

Acyclic indole and carbazole-based sulfate receptors

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Supplementary information

Experimental

General remarks: All reactions were performed using oven-dried glassware under slight positive pressure of nitrogen/argon (as specified). ¹H NMR (300 MHz) and ¹³C{¹H} NMR (75 MHz) spectra were determined on a Bruker AV300 spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were determined on a Bruker AV400 spectrometer. Chemical shifts for ¹H NMR are reported in parts per million (ppm), calibrated to the solvent peak set. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. Chemical shifts for ¹³C{¹H} NMR are reported in ppm, relative to the central line of a septet at $\delta = 39.52$ ppm for deuterio-dimethylsulfoxide. Infrared (IR) spectra were recorded on a Matterson Satellite (ATR). FTIR are reported in wavenumbers (cm⁻¹). All solvents and starting materials were purchased from chemical sources where available. NMR titrations were performed by adding aliquots of the putative anionic guest (as the TBA or TEA salt in the case of HCO₃⁻) salt (0.15 M) in a solution of the receptor (0.01M) in DMSO-*d*₆ to a solution of the receptor (0.01M).

7,7'-carbonylbis(azanediyl)bis(N-(1H-indol-7-yl)-1H-indole-2-carboxamide) (1)

N-(1H-indol-7-yl)-7-nitro-1H-indole-2-carboxamide A dry solution of 7-nitroindole-2-carboxylic acid (0.38 g, 1.85 mM), pyBOP (1.20 g, 2.31 mM) and a catalytic amount of HOBt was stirred in DMF (15 mL) for 30 mins. A dry solution of 7-aminoindole (0.24 g, 1.85 mM) and TEA (0.3 mL) was stirred in DMF (5 mL) for 30 mins. The amine solution was added dropwise to the acid solution and allowed to stir for four days at room temperature under nitrogen. The solution was then taken to dryness, dissolved in dichloromethane (30 mL) and washed with water (250 mL) and dried over MgSO₄. The filtrate was then reduced to half original volume and hexane added dropwise until a brown precipitate appeared which was removed by filtration. The filtrate was reduced *in vacuo* leaving an orange oil. The oil was dissolved in methanol (25 mL) which resulted in the formation of a yellow solid. The solid was removed by filtration and washed with diethylether (25 mL). Yield 41%; decomposed: 212°C; ¹H NMR (300 MHz, DMSO-*d*₆): δ : 6.51 (dd, $J_1 = 1.8$ Hz, $J_2 = 2.9$ Hz, 1H), 7.05 (t, $J = 7.7$ Hz, 1H), 7.31 (d, $J = 7.3$ Hz, 1H), 7.35-7.40 (m, 2H), 7.48 (d, $J = 7.7$ Hz, 1H), 7.64 (d, $J = 1.8$ Hz, 1H), 8.27 (d, $J = 2.6$ Hz, 1H), 8.30 (d, $J = 2.9$ Hz, 1H), 10.66 (s, NH, 1H), 10.90 (s, NH, 1H), 11.53 (s, NH, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ : 101.6 (ArCH), 107.2 (ArCH), 116.2 (ArCH), 117.9 (ArCH), 118.8 (ArCH), 120.1 (ArCH), 121.3 (ArCH), 122.1 (ArC), 125.5 (ArCH), 128.9 (ArC), 129.4 (ArC), 130.0 (ArC), 130.8 (ArCH), 131.0 (ArC), 133.1 (ArC), 1304.7 (ArC), 158.3 (CO); IR (film): $\nu = 3470$ and 3370 (indole NH stretching), 3290 (amide NH stretching), 1660 and 1550 (amide CO stretching); LRMS (ES⁺): m/z : 343.1 [M+Na]⁺; HRMS (ES⁺): m/z : act: 321.0979 [M+H]⁺ cal: 321.0982 [M+H]⁺.

7-amino-N-(1H-indol-7-yl)-1H-indole-2-carboxamide *N*-(1H-indol-7-yl)-7-nitro-1H-indole-2-carboxamide (0.20 g, 0.62 mM) and a Pd/C 10% catalyst (0.05 g) were suspended in ethanol (25 mL). The flask was then evacuated and the mixture placed under a hydrogen atmosphere and stirred vigorously for 2 hrs. After this time the palladium catalyst was removed by filtration through celite and the filtrate reduced *in vacuo* affording a light brown solid: Assumed yield 100%.

The light brown solid (0.18 g, 0.62 mM) was dissolved in a two phase solution of sat. NaHCO₃ (40 mL) and chloroform (40 mL). This solution was stirred vigorously under nitrogen at room temperature and triphosgene (0.19 g, 0.62 mM) added in two equal aliquots. The solution was allowed to stir overnight. The two phase solution was then filtered and a white solid sonicated in water (250 mL) for 30 mins. A white solid was then collected by filtration and washed with ether (100 mL). Yield 71%; mp. 204°C; ¹H NMR (400 MHz, DMSO-*d*₆): δ : 6.49 (s, 1H), 7.03 (t, $J = 8.0$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 7.37-7.45 (m, 4H), 7.54 (s, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 9.01 (s, NH, 1H), 10.17 (s, NH, 1H), 10.99 (s, NH, 1H), 11.59 (s, NH, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ : 101.6 (ArCH), 104.6 (ArCH), 114.2 (ArCH), 115.9 (ArCH), 116.3 (ArCH), 117.4 (ArCH), 118.9 (ArCH), 120.5 (ArCH), 122.6 (ArC), 125.0 (ArC), 125.3 (ArCH), 128.5 (ArC), 128.7 (ArC), 129.3 (ArC), 129.7 (ArC), 131.4 (ArC), 153.3 (CO), 159.8 (CO); IR (film): $\nu = 3350$ (indole NH stretching), 3250 (urea NH stretching), 1620 (urea CO stretching), 1550 (amide CO stretching); LRMS (ES⁻): m/z : 605.4 [M-H]⁻; HRMS (ES⁺): m/z : act: 629.2008 [M+Na]⁺ cal: 629.2020 [M+Na]⁺.

7,7'-carbonylbis(azanediyl)bis(N-(9H-carbazol-1-yl)-1H-indole-2-carboxamide) (2)

N-(9H-carbazol-1-yl)-7-nitro-1H-indole-2-carboxamide A dry solution of 7-nitroindole-2-carboxylic acid (0.29 g, 1.41 mM), pyBOP (0.92 g, 1.77 mM) and a catalytic amount of HOBt was stirred in DMF (15 mL) for 30 mins. A dry solution of 1-aminocarbazole (0.26 g, 1.41 mM) and TEA (0.3 mL) was stirred in DMF (5 mL) for 30 mins. The amine solution was added dropwise and allowed to stir for three days at room temperature under nitrogen. The solution was then reduced *in vacuo*, dissolved in dichloromethane (20 mL) and washed with water (150 mL) and the organic layer was placed in the freezer for 90 min. A yellow precipitate was removed by filtration. Yield 70%; mp. > 250°C; ¹H NMR (300 MHz, DMSO-*d*₆): δ : 7.17-7.25 (m, 2H), 7.37-7.44 (m, 2H), 7.53-7.59 (m, 2H), 7.7 (d, $J = 1.8$ Hz, 1H), 8.06 (d, $J = 7.7$ Hz, 1H), 8.15 (d, $J = 7.7$ Hz, 1H), 8.30-8.32 (m, 2H), 10.84 (s, NH, 1H), 11.01 (s, NH, 1H),

11.57 (s, NH, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ : 107.3 (ArCH), 111.3 (ArCH), 118.0 (ArCH), 118.6 (ArCH), 118.8 (ArCH), 120.2 (ArCH), 120.3 (ArCH), 121.3 (ArCH), 122.5 (ArC), 124.1 (ArC), 125.9 (ArCH), 128.9 (ArC), 130.9 (ArCH), 131.0 (ArC), 133.1 (ArC), 134.4 (ArC), 134.6 (ArC), 139.7 (ArCH), 158.4 (CO) (one ArC and one ArCH are absent and are presumably coincident with other resonances); IR (film): ν = 3370 (indole/carbazole NH stretching), 3250 (amide NH stretching), 1650 and 1550 (amide CO stretching); LRMS (ES^-): m/z : 369.2 [M-H] $^-$; HRMS (ES^+): m/z : act: 371.1134 [M+H] $^+$ cal: 371.1139 [M+H] $^+$.

7-amino-*N*-(9H-carbazol-1-yl)-1H-indole-2-carboxamide *N*-(1H-indol-7-yl)-7-nitro-1*H*-indole-2-carboxamide (0.20 g, 0.62 mM) and Pd/C 10% catalyst (0.05 g) were suspended in ethanol (25 mL) DMF (2.5 mL). The flask was then evacuated and the mixture placed under a hydrogen atmosphere and stirred vigorously for 24 hrs. After this time the palladium catalyst was removed by filtration through celite and the filtrate reduced in volume (1 mL) and placed under reduced pressure affording light brown oil in quantitative yield.

The light brown oil was dissolved in a two phase solution of sat. NaHCO_3 (40 mL), chloroform (20 mL) and ethyl acetate (20 mL). This solution was stirred vigorously under nitrogen at room temperature and triphosgene (0.18 g, 0.62 mM) added in two equal amounts. The solution was allowed to stir overnight. The two phase solution was then filtered and the residue, a white solid, sonicated in water (250 mL) for 30 mins. The white solid was then collected by filtration and washed with ether (100 mL). Yield 79 %; mp. > 250 $^\circ\text{C}$; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ : 7.10 (t, J = 7.0 Hz, 1H), 7.16-7.23 (m, 2H), 7.38-7.46 (m, 2H), 7.54-7.60 (m, 4H), 8.03 (d, J = 7.3 Hz, 1H), 8.14 (d, J = 7.3 Hz, 1H), 9.01 (s, NH, 1H), 10.38 (s, NH, 1H), 11.10 (s, NH, 1H), 11.65 (s, NH, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ : 104.6 (ArCH), 111.3 (ArCH), 114.2 (ArCH), 116.3 (ArCH), 117.6 (ArCH), 118.5 (ArCH), 118.8 (ArCH), 120.5 (ArCH), 121.2 (ArCH), 121.9 (ArC), 122.5 (ArC), 123.9 (ArC), 125.0 (ArC), 125.8 (ArCH), 128.5 (ArC), 128.7 (ArC), 131.3 (ArC), 134.2 (ArC), 139.7 (ArC), 153.3 (CO), 159.9 (CO); IR (film): ν = 3410 (carbazole NH stretching), 3370 (indole NH stretching), 3300 (urea NH stretching), 3220 (amide NH stretching), 1640 (urea CO stretching), 1540 (amide CO stretching); LRMS (ES^-): m/z : 705.5 [M-H] $^-$; HRMS (ES^+): m/z : act: 707.2497 [M+H] $^+$ cal: 707.2514 [M+H] $^+$.

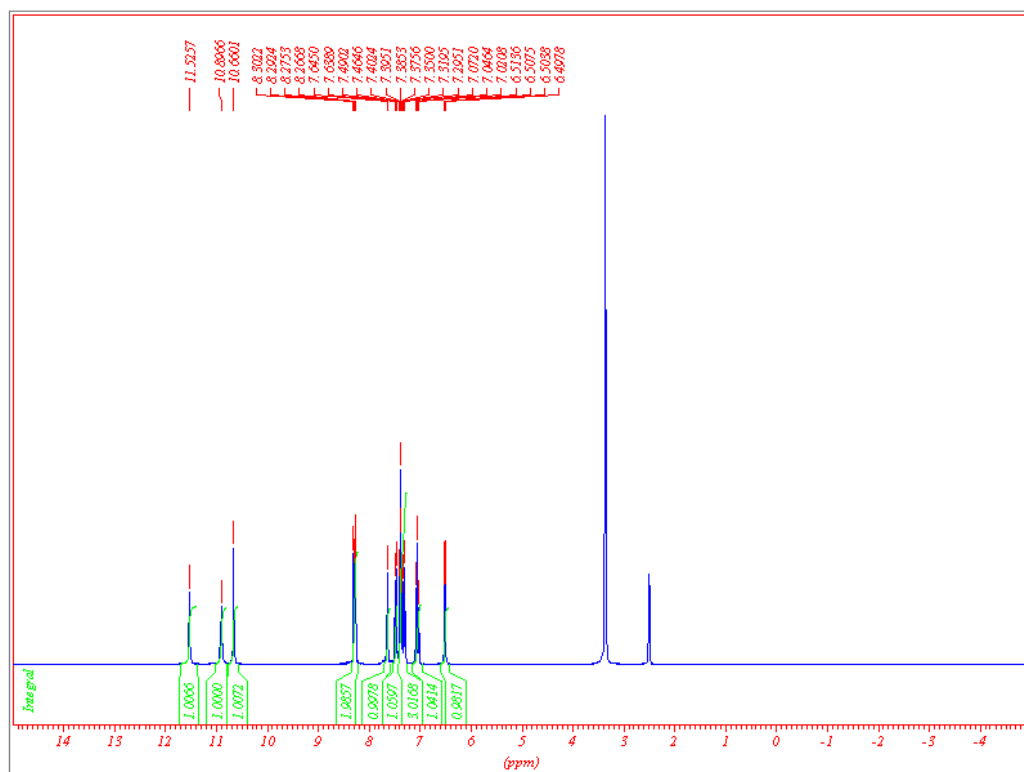


Figure S1 ^1H NMR spectrum of N-(1H-indol-7-yl)-7-nitro-1H-indole-2-carboxamide in $\text{DMSO-}d_6$.

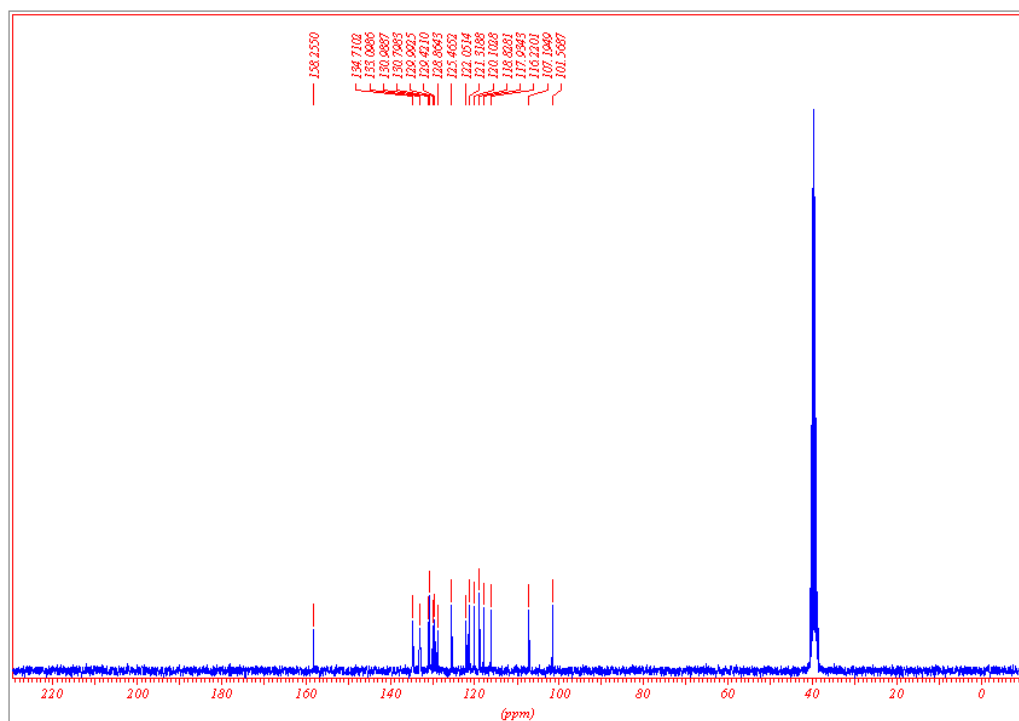


Figure S2 ^{13}C NMR spectrum of N-(1H-indol-7-yl)-7-nitro-1H-indole-2-carboxamide in $\text{DMSO-}d_6$.

