Electronic Supporting Information

Synthesis and anion binding studies of tris(3-aminopropyl)amine-based tripodal urea and thiourea receptors: Proton transfer-induced selectivity for hydrogen sulfate over sulfate

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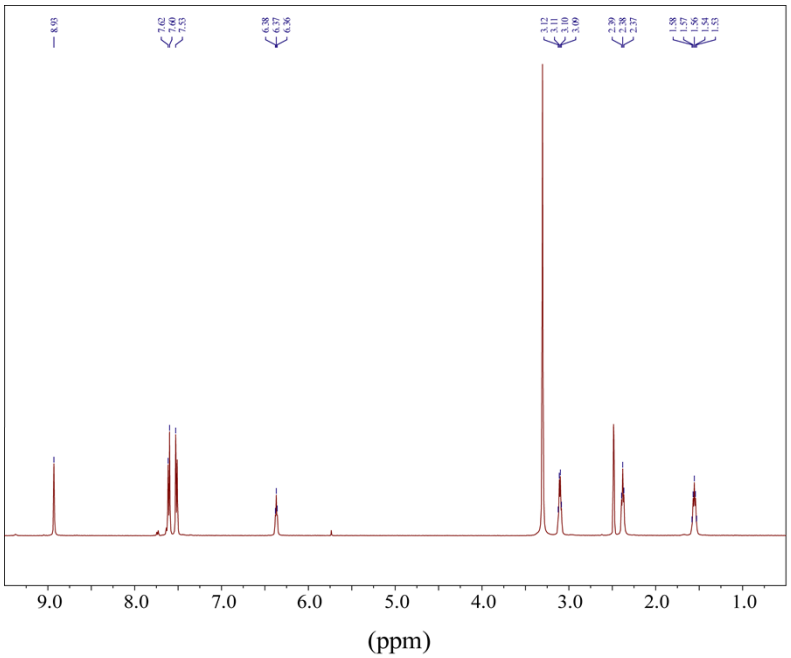


Figure S1. ^{1}H NMR spectra of **L1** in DMSO-d_6.

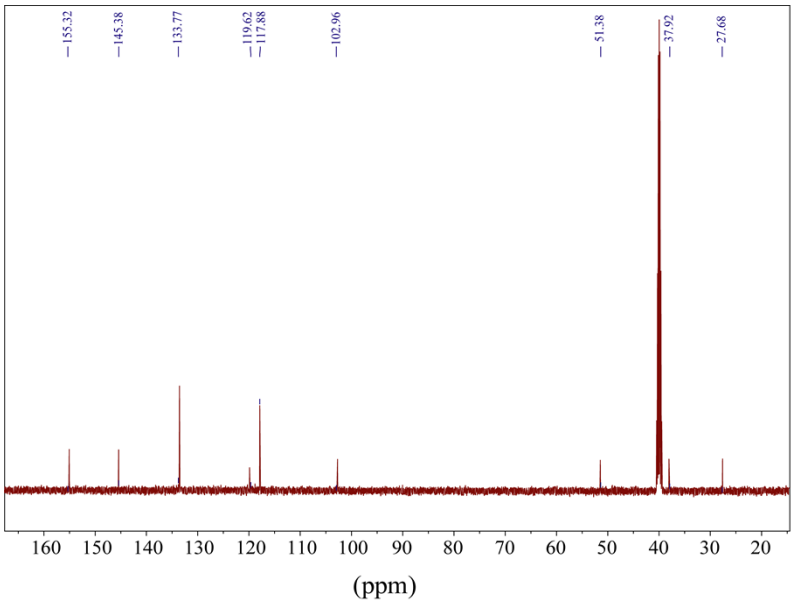


Figure S2. ^{13}C NMR spectra of **L1** in DMSO-d_6.

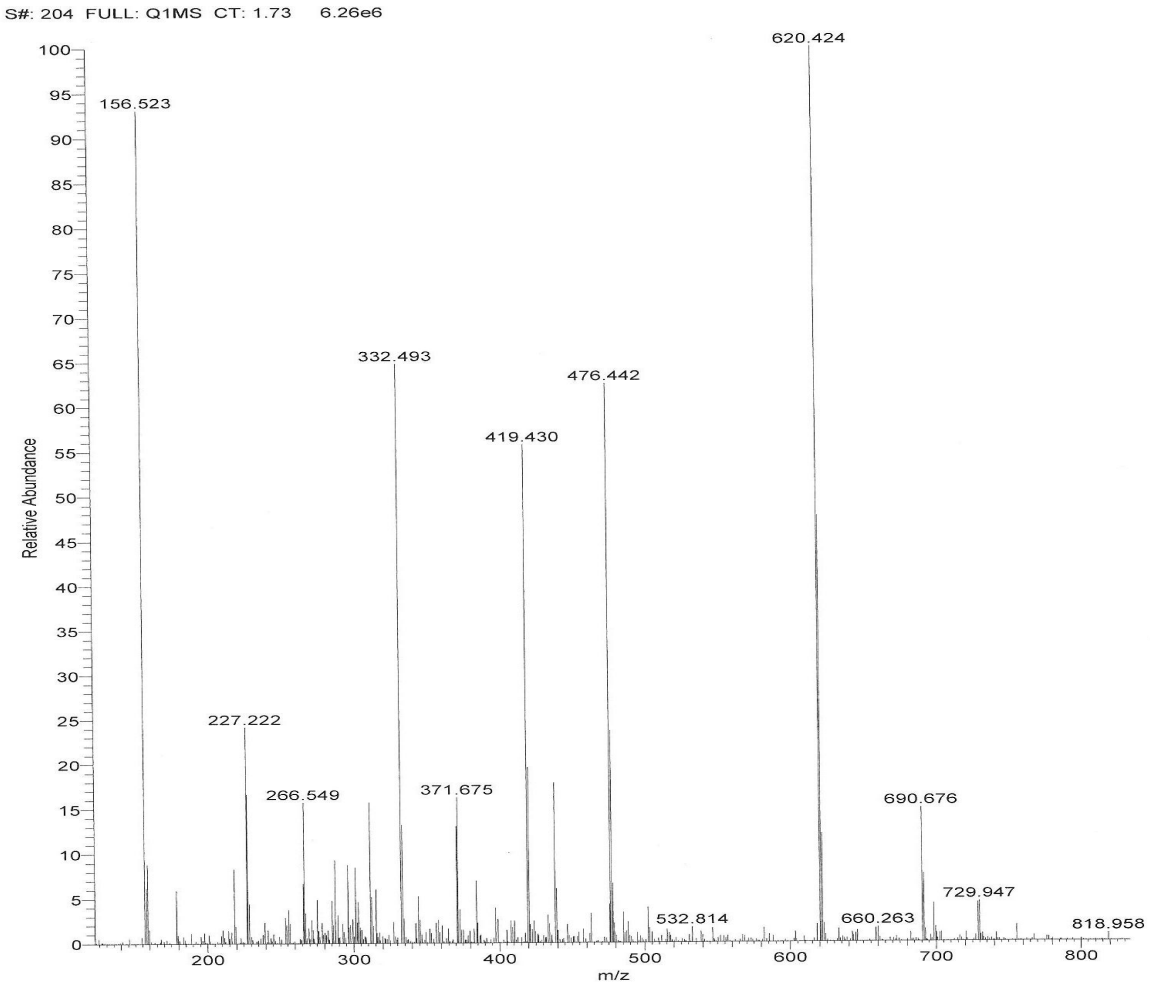


Figure S3. Mass spectra of **L1**

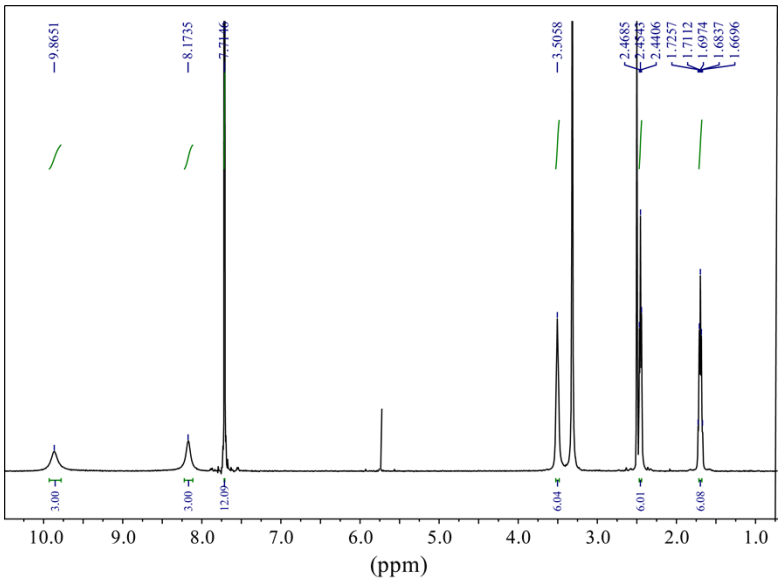


Figure S4. ^{1}H NMR spectra of **L2** in DMSO-d_6.

