Electronic Supplementary Material (ESI) for RSC Advances

SUPRAMOLECULAR "CONTAINERS": SELF-ASSEMBLY AND FUNCTIONALIZATION OF THIACALIX[4]ARENES FOR RECOGNITION OF AMINO- AND DICARBOXYLIC ACIDS

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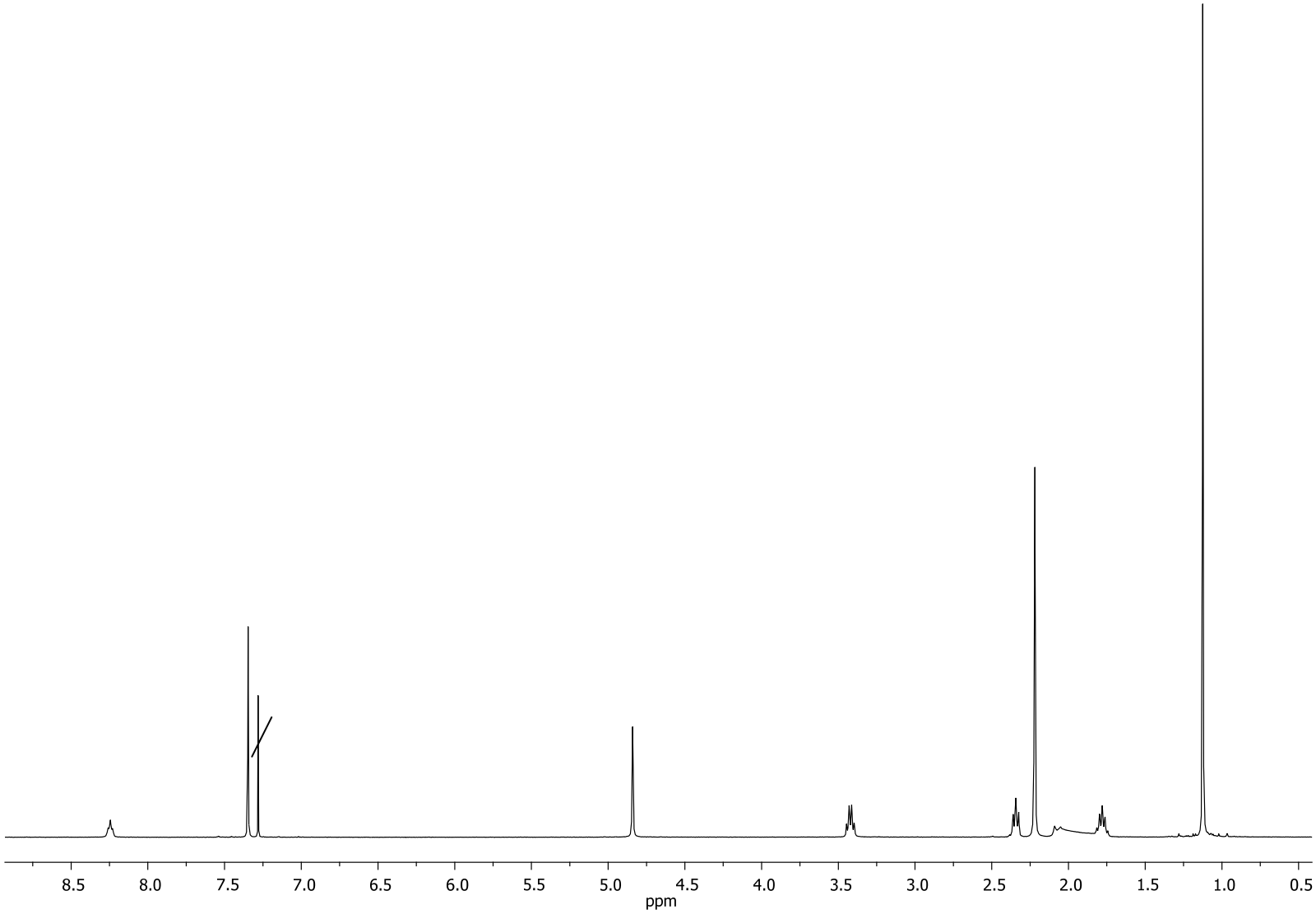
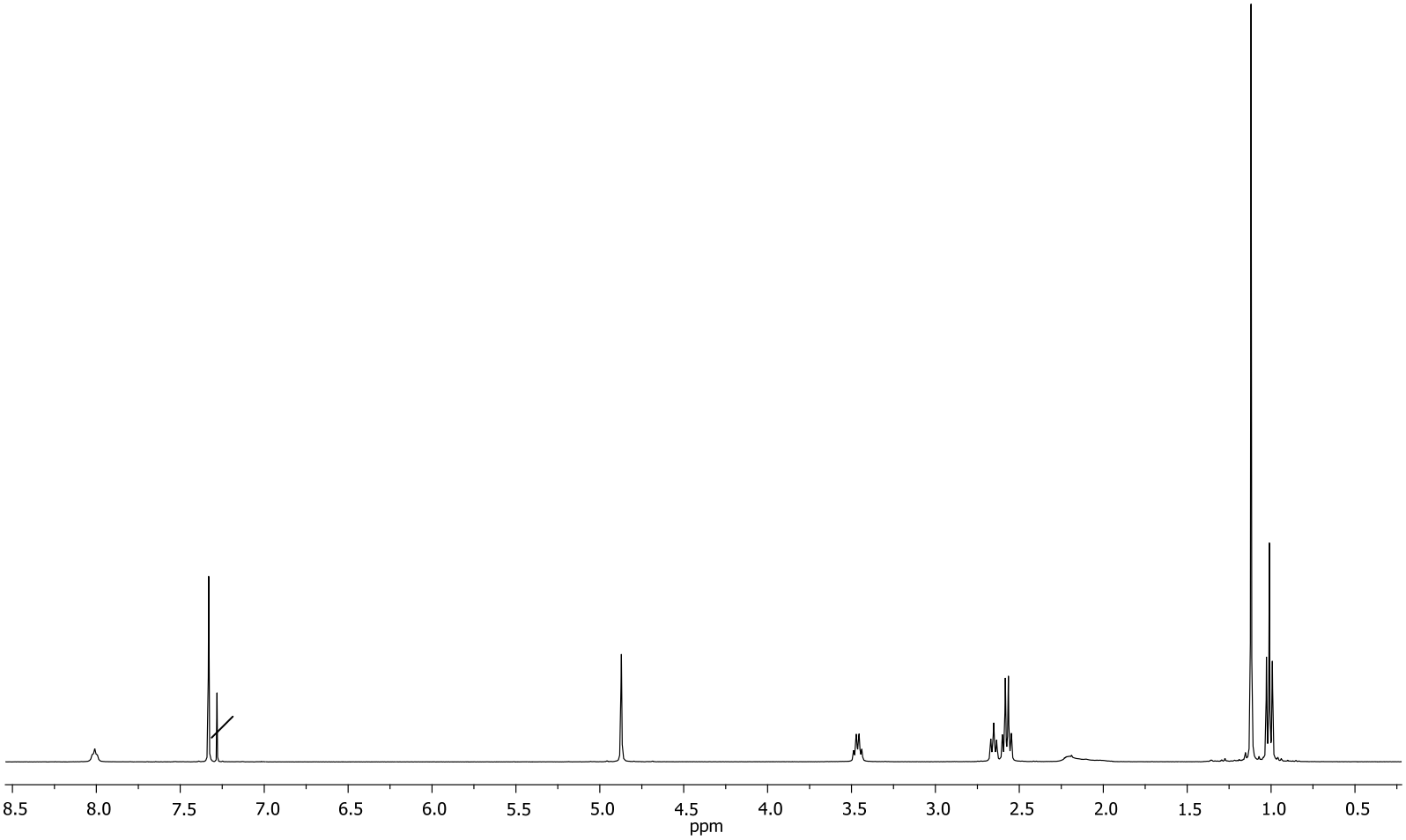
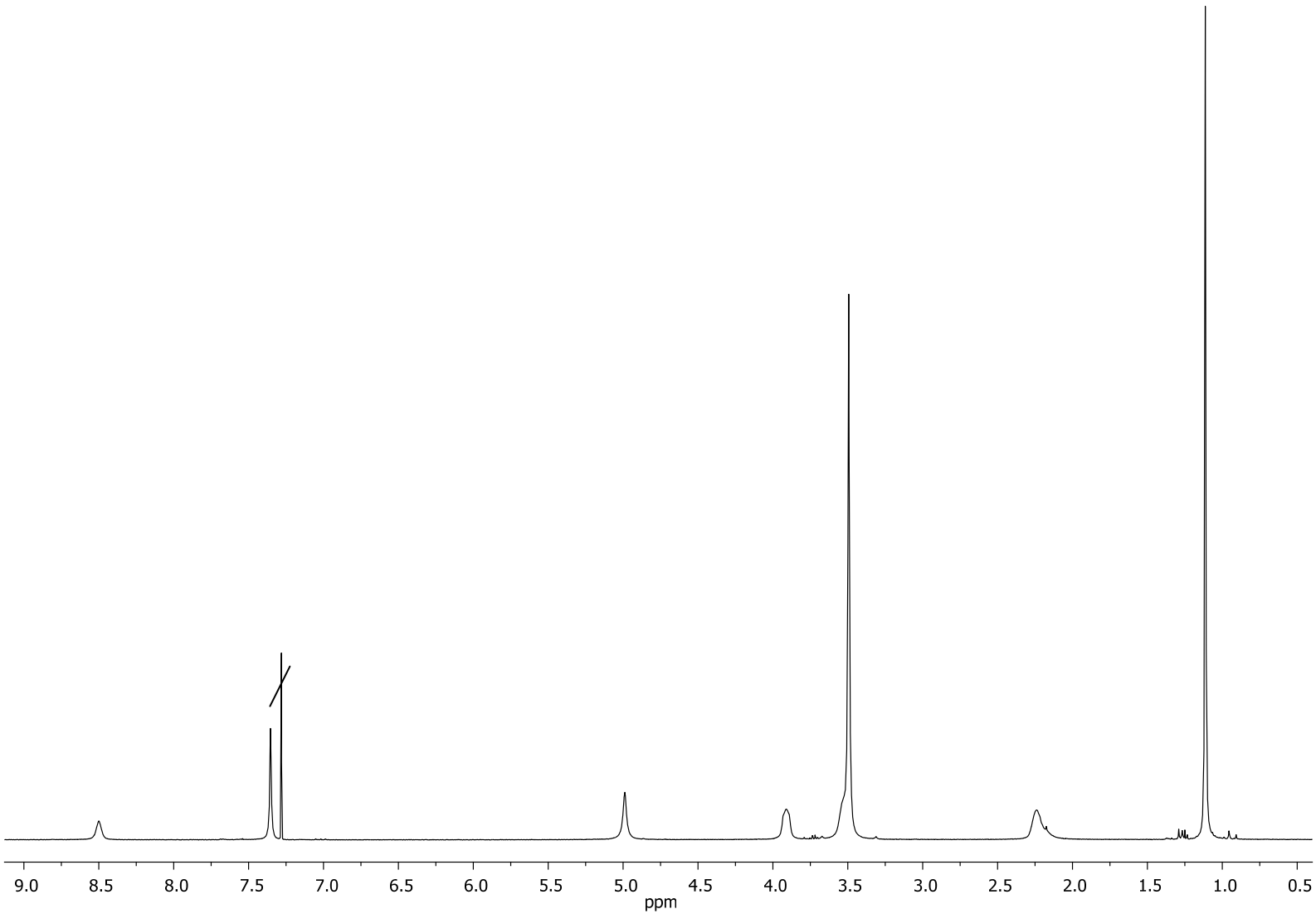
^{1}H NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(3',3'-dimethylaminopropyl)carbamoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone*-2), $CDCl_3$, 298 K, 400 MHz



