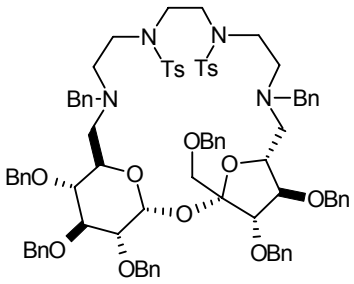
Synthesis of compound **7**:



Diamine **5** (180mg, 0.17 mmole) was dissolved in acetonitrile (10mL). Sodium carbonate (300mg) and the ditosylate of N,N'-ditosyl-N,N'-diethanol-ethylenediamine (155mg, 0.20 mmole) were added and the mixture was refluxed for 48h. Then ethyl acetate (20mL) and water (10mL) were added. The aqueous layer was extracted with ethyl acetate (2 x 20mL), dried over magnesium sulfate and evaporated. The mixture was separated by column chromatography using hexane : ethyl acetate = 3:2 as eluent. The macrocycle **7** was obtained as yellowish oil (130mg, 51% yield).

Data for **7**:

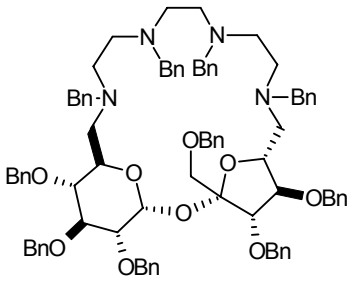
MS m/z: 1481.6 [$C_{88}H_{96}N_4O_{13}S_2 + H^+$] 1503.6 [$C_{88}H_{96}N_4O_{13}S_2 + Na^+$].

^{1}H NMR δ: 7.63 (d, 4H, $J_{1,2}$ = 8.27 Hz, H_{orto} – tosyl groups); 7.56 (d, 4H, $J_{1,2}$ = 8.27 Hz, H_{meta} – tosyl groups); 7.18 – 7.28 (m, 40H, H_{Ar}); 5.23 (d, 1H, $J_{1,2}$ = 3.22 Hz, H-1); 2.75-4.85 (range of multiplets, aliphatic hydrogens of the sucrose skeleton and the macrocyclic ring); 2.40 (s, 3H, CH_3 of tosyl group); 2.37 (s, 3H, CH_3 of tosyl group).

^{13}C NMR δ: 143.2, 143.1 (C_{quat}, tosyl groups); 138.80, 138.77, 138.5, 138.4, 138.3, 138.0, 137.93, 137.90 (C_{quat}, benzyl groups); 136.2, 135.6 (C_{quat}, tosyl groups); 127.0 – 129.7 (C_{Ar}); 104.0 (C-2'); 90.0 (C-1); 83.2, 82.5, 82.2, 79.8, 78.1, 77.2, 71.6 (C-2, C-3, C-3', C-4, C-4', C-5, C-5'); 75.6, 74.1, 73.3, 73.2, 72.4, 72.1, 71.8 (6 x OCH_2Ph, C-1'); 61.3, 57.8, 56.3, 55.1, 54.0, 53.8, 49.0, 48.8, 48.6, 47.6 (2 x NCH_2Ph, C-6, C-6', 3 x (NCH_2CH_2N)); 21.49, 21.45 (CH_3, tosyl groups).

Elem. analysis calcd. for $C_{88}H_{96}N_4O_{13}S_2$: C = 71.33%, H = 6.53%, N = 3.78%, S = 4.33%; found: C = 71.07%, H = 6.82%, N = 3.42%, S = 4.30%.

Synthesis of compound **8**:



Dimesylate **6** (110mg, 0.084 mmole) was dissolved in acetonitrile (8mL). Sodium carbonate (250mg) and N,N'-dibenzylethylenediamine (24mg, 0.1 mmole) were added and the mixture was refluxed for 48h. Then ethyl acetate (15mL) and water (5mL) were added. The aqueous layer was extracted with ethyl acetate (2 x 15mL), dried over magnesium sulfate and evaporated. The mixture was separated by column chromatography using hexane : ethyl acetate = 3:2 as eluent. The macrocycle **8** was obtained as colourless oil (60mg, 53% yield).

Data for **8**:

MS m/z: 1353.8 [$C_{88}H_{96}N_4O_9 + H^+$].

^{1}H NMR δ: 7.15 – 7.28 (m, 50H, HAr); 5.61 (d, 1H, $J_{1,2}$ = 3.47 Hz, H-1); 2.53 – 4.90 (range of multiplets, aliphatic hydrogens of the sucrose skeleton and the macrocyclic ring).

