**Electronic supplementary materials** *Mendeleev Commun.*, 2022, **32**, 670–671

# Targeted preparation of highly efficient lithium extractants based on 14-membered crown ethers

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**Content**

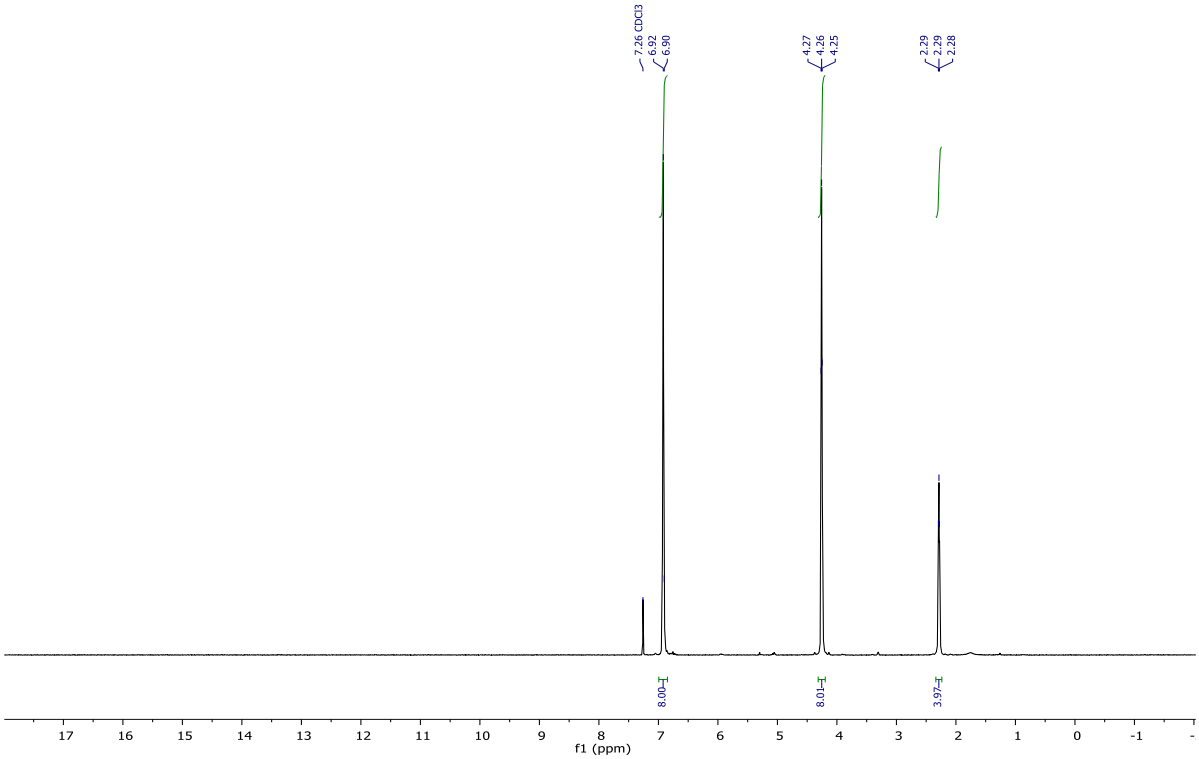


## 1. Synthesis and characterization of the 14-membered crown ethers

Dibenzo-14-crown-4 (**2**), di-*tert*-butylbenzo-14-crown-4 (**4**) and di-*tert*-butylcyclohexano-14-crown-4 (**5**) were synthesized in accordance with procedure described by C. Pedersen [S1], the synthesis of benzocyclohexano-14-crown-4 (**3**) has been described in paper[S2]. The macrocycles were characterized using NMR-spectrometry, FTIR-spectroscopy and DSC/TGA analysis. NMR spectra were measured with Bruker ‘‘Avance 600’’ NMR spectrometer (600 MHz $^{1}$H, 151 MHz $^{13}$C). Nicolet iS50FT-IR spectrometer was used to measure FTIR spectra in the range 4000−500 $cm^{-1}$ with a resolution of 2 $cm^{-1}$. The crown ethers were preliminary suspended in mineral oil. Thermo-chemical behavior was analyzed on a NETZSCH STA 449F3 apparatus. Samples was heated in $Al_2O_3$ pan with a vented cap in the temperature range from 306 K to 773 K at a heating rate of 10 K/min under dry argon flow of 30 ml/min. The results are given below.