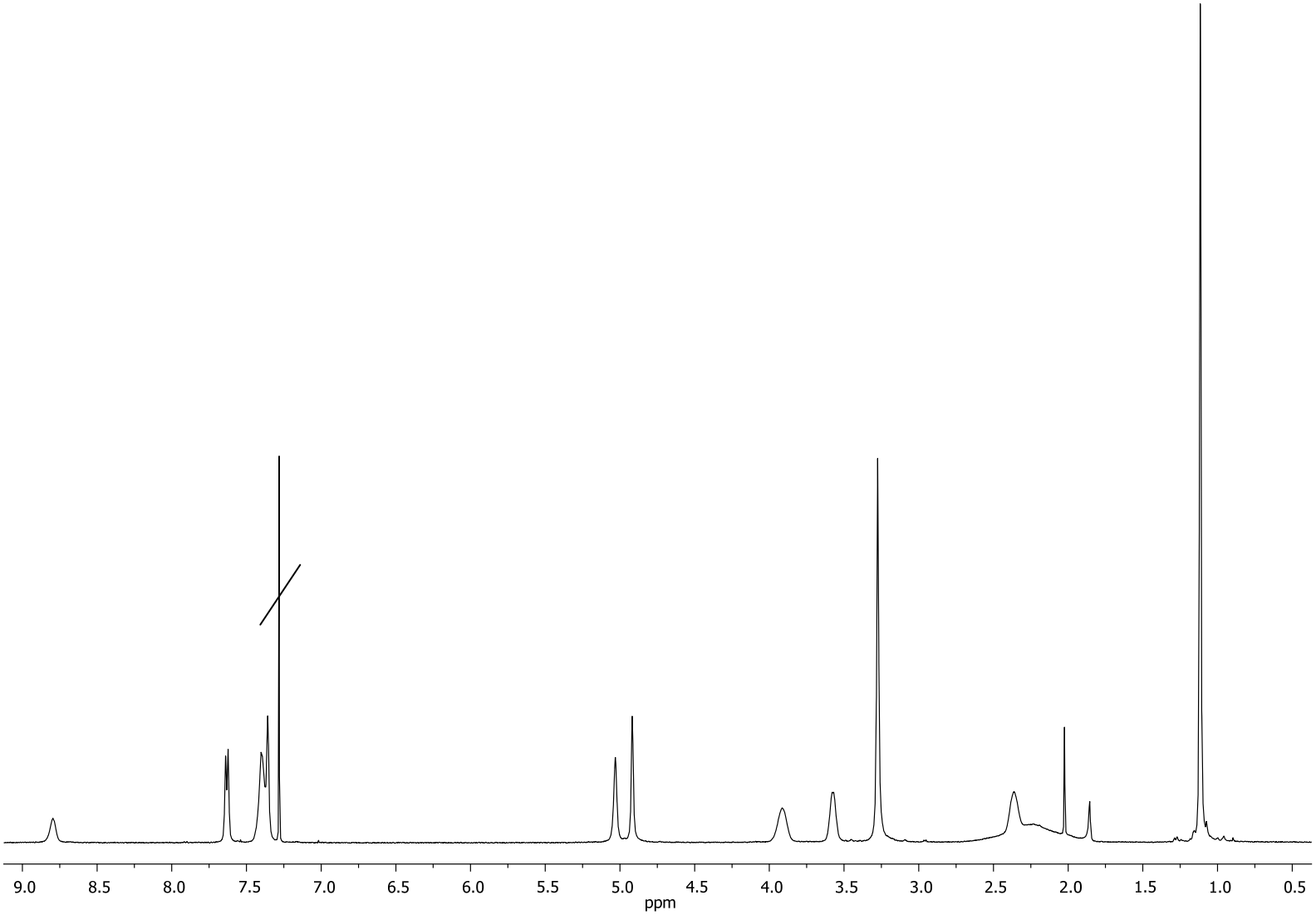
^{1}H NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(2',2'-diethylaminoethyl)carbamoylmethoxy]-2,8,14,20-thiacalix[4]arene (*cone*-3), $CDCl_3$, 298 K, 400 MHz



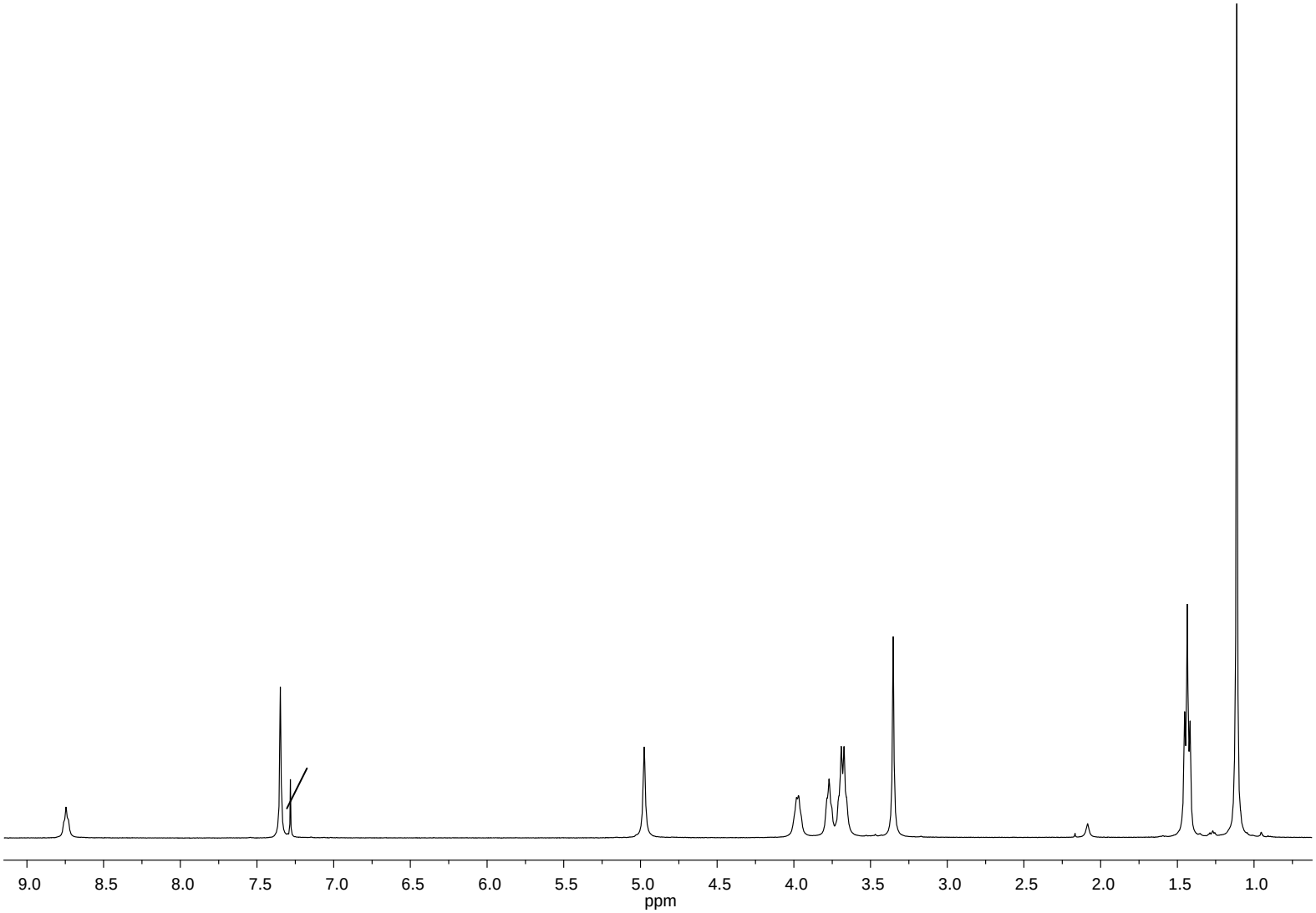
^{1}H NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(3',3',3'-trimethylammoniumpropyl)carbamoylmethoxy]-2,8,14,20-thiacalix[4]arene tetraiodide (*cone*-4), $CDCl_3$, 298 K, 400 MHz



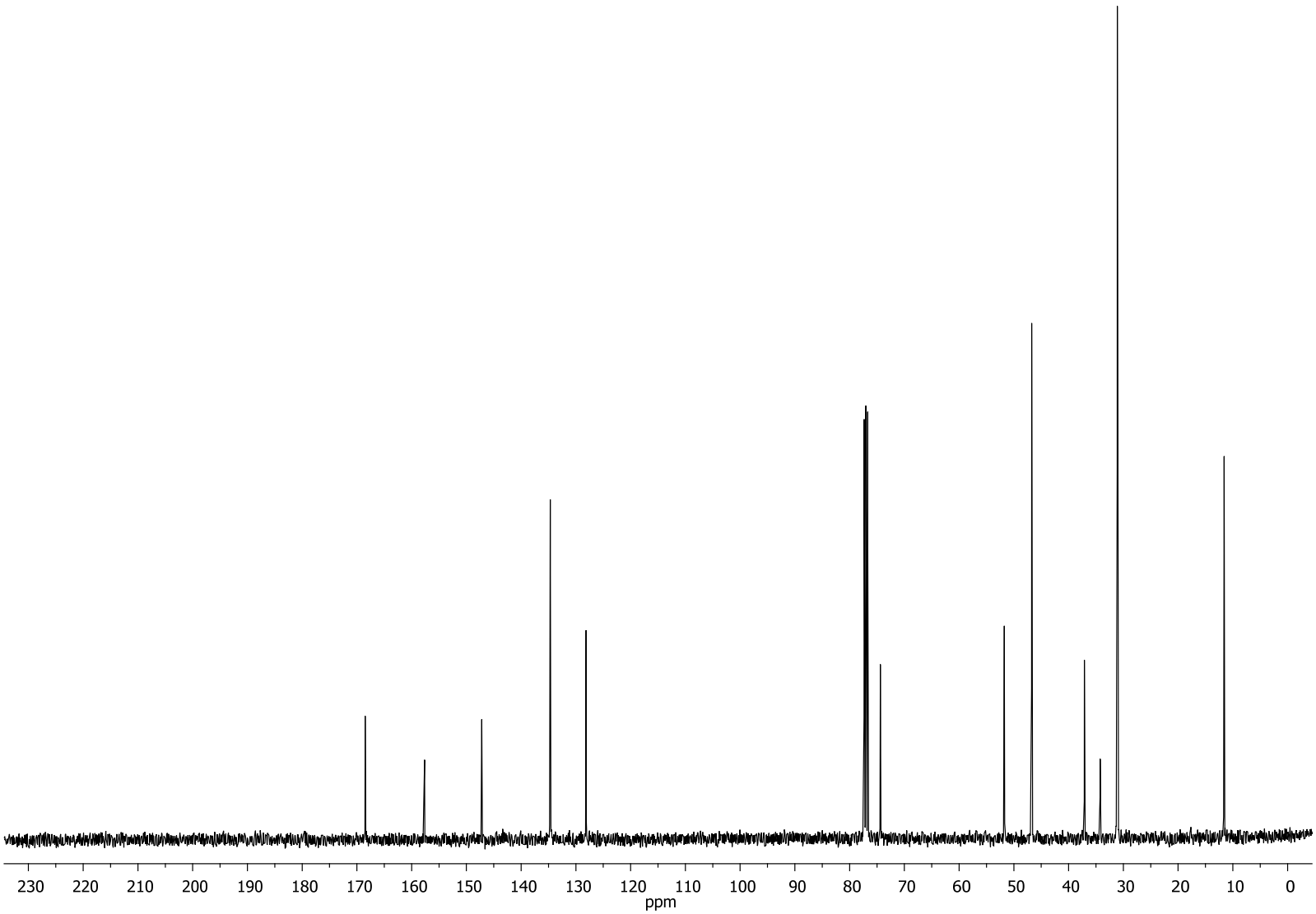
^{1}H NMR spectrum of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-[(N-(3',3'-dimethyl-3'-benzylammoniumpropyl) carbamoylmethoxy]-2,8,14 20-thiacalix[4]arene tetrabromide (*cone*-5), $CDCl_3$, 298 K, 400 MHz



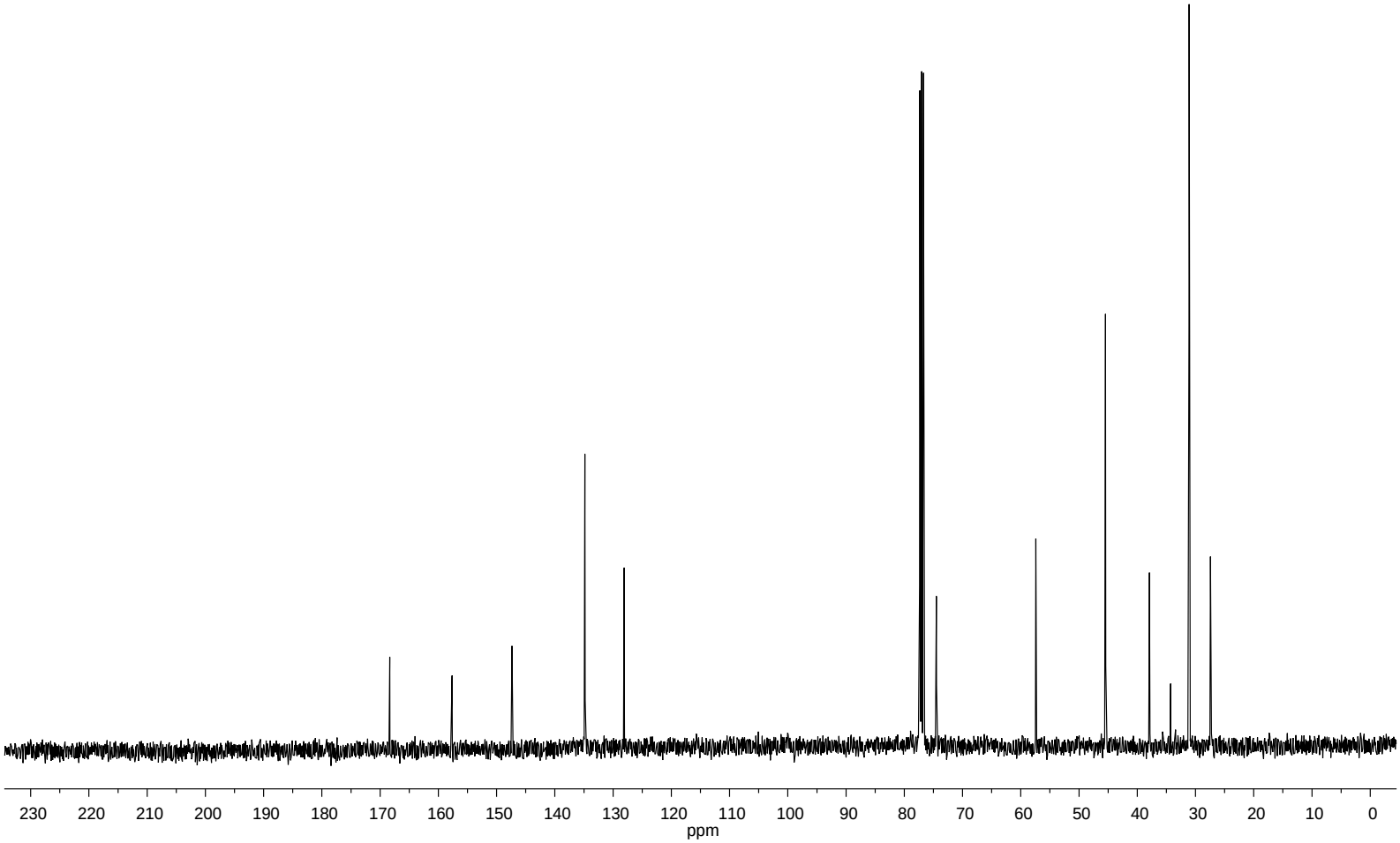
^{1}H NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(2'-methyl-2',2'-diethylammoniumethyl) carbamoylmethoxy]-2,8,14 20-thiacalix[4]arene tetraiodide (*cone*-6), $CDCl_3$, 298 K, 400 MHz



