Electronic Supplementary Material (ESI) for ChemComm.

Supplementary information

List of abbreviations

DMSO-d6	dimethyl sulfoxide
D_2O	deuterium oxide
TMS	tetramethylsilane
TBA	*n*-tetrabutylammonium
Me_2SO_2	dimethyl sulfone

General Methods. NMR spectra were recorded on a Bruker Avance III 500 spectrometer with working frequency 500.11 MHz for ^{1}H. The spectrometer was equipped with a BBFO probe. Low concentration experiments in D_2O were recorded on a Bruker Avance III HD 600 MHz spectrometer with working frequency 600.05 MHz for ^{1}H. The spectrometer was equipped with quadruple-resonance (^{1}H-^{31}P-^{13}C-^{15}N) inverse cryoprobe with cooled ^{1}H and ^{13}C preamplifiers. All experiments unless stated otherwise were recorded at 303.15 K. Experiments on 500 MHz spectrometer were measured with the zg30 pulse program as the flip angle of 30° allows for faster scan accumulation with shorter relaxation delay (d1 = 1s) and generally higher signal to noise ratio than 90° flip angle pulse with the same experimental time. For samples at milimolar concentrations typically 16 scans (t = 77 s) were enough to achieve sufficient signal to noise ratio. The influence of relaxation delay on quantitative studies was tested and it was found out that longer relaxation time is unnecessary for this system. Experiments in D_2O at micro and submicromolar concentrations were measured using water suppression pulse techniques. Either 1D ^{1}H sequence with presaturation (zgpr) or, to achieve flatter baseline, 1D ^{1}H NOE sequence with presaturation (noesygpps1d) and short mixing time of 10 μs was used. A 90° flip angle pulse was employed with appropriately longer relaxation delays (d1 = 5 or 10 s).

Materials. BU-1 and **BU-2**[11,12] were prepared as previously reported. Other compounds were purchased from Acros Organics or Sigma Aldrich and used as supplied. NMR solvents were purified with silver foil to remove traces of anions.

