Supporting Information

Halogen Bonding Assisted Selective Removal of Bromide

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Table of Contents

❖ Synthesis of 1-ethyl 2-iodo imidazole

1-ethyl imidazole (384 mg, 4mmol, 1 equivalent) was dissolved in 20 ml of dry tetrahydrofuran (THF) in a two neck 100 ml RB equipped with septum under argon (Ar) atmosphere and kept for stirring. The RB was kept in a low temperature bath to attain -78°C. 1.6M n-BuLi in hexane (3 ml, 5 mmol, 1.25 equv) was added with a syringe in drop by drop fashion to the solution at -78°C and kept for stirring till 1.5 hours. The solution turned colorless to dark yellow after complete addition of n-BuLi. Iodine (1.28g, 1.25 equiv.) was dissolved in 10 ml of dry THF and was added to the solution in drop by drop fashion over a time interval of 30 minutes. The resulting mixture was stirred form -78°C to room temperature over a time interval of 6 hours. After that solution was evaporated to dryness and the dried mass was thoroughly washed with sodium thiosulfate and extracted in DCM. Flash column (100 – 200 mesh) chromatography was performed in 0.25% methanol- DCM mixture to obtain pale yellow liquid as product.

Characterization data:

^{1}H NMR, 300 MHz ($CDCl_3$) δ ppm: 1.32-1.37 (t, 3H, -CH2CH3), 3.86-3.93 (m, 2H, -CH2CH3), 7.00-7.03 (d, 2H, -CH);

^{13}C NMR, 75 MHz ($CDCl_3$) δ ppm: 16.39, 45.08, 89.91, 122.61, 133.02.

Yield: 40%.

❖ General synthetic procedure of 1a, 1b & 1c

1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (1 equivalent) was dissolved in 50 ml acetonitrile (ACN) at 80°C under argon atmosphere. Then 1-ethyl-2-iodo imidazole or 1-ethyl imidazole (3.2 equivalents) was added in drop by drop fashion to the refluxing solution. After the addition was completed, thick white precipitate started coming (in cases of **1a** & **1b**) and then the reaction was continued till 24 hours. After completion, the solvent was evaporated to dryness under vacuum and the dried mass was dissolved in water. This bromide salt of ligand was then added in drop wise fashion to a saturated solution of KPF_6 and the corresponding PF_6 salt precipitated out immediately.

In case of **1c**, the precipitation of the salt was not observed. Hence after 24 hours reflux the reaction mixture was evaporated to dryness and the dry mass was dissolve in water. Then this bromide salt of ligand was then added in drop wise fashion to a saturated solution of KPF_6 and the corresponding PF_6 salt precipitated out immediately. **The precipitated compound was then dried in oven (at 60°C) for 72 hrs and then dried under vacuum to remove little trace of water.** In this way we prepared analytical pure and dry ligands **1a**, **1b** & **1c** whose characterization data are listed below.

❖ Characterization data of 1a:

Reagents: 1-ethyl-2-iodo imidazole (330mg, 1.5mM), 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (160mg, 0.4mM).

^{1}H NMR, 300 MHz (DMSO-d_6) δ ppm: 1.38-1.43 (t, 9H, -CH2CH3), 2.17-2.19 (s, 9H, -CH3), 4.19-4.26 (q, 6H, -CH2), 5.36 (s, 6H, -CH2), 7.28-7.29 (d, 3H, -CH), 8.00-8.04 (d, 3H, -CH).

^{13}C NMR, 75 MHz (DMSO-d_6) δ ppm: 15.71, 17.39, 48.13, 51.92, 102.63, 124.48, 125.63, 129.88, 142.41.

ESI-MS: 1115.16 (M^+).

Elemental (CHN) analysis: Calculated: C; 27.73, H; 3.40, N; 6.56, Found: C; 27.77, H; 3.38, N; 6.64.

Yield: 72%.

❖ Characterization data of 1b:

Reagents: 1-ethyl imidazole (192mg, 2mM), 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (228mg, 0.57mM).

^{1}H NMR, 300 MHz (DMSO-d_6) δ ppm: 1.38-1.42 (t, 9H, -CH2CH3), 2.30 (s, 9H, -CH3), 4.12-4.20 (q, 6H, -CH2), 5.53 (s, 6H, -CH2), 7.56-7.57 (d, 3H, -CH), 7.83-7.84 (d, 3H, -CH), 8.89 (s, 3H, -CH).

^{13}C NMR, 75 MHz (DMSO-d_6) δ ppm: 15.15, 16.23, 44.49, 47.64, 122.21, 129.39, 135.42, 141.05.

ESI-MS: 737.46 (M^+).

Elemental (CHN) analysis: Calculated: C; 38.21, H; 4.87, N; 9.22, Found: C; 38.16, H; 4.86, N; 9.30.

Yield: 90%.

❖ Characterization data of 1c:

Reagents: 1-ethyl-2-iodo imidazole (330mg, 1.5mM), 2-bromomethyl-1,3,5-trimethylbenzene (320mg, 1.5mM).

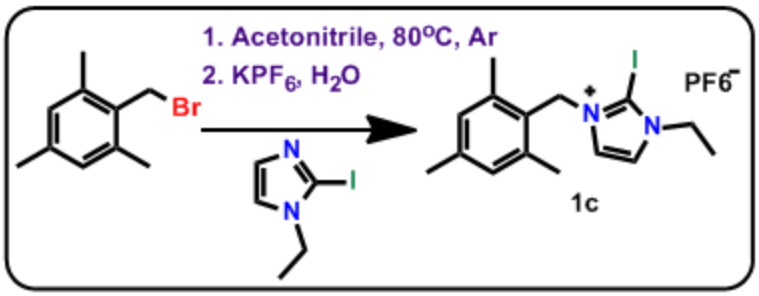
^{1}H NMR, 300 MHz (DMSO-d_6) δ ppm: 1.36-1.41 (t, 3H, -CH2CH3), 2.19 (s, 6H, -CH3), 2.26 (s, 3.17-4.24 (q, 2H, -CH2), 5.26 (s, 2H, -CH2), 6.99 (s, 2H, -CH), 7.14 (d, 1H, -CH), 7.96 (s, 1H, -CH).

^{13}C NMR, 75 MHz (DMSO-d_6) δ ppm: 14.76, 19.38, 20.60, 47.15, 50.20, 100.77, 123.88, 124.98, 126.27, 129.41, 138.14, 138.72.

ESI-MS: 354.77 (M^+).

Elemental (CHN) analysis: Calculated: C; 36.02, H; 4.03, N; 5.60, Found: C; 36.38, H; 4.04, N; 5.71.

Yield: 48%.



Synthetic scheme of **1c**.

❖ Characterization data of complex 1:

^{1}H NMR, 300 MHz (DMSO-d_6) δ ppm: 1.38-1.43 (t, 9H, -CH2CH3), 2.18 (s, 9H, -CH3), 4.19-4.26 (q, 6H, -CH2), 5.38 (s, 6H, -CH2), 7.30-7.31 (d, 3H, -CH), 8.02-8.04 (d, 3H, -CH).

^{13}C NMR, 125 MHz (DMSO-d_6) δ ppm: 14.82, 16.47, 47.02, 50.79, 123.57, 124.56, 129.04, 141.30.

Elemental (CHN) analysis: Calculated: C; 29.70, H; 3.21, N; 7.44, Found: C; 29.66, H; 3.20, N; 7.50.

Yield: 75%.

❖ Characterization data of complex 2:

^{1}H NMR, 300 MHz (DMSO-d_6) δ ppm: 1.37-1.42 (t, 9H, -CH2CH3), 2.18 (s, 9H, -CH3), 4.18-4.26 (q, 6H, -CH2), 5.38 (s, 6H, -CH2), 7.32 (d, 3H, -CH), 7.99 (d, 3H, -CH).

^{13}C NMR, 125 MHz (DMSO-d_6) δ ppm: 14.90, 16.50, 46.93, 50.73, 106.28, 123.50, 124.46, 129.19, 141.19.

Elemental (CHN) analysis: Calculated: C; 31.15, H; 3.49, N; 8.07, Found: C; 31.12, H; 3.47, N; 8.05.

Yield: 55%.

❖ Characterization data of complex 3:

^{1}H NMR, 300 MHz (DMSO-d_6) δ ppm: 1.35-1.40 (t, 9H, -CH2CH3), 2.16 (s, 9H, -CH3), 4.17-4.24 (q, 6H, -CH2), 5.37 (s, 6H, -CH2), 7.30-7.31 (d, 3H, -CH), 7.93-7.94 (d, 3H, -CH).

^{13}C NMR, 125 MHz (DMSO-d_6) δ ppm: 15.65, 17.13, 47.39, 51.19, 110.76, 123.86, 124.77, 129.99, 141.62.

Yield: 35%.

Experimental section:

❖ ^{13}C NMR titration studies:

^{13}C-NMR titration studies have been carried out in order to find out proper fitting model for host: guest binding. During titration, we have prepared a solution of **1a** (27.90 mM) in DMSO-d_6 which is titrated with a solution of TBACl (399.5 mM) in DMSO-d_6. During titration 10 µl aliquot of guest (overall anion equivalent is 0.3) is added directly to the NMR tube containing **1a**. By this way, we have titrated till addition of 4.45 equivalents of guest. Initially, the ^{13}C peak for iodine attached carbon atom is found to be present at 101.32 ppm. Till the addition of 3.2 equivalents of guest, this particular peak is found to be shifted to 109.6 (8.28 ppm). Further addition of guest aliquot till 4.45 equivalents leads to shift the peak to 110.15 ppm. Hence, the maximum peak shift occurs until addition of around 3 equivalents of guest. The anion equivalent plot of ^{13}C titration shows saturation around 3 equivalents of guest. Thus it is proved that the proper binding model (stoichiometry) for host: guest is 1:3. Initially, we have tried this experiment in ACN-d_3 solvent, but the host: guest adduct is found to be precipitated out of the solution after addition of 1 equivalents of guest. This is due to the large concentration factor. Hence the ^{13}C-titration study is performed in DMSO-d_6.

❖ Isothermal Titration Calorimetric studies:

The solution-state binding affinity of the receptors (**1a** & **1b**) with Cl^-, Br^- and I^- are performed by ITC experiments. In a typical ITC experiment, a solution of the anion as its tetrabutyl ammonium salt in dry acetonitrile is titrated into a solution of receptor at 298 K. Exothermic titration profiles are obtained for **1a** upon titration with guests and subsequent fitting to a 1:3 binding profile provide access to the stability constants (K1, K2, K3), enthalpy change (ΔH1, ΔH2, ΔH3), entropy change (TΔS1, TΔS2, TΔS3), and free energy change (ΔG1, ΔG2, ΔG3) of the binding processes. The titration data are fitted in a sequential site model (ligand in cell) with number of binding sites three. The titration data of **1b** exhibited good fitting in one set of site model even the stoichiometry matches with that of NMR titration. **We have tried to fit the data of 1a with other fitting models like, one set of site, two set of sites; but it did not fit properly. ^{13}C-NMR titration studies have shown host: guest binding model 1:3 which is detailed in the previous section. Again, shift in ^{1}H-NMR titration of 1a with gradual addition of TBACl was insignificant (-0.136 ppm) but it saturated after addition of 3 equivalents of guest. Hence, it satisfies the choice of fitting model also**. Dry ACN is used as a solvent during ITC titration studies. As the concentration of **1a** in ITC, is **100 folds** lower than that of the concentration maintained in ^{13}C-NMR titrations, hence we have not observed any precipitation of the host: guest adduct. Blank titration data is subtracted from the titration data in order to obtain accurate

thermodynamic parameters of binding. Origin 7.0 is used as software for analysis. The upper panel of the VP-ITC output figure shows the heat pulses which are observed experimentally in each titration step with respect to time. The lower panel reports the respective time integrals translating as the heat absorbed or evolved for each aliquot and its coherence to a 1:3, sequential binding model. During each titration, a solution of ligand ~ 0.2 mM is placed in the cell at 298 K temperature. This solution is then titrated with 28 injections of 10 μL each of a ~ 6 mM guest solution prepared dry acetonitrile. An initial delay of 240s is allowed before each titration. Interval of 220s is allowed between each injection and the stirring speed is set at 329 rpm.

❖ Single crystal X-ray crystallographic details.

The crystallographic details of complexes **1**-**3** are given in Table 1S & 2S. In each case, a crystal of suitable size is dipped in paratone oil after collecting from mother liquor. Then it is mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for all crystals are collected using MoKα (λ = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer equipped with a CCD area detector at 120 K. The data integration and reduction are processed with SAINT[1a] software. An empirical absorption correction is applied to the collected reflections with SADABS.[1b] The structures are solved by direct methods using SHELXTL[2] and are refined on F2 by the full-matrix least-squares technique using the SHELXL-97[3] program package. Graphics are generated using PLATON-97[4]and MERCURY 3.1.[5]

❖ ^{1}H-NMR titration studies.

^{1}H NMR titrations with **1a** with tetrabutyl ammonium salts of guest anions are carried out in a 300 MHz NMR instrument. The receptors are soluble in 0.45 ml of ACN-d_3 at 298K. The guest anion concentration is maintained almost 8 times more concentrated with respect to receptor concentration. 10 μL aliquot of anion prepared in ACN-d_3 is added and shaken well before recording the NMR data during titration. Imidazole C-H proton is monitored in all the cases to calculate stability constant values from WINEQNMR2 software.[6] The anion equivalent plot shows saturation beyond 1 equivalent of guest which justifies the 1:1 fitting model to calculate the stability constants (K) value. In case of **1a**, protons have not shifted with gradual addition of TBABr and TBAI. Even the shift of these protons with gradual addition of TBACl is insignificant (-0.136 ppm, after addition of 3.5 equivalents of guest).

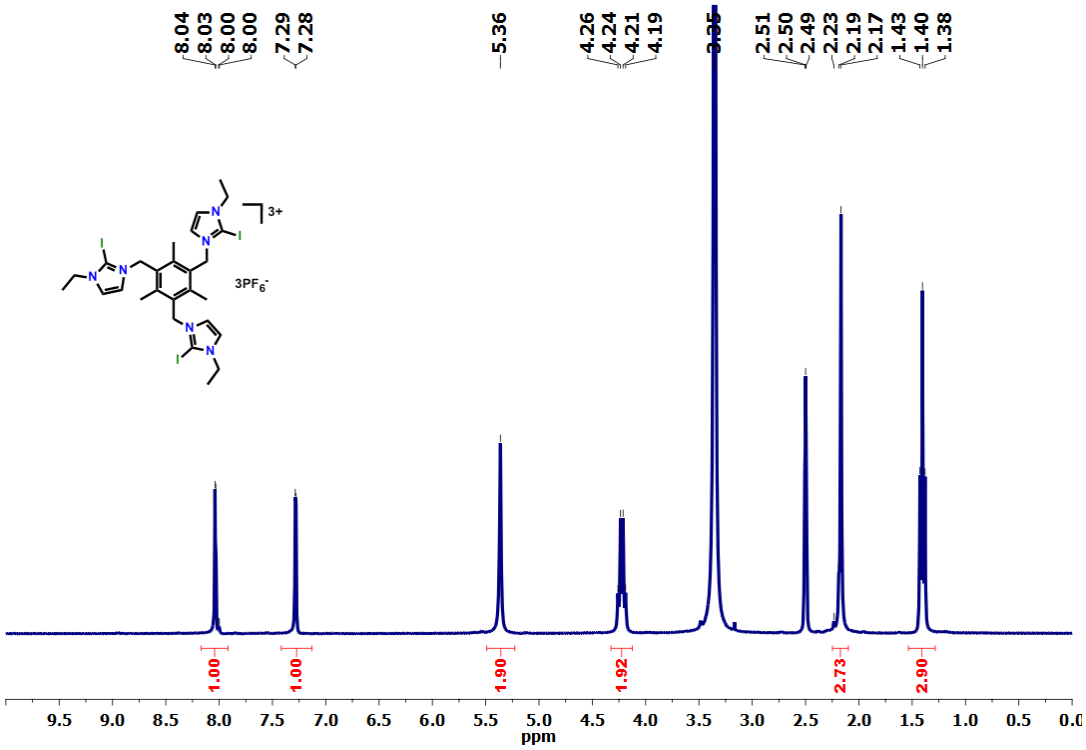


Fig. 1S: ^{1}H-NMR spectrum of **1a** in DMSO-d_6 at 298K.

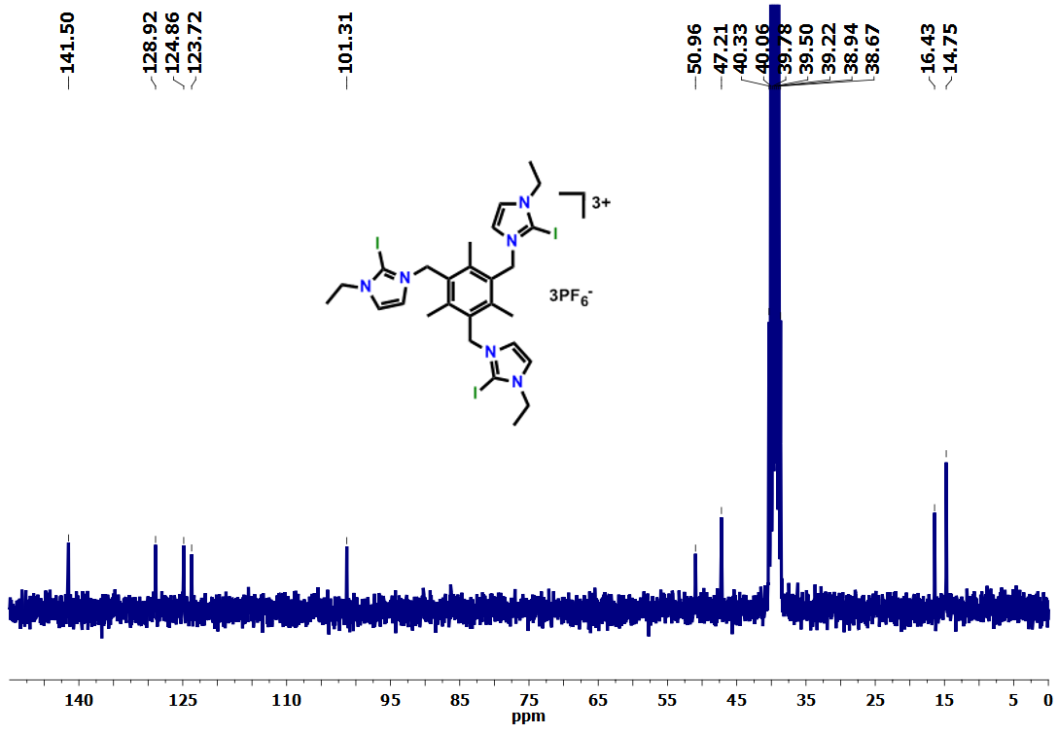


Fig. 2S: ^{13}C-NMR spectrum of **1a** in DMSO-d_6 at 298K.

