Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supporting Information

Metal ions as external stimuli in stereoselective self-sorting of koneramines and thiokoneramines

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Experimental Section

Materials.

Pyridine-2-carboxaldehyde (Sigma Aldrich), *N*-ethylethylenediamine (Alfa Aesar), *N*-phenylethylenediamine (TCI India), ethanethiol (Spectrochem), 2-mercaptoethanol (SDFCL), anhydrous $ZnCl_2$ (NICE), $CuCl_2\cdot 2H_2O$ (Merck), $CdCl_2$ (SDFCL), $NiCl_2\cdot 6H_2O$ (Rankem) and silver *p*-toluenesulfonate (Alfa Aesar) were used as received from commercial sources. Solvents were distilled under dry nitrogen atmosphere using conventional methods.

Methods.

NMR spectra were recorded on JEOL 500 MHz and JEOL 400 MHz spectrometers. Temperature was kept constant using a variable temperature unit within the error limit of ±1 K. The software MestReNova[1] was used for the processing of the NMR spectra. Tetramethylsilane (TMS) or the deuterated solvent residual peaks were used for calibration. Mass spectrometry experiments were performed on a Waters-Q-ToF-Premier-HAB213 equipped with an electrospray interface. Spectra were collected by constant infusion of the sample dissolved in methanol or acetonitrile with 0.1% formic acid.

Crystal Structure Determinations.

Single-crystal X-ray data were collected at 123 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The linear absorption coefficients, the scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Data integration and reduction were conducted with SAINT. An empirical absorption correction was applied to the collected reflections with SADABS using XPREP. Structures were determined by direct method using SHELXTL and refined on F^2 by a full-matrix least-squares technique using the SHELXL-97 program package. The lattice parameters and structural data are listed somewhere else in this Supporting Information.

Pyridine-2-carboxaldehyde and N-Phenylethylenediamine (2:1) with half equivalent of $CuCl_2{\cdot}2H_2O$ and $CdCl_2$ (1:1)

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (0.1072 g, 1 mmol) dissolved in 10 mL of methanol was added N-phenylethylenediamine (69 mg, 0.5 mmol), and the resulting yellow solution was stirred at room temperature for 24 hours. In a 5 mL vial $CuCl_2{\cdot}2H_2O$ (43 mg, 0.25 mmol) and $CdCl_2$ (46 mg, 0.25 mmol) mixed well as solid. The mixed metal salts were added all at once, the colour of the solution immediately turned into olive green. A precipitate appeared after 5 minutes, the reaction mixture further stirred at room temperature for 12 hours. The precipitate was filtered, washed with 20 mL methanol and the undissolved precipitate recovered as white solid. The filtrate volume reduced to half and slow addition of diethyl ether resulting in complete precipitation. Yield: Undissolved precipitate in methanol 0.109 g (84 % with respect to metal salt) and the precipitate dissolved in methanol 96 mg (76% with respect to metal salt).

^{1}H NMR (400.16 MHz, 25 ^{o}C, $CDCl_3$):

δ_H = 9.27 (d, 1H, J = 5.0 Hz, Py), 9.08 (d, 1H, J = 5.1 Hz, Py), 7.86 (t, 1H, J =7.7 Hz, Py), 7.69 (t, 1H, J = 7.7 Hz, Py), 7.55 (d, 1H, J = 7.9 Hz, Py), 7.41 (t, 1H, J = 6.3 Hz, Py), 7.36-7.45 (m, 2H, Py), 7.25 (t, 2H, J = 7.9 Hz, Ph), 6.83 (t, 1H, J = 7.3 Hz, Ph), 6.52 (d, 2H, J = 8.1 Hz, Ph), 5.91 (s, 1H, C*H), 5.17 (s, 1H, C*H), 4.08-4.13 (m, 1H, CH_2-Im), 3.90-3.98 (m, 1H, CH_2-Im), 3.73-3.81 (m, 1H, CH_2-Im), 3.63 (s, 3H, OCH_3), 3.55-3.59 ppm (m, 1H,CH_2-Im). See Figure S 1.

ESI-MS

Precipitate (insoluble in methanol)

m/z = 495.0526 (calcd. 495.0512) = $[Cd(L^{Ph}OMe)Cl]^+$. See Figure S 2.

Filtrate

m/z = 444.0771 (calcd.444.0778) = $[Cu(L^{Ph}OMe)Cl]^+$ = $[M-Cl]^+$, *m/z* = 454.1079 (calcd.454.1066) = $[M+HCOO-2Cl]^+$.Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 3.

Pyridine-2-carboxaldehyde and N-Phenylethylenediamine (2:1) with 1 equivalent of $CuCl_2 \cdot 2H_2O$ and $CdCl_2$ (1:1)

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (0.1072 g, 1 mmol) dissolved in 10 mL of methanol was added N-phenylethylenediamine (69 mg, 0.5 mmol), and the resulting yellow solution was stirred at room temperature for 24 hours. In a 5 mL vial $CuCl_2 \cdot 2H_2O$ (85 mg, 0.5 mmol) and $CdCl_2$ (92 mg, 0.5 mmol) mixed well as solid. The mixed metal salts were added all at once, the colour of the solution immediately turned into olive green. A precipitate appeared after 5 minutes, the reaction mixture further stirred at room temperature for 12 hours. The precipitate was filtered, washed once with 2 mL methanol. The filtrate volume reduced to half and slow addition of diethyl ether resulting in complete precipitation. Yield: Precipitate 0.199 g (83 %).

ESI-MS

Precipitate

m/z = 444.0771 (calcd.444.0778) = $[M\text{-}Cl]^+$, *m/z* = 454.1079 (calcd.454.1066) = $[M\text{+}HCOO\text{-}2Cl]^+$. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 4.

Filtrate

m/z = 444.0771 (calcd.444.0778) = $[M\text{-}Cl]^+$, *m/z* = 454.1079 (calcd.454.1066) = $[M\text{+}HCOO\text{-}2Cl]^+$. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 5.

Pyridine-2-carboxaldehyde and N-Phenylethylenediamine (2:1) with 1 equivalent of $CuCl_2{\cdot}2H_2O$ and $NiCl_2{\cdot}6H_2O$ (1:1)

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (53.5 mg, 0.5 mmol) dissolved in 10 mL of methanol was added N-phenylethylenediamine (34 mg, 0.25 mmol), and the resulting yellow solution was stirred at room temperature for 24 hours. In a 5 mL vial $CuCl_2{\cdot}2H_2O$ (0.0426 g, 0.25 mmol) and $NiCl_2{\cdot}6H_2O$ (0.0594 g, 0.25 mmol) mixed well as solid. The mixed metal salts were added all at once, the colour of the solution immediately turned into olive green. A dark green precipitate appeared after 5 minutes, the reaction mixture further stirred at room temperature for 12 hours. The dark green precipitate filtered, washed once with 2 mL methanol. The filtrate volume was reduced to half and slow addition of diethyl ether resulting in complete precipitation.

ESI-MS:

Precipitate

m/z = 444.0771 (calcd.444.0778) = $[M\text{-}Cl]^+$, *m/z* = 454.1079 (calcd.454.1066) = $[M+HCOO\text{-}2Cl]^+$.Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 6.

Filtrate

m/z = 444.0771 (calcd.444.0778) = $[M\text{-}Cl]^+$, *m/z* = 454.1079 (calcd.454.1066) = $[M+HCOO\text{-}2Cl]^+$.Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 7.

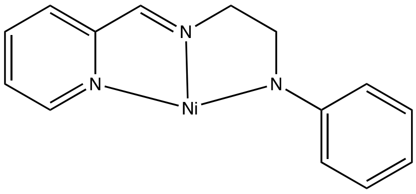
Pyridine-2-carboxaldehyde and N-Phenylethylenediamine (2:1) with 1 equivalent of $CdCl_2$ and $NiCl_2·6H_2O$ (1:1)

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (53.5 mg, 0.5 mmol) dissolved in 10 mL of methanol was added N-phenylethylenediamine (34 mg, 0.25 mmol), and the resulting yellow solution was stirred at room temperature for 24 hours. In a 5 mL vial $CdCl_2$ (46 mg, 0.25 mmol) and $NiCl_2·6H_2O$ (59 mg, 0.25 mmol) mixed well as solid. The mixed metal salts were added all at once, the colour of the solution immediately turned into green. A yellowish brown precipitate appeared after 30 minutes, the reaction mixture further stirred at room temperature for 12 hours. The yellowish brown precipitate filtered (Figure S 8), washed once with 2 mL methanol and the filtrate was kept at room temperature forms brown crystals (Figure S 9).

ESI-MS:

Precipitate

The ESI-MS of this precipitate shows a small peaks for $[Ni(L^{Ph}OMe)Cl]^+$ at 439.0837 (calculated *m/z* is 439.0836) but strong peak for $[Ni(sb^{Ph}\text{-}H)]^+$ at 282.0536 (calculated *m/z* is 282.0541). See Figure S 8.



$[Ni(sb^{Ph}\text{-}H)]^+$

Filtrate

m/z = 439.0837 (calcd. 439.0836) = $[M\text{-}Cl]^+$, *m/z* = 449.1080 (calcd.449.1124) = $[M+HCOO\text{-}2Cl]^+$. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. Figure S 9.

Pyridine-2-carboxaldehyde and N-Phenylethylenediamine (2:1) with 1 equivalent of $CdCl_2$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$ and $ZnCl_2$

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (0.214 g, 2 mmol) dissolved in 10 mL of methanol was added N-phenylethylenediamine (0.137 g, 1 mmol), and the resulting yellow solution was stirred at room temperature for 24 hours. In a 15 ml vial anhydrous $CdCl_2$ (0.183 g, 1 mmol), $CuCl_2{\cdot}2H_2O$ (0.1726 g, 1 mmol), $NiCl_2{\cdot}6H_2O$ (0.2382 g, 1 mmol) and anhydrous $ZnCl_2$ (0.1368 g, 1 mmol) mixed well as solid. The mixed metal salts were added all at once, the colour of the solution immediately turned into olive green. A brownish green precipitate appeared after 5 minutes, the reaction mixture further stirred at room temperature for 12 hours. The brownish green precipitate filtered, washed once with 2 ml methanol. The filtrate volume was reduced to half and slow addition of diethyl ether resulting in complete precipitation. Precipitate 0.2882 g (60 %).

