Electronic Supplementary Information (ESI)

Hybrid Cyclic Peptide – Thiourea Cryptands for Anion Recognition

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1. Synthesis and Characterisation Data

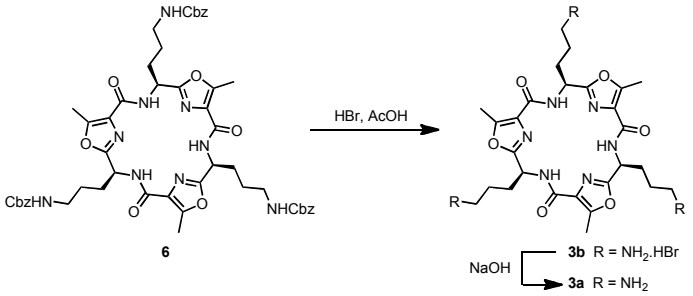
1.1 General Methods and Details

Melting points were measured using a Stanford Research Systems Optimelt melting apparatus and are uncorrected. Optical rotations were performed using a Perkin Elmer Model 341 polarimeter using the indicated spectroscopic grade solvents. ^{1}H nuclear magnetic resonance spectra were recorded using a Bruker Avance DPX 400 at a frequency of 400.13 MHz, a Bruker Avance DPX 300 at a frequency of 300.13 MHz, or a Bruker Avance DPX 200 at a frequency of 200.13 MHz are reported as parts per million (ppm) downfield shift from tetramethylsilane (δ_H 0.00), deuterochloroform ($CDCl_3$, δ_H 7.26 ppm) or deuterodimethlsulfoxide (DMSO-d_6, δ_H 2.50 ppm) as internal references, unless otherwise stated. The data is reported as chemical shift (δ), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J* Hz) and relative integral. ^{13}C nuclear magnetic resonance spectra were recorded using a Bruker Avance DPX 400 at a frequency of 100.61 MHz, a Bruker Avance DPX 300 at a frequency of 75.47 MHz, or a Bruker Avance DPX 200 at a frequency of 50.32 MHz and are reported as parts per million (ppm) downfield shift from deuterochloroform (δ_C 77.16 ppm) or deuterodimethlsulfoxide (δ_C 39.52 ppm) as internal references, unless otherwise stated. Low resolution electrospray ionisation (ESI) spectra were recorded a Thermo Finnigan LCQ Deca Ion Trap mass spectrometer. High resolution electrospray ionisation spectra were recorded on a Bruker BioApex Fourier Transform Ion Cyclotron Resonance mass spectrometer (FTICR) with an Analytica ESI source, operating at 4.7 T or a Bruker Daltonics Apex Ultra FTICR with an Apollo Dual source, operating at 7 T. Analytical thin layer chromatography (TLC) was performed using precoated silica gel plates (Merck Kieselgel 60 F254). Preparative column chromatography was carried out using Merck Kieselgel 60 silica gel (SiO_2; 0.040 – 0.065 mm) with the indicated solvents which were mixed v/v as specified. Analytical RF-HPLC was performed a Waters System 2695 Separations module consisting of an Alliance series column and 2420 ELS detector. An Alltech Alltima 5 μm column was used with 4.6 mm I.D. and 250 mm in length. The system was controlled and monitored using Waters Empower 2 Software. Preparative RF-HPLC was performed on a Waters 600E multisolvent delivery system with a Waters U6K injector, Waters 490E programmable multiwavelength detector, Waters busSAT/IN

module and Waters Empower 2 software. Separation was achieved on a Sunfire^{TM} PrepC_{18} OBD^{TM} column (5 μm, 150 x 19 mm ID). The elution rate was maintained at 7.0 mL/min over the stated linear gradient, comprised of solvent A (100:0.05 Milli-Q water/TFA) and solvent B (100:0.05 acetonitrile/TFA). Reactions were performed under an atmosphere of dry nitrogen. Dichloromethane and methanol were distilled from calcium hydride. *N,N*-dimethylformamide were obtained from LabScan and dried over molecular sieves. Chloroform was distilled from calcium chloride and passed through a column of basic alumina prior to use.

1.2 Experimental Details

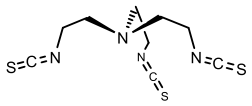
[Orn(NH_2.HBr)-Thr(Oxz)]$_3$ (3a) / [Orn(NH_2)-Thr(Oxz)]$_3$ (3b)



Cbz-protected cyclic peptide **6**[1] (1.23 g, 1.24 mmol) was treated with HBr in acetic acid (33 wt %, 10 mL) for 12 h. The resulting orange reaction mixture was then poured into anhydrous diethyl ether (30 mL). Tituration of the subsequent colourless precipitate with diethyl ether (approx. 300 mL) followed by drying under vacuum gave the desired tris-hydrobromide salt **3b** as a pale orange solid (1.02 g, quant.). To obtain tris-amine **3a**, **3b** was dissolved in $CHCl_3$/^{i}PrOH (3:1 v/v, 15 mL) and then washed with 1 M NaOH (15 mL). The basic extract was further washed with $CHCl_3$/^{i}PrOH (3:1 v/v, 3 x 15 mL) then the combined organics were dried ($MgSO_4$) and concentrated under reduced pressure to give **3a** as an off-white foam (690 mg, 95%); $[\alpha]_D^{20}$ = -28.1 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 6.6 Hz, 3 H), 5.15 (m, 3 H), 2.81-2.68 (partially obscured m, 6 H), 2.65 (s, 9 H), 2.21-2.07 (m, 3 H), 2.06-1.80 (overlapping peaks, m, 9 H), 1.75-1.58 (m, 3 H), 1.52-1.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.05, 161.01, 154.0, 128.6, 48.0, 41.8, 31.9, 28.3, 11.8. MS (ESI+) *m/z* = 586 $[M+H]^+$, *m/z* = 294

$[M+2H]^{2+}$. HRMS (ESI+) *m/z* calcd. for $C_{27}H_{40}N_9O_6$ $[M+H]^+$: 586.3102, found: 586.3106; *m/z* calcd. for $C_{27}H_{41}N_9O_6$ $[M+2H]^+$: 293.6584, found: 293.6586.

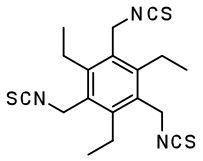
Tris-(2-isothiocyanatoethyl)amine (4)



4

Under an atmosphere of nitrogen, carbon disulfide (2.01 mL, 33.4 mmol) was added to a solution of tris-(2-aminoethyl)amine (250 μL, 1.67 mmol) in THF (25 mL) to give a cloudy solution. *N,N'*-dicyclohexylcarbodiimide (1.07 g, 5.18 mmol) was then added and the resulting reaction mixture was stirred overnight. The subsequent suspension was filtered three times, discarding the yellow precipitate. The filtrate was collected and concentrated under reduced pressure to give the crude product which was then purified by flash chromatography (silica gel; DCM). Combination of appropriate fractions and removal of the solvent gave the desired tris-isothiocyanate **4** as a pale yellow solid (289 mg, 64%); m.p. 47-49 °C (lit.[2] 48-49 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (t, *J* = 6.2 Hz, 6 H), 2.96 (t, *J* = 6.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 54.5, 44.4.

1,3,5-Tris(isothiocyanatomethyl)-2,4,6-triethylbenzene (5)

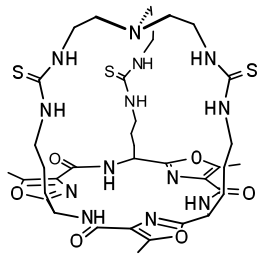


5

Under an atmosphere of nitrogen, carbon disulfide (0.60 mL, 10.0 mmol) was added to a solution of 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene[3] (125 mg, 0.50 mmol) in THF (5 mL) to produce a cloudy solution. *N,N'*-dicyclohexylcarbodiimide (320 mg, 1.55 mmol) was then added and the resulting reaction mixture was stirred for 18 h. The suspension thus obtained was then filtered and the filtrate was concentrated under reduced pressure to give the crude product as a

pale yellow oil. Subsequent purification by flash chromatography (silica gel; DCM) gave the desired tris-isothiocyanate **5** as a crystalline off-white solid (142 mg, 76 %); m.p. 110-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 6 H), 2.85 (q, *J* = 7.6 Hz, 6 H), 1.27 (t, *J* = 7.6 Hz, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 132.3, 130.1, 42.9, 23.2, 15.8. (^{1}H NMR data identical to that reported previously.[4])

Tren-capped cryptand (1)



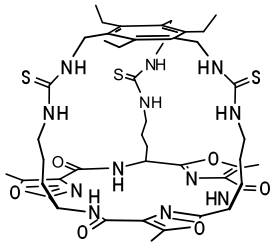
1

Method 1 – from* tris-*amine 3a: Under an atmosphere of nitrogen, a solution of tris-amine **3a** (15.4 mg, 26.3 μmol) in $CHCl_3$ (17 mL) and a separate solution of tris-isothiocyanate **4** (7.95 mg, 26.3 μmol) in $CHCl_3$ (17 mL) were added dropwise, via syringe pump (0.5 mL/h), to $CHCl_3$ (17 mL) at 35 °C. Following the addition the reaction mixture was stirred for a further 10 h then concentrated under reduced pressure and the crude product was subsequently purified by flash chromatography (silica gel; DCM/MeOH [10:1]) to provide desired tris-thiourea cryptand **1** as a colourless solid (12.3 mg, 54%); m.p. 212 °C (decomp). $[\alpha]_D^{20}$ = +19.1 [c 0.2, $CHCl_3$/MeOH (5:1)]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.46 (br s, 3 H), 8.08 (br s, 3 H), 7.38 (br s, 3 H), 5.23 (m, 3 H), 3.51-3.28 (partially obscured br m, 6 H), 3.23-2.86 (br m, 6 H), 2.59 (s, 9 H), 2.48-2.29 (m, 6 H), 2.27-2.13 (m, 3 H), 1.88-1.71 (m, 3 H), 1.51-1.34 (m, 3 H), 1.20-0.95 (m 3 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 182.1, 159.8, 159.1, 153.5, 127.5, 50.9, 47.0, 44.1, 39.9, 28.5, 21.5, 11.3. MS (ESI+) *m/z* = 858 $[M+H]^+$. HRMS (ESI+) *m/z* calcd. $C_{38}H_{51}N_{13}O_6S_3$ $[M+H]^+$: 858.3326, found: 858.3318.