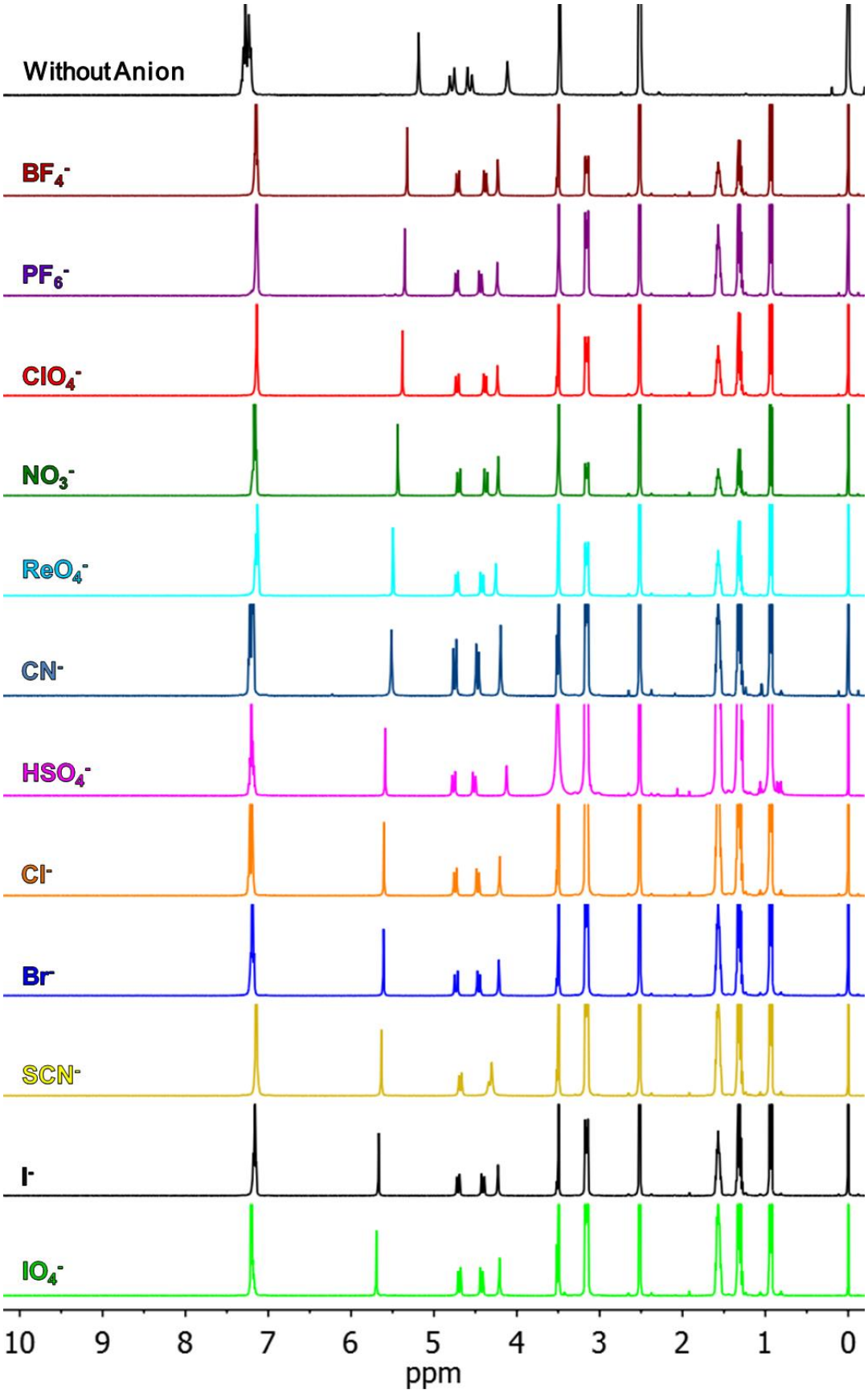


Figure S1. Full range of NMR spectra presented on Figure 2.

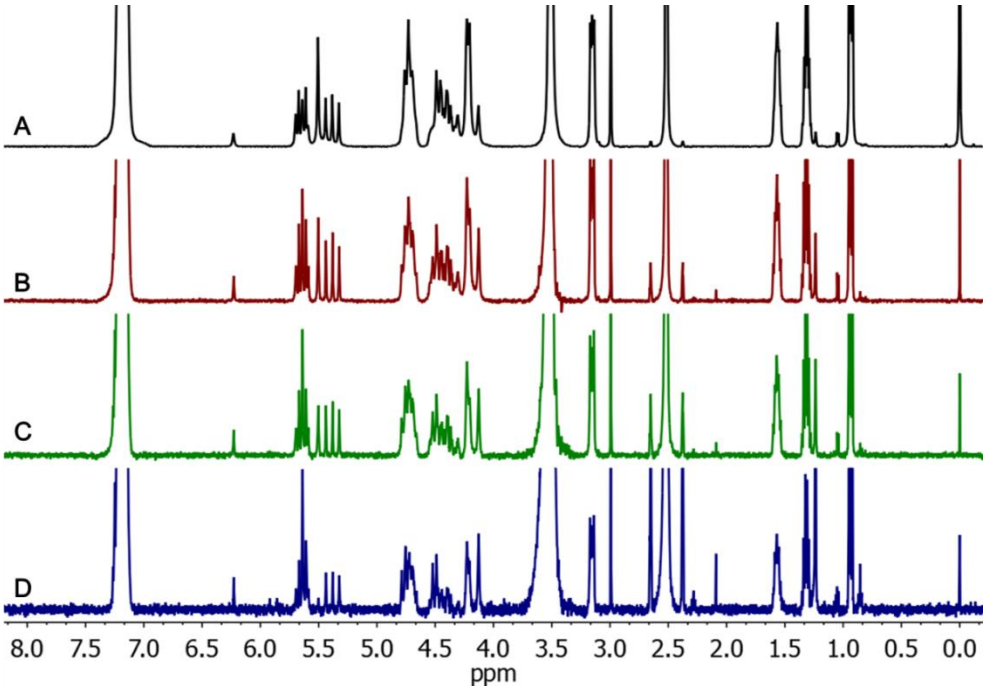
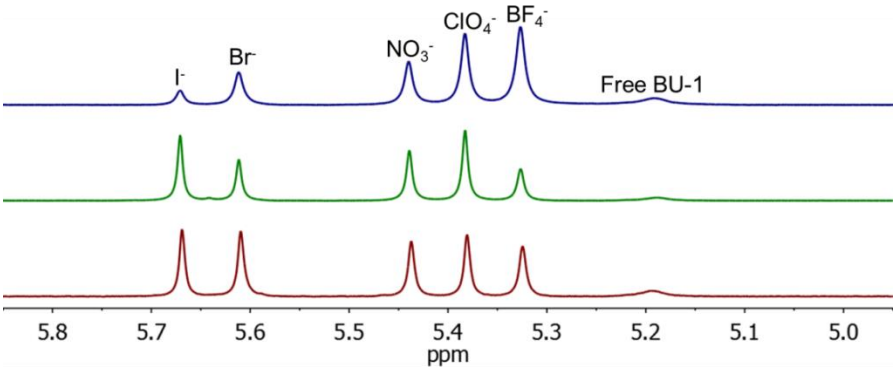


Figure S2. Full range of NMR spectra presented on Figure 3.