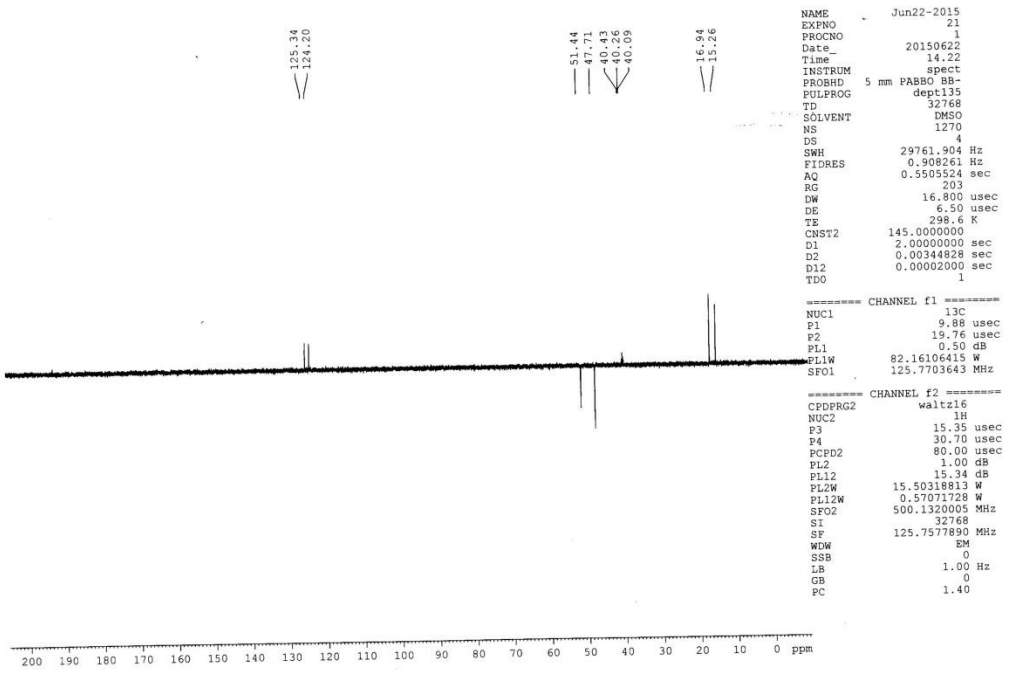


Fig. 3S: ^{13}C-DEPT spectrum of **1a** in DMSO-d_6 at 298K.

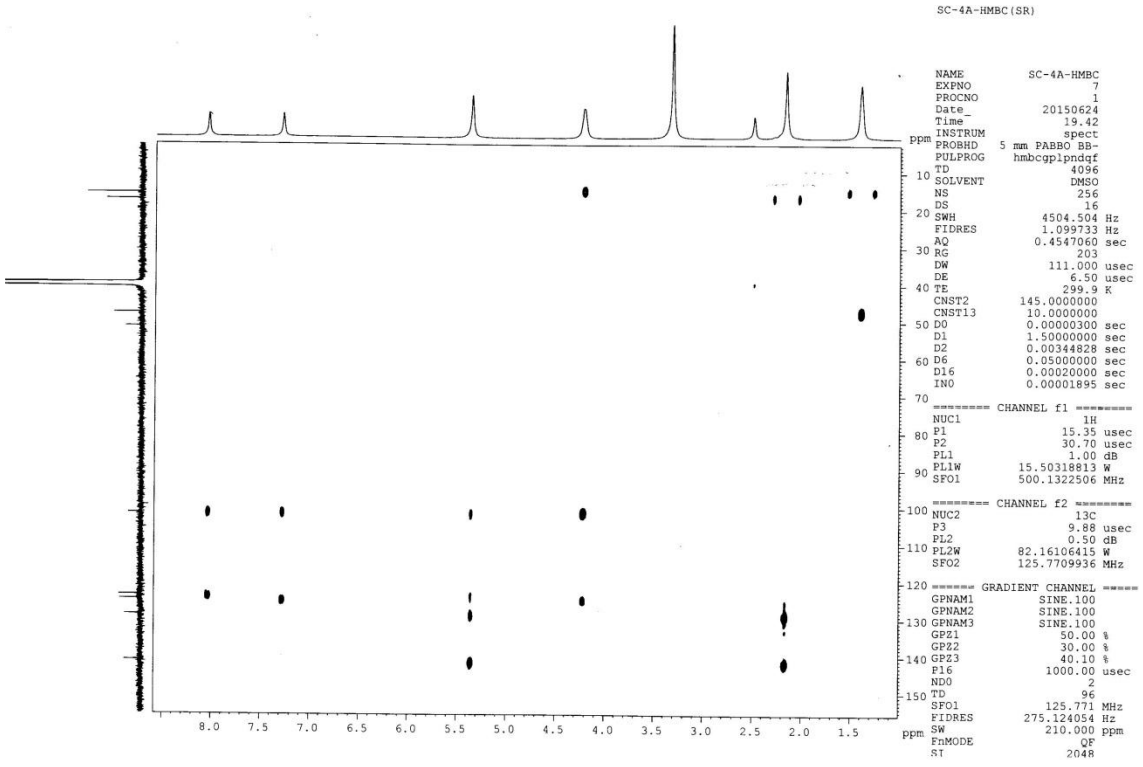


Fig. 4S: ^{13}C-^{1}H HMBC spectrum of **1a** in DMSO-d_6 at 298K.

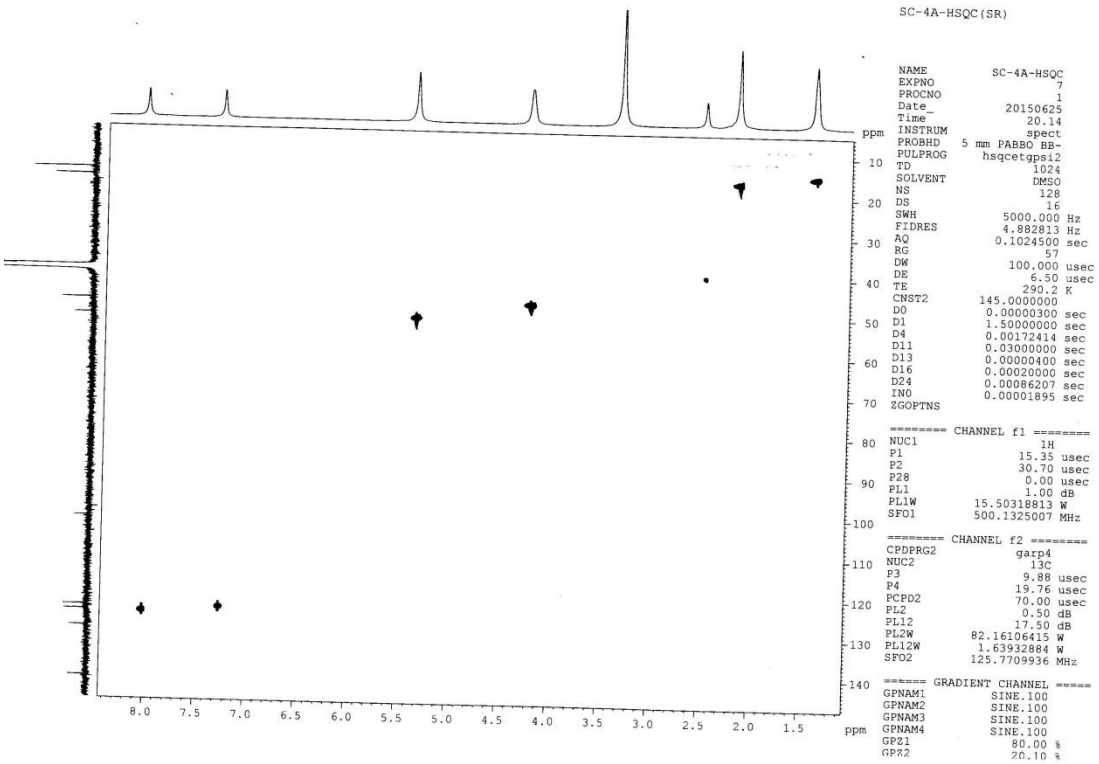


Fig. 5S: ^{13}C-^{1}H HSQC spectrum of **1a** in DMSO-d_6 at 298K.

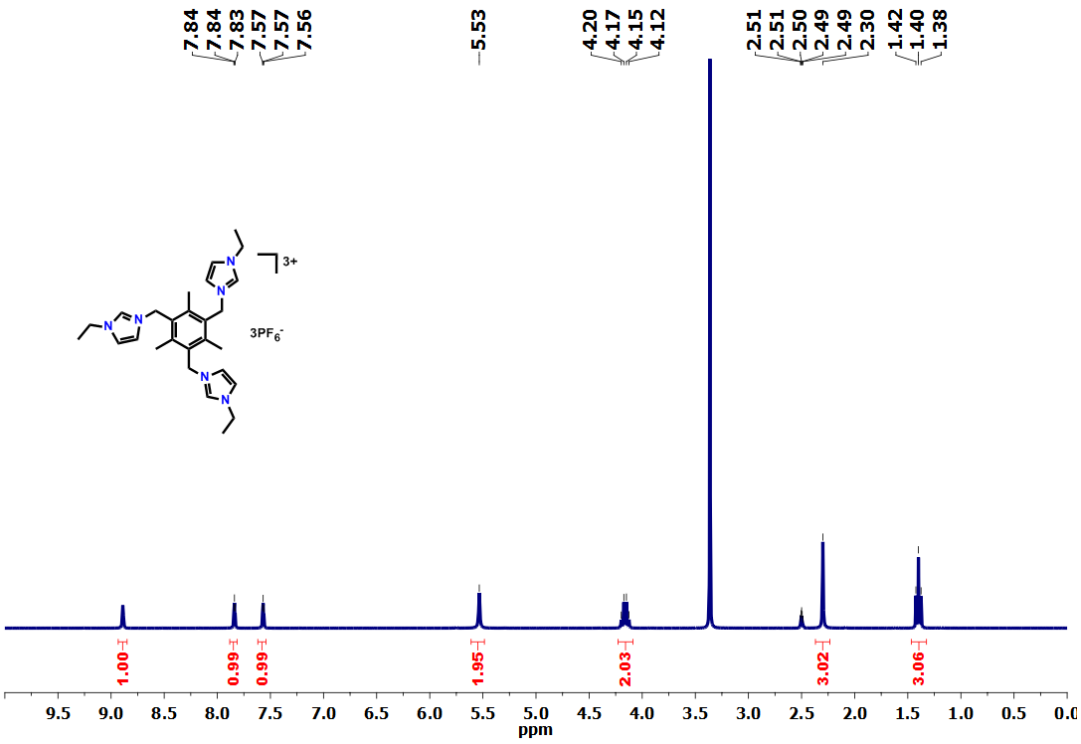


Fig. 6S: ^{1}H-NMR spectrum of **1b** in DMSO-d_6 at 298K.

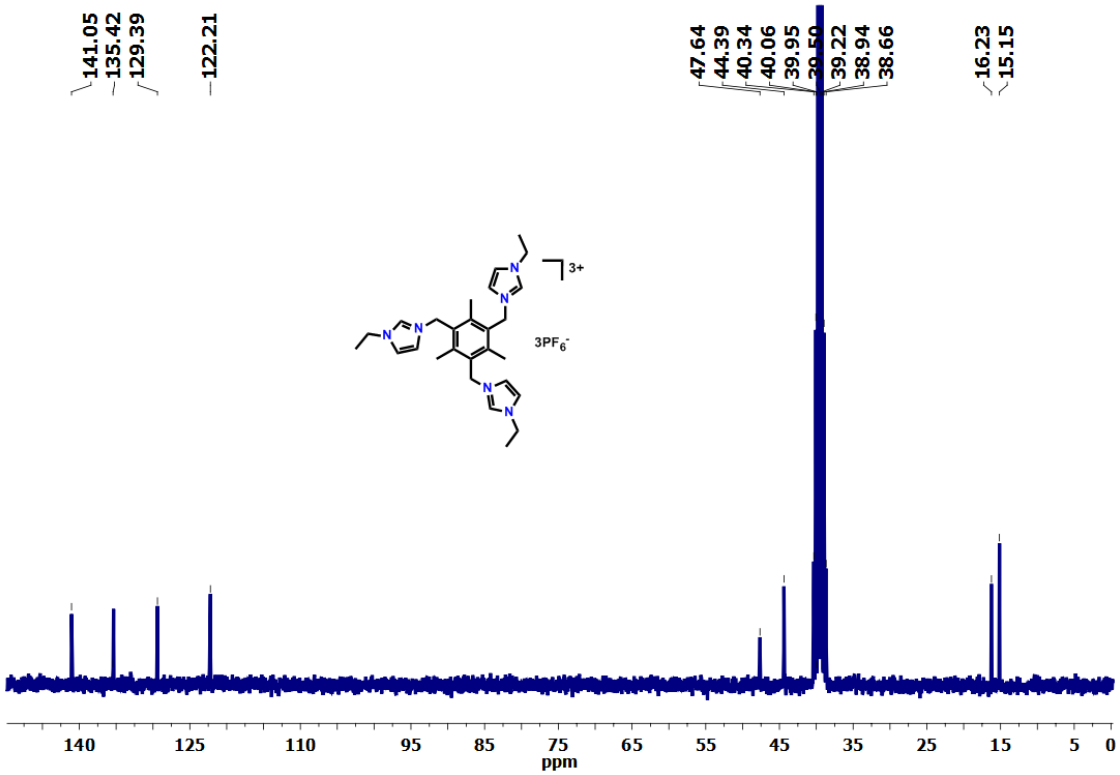


Fig. 7S: ^{13}C-NMR spectrum of **1b** in DMSO-d_6 at 298K.

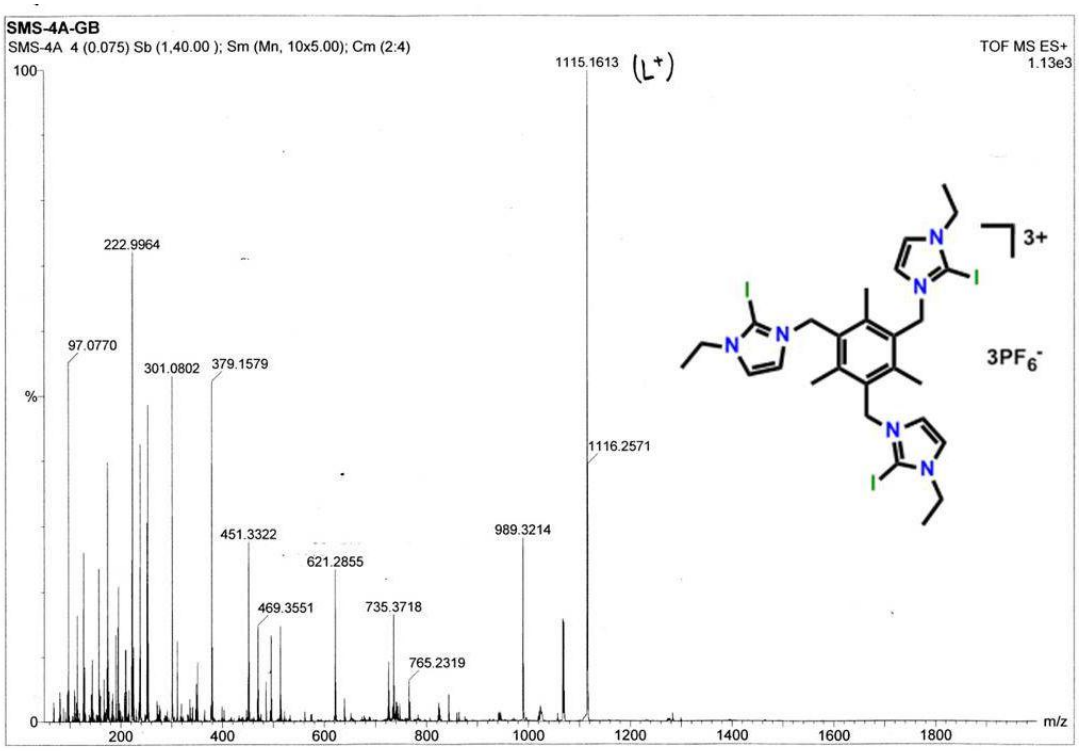


Fig. 8S: ESI-MS spectrum of **1a** in acetonitrile at 298K.

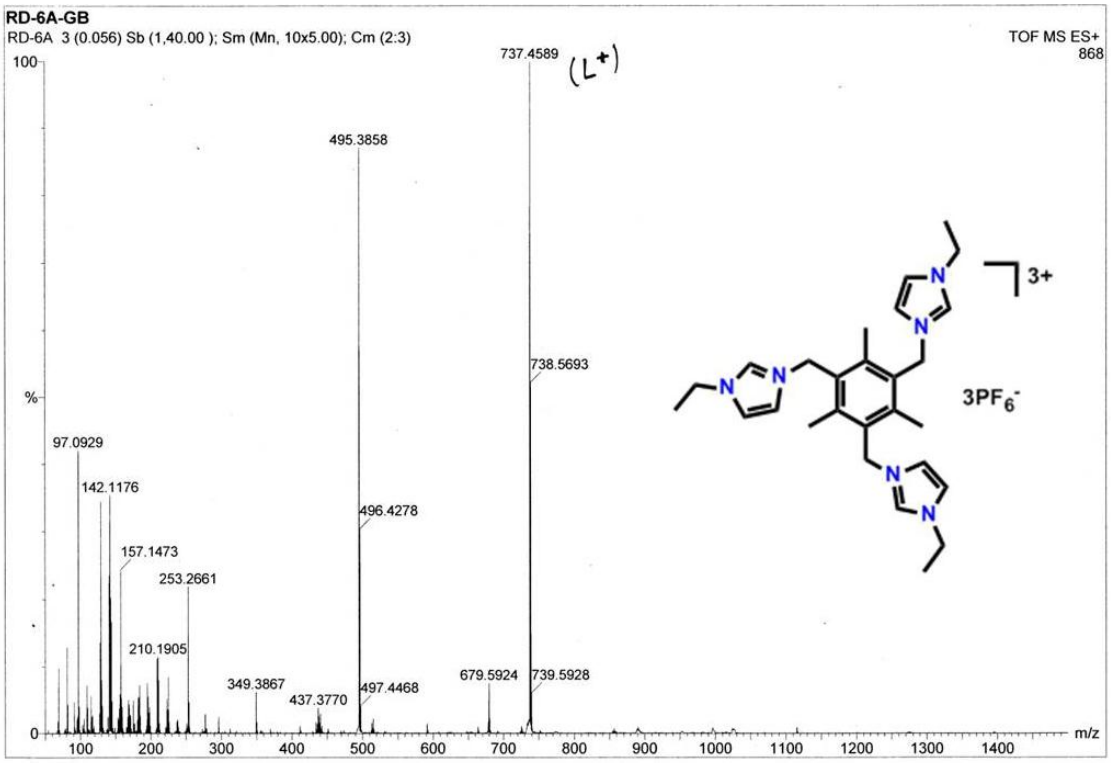


Fig. 9S: ESI-MS spectrum of **1b** in acetonitrile at 298K.