Method 2 – from* tris-*hydrobromide 3b: Under an atmosphere of nitrogen, tris-hydrobromide salt **3b** (40.0 mg, 47.7 μmol) was dissolved in $CHCl_3$ (11 mL), DMF (5 mL) and triethylamine (23.3 μL, 0.167 mmol). In a separate vessel, tris-isothiocyanate **4** (13.0 mg, 47.7 μmol) was

dissolved in $CHCl_3$ (16 mL). These two solutions were then added dropwise, via syringe pump (3 mL/h), to neat $CHCl_3$ at reflux. Following the addition the reaction mixture was allowed to proceed at reflux for a further 2 d and was then concentrated under reduced pressure to give a yellow-gold oil as the crude product. Subsequent purification by reverse phase preparative HPLC (95-50% A/5-50% B over 40 min; t_R = 33.9 min) gave the desired tris-thiourea cryptand **1** as an off-white solid (25.5 mg, 62%). Data identical to above.

1,3,5-Triethylbenzene-capped cryptand (2)



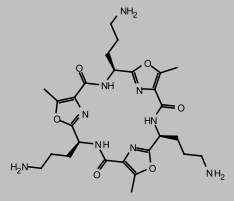
2

Method 1 – from* tris-*amine 3a: Under an atmosphere of nitrogen, a solution of tris-amine **3a** (30.0 mg, 51.2 μmol) in $CHCl_3$ (17 mL) and a separate solution of tris-isothiocyanate **5** (19.2 mg, 51.2 μmol) in $CHCl_3$ (17 mL) were added dropwise, via syringe pump (0.5 mL/h), to $CHCl_3$ (17 mL) at 40 °C. Following the addition the reaction mixture was stirred for a further 10 h and then concentrated under reduced pressure. The crude product was subsequently purified by flash chromatography (silica gel; DCM/EtOAc [1:1 to 1:5]) to give the desired tris-thiourea cryptand **2** as an off-white solid (34.0 mg, 69%); m.p. 205 °C (decomp). $[\alpha]_D^{20}$ = +1.65 (c 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.22 (d, *J* = 7.3 Hz, 3 H), 5.84 (br s, 3 H), 5.71 (br s, 3 H), 5.24-5.12 (m, 3 H), 4.91-4.67 (m, 6 H), 3.62-3.34 (m, 6 H), 2.60 (s, 9 H), 2.18-2.01 (m, 3 H), 1.87-1.62 (m, 4 H), 1.51-1.34 (m, 3 H), 1.17 (t, *J* = 7.1 Hz, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 182.5, 161.5, 161.2, 154.4, 144.3, 133.8, 128.9, 47.8, 44.4, 42.9, 33.4, 25.5, 24.4, 17.0, 11.9. MS (ESI+) *m/z* = 983 $[M+Na]^+$. HRMS (ESI+) *m/z* calcd. $C_{45}H_{60}N_{12}O_6S_3$ $[M+Na]^+$: 983.3819, found: 983.3795.

Method 2 – from* tris-*hydrobromide 3b: Under an atmosphere of nitrogen, tris-hydrobromide salt **3b** (15.0 mg, 18.1 μmol) was dissolved in $CHCl_3$ (3 mL), DMF (3 mL) and triethylamine (7.8 μL, 56.1 μmol). Separately, tris-isothiocyanate **5** (6.80 mg, 18.1 μmol) was dissolved in

$CHCl_3$ (6 mL) and the two solutions were then added simultaneously, via syringe pump (1 mL/h), to neat $CHCl_3$ (6 mL). The reaction mixture was allowed to proceed at reflux for a further 16 h, after which time it was concentrated under reduced pressure. The residue obtained was partitioned between 0.5 M HCl (20 mL) and $CHCl_3$ (20 mL) followed by further extraction of the aqueous phase with $CHCl_3$ (2 x 20 mL). The combined organics were then dried ($MgSO_4$) and concentrated under reduced pressure to provide the crude product as a golden oil. Purification with reverse phase preparative HPLC (100-50% A/0-50% B over 30 min; t_R = 25.4 min) provided the desired tris-thiourea cryptand **2** as an off-white solid (8.7 mg, 50 %). Data identical to above.

2. ^{1}H and ^{13}C NMR Spectra of New Compounds



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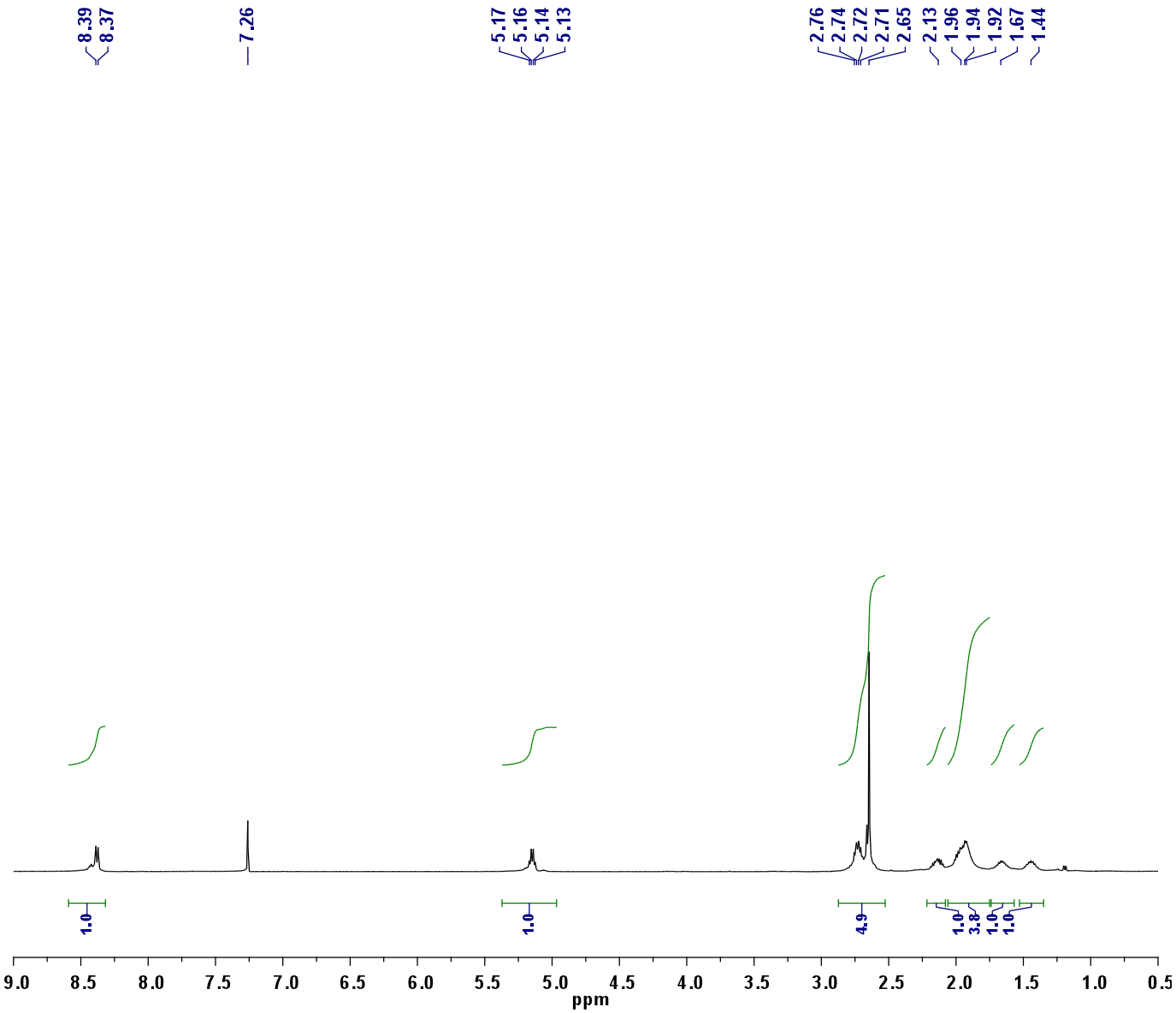

