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Synthesis of polyfunctional phosphorus-containing calixarenes in cycloaddition reactions of azides to alkynes

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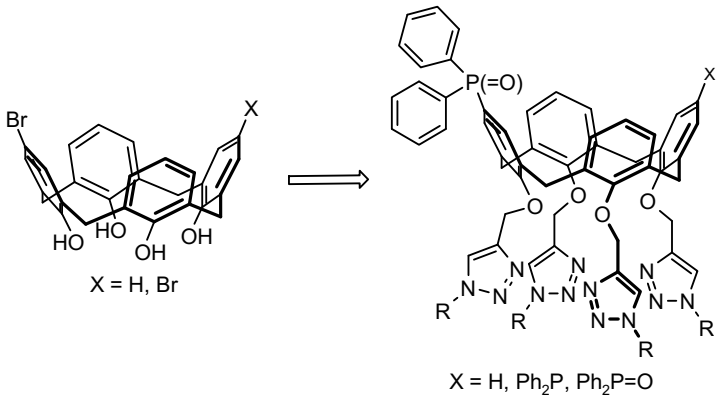


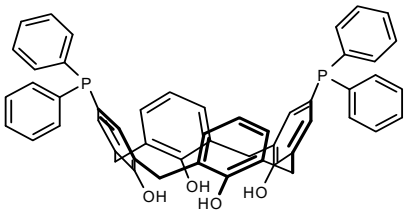
Mono- and dibromo derivatives of calix[4]arene were used for the first time in phosphorylation, alkylation, and azide-alkyne cycloaddition sequence in order to synthesize polyfunctional macrocycles containing phosphine oxide groups at the upper rim and 1,4-disubstituted triazole rings at the lower rim. The effect of reaction conditions onto the selectivity of the lower-rim alkylation of phosphorus-containing calixarenes and the ratio of spatial isomers in the exaustively alkylated products was studied. The reduction of phosphine oxide groups and modification of functional groups in the triazole rings were used for the synthesis of bulky hydrophilic phosphine-containing ligands. The catalytic activity of *in situ* obtained rhodium complexes of phosphine-containing calixarenes was preliminarily studied by 1-octene hydroformylation in ethanol.

Keywords: calixarenes, triazoles, click chemistry, hydroformylation, phosphines.

The rapid progress in the chemistry of calixarenes and related compounds over the past 30 years has led to the development of effective procedures for the functionalization of these macrocycles by selective and exhaustive modifications of the phenol hydroxy groups (the lower rim) and/or activated *para* positions of the phenolic moieties (the upper rim).[1] Thereby, calixarenes can now be considered as convenient scaffolds enabling the combination and spatial pre-organization of various functional groups and recognition units in one molecule, and, accordingly, for the design and synthesis of effective and selective receptor molecules.

Among the known calixarene derivatives, compounds containing phosphine substituents at the upper rim have a great potential for practical applications.[2] Thus, for example, nickel complexes of calixarenes **1**, **2** (Fig. 1) and their analogs containing alkyl groups at the lower rim have been found to be active catalysts of ethene or propene oligomerization reactions[3] and cross-coupling reactions (in various modifications).[4] Rhodium complexes of such calixarenes are effective in catalytic hydrogenation of linear and cyclic alkenes,[5] as well as in alkene hydroformylation reactions.[6] At the same time, the development of methods which allow the introduction of functional groups not directly participating in the formation of catalytically active complexes to the lower rim of compounds **1** and **2** would give an opportunity for the tuning of physicochemical characteristics of the catalysts and, in particular, for immobilization of the catalysts on extended surfaces.

The efficient building-block approach toward the synthesis of polyfunctional organic molecules is the Cu(I)-ca-



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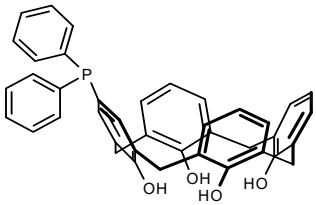

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Figure 1. Phosphorus-containing calixarenes **1** and **2**.

talyzed cycloaddition of azides to terminal alkynes (CuAAC), leading to the formation of 1,4-disubstituted triazoles. The data published so far indicate that the CuAAC reaction has features required by a universal method for the modification of polyfunctional molecules: high selectivity, tolerance to many functional groups and solvents of various nature.[7] CuAAC reactions have been used for the lower-rim modifications of calixarenes.[8] For example, we recently demonstrated that polyfunctional azides can be used for obtaining heteroditopic receptors based on calixarenes .[9] Besides that, it was found that the addition of first azide molecule to calixarenes containing between two, three, or four acetylene groups at the lower rim can initiate a cascade of sequential CuAAC reactions involving all propargyl groups available for the azide addition.[10]

In the current work, we studied the possibility of using CuAAC reactions as the key and universal step for the modification of phosphorus-containing calixarenes. A specific task of this study was also the creation of bulky ligands with good solubility in polar media, which could be used for rhodium-catalyzed hydroformylation of alkenes on membrane-separable catalysts.

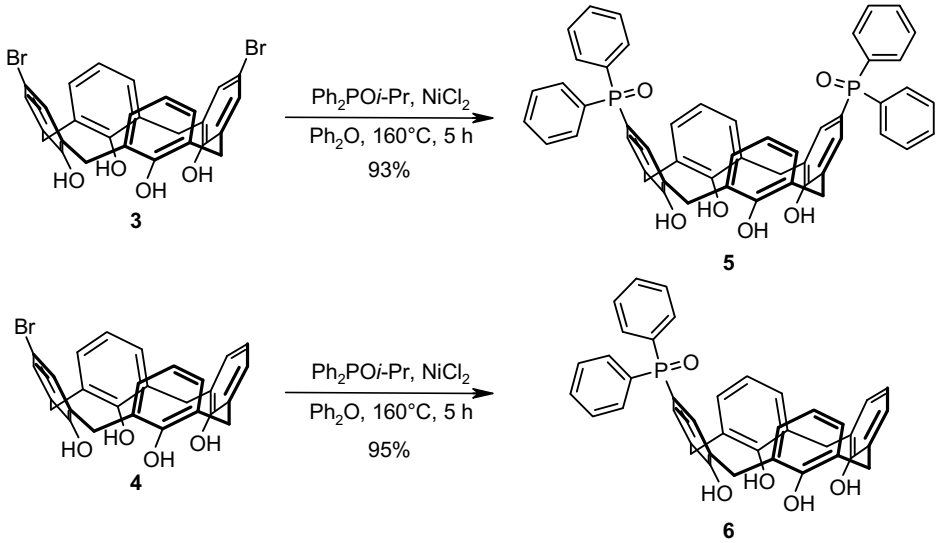
Direct modification of the lower rim in compounds **1** and **2** by alkylation reactions seems possible only with simultaneous quaternization of phosphine groups, leading to a loss of coordinating ability of P(III) atoms. Still, the synthesis of acetylene-containing phosphines on the basis of compounds **1** and **2** is theoretically possible by an alternative chain of transformations, but the introduction of such phosphines in CuAAC reaction would invariably lead to their oxidation to P(V) derivatives upon interaction with azides (the Staudinger reaction). For this reason, in this work we studied a different approach, including the transformations of calix[4]arenes containing a P=O group in alkylation and CuAAC reactions, followed by reduction of phosphine oxides to phosphines at the final steps of the synthesis.

Ni^{2+}-catalyzed Arbuzov reaction was used for introducing phosphorus-containing substituents at the upper rim of calixarenes.[11] The available bromides **3**[12] and **4**[13] were reacted with *O*-isopropyl diphenyl phosphinite in the presence of anhydrous $NiCl_2$, while heating in diphenyl ether. As a result, the phosphine oxides **5** and **6** were obtained in high yields (Scheme 1). Compound **6** was obtained for the first time, while the previously published procedure for the synthesis of calixarene **5** relied on a significantly larger number of steps.[5]

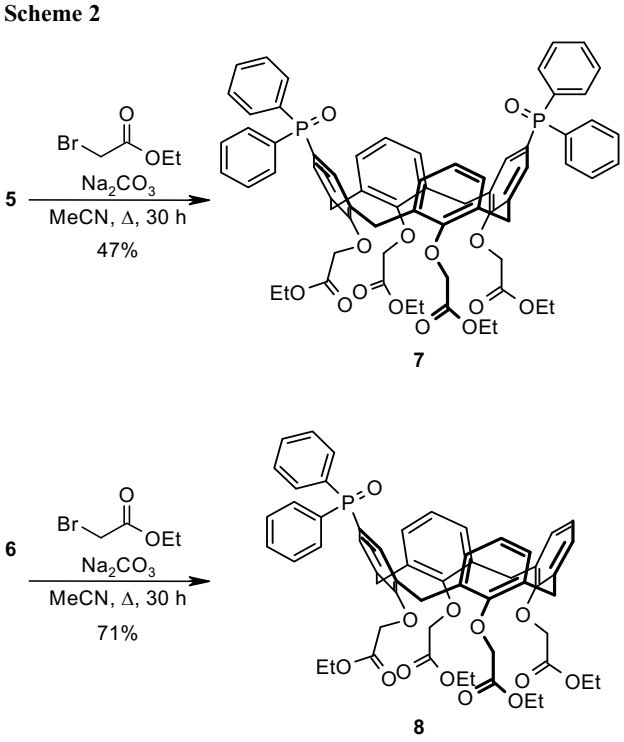
No literature references were found on the chemical modification of free hydroxy groups at the lower rim of calix[4]arenes containing diphenylphosphine oxide substituents at the upper rim. For this reason, in this work we performed optimization of reaction conditions for exhaustive alkylation of calixarenes **5** and **6** at the lower rim. The phosphine oxides **5** and **6** were used in reactions with an excess of ethyl 2-bromoacetate in the presence of Na_2CO_3, while refluxing in acetonitrile. As a result, the ester derivatives **7** and **8** fixed in the cone conformation were obtained for the first time (Scheme 2).

