

*Electronic Supplementary Information (ESI)*

**Selective recognition of sulfate ions by tripodal cyclic peptides functionalised with (thio)urea binding sites**

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## 1. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of new compounds

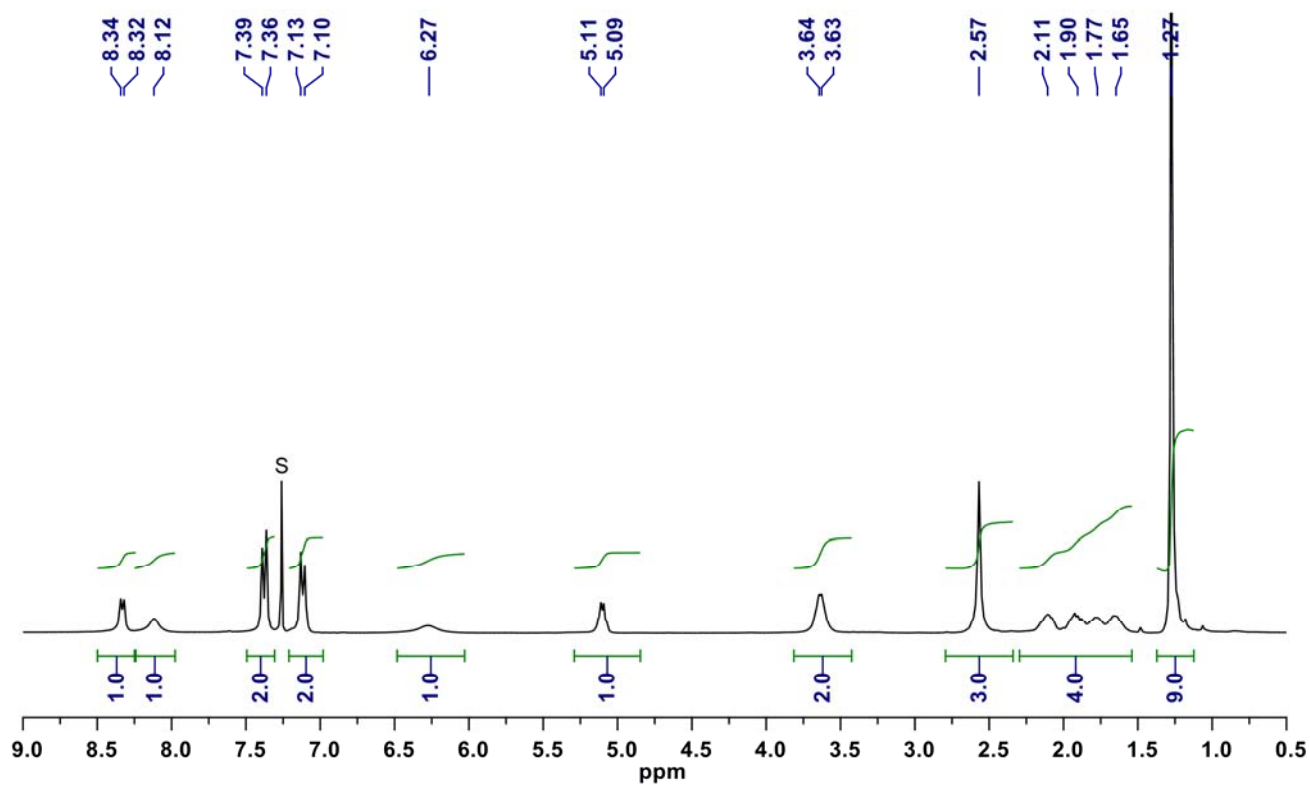


Figure S1  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K) spectrum of 1. S: solvent residual.

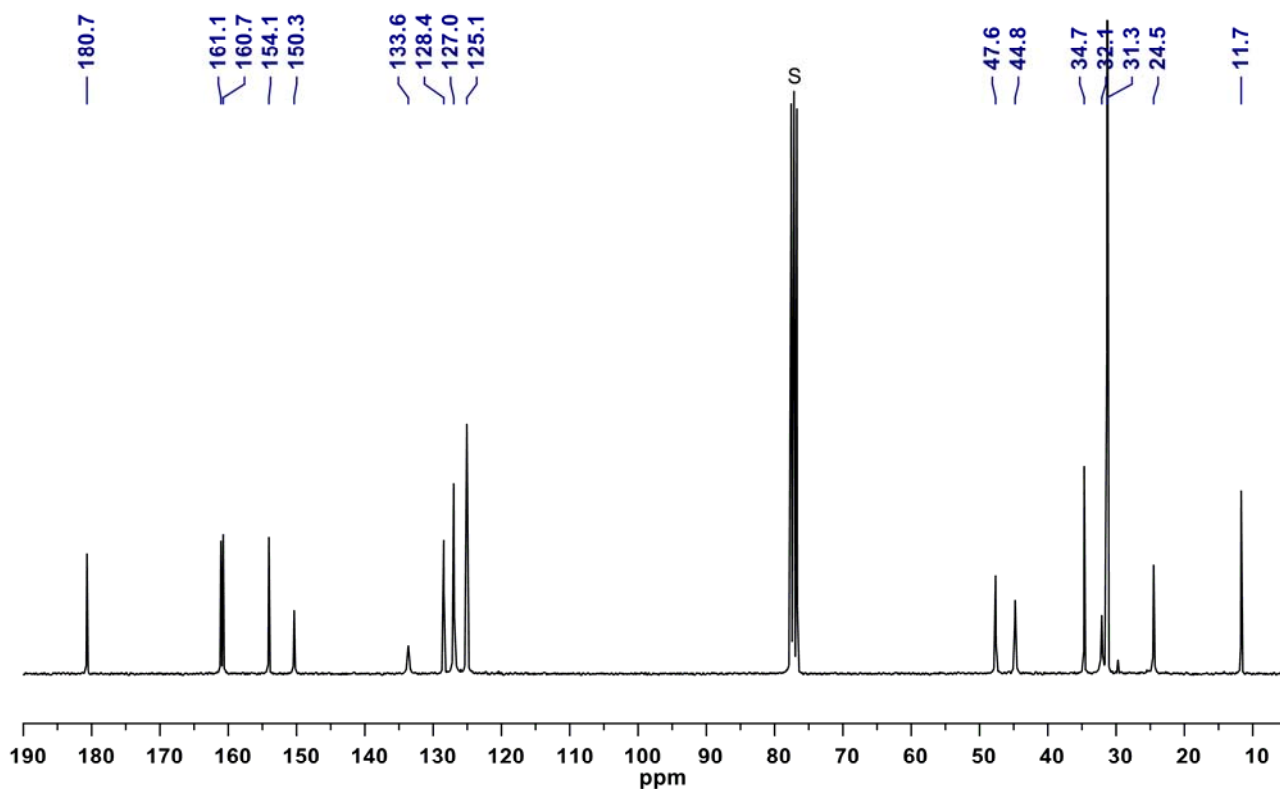


Figure S2  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298 K) spectrum of 1. S: solvent residual.

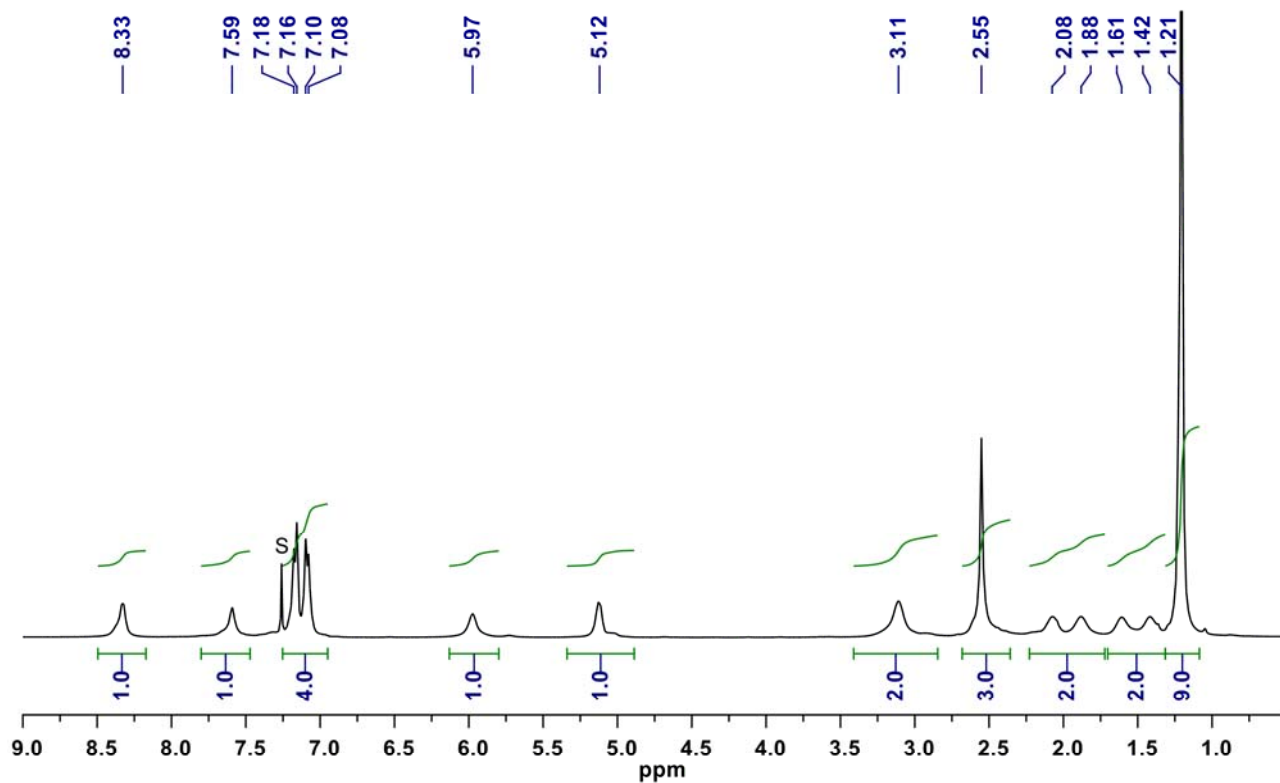


Figure S3  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of 2. S: solvent residual.

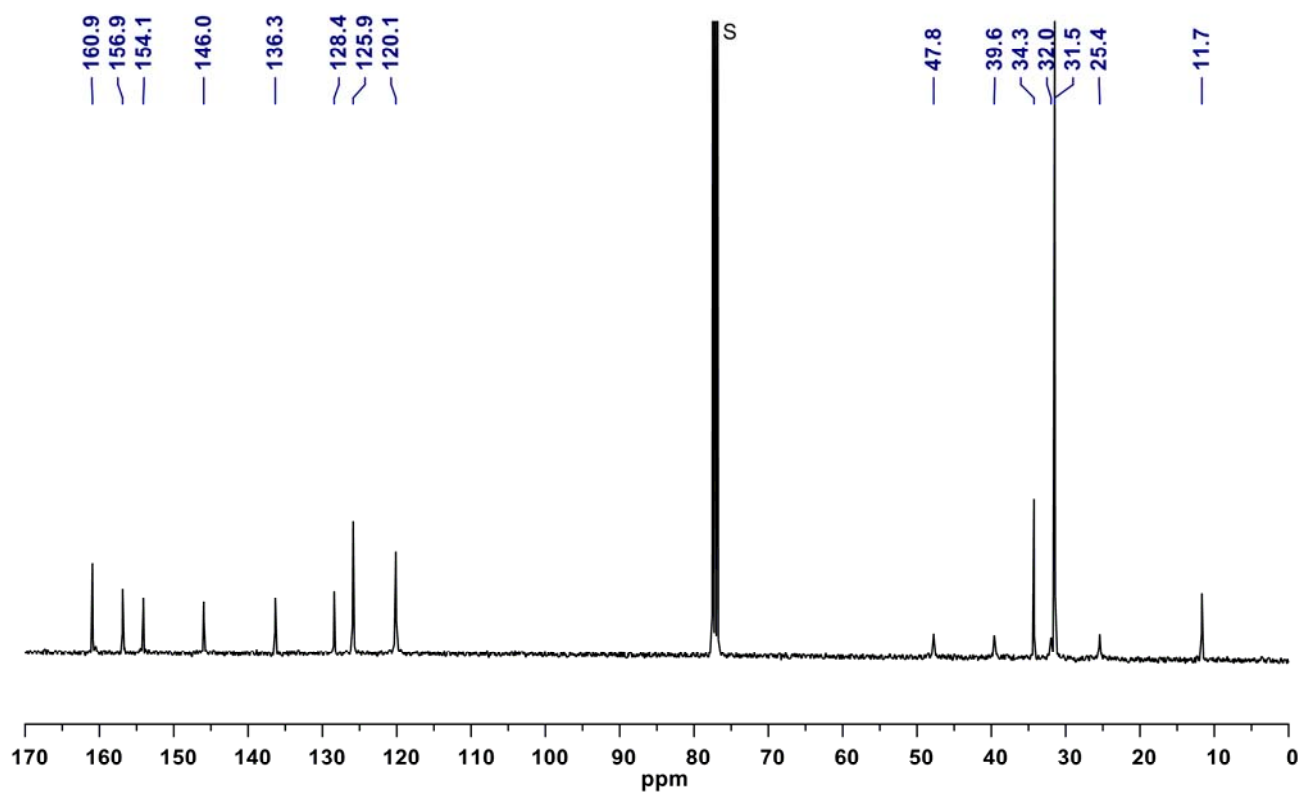


Figure S4  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of 2. S: solvent residual.

