Supplementary Material (ESI) for Chemical Communications

Metal-induced pre-organization for anion recognition in a neutral platinum-containing receptor

Claudia Caltagirone,* Andrea Mulas, Francesco Isaia, Vito Lippolis, Philip A. Gale and Mark E. Light

All reactions were performed in oven-dried glassware under a slight positive pressure of nitrogen. 2,2′-bipyridine-4,4′-dicarbonyl dichloride,[1] 7-aminoindole[2] and the complex *cis*-$[PtCl_2(DMSO)_2]$ [3] were synthesised following a literature procedure. ^{1}H-NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were determined on a Bruker AV300 spectrometer. ^{31}P-NMR (121 MHz) and ^{195}Pt NMR (64 MHz) were recorded on a Varian VXR-300 and the chemical shifts were recorded in ppm relative to H_3PO_4, 85% in water and K_2PtCl_6 in water, respectively. 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 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). UV-Vis spectra were recorded on a Thermo Nicolet Evolution 300 spectrophotometer. 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 (0.15 M) in a solution of the receptor (0.01M) in DMSO-d_6/0.5% water to a solution of the receptor (0.01M).

[1] Uppadine L. H., Keene F. R., Beer P. D., *Journal of the Chemical Society, Dalton Trans.*, 2001, **14**, 2188.

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

[3] Price J. H., Williamson A. N., Schramm R. S., Wayland B. B., *Inorg. Chem.*, 1972, **11**, 1280.

Synthesis of 4,4′-dicarboxamido-di(indol-7-yl)-2,2′-bipyridine 1

To a solution of 7-aminoindole (0.342 g, 2.59 mmol) in THF (15 mL) a solution of 2,2′-dipyridyl-4,4′-dicarbonyl dichloride (0.365 g, 1.30 mmol) in THF (75 mL) was added dropwise in the presence of 1.5 mL of triethylamine and a catalytic amount of DMAP. The reaction mixture was heated at 50°C under N_2 for 36 h. It was then filtered, and the solvent removed under reduced pressure. The residue (a brown oil) was dissolved in CH_2Cl_2 and washed with diethyl ether to precipitate the compound as a light brown powder. The solid was washed with CH_2Cl_2 (200 mL), filtered and dried under vacuum. Yield: 58% (0.356 g, 0.75 mmol). M.p. over 250°C; ^{1}H-NMR (300 MHz, DMSO-d_6, 298 K): δ_H 6.4-6.6 (m, 2H); 7.04 (t, J=7.68 Hz, 2H); 7.33 (d, J=7.32 Hz, 2H); 7.34-7.42 (m, 2H); 7.48 (d, J=8.04 Hz, 2H); 8.03-8.18 (m, 2H); 8.99 (d, J=5.10 Hz, 2H); 9.04 (s, 2H); 10.64 (s, 2H, NH amide); 10.97 (s, 2H, NH indole). ^{13}C-NMR (75 MHz, DMSO-d_6, 298 K): δ_C 101.47 (CH); 116.41 (CH); 117.95 (CH); 118.73 (CH); 119.00 (CH); 122.39 (C); 122.53 (CH); 125.35 (CH); 129.29 (C); 130.06 (C); 143.41 (C); 150.06 (CH); 155.53 (C); 163.97 (C). IR (KBr disk, cm^{-1}) ν = 3423, 3200 (s, NH stretching), 1650 (s, CO stretching); LRMS (ESI$^-$, m/z): 471.1 [M-H]$^-$. Elemental analysis: found (calculated for $C_{28}H_{20}N_6O_2$): C 71.21 (71.19); H 4.87 (4.24); N 17.78 (17.80).

Synthesis of 4,4′-dicarboxamido-di(indol-7-yl)-2,2′-bipyridine dichloro platinum (II) 2

To a solution of **1** (87.5 mg, 0.185 mmol) in MeCN (25 mL) [$PtCl_2(DMSO)_2$]*cis* (78.2 mg, 0.185 mmol) was added and the reaction mixture was refluxed under N_2 overnight. It was then filtered to give the desired compound as a brown orange solid. Yield: 75% (0.102 g, 0.139 mmol). M.p. over 250°C; ^{1}H-NMR (300 MHz, DMSO-d_6, 298 K): δ_H 6.4-6-6 (m, 2H); 7.05 (t, J=7.05 Hz, 2H); 7.32 (d, J=7.17 Hz, 2H); 7.35-7.45 (m, 2H); 7.50 (d, J=7.53 Hz, 2H); 8.44 (m, 2H); 9.20 (s, 2H); 9.77 (d, J=6.03 Hz, 2H); 10.82 (s, 2H, NH amide); 11.01 (s, 2H, NH indole). ^{13}C-NMR (75 MHz, DMSO-d_6, 298 K): δ_C 101.67 (CH); 116.37 (CH); 118.41 (CH); 118.83 (CH); 119.58 (CH); 121.79 (C); 123.50 (CH); 125.46 (CH); 129.33 (C); 130.00 (C); 149.01 (C); 150.67 (CH); 156.95 (C); 161.96 (C) IR (KBr disk, cm^{-1}): ν = 3386, 3344 (s, NH stretching), 1670 (s, CO stretching); LRMS (ESI$^-$, m/z): 736.1 [M-H]$^-$. Elemental analysis: found (calculated for $C_{28}H_{20}N_6O_2PtCl_2$): C 45.93 (45.54); H 2.62 (2.73); N 11.42 (11.38).

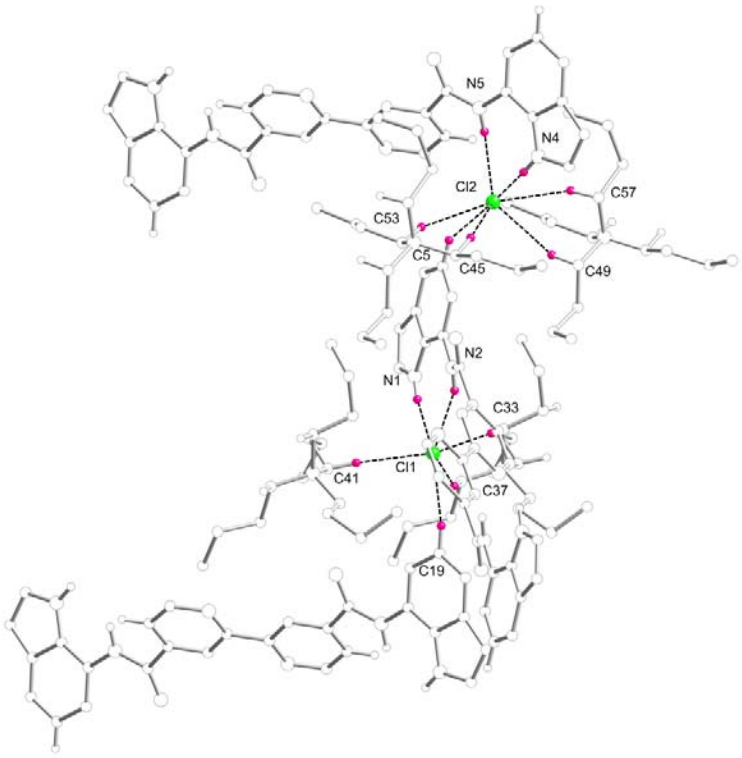
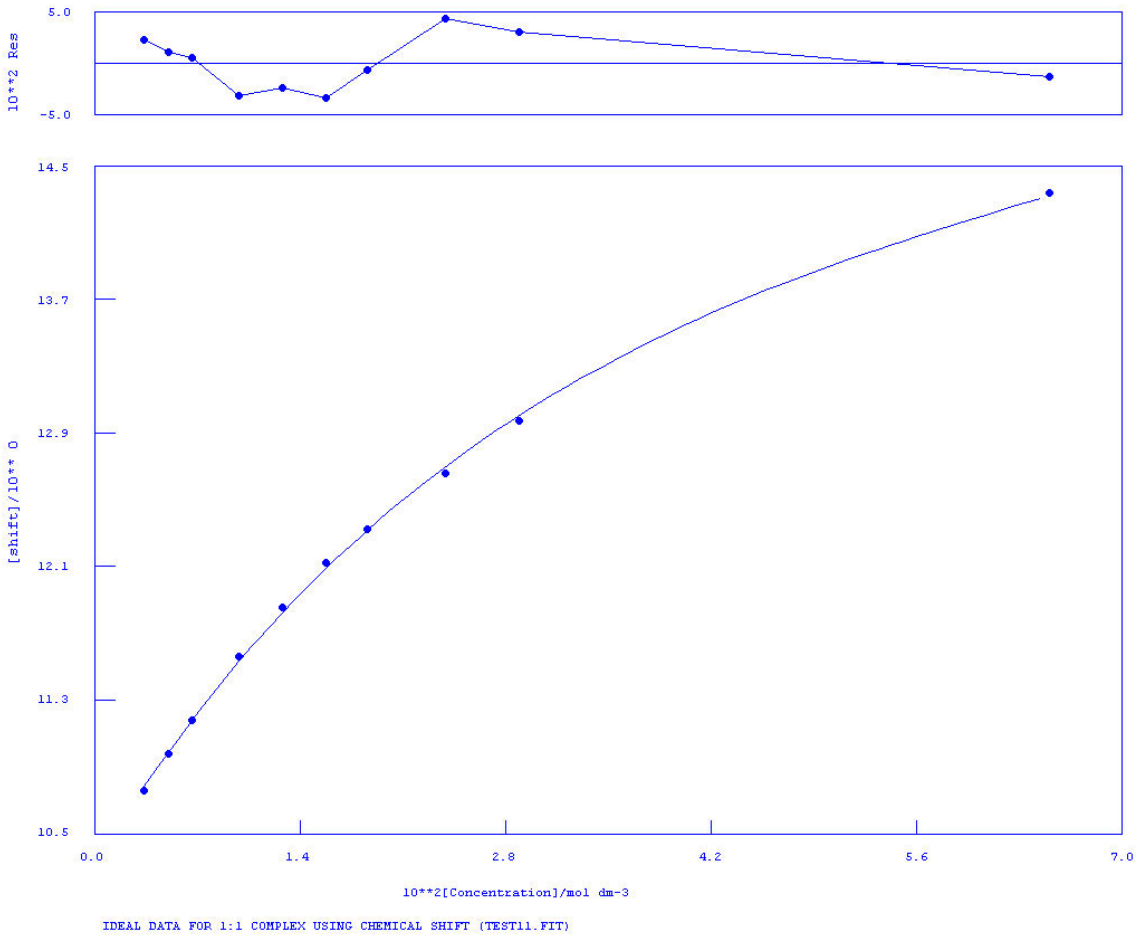


Figure S5 Hydrogen bonding environment in the crystal structure of compound **1** with chloride around Cl1 and Cl2. Additional C-H···O hydrogen bonds and contacts extend the structure into a 3D lattice.

