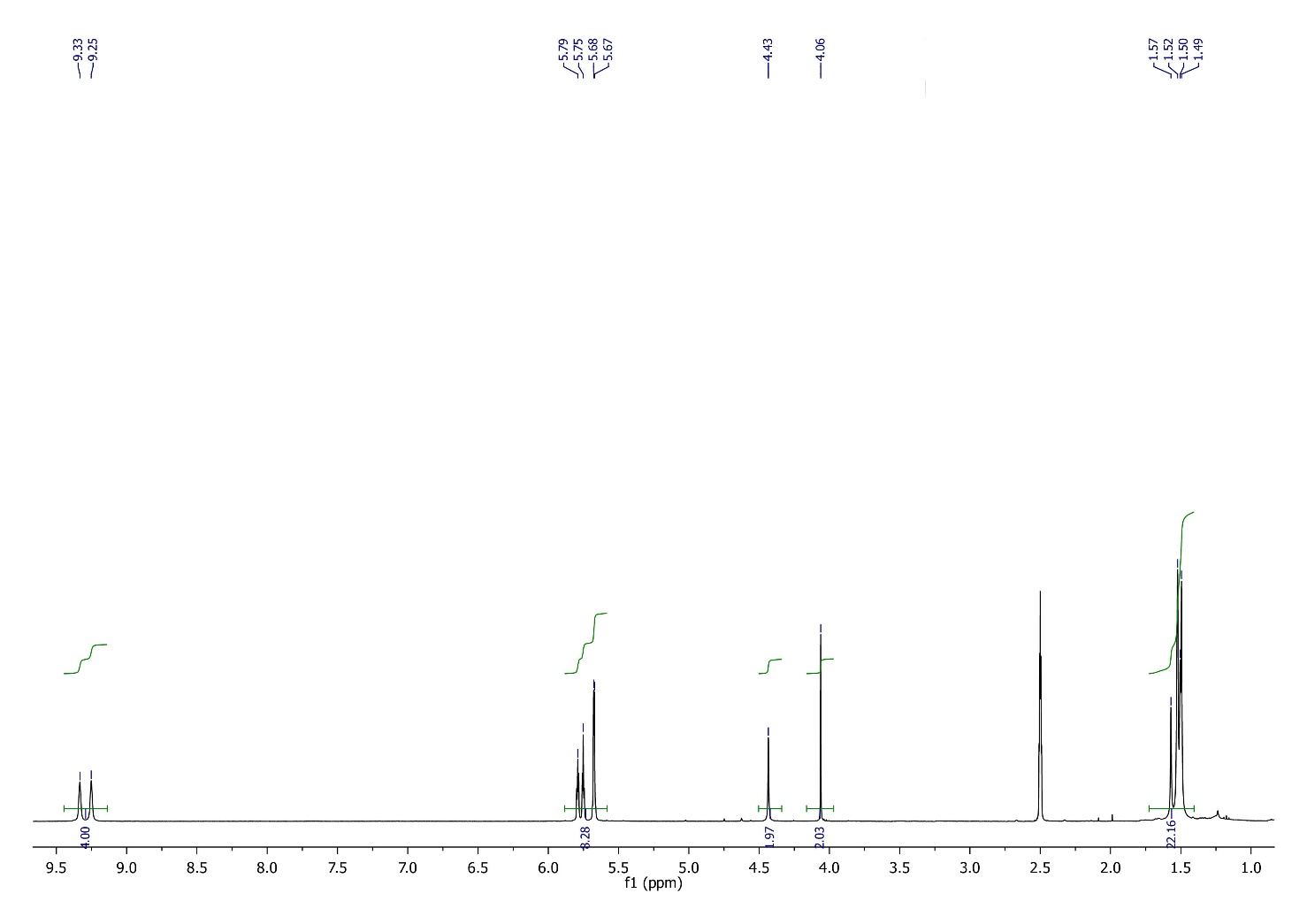
**Calix[4]pyrroles bearing quinolinium moiety for halide sensing in aqueous solution**

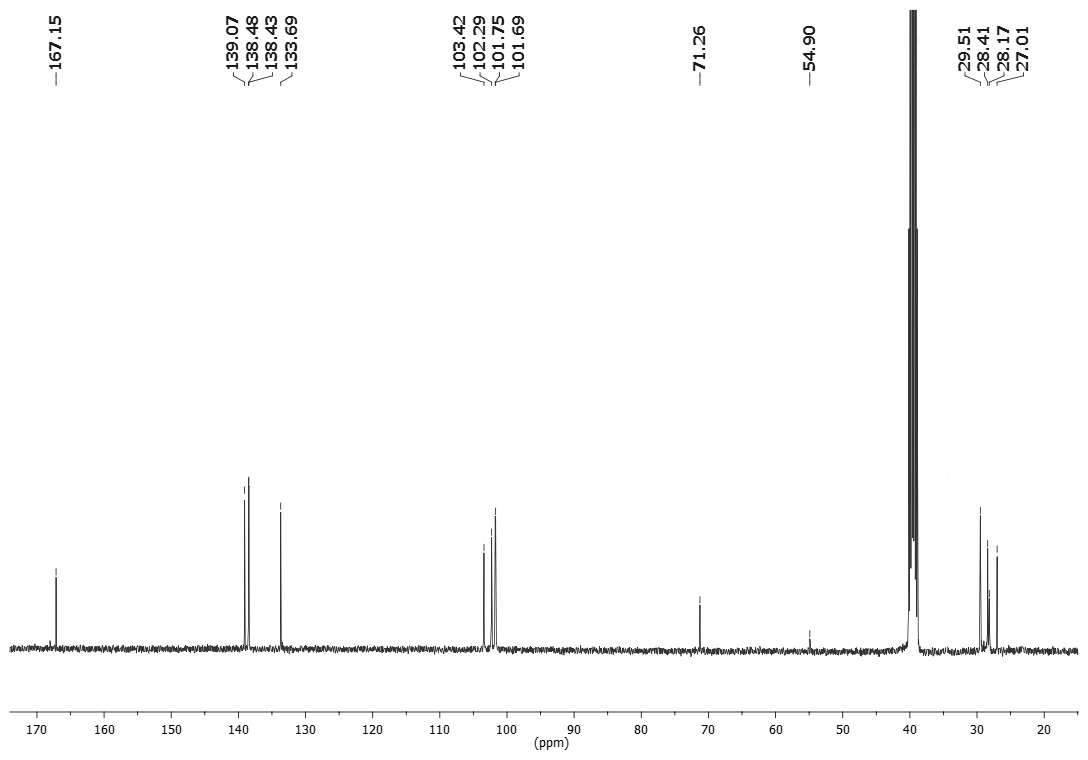
Evgeny A. Kataev, Nanett Backmann, Tobias Rüffer and Heinrich Lang