## 2. Maximum concentration dependent $^1\text{H}$ NMR chemical shifts for dimerisation experiments

Table S1 Changes in chemical shifts ( $\Delta\delta/\text{ppm}$ ) of various proton environments of 1 and 2 throughout  $^1\text{H}$  NMR concentration dependent titration experiments. <sup>[a]</sup>

Signal	Change in chemical shift ( $\Delta\delta/\text{ppm}$ )	
	Receptor 1	Receptor 2
NH <sup>a</sup>	0.25	0.63
NH <sup>b</sup>	0.02	0.45
CH <sub>2</sub> <sup>c</sup>	-0.01	-0.08
CH <sup>d</sup>	-0.01	-0.06
NH <sup>e</sup>	-0.02	-0.11
CH <sub>3</sub> <sup>f</sup>	-0.02	-0.07
C(CH <sub>3</sub> ) <sub>3</sub> <sup>g</sup>	-0.01	-0.05
ArH <sup>h</sup> /H <sup>i</sup> <sup>[b]</sup>	-0.01	-0.07

<sup>[a]</sup> Change in chemical shift ( $\Delta\delta$ ) =  $\delta_{\text{final}} - \delta_{\text{initial}}$ , where  $\delta_{\text{final}}$  is the final chemical shift at the end of the titration and  $\delta_{\text{initial}}$  is the initial chemical shift recorded for each respective proton environment listed. <sup>[b]</sup> Signal defined as the centre of the multiplet attributed to the *para*-substituted benzene ring.

### 3. $^1\text{H}$ NMR titration curves

Non-linear curve fitting of the experimentally obtained titration isotherms (equivalents of anion versus chemical shift of the [thio]urea NH protons) using the programme *Equilibria*<sup>1</sup> enabled the calculation of association constants ( $K_a/\text{M}^{-1}$ ). Final association constants for each anion are an average of the values obtained from monitoring  $\text{NH}^a$  and  $\text{NH}^b$  of receptor **1** or **2** (Figure S5) by  $^1\text{H}$  NMR spectroscopy (400 MHz, 300 K) in the stated deuterated solvents.

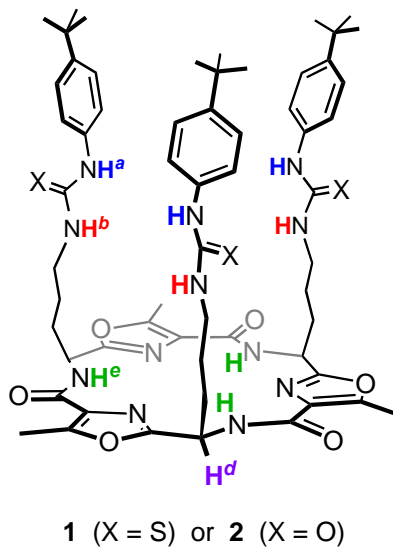


Figure S5 (Thio)urea protons,  $\text{NH}^a$  and  $\text{NH}^b$ , monitored over the course of each titration experiment with **1** (X = S) or **2** (X = O). Other proton environments referred to in the text are highlighted.

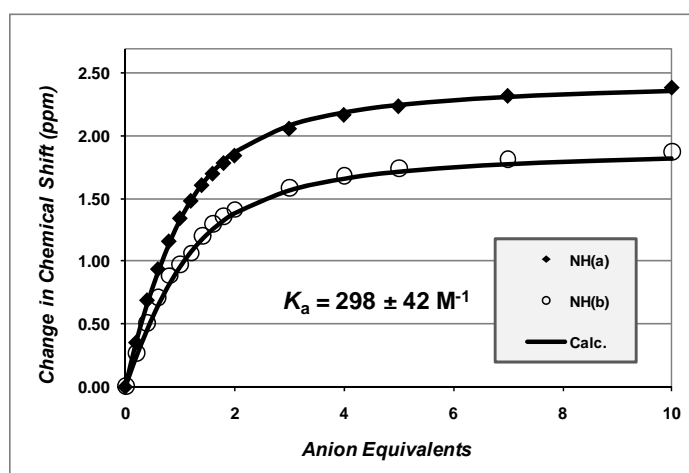


Figure S6 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{Cl}]$  in  $\text{CDCl}_3$ .

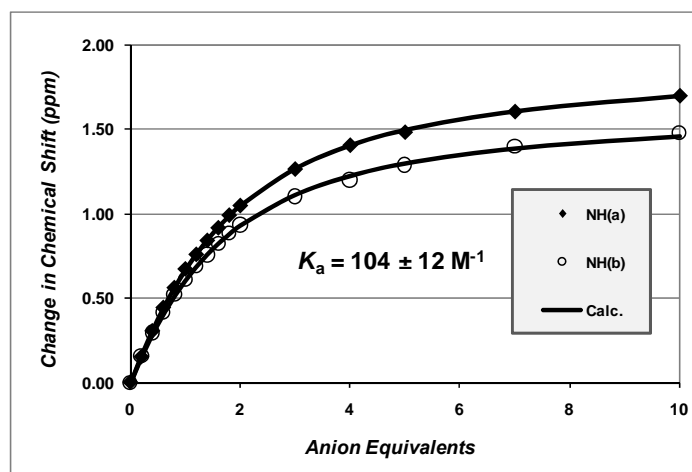


Figure S7 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{Br}]$  in  $\text{CDCl}_3$ .

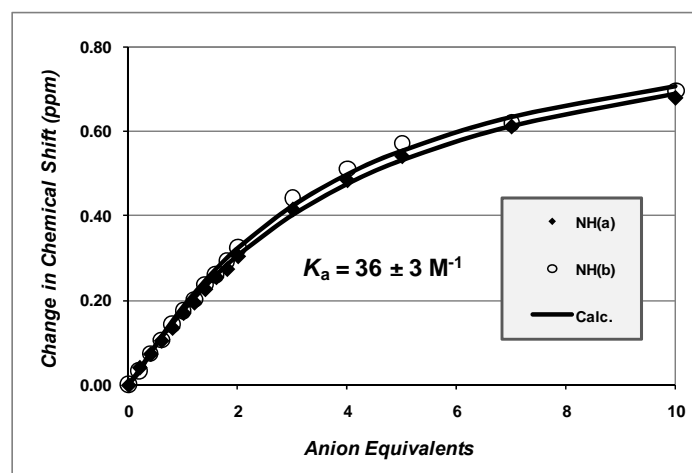


Figure S8 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{I}]$  in  $\text{CDCl}_3$ .

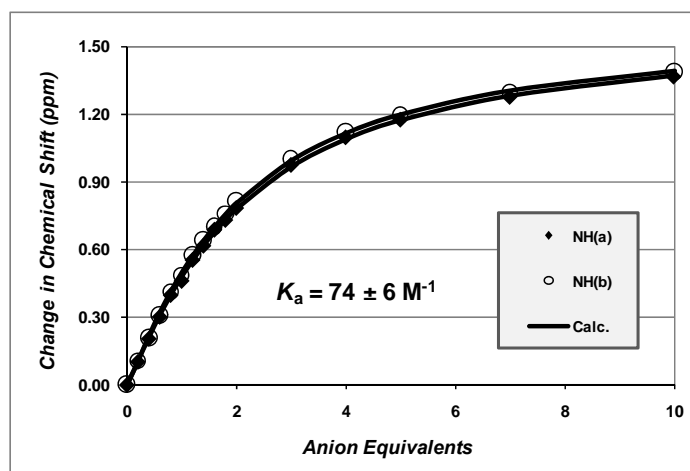


Figure S9 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{NO}_3]$  in  $\text{CDCl}_3$ .

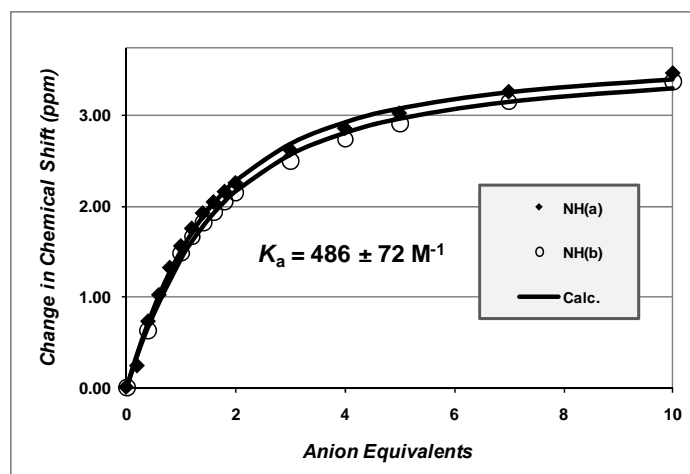


Figure S10 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{AcO}]$  in  $\text{CDCl}_3$ .

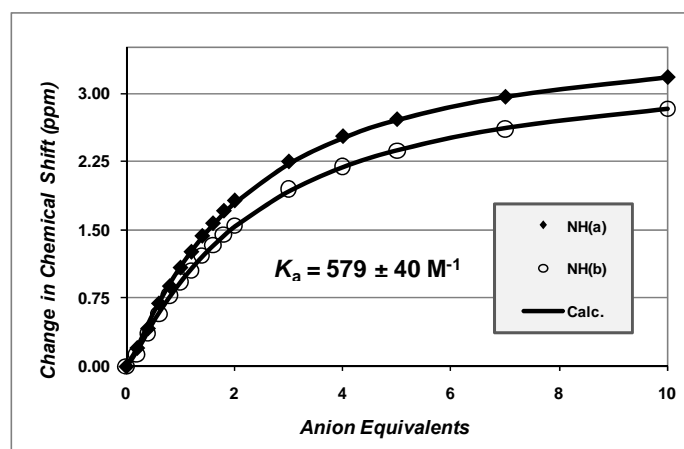


Figure S11 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{BzO}]$  in  $\text{CDCl}_3$ .

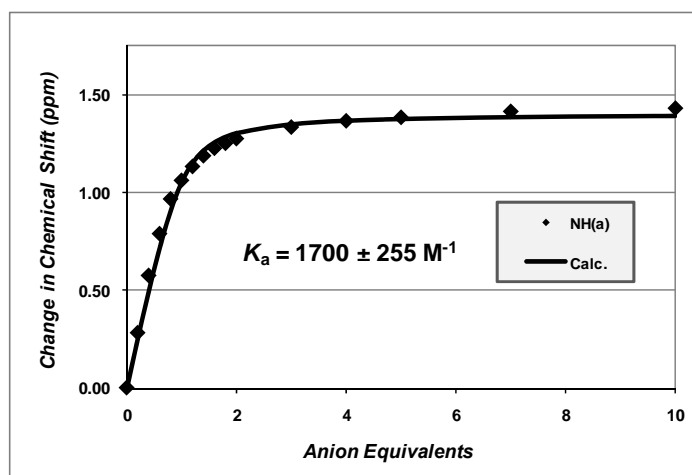


Figure S12 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{HSO}_4]$  in  $\text{CDCl}_3$ . Note: during the course of the titration the protons attributed to  $\text{NH}^b$  became obscured.

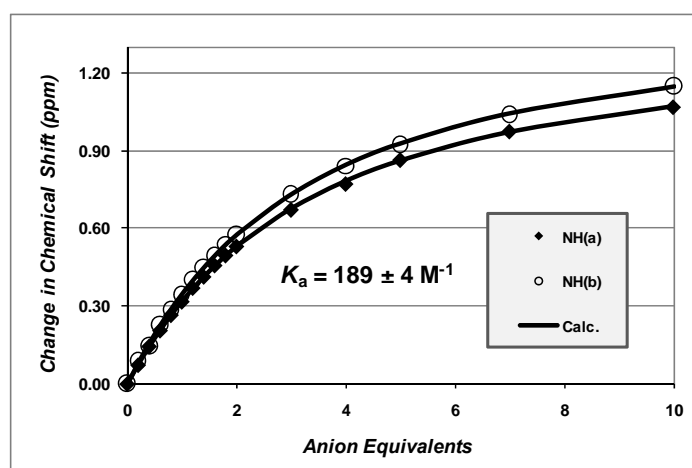


Figure S13 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{TfO}]$  in  $\text{CDCl}_3$ .