Exhaustive alkylation of compound **5** with the less reactive propargyl bromide could not be accomplished under the same conditions: mainly the starting calixarene was recovered from the reaction mixture, containing a

Scheme 1



Scheme 2



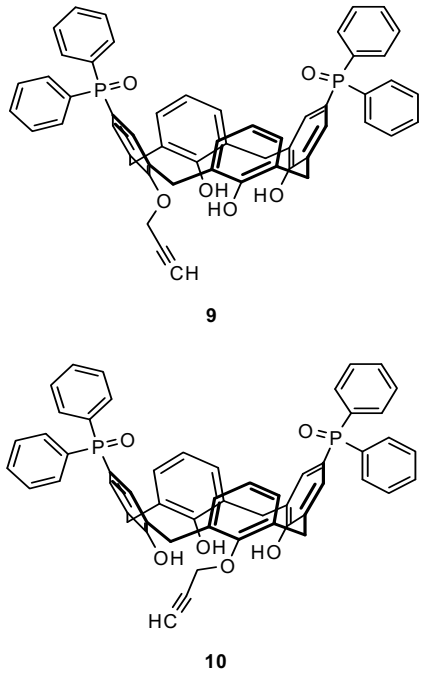


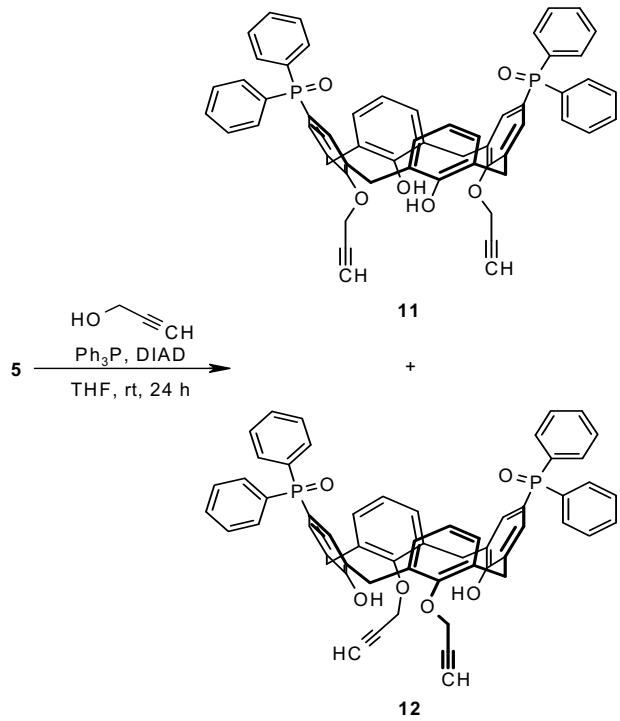
Figure 2. Monopropargyl ethers **9** and **10**, formed by reactions of calixarene **5** and propargyl bromide in the presence of potassium carbonate.

small amount of the monoalkylated products. When sodium carbonate was replaced with a stronger base, potassium carbonate, a complex mixture of products was obtained that did not contain the starting calixarene and gave ^{1}H NMR spectrum that allowed to identify only the isomeric monopropargyl ethers **9** and **10** (Fig. 2). The heating of calixarene **5** in a mixture with propargyl bromide and cesium carbonate in DMF led to the formation of a complex mixture of compounds, which was analyzed using ^{1}H NMR spectrum, but even the completeness of alkylation at the lower rim of calixarene could not be determined.

The Mitsunobu reaction, commonly used for the synthesis of calix[4]arenes distally disubstituted at the lower rim,[14] was also tested to get the dipropargyl ethers of compound **5**. However, despite the presence of bulky substituents both in the starting calixarene and in the reagent, the reaction of compound **5** with propargyl alcohol, triphenylphosphine, and diisopropylazodicarboxylate (DIAD) proceeded non-selectively, giving a mixture of isomeric ethers **11** and **12** according to ^{1}H NMR data, which could not be isolated and characterized as individual samples (Scheme 3).

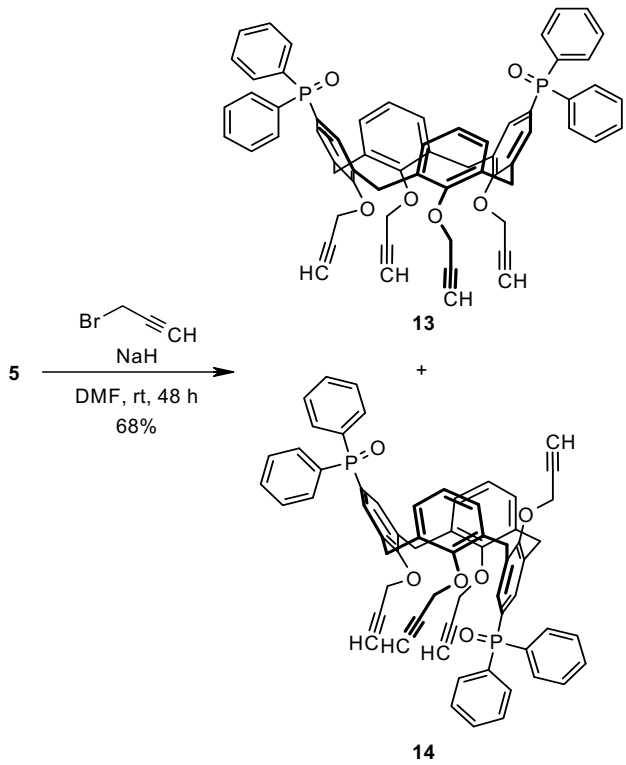
The complex mixture of compounds, including the tetrapropargyl ethers **13** and **14** fixed in cone and partial cone conformations, respectively, was obtained by alkylation of calixarene **5** with propargyl bromide in a DMSO–H_2O mixture, using NaOH as a base. Switching to another strong base, NaH, and performing the synthesis in THF with added DMF (5%)[15] allowed to obtain the target ether **13** as the main calixarene product of the reaction, albeit with a very low conversion of the starting material **5**. The use of neat DMF without adding other solvents allowed to achieve complete alkylation of the lower rim of

Scheme 3



calixarene **5** and to isolate a mixture of calixarenes **13** and **14** in 4:1 molar ratio and 68% overall yield. This mixture could not be separated either by crystallization from various solvents or by using column chromatography (Scheme 4). The ratio of compounds **13** and **14** in the mixture did not change after prolonged refluxing of its

Scheme 4



solution in toluene or during heating of a $CDCl_3$ solution while acquiring ^1H NMR spectrum, pointing to the conformational stability of the propargyl ethers. NMR spectra of a mixture of compounds **13** and **14** are given in Figure 3.

The structure of calixarene **13** fixed in the cone conformation was evidenced, for example, by the presence of a pair of ^1H NMR doublets due to $ArCH_2Ar$ protons at 4.59 and 3.19 ppm, two doublets (5.03 and 4.51 ppm), and two triplets (2.49 and 2.44 ppm) of the protons from two

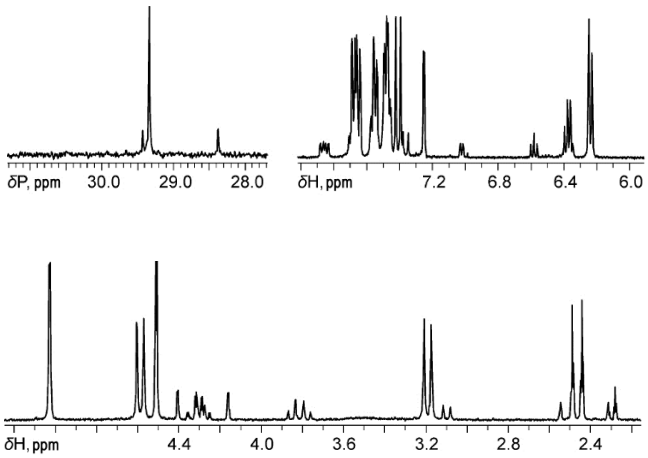
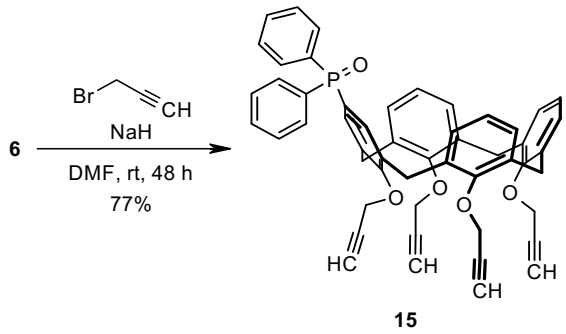


Figure 3. ^{31}P NMR (162 MHz) and ^1H NMR spectra (400 MHz) of a mixture of exhaustively propargylated calixarenes **13** and **14**, acquired in $CDCl_3$ at 25°C.

non-equivalent propargyl groups, as well as a single ^{31}P NMR signal at 29.3 ppm. A set of less intense ^1H NMR signals could correspond to the structures of two different tetraethers fixed in a partial cone conformation. However, there was not one, but rather two ^{31}P NMR signals of the minor isomer at 29.4 and 28.4 ppm, allowing to unequivocally assign them to the structure of compound **14** with alternating positions of two bulky substituents at the upper rim.

