

## ***N*-Aryl- and *N*-Vinyl-diaza-18-crown-6: Synthesis and Complexing Ability**

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**Abstract**—The nucleophilic aromatic and vinyl substitution using diaza-18-crown-6 as nucleophile afforded a number of its *N,N'*-diaryl- [aryl = 2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 4-C<sub>5</sub>F<sub>4</sub>N, 4-CF<sub>3</sub>C<sub>6</sub>F<sub>4</sub>] and *N,N'*-dialkenyl-substituted derivatives [alkenyl = PhC(O)CH=CH, MeOCOCH=CH, (EtO<sub>2</sub>C)<sub>2</sub>C=C(Ph), etc.]. Arylation of diaza-18-crown-6 with nonactivated aryl bromides, such as 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Br, 4-MeOC<sub>6</sub>H<sub>4</sub>Br, C<sub>6</sub>H<sub>5</sub>Br, and 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br, was effected under catalysis by palladium complexes. *N,N'*-Diaryldiaza-18-crowns-6 having electron-acceptor substituents in the aromatic rings turned out to be incapable of forming complexes with metal cations, while their analogs containing electron-donor *para*-methoxy and *para*-dimethylamino groups gave complexes with barium perchlorate.

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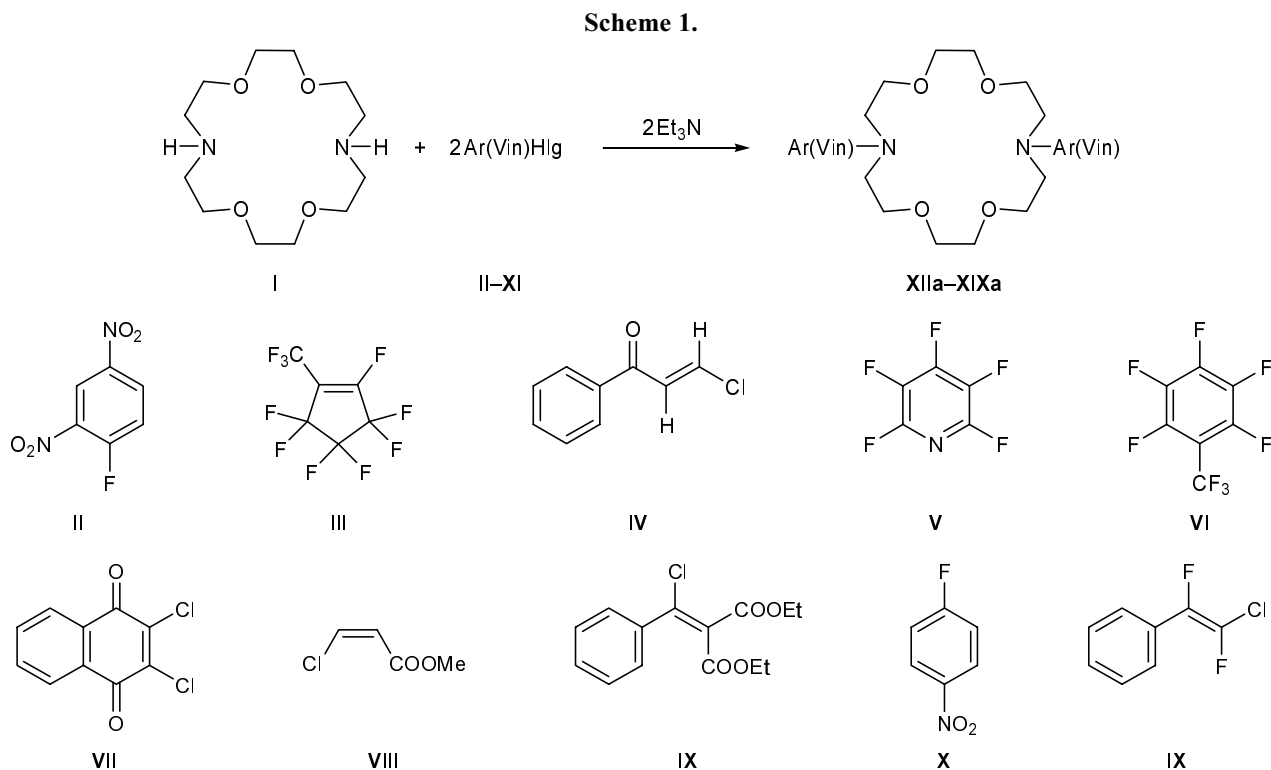
Aza crown ethers occupy a specific place among crown compounds due to their ability to be modified at the nitrogen atoms; the introduced substituents may thus be involved in direct conjugation with the donor center. This opens almost unlimited prospects in variation of coordinating properties of macrocyclic ligands, including its “fine tuning” to ensure high selectivity for a certain metal ion or a group of metal ions [1–13]. Depending on the substituent nature, such compounds may exhibit properties of fluoro- and chromoionophores [4, 9, 14–21] and di- and polytopic electro- and photoswitchable receptors [14, 22, 23]; they could also form the basis for creation of self-organizing supramolecular systems [1, 24].

Interaction of a substituent with the donor center (nitrogen atom) of an aza crown ether should be the strongest when the conjugation chain is continuous, e.g., when the substituent is linked to nitrogen through an unsaturated or aromatic bridging group. However, only a few examples of *N*-vinyl aza crown ethers have been reported so far [9, 25], and most of them belong to the quinone series [26–28]. *N*-Arylated aza crown compounds are much more readily accessible, but their syntheses are usually fairly laborious, and they include a number of steps [13, 29]. On the other hand, it is obvious that both *N*-vinyl and *N*-aryl aza crown ethers can readily be obtained in one step from aza crown ether and aryl or vinyl halide via nucleophilic aromatic

or vinyl substitution. In the recent years, some studies utilizing the above approach have been reported; nucleophilic substitution in weakly activated aryl halides was effected under high pressure [12] or in the presence of palladium complexes [19, 30]. Nevertheless, nucleophilic substitution in activated aryl and vinyl halides was used in the synthesis of substituted aza crown ethers fairly rarely.

