Anion complexation, transport and structural studies of a series of bis-methylurea compounds

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Electronic Supporting Information

1. Synthesis
2. Crystallizations
3. Single Crystal X-ray diffraction
4. Anion Transport Studies
5. Proton NMR titration fitting

1. Synthesis

All reactions were performed in oven-dried glassware under a slight positive pressure of nitrogen. ^{1}H-NMR (400 MHz, 500MHz) and ^{13}C NMR (100 MHz, 125MHz) spectra were determined on a Varian INOVA-400 spectrometer, and Varian INOVA-500 spectrometer. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet . Chemical shifts for ^{13}C NMR are reported in ppm, relative to the central line of a septet at δ = 39.52 ppm for deuterio-dimethylsulfoxide. Infrared (IR) spectra were recorded on a NICOLET 5700 FT-IR spectrophotometer and reported in wavenumbers (cm^{-1}). Microanalytical data were obtained using a Fisons EA CHNS-O instrument (T = 1000 °C). Fluorescence spectra were recorded on a Cary Eclypse spectrofluorimeter. All solvents and starting materials were purchased from commercial sources where available. Proton NMR titrations were performed by adding aliquots of the putative anionic guest (as the TBA salt, 0.075 M) in a solution of the receptor (0.005M) in DMSO-d_6/0.5% water to a solution of the receptor (0.005M).
The synthesis of pyridine-2,6-diyldimethanaminium chloride has already been reported in literature.[1]
[1] C. Nolan, T. Gunnlaugsson, Tetrahedron Lett., 2008, 49, 1993.

Synthesis of 1,1'-(1,3-phenylenebis(methylene))bis(3-(4-(trifluoromethyl)phenyl)urea) L^1

A solution of 4-(trifluoromethyl)phenyl isocyanate (0.550 g; 2.94 mmol) in 15 ml of DCM was added dropwise to a solution of m-xylylenediamine (0.200 g; 1.47 mmol) in 15 ml of DCM and was left stirring at reflux under N$_2$ atmosphere overnight. The precipitate thus formed was collected by filtration and dried under vacuum to give a white solid.
Yield: 97% (0.730 g; 1.43 mmol); M.p. 237°C; ^{1}H NMR (500 MHz, DMSO-d_6, 298K) δ_{CH} 4.3 (d, J=5 Hz, 4H); δ_{ArH} 6.78 (t, 2H, NH) 7.19 (d, J=10 Hz, 2H) 7.26 (s, 1H), 7.30 (t, J= Hz, 1H), 7.54 (d, J=10 Hz, 4H) 7.59 (d, J=10, 4H), 8.99 (s, 2H, NH); ^{13}C-NMR(100 MHz, DMSO-d_6, 298 K) δ_C 42.73; δ_{ArC} 117.29, 120. 90 (q, J= 100.8 Hz, CF$_3$), 125.66, 125. 85, 125. 88, 125.90, 128.31, 140. 16, 144.14, 154.82.

Synthesis of 1,1'-(pyridine-2,6-diylbis(methylene))bis(3-(4-(trifluoromethyl)phenyl)urea) L^2

A solution of 4-(trifluoromethyl)phenyl isocyanate (0.426 g; 2.28 mmol) in 15 ml of DCM was added dropwise to a stirred suspension of pyridine-2.6-diyldimethanamine dihydrocloride (0.240g; 1.14 mmol) and TEA (1 ml) in 15 ml of DCM. After the addition of isocyanate a colourless solution was obtained. The reaction was refluxed under N$_2$ atmosphere overnight. The solvent was evaporated *in vacuo* and the solid obtained was washed with water and then filtered off, dried under reduced pressure and isolated as a white solid.
Yield: 70% (0.340g, 0.73 mmol); M.p. 234°C; ^{1}H NMR(500 MHz, DMSO-d_6, 298K) δ_{CH} 4.425 (d, J=5.5 Hz, 4H); δ_{ArH} 6.91 (t, NH, 2H); 7.23 (d, J=7.5 Hz, ArH, 2H); 7.56-7.63 (m, 4H); 7.76 (t, J= 8 Hz, ArH, 1H); 9.20 (s, NH, 2H); ^{13}C-NMR(125 MHz, DMSO-d_6, 298 K) δ_C 44.66; δ_{ArC} 117.30, 119.12, 121.10 (q, j=128 Hz, CF$_3$), 123.27, 125.96, 137.45, 144.14, 154.88; δ_{CO} 158.26. LMRS (ES$^-$) m/z: 510.0381 [M-H$^+$]$^-$.

Synthesis of 1,1'-(1,3-phenylenebis(methylene))bis(3-(3,5-bis(trifluoromethyl)phenyl)urea) L^3

A solution of 3,5-Bis(trifluoromethyl)phenyl isocyanate (0.750 g; 2.94 mmol) in 15 ml of DCM was added dropwise to the solution of m-xylylenediamine (0.200g; 1.47 mmol) in 15 ml of DCM and was left stirring at reflux under N_2 atmosphere overnight. The precipitate thus formed was isolated by filtration, washed with MeOH and Et_2O and dried over vacuum.

Yield: 77% (0.730 g; 1.13 mmol); M.p. 245°C; ^{1}H NMR(500 MHz, DMSO-d_6, 298K) δ_{CH} 4.31 (d, J=6 Hz, 4H); δ_{ArH} 7.01 (t, J=6 Hz, NH, 2H); 7.18 (d, J=7.5 Hz, 2H); 7.25 (s, 1H); 7.30 (t, J=8 Hz, 1H); 7.50 (s, 2H); 8.07 (s, 4H); 9.35 (s, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 42.75, δ_{ArC} 113.41, 117.21, 123.33 (q, J=1080, CF_3), 125.59, 125.67, 128.28, 130.54 (q, J=128, CF_3), 140.11, δ_{CO} 154.83. LMRS (ES^-) m/z: 645.1481 $[M-H^+]^-$.

Synthesis of 1,1'-(pyridine-2,6-diylbis(methylene))bis(3-(3,5-bis(trifluoromethyl)phenyl)urea) L^4

A solution of 3,5-Bis(trifluoromethyl)phenyl isocyanate (0.619 g; 2.43 mmol) in 15 ml of DCM was added dropwise to the suspension of pyridine-2.6-diyldimethanamine dihydrocloride and TEA (1 ml) in 15 ml of DCM(0.255g; 1.21 mmol). After the addition of isocyanate a colourless solution was obtained. The mixture was heated to reflux under N_2 and stirred overnight. The solvent was removed under reduced pressure to give a white solid wich was washed with water and then with DCM, filtered off and dried over vacuum.

Yield: 74% (0.58 g; 0.89 mmol); M.p. >250°C; ^{1}H NMR (500 MHz, DMSO-d_6, 298K) δ_{CH} 4.43 (d, J=5.6 Hz, 4H); 7.10 (t, NH, 2H); 7.23 (d, J=8 Hz, 2H); 7.55 (s, 2H); 7.76 (t, J=8 Hz, 1H); 8.10 (s, 4H); 9.56 (s, NH, 2H); ^{13}C-NMR(125 MHz, DMSO-d_6, 298 K) δ_C 44.68, δ_{ArC} 113. 60, 117.213, 119. 04, 123.32 (q, J=1080, CF3), 130.60 (q, J=129.5, CF_3), 137.53, 142.49, 154.8, δ_{CO} 158.15. LMRS (ES^-) m/z: 646.0661 $[M-H^+]^-$.

Synthesis of 1,1'-(1,3-phenylenebis(methylene))bis(3-(4-nitrophenyl)urea) L^5

A solution of 4-nitrophenyl isocyanate (0.480 g; 2.94 mmol) in 15 ml of DCM was added to the solution of m-xylylenediamine (0.200g; 1.47 mmol) in 15 ml of DCM. After refluxing under stirring in N_2 atmosphere overnight, the precipitate was filtered off, washed with MeOH and dried over vacuum to give a yellow solid.

Yield: 88% (0.6 g; 1.29 mmol); M.p. 228°C; ^{1}H NMR(500 MHz, DMSO-d_6, 298K) δ_{CH} 4.32 (d, J=6 Hz, 4H); δ_{ArH} 6.93 (t, J=6 Hz, NH, 2H); 7.20 (d, J=7.5 Hz, 2H); 7.26 (s, 1H); 7.30 (t, J=8 Hz, 1H); 7.61 (d, J=9.5 Hz, 4H); 8.10 (d, J=9 Hz, 4H); 9.36 (s, NH, 2H); ^{13}C-NMR(125 MHz, DMSO-d_6, 298 K) δ_C 42.78; δ_{ArC} 116.88, 125.05, 125.72, 125.88, 128.37, 139.99, 140.43, 147.09; δ_{CO} 154.45

Synthesis of 1,1'-(pyridine-2,6-diylbis(methylene))bis(3-(4-nitrophenyl)urea) L^6

A solution of 4-nitrophenyl isocyanate (0.312 g; 1.9 mmol) in 10 ml of DCM was added to the stirring suspension of pyridine-2.6-diyldimethanamine dihydrocloride (0.200g; 0.95 mmol) and TEA (1 ml) in 15 ml of DCM. After the addition of isocyanate a yellow solution was obtained. The mixture of reaction was allowed to stir for 24h under a N_2 atmosphere at room temperature. The solvent was removed via reduced pressure to give a yellow solid which was washed with water and then with hot MeOH, filtered off and dried under vacuum.

Yield: 52% (0.23 g; 0.49 mmol); M.p. 232 °C; ^{1}H NMR(400 MHz, DMSO-d_6, 298K) δ_{CH} 4.44 (d, J=8 Hz, 4H); δ_{ArH} 7.06 (t, J=8 Hz, NH, 2H); 7.24 (d, J=8 Hz, 2H); 7.65 (d, J=8 Hz, 4H); 7.77 (t, J=8 Hz, 1H); 8.14 (d, J=8 Hz, 4H); 9.57 (s, NH, 1H); ^{13}C-NMR(125 MHz, DMSO-d_6 , 298 K) δ_C 44.68; δ_{ArC} 116.93, 119.21, 125.13, 137.51, 140.53, 147.08, 154.52; δ_{CO} 158.02. LMRS (ES^-) m/z: 463.9218 $[M-H^+]^-$.

2. Crystallizations

Table S1. Summary of the crystallization experiments in different solvents for the receptors **L^1-L^6**. Conditions yielding single crystals are indicated as (√). (●) indicates an unsuccessful experiment and (-) is used to indicate "not applied" experimental conditions.

Receptor	Host	solvent							
		MeOH	EtOH	EtOH/$MeNO_2$	THF /DMF	DMF	$MeNO_2$	MeCN	DMSO
L^1	-	-	-	-	●	-	-	-	●
L^1	AcO^-	-	-	-	√ L^1-AcO^-(1:2)	●	-	-	●
L^1	BzO^-	-	-	-	●	●	-	-	●
L^1	$HPpi^{2-}$	-	-	-	●	-	-	-	●
L^1	Cl^-	-	-	-	-	-	-	-	●
L^1	F^-	-	-	-	-	-	-	-	●
L^1	HCO_3^-	-	-	-	-	●	-	-	●
L^1	H_2PO_4	-	-	-	-	●	-	-	●
L^1	HSO_4^-	-	-	-	-	●	-	-	●
L^1	CN^-	-	-	-	-	-	-	-	-
L^2	-	-	-	-	●	●	-	-	●
L^2	AcO^-	-	-	-	-	●	-	-	●
L^2	BzO^-	-	-	-	-	-	-	-	●
L^2	$HPpi^{2-}$	-	-	-	-	-	-	-	●
L^2	Cl^-	-	-	-	-	-	-	-	●
L^2	F^-	-	-	-	-	-	-	-	●
L^2	HCO_3^-	-	-	-	-	-	-	-	●
L^2	H_2PO_4	-	-	-	-	●	-	-	●
L^2	HSO_4^-	-	-	-	-	-	-	-	√ L^2-SO_4^{2-}(3:1)
L^2	CN^-	-	-	-	-	-	-	-	-
L^3	-	-	-	-	-	-	-	-	√ L^3-DMSO
L^3	AcO^-	●	●	√ L^3-AcO^-(1:2)	●	●	●	●	●
L^3	BzO^-	●	●	●	-	●	●	●	●
L^3	$HPpi^{2-}$	●	●	●	-	●	●	●	●
L^3	Cl^-	-	-	-	-	-	-	-	●
L^3	F^-	-	-	-	-	-	-	-	●
L^3	HCO_3^-	-	-	-	-	-	-	-	●
L^3	H_2PO_4	-	-	-	-	-	-	-	●
L^3	HSO_4^-	-	-	-	-	-	-	-	-
L^3	CN^-	-	-	-	-	-	-	-	√L^3-CO_3^{2-} (2:1)
L^4	-	√L^4-MeOH		-	-	-	-	-	√ L^4-A
L^4	AcO^-	●	●	-	●	-	●	●	●
L^4	BzO^-	●	●	●	-	-	●	●	●
L^4	$HPpi^{2-}$	●	●	-	-	-	●	●	●
L^4	Cl^-	-	-	-	-	-	-	-	●
L^4	F^-	-	-	-	-	-	-	-	●
L^4	HCO_3^-	-	-	-	-	-	-	-	●
L^4	H_2PO_4	-	-	-	-	-	-	-	√L^4-HPO_4^{2-}-(2:1)
L^4	HSO_4^-	-	-	-	-	-	-	-	●
L^4	CN^-	-	-	-	-	-	-	-	●
L^5	-	-	-	-	-	●	-	-	●
L^5	AcO^-	-	-	-	-	●	●	●	●

L^5	BzO^-	-	-	-	-	-	●	●	●
L^5	$HPpi^{2-}$	-	-	-	-	-	●	●	●
L^5	Cl^-	-	-	-	-	-	●	●	●
L^5	F^-	-	-	-	-	-	-	-	●
L^5	HCO_3^-	-	-	-	-	-	●	●	●
L^5	H_2PO_4	-	-	-	-	●	-	-	●
L^5	HSO_4^-	-	-	-	-	-	-	-	●
L^5	CN^-	-	-	-	-	-	-	-	-
L^6	-	-	-	-	-	-	-	-	●
L^6	AcO^-	-	-	-	-	-	-	-	●
L^6	BzO^-	-							●
L^6	$HPpi^{2-}$	-	-	-	-	-	-	-	●
L^6	Cl^-	-	-	-	-	-	-	-	●
L^6	F^-	-	-	-	-	-	-	-	●
L^6	HCO_3^-	-	-	-	-	-	-	-	●
L^6	H_2PO_4	-	-	-	-	-	-	-	●
L^6	HSO_4^-	-	-	-	-	-	-	-	●
L^6	CN^-	-	-	-	-	-	-	-	-

3. Single Crystal X-ray diffraction

Data Collection: for the general procedure applied see "S. J. Coles and P. A. Gale, *Chem Sci.*, 2012, **3**, 683-689".

Graphics: all the graphics were generated by using Mercury 3.3.

L^3-DMSO (CCDC 1016980)

Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with VHF *Varimax* optics (70µm focus). **Cell determination and data collection**: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2013). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 3.1 b 27* (Rigaku, 2013). **Structure solution**: *SUPERFLIP* (Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790). **Structure refinement**: *SHELXL-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122).

Refine special details: One CF3 group and the DMSO solvent are disordered, and as such various geometrical (DFIX, SADI) and displacement (SIMU) restraints have been used and some of those atoms are left as isotropic. Both merohedral and non-merohedral twinning were investigated for this sample, but no viable twin law was discovered.

L^4-A (CCDC 1016981)

Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with VHF *Varimax* optics (70µm focus). **Cell determination and data collection**: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2013). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 3.1 b 27* (Rigaku, 2013). **Structure solution**: *SHELXS-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Structure refinement**: *SHELXL-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122).

Refine special details: The CF3 groups are disordered, and as such various geometrical (DFIX, SADI) and displacement (SIMU) restraints have been used and some of those atoms are left as isotropic.

L^4- MeOH (CCDC 1016982)

Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with HF *Varimax* optics (100µm focus). **Cell determination and data collection**: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2013). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 3.1 b27 (Rigaku, 2013).* **Structure solution**: *SHELXS-*

2013 (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Structure refinement**: *SHELXL-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122).

Refine special details: Electron density from disordered solvent (MeOH) was eliminated using the SMTBX solvent masking routine within Olex2, which is located within the channels (figure below).

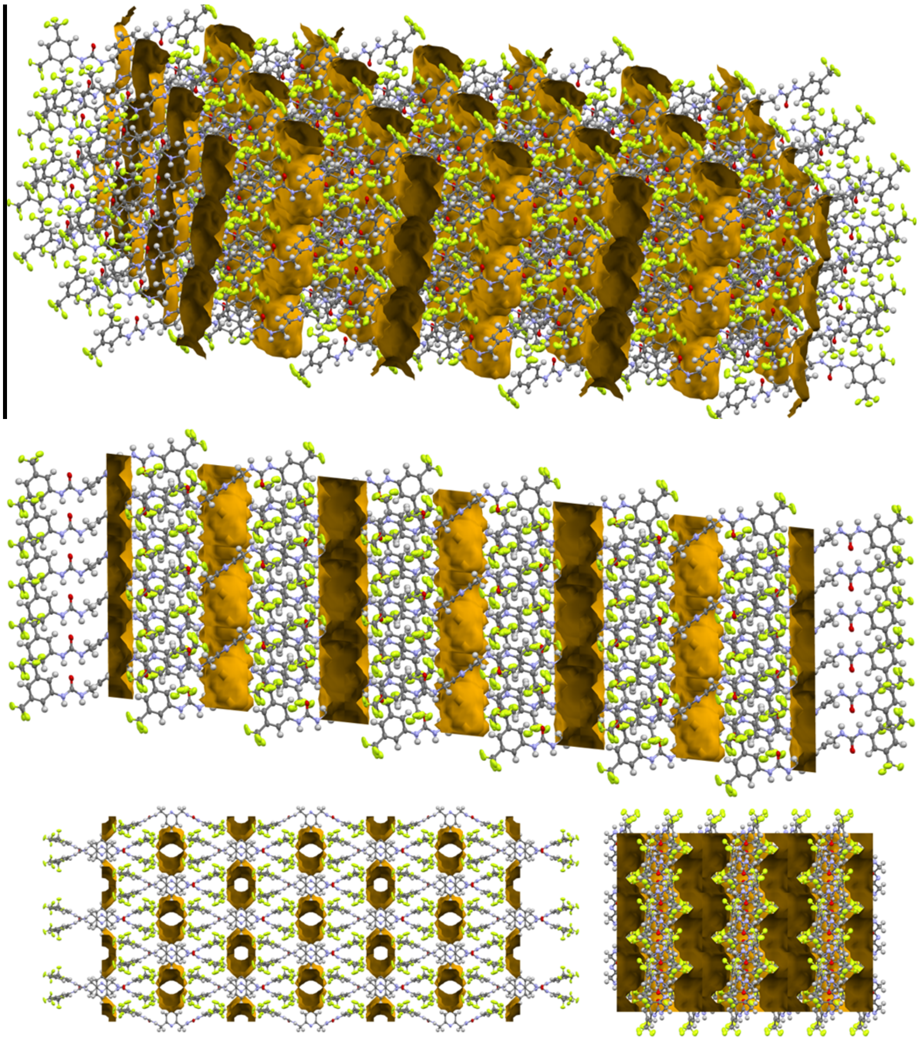


Figure Views of the open channels running through the structure in which the MeOH solvent is contained (disordered)

L^1-AcO$^-$ (1:2) (CCDC 1016983)

Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with HF *Varimax* optics (100µm focus). **Cell determination and data collection:** *CrystalClear-SM Expert 2.0 r7* (Rigaku, 2011). **Data reduction, cell refinement and absorption correction:** *CrystalClear-SM Expert 3.1 b27 (Rigaku, 2013).* **Structure solution: :** *SUPERFLIP* (Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790). **Structure refinement:** *SHELXL-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122).

Refine special details: One of the TBA arms is modelled as disordered using similarity restraints for the geometry.

L^3-AcO$^-$(1:2) (CCDC 1016984)
Diffractometer: Beamline I19 situated on an undulator insertion device with a combination of double crystal monochromator, vertical and horizontal focussing mirrors and a series of beam slits (primary white beam and either side of the focussing mirrors). The experimental hutch (EH1) is equipped with a Crystal Logic 4-circle kappa geometry goniometer with a Rigaku Saturn 724 CCD detector and an Oxford Cryosystems Cryostream plus cryostat (80-500K). For conventional service crystallography the beamline operates at a typical energy of 18 keV (Zr K absorption edge) and a Rigaku ACTOR robotic sample changing system is available. **Cell determination and data collection**: *CrystalClear-SM Expert 2.0 r5* (Rigaku, 2010). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 2.0 r5* (Rigaku, 2010). **Structure solution**: *SUPERFLIP* (Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790). S**tructure refinement**: *SHELXL-2013* (G Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.).

Refine special details: Refined as a 2-component twin. The crystal did not produce good diffraction images, even using synchrotron radiation, resulting in the high R(int) and R-values. However there is enough information to prove the location of the atoms in space,but due to the poor quality all the atoms were left isotropic and various geometrical (SAME, SADI) restraintshave been used.

L^3-CO$_3^{2-}$ (2:1) (CCDC 1016985)
Diffractometer: Beamline I19 situated on an undulator insertion device with a combination of double crystal monochromator, vertical and horizontal focussing mirrors and a series of beam slits (primary white beam and either side of the focussing mirrors). The experimental hutch (EH1) is equipped with a Crystal Logic 4-circle kappa geometry goniometer with a Rigaku Saturn 724 CCD detector and an Oxford Cryosystems Cryostream plus cryostat (80-500K). For conventional service crystallography the beamline operates at a typical energy of 18 keV (Zr K absorption edge) and a Rigaku ACTOR robotic sample changing system is available. **Cell determination and data collection**: *CrystalClear-SM Expert 2.0 r5* (Rigaku, 2010). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 2.0 r5* (Rigaku, 2010). **Structure solution**: *SUPERFLIP* (Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790). S**tructure refinement**: *SHELXL-2013* (G Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.).

Refine special details: Some of the CF3 groups and a DMSO solvent are disordered, and as such various geometrical (DFIX, SADI, BUMP) and displacement (SIMU, DELU) restraints have been used and some of those atoms are left as isotropic.

L^4-HPO$_4^{2--}$(2:1) (CCDC 1016986)
Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with HF *Varimax* optics (100µm focus). **Cell determination and data collection**: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2013). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 3.1 b27 (Rigaku, 2013).* **Structure solution**: *SHELXS-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Structure refinement**: *SHELXL-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122).

Refine special details: Disorder and 6 independent entities in the asymmetric unit require restraints to be applied, for full details see _olex2_refinement_description in the CIF

L^2-SO$_4^{2-}$ (3:1) (CCDC 1016987)
Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with HF *Varimax* optics (100µm focus). **Cell determination and data collection**: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2013). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 3.1 b27 (Rigaku, 2013).* **Structure solution**: *SHELXD-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Structure refinement**: *SHELXL-2013* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122).

Refine special details: Poor data quality, lots of disorder and 6 independent entities in the asymmetric unit require numerous restraints to be used, for full details see _olex2_refinement_description in the CIF

Table S2 . Crystal data and structure refinement details.

