Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A new family of bis-ureidic receptors for pyrophosphate optical sensing

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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).

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-phenylurea) L^1

A solution of phenyl isocyanate (0.3595g, 3.02mmol) in DCM (10 ml) was added dropwise to the solution of phenyl-1,3- dimethylamine (0.222g, 1.63 mmol) in DCM (20 ml) and was left stirring at ambient temperature under a N_2 atmosphere for 24h. The precipitate was collected by filtration, washed with diethyl ether and dried under reduced pressure to give the desired product as a white solid.

Yield: 80.14**%** (g 0.49g, 1 mmol); M.p.:222-225°C; ^{1}H NMR(400 MHz, DMSO-*d*$_6$, 298K) δH:4.25 (d, J=5.6 Hz, 4 H); 6.56 (t, J=5.6 Hz, NH, 2H); 6.84 (t, J=7.6 Hz, ArH, 2H); 7.13-7.20(m, ArH, 7H); 7.26 (t, J=7.6 Hz,ArH, 1H); 7.35 (d, J=8 Hz, 4H); 8.49(s, NH, 2H); ^{13}C-NMR(100 MHz, DMSO-d$_6$, 298 K) δ_C 42.77; δ_{ArH} 117.7, 121.1, 125.6, 126.0, 128.3, 128.7, 140.5; δ_{CO} 155.21

Synthesis of 1,1'-(1,3-phenylenebis(methylene))bis(3-(2-nitrophenyl)urea) L^2

A solution of 2-nitrophenyl isocyanate (0.4825 g, 2.94 mmol) in 10 ml of DCM was added dropwise to the solution of phenyl-1,3-dimethylamine (0.235 g, 1.47 mmol) in 20 ml of DCM and was stirred at room temperature under a N_2 atmosphere for 24h. The yellow solid formed was isolated by filtration, washed with dietyl ether and dried under vacuum.

Yield: 77.64% (0.53g, 1.1mmol); M.p.:236-240°C; ^{1}H NMR(400 MHz, DMSO-*d*$_6$, 298K) δH:4.32 (d, J=6 Hz, 4 H); 7.12 (t, J=8, ArH, 2H); 7.21 (d, J=7.2, ArH, 2H); 7.27 (s, ArH, 1H); 7.33 (t, J=7.2, ArH, 1H); 7.62 (t, J=8.4, ArH,2H); 8.00-8.06 (m, ArH, NH, 4H); 8.32 (d, J=8.4, 2H); 9.43 (s, NH, 2H); ^{13}C-NMR (100MHz, DMSO-*d*$_6$, 298 K) δ_C 42.94; δ_{ArC} 121.4, 122.4, 125.3, 125.9, 126.2, 128.4, 134.9,135.8,136.8, 139.8; δ_{CO} 154.28.

Synthesis of 1,1'-(1,3-phenylenebis(methylene))bis(3-(naphthalen-1-yl)urea) L^3

1-naphthyl isocyanate (0.5084 g 3.00 mmol) dissolved in DCM (10 ml) was added dropwise to a solution of phenyl-1,3-dimethylamine (0.233g, 1.63mmol) in 20 ml of DCM. The mixture of

reaction was allowed to stir for 24h under a N_2 atmosphere at room temperature. The resulting white precipitate was removed by filtration, washed with dietyl ether and dried under vacuum.

Yield: 67.22% (0.52 g, 1.1 mmol); M.p.: 245-248°C; ^{1}H NMR(500 MHz, DMSO-d_6, 298K) δ_{CH} 4.38 (d, J=6 Hz, 4 H); δ_{ArH} 7.04 (t, J=6 Hz, NH, 2H); 7.33-742 (m, ArH, 4H); 7.48-7.58 (m, ArH, 6H); 7.88 (d, J=7.5 Hz, ArH, 2H); 8.01 (d, J=7.5 Hz, ArH, 2H); 8.08 (d, J=8 Hz, ArH, 2H); 8.59 (s, NH, 2H) ^{13}C-NMR(100 MHz, DMSO-d$_6$, 298 K) δ_C 42.97; δ_{ArC} 116.4, 121.2, 122.1, 125.5,125.6, 125.7, 125.8,128.3, 133.7, 135.1, 140.7 δ_{CO} 155.6.

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

A solution of phenyl isocyanate (0.170 g; 1.42 mmol) in DCM (10 ml) was added dropwise to the suspension of pyridine-2.6-diyldimethanamine dihydrocloride (0.150g, 0.714 mmol) and TEA (1 ml) in DCM (20ml). The reaction mixture was refluxed for 24h under a N_2 atmosphere and the precipitate thus obtained was filtered off, washed with H_2O and dried over vacuum to give the product as a white solid.

Yield 53% (0.180 g; 0.378mmol) ; M.p. 225-226°C; ^{1}H NMR(500 MHz, DMSO-d_6, 298K) δ_{CH} 4.40 (d, J=5 Hz, 4 H); δ_{ArH} 6.73 (t, J=6 Hz, NH, 2H); 6.90 (t, 7Hz, ArH , 2H); 7.21-7.24 (m, ArH, 6H); 7.40 (d, J=8, ArH, 4H); 7.75 (t, J=8, ArH, 1H); 8.72 (s, NH, 2H); ^{13}C-NMR(125 MHz, DMSO-d$_6$, 298 K) δ_C 45.17; δ_{ArC} 118.19, 119.52, 121.61, 129.11, 137.84, 140.9, 155.7, δ_{CO}159.04.

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

A solution of 2-nitrophenyl isocyanate (0.468 g; 2.85 mmol) in 15 ml of DCM was added dropwise to a stirred suspension of pyridine-2.6-diyldimethanamine dihydrocloride and TEA (1 ml) in 20 ml of DCM. The reaction was refluxed under N_2 atmosphere overnight. The resulting precipitate was then filtered , washed with water and then whit MeOH, dried under reduced pressure and isolated as a yellow solid.

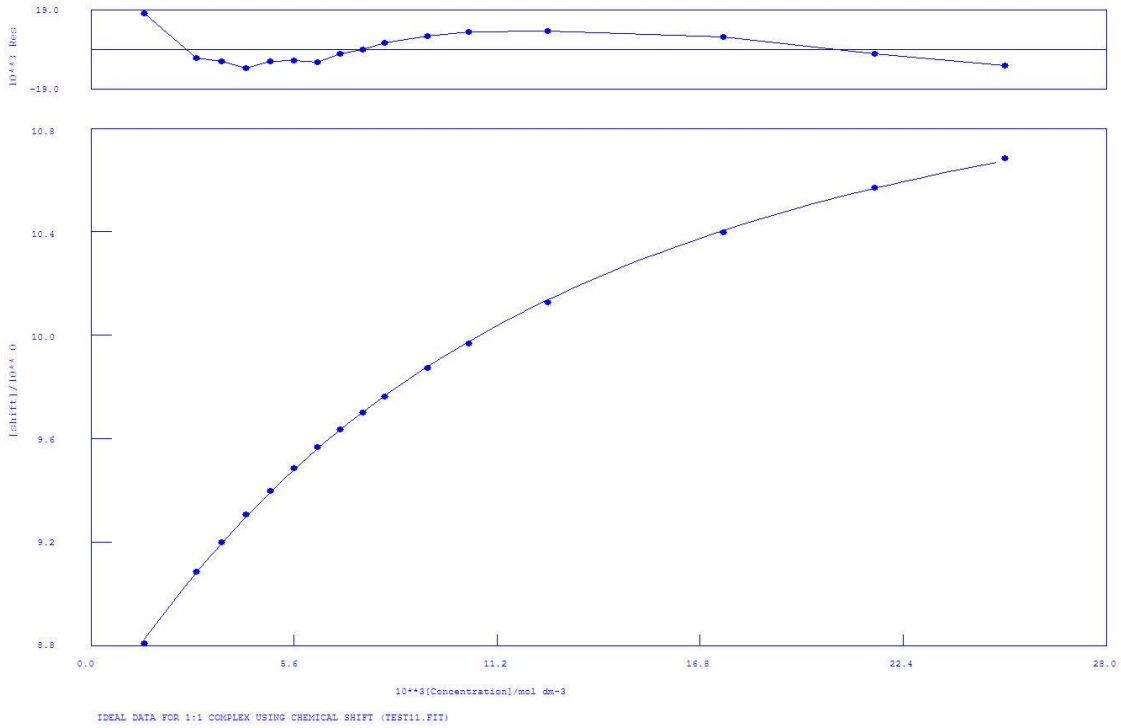
Yield: 51% (0.340g, 0.73 mmol); M.p. 234°C; ^{1}H NMR(500 MHz, DMSO-d_6, 298K) δ_{CH} 4.41 (d, J=6 Hz, 4 H); δ_{ArH} 7.14 (t, J=7 Hz, ArH, 2H); 7.25 (d, J=7.5Hz, ArH , 2H); 7.64 (t, J=7 ArH, 2H); 7.78 (t, J=8, ArH, 1H); 8.03-8.10 (m, 4H); 8.27 (d, J=8.5, ArH, 2H) 9.50 (s, NH, 2H) ^{13}C-NMR(125 MHz, DMSO-d$_6$, 298 K) δ_C 44.91; δ_{ArC} 119.22, 121.60, 122.20, 125.24, 134.82, 135.53, 137.25, 137.47, 154.41; δ_{CO} 158.25

Synthesis of 1,1'-(pyridine-2,6-diylbis(methylene))bis(3-(naphthalen1-yl)urea) L^6

A solution of 1-naphthyl isocyanate (0.320 g; 1.90 mmol) in DCM (15 ml) was added dropwise to a

stirred suspension of pyridine-2.6-diyldimethanamine dihydrocloride (0.200 g; 0.95 mmol) and TEA (1 ml) in DCM (15 ml). After refluxing under N_2 atmosphere overnight the white solid was isolated by filtration, washed with water and dried under reduced pressure.

Yield 59.7% (0.270 g; 0.57mmol); M.p. >250°C; ^{1}H NMR(500 MHz, DMSO-d_6, 298K) δ_{CH} 4.5 (d, J=6 Hz, 4 H); δ_{ArH} 7.20 (t, J=6 NH, 2H); 7.30 (d, J=8Hz, ArH , 2H); 7.43 (t, J=7.5 ArH, 2H); 7.49-7.59 (m, ArH, 6H); 7.80 (t, J=7.5, ArH, 1H); 7.90 (d, J=8, ArH, 2H); 8.00 (d, J=8, ArH, 2H); 8.14 (d, J=8, ArH, 2H); 8.77 (s, NH, 2H); ^{13}C-NMR(125 MHz, DMSO-d$_6$, 298 K) δ_C 44.89, δ_{ArC} 116.77, 119.14, 121.45, 122.24, 125.39, 125.71, 125.86, 128.28, 133.69, 135.03, 137.48, 155.65, δ_{CO} 158.61.

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Program run at 12:50:07   on 12/30/2011

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 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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   2  1  8.51926E+00 2.000E-01 9.384E-03 8.464E+00   SHIFT M
   3  1  1.15161E+01 1.000E+00 2.614E-02 3.230E+01    SHIFT ML

ORMS ERROR = 8.03E-03  MAX ERROR = 1.73E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 8.39E-04
 RFACTOR =     0.0744 PERCENT
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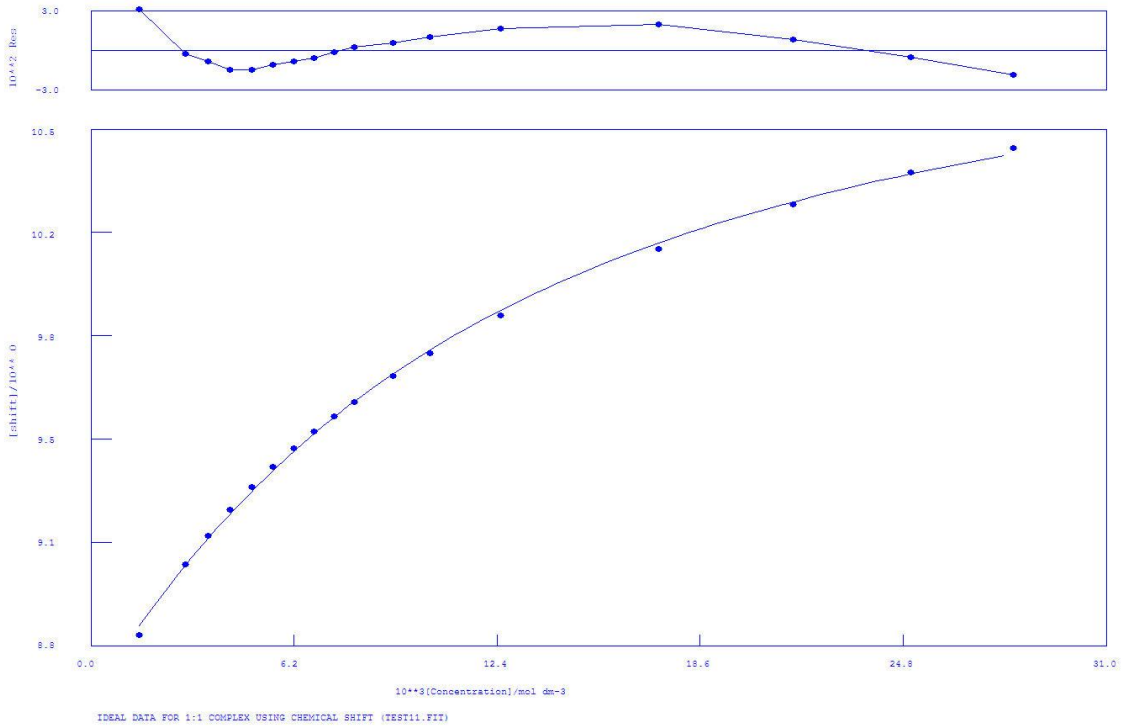
Figure S1 ^{1}H-NMR titration of $\mathbf{L^1}$ with TBAAcO in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:59:54   on 01/04/2012

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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  1.08941E+02 2.000E-01 5.928E+00 4.741E+01    K1
   2  1  8.62882E+00 2.000E-01 1.547E-02 7.546E+00   SHIFT M
   3  1  1.10901E+01 1.000E+00 4.079E-02 2.653E+01    SHIFT ML

0RMS ERROR = 1.45E-02  MAX ERROR = 3.11E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 2.93E-03
 RFACTOR =     0.1363 PERCENT
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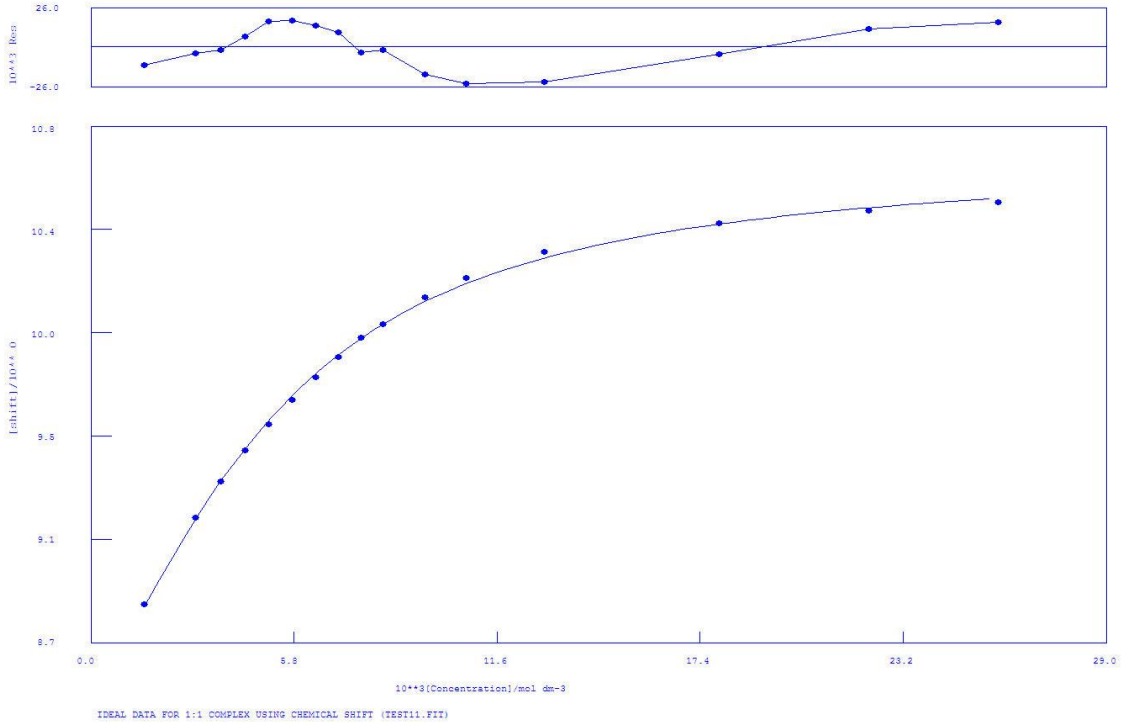
Figure S2 ^{1}H-NMR titration of $\mathbf{L^1}$ with TBABzO in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:06:06   on 12/29/2011

