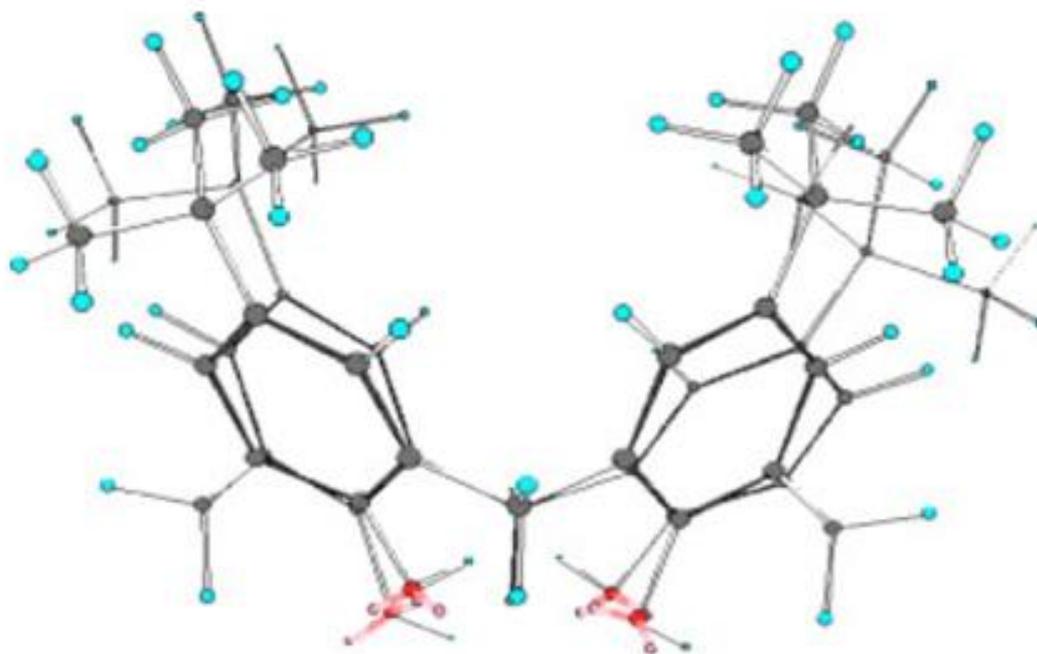
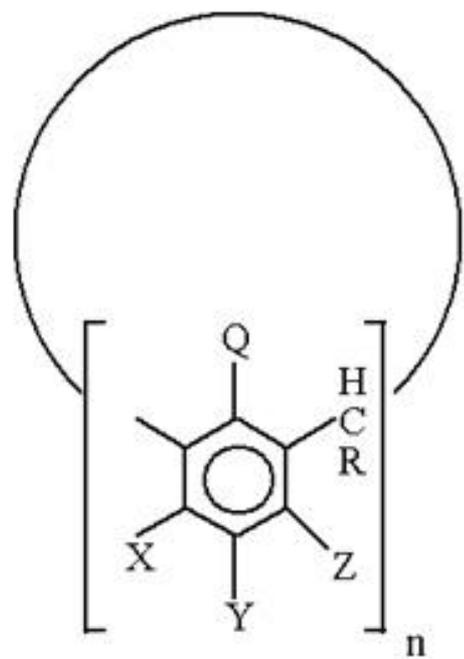
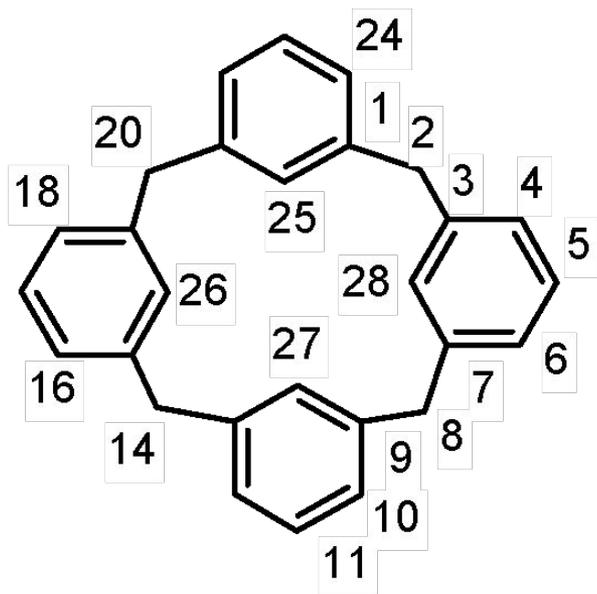


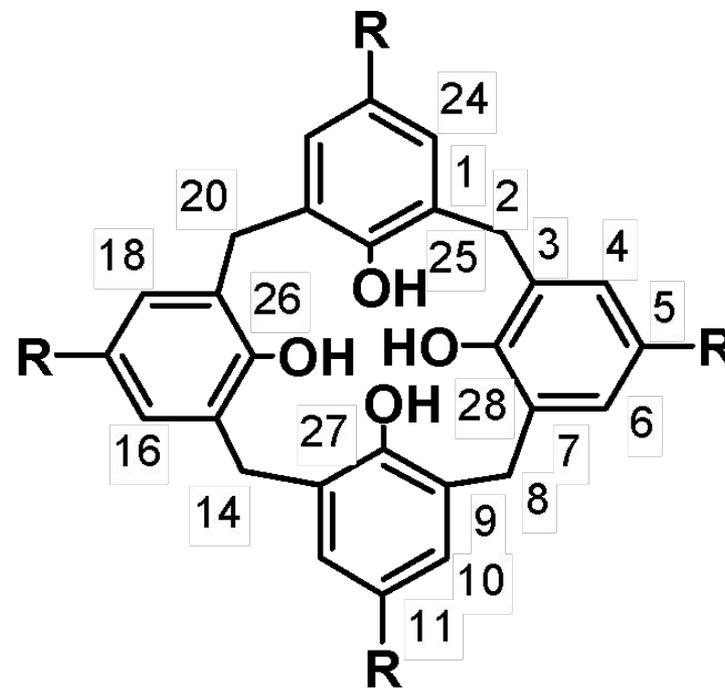
Каликсарены



Каликсарены

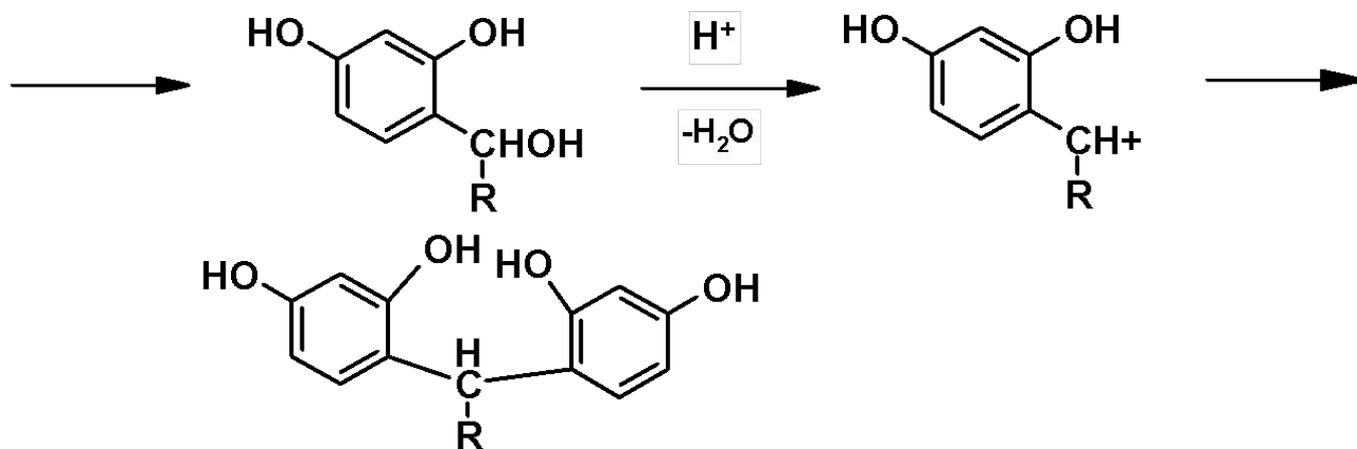
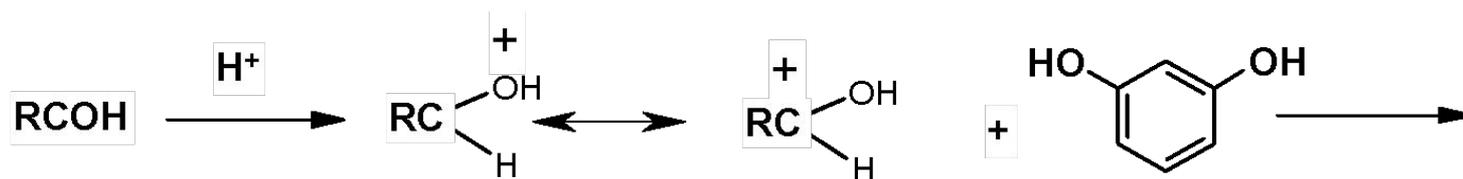
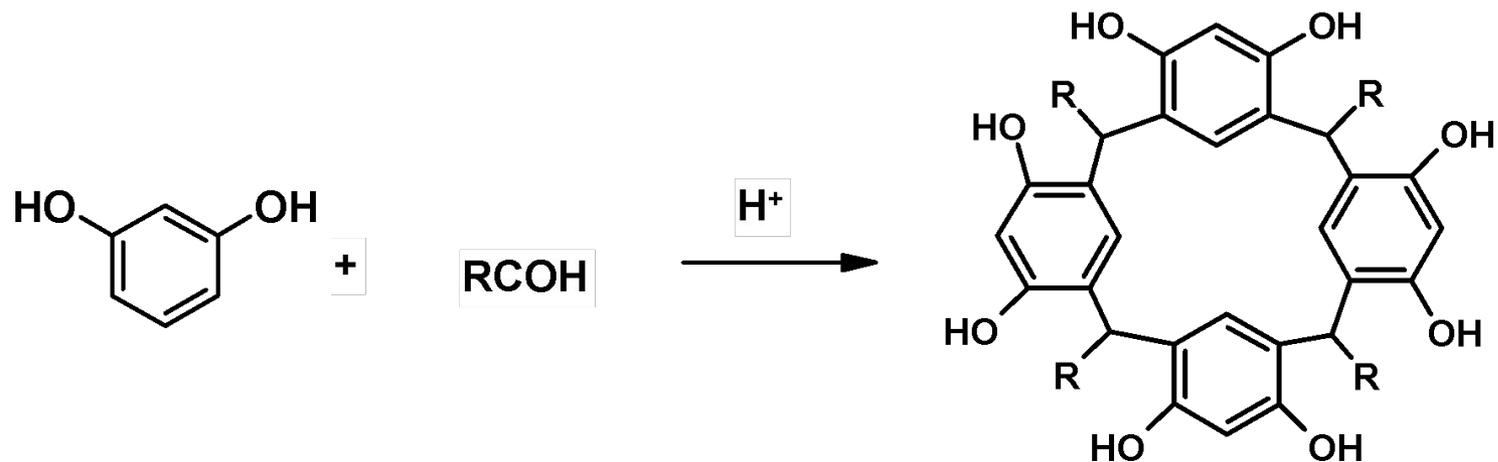


Пентацикло[19.3.1.1^{3,7}. 1^{9,13}.
1^{15,19}]
октакоза-1(25),3,5,7(28),9,11,
13(27),15,17,19(26),21,23-
додекаен

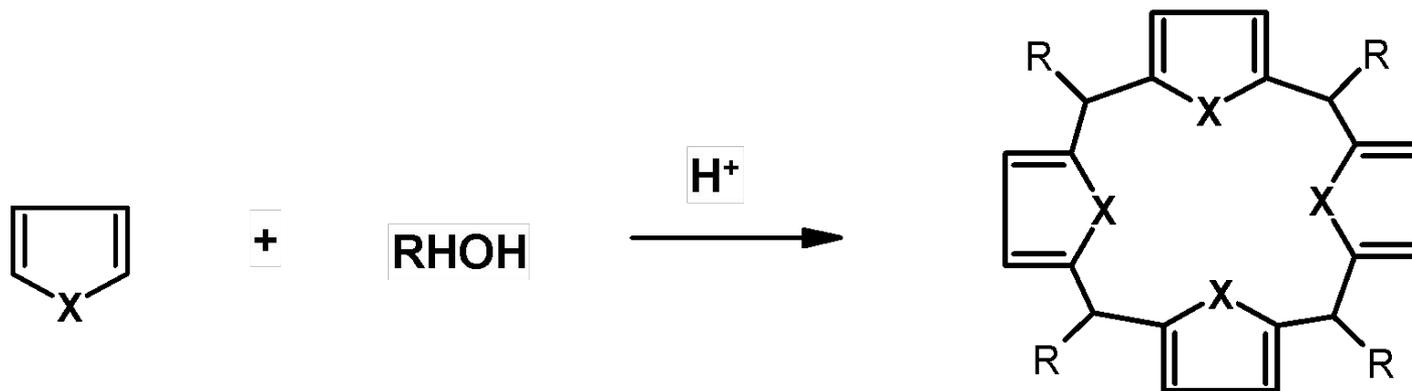
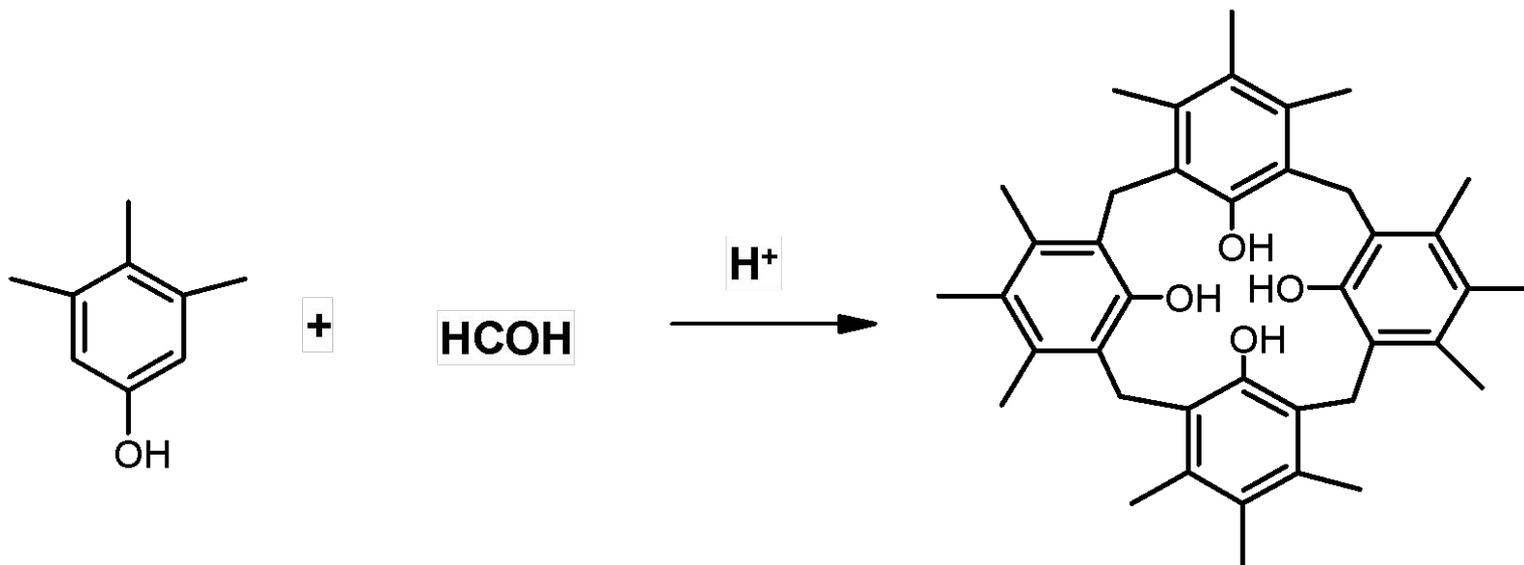


