Electronic Supplementary Information

Selective binding of (thio)sulfate and phosphate in water by quaternary ammonium functionalized oligo-ureas

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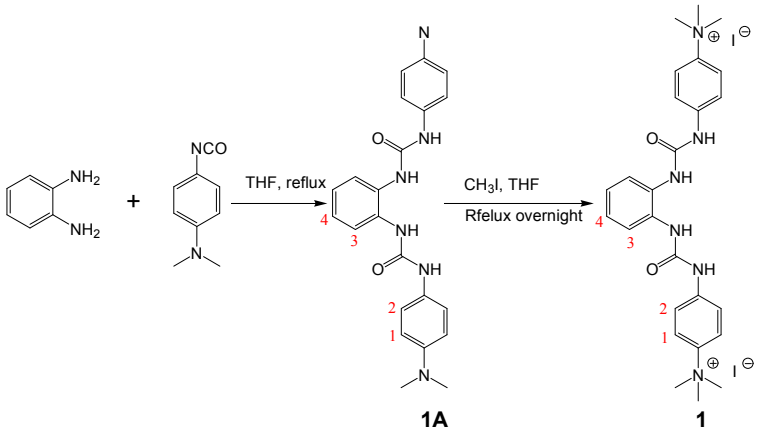
General

Tetrabutylammonium sulfate $(TBA)_2 \bullet SO_4$ (50%, w/w water solution) and *p*-nitro-phenylisocyanate were purchased from Aldrich and used as received. The concentrations of stock solutions of $(TBA)_2SO_4$ were corrected based on the integral of TBA^+/receptor. All solvents and other reagents were of reagent grade quality and purchased commercially.

^1H NMR and ^{13}C NMR spectra were recorded on a Mercury plus-400 spectrometer at 400 MHz and 100 MHz, respectively, ^1H and ^{13}C NMR chemical shifts were reported relative to residual solvent peaks (^1H NMR: 2.50 ppm for DMSO-d_6, 2.22 ppm for acetone-d_6 (as an internal standard in D_2O) respectively; ^{13}C NMR: 39.52 for DMSO-d_6).

Diffraction data were collected on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for the data. The structures were solved by direct methods using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL-97, and hydrogen atoms were included in idealized positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In the Checkcif file, alerts at level A and B were reported in the crystal of $[(\mathbf{2})_2^{2+} \cdot (SO_4)_2^{2-}]$. Although the diffraction dataset is of relatively good quality, the DMSO molecules included in the crystal are significantly disordered though low temperature 173 K was used for the data collection. The disordered DMSO molecules were all removed before applying SQUEEZE. As a result, the only level A and B alerts in the checkcif files are now related to the voids in the structure and the unusually low density, which are both attributed to the SQUEEZE routine.

1. Synthesis and characterization of receptors



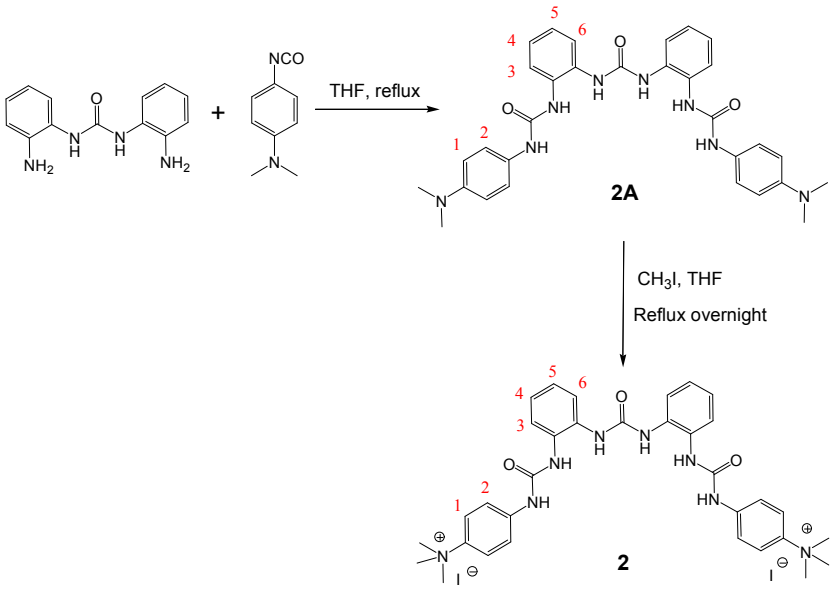
Scheme S1. Synthesis of the tris-urea receptors **1A** and **1**.

Synthesis and characterization of 1A

o-Phenylenediamine (0.16 g, 1.5 mmol) and 4-(dimethylamino)phenyl isocyanate (0.52 g, 3.2 mmol) in 20 mL THF solution was refluxed for 2 h and the precipitate thus obtained was filtered off and washed with THF and diethyl ether, and then dried over vacuum to yield **1A** as a white powder (0.52 g, 85%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.68 (s, 2H, urea H), 7.91 (s, 2H, urea H), 7.56 (dd, J = 3.6, 5.6 Hz, 2H, H3), 7.27 (d, J = 8.0 Hz, 4H, H1), 7.04 (dd, J = 3.6, 6.0 Hz, 2H, H4), 6.68 (d, 4H, J = 8.0 Hz, H2), 2.82 (s, 12H, CH_3).. ^{13}C NMR (100 MHz, DMSO-d_6), 153.5 (CO), 146.4 (C), 131.5 (C), 129.7 (C), 123.8 (CH), 123.6 (CH), 120.2(CH), 113.2 (CH), 40.7 (CH_3). Calculated mass for $C_{24}H_{28}N_6O_2$ + Na^+ 455.2166, found (HRMS-ESI$^+$) 455.2167.

Synthesis and characterization of 1

A suspension of **1A** (0.28 g, 0.6 mmol) in 10 mL iodomethane/15 mL THF was refluxed overnight and the solid was filtered off and washed with THF and diethyl ether, and then dried over vacuum to yield **1** as a pale yellow powder (0.36 g, 78%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.46 (s, 2H, urea H), 8.18 (s, 2H, urea H), 7.86 (d, J = 8.0 Hz, 4H, H1), 7.65 (d, 4H, J = 8.0 Hz, H2), 7.60 (dd, J = 3.6, 6.0 Hz, 2H, H3), 7.13 (dd, J = 3.6, 6.0 Hz, 2H, H4), 3.57 (s, 18H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6), 153.1 (CO), 141.1 (C), 140.7 (C), 131.1 (C), 124.5 (CH), 124.3 (CH), 121.1 (CH), 118.4 (CH), 56.5 (CH_3). Calculated mass for $C_{26}H_{34}I_2N_6O_2$ + Na^+ : 455.2166. Found (HRMS-ESI$^+$): 455.2167.



Scheme S2. Synthesis of the tris-urea receptors **2A** and **2**.

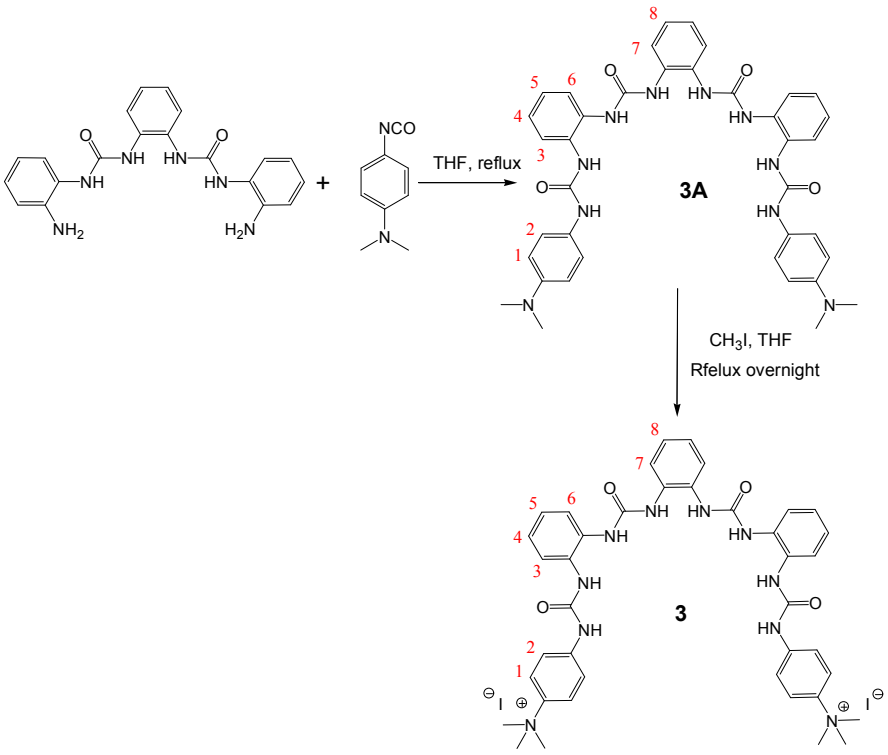
Synthesis and characterization of 2A

1,3-Bis(2-aminophenyl)urea[1] (0.33 g, 1.4 mmol) and 4-(dimethylamino)phenyl isocyanate (0.55 g, 3.4 mmol) was suspended in 30 mL THF. The mixture was refluxed for 16 h and the solid was filtered off and washed with THF and diethyl ether, and then dried over vacuum to yield **2A** as a pale-brown powder (0.67 g, 87%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.73 (s, 2H, urea H), 8.44 (s, 2H, urea H), 7.94 (s, 2H, urea H), 7.61 (d, J = 8.0 Hz, 2H, H6), 7.52 (d, J = 8.0 Hz, 2H, H3), 7.25 (d, 4H, J = 8.0 Hz, H1), 7.05 (m, H4 and H5), 6.67 (d, J = 8.0 Hz, 4H, H2), 2.81 (s, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6), 154.2 (CO), 153.4 (CO), 146.4 (C), 132.0 (C), 130.7 (C), 129.6 (C), 124.3 (CH), 124.1(CH), 123.6 (CH), 123.4 (CH), 120.2 (CH), 113.1(CH), 40.7 (CH_3). Calculated mass for $C_{31}H_{34}N_8O_3$ + Na^+: 589.2646. Found (HRMS-ESI$^+$): 589.2642.

Synthesis and characterization of 2

A suspension of **2A** (0.30 g, 0.5 mmol) in 10mL iodomethane /15 mL THF was refluxed overnight and the solid thus obtained was filtered off and washed with THF and diethyl ether, and then dried over vacuum to yield **2** as a pale-

brown powder (0.40 g, 88%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.55 (s, 2H, urea H), 8.45 (s, 2H, urea H), 8.23 (s, 2H, urea H), 7.85 (d, J = 8.0 Hz, 4H, H1), 7.63 (m, 6H, H2 and H3), 7.53 (d, J = 8.0 Hz, 2H, H6), 7.10 (m, 4H, H4 and H5), 3.57 (s, 18H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6), 154.2 (CO), 153.0 (CO), 141.1 (C), 140.7 (C), 131.3 (C), 131.1 (C), 124.5 (CH), 124.4(CH), 124.3 (CH), 124.1 (CH), 121.1 (CH), 118.4(CH), 56.5 (CH_3). Calculated mass for $C_{33}H_{40}I_2N_8O_3$ + Na^+: 589.2646. Found (HRMS-ESI$^+$): 589.2642.



Scheme S3. Synthesis of the tris-urea receptors **3A** and **3**.

Synthesis and characterization of 3A

1,2-Bis-(2-aminophenyl-urea)-benzene[2] (0.49 g, 1.3 mmol) and 4-(dimethylamino)phenyl isocyanate (0.54 g, 3.3 mmol) in 5 mL DMF/10 mL THF was mixed extensively in 80 ^{0}C oil bath for 3.5 h. The precipitate thus obtained was filtered out and washed with THF and diethyl ether, and then dried over vacuum to yield **3A** as a pale-brown powder (0.79 g, 86%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.72 (s, 2H, urea H), 8.49 (s, 2H, urea H), 8.46 (s, 2H, urea

H), 7.94 (s, 2H, urea H), 7.62 (d, J = 8.0 Hz, 2H, H6), 7.56 (dd, J = 3.6, 6.0 Hz, 4H, H7), 7.50 (d, 2H, J = 8.0 Hz, H3), 7.24 (d, 4H, J = 8.0 Hz, H1), 7.05 (m, 6H, H4, H5, H8), 6.66 (d, 4H, J = 8.0 Hz, H2), 2.81 (s, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6), 154.2 (CO), 153.4 (CO), 146.4 (C), 132.1 (C), 131.3 (C), 130.6 (C), 129.6(C), 124.4 (CH), 124.2(CH), 124.0 (CH), 123.6 (CH), 123.4 (CH), 120.2 (CH), 113.1 (CH), 40.7 (CH_3). Calculated mass for $C_{38}H_{40}N_{10}O_4$ + Na^+: 723.3126. Found (HRMS-ESI$^+$): 723.3130.

Synthesis and characterization of 3

A suspension of **3A** (0.26 g, 0.4 mmol) in 10mL iodomethane, 2 mL DMF and 10mL MeOH was stirred overnight in 70 ^{0}C oil bath. and the solid thus obtained was filtered off and washed with THF and diethyl ether, and then dried over vacuum to yield **2** as a pale-brown powder (0.40 g, 88%). ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 9.53 (s, 2H, urea H), 8.52 (s, 2H, urea H), 8.47 (s, 2H, urea H), 8.23 (s, 2H, urea H), 7.82 (d, J = 8.0 Hz, 2H, H1), 7.60 (m, 8H, H2, H3 and H6), 7.49 (d, 2H, J = 8.0 Hz, H7), 7.07 (m, 6H, H4, H5 and H8), 3.55 (s, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6), 154.2 (CO), 153.0 (CO), 141.1 (C), 140.6 (C), 131.4 (C), 131.0 (C), 124.5 (CH), 124.4(CH), 124.2 (CH), 124.0 (CH), 121.0 (CH), 118.4(CH), 56.5 (CH_3). Calculated mass for $C_{40}H_{46}I_2N_{10}O_4$ + Na^+: 1007.1685. Found (HRMS-ESI$^+$) 1007.1693.

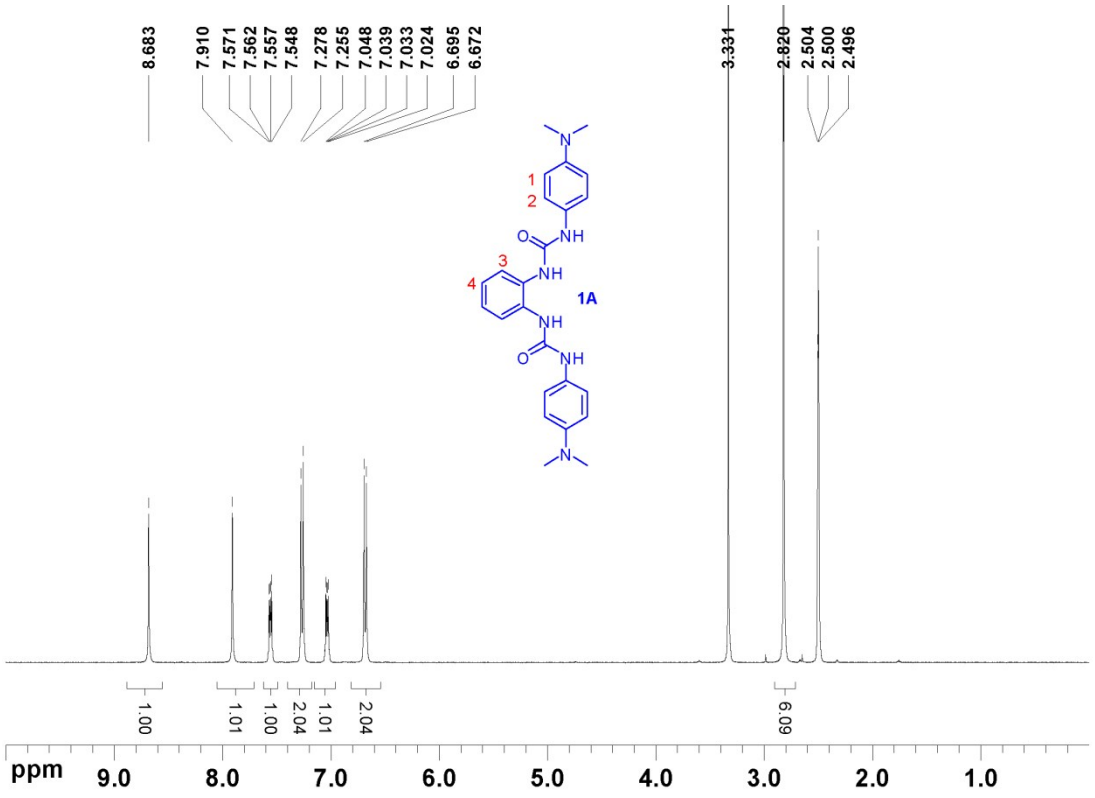


Fig. S1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **1A**.