A⁻	$c_{teor.}$ [mM]	$c_{calc.}$ [mM]	Error [%]	$c_{teor.}$ [mM]	$c_{calc.}$ [mM]	Error [%]	$c_{teor.}$ [mM]	$c_{calc.}$ [mM]	Error [%]
BF_4^-	1.59	1.51	4.8	0.571	0.592	3.6	0.347	0.348	0.5
ClO_4^-	1.31	1.24	5.6	1.12	1.10	1.6	0.378	0.376	0.8
NO_3^-	0.829	0.789	4.8	0.872	0.802	7.9	0.359	0.357	0.3
Br^-	0.571	0.599	4.9	0.646	0.600	7.1	0.377	0.392	4.2
I^-	0.265	0.247	6.6	0.937	0.888	5.3	0.368	0.369	0.4

Figure S3. ^{1}H NMR spectra (500 MHz, 5 % D_2O - DMSO-d_6, 30°C, TMS) of three independent quantitative analysis of anions mixtures. The results are summarized in the table and color of individual spectra matches corresponding text in the table.

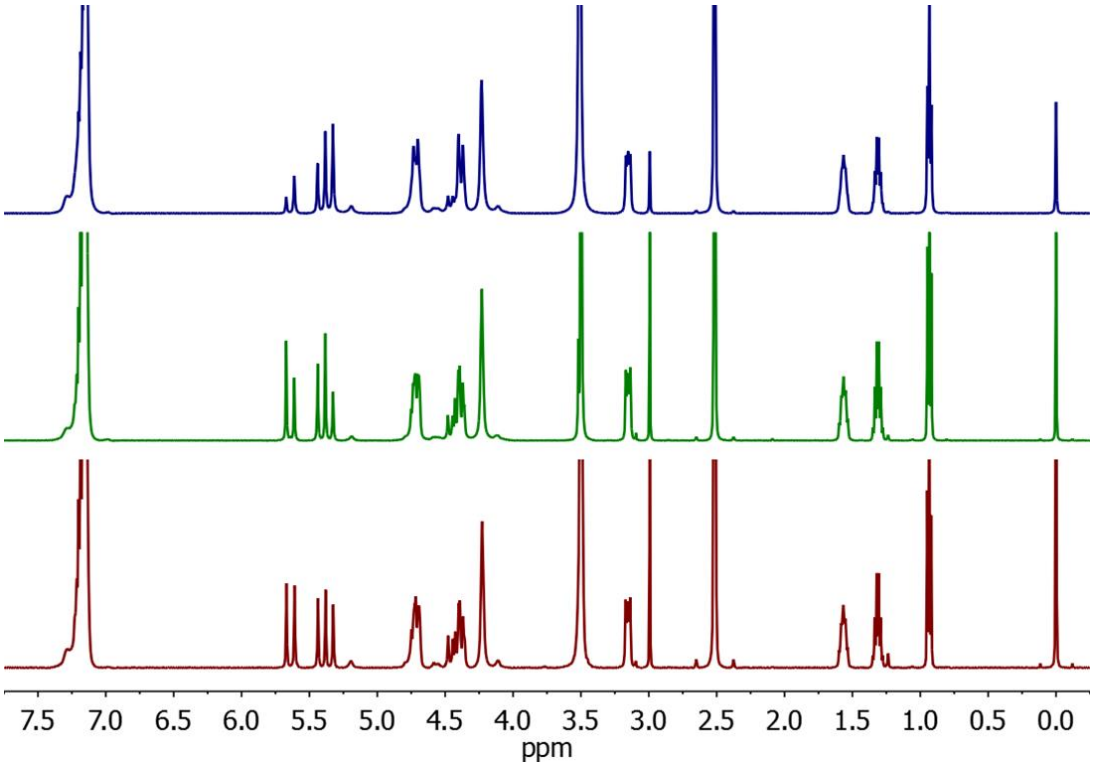


Figure S4. Full range of NMR spectra presented on Figure S3.

