Electronic Supplementary Material (ESI) for ChemComm.

Selenoureas for anion binding as molecular logic gates.

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Experimental methods

^{1}H NMR spectra were recorded on Bruker Avance-300 spectrometer with 300 MHz Larmor frequency at 300 K. Chemical shifts are reported in parts per million (ppm), referenced to the residual solvent peak. All solvents and starting materials were purchased from commercial sources where available. ^{1}H NMR titrations were performed by adding aliquots of a stock solution of the anionic guest (as tetrabutylamonium (TBA) salt, 0.075 M) to a solution of the receptor (0.005M) in DMSO-d_6. 2D NMR spectra acquisition was performed at 300K with an Agilent UNITY INOVA spectrometer operating at a ^{1}H frequency of 500 MHz. A ^{1}H(90°) pulse of 6.6 μs (90°) was applied over a spectral window of 8000 Hz, with 1 s recycle delay. Homonuclear gCOSY was collected by sampling each of the 256 increments with 2048 complex points. The same was carried out for TOCSY and ROESY by applying the mlev17 spin-lock scheme with 80 and 200 ms mixing time, respectively. Mass spectra (CI, EI, FAB and LSI) were recorded on Kratos MS-80-RFA and Micromass AutoSpec-Q mass spectrometers with a resolution of 1000 or 10,000 (10% valley definition). For the FAB and LSI spectra, ions were produced by a beam of xenon atoms and Cs^+ ions, respectively, by using 1-thioglycerol as matrix and NaI as additive. TLC was performed on aluminum pre-coated sheets (E. Merck Silica Gel 60 F_{254}); spots

were visualized under UV light, by charring with 10% H_2SO_4 in EtOH. Column chromatography was performed with E. Merck Silica Gel 60 (40–63 mm). All the reactions and purifications involving organoselenium derivatives were carried out in the darkness by using aluminium foil.

Synthetic procedures

Synthesis of L1

A solution of isoselenocyanatobenzene (0.200 g, 1.098 mmol) in dry DCM (2mL) was added dropwise to a solution of aniline (0.102 g, 1,098 mmol) in ethanol absolute (2mL) in the darkness under Ar. The mixture was stirred for 4h at room temperature and then it was filtered to give the desired compound as white solid. Yield 84 %(0,255 g, 0,927 mmol). ^{1}H-NMR (300 MHz,DMSO-d_6, 298K): δH: 10.14 (s, 1H); 7.41-7.31 (m, 8H); 7.15 (t, 7.1, Hz, 2H). ^{13}C-NMR (75.5 MHz, DMSO-d_6, 298 K), δC: 179.40, 140.06, 128.92, 125.54, 125.22. ESI m/z 299.0051 $[M+Na]^+$.

Synthesis of L2

A solution of 1-isoselenocyanatonaphtalene (0.200 g, 0,862 mmol) in dry DCM (2mL) was added dropwise to a solution of aniline (0.102 g, 0,862 mmol) in ethanol absolute (2mL) in the darkness under Ar. The mixture was stirred for 4h at room temperature and then it was filtered to give the desired compound as white solid. Yield 79 % (0,220 g, 0,676 mmol).^{1}H-NMR (300 MHz,DMSO-d_6, 298K): δH: 10.28 (s, 1H); 9.94 (s, 1H); 7.99-7.88 (m, 3H); 7.63-7.46 (m, 4H); 7.38 (d, J= 7.2 Hz, 2H); 7.30 (t, J= 7.8 Hz, 2H); 7.15 (t, J= 7.2 Hz, 1H). ^{13}C-NMR (75.5 MHz, DMSO-d_6, 298 K), δC: 180.30, 140.28, 136.07, 134.46, 130.35, 128.88,

128.58, 127.74, 126.75, 126.63, 126.22, 126.18, 125.95, 123.76. ESI m/z 349.0210 $[M+Na]^+$.

Synthesis of L3

A solution of 1-isoselenocyanatonaphtalene (0.200 g, 0,862 mmol) in dry DCM (2mL) was added dropwise to a solution of naphthalenamine (0.123 g, 0,862 mmol) in ethanol absolute (2mL) in the darkness under Ar. The mixture was stirred for 4h at room temperature and then it was filtered to give the desired compound as white solid. Yield 55 % (0.178 g, 0,474mmol).^{1}H-NMR (300 MHz,DMSO-d_6, 298K): δH: 10.14 (s, 1H); 7.95 (d, J= 7.9, Hz, 2H); 7.91-7.87 (m, 1H); 7.64-7.51 (m, 4H); 7.42-7.33 (m, 4H); 7.21 (t, 7.2 Hz, 1H). ^{13}C-NMR (75.5 MHz, DMSO-d_6, 298 K), δC: 181.30, 136.28, 134.40, 130.66, 128.53, 127.83, 126.77, 126.68, 126.62, 126.17, 123.78. ESI m/z 399.0367 $[M+Na]^+$.