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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  4.83740E+02 2.000E-01 2.235E+01 1.596E+01    K1
   2  1  8.40857E+00 2.000E-01 1.770E-02 3.921E+00   SHIFT M
   3  1  1.07129E+01 1.000E+00 1.774E-02 9.549E+00    SHIFT ML

ORMS ERROR = 1.51E-02  MAX ERROR = 2.38E-02 AT OBS.NO. 12
 RESIDUALS SQUARED = 2.97E-03
 RFACTOR =     0.1380 PERCENT
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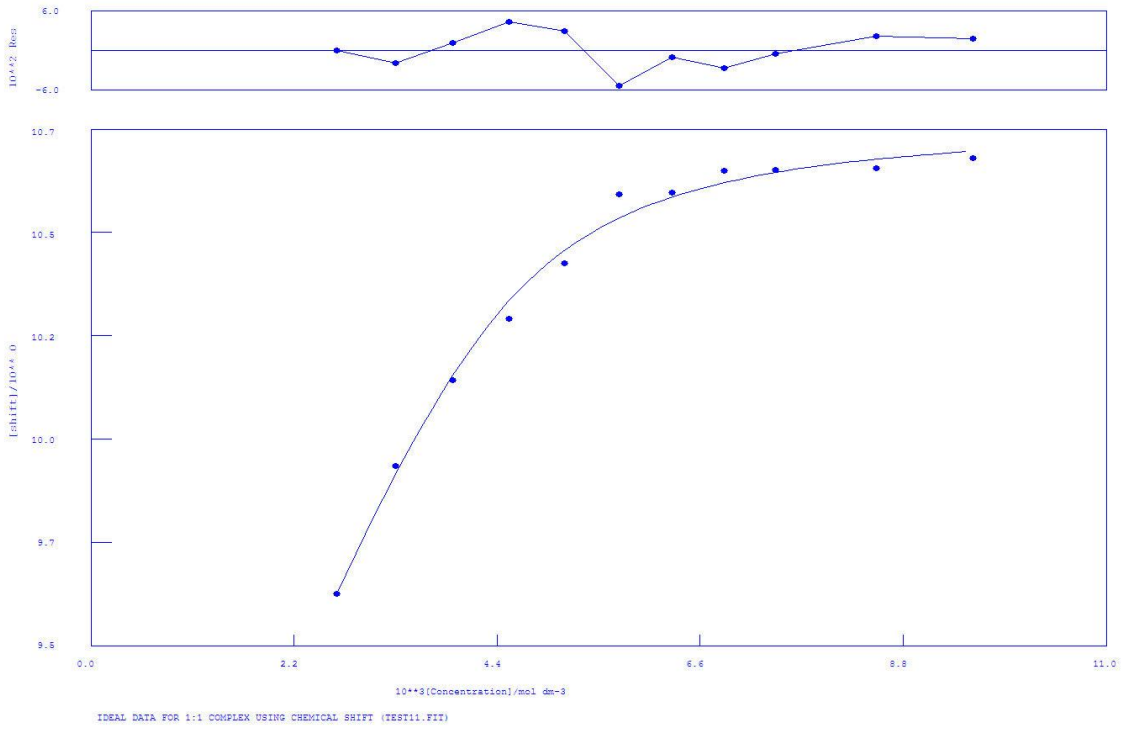
Figure S3 ^{1}H-NMR titration of $\mathbf{L^1}$ with $TBAH_2PO_4$ in DMSO-d_6.

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Program run at 12:59:10   on 02/08/2012

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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  5.48167E+03 2.000E-01 1.185E+03 1.181E+01    K1
   2  1  8.27172E+00 2.000E-01 7.242E-02 2.434E+00   SHIFT M
   3  1  1.07303E+01 1.000E+00 3.290E-02 9.007E+00    SHIFT ML

0RMS ERROR = 3.11E-02  MAX ERROR = 5.49E-02 AT OBS.NO.  6
 RESIDUALS SQUARED = 7.74E-03
 RFACTOR =     0.2562 PERCENT
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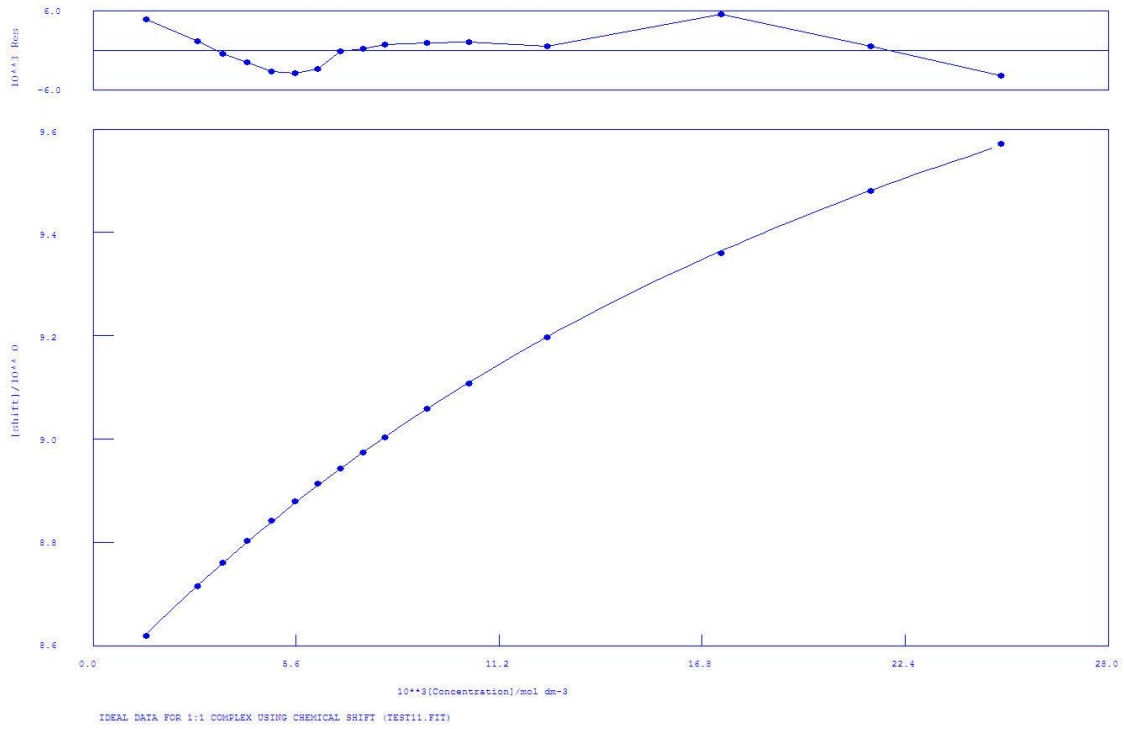
Figure S4 ^{1}H-NMR titration of **L**^{1} with $(TBA)_3HPpi$ in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 10:40:22   on 01/27/2012

 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  4.34068E+01 2.000E-01 1.224E+00 1.688E+02    K1
   2  1  8.51709E+00 2.000E-01 2.894E-03 9.815E+00   SHIFT M
   3  1  1.06512E+01 1.000E+00 2.964E-02 1.179E+02    SHIFT ML

0RMS ERROR = 2.87E-03  MAX ERROR = 5.48E-03 AT OBS.NO. 14
 RESIDUALS SQUARED = 1.07E-04
 RFACTOR =     0.0287 PERCENT
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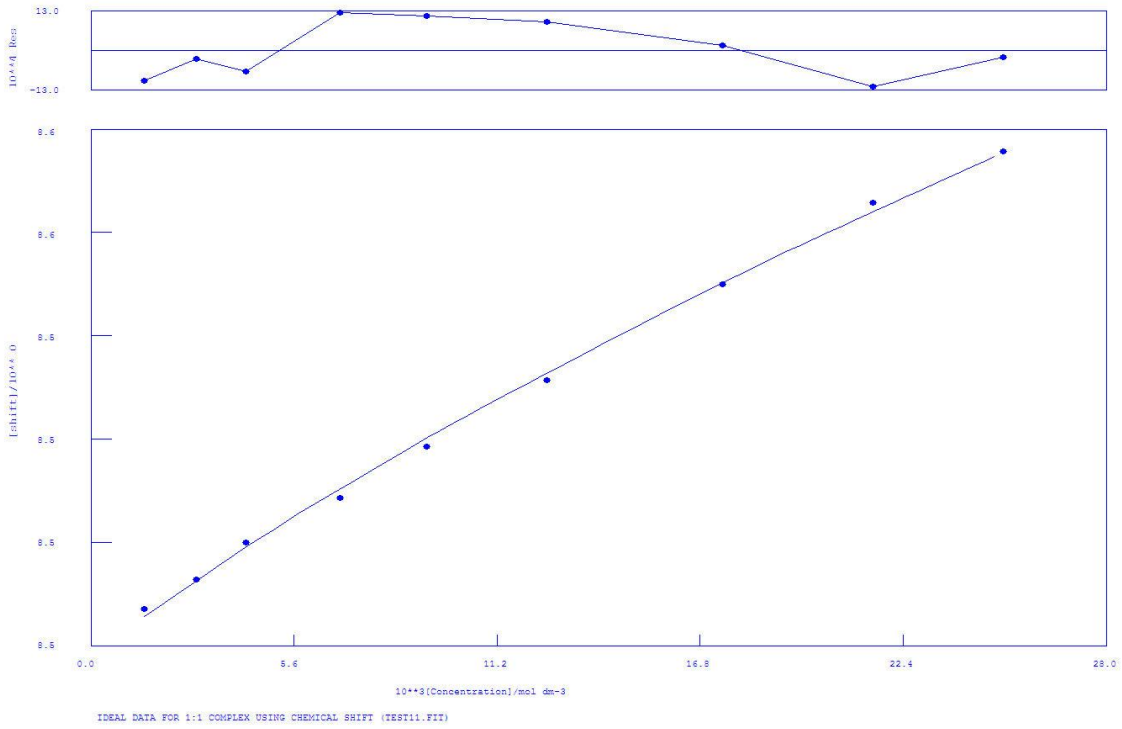
Figure S5 ^{1}H-NMR titration of **L**^{1} with $(TBA)_2Glu$ in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 10:50:01   on 01/27/2012

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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  1.12687E+01 2.000E-01 3.822E+00 9.005E+02    K1
   2  1  8.49895E+00 2.000E-01 1.054E-03 7.199E+00   SHIFT M
   3  1  8.81263E+00 1.000E+00 8.114E-02 8.025E+02    SHIFT ML

0RMS ERROR = 1.06E-03  MAX ERROR = 1.22E-03 AT OBS.NO.  4
 RESIDUALS SQUARED = 6.74E-06
 RFACTOR =     0.0101 PERCENT
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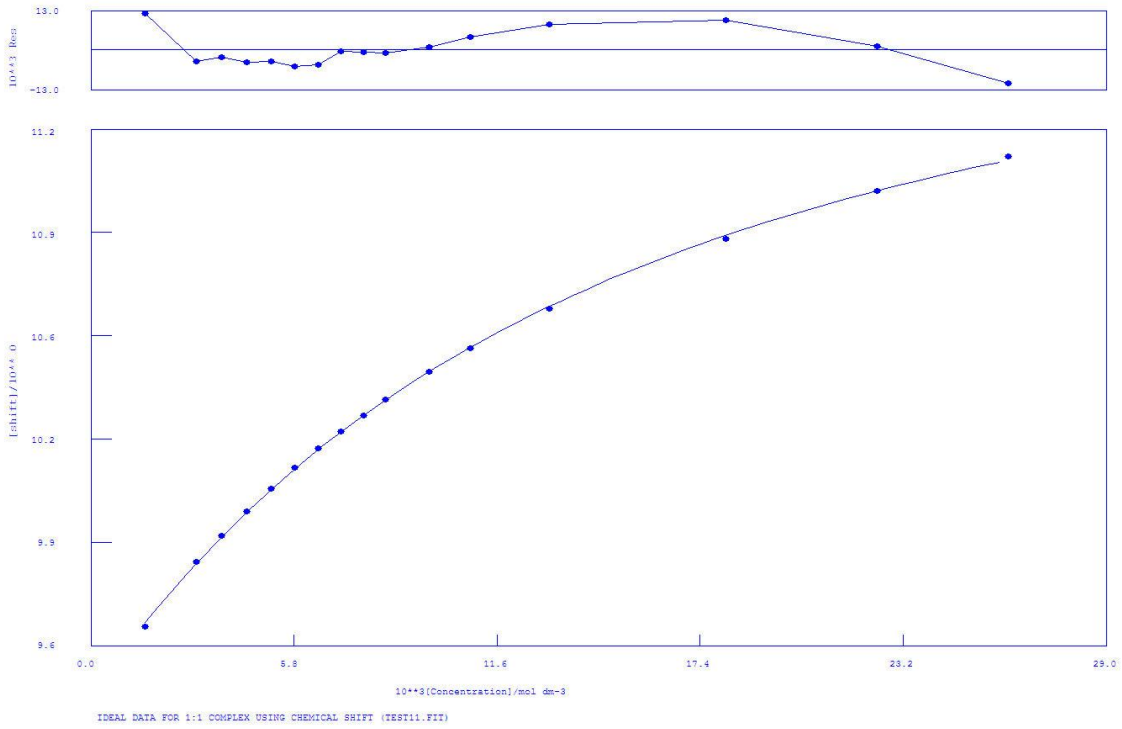
Figure S6 ^{1}H-NMR titration of $\mathbf{L^1}$ with $(TBA)_2Mal$ in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:23:03   on 12/16/2011

 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  8.83907E+01 2.000E-01 2.582E+00 6.315E+01    K1
   2  1  9.45328E+00 2.000E-01 7.234E-03 8.584E+00   SHIFT M
   3  1  1.19201E+01 1.000E+00 2.498E-02 3.644E+01    SHIFT ML

0RMS ERROR = 6.52E-03  MAX ERROR = 1.21E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 5.53E-04
 RFACTOR =     0.0568 PERCENT
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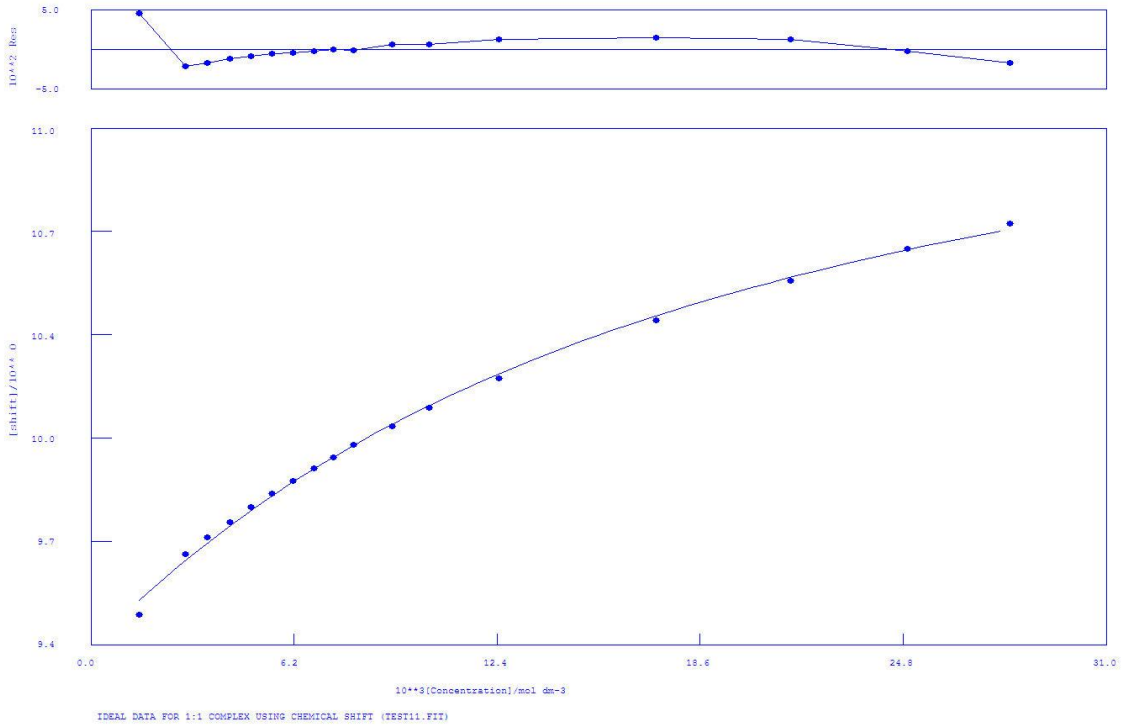
Figure S7 ^{1}H-NMR titration of $\mathbf{L}^{2}$ with TBAAcO in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:52:48   on 12/16/2011

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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  6.47549E+01 2.000E-01 6.441E+00 7.977E+01    K1
   2  1  9.39505E+00 2.000E-01 1.697E-02 8.514E+00   SHIFT M
   3  1  1.14835E+01 1.000E+00 8.118E-02 4.923E+01    SHIFT ML

