Electronic Supplementary Material (ESI) for Dalton Transactions.

Macrocyclic squaramides as ion pair receptors and fluorescent sensors selective towards sulfates

Marta Zaleskaya, Damian Jagleniec and Jan Romański*

*Faculty of Chemistry, University of Warsaw, Pasteura 1, PL 02-093 Warsaw, Poland

*jarom@chem.uw.edu.pl

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General information

Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. If necessary purification of products was performed using column chromatography on silica gel (Merck Kieselgel 60, 230-400 mesh) with mixtures of chloroform/methanol. Thin-layer chromatography (TLC) was performed on silica gel plates (Merck Kieselgel 60 F254).

^{1}H and ^{13}C NMR spectra used in the characterization of products were recorded on Bruker 300 spectrometer using a residual protonated solvent as internal standard.

^{1}H NMR DOSY, ROESY and HSQC experiments were conducted at 298 K on Varian VNMRS 600 MHz instruments with a residual solvent signal as an internal standard.

Mass spectra were measured on Quattro LC Micromass or Shimadzu LCMS-IT-TOF unit.

UV-vis analyses were performed using Thermo Spectronic Unicam UV500 Spectrophotometer.

NMR titration experiments

The ^{1}H NMR titration was conducted at 298K in DMSO-d_6. In each case, a 500 µL of freshly prepared 2.0 mM solution of **R1** (1.6 mM of **R3**; 1.7 mM of **R4**) was added to a 5 mm NMR tube. In the case of ion pair titration receptor was firstly pretreated with one or three equivalent of KPF_6 or $NaClO_4$. Then small aliquots of solution of TBAX, containing receptor at constant concentration, were added and a spectrum was acquired after each addition. The resulting titration data were analyzed using BindFit (v0.5) package, available online at http://supramolecular.org. Each titration was carried out in duplicate. Reported values are calculated as weighted arithmetic mean, where the weights were the errors obtained for each value separately. The given uncertainty of the association constants is the largest of the variance (external or internal).

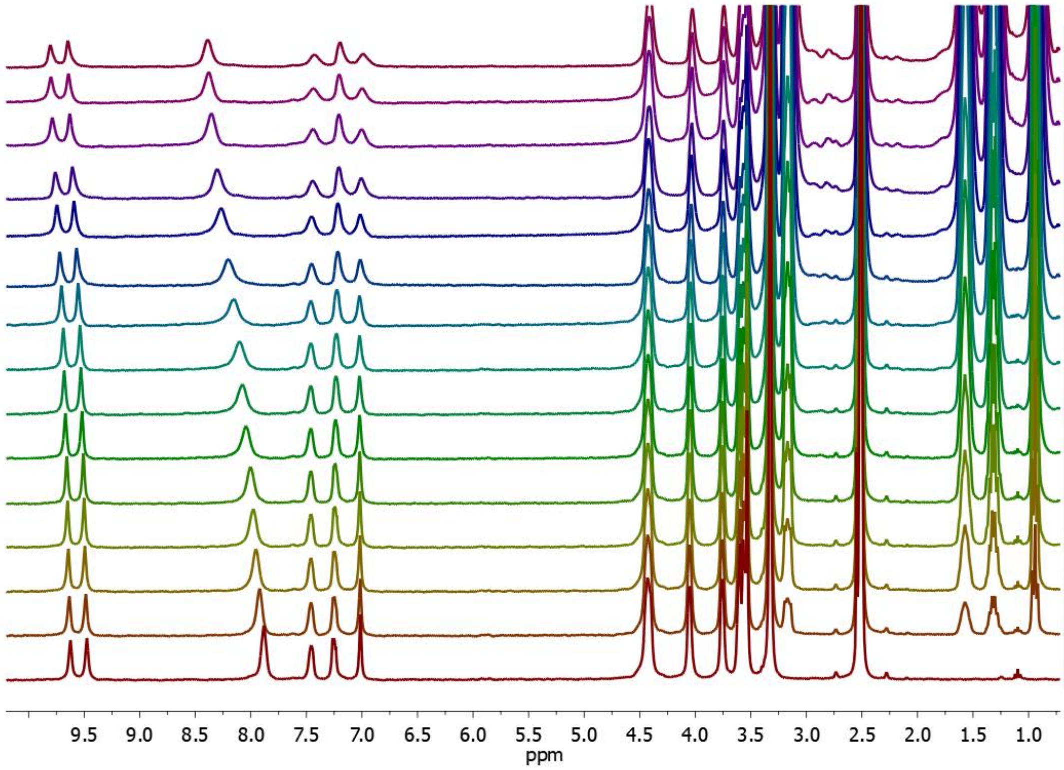

Fig. S1. Typical ^{1}H NMR spectra recorded upon titration of **R1** in DMSO-d_6 with TBACl.

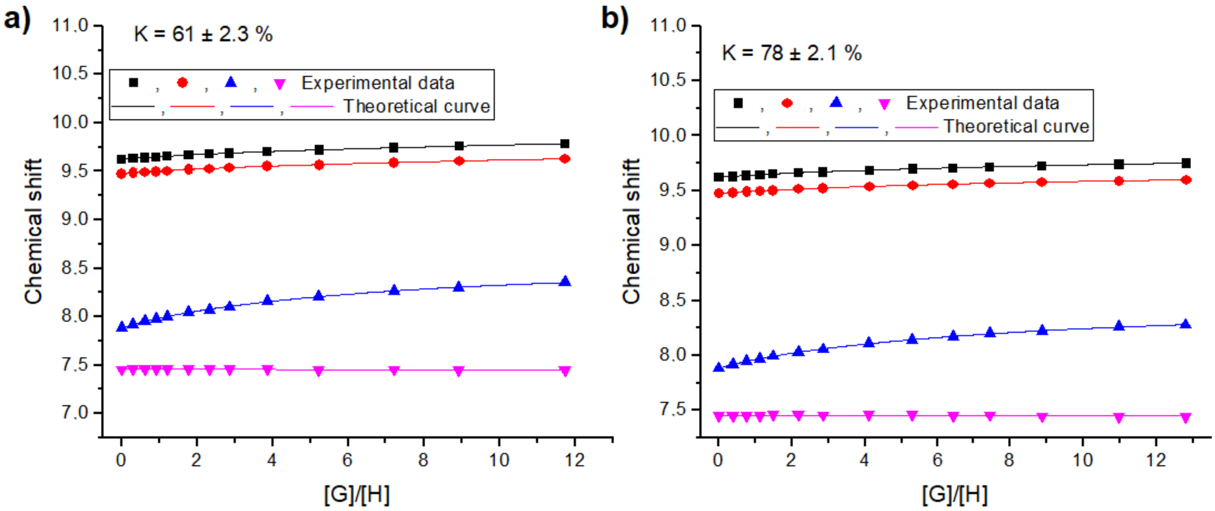

Fig. S2. ^{1}H NMR titration binding isotherms of **R1** in DMSO-d_6 upon addition of increasing amounts of TBACl (a) and of TBACl in the presence of 1 equiv. $NaClO_4$ (b).

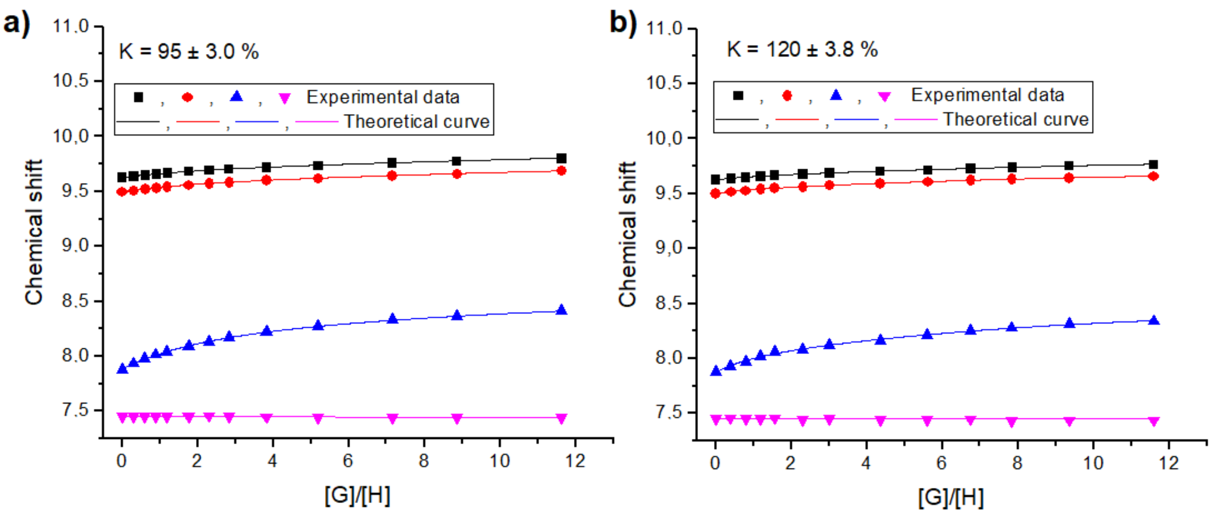

Fig. S3. ^{1}H NMR titration binding isotherms of **R1** in DMSO-d_6 upon addition of increasing amounts of TBACl in the presence of 1 equiv. KPF_6 (a) and of TBACl in the presence of 3 equiv. KPF_6 (b).

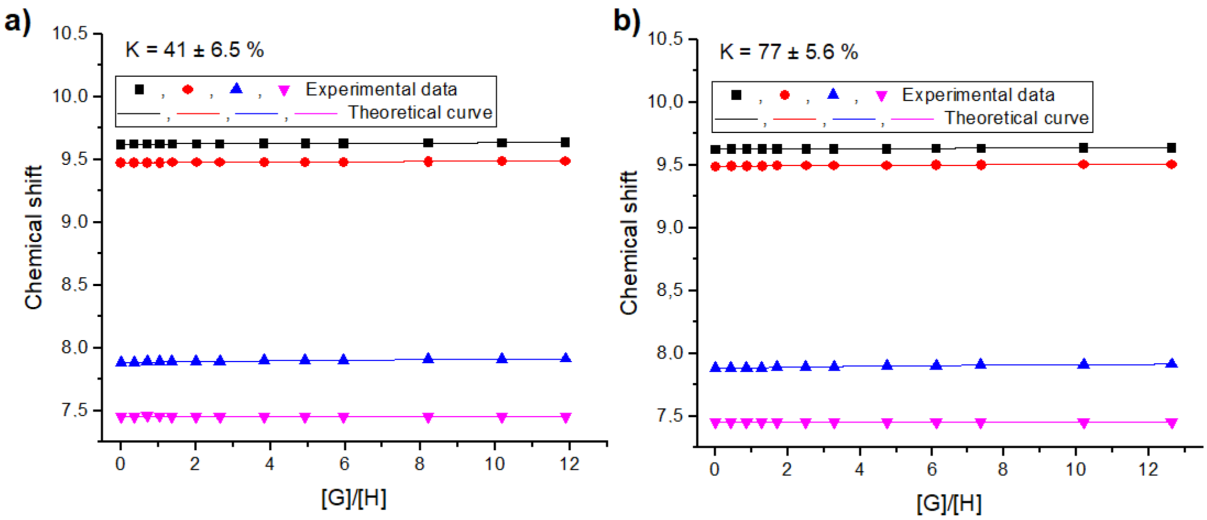

Fig. S4. ^{1}H NMR titration binding isotherms of **R1** in DMSO-d_6 upon addition of increasing amounts of TBABr (a) and of TBABr in the presence of 1 equiv. KPF_6 (b).

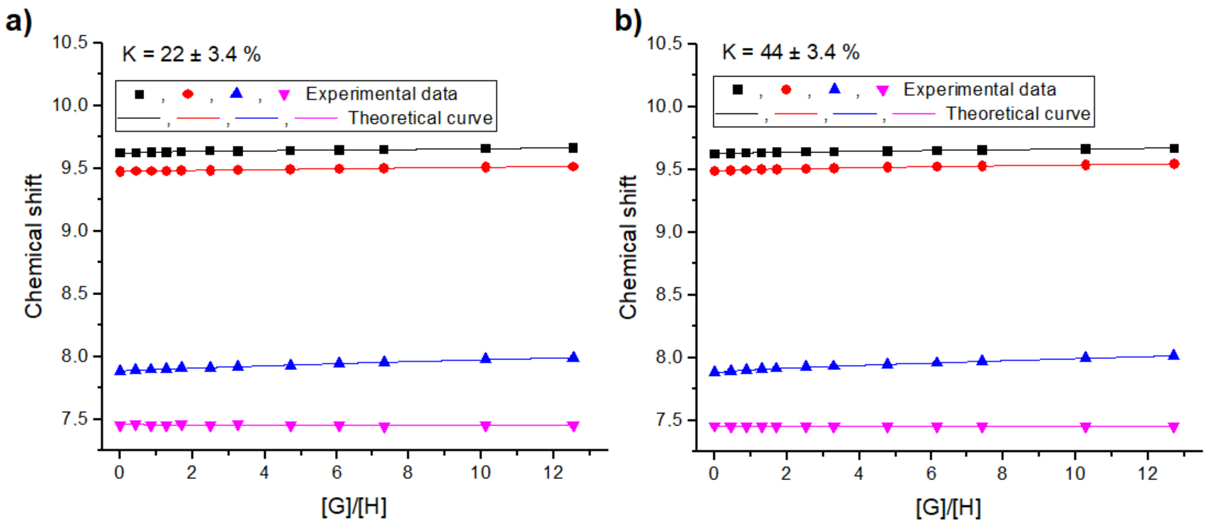

Fig. S5. ^{1}H NMR titration binding isotherms of **R1** in DMSO-d_6 upon addition of increasing amounts of $TBANO_2$ (a) and of $TBANO_2$ in the presence of 1 equiv. KPF_6 (b).