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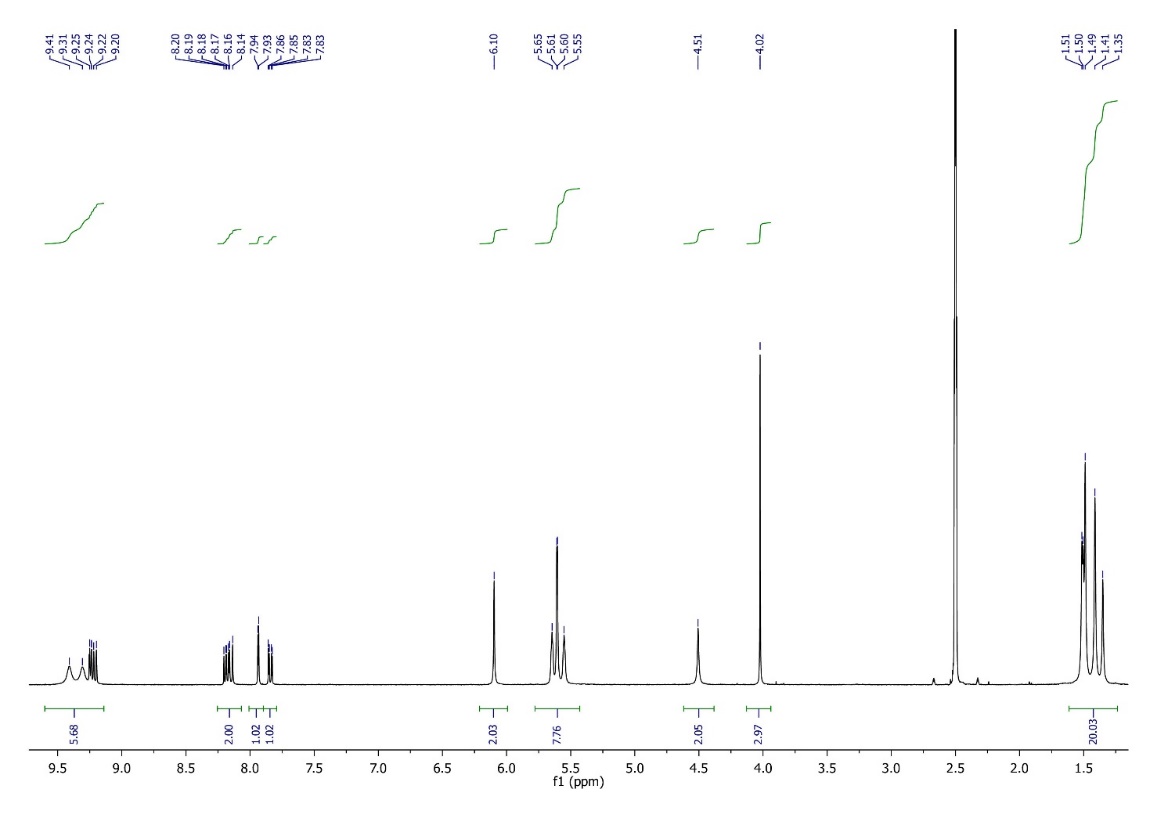
**NMR data**

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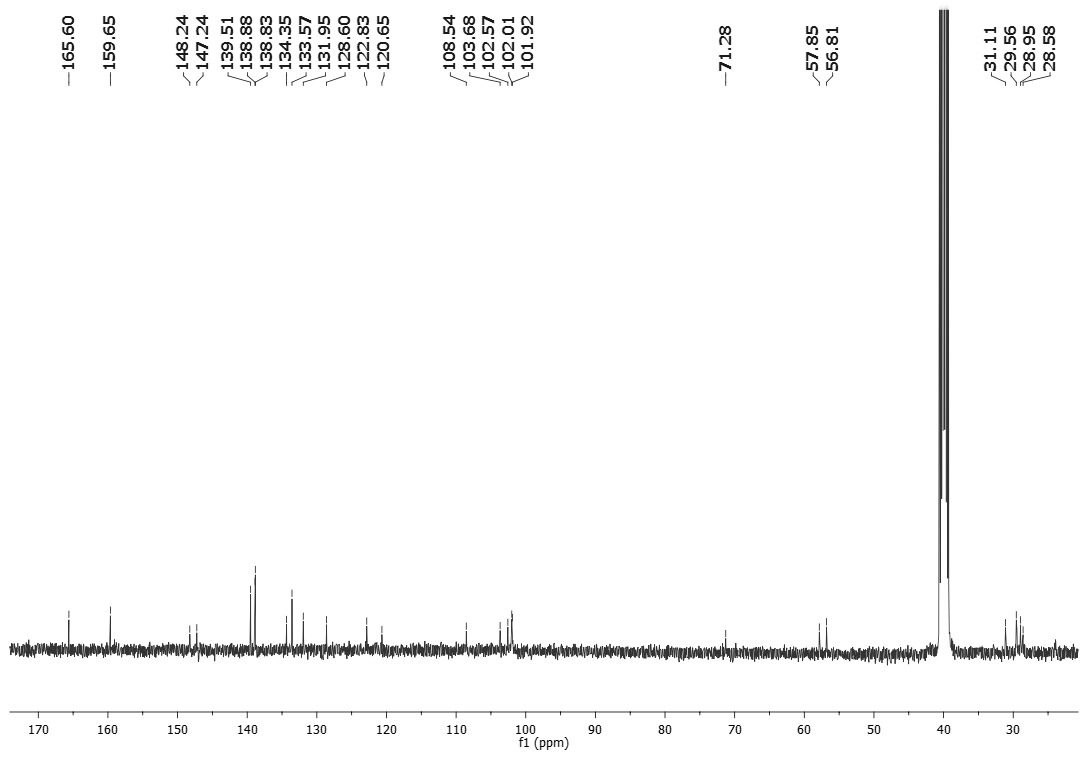
**Figure S1.** 1H NMR spectrum of monohydroxy-*meso*-octamethylCalix[4]pyrrole 2-bromacetate measured in DMSO-d6.



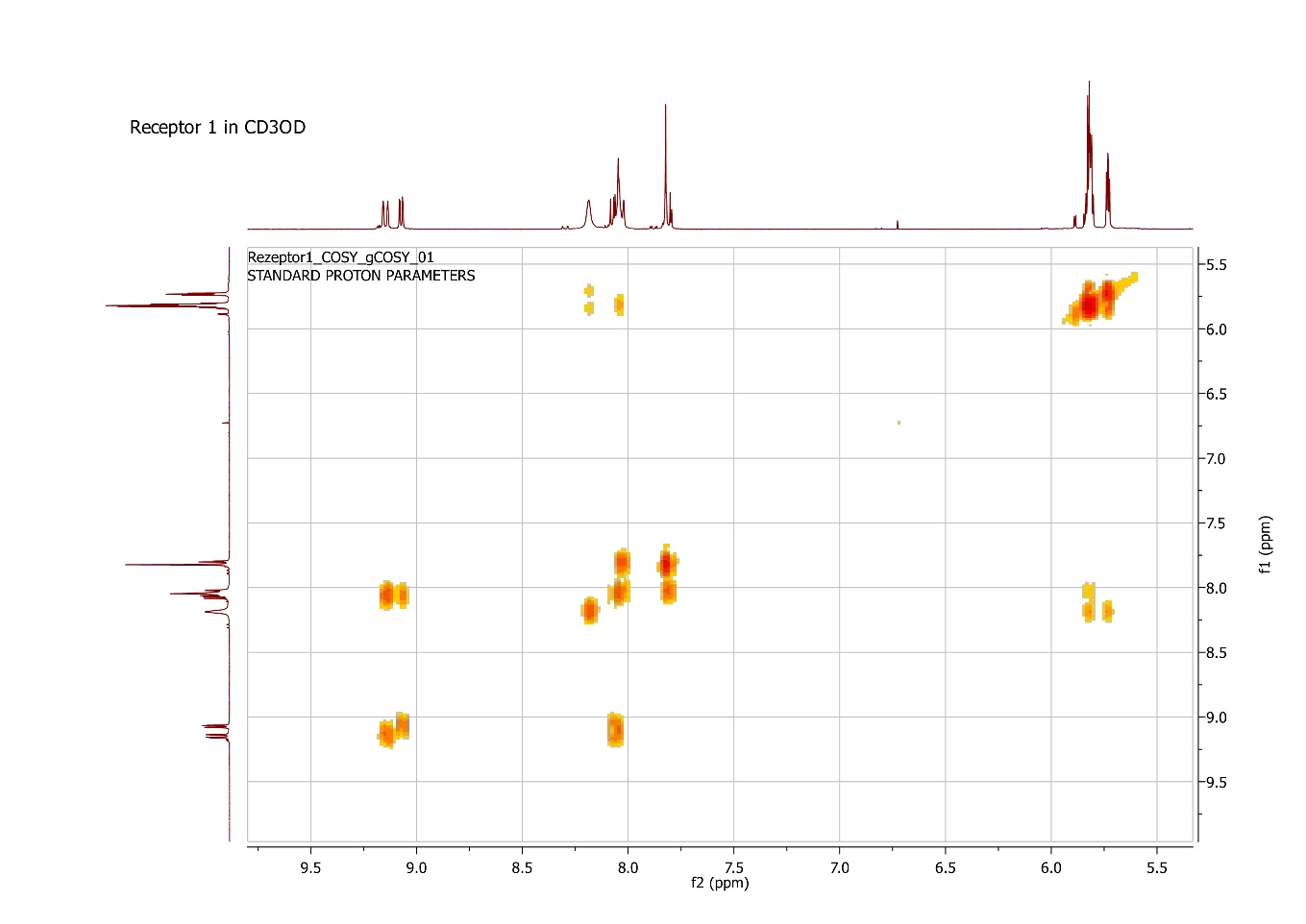
**Figure S2.** 13C NMR spectrum of monohydroxy-*meso*-octamethylCalix[4]pyrrole 2-bromacetate measured in DMSO-d6.

