Exploring the Chiral Recognition of Carboxylates by C_2-Symmetric Receptors Bearing Glucosamine Pendant Arms

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Supporting information

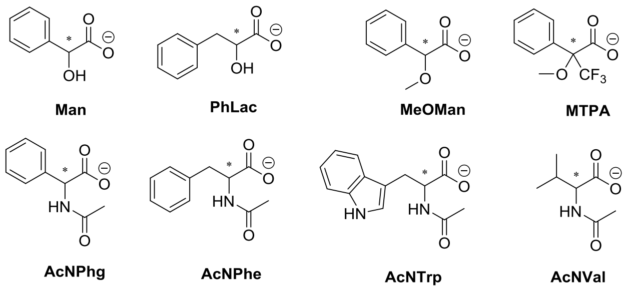
Contents

Binding studies

To quantify receptor–anion interactions in solution we followed the ^{1}H NMR titration protocol, which provides detailed insight into the complexation process. In all experiments we used a DMSO-water mixture (99.5:0.5 to 95:5) as a solvent, which is a rather competitive medium for anion recogniton.

General comments

Tetrabutylammonium (TBA) salts were used as a source of anions. TBA acetate and benzoate are commercially available. TBA salts of derivatives of mandelic acid and amino acids were prepared by addition of one equivalent of TBAOH to one equivalent carboxylic acid or N-Ac protected amino acid dissolved in MeOH. After evaporating MeOH in vacuo, salts were dried under high vacuum over P_2O_5. Distilled water was added to the commercially available DMSO-d6 of 99.8% isotopic purity to obtain the appropriate water concentration



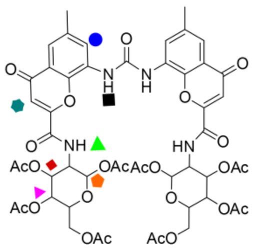
S1. Structures of the anionic guests investigated in this study, used as TBA salts.

^{1}H NMR titration experiments

The ligand solution (concentration from about 1.1 $\cdot 10^{-3}$ to 1.5 $\cdot 10^{-3}$ M, details are given in Tables S1 - S4) was titrated in the NMR tube with the solution of the respective TBA salt in ligand aliquots (salt concentration 0.11 – 0.2 M). 14 - 16 data points were recorded. The binding constants were calculated from the changes in chemical shifts of ligand protons which were shifted with $\Delta\delta_{max} > 0.1$ ppm during titration. Nonlinear curve fitting was carried out with HypNMR2008 Version 4.0.71 program with excellent fitting to the global binding model 1:1 receptor : anion stoichiometry as the most suitable for description of host – guest equilibria.

S1. The details of ^{1}H NMR titration in DMSO-d_6 + H_2O: concentrations used, titration curves ansd the results of data fitting, for receptor **1**

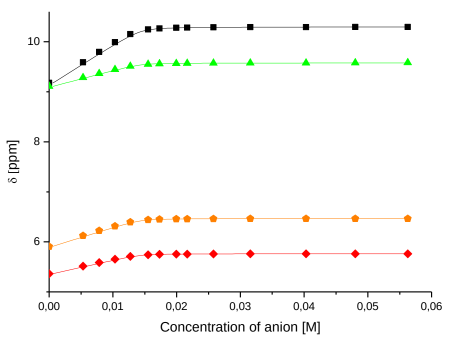
Receptor



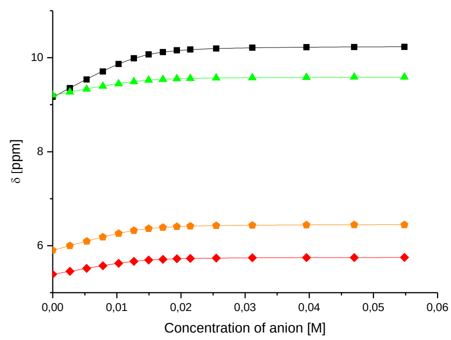
anion	water	L [mol · dm^{-3}]	A [mol · dm^{-3}]	logK	K
Cl^-	0. 5%	0.013893	0.178152	3.98(2)	9598
	5%	0.013919	0.164508	3.17(1)	1482
$C_6H_5CO_2^-$	0. 5%	0.013746	0.135084	4.05(3)	11306
	5%	0.013247	0.142663	3.4(1)	2576
$CH_3CO_2^-$	0. 5%	0.013746	0.167523	× [a]	× [a]
	5%	0.013247	0.137231	4.06(3)	11569
$Ph_2CHCO_2^-$	0. 5%	0.015032	0.155434	3.54(4)	3502
	5%	0.013616	0.138364	3.31(2)	2052
$H_2PO_4^-$	0. 5%	0.013893	0.158272	× [a]	× [a]
	5%	0.013919	0.149902	× [a]	× [a]

[a]Slow exchange in NMR scale

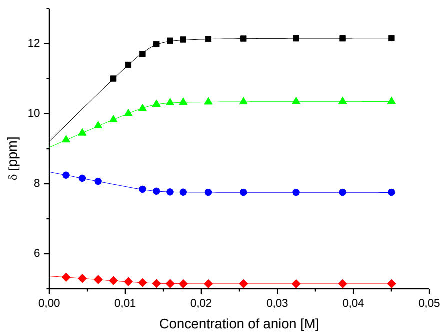
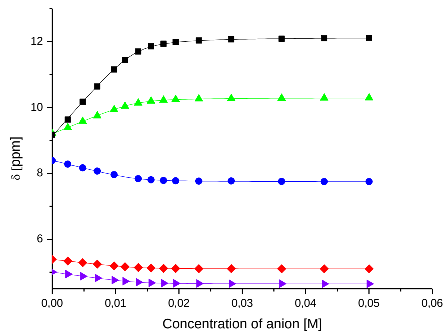
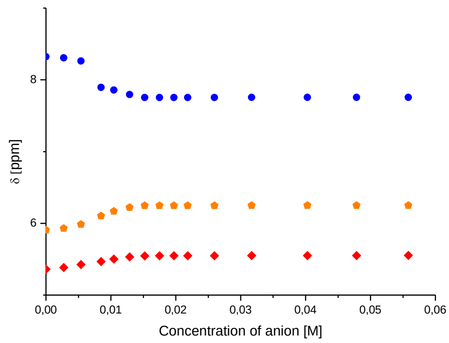
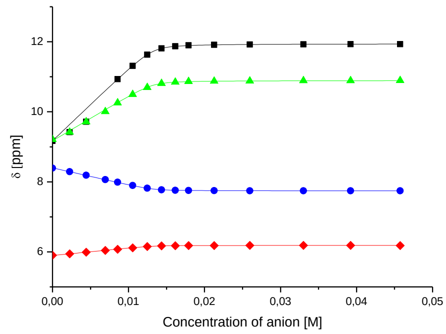
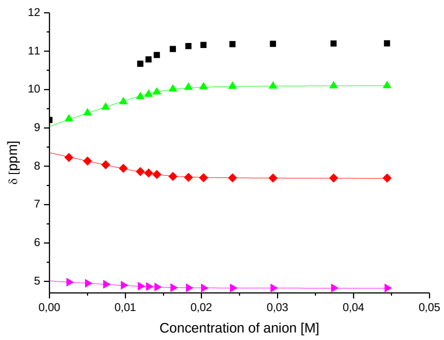
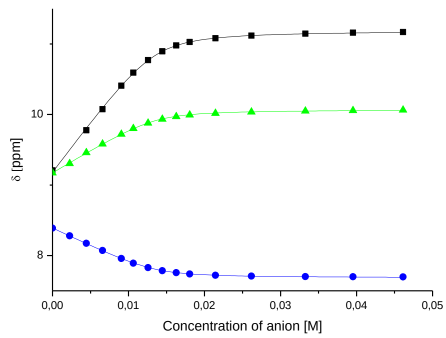
^{1}H NMR titrations curves



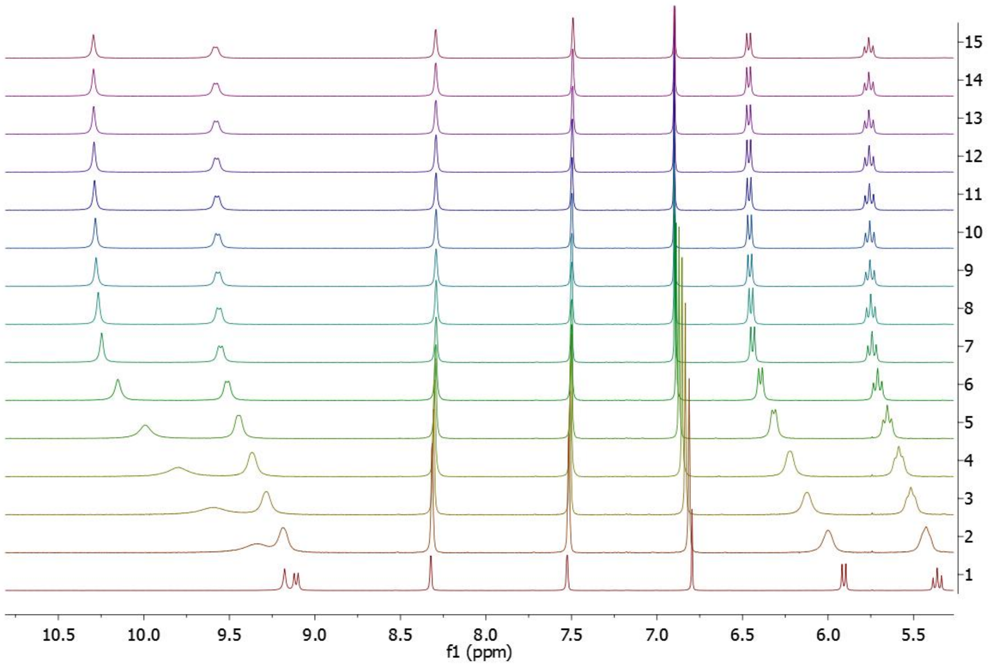
^{1}H NMR shifts signals upon addition of TBA chloride in DMSO-d_6 + 0.5% H_2O



^{1}H NMR shifts signals upon addition of TBA chloride in in DMSO-d_6 + 5% H_2O

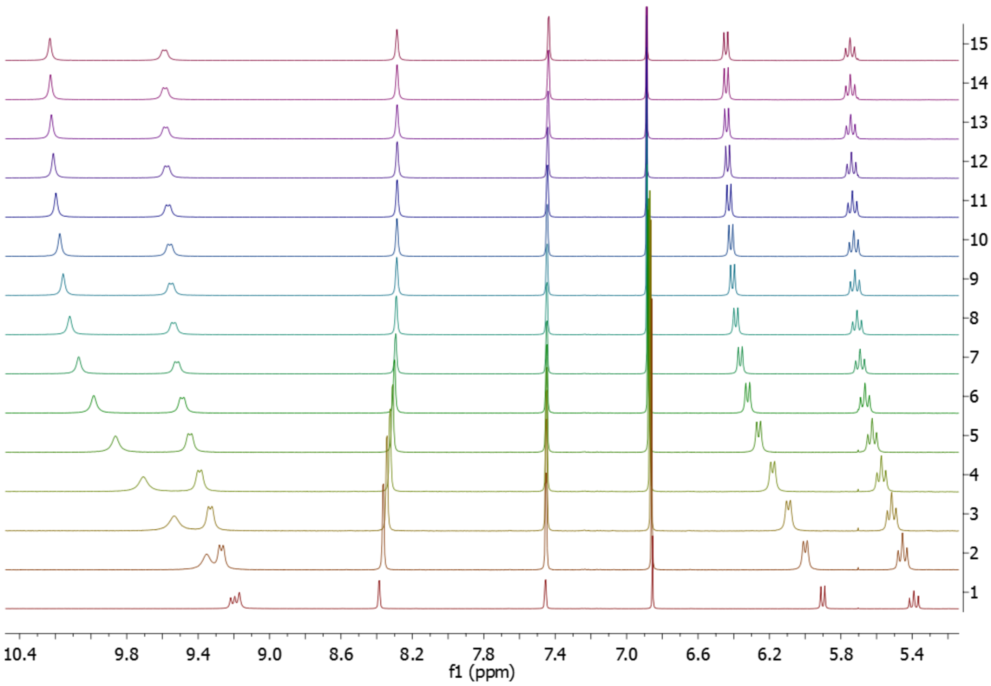
1H NMR titrations curves	 ^1H NMR shifts signals upon addition of TBA benzoate in DMSO-d_6 + 0.5% H_2O	 ^1H NMR shifts signals upon addition of TBA benzoate in DMSO-d_6 + 5% H_2O
1H NMR titrations curves	 ^1H NMR shifts signals upon addition of TBA acetate in DMSO-d_6 + 0.5% H_2O	 ^1H NMR shifts signals upon addition of TBA acetate in DMSO-d_6 + 5% H_2O
1H NMR titrations curves	 ^1H NMR shifts signals upon addition of TBA 2,2 – diphenylacetate DMSO-d_6 + 0.5% H_2O	 ^1H NMR shifts signals upon addition of TBA 2,2 – diphenylacetate DMSO-d_6 + 5% H_2O

Number of equivalents	
15	4.04
14	3.46
13	2.90
12	2.27
11	1.86
10	1.56
9	1.44
8	1.25
7	1.12
6	0.92
5	0.74
4	0.56
3	0.38
2	0.19
1	0.00



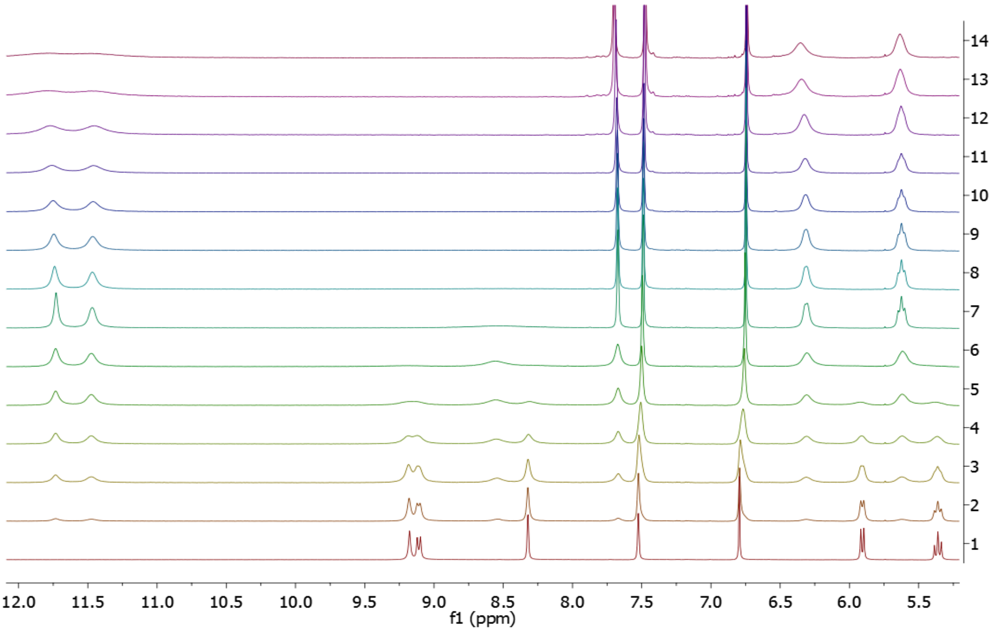
S2. [1]H NMR spectra changes upon titration receptor **1** with anions TBA chloride in DMSO-d_6 + 0.5% H_2O

Number of equivalents	
15	3.94
14	3.38
13	2.84
12	2.24
11	1.83
10	1.54
9	1.39
8	1.23
7	1.07
6	0.90
5	0.74
4	0.56
3	0.38
2	0.19
1	0.00



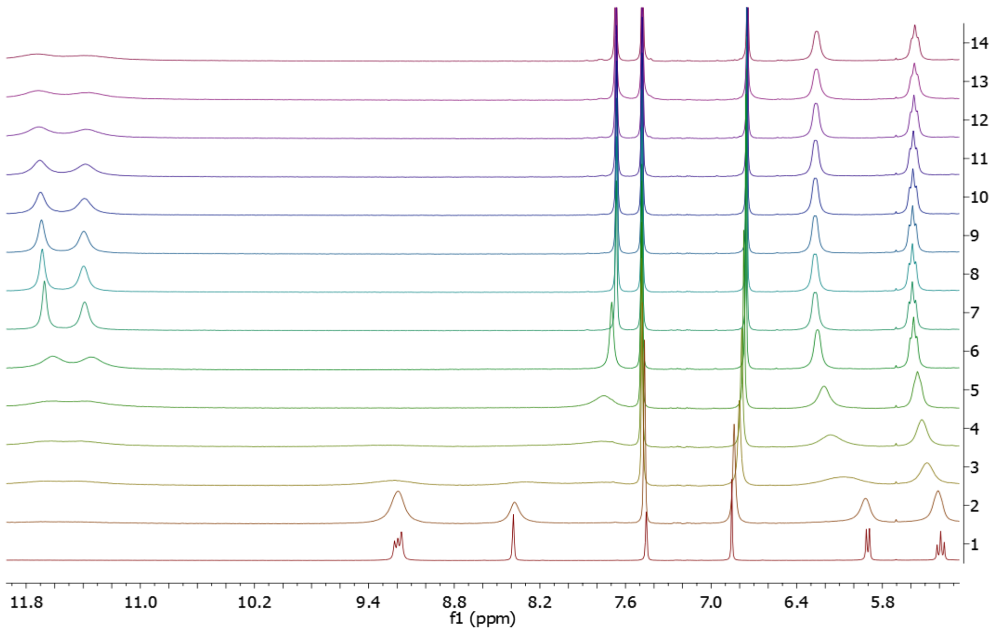
S3. [1]H NMR spectra changes upon titration receptor **1** with anions TBA chloride in DMSO-d_6 + 5% H_2O

Number of equivalents	
14	3.80
13	3.26
12	2.16
11	1.77
10	1.49
9	1.34
8	1.19
7	1.04
6	0.88
5	0.71
4	0.54
3	0.37
2	0.19
1	0.00



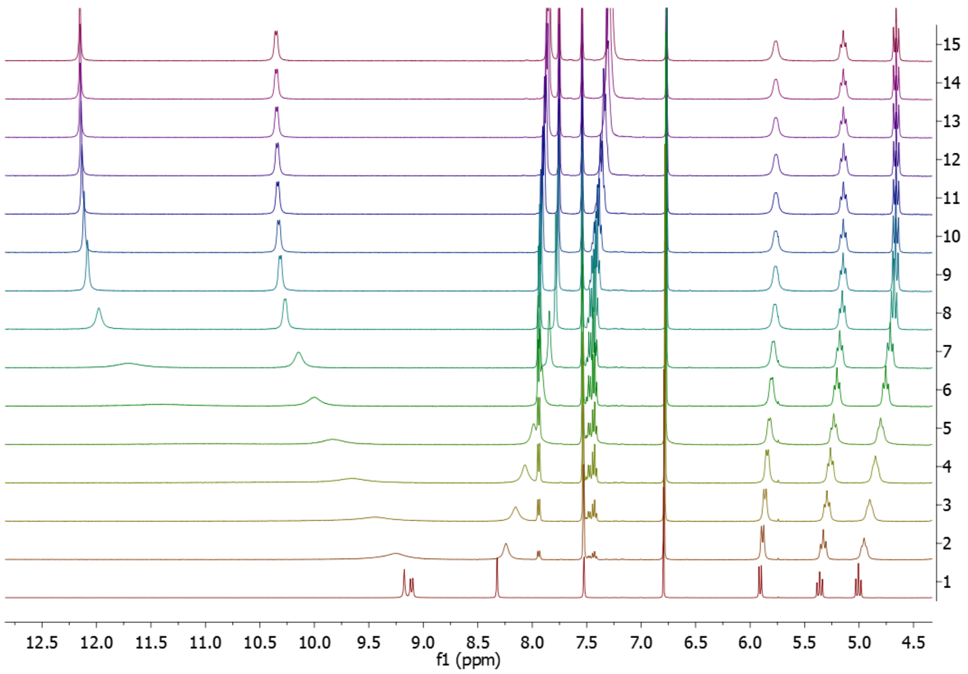
S4. ^{1}H NMR spectra changes upon titration receptor **1** with anion TBA dihydrophosphate in DMSO-d_6 + 0.5% H_2O

Number of equivalents	
14	3.5899
13	3.0771
12	2.5902
11	2.0375
10	1.6941
9	1.4048
8	1.2670
7	1.1252
6	0.9791
5	0.8284
4	0.6731
3	0.5128
2	0.1766
1	0.0000



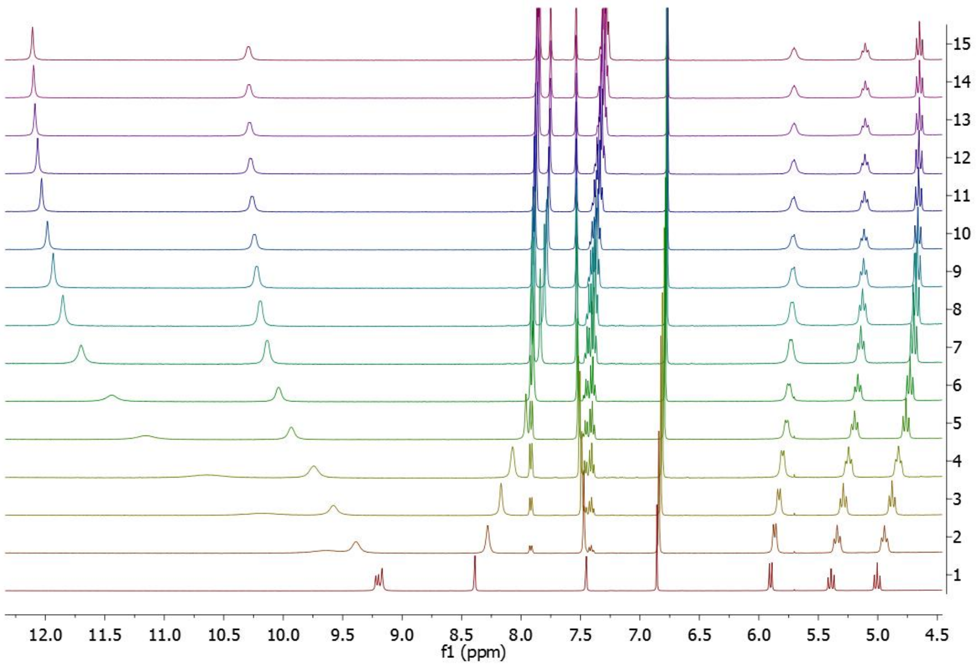
S5. ^{1}H NMR spectra changes upon titration receptor **1** with anion TBA dihydrophosphate in DMSO-d_6 + 5% H_2O

Number of equivalents	
15	3.28
14	2.81
13	2.36
12	1.86
11	1.52
10	1.28
9	1.16
8	1.03
7	0.89
6	0.76
5	0.61
4	0.47
3	0.32
2	0.16
1	0.00



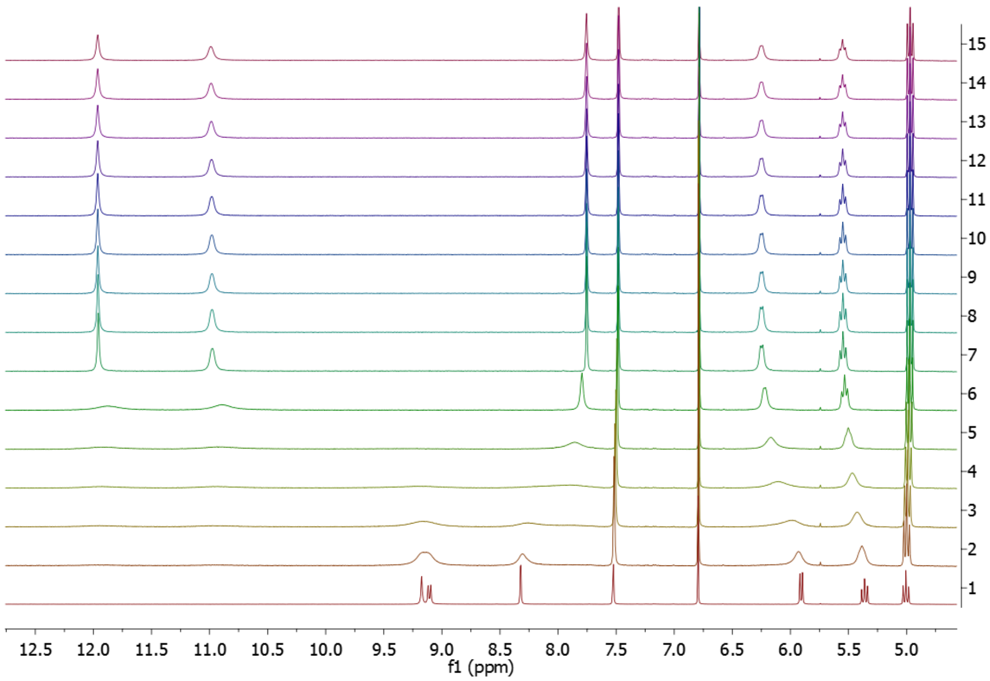
S6. ^{1}H NMR spectra changes upon titration receptor **1** with anions TBA benzoate in DMSO-d_6 + 0.5% H_2O

