Supporting information for

Tetraamidoindolyl Calix[4]arene as a Selective Ion Pair Receptor for LiCl

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1. General experimental and synthetic details

Solvents and reagents used for the synthetic work were purchased from Aldrich, TCI, or Alfa Aesar and used without further purification. Compound **2** was prepared as reported previously.[1] NMR spectra were recorded on a Bruker Advance-300 MHz instrument. The NMR spectra were referenced to residual solvent peaks and the spectroscopic solvents were purchased from either Cambridge Isotope Laboratories or Aldrich. Chemical ionization (CI) and electrospray ionization (ESI) mass spectra were recorded on a VG ZAB-2E instrument and a VG AutoSpec apparatus, respectively. TLC analyses were carried out using Sorbent Technologies silica gel (200 mm) sheets. Column chromatography was performed on Sorbent Technologies silica gel 60 (40–63 mm).

Receptor 1

Under a nitrogen atmosphere, compound **2** (500 mg, 0.82 mmol) and indole-2-carboxylic acid (538 mg, 3.34 mmol) were dissolved in 5 mL of a 2:1 v/v mixture of dichloromethane (DCM) and tetrahydrofuran (THF) in the presence of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI; 781 mg, 4.08 mmol) and 4-dimethylaminopyridine (438 mg, 3.59 mmol). The reaction mixture was allowed to stir for 4 h at room temperature. After the reaction was deemed complete (TLC), solvents were removed *in vacuo*. To the resulting yellowish solid, DCM (50 mL) and water (50 mL) were added. Then, organic phase was separated off and washed with water (30 mL) three times. The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo to give a yellow solid. Column chromatography over silica gel (eluent: ethyl acetate/hexanes (1:1)), followed by recrystallization from DCM and methanol, gave 0.5 g of receptor **1** (39% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (s, 4H), 9.88 (s, 4H), 7.44-7.42 (d, 4H, *J* = 8 Hz), 7.36-7.34 (d, 4H, *J* = 8 Hz), 7.24 (s, 8H), 7.21 (s, 4H), 7.13-7.09 (t, 4H, *J* = 8 Hz & *J* = 16 Hz), 6.96-6.92 (t, 4H, *J* = 8 Hz & *J* = 16 Hz), 4.47-4.44 (d, 4H, *J* = 12 Hz), 3.88-3.84 (t, 8H, *J* = 8 Hz & *J* = 16 Hz), 3.24-3.21 (d, 4H, *J* = 12 Hz), 2.02-1.93 (m, 8H), 1.01-0.97 (t, 9H, *J* = 8 Hz & *J* = 16 Hz), ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.8, 152.9, 137.0, 134.7, 133.3, 132.1, 127.5, 124.0, 122.1, 121.7, 120.2, 112.7, 104.0, 77.2, 23.2, 10.7. HR-ESI-MS calc. $C_{76}H_{72}N_8O_8Li$ 1231.56290; found 1231.5653 $[M+Li]^+$.

2. ^{1}H NMR spectra and mass spectra

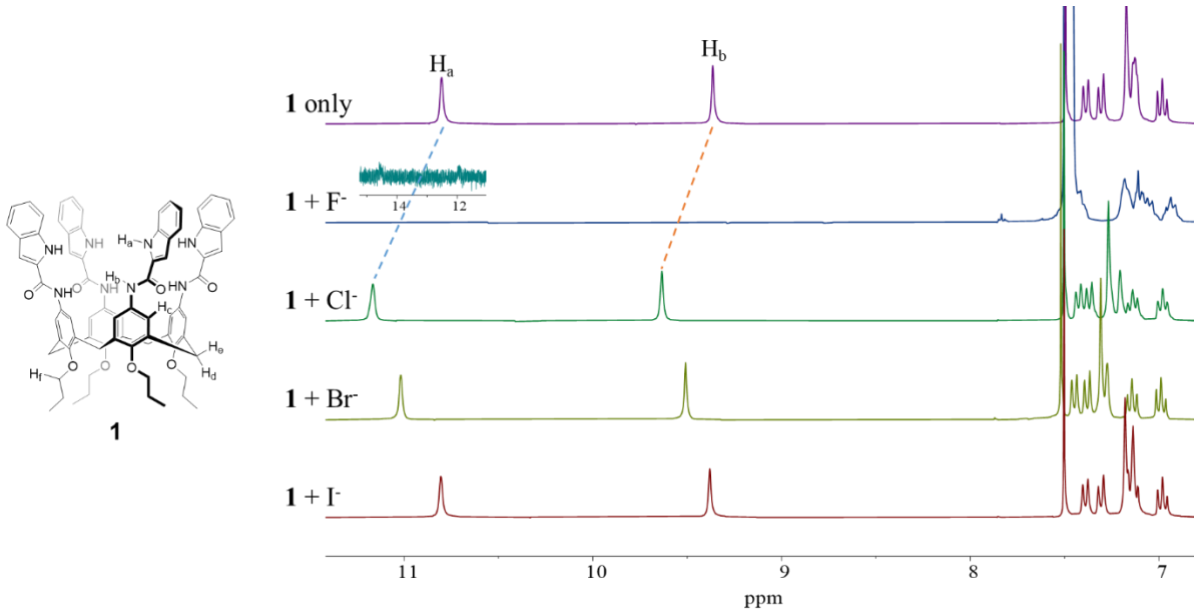


Figure S1. Partial ^{1}H NMR spectra of receptor **1** (3 mM) recorded in 10% DMSO-d_6 in $CDCl_3$ in the presence of TBAF, TBACl, TBABr, and TBAI (>50 equiv).

