.3.3. 11,23-Di-(*N*-methylacridinium-9-yl)-25,27-dihydroxy-26,28-bis(propyloxy)calix[4]arene-crown-7, 1,3-alternate bishexafluorophosphate (5c).** Compound **5c** was purified by CC (acetonitrile, aqueous solution of $NH_4PF_6$ (10%) 20:1); 0.5 g (14%)) yellow crystals, mp 203–205 °C. Anal. $C_{74}H_{78}F_{12}N_2O_8P_2$ (1429.39); HRMS (ESI): $[M-PF_6^-]^+$ calcd for $C_{74}H_{78}F_6N_2O_9P$: 1283.5349, found: 1283.5367; $[M-2PF_6^-]^{2+}$ calcd for $C_{74}H_{78}N_2O_9$: 569.2853, found: 569.2851. $^1$H NMR (600 MHz, $CD_3CN$, TMS): δ=*acridinium*: 8.63 (d, 2H, H-5), 8.46 (t, 2H, H-6), 8.24 (d, 2H, H-8), 8.06 (d, 2H, H-4), 8.03 (d, 2H, H-1), 7.93 (t, 2H, H-7), 7.27 (t, 2H, H-3), 6.72 (t, 2H, H-2), 4.75 (s, 6H, $N^+$–*CH*$_3$); *calixarene*: 7.45 (d, 4H, H-4, 6, 16, 18), 7.38 (s, 4H, H-10, 12, 22, 24), 6.95 (t, 2H, H-5, 17), 3.72 (m, 4H, H-2, 8, 14, 20), 3.62 (m, 4H, H-2, 8, 14, 20); *crown*: 4.10 (m, 4H, 2×$CH_2$), 3.99 (m, 4H, 2×$CH_2$), 3.88 (m, 4H, 2×$CH_2$), 3.82 (m, 12H, 6×$CH_2$); *ether*: 3.77 (m, 4H, –O*CH*$_2$CH$_2$CH$_3$), 1.61 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 0.60 (t, 6H, –OCH$_2$CH$_2$*CH*$_3$). $^{13}$C NMR (75 MHz, $CD_3CN$, TMS): δ=162.7 (C), 160.1 (C), 157.9 (C), 142.6 (C), 141.6 (C), 139.8 (CH), 137.2 (CH), 136.3 (C), 135 (CH), 133.9 (C), 132.8 (CH), 132.5 (CH), 132.2 (CH), 128.7 (CH), 127.1 (CH), 126.9 (C), 126.8 (C), 125.7 (C), 123.4 (CH), 119.3 (CH), 117.3 (CH), 77.1 (–O*CH*$_2$CH$_2$CH$_3$), 74.0, 71.7, 71.6, 71.5, 71.3 ($CH_2$-crown), 39.7 ($N^+$–$CH_3$), 36.7 ($CH_2$-calixarene), 24.4 (–OCH$_2$*CH*$_2$CH$_3$), 9.8 (–OCH$_2$CH$_2$*CH*$_3$).