In the present work we examined the synthetic potential of S<sub>N</sub>Ar (S<sub>N</sub>Vin) reactions as applied to the preparation of aryl- and alkenyl-substituted diaza-18-crowns-6. Electron-acceptor properties of activated aromatic and unsaturated systems should inevitably reduce the coordinating power of the resulting aza crown compounds but should simultaneously enhance their selectivity. In addition, we continued the study of palladium-catalyzed arylation of aza crown ethers, which was initiated by Witulski [19] and Buchwald [30] with monoaza crown ethers as examples; we extended the developed approach to diaza-18-crown-6 (**I**). Some of the prepared arylated and vinylated derivatives of diaza-18-crown-6 were tested for coordinating ability with respect to metal cations, mainly lanthanide cations.

Various aryl and vinyl halides, both perfluorinated and activated by nitro groups or (in the case of vinyl halides) other electron-acceptor substituents, were involved in reaction with diaza-18-crown-6 (**I**) (Table 1,



Scheme 1). Crown ether (**I**) reacted with the most active substrates, such as 2,4-dinitrofluorobenzene (**II**), perfluoro-(1-methylcyclopentene) (**III**), and  $\beta$ -chlorovinyl phenyl ketone (**IV**), even at room temperature. The reactions of **I** with pentafluoropyridine (**V**), perfluorotoluene (**VI**), 2,3-dichloro-1,4-naphthoquinone (**VII**), methyl *cis*-3-chloroacrylate (**VIII**), and diethyl  $\alpha$ -chlorobenzylidenemalonate (**IX**) required heating to 60–100°C. Less activated halogen derivatives, namely *p*-nitrofluorobenzene (**X**) and  $\beta$ -chloro- $\alpha,\beta$ -difluoro-

styrene (**XI**), failed to react with diaza-18-crown-6 (Table 1).

The nucleophilic substitution products, *N,N'*-disubstituted compounds **XIIa–XIXa**, can be obtained in nearly quantitative yield. In order to attain high yields in reactions with less activated aryl and vinyl halides **VI**, **VII**, and **IX**, the process should be performed in a more polar solvent such as dimethylformamide (DMF); in tetrahydrofuran (THF), the yield did not exceed 50–60% (Table 1, run nos. 6, 7, 9, 10). The

**Table 1.** Reaction of diaza-18-crown-6 (**I**) with activated aryl and vinyl halides

Run no.	Aryl (vinyl) halide no.	Solvent	Reaction time	Temperature, °C	Product no.	Yield, %
1	<b>II</b>	THF	<5 min	20	<b>XIIa</b>	95
2	<b>III</b>	THF	<5 min	20	<b>XIIIa</b>	90
3	<b>IV</b>	THF	<5 min	20	<b>XIVa</b>	80
4	<b>V</b>	THF	4 h	60	<b>XVa</b>	90
5	<b>VI</b>	DMF	4 h	100	<b>XVIa</b>	93
6	<b>VII</b>	THF	4 h	60	<b>XVIIa</b>	60
7	<b>VII</b>	DMF	4 h	90	<b>XVIIa</b>	90
8	<b>VIII</b>	THF	4 h	70	<b>XVIIIa</b>	90
9	<b>IX</b>	THF	20 h	100	<b>XIXa</b>	50
10	<b>IX</b>	DMF	4 h	100	<b>XIXa</b>	75
11	<b>X</b>	DMF	12 h	100	–	0
12	<b>XI</b>	THF	48 h	100	–	0

reaction of diaza-18-crown-6 (**I**) with chloroacrylate **VIII** gave only *trans* isomer **XVIIIa**, i.e., the configuration of the double bond was not retained.

The isolated diarylated diaza-18-crowns-6 are readily soluble in chloroform and methylene chloride, less readily soluble in acetone and methanol, and insoluble in petroleum ether. The solubility in acetone decreases in going from perfluorinated derivatives **XIIIa**, **XVa**, and **XVIa** to those containing ester groups, i.e., crown ether **XVIIIa** and especially **XIXa**.

The ability of *N,N'*-diaryldiaza-18-crowns-6 to form complexes with metals was studied by spectrophotometry (in methanol) and  $^1\text{H}$  NMR spectroscopy (in acetone- $d_6$ ). Shift of the UV absorption band of the ligand or shift and/or broadening of signals in the  $^1\text{H}$  NMR spectrum indicated formation of a complex. According to published data, complex formation of substituted aza crown ethers with diamagnetic metal cations is accompanied by an appreciable shift of the  $^1\text{H}$  NMR signals [5, 8, 12]. In the  $^1\text{H}$  NMR spectrum of the complex formed by praseodymium nitrate with initial crown ether **I** we observed strong paramagnetic shifts of signals from protons in the macroring (by up to 5 ppm both upfield and downfield) and line broadening.

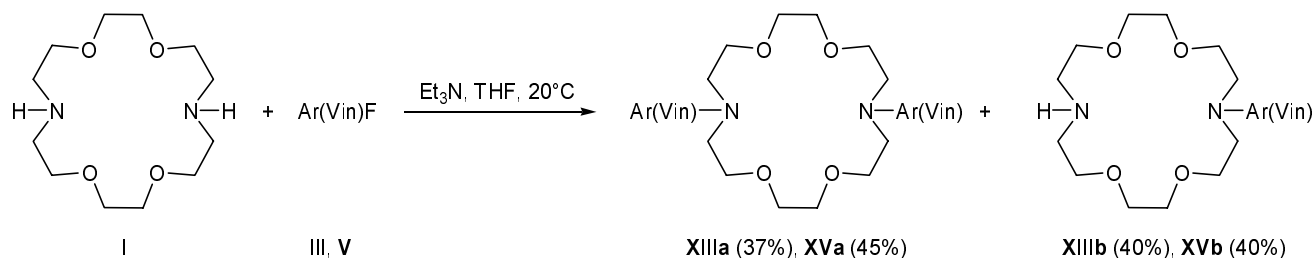
The  $^1\text{H}$  NMR spectrum of aza crown ether **XVa** ( $c \approx 2 \times 10^{-2}$  M) did not change on addition of an equimolar amount of  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  both in the presence and in the absence of  $\text{ZnCl}_2$  or  $\text{KCNS}$ . No variation of the absorption pattern was observed in the UV spectra of *N,N'*-diaryldiaza-18-crowns-6 **XIIIa**, **XVa**, and **XVIa** [ $\text{Ar} = 4\text{-C}_3\text{F}_4\text{N}$ ,  $4\text{-CF}_3\text{C}_6\text{F}_4$ ,  $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$ ] in the presence of a large excess of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{LiCl}$ , or  $\text{ZnCl}_2$ . We also failed to isolate crystalline complexes of the above crown compounds. Only the initial crown ether always crystallized from solutions containing metal salts. We can conclude that *N,N'*-diaryl diaza-18-crown-6 derivatives containing strong electron-acceptor substituents in the