ESI-MS:

Precipitate

m/z = 444.0771 (calcd.444.0778) = $[M-Cl]^+$, *m/z* = 454.1079 (calcd.454.1066) = $[M+HCOO-2Cl]^+$. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 11.

Filtrate

m/z = 444.0771 (calcd.444.0778) = $[M-Cl]^+$, *m/z* = 454.1079 (calcd.454.1066) = $[M+HCOO-2Cl]^+$. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 12.

Synthesis of *anti*-[Zn(L^{Ph}SEt)Cl_2]·CH_3CN:

To a solution of pyridine-2-carboxaldehyde (107 mg, 1 mmol) in 3 mL of ethanethiol was added *N*-ethylethylenediamine (68 mg, 0.5 mmol); resulting yellow solution was stirred for 24 hours at room temperature. The excess ethanethiol was removed under reduced pressure, resulting in brownish yellow oily compound. Subsequently, dissolved in 5 mL of acetonitrile was added an acetonitrile (3 mL) solution of anhydrous $ZnCl_2$ (65 mg, 0.5 mmol). The clear yellow solution was stirred at room temperature for 2 hours. The volume of the solution was reduced to half and allowed to stand at 0 °C for 24 hours to obtain crystals suitable for single crystal X-ray diffraction. Yield: 0.174 g (68 %).

^{1}H NMR (400.16 MHz, 25 °C, $CDCl_3$):

δ_H = 9.11 (d, 1H, *J* = 4.4 Hz, Py), 9.07 (d, 1H, *J* = 4.4 Hz, Py), 7.95 (t, 1H, *J* = 7.7 Hz, Py), 7.85 (t, 1H, *J* = 7.8 Hz, Py), 7.65 (d, 1H, *J* = 7.8 Hz, Py), 7.55 – 7.48 (m, 3H, Py), 7.35 (t, 2H, 7.9 Hz, Ph), 6.90 (t, 1H, *J* = 7.4 Hz, Ph), 6.76 (d, 2H, *J* = 8.6 Hz, Ph), 6.62 (s, 1H, C*H), 5.02 (s, 1H, C*H), 3.84 – 3.76 (m, 1H, CH_2-Im), 3.71 – 3.62 (m, 1H, CH_2-Im), 3.40 (t,1H, *J* = 8.4 Hz,), 3.18 (q, 1H, *J* = 13.0, 6.7 Hz, CH_2-S), 2.73 – 2.64 (m, 1H, CH_2-Im), 2.35 – 2.25 (m, 1H, CH_2-Im), 1.05 (t, 3H, *J* = 7.4 Hz, CH_3CH_2-S). See Figure S 13.

ESI-MS:

m/z = 475.0720 (calcd.475.0702) = $[M-Cl]^+$. See Figure S 14.

Synthesis of *anti*-[Zn($L^{Ph}SCH_2CH_2OH$)Cl_2]:

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (0.214 g, 2 mmol) was dissolved in 10 mL of acetonitrile and stirred for 5 minutes. N-phenylethylenediamine (0.141 g, 1 mmol) and 2-mercaptoethanol (1 mL, 14.2 mmol) was added drop-wise to the stirred aldehyde solution. The resulting yellow solution was stirred at room temperature for 24 hours and the anhydrous $ZnCl_2$ (0.137 g, 1 mmol) was added as solid. A white precipitate appeared within 3 hours, and the reaction mixture was continued to stir for 8 hours at room temperature. The white precipitate was filtered off and the precipitate was recrystallized in dichloromethane forms crystals suitable for single crystal X-ray diffraction. Yield: 0.5101 g, (97 %)

^{1}H NMR (400.16 MHz, 25 ^{o}C, $CDCl_3$):

δ_H = 8.95 (d, 1H, *J* = 6.0 Hz, Py), 8.92 (d, 1H, *J* = 5.5 Hz, Py), 7.94 (t, 1H, *J* = 7.7 Hz, Py), 7.84 (t, 1H, *J* = 7.8 Hz, Py), 7.69 (d, 1H, *J* = 7.9 Hz, Py), 7.50 (m, 3H, *J* = 7.6 Hz, Py), 7.34 (t, 2H, *J* = 8.0 Hz, Ph), 7.12 (s, 1H, C*H), 6.89 (t, 1H, *J* = 7.4 Hz, Ph), 6.82 (d, 2H, *J* = 8.0 Hz, Ph), 5.18 (s, 1H, C*H), 3.80 – 3.70 (m, 1H, CH_2-Im), 3.66 – 3.51 (m, 3H, CH_2-Im, OCH_2CH_2S), 3.41 (m, *J* = 8.3, 7.0 Hz, 2H, SCH_2CH_2OH), 3.13 – 3.04 (m, 1H, CH_2-Im), 2.53 (m, 1H, CH_2-Im). See Figure S 16.

ESI-MS:

m/z = 491.0679 (calcd.491.0651)=$[M-Cl]^+$. See Figure S 17.

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Synthesis of *anti*-[Ni(L^{Et}SEt)(H_2O)Cl_2]:

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (0.214 g, 2 mmol) was dissolved in 10 mL acetonitrile. *N*-Ethylethylenediamine (88 mg, 1 mmol) and ethanethiol (3 ml, 41.57 mmol) was added drop-wise into the stirred aldehyde solution. The light yellow solution was left to stir at room temperature for 24 hours. Excess ethanethiol was removed under reduced pressure to yield a brownish yellow oily compound. Subsequently, dissolved in 10 mL of acetonitrile and $NiCl_2 \cdot 6H_2O$ (0.236 g, 1 mmol) added as solid. After stirring for 2 hours at room temperature, a green precipitate was obtained. It was filtered off and the solvent was removed from the filtrate solution under reduced pressure resulting in a dark green solid. Yield: 0.4192 g, (84 %)

ESI-MS:

m/z = 421.0742 (calcd.421.0764) = $[M\text{-}Cl]^+$, *m/z* = 431.1033 (calcd.431.1052) = $[M\text{+}HCOO\text{-}2Cl]^+$. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample. See Figure S 21.

***anti*-[Ni(L^{Et}SEt)(H_2O)$(OTs)_2$] from *anti*-[Ni(L^{Et}SEt)(H_2O)Cl_2]:**

In an aluminium foil wrapped 15 mL culture tube, *anti*-[Ni(L^{Et}SEt)Cl_2H_2O] complex (0.4192 g, 0.84 mmol) was dissolved in 5 mL of acetonitrile. Silver p-toluenesulfonate (469.93 g, 1.68 mmol) was added as solid to the green solution, stirred at room temperature for 3 hours. The brown suspension was passed through celite pad and the solvent was removed under reduced pressure yields a brown solid. Yield: (0.5896 g, 93 %).

ESI-MS:

m/z = 557.1181 (calcd.557.1191) = $[M\text{-}OTs]^+$. See Figure S 22.

Synthesis of *anti*-[Cd($L^{Ph}SCH_2CH_2OH$)Cl_2]:

In a 50 mL round-bottom flask, pyridine-2-carboxaldehyde (0.214 g, 2 mmol) was dissolved in 10 mL of acetonitrile stirred for 5 minutes. N-Phenylethylenediamine (0.141 g, 1 mmol) and 2-mercaptoethanol (0.188 g, 2.45 mmol) was added drop-wise into the stirred aldehyde solution. The resulting yellow solution was stirred at room temperature for 24 hours and anhydrous $CdCl_2$ (0.183 g, 1 mmol) added as solid. A white precipitate appeared within 3 hours, after adding the metal salt. The reaction mixture was further stirred at room temperature for 8 hours. The white precipitate was filtered off and recrystallized in acetonitrile at 0 °C formed crystals suitable for single crystal X-ray diffraction. Yield: 0.501 g (87 %).

^{1}H NMR (400.16 MHz, 25 °C, $CDCl_3$):

δ_H = 9.03 (m, 1H, *J* =4.3 Hz , Py), 8.94 (d, 1H, *J* = 4.9 Hz, Py), 7.91 (m, 1H, Py), 7.75 (t, 1H, *J* =7.7 Hz, Py), 7.69 (d, 1H, *J* = 7.8 Hz, Py), 7.49 – 7.40 (m, 3H, Py), 7.31 (t, 2H *J* =7.5 Hz, Ph), 6.85 (t, 1H, *J* = 7.4 Hz, Ph), 6.65 (d, 2H, *J* =8.6 Hz, Ph), 6.08 (s, 1H, C*H), 5.80 (s, 1H, C*H), 4.02 – 3.98 (m, 1H, CH_2-Im), 3.78 – 3.73 (m, 1H, CH_2-Im), 3.38 (t, 2H, *J* = 8.1 Hz, $OHCH_2CH_2S$), 3.07 (t, 2H, *J* = 5.5 Hz, SCH_2CH_2OH), 2.86 – 2.79 (m, 1H, CH_2-Im), 2.73-2.59 (m, 2H, CH_2-Im). See Figure S 19.