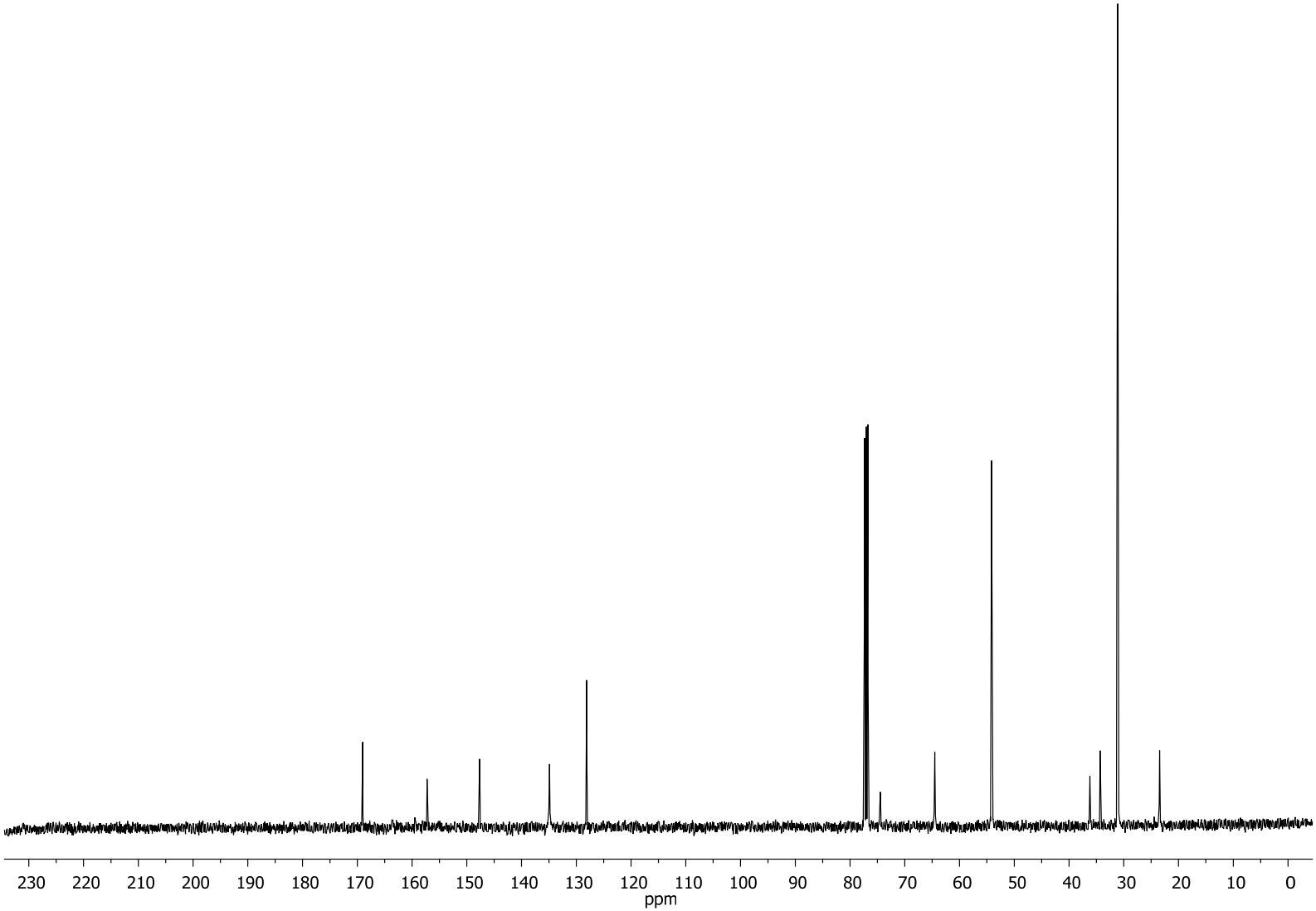
^{13}C NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(3',3'-dimethylaminopropyl)carbamoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone*-2), $CDCl_3$, 298 K, 400 MHz



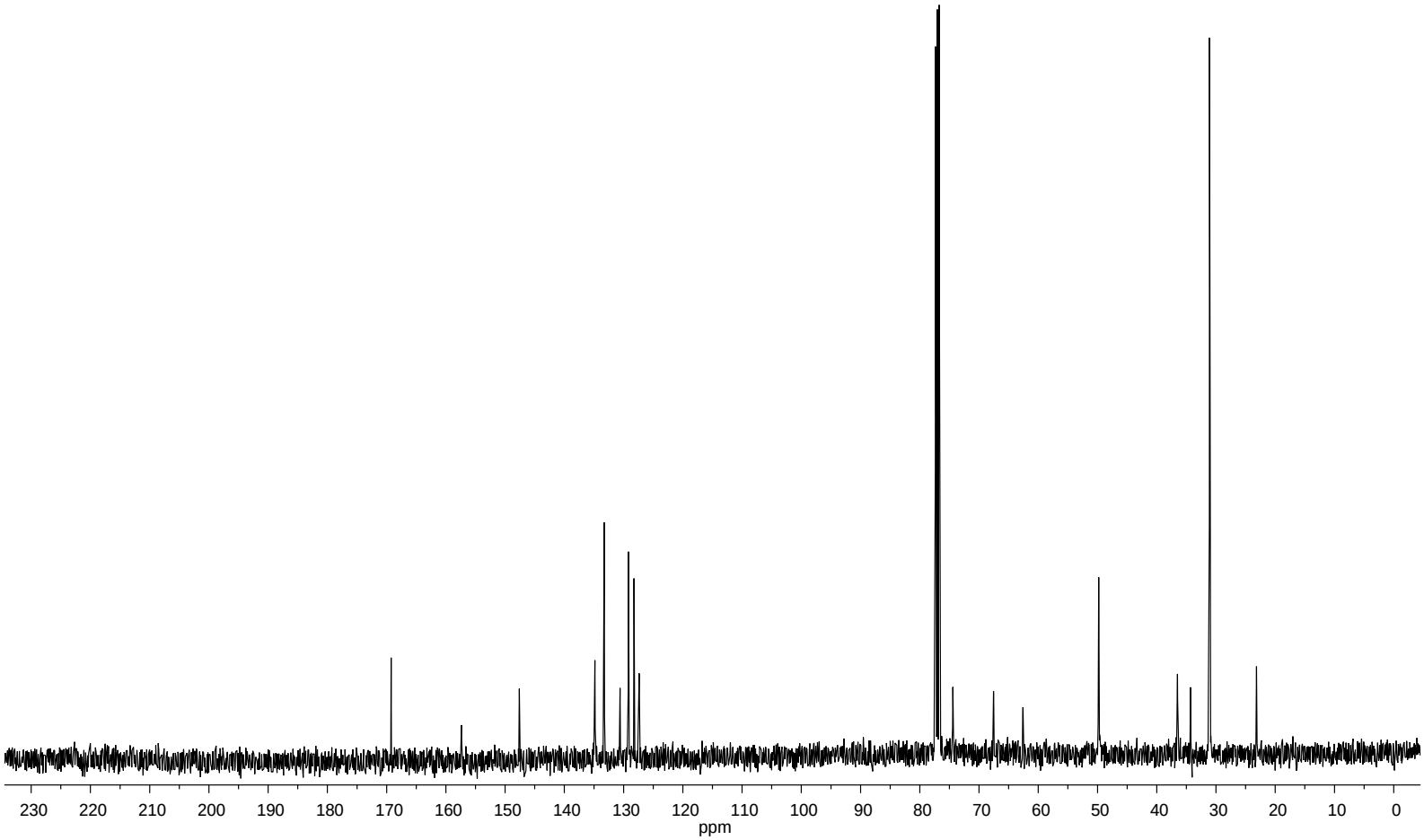
^{13}C NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(2',2'-diethylaminoethyl)carbamoylmethoxy]-2,8,14,20-thiacalix[4]arene (*cone*-3), $CDCl_3$, 298 K, 400 MHz



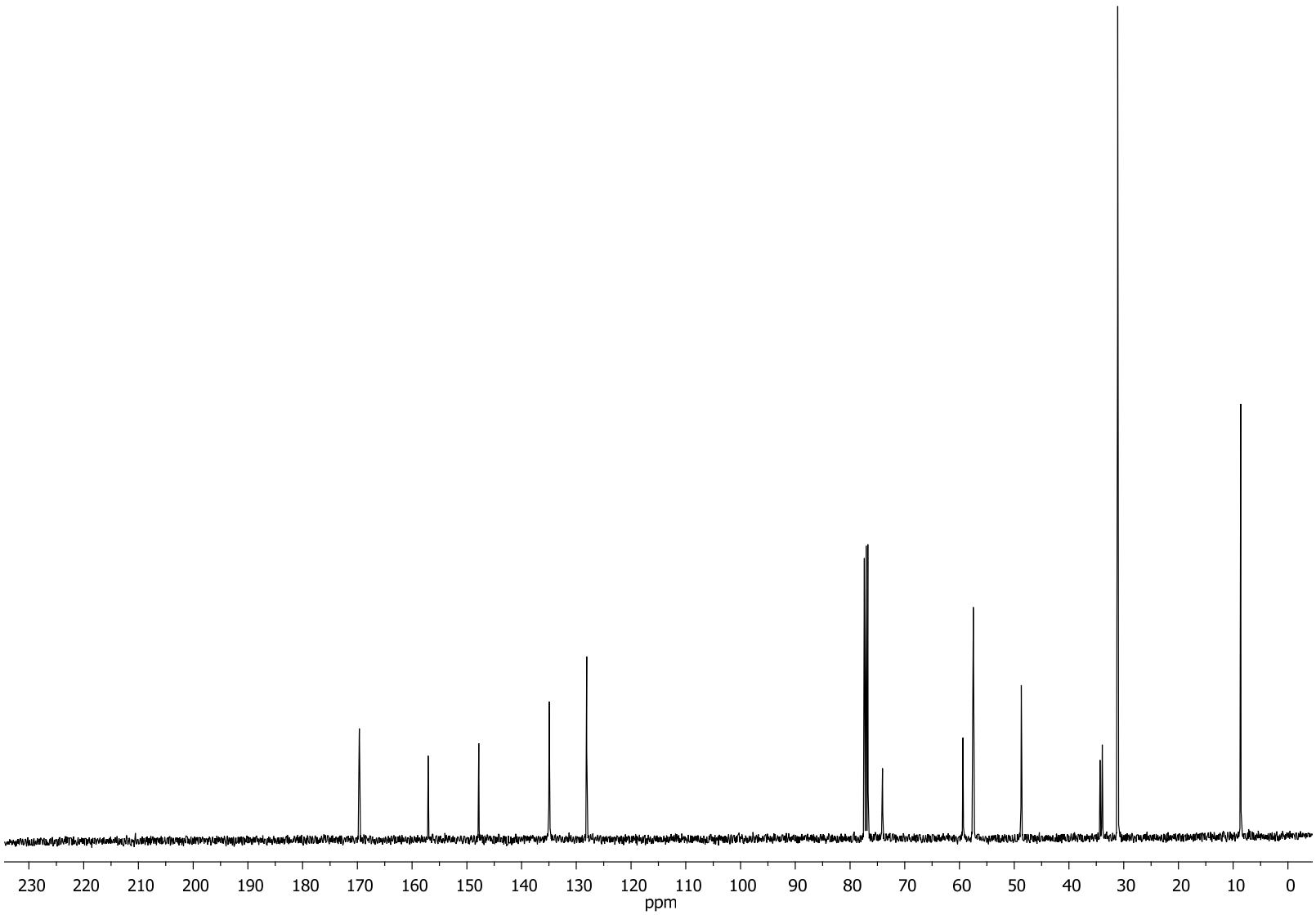
^{13}C NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(3',3',3'-trimethylammoniumpropyl)carbamoylmethoxy]-2,8,14,20-thiacalix[4]arene tetraiodide (*cone*-4), $CDCl_3$, 298 K, 400 MHz