aromatic rings and no additional coordination centers are incapable of binding metal cations. This conclusion is consistent with the extremely low coordinating power of *N,N'*-dipenyldiaza-18-crown-6 with respect to alkali and alkaline-earth metal cations, which was noted in [13]. It should also be emphasized that X-ray diffraction study of crown ethers **XIIIa**, **XVa**, and **XVIa** revealed considerable distortion of the shape of the macroring cavity, as compared to unsubstituted diaza-18-crown-6 [31, 32]; this factor, in combination with electronic effects, may be responsible for the weak complexing ability of these compounds.

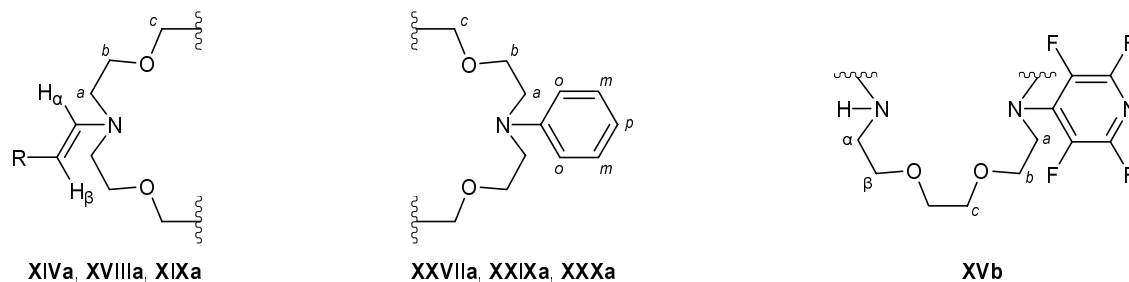
The alkenyl-substituted diaza crown ethers, except for perfluoro(methylcyclopentene) derivative **XIIIa**, contain a carbonyl group in the side chain; the carbonyl oxygen atom therein is also capable of coordinating metal ions. In fact, addition of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  to *N,N'*-dialkenyl-substituted compounds **XIVa**, **XVIIIa**, and **XIXa** induced more or less pronounced variations in the  $^1\text{H}$  NMR spectra (Table 2) and a red shift of the UV absorption maxima. Only naphthoquinone derivative **XVIIa** showed no indications of complex formation with  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $^1\text{H}$  NMR, UV). As shown in [33], bis(ketovinyl)-substituted aza crown ether **XIVa** was characterized by an unusual selectivity for rare-earth metal cations [33].

Taking into account the well-known ability of *N*-arylated monoaza crown compounds to bind various metal cations [4, 14, 15, 18–23], we made an attempt to synthesize monoaryl and monovinyl derivatives of diaza-18-crown-6 by treatment of the latter with an equimolar amount of pentafluoropyridine or perfluoro-(1-methylcyclopentene) in the presence of triethylamine. These reactions led to formation of mixtures of approximately equal amounts of the corresponding mono- and disubstituted compounds (**XIIIb/XIIIa** and **XVb/XVa**, Scheme 2) which can readily be separated by chromatography. We failed to obtain monosubstituted crown ether **XVb** as the only product by reaction of diaza-18-crown-6 dilithium salt (prepared by

Scheme 2.



**III, XIII**, Vin = perfluoro(2-methylcyclopentenylyl); **V, XV**, Ar = perfluoro(pyridin-4-yl).

**Table 2.** Variation of proton chemical shifts due to complex formation in the  $^1\text{H}$  NMR spectra of *N*-aryl- and *N*-alkenyl-substituted diaza crown ethers ( $c = 2 \times 10^{-2}$  M, acetone- $d_6$ , 20°C)

Crown ether no.	Metal salt <sup>a</sup>	$\Delta\delta = \delta(\text{complex}) - \delta(\text{crown ether})$							
		$\alpha$ -H	$\beta$ -H	$H_a$	$H_b$	$H_c$	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H
<b>XIVa<sup>b</sup></b>	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0.56	0.45	-0.12 to 0.05			0.18	-0.15 to 0.08	
<b>XVIIIa</b>	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0.20	0.10	0.02	0.03	0.01	–	–	–
<b>XIXa</b>	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	–	–	~0.05	0.51	~0.15	~0.15	~0.07	~0.20
<b>XVb</b>	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0.65	0.08 to 0.10				–	–	–
<b>XXIXa</b>	$\text{Ba}(\text{ClO}_4)_2$	–	–	-0.15	0.06	0.21	0.68	0.19	–
<b>XXXa</b>	$\text{Ba}(\text{ClO}_4)_2$	–	–	-0.15	0.06	0.22	0.61	0.08	–
<b>XXVIIa</b>	$\text{Ba}(\text{ClO}_4)_2$	–	–	-0.06	0.03	0.08	0.26	0.10	0.23