25,26,27,28-тетрагидрокси-
каликс[4]арен (R = H)

Одностадийный синтез каликсаренов



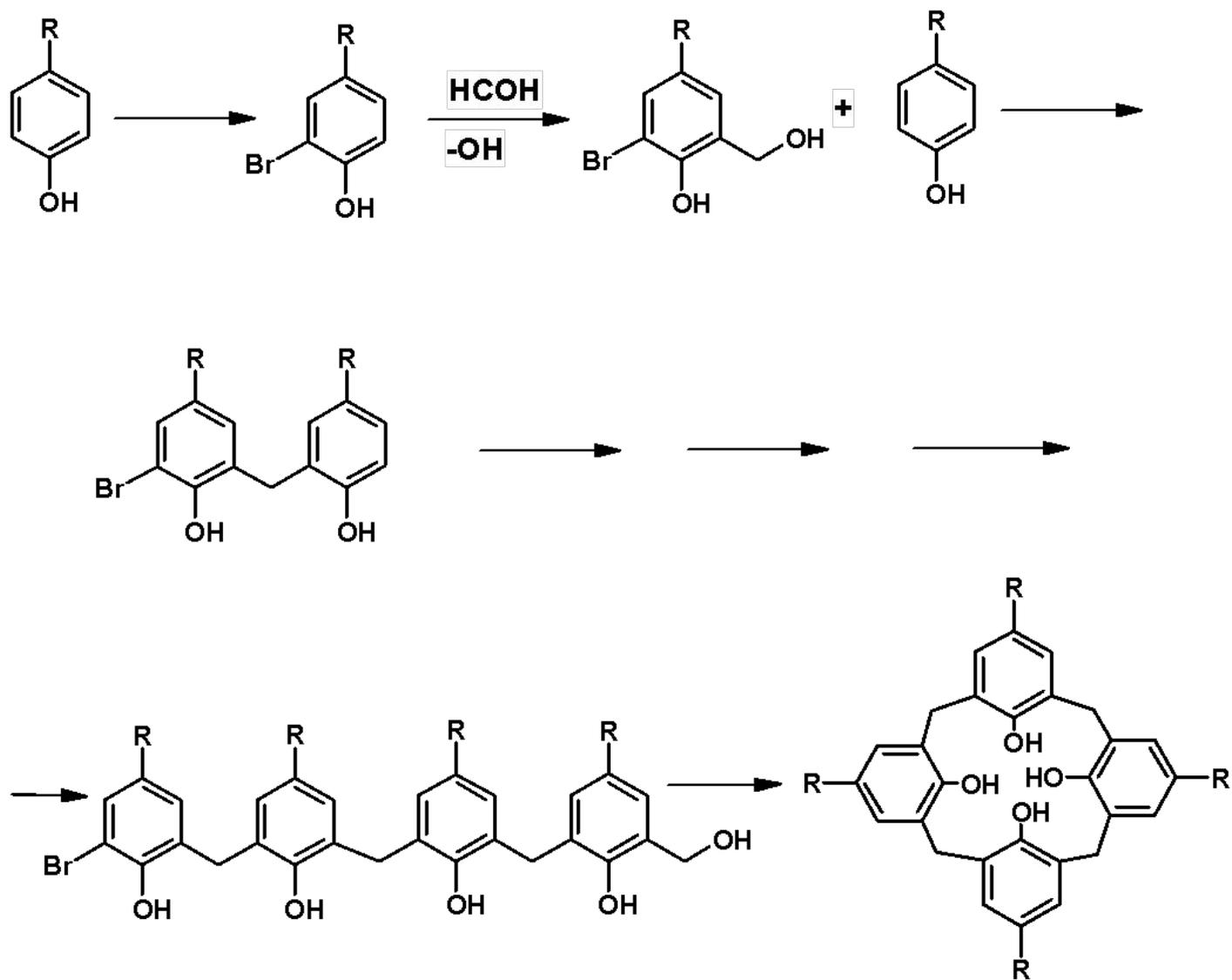
Одностадийный синтез каликсаренов



X = N, O, S; R = Me, Et

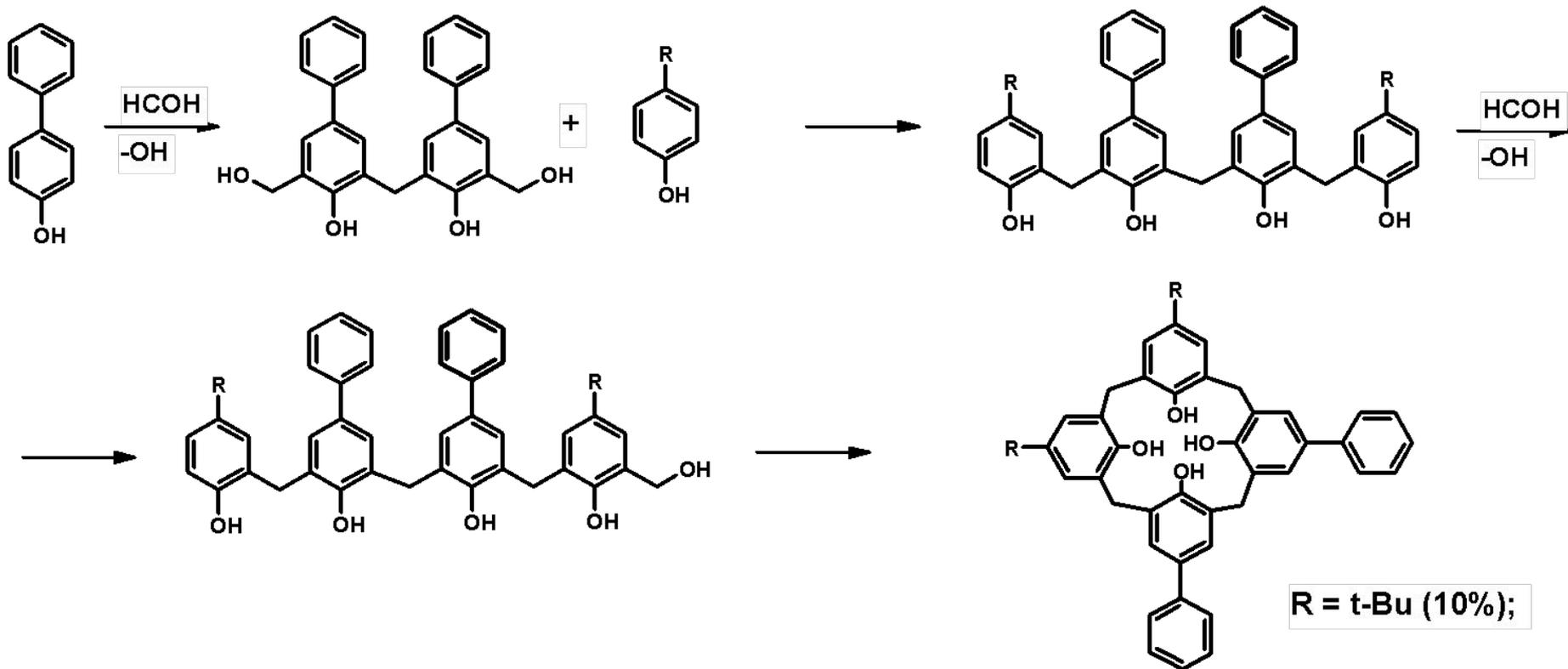
до 40%

Постадийный синтез каликсаренов. Метод Хейса-Хантера

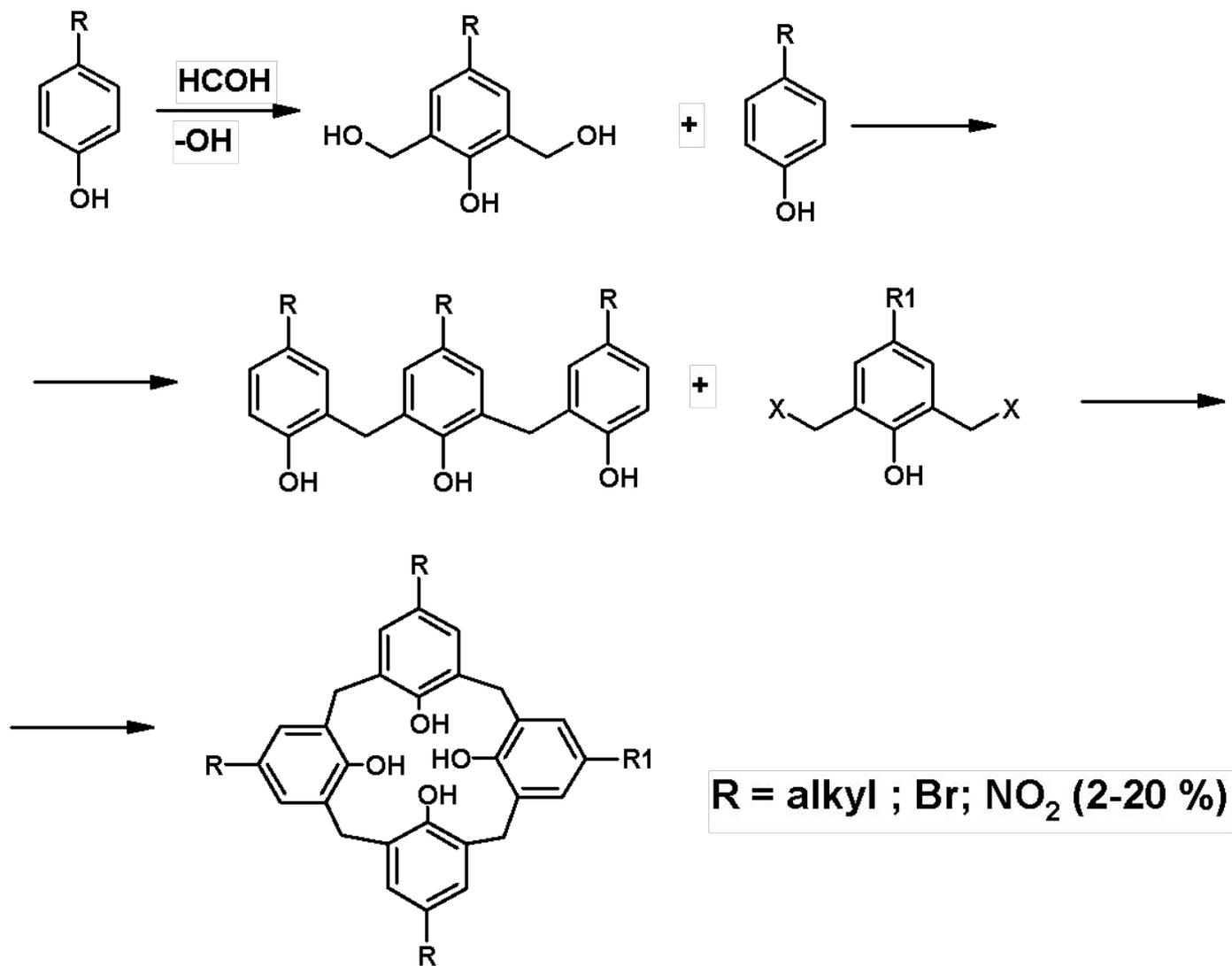


R = t-Bu (11%); Ph (0.5%)

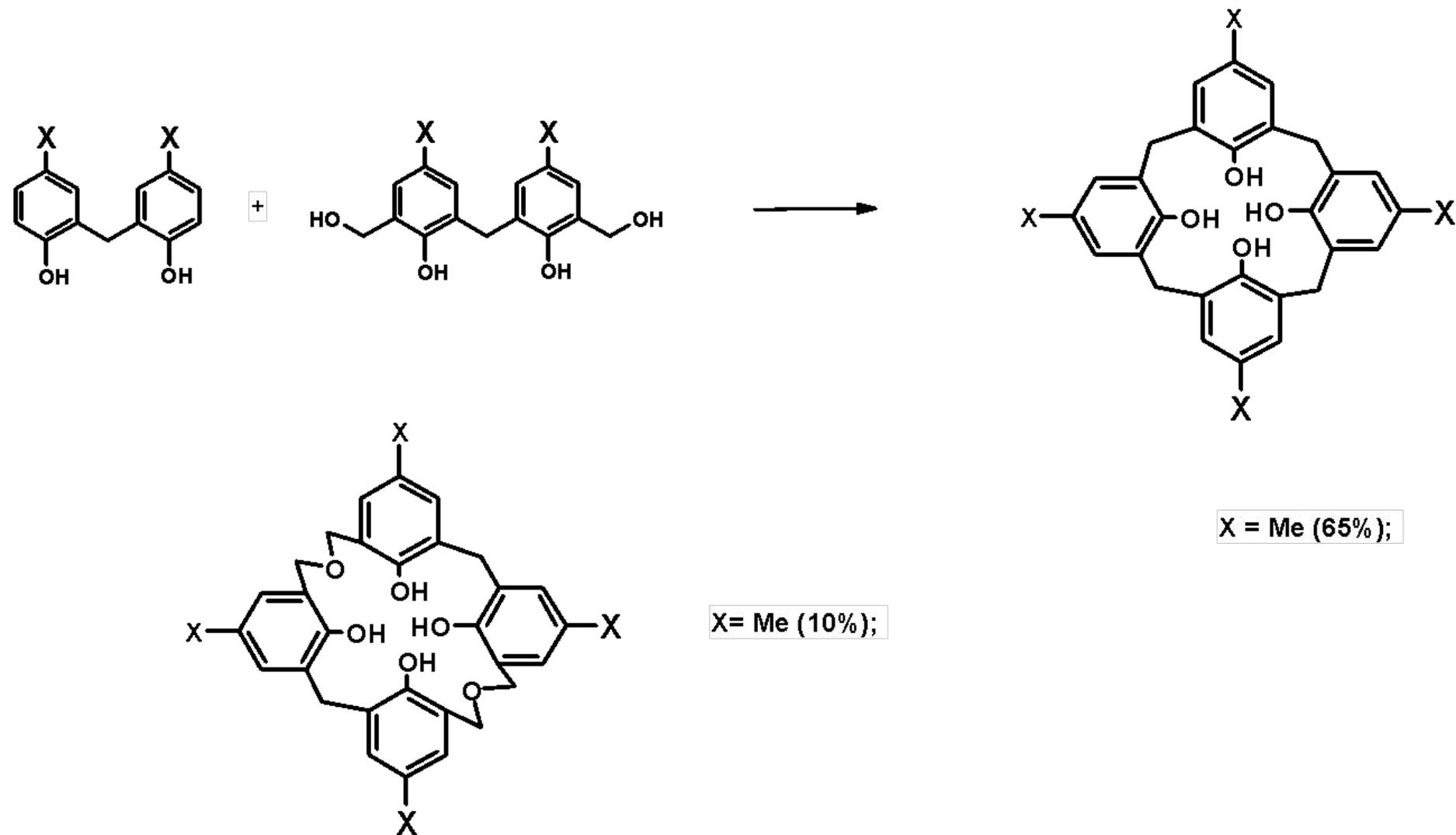
Постадийный синтез каликсаренов. Метод Ноу и Гютше



