Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

Nitrate anion templated assembly of a [2]rotaxane for selective nitrate recognition in aqueous solvent media

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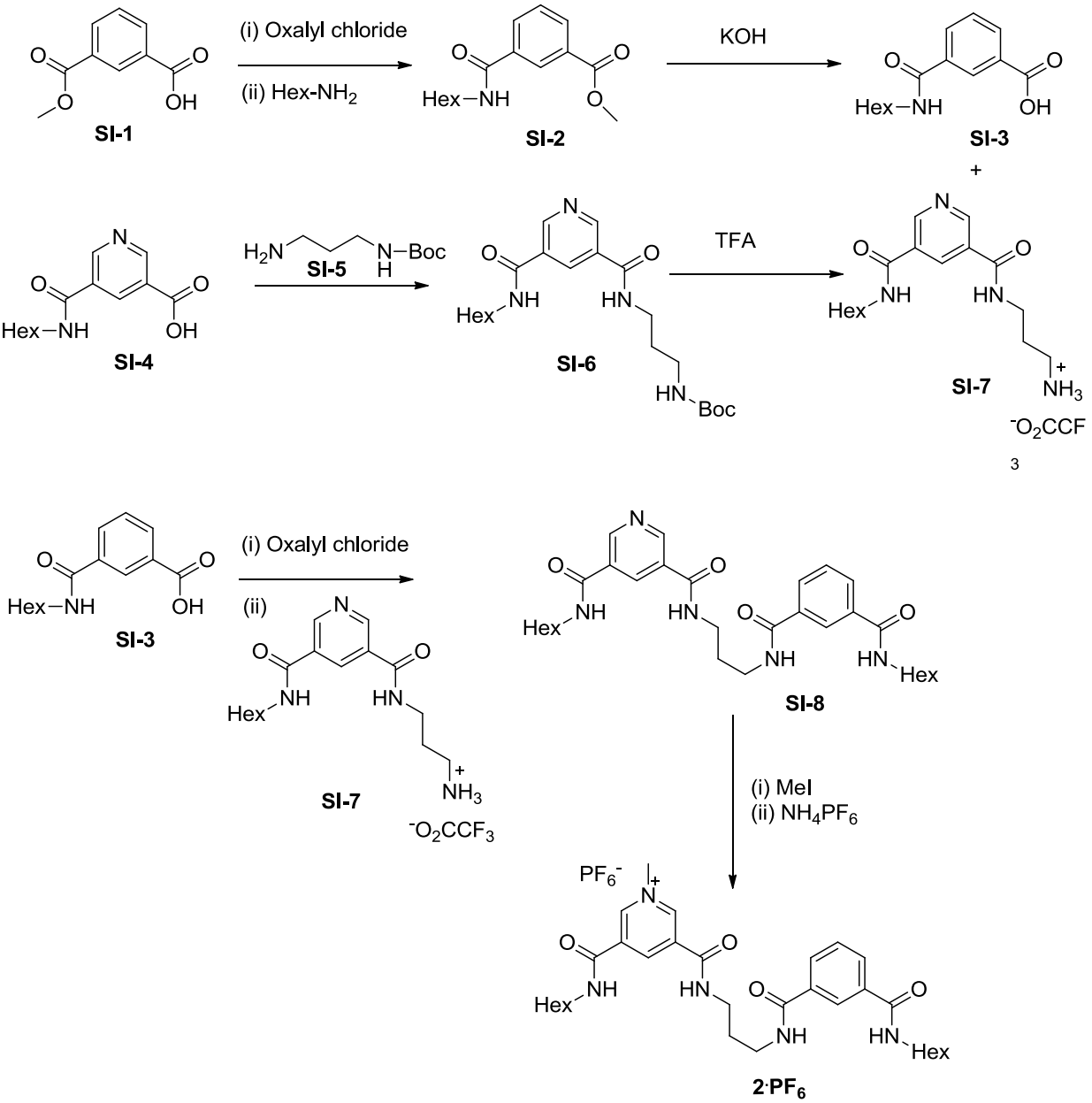
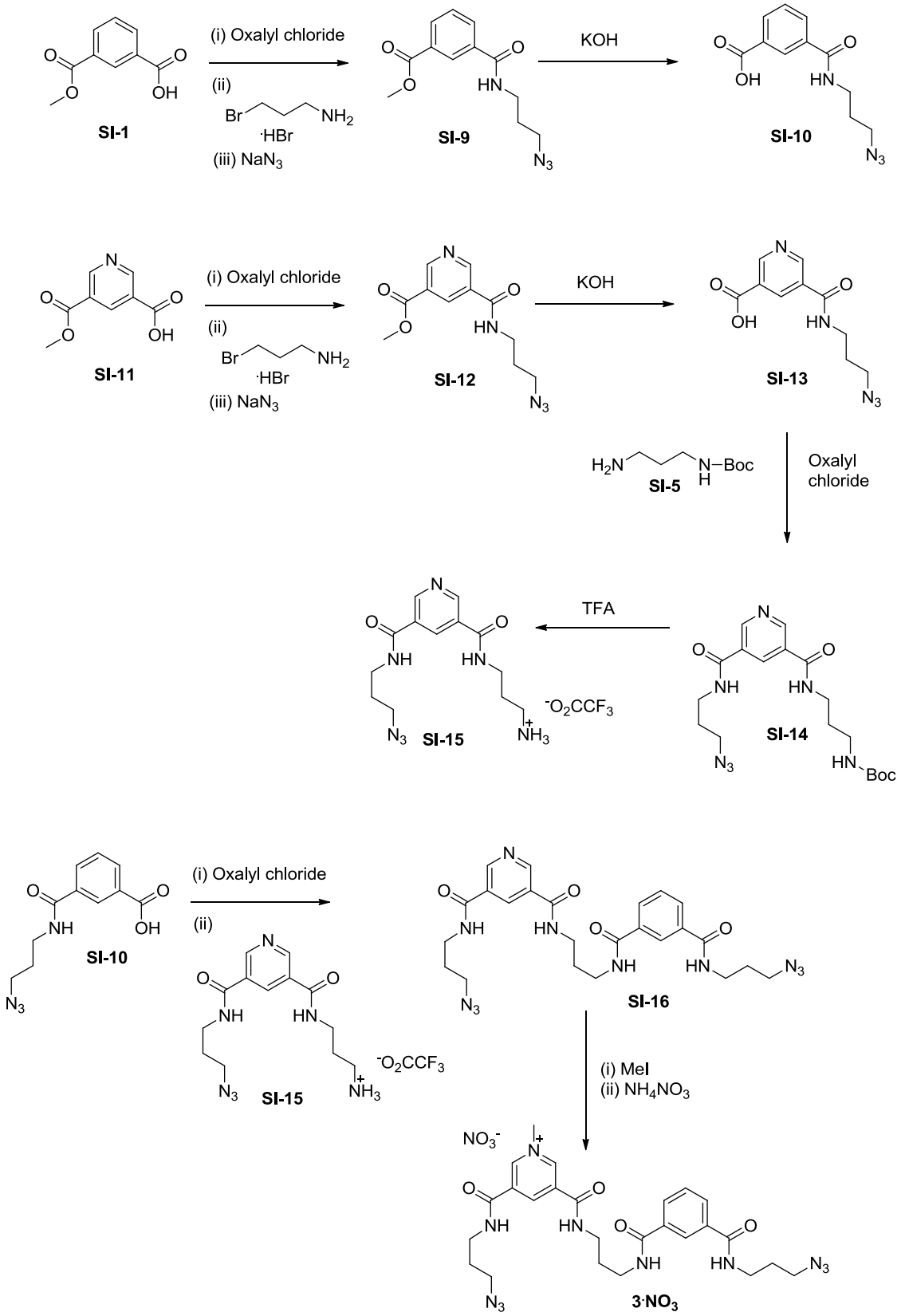
Contents

All reagents and solvents were purchased from commercial sources and used without further purification. Where necessary, solvents were dried by passing through a MBraun MPSP-800 column and degassed with nitrogen. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Size exclusion chromatography was carried out using Biobeads SX-3, with $CHCl_3$ as the eluent. Where mixtures of solvents were used, ratios reported are by volume. Triethylamine was distilled from and stored over potassium hydroxide. NMR spectra were recorded on Varian Mercury 300, Bruker AVII 500 (with cryoprobe) and Bruker AVIII 500 spectrometers. Mass spectra were carried out on a Waters Micromass LCT and Bruker microTOF spectrometers.

Section 1 – Synthesis and characterisation



Scheme SI-1 – Synthesis of thread **2·PF$_6$**



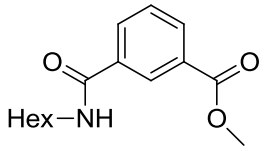
Scheme SI-2 – Synthesis of axle precursor **3·NO$_3$**

General procedure for acid chloride synthesis.

To convert carboxylic acids to their acid chloride derivatives the following general procedure was used. To a suspension of acid (1 mmol) in dry CH_2Cl_2 (10 mL) was added oxalyl chloride (2 mmol) dropwise under N_2. A drop of DMF (~0.01 mL, cat.) was added and the reaction refluxed at 40 °C under N_2 until the solution became homogeneous. The solvent was removed *in vacuo* to leave a yellow solid. This was immediately re-dissolved in dry CH_2Cl_2 and reacted on as desired. The yield was assumed to be quantitative.

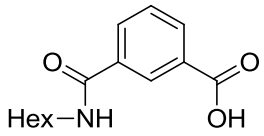
Compounds **SI-4**,[1] **SI-1**,[2], **SI-5**[3], **SI-11**[1] and stopper-alkyne **4**[4] were prepared according to literature procedures.

Compound SI-2:



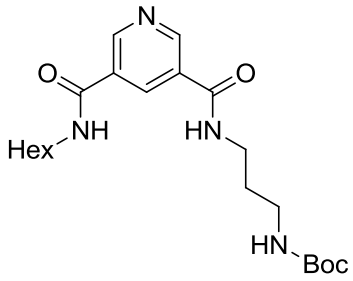
Acid **SI-1** (2.00 g, 11.1 mmol) was converted to its acid chloride using the general procedure**.** Assuming quantitative conversion, the crude acid chloride was immediately re-dissolved in CH_2Cl_2 (150 mL) and a solution of hexylamine (1.61 mL, 12.2 mmol), dry triethylamine (2.32 mL, 16.7 mmol) in CH_2Cl_2 (50 mL) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature under N_2 for 16 hrs and then washed with 10% citric acid (2 × 50 mL) and $NaHCO_3$ (2 × 50 mL). The organic layer was dried over $MgSO_4$ and solvent removed *in vacuo*. Purification by silica gel column chromatography (99:1 CH_2Cl_2/CH_3OH) to give a pale yellow oil. (1.31 g, 45 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.35 (t, ^4J = 1.7 Hz, 1H, Ar*H*), 8.15 (m, 1H, Ar*H*), 8.04 (m, 1H, Ar*H*), 7.52 (t, ^3J = 7.8 Hz, 1H, Ar*H*), 6.30 (br s, 1H, N*H*), 3.94 (s, 3H, OCH_3), 3.46 (m, 2H, CH_2NH), 1.63 (quintet, ^3J = 6.9 Hz, 2H, CH_2CH$_2$NH), 1.38 (m, 2H, hexyl CH_2), 1.32 (m, 4H, hexyl CH_2), 0.89 (t, ^3J = 7.2 Hz, 3H, CH_3).^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 166.4, 135.1, 132.2, 131.8, 130.4, 128.9, 127.4, 52.3, 40.2, 31.5, 29.6, 26.6, 22.5, 14.0, One peak missing, presumed overlapped. HRMS (ES +ve) *m/z*: 264.1601 ($[M + H]^+$, $C_{15}H_{22}NO_3$ requires 264.1594).