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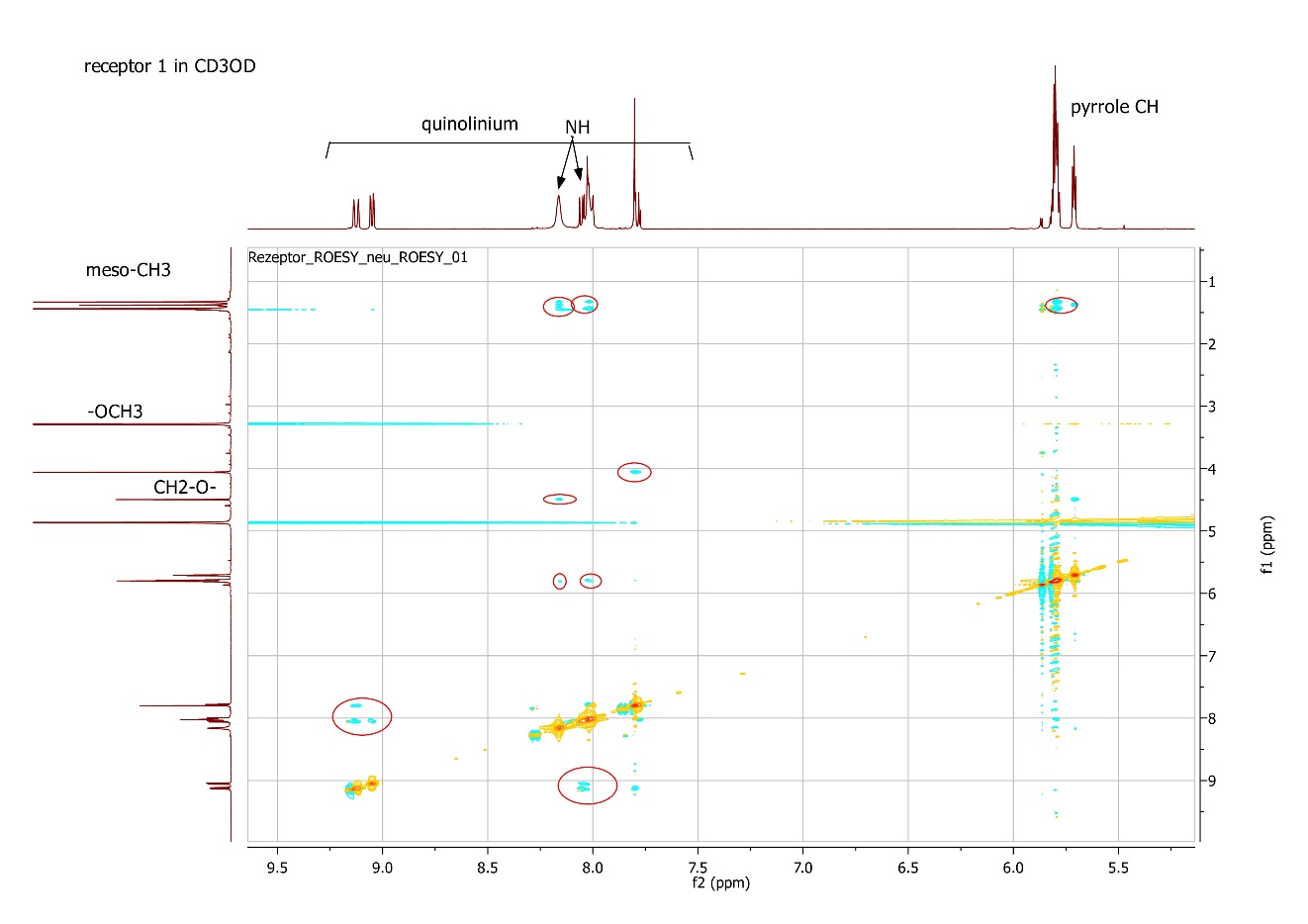
**Figure S3.** 1H NMR spectrum of **1** measured in DMSO-d6.

****

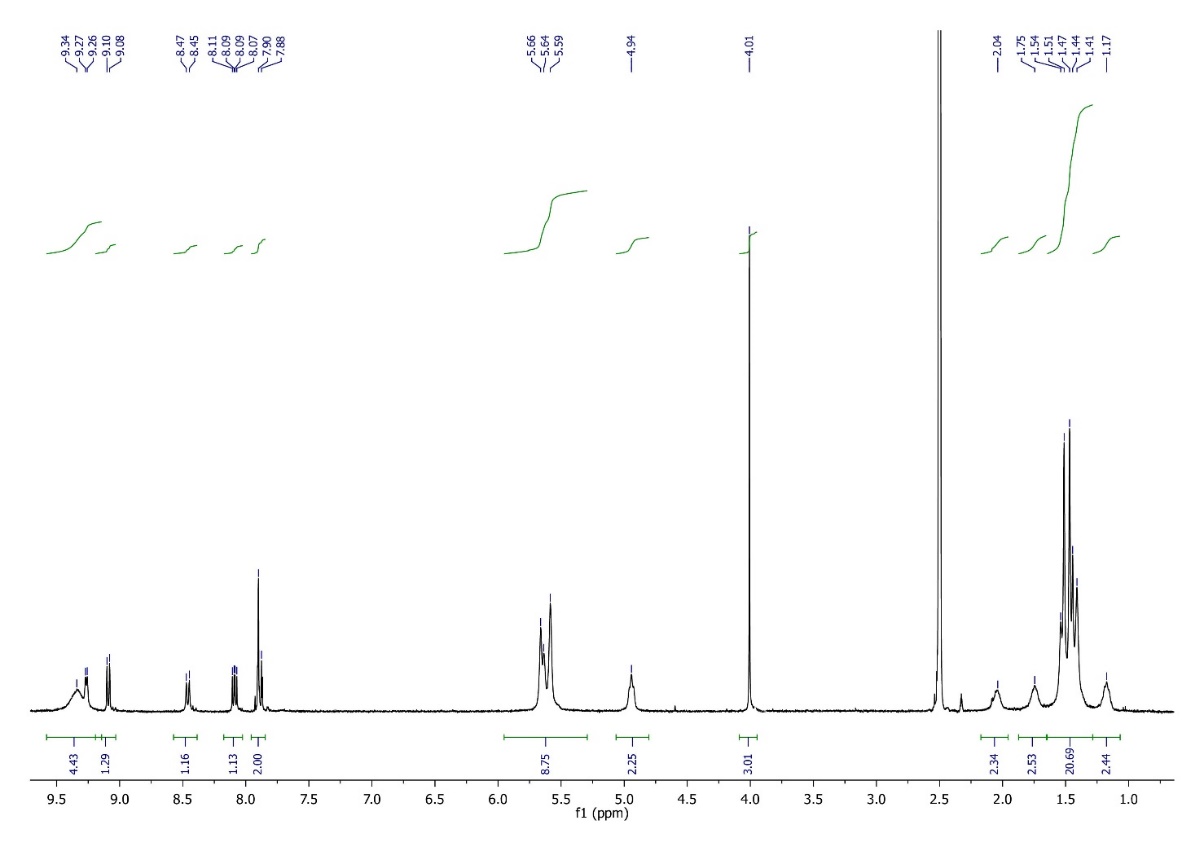
**Figure S4.** 13C NMR spectrum of **1** measured in DMSO-d6.