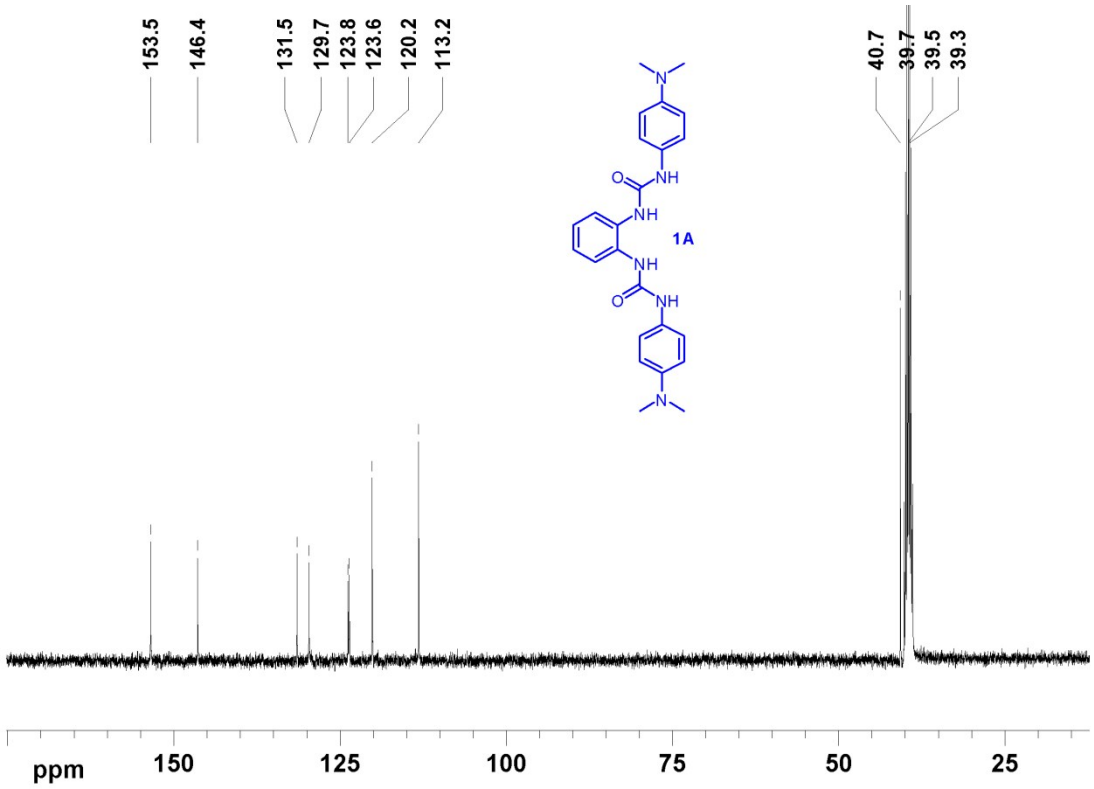
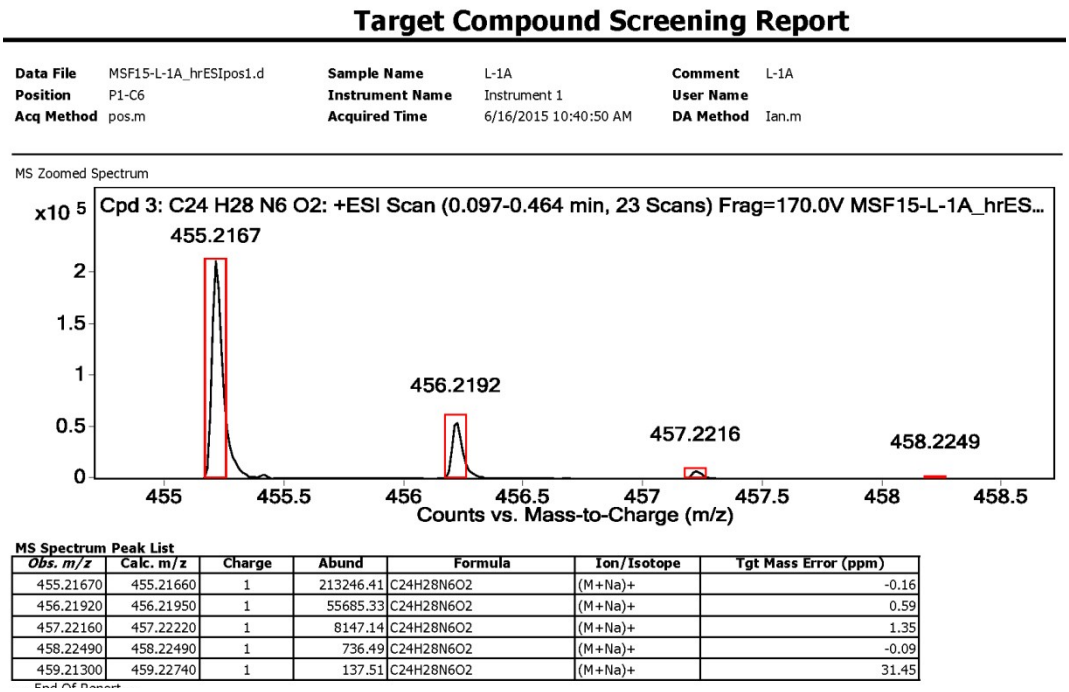


Fig. S2. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **1A**.



Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
455.21670	455.21660	1	213246.41	C24H28N6O2	(M+Na)+	-0.16
456.21920	456.21950	1	55685.33	C24H28N6O2	(M+Na)+	0.59
457.22160	457.22220	1	8147.14	C24H28N6O2	(M+Na)+	1.35
458.22490	458.22490	1	736.49	C24H28N6O2	(M+Na)+	-0.09
459.21300	459.22740	1	137.51	C24H28N6O2	(M+Na)+	31.45

Fig. S3. HRMS-ESI report of **1A**.

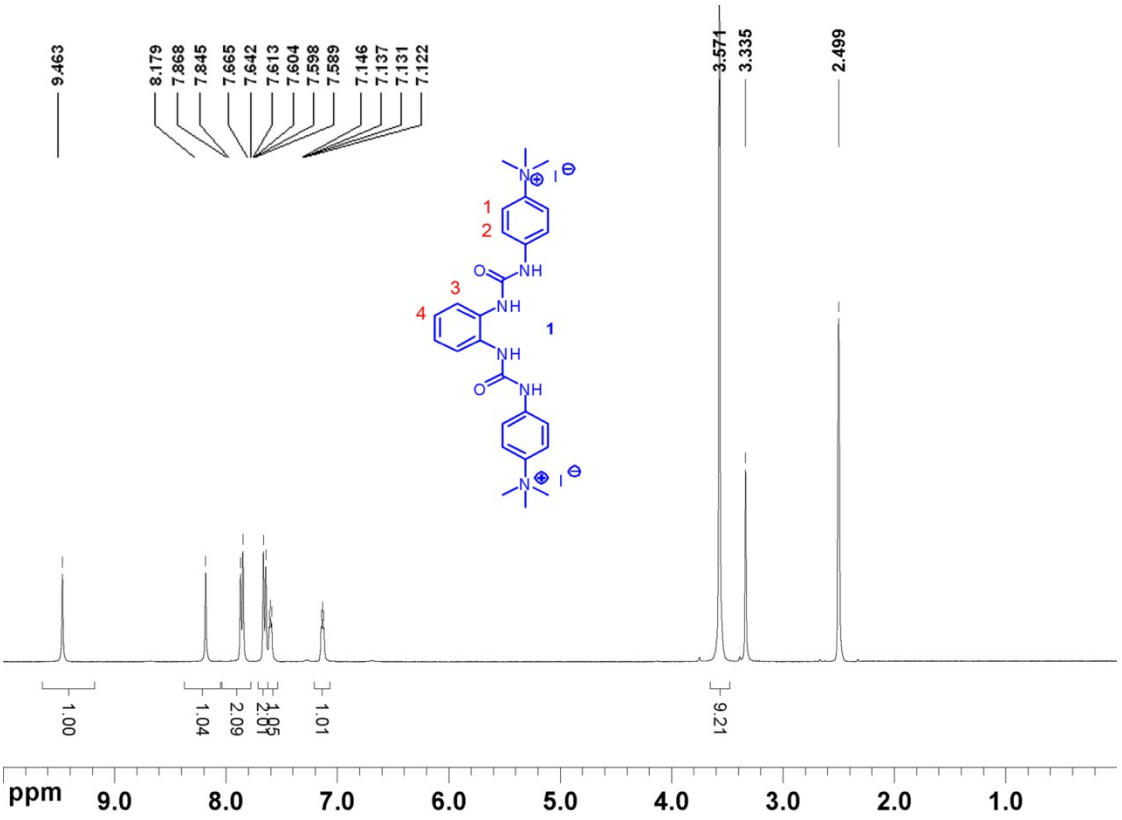


Fig. S4. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **1**.

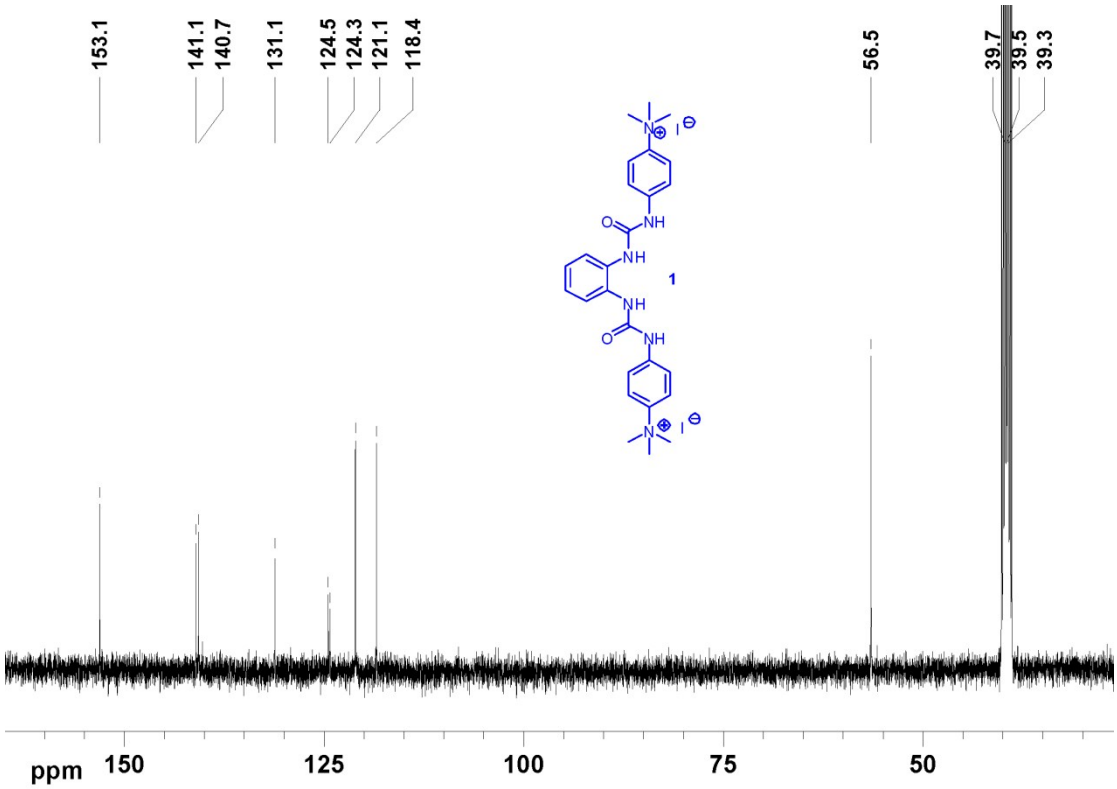


Fig. S5. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **1**.

Target Compound Screening Report

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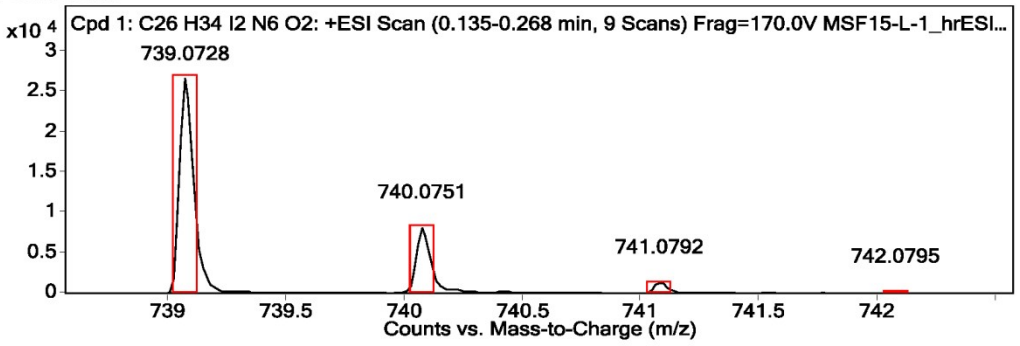
MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
739.07280	739.07250	1	26999.06	C26H34I2N6O2	(M+Na)+	-0.43
740.07510	740.07540	1	8187.51	C26H34I2N6O2	(M+Na)+	0.42
741.07920	741.07820	1	1350.41	C26H34I2N6O2	(M+Na)+	-1.34
742.07950	742.08090	1	203.43	C26H34I2N6O2	(M+Na)+	1.86

--- End Of Report ---

Fig. S6. HRMS-ESI report of **1**.

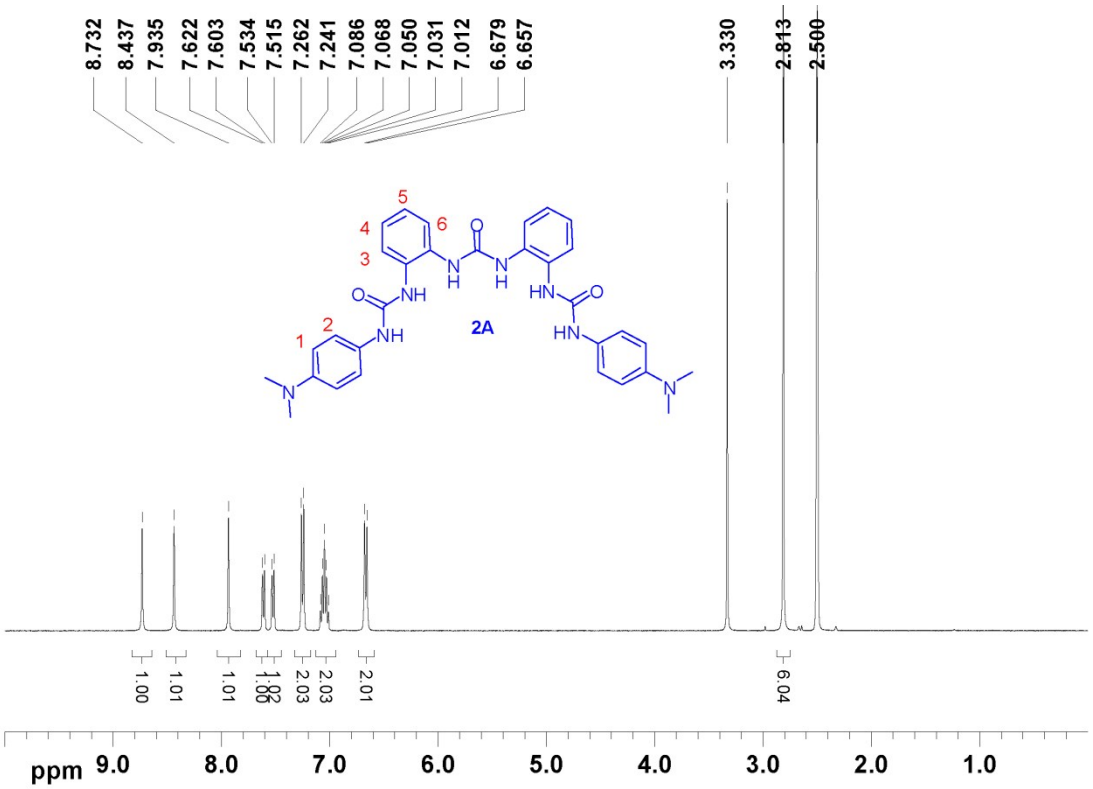


Fig. S7. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **2A**.