Compound SI-3



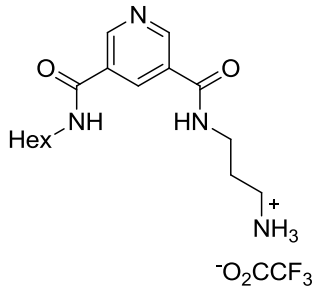
Ester **SI-2** (607 mg, 2.31 mmol) was dissolved with KOH (143 mg, 2.54 mmol) in MeOH (35 mL). The reaction mixture was stirred under N_2 for 16 hrs. The solvent removed *in vacuo* and re-dissolved in H_2O (50 mL) and washed with CH_2Cl_2 (2 × 20 mL). The aqueous layer was neutralised with 10% citric acid and the resulting precipitate was collected by vacuum filtration and washed with H_2O (10 mL), CH_2Cl_2 (10 mL) and dried to give a white solid. (445 mg, 77 %).^{1}H NMR (500 MHz, DMSO-d^6) δ (ppm): 8.65 (t, ^3J = 5.3 Hz, 1H, CON*H*), 8.42 (s, 1H, Ar*H*), 8.07 (dd, ^3J = 7.7 Hz ^4J = 1.8 Hz, 2H, Ar*H*), 7.59 (t, ^3J = 7.6 Hz, 1H, Ar*H*), 3.26 (m, 2H, CH_2NH), 1.53 (m, 2H, CH_2CH$_2$NH), 1.29 (m, 6H, CH_2) 0.88 (t, ^3J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, DMSO-d^6) δ (ppm): 167.0, 165.3, 135.0, 131.6, 131.4, 131.0, 128.7, 128.0, 31.0, 30.0, 26.2, 22.1, 13.9, One peak missing, presumed overlapped. HRMS (ES +ve) *m/z*: 272.1256 ($[M + Na]^+$, $C_{14}H_{19}NO_3Na$ requires 272.1257).

Compound SI-6



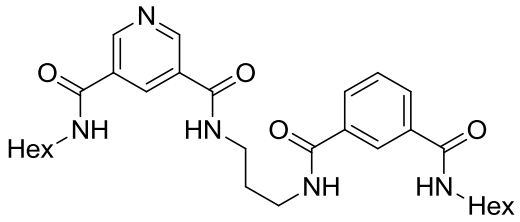
Acid **SI-4** (500 mg, 2.00 mmol) was converted to it's corresponding acid chloride using the general procedure. Assuming quantitative conversion, the crude acid chloride was immediately re-dissolved in CH_2Cl_2 (40 mL). A solution of **SI-5** (380 mg, 2.20 mmol) and dry triethylamine (0.42 mL, 3.00 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature under N_2 for 16 hrs and then washed with 10 % citric acid (2 × 30 mL) and $NaHCO_3$ (2 × 30 mL). The organic layer was dried over $MgSO_4$ and solvent removed *in vacuo*. Purification by silica gel column chromatography (95:5 CH_2Cl_2/CH_3OH) afforded the product as a pale yellow solid (490 mg, 60 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.19 (br s, 2H, pyridine Ar*H*), 8.57 (s, 1H, pyridine Ar*H*), 7.98 (br s, 1H, CON*H*), 6.78 (br s, 1H, CON*H*), 4.96 (br s, 1H, CON*H*), 3.53 (m, 2H, C*H*$_2$NH), 3.47 (m, 2H, C*H*$_2$NH), 3.26 (m, 2H, C*H*$_2$CH$_2$NH), 1.74 (m, 2H, C*H*$_2$), 1.63 (m, 2H, C*H*$_2$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 1.38 (m, 2H, C*H*$_2$), 1.31 (m, 4H, C*H*$_2$), 0.89 (t, ^3J = 6.6 Hz, 3H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 164.7, 164.6, 157.2, 150.7, 150.1, 133.5, 130.1, 129.9, 80.0, 40.3, 37.0, 36.1, 31.4, 29.8, 29.5, 28.4, 26.6, 22.5,14.0. HRMS (ES +ve) *m/z*: 429.2476 [[M + Na]$^+$, $C_{21}H_{34}N_4O_4Na$ requires 429.2472).

Compound SI-7



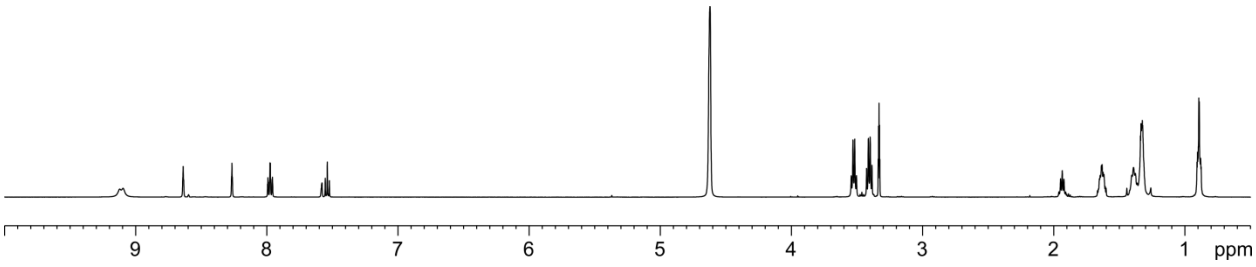
To a solution of **SI-6** (490 mg, 1.21 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added trifluoroacetic acid (5 mL) dropwise. The reaction mixture was allowed to warm to room temperature and stirred under N_2. The reaction was monitored using thin layer chromatography (9:1 CH_2Cl_2/CH_3OH) until all the amine had been deprotected. The solvent was removed *in vacuo* and re-dissolved in CH_3OH which was subsequently again removed *in vacuo*. This was repeated until all the excess TFA had been removed to give the trifluoroacetate salt of the product (423 mg, 83 %) ^{1}H NMR (500 MHz, CD_3OD) δ (ppm): 9.16 (br s, 2H, pyridine Ar*H*), 8.70 (s, 1H, pyridine Ar*H*), 3.57 (t, ^3J = 6.2 Hz, 2H, C*H*$_2^+$NH$_3$), 3.45 (t, ^3J = 6.8 Hz, 2H, C*H*$_2$NH), 3.06 (t, ^3J = 7.5 Hz, 2H, C*H*$_2$NH), 2.01 (quintet, ^3J = 7.0 Hz, 2H, C*H*$_2$CH$_2$NH), 1.66 (quintet, ^3J = 7.7 Hz, 2H, C*H*$_2$CH$_2$NH), 1.43 (m, 2H, hexyl-C*H*$_2$CH$_3$), 1.37 (m, 4H, C*H*$_2$), 0.94 (t, ^3J = 6.9 Hz, 3H, C*H*$_3$). ^{13}C NMR (125 MHz, CD_3OD) δ (ppm): 167.8, 166.9, 161.4, 159.0 (quartet, ^1J = 41.9 Hz, *C*F$_3$), 151.2, 151.1, 136.1, 117.2, 115.0, 41.4, 38.4, 37.8, 32.8, 30.5, 28.9, 28.0, 23.9, 14.6. HRMS (ES +ve) m/z: 307.2126 ([M + H]$^+$, $C_{16}H_{27}N_4O_2$ requires 307.2129).

Compound SI-8

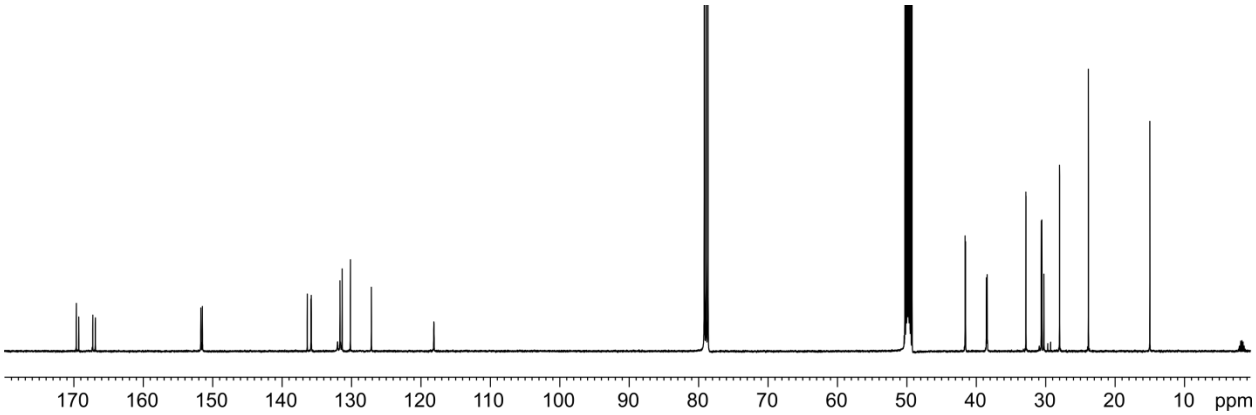


To a suspension of acid SI-**3** (68 mg, 0.272 mmol) in CH_2Cl_2 (10 mL) was added EDC·HCl (62.7 mg, 0.327 mmol), HOBt (50 mg, 0.327 mmol) and DMAP (cat. ~1 mg). This was stirred for 24 hrs under N_2 until the solution became homogeneous. To this was added dry triethylamine (0.19 mL, 1.36 mmol) and a solution of amine salt **SI-7** (100 mg, 0.327 mmol) in DMF (3 mL). The reaction mixture was stirred for 2 days under N_2 and washed with 10 % citric acid (2 × 5 mL) and $NaHCO_3$ (2 × 5 mL). The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo*. The product was purified using silica gel column chromatography (95:5 CH_2Cl_2/CH_3OH) to afford a yellow solid (79 mg, 54 %). ^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / CD_3OD) δ (ppm): 9.12 (s, 1H, pyridine Ar*H*), 9.10 (s, 1H, pyridine Ar*H*), 8.64 (s, 1H, pyridine Ar*H*), 7.98 (m, 2H, Ar*H*), 7.54 (t, ^3J = 7.73, 1H, Ar*H*), 3.52 (m, 4H, propyl CH_2NH), 3.41 (m, 4H, hexyl CH_2NH), 1.94 (m, 2H, propyl CH_2CH$_2$NH), 1.64 (m, 4H, hexyl CH_2CH$_2$NH), 1.39 (m, 4H, hexyl CH_2CH$_2$CH$_2$NH), 1.33 (m, 8H, hexyl CH_2), 0.90 (m, 6H, hexyl CH_3). ^{13}C NMR (125 MHz, 1:1 $CDCl_3$ / CD_3OD) δ (ppm): 169.6, 169.3, 167.3, 166.9, 151.7, 151.5, 136.4, 135.8, 135.8, 131.7, 131.3, 130.1, 127.1, 118.1, 41.6, 41.6, 38.5, 38.4, 32.8,32.8, 30.6, 30.5, 28.0, 28.0, 23.8, 15.0, Four peaks missing, presumed overlapped. HRMS (ES +ve) *m/z*: 560.3211 ([M + Na]$^+$, $C_{30}H_{43}N_5O_4Na$ requires 560.3207).