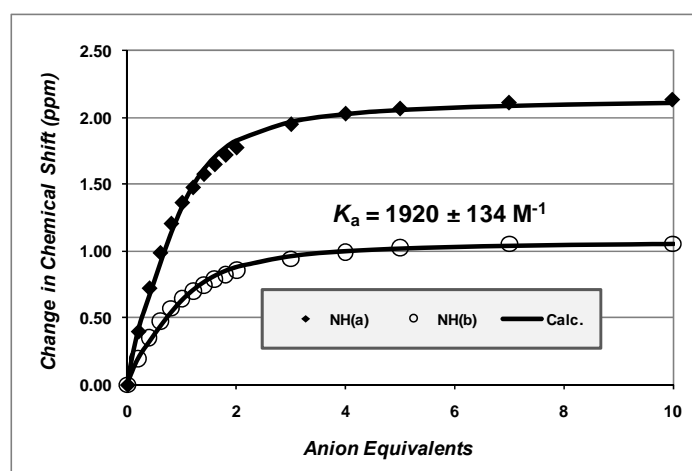


Figure S14 Titration of receptor 2 against  $[\text{Bu}_4\text{N}][\text{Cl}]$  in  $\text{CDCl}_3$ .



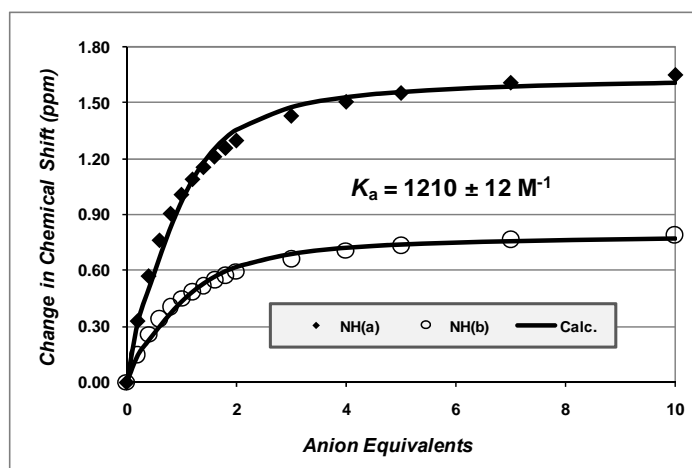


Figure S15 Titration of receptor 2 against  $[\text{Bu}_4\text{N}][\text{Br}]$  in  $\text{CDCl}_3$ .

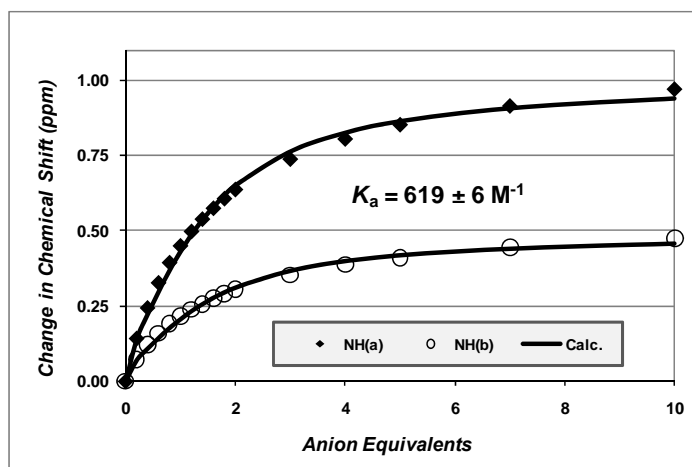


Figure S16 Titration of receptor 2 against  $[\text{Bu}_4\text{N}][\text{I}]$  in  $\text{CDCl}_3$ .

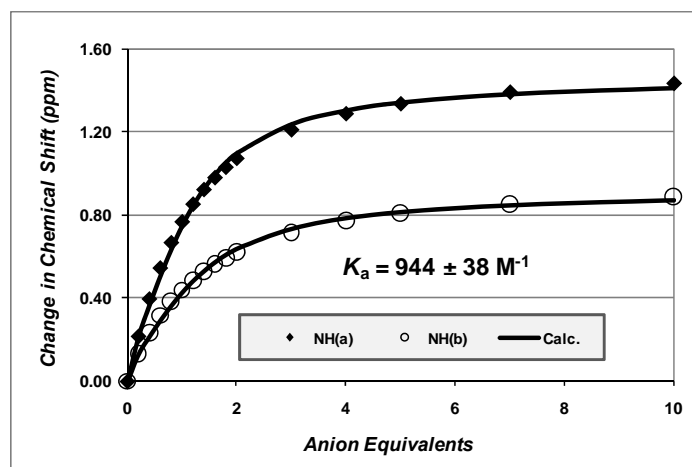


Figure S17 Titration of receptor 2 against  $[\text{Bu}_4\text{N}][\text{NO}_3]$  in  $\text{CDCl}_3$ .

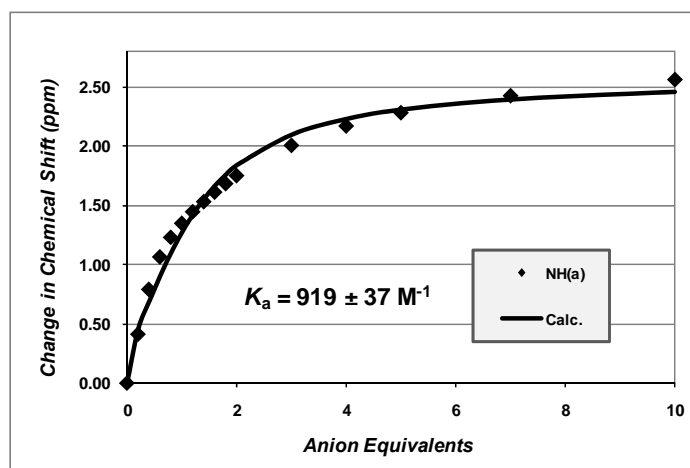


Figure S18 Titration of receptor 2 against [Bu<sub>4</sub>N][AcO] in CDCl<sub>3</sub>. Note: during the course of the titration the protons attributed to NH<sup>b</sup> became obscured.

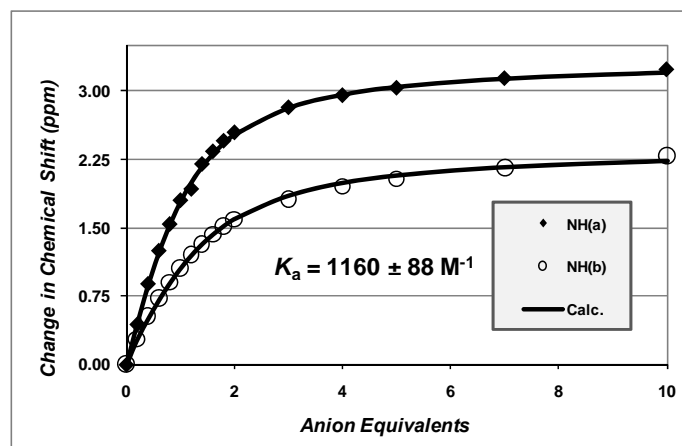


Figure S19 Titration of receptor 2 against [Bu<sub>4</sub>N][BzO] in CDCl<sub>3</sub>.

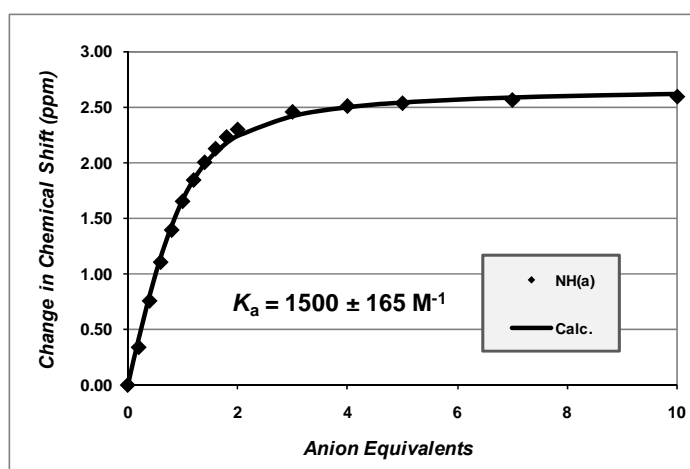


Figure S20 Titration of receptor 2 against [Bu<sub>4</sub>N][H<sub>2</sub>PO<sub>4</sub>] in CDCl<sub>3</sub>. Note: during the course of the titration the protons attributed to NH<sup>b</sup> became obscured.

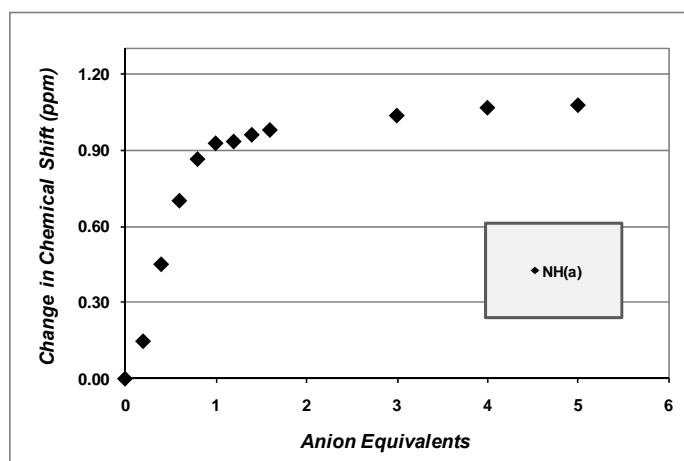


Figure S21 Titration of receptor 2 against  $[\text{Bu}_4\text{N}][\text{HSO}_4]$  in  $\text{CDCl}_3$ . Note: data could not be fitted to a suitable binding model. During the course of the titration the protons attributed to  $\text{NH}^b$  became obscured.

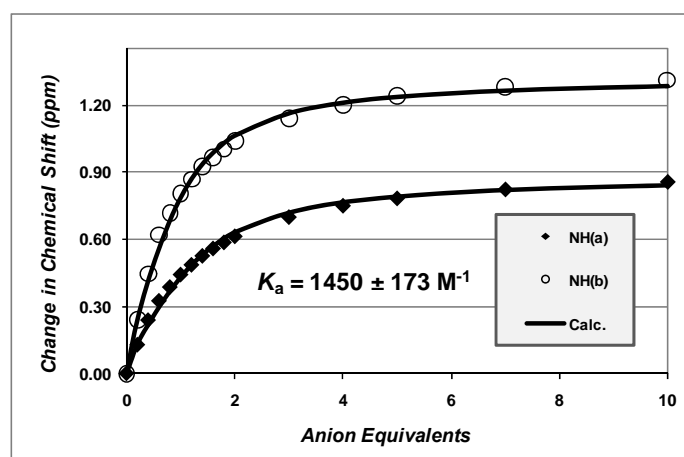


Figure S22 Titration of receptor 2 against  $[\text{Bu}_4\text{N}][\text{Tso}]$  in  $\text{CDCl}_3$ .

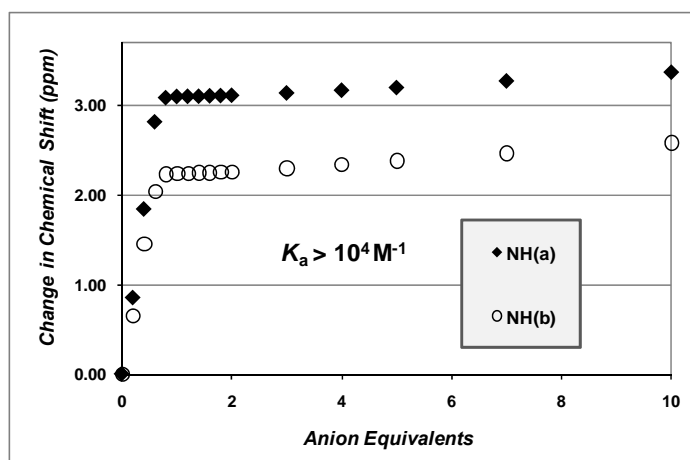


Figure S23 Titration of receptor 2 against  $[\text{Bu}_4\text{N}]_2[\text{SO}_4]$  in  $\text{CDCl}_3$ . Note: binding was too strong to accurately determine by NMR titration methods ( $K_a > 10^4 \text{ M}^{-1}$ ).

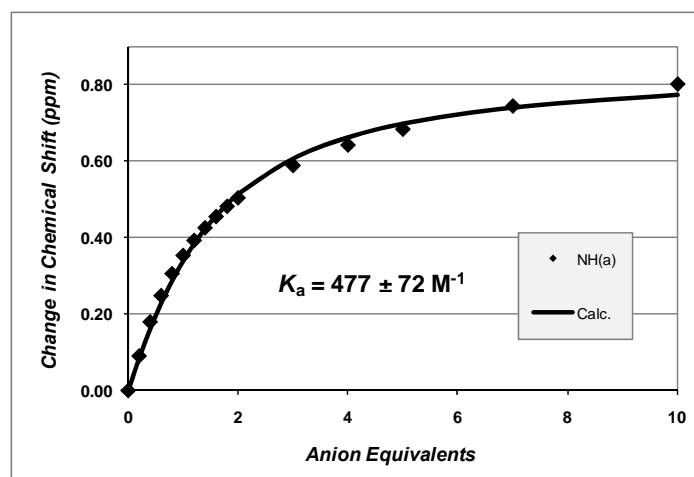


Figure S24 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{Cl}]$  in 10% v/v  $\text{DMSO-}d_6/\text{CDCl}_3$ . Note: during the course of the titration the protons attributed to  $\text{NH}^b$  became obscured.