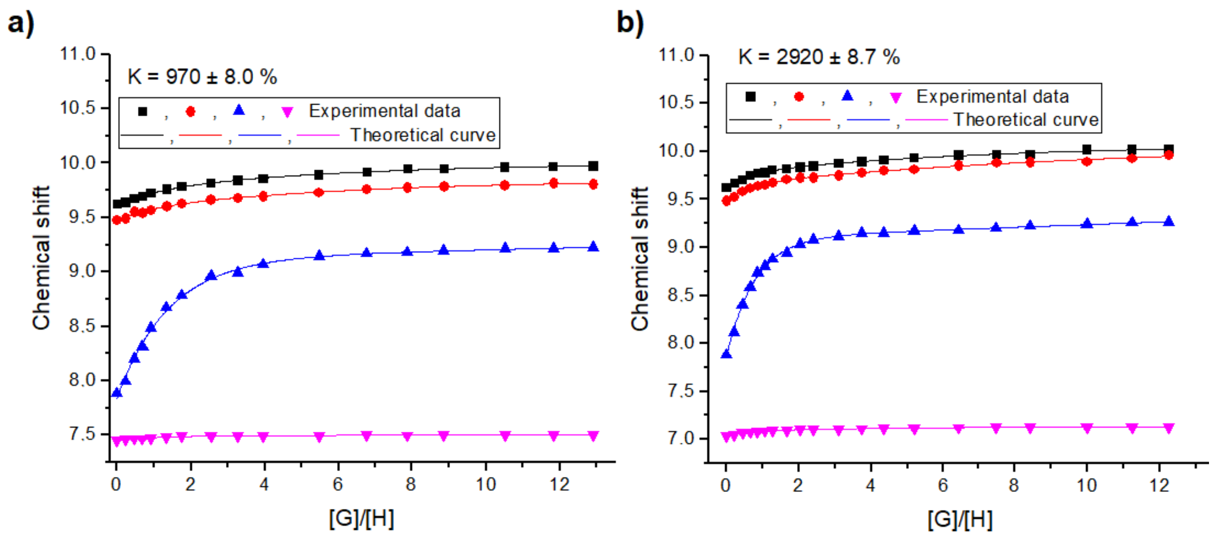

Fig. S6. ^{1}H NMR titration binding isotherms of **R1** in DMSO-d_6 upon addition of increasing amounts of TBAPhCOO (a) and of TBAPhCOO in the presence of 1 equiv. KPF_6 (b).

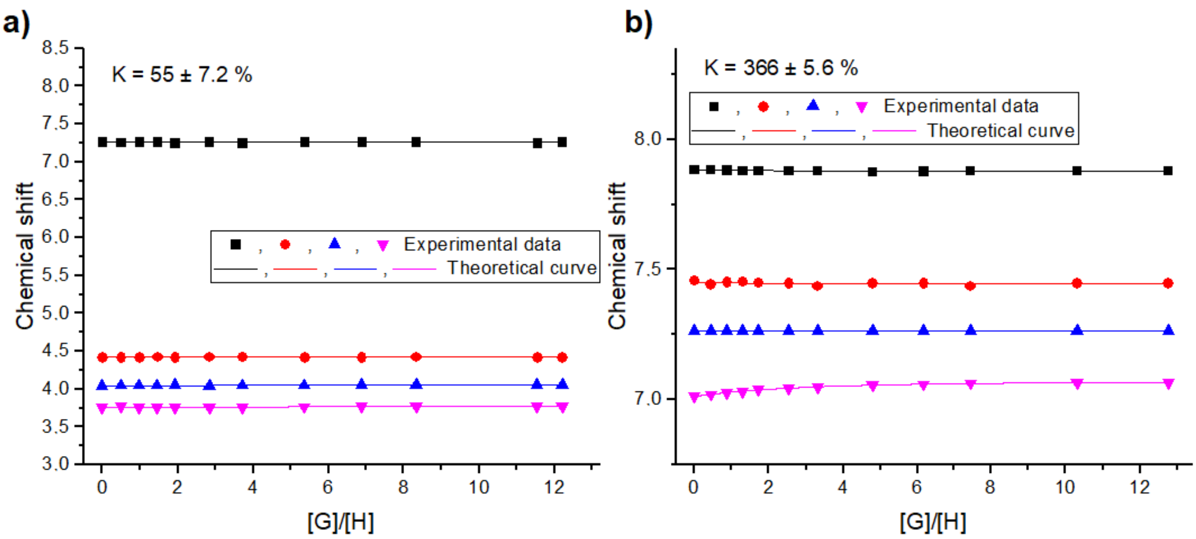

Fig. S7. ^{1}H NMR titration binding isotherms of **R1** in DMSO-d_6 upon addition of increasing amounts of $NaClO_4$ (a) and of KPF_6 (b).

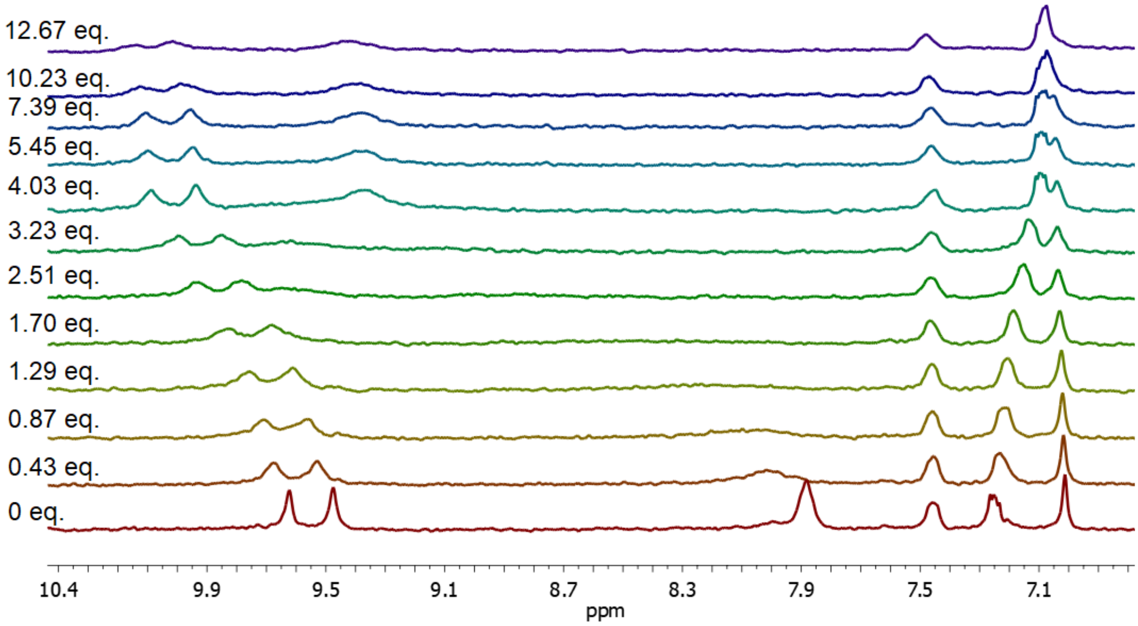

Fig. S8. Partial ^{1}HNMR spectra recorded upon titration of **R1** in DMSO-d$_6$ with TBA_2SO_4 (signals corresponding to amide and phenyl protons).

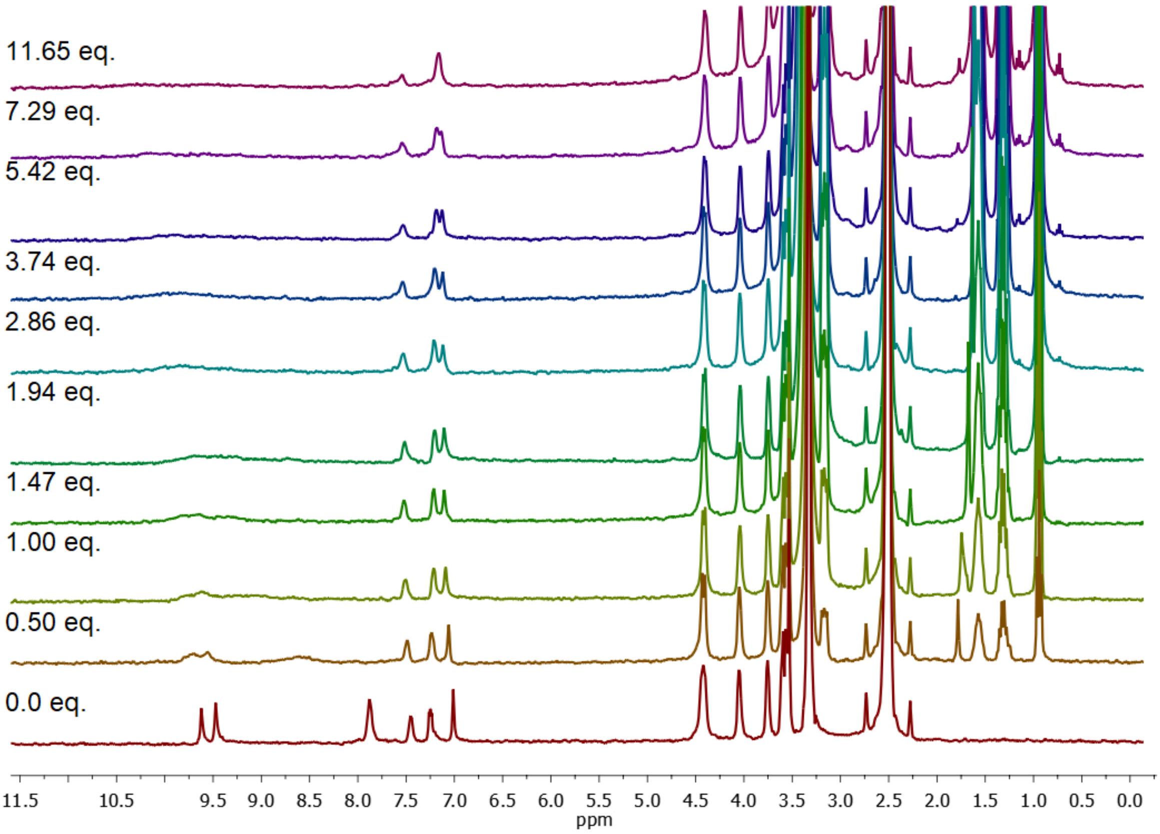

Fig. S9. ^{1}H NMR spectra recorded upon titration of **R1** in DMSO-d$_6$ with $TBACH_3COO$.

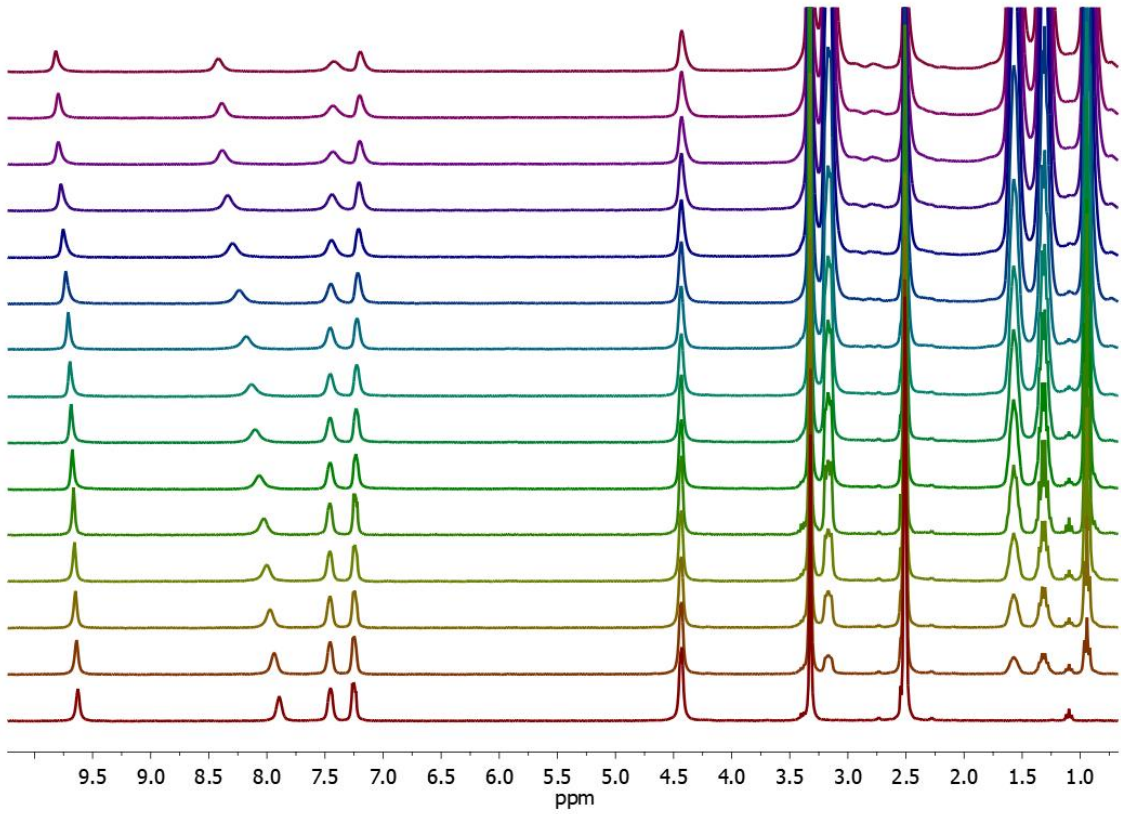

Fig. S10. Typical ^1H NMR spectra recorded upon titration of **R3** in DMSO-d_6 with TBACl.

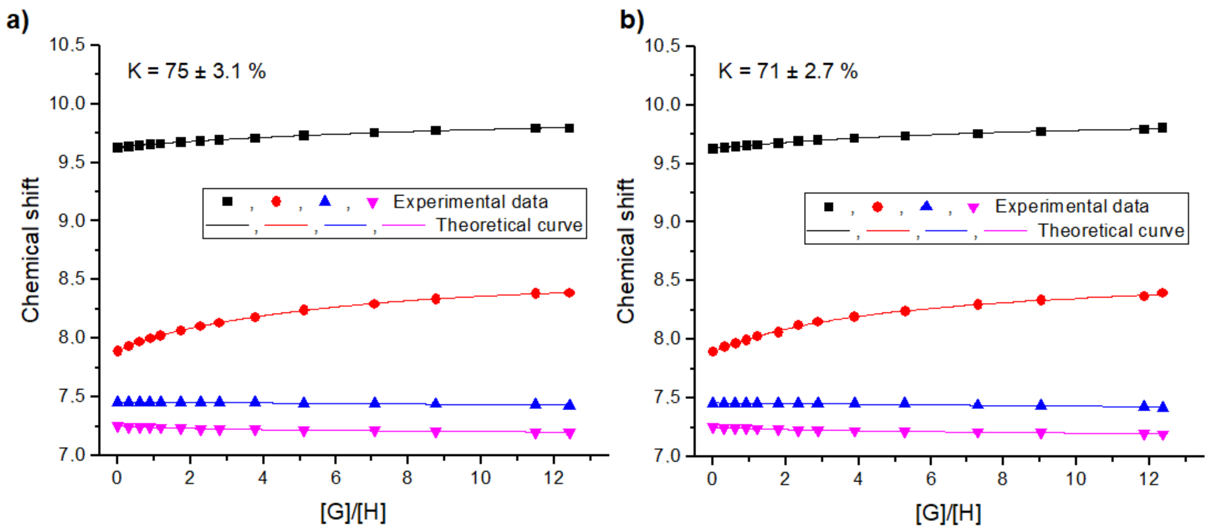

Fig. S11. ^1H NMR titration binding isotherms of **R3** in DMSO-d_6 upon addition of increasing amounts of TBACl (a) and of TBACl in the presence of 1 equiv. KPF_6 (b).