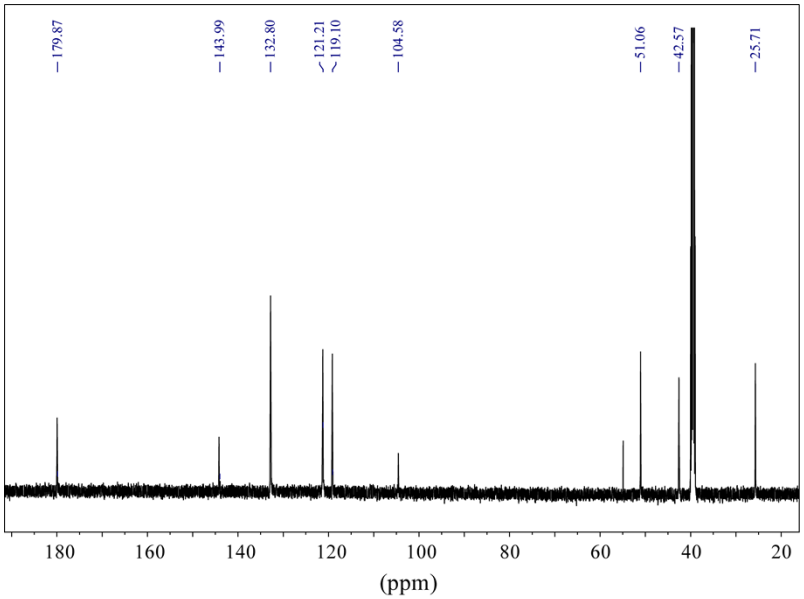


Figure S5. ^{13}C NMR spectra of **L2** in DMSO-d_6.

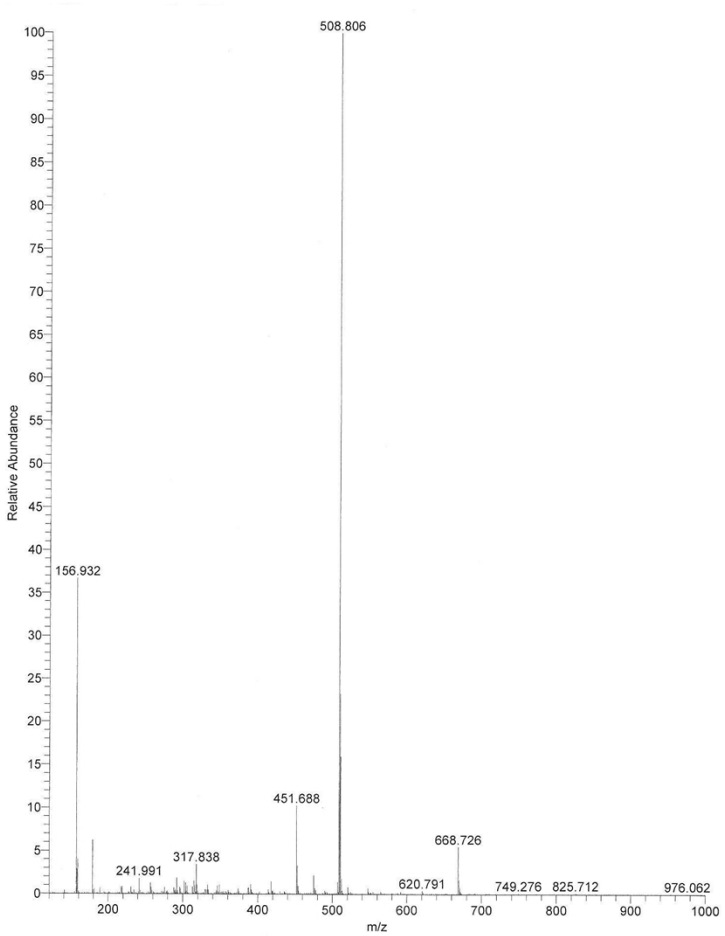
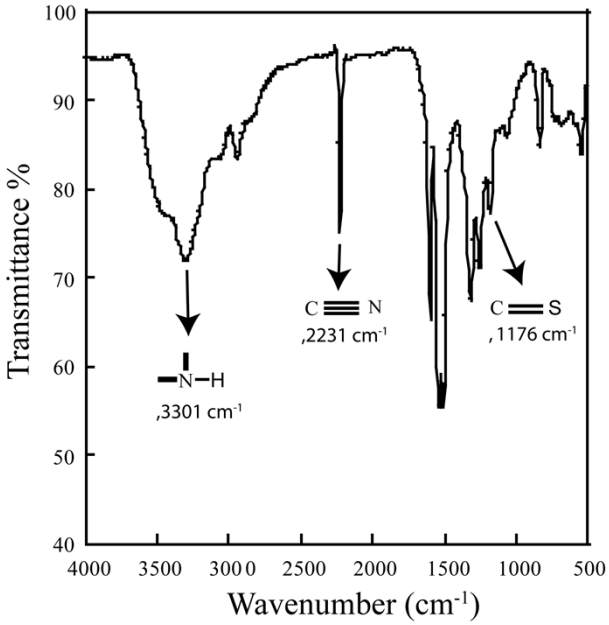


Figure S6. Mass spectra of **L2**



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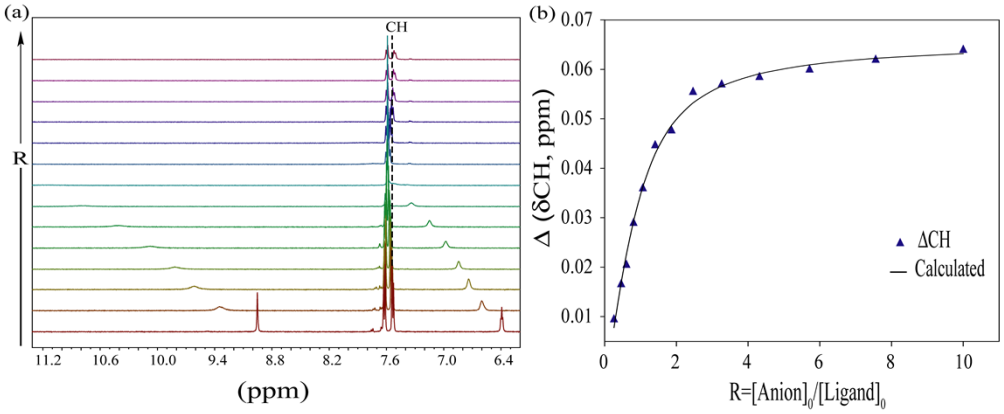
2. ^{1}H NMR Titrations



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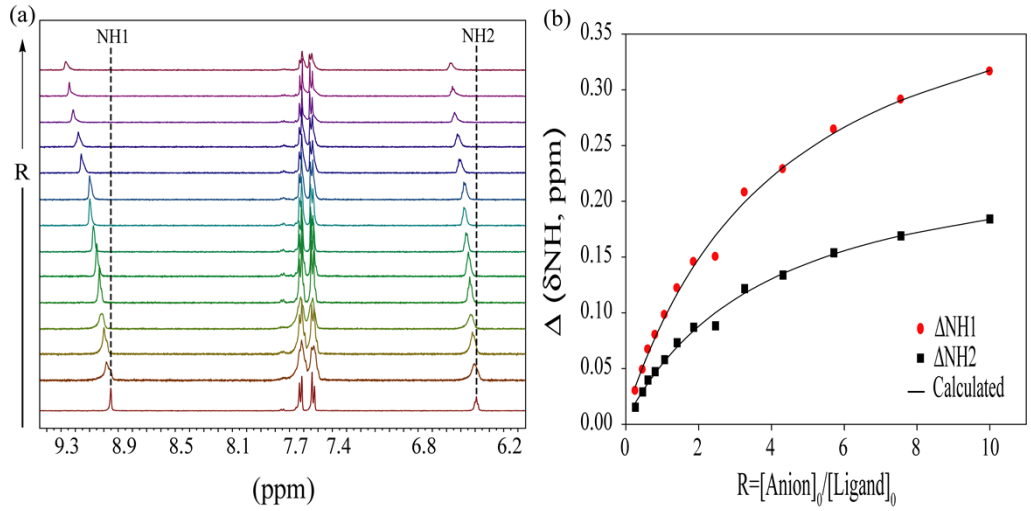

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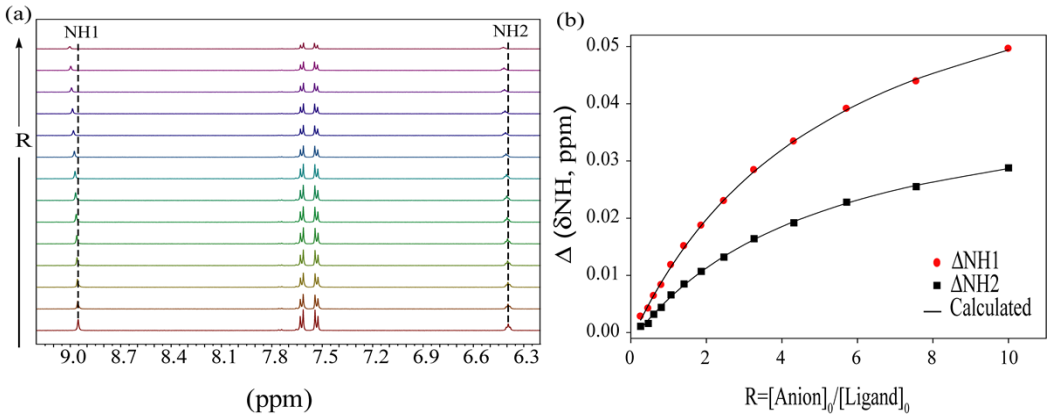