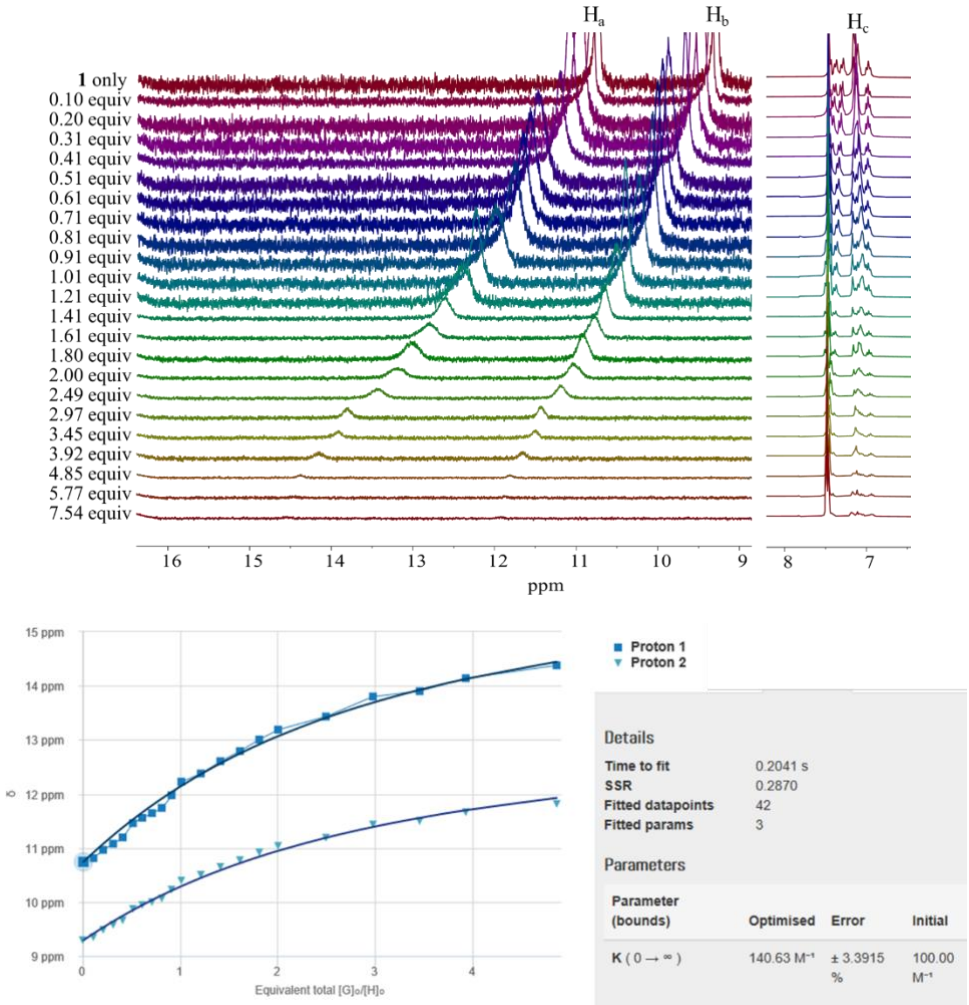


Figure S2. Top: Partial ^{1}H NMR spectra of receptor **1** (3 mM) recorded during the titration with F^{-} (as TBAF) in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

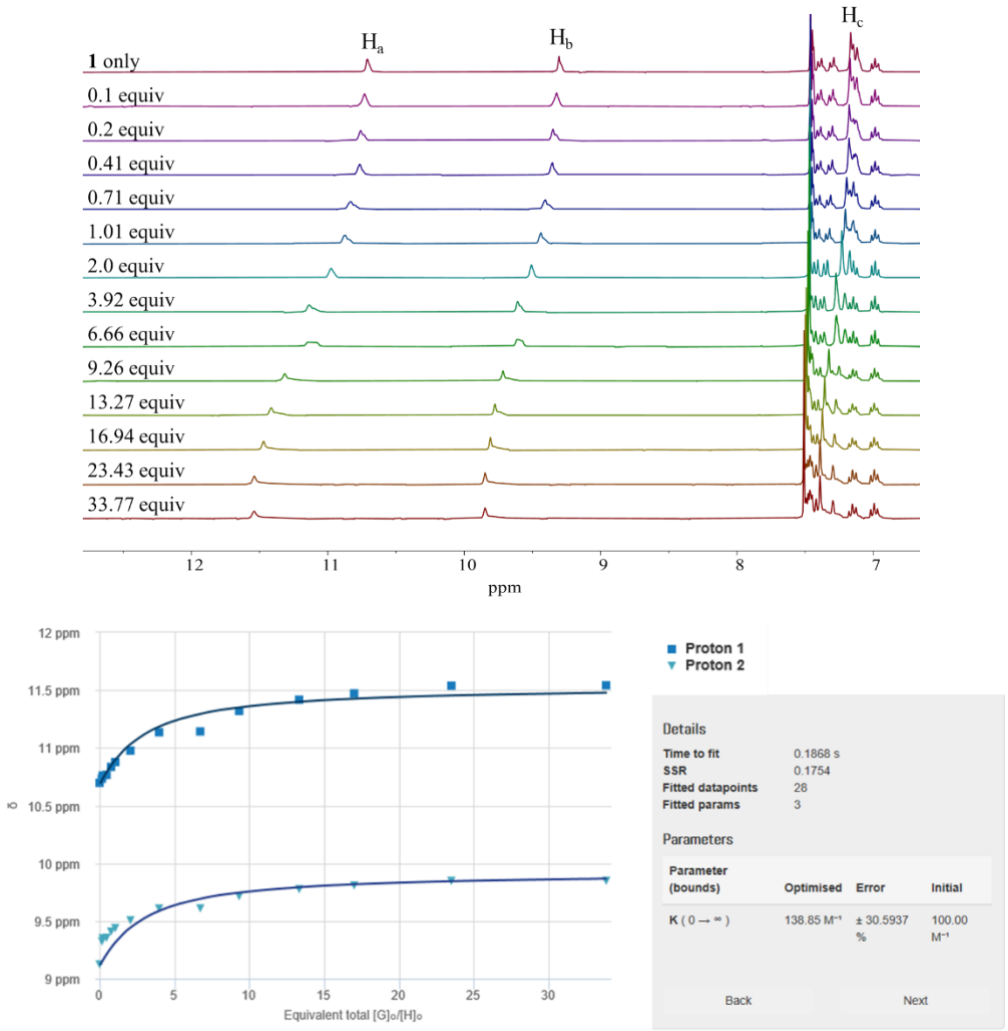


Figure S3. Top: Partial ^{1}H NMR spectra of receptor **1** (3 mM) recorded during the titration with Cl^{-} (as TBACl) in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