^{13}C NMR: 139.7 (double intensity), 139.5, 139.4, 139.2, 139.0, 138.8, 138.41, 138.34, 138,26, 138.2 (C_{quat}, benzyl groups); 126.6 – 129.1 (C_{Ar}); 104.6 (C-2'); 89.7 (C-1); 83.74, 83.68, 82.2, 81.5, 80.1, 79.0, 72.1 (C-2, C-3, C-3'. C-4, C-4', C-5, C-5'); 76.2, 75.5, 75.0, 74.0, 73.4, 73.2, 72.4 (6 x OCH_2Ph, C-1'); 61.7, 60.4, 59.9, 59.0, 58.3, 58.2, 56.1, 53.5, 53.0, 52.6, 52.4, 52.2 (4 x NCH_2Ph, C-6, C-1', C-6', 3 x (NCH_2CH_2N)).

Titration experiments (general procedure):

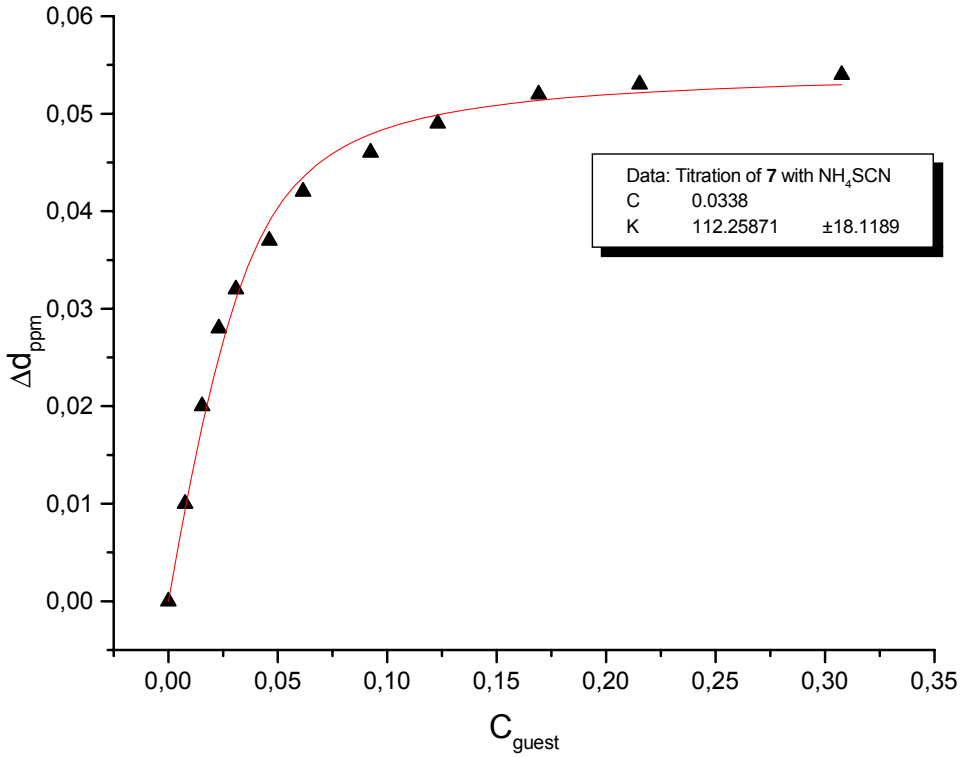
A solution of the macrocycle in 0.6mL of the respective solvent ($CDCl_3$ for the experiments with phenylethylammonium chlorides; acetone-d_6 for ammonium thiocyanate) was prepared (concentration given separately for each experiment) . The NMR spectrum was recorded. Subsequently small portions of the guest were added to the solution. After each addition of the ammonium salt NMR spectra's were recorded. The shift of the signal of anomeric proton of sucrose was followed. The additions of guest were continued until the constant value of the chemical shift of H-1 (anomeric). The value of the signal shift was then plotted against the concentration of the guest in solution. A curve was fitted to the plot, using the empirical equation described by Fielding (ref.18 of the article).

This allowed to determine the value of the association constant for the interaction between the macrocycle and the guest molecule. The above mentioned operations were carried out using the MicroCal Origin software.