	L^3-DMSO **CCDC c**	**L^4-MeOH** **CCDC 1016982**	**L^4-A** **CCDC 1016981**
Empirical formula	$C_{28}H_{24}F_{12}N_4O_3S$	$C_{25}H_{17}F_{12}N_5O_2$	$C_{25}H_{17}F_{12}N_5O_2$
Formula weight	724.57	647.44	647.43
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*	*P2/c*
a /Å	26.454(2)	26.210(7)	11.4364(9)
b /Å	12.7445(9)	12.739(3)	12.8183(10)
c /Å	8.9389(5)	8.981(2)	9.0313(7)
α / º	90	90	90
β / º	94.842(3)	96.618(5)	100.463(2)
γ / º	90	90	90
V /Å^3	3002.9(4)	2978.7(13)	1301.9(2)
T / K	100(2)	100(2)	100(2)
Crystal shape	Blade	Prism	Rod
Crystal size / m^3	0.130 × 0.100 × 0.040 mm^3	0.21 x 0.11 x 0.08 mm^3	0.220 × 0.050 × 0.040 mm^3
Colour	colourless	colourless	colourless
Z	4	4	2
θ range for data collection	2.946 – 27.485°	2.823 – 27.494°	3.092 – 27.467°
Index ranges	$-34 \leq h \leq 34$, $-16 \leq k \leq 16$, $-11 \leq l \leq 11$	$-34 \leq h \leq 29$, $-16 \leq k \leq 16$, $-11 \leq l \leq 7$	$-14 \leq h \leq 14$, $-12 \leq k \leq 16$, $-11 \leq l \leq 9$
Reflections collected	18400	10448	9371
Independent reflections	3436 [R_{int} = 0.1488]	3417 [R_{int} = 0.0461]	2968 [R_{int} = 0.0261]
Completeness	99.8 % (θ = 25.242°)	99.5 % (θ = 25.242°)	99.3 % (θ = 25.242°)
Absorption correction	Semi–empirical from equivalents	Semi–empirical from equivalents	Semi–empirical from equivalents
Max. and min. transmission	1.000 and 0.592	1.000 and 0.524	1.000 and 0.798
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3436 / 93 / 251	3417 / 281 / 262	2968 / 204 / 226
Goodness-of-fit on F^2	1.077	1.069	1.037
Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0751, *wR2* = 0.1893	*R1* = 0.0648, *wR2* = 0.1952	*R1* = 0.0381, *wR2* = 0.0974
***R* indices (all data)**	*R1* = 0.0908, *wR2* = 0.2007	*R1* = 0.0775, *wR2* = 0.2056	*R1* = 0.0465, *wR2* = 0.1025
Largest diff. peak and hole	0.486 and –0.507 e Å^{-3}	0.354 and –0.262 e Å^{-3}	0.390 and –0.246 e Å^{-3}

	L^1-AcO$^-$ (1:2) **CCDC 1016983**	**L^3-AcO$^-$(1:2)** **CCDC 1016984**	**L^3-CO_3^{2-} (2:1)** **CCDC 1016985**
Empirical formula	$C_{60}H_{104}F_6N_6O_9$	$C_{62}H_{96}F_{12}N_6O_6$	$C_{89}H_{120}F_{24}N_{10}O_9S_2$
Formula weight	1167.49	1249.44	1994.06
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*I2/a*	*I2/a*	*Pbca*
a /Å	34.550(2)	19.1107(15)	20.944(3)
b /Å	8.7957(5)	8.4202(7)	24.898(3)
c /Å	43.222(3)	42.107(3)	38.318(5)

α / º	90	90	90
β / º	91.801(4)	96.582(5)	90
γ / º	90	90	90
V /Å^3	13128.2(14)	6731.0(9)	19981(5)
T / K	100(2)	100(2)	100(2)
Crystal shape	Fragment	Plate	needle
Crystal size / m^3	0.12 × 0.06 × 0.06 mm^3	0.070 x 0.030 x 0.005 mm^3	0.120 x 0.015 x 0.015 mm^3
Colour	Colourless	colourless	colourless
Z	8	4	8
θ range for data collection	2.193 – 25.028°	2.832-24.415°	2.856 – 26.573°
Index ranges	$-41 \le h \le 41$, $-10 \le k \le 10$, $-51 \le l \le 51$	$-21 \le h \le 22$, $-9 \le k \le 10$, $-50 \le l \le 49$	$-27 \le h \le 22$, $-32 \le k \le 32$, $-49 \le l \le 49$
Reflections collected	222840	21286	181899
Independent reflections	11607 [R_{int} = 0.1182]	5879 [R_{int} = 0.3734]	22857 [R_{int}=0.0926]
Completeness	99.8 % (θ = 25.03°)	96.8 % (θ = 24.415°)	99.7 % (θ = 24.415°)
Absorption correction	Semi–empirical from equivalents	Semi–empirical from equivalents	Semi–empirical from equivalents
Max. and min. transmission	1.000 and 0.619	1.000 and 0.054	1.000 and 0.805
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11607 / 11 / 775	5879 / 45 / 192	22857 / 1568 / 1422
Goodness-of-fit on F^2	1.046	1.293	1.079
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0533, $wR2$ = 0.1468	$R1$ = 0.2097, $wR2$ = 0.4844	$R1$ = 0.0727, $wR2$ = 0.1646
R indices (all data)	$R1$ = 0.0842, $wR2$ = 0.1612	$R1$ = 0.3589, $wR2$ = 0.5516	$R1$ = 0.054, $wR2$ = 0.1835
Largest diff. peak and hole	0.691 and –0.308 e Å^{-3}	0.486 and –0.357 e Å^{-3}	0.757 and –0.557 e Å^{-3}

	L^4-HPO_4^{2-}(2:1) **CCDC 1016986**	**L^2-SO_4^{2-} (3:1)** **CCDC 1016987**
Empirical formula	$C_{84}H_{113}F_{24}N_{12}O_9PS$	$C_{101}H_{131}F_{18}N_{17}O_{11}S_1$
Formula weight	1953.90	2133.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a /Å	12.536(2)	29.281(6)
b /Å	32.550(4)	14.001(2)
c /Å	23.279(3)	28.838(6)
α / º	90	90
β / º	97.732(2)	113.087(3)
γ / º	90	90
V /Å^3	9413(2)	10876(4)
T / K	100(2)	100(2)
Crystal shape	Plate	Fragment
Crystal size / m^3	0.181 × 0.07 × 0.02 mm^3	0.2 × 0.15 × 0.1 mm^3
Colour	colourless	colourless
Z	4	4
θ range for data collection	1.964– 27.510°	2.430 – 25.081°
Index ranges	$-16 \le h \le 16$, $-42 \le k \le 41$,	$-34 \le h \le 24$, $-16 \le k \le 16$,

	$-30 \leq l \leq 29$	$-32 \leq l \leq 34$
Reflections collected	66676	62292
Independent reflections	21529 [R_{int} = 0.0703]	19019 [R_{int} = 0.0862]
Completeness	99.9 % (θ = 25.242°)	96.7 %
Absorption correction	Semi–empirical from equivalents	Semi–empirical from equivalents
Max. and min. transmission	1.000 and 0.715	1.000 and 0.574
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	21529 / 407 / 1280	19019 / 2570 / 1709
Goodness-of-fit on F^2	0.996	1.021
Final *R* indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.1274, $wR2$ = 0.1727	$R1$ = 0.1074, $wR2$ = 0.2648
***R* indices (all data)**	$R1$ = 0.0674, $wR2$ = 0.2000	$R1$ = 0.1533, $wR2$ = 0.2887
Largest diff. peak and hole	0.567 and –0.621 e Å^{-3}	0.518 and –0.314 e Å^{-3}

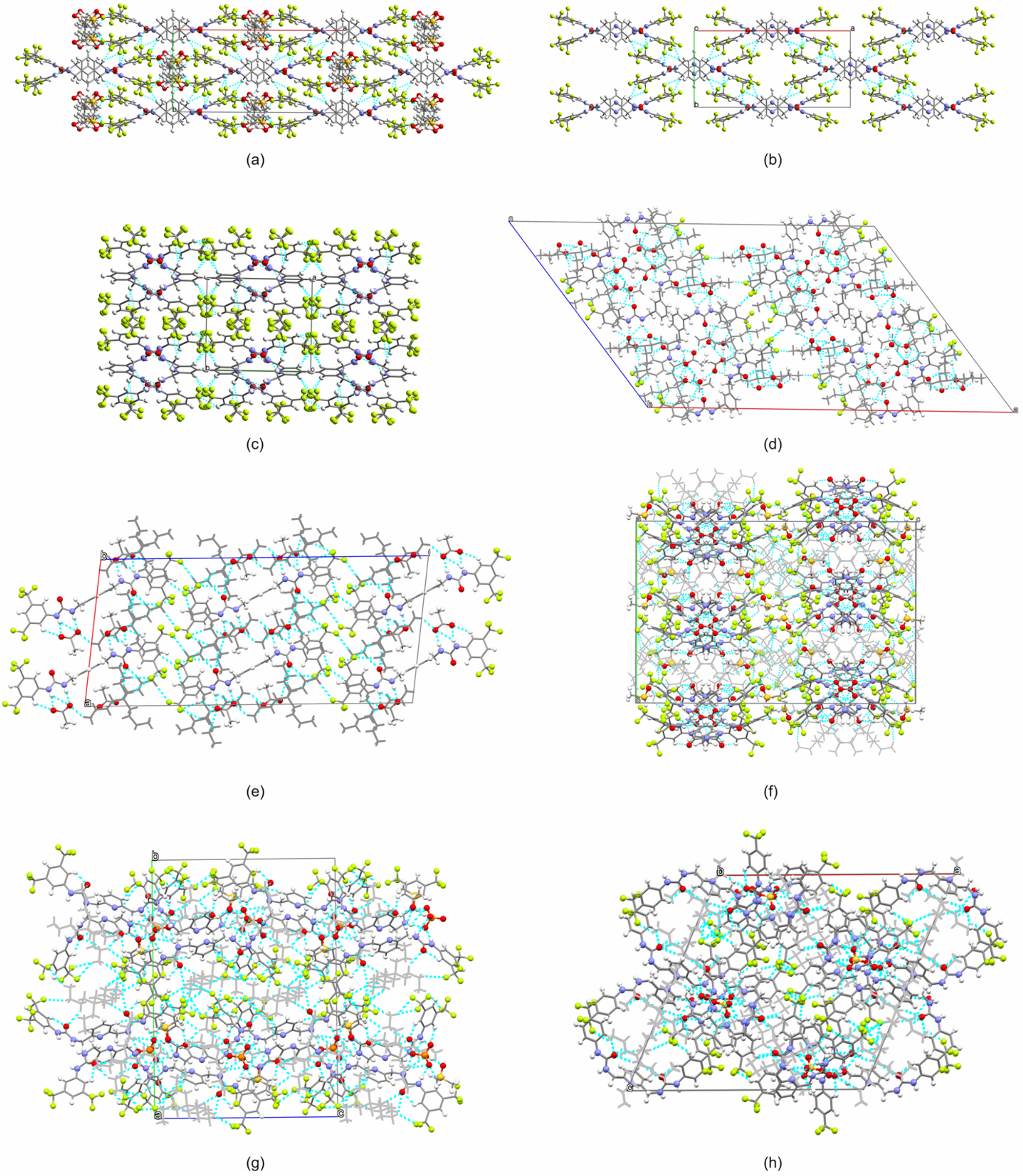


Figure S1. Crystal packing. a) L^3-DMSO; b) L^4-MeOH; c) L^4-A; d) L^1-AcO (1:2); e) L^3-AcO$^-$ (1:2); f) L^3-CO$_3^{2-}$ (2:1); g) L^4-HPO$_4^{2-}$(2:1); h) L^2-SO$_4^{2-}$(3:1). TBA$^+$ units are indicated as grey for clarity. intermolecular interactions are also reported as blue dashed lines.

Table S3. Main intermolecular interactions [Å and °]. (🟡) CH···F interactions; (🟢) receptor-anion binding, (🔴) receptor-anion binding above the 2.75 cut-off.

Phase		D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry	Fig
L^3-DMSO		N1–H1A···O1	0.88	2.13	2.812(3)	134	x,1-y,-1/2+z	2a
		N2–H2···O1	0.88	2.05	2.804(3)	143	x,1-y,-1/2+z	2a
		N2–H2···F5	0.88	2.50	3.181(3)	135	1/2-x,1/2-y,-z	-
	🟡	C4–H4···F3	0.95	2.76	3.379(4)	124	1/2-x,1/2-y,-z	-
	🟡	C5–H5A···F5	0.99	2.88	3.699(3)	141	1/2-x,-1/2+y,1/2-z	-
		C12–H12···O1 (intra)	0.95	2.27	2.837(3)	117	-	1a
L^4-MeOH		N2–H2A···O1	0.851(19)	2.13(2)	2.813(2)	137(3)	x,-y,-1/2+z	-
		N3–H3···O1	0.869(19)	2.00(2)	2.802(2)	153(2)	x,-y,-1/2+z	-
		N3–H3···F3	0.869(19)	2.52(2)	3.08(1)	123(2)	1/2-x,1/2-y,-z	-
	🟡	C4–H4B···F3	0.99	2.91	3.71(1)	139	-	-
	🟡	C4–H4B···F2	0.99	2.93	3.80(1)	147	-	-
	🟡	C7–H7···F6A	0.95	2.93	3.67(1)	136	-	
		C7–H7···O1 (intra)	0.95	2.27	2.840(3)	118	-	-
L^4-A		N2–H2A···O1	0.88	2.34	2.708(1)	105	-	
		N2–H2A···O1	0.88	2.25	3.028(2)	147	x,1-y,-1/2+z	2b
		N2–H2A···O1	0.88	1.99	2.822(1)	158	x,1-y,-1/2+z	2b
		N2–H2A···O1	0.95	2.46	2.917(2)	109	-	-
		N2–H2A...O1	0.95	2.38	2.717(2)	100	-	-
	🟡	C9–H9B···F5	0.95	2.67	3.405(2)	135	1-x,y,3/2-z	-
	🟡	C9–H9D···F5	0.95	2.62	3.517(2)	158	x,-y,-1/2+z	-
		C7–H7···O1 (intra)	0.95	2.46	2.917(2)	109	-	1a
L^1-AcO (1:2)	🟢	N1–H1···O5	0.88	1.94	2.810(2)	171	-	4, 5
	🟢	N2–H2···O6	0.88	1.94	2.804(3)	168	-	4, 5
	🟢	N4–H4···O4	0.88	1.95	2.763(3)	153	-	4, 5
		N3–H3···O7	0.88	2.13	2.899(2)	145	-	4, 5
		O7–H7A···O1	0.85	2.16	2.976(2)	161	3/2-x,1/2-y,1/2-z	4, 5
		O7–H7B···O3	0.85	1.91	2.755(2)	172	-	4, 5
		O8– H8A···O6	0.85	1.92	2.768(2)	175	-	4, 5
		O8– H8B···O2	0.85	1.95	2.792(2)	173	-	4, 5
		O9– H9C···O8	0.85	1.98	2.830(2)	172	1-x,-1/2+y,1/2-z	4, 5
		O9– H9D···O5	0.85	1.94	2.791(2)	178	-	4, 5
	🟡	C20–H20···F2	0.95	2.74	3.599(3)	151	x,1/2-y,1/2+z	-
	🟡	C44–H44A···F3	0.95	2.58	3.527(4)	164	3/2-x,-1+y,1-z	-
	🟡	C27–H27A···F4	0.95	2.65	3.520(3)	147	1-x,1/2+y,1/2-z	-
	🟡	C25–H25B···F4	0.95	2.57	3.464(3)	151	1-x,1/2+y,1/2-z	-
		C4–H4A···O1 (intra)	0.88	2.27	2.879(3)	121	-	3a
		C23–H23···O2 (intra)	0.88	2.35	2.866(3)	114	-	3a
L^3-AcO$^-$ (1:2)	🟢	N1–H1A···O41	0.88	1.90	2.78(2)	176	-	7
	🟢	N2–H2···O42	0.88	1.99	2.79(1)	150	-	7
	🟡	C28–H28C···F2	0.98	2.58	3.13(2)	115	-1/2+x,1-y,z	7
	🟡	C29–H29B···F1	0.98	2.68	3.58(2)	150	-1/2+x,-y,z	7
	🟡	C23–H23A···F6	0.98	2.57	3.53(2)	164	-	7

	🟡	C32–H32B···F5	0.98	2.69	3.57(2)	150	2-x,-1/2+y,1/2-z	7
	🟡	C28–H28B···F5	0.98	2.77	3.60(2)	157	x,-1+y,z	7
		C27–H27B···O1	0.99	2.47	3.32(2)	144	-	7
		C25–H25B···O1	0.99	2.48	3.34(2)	145	-	7
		C22–H22A···O1	0.99	2.42	3.40 (2)	174	-	7
		C25–H25A···O42	0.95	2.50	3.47 (2)	167	-1/2+x,1-y,z	7
		C8–H8···O42	0.95	2.58	3.33(2)	136	-	7
L^3-CO_3^{2-} (2:1)	🟢	N1–H1A···O201	0.88	1.95	2.822(3)	171	-1/2+x,y,1/2-z	8, 9
	🟢	N2–H2···O203	0.88	1.88	2.706(3)	155	-1/2+x,y,1/2-z	8, 9
	🟢	N3–H3A···O202	0.88	1.98	2.824(3)	160	-	8, 9
	🟢	N4–H4A···O201	0.88	2.06	2.900(3)	159	-	8, 9
	🟢	N31–H31A···O202	0.88	1.92	2.764(3)	161	-	8, 9
	🟢	N32–H32···O203	0.88	1.94	2.805(3)	167	-	8, 9
	🟢	N33–H33A···O201	0.88	2.04	2.915(3)	175	-1/2+x,y,1/2-z	8, 9
	🟢	N34–H34A···O202	0.88	2.00	2.817(3)	153	-1/2+x,y,1/2-z	8, 9
	🟡	C4–H4···F6	0.95	2.99	3.65(1)	128	-	9
	🟡	C33–H33···F41	0.95	2.49	3.19(1)	130	1/2+x,y,1/2-z	9
	🟡	C101–H10C···F1	0.98	2.78	3.58(1)	139	-	9
	🟡	C112–H11D···F40	0.98	2.08	2.99(4)	154	1-x,-1/2+y,1/2-z	-
		C12–H12···O1 (intra)	0.95	2.21	2.826(3)	122	-	3d 1
		C24–H24···O2 (intra)	0.95	2.45	2.984(3)	116	-	3d 1
		C42–H42···O31 (intra)	0.95	2.23	2.851(3)	122	-	3d 2
		C50–H50···O32 (intra)	0.95	2.27	2.855(3)	119	-	3d 2
L^4-HPO_4^{2-}(2:1)	🟢	N3 –H3A···O61	0.88(2)	1.87(2)	2.742(3)	177(3)	1/2+x,1/2-y,1/2+z	10, 11
	🟢	N35–H35···O61	0.85(3)	1.91(3)	2.742(3)	164(3)	1/2-x,1/2+y,3/2-z	10, 11
	🟢	N2 –H2A ···O62	0.86(2)	1.96(2)	2.814(3)	169(2)	1/2+x,1/2-y,1/2+z	10, 11
	🟢	N32–H32A···O62	0.86(2)	1.97(2)	2.826(3)	177(5)	-x,1-y,1-z	10, 11
	🟢	N4–H4A···O63	0.85(3)	2.23(3)	3.007(3)	152(3)	-	10, 11
	🟢	N5–H5···O63	0.87(3)	2.01(3)	2.853(3)	165(3)	-	10, 11
	🟢	N33 –H33A···O63	0.86(3)	2.06(3)	2.900(3)	165(3)	-x,1-y,1-z	10, 11
	🟢	N34–H34A···O63	0.87(2)	2.09(2)	2.950(3)	177(3)	1/2-x,1/2+y,3/2-z	10, 11
	🟢	N4–H4A···O64	0.85(3)	2.62(3)	3.153(3)	122(3)	-	10
	🟡	C2–H2···F35	0.95	2.70	3.511(4)	144	-x,1-y,1-z	11
	🟡	C2–H2···F36	0.95	2.77	3.471(4)	131	-x,1-y,1-z	11
	🟡	C46–H46B···F36	0.99	2.70	3.618(4)	154	-1/2+x,3/2-y,-1/2+z	11
	🟡	C112–H11E···F3	0.99	2.65	3.557(6)	155	-	-
		C9–H9···O1 (intra)	0.95	2.26	2.874(4)	122	-	3e1
		C19–H19···O2 (intra)	0.95	2.28	2.886(4)	122	-	3e 1
		C39–H39···O31 (intra)	0.95	2.19	2.808(4)	122	-	3e 2
		C49–H49···O32 (intra)	0.95	2.25	2.852(4)	120	-	3e 2
		C16–H16B···O111	0.99	2.74	3.611(4)	147	3/2-x,1/2+y,3/2-z	-
		O64–H64 ···S111	0.81(4)	2.79(4)	3.421(2)	136(3)	3/2-x,-1/2+y,3/2-z	-
		O64–H64 ···O111	0.81(4)	1.89(4)	2.674(3)	162(4)	3/2-x,-1/2+y,3/2-z	11
	🟢	N202–H202···O501	0.88(4)	2.04(5)	2.89(1)	161(4)	x,-1+y,z	12-15
	🟢	N204–H204···O501	0.88(5)	2.02 (5)	2.88(1)	166(5)	2-x,1-y,1-z	12-15
	🟢	N205–H205···O501	0.88(5)	2.31(5)	3.12(1)	155(4)	2-x,1-y,1-z	12-15

	●	N102–H102···O502	0.88(4)	2.23(5)	3.04(1)	154(4)	1-x,1-y,1-z	12-15
	●	N103–H103···O502	0.88(4)	2.00(4)	2.83(1)	156(5)	1-x,1-y,1-z	12-15
	●	N104–H104···O502	0.88(4)	2.29(4)	3.11(1)	155(3)	1-x,1-y,1-z	12-15
L^{2}-SO$_4$$^{2-}$(3:1)	●	N105–H105···O502	0.88	1.99	2.86(1)	173	1-x,1-y,1-z	12-15
	●	N2–H2···O503	0.880(5)	2.29(5)	3.15(1)	165(5)	1-x,-1/2+y,1/2-z	12-15
	●	N4–H4···O503	0.880(4)	2.44(3)	3.30(1)	165(7)	1-x,-1/2+y,1/2-z	12-15
	●	N203–H203···O503	0.88(4)	2.10 (4)	2.97 (1)	172(5)	x,-1+y,z	12-15
	●	N3–H3···O504	0.880(4)	2.01(4)	2.86(1)	162(4)	1-x,-1/2+y,1/2-z	12-15
	●	N5–H5A···O504	0.88	2.49	3.36(1)	166	1-x,-1/2+y,1/2-z	12-15
	●	N103–H103···O503	0.88(4)	2.93(5)	3.72(1)	156(4)	1-x,1-y,1-z	13
	●	N102–H102···O504	0.88(4)	2.81(5)	3.56(1)	144(3)	1-x,1-y,1-z	13
		O601–H60B··O2	0.85	2.15	2.99(1)	170	x,3/2-y,-1/2+z	12, 14, 15
		O601–H60A···O102	0.85	1.77	2.60 (1)	167	-	12, 14, 15
		C213–H213···O201 (intra)	0.95	2.25	2.87(1)	122	-	3b 1
		C218–H218···O202 (intra)	0.95	2.31	2.91(1)	120	-	3b 1
		C9–H9···O1 (intra)	0.95	2.29	2.88(1)	120	-	3b 2
		C22–H22···O2 (intra)	0.95	2.35	2.96 (1)	122	-	3b 2
		C109–H109···O101 (intra)	0.95	2.37	2.94(1)	118	-	3b 3
		C122–H122···O102 (intra)	0.95	2.55	3.17(1)	123	-	3b 3
	●	C110-H110...F101	0.95	2.77	3.41(1)	144	1-x,-y,1-z	14

4. Anion Transport Studies

Preparation of Vesicles

A lipid film of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) and cholesterol (0% or 30%) was formed from a chloroform solution under reduced pressure and dried under vacuum for at least 2 hours. The lipid film was rehydrated by vortexing with a internal solution (489 mM NaCl, 5 mM phosphate buffer at pH 7.2). The lipid suspension was then subjected to nine freeze-thaw cycles and allowed to age for 30 min at room temperature before extruding 20 times through a 200 nm polycarbonate membrane. The resulting unilamellar vesicles were dialyzed against the external solution to remove unencapsulated NaCl salts. The vesicles were diluted to 5mL with the external solution to form a stock solution of lipid.

Samples for assay were prepared by diluting lipid stock solution to 5mL (using the external solution) to give a solution of 1mM lipid. Chloride efflux was monitored using a chloride selective electrode (Accumet). To initiate the experiment compounds were added as solutions in DMSO, to give a 1:50 compound to lipid ratio (2mol%). At the end of the experiment detergent (octaethylene glycol monododecyl ether) was added to allow the determination of 100% chloride efflux. Experiments were repeated in triplicate and all traces presented are the average of three trials. The chloride electrode was calibrated against sodium chloride solutions of known concentration.

Chloride Transport Assays

Unilamellar POPC vesicles containing NaCl, prepared as described above, were suspended in 489 mM NaNO$_3$ buffered to pH 7.2 with 5 mM sodium phosphate salts. The lipid concentration per sample was 1 mM. A DMSO solution of the carrier molecule (10 mM) was added to start the experiment and the chloride efflux was monitored using a chloride sensitive electrode. At 5 min, the vesicles were lysed with 50 µl of octaethylene glycol monododecyl ether and a total chloride reading was taken at 7 min.