Number of equivalents	
15	3.78
14	3.24
13	2.73
12	2.13
11	1.75
10	1.47
9	1.33
8	1.18
7	1.02
6	0.87
5	0.74
4	0.54
3	0.36
2	0.18
1	0.00



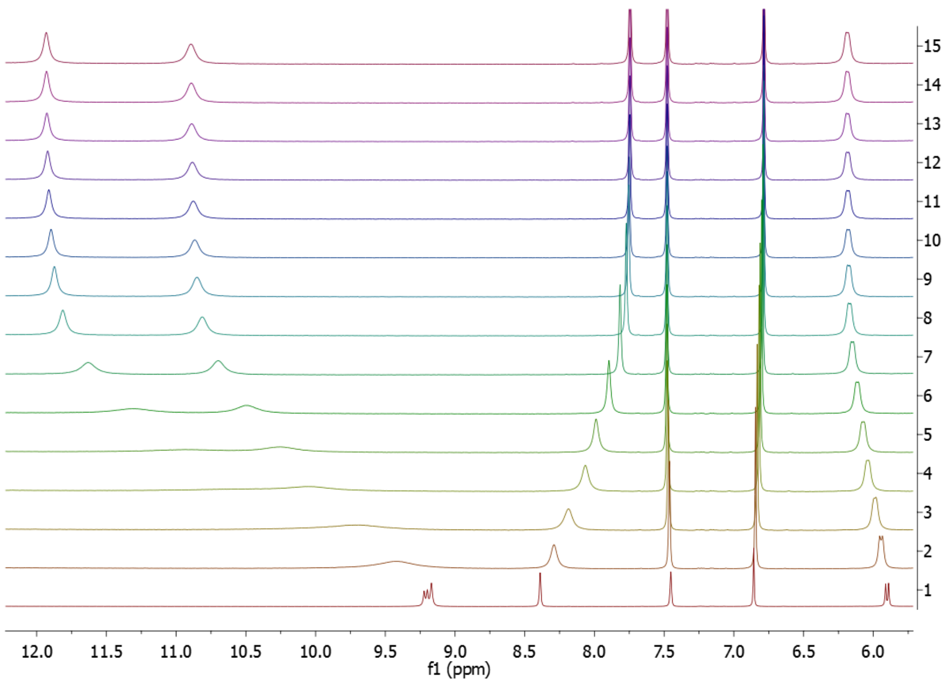
S7. ^{1}H NMR spectra changes upon titration receptor **1** anions TBA benzoate in DMSO-d_6 + 5% H_2O

Number of	equivalents
15	4.06
14	3.48
13	2.93
12	2.30
11	1.89
10	1.59
9	1.43
8	1.27
7	1.11
6	0.94
5	0.76
4	0.62
3	0.39
2	0.20
1	0.00



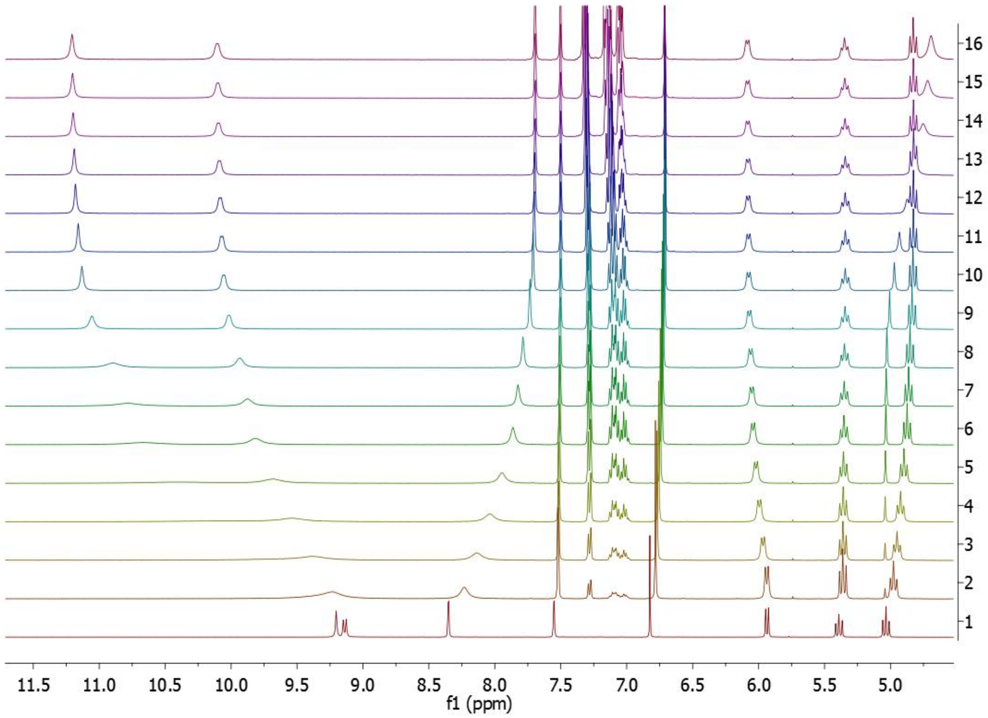
S8. [1]H NMR spectra changes upon titration receptor **1** with anions TBA acetate in DMSO-d_6 +0.5% H_2O

Number of	equivalents
15	3.26
14	2.79
13	2.35
12	1.85
11	1.51
10	1.27
9	1.15
8	1.02
7	0.89
6	0.75
5	0.61
4	0.50
3	0.32
2	0.16
1	0.00



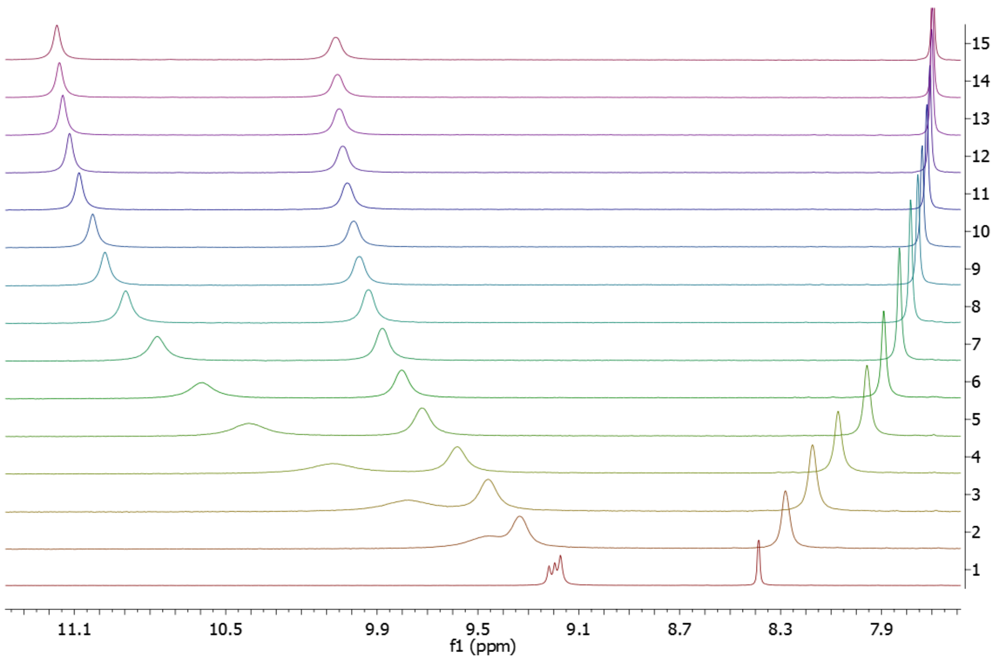
S9. [1]H NMR spectra changes upon titration receptor **1** anions TBA acetate in DMSO-d_6 + 5% H_2O

Number of equivalents	
16	3.45
15	2.95
14	2.49
13	1.96
12	1.60
11	1.35
10	1.22
9	1.08
8	0.94
7	0.87
6	0.80
5	0.65
4	0.49
3	0.33
2	0.17
1	0.00



S10. ^{1}H NMR spectra changes upon titration receptor **1** with TBA 2,2-diphenylacetate in DMSO-d_6 + 0.5% H_2O

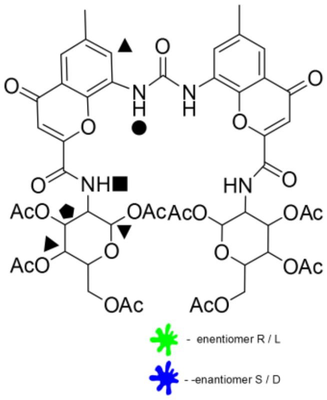
Number of equivalents	
15	3.39
14	2.90
13	2.44
12	1.92
11	1.57
10	1.32
9	1.20
8	1.06
7	0.92
6	0.78
5	0.66
4	0.48
3	0.33
2	0.17
1	0.00



S11. ^{1}H NMR spectra changes upon titration receptor **1** with TBA 2,2-diphenylacetate in DMSO-d_6 + 5% H_2O

S2. The details of ^{1}H NMR titration in DMSO-d_6 + H_2O: concentrations used, titration curves and the results of data fitting, for receptor **1**

Receptor

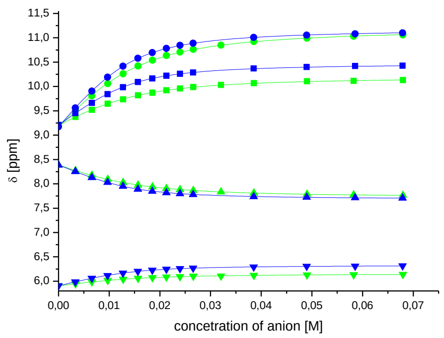


anion	L [mol · dm^{-3}]	A [mol · dm^{-3}]	logK	K	K_S/K_R (K_L/K_D)
(R)-Man	0.013789	0.203859	2.329(5)	213	1.76
(S) -Man	0.013789	0.203677	2.57(4)	375	
(L)-PhLac	0.014245	0.194745	2.797(6)	627	1.22
(D)-PhLac	0.014245	0.196096	2.709(6)	512	
(R)-MeOMan	0.014642	0.190076	3.59(1)	3890	2.00
(S)-MeOMan	0.014642	0.193102	3.89(2)	7801	
(R)-MTPA	0.014728	0.199292	1.785(5)	61.0	1.55
(S)-MTPA	0.014728	0.197628	1.9(7)	94.8	

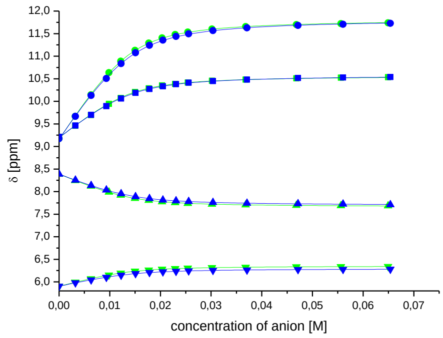
(L)-AcNPhg	0.014876	0.134192	2.391(9)	246	1.41
(D)-AcNPhg	0.014876	0.128878	2.241(1)	174	
(L)-AcNPhe	0.014544	0.179505	-[a]	- [a]	- [a]
(D) -AcNPhe	0.014544	0.178398	- [a]	- [a]	
(L)-AcNTrp	0.014045	0.14361	2.626(9)	423	1.25
(D)–AcNTrp	0.014045	0.139407	2.529(7)	338	
(L)-AcNVal	0.014246	0.164087	2.7(1)	514	1.26
(D)-AcNVal	0.014246	0.165148	2.6(1)	408	

[a] Data cannot be fit to a simple 1:1 model

^{1}H NMR titrations curves

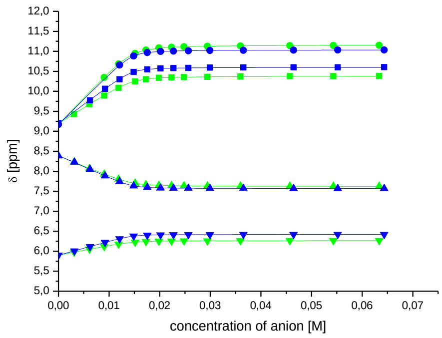


^{1}H NMR shifts signals upon addition both enantiomers of TBA Man

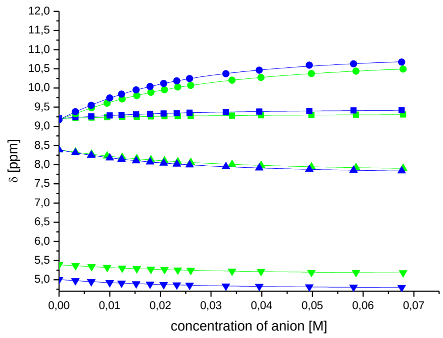


^{1}H NMR shifts signals upon addition both enantiomers of TBA PhLac

1H NMR titrations curves

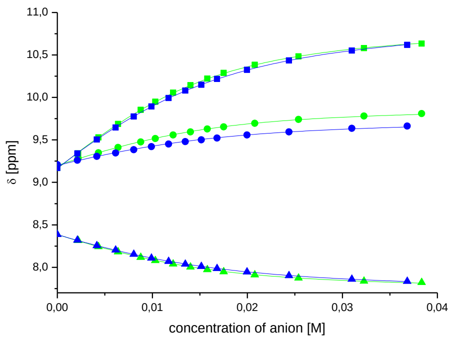


^{1}H NMR shifts signals upon addition both enantiomers of TBA MeOMan



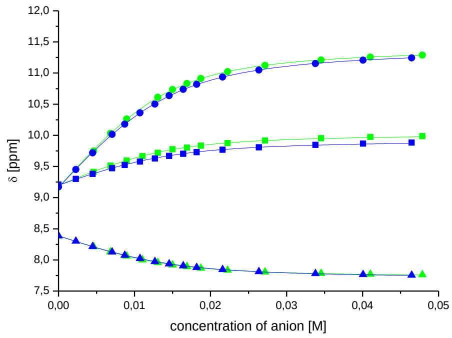
^{1}H NMR shifts signals upon addition both enantiomers of TBA TBA MTPA.

1H NMR titrations curves

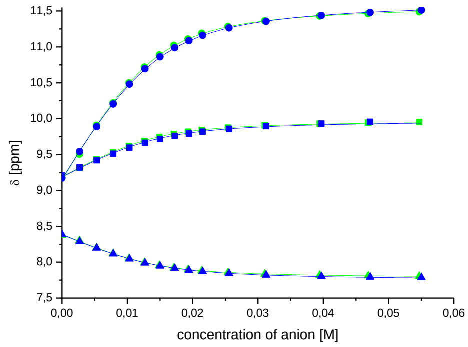


^{1}H NMR shifts signals upon addition both enantiomers of TBA Phg

1H NMR titrations curves

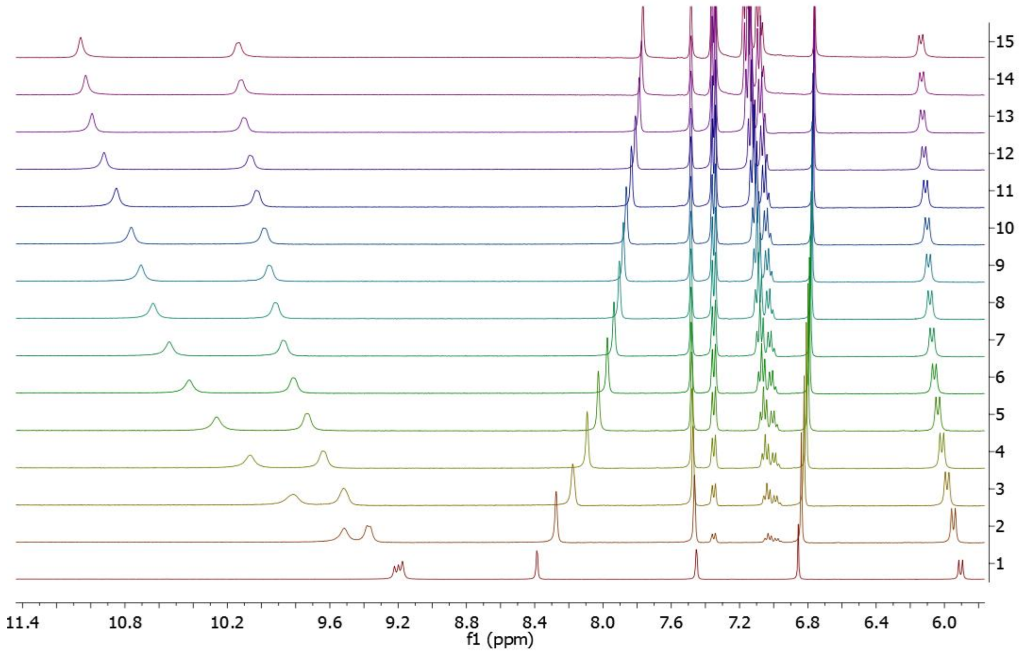


^{1}H NMR shifts signals upon addition both enantiomers of TBA AcNTrp



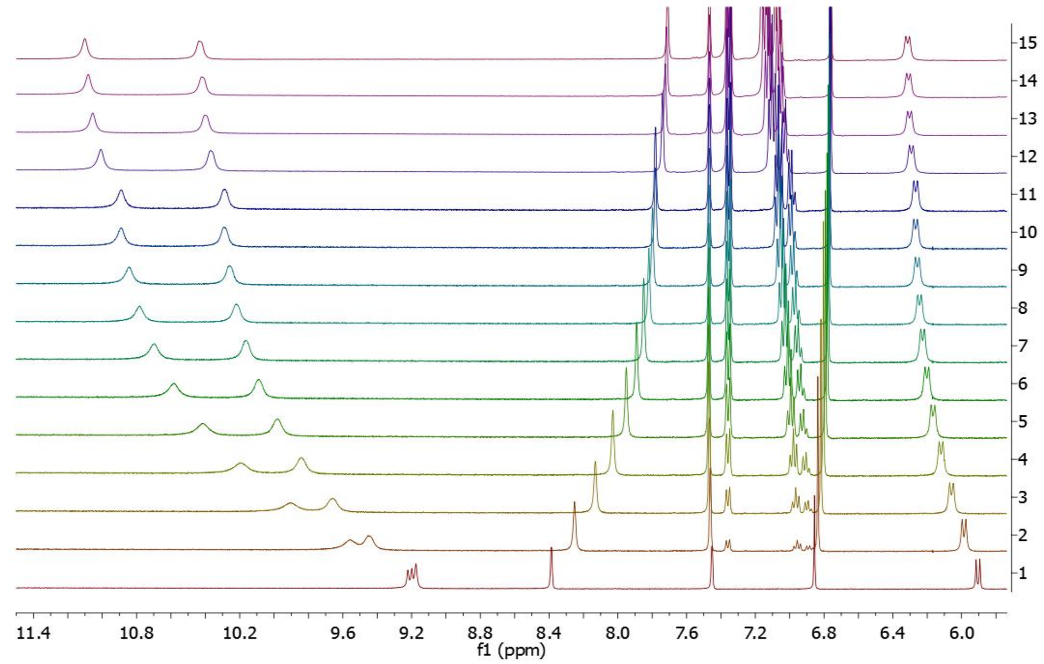
^{1}H NMR shifts signals upon addition both enantiomers of TBA AcNVal

Number of equivalents	
15	4.93
14	4.22
13	3.56
12	2.80
11	2.32
10	1.93
9	1.74
8	1.54
7	1.34
6	1.14
5	0.92
4	0.70
3	0.48
2	0.24
1	0.00



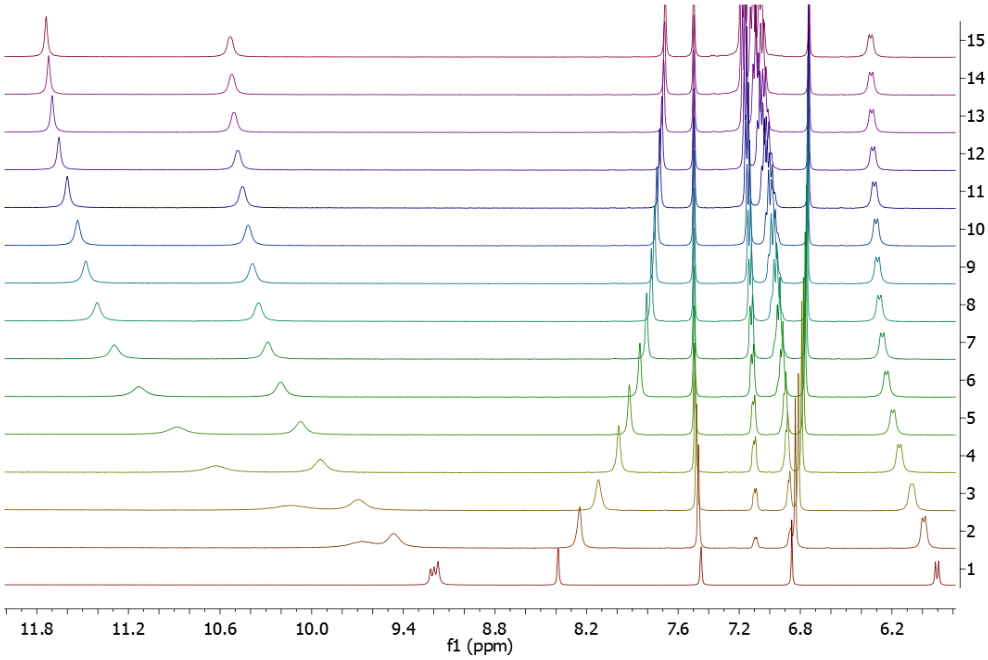
S12. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (R)-Man

Number of equivalents	
15	4.92
14	4.24
13	3.55
12	2.79
11	2.29
10	1.93
9	1.74
8	1.54
7	1.34
6	1.14
5	0.92
4	0.70
3	0.48
2	0.24
1	0.00



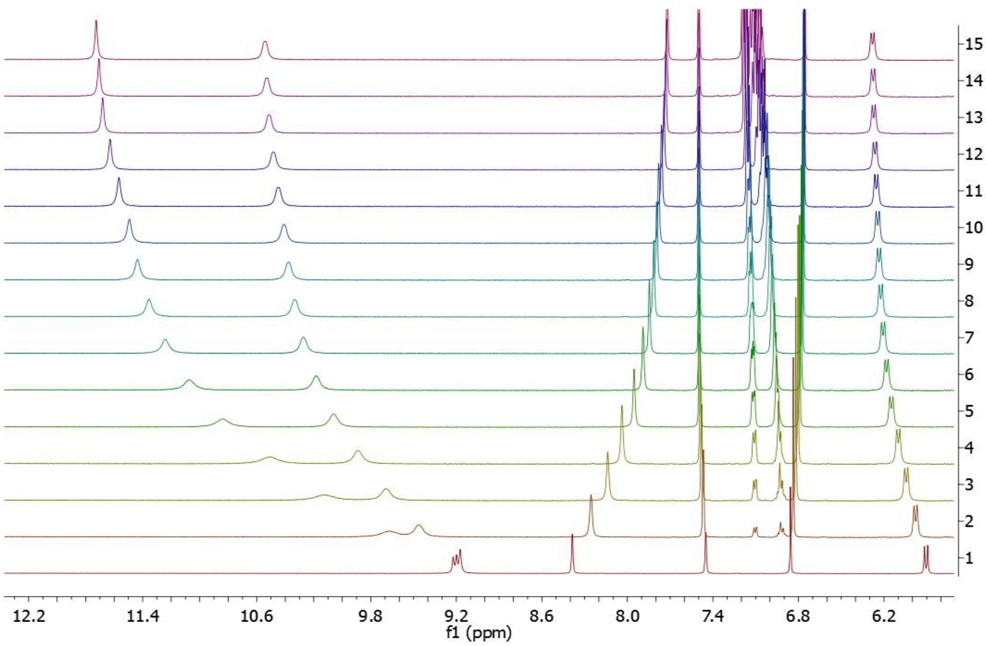
S13. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (S)-Man

Number of	equivalents
15	4.56
14	3.91
13	3.29
12	2.59
11	2.12
10	1.78
9	1.61
8	1.43
7	1.24
6	1.05
5	0.85
4	0.69
3	0.44
2	0.22
1	0.00