This methodology can be used for 1:1 complexes. If the method is applied succesfuly (the error of the K_a determination is not very high) the stoichiometry of the complex does not have to be additionaly proven by preparation of the Job plot. In the case of compound **4** the error of K_a value was quite high so we have additionaly prepared the Job plot. It has proven the 1:1 stoichiometry of the complex with S(-) phenylethylammonium chloride (see below).

Compound 7:

Complexation of NH_4SCN (acetone-d_6). Concentration of **7** in acetone, C_7 = 0.0338 M/L.

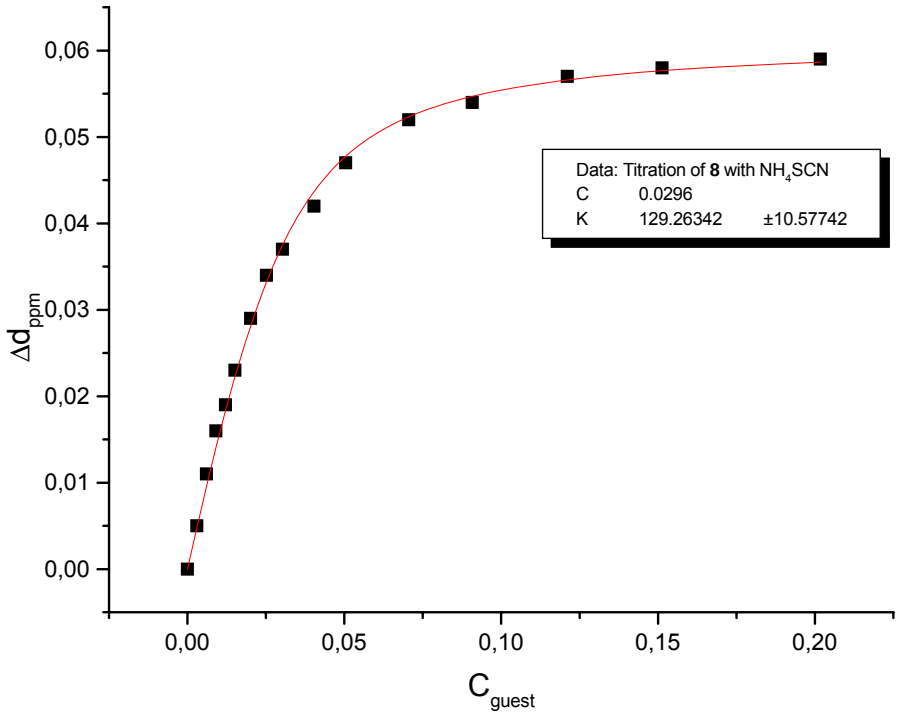


Concentration of NH_4SCN (M/L)	**Δd_{ppm}**
0	0
0.00769	0.01
0.01538	0.02
0.02308	0.028
0.03077	0.032
0.04615	0.037
0.06153	0.042
0.0923	0.046
0.1231	0.049
0.1692	0.052
0.2153	0.053
0.3077	0.054

K_a = 112 ± 18 M/L

Compound 8:

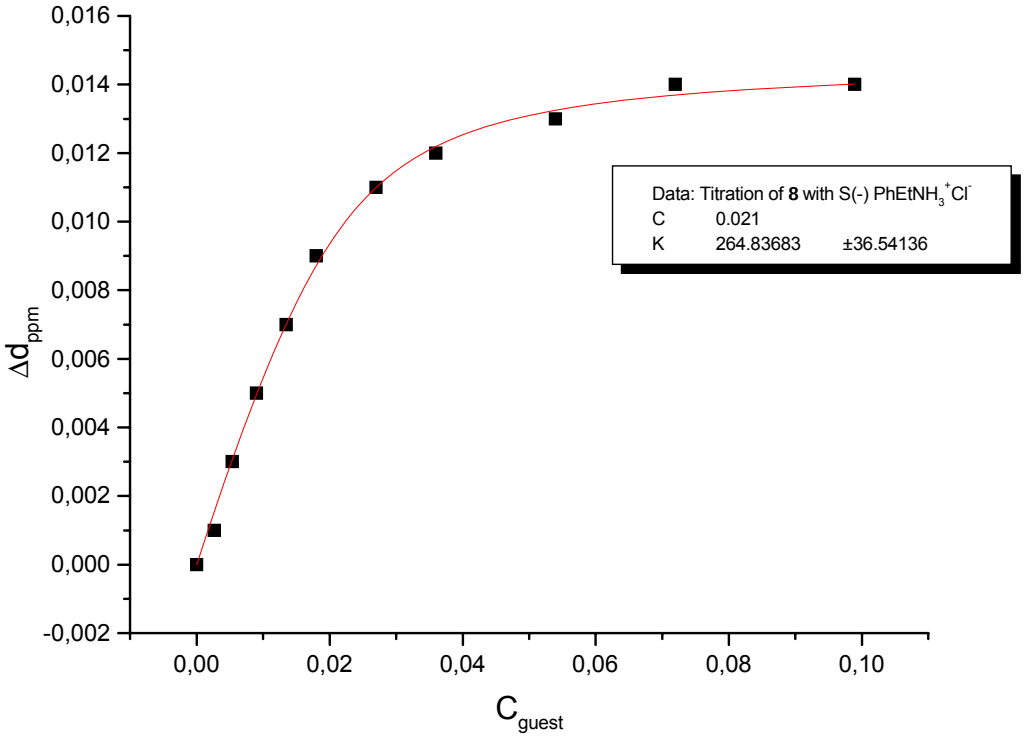
Complexation of NH_4SCN (acetone-d_6). Concentration of **8** in acetone, C_8 = 0.0296 M/L.