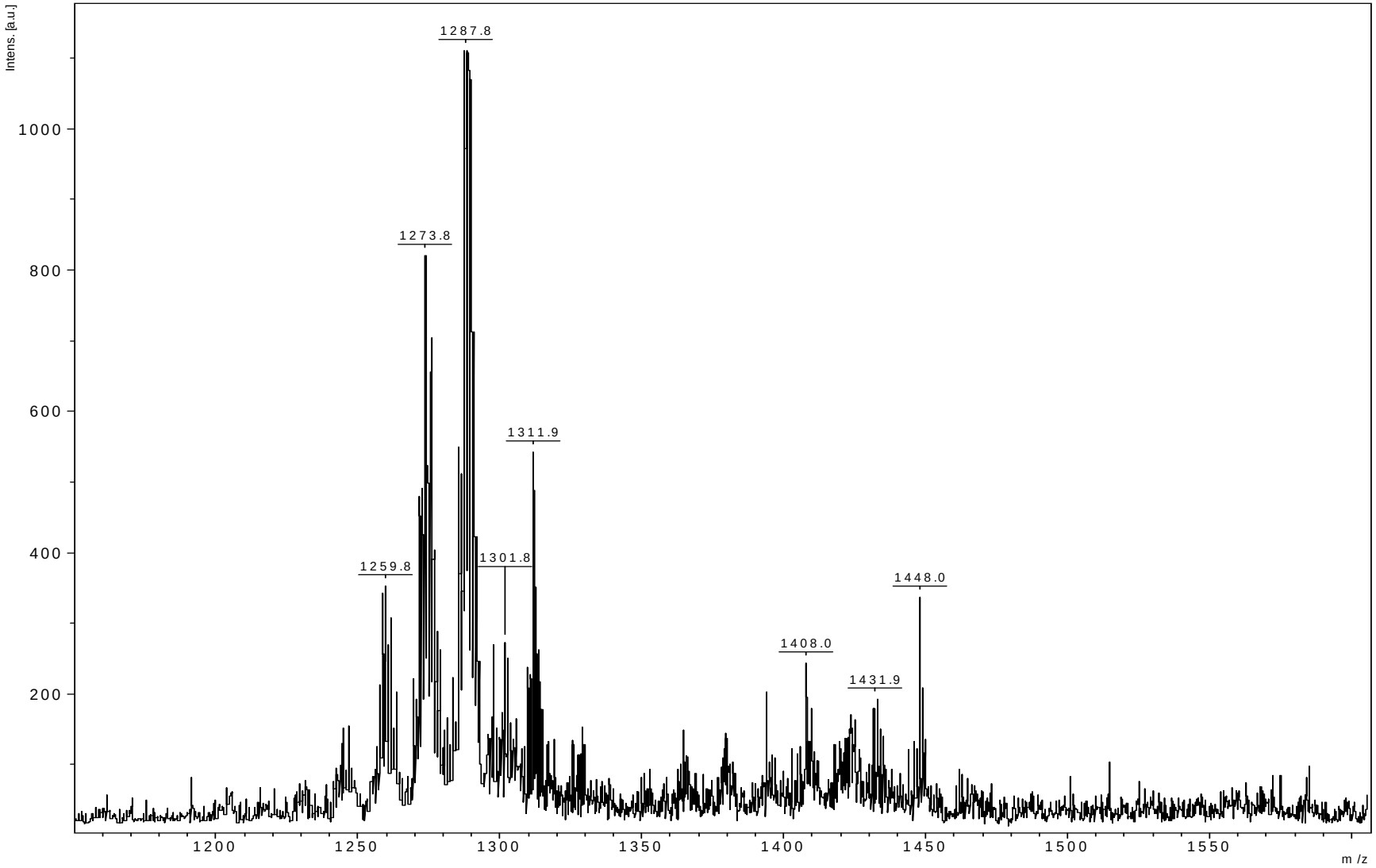
^{13}C NMR spectrum of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-[(N-(3',3'-dimethyl-3'-benzylammoniumpropyl) carbamoylmethoxy]-2,8,14 20-thiacalix[4]arene tetrabromide (*cone*-5), $CDCl_3$, 298 K, 400 MHz



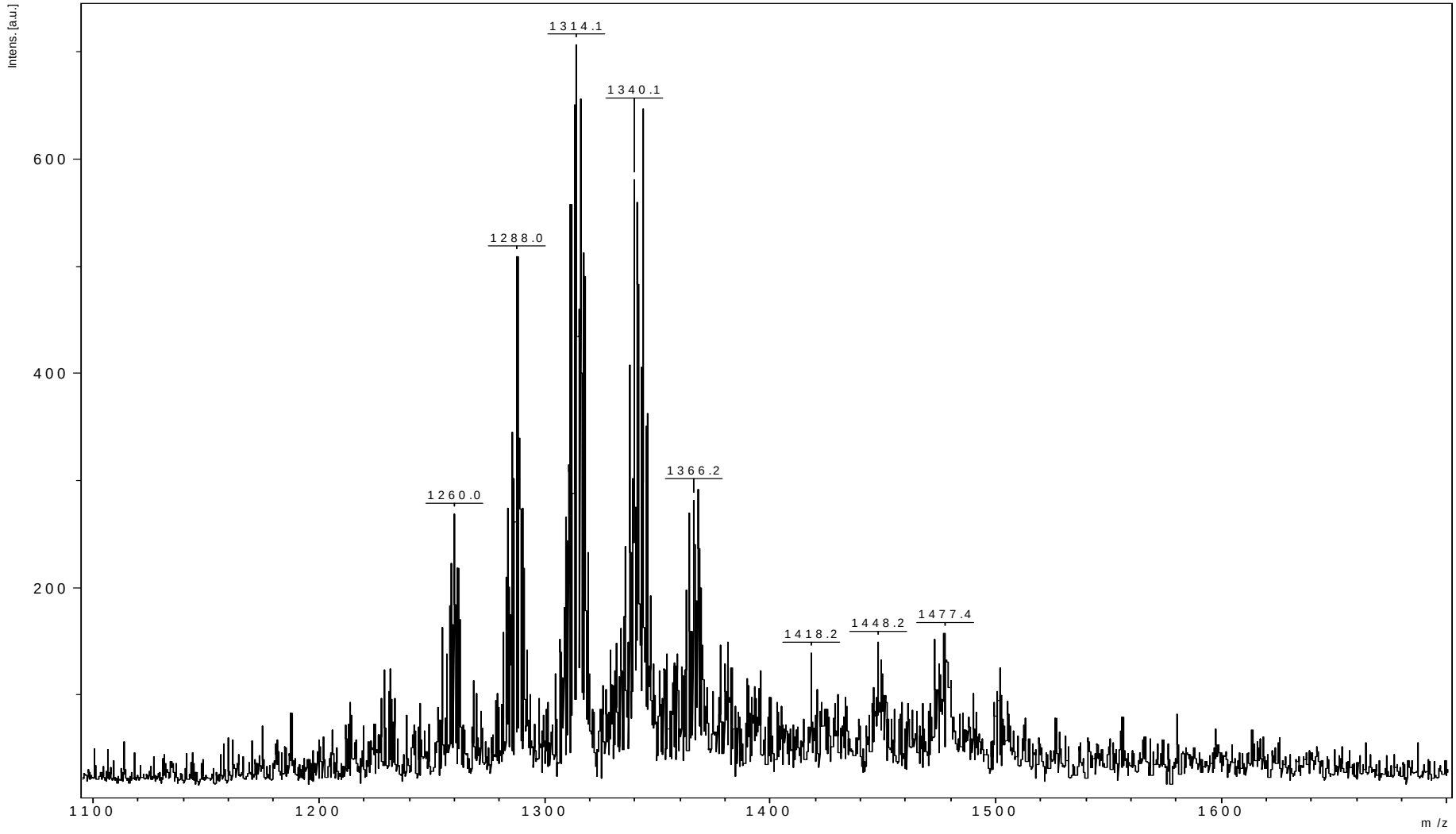
^{13}C NMR spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(2'-methyl-2',2'-diethylammoniumethyl) carbamoylmethoxy]-2,8,14 20-thiacalix[4]arene tetraiodide (*cone*-6), $CDCl_3$, 298 K, 400 MHz



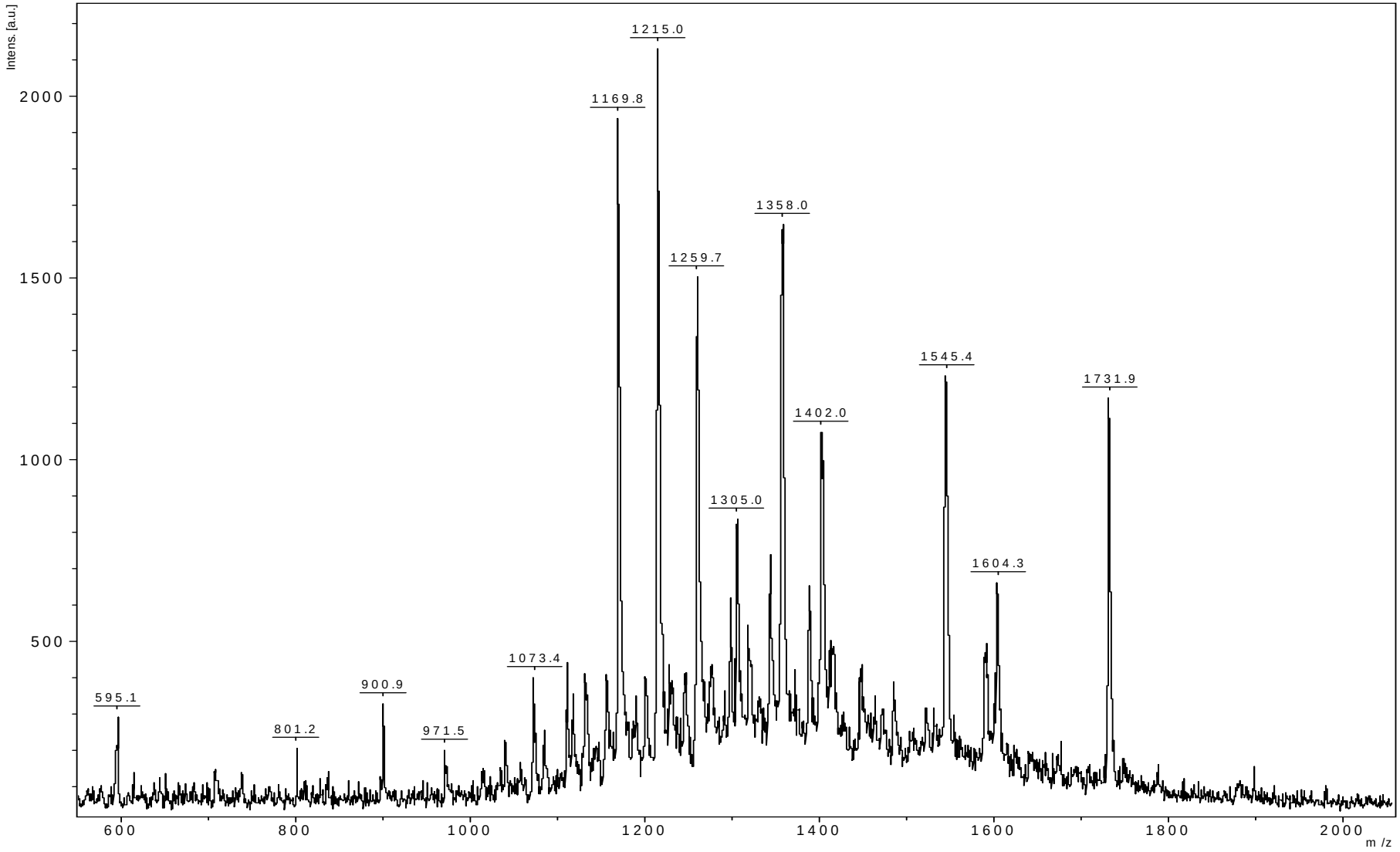
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(3',3'-dimethylaminopropyl)carbamoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone*-2)