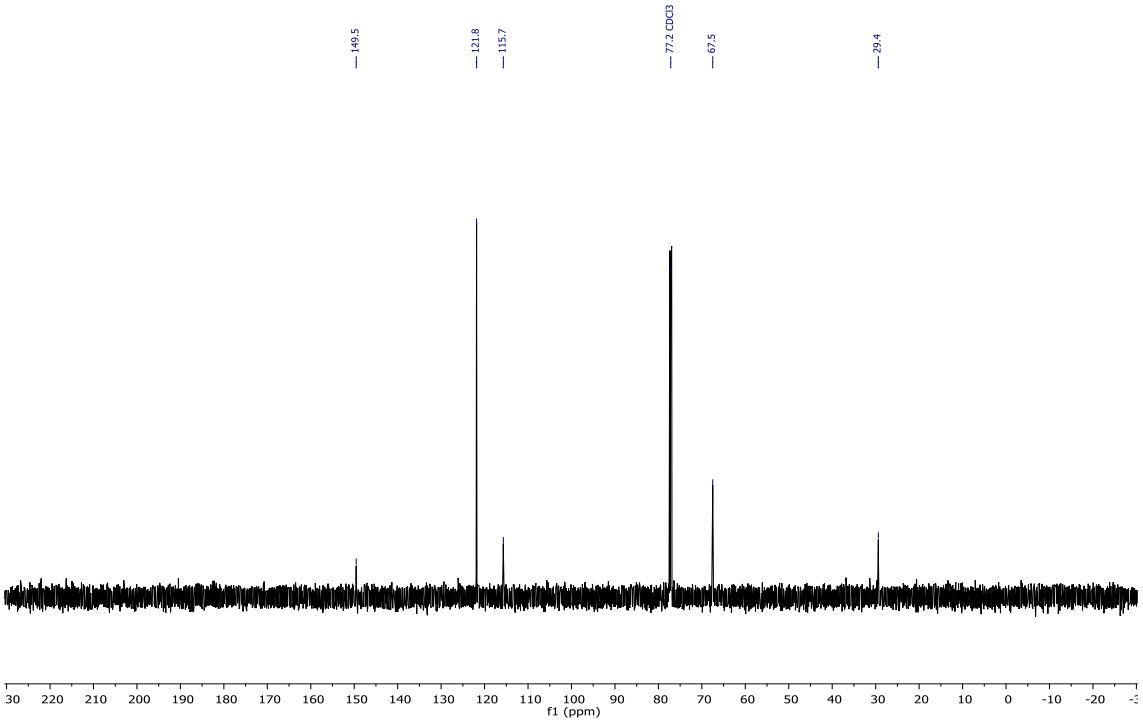
***Dibenzo-14-crown-4 (2)***

$^{1}$H NMR (600 MHz, $CDCl_3$): δ 6.91 (d, *J* = 9.6 Hz, 8H), 4.26 (t, *J* = 5.3 Hz, 8H), 2.34 – 2.24 (m, 4H).




**$^{1}$H NMR spectrum of 2**

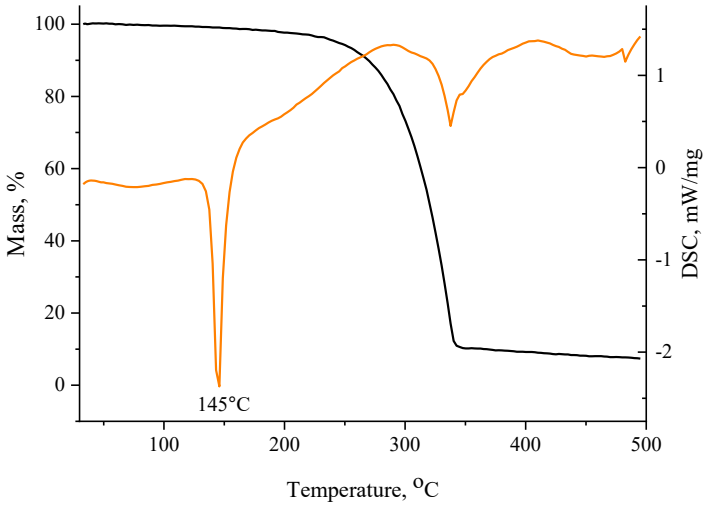
$^{13}$C NMR (151 MHz, $CDCl_3$): 149.5, 121.8, 115.7, 67.5, 29.4.




**$^{13}$C NMR spectrum of 2**

HRMS (ESI) calculated for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1439; found for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1435; calculated for $C_{18}H_{20}O_4Na$ $[M+Na]^+$: 323.1259; found for $C_{18}H_{20}O_4Na$ $[M+Na]^+$:323.1257.