Concentration of NH_4SCN (M/L)	Δd_{ppm}
0	0
0.00303	0.005
0.00605	0.011
0.00908	0.016
0.0121	0.019
0.01513	0.023
0.02017	0.029
0.02522	0.034
0.03026	0.037
0.04035	0.042
0.05044	0.047
0.07061	0.052
0.09079	0.054
0.12105	0.057
0.15132	0.058
0.20175	0.059

K_a = 129 ± 10 M/L

Complexation of **8** with S(-) phenylethylammonium chloride ($CDCl_3$). Concentration of **8** in chloroform, C_8 = 0.021 M/L.

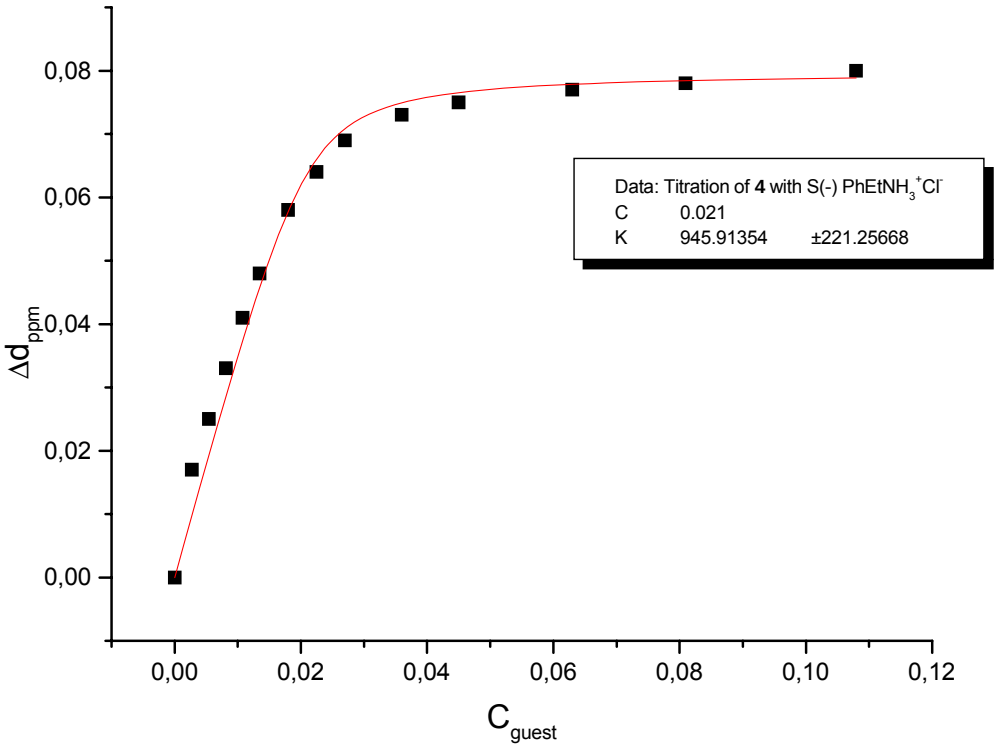


Concentration of S(-) $PhEtNH_3^+$ Cl^- (M/L)	**Δd_{ppm}**
0	0
0.0027	0.001
0.0054	0.003
0.00899	0.005
0.01349	0.007
0.01799	0.009
0.02698	0.011
0.03598	0.012
0.05397	0.013
0.07196	0.014
0.09894	0.014