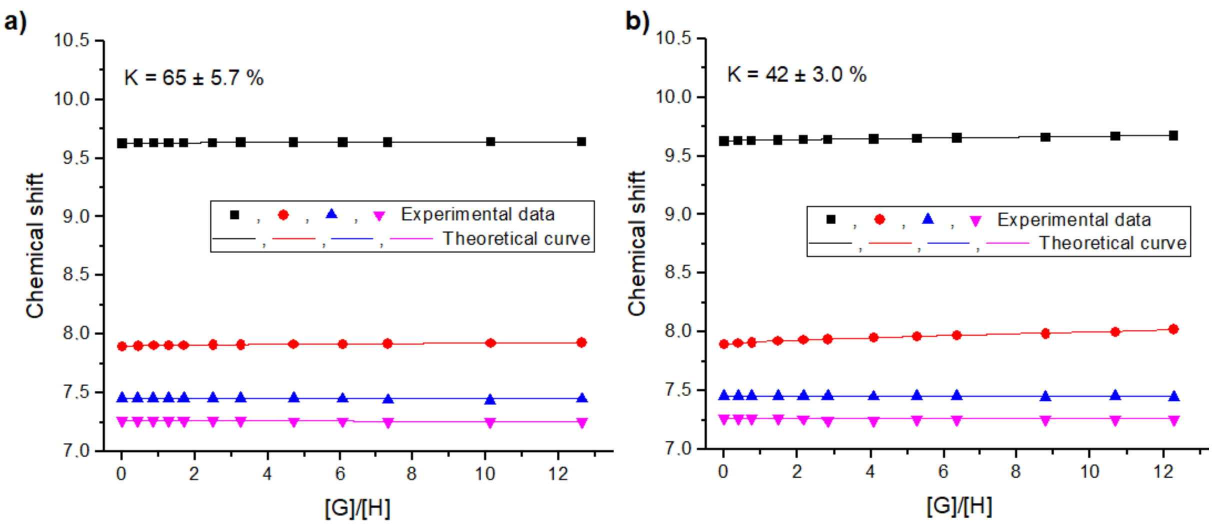

Fig. S12. ^{1}H NMR titration binding isotherms of **R3** in DMSO-d_6 upon addition of increasing amounts of TBABr (a) and of $TBANO_2$ (b).

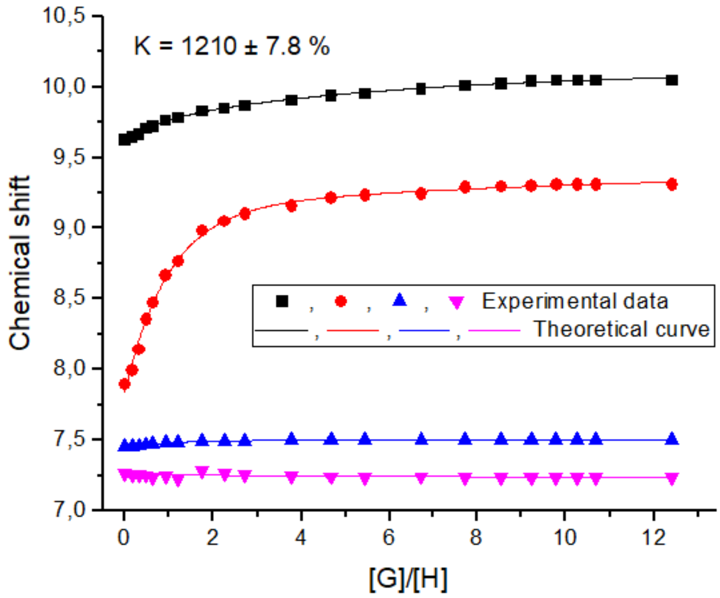

Fig. S13. ^{1}H NMR titration binding isotherms of **R3** in DMSO-d_6 upon addition of increasing amounts of TBAPhCOO.

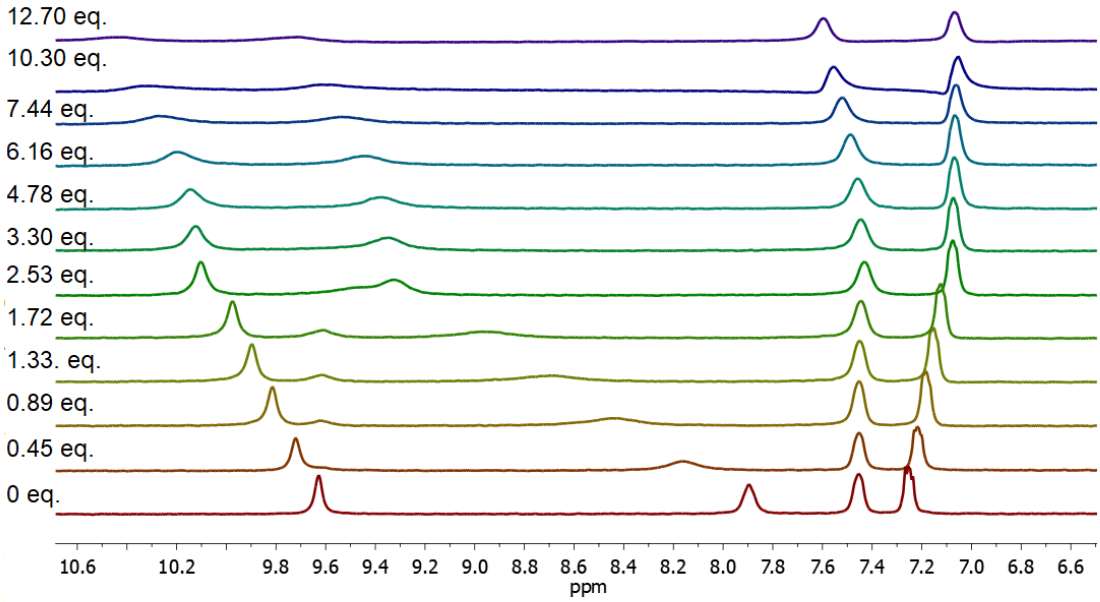

Fig. S14. Partial [1]HNMR spectra recorded upon titration of **R3** in DMSO-d_6 with TBA_2SO_4 (signals corresponding to amide and phenyl protons).

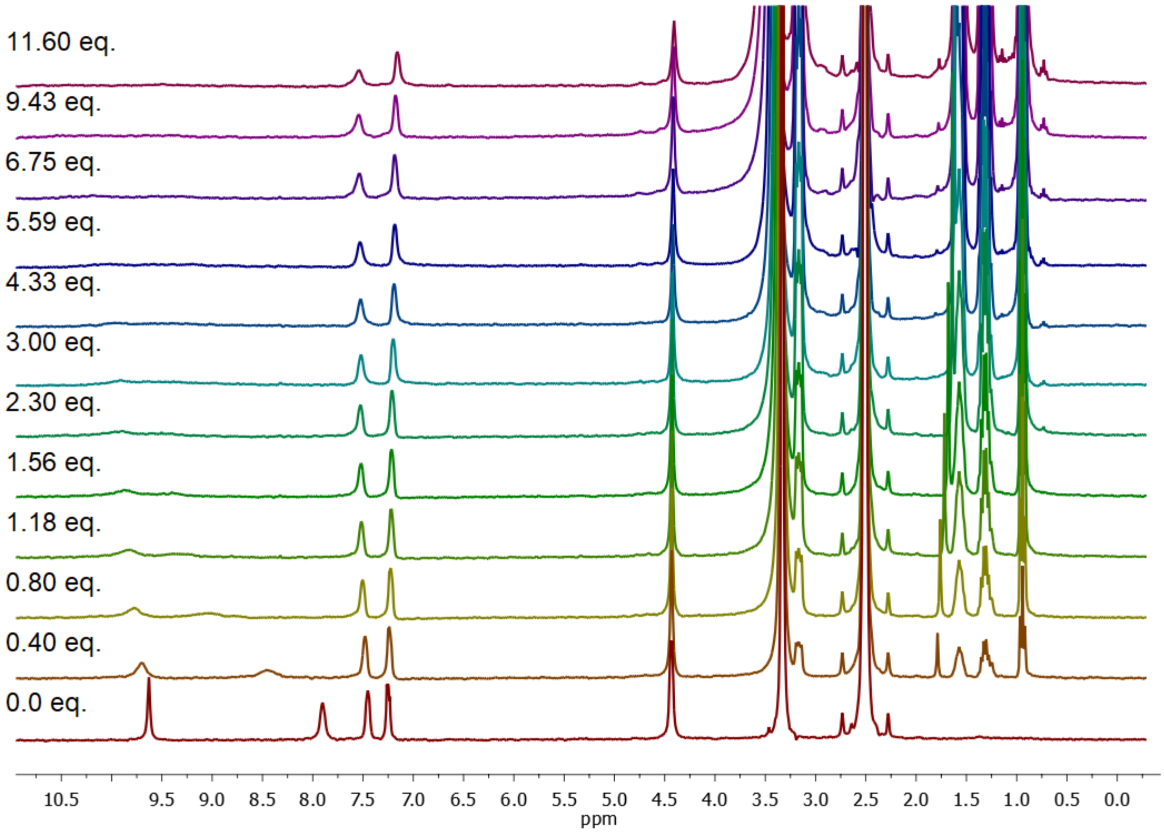

Fig. S15. ^{1}H NMR spectra recorded upon titration of **R3** in DMSO-d_6 with $TBACH_3COO$.

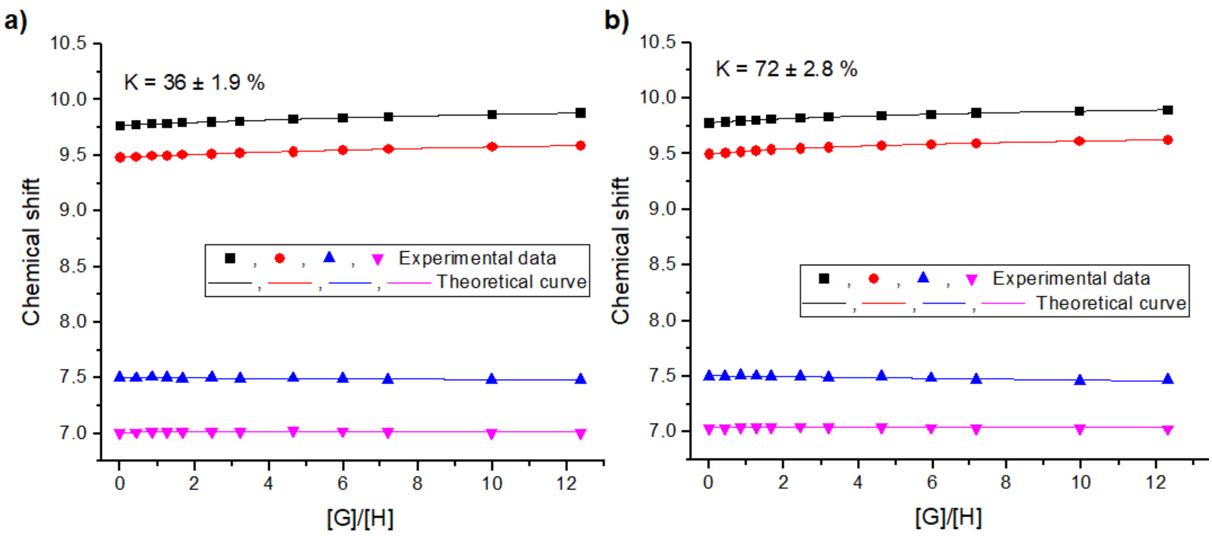

Fig. S16. ^{1}H NMR titration binding isotherms of **R4** in DMSO-d_6 upon addition of increasing amounts of TBACl (a) and of TBACl in the presence of 1 equiv. KPF_6 (b).

DOSY, ROESY and HSQC experiments

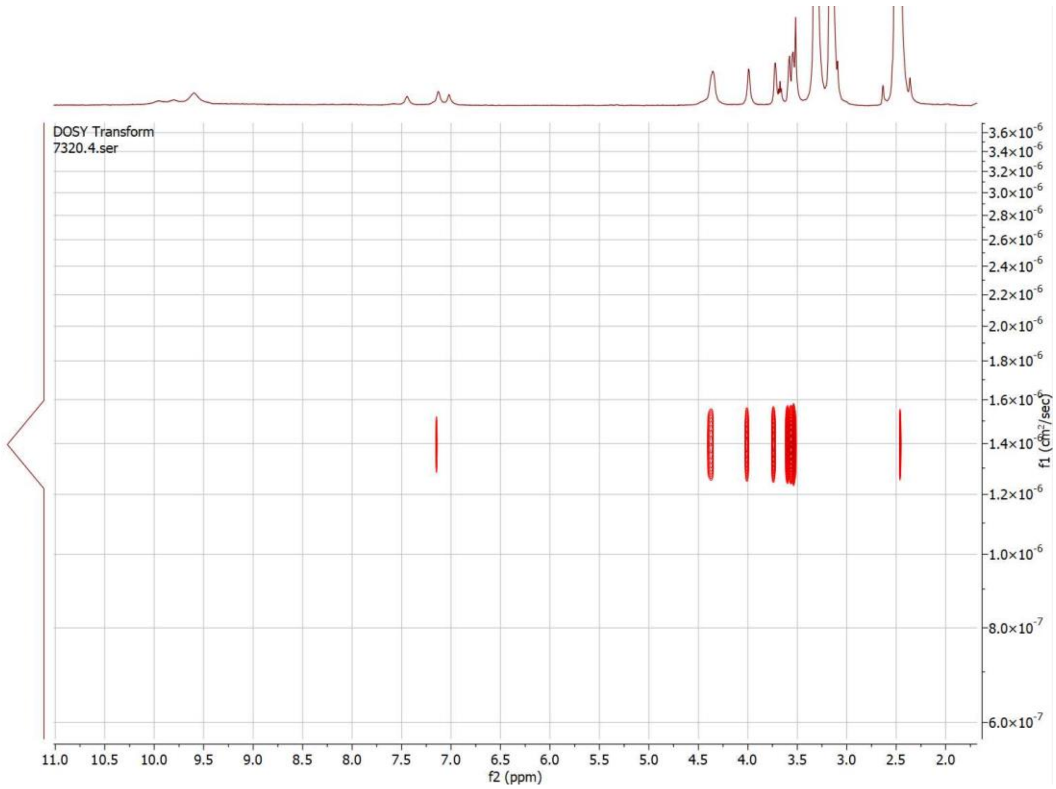

Fig. S17. DOSY experiment of **R1** (1.5 mM) + 3.2 eq. TBA_2SO_4 in DMSO-d_6.