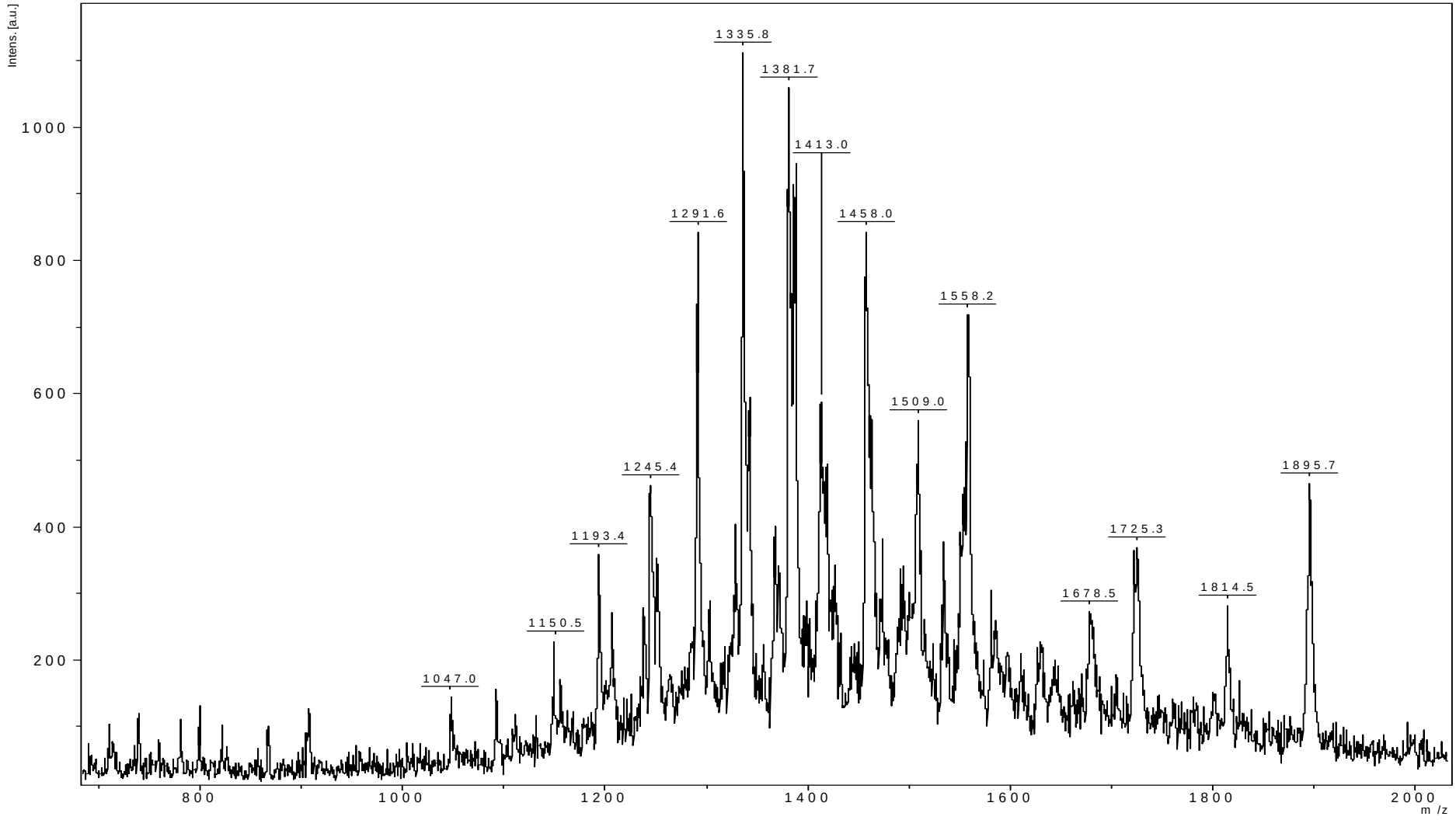
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(2',2'-diethylaminoethyl)carbamoylmethoxy]-2,8,14,20-thiacalix[4]arene (*cone*-3)



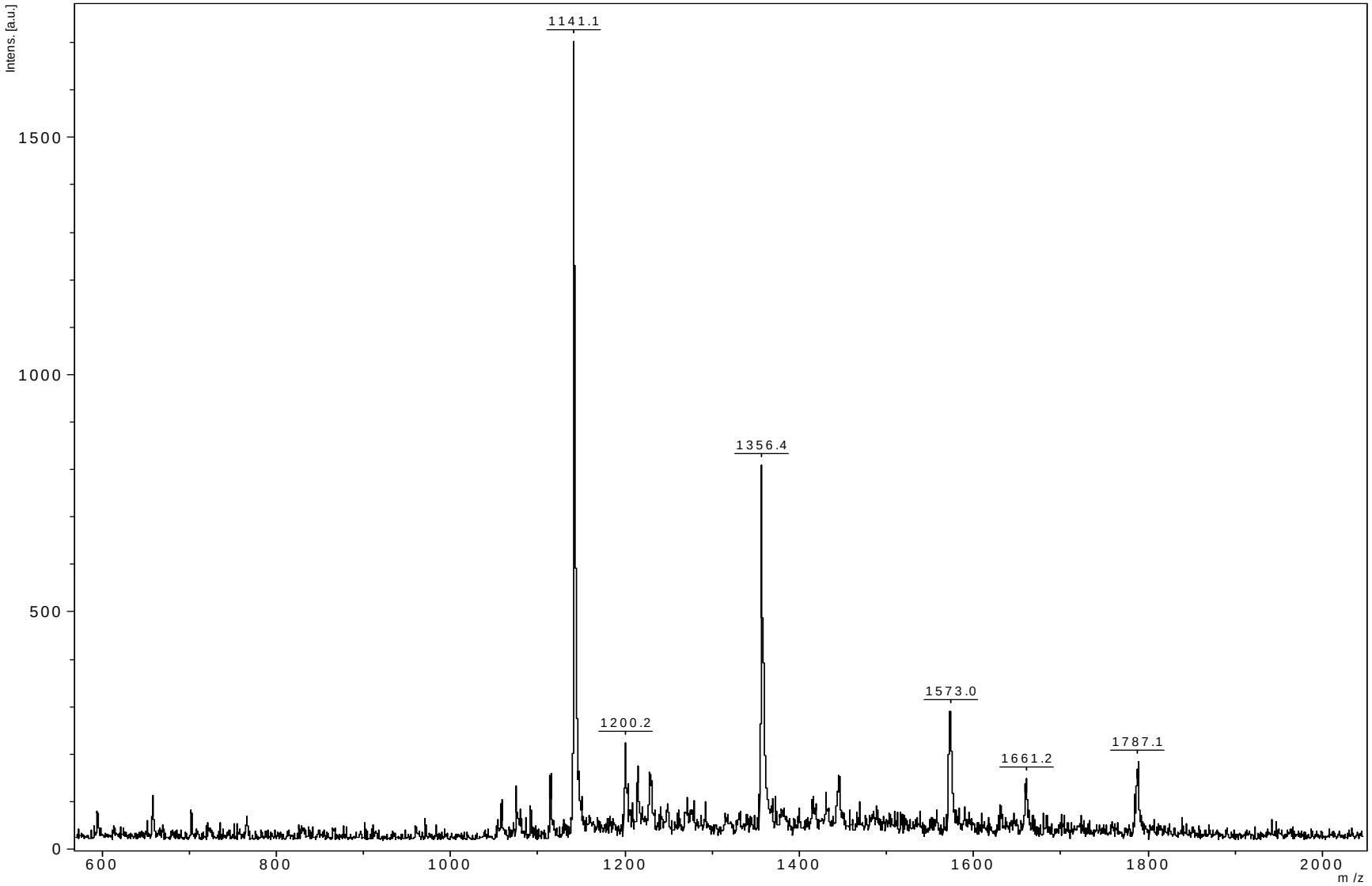
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(3',3',3'-trimethylammoniumpropyl)carbamoylmethoxy]-2,8,14,20-thiacalix[4]arene tetraiodide (*cone*-4)



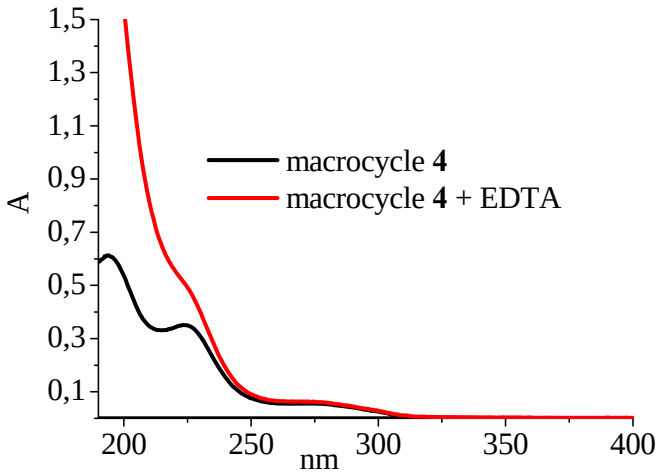
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-[(N-(3',3'-dimethyl-3'-benzylammoniumpropyl) carbamoylmethoxy]-2,8,14 20-thiacalix[4]arene tetrabromide (*cone*-5)



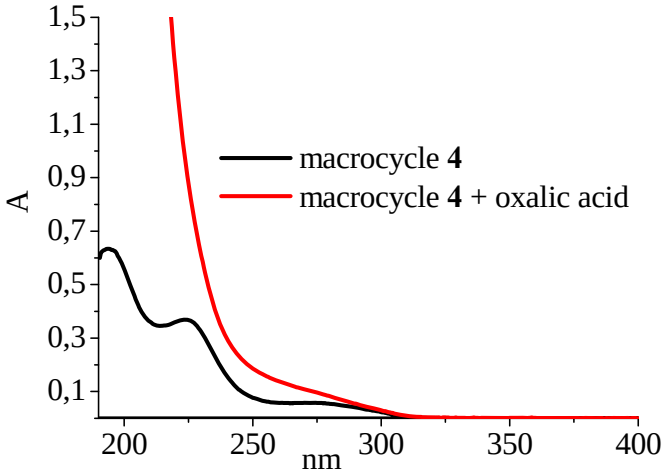
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(N-(2'-methyl-2',2'-diethylammoniumethyl) carbamoylmethoxy]-2,8,14 20-thiacalix[4]arene tetraiodide (*cone*-6)



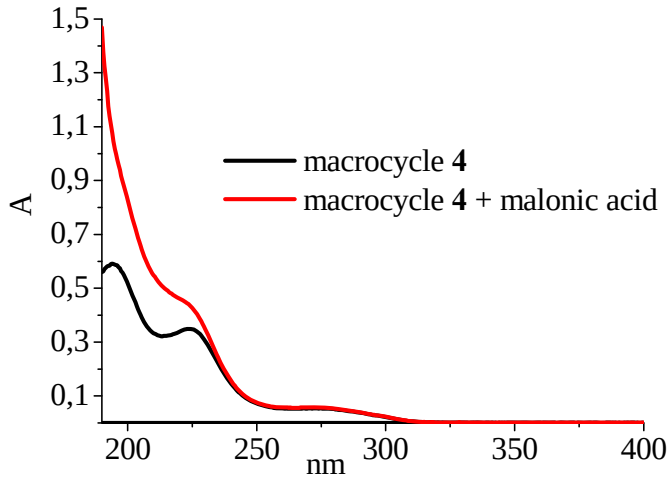
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of EDTA (c = $1.7 \cdot 10^{-4}$ M) in water.



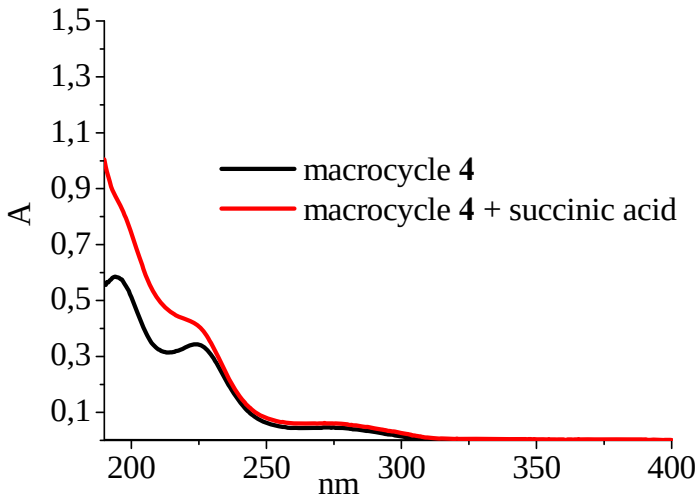
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of oxalic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



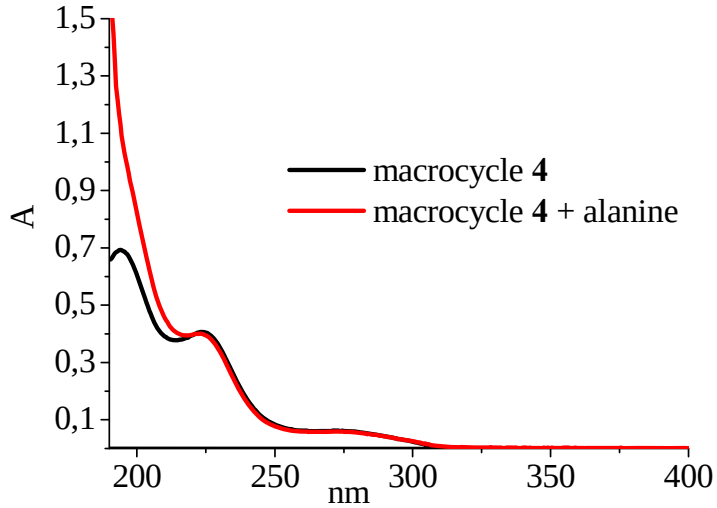
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of malonic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



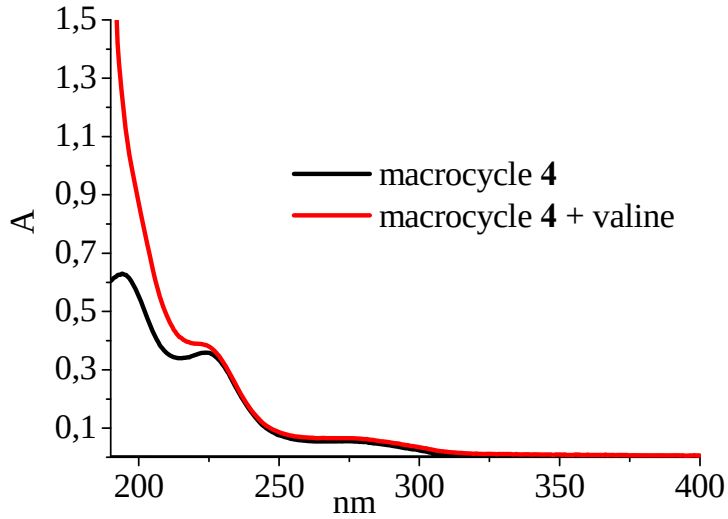
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of succinic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



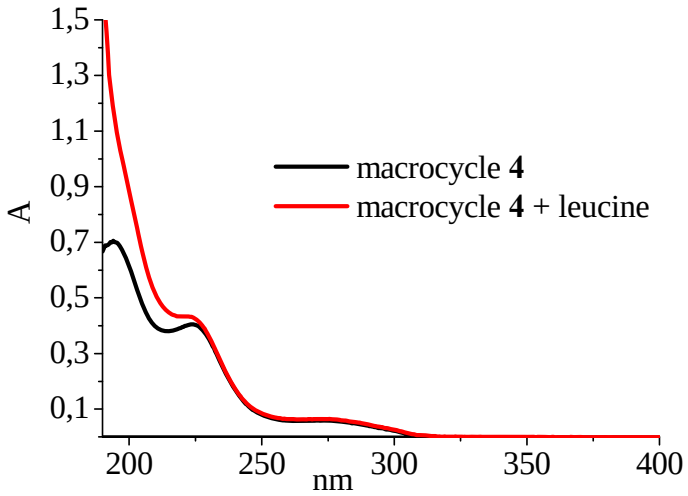
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of alanine (c = $1.7 \cdot 10^{-4}$ M) in water.