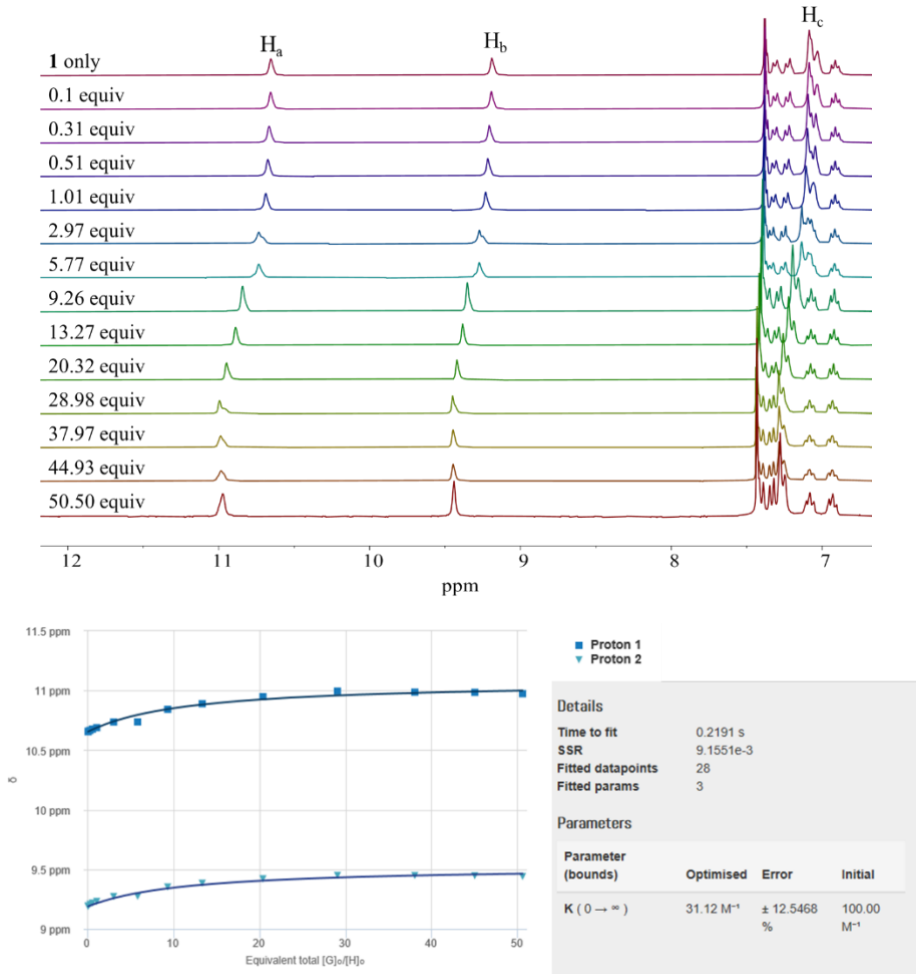


Figure S4. Top: Partial ^{1}H NMR spectra of receptor **1** (3mM) recorded during the titration with Br^{-} (as TBABr) in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

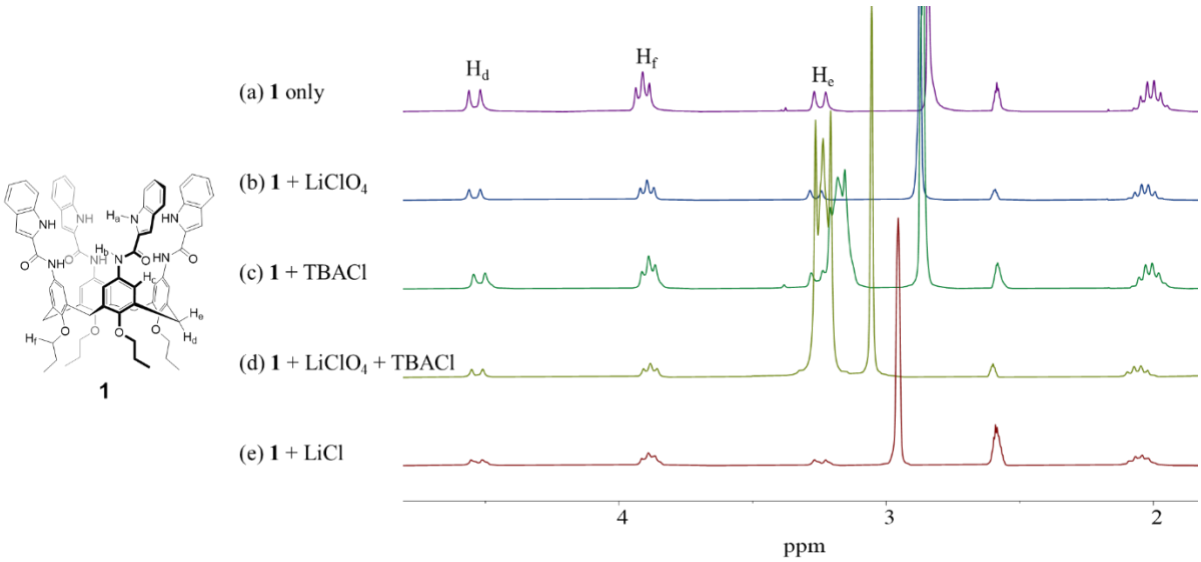


Figure S5. Partial ^{1}H NMR spectra of (a) receptor **1** only, (b) **1** + $LiClO_4$, (c) **1** + TBACl, (d) **1** + $LiClO_4$ + TBACl, and (e) **1** + LiCl in DMSO-d_6/$CDCl_3$ (1:9, v/v).

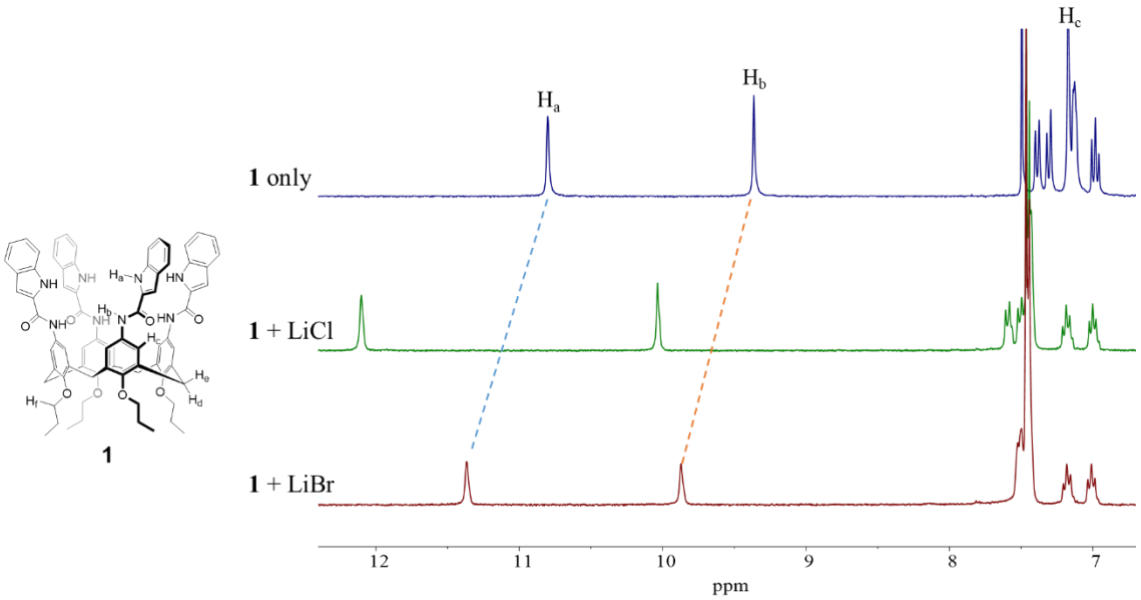


Figure S6. Partial ^{1}H NMR spectra of receptor **1** (3 mM) recorded in 10% DMSO-d_6 in $CDCl_3$ in the presence of LiCl (12 equiv), and LiBr (12 equiv).