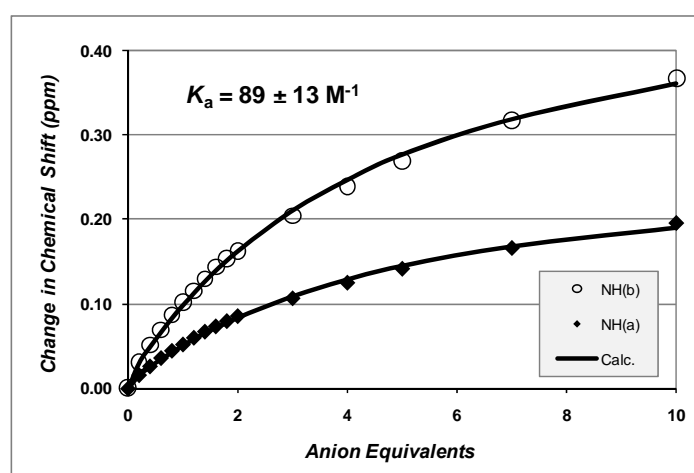


Figure S25 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{NO}_3]$  in 10% v/v  $\text{DMSO-}d_6/\text{CDCl}_3$ .

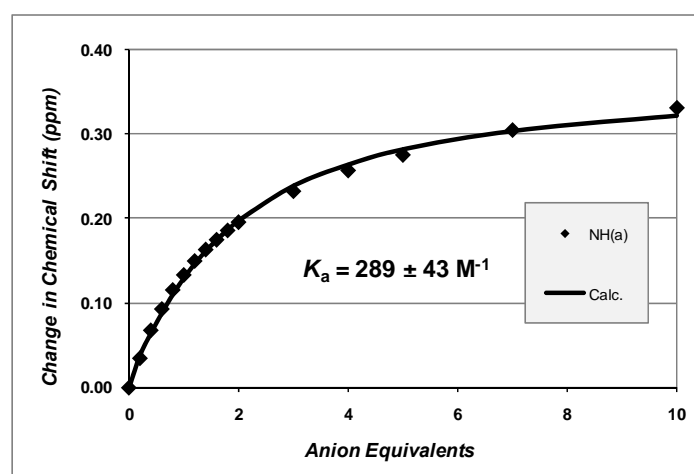


Figure S26 Titration of receptor 1 against  $[\text{Bu}_4\text{N}][\text{HSO}_4]$  in 10% v/v  $\text{DMSO-}d_6/\text{CDCl}_3$ . Note: during the course of the titration the protons attributed to  $\text{NH}^b$  became obscured.

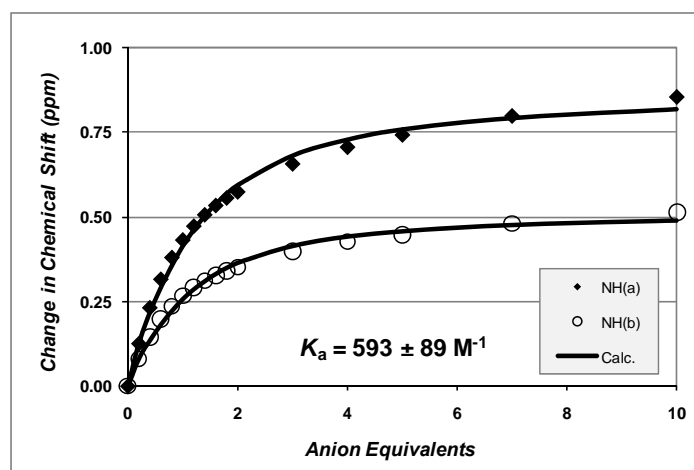


Figure S27 Titration of receptor 2 against [Bu<sub>4</sub>N][Cl] in 10% v/v DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>.

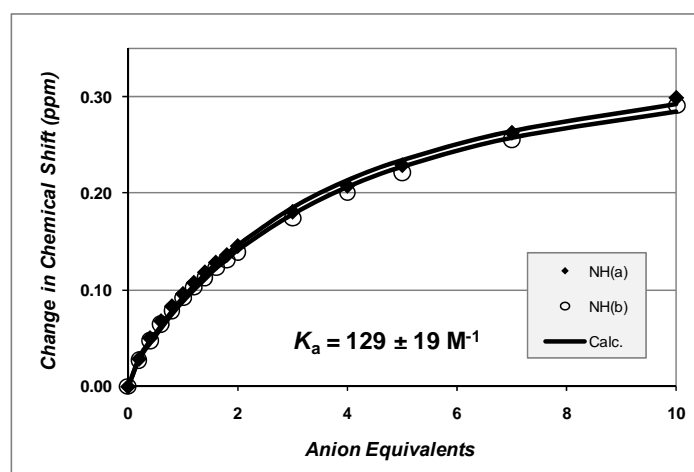


Figure S28 Titration of receptor 2 against [Bu<sub>4</sub>N][NO<sub>3</sub>] in 10% v/v DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>.

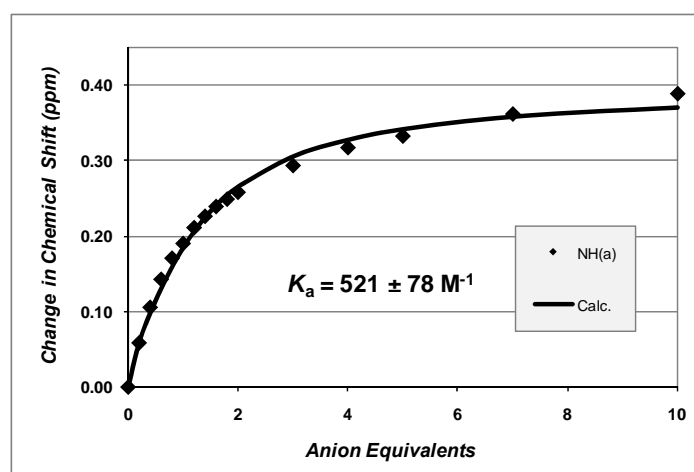


Figure S29 Titration of receptor 2 against [Bu<sub>4</sub>N][HSO<sub>4</sub>] in 10% v/v DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>. Note: during the course of the titration the protons attributed to NH<sup>b</sup> became obscured.

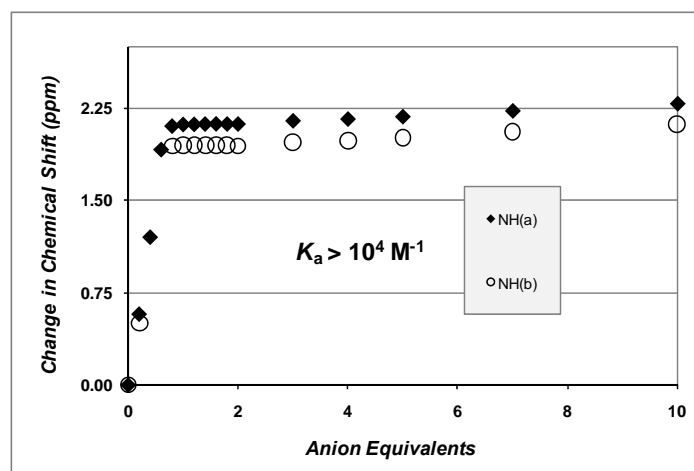


Figure S30 Titration of receptor 2 against  $[\text{Bu}_4\text{N}]_2[\text{SO}_4]$  in 10% v/v  $\text{DMSO-}d_6/\text{CDCl}_3$ . Note: binding was too strong to accurately determine by NMR titration methods ( $K_a > 10^4 \text{ M}^{-1}$ ).

## 4. Job plots

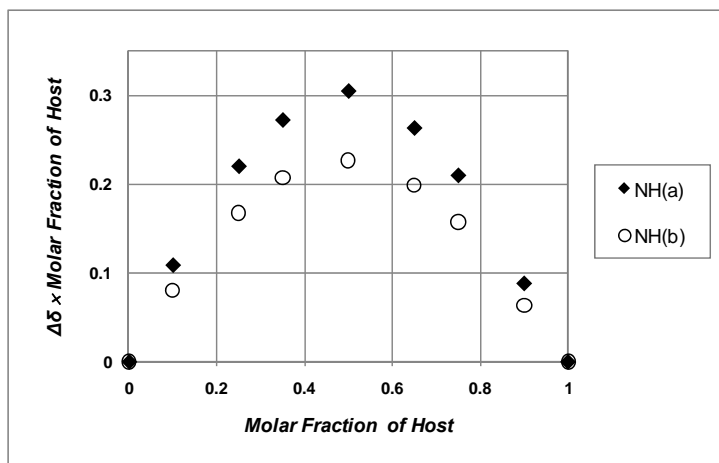


Figure S31 Job plot of receptor 1 against [Bu<sub>4</sub>N][Cl] in CDCl<sub>3</sub>.

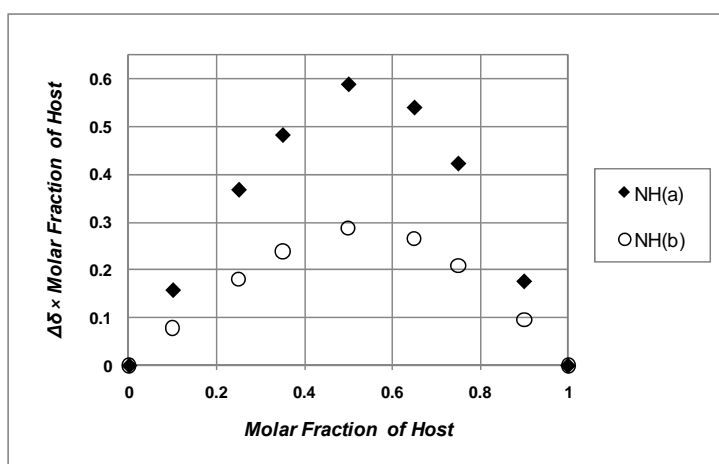


Figure S32 Job plot of receptor 2 against [Bu<sub>4</sub>N][Cl] in CDCl<sub>3</sub>.

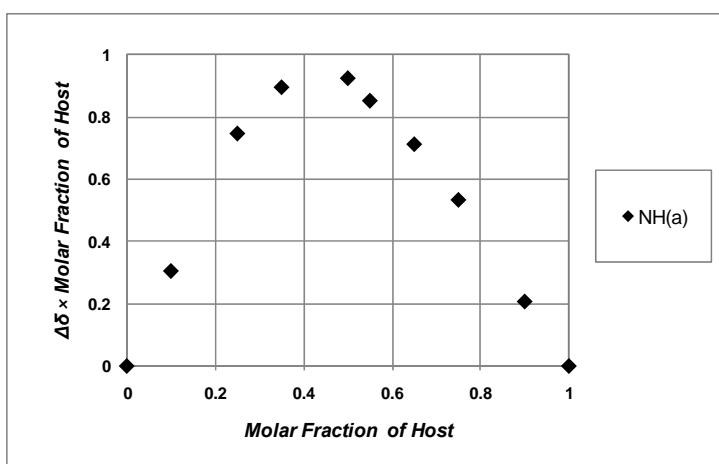


Figure S33 Job plot of receptor 2 against [Bu<sub>4</sub>N][H<sub>2</sub>PO<sub>4</sub>] in CDCl<sub>3</sub>. Note: during the course of the titration the protons attributed to NH<sup>b</sup> became obscured.

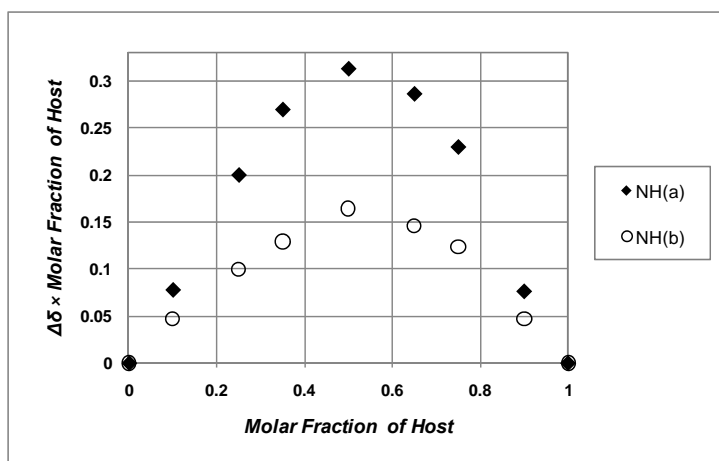


Figure S34 Job plot of receptor 1 against  $[\text{Bu}_4\text{N}][\text{HSO}_4]$  in  $\text{CDCl}_3$ .

