**Fluorescent asymmetric bis-ureas for pyrophosphate recognition in pure water**

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## General procedures

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). 7-aminoindole[1] was synthesised following a literature procedure.

Molecular modeling investigations on the adducts formed by the three ligands with $HPpi^{3-}$, in a 1 : 1 ligand-to-anion molar ratio have been performed by means of an empirical force field method (AMBER3),[2] evaluating the atomic partial charges at the PM3 semi-empirical level of theory[3] and using an implicit simulation of the solvent environment (ε = 4R). The potential energy surface of all the systems has been explored by means of simulated annealing (T = 600 K, equilibration time = 10 ps, run time = 10 ps and cooling time = 10 ps, time step = 1.0 fs). For each studied system, 80 conformations have been sampled.

Mass spectra in positive-ion mode were recorded on a triple quadruple QqQ Varian 310-MS mass spectrometer using the atmospheric-pressure ESI technique. The 20 μl of sample of binder in DMSO solutions were introduced into the ESI source by a Varian HPLC pump without column, at a flow rate of 250μL/min using a 1:1 /$CH_3OH$:$H_2O$ mixture . A dwell time of 4 s was used, needle voltage of 4000 V, shield voltage of 600 V, housing temperature of 60 °C, drying gas temperature

of 400 °C, nebuliser gas pressure of 46 PSI, drying gas pressure of 35 PSI and a detector voltage of 1490 V were used. Mass spectra were acquired in the 250-500amu range.

[1] T. Zielinski, P. Dydio, J. Jurczak, *Tetrahedron*, 2008**, 64,** 568**.**

[2] Hyperchem Release 7.51 for Windows MM System, Hypercube, Inc., Gainesville, FL, 2002.

[3] (a) J. J. P. J. Stewart, Comput. Chem., 1989, 10, 209–220; (b) J. J. P. J. Stewart, Comput. Chem., 1989, 10, 221–264.

**Synthesis of 1-(1H-indol-7-yl)-3-(2-nitrophenyl)urea (A)**

A solution of 1-isocyanate-2-nitrobenzene (0.3060g, 1.864 mmol) in dichloromethane (20ml) was added dropwise to a solution of 7-aminoindole (0.2445g, 1.85 mmol) in dichlomethane (10ml). The mixture was refluxed for 12h and then it was filtred to give the desired compound as a yellow solid. Yield 92% (0.5029g, 1.7 mmol); M.p.: 114°C; $^1$H-NMR (400 MHz,DMSO-$d_6$, 298K): δH: 10.68 (s, 1H); 9,71 (s, 1H); 9.56 (s, 1H); 8.42 (d, J= 8.3 Hz, 1H); 8.12 (d, J= 8.2 Hz, 1H); 7.71 (t, J= 7.5 Hz, 1H); 7.37-7.34(m, 2H); 7.22-7.17 (m, 2H); 6.97 (t, J= 7.6 Hz, 1H); 6.46 (s, 1H);IR: (KBr, cm-1): v CO: 1540.45 (CO stretching); v NH: 3321.60 (NH urea stretching).

**Synthesis of 1-(2-aminophenyl)-3-(1H-indol-7-yl)urea (D)**

Palladium on activate carbon 10% (0.01028g) was added to a solution of **A** (0.487g, 1.644 mmol) in ethanol (150ml) and then the mixture was stirred for a few minutes under inert atmosphere. Hydrazine (2,9ml ) was then added and the resulting mixture was refluxed for 30 minutes. The solution was filtered with CELITE to remove palladium and the filtrate was concentrated in vacuum to give a beige solid, which was washed in dichloromethane to give the desired compound as a white solid. Yield 79% (0.3471g, 1.303 mmol); M.p.: >250°C; $^1$H-NMR (500 MHz,DMSO-d6, 298K), δH: 10.64 (s, 1H); 8.44 (s, 1H); 8.39 (s, 1H); 7.32 (t, J= 2.7 Hz, 1H); 7.29 (d, J= 7.8 Hz, 1H); 7.09 (d, J= 7.4 Hz, 1H); 6.95-6.89 (m, 2H); 6.81 (s, 1H); 6.63 (d, J= 8.7 Hz, 1H); 6.44 (t, J= 2.6 Hz, 1H); 6.22 (d, J= 9.0 Hz, 1H); 4.94 (s, 2H).IR: (KBr, cm-1): v CO: 1566.69 (CO stretching); v NH: 3286.21 (NH urea stretching).

**Synthesis of L1**

A solution of naphtyl-isocyanate (0.0973g, 0.575mmol) in acetonitrile (10ml) was added dropwise to a solution of **D** (0.1531g, 0.575mmol), in acetonitrile (20ml). The mixture was refluxed for 12h and then it was filtred to give the desired compound as a beige solid. Yield 85% (0.2119g, 4,865 mmol); M.p.: > 211°C; $^{1}$H-NMR (500 MHz, DMSO-*d6*, 298 K), δH: 10.66 (s, 1H); 9.12 (s, 1H); 8.96 (s, 1H); 8.56 (s, 1H); 8.22 (s, 1H); 8.20 (d, J= 8.3 Hz, 1H); 8.02 (d, J= 7.6 Hz, 1H); 7.93 (d, J= 7.8 Hz, 1H); 7.69-7.63 (m, 3H); 7.59-7.52 (m, 2H); 7.47 (t, J= 7.8 Hz, 1H); 7.32-7.28 (m, 2H); 7.12 (t, J= 4.7 Hz, 4H); 6.93 (t, J= 7.7 Hz, 1H). $^{13}$C- NMR (100 MHz, DMSO-*d6*, 298 K), δC: 131.51; 129.29; 128.62; 126.03; 125.85; 125.59; 125.05; 124.44; 124.00; 122.98; 119.03; 117.77; 115.65; 113.16; 104.72; 101.47. IR: (KBr, cm$^{-1}$): v CO: 1565.82 (CO stretching); v NH: 3310.42 (NH urea stretching). LRMS (ES+): m/z: 458.2 $[M-Na]^{+}$

**Synthesi of 1-(1H-indol-7-yl)-3-(3-nitrophenyl)urea (B)**

A solution of 1-isocyanate-3-nitrobenzene (0.303g, 1.846 mmol) in dichloromethane (20ml) was added dropwise to a solution of 7-aminoindole (0.2445g, 1.85 mmol) in dichlomethane (10ml). The mixture was refluxed for 12h and then it was filtred to give the desired compound as a yellow solid. Yield 92% (0.503g, 1.7 mmol); M.p.: 114°C; ; $^{1}$H-NMR (400 MHz,DMSO-$d_6$, 298K): δH: 10.73 (s, 1H); 9.3 (s, 1H); 8.63 (s, 1H); 8.6(t, J= 2.0 Hz, 1H); 7.84-7.81 (m, 1H); 8.19-8.16 (m, 1H); 7.58 (t, J= 7.58, 1H); 7.36-7.33 (m, 2H); 7.10 (d, J=7.39, 1H); 6.96 (t, J= 7.7 Hz, 1H); 6.46-6.43 (m, 1H). IR: (KBr, cm-1): v CO: 1540.45 (CO stretching); v NH: 3321.60 (NH urea stretching).

**Synthesis of 1-(3-aminophenyl)-3-(1H-indol-7-yl)urea (E)**

Palladium on activate carbon 10% (0.01028g) was added to a solution of **B** (0.487g, 1.644 mmol) in ethanol (150ml) and then the mixture was stirred for a few minutes under inert atmosphere. Hydrazine (2,9ml ) was then added and the resulting mixture was refluxed for 30 minutes. The solution was filtered with CELITE to remove palladium and the filtrate was concentrated in vacuum to give a beige solid, which was washed in dichloromethane to give the desired compound as a white solid. Yield 79% (0.3471g, 1.303 mmol); M.p.: >250°C; 1H-NMR (500 MHz,DMSO-d6, 298K), δH: 10.64 (s, 1H); 8.44 (s, 1H); 8.39 (s, 1H); 7.32 (t, J= 2.7 Hz, 1H); 7.29 (d, J= 7.8 Hz, 1H); 7.09 (d, J= 7.4 Hz, 1H); 6.95-6.89 (m, 2H); 6.81 (s, 1H); 6.63 (d, J= 8.7 Hz, 1H); 6.44 (t, J= 2.6 Hz, 1H); 6.22 (d, J= 9.0 Hz, 1H); 4.94 (s, 2H).IR: (KBr, cm$^{-1}$): v CO: 1566.69 (CO stretching); v NH: 3286.21 (NH urea stretching).

**Synthesis of L2**

A solution of naphtyl-isocyanate (0.2204g, 1.303mmol) in acetonitrile (10ml) was added dropwise to a solution of **E** (0.3470g, 1.303mmol), in acetonitrile (20ml). The mixture was refluxed for 12h and then it was filtred to give the desired compound as a beige solid. Yield 84% (0.2756g, 2,034 mmol); M.p.: > 250°C; 1H-NMR (400 MHz,DMSO-d6, 298K): δH: 10.71 (s, 1H); 9.10 (s, 1H); 8.84 (s, 1H); 8.72 (s, 1H); 8.46 (s, 1H); 8.14 (d, J= 8.3 Hz, 1H); 8.06 (d, J= 7.5 Hz, 1H); 7.93 (d, J= 8.1 Hz, 1H); 7.76 (s, 1H); 7.62 (t, J= 8.3 Hz, 2H); 7.58-7.53 (m, 2H); 7.48 (t, J= 7.8 Hz, 1H); 7.33-7.29 (m, 2H); 7.21 (d, J= 4.6 Hz, 2H); 7.1 (d, J= 7.2 Hz, 2H); 6.94 (t, J= 7.7 Hz, 1H). 13C-NMR (126 MHz, DMSO-d6, 298 K), δC: 152.74; 134.32; 133.69; 129.23; 129.11; 128.97; 128.43; 125.86; 125.74; 125.67; 125.15; 123.72; 122.78; 121.18; 119.00; 117.02; 115.77; 113.64; 111.88; 111.54; 107.88; 101.49.IR: (KBr, cm-1): v CO: 1557.48 (CO stretching); v NH: 3275.42 (NH urea stretching). LRMS (ES+): m/z: 458.2 $[M-Na]^+$

**Synthesis of 1-(1H-indol-7-yl)-3-(4-nitrophenyl)urea (C)**

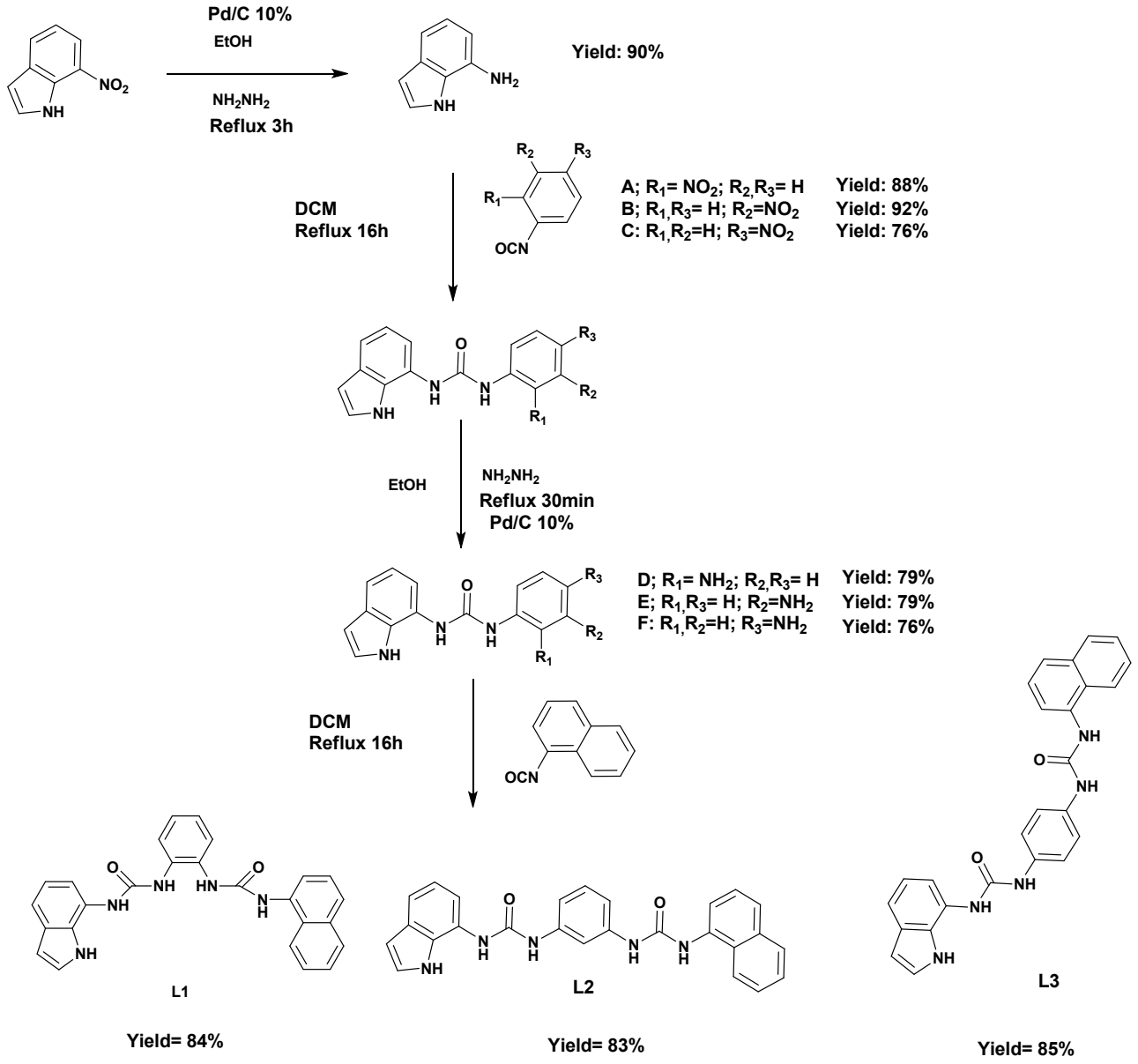
A solution of 1-isocyanate-4-nitrobenzene (0.4300g, 2.618 mmol) in dichloromethane (20ml) was added dropwise to a solution of 7-amino1-indole (0.3707 g, 2.80 mmol) in dichlomethane (10ml). The mixture was refluxed for 12h and then it was filtred to give the desired compound as a red solid. Yield 76% (0.6294 g, 8.028 mmol); M.p.:220°C; $^1$H-NMR (400 MHz,DMSO-$d_6$, 298K): δH: 10.7 (s, 1H); 9.69(s, 1H); 9.09 (s, 1H); 8.2 (d, J= 9.2 Hz, 2H); 7.74 (d, J=9.2, 2H); 7.36 (s, 1H); 7.34-7,32 (m, 1H); 7.13 (d, J=7.4, 1H); 6.96 (t, J=7.7, 1H); 6.45-6.43 (m, 1H). IR: (KBr, cm-1): v CO: 1302.05 (CO stretching); v NH: 3353.83 (NH urea stretching).

**Synthesis of 1-(4-aminophenyl)-3-(1H-indol-7-yl)urea (F)**

Palladium on activate carbon 10% (0.095 g) was added to a solution of **C** (0.6294 g, 2.124 mmol) in ethanol (100ml) and then the mixture was stirred for a few minutes under inert atmosphere. Hydrazine (1,7 ml ) was then added and the resulting mixture was refluxed for 30 minutes. The solution was filtred with CELITE to remove palladium and the filtrate was concentrated in vacuum to give a beige solid, which was washed in dichloromethane to give the desired compound as a white solid. Yield 55% (0.2138g, 1.303 mmol); M.p.: >250°C; $^1$H-NMR (500 MHz,DMSO-d6, 298K), δH: 10.74 (s, 1H, NH2 urea); 8.46 (s, 1H, NH2 urea); 8.36 (s, 1H, NH2 urea); 7.26-7.30 (m,1H); 7.26 (d, J= 7.6 Hz, 1H); 7.12 (d, J= 8.3 Hz, 2H); 7.06 (d, J= 7.5 Hz, 1H); 6.90 (t, J= 7.5 Hz, 1H); 6.53 (d, J= 8 Hz, 2H); 4.75 (s, 2H).IR: (KBr, cm-1): v CO: 1551.57 (CO stretching); v NH: 3292.99 (NH urea stretching).

**Synthesis of L3**

A solution of naphtyl-isocyanate (0.2204 g, 1.303 mmol) in acetonitrile (10 ml) was added dropwise to a solution of **F** (0.3470 g, 1.303 mmol), in acetonitrile (20ml). The mixture was refluxed for 12h and then it was filtred to give the desired compound as a beige solid. Yield 80% (0.2126 g, 4.882 mmol); M.p.: > 250°C; 1H-NMR (500 MHz, DMSO-d6, 298 K δH: 10.67 (s, 1H); 8.92 (s, 1H); 8.70 (s, 1H); 8.64 (s, 1H); 8.43 (s, 1H); 8.14 (d, J= 8.3 Hz, 1H); 8.03 (d, J= 7.4 Hz, 1H); 7.94 (d, J= 8.0 Hz, 1H); 7.64-7.58 (m, 2H); 7.55 (t, J= 7.4 Hz, 1H); 7.49-7.42 (m, 5H); 7.33 (t, J= 2.5 Hz, 1H); 7.30 (d, J=7 .9 Hz, 1H); 7.09 (d, J= 7.3 Hz, 1H); 6.94 (t, J= 7.7 Hz, 1H); 6.43 (t, J= 2.3 Hz, 1H). 13C-NMR (100 MHz, DMSO-d6, 298 K), δC: 212.10; 153.17; 153.00; 134.46; 134.34; 134.12; 133.73; 129.25; 128.89; 128.44; 125.89; 125.67; 125.17; 123.94; 122.74; 121.28; 119.24; 119.04; 118.87; 117.16; 115.64; 113.50; 101. LRMS (ES+): m/z: 458.2 $[M\text{-}Na]^+$




Scheme S1. Reaction scheme adopted for the synthesis of **L1**-**L3**.

**Synthesis of $(L2)(H_2PO_4^-)_2)(TBA)_2$**

A suspension of **L2** in $MeCN/MeNO_2$ was reacted with an excess of $TBAH_2PO_4$ at room temperature under stirring for 1 h. Crystals suitable of single crystal X-ray diffraction analysis were obtained by slow diffusion of $Et_2O$ vapours into the solution of the adduct. Elem. Anal. found (calc. for $C_{58}H_{97.5}N_7O_{10.25}P_2$): C 62.38 (62.26), H 8.70 (8.78), N 8.74 (8.76).

**Synthesis of (L2)($H_2$Ppi)($TBA)_2$**

A suspension of **L2** in MeCN/$MeNO_2$ was reacted with an excess of $TBA_3HPPi$ at room temperature under stirring for 1 h. Crystals suitable of single crystal X-ray diffraction analysis were obtained by slow diffusion of $Et_2O$ vapours into the solution of the adduct. Elem. Anal. found (calc. for $C_{58}H_{95}N_7O_9P_2$): C 63.59 (63.54), H 8.67 (8.73), N 8.81 (8.94).

