ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 4, pp. 745–752. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © O.S. Serkova, A.V. Burikhina, L.K. Vasyanina, O.S. Kuprina, V.I. Maslennikova, E.E. Nifantiev, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 4, pp. 670–678.

Pre-Organized Oligomodified Resorcinarene Ligands. Preparation, Structure, and Complex Formation

O. S. Serkova, A. V. Burikhina, L. K. Vasyanina, O. S. Kuprina, V. I. Maslennikova, and E. E. Nifantiev

Moscow Pedagogical State University, Nesvizhski per. 3, Moscow, 119021 Russia
e-mail: him-vim@mail.ru

Received June 20, 2013

Abstract—Interaction of various conformations of resorcinarenes with carbamoyl chloride, thiocarbamoyl chloride, and trifluoromethanesulfonic acid anhydride has resulted in a series of derivatives with certain pre-organization of the macrocyclic scaffold and the immobilized electron-donating groups. Complex formation of the selected prepared compounds towards Pd(II) derivatives has been studied.

Keywords: calix[4]resorcinarenes, conformation, carbamoylation, metalated cycle

DOI: 10.1134/S1070363214040240

Calix[4]resorcinarenes **I** containing four pairs of hydroxy groups per molecule are easily modified and are convenient precursors of receptors and coordination systems. Their conformation state depends on the nature of substituents in methylene bridges; hence, pre-organization of macrocyclic scaffold of the molecule can be achieved to form certain orientation of the functional groups, an important part of designing special purpose complexes [1–10].

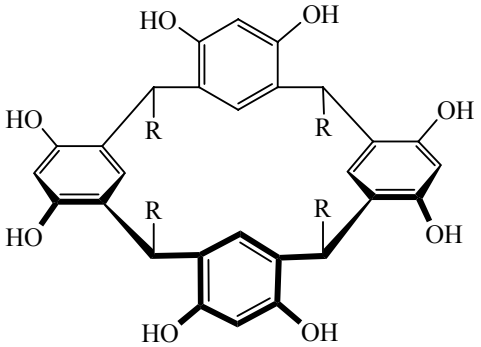
In this work we addressed the possibility to functionalize resorcinarenes **I** in order to construct pre-organized ligands with defined orientation of electron-donor groups capable of chelate complex formation.

The parent macrocycles were *rctt*-tetranaphthylresorcinarene **Ia** existing in the *chair* conformation and *rccc*-tetraalkylresorcinarenes **Ib**–**If** with preferential *crown* conformation. The following functionalized reagents were used: *N,N*-dimethylcarbamoyl chloride **IIa**, *N,N*-dimethylthiocarbamoyl chloride **IIb**, and trifluoromethanesulfonic acid anhydride **IIc** (Scheme 1).

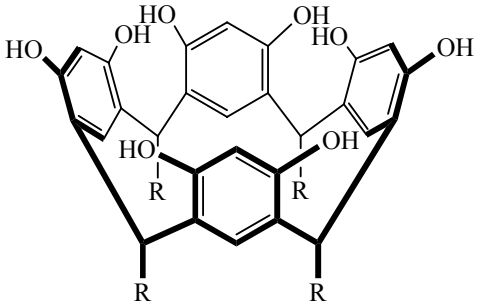
Reactions of resorcinarenes **I** with **IIa** and **IIb** were performed in acetone at 50–55°C in the presence of Cs_2CO_3 (Scheme 2).

The complete acylation of hydroxy groups occurred under the above conditions. Carbamoylation of **Ia**–**If**

Scheme 1.



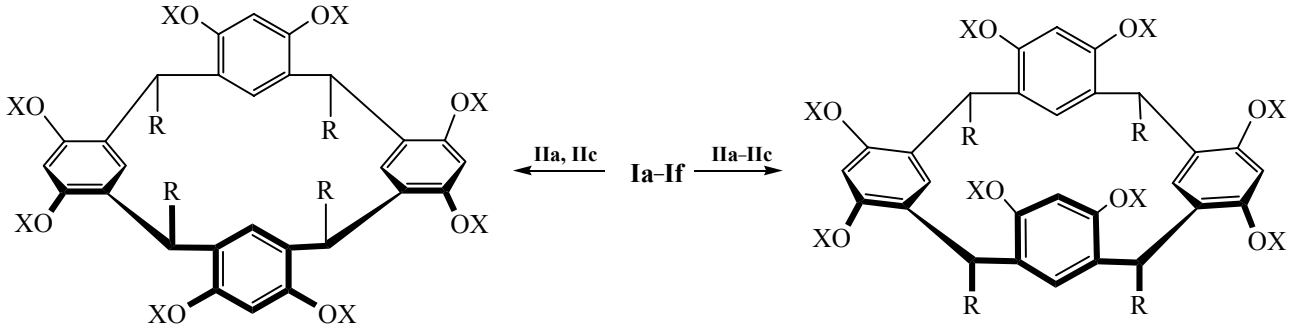
Ia



Ib–If

R = α-naphthyl (**a**), CH_3 (**b**), $CH_2CH_2C_6H_5$ (**c**), Pr (**d**), C_6H_{13} (**e**), C_9H_{19} (**f**).

Scheme 2.



IIIa, Va **IIIb–IIIf, IVa–IVc, Vb, Vc**

Va: X = SO_2CF_3; **II**: $ClC(O)N(CH_3)_2$ (**a**), $ClC(S)N(CH_3)_2$ (**b**), $(SO_2CF_3)_2O$ (**c**); **III**: X = $C(O)N(CH_3)_2$; R = α-naphthyl (**a**), CH_3 (**b**), CH_2CH_2Ph (**c**), C_3H_7 (**d**), C_6H_{13} (**e**), C_9H_{19} (**f**); **IV**: X = $C(S)N(CH_3)_2$, CH_3 (**a**), CH_2CH_2Ph (**b**), C_3H_7 (**c**); **V**: X = SO_2CF_3 (**a**), CH_3 (**b**), C_3H_7 (**c**).

was complete within 8 h; complete thiocarbamoylation of calixarenes **Ib–Id** took 48 h. Yields of *O*-(dimethyloctacarbamoyl)- and *O*-(dimethyloctathiocarbamoyl)resorcinarenes **III** and **IV** were 52–86% (Table 1).