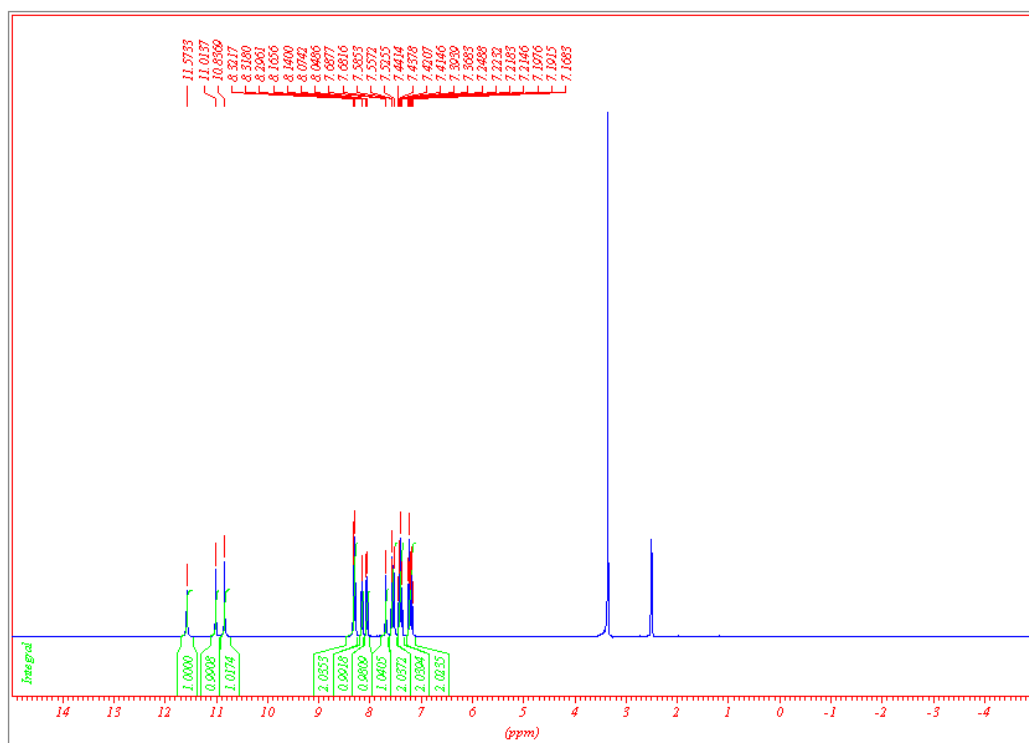


Figure S3 ^1H NMR spectrum of N-(9H-carbazol-1-yl)-7-nitro-1H-indole-2-carboxamide in $\text{DMSO-}d_6$.

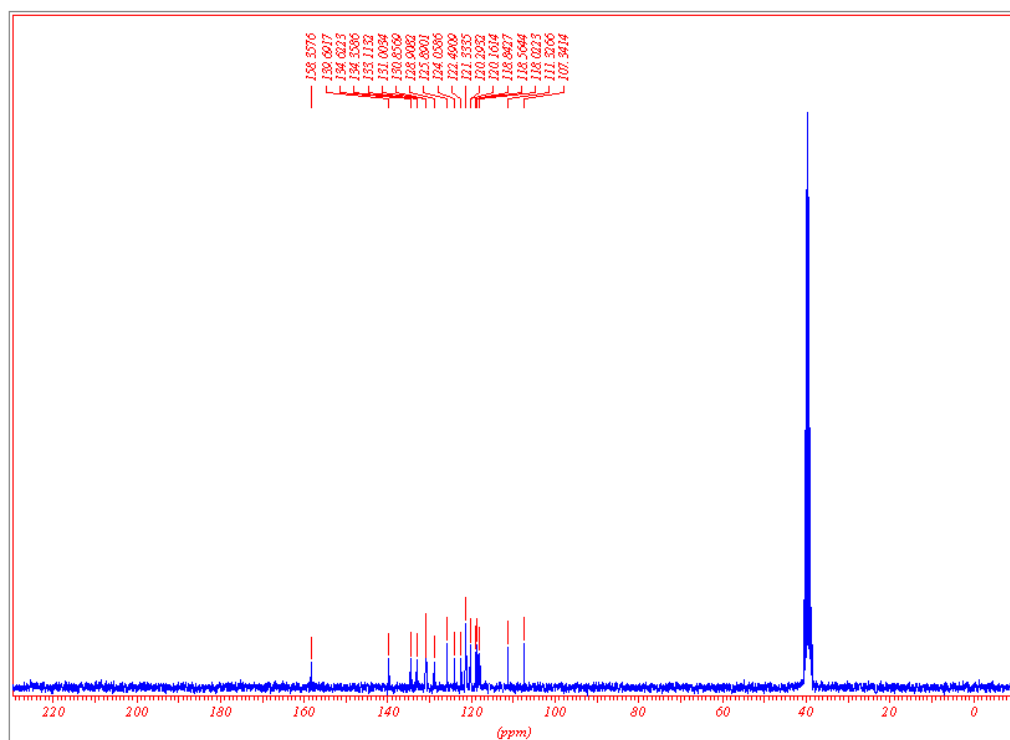


Figure S4 ^{13}C NMR spectrum of N-(9H-carbazol-1-yl)-7-nitro-1H-indole-2-carboxamide in $\text{DMSO-}d_6$.

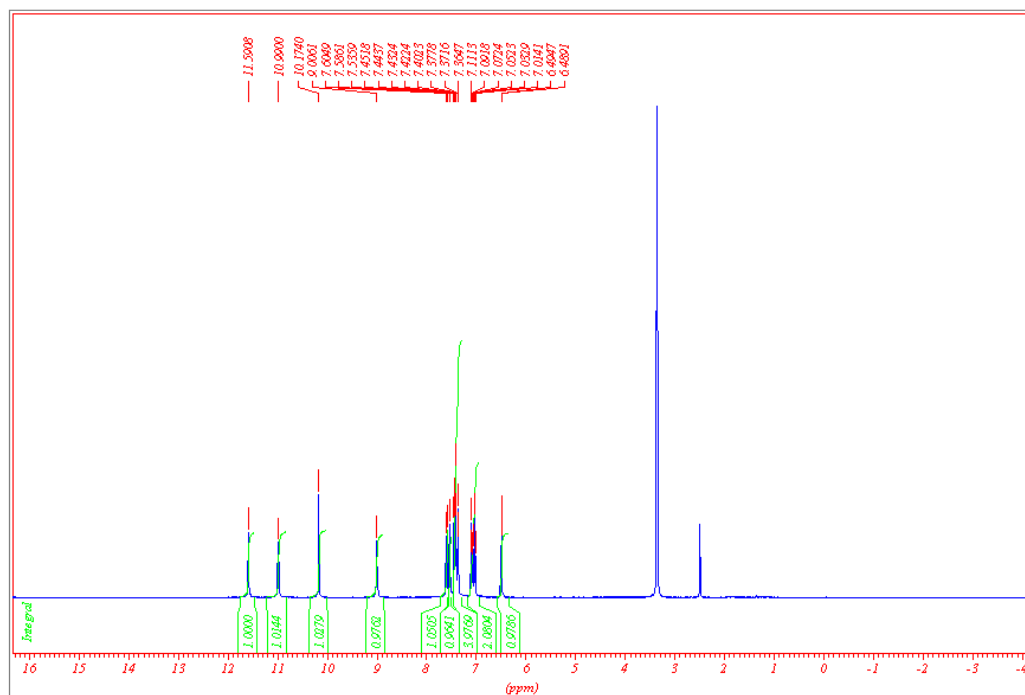


Figure S5 ^1H NMR spectrum of compound **1** in $\text{DMSO-}d_6$.

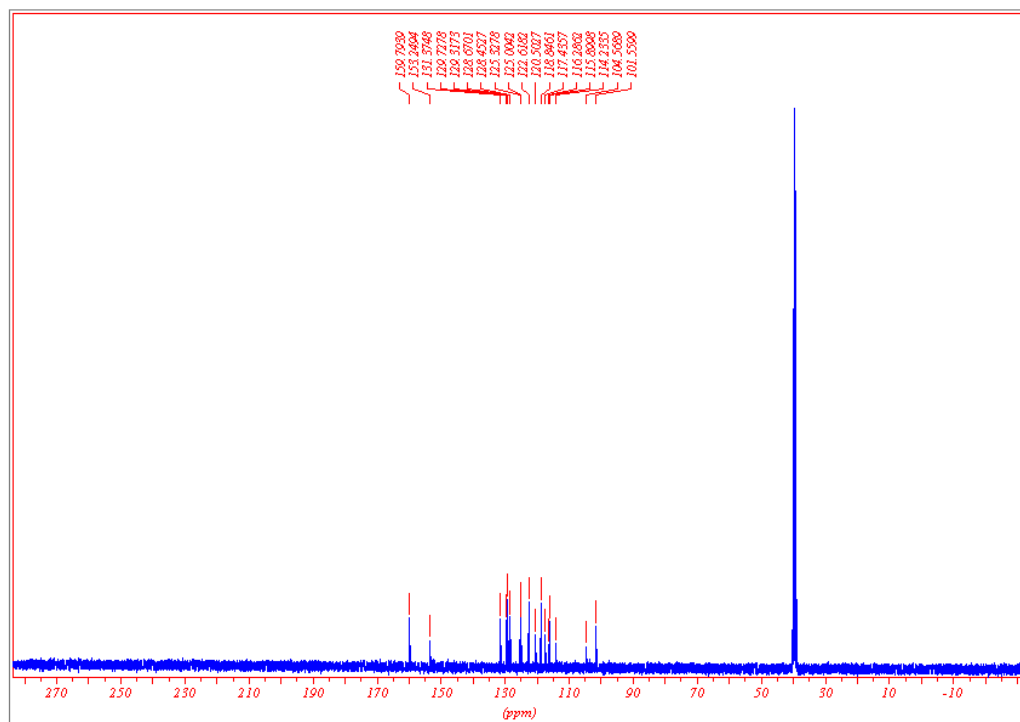


Figure S6 ^{13}C NMR spectrum of compound **1** in $\text{DMSO-}d_6$.

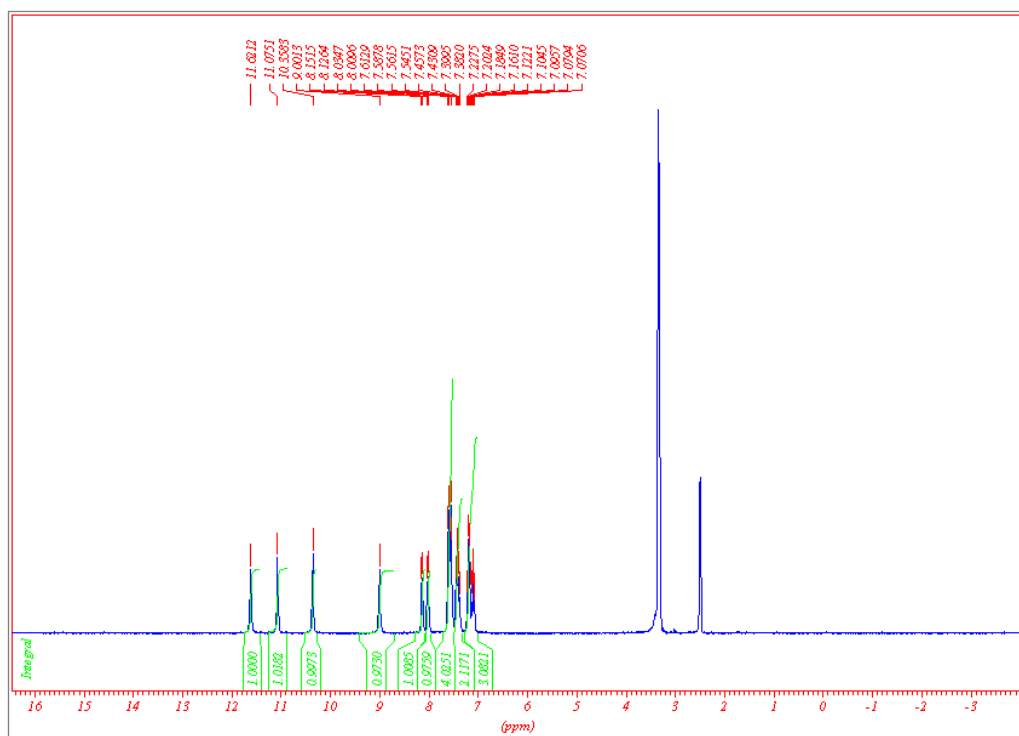


Figure S7 ^1H NMR spectrum of compound **2** in $\text{DMSO-}d_6$.

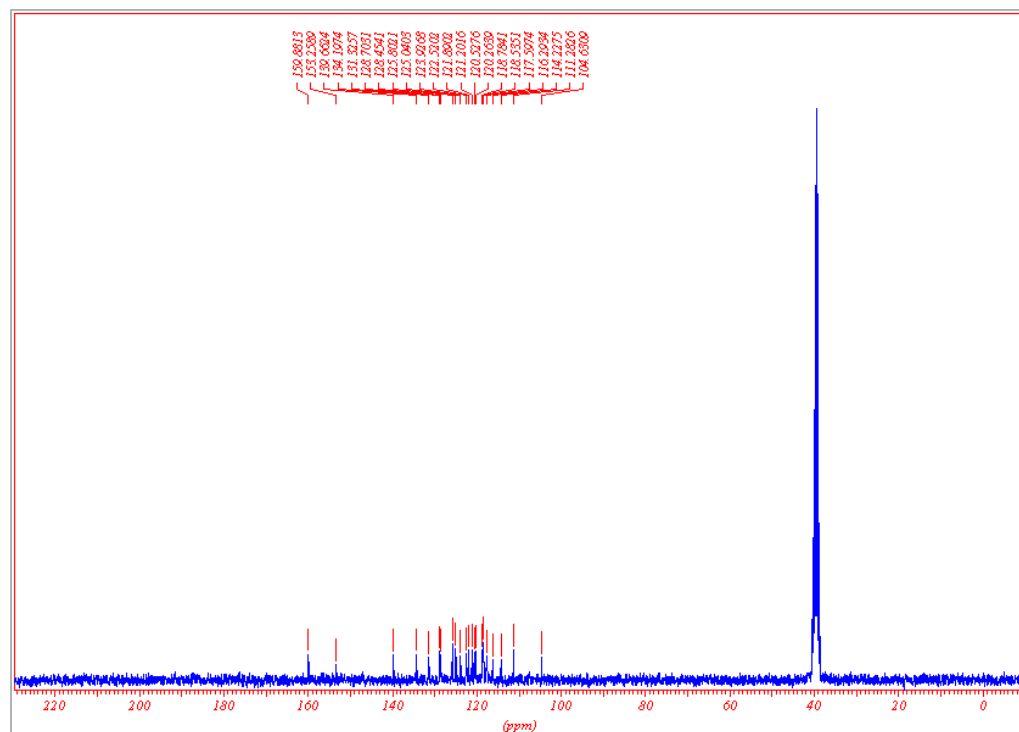


Figure S8 ^{13}C NMR spectrum of compound **2** in $\text{DMSO-}d_6$.