**4.3.4. 9-(4-Methoxyphenyl)-10-methyl-acridinium hexafluorophosphate (6).** Compound **6** was described in the literature.[18] However, experimental details and analytical data were not given. Compound **6** is, therefore, included. Butyllithium (1.6 M in hexane) (2 mL, 3.2 mmol) in THF solution (8 mL) was added dropwise to 4-bromoanisole (0.56 g, 3 mmol) dissolved in dry THF (50 mL) at −78 °C. After stirring for 0.5 h, *N*-methylacridone (0.630 g, 3 mmol) was added. After warming the solution to room temperature, stirring was continued for 1 h. The reaction was quenched with water (5 mL). The solvent was evaporated in vacuo and the residue was dissolved in acetonitrile (75 mL). The solution was then treated with $NH_4PF_6$ (1 g). After stirring for 0.5 h, the solvent was removed in vacuo. The resulting solid was three times washed with water. The crude product was purified by CC (methanol/acetonitrile/aqueous 10% $NH_4PF_6$ solution, 10:10:1.5) to afford yellow crystals, 0.51 g, 38%, mp 237–239 °C. Anal. Calcd for $C_{21}H_{18}F_6NOP$ (445.35): C, 56.64; H, 4.07; N, 3.15. Found: C, 56.70; H, 4.10; N, 3.45. $^1$H NMR (400 MHz, $CD_3CN$, TMS): δ=8.57 (d, 2H, H-1, 8), 8.35 (dt, 2H, H-2, 7), 8.10 (dd, 2H, H-4, 5), 7.84 (t, 2H, H-3, 6), 7.46 (d, 2H, $C_6H_4OCH_3$), 7.27 (d, 2H, $C_6H_4OCH_3$), 4.79 (s, 3H, –$OCH_3$), 3.95 (s, 3H, $N^+$–$CH_3$). $^{13}$C NMR (100 MHz, $CD_3CN$, TMS): δ=161.7 (C), 161.0 (C), 141.3 (C), 138.2 (CH), 131.6 (CH), 130.1 (CH), 127.3 (CH), 126.0 (C), 124.7 (C), 118.1 (CH), 114.0 (CH), 55.1 (–$OCH_3$), 38.3 ($N^+$–$CH_3$).

### 4.4. Calix[4]arenes 7–10: general procedure

The alcohol (1 mL) and $K_2CO_3$ (0.1 g) were added to the acridinium compounds **3**–**6** (0.1 mmol) in dry acetonitrile (10 mL). The suspension was stirred until decolorization of the solution (2–12 h). After filtration the solvent was removed in vacuo. The remaining residue was treated with chloroform (10 mL) and then filtered. The filtrate was evaporated in vacuo to yield a solid that was used without further purification.

**4.4.1. 11,23-Di-(10-methoxy-9,10-dihydro-9-methyl-acridin-9-yl)-25,27-dibenzyloxy-26,28-bis-(propyloxy)-calix[4]arene (7).** Colorless needles from acetone, 100 mg (90%), mp 144 °C, Anal. $C_{78}H_{74}N_2O_6$ (1135.46); HRMS (ESI): $[M-OCH_3]^+$ calcd for $C_{77}H_{71}N_2O_5$: 1103.5363, found: 1103.5367; $[M-2CH_3]^{2+}$ calcd for $C_{76}H_{68}N_2O_4$: 536.2590, found: 536.2589. $^1$H NMR (400 MHz, $CDCl_3$, TMS): δ=*acridane*: 7.34 (m, 4H, H-3, 6), 7.26 (m 4H, H-1, 8), 7.08 (d, *J*=8.0 Hz, 4H, H-2, 8), 6.98 (t, *J*=8.0 Hz, 4H, H-4, 5), 3.57 (s, 6H, –O*CH*$_3$), 2.91 (s, 6H, –NCH$_3$);

*calixarene*: 7.32 (m, 4H, *ortho* –O$CH_2C_6H_5$), 7.28 (m, 6H, –O$CH_2C_6H_5$), 7.06 (s, 4H, H-10, 12, 20, 24), 6.15 (t, 2H, $J$=7.5 Hz, H-5, 17), 5.91 (d, 4H, $J$=7.5 Hz, H-4, 6, 16, 18), 5.21 (–O$CH_2C_6H_5$), 4.15 (d, $J$=13.3 Hz, 4H, H-2, 8, 14, 20), 3.53 (t, $J$=7.0 Hz, 4H, –O$CH_2CH_2CH_3$), 2.90 (d, $J$=13.3 Hz, 4H, H-2, 8, 14, 20), 1.76 (m, 4H, –OCH$_2CH_2$CH$_3$), 0.99 (t, $J$=7.5 Hz, 6H, –OCH$_2CH_2CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): $\delta$=155.2 (C), 154.5 (C), 141.6 (C), 141.4 (C), 138.2 (C), 136.5 (C), 133.1 (C), 130.4 (CH), 128.4 (CH), 128.1 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 124.8 (C), 122.0 (CH), 119 (CH), 112.0 (CH), 78.9 (–O$CH_2CH_2CH_3$), 75.3 (–O$CH_2C_6H_5$), 51.0 (–$OCH_3$), 33.6 (–$NCH_3$), 31.4 (C-2, 8, 14, 20), 23.4 –OCH$_2CH_2$CH$_3$), 10.9 (–OCH$_2CH_2CH_3$).