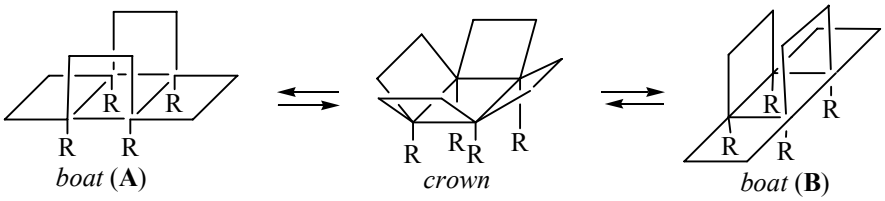
Elemental analysis data and mass spectra features of resorcinarenes **III** and **IV** (Table 1) along with the absence of ^{1}H NMR signals of hydroxy group protons and the ratio of integral intensities of the ^{1}H NMR signals of aminomethyl protons and those of resorcinarene scaffold confirmed the formation of perfunctionalized derivatives. In the ^{13}C NMR spectra the signals of carbon atoms of aminomethyl groups and of carbonyl (**III**) or thiocarbonyl (**IV**) groups were

Table 1. Yields, melting points, elemental analysis data, and mass spectra features of octafunctionalized resorcinarenes **III–V**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %			*m/z*
			C	H	N		C	H	N	
IIIa	83	260–262	70.77	5.65	7.15	$C_{92}H_{88}N_8O_{16}$	70.75	5.68	7.17	
IIIb	72	301–303	60.38	6.47	10.00	$C_{56}H_{72}N_8O_{16}$	60.42	6.52	10.07	1174 [$M^+ + Na^+ + K^+$]
IIIc	82	203–210[a]	68.41	6.55	7.62	$C_{84}H_{96}N_8O_{16}$	68.40	6.57	7.60	
IIId	84	310–314[a]	62.55	7.16	9.08	$C_{64}H_{88}N_8O_{16}$	62.73	7.24	9.14	1434.5 [M^+]
IIIe	71	257–260[a]	69.24	8.40	5.07	$C_{64}H_{92}N_4O_{12}$	69.29	8.36	5.05	1584 [$M^+ + Na^+$]
IIIf	66	270–274[a]	71.28	9.11	4.40	$C_{76}H_{116}N_4O_{12}$	71.44	9.15	4.38	
IVa	86	266–268[a]	50.68	5.46	8.38	$C_{56}H_{72}N_8O_8S_8 \cdot CHCl_3$	50.30	5.41	8.23	1241.4 [M^+]
IVb	86	196–198	62.51	6.02	6.63	$C_{84}H_{96}N_8O_8S_8$	62.97	6.04	6.99	1601.9 [M^+]
IVc	52	182–184[a]	57.00	6.52	8.25	$C_{64}H_{88}N_8O_8S_8$	56.77	6.55	8.28	
Va	60	268–270	44.35	2.04		$C_{76}H_{40}F_{24}O_{24}S_8$	44.54	1.98		2066 [$M^+ + H_2O$]
Vb	65	268–270	34.77	1.08		$C_{40}H_{24}F_{24}O_{24}S_8$	35.01	1.51		1409 [$M^+ - CF_3SO_2$]
Vc	61	281–283	33.44	2.37		$C_{48}H_{40}F_{24}O_{24}S_8$	33.65	2.35		

[a] Melting with decomposition.

Scheme 3.



observed. The IR spectra contained intense band at around 1660 cm^{-1} typical of C=O stretching vibrations (**III**) or around 1120 cm^{-1} (C=S stretching vibrations) (**IV**).

Introduction of eight functional groups into *rctt*-resorcinarene **Ia** containing distant benzene rings did not influence the macrocyclic scaffold conformation. Compound **IIIa**, similarly to **Ia**, existed in the *chair* conformation (C_{2h} symmetry) as evidenced by duplication of signals of protons and carbon atoms of benzene rings and of carbamate groups in ^1H and ^{13}C NMR spectra as well as by upfield shift (δ 5.24 ppm) of the benzene ring protons (H^{3h}) in ^1H NMR spectrum [11].

At the same time, ^1H and ^{13}C spectra of octacarbamate **IIIb** and octathiocarbamates **IVa** and **IVc** indicated the conformational changes of the resorcinarene scaffold. Regardless of the solvent used, their spectra contained signals of protons and carbon atoms oriented vertically and horizontally, typical of resorcinarenes in conformation of *hindered boat* (C^{2v} symmetry) [12]. The pointed structural changes resulted from slowing down of the *boat* (**A**)–*crown*-*boat* (**B**) interconversion due to immobilization of eight bulky functional groups at spatially close benzene rings of the macrocycle [13, 14] (Scheme 3).

Spatial orientation of octafunctionalized resorcinarenes **IIIc**–**IIIf** and **IVb** depended on the solvent used, as seen from the ^1H and ^{13}C NMR spectra (see Fig. 1). In chloroform, due to the repulsion of the carbamate groups and slowed interconversion the *boat* conformation was preferential (see Fig. 1a). In dimethylsulfoxide a strong liophilic interaction of the alkyl substituents R [15, 16] favored the *crown* conformation (C_{4v} symmetry) (see Fig. 1b), as evidenced by degeneracy of protons and carbon atoms signal in the NMR spectra.

O-Octatriflatoresorcinarenes **Va**–**Vc** were obtained via interaction of compounds **Ia**–**Ic**, respectively, with **IIc** in pyridine at 20–25°C (Scheme 2). The products were isolated in 60–65% yields. Elemental analysis and mass spectrometry data of compounds **Va**–**Vc** coincided with the theoretical predictions (Table 1). In the^1 H NMR spectra the hydroxy protons signals were absent thus confirming their complete substitution.