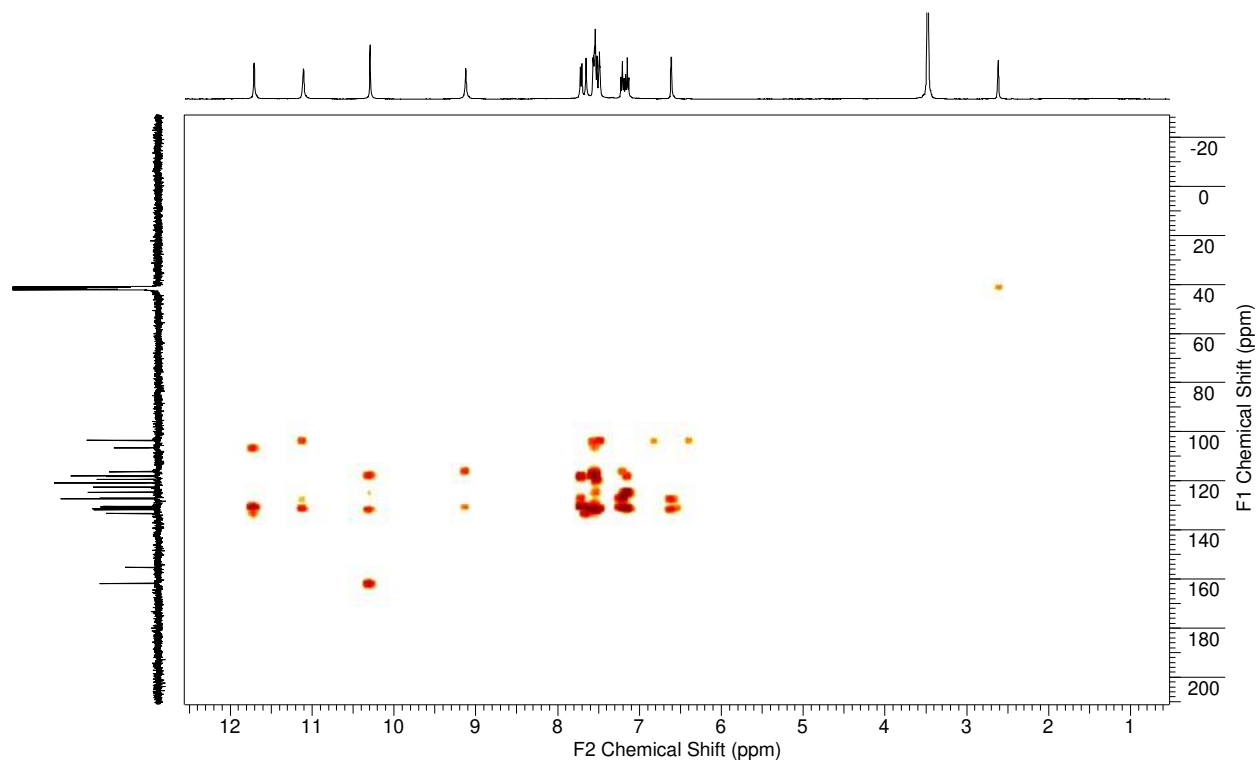


Figure S9 HMBC of compound **1** in DMSO-*d*₆

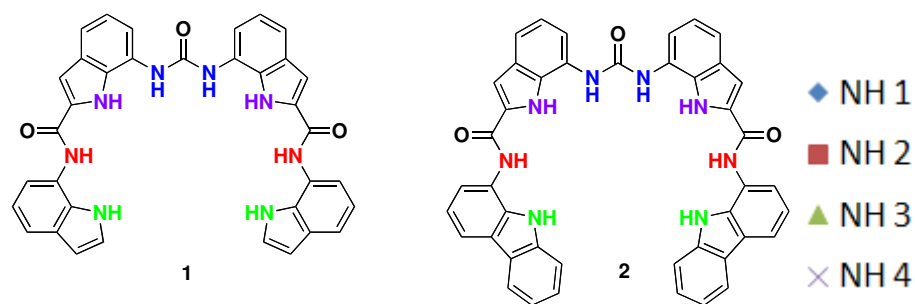


Figure 1: Structures of receptors **1** and **2** where the NH1 is the urea, NH4 is the indole NH nearest the urea, NH2 is the amide and NH3 is the indole/carbazole NH at the bottom of the molecule.

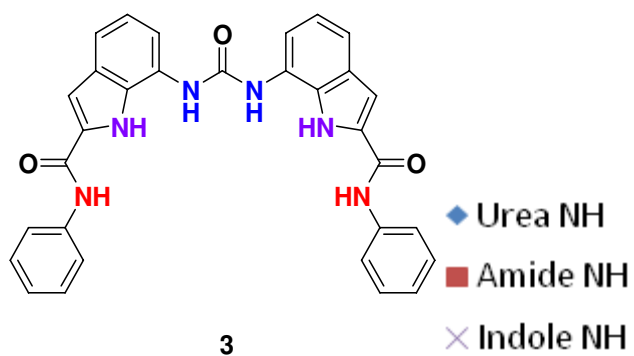


Figure 2: Structure of receptor **3**

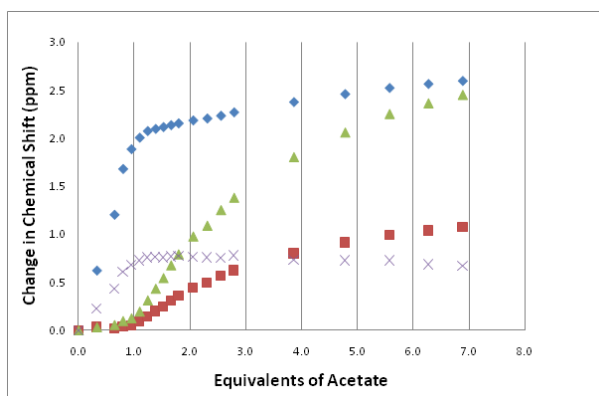


Figure S10 NMR titration of compound **1** vs. TBAOAc in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

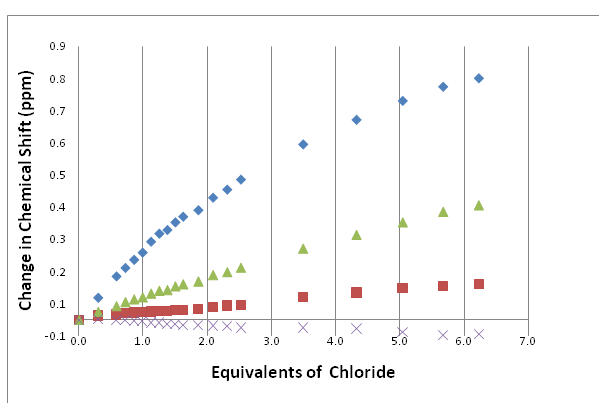


Figure S11 NMR titration of compound **1** vs. TBACl in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

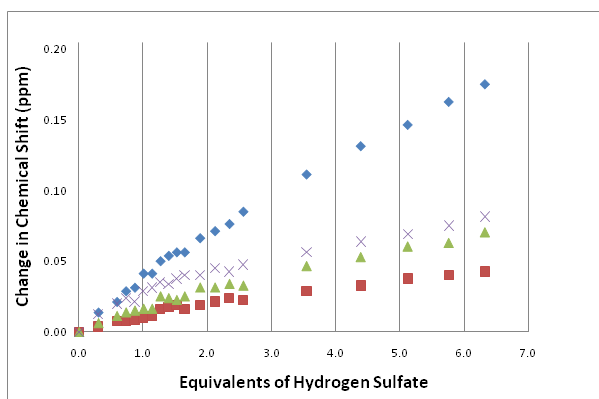


Figure S12 NMR titration of compound **1** vs. TBAHSO₄ in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

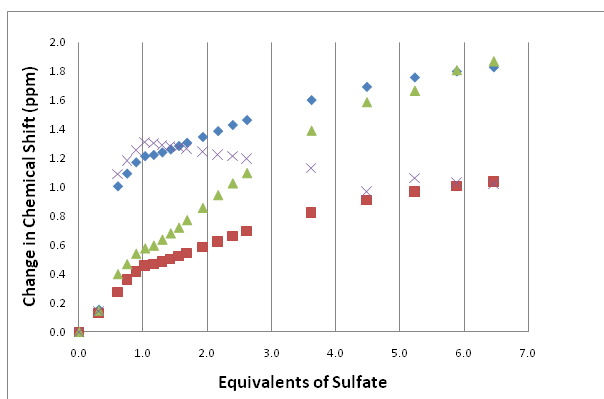


Figure S13 NMR titration of compound **1** vs. TBA_2SO_4 in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%. Monitoring change in chemical shift.

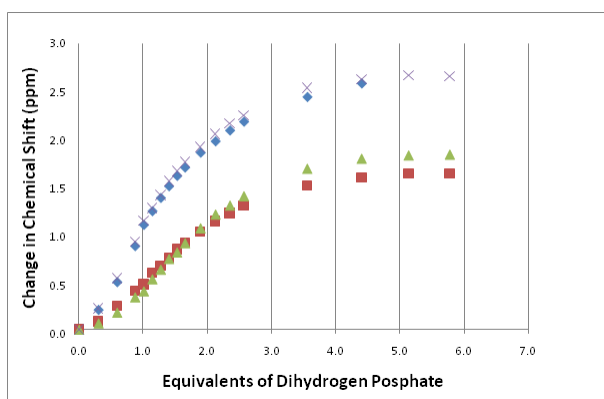


Figure S14 NMR titration of compound **1** vs. TBAH_2PO_4 in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 10%. Monitoring change in chemical shift.

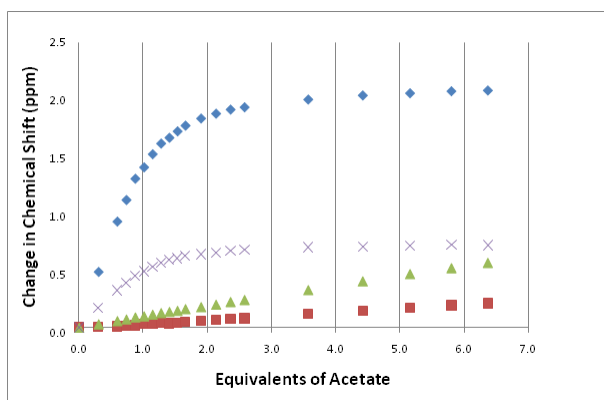


Figure S15 NMR titration of compound **1** vs. TBAOAc in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 10%. Monitoring change in chemical shift.

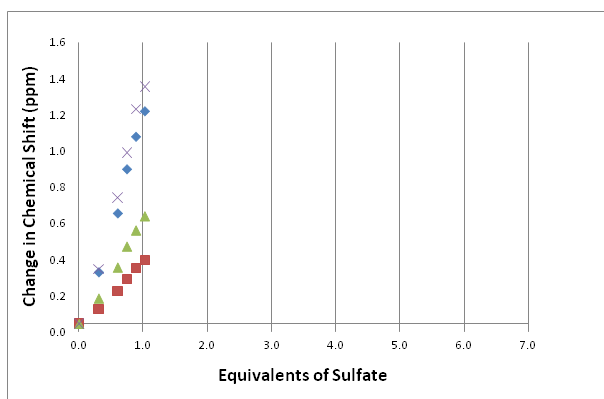


Figure S16 NMR titration of compound **1** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 10%. Monitoring change in chemical shift.

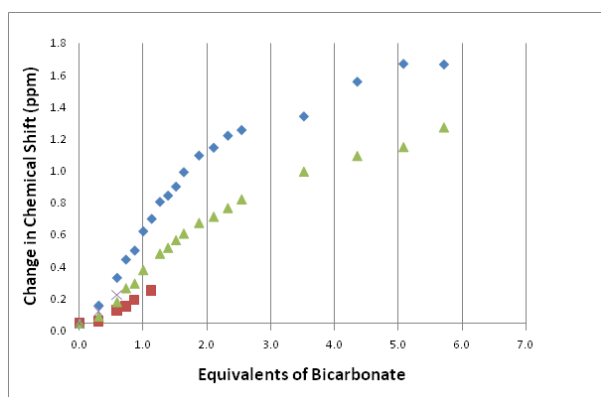


Figure S17 NMR titration of compound **1** vs. TEAHCO₃ in DMSO-*d*₆/H₂O 25%. Monitoring change in chemical shift.