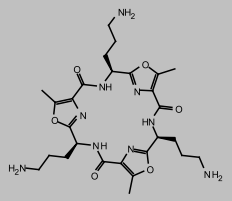

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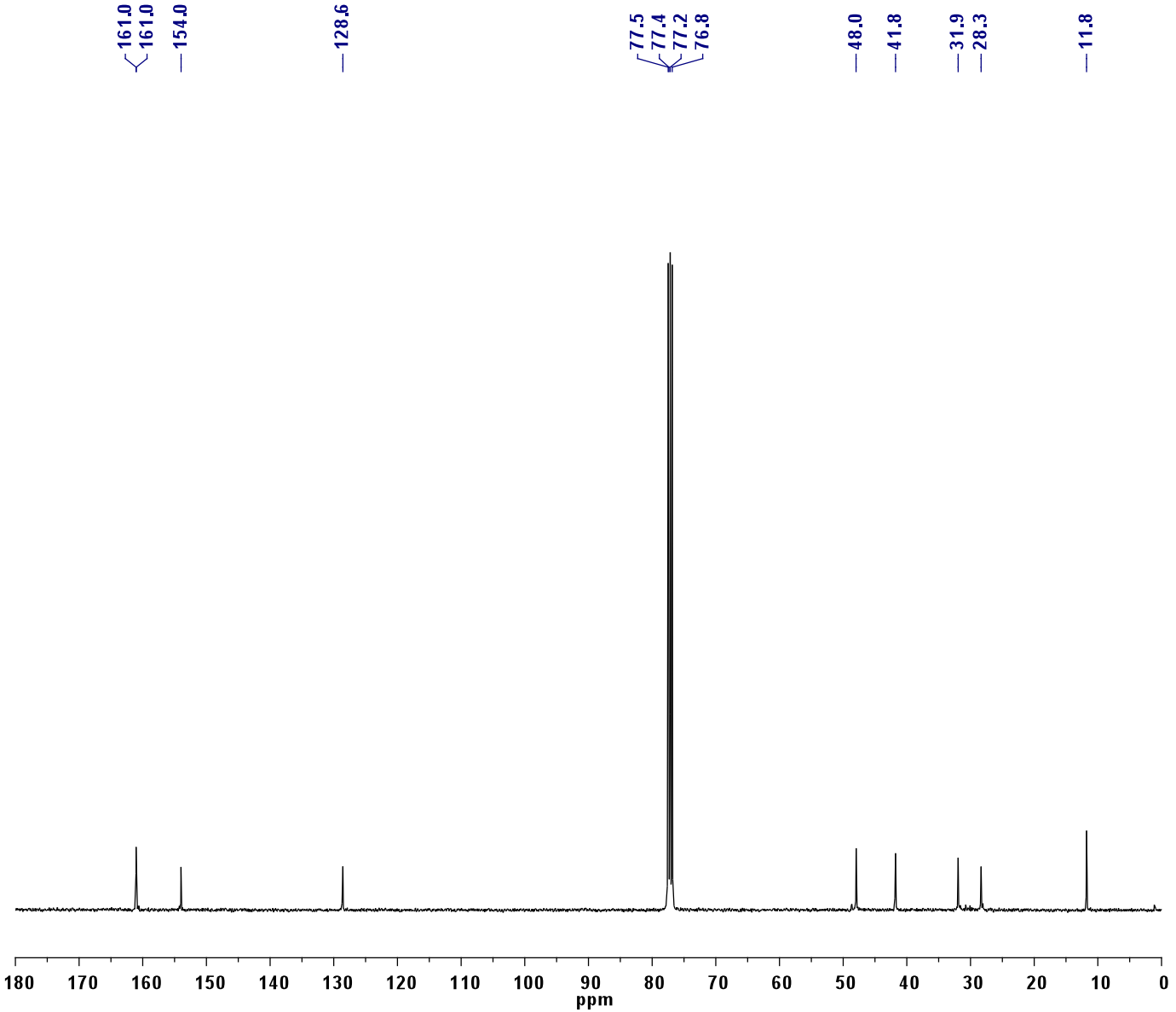

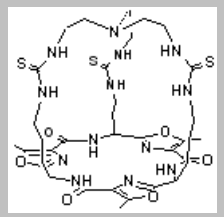

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Acquired Size	16384
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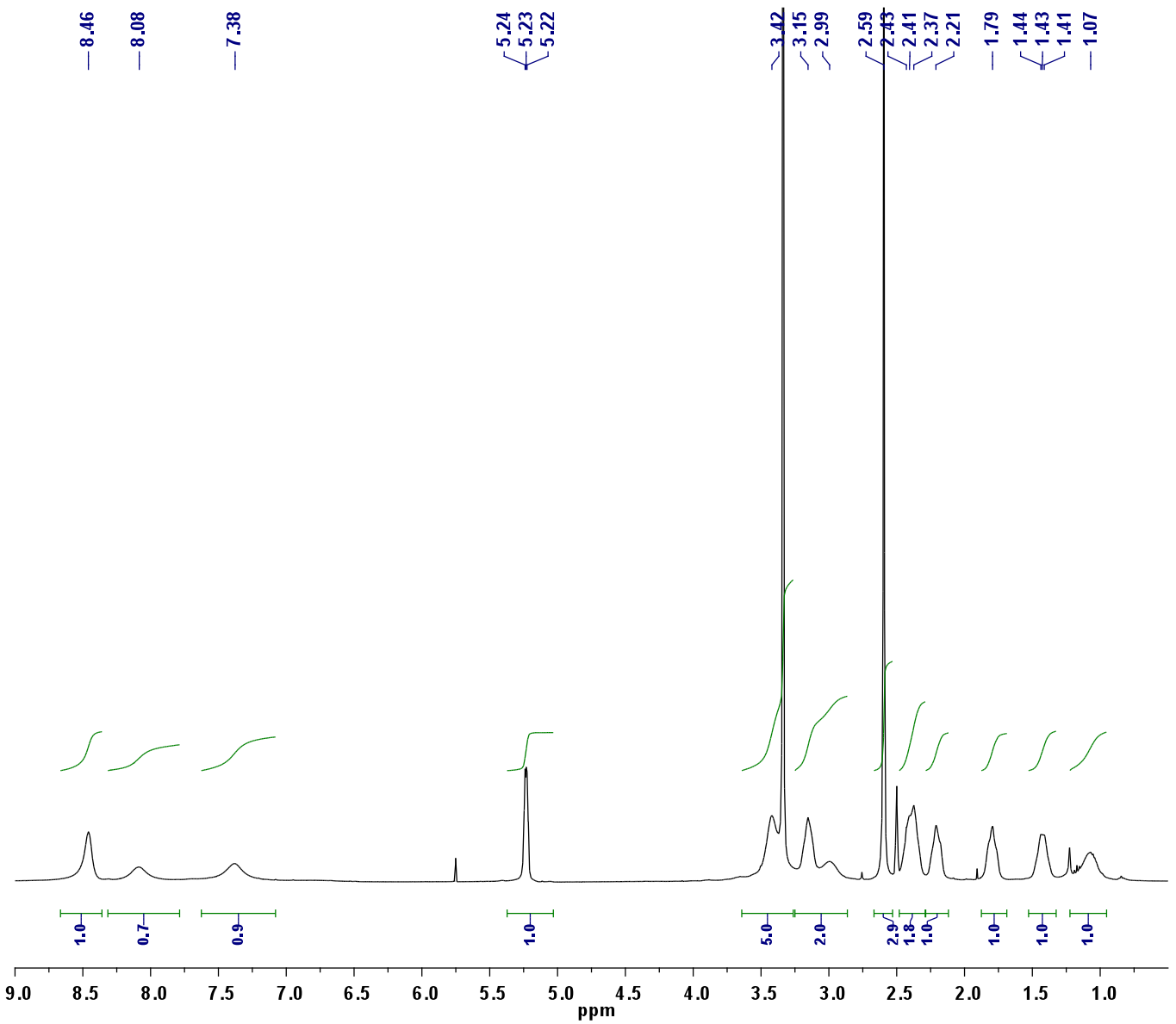