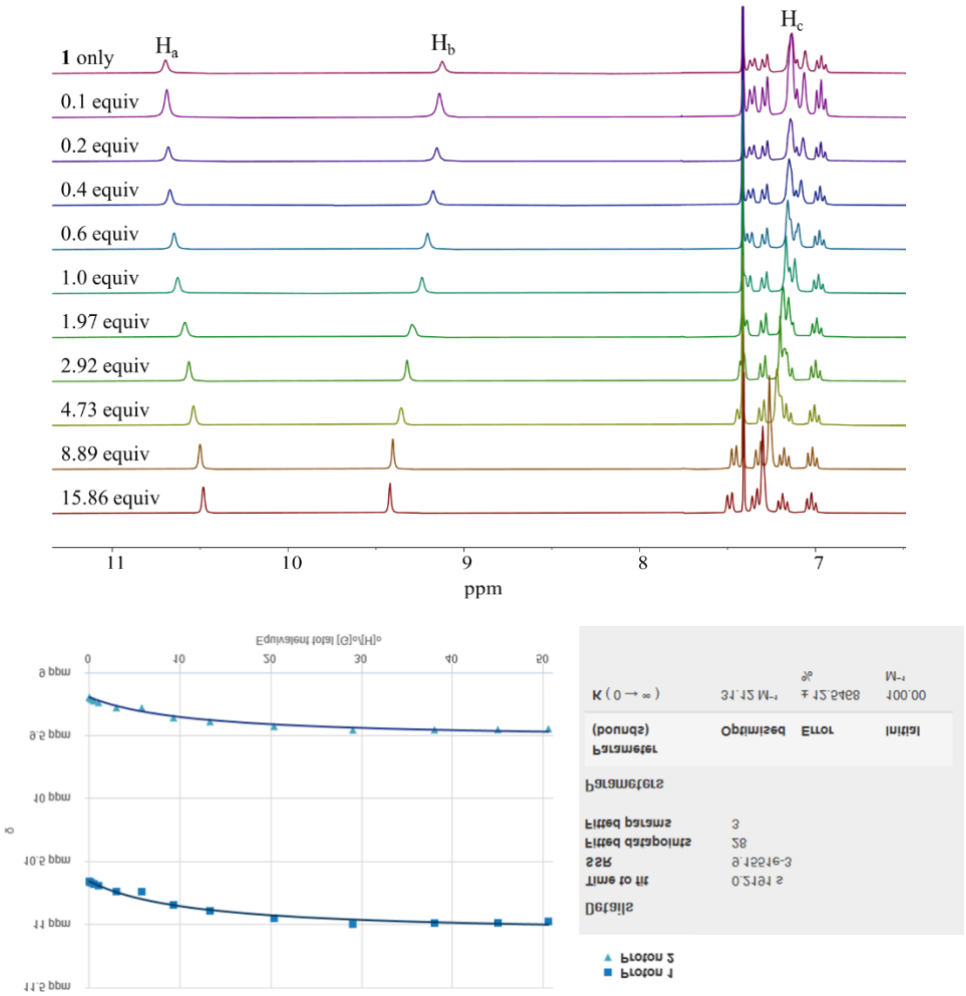


Figure S7. Top: Partial ^{1}H NMR spectra of receptor **1** (3 mM) recorded during the titration with Li^{+} (as $LiClO_4$) in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

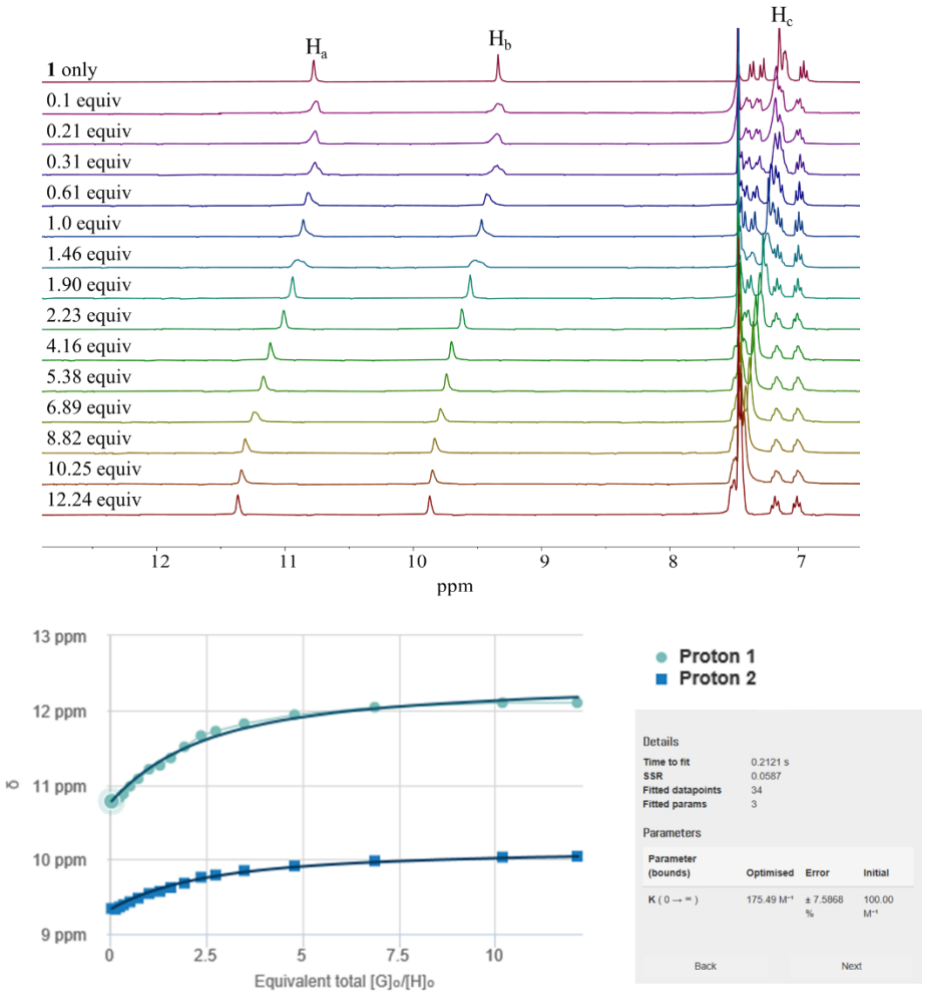


Figure S8. Top: Partial ^{1}H NMR spectra of receptor **1** (3 mM) recorded during the titration with LiBr in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