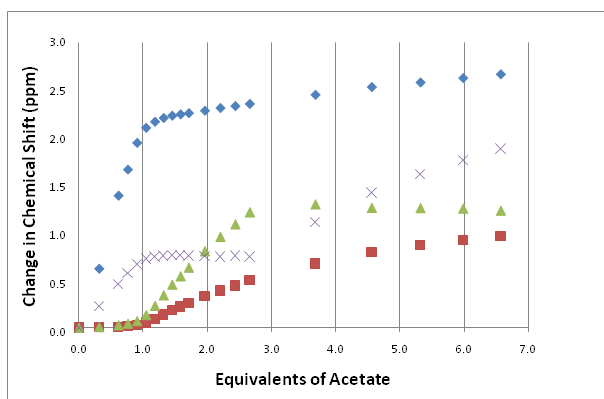


Figure S18 NMR titration of compound **2** vs. TBAOAc in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

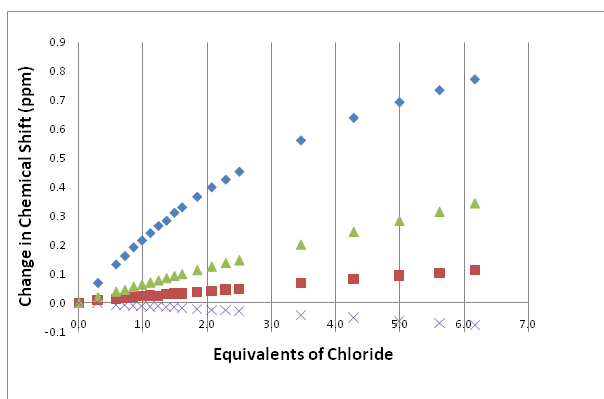


Figure S19 NMR titration of compound **2** vs. TBACl in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

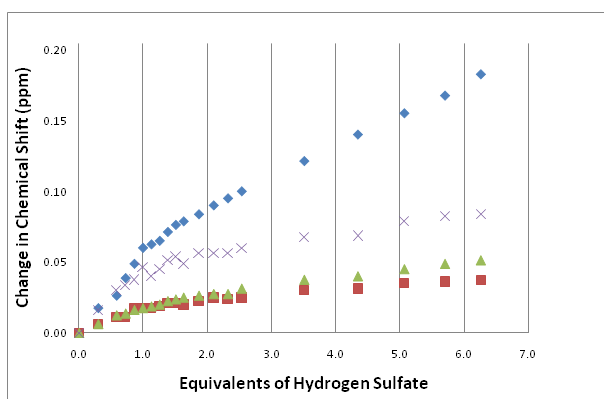


Figure S20 NMR titration of compound **2** vs. TBAHSO₄ in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

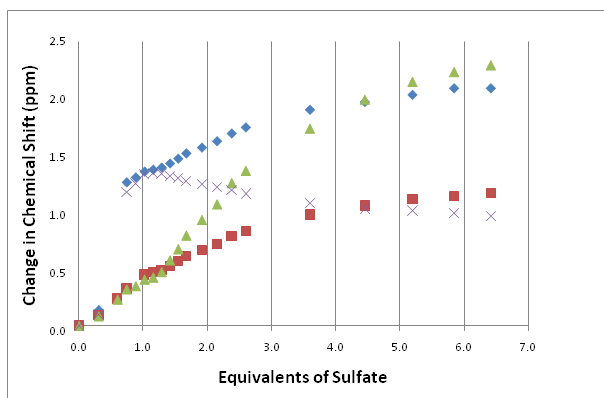


Figure S21 NMR titration of compound **2** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

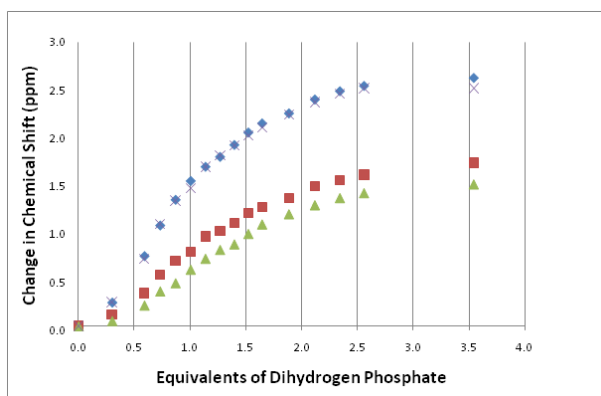


Figure S22 NMR titration of compound **2** vs. TBAH₂PO₄ in DMSO-*d*₆/H₂O 10%. Monitoring change in chemical shift.

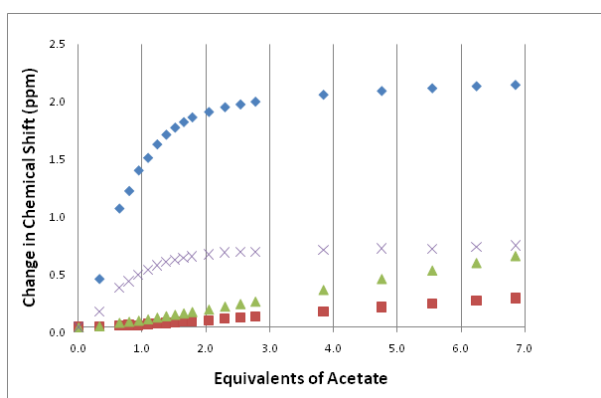


Figure S23 NMR titration of compound **2** vs. TBAOAc in DMSO-*d*₆/H₂O 10%. Monitoring change in chemical shift.

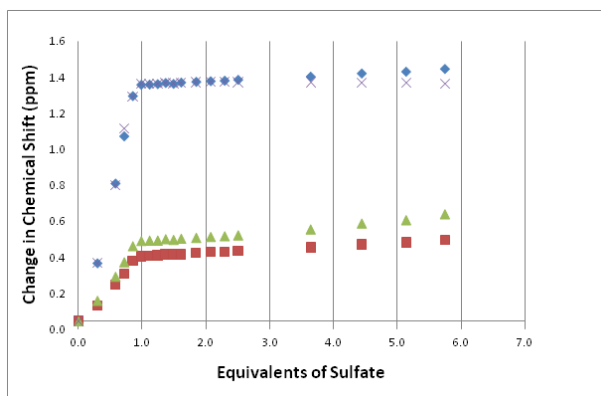


Figure S24 NMR titration of compound **2** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 10%. Monitoring change in chemical shift.

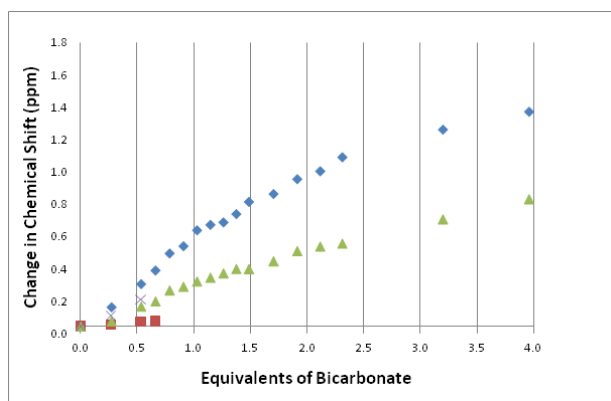


Figure S25 NMR titration of compound **2** vs. TEAHCO₃ in DMSO-*d*₆/H₂O 25%. Monitoring change in chemical shift.

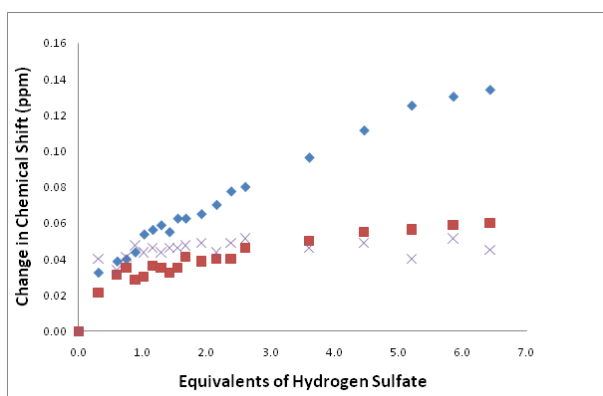


Figure S26 NMR titration of compound **3** vs. TBAHSO₄ in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

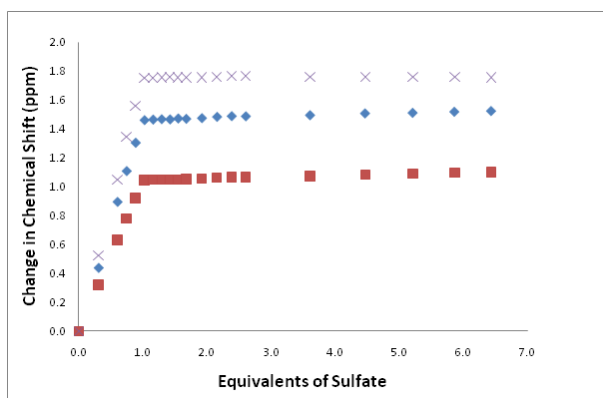


Figure S27 NMR titration of compound **3** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 0.5%. Monitoring change in chemical shift.

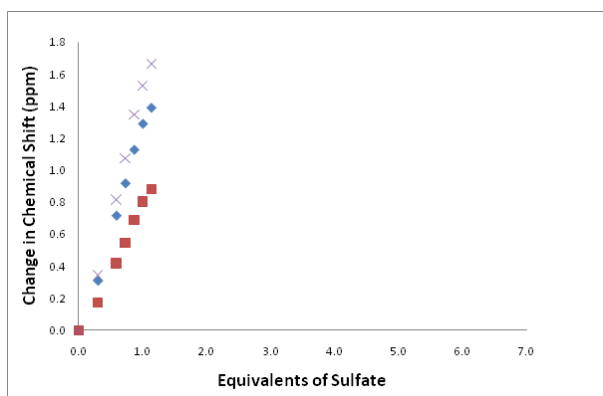


Figure S28 NMR titration of compound **3** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 10%. Monitoring change in chemical shift.

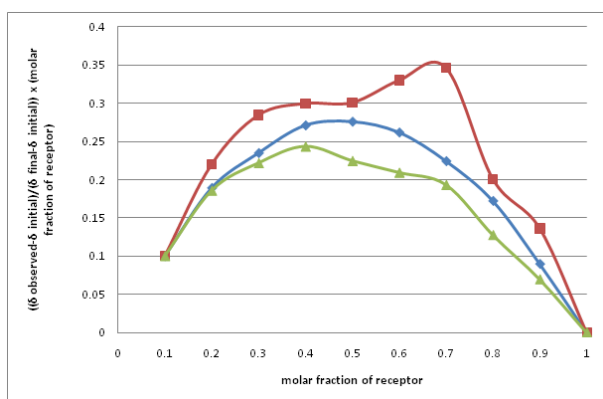


Figure S29 NMR job plot of compound **1** vs. TBACl in DMSO-*d*₆/H₂O 0.5%.

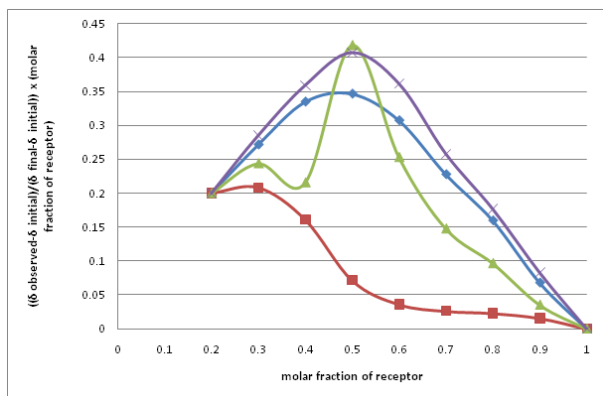


Figure S30 NMR job plot of compound **1** vs. TBAOAc in DMSO-*d*₆/H₂O 0.5%.

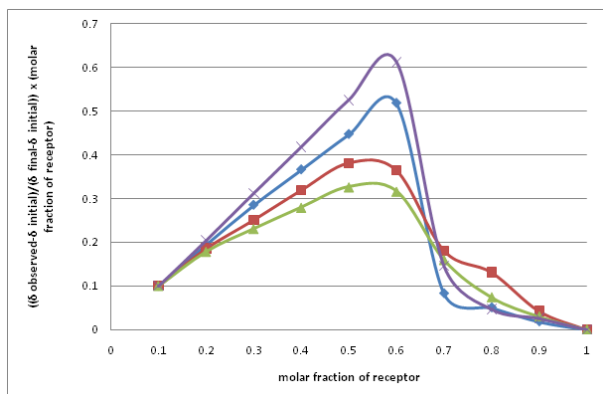


Figure S31 NMR job plot of compound **1** vs. TBA_2SO_4 in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%.

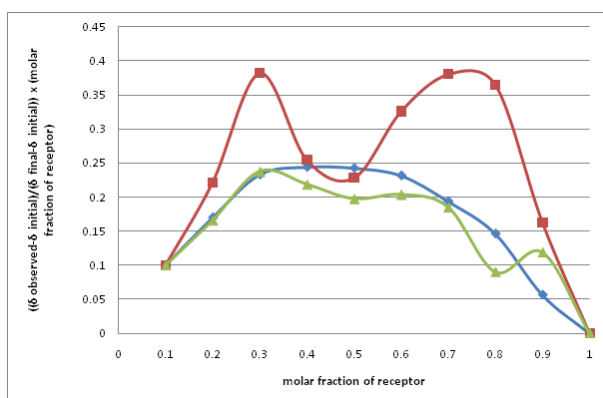


Figure S32 NMR job plot of compound **2** vs. TBACl in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%.

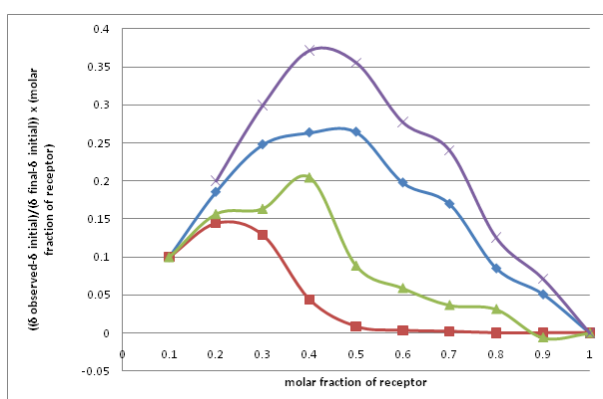


Figure S33 NMR job plot of compound **2** vs. TBAOAc in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%.

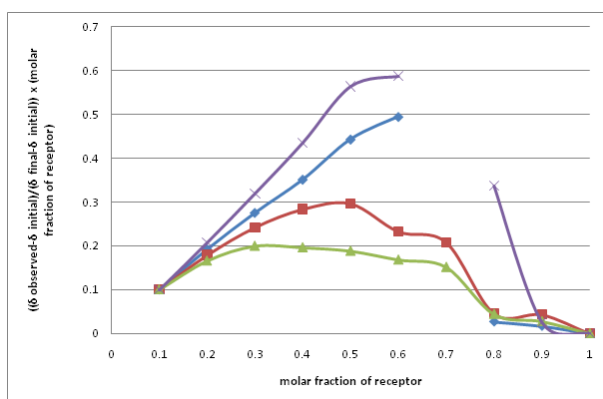
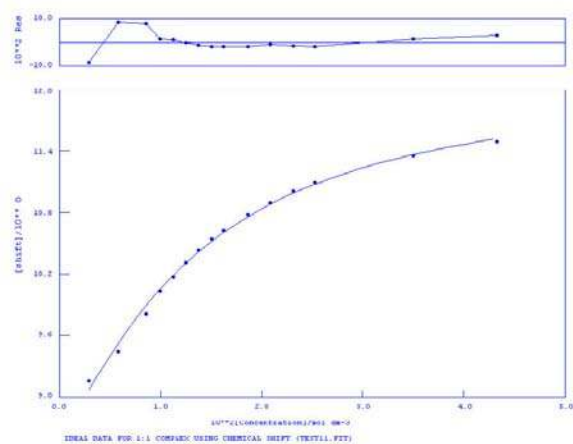
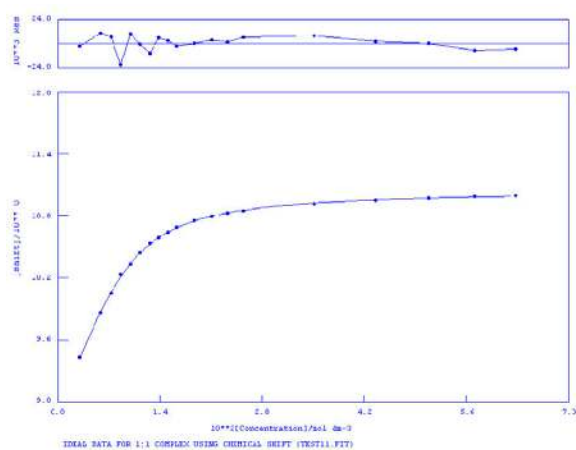


Figure S34 NMR job plot of compound **2** vs. TBA_2SO_4 in $\text{DMSO-}d_6/\text{H}_2\text{O}$ 0.5%.