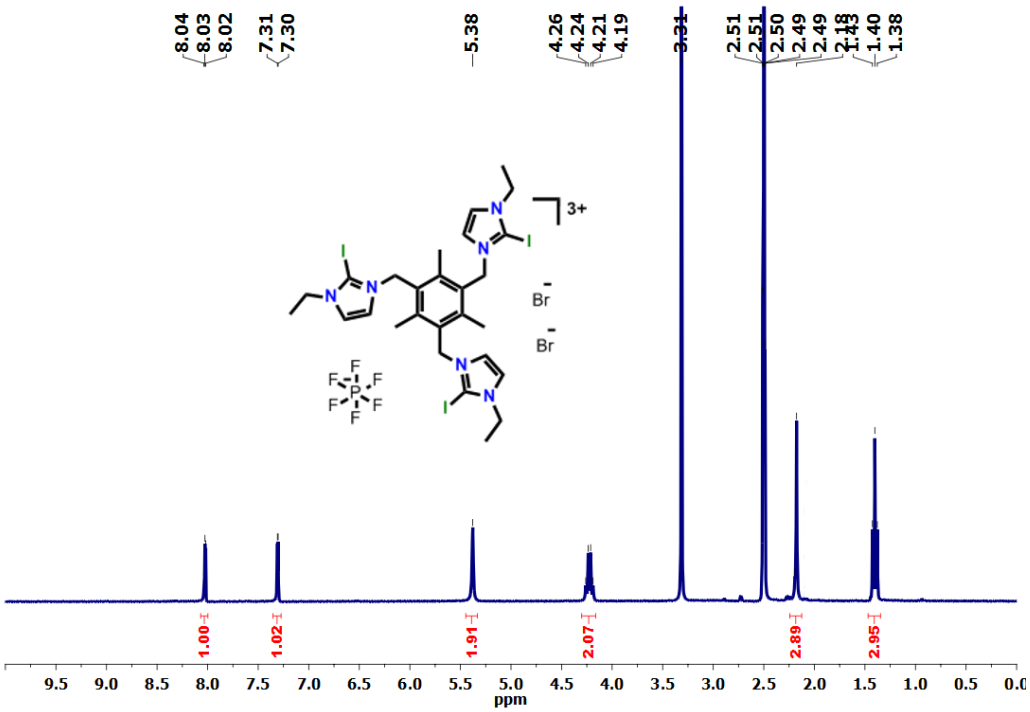


Fig. 10S: ^{1}H-NMR spectrum of **complex 1** in DMSO-d_6 at 298K.

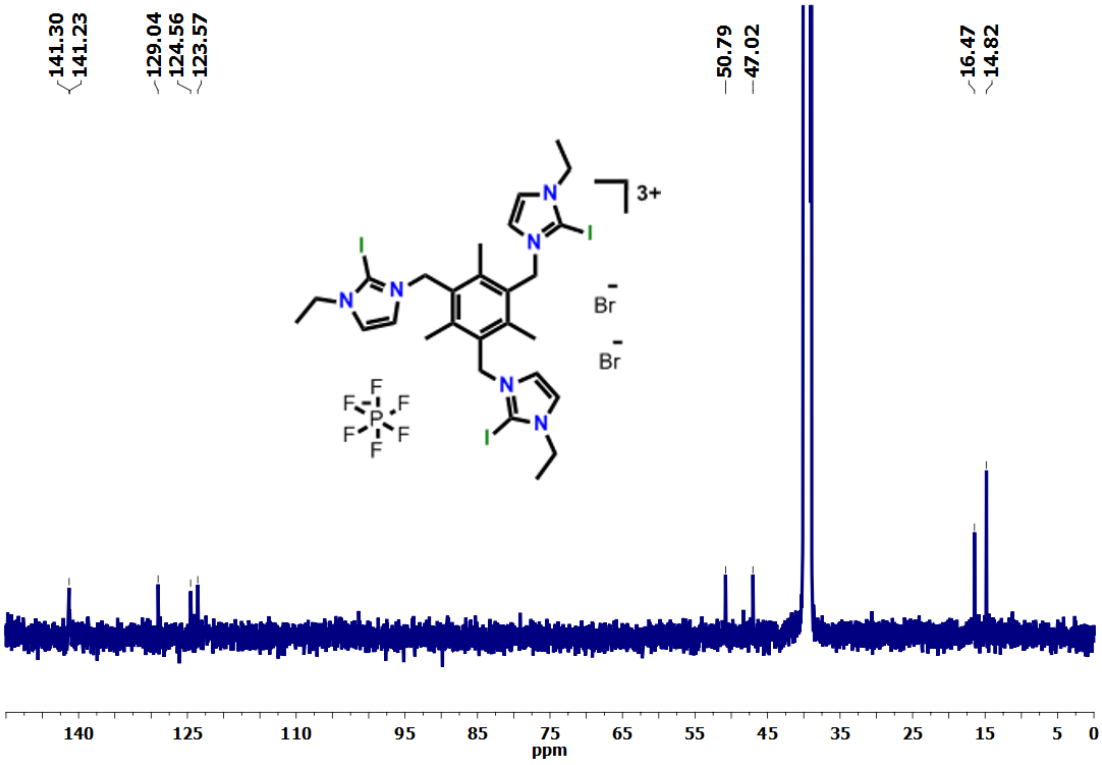


Fig. 11S: ^{13}C-NMR spectrum of complex **1** in DMSO-d_6 at 298K.

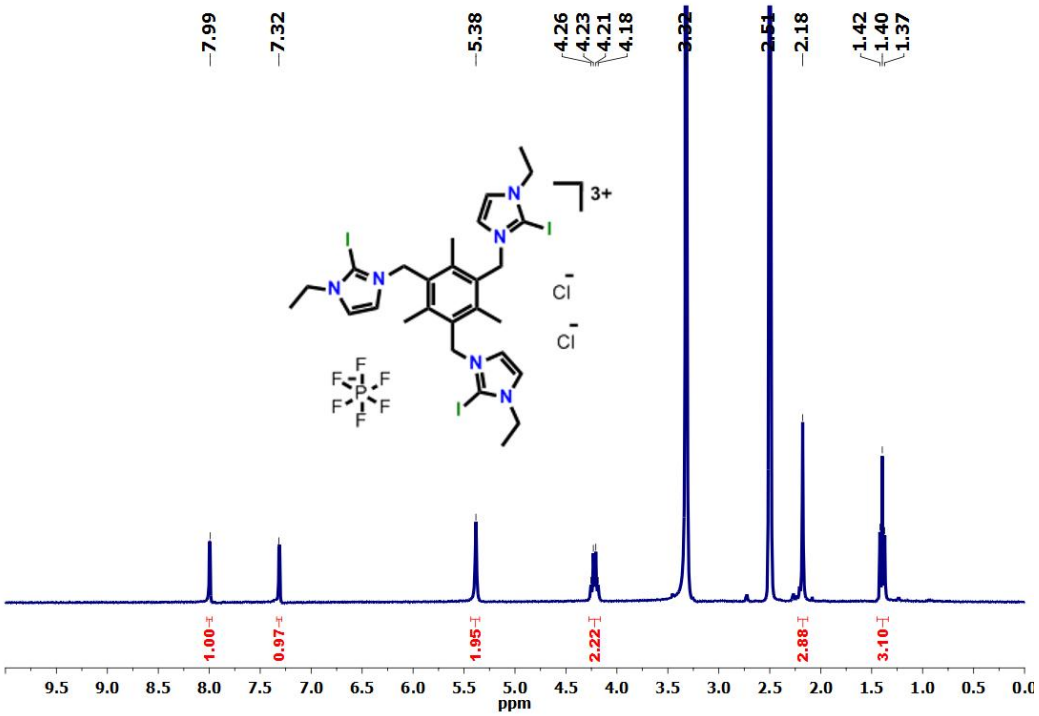


Fig. 12S: ^{1}H-NMR spectrum of **complex 2** in DMSO-d_6 at 298K.

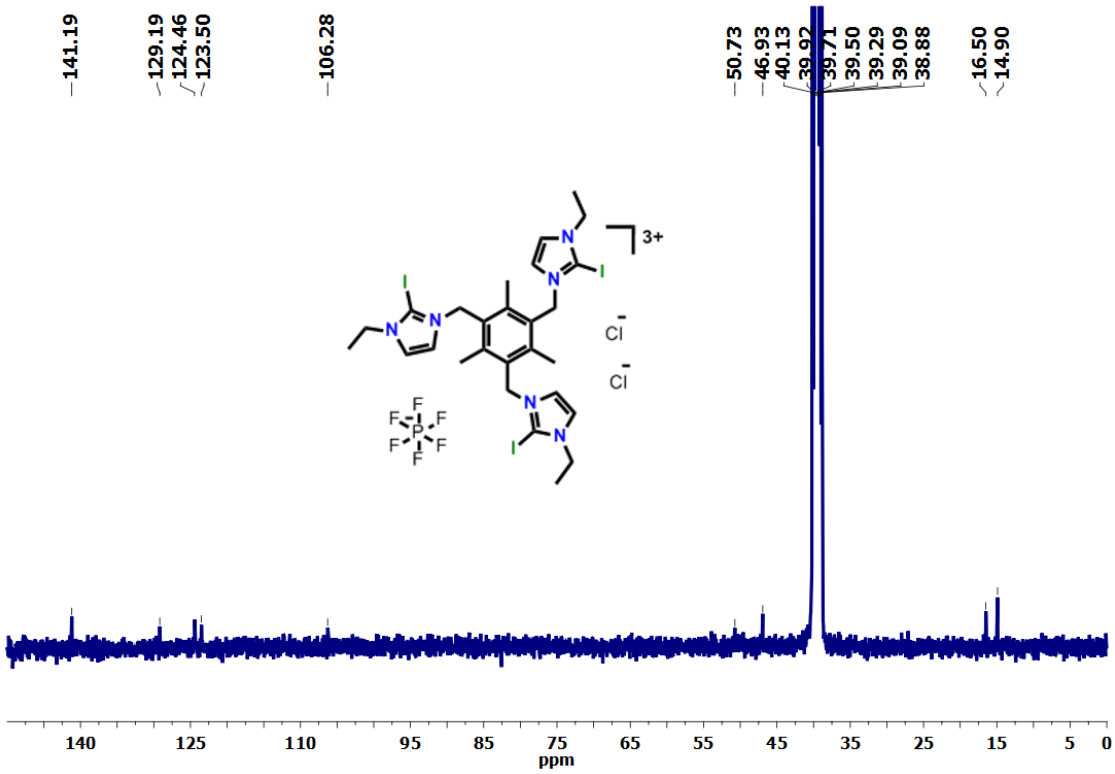


Fig. 13S: ^{13}C-NMR spectrum of **complex 2** in DMSO-d_6 at 298K.

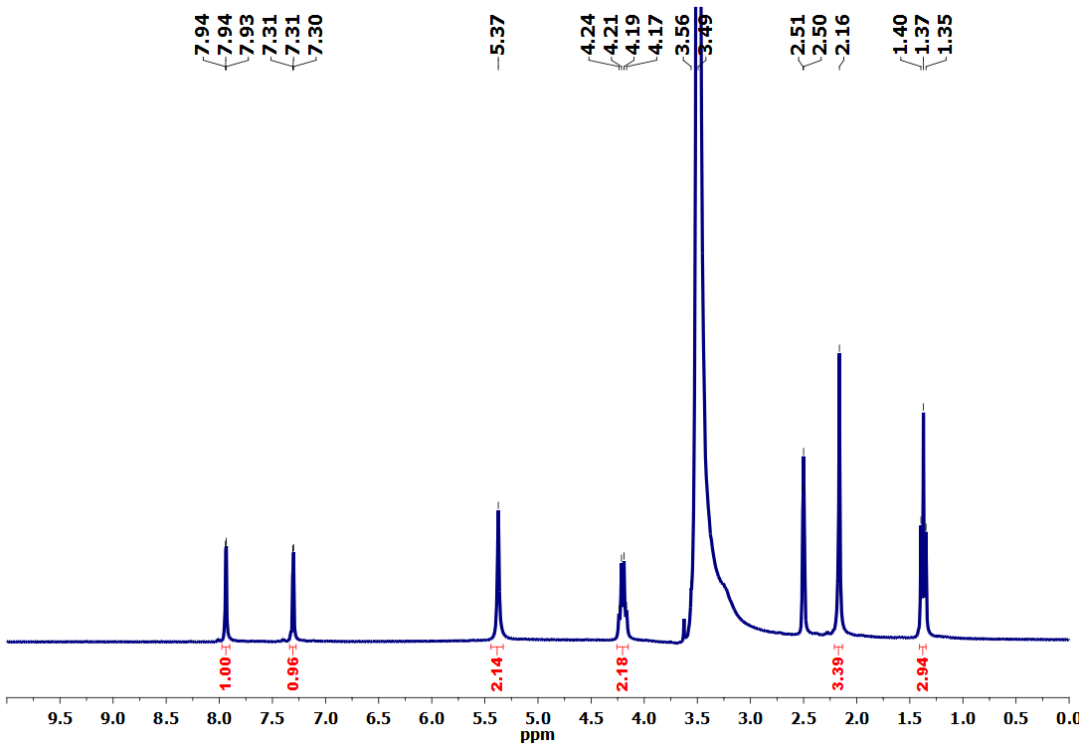


Fig. 14S: ^{1}H-NMR spectrum of **complex 3** in DMSO-d_6 at 298K.

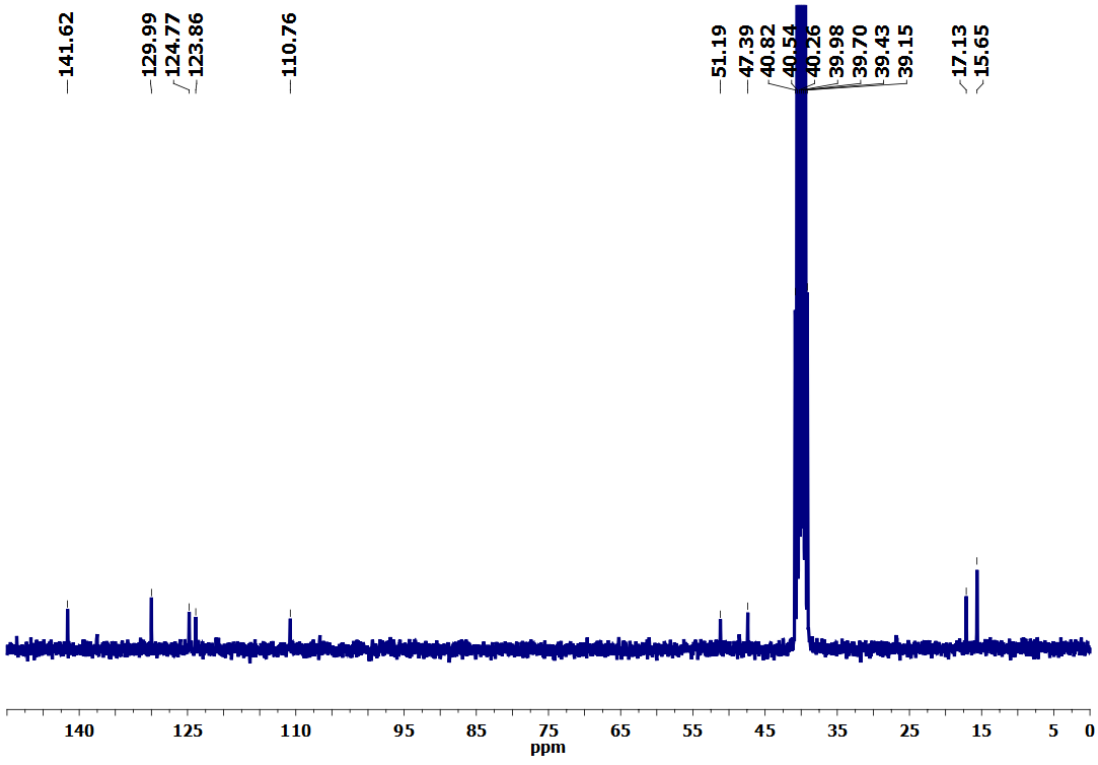


Fig. 15S: ^{13}C-NMR spectrum of **complex 3** in DMSO-d_6 at 298K.

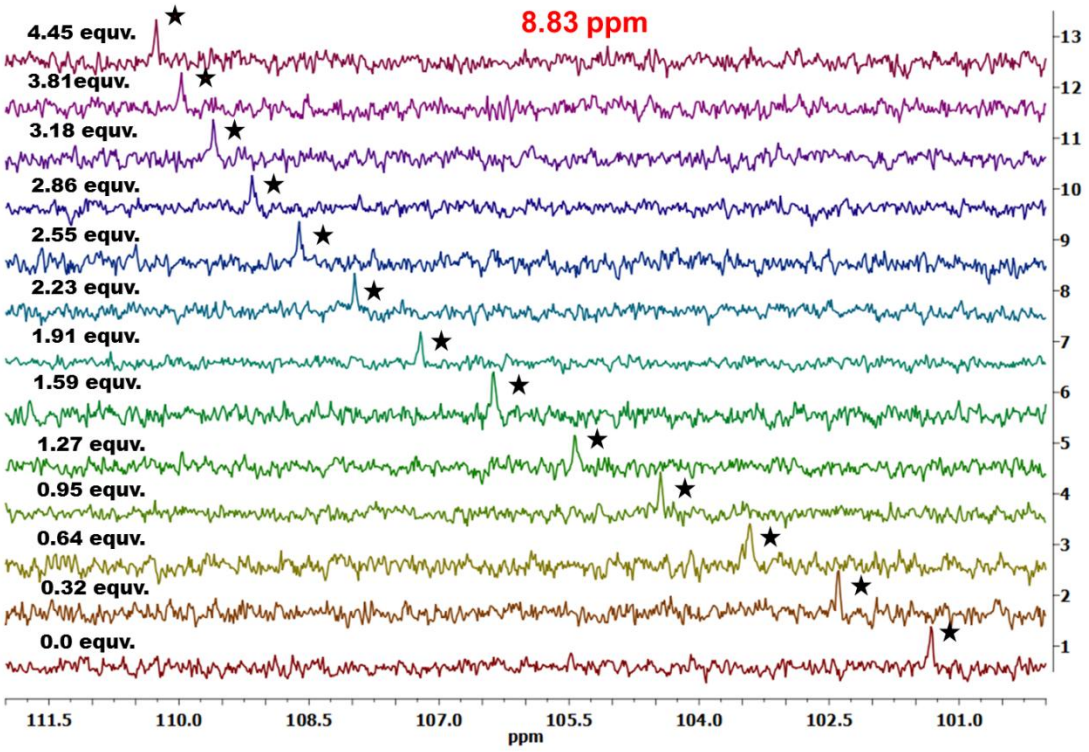


Fig. 16S: ^{13}C-NMR spectra of **1a** (27.90 mM) with TBACl (399.5 mM) in DMSO-d_6 at 298K.

