Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 119-120

Chemical aspects of the radiation stability of macrocyclic extractants designed for ^{90}Sr separation

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Contents

I. Experimental section

I.1. Materials

Cis-anti-cis-isomer of DCH18C6 was isolated from commercial product (Alfa Aesar, mixture of isomers, 97%) by using Izatt's procedure[S1]. Chloroform (99.2%, Khimmed, Russia), HBF_4 (Sigma-Aldrich, 48 wt. % in H_2O) and diethyl ether (analytical grade, Baum Lux, Russia) were used as received.

I.2. Synthesis

The synthesis of *cis-anti-cis*-DCH18C6·H_3O·BF_4 complex was carried out in accordance with published procedure[S2]. *Cis-anti-cis*-DCH18C6 (0.25 g, 0.67 mmol) was dissolved in 7 ml of

$CHCl_3$. The solution of tetrafluoroboric acid (48% wt. % in H_2O, 0.7 ml, 4.4 mmol) was added to the chloroform solution, and the reaction mixture was stirred for 30 min at room temperature. The organic phase was separated by using separation funnel. $CHCl_3$ was evaporated under vacuum, and resulting crystalline solids were washed with diethyl ether (3 × 1 ml). Residual $(C_2H_5)_2O$ was removed under vacuum to give 0.24 g *cis-anti-cis*- DCH18C6·H_3O·BF_4 complex with 74% yield**.**

The complex formation is described by the following reaction:

HBF_{4aq} + $DCH18C6_{org}$ + H_2O ↔ DCH18C6·H_3O·BF_4

I.3. Characterization

Cis-anti-cis-DCH18C6 and *cis-anti-cis*- DCH18C6·H_3O·BF_4 were characterized by NMR-, FTIR-spectroscopy and DSC/TGA analysis. FTIR spectra were measured in mineral oil using a Nicolet iS50 FT-IR spectrometer with a resolution of 2 cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker "Avance 600" spectrometer. The ^{1}H chemical shifts were referenced to the residual undeuterated solvent peak, ^{13}C chemical shifts were referenced to the solvent peak, ^{19}F NMR chemical shifts were referenced to external standard CF_3CO_2H (0.0 ppm). Thermogravimetric and differential scanning calorimetric analysis was carried out on a NETZSCH STA 449F3 apparatus. Samples were heated in the temperature range from 40 to 500°C at a heating rate of 10°C/min under argon flow of 30 ml/min.

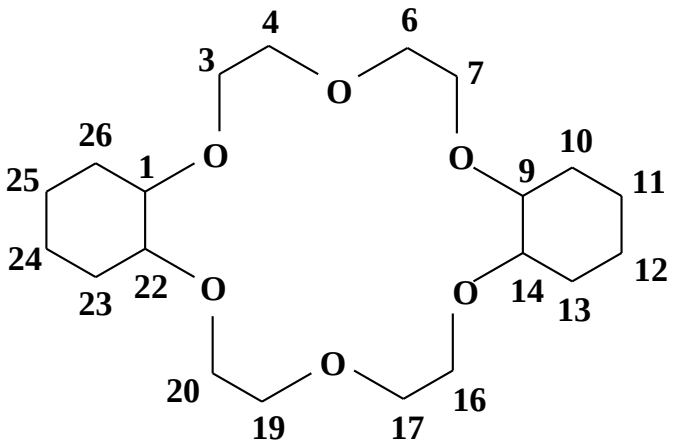
Cis-anti-cis-DCH18C6:

^{1}H NMR (300 MHz, $CDCl_3$) δ 1,20-1,27 (m); 1,37-1,44 (m); 1,52-1,60 (m); 1,78-1,88 (m); 3,49-3,50 (m); 3,51-3,52 (m); 3,61 (m); 3,63 (m); 3,65-3,66 (m); 3,69 (m); 3,70 (m), 3,72 (m); ^{13}C ЯМР (75 МГц, $CDCl_3$) δ 22,01 (C_{11}, C_{12}, C_{24}, C_{25}); 27,59 (C_{10}, C_{13}, C_{23}, C_{26}); 67,85 (C_3, C_7, C_{16}, C_{20}); 70,50 (C_4, C_6, C_{17}, C_{19}); 77,51 (C_1, C_9, C_{14}, C_{22}). DSC/TGA: m.p. = 69.8^{0}C, $T_{5\%}$= 257^{0}C.

