Electronic Supplementary Information

Simple pyrazoline and pyrazole "turn on" fluorescent sensors selective for Cd^{2+} and Zn^{2+} in MeCN

Alexander Ciupa, Mary F. Mahon, Paul A. De Bank* and Lorenzo Caggiano*

General Experimental

Chemicals, solvents and reagents were purchased from commercial sources and used without further purification. PE refers to petroleum ether, bp 40-60 °C. Spectroscopy was performed with CHROMASOLV® gradient grade acetonitrile for HPLC, ≥99.9%, from Sigma-Aldrich. The metal complexes used in this study were LiBr, NaCl, KCl, $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $ZnCl_2$, $RuCl_3$, $CoCl_2.6H_2O$, CrO_3, $MnCl_2.4H_2O$, $Pd(OAc)_2$, $Hg(OAc)_2$, $Cd(OAc)_2.2H_2O$ and $PbCl_2$.

TLCs were carried out on Merck Aluminium backed TLC plates Silica Gel 60 F254 and viewed using UV light of wavelength 254 nm and then stained with potassium permanganate. Merck Silica Gel (0.040-0.063 mm) was used for column chromatography. Compounds were loaded as an oil, CH_2Cl_2 solution or dry loaded by adsorption onto silica.

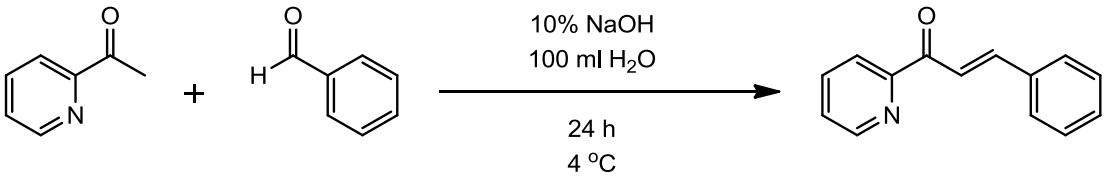
Melting points were obtained using a Reichert-Jung heated-stage microscope. Infrared spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR system and reported as cm^{-1}. NMR spectra were obtained on a Bruker Avance III (500 or 400 MHz) spectrometers. The chemical shifts are recorded in parts per million (ppm) with reference to tetramethylsilane. The coupling constants *J* are quoted to the nearest 0.5 Hz and are not corrected.

Mass spectra and high resolution mass spectra were obtained on a micrOTOF™ from Bruker Daltonics (Bremen, Germany) coupled with an electrospray source (ESI-TOF) using an autosampler in an Agilent 1100 LC system. Data was processed using external calibration with the Bruker Daltonics software, DataAnalysis™ as part of the overall hardware control software, Compass 1.1™.

UV/Vis spectroscopy studies were performed on a BMG labtech Fluostar plate reader with NUNC 96 well flat bottom plates at room temperature. Fluorescence studies were performed on a Hitachi F-2000 fluorescence spectrophotometer with a 150 W xenon lamp using a cuvette with 1 cm path length. Data processing and analysis was using performed using SigmaPlot 8.

Synthetic Procedures

Synthesis of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one



Following the procedure previously reported,[1,2] 2-acetylpyridine (1.331 g, 11 mmol) and benzaldehyde (1.06 g, 1.02 mL, 10 mmol) were added to 100 mL of distilled water cooled to 4 °C and shaken thoroughly forming a fine emulsion. 10 mL of 10% of NaOH aqueous solution was then added and shaken again for 30 seconds and the reaction left at 4 °C. After 24 h the solid product was filtered, dried and recrystallised from EtOH to give the chalcone (2.02 g, 97%) as pale green crystals.

M.p 72-74 °C (EtOH); Lit.[1] 74.5–75.3 °C (EtOH); Lit.[2] 74.8–75.5 °C (EtOH);

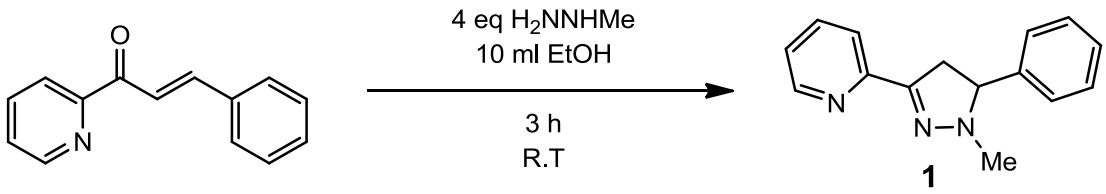
ν_{max}(film)/cm^{-1} 1667, 1601, 1337 and 1030;

^{1}H NMR δ_H (500 MHz; $CDCl_3$) 7.40-7.49 (4 H, m, CH), 7.72-7.73 (2 H, m, CH), 7.85-7.88 (1 H, m, CH), 7.94 (1 H, d, *J* = 16.0 Hz, CH), 8.18-8.19 (1 H, m, CH), 8.30 (1 H, d, *J* = 16.0 Hz, CH) and 8.74-8.76 (1 H, m, CH); consistent with the ^{1}H NMR spectroscopic data previously reported for this compound,[1]

^{13}C NMR δ_C (125 MHz; $CDCl_3$) 120.9 (CH), 122.9 (CH), 126.9 (CH), 128.8 (CH), 128.9 (CH), 130.6 (CH), 135.2 (Cq), 137.0 (CH), 144.8 (CH), 148.9 (CH), 154.3 (Cq) and 189.5 (Cq);

MS *m/z* (+ESI) 210 (100%, MH^+), 232 (42%, MNa^+) and 419 (17%, M_2H^+);
HRMS *m/z* (+ESI) Found 232.0749 (MNa^+). $C_{14}H_{11}NNaO$ (MNa^+) requires 232.0738.

Synthesis of 2-(1-methyl-5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)pyridine 1[3]



(*E*)-3-Phenyl-1-(pyridin-2-yl)prop-2-en-1-one (0.418 g, 2 mmol) was dissolved in EtOH (10 mL) and stirred for 10 min at room temperature until fully dissolved then methylhydrazine (0.368 g, 0.42 mL, 8 mmol) was added dropwise and stirred continued at room temperature for 3 h. The solvent was removed under reduced pressure and the resulting yellow oil purified by column chromatography with silica gel using PE:EtOAc 60:40 to afford pyrazoline **1** (0.34 g, 72%) as a yellow oil, which solidified upon cooling and was recrystallised from Et_2O to give pale yellow crystals.

M.p 52-55 ^{o}C (Et_2O);

V_{max}(film)/cm^{-1} 2971, 1570, 1456 and 1122;

DMSO-d_6
^{1}H NMR δ_H (400 MHz; DMSO) 2.80 (3 H, s, CH_3), 2.96 (1 H, dd, *J* = 17.0 and 14.5 Hz, C*H*$_A$H$_B$), 3.70 (1 H, dd, *J* = 17.0 and 10.5 Hz, CH$_A$*H*$_B$), 4.27 (1 H, dd, *J* = 14.5 and 10.5 Hz, C*H*Ph), 7.34-7.41 (2 H, m, Ph and py-C(5)H), 7.41-7.47 (2 H, m, Ph), 7.49-7.53 (2 H, m, Ph), 7.84 (1 H, td, *J* = 8.0 and 2.0 Hz, py-C(4)H), 7.94 (1 H, dt, *J* = 8.0 and 1.0 Hz, py-C(3)H) and 8.60 (1 H, ddd, *J* = 5.0, 1.5 and 1.0 Hz, py-C(6)H);

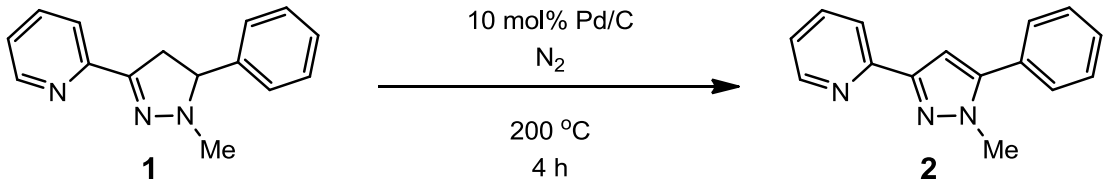
^{13}C NMR δ_C (100 MHz; DMSO) 40.8 (CH_3), 42.0 (CH_2), 72.6 (CH), 119.8 (CH), 123.0 (CH), 127.4 (CH), 127.7 (CH), 128.6 (CH), 136.3 (CH), 140.2 (Cq), 149.1 (CH), 149.9 (Cq) and 151.5 (Cq);

$CDCl_3$
^{1}H NMR δ_H (500 MHz; $CDCl_3$) 2.88 (3 H, s, CH_3), 3.08 (1 H, dd, *J* = 16.5 and 14.5 Hz, C*H*$_A$H$_B$), 3.71 (1 H, dd, *J* = 16.5 and 10.5 Hz, CH$_A$*H*$_B$), 4.21 (1 H, dd, *J* = 14.5 and 10.5 Hz, C*H*Ph), 7.18 (1 H, dd, *J* = 7.5 and 5.0 Hz, py-C(5)H), 7.29-7.34 (1 H, m, Ph), 7.35-7.40 (2 H, m, Ph), 7.45-7.48 (2 H, m, Ph), 7.66 (1 H, td, *J* = 7.5 and 1.0 Hz, py-C(4)H), 7.91 (1 H, dt, *J* = 8.0 and 1.0 Hz, py-C(3)H) and 8.56 (1 H, br.d, *J* = 5.0 Hz, py-C(6)H);

^{13}C NMR δ_C (125 MHz; $CDCl_3$) 41.1 (CH_3), 42.6 (CH_2), 73.5 (CH), 120.4 (CH), 122.6 (CH), 127.4 (CH), 127.8 (CH), 128.6 (CH), 136.0 (CH), 140.2 (Cq), 149.1 (CH), 150.4 (Cq) and 152.1 (Cq);

MS *m/z* (+ESI) 238 (100%, MH$^+$) and 260 (50%, MNa$^+$);
HRMS *m/z* (+ESI) Found 238.1339 (MH$^+$) and 260.1158 (MNa$^+$). $C_{15}H_{16}N_3$ (MH$^+$) requires 238.1344 and $C_{15}H_{15}N_3Na$ (MNa$^+$) requires 260.1164.

Synthesis of 2-(1-methyl-5-phenyl-1H-pyrazol-3-yl)pyridine 2[4]



Following the procedure previously reported for the oxidation of a 1,2,3,4-tetrahydro-*β*-carboline,[5] pyrazoline **1** (0.795 g, 3.35 mmol) was thoroughly ground together with 10 wt. % loading Pd/C (10 mol%, 0.355 g), placed under nitrogen and gradually heated to 200 °C and kept at 200 °C for 4 h. After 2 h the flask was cooled to room temperature and 50 mL of toluene added, heated and vigorously stirred for 10 min., the solution was then filtered through fluted filter paper and cotton wool. The solvent was removed under reduced pressure to give a brown oil which was purified by column chromatography with silica gel using PE:EtOAc 60:40 to afford pyrazole **2** (0.63 g, 80%) as a pale yellow solid, which was recrystallised from Et_2O to give pale yellow crystals.

M.p 108-110 °C (Et_2O);

V_{max}(film)/cm^{-1} 1598, 1477 and 1199;

DMSO-d_6
^{1}H NMR δ_H (500 MHz; DMSO) 3.98 (3 H, s, CH_3), 7.00 (1 H, s, CH), 7.33-7.38 (1 H, m, py-C(5)H), 7.50-7.55 (1 H, m, Ph), 7.58 (2 H, t, *J* = 7.5 Hz, Ph), 7.66 (2 H, d, *J* = 7.5 Hz, Ph), 7.86-7.92 (1 H, m, py-C(4)H), 8.00 (1 H, br.d, J = 8.0 Hz, py-C(3)H) and 8.63 (1 H, br.d, *J* = 4.5 Hz, py-C(6)H);

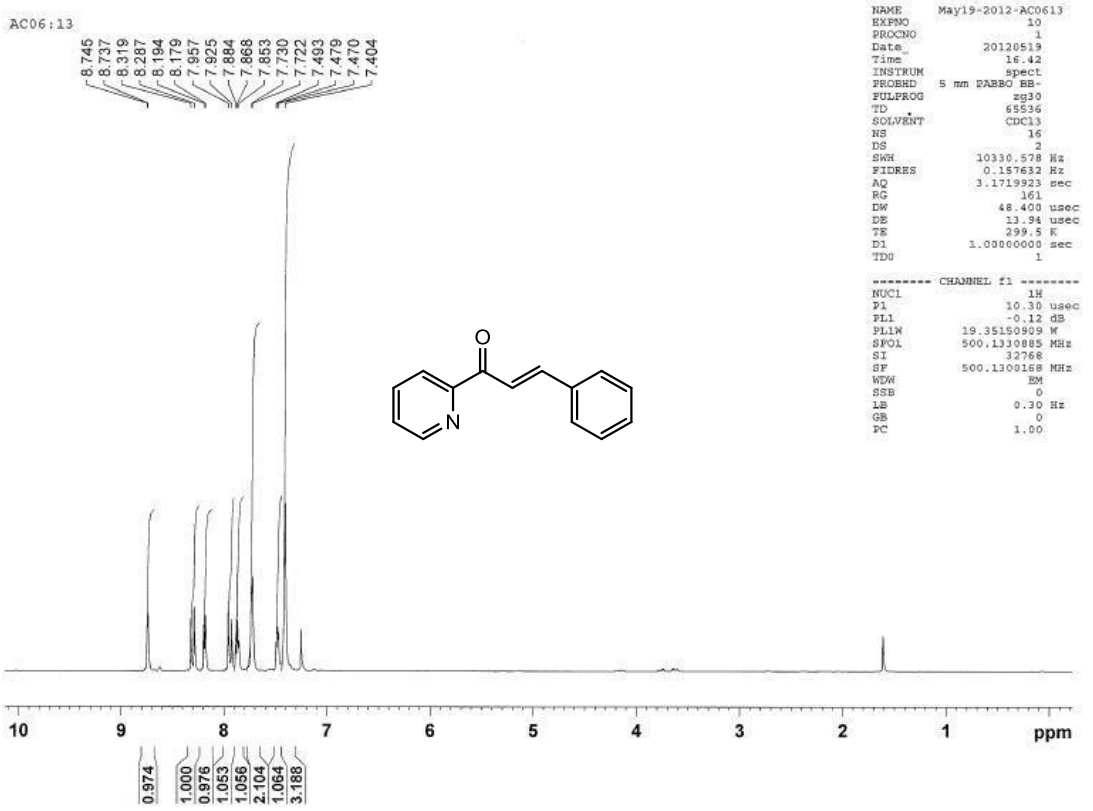
^{13}C NMR δ_C (125 MHz; DMSO) 37.9 (CH_3), 104.2 (CH), 119.1 (CH), 122.6 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.9 (Cq), 136.8 (CH), 144.6 (Cq), 149.2 (CH), 149.7 (Cq) and 151.7 (Cq);

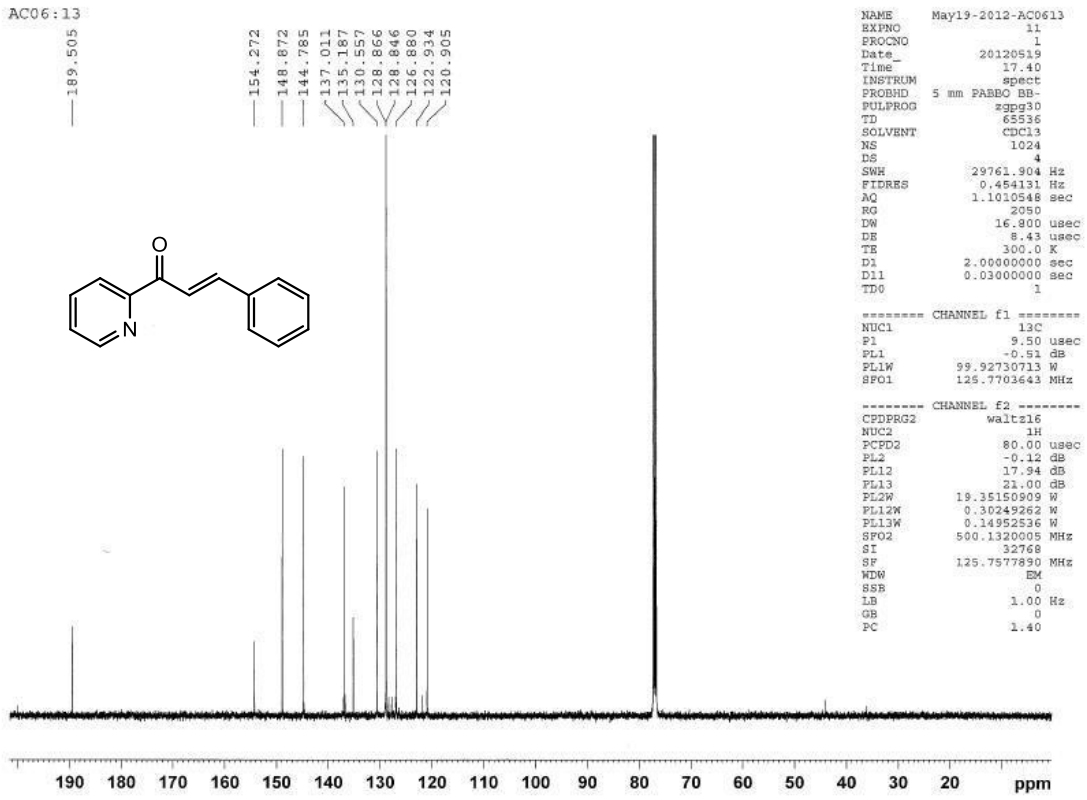
$CDCl_3$
^{1}H NMR δ_H (500 MHz; $CDCl_3$) 3.97 (3 H, s, CH_3), 6.94 (1 H, s, CH), 7.21 (1 H, ddd, *J* = 7.5, 4.5 and 1.0 Hz, py-C(5)H), 7.42-7.49 (5 H, m, Ph), 7.73 (1 H, td, *J* = 7.5 and 1.5 Hz, py-C(4)H), 7.95 (1 H, dt, *J* = 8.0 and 1.0 Hz, py-C(3)H) and 8.64 (1 H, ddd, *J* = 5.0, 1.5 and 1.0 Hz, py-C(6)H);

^{13}C NMR δ_C (125 MHz; $CDCl_3$) 37.9 (CH_3), 104.6 (CH), 119.9 (CH), 122.4 (CH), 128.6 (CH), 128.7 (2 x CH), 130.5 (Cq), 136.6 (CH), 145.2 (Cq), 149.4 (CH), 150.6 (Cq) and 152.2 (Cq); consistent with the ^{1}H and ^{13}C NMR spectroscopic data in $CDCl_3$ previously reported for this compound,[4]

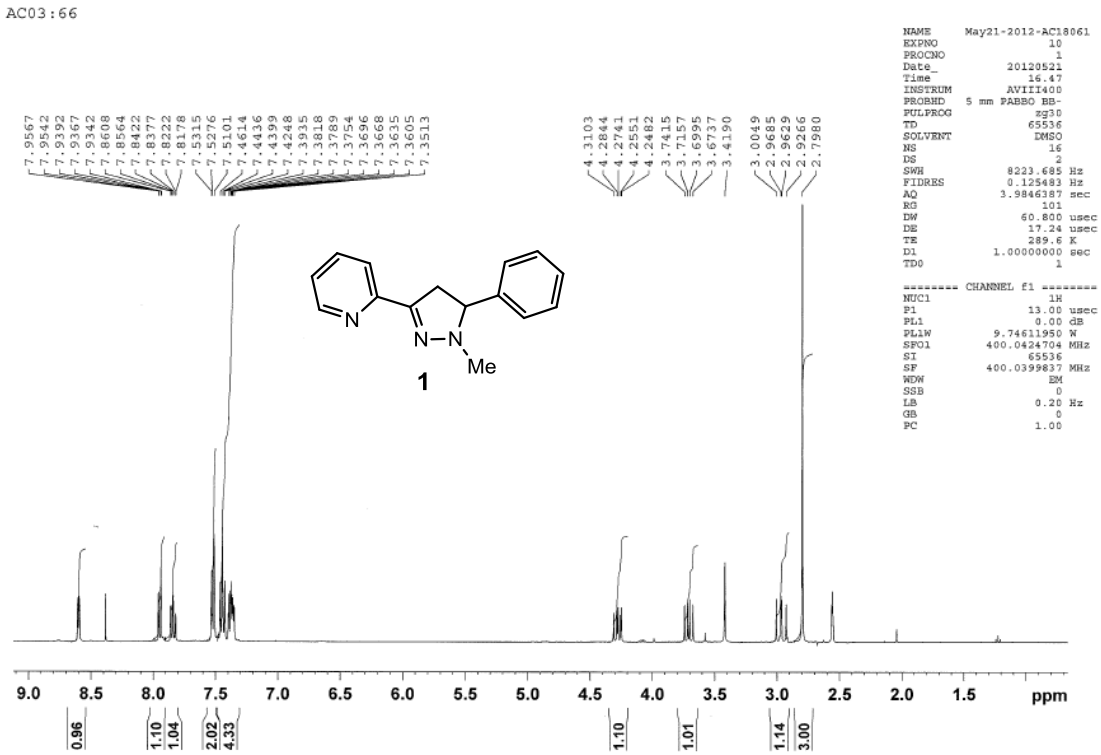
MS *m/z* (+ESI) 236 (26%, MH^+), 258 (50%, MNa^+) and 493 (100%, M_2Na^+);
HRMS *m/z* (+ESI) Found 236.1194 (MH^+). $C_{15}H_{14}N_3$ (MH^+) requires 236.1188.