It is likely that the steric repulsion between substituents in calixarene **5** had the key role in facilitating the formation of the isomer with partial cone conformation as the minor product during the synthesis of compound **13** (in the case of the ester derivative **7**, the additional stabilization of the isomer with cone conformation can be explained by the interaction of Na^+ ions with ester groups). This hypothesis was confirmed by the results obtained during exhaustive propargylation of calixarene **6**, which contained only a single phosphine oxide substituent at the upper rim: the reaction of compound **6** with propargyl bromide in DMF in the presence of sodium hydride gave only the ether **15**, fixed in the cone conformation, while no formation of other isomers was detected (Scheme 5).

Scheme 5

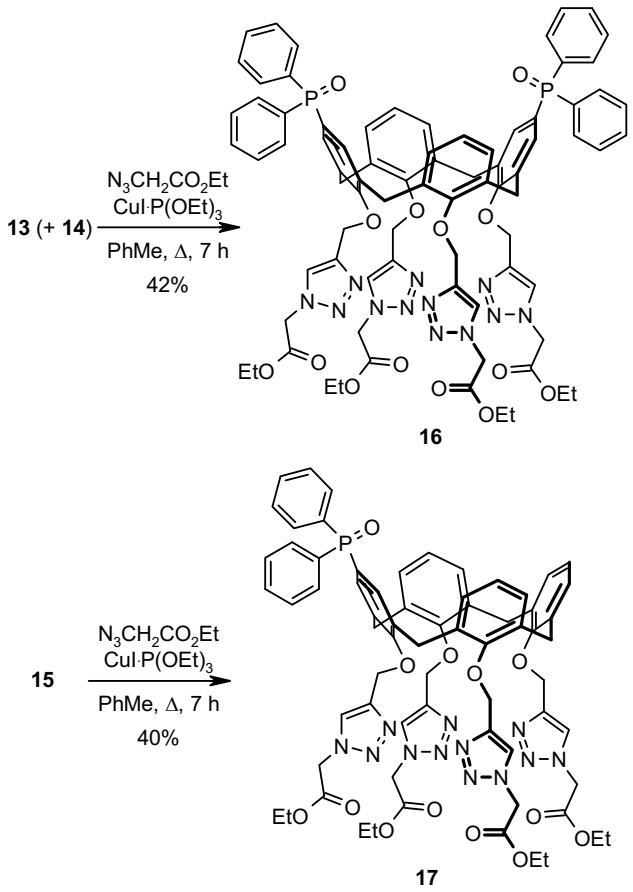


The propargylated calixarenes **13**–**15** were reacted with azides in the presence of $CuI{\cdot}P(OEt)_3$ by heating in toluene. In a reaction with ethyl 2-azidoacetate, the calixarene **15** was converted into compound **17** containing four ester groups in triazole substituents (Scheme 6). When a mixture of isomers **13** and **14** was used in a similar reaction, the expected mixture of triazole-containing calixarenes (cone and partial cone isomers) was obtained, from which the individual compound **16** was successfully isolated by column chromatography.

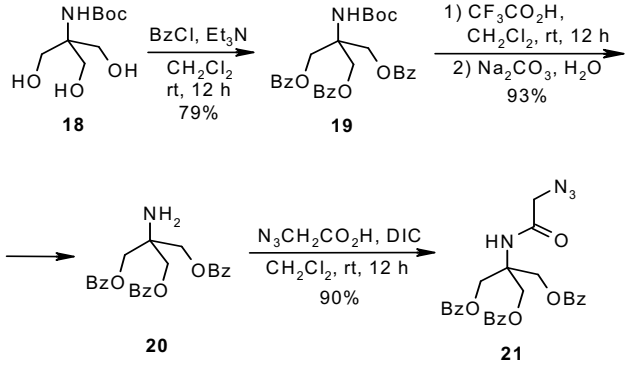
The polyfunctional azide **21** containing an *O*-benzoylated tris(hydroxymethyl)aminomethane fragment in its structure was also used as a component of CuAAC reactions. The synthesis of compound **21** was achieved by benzoylation of the *N*-protected tris(hydroxymethyl)-aminomethane **18**,[16] followed by removal of the protecting group from compound **19** and *N*-acylation of the amine **20** with azidoacetic acid that was activated with diisopropylcarbodiimide (DIC) (Scheme 7).

Despite the significantly stronger steric hindrance in the azide **21** compared to ethyl 2-azidoacetate, CuAAC reactions with the participation of this compound were successfully used for the synthesis of triazole-containing

Scheme 6



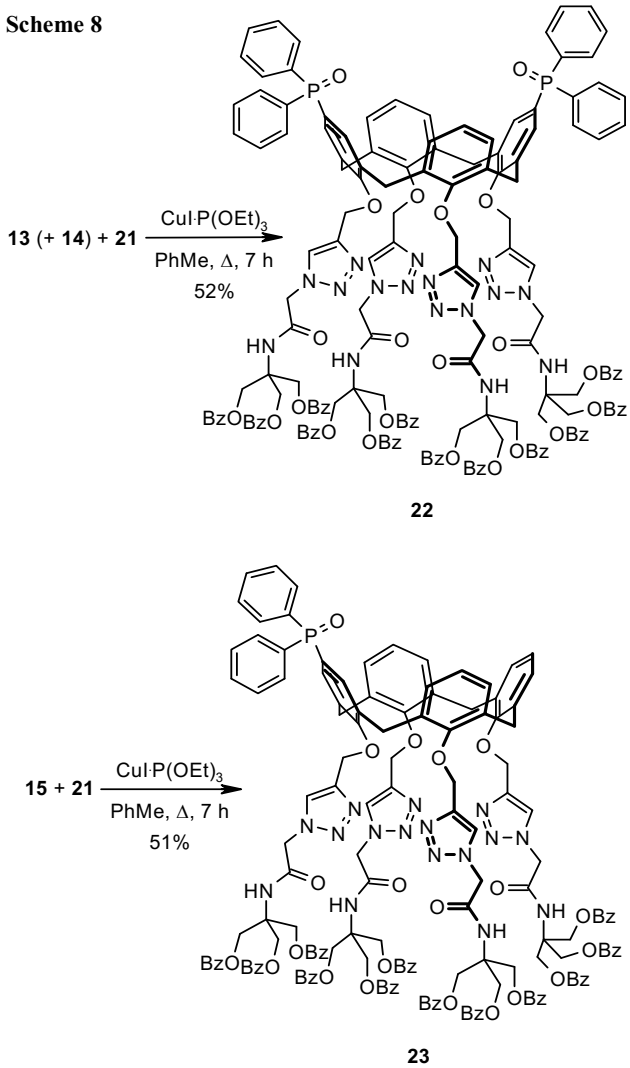
Scheme 7



calixarenes **22** and **23** (Scheme 8). Thus, the reaction of calixarene **15** and azide **21** was used to obtain compound **23**, fixed in the cone conformation and containing one diphenylphosphine oxide substituent at the upper rim, as well as four triazole substituents containing bulky groups at the lower rim. The mixture of isomeric triazole-containing calixarenes, formed in the reaction of propargyl ethers **13** and **14**, was successfully separated by using column chromatography, allowing to obtain of the calixarene **22** in a good yield .

The signals in ^{1}H NMR spectra of calixarenes **22** and **23** were broadened, but their positions and intensities corresponded to the proposed structures of these

Scheme 8



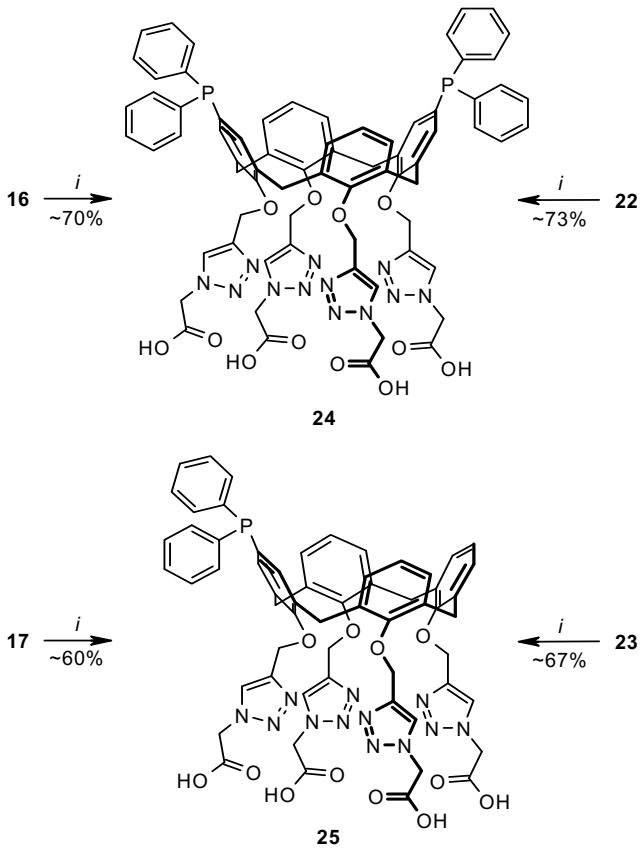
compounds. In particular, in ^{1}H NMR spectrum of compound **22**, the methylene bridges of the calixarene scaffold gave two broadened doublets, while ^{1}H NMR spectrum of compound **23** contained two pairs of doublets, pointing to *syn* orientation of all four aromatic rings of the calixarene macrocycle (cone isomers) in both cases. ^{13}C NMR spectra of compounds **22** and **23** provided little information – the majority of signals in these spectra were significantly broadened and/or substantially overlapped, that was likely caused by the slow conformational oscillations of the bulky substituents. The phosphine oxide groups gave ^{31}P NMR signals at 29.6 and 28.7 ppm in the case of compounds **22** and **23**, respectively. The mass spectral data also confirmed the structures of these compounds.