Table S1. Hydrogen bonds and short contacts [Å and °] in the chloride complex of **1**.

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
N1-H901···Cl1	0.88	2.21	3.083(8)	169.3
N2-H902···Cl1	0.88	2.42	3.249(8)	157.3
N4-H904···Cl2^{ii}	0.88	2.21	3.064(8)	164.6
N5-H905···Cl2^{ii}	0.88	2.45	3.315(8)	169.4
C5-H5···Cl2^{i}	0.95	2.80	3.569(10)	139.4
C6-H6···O1	0.95	2.36	2.898(12)	116.2
C11-H1···N3^{i}	0.95	2.49	2.808(12)	100.9
C19-H19···Cl1	0.95	2.68	3.524(11)	148.0
C20-H20···O2	0.95	2.29	2.885(12)	120.3
C33-H33B···Cl1^{iii}	0.99	2.72	3.651(10)	157.3
C37-H37A···Cl1^{iii}	0.99	2.74	3.601(11)	146.9
C41-H41A···Cl1	0.99	2.70	3.680(10)	172.5
C45-H45A···Cl2	0.99	2.76	3.697(10)	158.4
C45-H45B···O1^{i}	0.99	2.37	3.338(13)	167.3
C49-H49B···Cl2^{iv}	0.99	2.75	3.672(10)	155.9
C50-H50B···O1^{i}	0.99	2.58	3.276(14)	127.5
C53-H53A···Cl2	0.99	2.77	3.711(10)	159.2
C57-H57B···Cl2^{iv}	0.99	2.78	3.682(10)	152.1

Symmetry transformations used to generate equivalent atoms:
(i) = 1-x,1-y,1-z (ii) = 1-x,-y,1-z (iii) = -1+x,y,z (iv) = 1+x,y,z

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Program run at 10:50:39   on 03/05/2009

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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
   1  1  3.15279E+01 2.000E-01 1.924E+00 4.187E+01    K1
   2  1  1.03120E+01 2.000E-01 3.047E-02 5.478E+00   SHIFT M
   3  1  1.65012E+01 1.000E+00 1.499E-01 2.653E+01    SHIFT ML

0RMS ERROR = 3.02E-02  MAX ERROR = 4.28E-02 AT OBS.NO.  8
 RESIDUALS SQUARED = 6.40E-03
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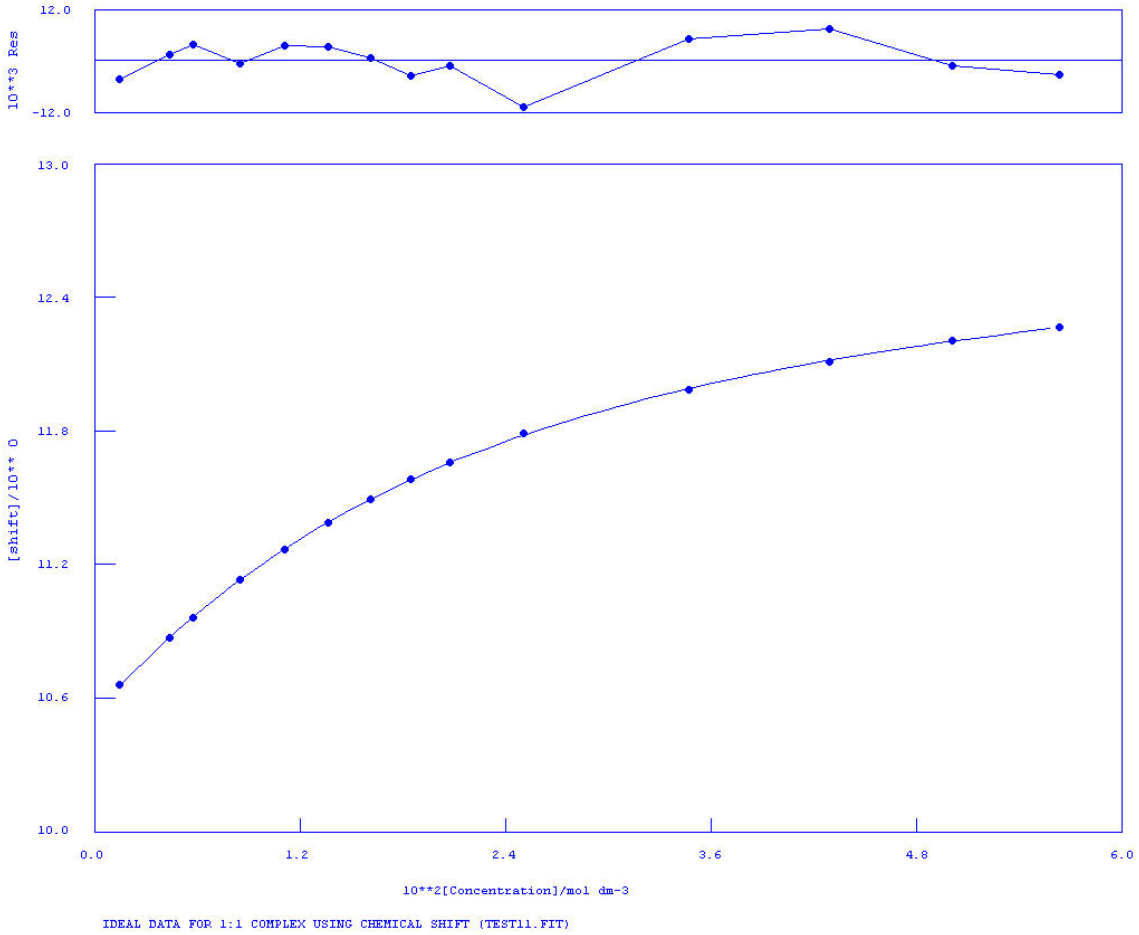
Figure S6 Proton NMR titration of compound **1** with TBAF in DMSO-d_6/0.5% water.

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Program run at 10:14:58   on 03/05/2009

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 FILE: TEST11.FIT
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 File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  5.81803E+01 2.000E-01 1.062E+00 3.131E+01    K1
   2  1  1.05346E+01 2.000E-01 4.521E-03 4.166E+00   SHIFT M
   3  1  1.28712E+01 1.000E+00 1.312E-02 2.092E+01    SHIFT ML

0RMS ERROR = 5.08E-03  MAX ERROR = 1.10E-02 AT OBS.NO. 10
 RESIDUALS SQUARED = 2.84E-04
 RFACTOR =     0.0390 PERCENT
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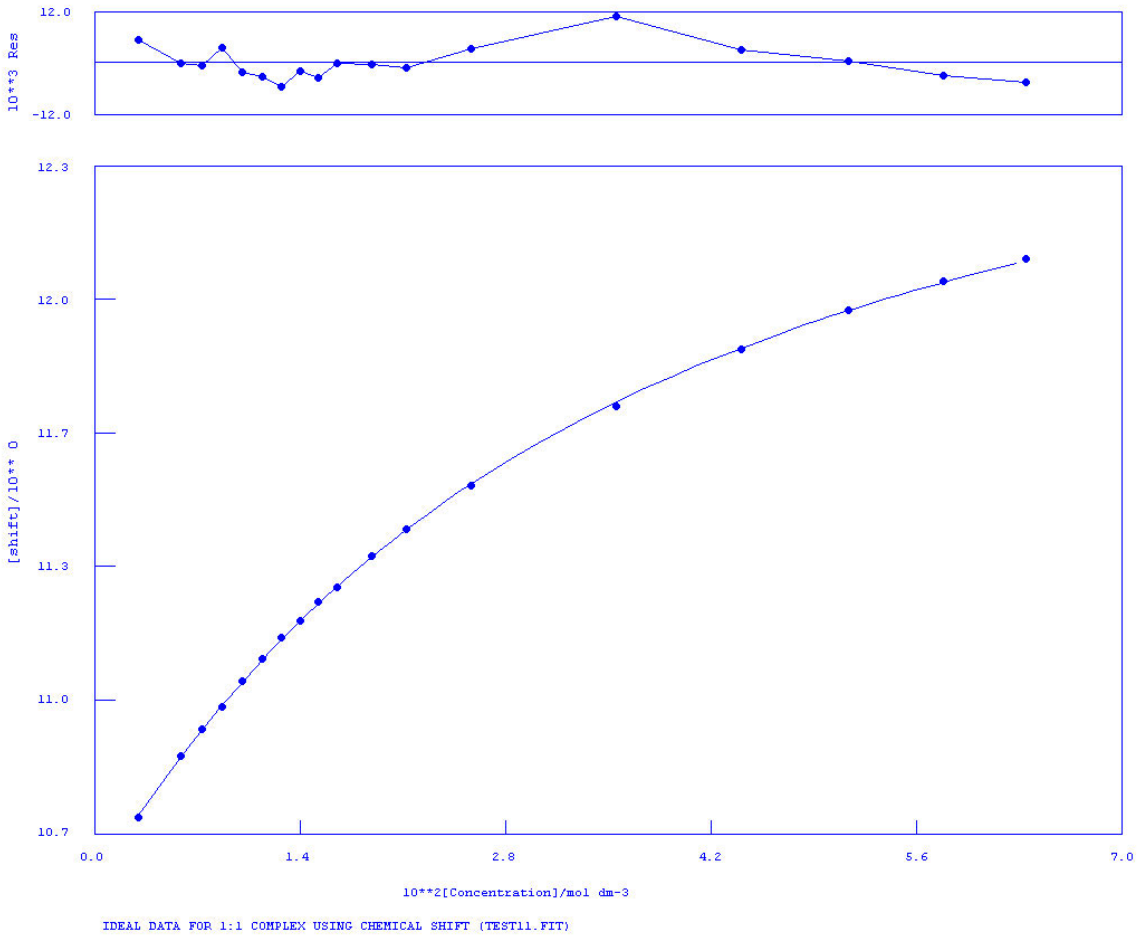
Figure S7 Proton NMR titration of compound **1** with TBAOAc in DMSO-d_6/0.5% water.