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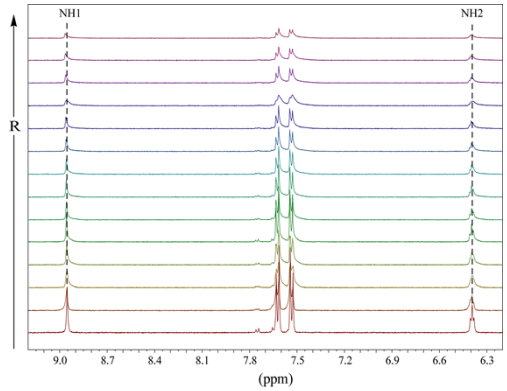

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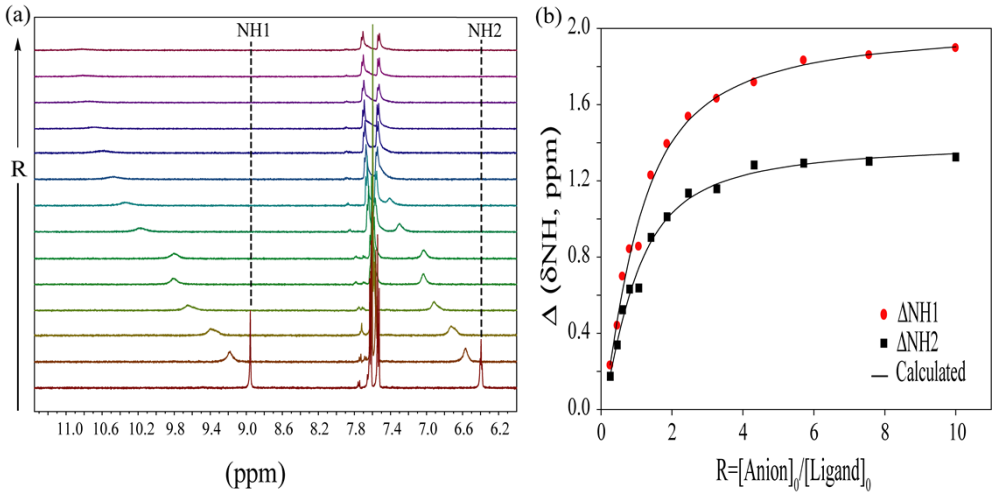

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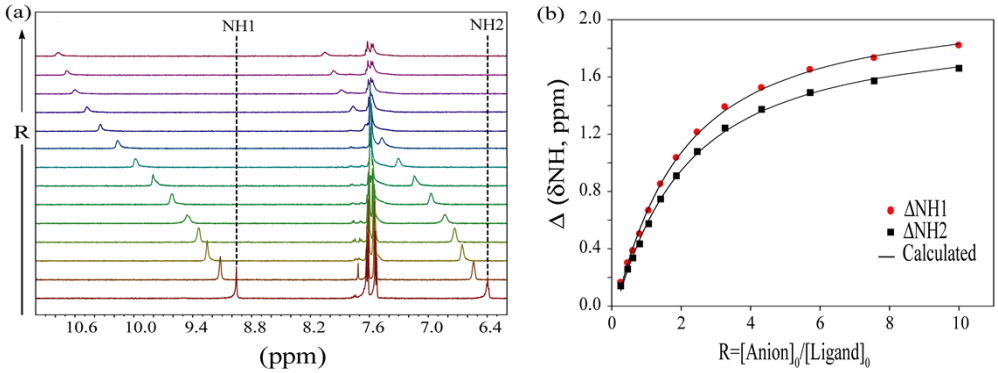

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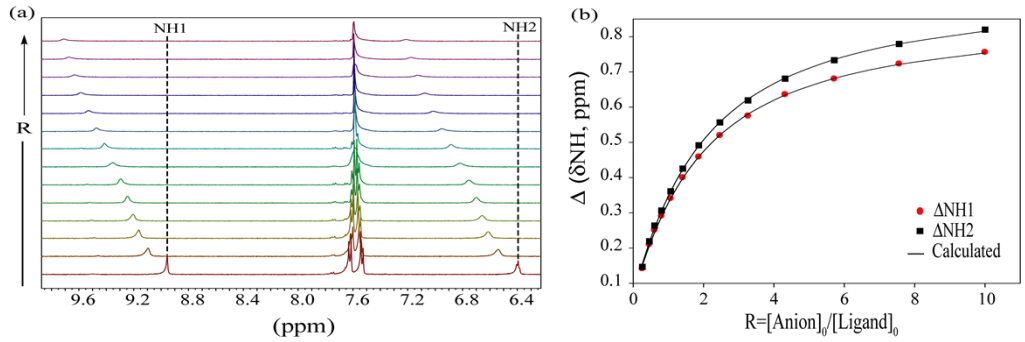

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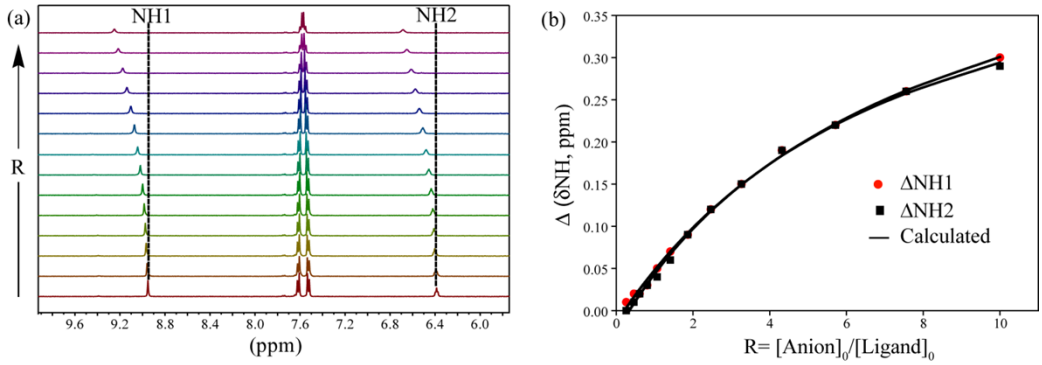

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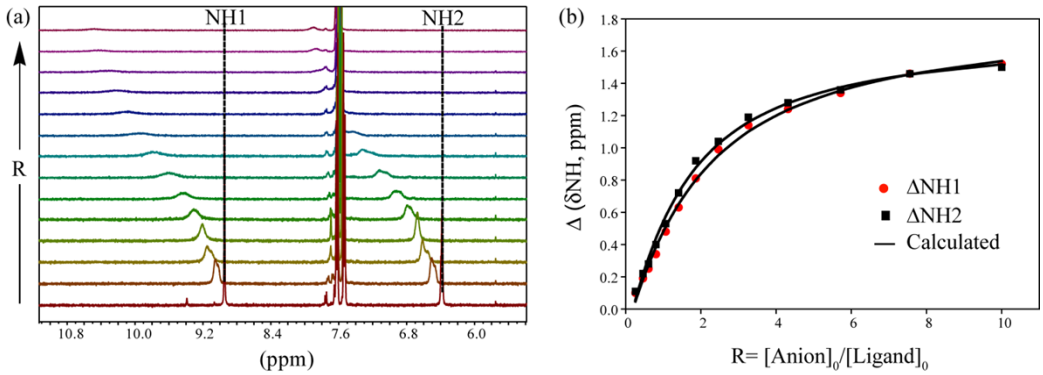

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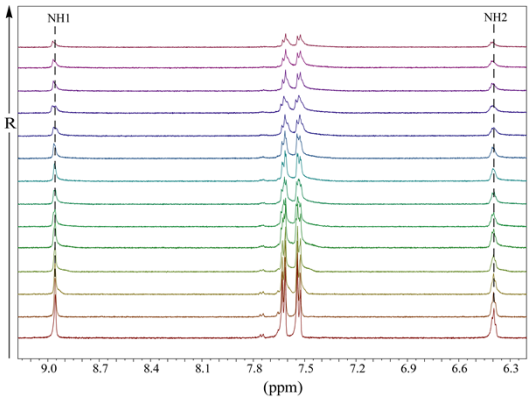

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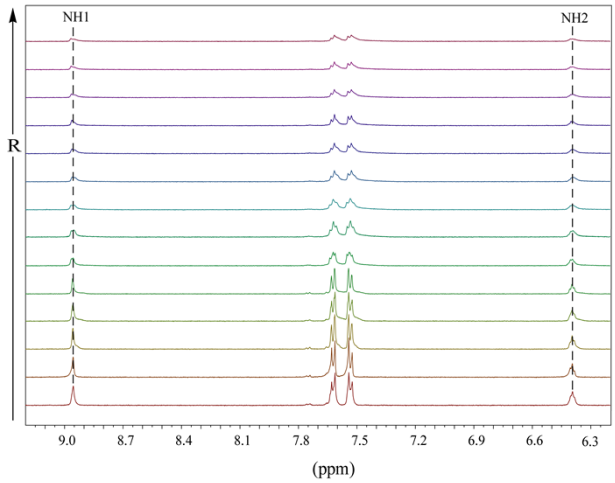