To get the phosphines capable of forming rhodium complexes, the calixarene phosphine oxides **16**, **17**, **22**, and **23** were reduced by phenylsilane upon prolonged refluxing under inert atmosphere (Scheme 9). The reaction mixtures after workup showed ^{1}H NMR signals corresponding to calixarene macrocycles, as well as triazole, ether, ester, and amide functional groups. The phosphorus atoms gave ^{31}P NMR signals between –5 and –7 ppm and the impurities gave minor signals (~10%) between

+28 and +30 ppm, indicating nearly complete reduction of phosphine oxide groups to the respective phosphines.

The obtained crude phosphines were subjected to hydrolysis reactions. According to the developed synthetic strategy, the ester hydrolysis reactions were expected to produce calixarenes containing one or two diphenylphosphine moieties at the upper rim and polar carboxy or hydroxymethyl groups as part of the substituents at the lower rim. The treatment of calixarenes **16** and **17** with potassium hydroxide in aqueous alcohol solution, followed by acidification allowed to successfully synthesize the tetracarboxylic acids **24** and **25** (Scheme 9). It was unexpectedly observed that even in the absence of heating the calixarenes **22** and **23** were hydrolyzed not only at the ester groups, but also at the amide bonds, therefore the acids **24** and **25** were obtained also in this case. Model reactions using non-reduced calixarenes **22** and **23** confirmed the low stability of the amide bond toward alkaline hydrolysis. Thus, the search of conditions suitable for selective removal of benzoyl protecting groups from *O*-benzoylated tris-(hydroxymethyl)methylamides required further experiments.

Scheme 9



i: 1) $PhSiH_3$, PhH, Δ, 48 h; 2) KOH, H_2O, THF, rt, 15 h; 3) HCl, H_2O

Calixarenes **24** and **25** were readily soluble in alcohols. ^{1}H NMR spectra acquired for their solutions in CD_3OD contained sets of signals corresponding to the structures of calixarenes **24** and **25** (data of ^{1}H–^{1}H COSY spectra were used for assigning the signals), as well as signals corresponding to the oxidized forms. ^{31}P NMR spectra contained characteristic phosphine signals at –6.6 and –4.8 ppm (for compounds **24** and **25**, respectively) along with the signals of the oxidized forms at ~30 ppm, but the content of the oxidized forms did not exceed 20%.

The possibility of using compounds **24** and **25** as ligands for alkene hydroformylation catalyzed by rhodium salts in ethanol medium was evaluated by performing hydroformylation of 1-octene as a model substrate. The rhodium complex $[Rh(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene) was used as rhodium source. In the course of these experiments, it was found that ethanol or methanol solutions of mixtures containing calixarene ligands and $[Rh(cod)_2]BF_4$ became cloudy after maintaining for 15–30 min at room temperature. ^{1}H NMR spectra of the solutions of such mixtures in CD_3OD (at the molar ratio of phosphine/Rh = 1:1), acquired within several minutes after preparation, featured broadened and shifted proton signals, which were assigned to compounds **24** and **25** (the characteristics of signals assigned to the oxidized forms of compounds **24** and **25** did not change). ^{1}H NMR spectra of the same samples, after maintaining for 2 h at room temperature and already containing apparent amounts of precipitate, featured signals that were assigned only to the oxidized forms of calixarenes **24** and **25** (along with the signals of 1,5-cyclooctadiene released during the formation of complexes). The obtained results allowed to propose that the reactions of compounds **24** and **25** with $[Rh(cod)_2]BF_4$ generated predominantly oligomeric/polymeric complexes that were insoluble in alcohols.

The addition of D_2SO_4 to solutions containing mixtures of ligands and $[Rh(cod)_2]BF_4$ (up to 1 % of D_2SO_4 in CD_3OD by volume) enabled to effectively suppress the formation of insoluble reaction products – the solutions remained homogeneous for at least 24 h. The signals of phosphines **24** and **25** in ^{1}H NMR spectra of samples obtained with added D_2SO_4 were broadened and shifted downfield, indicating the formation of cationic complexes. At the same time, ^{31}P NMR spectra contained signals due to the oxidized forms of ligands (at ~30 ppm) that did not participate in the reaction, as well as characteristic, extremely broadened signals at ~24 ppm, corresponding to the phosphorus atoms bonded to Rh^+ ions (in the case of the complex derived from calixarene **25**, containing only one phosphine moiety at the upper rim, ^{31}P NMR spectrum contained a well-visible broadened doublet with J_{RhP} ~143 Hz). The obtained data indicate that the calixarenes **24** and **25** in the presence of sulfuric acid were able to form alcohol-soluble rhodium complexes that were either monomeric or with a low degree of oligomerization. More accurate structural characterization of complexes obtained from calixarenes **24** and **25** with or without the presence of sulfuric acid would require additional experiments.

Due to the observed properties of rhodium complexes of calixarenes **24** and **25**, the preliminary study of the activity of these compounds in hydroformylation reactions of 1-octene were performed in the absence or in presence of H_2SO_4 by *in situ* preparation of the rhodium complexes directly in the autoclave. The reaction conditions used and

the obtained results of the experiments are presented in Table 1. From the data shown, it is evident that the addition of ligands **24** and **25** improved the conversion of 1-octene in all cases and facilitated an increase in the amount of reaction products having the normal structure. The addition of sulfuric acid allowed to achieve 100% conversion of alkene and to significantly lower the amount of hydrogenation products. It is probable that during the formation of oligomeric/polymeric complexes of compounds **24** and **25** in the absence of acid, the number of rhodium atoms available for the interaction with alkene was quite low, decreasing the rate of the desired hydroformylation reactions and, therefore, favoring the occurrence of side reactions, such as hydrogenation.

For the purpose of catalytic reactions with membrane separation of catalysts, the ligands and their complexes have to be not only sufficiently soluble in suitable solvents, but also must have the effective particle size corresponding to the separation characteristics of membranes used for the filtration.

The hydrodynamic radii of rhodium complexes of calixarenes **24** and **25** obtained in the presence of D_2SO_4 were evaluated from the self-diffusion coefficients, determined by using 2D DOSY NMR spectra acquired in CD_3OD at 30°C. The decimal logarithms of these values, expressed in m^2/s, were found to be –9.42 (D 3.8×10^{-6} cm^2/s) and –9.39 (D 4.1×10^{-6} cm^2/s) for the rhodium complexes of compounds **24** and **25**, respectively. The self-diffusion coefficient of PEG-1000 was determined for comparison under identical conditions (log$D$ (m^2/s) –9.24, D 5.7×10^{-6} cm^2/s). The hydrodynamic radius of PEG-1000 in methanol at 30°C, previously measured by the method of viscosimetry, was equal to 0.916–0.933 nm.[20]

The somewhat lower value of diffusion coefficient for the rhodium complex of calixarene **24**, compared to that of the complex of calixarene **25**, was obviously caused by the presence of not one, but two bulky substituents at the upper rim of the molecule of compound **24**, thus increasing the size of the molecule. Nevertheless, the similar diffusion coefficients for the complexes of calixarenes **24** and **25** indicate that the most significant contribution to the molecular size and hydrodynamic properties was not from the diphenylphosphine substituents, but rather from the four carboxymethyltriazolylmethyl groups, introduced at the lower rim. Since the diffusion coefficients of complexes obtained from calixarenes **24** and **25** were significantly lower than those for PEG-1000, and taking into account the fact that the diffusion coefficients are inversely proportional to the particle radii (in the approximation of Stokes–Einstein equation), the hydrodynamic radii of rhodium complexes of compounds **24** and **25** can be considered to be similar and exceeding 1 nm.

The obtained preliminary data allow to consider calixarenes **24** and **25** as promising ligands for performing alkene hydroformylation reactions catalyzed by rhodium complexes in alcohol media, and using catalyst separation by nanofiltration through membranes capable of separating particles with minimum diameter of 2 nm.

Thus, in the current work we have developed a method for the preparation of calix[4]arenes containing phosphine/phosphine oxide substituents at the upper rim and additional functional groups at the lower rim. A copper(I) salt-catalyzed cycloaddition reaction of azides to alkynes was used as the key step for introducing functional substituents at the lower rim. For the specific purpose of creating ligands soluble in polar media for applications in hydroformylation reactions, the first phosphine-containing calixarenes modified at the lower rim with carboxymethyltriazolylmethane moieties were created. Preliminary studies have demonstrated that the rhodium complexes prepared from the obtained phosphines showed catalytic activity in hydroformylation reactions. The estimated hydrodynamic radii of complexes indicated possibilities for using them in catalytic reactions with membrane separation of catalysts.