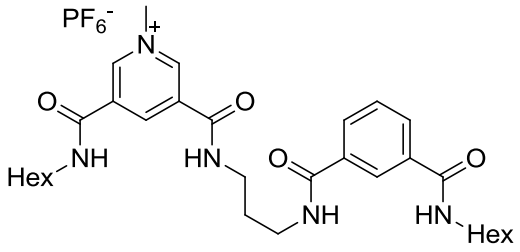
^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / CD_3OD)



^{13}C NMR (125 MHz, 1:1 $CDCl_3$ / CD_3OD)

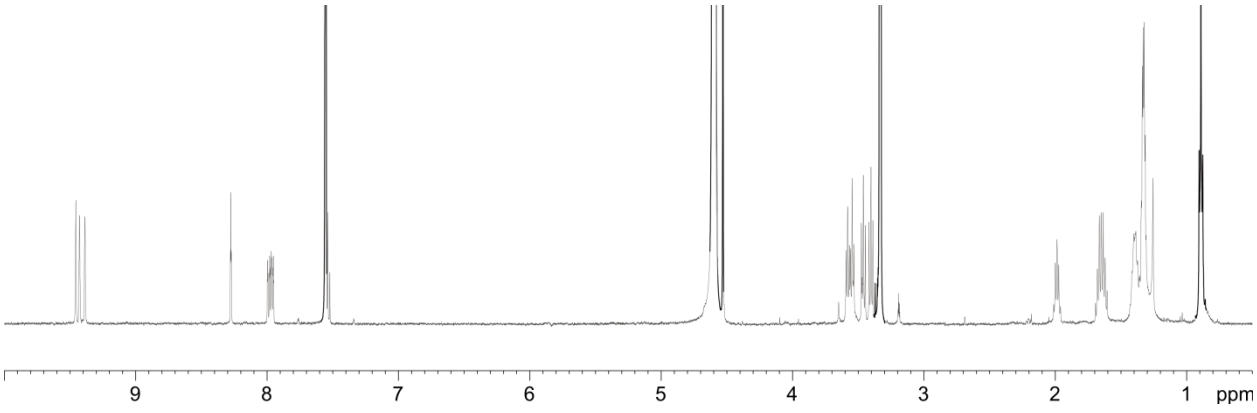


Compound 2·PF_6

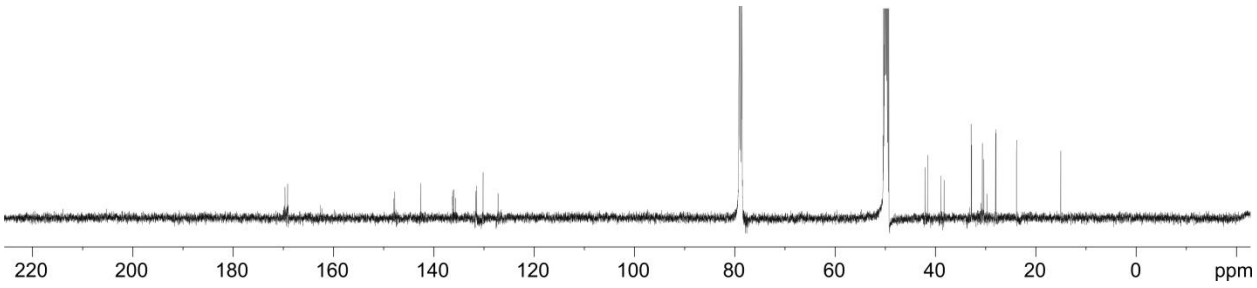


Methyl-iodide (2 mL) was added to a solution of **SI-8** (70 mg, 0.130 mmol) in DMF (2 mL) and stirred under N_2 for 16 hrs. The solvent was removed *in vacuo* to give compound **2** as the iodide salt. Ion exchange to the PF_6^- salt was achieved by washing a solution of **2·I** in CH_2Cl_2 (20 mL) with a solution of with a solution of aqueous ammonium hexaflurophosphate solution (8 × 12.5 mL of 0.1 M) and water (2 × 10 mL). The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo* to give **2·PF_6**. (70.0 mg, 77 %). ^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / CD_3OD) δ (ppm): 9.48 (s, 1H, pyridinium Ar*H*), 9.43 (s, 1H, pyridine Ar*H*), 9.39 (s, 1H, pyridinium Ar*H*), 8.28 (t, ^4J = 1.7 Hz, 1H, Ar*H*), 7.97 (m, 2H, Ar*H*), 7.54 (t, ^3J = 7.7 Hz, 1H, Ar*H*), 4.53 (s, 3H, N+CH_3), 3.58 (t, ^3J = 6.4 Hz, 2H, propyl CH_2NH), 3.55 (t, ^3J = 6.4 Hz, 2H, propyl CH_2NH), 3.46 (t, ^3J = 7.7 Hz, 2H, hexyl CH_2NH), 3.40 (t, ^3J = 7.2 Hz, 2H, hexyl CH_2NH), 1.99 (quintet, ^3J = 6.1 Hz, 2H, propyl C$H_2$$CH_2$NH), 1.65 (m, 4H, hexyl C$H_2$$CH_2$NH), 1.33 (m, 12H, hexyl CH_2), 0.89 (t, ^3J = 7.2 Hz, 6H, hexyl CH_3). ^{13}C NMR (125 MHz, 1:1 $CDCl_3$ /CD_3OD) δ (ppm): 169.7, 169.1, 162.6, 162.3, 148.0, 147.8, 142.6, 136.3, 136.2, 136.0, 135.7, 131.6, 131.5, 130.2, 127.2, 42.1, 41.6, 38.9, 38.3, 32.9, 32.8, 30.6, 30.4, 29.7, 28.0, 28.0, 23.9, 23.8, 15.0. Two peaks missing, presumed overlapped. ^{19}F NMR (282.5 MHz, 1:1 $CDCl_3$/CD_3OD) δ (ppm): -72.2 (d, ^1J = 717 Hz, PF_6^-). HRMS (ES +ve) *m/z*: 552.3544 ([M^+], $C_{31}H_{46}N_5O_4$ requires 552.3544).

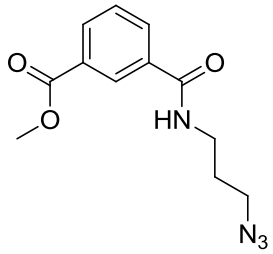
^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / CD_3OD)



^{31}C NMR (125 MHz, 1:1 $CDCl_3$ / CD_3OD)

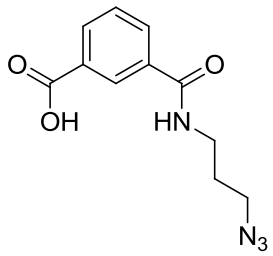


Compound SI-9



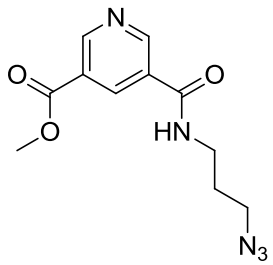
Mono-acid **SI-1** (1.50 g, 8.33 mmol) was converted to its respective acid chloride *via* the general procedure. Assuming quantitative yield the acid chloride was redissolved in dry CH_2Cl_2 (150 mL) and cooled to 0 °C. To this was added dry triethylamine (5.80 mL, 41.7 mmol) dropwise before adding 3-bromopropylamine hydrobromide (3.64 g, 16.7 mmol). The reaction mixture was allowed to warm to room temperature and stirred under N_2 for 16hrs. The solution was washed with 10 % citric acid (2 × 30 mL) and $NaHCO_3$ (2 x 30 mL) and the organic layer dried over $MgSO_4$ before removing the solvent *in vacuo* to give a pale yellow oil. This was dissolved in DMF (50 mL) before adding sodium azide (1.08 g, 16.7 mmol) to the solution. The reaction mixture was stirred under N_2 and refluxed at 70 °C for 16 hrs. The solution was allowed to cool to room temperature before pouring into H_2O (100 mL). The product was extracted into CH_2Cl_2 (3 × 40 mL) and the combined organic layers dried over $MgSO_4$. The solvent was removed *in vacuo* and the resulting oil purified via silica gel column chromatography (98:2 CH_2Cl_2/CH_3OH) to afford a pale yellow oil (1.89 g, 87 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.37 (t, ^4J = 1.7 Hz, 1H, Ar*H*), 8.18 (m, 1H, Ar*H*), 8.04 (m, 1H, Ar*H*), 7.55 (t, ^3J = 7.8 Hz, 1H, Ar*H*), 6.51 (br s, 1H, CON*H*), 3.95 (s, 3H, OCH_3), 3.59 (app quartet, ^3J = 6.5 Hz, 2H, CH_2NH), 3.47 (t, ^3J = 6.5 Hz, 2H, CH_2N_3) 1.94 (quintet, J = 6.7 Hz, CH_2CH_2N_3).^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 166.5. 166.3, 134.7, 132.5, 131.8, 130.5, 129.0, 127.4, 52.4, 49.5, 37.9, 28.7. HRMS (ES +ve) *m/z*: 285.0960 ($[M + Na]^+$, $C_{12}H_{14}N_4O_3Na$ requires 285.0958).

Compound SI-10



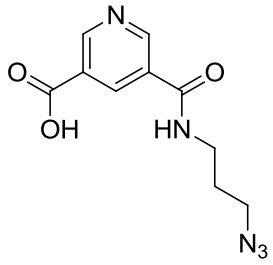
Ester **SI-9** (1.04 g, 3.97 mmol) and KOH (0.24 g, 4.37 mmol) were dissolved in CH_3OH (55 mL) was stirred for 16 hrs under N_2. The solvent was removed *in vacuo* and the residue was dissolved in H_2O (100 mL) and washed with CH_2Cl_2 (3 × 50 mL) The aqueous layer was neutralised by addition of 10 % citric acid dropwise and the white precipitate was collected through vacuum filtration and washed with H_2O (10 mL) and CH_2Cl_2 (10 mL). The product was dried under vacuum to afford a white solid (536 g, 54 %). ^{1}H NMR (500 MHz, DMSO-d^6) δ (ppm): 8.73 (app t, ^3J = 5.4 Hz, 1H, CON*H*), 8.43 (t, ^4J = 1.6 Hz, 1H, Ar*H*), 8.08 (m, 2H, Ar*H*), 7.16 (t, ^3J = 7.9 Hz, 1H, Ar*H*), 3.43 (t, ^3J = 6.9 Hz, 2H, CH_2NH), 3.36 (t, ^3J = 6.7 Hz, 2H, CH_2N_3), 1.80 (quintet, ^3J = 6.5 Hz, 2H, CH_2CH_2NH). ^{13}C NMR (125 MHz, DMSO-d^6) δ (ppm): 166.9, 165.5, 134.8, 131.8, 131.5, 131.0, 128.7, 128.0, 48.5, 36.7, 28.3. HRMS (ES +ve) *m/z*: 271.0810 ($[M + Na]^+$, $C_{11}H_{12}N_4O_3Na$ requires 271.0802).

Compound SI-12



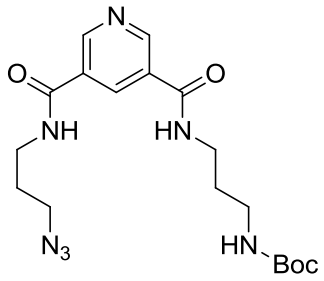
Acid **SI-10** (1.41 g, 7.79 mmol) was converted to its respective acid chloride by the general method. Assuming quantitative yield, the acid chloride was immediately re-dissolved in dry CH_2Cl_2 (150 mL) and cooled to 0 °C. To this was added dry triethylamine (5.43 mL, 39.0 mmol) dropwise before adding 3-bromopropylamine hydrobromide (3.42 g, 15.6 mmol). The reaction mixture was allowed to warm to room temperature and stirred under N_2 for 16 hrs. The solution was washed with 10 % citric acid (2 × 50 mL) and $NaHCO_3$ (2 × 50 mL) and the organic layer dried over $MgSO_4$ before removing the solvent *in vacuo* to give a pale yellow oil. This was dissolved in DMF (50 mL) before adding sodium azide (1.01 g, 15.6 mmol) to the solution. The reaction mixture was stirred under N_2 and refluxed at 70 °C for 16 hrs. The solution was allowed to cool to room temperature before pouring into H_2O (100 mL). The product was extracted into CH_2Cl_2 (3 × 40 mL) and the combined layers dried over $MgSO_4$. The solvent was removed *in vacuo* and the resulting oil purified via silica gel column chromatography (98:2 CH_2Cl_2/ CH_3OH) to afford a pale yellow oil (0.85 g, 41 %). ^{1}H NMR (500 MHz, DMSO-*d*^{6}) δ (ppm): 9.22 (d, ^4J = 2.2 Hz, 1H, pyridine Ar*H*), 9.21 (d, ^4J = 2.1 Hz, 1H, pyridine Ar*H*), 8.94 (br s, 1H, CON*H*), 8.69 (t, ^4J = 2.2 Hz, 1H, pyridine Ar*H*), 3.94 (s, 3H, OCH_3), 3.44 (t, ^3J = 6.6 Hz, 2H, N_3CH_2), 3.38 (m, 2H, NHCH_2), 1.81 (quintet, ^3J = 6.8 Hz, 2H, CH_2CH$_2$NH). ^{13}C NMR (125 MHz, DMSO-*d*^{6}) δ (ppm): 164.8, 163.8, 152.3, 151.9, 135.4, 129.8, 125.3, 52.7, 48.5, 36.8, 28.1. HRMS (ES +ve) *m/z*: 286.0902 ([M + Na]$^+$, $C_{11}H_{13}N_5O_3Na$ requires 286.0911).