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Program run at 14:52:27   on 03/05/2009

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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  3.46749E+01 2.000E-01 6.495E-01 5.766E+01    K1
   2  1  1.05794E+01 2.000E-01 4.228E-03 8.041E+00   SHIFT M
   3  1  1.28269E+01 1.000E+00 1.469E-02 3.317E+01    SHIFT ML

0RMS ERROR = 4.25E-03  MAX ERROR = 1.09E-02 AT OBS.NO. 14
 RESIDUALS SQUARED = 2.71E-04
 RFACTOR =     0.0341 PERCENT
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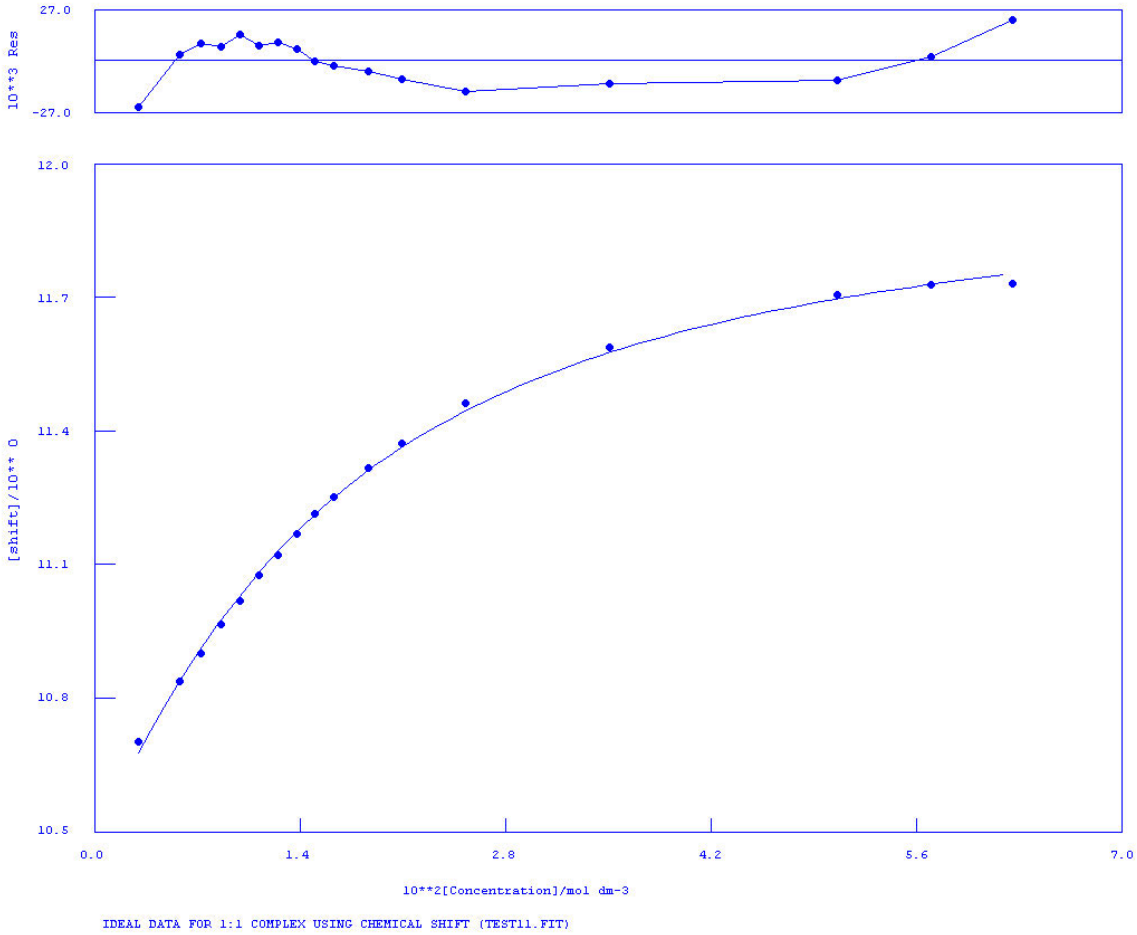
Figure S8 Proton NMR titration of compound **1** with TBAOBz in DMSO-d_6/0.5% water.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 15:11:29   on 03/05/2009

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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  9.01778E+01 2.000E-01 5.129E+00 2.396E+01    K1
   2  1  1.04783E+01 2.000E-01 1.398E-02 6.041E+00   SHIFT M
   3  1  1.20118E+01 1.000E+00 1.973E-02 1.204E+01    SHIFT ML

0RMS ERROR = 1.26E-02  MAX ERROR = 2.42E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 2.24E-03
 RFACTOR =     0.1020 PERCENT
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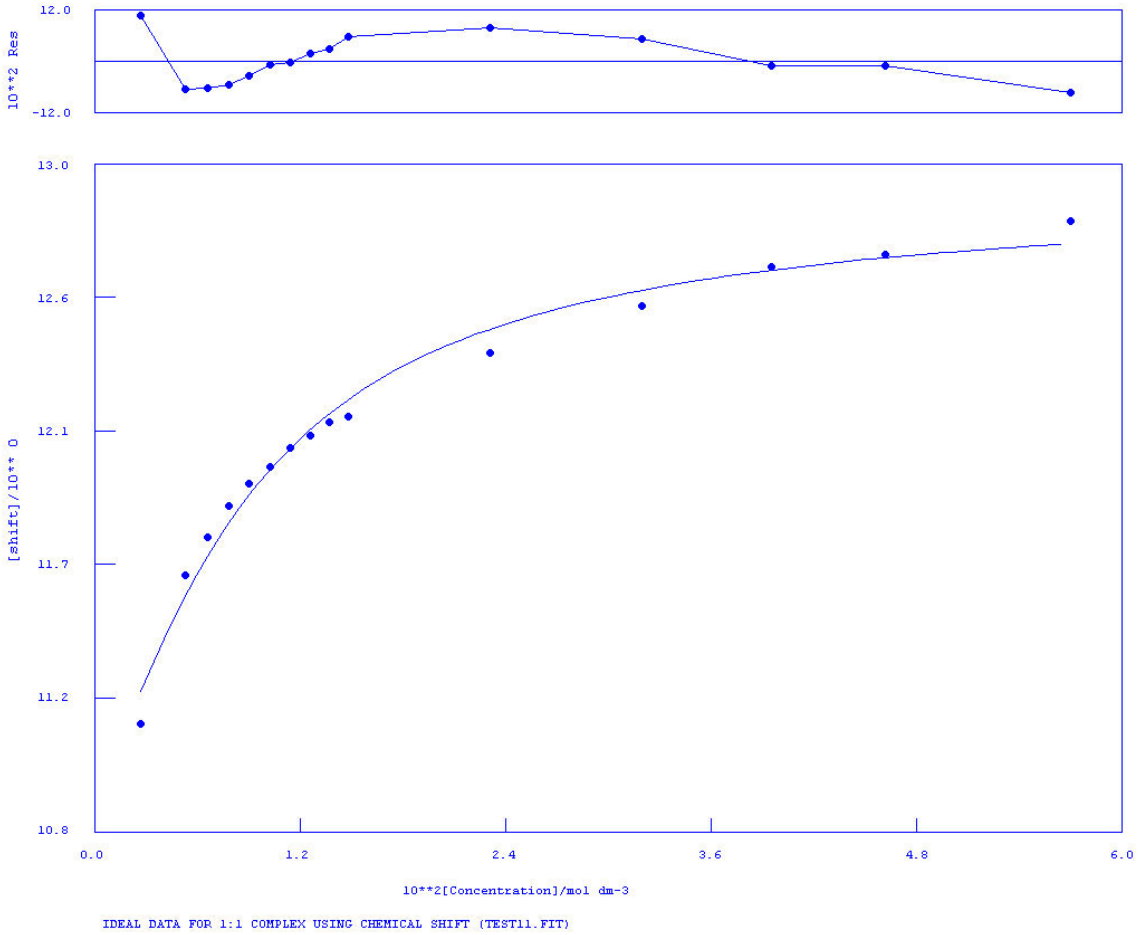
Figure S9 Proton NMR titration of compound **1** with $TBAH_2PO_4$ in DMSO-d_6/0.5% water.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 09:28:46   on 03/17/2009

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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  1.88796E+02 2.000E-01 3.556E+01 1.643E+01    K1
   2  1  1.08438E+01 2.000E-01 8.892E-02 6.327E+00   SHIFT M
   3  1  1.29327E+01 1.000E+00 6.112E-02 6.651E+00    SHIFT ML