^{19}F NMR spectra of compounds **Va** and **Vb** contained pairs of singlet signals of fluorine atoms of triflate fragments of vertically and horizontally oriented benzene rings of resorcinarene scaffold. The downfield part of ^1H and ^{13}C NMR spectra of octatriflates **Va** and **Vb** (reflecting the molecules conformation) corresponded to C_2 symmetry of the macrocyclic scaffolds. In ^{19}F and ^1H NMR spectra of tetrapropylcalixarene **Vc** the signals of the corresponding nuclei were degenerate, typical of *crown* conformation of resorcinarenes C_{4v} symmetry). Comparison of NMR spectra of **Va**–**Vc** and of **IIIa**, **IIIb**, **IIId** confirmed their structural similarity.

The prepared perfunctionalized resorcinarenes **III**–**V** were octadental ligands capable of chelate formation with transition metals, due to spatially close electron-donor substituents of benzene rings of macrocyclic scaffold. Depending on the ligand conformation, the metal ion could coordinate at functional groups of one of the benzene rings [*chair* (**IIIa**)*, hindered boat* (**IIIb**, **IVa**, and **IVc**)], at two adjacent benzene rings [*crown* (**IIIc**–**IIIf** and **IVb**)], or at distal vertically oriented benzene rings [*boat* (**IIIb**, **IVa**, **IVc**, and **Va**–**Vc**)] of the macrocyclic scaffold.

Using the ligands (**IIIa**–**IIIc**, **IVa**, and **IVb**) existing in different conformational states and Pd(II) derivatives we prepared a series of complexes with metal to ligand ratio of 4 : 1 (**VIa**, **VIb**, and **VIIa**–**VIIc**) or 2 : 1 (**VIII**) (Scheme 4). Conditions of the complex formation were slightly different depending on the reagents used. In particular, complex formation of compounds **III** and **IV** with $Pd[C_6H_5CN]_2Cl_2$ occurred at room temperature within 6 h (**III**) or 24 h (**IV**). In the case of compounds **IV** interaction with $PdCl_2$ the reaction mixture was refluxed during 20 min, and then stirred during 24 h at room temperature;

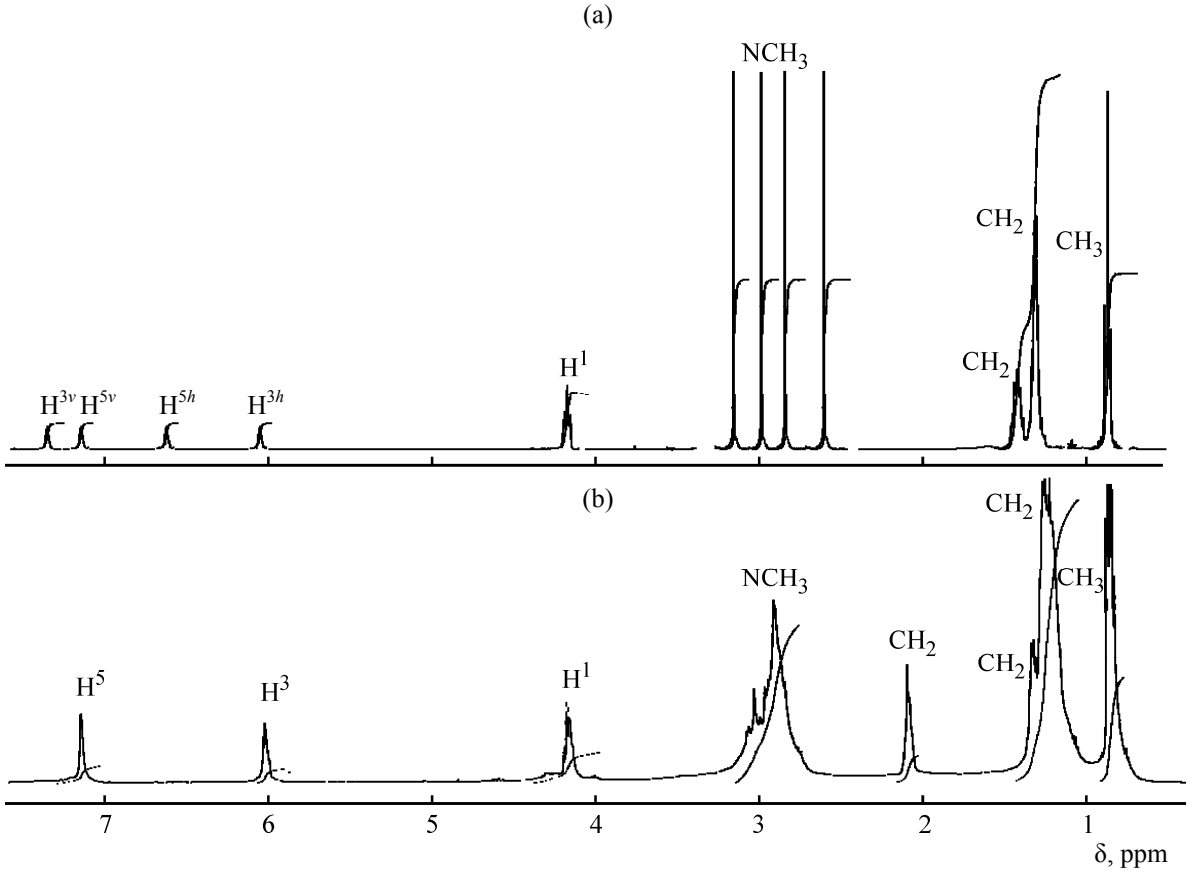


Fig. 1. [1]H NMR spectra of *O*-(dimethyloctacarbamoyl)(tetrahexyl)resorcinarene **IIIe** in $CDCl_3$ (a) and in DMSO-d_6 (b).

in the case of compounds **III** the reaction was complete within 46 h at 35–40°C or within 8 h at 75°C.

Complexes **VI**–**VIII** were yellow powders melting with decomposition (Table 2), insoluble in the majority of organic solvents. Their yields were 62–94%. From elemental analysis data complexes **VI** and **VII** contained four cyclopalladated fragments, whereas two such fragments were found in **VIII**.