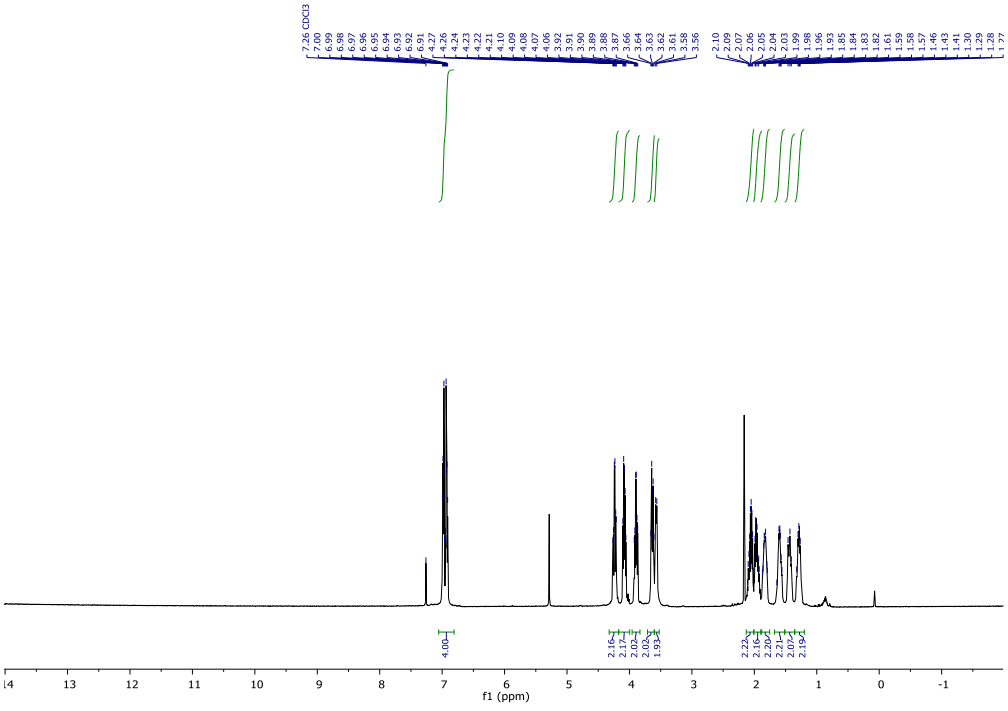
FTIR (mineral oil, 1700–400 $cm^{-1}$): 1592, 1507, 1258, 1234, 1123, 1051, 736 $cm^{-1}$.