0RMS ERROR = 5.95E-02  MAX ERROR = 1.06E-01 AT OBS.NO.  1
 RESIDUALS SQUARED = 4.24E-02
 RFACTOR =     0.4382 PERCENT
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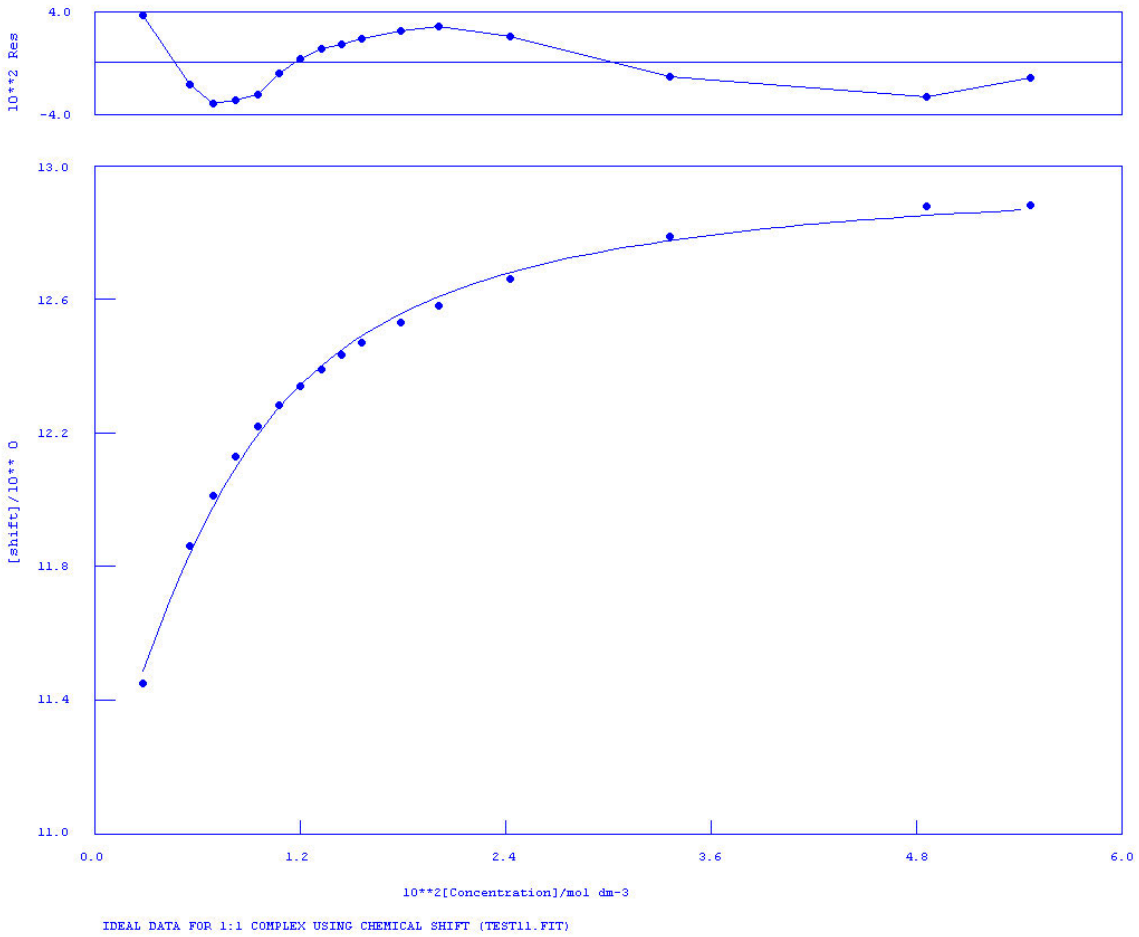
Figure S10 Proton NMR titration of compound **2** with TBAOAc in DMSO-d_6/0.5% water.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
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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  2.80122E+02 2.000E-01 2.443E+01 1.872E+01    K1
   2  1  1.10167E+01 2.000E-01 4.161E-02 6.473E+00   SHIFT M
   3  1  1.30055E+01 1.000E+00 2.424E-02 7.937E+00    SHIFT ML

0RMS ERROR = 2.42E-02  MAX ERROR = 3.69E-02 AT OBS.NO.  1
 RESIDUALS SQUARED = 7.63E-03
 RFACTOR =     0.1765 PERCENT
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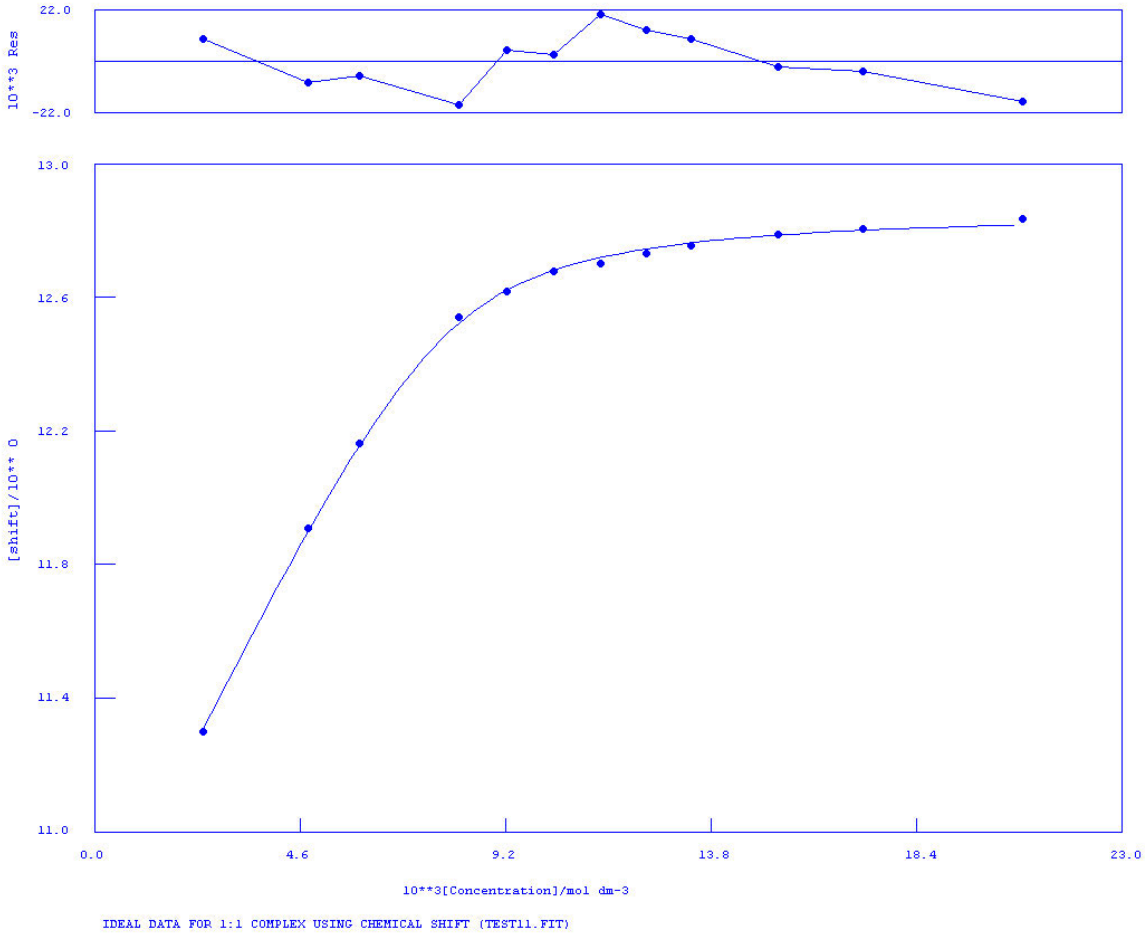
Figure S11 Proton NMR titration of compound **2** with TBAOBz in DMSO-d_6/0.5% water.

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

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  3.64407E+03 2.000E-01 3.063E+02 6.116E+00    K1
   2  1  1.06580E+01 2.000E-01 1.661E-02 1.323E+00   SHIFT M
   3  1  1.28607E+01 1.000E+00 1.077E-02 5.770E+00    SHIFT ML

0RMS ERROR = 1.33E-02  MAX ERROR = 1.99E-02 AT OBS.NO.  7
 RESIDUALS SQUARED = 1.58E-03
 RFACTOR =     0.0919 PERCENT
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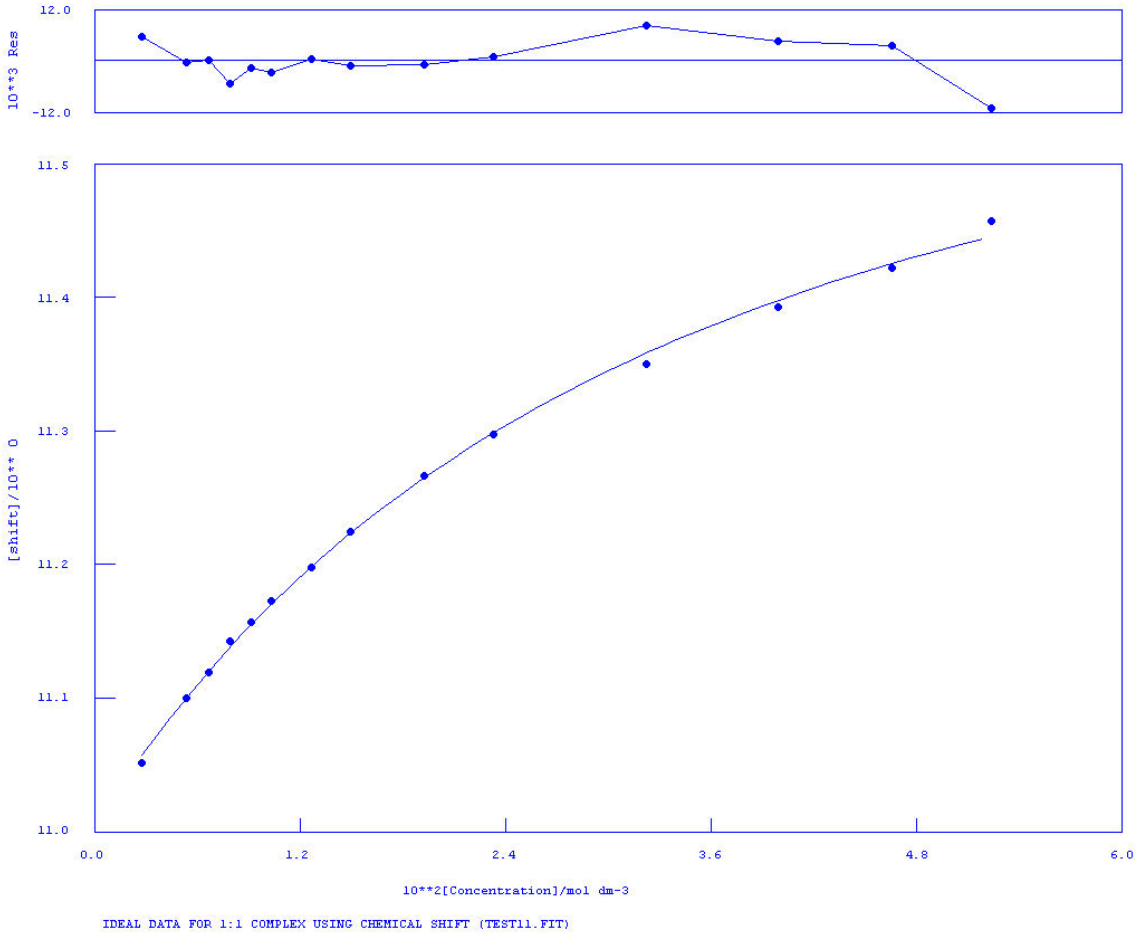
Figure S12 Proton NMR titration of compound **2** with $TBAH_2PO_4$ in DMSO-d_6/0.5% water.