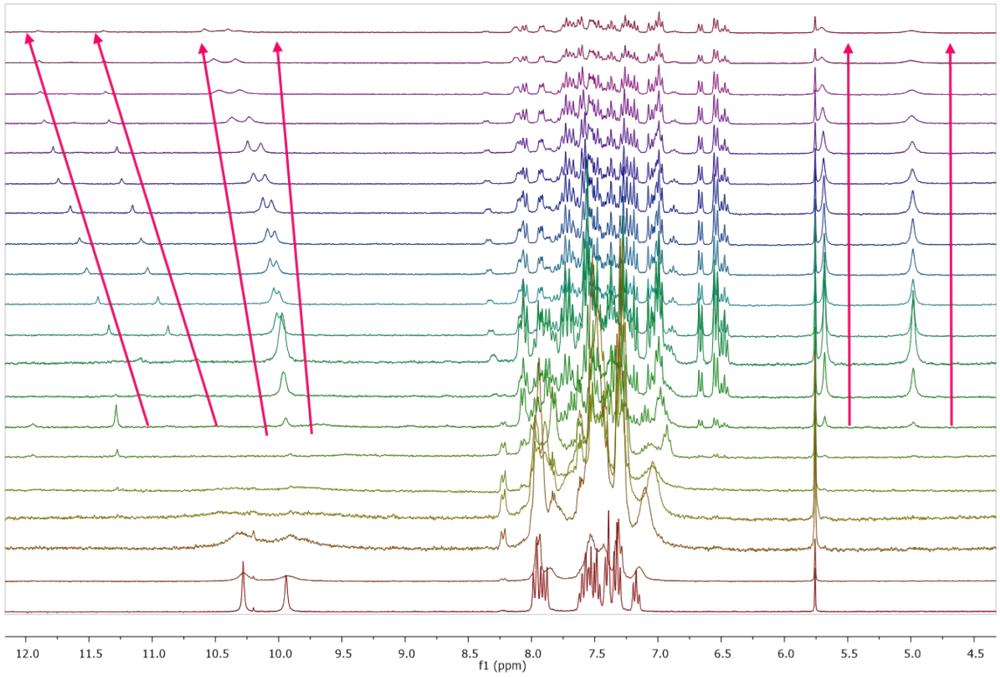


Figure S1 Titration of **L2** (0.005M) with acetate as TBA salt (0.075M) in DMSO-d_6.

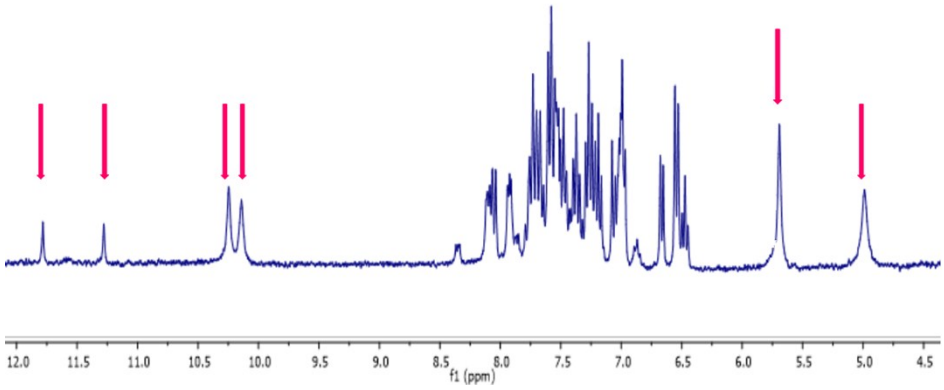


Figure S2 Spectrum of **L2** (0.005M) in the presence of 2.5 equivalents of acetate as TBA salt (0.075M) in DMSO-d_6.

Discussion of 2D-NMR experiments

In the gCOSY spectrum, no correlation (scalar coupling) was found among the six singlets indicated by arrows in Fig. S2, confirming their multiplicity. The analysis revealed eight different spin systems comprising three aromatic protons each. One additional spin system could not be accurately identified together with several resonances belonging to other spin systems as illustrated in Fig. S3, because of resonances partial overlap with insufficient spectral resolution. TOCSY and ROESY spectra confirmed the correlation between the NH proton signals and the different aromatic spin systems identified in the gCOSY. By taking all the results together into consideration, including frequency order and range for each of the spin systems, the assignments shown in Fig. S3 emerged, indicating the co-existence of three different species in the solution. The only ROEs (dipolar interaction) among HN protons was found for the two with the highest frequency, namely, at 11.65 and 11.15 ppm, clearly indicating that these belonged to the same species. Such a through-space direct interaction between two protons indicates that they are relatively still over time in close proximity with each other (usually at a distantce < 5Å). This led to their attribution to the bi-coordinated adduct, since the interaction with the anion is expected to keep the two NHs directed towards the same direction and to shift their resonance frequency to rather high values. As far as the remaining NH signals are concerned, they were categorized into two couples, one at intermediate frequencies (at 10.11 and 10.04 ppm) and the other at low frequencies (at 4.97 and 5.67 ppm). As already discussed in the main paper, on the basis of the work by Roberts and co-workers it was possible to attribute these to coordinating and non-coordinating NHs in two different mono-coordinated adducts. In one of the latter, the NH on the phenyl side interacted with the acetate anion while the other NH pointed to the opposite direction,

thus, towards the side of the chalcogen atom. In a second mono-coordinated adducts, the NH on the naphthyl side interacted with the anion, while the other NH pointed to the chalcogen side. This interpretation is bolstered by evidence from the literature and explains the large difference in frequency among the NHs.

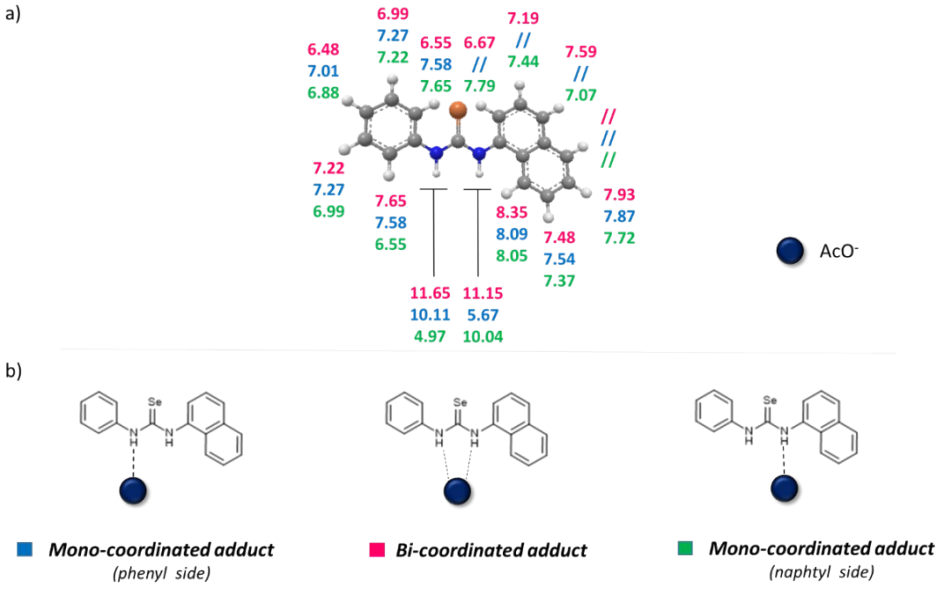


Figure S3 a)^{1}H-NMR frequencies attribution of receptor **L2** in the presence of 2.5 equivalents of TBAAcO in DMSO-d_6 and b) structures of the hypothesised mono and bi-coordinated adducts with acetate.