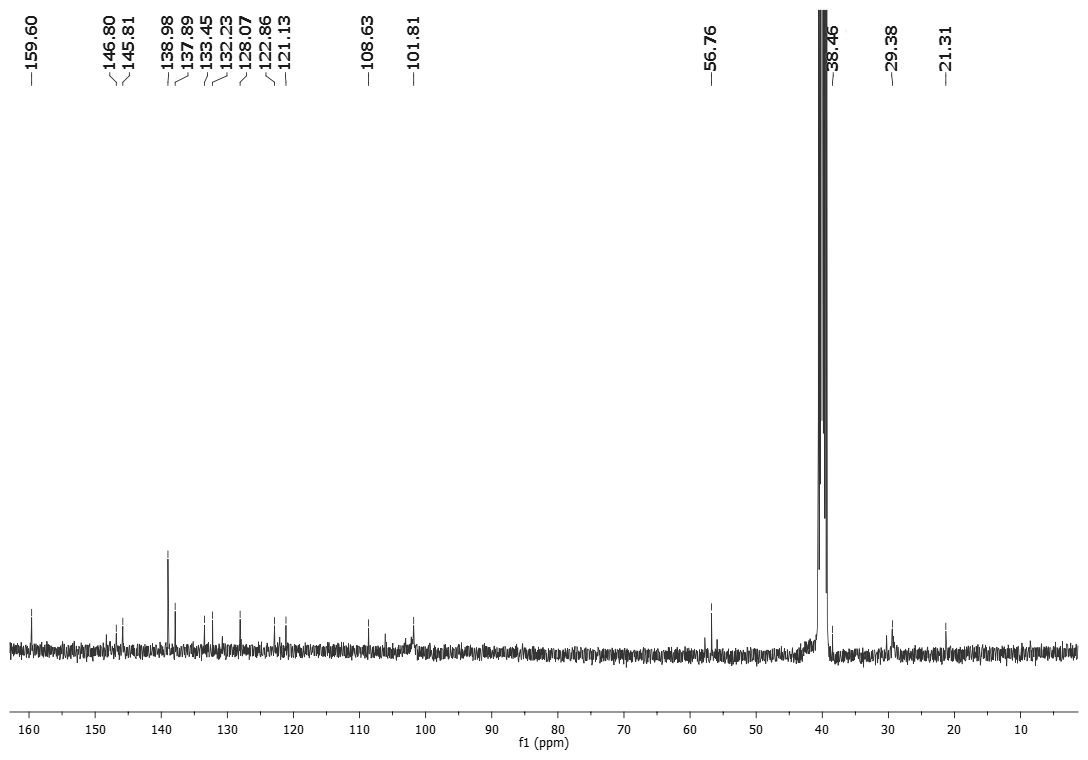
**Figure S5.** COSY spectrum of **1** in CD3OD.



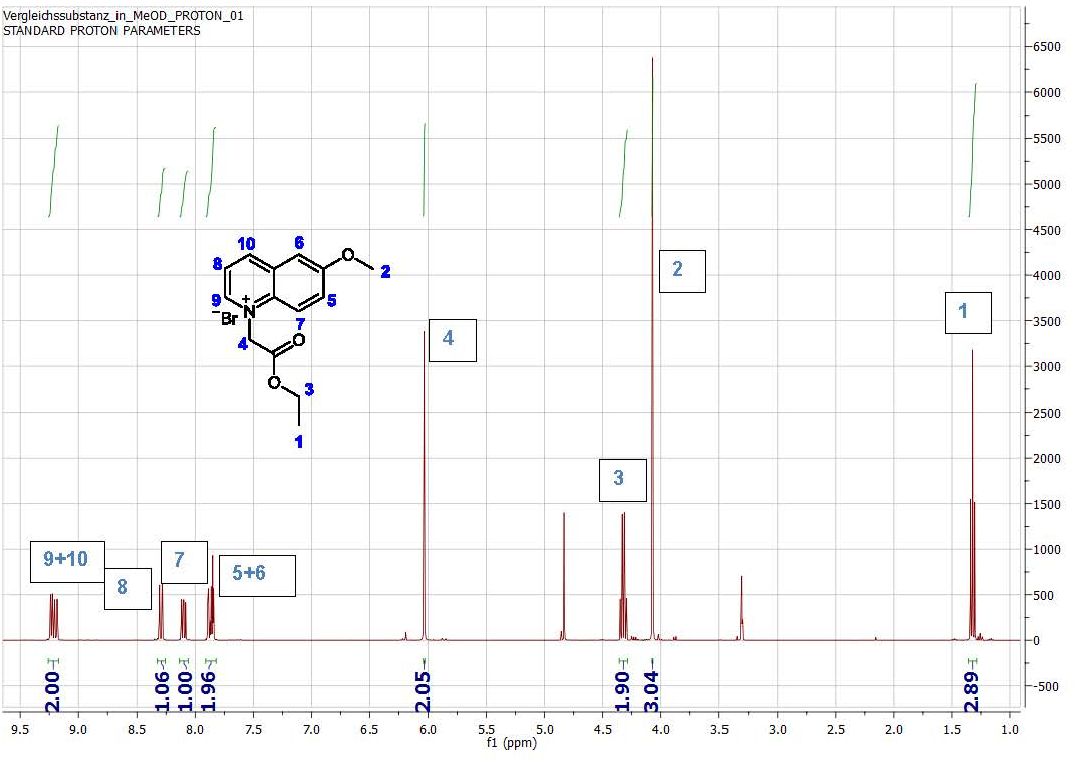
**Figure S6.** ROESY spectrum of **1** in CD3OD.