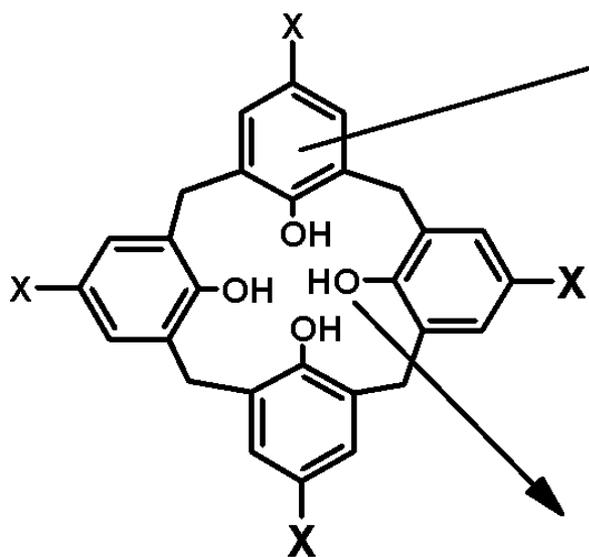
Постадийный синтез каликсаренов. Метод Бемера-Чхима-Каммерера



Постадийный синтез каликсаренов. Метод Мошфеха и Хакимелахи



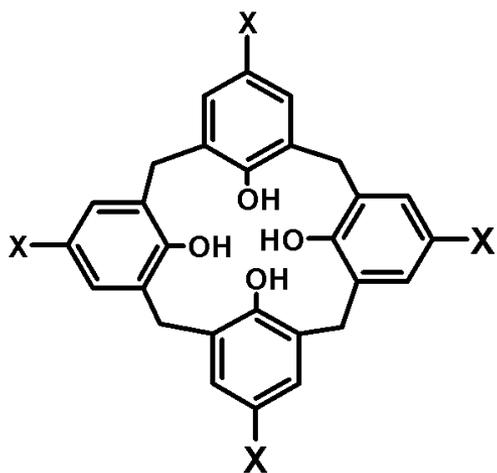
Модификация каликсаренов



Введение новых заместителей

**Модификация заместителей,
(получение простых и сложных
эфиров)**

Модификация каликсаренов



AlkylHal



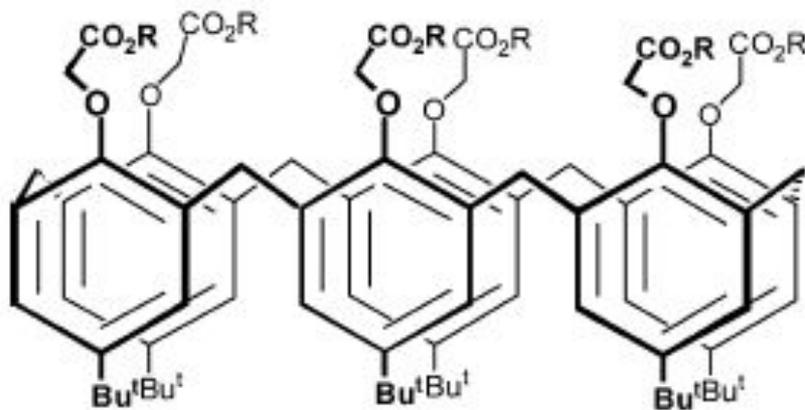
NaH or MOH

простые эфиры

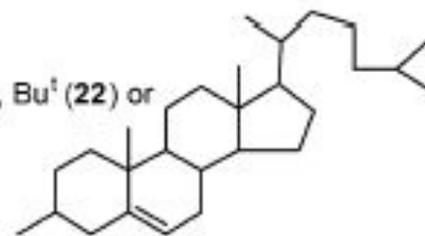
Hal - C(=O) - R



сложные эфиры

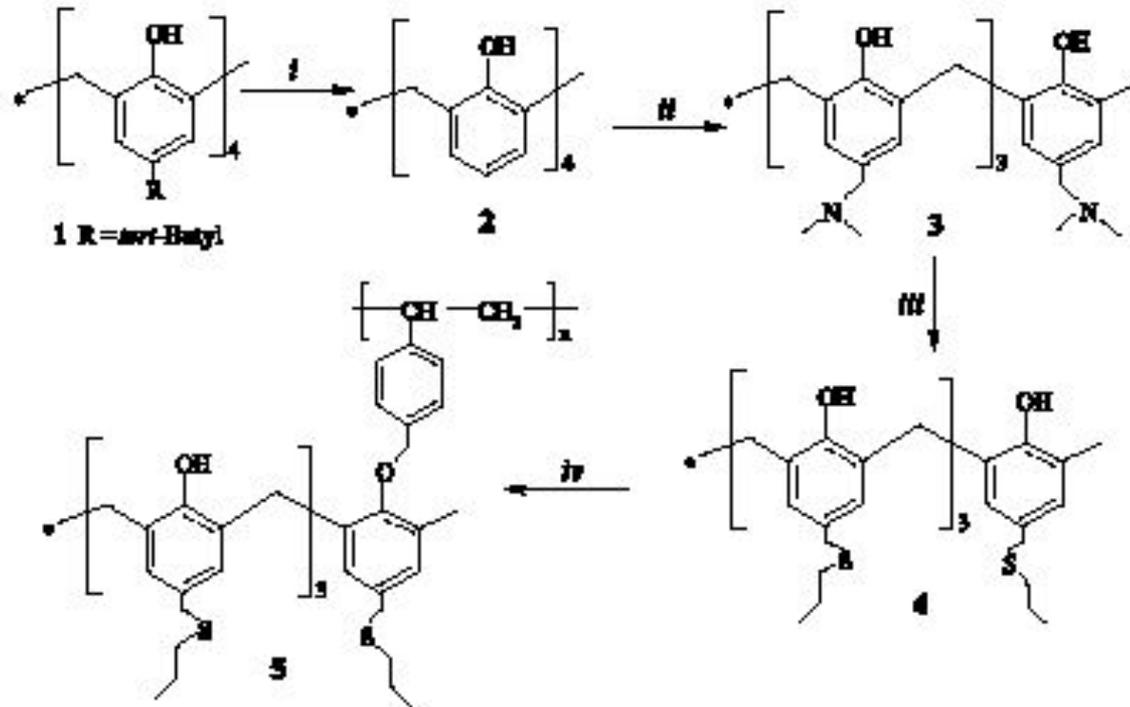


R = Et (21), Bu^t (22) or



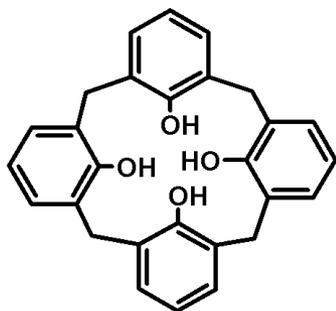
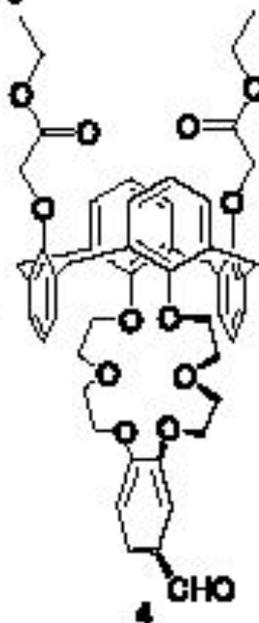
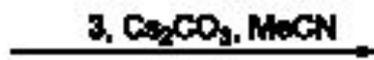
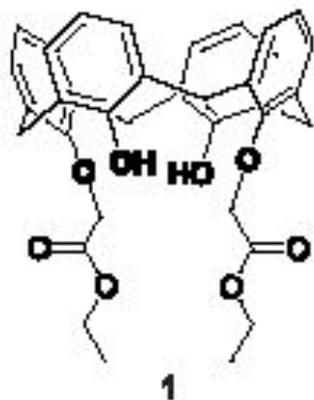
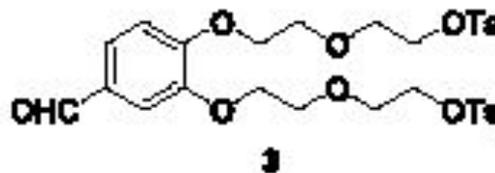
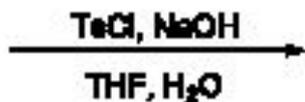
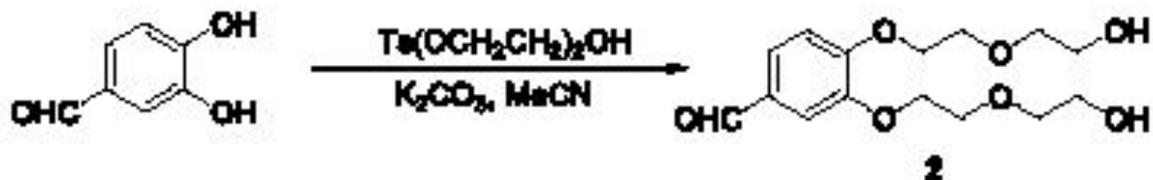
(23)

Модификация каликсаренов



Scheme 1. (i) Toluene, phenol, AlCl_3 (ii) THF, CH_3COOH , HCHO , $\text{NH}(\text{CH}_3)_2$ (iii) DMSO, CH_3I , 1-propanthiol, $\text{N}(\text{C}_2\text{H}_5)_3$ (iv) DMF, Merrifield's resin, NaI , NaH .

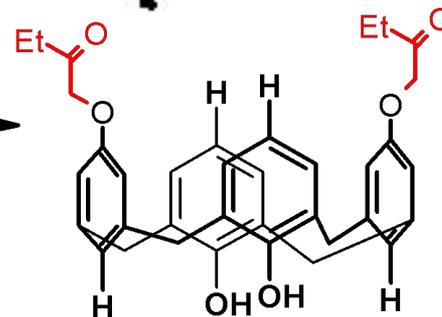
Модификация каликсаренов

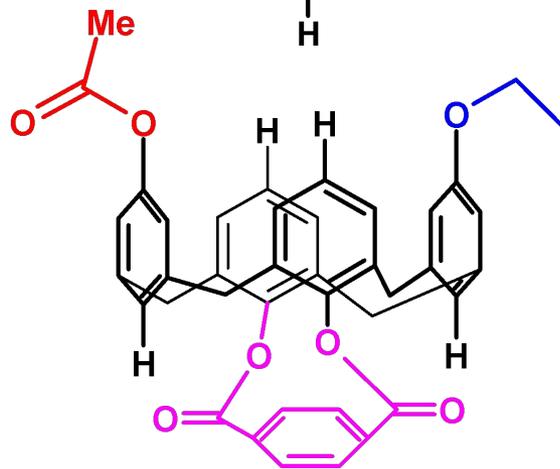
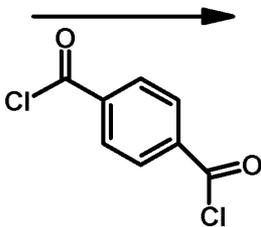
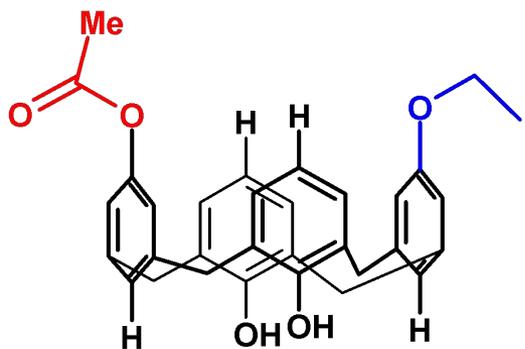
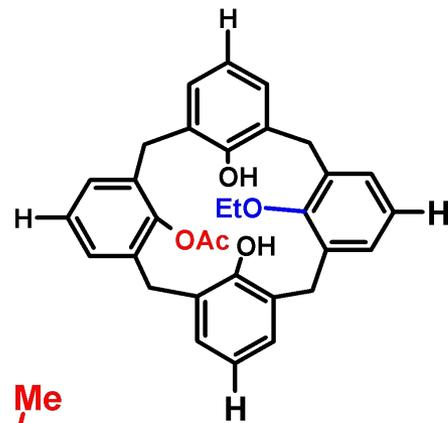
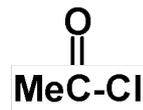
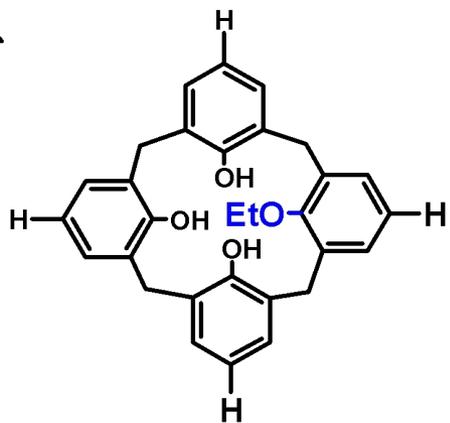
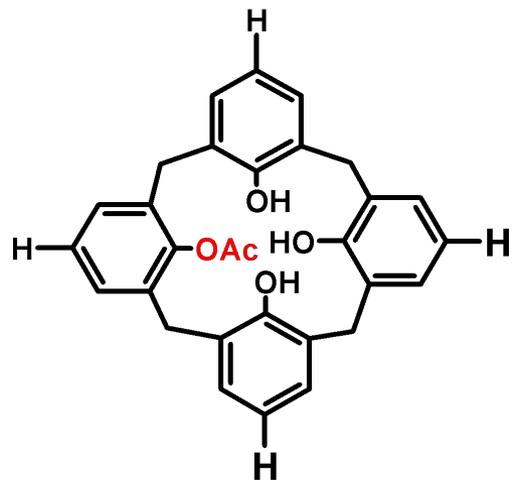
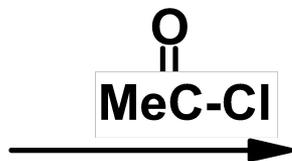
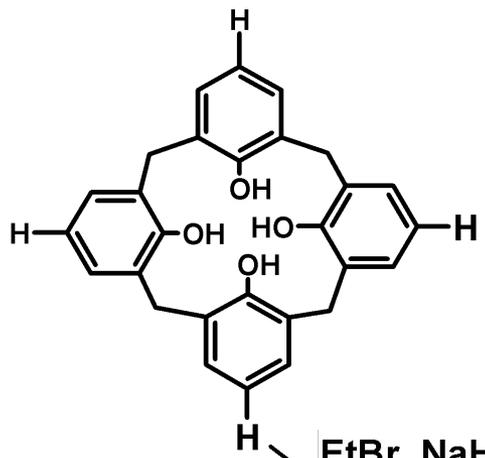