0RMS ERROR = 1.69E-02  MAX ERROR = 4.48E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 3.98E-03
 RFACTOR =     0.1521 PERCENT
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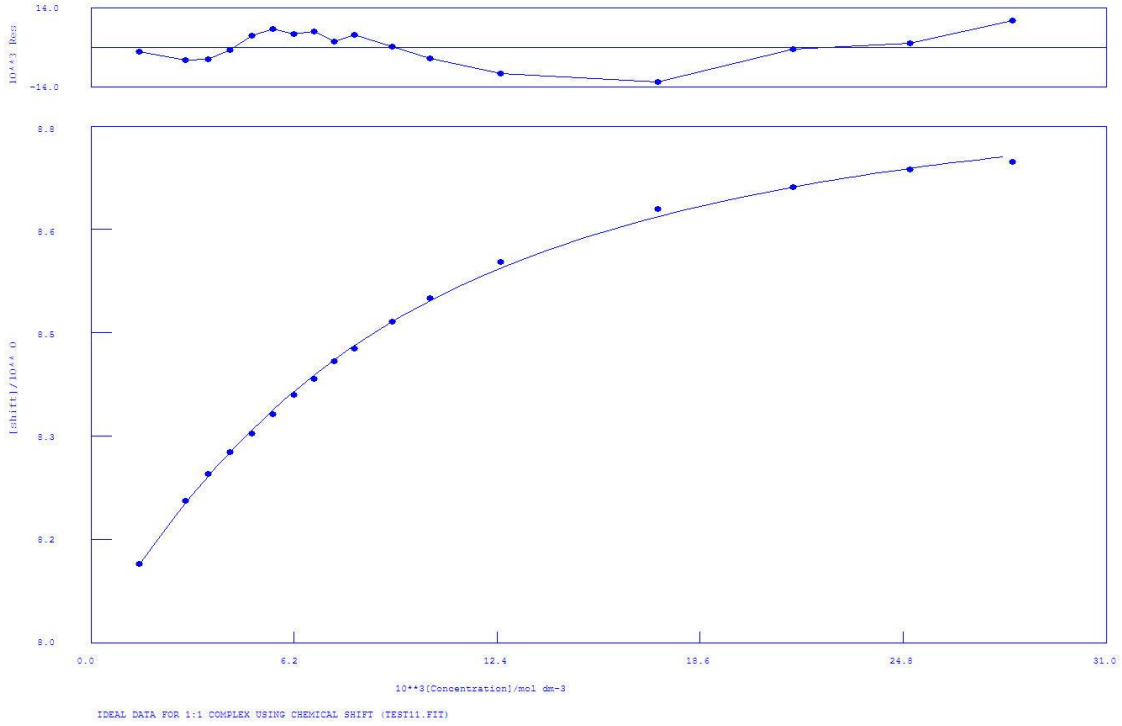
Figure S8 ^{1}H-NMR titration of **L**^{2} with TBABzO in DMSO-*d*$_6$.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:15:07   on 12/16/2011

 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  1.80508E+02 2.000E-01 9.117E+00 2.953E+01    K1
   2  1  8.00609E+00 2.000E-01 6.519E-03 5.914E+00   SHIFT M
   3  1  8.92857E+00 1.000E+00 1.136E-02 1.626E+01    SHIFT ML

0RMS ERROR = 6.08E-03  MAX ERROR = 1.23E-02 AT OBS.NO. 14
 RESIDUALS SQUARED = 5.18E-04
 RFACTOR =     0.0653 PERCENT
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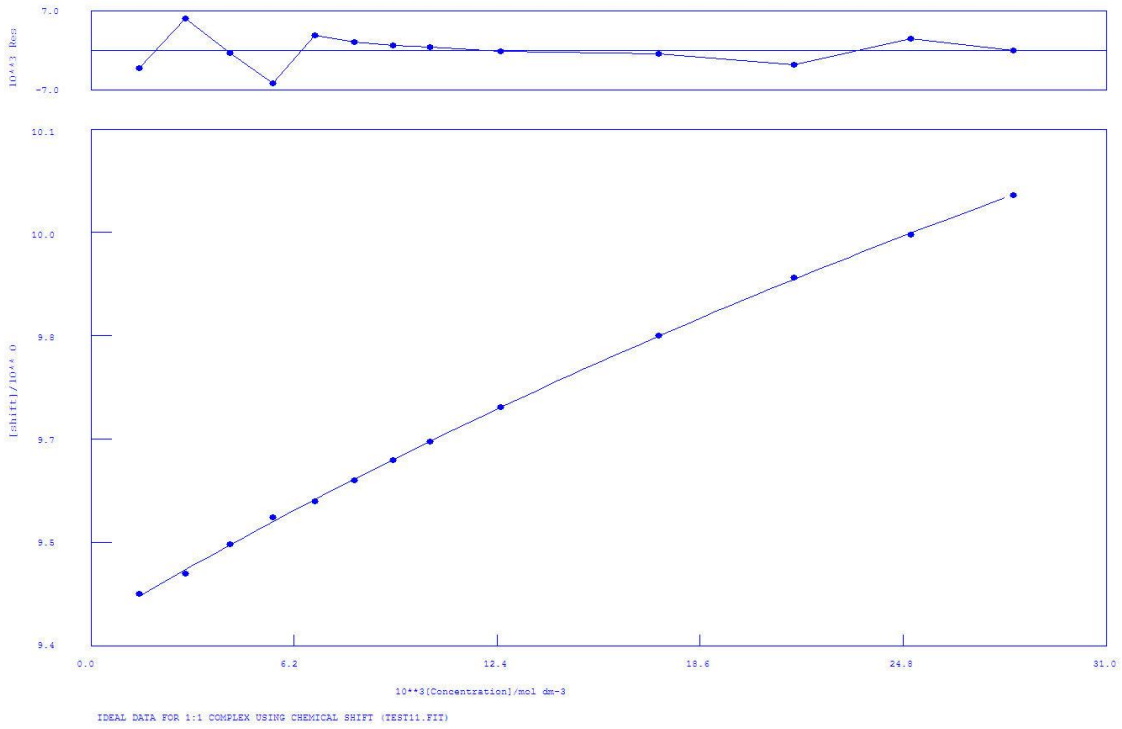
Figure S9 ^{1}H-NMR titration of $\mathbf{L^2}$ with $TBAH_2PO_4$ in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:40:12   on 01/27/2012

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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  1.04984E+01 2.000E-01 1.028E+00 8.119E+02    K1
   2  1  9.42859E+00 2.000E-01 2.719E-03 7.974E+00   SHIFT M
   3  1  1.20573E+01 1.000E+00 1.932E-01 7.114E+02    SHIFT ML

ORMS ERROR = 3.13E-03  MAX ERROR = 5.92E-03 AT OBS.NO.  4
 RESIDUALS SQUARED = 9.79E-05
 RFACTOR =     0.0283 PERCENT
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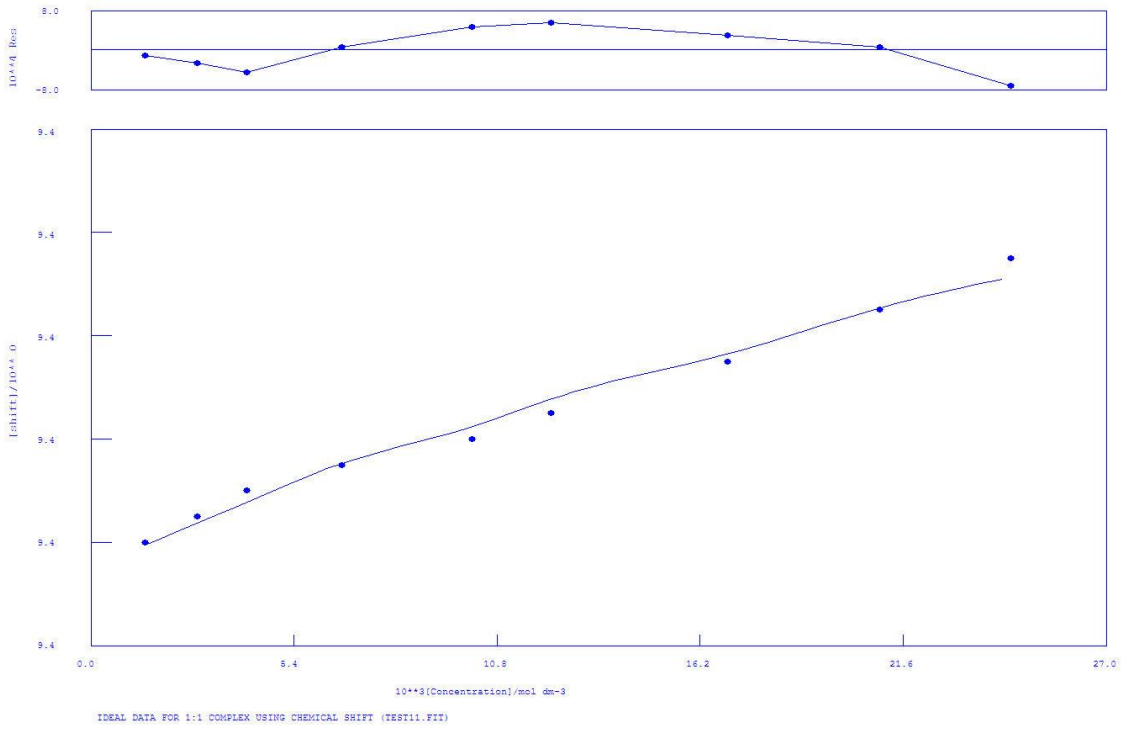
Figure S10 ^{1}H-NMR titration of $\mathbf{L^2}$ with $(TBA)_2Glu$ in DMSO-d_6.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:49:43   on 01/27/2012

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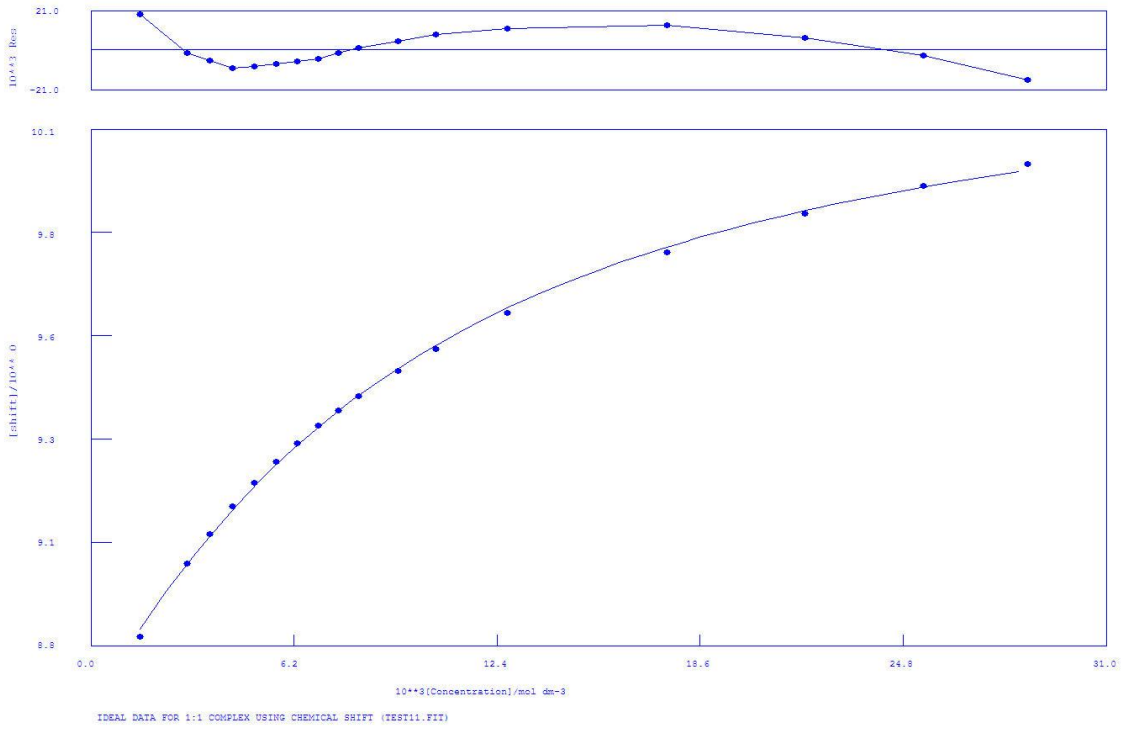
  Reaction:   M + L = ML
 FILE: TEST11.FIT
 IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
 File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  7.58123E+00 2.000E-01 7.427E-01 9.636E+00    K1
   2  1  9.42298E+00 2.000E-01 2.983E-04 2.867E+00   SHIFT M
   3  1  9.49195E+00 1.000E+00 6.581E-03 1.229E+01    SHIFT ML

0RMS ERROR = 4.91E-04  MAX ERROR = 7.30E-04 AT OBS.NO.  9
 RESIDUALS SQUARED = 1.44E-06
 RFACTOR =     0.0042 PERCENT
```

Figure S11 ^{1}H-NMR titration of $\mathbf{L}^{2}$ with con $(TBA)_2Mal$ in DMSO-d_6.



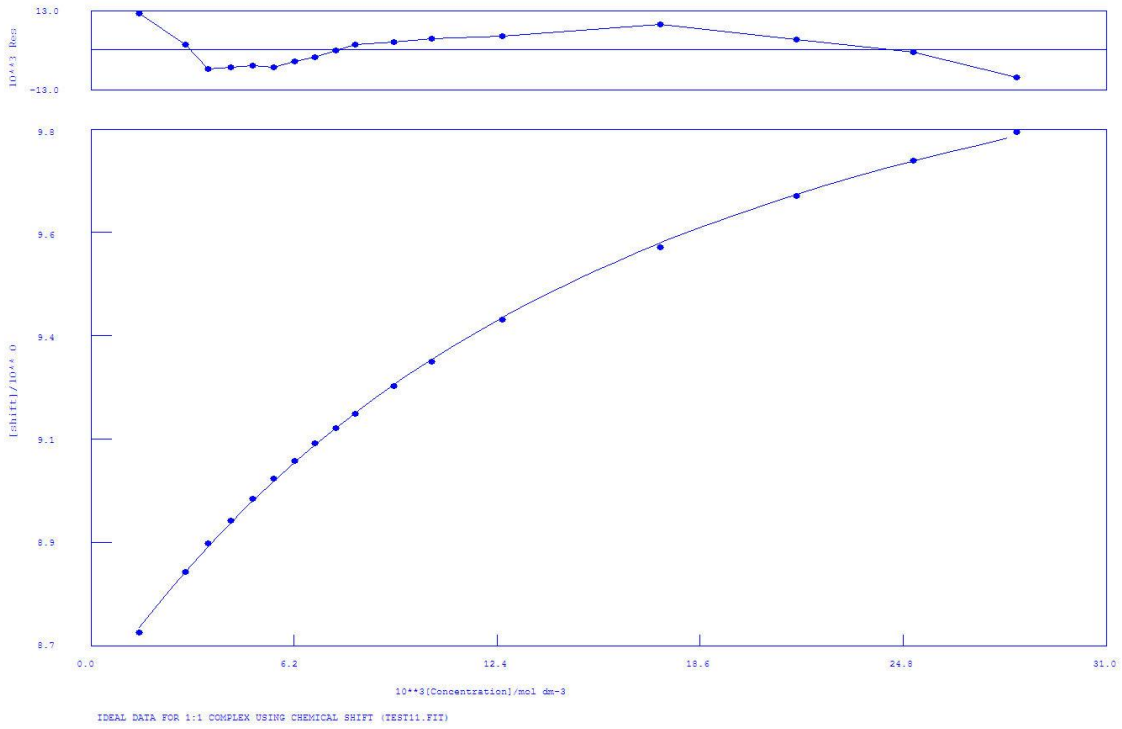

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 12:08:55   on 01/05/2012

 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  1.36759E+02 2.000E-01 6.352E+00 3.705E+01    K1
   2  1  8.64369E+00 2.000E-01 1.102E-02 7.098E+00   SHIFT M
   3  1  1.03948E+01 1.000E+00 2.188E-02 1.974E+01    SHIFT ML

0RMS ERROR = 9.92E-03  MAX ERROR = 1.91E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 1.38E-03
 RFACTOR =     0.0954 PERCENT
```

Figure S12 ^{1}H-NMR titration of $\mathbf{L^3}$ with TBAAcO in DMSO-d_6.