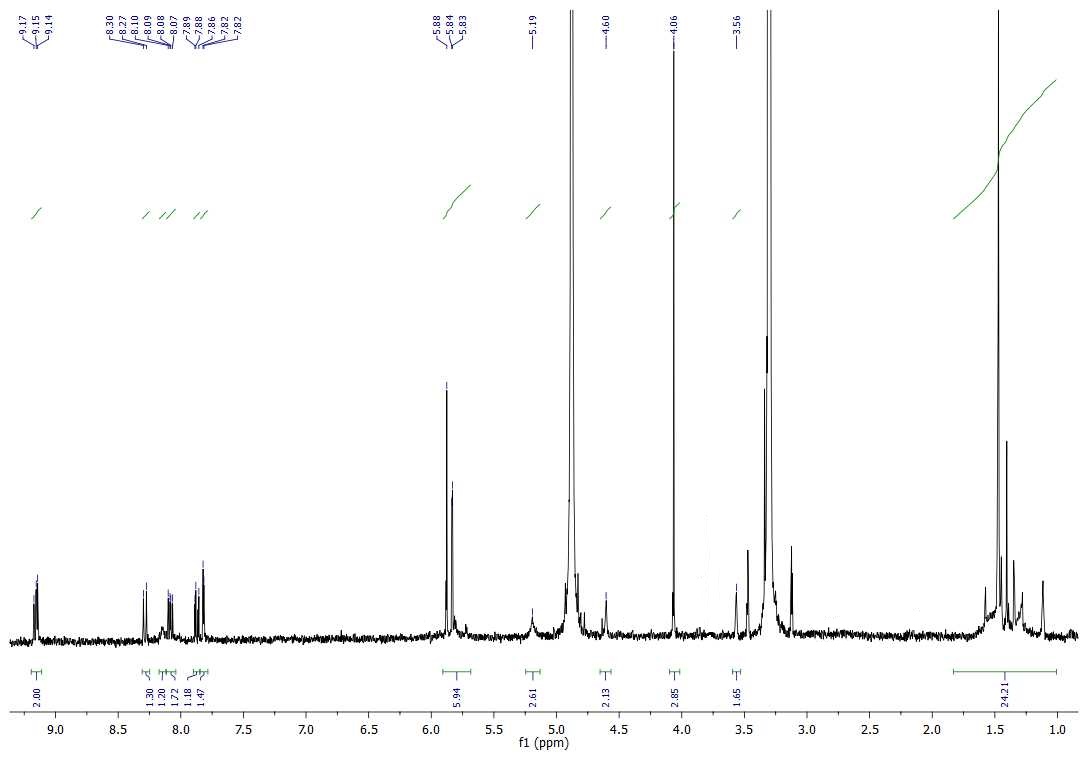
**Figure S7.** 1H NMR spectrum of **2** measured in DMSO-d6



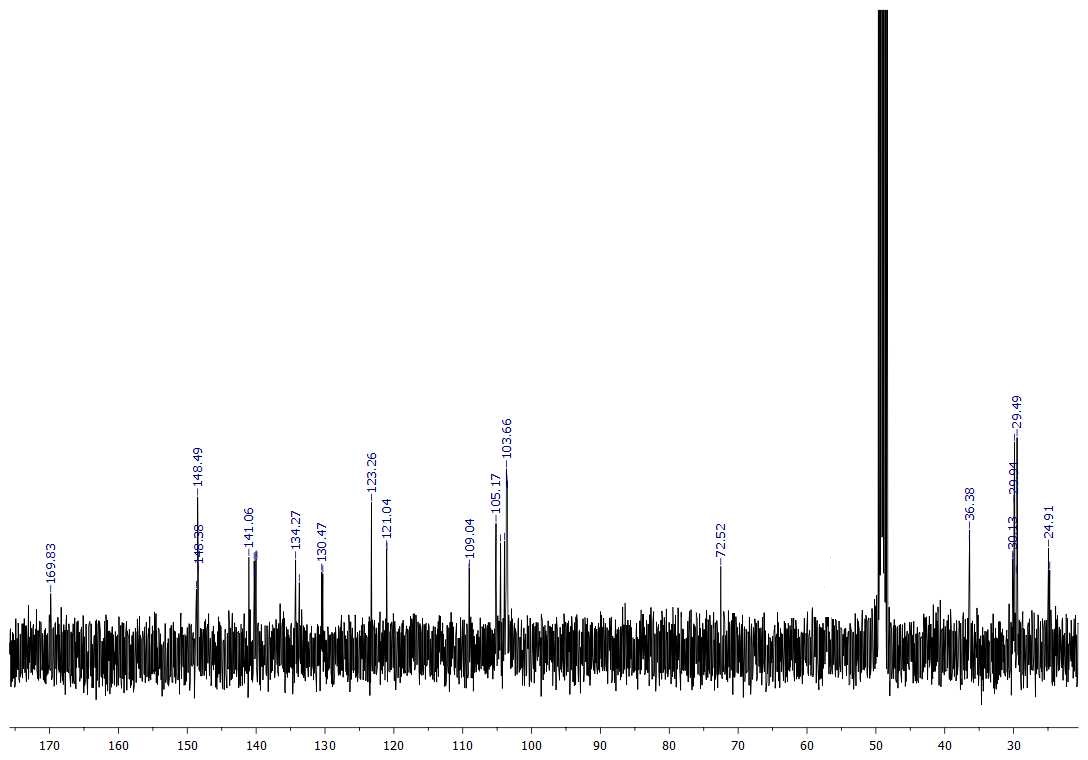
**Figure S8.** 13C NMR spectrum of **2** measured in DMSO-d6.



