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Functionalized thiacalix- and calix[4]arene-based Ag^+ ionophores: synthesis and comparative NMR study

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Abstract—Thiacalix[4]arene ionophores comprised of cyclic or linear *O*,*S*,*N* ligating and/or π-coordinate groups on the lower rim were synthesized and their Ag^+ binding was studied by ^1H NMR methods in comparison with the respective known and novel calix[4]arene counterparts. Calix[4](*O*,*S*,*N*)crowns were found stronger binders than the π-coordinate molecules and thiacalixarene ionophores were generally superior to calixarenes. This study helped to develop silver ion-selective electrodes working in the subnanomolar region.

1. Introduction

Over the last two decades, considerable efforts have been devoted to the design and synthesis of calixarene (CA)-based ionophores and a number of functionalized derivatives have been applied as extractants and sensors in analytical and separation chemistry.[1,2] In fact, many calixarenes containing pendant ether, ester, amide and ketonic groups, in addition to calix(mono- and biscrowns) have been used as neutral carriers in ion-selective electrodes (ISE) exhibiting selective responses to main group metal ions, such as Na^+, K^+ and Cs^+.[3–14] Transition metal ion (Ag^+, Hg^{2+}, Pb^{2+} etc.) selective receptors are less prevalent in calixarene chemistry,[15–19] but recently Zhang's group has published a series of Ag^+ ionophores comprised of sulfur, selenium, nitrogen and phosphorus atoms in the ligating groups attached to the lower rim.[20–26] The binding ability of these ligands is based alike on the preferred interaction between the soft donor atoms (S, Se, N) and the soft Ag^+ ion. At the same time, some recent works have demonstrated that a π-system can be suitable binding site for soft cations via π-cation interaction[27] and in fact, a π-coordinate tetraallyloxy-CA was already utilized in the development of a calixarene-based Ag^+ ISE.[28] Although thiacalix[4]arenes (TCA) have received growing interest since their discovery in 1997,[29] so far the synthesis and application of the respective thiacalixarene ionophores have remained unexplored. The investigation of cation extraction ability of the parent TCA revealed that it efficiently extracts a number of transition metal ions without any selectivity at pH 7.5.[30,31] Obviously, similar to calix[4]arenes, appropriate functionalization on the lower rim is required to achieve cation selectivities of practical value. Probably, synthetic difficulties aroused on the regio- and stereoselective functionalization of TCA have prevented an extended research in this field.[32] In fact, only a few thiacalix[4]crown-6 ethers (**I**) have been reported to display Cs^+ selectivity in extraction experiments[33,34] and utilized as neutral carriers in ISEs.[35,36] Besides, the selective cation extraction ability of 24,26-bis(3-hydroxypropoxy)-*p*-*tert*-butyl-TCA (Ag^+)[31] and 24,25,26,27-tetrakis(diethylcarbamoylmethoxy)-*p*-*tert*-butyl-TCA (Pb^{2+})[37] are worth mentioning.

Seeking a selective method for the distal dialkylation and ring closure of TCA, we have recently recognized that the Mitsunobu reaction is an extremely simple, efficient and mild method to diametrically alkylate and cyclize TCA with alcohols and diols.[38–40]

In this way, we have prepared a series of thiacalix[4](*O*,*S*,*N*-crown-5)ethers[40] and herein our studies with selected derivatives, completed by new molecules containing known soft ligating functions, are reported. For comparison, the respective calixarene counterparts including known and new ionophores were synthesized and their Ag^+ sensing was also investigated by ^1H NMR under similar conditions. Our final goal was to find TCA ligands for developing silver ISEs

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possessing high stability and sensitivity in the subnanomolar region without the drawbacks of the known sensors. The electroanalytical evaluation of ISEs fabricated from our best ligands has been published elsewhere.[41]

2. Results and discussion

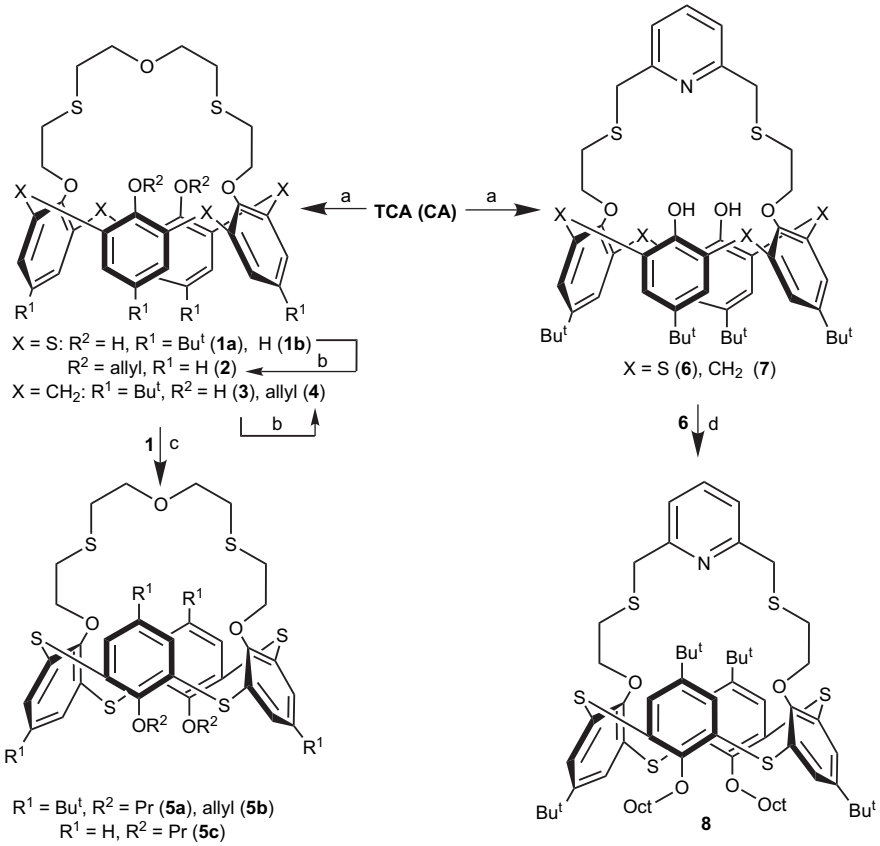
The potential silver sensing ligands are surveyed in Schemes 1 and 2. The selection of molecules requires some comments. A number of thiacrown ethers were designed as neutral carriers for Ag^+ ISEs.[1d] However, the binding of Ag^+ with the crown-ring sulfur atoms is strong, often causing slow metal ion exchange equilibrium in the membrane interface, which results in slow sensor response and poor selectivity. These disadvantages and the alkali- and alkaline earth metal ion interference were expected to be eliminated by designing calix[4](*O*,*S*,*N*-crown-5) ethers (cone **1**–**4**, **6**, **7** and 1,3-alt **5** and **8**), where the calixarene skeleton and the conformation were varied (Scheme 1).