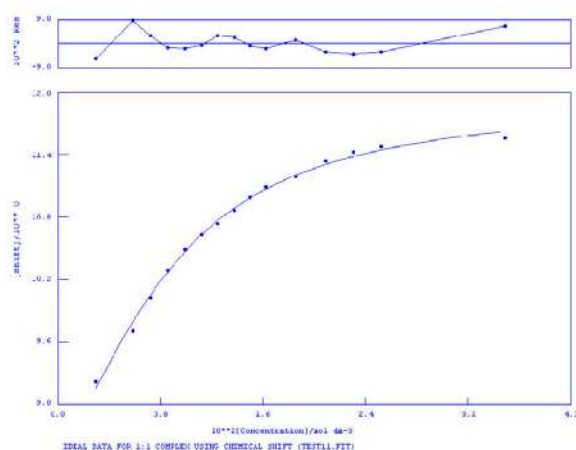
$K_a = 122 \text{ M}^{-1}$ Error = 11 %

Figure S35 NMR titration of compound **1** vs. TBAH₂PO₄ in DMSO-*d*₆/H₂O 10%. Following the urea NH.



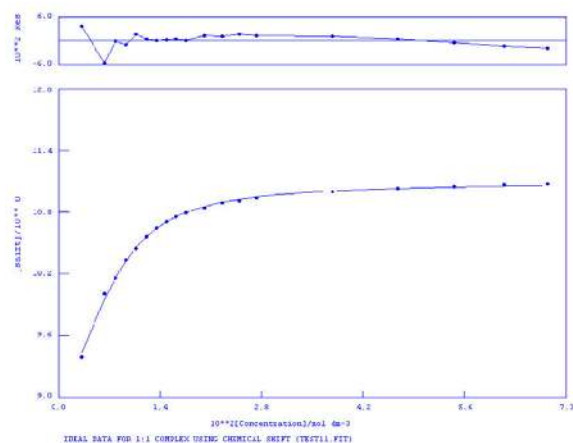
$K_a = 602 \text{ M}^{-1}$ Error = 2 %

Figure S36 NMR titration of compound **1** vs. TBAOAc in DMSO-*d*₆/H₂O 10%. Following the urea NH.



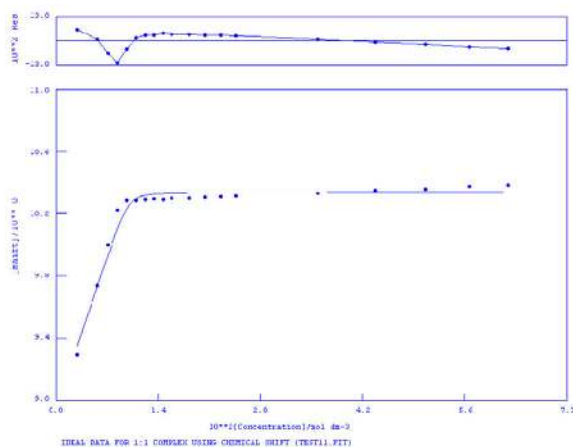
$K_a = 315 \text{ M}^{-1}$ Error = 11 %

Figure S37 NMR titration of compound **2** vs. TBAH₂PO₄ in DMSO-*d*₆/H₂O 10%. Following the urea NH.



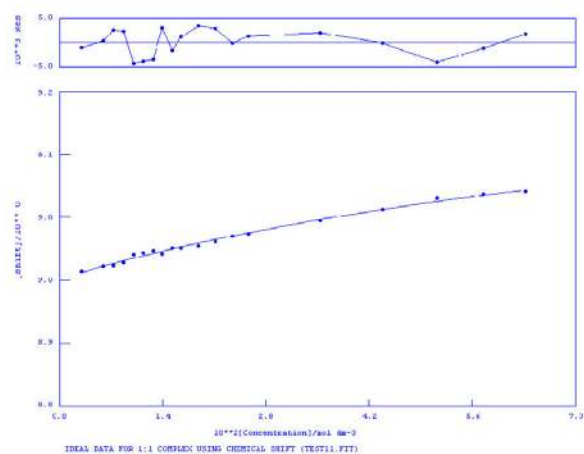
$K_a = 691 \text{ M}^{-1}$ Error = 5 %

Figure S38 NMR titration of compound **2** vs. TBAOAc in DMSO-*d*₆/H₂O 10%. Following the urea NH.



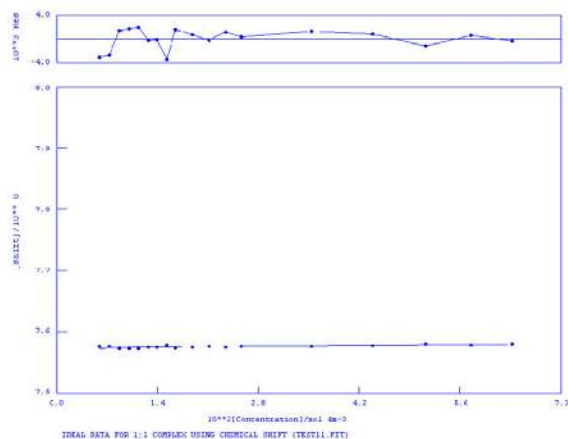
$K_a = >10^4 \text{ M}^{-1}$

Figure S39 NMR titration of compound **2** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 10%. Following the urea NH.



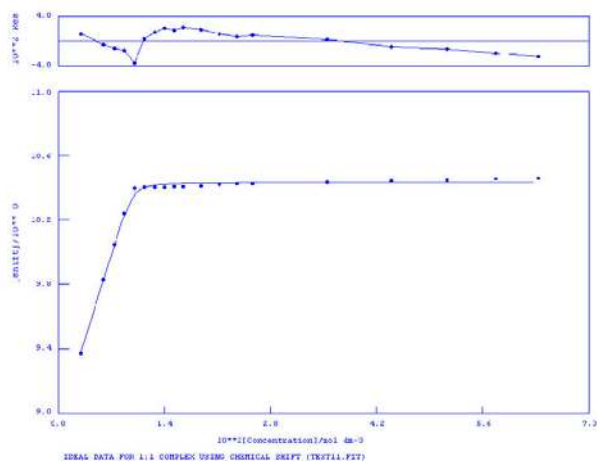
$K_a = \leq 10 \text{ M}^{-1}$

Figure S40 NMR titration of compound **3** vs. TBAHSO₄ in DMSO-*d*₆/H₂O 0.5%. Following the urea NH.



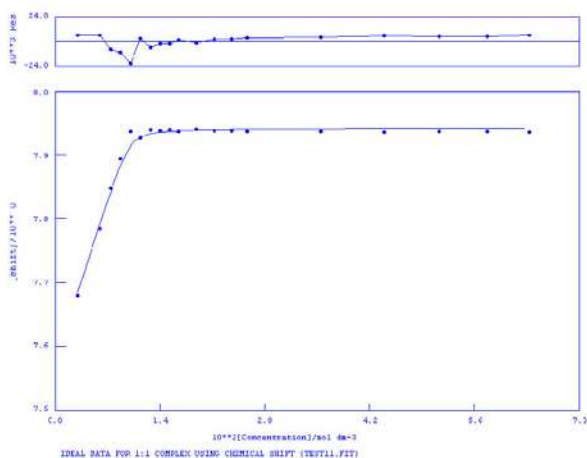
$K_a = 18 \text{ M}^{-1}$ Error = 14 %

Figure S41 NMR titration of compound **3** vs. TBAHSO₄ in DMSO-*d*₆/H₂O 0.5%. Following the aromatic CH.



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

Figure S42 NMR titration of compound **3** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 0.5%. Following the urea NH.



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

Figure S43 NMR titration of compound **3** vs. TBA₂SO₄ in DMSO-*d*₆/H₂O 0.5%. Following the aromatic CH.

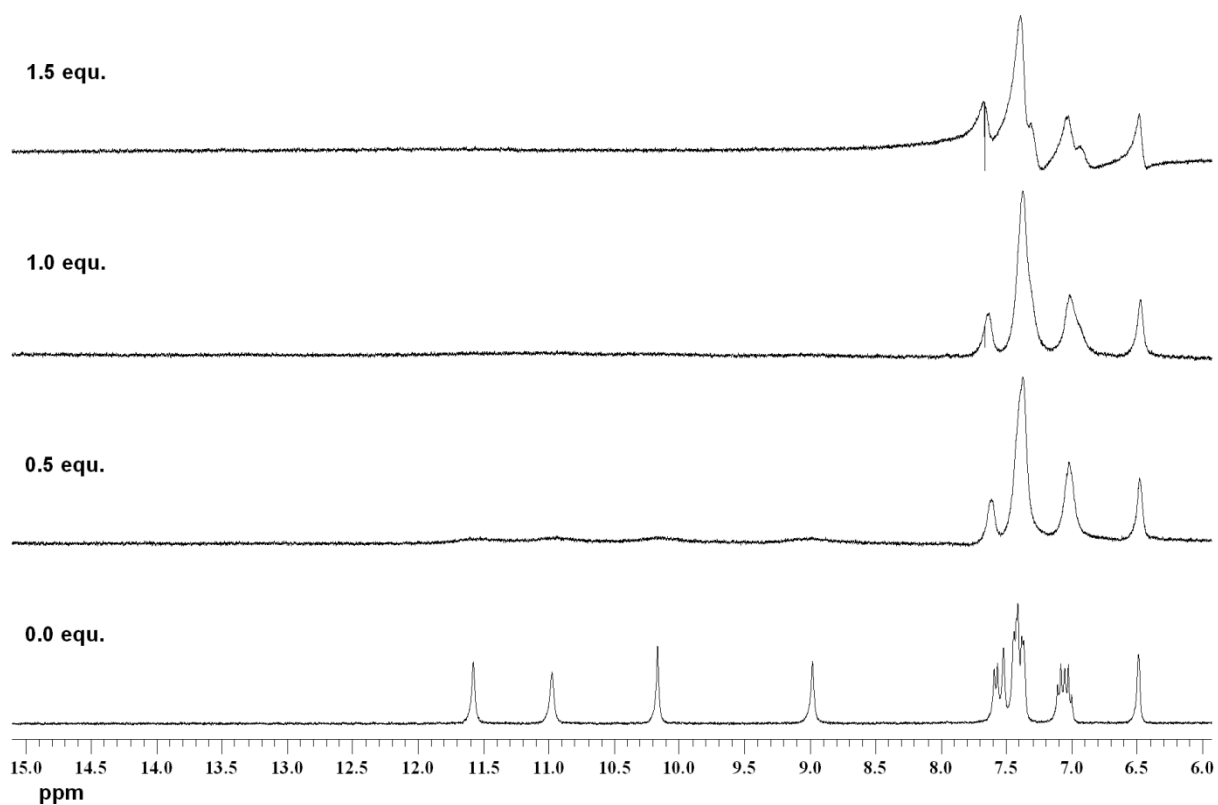


Figure S44 NMR stack plot of compound **1** vs. TBAOH in DMSO-*d*₆/H₂O 0.5%.

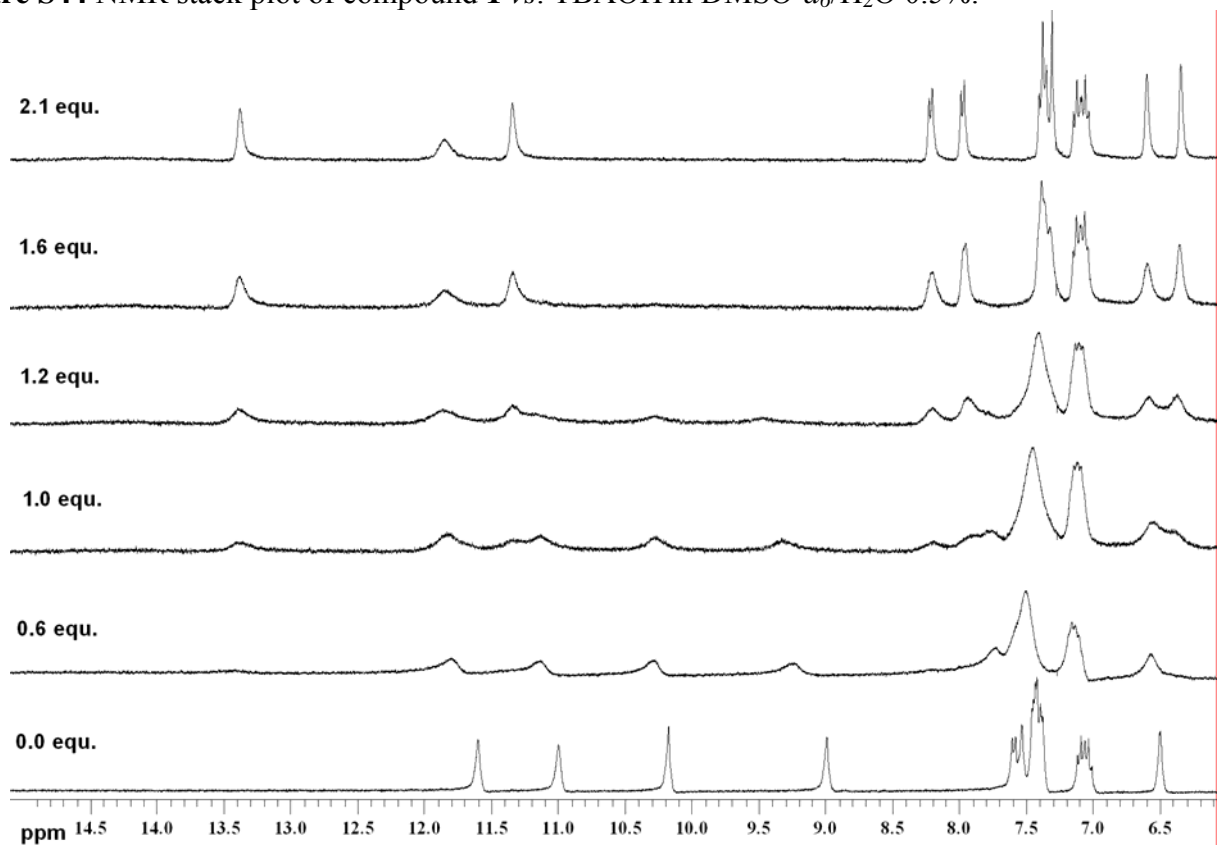


Figure S45 NMR stack plot of compound **1** vs. TBAHCO₃ in DMSO-*d*₆/H₂O 0.5%.

