Benzimidazole-based anion receptors: tautomeric switching and selectivity

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Electronic supplementary information

Experimental

General procedures

Where necessary, solvents were purified prior to use. Anhydrous DMF puriss, over molecular sieves, was purchased from Fluka. Pyridine and triethylamine were distilled over KOH. Pyridine was used directly after distillation. Triethylamine was stored over KOH under a nitrogen atmosphere. All solvents and starting materials are commercial grade and used as purchased from chemical sources such as Sigma Aldrich and Fisher Scientific. Reagents obtained via literature procedures have been referenced accordingly. All reactions were performed using oven-dried glassware under a slight positive pressure of nitrogen or argon unless otherwise specified. Tetrabutylammonium and tetraethylammonium salts of the anions used for 1H NMR studies were dried thoroughly overnight on a high vacuum line. Dry tetrabutylammonium sulfate was obtained from a 50% (w/w) water solution removed by distillation to remove the water. The tetrabutylammonium sulfate crystals were then stored on a high vacuum line.

The 1H NMR (300 MHz) and 13C{1H} NMR (75 MHz) spectra were determined on Bruker AV300 and AC300 spectrometers. 1H NMR (400 MHz) and 13C NMR (100 MHz) spectra were determined on a Bruker AV400 spectrometer. Chemical shifts for 1H NMR are reported in parts per million (ppm), calibrated to the solvent peak set. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet. Chemical shifts for 13C{1H} NMR are reported in ppm, calibrated to the solvent peak set. Infra-red (IR) spectra were recorded on a Matterson Satellite (ATR). FTIR are reported in wavenumbers (cm⁻¹). Low resolution mass spectra were recorded on a Micromass Platform II Single Quadrupole mass spectrometer. High resolution mass spectra were recorded on a VG 70-250-SE normal geometry double focusing mass spectrometer by the
Mass Spectrometry Service at the University of Southampton. Melting points were recorded in open capillaries on a Gallenkamp melting point apparatus and are uncorrected.

**1H NMR Titration Method**

1.5 mL of a 0.01 M solution of receptor was prepared. Of this solution, 0.5 mL was added to an NMR tube, which was then sealed with an air tight suba seal. The remaining 1 mL of the receptor solution was used to prepare a 0.15 M solution of the tetrabutylammonium/tetraethylammonium salt of the anion. The anion/receptor solution was titrated into the NMR tube in aliquots and a 1H NMR taken after each addition. This allows the concentration of the anion in the NMR tube to increase whilst the concentration of receptor remains constant. Chemical shifts for each 1H NMR spectra were recorded in ppm and calibrated to the solvent peak set. The computer program WINEQNMRI [Hynes, 1993 #16] was then used to interpret the data to determine the binding constant(s).

**Job Plot method**

Two solutions were prepared; the first was a 3 mL, 0.01M solution of receptor and the second was a 3 mL, 0.01M solution of tetrabutylammonium (TBA)/ tetraethylammonium (TEA) salt of the anion. 0.5 mL of the receptor solution was added to an NMR tube. The amount of the receptor solution was then decreased by 0.05 mL and the amount of anion solution increased by 0.05 mL for each successive NMR tube until a 9:1 anion:receptor ratio was reached. A 1H NMR spectra was then taken for each of the ten NMR tubes and calibrated to the solvent peak set. This data was then used to produce a Job plot in accordance with the methods described by Job [Job, 1928 #15]. Plotting the molar fraction of the receptor against the values given by the formula; \[
\frac{\delta_{obs} - \delta_{int}}{\delta_{fin} - \delta_{int}} \times x_r
\]
where \(\delta_{obs}\) is the observed chemical shift, \(\delta_{int}\) is the initial chemical shift, \(\delta_{fin}\) is the final chemical shift and \(x_r\) is the molar fraction of the receptor.