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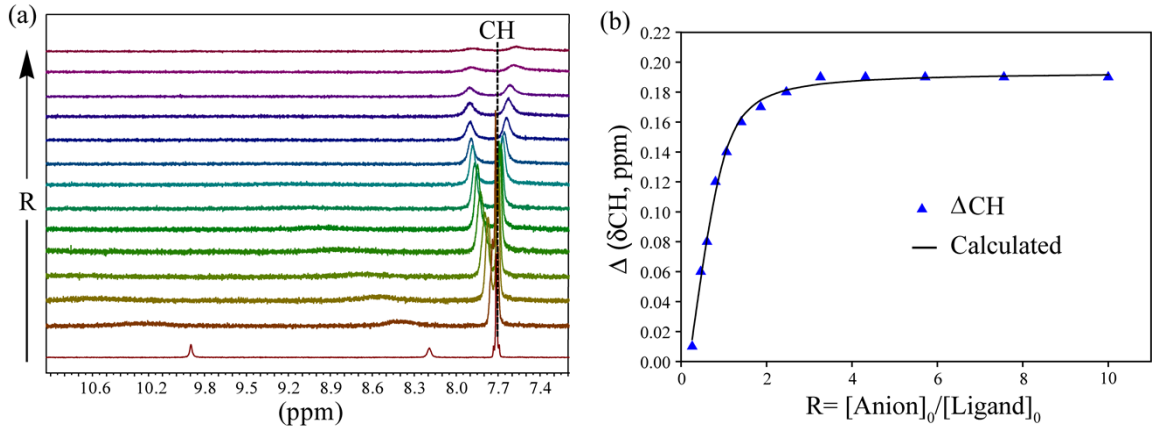

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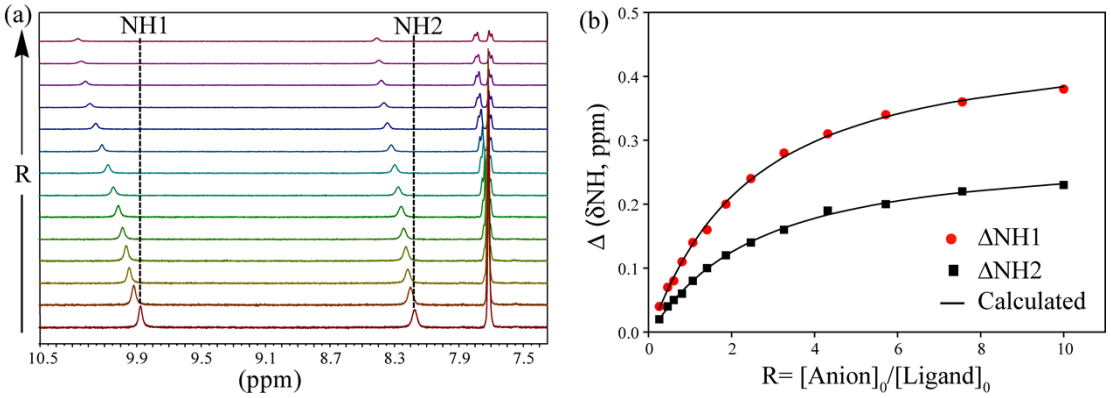

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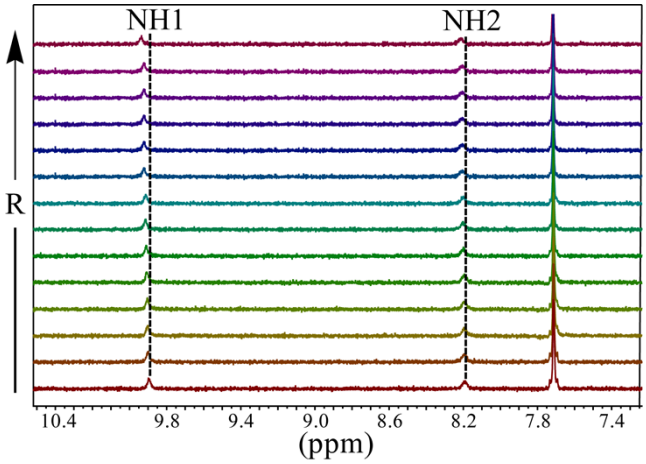


Figure S21. Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of TBABr (R = [TBABr] /[**L2**]) in DMSO-d_6. H1 = CSN*H*Ar and H2 = CH_2N*H*CS.

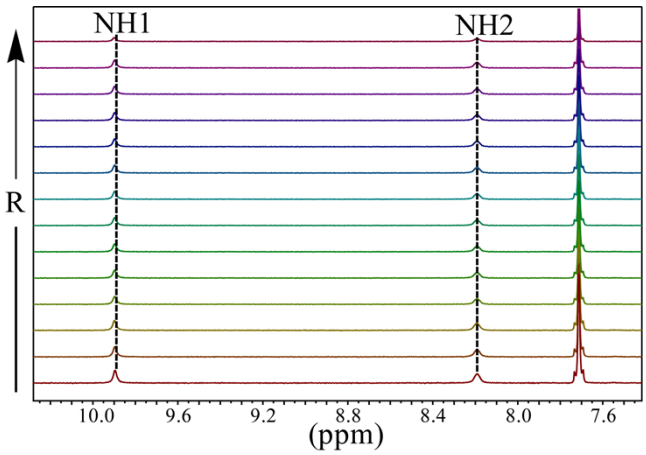


Figure S22. Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of TBAI (R = [TBAI] /[**L2**]) in DMSO-d_6. H1 = CSN*H*Ar and H2 = CH_2N*H*CS.

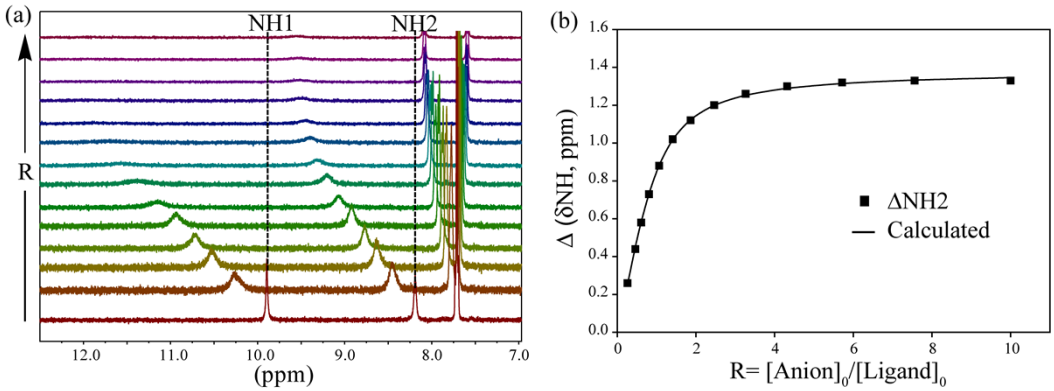


Figure S23. (a) Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of $TBAH_2PO_4$ (R = [$TBAH_2PO_4$] /[**L2**]) in DMSO-d_6 (b) Titration curves of **L2** with $TBAH_2PO_4$ showing changes in the chemical shifts of NH against the increasing amount of anion. H1 = CSN*H*Ar and H2 = CH_2N*H*CS.

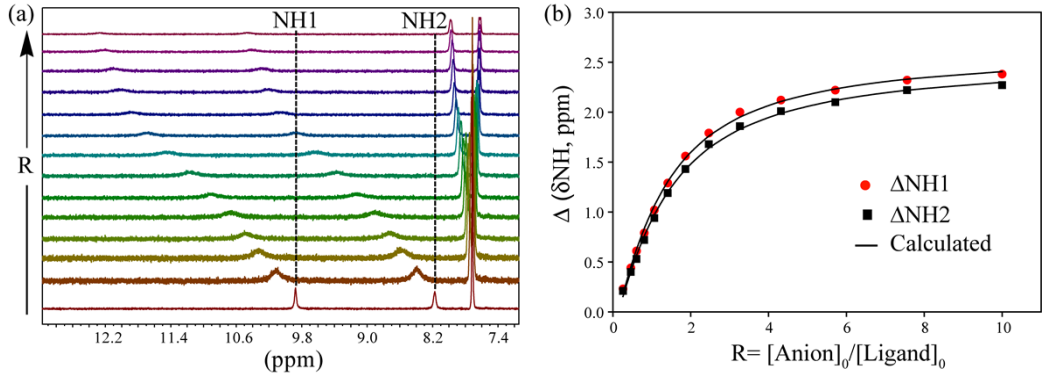
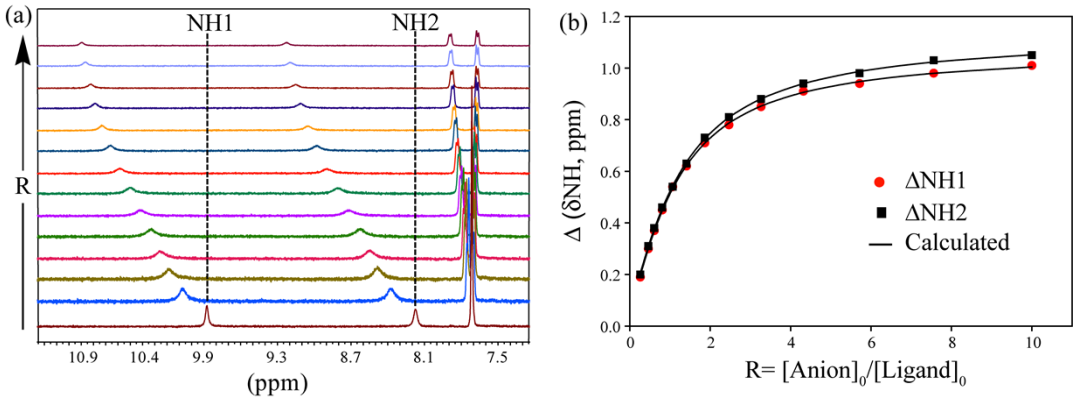


Figure S24. (a) Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of $TBACH_3COO$ (R = [$TBACH_3COO$] /[**L2**]) in DMSO-d_6 (b) Titration curves of **L2** with $TBACH_3COO$ showing changes in the chemical shifts of NH against the increasing amount of anion. H1 = CSN*H*Ar and H2 = CH_2N*H*CS.