**DSC/TGA analysis of 2** (m.p. = 145°C)

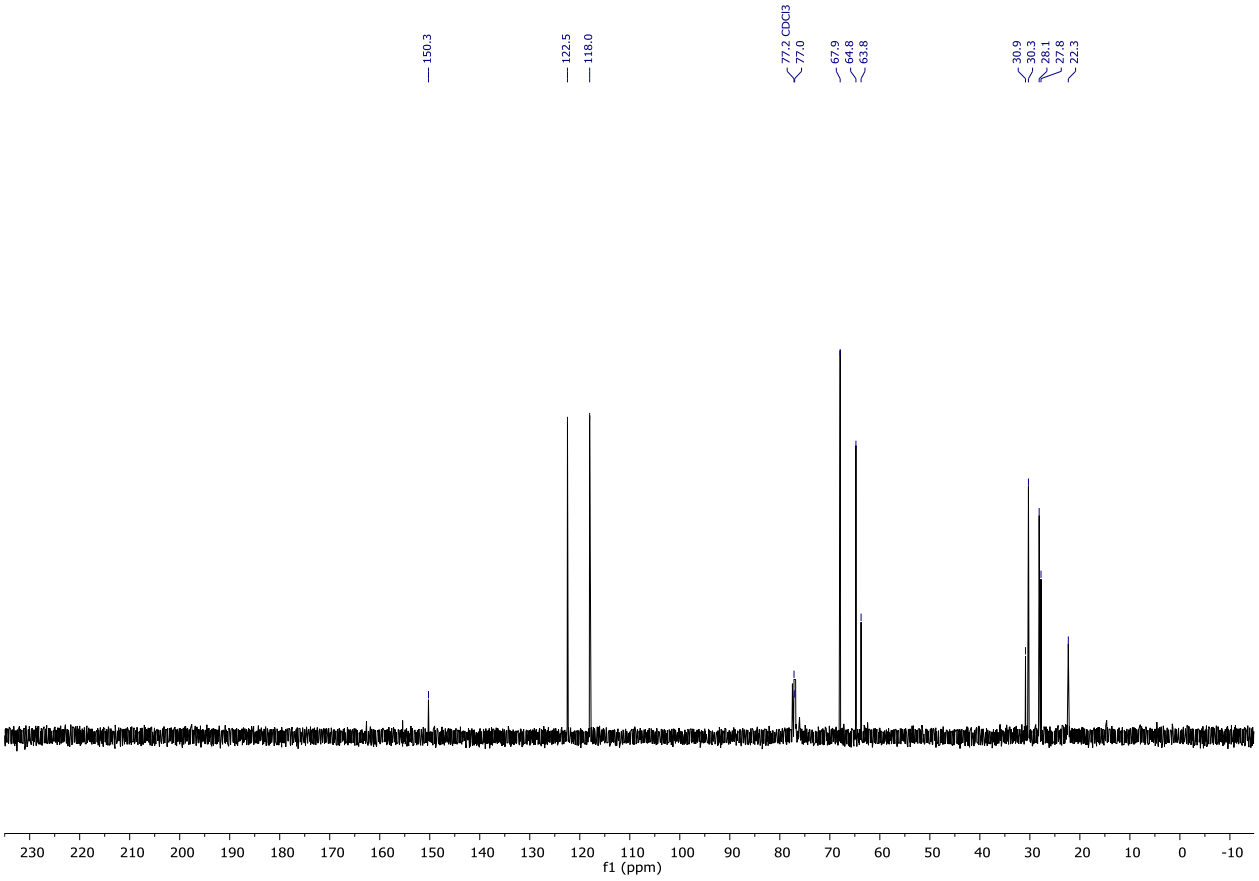
***Benzocyclohexano-14-crown-4 (3)***

$^1$H NMR (600 MHz, $CDCl_3$) δ 7.06 – 6.81 (m, 4H), 4.24 (td, *J* = 9.1, 3.8 Hz, 2H), 4.17 – 4.00 (m, 2H), 3.90 (td, *J* = 8.9, 4.5 Hz, 2H), 3.71 – 3.60 (m, 2H), 3.57 (d, *J* = 7.4 Hz, 2H), 2.13 – 2.01 (m, 2H), 2.01 – 1.88 (m, 2H), 1.90 – 1.75 (m, 2H), 1.68 – 1.51 (m, 2H), 1.51 – 1.35 (m, 2H), 1.35 – 1.20 (m, 2H).



**$^{1}$H NMR spectrum of 3**

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.3, 122.5, 118.0, 77.0, 67.9, 64.8, 63.8, 30.9, 30.3, 28.1, 27.8, 22.3.

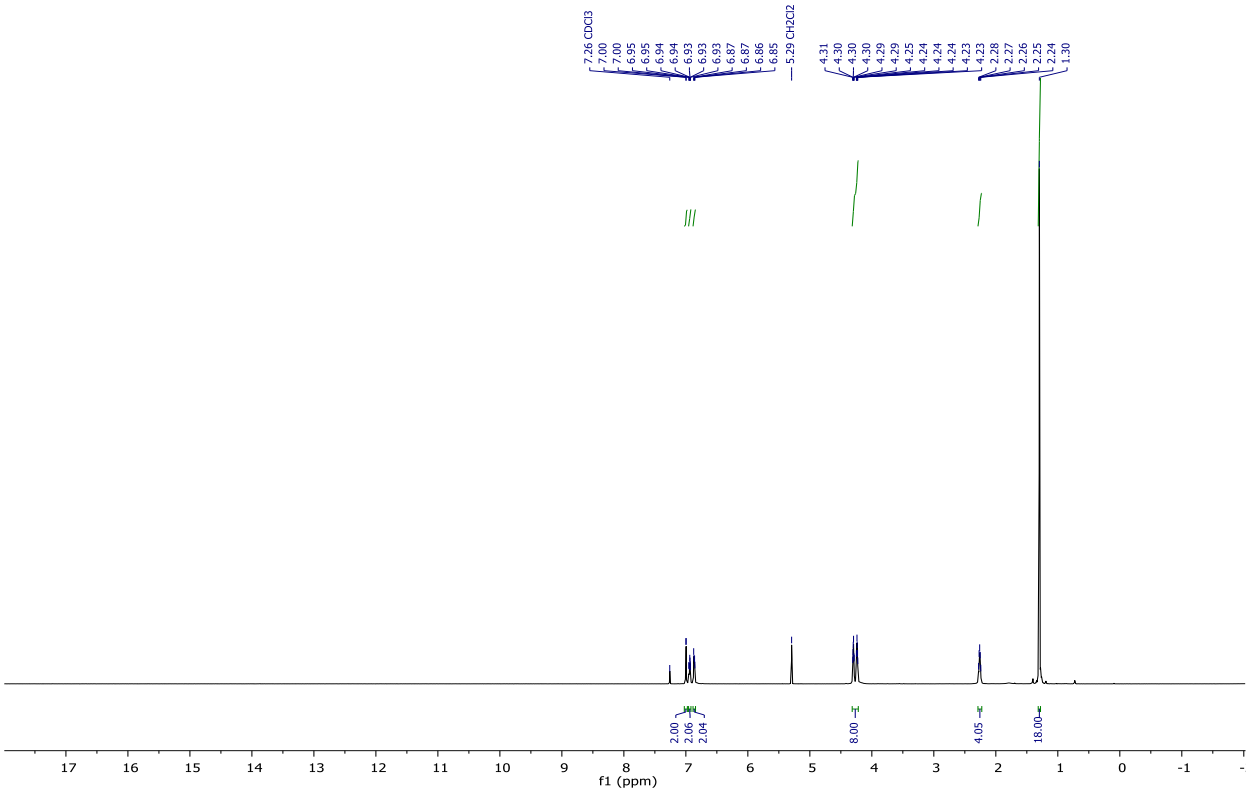



**$^{13}$C NMR spectrum of 3**

HRMS (APPI) calculated for $C_{18}H_{26}O_4$ $[M]^+$: 306.1826, 307.1859; found for $C_{18}H_{26}O_4$ $[M]^+$: 306.1826, 307.1873.