+

2 $\text{BrCH}_2\text{COOEt}$

$\xrightarrow{\text{NaOH}}$





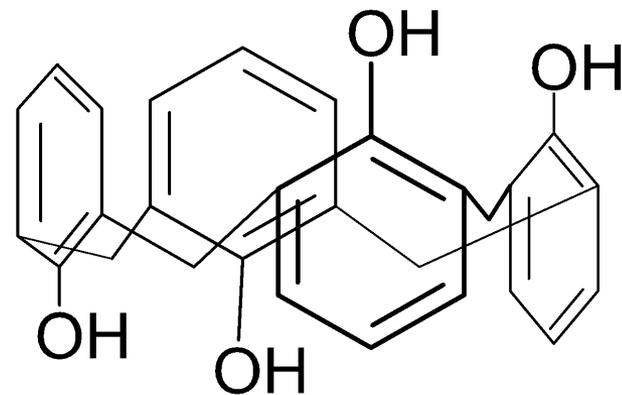
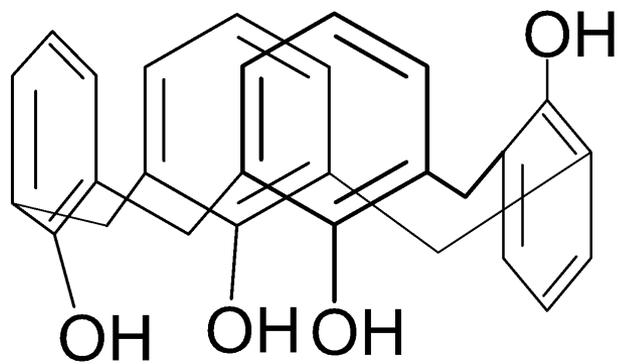
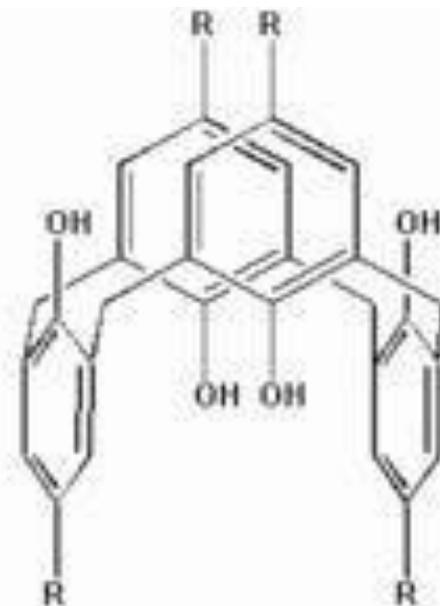
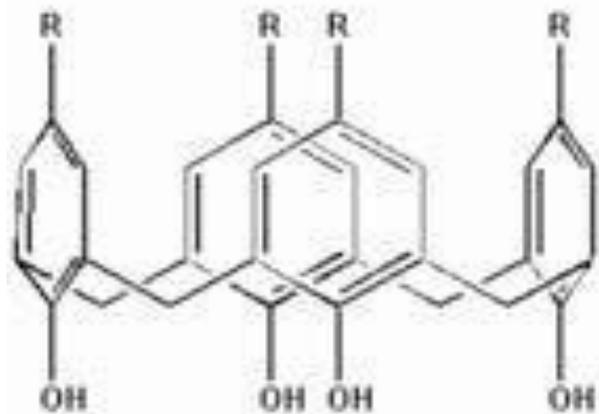
Особенности каликсаренов:

- **высокая температура плавления**
- **низкая растворимость в органических растворителях**

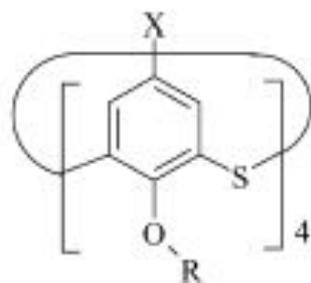
Физико-химические методы исследования

- **ИК-спектры: валентные колебания ОН-групп в области 3200 см^{-1}**
- **В УФ-спектрах имеется полоса поглощения при 280-288 нм**
- **ЯМР-спектры: более простые спектры по сравнению с линейными аналогами**
- **Масс-спектры: распад с сохранением циклической структуры и отщеплением заместителей**

Конформация каликсаренов



Конформация каликсаренов



1a, R = H, X = Bu^t;
1b, R = H, X = H;
2a, R = Me, X = Bu^t;
2b, R = Me, X = H,

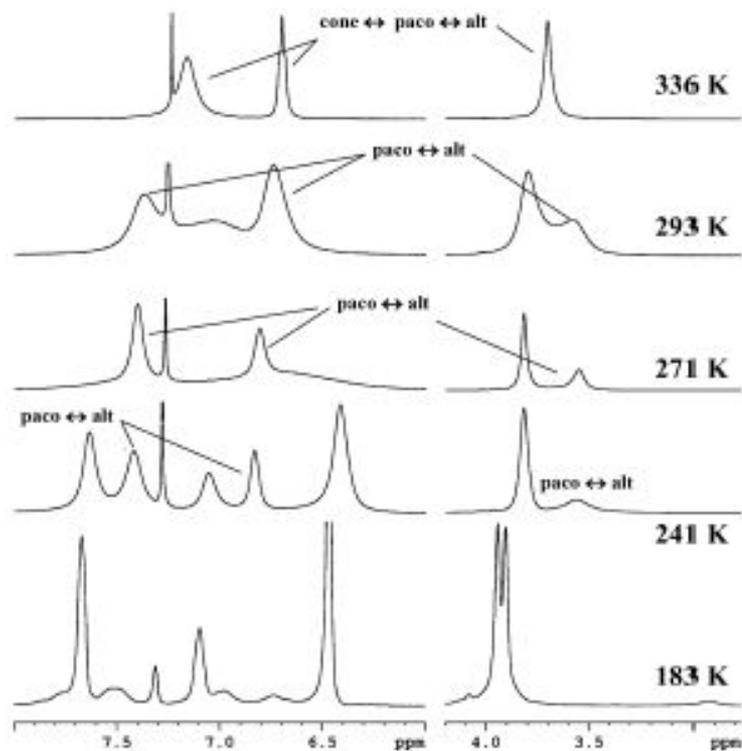
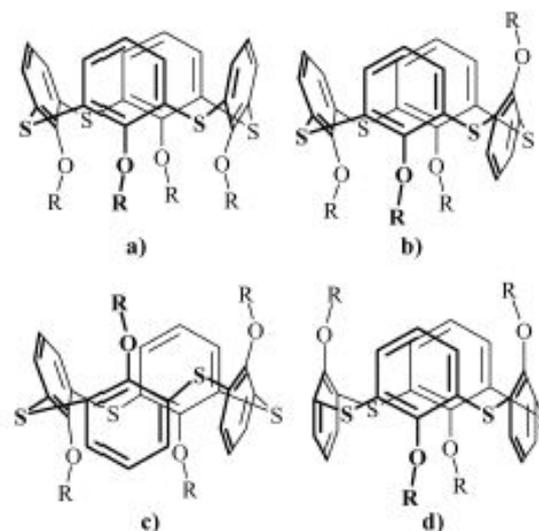


Figure 1. Temperature dependent ¹H NMR spectra of **2b** (CDCl₃, 500 MHz, spectrum at 183–336 K). Assignment of the individual conformers is shown.



Scheme 1. Conformers of thiacalix[4]arene: (a) *cone*, (b) *partial cone*, (c) *1,2-alternate*, (d) *1,3-alternate*.

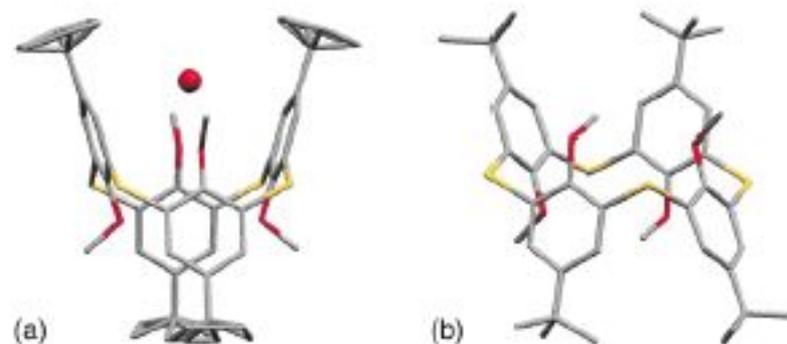
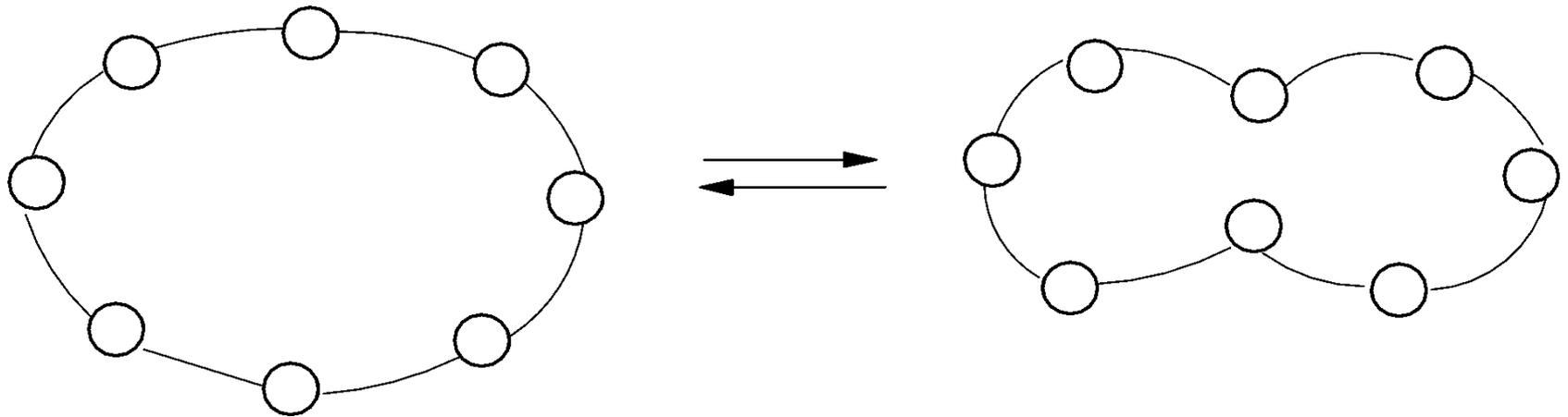


Figure 4. (a) Crystal structure of **2a** (*1,3-alternate* conformation) with included H₂O molecule; (b) crystal structure of **2a** (*1,2-alternate*). Hydrogen atoms were omitted for better clarity.

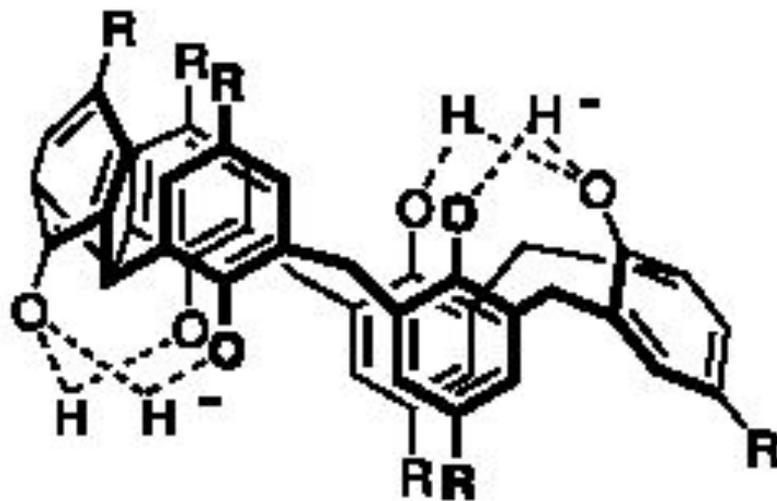
Конформация каликсаренов



Бензол - ?