**Figure S9.** 1H NMR spectrum of **3** measured in CD3OD.

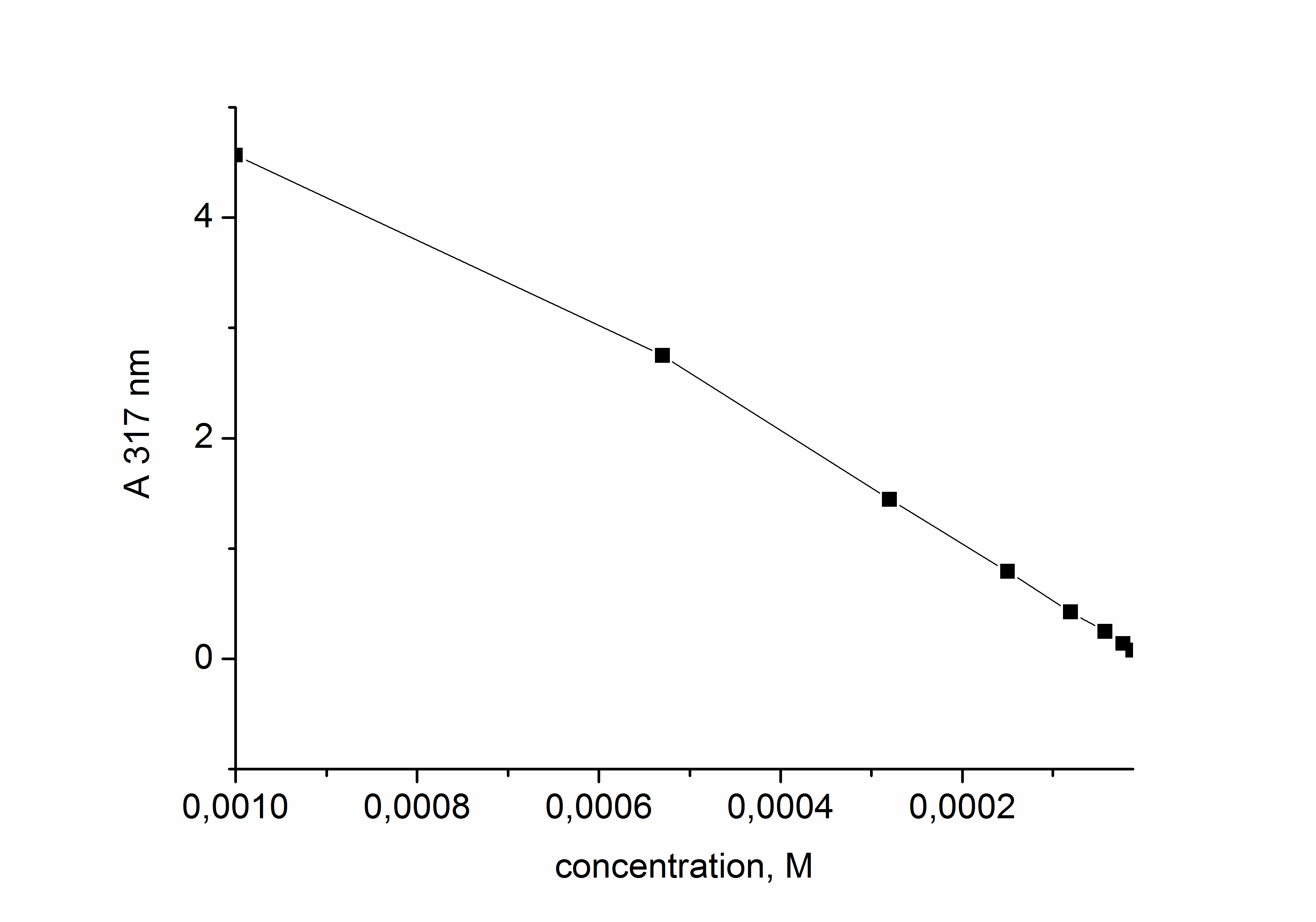
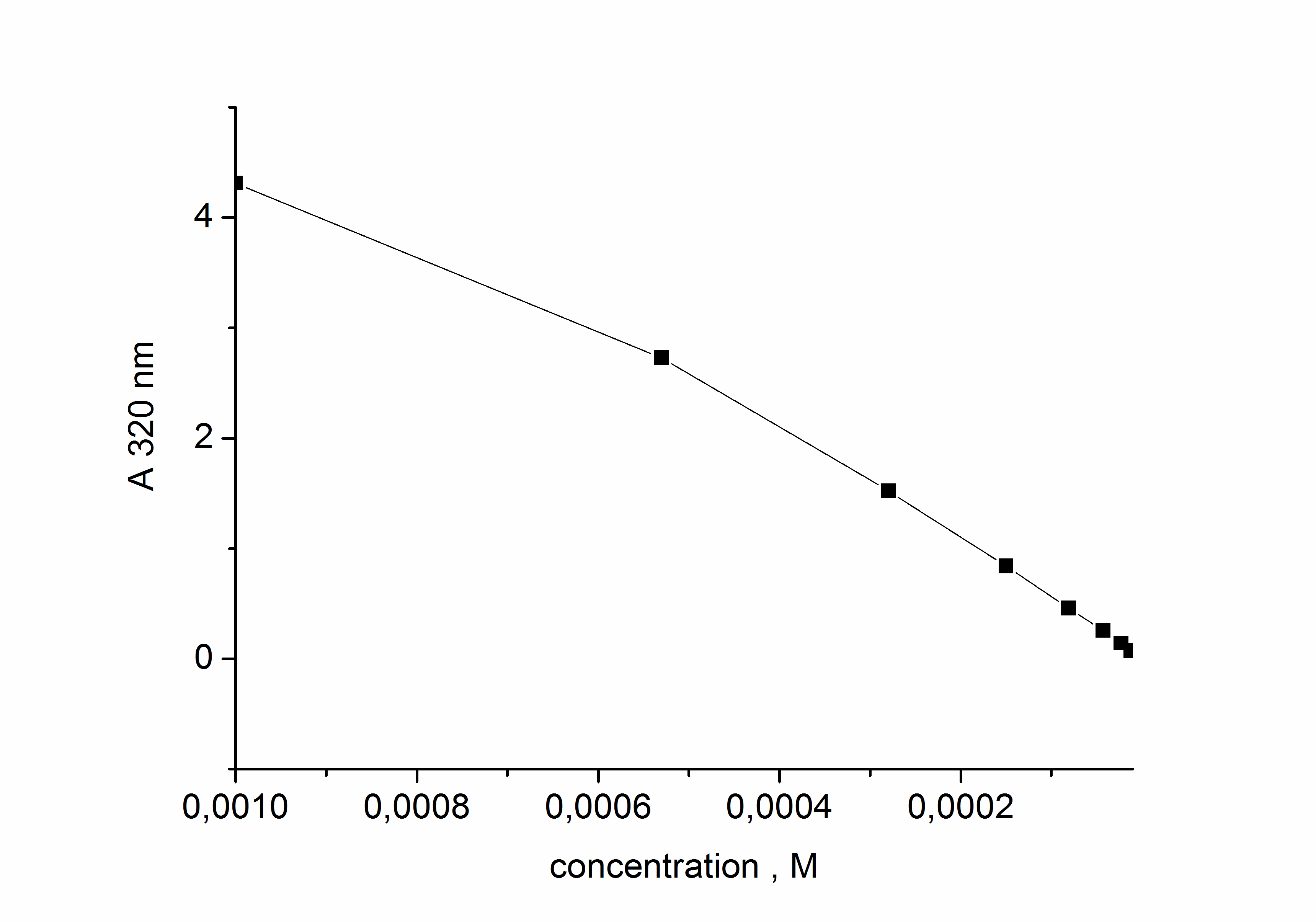