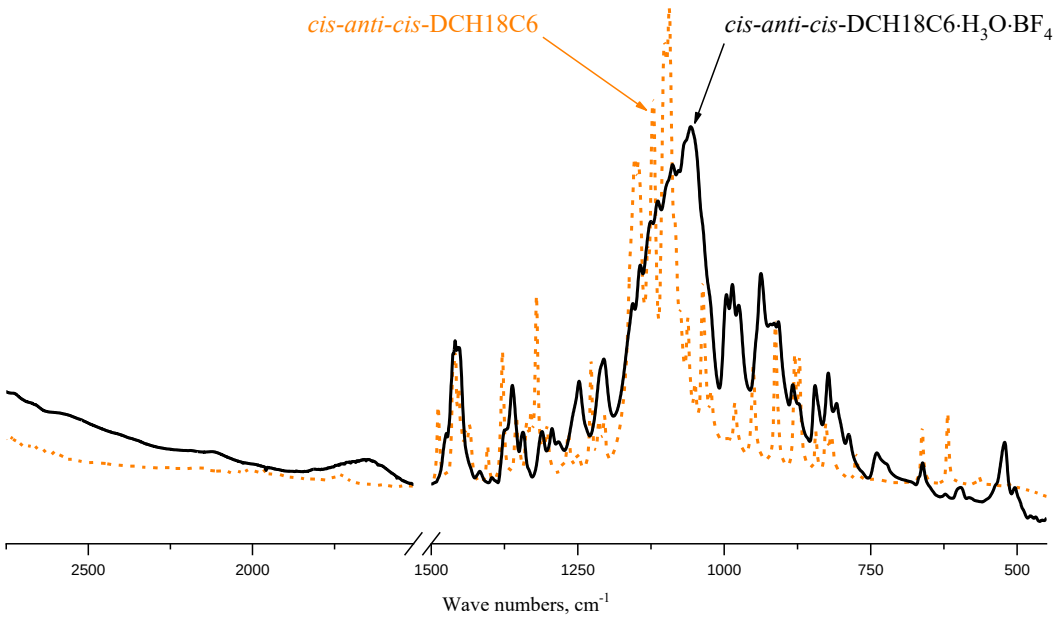
Cis-anti-cis-DCH18C6·H_3O·BF_4:

^{1}H NMR (600 MHz, $CDCl_3$, 323K) δ 1.31–1.33 (m, 4H), 1.57–1.62 (m, 8H), 1.89–1.94 (m, 4H), 3.67–3.86 (m, 20H), 8.80 (br.s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*, 323K) δ 21.53 (C_{11}, C_{12}, C_{24}, C_{25}), 26.08 (C_{10}, C_{13}, C_{23}, C_{26}), 67.12 (C_3, C_7, C_{16}, C_{20}) ,70.76(C_4, C_6, C_{17}, C_{19}), 79.00 (C_1, C_9, C_{14}, C_{22}); ^{11}B NMR (64 MHz, Chloroform-d, 298K) δ -0.95; ^{19}F NMR (188 MHz, Chloroform-d, 298K) δ -151.46, -151.52, -155.48, -155.53. DSC/TGA: $T_{5\%}$= 140^{0}C