**4.4.2. 11,23-Di-(10-methoxy-9,10-dihydro-9-methyl-acridin-9-yl)-25,27-dihydroxy-26,28-bis-(propyloxy)calix[4]-arene-crown-5, 1,3-alternate (8a).** Colorless crystals, 100 mg (90%), mp 188–190 °C, Anal. $C_{72}H_{76}N_2O_9$ (1113.41); HRMS (ESI): [M+K$^+$] calcd for $C_{72}H_{76}KN_2O_9$: 1151.5188, found: 1151.5187; [M−$OCH_3$]$^+$ calcd for $C_{71}H_{73}N_2O_8$: 1081.5367, found: 1081.5372; [M+K$^+$−$OCH_3$]$^{2+}$ calcd for $C_{71}H_{73}KN_2O_9$: 560.2502, found: 560.2504; [M−2$CH_3$]$^{2+}$ calcd for $C_{70}H_{70}N_2O_7$: 525.2592, found: 525.2593. $^1$H NMR (400 MHz, $(CD_3)_2CO$, TMS): $\delta$= 7.49–6.49 (m, 26H), 3.94–3.36 (m, 40H), 1.28 (m, 4H), 0.68 (t, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): $\delta$=157.9 (C), 153.5 (C), 144.2 (C), 141.2 (C), 135.9 (C), 132.3 (C), 130.6 (CH), 129.6 (CH), 128.9 (CH), 128.3 (CH), 124.3 (C), 121.5 (CH), 120.4 (CH), 112.1 (CH), 78.4 (C), 73.8 (–O$CH_2$CH$_2$CH$_3$), 73.7, 70.8, 70.7, 70.0 ($CH_2$-crown), 51.3 (–$OCH_3$), 37.7 ($CH_2$-cailxarene), 33.5 (–$NCH_3$), 22.8 (–OCH$_2CH_2$CH$_3$), 9.7 (–OCH$_2$CH$_2CH_3$).

**4.4.3. 11,23-Di-(10-methoxy-9,10-dihydro-9-methyl-acridin-9-yl)-25,27-dihydroxy-26,28-bis-(propyloxy)calix[4]-arene-crown-6, 1,3-alternate (9a).** Colorless crystals, 97 mg (84%), mp 149–151 °C. Anal. $C_{74}H_{80}N_2O_{10}$ (1157.46); HRMS (ESI): [M+Na$^+$]$^+$ calcd for $C_{74}H_{80}N_2NaO_{10}$: 1179.5711, found: 1179.5636; [M−$OCH_3$]$^+$ calcd for $C_{73}H_{77}N_2O_9$: 1125.5629, found: 1125.5562. $^1$H NMR (400 MHz, $(CD_3)_2CO$, TMS): $\delta$=*acridane*: 7.52 (d, 4H, $J$=7.8 Hz, H-1, 8), 7.41 (t, 4H, $J$=7.8 Hz, H-3, 6), 7.24 (d, 4H, $J$=7.8 Hz, H-4, 5), 7.12 (t, 4H, $J$=7.8 Hz, H-2, 7), 3.62 (s, 6H, –N–$CH_3$), 3.09 (s, 6H, –O$CH_3$); *calixarene*: 7.29 (d, 4H, $J$=7.5 Hz, H-4, 6, 16, 18), 7.19 (s, 4H, H-10, 12, 20, 24), 6.94 (t, 2H, $J$=7.5 Hz, H-5, 17), 3.86 (m, 4H, H-2, 8, 14, 20), 3.70 (m, 4H, H-2, 8, 14, 20); *crown*: 3.79 (br s, 20H); *ether*: 3.38 (m, 4H, –O$CH_2$CH$_2$CH$_3$), 1.25 (m, 4H, –OCH$_2CH_2$CH$_3$), 0.72 (t, 6H, $^3J$=7.5 Hz, –OCH$_2$CH$_2CH_3$). $^{13}$C NMR (100 MHz, $(CD_3)_2CO$, TMS): $\delta$=*acridane*: 141.2 (C-4a, 5a), 129.1 (C-1, 8), 128.1 (C-3, 6), 124.3 (C-1a, 8a), 120.1 (C-2, 7), 112.4 (C-4, 5), 50.3 (–$OCH_3$), 32.9 (–$NCH_3$); *calixarene*: 135.3 (C-1, 9, 13, 21), 132.5 (C-3, 7, 15, 19), 130.0 (C-4, 6, 16, 18), 128.2 (C-10, 12, 20, 24), 121.4 (C-5, 17), 73.0 (–O$CH_2$CH$_2$CH$_3$), 37.4 (C-2, 8, 14, 20), 22.4 (–OCH$_2CH_2$CH$_3$), 9.3 (–OCH$_2$CH$_2CH_3$); *crown*: 70.5 (4C, $CH_2$), 69.8 (2C, $CH_2$), 69.7 (2C, $CH_2$), 69.1 (2C, $CH_2$).