Figure S 1. ^{1}H NMR of the white precipitate from *N*-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with half equivalent of $CuCl_2{\cdot}2H_2O$ and half equivalent of $CdCl_2$. It is as same as the data reported in literature.[2]

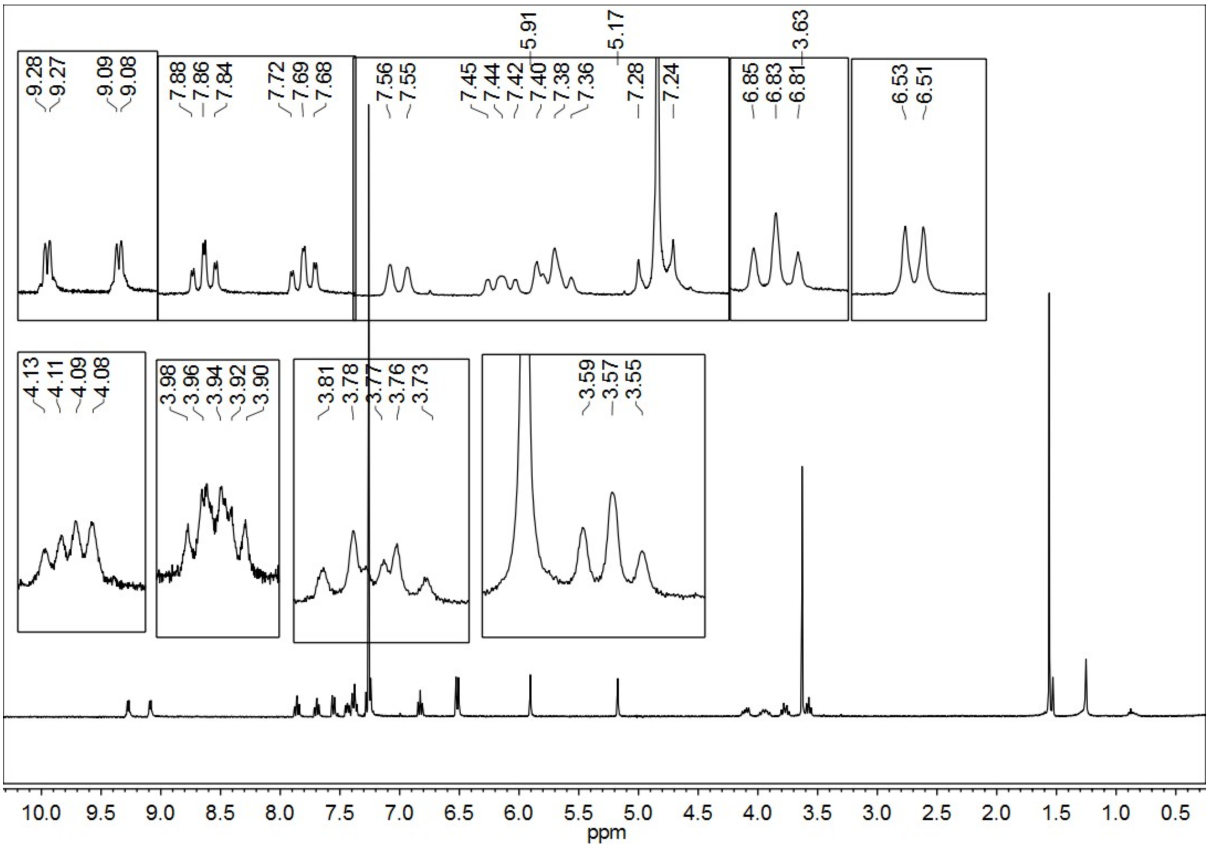
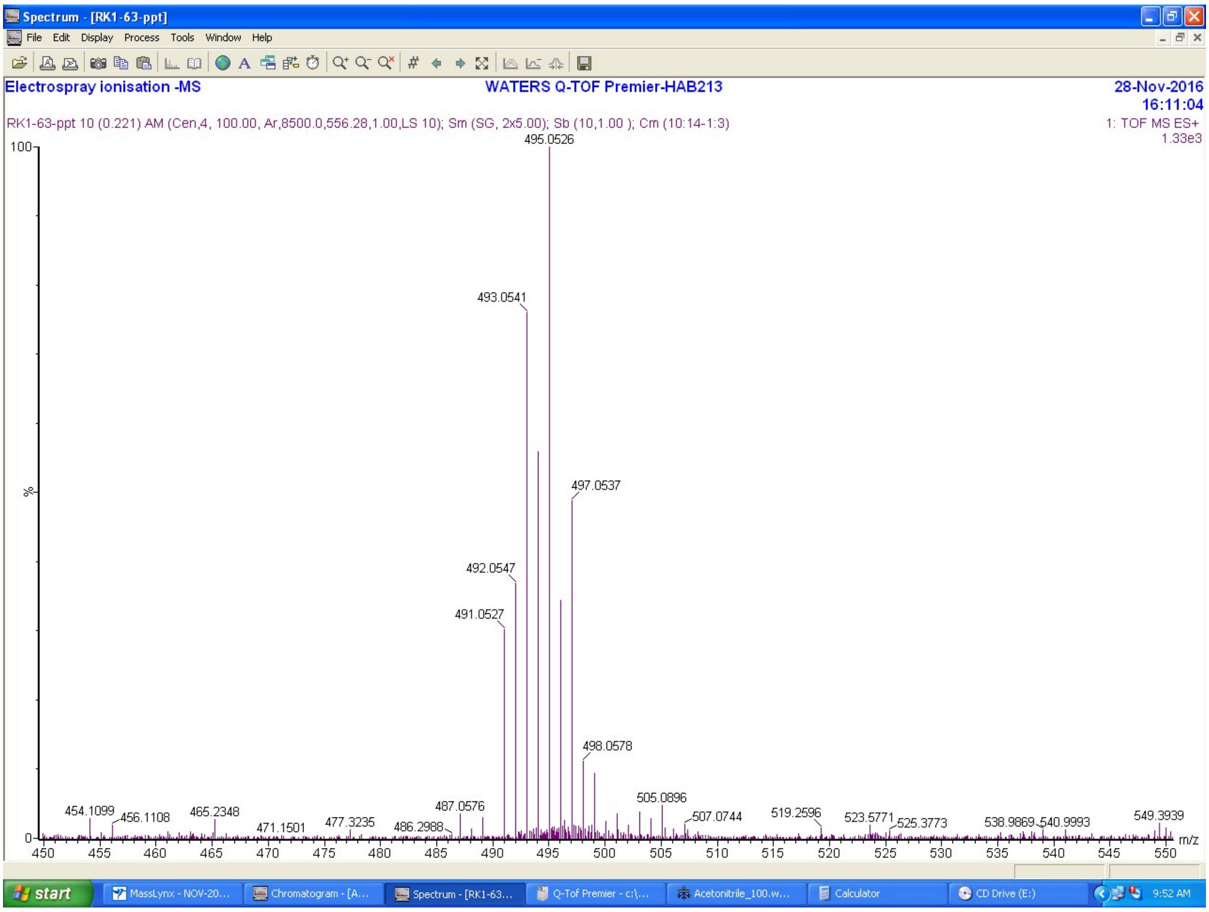


Figure S 2. ESI-MS of the white precipitate from *N*-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with half equivalent of $CuCl_2{\cdot}2H_2O$ and half equivalent of $CdCl_2$. It is as same as the data reported in literature.[2]



Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

28-Nov-2016
16:11:04

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1: TOF MS ES+
1.33e3

Calculated *m/z* for $[Cd(L^{Ph}OMe)Cl]^+$ = 495.0512; Observed *m/z* is 495.0526.

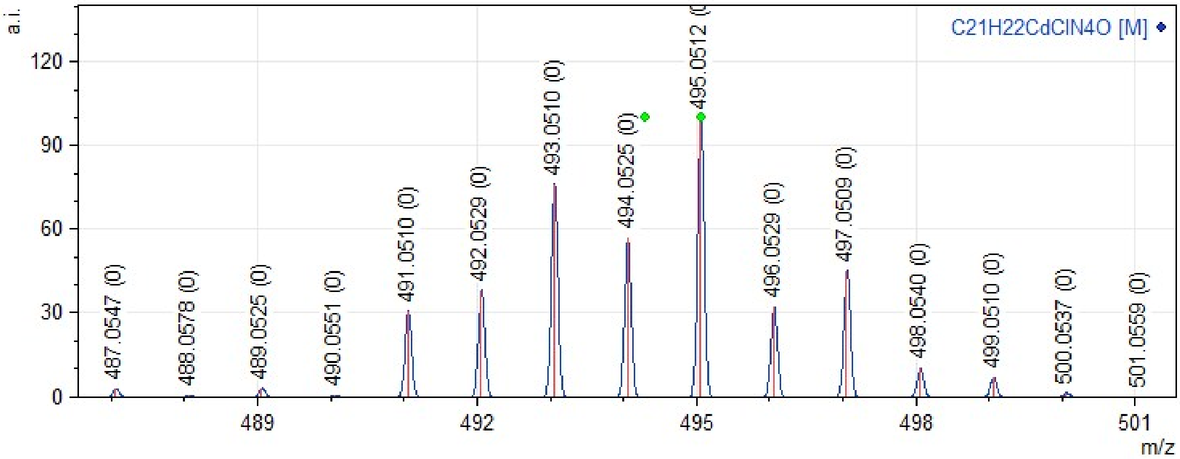
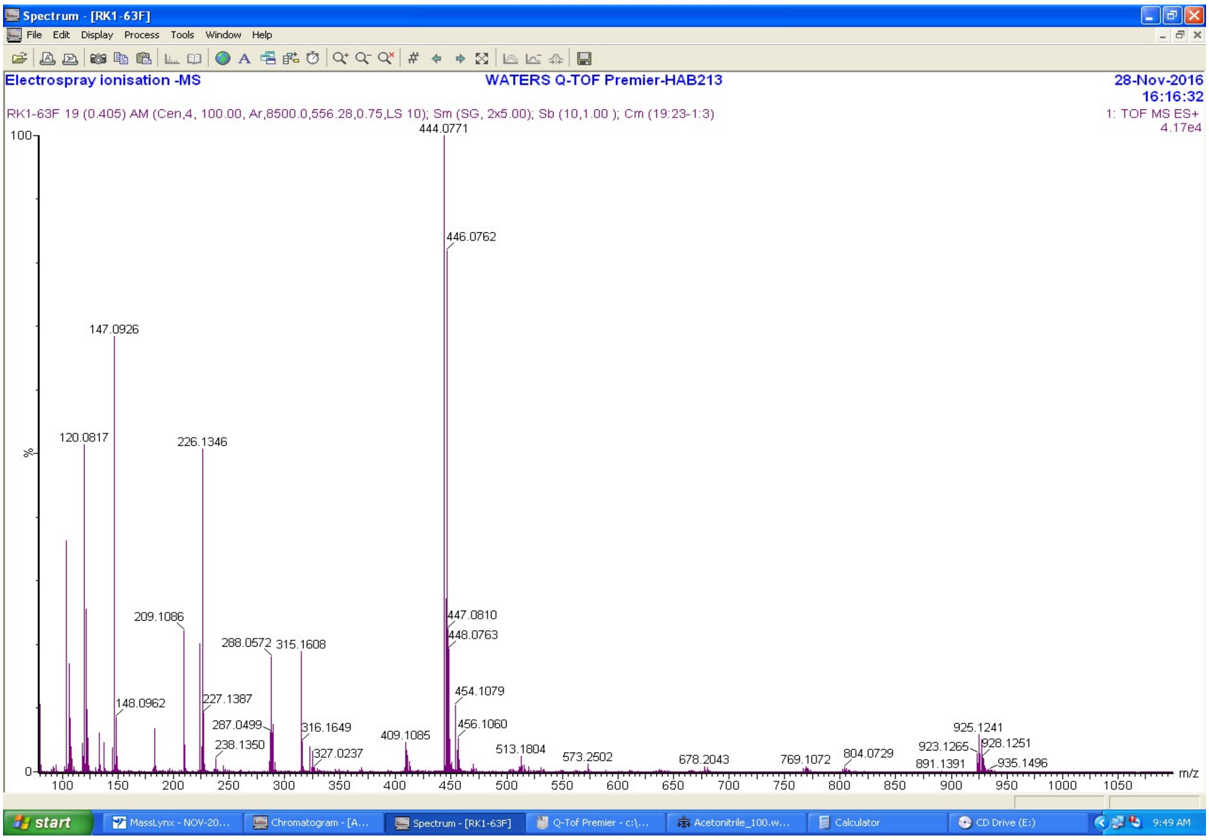