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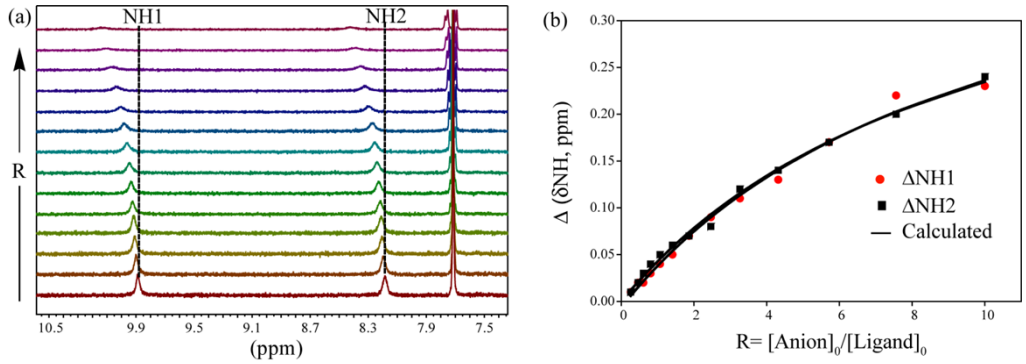

Figure S26. (a) Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of $(TBA)_2SO_4$ (R = [$(TBA)_2SO_4$] /[**L2**]) in DMSO-d_6 (b) Titration curves of **L2** with $(TBA)_2SO_4$ showing changes in the chemical shifts of NH against the increasing amount of anion. H1 = CON*H*Ar and H2 = CH_2N*H*CO.

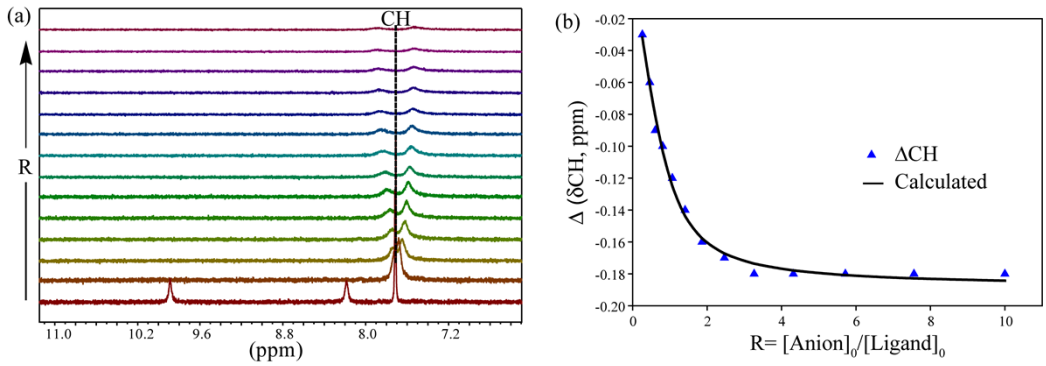

Figure S27. (a) Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of $TEAHCO_3$ (R = [$TEAHCO_3$] /[**L2**]) in DMSO-d_6 (b) Titration curves of **L2** with $TEAHCO_3$ showing changes in the chemical shifts of CH against the increasing amount of anion.

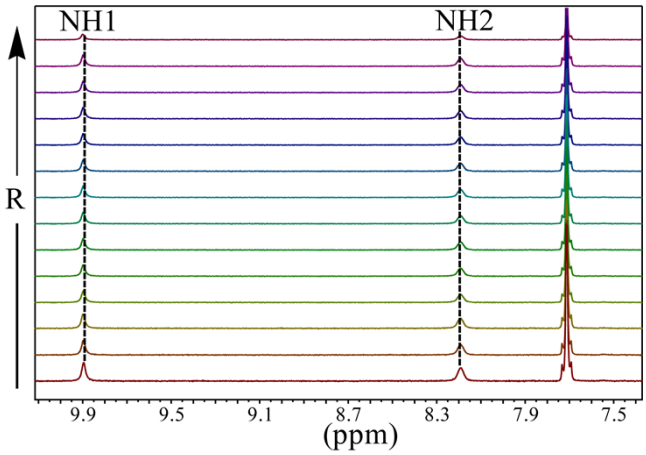

Figure S28. Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of $TBANO_3$ (R = $[TBANO_3]$ /[**L2**]) in DMSO-d_6. H1 = CSN*H*Ar and H2 = CH_2N*H*CS.

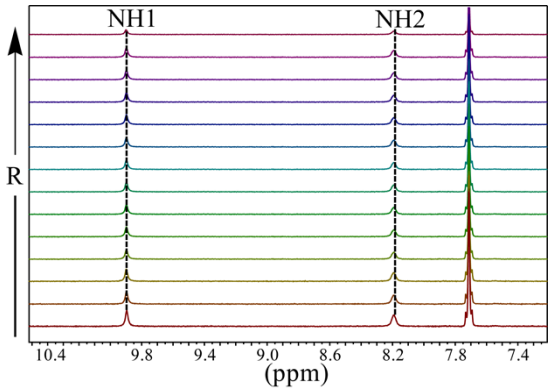

Figure S29. Partial ^{1}H NMR spectra of **L2** (2mM) with an increasing amount of $TBAClO_4$ (R = $[TBAClO_4]$ /[**L2**]) in DMSO-d_6. H1 = CSN*H*Ar and H2 = CH_2N*H*CS.

3. Job's Plots

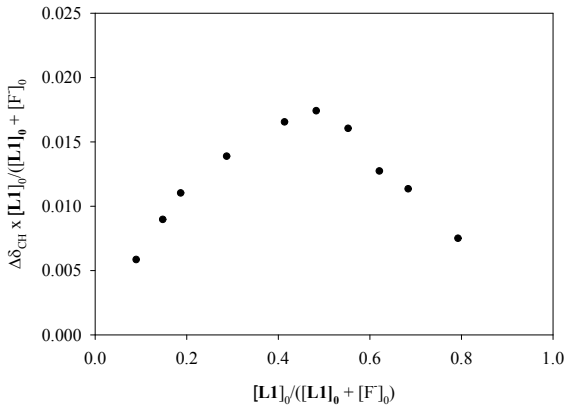

Figure S30. Job's plot for the formation of the fluoride complex with **L1**. The chemical shift changes are shown for C*H*CNH obtained from the ^{1}H NMR titrations of **L1** with F^-.

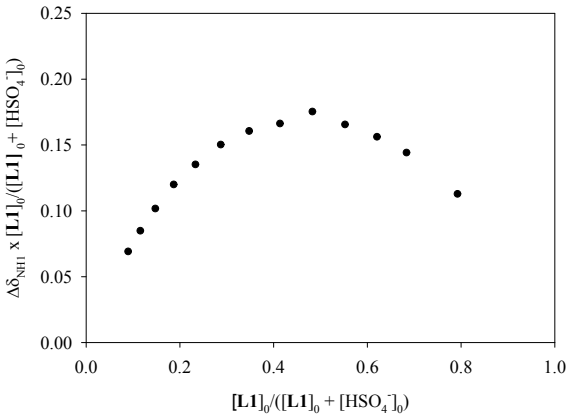

Figure S31. Job's plot for the formation of the hydrogen sulfate complex with **L1**. The chemical shift changes are shown for NH1 obtained from the ^{1}H NMR titrations of **L1** with HSO_4^-.