Podands **9** and **10**, containing the same 1,3-benzothiazole binding site attached to different calixarenes in distal position through a spacer, represent the flexible version of receptors that may have advantages over rigid ionophores. The π–cation interaction of soft Ag^+ is relatively weak, but quite selective, thereby providing another way of sensing.[28] Therefore, it seemed to be promising to test the binding ability of ligands **11**–**16** (including **14** as reference[28]), where the number of π-donor allyl groups, the calixarene scaffold and the conformation were varied (Scheme 2).

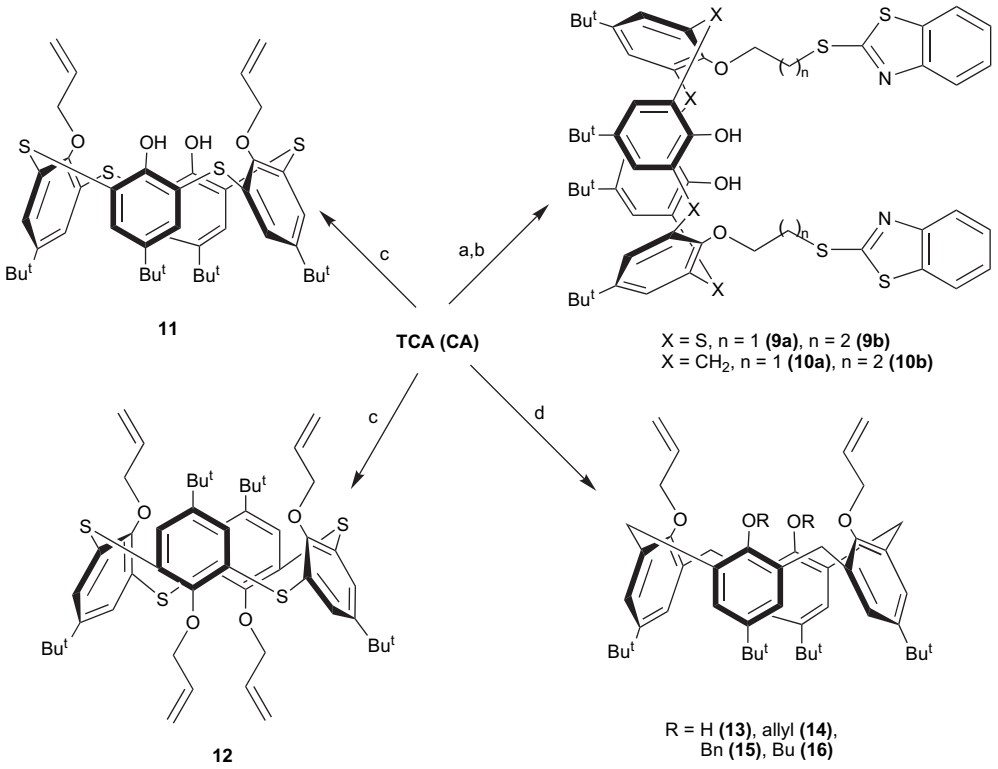
2.1. Synthesis

Thiacalix[4](*O*,*S*,*N*-crown-5)ethers **1a**, **6** and **8** were described by us[40] and the analogous **1b**, **3** and **7** were prepared similarly by the Mitsunobu cyclization of TCA or *p*-Bu^{t}CA with diols using triphenylphosphine (TPP) and diethyl azodicarboxylate (DEAD) coupling agents.

The O-alkylation of **1b** and **3** was performed with allylbromide under PTC conditions (50% aq $NaOH/Bu_4N^+Br^-$)[42] to afford cone **2** and **4**, and with PrI or allylbromide/Cs_2CO_3 to give 1,3-alt **5a**–**c**. Bis(1,3-benzothiazol-2-yl)-CA derivatives **10a**,**b** were described by Zhang using the weak base-promoted S-alkylation of 2-mercapto-1,3-benzothiazole with 25,27-bis(bromoalkoxy)-*p*-*tert*-butylcalix[4]-arene.[23,25] The TCA analogue **9a** was obtained by slight modification of the literature method developed for **10a**,**b**[23] but this procedure failed to give **9b**. Instead, the Mitsunobu alkylation of *p*-Bu^t-TCA with 2-(3-hydroxypropylthio)-1,3-benzothiazole led to success. The π-coordinate allyloxy-TCA ligands **11** and **12** were obtained by our regio- and conformation-selective alkylation of TCA with allylalcohol under Mitsunobu condition,[38] while 25,27-diallyloxy-CA **13** was prepared as described earlier.[43] Tetrasubstituted CA ionophores **14**–**16** were synthesized by our PTC alkylation method of CA with allylbromide (**14**), and



Scheme 1. Survey and synthesis of calix[4]crown ionophores to be tested for Ag^+ sensing. Reagents and conditions: (a) diol, TPP/DEAD, toluene, rt (**1a**,**b**, **3**, **6**, **7**); (b) **1b** or **3**, allylbromide, aq NaOH, PTC (**2**, **4**); (c) allylbromide or PrI, Cs_2CO_3, MeCN, 80 °C (**5a**–**c**); (d) OctOH, TPP/DEAD, toluene, 80 °C.



Scheme 2. Survey and synthesis of open-chain calix[4]arene ionophores to be tested for Ag^+ sensing. Reagents and conditions: (a1) (i) *p*-Bu^t-TCA, 2-bromoethanol, TPP/DEAD, toluene, rt; (ii) 2-mercapto-1,3-benzothiazole, $NaHCO_3$, MeCN, 80 °C (**9a**); (a2) (i) *p*-Bu^t-CA, 1,2-dibromoethane, K_2CO_3, MeCN, 80 °C; (ii) 2-mercapto-1,3-benzothiazole, $NaHCO_3$, aq THF (**10a**,**b**); (b) *p*-Bu^t-TCA, 2-(3-hydroxypropylthio)-1,3-benzothiazole, TPP/DEAD, toluene, rt (**9b**); (c) allylalcohol, TPP/DEAD, toluene, rt (**11**) or 80 °C (**12**); (d1) *p*-Bu^t-CA, allylbromide, K_2CO_3, acetone, 56 °C (**13**); (d2) *p*-Bu^t-CA, allylbromide, aq NaOH, PTC (**14**); (d3) **13**, aq NaOH, PTC, BnBr (**15**) or BuBr (**16**).