Experimental

^1H, ^{13}C, and ^{31}P NMR spectra were acquired on a Bruker Avance 400 instrument (400, 100, and 162 MHz, respectively), the chemical shifts (δ) are reported relative to TMS (for ^1H and ^{13}C nuclei) and 85% H_3PO_4 (for ^{31}P nuclei); the signals were assigned on the basis of ^1H–^1H COSY and ^{13}C APT NMR spectra. The 2D DOSY spectra

Table 1. Reaction conditions and results of 1-octene hydroformylation*

Ligand	Octene conversion, %	Composition of reaction product mixture, %				
		Isomerization products	Hydrogenation products	Aldehydes	Acetals	*n*-/*iso*- (aldehydes + acetals)
–	74	5	15	73	7	1.5
24	84	5	15	33	28	2
24**	100	5	6	72	16	2
25	92	10	18	49	23	2.5
25**	100	4	2	92	6	2

* Reaction conditions: p($CO–H_2$, 1:1) 5 MPa, temperature 80°C, time 3 h, 2 μmol of $[Rh(cod)_2]BF_4$, 1.9 mmol of 1-octene, 4 μmol of ligand **24** or **25**, 2.5 ml of EtOH.

** Added 2 μmol of H_2SO_4.

were acquired on a Bruker Avance 600 instrument (600 MHz), using ledbpgp2s pulse sequence[21] with stimulated spin echo, sinusoidal shaped gradient pulses of magnetic field and time delay compensating for the influence of longitudinal eddy currents; the change of current in the gradient coil was stepwise (64 steps) from 2 to 95% of the maximum value (10 A); the maximum value of magnetic field gradient (at the current of 10 A) *G* 53.5 Gauss/cm, the diffusion time delay was 40 ms, the gradient pulse length was 2 ms, relaxation delay was 1 s; the obtained array of diffusion data was processed using the Bruker XWinNMR 3.5 software suite. High-resolution mass spectra were recorded on a Thermo Scientific LTQ Orbitrap instrument with electrospray ionization. Melting points were determined on a Stuart SMP3 apparatus and were not corrected. The composition of product mixtures from catalytic reactions was analyzed by gas-liquid chromatography on an HP G1530A chromatograph with a flame ionization detector, capillary column (30 m) with SE-30 phase, with the temperature programmed from 60 to 230°C, carrier gas – helium. Commercially available reagents were used without additional purification. The solvents were purified and dried according to standard procedures. Ethyl 2-azidoacetate,[17] azidoacetic acid,[18] *O*-isopropyl diphenyl phosphinite,[19] compound **18**,[16] and calixarenes **3**,[12] **4**[13] were synthesized according to published procedures.

5,17-Bis(diphenylphosphoryl)-25,26,27,28-tetrahydroxycalix[4]arene (5).[5] A mixture of calixarene **3** (1.46 g, 2.5 mmol), $NiCl_2$ (0.065 g, 0.5 mmol), and diphenyl ether (30 ml) was stirred for 10 min at 160°C. Then a solution of *O*-isopropyl diphenyl phosphinite (1.46 g, 6.0 mmol) in diphenyl ether (15 ml) was added and the reaction mixture was stirred for 5 h at 160°C. The reaction mixture was then cooled and diluted with CH_2Cl_2 (50 ml), treated by the addition of 15% aqueous $Na_2S_2O_3$ solution (25 ml), and vigorously stirred for 2 h. The organic layer was separated and the aqueous layer was washed with CH_2Cl_2. The combined organic extracts were washed with 2 N HCl solution and water, filtered through a paper filter and concentrated at reduced pressure. Hexane was added to the obtained solution, the precipitate that formed was filtered off, dried, and separated by chromatography (eluting with a concentration gradient of CH_2Cl_2–EtOH). Yield 1.92 g (93%), white crystals, mp 258–260°C (EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 10.15 (4H, br. s, OH); 7.67–7.59 (8H, m, H Ph); 7.56–7.50 (4H, m, H Ph); 7.47–7.36 (12H, m, H Ar, H Ph); 6.86 (4H, d, ^3J = 7.5, H Ar); 6.66 (2H, t, ^3J = 7.5, H Ar); 4.21 (4H, br. s, $ArCH_2Ar$); 3.52 (4H, br. s, $ArCH_2Ar$).

5-Diphenylphosphoryl-25,26,27,28-tetrahydroxycalix[4]arene (6) was obtained analogously to the procedure for obtaining compound **5**, using calixarene **4** (1.67 g, 3.3 mmol), $NiCl_2$ (0.044 g, 0.33 mmol), *O*-isopropyl diphenyl phosphinite (0.98 g, 3.96 mmol), and diphenyl ether (54 ml). Yield 1.96 g (95%), white crystals, mp 166–168°C (hexane). ^{1}H NMR spectrum ($CDCl_3$,), δ, ppm (*J*, Hz): 10.21 (4H, br. s, OH); 7.67–7.59 (4H, m, H Ph); 7.55–7.48 (2H, m, H Ph); 7.46–7.39 (4H, m, H Ph); 7.39 (2H, d, J_{PH} = 11.9, H Ar); 7.11 (2H, d, ^3J = 7.6, H Ar); 7.06 (2H, dd, ^3J = 7.6, ^4J = 1.5, H Ar); 6.88 (2H, dd, ^3J = 7.6, ^4J = 1.5, H Ar); 6.79 (1H, t, ^3J = 7.6, H Ar); 6.71 (2H, t, ^3J = 7.6, H Ar); 4.24 (4H, br. s, $ArCH_2Ar$); 3.56 (4H, br. s, $ArCH_2Ar$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 152.6 (d, J_{PC} = 3.0, C Ar); 149.0, 148.3 (C Ar); 133.2 (d, J_{PC} = 10.8, CH Ar); 132.6 (d, J_{PC} = 104.3, C Ph); 132.1 (d, J_{PC} = 10.0, CH Ph); 131.8 (d, J_{PC} = 2.7, CH Ph); 129.2, 129.1, 128.9 (CH Ar); 128.6 (d, J_{PC} = 13.2, C Ar); 128.3 (d, J_{PC} = 12.2, CH Ph); 128.1, 128.0, 127.5 (C Ar); 124.8 (d, J_{PC} = 108.0, C Ar); 122.5, 122.1 (CH Ar); 31.6, 31.5 ($ArCH_2Ar$). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 30.1 (P=O). Found, *m*/*z*: 625.2145 $[M+H]^+$. $C_{40}H_{34}O_5P$. Calculated, *m*/*z*: 625.2139.

5,17-Bis(diphenylphosphoryl)-25,26,27,28-tetra(ethoxycarbonylmethoxy)calix[4]arene (7). A mixture of calixarene **5** (0.063 g, 0.076 mmol), freshly calcined Na_2CO_3 (0.057 g, 0.54 mmol), and anhydrous acetonitrile (2 ml) was refluxed with stirring for 1 h, treated with ethyl 2-bromoacetate (0.080 ml, 0.693 mmol), then the reaction mixture was refluxed with stirring for additional 30 h and cooled. The precipitate was filtered off, washed with dichloromethane, and the combined filtrate was evaporated by heating under vacuum. The residue after evaporation of the solvent was separated by chromatography (eluting with a concentration gradient of CH_2Cl_2–EtOH). Yield 0.043 g (47%), white crystals, mp 160–162°C (ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.75–7.64 (8H, m, H Ph); 7.59–7.36 (16H, m, H Ar, H Ph); 6.29 (2H, t, ^3J = 7.6, H Ar); 6.09 (4H, d, ^3J = 7.6, H Ar); 4.99 (4H, s, CH_2CO); 4.84 (4H, d, ^2J = 13.7, $ArCH_2Ar$); 4.42 (4H, s, CH_2CO); 4.20 (4H, q, ^3J = 7.2, $C\underline{H}_2CH_3$); 4.16 (4H, q, ^3J = 7.2, $C\underline{H}_2CH_3$); 3.20 (4H, d, ^2J = 13.7, $ArCH_2Ar$); 1.26 (6H, t, ^3J = 7.2, $CH_2C\underline{H}_3$); 1.25 (6H, t, ^3J = 7.2, $CH_2C\underline{H}_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 170.3, 169.3 (C=O); 160.3 (d, J_{PC} = 3.3, C Ar); 154.6 (C Ar); 136.9 (d, J_{PC} = 13.2, C Ar); 133.3 (d, J_{PC} = 10.6, CH Ar); 132.9 (d, J_{PC} = 103.9, C Ph); 132.1 (d, J_{PC} = 9.9, CH Ph); 132.0 (C Ar); 131.8 (d, J_{PC} = 2.6, CH Ph); 128.4 (d, J_{PC} = 12.1, CH Ph); 128.1 (CH Ar); 126.1 (d, J_{PC} = 106.8, C Ar); 123.2 (CH Ar); 71.7, 71.0 ($\underline{C}H_2CO$); 60.8, 60.5 ($\underline{C}H_2CH_3$); 31.3 ($ArCH_2Ar$); 14.2, 14.1 (CH_3). ^{31}P NMR spectrum (DMSO-d_6), δ, ppm: 25.6 (P=O). Found, *m*/*z*: 1191.3797 $[M+Na]^+$. $C_{68}H_{66}NaO_{14}P_2$. Calculated, *m*/*z*: 1191.3820.