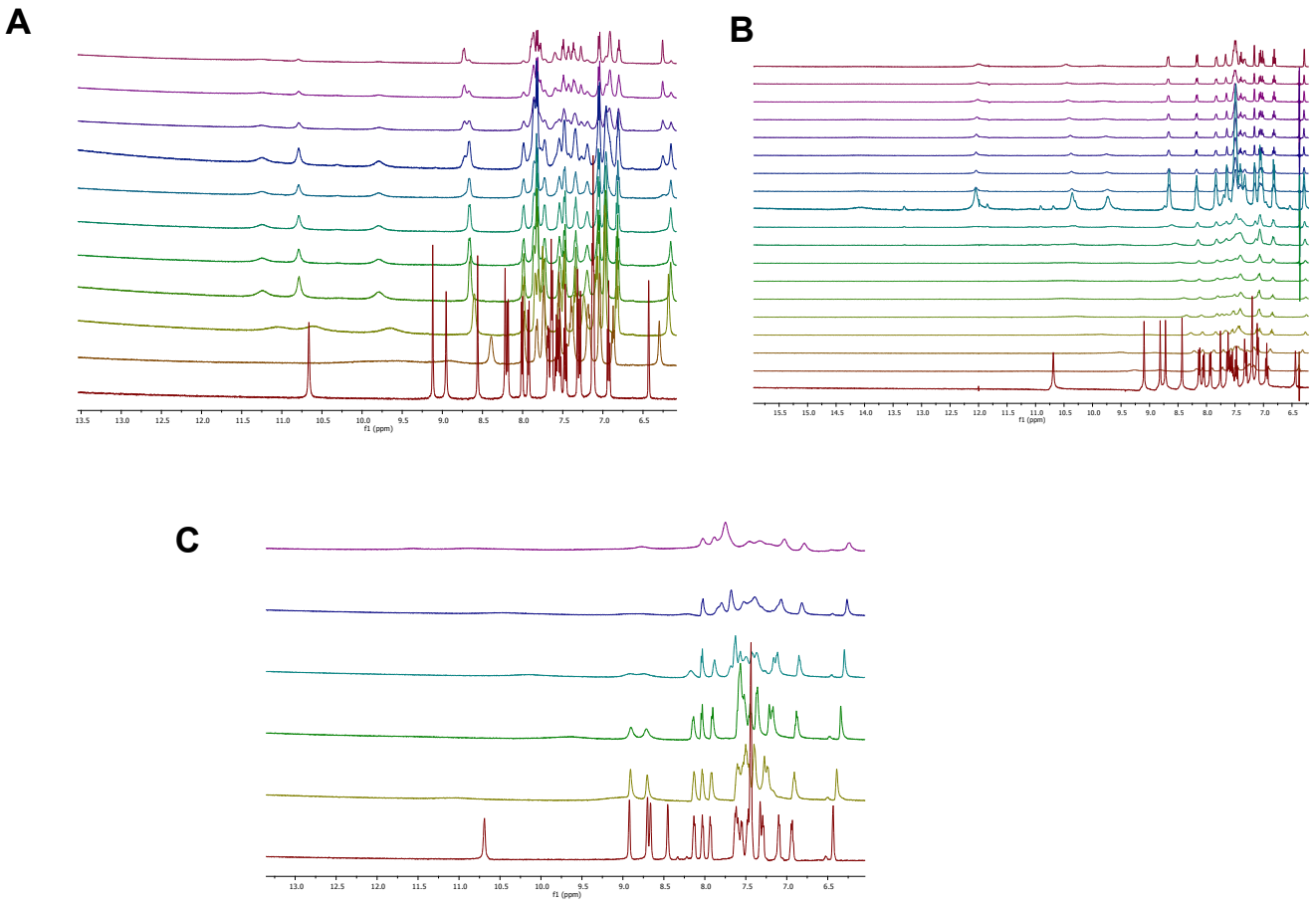



Figure S1 Stack plot of a DMSO-$d_6$ solution **L1** (A), **L2** (B) and **L3** (C) (0.005 M) upon addition of $Hppi^{3-}$ (0.075 M).

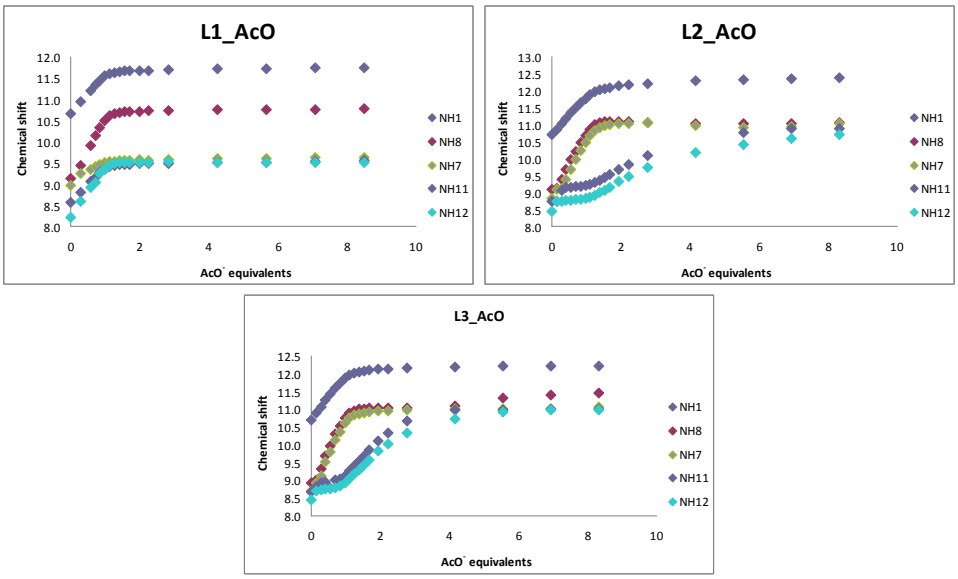



Figure S2. Shift of the NH protons upon addition of $AcO^-$ to a DMSO-$d_6$ solution of **L1**, **L2** , and **L3**.

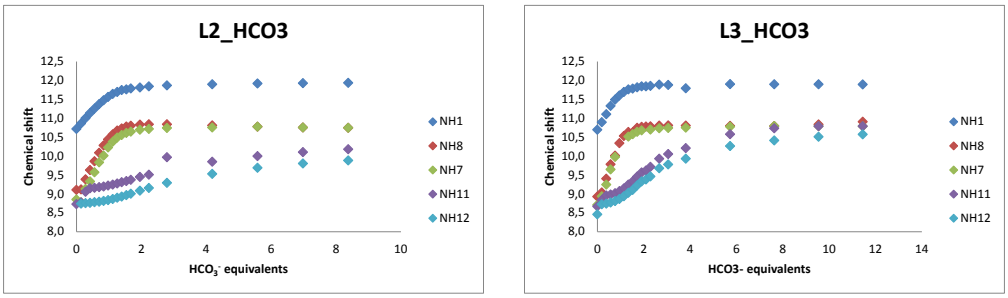



Figure S3. Shift of the NH protons upon addition of $HCO_3^-$ to a DMSO-$d_6$ solution of **L2** and **L3**.

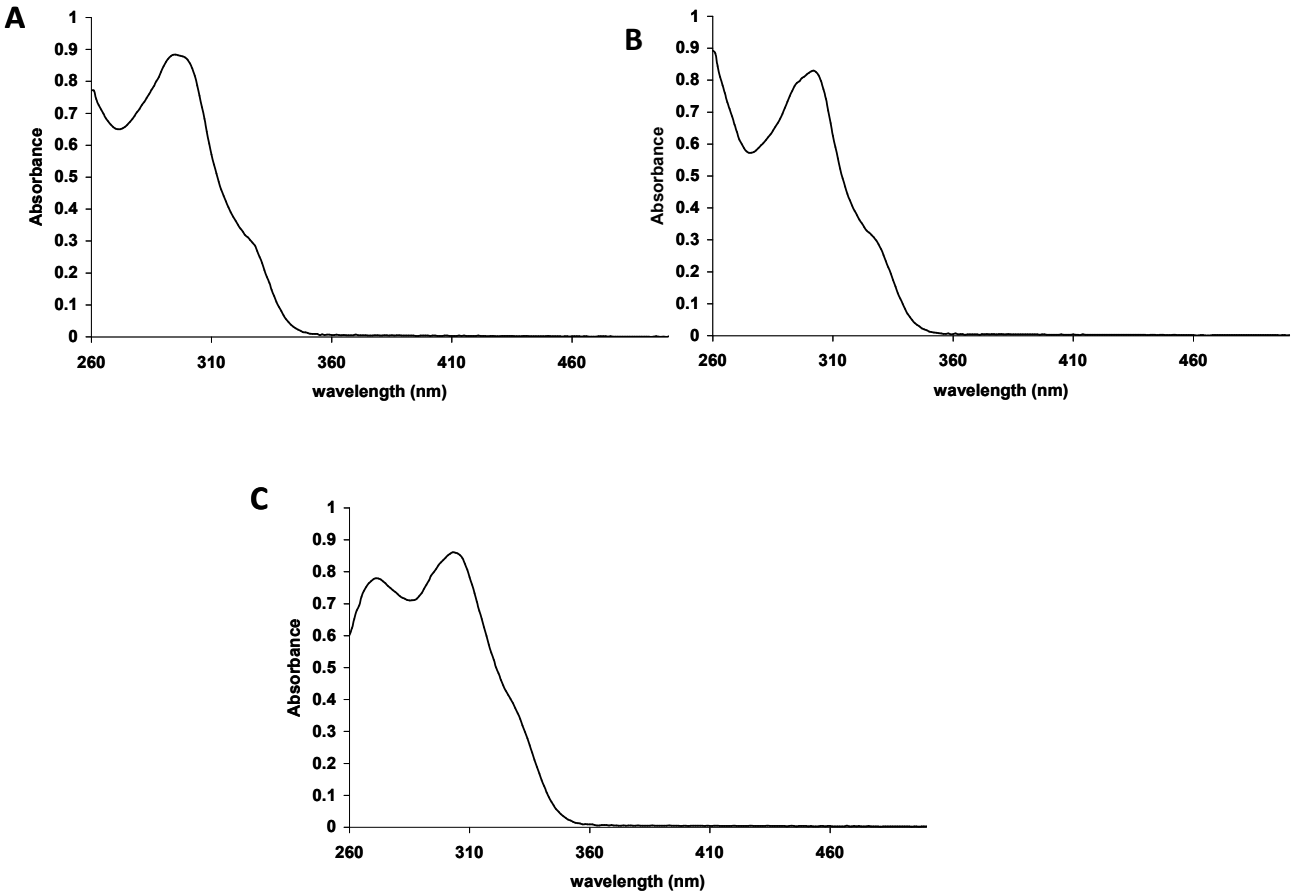



Figure S4. Absorption spectra of **L1** (A), **L2** (B), and **L3** (C) in DMSO (conc. = $3.0 \cdot 10^{-5}$ M)

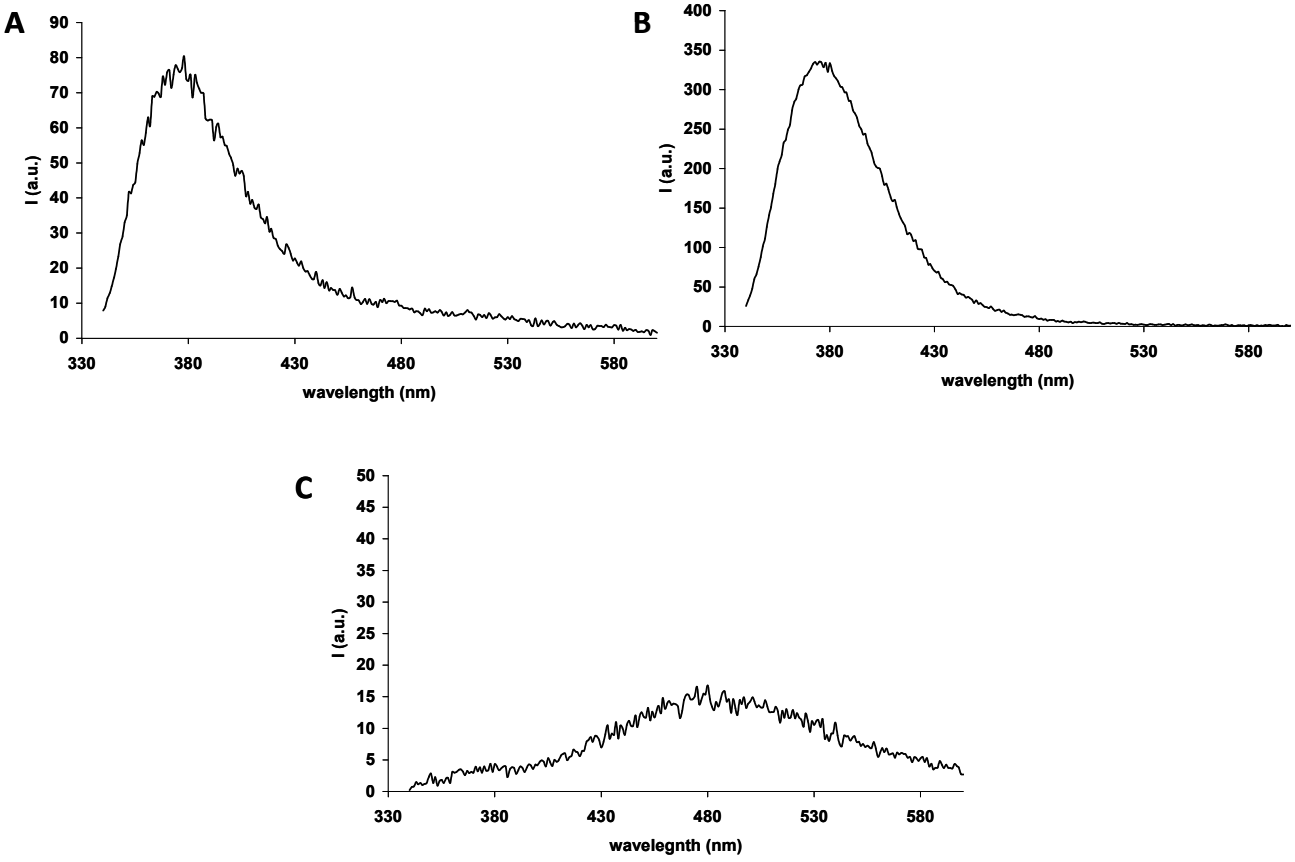


Figure S5. Emission spectra of **L1** (A), **L2** (B), and **L3** (C) in DMSO (conc. = $3.0 \cdot 10^{-5}$ M).

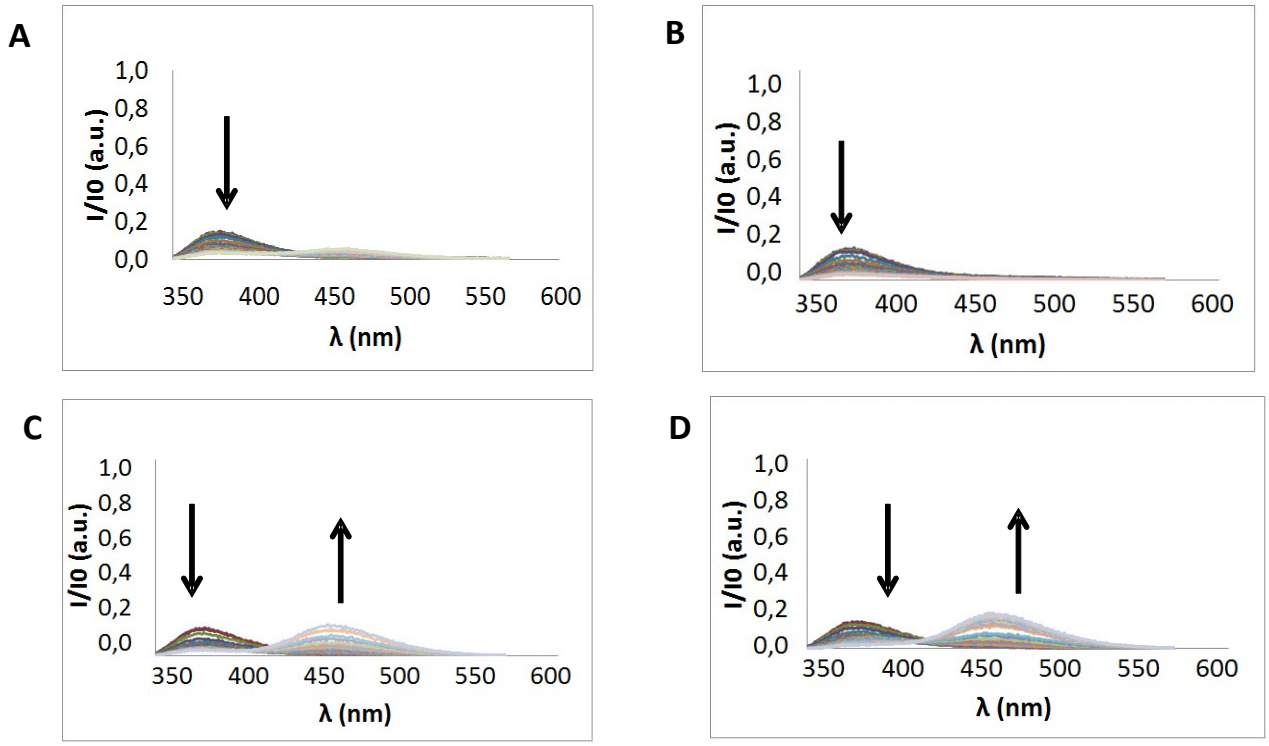



Figure S6 Changes in the fluorescence spectra of **L1** ($3.0 \cdot 10^{-5}$ M) upon addition of increasing amounts of $AcO^-$ (A), $HCO_3^-$ (B), $H_2PO_4^-$ (C), and $F^-$ (D) in DMSO.

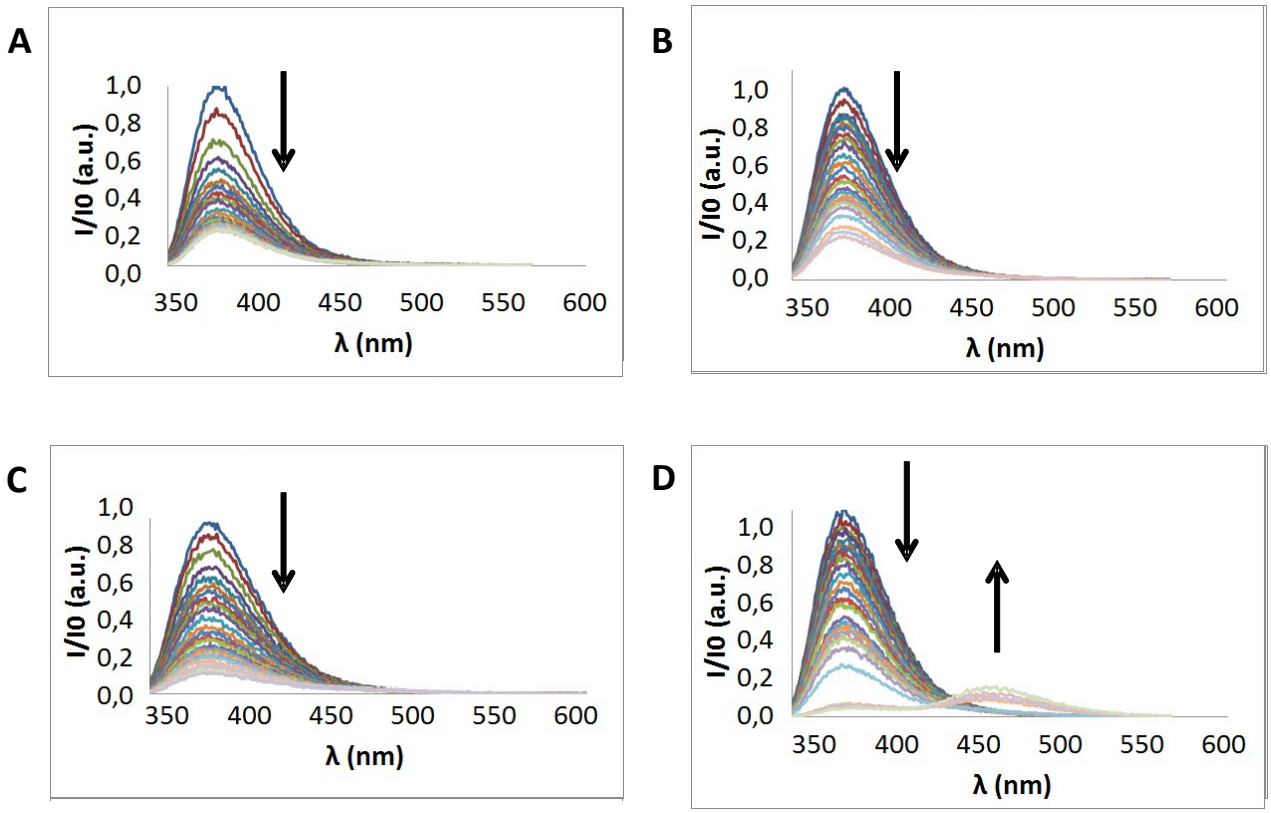



Figure S7 Changes in the fluorescence spectra of **L2** ($3.0 \cdot 10^{-5}$ M) upon addition of increasing amounts of $AcO^-$ (A), $HCO_3^-$ (B), $H_2PO_4^-$ (C), and $F^-$ (D) in DMSO.