**Dilution Studies**

A 0.54 M solution of receptor (0.5 mL) was prepared and added to an NMR tube, which was then sealed with an air tight suba seal. A solution of the NMR solvent mixture was then titrated into the NMR tube in 0.5 mL aliquots and a 1H NMR taken after each addition.
Receptor Synthesis

7-Nitrobenzimidazole: This was synthesised by a literature method. {Devlin, 1995 #1}

4-Aminobenzimidazole: A solution of 7-nitrobenzimidazole (0.20 g, 1.23 mM) with a Pd/C 10% catalyst (0.02 g) in DMF (5 mL) was stirred at room temperature under a hydrogen atmosphere for four hours. The palladium catalyst was then removed by filtration and the DMF was then removed under reduced pressure and the grey solid/oil was used immediately without purification in the next step of the reaction. Assumed 100 % yield. Reaction conditions adapted from another literature source. {Mewshaw, 1998 #2}

7-Aminoindole: A solution of 7-nitroindole (0.20 g, 1.23 mM) with a Pd/C 10% catalyst (0.02 g) in ethanol (10 mL) was stirred at room temperature under a hydrogen atmosphere for two hours. The palladium catalyst was then removed by filtration and the ethanol was then removed under reduced pressure and the white crystalline product was used immediately without purification in the next step of the reaction. Assumed 100 % yield. Reaction adapted from other literature sources. {Bell, 2007 #14; COMPANY, 2005 #13}

N-(1H-indol-7-yl)-1H-imidazole-1-carboxamide: A solution of carbonyldiimidazole (CDI) (1.50 g, 9.25 mM) and dichloromethane (50 mL) was stirred until the solution was clear. 7-Aminoindole (0.41 g, 3.08 mM) was then added in dichloromethane (5 mL) and allowed to stir overnight at room temperature. The white precipitate was then collected by filtration. It was not purified but used impure in further reactions. Approximate yield 72 - 82 %. {Andrews, 2011 #6}

1-Methyl-4-nitrobenzimidazole: Methyliodide (2.30 mL, 18.39 mM) was added dropwise to a stirring solution of 7-nitrobenzimidazole (1.0 g, 6.13 mM) in acetone (10 mL) and the solution was heated to 50 °C overnight. The yellow solid was formed isolated by filtration, washed with acetone (20 mL) and dried. The solid was then dissolved in water and an aqueous solution of sodium hydroxide added until a white precipitate had formed. The solid was isolated by filtration and washed with water (20 mL) and diethylether (20 mL). Yield 60%, 0.65 g; M.P.: 159 °C; 1H NMR: (400 MHz, DMSO-d₆): δ: 4.13 (s, 1 CH₃), 7.81 (t, J = 8.08 Hz, ArCH), 8.44 (dd, J₁ = 8.08 Hz, J₂ = 3.56 Hz, ArCH), 9.69 (s, 1 ArCH); 13C NMR: (100 MHz, DMSO-d₆): δ: 33.36 (CH₃), 120.6 (ArCH), 121.9 (ArCH), 125.2 (ArCH), 126.5 (ArC), 134.8 (ArC), 135.5 (ArC), 145.8 (ArCH); IR (film): ν = 1500, 1340
(conjugated nitro stretching); **LRMS (ESI⁺):** m/z 178 [M+H]+; **HRMS (ES⁺):** m/z: act: 178.0612 [M+H]+ cal: 178.0611 [M+H]+. Although not by this method this compound has previously been synthesized by a number of different methods. {Bella, 2008 #8; Leandri, 1955 #9; Megger, 2010 #7; Pappalardo, 1975 #12; Reddy, 1979 #10; Simonov, 1970 #11}

**1-Methyl-4-aminobenzimidazole:** A solution of 7-nitrobenzimidazole (0.33 g, 1.84 mM) with a Pd/C 10% catalyst (0.03 g) in ethanol (20 mL) was stirred at room temperature under a hydrogen atmosphere for four hours. The palladium catalyst was then removed by filtration and the ethanol was then removed under reduced pressure and the while crystalline product was used immediately without purification in the next step of the reaction. Assumed 100 % yield. Reaction adapted from another literature source. {Sun, 2004 #4}

**Receptor 1:** Pentafluorophenylisocyanate (0.35 mL, 2.70 mM) was added to a stirred solution of 7-aminobenzimidazole (0.33 g, 2.45 mM) in dry pyridine (10mL) and the mixture was heated at 50 °C overnight. The solution was then taken to dryness and the product recrystalised from hot methanol. The white solid was then collected by filtration and dried under reduced pressure. **Yield 76%, 0.64 g; M.P.:** > 250 °C; **¹H NMR:** (400 MHz, DMSO-d₆): δ: 7.10-7.17 (m, 2 ArCH), 7.82 (d, J = 7.08 Hz, ArCH), 8.22 (s, 1 ArCH), 9.24 (s, NH urea), 9.31 (s, NH urea), 12.54 (s, NH imidazole); **¹³C NMR:** (100 MHz, DMSO-d₆): δ: 105.7 (ArCH), 108.6 (ArCH), 123.0 (ArCH), 130.2 (ArC), 133.2 (ArC), 133.3 (ArC), 140.6 (ArCH), 150.7 (CO); **IR (film):** ν = 3230 (imidazole NH stretching) , 3080 (urea NH stretching), 1650 (urea CO stretching); **LRMS (ESI⁺):** m/z 343 [M+H]+; **HRMS (ES⁺):** m/z: act: 343.0615 [M+H]+ cal: 343.0613 [M+H]+.