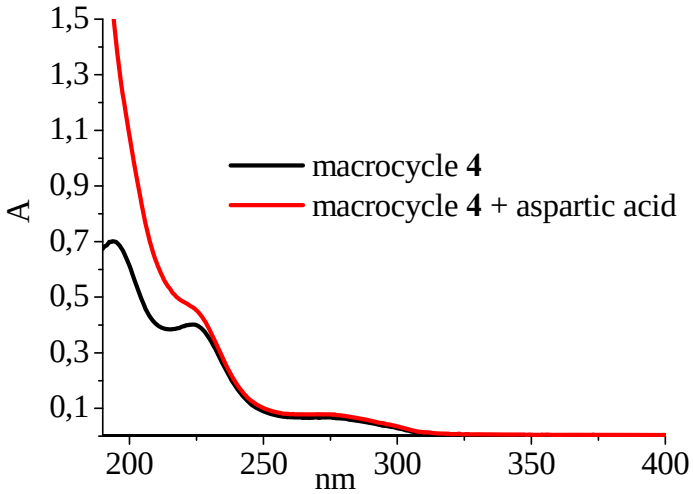
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of valine (c = $1.7 \cdot 10^{-4}$ M) in water.



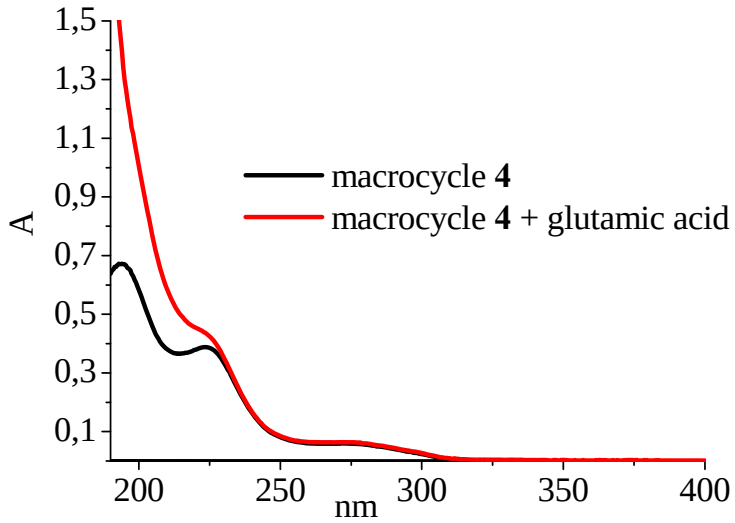
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of leucine (c = $1.7 \cdot 10^{-4}$ M) in water.



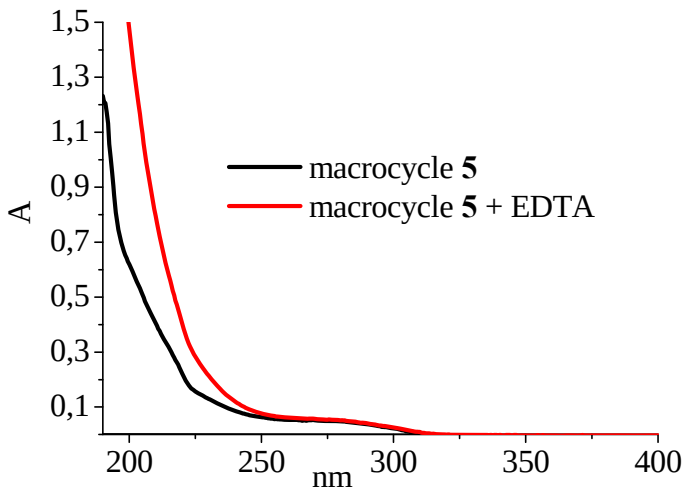
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of aspartic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



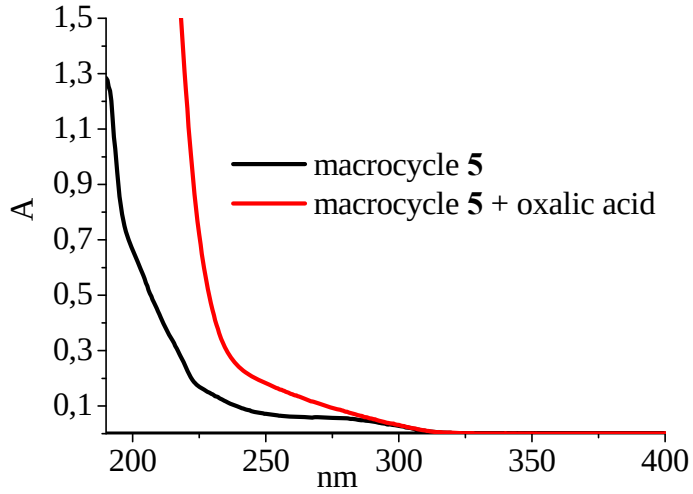
UV spectra of *p-tert*-butylcalix[4]arene **4** (c = $1 \cdot 10^{-6}$ M) after the addition of glutamic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



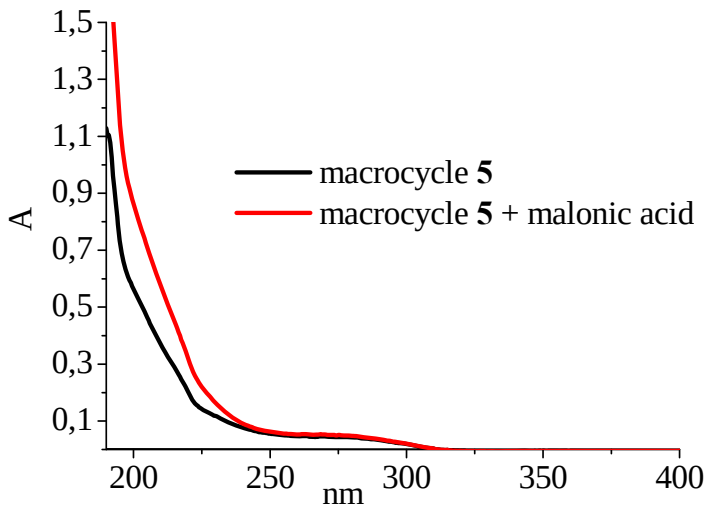
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of EDTA (c = $1.7 \cdot 10^{-4}$ M) in water.



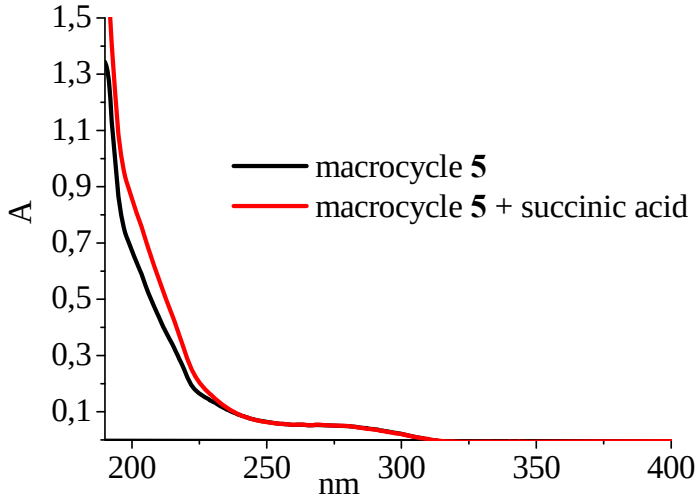
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of oxalic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



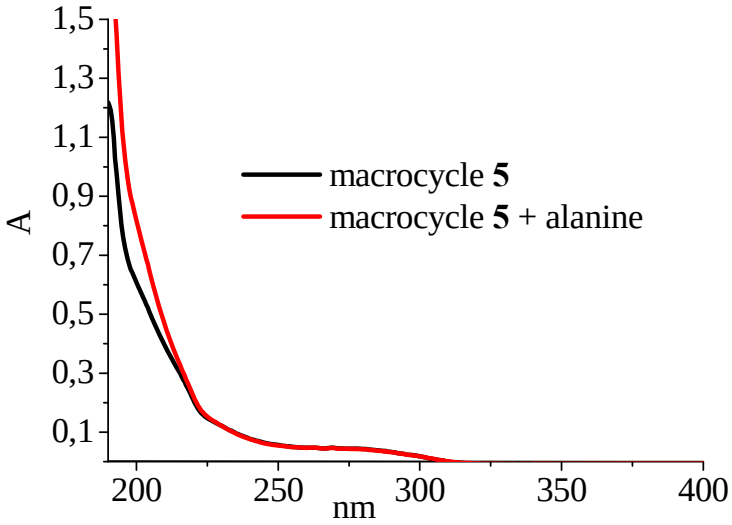
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of malonic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



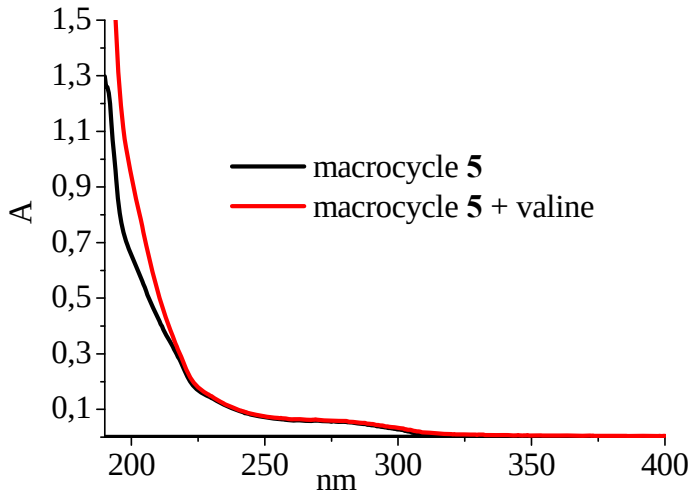
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of succinic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



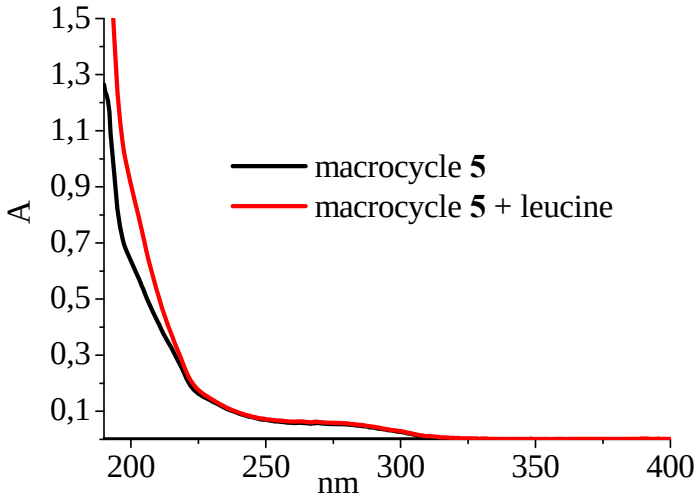
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of alanine (c = $1.7 \cdot 10^{-4}$ M) in water.