Compound SI-13



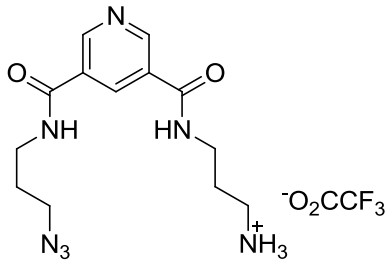
Ester **SI-12** (850 mg, 3.23 mmol) and KOH (199 g, 3.55 mmol) were dissolved in CH_3OH (48 mL) and stirred for 16 hrs under N_2. The solvent was removed *in vacuo* and the resulting solid re-dissolved in H_2O (75 mL). This solution was washed with CH_2Cl_2 (3 × 30 mL) and the aqueous layer neutralised by addition of 10 % citric acid dropwise. The resulting white precipitate was collected through vacuum filtration, washed with H_2O (10 mL) and CH_2Cl_2 (10 mL). It was dried under vacuum to afford a white solid (547 g, 68 %). ^{1}H NMR (500 MHz, DMSO-*d*^{6}) δ (ppm): 9.19 (d,^4J = 2.2 Hz, 1H, pyridine Ar*H*), 9.17 (d, ^4J = 2.2 Hz, 1H, pyridine Ar*H*), 8.92 (t, ^3J = 2.2 Hz, 1H, N*H*), 8.68 (t, ^4J = 2.2 Hz, 1H, pyridine Ar*H*), 3.44 (t, ^3J = 6.7 Hz, 2H, CH_2N_3), 3.36 (m, 2H, CH_2NH), 1.81 (quintet, ^3J = 6.7 Hz, 2H, CH_2CH$_2$NH). ^{13}C NMR (125 MHz, DMSO-*d*^{6}) δ (ppm): 165.8, 164.0, 152.2, 151.0, 135.5, 129.7, 126.5, 48.5, 36.7, 28.2. HRMS (ES +ve) *m/z*: 272.0750 ([M + Na]$^+$, $C_{10}H_{11}N_5O_3Na$ requires 272.0754).

Compound SI-14



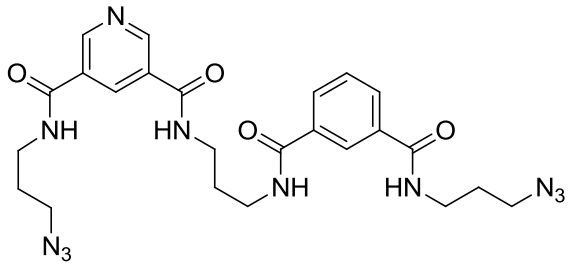
Mono-acid **SI-13** (200 mg, 0.803 mmol) was converted to an acid chloride *via* the general method**.** Assuming quantitative yield the acid chloride was immediately re-dissolved in CH_2Cl_2 (25 mL) and a solution of protected amine **SI-5** (209 mg, 1.21 mmol), dry triethylamine (0.168 mL, 1.21 mmol) in CH_2Cl_2 (5 mL) was added dropwise at 0°C. The reaction mixture was stirred at room temperature under N_2 for 16hrs and then washed with 10 % citric acid (2 ×10 mL) and $NaHCO_3$ (2 × 10 mL). The organic layer was dried over $MgSO_4$ and solvent removed *in vacuo*. Silica gel column chromatography (98:2 CH_2Cl_2/CH_3OH then 96:4) was used to purify giving a pale yellow solid (224 mg, 69 %).^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.16 (br s, 2H, pyridine Ar*H*), 8.55 (br s, 1H, pyridine Ar*H*), 8.04 (br s, 1H, CON*H*), 7.44 (br s, 1H, CON*H*), 5.02 (br s, 1H CON*H*), 3.56 (m, 2H, C*H*$_2$NH), 3.50 (m, 2H, C*H*$_2$NH), 3.44 (t, ^3J = 6.6 Hz, 2H, C*H*$_2$N$_3$), 3.23 (m, 2H, C*H*$_2$NH), 1.92 (quintet, ^3J = 6.6 Hz, 2H, CH$_2$C*H*$_2$NH), 1.72 (m, 2H, C*H*$_2$CH$_2$NH), 1.44 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 165.2, 164.8, 157.2, 150.8, 150.4, 133.5, 129.9, 129.8, 79.9, 53.4, 37.8, 37.1, 36.3, 30.9, 29.8, 28.7. HRMS (ES +ve) *m/z*: $[M + Na]^+$ 428.2019 $C_{18}H_{27}N_7O_4Na$ (calc. 428.2017).

Compound SI-15



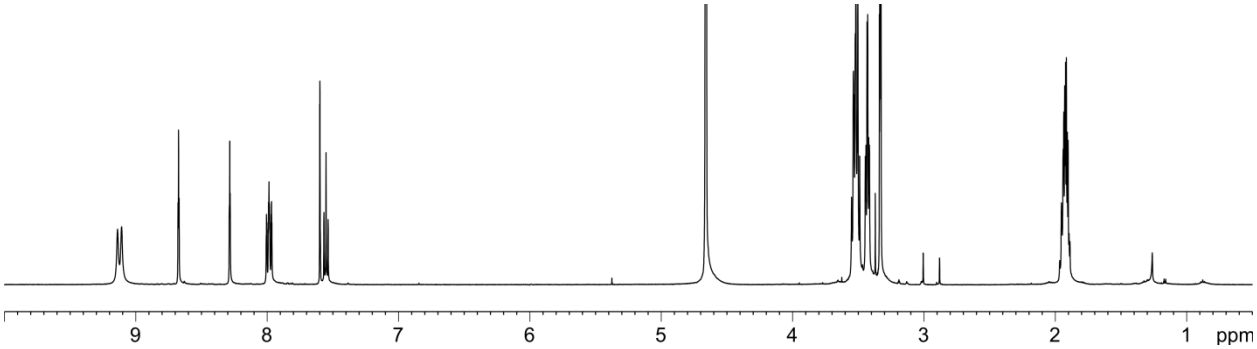
To a solution of **SI-14** (220 mg, 0.543 mmol) in CH_2Cl_2 (10 mL) at 0 °C, was added trifluoroacetic acid (2 mL) dropwise. The reaction mixture was allowed to warm to room temperature and stirred under N_2. The reaction was monitored using thin layer chromatography (9:1 CH_2Cl_2/CH_3OH) until all the amine had been deprotected. The solvent was removed *in vacuo* and re-dissolved in CH_3OH. The CH_3OH was removed *in vacuo* and this was repeated until all the excess TFA had been removed to give the trifluoroacetate salt of the product in a quantitative yield (228 mg).^{1}H NMR (500 MHz, CD_3OD) δ (ppm): 9.13 (br s, 2H pyridine Ar*H*), 8.67 (t, ^4J = 1.9 Hz, 1H, pyridine Ar*H*), 8.00 (bs, 1H, CON*H*), 3.56 (t, ^3J = 6.7 Hz, 2H, C*H*$_2$), 3.52 (t, ^3J = 6.9 Hz, 2H, C*H*$_2$), 3.45 (t, ^3J = 6.6 Hz, 2H, C*H*$_2$), 3.06 (t, ^3J = 7.5 Hz, 2H, C*H*$_2$), 2.02 (quintet, ^3J = 7.2 Hz, 2H, CH$_2$C*H*$_2$CH$_2$), 1.92 (quintet, ^3J = 6.7 Hz, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C NMR (125 MHz, CD_3OD) δ (ppm): 167.7, 167.2, 164.9 (quartet, ^1J = 34.7 Hz, *C*F$_3$), 162.9, 151.5, 151.4, 135.9, 131.8, 131.4, 50.2, 38.6, 38.4, 37.7, 29.7, 28.8. HRMS (ES +ve) *m/z*: 306.1662 ($[M + H]^+$, $C_{13}H_{20}N_7O_2$ requires 306.1673).

Compound SI-16

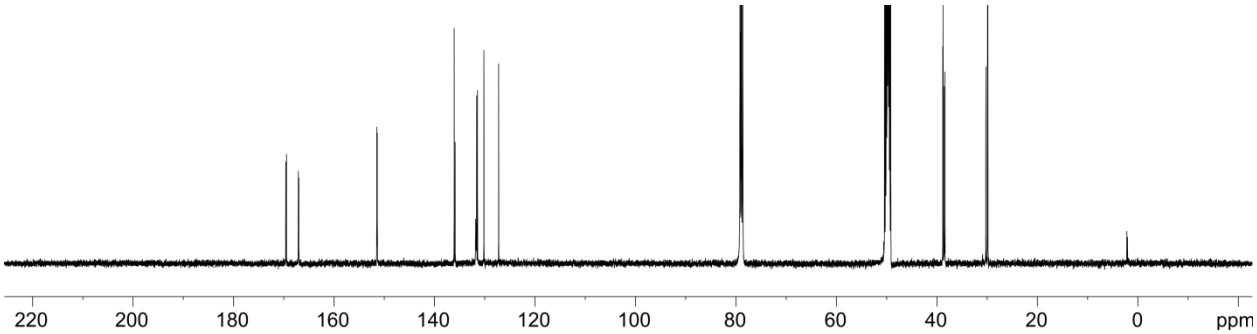


To a suspension of acid **SI-10** (64 mg, 0.257 mmol) in CH_2Cl_2 (10 mL) was added EDC·HCl (59 mg, 0.308 mmol), HOBt (47 mg, 0.308 mmol) and DMAP (cat. ~ 1 mg). This was stirred for 2 hrs under N_2 until the solution became homogeneous. To this was added dry triethylamine (0.18 mL, 1.29 mmol) and a solution of amine **SI-15** (140 mg, 0.344 mmol) in DMF (3 mL). The reaction mixture was stirred for 4 days under N_2 and then the solvent removed *in vacuo*. The solution was washed with 10 % citric acid (2 × 5 mL) and $NaHCO_3$ (2 × 5 mL). The organic layer was dried with $MgSO_4$ and the solvent removed *in vacuo*. The product was purified using silica gel column chromatography (96:4 CH_2Cl_2/CH_3OH) to afford a white solid (52 mg, 38 %).^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / CD_3OD) δ (ppm): 9.14 (br s, 1H, pyridine Ar*H*), 9.11 (br s, 1H, pyridine Ar*H*), 8.67 (t, ^4J = 2.0 Hz, 1H, pyridine Ar*H*), 8.28 (t, ^4J = 1.7 Hz, 1H, Ar*H*), 7.98 (m, 2H, Ar*H*), 7.55 (t, ^3J = 7.7 Hz, 1H, Ar*H*), 3.52 (m, 8H, CH_2NH), 3.43 (m, 4H, CH_2N_3), 1.92 (m, 6H, CH_2CH_2NH). ^{13}C NMR (125 MHz, 1:1 $CDCl_3$ / CD_3OD) δ (ppm): 169.6,169.5, 167.1, 167.0, 151.5, 151.4, 136.1, 135.9, 131.6, 131.4, 130.2, 127.2, 50.4, 50.3, 38.8, 38.7, 38.5, 38.4, 30.2, 29.9, 29.8, Three peaks missing, presumed overlapped. HRMS (ES +ve) *m/z*: 558.2287, ($[M + Na]^+$, $C_{24}H_{29}N_{11}O_4Na$ requires 558.2296).