**Receptor 2:** Hexylisocyanate (0.39 mL, 2.70 mM) was added to a stirred solution of 7-aminobenzimidazole (0.33 g, 2.45 mM) in dry pyridine (10mL) and the mixture heated at 110 °C overnight. The solution was then taken to dryness and the product recrystalised from hot ethylacetate. The white solid was then collected by filtration and dried under reduced pressure. **Yield 46%, 0.30 g; M.P.:** 139 °C; **¹H NMR:** (300 MHz, DMSO-d₆): δ: 0.87 (t, J = 6.60 Hz, CH₃), 1.28-1.43 (m, 4 CH₂), 3.10 (dd, J₁ = 12.45 Hz, J₂ = 6.60 Hz, CH₂), 6.70-7.05 (m, 2 ArCH, NH urea), 7.86 (dd, J₁ = 6.96 Hz, J₂ = 2.22 Hz, ArCH), 8.13 (s, 1 ArCH), 8.53 (s, NH urea), 12.40 (s, NH imidazole); **¹³C NMR:** (75 MHz, DMSO-d₆): δ: 13.9 (CH₃), 22.1 (CH₂), 26.1 (CH₂), 29.7 (CH₂), 31.0 (CH₂), 38.9 (CH₂), 103.9 (ArCH), 107.8 (ArCH), 122.9
Receptor 3: A solution of 4-aminobenzimidazole (0.20 g, 1.23 mM) in dichloremethane (10 mL) was added to a stirring solution of CDI (0.60 g, 3.70 mM) in dichloromethane (10 mL). The mixture was stirred at room temperature under nitrogen for 4 hrs. A pale lilac solid was isolated by filtration. This solid was then dissolved in dry pyridine (10 mL) and added to a stirring solution of 7-aminobenzimidazole (0.20 g, 1.23 mM) in dry pyridine (10 mL). The solution was then heated to 65 ºC overnight. A grey solid was then removed by filtration and washed with dichloromethane (20 mL) and dried under reduced pressure. Yield 45 %, 0.16 g; M.P.: 164 ºC; $^{1}$H NMR: (300 MHz, DMSO-d$_6$): 7.12-7.13 (m, 2 ArCH), 7.95 (br s, ArCH), 8.19 (s, 1 ArCH), 9.82 (s, NH urea), 12.46 (s, NH imidazole); $^{13}$C NMR: (100 MHz, DMSO-d$_6$): δ: 107.7 (ArCH), 112.9 (ArCH), 124.5 (ArCH), 128.1 (ArC), 128.4 (ArC), 133.5 (ArC), 140.1 (ArCH), 152.7 (CO); IR (film): ν = 3260 (imidazole NH stretching), 3080 (urea NH stretching), 1640 (urea CO stretching); LRMS (ESI$^+$): m/z 293 [M+H]$^+$; HRMS (ES$^+$): m/z: act: 293.1146 [M+H]$^+$ cal: 293.1145 [M+H]$^+$.