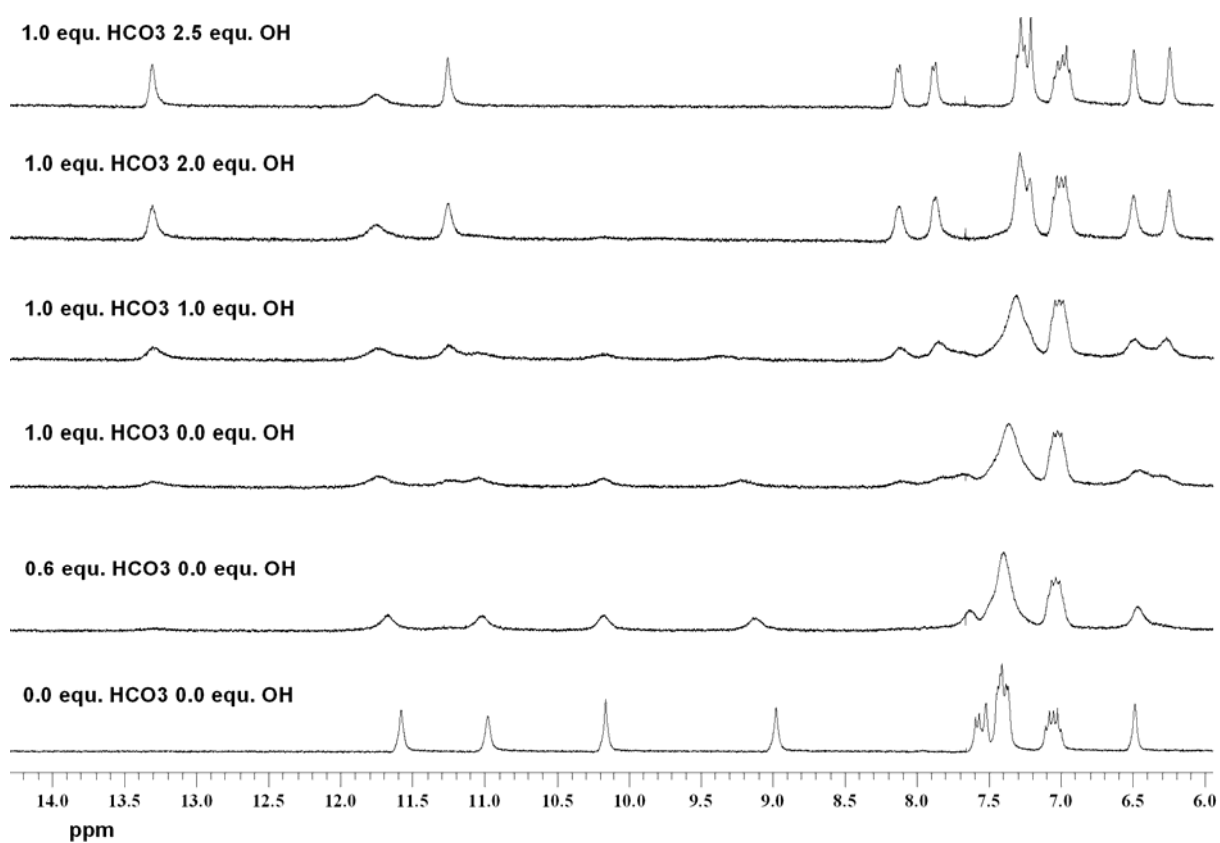


Figure S46 NMR stack plot of compound **1** vs. TBAHCO₃ and TBAOH in DMSO-*d*₆/H₂O 0.5%.

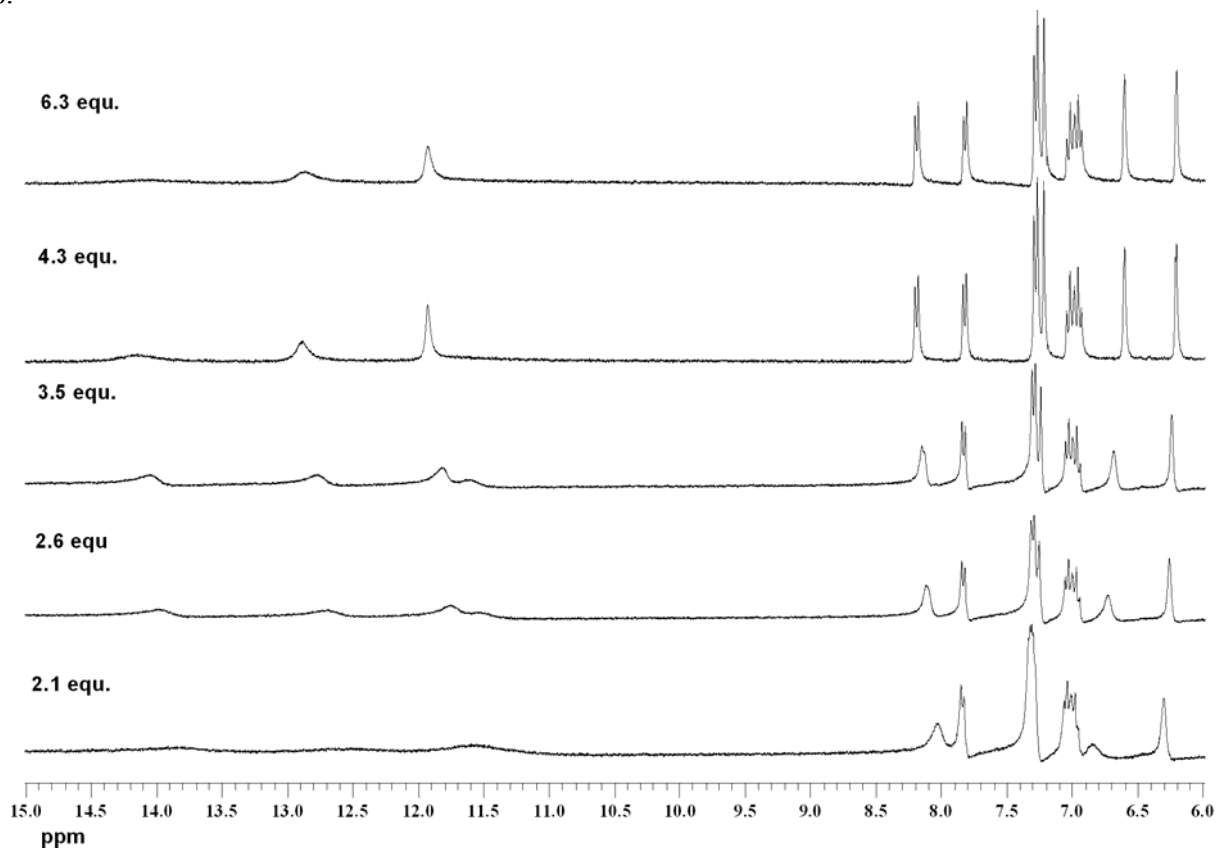


Figure S47a NMR stack plot of compound **1** vs. TBAH₂PO₄ in DMSO-*d*₆/H₂O 0.5%.

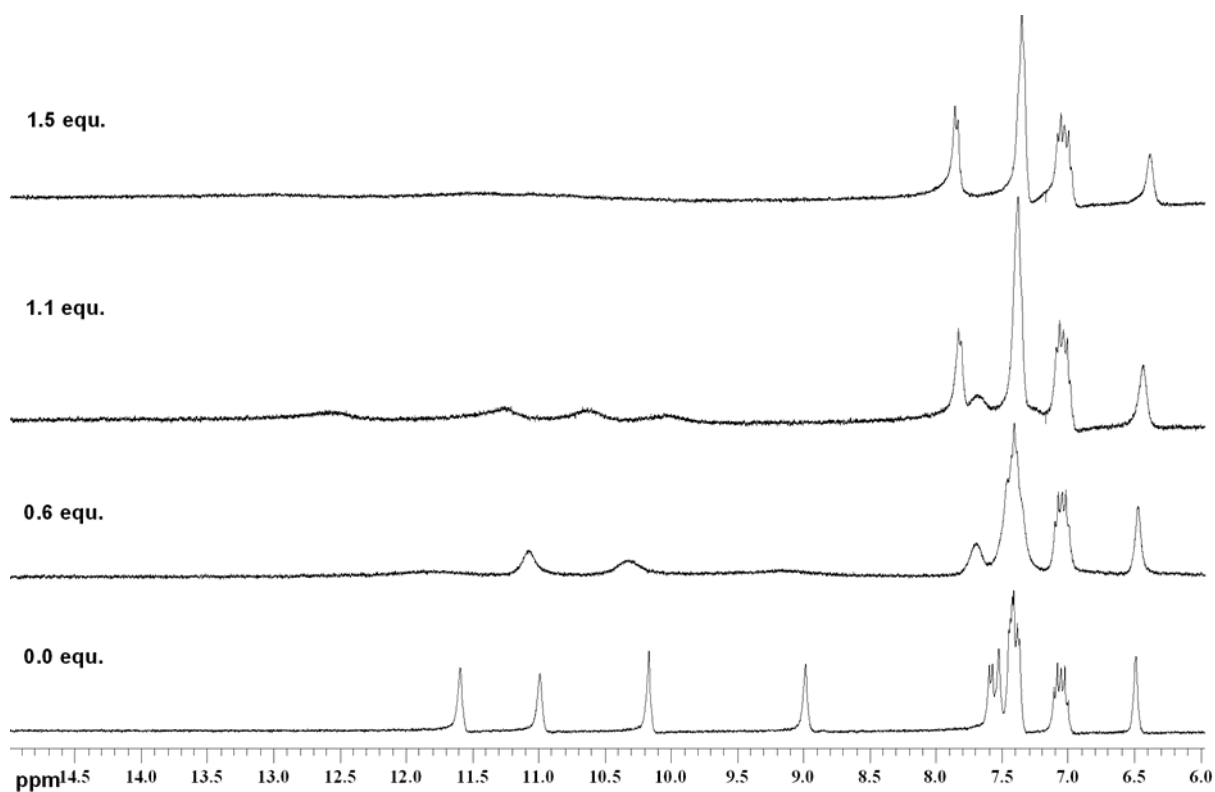


Figure S47b NMR stack plot of compound **1** vs. TBAH₂PO₄ in DMSO-*d*₆/H₂O 0.5%.

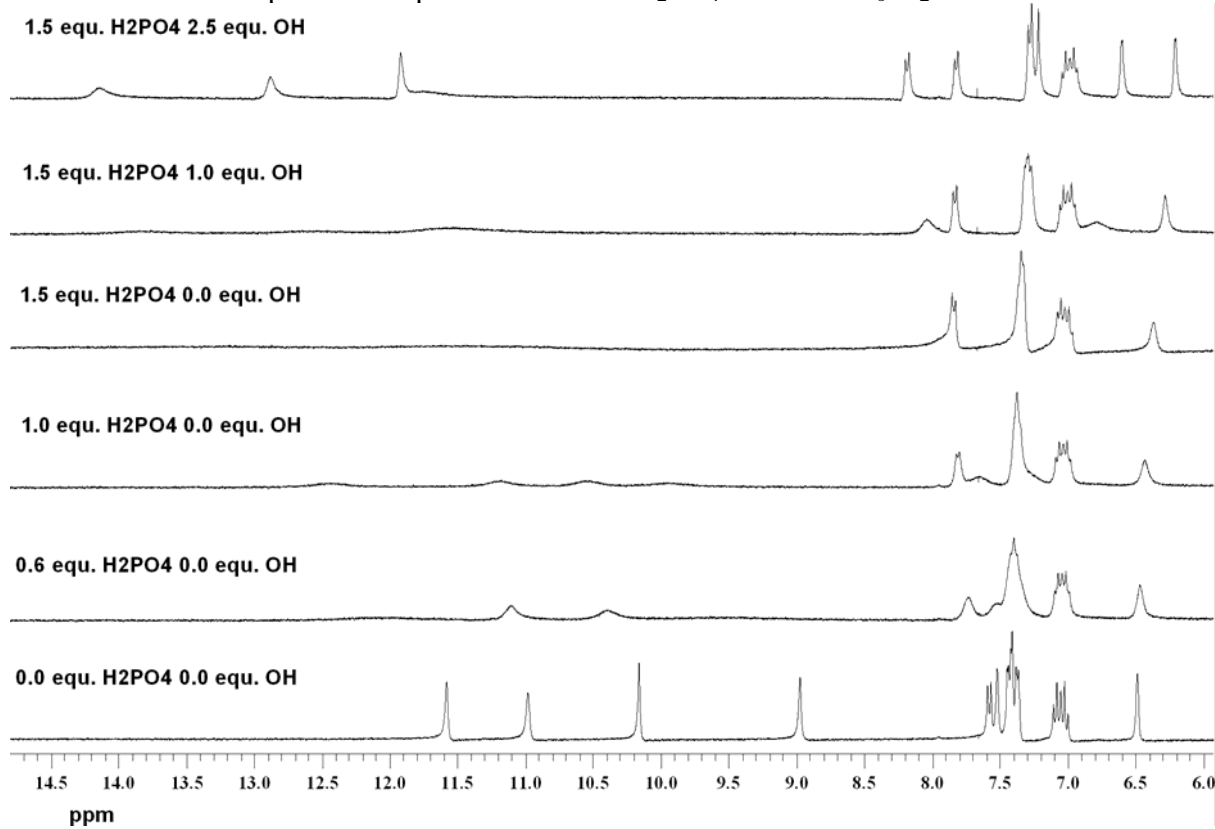


Figure S48 NMR stack plot of compound **1** vs. TBAH₂PO₄ and TBAOH in DMSO-*d*₆/H₂O 0.5%.

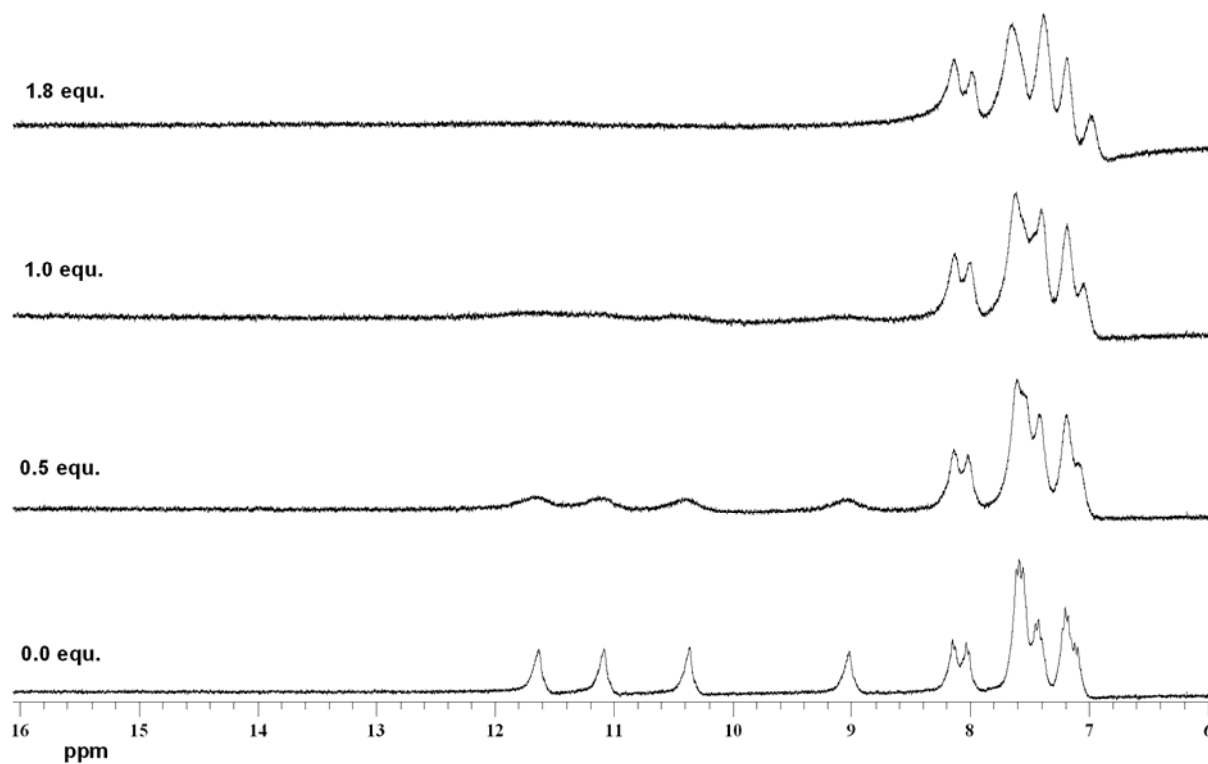


Figure S49 NMR stack plot of compound **2** vs. TBAOH in DMSO-*d*₆/H₂O 0.5%.

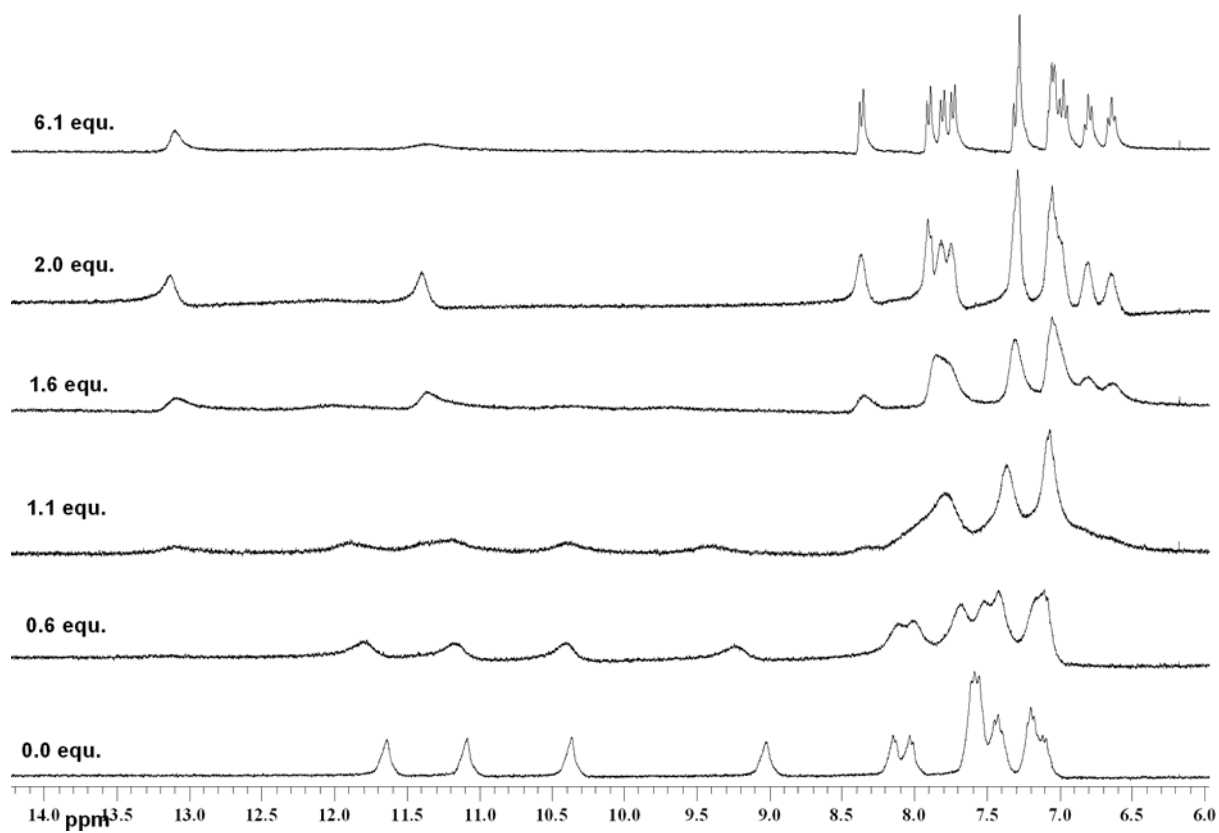


Figure S50 NMR stack plot of compound **2** vs. TBAHCO₃ in DMSO-*d*₆/H₂O 0.5%.

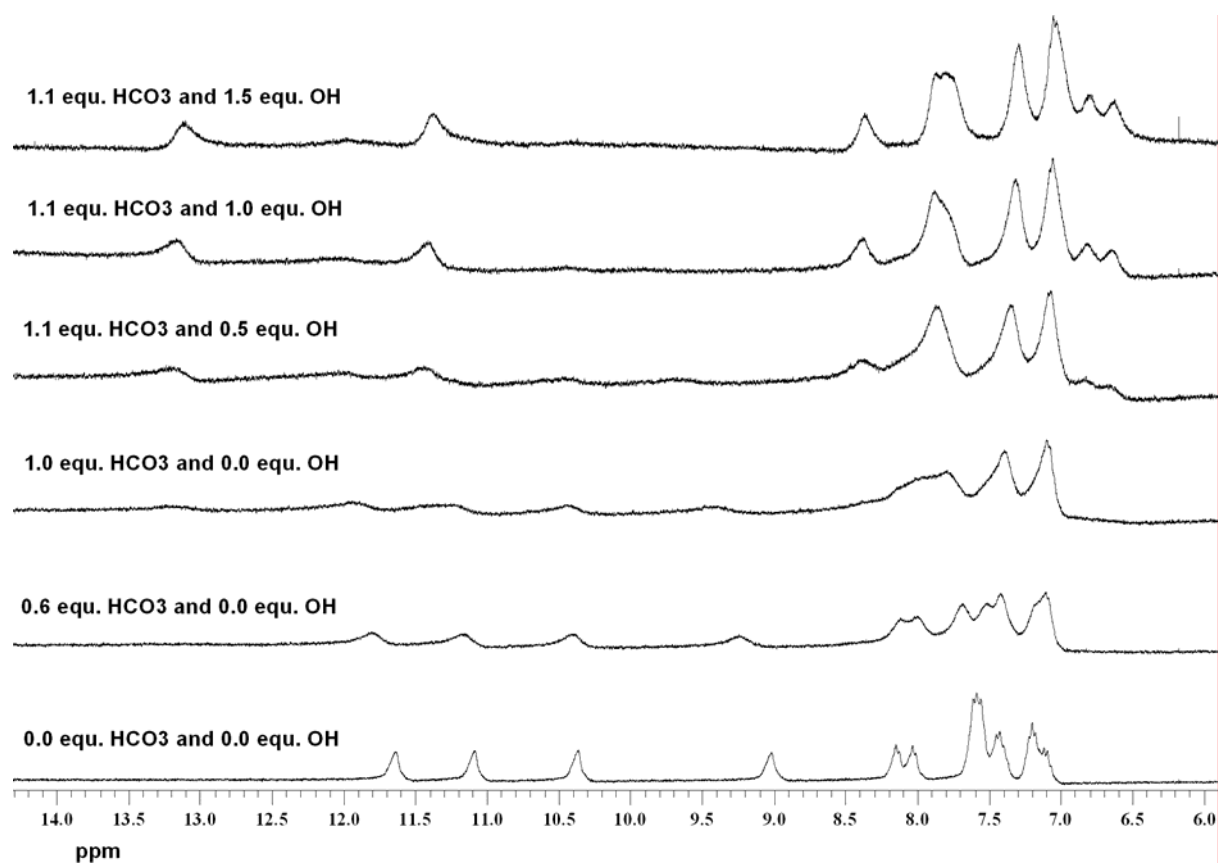


Figure S51 NMR stack plot of compound **2** vs. TBAHCO₃ and TBAOH in DMSO-*d*₆/H₂O 0.5%.

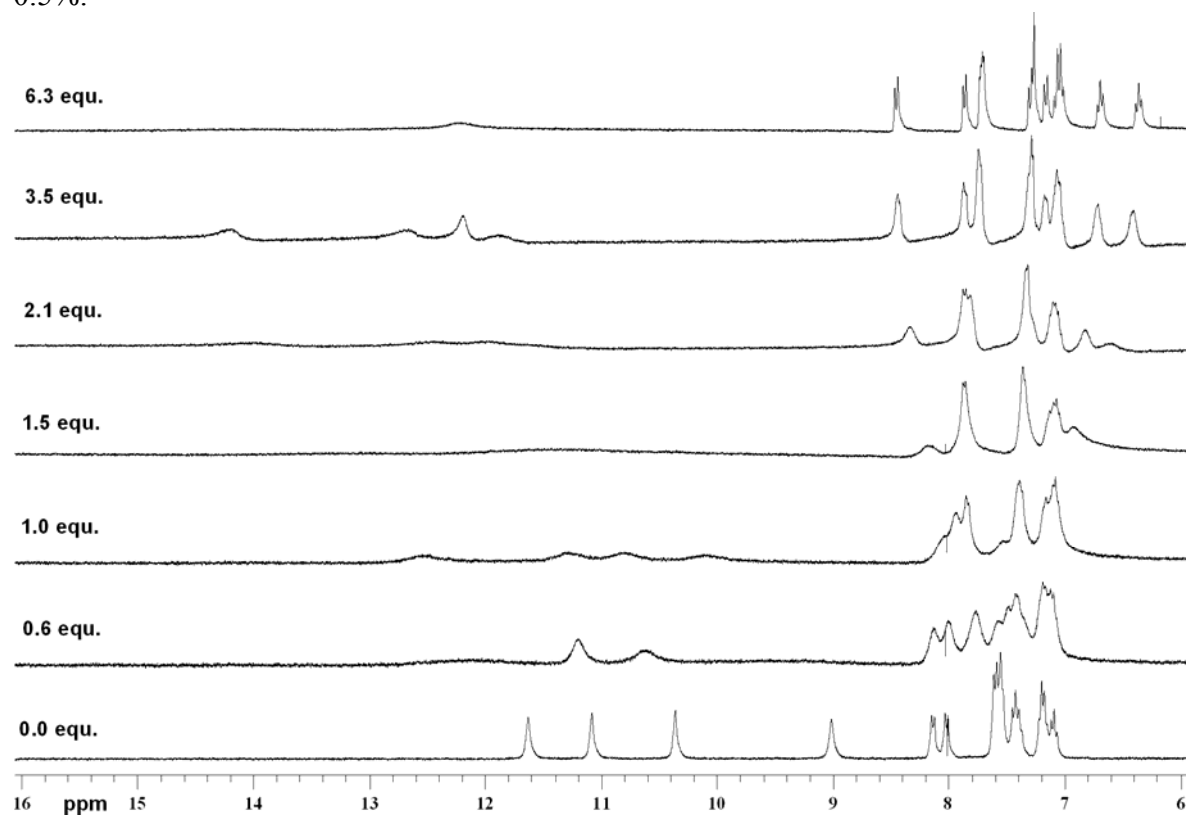


Figure S52 NMR stack plot of compound **2** vs. TBAH₂PO₄ in DMSO-*d*₆/H₂O 0.5%.

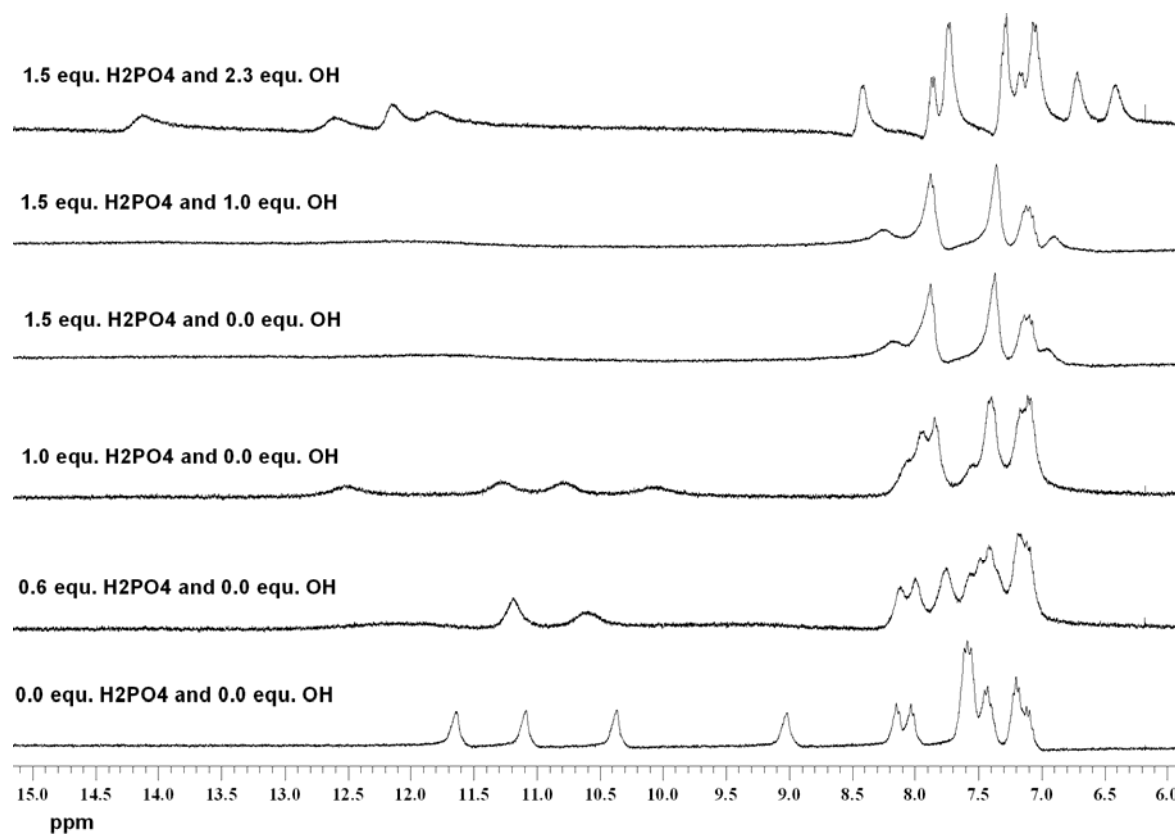


Figure S53 NMR stack plot of compound **2** vs. TBAH₂PO₄ and TBAOH in DMSO-*d*₆/H₂O 0.5%.