**4.4.4. 11,23-Di-(10-ethoxy-9,10-dihydro-9-methyl-acridin-9-yl)-25,27-dihydroxy-26,28-bis-(propyloxy)calix[4]-arene-crown-6, 1,3-alternate (9b).** Beige crystals, 110 mg (93%), mp 155–160 °C. Anal. $C_{76}H_{84}N_2O_{10}$ (1185.52); HRMS (ESI): [M+K$^+$]$^+$ calcd for $C_{76}H_{84}KN_2O_{10}$: 1223.5763, found: 1223.5703; [M−$OC_2H_5$]$^+$ calcd for $C_{74}H_{79}N_2O_9$: 1139.5785, found: 1139.5737. $^1$H NMR (400 MHz, $CD_3CN$, TMS): $\delta$=*acridane*: 7.43 (dd, $J$= 9.3 Hz, 4H), 7.31 (m, 4H), 7.11 (m, 4H), 7.01 (t, $J$= 9.3 Hz, 4H), 3.49 (s, 6H, –$NCH_3$), 3.08 (q, $J$=7.1 Hz, 4H, –O$CH_2CH_3$), 1.18 (t, $J$=7.1 Hz, 6H, –OCH$_2CH_3$); *calixarene*: 7.14 (d, $J$=8.0 Hz, 4H, H-4, 6, 16, 18), 7.09 (s, 4H, H-10, 12, 20, 24), 6.82 (t, $J$=8.0 Hz, 2H, H-5, 17), 3.64 (m, 8H, –$CH_2$), 3.25 (m, 4H, –O$CH_2CH_2CH_3$), 1.17 (m, 4H, –OCH$_2CH_2$CH$_3$), 0.61 (t, 6H, –OCH$_2$CH$_2CH_3$); *crown*: 3.71 (m, 6H), 3.65 (m, 12H), 3.57 (m, 6H). $^{13}$C NMR (75 MHz, $CD_3CN$, TMS): $\delta$=*acridane*: 141.0 (C-4a, 5a), 129.1 (C-1, 8), 128.3 (C-3, 6), 125.2 (C-1a, 8a), 120.1 (C-2, 7), 112.5 (C-4, 5), 58.4 (–O$CH_2CH_3$), 33.2 (–$NCH_3$), 15.0 (–OCH$_2CH_3$); *calixarene*: 143.9 (C-11, 23), 136.1 (C-1, 9, 13, 21), 132.5 (C-3, 7, 15, 19), 130.4 (C-4, 6, 16, 18), 128.4 (C-10, 12, 20, 24), 120.4 (C-5, 17), 73.4 (–O$CH_2$CH$_2$CH$_3$), 37.4 (C-2, 8, 14, 20), 22.2 (–OCH$_2CH_2$CH$_3$), 9.3 (–OCH$_2$CH$_2CH_3$); *crown*: 73.0 (2C, $CH_2$), 70.3 (2C, $CH_2$), 70.2 (2C, $CH_2$), 70.0 (4C, $CH_2$).