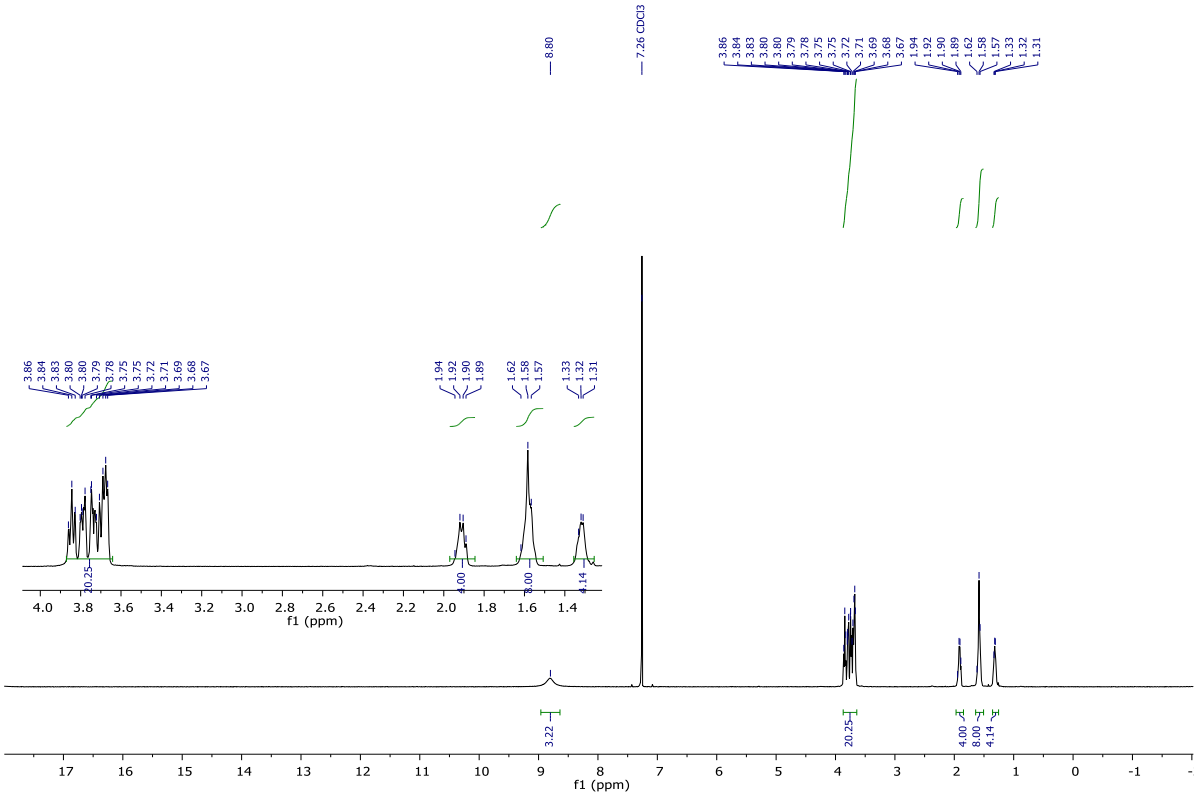
The positions of carbon atoms in DCH18C6 are given in the scheme below:



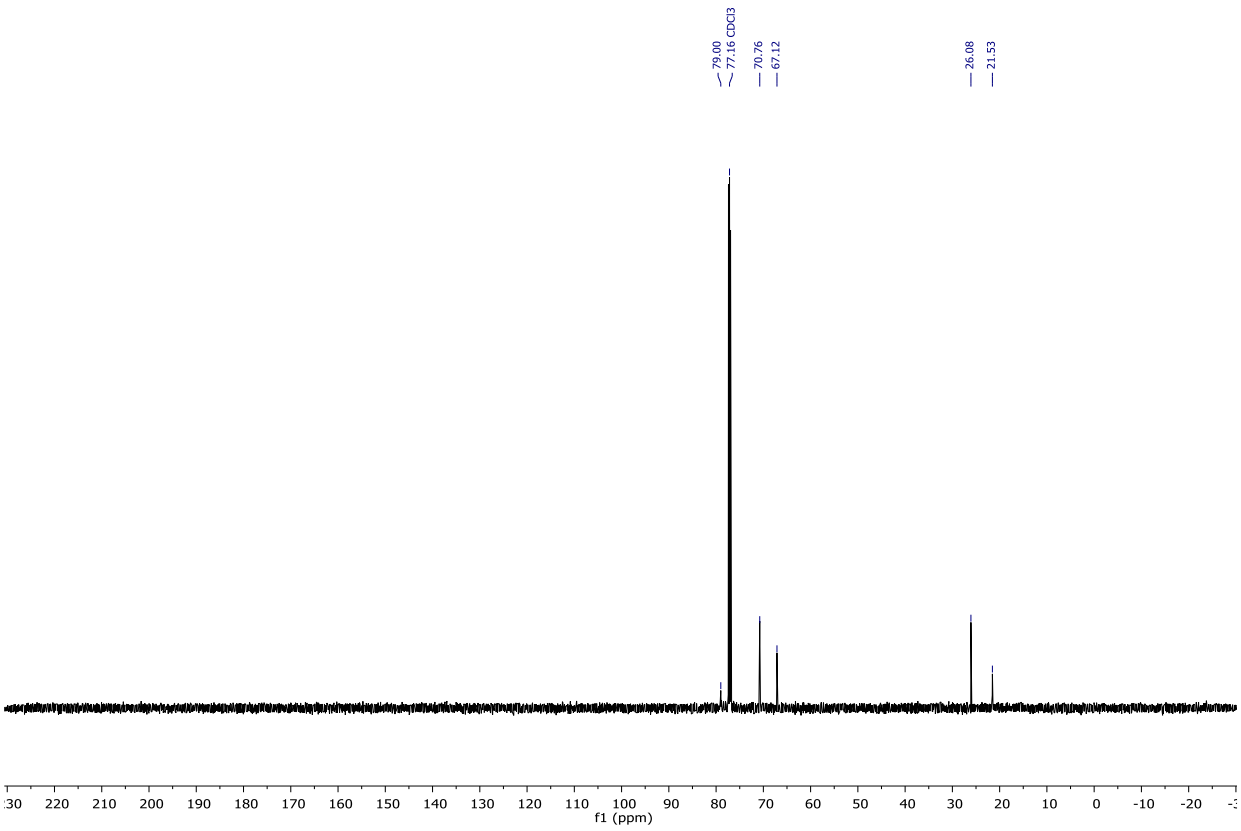
FTIR spectra of *cis-anti-cis*-DCH18C6 and *cis-anti-cis*- DCH18C6·H_3O·BF_4 suspended in mineral oil are given below:



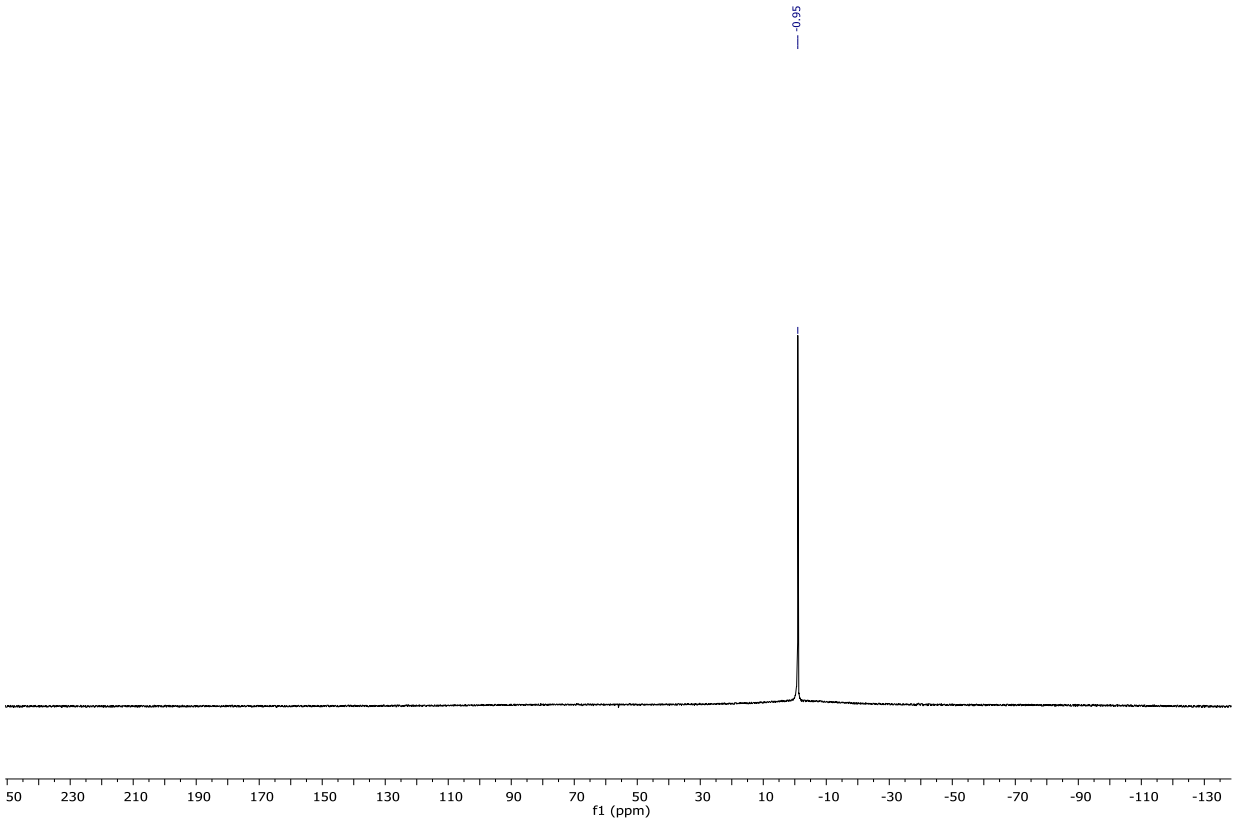
NMR spectra of synthesized *cis-anti-cis*-DCH18C6·H_3O·BF_4 complex in deuterated chloroform:



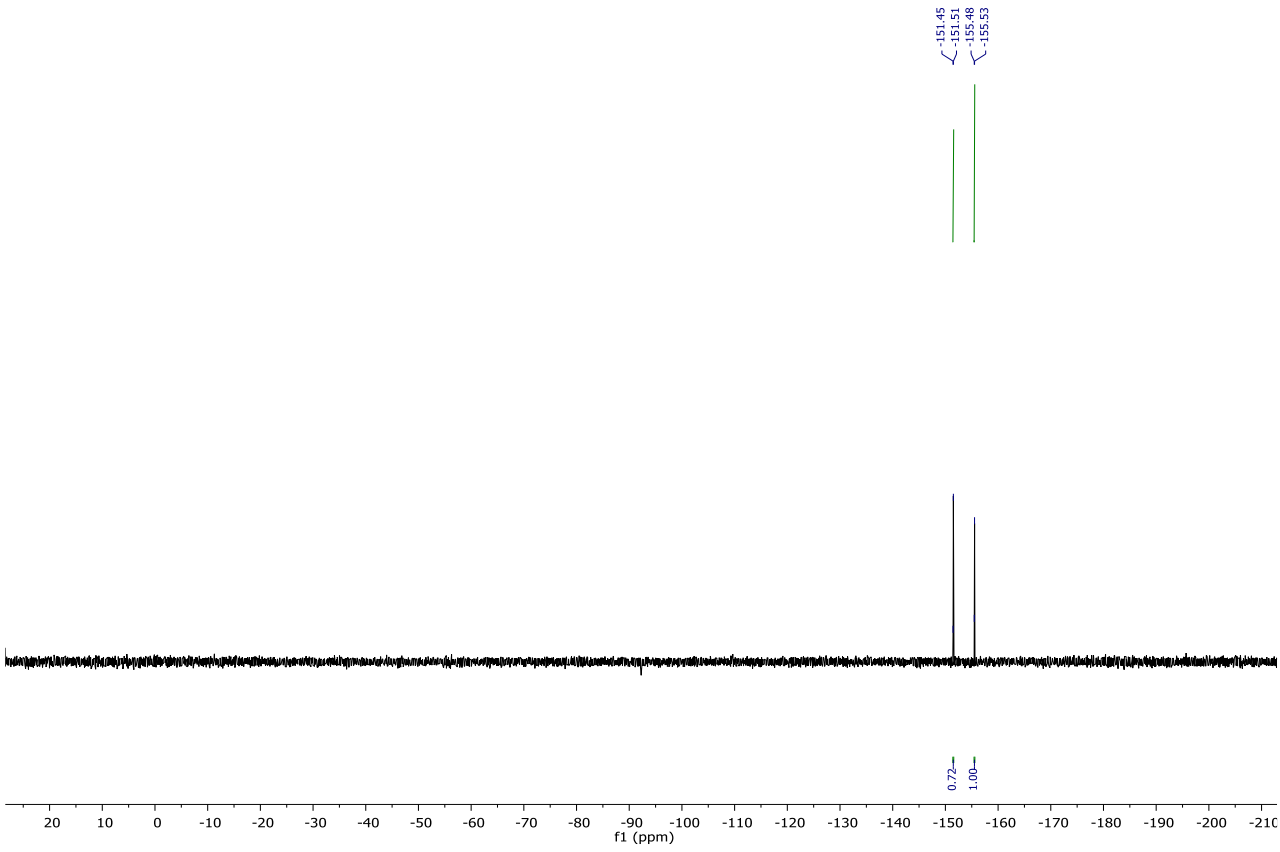
Cis-anti-cis-DCH18C6·H_3O·BF_4 - ^{1}H NMR