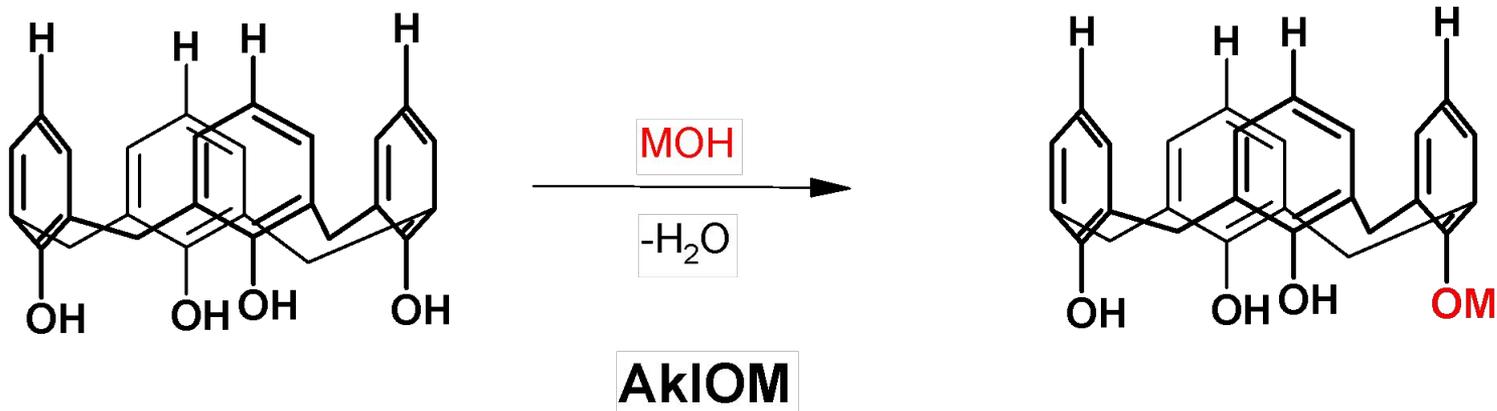
Пропанол - ?

Конформация каликс[6]аренов

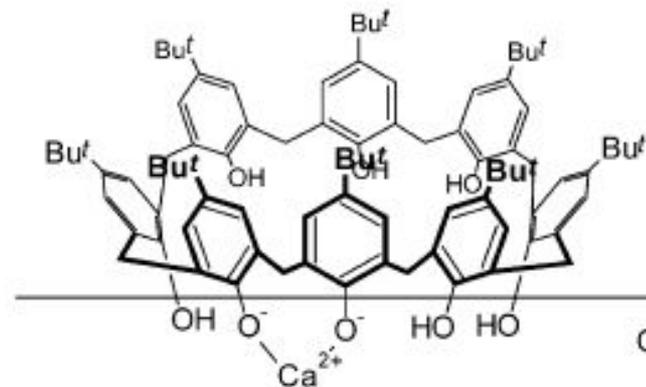


(18, $\text{R} = \text{SO}_3^-$)

Комплексообразование с катионами металлов

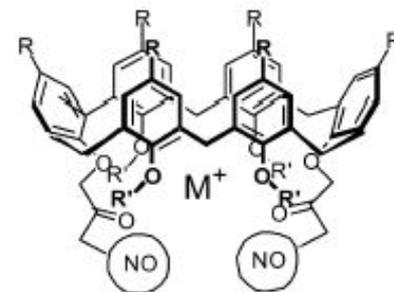
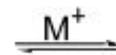
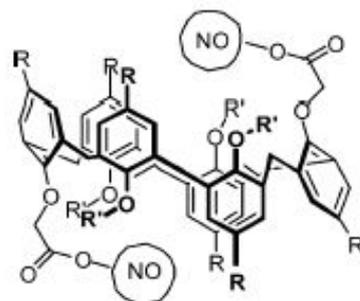
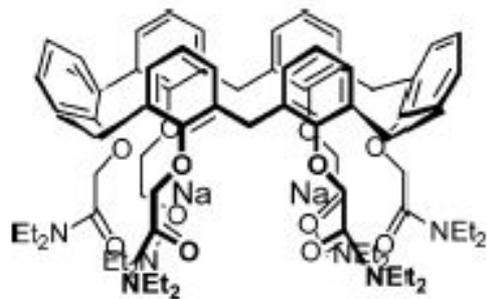


LiOH	Поток, 10^{-8} моль·с ⁻¹ ·м ⁻²
<i>Трет-бутилфенол</i>	0.9
<i>Трет-бутилкаликс[4]арен</i>	0
<i>Трет-бутилкаликс[6]арен</i>	10
<i>Трет-бутилкаликс[8]арен</i>	2



Комплексообразование с катионами металлов

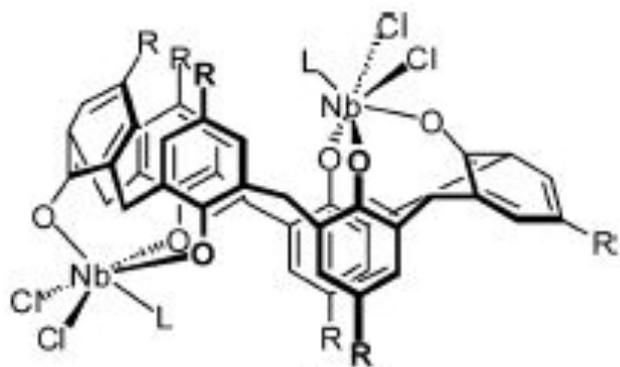
Cs^+



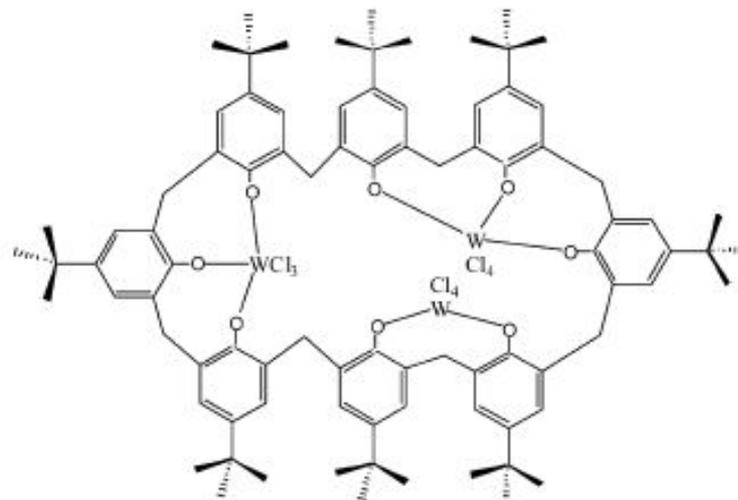
1,2,3-alternate (26)

$\text{R} = \text{Bu}^t, \text{R}' = \text{CH}_2\text{COOEt}$

Cone (27)

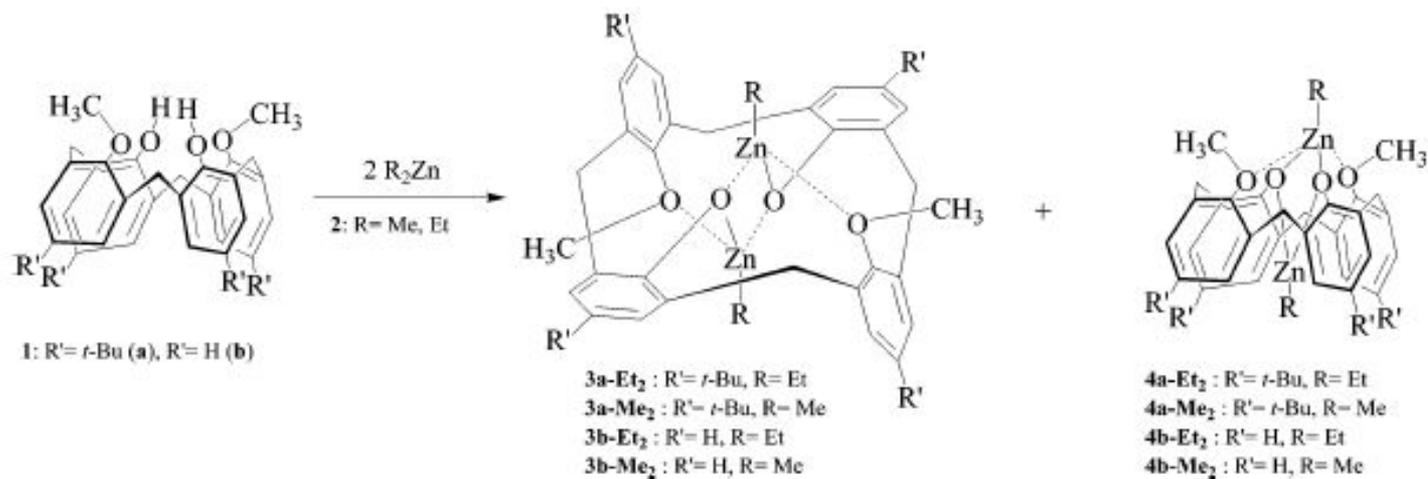


41 $\text{R} = \text{Bu}^t, \text{L} = \text{MeCN}$

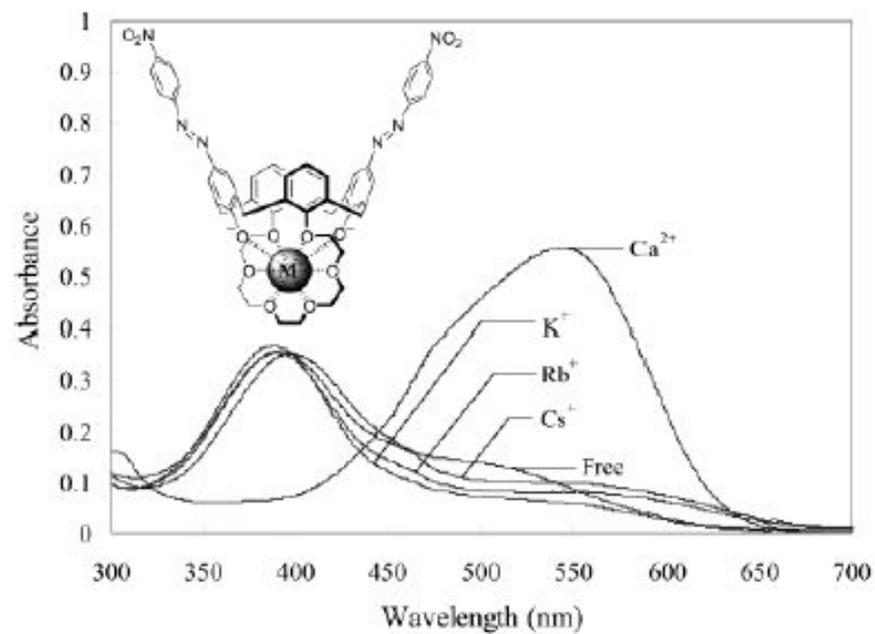
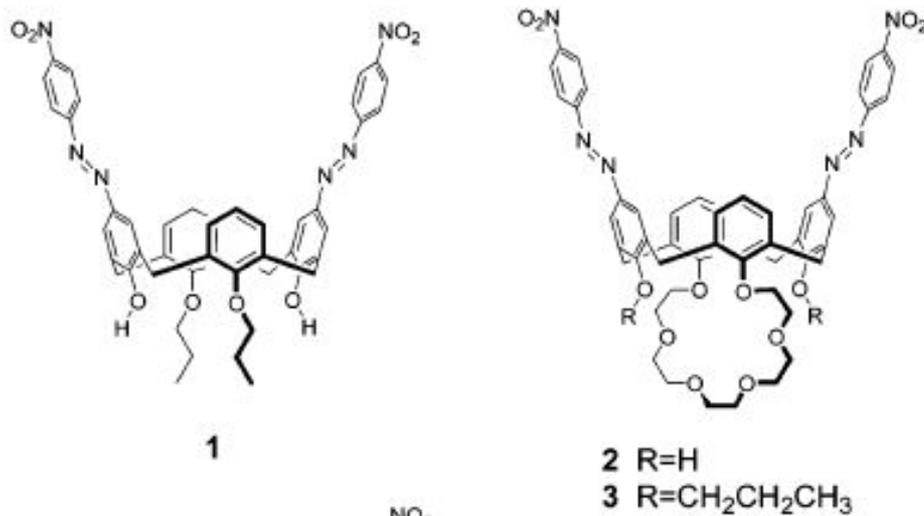


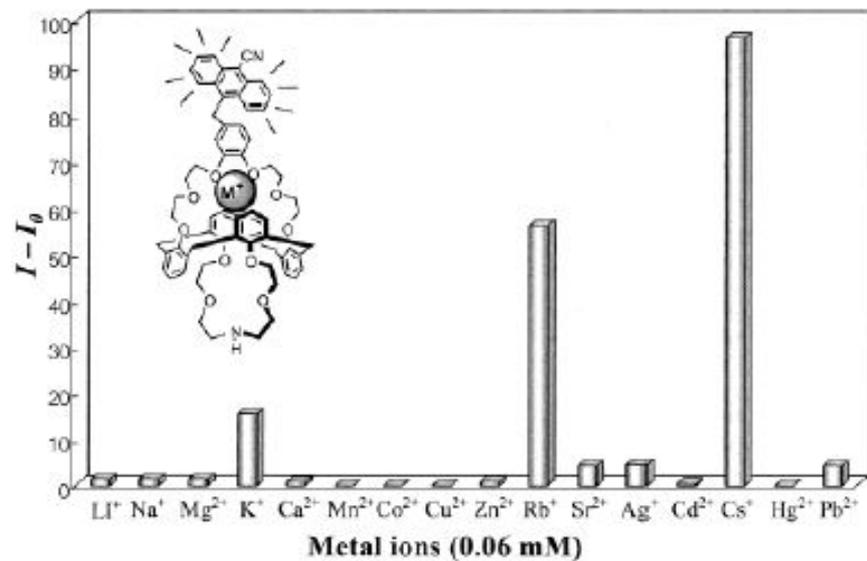
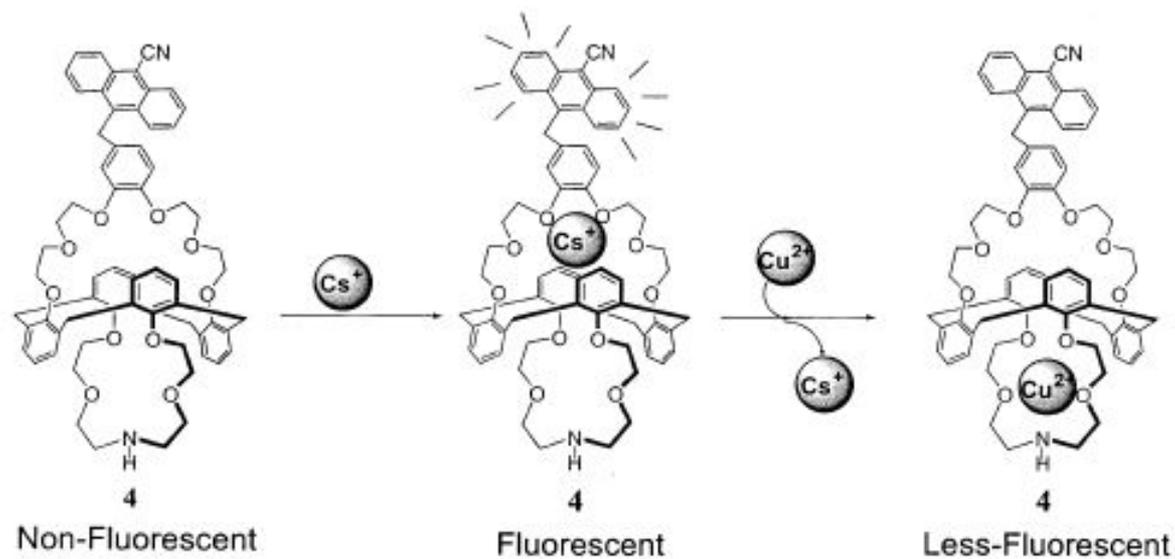
53 $\text{L} = \text{MeCN}$