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Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 17:23:39   on 03/17/2009

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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
   1  1  3.68298E+01 2.000E-01 3.284E+00 6.278E+01    K1
   2  1  1.10071E+01 2.000E-01 5.477E-03 7.398E+00   SHIFT M
   3  1  1.16974E+01 1.000E+00 2.265E-02 3.849E+01    SHIFT ML

0RMS ERROR = 5.18E-03  MAX ERROR = 1.11E-02 AT OBS.NO. 14
 RESIDUALS SQUARED = 2.96E-04
 RFACTOR =     0.0409 PERCENT
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Figure S13 Proton NMR titration of compound **2** with TBACl in DMSO-d_6/0.5% water.

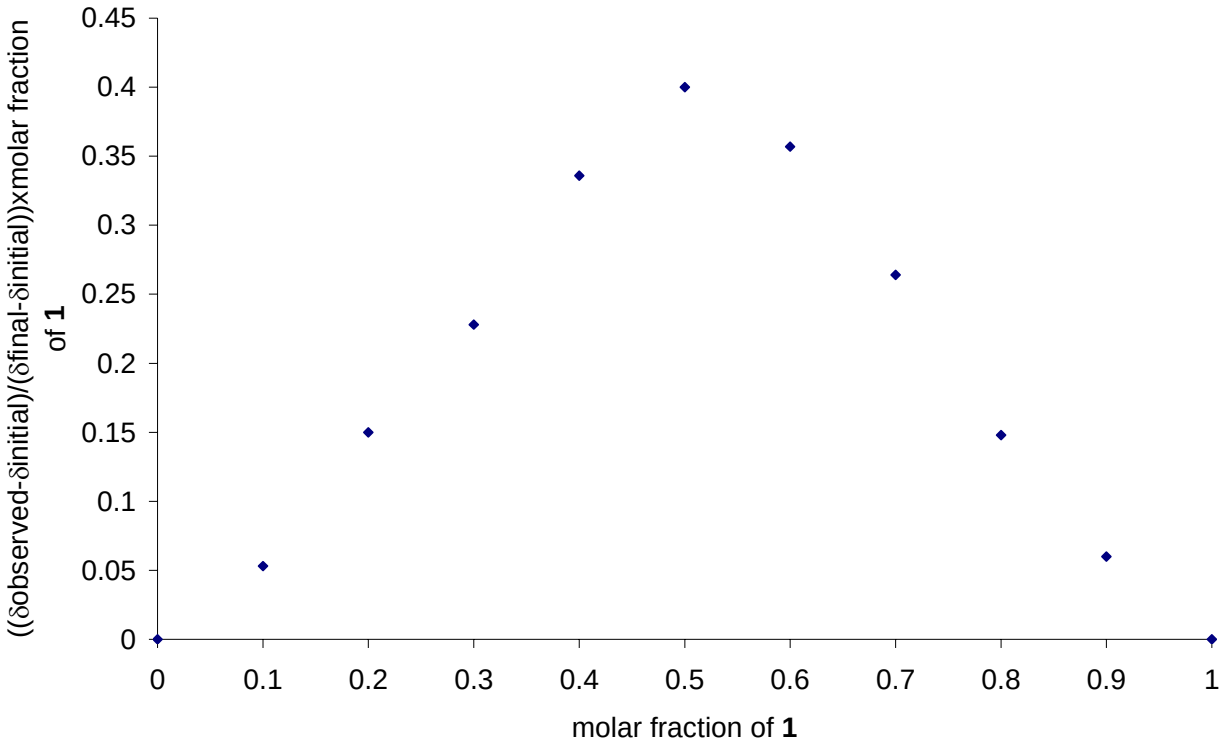

Figure S14 Job plot of **1** with TBAF in DMSO-d_6/0.5% water.

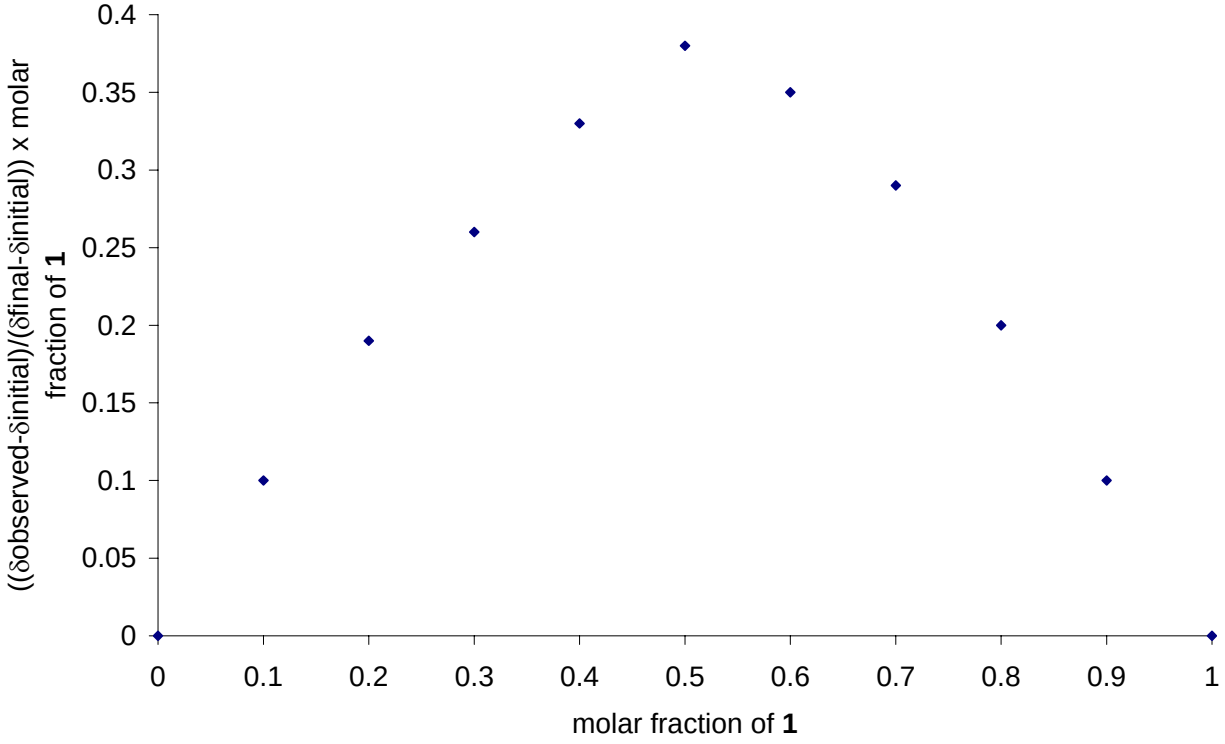

Figure S15 Job plot of **1** with TBAOAc in DMSO-d_6/0.5% water.

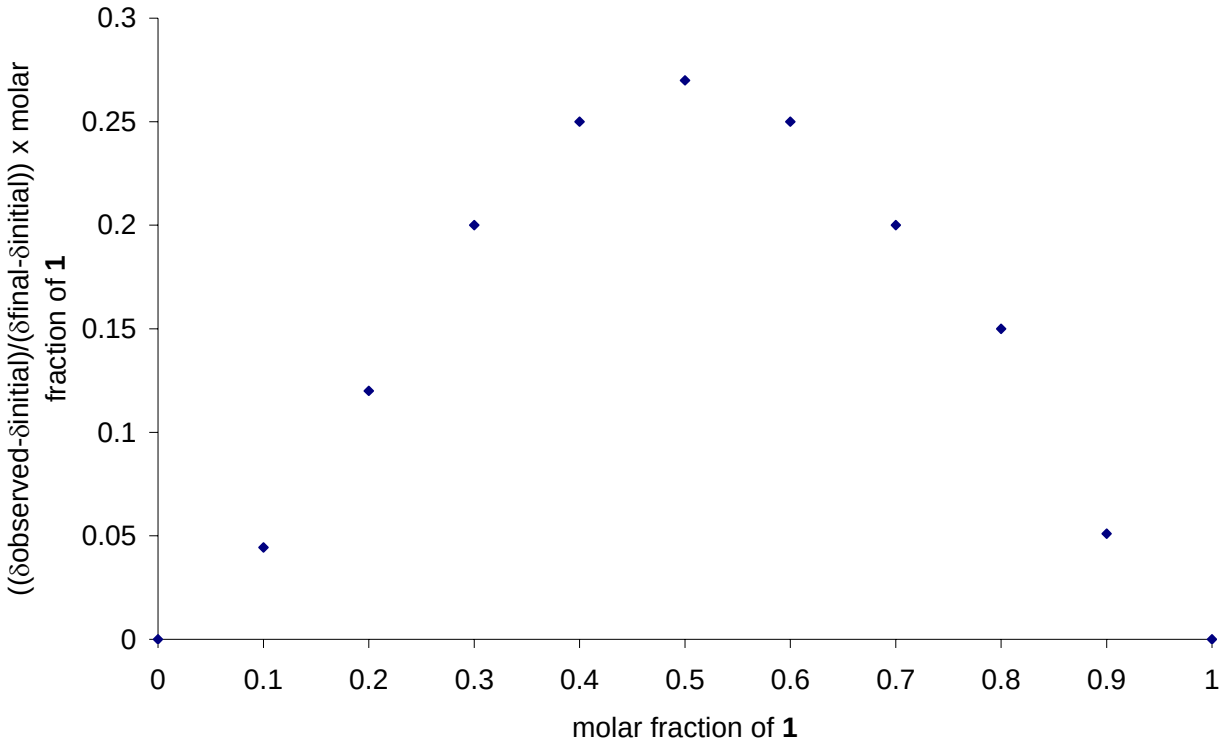

Figure S16 Job plot of **1** with $TBAH_2PO_4$ in DMSO-d_6/0.5% water.