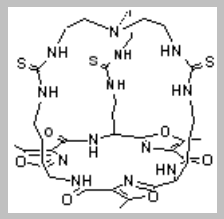

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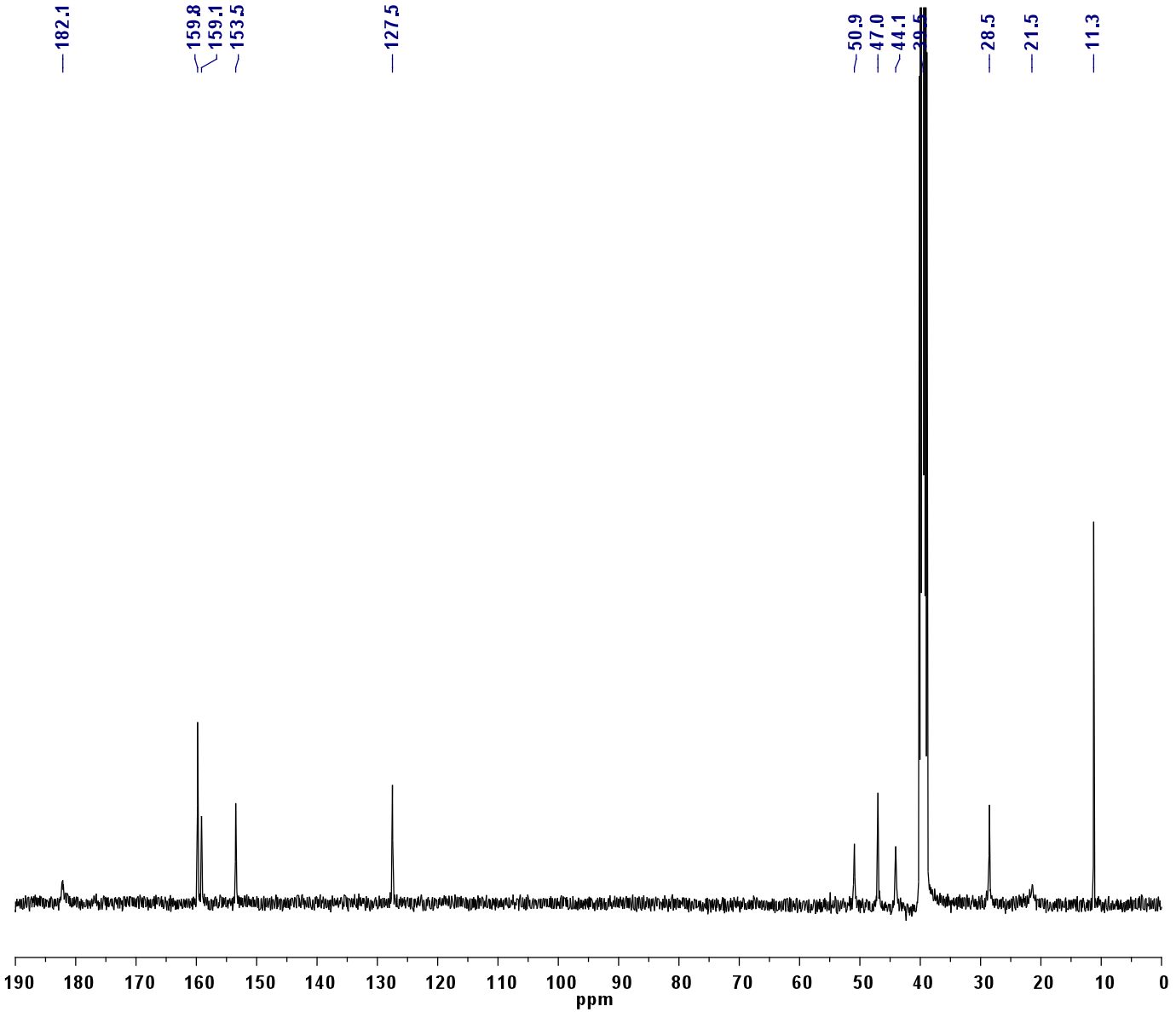

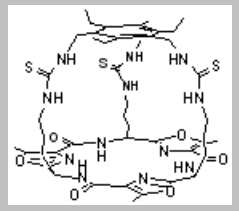

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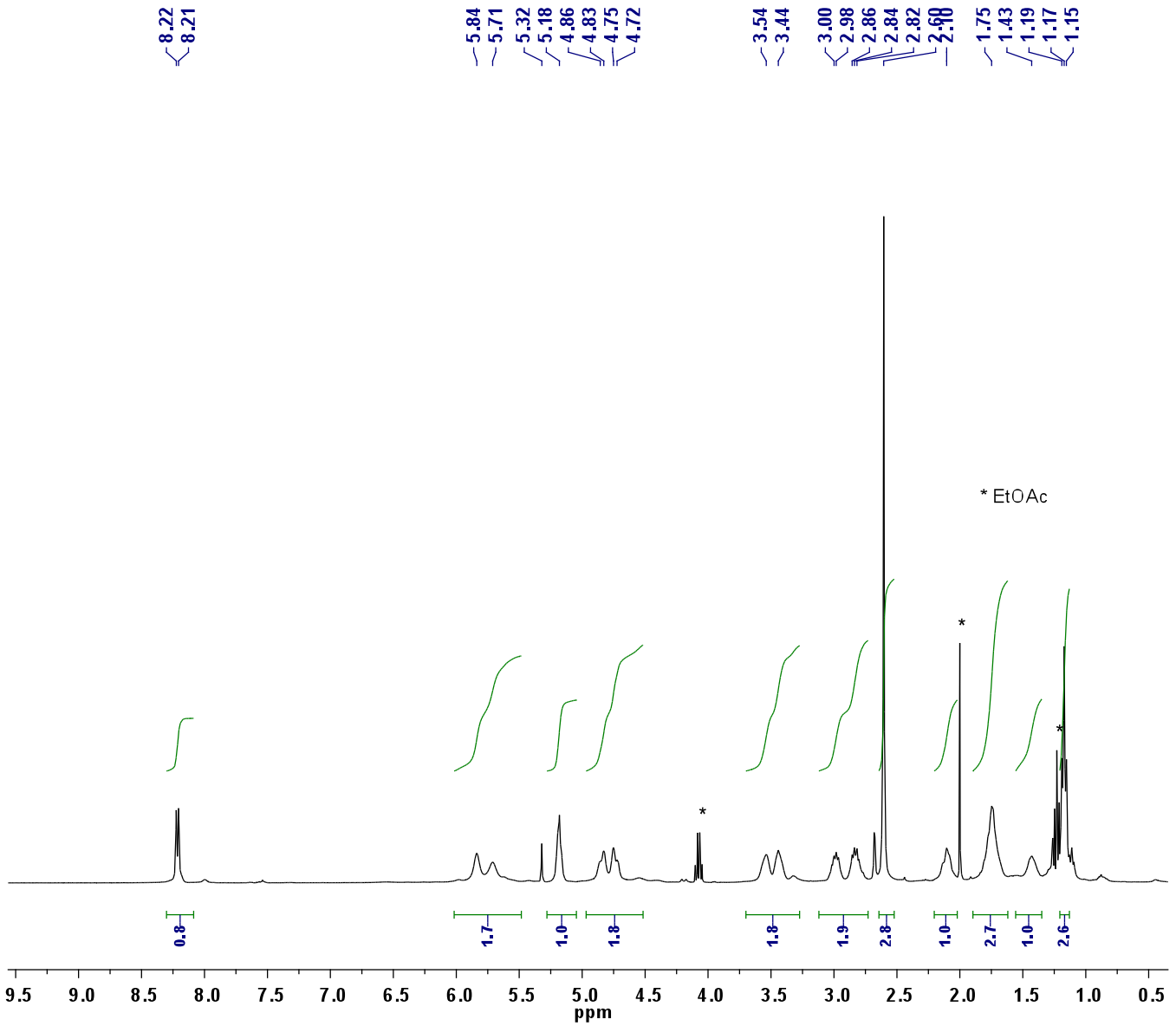

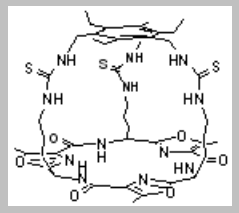

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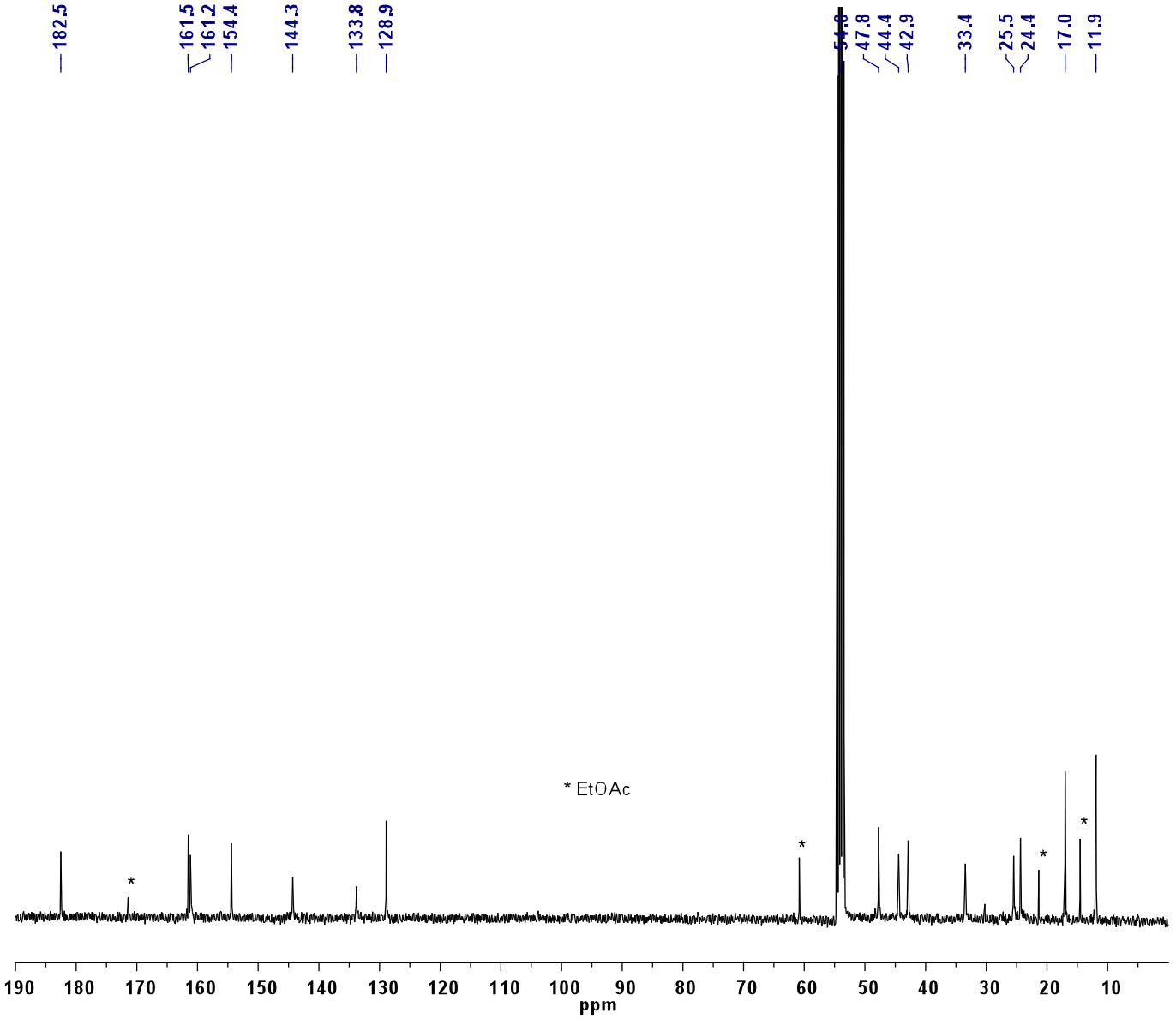