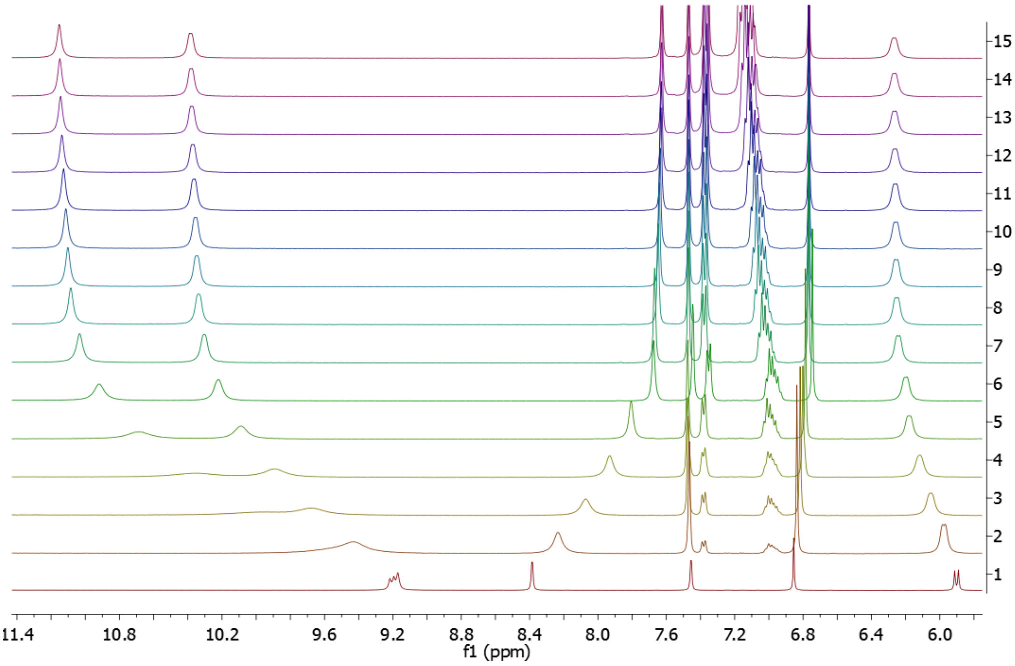
S14. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (L)-PhLac

Number of	equivalents
15	4.59
14	3.93
13	3.31
12	2.60
11	2.13
10	1.80
9	1.62
8	1.44
7	1.25
6	1.06
5	0.86
4	0.66
3	0.44
2	0.22
1	0.00



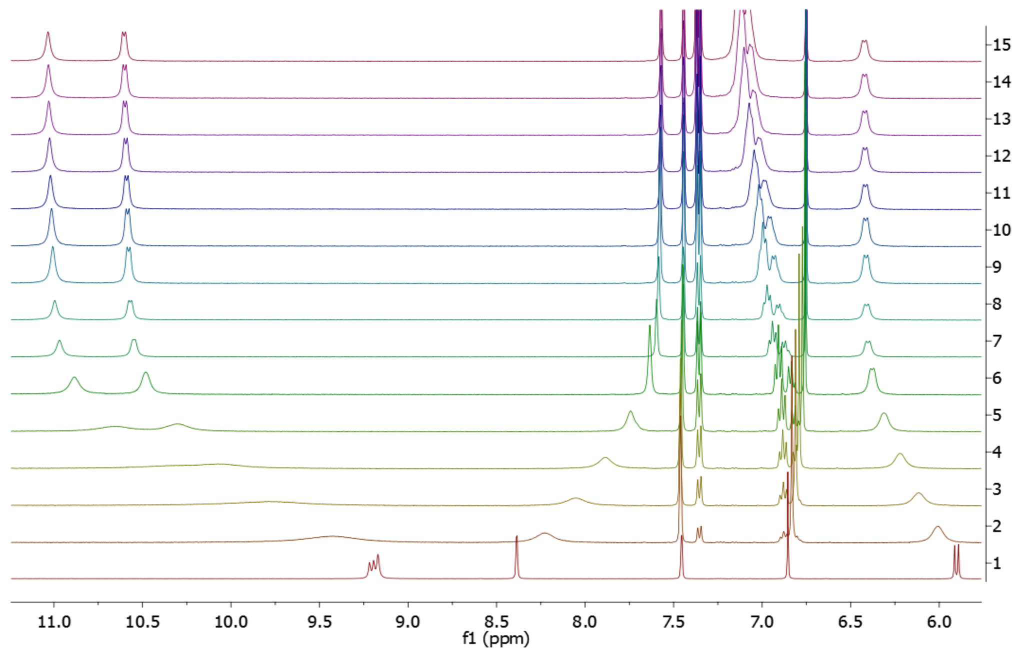
S15. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (D)-PhLac

Number of	equivalents
15	4.33
14	3.71
13	3.12
12	2.46
11	2.01
10	1.69
9	1.53
8	1.36
7	1.18
6	1.04
5	0.81
4	0.62
3	0.42
2	0.21
1	0.00



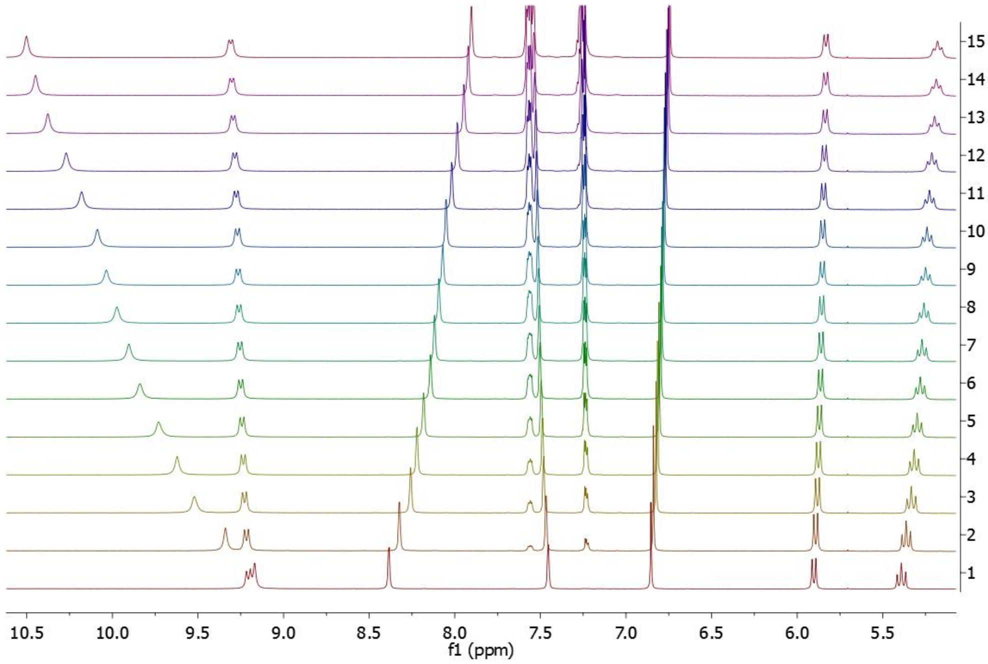
S16. [1]H NMR spectra changes upon titration receptor **1** with TBA (R)-MeOMan

Number of	equivalents
15	4.40
14	3.77
13	3.17
12	2.50
11	2.04
10	1.75
9	1.55
8	1.38
7	1.20
6	1.01
5	0.82
4	0.63
3	0.42
2	0.22
1	0.00



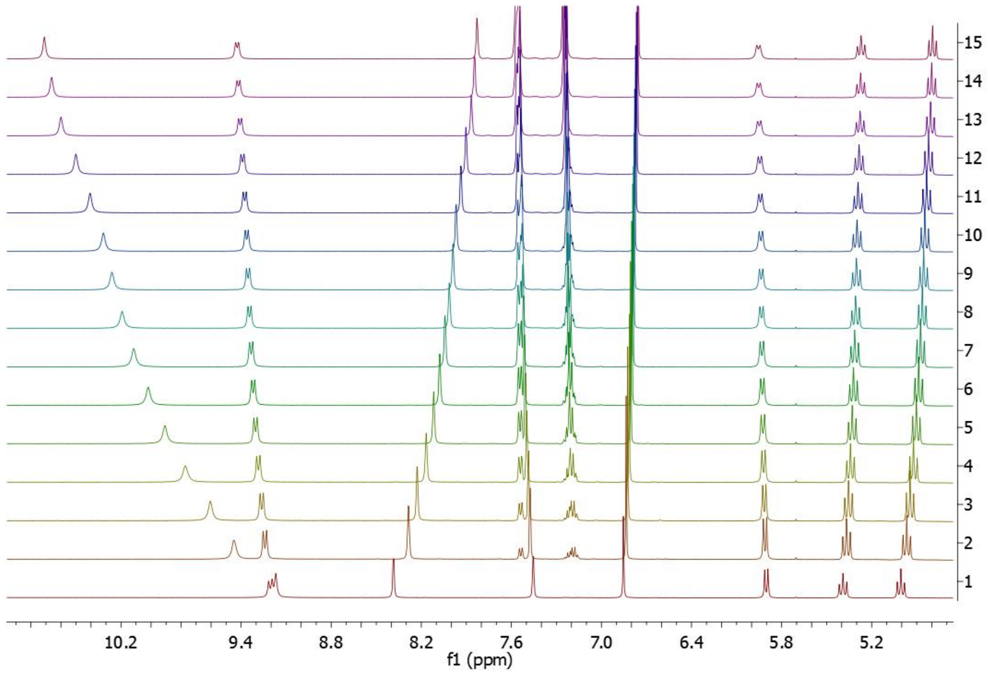
S17. [1]H NMR spectra changes upon titration receptor **1** with TBA(S)-MeOMan

Number of equivalents	
15	4.61
14	3.98
13	3.38
12	2.71
11	2.32
10	1.76
9	1.59
8	1.41
7	1.23
6	1.04
5	0.84
4	0.64
3	0.44
2	0.22
1	0.00



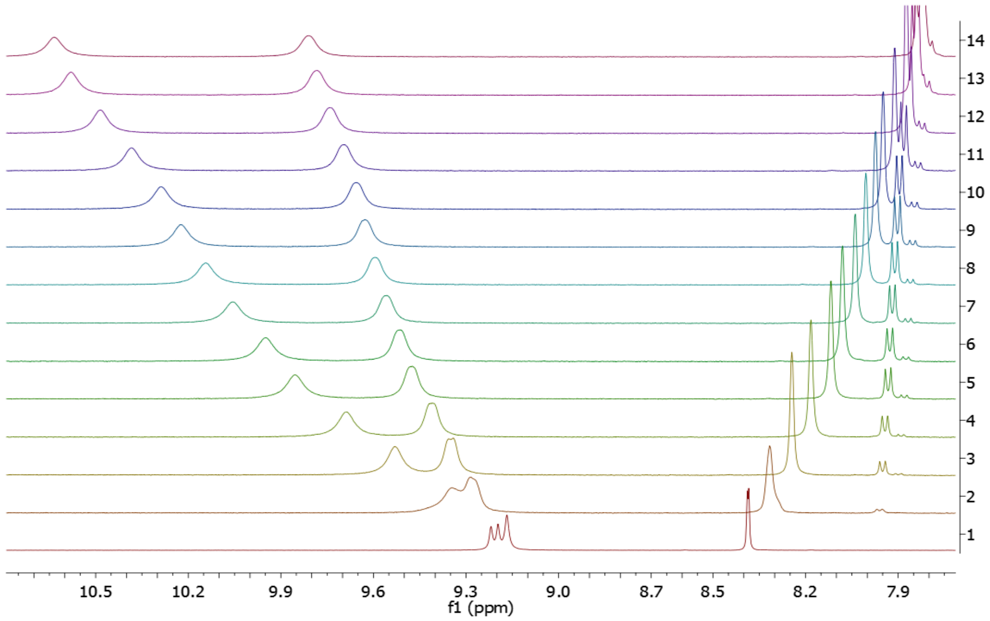
S18. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (R)-MTPA

Number of equivalents	
15	4.59
14	3.95
13	3.35
12	2.68
11	2.24
10	1.75
9	1.58
8	1.40
7	1.22
6	1.03
5	0.84
4	0.68
3	0.43
2	0.22
1	0.00



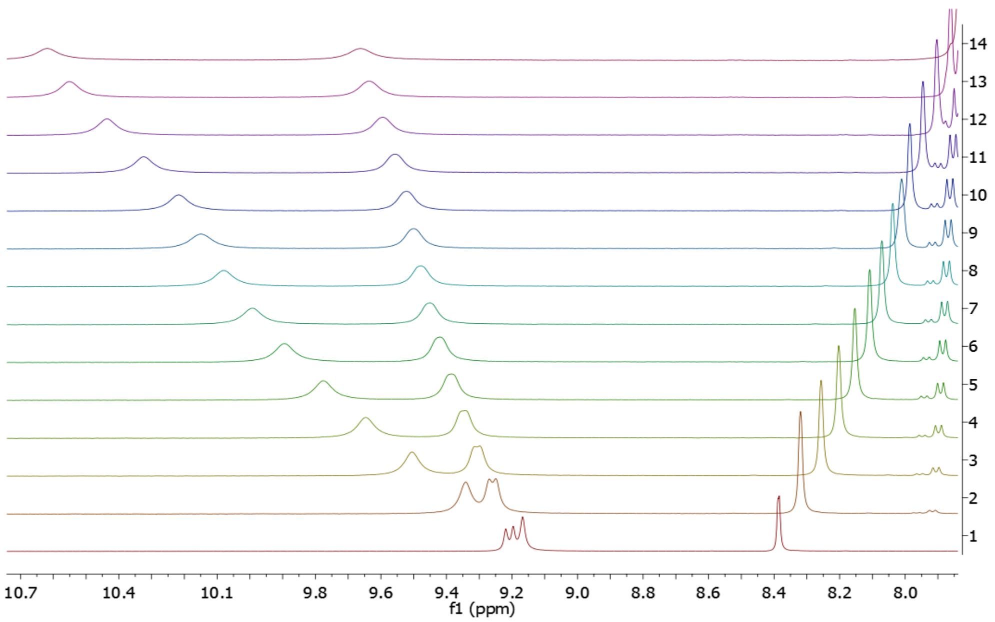
S19. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (S)-MTPA

Number of	equivalents
14	2.58
13	2.17
12	1.71
11	1.40
10	1.18
9	1.06
8	0.94
7	0.82
6	0.69
5	0.59
4	0.43
3	0.29
2	0.15
1	0.00



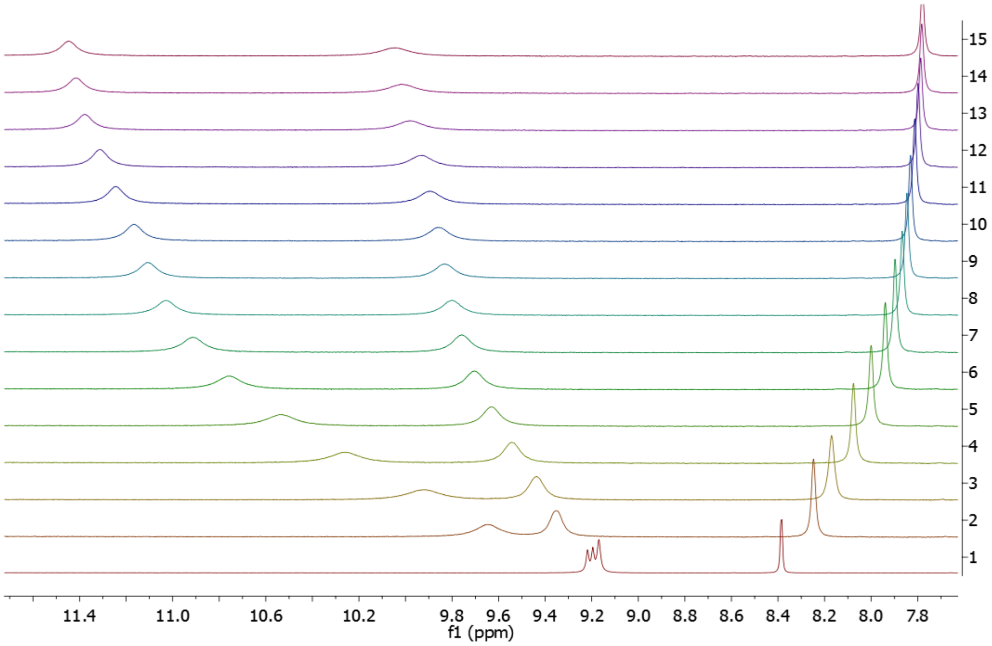
S20. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (L)-AcNPhg

Number of	equivalents
14	2.48
13	2.08
12	1.64
11	1.34
10	1.13
9	1.02
8	0.90
7	0.79
6	0.67
5	0.54
4	0.41
3	0.28
2	0.14
1	0.00



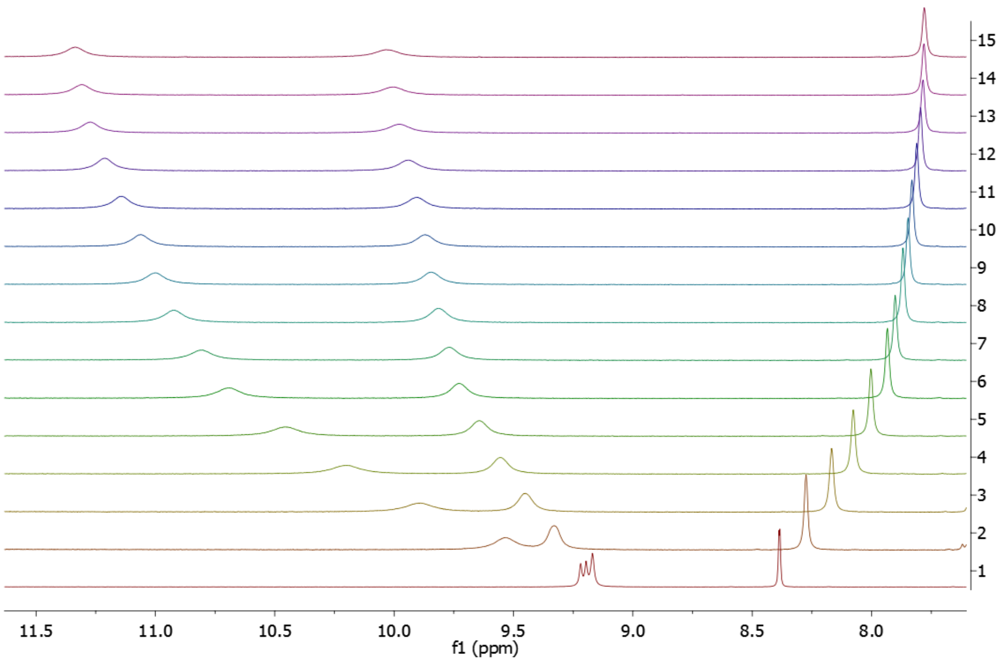
S21. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (D)-AcNPhg

Number of equivalents	
15	4.11
14	3.53
13	2.97
12	2.33
11	1.91
10	1.61
9	1.45
8	1.29
7	1.12
6	0.95
5	0.77
4	0.59
3	0.40
2	0.24
1	0.00



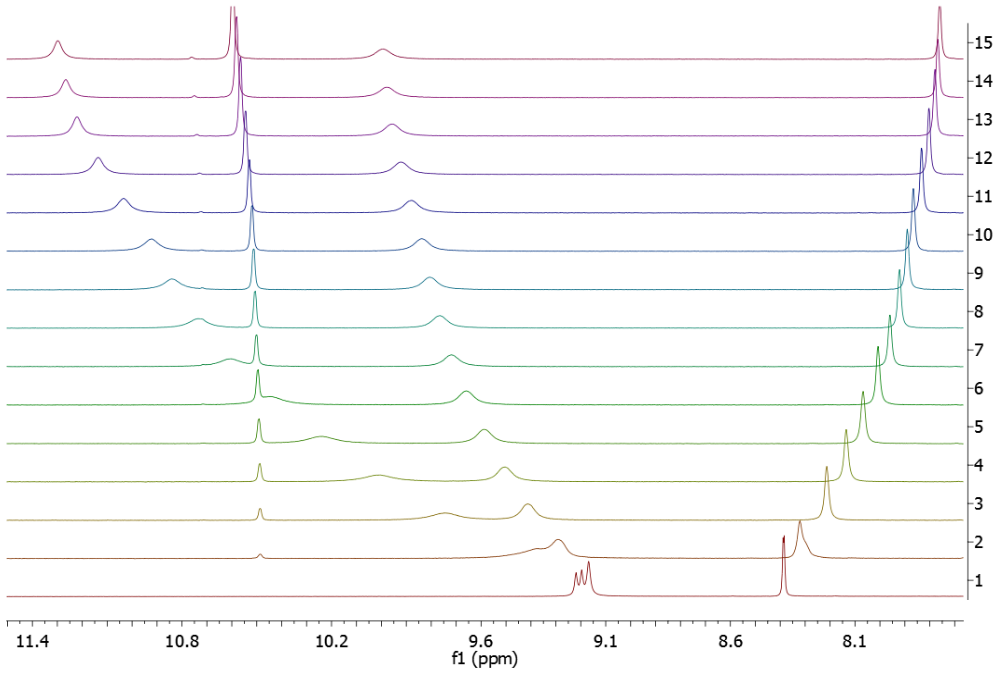
S22. ^1H NMR spectra changes upon titration receptor **1** with TBA (L)-AcNPhe

Number of equivalents	
15	4.0888
14	3.50
13	2.95
12	2.32
11	1.90
10	1.60
9	1.44
8	1.28
7	1.12
6	0.94
5	0.77
4	0.58
3	0.40
2	0.20
1	0.00



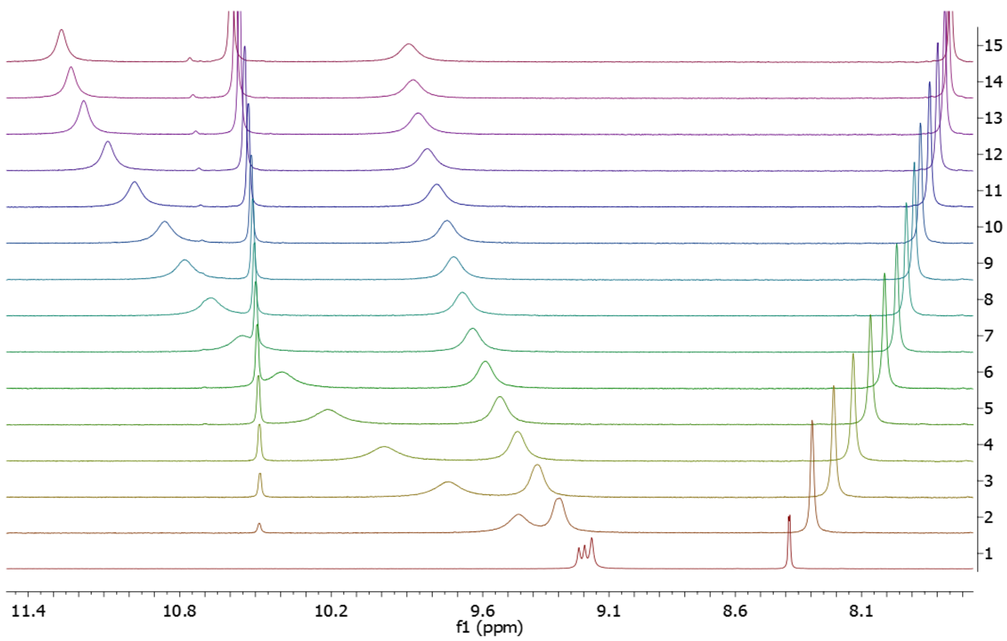
S23. ^1H NMR spectra changes upon titration receptor **1** with TBA (L)-AcNPhe

	Number of equivalents
15	3.40
14	2.92
13	2.46
12	1.93
11	1.58
10	1.33
9	1.20
8	1.07
7	0.93
6	0.79
5	0.64
4	0.49
3	0.33
2	0.17
1	0.00



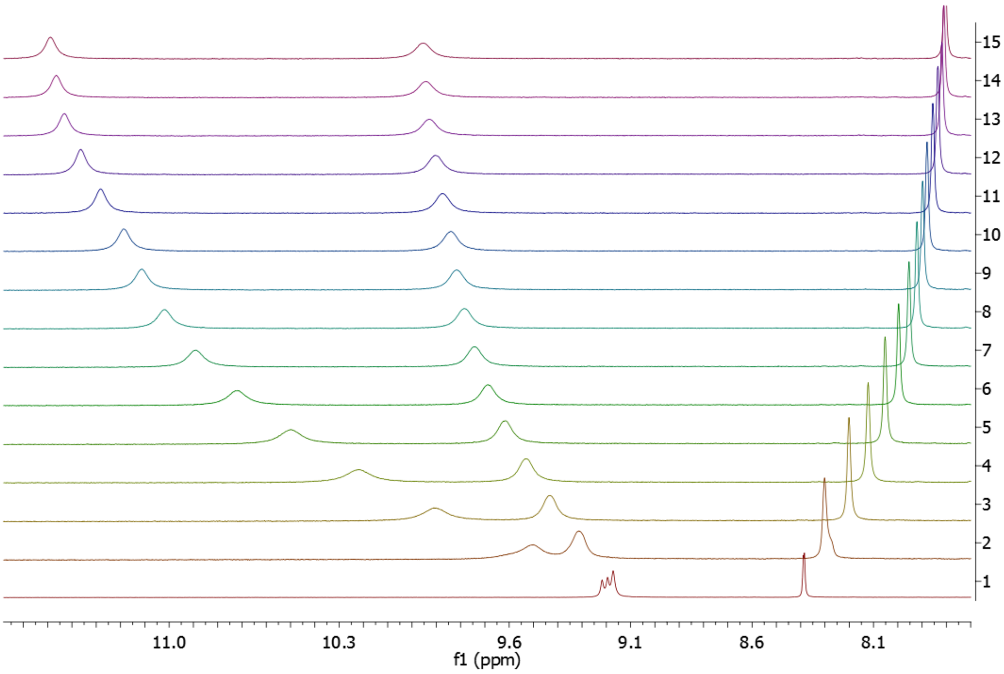
S24. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (L)-AcNTrp