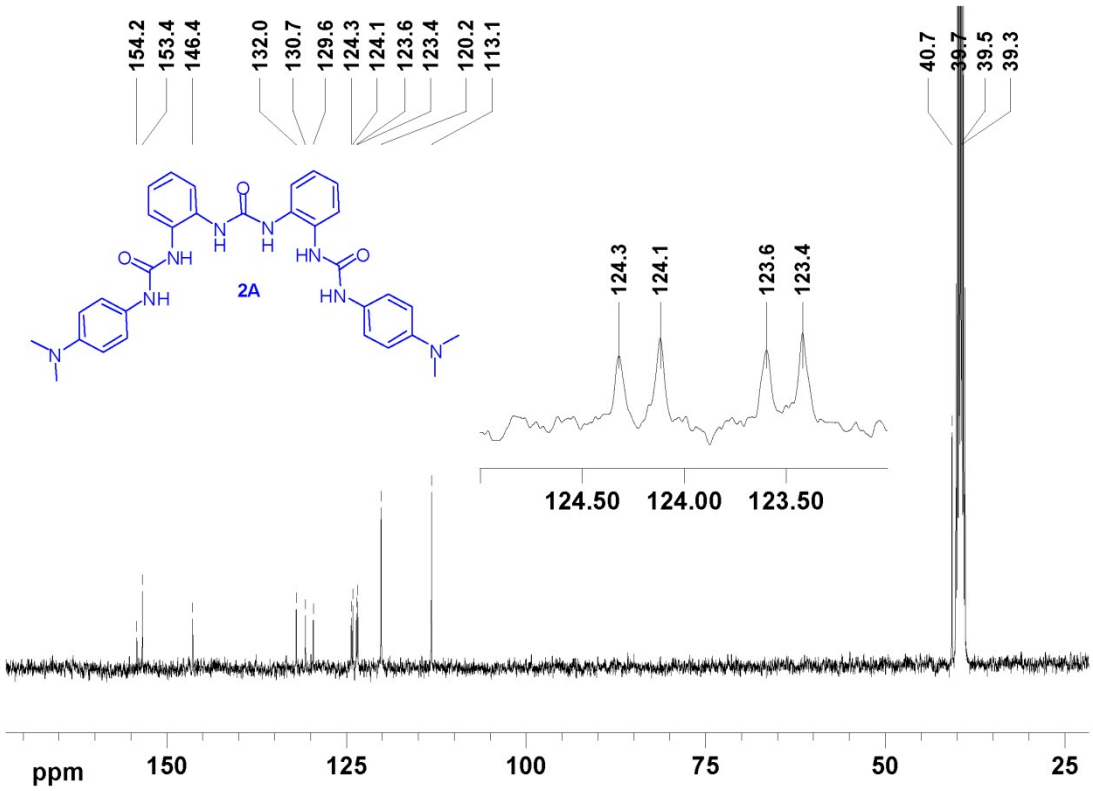


Fig. S8. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **2A** (insert: expanding spectrum of 123-125 ppm).

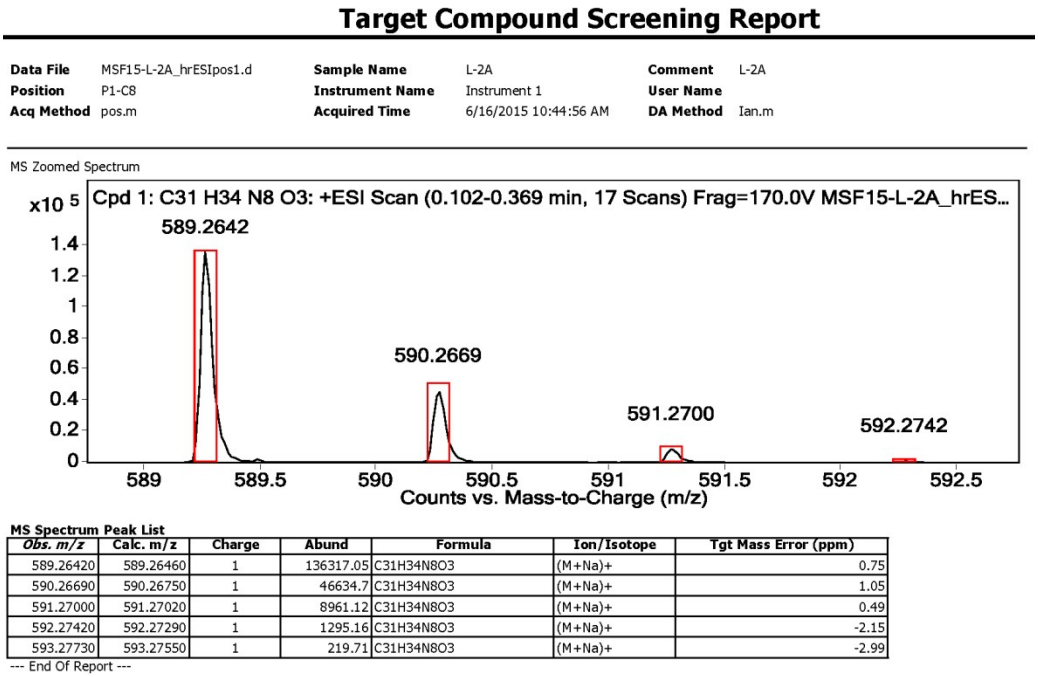


Fig. S9. HRMS-ESI report of **2A**.

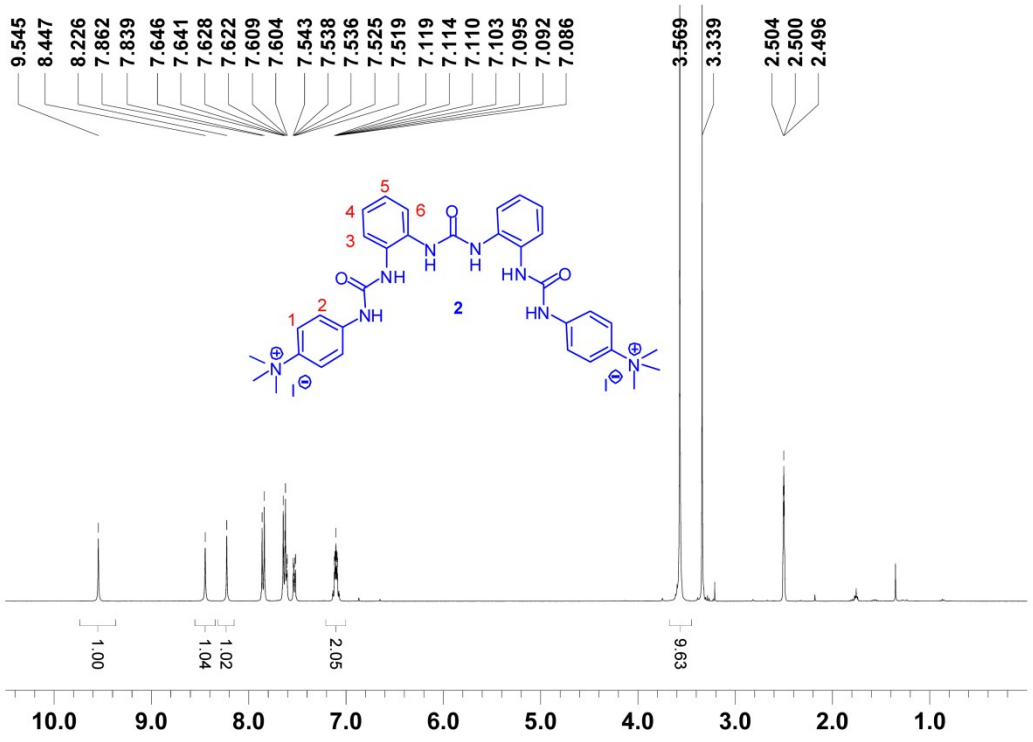


Fig. S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **2**.

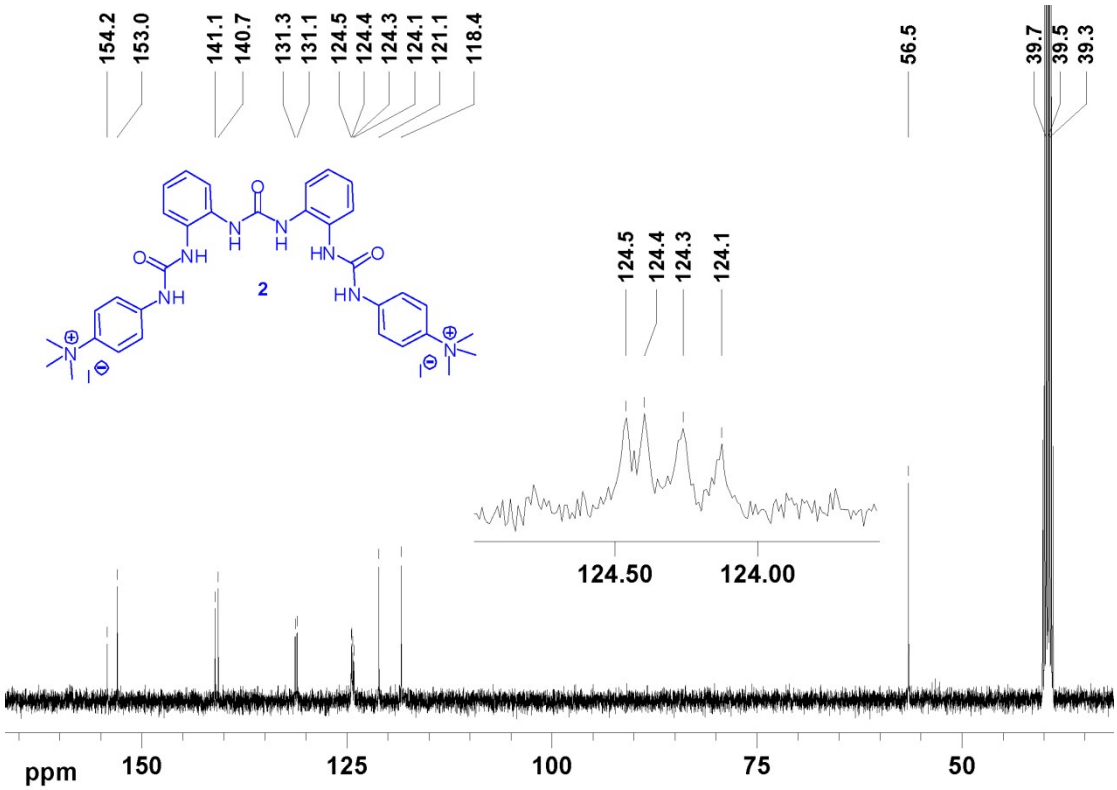


Fig. S11. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **2** (insert: expanding spectrum of 123-125 ppm).

Target Compound Screening Report

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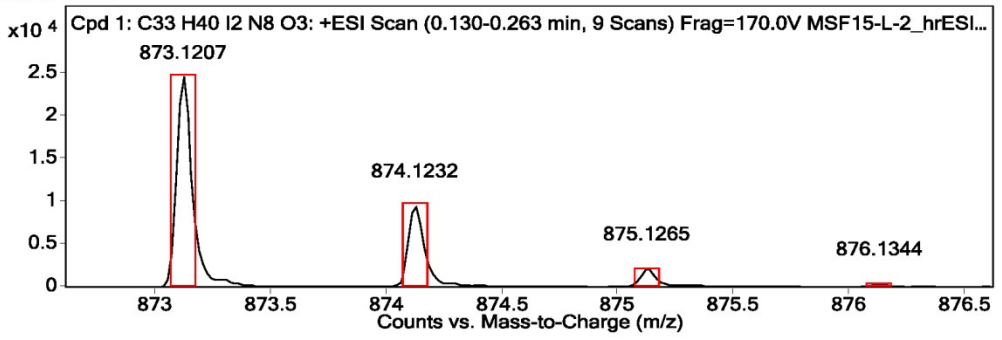
MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
873.12070	873.12050	1	24543.76	C33H40I2N8O3	(M+Na)+	-0.25
874.12320	874.12340	1	9476.29	C33H40I2N8O3	(M+Na)+	0.21
875.12650	875.12620	1	2136.7	C33H40I2N8O3	(M+Na)+	-0.35
876.13440	876.12890	1	374.71	C33H40I2N8O3	(M+Na)+	-6.3

--- End Of Report ---

Fig. S12. HRMS-ESI report of **2**.

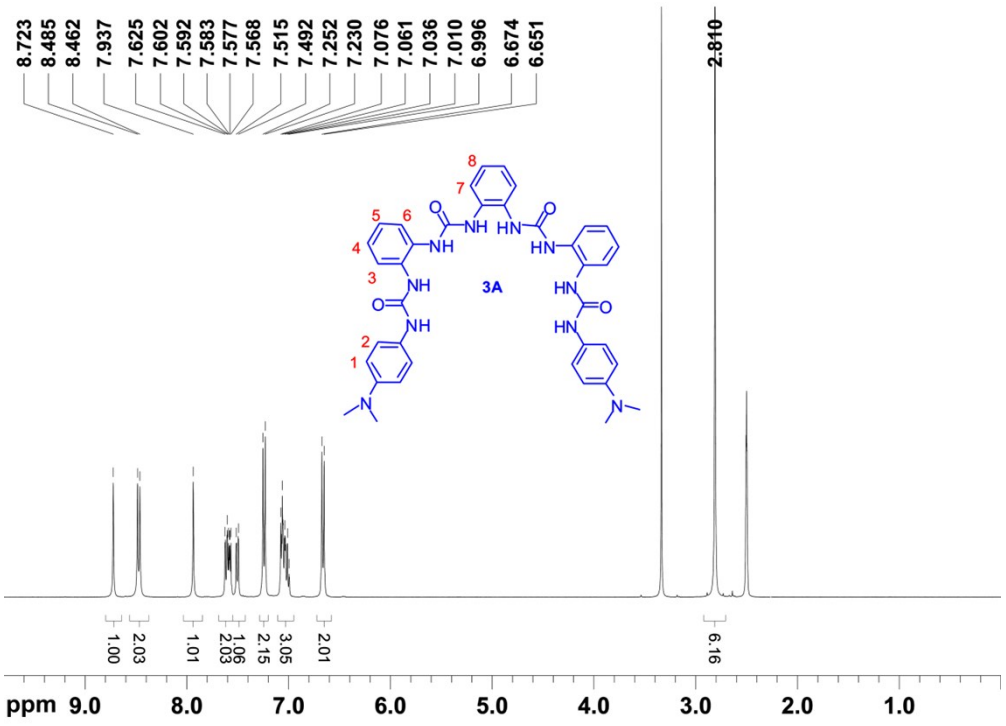


Fig. S13. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **3A**.