5-Diphenylphosphoryl-25,26,27,28-tetra(ethoxycarbonylmethoxy)calix[4]arene (8) was obtained analogously to the procedure for preparation of compound **7** from calixarene **6** (0.125 g, 0.20 mmol), freshly calcined Na_2CO_3 (0.148 g, 1.40 mmol), ethyl 2-bromoacetate (0.208 ml, 1.80 mmol), and anhydrous acetonitrile (5 ml). Yield 0.138 g (71%), white crystals, mp 84–89°C (ethanol). ^{1}H NMR spectrum ($CDCl_3$,), δ, ppm (*J*, Hz): 7.50–7.42 (2H, m, H Ph); 7.41–7.28 (8H, m, H Ph); 6.88 (2H, d, J_{PH} = 12.2, H Ar); 6.83 (2H, d, ^3J = 6.8, H Ar); 6.71 (2H, d, ^3J = 6.8, H Ar); 6.61 (2H, d, ^3J = 7.4, H Ar); 6.57 (2H, t, ^3J = 6.8, H Ar); 6.51 (1H, t, ^3J = 7.4, H Ar); 4.91 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 4.88 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 4.87 (2H, d, ^2J = 16.3, OCH_2); 4.80 (2H, d, ^2J = 16.3, OCH_2); 4.69 (2H, s, OCH_2); 4.67 (2H, s, OCH_2); 4.22 (2H, q, ^3J = 7.2, $C\underline{H}_2CH_3$); 4.20 (2H, q, ^3J = 7.2, $C\underline{H}_2CH_3$); 4.17 (4H, q, ^3J = 7.1, $C\underline{H}_2CH_3$); 3.27 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 3.18

(2H, d, ^2J = 13.4, $ArCH_2Ar$); 1.29 (3H, t, ^3J = 7.2, $CH_2C\underline{H}_3$); 1.27 (3H, t, ^3J = 7.2, $CH_2C\underline{H}_3$); 1.26 (6H, t, ^3J = 7.1, $CH_2C\underline{H}_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 170.1, 169.7, 169.4 (C=O); 158.7 (d, J_{PC} = 3.3, C Ar); 155.7, 155.5 (C Ar); 134.8 (C Ar); 134.7 (d, J_{PC} = 13.2, C Ar); 134.3, 134.2 (C Ar); 132.9 (d, J_{PC} = 11.3, CH Ar); 132.5 (d, J_{PC} = 104.0, C Ph); 131.8 (d, J_{PC} = 9.9, CH Ph); 131.3 (d, J_{PC} = 2.6, CH Ph); 128.8, 128.6, 128.3 (CH Ar); 128.1 (d, J_{PC} = 12.1, CH Ph); 125.4 (d, J_{PC} = 107.6, C Ar); 123.3, 123.0 (CH Ar); 71.6, 71.3, 71.1 ($\underline{C}H_2CO$); 60.6, 60.5, 60.4 ($\underline{C}H_2CH_3$); 31.4, 31.2 ($ArCH_2Ar$); 14.1 (CH_3). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 28.8 (P=O). Found, *m*/*z*: 991.3433 $[M+Na]^+$. $C_{56}H_{57}NaO_{13}P$. Calculated, *m*/*z*: 991.3430.

5,17-Bis(diphenylphosphoryl)-25,26,27,28-tetra(2-propynyloxy)calix[4]arene (13) (in a mixture with compound **14**). A suspension of calixarene **5** (1.14 g, 1.38 mmol) in anhydrous DMF (35 ml) was treated with sodium hydride (60% suspension in mineral oil, 0.33 g). The mixture was stirred under moisture-free atmosphere for 1 h. Propargyl bromide (80% solution in toluene, 1.19 ml, 11.0 mmol) was added with stirring. The reaction mixture was stirred in a sealed flask at room temperature for 48 h. Water (80 ml) was added with caution while stirring and the reaction products were extracted with CH_2Cl_2 (5×30 ml). The combined organic extracts were washed with water, filtered through a paper filter, and evaporated at reduced pressure. The residue was separated by chromatography (eluting with a concentration gradient of CH_2Cl_2–EtOH). Yield (4:1 mixture of compounds **13**/**14**) 0.92 g (68%), yellowish-brown solid. ^1H NMR spectrum ($CDCl_3$, signals reported only for compound **13**), δ, ppm (*J*, Hz): 7.72–7.62 (8H, m, H Ph); 7.60–7.36 (16H, m, H Ar, H Ph); 6.38 (2H, t, ^3J = 7.5, H Ar); 6.24 (4H, d, ^3J = 7.5, H Ar); 5.03 (4H, d, ^4J = 2.4, OCH_2); 4.59 (4H, d, ^2J = 13.5, $ArCH_2Ar$); 4.51 (4H, d, ^4J = 2.4, OCH_2); 3.19 (4H, d, ^2J = 13.5, $ArCH_2Ar$); 2.49 (2H, t, ^4J = 2.4, CCH); 2.44 (2H, t, ^4J = 2.4, CCH). ^{31}P NMR spectrum ($CDCl_3$, only the signal of compound **13** reported), δ, ppm: 29.3 (P=O). Found, *m*/*z*: 977.3163 $[M+H]^+$. $C_{64}H_{51}O_6P_2$. Calculated, *m*/*z*: 977.3156.

5-Diphenylphosphoryl-25,26,27,28-tetra(2-propynyloxy)-calix[4]arene (15) was obtained analogously to the procedure for preparation of compound **13**, using calixarene **6** (1.32 g, 2.12 mmol), sodium hydride (60% suspension in mineral oil, 0.51 g, 12.7 mmol), propargyl bromide (80% solution in toluene, 1.83 ml, 17.0 mmol), and anhydrous DMF (40 ml). Yield 1.26 g (77%), yellowish-brown crystals, mp 117–119°C (ethanol). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.47–7.41 (2H, m, H Ph); 7.31–7.20 (8H, m, H Ph); 7.02–6.97 (2H, m, H Ar); 6.78 (2H, d, J_{PH} = 12.3, H Ar); 6.73–6.70 (6H, m, H Ar); 6.68 (2H, d, ^3J = 7.5, H Ar); 6.47 (1H, t, ^3J = 7.5, H Ar); 4.96 (2H, dd, ^2J = 16.2, ^4J = 2.4, OCH_2); 4.90 (2H, dd, ^2J = 16.2, ^4J = 2.4, OCH_2); 4.68 (2H, d, ^4J = 2.4, OCH_2); 4.67 (2H, d, ^4J = 2.4, OCH_2); 4.64 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 4.63 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 3.27 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 3.15 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 2.50 (1H, t, ^4J = 2.4, CCH); 2.47 (2H, t, ^4J = 2.4, CCH); 2.46 (1H, t, ^4J = 2.4, CCH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 157.6 (d, J_{PC} = 3.1, C Ar); 155.0, 154.6, 136.3, 135.9 (C Ar); 135.0 (d, J_{PC} = 13.2, C Ar); 134.5 (C Ar); 132.7 (d, J_{PC} = 11.3, CH Ar); 132.5 (d, J_{PC} = 103.5, C Ph); 131.7 (d, J_{PC} = 9.7, CH Ph); 131.2 (d, J_{PC} = 2.8, CH Ph); 128.6, 128.4 (CH Ar); 128.0 (d, J_{PC} = 12.0, CH Ph); 127.8 (CH Ar); 125.8 (d, J_{PC} = 106.7, C Ar); 123.8, 123.3 (CH Ar); 80.6, 79.9, 79.3 ($\underline{C}CH$); 75.4, 75.0, 74.8 ($C\underline{C}H$); 61.8 (2C), 60.6 (OCH_2); 31.9, 31.7 ($ArCH_2Ar$). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 28.5 (P=O). Found, *m*/*z*: 777.2768 $[M+H]^+$. $C_{52}H_{42}O_5P$. Calculated, *m*/*z*: 777.2765.