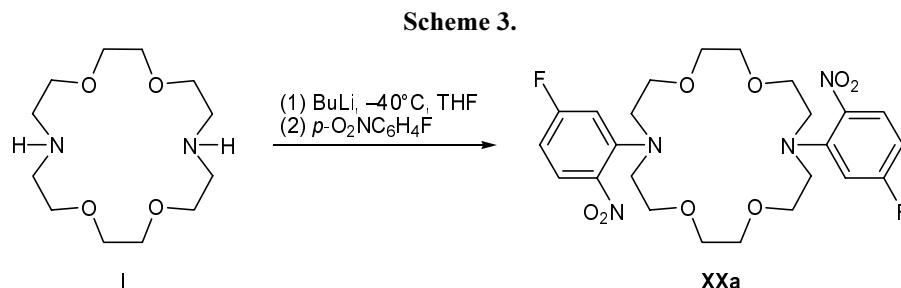
<sup>a</sup> 2 equiv.<sup>b</sup> In the presence of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , the alkenyl groups become nonequivalent; given are the largest variations in the chemical shifts.

metalation of crown ether **I** with butyllithium) with an equimolar amount of pentafluoropyridine. Moreover, the expected product was not formed at all. Apart from a considerable amount of disubstituted compound **XVa**, the reaction mixture contained a number of unidentified products which were difficult to separate.

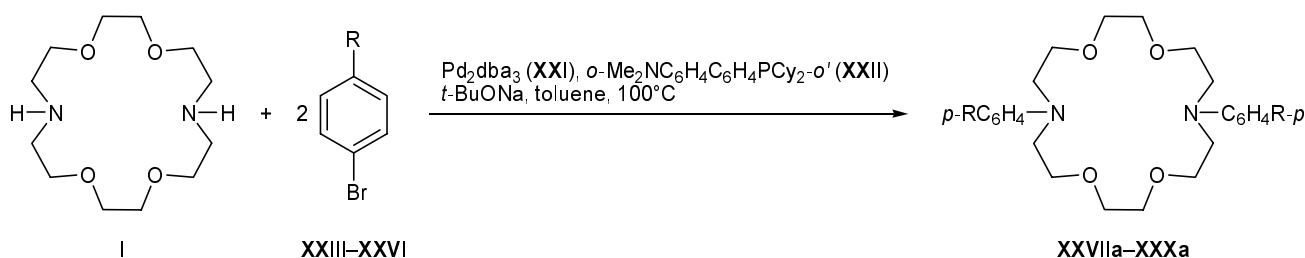
Unusual results were obtained in the reaction of diaza-18-crown-6 dilithium salt with weakly activated *p*-nitrofluorobenzene (**X**) which was inert toward crown ether **I** in the presence of a base (Table 1, run no. 11). We succeeded in isolating from the reaction mixture only two products, one of which was disubstituted diaza-18-crown-6 **XXa** and the other was a mixture of *N*-aryl derivatives presumably formed via opening or rearrangement of the macroring. The aromatic residue in the products was 2-nitro-5-fluoro-

phenyl rather than 4-nitrophenyl, i.e., the reaction occurred as replacement of hydrogen rather than fluorine atom (Scheme 3). Nucleophilic substitution of hydrogen in aromatic compounds ( $\text{S}_{\text{N}}\text{H}_{\text{Ar}}$ ) is well known; it often occurs by the action of strongly basic nucleophiles (e.g., Grignard compounds, amide ions, etc.) which give rise to stable anionic  $\sigma$  complexes; the subsequent oxidation of the latter, e.g., with the initial nitroaromatic compound, yields final hydrogen replacement products [34].

Despite the presence of electron-acceptor tetrafluoropyridin-4-yl substituent, monoarylated diaza-18-crown-6 **XVb** gave fairly stable complexes with metal cations, e.g., with  $\text{La}^{3+}$ , as followed from the observed variations in the  $^1\text{H}$  NMR spectrum of **XVb** in the presence of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Table 2).



## Scheme 4.



**XXIII, XXVIIa**, R = H; **XXIV, XXVIII**, R = CF<sub>3</sub>; **XXV, XXIXa**, R = MeO; **XXVI, XXXa**, R = Me<sub>2</sub>N.

Another approach to coordinately active *N*-aryl derivatives of diaza-18-crown-6 implies introduction of aromatic groups having electron-donor substituents to the nitrogen atoms. The corresponding aryl halides are not activated to S<sub>N</sub>Ar reactions, and they do not react with aza crown ethers. However, Zhang and Buchwald [30] recently showed that monoaza crown ethers can successfully be arylated with nonactivated and deactivated aryl halides in the system Pd<sub>2</sub>dba<sub>3</sub>·CHCl<sub>3</sub> (**XXI**)–*N,N*-dimethyl-2'-dicyclohexylphosphinobiphenyl-2-amine (**XXII**)–*t*-BuONa–toluene [30]. We tried to apply the same conditions to the arylation of diaza-18-crown-6 (**I**). We examined arylation of diaza-18-crown-6 (**I**) with bromobenzene (**XXIII**) and aryl bromides containing both electron-acceptor (**XXIV**, R = *p*-CF<sub>3</sub>) and electron-donor substituents (**XXV**, R = *p*-OMe; **XXVI**, R = *p*-Me<sub>2</sub>N). In all cases, the corresponding bis-arylation products, *N,N'*-diaryl diaza crown ethers **XXVIIa–XXXa**, were obtained in good yields, the conversion of the initial aryl bromide being complete (Scheme 4, Table 3). It should be noted that the use of such a universal phosphine ligand as Xantphos [9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene] instead of ligand **XXII** afforded only 80% conversion of *p*-bromotrifluoromethylbenzene in 20 h.