Figure S 3. ESI-MS of filtrate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with half equivalent of $CuCl_2{\cdot}2H_2O$ and half equivalent of $CdCl_2$. It is as same as the data reported in literature.[2]



Calculated *m/z* for $[Cu(L^{Ph}OMe)Cl]^+$ = 444.0778; Observed *m/z* is 444.0771;. Calculated *m/z* for $[Cu(L^{Ph}OMe)HCOO]^+$ = 454.1066; Observed *m/z* is 454.1079. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

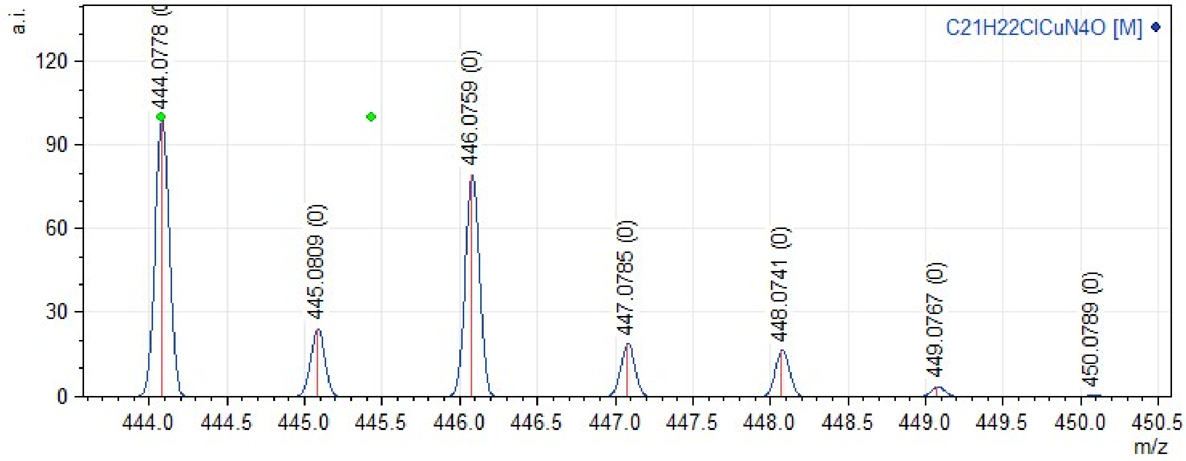


Figure S 4. ESI-MS of precipitate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with one equivalent of $CuCl_2{\cdot}2H_2O$ and one equivalent of $CdCl_2$. It is as same as the data reported in literature.[2]

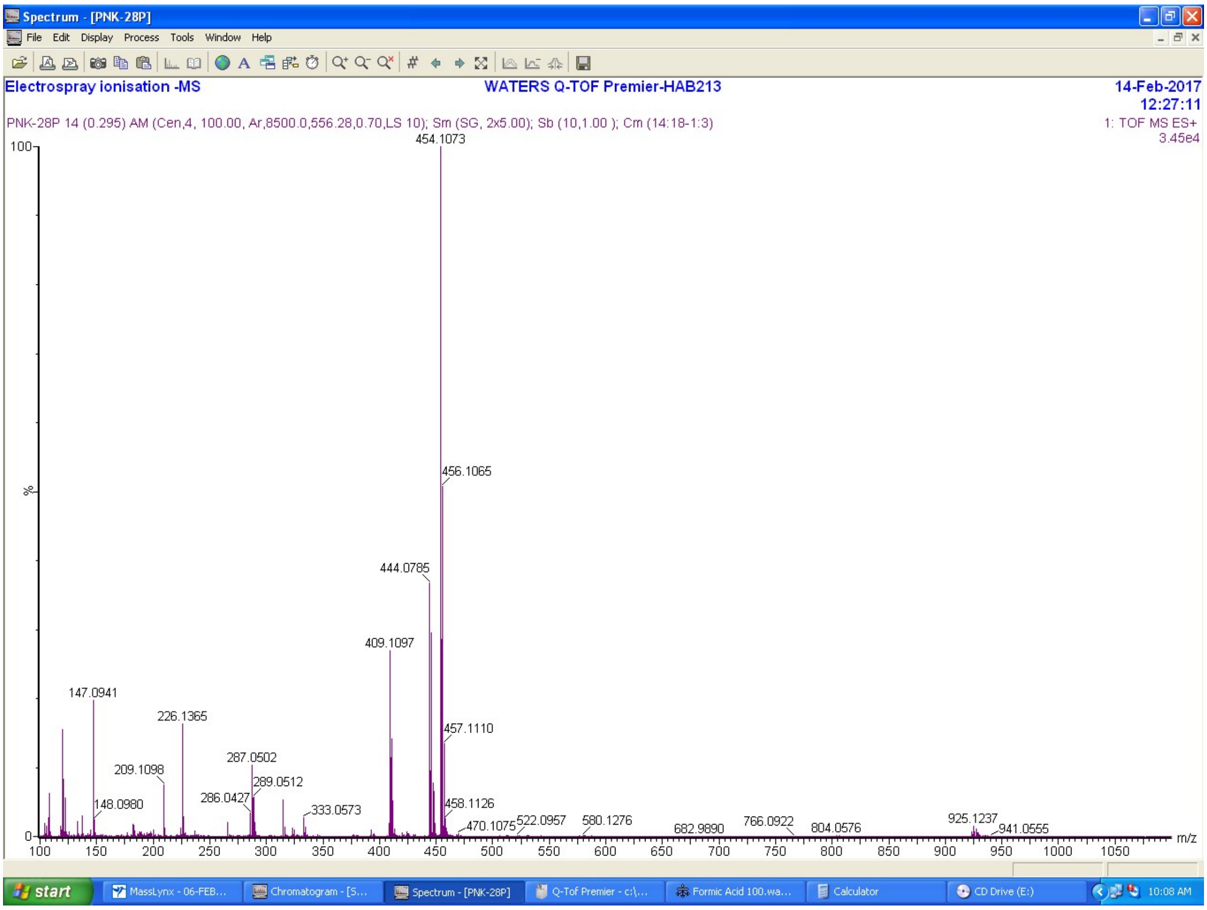


Figure S 5. ESI-MS of filtrate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with one equivalent of $CuCl_2{\cdot}2H_2O$ and one equivalent of $CdCl_2$. It is as same as the data reported in literature.[2]