Комплексообразование с катионами металлов

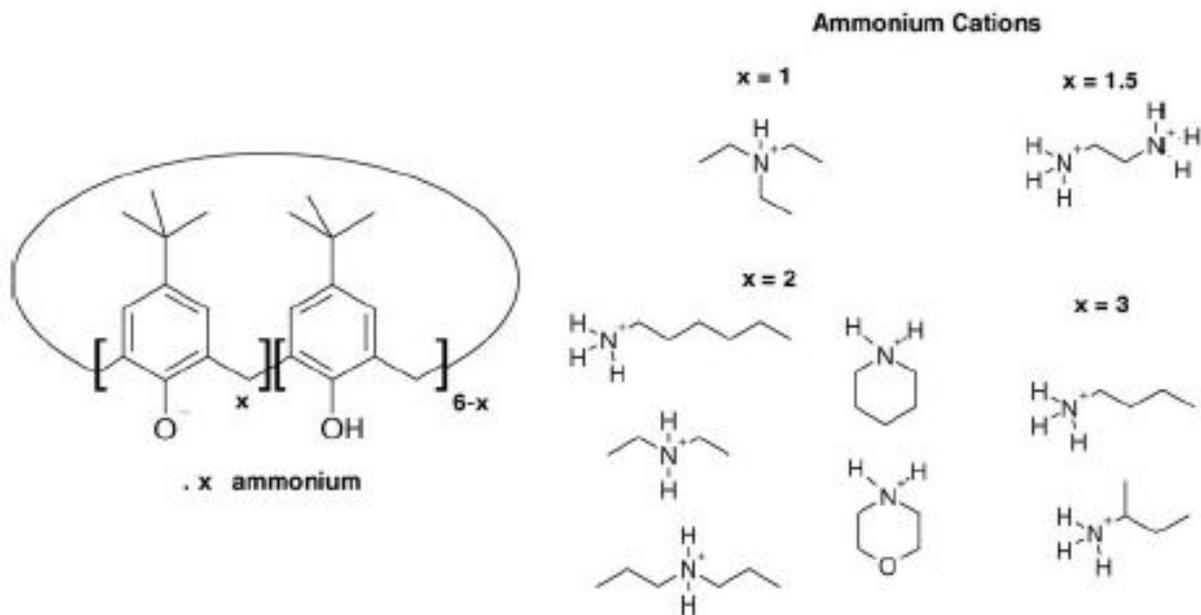


Комплексообразование

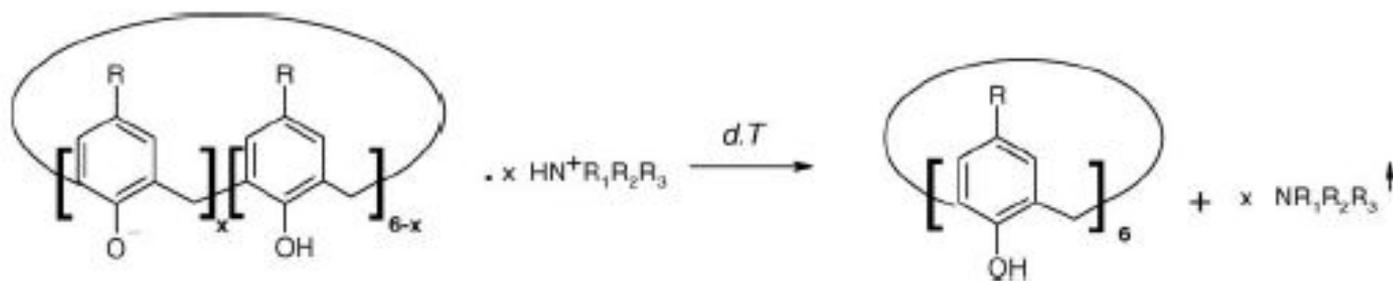




Комплексообразование с катионами аммония



Scheme 1. Ammonium *p-tert*-butylcalix[6]arene salts analyzed.



Scheme 2. Decomplexation of ammonium cations by temperature.

Комплексообразование с катионами аммония

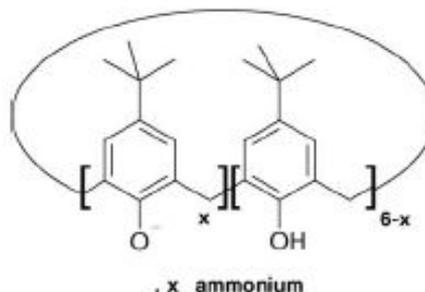
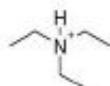


Table 1
values of decomplexation temperatures

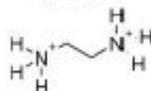
Amine	Amine:calix	ΔT ($^{\circ}\text{C}$)	bp ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)
Butylamine	3:1	196	78	118
<i>s</i> -Butylamine	3:1	194; 201	63	131; 138
Dibutylamine	2:1	136	159	-23
Diethylamine	2:1	176; 188	55	121; 133
Hexylamine	2:1	146; 178	132	12; 46
dipropylamine	2:1	142	110	32
Triethylamine	1:1	159	89	70
Piperidine	2:1	200; 217	106	92; 111
Morpholine	2:1	177	129	48
Ethylenediamine	3:2	200	118	82

Ammonium Cations

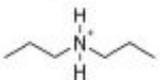
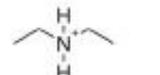
x = 1



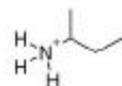
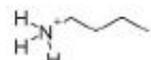
x = 1.5



x = 2



x = 3



Комплексообразование с катионами аммония

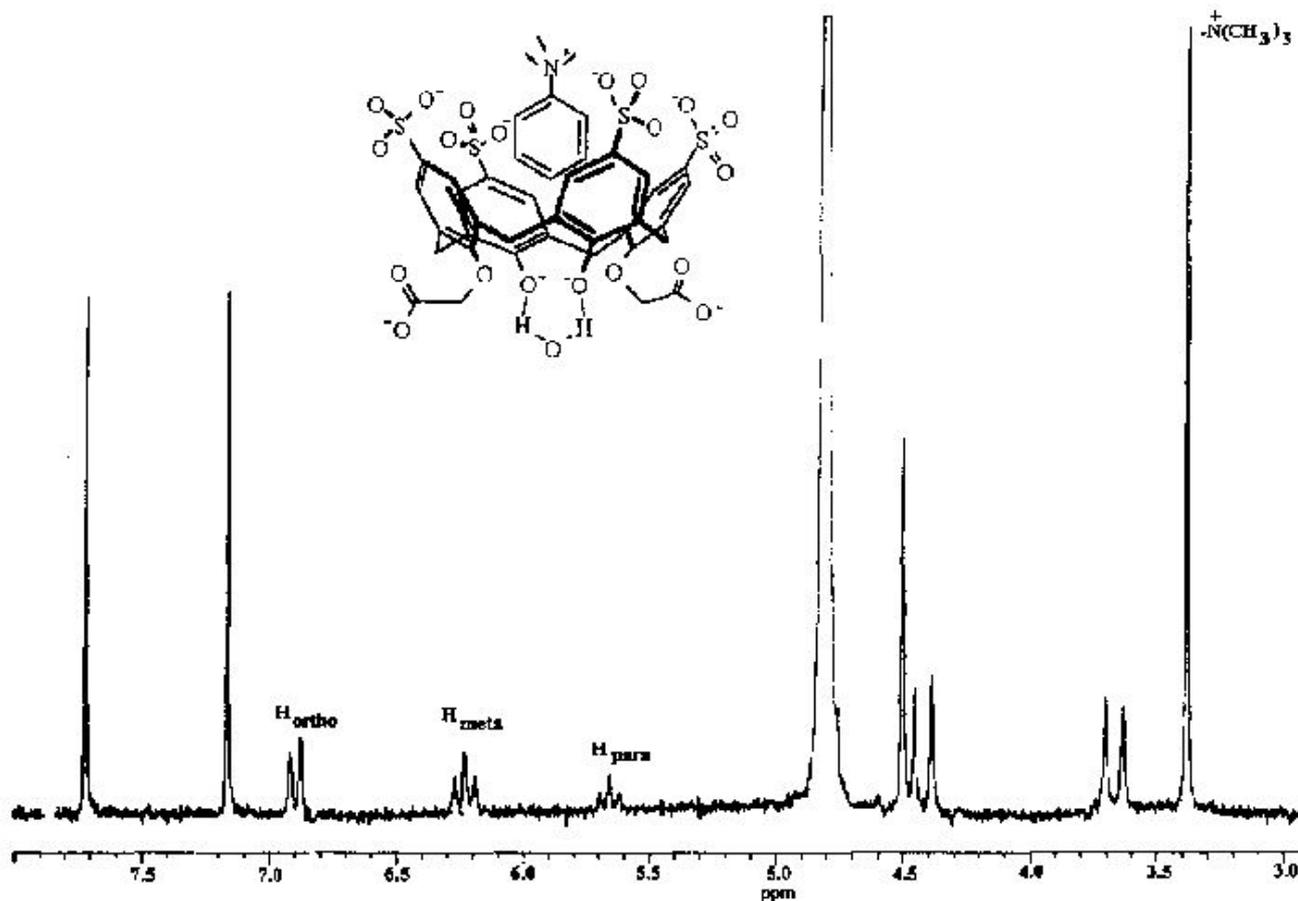
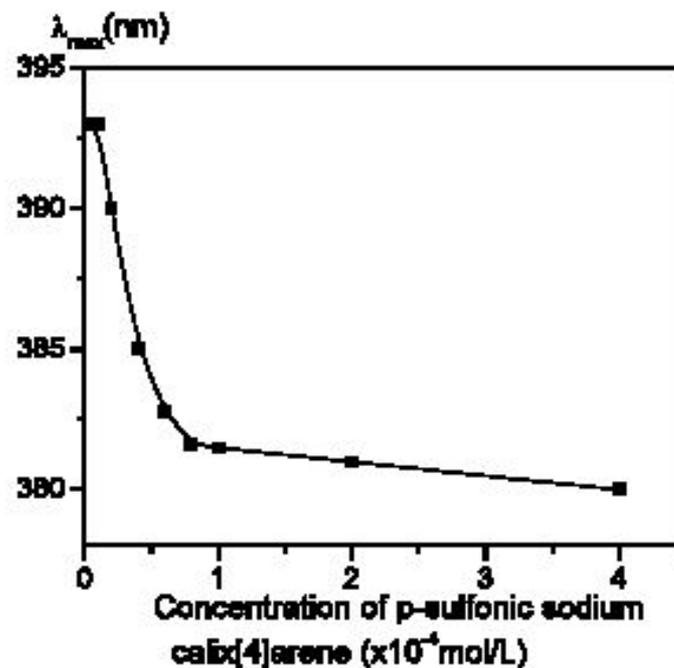
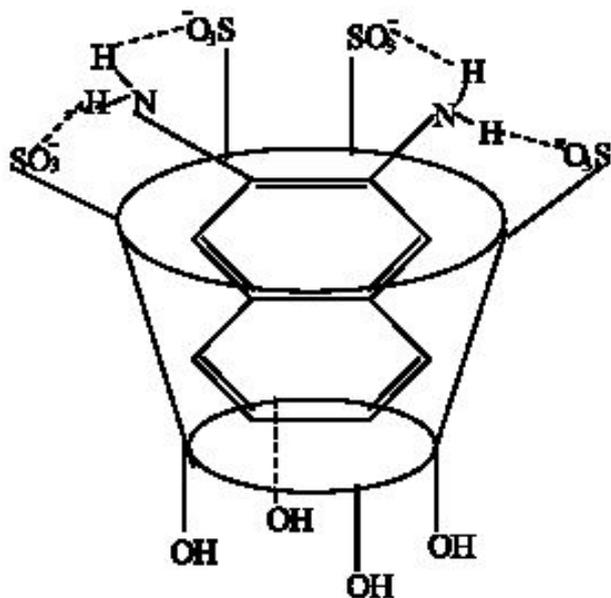
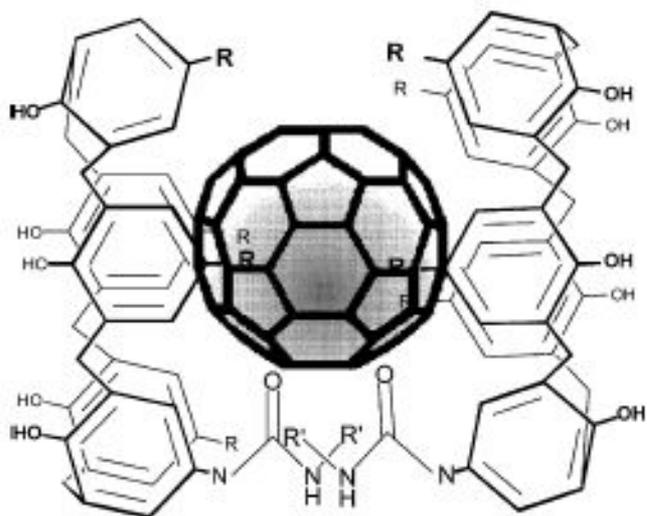


Figure 1. ¹H NMR spectrum of the 4-TMA system (D₂O, [4] = [TMA] = 1 × 10⁻³ mol dm⁻³, pD = 7.3, 25° C, 200 MHz). δ values (ppm) of free TMA (D₂O, pD = 7.3, [TMA] = 1 × 10⁻³ mol dm⁻³) H_{ortho} = 7.83, H_{meta} = 7.65, H_{para} = 7.61, N(CH₃)₃ = 3.64.