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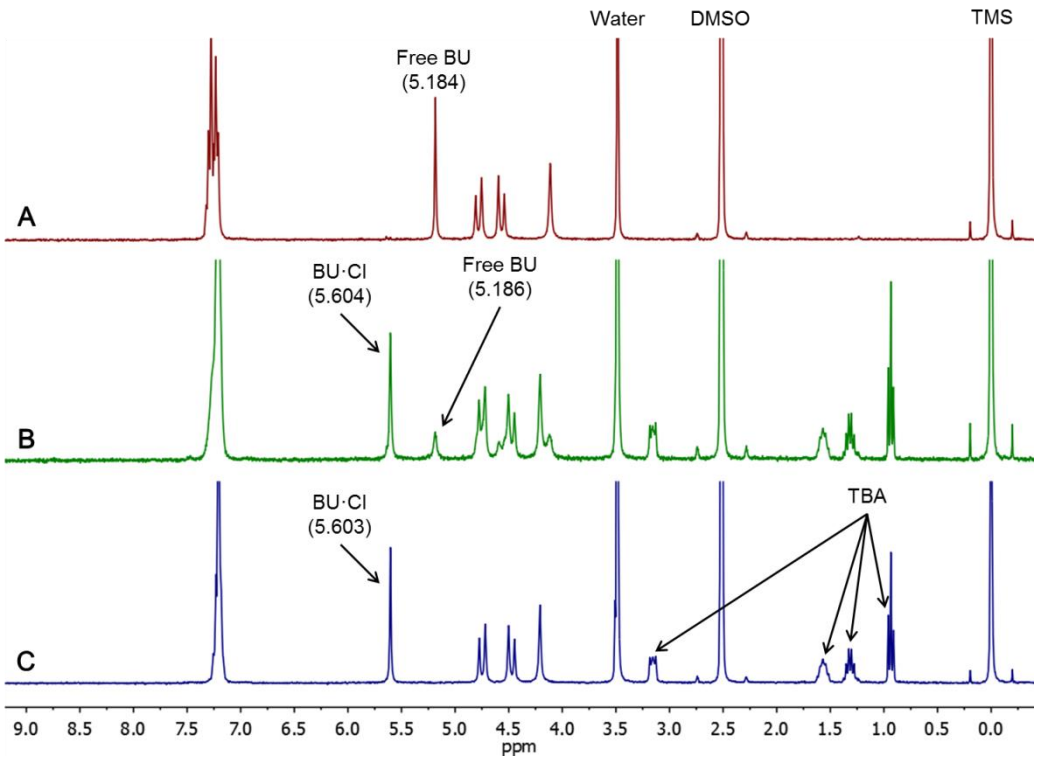

Figure S5. ^{1}H NMR spectra (500 MHz, 5 % D_2O - DMSO-d_6, 30°C, TMS) of A) free **BU-1** (c = 1×10^{-3} M) B) 0.65 eqv. C) 1.03 eqv. of TBACl.

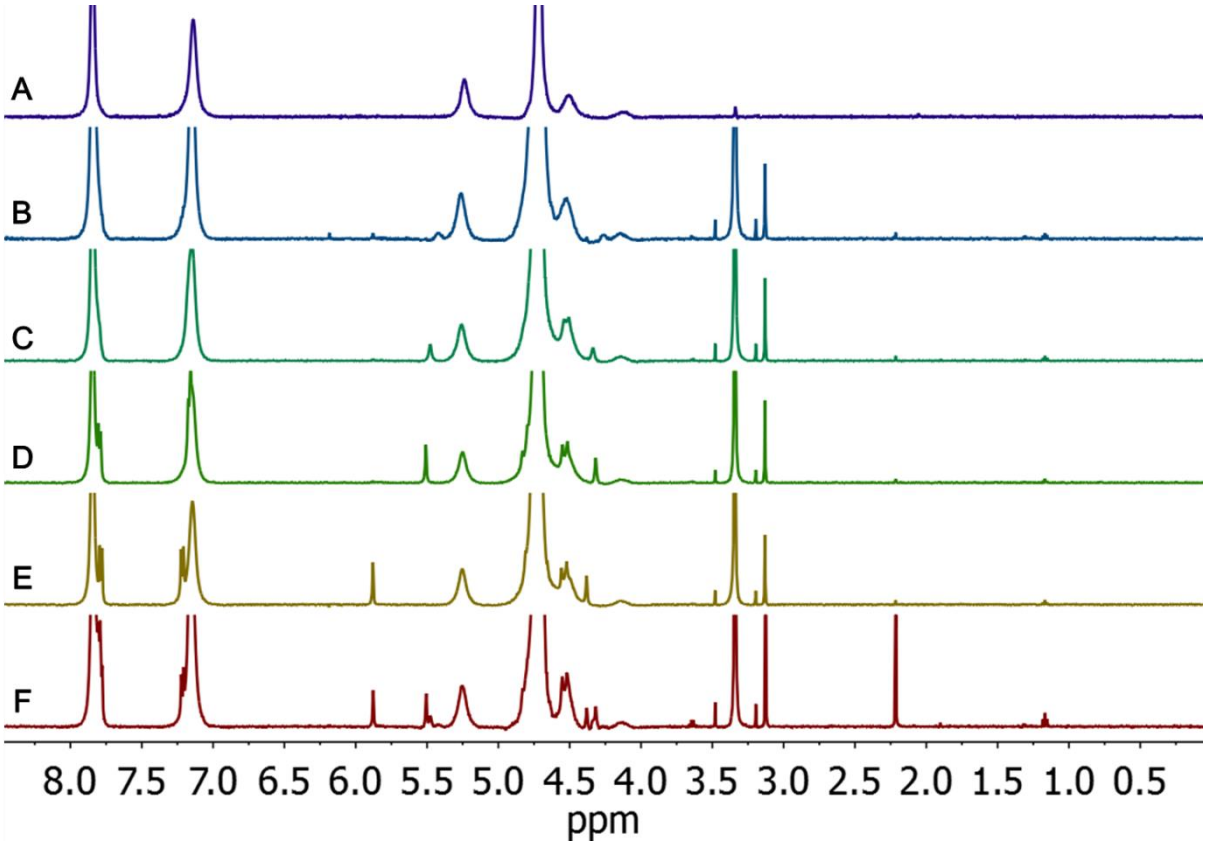

Figure S6. Full range of NMR spectra presented on Figure 5.