Bicarbonate Transport Assay

Unilamellar POPC vesicles containing 451 mM NaCl solution buffered to pH 7.2 with 20 mM sodium phosphate salts, prepared as described above, were suspended in 150 mM Na_2SO_4 solution buffered to pH 7.2 with sodium phosphate salts. The lipid concentration per sample was 1 mM. A DMSO solution of the carrier molecule (10 mM) was added to start the experiment and chloride efflux was monitored using a chloride sensitive electrode. At 2 min, $NaHCO_3$ solution (1 M in 150 mM Na_2SO_4 buffered to pH 7.2 with 20 mM sodium phosphate salts) was added so that the outer solution contained 40 mM $NaHCO_3$. At 7 min, the vesicles were lysed with 50 µl of octaethylene glycol monododecyl ether and a total chloride reading was taken at 9 min.

Cl^-/NO_3^- antiport assays

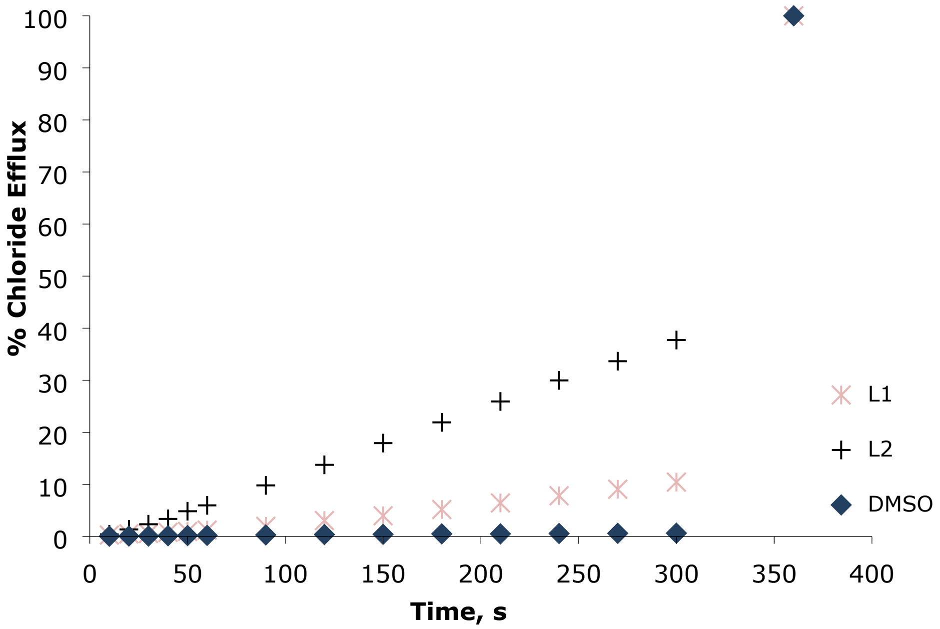


Figure S2 Comparison of chloride efflux promoted by a DMSO solution of compounds **L^1** and L^2 (2% carrier to lipid) from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5 mM sodium phosphate salts. The vesicles were dispersed in 489 mM $NaNO_3$ buffered to pH 7.2 with 5 mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.

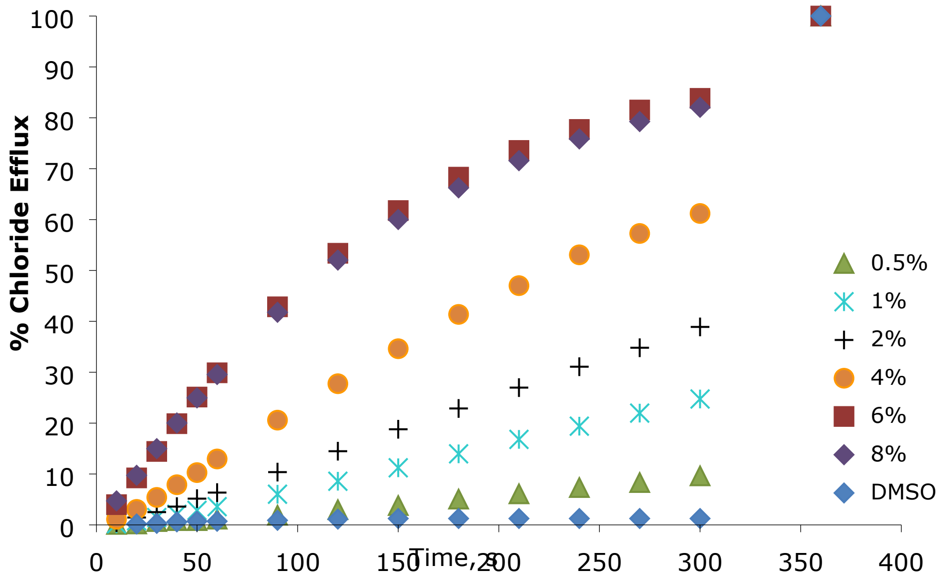
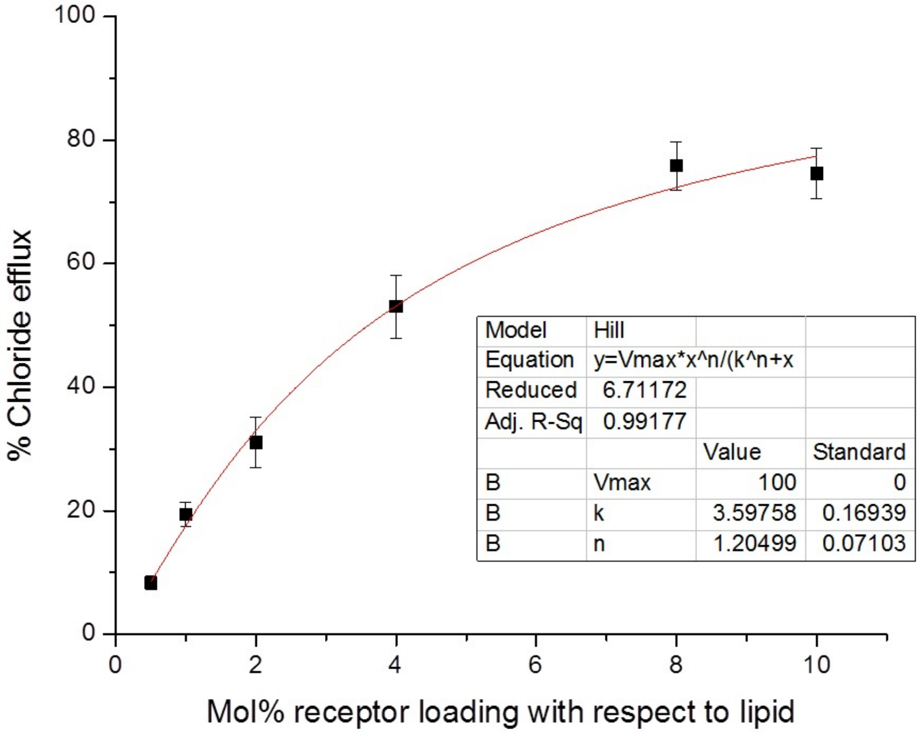


Figure S3 Chloride efflux promoted by variuos concentrations of $\mathbf{L^2}$ from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5 mM sodium phosphate salts. The vesicles were dispersed in 489 mM $NaNO_3$ buffered to pH 7.2 with 5 mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equation	y=Vmax*x^n/(k^n+x		
Reduced	6.71172		
Adj. R-Sq	0.99177		
		Value	Standard
B	Vmax	100	0
B	k	3.59758	0.16939
B	n	1.20499	0.07103

Figure S4 Hill plot of chloride efflux promoted by varying concentrations of compound $\mathbf{L^2}$ from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489 mM $NaNO_3$ buffered at pH 7.2 with 5mM sodium phosphate salts. Each point represents an average of 3 trials.

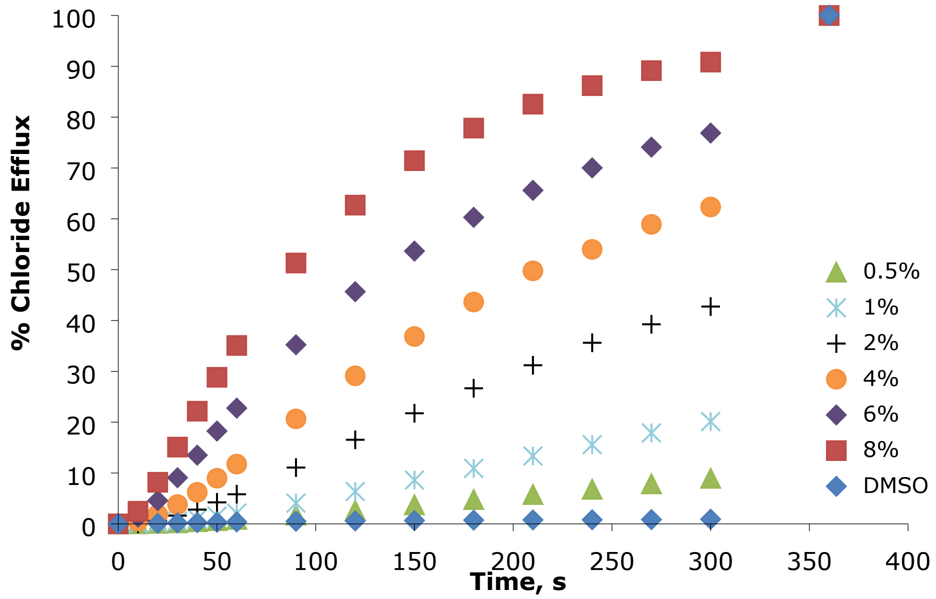


Figure S5 Chloride efflux promoted by variuos concentrations of **L**^{3} from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5 mM sodium phosphate salts. The vesicles were dispersed in 489 mM $NaNO_3$ buffered to pH 7.2 with 5 mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.

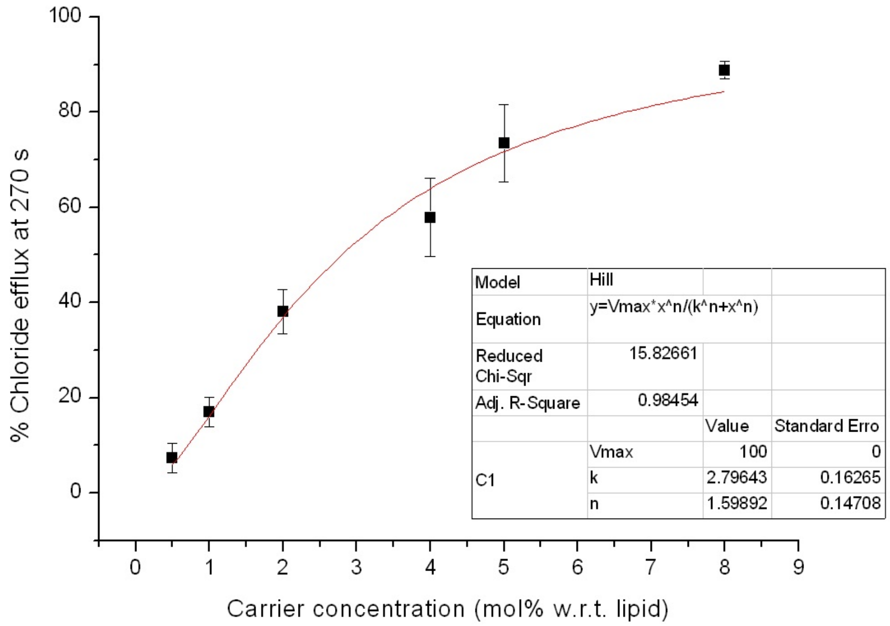


Figure S6 Hill plot of chloride efflux promoted by varying concentrations of compound **L**^{3} from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489 mM $NaNO_3$ buffered at pH 7.2 with 5mM sodium phosphate salts. Each point represents an average of 3 trials.

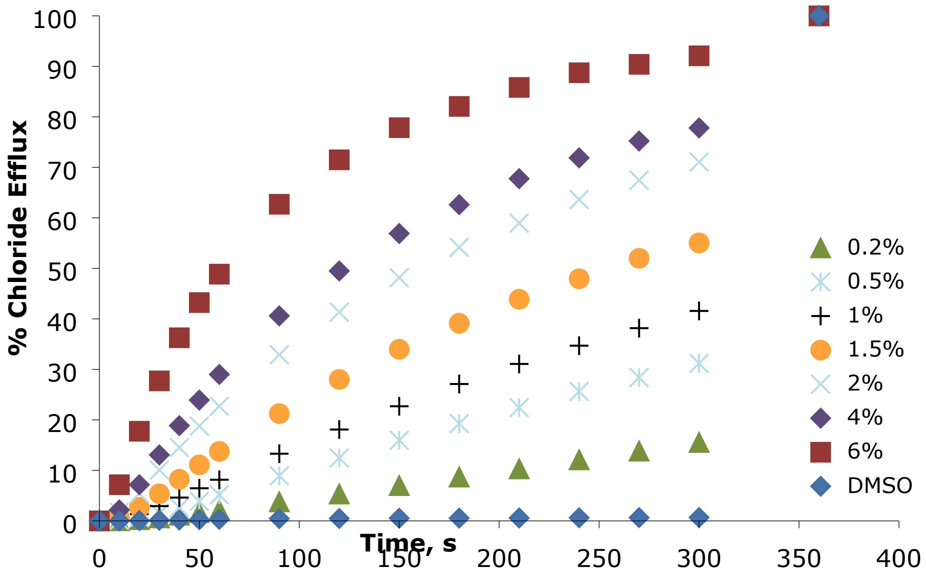
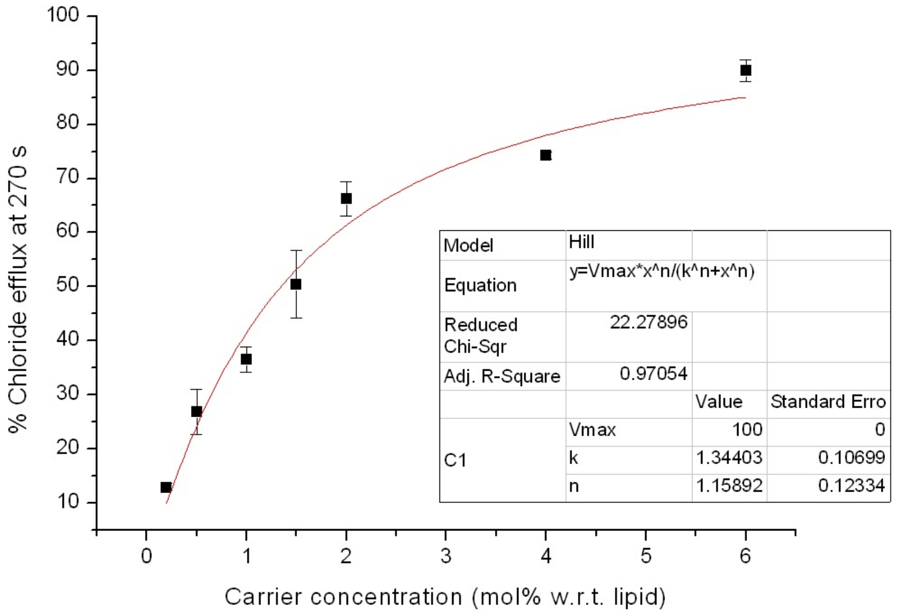


Figure S7 Chloride efflux promoted by variuos concentrations of **L^4** from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5 mM sodium phosphate salts. The vesicles were dispersed in 489 mM $NaNO_3$ buffered to pH 7.2 with 5 mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equation	y=Vmax*x^n/(k^n+x^n)		
Reduced Chi-Sqr	22.27896		
Adj. R-Square	0.97054		
		Value	Standard Erro
C1	Vmax	100	0
	k	1.34403	0.10699
	n	1.15892	0.12334

Figure S8 Hill plot of chloride efflux promoted by varying concentrations of compound **L^4** from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489 mM $NaNO_3$ buffered at pH 7.2 with 5mM sodium phosphate salts. Each point represents an average of 3 trials.

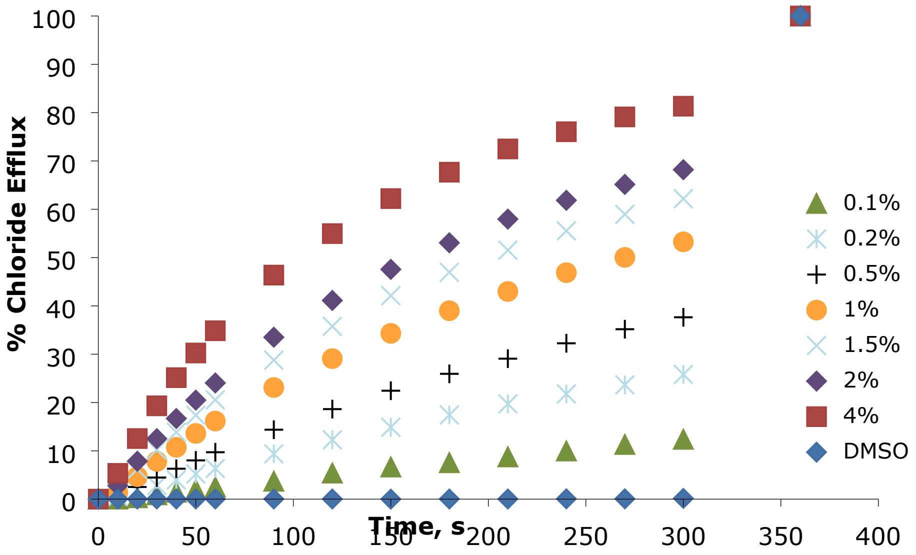
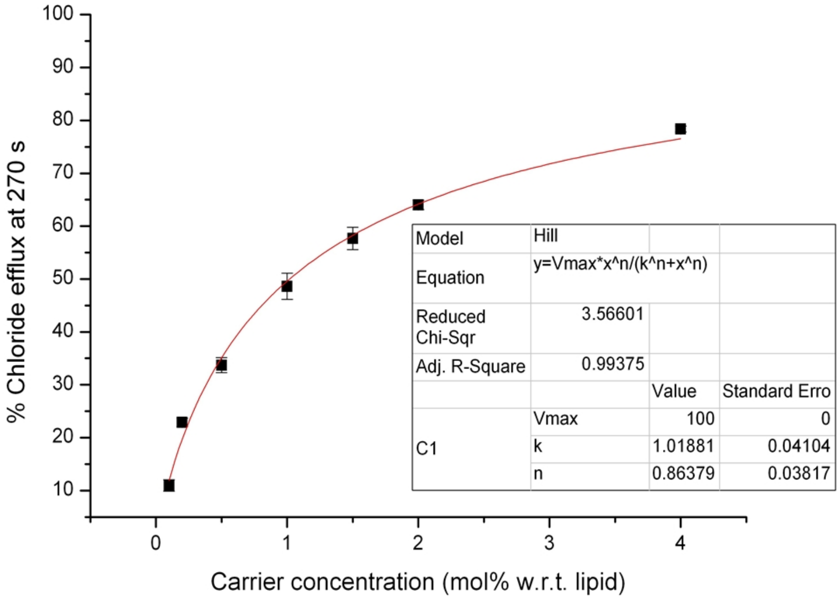


Figure S9. Chloride efflux promoted by variuos concentrations of **L**^{5} from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5 mM sodium phosphate salts. The vesicles were dispersed in 489 mM NaNO$_3$ buffered to pH 7.2 with 5 mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equation	y=Vmax*x^n/(k^n+x^n)		
Reduced Chi-Sqr	3.56601		
Adj. R-Square	0.99375		
		Value	Standard Erro
C1	Vmax	100	0
	k	1.01881	0.04104
	n	0.86379	0.03817

Figure S10. Hill plot of chloride efflux promoted by varying concentrations of compound **L**^{5} from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489 mM NaNO$_3$ buffered at pH 7.2 with 5mM sodium phosphate salts. Each point represents an average of 3 trials.

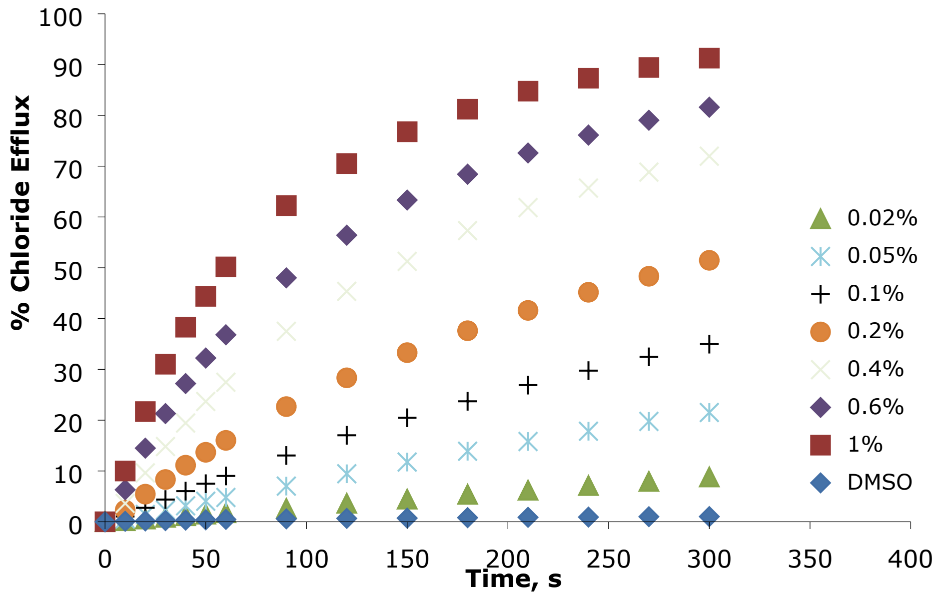
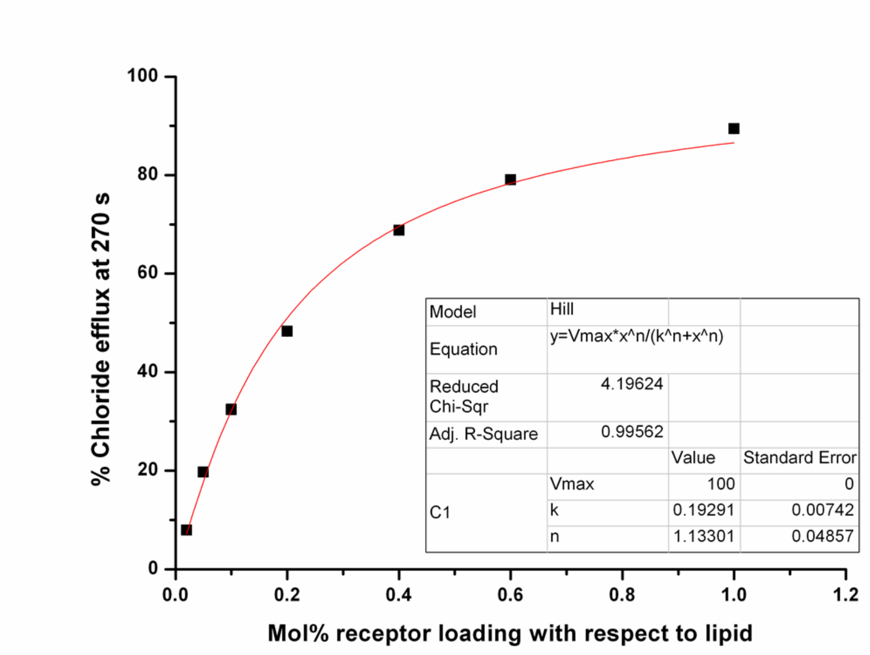


Figure S11 Chloride efflux promoted by variuos concentrations of **L^6** from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5 mM sodium phosphate salts. The vesicles were dispersed in 489 mM NaNO$_3$buffered to pH 7.2 with 5 mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equation	y=Vmax*x^n/(k^n+x^n)		
Reduced Chi-Sqr	4.19624		
Adj. R-Square	0.99562		
		Value	Standard Error
C1	Vmax	100	0
	k	0.19291	0.00742
	n	1.13301	0.04857

Figure S12 Hill plot of chloride efflux promoted by varying concentrations of compound **L^6** from unilamellar POPC vesicles loaded with 489 mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489 mM NaNO$_3$ buffered at pH 7.2 with 5mM sodium phosphate salts. Each point represents an average of 3 trials.