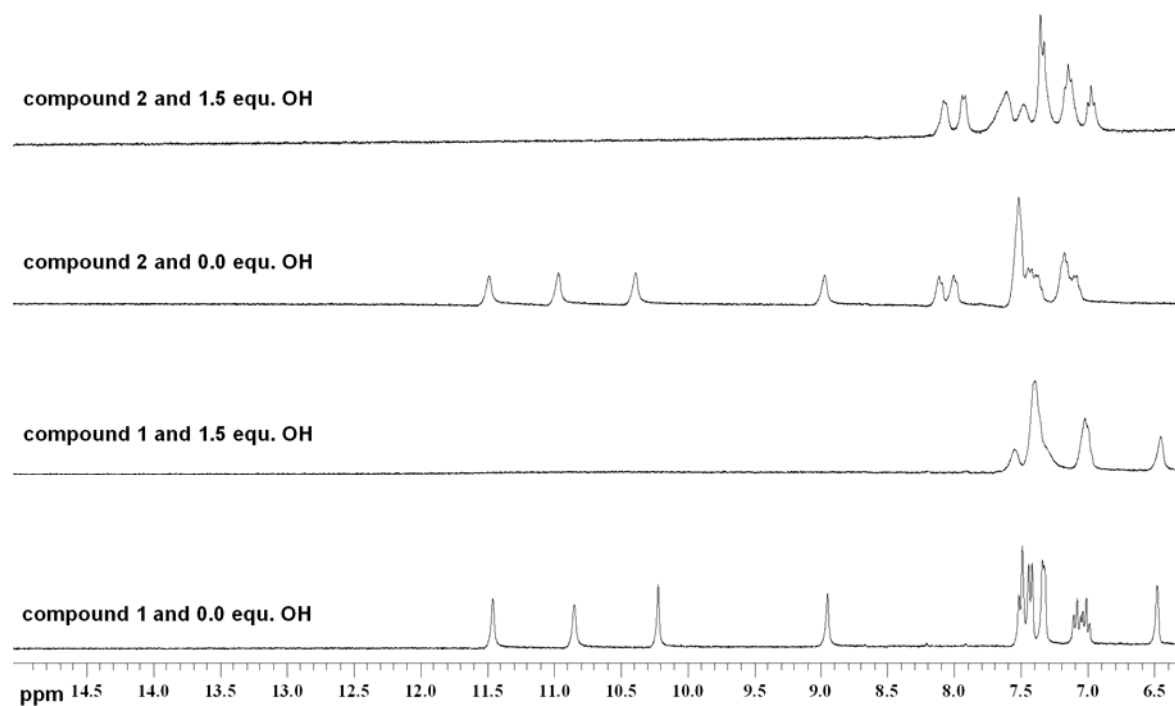


Figure S54 NMR stack plot of compound **1** and **2** vs. TBAOH in DMSO-*d*₆/H₂O 10%.

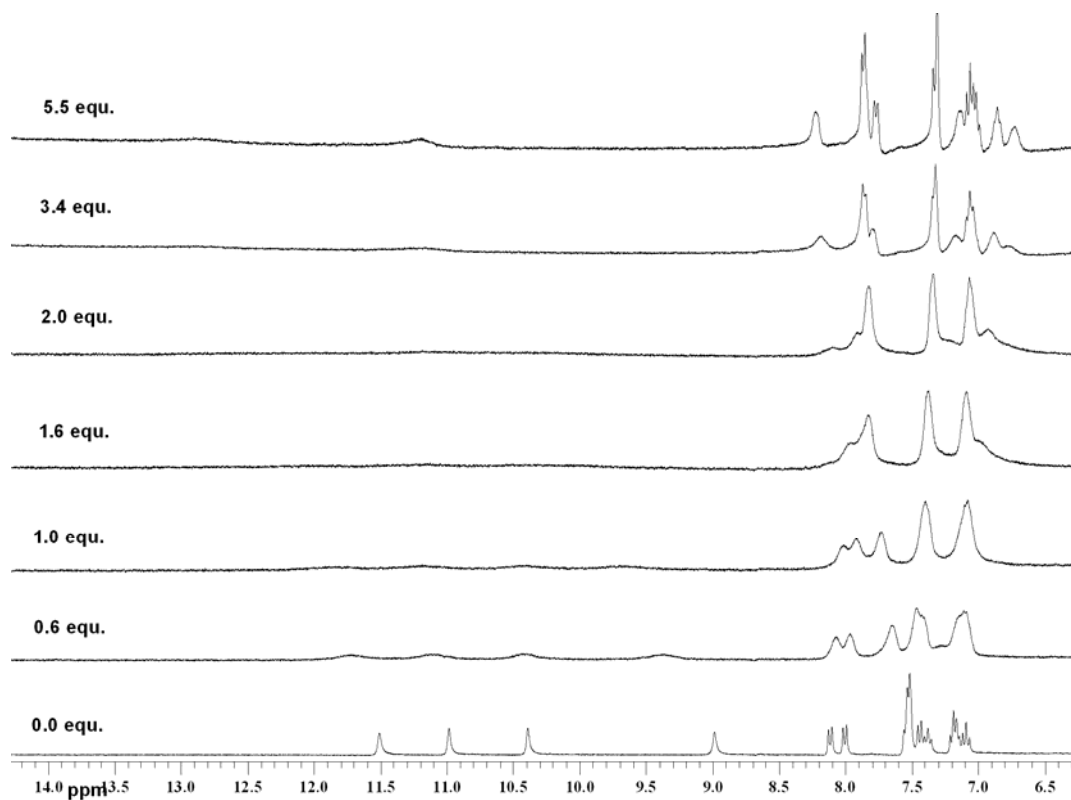


Figure S55 NMR stack plot of compound **1** vs. TBAHCO₃ in DMSO-*d*₆/H₂O 10%.

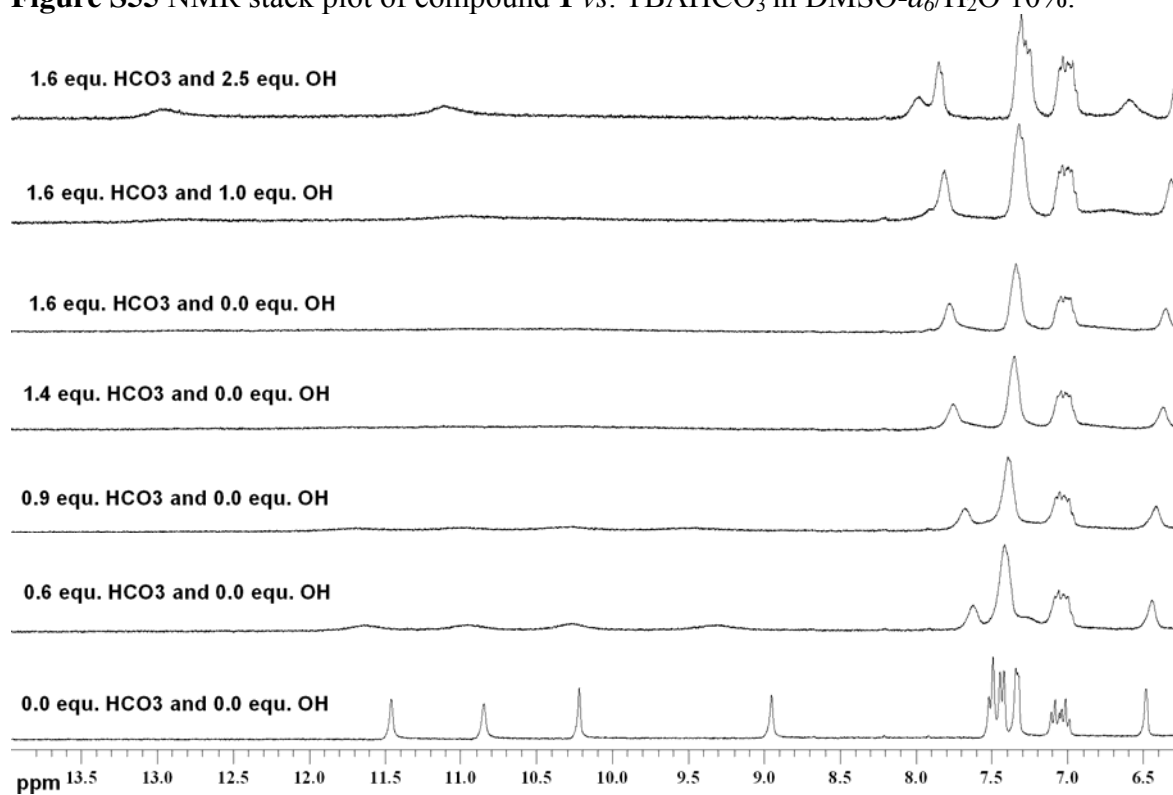


Figure S56 NMR stack plot of compound **1** vs. TBAHCO₃ and TBAOH in DMSO-*d*₆/H₂O 10%.

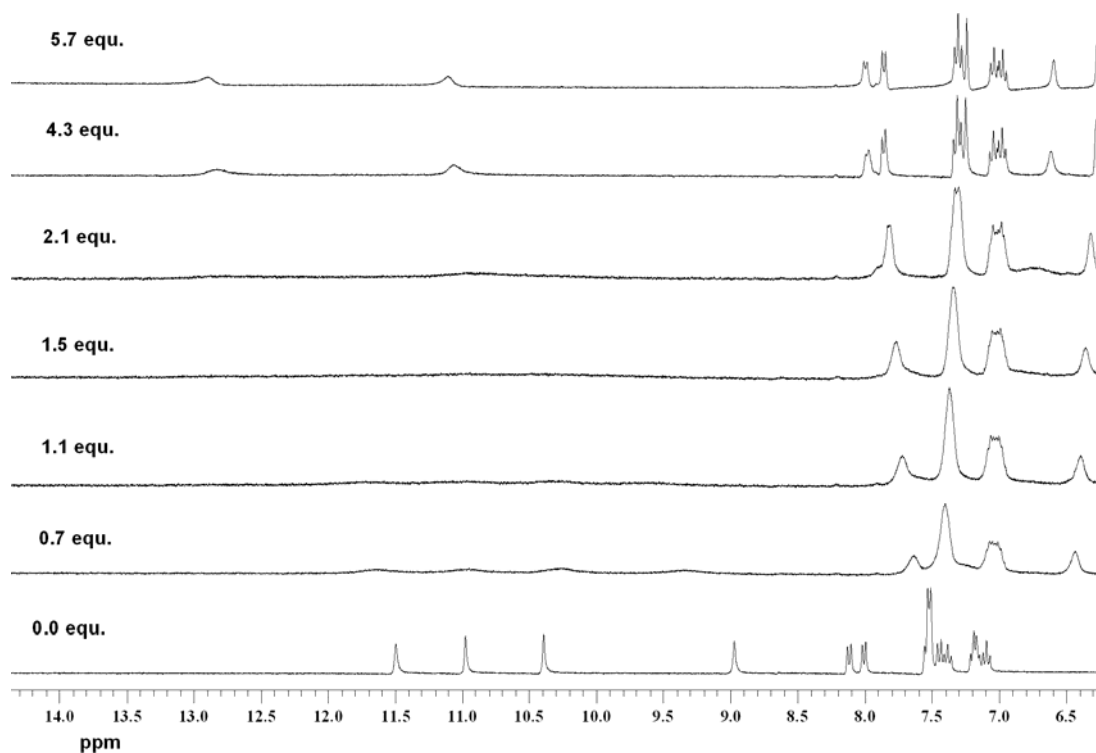


Figure S57 NMR stack plot of compound **2** vs. TBAHCO₃ in DMSO-*d*₆/H₂O 10%.

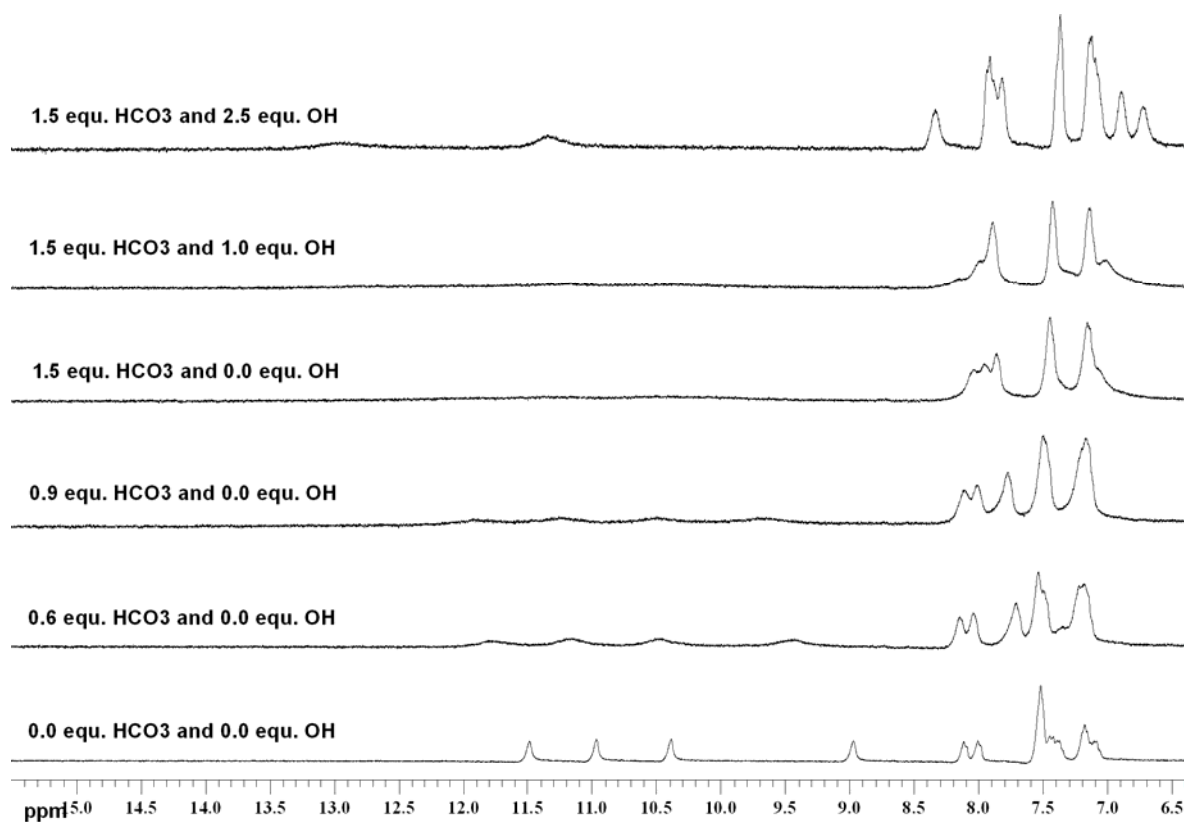


Figure S58 NMR stack plot of compound **2** vs. TBAHCO₃ and TBAOH in DMSO-*d*₆/H₂O 10%.