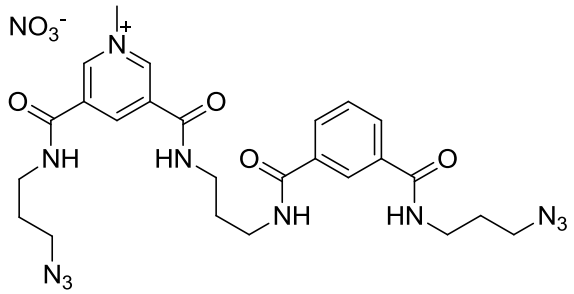
^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / CD_3OD)



^{13}C NMR (125 MHz, 1:1 $CDCl_3$ / CD_3OD)

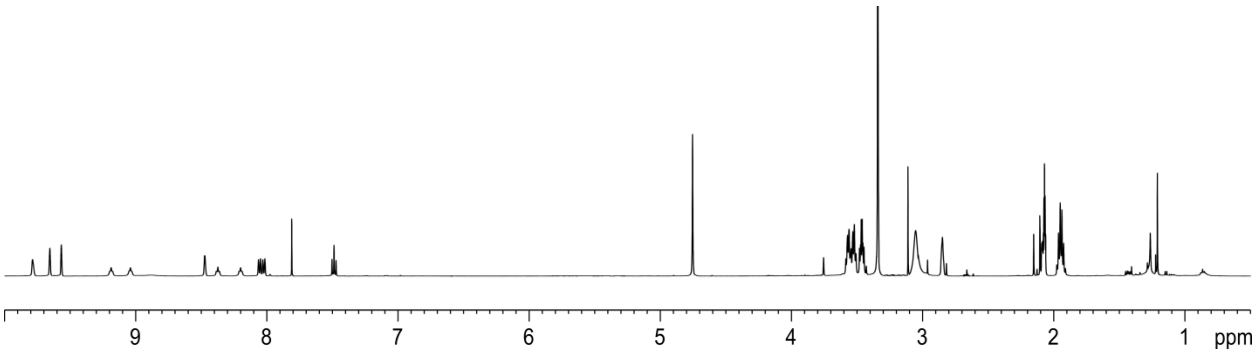


Compound 3·NO_3

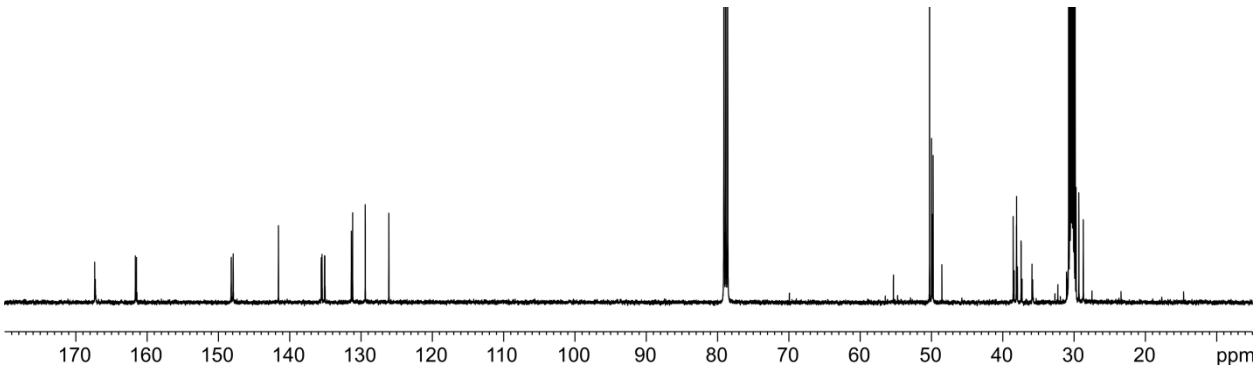


Methyl-iodide (2 mL) was added to a solution of **SI-16** (48 mg, 0.089 mmol) in DMF (2 mL) and stirred under N_2 for 16 hrs. The solvent was removed *in vacuo*. Ion exchange to the nitrate salt was achieved by passing down a nitrate loaded Amberlite® column in 9:1 acetone/water. The solvent was removed *in vacuo* to leave a pale yellow oil (52 mg, 94 %).^{1}H NMR (500 MHz, 1:1 $CDCl_3$/ d_6-acetone) δ (ppm): 9.79 (br s, 1H, pyridinium Ar*H*), 9.65 (bs, 1H, pyridinium Ar*H*), 9.57 (br s, 1H, pyridinium Ar*H*), 9.19 (t, ^{3}J = 5.4 Hz, 1H, CON*H*), 9.04 (t, ^{3}J = 5.3 Hz, 1H, CON*H*), 8.47 (br s, 1H, Ar*H*), 8.37 (t, ^{3}J = 5.9 Hz, 1H, CON*H*), 8.20 (t, ^{3}J = 5.3 Hz, 1H, CON*H*), 8.05 (d, ^{3}J = 7.8 Hz, 1H, Ar*H*), 8.02 (d, ^{3}J = 7.8 Hz, 1H, Ar*H*), 7.49 (t, ^{3}J = 7.8 Hz, 1H, Ar*H*), 4.75 (s, 3H, $N^{+}CH_3$), 3.56 (m, 4H, CH_2NH), 3.52 (m, 4H, CH_2NH), 3.46 (m, 4H, CH_2N_3), 1.94 (m, 6H, CH_2CH_2NH).^{13}C NMR (125 MHz, 1:1 $CDCl_3$:d_6-acetone) δ (ppm): 167.3, 167.3, 161.6, 161.5, 148.2, 147.9, 141.6, 135.6, 135.1, 135.1, 135.1, 131.4, 131.2, 129.4, 126.1, 50.3, 50.0, 49.9, 49.8, 38.5, 38.1, 37.4, 29.7, 29.3, 28.7. HRMS (ES +ve) *m/z*: 550.2613 ($[M]^{+}$, $C_{25}H_{32}N_{11}O_4$ requires 550.2633).

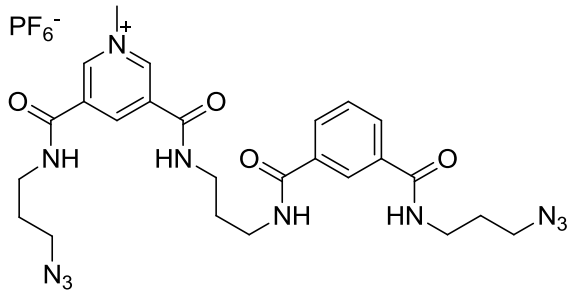
^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / d_6-acetone)



^{13}C NMR (125 MHz, 1:1 $CDCl_3$ / d_6-acetone)

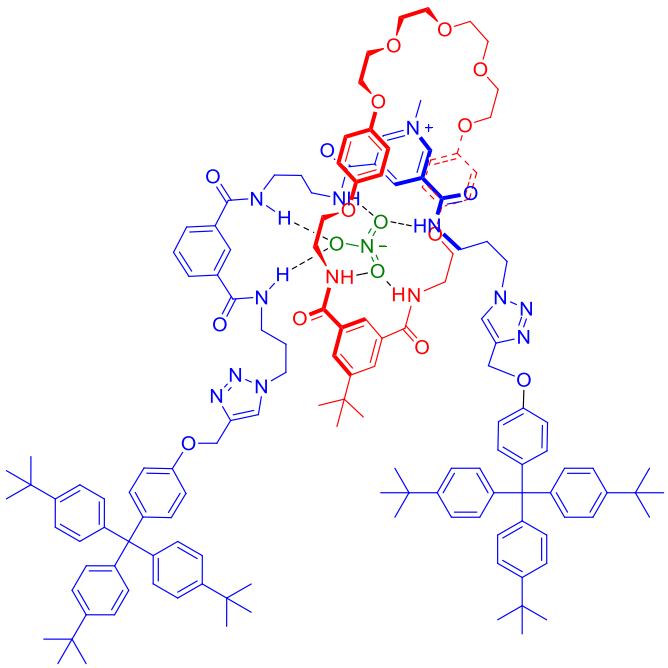


Compound 3·PF_6



Anion exchange of a further sample of **3**·NO_3 to the PF_6^- salt was achieved by passing down a PF_6^- loaded Amberlite® column in 9:1 acetone/water. ^{1}H NMR (500 MHz, 1:1 $CDCl_3$/CD_3OD) δ (ppm): 9.61 (s, 1H, pyridinium Ar*H*), 9.56 (s, 1H, pyridinium Ar*H*), 9.49 (s, pyridinium Ar*H*), 8.38 (s, 1H, Ar*H*), 8.05 (d, ^3J = 7.8 Hz, 1H, Ar*H*), 8.00 (d, ^3J = 7.8 Hz, 1H, Ar*H*), 7.61 (t, ^3J = 7.8 Hz, 1H, Ar*H*), 4.56 (s, 3H, N^+CH_3), 3.56 (m, 4H, CH_2NH), 3.52 (m, 4H, CH_2NH), 3.46 (m, 4H, CH_2N_3), 1.94 (m, 6H, CH_2CH_2NH). ^{19}F NMR (282.5 MHz, 1:1 $CDCl_3$ / CD_3OD) δ (ppm): -73.5 (d, ^1J = 712 Hz, PF_6^-).