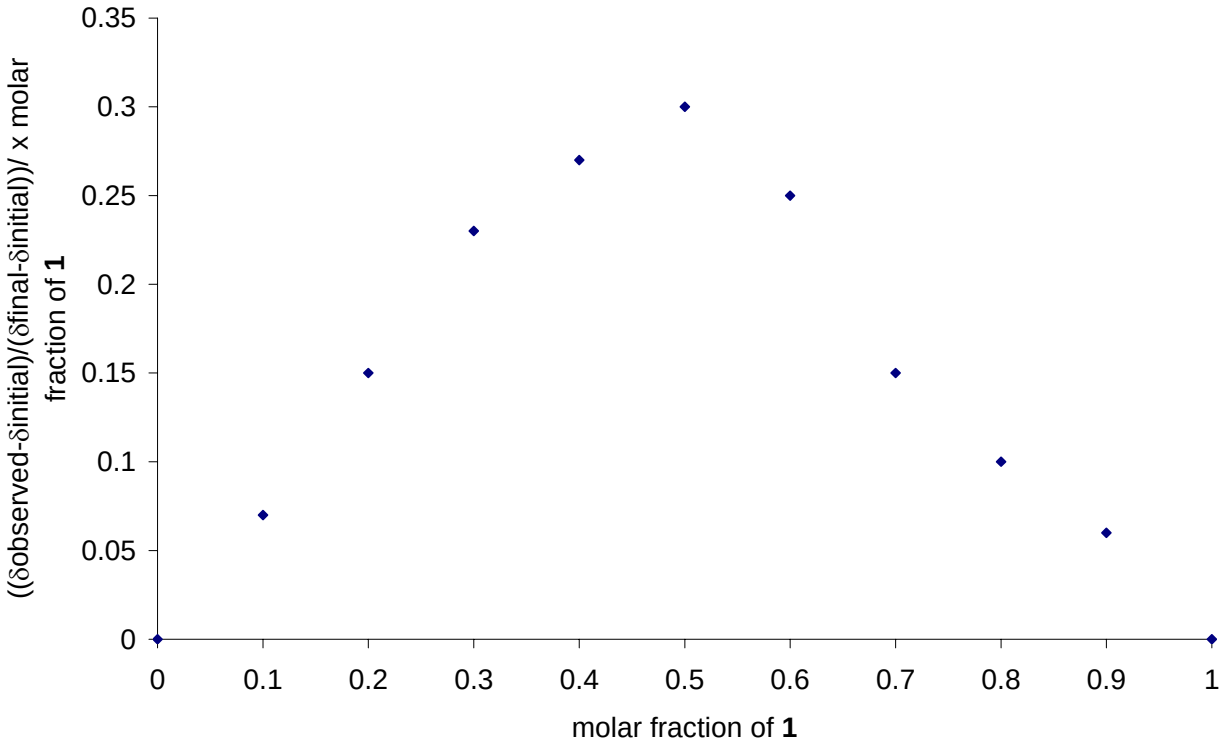

Figure S17 Job plot of **1** with TBAOBz in DMSO-d_6/0.5% water.

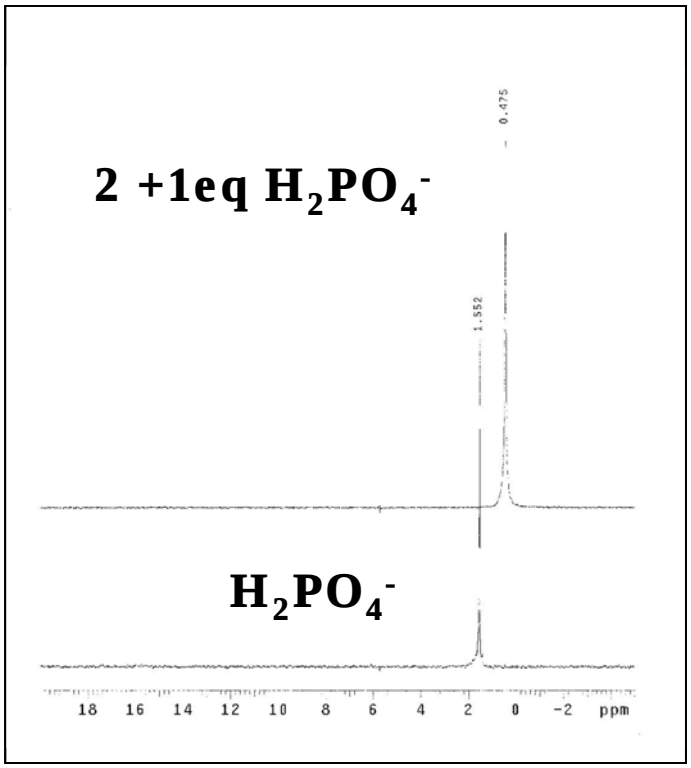

Figure S18 ^{31}P NMR of $TBAH_2PO_4$ and compound **2** with one equivalent of $H_2PO_4^-$ in DMSO-d_6/0.5% water.

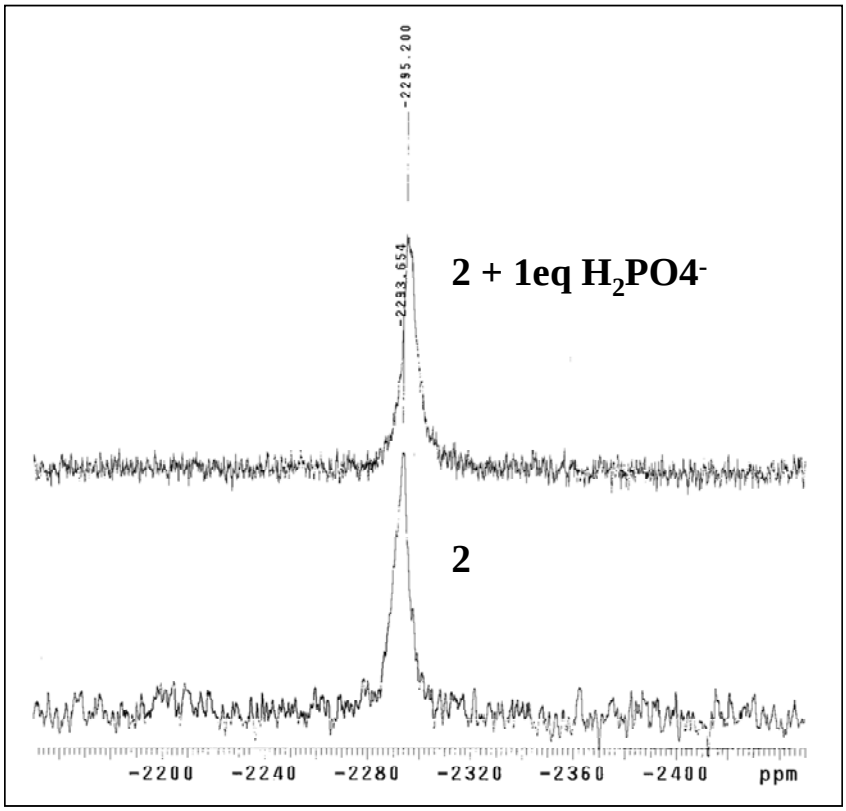

Figure S19 ^{195}Pt NMR of free compound **2** and after the addition of one equivalent of $TBAH_2PO_4$ in DMSO-d_6/0.5% water.

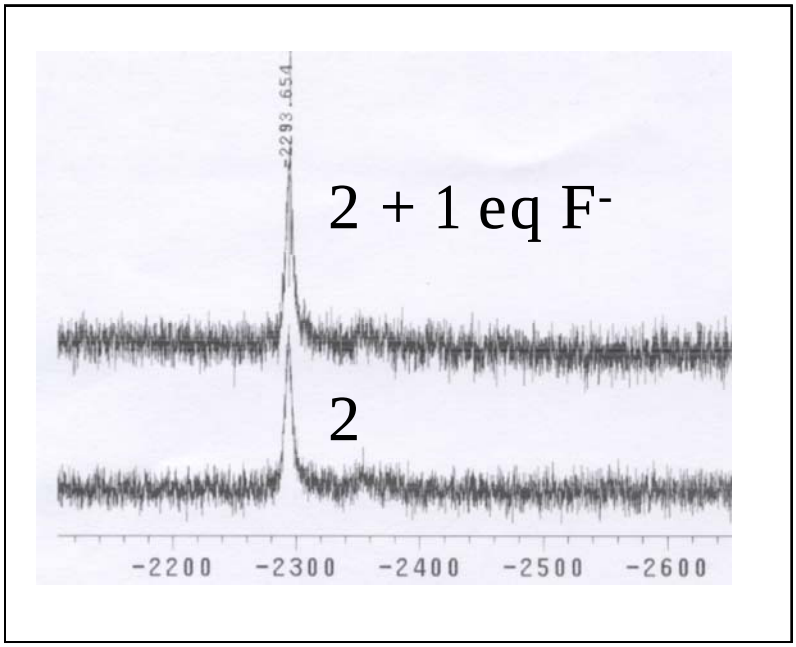

Figure S20 ^{195}Pt NMR of free compound **2** and after the addition of one equivalent of TBAF in DMSO-d_6/0.5% water.