Taking into account the ligands pre-organization, we suggest that the cyclopalladation of resorcinarenes with C_2 symmetry [*chair* (**IIIa**) and *hindered boat* (**IIIb**, **IVa**, and **IVb**) conformations with spatially isolated functional groups of the adjacent aromatic rings] occurred via coordination of Pd with functional groups of the same benzene ring. That led to the formation of complexes **VI** and **VII** with four 10-membered metalated cycles, two of which located in the macrocycle plane, and two others located perpendicular to it to the same side (**VIb**, **VIIa**, and **VIIb**) or to different sides (**VIa**) of the plane (Scheme 4).

The interaction of Pd(II) derivatives with *rccc*-octacarbamoylresorcinarene **IIIc** with C_{4v} symmetry (preferential *crown* conformation with spatially close carbamoyl groups located at the adjacent aromatic rings) could lead to the formation of metalated cavitand **VIII** containing two diagonally located 12-membered metalated cycles. Other carbamate groups became distant and lost the ability of chelate formation.

To conclude, the prepared octafunctionalized resorcinarenes **III**–**V** were pre-organized oligodental ligands capable of formation of complexes with defined orientation of metalated fragments. Therefore, they can serve as basis for constructing various supramolecular systems.

EXPERIMENTAL

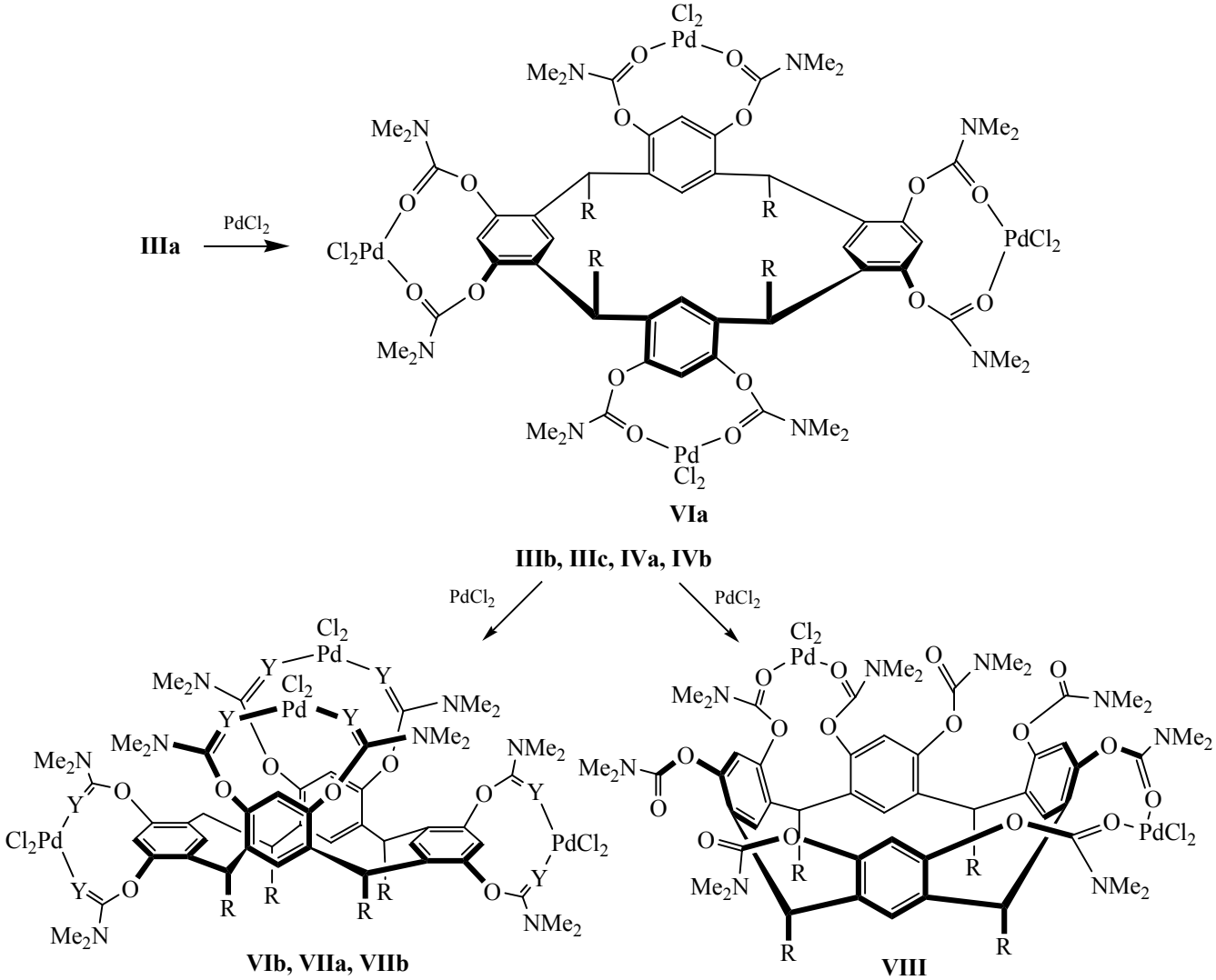
^{1}H and ^{13}C NMR spectra (TMS as internal reference), ^{31}P NMR spectra (85% H_3PO_4 as external reference) were recorded using a Jeol ECX-400 spectrometer [400 (^{1}H) and 100.5 (^{13}C) MHz] at 25°C.

Table 2. Yields, melting points, and elemental analysis data of complexes **VI–VIII**

Comp. no.	Yield, %	Mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
VIa	82[a], 80[b]	205–207[c]	48.55	3.76	4.92	$C_{92}H_{88}Cl_8N_8O_{16}Pd_4$	48.46	3.91	4.94
VIb	88[a], 94[b]	240–242	36.85	3.90	6.11	$C_{56}H_{72}Cl_8N_8O_{16}Pd_4$	36.90	3.98	6.15
VIIa	62[a], 62[b]	291–295[c]	42.14	4.52	6.58	$C_{56}H_{72}Cl_8N_8O_8Pd_4S_8$	42.13	4.55	7.02
VIIb	90[a], 88[b]	290–293[c]	44.63	4.15	4.68	$C_{84}H_{96}Cl_8N_8O_8Pd_4S_8$	45.08	4.62	4.67
VIII	88[a], 83[b]	285–289[c]	46.26	4.41	5.11	$C_{84}H_{96}Cl_4N_8O_{16}Pd_2$	46.22	4.41	5.13

[a] Method *a*. [b] Method *b*. [c] Melting with decomposition.