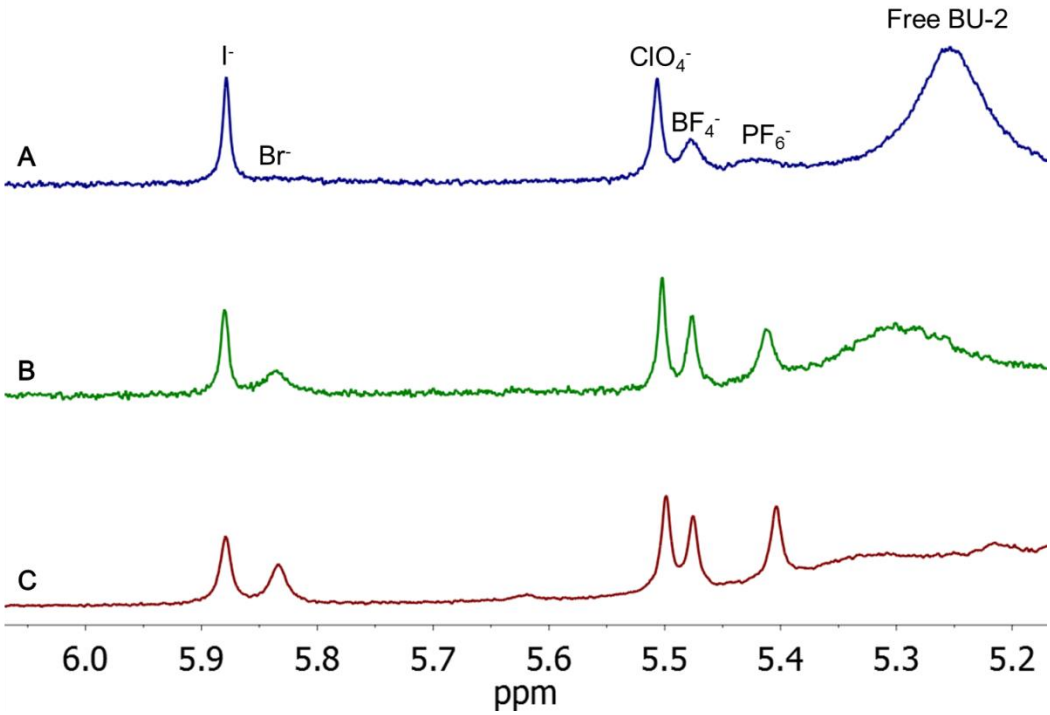

Figure S7. ^{1}H NMR spectra (500 MHz, D_2O, 20 mM K_2DPO_4, 5 – 30°C,) of **BU-2** - anion mixture (I^-, Br^-, BF_4^-, ClO_4^- and PF_6) at different temperatures A) 30 B) 15 and C) 5 °C. Signal of **BU-2**·I^- (5.879 ppm) was used to standardize chemical shifts at lower temperatures.