	Number of equivalents
15	3.41
14	2.92
13	2.46
12	1.93
11	1.58
10	1.33
9	1.20
8	1.07
7	0.93
6	0.79
5	0.64
4	0.49
3	0.33
2	0.17
1	0.00



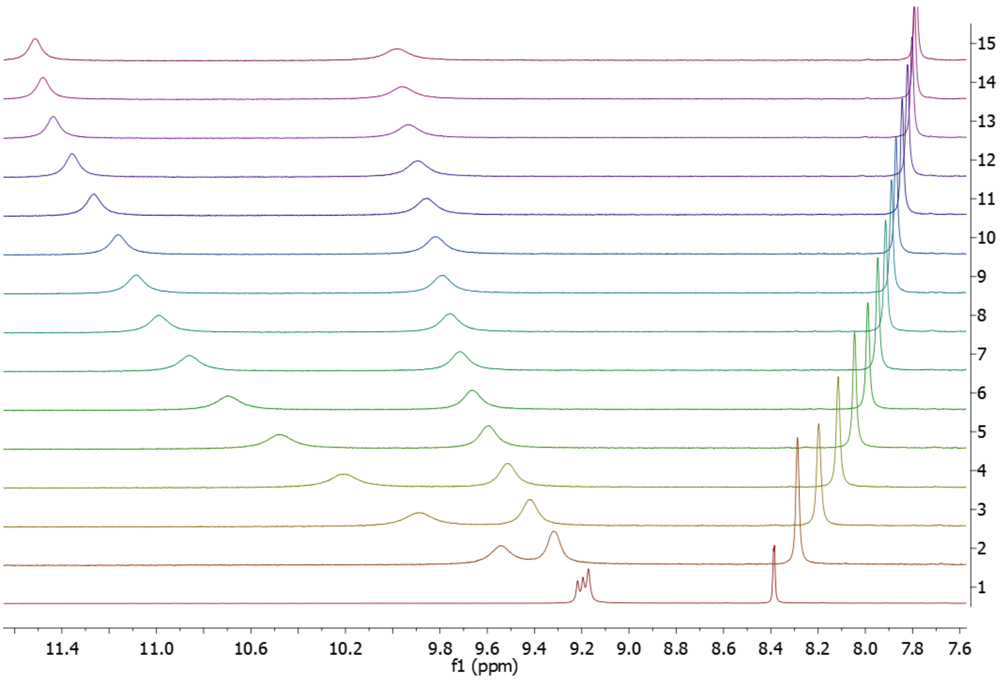
S25. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (D)-AcNTrp

Number of	equivalents
15	3.84
14	3.29
13	2.77
12	2.18
11	1.78
10	1.50
9	1.36
8	1.20
7	1.05
6	0.89
5	0.72
4	0.55
3	0.37
2	0.19
1	0.00



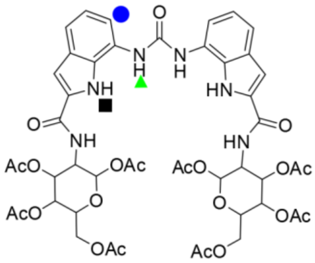
S26. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (L)-AcNVal

Number of	equivalents
15	3.86
14	3.31
13	2.79
12	2.19
11	1.80
10	1.51
9	1.36
8	1.21
7	1.05
6	0.89
5	0.72
4	0.55
3	0.37
2	0.19
1	0.00



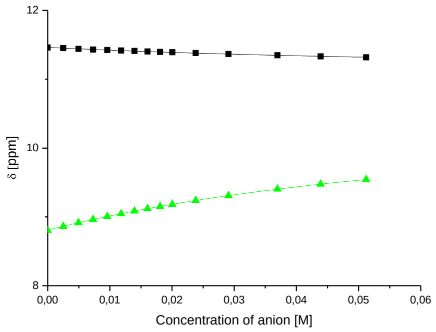
S27. ^{1}H NMR spectra changes upon titration receptor **1** with TBA (D)-AcNVal

S3. The details of ^1H NMR titration in DMSO-d_6 + H_2O: concentrations used, titration curves and the results of data fitting, for receptor **2**

Receptor					
anion	water	L [mol · dm^{-3}]	A [mol · dm^{-3}]	logK	K
Cl^-	0. 5%	0.014796	0.153654	1.21(6)	16
$C_6H_5CO_2^-$	0. 5%	0.014688	0.134718	4.19(5)	>10^4
	5%	0.015014	0.139544	3.24(1)	1742
$CH_3CO_2^-$	0. 5%	0.014688	0.160224	4.22(5)	>10^4
	5%	0.015014	0.157186	3.307(7)	2028
$Ph_2CHCO_2^-$	0. 5%	0.011618	0.13721	3.41(1)	2570
	5%	0.013502	0.143011	2.883(8)	765
$H_2PO_4^-$	0. 5%	0.014796	0.162175	×[a]	×[a]

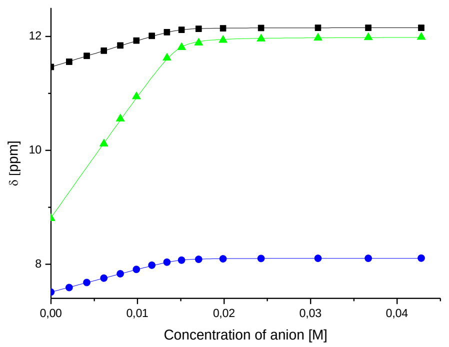
[a]Deprotonation

^1H NMR titrations curves

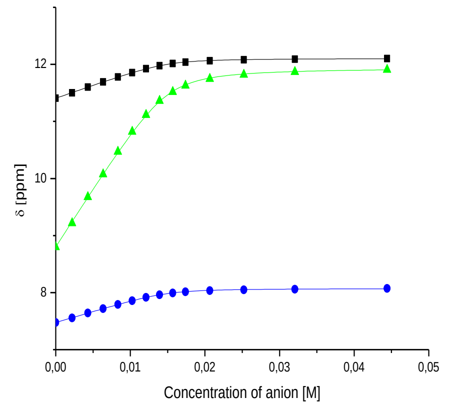


^1H NMR shifts signals upon addition of TBA chloride in DMSO-d_6 + 0.5% H_2O

1H NMR titrations curves

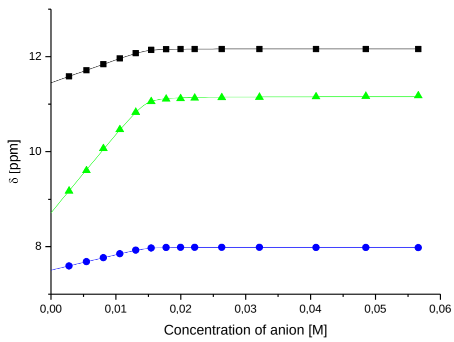


^{1}H NMR shifts signals upon addition of TBA benzoate in DMSO-d_6 + 0.5% H_2O

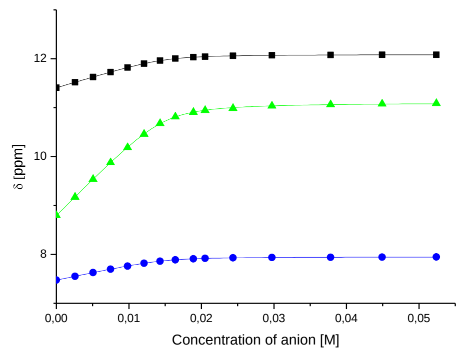


^{1}H NMR shifts signals upon addition of TBA benzoate in DMSO-d_6 + 5% H_2O

1H NMR titrations curves

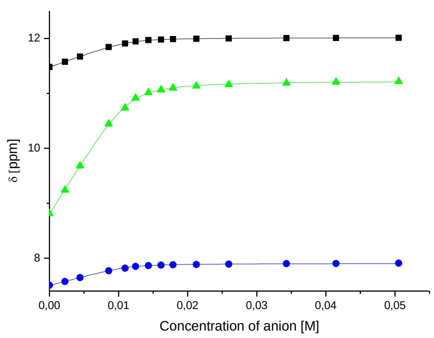


^{1}H NMR shifts signals upon addition of TBA acetate in DMSO-d_6 + 0.5% H_2O

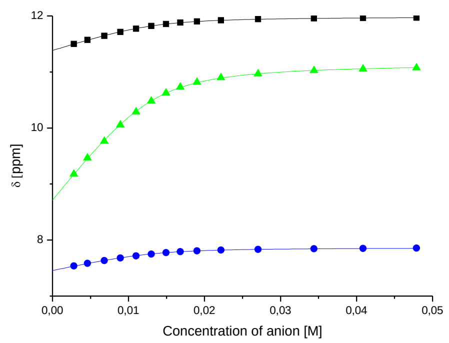


^{1}H NMR shifts signals upon addition of TBA acetate in DMSO-d_6 + 5% H_2O

1H NMR titrations curves

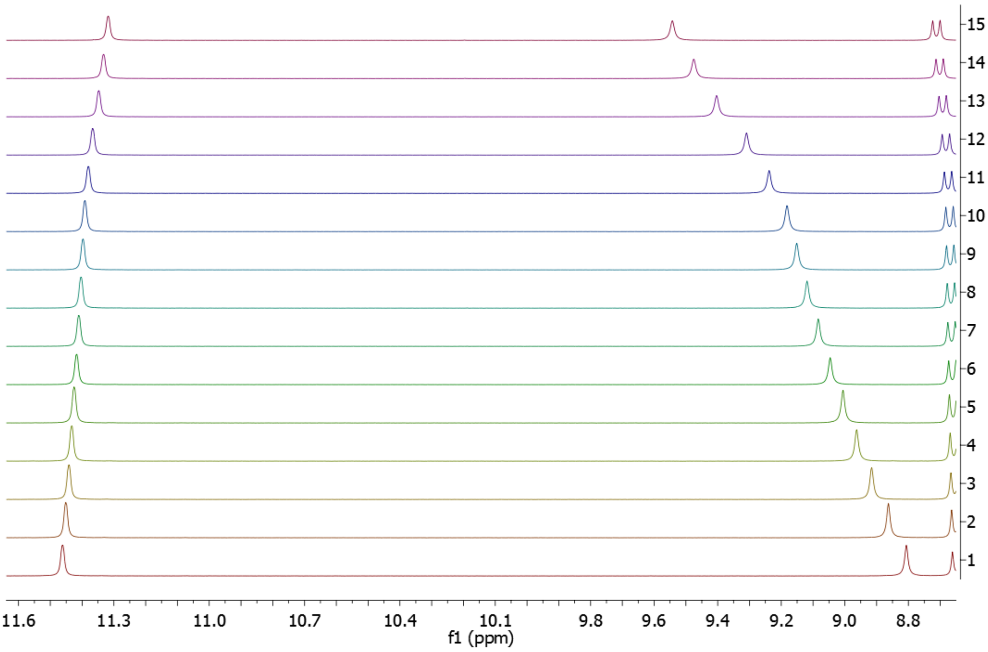


^{1}H NMR shifts signals upon addition of TBA 2,2 – diphenylacetate DMSO-d_6 + 0.5% H_2O



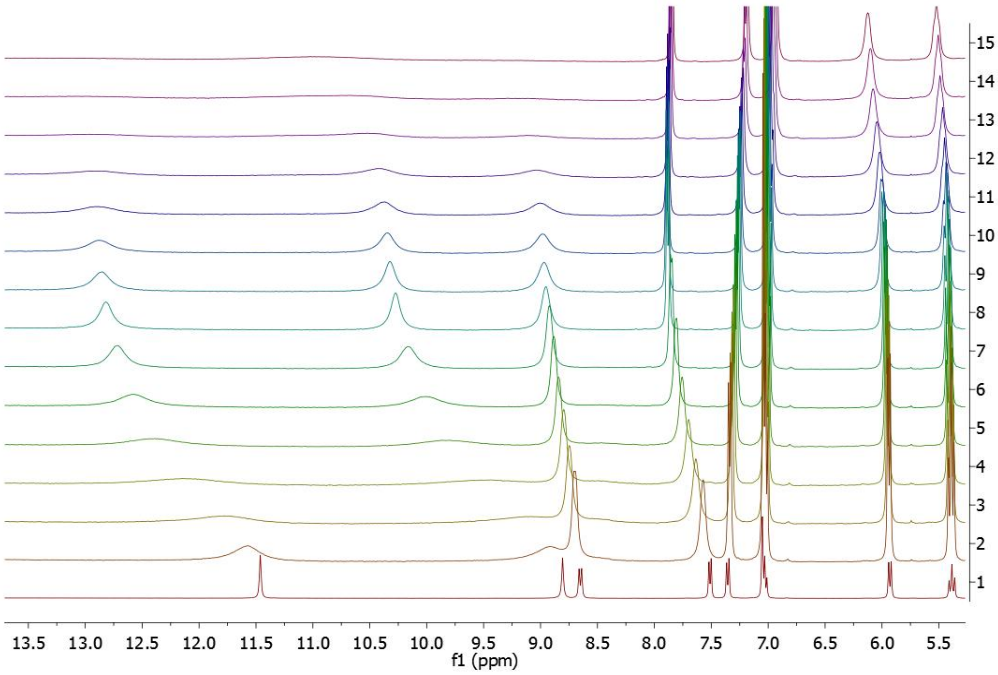
^{1}H NMR shifts signals upon addition of TBA 2,2 – diphenylacetate DMSO-d_6 + 5% H_2O

Number of equivalents	
15	3.46
14	2.97
13	2.50
12	1.96
11	1.61
10	1.35
9	1.22
8	1.08
7	0.94
6	0.80
5	0.65
4	0.49
3	0.34
2	0.17
1	0.00



S28. ^{1}H NMR spectra changes upon titration receptor **2** with TBA chloride in DMSO-d_6 + 0.5% H_2O

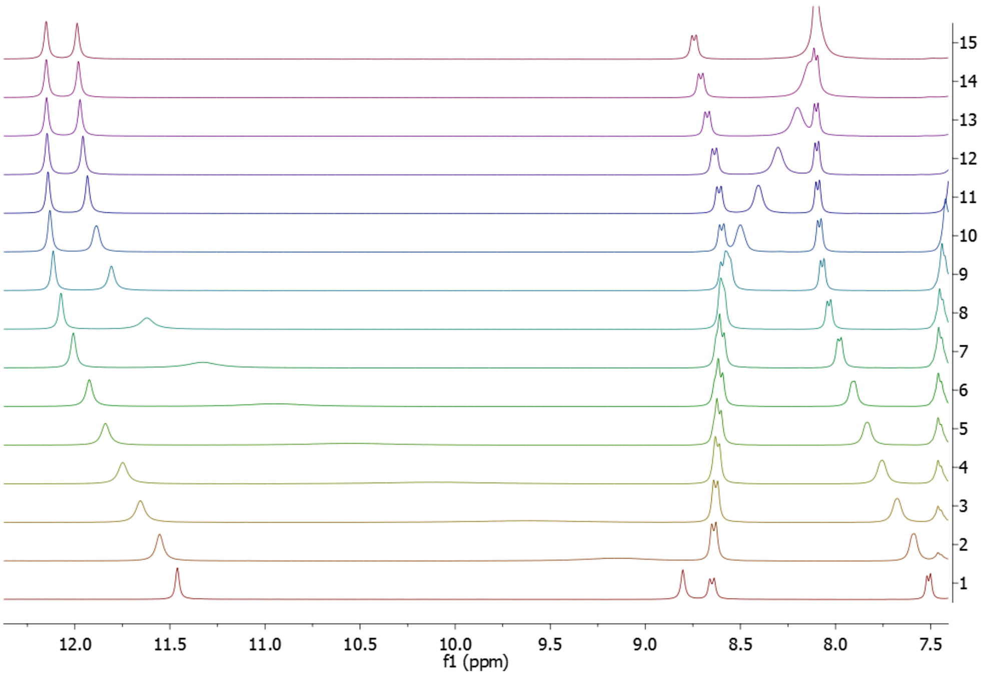
Number of equivalents	
15	3.65
14	3.13
13	2.64
12	2.07
11	1.70
10	1.43
9	1.29
8	1.14
7	1.00
6	0.84
5	0.68
4	0.52
3	0.35
2	0.18
1	0.00



S29. ^{1}H NMR spectra changes upon titration receptor **2** with dihydrogenphosphate in DMSO-d_6 + 0.5% H_2O

Number of equivalents

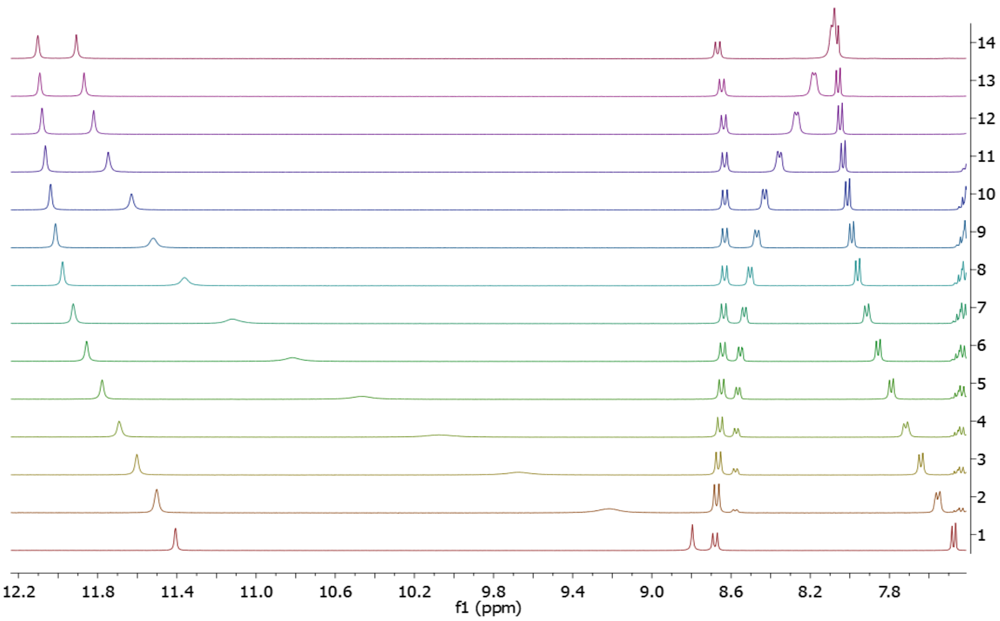
15	3.06
14	2.62
13	2.20
12	1.74
11	1.42
10	1.20
9	1.08
8	0.96
7	0.83
6	0.70
5	0.57
4	0.44
3	0.30
2	0.15
1	0.00



S30. ^{1}H NMR spectra changes upon titration receptor **2** with anions TBA benzoate in DMSO-d_6 + 0.5% H_2O

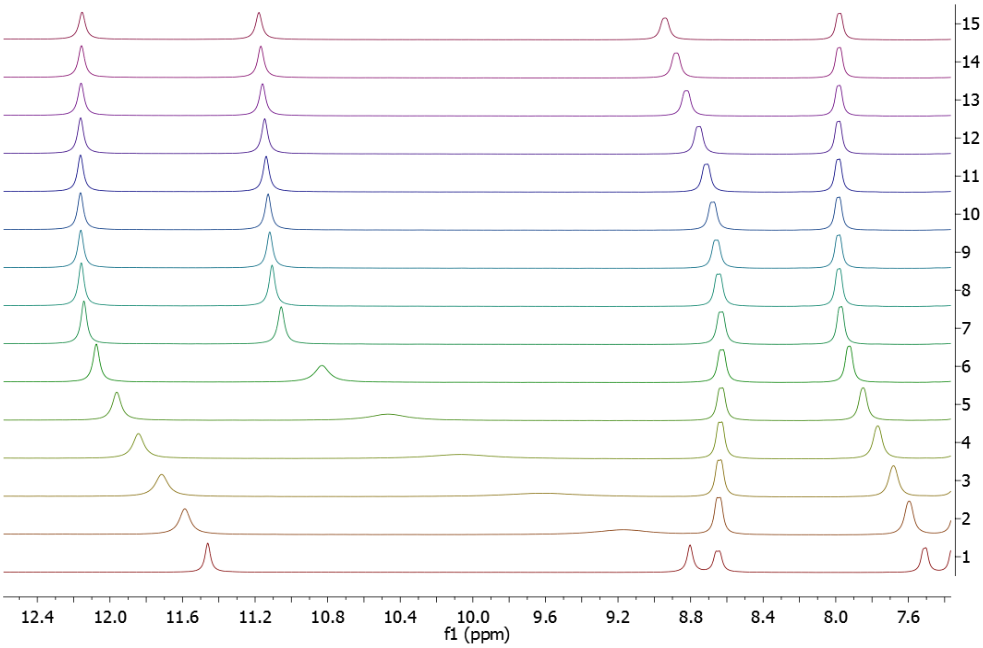
Number of equivalents

14	3.10
13	2.24
12	1.76
11	1.44
10	1.21
9	1.09
8	0.97
7	0.84
6	0.71
5	0.58
4	0.44
3	0.30
2	0.15
1	0.00



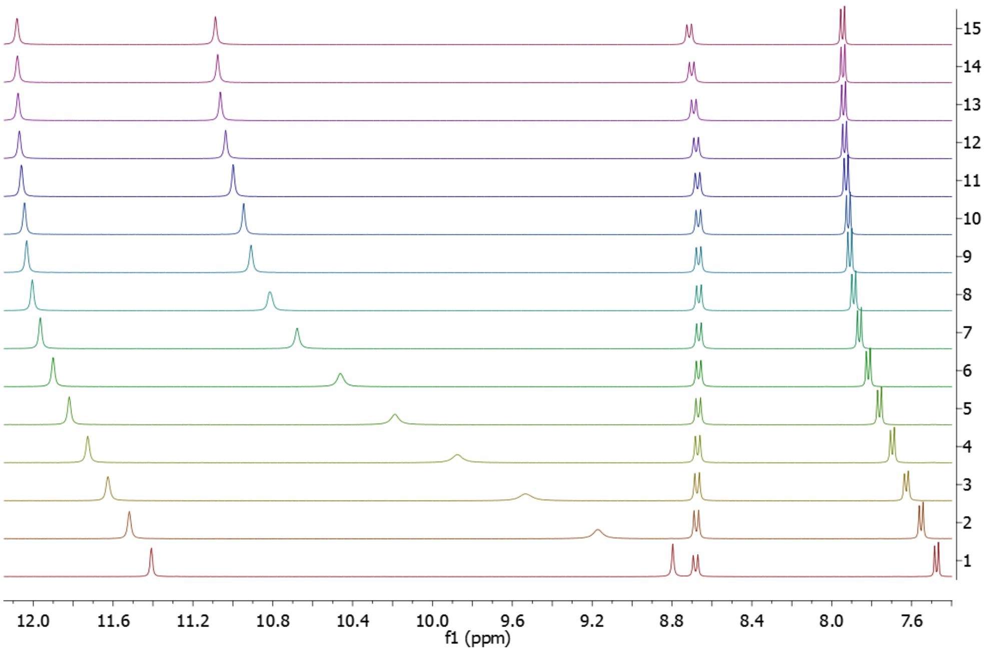
S31. ^{1}H NMR spectra changes upon titration receptor **2** with anions TBA benzoate in DMSO-d_6 + 5% H_2O

Number of equivalents	
15	3.64
14	3.12
13	2.62
12	2.06
11	1.69
10	1.42
9	1.28
8	1.14
7	0.99
6	0.84
5	0.68
4	0.52
3	0.35
2	0.18
1	0.00



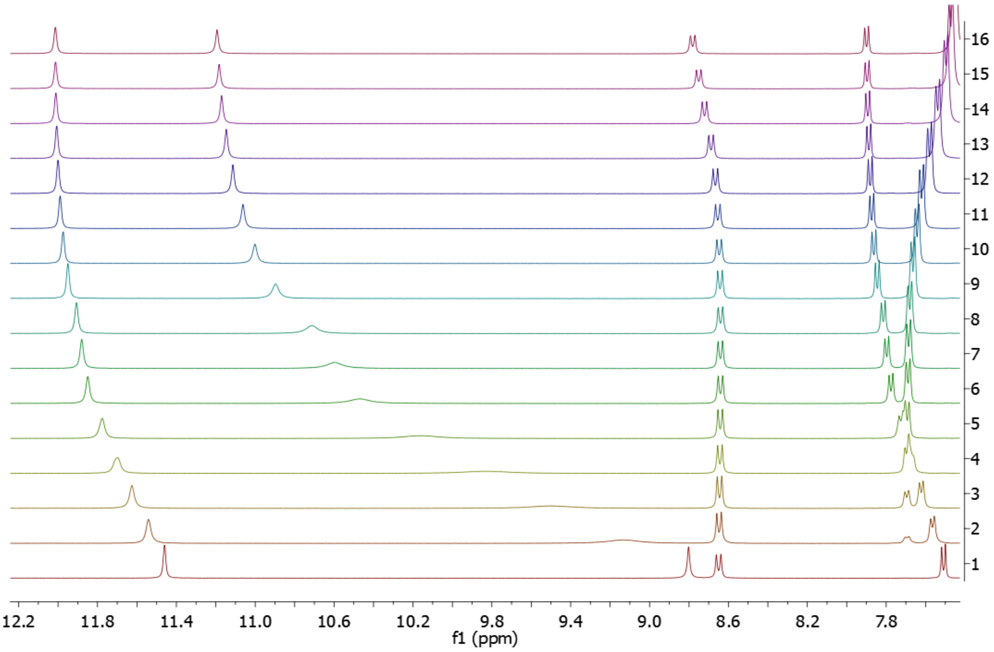
S32. ^1H NMR spectra changes upon titration receptor **2** with anions TBA acetate in DMSO-d_6 + 0.5% H_2O