The whole series of *N,N'*-diaryldiaza-18-crowns-6 prepared by palladium-catalyzed arylation of crown

ether **I** was tested for complexing ability with respect to Ba(ClO<sub>4</sub>)<sub>2</sub>. Addition of Ba(ClO<sub>4</sub>)<sub>2</sub> to solutions (acetone-*d*<sub>6</sub>) of crown ethers **XXIXa** and **XXXa** having electron-donor substituents in the aromatic rings induced considerable shifts of <sup>1</sup>H NMR signals from protons both in the macroring and in the aromatic fragments (Table 2). In the electron absorption spectra (methanol) we observed a blue shift of the absorption maxima. These data indicated formation of complexes with Ba<sup>2+</sup> ion; the complexes are likely to have a symmetric structure with central coordination of the metal ion by the macroring cavity. Analogous, though smaller (in absolute value), variations were observed in the <sup>1</sup>H NMR spectrum of *N,N'*-diphenyldiaza-18-crown-6 (**XXVIIa**) in the presence of Ba(ClO<sub>4</sub>)<sub>2</sub> (Table 2). In this case, the smaller shifts due to complex formation may be interpreted as incomplete coordination. The effect of lanthanide metal salts (La<sup>3+</sup>, Lu<sup>3+</sup>, Yb<sup>3+</sup>) on the <sup>1</sup>H NMR and UV spectra of crown ethers **XXIXa** and **XXXa** cannot be interpreted with equal unambiguity, in particular because of strong signal broadening in the <sup>1</sup>H NMR spectra. Presumably, the main factor is not complex formation but protonation of the crown ether with the acid released as a result of hydrolysis of Ln<sup>3+</sup> salt. In any case, the influence of LuCl<sub>3</sub> on the UV spectrum of crown ether **XXXa** is qualitatively different from that observed in the presence of Ba(ClO<sub>4</sub>)<sub>2</sub> but is exactly the same as that

**Table 3.** Palladium-catalyzed arylation<sup>a</sup> of diaza-18-crown-6 (**I**)

Aryl halide no.	R	Reaction time, h	[Pd], mol %	Product	Yield, %
<b>XXIV</b>	CF <sub>3</sub>	4	2	<b>XXVIIIa</b>	75
<b>XXIII</b>	H	20	4	<b>XXVIIa</b>	90
<b>XXV</b>	MeO	20	4	<b>XXIXa</b>	85
<b>XXVI</b>	Me <sub>2</sub> N	20	4	<b>XXXa</b>	90
<b>XXVI</b>	Me <sub>2</sub> N	40	2	<b>XXXa</b>	85

<sup>a</sup> The reactions were carried out with ~1.1 equiv of aryl halide, 1.5 equiv of *t*-BuONa, and a Pd–ligand ratio of 2:3; the reaction time was not optimized.

produced by addition of HCl. Finally, crown ether **XXVIIIa** having an electron-acceptor trifluoromethyl group in the aromatic ring showed signs of complex formation with neither  $\text{Ba}^{2+}$  ion nor  $\text{La}^{3+}$  ion.

### EXPERIMENTAL

The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on Varian VXR-400 and Bruker Avance spectrometers at 400 and 376.3 MHz, respectively. The mass spectra (electron impact, 70 eV) were obtained on Kratos MS-30 and MS-890 instruments. The electron absorption spectra were measured on a Hewlett-Packard 8452-A spectrophotometer from solutions in methanol. Chromatographic analysis was performed on an Agat-9 chromatograph equipped with a flame-ionization detector (2.5-m $\times$ 5-mm column packed with OV-17 on Inerton Super, 160-200  $\mu\text{m}$ ; carrier gas nitrogen).

$\beta$ -Chlorovinyl phenyl ketone (**IV**) was synthesized by the Kondakov reaction [35]. Methyl *cis*-3-chloroacrylate (**VIII**) was prepared by addition of hydrogen chloride to methyl propynoate in the presence of CuCl as catalyst [36]. Diethyl  $\alpha$ -chlorobenzylidenemalonate (**IX**) was obtained from diethyl benzylidenemalonate by successive addition of chlorine and dehydrochlorination by the action of 1,8-diazabicyclo[5.4.0]-undec-7-ene [37]. (*Z*)- $\beta$ -Chloro- $\alpha,\beta$ -difluorostyrene (**XI**) was synthesized as described in [38]. The other aryl and vinyl halides, 2'-(dicyclohexylphosphino)-*N,N*-dimethylbiphenyl-2-amine (**XXII**), and sodium *tert*-butoxide were commercial products. Diaza-18-crown-6 was kindly provided by Dr. Yu.G. Gorbunova (Institute of General and Inorganic Chemistry, Russian Academy of Sciences) and was additionally purified by vacuum sublimation ( $10^{-2}$  mm). Rare-earth metal nitrates were used as hexahydrates. Barium perchlorate was prepared by dissolution of barium carbonate in aqueous perchloric acid, followed by evaporation of the solution and drying of the residue under reduced pressure at 100–180°C over  $\text{P}_2\text{O}_5$  (2–4 h). Cesium carbonate was dried in a similar way. Xantphos [39], and  $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$  [40] were synthesized by known methods.

The solvents were dried and purified by standard procedures. Toluene was additionally purified by stirring over sodium amalgam; dioxane, toluene, and THF were stored over potassium diphenylketyl under reduced pressure.

**Arylation of diaza-18-crown-6 (I) with activated aryl and vinyl halides.** A Schlenk vessel was charged

with diaza-18-crown-6, 1–2 ml of THF was recondensed thereto through a vacuum line or 1–2 ml of DMF was added, the flask was filled with argon, aryl or vinyl halide and triethylamine (20–100% excess relative to 1:1 or 1:2 stoichiometry) were added, and the mixture was stirred using a magnetic stirrer. The reaction temperature and time are specified in Table 1. The product was isolated following one of the procedures given below (*a–d*).

*a.* The reaction mixture was poured into a saturated solution of potassium chloride, the mixture was cooled, and the precipitate was filtered off. It contained *N,N'*-diaryldiaza-18-crown-6 and a small amount of triethylamine hydrochloride. The precipitate was dried and dissolved in benzene, the solution was filtered, the filtrate was evaporated, and the residue was purified by recrystallization.