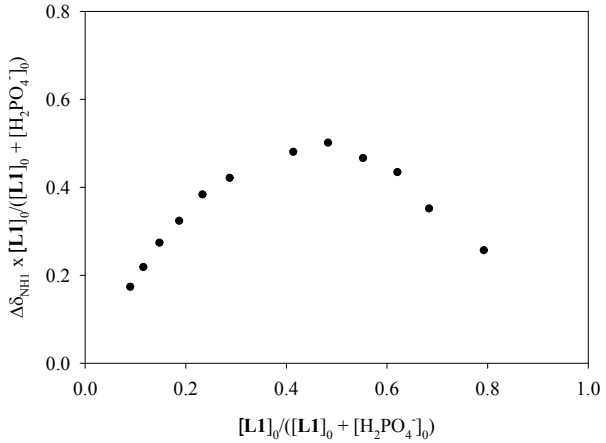

Figure S32. Job's plot for the formation of the dihydrogen phosphate complex with **L1**. The chemical shift changes are shown for NH1 obtained from the ^{1}H NMR titrations of **L1** with $H_2PO_4^-$.

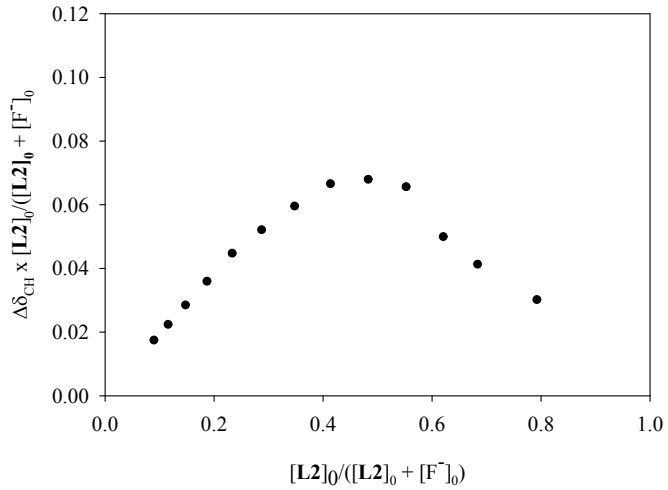

Figure S33. Job's plot for the formation of the fluoride complex with **L2**. The chemical shift changes are shown for C*H*CNH obtained from the ^{1}H NMR titrations of **L2** with F^-.

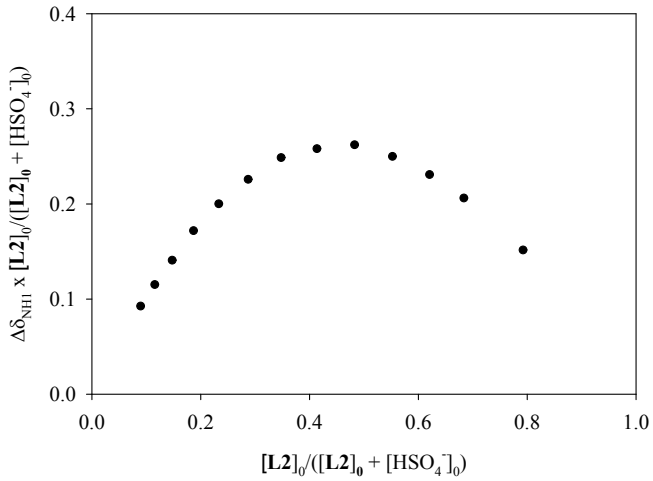

Figure S34. Job's plot for the formation of the hydrogen sulfate complex with **L2**. The chemical shift changes are shown for NH1 obtained from the ^{1}H NMR titrations of **L2** with HSO_4^-.

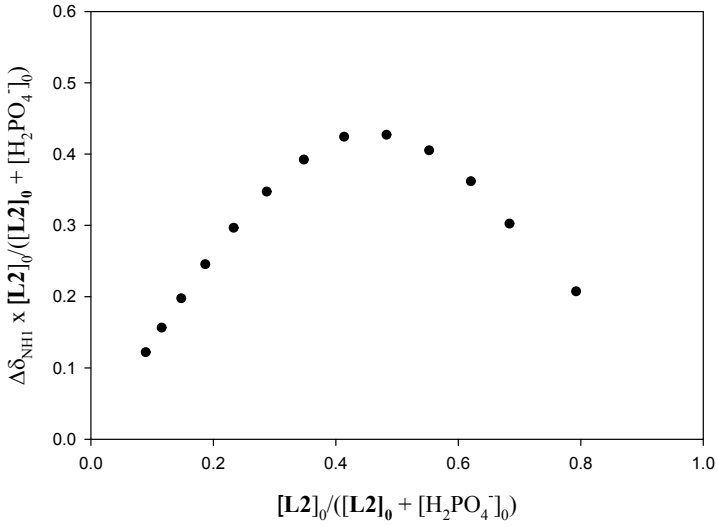

Figure S35. Job's plot for the formation of the dihydrogen phosphate complex with **L2**. The chemical shift changes are shown for NH1 obtained from the ^{1}H NMR titrations of **L2** with $H_2PO_4^-$.

4. 2D NOESY NMR experiments

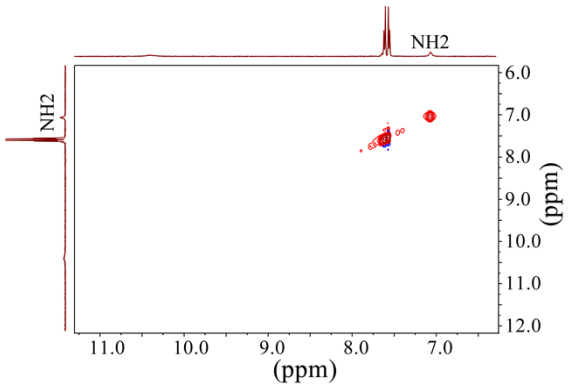

Figure S36. 2D NOESY NMR spectra of TBAF complex of **L1** in DMSO-d_6 at room temperature.

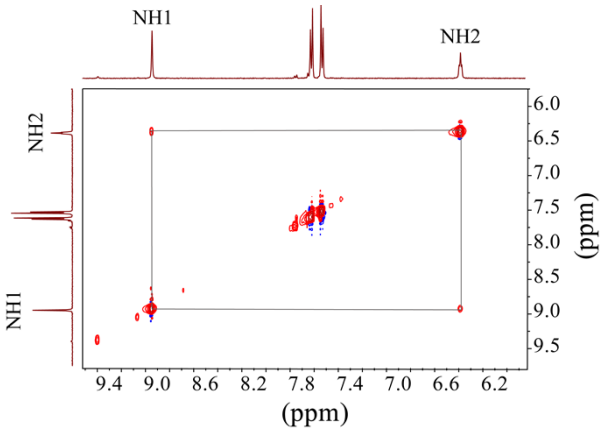

Figure S37. 2D NOESY NMR spectra of TBACl complex of **L1** in DMSO-d_6 at room temperature.

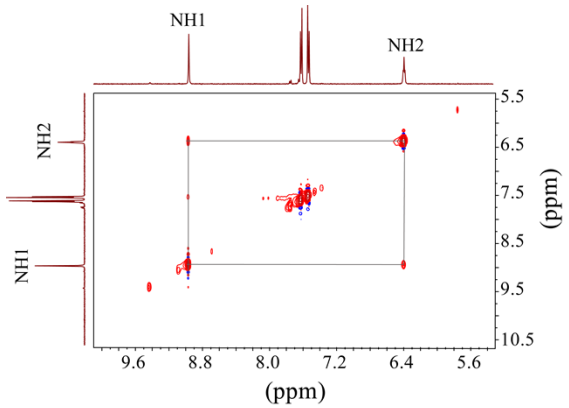

Figure S38. 2D NOESY NMR spectra of TBABr complex of **L1** in DMSO-d_6 at room temperature.

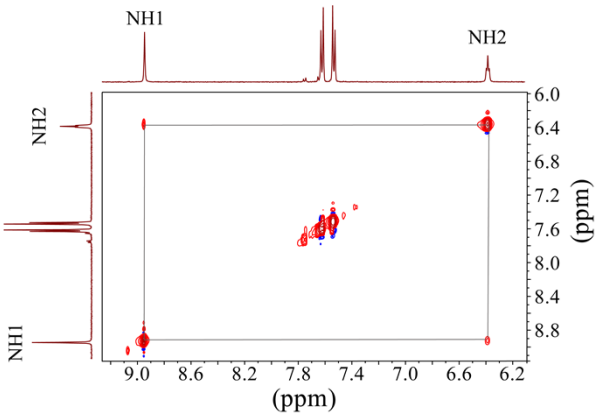

Figure S39. 2D NOESY NMR spectra of TBAI complex of **L1** in DMSO-d_6 at room temperature.

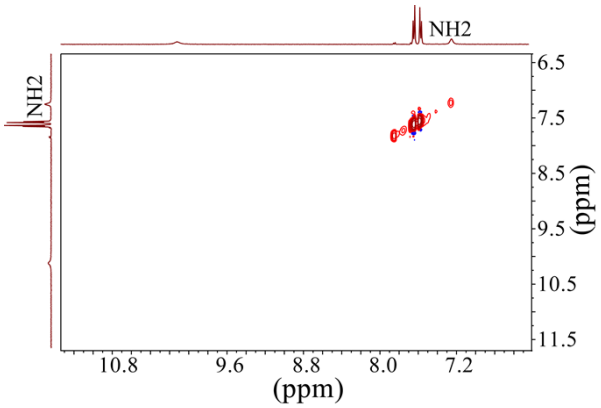

Figure S40. 2D NOESY NMR spectra of $TBAH_2PO_4$ complex of **L1** in DMSO-d_6 at room temperature.