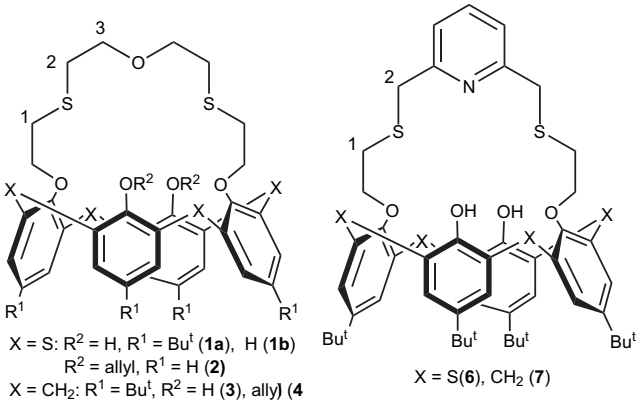
by that of **13** with BnBr (**15**) or BuBr (**16**)[42] (Schemes 1 and 2).

2.2. Investigation of Ag^+ binding by ^{1}H NMR methods

Among ionophores only calix[4]arene derivatives **10a**,**b** and **14** were applied to fabricate silver ISEs,[23,25,28] therefore, they served as references in the NMR measurements of TCA ligands. Our aim was to recognize the dominant binding sites and events by comparing the respective ^{1}H chemical shift differences. Stability constants were not calculated, although they are useful but not indispensable to estimate the binding affinities (in ISE experiments these data are significantly affected by the membrane composition[44]). The NMR measurements were performed with equimolar quantity of $AgClO_4$ (excess of Ag^+ did not change the spectra) in $CDCl_3$ (TCA) or $CDCl_3$–CD_3OD=4:1 (CA) solvents at 25 °C and the chemical shift differences ($\Delta\delta=\delta$ (in the presence of Ag^+)$-\delta$ (metal free)) are summarized in Tables 1–4.

The spectral changes of ligands **1a**–**4** clearly show that the SCH_2 protons exhibit the largest $\Delta\delta$ values suggesting that the soft sulfur atoms are primarily involved in complexation. The central hard oxygen atom also takes part in binding but, as expected, to a lesser extent. The allyl groups of **2** and **4** are assumed not to be involved in binding (little $\Delta\delta$ values as compared to those in Table 4). In the pyridinocrown derivative **6** the central sp^2 nitrogen together with the sulfur atoms efficiently coordinates the silver ion as reflected by the significant downfield shifts of the heteroaromatic *m*- and *p*-protons (0.28, 0.34) and the SCH_2 protons as well. In contrast, the three-point ligation involving the sp^2 nitrogen in the CA counterpart **7** is suppressed (PyH 0.03*m*, 0.05*p* ppm), similar to the respective OS_2 ligand **3** (Table 1).

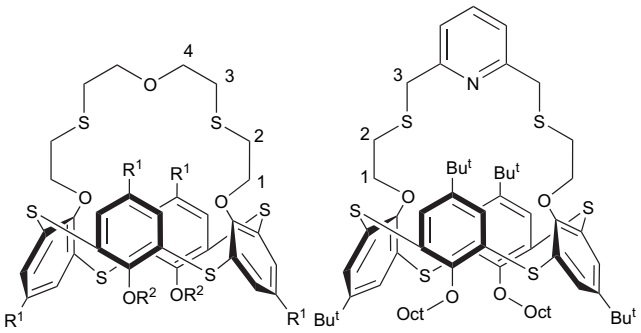
Table 1. Chemical shift differences ($\Delta\delta$, ppm) of cone thiacalix- and calix[4]crowns **1a**, **2**–**4**, **6** and **7** upon addition of $AgClO_4$ ([L]/[Ag^+]=1:1)



L	CH_2-3	SCH_2-1,2	PyH	=CH	$=CH_2$
1a[a]	0.39	0.51, 0.67	—	—	—
2	0.15	0.19, 0.18	—	0.19	0.06*t*, 0.19*c*
3	0.03	0.27, 0.17	—	—	—
4	0.16	0.41, 0.16	—	0.04	0.03*t*, 0.12*c*
6	—	0.36, 0.65	0.28*m*, 0.34*p*	—	—
7	—	0.22, 0.17	0.03*m*, 0.05*p*	—	—

[a] Ligand **1b** did not give well-resolved signals on exposure to Ag^+.

Table 2. Chemical shift differences ($\Delta\delta$, ppm) of 1,3-alt thiacalix[4]crowns **5a–c** and **8** upon addition of $AgClO_4$ ([L]/[Ag^+]=1:1)



R^1 = Bu^t, R^2 = Pr (**5a**), allyl (**5b**)
R^1 = H, R^2 = Pr (**5c**)

8

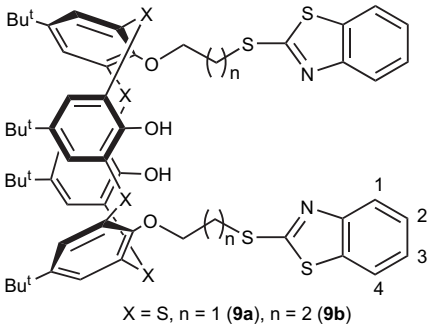
L	OCH_2-1	OCH_2-4	SCH_2-2,3	PyH
5a	0.53	0.16	0.84, 0.54	—
5b[a,b]	0.44	0.17	0.78, 0.56	—
5c	0.46	0.17	1.02, 0.63	—
8	0.47	—	0.79, 0.61	0.35*m*, 0.27*p*

[a] =CH −0.01.
[b] $=CH_2$ 0.10 (*cis*), 0.05 (*trans*).

The bulky *p*-Bu^t groups of 1,3-alt **5a**,**b** and **8** do not prevent the Ag^+ ion from accessing the crown ring, where it is bound analogously to the cone TCA ligands **1a** and **6**. The significant increase in the $\Delta\delta$ values of the SCH_2 protons of **5** and **8** (Table 2) as compared with those of cone **1**–**4** (Table 1) reveals that the 1,3-alt conformation is superior to the cone for binding, meanwhile the coordination power of the central oxygen and nitrogen atoms is kept.