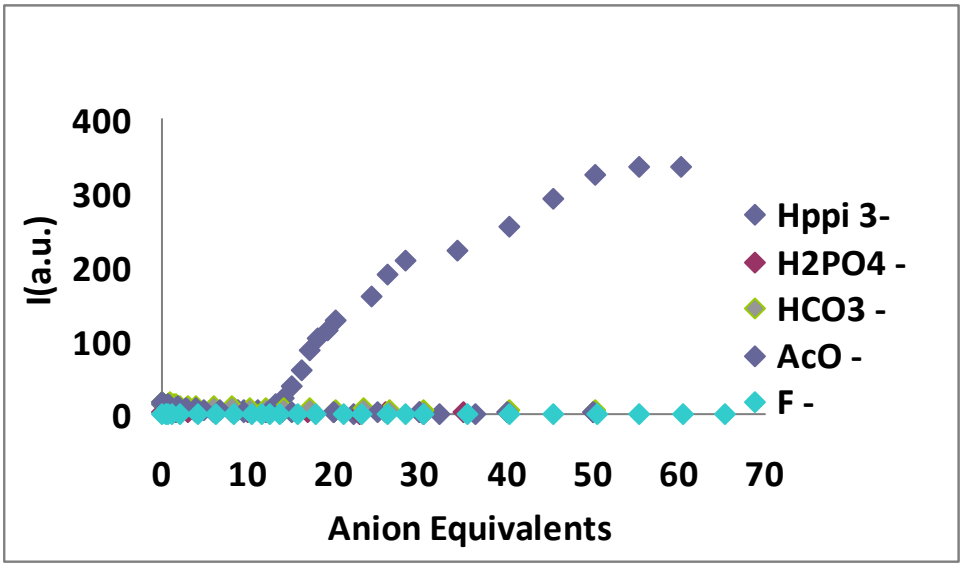



Figure S8 Plot of I vs anion equivalents at 483 nm for **L3**.

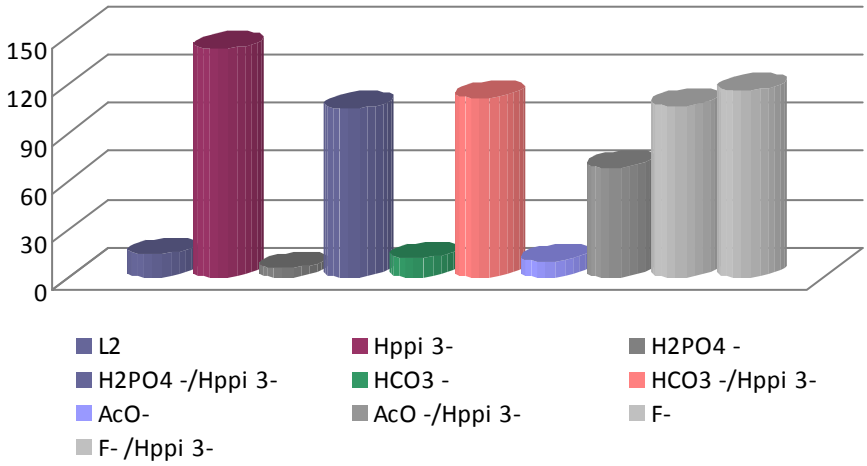



Figure S9 Anion competition study for **L2** [$3.0 \cdot 10^{-5}$ M] in the presence of 20 equivalents of $HPpi^{3-}$ and 50 equivalents of the other anions in DMSO ($\lambda_{em}$ = 476 nm, $\lambda_{exc}$ = 330 nm).

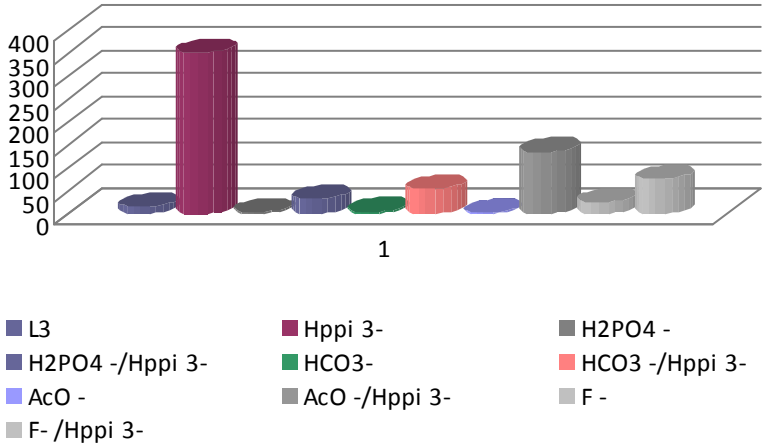



Figure S10 Anion competition study for **L3** [$3.0 \cdot 10^{-5}$ M] in the presence of 20 equivalents of $HPpi^{3-}$ and 50 equivalents of the other anions in DMSO ($\lambda_{em}$ = 483 nm, $\lambda_{exc}$ = 330 nm).

Table S1 Limit of detection (LOD) for HPpi3 with **L1** (both in DMSO and in $H_2O$) and **L2** (in DMSO).

| Receptor | LOD |
|---|---|
| **L1** (DMSO) | $2.0 \cdot 10^{-5}$ M |
| **L1** ($H_2O$) | $1.5 \cdot 10^{-4}$ M |
| **L2**(DMSO) | $1.0 \cdot 10^{-5}$ M |
| **L3** (DMSO) | $2.0 \cdot 10^{-5}$ M |

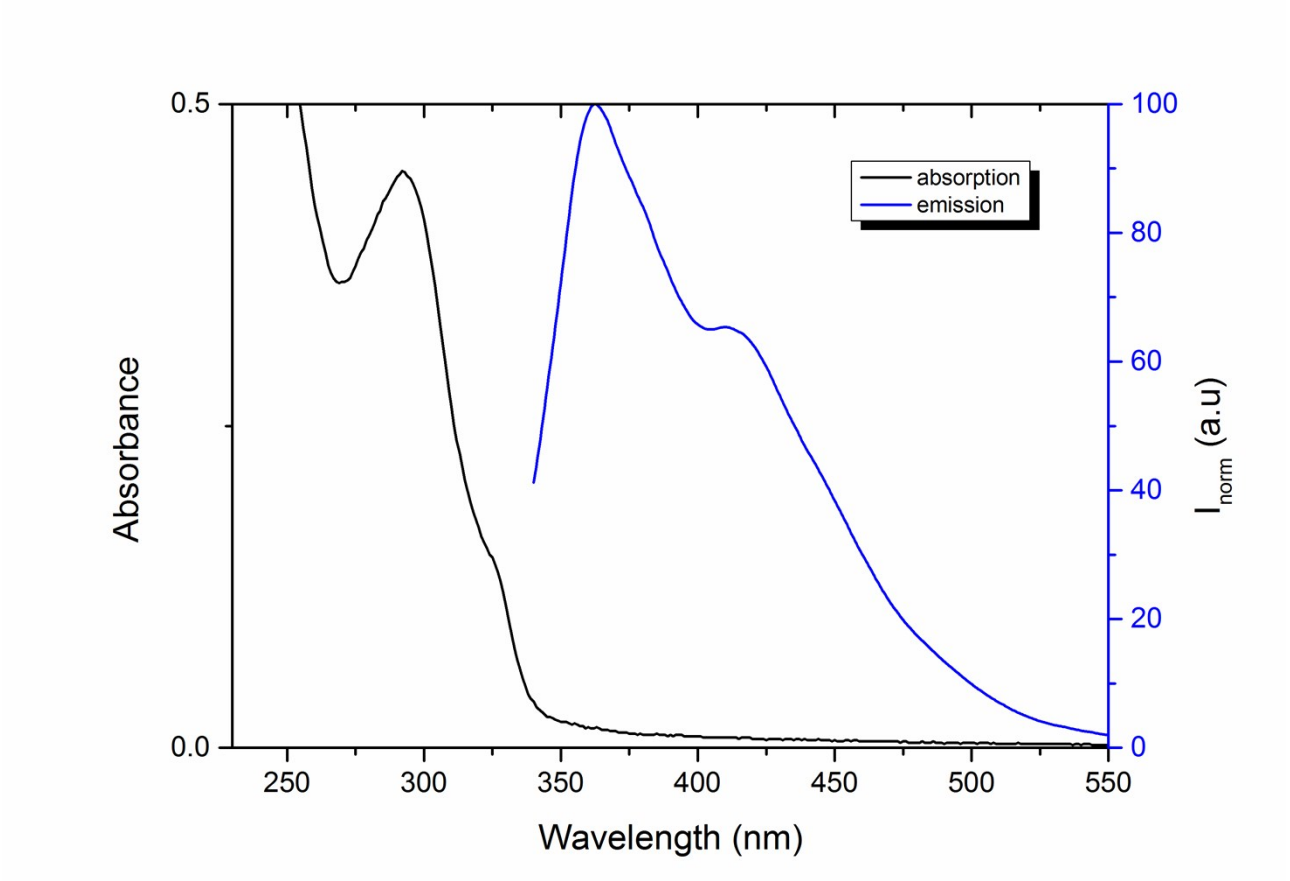



Figure S11. Absorption (black) and emission (blue) spectra of **L1** in CTAB micelles.

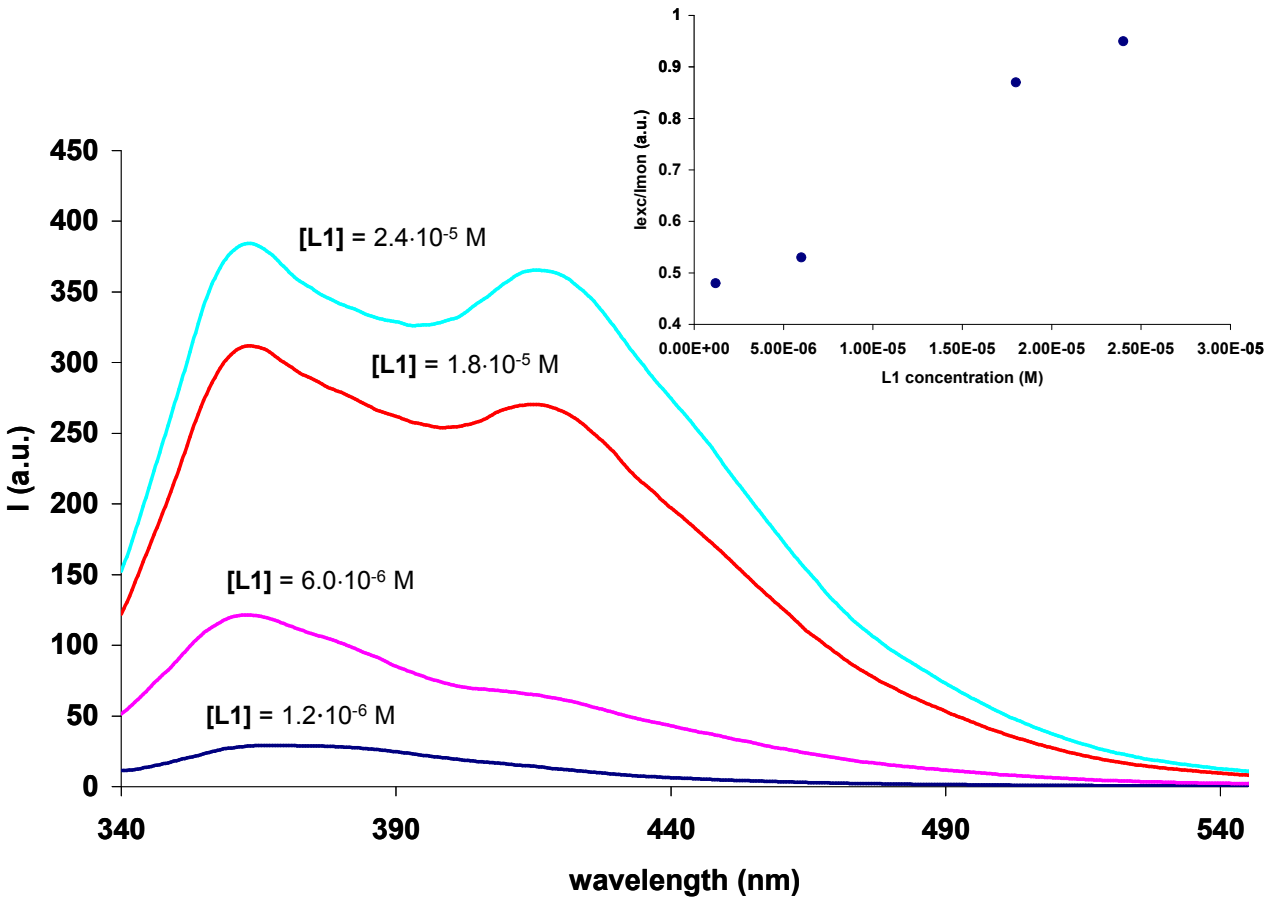



Figure S12 Emission spectra of **L1** in water at pH 7 with 0.01 M CTAB at different concentrations. Inset: Plot of the $I_{excimer}/I_{monomer}$ vs concentration.

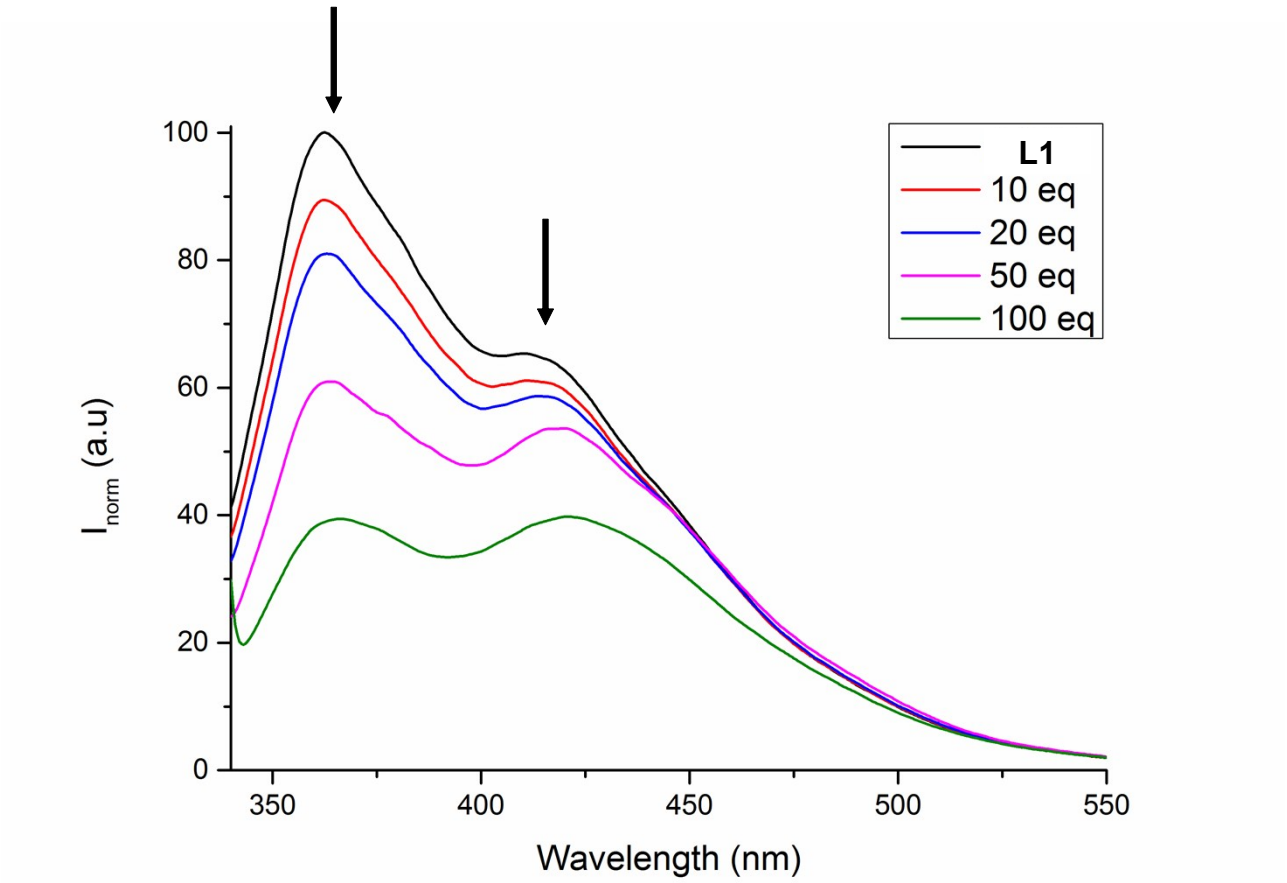



Figure S13 Changes in the emission spectra of **L1** in water at pH 7 with 0.01 M CTAB upon addition of increasing amounts of $HPpi^{3-}$.