*b.* When the reaction was performed in THF, the precipitate of triethylamine hydrochloride was filtered off and washed with diethyl ether, the filtrate was combined with the washings and evaporated, and the residue was subjected to column chromatography on silica gel (40–63  $\mu\text{m}$ , Merck). Disubstituted diaza crown ethers were eluted with petroleum ether–methylene chloride–ethyl acetate [3:3:(1–4)]. More polar derivatives **XIVa**, **XVIIIa**, and **XIXa** were isolated by elution with the same solvent system containing additionally 2–7% of methanol. In the case of monosubstituted compounds **XIIIb** and **XVb**, the concentration of methanol in the eluent was raised to 20% and more. Disubstituted diaza crown ethers were additionally purified by recrystallization.

*c.* The mixture was treated with a solution of sodium carbonate, the products were extracted into chloroform, the extract was evaporated, and the residue was purified by recrystallization.

*d.* The mixture was treated as described in *c*, but the products were isolated by column chromatography as described in *b*.

**7,16-Bis(2,4-dinitrophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XIIa)** was synthesized from 131 mg (0.5 mmol) of crown ether **I**, 186 mg (1 mmol) of 2,4-dinitrofluorobenzene (**II**), and 270  $\mu\text{l}$  of triethylamine in 2 ml of THF. Following method *a*, we isolated 281 mg (95%) of compound **XIIa**, mp 140–142°C (from  $\text{CH}_2\text{Cl}_2$ –petroleum ether, 1:5). UV spectrum:  $\lambda_{\text{max}}$  370 nm.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.56 s, 3.61 t (16H), 3.71 t (8H), 7.25 d (2H,  $J \approx 9$  Hz), 8.19 d.d (2H,  $J = 9.5, 2.7$  Hz),

8.59 d (2H,  $J = 2.7$  Hz). Found, %: C 48.50; H 5.17; N 14.31.  $C_{24}H_{30}N_6O_{12}$ . Calculated, %: C 48.48; H 5.09; N 14.14.

**7,16-Bis[perfluoro(2-methylcyclopent-1-enyl)]-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XIIIa)** was synthesized from 34 mg (0.13 mmol) of crown ether **I**, 77 mg (0.294 mmol) of perfluoro(1-methylcyclopentene) (**III**), and 40  $\mu$ l of triethylamine in 1 ml of THF. Following method *b*, we isolated 88 mg (90%) of compound **XIIIa**, mp 79–80°C (from  $CH_2Cl_2$ –petroleum ether, 1:5). UV spectrum:  $\lambda_{max}$  258 nm.  $^1H$  NMR spectrum ( $CDCl_3$ ),  $\delta$ , ppm: 3.601 s (8H), 3.69–3.74 m (16H).  $^{19}F$  NMR spectrum ( $CDCl_3$ ),  $\delta_F$ , ppm: –54.18 m (6F), –104.49 m (4F), –113.46 m (4F), –132.68 m (4F). Found, %: C 38.83; H 3.12; N 3.74.  $C_{24}H_{24}F_{18}N_2O_4$ . Calculated, %: C 38.62; H 3.24; N 3.75.

**(2E,2'E)-3,3'-(1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)bis(1-phenylprop-2-en-1-one) (XIVa)** was synthesized from 131 mg (0.5 mmol) of crown ether **I**, 200 mg (1.20 mmol) of  $\beta$ -chlorovinyl phenyl ketone (**IV**), and 130  $\mu$ l of triethylamine in 2 ml of THF. Following method *b*, we isolated 210 mg (80%) of compound **XIVa**, mp 117–119°C (from petroleum ether–benzene, 4:1). UV spectrum:  $\lambda_{max}$  342 nm.  $^1H$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 3.62 br.m (8H), 3.66 s (8H), 3.76 br.m (8H), 5.95 d (2H,  $J = 12.5$  Hz), 7.37–7.47 m (6H), 7.75 d (2H,  $J = 12.5$  Hz), 7.91 d (4H). Found, %: C 68.90; H 7.36; N 5.41.  $C_{30}H_{38}N_2O_4$ . Calculated, %: C 68.94; H 7.33; N 5.36.

**7,16-Bis(tetrafluoropyridin-4-yl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XVa)** was synthesized from 131 mg (0.5 mmol) of crown ether **I**, 203 mg (1.21 mmol) of pentafluoropyridine (**V**), and 290  $\mu$ l of triethylamine in 2 ml of THF. Following method *a*, we isolated 255 mg (90%) of compound **XVa**, mp 115–116°C (from methanol). UV spectrum:  $\lambda_{max}$  266 nm.  $^1H$  NMR spectrum ( $CDCl_3$ ),  $\delta$ , ppm: 3.60 s (8H), 3.71–3.76 m (16H).  $^{19}F$  NMR spectrum (acetone- $d_6$ ),  $\delta_F$ , ppm: –95.49 m (4F), –154.50 m (4F). Found, %: C 47.04; H 4.33; N 9.71.  $C_{22}H_{24}F_8N_4O_4$ . Calculated, %: C 47.15; H 4.32; N 10.00.

**7,16-Bis(octafluoro-*p*-tolyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XVIa)** was synthesized from 131 mg (0.5 mmol) of crown ether **I**, 285 mg (1.22 mmol) of octafluorotoluene (**VI**), and 270  $\mu$ l of triethylamine in 2 ml of DMF. Following method *a*, we isolated 324 mg (93%) of compound **XVIa**, mp 110–113°C (from petroleum ether). UV spectrum:

$\lambda_{max}$  283 nm.  $^1H$  NMR spectrum ( $CDCl_3$ ),  $\delta$ , ppm: 3.61 s and 3.62 t (16H), 3.71 t (8H).  $^{19}F$  NMR spectrum ( $CDCl_3$ ),  $\delta_F$ , ppm: –54.64 t (6F), –141.98 m (4F), –148.67 m (4F). Found, %: C 44.80; H 3.47; N 3.90.  $C_{26}H_{24}F_{14}N_2O_4$ . Calculated, %: C 44.97; H 3.48; N 4.03.