Receptor 4: Triphosgene (0.55 g, 1.84 mM) was added portionwise to a stirred solution of 1-methyl-4-aminobenzimidazole (0.27 g, 1.84 mM) in dichloromethane (20 mL) and sat. NaHCO$_3$ (20 mL) overnight. A white solid was then isolated from the reaction mixture by filtration which was shown to be a first crop of the product. The organic phase was then washed with water (2 x 40 mL), dried with magnesium sulfate and the solvent removed under reduced pressure. The yellow solid obtained was recrystalised from methanol to yield a second crop of product. Yield 42 %, 0.12 g; M.P.: 132 ºC; $^{1}$H NMR: (400 MHz, DMSO-d$_6$): δ: 3.83 (s, J = 6.60 Hz, CH$_3$), 7.14-7.22 (m, 2 ArCH), 8.01 (d, J = 7.56 Hz, ArCH), 8.16 (s, 1 ArCH), 9.85 (s, NH urea); $^{13}$C NMR: (100 MHz, DMSO-d$_6$): δ: 30.8 (CH$_3$), 103.4 (ArCH), 109.4 (ArCH), 122.9 (ArCH), 131.3 (ArC), 133.8 (ArC), 134.8 (ArC), 142.8 (ArCH), 152.8 (CO); IR (film): ν = 3060 (urea NH stretching), 1690 (urea CO stretching); LRMS (ESI$^+$): m/z 321 [M+H]$^+$; HRMS (ES$^+$): m/z: act: 321.1460 [M+H]$^+$ cal: 321.1458 [M+H]$^+$.
**Receptor 5:** Methyl-4-aminobenzimidazole (0.20 g, 1.35 mM) and N-(1H-indol-7-yl)-1H-imidazole-1-carboxamide (0.31 g, 1.35 mM) were dissolved in chloroform (30 mL), triethylamine (0.3 mL) and DMF (1 mL). The mixture was then heated to 70 °C overnight with stirring. The solution was allowed to cool and water (30 mL) and hexane (30 mL) were added. The white precipitate formed was isolated by filtration and titurated in MeOH (10 mL) for 15 mins. The white solid was then isolated again by filtration and dried under reduced pressure. **Yield** 27 %, 0.11 g; **M.P.:** 103 °C (decomposed); **¹H NMR:** (300 MHz, DMSO-d₆): δ: 3.85 (s, CH₃), 6.45 (dd, J₁ = 2.94 Hz, J₂ = 1.83 Hz ArCH), 6.96 (t, J = 7.68 Hz, ArCH), 7.17-7.31 (m, 4 ArCH), 7.35 (t, J = 2.55 Hz, ArCH), 8.01 (dd, J₁ = 7.32 Hz, J₂ = 1.83 Hz, ArCH), 8.19 (s, 1 ArCH), 8.88 (s, NH urea), 9.29 (s, NH urea), 10.57 (s, NH indole); **¹³C NMR:** (100 MHz, DMSO-d₆): δ: 30.8 (CH₃), 101.6 (ArCH), 103.4 (ArCH), 108.5 (ArCH), 112.8 (ArCH), 115.6 (ArCH), 119.1 (ArCH), 123.0 (ArCH), 123.9 (ArC), 125.2 (ArCH), 128.5 (ArC), 129.1 (ArC), 131.1 (ArC), 133.3 (ArC), 134.6 (ArC), 142.9 (ArCH), 152.7 (CO); **IR (film):** ν = 3270 (indole NH stretching), 3010 (urea NH stretching), 1640 (urea CO stretching); **LRMS (ESI⁺):** m/z 306 [M+H]+; **HRMS (ES⁺):** m/z: act: 306.1349 [M+H]+ cal: 306.1349 [M+H]+.
**NMR data**

Figure S1 $^1$H NMR spectrum of compound 1-methyl-4-nitrobenzimidazole in DMSO-$d_6$.

Figure S2 $^{13}$C NMR spectrum of compound 1-methyl-4-nitrobenzimidazole in DMSO-$d_6$. 
Figure S3 $^1$H NMR spectrum of compound 1 in DMSO-$d_6$.

Figure S4 $^{13}$C NMR spectrum of compound 1 in DMSO-$d_6$. 
Figure S5 $^1$H NMR spectrum of compound 2 in DMSO-$d_6$.

Figure S6 $^{13}$C NMR spectrum of compound 2 in DMSO-$d_6$. 
**Figure S7** $^1$H NMR spectrum of compound 3 in DMSO-$d_6$.

**Figure S8** $^{13}$C NMR spectrum of compound 3 in DMSO-$d_6$. 
Figure S9 $^1$H NMR spectrum of compound 4 in DMSO-$d_6$.

Figure S10 $^{13}$C NMR spectrum of compound 4 in DMSO-$d_6$. 
Figure S11 $^1$H NMR spectrum of compound 5 in DMSO-$d_6$.

Figure S12 $^{13}$C NMR spectrum of compound 5 in DMSO-$d_6$. 
**Variable Temperature $^{19}$F + $^1$H NMR**

Figure S13 $^{19}$F NMR spectra of compound 1 in DMSO-$d_6$/H$_2$O 0.5% at variable temperatures.