The ^1H NMR titration of ligands **5a** with $AgClO_4$ demonstrates that the SCH_2-2,3 signals are gradually broadening and coalesce at ligand/Ag^+=0.5 ratio. Increasing further the Ag^+ ratio, the signal was enhanced reaching the final point at 1:1 stoichiometry. A similar phenomenon appears with the OCH_2-4 signal, while the PrO group, being far from the binding site, is lesser affected. The involvement

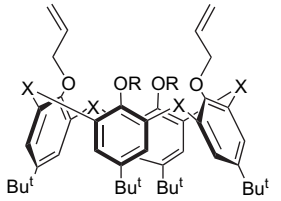
Table 3. Chemical shift differences ($\Delta\delta$, ppm) of open-chain thiacalix- and calix[4]arenes **9**–**11** upon addition of $AgClO_4$ ([L]/[Ag^+]=1:1, $CDCl_3$, 25 °C)



X = S, n = 1 (**9a**), n = 2 (**9b**)
X = CH_2, n = 1 (**10a**), n = 2 (**10b**)

L	BtH-1	BtH-2	BtH-3	BtH-4
9a	0.17	0.13	0.16	0.09
9b	0.42	0.12	0.13	0.06
10a	0.19	0.23	0.25	0.20
10b	0.35	0.25	0.21	0.18

Table 4. Chemical shift differences ($\Delta\delta$, ppm) of open-chain thiacalix- and calix[4]arenes **11**, **13**, **14**–**16** upon addition of $AgClO_4$ ([L]/[Ag^+]=1:1, $CDCl_3$, 25 °C)



X = S, R = H (**11**)
X = CH_2, R = H (**13**), allyl (**14**), Bn (**15**), Bu (**16**)

L	=CH	$=CH_2$ *cis*	$=CH_2$ *trans*	BnH
11	0.45	0.38	0.27	—
13	0.34	0.21	0.12	—
14	0.27 (0.26)[28]	0.48 (0.51)[28]	0.56 (0.62)[28]	—
15	0.11	0.02	0.27	0.28*o*,*p*, 0.09*m*
16	0.32	0.66	0.68	—

of two phenol-etheric oxygen atoms (OCH_2-1), as part of the crown ring, in ligation is possible but not sure, since the large downfield shifts of $ArOCH_2$ protons (0.53 ppm for **5a**) may originate from a complexation-induced conformational distortion of the calixarene skeleton (Fig. 1).

On the basis of data shown in Tables 1 and 2, we concluded that the 1,3-alt crowned TCA ligands **5** and **8** can sense the silver ion more efficiently than the respective cone TCA or CA counterparts **1**–**4**, **6** and **7**.

The largest upfield shifts of ligands **9** and **10** were measured for the benzothiazole aromatic protons (BtH) as shown in Table 3. In fact, the benzothiazole rings constitute the binding site, but in TCA compounds **9** they seem not to form a sandwich-like complex with Ag^+, only a two-point ligation occurs with the primary donor nitrogen atoms, where the cation is located in the plane of the aromatic rings. In this case the sulfur atoms do not play considerable role in complexation as reflected by the small $\Delta\delta$ values of BtH-4=0.06–0.09 ppm. The longer chain in ligand **9b** is more flexible than the shorter one in **9a**, thereby it provides a more favourable steric arrangement of the ligating site for binding, which

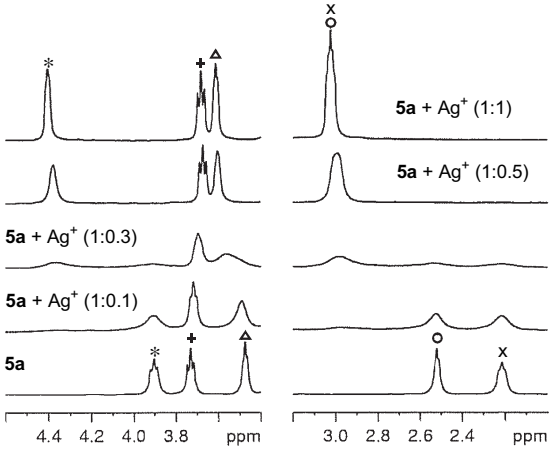


Figure 1. ^1H NMR titration of **5a** with $AgClO_4$ in $CDCl_3$ (labelled protons: SCH_2-2$^{\times}$, 3$^{\bigcirc}$; OCH_2-4$^{\triangle}$, (Pr)OCH_2^+, OCH_2-1*).

is shown by the larger downfield shift of the BtH-1 protons (0.42 vs 0.17 ppm). A similar result was obtained with the CA ligands **10a**,**b**, where again **10b** coordinates Ag^+ more strongly than **10a** (BtH-1 0.35 vs 0.19 ppm). It is notable, however, that in the latter ionophores the benzothiazole sulfur atom acts as an assistant donor besides the primary donor nitrogen providing a four-point ligation by the two benzothiazole rings (BtH-4 0.2, 0.18 ppm). Recent comprehensive ISE membrane experiments and X-ray studies with CA ligands **10** and related molecules[23] give strong evidences for this complexation pattern.

Diallyloxy-TCA ligand **11**, in contrast to the allyl derivatives of crowns **2**, **4** and **5b**, exhibits significant downfield shifts of the CH=CH_2 protons indicating a powerful π–cation interaction. Similar or larger $\Delta\delta$ values were measured for the CA ligands **13**, **14** and **16** containing two or four allyloxy groups. Diallyloxy-dibenzyloxy derivative **15**, however, behaves quite differently, here the Ag^+ ion is probably bound by the π-system of two parallel benzyl groups (*o*- and *p*-BnH 0.28 ppm) and the allyl groups are not involved in ligation. The measured small downfield shifts of the =CH and =CH_2 protons cannot stem from complexation, as only the trans proton of the terminal =CH_2 group is shifted due to the anisotropy caused by the ring current of benzyl groups (Table 4).

The behaviour of 1,3-alt tetraallyloxy-TCA **12** is worth discussing in detail. NMR titration did not indicate notable spectral changes referring to complexation up to 1 equiv $AgClO_4$. When **12** was exposed to a large quantity of Ag^+, however, the originally 1,3-alt conformation gradually changed and after 24 h, ca. 15% of 1,3-alt (free) and 85% of partial cone (complexed) ligands were detected (Fig. 2).