Scheme 4.



VI, Y = O, R = α-naphthyl (**a**), CH_3 (**b**); **VII**, Y = S, R = Me (**a**), CH_2CH_2Ph (**b**); **VIII**, R = CH_2CH_2Ph.

Mass spectra (MALDI–TOF) were recorded using the Bruker Ultra-flex TOF/TOF spectrometer (Bruker Daltonics GmbH), using 1,8,9-trihydroxyantracene as matrix. IR spectra (4000–500 cm^{-1}, mull in nujol) were registered using a NICOLETTE 380 Thermo spectrometer in reflection mode. Elemental analysis was carried out with a Thermo Flash EA112 CHN-analyzer.

Calix[4]resorcinarenes **Ia–If** were obtained as described in [16, 17].

Carbamoylation of resorcinarenes I. *N,N*-Dimethylcarbamoyl chloride (2.4 mmol) was added to suspension of the corresponding compound **I** (0.2 mmol) and cesium carbonate (2.42 mmol) in 10 mL of acetone. The reaction mixture was refluxed during 8 h at stirring. Then acetone was distilled off, and 10 mL of 5% aqueous sulfuric acid solution was added to the residue. The formed precipitate was filtered off, washed with water (60 mL) and hexane (20 mL), and dried during 5 h at 80–90°C (1 mmHg). In the cases of Ie and **If**, the reaction product was extracted with chloroform (3 × 5 mL) after addition of sulfuric acid. Organic layers were combined, chloroform was distilled off, and the residue was dried during 6 h at 75–80°C (1 mmHg).

***O*-Octa(dimethylcarbamoyl)(tetranaphth-1-yl)-calix[4]resorcinarene (IIIa).** IR spectrum (nujol), ν, cm^{-1}: 1714.3 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 s, 2.35 s, 2.68 s, 2.92 s (12H each, NCH_3); 5.25 s (2H, H^{3h}), 6.20 s (2H, H^{3v}) 6.21 s (4H, H^1), 6.50 d (4H, H^2-Naphth, $^3J_{HH}$ 6.8 Hz), 6.93 d.d (4H, H^7-Naphth, $^3J_{HH}$ 6.8, $^3J_{HH}$ 8.0 Hz), 6.95 d.d (4H, H^3-Naphth, $^3J_{HH}$ 7.3, $^3J_{HH}$ 6.8 Hz), 7.03 d.d (4H, H^6-Naphth, $^3J_{HH}$ 7.1, $^3J_{HH}$ 6.8 Hz), 7.14 s (2H, H^{5h}), 7.17 s (2H, H^{5v}), 7.39 d (4H, H^4-Naphth, $^3J_{HH}$ 8.0 Hz), 7.41 d (4H, H^5-Naphth, $^3J_{HH}$ 7.8 Hz), 7.44 d (4H, H^8-Naphth, $^3J_{HH}$ 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$, 25°C), δ_C, ppm: 34.72 (C^1), 35.25 (NCH_3), 36.13 (NCH_3), 36.14 (NCH_3), 36.21 (NCH_3), 116.70 (C^{5h}), 117.50 (C^{5v}); 124.10, 124.42, 124.53, 124.79, 126.23, 126.34, 127.82, 128.01 s ($C_{Napht}H$); 128.57 (C^{2v}); 128.55 (C^{2h}); 130.62 (C^{3h}), 130.84 (C^{3v}), 147.74 (C^{4h}); 148.50 (C^{4v}), 152.82 (C=O), 153.77 (C=O).

***O*-Octa(dimethylcarbamoyl)(tetramethyl)calix-[4]resorcinarene (IIIb).** IR spectrum (nujol), ν, cm^{-1}: 1720.6 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.46 d (12H, CH_3, $^3J_{HH}$ 6.9 Hz); 2.61 s, 2.82 s, 3.01, 3.09 s (12H each, NCH_3); 4.40 q (4H, H^1, $^3J_{HH}$ 6.8 Hz), 6.01 s (2H, H^{3h}), 6.77 s (2H, H^{5h}), 7.16 s (2H, H^{5v}), 7.37 s (2H, H^{3v}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.31 (CH_3), 32.26 (C^1); 35.99, 36.48, 36.83 (NCH_3); 115.87 (C^{5h}), 116.90 (C^{5v}), 125.26 (C^{3h}), 125.68 (C^{3v}), 131.97 (C^{2v}); 135.68 (C^{2h}), 146.22 (C^{4h}), 148.22 (C^{4v}), 153.89 (C=O), 154.43 (C=O).

***O*-Octa(dimethylcarbamoyl)[tetra(2-phenyl-ethyl)]calix[4]resorcinarene (IIIc).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.23 m (8H, $C\underline{H}_2CH_2PH$), 2.55 br.t (8H, $CH_2C\underline{H}_2PH$), 2.78 s (24H, NCH_3) 2.85 s (24H, NCH_3), 4.33 t (4H, H^1, $^3J_{HH}$ 7.3 Hz), 7.04 m (10H, H^3, *o*-PH), 7.16 m (14H, H^5, *p,m*-PH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 33.92 ($CH_2\underline{C}H_2PH$), 35.47 ($\underline{C}H_2CH_2PH$), 35.88 (NCH_3), 36.03 (C^1), 36.19 (NCH_3), 116.41 (C^5), 125.66 (C^2), 126.08 (C^3), 128.10 (PH), 128.14 (PH), 141.39 (C^4), 153.35 (C=O).