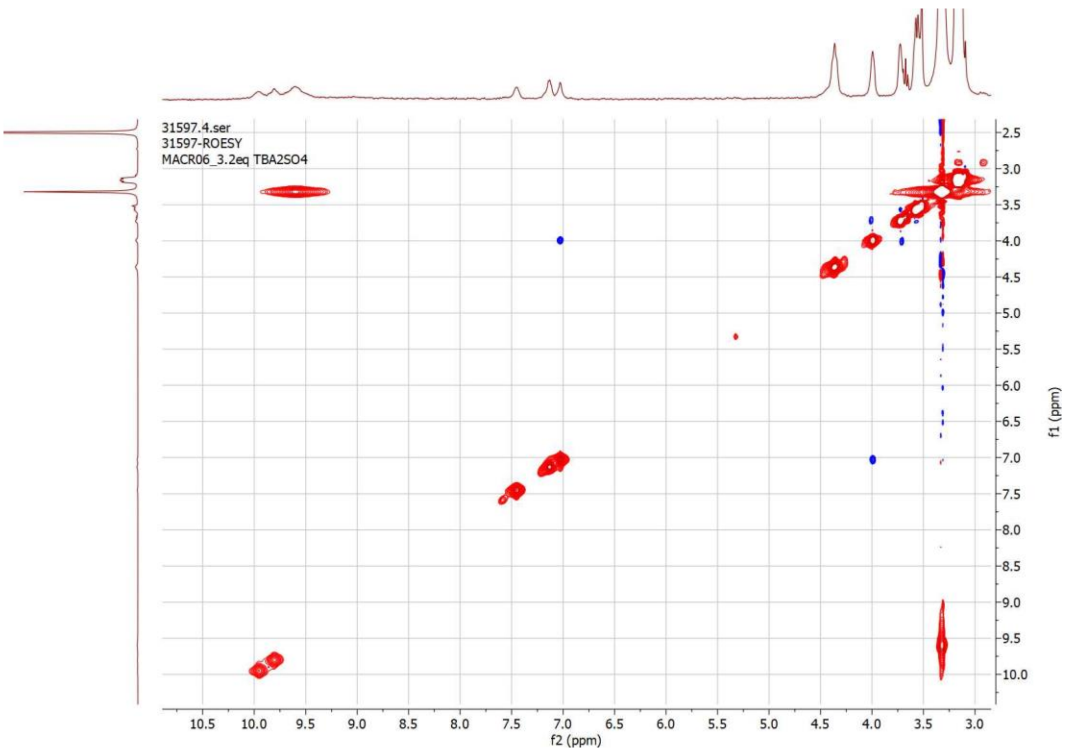

Fig. S18. ROESY NMR spectrum of **R1** (1.5 mM) + 3.2 eq. TBA_2SO_4 in DMSO-d_6.

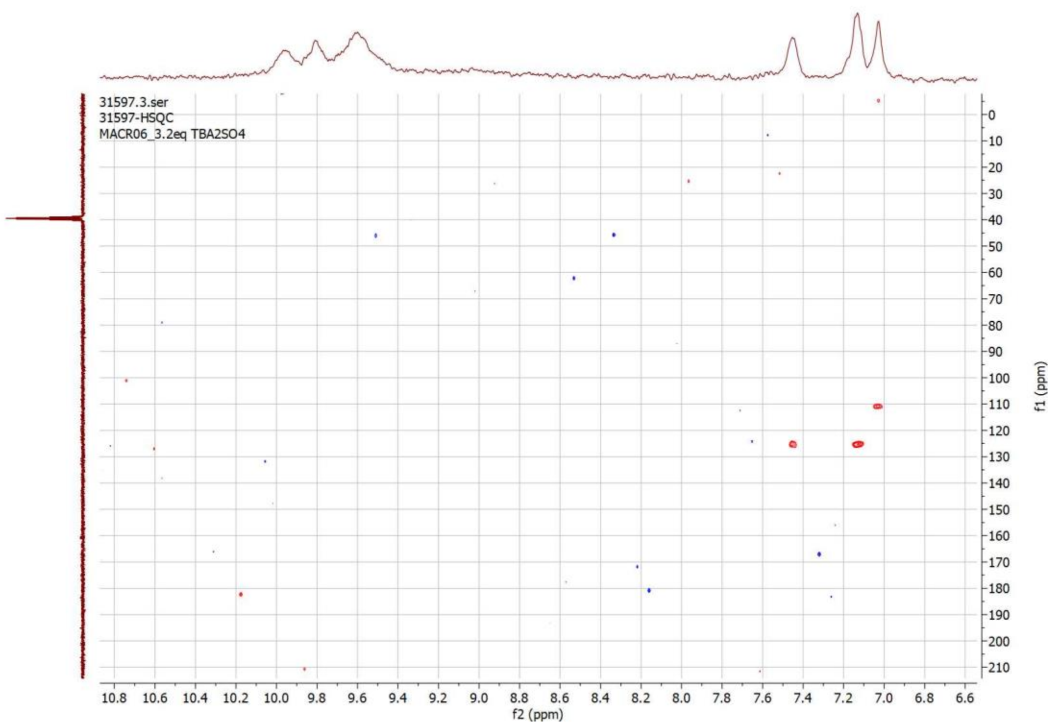

Fig. S19. HSQC NMR spectrum of **R1** (1.5 mM) + 3.2 eq. TBA_2SO_4 in DMSO-d_6.

UV-Vis and Emission spectra

UV-vis experiments were performed on a Thermo Spectronic Unicam UV 500 spectrophotometer in DMSO solution at 298K. To 10 mm cuvette was added 2.5 mL of freshly prepared solution of **R4** (c=1.0 $\times 10^{-5}$ M) and small aliquots of TBAX solution containing **R4** at the same concentration as in cuvette, were added and a spectrum was acquired after each addition.

Fluorescence emission spectra were measured on a Hitachi F-7100 Fluorescence Spectrophotometer. Solution of **R4** (c=1.0 × 10^{-5} M) in DMSO were titration with small aliquots of TBAX solution containing **R4** at the same concentration as in cuvette. Successive scans were performed measuring fluorescence (λ_{ex}= 340 nm) emission between 355 and 650 nm.

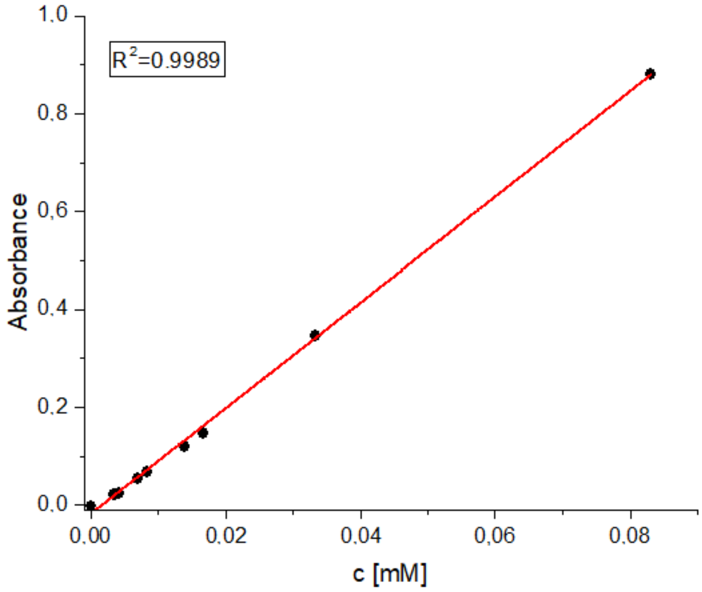

Fig. S20. Dilution curve of **R4** in DMSO.

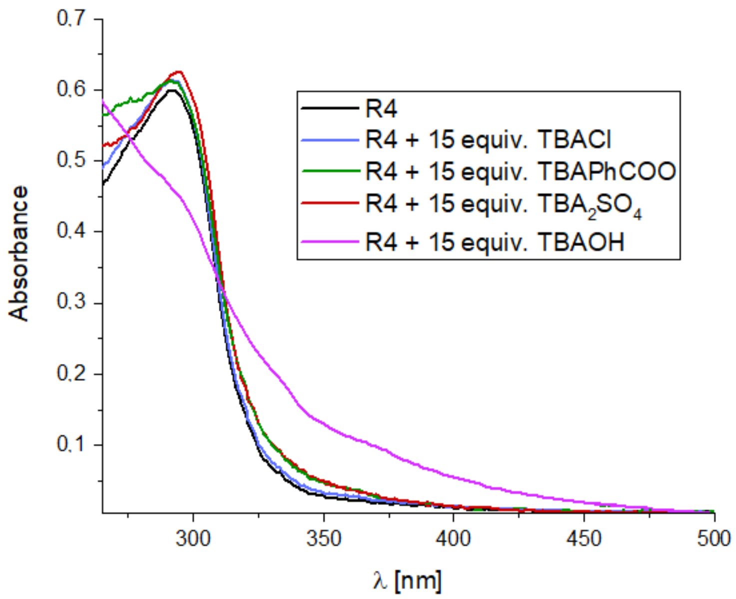

Fig. S21. UV-Vis absorption spectra of **R4** (1.0 × 10^{-5} M) and upon addition of TBA salts.

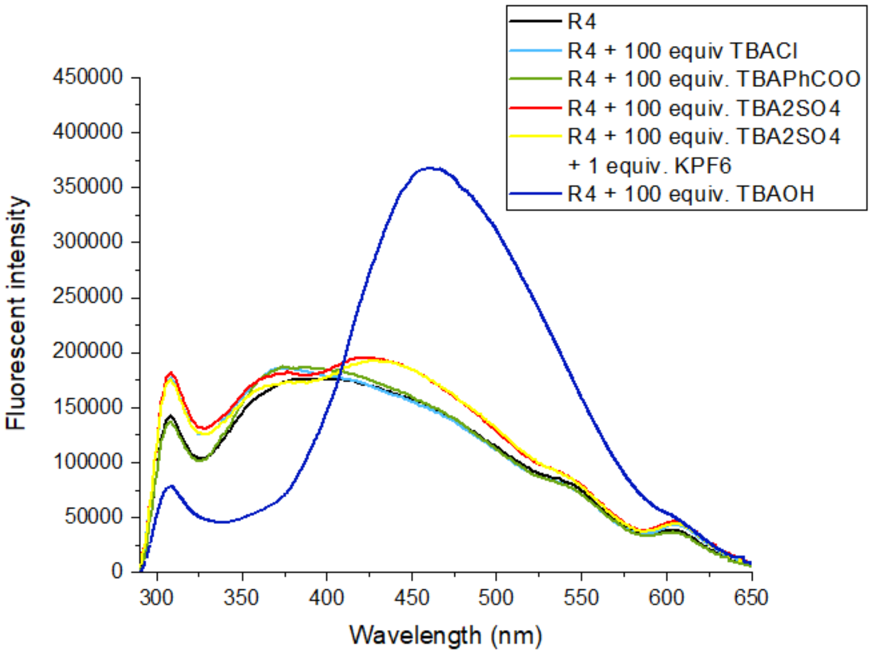

Fig. S22. Emission spectra of **R4** (1.0×10^{-5} M) and upon addition of TBA salts (excitation at 300 nm).

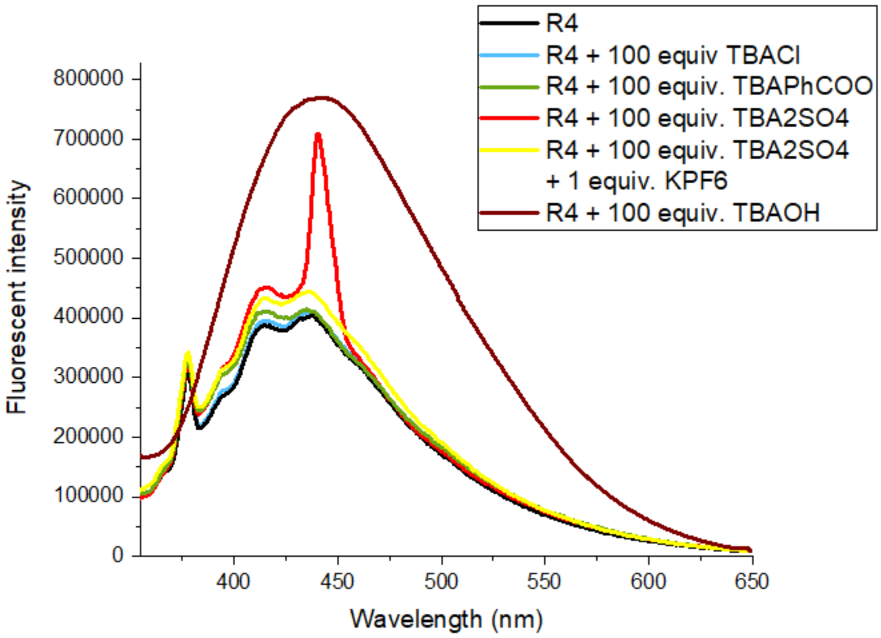

Fig. S23. Emission spectra of **R4** (1.0×10^{-5} M) and upon addition of TBA salts (excitation at 340 nm).

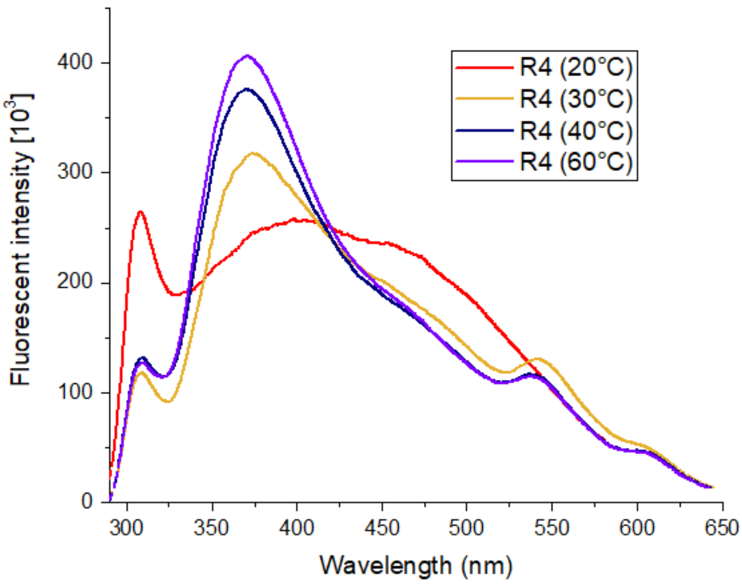

Fig. S24. Emission spectra of **R4** (1.0×10^{-5} M) λ excitation = 300 nm.