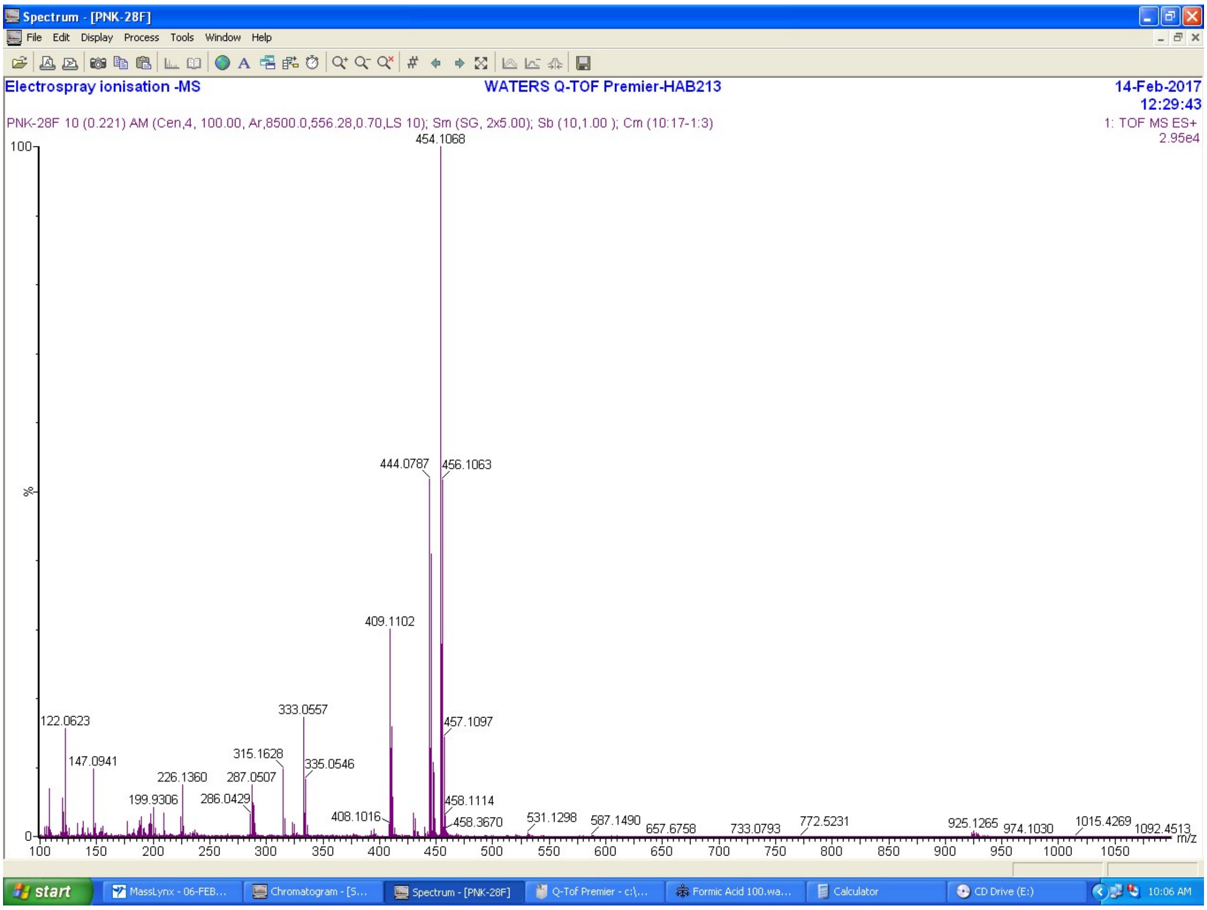
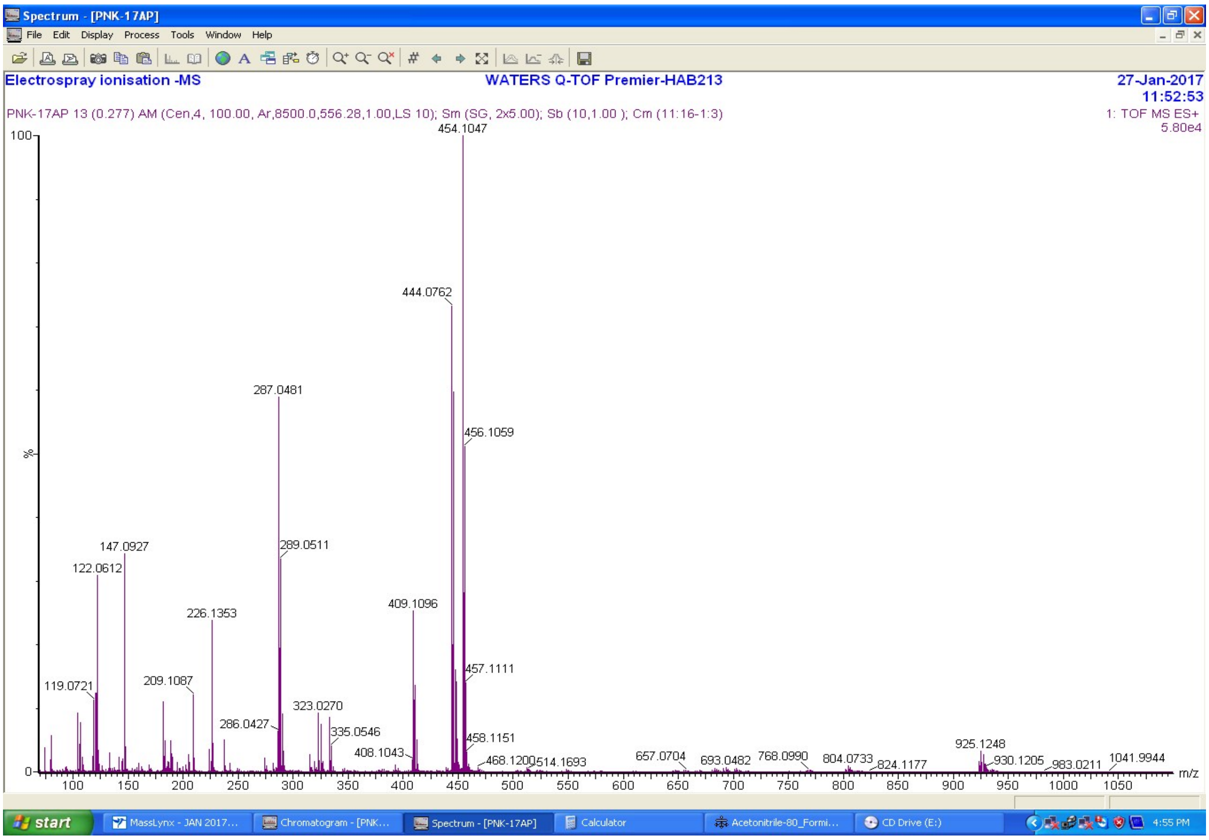
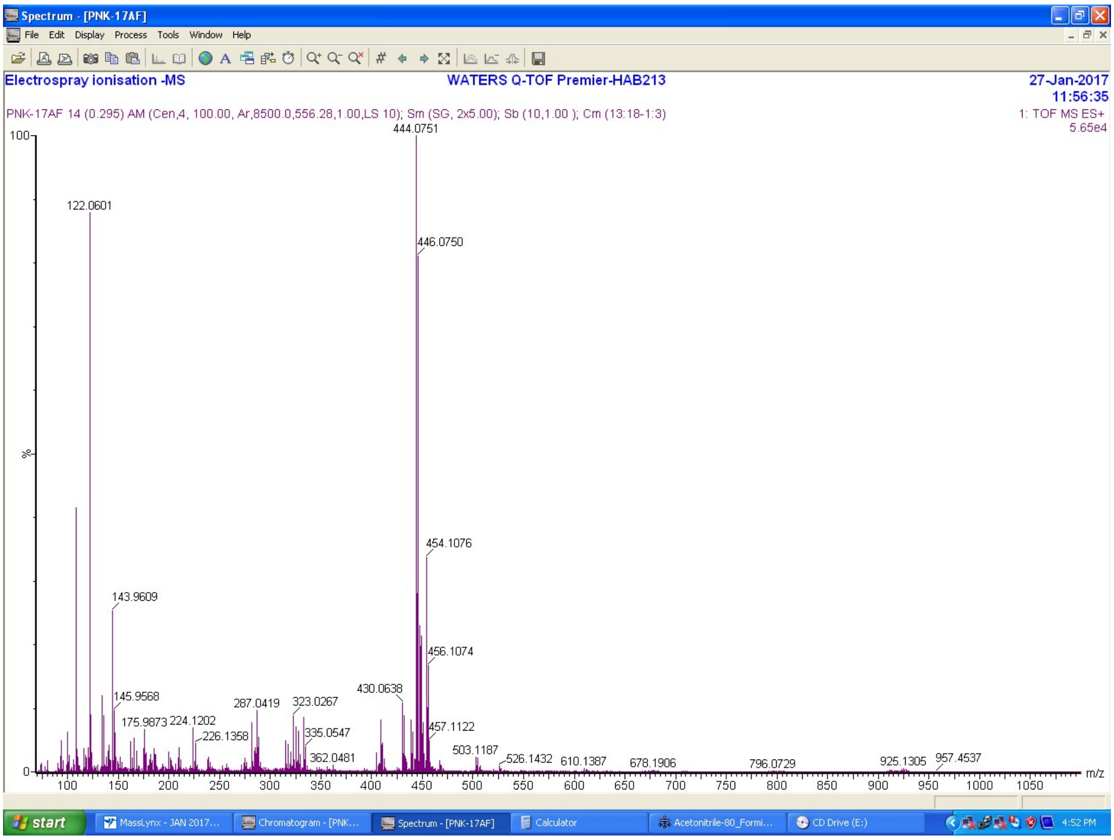


Figure S 6. ESI-MS of precipitate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with one equivalent of $CuCl_2{\cdot}2H_2O$ and one equivalent of $NiCl_2{\cdot}6H_2O$.



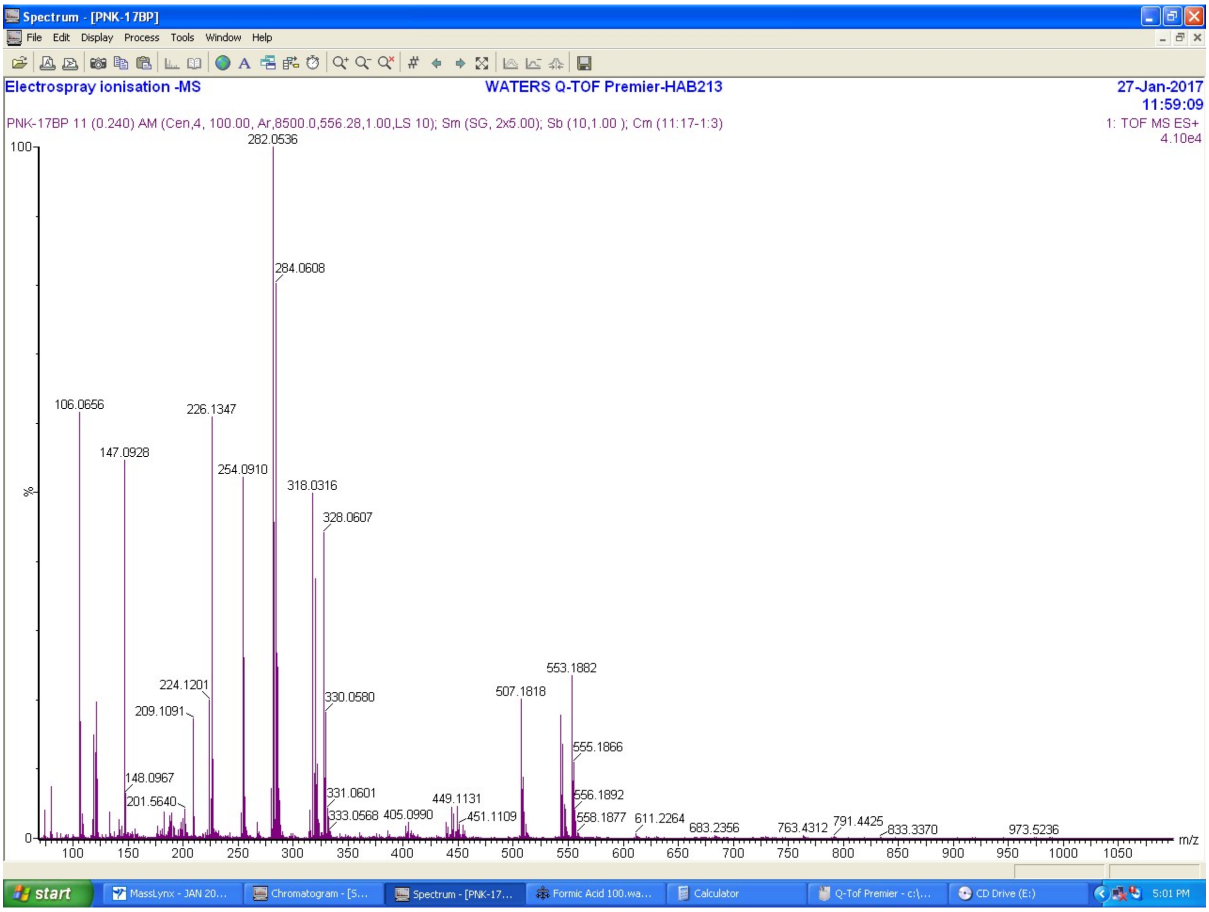
Calculated *m/z* for $[Cu(L^{Ph}OMe)Cl]^+$ = 444.0778; Observed *m/z* is 444.0771;. Calculated *m/z* for $[Cu(L^{Ph}OMe)HCOO]^+$ = 454.1066; Observed *m/z* is 454.1079. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

Figure S 7. ESI-MS of filtrate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with one equivalent of $CuCl_2{\cdot}2H_2O$ and one equivalent of $NiCl_2{\cdot}6H_2O$.