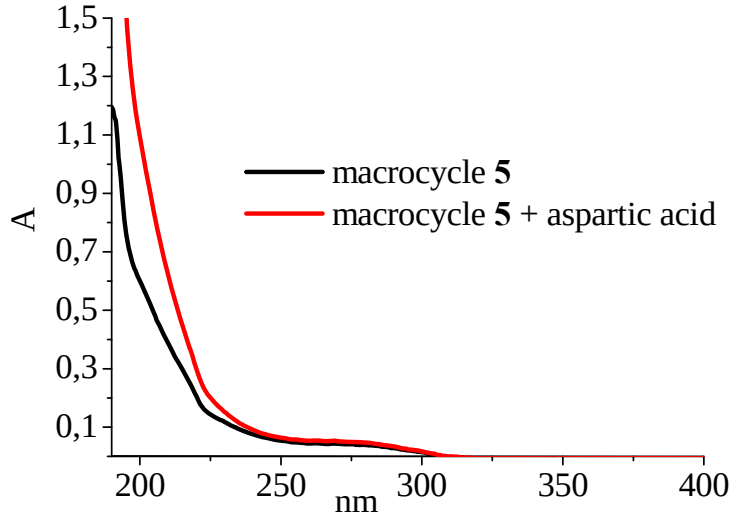
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of valine (c = $1.7 \cdot 10^{-4}$ M) in water.



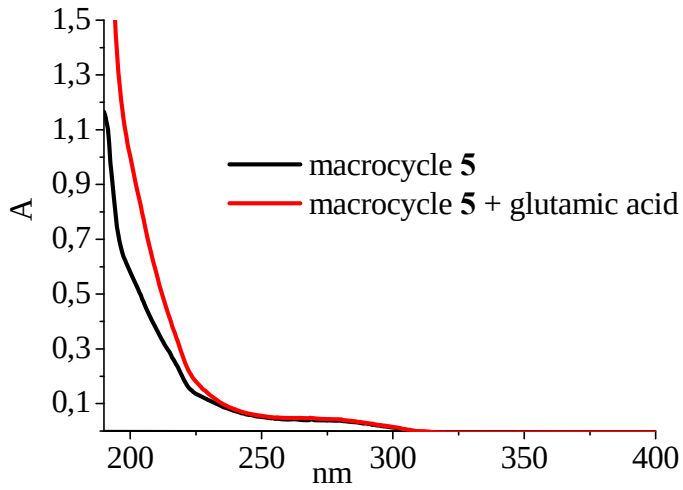
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of leucine (c = $1.7 \cdot 10^{-4}$ M) in water.



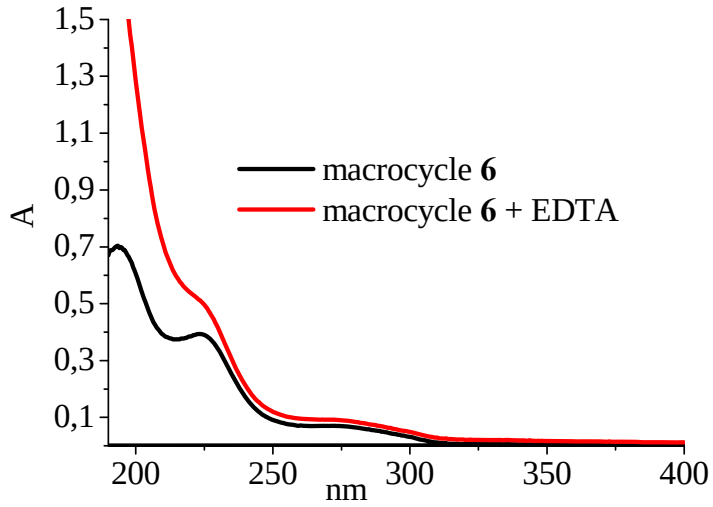
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of aspartic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



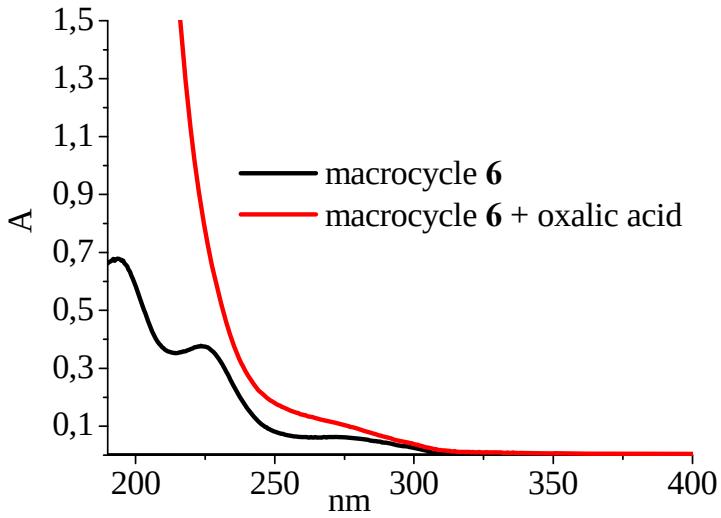
UV spectra of *p-tert*-butylcalix[4]arene **5** (c = $1 \cdot 10^{-6}$ M) after the addition of glutamic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



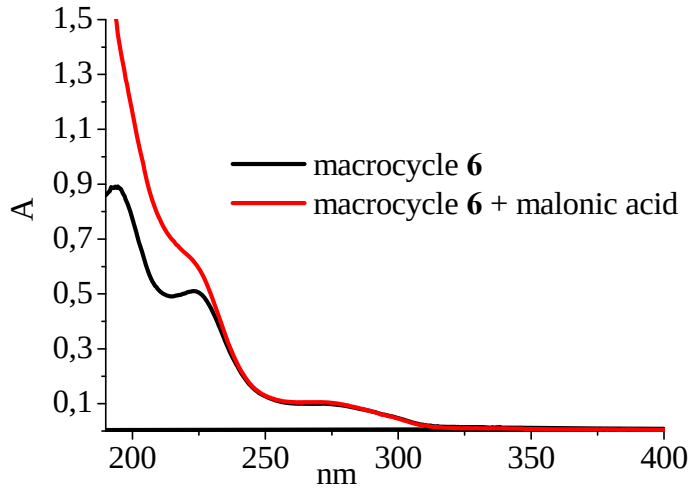
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of EDTA (c = $1.7 \cdot 10^{-4}$ M) in water.



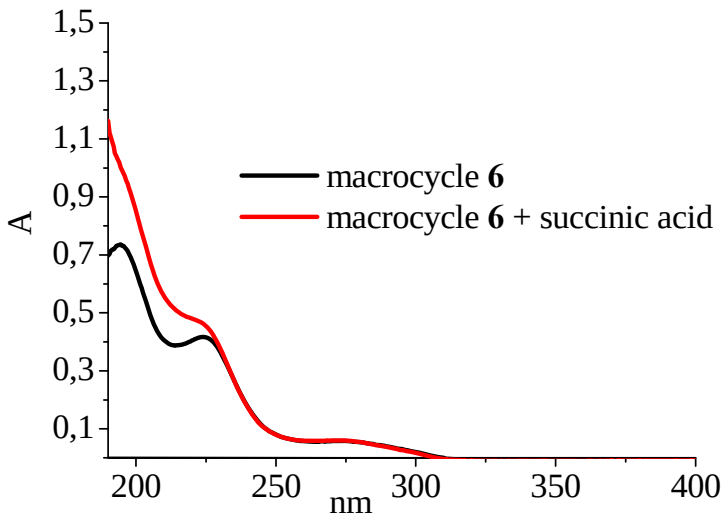
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of oxalic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



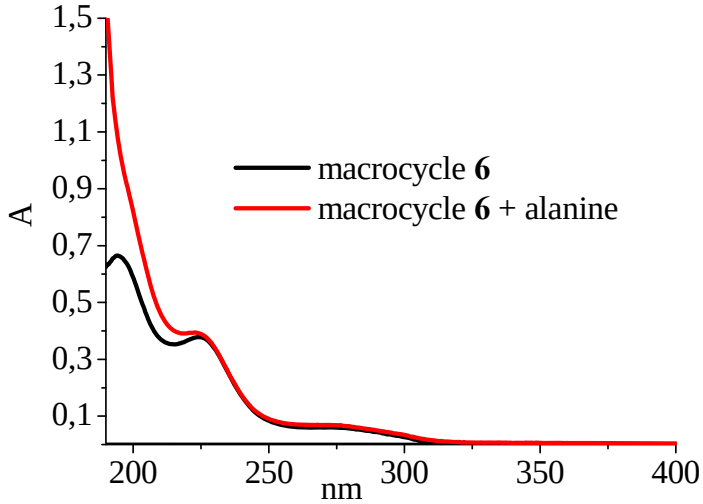
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of malonic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



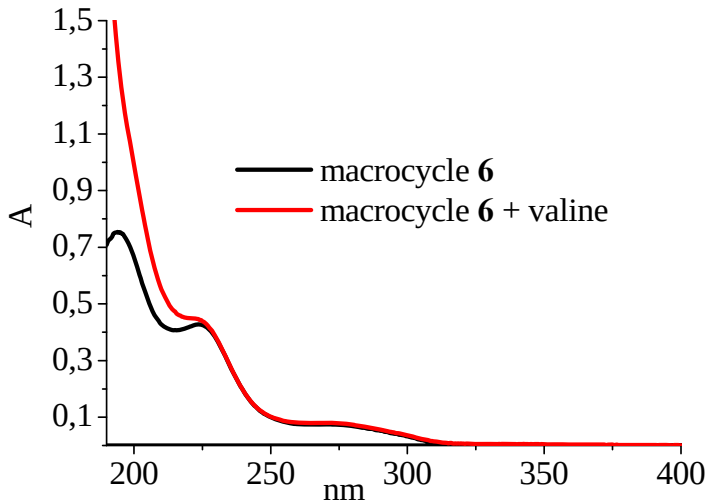
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of succinic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



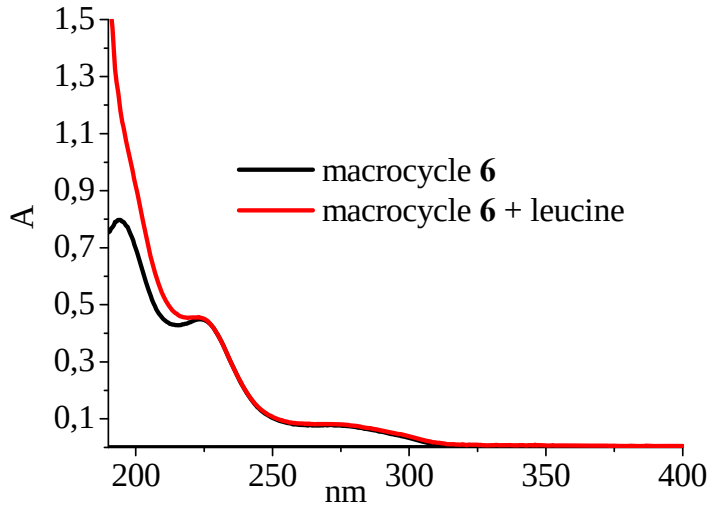
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of alanine (c = $1.7 \cdot 10^{-4}$ M) in water.



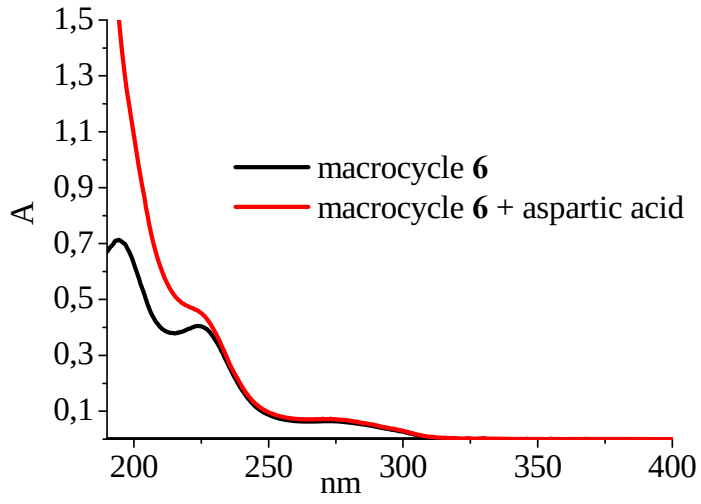
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of valine (c = $1.7 \cdot 10^{-4}$ M) in water.



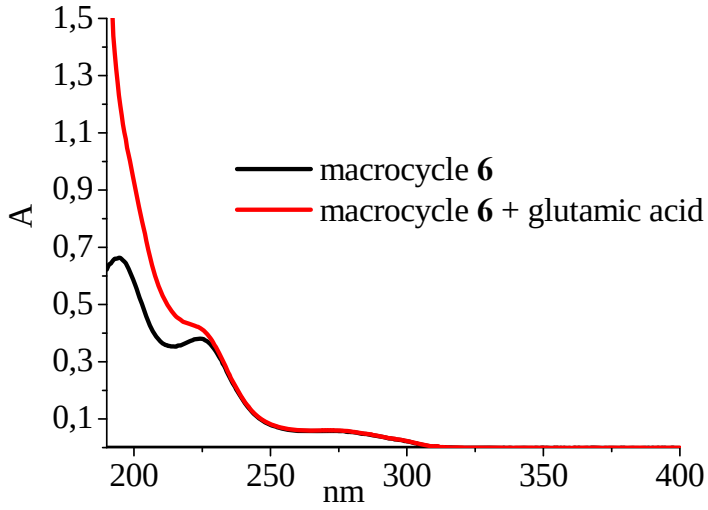
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of leucine (c = $1.7 \cdot 10^{-4}$ M) in water.