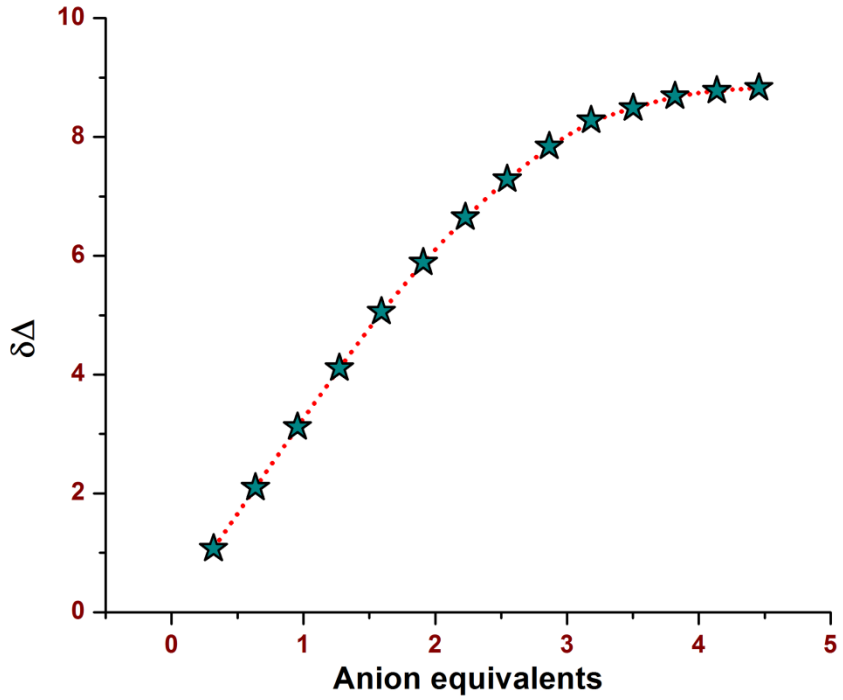


Fig. 17S: Anion equivalent plot of ^{13}C-NMR titration of **1a** with TBACl in DMSO-d_6

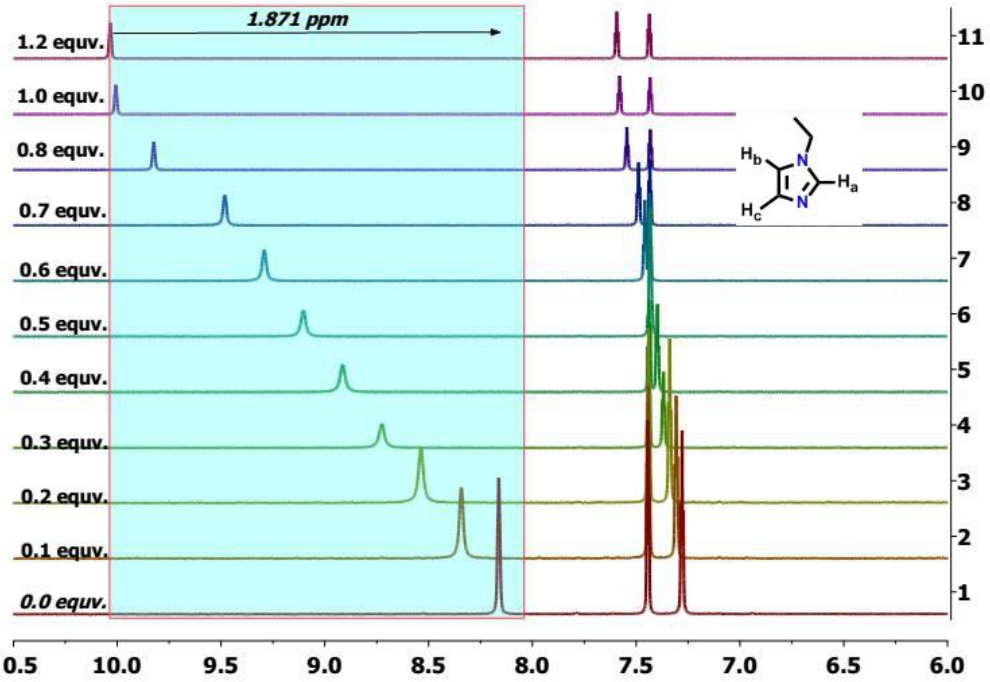


Fig. 18S: ^{1}H-NMR titration profile of **1b** with TBACl in ACN-d_3. [**1b**] = 4.88 mM, [Cl^{-}] = 28.80 mM.

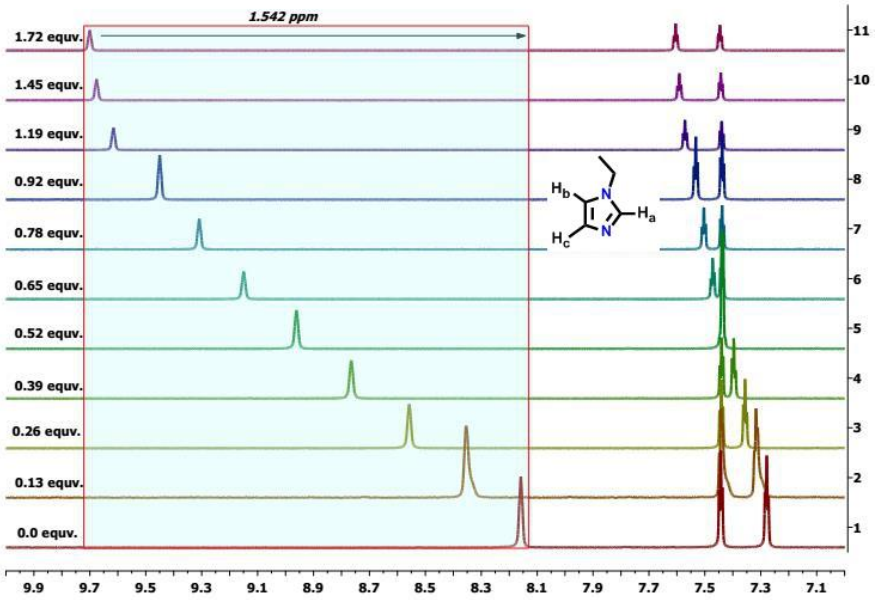


Fig. 19S: ^{1}H-NMR titration profile of **1b** with TBABr in ACN-d_3. [**1b**] = 5.39 mM, [Br^{-}] = 32.13 mM.

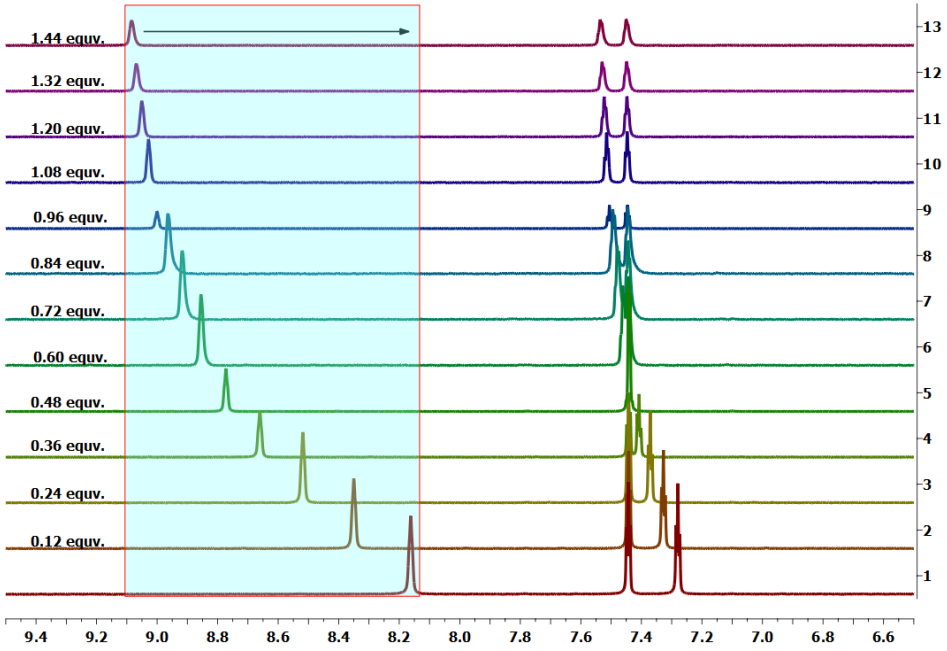


Fig. 20S: ^{1}H-NMR titration profile of **1b** with TBAI in ACN-d_3. [**1b**] = 5.36 mM, [I^{-}] = 29.13 mM.

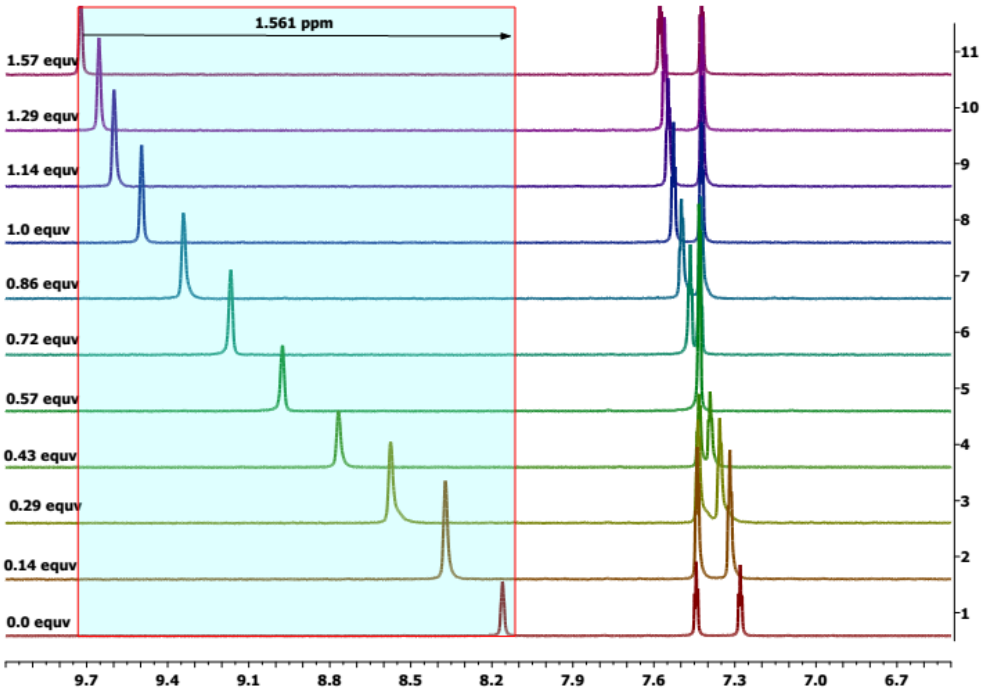


Fig. 21S: ^{1}H-NMR titration profile of **1b** with TBAAcO in ACN-d_3. [**1b**] = 6.24 mM, [AcO^{-}] = 40.19 mM.

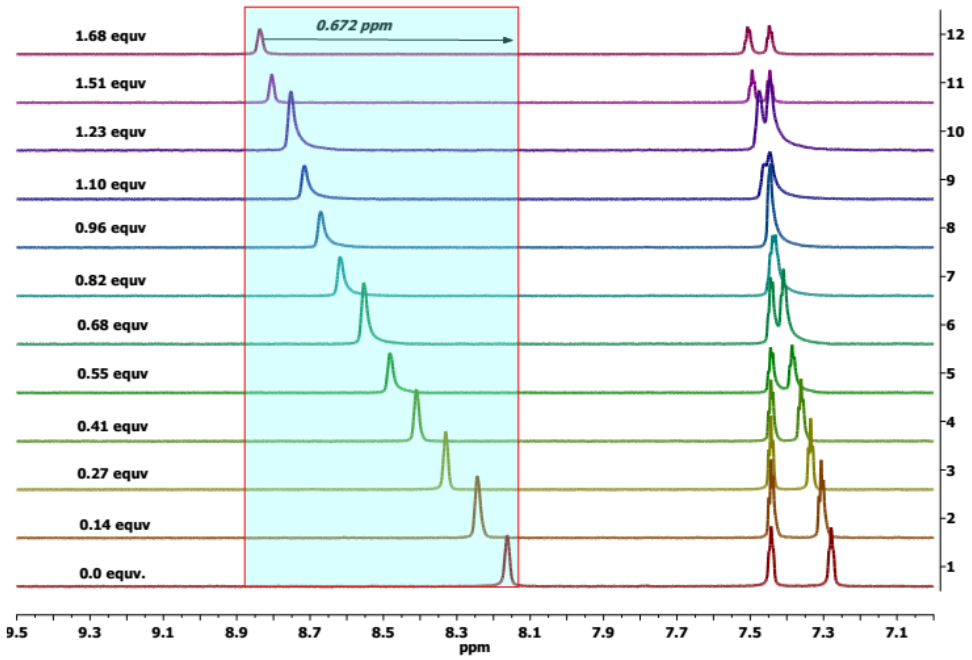


Fig. 22S: ^{1}H-NMR titration profile of **1b** with $TBANO_3$ in ACN-d_3. [**1b**] = 5.29 mM, [NO_3^-] = 32.58 mM.

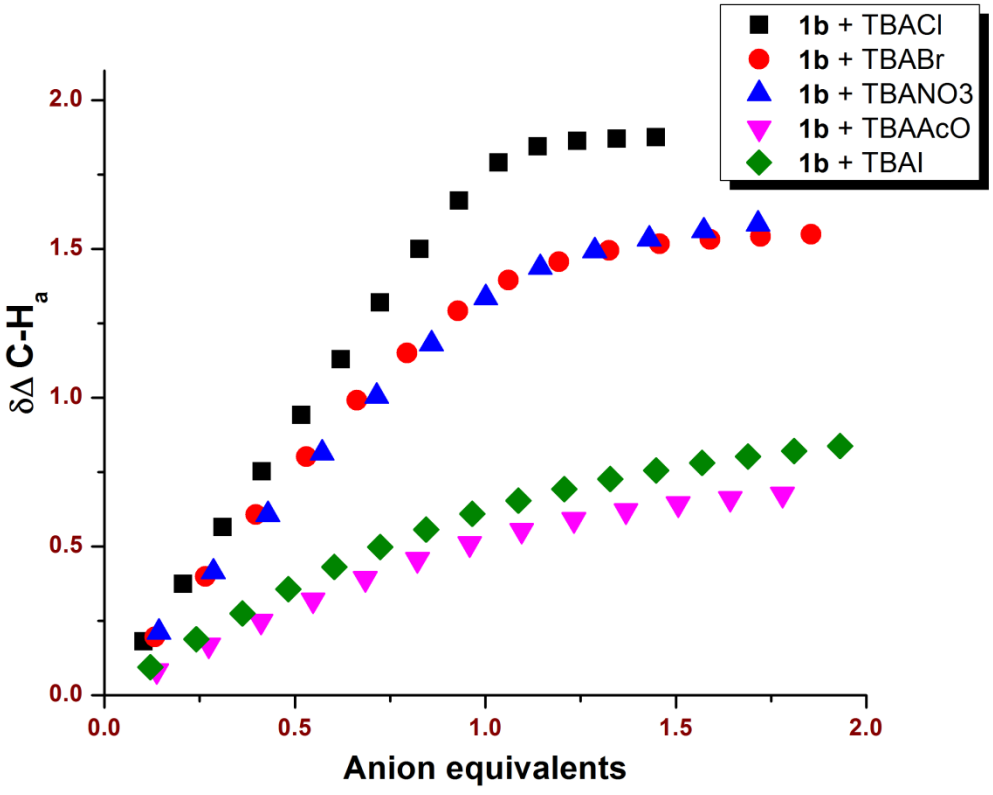


Fig. 23S: Anion equivalent plot of **1b** with guests.

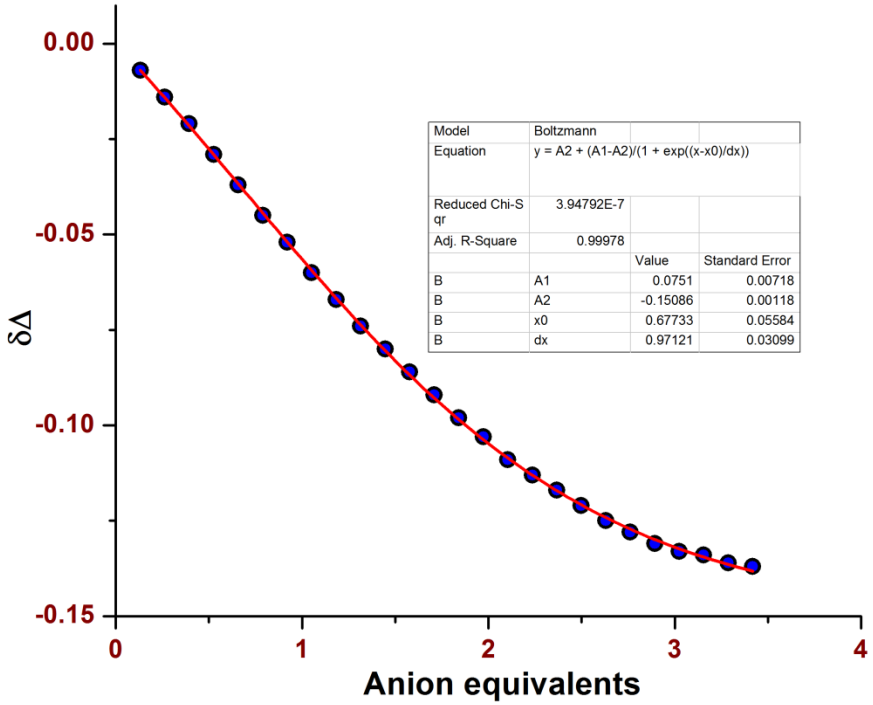


Fig. 24S: Anion Equivalents plot of **1a** with TBACl in ACN-d_3 solvent. The plot shows saturation attained after addition of 3 equivalents of guests.

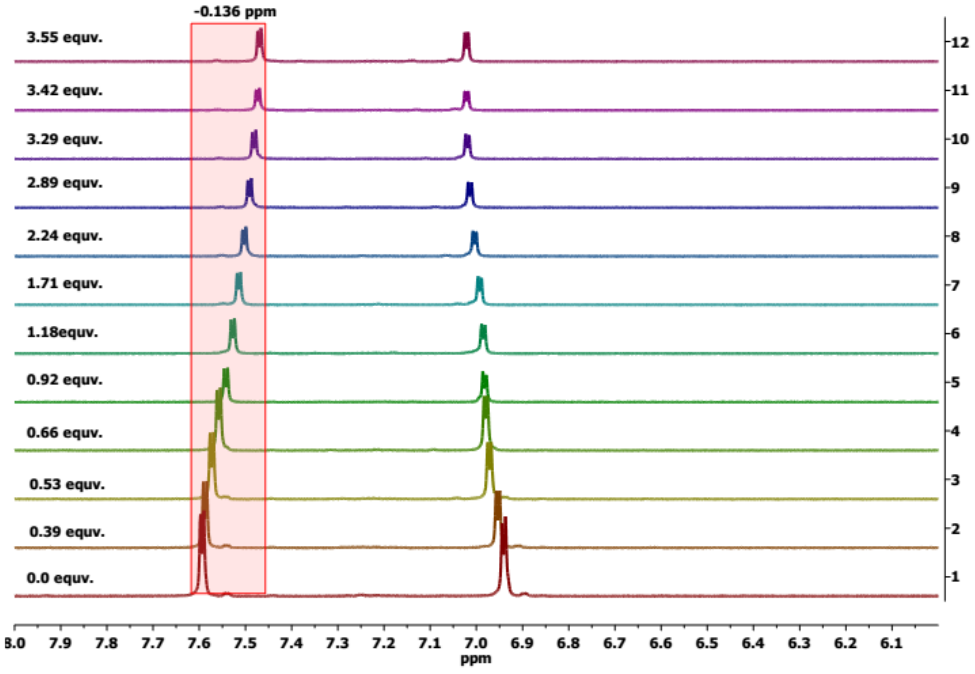


Fig. 25S: ^{1}H-NMR titration profile of **1a** with TBACl in ACN-d_3. [**1a**] = 3.32 mM, [Cl^-] = 21.8 mM.