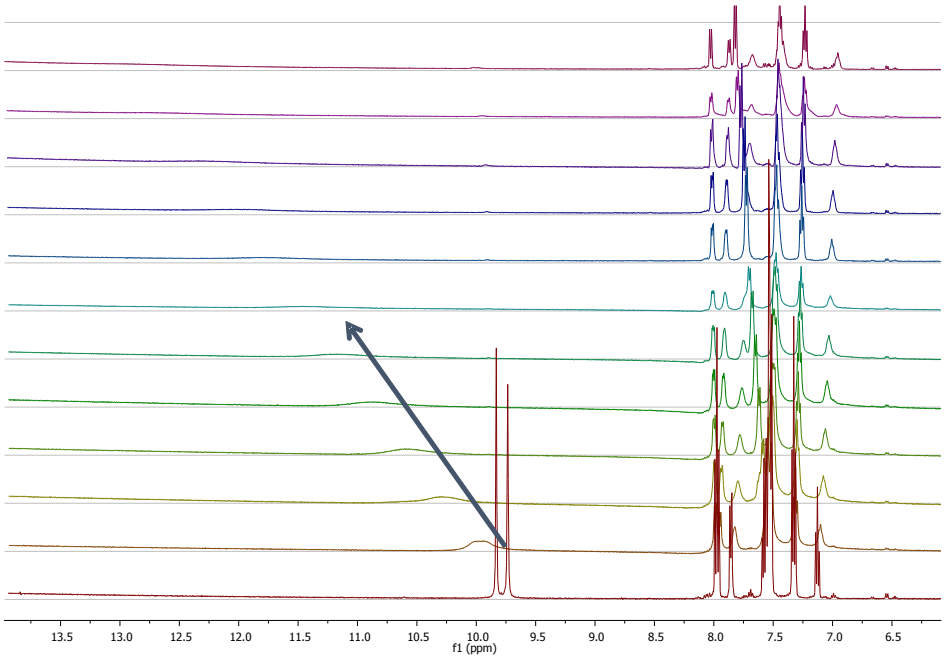
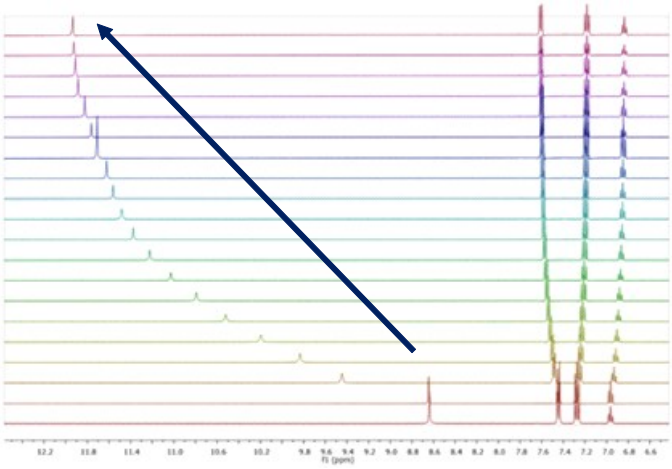


Figure S4 Stack plot of the titrations of **L5** (0.005M) with TBAAcO (0.075M) (in DMSO-d_6.

a)