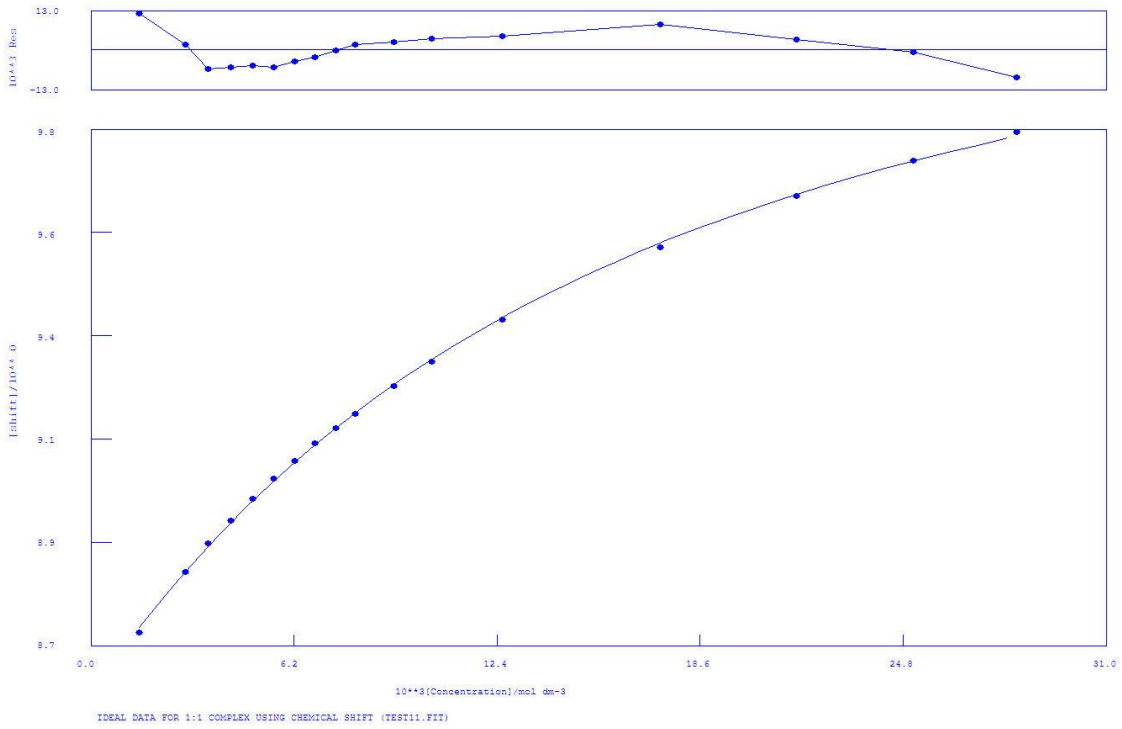

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 12:14:41   on 01/05/2012

 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  7.83725E+01 2.000E-01 2.803E+00 6.018E+01    K1
   2  1  8.60057E+00 2.000E-01 6.112E-03 7.970E+00   SHIFT M
   3  1  1.03937E+01 1.000E+00 2.247E-02 3.531E+01    SHIFT ML

0RMS ERROR = 6.02E-03  MAX ERROR = 1.20E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 5.07E-04
 RFACTOR =     0.0592 PERCENT
```

Figure S13 ^{1}H-NMR titration of $\mathbf{L}^{3}$ with TBABzO in DMSO-d_6.



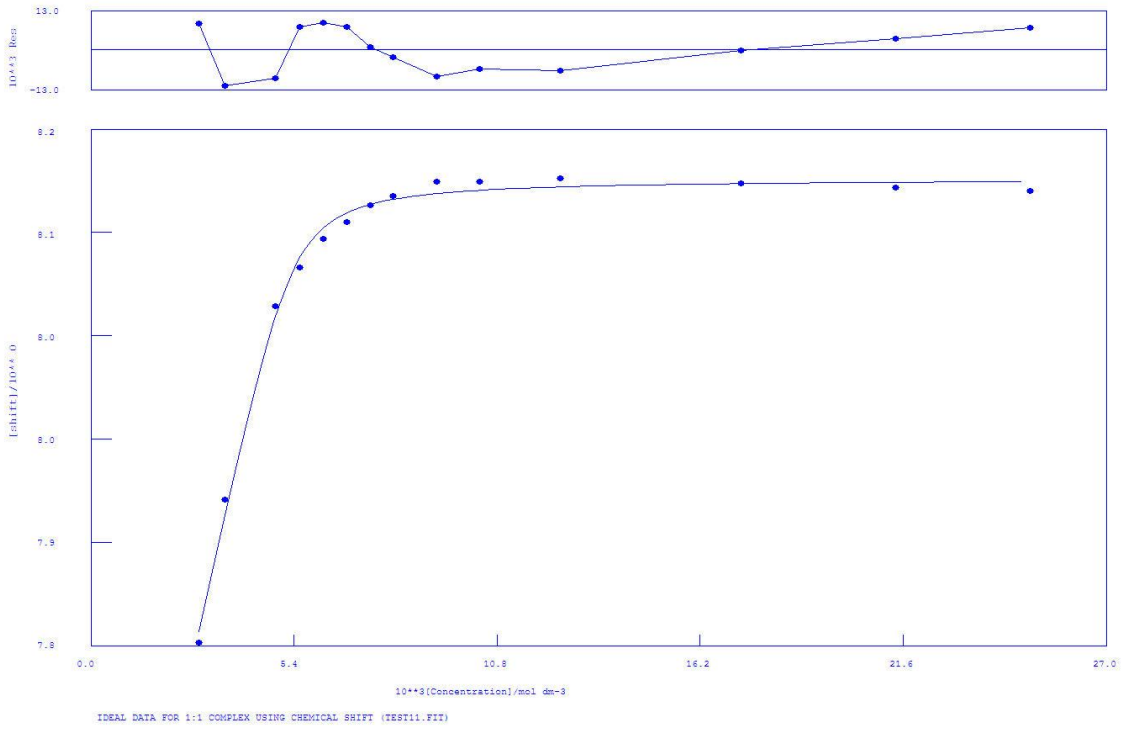

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:30:21   on 01/04/2012

 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  4.35285E+02 2.000E-01 1.209E+01 1.759E+01    K1
   2  1  8.50083E+00 2.000E-01 8.853E-03 4.244E+00   SHIFT M
   3  1  1.04192E+01 1.000E+00 9.400E-03 1.028E+01    SHIFT ML

0RMS ERROR = 7.52E-03  MAX ERROR = 1.86E-02 AT OBS.NO. 15
 RESIDUALS SQUARED = 7.34E-04
 RFACTOR =     0.0700 PERCENT
```

Figure S14 ^{1}H-NMR titration of $\mathbf{L^3}$ with $TBAH_2PO_4$ in DMSO-d_6.



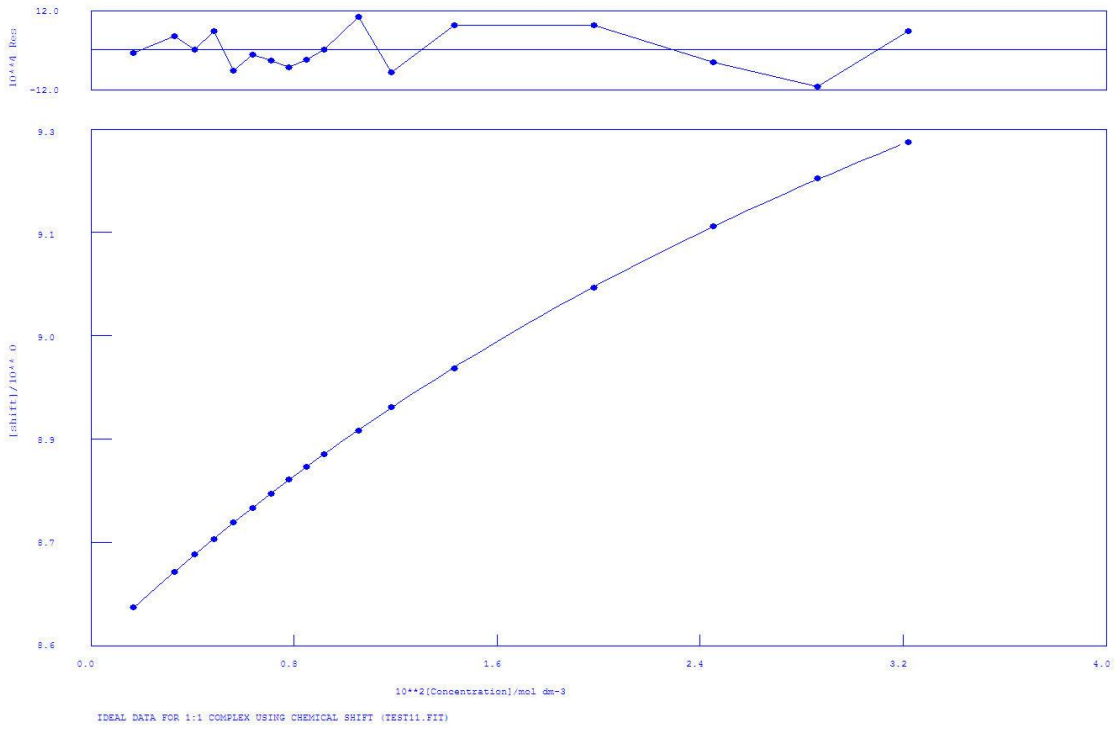

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:22:35   on 01/04/2012

 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  1.60759E+04 2.000E-01 2.052E+03 1.981E+00    K1
   2  1  7.41311E+00 2.000E-01 1.563E-02 1.362E+00   SHIFT M
   3  1  8.16089E+00 1.000E+00 3.130E-03 1.759E+00    SHIFT ML

0RMS ERROR = 8.15E-03  MAX ERROR = 1.16E-02 AT OBS.NO.  2
 RESIDUALS SQUARED = 7.31E-04
 RFACTOR =     0.0892 PERCENT
```

Figure S15 ^{1}H-NMR titration of $\mathbf{L^3}$ with $(TBA)_3HPpi$ in DMSO-d_6.



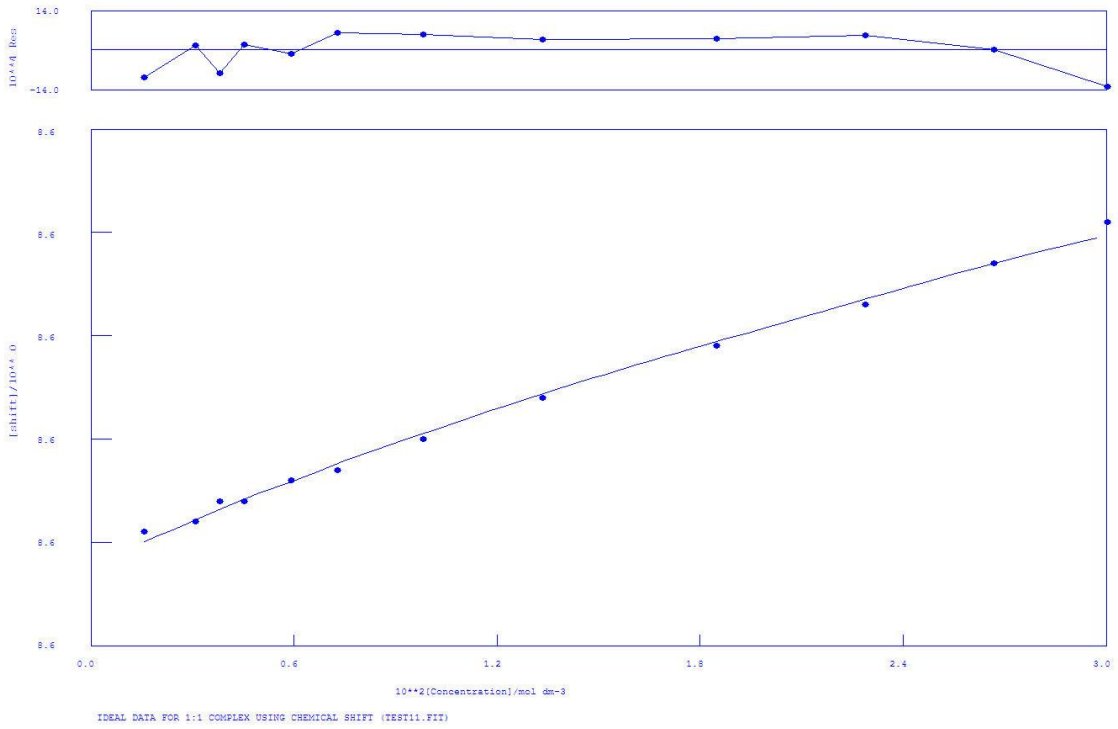

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:56:31   on 01/23/2012

 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  1.98147E+01 2.000E-01 1.999E-01 2.863E+02    K1
   2  1  8.54750E+00 2.000E-01 5.498E-04 9.004E+00   SHIFT M
   3  1  1.05114E+01 1.000E+00 1.200E-02 2.226E+02    SHIFT ML

0RMS ERROR = 6.37E-04  MAX ERROR = 1.11E-03 AT OBS.NO. 16
 RESIDUALS SQUARED = 5.67E-06
 RFACTOR =     0.0065 PERCENT
```

Figure S16 ^{1}H-NMR titration of $\mathbf{L^3}$ with $(TBA)_2Glu$ in DMSO-d_6.



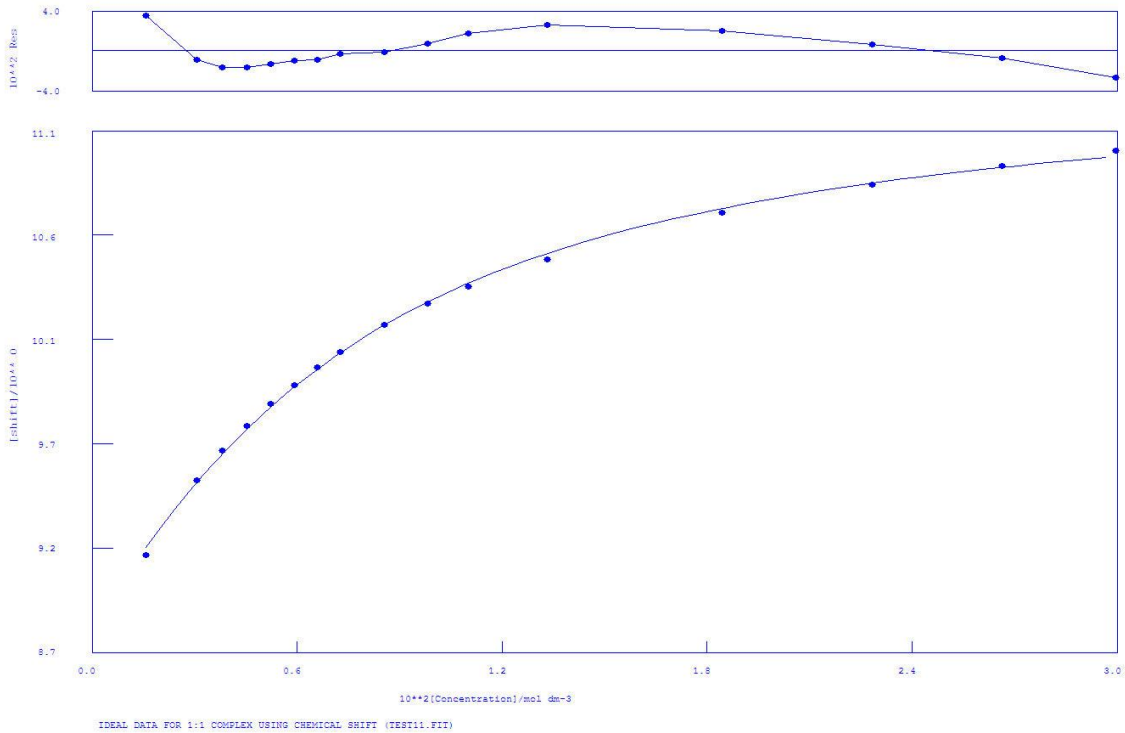

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:07:16   on 01/23/2012

 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  9.79880E+00 2.000E-01 1.173E+00 5.838E+01    K1
   2  1  8.58775E+00 2.000E-01 3.937E-04 2.958E+00   SHIFT M
   3  1  8.72901E+00 1.000E+00 1.238E-02 5.177E+01    SHIFT ML

0RMS ERROR = 7.17E-04  MAX ERROR = 1.30E-03 AT OBS.NO. 12
 RESIDUALS SQUARED = 4.63E-06
 RFACTOR =     0.0072 PERCENT
```

Figure S17 ^{1}H-NMR titration of $\mathbf{L}^{3}$ with $(TBA)_2Mal$ in DMSO-d_6.



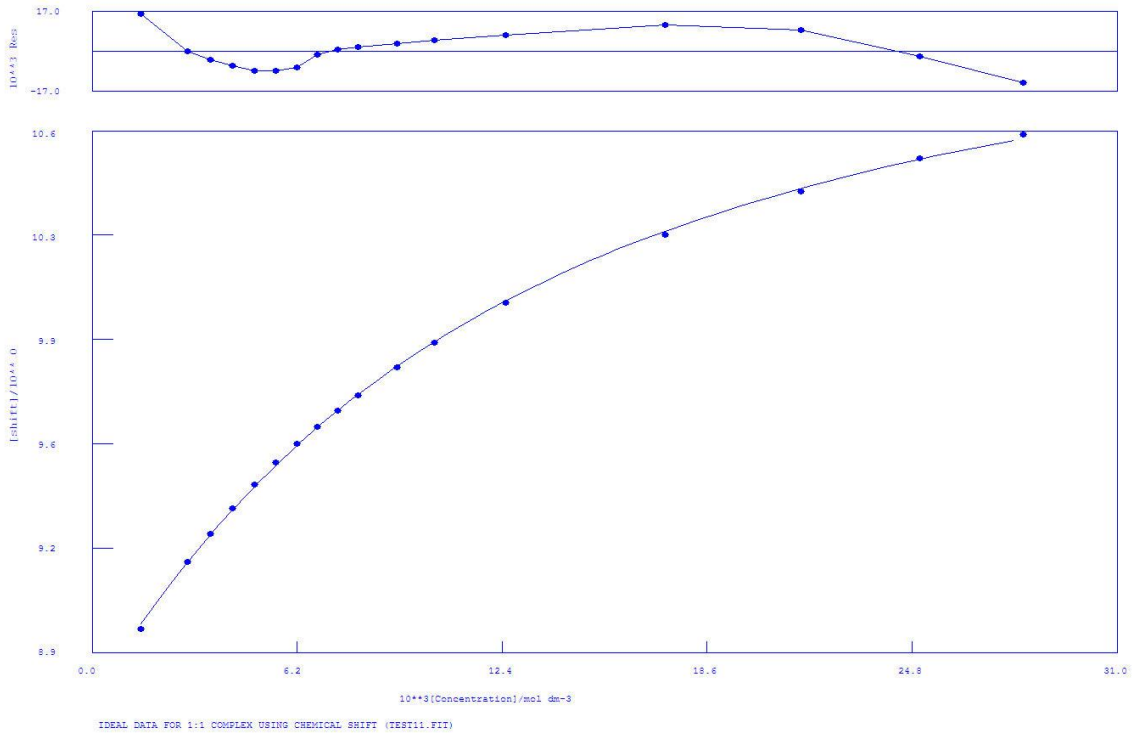

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:47:29   on 06/06/2012

 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  1.97486E+02 2.000E-01 1.029E+01 2.566E+01    K1
   2  1  8.80900E+00 2.000E-01 2.233E-02 6.163E+00   SHIFT M
   3  1  1.14063E+01 1.000E+00 2.981E-02 1.301E+01    SHIFT ML

0RMS ERROR = 1.86E-02  MAX ERROR = 3.52E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 4.49E-03
 RFACTOR =     0.1644 PERCENT
```

Figure S18 ^{1}H-NMR titration of $\mathbf{L^4}$ with TBAAcO in DMSO-d_6.