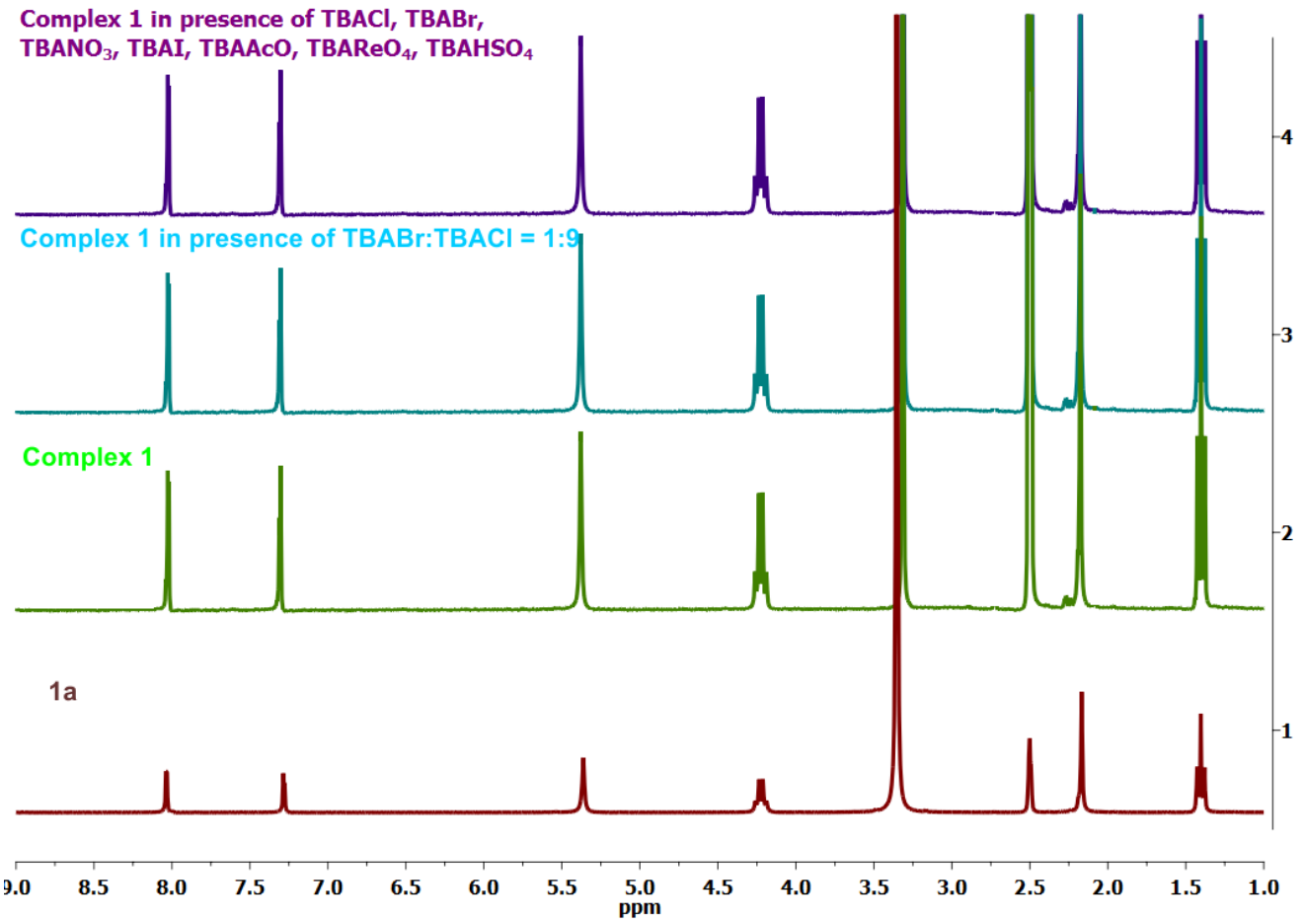


Fig. 26S: Comparative ^{1}H-NMR spectra of **1a**, complex **1** and complex **1** isolated *via* competitive crystallization in DMSO-d_6.

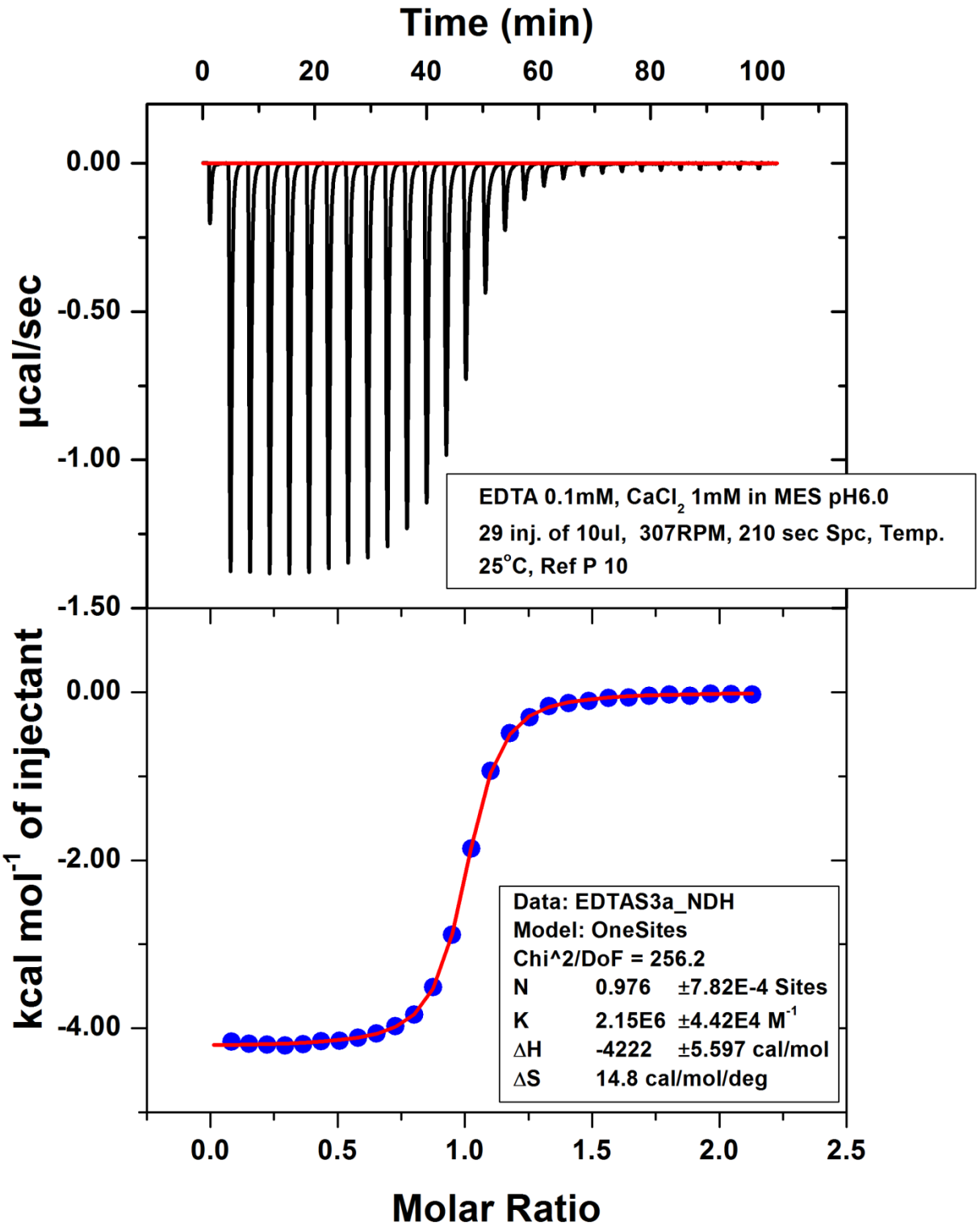


Fig. 27S: ITC accuracy check experiment with EDTA and $CaCl_2$ in MES buffer at pH = 6.0.

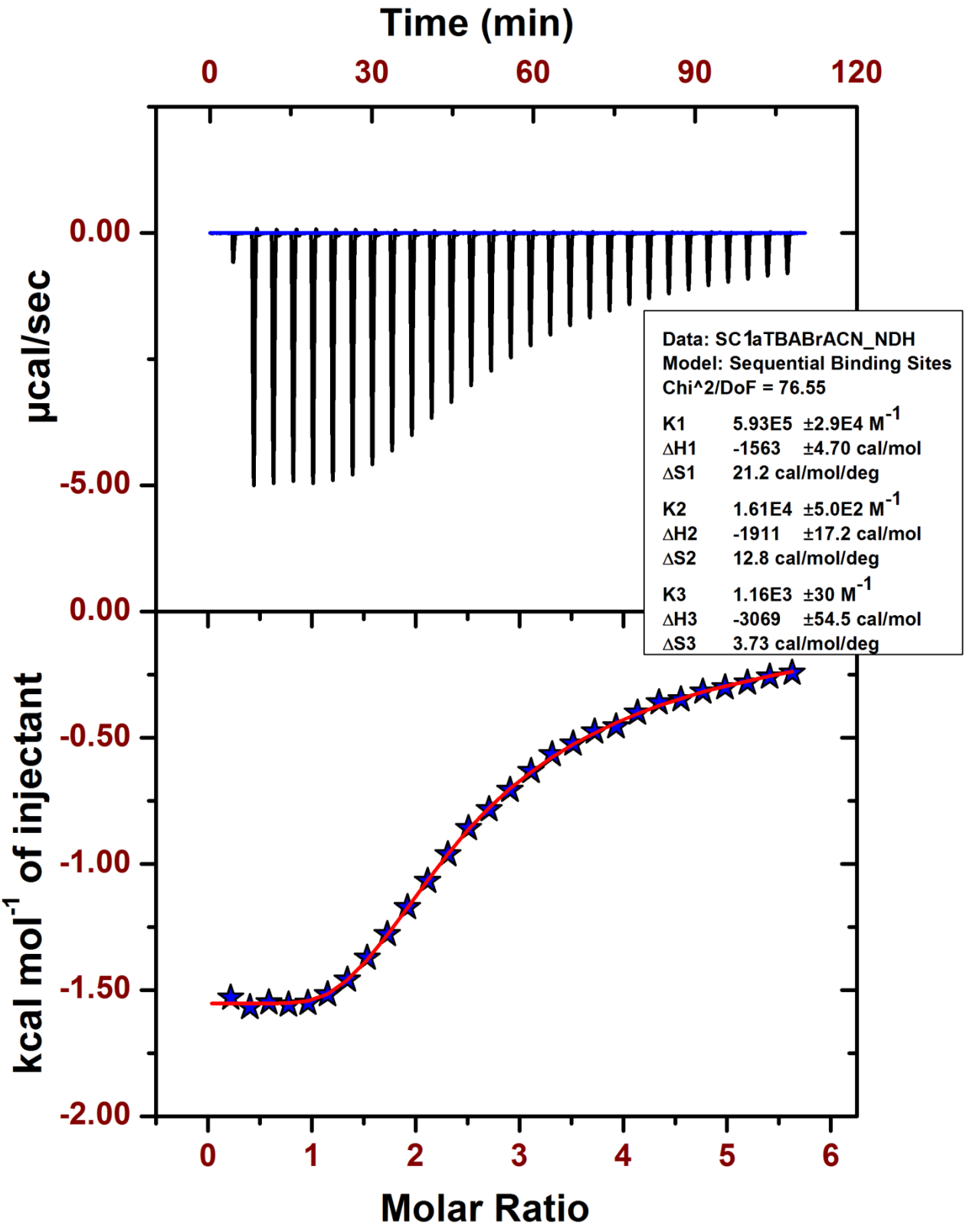


Fig. 28S: ITC profile of **1a** (0.2 mM) with TBABr (5.7 mM) in ACN at 298K.

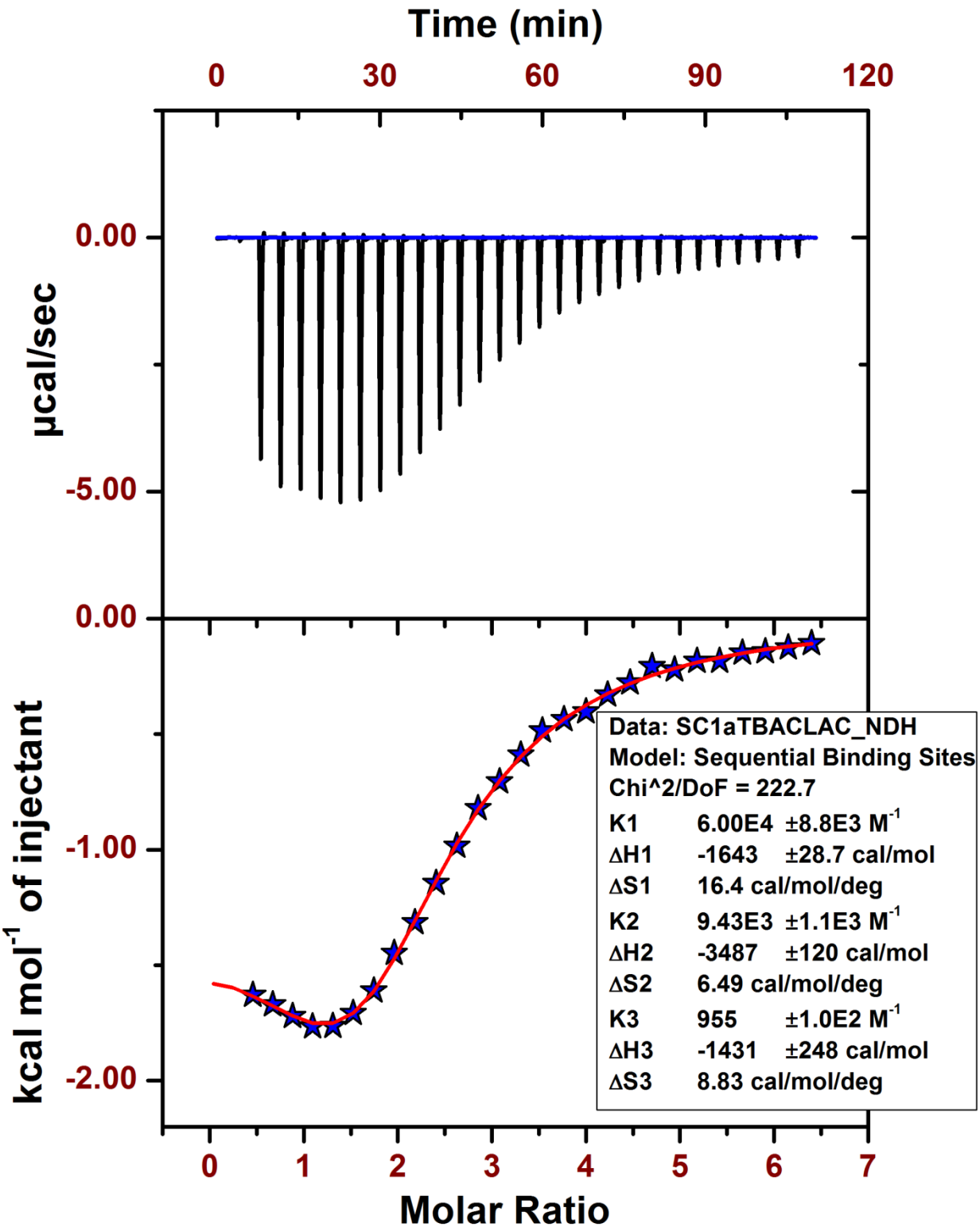


Fig. 29S: ITC profile of **1a** (0.2 mM) with TBACl (6.5 mM) in ACN at 298K.

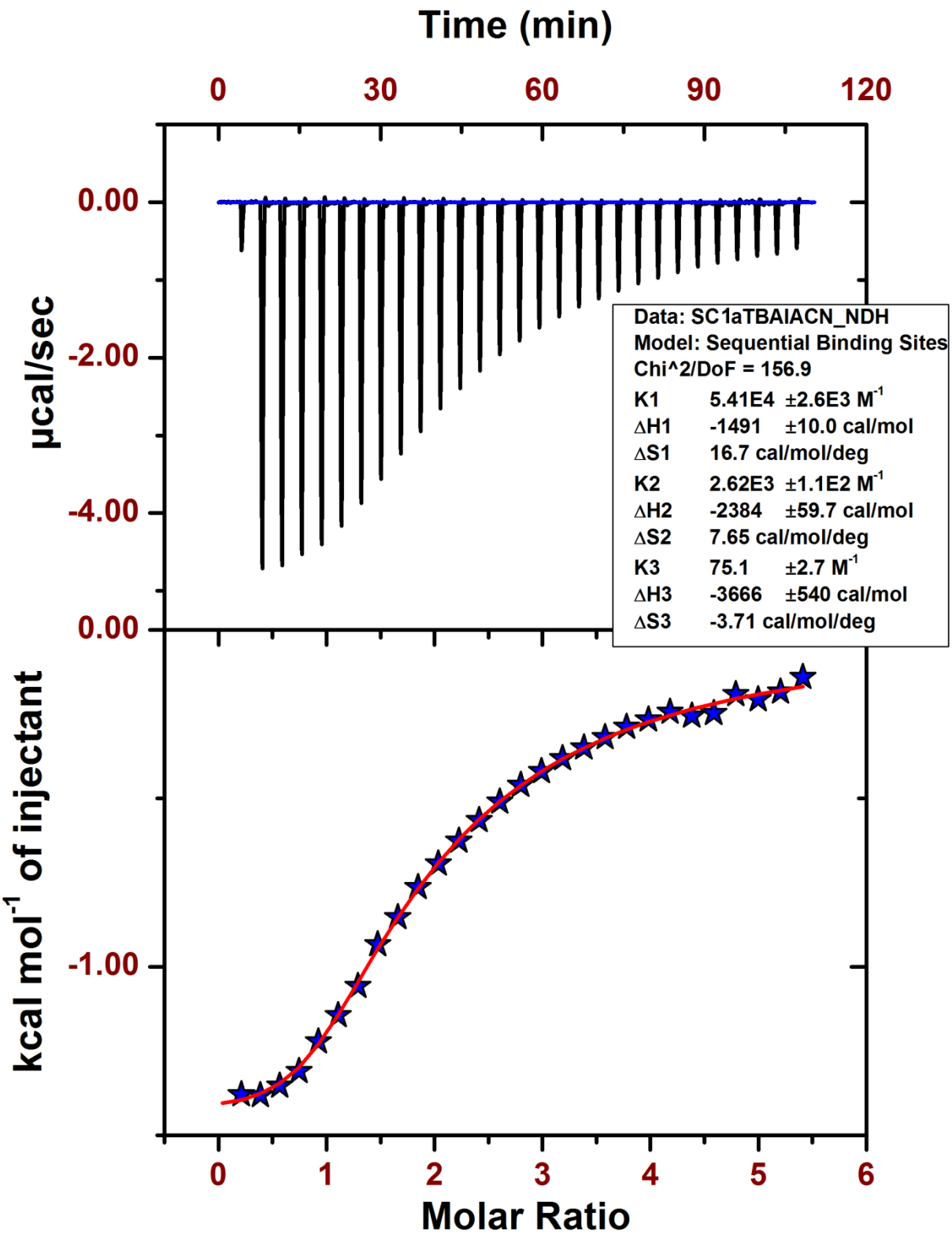


Fig. 30S: ITC profile of **1a** (0.2 mM) with TBAI (5.5 mM) in ACN at 298K.