3. Binding Studies

General notes for ^{1}H NMR titration experiments: Typically, a 2-5 mM stock solution of **1** or **2** was prepared in 0.5% (v/v) H_2O/DMSO-d_6 using a volumetric flask. Solutions of anions to be titrated were then prepared in separate volumetric flasks using the same host solution so that the concentration of the host remained constant throughout a given titration experiment. The concentration of anion solutions were made 50 times that of the host (i.e. 0.1-0.25 M). In each case, 500 μL of host solution in a NMR tube was titrated with aliquots of anion stock solution and after each addition the ^{1}H NMR spectrum was recorded after thorough mixing. Typically this was performed in the following order: 10 × 2 μL, 3 × 10 μL, 20 μL then 30 μL (total 100 μL / 10 equivalents). Non-linear curve fitting of the experimentally obtained titration isotherms (equivalents of anion vs. chemical shift of thiourea protons) using the programme *Equilibria*[5] enabled the calculation of association constants (K_a/M^{-1}). In all cases the complete dissociation of the tetrabutylammonium salts was assumed and the data was fitted to a 1:1 binding model. In the case of titrations carried out with **1**, at low millimolar concentrations broad peaks were observed at 300 K and as a result experiments were conducted at 330 K. Final association constants are an average of the values obtained from monitoring N*H*^{1} and N*H*^{2} (Figure S1). All titrations were performed in duplicate.

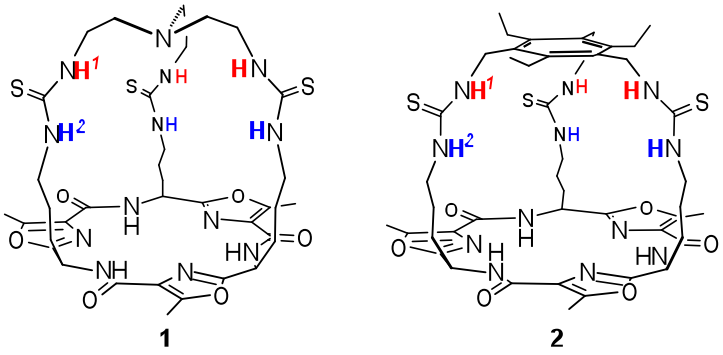
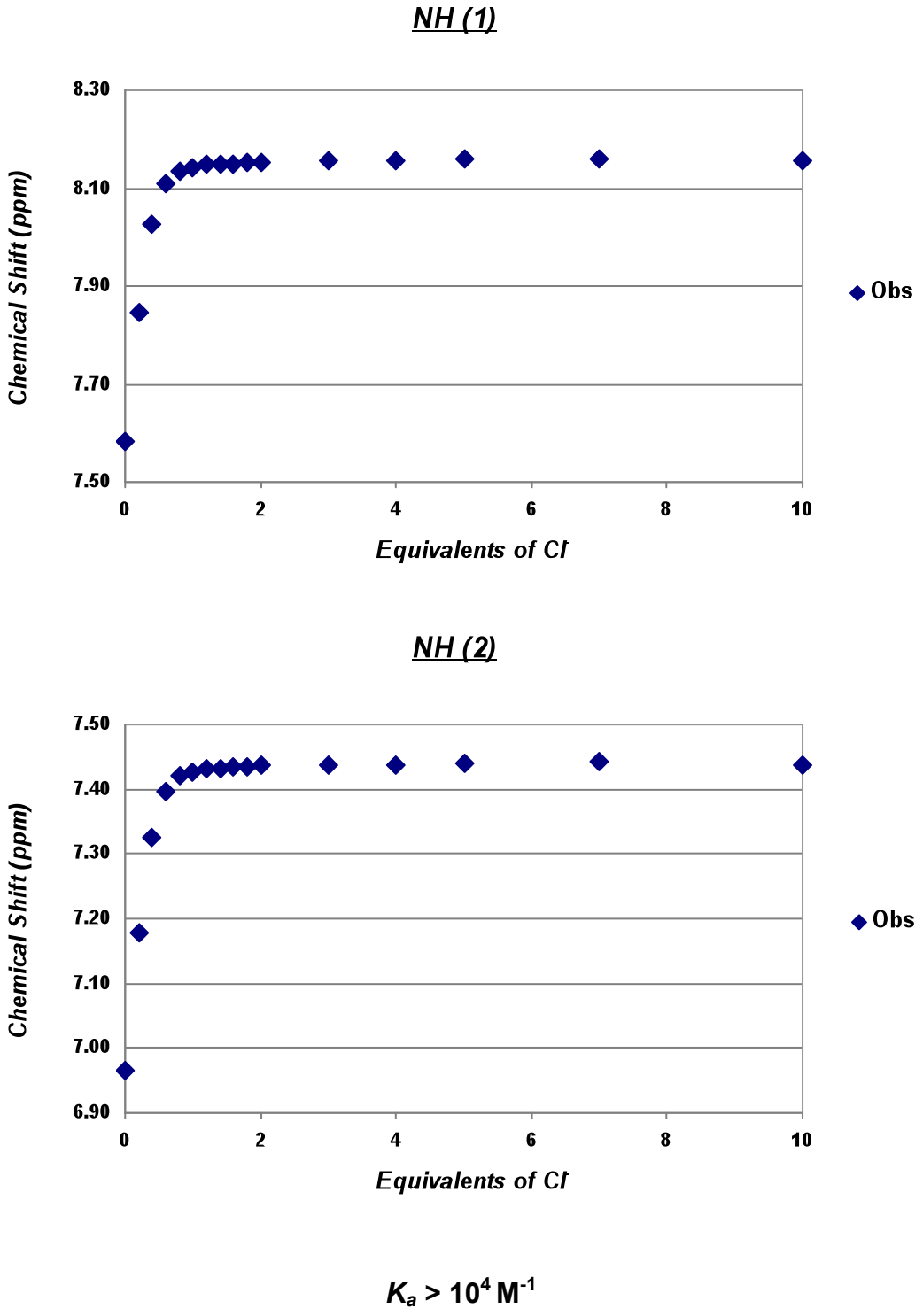


Figure S1. Thiourea protons, NH^1 and NH^2, monitored over the course of each titration experiment.

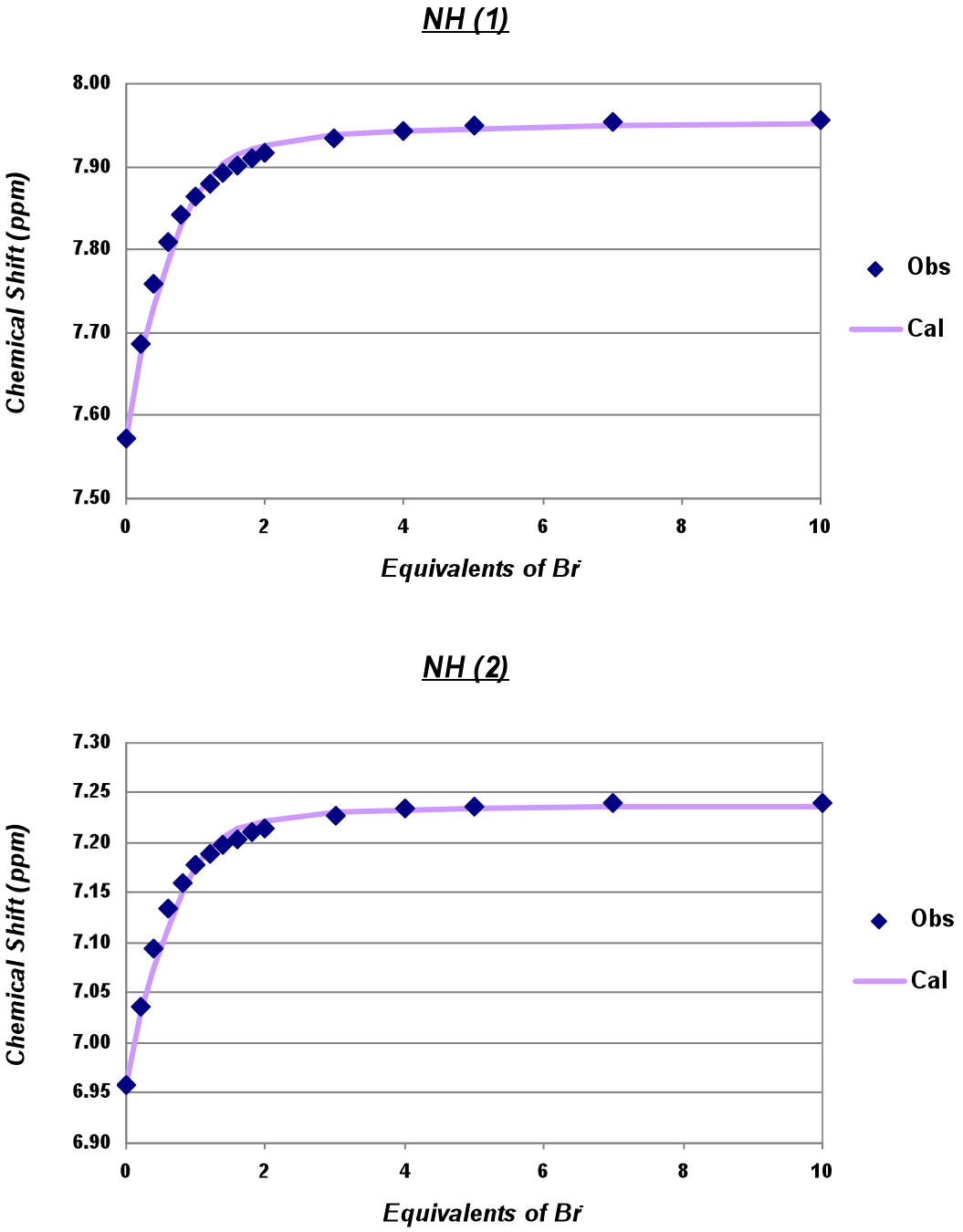
❖ ***Receptor 1 + Cl^-***



$K_a > 10^4\ M^{-1}$

Figure S2. NMR titration of **1** *vs.* TBA-Cl in 0.5% (v/v) H_2O/DMSO-d_6.