***O*-Octa(dimethylcarbamoyl)(tetrapropyl)calix[4]-resorcinarene (IIId).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.83 t (12H, $CH_2CH_2C\underline{H}_3$, $^3J_{HH}$ 7.3 Hz), 1.14 m (8H, $CH_2C\underline{H}_2CH_3$, $^3J_{HH}$ 7.4 Hz), 2.03 m (8H, $C\underline{H}_2CH_2CH_3$); 2.46 s (24H, NCH_3), 2.64 s (24H, NCH_3), 4.16 t (4H, $^3J_{HH}$ 7.4 Hz), 6.10 s (4H, H^3), 7.19 s (4H, H^5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.39 s (CH_3), 20.90 s (CH_2), 21.19 s (CH_2), 33.09 s (C^1); 36.10 s, 36.75 s, 38.77 s; 40.01 s (NCH_3); 102.92 s (C^5), 123.78 s (C^3), 125.48 s (C^2), 152.11 s (C^4), 154.02 s (C=O).

***O*-Octa(dimethylcarbamoyl)(tetrahexyl)calix[4]-resorcinarene (IIIe).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.83 t [12H, $CH_2(CH_2)_4C\underline{H}_3$, $^3J_{HH}$ 6.4 Hz], 1.22 m [32H, $CH_2(C\underline{H}_2)_4CH_3$], 1.75 m [8H, $C\underline{H}_2(CH_2)_4CH_3$]; 2.62 s, 2.80 s, 3.00 s, 3.08 s (12H each, NCH_3); 4.26 t (4H, H^1, $^3J_{HH}$ 6.8 Hz), 6.06 s (2H, H^{3h}), 6.69 s (2H, H^{5h}), 7.19 s (2H, H^{5v}), 7.32 s (2H, H^{3v}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.84 t [12H, $CH_2(CH_2)_4C\underline{H}_3$, $^3J_{HH}$ 6.8 Hz], 1.25 m [32H, $CH_2(C\underline{H}_2)_4CH_3$], 2.08 m [8H, $C\underline{H}_2(CH_2)_4CH_3$], 2.89 s (24H, NCH_3), 2.91 s (24H, NCH_3), 4.16 t (4H, H^1, $^3J_{HH}$ 7.55 Hz), 6.00 s (4H, H^3), 7.12 s (4H, H^5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.11 (CH_3), 22.80 (CH_2), 23.05 (CH_2), 28.20 (CH_2), 29.71 (CH_2), 31.84 (CH_2), 33.09 (C^1); 36.47, 36.60, 36.74, 36.78 (NCH_3); 115.88 (C^5), 117.08 (C^5), 125.94 (C^3), 126.03 (C^3), 130.03 (C^2), 134.62 (C^2), 146.04 (C^4), 148.75 (C^4), 153.93 (C=O), 154.28 (C=O). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.76 (CH_3), 22.04 (CH_2), 27.60 (CH_2), 28.85 (CH_2), 31.17 (CH_2), 31.51 (CH_2), 35.49 (C^1), 36.28 (NCH_3), 38.18 (NCH_3), 102.57 (C^5), 123.08 (C^3), 125.66 (C^2), 151.65 (C^4), 153.48 (C=O).

***O*-Octa(dimethylcarbamoyl)(tetranonyl)calix[4]-resorcinarene (IIIf).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.84 t [12H, $CH_2(CH_2)_7C\underline{H}_3$, $^3J_{HH}$ 6.9 Hz], 1.22 m [56H, $CH_2(C\underline{H}_2)_7CH_3$], 2.00 m [8H, $C\underline{H}_2(CH_2)_7CH_3$], 2.88 br.s (48H, NCH_3), 4.17 t (2H, H^1, $^3J_{HH}$ 7.4 Hz), 4.22 t (2H, H^1, $^3J_{HH}$ 7.6 Hz), 6.15 s (4H, H^3), 7.12 s (4H, H^5). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.40 (CH_3), 22.90 (CH_2), 21.18 (CH_2), 33.09 (C^1), 36.10 (NCH_3), 36.75 (NCH_3), 102.92 (C^5), 123.72 (C^2), 125.48 (C^3), 152.11 (C^4), 154.28 (C=O).

Thiocarbamoylation of resorcinarenes I. *N,N*-Dimethylthiocarbamoyl chloride (9.6 mmol) was added to suspension of the corresponding compound **I** (0.8 mmol) and cesium carbonate (9.6 mmol) in 10 mL of acetone. The reaction mixture was refluxed during 48 h at stirring. Then acetone was distilled off, and 10 mL of 5% sulfuric acid was added to the residue. The precipitate was filtered off, washed with water (60 mL) and hexane (20 mL), and dried during 5 h at 80–90°C (1 mmHg).

***O*-Octa(dimethylthiocarbamoyl)(tetramethyl)-calix[4]resorcinarene (IVa).** IR spectrum (nujol), ν, cm^{-1}: 1173.4 (C=S), 1135.6 (C=S). ^{1}H NMR spectrum ($CDCl_3$, 25°C), δ, ppm: 1.56 d (12H, CH_3, $^3J_{HH}$ 6.9 Hz); 2.95 s, 3.23 s, 3.35 s, 3.44 s (12H each, NCH_3); 4.35 q (4H, H^1, $^3J_{HH}$ 7.3 Hz), 6.47 s (2H, H^{3h}), 6.89 s (2H, H^{5v}), 7.25 s (2H, H^{5h}), 7.47 s (2H, H^{3v}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.45 (CH_3), 32.17 (C^1); 38.42, 39.36, 42.98, 43.52 (NCH_3); 119.43 (C^{5h}, C^{5v}), 126.18 (C^{3h}), 126.79 (C^{3v}), 132.63 (C^{2v}), 136.50 (C^{2h}), 148.61 (C^{4h}); 150.55 (C^{4v}), 186.30 (C=S), 187.09 (C=S).