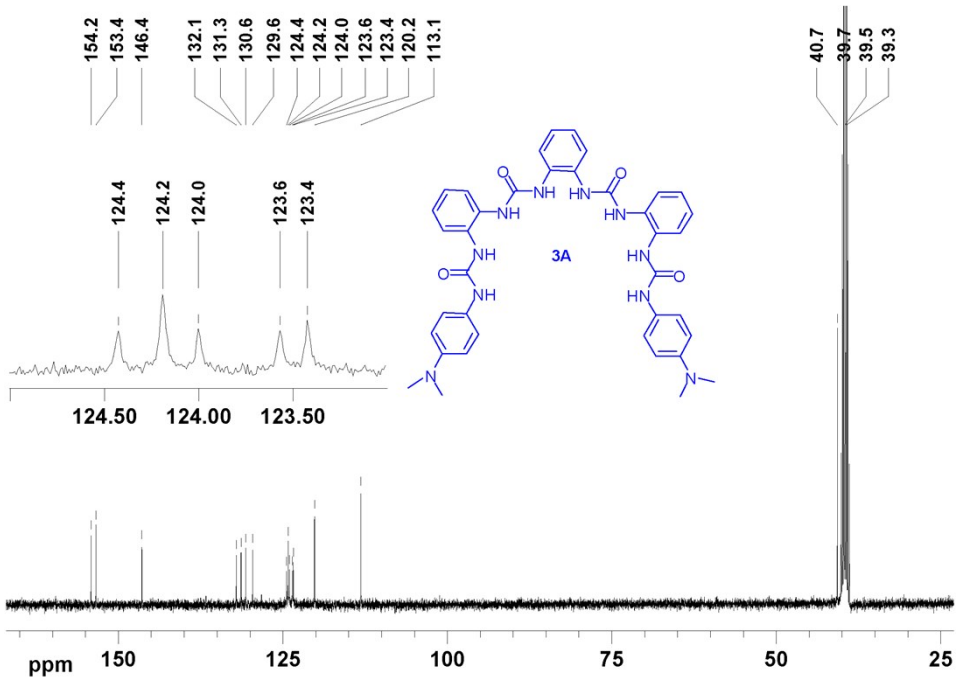
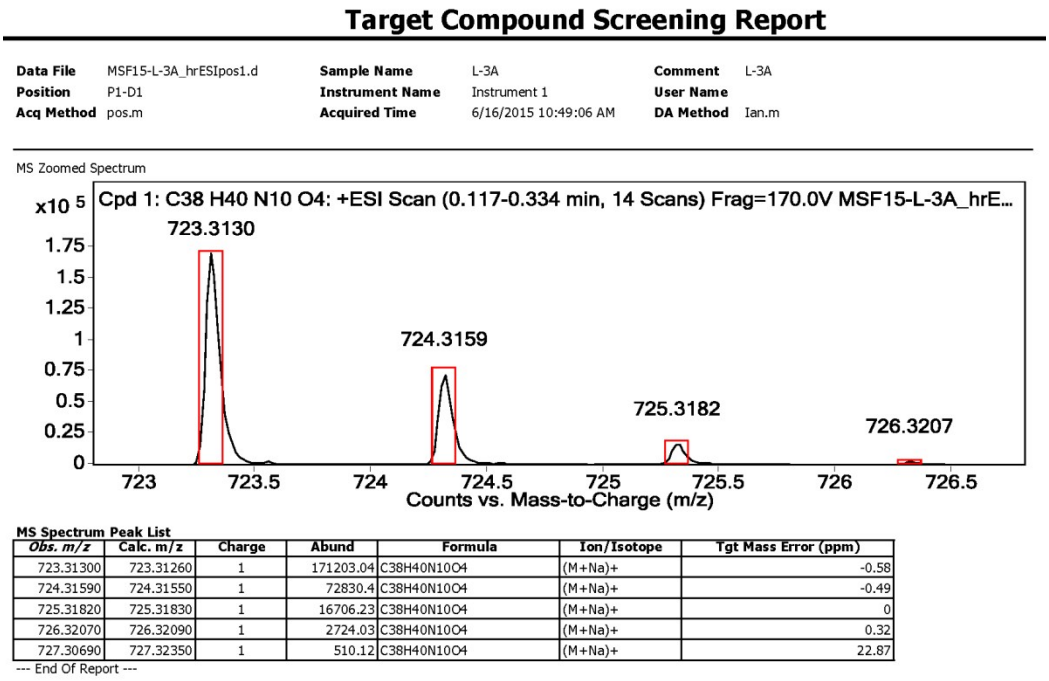


Fig. S14. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **3A** (left insert: expanding spectrum of 123-125 ppm).



Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
723.31300	723.31260	1	171203.04	C38H40N10O4	(M+Na)+	-0.58
724.31590	724.31550	1	72830.4	C38H40N10O4	(M+Na)+	-0.49
725.31820	725.31830	1	16706.23	C38H40N10O4	(M+Na)+	0
726.32070	726.32090	1	2724.03	C38H40N10O4	(M+Na)+	0.32
727.30690	727.32350	1	510.12	C38H40N10O4	(M+Na)+	22.87

Fig. S15. HRMS-ESI report of **3A**.

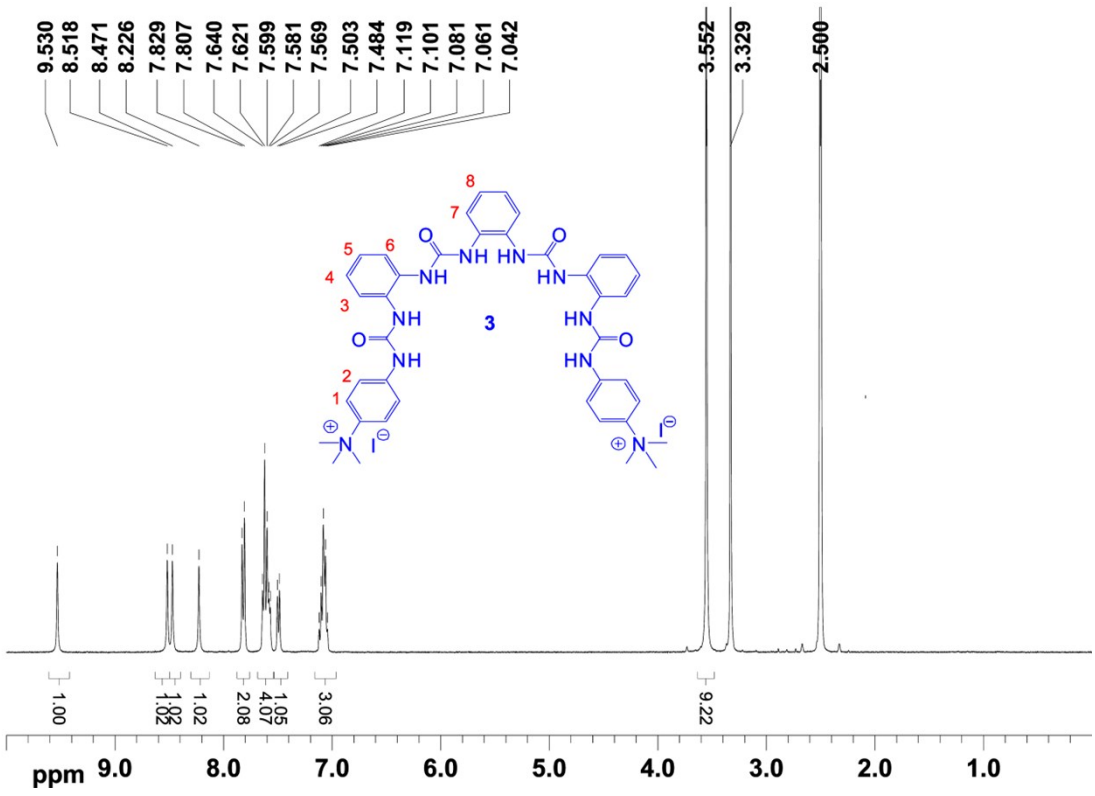


Fig. S16. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **3**.

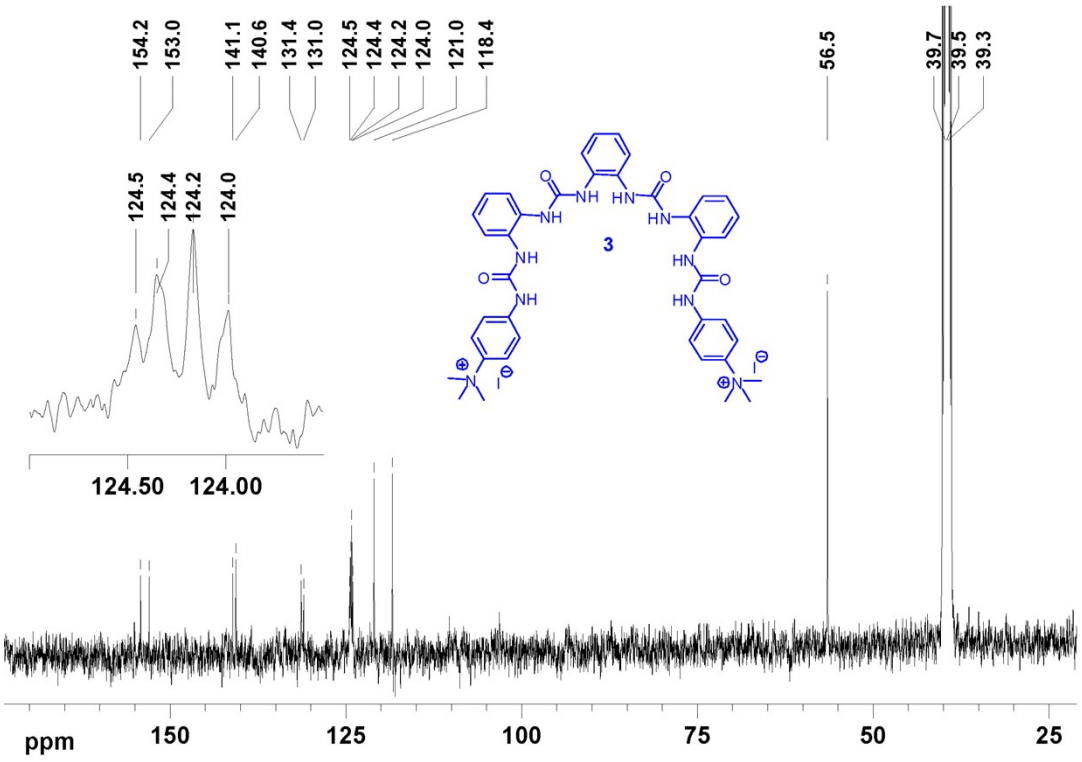
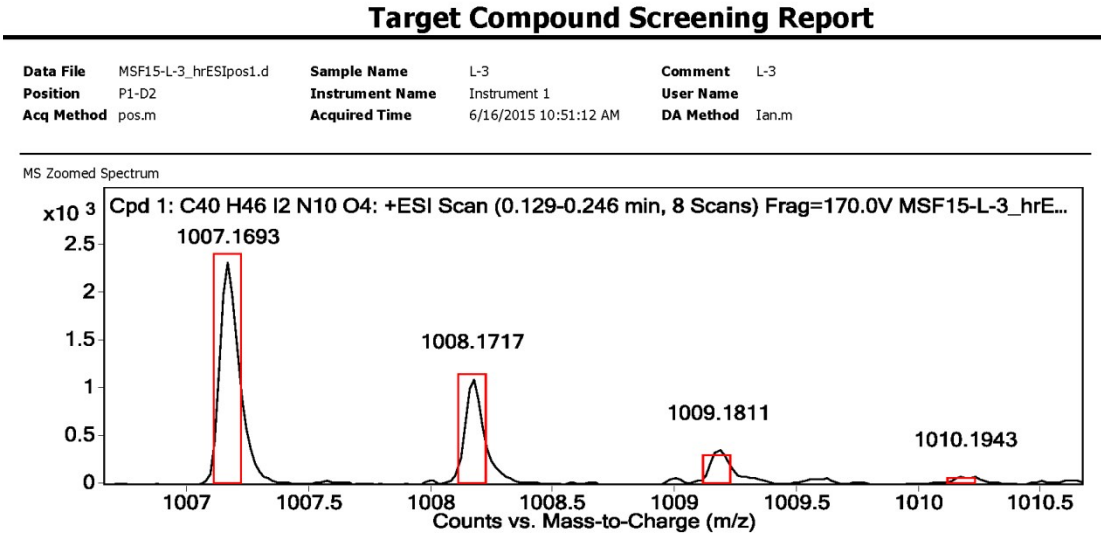


Fig. S17. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **3** (left insert: expanding spectrum of 123-125 ppm).



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
1007.16930	1007.16850	1	2327.78	C40H46I2N10O4	(M+Na)+	-0.77
1008.17170	1008.17140	1	1112.06	C40H46I2N10O4	(M+Na)+	-0.29
1009.18110	1009.17420	1	363.23	C40H46I2N10O4	(M+Na)+	-6.85
1010.19430	1010.17690	1	81.19	C40H46I2N10O4	(M+Na)+	-17.26

--- End Of Report ---

Fig. S18. HRMS-ESI report of **3**.

2. Binding Studies

All anions used in binding studies are tetrabutyl ammonium (TBA) or sodium salts as noted. Since the $(TBA)_2SO_4$ was purchased in a 50% H_2O% solution (Sigma Aldrich), stock solutions were prepared in DMSO-d_6 with aliquots diluted with DMSO-d_6 according to desired water concentrations, and were corrected based on the integral of TBA^+/receptor.

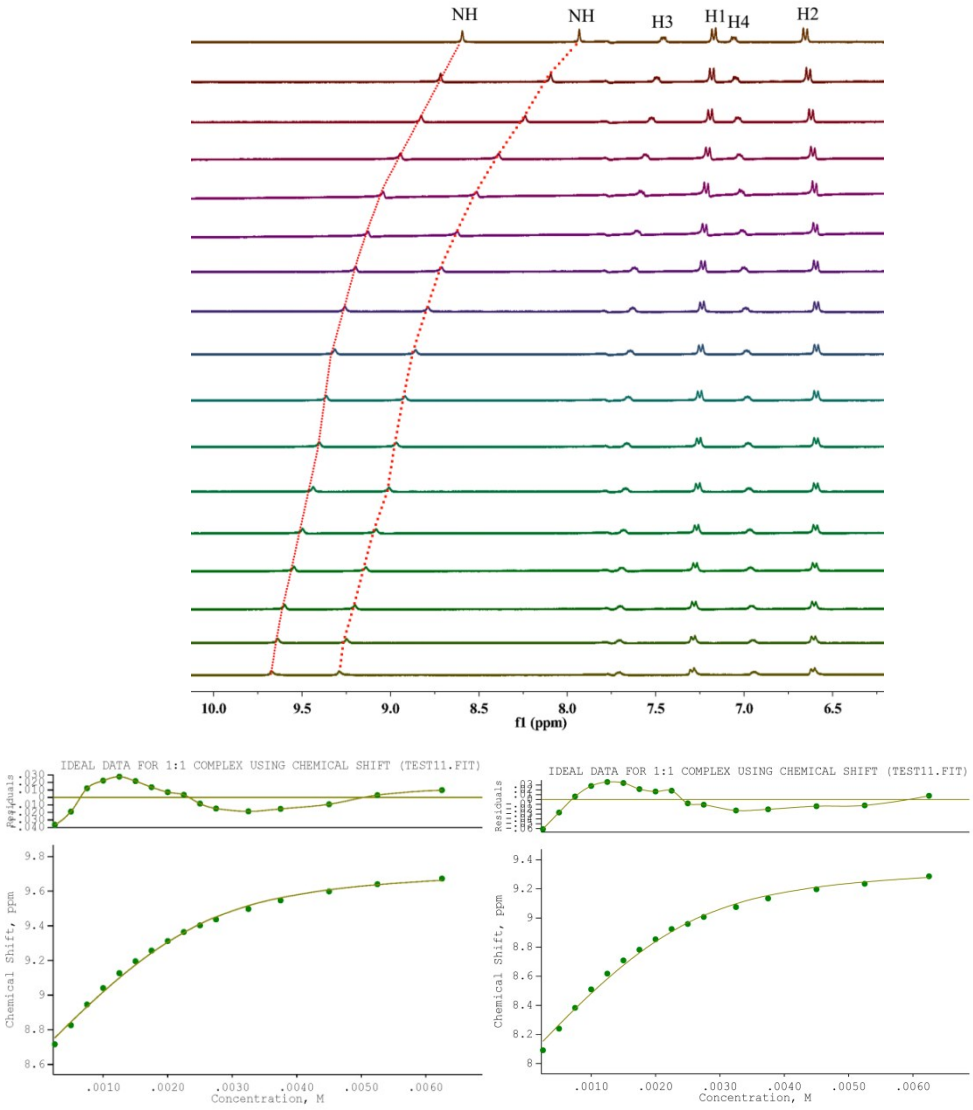
Binding constants were calculated by fitting titration profiles of clearly-shifting protons with the WinEQNMR2 software.[3] For accuracy, each binding constant was calculated at least twice by fitting the titration profiles of clearly-shifting protons showing the most significant chemical shifts, and the result with the smallest error value was selected to use. In each case, all results showed expected consistency (differences within 10%).

Job's plots were determined using ^{1}H NMR spectroscopy. Stock solutions of host and the guest anion were prepared respectively with desired solvents (5.0 mL, 2.5 mM or 1.25 mM as noted). 5 mm-o.d. NMR tubes were separately filled with a total of 500 μL solution of the host and guest in the following ratios (μL, host/guest) at 297 K: 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9. The ^{1}H NMR spectra were obtained for each tube. $[H]_{complexed} = [H]_{all} \times (\delta_{obsd} - \delta_{free})/(\delta_{com} - \delta_{free})$, where $[H]_{all}$ is the total concentration of the host, δ_{obsd} is the chemical shift observed on every point, δ_{free} and δ_{com} corresponds to the chemical shifts of the free receptor and the complex. This value was plotted against the mole fraction of the host.