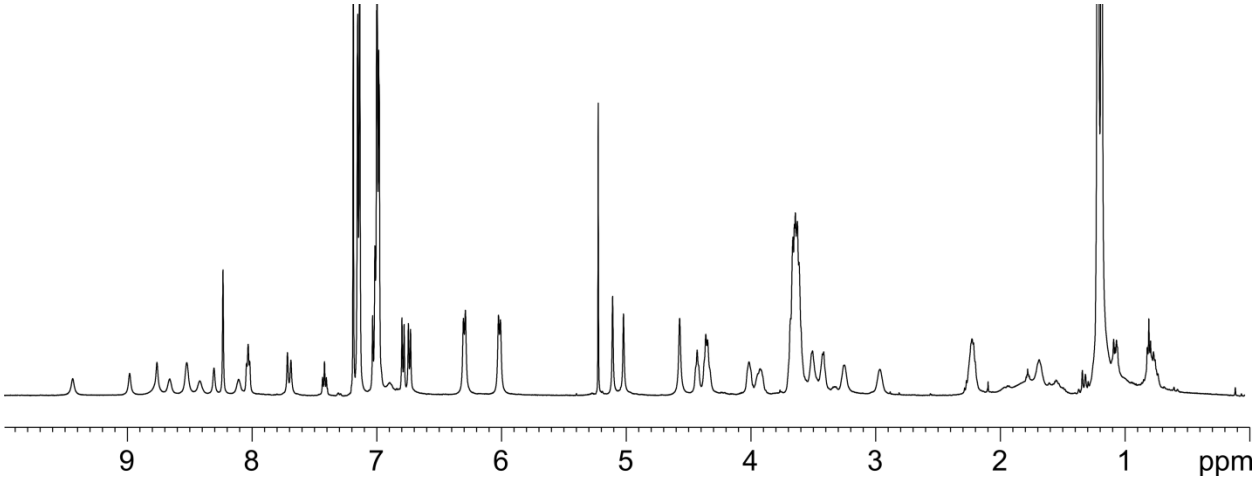
Rotaxane 5·NO_3



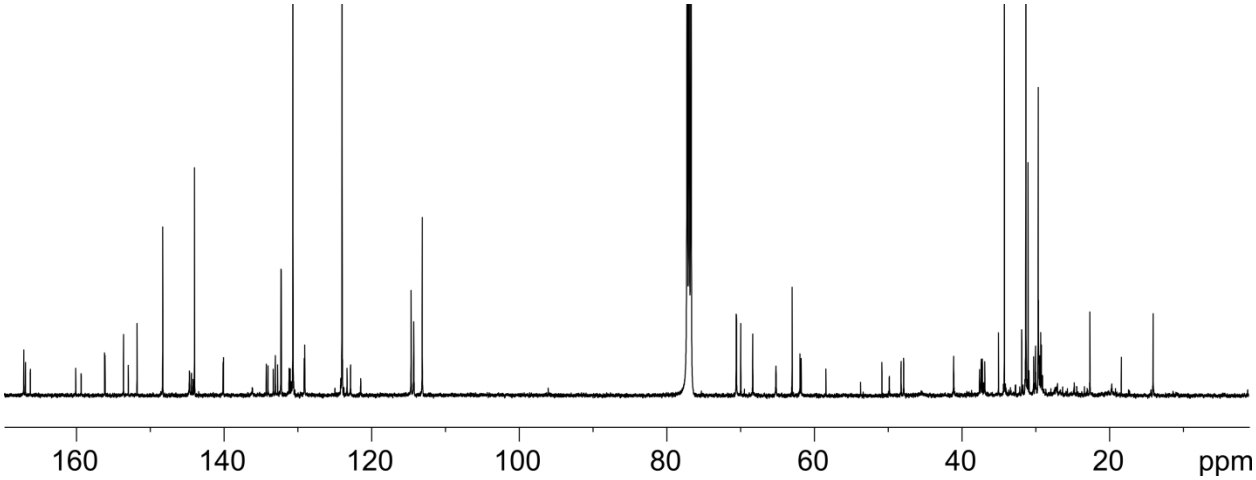
A solution of thread **3**·NO_3 (26 mg, 0.0425 mmol) and macrocycle **1** (25.1 mg, 0.0386 mmol) was stirred for 30 mins under N_2 in dry 4:1 CH_2Cl_2/Acetone (2 mL. A solution of stopper alkyne **4** (46.1 mg, 0.0849 mmol) in dry 4:1 CH_2Cl_2/Acetone (0.5 mL) was prepared. Half of this solution, $Cu(CH_3CN)_4PF_6$ (4.85 mg, 0.0155 mmol) and TBTA (5.19 mg, 0.0155 mmol) was added to reaction mixture and allowed to stir for a further 30 mins. The remaining stopper alkyne **4** solution was added and the reaction mixture stirred under N_2 for 3 days. The reaction was then washed with 0.1 M ETDA solution (3 mL), H_2O (3 mL) and the organic layer dried over $MgSO_4$. The solvent was removed *in vacuo*. Size exclusion chromatography ($CHCl_3$) was used to remove any remaining macrocycle **1** followed by silica gel chromatography (97:3 CH_2Cl_2/CD_3OD). A final preparative thin layer chromatography (Acetone) was used to afford rotaxane **3**·NO_3 as a yellow solid (22 mg, 24 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.53 (br s, 1H, pyridinium Ar*H*), 9.08 (br s, 1H, isophthalamide macrocycle Ar*H*), 8.84 (br s, 2H, pyridinium Ar*H*), 8.76 (br s, 1H, CON*H*), 8.63 (br s, 1H, CON*H*), 8.50 (br s, 1H, CON*H*), 8.39 (br s, 1H, CON*H*), 8.31 (s, 2H, isophthalamide macrocycle Ar*H*), 8.22 (br s, 1H, isophthalamide Ar*H*), 8.12 (m, 2H, isophthalamide Ar*H*), 7.82 (s, 1H, triazole C*H*), 7.80 (s, 1H, triazole C*H*), 7.51 (t, 1H, ^{3}J = 7.7 Hz, isophthalamide Ar*H*), 7.23 (m, 12H, stopper Ar*H*), 7.09 (m, 4H, stopper Ar*H*), 7.07 (m, 12H, stopper Ar*H*), 6.87 (d, ^{3}J = 8.8 Hz, 2H, stopper Ar*H*), 6.82 (d, ^{3}J = 9.0 Hz, 2H, stopper Ar*H*) , 6.37 (d, ^{3}J = 8.7 Hz, 4H, hydroquinone Ar*H*), 6.10 (d, ^{3}J = 7.7 Hz, 4H, hydroquinone Ar*H*), 5.19 (s, 2H, CH_2-C triazole), 5.11 (s, 2H, CH_2-C triazole), 4.66 (s, 3H, $N^{+}CH_3$), 4.52 (br m, 2H, CH_2-N triazole), 4.45 (br m, 2H, CH_2-N triazole) 4.09 (br m, 2H, CH_2NH macrocycle), 4.01 (br m, 2H, CH_2NH macrocycle), 3.82 – 3.64 (br m, 20H, CH_2O macrocycle), 3.63 – 2.97 (br m, 8H, CH_2NH), 2.04 – 1.41 (br m, 6H, CH_2CH_2NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 167.1, 166.9, 166.2, 160.1, 159.4, 156.2, 153.6, 153.0, 151.8, 148.3, 144.7, 144.4, 144.2, 144.0, 140.2, 140.1, 132.3, 132.3, 130.7, 129.2, 129.1, 124.0, 123.4, 122.9, 121.5, 114.7, 114.3, 113.2, 70.6, 70.6, 70.0, 68.4, 65.2, 63.0, 62.0, 61.8, 58.4, 50.9, 49.9, 48.3, 47.9, 41.1, 37.6, 37.4, 37.2, 37.1, 36.9, 35.1, 34.4, 34.3, 31.0, 30.3, 30.0, 29.7, 29.5, 29.3. Thirteen peaks missing, presumed overlapped due to apparent symmetry.

^{1}H NMR (500 MHz, $CDCl_3$)



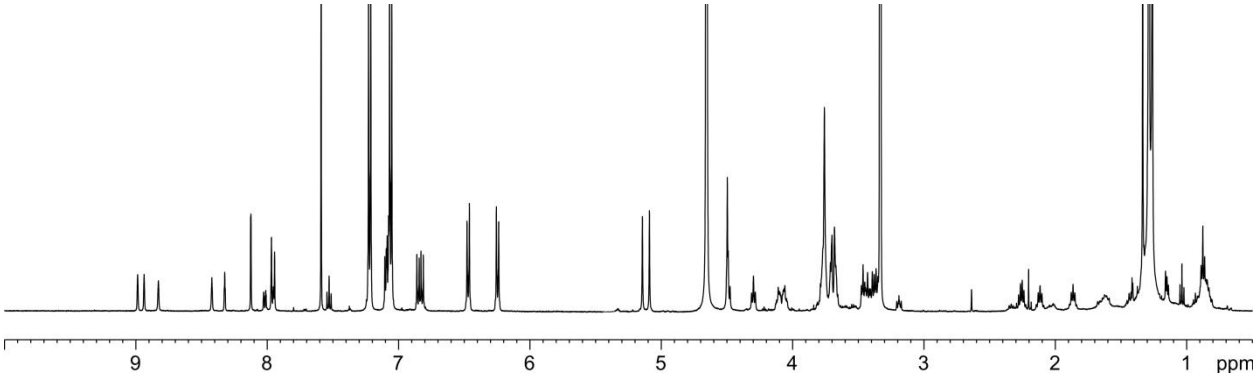
^{13}C NMR (125 MHz, $CDCl_3$)



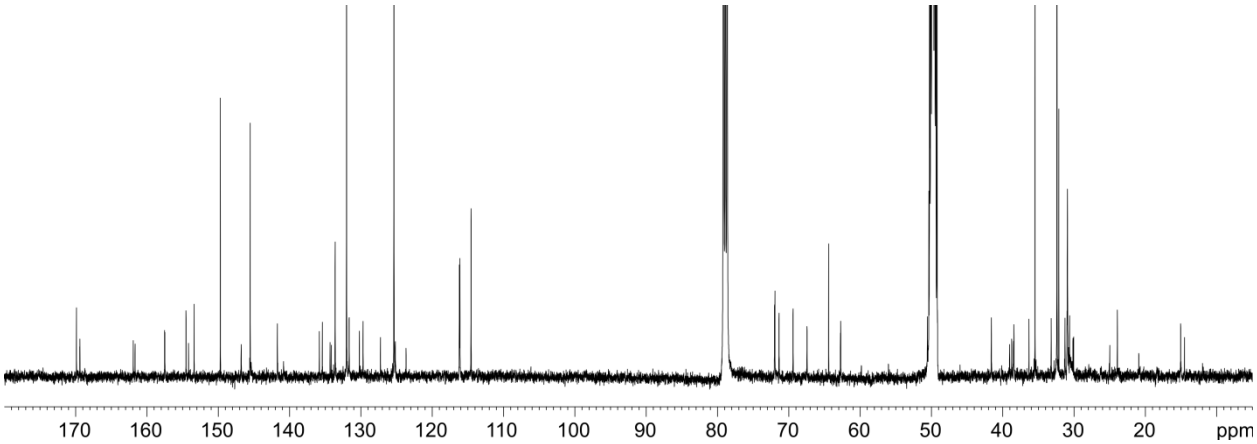
Rotaxane 3·PF$_6$

Anion exchange to the hexaflurophosphate salt was achieved by passing **3·NO$_3$** down a hexaflurophosphate loaded Amberlite® column (9:1 Acetone/H_2O). The solvent was removed *in vacuo* to afford **3·PF$_6$** in quantitative yield. ^{1}H NMR (500 MHz, 1:1 $CDCl_3/CD_3OD$) δ (ppm): 8.98 (s, 1H, pyridinium Ar*H*), 8.93 (s, 1H, pyridinium Ar*H*), 8.82 (s, 1H, pyridinium Ar*H*), 8.42 (app s, 1H, isophthalamide macrocycle Ar*H*), 8.32 (t, ^4J = 1.4 Hz, 1H, isophthalamide Ar*H*), 8.12 (d, ^4J = 1.6 Hz, 2H isophthalamide macrocycle Ar*H*), 7.97 (s, 1H, C*H* triazole), 7.96 (m, 2H, isophthalamide Ar*H*), 7.94 (s, 1H, C*H* triazole), 7.53 (t, ^3J = 7.9 Hz, 1H, isophthalamide Ar*H*), 7.22 (m, 12H, stopper Ar*H*), 7.11-7.07 (m, 4H, stopper Ar*H*), 7.06 (m, 12H, stopper Ar*H*), 6.85 (d, ^3J = 9.1 Hz, 2H, stopper Ar*H*), 6.82 (d, ^3J = 9.1 Hz, 2H, stopper Ar*H*), 6.47 (d, ^3J = 9.0 Hz, 4H, hydroquinone Ar*H*), 6.25 (d, ^3J = 9.1 Hz, 4H, hydroquinone Ar*H*), 5.14 (s, 2H, CH_2-C triazole), 5.09 (s, 2H, CH_2-C triazole), 4.50 (s, 3H, N^+CH_3), 4.49 (t, ^3J = 7.0 Hz, 2H, CH_2-N triazole), 4.30 (t, ^3J = 7.0 Hz, 2H, CH_2-N triazole), 4.14 – 4.02 (m, 4H, CH_2NH macrocycle), 3.81 – 3.65 (m, 20H, CH_2O macrocycle), 3.49 – 3.34 (m, 8H, CH_2NH), 2.25 (quintet, ^3J = 6.5 Hz, 2H, CH_2CH_2NH), 2.12 (quintet, ^3J = 6.5 Hz, 2H, CH_2CH_2NH), 1.86 (quintet, ^3J = 6.5 Hz, 2H, CH_2CH_2NH). ^{13}C NMR (125 MHz, 1:1 $CDCl_3/CD_3OD$) δ (ppm): 169.9, 169.4, 169.4, 161.9, 161.7, 157.4, 157.5, 157.5, 154.5, 154.2, 153.4, 149.7, 145.5, 141.7, 135.9, 135.5, 133.6, 132.0, 131.7, 130.2, 129.7, 127.3, 125.4, 125.2, 123.7, 116.2, 116.1, 114.5, 72.0, 71.9, 71.4, 69.4, 67.4, 64.4, 62.7, 62.7, 41.6, 39.1, 38.7, 38.5, 38.4, 36.4, 35.5, 33.2, 32.4, 32.1, 31.3, 30.9, 30.6. Twenty peaks missing, presumed overlapped due to apparent symmetry. ^{19}F NMR (282.5 MHz, 1:1 $CDCl_3/CD_3OD$) δ (ppm): -73.2 (d, ^1J = 710 Hz, PF_6^-). HRMS (ES +ve) m/z: 2286.2915 ($[M]^+$, $C_{141}H_{170}N_{13}O_{15}$ requires 2286.2966).