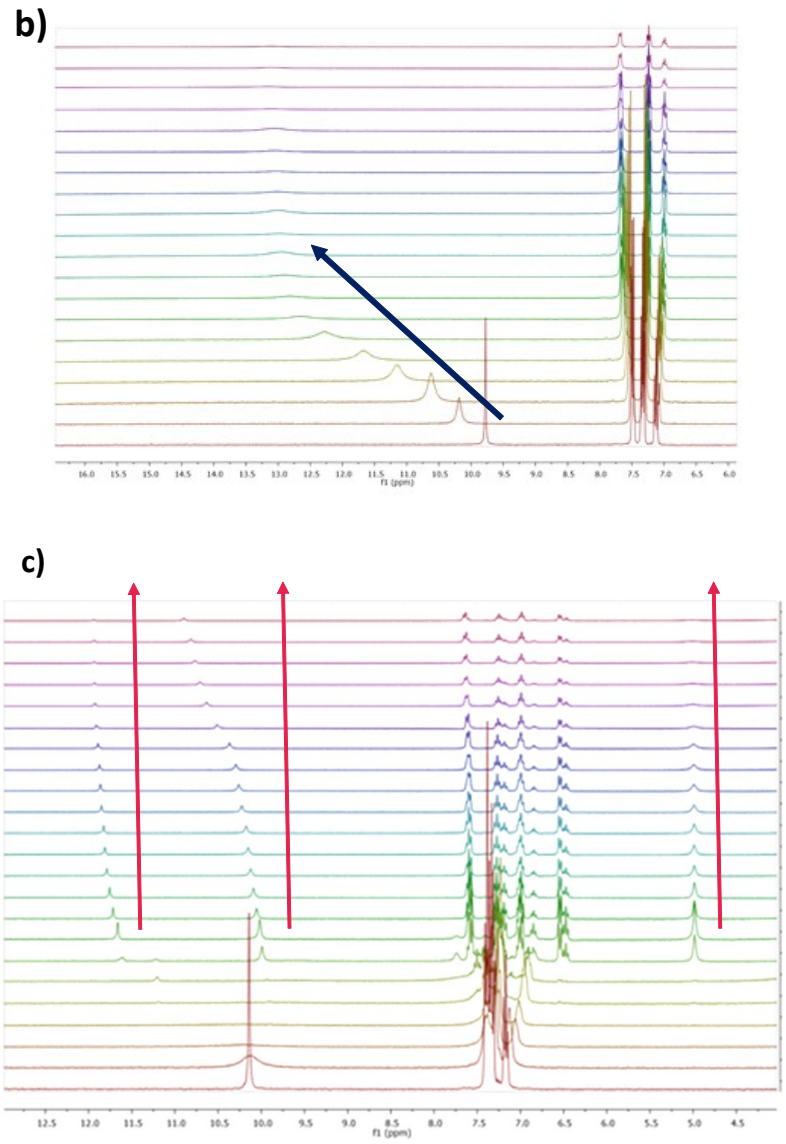
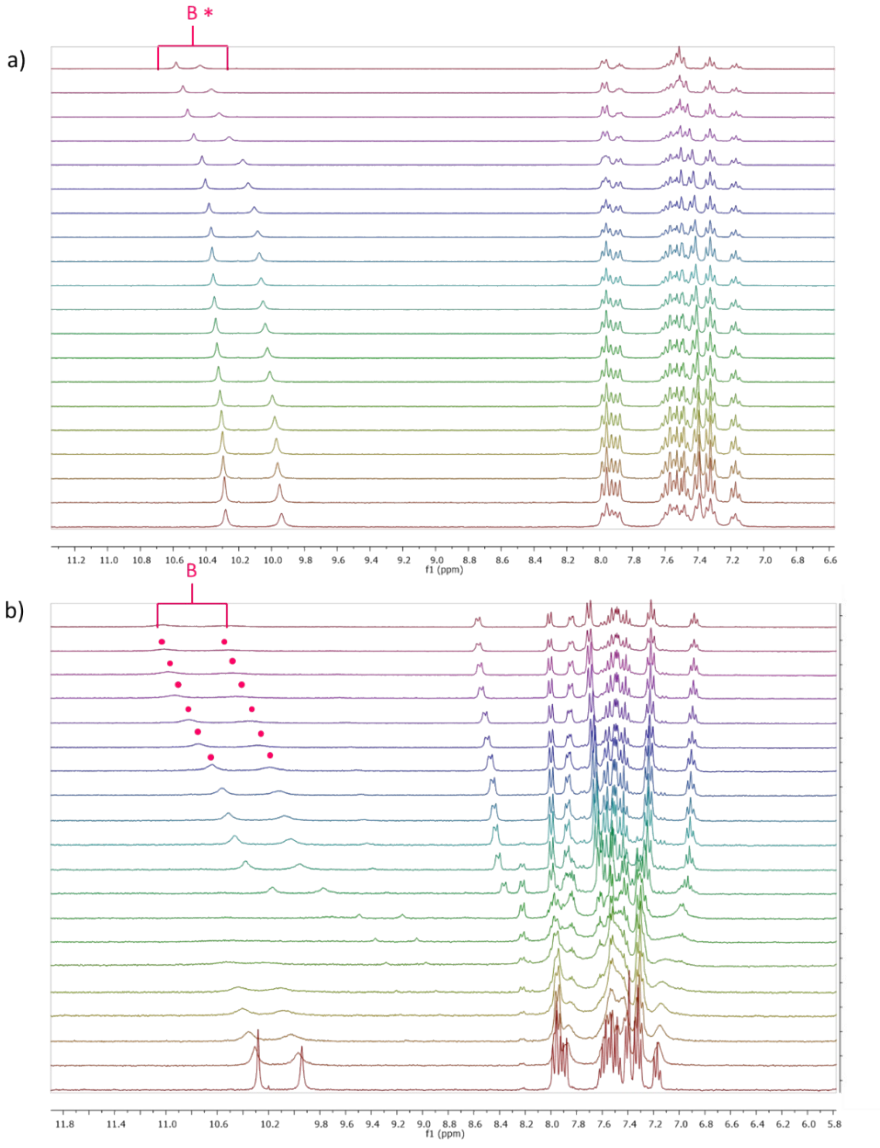


Figure S5 Stack plots of the titrations of **L4**, **L7**, and **L1** (0.005M) with TBAAcO (0.075M) (a, b and c for the titration of **L4**, **L7**, and **L1**, respectively) in DMSO-d_6.


a)
B *
11.2 11.0 10.8 10.6 10.4 10.2 10.0 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
f1 (ppm)
b)
B
11.8 11.4 11.0 10.6 10.2 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8
f1 (ppm)