**Figure S10**. 1H NMR spectrum of **4** measured in CD3OD.

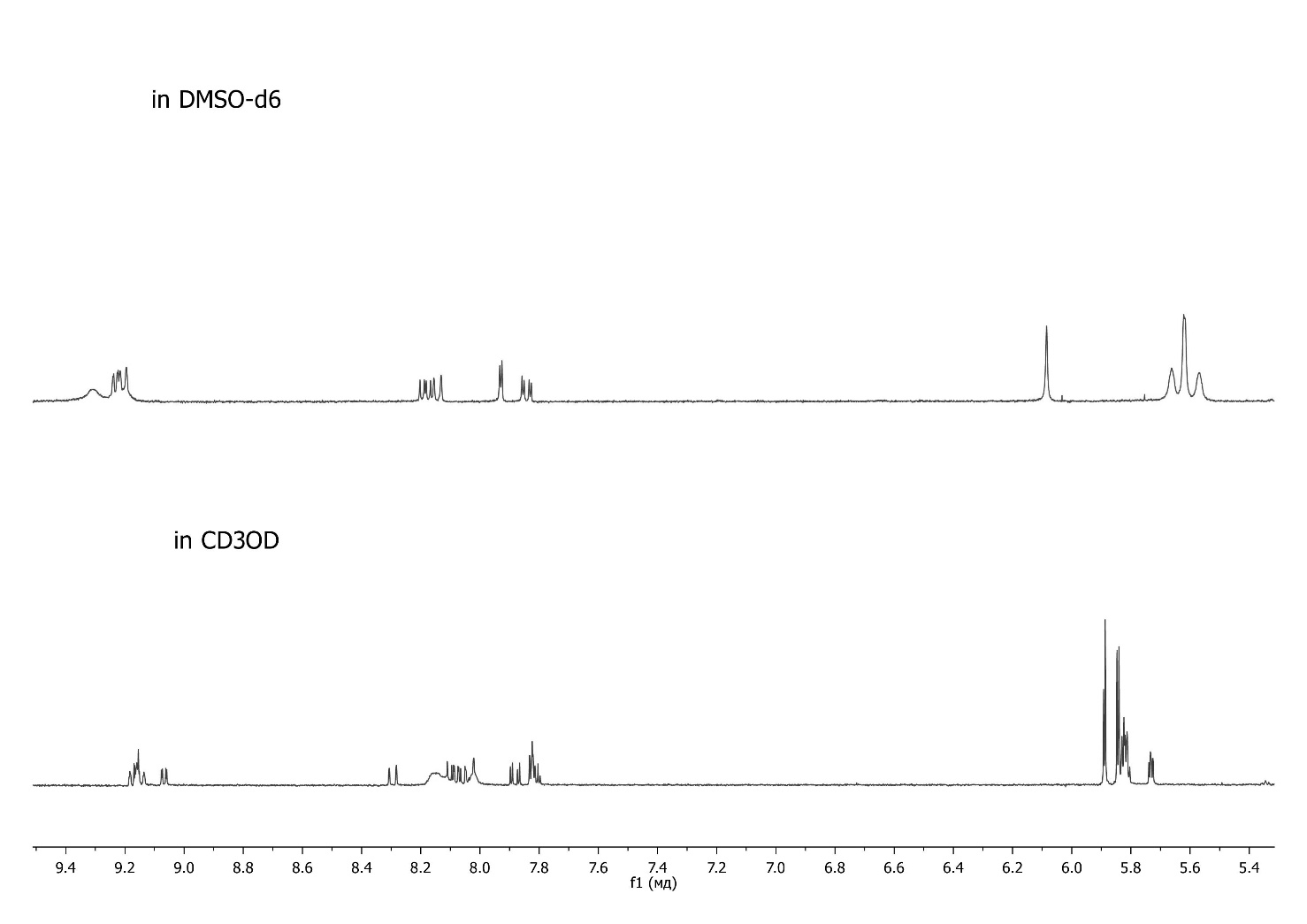


**Figure S11**. 13C NMR spectrum of **4** measured in CD3OD.

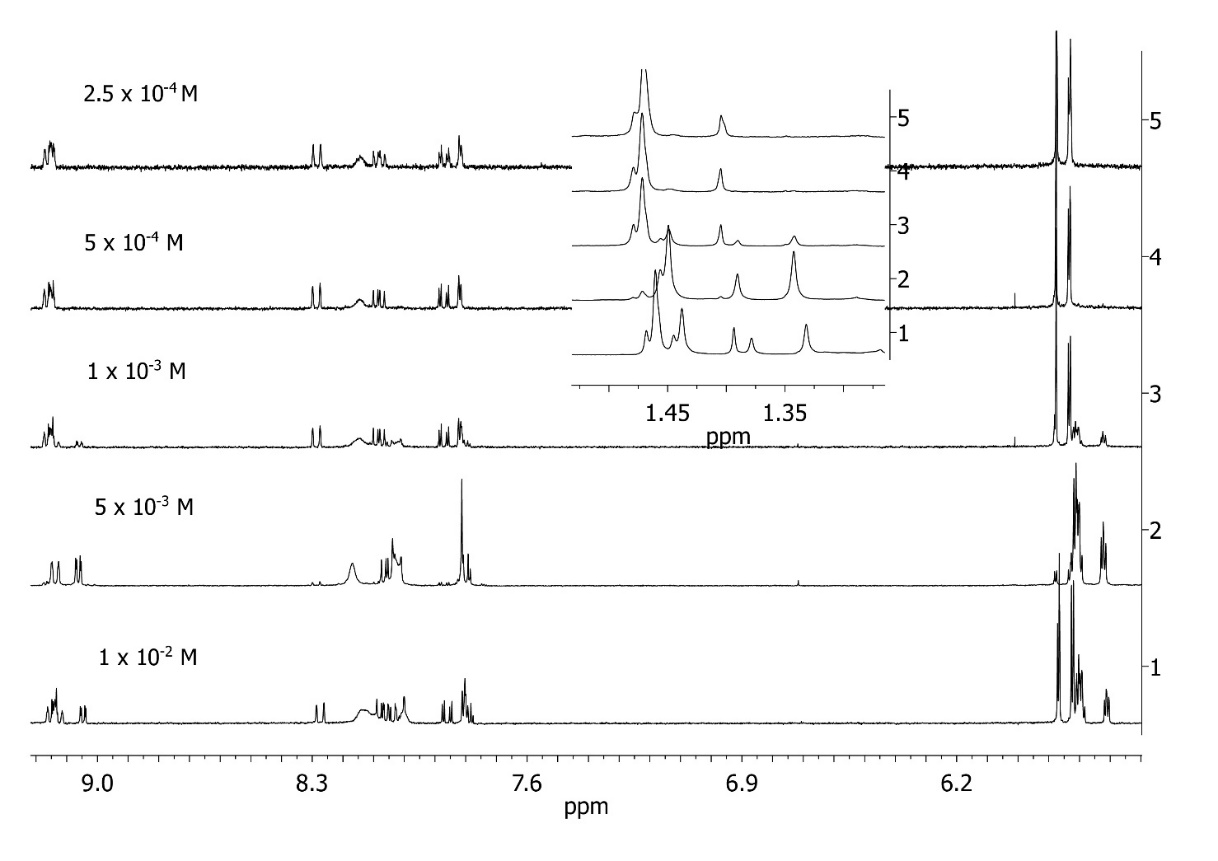
**Dilution experiments**



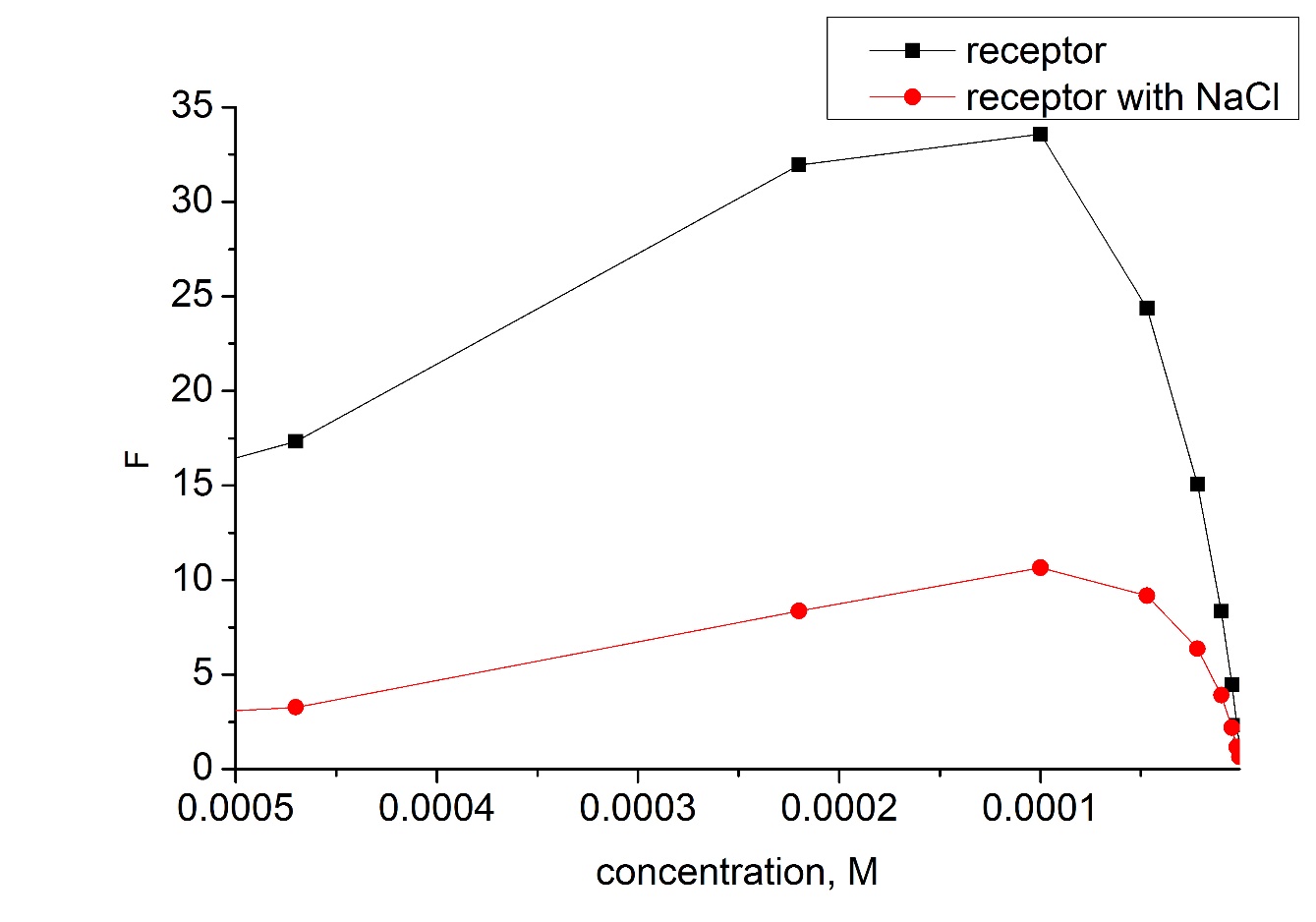
**Figure S12.** Changes in absorption (A) of receptor **1**(left) and **2**(right) depending on their concentration in a methanol-water 1:1 mixture.