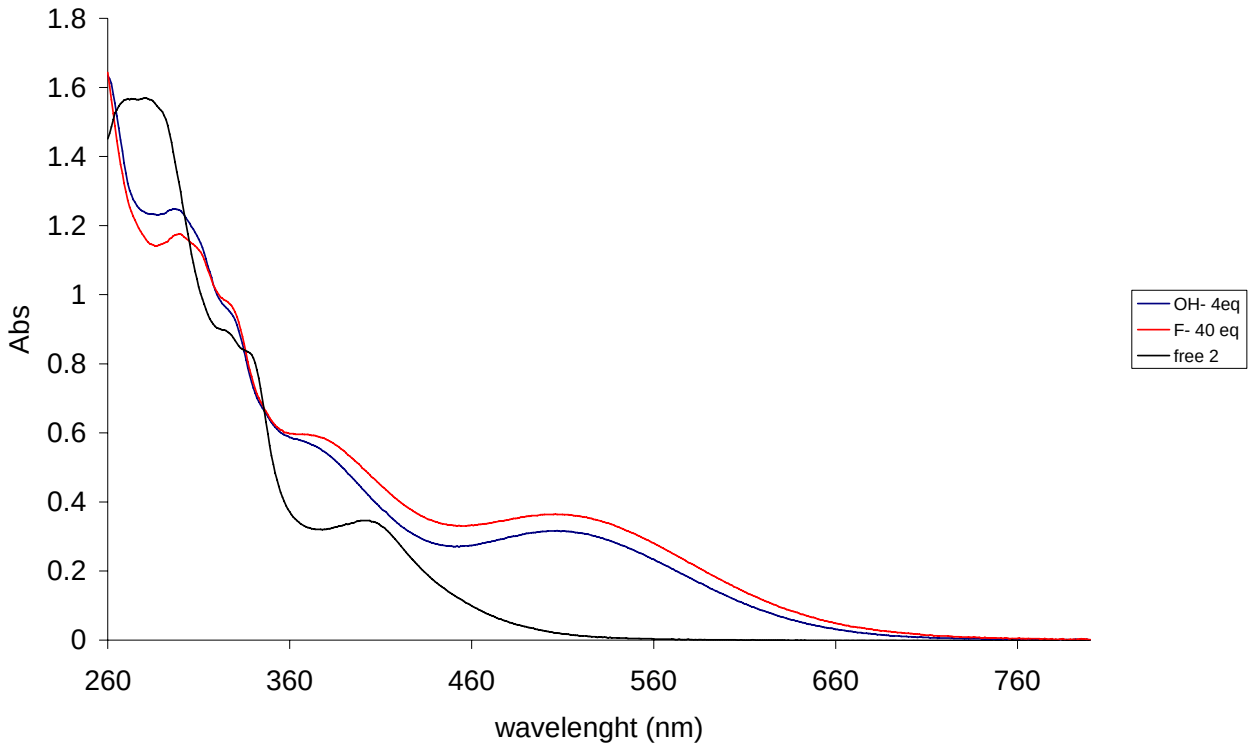

Figure S21 Changes in the UV-Vis spectrum of compound **2** (5.5×10^{-5} M) upon addition of 40 equivalents TBAF and 4 equivalents of TEAOH in DMSO/0.5% water.

Figure S22 Colour changes of compound **2** (1.6×10^{-4} M) upon addition of 60 equivalents of anions as tetrabutylammonium salts in DMSO/0.5% water. From left to right: free **2**, **2** $+F^-$, **2** + ACO^-, **2** + BzO^-, **2** + $H_2PO_4^-$, **2** + Cl^-.

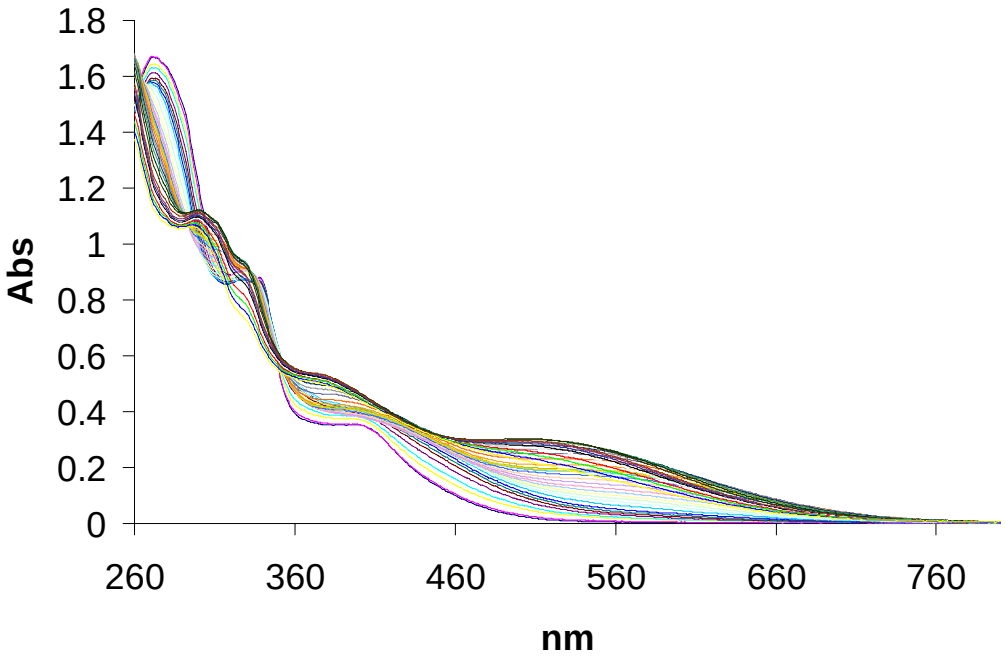

Figure S23 Full UV-Vis titration of compound **2** (1.6×10^{-4} M) in the presence of TBAF in DMSO/0.5% water.

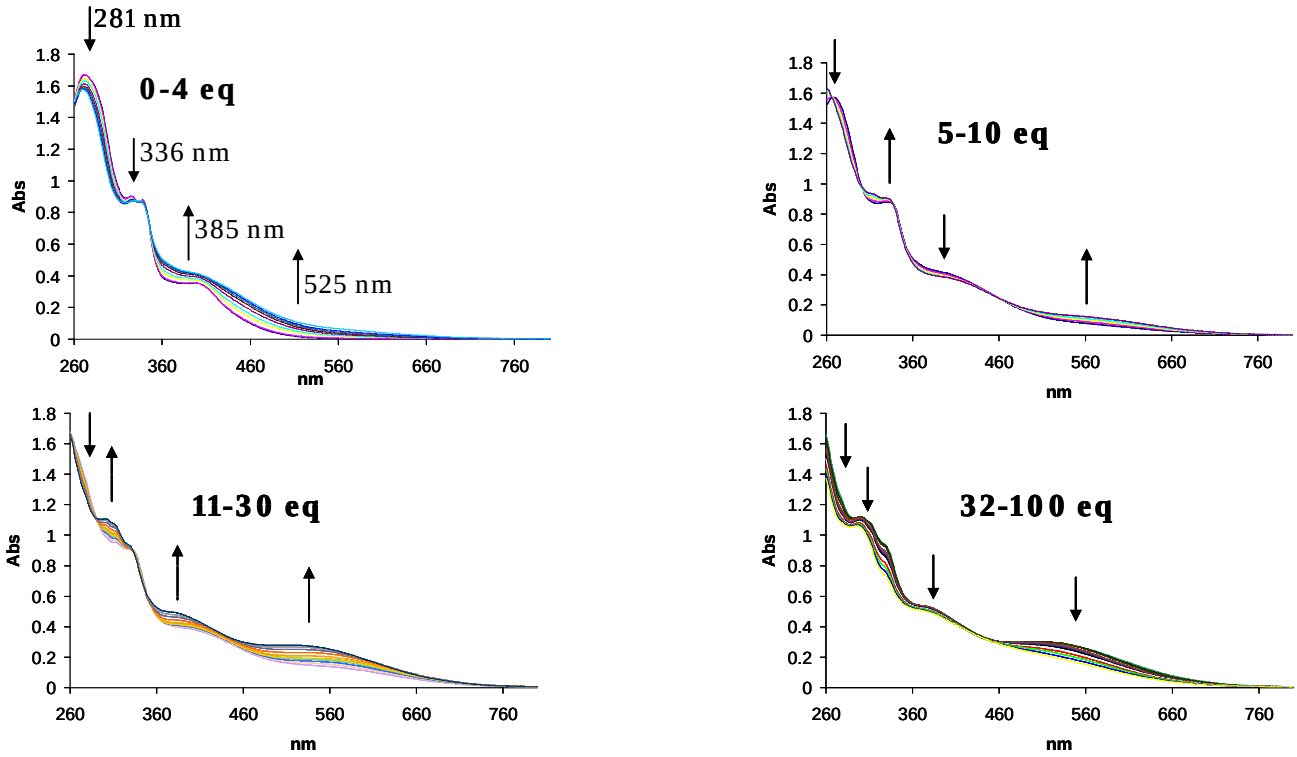

Figure S24 Portions of the full UV-Vis titration shown in Fig. S23 of compound **2** (1.6×10^{-4} M) in the presence of increasing amounts of TBAF.

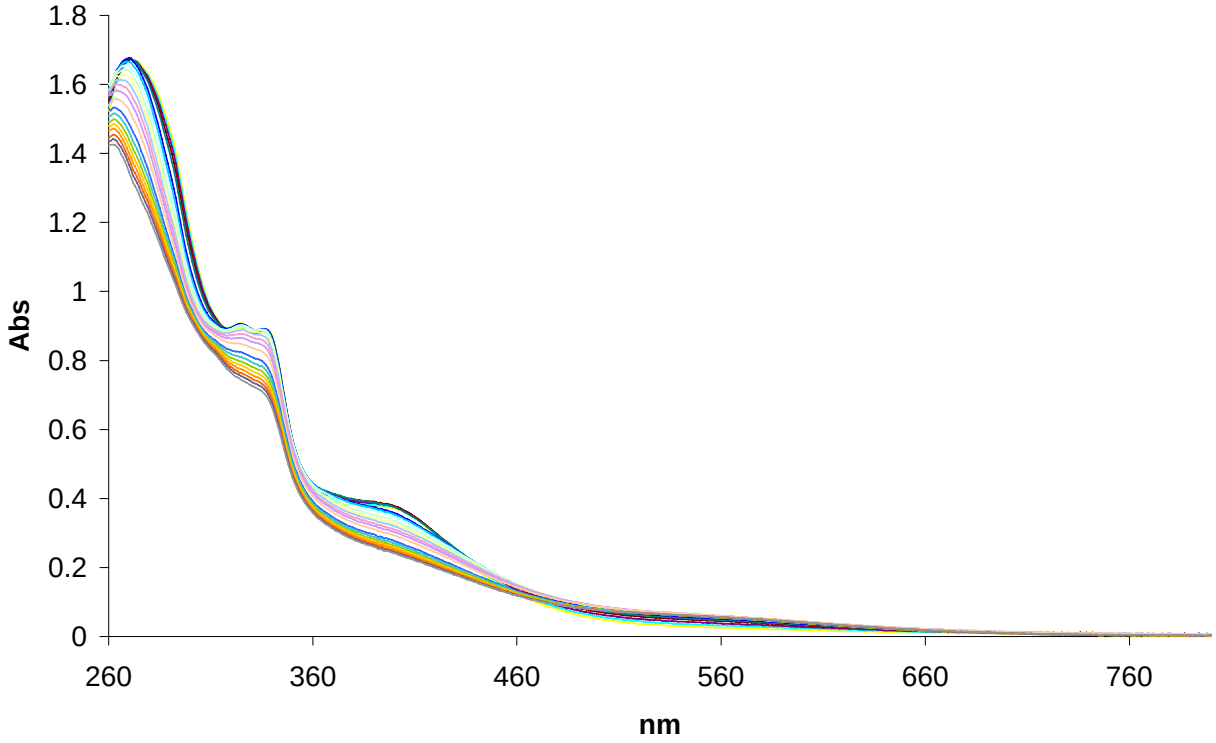

Figure S25 Full UV-Vis titration of compound **2** (1.6×10^{-4} M) in the presence of TBAOAc in DMSO/0.5% water.