In titrations conducted in DMSO-d_6/20% H_2O and DMSO-d_6/50% H_2O, DMSO-d_6/0.5% water (Sigma Aldrich) was used to prepare DMSO solutions with desired H_2O concentration (v/v). Titration profiles were recorded according to the shifts of NH or CH protons. Since all receptors contain more than one type of NH group, all the titration profiles were fitted and the one shows the lowest error was selected in each case. In the titration of **2** conducted in D_2O, 0.4% (v/v) acetone-d_6 was added as an internal standard (2.22 ppm). Since all signals of NH disappeared due to proton exchange with D_2O, and all titration profiles were obtained by tracking the shifts of CH1 except in the cases of HPO_4^{2-} and ATP^{2-},

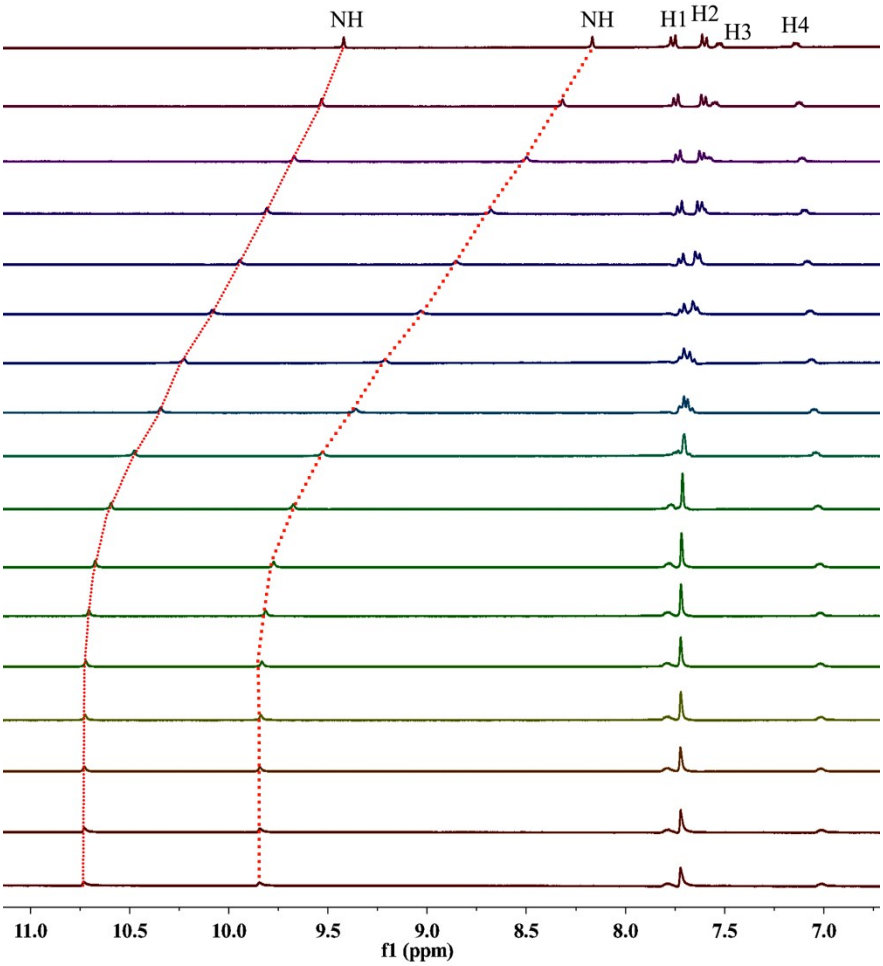
where the shifts of CH1 can hardly been tracked due to signals broadening and the shifts of NMe_3 were tracked instead

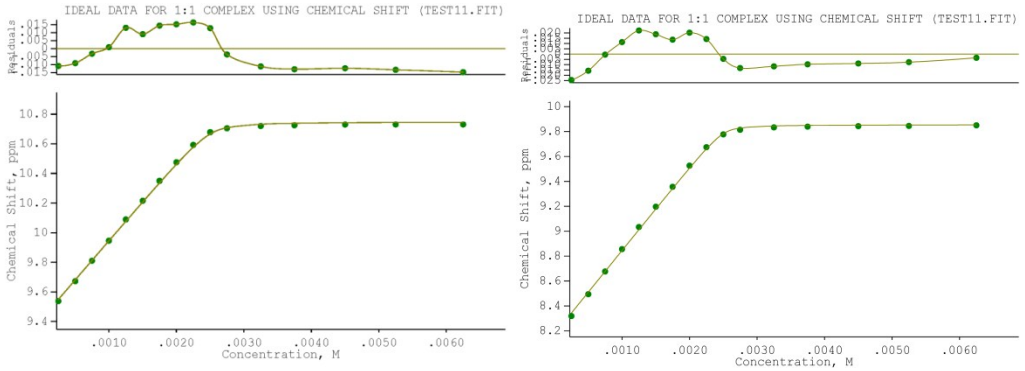
2.1. Anion binding studies of receptors with $(TBA)_2SO_4$



K_a = 2791 M^{-1}, Error = 4%; K_a = 2813 M^{-1}, Error = 8%

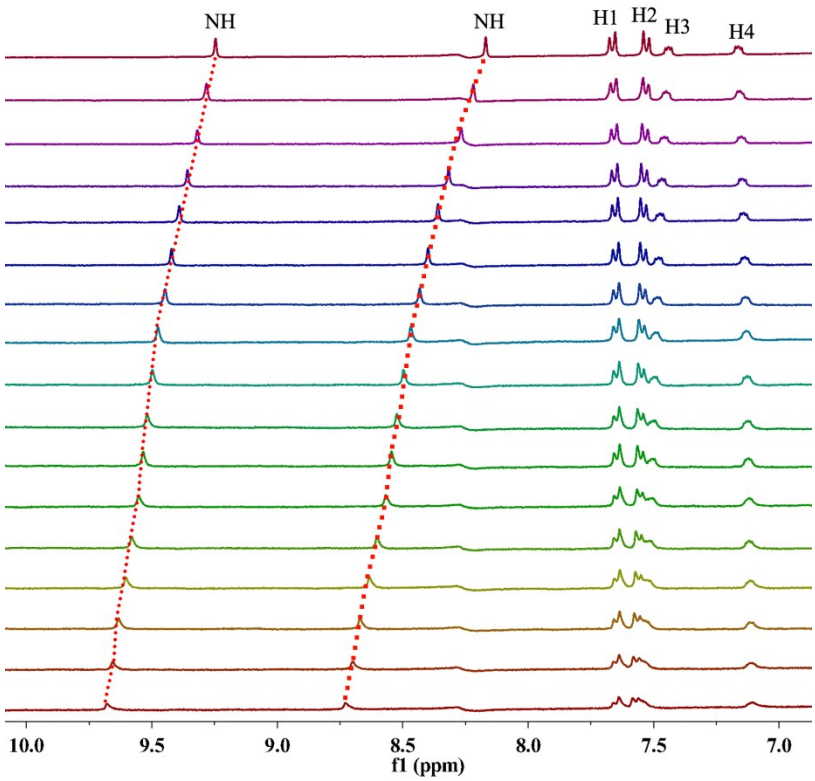
Fig. S19. ^1H NMR Stack plot of receptor **1A** (2.5 mM) with 0-2.5 equiv. of $(TBA)_2SO_4$ in DMSO-d_6/20% H_2O and the WinEQNMR2 fitted titration profiles by following the shifts of NH at 8.59 ppm and 7.93 ppm.

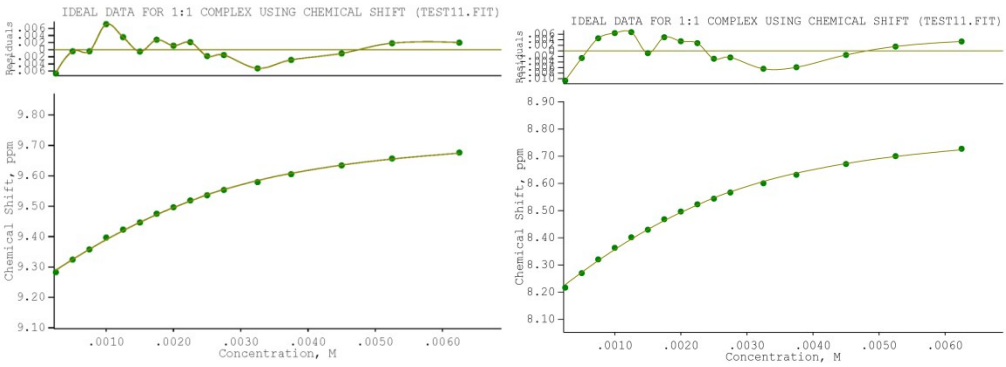




K_a **> 10^4 M^{-1};** K_a **> 10^4 M^{-1}**

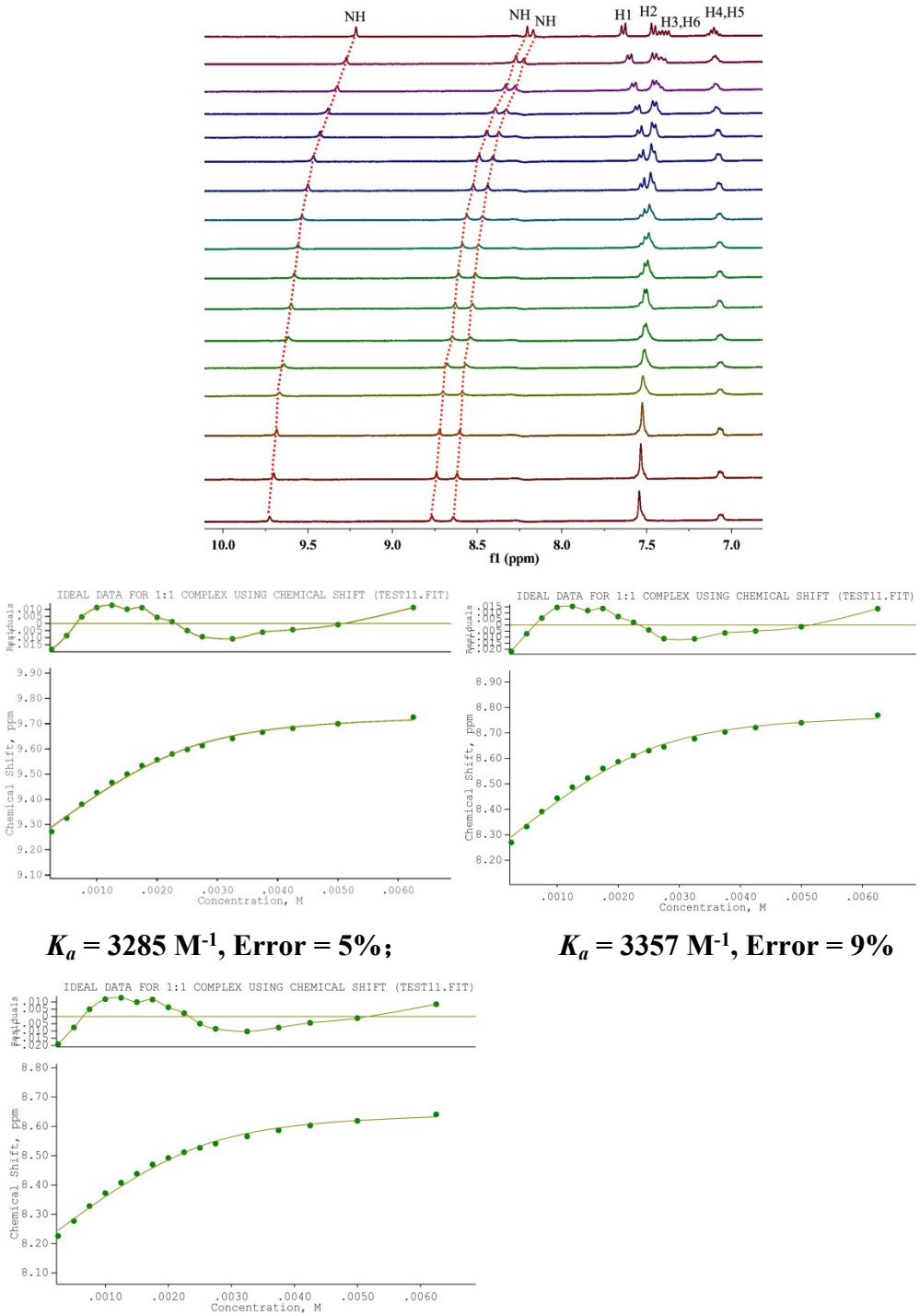
Fig. S20. ^{1}H NMR Stack plot of receptor **1** (2.5 mM) with 0-2.5 equiv. of $(TBA)_2SO_4$ in DMSO-d_6/20% H_2O and the WinEQNMR2 fitted titration profile by following the shifts of NH at 9.42 ppm and 8.17 ppm.





K_a = 1145 M^{-1}, Error = 8%; **K_a = 1132 M^{-1}, Error = 9%**

Fig. S21. ^{1}H NMR Stack plot of receptor **1** (2.5 mM) with 0-2.5 equiv. of $(TBA)_2SO_4$ in DMSO-d_6/50% H_2O and the WinEQNMR2 fitted titration profile by following the shifts of NH at 9.25 ppm and 8.17 ppm.

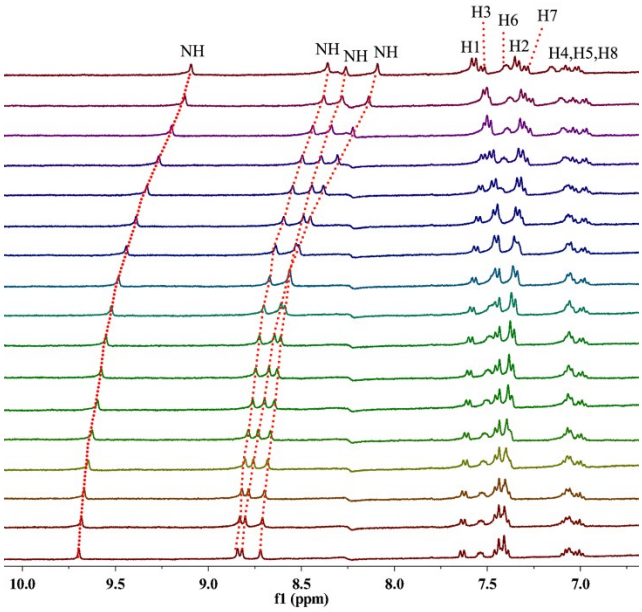


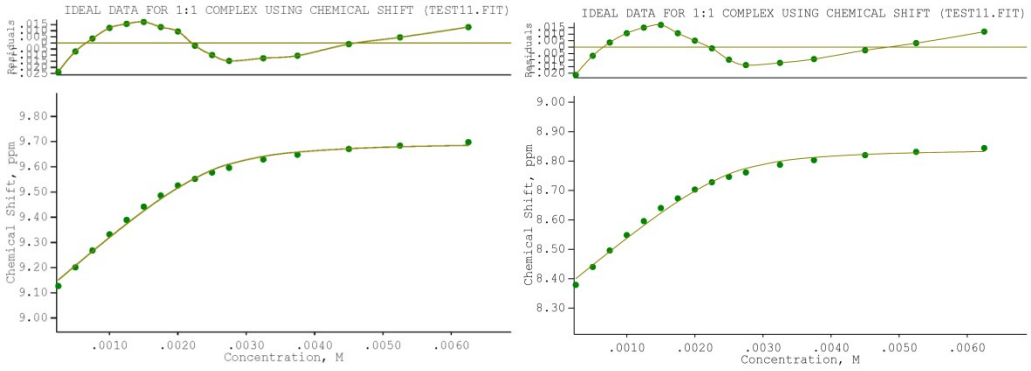
K_a = 3285 M^{-1}, Error = 5%;

K_a = 3357 M^{-1}, Error = 9%

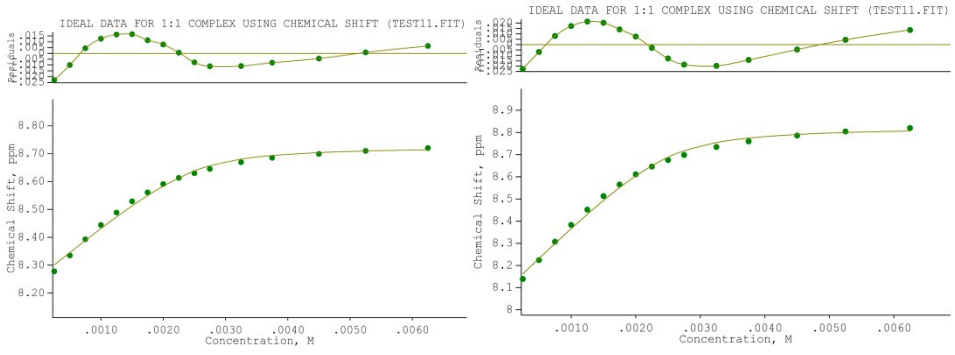
K_a = 3425 M^{-1}, Error = 4%

Fig. S22. ^{1}H NMR Stack plot of receptor **2** (2.5 mM) with 0-2.5 equiv. of $(TBA)_2SO_4$ in DMSO-d_6/50% H_2O and the WinEQNMR2 fitted titration profile by following the shifts of NH at 9.22 ppm, 8.25 ppm and 8.21 ppm.