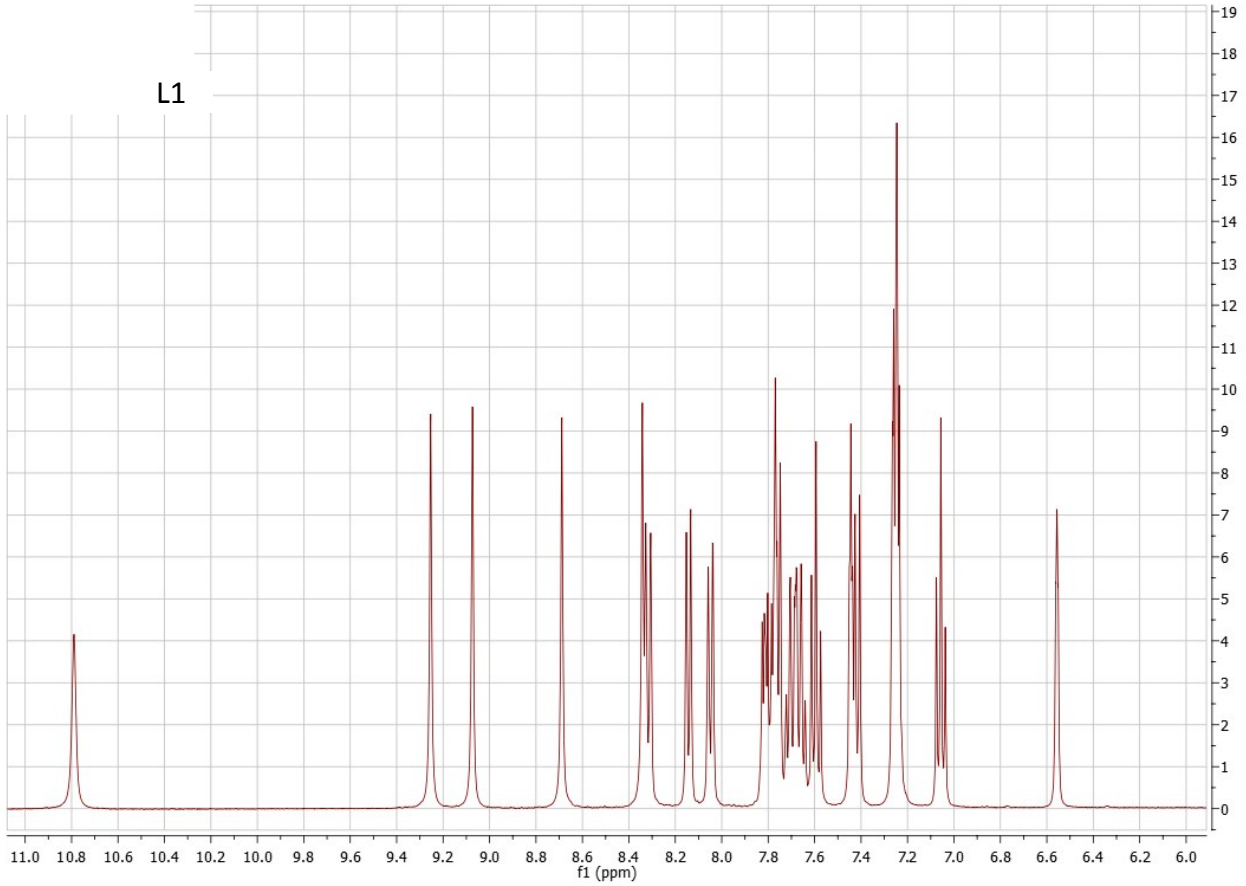



Figure S14 $^{1}$H-NMR spectrum of **L1** in DMSO-$d_6$.

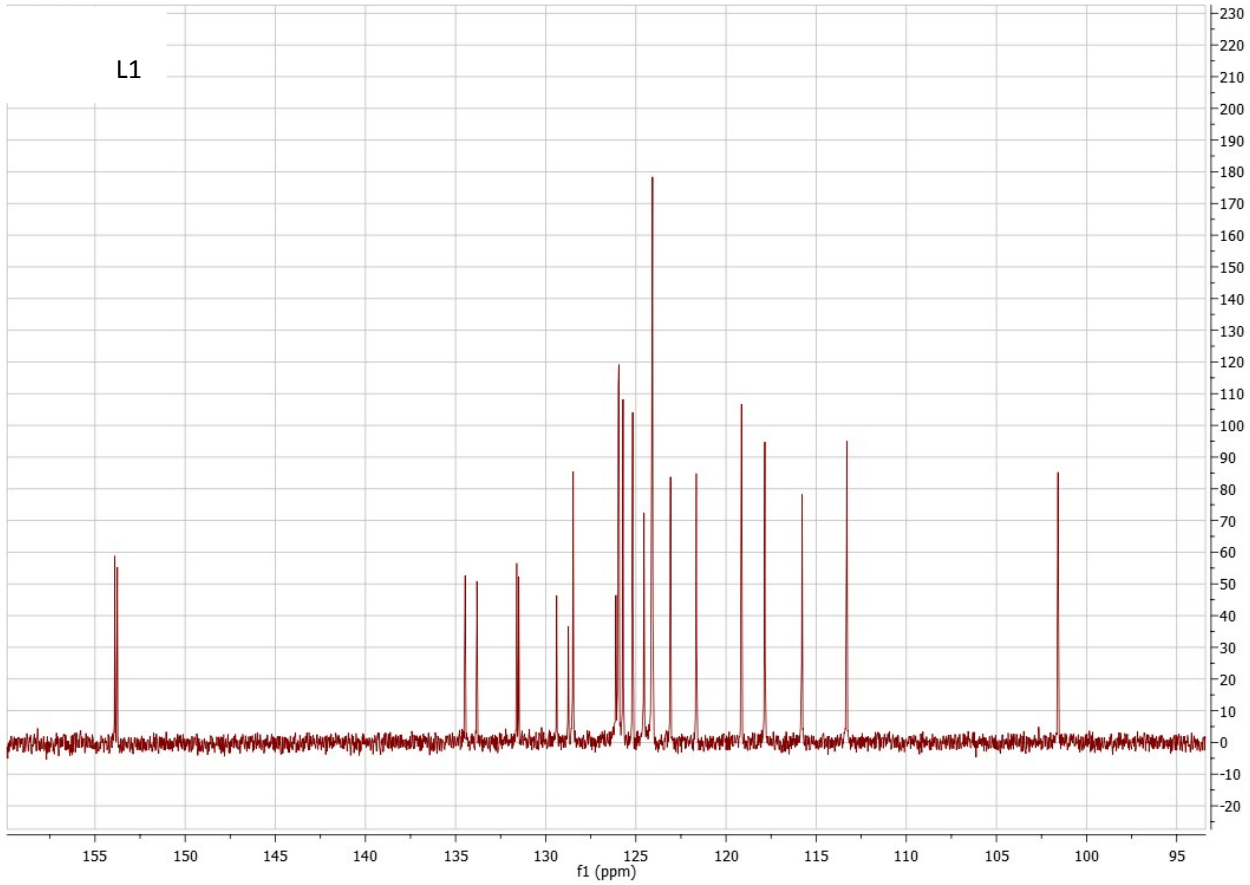



Figure S15 $^{13}$C-NMR spectrum of **L1** in DMSO-$d_6$.

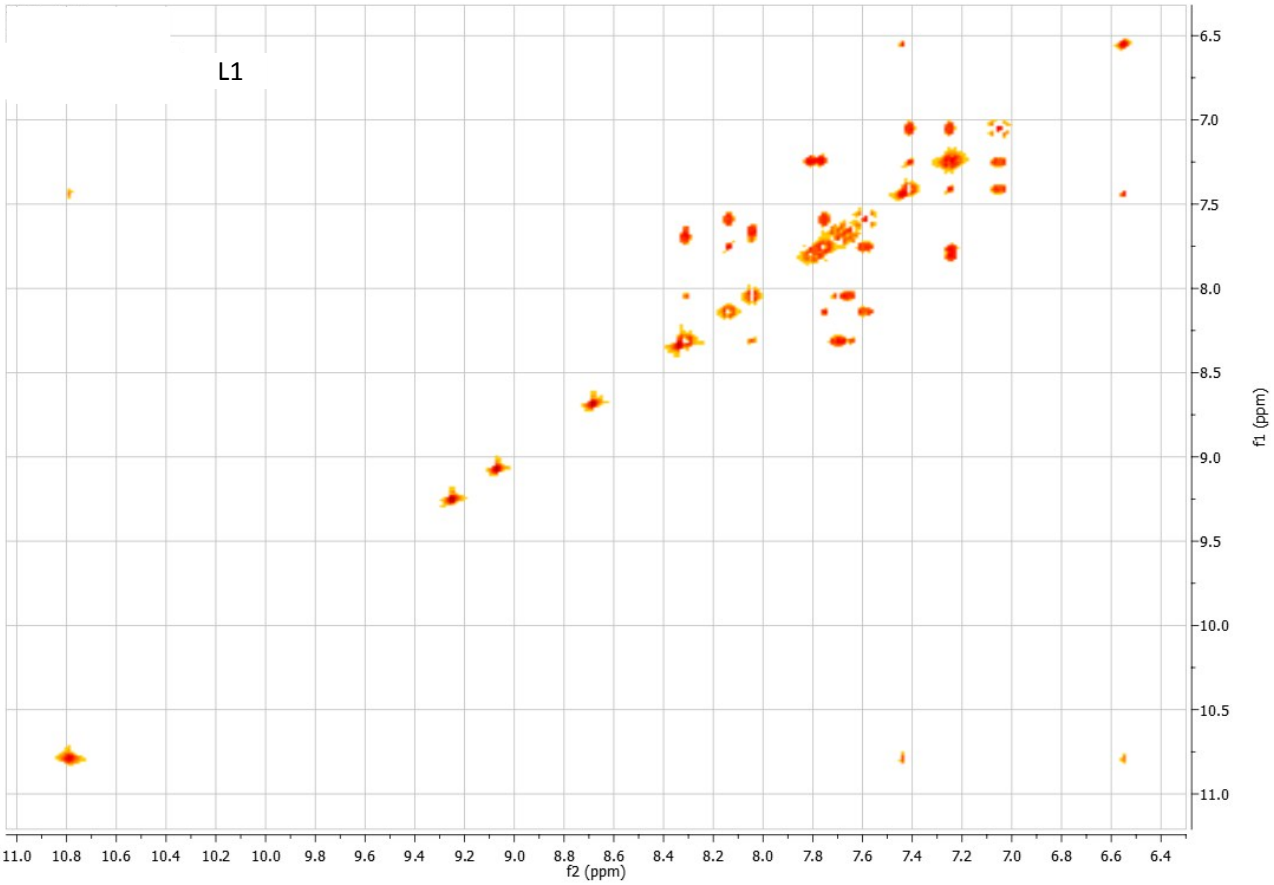



Figure S16 COSY spectrum of **L1** in DMSO-$d_6$.

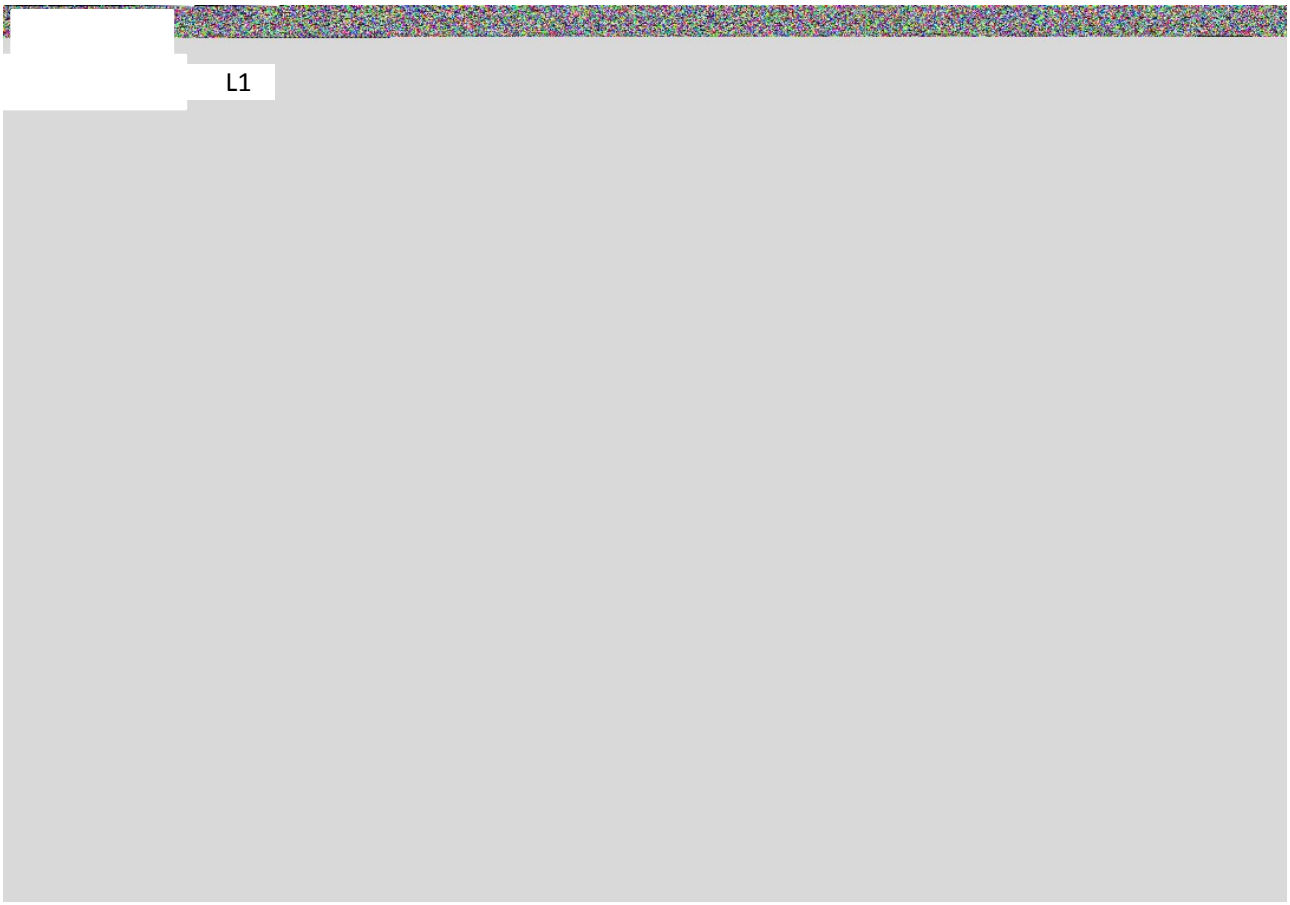


Figure S17 TOCSY spectrum of **L1** in DMSO-$d_6$.

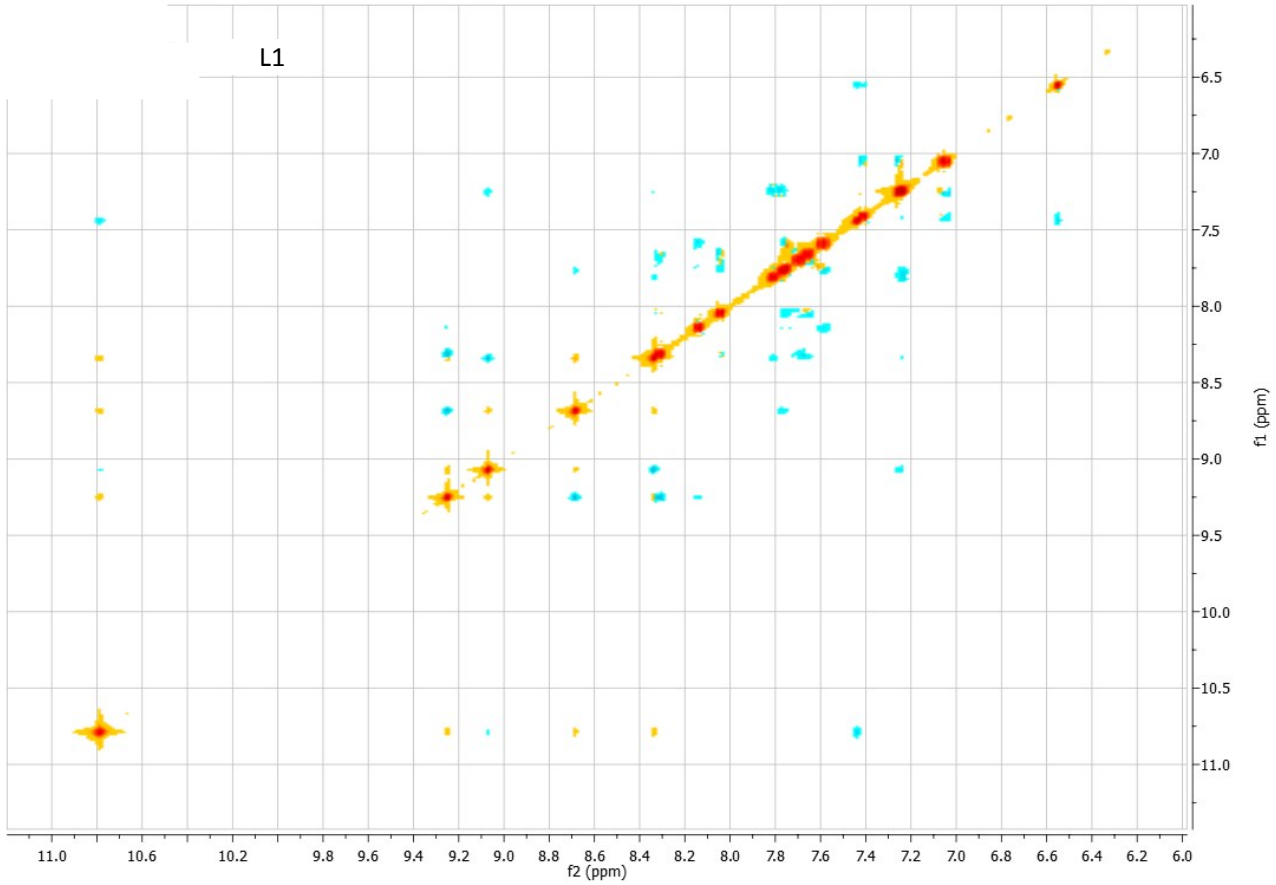



Figure S18 TROESY spectrum of **L1** in DMSO-$d_6$.

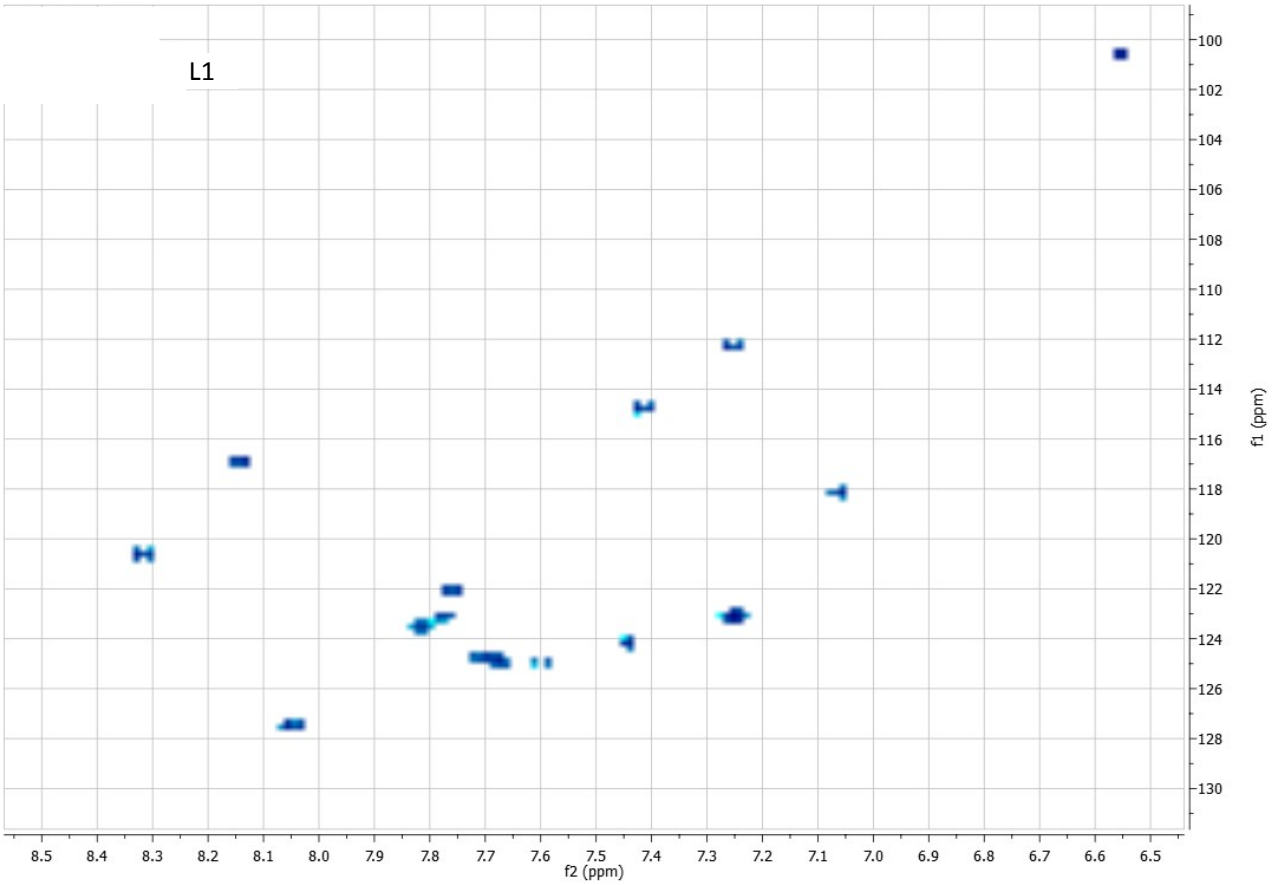



Figure S19 ghsqc spectrum of **L1** in DMSO-$d_6$.