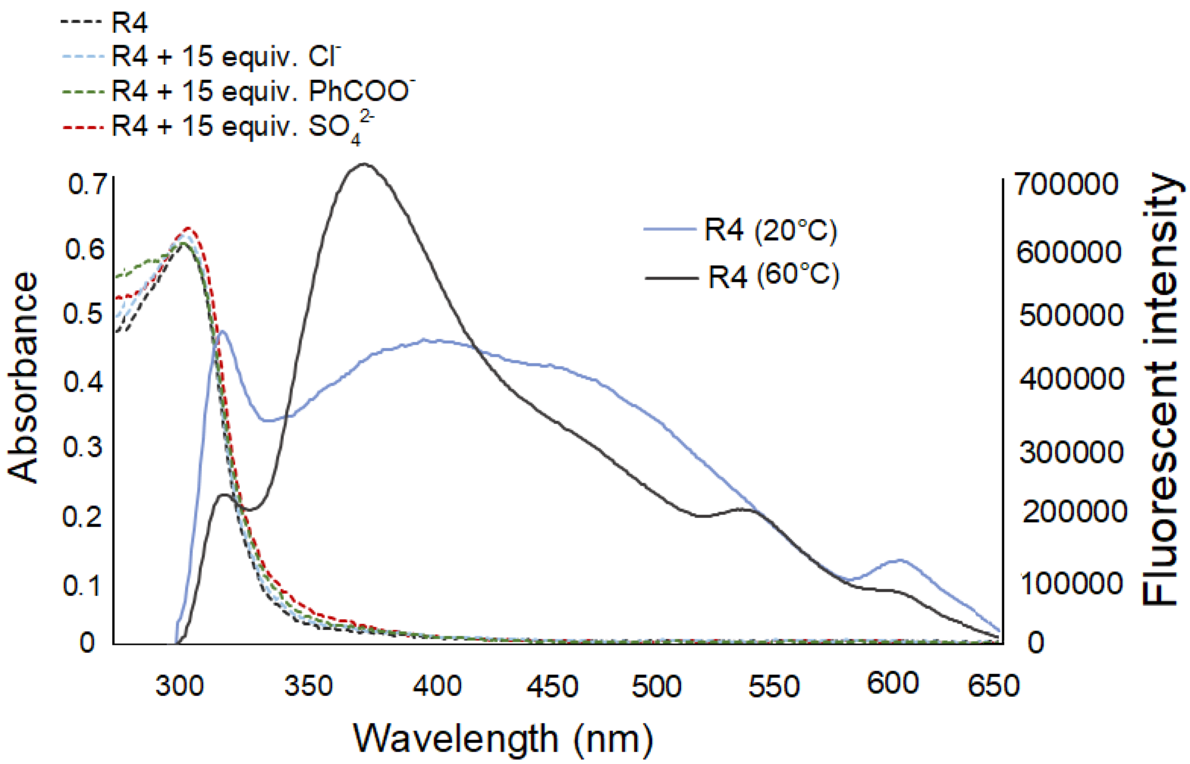

Fig. S25. UV-Vis absorption and emission (excitation at 300 nm) spectra of **R4** (1.0×10^{-5} M) and upon addition of TBA salts in DMSO.

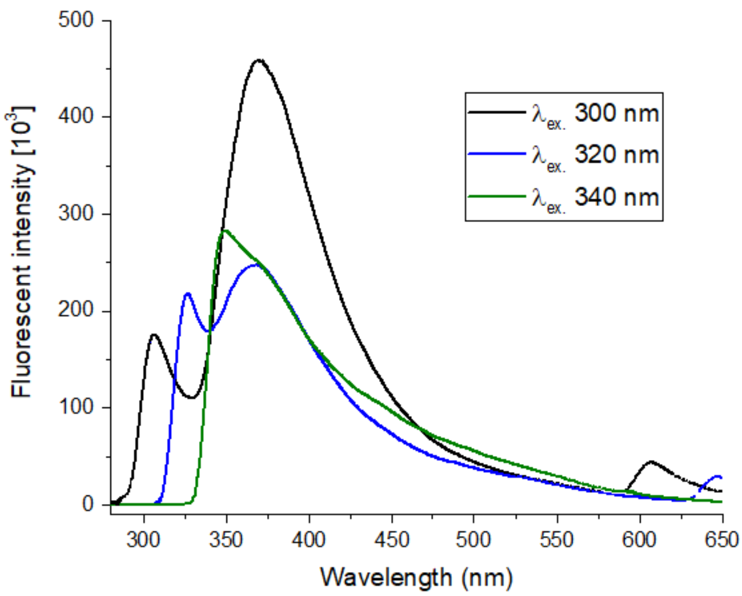

Fig. S26. Emission spectra of **A3** (1.0×10^{-5} M) in DMSO.

Molecular modelling

Molecular modelling of receptor **R3** was performed using Spartan 10 for Windows (Wavefunction, Inc. Irvine, CA). The structure of receptor **R3** was energy minimized using molecular mechanics and Cl^-, SO_4^{2-} and $PhCOO^-$ molecule was placed into the center of macrocycle and the optimized by density functional theory (DFT) calculations was performed at B3LYP/6-31G* level of theory.

Table S1: Atomic coordinates for complex **R3** and TBACl.

Atom	X	Y	Z	26H	1,80796	-4,08323	1,990317
1O	5,67984	-2,71472	1,136771	27C	-2,41642	3,493534	1,648313
2O	6,246003	0,547883	1,033326	28H	-2,08956	3,986783	2,574314
3N	2,519691	-2,12896	1,755624	29H	-3,4329	3,836314	1,436272
4H	1,626888	-1,62565	1,801118	30C	-1,51759	4,028645	0,523257
5N	3,056433	1,082999	1,691543	31O	-1,35265	5,228986	0,383273
6H	2,053331	0,905071	1,785223	32C	3,175064	2,928259	-0,01579
7C	3,614795	-1,37721	1,562325	33C	2,015541	-3,62581	-0,14286

8C	3,85002	0,012406	1,53926	34O	4,056371	3,23689	-0,81068
9C	5,294664	-0,18425	1,255996	35O	2,819466	-3,61617	-1,07289
10C	5,032412	-1,68791	1,29815	36N	1,841762	2,98381	-0,29282
11O	-6,14548	-0,5807	0,817483	37H	1,197306	2,719754	0,440589
12O	-5,48069	2,699489	0,843396	38N	0,660624	-3,66419	-0,2967
13N	-3,11808	-1,16205	1,848738	39H	0,091987	-3,56248	0,53756
14H	-2,1495	-1,04835	2,140213	40C	-3,65183	-2,49882	1,632225
15N	-2,44566	2,052222	1,813517	41H	-3,51315	-3,1162	2,528985
16H	-1,59206	1,563987	2,070267	42H	-4,72821	-2,41802	1,456029
17C	-3,81281	-0,05566	1,525127	43C	-3,08298	-3,29213	0,441042
18C	-3,53114	1,310156	1,517362	44O	-3,6095	-4,33659	0,094205
19C	-4,90177	1,658065	1,071191	45N	-0,92771	3,077442	-0,28233
20C	-5,20921	0,153726	1,068002	46H	-1,15586	2,099555	-0,1128
21C	3,516799	2,439752	1,408424	47N	-1,94969	-2,77483	-0,15758
22H	4,603566	2,466025	1,490075	48H	-1,61778	-1,86176	0,149427
23H	3,086988	3,125368	2,149155	49H	-0,76087	4,515044	-4,65585
24C	2,477163	-3,52426	1,323388	50C	-0,21293	4,202594	-3,7706
25H	3,482675	-3,94453	1,389021	51C	1,199067	3,401879	-1,47707
52C	1,181669	4,17763	-3,77025				
53C	-0,90182	3,830982	-2,61598				
54C	-0,21237	3,430761	-1,47309				
55C	1,892381	3,783559	-2,63646				
56H	1,731942	4,481699	-4,66006				
57H	-1,98886	3,855604	-2,58182				

58H	2,974179	3,779471	-2,62542				
59C	-0,09502	-3,66784	-1,48843				
60C	-1,74886	-3,77226	-3,75128				
61C	0,42365	-4,09252	-2,71954				
62C	-1,44486	-3,26905	-1,40054				
63C	-2,26329	-3,33996	-2,53006				
64C	-0,40441	-4,13641	-3,84227				
65H	1,461284	-4,39272	-2,77904				
66H	-3,30453	-3,04974	-2,43939				
67H	0,006448	-4,47871	-4,78863				
68H	-2,3925	-3,81631	-4,62418				
69Cl	-0,00958	-0,11118	1,546503				

Table S2: Atomic coordinates for complex **R3** and TBAPhCOO.

Atom	X	Y	Z	31O	-6,19197	-0,26908	-0,37784
1O	4,830755	2,931988	-2,40522	32C	-1,96229	2,484849	-1,71448
2O	1,813263	3,919161	-3,48091	33C	4,947466	-0,51323	-0,34943
3N	3,370045	1,416938	0,120149	34O	-3,03133	3,058478	-1,60076
4H	2,659195	1,204268	0,8288	35O	6,053465	-0,84538	-0,7514
5N	0,442102	2,258938	-1,00853	36N	-1,82113	1,206937	-2,22309
6H	0,391254	1,763861	-0,11032	37H	-0,86425	0,913589	-2,38902
7C	2,96099	2,102155	-0,96487	38N	3,837789	-1,31779	-0,34073
8C	1,704775	2,510653	-1,42748	39H	3,001498	-0,95081	0,100263
9C	2,27675	3,241744	-2,57917	40C	0,741501	-2,73832	2,797403

10C	3,667052	2,793972	-2,07917	41H	1,109238	-2,28119	3,722382
11O	-1,74379	-4,93033	2,42917	42H	0,374492	-3,74197	3,039686
12O	-4,72368	-3,51451	1,849549	43C	1,954995	-2,92291	1,878846
13N	-0,35329	-1,96706	2,230002	44O	3,058761	-3,16982	2,333654
14H	-0,28855	-0,94115	2,27687	45N	-3,96327	-0,01185	-0,902
15N	-3,24187	-0,57934	1,725565	46H	-3,05518	0,114657	-0,46996
16H	-2,57873	0,145037	2,014851	47N	1,679183	-2,83902	0,527879
17C	-1,60713	-2,45523	2,154675	48H	0,699741	-2,72918	0,29038
18C	-2,85045	-1,85863	1,909941	49H	-5,7465	-1,00023	-5,02203
19C	-3,56308	-3,16188	1,957065	50C	-4,93224	-0,56084	-4,45159
20C	-2,19241	-3,8149	2,221741	51C	-2,86694	0,580069	-2,97059
21C	-0,64956	3,171848	-1,32629	52C	-3,81172	-0,05215	-5,11048
22H	-0,34088	3,791376	-2,1761	53C	-5,02224	-0,52699	-3,06241
23H	-0,87524	3,843322	-0,48906	54C	-3,97871	0,025681	-2,30407
24C	4,725226	0,901625	0,225719	55C	-2,78841	0,527113	-4,36295
25H	5,405608	1,556011	-0,32329	56H	-3,74167	-0,08689	-6,19393
26H	5,030957	0,894566	1,278529	57H	-5,88644	-0,92362	-2,54728
27C	-4,63207	-0,25204	1,446042	58H	-1,92189	0,964453	-4,85219
28H	-4,87254	0,716718	1,89746	59C	3,704331	-2,6195	-0,8477
29H	-5,29207	-1,00397	1,884698	60C	3,21522	-5,15884	-1,9514
30C	-5,01834	-0,18524	-0,04599	61C	4,604499	-3,17712	-1,76834
62C	2,574523	-3,36586	-0,45431				
63C	2,33548	-4,62107	-1,01384				
64C	4,353919	-4,43587	-2,30992				

65H	5,484999	-2,6135	-2,04411				
66H	1,459404	-5,17618	-0,68899				
67H	5,058183	-4,85	-3,02695				
68H	3,021776	-6,1379	-2,38037				
69H	0,549749	6,470878	4,328306				
70C	0,455857	5,462476	3,932249				
71C	0,211803	2,864507	2,905168				
72C	-0,59136	4,638478	4,353258				
73C	1,382208	4,987899	3,001079				
74C	1,261445	3,694941	2,491996				
75C	-0,71191	3,34795	3,841309				
76H	-1,31397	5,003868	5,079021				
77H	2,199075	5,62504	2,67113				
78H	1,982582	3,318453	1,774487				
79H	-1,51576	2,689905	4,153981				
80C	0,059672	1,459852	2,357614				
81O	-0,93109	0,785991	2,752724				
82O	0,923834	1,032895	1,524794				

Table S3: Atomic coordinates for complex **R3** and TBA_2SO_4.

Atom	X	Y	Z	31O	-3,25698	4,384861	-0,60838
1O	5,96567	-1,65861	0,046258	32C	2,646957	3,545584	0,018678
2O	5,96255	1,68571	0,050655	33C	2,549519	-3,62118	0,149596
3N	3,098534	-1,6151	1,615586	34O	3,256424	4,366762	-0,63876

4H	2,285752	-1,25449	2,15821	35O	2,989639	-4,64407	-0,34152
5N	3,090632	1,632789	1,60996	36N	1,430556	2,985422	-0,3138
6H	2,291287	1,280687	2,161869	37H	0,987113	2,400344	0,40653
7C	3,926633	-0,70289	1,136766	38N	1,447997	-2,93187	-0,28854
8C	3,925338	0,722016	1,135055	39H	1,116202	-2,1272	0,250642
9C	5,246142	0,787612	0,424634	40C	-3,25878	-3,05509	1,396877
10C	5,248528	-0,7627	0,424142	41H	-2,89875	-3,59217	2,279949
11O	-5,95442	-1,68499	0,043928	42H	-4,31543	-3,28281	1,250437
12O	-5,96116	1,660193	0,042234	43C	-2,53364	-3,63156	0,148479
13N	-3,09097	-1,63028	1,618139	44O	-2,96775	-4,65707	-0,34259
14H	-2,28099	-1,26725	2,162561	45N	-1,44835	2,976275	-0,30925
15N	-3,09782	1,618944	1,614892	46H	-1,00672	2,379845	0,4026
16H	-2,29828	1,270746	2,16896	47N	-1,43836	-2,93386	-0,29184
17C	-3,92165	-0,72085	1,138109	48H	-1,10705	-2,13141	0,251382
18C	-3,92595	0,704024	1,136276	49H	-1,27043	4,065748	-4,74684
19C	-5,24412	0,76442	0,42091	50C	-0,71989	3,84597	-3,83724
20C	-5,24116	-0,786	0,422152	51C	0,703561	3,274343	-1,48133
21C	3,238133	3,060631	1,372635	52C	0,683922	3,848404	-3,84049
22H	4,29527	3,327095	1,341404	53C	-1,41165	3,557057	-2,67293
23H	2,752388	3,593341	2,195179	54C	-0,72584	3,270658	-1,47854
24C	3,272938	-3,03954	1,396677	55C	1,382681	3,56298	-2,67951
25H	4,330478	-3,26199	1,249382	56H	1,229423	4,070534	-4,75255
26H	2,916994	-3,57697	2,281018	57H	-2,49276	3,561693	-2,66276
27C	-3,25441	3,046305	1,380282	58H	2,463608	3,573237	-2,67459

28H	-2,7797	3,580857	2,207844	59C	0,714479	-3,29778	-1,44427
29H	-4,31343	3,304194	1,342343	60C	-0,69137	-4,03872	-3,75599
30C	-2,65749	3,544949	0,034073	61C	1,401537	-3,66428	-2,61155
62C	-0,70144	-3,29829	-1,44574				
63C	-1,38591	-3,66463	-2,61475				
64C	0,70948	-4,0388	-3,75422				
65H	2,484147	-3,66577	-2,60019				
66H	-2,46859	-3,66602	-2,60573				
67H	1,259373	-4,3264	-4,64505				
68H	-1,23922	-4,32494	-4,64866				
69S	-0,0004	0,161963	2,070529				
70O	0,000522	-0,72914	0,851481				
71O	-0,00435	1,626805	1,656487				
72O	-1,25085	-0,08549	2,883953				
73O	1,253309	-0,07926	2,881118				