Cis-anti-cis-DCH18C6·H_3O·BF_4 - ^{13}C NMR



Cis-anti-cis-DCH18C6·H_3O·BF_4 - ^{11}B NMR



Cis-anti-cis-DCH18C6·H_3O·BF_4 - ^{19}F NMR

The values of chemical shifts, vibrational frequencies, and melting point of isolated *cis-anti-cis*-DCH18C6 were in full accordance with literature data[S3,S4].

I.4. X-rays irradiation and EPR spectroscopy

The samples were preliminary deoxygenated in SK-4B (Russia) glass ampoules by vacuum pumping to a residual pressure of ~0.13 Pa. The ampoules were sealed and subsequently irradiated at 77 K using X-ray tube (5-BKhV-6) with a tungsten anode. The effective energy of photons was ca. 20 keV. The absorbed doses (D_{sampl}) were calculated using the data of ferrous sulfate dosimetry (fsd) and conversion factors (K) considering the difference in mass energy-absorption coefficients (μ_{en}/ρ)[S5] of the DCH18C6, DCH18C6·H_3O·BF_4 and the dosimetric system: $D_{sampl} = D_{fsd} \cdot K$, where D_{fsd} is a dose absorbed by fsd system. The K values of 0.49 and 0.40 were calculated for "free" crown ether and its complex, respectively. The dose rate in accordance with the data of fsd was 3.5 Gy/s. X-band spectrometer with a 100-kHz high-frequency modulation (SPIN, Russia) was used to record EPR spectra. Relative concentrations of radicals were measured by double integrating the experimental spectra normalized to the EPR signals from Mn^{2+} standard. Relative error of measuring the concentration of the radical intermediates stabilized in the irradiated samples was within 10%.