K_a = 264 ± 36 M/L

Compound 4:

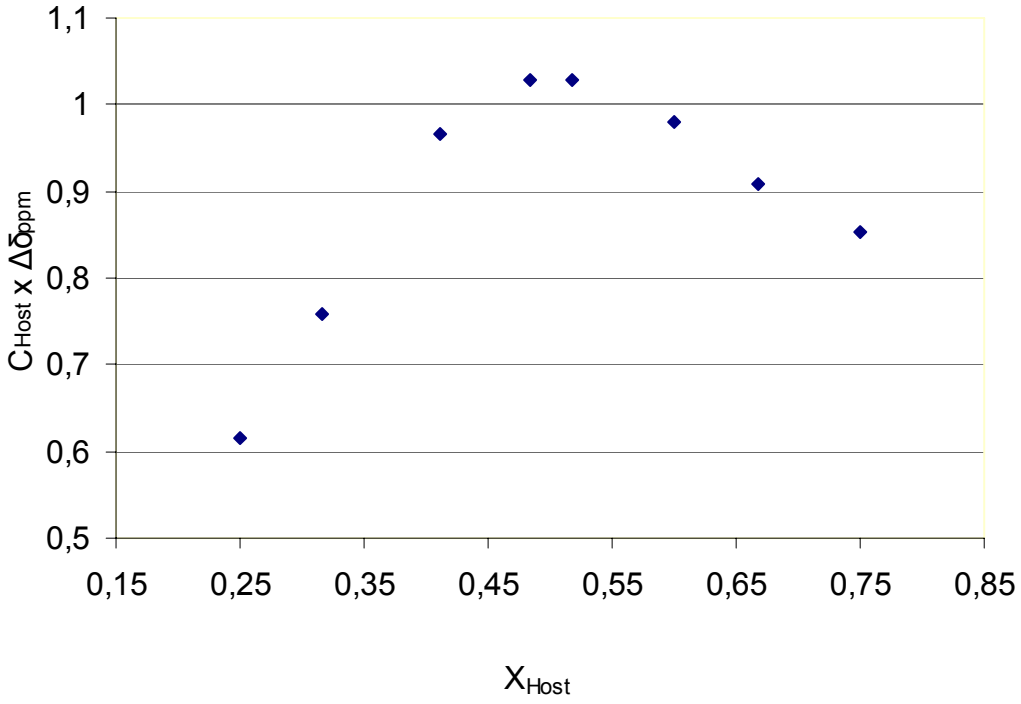
Complexation of **4** with S(-) phenylethylammonium chloride. Concentration of **4** in chloroform, C_4 = 0.021 M/L.



Concentration of S(-) $PhEtNH_3^+$ Cl^- (M/L)	**Δd_{ppm}**
0	0
0.0027	0.017
0.0054	0.025
0.00809	0.033
0.01079	0.041
0.01349	0.048
0.01799	0.058
0.02249	0.064
0.02698	0.069
0.03598	0.073
0.04497	0.075
0.06296	0.077
0.08095	0.078
0.10794	0.080