Number of equivalents	
15	3.49
14	2.99
13	2.52
12	1.98
11	1.62
10	1.36
9	1.26
8	1.09
7	0.95
6	0.80
5	0.65
4	0.50
3	0.34
2	0.17
1	0.00



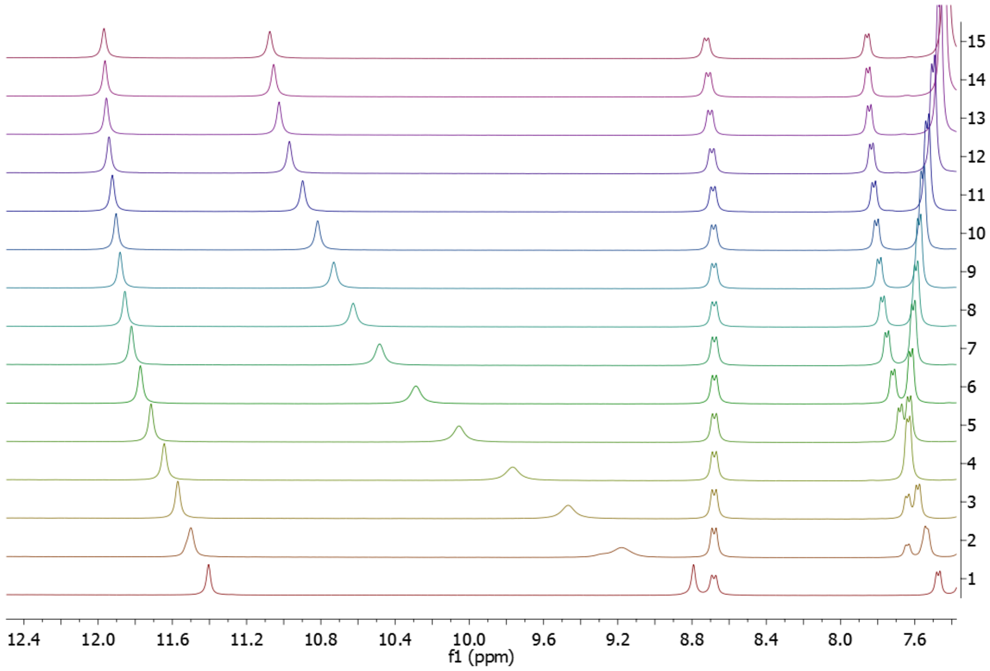
S33. ^1H NMR spectra changes upon titration receptor **2** anions TBA acetate in DMSO-d_6 + 5% H_2O

Number of equivalents	
15	4.35
14	3.57
13	2.95
12	2.23
11	1.83
10	1.54
9	1.39
8	1.23
7	1.07
6	0.94
5	0.74
4	0.60
3	0.38
2	0.19
1	0.00



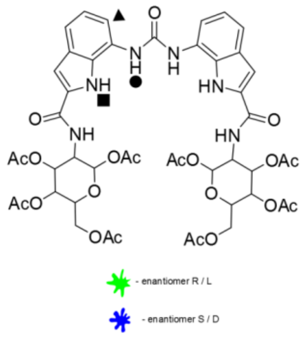
S34. ^{1}H NMR spectra changes upon titration receptor **2** with TBA 2,2-diphenylacetate in DMSO-d_6 + 0.5% H_2O

Number of equivalents	
15	3.55
14	3.03
13	2.55
12	2.00
11	1.64
10	1.41
9	1.25
8	1.11
7	0.96
6	0.81
5	0.66
4	0.50
3	0.34
2	0.21
1	0.00

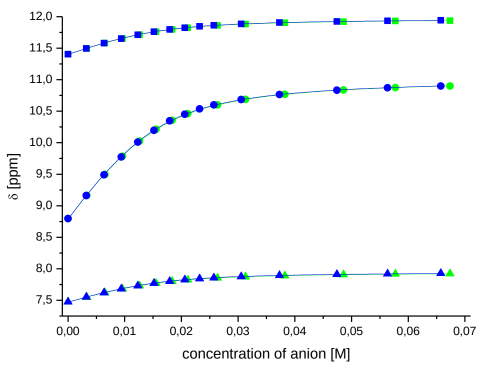
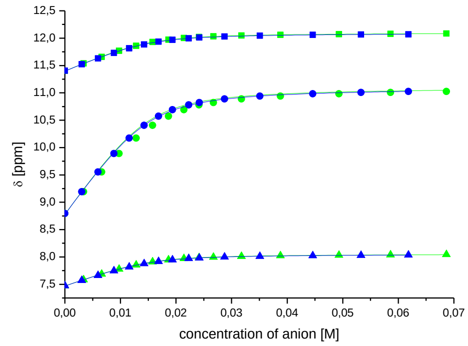
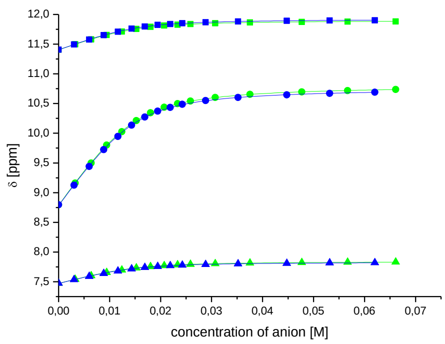
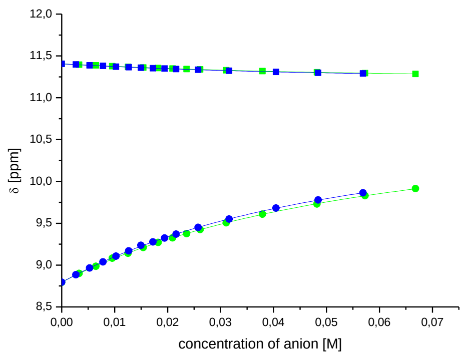


S35. ^{1}H NMR spectra changes upon titration receptor **2** with TBA 2,2-diphenylacetate in DMSO-d_6 + 5% H_2O

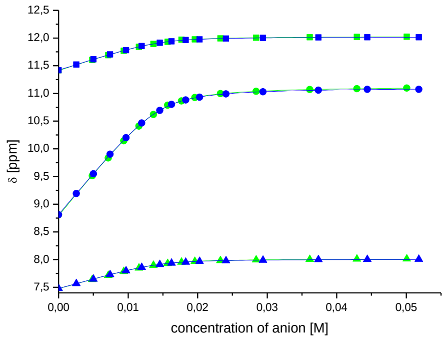
S4. The details of ^{1}H NMR titration in DMSO-d_6 + H_2O: concentrations used, titration curves and the results of data fitting, for receptor **2**

Receptor					
anion	L [mol · dm^{-3}]	A [mol · dm^{-3}]	logK	K	K_S/K_R (K_L/K_D)
(R)-Man	0.015391	0.202118	2.4703	298	1.03
(S) -Man	0.015391	0.197238	2.487(4)	307	
(L)-PhLac	0.015194	0.205062	2.847(9)	704	1.07
(D)-PhLac	0.015194	0.185456	2.817(1)	656	
(R)-MeOMan	0.01483	0.198377	2.695(5)	496	1.04
(S)-MeOMan	0.01483	0.186048	2.711(8)	515	
(R)-MTPA	0.015023	0.200484	1.313(8)	20	1.13
(S)-MTPA	0.015023	0.189655	1.365(7)	23	
(L)-AcNPhg	0.014693	0.150199	3.22(1)	1663	0.91
(D)-AcNPhg	0.014693	0.155414	3.254(7)	1810	
L-AcNPhe	0.01418	0.184201	3.46(1)	2890	1.1

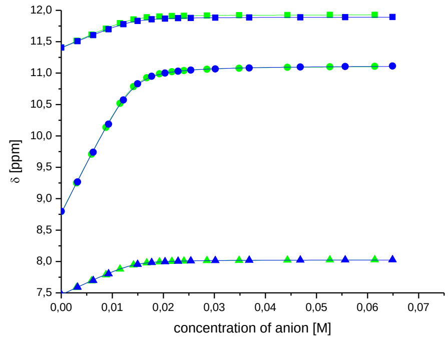
D -AcNPhe	0.01418	0.1947	3.4(2)	2630	
(L)-AcNTrp	0.011423	0.119502	3.43(2)	2705	1.02
(D)–AcNTrp	0.011423	0.106396	3.42(1)	2636	
(L)-AcNVal	0.015331	0.164775	3.59(1)	3900	1.04
(D)-AcNVal	0.015331	0.161986	3.57(2)	3734	

1H NMR titrations curves	 ¹H NMR shifts signals upon addition both enantiomers of TBA Man	 ¹H NMR shifts signals upon addition both enantiomers of TBA PhLac
1H NMR titrations curves	 ¹H NMR shifts signals upon addition both enantiomers of TBA MeOMan	 ¹H NMR shifts signals upon addition both enantiomers of TBA MTPA

1H NMR titrations curves

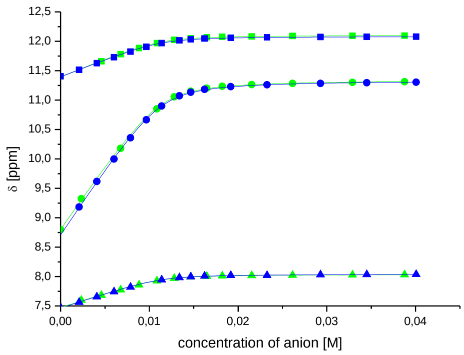


^{1}H NMR shifts signals upon addition both enantiomers of TBA AcNPhg

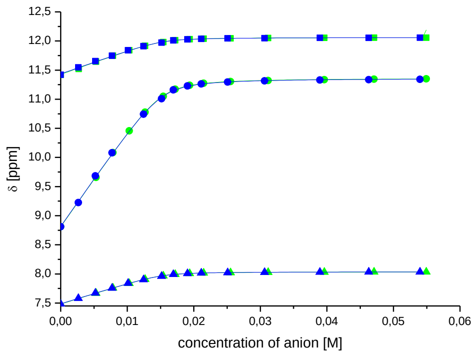


^{1}H NMR shifts signals upon addition both enantiomers of TBA AcNPhe

1H NMR titrations curves

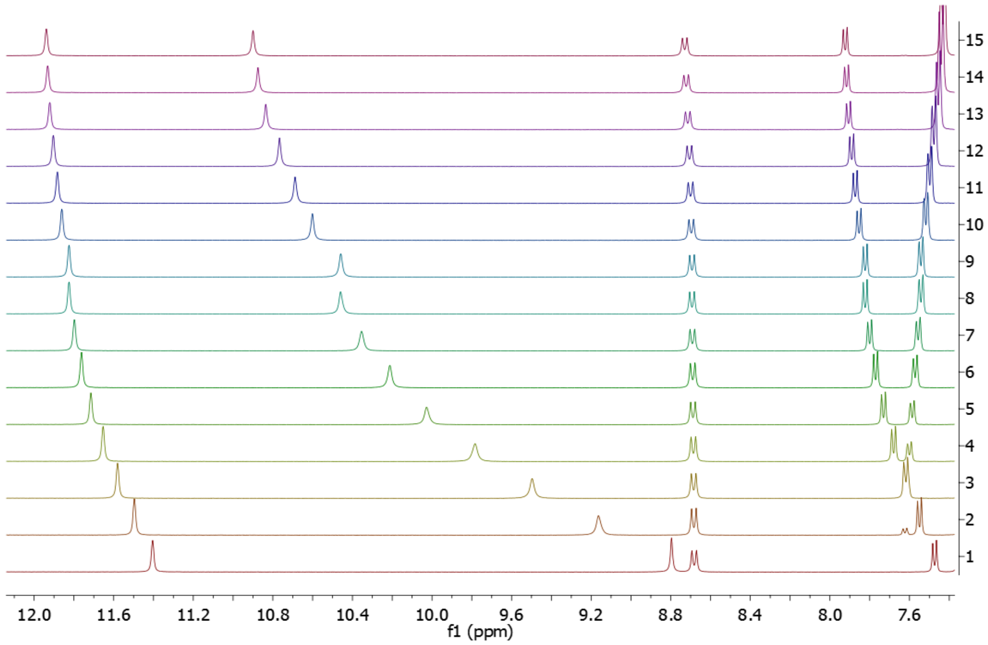


^{1}H NMR shifts signals upon addition both enantiomers of TBA AcNTrp



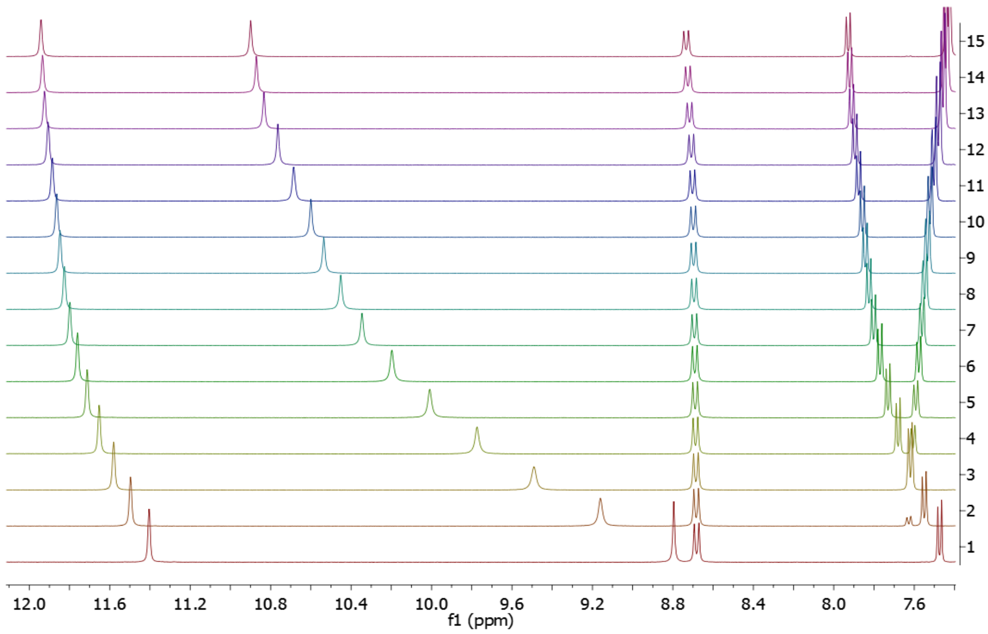
^{1}H NMR shifts signals upon addition both enantiomers of TBA AcNVal

Number of equivalents	
15	4.38
14	3.75
13	3.16
12	2.48
11	2.03
10	1.71
9	1.54
8	1.37
7	1.19
6	1.01
5	0.82
4	0.62
3	0.42
2	0.22
1	0.00



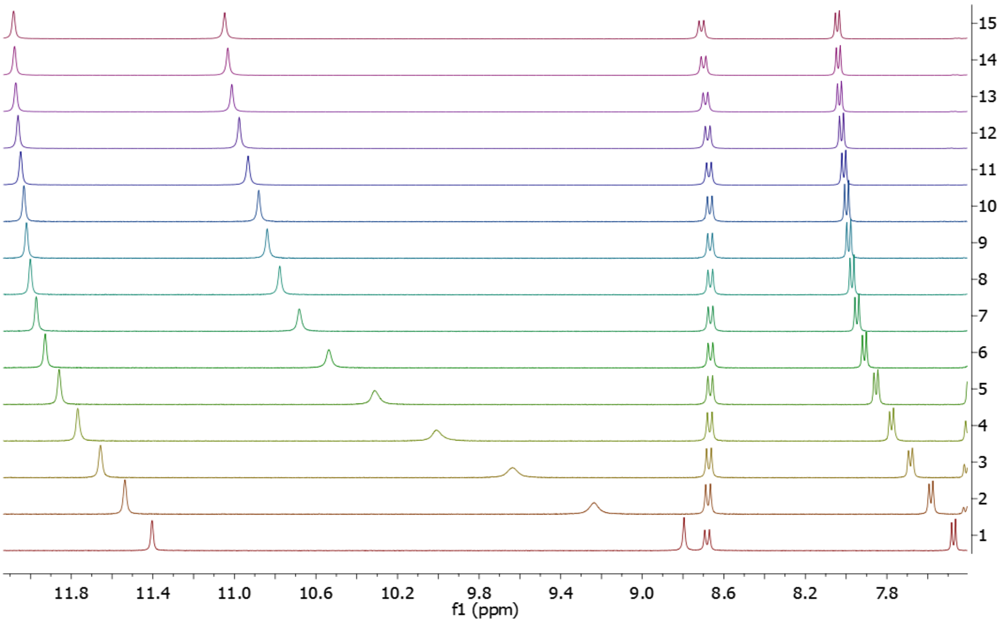
S36. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (R)-Man

Number of equivalents	
15	4.27
14	3.66
13	3.08
12	2.42
11	1.98
10	1.67
9	1.51
8	1.34
7	1.16
6	0.98
5	0.80
4	0.61
3	0.41
2	0.21
1	0.00



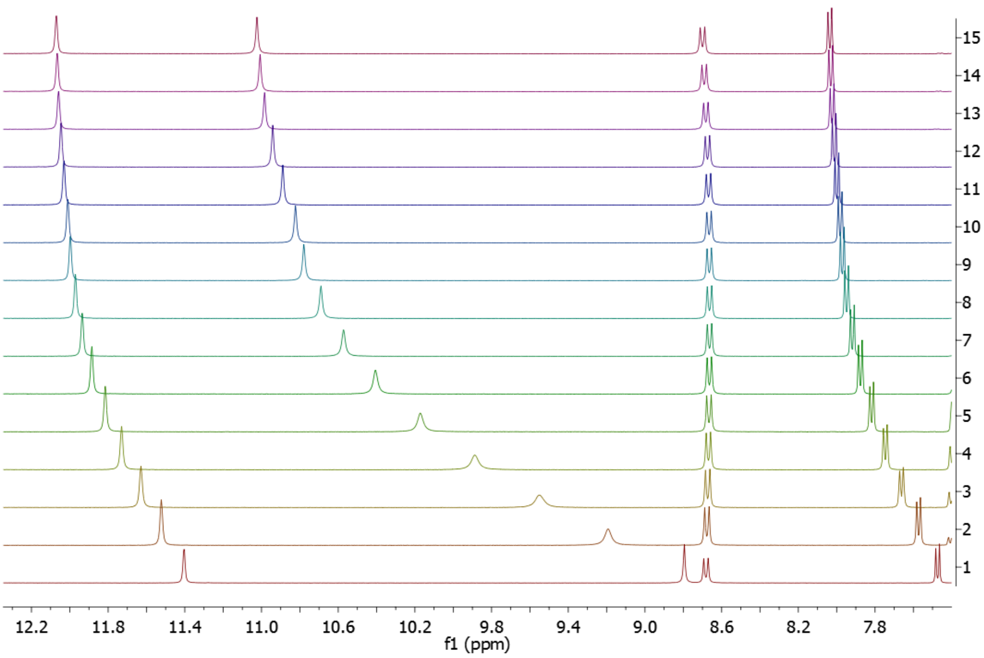
S37. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (S)-Man

Number of	equivalents
15	4.52
14	3.86
13	3.25
12	2.55
11	2.09
10	1.76
9	1.59
8	1.41
7	1.23
6	1.04
5	0.84
4	0.64
3	0.44
2	0.22
1	0.00



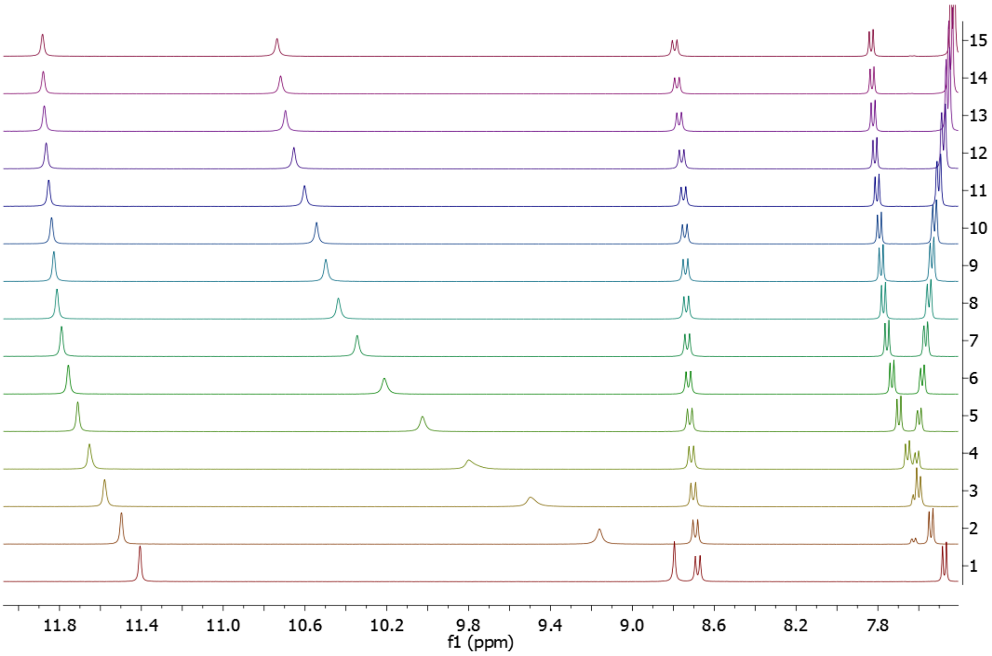
S38. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (L)-PhLac

Number of	equivalents
15	4.07
14	3.51
13	2.94
12	2.31
11	1.89
10	1.59
9	1.47
8	1.28
7	1.11
6	0.94
5	0.76
4	0.58
3	0.39
2	0.20
1	0.00



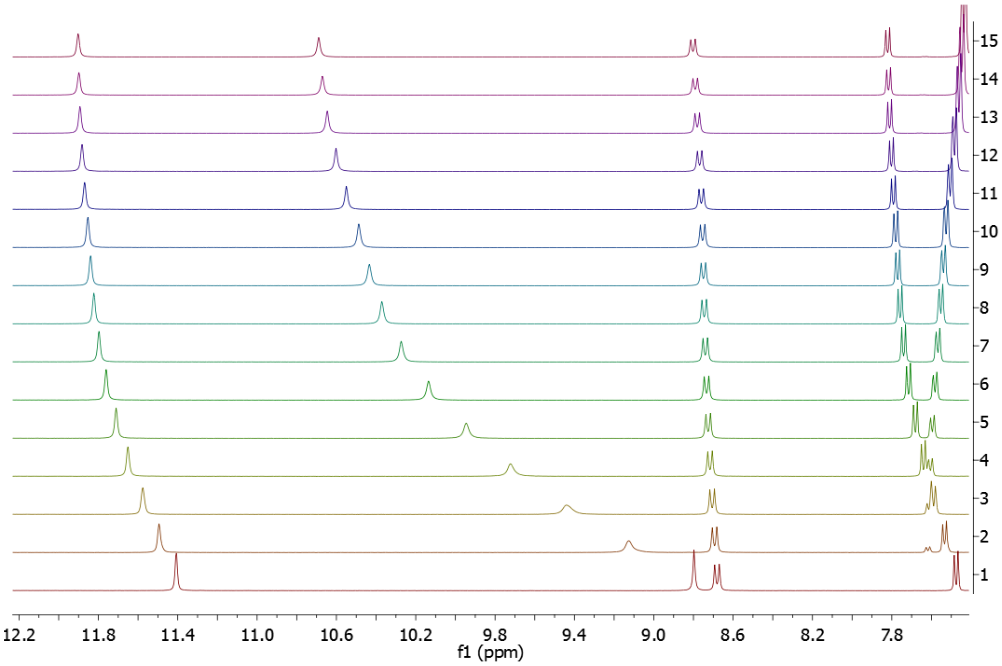
S39. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (D)-PhLac

Number of	equivalents
15	4.46
14	3.82
13	3.22
12	2.53
11	2.07
10	1.74
9	1.57
8	1.40
7	1.22
6	1.03
5	0.84
4	0.64
3	0.43
2	0.22
1	0.00