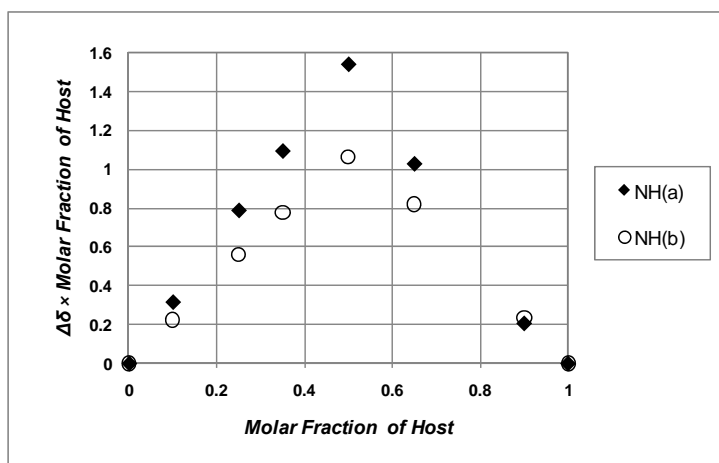


Figure S35 Job plot of receptor 2 against  $[\text{Bu}_4\text{N}]_2[\text{SO}_4]$  in  $\text{CDCl}_3$ .



## 5. Selected $^1\text{H}$ NMR titration spectra

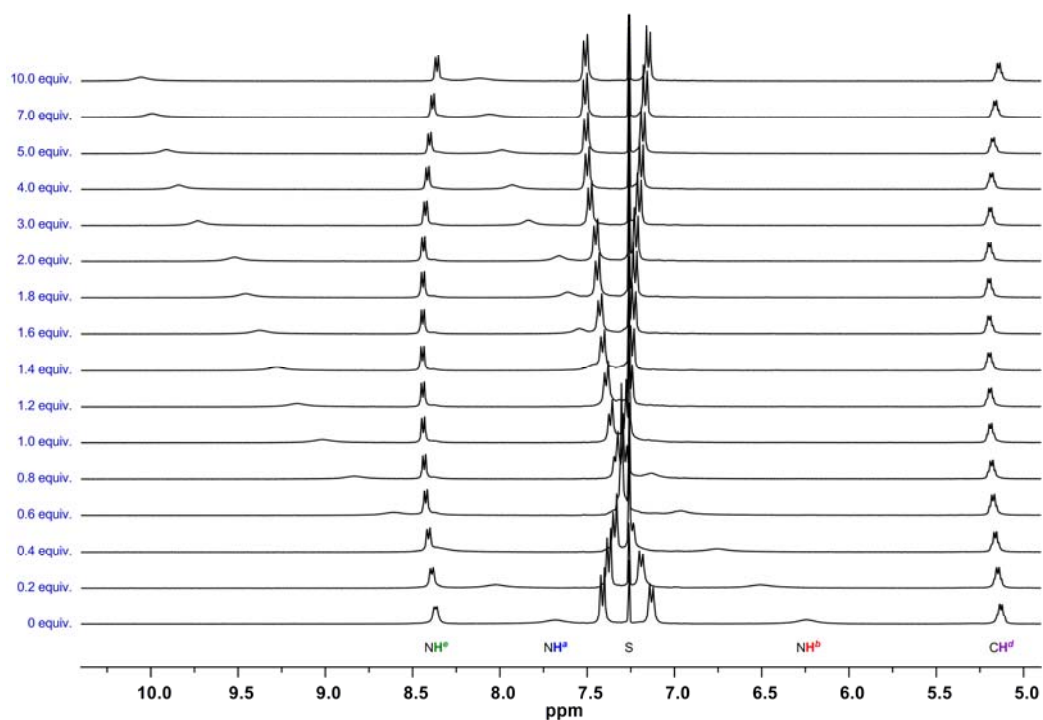


Figure S36 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 1 with  $[\text{Bu}_4\text{N}][\text{Cl}]$  in  $\text{CDCl}_3$ . S: solvent residual.

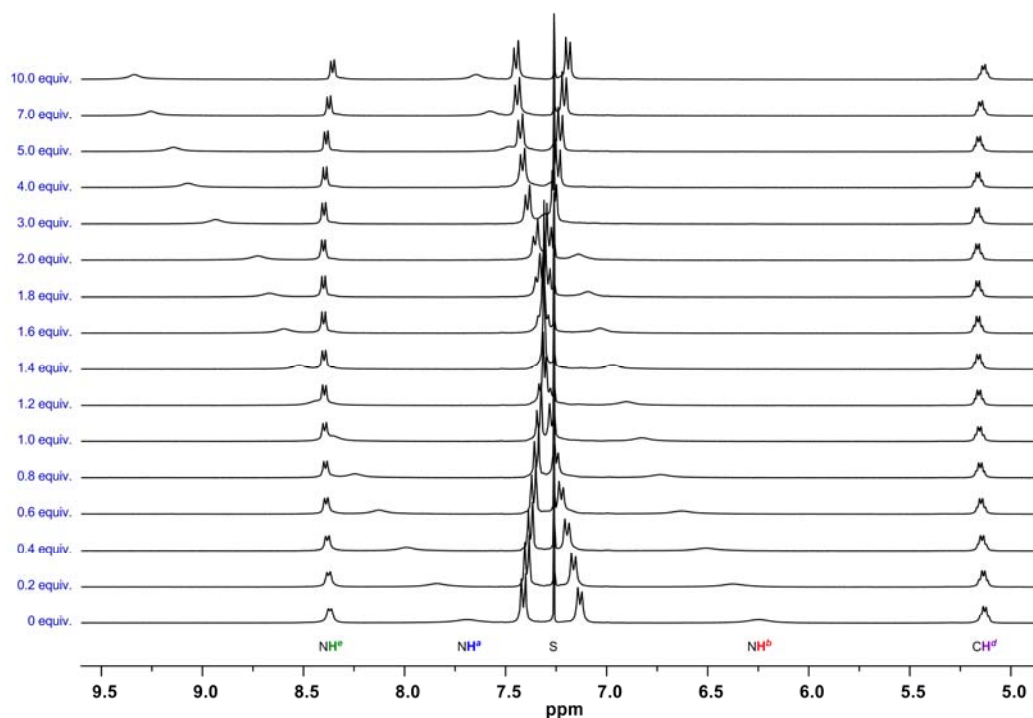


Figure S37 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 1 with  $[\text{Bu}_4\text{N}][\text{Br}]$  in  $\text{CDCl}_3$ . S: solvent residual.

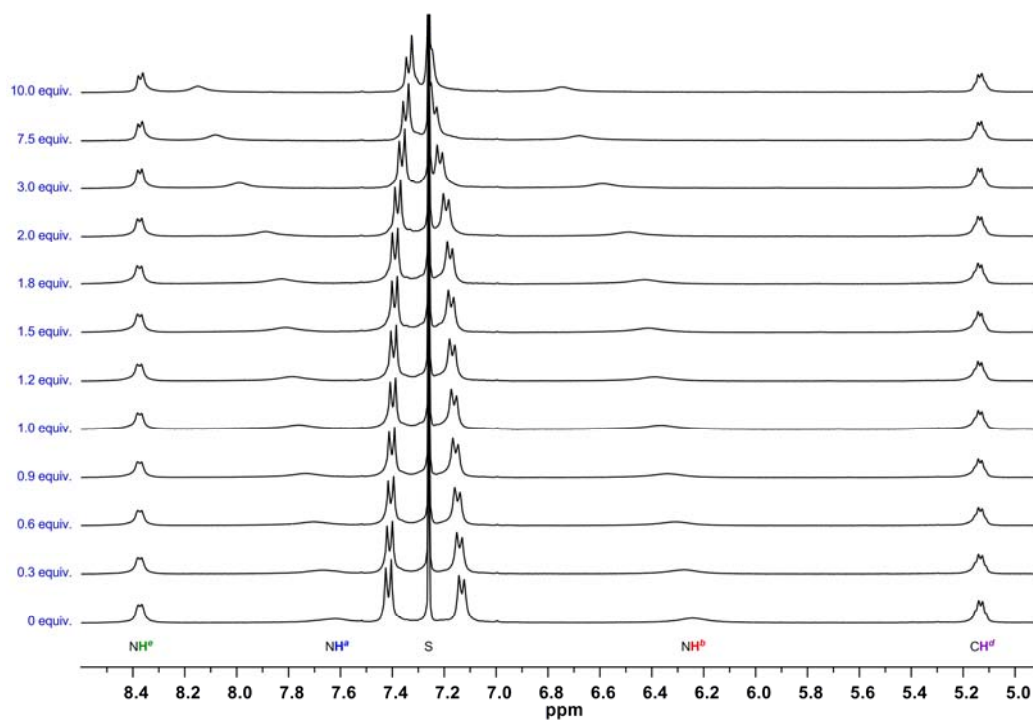


Figure S38 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 1 with  $[\text{Bu}_4\text{N}][\text{I}]$  in  $\text{CDCl}_3$ . S: solvent residual.

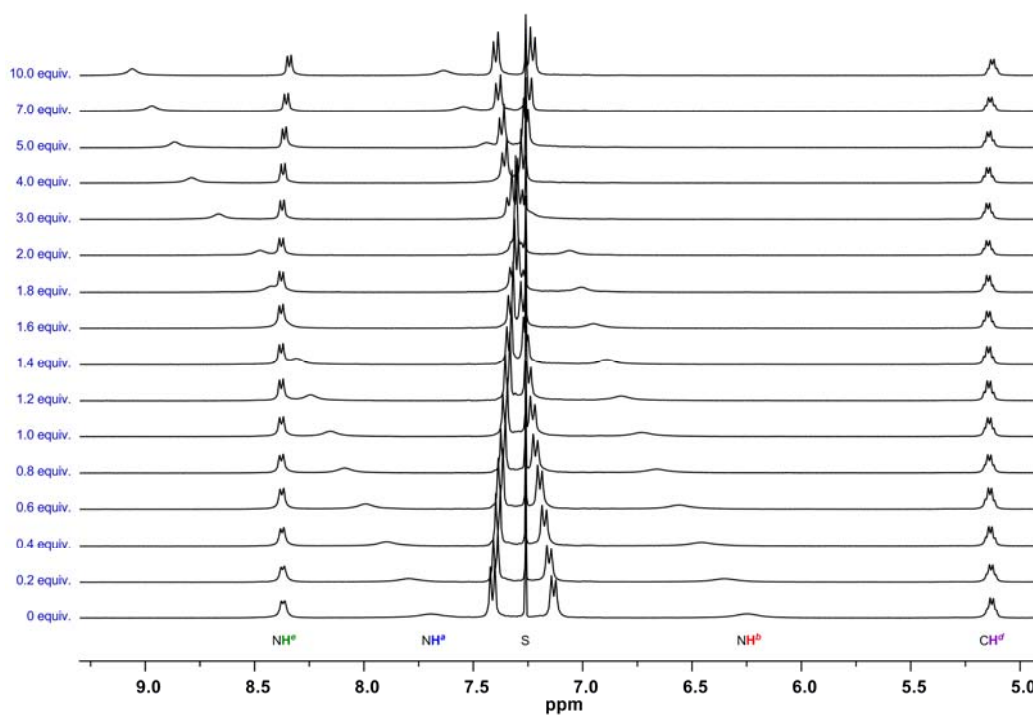


Figure S39 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 1 with  $[\text{Bu}_4\text{N}][\text{NO}_3]$  in  $\text{CDCl}_3$ . S: solvent residual.

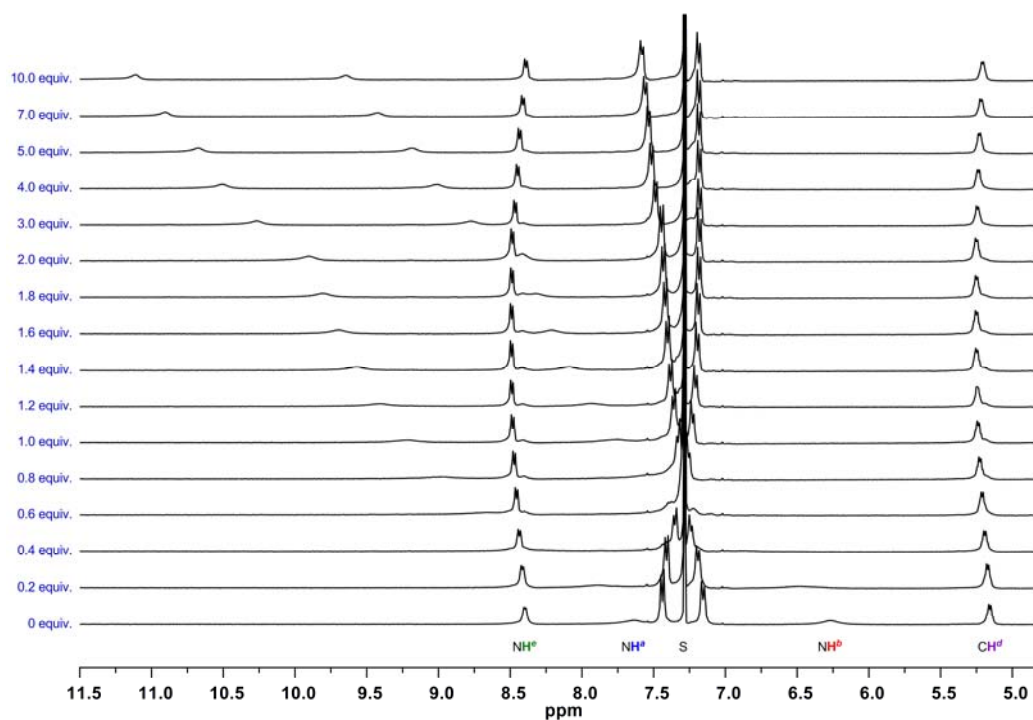


Figure S40 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of **1** with  $[\text{Bu}_4\text{N}][\text{AcO}]$  in  $\text{CDCl}_3$ . S: solvent residual.