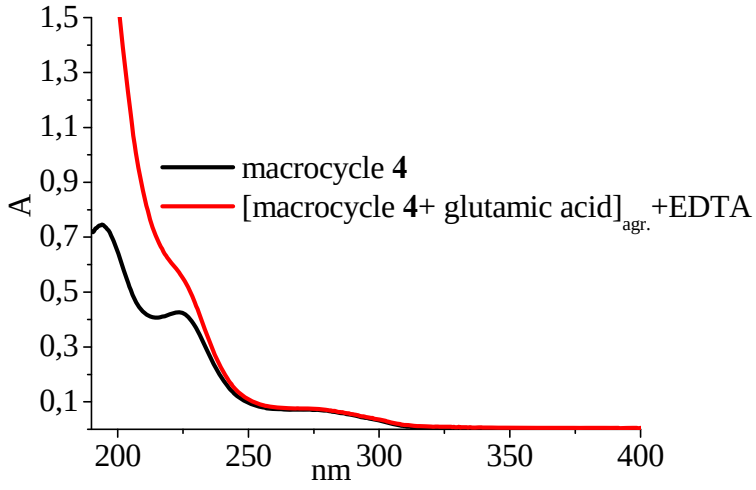
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of aspartic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



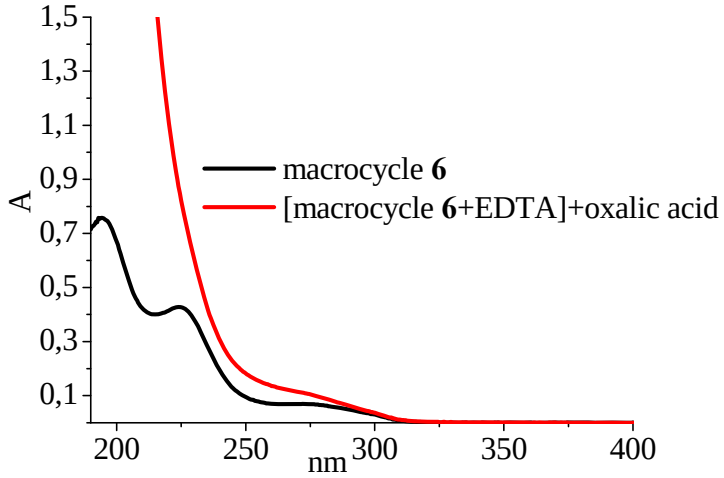
UV spectra of *p-tert*-butylcalix[4]arene **6** (c = $1 \cdot 10^{-6}$ M) after the addition of glutamic acid (c = $1.7 \cdot 10^{-4}$ M) in water.



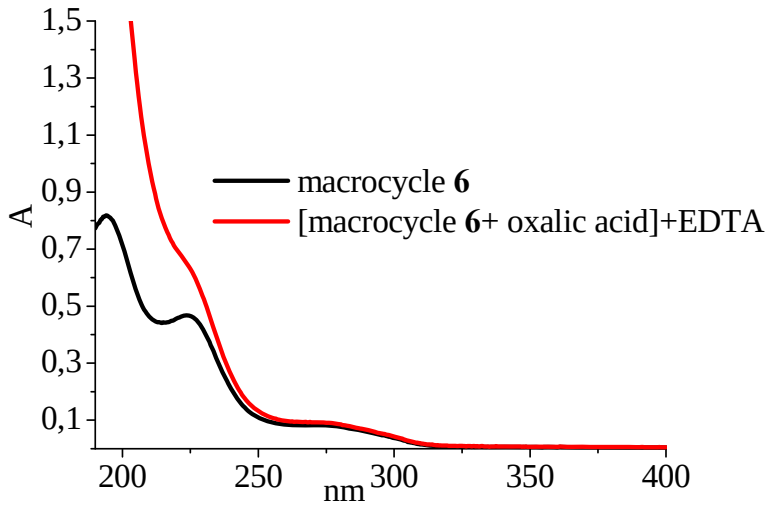
UV spectra (c = $1 \cdot 10^{-6}$ M) of cascade system based on [*p-tert*-butyl thiacalix[4]arene **4**+ glutamic acid]$_{agr.}$+EDTA.



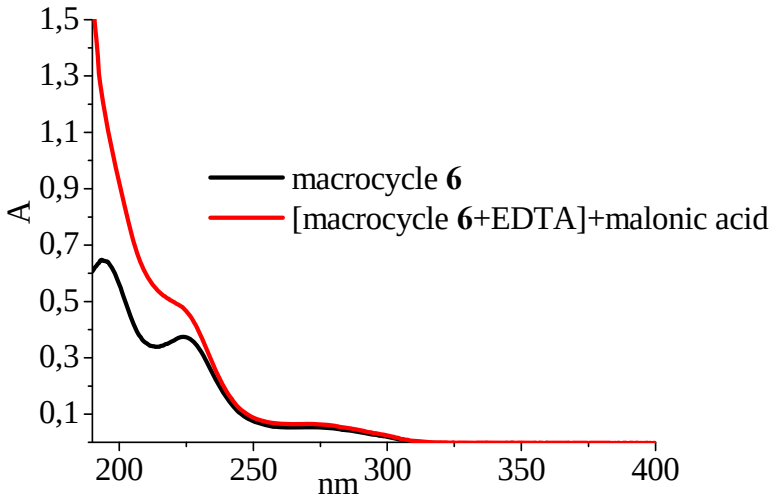
UV spectra (c = $1 \cdot 10^{-6}$ M) of commutative system based on [*p-tert*-butyl thiacalix[4]arene **6**+ EDTA]+ oxalic acid.



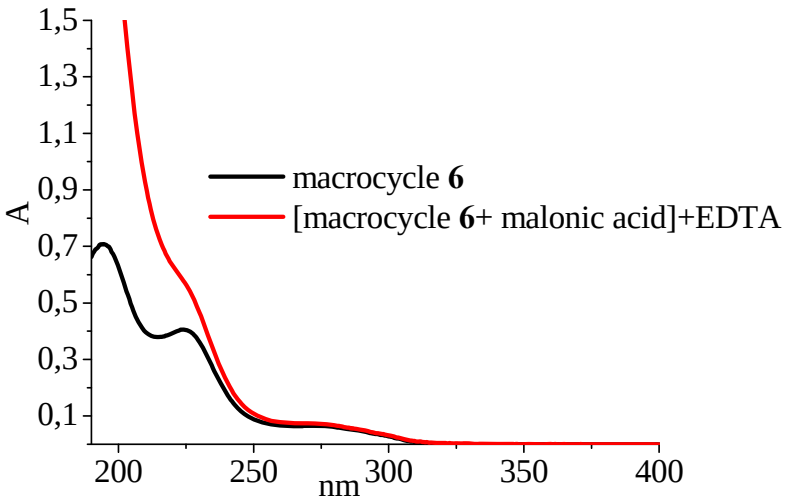
UV spectra (c = $1 \cdot 10^{-6}$ M) of commutative system based on [*p-tert*-butyl thiacalix[4]arene **6**+oxalic acid]+EDTA.



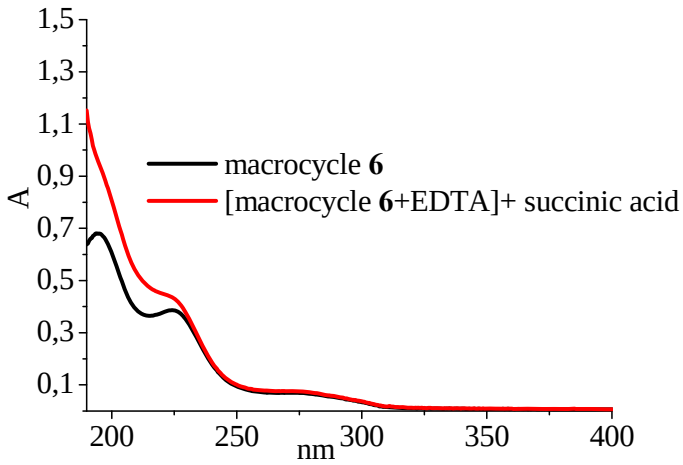
UV spectra (c = $1 \cdot 10^{-6}$ M) of commutative system based on [*p-tert*-butyl thiacalix[4]arene **6**+ EDTA]+ malonic acid.



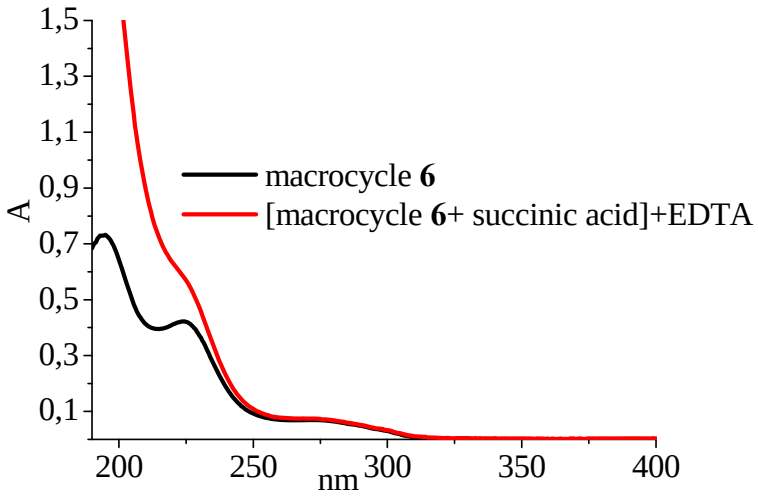
UV spectra (c = $1 \cdot 10^{-6}$ M) of commutative system based on [*p-tert*-butyl thiacalix[4]arene **6**+malonic acid]+EDTA.



UV spectra (c = $1 \cdot 10^{-6}$ M) of commutative system based on [*p-tert*-butyl thiacalix[4]arene **6**+ EDTA]+ succinic acid.



UV spectra (c = $1 \cdot 10^{-6}$ M) of commutative system based on [*p-tert*-butyl thiacalix[4]arene **6**+ succinic acid]+EDTA.



Determination of the stability constant and stoichiometry of the complex by UV titration.

The stability constant and stoichiometry of complexes were calculated as described below.

The system equilibrium is described by Eq. (1), where H, G, and G_nH denote the ligands (receptor **4-6** or nanoparticles based on macrocycles **4-6** and substrates), substrates (dicarboxylic acids (oxalic, malonic, succinic acids), amino acids (DL-alanine, DL-valine, DL-leucine, DL-aspartic acid and DL-glutamic acid), and EDTA), and complex with substrate.

$$nG + H \Leftrightarrow G_nH \qquad (1)$$

The association constant, K_{ass}, is defined by Eq. (2).

$$K_{ass} = [G_nH] / [G]^n [H] \qquad (2)$$

To determine the stoichiometry coefficient, n of the complexes formed in the organic phase, Eq. (2) was converted to Eq. (3).

$$\lg K_{ass} = \lg [G_nH] - n \lg [G] - \lg [H] \qquad (3)$$

The absorbance A, a sum of those related to the complex, ligand and substrate (A_{GnH}, A_H and A_G, respectevly) is equal to:

$$A = A_{GnH} + A_H + A_G \qquad (4)$$

Assuming that the Beer-lambert law is obeyed for all the components considered, the absorbance A is expressed as

$$A_i = C_i \varepsilon_i l \qquad (5)$$

where c_i is the molar concentration of i-species, ε_i the molar absorptivity, and l the cell thickness. For complexation between the ligand and substrate, the absorbance mesurement is usually conducted in the wavelength for maximum absorbance in the charge-transfer region where A_G=0. This gives Eq. 6

$A = A_{GnH} + A_H$ (6)

Concentration of the complex $[G_nH]$ in the system is calculated according to equations (5) and (6).

The plot of lg $[G_nH]$- lg [H] versus lg [G] (Fig. 1) presents a straight line, slope of which equals to n. Association constants K_{ass} are calculated using the intercept values (b).

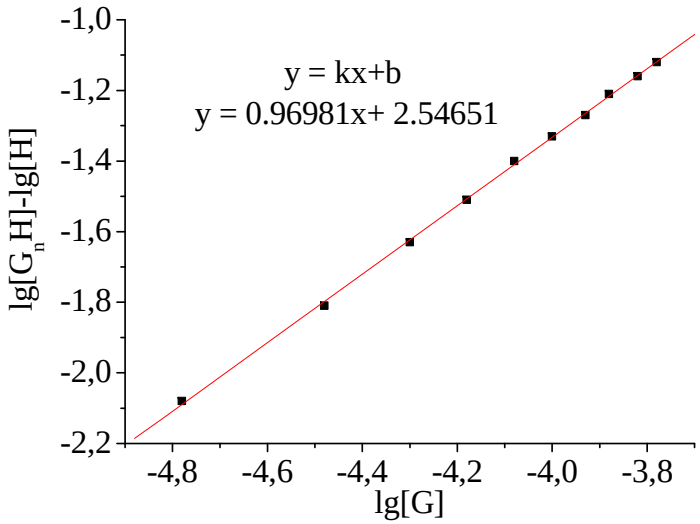


Figure 1. Plot of lg $[G_nH]$- lg [H] versus lg [G].

$b = \lg K_{ass}$ (7)

Origin 7.0 (Origin-Lab Corporation) was used for all the calculations.