NMR spectra of new compounds

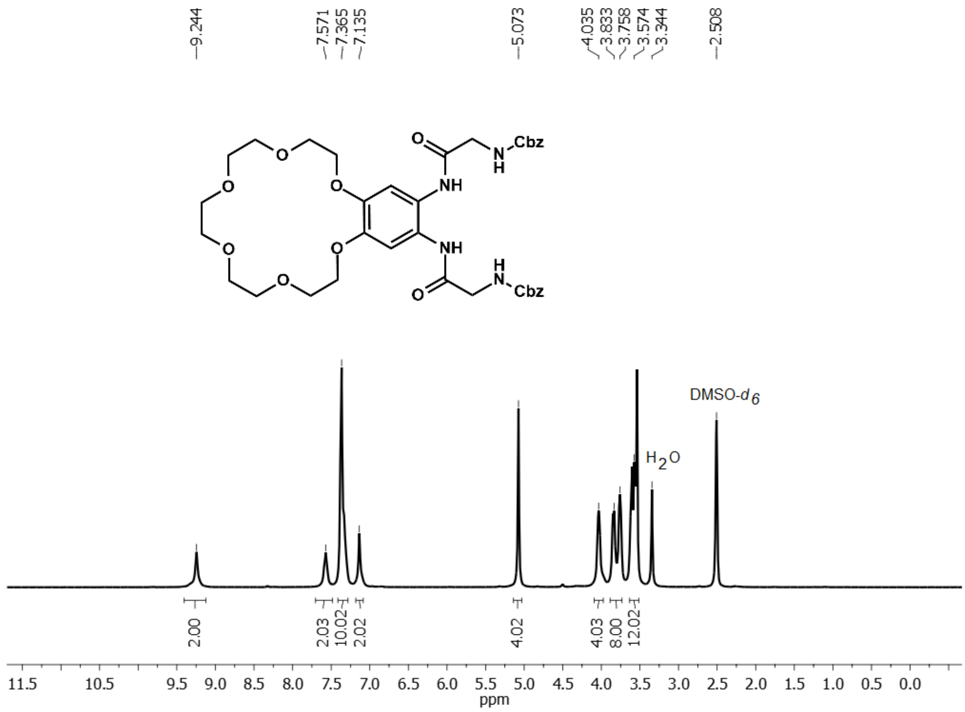

Fig. S27. ^{1}H NMR spectrum of **D1** in DMSO-d$_6$.

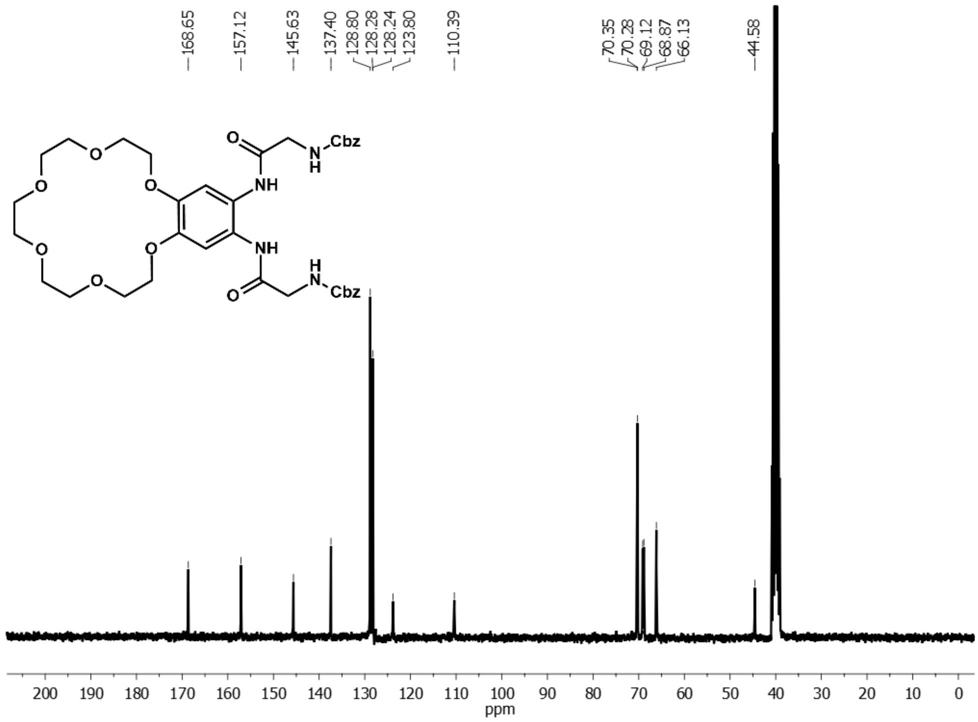

Fig. S28. ^{13}C NMR spectrum of **D1** in DMSO-d$_6$.

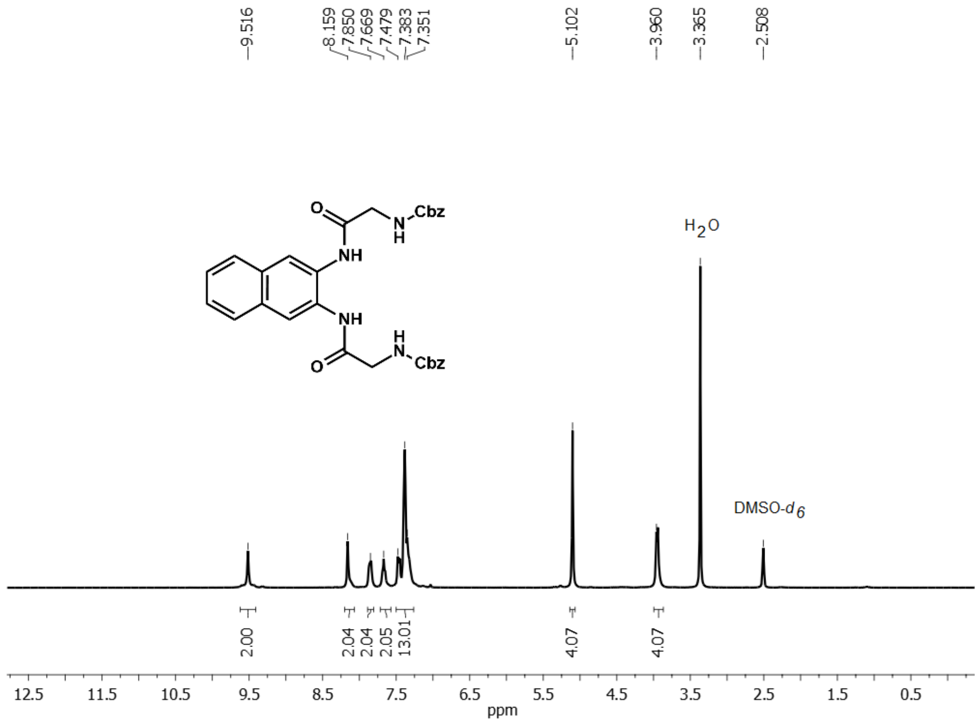

Fig. S29. ^{1}H NMR spectrum of **D3** in DMSO-d_6.

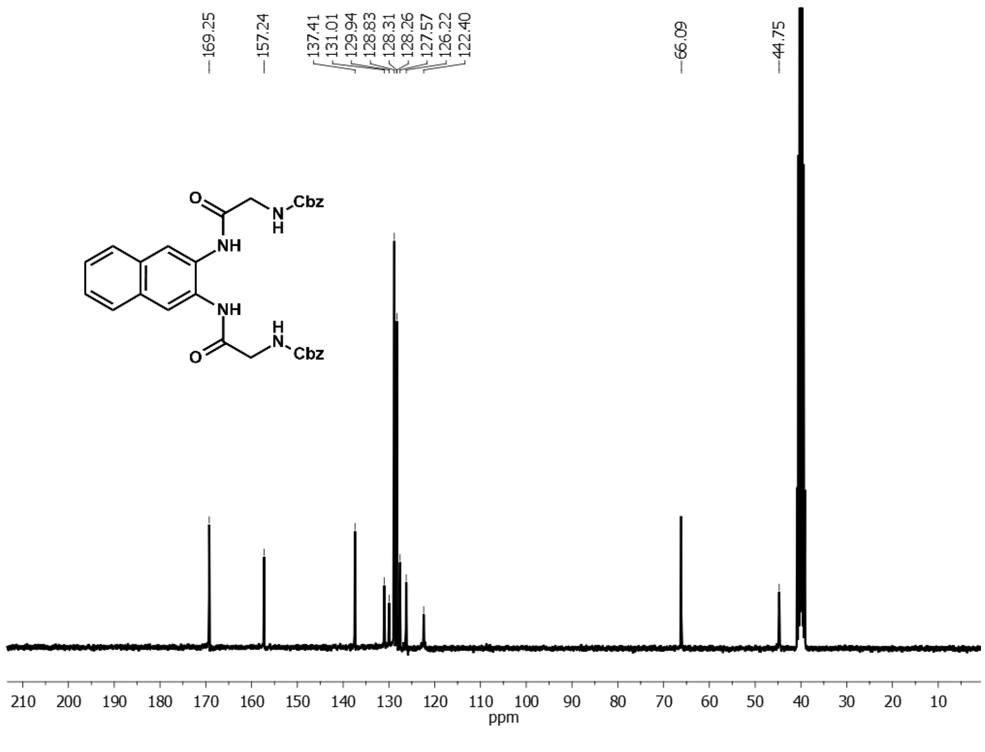

Fig. S30. ^{13}C NMR spectrum of **D3** in DMSO-d_6.

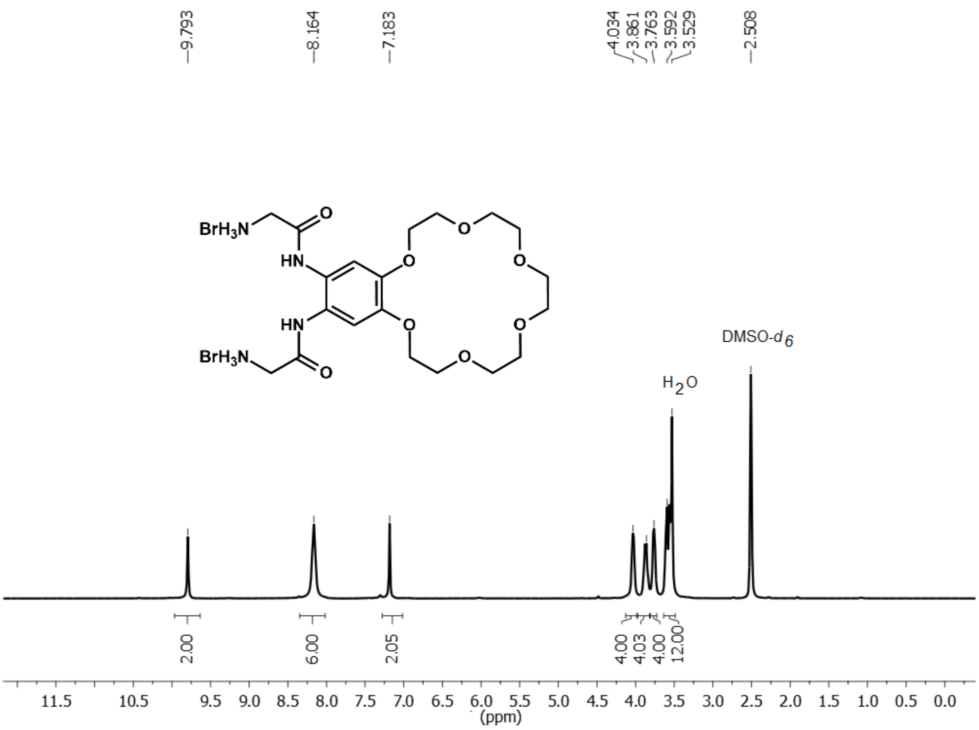

Fig. S31. ^{1}H NMR spectrum of **A1** in DMSO-d$_6$.

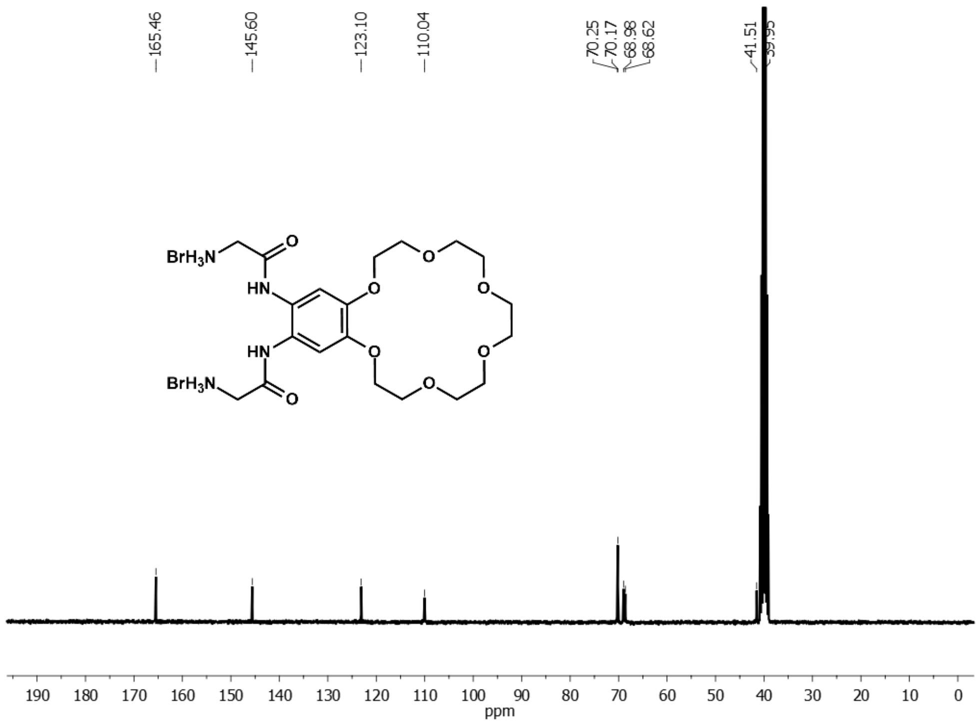

Fig. S32. ^{13}C NMR spectrum of **A1** in DMSO-d$_6$.