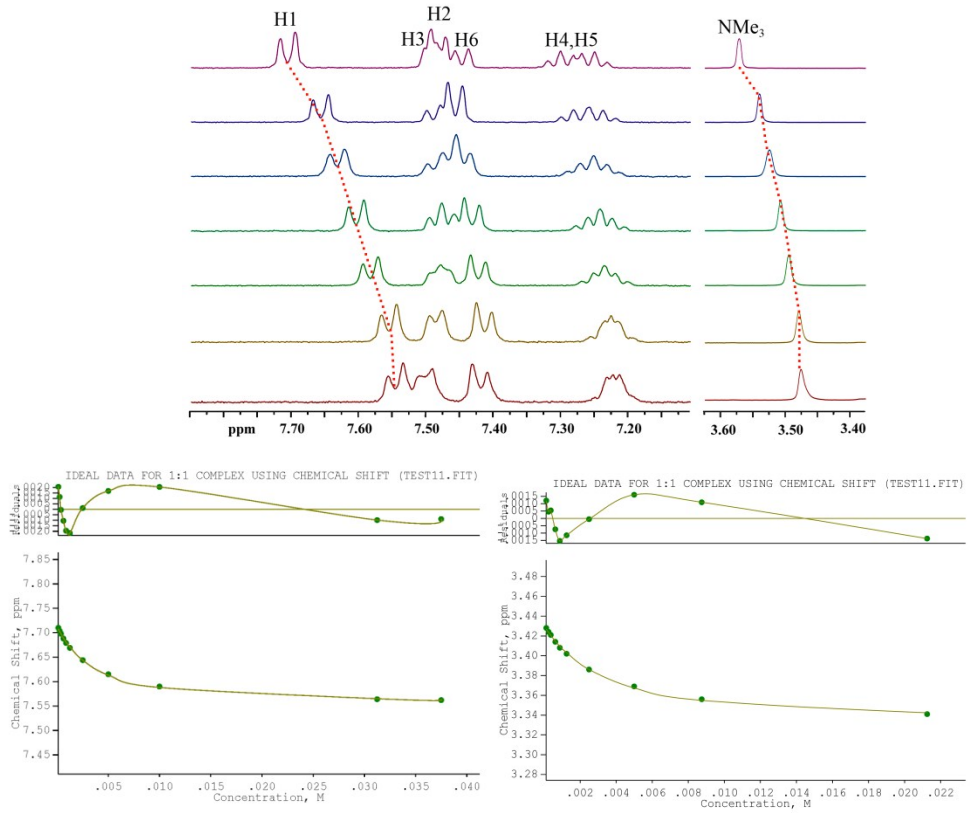


K_a = 9013 , Error = 11%; K_a = 9139 , Error = 4%



K_a = 9012 M^{-1}, Error = 2%; K_a = 9018 M^{-1}, Error = 2%

Fig. S23. ^{1}H NMR Stack plot of receptor **3** (2.5 mM) with 0-2.5 equiv. of $(TBA)_2SO_4$ in DMSO-d_6/50% H_2O and the WinEQNMR2 fitted titration profile by following the shifts of NH at 9.09 ppm, 8.32 ppm, 8.26 ppm, 8.13 ppm, respectively.



K_a = 390 M^{-1}, Error = 5%; K_a = 425 M^{-1}, Error = 7%

Fig. S24. ^{1}H NMR Stack plot of receptor **2** (1.25 mM) with 0-30 equiv. of $(TBA)_2SO_4$ in D_2O and the WinEQNMR2 fitted titration profile by following the shifts of CH at 7.72 ppm and 3.43 ppm.

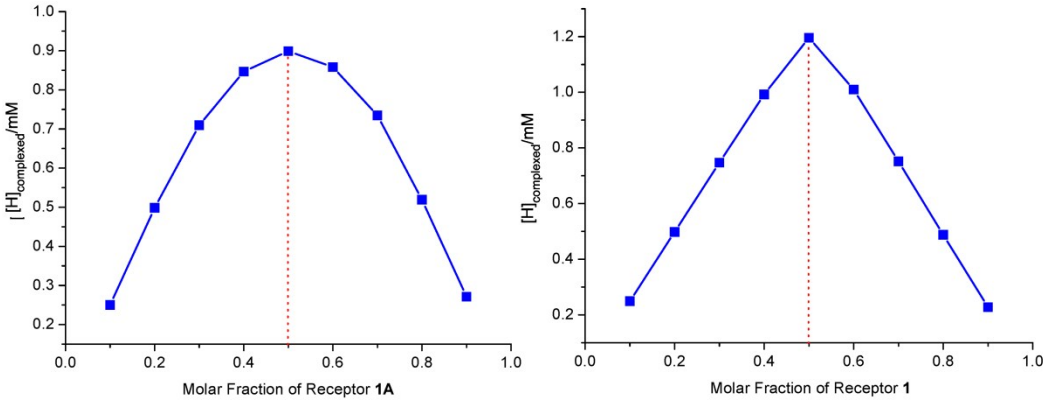


Fig. S25. Job plots between receptors (**1A**, **1)** and SO_4^{2-} in DMSO-d_6/20% H_2O . Points were obtained based on changes of the signals used for calculation of binding constants. The [host] + [SO_4^{2-}] = 2.5 mM.

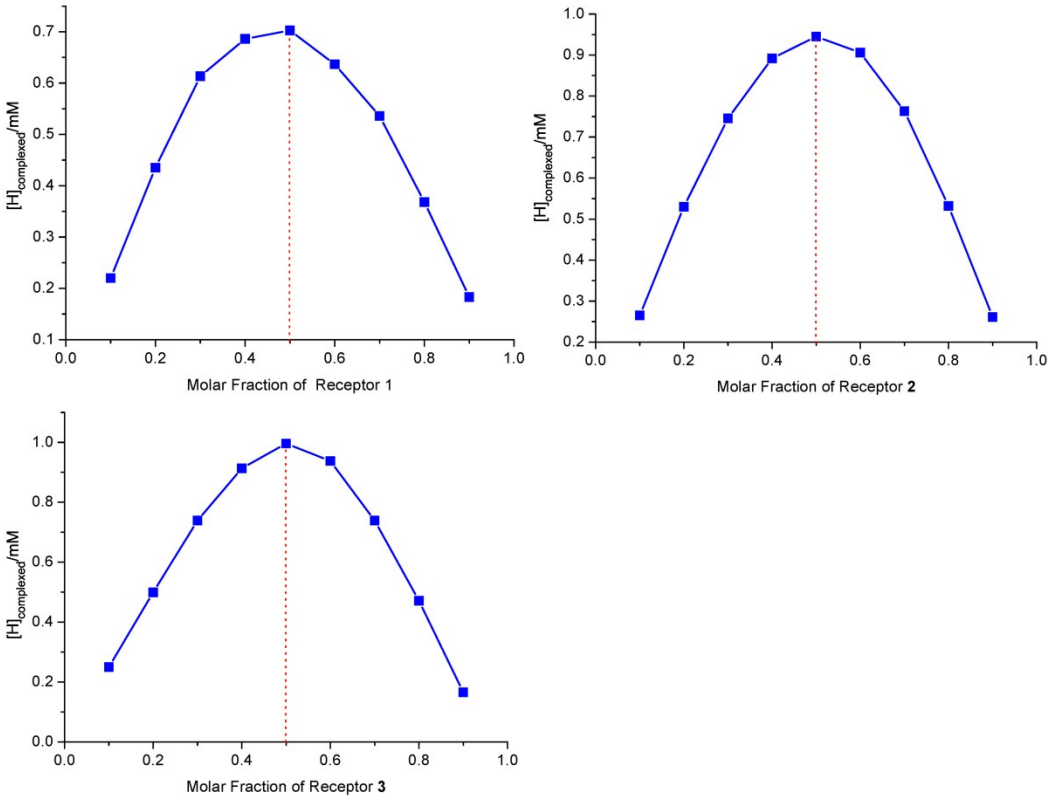


Fig. S26. Job plots between receptors (**1**, **2**, **3**) and SO_4^{2-} in DMSO-d_6/50% H_2O . Points were obtained based on changes of the signals used for calculation of binding constants. The [host] + [SO_4^{2-}] = 2.5 mM.

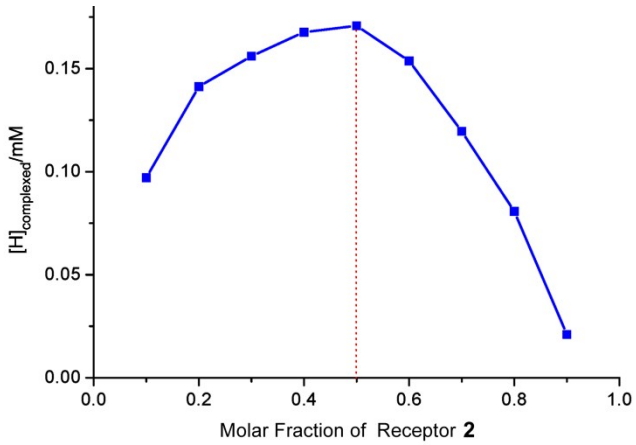


Fig. S27. Job plots between receptor **2** and SO_4^{2-} in D_2O. Points were obtained based on changes of the signals used for calculation of binding constants. The [host] + [SO_4^{2-}] = 1.25 mM.

2.2. Stacked ^{1}H NMR spectra (400 MHz, DMSO-d_6) of 2A and 2.

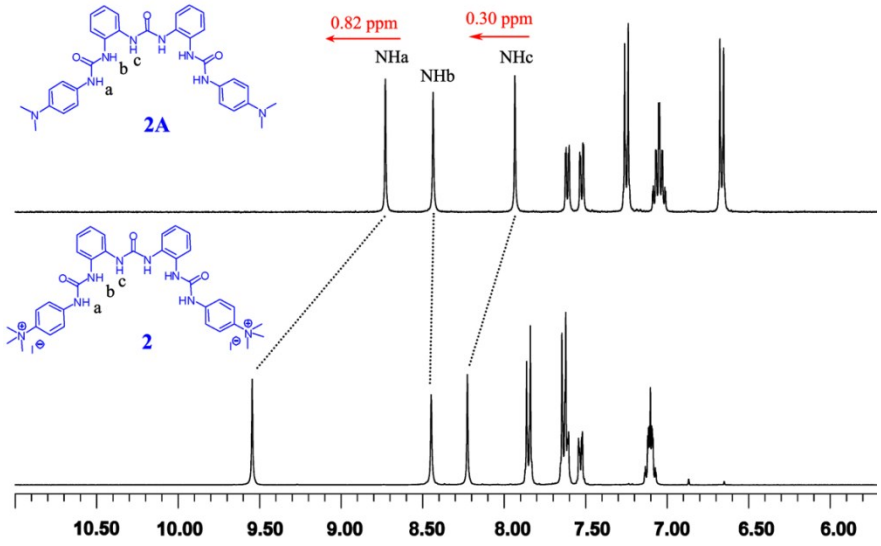


Fig. S28. Stacked ^{1}H NMR spectra (400 MHz, DMSO-d_6) of **2A** and **2**.

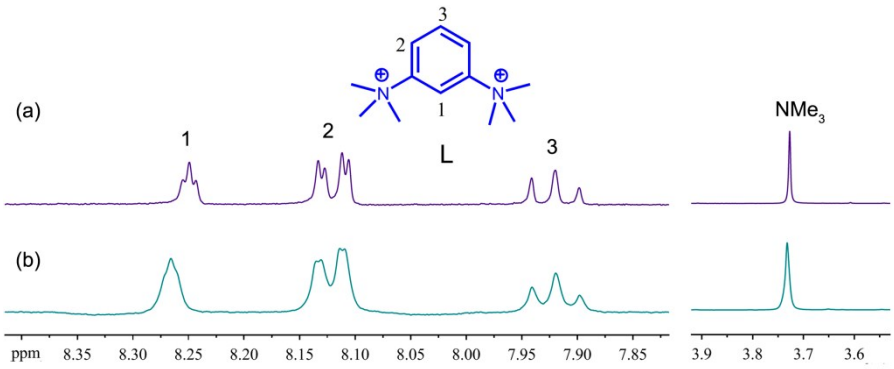


Fig. S29 Partial ^{1}H NMR spectra (400 MHz, 298 K, D_2O) of (a) control molecule **L** (2.5 mM) and (b) **L**/25 $(TBA)_2SO_4$.

2.3. Crystal structural data of $[(2)_2^{2+}\cdot(SO_4)_2^{2-}]$

Crystals suitable for X-ray diffraction was obtained by slow evaporation of a DMSO solution of **2** in the presence of one equiv. of $(TBA)_2SO_4$.

Table S1. Hydrogen bonds [Å and °] in the crystal structure, $[(\mathbf{2})^{2+}\cdot(SO_4)^{2-}]$.

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
N2–H2···O1	0.88	2.02	2.8990(57)	175
N3–H3···O2	0.88	1.93	2.8094(59)	167
N4–H4···O2	0.88	2.01	2.8913(56)	147
N5–H5···O3	0.88	2.02	2.8989(55)	159
N6–H6···O3	0.88	1.96	2.8423(55)	164
N7–H7···O1	0.88	2.02	2.8969(58)	166
Average	0.88	1.99	2.8730	163
D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
C3–H3A···O4	0.98	2.34	3.3234(72)	161
C9–H9···O4	0.95	2.40	3.3482(81)	170
C29–H29···O4	0.95	2.45	3.4035(62)	161
C33–H33A···O4	0.98	2.38	3.3581(57)	172
Average	0.97	2.39	3.3583	166

2.4. DOSY spectra of 2 and 2/5 SO_4^{2-}

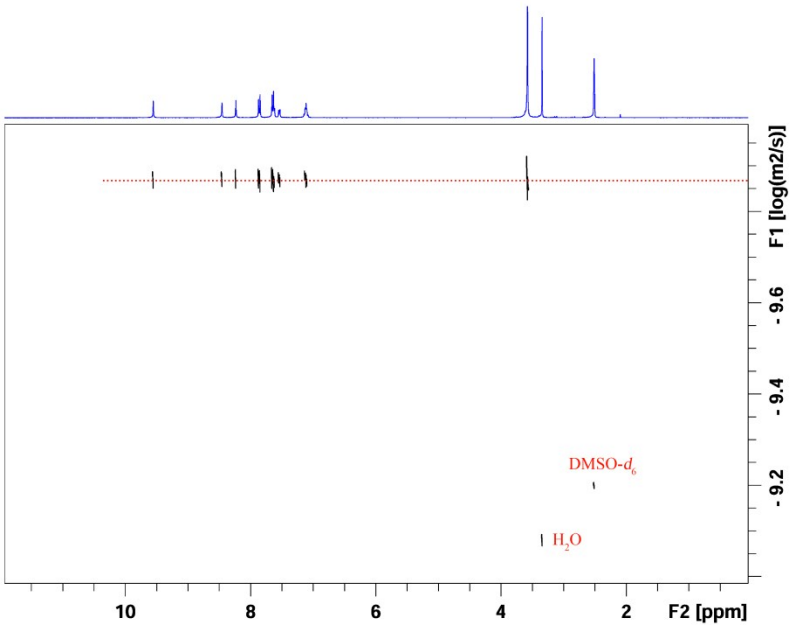


Fig. S30 ^{1}H DOSY (400 MHz, DMSO-d_6, 293 K) spectrum of receptor **2** (10 mM), showing D(**2**) = 1.33 × 10^{-10} m^2 s^{-1}.

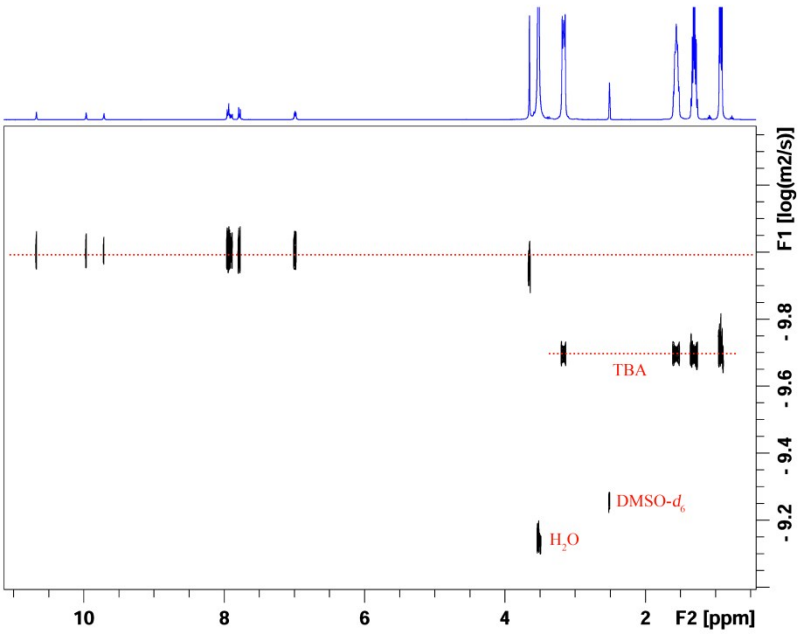


Fig. S31 ^{1}H DOSY (400 MHz, DMSO-d_6, 293 K) spectrum of receptor **2** (10 mM) + 5 equiv. of $(TBA)_2SO_4$, showing a D(**2•SO$_4$**) = 1.02 × 10^{-10} m^2 s^{-1}.