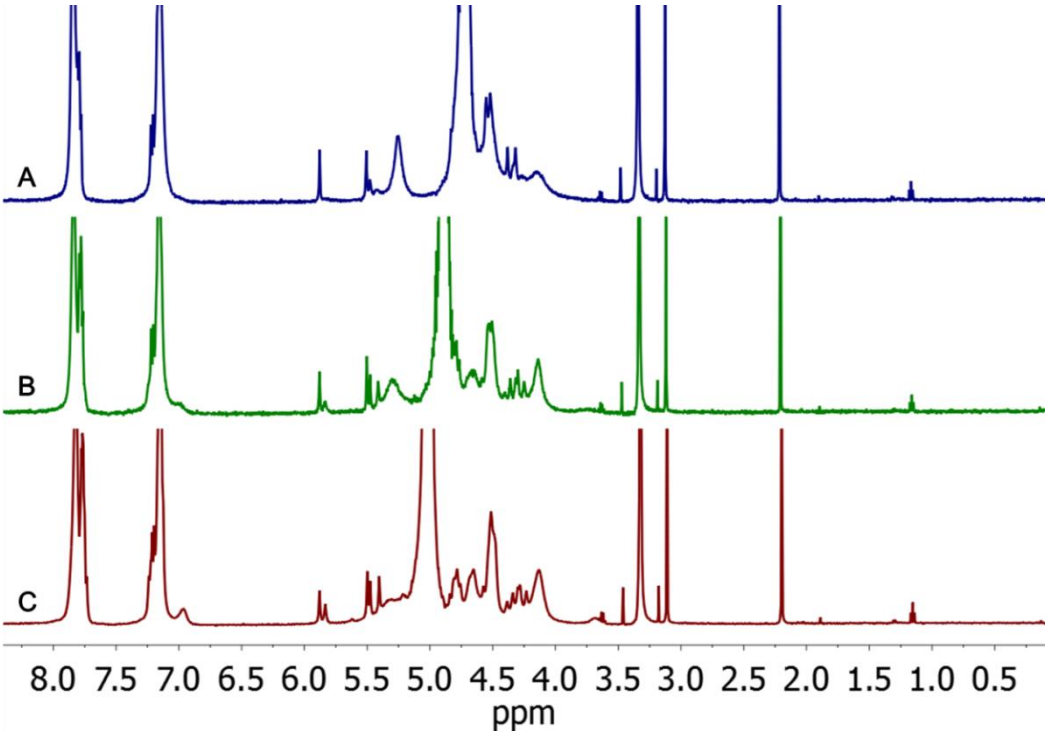

Figure S8. Full range of NMR spectra presented on Figure S7.

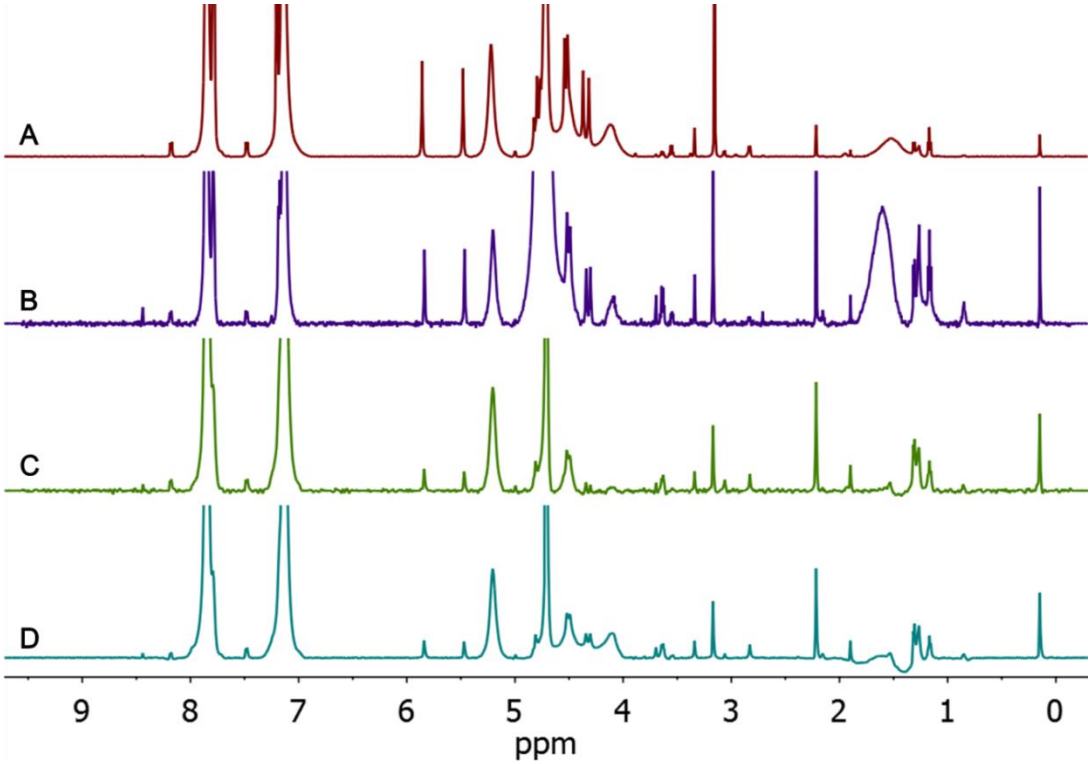

Figure S9. Full range of NMR spectra presented on Figure 6.