II. EPR spectra of radicals stabilized in irradiated samples

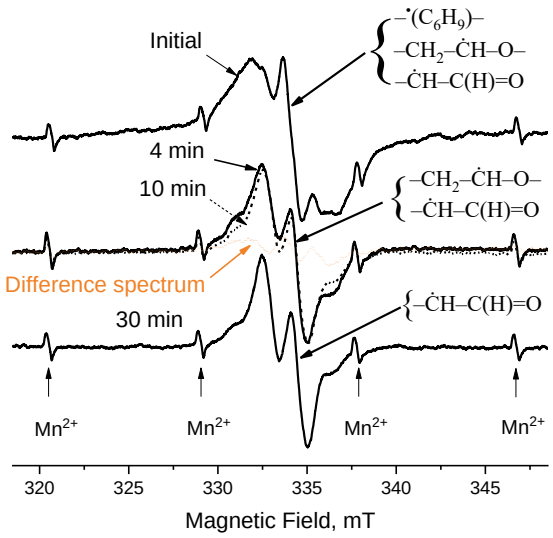


Figure S1. EPR spectra of *cis-anti-cis*-DCH18C6 irradiated at 77 K and subjected to thermal annealing at 313 K. Annealing times are given in the figure. Difference spectrum (orange line) corresponds to the signal of macrocyclic –CH_2–ĊH–O– radicals. All spectra were measured at 77 K. Mn^{2+} arrows shown the positions of lines from manganese standard.

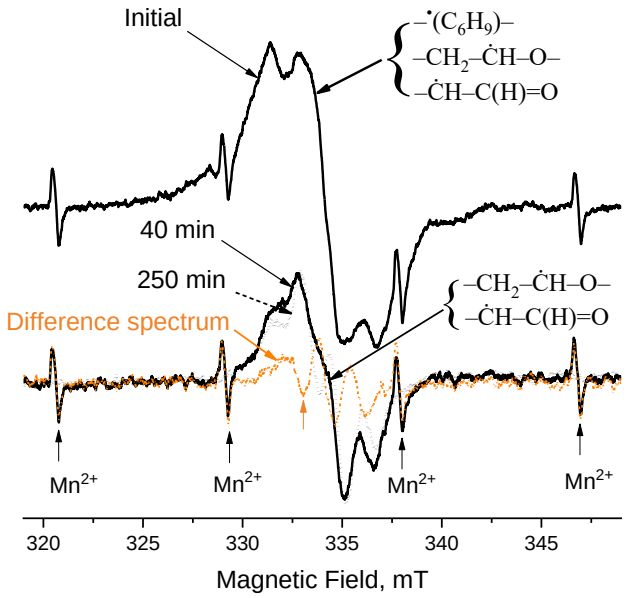


Figure S2. EPR spectra of *cis-anti-cis*-DCH18C6·H_3O^+·BF_4^- complex irradiated at 77 K and subjected to thermal annealing at 297 K. Annealing times are given in the figure. Difference spectrum (orange line) corresponds to the signal of macrocyclic –CH_2–ĊH–O– radicals. All spectra were measured at 77 K. Mn^{2+} arrows shown the positions of lines from manganese standard.

III. References

S1. R. M. Izatt, B. L. Haymore, J. S. Bradshaw and J. J. Christensen, Facile separation of the cis isomers of dicyclohexyl-18-crown-6, *Inorg. Chem.*, 1975, **14**, 3132. http://dx.doi.org/10.1021/ic50154a059.

S2. R. Chenevert, A. Rodrigue, P. Beauchesne and R. Savoi, New complexes of the hydronium ion with crown ethers: synthesis and vibrational spectra, *Can. J. Chem*., 1984, **62,** 2293. http://dx.doi.org/10.1139/v84-390.

S3. S. Z. Kusov, E. G. Lubenets, V. S. Kobrin, O. P. Sheremet and A. G. Khmel'nitskii, Catalytic activity of diastereomers of dicyclohexano-18-crown-6, *Russ. Chem. Bull.*, 1986, **35**, 650. https://doi.org/10.1007/BF00953252.

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S5. J. H. Hubbell, S. M. Seltzer, 2004. Tables of x-ray mass attenuation coefficients and mass energy-absorption coefficients (version1.4). National Institute of Standards and Technology, Gaithersburg, MD [2015.05.07.]. https://dx.doi.org/10.18434/T4D01F.