^{1}H NMR (500 MHz, 1:1 $CDCl_3$ / CD_3OD)



^{13}C NMR (125 MHz, 1:1 $CDCl_3$ / CD_3OD)



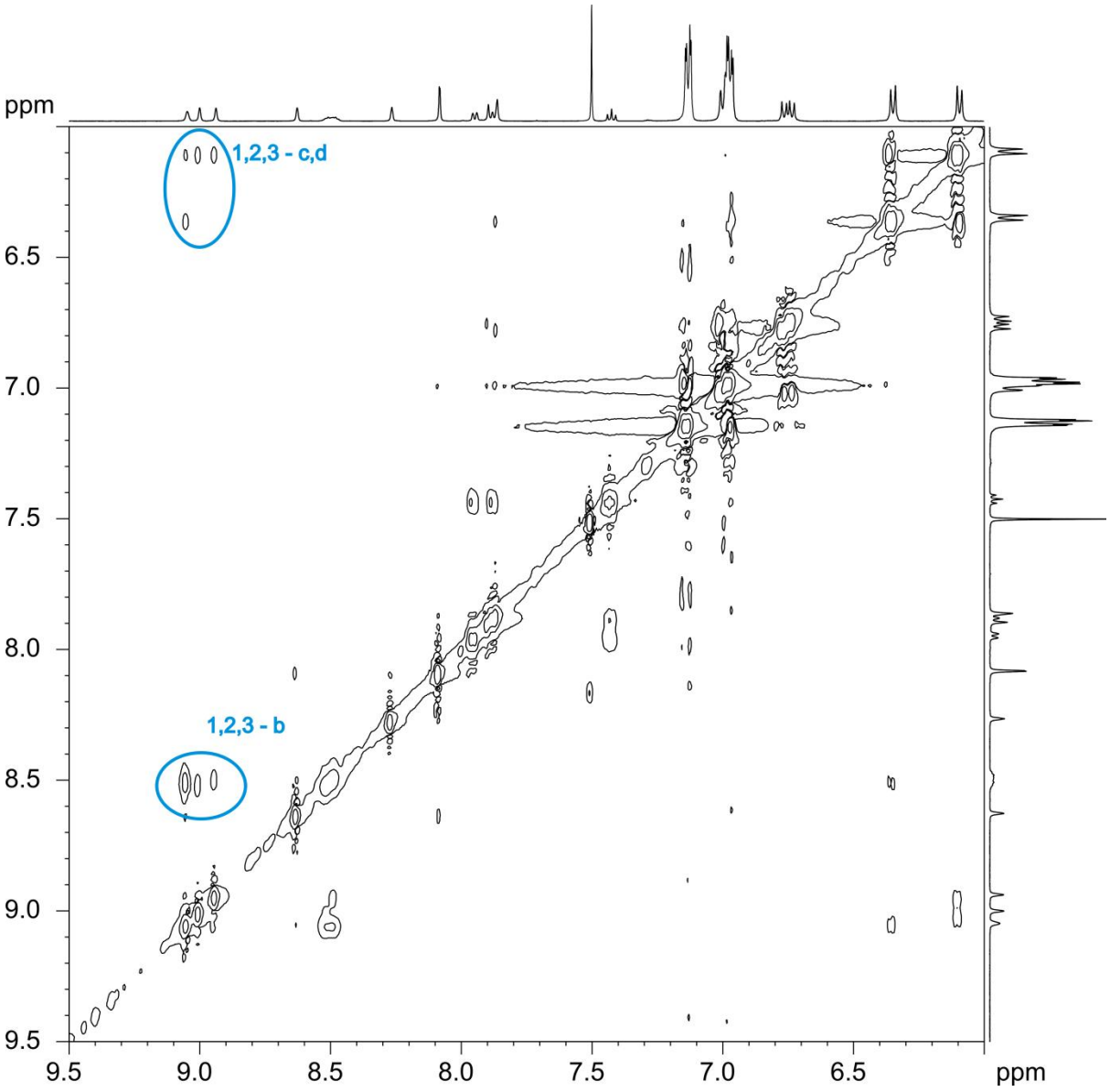


Figure SI-1 ^{1}H ROESY NMR spectrum of **5**$^{\cdot}$**NO$_3$** (1:1 $CDCl_3$/CD_3OD). Selected cross-peaks indicating through space interactions between the interlocked macrocycle and axle components are highlighted.

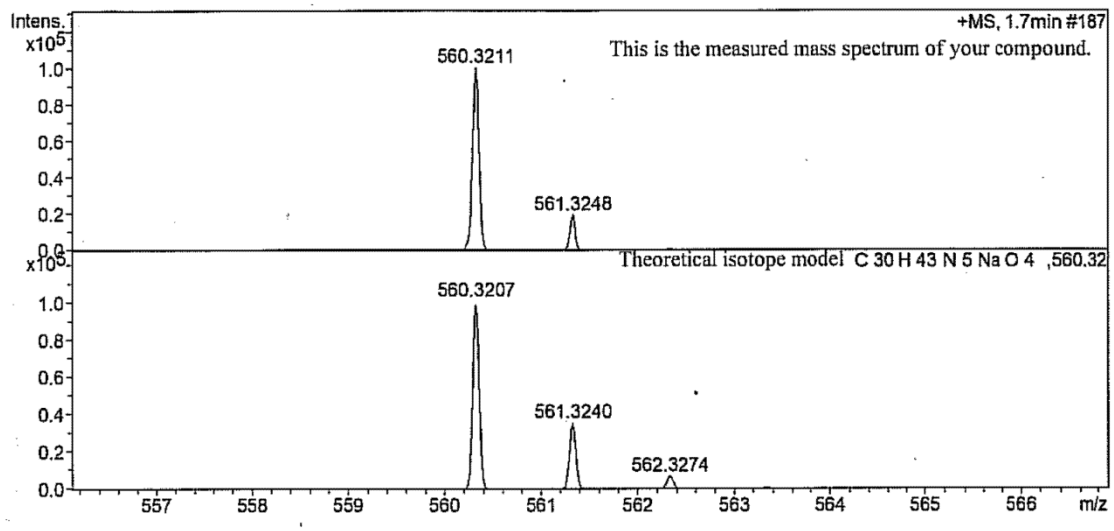


Figure SI-2 Electrospray mass spectrum of **SI-8**(top) with theoretical isotope model for $[M+Na]^+$ (bottom)

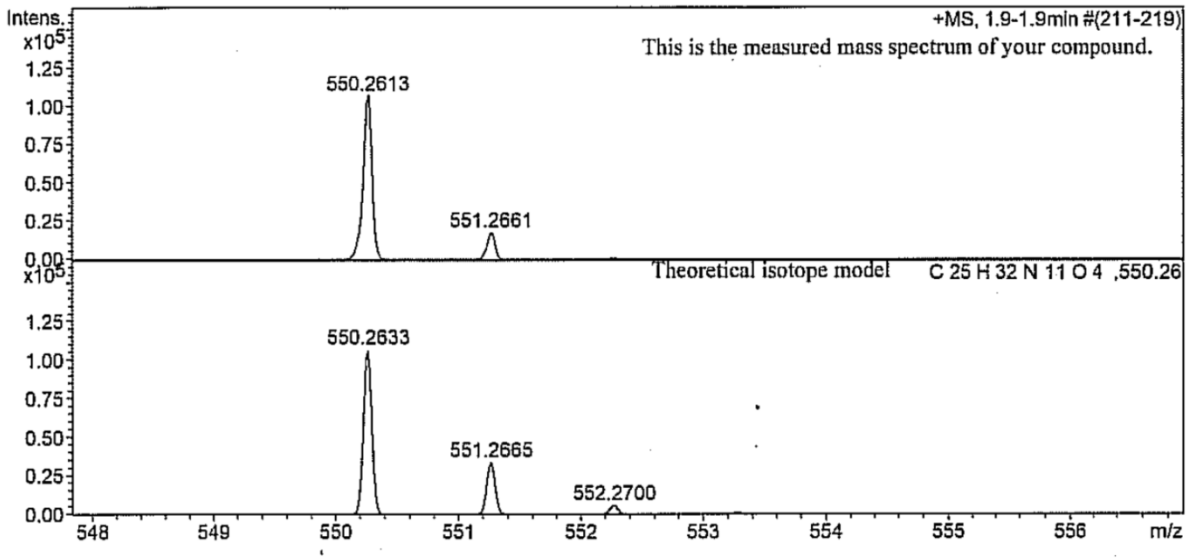


Figure SI-3 Electrospray mass spectrum of **2**·$\mathbf{PF_6}$ (top) with theoretical isotope model for $[M-PF_6]^+$ (bottom)

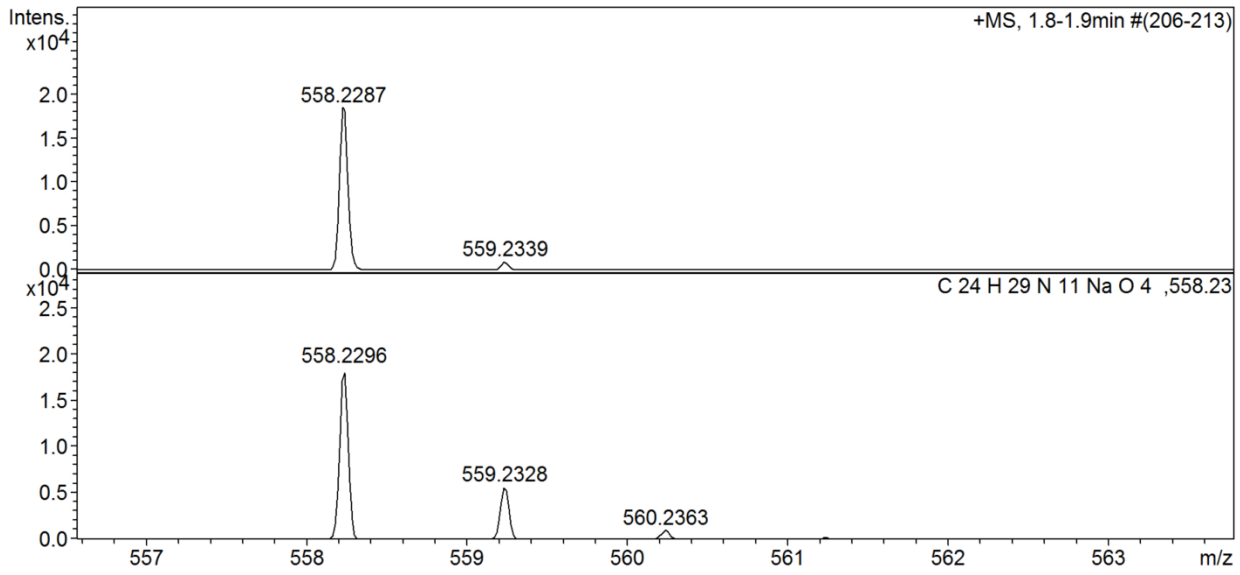


Figure SI-4 Electrospray mass spectrum of **SI-16** (top) with theoretical isotope model for $[M+Na]^+$ (bottom)