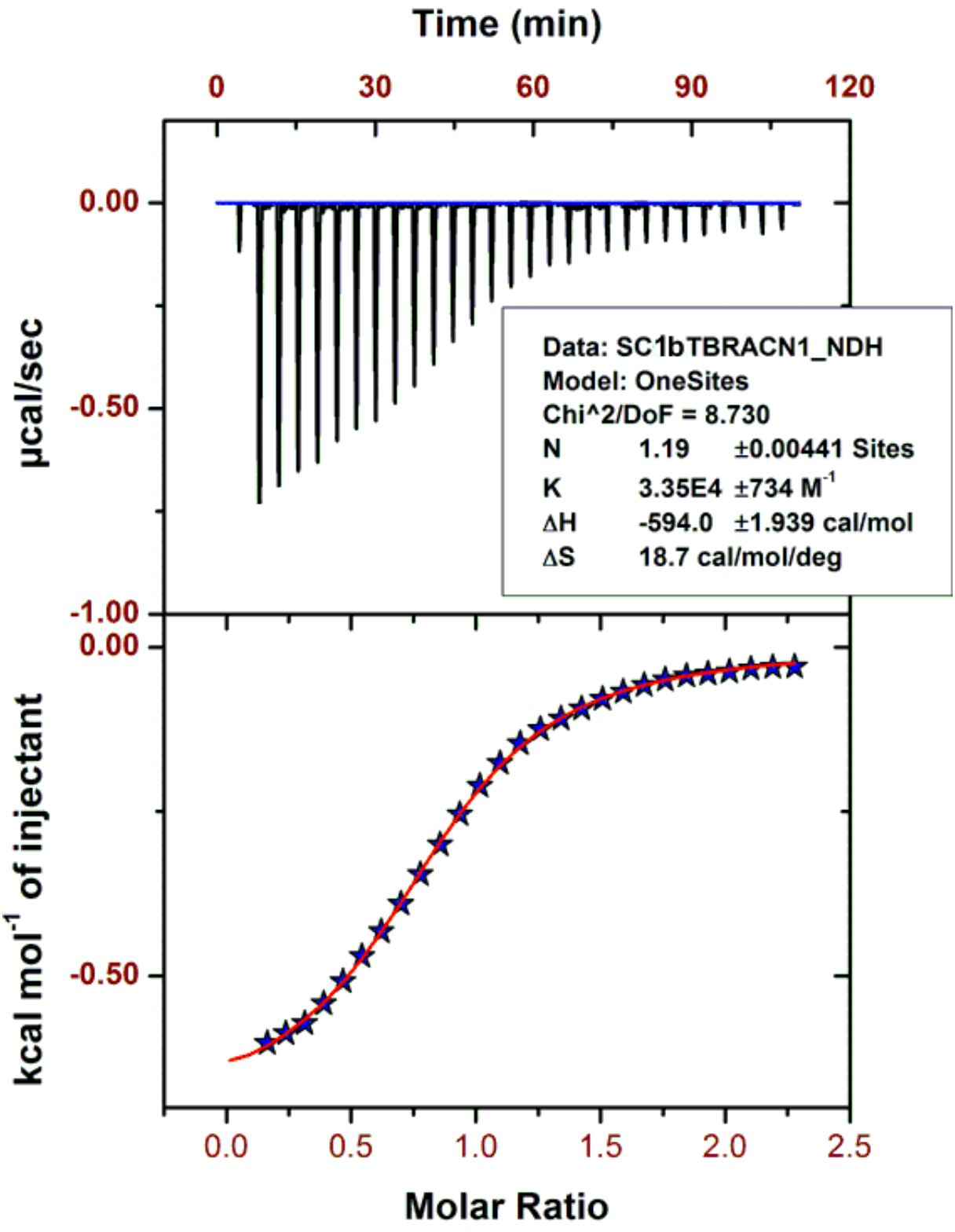


Fig. 31S: ITC profile of **1b** (0.25 mM) with TBABr (2.61 mM) in ACN at 298K.

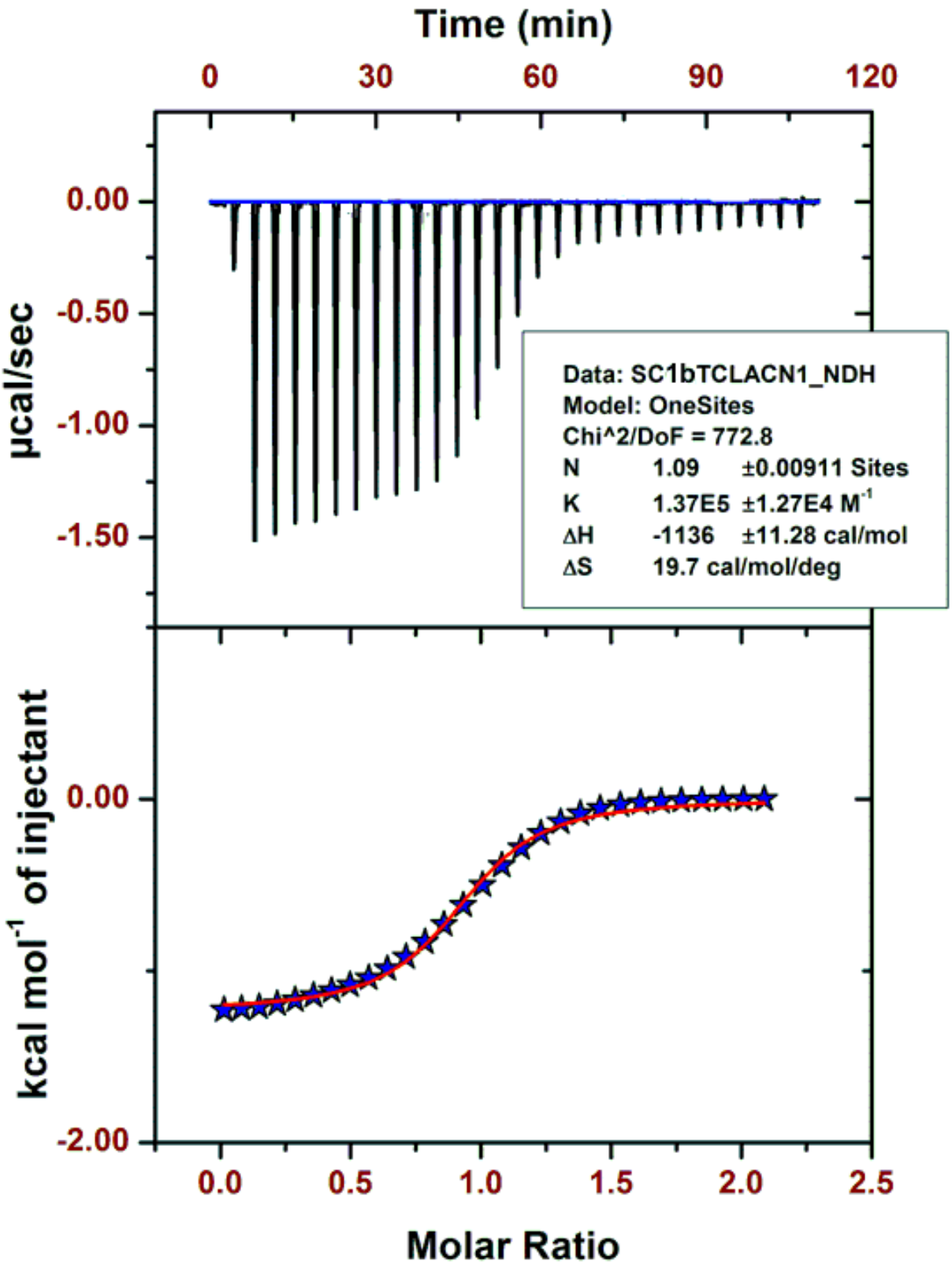


Fig. 32S: ITC profile of **1b** (0.31 mM) with TBACl (3.14 mM) in ACN at 298K.

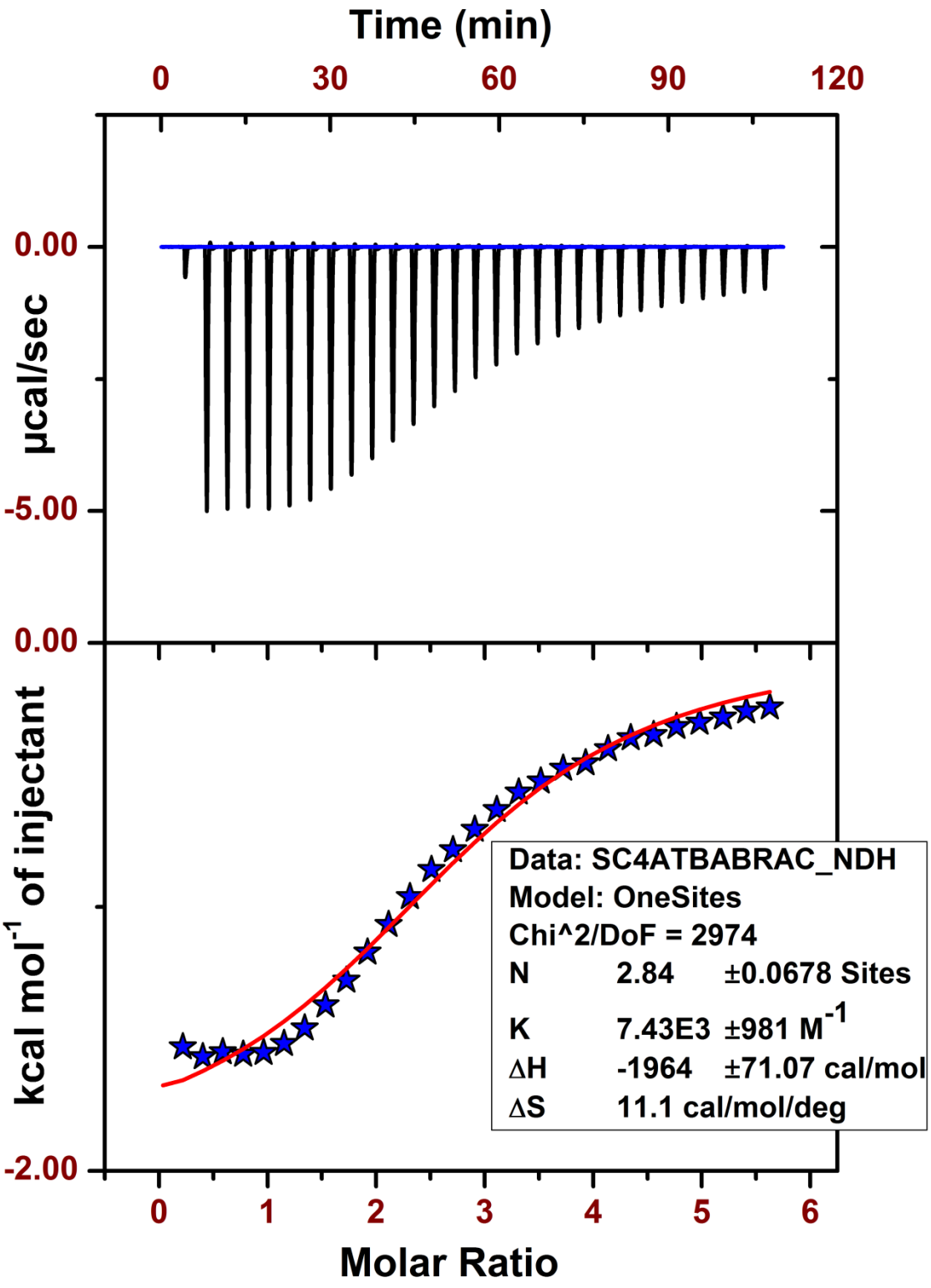


Fig. 33S: ***<u>One set of site model</u>*** fitting of ITC profile of **1a** (0.2 mM) with TBABr (5.7 mM) in ACN at 298K.

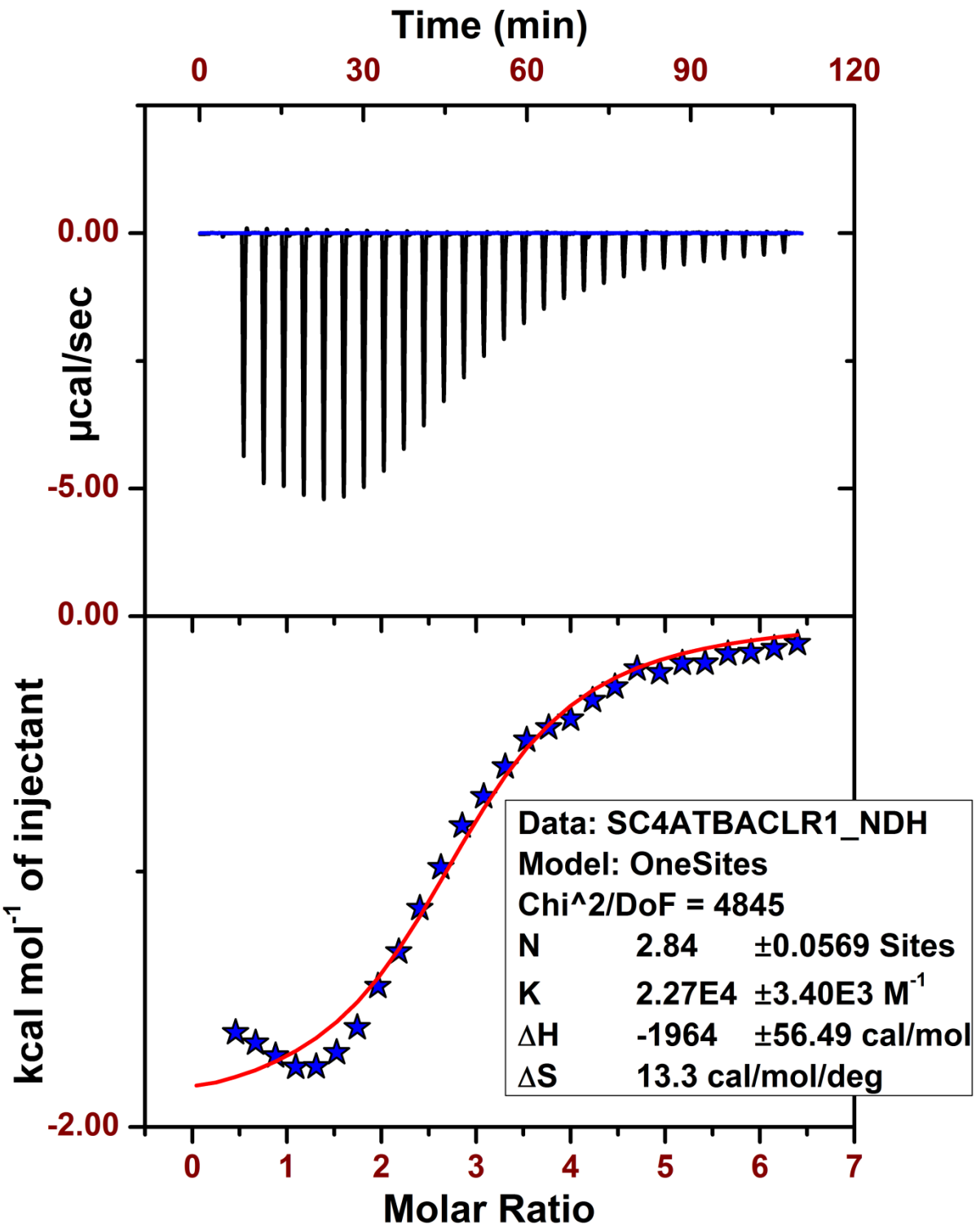


Fig. 34S: ***<u>One set of site model</u>*** fitting of ITC profile of **1a** (0.2 mM) with TBACl (6.5 mM) in ACN at 298K.

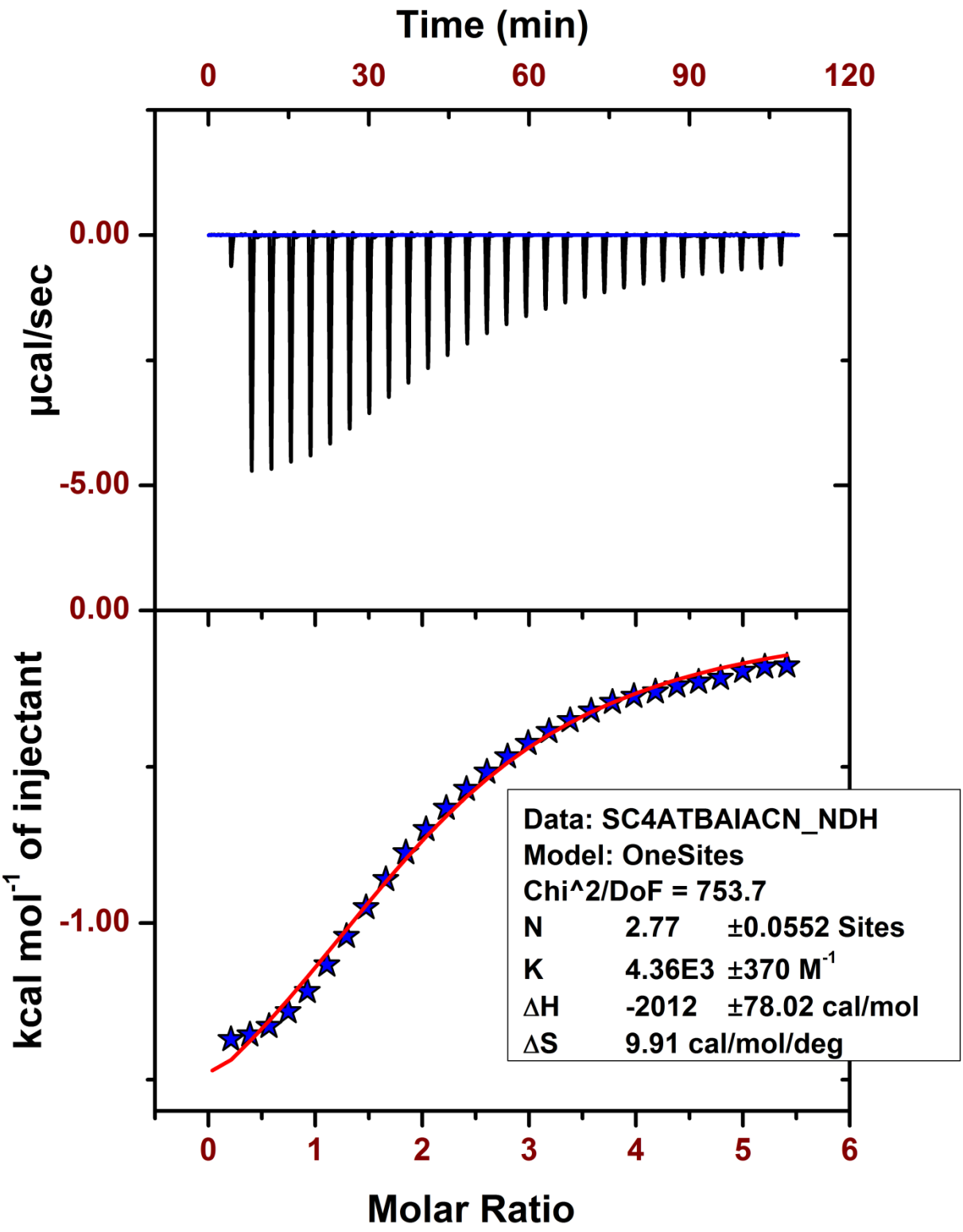


Fig. 35S: ***<u>One set of site model</u>*** fitting of ITC profile of **1a** (0.2 mM) with TBAI (5.5 mM) in ACN at 298K.

Complexes	I···X	I···X distance	< C-I···X	< C-I···X value	I···X Vander wall Radii (%)
Complex 1	I1···Br5	3.155Å	C13-I1···Br5	178.71°	82.3
	I3···Br5	3.125Å	C16-I3···Br5	174.85°	81.6
	I2···Br4	3.084Å	C17-I2···Br4	175.34°	80.4
Complex 2	I2···Cl5	2.992Å	C12-I2···Cl5	176.93°	80.2
	I3···Cl5	3.012Å	C13-I3···Cl5	173.79°	80.7
	I1···Cl4	2.927Å	C18-I1···Cl4	173.25°	78.4
Complex 3	I3···Cl1	3.099Å	C24-I3···Cl1	177.35°	83.1
	I1···Cl2	2.988Å	C13-I1···Cl2	176.72°	80.1
	I2···Cl2	3.081Å	C14-I2···Cl2	173.07°	82.6

Table 1S: The halogen bonding parameters of complexes **1**, **2** & **3**.