The sphere's hydrodynamic radius was estimated according to the Stokes-Einstein Equation, $D = kT/6\pi\mu r$, where D is the diffusion constant, k is the Boltzmann's constant, T is the temperature, μ is the viscosity of solvents, and r is the radius. r(**2•SO$_4$**)/r(**2**) = D(**2**)/D(**2•SO$_4$**) = 1.30.

2.5. Anion selectivity studies of receptors 2 with various anions

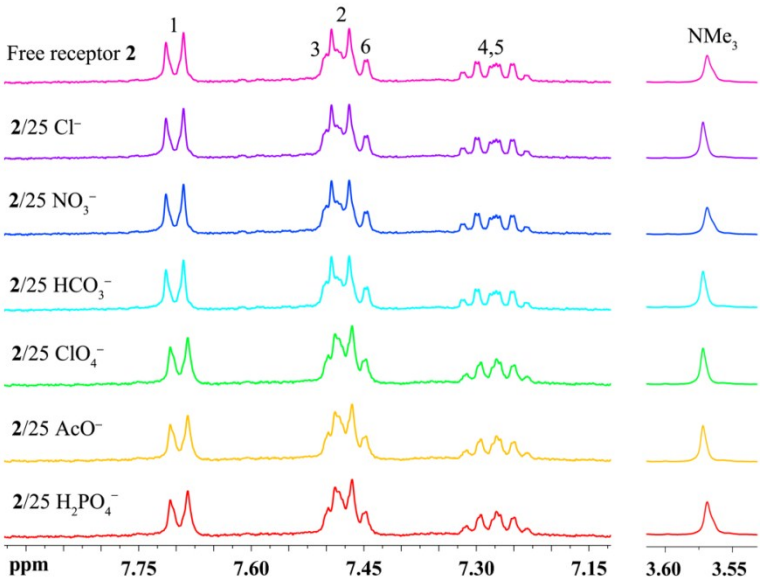


Fig. S32. Partial ^{1}H NMR spectra (400 MHz, 298 K, pH 7.4 D_2O buffered by 20 mM HEPES) of receptor **2** (1.25 mM) alone and in the presence of 25 equiv. of Cl^-, NO_3^-, HCO_3^-, ClO_4^-, AcO^- and $H_2PO_4^-$, respectively, (all anions added as sodium salts).

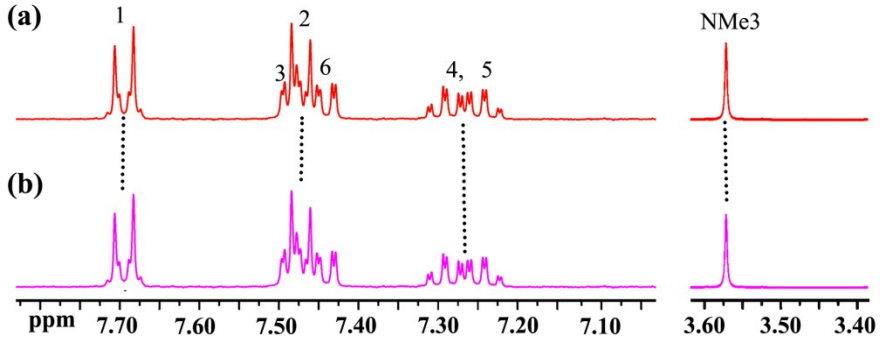
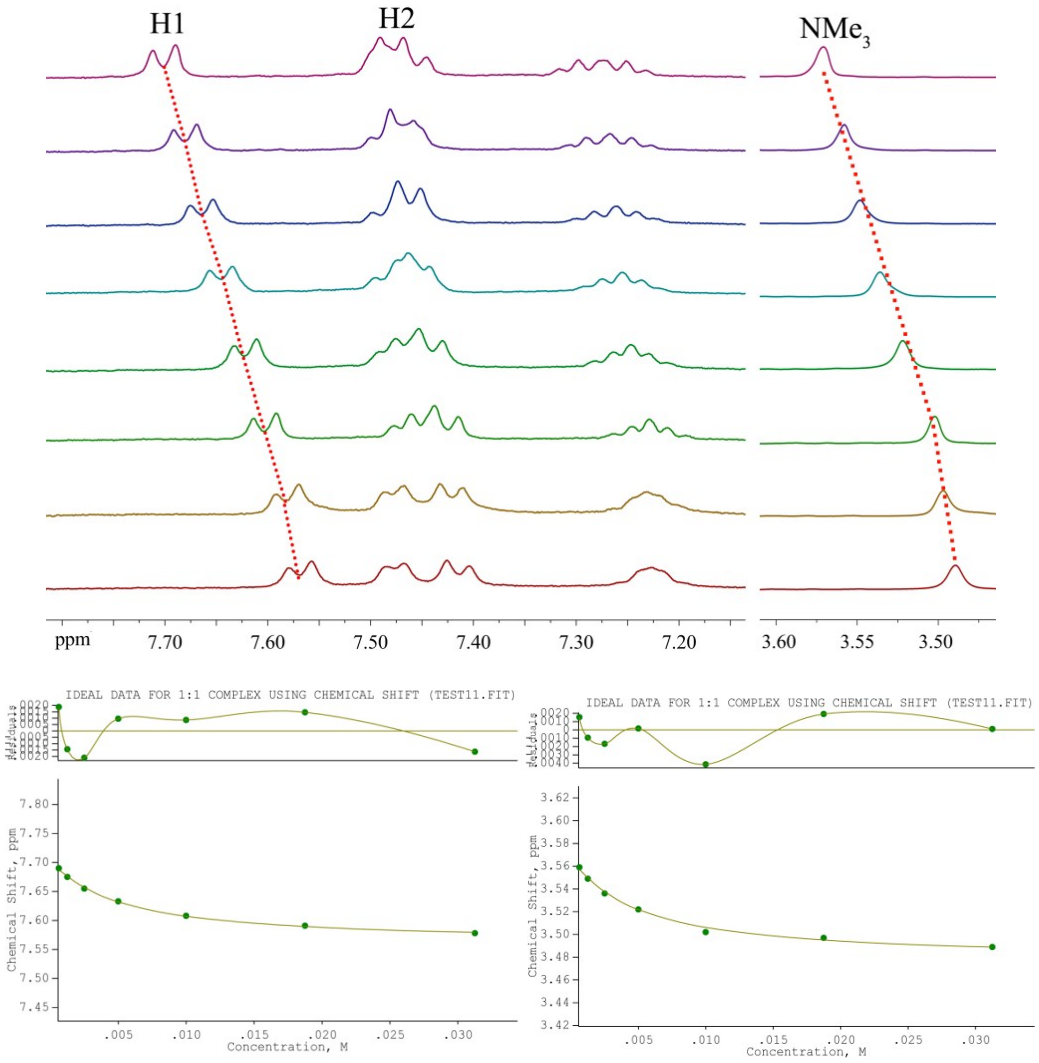
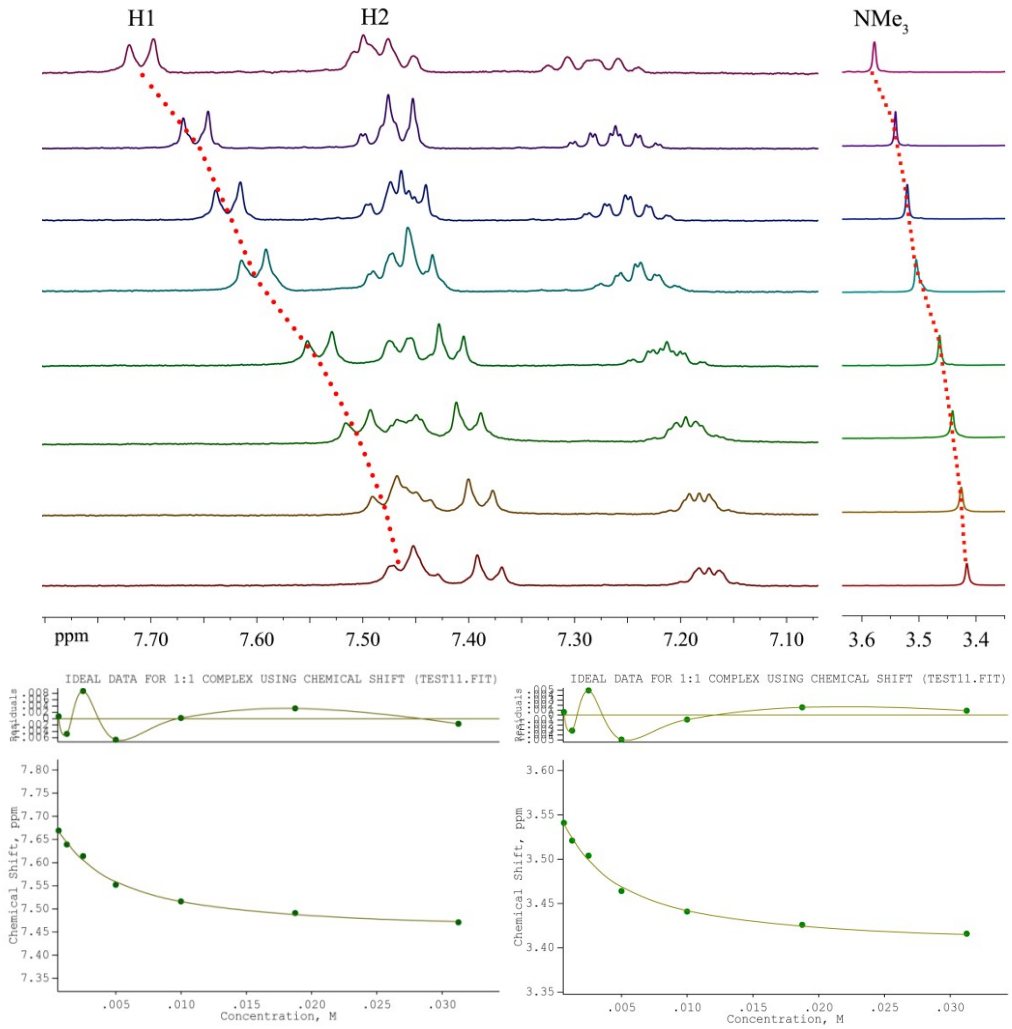


Fig. S33. Partial ^{1}H NMR spectra (400 MHz, 298 K, D_2O) of receptor **2** (1.25 mM) (a) alone and (b) in the presence of 25 equiv. of Cl^-, NO_3^-, HCO_3^-, ClO_4^-, AcO^- and $H_2PO_4^-$ (all anions added as sodium salts).



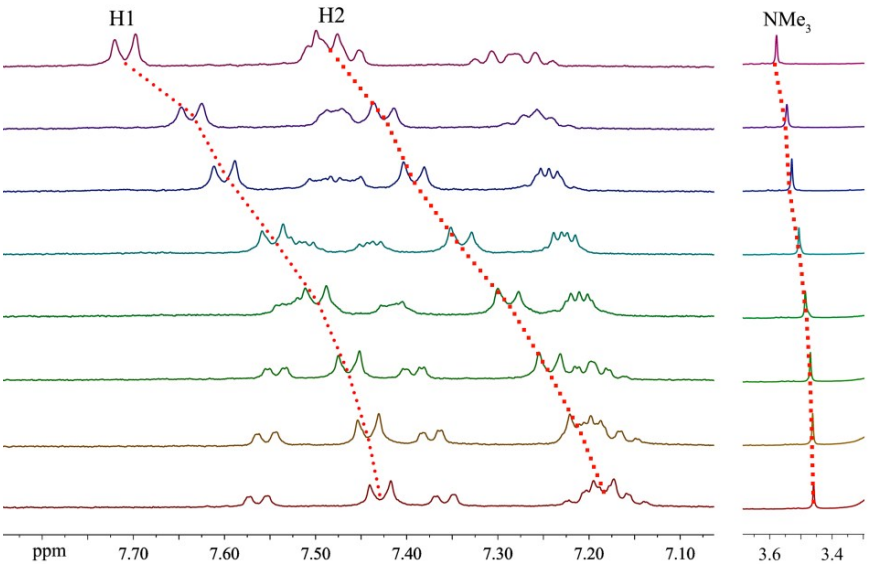
K_a = 235 M^{-1}, Error = 9%; K_a = 237 M^{-1}, Error = 5%

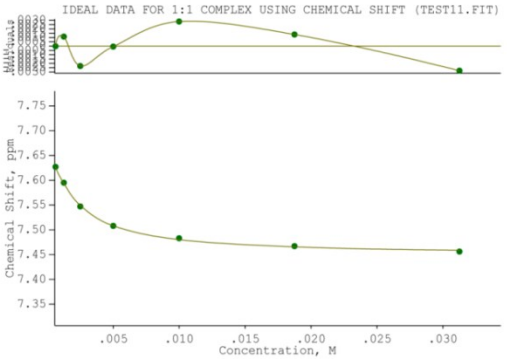
Fig. S34. ^{1}H NMR Stack plot of receptor **2** (1.25 mM) with 0-25 equiv. of Na_2SO_4 in a pH 7.4 D_2O buffer (20 mM HEPES) and the WinEQNMR2 fitted titration profile by following the shifts of CH at 7.72 ppm and 3.58 ppm.



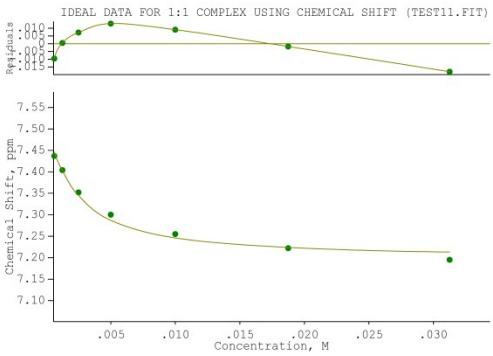
K_a = 295 M^{-1}, Error = 1%; K_a = 310 M^{-1}, Error = 5%

Fig. S35. ^{1}H NMR Stack plot of receptor **2** (1.25 mM) with 0-25 equiv. of $Na_2S_2O_3$ in a pH 7.4 D_2O buffer (20 mM HEPES) and the WinEQNMR2 fitted titration profile by following the shifts of CH at 7.72 ppm and 3.58 ppm.