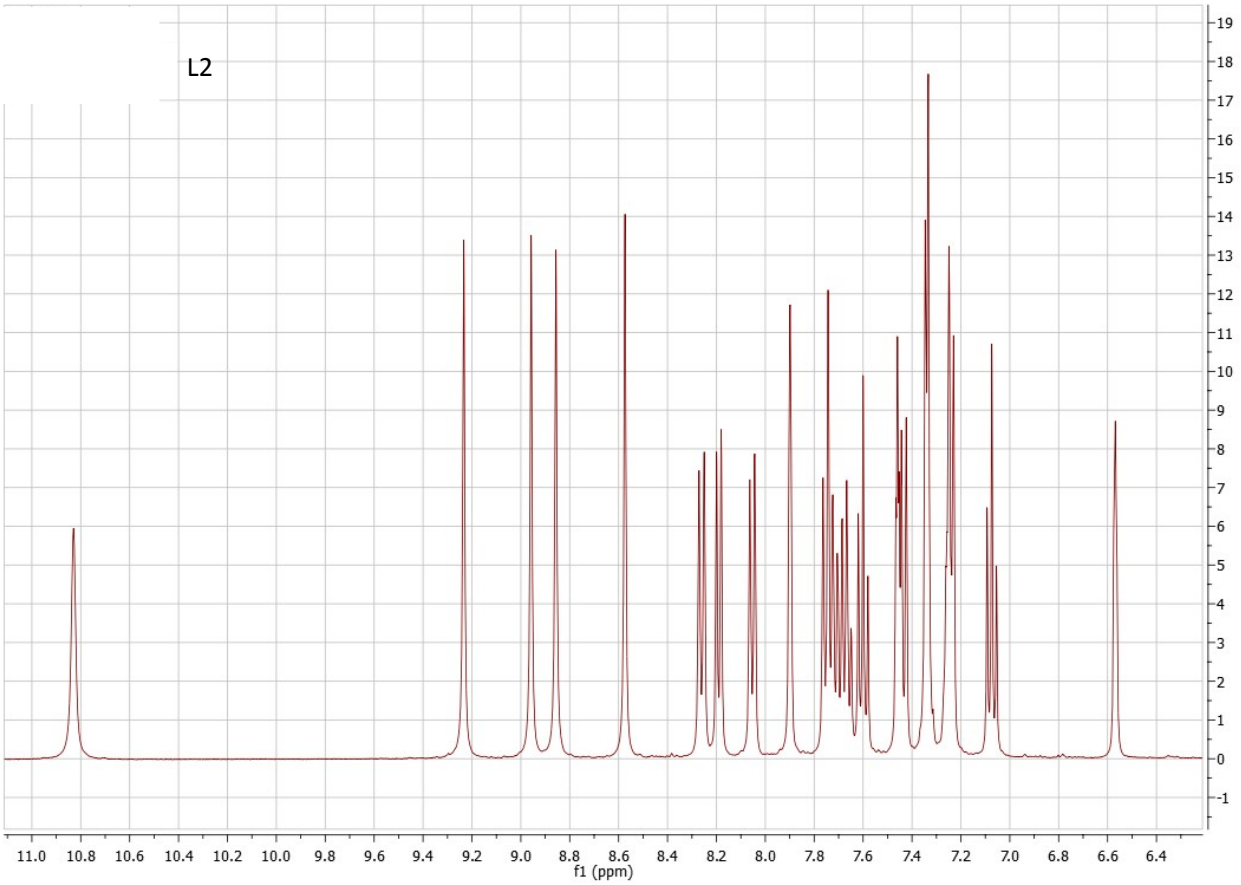



Figure S20 $^{1}$H-NMR spectrum of **L2** in DMSO-$d_6$.

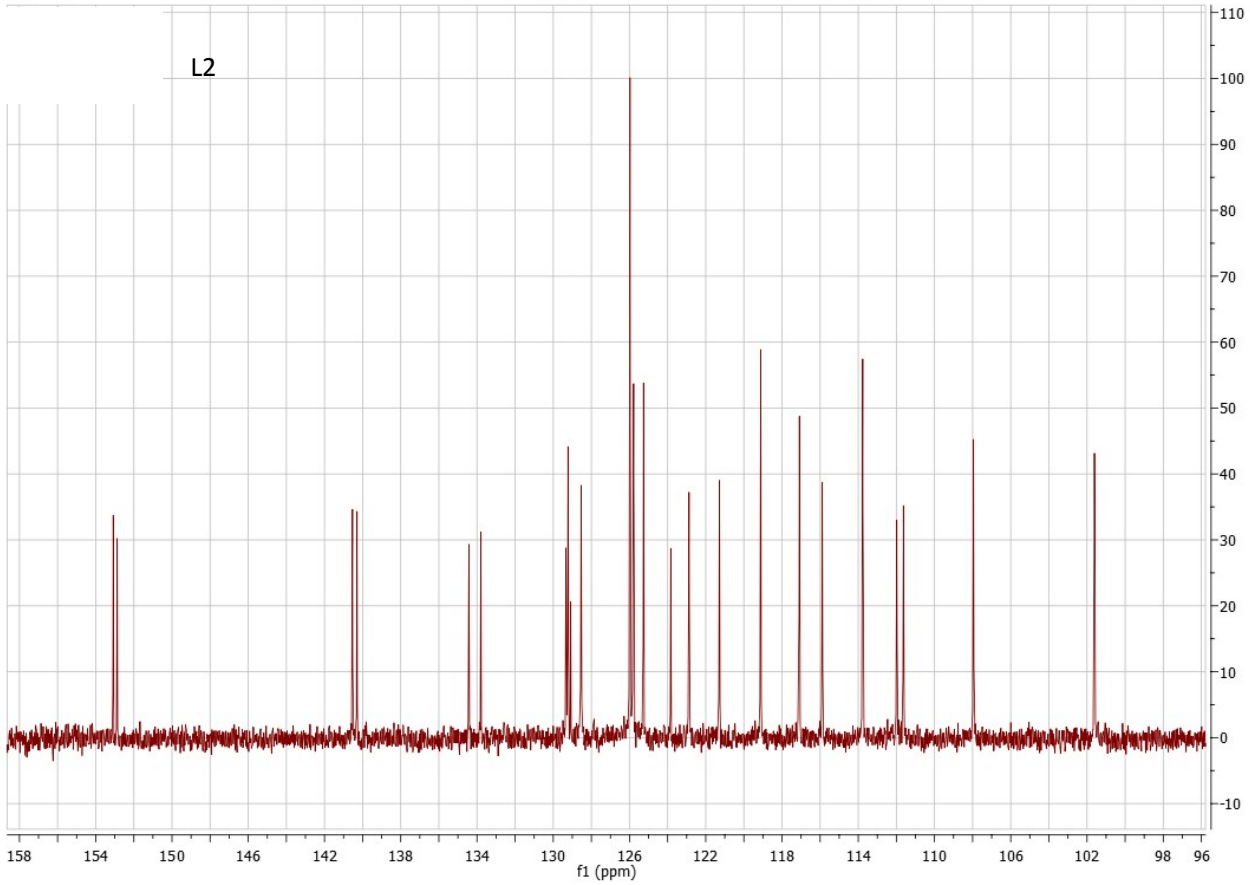



Figure S21 $^{13}$C-NMR spectrum of **L2** in DMSO-$d_6$.

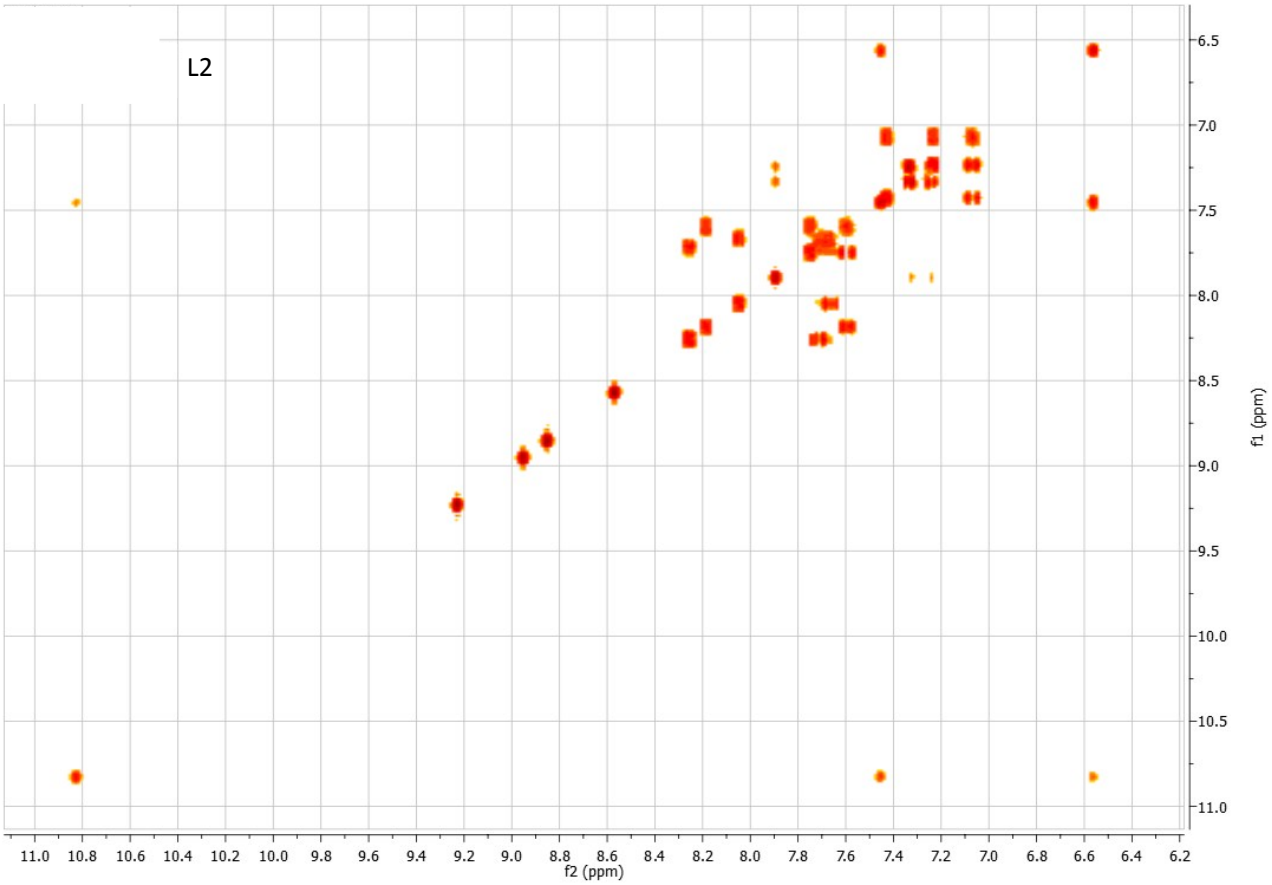



Figure S22 COSY spectrum of **L2** in DMSO-$d_6$.

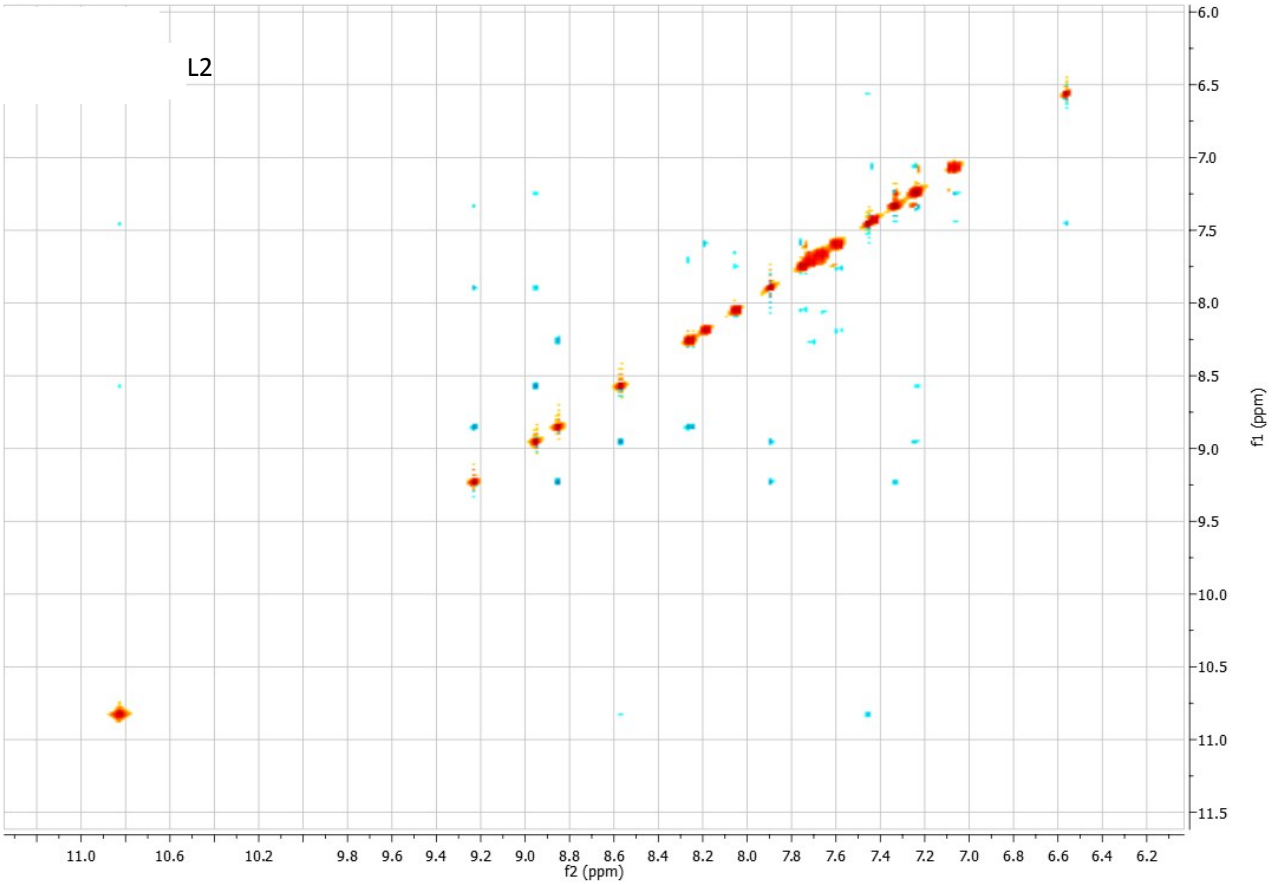



Figure S23 TROESY spectrum of **L2** in DMSO-$d_6$.

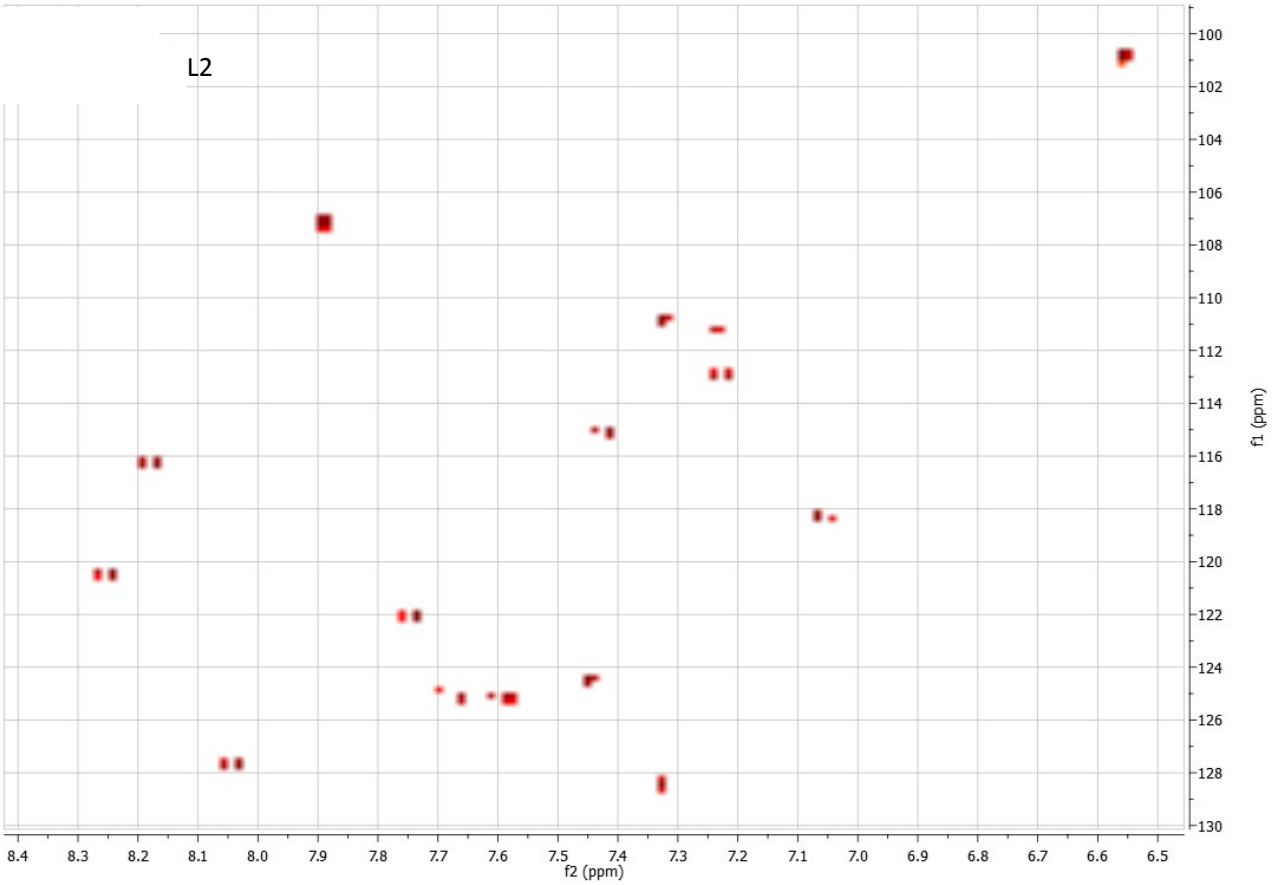



Figure S24 ghsqc spectrum of **L2** in DMSO-$d_6$.