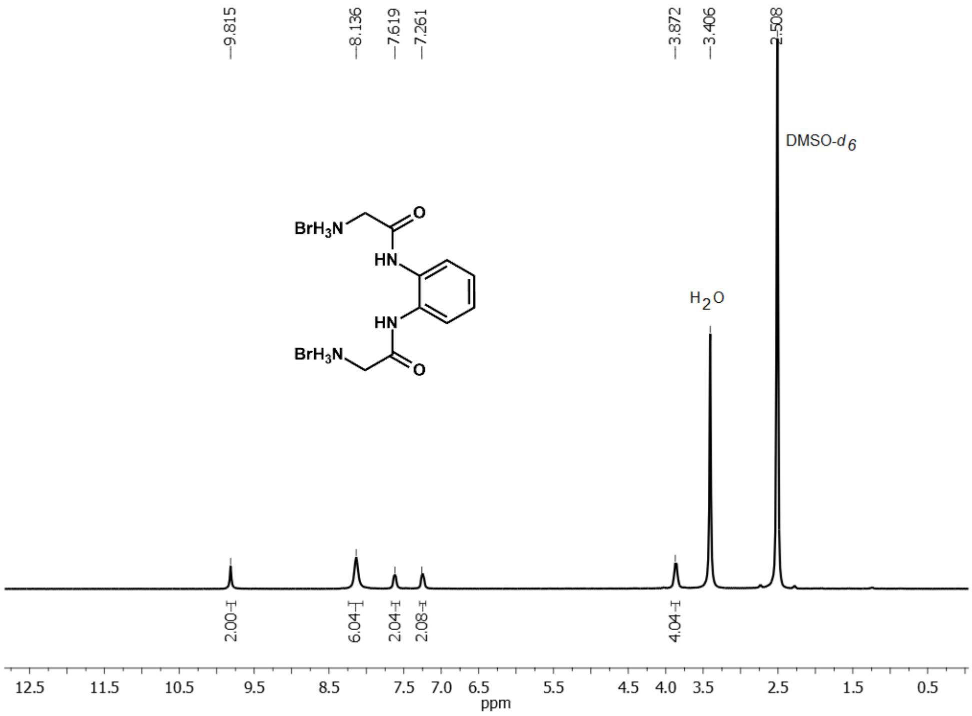

Fig. S33. ^{1}H NMR spectrum of **A2** in DMSO-d_6.

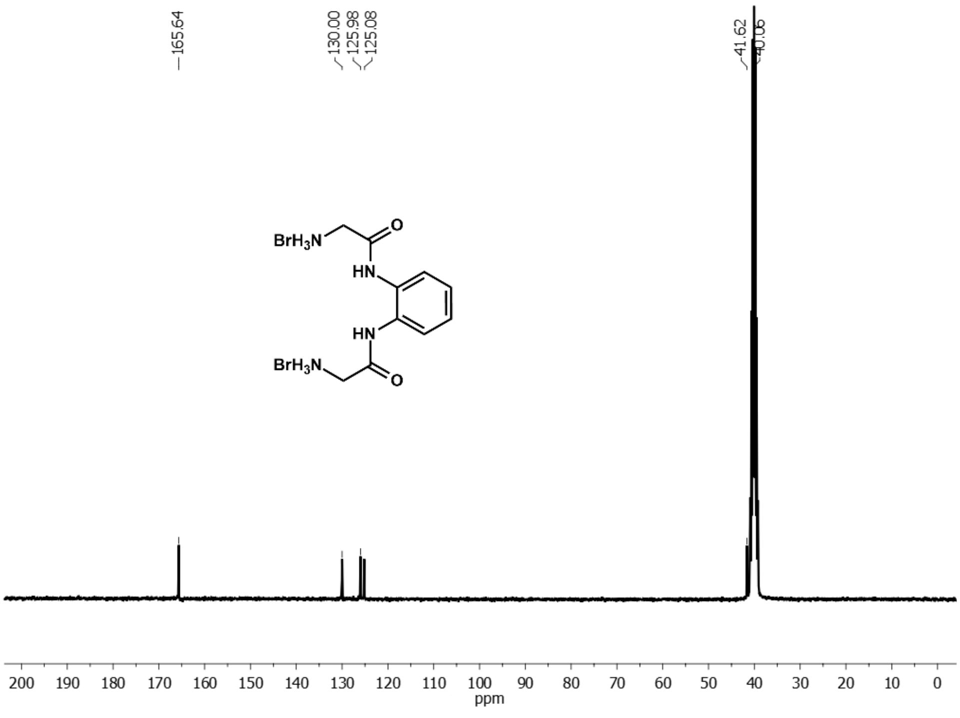

Fig. S34. ^{13}C NMR spectrum of **A2** in DMSO-d_6.

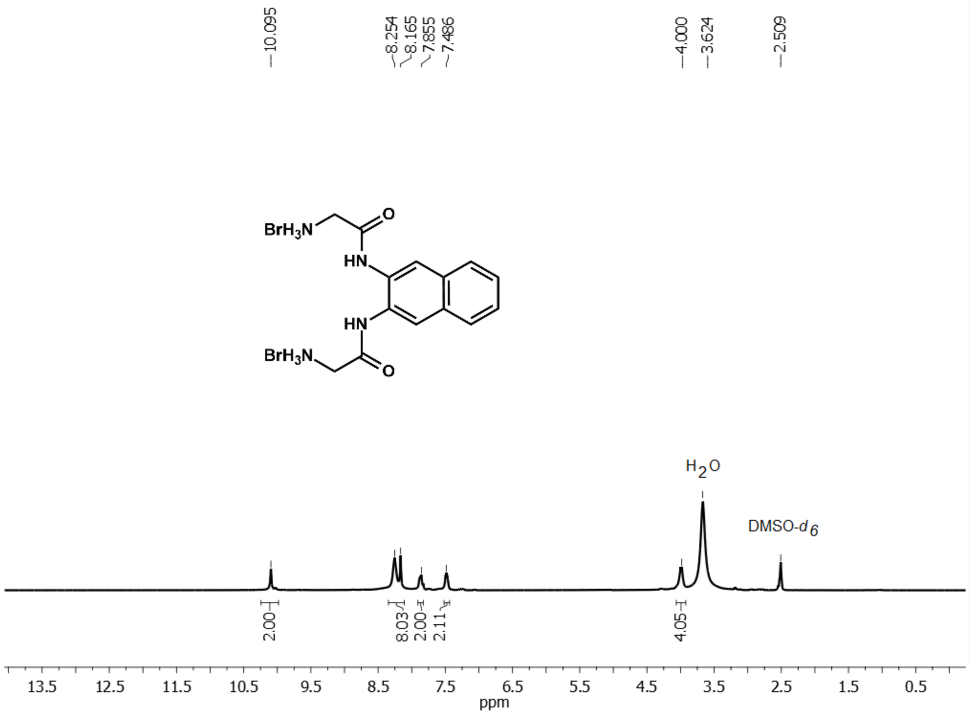

Fig. S35. ^{1}H NMR spectrum of **A3** in DMSO-d$_6$.

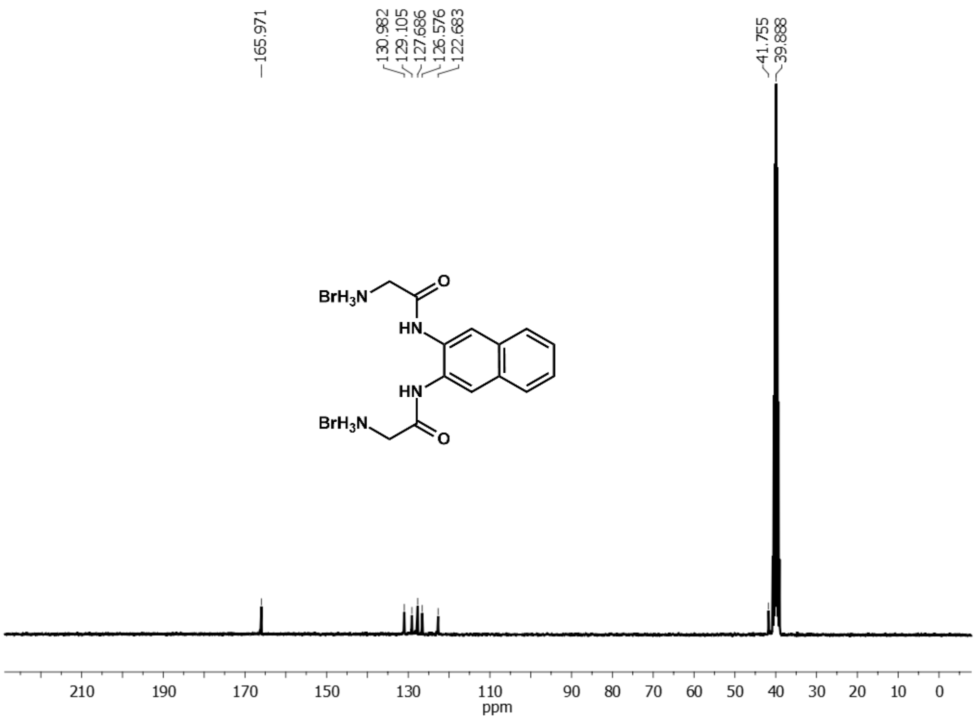

Fig. S36. ^{13}C NMR spectrum of **A3** in DMSO-d$_6$.

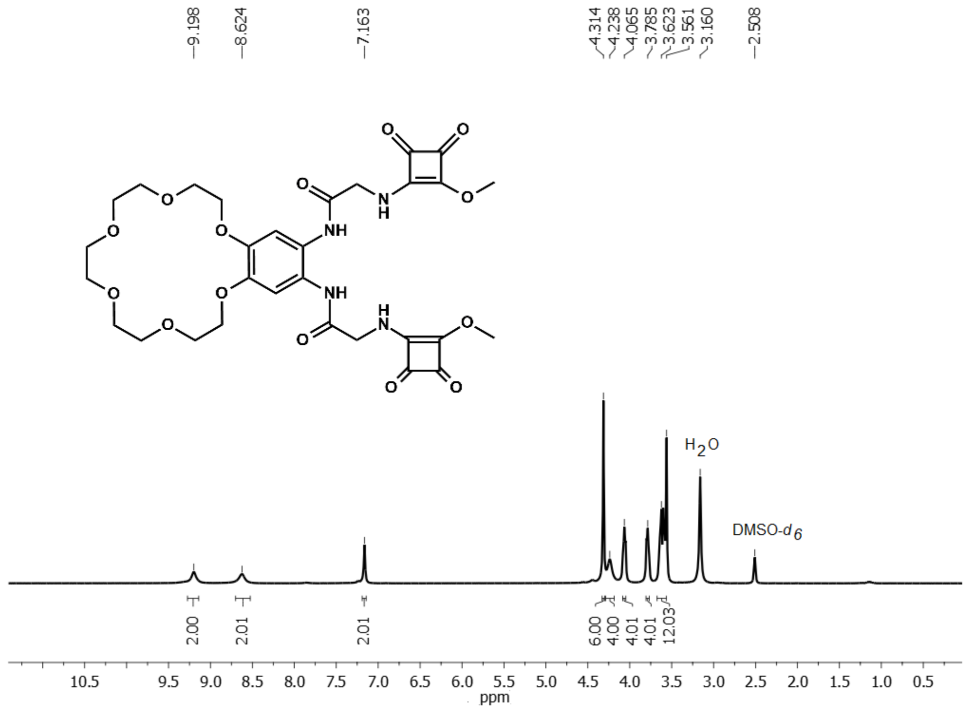

Fig. S37. ^{1}H NMR spectrum of **E1** in DMSO-d$_6$ (80°C).

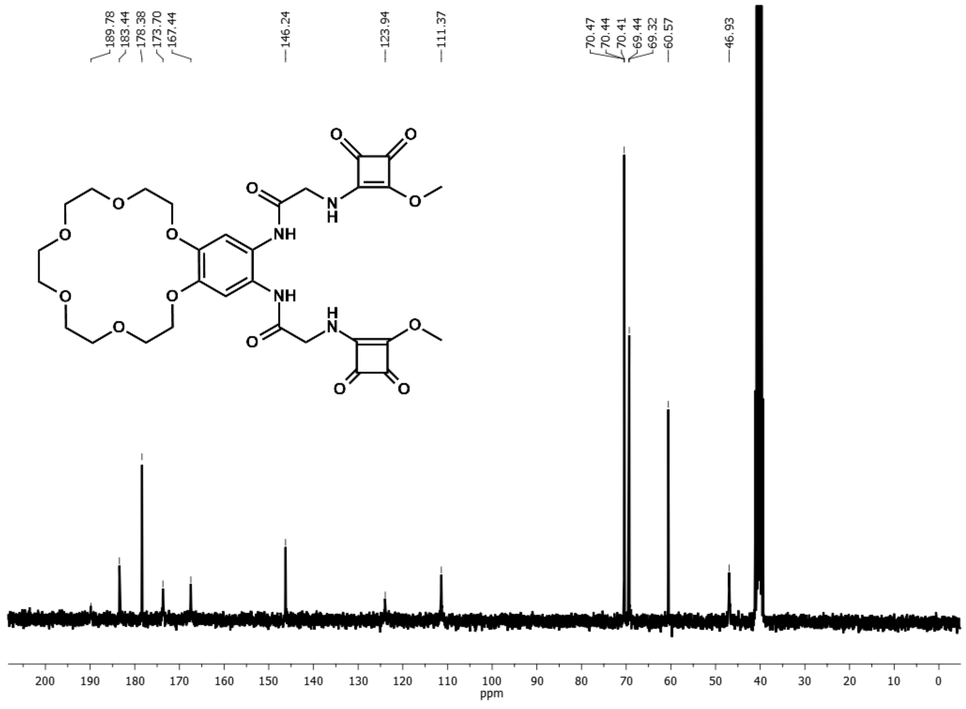

Fig. S38. ^{13}C NMR spectrum of **E1** in DMSO-d$_6$ (80°C).

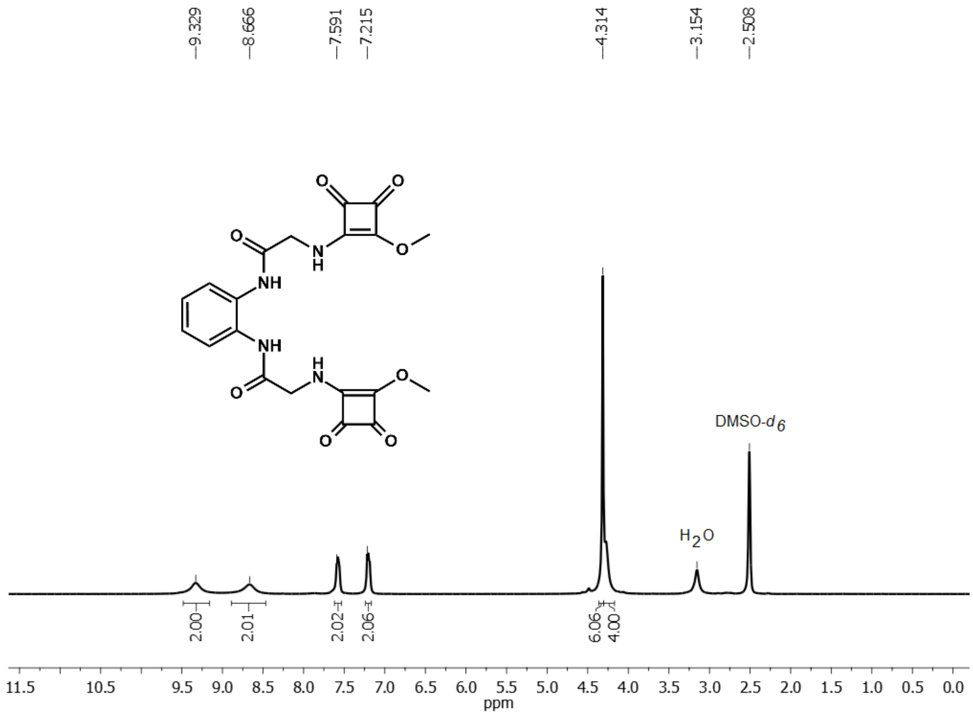

Fig. S39. ^{1}H NMR spectrum of **E2** in DMSO-d$_6$ (80°C).