**4.4.5. 11,23-Di-(9,10-dihydro-9-methyl-10-methoxy-acridin-9-yl)-25,27-dihydroxy-26,28-bis-(propyloxy)calix[4]-arene-crown-7, 1,3-alternate (10a).** Colorless crystals, 102 mg (85%), mp 140–142 °C. Anal. $C_{76}H_{84}N_2O_{11}$ (1201.51); HRMS (ESI): [M−OMe]$^+$ calcd for $C_{75}H_{81}N_2O_{10}$: 1169.5891, found: 1169.5861; [M−2-OMe]$^{2+}$ calcd for $C_{74}H_{78}N_2O_9$: 569.2853, found: 569.2849. $^1$H NMR (400 MHz, $(CD_3)_2CO$, TMS): $\delta$=*acridane*: 7.44 (dd, $J$= 7.8 Hz, 4H, H-1, 8), 7.35 (dt, $J$=7.0 Hz, 4H, H-3, 6), 7.19 (d, $J$=7.0 Hz, 4H, H-4, 5), 7.05 (t, $J$=7.8 Hz, 4H, H-2, 7), 3.56 (s, 6H, –$NCH_3$), 3.01 (s, 6H, O–$CH_3$); *calixarene*: 7.13 (d, $J$=7.3 Hz, 4H, H-4, 6, 16, 18), 7.08 (s, 4H, H-10, 12, 22, 24), 6.85 (t, $J$=7.3 Hz, 4H, H-5, 17), 3.75 (d, $^2J$=15.8 Hz, 4H, H-2, 8, 14, 20), 3.71 (d, $^2J$=15.8 Hz, 4H, H-2, 8, 14, 20), 3.22 (m, 4H, –O$CH_2$CH$_2$CH$_3$), 1.06 (m, 4H, –OCH$_2CH_2$CH$_3$), 0.60 (t, 6H, –OCH$_2$CH$_2CH_3$); *crown*: 3.68–3.59 (m, 20H), 3.32 (m, 4H). $^{13}$C NMR (100 MHz, $(CD)_3CO$, TMS): $\delta$=*acridane*: 142.1 (C-4a, 5a), 130.0 (C-1, 8), 128.6 (C-3, 6), 125.4 (C-1a, 8a), 121.1 (C-2, 7), 113.4 (C-4, 5), 51.3 (–$OCH_3$), 33.9 (–$NCH_3$); *calixarene*: 158.4 (C-25, C-27), 154.9 (C-26, C-27), 145.0 (C-11, 23), 138.7 (C-1, 9, 13, 21), 135.8 (C-3, 7, 15, 19), 131.0 (C-4, 6, 16, 18), 129.2 (C-10, 12, 20, 24), 122.8 (C-5, 17), 73.7 (–O$CH_2$CH$_2$CH$_3$), 38.5 (C-2, 8, 14, 20), 23.4 (–OCH$_2CH_2$CH$_3$), 10.4 (–OCH$_2$CH$_2CH_3$); *crown*: 71.4 (2C, $CH_2$), 71.3 (2C, $CH_2$), 71.2 (2C, $CH_2$), 71.1 (2C, $CH_2$), 70.8 (2C, $CH_2$), 70.1 (2C, $CH_2$).

**4.4.6. 11,23-Di-(10-ethoxy-9,10-dihydro-9-methyl-acridin-9-yl)-25,27-dihydroxy-26,28-bis-(propyloxy)calix[4]-arene-crown-7, 1,3-alternate (10b).** Beige crystals, 117 mg (95%), mp 136–139 °C. Anal. $C_{78}H_{88}N_2O_{11}$ (1229.57); HRMS (ESI): [M+K$^+$]$^+$ calcd for $C_{78}H_{88}KN_2O_{11}$: 1267.6025, found: 1267.5995; [M−OEt]$^+$ calcd for $C_{76}H_{83}N_2O_{10}$: 1183.6048, found: 1183.6017; [M−2-OEt]$^{2+}$ calcd for $C_{74}H_{78}N_2O_9$: 569.2853, found: 569.2851. $^1$H NMR (400 MHz, $CD_3CN$, TMS): $\delta$=*acridane*: 7.42 (d, 4H, H-1, 8), 7.31 (t, 4H, H-3, 6), 7.12 (d, 4H, H-4, 5), 7.01 (t, 4H, H-2, 7), 3.48 (s, 6H, N–$CH_3$), 3.08 (q, 4H, O–$CH_2CH_3$), 1.25 (t, 6H, O–CH$_2CH_3$); *calixarene*: 7.17