Cl^-/HCO_3^- antiport assays

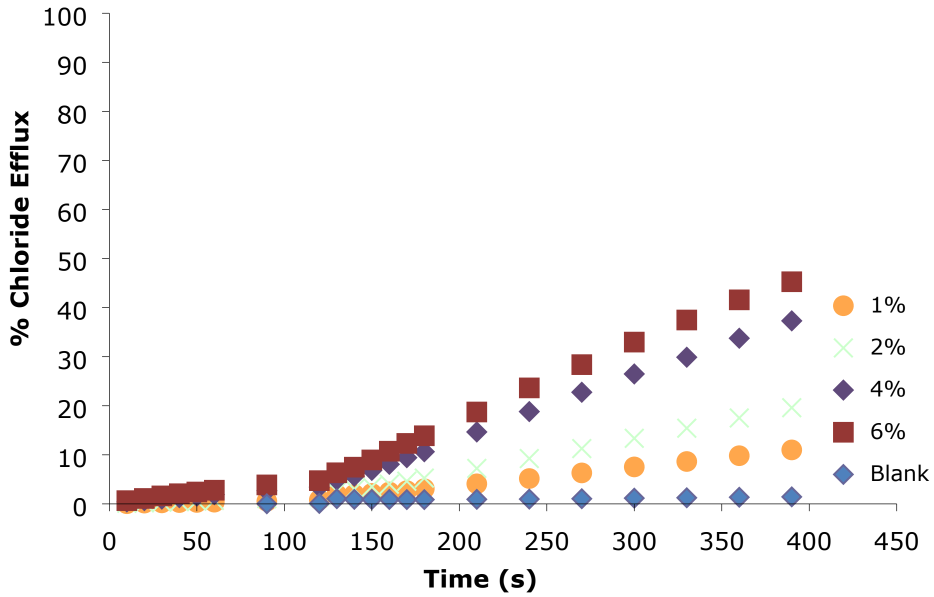
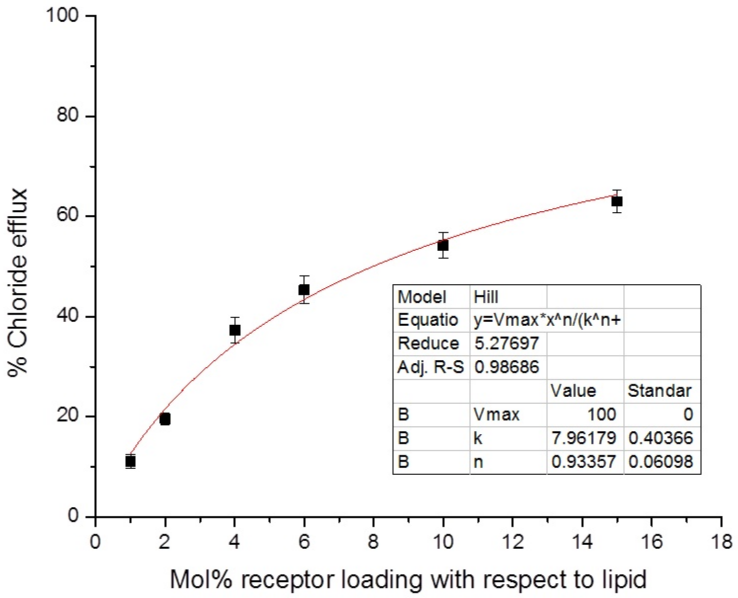


Figure S13 Chloride efflux promoted by various concentrations of **L**^{3} from unilamellar POPC vesicles loaded with 451 mM NaCl buffered to pH 7.2 with 20 mM sodium phosphate salts. The vesicles were dispersed in 150 mM Na_2SO_4 buffered to pH 7.2 with 20 mM sodium phosphate salts. At t. 120 s a solution of sodium bicarbonate was added such that the external concentration of bicarbonate was 40 mM. At the end of the experiment, detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equatio	y=Vmax*x^n/(k^n+		
Reduce	5.27697		
Adj. R-S	0.98686		
		Value	Standar
B	Vmax	100	0
B	k	7.96179	0.40366
B	n	0.93357	0.06098

Figure S14 Hill plot of chloride efflux promoted varying concentrations of compound **L**^{3} from unilamellar POPC vesicles loaded with 451mM NaCl buffered to pH 7.2 with 20mM sodium phosphate salts upon addition of a bicarbonate ‘pulse’, bringing the external concentration of bicarbonate to 40mM. The vesicles were dispersed in 150mM Na_2SO_4 buffered to pH 7.2 with 20mM sodium phosphate salts. Each point represents an average of 3 trials.

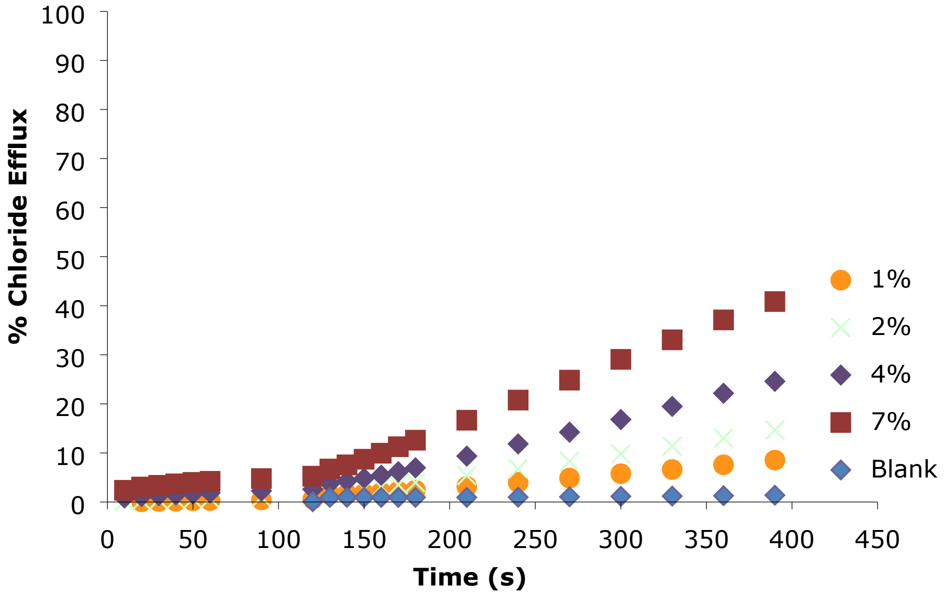
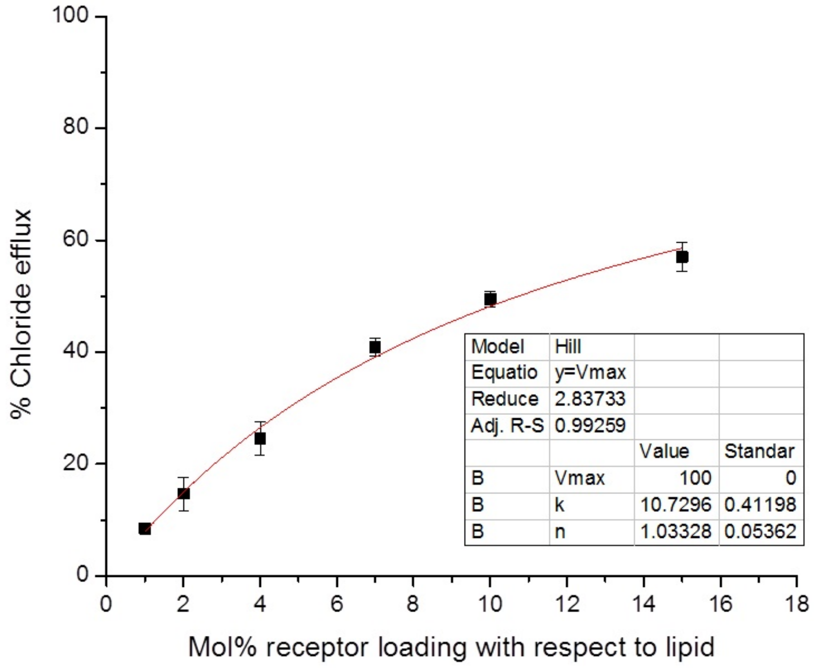


Figure S15 Chloride efflux promoted by various concentrations of **L**^{4} from unilamellar POPC vesicles loaded with 451 mM NaCl buffered to pH 7.2 with 20 mM sodium phosphate salts. The vesicles were dispersed in 150 mM Na_2SO_4 buffered to pH 7.2 with 20 mM sodium phosphate salts. At t. 120 s a solution of sodium bicarbonate was added such that the external concentration of bicarbonate was 40 mM. At the end of the experiment, detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equatio	y=Vmax		
Reduce	2.83733		
Adj. R-S	0.99259		
		Value	Standar
B	Vmax	100	0
B	k	10.7296	0.41198
B	n	1.03328	0.05362

Figure S16 Hill plot of chloride efflux promoted varying concentrations of compound **L**^{4} from unilamellar POPC vesicles loaded with 451mM NaCl buffered to pH 7.2 with 20mM sodium phosphate salts upon addition of a bicarbonate 'pulse', bringing the external concentration of bicarbonate to 40mM. The vesicles were dispersed in 150mM Na_2SO_4 buffered to pH 7.2 with 20mM sodium phosphate salts. Each point represents an average of 3 trials.

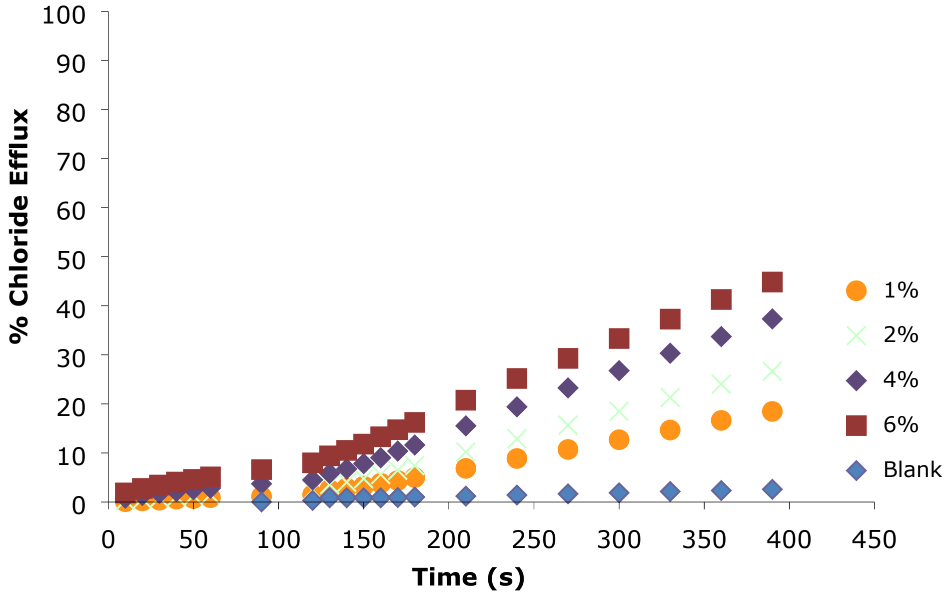
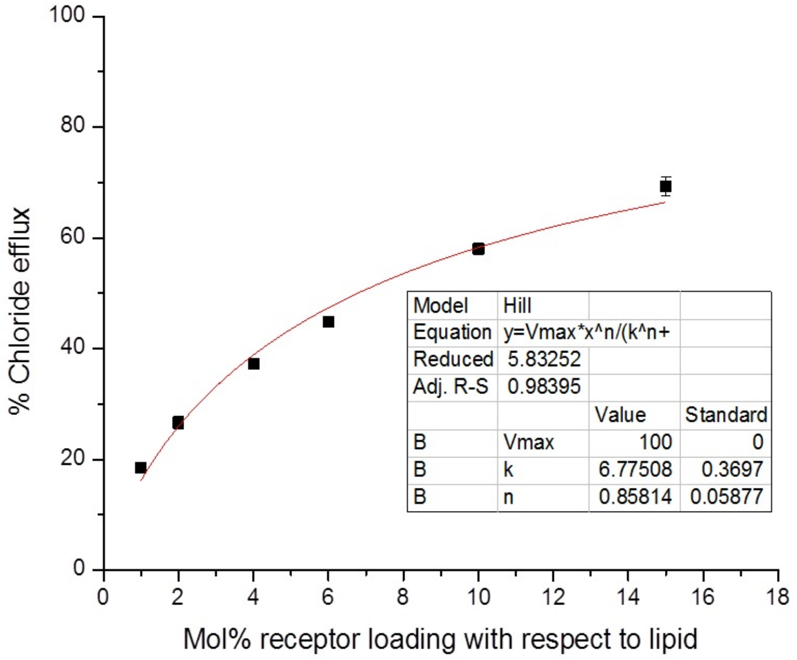


Figure S17 Chloride efflux promoted by various concentrations of **L**^{5} from unilamellar POPC vesicles loaded with 451 mM NaCl buffered to pH 7.2 with 20 mM sodium phosphate salts. The vesicles were dispersed in 150 mM Na_2SO_4 buffered to pH 7.2 with 20 mM sodium phosphate salts. At t. 120 s a solution of sodium bicarbonate was added such that the external concentration of bicarbonate was 40 mM. At the end of the experiment, detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equation	y=Vmax*x^n/(k^n+		
Reduced	5.83252		
Adj. R-S	0.98395		
		Value	Standard
B	Vmax	100	0
B	k	6.77508	0.3697
B	n	0.85814	0.05877

Figure S18 Hill plot of chloride efflux promoted varying concentrations of compound **L**^{5} from unilamellar POPC vesicles loaded with 451mM NaCl buffered to pH 7.2 with 20mM sodium phosphate salts upon addition of a bicarbonate 'pulse', bringing the external concentration of bicarbonate to 40mM. The vesicles were dispersed in 150mM Na_2SO_4 buffered to pH 7.2 with 20mM sodium phosphate salts. Each point represents an average of 3 trials.

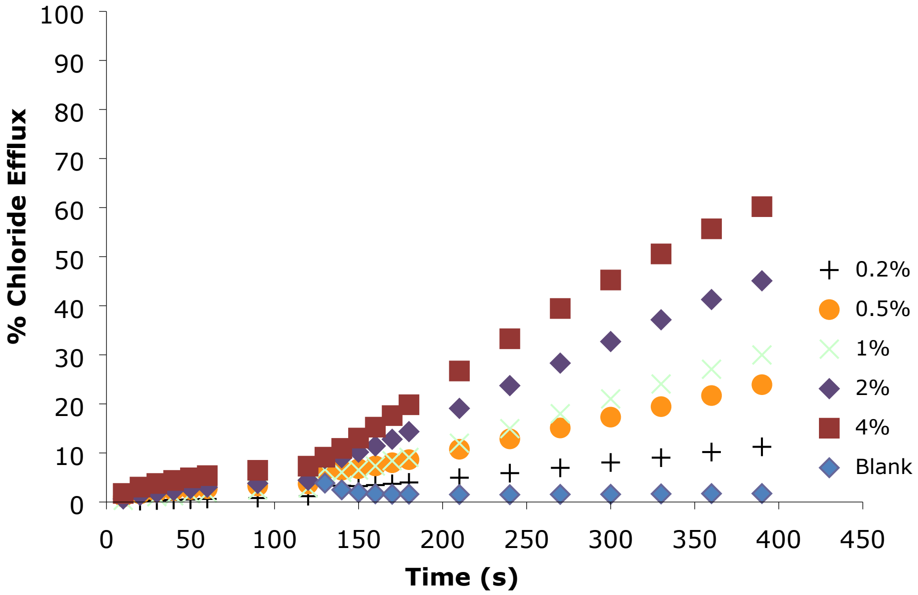
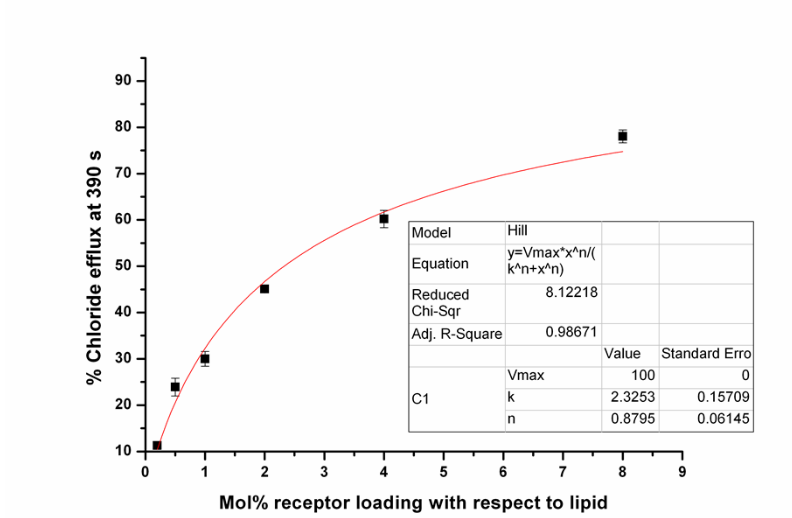


Figure S19 Chloride efflux promoted by various concentrations of **L**^{6} from unilamellar POPC vesicles loaded with 451 mM NaCl buffered to pH 7.2 with 20 mM sodium phosphate salts. The vesicles were dispersed in 150 mM Na_2SO_4 buffered to pH 7.2 with 20 mM sodium phosphate salts. At t. 120 s a solution of sodium bicarbonate was added such that the external concentration of bicarbonate was 40 mM. At the end of the experiment, detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.



Model	Hill		
Equation	y=Vmax*x^n/(k^n+x^n)		
Reduced Chi-Sqr	8.12218		
Adj. R-Square	0.98671		
		Value	Standard Erro
C1	Vmax	100	0
	k	2.3253	0.15709
	n	0.8795	0.06145

Figure S20 Hill plot of chloride efflux promoted varying concentrations of compound **L**^{6} from unilamellar POPC vesicles loaded with 451mM NaCl buffered to pH 7.2 with 20mM sodium phosphate salts upon addition of a bicarbonate ‘pulse’, bringing the external concentration of bicarbonate to 40mM. The vesicles were dispersed in 150mM Na_2SO_4 buffered to pH 7.2 with 20mM sodium phosphate salts. Each point represents an average of 3 trials.

Cation dependence

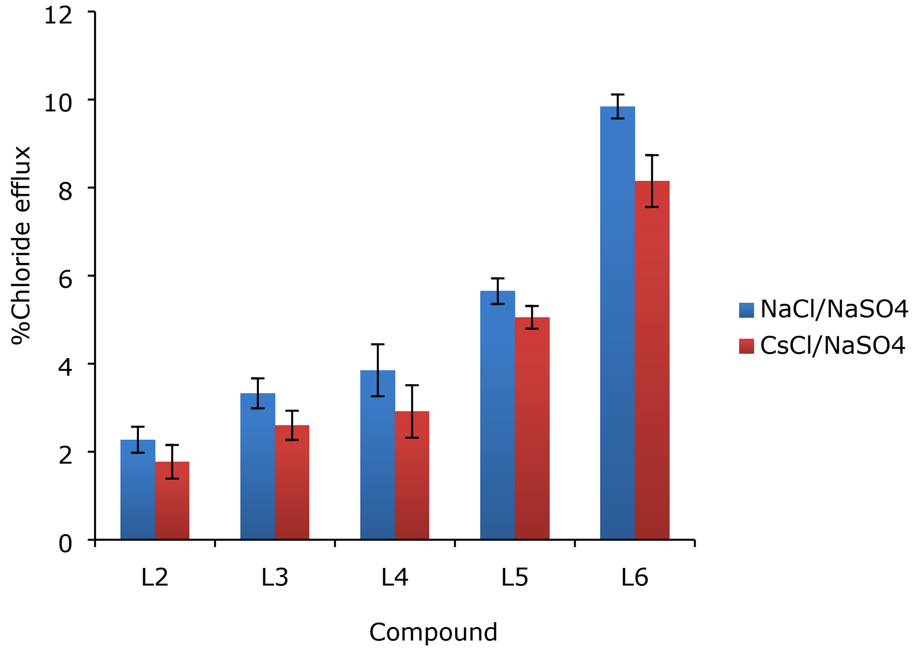


Figure S21. Chloride efflux promoted by a DMSO solution of compounds **L^2**-**L^6** from unilamellar POPC vesicles loaded with either 451mM NaCl (red) or 451mM CsCl (blue) buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 150 mM Na_2SO_4 buffered to pH 7.2 with 5mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.

Cholesterol assays

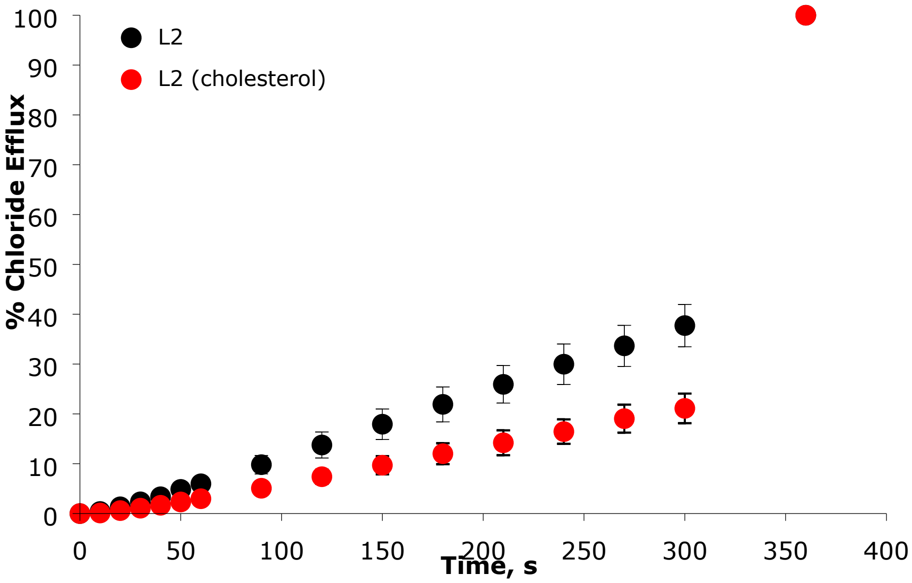


Figure S22 Chloride efflux promoted by a DMSO solution of compound **L²** (2mol% carrier to lipid) from unilamellar vesicles comprising of either POPC or POPC/cholesterol (7:3 molar ratio), loaded with 489mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489mM $NaNO_3$ buffered to pH 7.2 with 5mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.

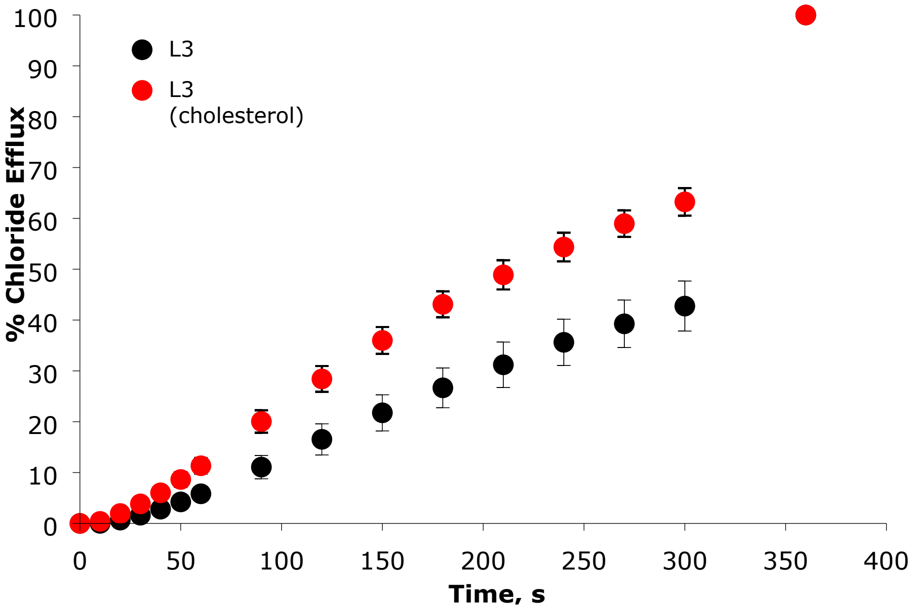


Figure S23. Chloride efflux promoted by a DMSO solution of compound **L³** (2mol% carrier to lipid) from unilamellar vesicles comprising of either POPC or POPC/cholesterol (7:3 molar ratio), loaded with 488mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489mM $NaNO_3$ buffered to pH 7.2 with 5mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.

The U-Tube test could not be performed for solubility reasons.