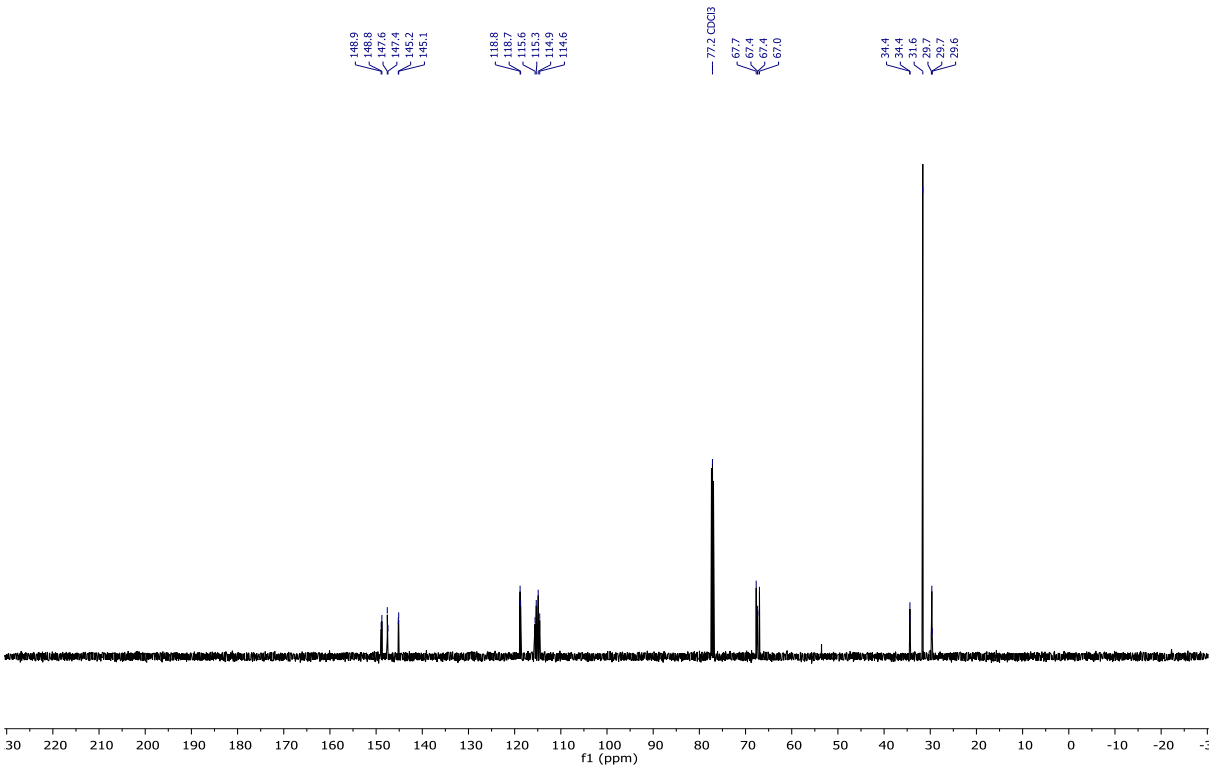
***Di-tert-butylbenzo-14-crown-4 (4)***

$^{1}$H NMR (600 MHz, $CDCl_3$): δ 7.00 (d, *J* = 2.1 Hz, 2H), 6.94 (ddd, *J* = 7.1, 4.8, 2.2 Hz, 2H), 6.86 (dd, *J* = 8.4, 3.2 Hz, 2H), 4.27 (dtd, *J* = 35.2, 5.5, 2.3 Hz, 8H), 2.26 (dt, *J* = 10.7, 5.2 Hz, 4H), 1.30 (s, 18H).




**$^{1}$H NMR spectrum of 4**

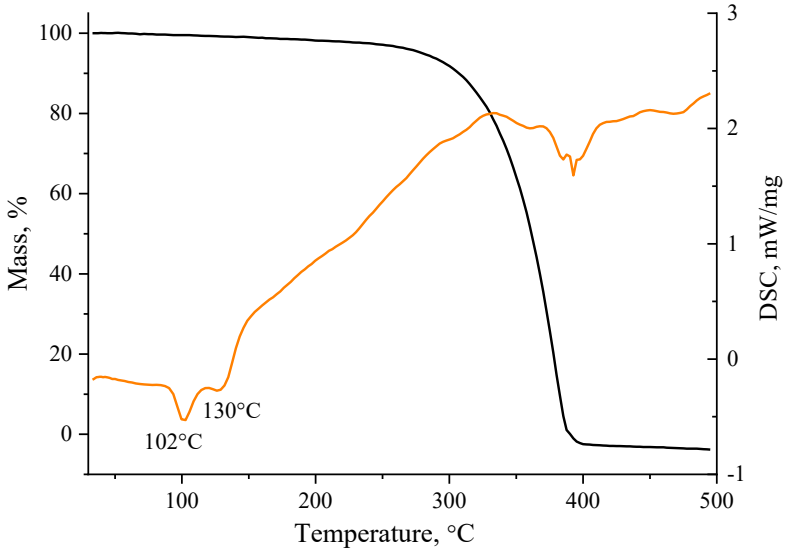
$^{13}$C NMR (151 MHz, $CDCl_3$): 148.9, 148.8, 147.6, 147.4, 145.2, 145.1, 118.8, 118.7, 115.6, 115.3, 114.9, 114.6, 67.7, 67.4, 67.4, 67.0, 34.4, 31.6, 29.7, 29.6.