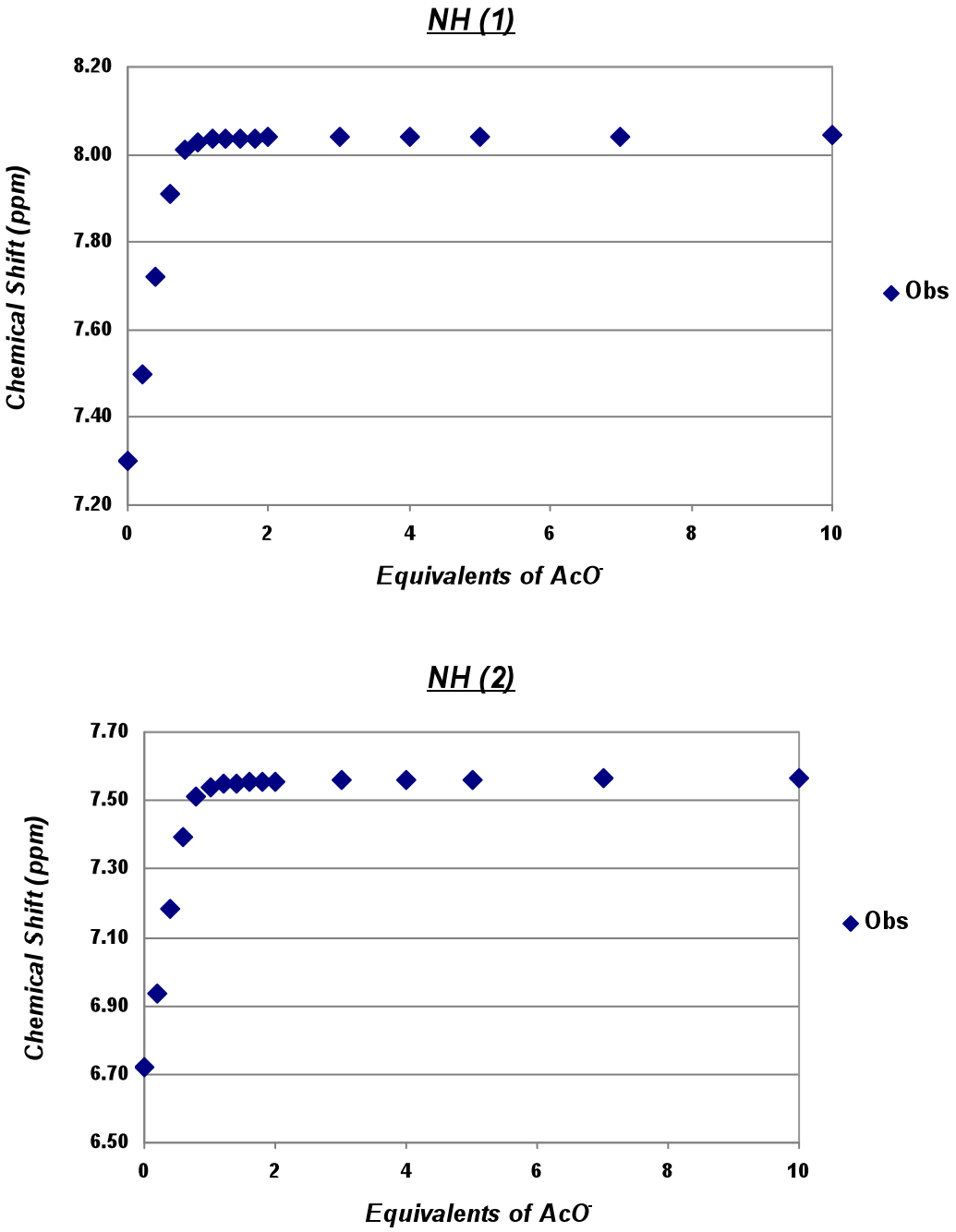
❖ ***Receptor 1 + Br^-***



K_a = 2.7 (± 0.2) x 10^3 M^{-1}

Figure S3. NMR titration of **1** *vs.* TBA-Br in 0.5% (v/v) H_2O/DMSO-d_6.

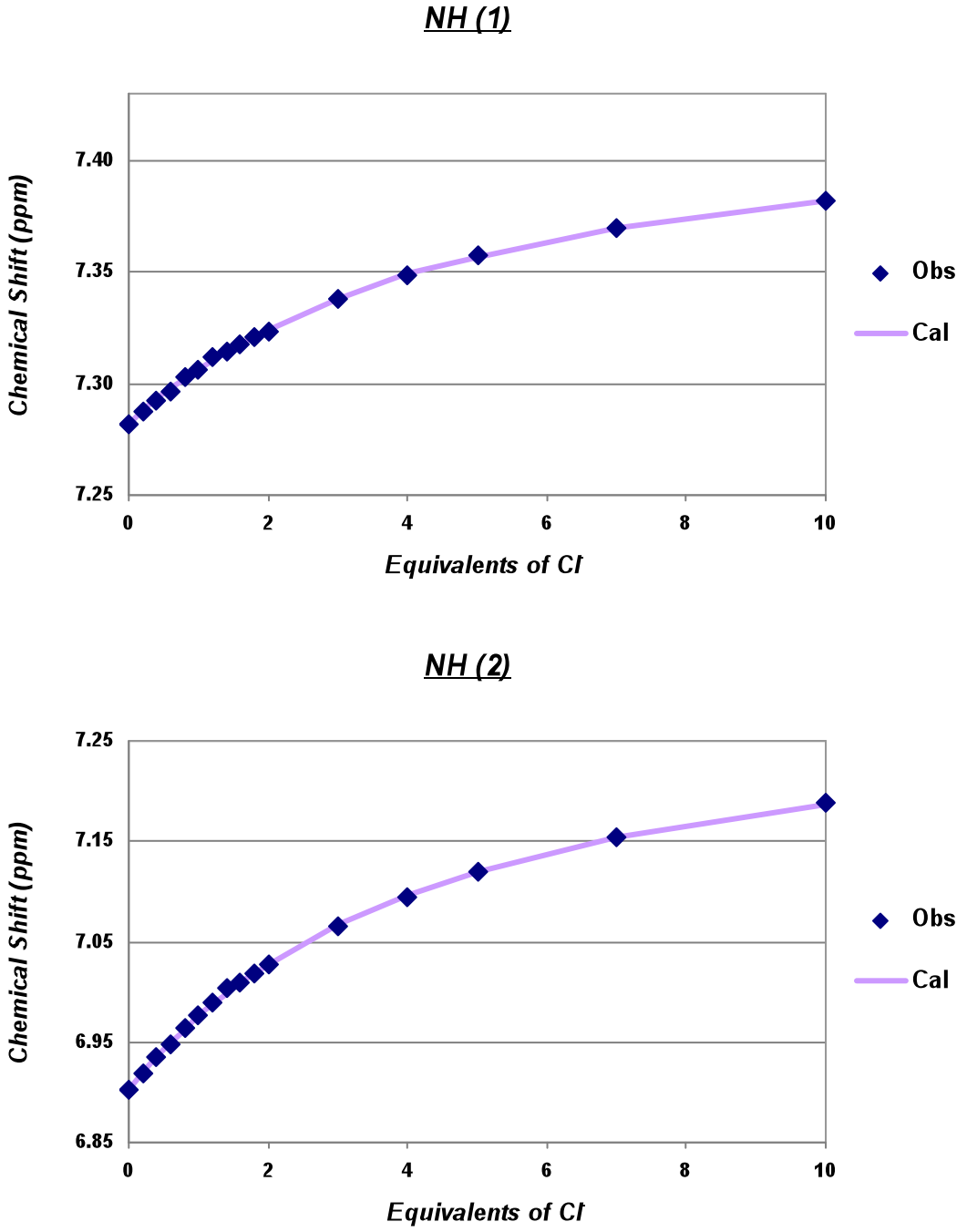
❖ ***Receptor 1 + AcO⁻***



$K_a > 10^4\ M^{-1}$

Figure S4. NMR titration of **1** *vs.* TBA-AcO in 0.5% (v/v) H_2O/DMSO-d_6.