Compound reference	**Complex 1**	**Complex 2**	**Complex 3**
Chemical formula	$C_{27}H_{31}Br_2F_6I_3N_6OP$	$C_{27}H_{33}Cl_2F_6I_3N_6OP$	$C_{54}H_{72}Cl_3I_6N_{12}$
Formula Mass	1141.07	1054.16	1756.99
Crystal system	Triclinic	Triclinic	Monoclinic
***a*/Å**	10.9697(14)	10.6955(13)	29.993(3)
***b*/Å**	14.1499(18)	13.5915(17)	12.6135(12)
***c*/Å**	16.420(2)	16.862(2)	21.963(2)
***α*/°**	93.110(3)	93.543(3)	90.00
***β*/°**	108.455(3)	107.602(3)	109.059(2)
***γ*/°**	112.057(3)	110.756(3)	90.00
Unit cell volume/Å^3	2196.9(5)	2145.1(5)	7853.5(13)
Temperature/K	150(2)	150(2)	150(2)
Space group	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
No. of formula units per unit cell, *Z*	2	2	4
No. of reflections measured	25065	7524	6916
No. of independent reflections	7711	7524	6916
Final R_1 values ($I > 2\sigma(I)$)	0.0531	0.0411	0.0484
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1583	0.1427	0.1509
Final R_1 values (all data)	0.0661	0.0465	0.0569
Final $wR(F^2)$ values (all data)	0.1751	0.1474	0.1623
Goodness of fit on F^2	0.609	1.223	0.592
CCDC number	1049817	1049818	1049819

Table 2S: Crystallographic Tables of complex **1**, **2** & **3**

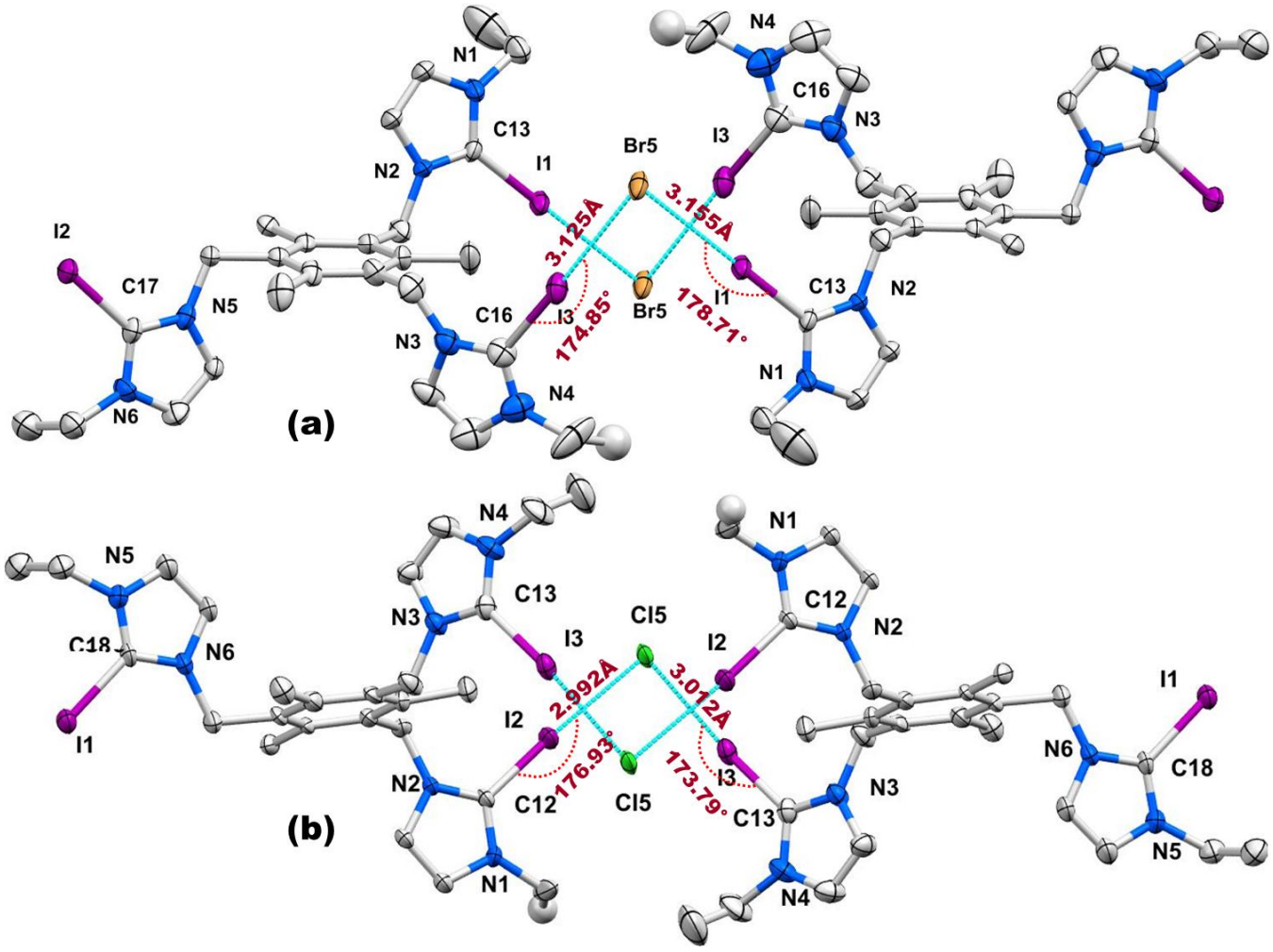


Fig. 36S: Single crystal X-ray structures of represents XB present in (a) complex **1**; (b) complex **2**. All the hydrogen atoms are omitted for clarity.

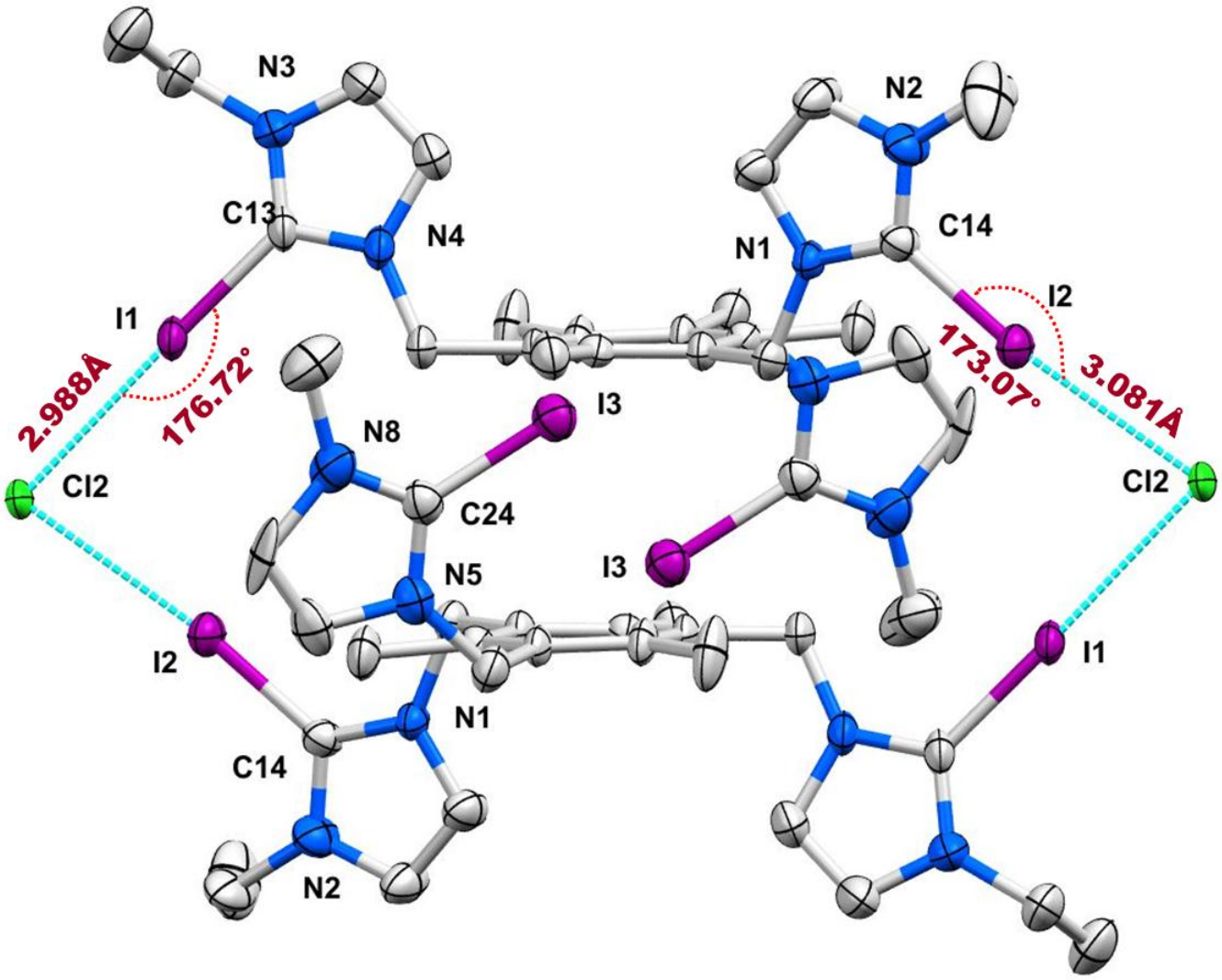


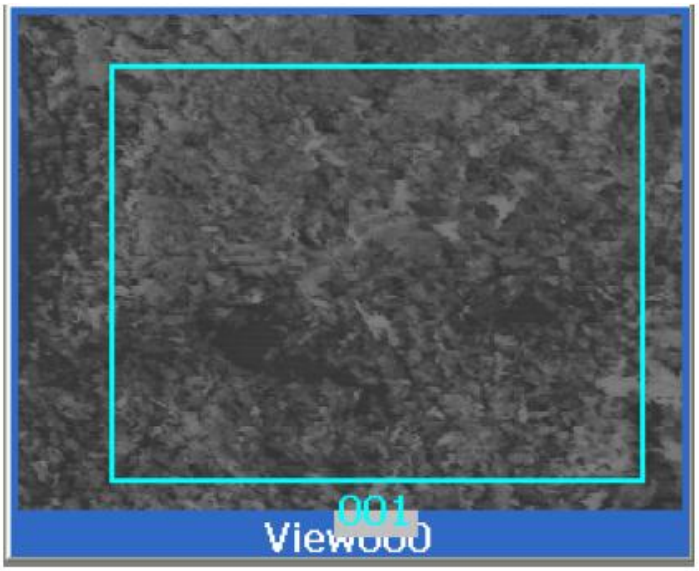
Fig. 37S: Single crystal X-ray structures of represents XB present in complex **3**. All the hydrogen atoms are omitted for clarity.

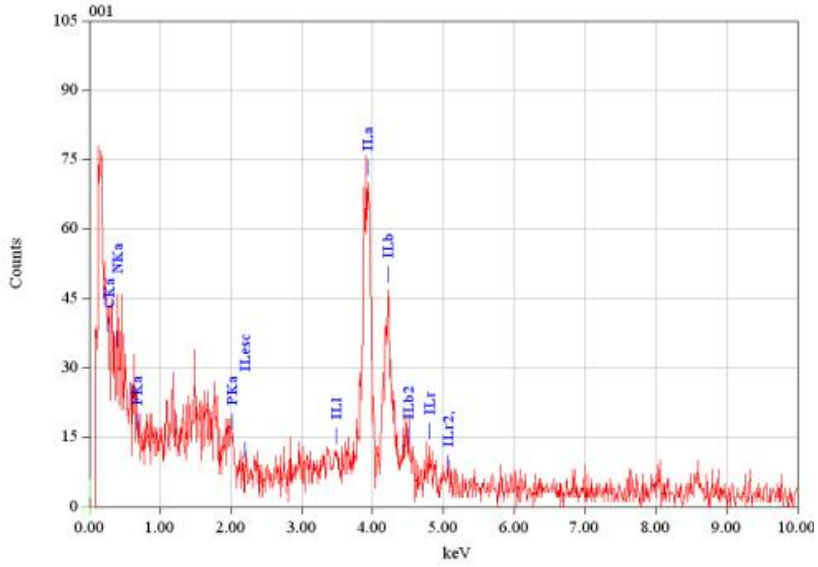
Batch	Wt. of Ligand taken (mg)	Wt. of Br^- taken (mg)	Wt. of Cl^- taken (mg)	Wt. of I^- taken (mg)	Wt. of NO_3^- taken (mg)	Wt. of ReO_4^- taken (mg)	Wt. of HSO_4^- taken (mg)	Wt. of complex (mg)	%Yield
1	11.87	10.0	11.1	11	11.9	14.5	12.3	**6.38**	**60%**
2	8.0	10	8.6	×	×	×	×	**3.51**	**49%**
3	8.75	11.3	29.2	×	×	×	×	**2.67**	**34%**
4	8.14	10	77	×	×	×	×	**1.68**	**23%**
5	10	15	×	×	×	×	×	**6.72**	**75%**
6	12	×	16.6	×	×	×	×	**5.92**	**55%**
7	10.6	×	15	12.6	14.2	11.9	15.4	**3.06**	**35%**

Table 3S: Crystallization details & yield calculation.

❖ Crystallization details:

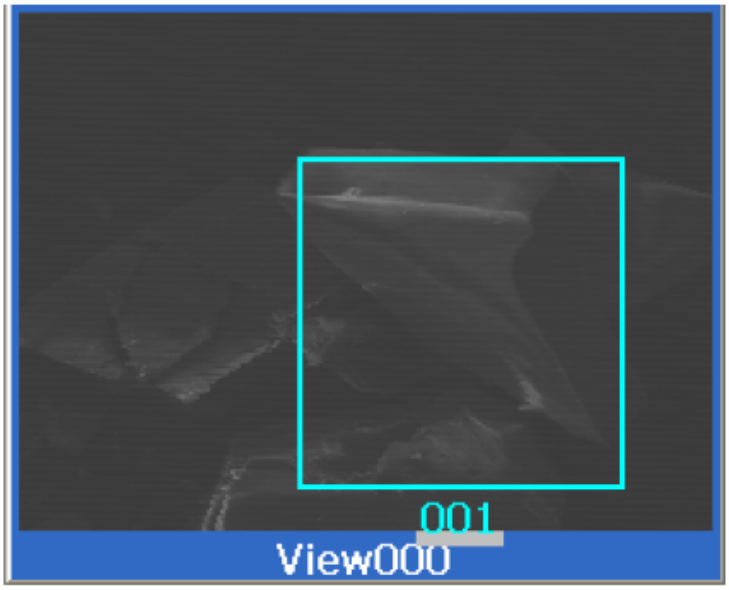
The crystallization is performed in DCM-DMF binary solvent mixture. During crystallization the total content of DMF was fixed at 1 ml. Then DCM was mixed into the solution through vapor diffusion. Each time we have obtained crystals as **complex 1** which was analyzed by single crystal X-ray crystallographic studies. We have observed that the crystals contained two bromides and one PF6 as counter anions. Apparently, the study reveals that **1a** is selective towards Br^- over other investigated anions. Later on, same selectivity studies have been carried out with Cl^- in absence of Br^- (entry 7, table 3S). This experiment revealed that Cl^- is found to be forming **complex 3** in absence of Br^-. This experiment was repeated thrice and each time we observed crystals of **complex 3** which were analyzed by single crystal X-ray structural studies. In **complex 3**, we don't see any PF_6 fragment at all. The Cl^- occupies special positions to maintain overall neutral nature of the complex. Yield of crystallization calculated on the basis of molecular weight of complex **1**. In case of entry 7 in table 3S, Yield of crystallization calculated on the basis of molecular weight of complex **3**.

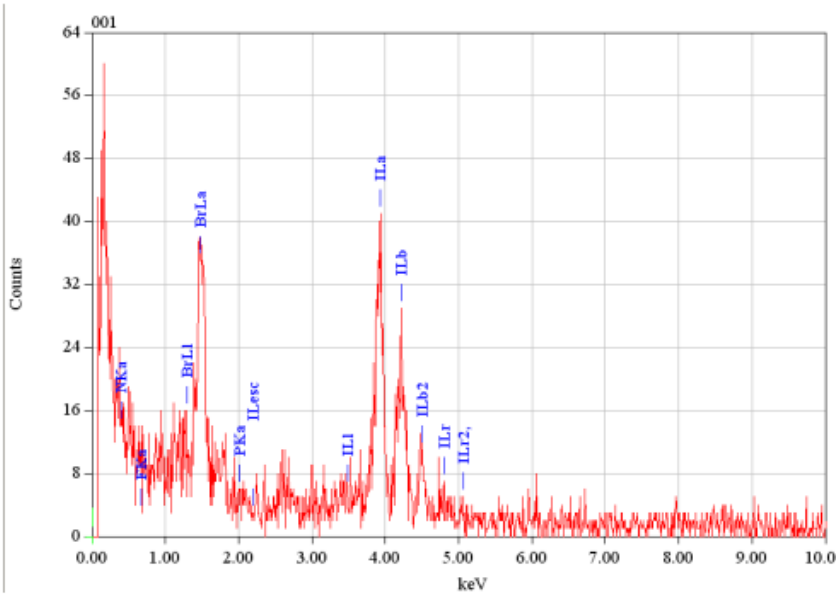




Ele...	Cl...	(keV)	mass%	Error%	At%
C	K*				
N	K*	0.392	13.14	1.05	45.37
F	K*	0.677	8.78	2.12	22.35
P	K*	2.013	2.12	0.60	3.32
I	L	3.936	75.96	1.50	28.96
Total			100.00		100.00

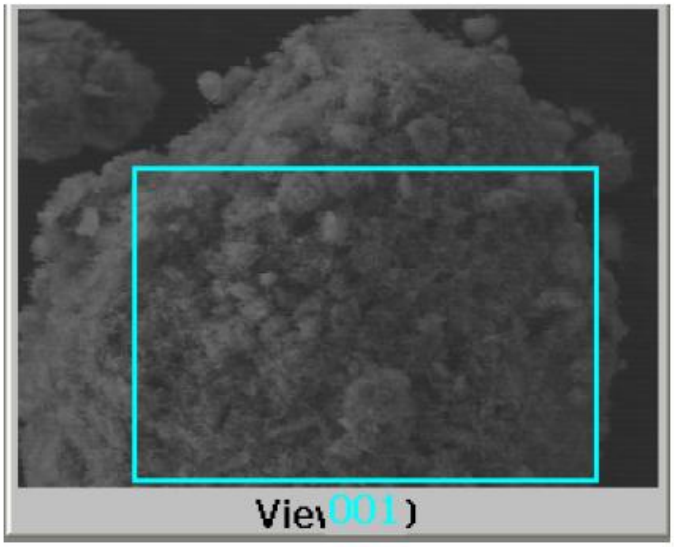
Fig. 38S: Energy dispersive X-ray spectroscopy (SEM-EDX) of **1a**.

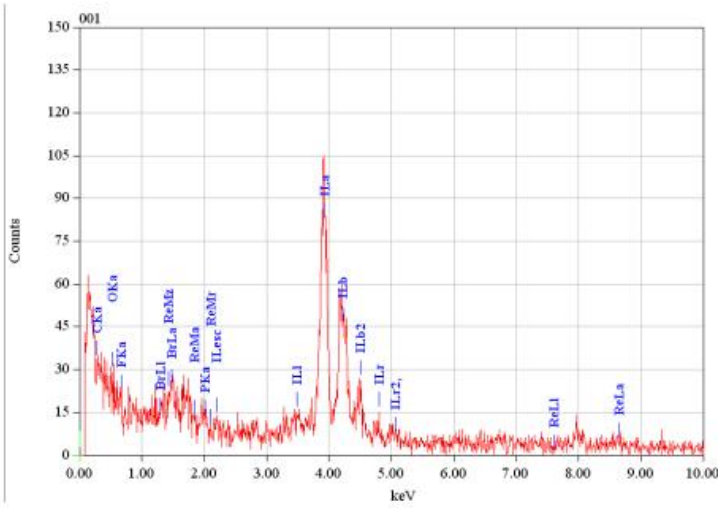




Ele...	Cl...	(keV)	mass%	Error%	At%
N K*		0.392	26.06	1.14	67.98
F K*		0.677	4.26	1.39	8.20
P K*					
Br L		1.480	22.15	0.90	10.13
I L		3.936	47.52	1.12	13.69
Total			100.00		100.00

Fig. 39S: Energy dispersive X-ray spectroscopy (SEM-EDX) of complex **1** isolated in presence of chloride (Batch 2 in Table 3S).