Calculated *m/z* for $[Cu(L^{Ph}OMe)Cl]^+$ = 444.0778; Observed *m/z* is 444.0771;. Calculated *m/z* for $[Cu(L^{Ph}OMe)HCOO]^+$ = 454.1066; Observed *m/z* is 454.1079. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

Figure S 8. ESI-MS of precipitate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with one equivalent of $NiCl_2{\cdot}6H_2O$ and one equivalent of $CdCl_2$.



Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

27-Jan-2017
11:59:09

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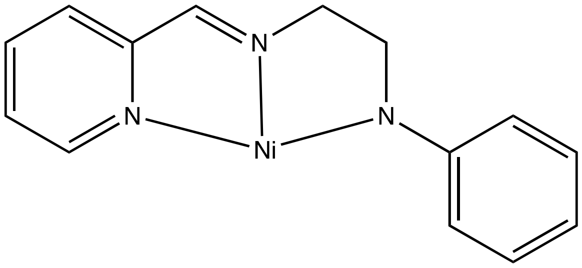
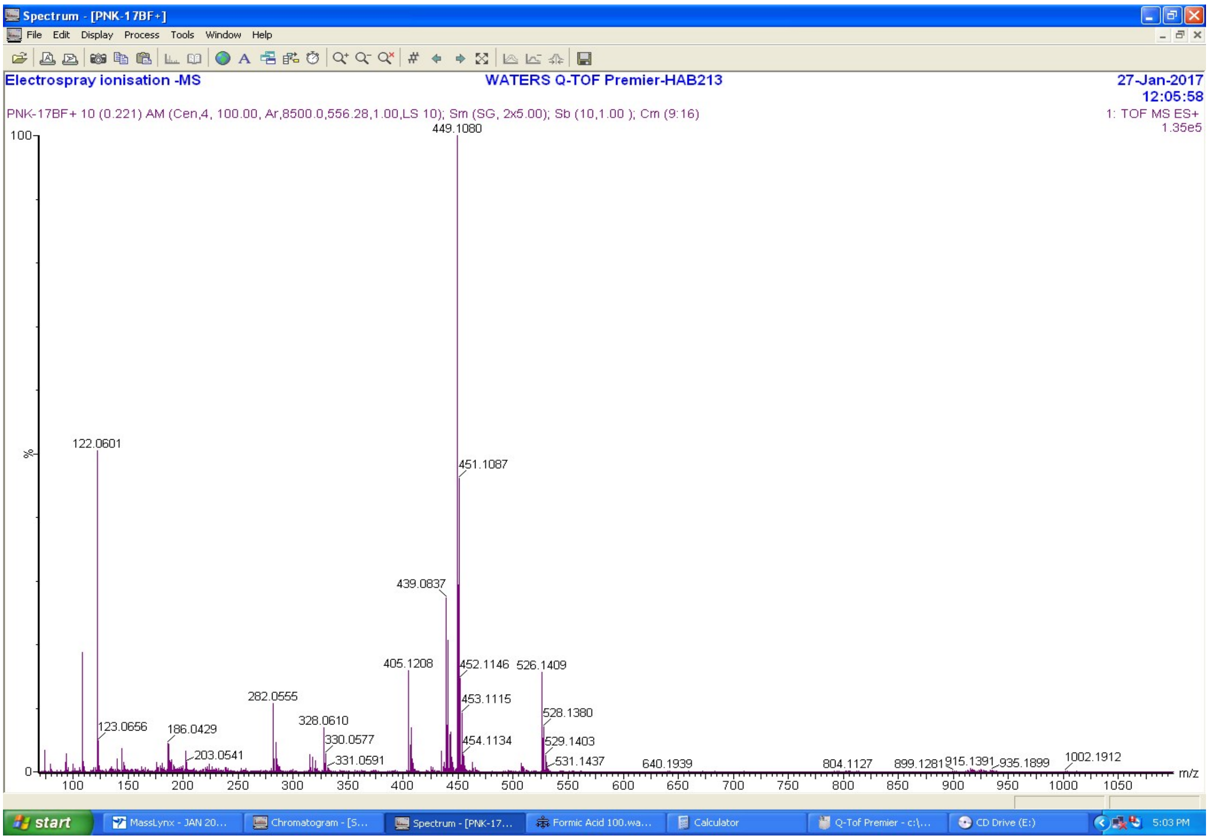
1: TOF MS ES+
4.10e4

The ESI-MS a small peaks for $[Ni(L^{Ph}OMe)Cl]^+$ at 439.0837 (calculated *m/z* is 439.0836) but strong peak for $[Ni(sb^{Ph}\text{-}H)]^+$ at 282.0536 (calculated *m/z* is 282.0541). See Figure S 8.



$[Ni(sb^{Ph}\text{-}H)]^+$

Figure S 9. ESI-MS of filtrate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with one equivalent of $NiCl_2{\cdot}6H_2O$ and one equivalent of $CdCl_2$.



Calculated *m/z* for $[Ni(L^{Ph}OMe)Cl]^+$ = 439.0836; Observed *m/z* is 439.0837;. Calculated *m/z* for $[Ni(L^{Ph}OMe)HCOO]^+$ = 449.1124; Observed *m/z* is 449.1080. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

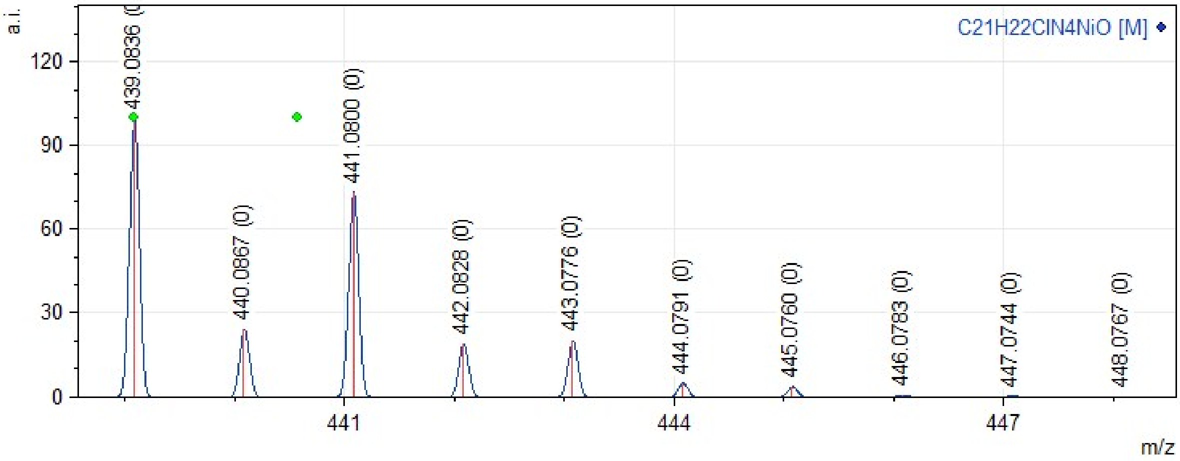
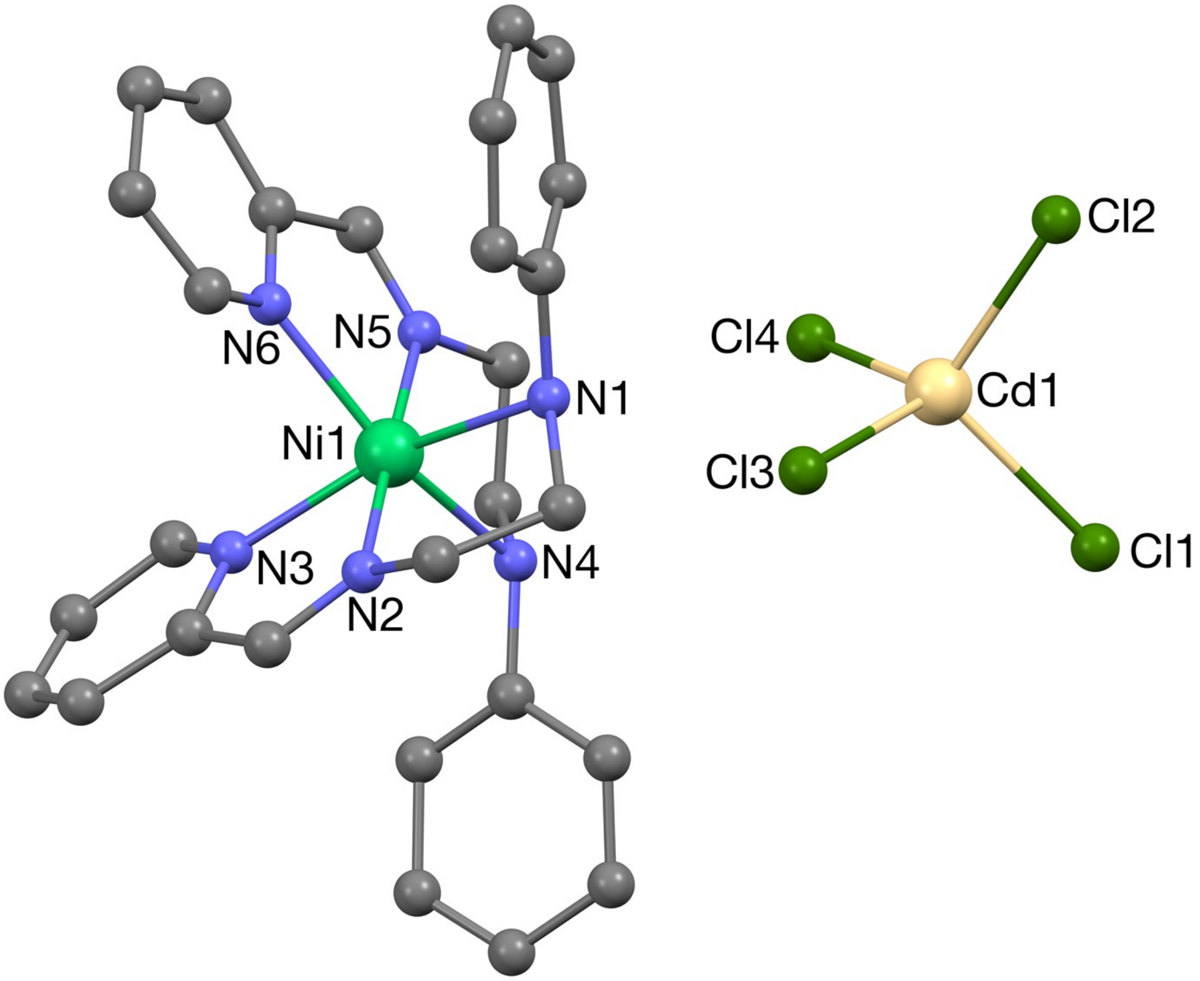


Figure S 10. X-ray structure of $[Ni(sb^{Ph})_2](CdCl_4)$.