(d, 4H, H-4, 6, 16, 18), 7.08 (s, 4H, H-10, 12, 22, 24), 6.88 (t, 2H, H-5, 17), 3.70–3.55 (m, 32H, 8×$CH_2$ and 12×$CH_2$-crown), 3.24 (m, 4H, –O$CH_2$$CH_2CH_3$), 1.15 (m, 4H, –$OCH_2CH_2$$CH_3$), 0.60 (t, 6H, –$OCH_2CH_2CH_3$). $^{13}$C NMR (100 MHz, $(CD)_3CO$, TMS): $\delta$=*acridane*: 141.9 (C-4a, 5a), 130.1 (C-1, 8), 128.7 (C-3, 6), 126.1 (C-1a, 8a), 121.0 (C-2, 7), 113.3 (C-4, 5), 59.1 (–O$CH_2CH_3$), 33.9 (–$NCH_3$), 16.0 (–$OCH_2CH_3$); *calixarene*: 158.5 (C-25, C-27), 154.9 (C-26, C-27), 145.4 (C-11, 23), 135.9 (C-1, 9, 13, 21), 133.8 (C-3, 7, 15, 19), 131.1 (C-4, 6, 16, 18), 129.1 (C-10, 12, 20, 24), 122.8 (C-5, 17), 73.9 (–O$CH_2CH_2CH_3$), 38.6 (C-2, 8, 14, 20), 23.5 (–$OCH_2CH_2CH_3$), 10.5 (–$OCH_2CH_2CH_3$); *crown*: 71.5 (2C, $CH_2$), 71.4 (2C, $CH_2$), 71.3 (2C, $CH_2$), 71.2 (2C, $CH_2$), 70.8 (2C, $CH_2$), 70.1 (2C, $CH_2$).

**4.4.7. 9,10 Dihydro-9-methoxy-9-(4-methoxyphenyl)-10-methyl-acridine (11).** Colorless crystals, 70 mg (94%), mp 137–140 °C. Anal. $C_{22}H_{21}NO_2$ (331.42); HRMS (ESI): $[M+Na^+]^+$ calcd for $C_{22}H_{21}NNaO_2$: 354.1467, found: 354.1462; $[M-OCH_3]^+$ calcd for $C_{21}H_{18}NO$: 300.1388, found: 300.1381. $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$=7.28 (dt, 2H, H-1, 8), 7.25 (dd, 2H, H-3, 6), 7.14 (d, 2H, $C_6H_4OCH_3$), 7.12 (d, 2H, H-4, 5), 6.90 (dt, 2H, H-2, 7), 6.74 (d, 2H $C_6H_4OCH_3$), 3.73 (s, 3H, $OCH_3$), 3.50 (s, 3H, $OCH_3$), 2.97 (s, 3H, –$NCH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$=158.1 (*p*-$C_6H_4OCH_3$), 142.2 (*ipso*-$C_6H_4OCH_3$), 141.2 (C-4a, 5a), 129.5 (*o*-$C_6H_4OCH_3$), 128.5 (C-1, 8), 127.6 (C-3, 6), 124.8 (C-1a, 8a), 120.4 (*m*-$C_6H_4OCH_3$), 113.2 (C-2, 7), 112.4 (C-1, 8), 78.5 (C-9), 55.4 (–$C_6H_4O$$CH_3$), 51.4 (–$OCH_3$), 36.7 (–$NCH_3$).

## Acknowledgements

Financial support provided by Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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