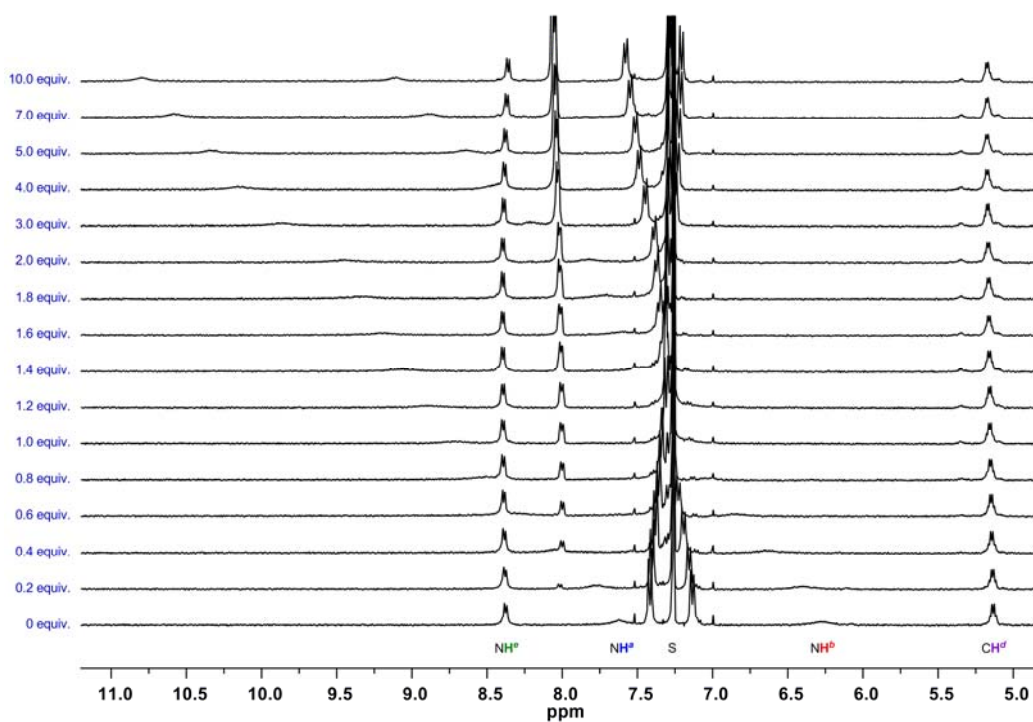


Figure S41 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of **1** with  $[\text{Bu}_4\text{N}][\text{BzO}]$  in  $\text{CDCl}_3$ . S: solvent residual.

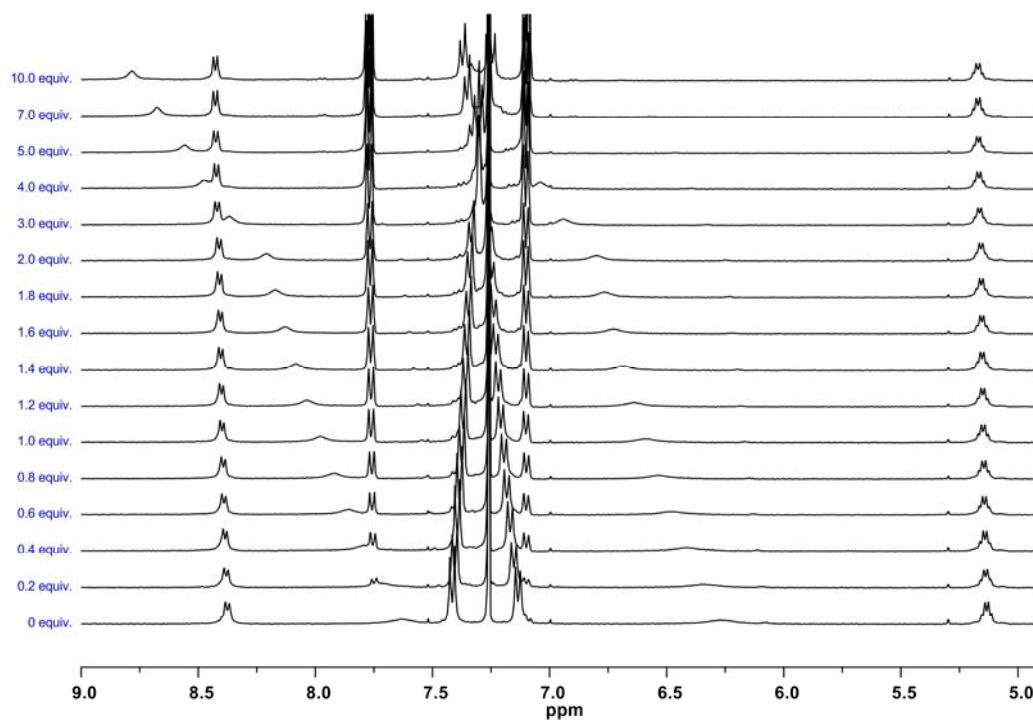


Figure S42 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of **1** with  $[\text{Bu}_4\text{N}][\text{TsO}]$  in  $\text{CDCl}_3$ . S: solvent residual.

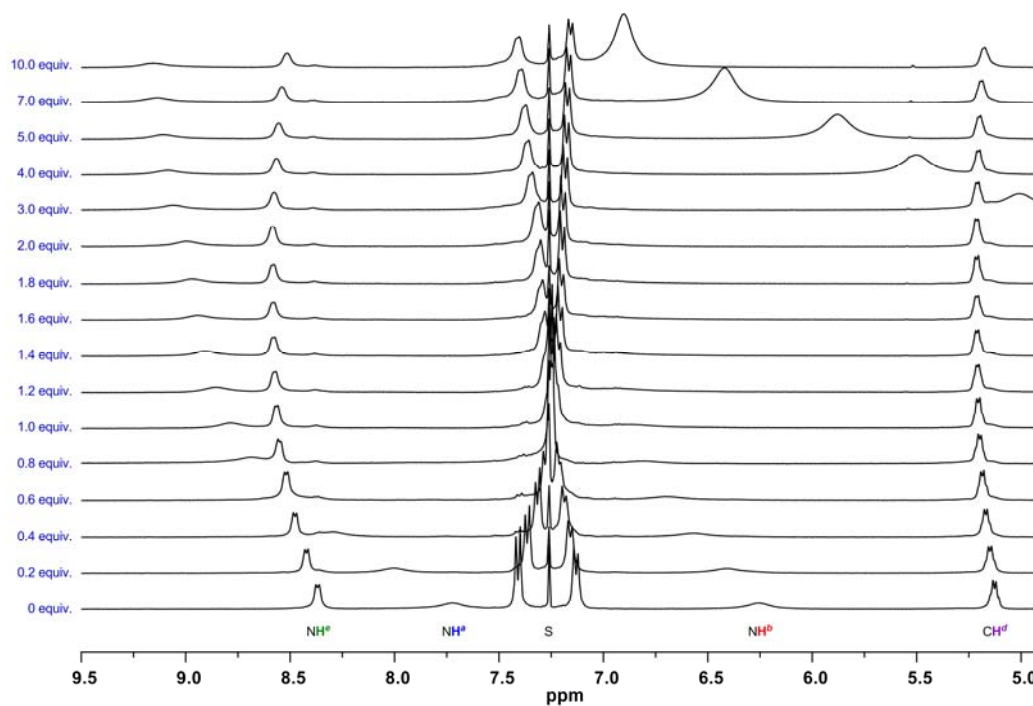


Figure S43 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of **1** with  $[\text{Bu}_4\text{N}][\text{HSO}_4]$  in  $\text{CDCl}_3$ . S: solvent residual.

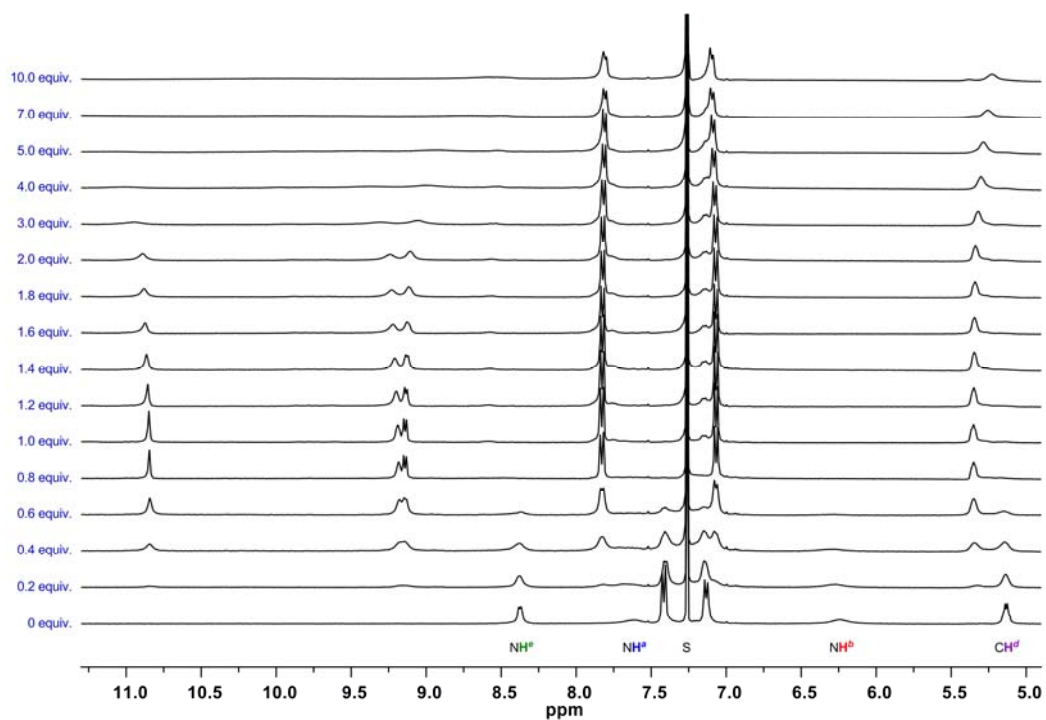


Figure S44 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 1 with  $[\text{Bu}_4\text{N}]_2[\text{SO}_4]$  in  $\text{CDCl}_3$ . S: solvent residual.

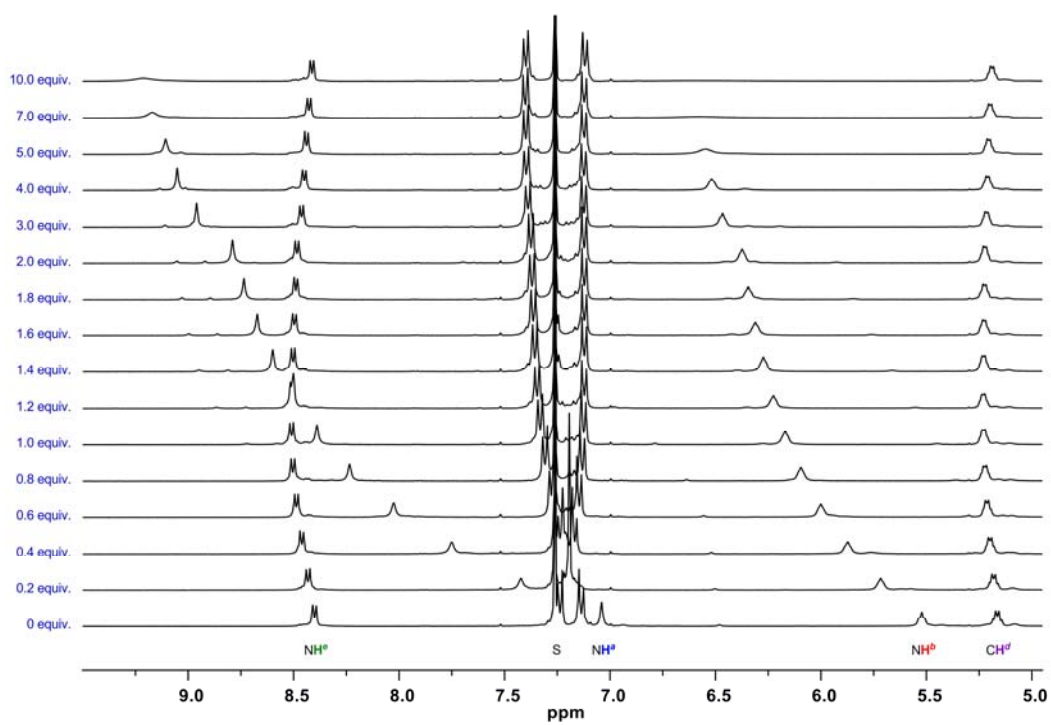


Figure S45 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 2 with  $[\text{Bu}_4\text{N}][\text{Cl}]$  in  $\text{CDCl}_3$ . S: solvent residual.