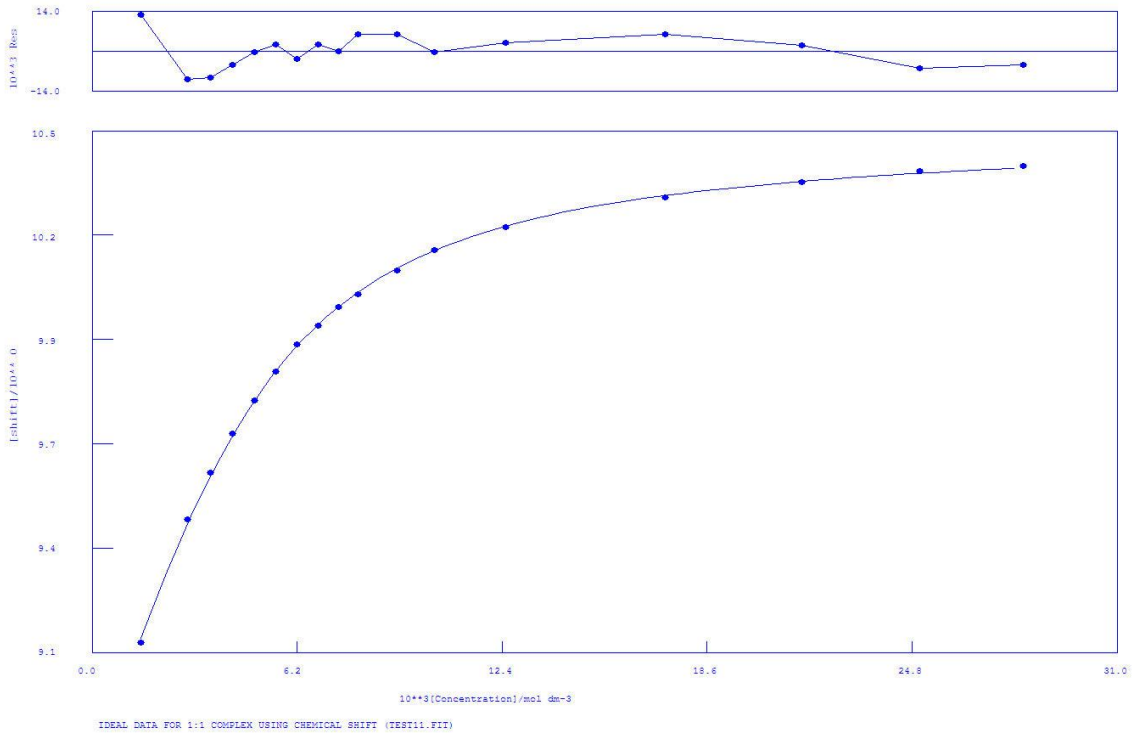

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:08:11   on 06/06/2012

 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  1.06438E+02 2.000E-01 3.285E+00 4.759E+01    K1
   2  1  8.75456E+00 2.000E-01 8.965E-03 7.752E+00   SHIFT M
   3  1  1.12730E+01 1.000E+00 2.354E-02 2.626E+01    SHIFT ML

0RMS ERROR = 8.32E-03  MAX ERROR = 1.59E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 9.68E-04
 RFACTOR =     0.0772 PERCENT
```

Figure S19 ^{1}H-NMR titration of **L**^{4} with TBABzO in DMSO-*d*$_6$.



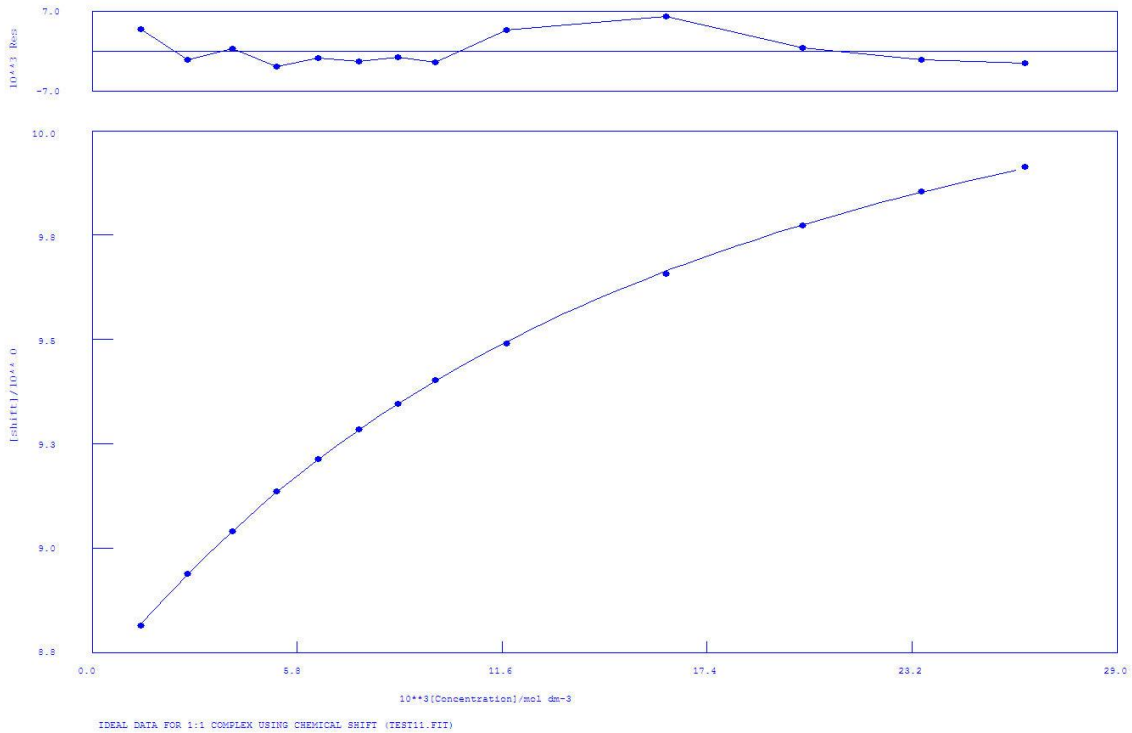

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:59:57   on 06/06/2012

 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  6.98292E+02 2.000E-01 1.614E+01 1.074E+01    K1
   2  1  8.76393E+00 2.000E-01 7.809E-03 3.386E+00   SHIFT M
   3  1  1.04988E+01 1.000E+00 5.360E-03 6.271E+00    SHIFT ML

0RMS ERROR = 6.38E-03  MAX ERROR = 1.28E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 5.70E-04
 RFACTOR =     0.0581 PERCENT
```

Figure S20 ^{1}H-NMR titration of **L**^{4} with $TBAH_2PO_4$ in DMSO-d_6.



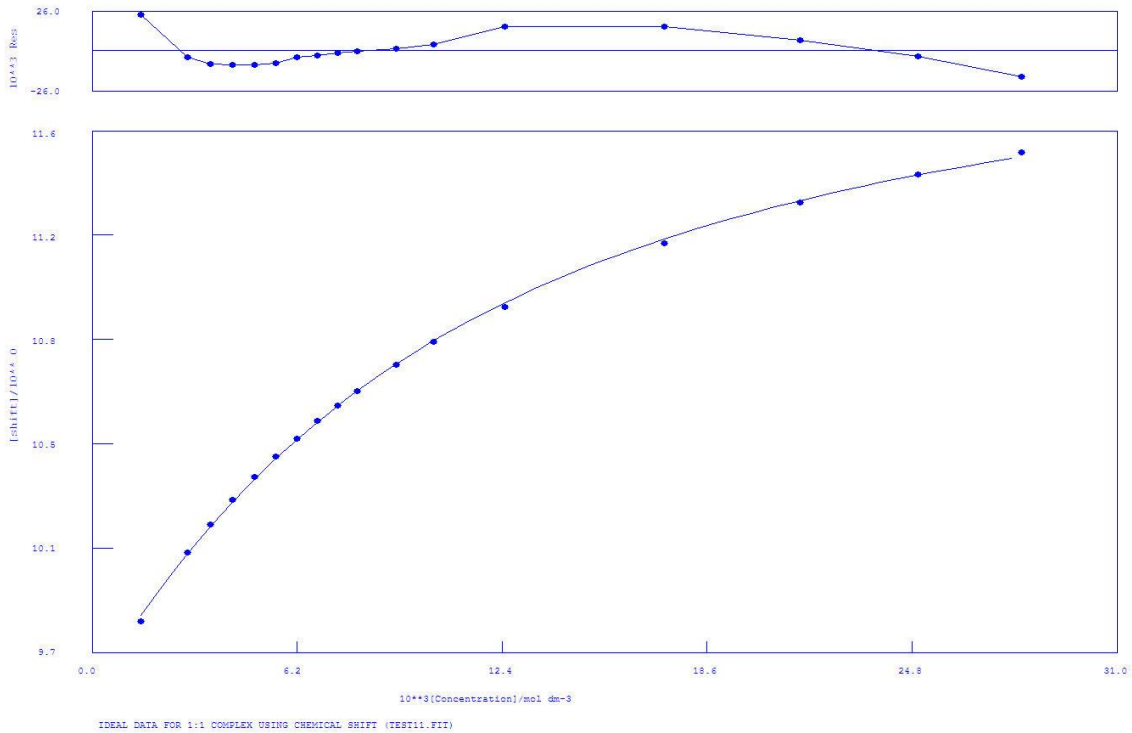

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:21:44   on 06/06/2012

 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  7.71037E+01 2.000E-01 1.590E+00 6.830E+01    K1
   2  1  8.73194E+00 2.000E-01 3.174E-03 6.310E+00   SHIFT M
   3  1  1.05761E+01 1.000E+00 1.407E-02 4.574E+01    SHIFT ML

0RMS ERROR = 3.02E-03  MAX ERROR = 5.99E-03 AT OBS.NO. 10
 RESIDUALS SQUARED = 9.10E-05
 RFACTOR =     0.0281 PERCENT
```

Figure S21 ^{1}H-NMR titration of $\mathbf{L^4}$ with $(TBA)_2Glu$ in DMSO-d_6.



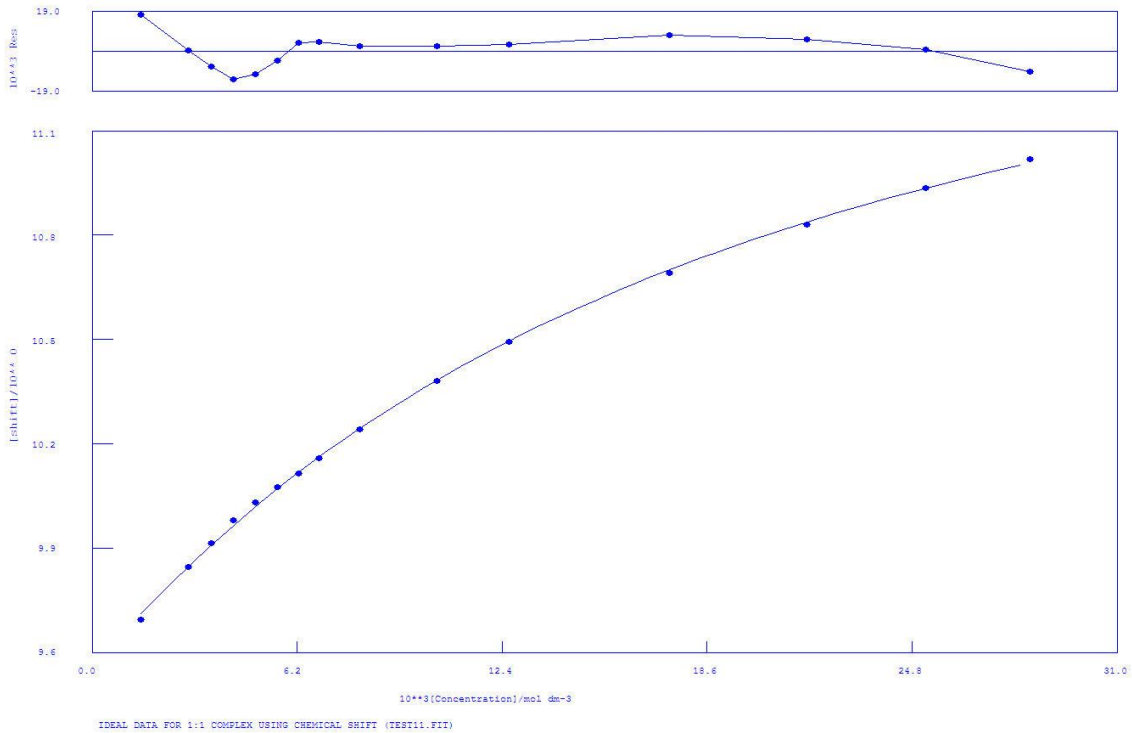

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:48:56   on 06/06/2012

 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  1.21073E+02 2.000E-01 4.592E+00 4.259E+01    K1
   2  1  9.56785E+00 2.000E-01 1.224E-02 7.395E+00   SHIFT M
   3  1  1.21602E+01 1.000E+00 2.839E-02 2.325E+01    SHIFT ML

0RMS ERROR = 1.12E-02  MAX ERROR = 2.33E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 1.77E-03
 RFACTOR =     0.0954 PERCENT
```

Figure S22 ^{1}H-NMR titration of **L**[5] with TBAAcO in DMSO-d_6.