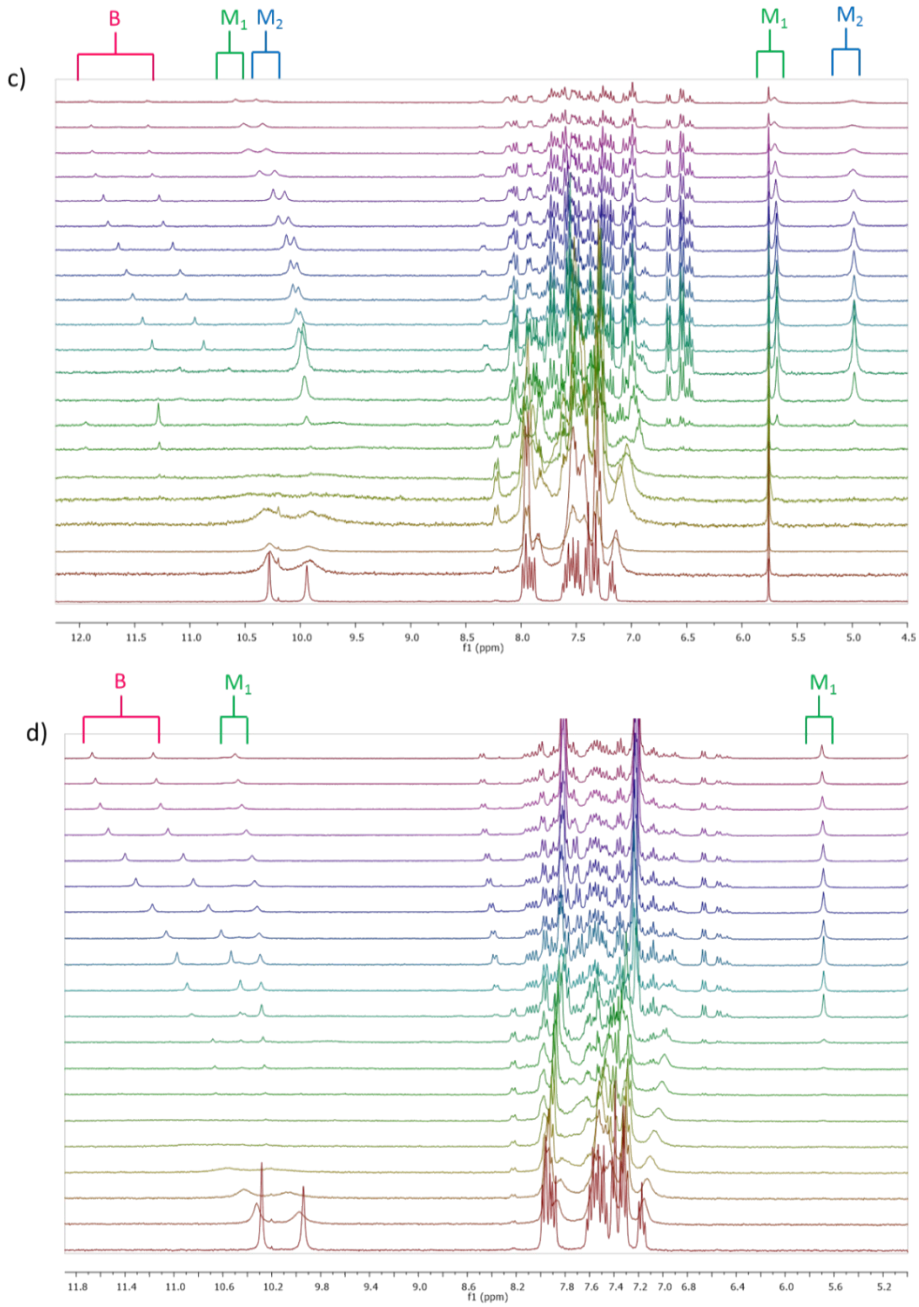


Figure S6 Titration in DMSO-d_6 of **L2** (0.005M) with Cl^-, $H_2PO_4^-$, AcO- and BzO^- (figure a, b, c and d respectively) as TBA salt (0.075M). The label B, M1 and M2 indicate the bi-coordinated adduct and the two mono-coordinated forms, respectively. *In Figure b the presence of poorly visible peaks is indicated by red dots.

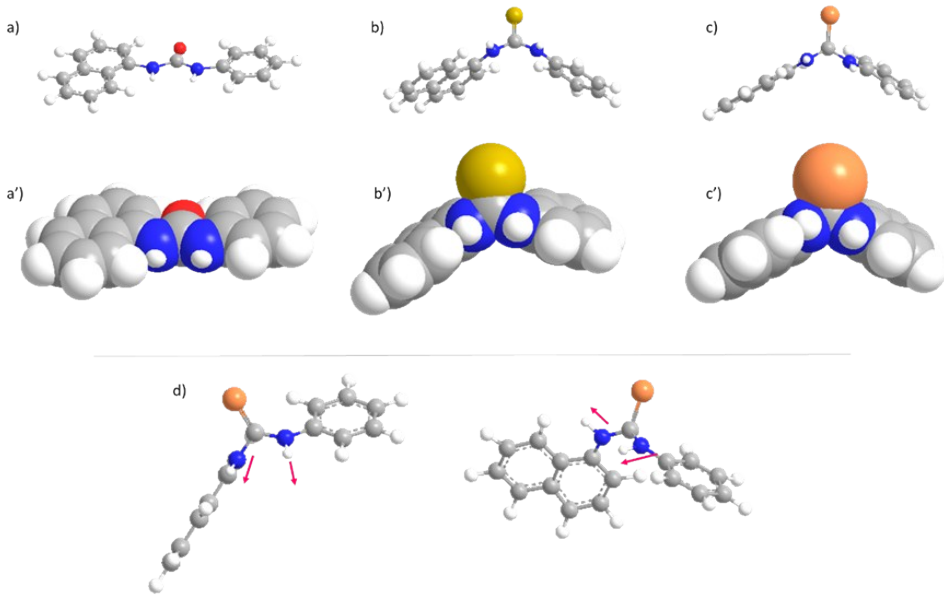
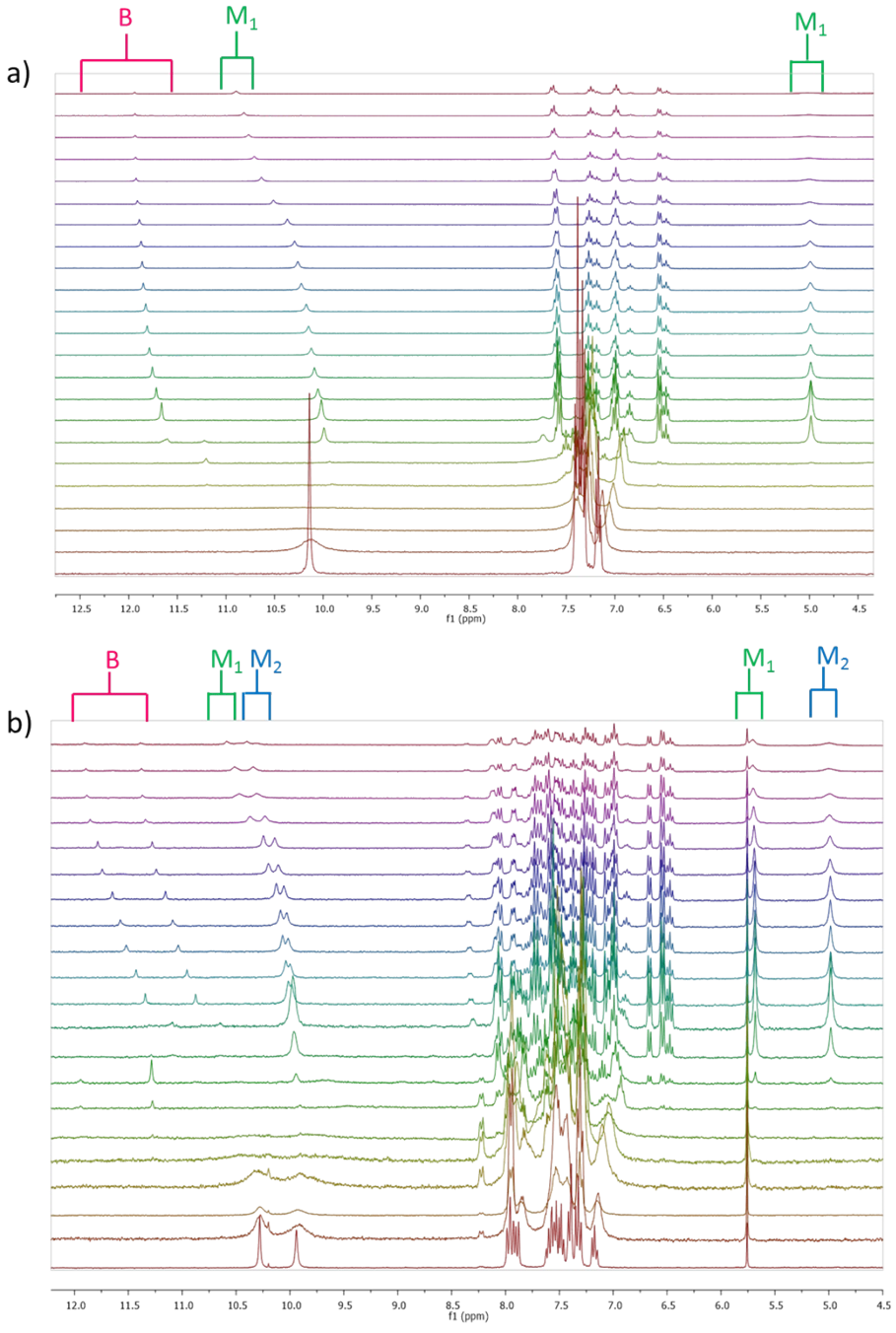