Figure S14 $^1$H NMR spectra of compound 1 in DMSO-$d_6$/H$_2$O 0.5% at variable temperatures.
**Dilution Study Data**

Figure S15 Dilution study of compound 1 in DMSO-$d_6$/H$_2$O 0.5%.

Figure S16 Dilution study of compound 2 in DMSO-$d_6$/H$_2$O 0.5%.
Titration data

2D NMR

Figure S17 Full HMBC NMR spectrum of compound 1 in DMSO-d$_6$/H$_2$O 0.5\%.
Figure S18 Expansion of HMBC NMR spectrum of compound 1 in DMSO-$d_6$/H$_2$O 0.5%.
Figure S19 Full HMBC NMR spectrum of compound 1 and 0.5 equivalents of TBA$_2$SO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
Figure S20 Expansion of HMBC NMR spectrum of compound 1 and 0.5 equivalents of TBA₂SO₄ in DMSO-	extit{d}_6/H₂O 0.5%.
Figure S21 Full HMBC NMR spectrum of compound 1 and 1.0 equivalents of TBA₂SO₄ in DMSO-
$\text{d}_6$/H₂O 0.5%.
Figure S22 Expansion of HMBC NMR spectrum of compound 1 and 1.0 equivalents of TBA$_2$SO$_4$ in DMSO-$d_6$/$H_2$O 0.5%. 
Figure S23 Full HMBC NMR spectrum of compound 1 and 2.0 equivalents of TBA$_2$SO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
Figure S24 Expansion of HMBC NMR spectrum of compound 1 and 2.0 equivalents of TBA$_2$SO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
Figure S25 Expansion stack plot of $^1$H NMR from HMBC NMR spectrum of compound 1 with equivalents of TBA$_2$SO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
Figure S26 Stack plot of $^{19}$F NMR spectrum of compound 1 (a) with 0.45 equivalents of TBA$_2$SO$_4$ at 298 K (b), 1.10 equivalents of TBA$_2$SO$_4$ at 298 K (c), 1.00 equivalents of TBAOBz at 298 K (d) and 1.00 equivalents of TBACL at 333 K (e) in DMSO-$d_6$/$\text{H}_2\text{O}$ 0.5%. 
### Change in Chemical Shift

#### Figure S27
NMR titration of compound 1 vs. TBAOAc in DMSO-$d_6$/$H_2$O 0.5%.

#### Figure S28
$^1$H NMR stack plot of compound 1 vs. TBAOAc in DMSO-$d_6$/$H_2$O 0.5%.
Figure S29 NMR titration of compound 1 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.

Figure S30 NMR titration of compound 1 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5% at 333 K.
Figure S31 NMR titration of compound 1 vs. TBAH₂PO₄ in DMSO-d₆/H₂O 0.5%.

Figure S32 ¹H NMR stack plot of compound 1 vs. TBAH₂PO₄ in DMSO-d₆/H₂O 0.5%.
**Figure S33** $^1$H NMR stack plot of compound 1 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/$H_2$O 0.5%.

**Figure S34** $^1$H NMR stack plot of compound 1 vs. TBA$_2$SO$_4$ in DMSO-$d_6$/$H_2$O 0.5%.
**Figure S35** $^1$H NMR stack plot of compound 1 vs. TBA$_2$SO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.

**Figure S36** NMR titration of compound 1 vs. TBAHSO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
**Figure S37** NMR titration of compound 1 vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%.

**Figure S38** $^1$H NMR stack plot of compound 1 vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%.
Figure S39 $^1$H NMR stack plot of compound 1 vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%.

Figure S40 NMR titration of compound 1 vs. TEA$\text{HCO}_3$ in DMSO-$d_6$/H$_2$O 0.5%.
**Figure S41** NMR titration of compound 1 vs. TBANO₃ in DMSO-d₆/H₂O 0.5%.

**Figure S42** NMR Job Plot of compound 1 vs. TBAOAc in DMSO-d₆/H₂O 0.5%.
**Figure S43** NMR titration of compound 2 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.

**Figure S44** NMR titration of compound 2 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
**Figure S45** Expanded NMR titration of compound 2 vs. TBAH₂PO₄ in DMSO-øre/H₂O 0.5%.