**2,2'-(1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)bis(3-chloro-1,4-naphthoquinone) (XVIIa)** was synthesized from 52 mg (0.20 mmol) of crown ether **I**, 104 mg (0.46 mmol) of dichloronaphthoquinone **VII**, and 70  $\mu$ l of triethylamine in 1 ml of DMF. Following method *c*, we isolated 118 mg (90%) of compound **XVIIa**, mp 145–146°C (from  $CH_2Cl_2$ –methanol, 1:5). UV spectrum:  $\lambda_{max}$  492 nm.  $^1H$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 3.576 s (8H), 3.789 t (8H), 3.895 t (8H), 7.77–7.84 m (4H), 8.00–8.06 m (4H). Found, %: C 59.55; H 4.73; N 4.44.  $C_{32}H_{32}N_2O_8$ . Calculated, %: C 59.73; H 5.01; N 4.35.

**Dimethyl (2E,2'E)-3,3'-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)bis(prop-2-enoate) (XVIIIa)** was synthesized from 51 mg (0.195 mmol) of crown ether **I**, 60 mg (0.50 mmol) of methyl *cis*-3-chloroprop-2-enoate (**VIII**), and 70  $\mu$ l of triethylamine in 1 ml of THF. Following method *c*, we isolated 75 mg (90%) of compound **XVIIIa**, mp 146–148°C (from  $CH_2Cl_2$ –methanol, 1:5). UV spectrum:  $\lambda_{max}$  280 nm.  $^1H$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 3.47 br.t (8H), 3.53 s (6H), 3.62 s (8H), 3.67 t (8H), 4.54 d (2H,  $J = 13$  Hz), 7.43 d (2H,  $J = 13$  Hz). Found, %: C 56.12; H 8.08; N 6.85.  $C_{20}H_{34}N_2O_8$ . Calculated, %: C 55.80; H 7.96; N 6.51.

**Tetraethyl  $\alpha,\alpha'$ -(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)bis(benzylidenemalonate) (XIXa)** was synthesized from 55 mg (0.21 mmol) of crown ether **I**, 132 mg (0.47 mmol) of diethyl  $\alpha$ -chlorobenzylidenemalonate (**IX**), and 70  $\mu$ l of triethylamine in 1 ml of DMF. Following method *d*, we isolated 118 mg (75%) of compound **XIXa**, mp 195–196°C (from  $CH_2Cl_2$ –petroleum ether, 1:3). UV spectrum:  $\lambda_{max}$  334 nm.  $^1H$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 0.98 br.m (12H), 3.40 t (8H), 3.55 s (8H), 3.66 t (8H), 3.90 br.m (8H), 7.41–7.50 m (10H). Found, %: C 63.63; H 7.27; N 3.59.  $C_{40}H_{54}N_2O_{12}$ . Calculated, %: C 63.64; H 7.21; N 3.71.

**7-[Perfluoro(2-methylcyclopent-1-enyl)]-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XIIIb)** was synthesized from 95 mg (0.36 mmol) of crown ether **I**, 95 mg (0.36) of perfluoro(1-methylcyclopentene) (**III**), and 50  $\mu$ l of triethylamine in 2 ml of THF (20°C, 15 min). Following method *b*, we isolated (in the order of elution) 50 mg (37%) of disubstituted

crown ether **XIIIa** and 78 mg (40%) of compound **XIIIb**.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.19 m (4H), 3.66 m (4H), 3.71 m (4H), 3.76–3.82 m (8H), 3.94 m (4H).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta_{\text{F}}$ , ppm: –53.92 m (3F), –104.30 m (2F), –113.13 m (2F), –132.57 m (2F). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 504 (3)  $[M]^+$ , 485 (3), 445 (3), 427 (10), 409 (7), 354 (12), 298 (15), 266 (12), 224 (10), 148 (40), 118 (40), 100 (100).

**7-(Tetrafluoropyridin-4-yl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XVb)** was synthesized from 131 mg (0.5 mmol) of crown ether **I**, 175 mg (1.04 mmol) of pentafluoropyridine (**V**), and 170  $\mu\text{l}$  of triethylamine in 2 ml of THF (20°C, 100 h). Following method *b*, we isolated (in the order of elution) 125 mg (45%) of disubstituted crown ether **XVa** and 82 mg (40%) of compound **XVb**.  $^1\text{H}$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 2.74 m (4H), 3.54–3.62 m (12H), 3.78 m (8H).  $^{19}\text{F}$  NMR spectrum (acetone- $d_6$ ),  $\delta_{\text{F}}$ , ppm: –95.05 m (2F), –153.59 m (2F). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 411 (20)  $[M]^+$ , 381 (5), 354 (10), 336 (50), 324 (30), 310 (10), 218 (20), 206 (25), 193 (60), 118 (100), 100 (80).

**Reaction of diaza-18-crown-6 dilithium salt with pentafluoropyridine (V).** A suspension of 262 mg (1 mmol) of diaza-18-crown-6 (**I**) in 4 ml of THF was cooled to –40°C, 1.1 ml (2 mmol) of a 1.8 M solution of butyllithium in petroleum ether was added under stirring, the mixture was stirred for 15 min, and 169 mg (1 mmol) of pentafluoropyridine (**V**) was added. The mixture was stirred for a short time at –40°C, treated with an aqueous solution of ammonium chloride, and extracted with chloroform. A sample of the mixture was analyzed by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy, but no signals assignable to monoarylated crown ether **XVb** were detected. Apart from signals belonging to disubstituted derivative **XVa**, the spectrum contained a number of broadened signals which were not assigned.