Figure S7 Balls and sticks and space fill representations of the 1-naphtyl-3phenyl urea (a and a'), thiourea (b and b') and selenourea (c and c') and NH hydrogen bonding directionality (d) in the case of 1-naphtyl-3phenyl selenourea obtained using ChemBio3D (12.0 Version) software.


a)
B
M1
M1
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5
f1 (ppm)
b)
B
M1
M2
M1
M2
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5
f1 (ppm)

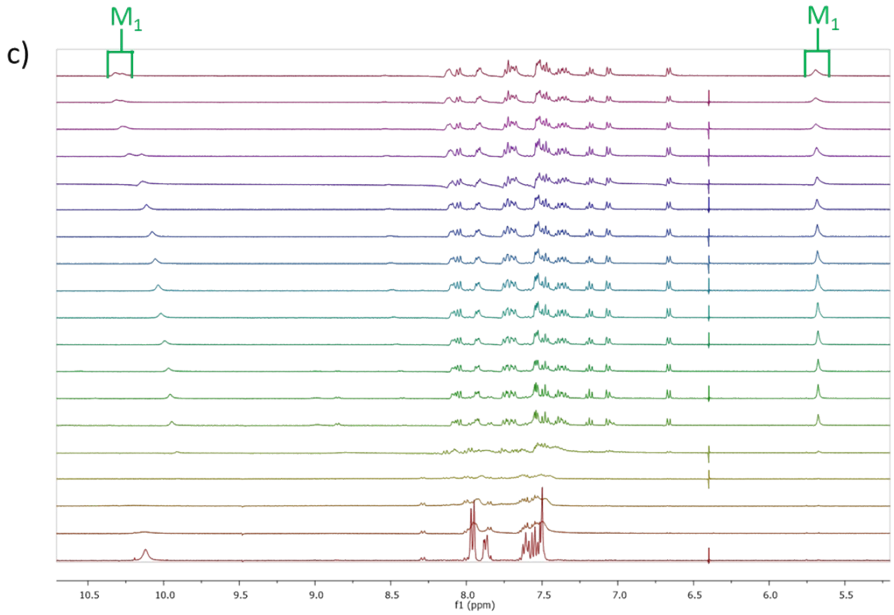
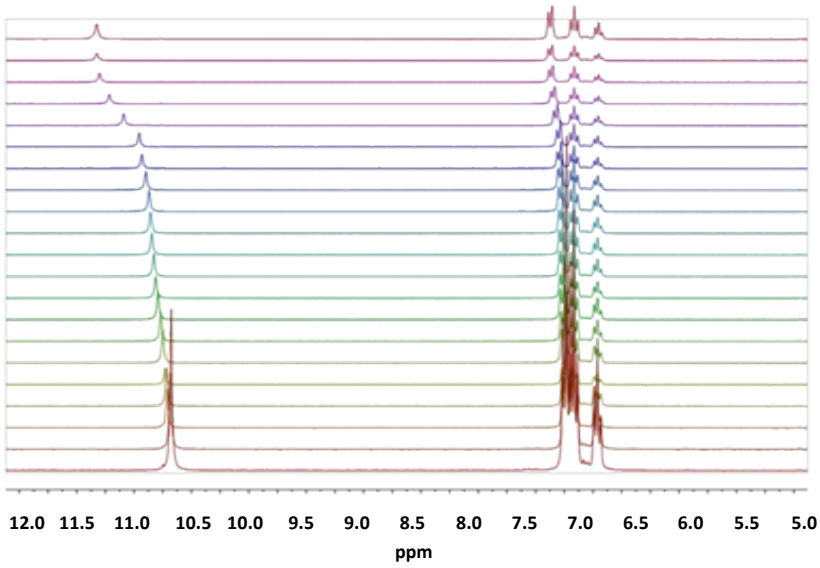
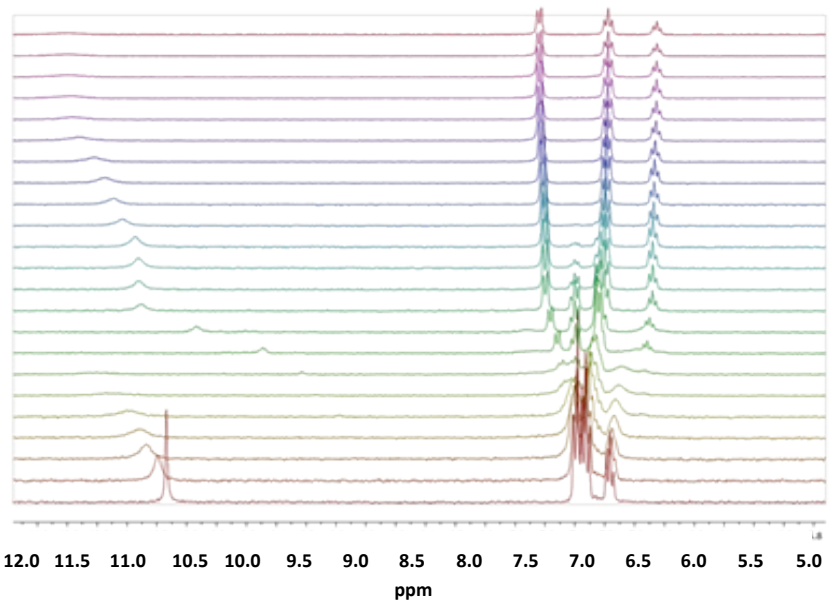