**Figure S46** ¹H NMR stack plot of compound 2 vs. TBAH₂PO₄ in DMSO-øre/H₂O 0.5%.
**Figure S47** $^1$H NMR stack plot of compound 2 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.

**Figure S48** NMR titration of compound 2 vs. TEA$\text{HCO}_3$ in DMSO-$d_6$/H$_2$O 0.5%.
**Figure S49** NMR titration of compound 2 vs. TBAHSO₄ in DMSO-d₆/H₂O 0.5%.

**Figure S50** NMR titration of compound 2 vs. TBAOAc in DMSO-d₆/H₂O 0.5%.
Figure S51 NMR titration of compound 2 vs. TBA₂SO₄ in DMSO-d₆/H₂O 0.5%.

Figure S52 ¹H NMR stack plot of compound 2 vs. TBA₂SO₄ in DMSO-d₆/H₂O 0.5%.
Figure S53 $^1$H NMR stack plot of compound 2 vs. TBA$_2$SO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.

Figure S54 $^1$H NMR stack plot of compound 2 vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%. 

Figure S55 NMR titration of compound 3 vs. TBAOAc in DMSO-\(d_6\)/H\(_2\)O 0.5%.

Figure S56 NMR titration of compound 3 with 2 equivalents of HPF\(_6\) vs. TBAOAc in DMSO-\(d_6\)/H\(_2\)O 0.5%.
Figure S57 NMR titration of compound 3 vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%.

Figure S58 NMR titration of compound 3 with 2 equivalents of HPF$_6$ vs. TBAOBz in DMSO-$d_6$/H$_2$O 0.5%.
Figure S59 NMR titration of compound 3 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.

Figure S60 NMR titration of compound 3 with 2 equivalents of HPF$_6$ vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.
Figure S61 NMR titration of compound 3 vs. TBANO₃ in DMSO-d₆/H₂O 0.5%.

Figure S62 NMR titration of compound 3 with 2 equivalents of HPF₆ vs. TBANO₃ in DMSO-d₆/H₂O 0.5%.
**Figure S63** NMR titration of compound 3 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.

**Figure S64** $^1$H NMR stack plot of compound 3 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
Figure S65 NMR titration of compound 3 with 2 equivalents of HPF$_6$ vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.

Figure S66 NMR titration of compound 3 vs. TEA$\mathrm{HCO}_3$ in DMSO-$d_6$/H$_2$O 0.5%.
Figure S67 NMR titration of compound 3 with 2 equivalents of HPF₆ vs. TEAHCO₃ in DMSO-d₆/H₂O 0.5%.

Figure S68 "H NMR stack plot of compound 3 vs. TBA₂SO₄ in DMSO-d₆/H₂O 0.5%.
Figure S69  NMR titration of compound 3 with 2 equivalents of HPF₆ vs. TBA₂SO₄ in DMSO-\textit{d}_6/H₂O 0.5%.

Figure S70  $^1$H NMR titrations of compound 4 vs. TBA/TEA salts of the anion in DMSO-\textit{d}_6/H₂O 0.5%, following the urea NH.
Figure S71 NMR titration of compound 5 vs. TBACl in DMSO-$d_6$/H$_2$O 0.5%.

Figure S72 NMR titration of compound 5 vs. TBAH$_2$PO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
Figure S73 NMR titration of compound 5 vs. TEA$\text{HCO}_3$ in DMSO-$d_6$/H$_2$O 0.5%.

Figure S74 NMR titration of compound 5 vs. TBA$_2$SO$_4$ in DMSO-$d_6$/H$_2$O 0.5%.
**Figure S75** NMR titration of compound 5 vs. TBANO₃ in DMSO-ᴅ/H₂O 0.5%.

**Figure S76** NMR titration of compound 5 vs. TBAOAc in DMSO-ᴅ/H₂O 0.5%.
Figure S77 NMR titration of compound 5 vs. TBAOBz in DMSO-$d_6$/$H_2O$ 0.5%.
**Binding Studies**

\[ K_a = 130 \text{ M}^{-1} \]  Error = >10 %

**Figure S78** NMR titration of compound 2 vs. TEAHCO\(_3\) in DMSO-\(d_6\)/H\(_2\)O 0.5%.

\[ K_a = 422 \text{ M}^{-1} \]  Error = 4 %

**Figure S79** NMR titration of compound 5 vs. TEAHCO\(_3\) in DMSO-\(d_6\)/H\(_2\)O 0.5%.