***O*-Octa(dimethylthiocarbamoyl)[tetra(2-phenyl-ethyl)]calix[4]resorcinarene (IVb).** IR spectrum (nujol), ν, cm^{-1}: 1170.6 (C=S), 1128.8 (C=S). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.31 m (8H, $C\underline{H}_2CH_2Ph$, $^3J_{HH}$ 6.9, $^3J_{HH}$ 7.3 Hz), 2.57 m (4H, $CH_2C\underline{H}_2Ph$, $^3J_{HH}$ 7.8 Hz), 2.75 m (4H, $CH_2C\underline{H}_2Ph$, $^3J_{HH}$ 6.4 Hz); 2.92 s, 3.05 s, 3.18 s, 3.31 s (12H, NCH_3); 4.24 t (4H, H^1, $^3J_{HH}$ 6.4 Hz), 6.61 s (2H, H^{3h}), 6.65 s (2H, H^{5v}), 6.80 s (2H, H^{5h}), 7.06–7.15 m (20H, PH) 7.59 s (2H, H^{3v}). ^{1}H NMR spectrum (DMSO-d_6), δ_C, ppm: 2.46 m (8H, $C\underline{H}_2CH_2PH$), 2.95 m (8H, $CH_2C\underline{H}_2PH$), 3.21 s (24H, NCH_3), 3.30 s (24H, NCH_3), 4.25 t (4H, H^1, $^3J_{HH}$ 6.4 Hz), 7.00 m (10H, Ph, H^{3h}), 7.11 s (16H, Ph, H^{5v}). ^{13}C NMR spectrum ($CDCl_3$, δ_C, ppm: 34.19 ($CH_2\underline{C}H_2PH$), 36.27 ($\underline{C}H_2CH_2PH$), 36.54 (C^1); 38.61, 39.36, 42.92, 43.42 s (NCH_3); 119.47 (C^{5h}), 120.63 (C^{5v}), 125.61 (PH), 127.32 (C^{3h}), 128.68 (PH), 129.10 (PH), 129.82 (C^{3v}), 135.22 (C^{2v}), 141.59 (C^{2h}); 148.63 (C^{4h}), 151.77 (C^{4v}), 186.29 (C=S), 186.67 (C=S). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 34.48 (CH_2), 36.27 (CH_2), 36.97 (C^1), 38.77 (NCH_3), 43.34 (NCH_3), 119.41 (C^5), 126.08 (PH), 127.00 (C^3), 128.61 (PH), 128.81 (PH), 141.87 (C^2); 148.63 (C^4), 186.26 (C=S).

***O*-Octa(dimethylthiocarbamoyl)(tetrapropyl)-calix[4]resorcinarene (IVc).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.80 br.s (12H, $CH_2CH_2C\underline{H}_3$), 1.20 br.s (8H, $CH_2C\underline{H}_2CH_3$), 1.83 br.s (8H, $C\underline{H}_2CH_2CH_3$), 2.46 s (24H, NCH_3), 2.89 s (24H, NCH_3), 4.19 br.t (4H, H^1), 6.27 br.s (2H, H^{3h}), 6.56 br.s (2H, H^{5v}), 6.84 br.s (2H, H^{5h}), 7.42 br.s (2H, H^{3v}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.03 (CH_3), 20.77 ($\underline{C}H_2CH_3$), 20.93 ($CH\underline{C}H_2$), 32.20 (C^1); 38.61, 39.86, 40.28, 40.49 (NCH_3); 118.26 (C^5), 126.49 (C^3), 132.10 (C^2), 153.79 (C^4), 185.90 (C=S), 186.16 (C=S).

Triflate derivatives of resorcinarenes I. Trifluoromethylsulfonic acid anhydride (2.8 mmol) was added dropwise to a solution of 0.3 mmol of the corresponding compound **I** in 3 mL of pyridine at cooling to 0°C. The reaction mixture was maintained during 24 h at room temperature, and then 20 mL of water was added. The formed precipitate was filtered off, washed with 5% hydrochloric acid (20 mL) and with water till neutral reaction, and with hexane (20 mL). The precipitate was dried at 80–90°C (1 mmHg).

***O*-Octa(trifluoromethylsulfonyl)(tetranaphth-1-yl)calix[4]resorcinarene (Va).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.80 s (2H, H^{3h}), 6.29 d (4H, H^2-Napht, $^3J_{HH}$ 6.9 Hz), 6.35 s (2H, H^{3v}), 6.59 s (4H, H^1), 6.98 d.d (8H, H^3-Napht, H^7-Napht, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.7 Hz), 7.21 d (4H, H^8-Napht, $^3J_{HH}$ 8.3 Hz), 7.25 d.d (4H, H^6-Napht, $^3J_{HH}$ 7.4, $^3J_{HH}$ 6.8 Hz), 7.61 d (4H, H^4-Napht, $^3J_{HH}$ 8.3Hz), 7.63 s (2H, H^{5h}), 7.65 d (4H, H^5-Napht, $^3J_{HH}$ 8.2 Hz), 7.88 s (2H, H^{5v}). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 38.74 (C^1), 102.57 (C^5), 122.55 q (CF, $^3J_{CF}$ 308.6 Hz), 124.08 ($C_{Napht}H$), 124.25 ($C_{Napht}H$), 124.41 ($C_{Napht}H$), 124.47 ($C_{Napht}H$), 124.63 ($C_{Napht}H$), 125.13 ($C_{Napht}H$), 126.01 ($C_{Napht}H$), 128.20 (C^{2h}), 128.37 (C^{2v}), 131.67 (C^3, $C_{Napht}H$), 133.50 (C^3, $C_{Napht}H$), 141.25 ($C_{Napht}H$), 152.70 (C^{4h}), 153.64 (C^{4v}). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: –74.49, –75.35.

***O*-Octa(trifluoromethylsulfonyl)(tetramethyl)-calix[4]resorcinarene (Vb).** ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.79 d (12H, CH_3, $^3J_{HH}$ 6.9 Hz), 4.79 q (4H, CH, $^3J_{HH}$ 6.9 Hz), 6.77 s (2H, H^{3h}), 7.14 s (2H, H^{5v}), 7.47 s (2H, H^{5h}), 7.66 s (2H, H^{3v}). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 19.24 (CH_3), 32.39

(C^1), 114.52 (C^5), 118.50 q (CF, $^3J_{CF}$ 319.2 Hz), 129.33 (C^2), 129.59 (C^3), 145.66 (C^4). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: –73.71, –74.17.