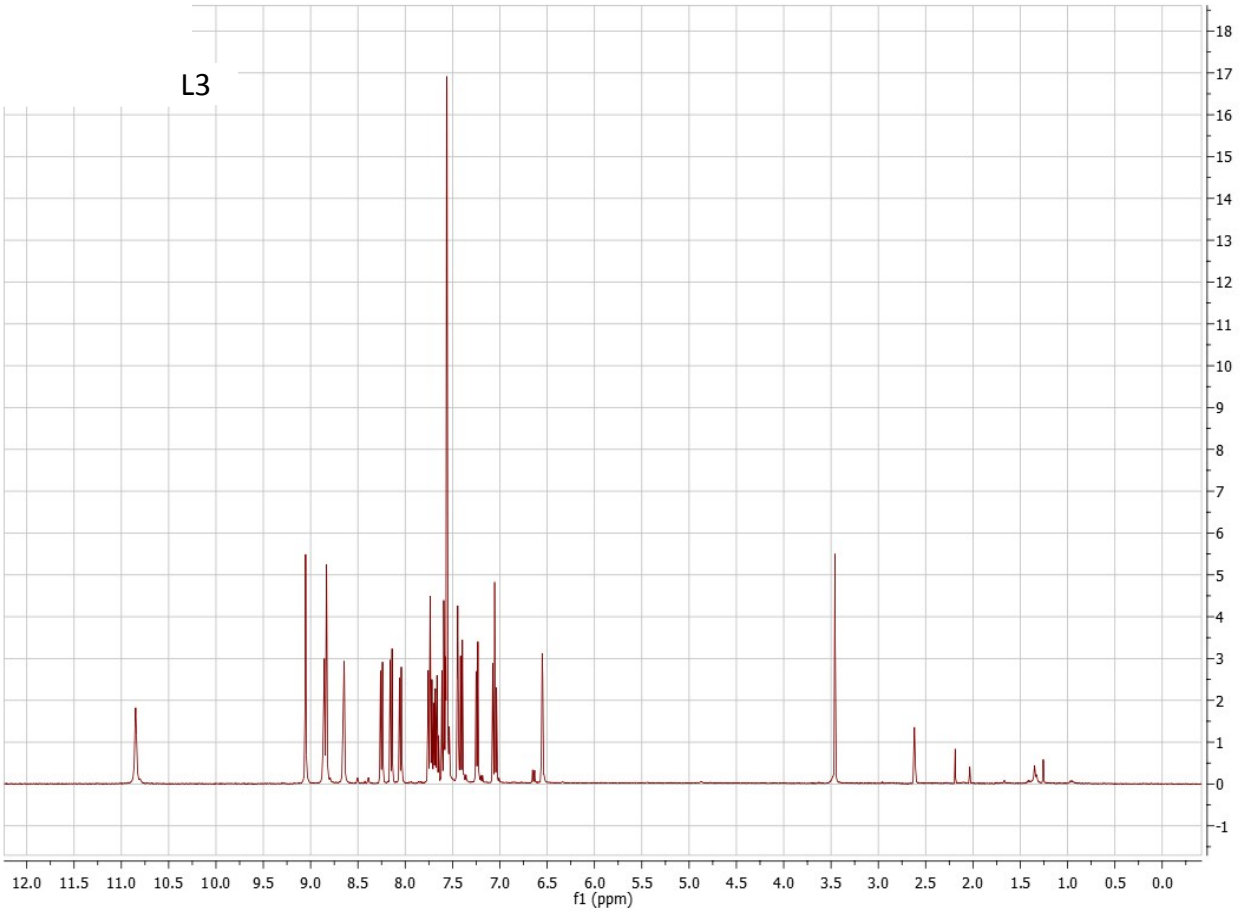



Figure S25 $^{1}$H-NMR spectrum of **L3** in DMSO-$d_6$.

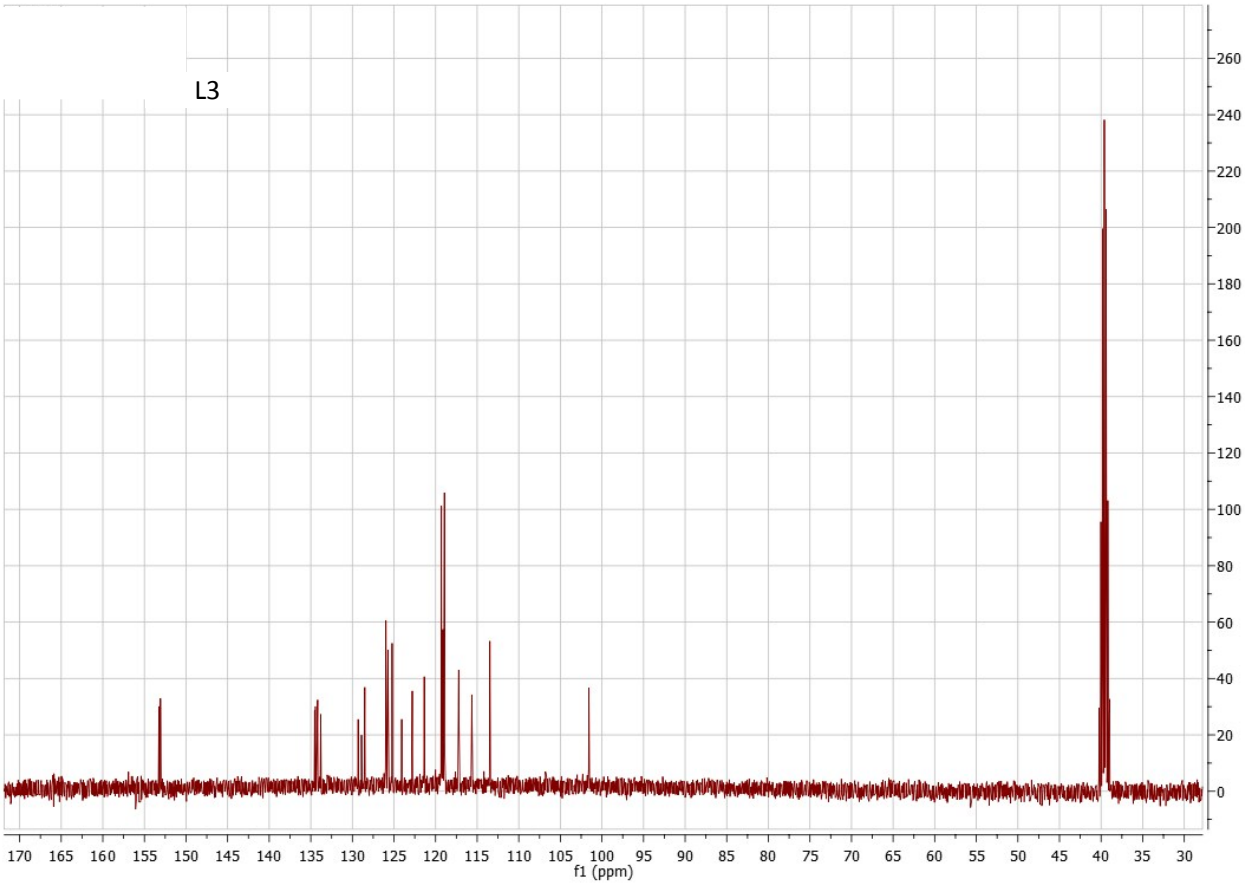



Figure S26 $^{13}$C-NMR spectrum of **L3** in DMSO-$d_6$.

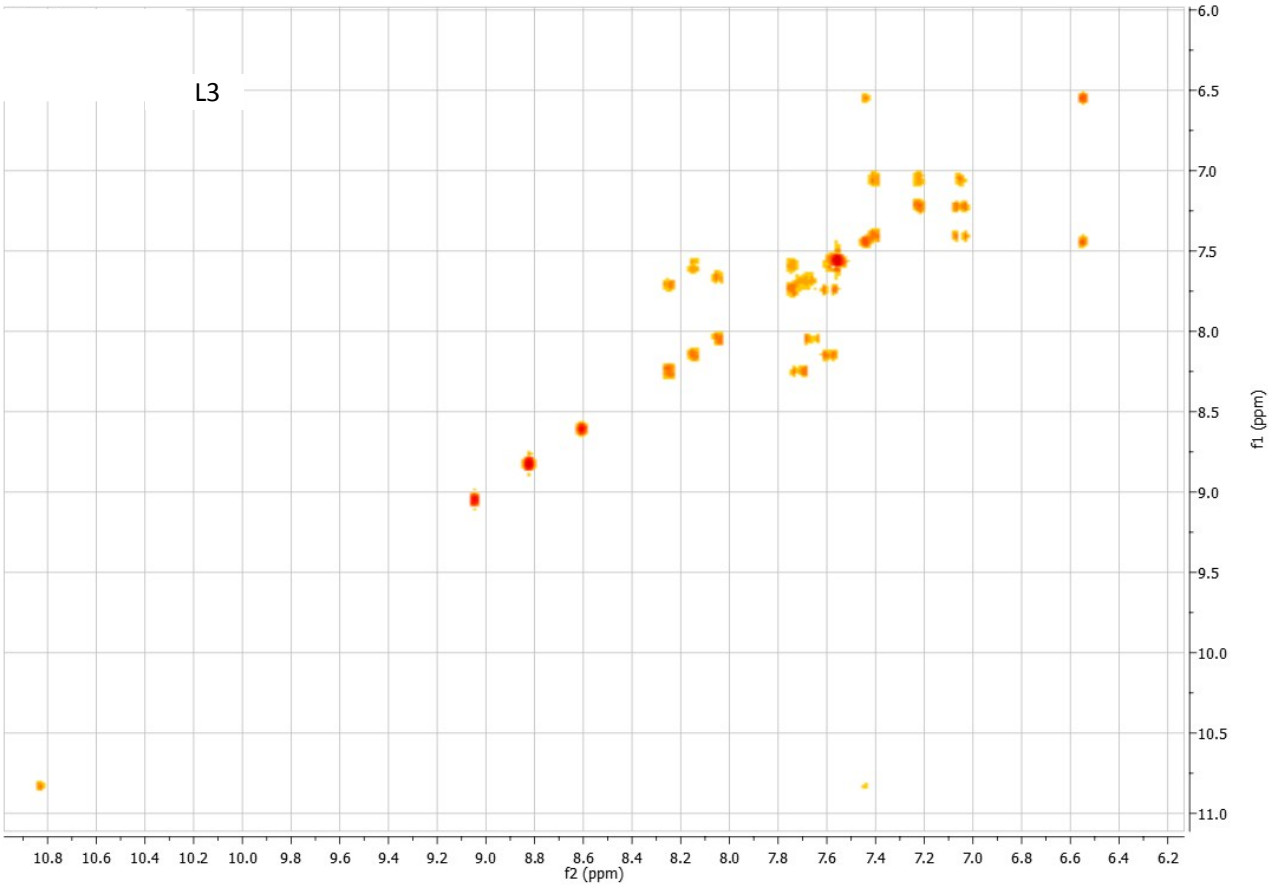



Figure S27 COSY spectrum of **L3** in DMSO-$d_6$.

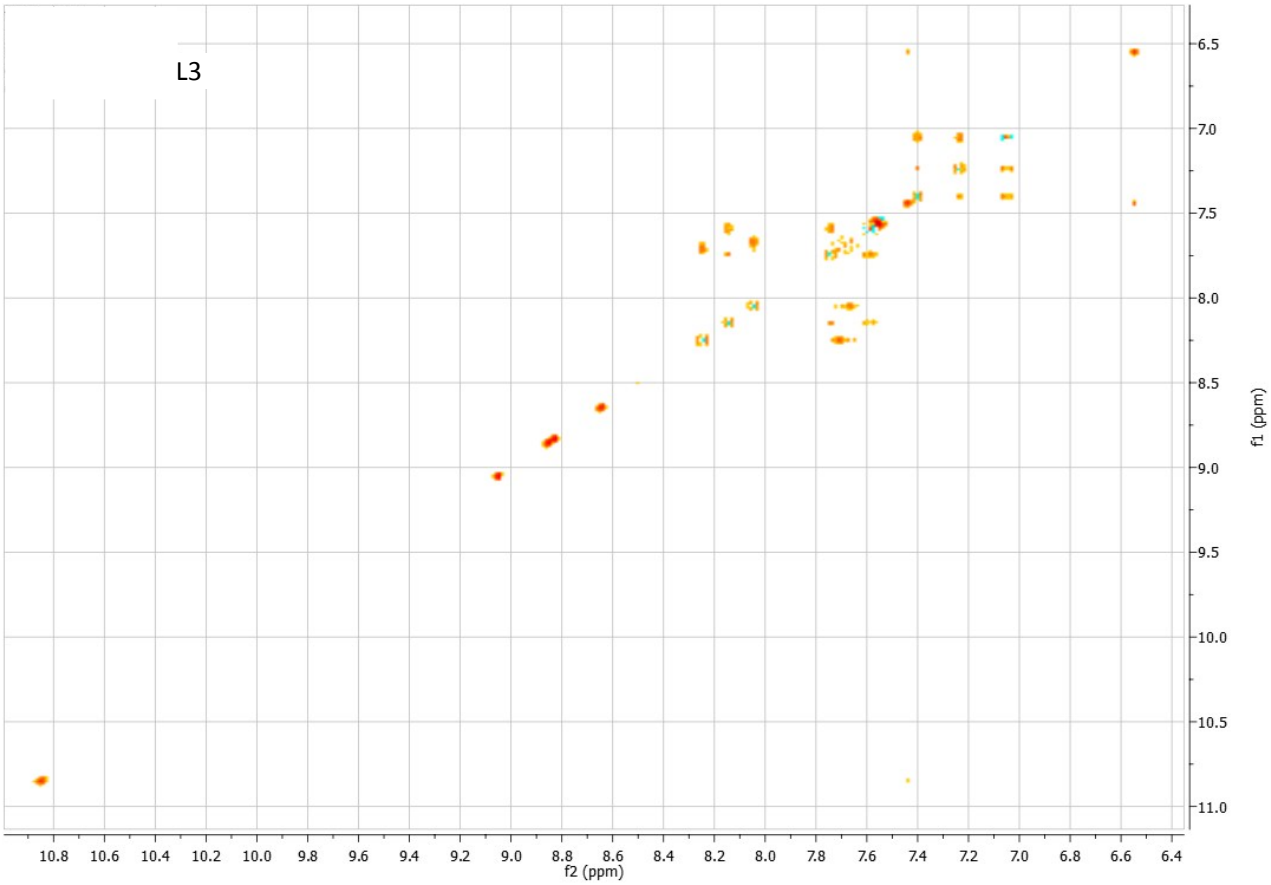



Figure S28 TOCSY spectrum of **L3** in DMSO-$d_6$.

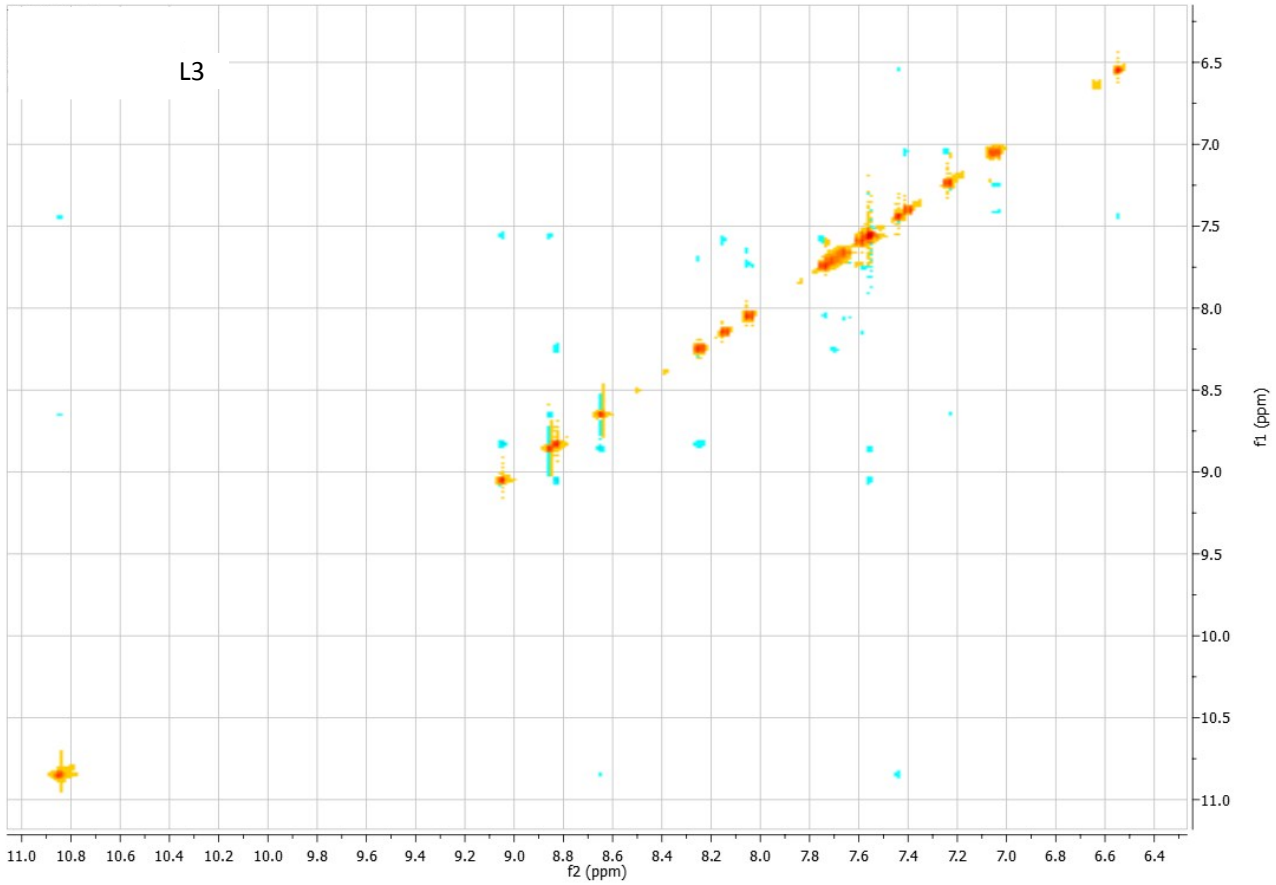



Figure S29 TROESY spectrum of **L3** in DMSO-$d_6$.