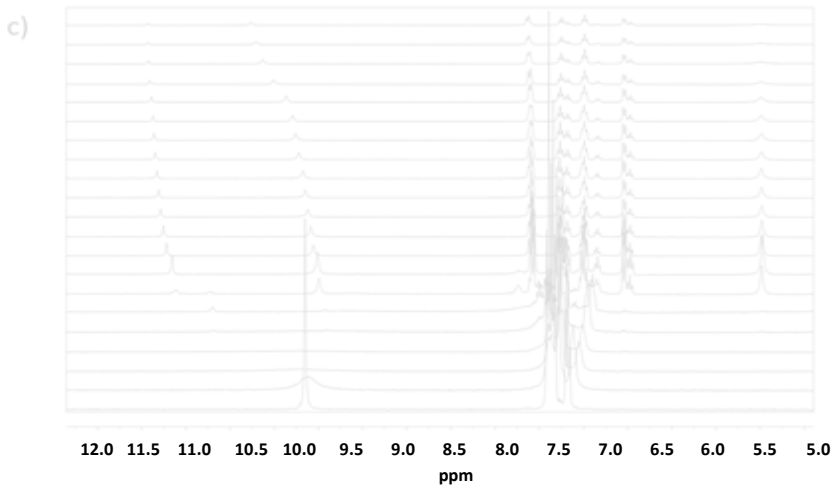
Figure S8 Stack plots of the Titrations of **L1**, **L2** and **L3** (0.005M) (figure a, b and c, respectively) with acetate as TBA salt (0.075M) in DMSO-d_6

a)


12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
ppm

b)


12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
ppm



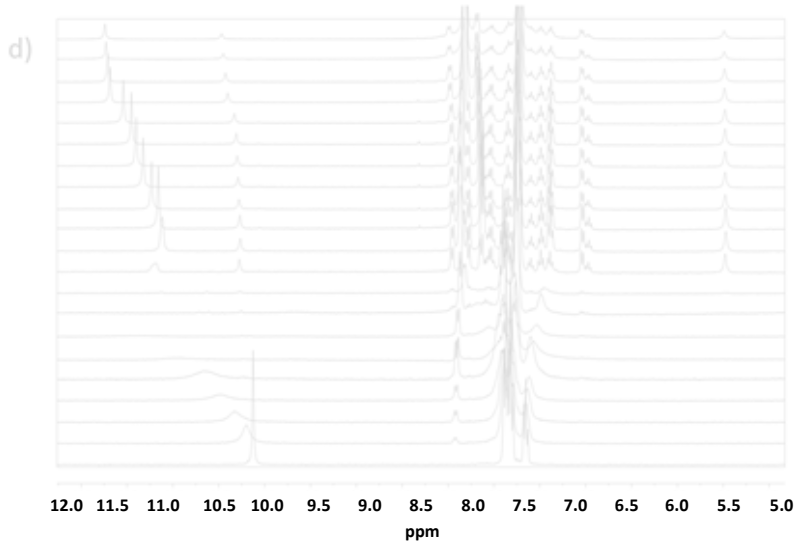
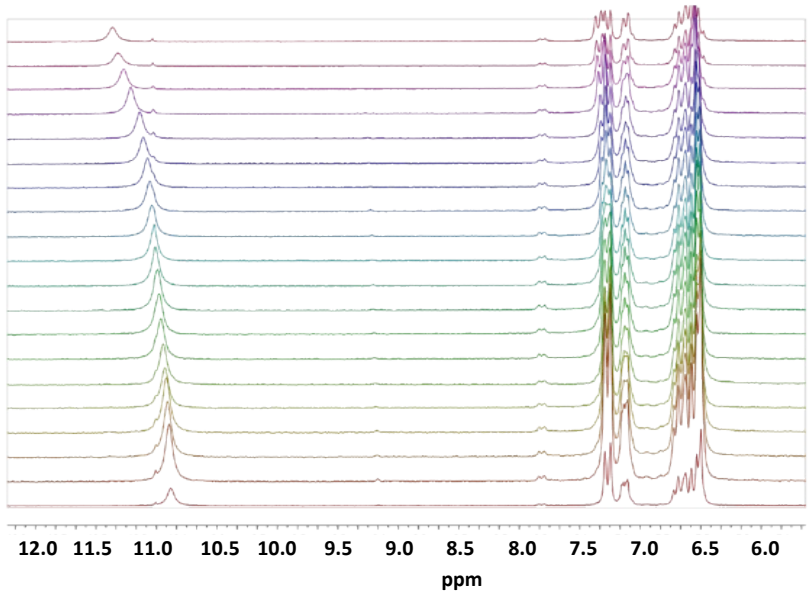
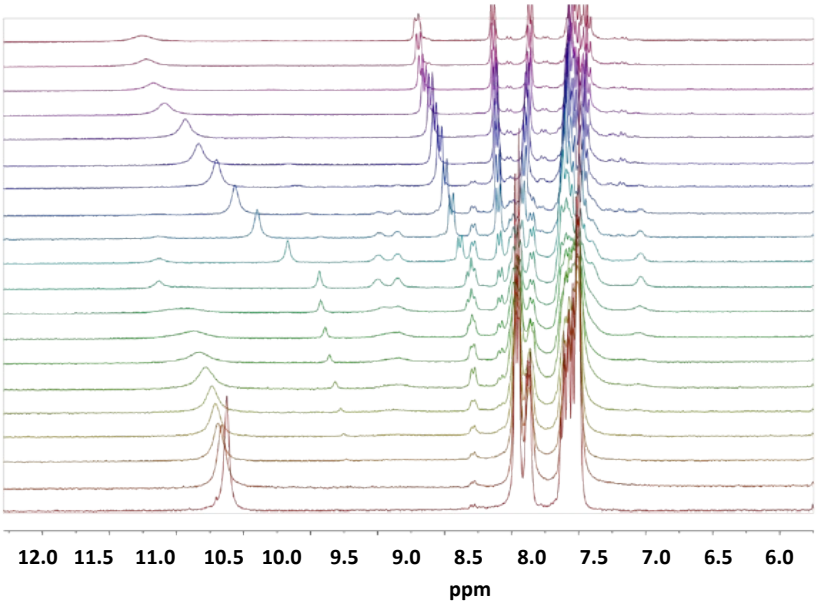