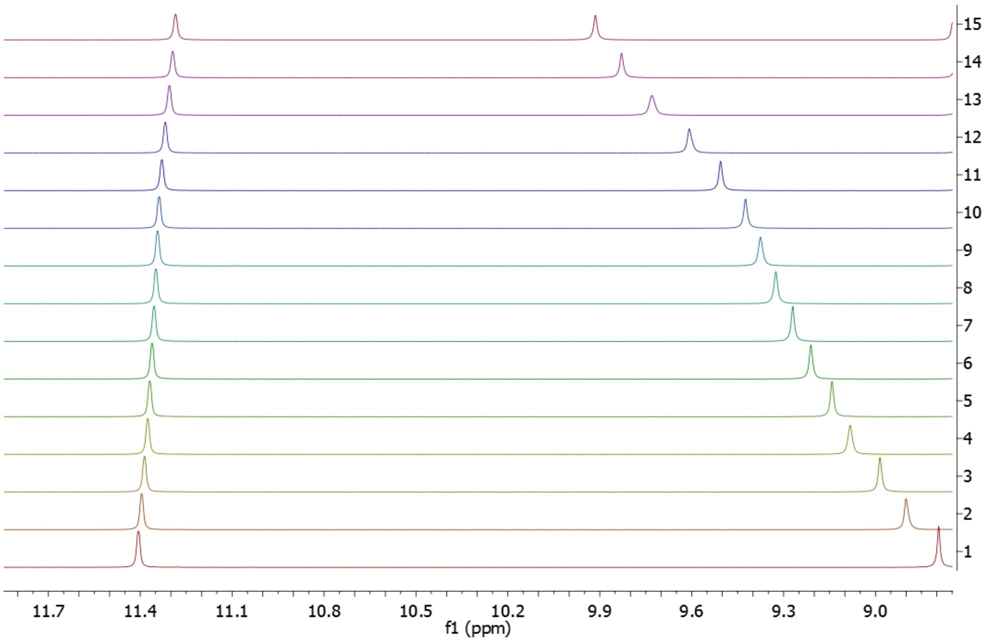
S40. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (R)-MeOMan

Number of	equivalents
15	4.18
14	3.58
13	3.02
12	2.37
11	1.94
10	1.64
9	1.48
8	1.31
7	1.14
6	0.96
5	0.78
4	0.60
3	0.40
2	0.20
1	0.00



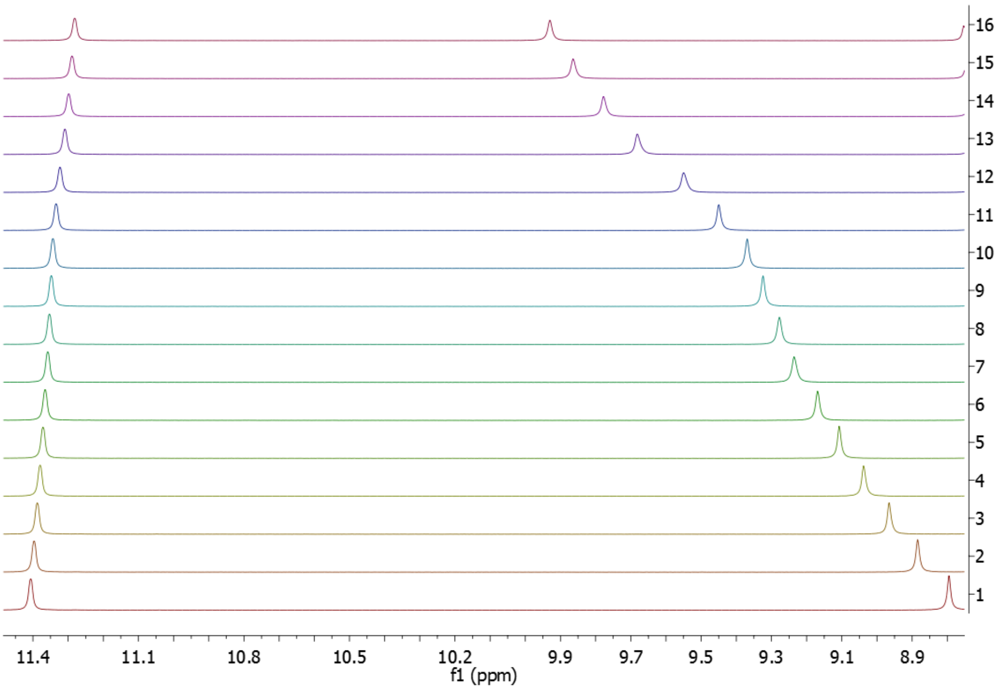
S41. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (S)-MeOMan

Number of	equivalents
15	4.45
14	3.81
13	3.21
12	2.52
11	2.07
10	1.74
9	1.57
8	1.39
7	1.21
6	1.03
5	0.83
4	0.64
3	0.43
2	0.22
1	0.00



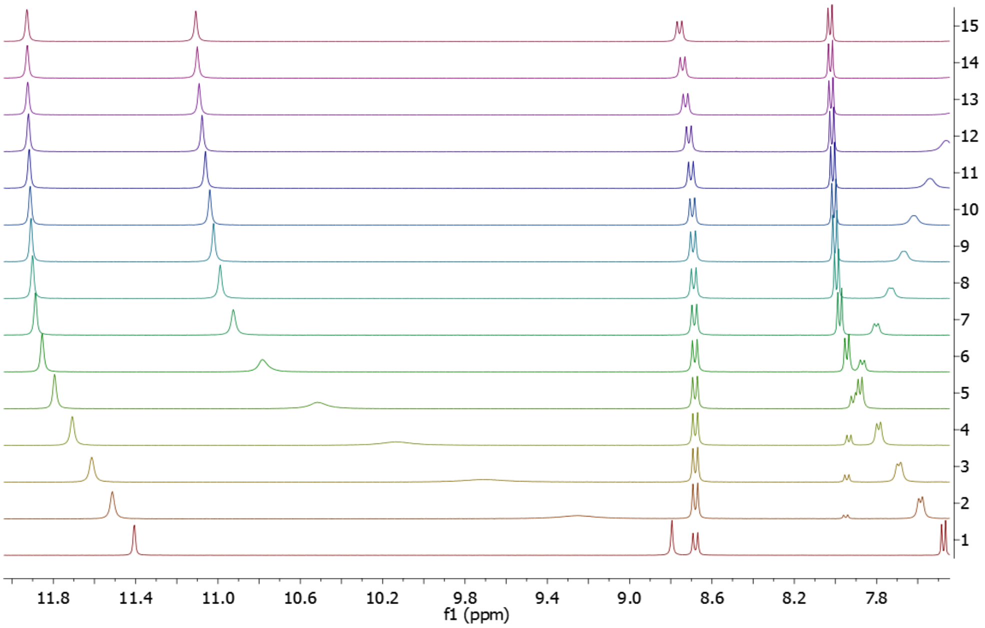
S42. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (R)-MTPA

Number of	equivalents
16	4.29
15	3.79
14	3.22
13	2.70
12	2.10
11	1.71
10	1.44
9	1.29
8	1.15
7	1.00
6	0.84
5	0.68
4	0.52
3	0.35
2	0.18
1	0.00



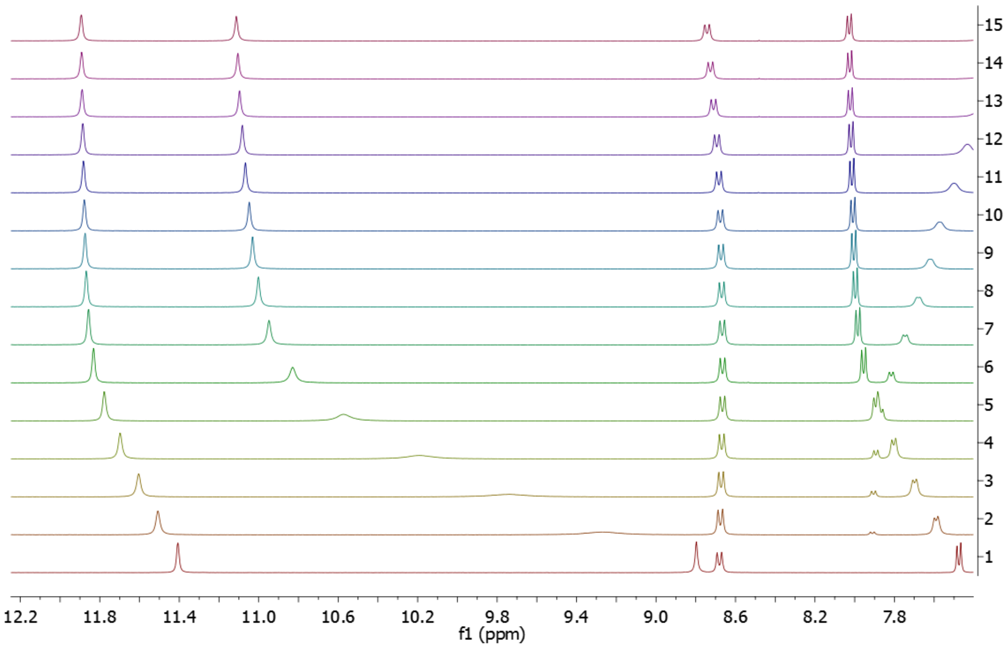
S43. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (S)-MTPA

Number of	equivalents
15	4.33
14	3.71
13	3.12
12	2.46
11	2.01
10	1.69
9	1.53
8	1.36
7	1.18
6	1.00
5	0.81
4	0.62
3	0.42
2	0.21
1	0.00



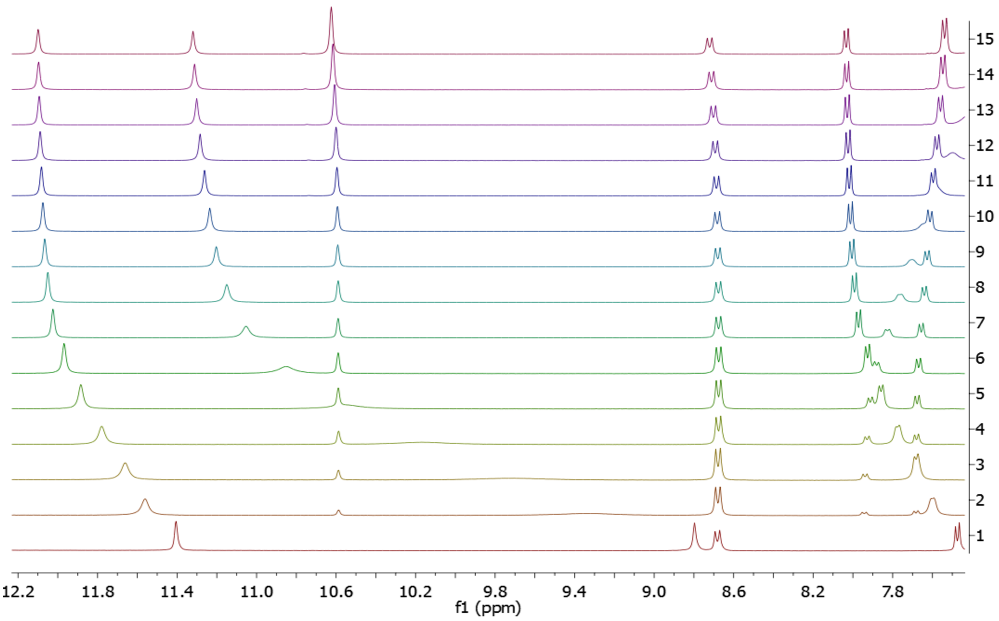
S44. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (L)-AcNPhe

Number of	equivalents
15	4.58
14	3.92
13	3.30
12	2.60
11	2.13
10	1.79
9	1.62
8	1.43
7	1.25
6	1.06
5	0.83
4	0.65
3	0.44
2	0.22
1	0.00



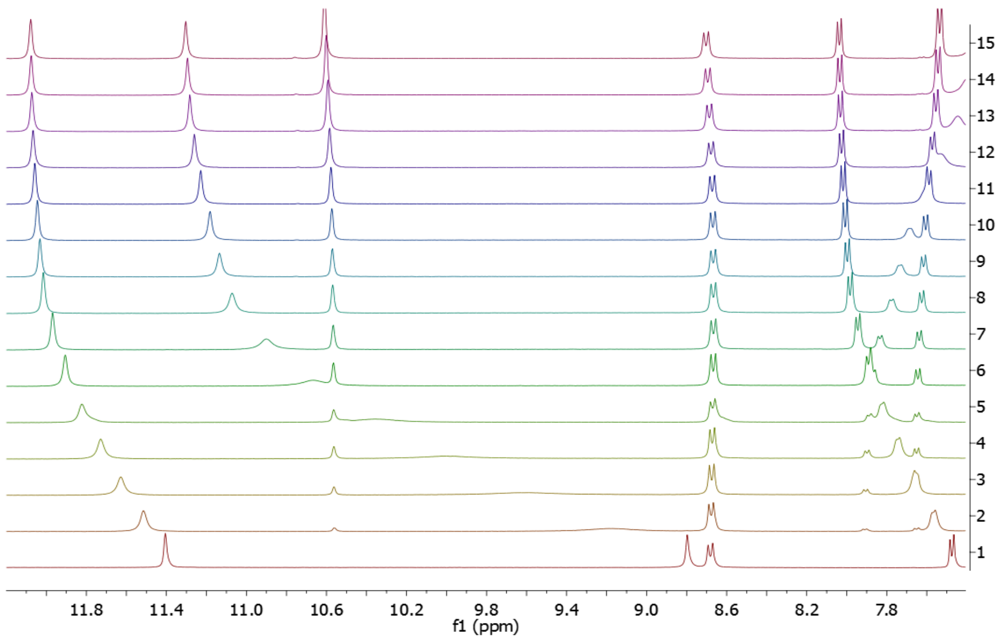
S45. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (D)-AcNPhe

Number of equivalents	
15	3.92
14	3.39
13	2.88
12	2.29
11	1.89
10	1.60
9	1.44
8	1.28
7	1.12
6	0.95
5	0.77
4	0.59
3	0.40
2	0.20
1	0.00



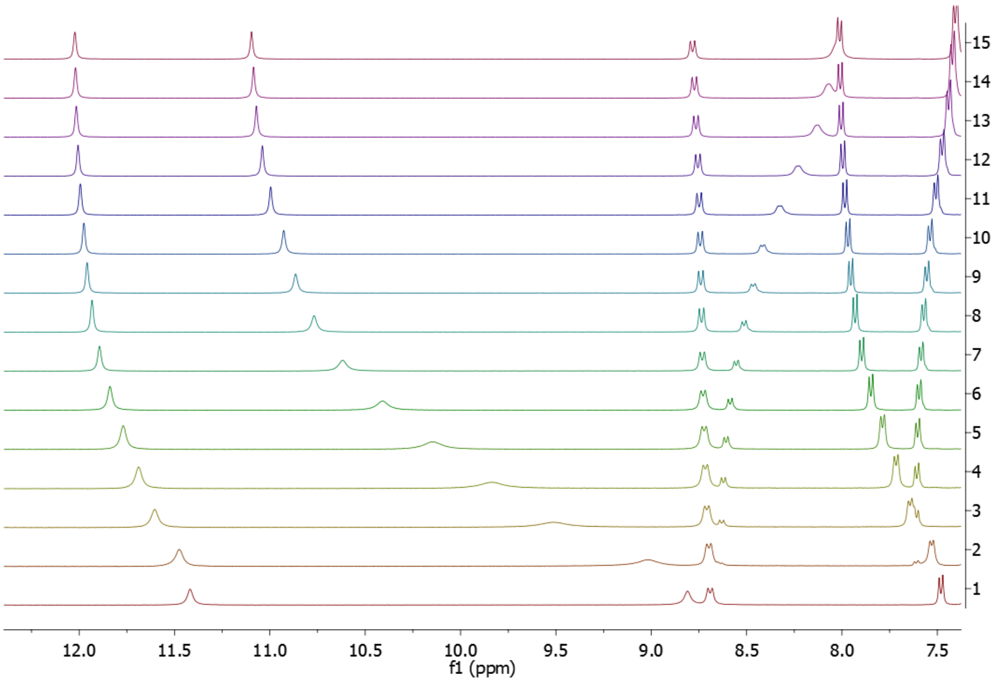
S46. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (L)-AcNTrp

Number of equivalents	
15	3.51
14	3.02
13	2.56
12	2.04
11	1.68
10	1.42
9	1.28
8	1.17
7	1.00
6	0.85
5	0.70
4	0.53
3	0.36
2	0.18
1	0.00



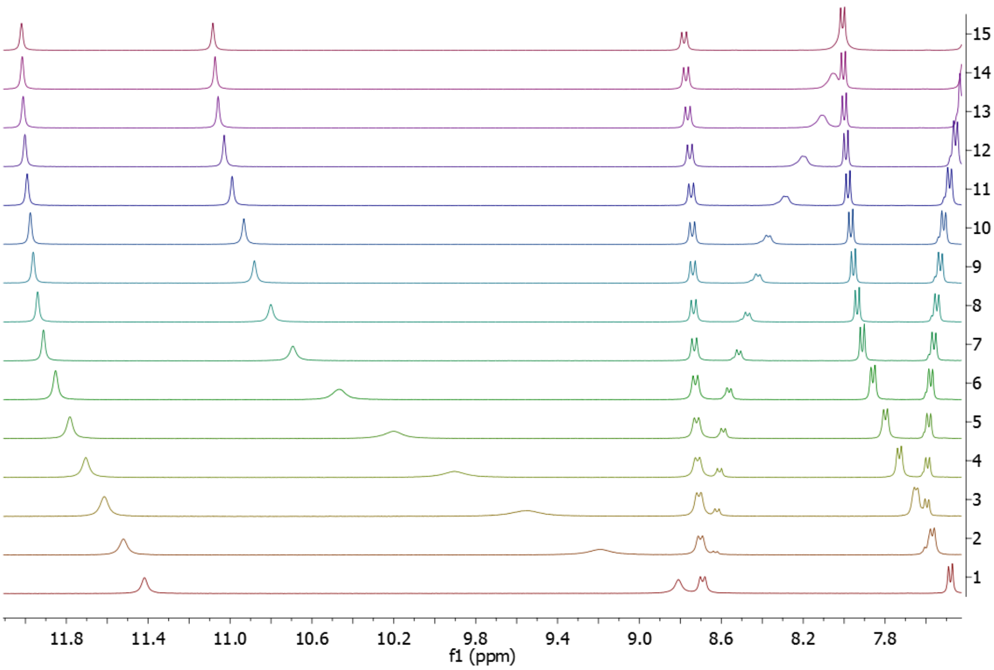
S47. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (D)-AcNTrp

Number of	equivalents
15	3.41
14	2.92
13	2.46
12	1.93
11	1.58
10	1.33
9	1.20
8	1.07
7	0.93
6	0.79
5	0.64
4	0.49
3	0.33
2	0.17
1	0.00



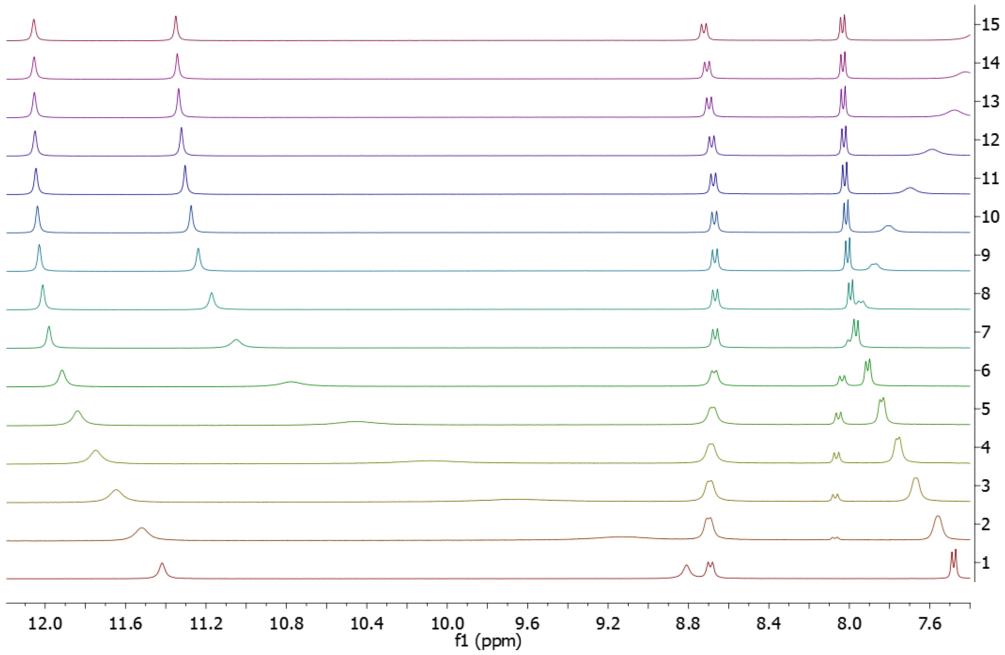
S48. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (L)-AcNTrp

Number of	equivalents
15	3.52
14	3.02
13	2.54
12	2.00
11	1.64
10	1.38
9	1.24
8	1.10
7	0.99
6	0.81
5	0.66
4	0.50
3	0.34
2	0.17
1	0.00



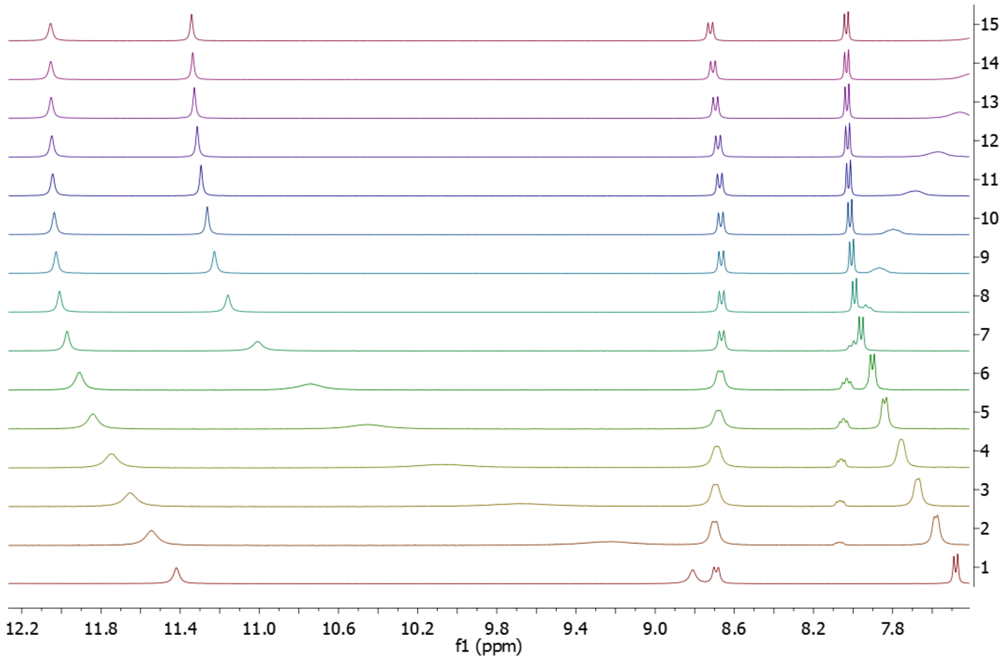
S49. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (D)-AcNTrp

	Number of equivalents
15	3.58
14	3.07
13	2.58
12	2.03
11	1.66
10	1.40
9	1.26
8	1.12
7	1.01
6	0.83
5	0.67
4	0.51
3	0.35
2	0.18
1	0.00



S50. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (L)-AcNVal

	Number of equivalents
15	3.52
14	3.02
13	2.54
12	2.00
11	1.64
10	1.38
9	1.24
8	1.10
7	0.99
6	0.81
5	0.66
4	0.50
3	0.34
2	0.17
1	0.00