**The reaction of diaza-18-crown-6 dilithium salt with *p*-nitrofluorobenzene (X)** was carried out in a similar way using 262 mg (1 mmol) of diaza-18-crown-6 (**I**), 0.58 ml (1 mmol) of a 1.74 M solution of butyllithium, and 141 mg (1 mmol) of *p*-nitrofluorobenzene (**X**) in 4 ml of THF (–40°C). The mixture was subjected to column chromatography on silica gel (40–63  $\mu\text{m}$ , Merck) using petroleum ether–methylene chloride–ethyl acetate [3:3:(1–4)] as eluent. The first fraction (18 mg) contained 7,16-bis(5-fluoro-2-nitrophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**XXa**).  $^1\text{H}$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 3.49 t

(8H), 3.56 s (8H), 3.65 t (8H), 6.76 d.d.d (2H,  $J = 9.1, 7.3, 2.6$  Hz), 7.23 d.d (2H,  $J = 12, 2.6$  Hz), 7.80 d.d (2H,  $J = 9.1, 6.2$  Hz).  $^{19}\text{F}$  NMR spectrum (acetone- $d_6$ ),  $\delta_{\text{F}}$ , ppm: –103.8 d.t ( $J_{\text{d}} = 12, J_{\text{t}} \approx 6$  Hz). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 540 (10)  $[M]^+$ , 313 (10), 299 (5), 283 (5), 222 (10), 207 (10).

**Second fraction (5 mg).**  $^{19}\text{F}$  NMR spectrum (acetone- $d_6$ ):  $\delta_{\text{F}}$  –103.8 ppm, br.m. The  $^1\text{H}$  NMR spectrum in acetone- $d_6$  contained signals in the aromatic region at the same positions as in the spectrum of the first fraction, but the signals had a more complex shape. Each of the signals may be considered to be a superposition of several multiplets located very close to each other. The spectrum of the second fraction in the  $\delta$  region 3–4 ppm was also much more complex than that of the first fraction. These data indicate that the second fraction consists of 1-amino-2-nitro-5-fluorophenyl derivatives with unknown structure.

**Arylation of diaza-18-crown-6 (I) with nonactivated aryl halides in the presence of palladium complexes.** A Schlenk vessel was charged with diaza-18-crown-6 (**I**), 140 mol % of *t*-BuONa, 110–120 mol % of aryl bromide, 1–2 mol % of  $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$  (**XXI**), 3–6 mol % of ligand **XXII**, and durene as reference for GLC. The mixture was cooled with liquid nitrogen and evacuated, toluene was recondensed thereto through a vacuum line, and the vessel was filled with argon. The mixture was stirred at 100°C over a period indicated in Table 2. The conversion of aryl bromide was determined by GLC, the mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and filtered through a layer of celite, the filtrate was evaporated, and the residue was subjected to column chromatography on silica gel (40–63  $\mu\text{m}$ , Merck). The product was eluted with petroleum ether–methylene chloride–ethyl acetate, 3:3:(1–4).

**7,16-Diphenyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XXVIIa)** was synthesized from 65.5 mg of crown ether **I**, 103 mg of bromobenzene (**XXIII**), 67 mg of *t*-BuONa, 10.3 mg of  $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$  (**XXI**), and 11.8 mg of ligand **XXII** in 1 ml of toluene. Yield 97 mg (94%), mp 97–98°C (from  $\text{CH}_2\text{Cl}_2$ –petroleum ether); published data [13]: mp 90°C. UV spectrum,  $\lambda_{\text{max}}$ , nm: 256, 300.  $^1\text{H}$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 3.61 s and 3.61 t (16H), 3.69 t (8H), 6.58 t (2H), 6.70 d (4H), 7.14 m (4H).

**7,16-Bis(4-trifluoromethylphenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XXVIIIa)** was synthesized from 131 mg of crown ether **I**, 250 mg of *p*-bromotrifluoromethylbenzene (**XXIV**), 134 mg of *t*-BuONa, 10.3 mg of  $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$  (**XXI**), and



15.7 mg of ligand **XXII** in 2 ml of toluene. Yield 210 mg (75%), mp 137–138°C (from CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether). UV spectrum,  $\lambda_{\max}$ , nm: 266, 300 sh. <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ , ppm: 3.63 s (8H), 3.67–3.74 (*AA'BB'* system, 16H), 6.83 d (4H), 7.43 d (4H). Found, %: C 56.68; H 5.98; N 5.13. C<sub>26</sub>H<sub>32</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub>. Calculated, %: C 56.70; H 5.84; N 5.10.

**7,16-Bis(4-methoxyphenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XXIXa)** was synthesized from 65.5 mg of crown ether **I**, 103 mg of *p*-bromoanisole (**XXV**), 67 mg of *t*-BuONa, 10.3 mg of Pd<sub>2</sub>dba<sub>3</sub>·CHCl<sub>3</sub> (**XXI**), and 11.8 mg of ligand **XXII** in 1 ml of toluene. Yield 100 mg (85%), mp 93–94°C (from CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether). UV spectrum,  $\lambda_{\max}$ , nm: 254, 320. <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ , ppm: 3.54 t (8H), 3.59 s (8H), 3.65 t (8H), 3.69 s (6H), 6.68 d (4H), 6.78 d (4H). Found, %: C 65.73; H 8.14; N 5.76. C<sub>26</sub>H<sub>38</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 65.80; H 8.07; N 5.90.

**7,16-Bis(4-dimethylaminophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (XXXa)** was synthesized from 70 mg of crown ether **I**, 120 mg of *N,N*-dimethyl-*p*-bromoaniline (**XXVI**), 71 mg of *t*-BuONa, 11 mg of Pd<sub>2</sub>dba<sub>3</sub>·CHCl<sub>3</sub> (**XXI**), and 13.7 mg of ligand **XXII** in 1 ml of toluene. Yield 120 mg (90%), mp 117–118°C (from CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether). UV spectrum,  $\lambda_{\max}$ , nm: 264, 318. <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ , ppm: 2.77 br.s (12H), 3.51 br.s (8H), 3.59 s (8H), 3.64 t (8H), 6.73 br and 6.70 br (8H, *AB* quartet). Strong signal broadening was observed even in the presence of a very small amount of water. Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 500 (30) [*M*]<sup>+</sup>, 250 (8), 237 (40), 220 (8), 206 (12), 189 (10), 175 (20), 163 (60), 148 (100), 134 (30). Found, %: C 66.93; H 9.02; N 10.98. C<sub>28</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>. Calculated, %: C 67.17; H 8.86; N 11.19.

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