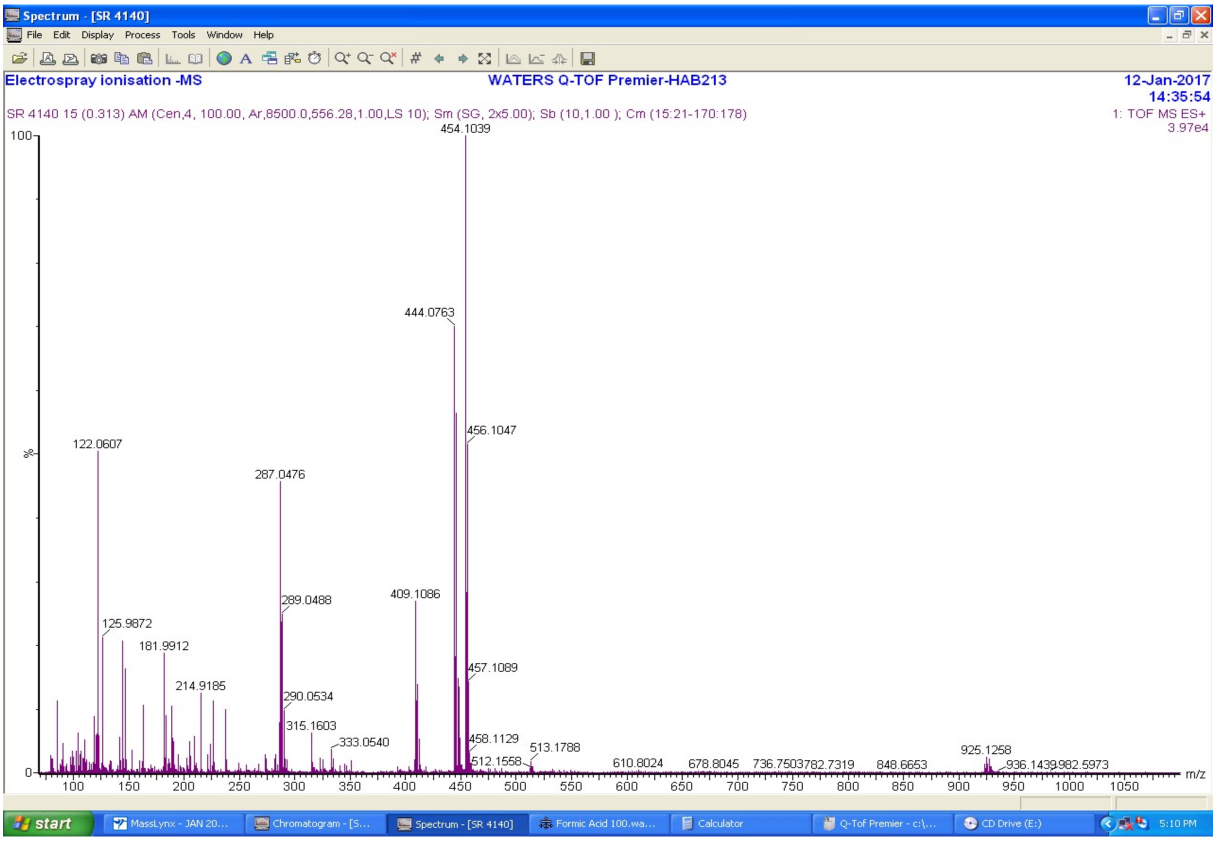


CCDC-1534802. Solvated acetonitrile and hydrogens except those bound to the stereogenic centres are omitted for clarity. Selected bond distances (Å): Ni(1)-N(2), 1.950(13); Ni(1)-N(5), 1.997(12); Ni(1)-N(6), 2.107(10); Ni(1)-N(3), 2.122(13); Ni(1)-N(1), 2.215(13); Ni(1)-N(4), 2.241(10); Cd(1)-Cl(4), 2.438(4); Cd(1)-Cl(2), 2.446(4); Cd(1)-Cl(1), 2.457(4); Cd(1)-Cl(3), 2.482(3). Selected angles (deg): N(2)-Ni(1)-N(5), 178.9(5); N(2)-Ni(1)-N(6), 103.6(5); N(5)-Ni(1)-N(6), 77.3(4); N(2)-Ni(1)-N(3), 78.8(6); N(5)-Ni(1)-N(3), 101.9(5); N(6)-Ni(1)-N(3), 88.4(4); N(2)-Ni(1)-N(1), 81.8(6); N(5)-Ni(1)-N(1), 97.5(5); N(6)-Ni(1)-N(1), 97.6(4); N(3)-Ni(1)-N(1), 160.5(5); N(2)-Ni(1)-N(4), 101.5(4); N(5)-Ni(1)-N(4), 77.7(4); N(6)-Ni(1)-N(4), 154.4(4); N(3)-Ni(1)-N(4), 91.3(4); N(1)-Ni(1)-N(4), 91.1(4); Cl(4)-Cd(1)-Cl(2), 115.57(12); Cl(4)-Cd(1)-Cl(1), 109.78(13); Cl(2)-Cd(1)-Cl(1), 105.45(15); Cl(4)-Cd(1)-Cl(3), 109.48(13); Cl(2)-Cd(1)-Cl(3), 105.29(13); Cl(1)-Cd(1)-Cl(3), 111.17(15).

Table S 1. Crystallographic data of $[Ni(sb^{Ph})_2](CdCl_4)$.

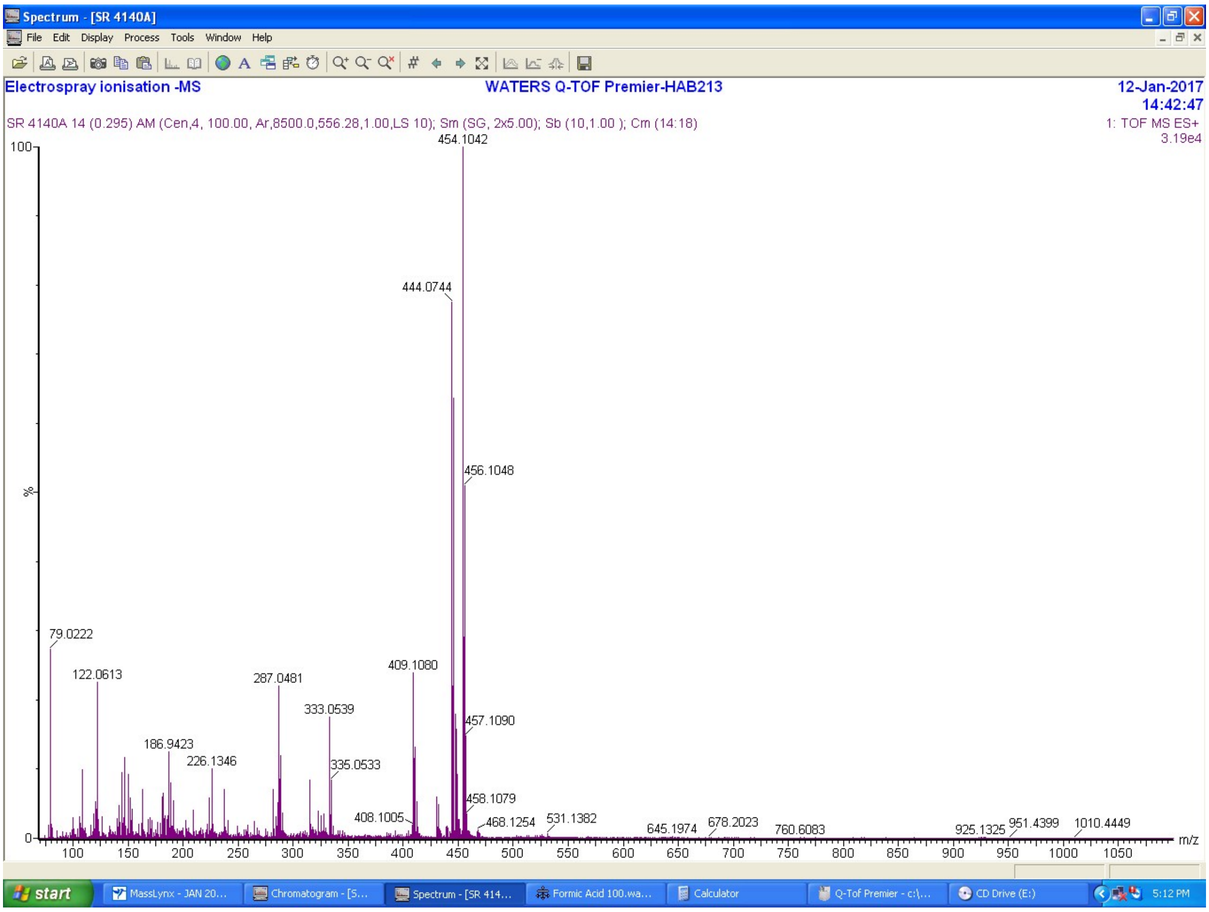
Identification code	$[Ni(sb^{Ph})_2](CdCl_4)$	CCDC-1534802
Empirical formula	C28 H30 Cd Cl4 N6 Ni	
Formula weight	763.49	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.202(2) Å	α = 90°
	b = 17.783(4) Å	β = 102.04(3)°
	c = 17.633(4) Å	γ = 90°
Volume	3128.6(11) $Å^3$	
Z	4	
Density (calculated)	1.621 Mg/m^3	
Absorption coefficient	1.652 mm^{-1}	
F(000)	1536	
Crystal size	0.22 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.04 to 25.13°.	
Index ranges	-12<=h<=12, -21<=k<=21, -21<=l<=21	
Reflections collected	31924	
Independent reflections	5575 [R(int) = 0.0647]	
Completeness to theta = 25.13°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5575 / 6 / 361	
Goodness-of-fit on F^2	2.210	
Final R indices [I>2sigma(I)]	R1 = 0.1113, wR2 = 0.3075	
R indices (all data)	R1 = 0.1450, wR2 = 0.3225	
Largest diff. peak and hole	2.832 and -1.477 e.$Å^{-3}$	

Figure S 11. ESI-MS of precipitate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with 1 eq. of $CuCl_2{\cdot}2H_2O$, 1 eq. of $NiCl_2{\cdot}6H_2O$, 1 eq. of $ZnCl_2$ and 1 eq. $CdCl_2$.