NMR Spectra of Chalcone





NMR Spectra of Pyrazoline 1 in DMSO-d_6



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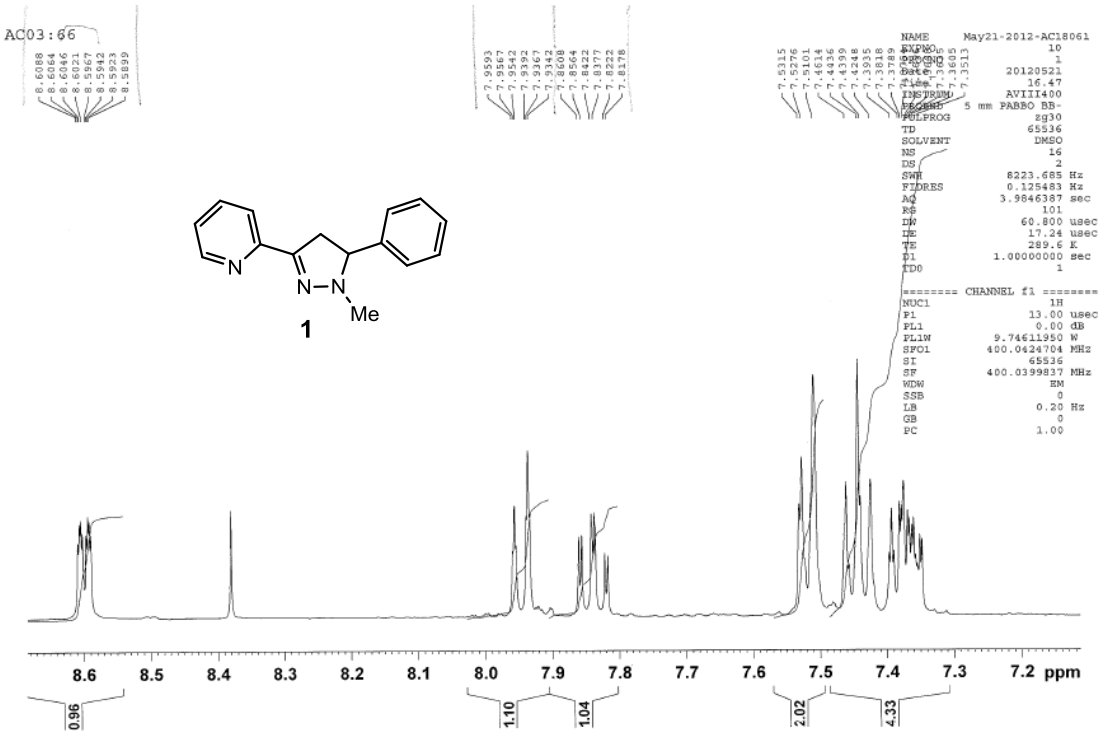
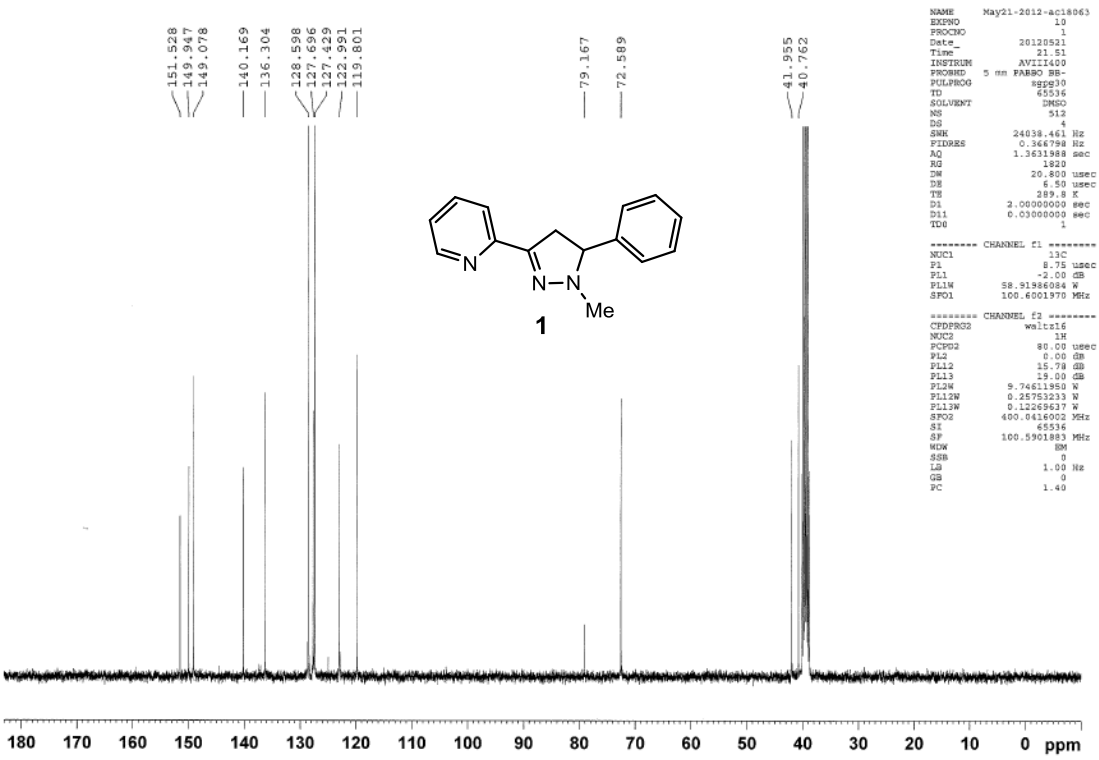
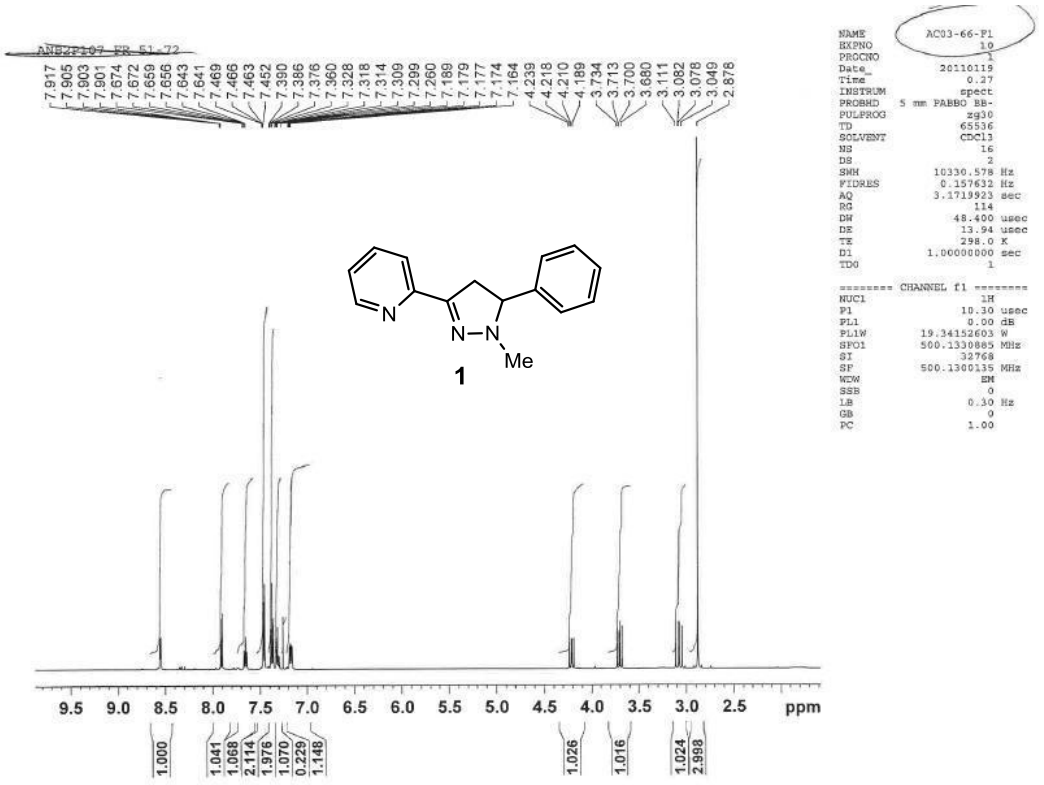




NMR Spectra of Pyrazoline 1 in $CDCl_3$



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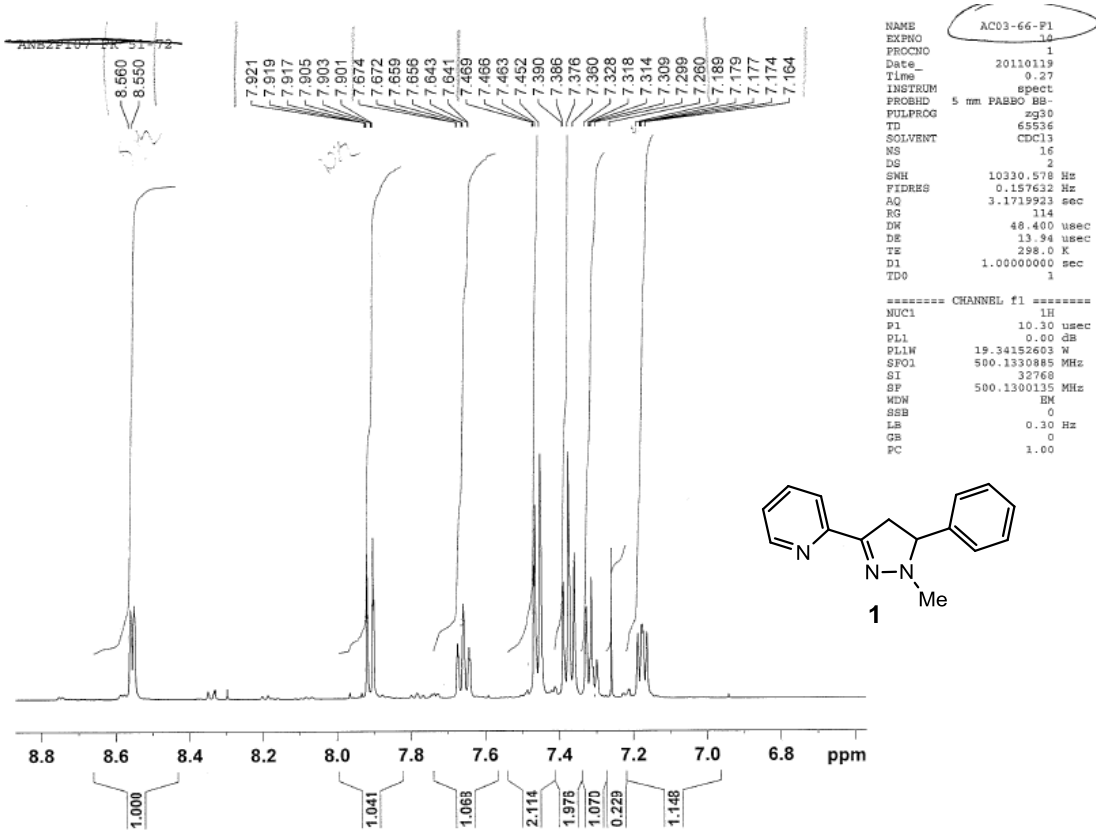

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EXPNO 10
PROCNO 1
Date_ 20110119
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INSTRUM spect
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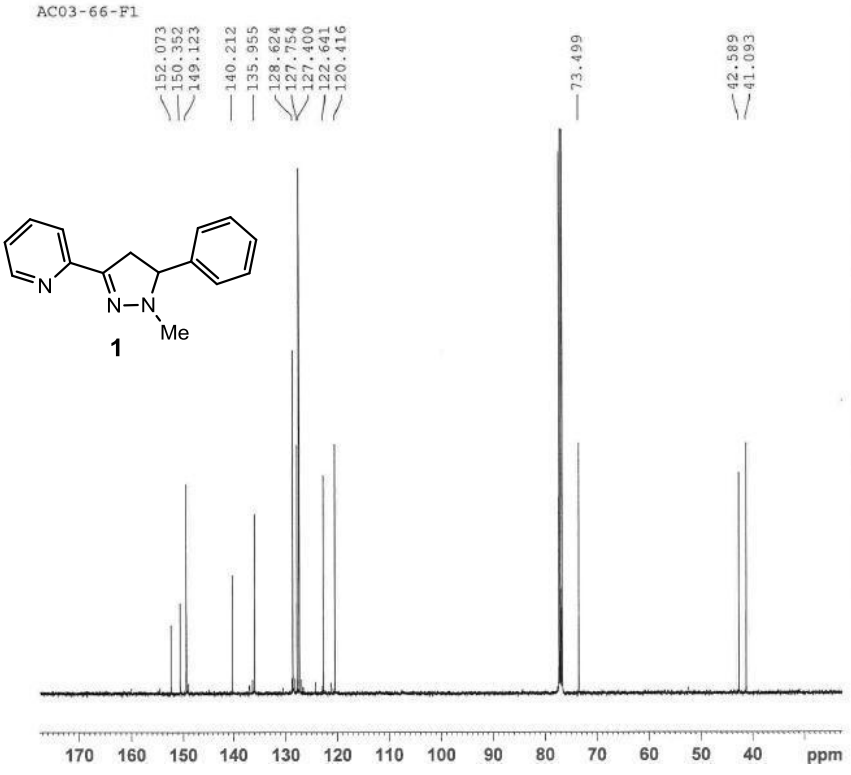
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 114
DW 48.400 usec
DE 13.94 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 0.00 dB
PL1W 19.34152603 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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PROCNO 1
Date_ 20110119
Time 1.23
INSTRUM spect
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SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 9.48 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 14.50 usec
PL1 0.00 dB
PL1W 114.29083252 W
SFO1 125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.06 dB
PL13 21.00 dB
PL2W 19.34152603 W
PL12W 0.30233663 W
PL13W 0.15363520 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577965 MHz
WDW EM
SSB 0
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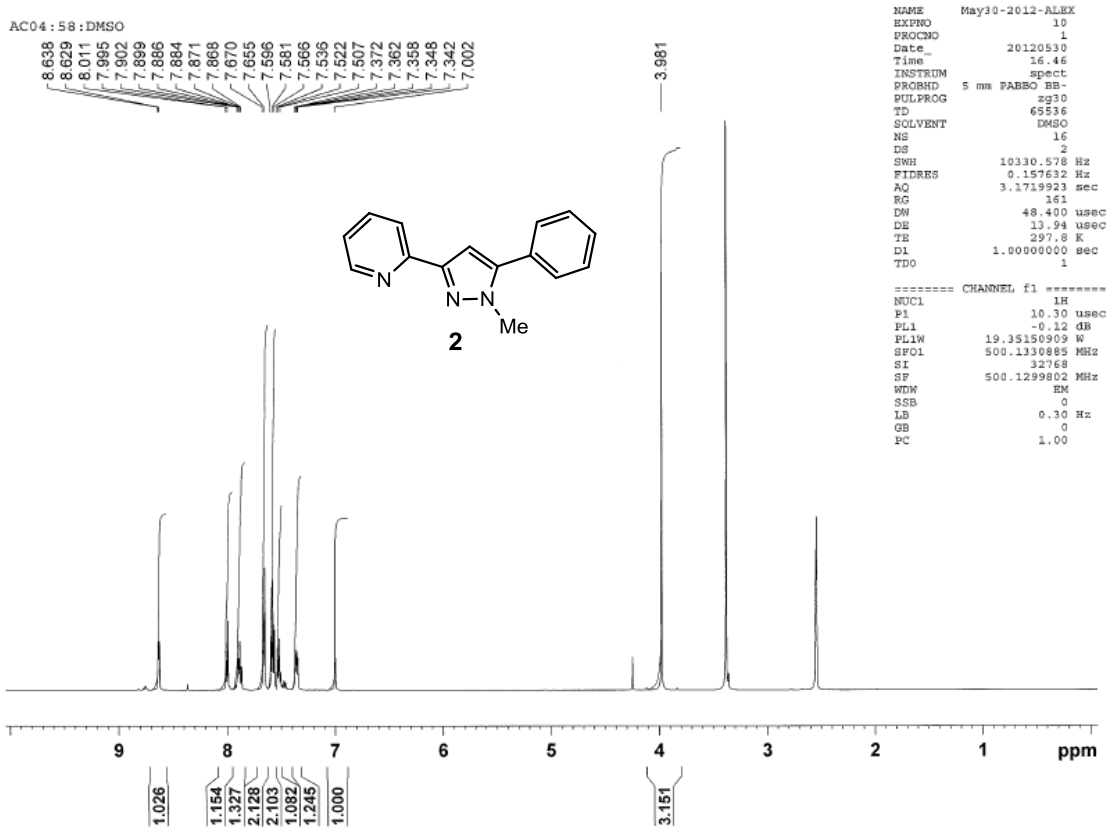
PC 1.40

NMR Spectra of Pyrazole 2 in DMSO-d_6



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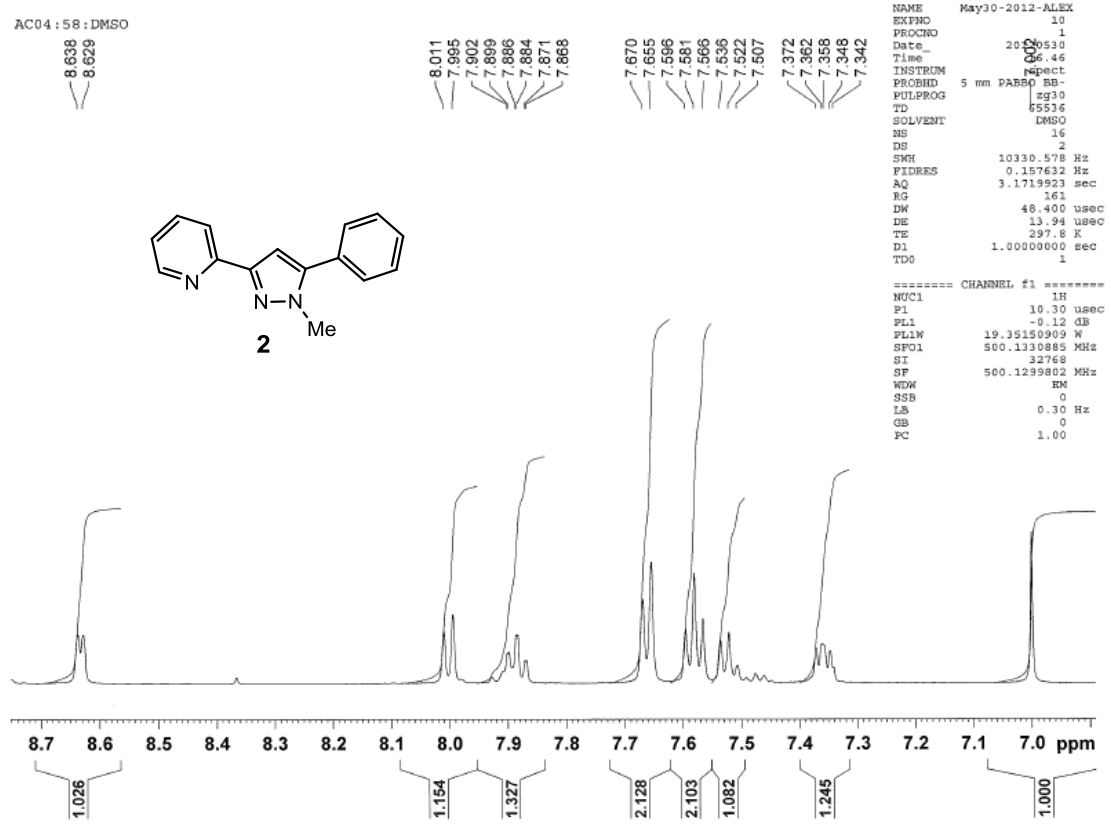
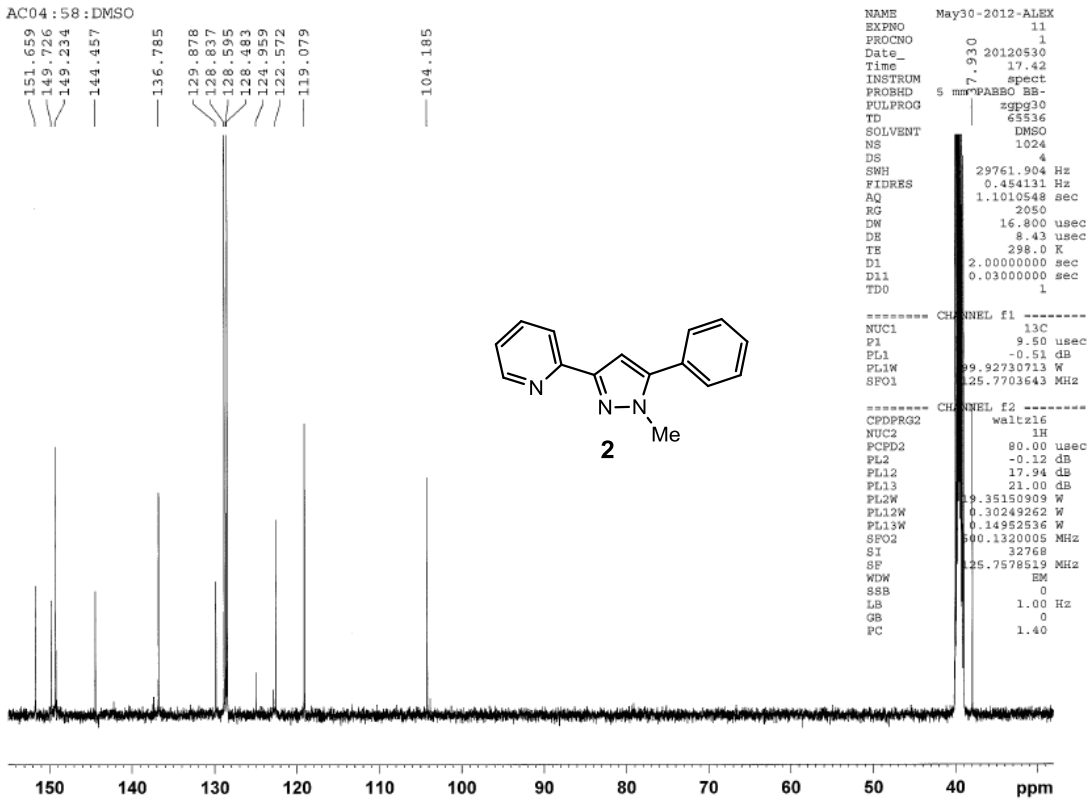
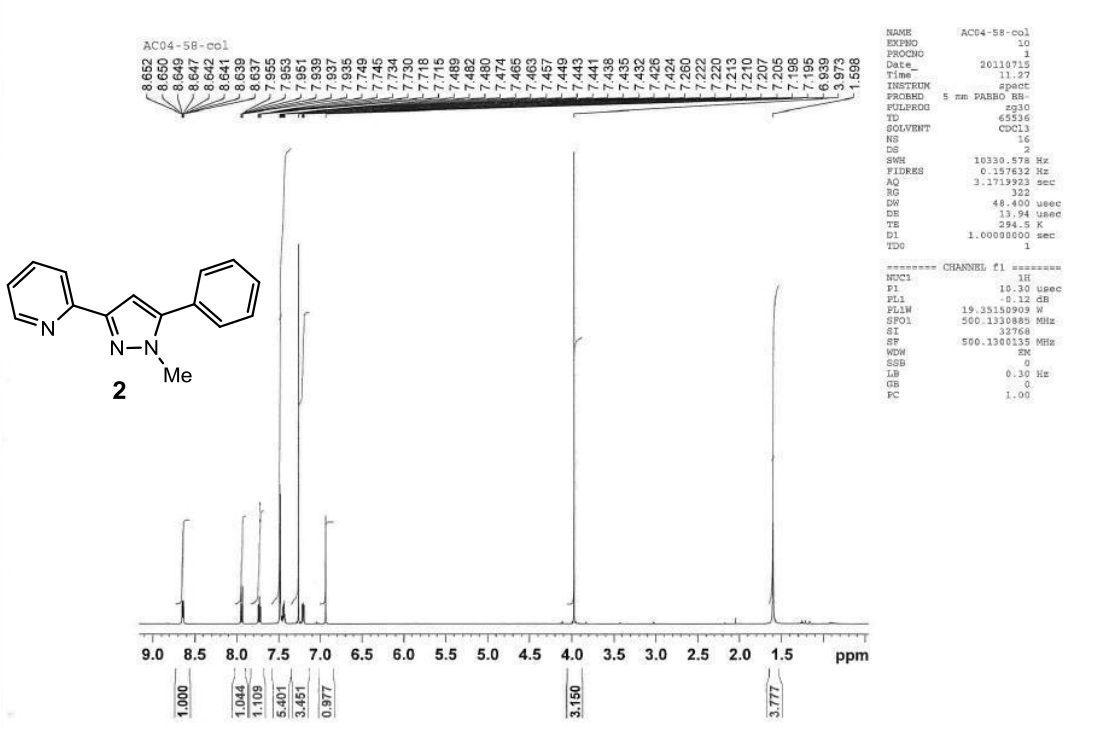




NMR Spectra of Pyrazole 2 in $CDCl_3$



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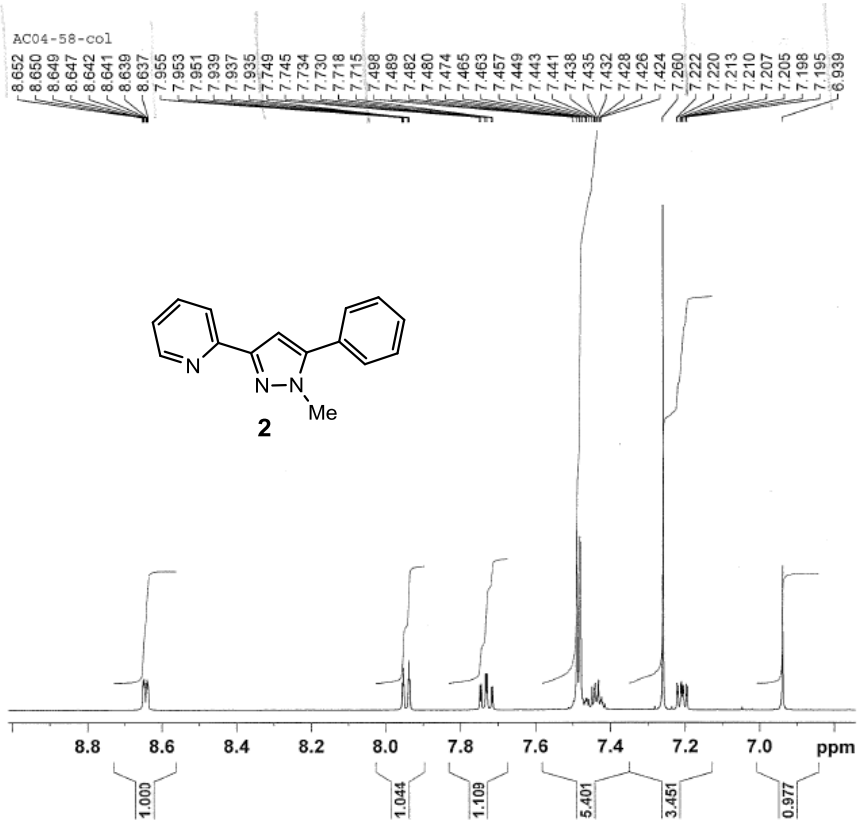

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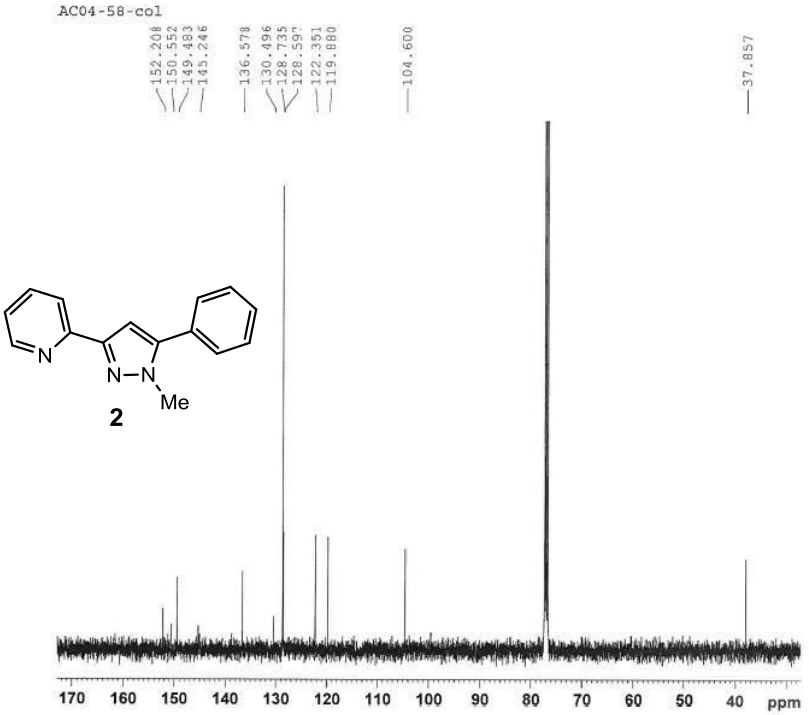
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	322
DW	48.400 usec
DE	13.94 usec
TE	294.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.30 usec
PL1	-0.12 dB
PL1W	19.35150909 W
SFO1	500.1330885 MHz
SI	32768
SF	500.1300135 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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PROCNO	1
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TD	65536
SOLVENT	CDCl3
NS	749
DS	4
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	2050
DW	16.800 usec
DE	8.43 usec
TE	295.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-0.51 dB
PL1W	99.92730713 W
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-0.12 dB
PL12	17.94 dB
PL13	21.00 dB
PL2W	19.35150909 W
PL12W	0.30249262 W
PL13W	0.14952536 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577929 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
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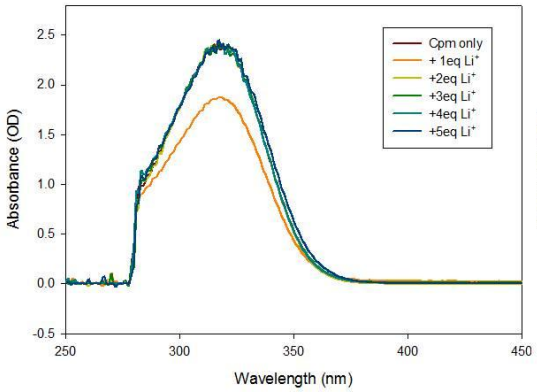
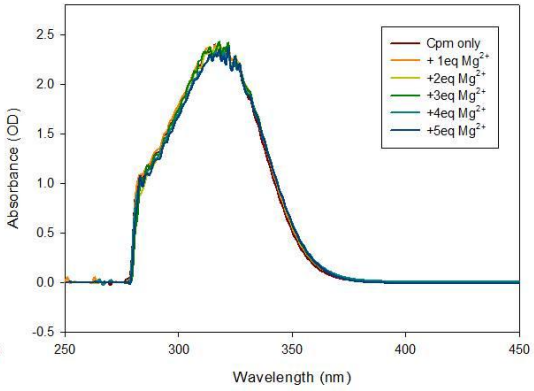
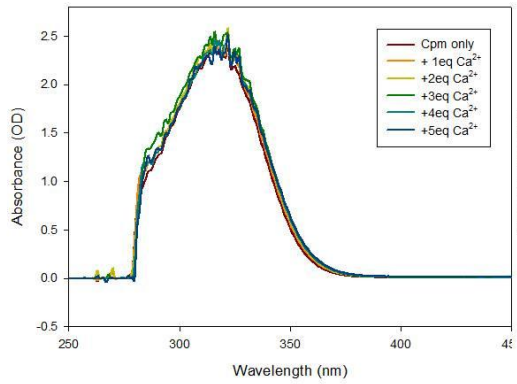
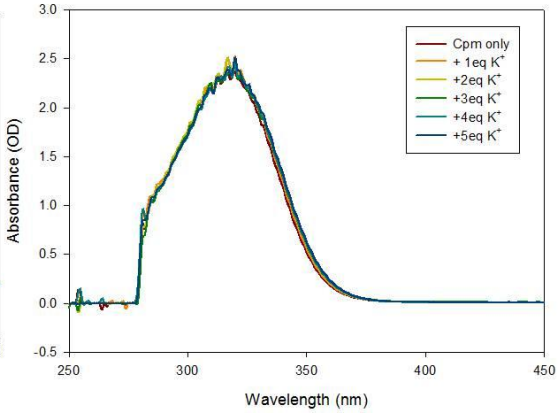
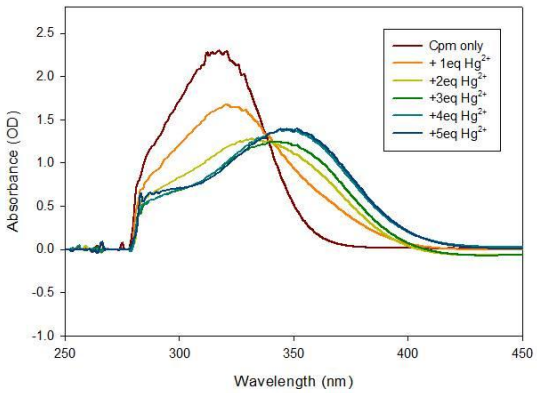
Absorbance Spectra for Pyrazoline Ligand 1 (MeCN, 500 μM) - Metal Screen

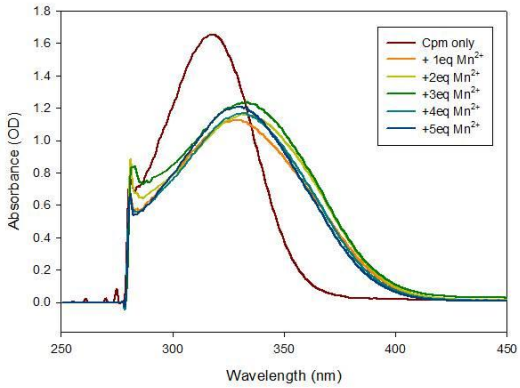


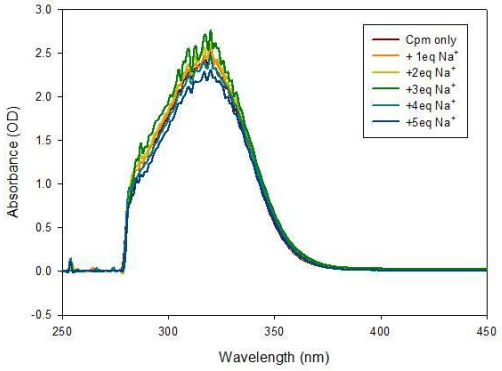


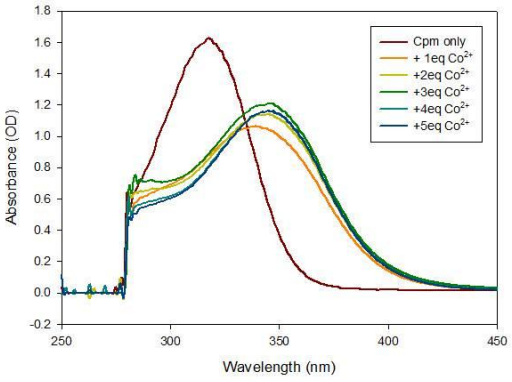


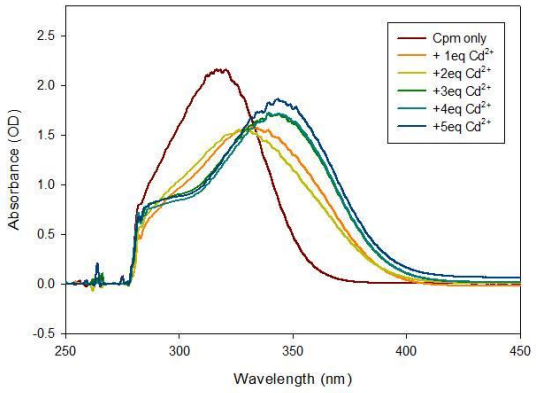


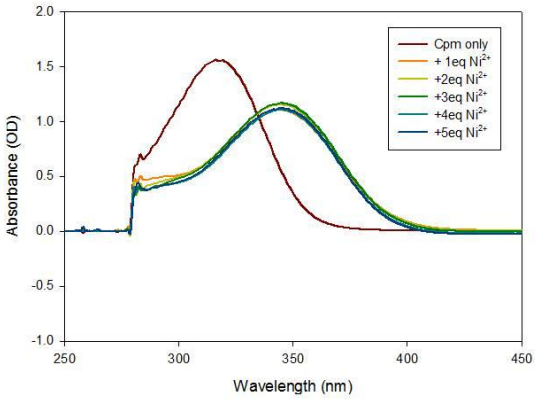


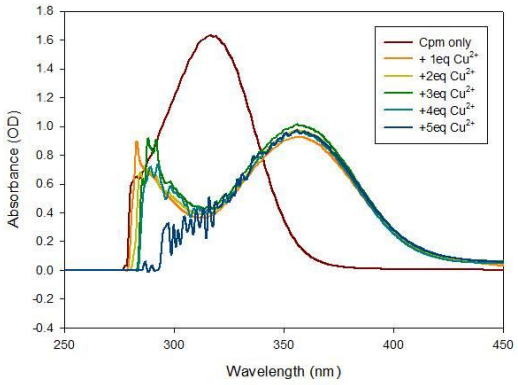


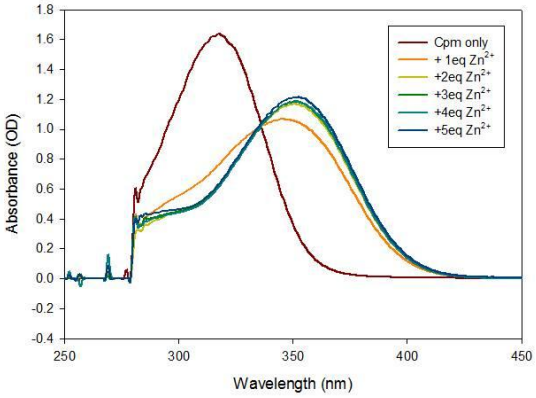


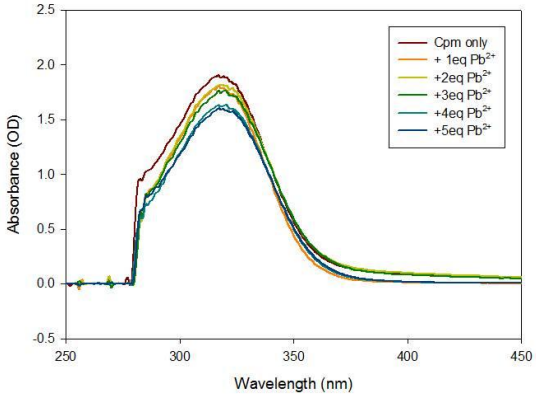


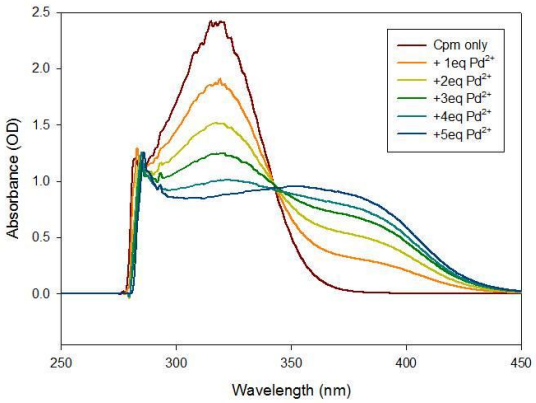


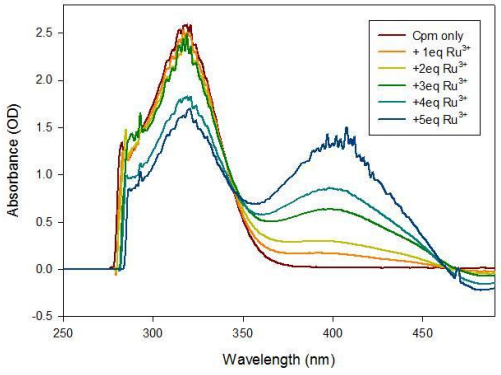




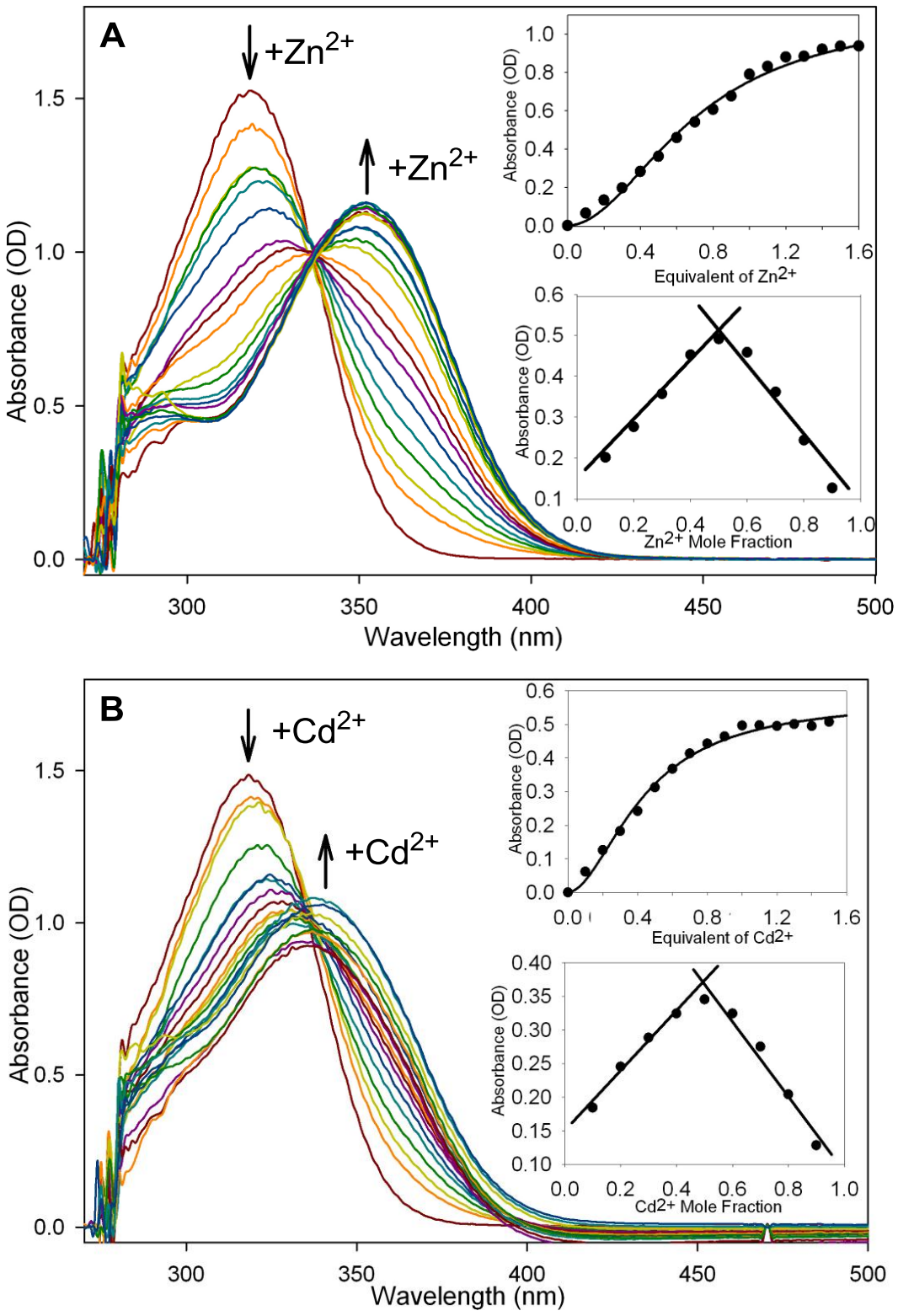






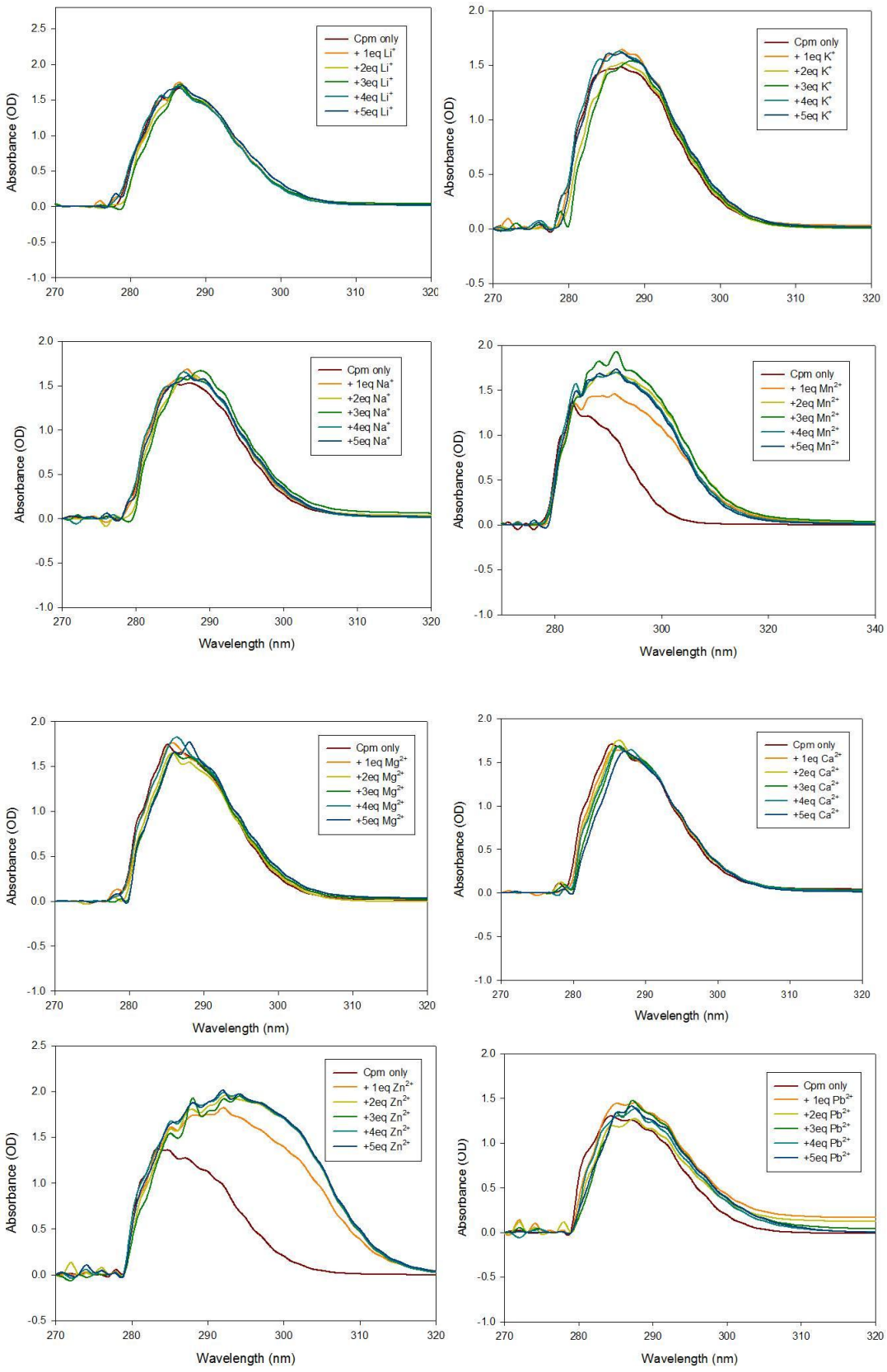


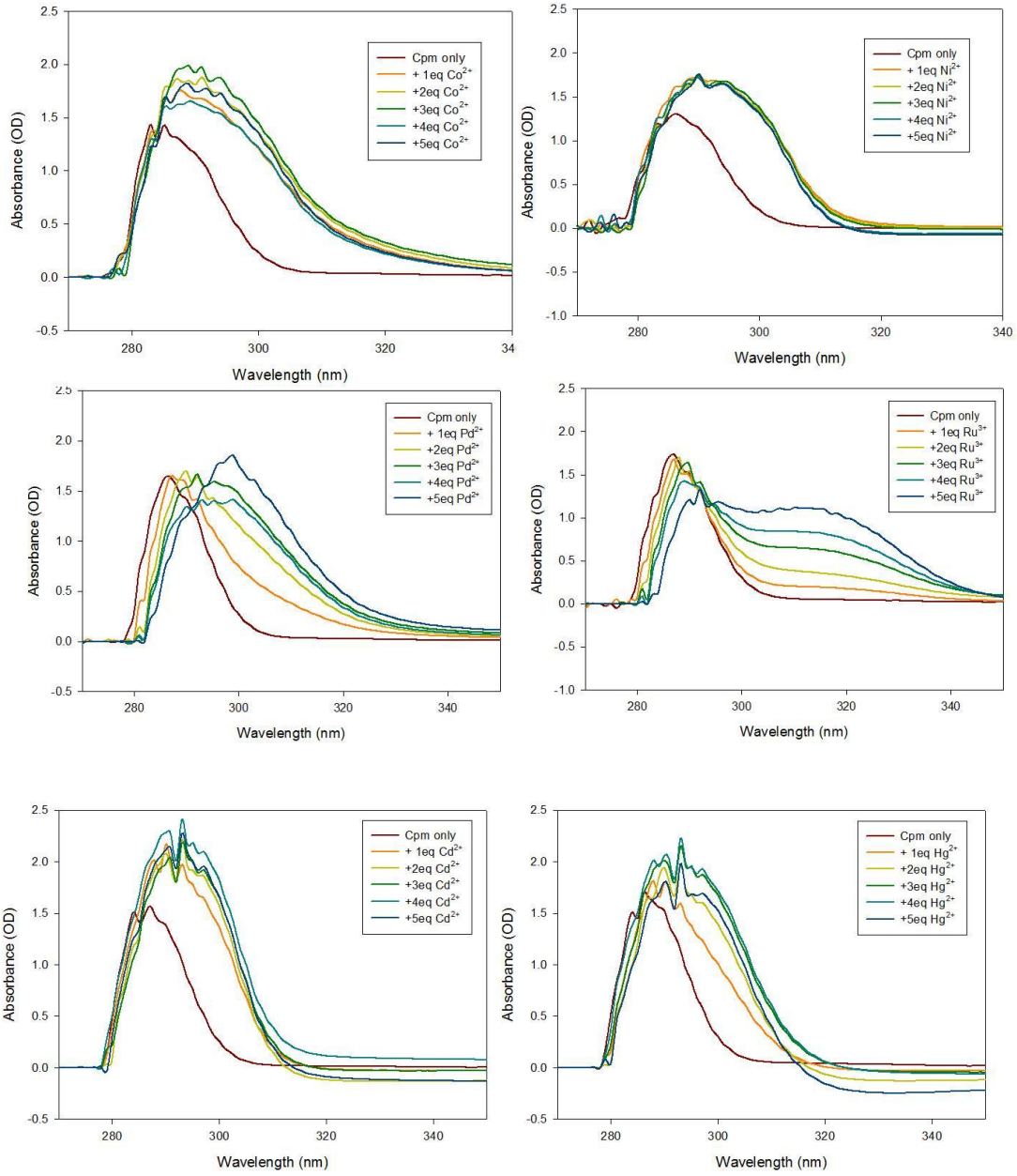
Absorbance Spectra for Pyrazoline Ligand 1 – Titration and Job Plot



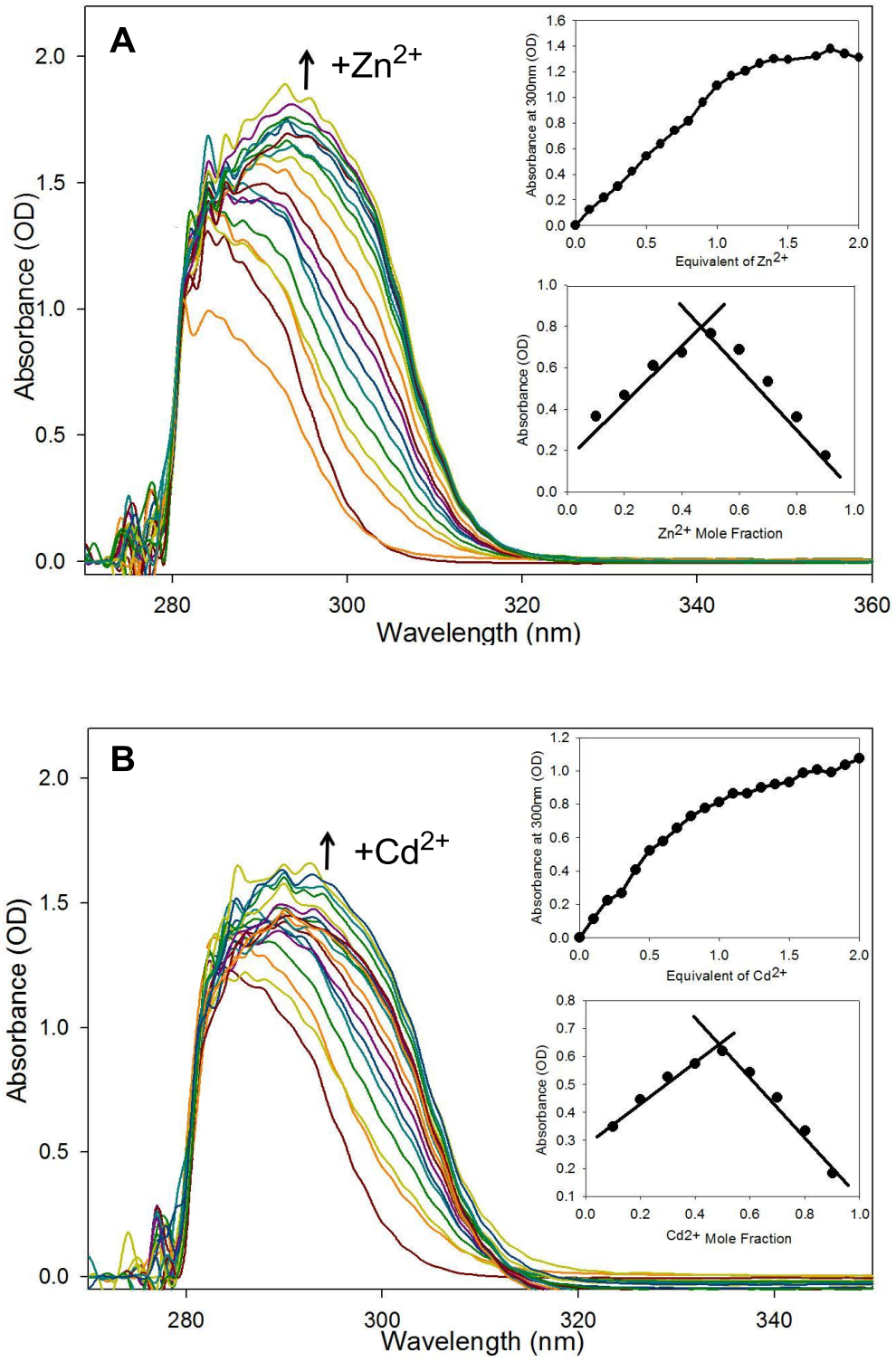
Absorbance spectra of pyrazoline **1** (MeCN, 500 μM) with the addition of 0-1.5 equiv. (0.1 increments) of Zn^{2+} (**A**) and Cd^{2+} (**B**). Insets at λ_{em} = 370 nm. Lower inset Job plot ([Metal]+[ligand]=500 μM).

Absorbance Spectra for Pyrazole Ligand 2 (MeCN, 500 μM) – Metal Screen





Absorbance Spectra for Pyrazole Ligand 2 – Titration and Job Plot



Absorbance spectra of pyrazole **2** (MeCN, 500 μM) with the addition of 0-2.0 equiv. (0.1 increments) of Zn^{2+} (**A**) and Cd^{2+} (**B**). Insets at λ_{em} = 305 nm. Lower inset Job plot ([Metal]+[ligand]=500 μM).

Extinction Co-efficients

Ligand concentration 20 μM, path length 1 cm

Pyrazoline **1** only, abs. @ 320 nm = 0.296; ε = 14800 $M^{-1}cm^{-1}$

Pyrazoline **1** + 5 equiv. Zn^{2+}, abs. @ 360 nm = 0.173; ε = 8650 $M^{-1}cm^{-1}$

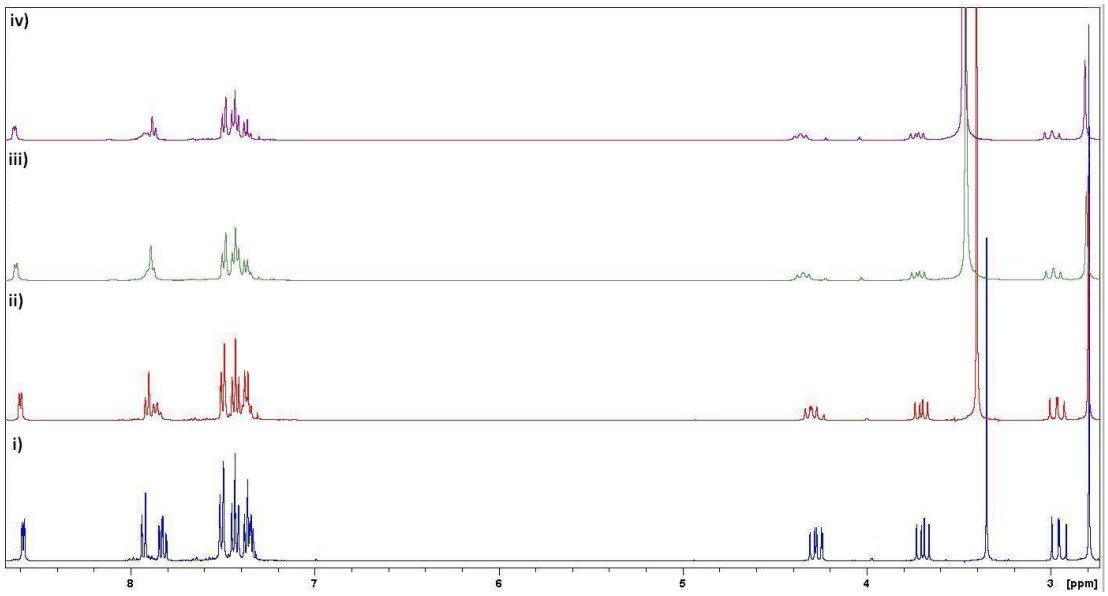
Pyrazoline **1** + 5 equiv. Cd^{2+}, abs. @ 350 nm = 0.153; ε = 7650 $M^{-1}cm^{-1}$

Pyrazole **2** only, abs. @ 285 nm = 0.237; ε = 11850 $M^{-1}cm^{-1}$

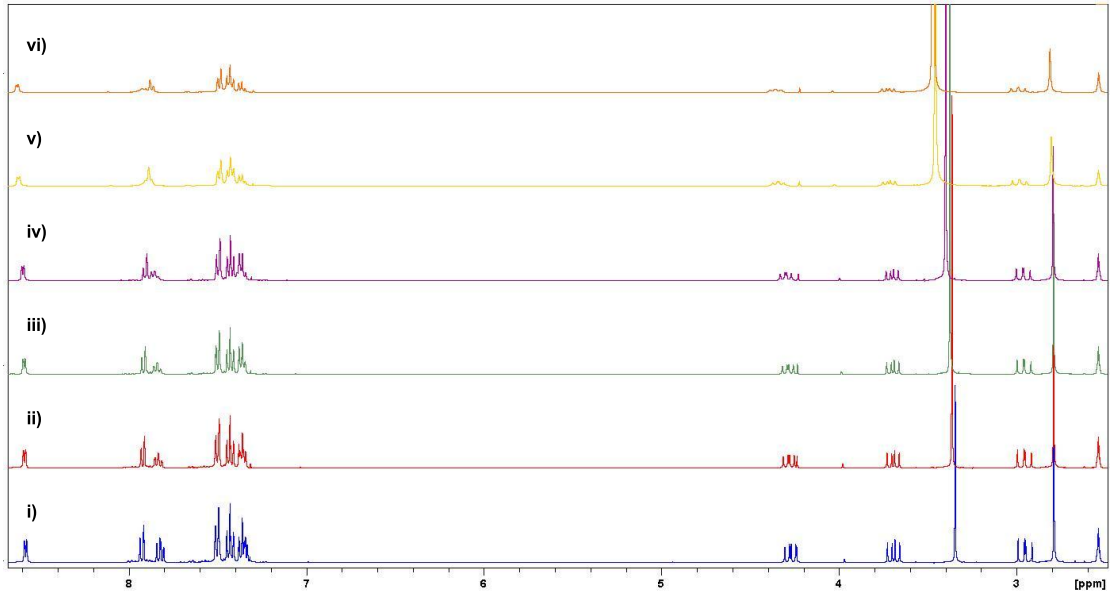
Pyrazole **2** + 5 equiv. Zn^{2+}, abs. @ 290 nm = 0.309; ε = 15450 $M^{-1}cm^{-1}$

Pyrazole **2** + 5 equiv. Cd^{2+}, abs. @ 290 nm = 0.261; ε = 13050 $M^{-1}cm^{-1}$

NMR Spectra for Pyrazoline Ligand 1 – Zn^{2+} Titration

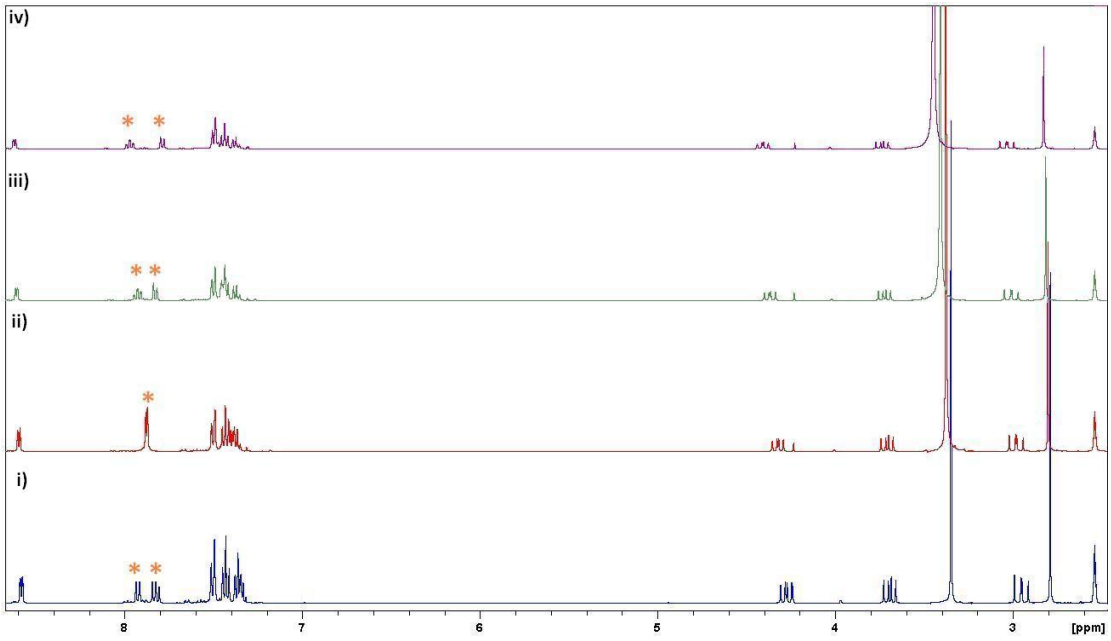


^{1}H NMR spectra of i) pyrazoline **1** (DMSO-d_6, 63 mM) with ii) 0.9, iii) 2.0 and iv) 3.0 equiv. Zn^{2+}.

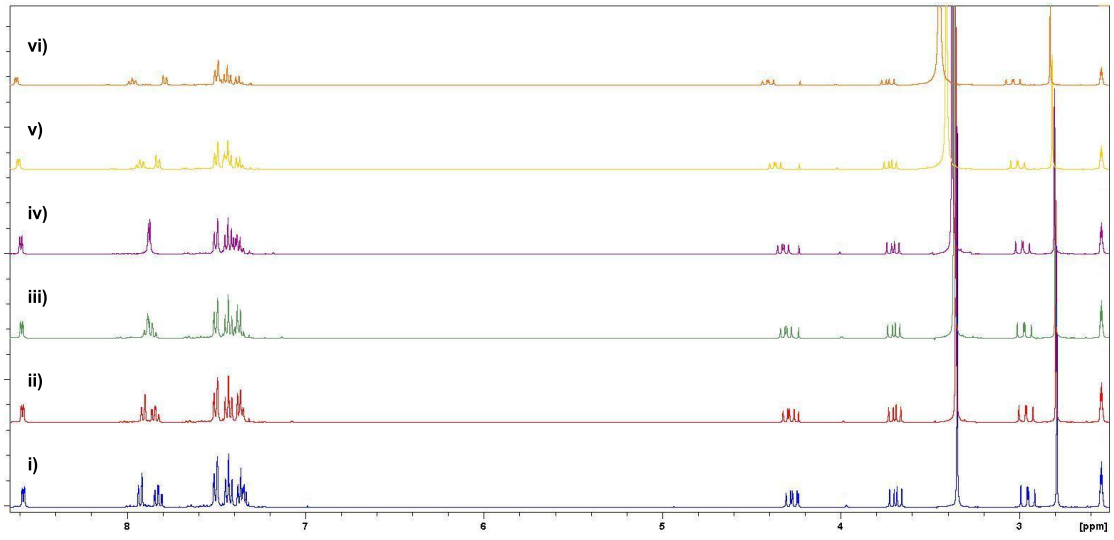


^{1}H NMR spectra of i) pyrazoline **1** (DMSO-d_6, 63 mM) with ii) 0.3, iii) 0.6, iv) 0.9, v) 2.0 and vi) 3.0 equiv. Zn^{2+}.

NMR Spectra for Pyrazoline Ligand 1 – Cd^{2+} Titration

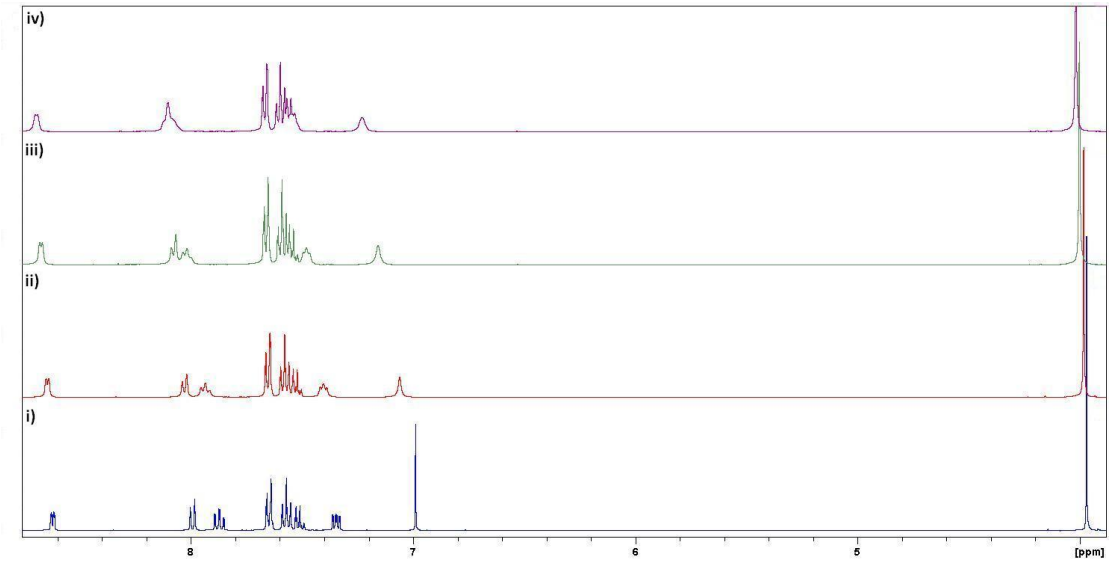


^{1}H NMR spectra of i) pyrazoline **1** (DMSO-d_6, 63 mM) with ii) 0.9, iii) 2.0 and iv) 3.0 equiv. Cd^{2+}.

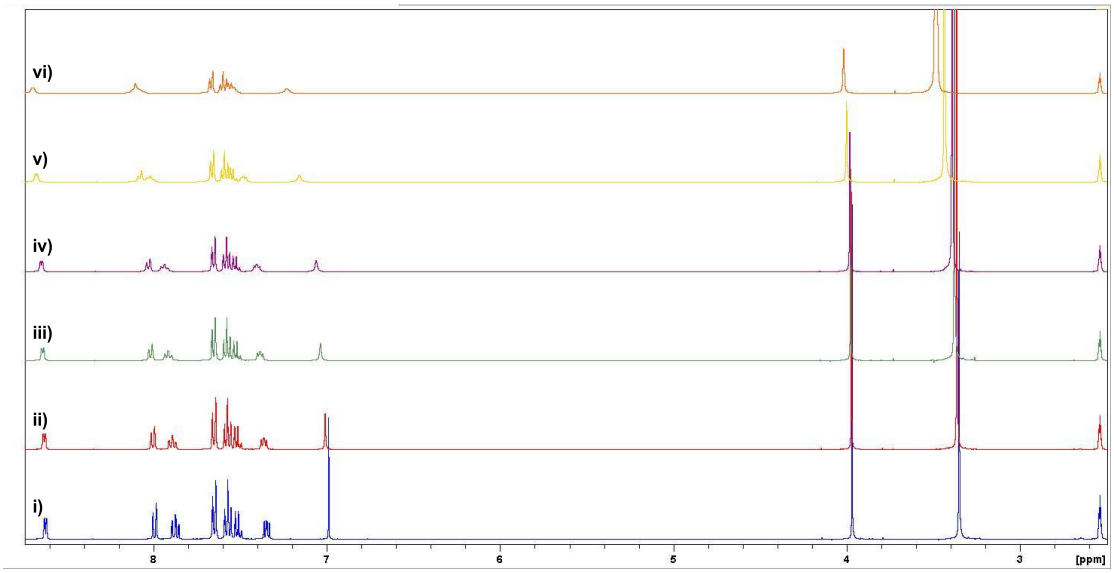


^{1}H NMR spectra of i) pyrazoline **1** (DMSO-d_6, 63 mM) with ii) 0.3, iii) 0.6, iv) 0.9, v) 2.0 and vi) 3.0 equiv. Cd^{2+}.

NMR Spectra for Pyrazole Ligand 2 - Zn^{2+} Titration

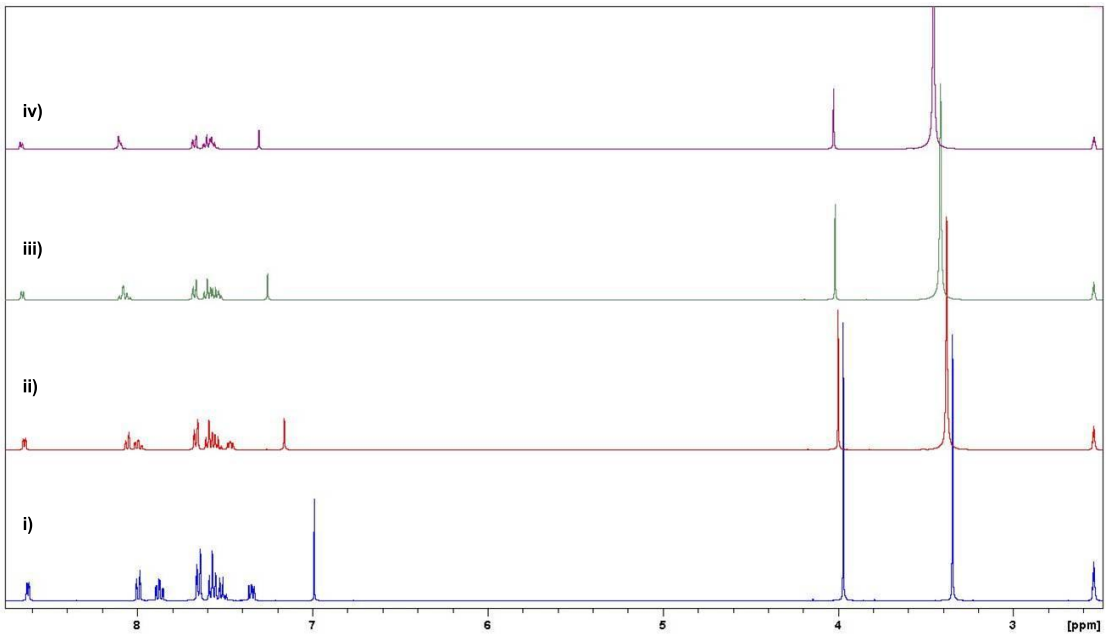


^{1}H NMR spectra of i) pyrazole **2** (DMSO-d_6, 63 mM) with ii) 0.9, iii) 2.0 and iv) 3.0 equiv. Zn^{2+}.

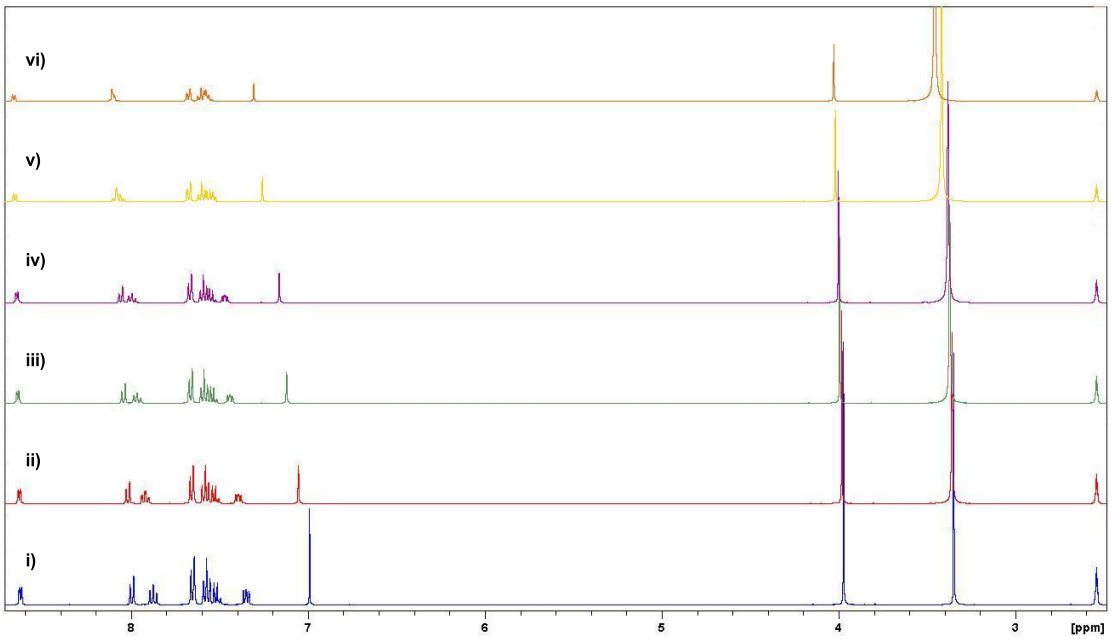


^{1}H NMR spectra of i) pyrazole **2** (DMSO-d_6, 63 mM) with ii) 0.3, iii) 0.6, iv) 0.9, v) 2.0 and vi) 3.0 equiv. Zn^{2+}.

NMR Spectra for Pyrazole Ligand 2 - Cd^{2+} Titration

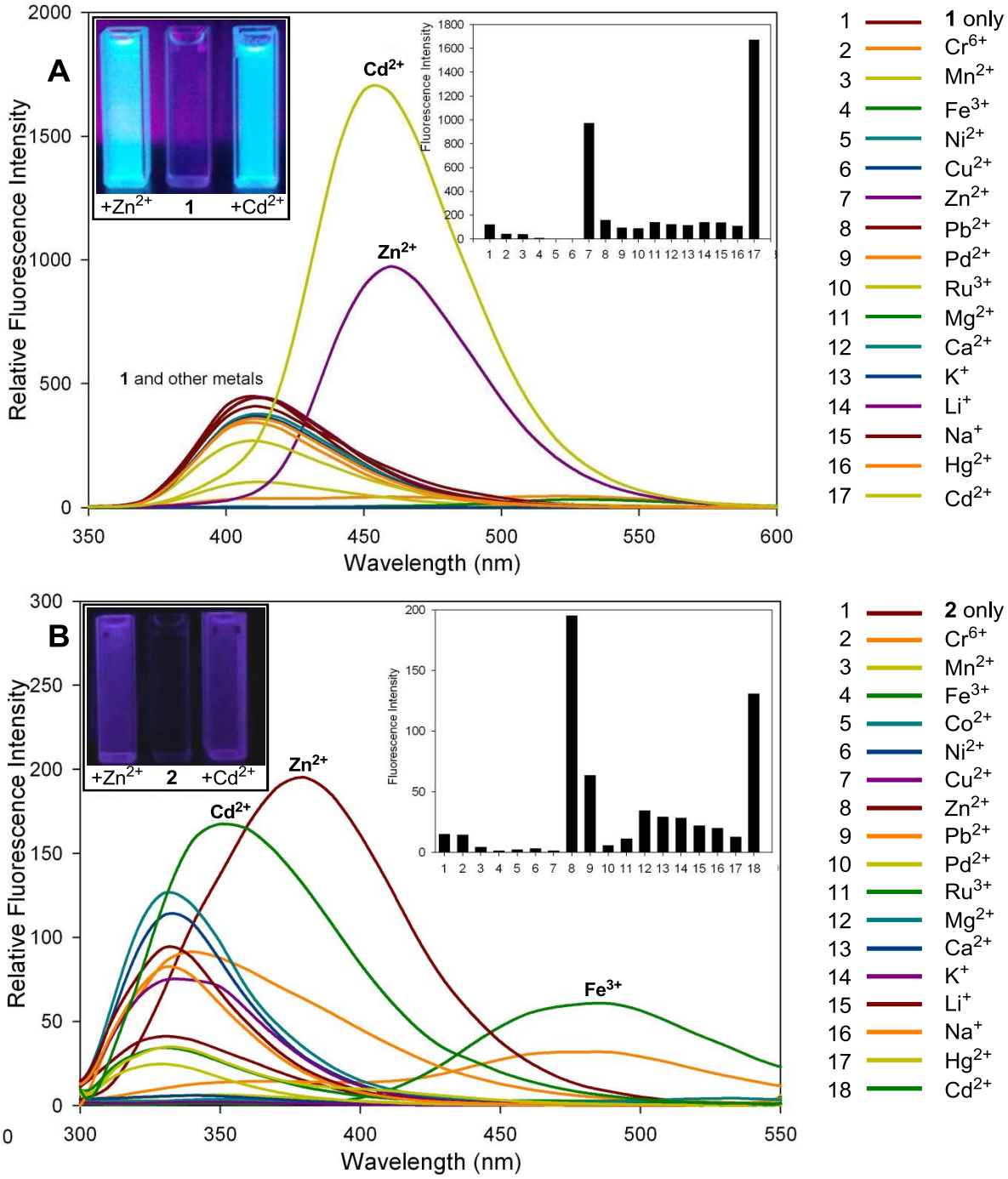


^{1}H NMR spectra of i) pyrazole **2** (DMSO-d_6, 63 mM) with ii) 0.9, iii) 2.0 and iv) 3.0 equiv. Cd^{2+}.



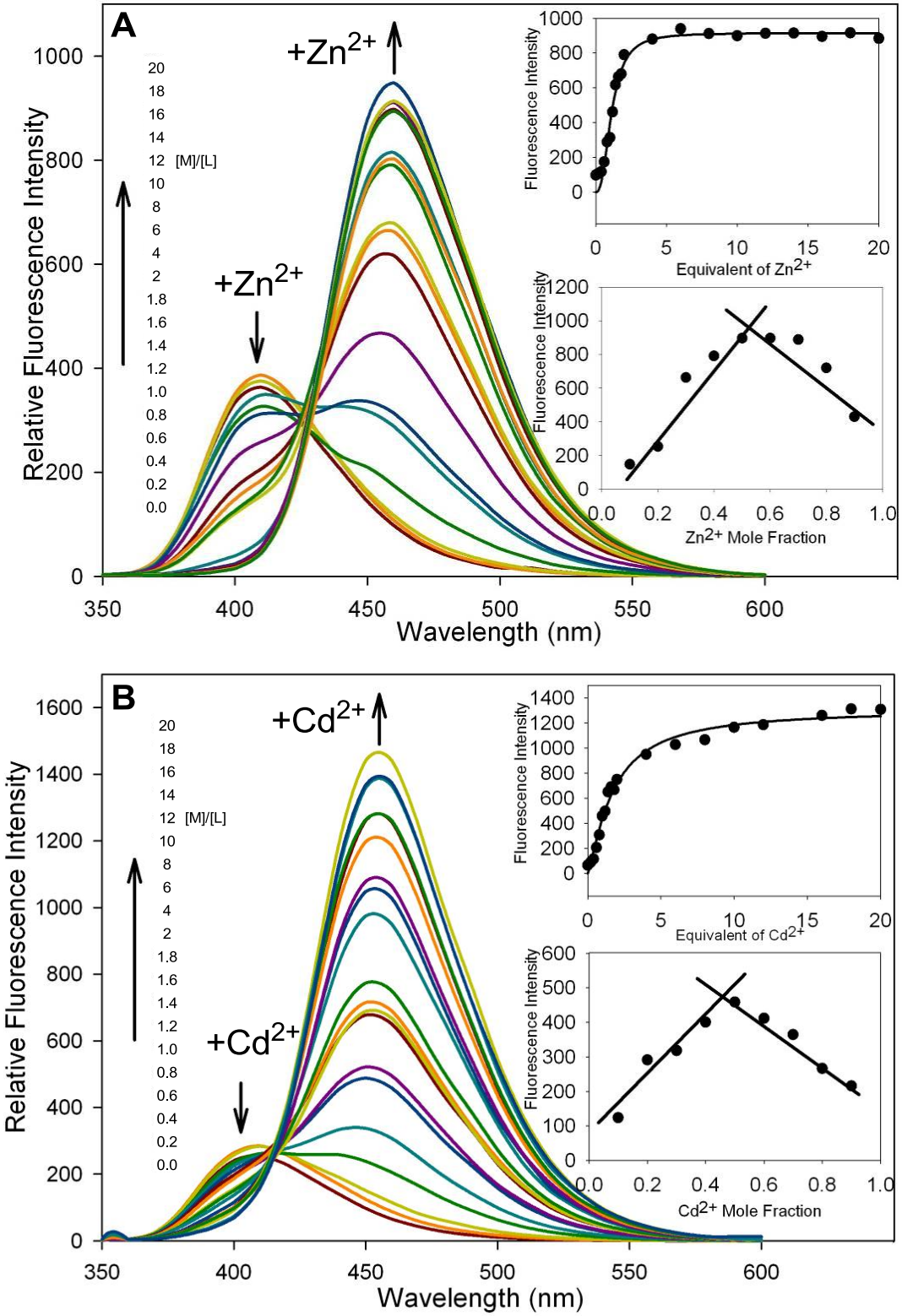
^{1}H NMR spectra of i) pyrazole **2** (DMSO-d_6, 63 mM) with ii) 0.3, iii) 0.6, iv) 0.9, v) 2.0 and vi) 3.0 equiv. Cd^{2+}.

Fluorescence Spectra – Metal Screen



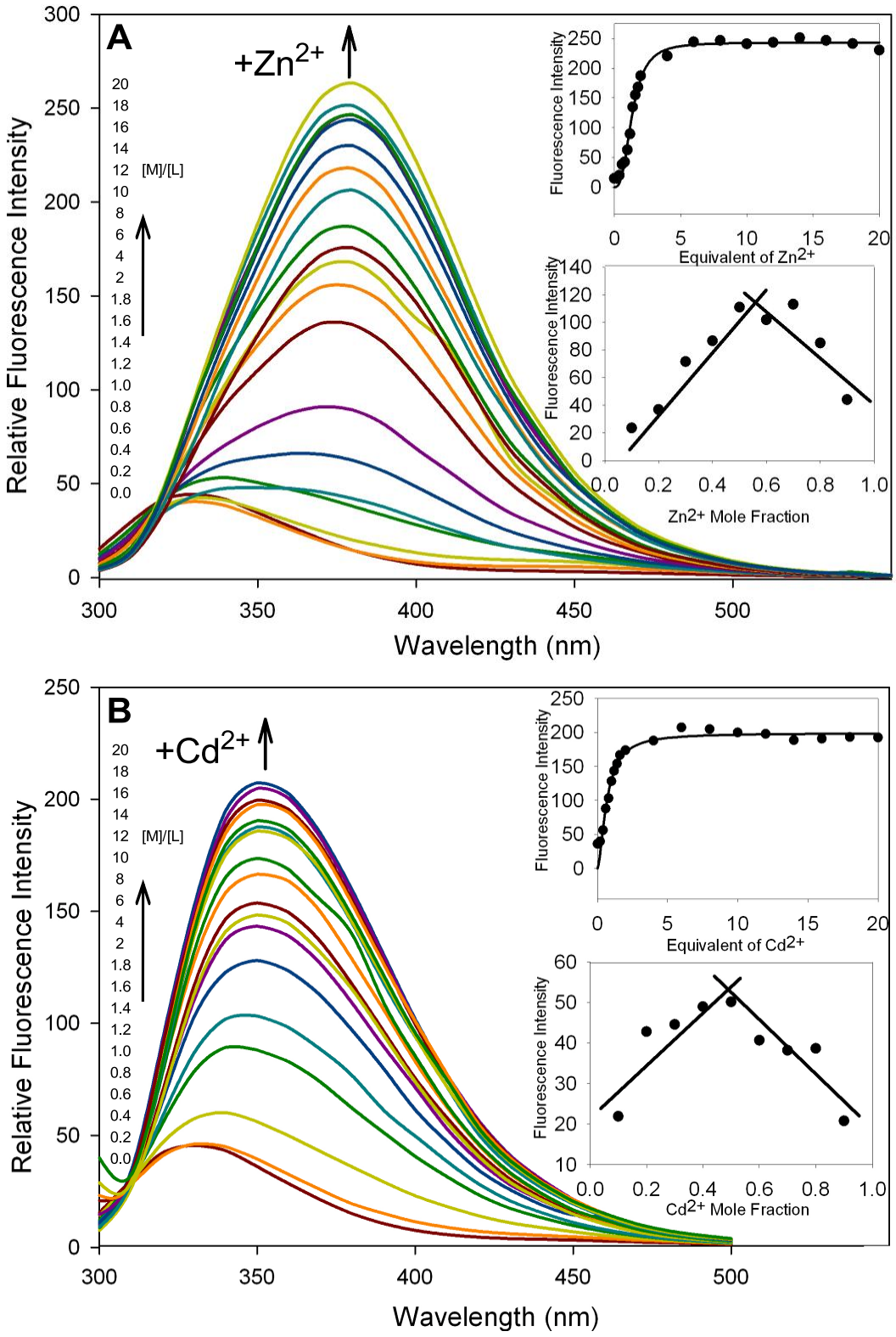
Fluorescence spectra of pyrazoline **1** (**A**, λ_{ex} = 320 nm) and pyrazole **2** (**B**, λ_{ex} = 285 nm, MeCN, 20 μM), upon addition of 5 equiv. of metal. Metal screen at λ_{em} = 460 nm (**A**) and 380 nm (**B**). Inset shows fluorescence with Zn^{2+} and Cd^{2+} at 313 nm (**A**) and 254 nm (**B**).

Fluorescence Spectra for Pyrazoline Ligand 1 – Titration and Job Plot



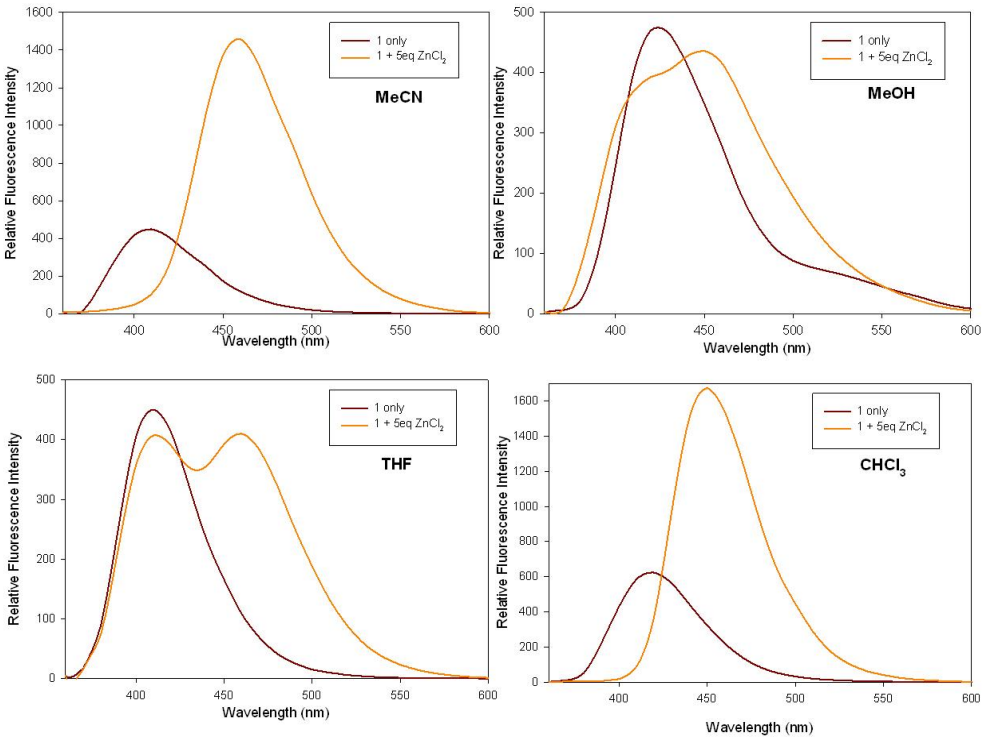
Fluorescence spectra of pyrazoline **1** (MeCN, 20 μM, λ_{ex} = 320 nm) upon addition of 0-20 equiv. Zn^{2+} (**A**) and Cd^{2+} (**B**). Insets at λ_{em} = 460 nm upon addition of cation. Lower inset Job plot ([Metal]+[ligand]=20 μM).

Fluorescence Spectra for Pyrazole Ligand 2 – Titration and Job Plot

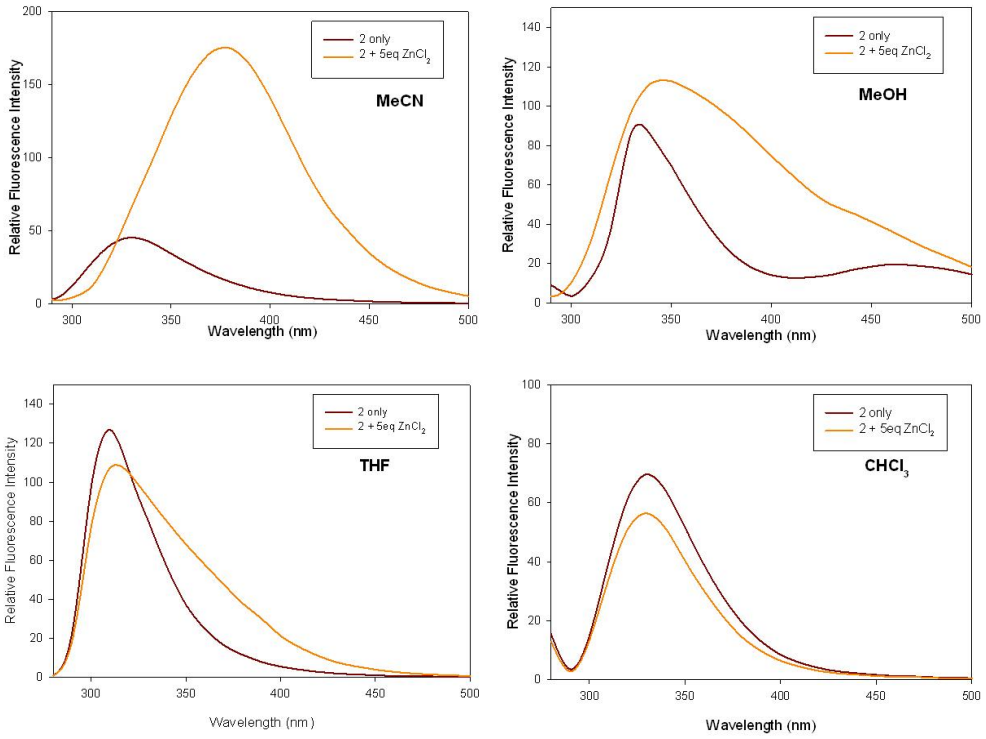


Fluorescence spectra of pyrazole **2** (MeCN, 20 μM, λ_{ex} = 285 nm) upon addition of 0-20 equiv. Zn^{2+} (**A**) and Cd^{2+} (**B**). Insets at λ_{em} = 380 nm (**A**) and 350 nm (**B**) upon addition of cation. Lower inset Job plot ([Metal]+[ligand]=20 μM).

Fluorescence Spectra in Various Solvents



Pyrazoline **1** (20 μM, λ_{ex} = 330 nm) with 5 equiv. $ZnCl_2$



Pyrazole **2** (20 μM, λ_{ex} = 270 nm) with 5 equiv. $ZnCl_2$

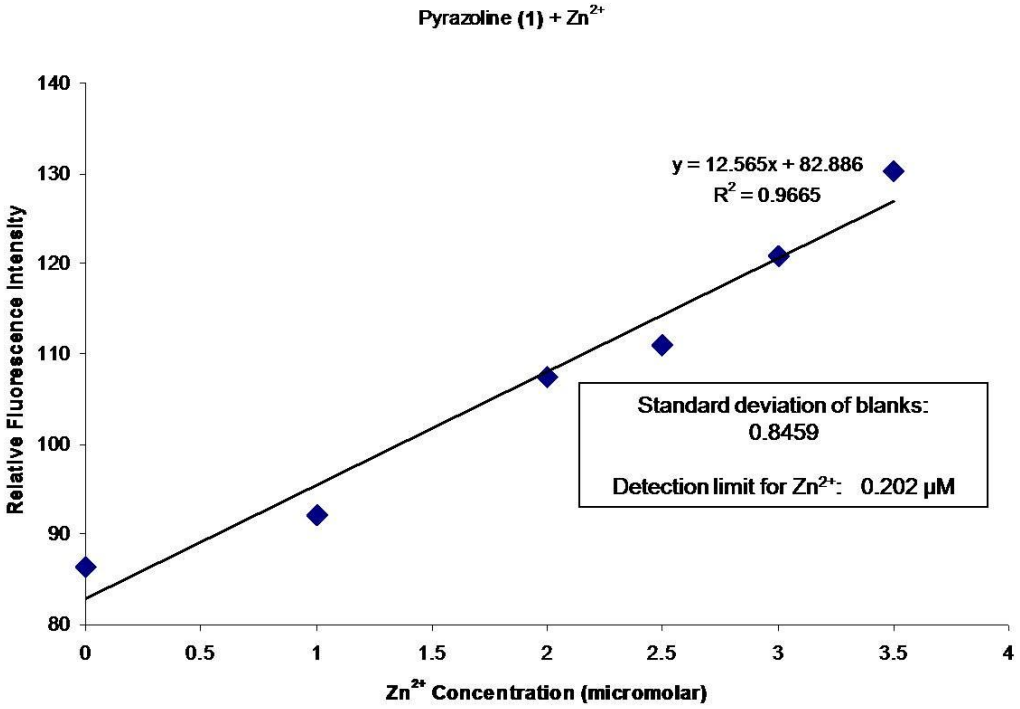
Water and even water mixtures with MeCN completely quenched fluorescence (results not shown).

Limit of Detection Calculations

The detection limit was calculated using fluorescence titration following the procedure reported by Lee *et al*.[6] Initially, the emission intensity of pyrazoline **1** and pyrazole **2** was measured in the absence of any metals and the standard deviation determined. Three independent measurements of emission intensity in the presence of either Zn^{2+} or Cd^{2+} was then performed and the average fluorescence intensities plotted against the concentration of metal ions. The detection limit was then calculated from the following equation.[6,7] Where σ_{bi} is the standard deviation of blank measurements and m is the slope of fluoresce intensity versus sample concentration.

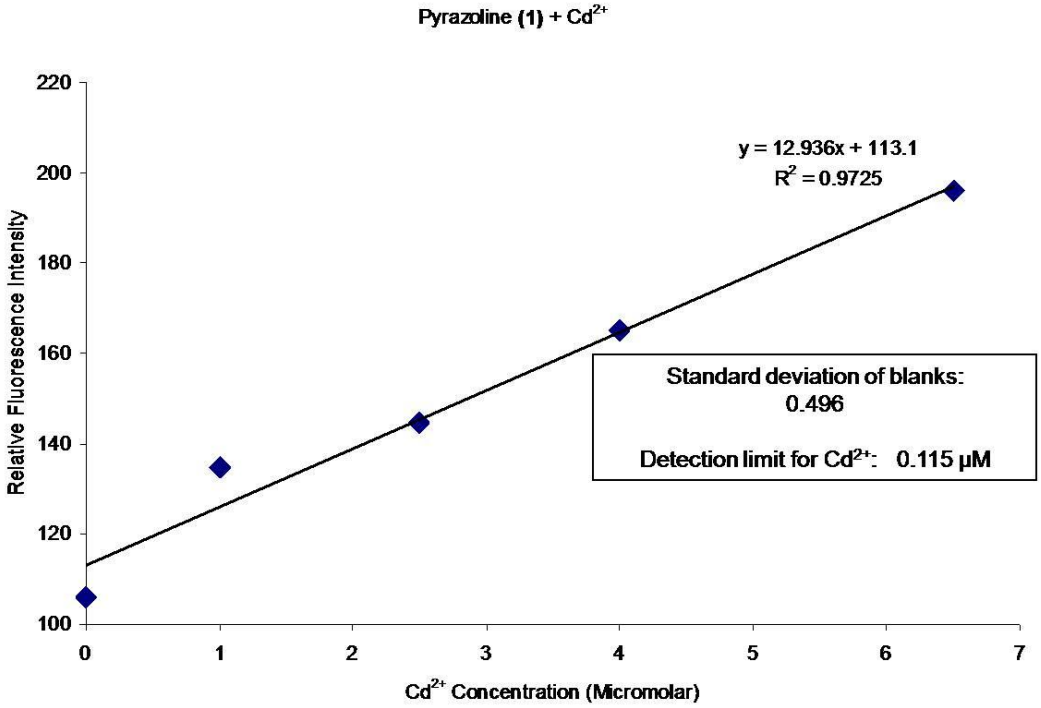
$$\text{Limit of Detection (LOD)} = 3\sigma_{bi} / m$$

Zn^{2+} Detection Limit for Pyrazoline Ligand 1



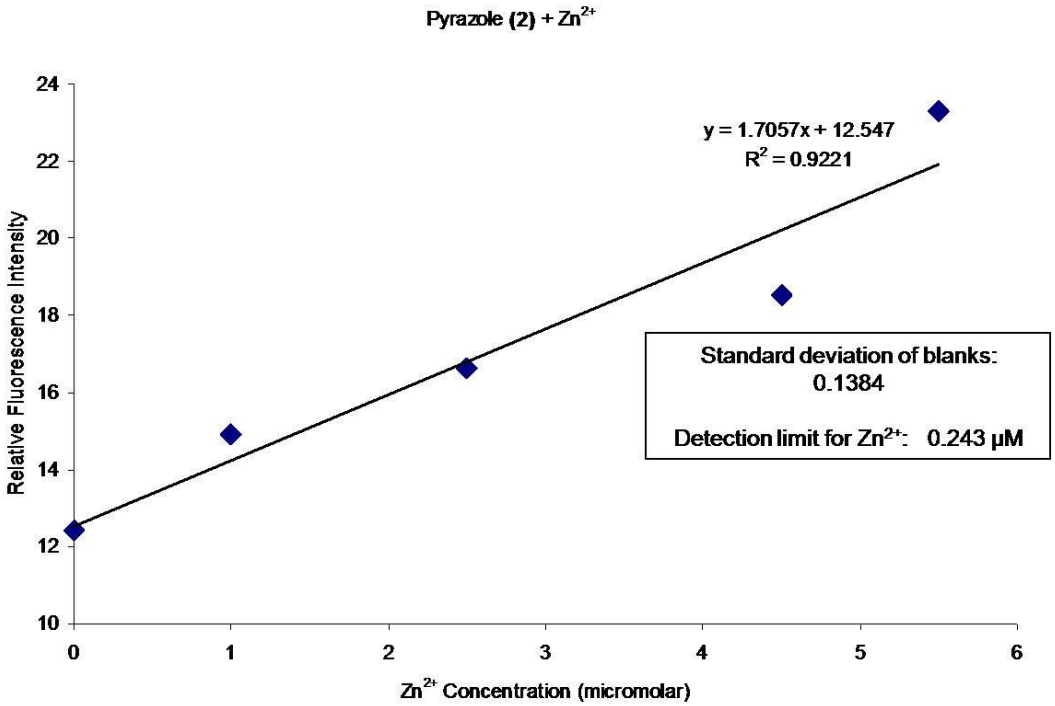
Zn^{2+} detection with pyrazoline **1** (MeCN, 20 μM, λ_{ex} = 320 nm, λ_{em} = 460 nm)

Cd^{2+} Detection Limit for Pyrazoline Ligand 1



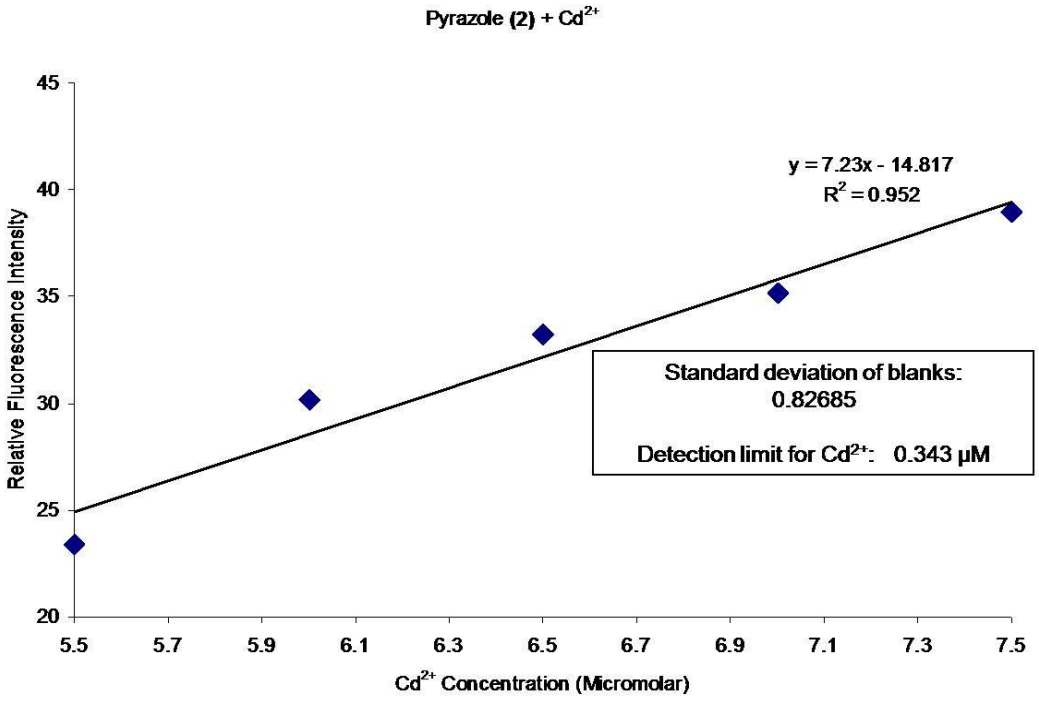
Cd^{2+} detection with pyrazoline **1** (MeCN, 20 μM, λ_{ex} = 320 nm, λ_{em} = 460 nm)

Zn^{2+} Detection Limit for Pyrazole Ligand 2



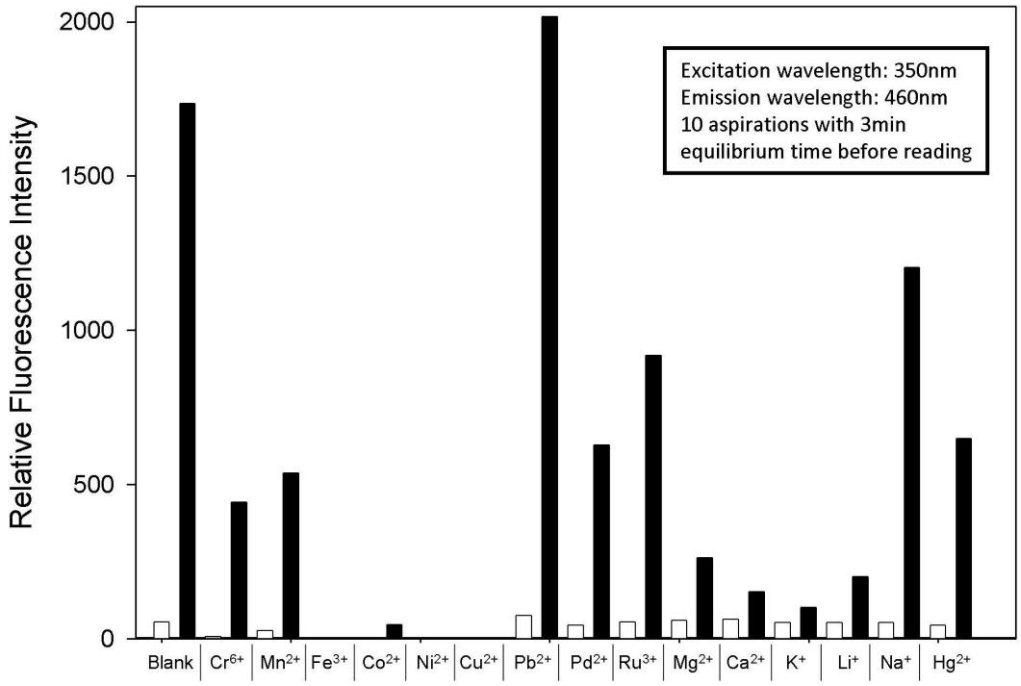
Zn^{2+} detection with pyrazole **2** (MeCN, 20 μM, λ_{ex} = 285 nm, λ_{em} = 380 nm)

Cd^{2+} Detection Limit for Pyrazole Ligand 2



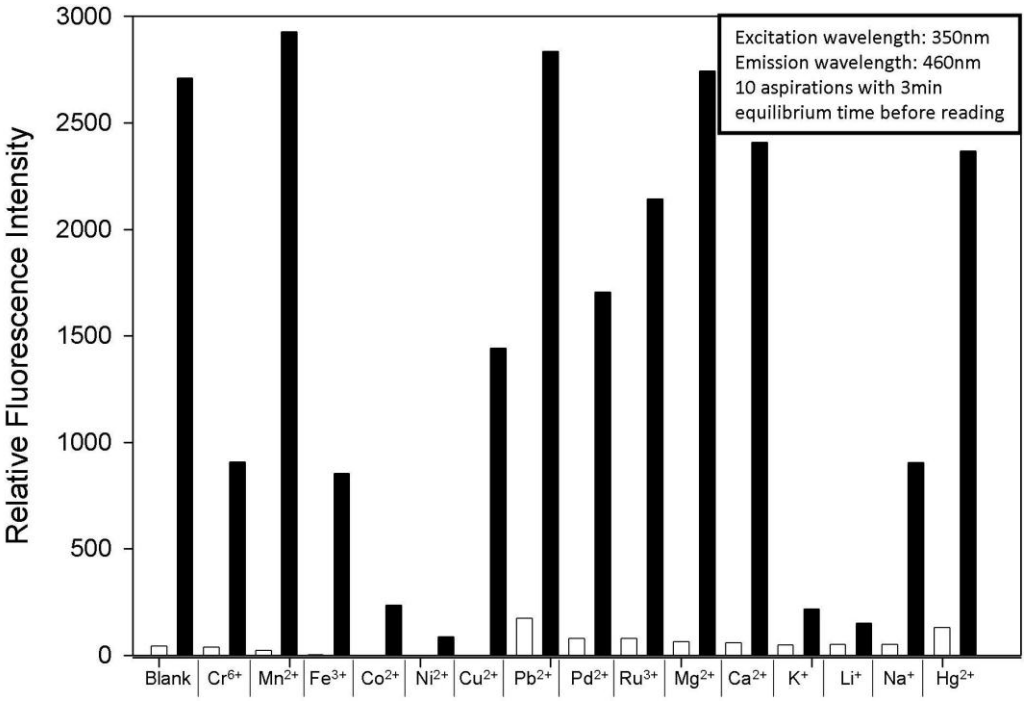
Cd^{2+} detection with pyrazole **2** (MeCN, 20 μM, λ_{ex} = 285 nm, λ_{em} = 350 nm)

Competition Experiments for Pyrazoline Ligand 1 - Zn^{2+}



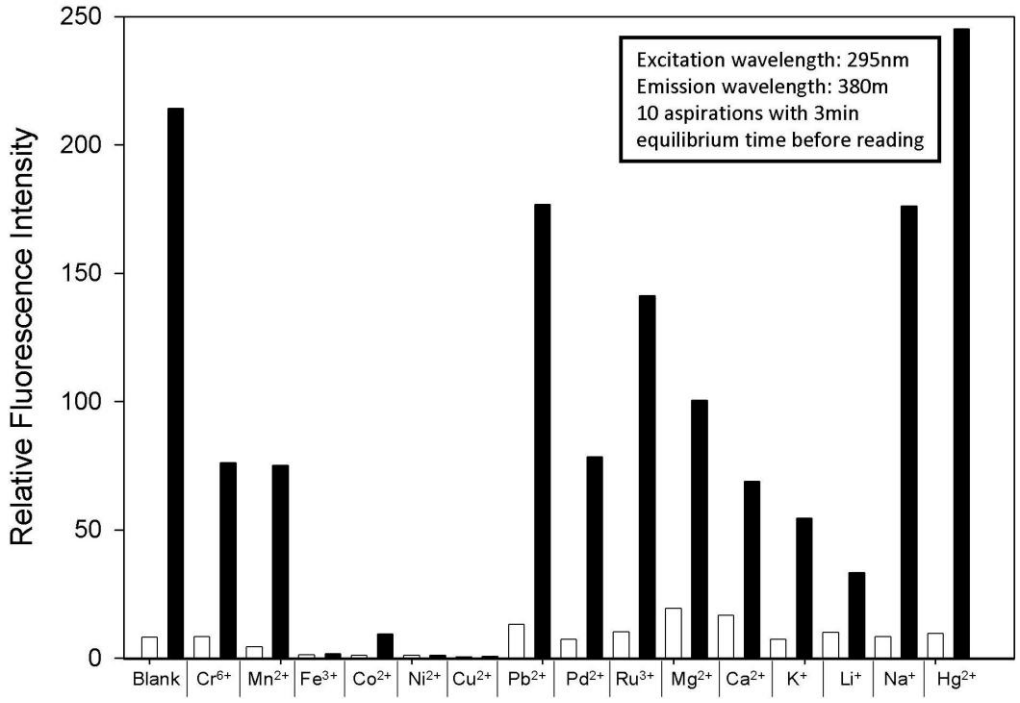
The white bar represents pyrazoline **1** (MeCN, 20 μM) and 5 equiv. of the cation; the black bar is the same plus 5 equiv. Zn^{2+}

Competition Experiments for Pyrazoline Ligand 1 - Cd^{2+}



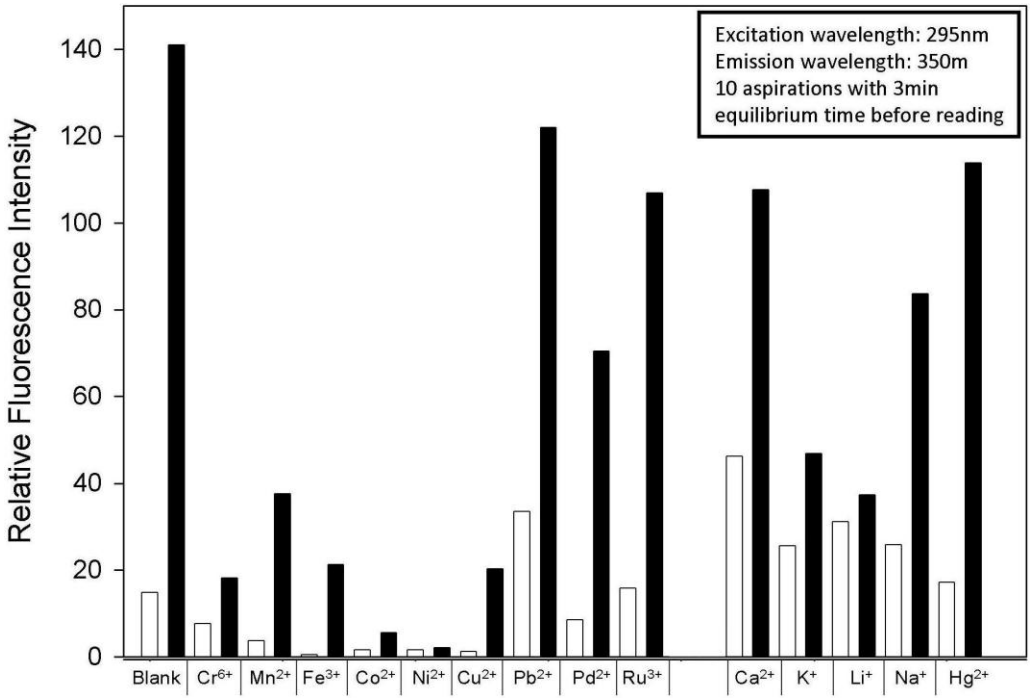
The white bar represents pyrazoline **1** (MeCN, 20 μM) and 5 equiv. of the cation; the black bar is the same plus 5 equiv. Cd^{2+}

Competition Experiments for Pyrazole Ligand 2 - Zn^{2+}



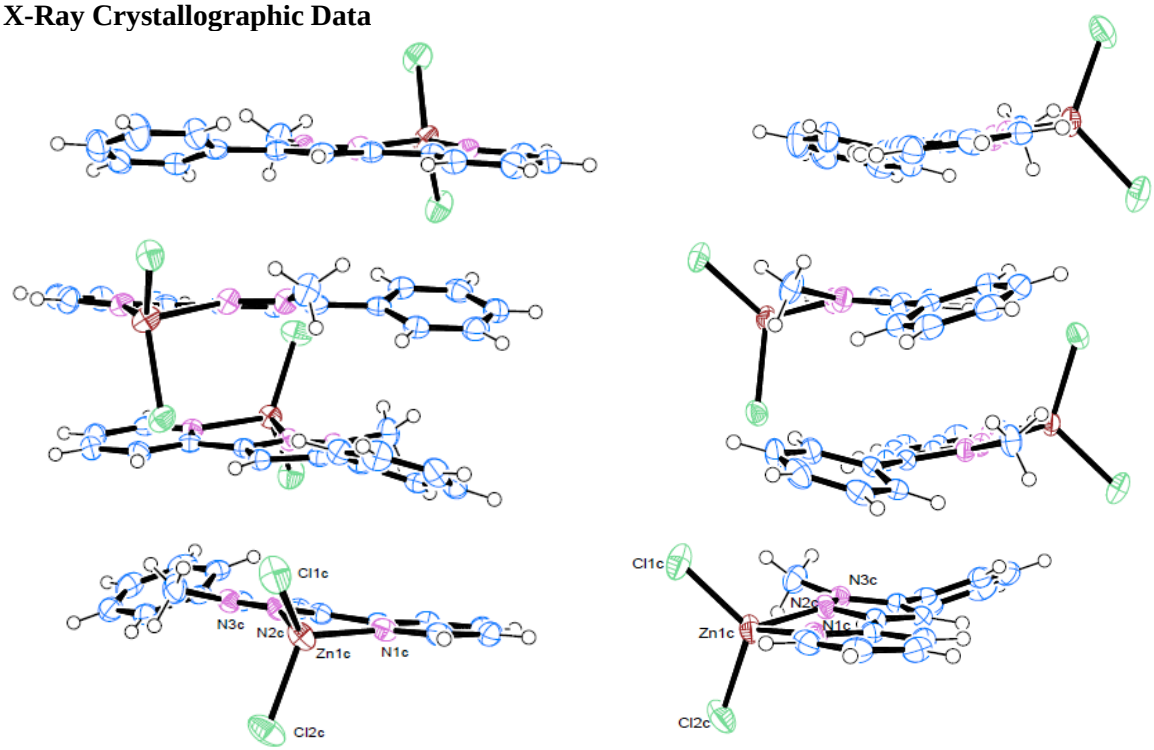
The white bar represents pyrazole **2** (MeCN, 20 μM) and 5 equiv. of the cation; the black bar is the same plus 5 equiv. Zn^{2+}

Competition Experiments for Pyrazole Ligand 2 - Cd^{2+}

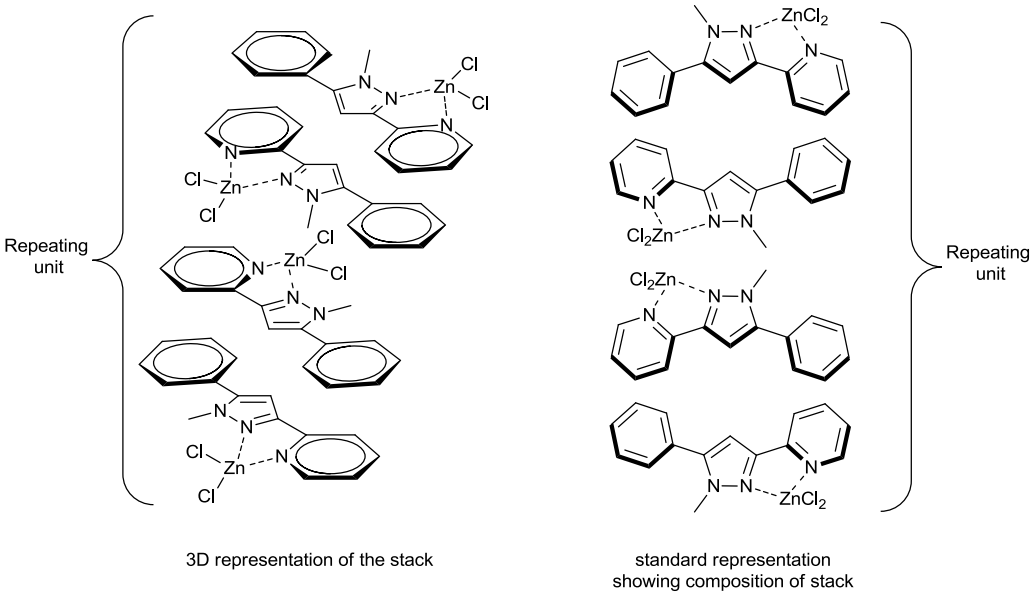


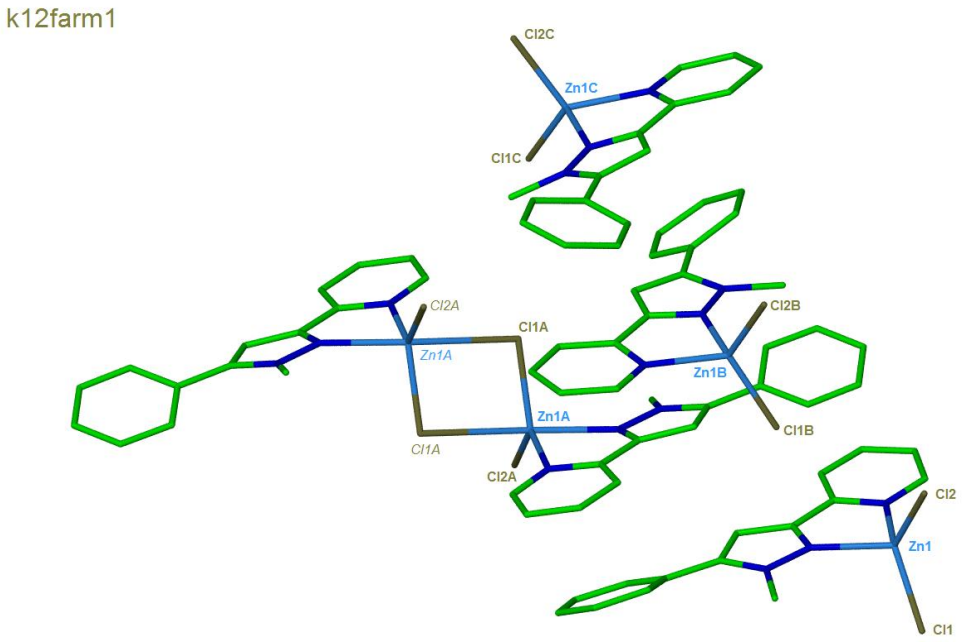
The white bar represents pyrazole **2** (MeCN, 20 μM) and 5 equiv. of the cation; the black bar is the same plus 5 equiv. Cd^{2+}

X-Ray Crystallographic Data



Ortep3 representations, showing the four independent structures. Right – highlighting the alternating positions of the bound metal. All ellipsoids are shown at 50% probability.[8]





The fragment based on Zn1A forms part of a dimer in the gross structure, while the entities based on Zn1, Zn1B and Zn1C do not (the chlorines in the latter 3 molecules are not close enough to any other Zn centre that would facilitate dimer formation).

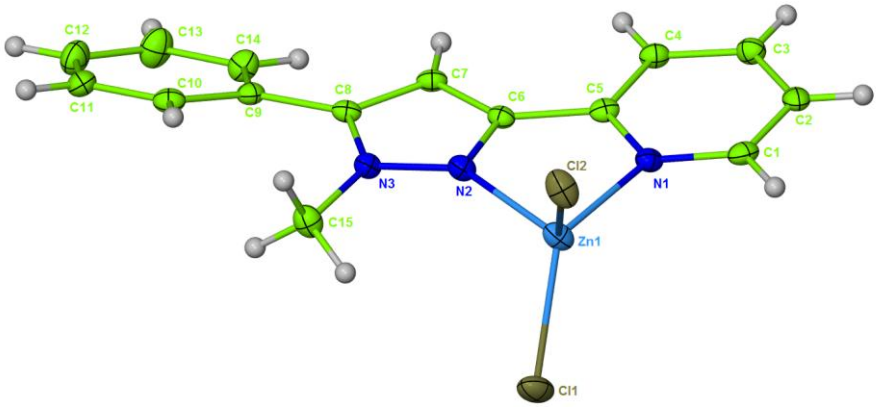


Table 1 Crystal data and structure refinement for pyrazole **2** and $ZnCl_2$

Identification code	k12farm1
Empirical formula	C60 H52 Cl8 N12 Zn4
Formula weight	1486.22
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 14.2600(2)Å alpha = 90°
	b = 26.1400(4)Å beta = 101.476(1)°
	c = 16.8220(2)Å gamma = 90°
Volume	6145.15(15) $Å^3$
Z	4
Density (calculated)	1.606 Mg/m^3
Absorption coefficient	1.941 mm^{-1}
F(000)	3008
Crystal size	0.40 x 0.25 x 0.14 mm
Theta range for data collection	3.51 to 27.47°
Index ranges	-18<=h<=18; -33<=k<=33; -21<=l<=21
Reflections collected	99814
Independent reflections	14032 [R(int) = 0.0737]
Reflections observed (>2sigma)	9917
Data Completeness	0.997
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.565 and 0.457
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14032 / 0 / 761
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0452 wR2 = 0.1015
R indices (all data)	R1 = 0.0782 wR2 = 0.1156
Largest diff. peak and hole	2.273 and -0.882 $eÅ^{-3}$

Notes:

4 independent molecules in the asymmetric unit. Largest residual peak in difference Fourier electron density map is at a chemically insignificantly distance from Zn1A.

Table 2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for pyrazole **2** and $ZnCl_2$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Zn(1)	1522(1)	3005(1)	4492(1)	34(1)
Cl(1)	184(1)	3211(1)	4892(1)	50(1)
Cl(2)	2821(1)	2998(1)	5450(1)	46(1)
N(1)	1540(2)	2451(1)	3607(1)	29(1)
N(2)	1582(2)	3462(1)	3500(1)	29(1)
N(3)	1565(2)	3963(1)	3307(1)	28(1)
C(1)	1583(2)	1943(1)	3708(2)	33(1)
C(2)	1606(2)	1608(1)	3074(2)	35(1)
C(3)	1577(2)	1804(1)	2309(2)	36(1)
C(4)	1545(2)	2325(1)	2197(2)	31(1)
C(5)	1536(2)	2641(1)	2854(2)	28(1)
C(6)	1536(2)	3202(1)	2806(2)	28(1)
C(7)	1503(2)	3539(1)	2163(2)	28(1)
C(8)	1528(2)	4027(1)	2493(2)	28(1)
C(9)	1500(2)	4522(1)	2074(2)	30(1)
C(10)	1826(2)	4980(1)	2452(2)	33(1)
C(11)	1761(2)	5432(1)	2013(2)	39(1)
C(12)	1394(3)	5430(2)	1191(2)	48(1)
C(13)	1097(3)	4974(2)	808(2)	54(1)
C(14)	1139(3)	4523(1)	1237(2)	40(1)
C(15)	1549(3)	4332(1)	3955(2)	40(1)
Zn(1A)	4005(1)	4683(1)	458(1)	33(1)
Cl(1A)	5541(1)	4459(1)	390(1)	36(1)
Cl(2A)	2798(1)	4447(1)	-528(1)	39(1)
N(1A)	4013(2)	5165(1)	1446(1)	28(1)
N(2A)	3841(2)	4157(1)	1413(1)	30(1)
N(3A)	3807(2)	3645(1)	1534(1)	30(1)
C(1A)	3987(2)	5677(1)	1428(2)	34(1)
C(2A)	4093(2)	5972(1)	2122(2)	35(1)
C(3A)	4237(2)	5729(1)	2866(2)	33(1)
C(4A)	4249(2)	5201(1)	2899(2)	29(1)
C(5A)	4122(2)	4929(1)	2177(2)	26(1)
C(6A)	4063(2)	4369(1)	2148(2)	28(1)
C(7A)	4171(2)	3997(1)	2750(2)	28(1)
C(8A)	4001(2)	3531(1)	2345(2)	28(1)
C(9A)	4034(2)	3014(1)	2690(2)	29(1)
C(10A)	4252(2)	2576(1)	2286(2)	32(1)
C(11A)	4301(2)	2101(1)	2655(2)	38(1)
C(12A)	4148(2)	2052(1)	3440(2)	40(1)
C(13A)	3941(2)	2482(1)	3847(2)	39(1)
C(14A)	3880(2)	2958(1)	3486(2)	34(1)
C(15A)	3457(3)	3320(1)	829(2)	40(1)
Zn(1B)	6478(1)	4369(1)	4600(1)	29(1)
Cl(1B)	5060(1)	4224(1)	4899(1)	43(1)

Cl(2B)	7730(1)	4325(1)	5602(1)	44(1)
N(1B)	6581(2)	4960(1)	3800(1)	26(1)
N(2B)	6571(2)	3955(1)	3576(1)	26(1)
N(3B)	6526(2)	3464(1)	3323(1)	25(1)
C(1B)	6628(2)	5462(1)	3950(2)	30(1)
C(2B)	6702(2)	5825(1)	3373(2)	34(1)
C(3B)	6710(2)	5660(1)	2593(2)	35(1)
C(4B)	6664(2)	5143(1)	2420(2)	29(1)
C(5B)	6613(2)	4800(1)	3037(2)	25(1)
C(6B)	6596(2)	4243(1)	2926(2)	25(1)
C(7B)	6582(2)	3941(1)	2252(2)	25(1)
C(8B)	6531(2)	3440(1)	2513(2)	24(1)
C(9B)	6462(2)	2964(1)	2032(2)	26(1)
C(10B)	6781(2)	2490(1)	2355(2)	27(1)
C(11B)	6654(2)	2060(1)	1863(2)	35(1)
C(12B)	6225(3)	2096(1)	1050(2)	38(1)
C(13B)	5945(3)	2567(1)	724(2)	38(1)
C(14B)	6064(2)	3000(1)	1200(2)	31(1)
C(15B)	6413(3)	3065(1)	3900(2)	37(1)
Zn(1C)	8769(1)	3081(1)	472(1)	34(1)
Cl(1C)	7528(1)	3147(1)	-539(1)	50(1)
Cl(2C)	10158(1)	3263(1)	124(1)	53(1)
N(1C)	8853(2)	2515(1)	1360(2)	30(1)
N(2C)	8725(2)	3519(1)	1490(1)	28(1)
N(3C)	8748(2)	4018(1)	1684(1)	28(1)
C(1C)	8811(2)	2007(1)	1261(2)	34(1)
C(2C)	8945(2)	1666(1)	1908(2)	36(1)
C(3C)	9139(2)	1859(1)	2690(2)	36(1)
C(4C)	9168(2)	2384(1)	2806(2)	30(1)
C(5C)	9014(2)	2701(1)	2128(2)	26(1)
C(6C)	8979(2)	3261(1)	2186(2)	27(1)
C(7C)	9155(2)	3596(1)	2837(2)	27(1)
C(8C)	9009(2)	4081(1)	2507(2)	27(1)
C(9C)	9111(2)	4574(1)	2925(2)	29(1)
C(10C)	9417(2)	5018(1)	2594(2)	33(1)
C(11C)	9545(2)	5470(1)	3039(2)	40(1)
C(12C)	9371(3)	5485(1)	3819(2)	45(1)
C(13C)	9067(2)	5046(1)	4155(2)	40(1)
C(14C)	8936(2)	4597(1)	3715(2)	32(1)
C(15C)	8418(3)	4386(1)	1042(2)	39(1)

Table 3 Bond lengths [Å] and angles [°] for pyrazole **2** and $ZnCl_2$

Zn(1)-N(2)	2.066(2)	Zn(1)-N(1)	2.081(2)
Zn(1)-Cl(2)	2.2012(9)	Zn(1)-Cl(1)	2.2124(10)
N(1)-C(1)	1.338(4)	N(1)-C(5)	1.359(4)
N(2)-C(6)	1.341(4)	N(2)-N(3)	1.349(3)
N(3)-C(8)	1.371(4)	N(3)-C(15)	1.459(4)
C(1)-C(2)	1.387(4)	C(2)-C(3)	1.379(4)
C(3)-C(4)	1.373(4)	C(4)-C(5)	1.384(4)
C(5)-C(6)	1.469(4)	C(6)-C(7)	1.389(4)

C(7)-C(8)	1.388(4)	C(8)-C(9)	1.470(4)
C(9)-C(10)	1.391(4)	C(9)-C(14)	1.399(4)
C(10)-C(11)	1.386(4)	C(11)-C(12)	1.379(5)
C(12)-C(13)	1.381(5)	C(13)-C(14)	1.378(5)
Zn(1A)-N(1A)	2.084(2)	Zn(1A)-N(2A)	2.162(2)
Zn(1A)-Cl(2A)	2.2261(9)	Zn(1A)-Cl(1A)	2.2932(9)
Zn(1A)-Cl(1A)#1	2.8025(9)	Cl(1A)-Zn(1A)#1	2.8026(9)
N(1A)-C(1A)	1.339(4)	N(1A)-C(5A)	1.358(4)
N(2A)-C(6A)	1.335(4)	N(2A)-N(3A)	1.356(3)
N(3A)-C(8A)	1.369(4)	N(3A)-C(15A)	1.465(4)
C(1A)-C(2A)	1.382(4)	C(2A)-C(3A)	1.380(4)
C(3A)-C(4A)	1.382(4)	C(4A)-C(5A)	1.389(4)
C(5A)-C(6A)	1.466(4)	C(6A)-C(7A)	1.390(4)
C(7A)-C(8A)	1.391(4)	C(8A)-C(9A)	1.469(4)
C(9A)-C(10A)	1.397(4)	C(9A)-C(14A)	1.408(4)
C(10A)-C(11A)	1.383(4)	C(11A)-C(12A)	1.386(5)
C(12A)-C(13A)	1.378(5)	C(13A)-C(14A)	1.379(4)
Zn(1B)-N(2B)	2.062(2)	Zn(1B)-N(1B)	2.072(2)
Zn(1B)-Cl(2B)	2.2002(9)	Zn(1B)-Cl(1B)	2.2107(9)
N(1B)-C(1B)	1.337(4)	N(1B)-C(5B)	1.359(3)
N(2B)-C(6B)	1.333(4)	N(2B)-N(3B)	1.349(3)
N(3B)-C(8B)	1.365(3)	N(3B)-C(15B)	1.457(4)
C(1B)-C(2B)	1.375(4)	C(2B)-C(3B)	1.383(4)
C(3B)-C(4B)	1.382(4)	C(4B)-C(5B)	1.384(4)
C(5B)-C(6B)	1.467(4)	C(6B)-C(7B)	1.379(4)
C(7B)-C(8B)	1.387(4)	C(8B)-C(9B)	1.475(4)
C(9B)-C(10B)	1.393(4)	C(9B)-C(14B)	1.406(4)
C(10B)-C(11B)	1.388(4)	C(11B)-C(12B)	1.385(5)
C(12B)-C(13B)	1.375(5)	C(13B)-C(14B)	1.376(4)
Zn(1C)-N(2C)	2.071(2)	Zn(1C)-N(1C)	2.089(3)
Zn(1C)-Cl(1C)	2.2032(9)	Zn(1C)-Cl(2C)	2.2259(10)
N(1C)-C(1C)	1.338(4)	N(1C)-C(5C)	1.355(4)
N(2C)-C(6C)	1.338(4)	N(2C)-N(3C)	1.344(3)
N(3C)-C(8C)	1.370(4)	N(3C)-C(15C)	1.453(4)
C(1C)-C(2C)	1.390(4)	C(2C)-C(3C)	1.385(5)
C(3C)-C(4C)	1.385(4)	C(4C)-C(5C)	1.392(4)
C(5C)-C(6C)	1.469(4)	C(6C)-C(7C)	1.387(4)
C(7C)-C(8C)	1.383(4)	C(8C)-C(9C)	1.463(4)
C(9C)-C(10C)	1.393(4)	C(9C)-C(14C)	1.400(4)
C(10C)-C(11C)	1.393(4)	C(11C)-C(12C)	1.385(5)
C(12C)-C(13C)	1.386(5)	C(13C)-C(14C)	1.379(4)
N(2)-Zn(1)-N(1)	79.45(10)	N(2)-Zn(1)-Cl(2)	115.60(8)
N(1)-Zn(1)-Cl(2)	112.91(7)	N(2)-Zn(1)-Cl(1)	106.41(7)
N(1)-Zn(1)-Cl(1)	121.40(8)	Cl(2)-Zn(1)-Cl(1)	115.48(4)
C(1)-N(1)-C(5)	118.3(3)	C(1)-N(1)-Zn(1)	127.3(2)
C(5)-N(1)-Zn(1)	114.4(2)	C(6)-N(2)-N(3)	106.6(2)
C(6)-N(2)-Zn(1)	114.0(2)	N(3)-N(2)-Zn(1)	138.94(19)
N(2)-N(3)-C(8)	110.7(2)	N(2)-N(3)-C(15)	117.7(2)
C(8)-N(3)-C(15)	131.5(3)	N(1)-C(1)-C(2)	122.5(3)
C(3)-C(2)-C(1)	118.8(3)	C(4)-C(3)-C(2)	119.5(3)
C(3)-C(4)-C(5)	119.2(3)	N(1)-C(5)-C(4)	121.8(3)
N(1)-C(5)-C(6)	114.6(3)	C(4)-C(5)-C(6)	123.6(3)

N(2)-C(6)-C(7)	110.2(3)	N(2)-C(6)-C(5)	117.3(3)
C(7)-C(6)-C(5)	132.5(3)	C(8)-C(7)-C(6)	106.0(3)
N(3)-C(8)-C(7)	106.3(3)	N(3)-C(8)-C(9)	125.3(3)
C(7)-C(8)-C(9)	128.4(3)	C(10)-C(9)-C(14)	118.8(3)
C(10)-C(9)-C(8)	124.3(3)	C(14)-C(9)-C(8)	116.9(3)
C(11)-C(10)-C(9)	120.5(3)	C(12)-C(11)-C(10)	120.3(3)
C(11)-C(12)-C(13)	119.3(3)	C(14)-C(13)-C(12)	121.2(3)
C(13)-C(14)-C(9)	119.8(3)	N(1A)-Zn(1A)-N(2A)	77.08(9)
N(1A)-Zn(1A)-Cl(2A)	130.00(7)	N(2A)-Zn(1A)-Cl(2A)	101.27(7)
N(1A)-Zn(1A)-Cl(1A)	109.91(7)	N(2A)-Zn(1A)-Cl(1A)	96.89(7)
Cl(2A)-Zn(1A)-Cl(1A)	119.76(3)	N(1A)-Zn(1A)-Cl(1A)#1	87.49(7)
N(2A)-Zn(1A)-Cl(1A)#1	163.17(7)	Cl(2A)-Zn(1A)-Cl(1A)#1	93.76(3)
Cl(1A)-Zn(1A)-Cl(1A)#1	81.93(3)	Zn(1A)-Cl(1A)-Zn(1A)#1	98.06(3)
C(1A)-N(1A)-C(5A)	118.3(3)	C(1A)-N(1A)-Zn(1A)	126.2(2)
C(5A)-N(1A)-Zn(1A)	115.3(2)	C(6A)-N(2A)-N(3A)	106.1(2)
C(6A)-N(2A)-Zn(1A)	112.6(2)	N(3A)-N(2A)-Zn(1A)	138.77(18)
N(2A)-N(3A)-C(8A)	111.0(2)	N(2A)-N(3A)-C(15A)	117.9(2)
C(8A)-N(3A)-C(15A)	130.5(3)	N(1A)-C(1A)-C(2A)	122.6(3)
C(3A)-C(2A)-C(1A)	118.8(3)	C(2A)-C(3A)-C(4A)	119.6(3)
C(3A)-C(4A)-C(5A)	118.6(3)	N(1A)-C(5A)-C(4A)	122.0(3)
N(1A)-C(5A)-C(6A)	115.5(2)	C(4A)-C(5A)-C(6A)	122.5(3)
N(2A)-C(6A)-C(7A)	110.9(3)	N(2A)-C(6A)-C(5A)	116.4(3)
C(7A)-C(6A)-C(5A)	132.7(3)	C(6A)-C(7A)-C(8A)	105.8(3)
N(3A)-C(8A)-C(7A)	106.2(3)	N(3A)-C(8A)-C(9A)	125.3(3)
C(7A)-C(8A)-C(9A)	128.6(3)	C(10A)-C(9A)-C(14A)	118.0(3)
C(10A)-C(9A)-C(8A)	123.8(3)	C(14A)-C(9A)-C(8A)	118.2(3)
C(11A)-C(10A)-C(9A)	120.8(3)	C(10A)-C(11A)-C(12A)	120.5(3)
C(13A)-C(12A)-C(11A)	119.3(3)	C(12A)-C(13A)-C(14A)	121.1(3)
C(13A)-C(14A)-C(9A)	120.4(3)	N(2B)-Zn(1B)-N(1B)	79.84(9)
N(2B)-Zn(1B)-Cl(2B)	115.82(7)	N(1B)-Zn(1B)-Cl(2B)	112.65(7)
N(2B)-Zn(1B)-Cl(1B)	108.29(7)	N(1B)-Zn(1B)-Cl(1B)	117.44(7)
Cl(2B)-Zn(1B)-Cl(1B)	117.15(4)	C(1B)-N(1B)-C(5B)	118.0(3)
C(1B)-N(1B)-Zn(1B)	128.2(2)	C(5B)-N(1B)-Zn(1B)	113.86(19)

C(6B)-N(2B)-N(3B)	106.6(2)	C(6B)-N(2B)-Zn(1B)	113.92(19)
N(3B)-N(2B)-Zn(1B)	139.10(18)	N(2B)-N(3B)-C(8B)	110.5(2)
N(2B)-N(3B)-C(15B)	118.4(2)	C(8B)-N(3B)-C(15B)	130.9(2)
N(1B)-C(1B)-C(2B)	123.6(3)	C(1B)-C(2B)-C(3B)	118.1(3)
C(4B)-C(3B)-C(2B)	119.6(3)	C(3B)-C(4B)-C(5B)	118.9(3)
N(1B)-C(5B)-C(4B)	121.7(3)	N(1B)-C(5B)-C(6B)	115.0(2)
C(4B)-C(5B)-C(6B)	123.3(3)	N(2B)-C(6B)-C(7B)	110.6(3)
N(2B)-C(6B)-C(5B)	117.3(2)	C(7B)-C(6B)-C(5B)	132.1(3)
C(6B)-C(7B)-C(8B)	105.9(2)	N(3B)-C(8B)-C(7B)	106.4(2)
N(3B)-C(8B)-C(9B)	125.0(3)	C(7B)-C(8B)-C(9B)	128.6(3)
C(10B)-C(9B)-C(14B)	118.8(3)	C(10B)-C(9B)-C(8B)	123.7(3)
C(14B)-C(9B)-C(8B)	117.4(3)	C(11B)-C(10B)-C(9B)	119.7(3)
C(12B)-C(11B)-C(10B)	120.8(3)	C(13B)-C(12B)-C(11B)	119.5(3)
C(12B)-C(13B)-C(14B)	120.7(3)	C(13B)-C(14B)-C(9B)	120.3(3)
N(2C)-Zn(1C)-N(1C)	78.90(10)	N(2C)-Zn(1C)-Cl(1C)	116.30(8)
N(1C)-Zn(1C)-Cl(1C)	122.03(7)	N(2C)-Zn(1C)-Cl(2C)	105.88(7)
N(1C)-Zn(1C)-Cl(2C)	114.33(8)	Cl(1C)-Zn(1C)-Cl(2C)	113.61(4)
C(1C)-N(1C)-C(5C)	118.0(3)	C(1C)-N(1C)-Zn(1C)	128.3(2)
C(5C)-N(1C)-Zn(1C)	113.7(2)	C(6C)-N(2C)-N(3C)	106.7(2)
C(6C)-N(2C)-Zn(1C)	113.4(2)	N(3C)-N(2C)-Zn(1C)	137.31(19)
N(2C)-N(3C)-C(8C)	110.5(2)	N(2C)-N(3C)-C(15C)	118.2(2)
C(8C)-N(3C)-C(15C)	130.9(3)	N(1C)-C(1C)-C(2C)	122.9(3)
C(3C)-C(2C)-C(1C)	118.7(3)	C(2C)-C(3C)-C(4C)	119.3(3)
C(3C)-C(4C)-C(5C)	118.6(3)	N(1C)-C(5C)-C(4C)	122.4(3)
N(1C)-C(5C)-C(6C)	114.8(3)	C(4C)-C(5C)-C(6C)	122.7(3)
N(2C)-C(6C)-C(7C)	110.4(3)	N(2C)-C(6C)-C(5C)	116.8(3)
C(7C)-C(6C)-C(5C)	132.8(3)	C(8C)-C(7C)-C(6C)	105.8(3)
N(3C)-C(8C)-C(7C)	106.6(3)	N(3C)-C(8C)-C(9C)	124.9(3)
C(7C)-C(8C)-C(9C)	128.5(3)	C(10C)-C(9C)-C(14C)	118.2(3)
C(10C)-C(9C)-C(8C)	123.4(3)	C(14C)-C(9C)-C(8C)	118.3(3)
C(11C)-C(10C)-C(9C)	120.6(3)	C(12C)-C(11C)-C(10C)	120.3(3)
C(11C)-C(12C)-C(13C)	119.5(3)	C(14C)-C(13C)-C(12C)	120.4(3)
C(13C)-C(14C)-C(9C)	121.0(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

Table 4 Anisotropic displacement parameters ($Å^2$ x 10^3) for pyrazole **2** and $ZnCl_2$. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Zn(1)	43(1)	39(1)	20(1)	2(1)	6(1)	12(1)
Cl(1)	59(1)	58(1)	40(1)	10(1)	27(1)	15(1)
Cl(2)	61(1)	44(1)	27(1)	-4(1)	-7(1)	11(1)
N(1)	26(1)	34(2)	26(1)	1(1)	5(1)	4(1)
N(2)	32(2)	34(2)	22(1)	0(1)	5(1)	6(1)
N(3)	30(2)	31(1)	23(1)	2(1)	4(1)	5(1)
C(1)	24(2)	42(2)	32(2)	5(1)	6(1)	0(1)
C(2)	31(2)	33(2)	43(2)	1(2)	11(2)	1(1)
C(3)	37(2)	36(2)	36(2)	-8(2)	10(2)	-2(2)
C(4)	31(2)	40(2)	23(2)	0(1)	6(1)	1(1)
C(5)	23(2)	36(2)	23(1)	1(1)	5(1)	1(1)
C(6)	24(2)	35(2)	24(2)	-2(1)	6(1)	1(1)
C(7)	25(2)	40(2)	20(1)	-1(1)	5(1)	2(1)
C(8)	22(2)	37(2)	23(1)	-2(1)	3(1)	2(1)
C(9)	22(2)	41(2)	27(2)	4(1)	7(1)	2(1)
C(10)	27(2)	42(2)	30(2)	-3(1)	6(1)	0(1)
C(11)	35(2)	38(2)	45(2)	1(2)	15(2)	-4(2)
C(12)	58(3)	42(2)	48(2)	10(2)	17(2)	-2(2)
C(13)	72(3)	54(2)	32(2)	11(2)	6(2)	-6(2)
C(14)	50(2)	41(2)	28(2)	3(2)	5(2)	-5(2)
C(15)	57(2)	37(2)	27(2)	-4(1)	8(2)	6(2)
Zn(1A)	35(1)	41(1)	21(1)	-5(1)	2(1)	7(1)
Cl(1A)	40(1)	42(1)	27(1)	8(1)	10(1)	12(1)
Cl(2A)	45(1)	42(1)	25(1)	2(1)	-4(1)	-5(1)
N(1A)	29(1)	35(2)	20(1)	-1(1)	6(1)	4(1)
N(2A)	35(2)	30(2)	23(1)	-2(1)	4(1)	3(1)
N(3A)	33(2)	31(2)	24(1)	-2(1)	2(1)	2(1)
C(1A)	41(2)	34(2)	28(2)	4(1)	9(1)	5(2)
C(2A)	38(2)	34(2)	34(2)	0(1)	10(2)	1(2)
C(3A)	34(2)	36(2)	27(2)	-8(1)	5(1)	-1(1)
C(4A)	28(2)	36(2)	21(1)	1(1)	6(1)	2(1)
C(5A)	22(2)	36(2)	22(1)	-1(1)	5(1)	3(1)
C(6A)	23(2)	37(2)	23(1)	-1(1)	5(1)	1(1)
C(7A)	24(2)	36(2)	23(1)	0(1)	5(1)	3(1)
C(8A)	22(2)	36(2)	26(2)	-1(1)	2(1)	1(1)
C(9A)	18(2)	36(2)	32(2)	-1(1)	0(1)	-2(1)
C(10A)	26(2)	37(2)	32(2)	-2(1)	5(1)	-2(1)
C(11A)	30(2)	39(2)	45(2)	-4(2)	4(2)	0(2)
C(12A)	30(2)	40(2)	49(2)	8(2)	3(2)	-3(2)
C(13A)	31(2)	52(2)	33(2)	7(2)	4(1)	-2(2)
C(14A)	28(2)	41(2)	32(2)	-1(1)	6(1)	2(1)
C(15A)	52(2)	34(2)	30(2)	-7(1)	-6(2)	2(2)
Zn(1B)	33(1)	35(1)	18(1)	0(1)	3(1)	-1(1)
Cl(1B)	41(1)	63(1)	28(1)	-4(1)	13(1)	-6(1)
Cl(2B)	49(1)	47(1)	29(1)	1(1)	-11(1)	1(1)

N(1B)	23(1)	30(1)	23(1)	0(1)	3(1)	-1(1)
N(2B)	28(1)	27(1)	21(1)	2(1)	3(1)	-2(1)
N(3B)	27(1)	28(1)	20(1)	1(1)	4(1)	-1(1)
C(1B)	22(2)	37(2)	30(2)	-4(1)	3(1)	2(1)
C(2B)	32(2)	27(2)	42(2)	-3(1)	6(2)	0(1)
C(3B)	35(2)	30(2)	41(2)	5(1)	11(2)	0(1)
C(4B)	28(2)	35(2)	26(2)	2(1)	8(1)	-1(1)
C(5B)	21(2)	31(2)	23(1)	-3(1)	5(1)	0(1)
C(6B)	22(2)	33(2)	21(1)	3(1)	5(1)	0(1)
C(7B)	24(2)	31(2)	20(1)	2(1)	5(1)	1(1)
C(8B)	21(2)	30(2)	21(1)	0(1)	5(1)	-1(1)
C(9B)	22(2)	35(2)	24(2)	1(1)	10(1)	-2(1)
C(10B)	21(2)	33(2)	28(2)	1(1)	7(1)	-2(1)
C(11B)	34(2)	32(2)	42(2)	1(1)	18(2)	-2(1)
C(12B)	46(2)	34(2)	37(2)	-9(2)	19(2)	-7(2)
C(13B)	47(2)	47(2)	21(2)	-6(1)	8(2)	-1(2)
C(14B)	35(2)	34(2)	25(2)	1(1)	9(1)	1(1)
C(15B)	53(2)	33(2)	26(2)	5(1)	10(2)	-1(2)
Zn(1C)	40(1)	40(1)	23(1)	-4(1)	8(1)	-12(1)
Cl(1C)	60(1)	52(1)	31(1)	1(1)	-5(1)	-12(1)
Cl(2C)	56(1)	66(1)	45(1)	-16(1)	28(1)	-22(1)
N(1C)	27(1)	33(2)	30(1)	-5(1)	9(1)	-5(1)
N(2C)	30(1)	30(1)	26(1)	1(1)	8(1)	-3(1)
N(3C)	28(1)	31(1)	26(1)	2(1)	4(1)	-3(1)
C(1C)	30(2)	37(2)	38(2)	-7(2)	12(1)	-4(1)
C(2C)	31(2)	28(2)	49(2)	-4(2)	9(2)	1(1)
C(3C)	29(2)	35(2)	42(2)	4(2)	4(2)	0(1)
C(4C)	28(2)	35(2)	29(2)	-2(1)	6(1)	-2(1)
C(5C)	21(2)	32(2)	27(2)	-2(1)	6(1)	-4(1)
C(6C)	24(2)	33(2)	25(2)	1(1)	7(1)	-2(1)
C(7C)	24(2)	34(2)	24(2)	-1(1)	7(1)	-1(1)
C(8C)	22(2)	33(2)	26(2)	-1(1)	6(1)	-2(1)
C(9C)	18(2)	32(2)	35(2)	-2(1)	2(1)	2(1)
C(10C)	24(2)	34(2)	40(2)	0(2)	4(1)	2(1)
C(11C)	32(2)	32(2)	55(2)	-1(2)	3(2)	-1(1)
C(12C)	36(2)	34(2)	58(2)	-17(2)	-2(2)	3(2)
C(13C)	33(2)	47(2)	37(2)	-12(2)	1(2)	5(2)
C(14C)	24(2)	36(2)	35(2)	-6(1)	3(1)	0(1)
C(15C)	43(2)	38(2)	33(2)	9(2)	2(2)	0(2)

Table 5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for pyrazole **2** and $ZnCl_2$

Atom	x	y	z	U(eq)
H(1)	1597	1808	4235	39
H(2)	1642	1249	3165	42
H(3)	1578	1582	1863	43
H(4)	1528	2466	1674	38
H(7)	1470	3453	1609	34
H(10)	2096	4983	3016	39
H(11)	1971	5743	2280	46
H(12)	1346	5740	890	58
H(13)	860	4971	239	64
H(14)	922	4214	966	48
H(15A)	1287	4169	4388	61
H(15B)	1147	4624	3738	61
H(15C)	2201	4451	4172	61
H(1A)	3891	5845	917	41
H(2A)	4067	6334	2089	42
H(3A)	4328	5924	3352	39
H(4A)	4342	5028	3406	34
H(7A)	4328	4049	3320	33
H(10A)	4367	2604	1751	38
H(11A)	4440	1807	2369	46
H(12A)	4185	1726	3693	48
H(13A)	3839	2450	4386	47
H(14A)	3733	3249	3776	40
H(15D)	4002	3174	633	60
H(15E)	3069	3525	397	60
H(15F)	3066	3043	984	60
H(1B)	6609	5575	4483	36
H(2B)	6746	6178	3506	41
H(3B)	6747	5901	2178	41
H(4B)	6666	5024	1887	35
H(7B)	6602	4052	1718	30
H(10B)	7085	2462	2910	33
H(11B)	6864	1736	2086	42
H(12B)	6124	1798	721	45
H(13B)	5667	2595	163	46
H(14B)	5876	3324	965	37
H(15G)	7044	2934	4159	55
H(15H)	6028	2785	3615	55
H(15I)	6091	3206	4315	55
H(1C)	8683	1873	725	41
H(2C)	8904	1307	1815	43
H(3C)	9252	1634	3143	43
H(4C)	9290	2524	3337	37
H(7C)	9338	3510	3396	33
H(10C)	9540	5011	2059	40
H(11C)	9753	5770	2805	48

H(12C)	9460	5794	4123	53
H(13C)	8947	5054	4690	48
H(14C)	8725	4300	3951	38
H(15J)	8960	4499	808	58
H(15K)	8135	4681	1265	58
H(15L)	7936	4225	619	58

Table 6 Dihedral angles [^{o}] for pyrazole **2** and $ZnCl_2$

Atom1 - Atom2 - Atom3 - Atom4	Dihedral
N(2) - Zn(1) - N(1) - C(1)	175.1(3)
Cl(2) - Zn(1) - N(1) - C(1)	61.6(3)
Cl(1) - Zn(1) - N(1) - C(1)	-82.1(3)
N(2) - Zn(1) - N(1) - C(5)	-2.8(2)
Cl(2) - Zn(1) - N(1) - C(5)	-116.25(19)
Cl(1) - Zn(1) - N(1) - C(5)	100.1(2)
N(1) - Zn(1) - N(2) - C(6)	4.3(2)
Cl(2) - Zn(1) - N(2) - C(6)	114.8(2)
Cl(1) - Zn(1) - N(2) - C(6)	-115.5(2)
N(1) - Zn(1) - N(2) - N(3)	176.1(3)
Cl(2) - Zn(1) - N(2) - N(3)	-73.4(3)
Cl(1) - Zn(1) - N(2) - N(3)	56.3(3)
C(6) - N(2) - N(3) - C(8)	-1.2(3)
Zn(1) - N(2) - N(3) - C(8)	-173.4(2)
C(6) - N(2) - N(3) - C(15)	176.3(3)
Zn(1) - N(2) - N(3) - C(15)	4.1(4)
C(5) - N(1) - C(1) - C(2)	-1.2(4)
Zn(1) - N(1) - C(1) - C(2)	-178.9(2)
N(1) - C(1) - C(2) - C(3)	-0.5(5)
C(1) - C(2) - C(3) - C(4)	1.3(5)
C(2) - C(3) - C(4) - C(5)	-0.4(5)
C(1) - N(1) - C(5) - C(4)	2.1(4)
Zn(1) - N(1) - C(5) - C(4)	-179.8(2)
C(1) - N(1) - C(5) - C(6)	-177.1(3)
Zn(1) - N(1) - C(5) - C(6)	0.9(3)
C(3) - C(4) - C(5) - N(1)	-1.4(5)
C(3) - C(4) - C(5) - C(6)	177.8(3)
N(3) - N(2) - C(6) - C(7)	0.8(3)
Zn(1) - N(2) - C(6) - C(7)	175.2(2)
N(3) - N(2) - C(6) - C(5)	-179.6(2)
Zn(1) - N(2) - C(6) - C(5)	-5.2(3)
N(1) - C(5) - C(6) - N(2)	2.9(4)
C(4) - C(5) - C(6) - N(2)	-176.4(3)
N(1) - C(5) - C(6) - C(7)	-177.6(3)
C(4) - C(5) - C(6) - C(7)	3.1(5)
N(2) - C(6) - C(7) - C(8)	-0.2(3)
C(5) - C(6) - C(7) - C(8)	-179.7(3)
N(2) - N(3) - C(8) - C(7)	1.1(3)
C(15) - N(3) - C(8) - C(7)	-176.0(3)
N(2) - N(3) - C(8) - C(9)	179.9(3)

C(15) - N(3) - C(8) - C(9)	2.9(5)
C(6) - C(7) - C(8) - N(3)	-0.5(3)
C(6) - C(7) - C(8) - C(9)	-179.3(3)
N(3) - C(8) - C(9) - C(10)	22.9(5)
C(7) - C(8) - C(9) - C(10)	-158.6(3)
N(3) - C(8) - C(9) - C(14)	-158.5(3)
C(7) - C(8) - C(9) - C(14)	20.0(5)
C(14) - C(9) - C(10) - C(11)	2.3(5)
C(8) - C(9) - C(10) - C(11)	-179.1(3)
C(9) - C(10) - C(11) - C(12)	-1.6(5)
C(10) - C(11) - C(12) - C(13)	-0.4(6)
C(11) - C(12) - C(13) - C(14)	1.7(6)
C(12) - C(13) - C(14) - C(9)	-1.0(6)
C(10) - C(9) - C(14) - C(13)	-1.0(5)
C(8) - C(9) - C(14) - C(13)	-179.7(3)
N(1A) - Zn(1A) - Cl(1A) - Zn(1A)#1	-84.35(8)
N(2A) - Zn(1A) - Cl(1A) - Zn(1A)#1	-163.07(7)
Cl(2A) - Zn(1A) - Cl(1A) - Zn(1A)#1	89.73(4)
Cl(1A)#1 - Zn(1A) - Cl(1A) - Zn(1A)#1	0.0
N(2A) - Zn(1A) - N(1A) - C(1A)	-171.5(3)
Cl(2A) - Zn(1A) - N(1A) - C(1A)	-77.5(3)
Cl(1A) - Zn(1A) - N(1A) - C(1A)	95.8(3)
Cl(1A)#1 - Zn(1A) - N(1A) - C(1A)	15.3(3)
N(2A) - Zn(1A) - N(1A) - C(5A)	13.3(2)
Cl(2A) - Zn(1A) - N(1A) - C(5A)	107.2(2)
Cl(1A) - Zn(1A) - N(1A) - C(5A)	-79.5(2)
Cl(1A)#1 - Zn(1A) - N(1A) - C(5A)	-160.0(2)
N(1A) - Zn(1A) - N(2A) - C(6A)	-15.6(2)
Cl(2A) - Zn(1A) - N(2A) - C(6A)	-144.4(2)
Cl(1A) - Zn(1A) - N(2A) - C(6A)	93.3(2)
Cl(1A)#1 - Zn(1A) - N(2A) - C(6A)	8.4(4)
N(1A) - Zn(1A) - N(2A) - N(3A)	-174.4(3)
Cl(2A) - Zn(1A) - N(2A) - N(3A)	56.8(3)
Cl(1A) - Zn(1A) - N(2A) - N(3A)	-65.5(3)
Cl(1A)#1 - Zn(1A) - N(2A) - N(3A)	-150.4(2)
C(6A) - N(2A) - N(3A) - C(8A)	0.3(3)
Zn(1A) - N(2A) - N(3A) - C(8A)	160.0(2)
C(6A) - N(2A) - N(3A) - C(15A)	172.4(3)
Zn(1A) - N(2A) - N(3A) - C(15A)	-27.9(4)
C(5A) - N(1A) - C(1A) - C(2A)	1.9(5)
Zn(1A) - N(1A) - C(1A) - C(2A)	-173.2(2)
N(1A) - C(1A) - C(2A) - C(3A)	0.3(5)
C(1A) - C(2A) - C(3A) - C(4A)	-1.6(5)
C(2A) - C(3A) - C(4A) - C(5A)	0.5(5)
C(1A) - N(1A) - C(5A) - C(4A)	-3.0(4)
Zn(1A) - N(1A) - C(5A) - C(4A)	172.6(2)
C(1A) - N(1A) - C(5A) - C(6A)	175.0(3)
Zn(1A) - N(1A) - C(5A) - C(6A)	-9.4(3)
C(3A) - C(4A) - C(5A) - N(1A)	1.8(4)
C(3A) - C(4A) - C(5A) - C(6A)	-176.0(3)
N(3A) - N(2A) - C(6A) - C(7A)	-0.2(3)
Zn(1A) - N(2A) - C(6A) - C(7A)	-165.8(2)
N(3A) - N(2A) - C(6A) - C(5A)	-178.6(2)

Zn(1A) - N(2A) - C(6A) - C(5A)	15.7(3)
N(1A) - C(5A) - C(6A) - N(2A)	-4.8(4)
C(4A) - C(5A) - C(6A) - N(2A)	173.2(3)
N(1A) - C(5A) - C(6A) - C(7A)	177.2(3)
C(4A) - C(5A) - C(6A) - C(7A)	-4.8(5)
N(2A) - C(6A) - C(7A) - C(8A)	0.0(3)
C(5A) - C(6A) - C(7A) - C(8A)	178.1(3)
N(2A) - N(3A) - C(8A) - C(7A)	-0.4(3)
C(15A) - N(3A) - C(8A) - C(7A)	-171.1(3)
N(2A) - N(3A) - C(8A) - C(9A)	-179.3(3)
C(15A) - N(3A) - C(8A) - C(9A)	10.0(5)
C(6A) - C(7A) - C(8A) - N(3A)	0.2(3)
C(6A) - C(7A) - C(8A) - C(9A)	179.1(3)
N(3A) - C(8A) - C(9A) - C(10A)	26.7(5)
C(7A) - C(8A) - C(9A) - C(10A)	-152.0(3)
N(3A) - C(8A) - C(9A) - C(14A)	-156.3(3)
C(7A) - C(8A) - C(9A) - C(14A)	25.1(5)
C(14A) - C(9A) - C(10A) - C(11A)	0.9(4)
C(8A) - C(9A) - C(10A) - C(11A)	177.9(3)
C(9A) - C(10A) - C(11A) - C(12A)	-0.9(5)
C(10A) - C(11A) - C(12A) - C(13A)	0.3(5)
C(11A) - C(12A) - C(13A) - C(14A)	0.3(5)
C(12A) - C(13A) - C(14A) - C(9A)	-0.3(5)
C(10A) - C(9A) - C(14A) - C(13A)	-0.2(4)
C(8A) - C(9A) - C(14A) - C(13A)	-177.5(3)
N(2B) - Zn(1B) - N(1B) - C(1B)	-176.6(3)
Cl(2B) - Zn(1B) - N(1B) - C(1B)	-62.7(3)
Cl(1B) - Zn(1B) - N(1B) - C(1B)	78.0(2)
N(2B) - Zn(1B) - N(1B) - C(5B)	2.60(19)
Cl(2B) - Zn(1B) - N(1B) - C(5B)	116.47(18)
Cl(1B) - Zn(1B) - N(1B) - C(5B)	-102.84(19)
N(1B) - Zn(1B) - N(2B) - C(6B)	-3.3(2)
Cl(2B) - Zn(1B) - N(2B) - C(6B)	-113.66(19)
Cl(1B) - Zn(1B) - N(2B) - C(6B)	112.41(19)
N(1B) - Zn(1B) - N(2B) - N(3B)	-175.1(3)
Cl(2B) - Zn(1B) - N(2B) - N(3B)	74.5(3)
Cl(1B) - Zn(1B) - N(2B) - N(3B)	-59.4(3)
C(6B) - N(2B) - N(3B) - C(8B)	0.6(3)
Zn(1B) - N(2B) - N(3B) - C(8B)	172.7(2)
C(6B) - N(2B) - N(3B) - C(15B)	-175.2(3)
Zn(1B) - N(2B) - N(3B) - C(15B)	-3.0(4)
C(5B) - N(1B) - C(1B) - C(2B)	0.4(4)
Zn(1B) - N(1B) - C(1B) - C(2B)	179.5(2)
N(1B) - C(1B) - C(2B) - C(3B)	1.2(5)
C(1B) - C(2B) - C(3B) - C(4B)	-1.3(5)
C(2B) - C(3B) - C(4B) - C(5B)	-0.2(5)
C(1B) - N(1B) - C(5B) - C(4B)	-2.0(4)
Zn(1B) - N(1B) - C(5B) - C(4B)	178.7(2)
C(1B) - N(1B) - C(5B) - C(6B)	177.7(3)
Zn(1B) - N(1B) - C(5B) - C(6B)	-1.6(3)
C(3B) - C(4B) - C(5B) - N(1B)	1.9(4)
C(3B) - C(4B) - C(5B) - C(6B)	-177.8(3)
N(3B) - N(2B) - C(6B) - C(7B)	-0.9(3)

Zn(1B) - N(2B) - C(6B) - C(7B)	-175.26(19)
N(3B) - N(2B) - C(6B) - C(5B)	177.9(2)
Zn(1B) - N(2B) - C(6B) - C(5B)	3.5(3)
N(1B) - C(5B) - C(6B) - N(2B)	-1.3(4)
C(4B) - C(5B) - C(6B) - N(2B)	178.4(3)
N(1B) - C(5B) - C(6B) - C(7B)	177.1(3)
C(4B) - C(5B) - C(6B) - C(7B)	-3.2(5)
N(2B) - C(6B) - C(7B) - C(8B)	0.8(3)
C(5B) - C(6B) - C(7B) - C(8B)	-177.7(3)
N(2B) - N(3B) - C(8B) - C(7B)	0.0(3)
C(15B) - N(3B) - C(8B) - C(7B)	175.0(3)
N(2B) - N(3B) - C(8B) - C(9B)	-178.2(3)
C(15B) - N(3B) - C(8B) - C(9B)	-3.1(5)
C(6B) - C(7B) - C(8B) - N(3B)	-0.5(3)
C(6B) - C(7B) - C(8B) - C(9B)	177.6(3)
N(3B) - C(8B) - C(9B) - C(10B)	-28.5(4)
C(7B) - C(8B) - C(9B) - C(10B)	153.8(3)
N(3B) - C(8B) - C(9B) - C(14B)	152.6(3)
C(7B) - C(8B) - C(9B) - C(14B)	-25.1(4)
C(14B) - C(9B) - C(10B) - C(11B)	-3.5(4)
C(8B) - C(9B) - C(10B) - C(11B)	177.6(3)
C(9B) - C(10B) - C(11B) - C(12B)	0.9(5)
C(10B) - C(11B) - C(12B) - C(13B)	1.8(5)
C(11B) - C(12B) - C(13B) - C(14B)	-1.8(5)
C(12B) - C(13B) - C(14B) - C(9B)	-0.9(5)
C(10B) - C(9B) - C(14B) - C(13B)	3.5(5)
C(8B) - C(9B) - C(14B) - C(13B)	-177.5(3)
N(2C) - Zn(1C) - N(1C) - C(1C)	171.8(3)
Cl(1C) - Zn(1C) - N(1C) - C(1C)	57.6(3)
Cl(2C) - Zn(1C) - N(1C) - C(1C)	-85.6(3)
N(2C) - Zn(1C) - N(1C) - C(5C)	-11.3(2)
Cl(1C) - Zn(1C) - N(1C) - C(5C)	-125.54(19)
Cl(2C) - Zn(1C) - N(1C) - C(5C)	91.2(2)
N(1C) - Zn(1C) - N(2C) - C(6C)	14.0(2)
Cl(1C) - Zn(1C) - N(2C) - C(6C)	134.34(19)
Cl(2C) - Zn(1C) - N(2C) - C(6C)	-98.4(2)
N(1C) - Zn(1C) - N(2C) - N(3C)	172.6(3)
Cl(1C) - Zn(1C) - N(2C) - N(3C)	-67.0(3)
Cl(2C) - Zn(1C) - N(2C) - N(3C)	60.2(3)
C(6C) - N(2C) - N(3C) - C(8C)	-0.5(3)
Zn(1C) - N(2C) - N(3C) - C(8C)	-160.0(2)
C(6C) - N(2C) - N(3C) - C(15C)	-174.6(3)
Zn(1C) - N(2C) - N(3C) - C(15C)	25.8(4)
C(5C) - N(1C) - C(1C) - C(2C)	-1.5(5)
Zn(1C) - N(1C) - C(1C) - C(2C)	175.2(2)
N(1C) - C(1C) - C(2C) - C(3C)	-0.5(5)
C(1C) - C(2C) - C(3C) - C(4C)	1.8(5)
C(2C) - C(3C) - C(4C) - C(5C)	-1.0(5)
C(1C) - N(1C) - C(5C) - C(4C)	2.4(4)
Zn(1C) - N(1C) - C(5C) - C(4C)	-174.8(2)
C(1C) - N(1C) - C(5C) - C(6C)	-175.6(3)
Zn(1C) - N(1C) - C(5C) - C(6C)	7.2(3)
C(3C) - C(4C) - C(5C) - N(1C)	-1.1(4)

C(3C) - C(4C) - C(5C) - C(6C)	176.7(3)
N(3C) - N(2C) - C(6C) - C(7C)	0.8(3)
Zn(1C) - N(2C) - C(6C) - C(7C)	165.9(2)
N(3C) - N(2C) - C(6C) - C(5C)	-179.6(2)
Zn(1C) - N(2C) - C(6C) - C(5C)	-14.6(3)
N(1C) - C(5C) - C(6C) - N(2C)	4.9(4)
C(4C) - C(5C) - C(6C) - N(2C)	-173.1(3)
N(1C) - C(5C) - C(6C) - C(7C)	-175.6(3)
C(4C) - C(5C) - C(6C) - C(7C)	6.4(5)
N(2C) - C(6C) - C(7C) - C(8C)	-0.8(3)
C(5C) - C(6C) - C(7C) - C(8C)	179.7(3)
N(2C) - N(3C) - C(8C) - C(7C)	0.0(3)
C(15C) - N(3C) - C(8C) - C(7C)	173.1(3)
N(2C) - N(3C) - C(8C) - C(9C)	179.5(3)
C(15C) - N(3C) - C(8C) - C(9C)	-7.3(5)
C(6C) - C(7C) - C(8C) - N(3C)	0.5(3)
C(6C) - C(7C) - C(8C) - C(9C)	-179.0(3)
N(3C) - C(8C) - C(9C) - C(10C)	-32.7(5)
C(7C) - C(8C) - C(9C) - C(10C)	146.7(3)
N(3C) - C(8C) - C(9C) - C(14C)	150.4(3)
C(7C) - C(8C) - C(9C) - C(14C)	-30.1(5)
C(14C) - C(9C) - C(10C) - C(11C)	0.0(4)
C(8C) - C(9C) - C(10C) - C(11C)	-176.8(3)
C(9C) - C(10C) - C(11C) - C(12C)	0.2(5)
C(10C) - C(11C) - C(12C) - C(13C)	-0.2(5)
C(11C) - C(12C) - C(13C) - C(14C)	0.0(5)
C(12C) - C(13C) - C(14C) - C(9C)	0.2(5)
C(10C) - C(9C) - C(14C) - C(13C)	-0.2(5)
C(8C) - C(9C) - C(14C) - C(13C)	176.8(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

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