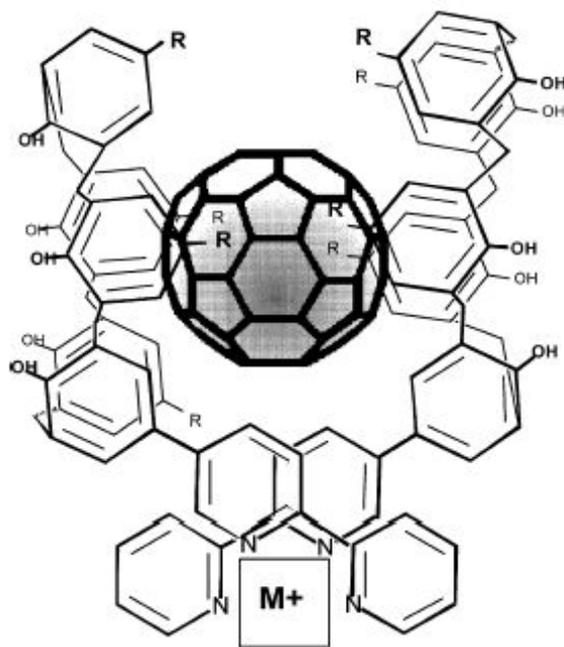
Комплексообразование с с органическими молекулами



Комплексообразование с органическими молекулами

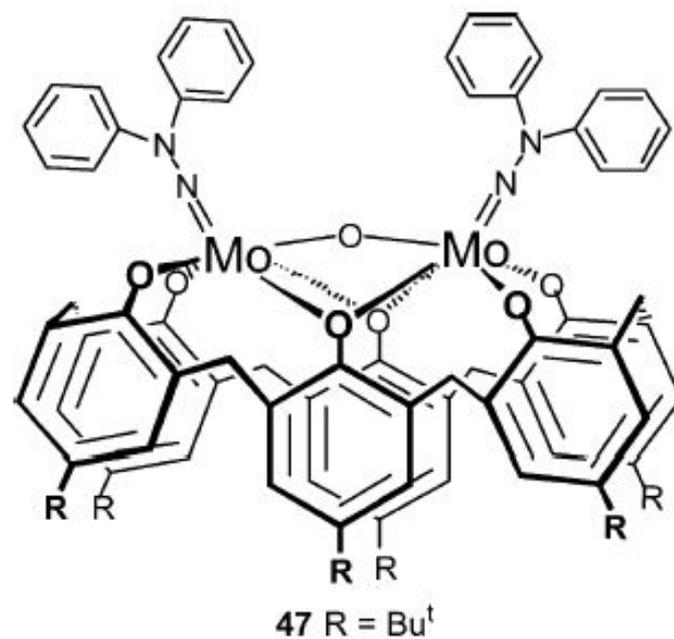
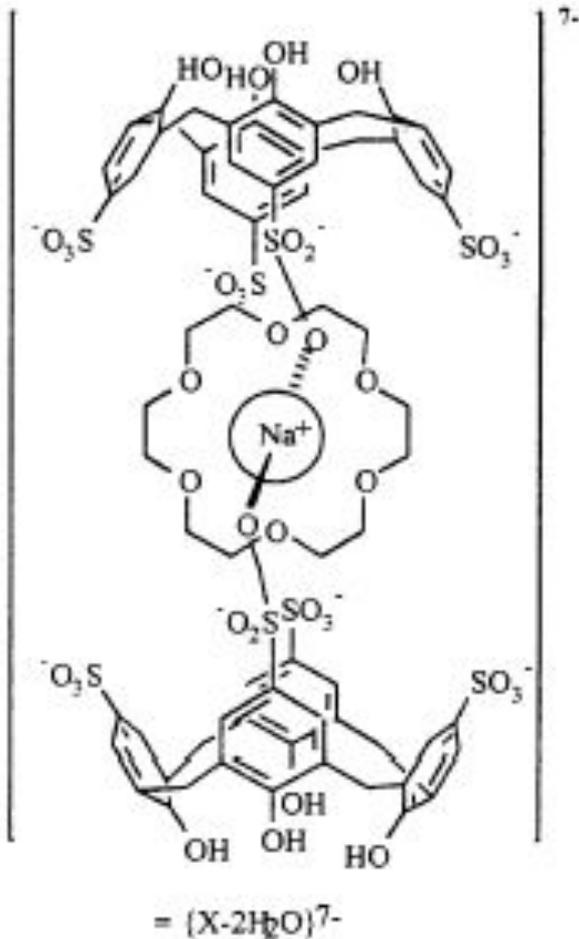


105 R = Me, R' = (CH₂)₆CH₃



106 R = Me

Смешанное комплексообразование



Комплексообразование

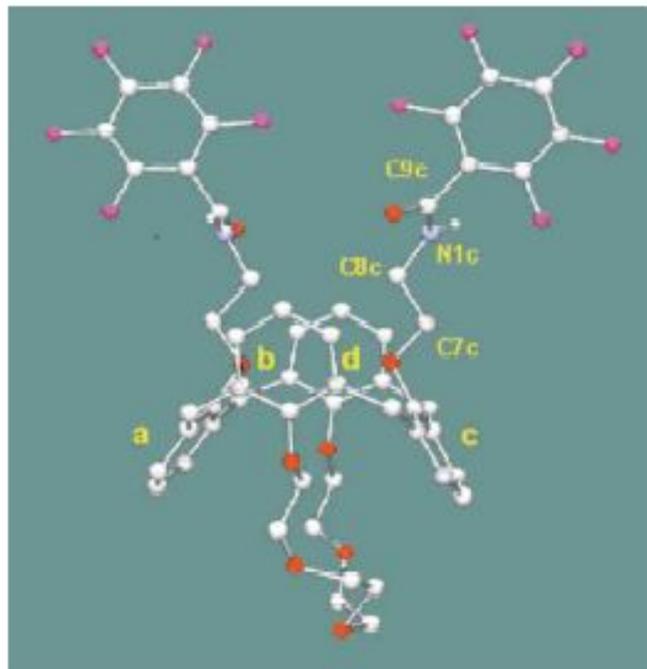
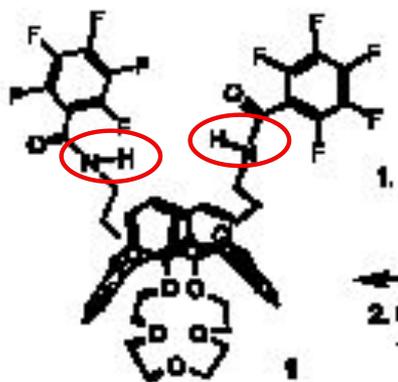
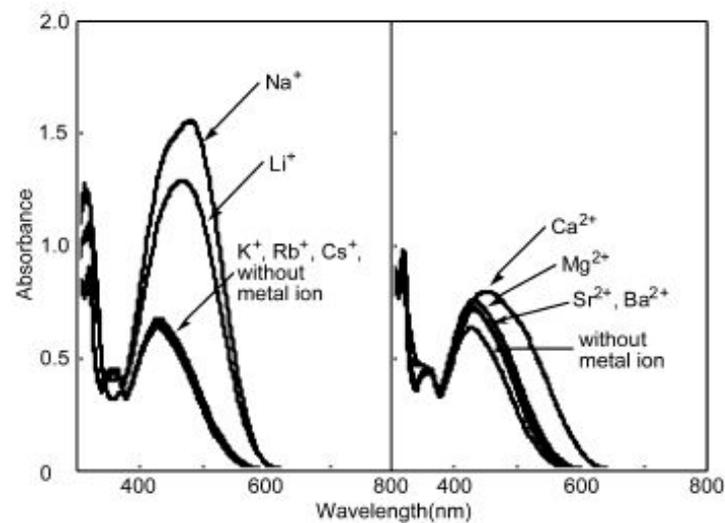
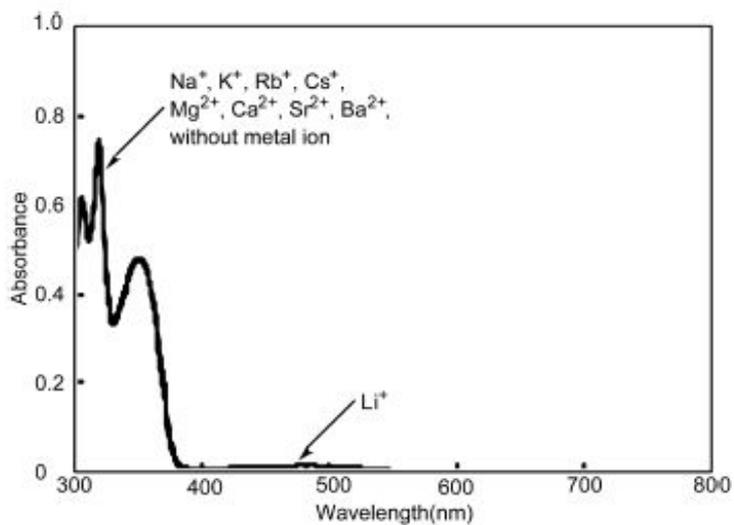
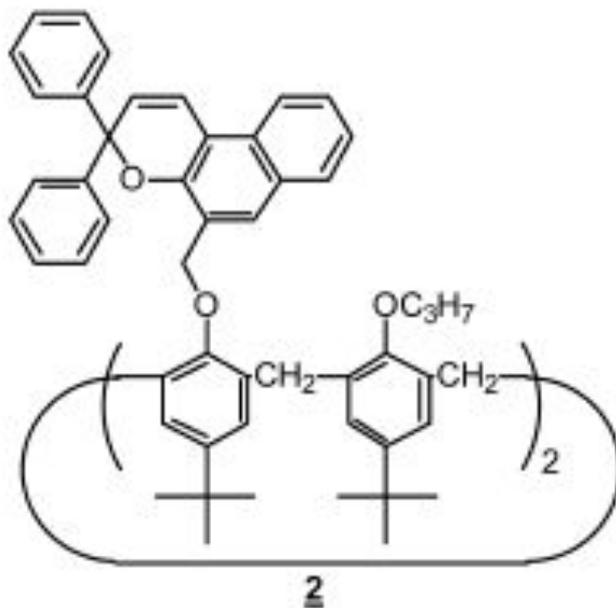


Figure 1. Perspective view of the free ligand 1 (colour key: carbon, white; oxygen, red; nitrogen, blue; hydrogen, white; fluorine, cyano).



Figure 2. A self-assembled superstructure held by anion-ligand and H-bonding (colour key: carbon, white; oxygen, red; nitrogen, blue; hydrogen, white; fluorine, cyano).

Комплексообразование



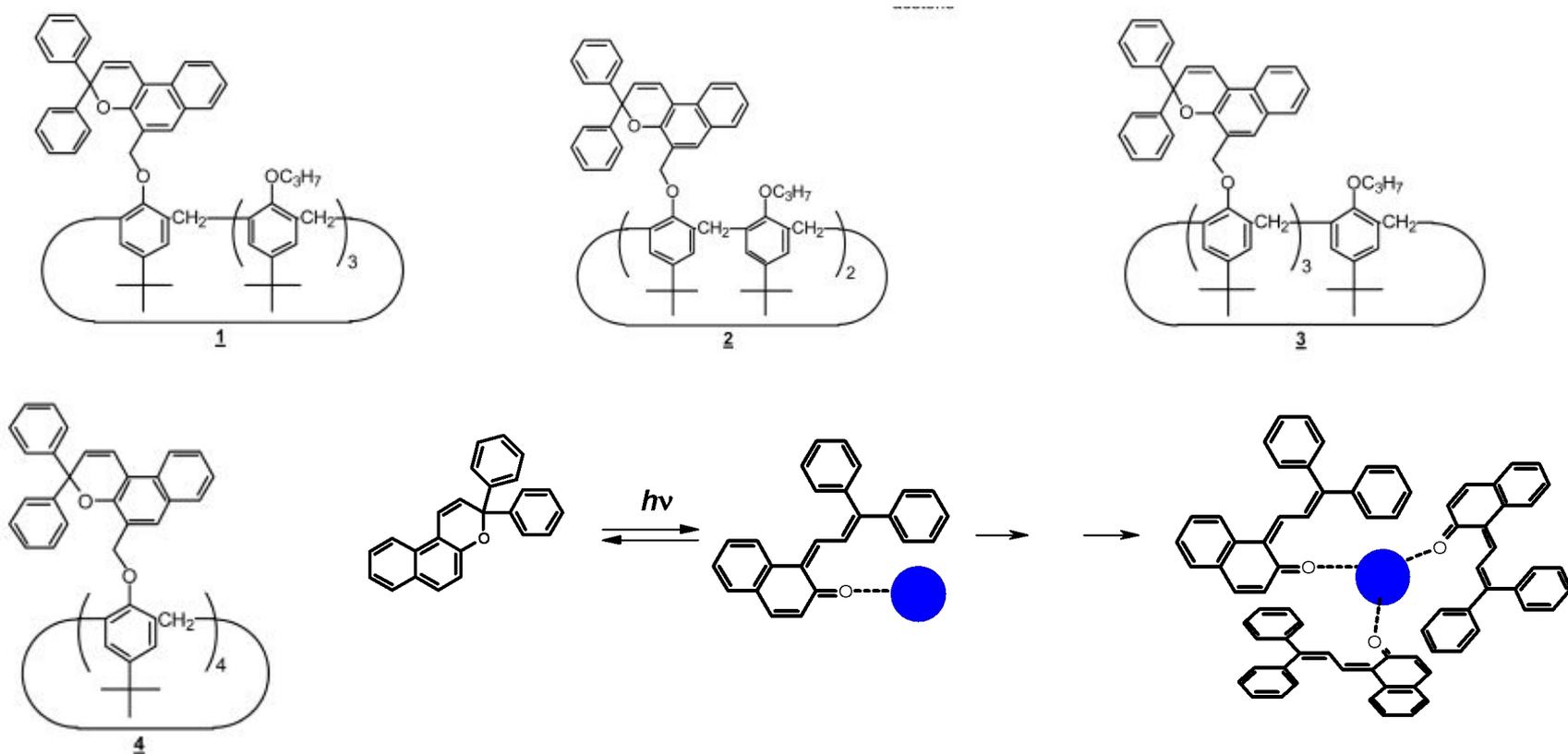
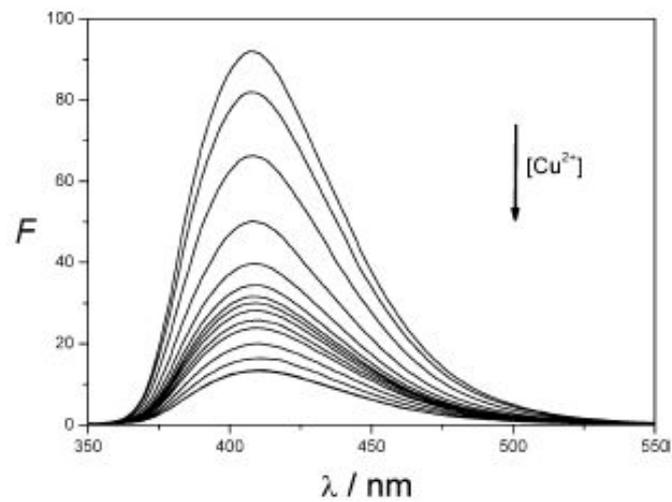
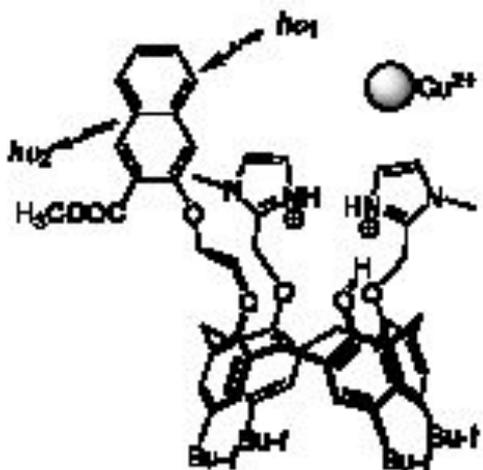
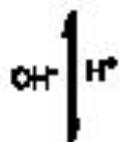
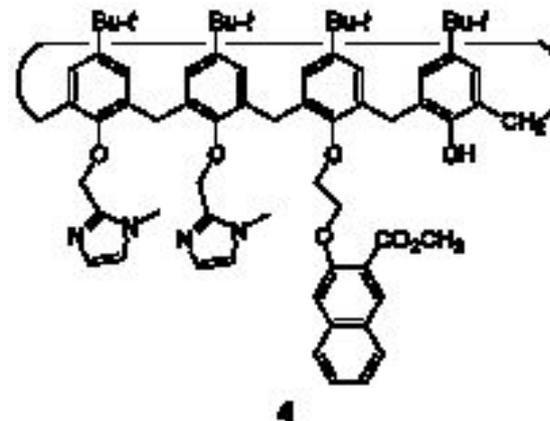
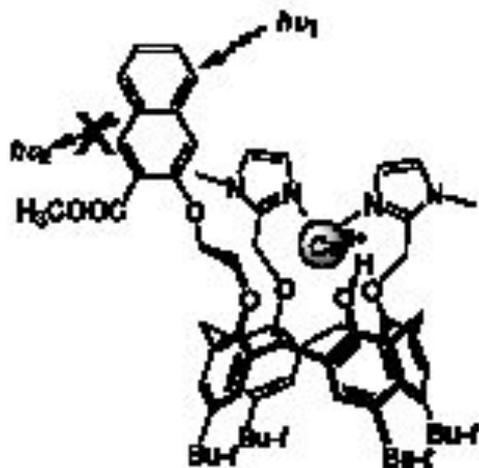