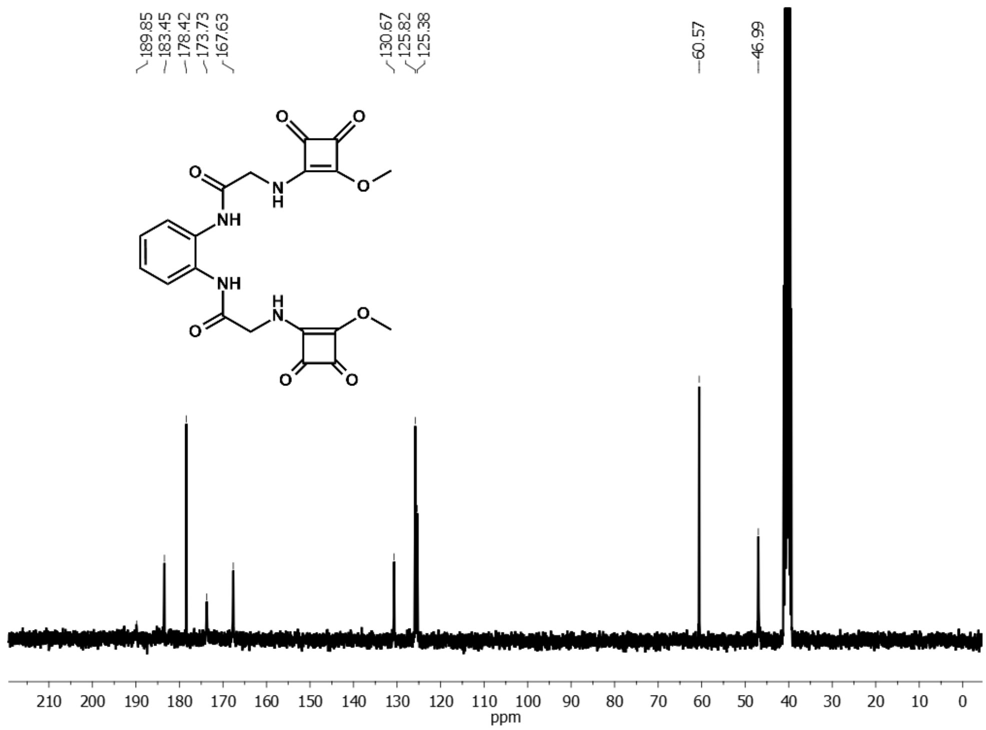

Fig. S40. ^{13}C NMR spectrum of **E2** in DMSO-d$_6$ (80°C).

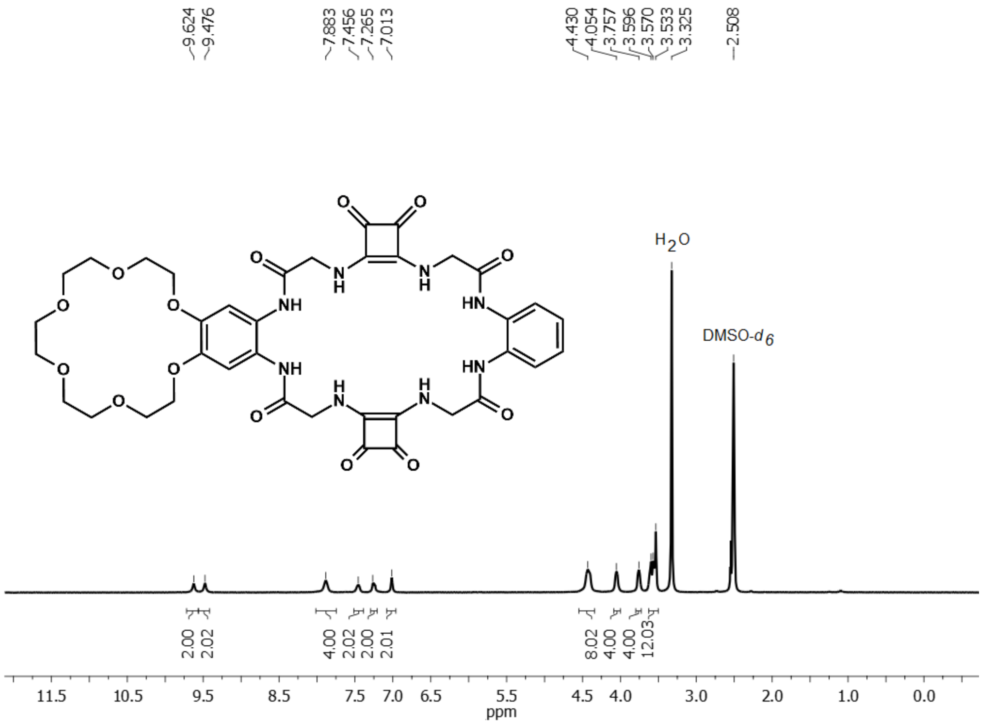

Fig. S41. ^{1}H NMR spectrum of **R1** in DMSO-d_6.

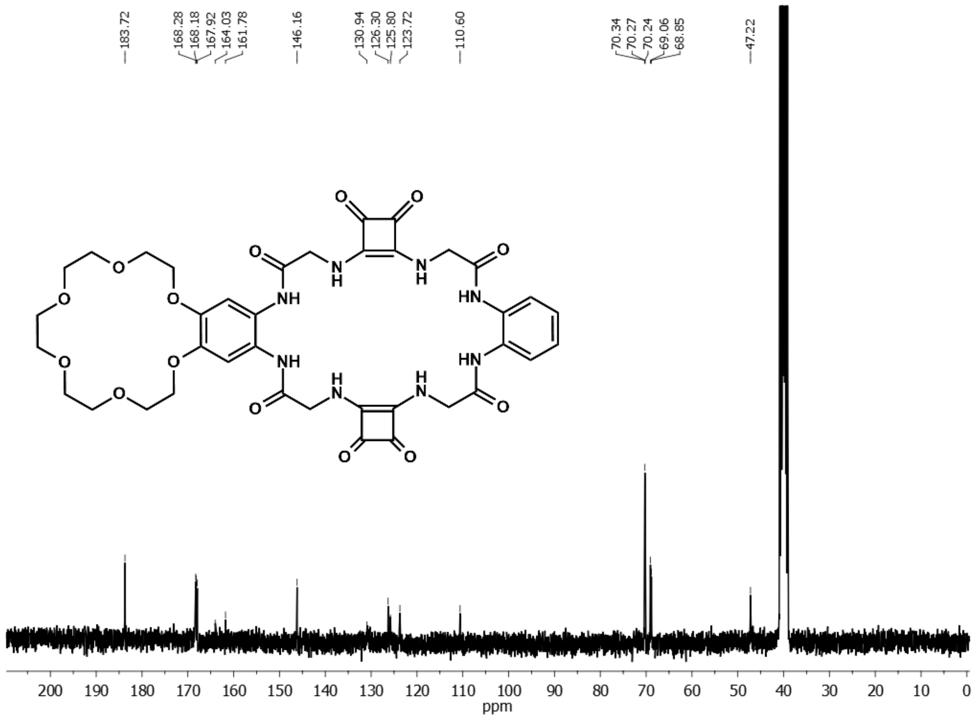

Fig. S42. ^{13}C NMR spectrum of **R1** in DMSO-d_6.

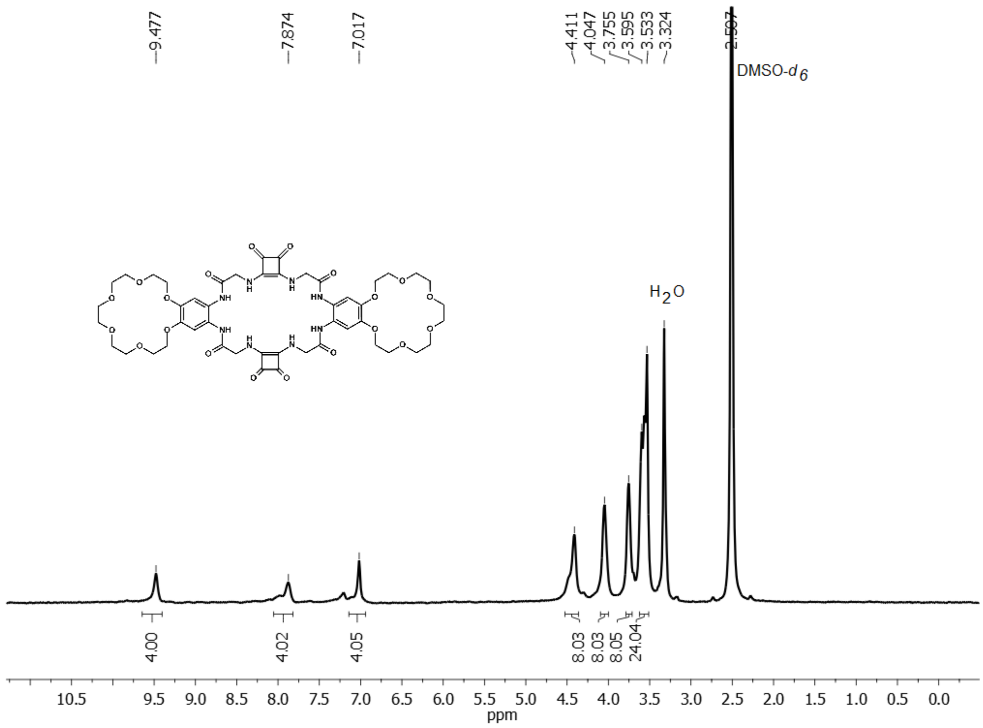

Fig. S43. ^{1}H NMR spectrum of **R2** in DMSO-d$_6$.

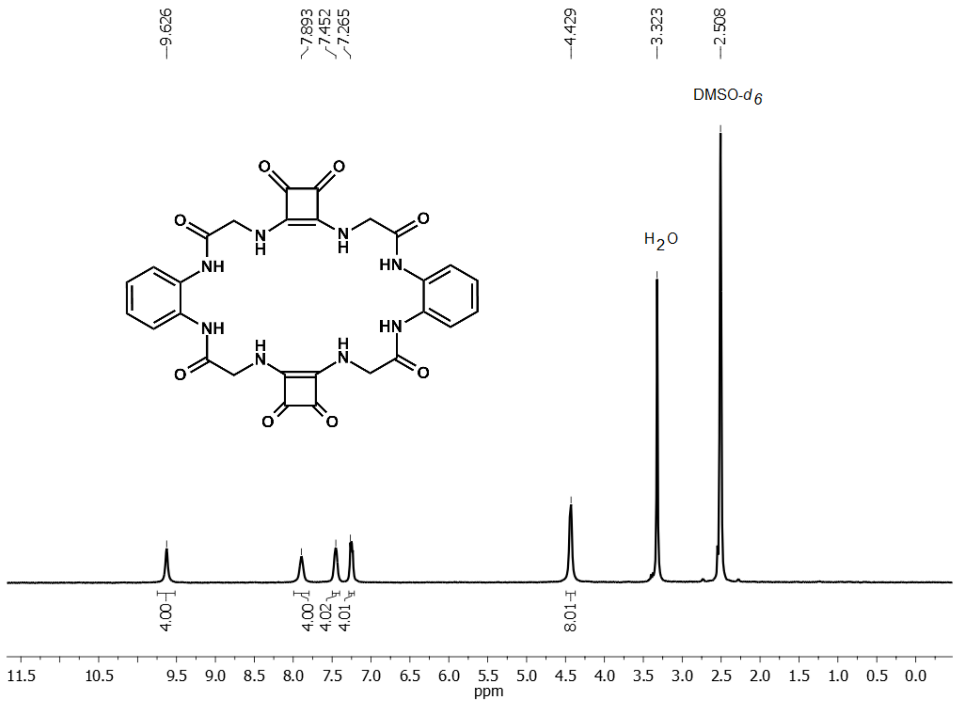

Fig. S44. ^{1}H NMR spectrum of **R3** in DMSO-d$_6$.

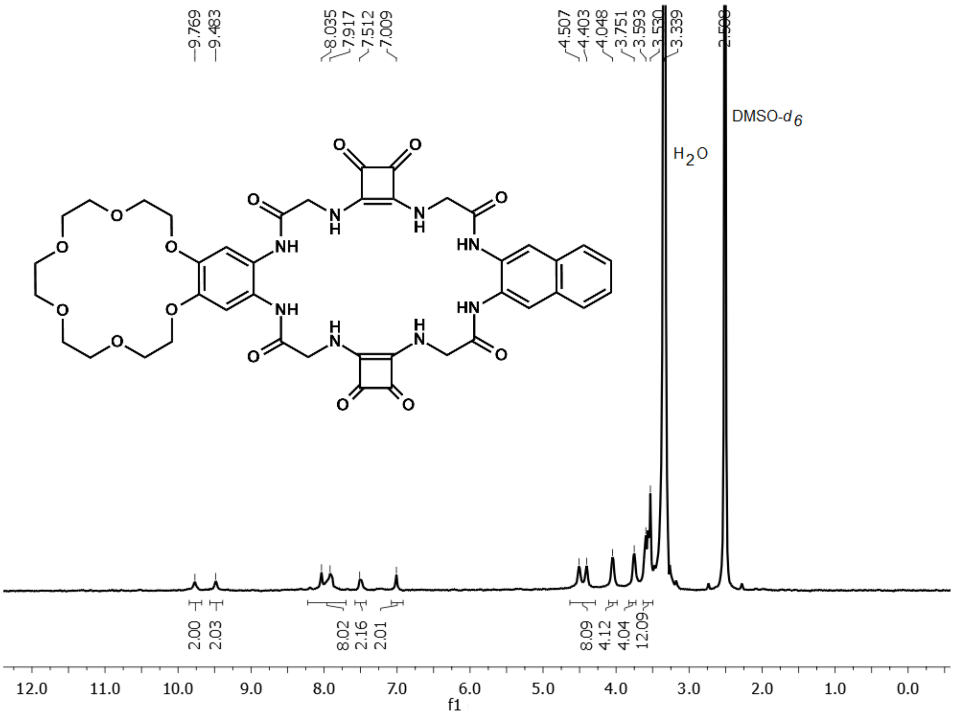

Fig. S45. ^1H NMR spectrum of **R4** in DMSO-d_6.