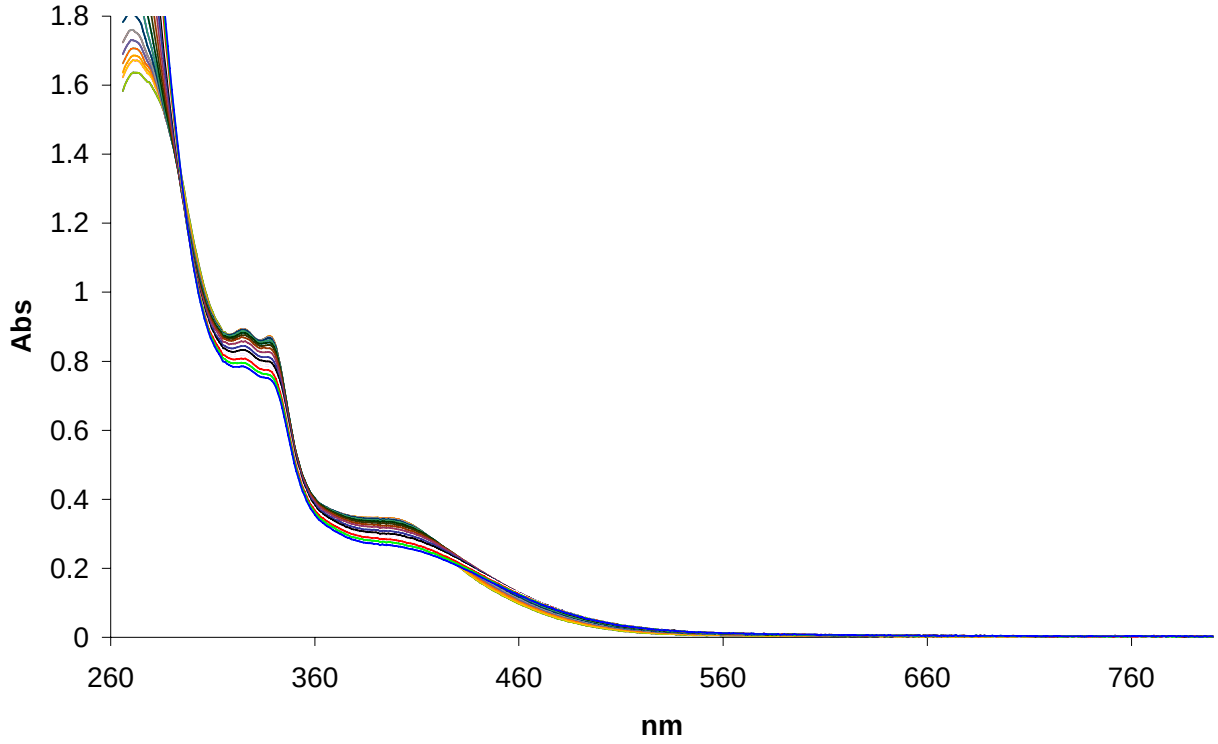

Figure S26 Full UV-Vis titration of compound **2** (1.6×10^{-4} M) in the presence of TBAOBz in DMSO/0.5% water.

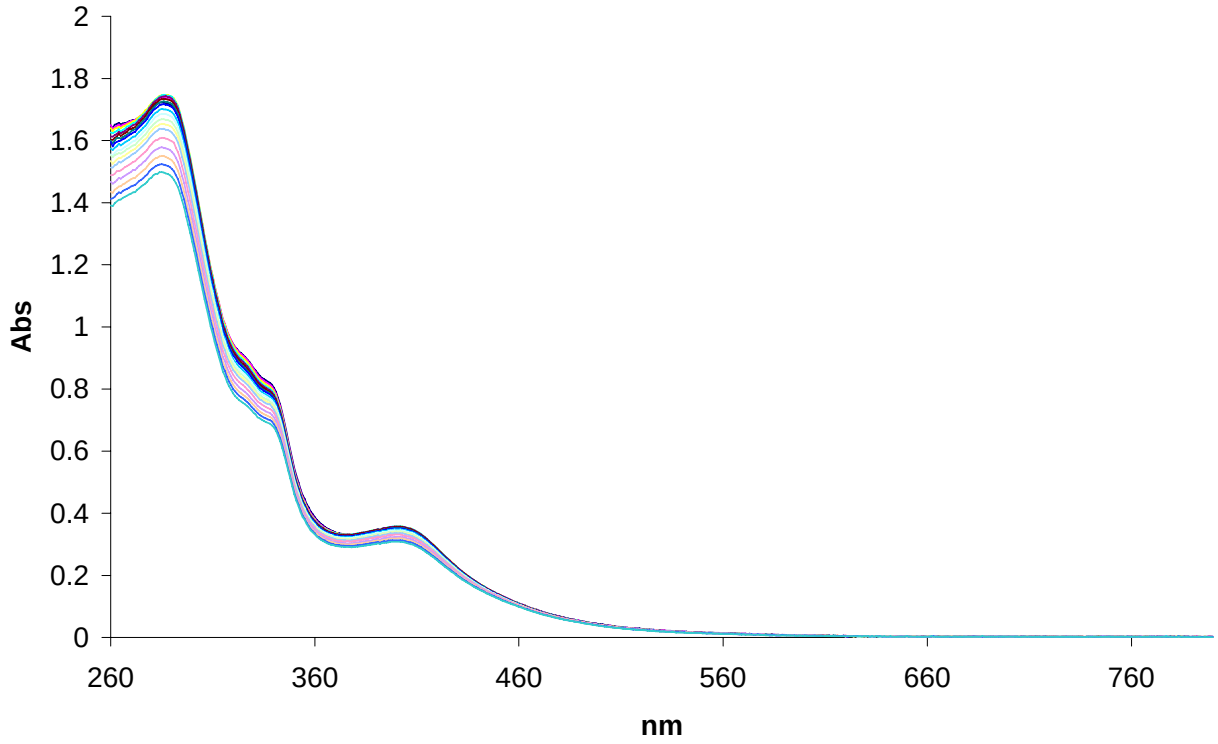

Figure S27 Full UV-Vis titration of compound **2** (1.6×10^{-4} M) in the presence of TBACl in DMSO/0.5% water.

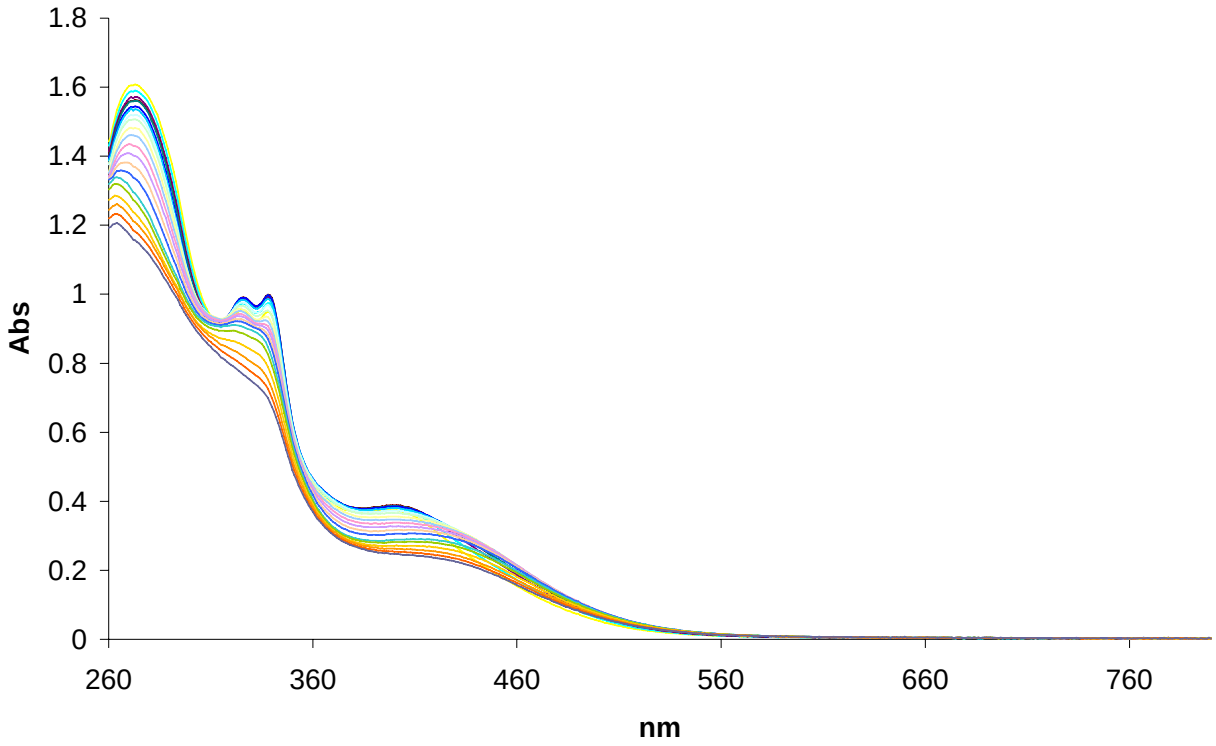

Figure S28 Full UV-Vis titration of compound **2** (1.6×10^{-4} M) in the presence of $TBAH_2PO_4$ in DMSO/0.5% water.