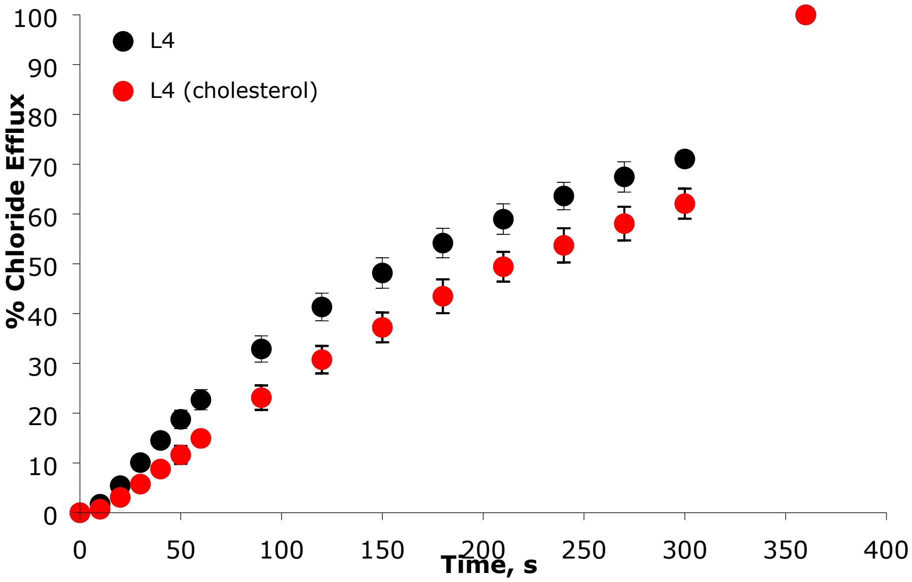


Figure S24. Chloride efflux promoted by a DMSO solution of compound **L**^{4} (2mol% carrier to lipid) from unilamellar vesicles comprising of either POPC or POPC/cholesterol (7:3 molar ratio), loaded with 489mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489mM $NaNO_3$ buffered to pH 7.2 with 5mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.

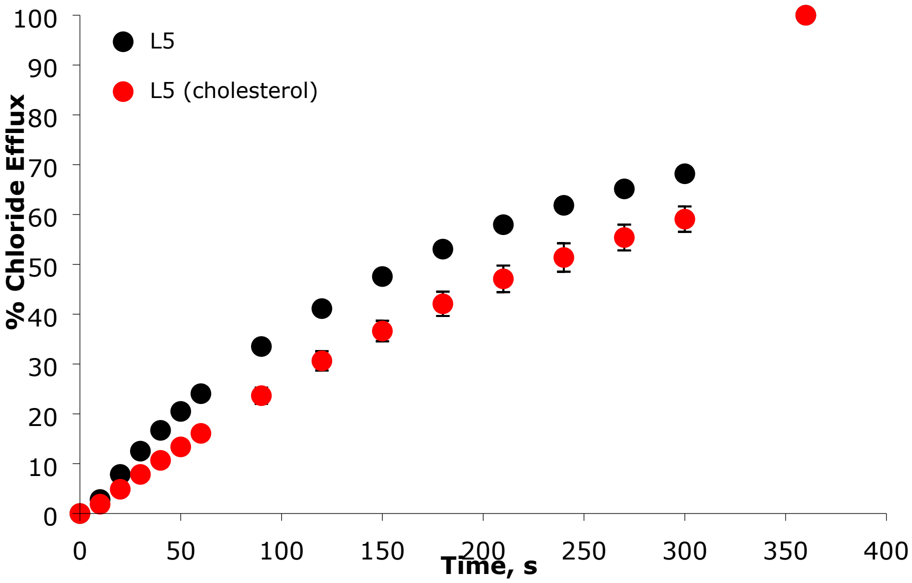
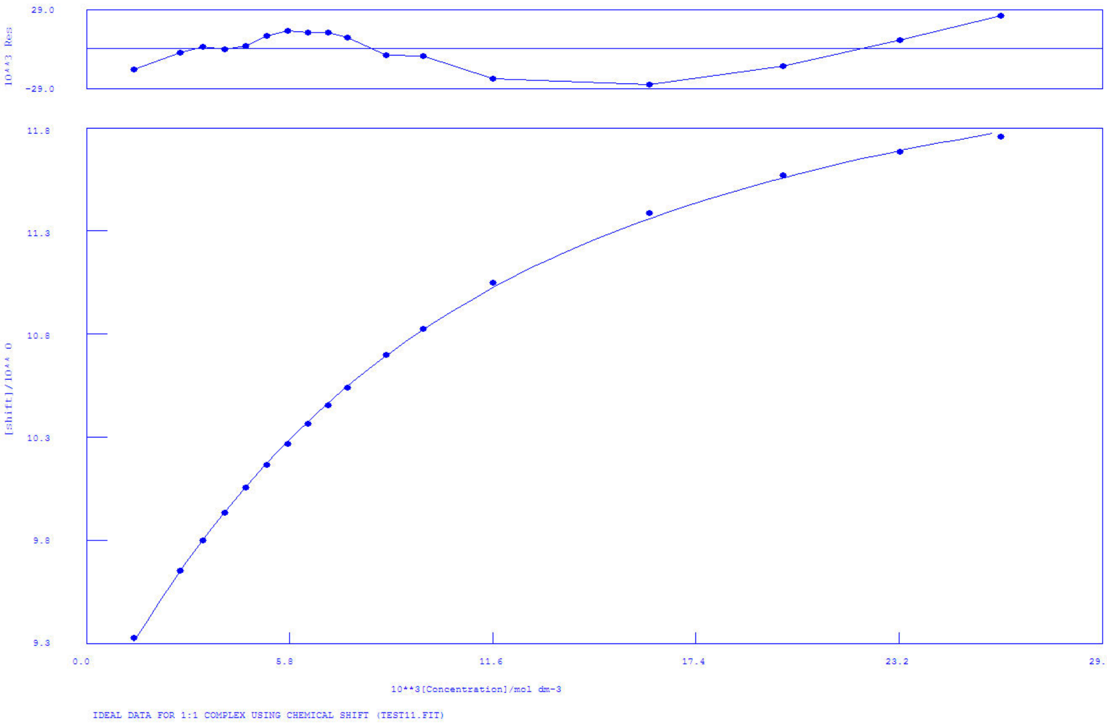


Figure S25. Chloride efflux promoted by a DMSO solution of compound **L**^{5} (2mol% carrier to lipid) from unilamellar vesicles comprising of either POPC or POPC/cholesterol (7:3 molar ratio), loaded with 489mM NaCl buffered to pH 7.2 with 5mM sodium phosphate salts. The vesicles were dispersed in 489mM $NaNO_3$ buffered to pH 7.2 with 5mM sodium phosphate salts. At the end of the experiment detergent was added to lyse the vesicles and calibrate the ISE to 100% chloride efflux. Each point represents an average of three trials. DMSO was used as a control.

5. Proton NMR titration fitting



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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
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  Reaction:   M + L = ML
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 FILE: TEST11.FIT
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 File prepared by M. J. Hynes, October 22 2000

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  2  1  8.90732E+00 2.000E-01 1.557E-02 6.994E+00   SHIFT M
  3  1  1.26326E+01 1.000E+00 3.314E-02 2.139E+01    SHIFT ML
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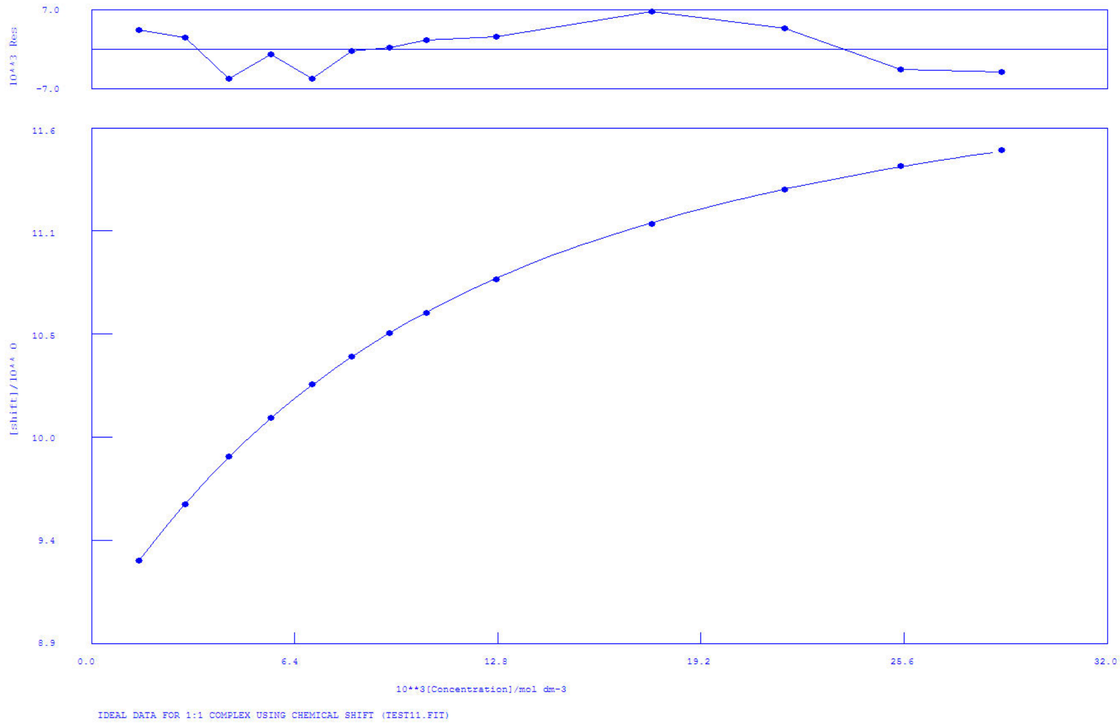
Figure S26. ^{1}H-NMR of **L^1** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



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File prepared by M. J. Hynes, October 22 2000

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3  1  1.22857E+01 1.000E+00 1.052E-02 2.225E+01    SHIFT ML
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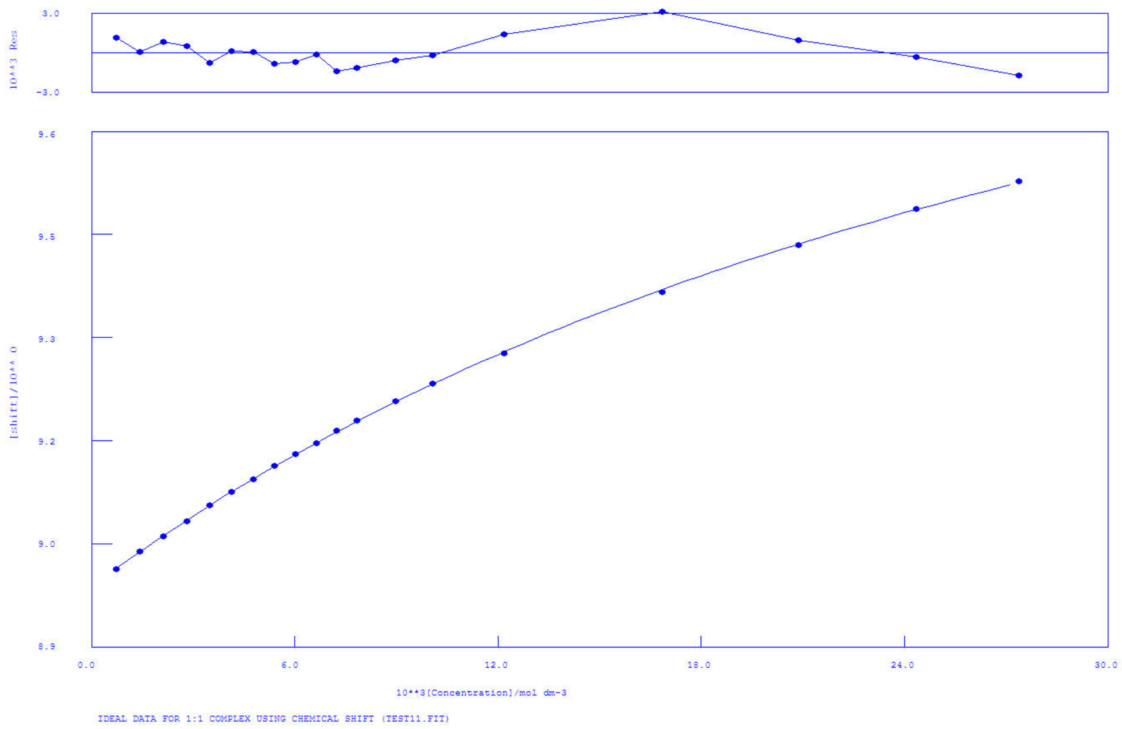
Figure S27. ^{1}H-NMR of **L^1** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



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Program run at 16:02:41   on 01/28/2014

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Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
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3  1  1.02040E+01 1.000E+00 1.258E-02 1.035E+02    SHIFT ML
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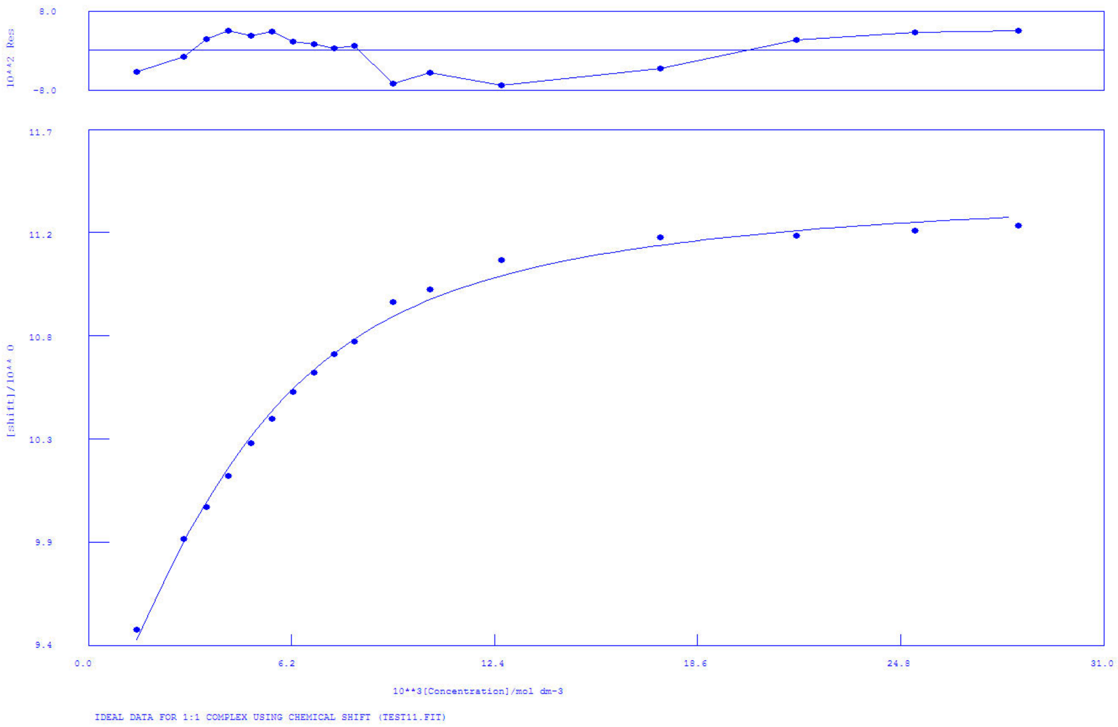
Figure S28. ^{1}H-NMR of **L^1** with TBACl in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



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 File prepared by M. J. Hynes, October 22 2000

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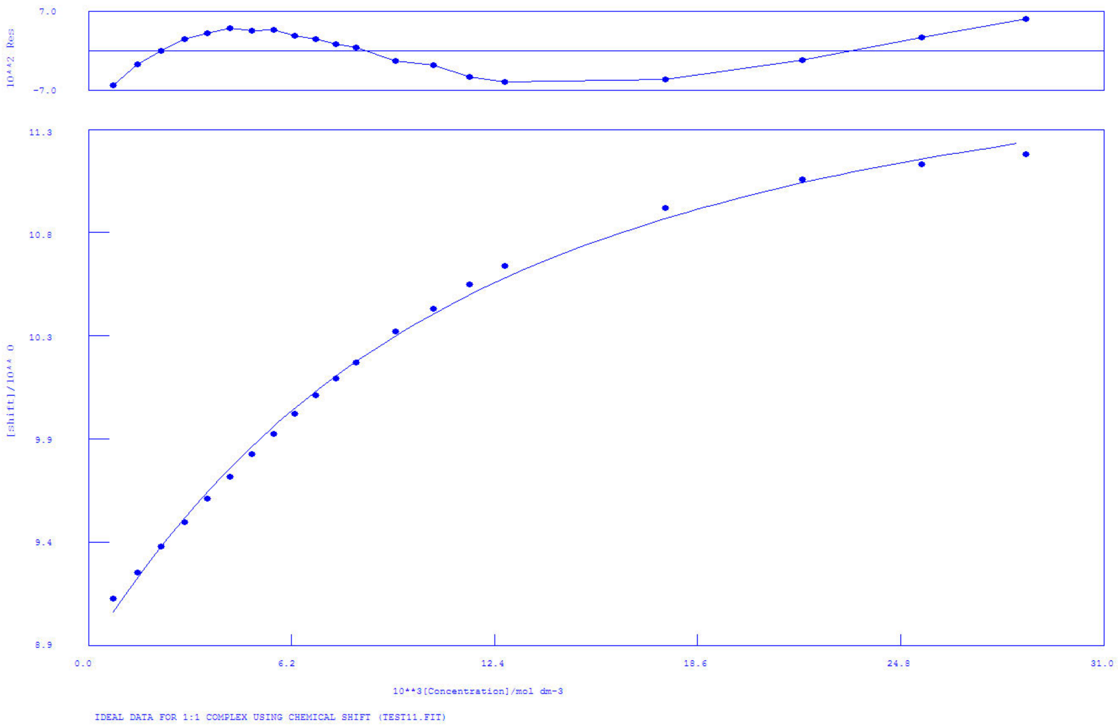
   3  1  1.14839E+01 1.000E+00 3.661E-02 6.717E+00    SHIFT ML
```

Figure S29. ^{1}H-NMR of **L^1** with $TBAH_2PO_4$ in DMSO-*d*$_6$/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:07:10   on 01/28/2014

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Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.24080E+02 2.000E-01 1.052E+01 3.002E+01    K1
2  1  8.87977E+00 2.000E-01 2.858E-02 4.552E+00   SHIFT M
3  1  1.20037E+01 1.000E+00 8.093E-02 1.913E+01    SHIFT ML
```
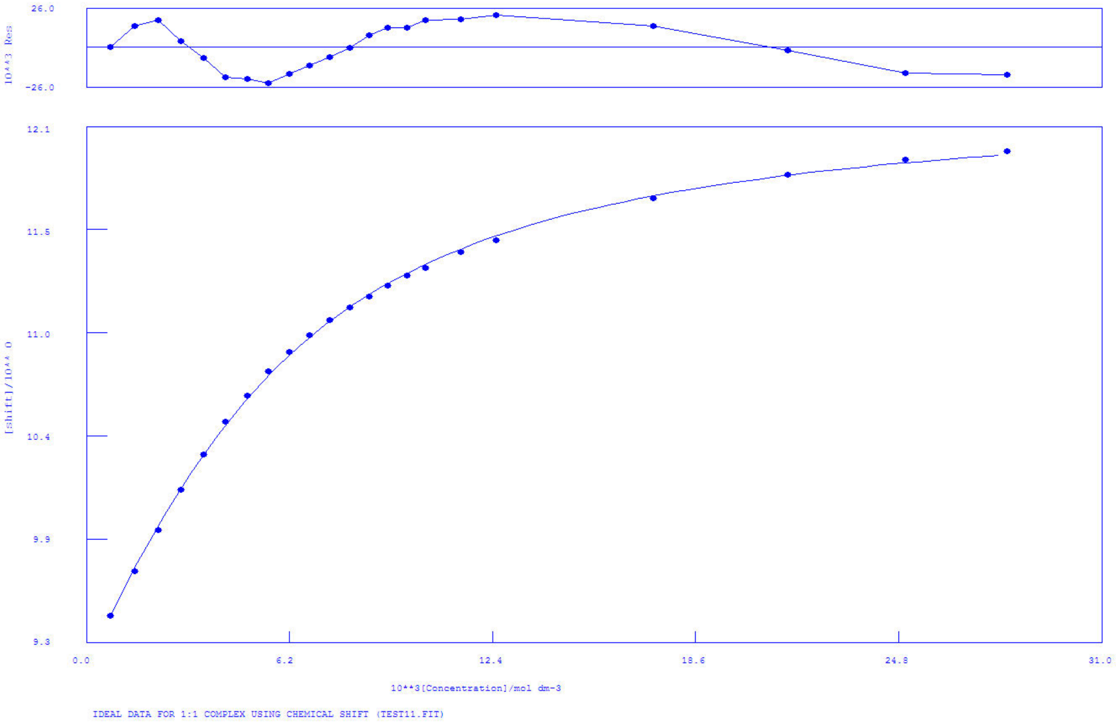
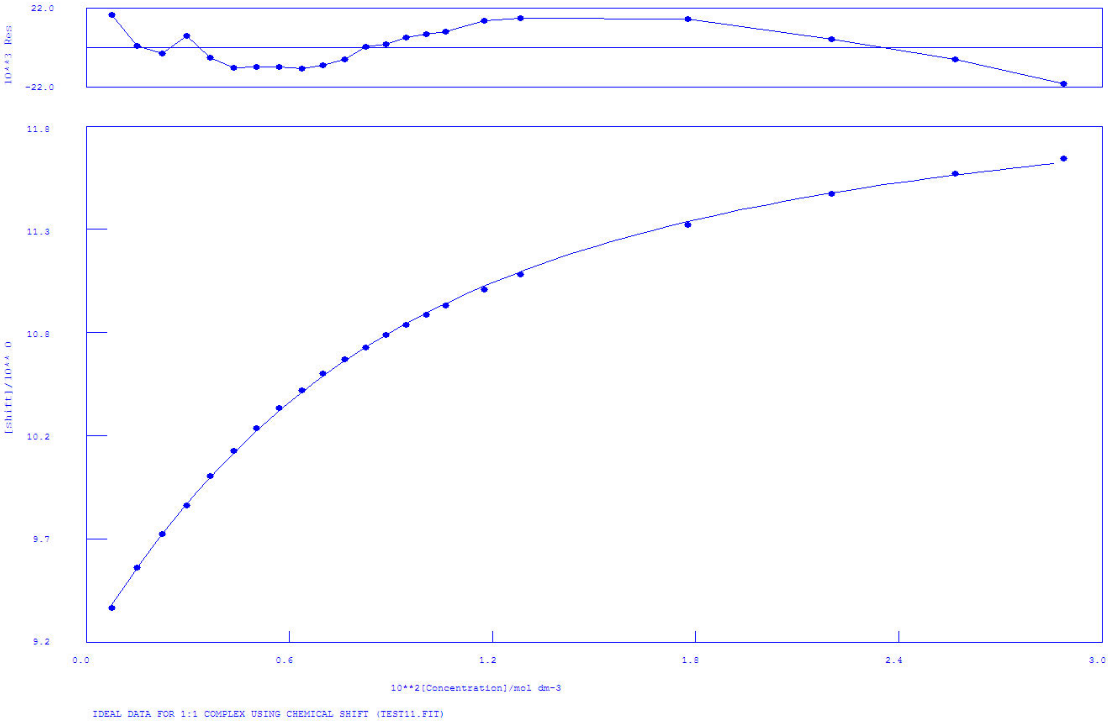

Figure S30. ^{1}H-NMR of **L^1** with TEAHCO$_3$ in DMSO-*d$_6$*/0.5%H$_2$O. The fitting has been obtained following the most downfield shifted NH proton.



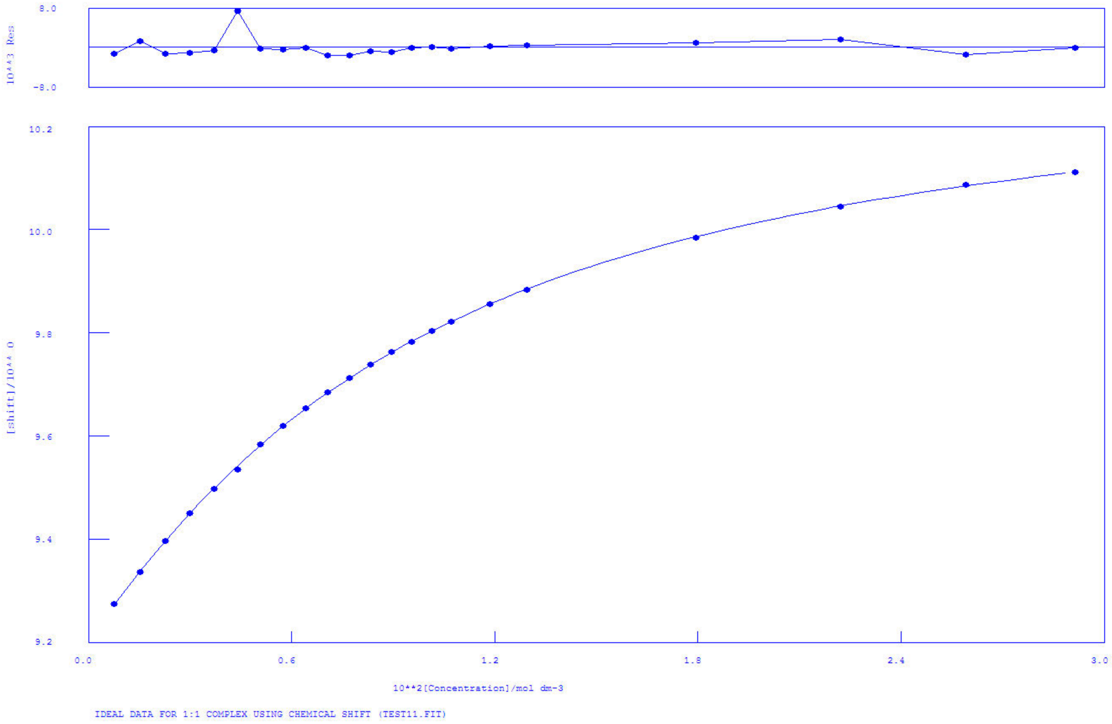
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 17:44:44   on 09/19/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  3.42611E+02 2.000E-01 9.574E+00 1.543E+01    K1
2  1  9.16612E+00 2.000E-01 1.227E-02 3.112E+00   SHIFT M
3  1  1.22897E+01 1.000E+00 1.779E-02 1.039E+01    SHIFT ML
```

Figure S31. ^{1}H-NMR of **L^2** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



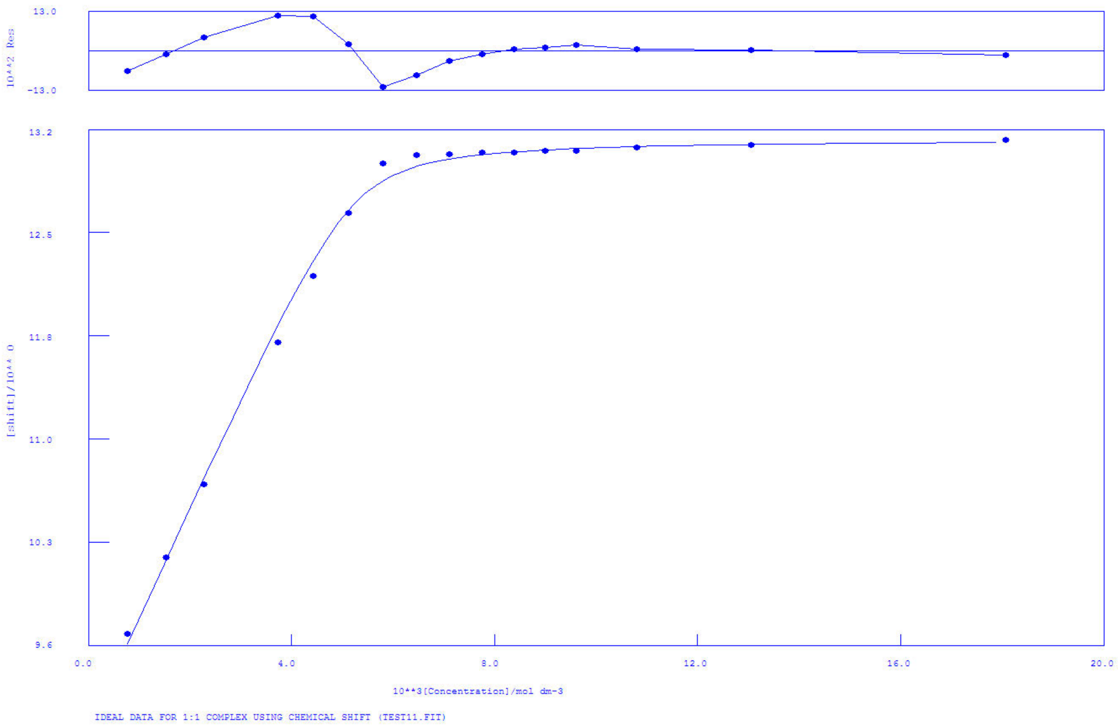
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:23:20   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.73966E+02 2.000E-01 3.942E+00 2.400E+01    K1
2  1  9.18417E+00 2.000E-01 8.745E-03 4.200E+00   SHIFT Sn
3  1  1.21793E+01 1.000E+00 1.842E-02 1.523E+01    SHIFT Sn(L)
```

Figure S32. ^{1}H-NMR of **L^2** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



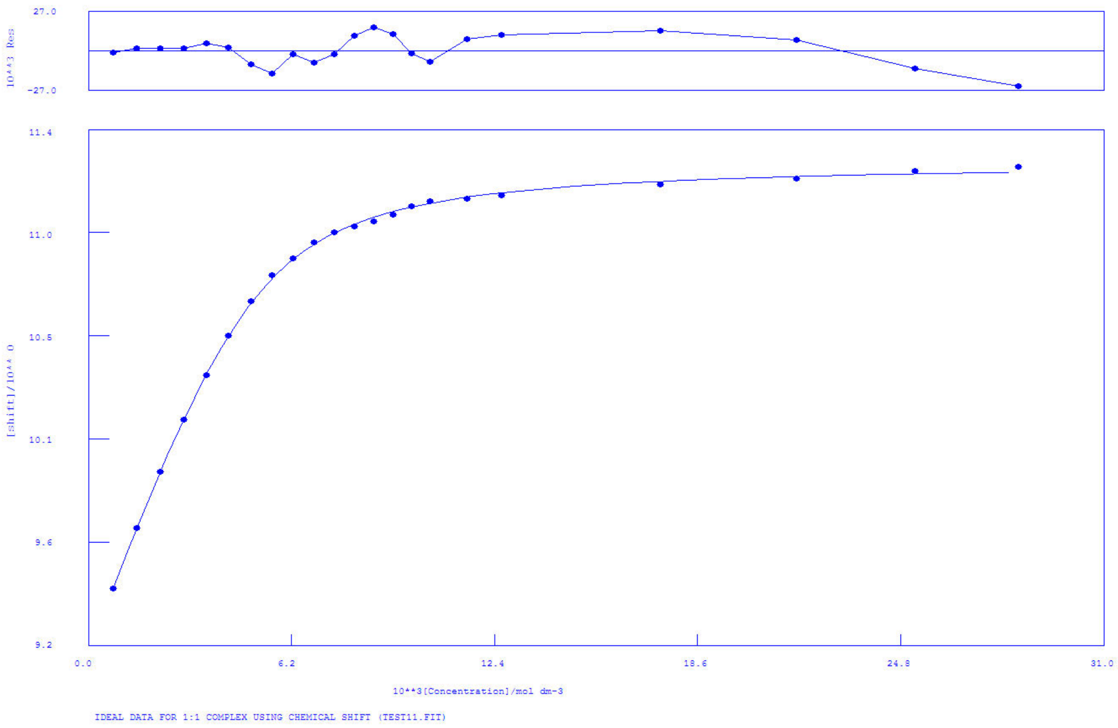
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:31:04   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.41834E+02 2.000E-01 1.508E+00 2.782E+01    K1
2  1  9.20194E+00 2.000E-01 1.469E-03 4.399E+00   SHIFT Sn
3  1  1.03656E+01 1.000E+00 3.696E-03 1.788E+01    SHIFT Sn(L)
```

Figure S33. ^{1}H-NMR of **L^2** with TBACl in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



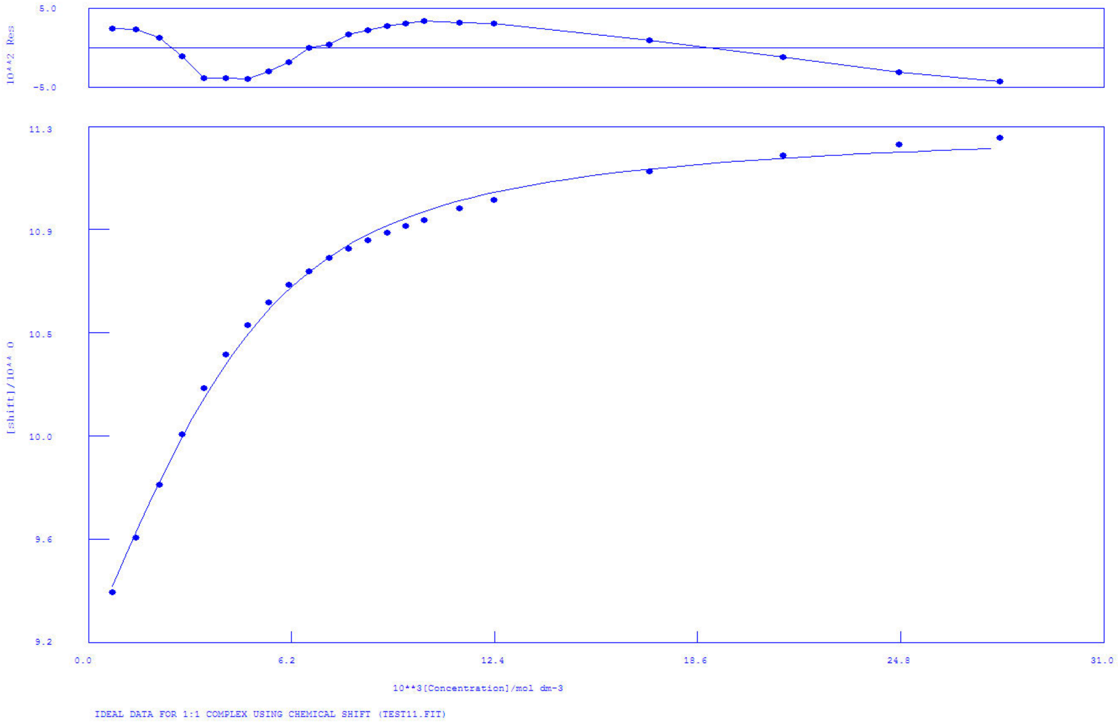
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes

Program run at 10:37:50   on 06/28/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.39502E+04 2.000E-01 3.049E+03 2.466E+00    K1
2  1  9.00793E+00 2.000E-01 5.287E-02 1.123E+00   SHIFT M
3  1  1.31304E+01 1.000E+00 2.986E-02 2.412E+00    SHIFT ML
```

Figure S34. ^{1}H-NMR of **L^2** with TBAF in DMSO-*d*$_6$/0.5%H$_2$O. The fitting has been obtained following the most downfield shifted NH proton.



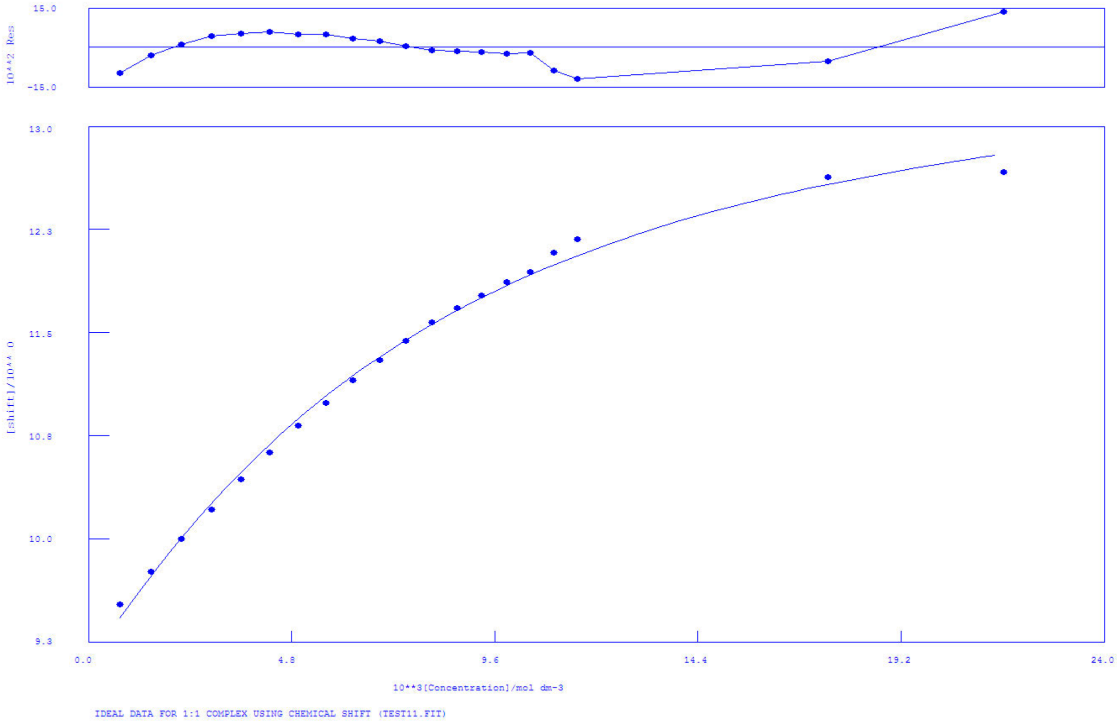
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 18:20:22   on 09/19/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.84167E+03 2.000E-01 6.193E+01 6.089E+00    K1
2  1  9.16573E+00 2.000E-01 8.302E-03 1.576E+00   SHIFT M
3  1  1.12642E+01 1.000E+00 6.453E-03 5.075E+00    SHIFT ML
```

Figure S35. ^{1}H-NMR of **L^2** with TBAH_2PO_4 in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



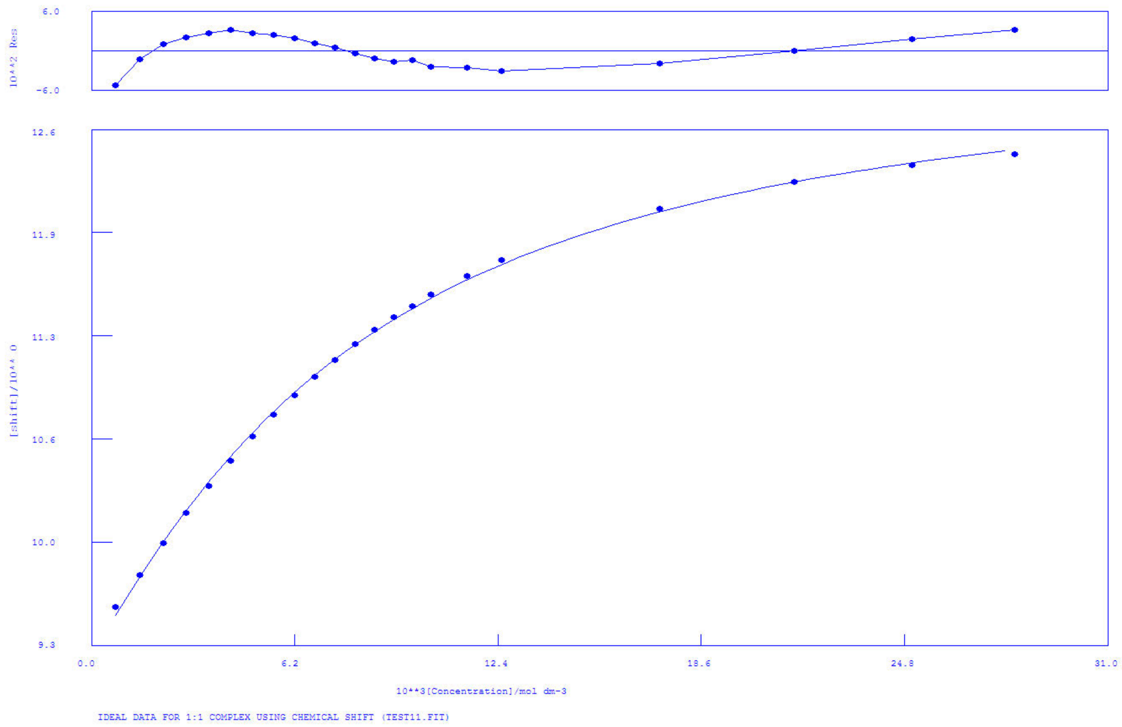
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:59:12   on 06/26/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  7.95574E+02 2.000E-01 5.900E+01 9.118E+00    K1
2  1  9.18599E+00 2.000E-01 2.241E-02 2.137E+00   SHIFT M
3  1  1.13205E+01 1.000E+00 2.248E-02 6.825E+00    SHIFT ML
```

Figure S36. ^{1}H-NMR of **L^2** with TEAHCO$_3$ in DMSO-*d$_6$*/0.5%H$_2$O. The fitting has been obtained following the most downfield shifted NH proton.



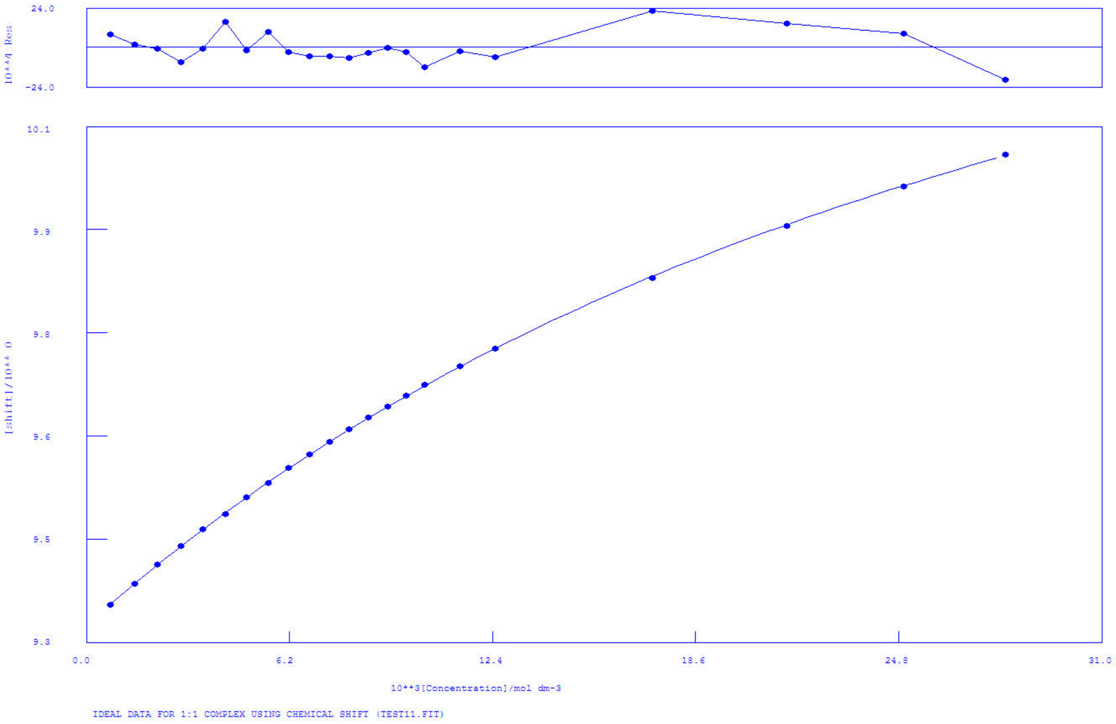
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:59:14   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.94560E+02 2.000E-01 2.241E+01 3.979E+01    K1
2  1  9.14315E+00 2.000E-01 5.102E-02 4.276E+00   SHIFT Sn
3  1  1.38697E+01 1.000E+00 1.556E-01 2.828E+01    SHIFT Sn(L)
```

Figure S37. ^{1}H-NMR of **L^3** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



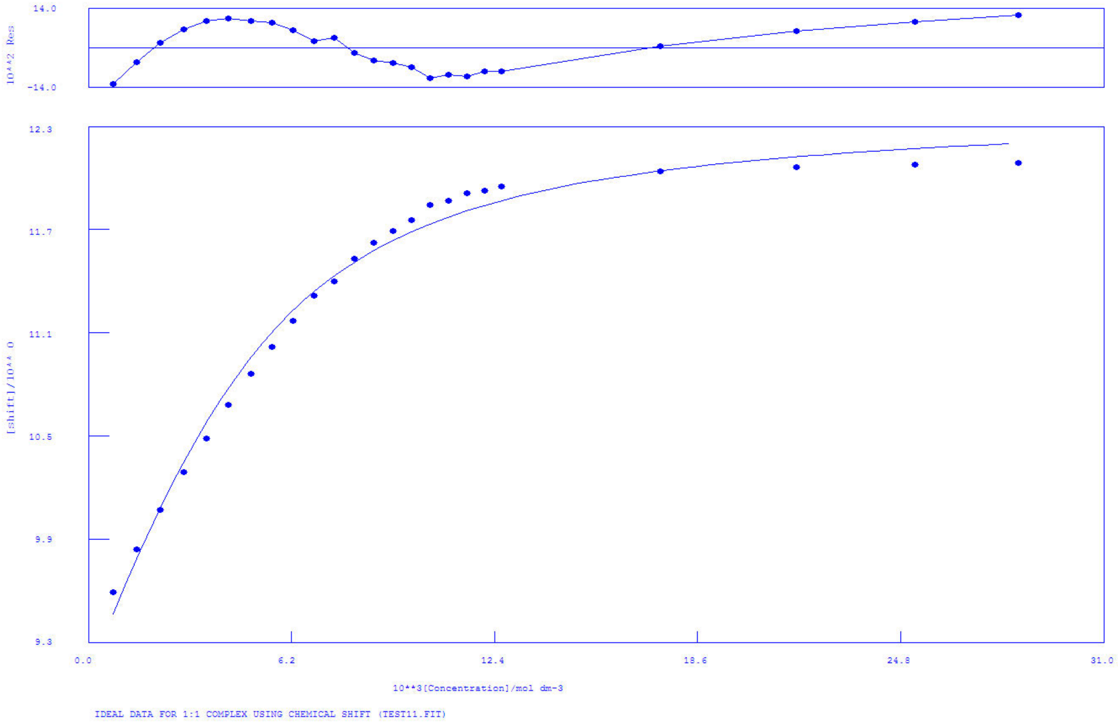
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:01:51   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.80886E+02 2.000E-01 6.609E+00 2.400E+01    K1
2  1  9.21685E+00 2.000E-01 1.874E-02 4.159E+00   SHIFT Sn
3  1  1.32149E+01 1.000E+00 3.983E-02 1.530E+01    SHIFT Sn(L)
```

Figure S38. ^{1}H-NMR of **L^3** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



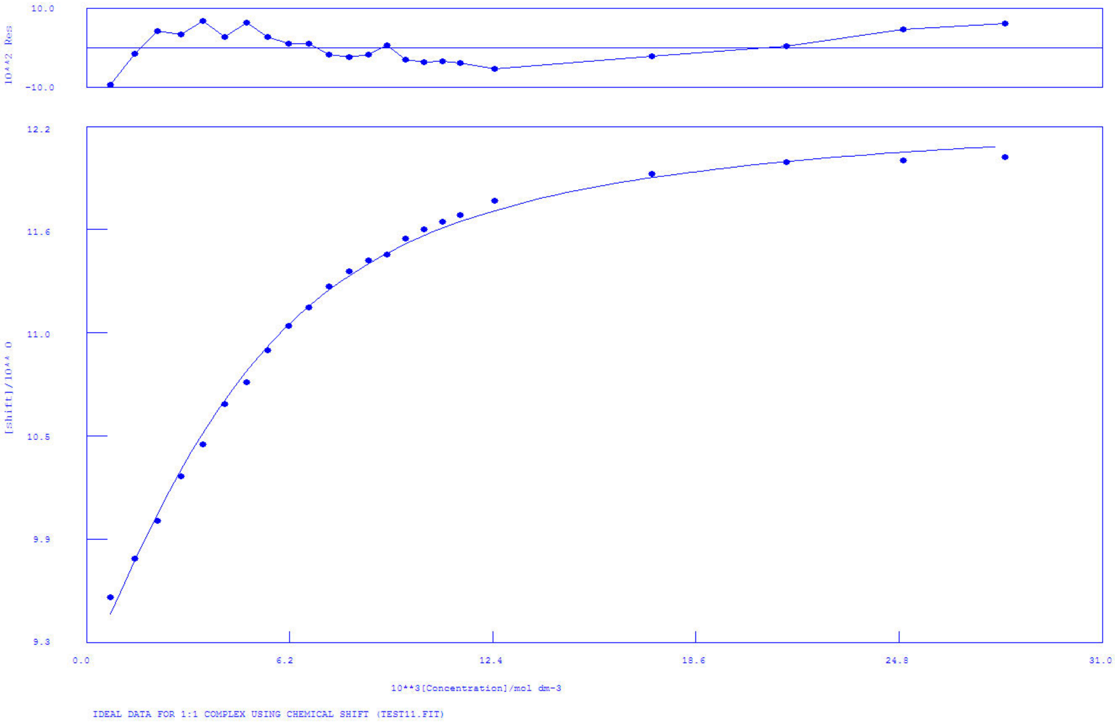
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:04:11   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  3.46683E+01 2.000E-01 3.688E-01 1.263E+02    K1
2  1  9.32563E+00 2.000E-01 6.642E-04 6.151E+00   SHIFT Sn
3  1  1.08721E+01 1.000E+00 8.872E-03 9.555E+01    SHIFT Sn(L)
```

Figure S39. ^{1}H-NMR of **L^3** with TBACl in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



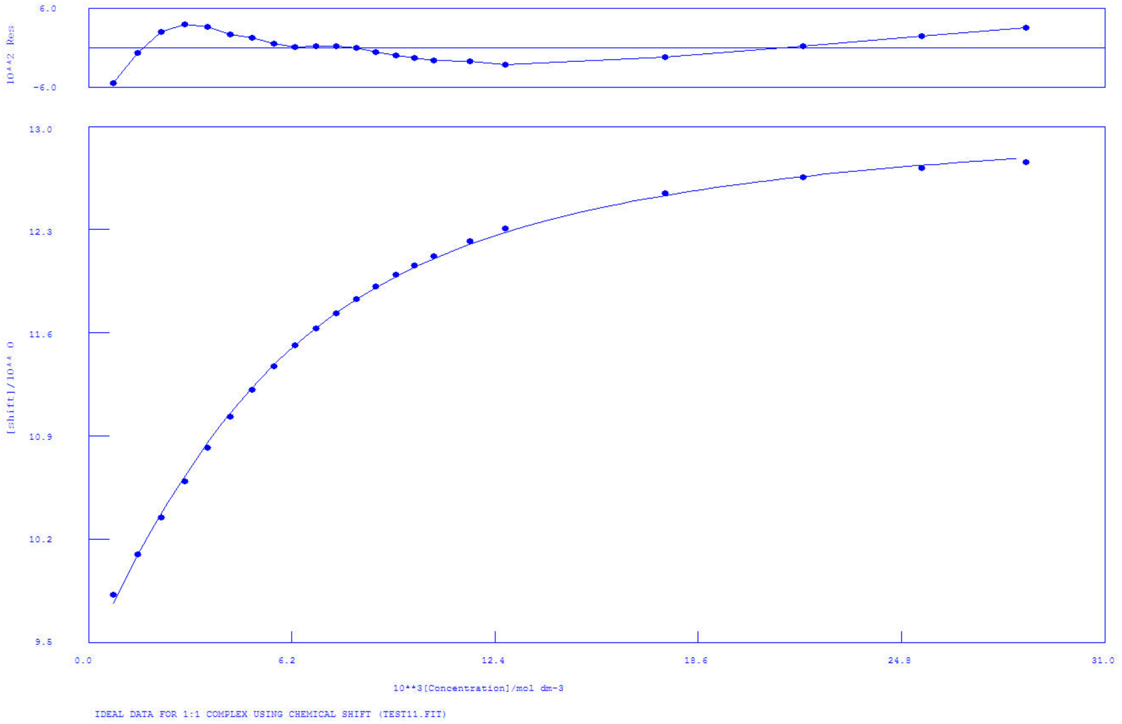
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:06:56   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  5.92470E+02 2.000E-01 7.931E+01 1.178E+01    K1
2  1  9.10526E+00 2.000E-01 6.554E-02 2.463E+00   SHIFT Sn
3  1  1.24211E+01 1.000E+00 7.136E-02 8.511E+00    SHIFT Sn(L)
```

Figure S40. ^{1}H-NMR of **L³** with $TBAH_2PO_4$ in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



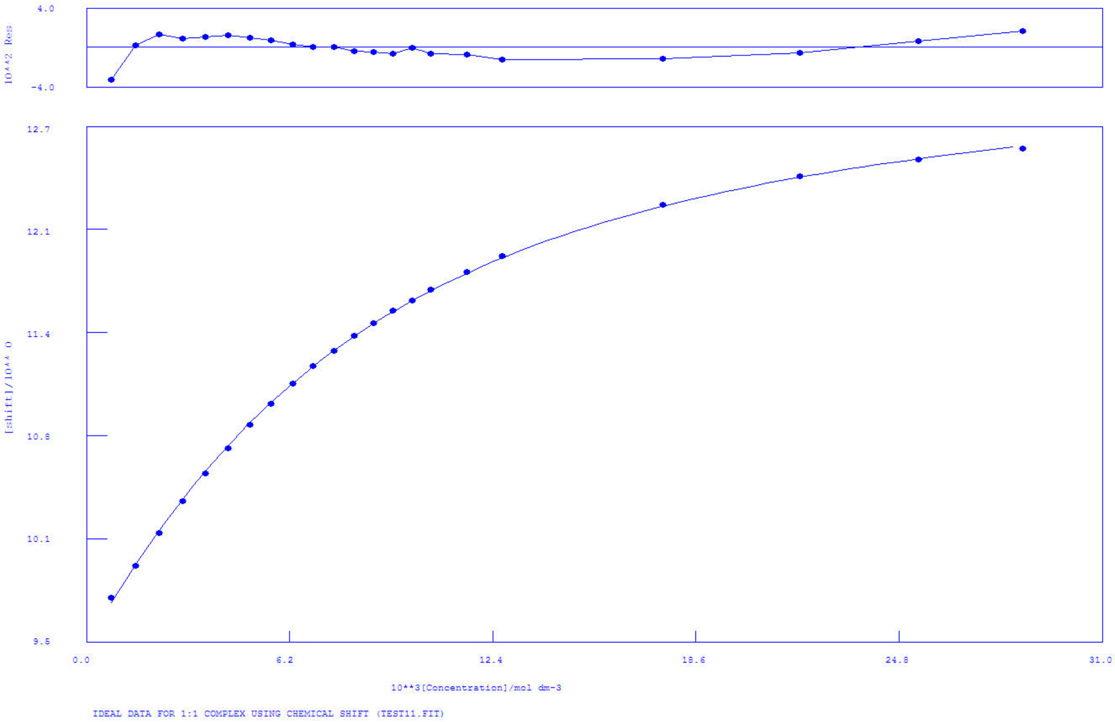
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:10:12   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  5.06561E+02 2.000E-01 3.641E+01 1.244E+01    K1
2  1  9.12879E+00 2.000E-01 3.376E-02 2.624E+00   SHIFT Sn
3  1  1.23375E+01 1.000E+00 4.004E-02 8.802E+00    SHIFT Sn(L)
```

Figure S41. ^{1}H-NMR of **L^3** with TEAHCO$_3$ in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



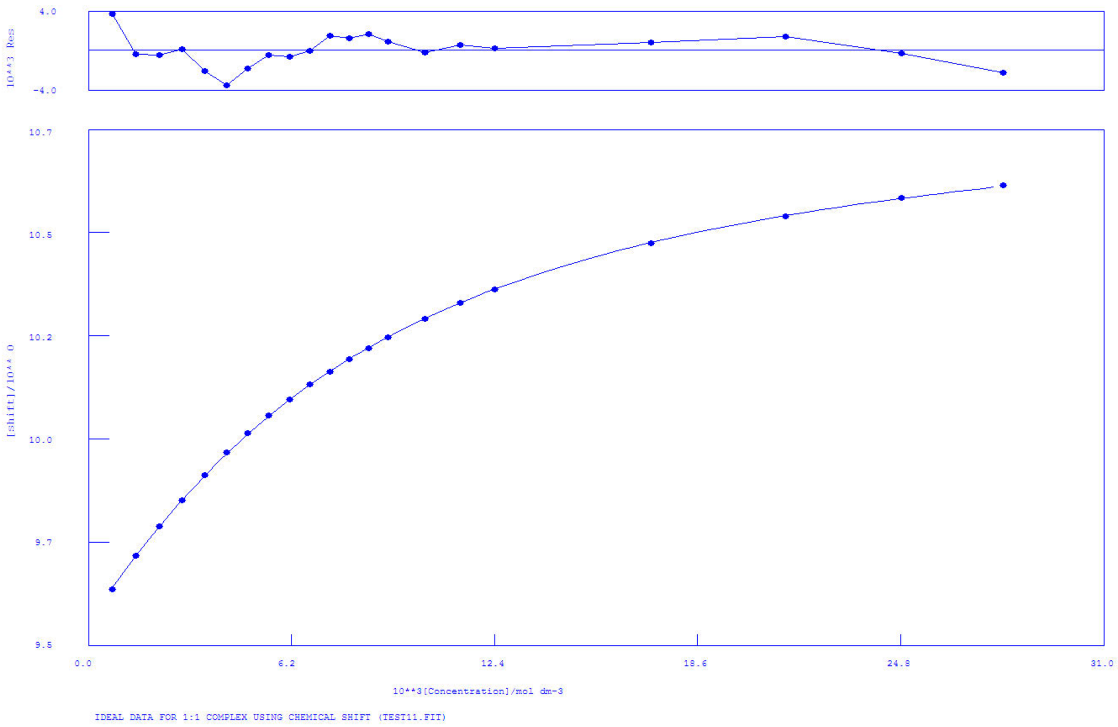
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:12:44   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  3.57372E+02 2.000E-01 1.146E+01 1.452E+01    K1
2  1  9.41181E+00 2.000E-01 1.806E-02 3.106E+00   SHIFT Sn
3  1  1.31764E+01 1.000E+00 2.416E-02 9.653E+00    SHIFT Sn(L)
```

Figure S42. ^{1}H-NMR of **L^4** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



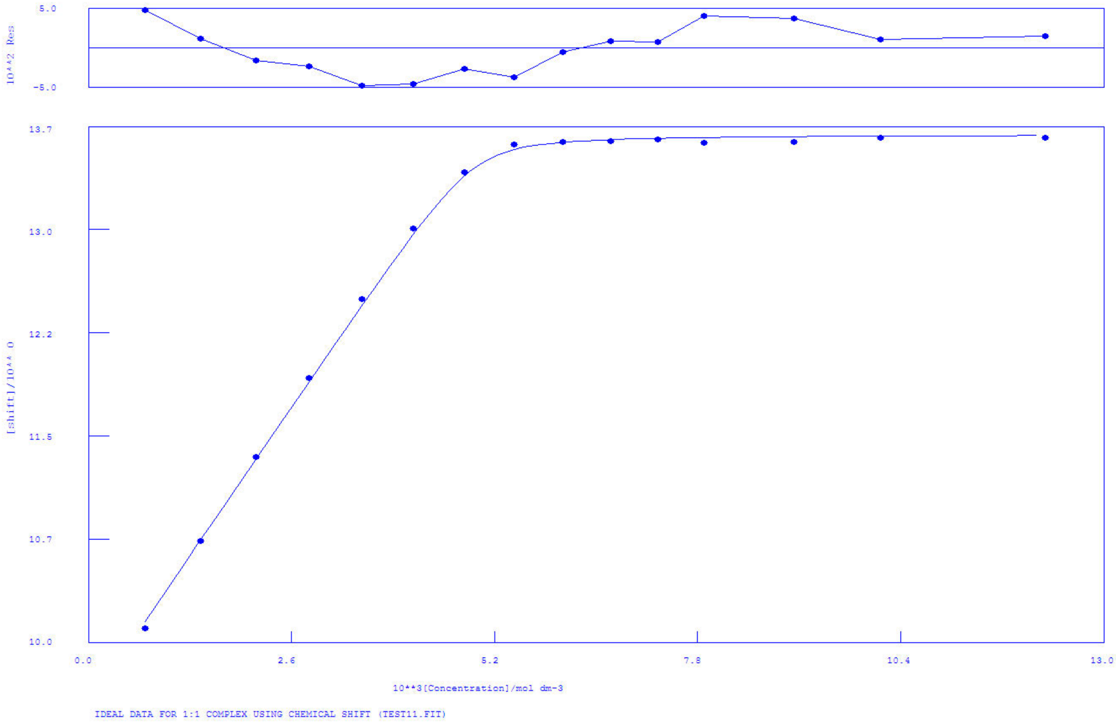
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:15:21   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.83482E+02 2.000E-01 3.375E+00 2.352E+01    K1
2  1  9.48041E+00 2.000E-01 8.831E-03 4.060E+00   SHIFT Sn
3  1  1.32699E+01 1.000E+00 1.864E-02 1.512E+01    SHIFT Sn(L)
```

Figure S43. ^{1}H-NMR of **L^4** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



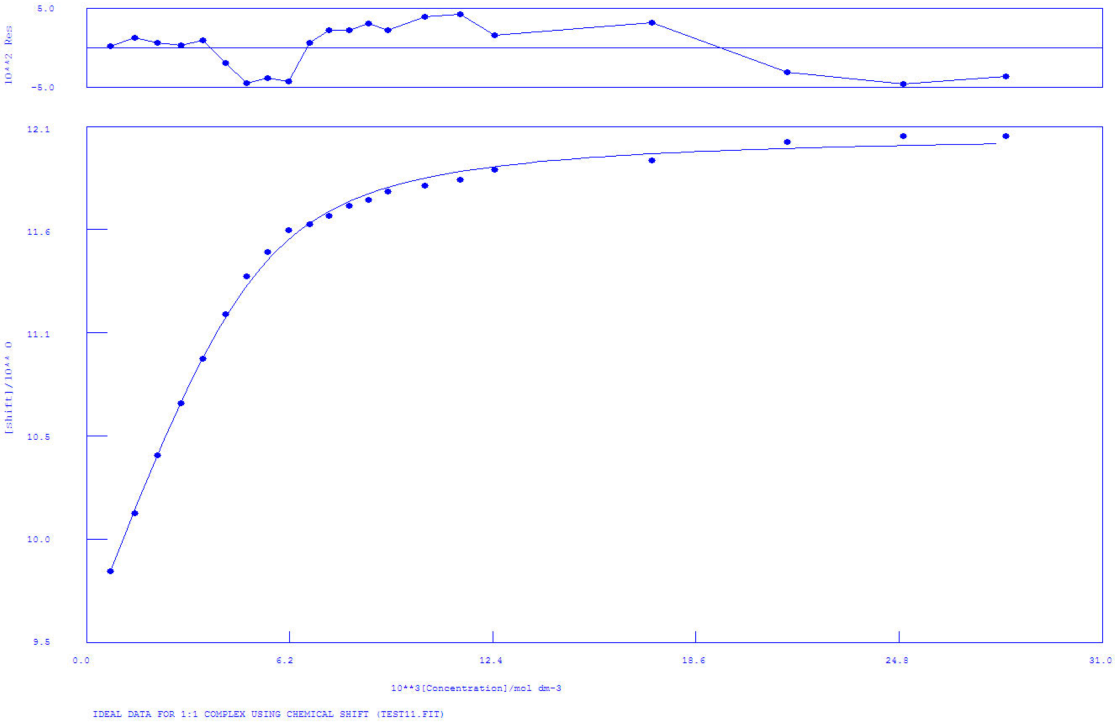
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:18:20   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.68534E+02 2.000E-01 1.382E+00 2.437E+01    K1
2  1  9.55125E+00 2.000E-01 1.273E-03 4.135E+00   SHIFT Sn
3  1  1.08181E+01 1.000E+00 2.902E-03 1.559E+01    SHIFT Sn(L)
```

Figure S44. ^{1}H-NMR of **L^4** with TBACl in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



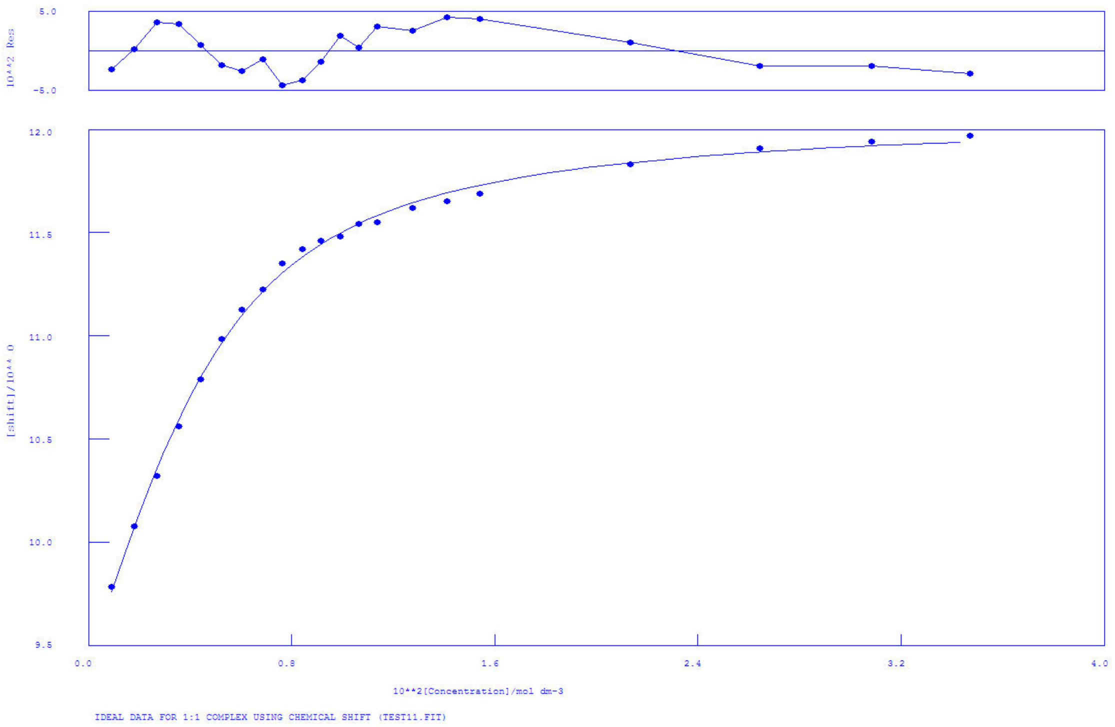
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:30:16   on 09/19/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  5.76469E+04 2.000E-01 5.039E+03 1.439E+00    K1
2  1  9.54863E+00 2.000E-01 2.644E-02 1.186E+00   SHIFT M
3  1  1.36427E+01 1.000E+00 1.284E-02 1.568E+00    SHIFT ML
```

Figure S45. ^{1}H-NMR of **L**^{4} with TBAF in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



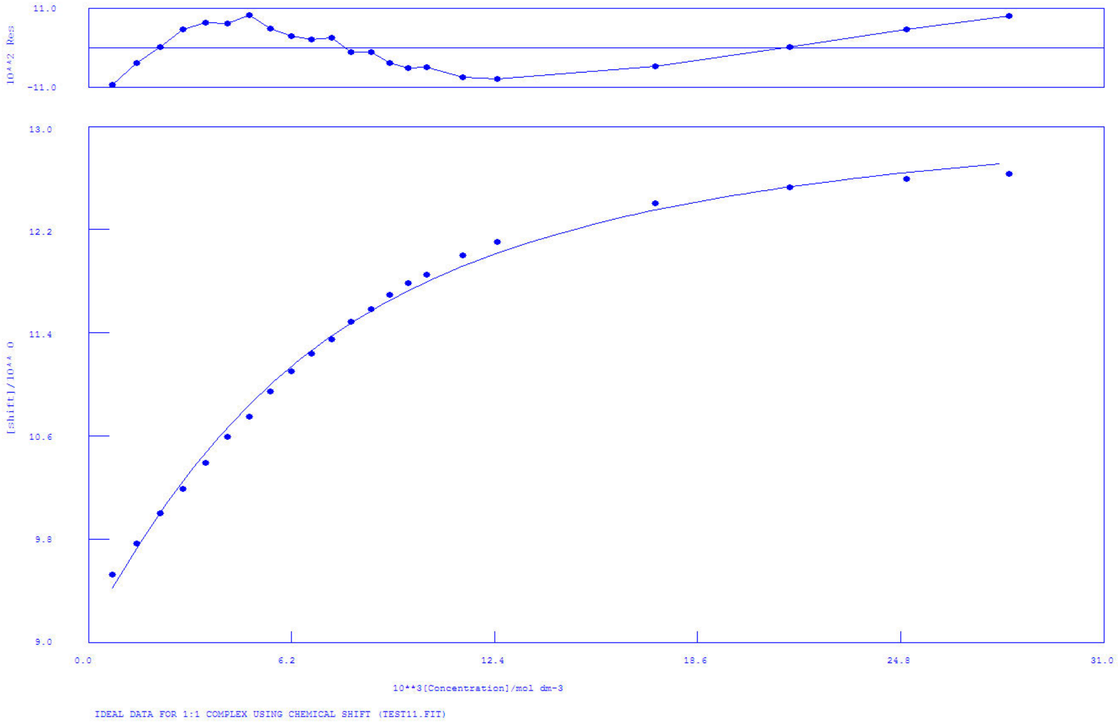
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:44:37   on 09/19/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.72815E+03 2.000E-01 1.383E+02 5.912E+00    K1
2  1  9.53498E+00 2.000E-01 2.411E-02 1.599E+00   SHIFT M
3  1  1.20740E+01 1.000E+00 1.939E-02 4.894E+00    SHIFT ML
```

Figure S46. ^{1}H-NMR of **L^4** with TBAH$_2$PO$_4$ in DMSO-*d$_6$*/0.5%H$_2$O. The fitting has been obtained following the most downfield shifted NH proton.