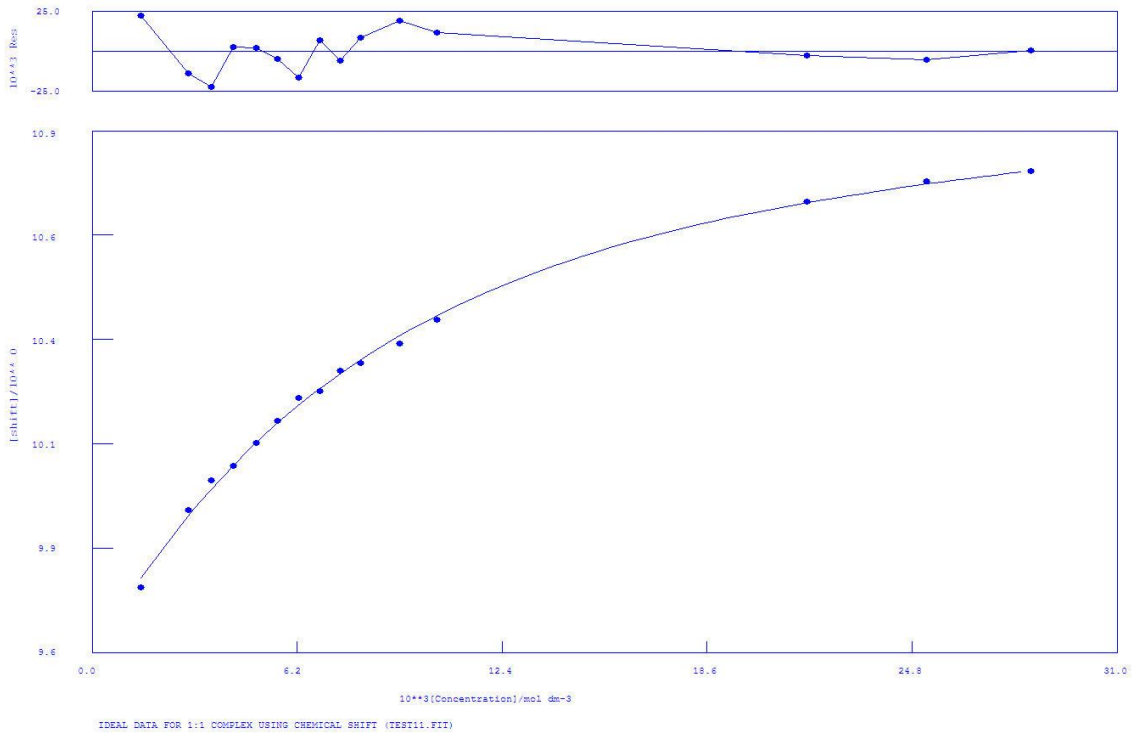

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:03:17   on 06/06/2012

 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  6.03580E+01 2.000E-01 3.150E+00 9.171E+01    K1
   2  1  9.55363E+00 2.000E-01 9.247E-03 8.442E+00   SHIFT M
   3  1  1.19574E+01 1.000E+00 4.975E-02 5.886E+01    SHIFT ML

0RMS ERROR = 8.78E-03  MAX ERROR = 1.72E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 9.25E-04
 RFACTOR =     0.0762 PERCENT
```

Figure S23 ^{1}H-NMR titration of **L**[5] with TBABzO in DMSO-d_6.



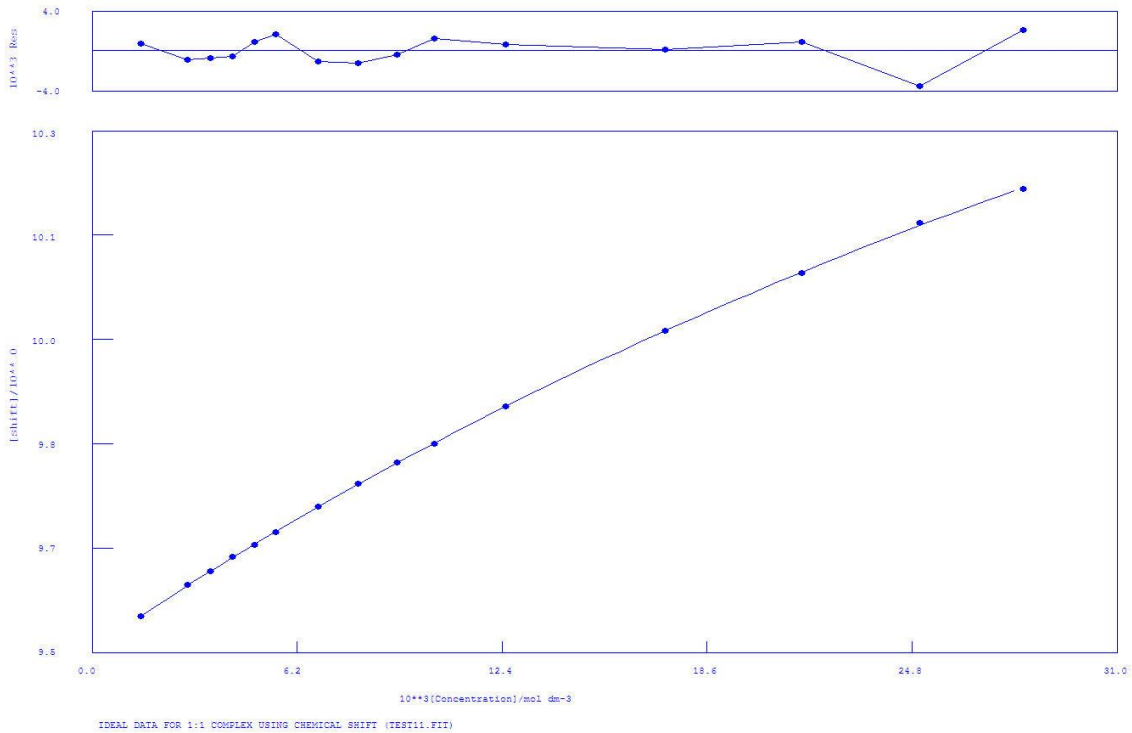

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 14:36:47   on 06/06/2012

 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  1.66748E+02 2.000E-01 1.195E+01 2.979E+01    K1
   2  1  9.59614E+00 2.000E-01 1.690E-02 7.748E+00   SHIFT M
   3  1  1.10940E+01 1.000E+00 2.570E-02 1.365E+01    SHIFT ML

0RMS ERROR = 1.35E-02  MAX ERROR = 2.25E-02 AT OBS.NO.  3
 RESIDUALS SQUARED = 2.18E-03
 RFACTOR =     0.1170 PERCENT
```

Figure S24 ^{1}H-NMR titration of **L**[5] with $TBAH_2PO_4$ in DMSO-d_6.



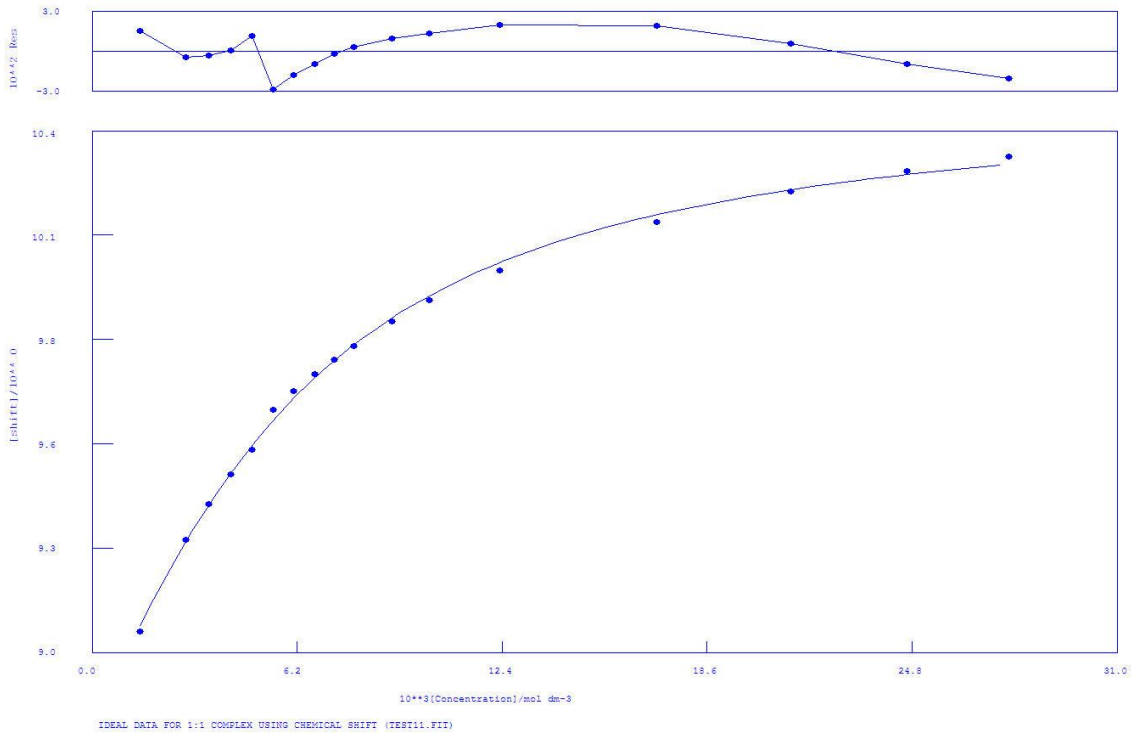

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:26:34   on 06/06/2012

 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  1.52949E+01 2.000E-01 4.882E-01 4.931E+02    K1
   2  1  9.50565E+00 2.000E-01 1.295E-03 8.319E+00   SHIFT M
   3  1  1.19438E+01 1.000E+00 5.325E-02 4.130E+02    SHIFT ML

0RMS ERROR = 1.53E-03  MAX ERROR = 3.52E-03 AT OBS.NO. 14
 RESIDUALS SQUARED = 2.80E-05
 RFACTOR =     0.0139 PERCENT
```

Figure S25 ^{1}H-NMR titration of **L**^{5} with $(TBA)_2Glu$ in DMSO-d_6.



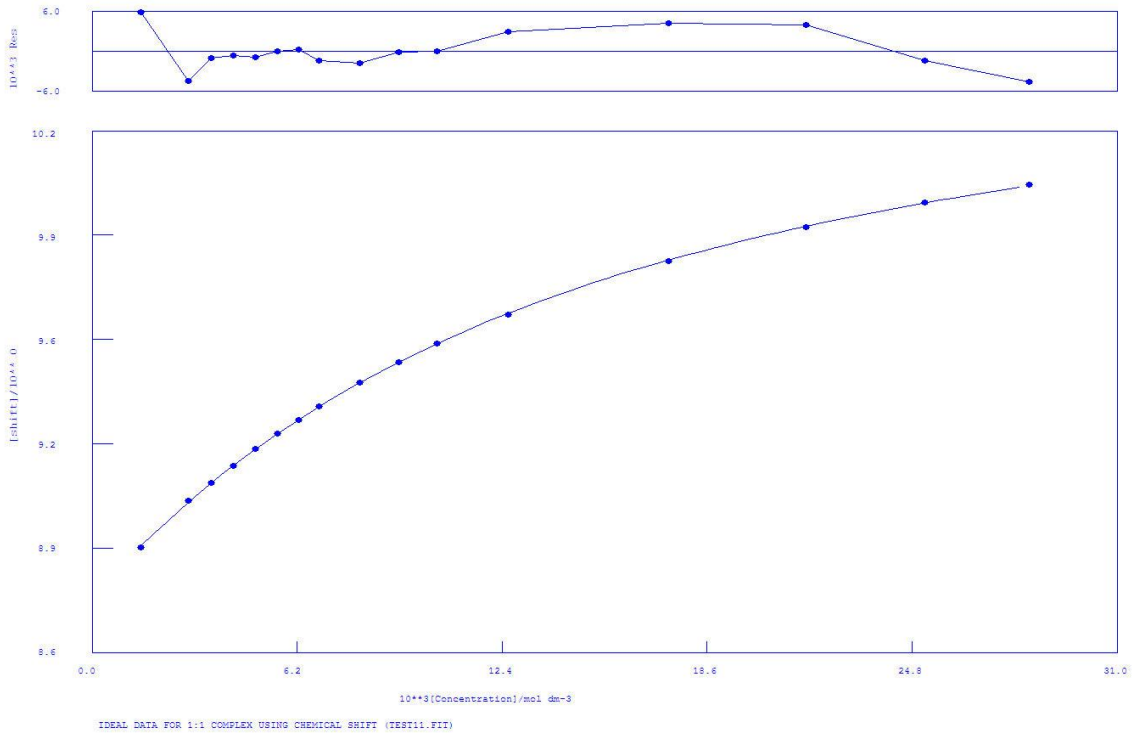

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 11:44:14   on 02/08/2012

 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  2.99470E+02 2.000E-01 1.765E+01 1.905E+01    K1
   2  1  8.79504E+00 2.000E-01 1.701E-02 4.785E+00   SHIFT M
   3  1  1.05260E+01 1.000E+00 1.959E-02 1.045E+01    SHIFT ML

0RMS ERROR = 1.52E-02  MAX ERROR = 2.90E-02 AT OBS.NO.  6
 RESIDUALS SQUARED = 3.22E-03
 RFACTOR =     0.1405 PERCENT
```

Figure S26 ^{1}H-NMR titration of **L^{6}** with TBAAcO in DMSO-*d*$_{6}$.



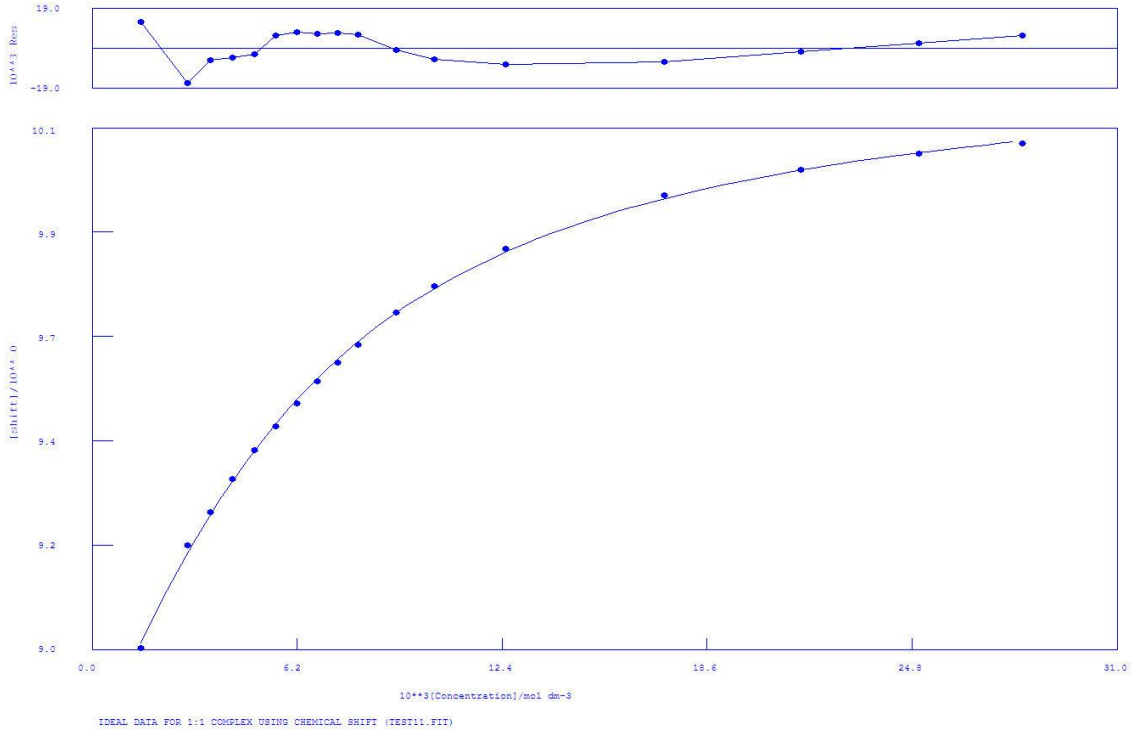

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 17:06:57   on 03/01/2012

 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  8.79467E+01 2.000E-01 1.500E+00 5.130E+01    K1
   2  1  8.77283E+00 2.000E-01 3.254E-03 7.445E+00   SHIFT M
   3  1  1.06041E+01 1.000E+00 1.029E-02 2.960E+01    SHIFT ML

0RMS ERROR = 3.12E-03  MAX ERROR = 5.76E-03 AT OBS.NO.  1
 RESIDUALS SQUARED = 1.26E-04
 RFACTOR =     0.0297 PERCENT
```

Figure S27 ^{1}H-NMR titration of **L**^{6} with TBABzO in DMSO-*d*$_6$.



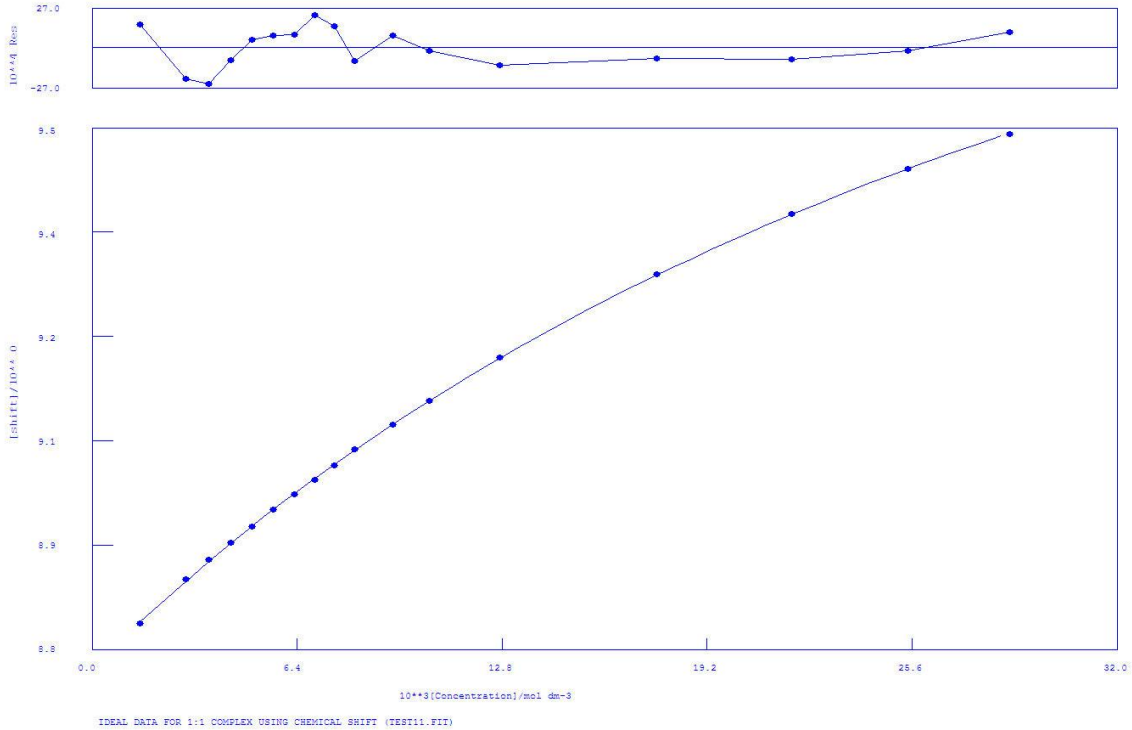

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 12:10:49   on 02/08/2012

 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  2.73005E+02 2.000E-01 1.018E+01 2.087E+01    K1
   2  1  8.78206E+00 2.000E-01 9.409E-03 5.442E+00   SHIFT M
   3  1  1.02701E+01 1.000E+00 1.072E-02 1.076E+01    SHIFT ML

0RMS ERROR = 8.03E-03  MAX ERROR = 1.69E-02 AT OBS.NO.  2
 RESIDUALS SQUARED = 9.02E-04
 RFACTOR =     0.0757 PERCENT
```

Figure S28 ^{1}H-NMR titration of **L**^{6} with $TBAH_2PO_4$ in DMSO-d_6.