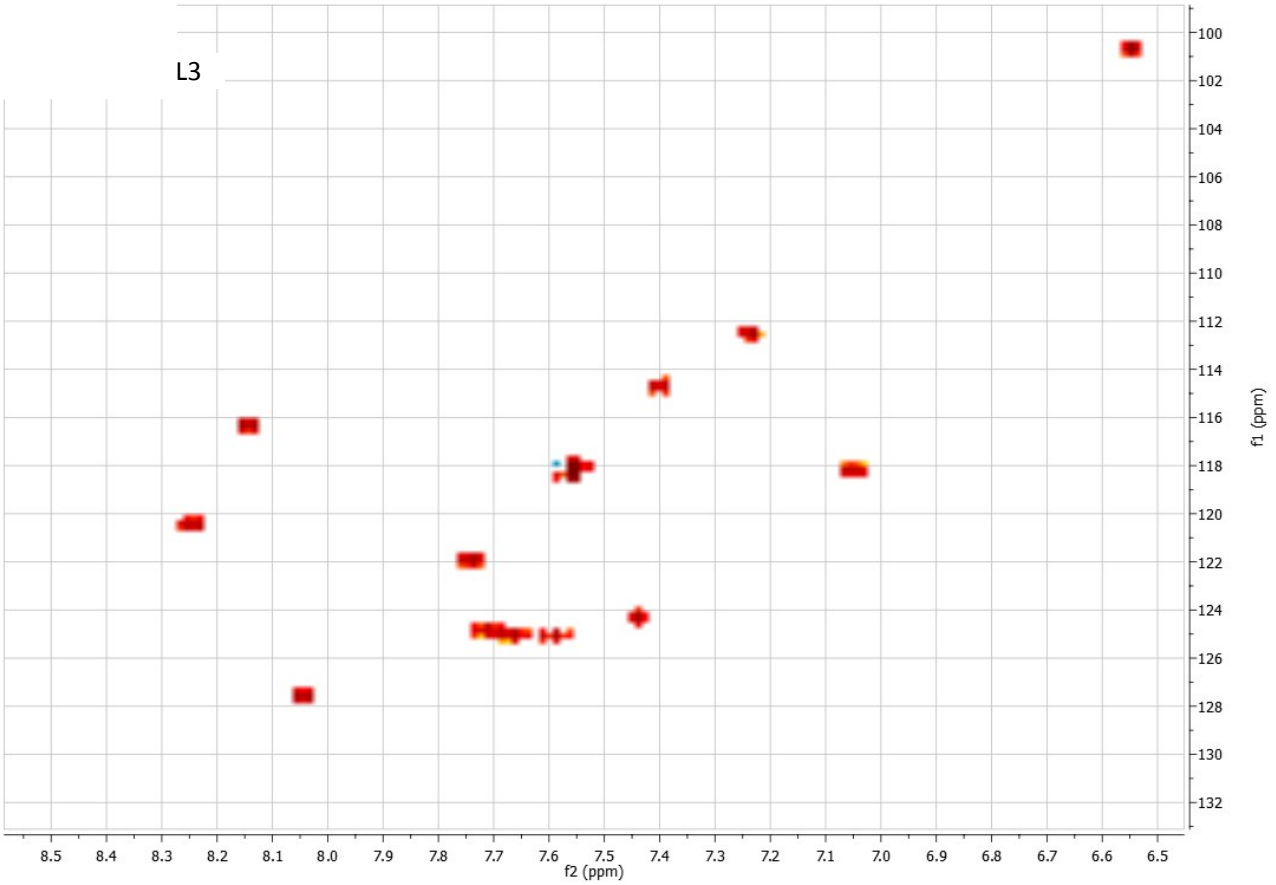
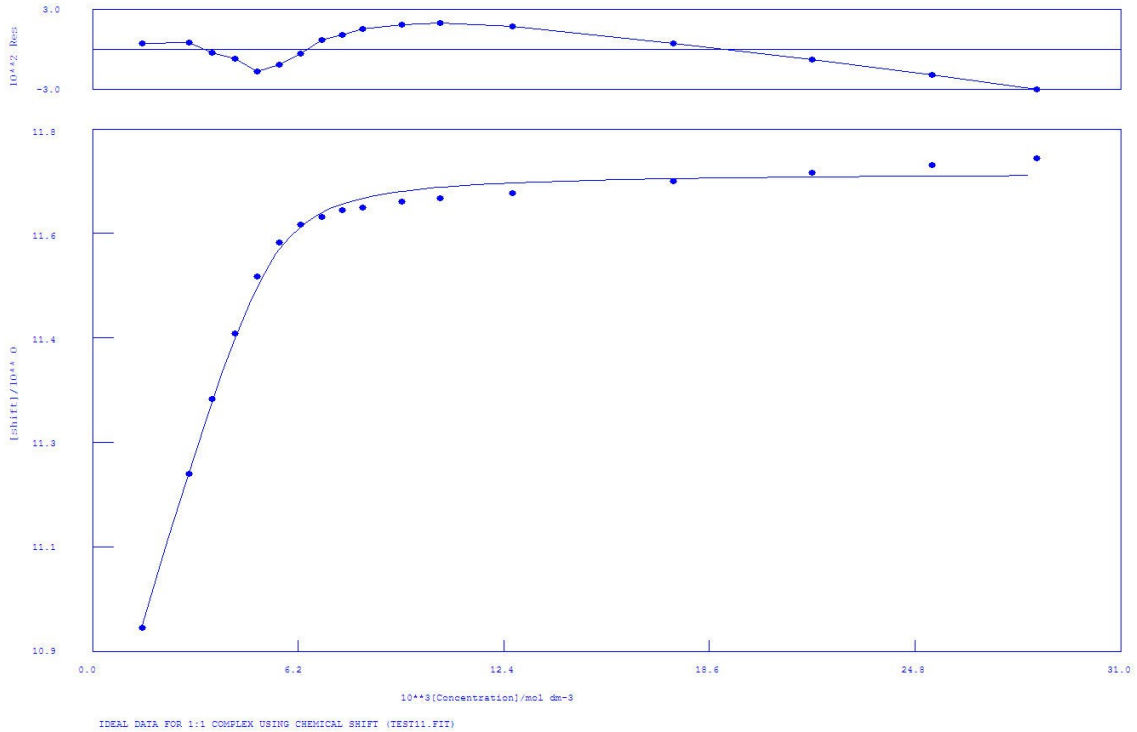



Figure S30 ghsqc spectrum of **L3** in DMSO-$d_6$.



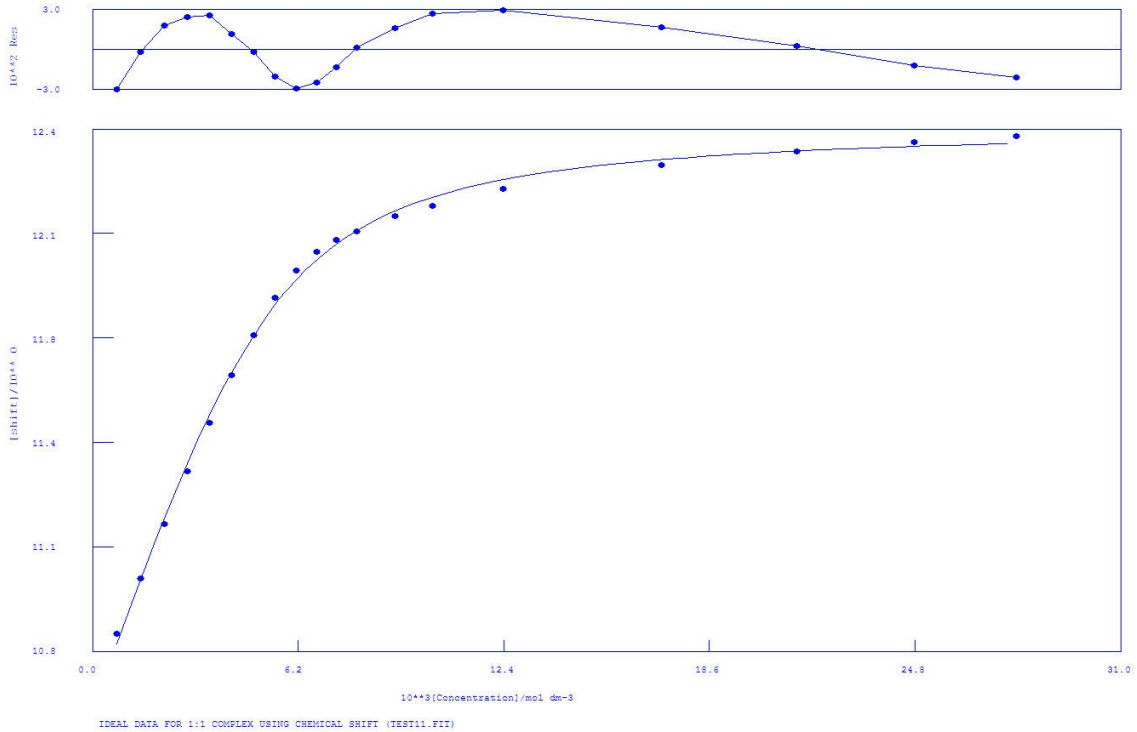

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:20:17   on 05/21/2014

 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  7.43233E+03 2.000E-01 1.010E+03 2.593E+00    K1
   2  1  1.06595E+01 2.000E-01 1.664E-02 1.230E+00   SHIFT M
   3  1  1.17248E+01 1.000E+00 6.791E-03 2.557E+00    SHIFT ML

0RMS ERROR = 1.53E-02  MAX ERROR = 3.03E-02 AT OBS.NO. 17
 RESIDUALS SQUARED = 3.29E-03
 RFACTOR =     0.1202 PERCENT
```

Figure S31 $^{1}$H-NMR titration of **L1** with TBAAcO in DMSO-$d_6$.



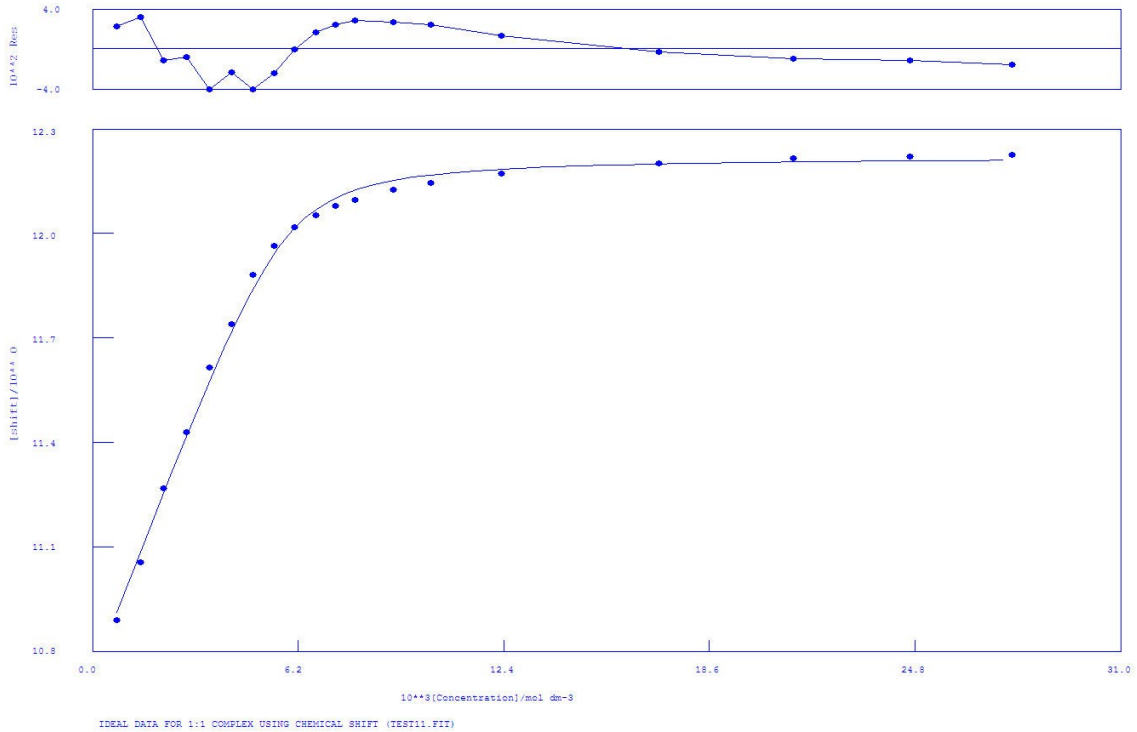

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:00:08   on 07/18/2014

 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  1.25223E+03 2.000E-01 3.870E+01 1.622E+00    K1
   2  1  1.06110E+01 2.000E-01 1.518E-02 1.521E+00   SHIFT M
   3  1  1.24161E+01 1.000E+00 8.525E-03 1.606E+00    SHIFT ML

0RMS ERROR = 2.15E-02  MAX ERROR = 3.04E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 7.40E-03
 RFACTOR =     0.1664 PERCENT
```

Figure S32 $^{1}$H-NMR titration of **L2** with TBAAcO in DMSO-$d_6$.



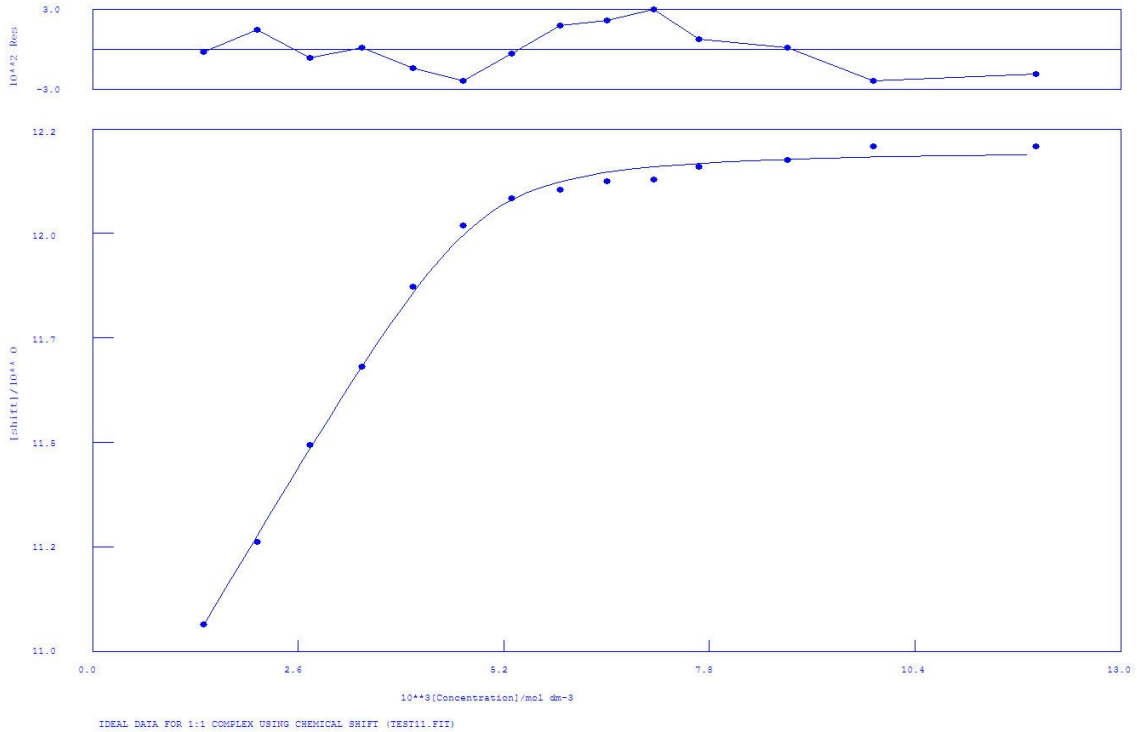

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:30:12   on 07/18/2014

 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  5.82968E+03 2.000E-01 8.591E+02 3.190E+00    K1
   2  1  1.07293E+01 2.000E-01 1.716E-02 1.217E+00   SHIFT M
   3  1  1.22204E+01 1.000E+00 1.223E-02 3.053E+00    SHIFT ML

0RMS ERROR = 2.46E-02  MAX ERROR = 4.02E-02 AT OBS.NO.  5
 RESIDUALS SQUARED = 9.68E-03
 RFACTOR =     0.1902 PERCENT
```

Figure S33 $^{1}$H-NMR titration of **L3** with TBAAcO in DMSO-$d_6$.



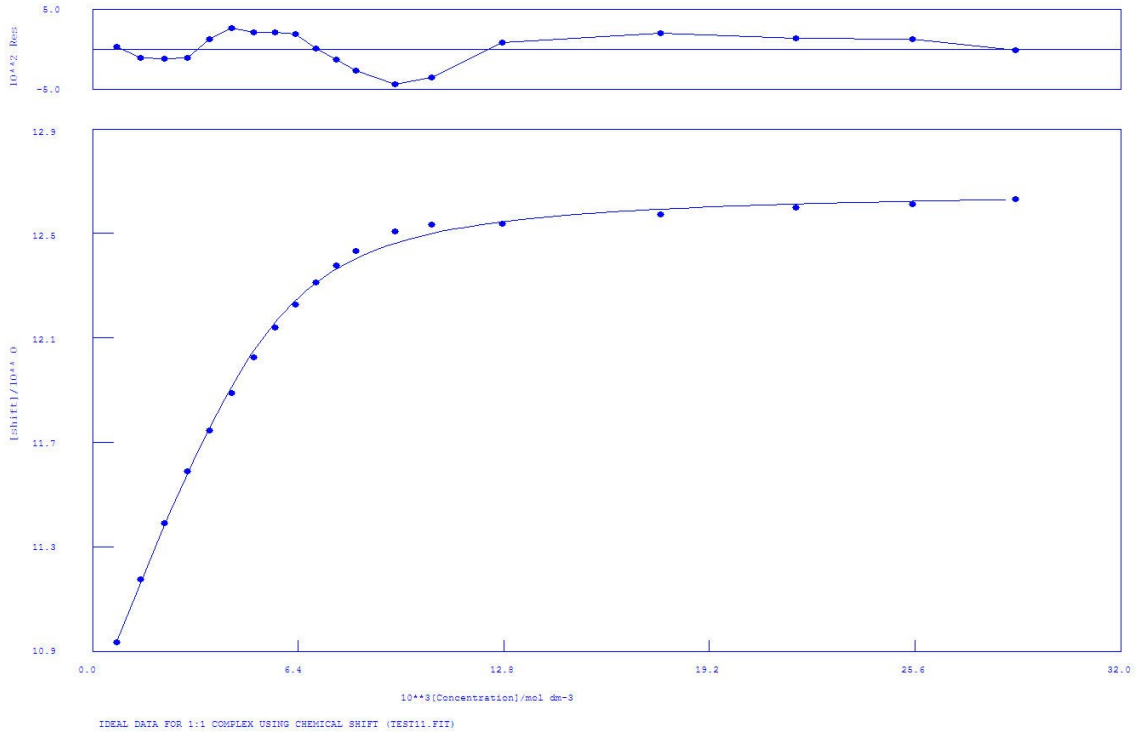

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:04:38   on 05/22/2014

 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  1.44560E+04 2.000E-01 2.735E+03 4.069E+00    K1
   2  1  1.06252E+01 2.000E-01 1.821E-02 1.225E+00   SHIFT M
   3  1  1.21546E+01 1.000E+00 1.174E-02 4.070E+00    SHIFT ML

0RMS ERROR = 1.83E-02  MAX ERROR = 2.96E-02 AT OBS.NO. 10
 RESIDUALS SQUARED = 3.68E-03
 RFACTOR =     0.1366 PERCENT
```

Figure S34 $^{1}$H-NMR titration of **L1** with $TBAH_2PO_4$ in DMSO-$d_6$.