**$^{13}$C NMR spectrum of 4**

HRMS (ESI) calculated for $C_{26}H_{37}O_4$ $[M+H]^+$: 413.2691; found for $C_{26}H_{37}O_4$ $[M+H]^+$: 413.2696; calculated for $C_{26}H_{36}O_4Na$ $[M+Na]^+$: 435.2511; found for $C_{26}H_{36}O_4Na$ $[M+Na]^+$:435.2516.

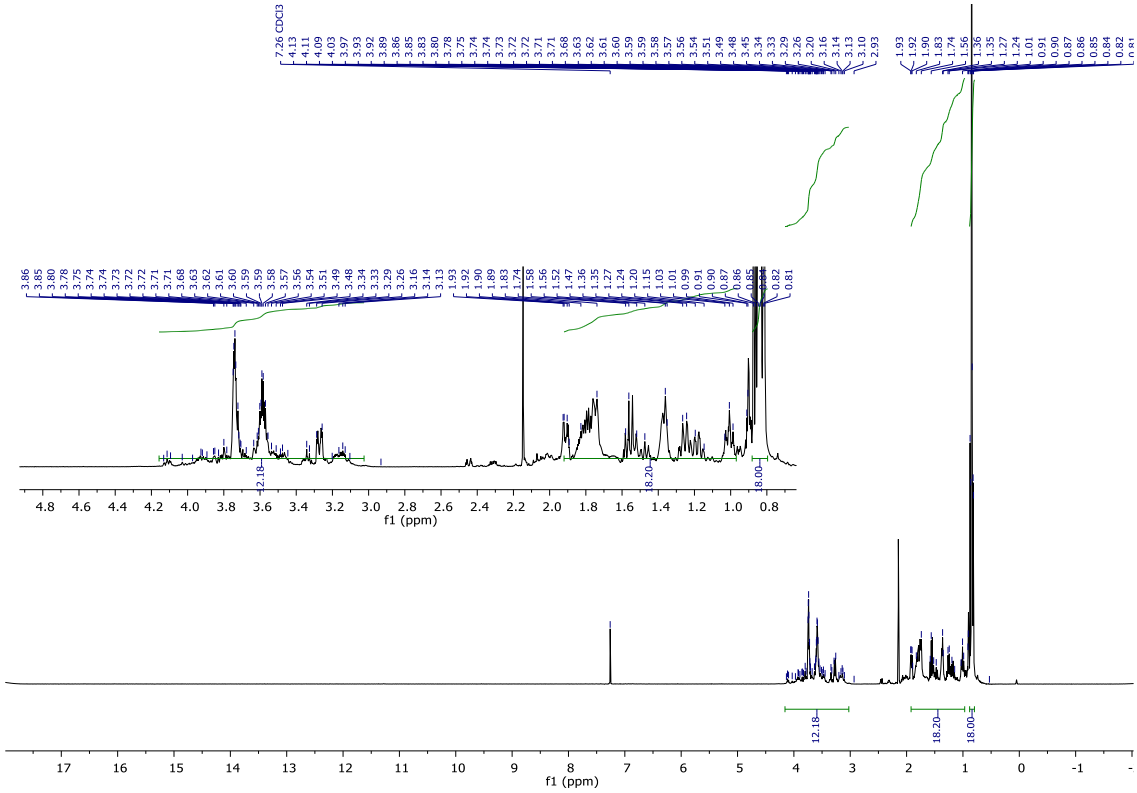
FTIR (mineral oil, 1700–400 $cm^{-1}$): 1606, 1577, 1505, 1266, 1207, 1131, 1103, 1050 $cm^{-1}$.




**DSC/TGA analysis of 4 (**m.p. = 102°C and 130°C, mixture of isomers)

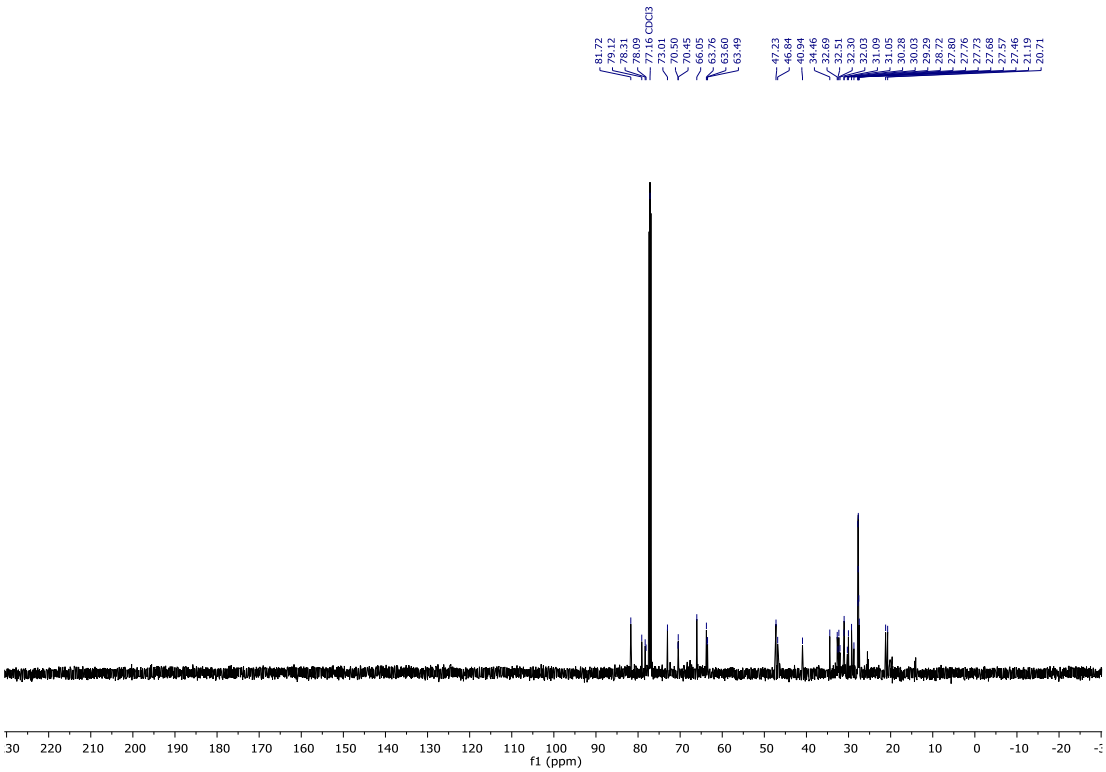
***Di-tert-butylcyclohexano-14-crown-4 (5)***

$^{1}$H NMR (600 MHz, $CDCl_3$) δ 4.16 – 3.03 (m, 12H), 1.92 – 0.97 (m, 18H), 0.88 – 0.80 (m, 18H).




**$^{1}$H NMR spectrum of 5**

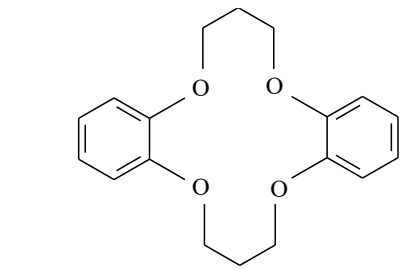
$^{13}$C NMR (151 MHz, $CDCl_3$) δ 81.72, 79.12, 78.31, 73.01, 70.50, 70.45, 66.05, 63.76, 63.60, 63.49, 47.23, 46.84, 40.94, 34.46, 32.69, 32.51, 32.30, 32.03, 31.09, 31.05, 30.28, 30.03, 29.29, 28.72, 27.80, 27.76, 27.73, 27.68, 27.57, 27.46, 21.19, 20.71.



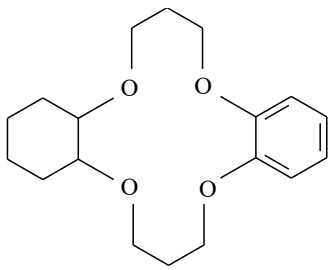

**$^{13}$C NMR spectrum of 5**

HRMS (ESI) calculated for $C_{26}H_{49}O_4$ $[M+H]^+$: 425.3625, 426.3659; found for $C_{26}H_{49}O_4$ $[M+H]^+$: 425.3626, 426.3661; calculated for $C_{26}H_{48}O_4Na$ $[M+Na]^+$: 447.3445; found for $C_{26}H_{48}O_4Na$ $[M+Na]^+$: 447.3442.

**Structural formulas of 14-membered crown ethers**



**2**



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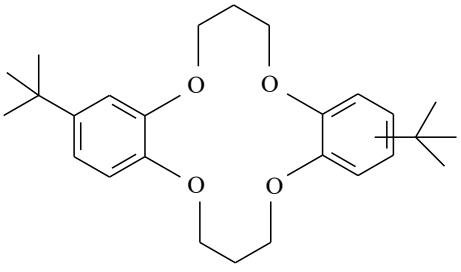
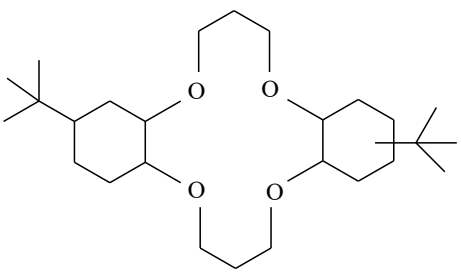


**4**



**5**

## 2. Distribution of macrocyclic ligand between chloroform and the aqueous phase

The distribution of aromatic macrocycles between the organic (0.1 M solution of CE in $CHCl_3$) and aqueous (2 M solution of LiBr in $H_2O$) phases was estimated using the technique described in the paper [S3]. The aqueous phase was analyzed by UV-spectrophotometry either directly (as for **1**), or after re-extraction of CE from aqueous phase into chloroform (for the other CEs). In the second case, the ratio of the aqueous and organic phases of 15:5 was used at the stage of CE re-extraction in order to increase the macrocycle concentration of in the analyzed sample. The distribution of **5** was studied by a modified extraction-spectrophotometric technique [S4]. It is based on the ability of the CE to form a stable, colored $CE{\cdot}Me^{n+}$ $BTS^{-}_{n}$ macrocyclic complex, which is quantitatively re-extracted from aqueous phase into an organic solvent. In the formula $Me^{n+}$ presents metal cation and $BTS^{-}$ is a colored organic anion. At the stage of the CE re-extraction from aqueous phase, the sodium form of bromothymol blue, $Na^{+}{\cdot}BTS^{-}$, and toluene were chosen as the dye salt and the solvent, respectively.