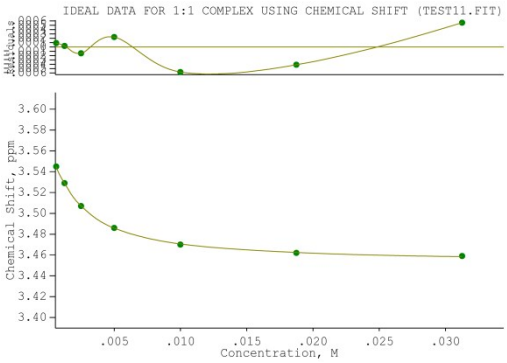




K_a = 549 M^{-1}, Error = 3%;

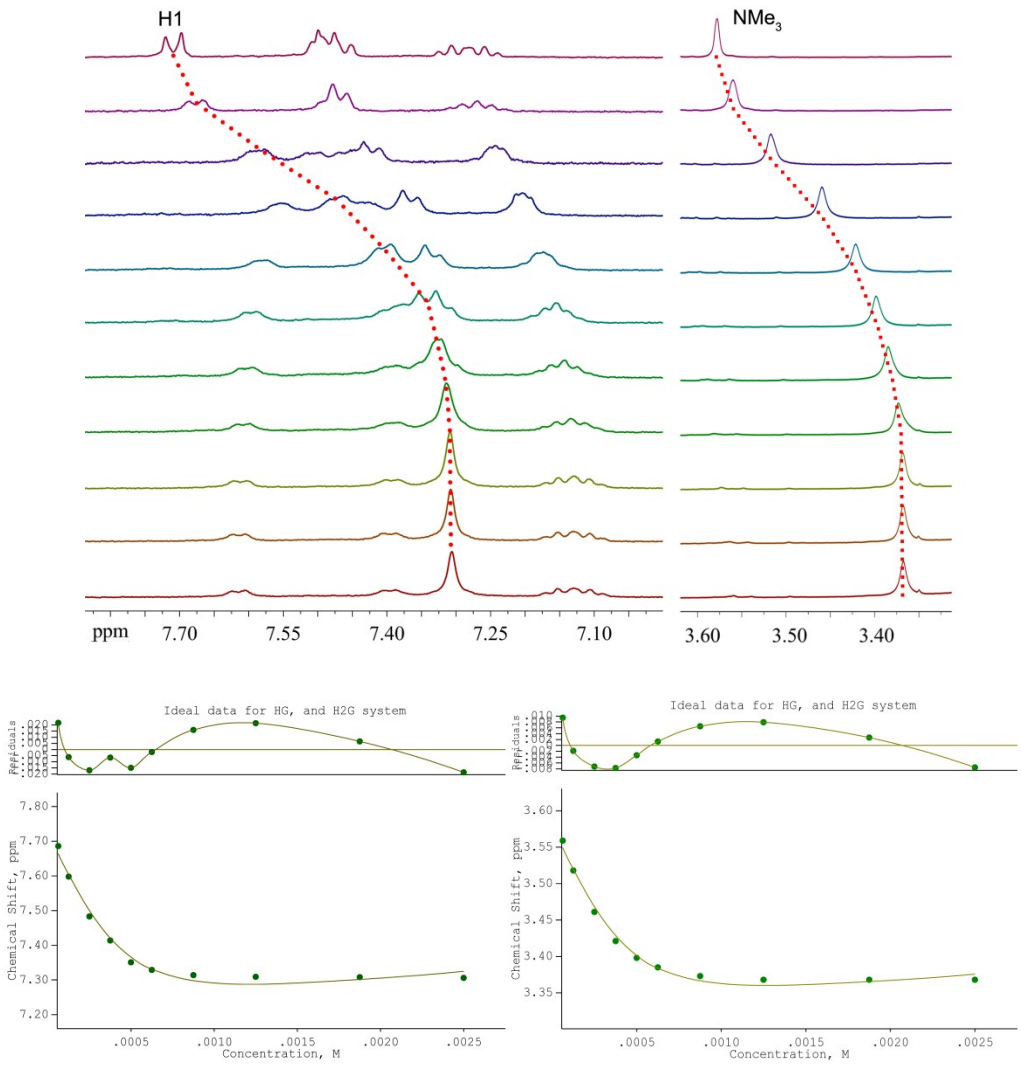


K_a = 587 M^{-1}, Error = 5%;



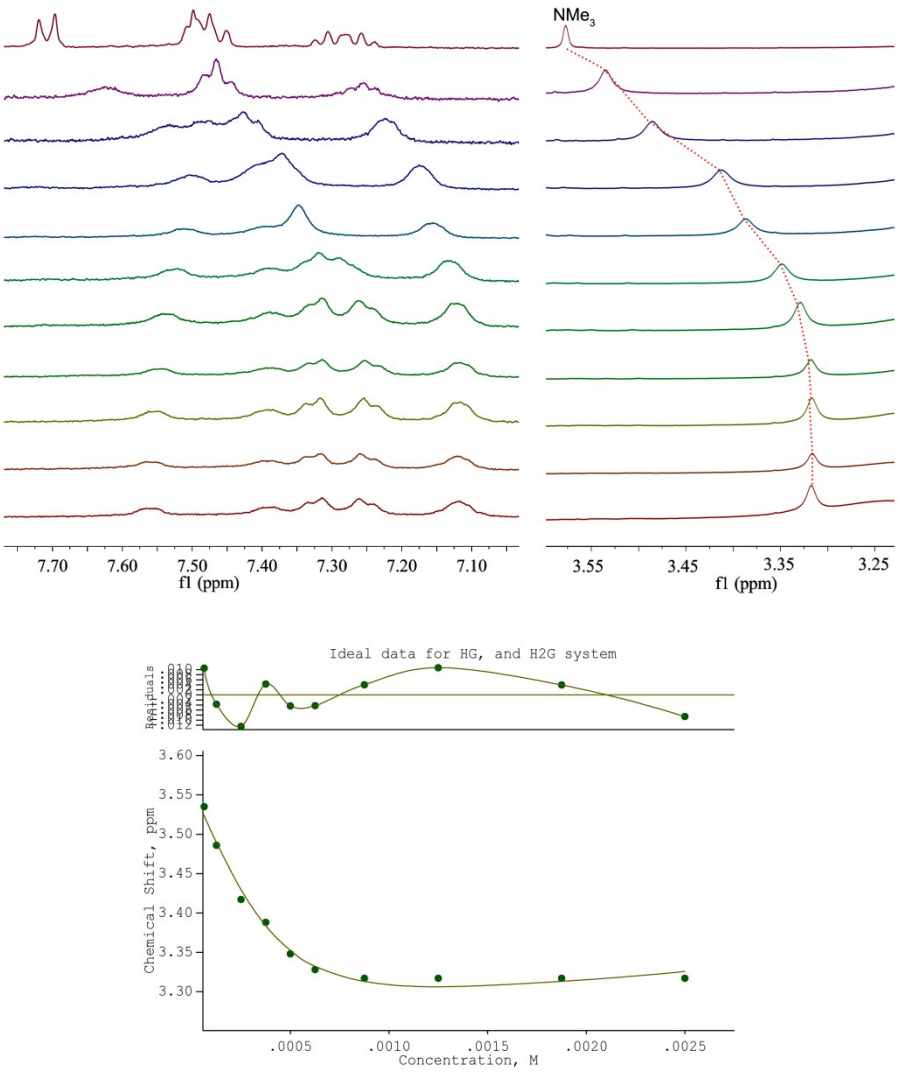
K_a = 590 M^{-1}, Error = 5%;

Fig. S36. ^{1}H NMR Stack plot of receptor **2** (1.25 mM) with 0-25 equiv. of AMP^{2-} (used as sodium salts) in a pH 7.4 D_2O buffer (20 mM HEPES) and the WinEQNMR2 fitted titration profile by following the shifts of CH at 7.72 ppm, 7.48 ppm and 3.58 ppm.



$K_a(H_2G) > 10^4\ M^{-2}$; $K_a(H_2G) > 10^4\ M^{-2}$;

Fig. S37. ^{1}H NMR Stack plot of receptor **2** (1.25 mM) with 0-2.0 equiv. of ADP^{2-} (used as sodium salts) in a pH 7.4 D_2O buffer (20 mM HEPES) and the WinEQNMR2 fitted titration profile by following the shifts of CH at 7.72 ppm, 7.48 ppm and 3.58 ppm (H = host, G = guest).



$$K_a(H_2G) > 10^4\ M^{-2}$$

Fig. S38. ^{1}H NMR Stack plot of receptor **2** (1.25 mM) with 0-2.0 equiv. of ATP^{2-} (used as sodium salts) in a pH 7.4 D_2O buffer (20 mM HEPES) and the WinEQNMR2 fitted titration profile by following the shifts of CH at 3.58 ppm (H = host, G = guest).

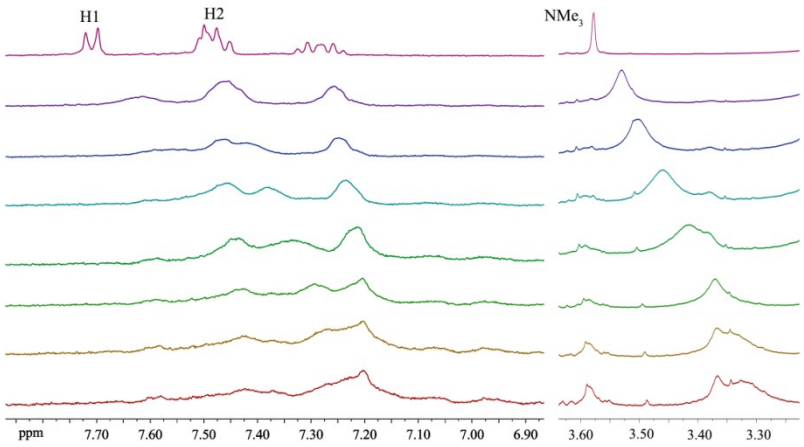


Fig. S39. ^{1}H NMR Stack plot of receptor **2** (1.25 mM) with 0-25 equiv. of Na_2HPO_4 in a pH 7.4 D_2O buffer (20 mM HEPES).

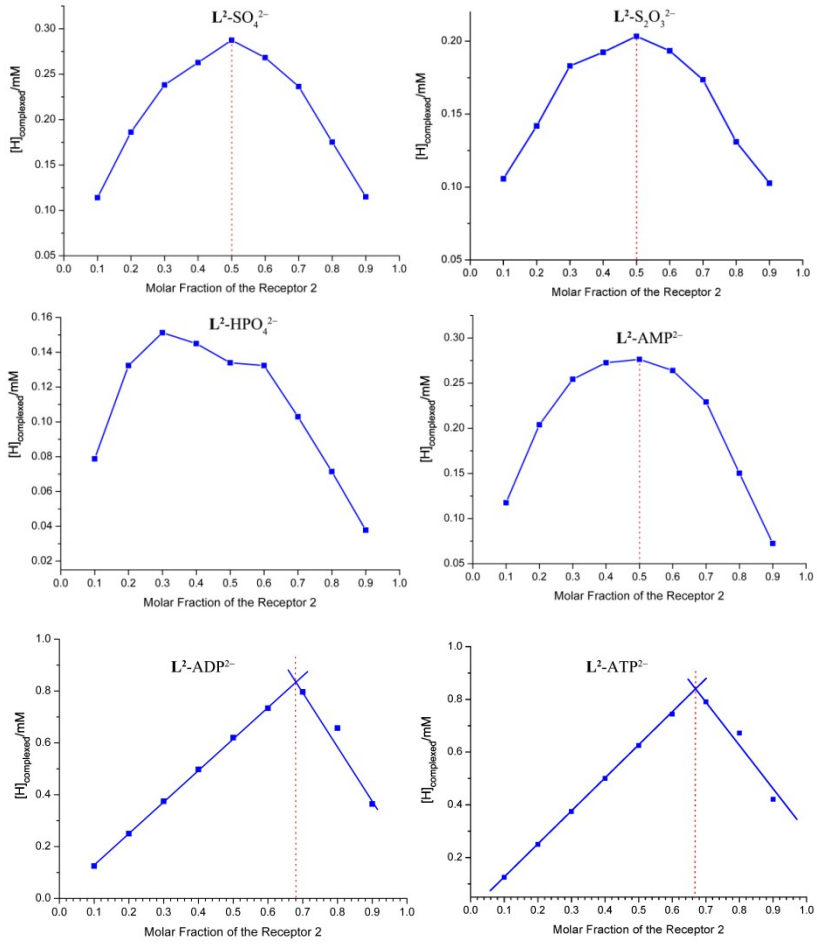


Fig. S40. Job plots between receptor **2** and SO_4^{2-}, $S_2O_3^{2-}$, HPO_4^{2-}, AMP^{2-}, ADP^{2-}, ATP^{2-} (all anions used as as sodium salts) in a pH 7.4 D_2O buffer (20 mM HEPES). Points were obtained based on changes of the signals used for calculation of binding constants. The [host] + [anion] = 1.25 mM.

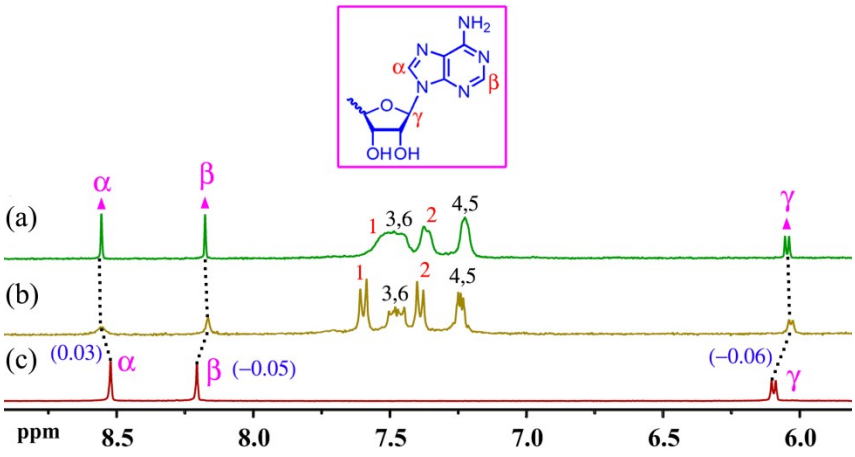


Fig. S41 Partial ^{1}H NMR spectra (400 MHz, 298 K, pH 7.4 D_2O buffered by 20 mM HEPES) of (a) receptor **2**/1.0 (AMP^{2-}, SO_4^{2-}, HPO_4^{2-} and $S_2O_3^{2-}$), (b) receptor **2**/1.0 AMP^{2-} and (c) free AMP^{2-} (all anions used as sodium salts, AMP^{2-}, ▲, inset: proton numbering of the adenosine group).

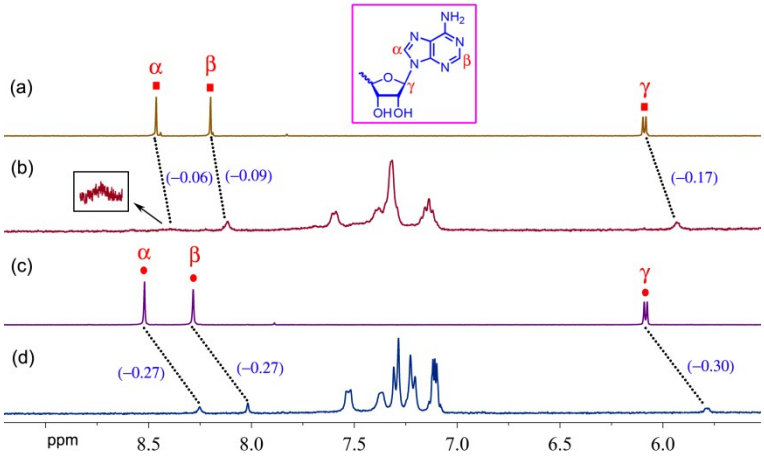


Fig. S42 Partial ^{1}H NMR spectra (400 MHz, 298 K, pH 7.4 D_2O buffered by 20 mM HEPES) of (a) ADP^{2-} ■), (b) receptor **2**/0.5 ADP^{2-}, (c) ATP^{2-} (●) and (d) receptor **2**/0.5 ATP^{2-} (all anions used as sodium salts, inset: proton numbering of the adenosine group).

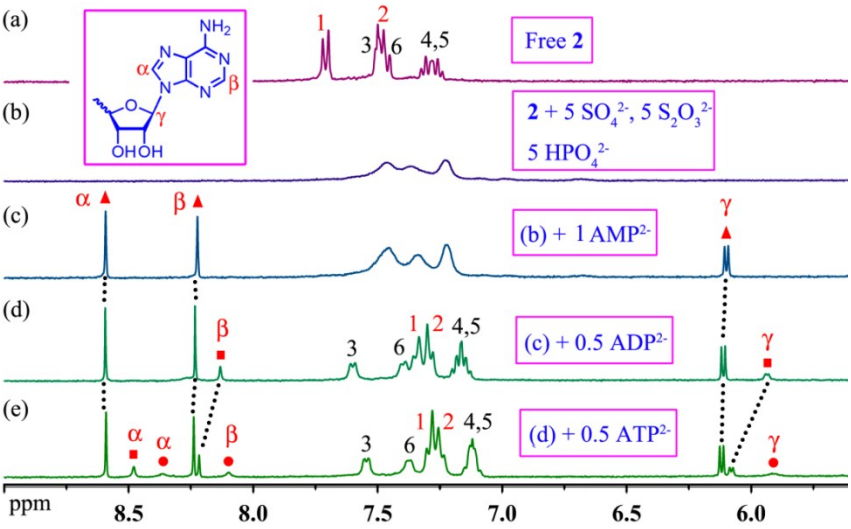


Fig. S43 Partial ^{1}H NMR spectra (400 MHz, 298 K, pH 7.4 D_2O buffered by 20 mM HEPES) of receptor **2** (1.25 mM) (a) alone and (b) after successively adding 5.0 equiv. of SO_4^{2-}, HPO_4^{2-}, $S_2O_3^{2-}$, (c) 1.0 equiv. of AMP^{2-} (▲), (d) 0.5 equiv. of ADP^{2-} (■), and (e) 0.5 equiv. of ATP^{2-} (●) (all anions used as sodium salts, inset: proton numbering of the adenosine group).

3. References

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