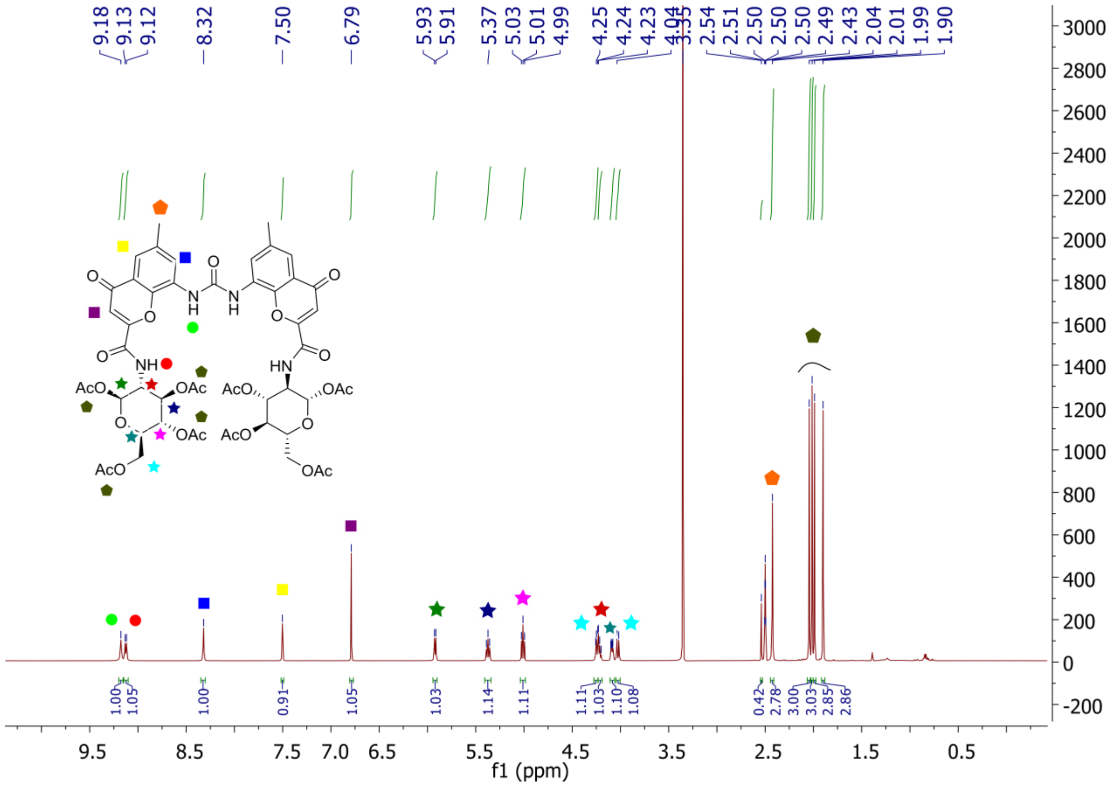


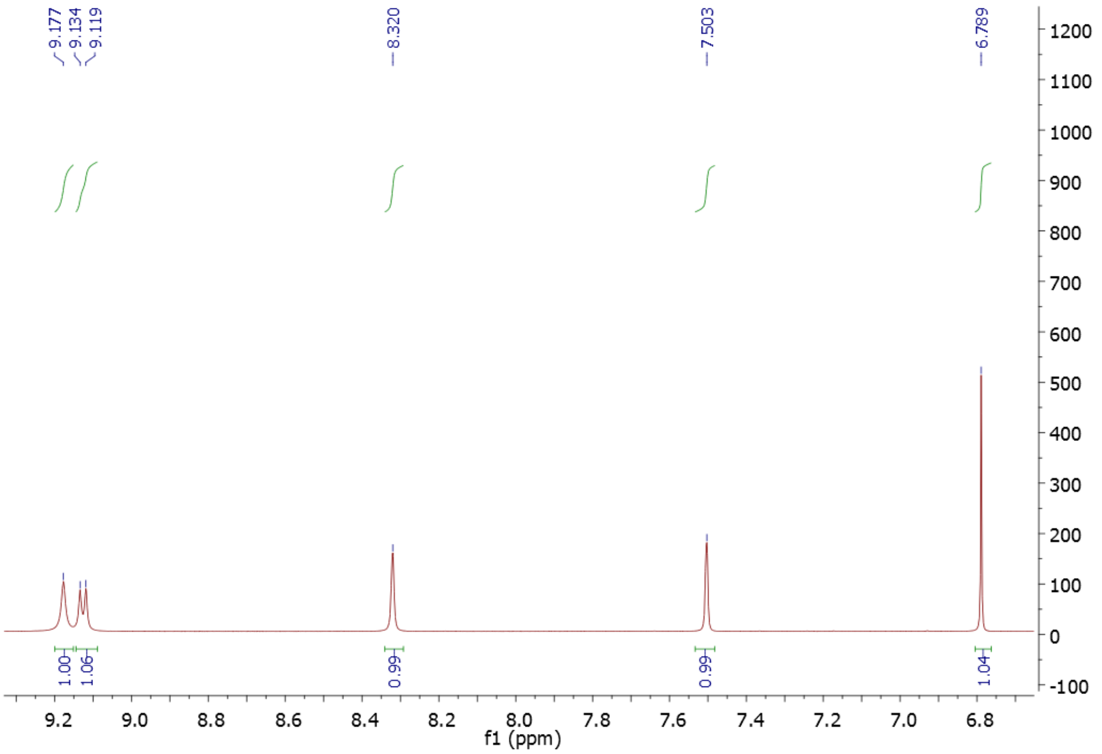
S51. ^{1}H NMR spectra changes upon titration receptor **2** with TBA (D)-AcNVal

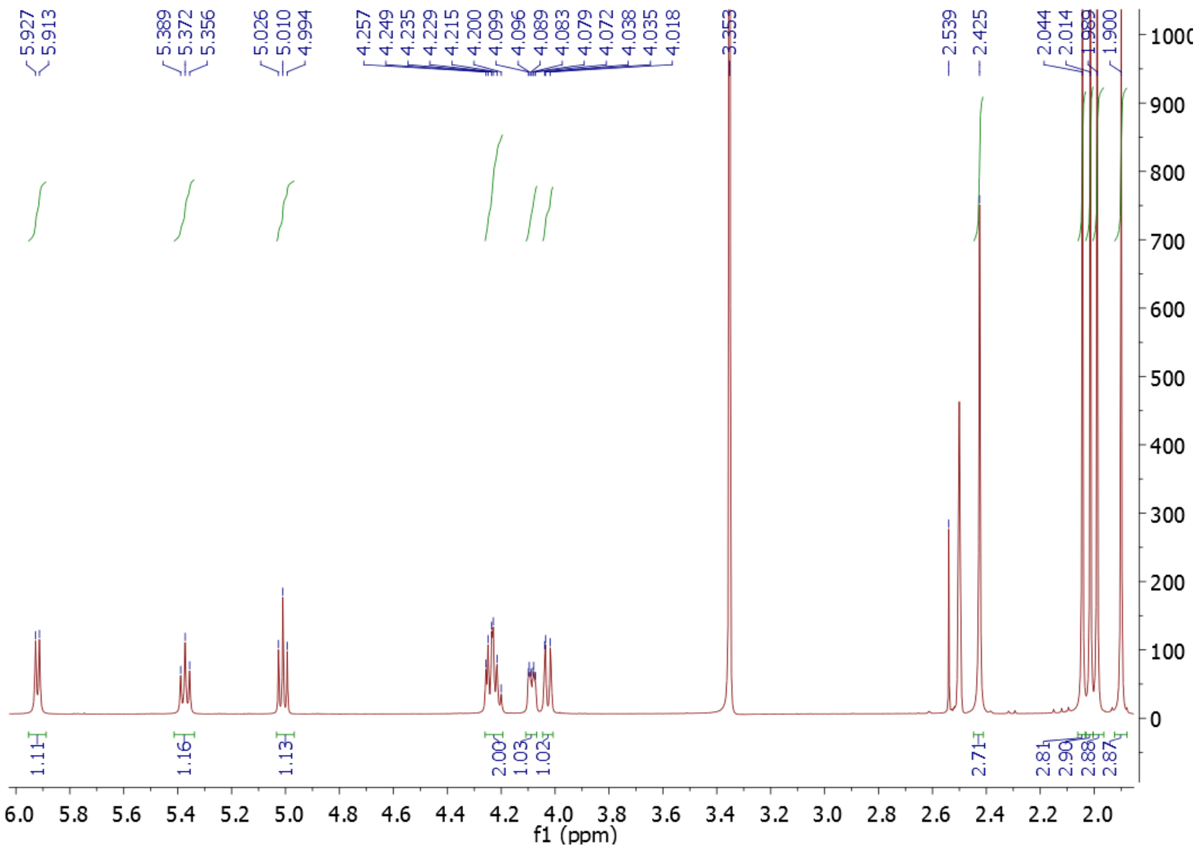
NMR SPECTRA

Receptor 1

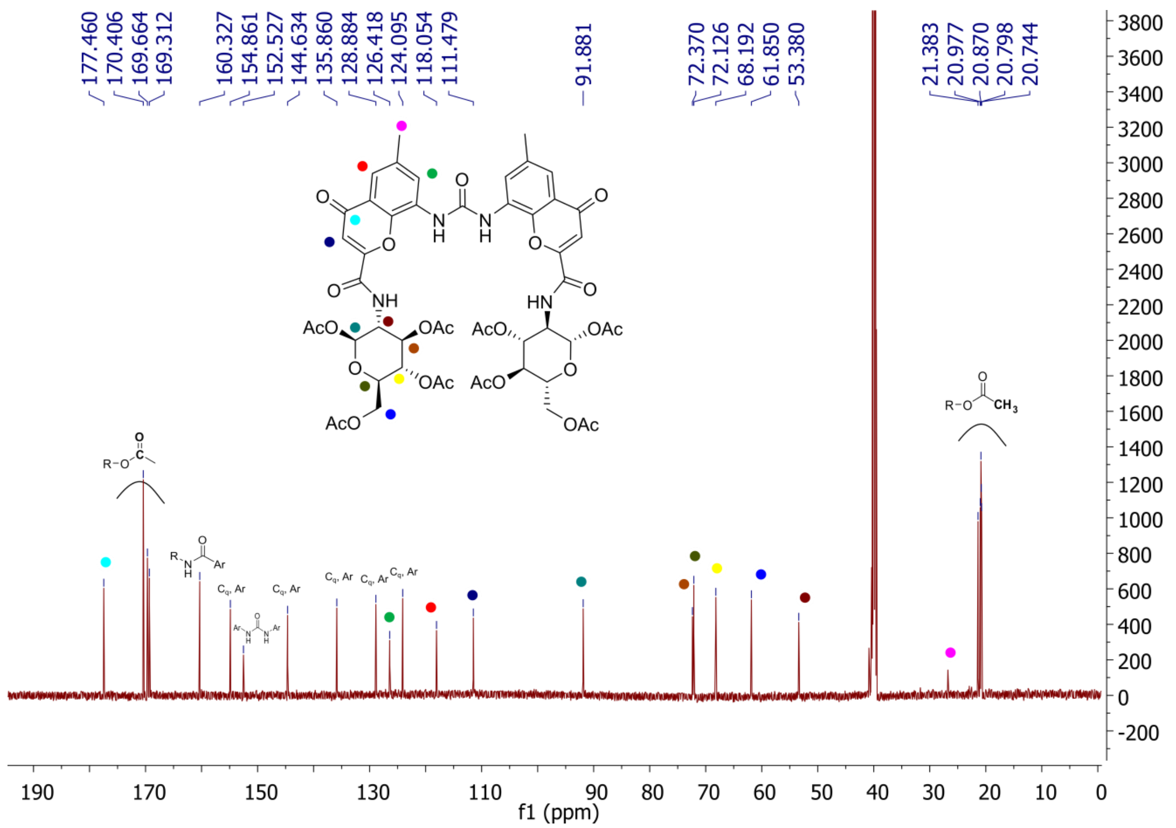
^{1}H NMR (600 MHz, DMSO)





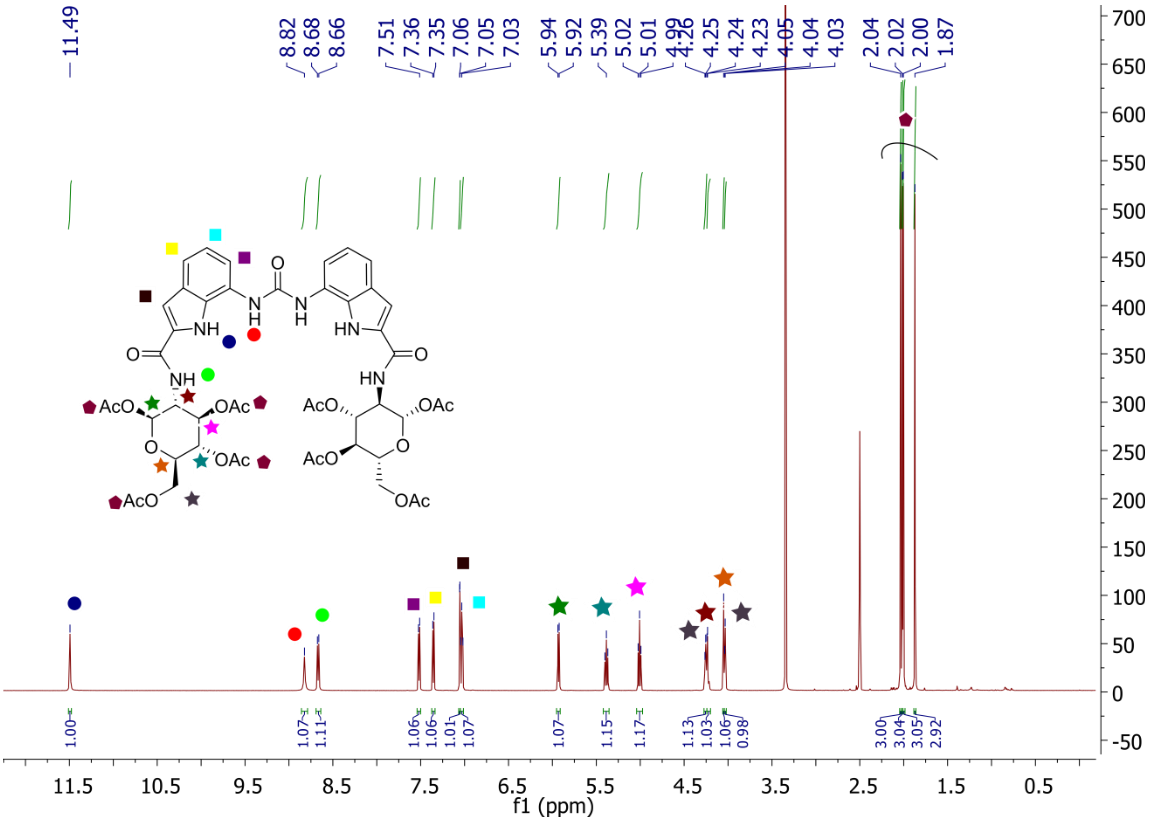


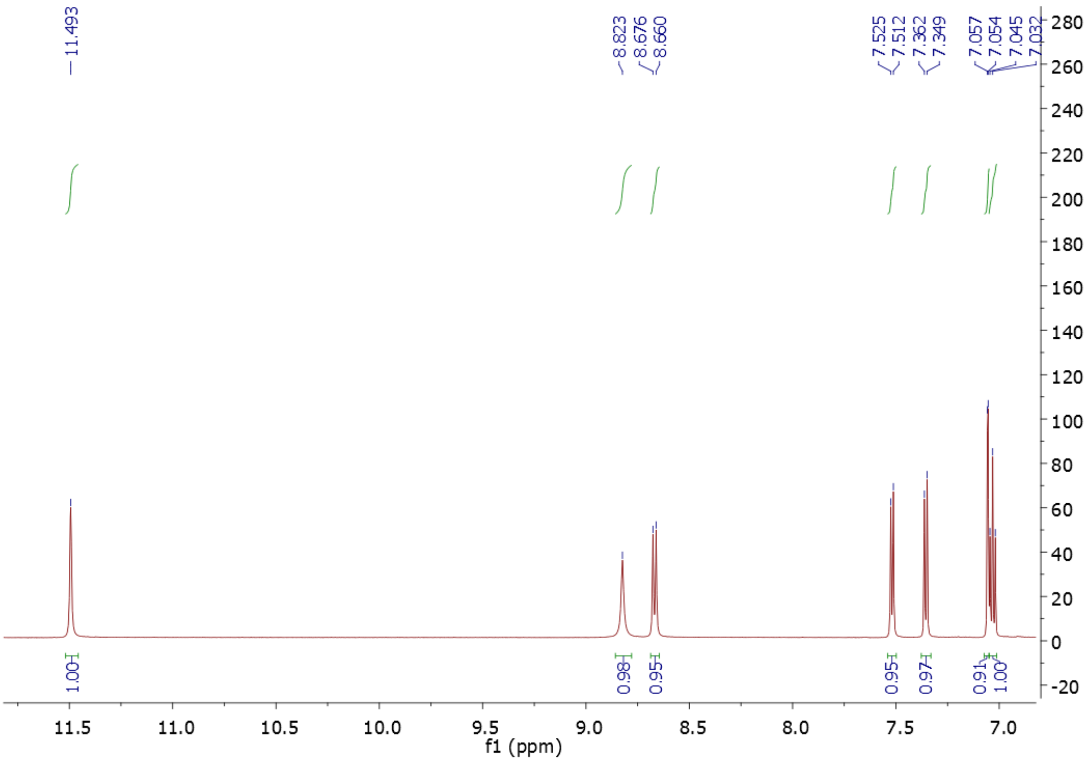
^{13}C (151MHz, DMSO)

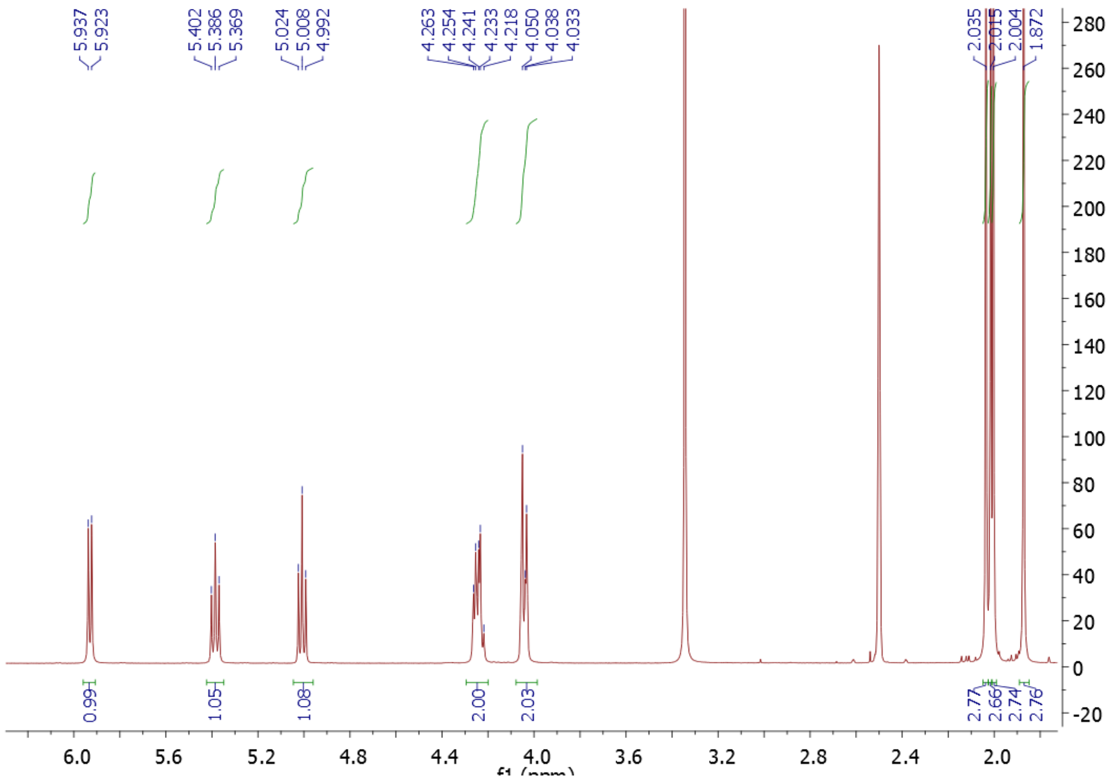


Receptor 2

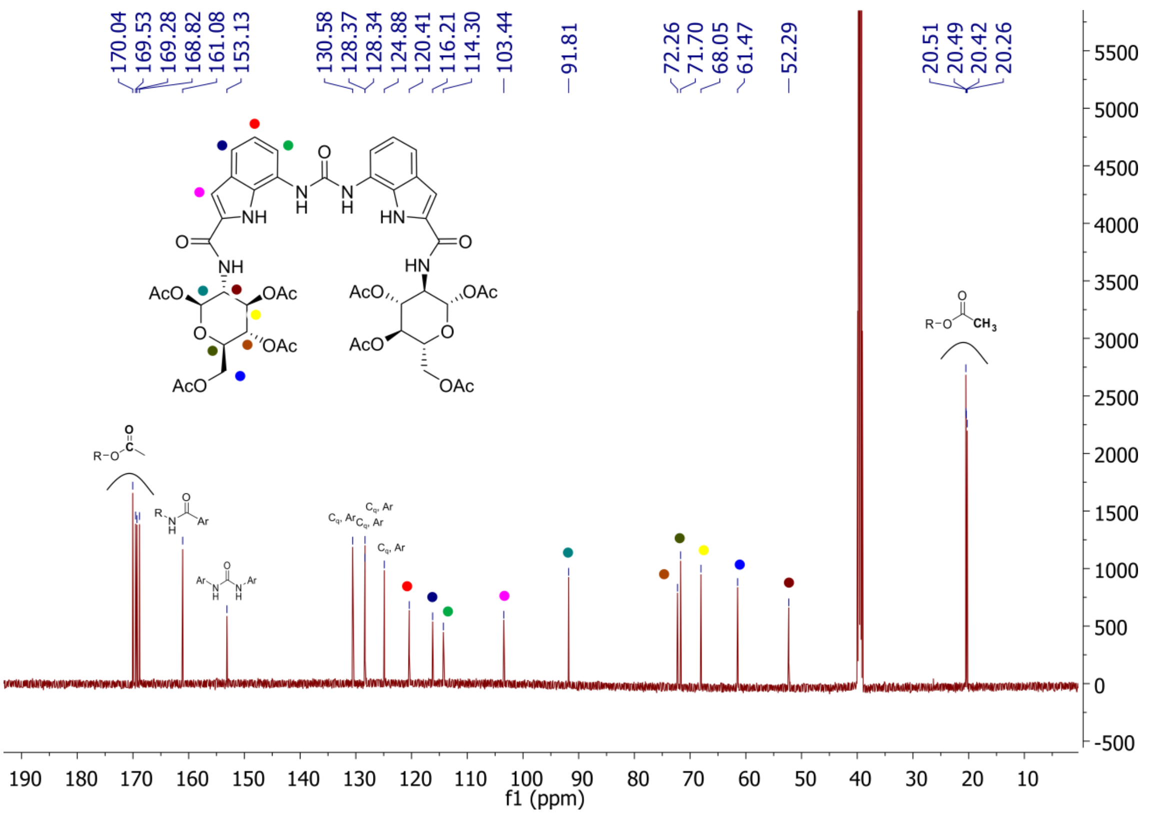
^{1}H NMR (600 MHz, DMSO)





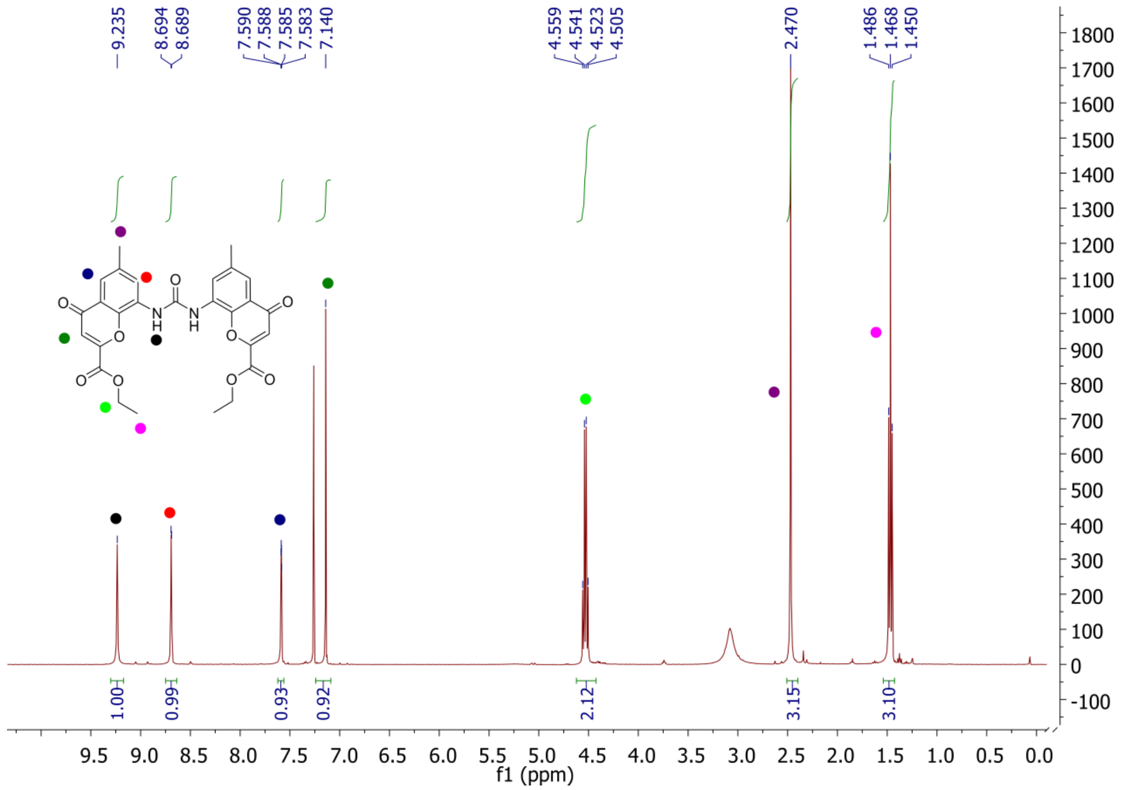


^{13}C (151MHz, DMSO)