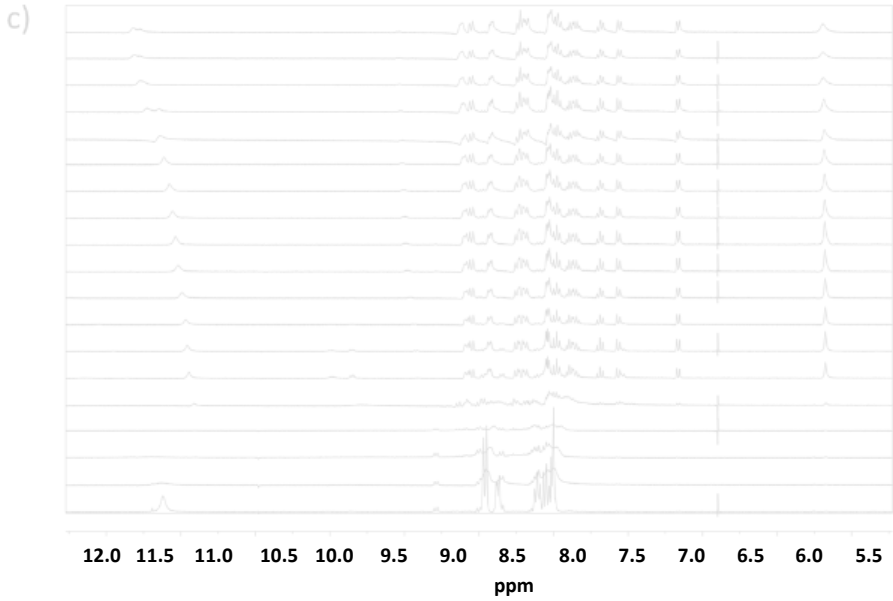
Figure S9. Changes in the ^{1}H-NMR spectra of **L1** (0.005M) upon addition of increasing amounts of Cl^- (a), $H_2PO_4^-$ (b), AcO^- (c) and BzO^- (d) (0.075M) in DMSO.

a)


12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0
ppm

b)


12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0
ppm



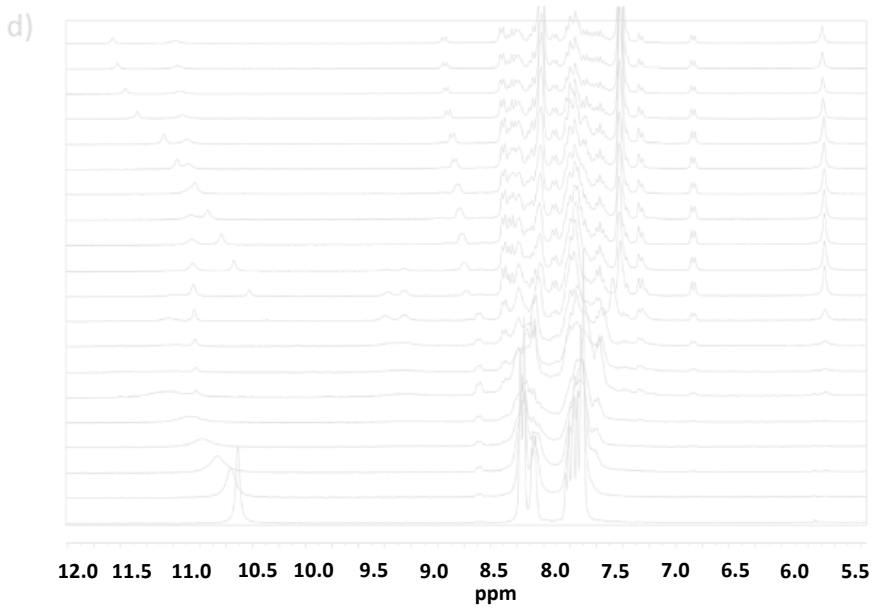


Figure S10. Changes in the ^{1}H-NMR spectra of **L3** (0.005M) upon addition of increasing amounts of Cl^- (a), $H_2PO_4^-$ (b), AcO^- (c) and BzO^- (d) (0.075M) in DMSO. In the case of

BzO-, we observed an exception: the high frequency NHs resonances due to the bi- and mono- coordinated adducts inverted along the titration.