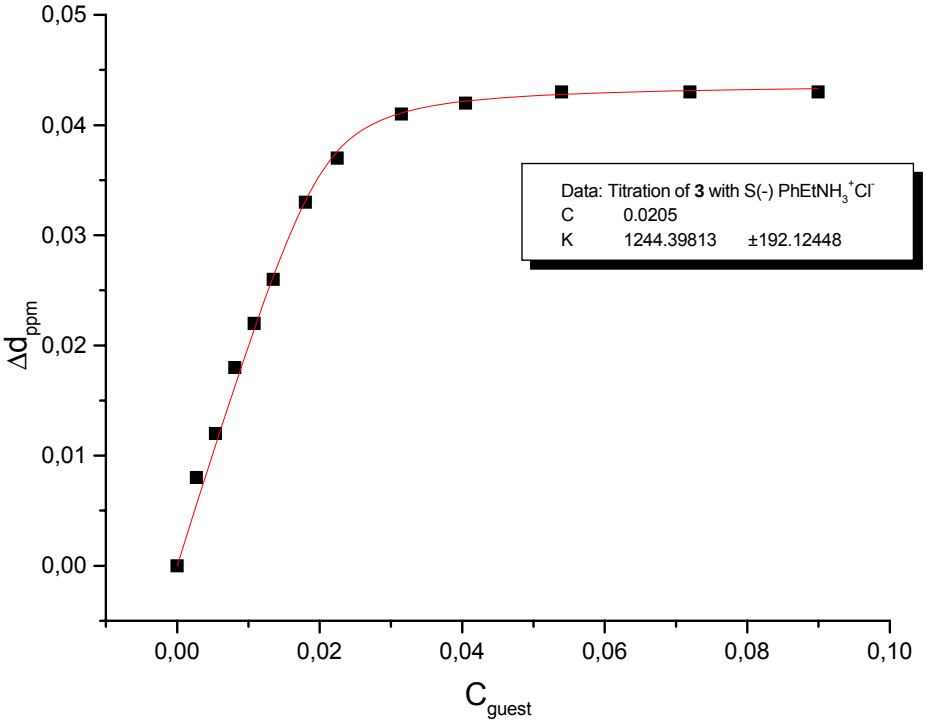
K_a = 945 ± 221 M/L

Job plot for the interaction between **4** and S(-) $PhEtNH_3^+Cl^-$.



Compound 3:

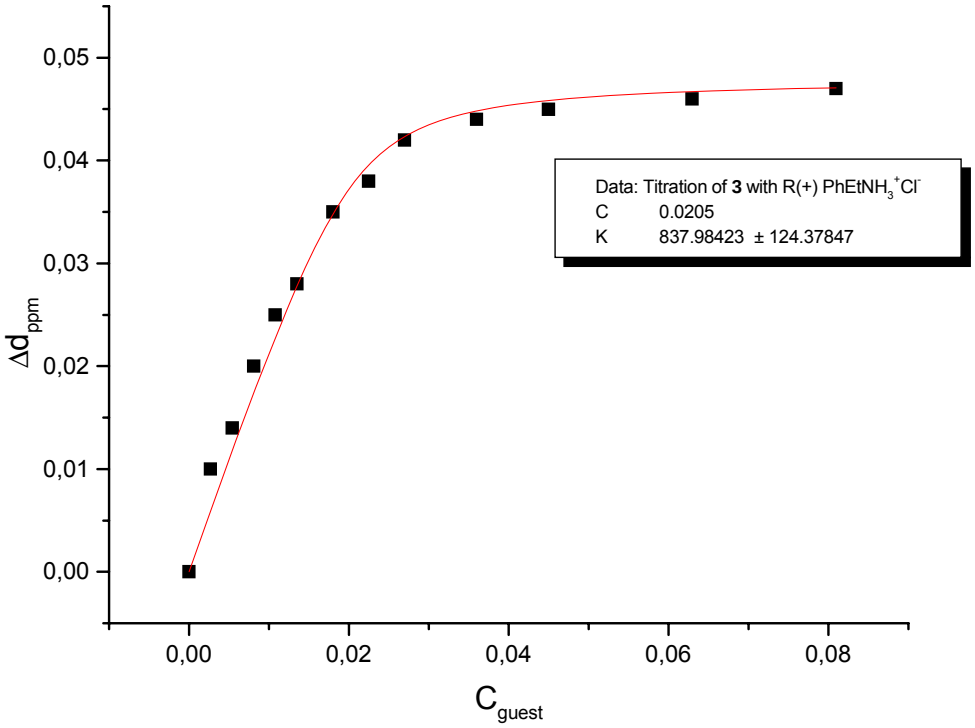
Complexation of **3** with S(-) phenylethylammonium chloride. Concentration of **3** in chloroform, C_3 = 0.0205 M/L.



Concentration of S(-) $PhEtNH_3^+$ Cl^- (M/L)	**Δd_{ppm}**
0	0
0.0027	0.008
0.0054	0.012
0.00809	0.018
0.01079	0.022
0.01349	0.026
0.01799	0.033
0.02249	0.037
0.03148	0.041
0.04048	0.042
0.05397	0.043
0.07196	0.043
0.08995	0.043

K_a = 1244 ± 192 M/L

Complexation of **3** with R(+) phenylethylammonium chloride. Concentration of **3** in chloroform, C_3 = 0.0205 M/L.



Concentration of R(+) $PhEtNH_3^+$ Cl^- (M/L)	**Δd_{ppm}**
0	0
0.0027	0.010
0.0054	0.014
0.00809	0.020
0.01079	0.025
0.01349	0.028
0.01799	0.035
0.02249	0.038
0.02698	0.042
0.03598	0.044
0.04497	0.045
0.06296	0.046
0.08095	0.047

K_a = 837 ± 124 M/L