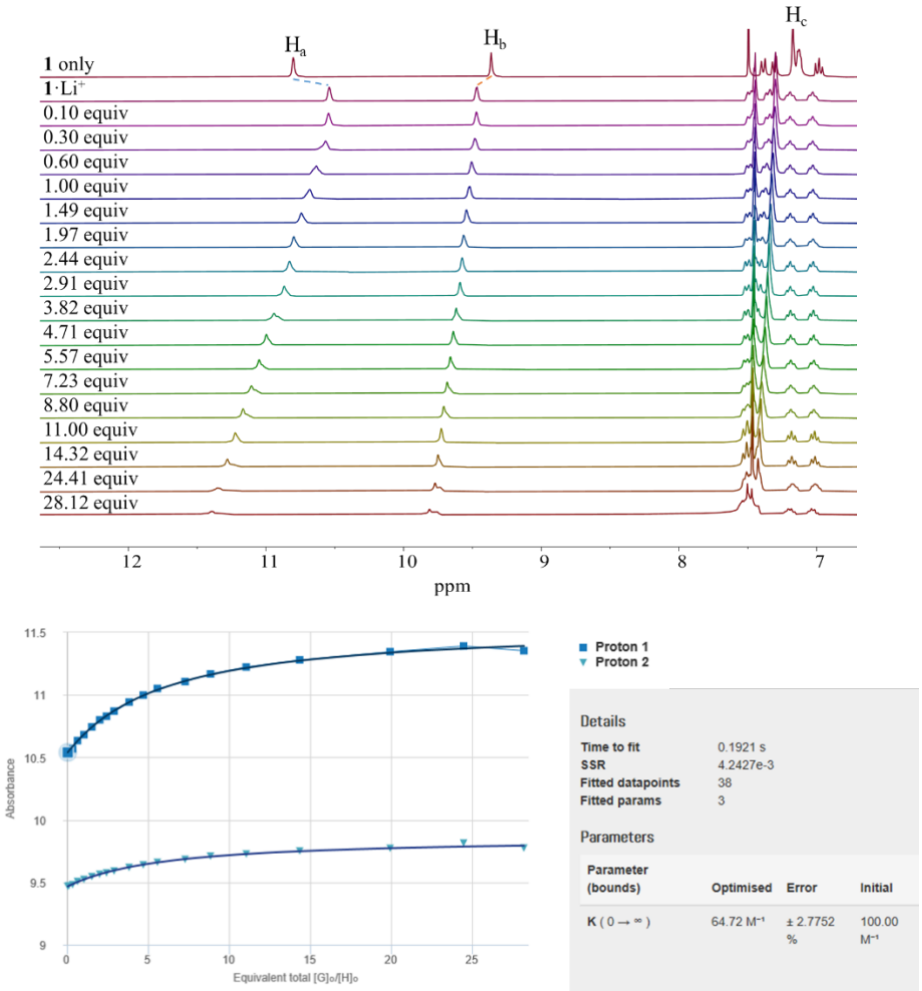


Figure S9. Top: Partial ^{1}H NMR spectra of receptor **1**•Li^{+} (3 mM; produced from **1** and $LiClO_4$) recorded upon titration with Br^{-} (as TBABr) in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

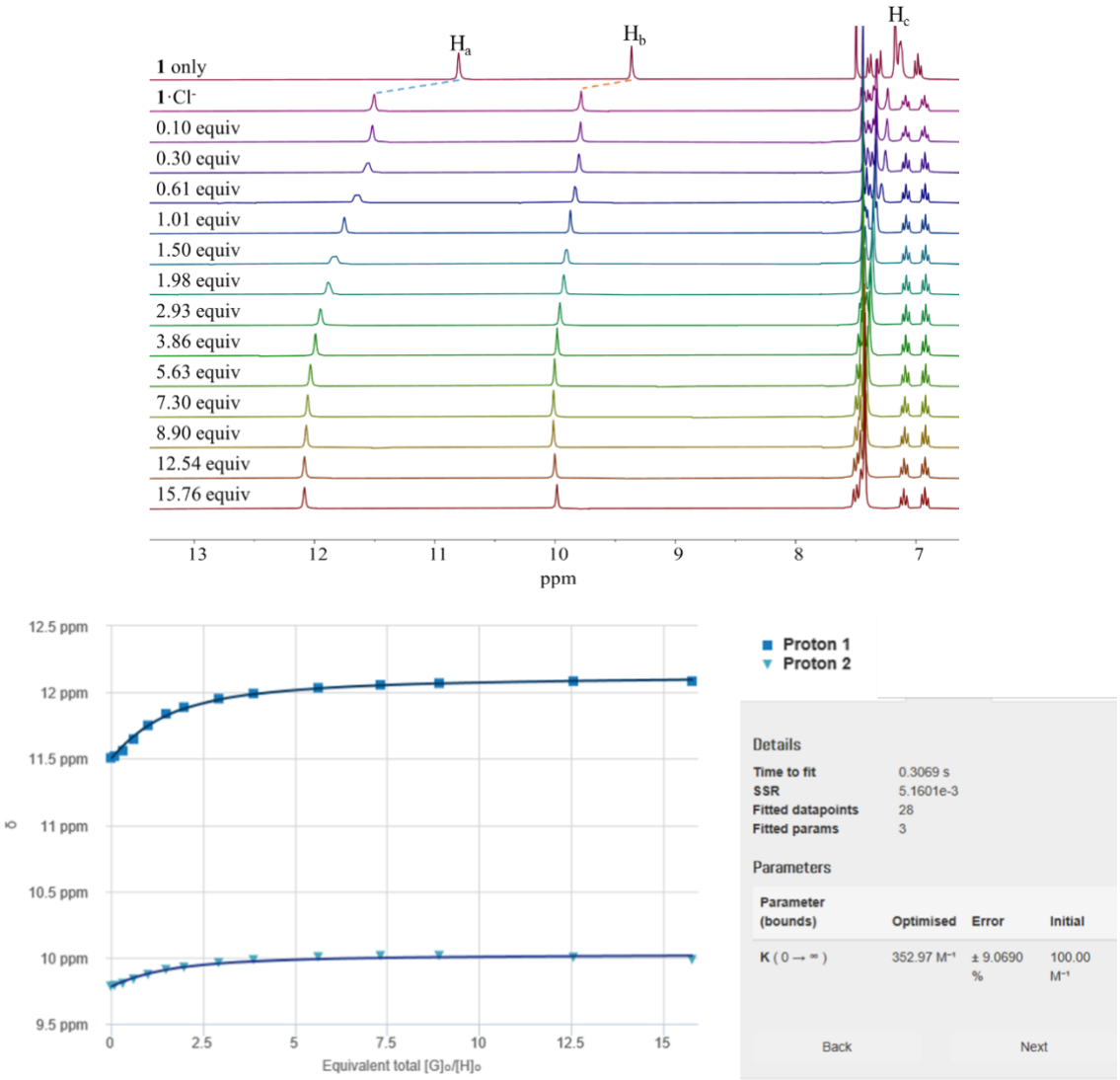


Figure S10. Top: Partial ^{1}H NMR spectra of receptor **1**•Cl^{-} (3 mM produced from **1** and TBACl) recorded upon titration with Li^{+} (as the perchlorate salt) in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

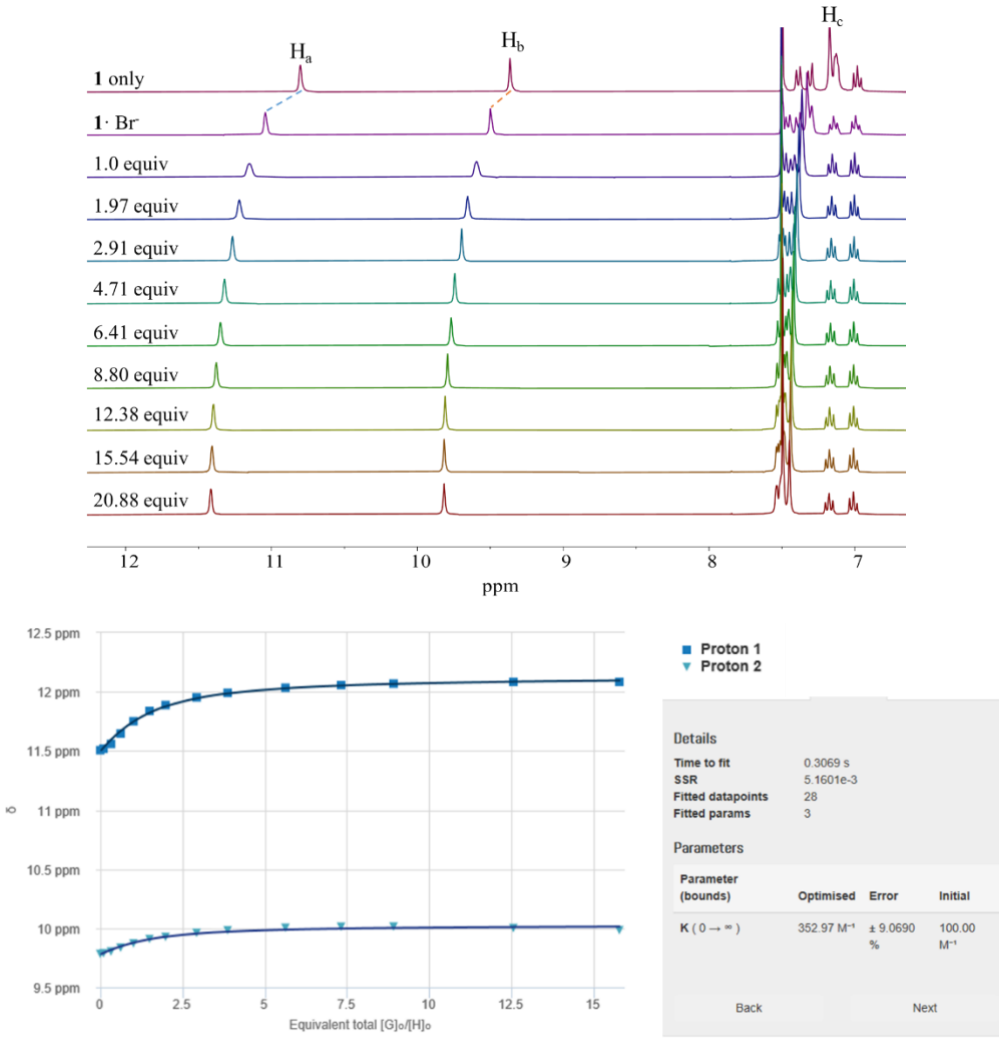


Figure S11. Top: Partial ^{1}H NMR spectra of receptor **1**·Br^{-} (3 mM, produced from **1** and TBABr) recorded upon titration with Li^{+} (as the perchlorate salt) in 10% DMSO-d_6 in $CDCl_3$. Bottom: The corresponding binding isotherms.

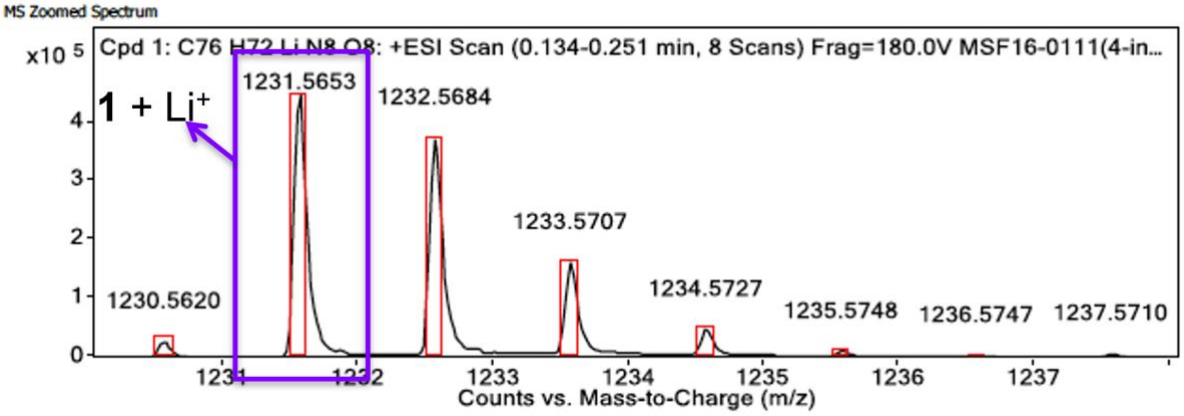


Figure S12. HRMS spectrum of the lithium cation complex of receptor **1**.

3. X-ray Experimental for 1•LiCl•2CH_3OH

Crystals grew as colorless plates by slow evaporation of a $CHCl_3/CH_3CN/CH_3OH$ solution of receptor **1** in the presence of excess lithium chloride. The data crystal was separated from a cluster of crystals and had approximate dimensions; 0.23 x 0.063 x 0.045 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418 Å) with collimating mirror monochromators using a Saturn S2 CCD detector. A total of 1010 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 25 seconds per frame for frames collected with a detector offset of 0.0° and 40 seconds per frame with frames collected with a detector offset of +/- 53.8°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.70a.[3] The structure was solved by direct methods using SHELXT[4] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.[5] Structure analysis was aided by use of the programs PLATON[6] and OLEX2[7]. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

Two regions of disordered solvent were observed in the unit cell. The solvent appeared to be composed of mostly methanol. The solvent mix could not be satisfactorily modeled. The contributions to the scattering factors due to these solvent molecules were removed by using SQUEEZE.[8]

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.0785*P)^2 + (10.6814*P)]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_w(F^2)$ refined to 0.170, with R(F) equal to 0.0649 and a goodness of fit, S, = 0.992. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[9] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[10] All figures were generated using SHELXTL/PC.[11] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures may be obtained from the Cambridge Crystallographic Centre by referencing CCDC number 2209048.

Table S1. Crystal data and structure refinement for **1**•LiCl.

Empirical formula	C78 H80 Cl Li N8 O10	
Formula weight	1331.89	
Temperature	100.15 K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.6204(4) Å	α = 90°.
	b = 34.8192(10) Å	β = 105.015(4)°.
	c = 20.2204(9) Å	γ = 90°.
Volume	7902.2(5) $Å^3$	
Z	4	
Density (calculated)	1.120 Mg/m^3	
Absorption coefficient	0.898 mm^{-1}	
F(000)	2816	
Crystal size	0.23 x 0.063 x 0.045 mm^3	
Theta range for data collection	2.594 to 44.995°.	
Index ranges	-10<=h<=10, -31<=k<=31, -18<=l<=18	
Reflections collected	30780	
Independent reflections	6341 [R(int) = 0.0642]	
Completeness to theta = 44.995°	99.2 %	
Absorption correction	Gaussian and multi-scan	
Max. and min. transmission	1.00 and 0.677	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6341 / 611 / 905	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0649, wR2 = 0.1559	
R indices (all data)	R1 = 0.0879, wR2 = 0.1703	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.291 and -0.260 $e.Å^{-3}$	

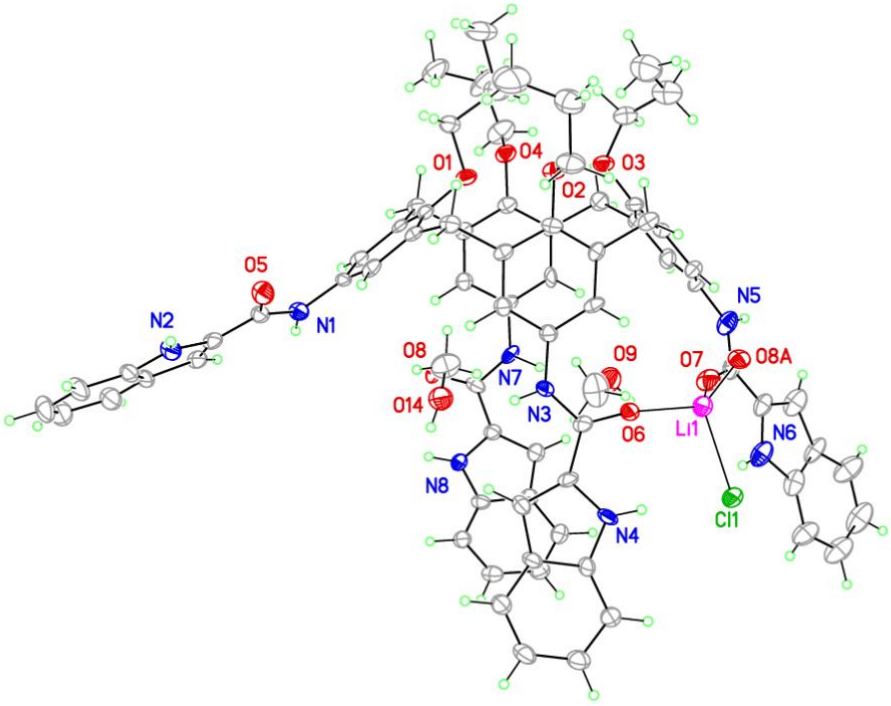


Figure S13. View of the LiCl complex in **1** showing the heteroatom labeling scheme. Displacement ellipsoids are scaled to the 30% probability level.

4. NMR spectra and HRMS data

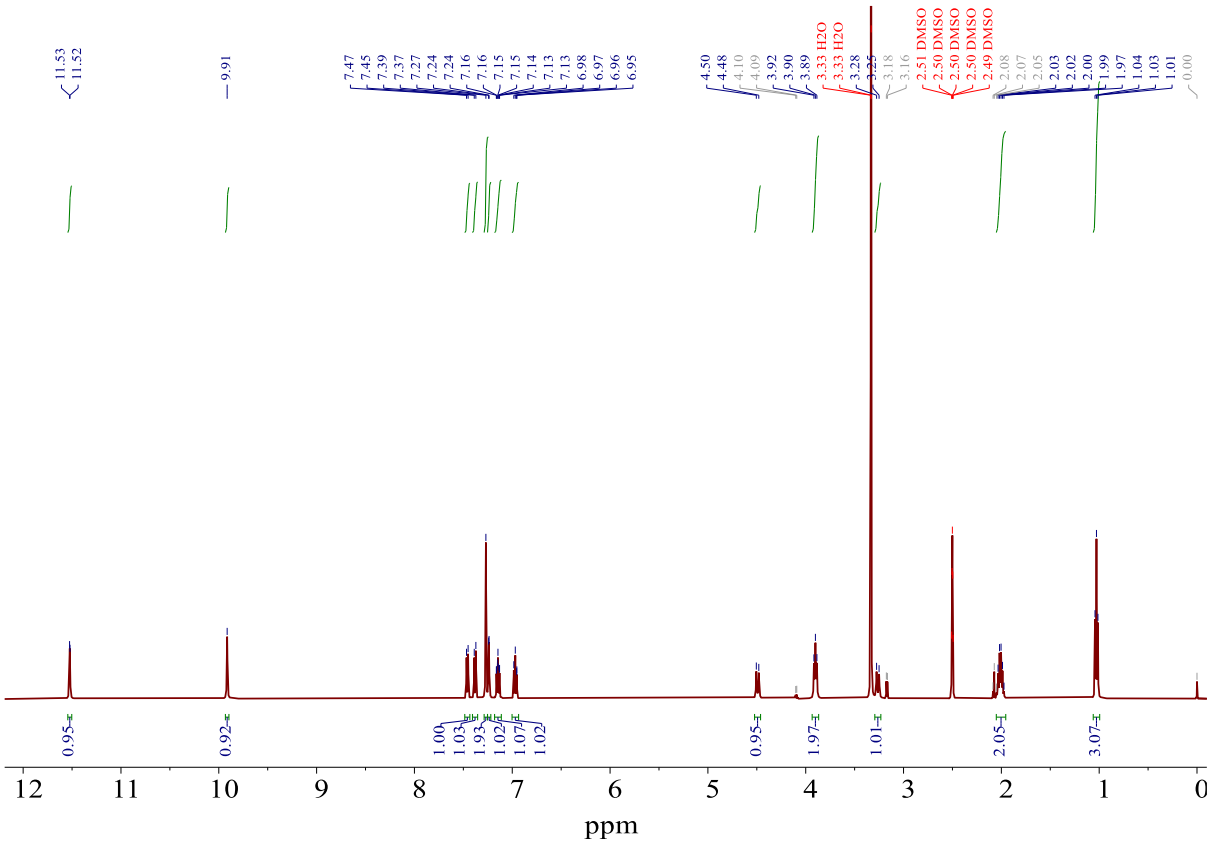


Figure S14. ^{1}H NMR spectrum of **1** (3 mM) recorded in DMSO-d_6.