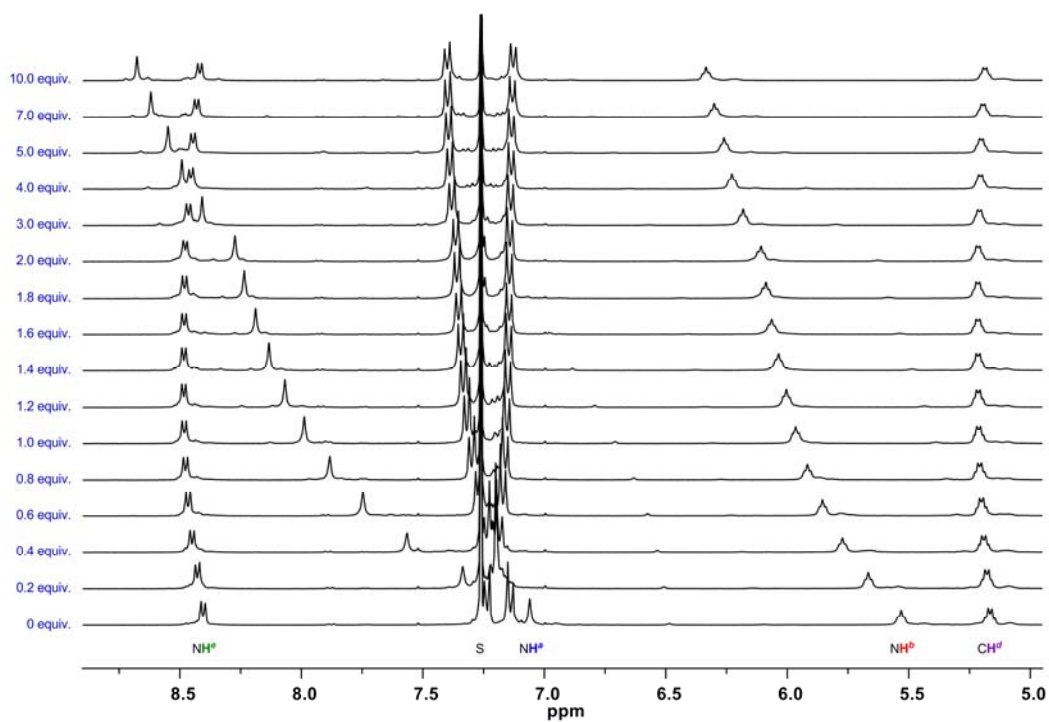


Figure S46 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 2 with  $[\text{Bu}_4\text{N}][\text{Br}]$  in  $\text{CDCl}_3$ . S: solvent residual.

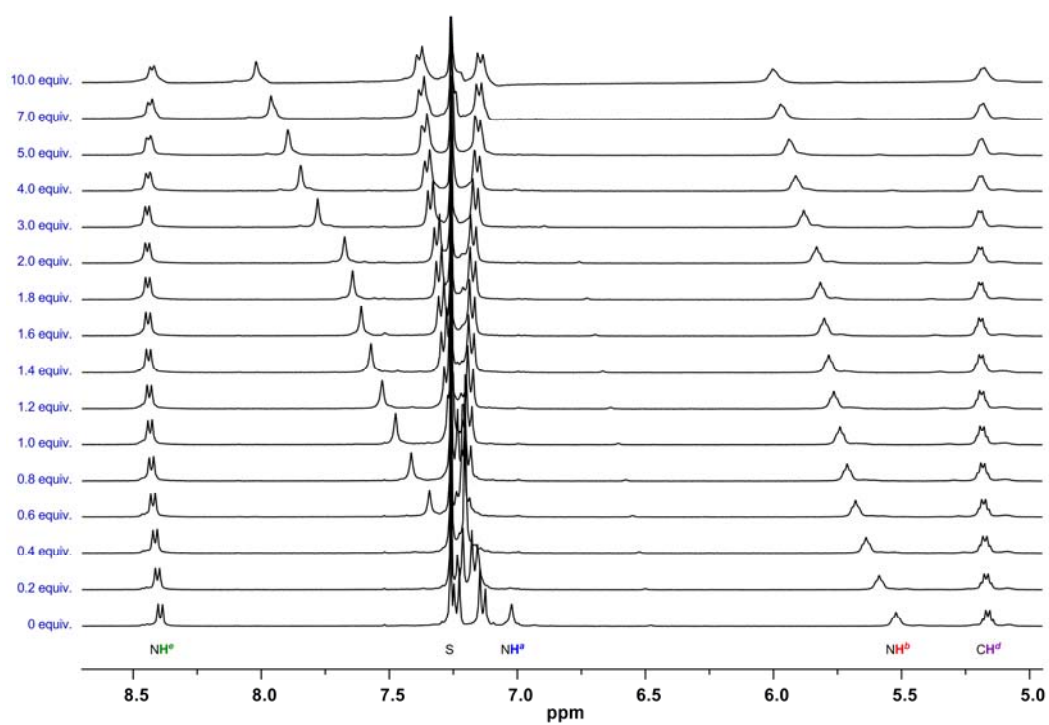


Figure S47 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 2 with  $[\text{Bu}_4\text{N}][\text{I}]$  in  $\text{CDCl}_3$ . S: solvent residual.



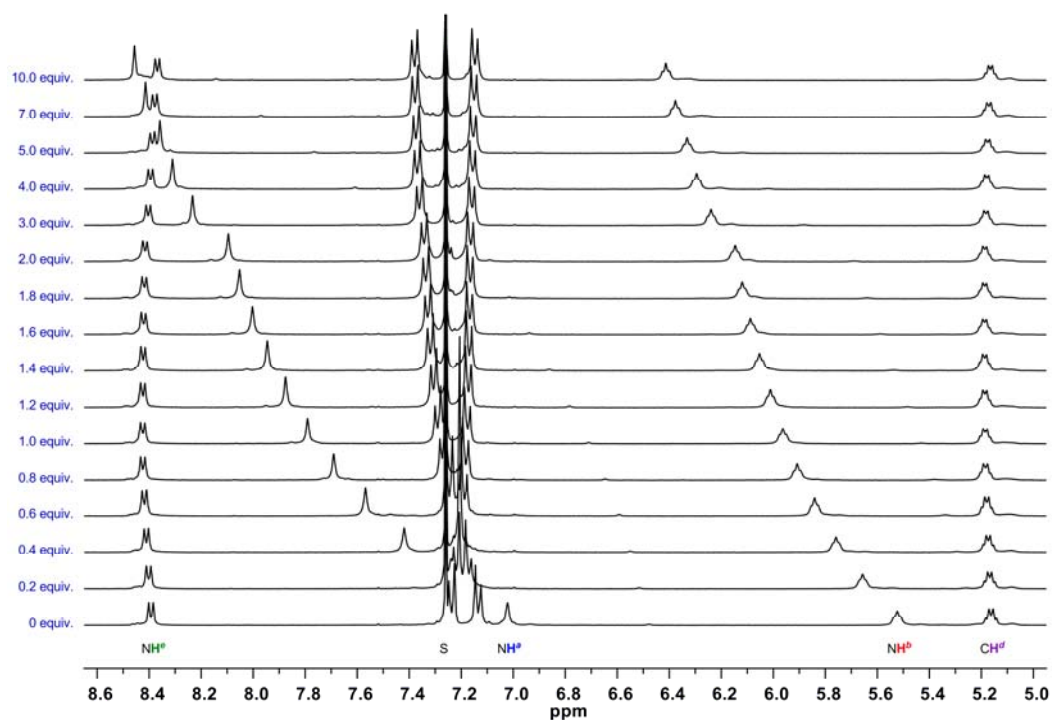


Figure S48 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of **2** with  $[\text{Bu}_4\text{N}][\text{NO}_3]$  in  $\text{CDCl}_3$ . S: solvent residual.

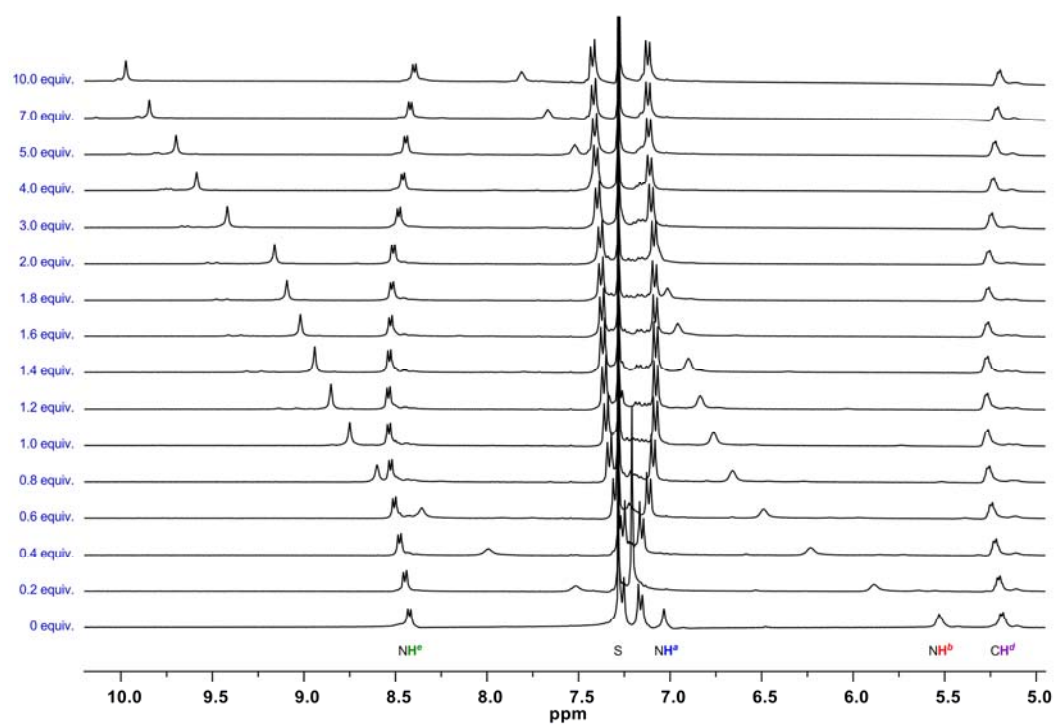


Figure S49 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of **2** with  $[\text{Bu}_4\text{N}][\text{AcO}]$  in  $\text{CDCl}_3$ . S: solvent residual.

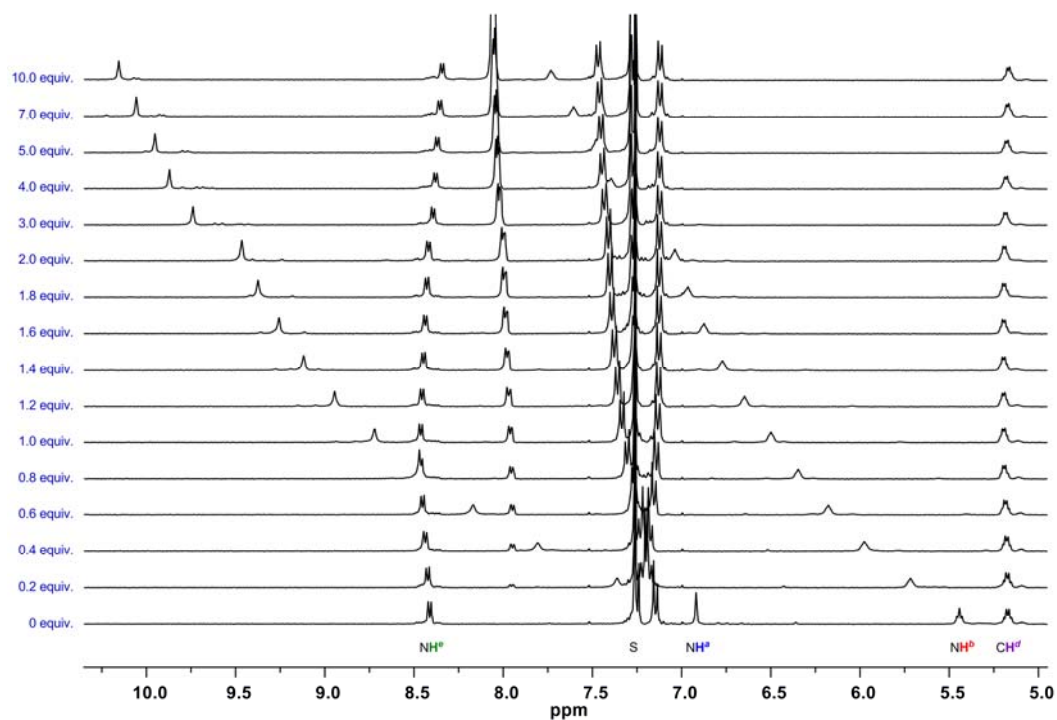


Figure S50 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 2 with  $[\text{Bu}_4\text{N}][\text{BzO}]$  in  $\text{CDCl}_3$ . S: solvent residual.