The structure elucidation using APT, COSY, HMQC, HMBC and ROESY methods was based on the unambiguous assignment of allyl protons (Table 5).

The partial cone conformer of **12**-Ag^+ complex contains three *syn* (**I** and **II**) and one *anti* (**III**) allyl groups. It would be reasonable to assume the involvement of the *syn* allyl groups in binding, but this process should be reflected by

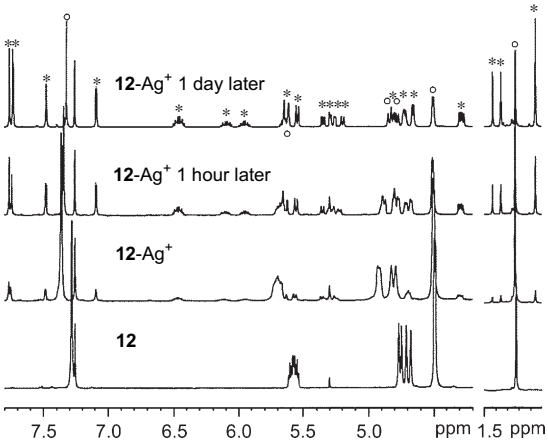


Figure 2. Time-dependent partial ^{1}H NMR spectra of **12** on exposure to 5 equiv Ag^+ in $CDCl_3$ (labelled protons: 1,3-alt-○ and paco* conformation; $CHCl_3$: 7.25 ppm).

Table 5. Allyl proton shifts of 1,3-alt **12**-Ag^+ complex

	OCH_2	=CH	=CH_2 *cis*	=CH_2 *trans*
I *syn*	4.70	5.99	5.38	5.29
II *syn*[a]	4.30, 4.77	6.49	5.55	5.62
III *anti*	4.62	6.05	5.14	5.18
12 (free)	4.49	5.58	4.76	4.69

[a] Two distal allyl groups.

downfield shifts. In contrast, the measured chemical shifts of the complex actually fell in the region of the uncomplexed allyl groups located in cone conformation. The *anti* (**III**) allyl group, however, shows significant downfield shifts ($\Delta\delta$ =CH 0.5, =CH_2 0.4 ppm) suggesting that the silver ion is probably located in the calixarene cavity surrounded by *syn* phenyl rings with two bridging sulfur donor atoms that can sufficiently stabilize the thiophil cation with the assistance of the *anti* allyl group (Fig. 3).

Since the 1,3-alt conformation of free **12** is stable, the binding process as a whole is assumed to take place through at least two consecutive equilibria. First, it starts with a weak coordination of Ag^+ of the 1,3-alt conformer followed by a slow conformational change to paco resulting in the thermodynamically more stable complex.

Simultaneously with the binding studies, ligands 1,3-alt **5a**, **8** and cone **14** (as reference[28])–**16** were selected for ISE screening experiments.[41] Though a poor binder, ligand **12** was also included to affirm (or to disprove) our expectation under quite different conditions. The potentiometric selectivity coefficients were determined in PVC membranes containing *o*NPOE plasticizer, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate lipophilic anion additive and the ionophores. We have found that ISEs based on π-coordinate ligands **14**–**16** are significantly less sensitive and selective towards a series of cations than crowns **5a** and **8**. Ligands **15** and **16** exhibited similar or slightly better characteristics of Ag^+ sensing than the reference **14**[28] as supported by the NMR binding studies. Ligand **12** proved to be inferior in respect of selectivity and responses affirming the result of NMR studies.

ISEs fabricated from **5a** and **8** were chosen for further evaluation and we established that both have excellent electroanalytical characteristics including high selectivities over a number of relevant cations (selected data are given

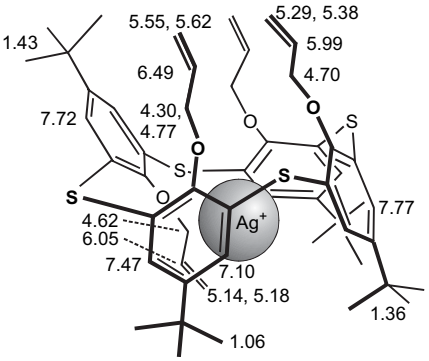


Figure 3. Proposed structure of **12**-Ag^+ complex based on ^{1}H NMR measurements.

Table 6. Potentiometric selectivity coefficients, log $K_{Ag/M}$

L	H^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cu^{2+}	Pb^{2+}
5a	−10.2	−10.3	−8.4	−11.4	−11.3	−11.1	−10.4
CAb[a]	−8.9	−9.0	−8.4	−10.1	−10.2	−9.0	−8.7

[a] So far the best calix[4]arene-based Ag^+ ISE containing 25,27-bis(2-methylthioethoxy)-*p*-Bu^t-CA sensing ligand.[16]

in Table 6). For practical use, **5a** is superior to **8** (due to proton interference of the basic nitrogen) and it has the lowest detection limit of sensing yet measured.[41,45]

3. Conclusions

A series of cone- and 1,3-alt thiacalix[4]arene-based ionophores comprised of distal *O*,*S*,*N*-crown-5 bridges and soft open-chained ligating functions, respectively, were synthesized and investigated as Ag^+ sensing ligands in comparison with known and new calix[4]arene counterparts. The complexation was detected in solution by ^{1}H NMR measurements and evaluated by comparing the characteristic $\Delta\delta$ values of groups involved in binding. In summary, we concluded that crowned 1,3-alt TCA ligands OS_2-**5** and S_2N-**8** exhibit much stronger binding with Ag^+ than the cone counterparts irrespective of the calixarene skeleton. Ligands 1,3-alt **5a**, **8**, **12** and cone **14** (as reference)–**16** were selected as promising candidates for potentiometric ISE membrane screening experiments. Comprehensive electroanalytical evaluation revealed[41] that the π-coordinate ligands were significantly less sensitive and selective over a series of cations than crowns **5a** and **8**. To the best of our knowledge, the ISE based on **5a** has the lowest detection limit in Ag^+ sensing that has been measured until now.

4. Experimental

4.1. General

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ at 500/125 MHz on a Bruker Avance DRX-500 spectrometer. FAB mass spectra were taken on a Finnigan MAT 8430 spectrometer (ion source temperature: 25 °C, matrix: *m*-nitrobenzyl alcohol, gas: xenon, accelerating voltage: 9 kV). Precoated silica gel plates (Merck 60 F_{254}) were used for analytical TLC and Kieselgel 60 for column chromatography. All chemicals were of reagent grade and used without further purification. DEAD[46] (Caution! DEAD may explode if exposed to shock, friction or heating) and ligands **1a**, **5a**, **8**,[40] **10a**,**b**,[23] **13**,[43] **14**–**16**[42] were synthesized as described in the literature.