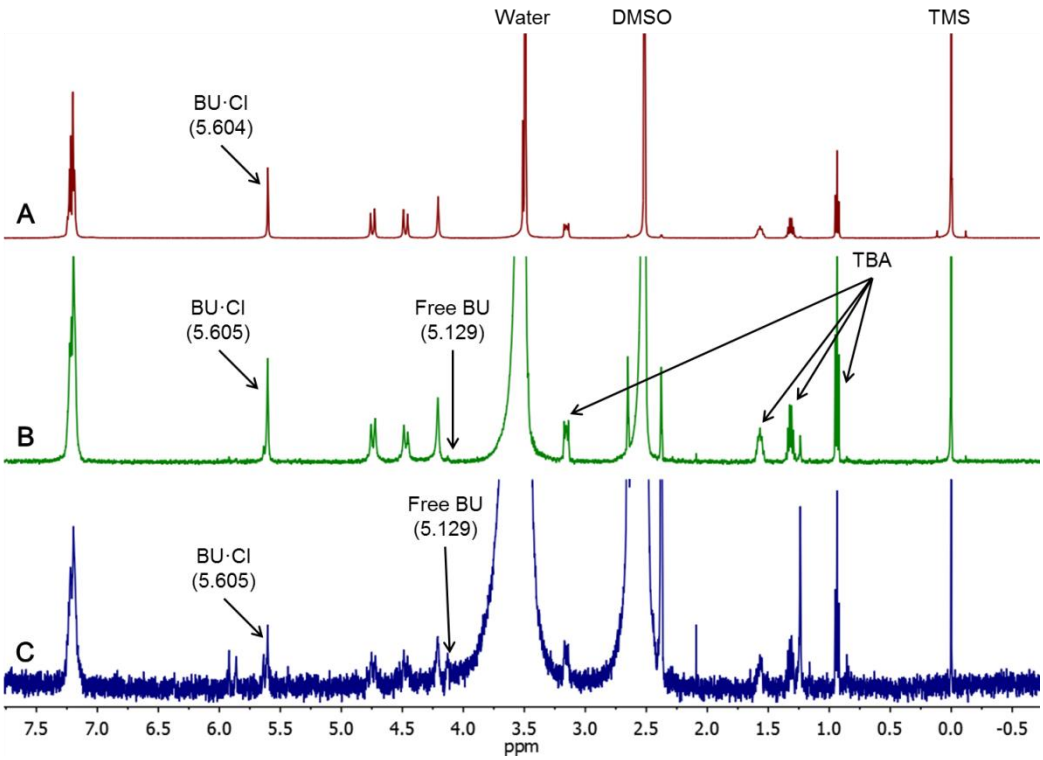

Figure S10. ^{1}H NMR spectra (500 MHz, 5 % D_2O - DMSO-d_6, 30°C, TMS) of **BU-1** and 1.03 eqv. TBACl A) $c_{(BU\text{-}1)} = 1 \times 10^{-3}$ M B) $c_{(BU\text{-}1)} = 1 \times 10^{-4}$ M and C) $c_{(BU\text{-}1)} = 1 \times 10^{-5}$ M.

Evaluation of affinity of BU-1 and anions which where used in quantitative NMR analysis in d_6-DMSO containing 5% D_2O

First we determined association constant for the nitrate-bambusuril complex to be 1×10^6 M^{-1} using isothermal titration calorimetry (ITC). Then we used competitive ^1H NMR to find out, that BF_4^- is the anion which is bound by bambusuril with the lowest affinity among all anions tested in quantitative analysis. The association constant of the BF_4^--BU-1 complex was calculated to be 2.2×10^5 M^{-1}

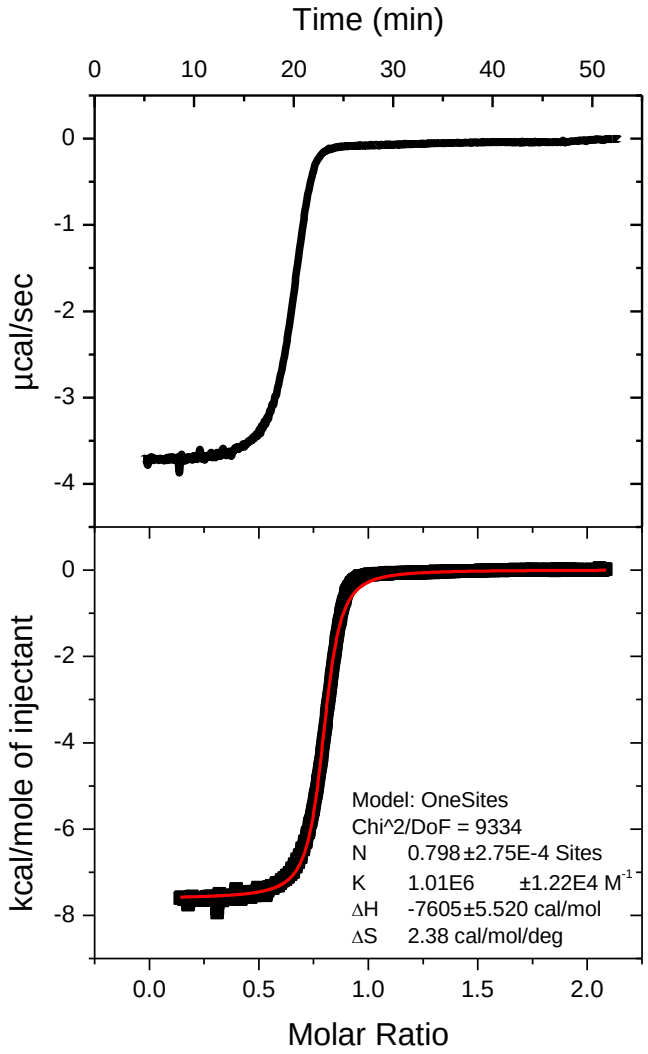

Figure S11. Isothermal titration calorimetry of NO_3^- binding to **BU-1** using VP-ITC microcalorimeter (Microcal, GE-Healthcare) at 30 °C in 5 % H_2O - DMSO. Top: Data obtained from a single injection of $TBANO_3$ solution (4.82 mM) to **BU-1** (0.499 mM). Bottom: Plot of the total heat released as a function of total ligand concentration for the titration shown in the upper panel. Integrated heat effects were analyzed by non-linear regression using a one site binding model (Microcal Origin 7). The red solid line represent least-squares fit of the data. Heats of dilution were subtracted from the end interval of titration using subtract straight line option.