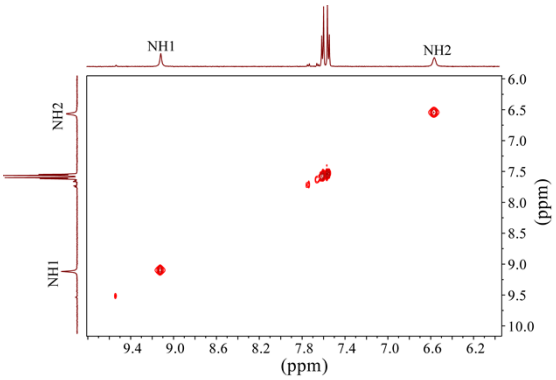

Figure S41. 2D NOESY NMR spectra of $ZnSO_4$ complex of **L1** in DMSO-d_6 at room temperature.

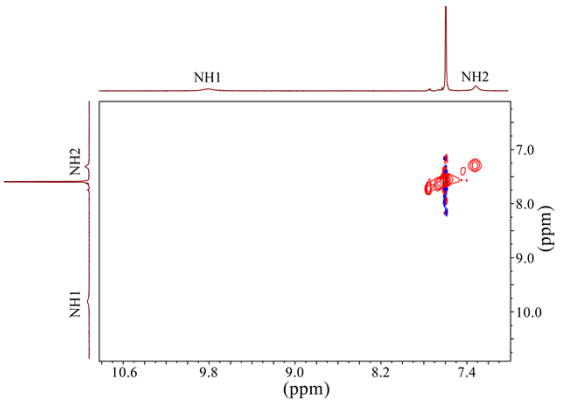

Figure S42. 2D NOESY NMR spectra of $TEAHCO_3$ complex of **L1** in DMSO-d_6 at room temperature.

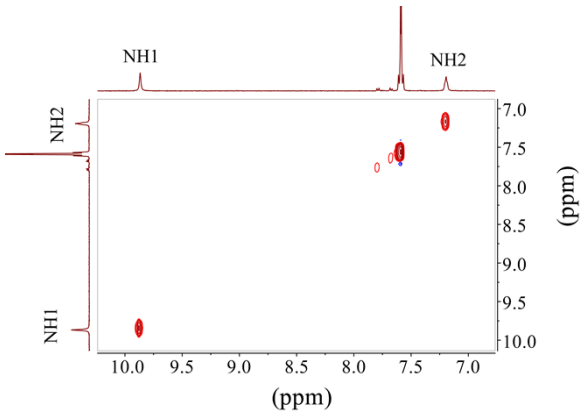

Figure S43. 2D NOESY NMR spectra of $TBA(CH_3COO)$ complex of **L1** in DMSO-d_6 at room temperature.

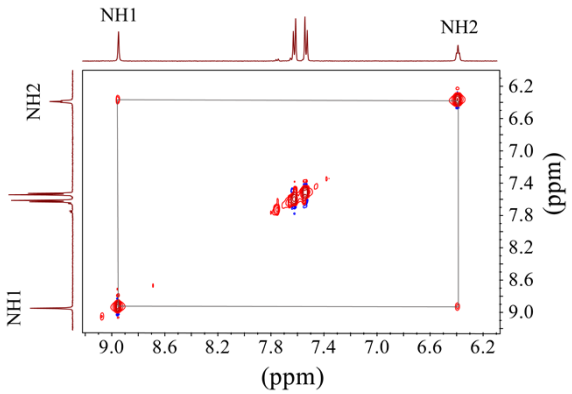

Figure S44. 2D NOESY NMR spectra of $TBANO_3$ complex of **L1** in DMSO-d_6 at room temperature.

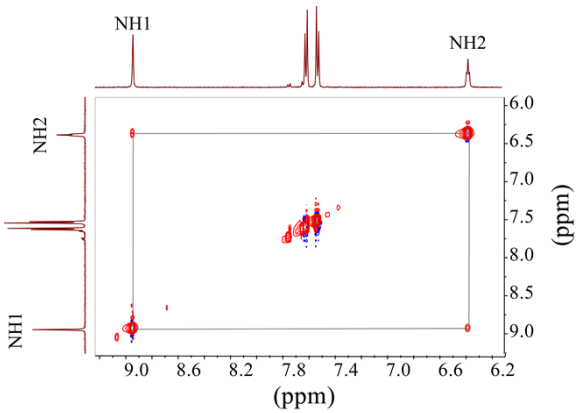

Figure S45. 2D NOESY NMR spectra of $TBAClO_4$ complex of **L1** in DMSO-d_6 at room temperature.

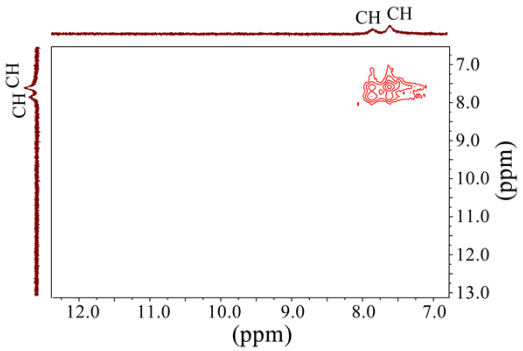

Figure S46. 2D NOESY NMR spectra of TBAF complex of **L2** in DMSO-d_6 at room temperature.

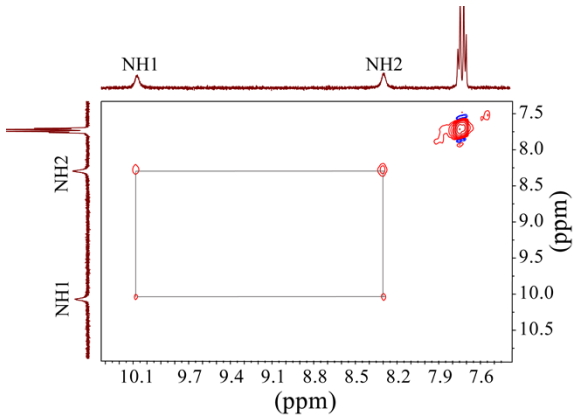

Figure S47. 2D NOESY NMR spectra of TBACl complex of **L2** in DMSO-d_6 at room temperature.

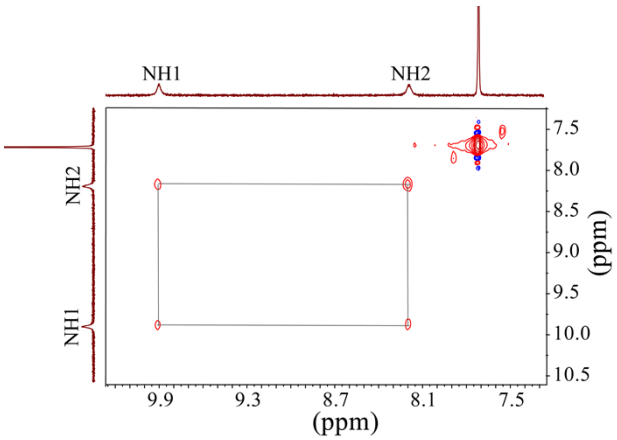

Figure S48. 2D NOESY NMR spectra of TBABr complex of **L2** in DMSO-d_6 at room temperature.

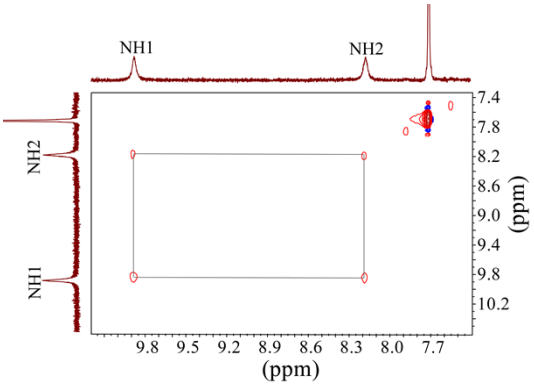

Figure S49. 2D NOESY NMR spectra of TBAI complex of **L2** in DMSO-d_6 at room temperature.

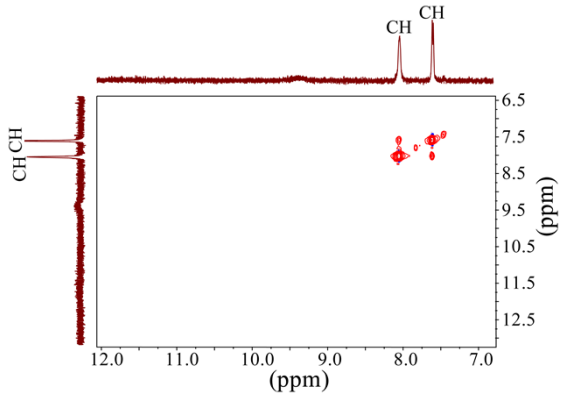

Figure S50. 2D NOESY NMR spectra of $TBAH_2PO_4$ complex of **L2** in DMSO-d_6 at room temperature.