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**Figure S13**. Comparison of 1H NMR spectra of receptor **1** recorded in DMSO-d6 and methanol-d4. The complex structure of signal in the spectrum measured in methanol-d4 indicates that the receptor forms aggregates.



**Figure S14**. 1H NMR spectra of receptor **1** in CD3OD



**Figure S15**. Changes in fluorescence of free receptor **1** andwith 10 equiv. NaCldepending on their concentration in CH3OH.

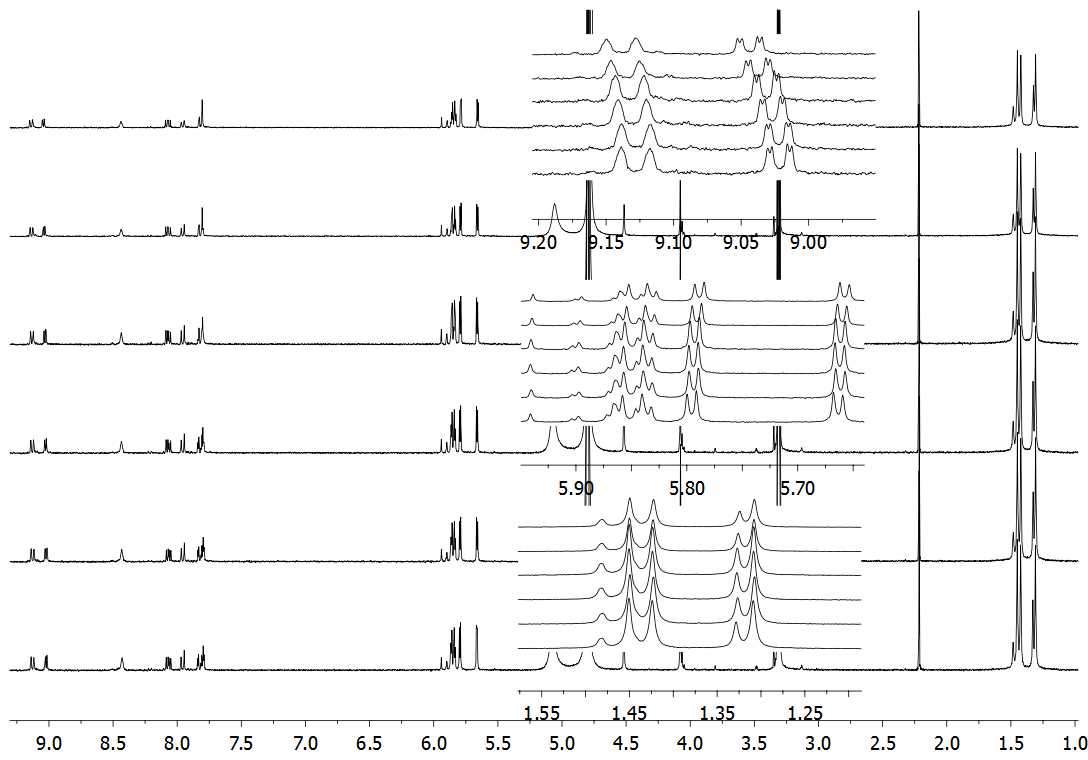
**UV-Vis titrations**

|  |  |
| --- | --- |
| G:\papers\15 calix-quinoline\SC\Graphs\Comp1_Cl_all_1.jpg | G:\papers\15 calix-quinoline\SC\Graphs\Comp1_Br_all_1.jpg |
| **1+NaCl** | **1+NaBr** |
| G:\papers\15 calix-quinoline\SC\Graphs\Comp1_I_all_1.jpg | G:\papers\15 calix-quinoline\SC\Graphs\Comp2_I_all_1.jpg |
| **1+NaI** | **2+NaI** |

**Figure S16**. Changes in UV-Vis spectra of receptors upon addition of anions.

|  |  |
| --- | --- |
| G:\papers\15 calix-quinoline\SC\Graphs\Comp1_Cl_fit_1.jpg | G:\papers\15 calix-quinoline\SC\Graphs\Comp1_Br_fit_1.jpg |
| **1+NaCl** | **1+NaBr** |
| G:\papers\15 calix-quinoline\SC\Graphs\Comp1_I_fit_1.jpg | G:\papers\15 calix-quinoline\SC\Graphs\Comp2_I_fit_1.jpg |
| **1+NaI** | **2+NaI** |

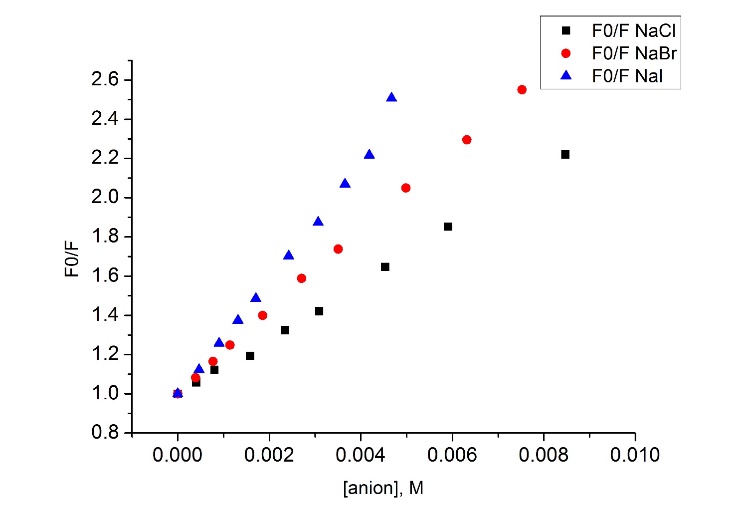
**Figure S17**. Fitting of binding curves obtained in UV-Vis titraions.



**Figure S18.** 1H NMR titration of **1** (5 x 10-4 M) with NaCl (from the bottom: 0, 10, 20, 60, 120, 200 equivalents) in a 1:1 CD3OD-D2O solution.

|  |  |
| --- | --- |
| G:\papers\15 calix-quinoline\SC\Graphs\fitting 1 with Cl_1.jpg | G:\papers\15 calix-quinoline\SC\Graphs\fitting 1 with Br_1.jpg |
| **1+NaCl** | **1+NaBr** |

**Figure S19**. Fitting of binding curves obtained in 1H NMR titration of compounds **1**.



**Figure S20.** Quenching of fluorescence of receptor **4** by anions.