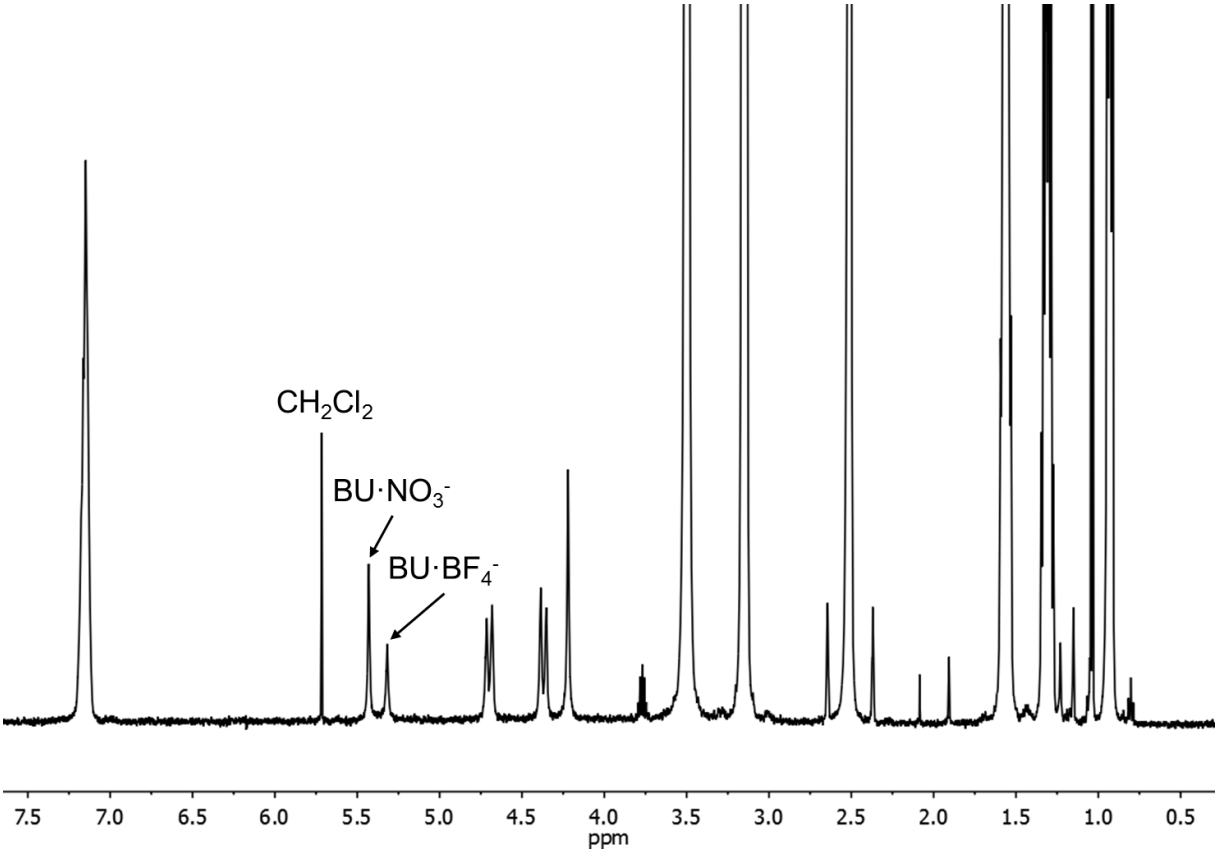

Figure S11. ^{1}H NMR spectra (500 MHz, 5 % D_2O - DMSO-d_6, 30°C) of competition experiment **BU-1** (c = 1.0 × 10^{-4} M), $TBABF_4$ (c = 1.3 × 10^{-3} M) $TBANO_3$ (c = 4.3 × 10^{-4} M)

$$BU{\cdot}BF_4^- + NO_3^- \rightleftharpoons BU{\cdot}NO_3^- + BF_4^-$$

$$K_{a(BF_4^-)} = K_{a(NO_3^-)} \div \frac{[BUNO_3^-] \times [BF_4^-]}{[BUBF_4^-] \times [NO_3^-]}$$

$$K_{a(BF_4^-)} = 1.1 \times 10^6 \div \frac{[5.98 \times 10^{-5}] \times [1.21 \times 10^{-3}]}{[3.98 \times 10^{-5}] \times [3.66 \times 10^{-4}]} = 2.2 \times 10^5\ M^{-1}$$