***O*-Octa(trifluoromethylsulfonyl)(tetrapropyl)-calix[4]resorcinarene (Vc).** ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.99 t (12H, $CH_2CH_2C\underline{H}_3$, $^3J_{HH}$ 6.9 Hz), 1.41 m (8H, $CH_2C\underline{H}_2CH_3$), 2.02 m (8H, $C\underline{H}_2CH_2CH_3$), 4.57 t (4H, CH, $^3J_{HH}$ 7.4 Hz), 8.04 s (4H, H^5), 8.89 s (4H, H^3). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 13.27 (CH_3), 20.84 (CH_2), 35.75 (CH_2), 37.38 (C^1), 114.57 (C^5), 118.39 q (CF, $^3J_{CF}$ 320.2 Hz), 129.86 (C^2), 135.16 (C^3), 146.07 (C^4). ^{19}F NMR spectrum (acetone-d_6): δ_F –74.08 ppm

Complex VIa. *a*. 0.02 mmol of palladium chloride was added to solution of 0.005 mmol of compound **IIIa** in 4 mL of methylene chloride. The reaction mixture was kept during 46 h at 35–40°C. Methylene chloride was distilled off, 4 mL of chloroform was added to the residue, and the mixture was heated during 8 h at 75°C. 10 mL oh hexane was added, the formed precipitate was filtered off, washed with 15 mL of hexane, and dried at 80–90°C (1 mmHg) during 5 h.

b. 0.012 mmol of palladium chloride adduct with benzonitrile was added to solution of 0.003 mmol of compound **IIIa** in 4 mL methylene chloride. The reaction mixture was kept during 6 h at room temperature, then 10 mL of hexane was added to the mixture, the formed precipitate was filtered off, washed with 15 mL of hexane, and dried at 80–90°C (1 mmHg) during 5 h.

Complex **VIb** was prepared similarly via interaction of 0.005 mmol of **IIIb** with 0.02 mmol of the corresponding palladium salt (methods *a* and *b*).

Complex VIIa. *a*. 0.26 mmol of palladium chloride was added to solution of 0.065 mmol of compound **IVa** in 4 mL of methylene chloride. The reaction mixture was kept during 20 min at 35–40°C and then 24 h at 20–25°C. 5 mL of hexane was added to the mixture, the formed precipitate was filtered off, washed with 15 mL of hexane, and dried at 20–25°C (1 mmHg) during 6 h.

b. 0.012 mmol of palladium chloride adduct with benzonitrile was added to solution of 0.003 mmol of compound **IVa** in 4 mL methylene chloride. The reaction mixture was kept during 24 h at room temperature, then 5 mL of hexane was added to the mixture, the formed precipitate was filtered off, washed with 15 mL of hexane, and dried at 20–25°C (1 mmHg) during 8 h.

Complex **VIIb** was prepared similarly via interaction of 0.046 mmol of **IVb** and 0.18 mmol of the corresponding palladium salt (methods *a* and *b*).

Complex **VIII** was prepared similarly to **VIa** via interaction of 0.003 mmol of **IIIc** with 0.012 mmol of the corresponding palladium salt (methods *a* and *b*).

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 12-03-00213a).

REFERENCES

1. Steed, J.W. and Atwood, J.L., *Supramolecular Chemistry*, Wiley, 2009.
2. Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, Wiley, 1995.
3. Wieser, C., Dieleman, C.B., and Matt, D., *Coord. Chem. Rev*., 1997, vol. 165, p. 93.
4. Asfari, Z., Boehmer, V., Harrowfield, J., and Vicens, J., *Calixarenes*, Dordrecht: Kluwer Academic Publishers, 2001, p. 24.
5. Dutasta, J.-P., *Top. Curr. Chem*., 2004, vol. 232, no. 3, p. 55.
6. Nifantyev, E.E., Maslennikova, V.I., and Merkulov, R.V., *Acc. Chem. Res*., 2005, vol. 38, no. 2, p. 108.
7. Botta, B., Cassani, M., D'Acquarica, I., Misiti, D., Subissati, D., and Delle Monache, G., *Cur. Org. Chem*., 2005, vol. 9, p. 337.
8. Dubessy, B., Harthong, S., Aronica, C., Bouchu, D., Busi, M., Dalcanale, E., and Dutasta, J.-P., *J. Org. Chem*., 2009, vol. 74, p. 3923.
9. Cram, D.J., *Angew. Chem. Int. Ed. Engl*., 1988, no. 27, p. 1009.
10. Timmerman, P., Verboom, W., and Reinhoudt, D.N., *Tetrahedron*., 1996, vol. 52, no. 8, p. 2663.
11. Maslennikova, V.I., Serkova, O.S., Guzeeva, T.V., Vasyanina, L.K., Lysenko, K.A., Kopteva, V.V., and Nifantiev, E.E., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 3, p. 392.
12. Maslennikova, V.I., Serkova, O.S., Gruner, M., Goutal, S., Bauer, I., Habicher, W.D., Lyssenko, K.A., Antipin, M.Yu., and Nifantiev, E.E., *Eur. J. Org. Chem*., 2004, vol. 23, p. 4884.
13. Högberg, A.G.S., *J. Am. Chem. Soc*., 1980, vol. 102, p. 6046.
14. Abis, L., Dalcanale, E., Du Vosel, A., and Spera, S., *J. Chem. Soc., Perkin Trans 2*, 1990, no. 12, p. 2075.
15. Cram, D.J., Karbach, S., Kim, H.-E., Knobler, C.B., Maverick, E.F., Ericson, J.L., and Helgeson, R.C., *J. Am. Chem. Soc*., 1988, vol. 110, no. 7, p. 2229.
16. Tunstad, L.M., Tucker, J.A., Dalkanale, E., Weiser, J., Bryant, J.A., Sherman, J.C., Helgeson, R.C., Knobler, C.B., and Cram, D.J., *J. Org. Chem*., 1989, vol. 54, no. 6, p. 1305.
17. Sakhaii, P., Neda, I., Freytag, M., Thonnessen, H., Jones, P.G., and Schmutzler, R., *Z. Anorg. Allg. Chem*., 2000, no. 626, p. 1246.