Ele...	Cl...	(keV)	mass%	Error%	At%
C	K*				
O	K*				
F	K*	0.677	8.56	1.63	36.27
P	K*	2.013	1.57	0.56	4.09
Br	L*	1.480	7.06	1.31	7.11
I	L	3.936	82.81	1.33	52.54
Re	M*				
Total			100.00		100.00

Fig. 40S: Energy dispersive X-ray spectroscopy (SEM-EDX) of complex **1** isolated in presence of chloride and all interfering anions (Batch 1 in Table 3S).

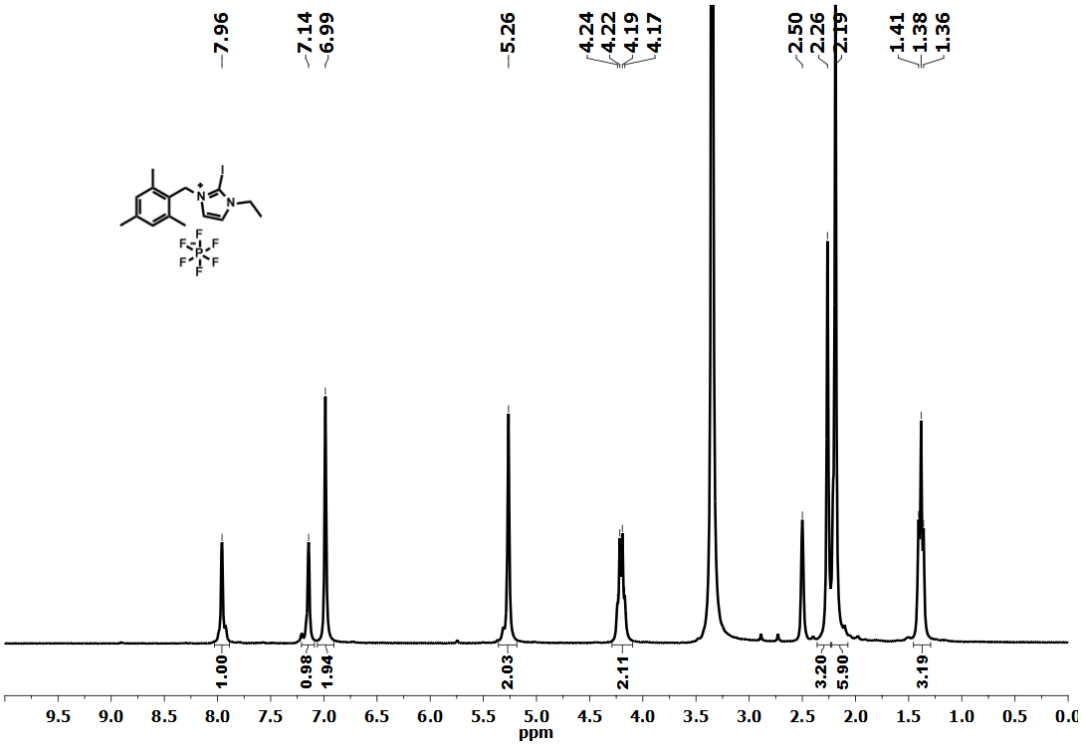


Fig. 41S: ^{1}H-NMR spectrum of **1c** in DMSO-d_6 at 298K.

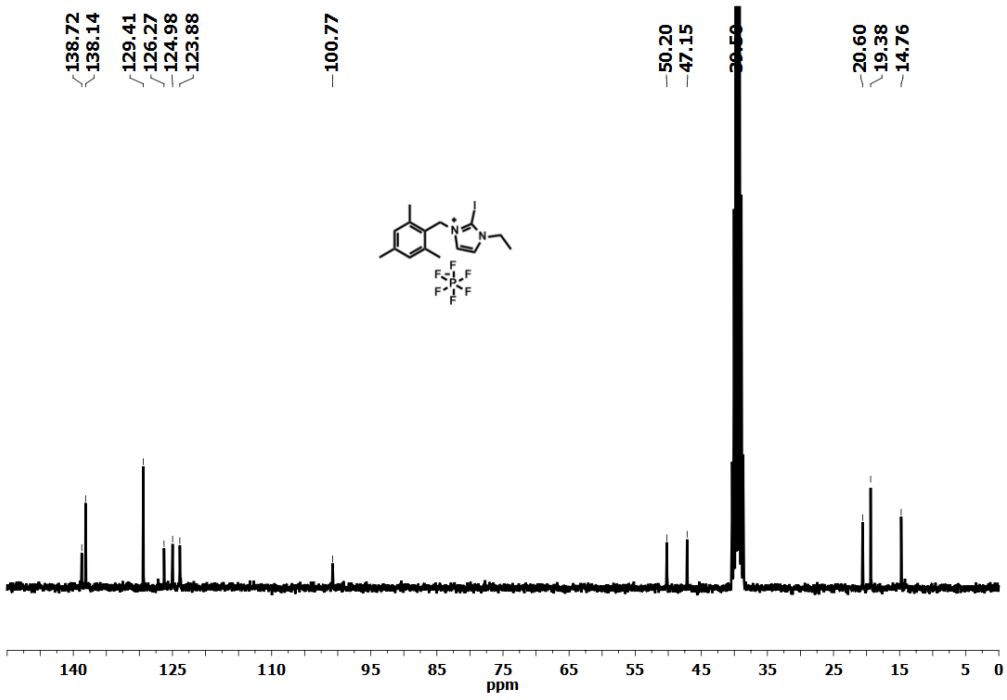


Fig. 42S: ^{13}C-NMR spectrum of **1c** in DMSO-d_6 at 298K.

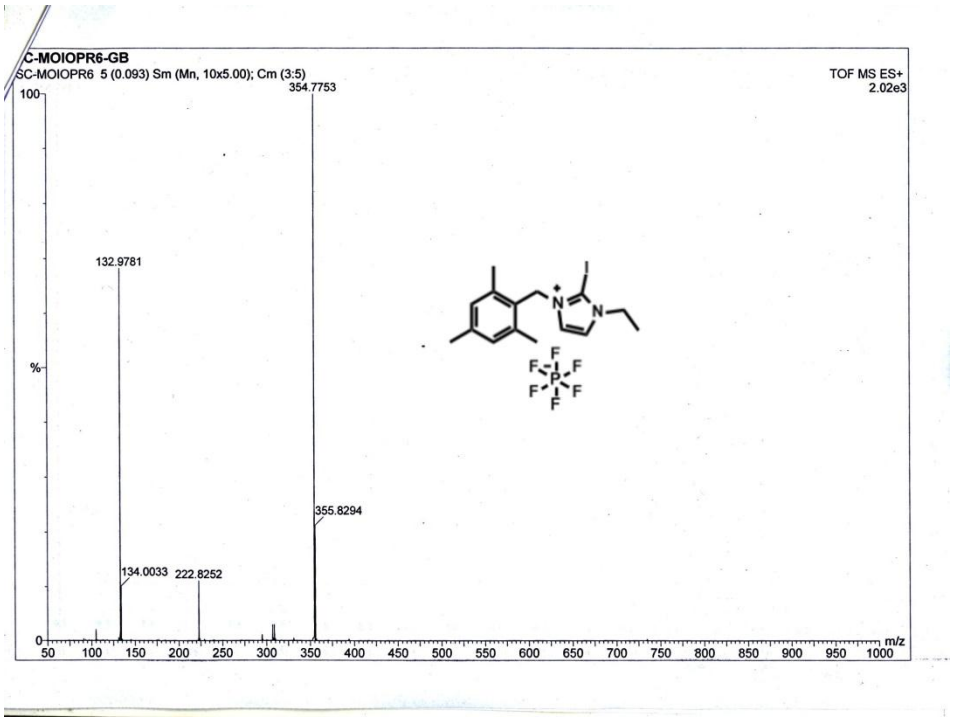


Fig. 43S: ESI-MS spectrum of **1c** in acetonitrile at 298K.

Guest	***K***	***ΔH (KJ/mol)***	***TΔS (KJ/mol)***	***ΔG (KJ/mol)***
Cl^-	*$2.12*10^3$*	*-13.2*	*5.8*	*-19*
Br^-	*$2.66*10^3$*	*-14.8*	*4.7*	*-19.5*
I^-	*$1.49*10^3$*	*-13.4*	*4.6*	*-18*

Table 4S: Thermodynamic parameters obtained from ITC titration study.

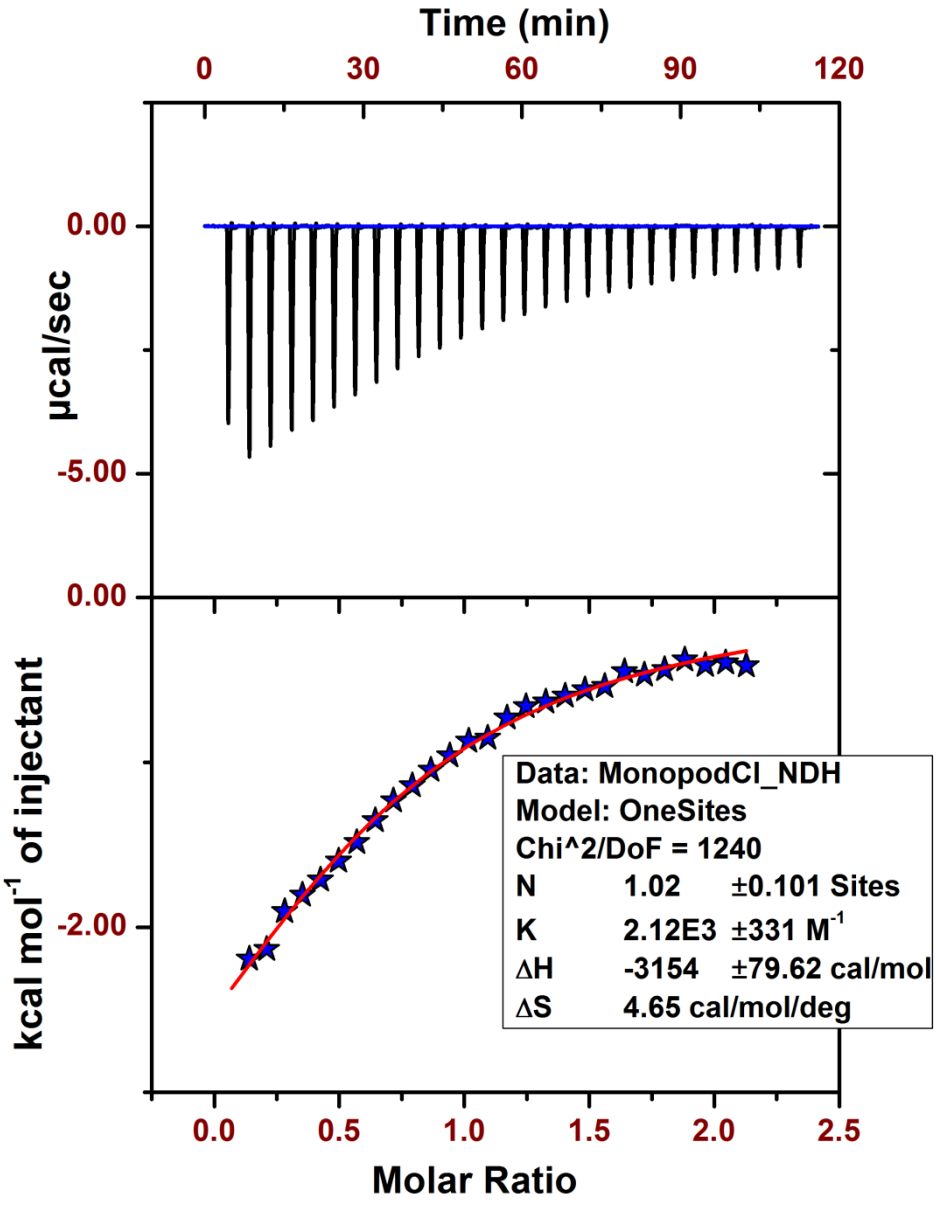


Figure 44s. ITC titration profiles of **1c** with Cl^-. Concentration; [1c] = 0.5018 mM, [Cl^-] = 5.0554 mM.

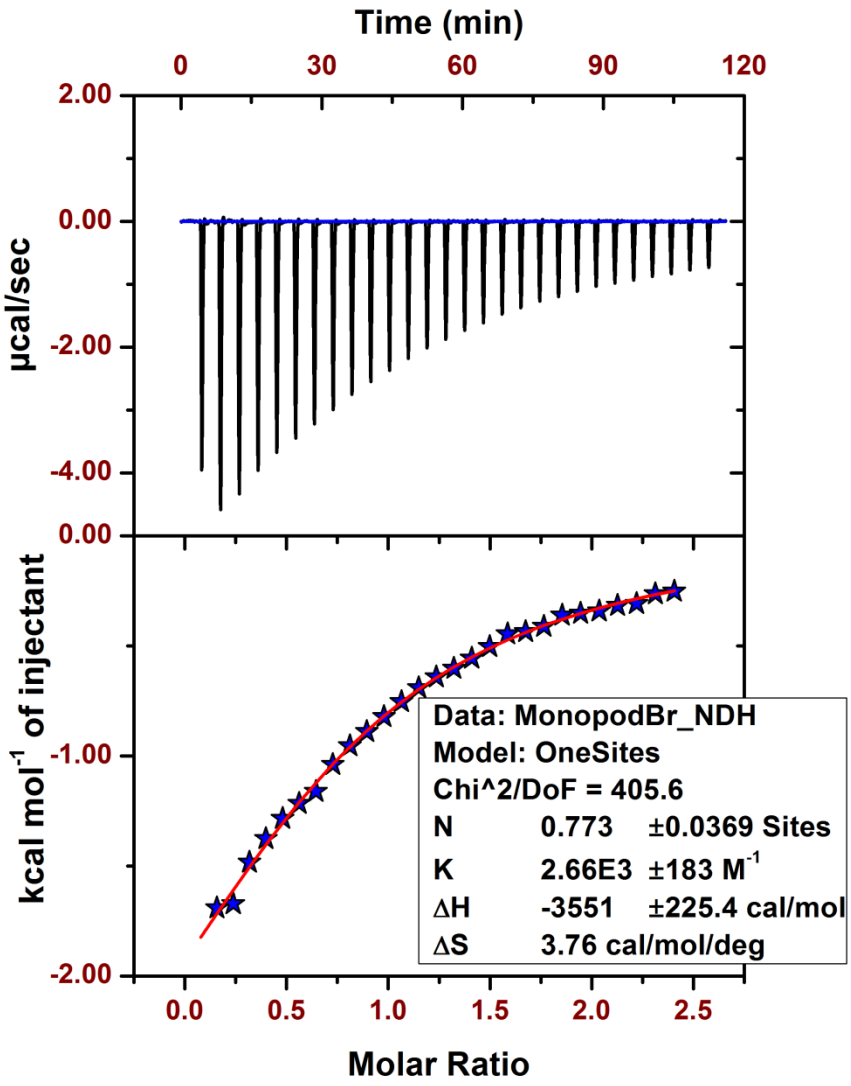


Figure 45S. ITC titration profiles of **1c** with Br^{-}. Concentration; [1c] = 0.5118 mM, [Cl^{-}] = 4.913 mM.

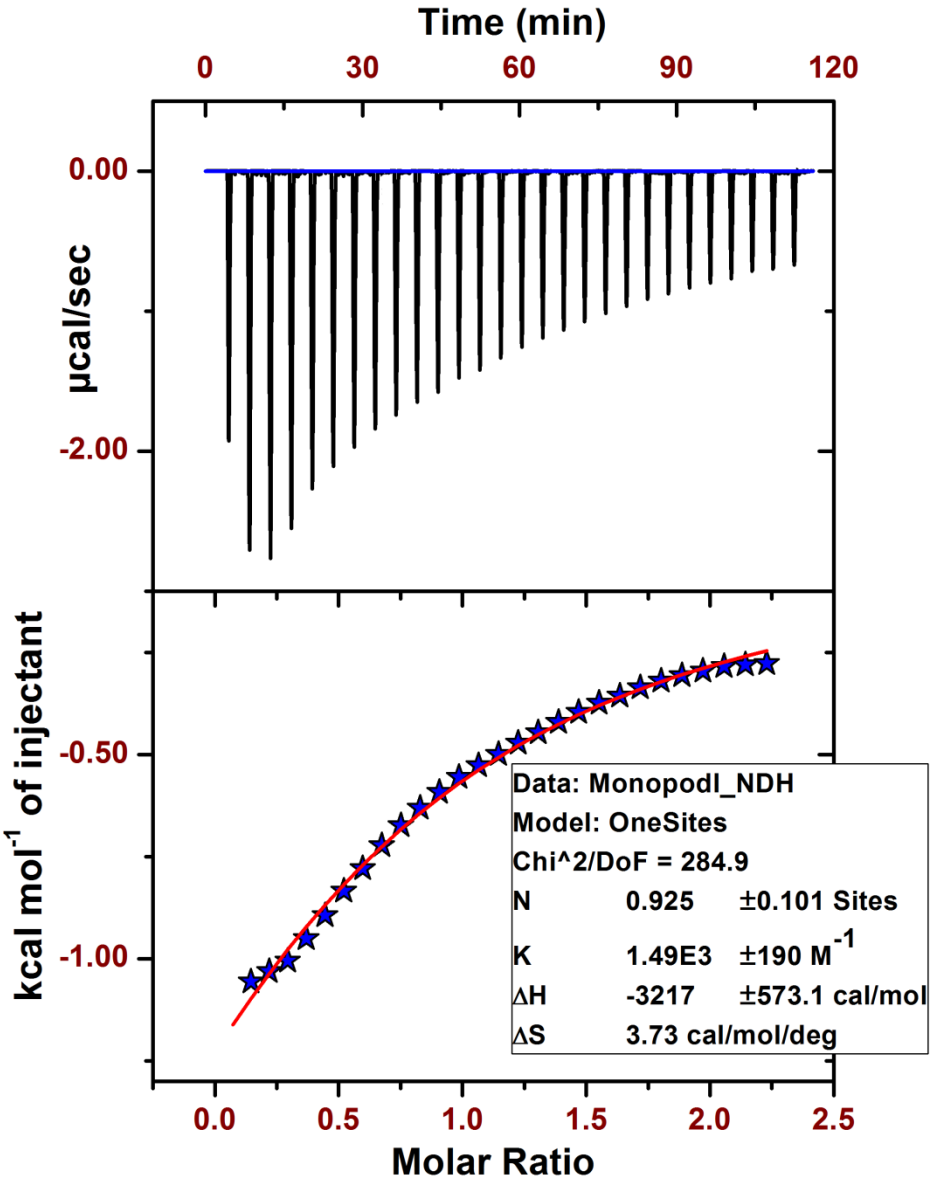


Figure 46S. ITC titration profiles of **1c** with I^-. Concentration; [1c] = 0.5459 mM, [I^-] = 5.76 mM.

References:

1. (a) SAINT and XPREP, version 5.1; Siemens Industrial Automation Inc.: Madison, WI, 1995; (b) Sheldrick, G. M.; SADABS, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany, **1997**.

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6. Hynes, M. J.; *J. Chem. Soc. Dalton. Trans.*, **1993**, 311-312.