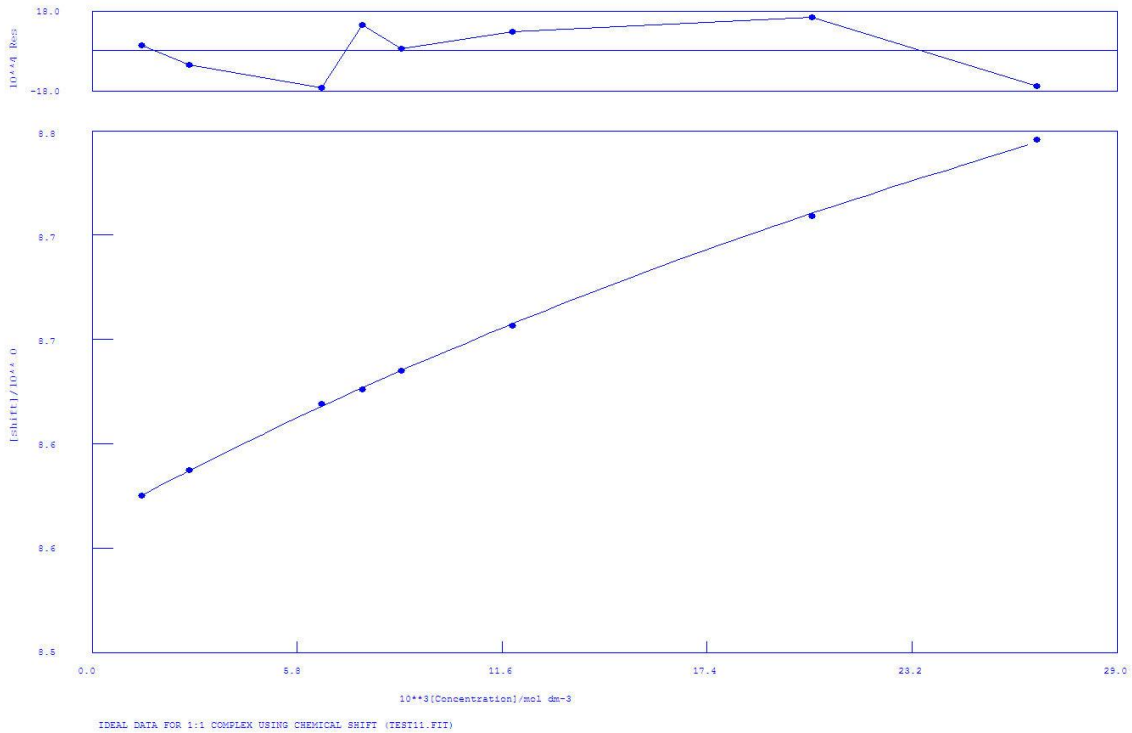

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 16:06:56   on 03/01/2012

 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  3.02974E+01 2.000E-01 5.495E-01 1.614E+02    K1
   2  1  8.77531E+00 2.000E-01 1.252E-03 8.871E+00   SHIFT M
   3  1  1.03904E+01 1.000E+00 1.555E-02 1.151E+02    SHIFT ML

0RMS ERROR = 1.40E-03  MAX ERROR = 2.43E-03 AT OBS.NO.  3
 RESIDUALS SQUARED = 2.74E-05
 RFACTOR =     0.0139 PERCENT
```

Figure S29 ^{1}H-NMR titration of $\mathbf{L}^{6}$ with $(TBA)_2Glu$ in DMSO-d_6.



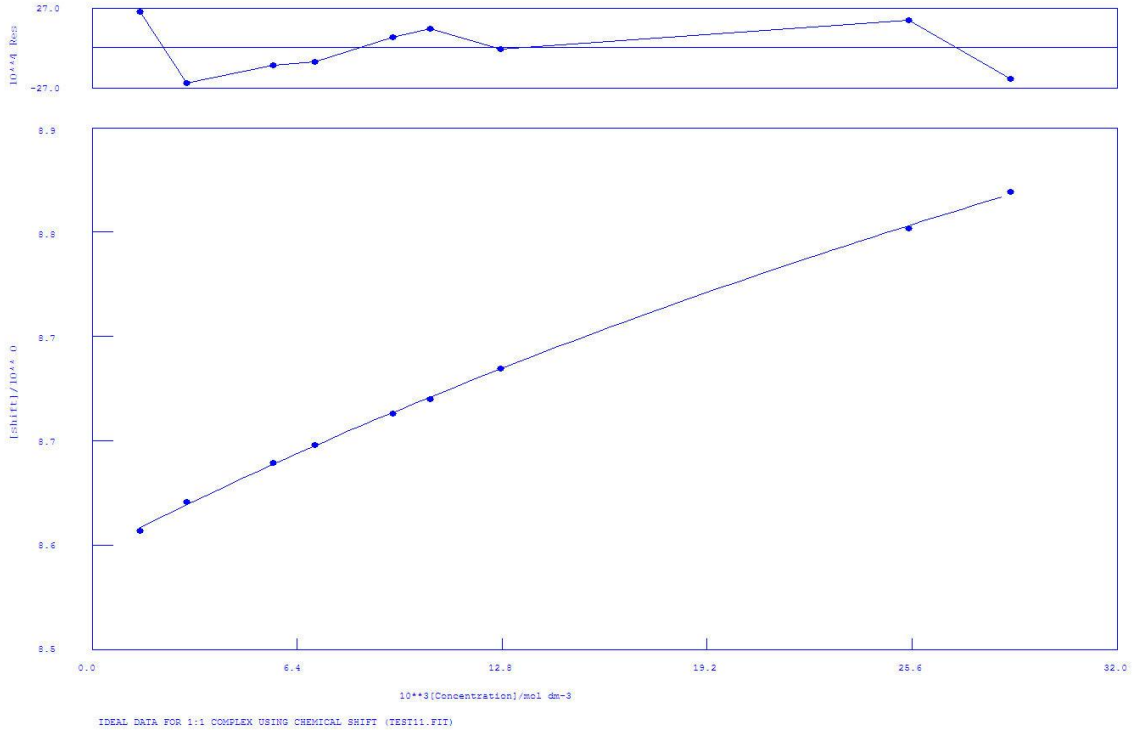

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:22:08   on 07/25/2012

 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  1.47071E+01 2.000E-01 1.452E+00 2.970E+02    K1
   2  1  8.57506E+00 2.000E-01 1.292E-03 5.168E+00   SHIFT M
   3  1  9.37610E+00 1.000E+00 5.472E-02 2.557E+02    SHIFT ML

0RMS ERROR = 1.42E-03  MAX ERROR = 1.65E-03 AT OBS.NO.  3
 RESIDUALS SQUARED = 1.01E-05
 RFACTOR =     0.0129 PERCENT
```

Figure S30 ^{1}H-NMR titration of **L**^{3} with TBAAcO in DMSO-d_6/0.5%H_2O.



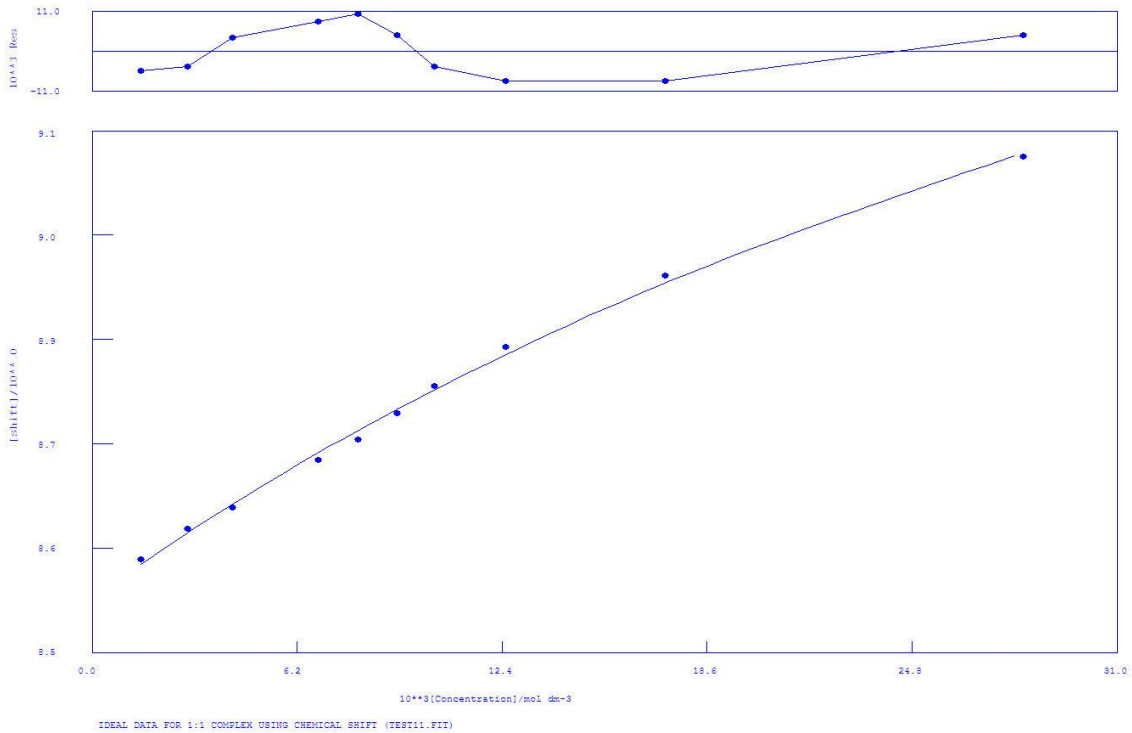

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:29:07   on 07/25/2012

 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  1.14006E+01 2.000E-01 1.607E+00 5.616E+02    K1
   2  1  8.57504E+00 2.000E-01 2.008E-03 7.313E+00   SHIFT M
   3  1  9.71930E+00 1.000E+00 1.117E-01 4.838E+02    SHIFT ML

0RMS ERROR = 1.99E-03  MAX ERROR = 2.45E-03 AT OBS.NO.  1
 RESIDUALS SQUARED = 2.39E-05
 RFACTOR =     0.0187 PERCENT
```

Figure S31 ^{1}H-NMR titration of **L**^{3} with TBABzO in DMSO-d_6/0.5%H_2O.



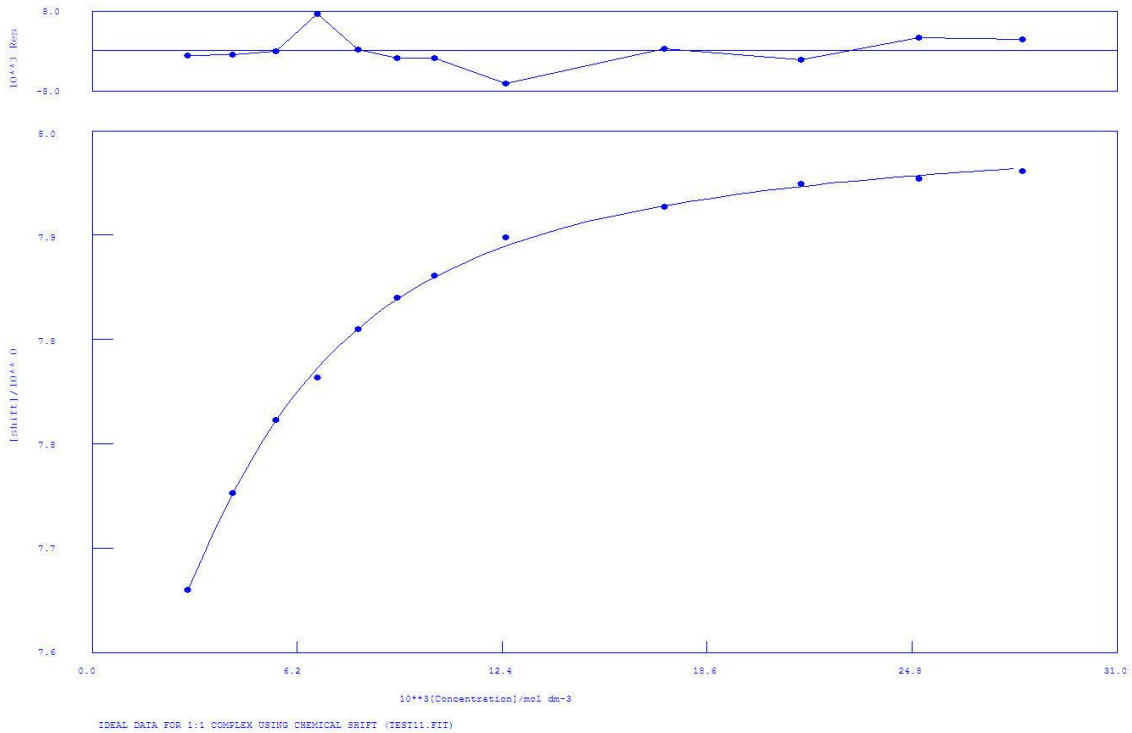

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:34:19   on 07/25/2012

 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  2.07454E+01 2.000E-01 4.325E+00 2.344E+02    K1
   2  1  8.56248E+00 2.000E-01 7.751E-03 7.191E+00   SHIFT M
   3  1  1.00055E+01 1.000E+00 1.895E-01 1.860E+02    SHIFT ML

0RMS ERROR = 7.80E-03  MAX ERROR = 1.02E-02 AT OBS.NO.  5
 RESIDUALS SQUARED = 4.26E-04
 RFACTOR =     0.0743 PERCENT
```

Figure S32 ^{1}H-NMR titration of $\mathbf{L}^{3}$ with $TBAH_2PO_4$ in DMSO-d_6/0.5%H_2O.