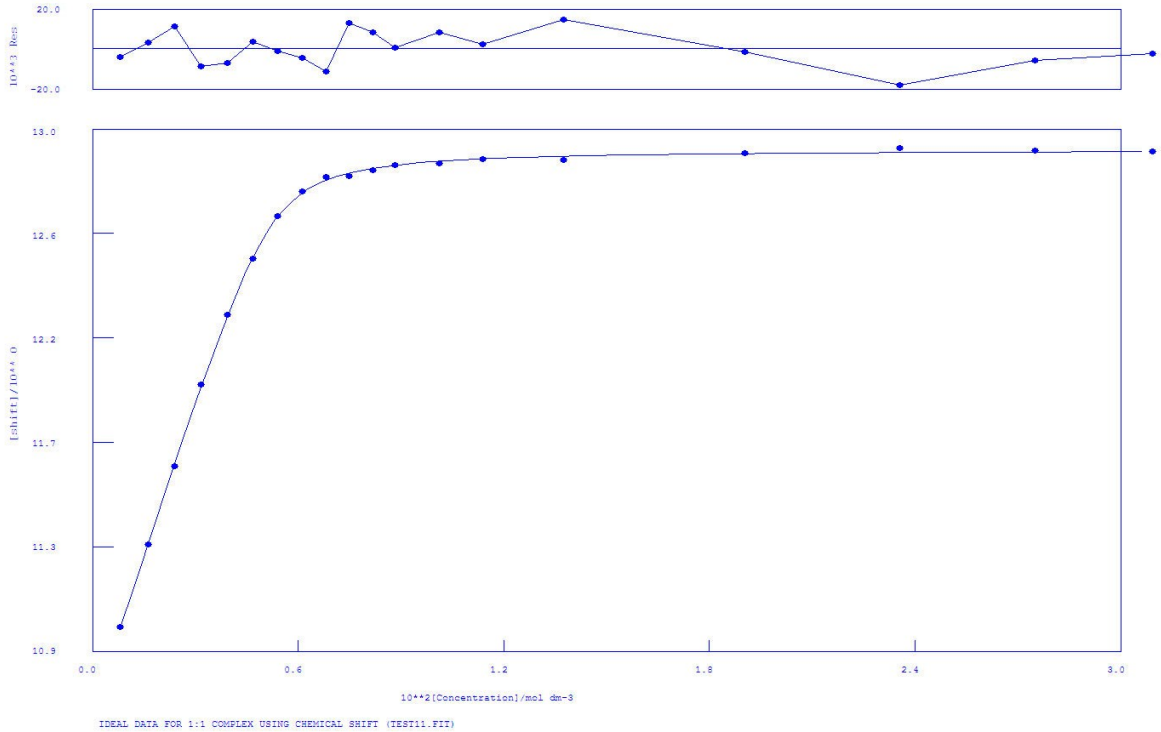

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:13:16   on 07/18/2014

 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  1.91221E+03 2.000E-01 1.428E+02 5.100E+00    K1
   2  1  1.06971E+01 2.000E-01 1.578E-02 1.485E+00   SHIFT M
   3  1  1.26723E+01 1.000E+00 1.361E-02 4.412E+00    SHIFT ML

0RMS ERROR = 2.16E-02  MAX ERROR = 4.46E-02 AT OBS.NO. 13
 RESIDUALS SQUARED = 7.43E-03
 RFACTOR =     0.1631 PERCENT
```

Figure S35 $^{1}$H-NMR titration of **L2** with $TBAH_2PO_4$ in DMSO-$d_6$.



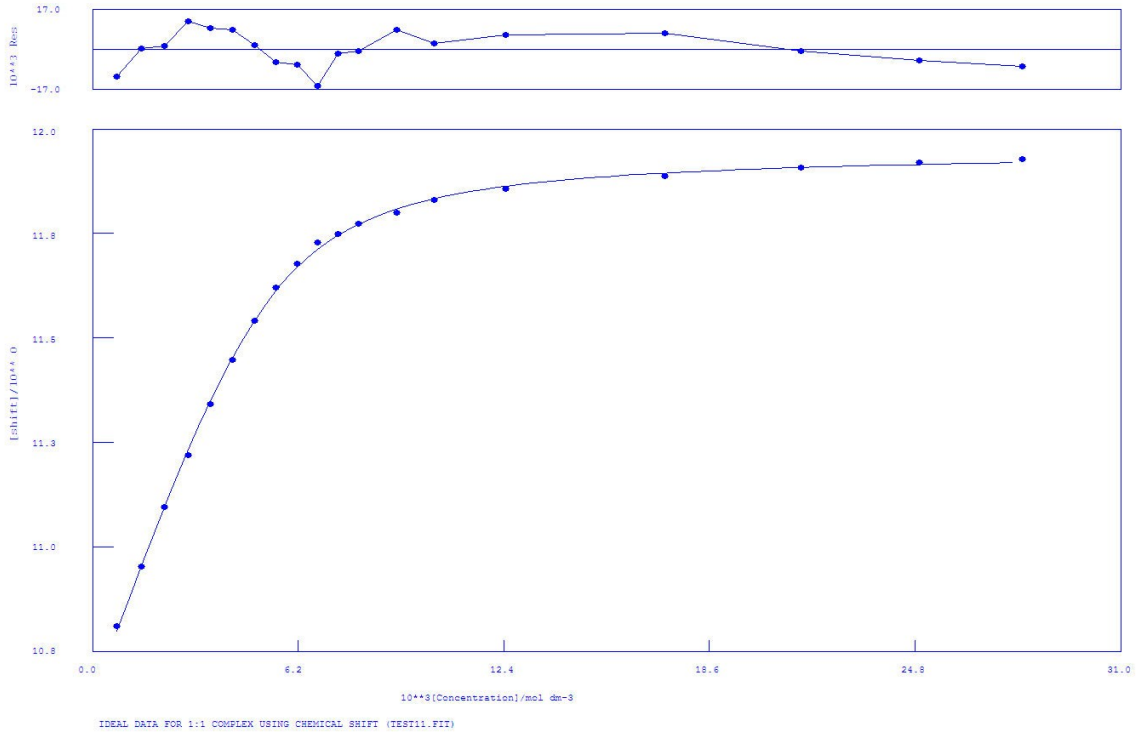

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 09:16:03   on 07/18/2014

 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  9.19353E+03 2.000E-01 4.203E+02 2.342E+00    K1
   2  1  1.06469E+01 2.000E-01 7.317E-03 1.173E+00   SHIFT M
   3  1  1.29169E+01 1.000E+00 3.655E-03 2.222E+00    SHIFT ML

0RMS ERROR = 9.17E-03  MAX ERROR = 1.83E-02 AT OBS.NO. 17
 RESIDUALS SQUARED = 1.34E-03
 RFACTOR =     0.0672 PERCENT
```

Figure S36 $^{1}$H-NMR titration of **L3** with $TBAH_2PO_4$ in DMSO-$d_6$.



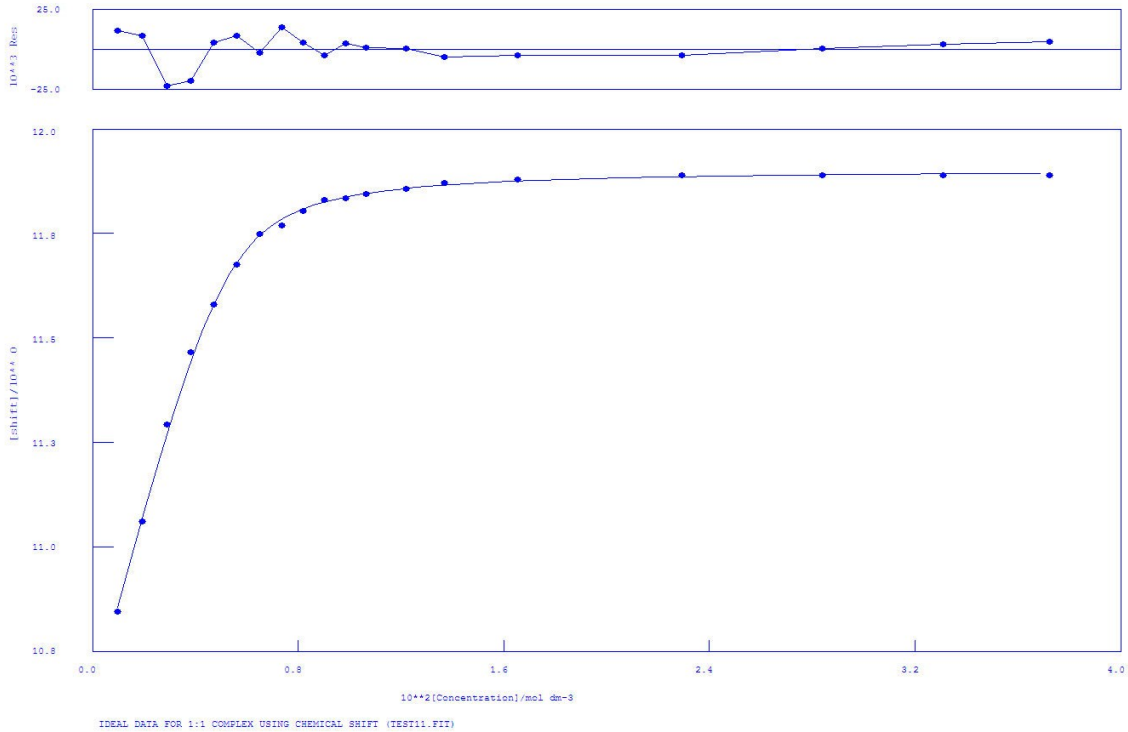

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:19:37   on 07/18/2014

 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  1.90062E+03 2.000E-01 7.965E+01 5.211E+00    K1
   2  1  1.06892E+01 2.000E-01 5.872E-03 1.523E+00   SHIFT M
   3  1  1.19499E+01 1.000E+00 4.938E-03 4.431E+00    SHIFT ML

0RMS ERROR = 7.83E-03  MAX ERROR = 1.56E-02 AT OBS.NO. 10
 RESIDUALS SQUARED = 9.82E-04
 RFACTOR =     0.0619 PERCENT
```

Figure S37 $^{1}$H-NMR titration of **L2** with $TEAHCO_3$ in DMSO-$d_6$.




```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:47:18   on 07/18/2014

 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  3.59363E+03 2.000E-01 2.364E+02 3.495E+00    K1
   2  1  1.06851E+01 2.000E-01 8.936E-03 1.342E+00   SHIFT M
   3  1  1.19077E+01 1.000E+00 4.589E-03 3.031E+00    SHIFT ML

0RMS ERROR = 9.82E-03  MAX ERROR = 2.29E-02 AT OBS.NO.  3
 RESIDUALS SQUARED = 1.54E-03
 RFACTOR =     0.0771 PERCENT
```

Figure S38 $^{1}$H-NMR titration of **L3** with $TEAHCO_3$ in DMSO-$d_6$.

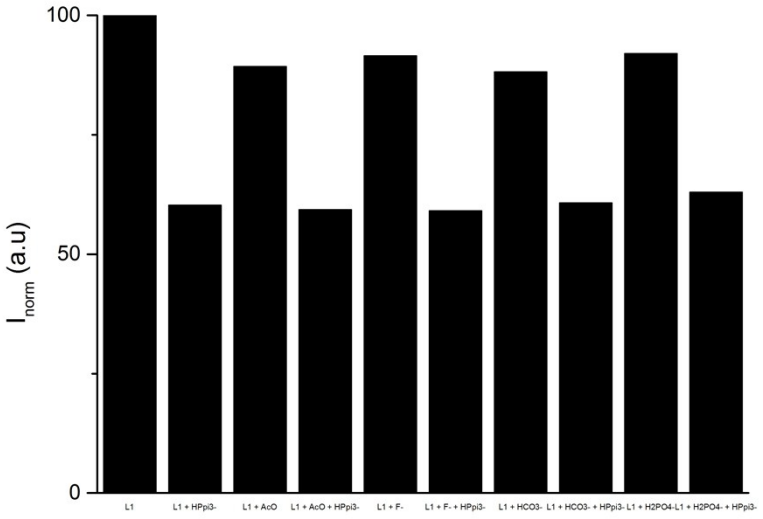



Figure S39 Anion competition study for **L1** [$3.0 \cdot 10^{-5}$ M] in the presence of 50 equivalents of $HPpi^{3-}$ and 70 equivalents of the other anions in in water at pH 7 with 0.01 M CTAB ($\lambda_{em}$ = 363 nm, $\lambda_{exc}$ = 326 nm).

## Crystallography

CCDC1435845 and 1435846 contains supplementary X-ray crystallographic data for **L2-$H_2PO_4^-$** and **L2-$H_2PPi^{2-}$** respectively. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or email: deposit@ccdc.cam.ac.uk.

**Table S2.** Crystal data and structure refinement details for **$(L2)(H_2PO_4^-)_2)(TBA)_2$**

| | | |
|---|---|---|
| CCDC dep. number | **1435845** | |
| Empirical formula | $C_{116}H_{195}N_{14}O_{20.50}P_4$ | |
| Formula weight | 2237.73 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71075 Å | |
| Crystal system | Orthorhombic | |
| Space group | $Pca2_1$ | |
| Unit cell dimensions | $a$ = 16.1474(7) Å | $\alpha$ = 90° |
| | $b$ = 28.4487(12) Å | $\beta$ = 90° |
| | $c$ = 26.5040(9) Å | $\gamma$ = 90° |
| Volume | 12175.2(8) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.221 Mg / m$^3$ | |
| Absorption coefficient | 0.133 mm$^{-1}$ | |
| *F(000)* | 4852 | |
| Crystal | Prism; Colourless | |
| Crystal size | 0.24 × 0.22 × 0.22 mm$^3$ | |
| $\theta$ range for data collection | 2.113 – 27.503° | |
| Index ranges | $-20 \le h \le 20$, $-35 \le k \le 36$, $-31 \le l \le 34$ | |
| Reflections collected | 106562 | |
| Independent reflections | 27595 [$R_{int}$ = 0.0402] | |
| Completeness to $\theta$ = 25.242° | 99.8 % | |
| Absorption correction | Semi–empirical from equivalents | |
| Max. and min. transmission | 1.000 and 0.688 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 27595 / 1341 / 1712 | |
| Goodness-of-fit on $F^2$ | 1.039 | |
| Final $R$ indices [$F^2 > 2\sigma(F^2)$] | *R1* = 0.0511, *wR2* = 0.1288 | |
| $R$ indices (all data) | *R1* = 0.0602, *wR2* = 0.1355 | |
| Absolute structure parameter | 0.03(2) | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.733 and –0.324 e Å$^{-3}$ | |

**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-2014* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Graphics:** *OLEX2* (Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339-341).

**Special details:**

Whole molecule disorder observed in one ligand molecule but only required to model the pendant side-arms as such. The second ligand molecule also shows some signs of disorder however attempts at modelling this did not improve the model.
A partially occupied water was allowed to refine occupancy and then set to 50%.
There was also disorder for some of the butyl chains of the TBA cations.
Due to the above various geometrical (SAME, SADI, DFIX, BUMP) and displacement (RIGU) restraints were employed.

**Table S3.** Hydrogen bonds [Å and °] for **(L2)($H_2PO_4^-$)$_2$)(TBA)$_2$**

| *D*–H···*A* | *d*(*D*–H) | *d*(H···*A*) | *d*(*D*···*A*) | ∠(*D*H*A*) |
|---|---|---|---|---|
| N32–H32A···O42$^{i}$ | 0.88 | 1.92 | 2.758(4) | 159.4 |
| N33–H33···O42$^{i}$ | 0.88 | 2.31 | 3.070(6) | 145.3 |
| N34–H34···O55 | 0.88 | 1.97 | 2.795(4) | 155.7 |
| N35–H35A···O55 | 0.88 | 1.93 | 2.771(4) | 158.2 |
| N31–H31···O42$^{i}$ | 0.88 | 2.23 | 3.034(13) | 152.3 |
| N31A–H31A···O55 | 0.88 | 2.24 | 3.07(2) | 157.3 |
| N1–H1···O52 | 0.88 | 1.99 | 2.832(5) | 161.1 |
| N2–H2···O52 | 0.88 | 1.91 | 2.787(4) | 175.5 |
| N3–H3···O52 | 0.88 | 2.54 | 3.305(5) | 145.2 |
| N4–H4···O45 | 0.88 | 1.97 | 2.779(4) | 152.1 |
| N5–H5···O45 | 0.88 | 2.01 | 2.833(4) | 154.6 |
| O47–H47···O51 | 0.84 | 1.85 | 2.624(4) | 152.2 |
| O43–H43A···O56$^{ii}$ | 0.84 | 1.80 | 2.605(4) | 160.3 |
| O44–H44···O46 | 0.84 | 1.82 | 2.643(4) | 165.7 |
| O53–H53B···O46 | 0.84 | 1.80 | 2.636(4) | 171.2 |
| O54–H54B···O56$^{ii}$ | 0.84 | 1.77 | 2.602(4) | 171.4 |
| O57–H57···O51$^{i}$ | 0.84 | 1.79 | 2.615(4) | 168.7 |
| O58–H58···O41$^{i}$ | 0.84 | 1.81 | 2.620(4) | 162.8 |
| O201–H20J···O42 | 0.87 | 2.52 | 3.316(10) | 153.4 |
| O201–H20J···O44 | 0.87 | 2.11 | 2.840(10) | 141.5 |
| O201–H20K···O48 | 0.87 | 2.40 | 2.974(9) | 123.8 |

Symmetry transformations used to generate equivalent atoms:
(i) –x+1,–y+1,z–1/2 (ii) –x+1,–y+1,z+1/2

**Table S4.** Crystal data and structure refinement details for **(L2)($H_2$Ppi)(TBA)$_2$**

| | | |
|---|---|---|
| CCDC dep. number | **1435846** | |
| Empirical formula | $C_{58}H_{95}N_7O_9P_2$ | |
| Formula weight | 1096.34 | |
| Temperature | 100.15 K | |
| Wavelength | 0.71075 Å | |
| Crystal system | Orthorhombic | |
| Space group | *Pban* | |
| Unit cell dimensions | $a$ = 22.394(12) Å | $\alpha$ = 90° |
| | $b$ = 16.369(8) Å | $\beta$ = 90° |
| | $c$ = 17.539(10) Å | $\gamma$ = 90° |
| Volume | 6429(6) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.133 Mg / m$^3$ | |
| Absorption coefficient | 0.123 mm$^{-1}$ | |
| *F(000)* | 2376 | |
| Crystal | Plate; colourless | |
| Crystal size | 0.08 × 0.08 × 0.01 mm$^3$ | |
| $\theta$ range for data collection | 2.158 – 25.027° | |
| Index ranges | $0 \le h \le 26$, $0 \le k \le 19$, $0 \le l \le 20$ | |
| Reflections collected | 5686 | |
| Independent reflections | 5685 [$R_{int}$ = 0.0000] | |
| Completeness to $\theta$ = 25.027° | 99.9 % | |
| Absorption correction | Semi–empirical from equivalents | |
| Max. and min. transmission | 1.000 and 0.534 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5685 / 1691 / 878 | |
| Goodness-of-fit on $F^2$ | 1.043 | |
| Final $R$ indices [$F^2 > 2\sigma(F^2)$] | *R1* = 0.0839, *wR2* = 0.2651 | |
| $R$ indices (all data) | *R1* = 0.1566, *wR2* = 0.3026 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.360 and –0.347 e Å$^{-3}$ | |

**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-2014* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Graphics:** *OLEX2* (Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339-341).

**Special details**:

Electron density from disordered solvent, likely to be comprised of a mixture of CH3CN/CH3NO2/DMSO/Diethyl ether, was eliminated using the SMTBX solvent masking routine within Olex2.
Low angle data only obtained - structure shows connectivity only.
The asymmetric unit actually only comprises of one TBA, along with just half the ligand and PPi moieties each lying over symmetry operators. Both the ligand and PPi show whole molecule disorder. To appropriately model this, two complete moieties of each were required at 25% occupancy.
Due to the above various geometrical (DFIX, SADI, SAME) and displacement (SIMU, RIGU) restraints were employed, along with geometrical constraints on the benzene and naphthalene rings.

**Table S5.** Hydrogen bonds [Å and °] for (**L2**)(HPpi)$(TBA)_2$.

| *D*–H···*A* | *d*(*D*–H) | *d*(H···*A*) | *d*(*D*···*A*) | ∠(*D*H*A*) |
|---|---|---|---|---|
| N1–H1···O12 | 0.88 | 2.10 | 2.90(4) | 150.7 |
| N2–H2···O11 | 0.88 | 2.06 | 2.92(4) | 163.7 |
| N3–H3···O22 | 0.88 | 2.67 | 3.42(4) | 145.0 |
| N4–H4···O21 | 0.88 | 1.98 | 2.85(4) | 172.2 |
| N5–H5···O11 | 0.88 | 1.84 | 2.66(3) | 153.6 |
| O12–H12···O22 | 0.84 | 1.78 | 2.535(16) | 149.3 |
| O16–H16···O26 | 0.84 | 1.77 | 2.567(16) | 158.5 |
| O23–H23A···O17 | 0.84 | 1.80 | 2.592(15) | 155.5 |
| O27–H27···O13 | 0.84 | 1.79 | 2.604(16) | 162.5 |
| N51–H51···O26 | 0.88 | 2.43 | 3.26(6) | 157.3 |
| N52–H52···O25 | 0.88 | 2.06 | 2.94(4) | 175.6 |
| N53–H53···O16 | 0.88 | 2.17 | 2.99(5) | 153.8 |
| N54–H54···O15 | 0.88 | 1.78 | 2.53(4) | 141.0 |
| N55–H55···O25 | 0.88 | 2.05 | 2.89(3) | 159.8 |

Symmetry transformations used to generate equivalent atoms: