Anion receptors based on 7,7'-diamido-2,2'-diindolylmethane

Paweł Dydio[a,b], Tomasz Zieliński[a], Janusz Jurczak[a,b]

[a] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*

Supporting information

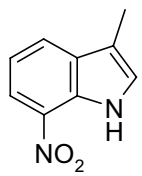
Contents

Synthesis

General remarks

All precursors for syntheses were obtained from Aldrich or Fluka and were used without further purification. The flash chromatography was carried out using Merck Kieselgel 60 (63–100 μm mesh size), TLC was carried out on Merck Kieselgel F254 plates.

3-Methyl-7-nitro-1H-indole (4)



1,2-dinitrobenzene (2.8 g, 16.7 mmol) was dissolved in dry THF (75 ml) in a two-neck flask equipped with a thermometer and a dropping funnel. The resulting mixture was cooled down to -60˚C and stirred under inert atmosphere. Then the 0.5M solution of 1-propenylmagnesiumbromide in THF (100 ml, 50 mmol) was added dropwise slowly enough to keep the temperature between -60˚C and -50˚C (which took about 1 hour). After addition of the Gringard's reagent, the reaction mixture was stirred at -60˚C for the next 4 hours and then the reaction was quenched with ammonium chloride (6g) in water (70 ml). THF was removed *in vacuo* from the solution, and the remaining water phase was extracted with $CHCl_3$. The $CHCl_3$ portions were combined, dried over $MgSO_4$, and the solvent was evaporated. The product was purified by column chromatography on silica gel, with hexane : ethyl acetate (99 : 1) mixture as an eluent. The product was crystallized from hexane : ethyl acetate mixture yielding 1.1 g (37%) of the methylnitroindole **4** as yellow crystals, m.p. 138-140˚C.

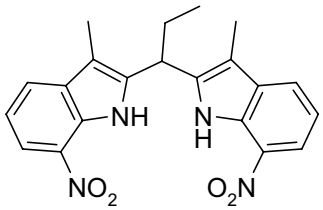
^{1}H NMR (200 MHz, $CDCl_3$) δ = 9.57 (bs, 1H, N*H*), 8.07 (d, 1H, J_1 = 8.0 Hz), 7.83 (d, 1H, J_1 = 7.8 Hz), 7.11 (t, 1H, J_1 = 7.8 Hz), 7.07 (s, 1H), 2.29 (s, 3H, CH_3);

^{13}C NMR (50 MHz, $CDCl_3$) δ = 132.2, 129.6, 126.9, 123.9, 119.1, 118.4, 113.1, 9.4;

HR ESI calcd. for $C_9H_8N_2O_2Na$ $[M+Na]^+$: 199.0478, found: 199.04845;

Elemental analysis (%) calcd. for $C_9H_8N_2O_2$: C 61.36, H 4.58, N 15.90, found: C 61.10, H 4.45, N 15.87.

1,1-Bis-(-3-methyl-7-nitro-1H-indol-2-yl)-propane (5)



Well powdered 3-methyl-7-nitro-1H-indole (**4**) (176mg, 1mmol) and propionaldehyde (0.22ml, 3mmol) were suspended in

concentrated HCl (10ml), and heated at 100˚C over 2 hours in a sealable tube. After cooling down, the suspension was carefully poured into $Na_2CO_{3(sat)}$ (20ml) and $CHCl_3$ was added to dissolve the precipitate formed. The layers were separated and the remaining water phase was extracted with $CHCl_3$. The $CHCl_3$ extracts were combined, washed with water, dried over $MgSO_4$, and evaporated. The product was further purified by column chromatography on silica gel, with hexane : ethyl acetate (gradient: 99:1 to 95:5) mixture as an eluent, followed by crystallization from hexane : ethyl acetate mixture yielding 137mg (70%) of the desired compound **5**, m.p. 198-200˚C.

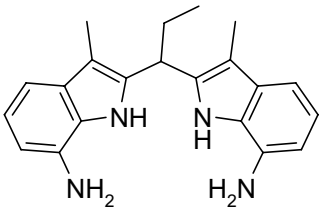
^{1}H NMR (200 MHz, $CDCl_3$) δ = 9.72 (bs, 2H, N*H*), 8.09 (d, 2H, J_1 = 8.1 Hz), 7.84 (d, 2H, J_1 = 7.8 Hz), 7.17 (t, 2H, J_1 = 8.2 Hz), 4.56 (t, 1H, J_1 = 8.2Hz), 2.37 (m, 2H, CH_2), 2.34 (s, 6H, CH_3), 1.08 (t, 3H, J_1 = 7.2 Hz, CH_3CH$_2$);

^{13}C NMR (50 MHz, $CDCl_3$) δ = 136.5, 133.1, 132.5, 128.9, 126.3, 118.8, 109.5, 37.1, 26.4, 12.4, 8.7;

HR EI calcd. for $C_{21}H_{20}N_4O_4$ M^+: 392.14846, found: 392.14746;

Elemental analysis (%) calcd. for $C_{21}H_{20}N_4O_4$: C 64.28, H 5.14, N 14.28, found: C 64.16, H 5.13, N 14.15.

1,1-bis-(-7-amino-3-methyl-1H-indol-2-yl)-propane (6)



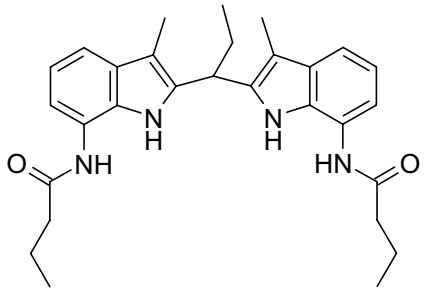
1,1-Bis-(-3-methyl-7-nitro-1H-indol-2-yl)-propane (**5**) (392mg, 1 mmol) was dissolved in methanol (20 ml) and 5% palladium on charcoal was added (0.1g). The reaction mixture was vigorously stirred under hydrogen atmosphere. The progress of the reaction was monitored on TLC, and after completion (about one hour), the catalyst was filtered off on Celite®. The solvent was evaporated, and the crude amine **6** was immediately used in a subsequent reaction with the appropriate acetic chloride assuming a complete transformation of substrate **5** into the desired amine **6**.

^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.18 (bs, 2H, N*H*-indole), 7.07 (d, 2H, J_1 = 8.0 Hz), 6.92 (t, 2H, J_1 = 7.6 Hz), 6.42 (d, 2H, *J1* = 7.0 Hz), 4.23 (t, 1H, *J1* = 7.6Hz), 3.17 (bs, 4H, NH_2), 2.23 (s, 6H, CH_3), 2.09 (m, 2H, CH_2), 0.95 (t, 3H, J_1 = 7.2 Hz, CH_3CH$_2$).

General Procedure for Preparation of the Ligands 1a-c

Triethylamine was added (0.42ml, 3mmol) to the cooled (0˚C) solution of crude diamine **6** (1mmol) in dry CH_2Cl_2 (60ml). Subsequently, appropriate acid chloride was added slowly dropwise to the stirred solution under Ar atmosphere. Afterwards, the cooling bath was removed and the stirring was continued overnight. The organic layer was washed with $NaHCO_{3(sat.)}$ (2•50 ml), water (50ml), dried over $MgSO_4$, and then the solvent was evaporated. The crude product was purified by column chromatography on silica gel, with CH_2Cl_2 : methanol (250:1) mixture as an eluent.

1,1-bis-(-7-butyrylamino-3-methyl-1H-indol-2-yl)-propane (1a)



Butanoic acid chloride (0.26ml, 2.5mmol) was used as the acyl reagent, yielding 0.412g (87%) of product, which was recrystallized from hot ethyl acetate giving colorless crystals, m.p. 242-243˚C.

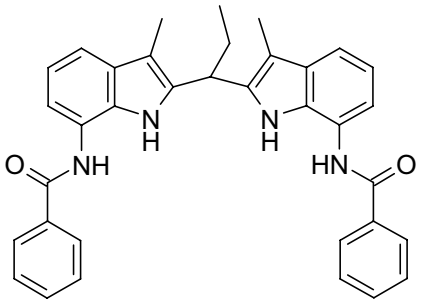
^{1}H NMR (500 MHz, DMSO) δ = 10.16 (bs, 2H, N*H*-indole), 9.66 (bs, 2H, N*H*), 7.43 (d, 2H, J_1 = 7.5 Hz), 7.16 (d, 2H, J_1 = 7.8 Hz), 6.90 (t, 2H, J_1 = 7.7 Hz), 4.46 (t, 1H, J_1 = 8.0Hz, C*H*CH_2CH_3), 2.38 (t, 4H, J_1 = 7.4 Hz, COC*H*$_2$), 2.20 (m, 2H, CHC*H*$_2$$CH_3$), 2.16 (s, 6H, C*H*$_3$), 1.66 (m, 4H, $COCH_2$C*H*$_2$), 0.94 (t, 6H, J_1 = 7.4 Hz, $COCH_2CH_2$C*H*$_3$), 0.92 (t, 3H, J_1 = 7.4 Hz, $CHCH_2$C*H*$_3$);

^{13}C NMR (50 MHz, DMSO) δ = 171.5, 135.7, 130.8, 127.1, 123.1, 118.9, 114.1, 112.7, 107.0, 36.6, 27.0, 19.1, 14.1, 12.6, 9.0;

HR ESI calcd. for $C_{29}H_{36}N_4O_2Na$ $[M+Na]^+$: 495.27305, found: 495.27522;

Elemental analysis (%) calcd. for $(C_{29}H_{36}N_4O_2)_4 \cdot CH_3CO_2C_2H_5$[i]: C 72.84, H 7.74, N 11.33, found: C 72.85, H 7.96, N 11.52.

1,1-Bis-(-7-benzoylamino-3-methyl-1H-indol-2-yl)-propane (1b)

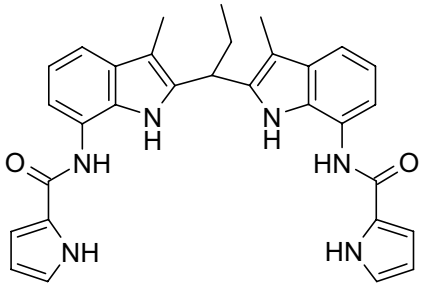


Benzoyl chloride (0.29ml, 2.5mmol) was used as the acyl reagent, yielding 0.500g (92%) of product, which was recrystallized from ethyl acetate – hexane mixture giving off-white powder, m.p. 270˚C (decomp).

[i] (4·Ligands **1a**·Ethyl acetate – as observed on ^{1}H NMR spectra)

^{1}H NMR (500 MHz, DMSO) δ = 10.23 (bs, 2H, N*H*-indole), 10.06 (bs, 2H, N*H*), 7.94 (d, 4H, J_1 = 7.4 Hz), 7.58 (t, 2H, J_1 = 7.4 Hz), 7.48 (t, 4H, J_1 = 7.7 Hz), 7.37 (d, 2H, J_1 = 7.5 Hz), 7.26 (d, 2H, J_1 = 7.8 Hz), 6.96 (t, 2H, J_1 = 7.7 Hz), 4.50 (t, 1H, J_1 = 8.0Hz, C*H*CH_2CH_3), 2.23 (s, 6H, C*H*$_3$), 2.20 (m, 2H, CHC*H*$_2$$CH_3$), 0.91 (t, 3H, J_1 = 7.2 Hz, $CHCH_2$C*H*$_3$);
^{13}C NMR (50 MHz, DMSO) δ = 166.1, 136.1, 135.5, 131.8, 130.8, 128.8, 128.3, 123.2, 118.8, 115.4, 115.2, 106.8, 79.6, 36.5, 27.0, 12.7, 9.1;
HR ESI calcd. for $C_{35}H_{32}N_4O_2Na$ $[M+Na]^+$: 563.24175, found: 563.24443;
Elemental analysis (%) calcd. for $C_{35}H_{32}N_4O_2 \cdot H_2O$[ii]: C 75.24, H 6.13, N 10.03, found: C 75.03, H 6.66, N 10.26.

1,1-Bis-(-3-methyl-7-(1H-pyrrole-2-carboxyl)-amino-1H-indol-2-yl)-propane (1c)



1*H*-pyrrole-2-carboxylic acid chloride (0.58g, 4.5mmol) in dry CH_2Cl_2 (20 ml) was used as an acyl reagent. Larger amount of triethylamine (0.81ml, 10mmol) was employed. 0.410g (79%) of product was obtained, which was crystallized from hot ethyl acetate – hexane mixture giving off-white powder, m.p. 135°C (decomp).

^{1}H NMR (500 MHz, DMSO) δ = 11.62 (bs, 2H, N*H*-pyrrole), 10.28 (bs, 2H, N*H*-indole), 9.59 (bs, 2H, N*H*), 7.25 (d, 2H, J_1 = 7.5 Hz), 7.22 (d, 2H, J_1 = 7.7 Hz), 7.06 (m, 2H), 6.96 (m, 2H), 6.93 (d, 2H, J_1 = 7.7 Hz), 6.17 (dt, 2H, J_1 = 3.7 Hz, J_1 = 2.4 Hz), 4.50 (t, 1H, J_1 = 8.1 Hz, C*H*CH_2CH_3), 2.23 (s, 6H, C*H*$_3$), 2.21 (m, 2H, CHC*H*$_2$$CH_3$), 0.91 (t, 3H, J_1 = 7.3 Hz, $CHCH_2$C*H*$_3$);
^{13}C NMR (125 MHz, DMSO) δ = 159.3, 135.7, 130.2, 128.7, 126.1, 122.5, 122.2, 118.3, 115.0, 114.4, 111.6, 108.8, 106.2, 35.8, 26.2, 12.2, 8.5;
HR ESI calcd. for $C_{31}H_{30}N_6O_2Na$ $[M+Na]^+$: 541.23225, found: 541.23049;
Elemental analysis (%) calcd. for $(C_{31}H_{30}N_6O_2)_2 \cdot H_2O$: C 70.57, H 5.92, N 15.93, found: C 70.95, H 6.17, N 15.21.

[ii] Monohydrate as observed X-ray structure

Binding studies

General comments

As the source of anions, commercially available tetrabutylammonium salts were used which were pre-dried overnight under high vacuum at 60ºC.
Distilled water was added to the commercially available DMSO-d_6 of 99.9% isotopic purity (purchased from ARMAR AG) to obtain the appropriate water concentration.

^{1}H NMR titration experiments

The ligand solution (concentration about $1.5 \cdot 10^{-2}$ M, details are given in Tables S1-S4) was titrated in the NMR tubes with the solution of the respective tetrabutylammonium salt in ligand aliquots (salt concentration about 0.1-0.2 M). 14-18 data points were recorded. The binding constants were calculated from the changes in chemical shifts of ligand protons. Nonlinear curve fitting for 1:1 binding model was carried out with the Origin program. The binding constants K and the asymptotic change in chemical shift $\Delta\delta_{max}$ were chosen as the free parameters for fitting.

^{1}H NMR Job plot experiments

0.40ml of the ligand solution (C about $2 \cdot 10^{-2}$ M) was titrated in the NMR tubes with aliquots (50µl) of the equimolar solution of the respective tetrabutylammonium salt, to the point of 1 : 1 ligand : anion ratio. Similarly, the anion solution was titrated with the ligand solution. 17 data points were recorded, which were used to obtain the Job plot.

Table S1. The details of ^{1}H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand **1a**

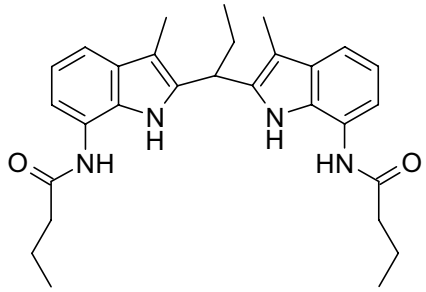
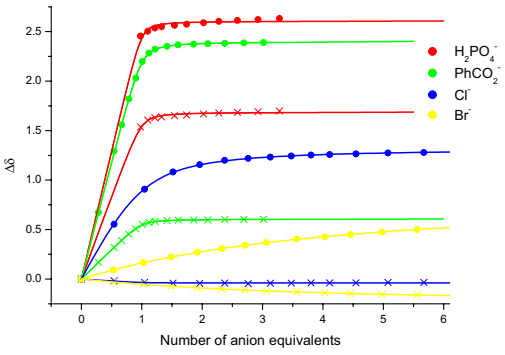
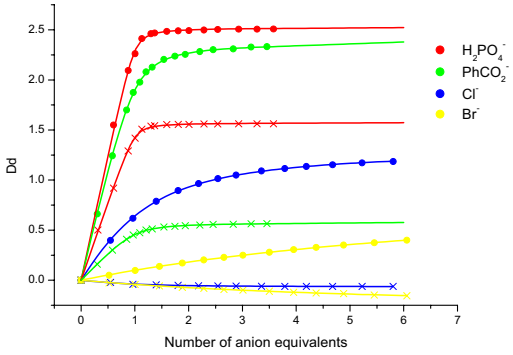
Ligand								
Solvent	DMSO-d_6 + 0.5% H_2O				DMSO-d_6 + 5% H_2O			
Anion	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]
Br^-	0.014608	0.22078	20.1 ± 0.2 21.5 ± 1.1	0.84 ($NH_{ind.}$) -0.26 (NH_{amde})	0.014440	0.21406	9.2 ± 0.2 12.5 ± 0.8	0.94 ($NH_{ind.}$) -0.31 (NH_{amde})
Cl^-	0.013800	0.22491	470 ± 4 -	1.33 ($NH_{ind.}$) -0.04 (NH_{amde})	0.014472	0.21478	145 ± 0.2 244 ± 24	1.29 ($NH_{ind.}$) 0.09 (NH_{amde})
$PhCOO^-$	0.010098	0.07396	> 10 000 > 10 000	2.40 ($NH_{ind.}$) 0.61 (NH_{amde})	0.011755	0.094172	2061 ± 44 1884 ± 47	2.38 ($NH_{ind.}$) 0.58 (NH_{amde})
$H_2PO_4^-$	0.01088	0.07221	> 10 000 > 10 000	2.63 ($NH_{ind.}$) 1.70 (NH_{amde})	0.011268	0.100252	> 10 000 > 10 000	2.52 ($NH_{ind.}$) 1.57 (NH_{amde})
^{1}H NMR titration curves	 ^{1}H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.				 ^{1}H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.			

Table S2. The details of ^{1}H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand **1a**

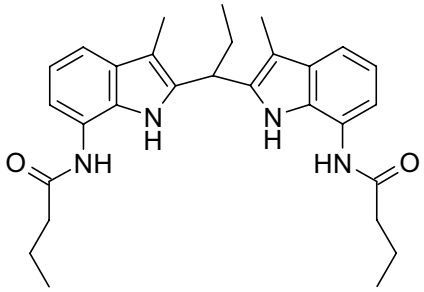
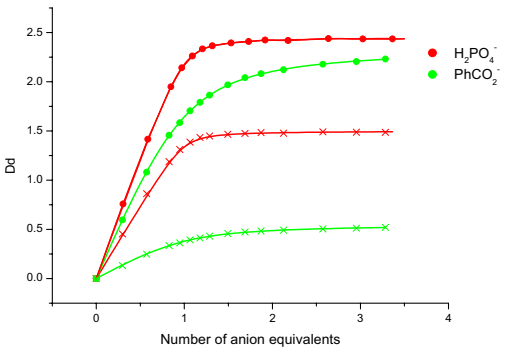
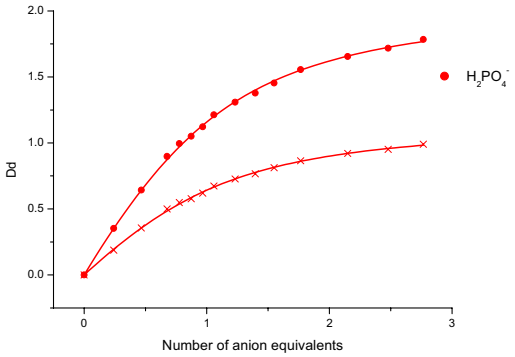
Ligand								
Solvent	DMSO-d_6 + 10% H_2O				DMSO-d_6 + 25% H_2O			
Anion	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]
Br^-								
Cl^-								
$PhCOO^-$	0.013174	0.101716	585 ± 8 537 ± 19	2.35 ($NH_{ind.}$) 0.55 (NH_{amde})				
$H_2PO_4^-$	0.012711	0.100527	5644±397 5981±355	2.46 ($NH_{ind.}$) 1.50 (NH_{amde})	0.012870	0.088522	211 ± 11 206 ± 11	2.11 ($NH_{ind.}$) 1.17 (NH_{amde})
^{1}H NMR titration curves	 ^{1}H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.				 ^{1}H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.			

Table S3. The details of ^{1}H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand **1b**

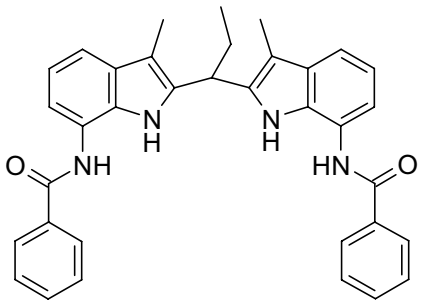
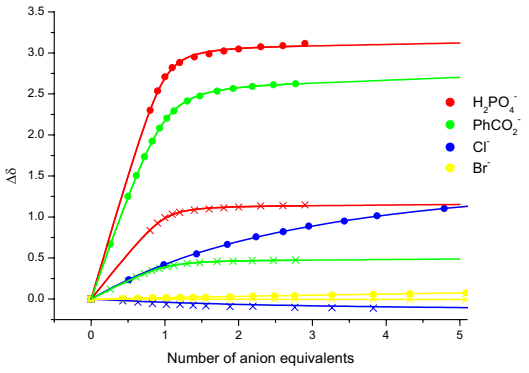
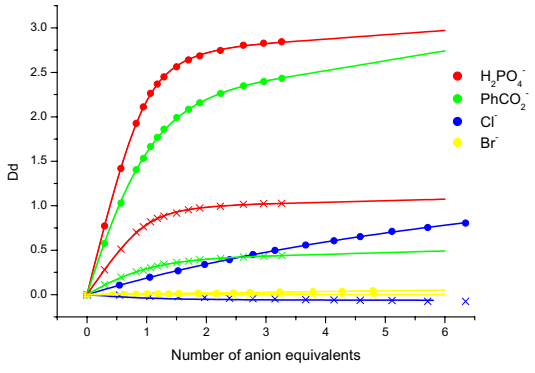
Ligand								
Solvent	DMSO-d_6 + 0.5% H_2O				DMSO-d_6 + 5% H_2O			
Anion	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]
Br^-	0.016321	0.199893	< 2 -	~0.57 ($NH_{ind.}$) - (NH_{amde})	0.015971	0.193605	< 2	-
Cl^-	0.014682	0.213520	29.5 ± 0.5 30.2 ± 3.8	1.72 ($NH_{ind.}$) -0.16 (NH_{amde})	0.014602	0.226743	7.5 ± 0.2 7.2 ± 1.6	2.25 ($NH_{ind.}$) -0.20 (NH_{amde})
$PhCOO^-$	0.010419	0.070163	2141 ± 67 2012 ± 53	2.69 ($NH_{ind.}$) 0.49 (NH_{amde})	0.011755	0.094172	340 ± 7 360 ± 13	2.64 ($NH_{ind.}$) 0.47 (NH_{amde})
$H_2PO_4^-$	0.010419	0.074015	4461 ± 349 3850 ± 321	3.12 ($NH_{ind.}$) 1.15 (NH_{amde})	0.011193	0.072967	981 ± 18 985 ± 41	2.63 ($NH_{ind.}$) 1.06 (NH_{amde})
^{1}H NMR titration curves	 ^{1}H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.				 ^{1}H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.			

Table S4. The details of ^{1}H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand **1c**

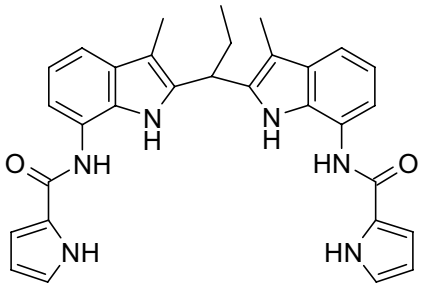
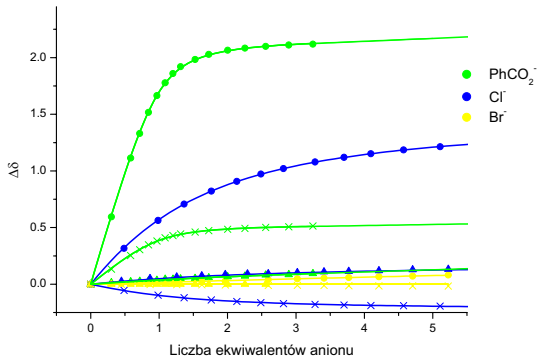
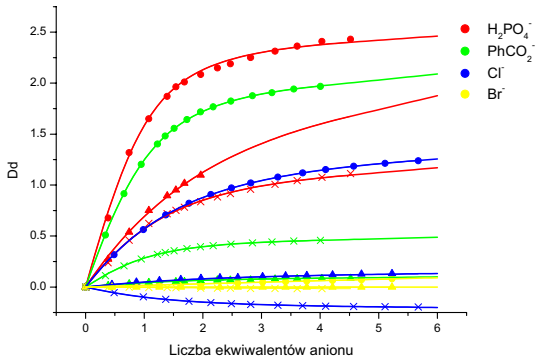
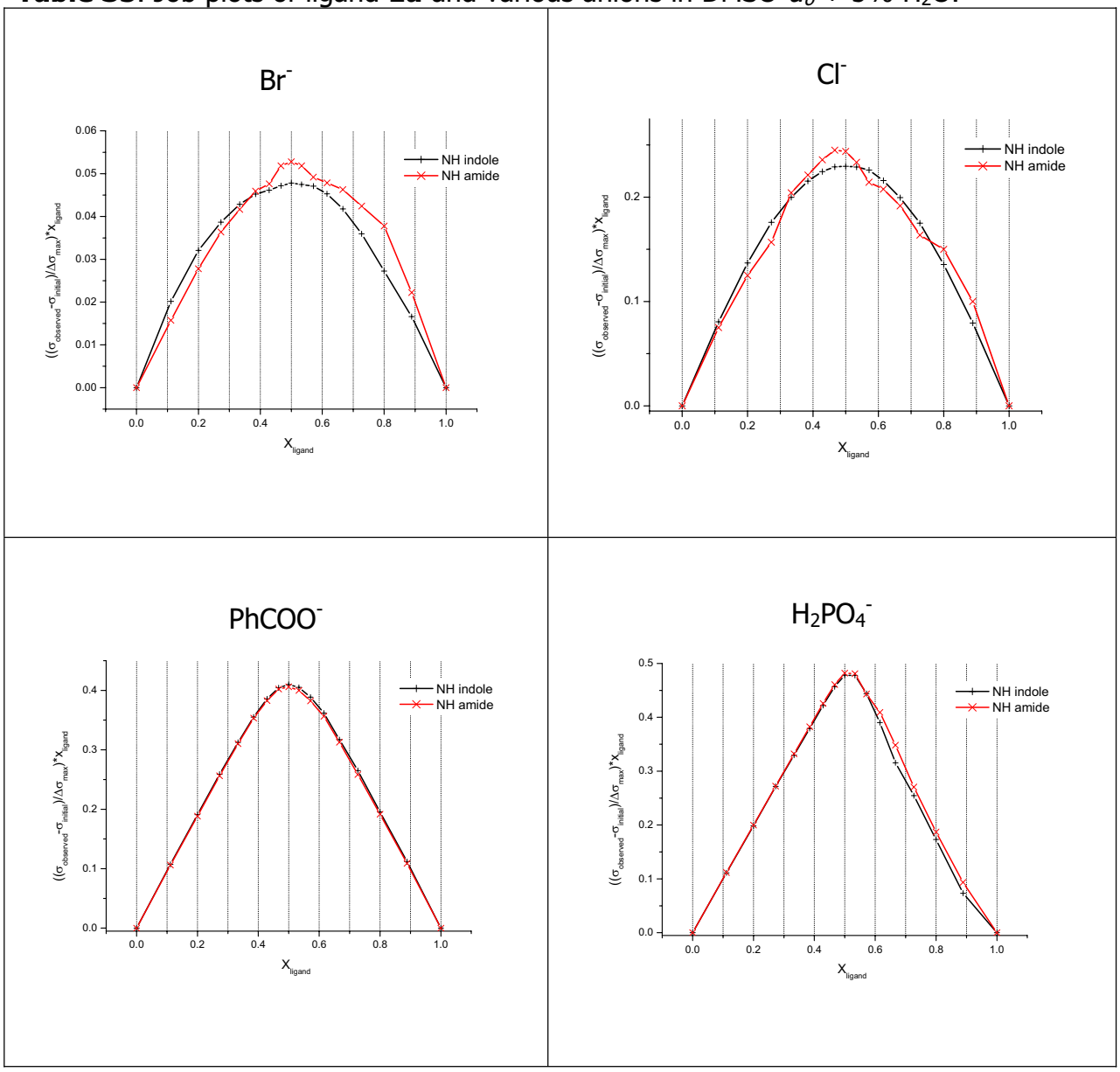
Ligand								
Solvent	DMSO-d_6 + 0.5% H_2O				DMSO-d_6 + 5% H_2O			
Anion	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]	L [mol·dm^{-3}]	A [mol·dm^{-3}]	K [M^{-1}]	$\Delta\delta_{max}$[ppm]
Br^-	0.015761	0.201625	- < 2 < 2	- ($NH_{pyrr.}$) ~2.6 ($NH_{ind.}$) ~-0.2 (NH_{amde})	0.018054	0.224955	< 2	-
Cl^-	0.018086	0.226384	35.3 ± 2.0 82.8 ± 0.5 131 ± 7	0.20 ($NH_{pyrr.}$) 1.47 ($NH_{ind.}$) -0.21 (NH_{amde})	0.018054	0.228085	18.9 ± 2.2 20.5 ± 0.3 21.9 ± 0.9	0.19 ($NH_{pyrr.}$) 1.64 ($NH_{ind.}$) -0.28 (NH_{amde})
$PhCOO^-$	0.009483	0.074793	21 ± 3 1657 ± 56 1023 ± 55	0.26 ($NH_{pyrr.}$) 2.18 ($NH_{ind.}$) 0.53 (NH_{amde})	0.010695	0.103261	88 ± 12 295 ± 4 263 ± 6	0.12 ($NH_{pyrr.}$) 2.17 ($NH_{ind.}$) 0.51 (NH_{amde})
$H_2PO_4^-$	0.008900	0.074186	-	-	0.010695	0.117226	50 ± 11 400 ± 38 125 ± 7	2.49 ($NH_{pyrr.}$) 2.56 ($NH_{ind.}$) 1.32 (NH_{amde})
^{1}H NMR titration curves	 ^{1}H NMR shifts of the indole (•), pyrrole (Δ) and amide NH (x) signals upon addition of various anions salts.				 ^{1}H NMR shifts of the indole (•), pyrrole (Δ) and amide NH (x) signals upon addition of various anions salts.		

Table S5. Job plots of ligand **1a** and various anions in DMSO-d_6 + 5% H_2O.



Crystal data

The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Lab. at the Chemistry Department of the University of Warsaw. Crystallographic data (excluding structure factors) for the structures discussed in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

All measurements of crystal were performed on a KM4CCD κ-axis diffractometer with graphite-monochromated MoKa radiation. The crystals were positioned at 62 mm from the CCD camera. 1200 frames were measured at 0.5°/1° intervals (for the chloride complex/ for the benzoate complex and the free ligand structures, respectively) with a counting time of 10, 22, and 21 sec (for the chloride complex of **1c**, the benzoate complex of **1a**, and monohydrate of **1b**, respectively). The data were corrected for Lorentz and polarization effects. Empirical correction for absorption was applied. Data reduction and analysis were carried out with the Oxford Diffraction programs.

The structure was solved by direct methods and refined using SHELXL. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $Fo^2>2\sigma$ (Fo^2) criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F.

Crystal data for **1a***TBAPhCOO: **CCDC** number 725837. $C_{52}H_{77}N_5O_4$, M = 836.19, Triclinic, *P-1*, a = 13.4563(10) Å, b = 13.7844(11) Å, c = 27.517(2) Å, α = 101.614(7)°, β = 100.781(7)°, γ = 94.217(6)°, V = 4878.4(7) Å^3, T = 100(2) K, Z = 4, μ(Mo-K_α) = 0.072 mm^{-1}, 88056 reflections measured, 21275 unique (R(int) = 0.0403) which were used in all calculations. The final R indices [I>2σ(I)]: R1(F^2)= 0.0423 and wR2(F^2)= 0.0940, for all data: R1(F^2)= 0.1028 and wR2(F^2)= 0.10062. Three disordered carbon atoms were refined with isotropic temperature factors due to low occupancy (below 20%). All hydrogen atoms were located geometrically and their position and temperature factors were not refined except eight ones engaged in hydrogen bonds. Scattering factors were taken from Tables

6.1.1.4 and 4.2.4.2 in *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer : Dordrecht, **1992**, Vol.C.
Diffraction grade crystal was obtained by slow diffusion of water and slow evaporation of a DMSO solution of the ligand **1a** in the presence of excess tetrabutylammonium benzoate.

Crystal data for **1b***H_2O: **CCDC** number 707058. $C_{35}H_{34}N_4O_3$, M = 558.66, Monoclinic, *P21/c*, *a* = 14.5822(6) Å, *b* = 13.6329(5) Å, *c* = 15.4897(5) Å, α = 90°, β = 112.956(4) °, γ = 90°, V = 2835.45(18) Å^3, *T* = 110(2) K, Z = 4, μ(Mo-K$_\alpha$) = 0.085 mm^{-1}, 26227 reflections measured, 6833 unique (R(int) = 0.0207) which were used in all calculations. The final R indices [I>2σ(I)]: R1(F^2)= 0.0361 and wR2(F^2)= 0.0868, for all data: R1(F^2)= 0.0599 and wR2(F^2)= 0.0906. All hydrogen atoms were located geometrically. Positions and temperature factors of most of them were not refined. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer : Dordrecht, **1992**, Vol.C.
Diffraction grade crystal was obtained by slow evaporation of an acetone - water solution of the ligand **1b**.

Crystal data for **1c***TBA-Cl: **CCDC** number 707057. $C_{47}H_{66}ClN_7O_2$, M = 796.52, Triclinic, *P-1*, *a* = 10.7982(7) Å, *b* = 20.0727(13) Å, *c* = 22.7848(14) Å, α = 65.331(6)°, β = 80.937(5)°, γ = 86.475(5)°, V = 4431.8(5) Å^3, *T* = 100(2) K, Z = 4, μ(Mo-K$_\alpha$) = 0.132 mm^{-1}, 84109 reflections measured, 21476 unique (R(int) = 0.0372) which were used in all calculations. The final R indices [I>2σ(I)]: R1(F^2) = 0.0406 and wR2(F^2) = 0.0951, for all data: R1(F^2) = 0.0839 and wR2(F^2) = 0.1038. All hydrogen atoms were located geometrically and their positions and temperature factors were not refined except those atoms engaged in hydrogen bonds. Hydrogen atoms of the methyl groups (C21A, C33A, C21B, C33B) are disordered, and they are refined in two positions (AFIX 123). Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer : Dordrecht, **1992**, Vol.C.
Diffraction grade crystal was obtained by slow diffusion of pentane to a solution of ligand **1c** in $C_2H_4Cl_2$ – ethyl acetate mix in the presence of excess tetrabutylammonium chloride.

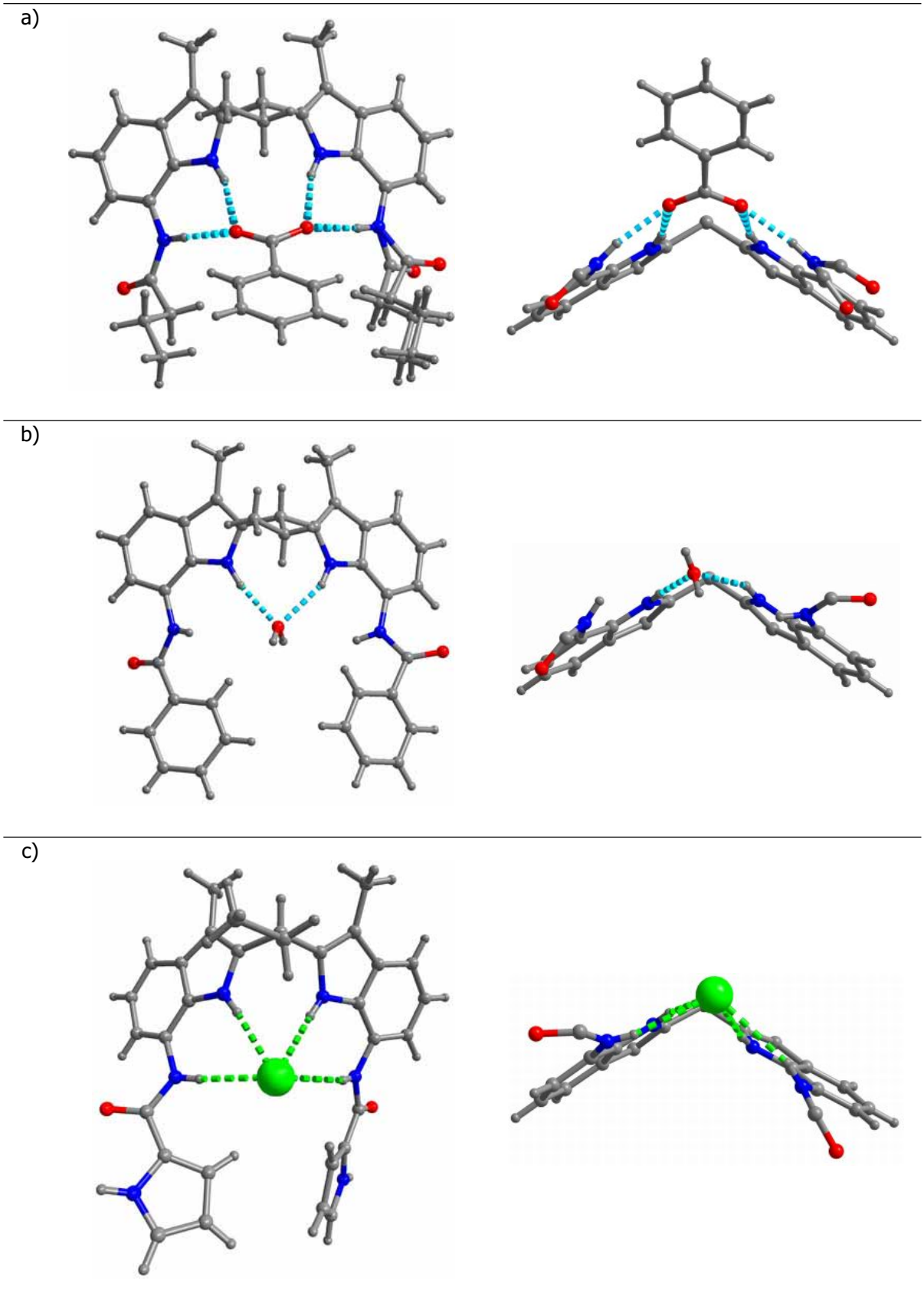


Figure S1. Different views of crystal structures of a) the benzoate complex of **1a**; b) **1b**·H_20; and c) the chloride complex of **1c**; some parts omitted for clarity.

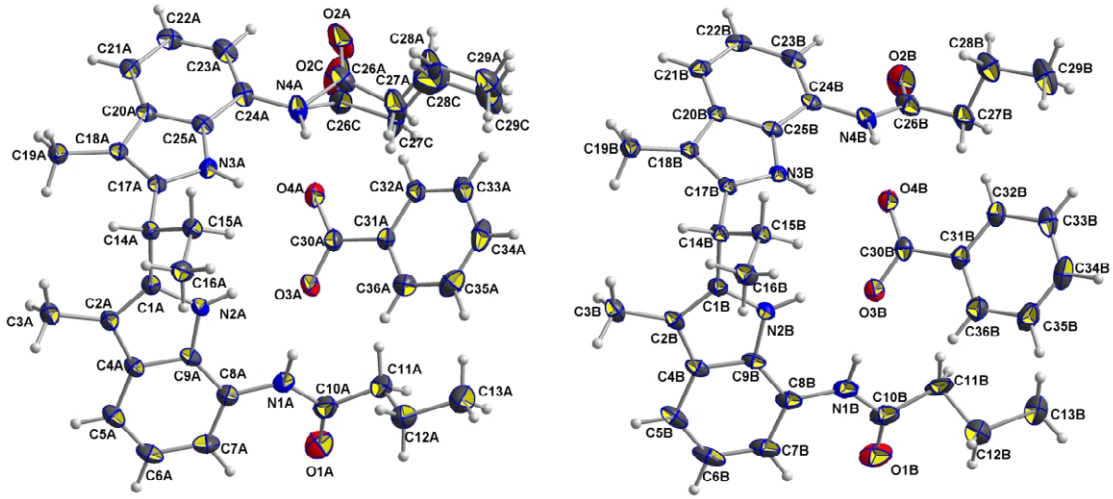


Figure S2. ORTEP presentation of two forms of the benzoate complex of ligand **1a**.

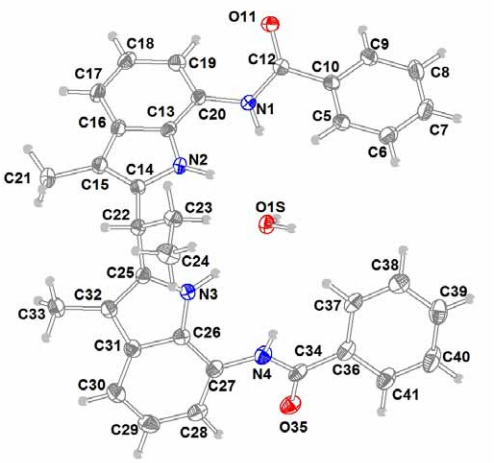


Figure S3. ORTEP presentation of the ligand **1b***H_2O.

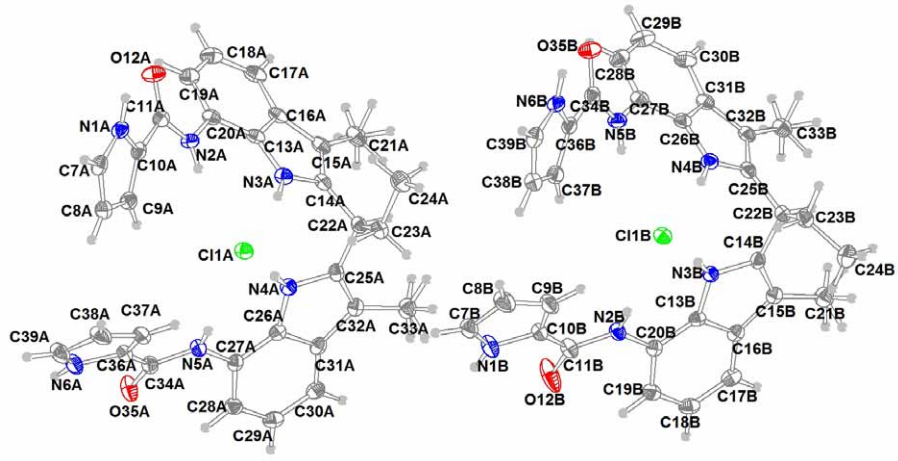
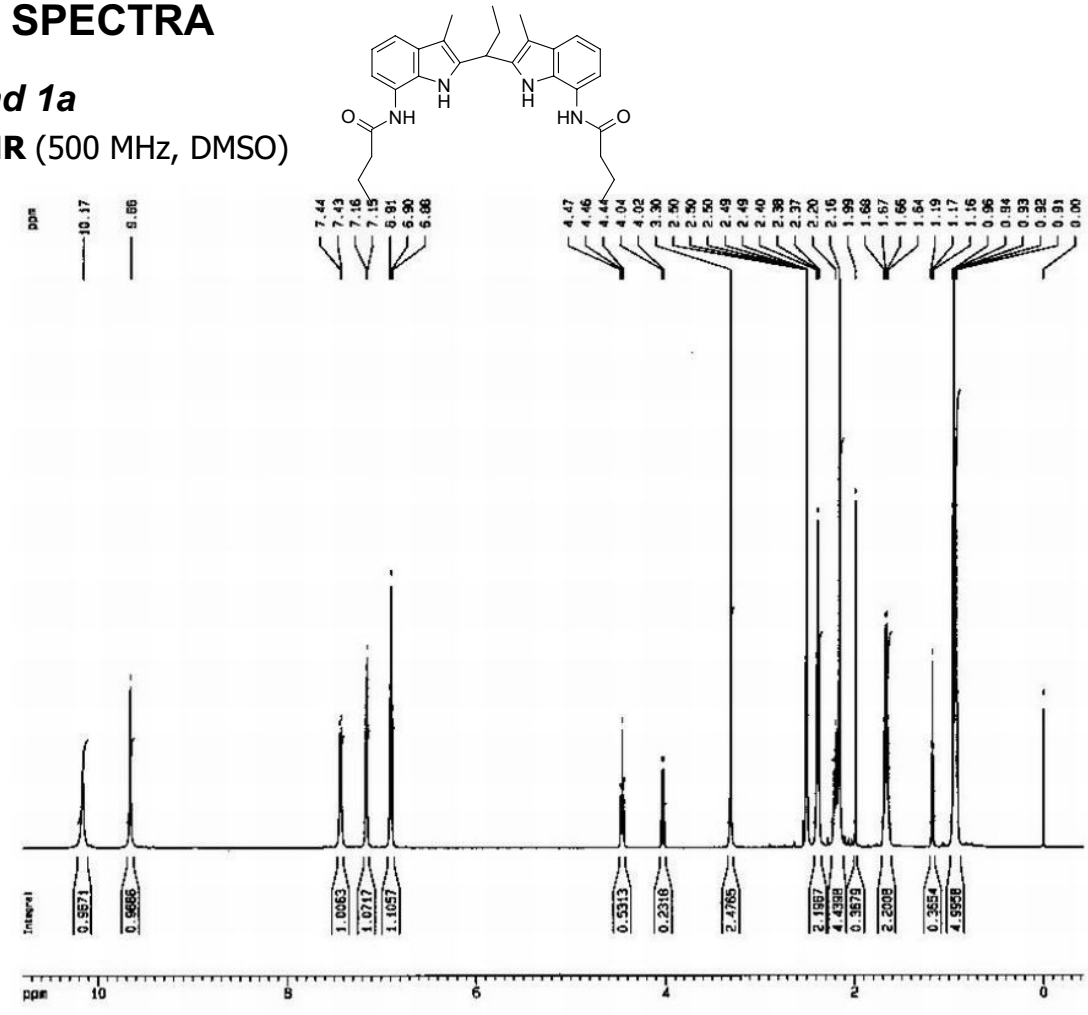


Figure S4. ORTEP presentation of two forms of the chloride complex of the ligand **1c**.

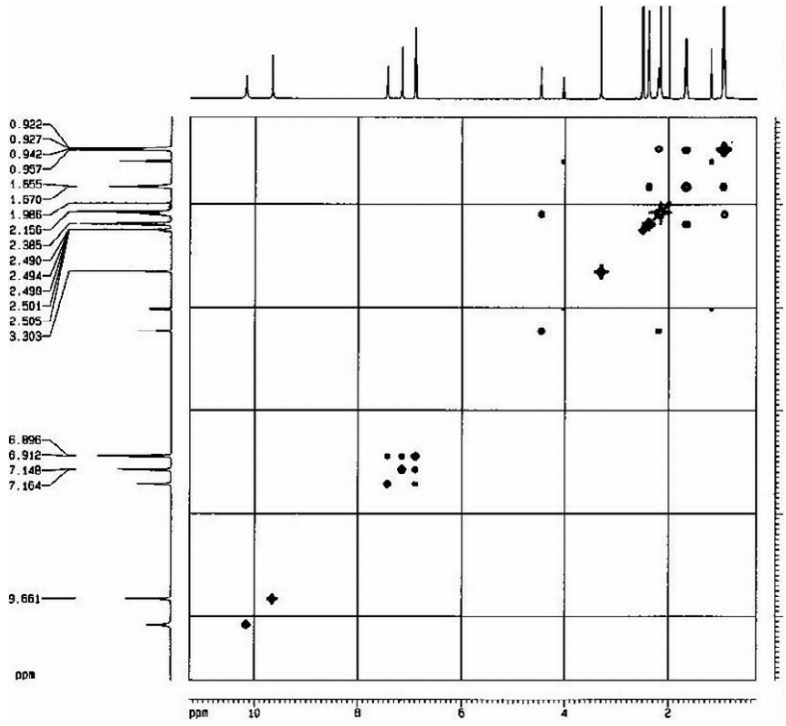
NMR SPECTRA

Ligand 1a

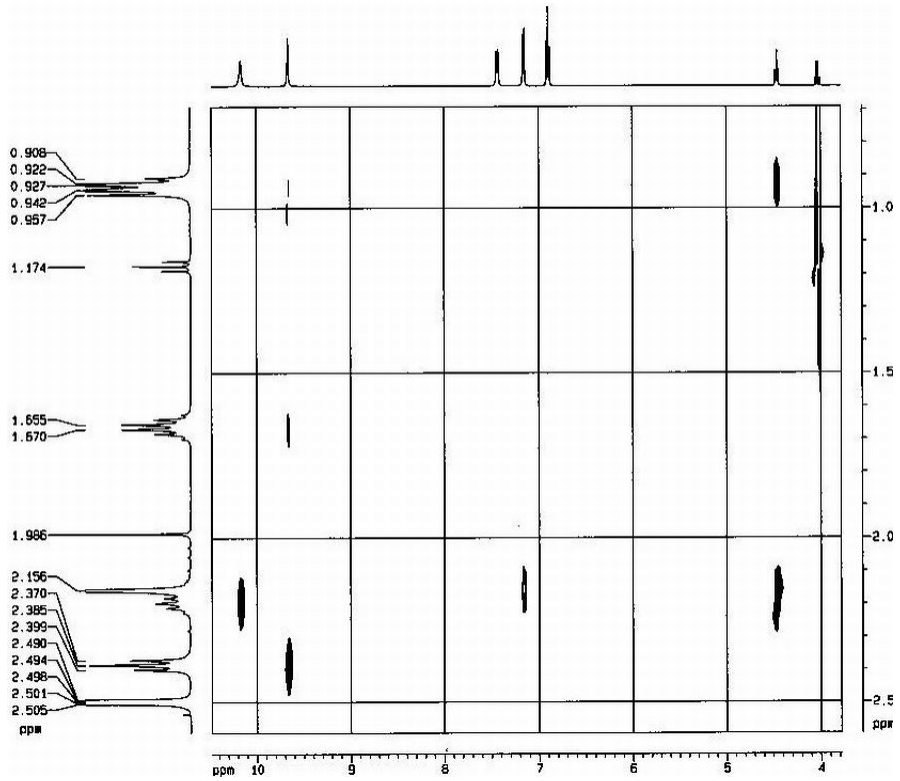
^{1}H NMR (500 MHz, DMSO)



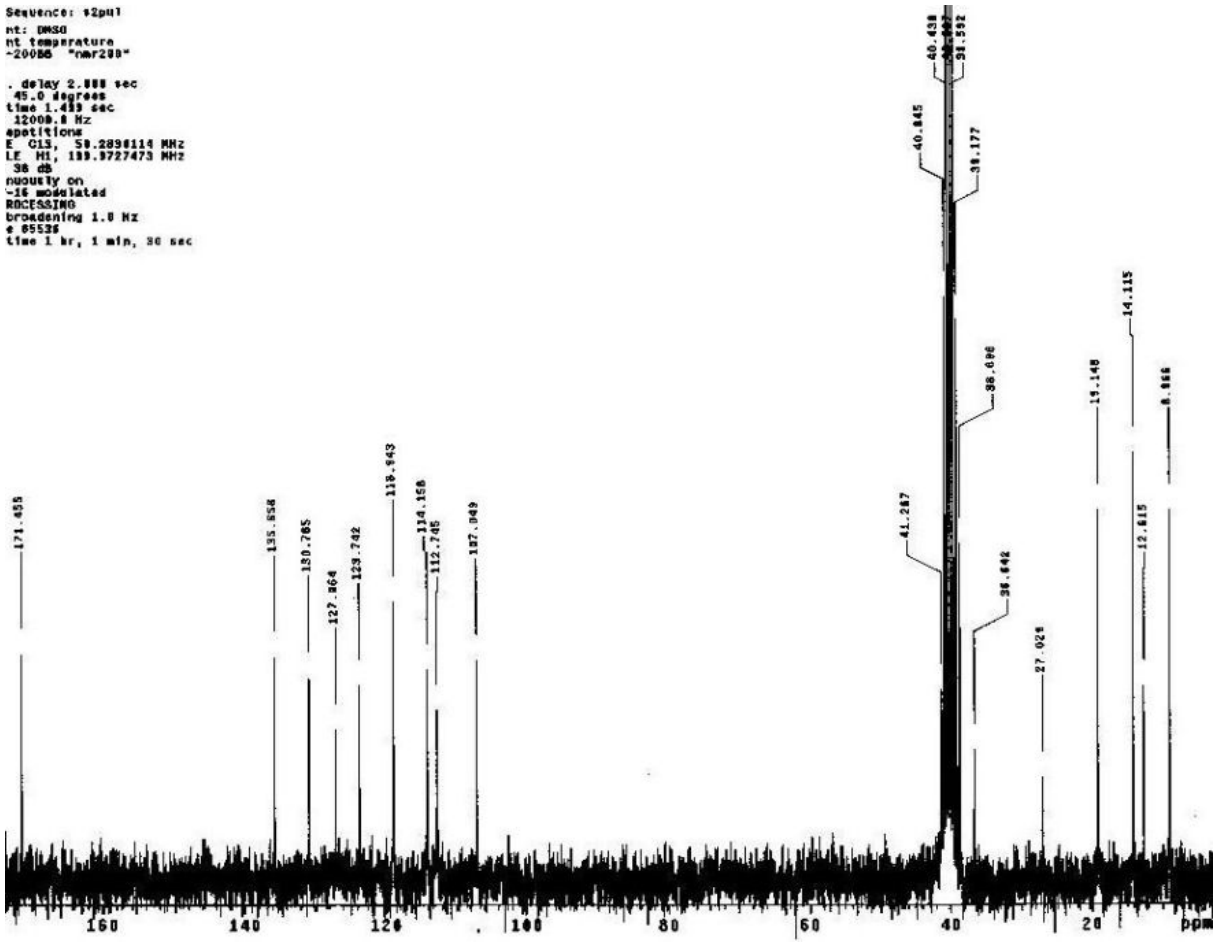
COSY (500 MHz, DMSO)



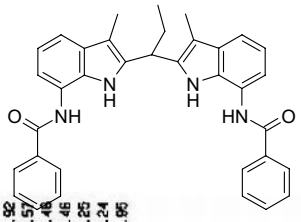
NOESY (500 MHz, DMSO)



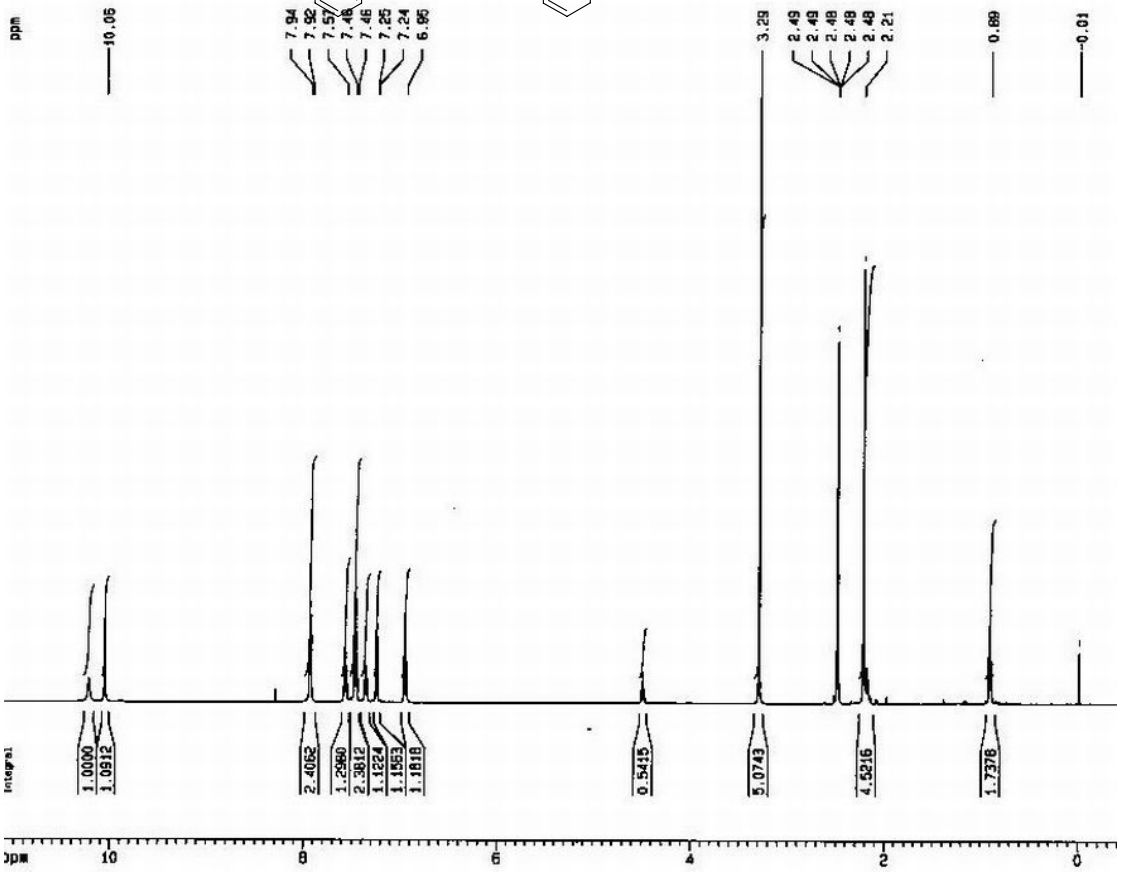
^{13}C NMR (200 MHz, DMSO)



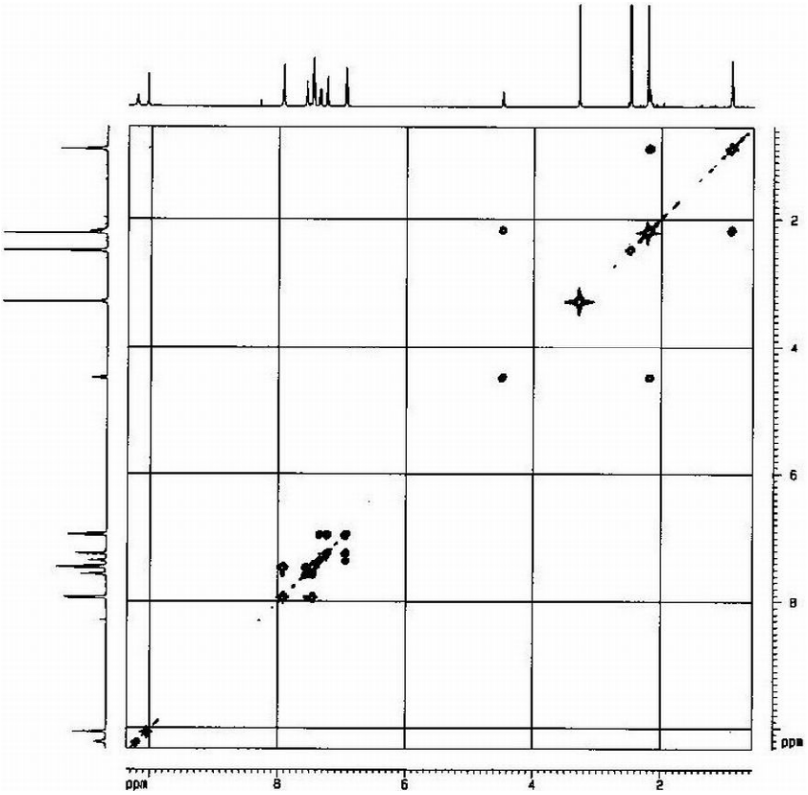
Ligand 1b



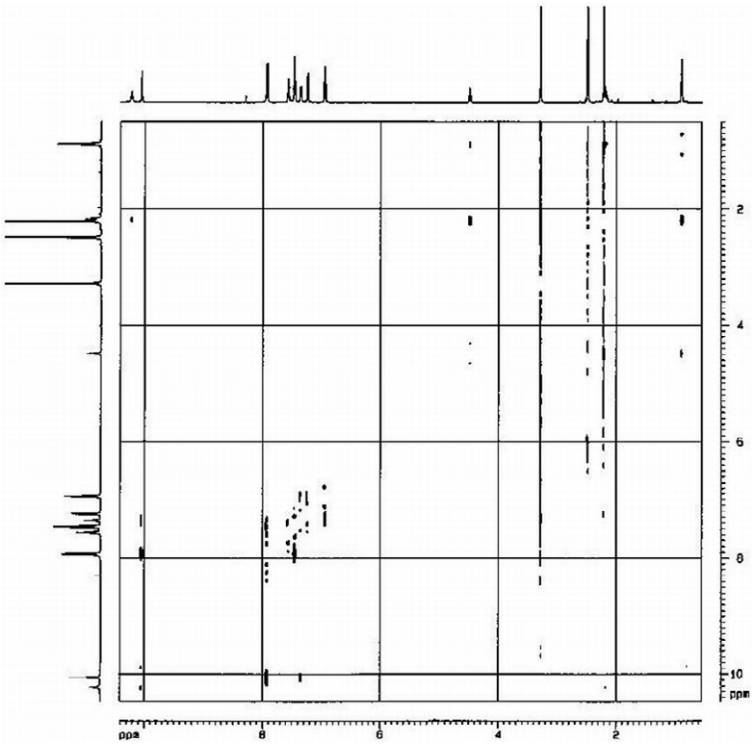
^{1}H NMR (500 MHz, DMSO)



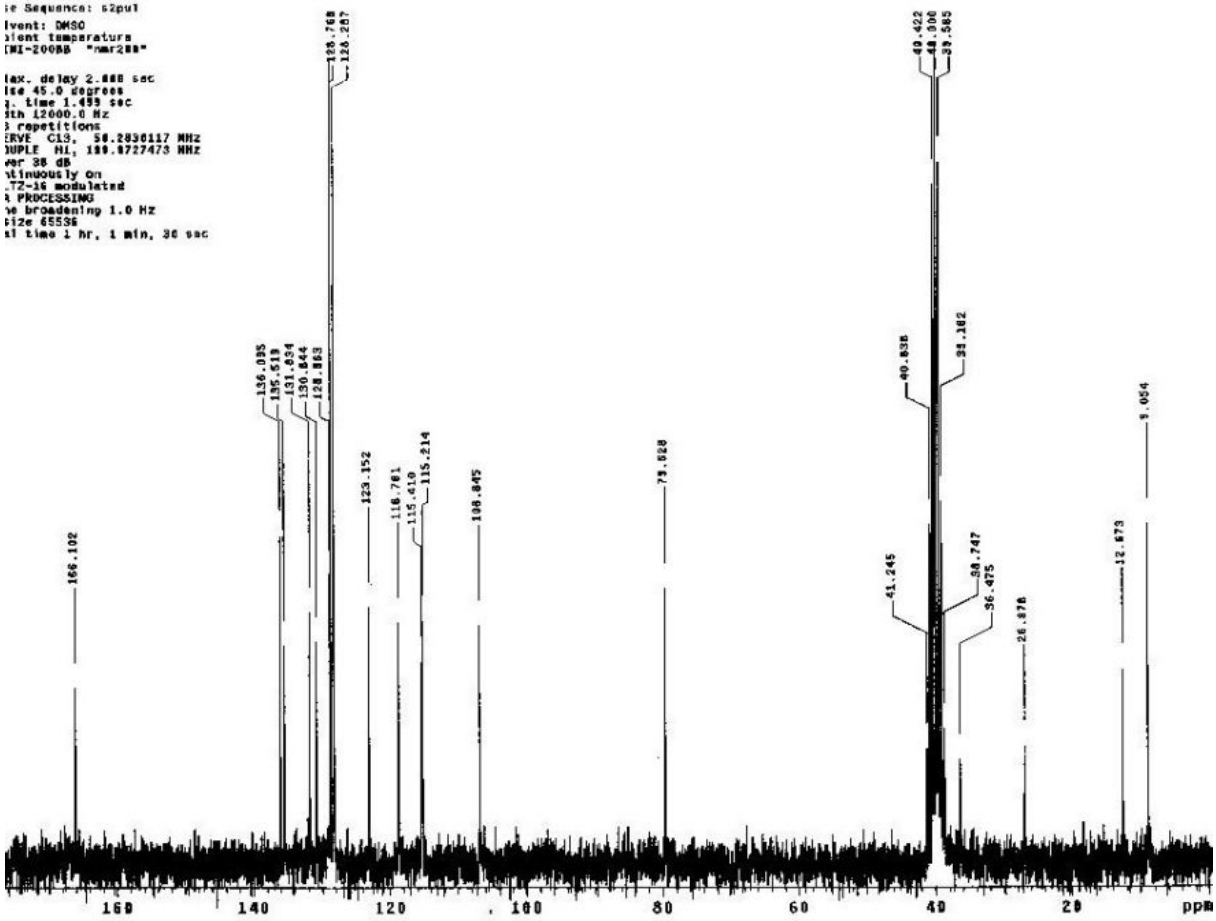
COSY (500MHz, DMSO)



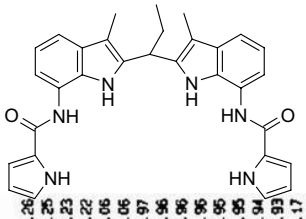
NOESY (500MHz, DMSO)



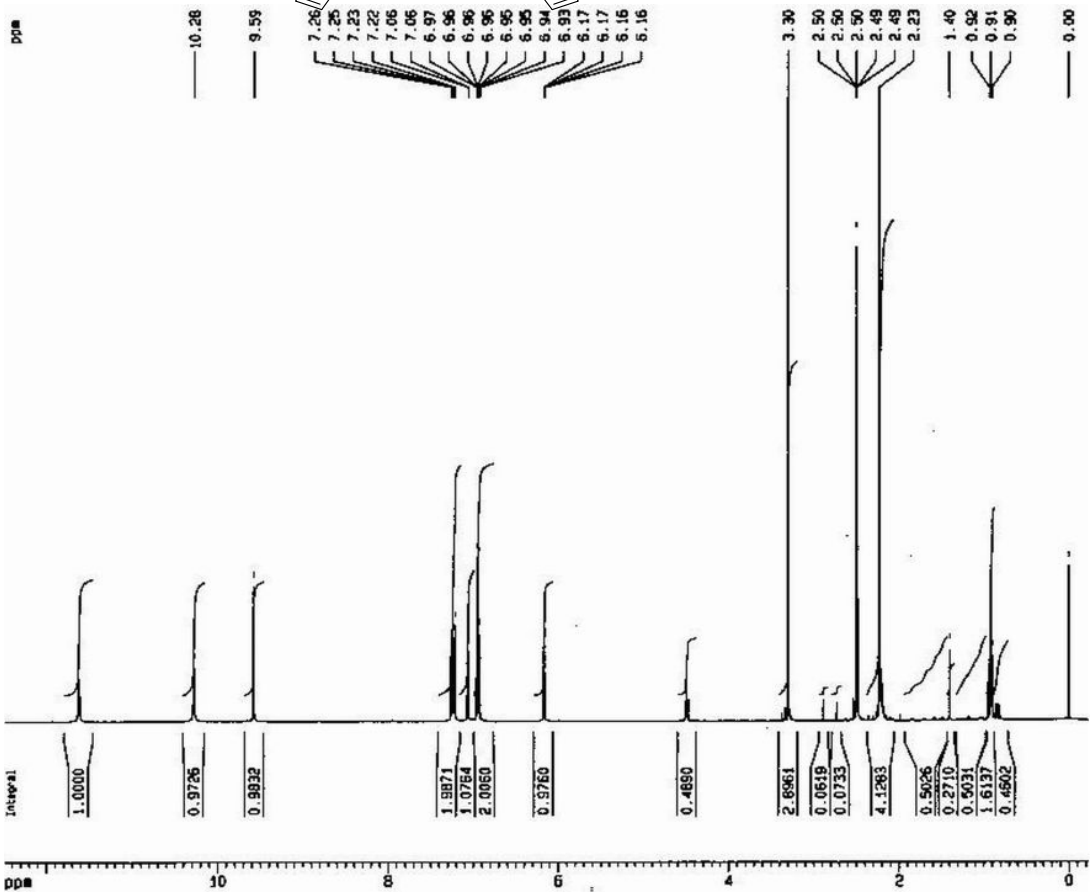
^{13}C NMR (200 MHz, DMSO)



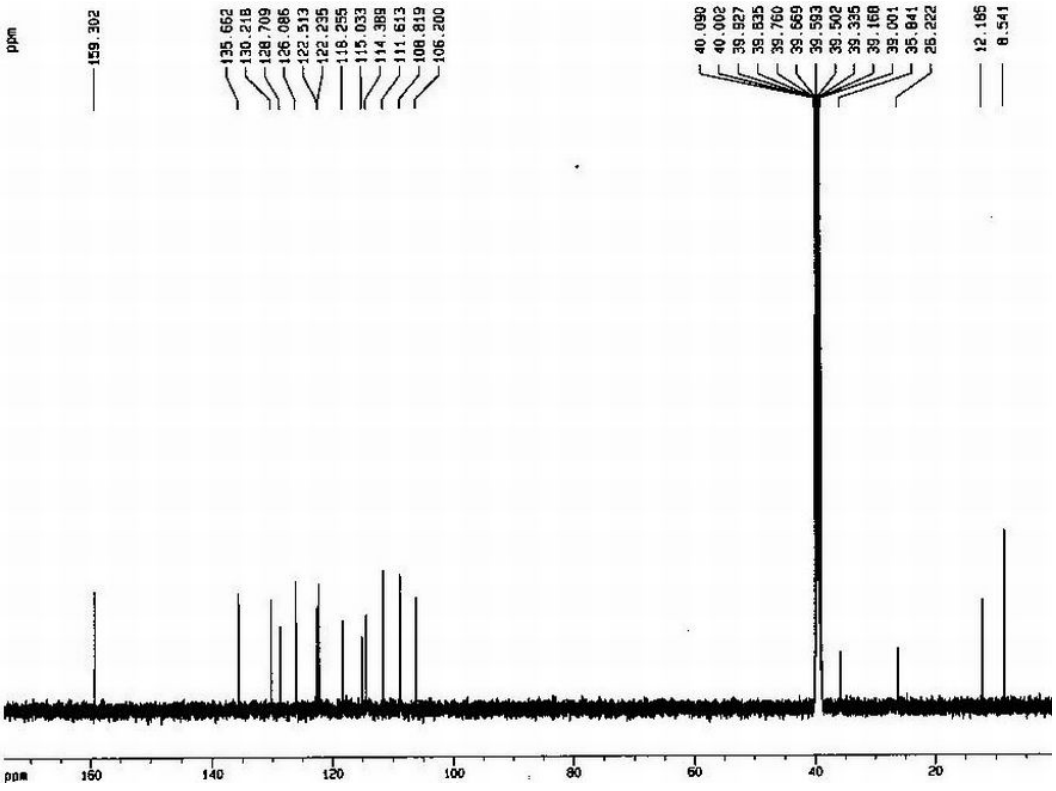
Ligand 1c



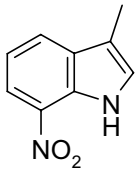
^{1}H NMR (500 MHz, DMSO)



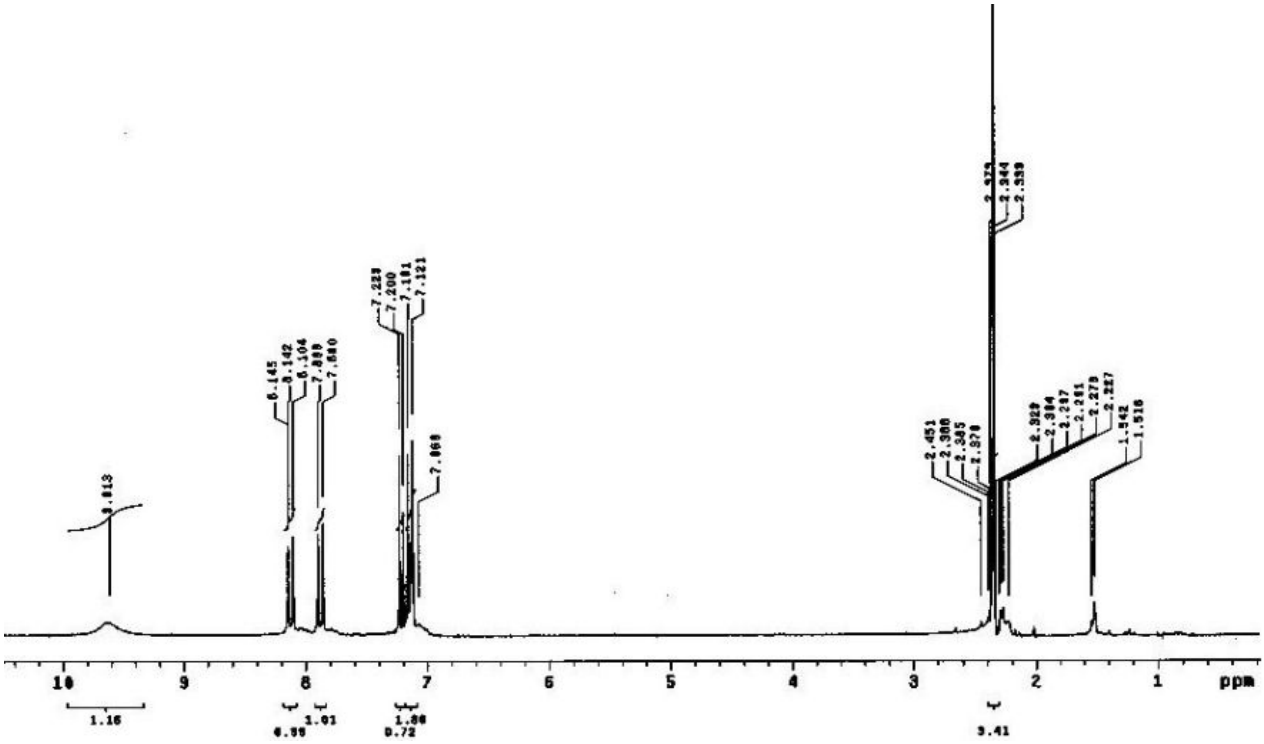
^{13}C NMR (500 MHz, DMSO)