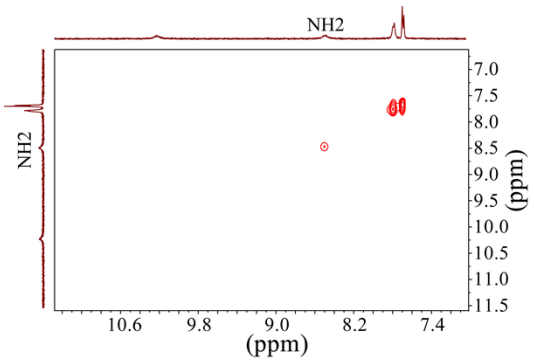

Figure S51. 2D NOESY NMR spectra of $ZnSO_4$ complex of **L2** in DMSO-d_6 at room temperature.

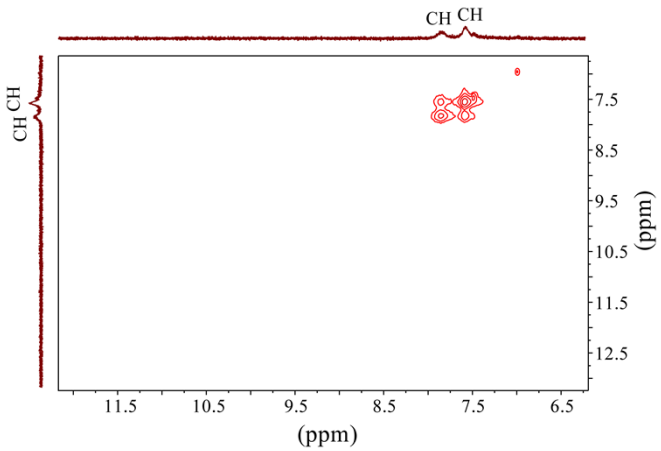

Figure S52. 2D NOESY NMR spectra of $TEAHCO_3$ complex of **L2** in DMSO-d_6 at room temperature.

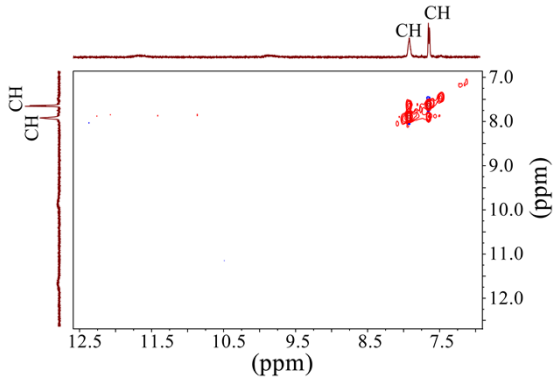

Figure S53. 2D NOESY NMR spectra of $TBA(CH_3COO)$ complex of **L2** in DMSO-d_6 at room temperature.

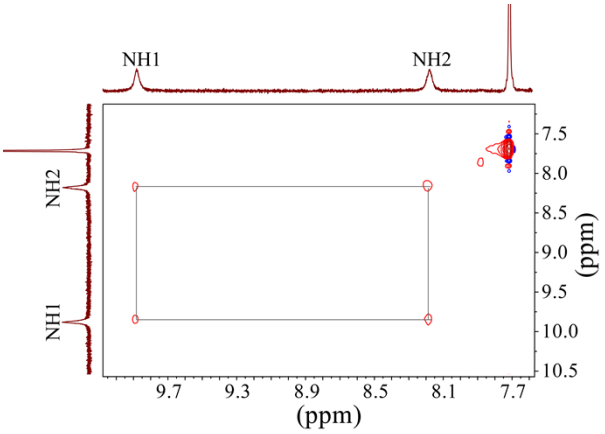

Figure S54. 2D NOESY NMR spectra of $TBANO_3$ complex of **L2** in DMSO-d_6 at room temperature.

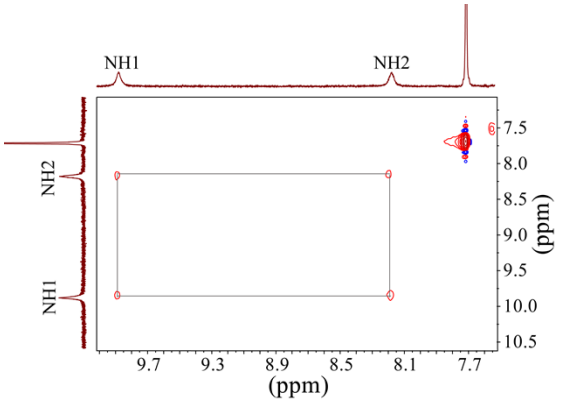

Figure S55. 2D NOESY NMR spectra of $TBAClO_4$ complex of **L2** in DMSO-d_6 at room temperature.

4. Fluoride Extraction Studies

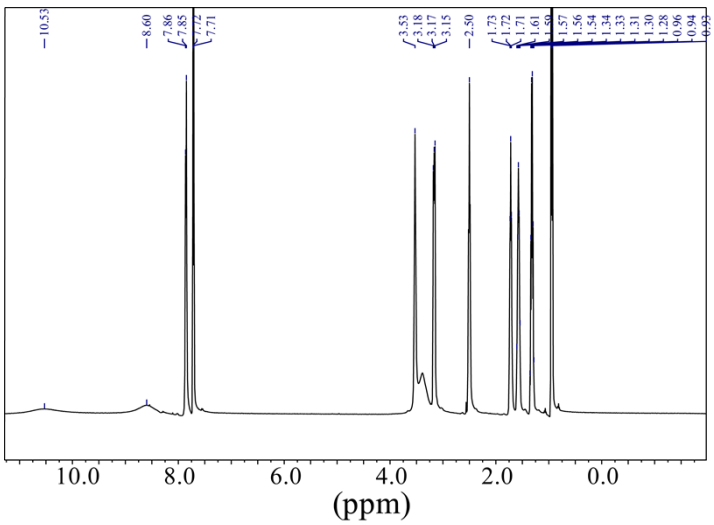

Figure S56. ^{1}H NMR spectra of extracted fluoride-**L2** complex in DMSO-d_6.

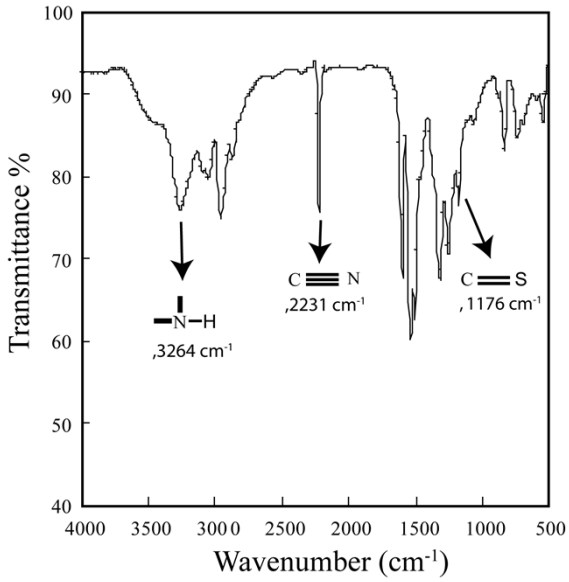

Figure S57. FT-IR spectra of extracted fluoride-**L2** complex in KBr.

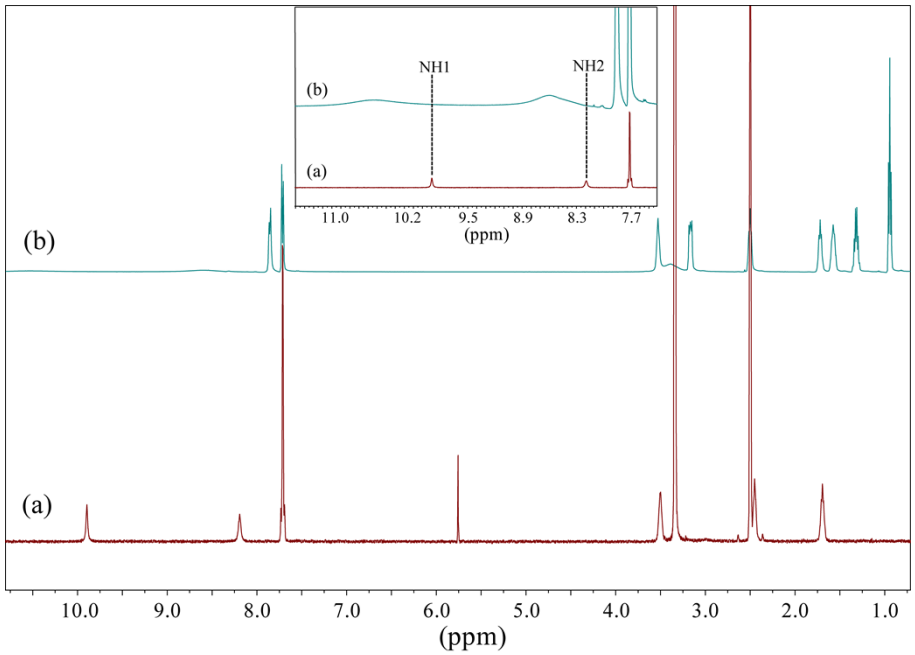

Figure S58. Comparative ^{1}H NMR spectra of (a) **L2**, (b) Extracted fluoride complex. Inset shows the expanded partial ^{1}H NMR spectra of **L2** and the complex.