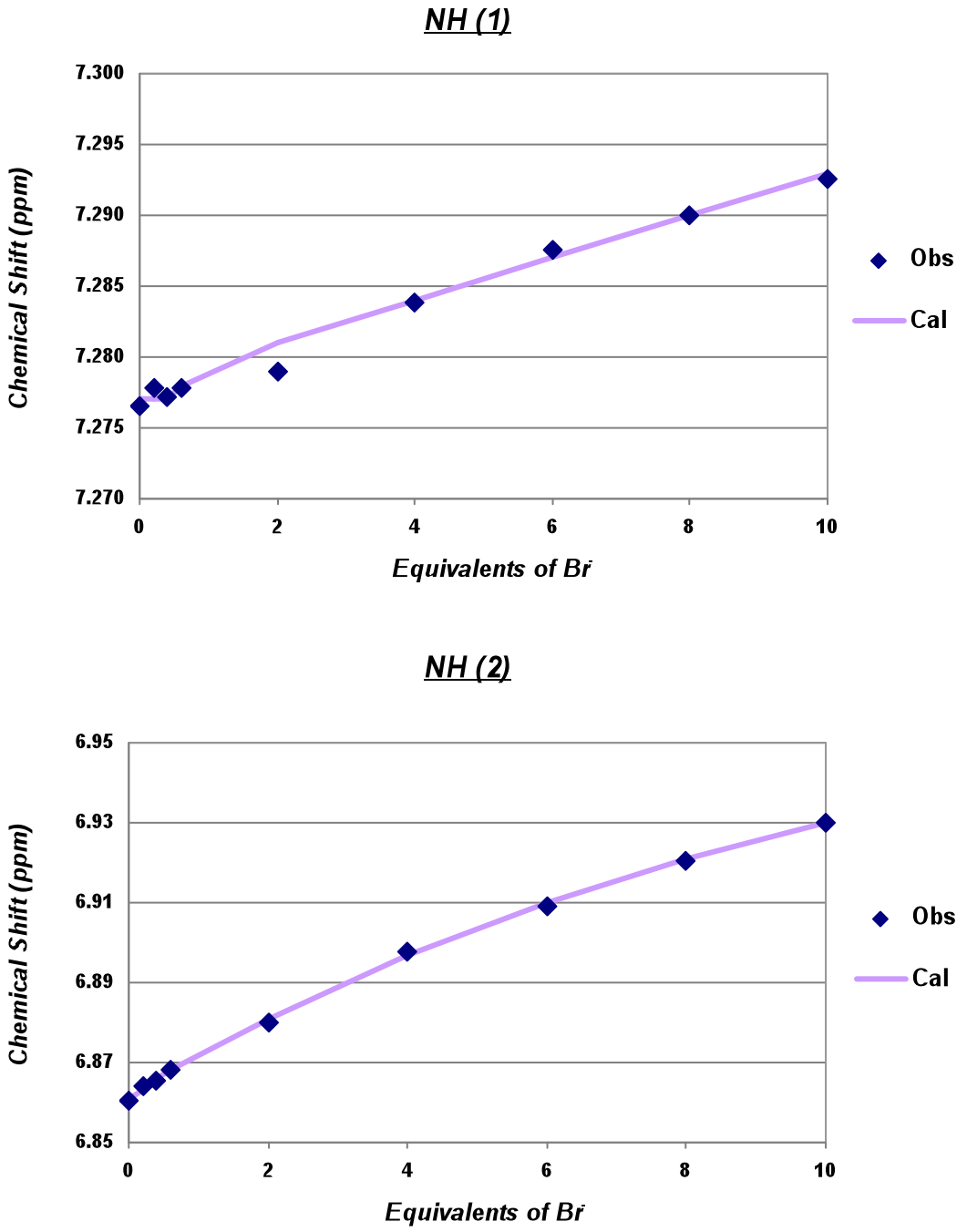
❖ *Receptor 2 + Cl^-*



K_a = 87 (± 6.1) M^{-1}

Figure S5. NMR titration of **2** *vs.* TBA-Cl in 0.5% (v/v) H_2O/DMSO-d_6.

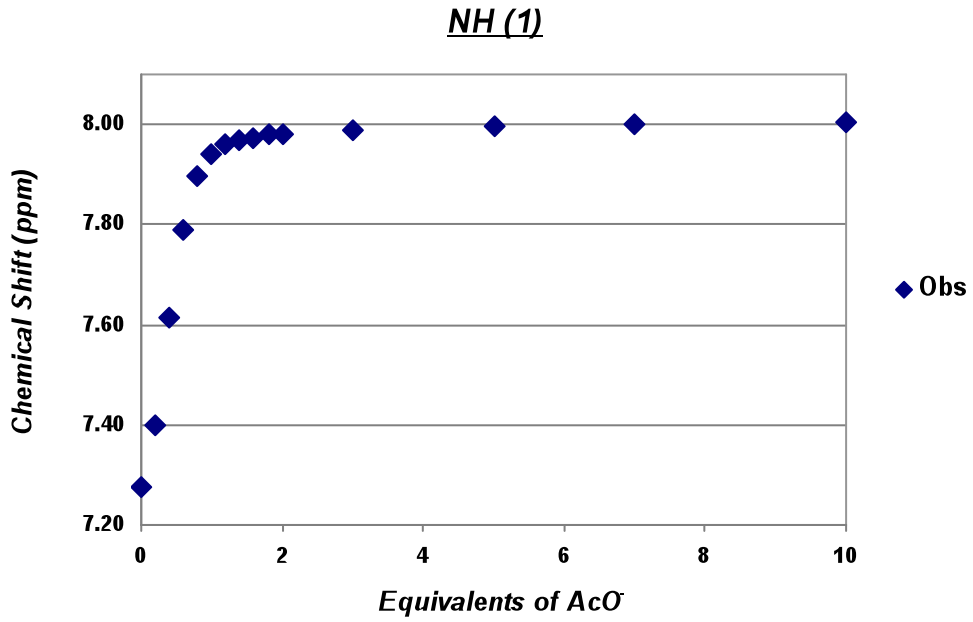
❖ ***Receptor 2 + Br^-***

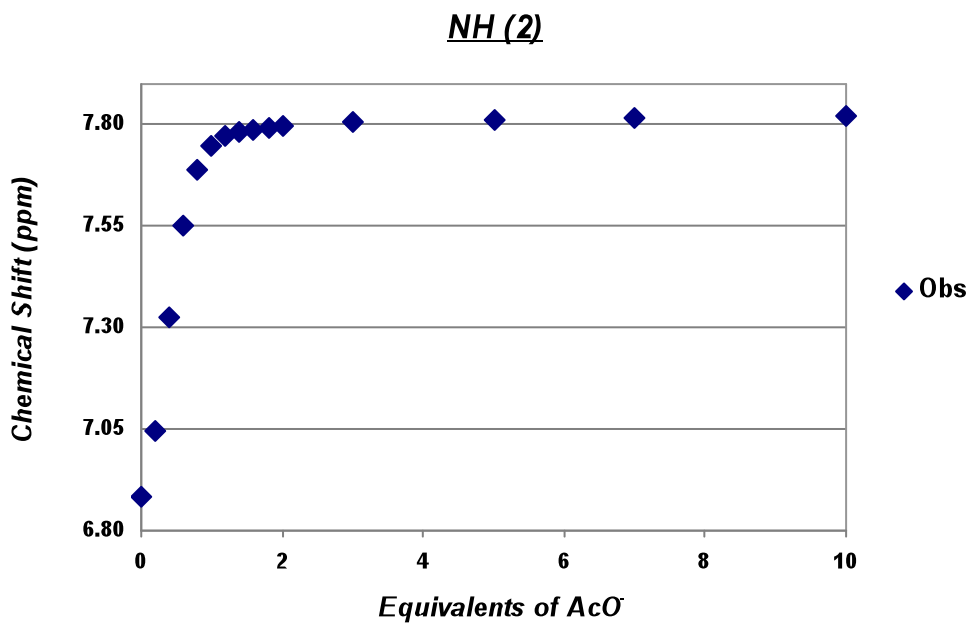


K_a = 11 (±6) M^{-1}

Figure S6. NMR titration of **2** *vs.* TBA-Br in 0.5% (v/v) H_2O/DMSO-d_6.

❖ ***Receptor 2 + AcO^-***





$K_a > 10^4\ M^{-1}$

Figure S7. NMR titration of **2** *vs.* TBA-AcO in 0.5% (v/v) H_2O/DMSO-d_6.

4. X-Ray Crystal Structure Data for Cryptands 1 and 2

Experimental

Data for [MeOH⊂**1**]·TFA·0.875MeOH·0.625H_2O collected at approximately 120 K using silicon monochromated synchrotron radiation (0.65256 Å) at 3-BM1 at the Australian Synchrotron.[6] Data collection was limited to a 360 ° φ scans and a resolution of approximately 0.9 Å. Data for {[$(H_2O)_2$MeCN⊂**2**] [$(H_2O)_3$⊂**2**]}·14.5H_2O were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with ω and φ scans at 150(2) K. Data integration and reduction were undertaken with XDS[7] and SAINT and XPREP.[8] Subsequent computations were carried out using the WinGX-32 graphical user interface.[9] Structures were solved by direct methods using SIR97[10] and SHELXS-97.[11] Multi-scan empirical absorption corrections, when applied, were applied to the data set using the program SADABS.[12] Data were refined and extended with SHELXL-97.[13] In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound, Nitrogen-bound and Alcoholic hydrogen atoms were included in idealised positions and refined using a riding model. Water hydrogen atoms were first located in the difference Fourier map before refinement. Where these hydrogen atoms could not be located, they were not modeled. Specific details regarding the crystal structure refinement are given below.