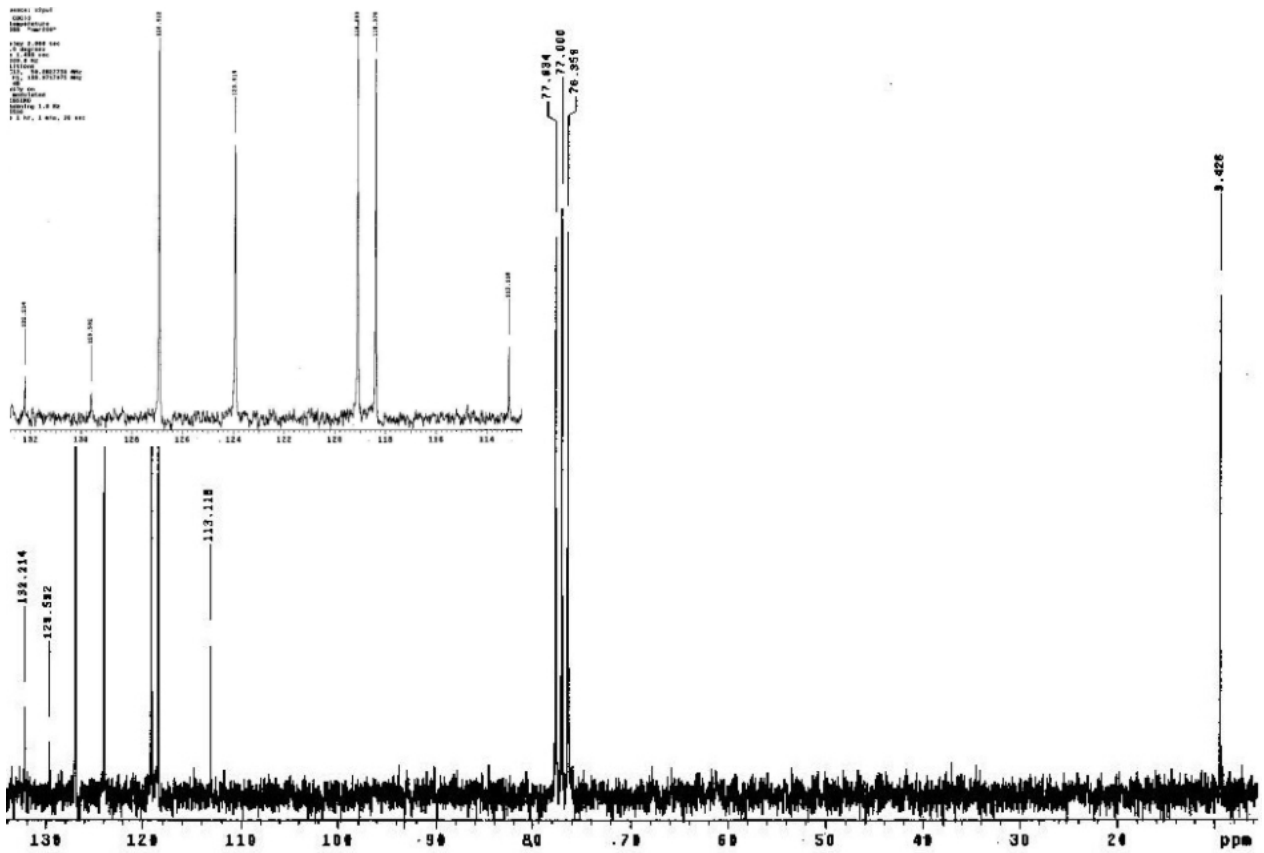
Compound 4



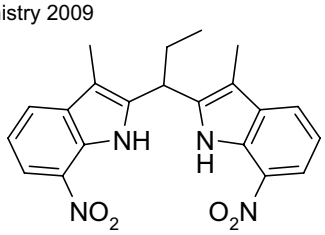
^{1}H NMR (200 MHz, $CDCl_3$)



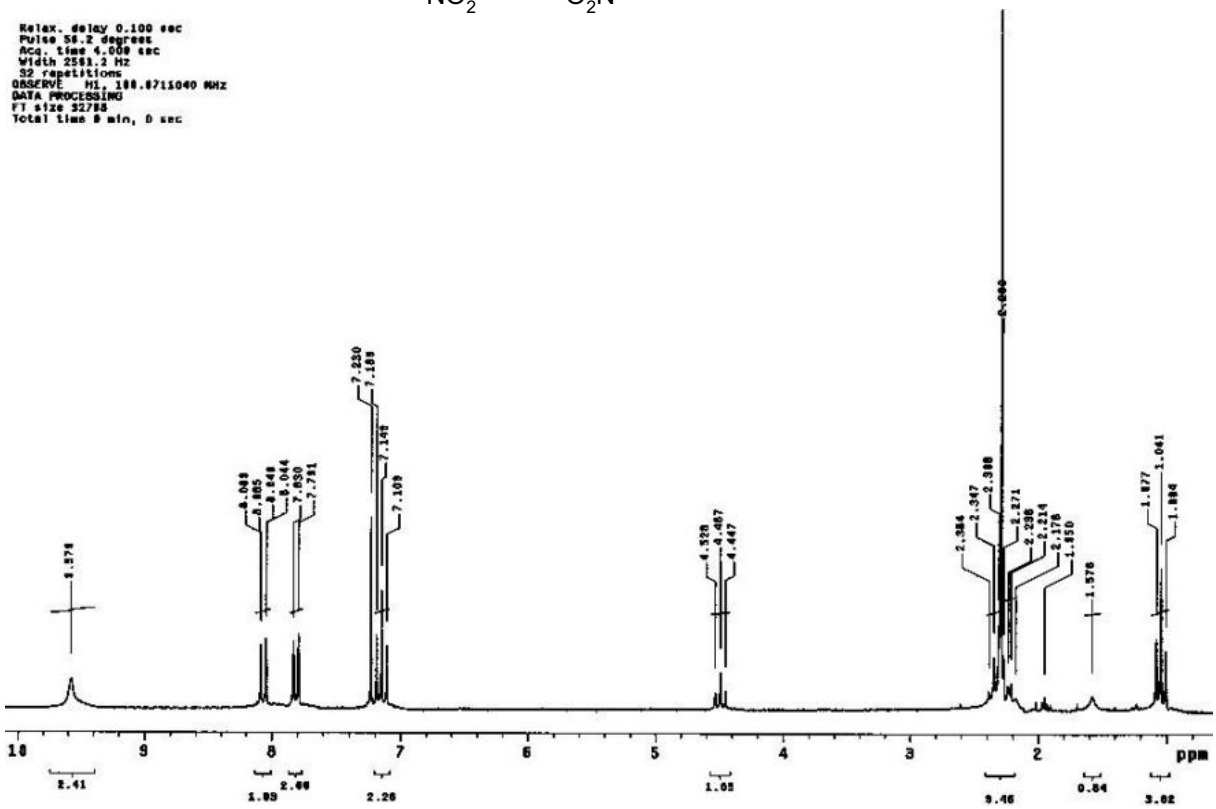
^{13}C NMR (200 MHz, $CDCl_3$)



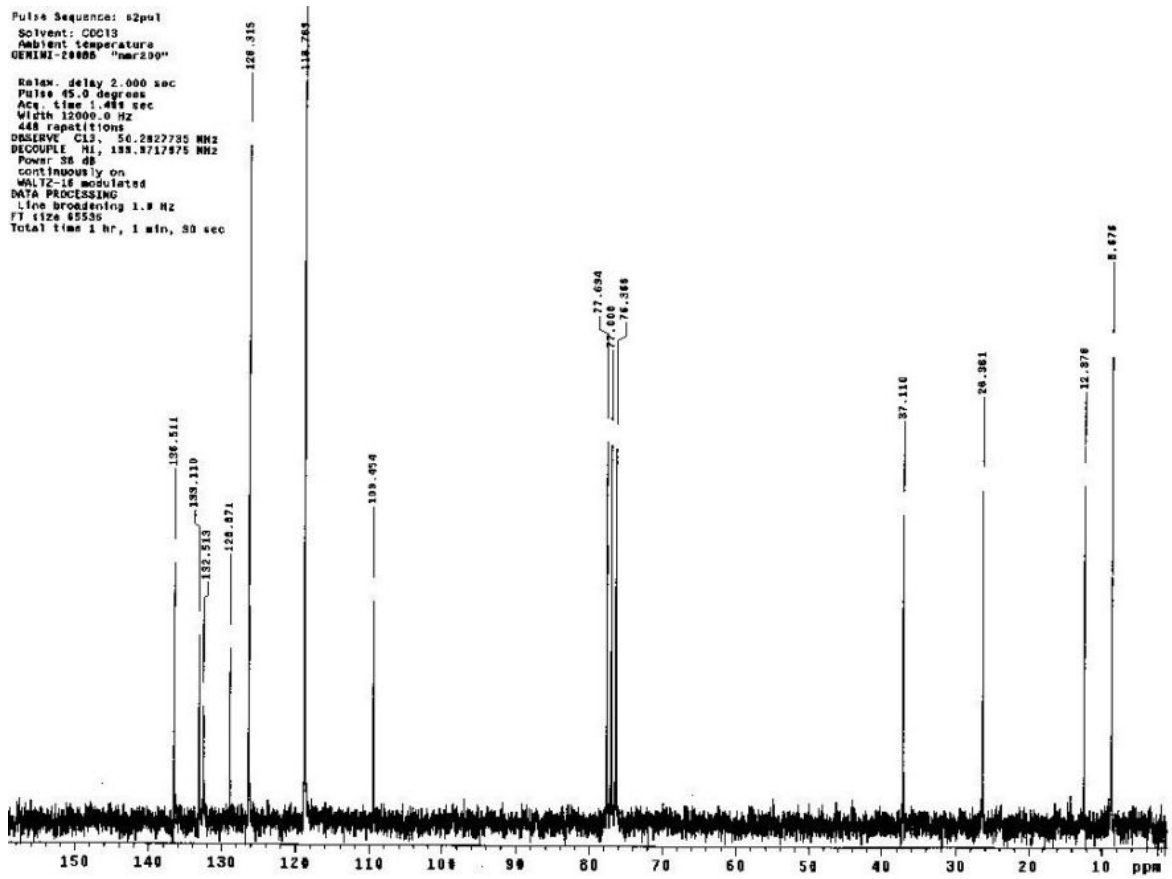
Compound 5



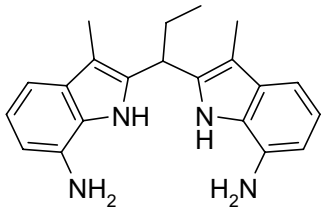
^{1}H NMR (200 MHz, $CDCl_3$)



^{13}C NMR (200 MHz, $CDCl_3$)



Compound 6



^{1}H NMR (200 MHz, $CDCl_3$)