## 3. Calculation of the lithium distribution coefficient $D_{Li}$

The extractability of LiBr was estimated by the values of the Li+ distribution coefficients ($D_{Li}$):

$$D_{Li} = [Li_{org.}]^{eq}/[Li_{aq}]^{eq},$$

where $[Li_{opr.}]^{eq}$ represents the equilibrium concentration of lithium cations in the organic phase, and $[Li_{aq.}]^{eq}$ - the equilibrium concentration of $Li^{+}$ in the aqueous phase.

An aqueous 2 M solution of LiBr was extracted with 0.1 M solution of CE in $CHCl_3$ at a phase ratio of 1:1 using a laboratory shaker PE-6410 (Ekros, Russia) for 30 min. The obtained phases were divided on a laboratory centrifuge PE-6926 (Ekros, Russia). The rotation speed was 2500 rpm, the phase separation time was 5 min. The organic phase was separated (17 ml) and the extracted lithium was re-extracted with an equal volume of deionized water with a resistivity of 18 MOm·cm.

The concentration of the re-extracted $Li^{+}$ in the resulting aqueous phase was determined using a lithium-selective electrode "Alice-142Li" ("Measuring Equipment", Russia) and the analyzer "Expert-001-3" (Econix-Expert, Russia). The pH of the analyzed solution was controlled using a glass combined electrode ESC-100603/7. The lithium-selective electrode was pre-calibrated using solutions with a known concentration of $Li^{+}$ in the range from $1{\cdot}10^{-4}$ to 0.1 M.

The calibration graph is shown in Figure S1. Dependence of emf (E, mV) of the electrode system from the concentration of the $Li^+$ solution is described by the equation:

$$E = -(2510\pm2) - (53\pm1)\cdot pX, \text{ where } pX = -\lg[Li_{aq}]$$

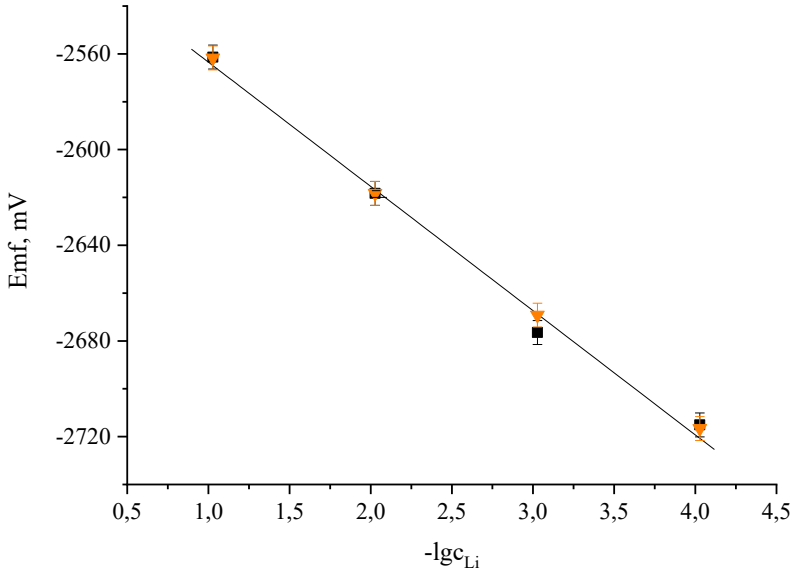



Figure S1. The calibration curve for the lithium-selective electrode at aqueous phase pH of 7.7-8.3, the symbols (▼) и (■) refer to the solutions saturated and unsaturated with chloroform

Considering the completeness of $Li^+$ re-extraction from the organic phase to the aqueous phase at a phase ratio of 1:1, the resulting concentration value was $[Li_{org}]^{eq}$. The equilibrium concentration of $Li^+$ in the aqueous phase ($[Li_{aq}]^{eq}$) was calculated by the formula:

$$[Li_{aq}]^{eq} = [Li_{aq}]^0 - [Li_{org}]^{eq},$$

in which $[Li_{aq}]^0$ represents the initial concentration of $Li^+$ cations in the aqueous phase.

The $D_{Li}$ values were averaged based on the results of three parallel tests.

**References**

**S1**. C. J. Pedersen. *J. Am. Chem. Soc.* 1967, **89**, 7017.

**S2**. J. C. Bryan, R. A. Sachleben. *Acta Cryst.* 2000, **C56**, 1104.

**S3**. O.A. Zakurdaeva, A.F. Asachenko, M.A. Topchiy, S.V. Nesterov. *J. Radioanal. Nucl. Chem.*, 2018, **316**, 535.

**S4**. O. A. Zakurdaeva, S. V. Nesterov. *J. Radioanal. Nucl. Chem.*, 2015, **303**, 1737.