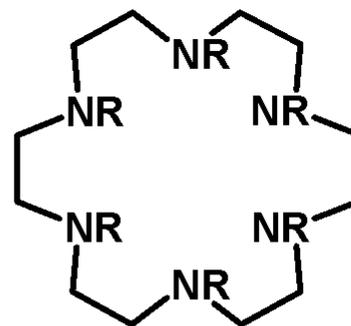
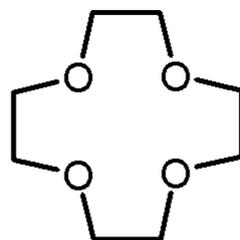
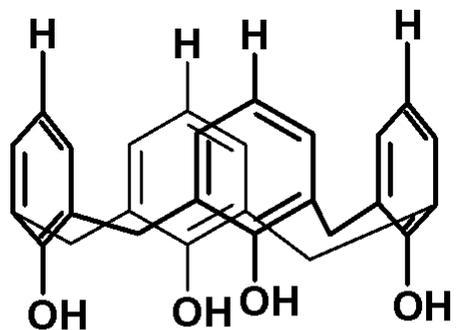
Table 1. Decoloration rate constants (10^{-2} s^{-1})

	Without metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	2.4	0.28	1.6	2.5	2.3	2.3	2.0	2.1	2.5	2.3
2	2.0	1.1	0.20	1.6	1.7	1.9	1.5	0.62	1.5	1.8
3	1.9	1.5	0.54	1.6	1.6	1.6	1.7	0.29	0.83	0.44
4	2.0	1.6	0.71	0.59	1.0	1.8	1.2	0.32	0.18	0.11

For **1**, a mixture of acetonitrile and chloroform, 7:1 (vol.) was used as a solvent while acetonitrile was used for **2–4**.

Комплексообразование





LiClO₄

LiOH

NH₄ClO₄

Экстракция из воды в органическую фазу

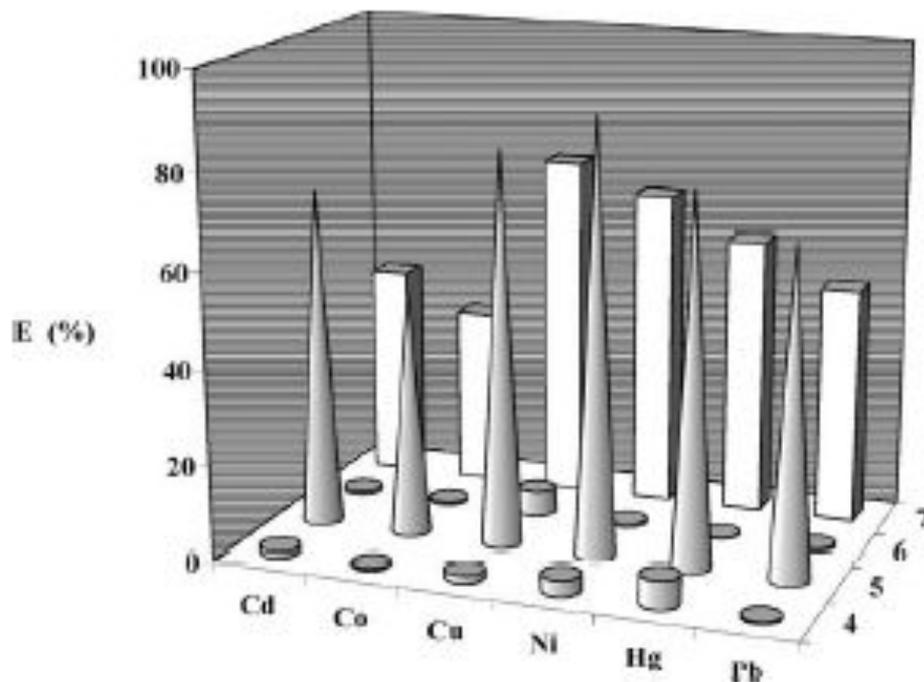
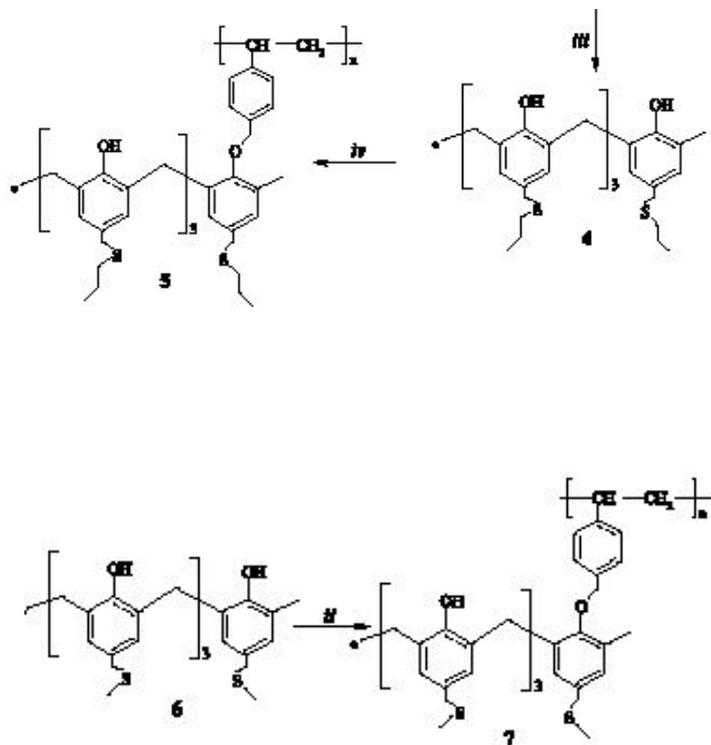
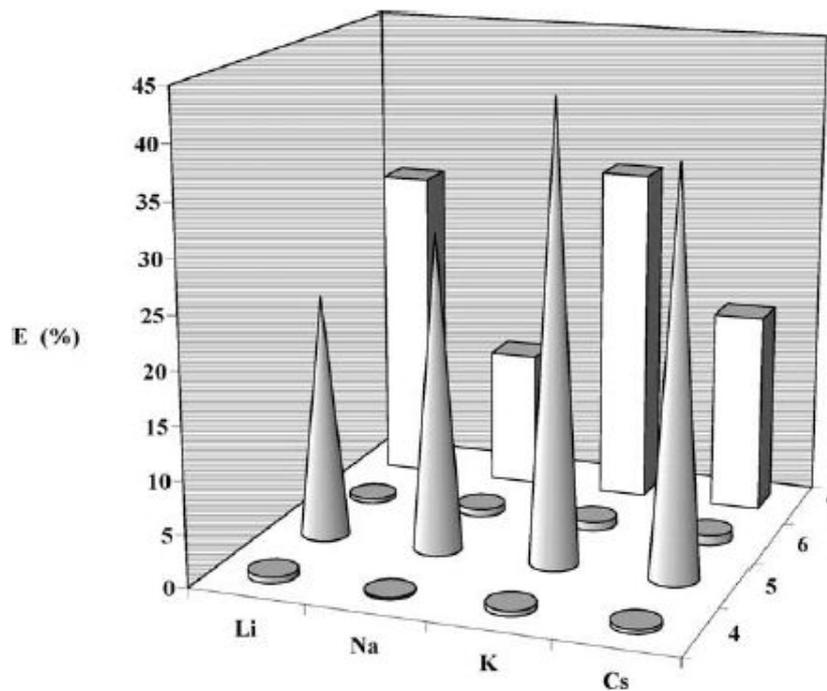
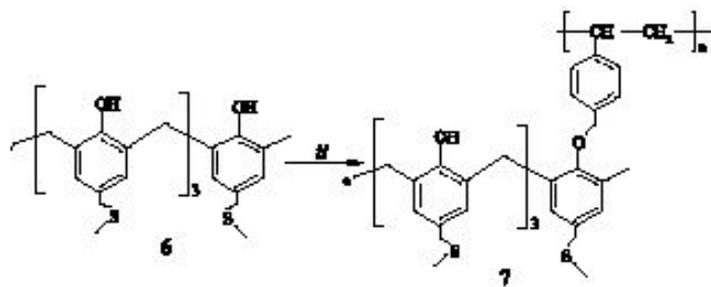
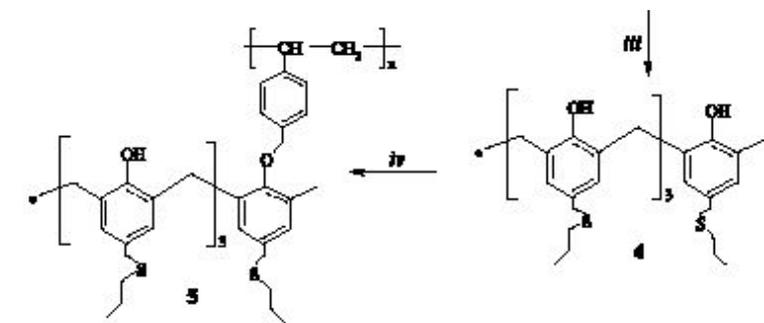


Fig. 1. Extraction percentage of the transition and post-transition metal picrates versus ligands 4–7. Aqueous phase, [metal picrate] = 2.0×10^{-5} M; organic phase, chloroform, [ligand] = 1.0×10^{-3} M or a 1.0×10^{-3} M solution of calix[4]arene unit/g polymer resin at 25 °C, for 1 h.

Экстракция из воды в органическую фазу



Экстракция из воды в органическую фазу

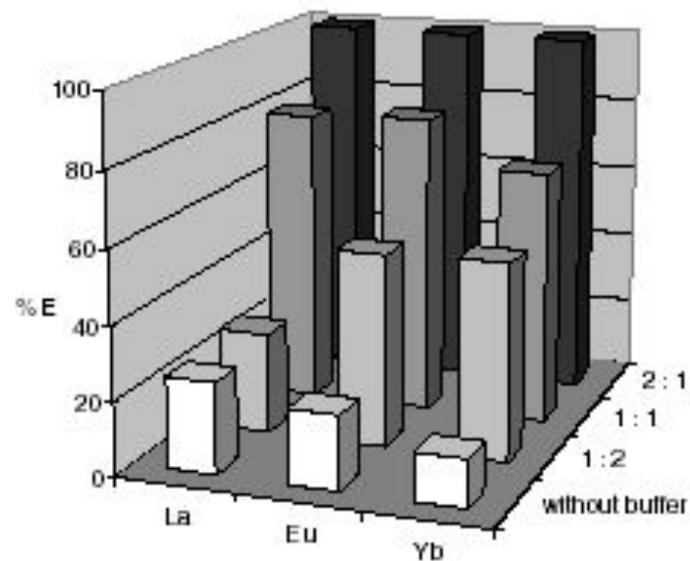
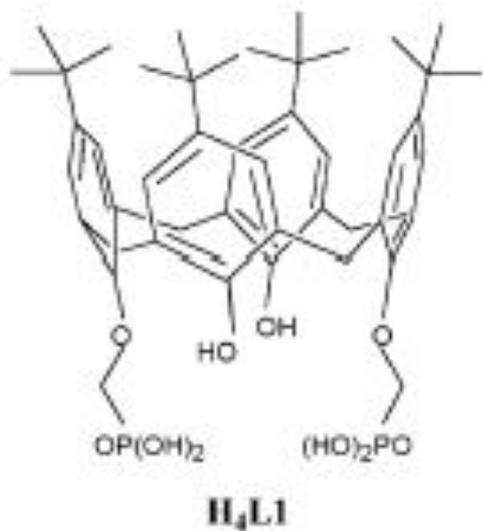


Fig. 4. Extraction efficiencies (%E) for the extraction of chosen lanthanide ions, using molar ratio (ligand **1b**/lanthanide ions), different pH (2 or 5.5) with compound **1b**. The signature without buffer means that the experiment was done with pH 2 in the aqueous phase.

Экстракция из воды в органическую фазу