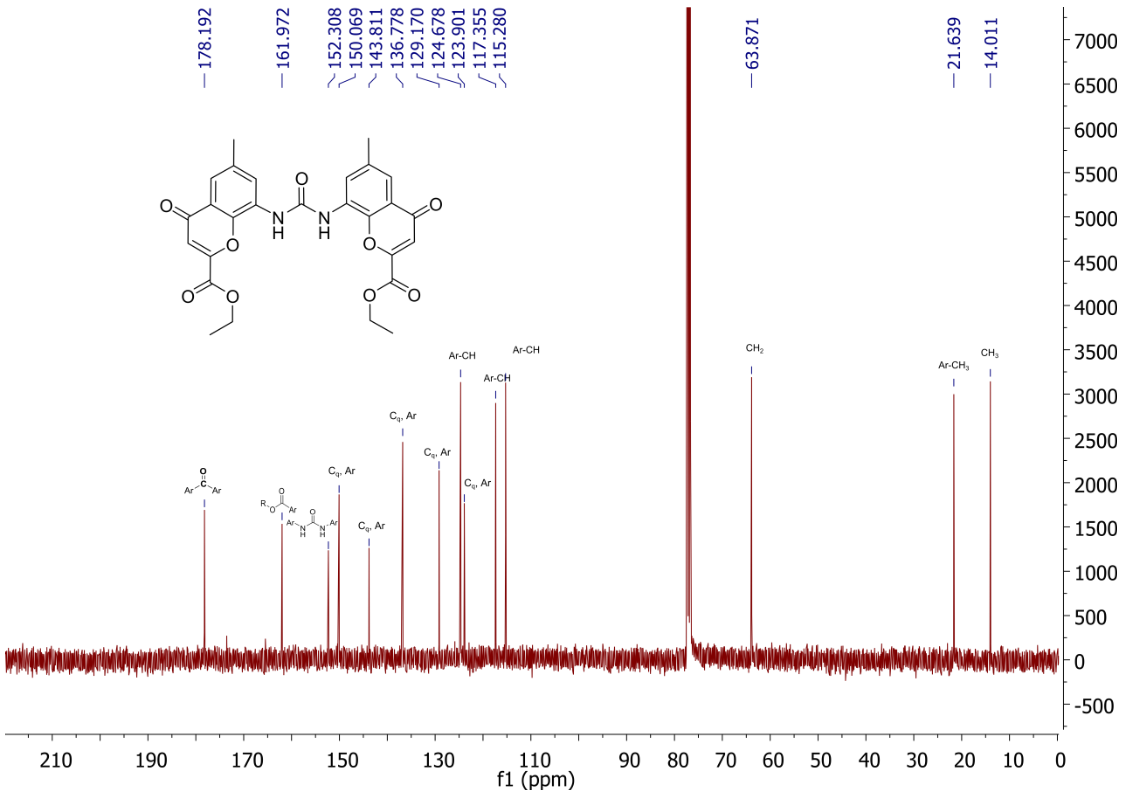


Compound 4

^{1}H NMR (400 MHz, $CDCl_3$)

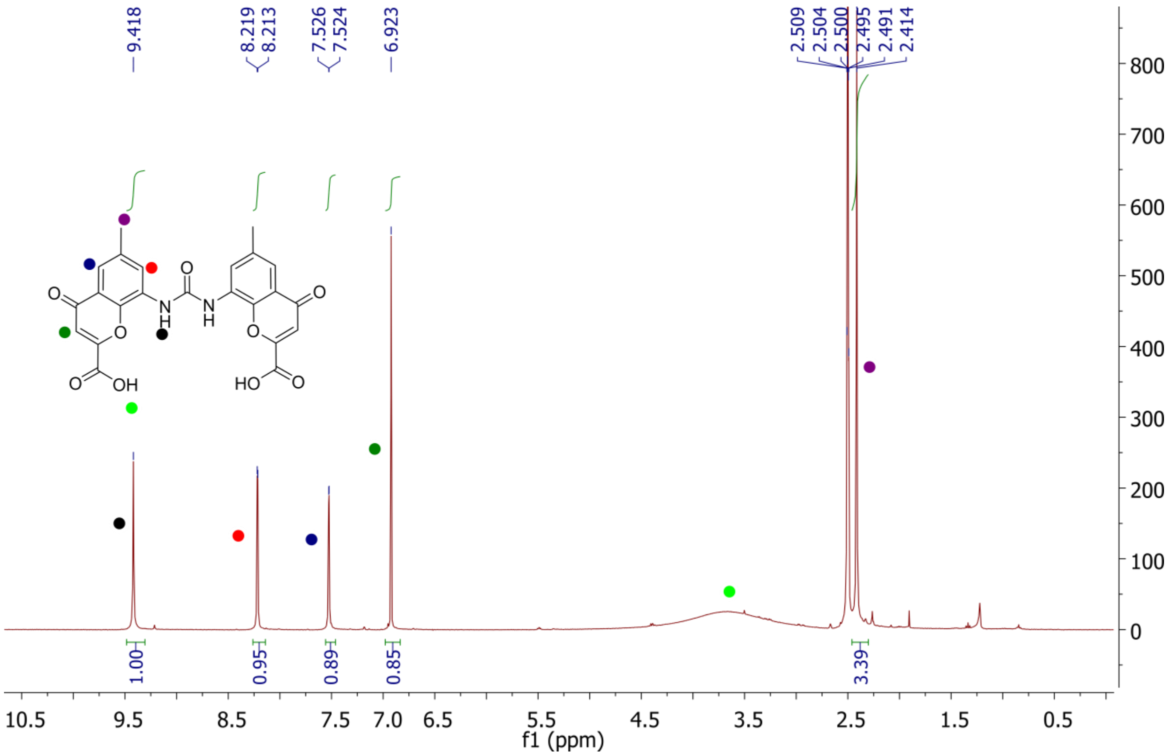


^{13}C (101MHz, $CDCl_3$)

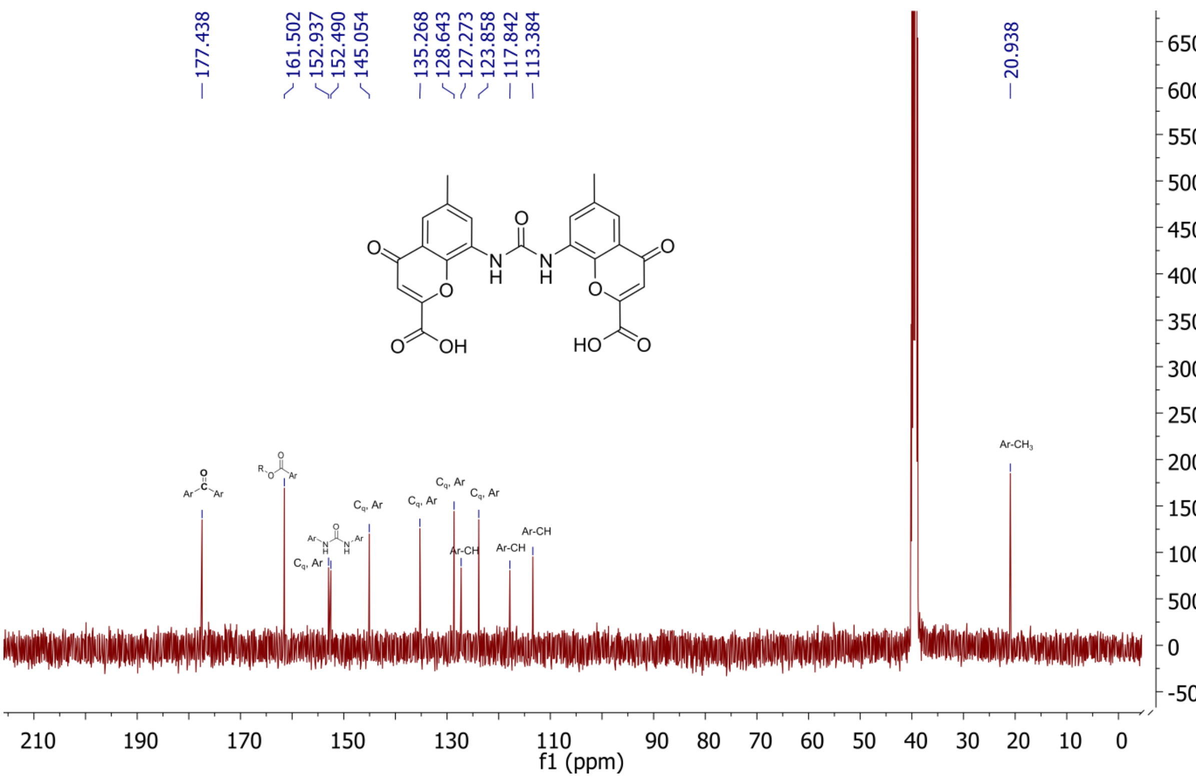


Compound 5

^{1}H NMR (400 MHz, DMSO)

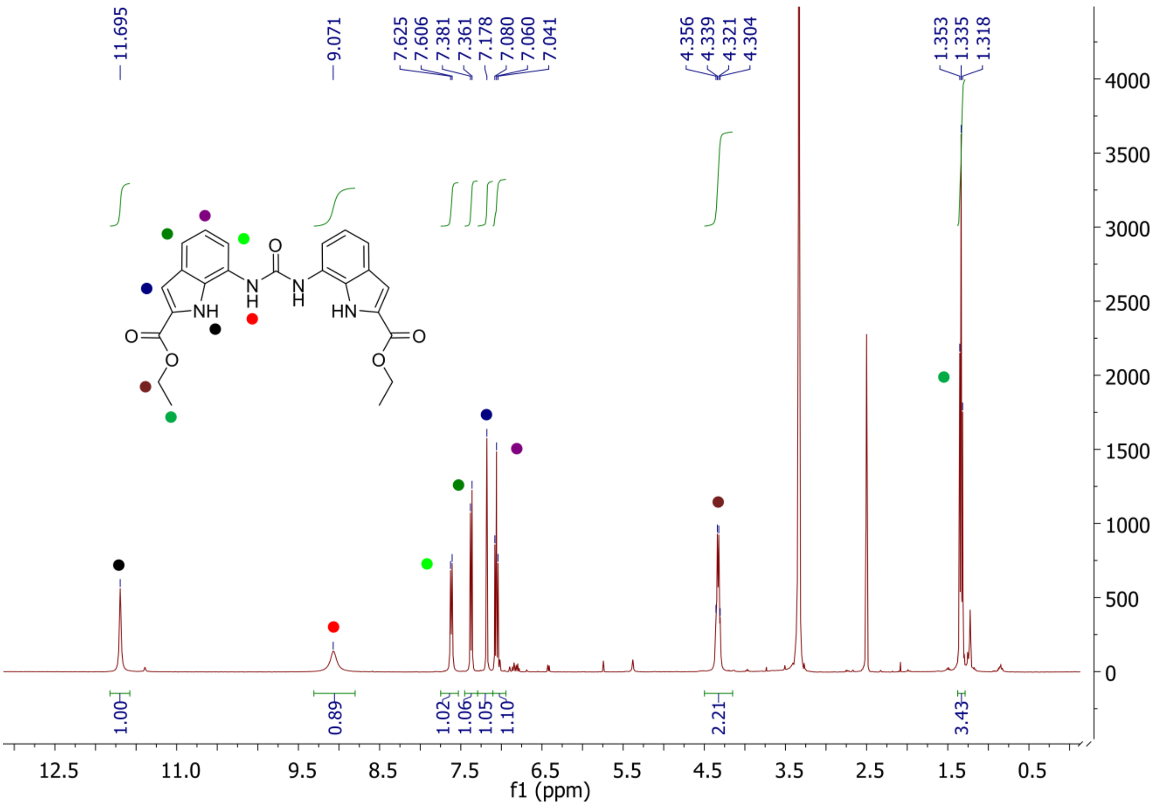


^{13}C (101MHz, DMSO)

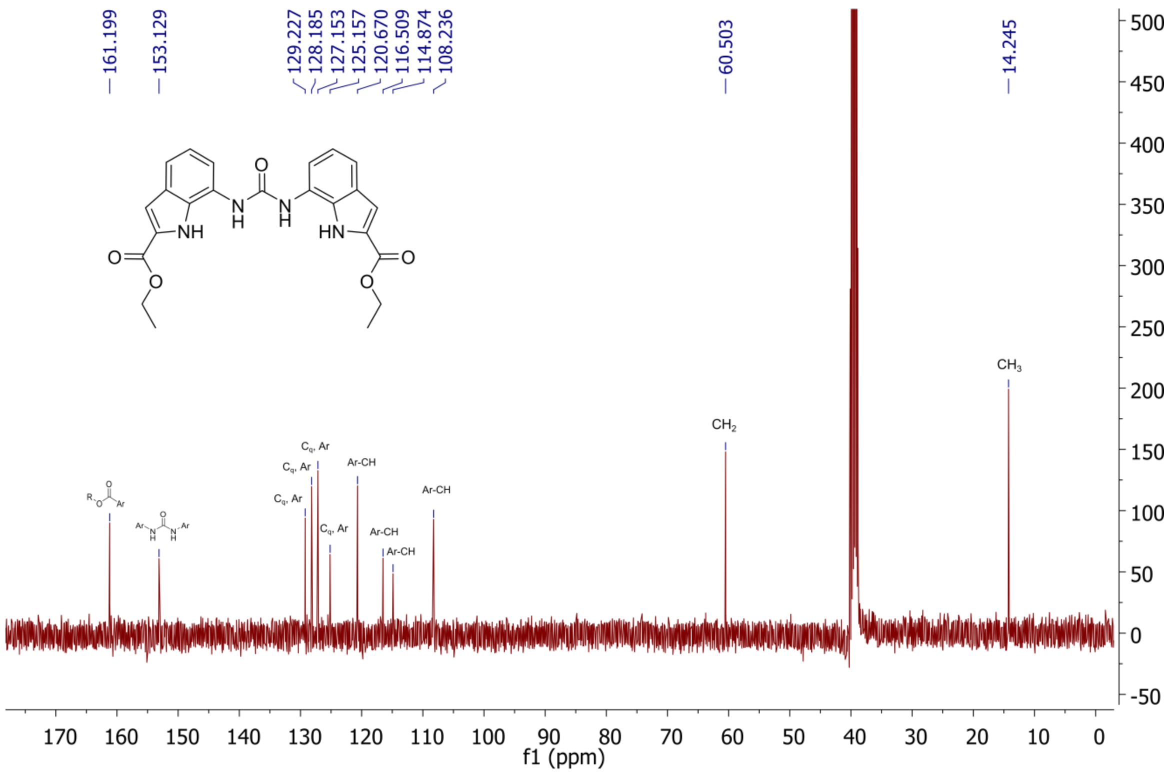


Compound 7

^{1}H NMR (400 MHz, DMSO)

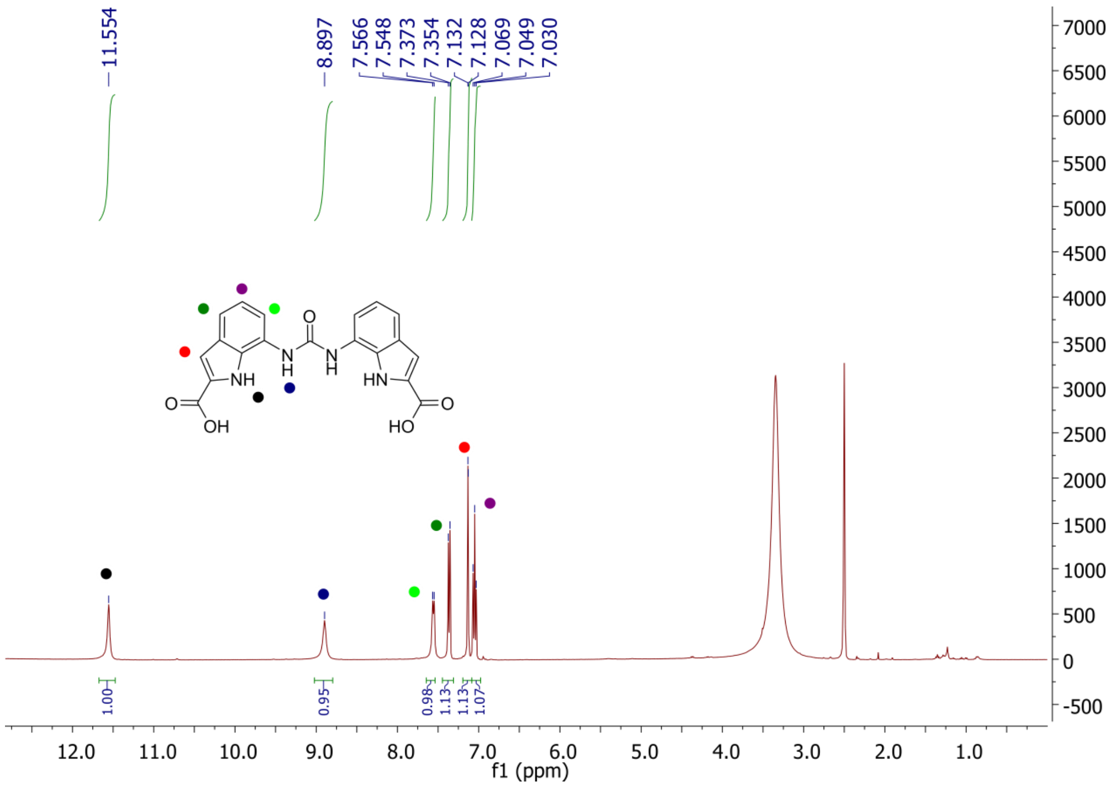


^{13}C (101MHz, DMSO)

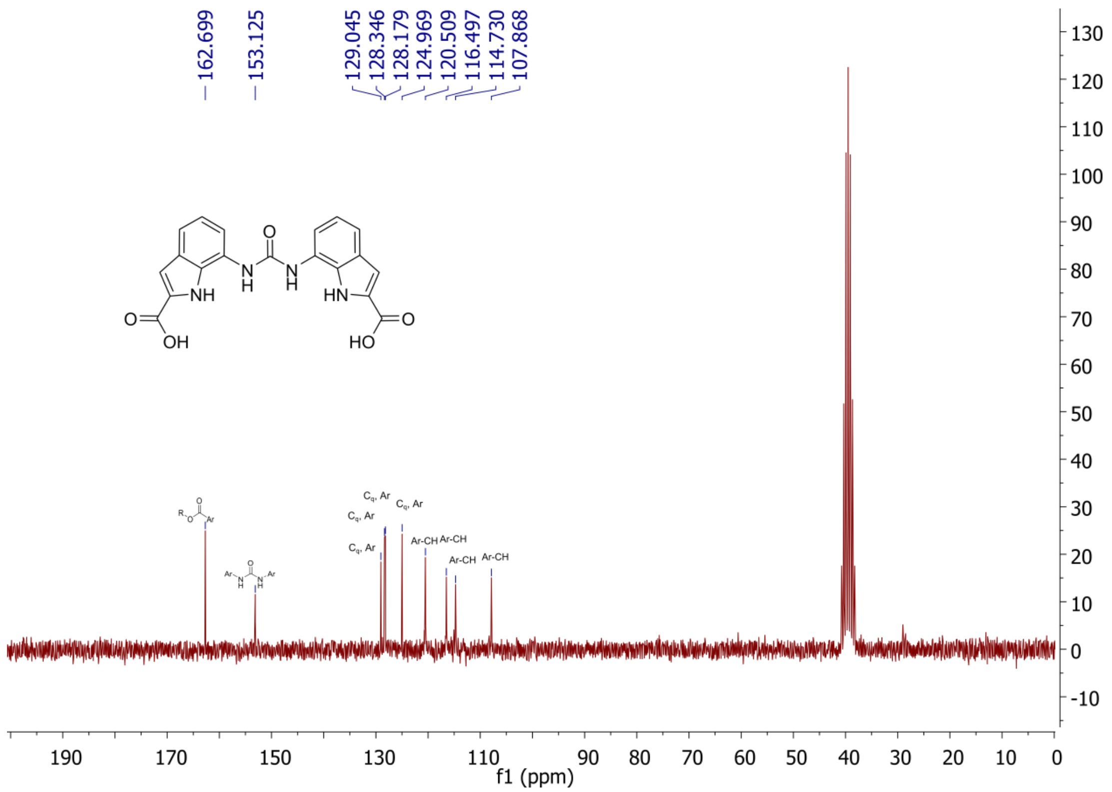


Compound 8

¹H NMR (400 MHz, DMSO)



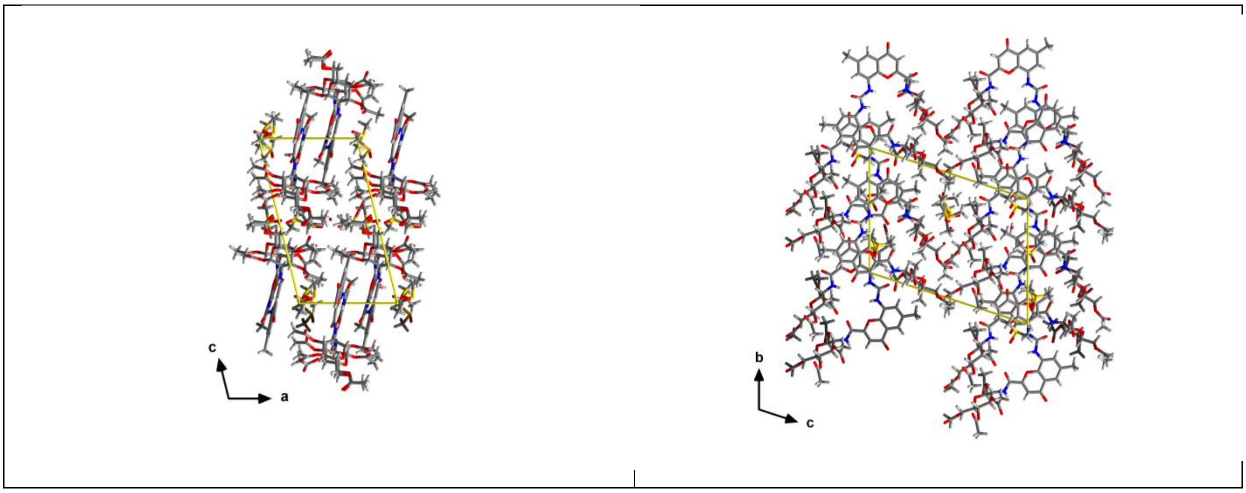
¹³C (101MHz, DMSO)

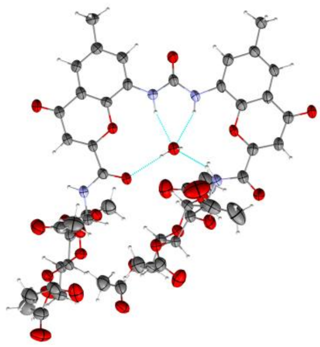


Crystal data

The X-ray structure was determined in the Advanced Crystal Engineering Laboratory (aceLAB) at the Chemistry Department of the University of Warsaw. Crystallographic data (excluding structure factors) for the structures discussed in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. All measurements of crystal were performed on a Bruker D8 Venture Photon100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ=1.54178 Å).

Crystal data for monohydrate **1**: **CCDC** number 1437145: The structure was solved and refined using SHELXTL Software Package using the space group P1, with Z = 1 for the formula unit, $C_{111.30}H_{139.90}N_8O_{58.50}S_{4.65}$. The final cell constants of a = 11.3435(3) Å, b = 15.0588(5) Å, c = 20.0689(6) Å, α = 105.6600(10)°, β = 100.4930(10)°, γ = 99.5980(10)°, volume = 3160.20(17) Å^3, T = 100(2) K. The integration of the data using a triclinic unit cell yielded a total of 72460 reflections to a maximum θ angle of 133.00° (0.84 Å resolution), of which 21810 were independent (average redundancy 3.322, completeness = 99.8%, R_{int} = 2.40%, R_{sig} = 2.12%) and 21145 (96.95%) were greater than 2σ(F^2). Thermal ellipsoids parameters are presented at 50% probability level.





Crystal data for complex **2** with (R)-PhLac: **CCDC** number 1437146: The structure was solved and refined using SHELXTL Software Package using the space group *P*1, with *Z*=1 for the formula unit, $C_{154}H_{226}N_{14}O_{54}S_5$ and the Flack parameter equal to 0.035(8). The final cell constants of *a*=9.5057(4) Å, *b*=18.8467(8) Å, *c*=23.7866(10) Å, *α*=86.241(2)°, *β*=85.5566(19)°, *γ*=89.253(2)°, *V*=3160.20(17) Å^3, T = 100(2) K. The integration of the data using a triclinic unit cell yielded a total of 81132 reflections to a maximum θ angle of 119.00° (0.89 Å resolution), of which 23726 were independent (average redundancy 3.419, completeness = 95.8%, Rint=4.75%, Rsig=4.23%) and 21848 (92.08%) were greater than 2σ(F2). The investigated small crystal was very weakly diffracting thus it was not possible to record intensity of all reflections up to 2*θ* equal to 133° resulting in Alert B in the Checkcif report. The unit cell of the investigated sample contains two ligands, two carboxylate anions, two tetrabuylammonium, five DMSO molecule and one H_2O. One TBA cation and one carboxylate anion are partially disordered over two positions. Three DMSO molecules are disordered as well. To model the disorder a number of geometry and ADP constraints were used. Most of non-hydrogen atoms were refined anisotropically. The isotropic approach was applied for atoms of disordered fragments in organic ions and heavily disordered solvent molecules. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. Coordinates of hydrogen atoms of the water molecule were assigned to form reasonable hydrogen bonds with neighboring molecules. The temperature factors of the hydrogen atoms were not refined and were set to be equal to either 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. The partial occupancies of disordered solvent molecules were refined.Thermal ellipsoids parameters are presented at 50% probability level.