5,17-Bis(diphenylphosphoryl)-25,26,27,28-tetra-(1-ethoxycarbonylmethyl-4-triazolylmethoxy)calix[4]arene (16). A mixture of calixarenes **13** and **14** (0.39 g, 0.4 mmol), ethyl 2-azidoacetate (0.26 g, 2.0 mmol), $CuI{\cdot}P(OEt)_3$ (0.02 g, 0.06 mmol), and anhydrous toluene (12 ml) was refluxed with stirring for 7 h. The solvent was evaporated, the residue was diluted with CH_2Cl_2, and the solution was washed with 2 N HCl. The organic extracts were washed with water, filtered through a paper filter and evaporated at reduced pressure. The residue was separated by chromatography (eluting with a concentration gradient of CH_2Cl_2–EtOH). Yield 0.25 g (42%), white crystals, mp 124–126°C (ethanol). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.91 (2H, s, H triazole); 7.79 (2H, s, H triazole); 7.67–7.40 (20H, m, H Ph); 7.29 (4H, d, J_{PH} = 12.0, H Ar); 6.28 (2H, t, ^3J = 7.6, H Ar); 6.08 (4H, d, ^3J = 7.6, H Ar); 5.21 (4H, s, OCH_2); 5.14 (4H, s, NCH_2); 5.13 (4H, s, NCH_2); 4.83 (4H, s, OCH_2); 4.24 (4H, d, ^2J = 13.5, $ArCH_2Ar$); 4.18 (4H, q, ^3J = 7.1, $C\underline{H}_2CH_3$); 4.13 (4H, q, ^3J = 7.1, $C\underline{H}_2CH_3$); 3.00 (4H, d, ^2J = 13.5, $ArCH_2Ar$); 1.23 (6H, t, ^3J = 7.1, $CH_2C\underline{H}_3$); 1.19 (6H, t, ^3J = 7.1, $CH_2C\underline{H}_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 166.6, 166.2 (C=O); 159.0 (d, J_{PC} = 2.9, C Ar); 154.2 (C Ar); 144.2, 143.9 (C triazole); 137.7 (d, J_{PC} = 13.4, C Ar); 132.9 (d, J_{PC} = 11.5, CH Ar); 132.8 (d, J_{PC} = 104.3, C Ph); 132.5 (C Ar); 132.1 (d, J_{PC} = 9.9, CH Ph); 131.7 (d, J_{PC} = 2.2, CH Ph); 128.4 (d, J_{PC} = 12.1, CH Ph); 127.9 (CH Ar); 126.1 (CH triazole); 125.9 (d, J_{PC} = 107.0, C Ar); 125.4 (CH triazole); 123.0 (CH Ar); 67.8, 65.6 (OCH_2); 62.2, 62.0 ($\underline{C}H_2CH_3$); 50.8, 50.7 (NCH_2); 31.1 ($ArCH_2Ar$); 14.0, 13.9 (CH_3). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 29.8 (P=O). Found, *m*/*z*: 747.2683 $[M+2H]^{2+}$. $C_{80}H_{80}N_{12}O_{14}P_2$. Calculated, *m*/*z*: 747.2691.

5-Diphenylphosphoryl-25,26,27,28-tetra(1-ethoxy-carbonylmethyl-4-triazolylmethoxy)calix[4]arene (17) was obtained analogously to the procedure for preparation of compound **16**, using calixarene **15** (0.39 g, 0.5 mmol), ethyl 2-azidoacetate (0.32 g, 2.5 mmol), $CuI{\cdot}P(OEt)_3$ (0.03 g, 0.08 mmol), and toluene (15 ml). Yield 0.26 g (40%), white crystals, mp 110–112°C (ethanol). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.98 (1H, s, H triazole); 7.82 (1H, s, H triazole); 7.78 (2H, s, H triazole); 7.47–7.42 (2H, m, H Ph); 7.33–7.27 (8H, m, H Ph); 6.87–6.82 (2H, m, H Ar); 6.78 (2H, d, J_{PH} = 12.3, H Ar); 6.67 (2H, d, ^3J = 7.5, H Ar); 6.59 (2H, t, ^3J = 7.5, H Ar); 6.55–6.51 (2H, br. d, H Ar); 6.46 (1H, t, ^3J = 7.5, H Ar); 5.17 (2H, s, NCH_2); 5.15 (4H, s, NCH_2); 5.14 (2H, s, NCH_2); 5.10 (2H, d, ^2J = 12.6, OCH_2); 5.04 (2H, d, ^2J = 12.6, OCH_2); 5.01 (2H, s, OCH_2); 5.00 (2H, s, OCH_2); 4.34 (2H, d, ^2J = 13.3,

$ArCH_2Ar$); 4.21 (2H, q, ^3J = 7.1, $C\underline{H}_2CH_3$); 4.20 (4H, q, ^3J = 7.1, $C\underline{H}_2CH_3$); 4.19 (2H, q, ^3J = 7.1, $C\underline{H}_2CH_3$); 4.18 (2H, d, ^2J = 13.3, $ArCH_2Ar$); 3.14 (2H, d, ^2J = 13.3, $ArCH_2Ar$); 2.93 (2H, d, ^2J = 13.3, $ArCH_2Ar$); 1.26 (9H, t, ^3J = 7.1, $CH_2C\underline{H}_3$); 1.25 (3H, t, ^3J = 7.1, $CH_2C\underline{H}_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 166.6, 166.5, 166.4 (C=O); 158.0 (d, J_{PC} = 2.6, C Ar); 155.0, 154.8 (C Ar); 144.5, 144.4, 143.9 (C triazole); 135.9, 135.3 (C Ar); 135.2 (d, J_{PC} = 13.5, C Ar); 134.7 (C Ar); 132.9 (d, J_{PC} = 11.5, CH Ar); 132.7 (d, J_{PC} = 102.7, C Ph); 131.9 (d, J_{PC} = 9.5, CH Ph); 131.2 (d, J_{PC} = 2.0, CH Ph); 128.7, 128.4 (CH Ar); 128.1 (d, J_{PC} = 11.8, CH Ph); 128.1 (CH Ar); 125.9, 125.8 (2C) (CH triazole); 125.4 (d, J_{PC} = 108.1, C Ar); 123.3, 122.9 (CH Ar); 67.6, 67.3, 66.2 (OCH_2Trz); 62.2 ($\underline{C}H_2CH_3$); 50.9, 50.8 (2C) (NCH_2); 31.3, 31.1 ($ArCH_2Ar$); 14.1 (br. s, CH_3). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 28.9 (P=O). Found, *m*/*z*: 647.2490 $[M+2H]^{2+}$. $C_{68}H_{71}N_{12}O_{13}P$. Calculated, *m*/*z*: 647.2496.

***tert*-Butyl-*N*-[tris(benzoyloxymethyl)methyl]carbamate (19)**. A mixture of carbamate **18** (10.70 g, 48.4 mmol), Et_3N (23.3 ml, 167.4 mmol), and anhydrous CH_2Cl_2 (160 ml) was stirred and slowly treated by dropwise addition of a solution of benzoyl chloride (18.3 ml, 157.7 mmol) in CH_2Cl_2 (40 ml). The reaction mixture was stirred for 12 h. The obtained mixture was quenched with water and portionwise addition of $NaHCO_3$ until the evolution of gas ceased. The organic layer was separated, and the aqueous layer was washed with CH_2Cl_2. The combined organic extracts were washed with water, filtered through a paper filter, and evaporated. The residue after evaporation of solvent was recrystallized from ethanol and separated by chromatography (eluting with a concentration gradient of CH_2Cl_2–EtOH). Yield 20.4 g (79%), white crystals, mp 124–126°C (ethanol). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.01 (6H, d, ^3J = 7.6, H Ph); 7.55 (3H, t, ^3J = 7.6, H Ph); 7.40 (6H, t, ^3J = 7.6, H Ph); 5.25 (1H, s, NH); 4.82 (6H, s, OCH_2); 1.41 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 166.0, 154.4 (C=O); 133.3, 129.7 (CH Ph); 129.4 (C Ph); 128.4 (CH Ph); 80.2 ($O\underline{C}(CH_3)_3$) 64.0 (OCH_2); 57.5 ($N\underline{C}(CH_2)_3$); 28.2 ($C(\underline{C}H_3)_3$). Found, *m*/*z*: 534.2098 $[M+H]^+$. $C_{30}H_{32}NO_8$. Calculated, *m*/*z*: 534.2122.

Tris(benzoyloxymethyl)methylamine (20). A solution of carbamate **19** (8.00 g, 15.0 mmol) in CH_2Cl_2 (120 ml) was treated by the addition of CF_3CO_2H (11.5 ml, 150.0 mmol). The reaction mixture was stirred at room temperature for 12 h. The mixture was poured into 0.1 M aqueous solution of Na_2CO_3 and stirred until complete dissolution of the precipitate. The organic layer was separated and the aqueous layer was washed with CH_2Cl_2. The combined organic extracts were washed with water, filtered through paper filter, and evaporated. Yield 6.04 g (93%), white crystals, mp 107–109°C (dichloromethane). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.03 (6H, d, ^3J = 7.6, H Ph); 7.55 (3H, t, ^3J = 7.6, H Ph); 7.41 (6H, t, ^3J = 7.6, H Ph); 4.52 (6H, s, OCH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 166.0 (C=O); 133.3, 129.6 (CH Ph); 129.4 (C Ph); 128.5 (CH Ph); 66.4 (OCH_2); 54.9 (CNH_2). Found, *m*/*z*: 434.1602 $[M+H]^+$. $C_{25}H_{24}NO_6$. Calculated, *m*/*z*: 434.1598.

Tris(benzoyloxymethyl)methylamide of 2-azidoacetic acid (21). A mixture of amine **20** (6.00 g, 13.9 mmol), 2-azidoacetic acid (1.60 g, 15.8 mmol), and anhydrous CH_2Cl_2 (80 ml) was treated with diisopropylcarbodiimide (2.28 ml, 14.7 mmol). The reaction mixture was stirred at room temperature for 12 h. The obtained mixture was treated with 2 N HCl and vigorously stirred for 1 h. The organic layer was separated, and the aqueous layer was washed with CH_2Cl_2. The combined organic extracts were washed with water, filtered through a paper filter, and evaporated. Yield 6.44 g (90%), white crystals, mp 119–121°C (dichloromethane). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.04–7.95 (6H, m, H Ph); 7.59–7.51 (3H, m, H Ph); 7.45–7.36 (6H, m, H Ph); 7.21 (1H, s, NH); 4.90 (6H, s, OCH_2); 3.95 (2H, s, CH_2N_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 167.1, 166.1 (C=O); 133.5, 129.7 (CH Ph); 129.1 (C Ar); 128.5 (CH Ar); 63.5 (OCH_2); 59.2 ($N\underline{C}(CH_2)_3$); 53.0 (N_3CH_2). Found, *m*/*z*: 539.1556 $[M+Na]^+$. $C_{27}H_{24}NaN_4O_7$. Calculated, *m*/*z*: 539.1538).