4.2. General procedure for the synthesis of calix[4](O_3S_2-crown-5)ethers (1b, 3 and 7)

To the stirred mixture of thiacalix[4]arene (0.5 g, 1 mmol for **1b**) or *p*-*tert*-butylcalix[4]arene (0.65 g, 1 mmol for **3** and **7**), TPP (0.8 g, 3 mmol), 3,9-dioxa-6-thia-undecane-1,11-diol (for **1b** and **3**) or 2,6-bis(1-hydroxy-3-thiabutyl)pyridine (for **7**) (1.5 mmol each) in 20 ml toluene, a 40% toluene solution of DEAD (1.3 ml, 3 mmol) was added at room temperature and allowed to react for 1 h (**1b** and **3**) or refluxed (**7**). The solvent was then removed under reduced pressure and the residue was triturated with MeOH to free from by-products. Thereafter, the insoluble part was purified by chromatography on silica with hexane–EtOAc=8:2 eluent to give white solids.

4.2.1. Compound 1b. Yield: 95%, mp 127–129 °C; ^{1}H NMR δ 7.64 (d, 4H, *J*=7.5, Ar*H*), 7.54 (s, 4H, O*H*), 6.87 (d, 4H, *J*=7.5, Ar*H*), 6.84 (t, 2H, *J*=7.5, Ar*H*), 6.53 (t, 2H, *J*=7.5, Ar*H*), 4.71 (t, 4H, *J*=7.0, ArOCH_2), 3.80 (t, 4H, *J*=5.5, OCH_2), 3.34 (t, 4H, *J*=7.0, SCH_2), 2.99 (t, 4H, *J*=5.5, SCH_2); ^{13}C NMR δ 158.2, 158.0, 136.9, 135.2, 130.0, 125.5, 123.1, 119.8 (Ar), 74.8, 71.7 (O*C*H$_2$), 32.4, 34.2 (S*C*H$_2$); FABMS *m*/*z*: 688.2 [M+H]$^+$. Anal. Calcd for $C_{32}H_{30}O_5S_6$ (686.04): C, 55.95; H, 4.40; S, 28.01. Found: C, 55.69; H, 4.35; S, 27.67%.

4.2.2. Compound 3. Yield: 40%, mp 221–224 °C; ^{1}H NMR δ 7.07 (s, 4+2H, Ar*H*, O*H*), 6.76 (s, 2H, Ar*H*), 4.37 (d, 4H, *J*=13.0, ArCH_2Ar), 4.19 (t, 4H, *J*=6.3, OCH_2), 3.86 (t, 4H, *J*=5.8, OCH_2), 3.33 (t, 4H, *J*=6.3, SCH_2), 3.31 (d, 4H, *J*=13.0, ArCH_2Ar), 3.04 (t, 4H, *J*=5.8, SCH_2), 1.26 (s, 18H, C(CH_3)$_3$), 1.04 (s, 18H, C(CH_3)$_3$); ^{13}C NMR δ 150.8, 150.1, 147.1, 132.6, 128.1, 125.7, 125.3 (Ar), 76.8, 72.5 (O*C*H$_2$), 34.1, 34.0 (*C*(CH$_3$)$_3$), 33.1, 32.8 (S*C*H$_2$), 31.9, 31.2 (*C*H$_3$), 31.9 (Ar*C*H$_2$Ar); FABMS *m*/*z*: 841.2 [M+H]$^+$. Anal. Calcd for $C_{52}H_{70}O_5S_2$ (839.24): C, 74.42; H, 8.41; S, 7.62. Found: C, 74.08; H, 8.49; S, 7.48%.

4.2.3. Compound 7. Yield: 37%, mp 234–237 °C; ^{1}H NMR δ 7.89 (s, 2H, O*H*), 7.76 (t, 1H, *J*=7.5, Ar*H*), 7.39 (d, 2H, *J*=7.5, Ar*H*), 7.03 (s, 4H, Ar*H*), 7.02 (s, 4H, Ar*H*), 4.29 (d, 4H, *J*=13.0, ArCH_2Ar), 4.17 (t, 4H, *J*=7.5, OCH_2), 4.03 (s, 4H, SCH_2), 3.35 (d, 4H, *J*=13.0, ArCH_2Ar), 3.26 (t, 4H, *J*=7.5, SCH_2), 1.19 (s, 18H, C(CH_3)$_3$), 1.06 (s, 18H, C(CH_3)$_3$); ^{13}C NMR δ 158.7, 150.6, 150.1, 147.4, 141.9, 138.1, 133.3, 128.1, 126.0, 125.4, 121.5 (Ar), 75.7 (O*C*H$_2$), 38.8, 30.8 (S*C*H$_2$), 34.3, 34.0 (*C*(CH$_3$)$_3$), 32.5 (Ar*C*H$_2$Ar), 31.9, 31.3 (*C*H$_3$); FABMS *m*/*z*: 874.2 [M+H]$^+$. Anal. Calcd for $C_{55}H_{69}NO_4S_2$ (872.27): C, 75.73; H, 7.97; S, 7.34. Found: C, 75.28; H, 8.03; S, 7.27%.

4.3. General procedure for the cone-selective allylation of 1b and 3

The same method was used as described for the PTC alkylation of calix[4]arenes.[42] Thus, ligands **1b** or **3** (0.5 mmol), allylbromide (2.5 mmol), 50% aqueous NaOH (1 ml) and TBAB catalyst (0.05 g) in toluene (10 ml) were refluxed for 6 h under vigorous stirring to give **2** and **4** as white solids (purified by chromatography on silica with hexane–EtOAc=8:2 eluent).

4.3.1. Compound 2. Yield: 52%, mp 147–148 °C; ^{1}H NMR δ 7.62 (d, 4H, *J*=8.0, Ar*H*), 7.04 (t, 2H, *J*=8.0, Ar*H*), 6.34 (t, 2H, Ar*H*), 6.32 (d, 4H, Ar*H*), 6.17 (m, 2H, =C*H*), 5.42 (d, 2H, *J*=17.0, =CH_2 *trans*), 5.28 (d, 2H, *J*=10.0, =CH$_2$ *cis*), 4.51 (t, 4H, *J*=7.5, ArOCH_2), 4.44 (d, 4H, *J*=5.5, OCH_2), 3.78 (t, 4H, *J*=6.0, OCH_2), 3.05 (t, 4H, *J*=7.5, SCH_2), 2.84 (t, 4H, *J*=6.0, SCH_2); ^{13}C NMR δ 160.6, 157.3, 136.8, 133.5, 132.1, 131.6, 124.8, 123.3 (Ar), 133.9, 118.7 (allyl), 77.6, 72.9, 71.2 (O*C*H$_2$), 32.0, 30.7 (S*C*H$_2$); FABMS *m*/*z*: 768 [M+H]$^+$. Anal. Calcd for $C_{38}H_{38}O_5S_6$

(766.10): C, 59.50; H, 4.99; S, 25.08. Found: C, 59.28; H, 5.03; S, 24.89%.

4.3.2. Compound 4. Yield: 78%, mp 214–217 °C; ^{1}H NMR δ 7.12 (s, 4H, Ar*H*), 6.45 (s, 4H, Ar*H*), 6.35 (m, 2H, =C*H*), 5.42 (d, 2H, *J*=17.0, =CH_2 *trans*), 5.32 (d, 2H, *J*=10.0, =CH_2 *cis*), 4.37 (d, 4H, *J*=12.5, ArCH_2Ar), 4.26 (d, 4H, *J*=6.5, OCH_2), 4.21 (t, 4H, *J*=6.5, ArOCH_2), 3.81 (t, 4H, *J*=6.0, OCH_2), 3.27 (t, 4H, *J*=6.5, SCH_2), 3.15 (d, 4H, *J*=12.5, ArCH_2Ar), 2.83 (t, 4H, *J*=6.0, SCH_2), 1.34 (s, 18H, C(CH_3)$_3$), 0.81 (s, 18H, C(CH_3)$_3$); ^{13}C NMR δ 153.7, 151.9, 145.3, 144.4, 135.6, 131.8, 125.5, 124.5 (Ar), 135.2, 118.3 (allyl), 77.0, 73.8, 71.9 (OCH_2), 34.1, 33.6 (*C*(CH$_3$)$_3$), 31.7, 31.1 (*C*H$_3$), 31.5 (ArCH_2Ar), 31.4, 31.3 (SCH_2); FABMS *m*/*z*: 921.4 [M+H]$^+$. Anal. Calcd for $C_{58}H_{78}O_5S_2$ (919.37): C, 75.77; H, 8.55; S, 6.96. Found: C, 75.31; H, 8.62; S, 6.88%.

4.4. General procedure for the 1,3-alt-selective alkylation of 1b

The same method was used as described for the preparation of **5a**.[40] Thus, **1b** (1 mmol) was treated with allylbromide or PrI (5 mmol), Cs_2CO_3 (8 mmol) in MeCN (20 ml) under reflux for 12 h to give **5b**,**c** as white solids.

4.4.1. Compound 5b. Yield: 93%, mp 280–282 °C; ^{1}H NMR δ 7.34 (s, 4H, Ar*H*), 7.25 (s, 4H, Ar*H*), 5.39 (m, 2H, =C*H*), 4.66 (dd, 2H, *J*=10.5, 1.5, =CH_2 *cis*), 4.62 (dd, 2H, *J*=12.5, 1.5, =CH_2 *trans*), 4.39 (d, 4H, *J*=3.5, OCH_2), 3.95 (t, 4H, *J*=8.0, ArOCH_2), 3.47 (t, 4H, *J*=5.0, OCH_2), 2.50 (t, 4H, *J*=5.0, SCH_2), 2.29 (t, 4H, *J*=7.5, SCH_2), 1.35 (s, 18H, C(CH_3)$_3$), 1.22 (s, 18H, C(CH_3)$_3$); ^{13}C NMR δ 156.8, 156.3, 146.5, 146.0, 133.8, 128.7, 128.5, 127.5, 126.6 (Ar), 133.8, 115.6 (allyl), 74.1, 69.2, 68.2 (OCH_2), 34.6, 34.4 (*C*(CH$_3$)$_3$), 33.8, 33.3 (SCH_2), 31.7, 31.5 (C(*C*H$_3$)$_3$); FABMS *m*/*z*: 992.4 [M+H]$^+$. Anal. Calcd for $C_{54}H_{70}O_5S_6$ (990.35): C, 65.41; H, 7.12; S, 19.40. Found: C, 65.19; H, 7.06; S, 19.23%.

4.4.2. Compound 5c. Yield: 60%, mp 199–200 °C; ^{1}H NMR δ 7.42 (d, 4H, *J*=7.5, Ar*H*), 7.31 (d, 4H, *J*=8.0, Ar*H*), 6.93 (t, 2H, *J*=8.0, Ar*H*), 6.89 (t, 2H, *J*=7.5, Ar*H*), 3.94 (t, 4H, *J*=8.5, ArOCH_2), 3.86 (t, 4H, *J*=7.0, ArOCH_2), 3.62 (t, 4H, *J*=5.0, OCH_2), 2.62 (t, 4H, *J*=5.0, SCH_2), 2.15 (t, 4H, *J*=8.0, SCH_2), 1.14 (m, 4H, CH_2), 0.59 (t, 6H, *J*=7.0, CH_3); ^{13}C NMR δ 160.1, 158.6, 131.3, 130.6, 128.9, 128.8, 123.5, 123.4 (Ar), 73.7, 70.7, 67.7 (OCH_2), 33.6, 32.5 (SCH_2), 22.5 (CH_2), 10.3 (CH_3); FABMS *m*/*z*: 771.14 [M+H]$^+$. Anal. Calcd for $C_{38}H_{42}O_5S_6$ (770.14): C, 59.19; H, 5.49; S, 24.95. Found: C, 59.28; H, 5.42; S, 24.69%.

4.5. Synthesis of 25,27-bis[1,3-benzothiazole-2-(1-thioalkoxy)]-*p*-Bu^{t}TCA (9a,b)

Ligand **9a** was prepared according to literature analogy by the $NaHCO_3$ promoted alkylation of 2-mercapto-1,3-benzothiazole with 25,27-bis(2-bromoethoxy)-*p*-Bu^{t}TCA[38] changing the solvent from aqueous THF[23] to boiling MeCN. Ligand **9b** was synthesized by the Mitsunobu alkylation of *p*-Bu^{t}TCA (0.72 g, 1 mmol) with 2-(3-hydroxypropylthio)-1,3-benzothiazole (0.56 g, 2.5 mmol) using TPP/DEAD (3 mmol) coupling agents following the procedure described in Section 4.2. The crude product was purified by recrystallization from EtOAc–hexane.

4.5.1. Compound 9a. Yield: 52%, mp 148–150 °C; ^{1}H NMR δ 7.82 (d, 2H, *J*=8.0, Ar*H*), 7.79 (s, 2H, O*H*), 7.68 (d, 2H, *J*=8.0, Ar*H*), 7.66 (s, 4H, Ar*H*), 7.36 (t, 2H, *J*=8.0, Ar*H*), 7.24 (t, 2H, *J*=8.0, Ar*H*), 6.95 (s, 4H, Ar*H*), 4.95 (t, 4H, *J*=6.0, ArOCH_2), 4.02 (t, 4H, *J*=6.0, SCH_2), 1.34 (s, 18H, C(CH_3)$_3$), 0.79 (s, 18H, C(CH_3)$_3$); ^{13}C NMR δ 166.6, 156.0, 155.9, 153.4, 148.4, 143.0, 135.7, 134.6, 133.0, 129.2, 126.1, 124.3, 122.3, 121.8, 121.1 (Ar), 73.3 (OCH_2), 34.4, 34.2 (*C*(CH$_3$)$_3$), 33.4 (SCH_2), 31.7, 31.0 (C(*C*H$_3$)$_3$); FABMS *m*/*z*: 1108.2 [M+H]$^+$. Anal. Calcd for $C_{58}H_{62}N_2O_4S_8$ (1106.25): C, 62.89; H, 5.64; N, 2.53; S, 23.16. Found: C, 62.57; H, 5.70; N, 2.49; S, 23.05%.

4.5.2. Compound 9b. Yield: 63%, mp 154–156 °C; ^{1}H NMR δ 7.90 (s, 2H, O*H*), 7.83 (d, 2H, *J*=8.0, Ar*H*), 7.68 (d, 2H, *J*=8.0, Ar*H*), 7.66 (s, 4H, Ar*H*), 7.34 (t, 2H, *J*=8.0, Ar*H*), 7.22 (t, 2H, *J*=8.0, Ar*H*), 7.00 (s, 4H, Ar*H*), 4.67 (t, 4H, *J*=6.5, ArOCH_2), 3.76 (t, 4H, *J*=6.5, SCH_2), 2.53 (quint., 4H, *J*=6.5, CH_2), 1.34 (s, 18H, C(CH_3)$_3$), 0.82 (s, 18H, C(CH_3)$_3$); ^{13}C NMR δ 167.3, 156.3, 156.0, 153.6, 148.4, 143.0, 135.5, 134.6, 133.3, 129.1, 126.1, 124.2, 122.2, 121.8, 121.1 (Ar), 74.0 (OCH_2), 34.4, 34.3 (*C*(CH$_3$)$_3$), 31.7, 31.0 (C(*C*H$_3$)$_3$), 30.7 (SCH_2), 30.3 (CH_2); FABMS *m*/*z*: 1136.3 [M+H]$^+$. Anal. Calcd for $C_{60}H_{66}N_2O_4S_8$ (1134.28): C, 63.45; H, 5.86; N, 2.47; O, 5.64; S, 22.59. Found: C, 63.11; H, 5.83; N, 2.43; S, 22.34%.

4.6. Synthesis of 25,27-diallyloxy- and 25,26,27,28-tetraallyloxy-*p*-Bu^{t}TCA (11 and 12)

To the stirred mixture of *p*-*tert*-butylthiacalix[4]arene (0.72 g, 1 mmol), TPP (0.8 g, 3 mmol for **11** and 1.6 g, 6 mmol for **12**), allylalcohol (0.13 g, 2.2 mmol for **11** and 0.58 g, 10 mmol for **12**) in 20 ml toluene, a 40% toluene solution of DEAD (1.3 ml, 3 mmol for **11** and 2.6 ml, 6 mmol for **12**) was added at room temperature and allowed to react for 0.5 h (**11**) or refluxed for 12 h (**12**). The solvent was then removed under reduced pressure and the residue was triturated with hot acetone (20 ml) and filtered to give white solid in essentially pure form.

4.6.1. Compound 11. Yield: 85%, mp 222–224 °C; ^{1}H NMR δ 7.87 (s, 2H, O*H*), 7.66 (s, 4H, Ar*H*), 6.97 (s, 4H, Ar*H*), 6.32 (m, 2H, =C*H*), 5.55 (d, 2H, *J*=17.0, =CH_2 *trans*), 5.37 (d, 2H, *J*=10.0, =CH_2 *cis*), 5.01 (d, 4H, *J*=5.5, OCH_2), 1.33 (s, 36H, C(CH_3)$_3$), 0.80 (s, 36H, C(CH_3)$_3$); ^{13}C NMR δ 156.2, 156.0, 148.2, 142.8, 134.6, 133.0, 129.3, 122.3 (Ar), 133.6, 118.9 (allyl), 76.6 (OCH_2), 34.4, 34.2 (*C*(CH$_3$)$_3$), 31.8, 31.0 (C(*C*H$_3$)$_3$); FABMS *m*/*z* (%): 801 [M+H]$^+$. Anal. Calcd for $C_{46}H_{56}O_4S_4$ (800.31): C, 68.96; H, 7.05; S, 16.01. Found: C, 69.16; H, 6.98; S, 16.18%.

4.6.2. Compound 12. Yield: 90%, mp 245–247 °C; ^{1}H NMR δ 7.28 (s, 8H, Ar*H*), 5.58 (m, 4H, =C*H*), 4.76 (d, 2H, *J*=10.5, =CH_2 *cis*), 4.69 (d, 2H, *J*=17.5, =CH_2 *trans*), 4.49 (d, 2H, *J*=4.0, OCH_2), 1.22 (s, 36H, C(CH_3)$_3$); ^{13}C NMR δ 156.9, 145.8, 129.4, 128.5 (Ar), 133.9, 115.6 (allyl), 69.4 (OCH_2), 34.4 (*C*(CH$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$); FABMS *m*/*z* (%): 882.4 [M+H]$^+$. Anal. Calcd for $C_{52}H_{64}O_4S_4$ (880.37): C,

70.84; H, 7.32; S, 14.55. Found: C, 70.47; H, 7.36; S, 14.39%.

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