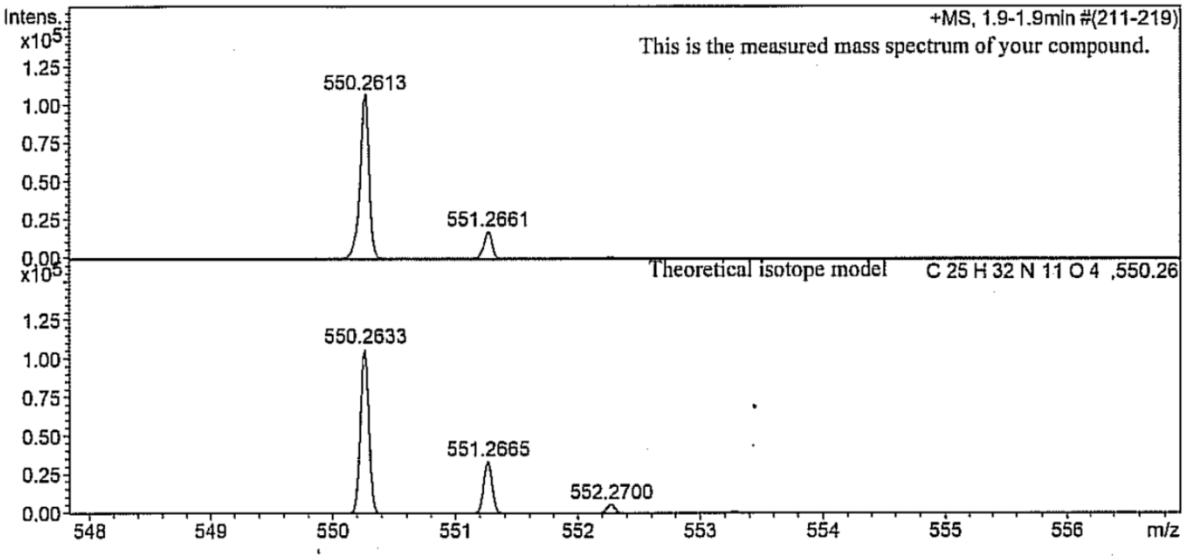


Figure SI-5 Electrospray mass spectrum of **3**$\cdot$**NO$_3$** (top) with theoretical isotope model for $[M-NO_3]^+$ (bottom)

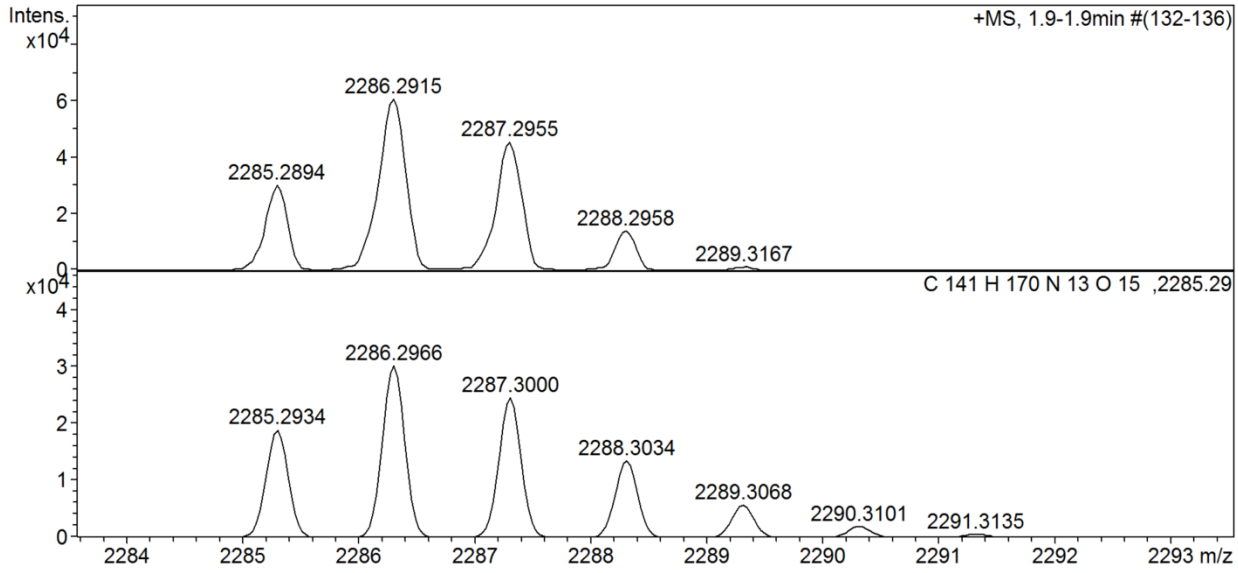


Figure SI-6 Electrospray mass spectrum of **5**·**NO$_3$** (top) with theoretical isotope model for $[M-NO_3]^+$ (bottom)

Section 2 – Additional pseudorotaxane studies

The lack of formation of a pseudorotaxane in the absence of the nitrate anion template is demonstrated by a ^{1}H NMR study in which the thread and pyridinium protons are not perturbed upon mixing (Figure SI-2)

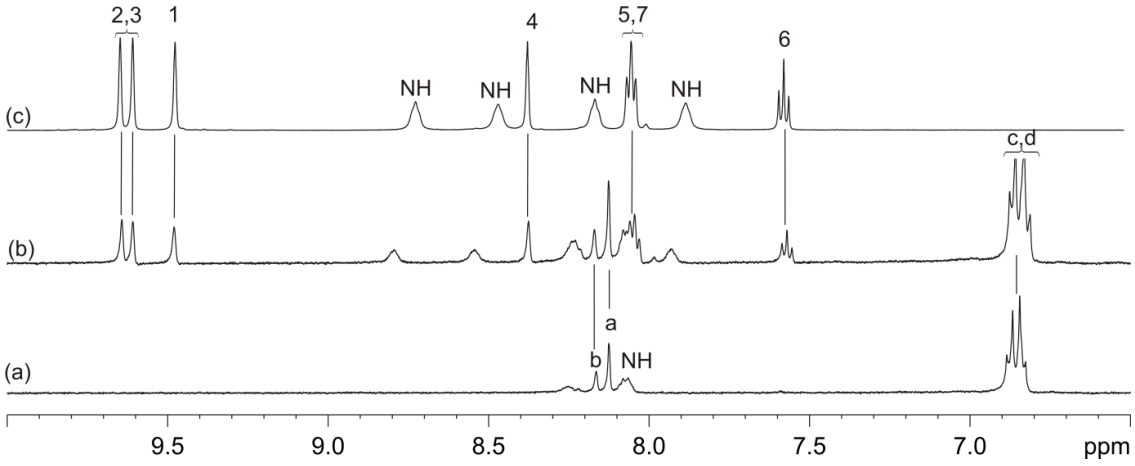


Figure SI-7 – ^{1}H NMR spectra (a) Macrocycle **1**, (b) 1:1 mixture of **1** and thread **2**·**PF$_6$** and (c) Thread **2**·**PF$_6$** in d_6-acetone (500 MHz).

Section 3 – ^{1}H NMR titrations

^{1}H NMR spectra were recorded on a Bruker AVIII 500 spectrometer. A solution of the anion guest, as the non-complexing tetrabutylammonium (TBA) salt (or in the case of hydrogen carbonate, as the triethylammonium (TEA) salt), was added to a solution of the host at 298 K. The chemical shift of the axle pyridinium proton *1* was monitored for seventeen titration points (for 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10.0 equivalents of guest added). The resulting data were analysed using the WinEqNMR2[5] computer program. (In all experiments the association of guest and host was fast on the NMR timescale).

The anion guest was titrated into a solution of host species [2]rotaxane **8**$\cdot$**PF$_6$** in 45:45:10 $CDCl_3/CD_3OD/D_2O$, A 75 mM solution of anion was added to 0.5 mL of a 1.5 mM solution of [3]rotaxane. The volumes of salt solution added were 10 x 2 μL, 2 x 5 μL, 2 x 10 μL, 1 x 20 μL, and 1 x 30 μL. The values of the observed chemical shift and the guest concentration were entered into winEQNMR2 for every titration point and estimates for the binding constant and limiting chemical shifts were made. The parameters were refined using non-linear squares analysis to obtain the best fit between observed and calculated chemical shifts for a 1:1 host-guest binding stoichiometry. The input parameters were varied until the best-fit values of the stability constants, and their errors, converged.

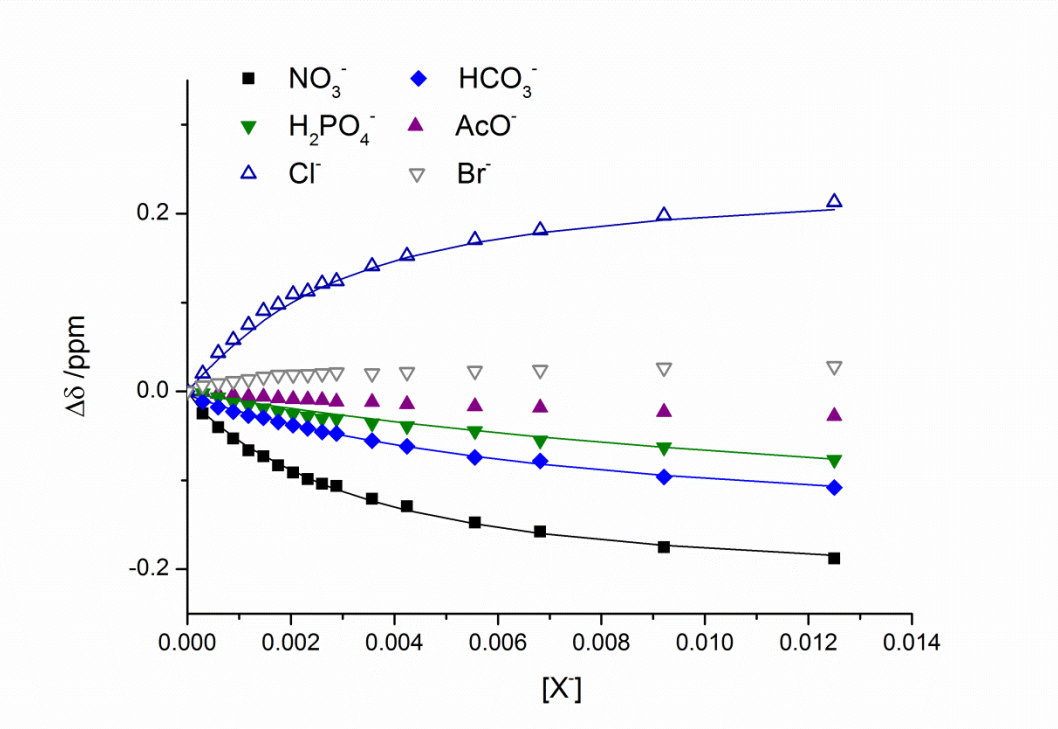


Figure SI-8. Plots of change in chemical shift against anion concentration in 45:45:10 $CDCl_3/CD_3OD/D_2O$, at 298 K. Observed data (solid points) and fitted isotherms (lines), monitoring proton *1*.

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