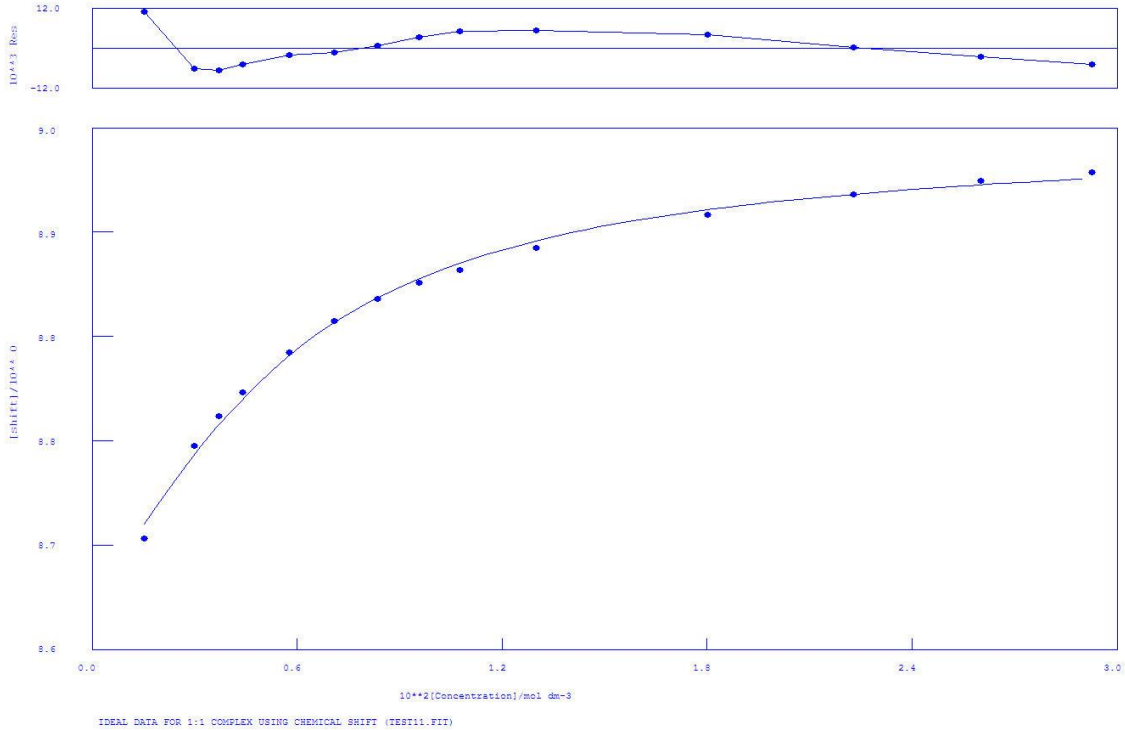

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 17:52:28   on 06/21/2012

 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  5.69754E+02 2.000E-01 3.132E+01 1.634E+01    K1
   2  1  7.43388E+00 2.000E-01 8.033E-03 5.719E+00   SHIFT M
   3  1  8.01066E+00 1.000E+00 3.742E-03 7.258E+00    SHIFT ML

0RMS ERROR = 3.64E-03  MAX ERROR = 7.45E-03 AT OBS.NO.  4
 RESIDUALS SQUARED = 1.19E-04
 RFACTOR =     0.0401 PERCENT
```

Figure S33 ^{1}H-NMR titration of $\mathbf{L}^{3}$ with $(TBA)_3HPpi$ in DMSO-d_6/0.5%H_2O.



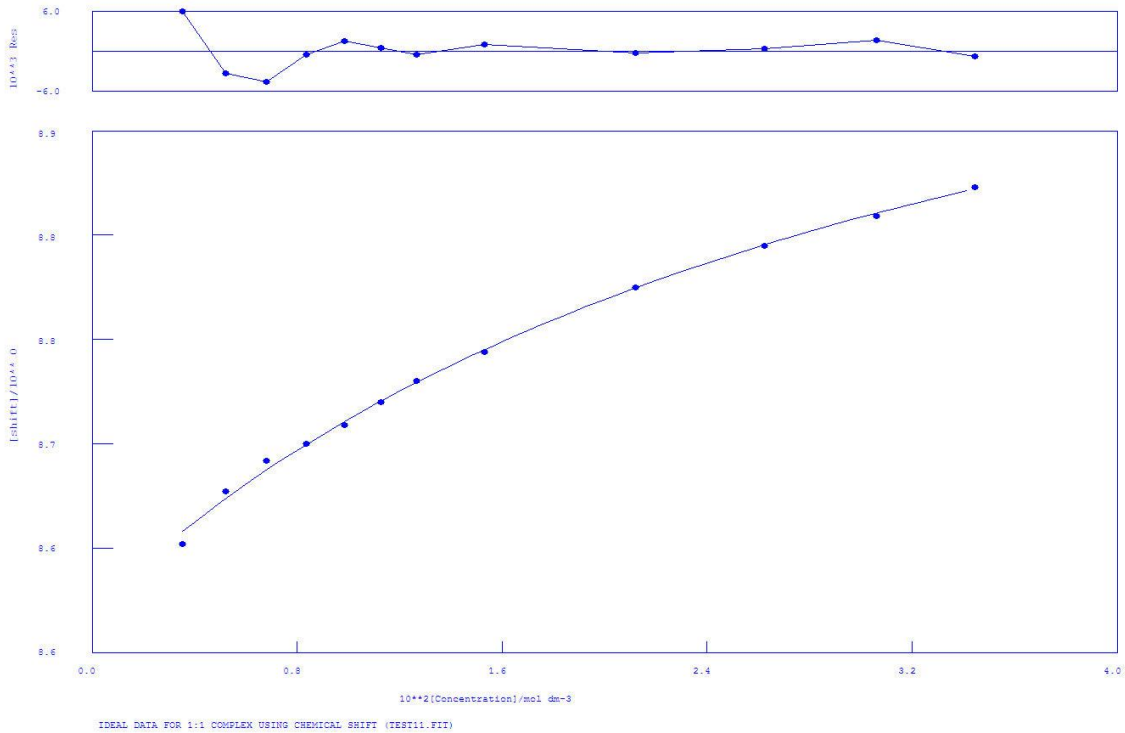

```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 17:41:55   on 06/06/2012

 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  3.68944E+02 2.000E-01 3.693E+01 1.359E+01    K1
   2  1  8.62850E+00 2.000E-01 6.646E-03 3.673E+00   SHIFT M
   3  1  8.99647E+00 1.000E+00 6.268E-03 7.884E+00    SHIFT ML

0RMS ERROR = 5.57E-03  MAX ERROR = 1.08E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 3.41E-04
 RFACTOR =     0.0557 PERCENT
```

Figure S34 ^{1}H-NMR titration of $\mathbf{L}^{3}$ with NaAMP in DMSO-d_6.




```
Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 18:02:50   on 06/21/2012

 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  3.53294E+01 2.000E-01 5.083E+00 1.465E+02    K1
   2  1  8.62097E+00 2.000E-01 3.994E-03 1.175E+01   SHIFT M
   3  1  9.00015E+00 1.000E+00 2.445E-02 9.371E+01    SHIFT ML

0RMS ERROR = 2.88E-03  MAX ERROR = 5.89E-03 AT OBS.NO.  1
 RESIDUALS SQUARED = 7.47E-05
 RFACTOR =     0.0286 PERCENT
```

Figure S35 ^{1}H-NMR titration of $\mathbf{L}^{3}$ with NaAMP in DMSO-d_6/0.5%H_2O.

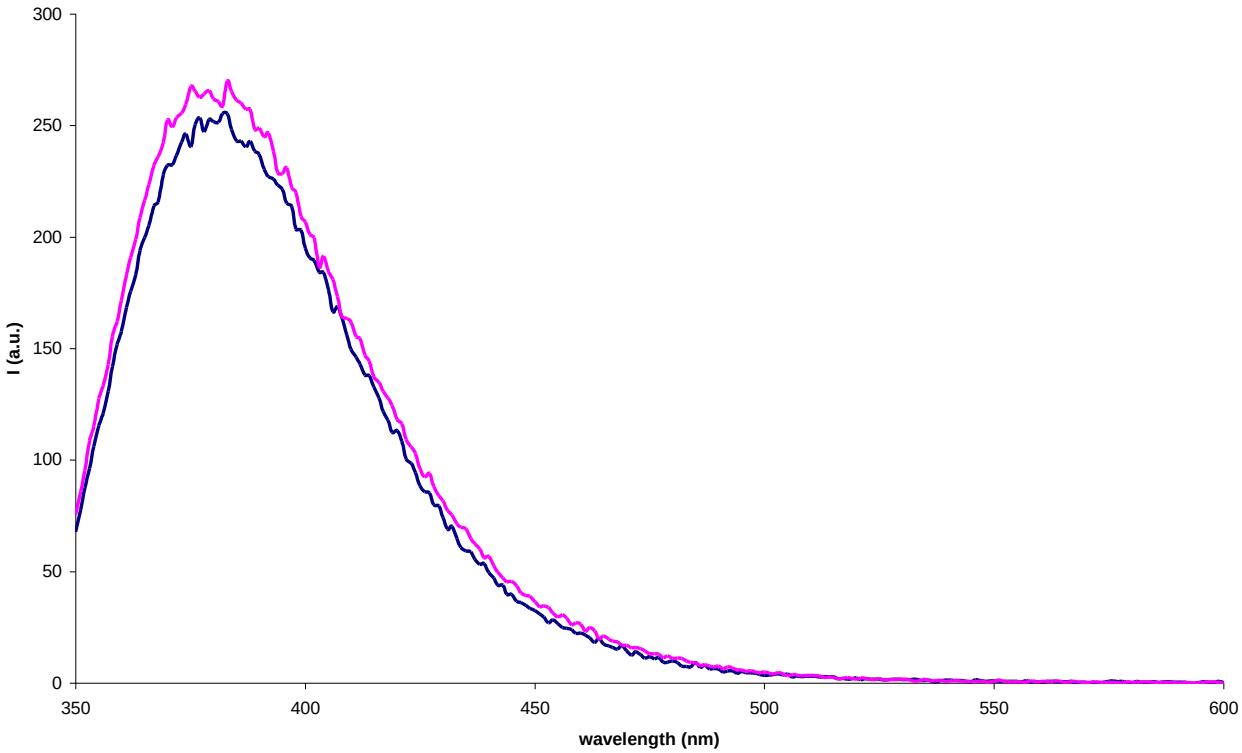


Figure S35 Emission spectra of $\mathbf{L^3}$ ($1.50 \cdot 10^{-4}$ M) (pink line) and of L^3 in the presence of 1 equivalent of TBAOH (blue line) in DMSO.

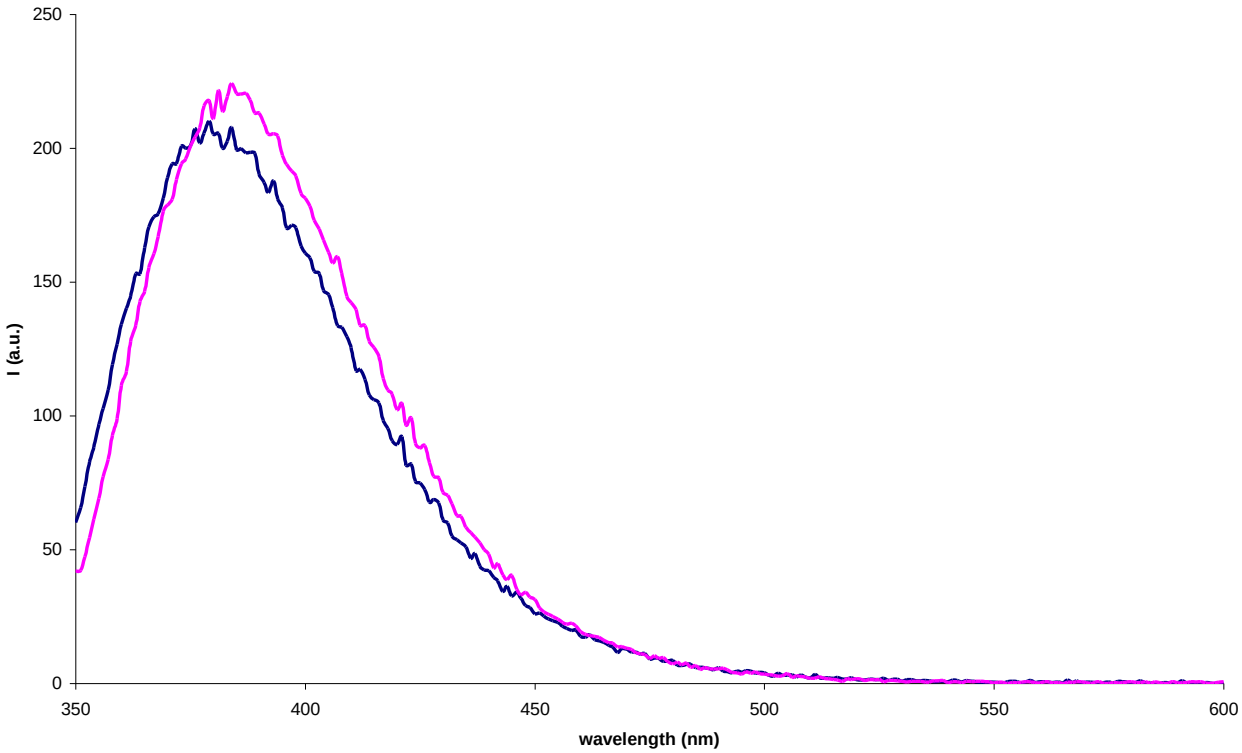


Figure S36 Emission spectra of $\mathbf{L^6}$ ($8.5 \cdot 10^{-5}$ M) (pink line) and of $\mathbf{L^6}$ in the presence of 1 equivalent of TBAOH (blue line) in DMSO.

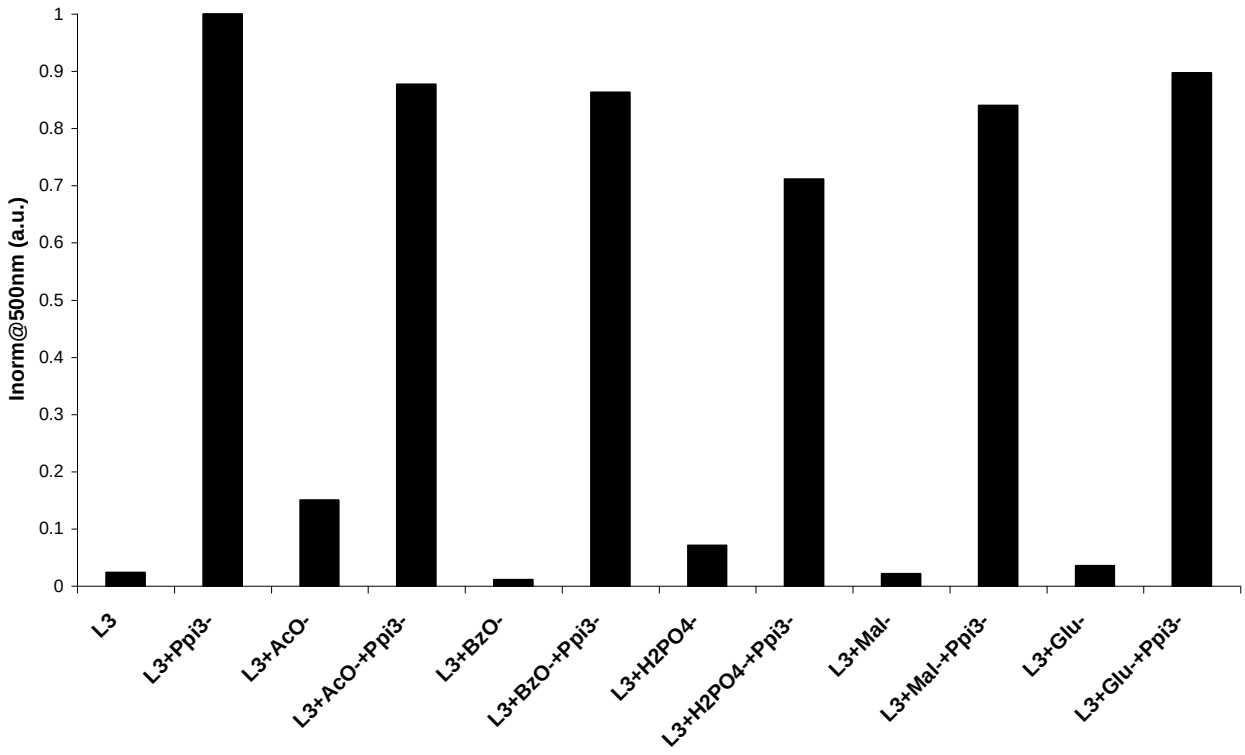


Figure S37 Changes in the intensity emission of $\mathbf{L^3}$ ($1.50 \cdot 10^{-4}$ M)at 500 nm after addition of 10 equivalents of $HPpi^{3-}$ and 20 equivalents of the other anions in DMSO.

Table S1. Crystal data and structure refinement details.

Identification code	**2012acc0042** (MAR94_4 BENZOATO)
Empirical formula	$C_{75}H_{107}N_7O_6$ $C_{29}H_{25}N_5O_2$, 2($C_{16}H_{36}N$), 2($C_7H_5O_2$)
Formula weight	1202.68
Temperature	100(2) K
Wavelength	0.71075 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.623(3) Å b = 41.598(13) Å β = 100.518(5)° c = 19.413(6) Å
Volume	6846(4) Å^3
Z	4
Density (calculated)	1.167 Mg / m^3
Absorption coefficient	0.074 mm^{-1}
$F(000)$	2616
Crystal	Rod; Colourless
Crystal size	0.22 × 0.04 × 0.02 mm^3
θ range for data collection	2.94 – 25.03°
Index ranges	$-10 \le h \le 9$, $-49 \le k \le 44$, $-13 \le l \le 23$
Reflections collected	26420
Independent reflections	12037 [R_{int} = 0.0798]
Completeness to θ = 25.03°	99.5 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.9985 and 0.9840
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12037 / 0 / 801
Goodness-of-fit on F^2	1.196
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.1018, $wR2$ = 0.1504
R indices (all data)	$R1$ = 0.1606, $wR2$ = 0.1762
Largest diff. peak and hole	0.384 and –0.249 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, Data collection, Data reduction and cell refinement & Absorption correction**: CrystalClear-SM Expert 2.0 r7 (Rigaku, 2011) , **Structure solution**: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). **Structure refinement**: SHELXL97 (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** CrystalMaker: a crystal and molecular structures program for Mac and Windows. CrystalMaker Software Ltd, Oxford, England (www.crystalmaker.com)

Table S2. Hydrogen bonds [Å and °].

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
N1–H901···O3	0.88	1.94	2.816(4)	171.9
N2–H902···O4	0.88	1.95	2.809(4)	166.1
N4–H904···O5	0.88	1.96	2.831(4)	170.1
N5–H905···O6	0.88	1.91	2.760(4)	161.6