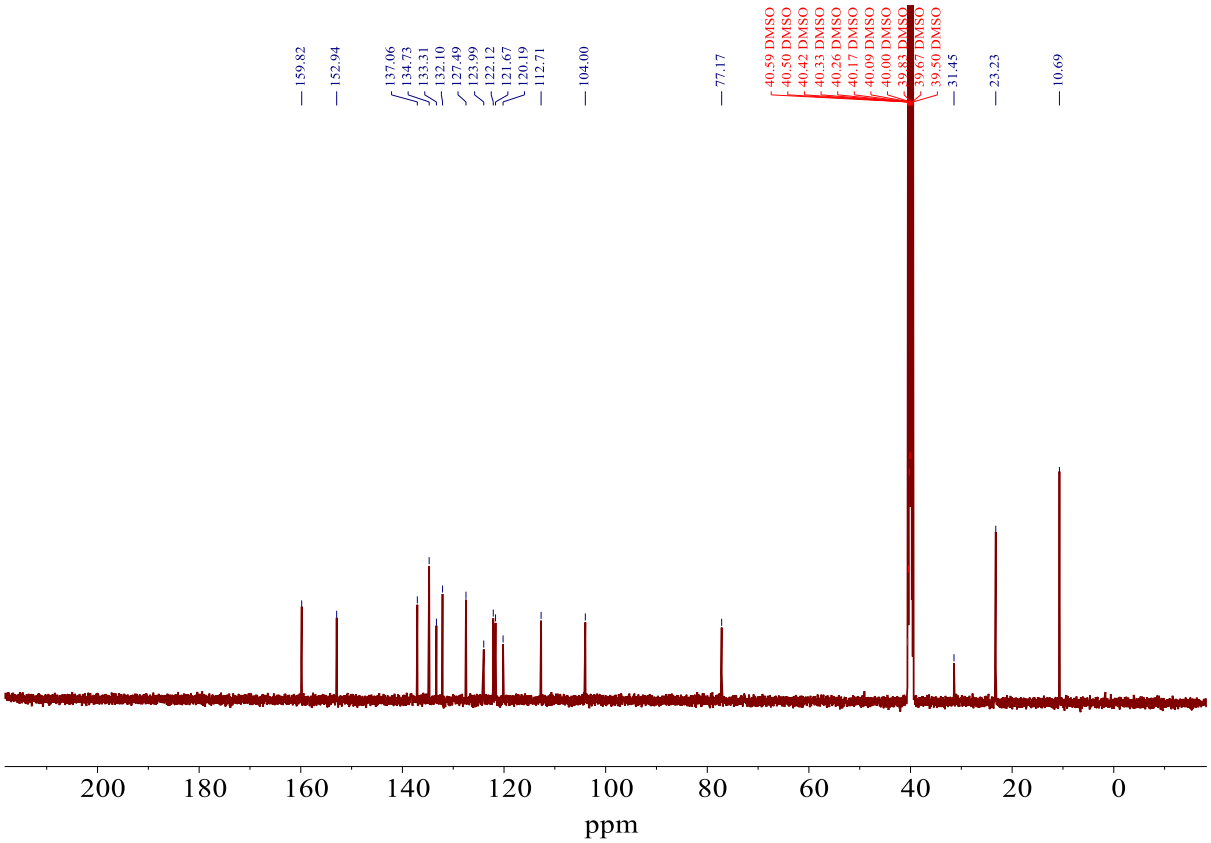
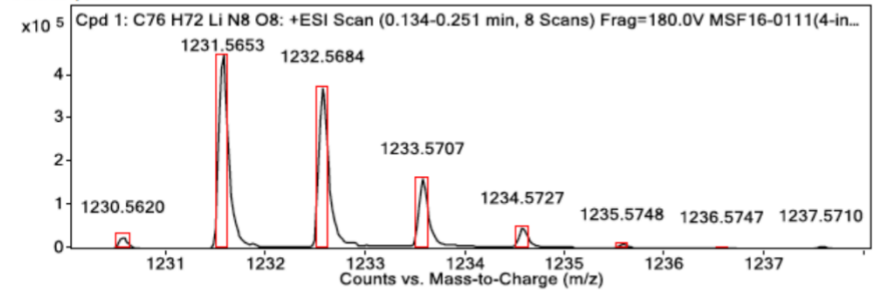


Figure S15. ^{13}C NMR spectrum of **1** (5 mM) recorded in DMSO-d_6.

Target Compound Screening Report

Data File	MSF16-0111(4-indole calix[4]arene + LiCl)_hrESIpos1.d	**Sample Name**	0111(4-indole calix[4]arene + LiCl)	**Comment**	0111(4-indole calix[4]arene + LiCl)
Position	P1-E8	**Instrument Name**	Instrument 1	**User Name**	
Acq Method	pos.m	**Acquired Time**	1/6/2016 5:10:07 PM	**DA Method**	Ian.m

MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
1230.56200	1230.56190	1	26435.12	C76H72LiN8O8	M+	-0.08
1231.56530	1231.56290	1	446090.77	C76H72LiN8O8	M+	-1.96
1232.56840	1232.56600	1	372871.35	C76H72LiN8O8	M+	-1.95
1233.57070	1233.56910	1	160835.09	C76H72LiN8O8	M+	-1.35
1234.57270	1234.57210	1	47128.44	C76H72LiN8O8	M+	-0.5
1235.57480	1235.57500	1	9368.6	C76H72LiN8O8	M+	0.12
1236.57470	1236.57790	1	2551.02	C76H72LiN8O8	M+	2.58
1237.57100	1237.58070	1	5824.89	C76H72LiN8O8	M+	7.84
1238.57360	1238.58350	1	4552.18	C76H72LiN8O8	M+	8.04

--- End Of Report ---

Figure S16. ESI HRMS of [**1** + Li]$^+$.

5. References

1. W. Verboom, A. Durie, R. J. M. Egberink, Z. Asfari, D. N. Reinhoudt, *J. Org. Chem.*, 1992, **57**, 1313–1316.
2. F. Troisi, C. Gaeta, T. Pierro, P. Neri, *Tetrahedron Lett.*, 2009, **50**, 5113-5115.
3. CrysAlisPro. Rigaku Oxford Diffraction (2020). CrysAlisPro Software System, 1.171.41.70a.
4. SHELXT. G. M. Sheldrick, A program for crystal structure solution. Acta Cryst. A, 2015, **71**, 3-8.
5. G. M. Sheldrick, SHELXL-2018/3. Program for the Refinement of Crystal Structures. Acta Cryst., 2015, **C71**, 3-8.
6. A. L. Spek PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D, 2009, **65**, 148-155.
7. OLEX2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Cryst., 2009, **42**, 339-341.
8. A. L. Spek, SQUEEZE. Acta Cryst. C, 2015, **71**, 9-18.
9. $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.

   $R(F) = \Sigma(|F_o| - |F_c|)/ \Sigma|F_o|\}$ for reflections with $F_o > 4(\Sigma(F_o))$.

   $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
10. International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
11. G. M. Sheldrick, (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.