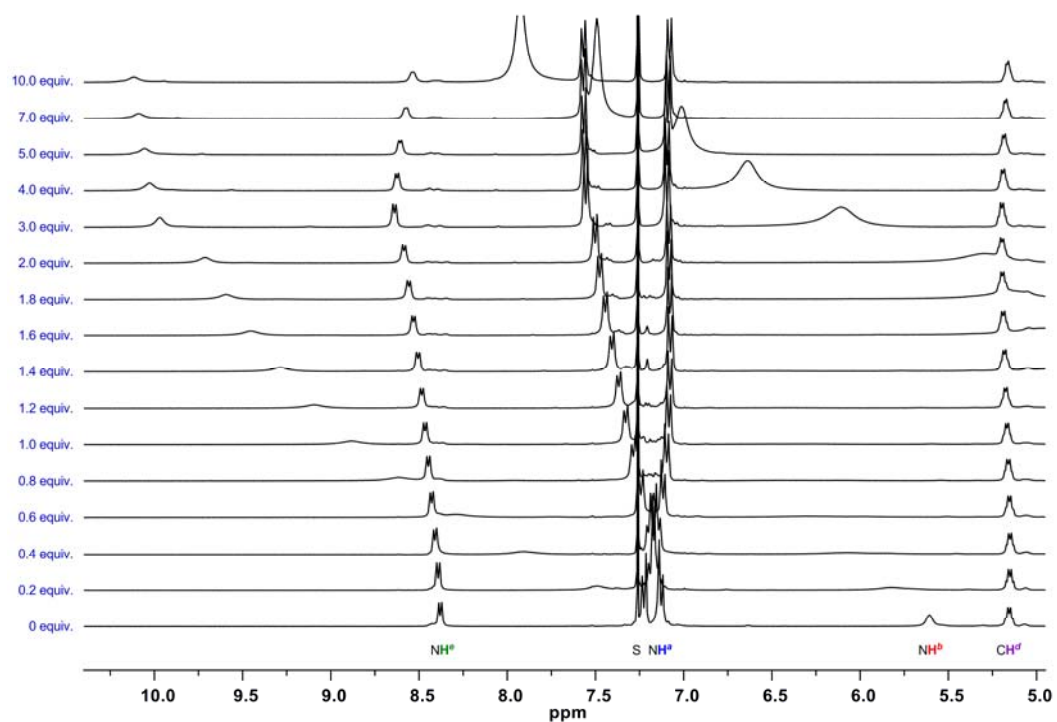


Figure S51 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 2 with  $[\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$  in  $\text{CDCl}_3$ . S: solvent residual.



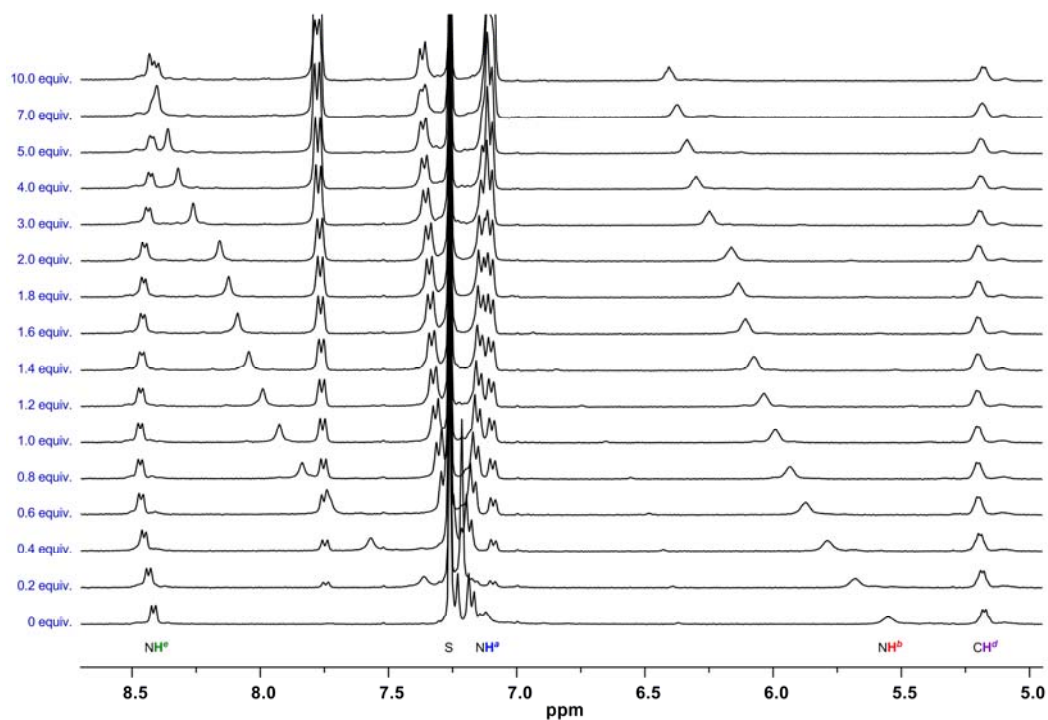


Figure S52 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 2 with  $[\text{Bu}_4\text{N}][\text{TsO}]$  in  $\text{CDCl}_3$ . S: solvent residual.

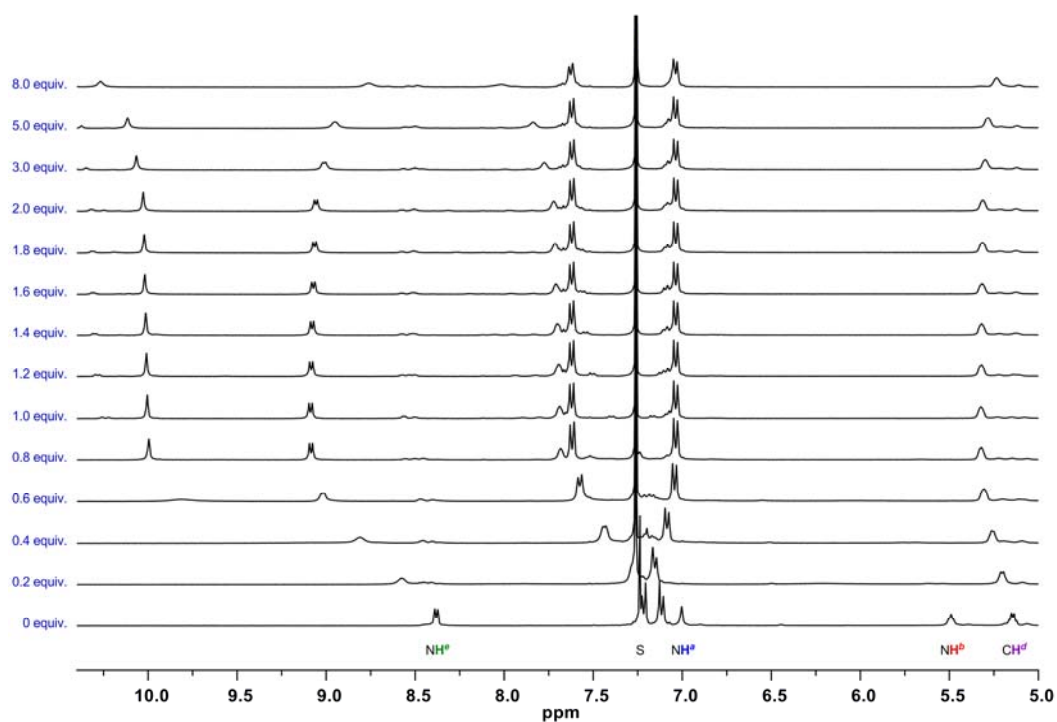
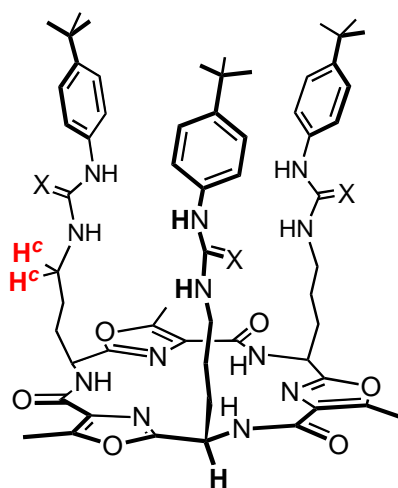
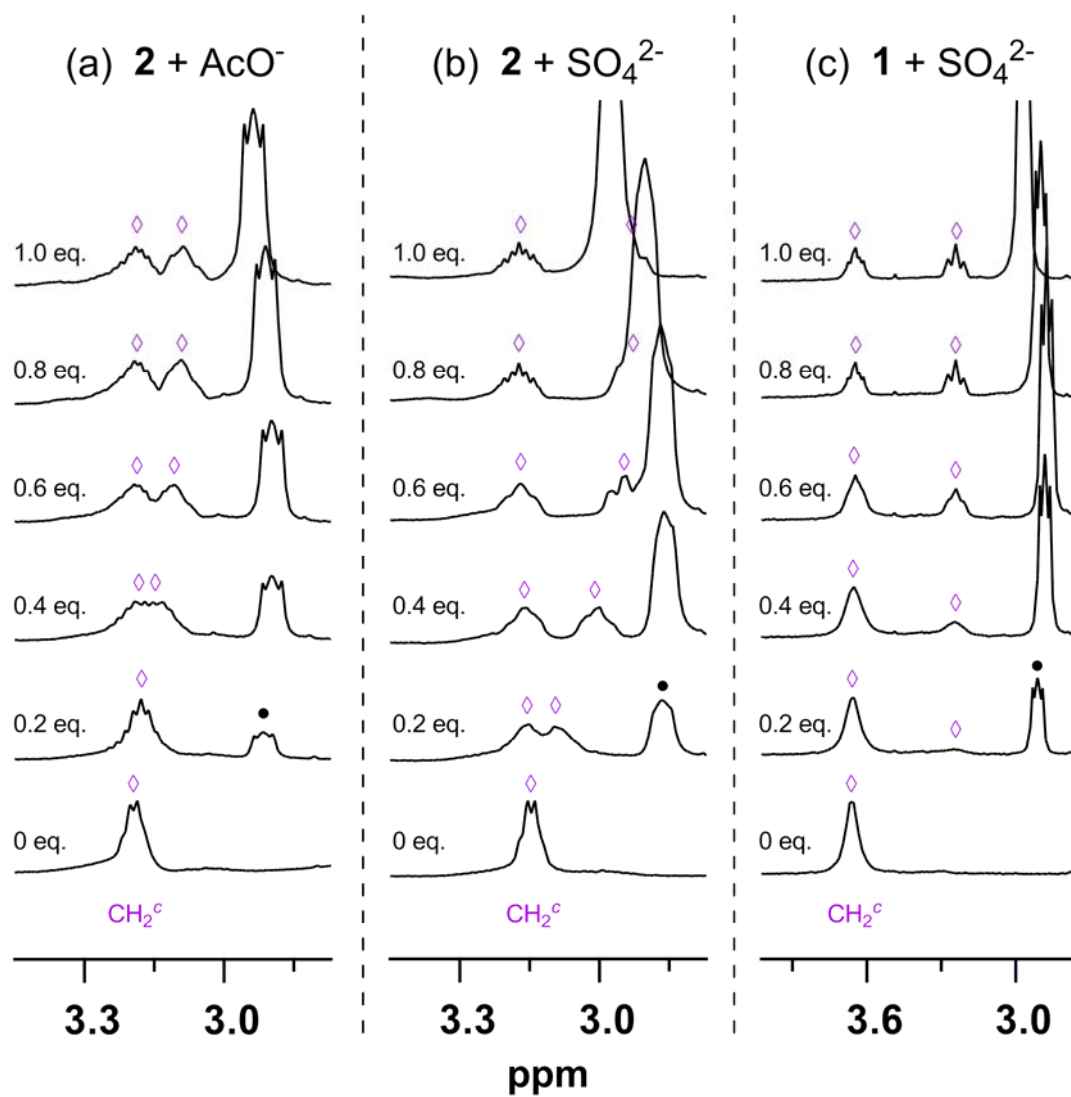


Figure S53 Partial  $^1\text{H}$  NMR (400 MHz, 300 K) spectra from titration of 2 with  $[\text{Bu}_4\text{N}]_2[\text{SO}_4]$  in  $\text{CDCl}_3$ . S: solvent residual.



**1** (X = S) or **2** (X = O)

**Figure S54:** Partial <sup>1</sup>H NMR spectra illustrating the splitting of the signals attributable to the diastereotopic CH<sub>2</sub><sup>c</sup> protons (labeled ◇) upon anion complexation; signals attributable to the tetrabutylammonium counterion are labeled ●.

## 7. References

1. C. E. Marjo, *Equilibria*, University of New South Wales Analytical Centre, Sydney, Australia; <http://www.sseau.unsw.edu.au/Index.htm>, 2009.