5,17-Bis(diphenylphosphoryl)-25,26,27,28-tetra-[1-tris(benzoyloxymethyl)methylaminocarbonylmethyl-4-triazolylmethoxy]calix[4]arene (22) was prepared analo-gously to the procedure for obtaining compound **16**, by using a mixture of calixarenes **13** and **14** (0.49 g, 0.5 mmol), azide **21** (1.29 g, 2.5 mmol), $CuI{\cdot}P(OEt)_3$ (0.03 g, 0.08 mmol), and toluene (30 ml). Yield 0.79 g (52%), yellow crystals, mp 163–165°C (ethanol). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.05 (2H, br. s, H triazole); 8.01–7.80 (26H, m, H Ph, H triazole); 7.71–7.60 (10H, m, H Ph); 7.55–7.20 (54H, m, H Ar, H Ph, NH); 6.27 (2H, t, ^3J = 7.6, H Ar); 6.05 (4H, d, ^3J = 7.6, H Ar); 5.15 (4H, s, NCH_2); 4.98 (4H, s, NCH_2); 4.90 (4H, s, OCH_2); 4.81 (12H, s, CH_2OBz); 4.80 (12H, s, CH_2OBz); 4.65 (4H, s, OCH_2); 4.25 (4H, br. d, ^2J = 13.1, $ArCH_2Ar$); 3.02 (4H, br. d, ^2J = 13.1, $ArCH_2Ar$). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 29.6 (P=O). Found, *m*/*z*: 1521.4914 $[M+2H]^{2+}$. $C_{172}H_{148}N_{16}O_{34}P_2$. Calculated, *m*/*z*: 1521.4904.

5-Diphenylphosphoryl-25,26,27,28-tetra[1-tris(benzoyloxymethyl)methylaminocarbonylmethyl-4-triazolylmethoxy]calix[4]arene (23) was prepared analogously to the procedure for obtaining compound **16**, using calixarene **15** (0.55 g, 0.7 mmol), azide **21** (1.81 g, 3.5 mmol), $CuI{\cdot}P(OEt)_3$ (0.04 g, 0.11 mmol), and toluene (35 ml). Yield 1.02 g (51%), yellow crystals, mp 153–155°C (ethanol). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.98–7.82 (28H, m, H triazole, H Ph); 7.67 (2H, s, H triazole); 7.49–7.33 (20H, m, H Ph); 7.32–7.19 (28H, m, H Ph, NH); 6.81 (2H, d, ^3J = 7.6, H Ar); 6.67 (2H, d, J_{PH} = 12.0, H Ar); 6.55 (2H, d, ^3J = 7.6, H Ar); 6.54 (2H, t, ^3J = 7.6, H Ar); 6.43 (2H, d, ^3J = 7.1, H Ar); 6.35 (1H, t, ^3J = 7.1, H Ar); 5.08 (2H, s, NCH_2); 5.07 (2H, s, NCH_2); 5.01 (4H, s, NCH_2); 4.91 (4H, s, OCH_2Trz); 4.84 (4H, s, OCH_2Trz); 4.83 (24H, s, CH_2OBz); 4.26 (2H, d, ^2J = 13.2, $ArCH_2Ar$); 4.15 (2H, d, ^2J = 13.2, $ArCH_2Ar$); 3.03 (2H, d, ^2J = 13.3, $ArCH_2Ar$); 2.82 (2H, d, ^2J = 13.3, $ArCH_2Ar$). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 28.7 (P=O). Found, *m*/*z*: 1421.4705 $[M+2H]^{2+}$. $C_{160}H_{139}N_{16}O_{33}P$. Calculated, *m*/*z*: 1421.4709.

5,17-Bis(diphenylphosphanyl)-25,26,27,28-tetra-(1-carboxymethyl-4-triazolylmethoxy)calix[4]arene

(**24**). A suspension of calixarene **16** or calixarene **22** (0.1 mmol) in anhydrous toluene (3 ml) was treated with $PhSiH_3$ (0.74 ml, 6.0 mmol). The obtained solution was refluxed for 48 h in a flask with reflux condenser under argon atmosphere. The solvent was evaporated under vacuum at room temperature, the residue was dissolved in CH_2Cl_2 and diluted with methanol. The precipitate that formed was filtered off, dissolved in a mixture of ethanol (10 ml) and tetrahydrofuran (5 ml), and treated with a solution of 90% KOH (0.32 g, 5.3 mmol) in water (5 ml). The solution was stirred for 15 h at room temperature. The organic solvents were evaporated under vacuum, and the residue was treated with 5 N HCl (20 ml). The precipitate that formed was filtered off, washed with water (5 ml), diethyl ether (5 ml), and dried. Yield (including the oxidized form as impurity) 0.094 g (~70% from compound **16**), 0.098 g (~73% from compound **22**), white crystals. ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 8.01 (2H, s, H triazole); 8.00 (2H, s, H triazole); 7.38–7.11 (20H, m, H Ph); 6.82 (4H, d, J_{PH} = 7.8, H Ar); 6.36–6.30 (6H, m, H Ar); 5.28 (4H, s), 5.26 (4H, s), 5.20 (4H, s) and 5.02 (4H, s, NCH_2, OCH_2); 4.19 (4H, d, ^2J = 13.4, $ArCH_2Ar$); 2.91 (4H, d, ^2J = 13.4, $ArCH_2Ar$). ^{31}P NMR spectrum (CD_3OD), δ, ppm: –6.6 (P). Found, *m*/*z*: 1347.4012 $[M–H]^-$. $C_{72}H_{61}N_{12}O_{12}P_2$. Calculated, *m*/*z*: 1347.4002. Found, *m*/*z*: 1363.3922 $[M(O)–H]^-$. $C_{72}H_{61}N_{12}O_{13}P_2$. Calculated, *m*/*z*: 1363.3951. Found, *m*/*z*:1379.3855 $[M(O)_2–H]^-$. $C_{72}H_{61}N_{12}O_{14}P_2$. Calculated, *m*/*z*: 1379.3900.

5-Diphenylphosphanyl-25,26,27,28-tetra(1-carboxymethyl-4-triazolylmethoxy)calix[4]arene (**25**) was prepared analogously to the procedure for obtaining compound **24** by using calixarene **17** or calixarene **23** (0.15 mmol), $PhSiH_3$ (0.55 ml, 4.5 mmol), toluene (2.5 ml), 90% KOH (0.48 g, 7.7 mmol), ethanol (15 ml), tetrahydrofuran (7.5 ml), and water (7.5 ml). Yield (including the oxidized form as impurity) 0.105 g (~60% from compound **17**), 0.118 g (~67% from compound **23**), white crystals. ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 8.03 (1H, s, H triazole); 8.02 (1H, s, H triazole); 8.00 (2H, s, H triazole); 7.31–7.26 (2H, m, H Ph); 7.25–7.19 (4H, m, H Ph); 7.01–6.95 (4H, m, H Ph); 6.82 (2H, dd, ^3J = 7.3, ^4J = 1.8, H Ar); 6.63–6.60 (2H, m, H Ar); 6.60 (2H, d, ^3J = 7.5, H Ar); 6.57 (2H, dd, ^3J = 7.3, ^4J = 1.8, H Ar); 6.45 (1H, t, ^3J = 7.5, H Ar); 6.44 (2H, d, J_{PH} = 7.8, H Ar); 5.30 (4H, s, NCH_2); 5.29 (2H, s, NCH_2); 5.25 (2H, s, NCH_2); 5.19 (4H, br. s, OCH_2); 5.06 (4H, br. s, OCH_2); 4.22 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 4.14 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 3.04 (2H, d, ^2J = 13.4, $ArCH_2Ar$); 2.89 (2H, d, ^2J = 13.4, $ArCH_2Ar$). ^{31}P NMR spectrum (CD_3OD), δ, ppm: –4.8 (P). Found, *m*/*z*: 1165.3741 $[M+H]^+$. $C_{60}H_{54}N_{12}O_{12}P$. Calculated, *m*/*z*: 1165.3716. Found, *m*/*z*: 1181.3695 $[M(O)+H]^+$. $C_{60}H_{54}N_{12}O_{13}P$. Calculated, *m*/*z*: 1181.3665.

Catalytic experiments were performed in a 25-ml steel autoclave that was equipped with a magnetic stirrer and a thermostat. The autoclave was charged with $[Rh(cod)_2]BF_4$ (0.8 mg, 0.002 mmol), 1-octene (0.3 ml, 1.9 mmol), ethyl alcohol, and the calculated mass of ligand (Table 1). The autoclave was purged twice with argon, filled with synthesis gas ($CO–H_2$, 1:1) to 5.0 MPa pressure, heated to 80°C, and maintained at this temperature for 3 h with constant stirring. The analysis of reaction product mixtures was performed in the presence of internal standard – *n*-nonane.

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