Data for 1

[MeOH⊂**1**]·TFA·0.875MeOH·0.625H_2O

Specific Details:

A very small crystal was employed in this study. In part due to the crystal size and in part due to the limitations of the synchrotron source employed no useable data was recorded above 0.9 Å resolution. One of the ethylene groups is disordered over two positions and was modelled over two equal occupancy positions with bond length restraints and identical thermal parameters. A number of the solvent methanol molecules are also disordered and were treated similarly. The CF_3 group of one of the TFA molecules is also disordered over two positions and was treated

similarly. The refined Flack parameter (0.01(1))[14] confirms (with reference to the synthetic procedure employed) the enantiopurity of the cryptate.

Hydrogen Bond Geometry

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA Angle(º)
N(13A)	H(13A)	S(35B)	0.88	2.74	3.544(13)	152.6
N(16A)	H(16A)	O(1C)	0.88	2.03	2.890(12)	164.8
N(23A)	H(23A)	O(1J)^{i}	0.88	2.18	2.95(2)	146.8
N(26A)	H(26A)	S(25B)^{ii}	0.88	2.99	3.662(16)	135.1
N(33A)	H(33A)	S(35B)	0.88	2.64	3.504(12)	165.6
N(36A)	H(36A)	F(1C)	0.88	2.39	3.144(9)	143.8
N(36A)	H(36A)	O(2C)	0.88	2.59	3.046(11)	113.0
N(49A)	H(49A)	N(43A)	0.88	2.22	2.701(11)	113.8
N(59A)	H(59A)	N(63A)	0.88	2.33	2.780(11)	111.5
N(13B)	H(13B)	S(25A)^{iii}	0.88	2.80	3.450(14)	132.2
N(16B)	H(16C)	O(1D)	0.88	2.16	2.922(19)	144.5
N(23B)	H(23B)	O(1C)	0.88	2.26	2.866(13)	126.1
N(26B)	H(26B)	O(70A)	0.88	2.53	3.289(13)	144.4
N(33B)	H(33B)	S(25A)^{iii}	0.88	2.75	3.569(14)	154.6
N(36B)	H(36B)	O(2D)	0.88	2.03	2.878(18)	161.9
O(2C)	H(2C)	O(1E)	0.84	1.89	2.648(10)	149.2
O(1D)	H(1D)	O(1F)	0.84	1.91	2.661(18)	148.3
O(1E)	H(1E)	N(1A)	0.84	1.96	2.743(13)	153.9
O(1F)	H(1F)	N(1B)	0.84	1.95	2.789(13)	172.3
O(1G)	H(1G)	O(1I)iv	0.82	1.60	2.05(3)	112.1
O(1G)	H(1G)	O(1H)	0.82	2.04	2.85(4)	168.5

O(2W)	H(1I3)	O(1I)	1.22	1.97	2.87(3)	126.1

Symmetry Operators
[i] –x+1, y+1/2, -z+1 [ii] x+1, y, z [iii] –x+1, y-1/2, -z+2 [iv] –x+1, y+1/2, -z+1 (1) x, y, z

Data for 2

{[$(H_2O)_2$MeCN⊂**2**] [$(H_2O)_3$⊂**2**]}·14.5H_2O

Specific Details:

The crystal employed in this study was very small and weakly diffracting. Despite the use of a low temperature device, a high-powered laboratory X-ray source (5 kW) and long exposure times, little diffraction was observed beyond 1 Å resolution. In addition there is some disorder present in the lattice with one of the ethylene chains modeled over two positions with occupancies of 0.75 and 0.25 respectively. A number of bond-length and angle restraints were required in this region to facilitate realistic modelling. The S(4) sulfur atom was also disordered and modelled over two positions with identical thermal parameters and a total occupancy of 1. A number of the solvent water molecules are also disordered and their hydrogen atoms could not be located in the difference Fourier map and were not modelled. The refined Flack parameter (0.01(7))[14] confirms (with reference to the synthetic procedure employed) the enantiopurity of the cryptate.

Hydrogen Bond Geometry

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA Angle(º)
N(2)	H(2)	N(1)	0.88	2.24	2.693(7)	111.8
N(6)	H(6A)	N(5)	0.88	2.27	2.712(7)	111.3
N(7)	H(7)	O(1W)	0.88	2.15	2.949(7)	151.5
N(8)	H(8)	O(1W)	0.88	2.24	3.033(8)	150.7
N(9)	H(9)	O(3W)	0.88	2.11	2.986(6)	171.7
N(10)	H(10)	O(3W)	0.88	2.60	3.360(7)	145.7
N(11)	H(11)	O(2W)	0.88	2.15	2.959(7)	152.2

N(12)	H(12A)	O(2W)	0.88	2.08	2.899(7)	155.5
N(14)	H(14)	N(13)	0.88	2.26	2.706(7)	111.0
N(16)	H(16)	N(15)	0.88	2.28	2.729(7)	111.4
N(19)	H(19)	O(15W)	0.88	2.12	2.949(9)	156.7
N(20)	H(20)	O(15W)	0.88	2.31	3.102(9)	150.0
N(21)	H(21)	O(10W)	0.88	2.29	3.126(9)	159.5
N(22)	H(22)	O(10W)	0.88	2.19	3.020(7)	156.5
N(23)	H(23)	O(12W)	0.88	2.37	2.976(7)	126.5
N(24)	H(24)	O(10W)	0.88	2.48	3.353(9)	174.0
O(1W)	H(1O)	N(1A)	0.87(4)	2.29(5)	3.148(12)	170(6)
O(2W)	H(3O)	O(3W)	0.87(4)	1.97(6)	2.831(7)	169(8)
O(2W)	H(4O)	N(1A)	0.87(4)	2.06(5)	2.925(10)	171(8)
O(3W)	H(5O)	O(4W)	0.87(4)	1.82(4)	2.690(7)	171(7)
O(3W)	H(6O)	S(5)^{ii}	0.87(4)	2.46(4)	3.328(5)	178(5)
O(4W)	H(7O)	O(5W) ^{ii}	0.87(4)	1.97(5)	2.824(7)	166(7)
O(4W)	H(8O)	O(12) ^{iii}	0.87(4)	1.93(4)	2.792(7)	170(8)
O(5W)	H(9O)	O(10)	0.87(4)	2.01(6)	2.848(7)	160(6)
O(5W)	H(10O)	O(6W)	0.87(4)	2.17(4)	3.002(9)	163(5)
O(6W)	H(11O)	O(7W)	0.87(4)	1.85(6)	2.688(8)	164(6)
O(6W)	H(12O)	O(5W)	0.87(4)	2.58(8)	3.002(9)	111(7)
O(7W)	H(13O)	S(5)	0.870(16)	2.49(3)	3.318(5)	158(7)
O(7W)	H(14O)	O(8W)	0.87(4)	1.92(7)	2.789(8)	180(9)
O(8W)	H(15O)	O(16W)	0.87(4)	2.24(4)	2.873(10)	130(4)
O(8W)	H(16O)	S(6)^{i}	0.87(4)	2.55(4)	3.390(6)	165(5)
O(9W)	H(17O)	S(1)	0.87(4)	2.76(6)	3.426(7)	134(7)
O(9W)	H(18O)	O(16W)^{iv}	0.87(4)	2.14(7)	2.768(10)	129(7)
O(10W)	H(19O)	O(18W)	0.87(4)	2.03(5)	2.788(11)	145(8)

O(10W)	H(19O)	O(19W)	0.87(4)	2.09(8)	2.572(19)	114(7)
O(10W)	H(20O)	O(12W)	0.87(4)	1.87(7)	2.731(8)	172(8)
O(11W)	H(21O)	O(13W)	0.87(4)	2.04(5)	2.748(7)	137(6)
O(12W)	H(23O)	O(11W)^{v}	0.87(4)	1.95(7)	2.788(7)	165(8)
O(12W)	H(24O)	S(3)^{vi}	0.87(4)	2.42(5)	3.259(5)	163(7)
O(13W)	H(25O)	O(4)^{vi}	0.87(4)	2.00(7)	2.843(6)	161(7)
O(13W)	H(26O)	O(8)^{vii}	0.87(4)	2.14(4)	2.933(7)	151(7)
O(14W)	H(27O)	O(8)^{vii}	0.87(4)	2.05(3)	2.888(7)	160(7)
O(14W)	H(28O)	O(23W)	0.87(4)	2.34(4)	3.17(3)	160(6)
O(15W)	H(29O)	O(6W)	0.87(4)	2.22(6)	2.895(10)	134(7)
O(15W)	H(30O)	O(19W)	0.87(4)	1.71(2)	2.58(2)	175(9)
O(15W)	H(30O)	O(18W)	0.87(4)	2.46(7)	3.028(12)	123(7)
O(16W)	H(31O)	O(8W)	0.87(4)	2.26(6)	2.873(10)	128(6)
O(16W)	H(32O)	O(17W)^{i}	0.87(4)	1.99(4)	2.714(11)	140(6)
O(16W)	H(32O)	O(26W)^{i}	0.87(4)	2.46(7)	2.94(3)	115(5)

Symmetry Operators

^{i} x+1, y, z ^{ii} x, y+1, z ^{iii} x+1, y+1, z ^{iv} x, y, z+1 ^{v} x-1, y, z ^{vi} x, y-1, z ^{vii} x+1, y, z+1

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