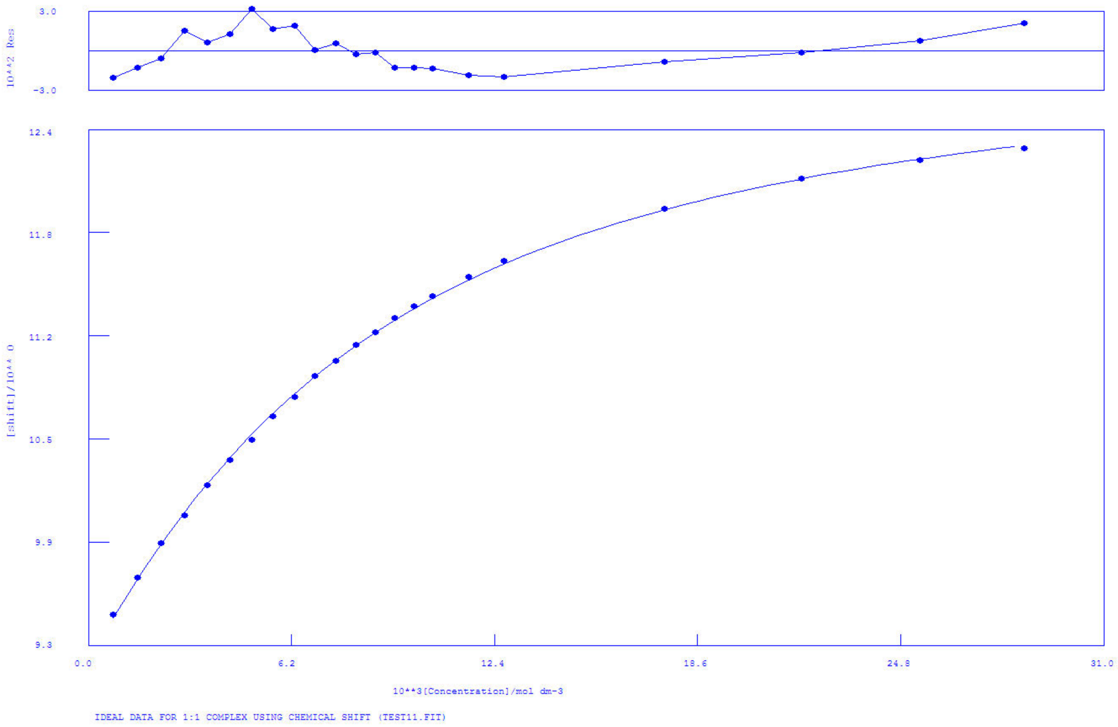
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:52:07   on 09/19/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  5.94298E+02 2.000E-01 3.296E+01 9.007E+00    K1
2  1  9.40172E+00 2.000E-01 2.580E-02 2.498E+00   SHIFT M
3  1  1.20809E+01 1.000E+00 2.124E-02 6.076E+00    SHIFT ML
```

Figure S47. ^{1}H-NMR of **L^4** with TEAHCO$_3$ in DMSO-d_6/0.5%H$_2$O. The fitting has been obtained following the most downfield shifted NH proton.



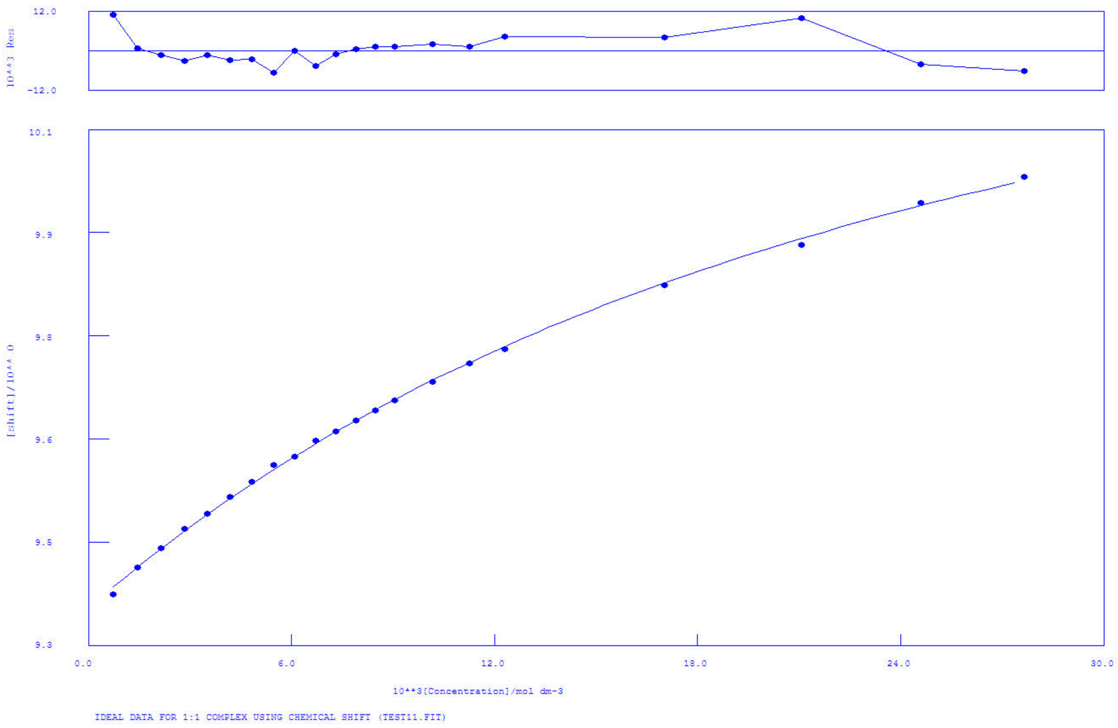
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:11:10   on 09/16/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  2.41661E+02 2.000E-01 2.004E+01 1.989E+01    K1
2  1  9.08094E+00 2.000E-01 4.968E-02 3.870E+00   SHIFT M
3  1  1.33459E+01 1.000E+00 8.387E-02 1.254E+01    SHIFT ML
```

Figure S48. ^{1}H-NMR of **L^5** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



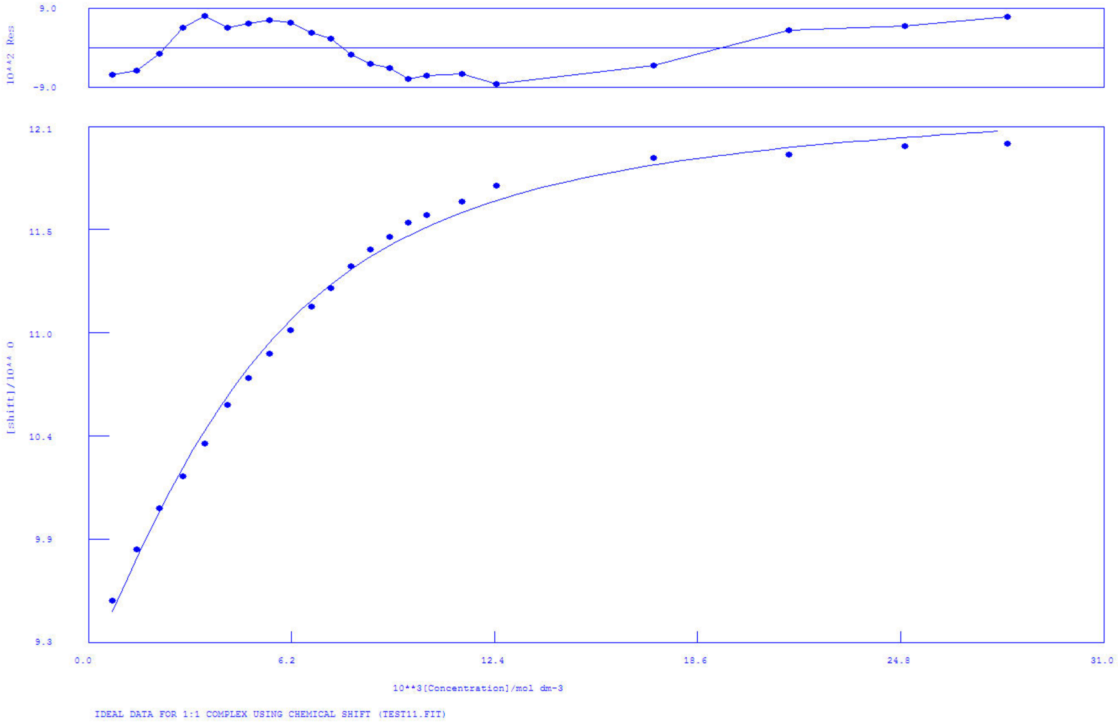
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:35:14   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.71752E+02 2.000E-01 4.191E+00 2.462E+01    K1
2  1  9.20606E+00 2.000E-01 1.180E-02 4.206E+00   SHIFT Sn
3  1  1.30398E+01 1.000E+00 2.579E-02 1.571E+01    SHIFT Sn(L)
```

Figure S49. ^{1}H-NMR of **L^5** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



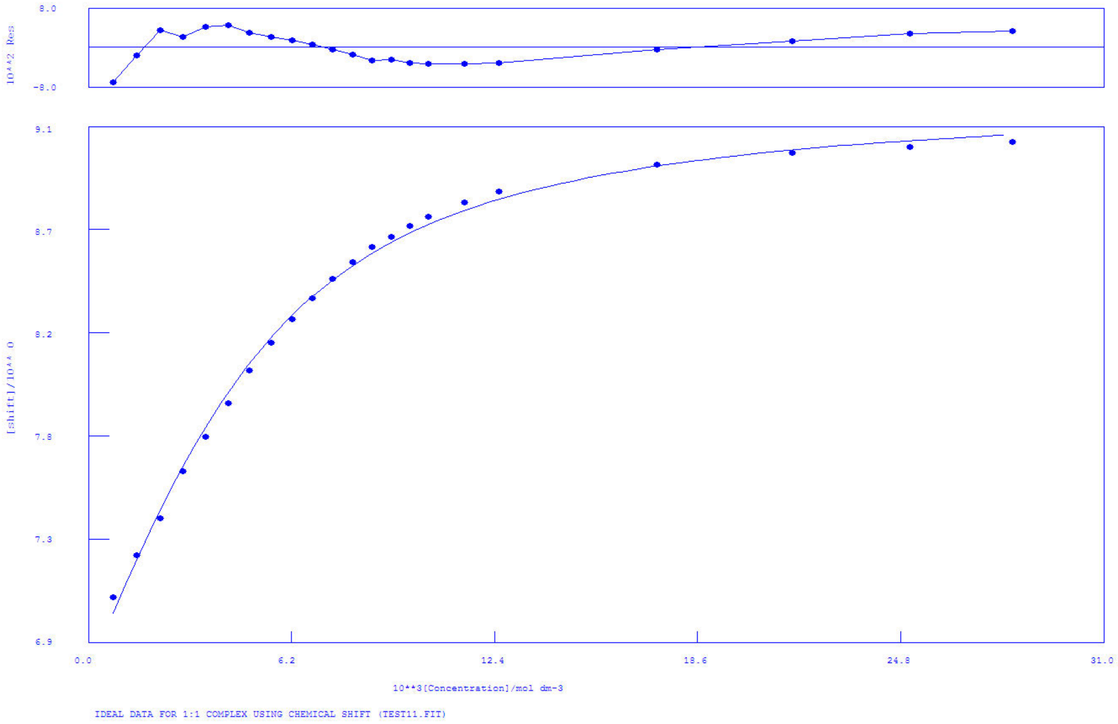
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:39:07   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  4.44922E+01 2.000E-01 2.233E+00 9.052E+01    K1
2  1  9.35733E+00 2.000E-01 3.252E-03 5.825E+00   SHIFT Sn
3  1  1.06151E+01 1.000E+00 3.110E-02 6.584E+01    SHIFT Sn(L)
```

Figure S50. ^{1}H-NMR of **L^5** with TBACl in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



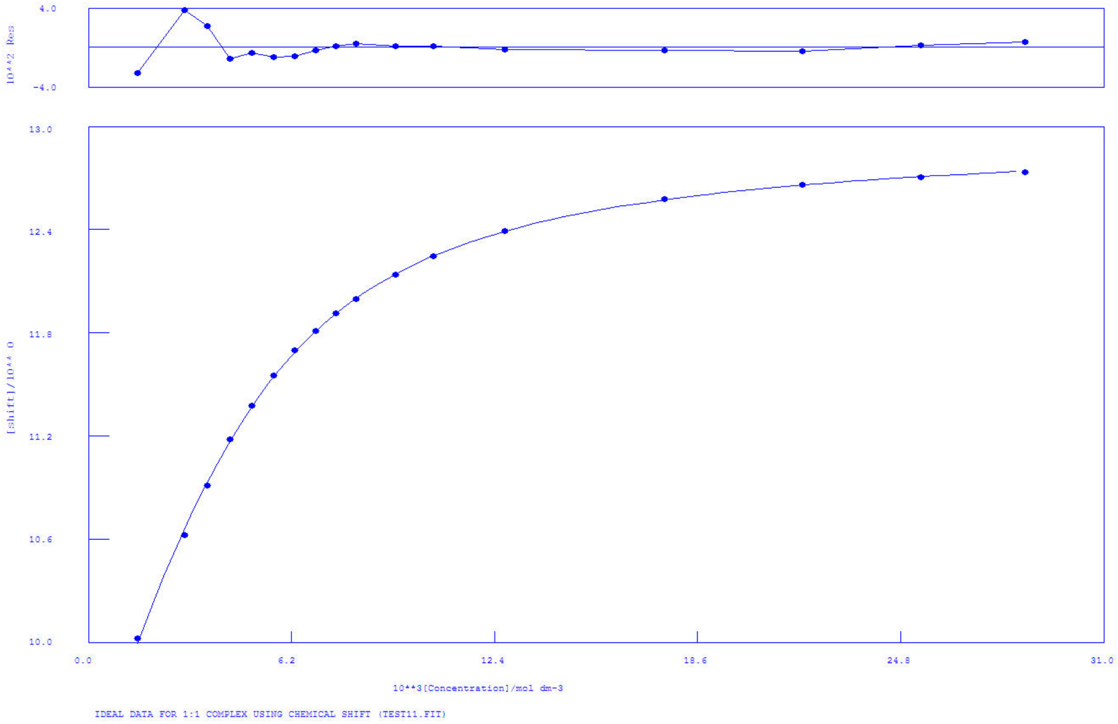
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:40:30   on 01/09/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   Sn + L = Sn(L)
FILE: TEST11.FIT (Measured shift is on 119Sn)
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  4.75339E+02 2.000E-01 4.375E+01 1.167E+01    K1
2  1  9.15035E+00 2.000E-01 4.421E-02 2.680E+00   SHIFT Sn
3  1  1.23385E+01 1.000E+00 5.279E-02 8.072E+00    SHIFT Sn(L)
```

Figure S51. ^{1}H-NMR of **L^5** with TBAH$_2$PO$_4$ in DMSO-d_6/0.5%H$_2$O. The fitting has been obtained following the most downfield shifted NH proton.



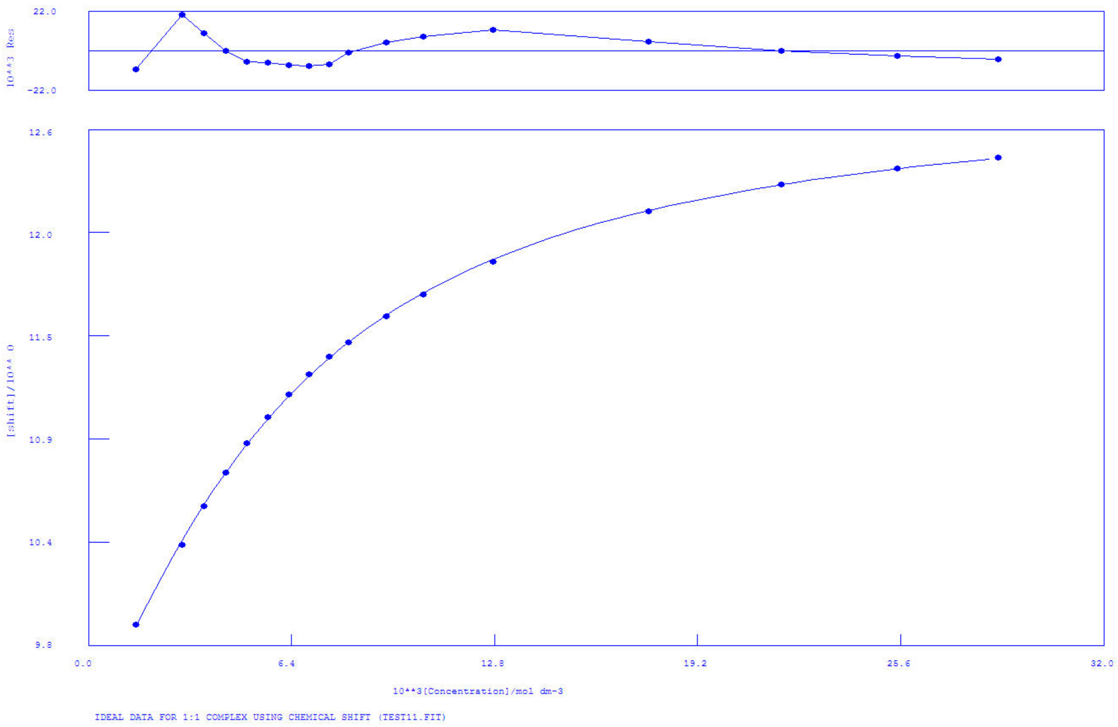
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 17:42:22   on 03/25/2013
IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  5.22724E+02 2.000E-01 3.653E+01 1.156E+01    K1
2  1  6.76960E+00 2.000E-01 2.518E-02 2.550E+00   SHIFT M
3  1  9.25140E+00 1.000E+00 2.967E-02 8.191E+00    SHIFT ML
```

Figure S52. ^{1}H-NMR of **L^5** with TEAHCO$_3$ in DMSO-d_6/0.5%H$_2$O. The fitting has been obtained following the most downfield shifted NH proton.



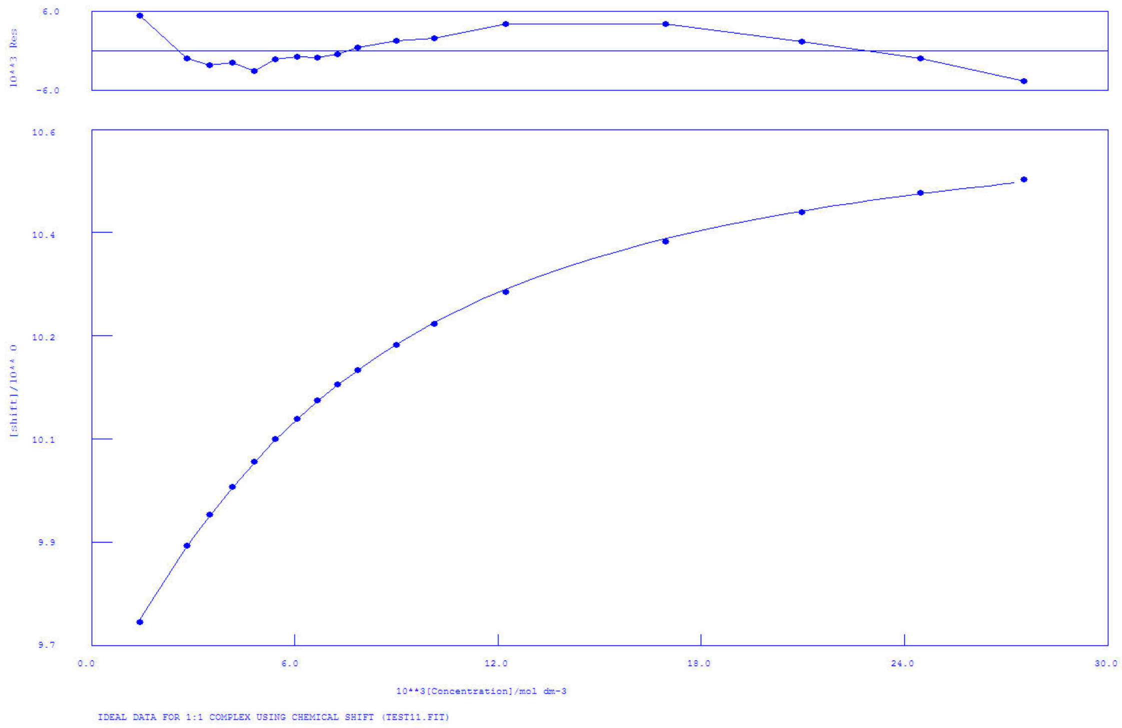
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:24:59   on 02/28/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  6.57069E+02 2.000E-01 1.598E+01 1.098E+01    K1
2  1  9.18134E+00 2.000E-01 1.814E-02 3.505E+00   SHIFT M
3  1  1.29651E+01 1.000E+00 1.244E-02 6.291E+00    SHIFT ML
```

Figure S53. ^{1}H-NMR of **L^6** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



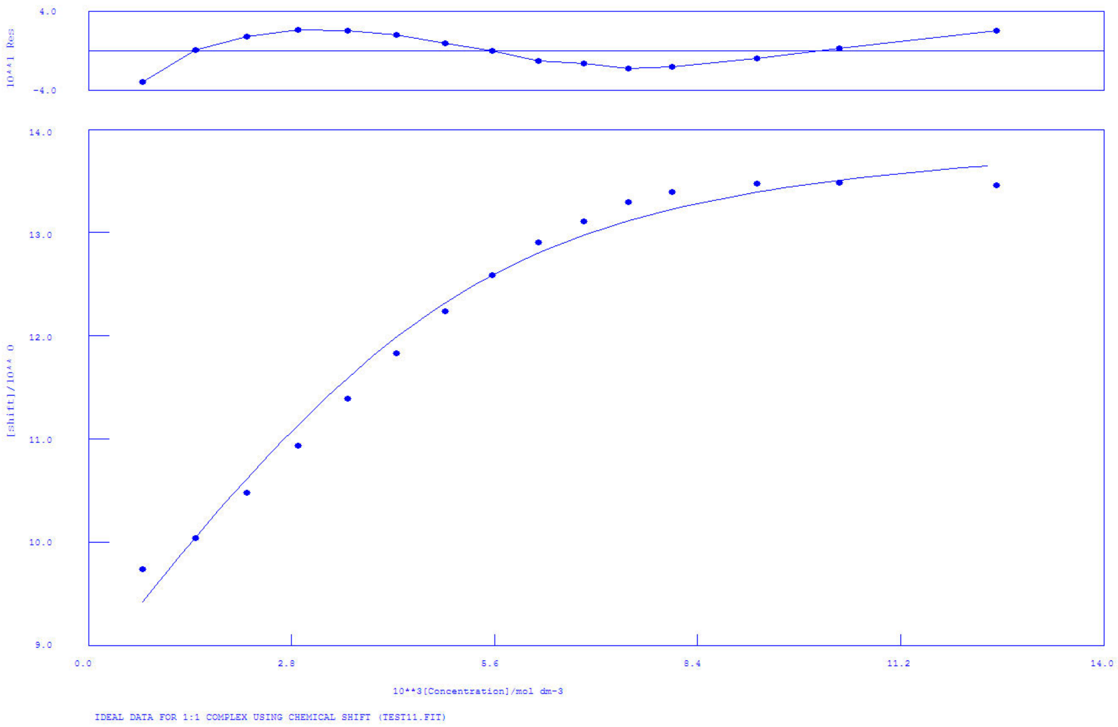
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:30:17   on 02/28/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  2.76781E+02 2.000E-01 4.738E+00 2.063E+01    K1
2  1  9.32631E+00 2.000E-01 1.084E-02 5.449E+00   SHIFT M
3  1  1.29059E+01 1.000E+00 1.188E-02 1.058E+01    SHIFT ML
```

Figure S54. ^{1}H-NMR of **L^6** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



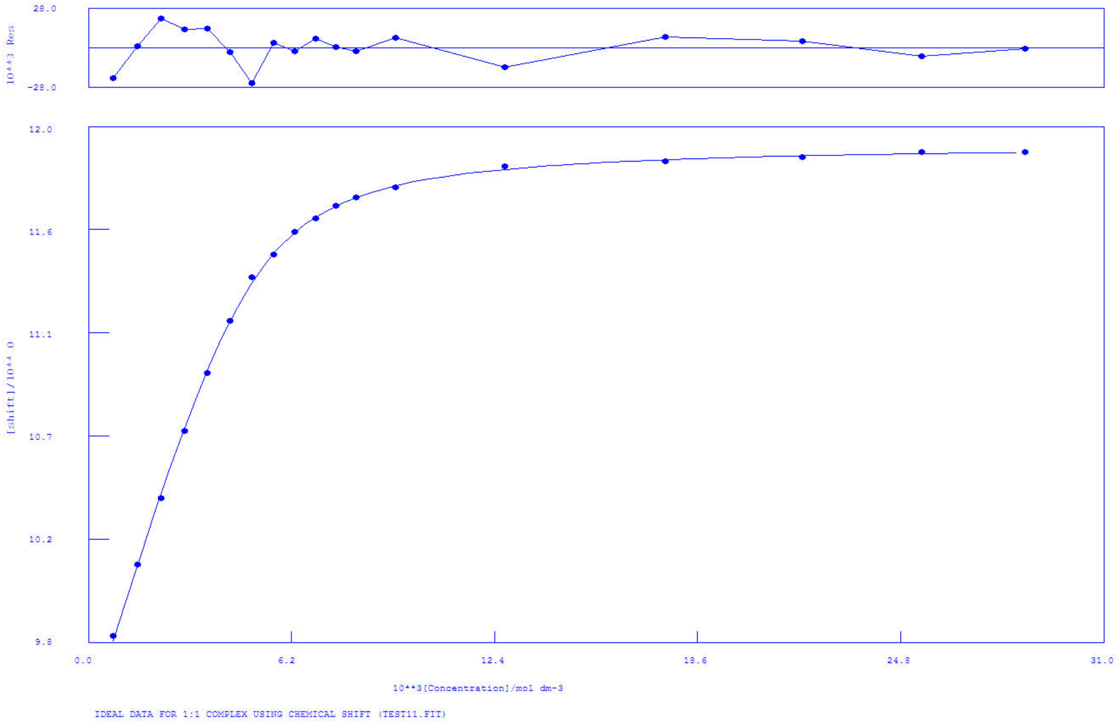
```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:36:21   on 02/28/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  2.28604E+02 2.000E-01 4.255E+00 2.332E+01    K1
2  1  9.59087E+00 2.000E-01 3.179E-03 5.498E+00   SHIFT M
3  1  1.06794E+01 1.000E+00 4.349E-03 1.246E+01    SHIFT ML
```

Figure S55. ^{1}H-NMR of **L^6** with TBACl in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 12:02:03   on 02/28/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  1.30128E+03 2.000E-01 4.956E+02 2.113E+01    K1
2  1  8.75789E+00 2.000E-01 1.389E-01 1.788E+00   SHIFT M
3  1  1.41345E+01 1.000E+00 2.932E-01 1.897E+01    SHIFT ML
```

Figure S56. ^{1}H-NMR of **L^6** with TBAF in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.



```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:43:49   on 02/28/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction:   M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
1  1  2.65186E+03 2.000E-01 9.750E+01 4.471E+00    K1
2  1  9.46586E+00 2.000E-01 9.891E-03 1.461E+00   SHIFT M
3  1  1.19268E+01 1.000E+00 7.215E-03 3.812E+00    SHIFT ML
```

Figure S57. ^{1}H-NMR of **L^6** with TBAH_2PO_4 in DMSO-*d*$_6$/0.5%H_2O. The fitting has been obtained following the most downfield shifted NH proton.