Calculated *m/z* for $[Cu(L^{Ph}OMe)Cl]^+$ = 444.0778; Observed *m/z* is 444.0771;. Calculated *m/z* for $[Cu(L^{Ph}OMe)HCOO]^+$ = 454.1066; Observed *m/z* is 454.1079. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

Figure S 12. ESI-MS of filterate from N-phenylethylenediamine and pyridine-2-carboxldehyde (1:2) in methanol with 1 eq. of $CuCl_2{\cdot}2H_2O$, 1 eq. of $NiCl_2{\cdot}6H_2O$, 1 eq. of $ZnCl_2$ and 1 eq. $CdCl_2$.



Calculated *m/z* for $[Cu(L^{Ph}OMe)Cl]^+$ = 444.0778; Observed *m/z* is 444.0771;. Calculated *m/z* for $[Cu(L^{Ph}OMe)HCOO]^+$ = 454.1066; Observed *m/z* is 454.1079 and Calculated *m/z* for $[Ni(L^{Ph}OMe)Cl]^+$ = 439.0836; Observed *m/z* is 439.0837;. Calculated *m/z* for $[Ni(L^{Ph}OMe)HCOO]^+$ = 449.1124; Observed *m/z* is 449.1080. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

Figure S 13. ^{1}H NMR of [Zn(L^{Ph}SEt)Cl$_2$].

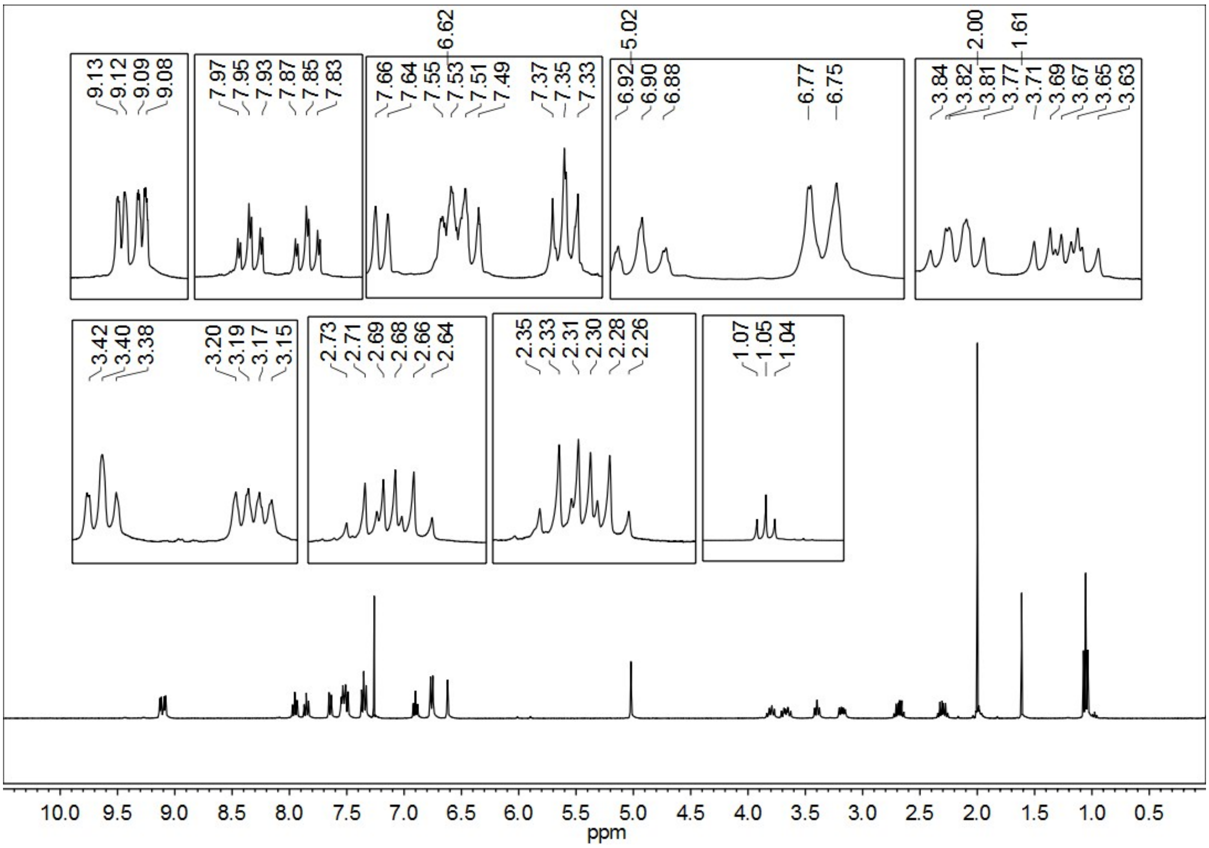
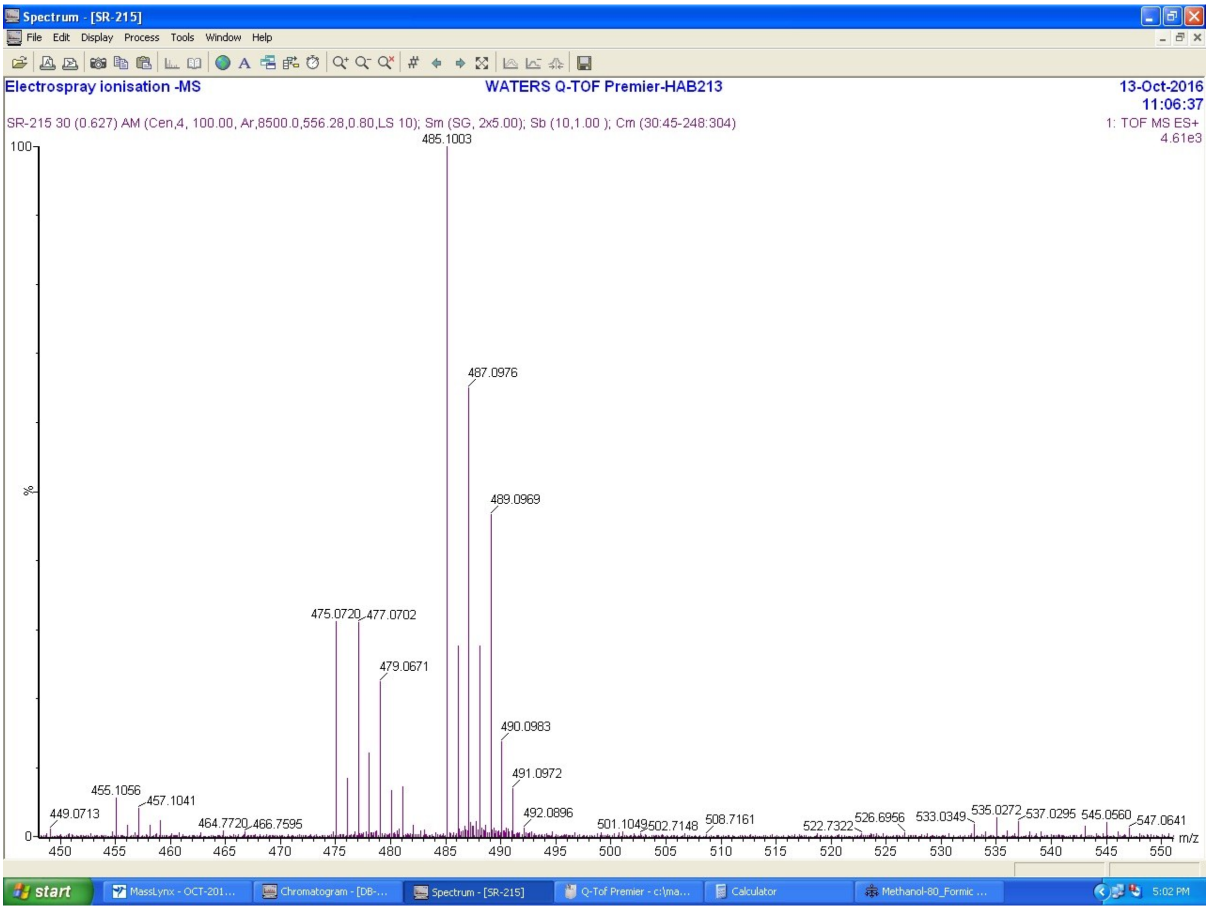


Figure S 14. ESI-MS of [Zn(L^{Ph}SEt)Cl$_2$].



Calculated *m/z* for [Zn(L^{Ph}SEt)Cl]$^+$ = 475.0702; Observed *m/z* is 475.0720. Calculated *m/z* for [Zn(L^{Ph}SEt)(HCOO)]$^+$ = 485.0990; Observed *m/z* is 485.1003. Formate must have originated from the acetonitrile (with 0.1% HCOOH) used to infuse the sample.

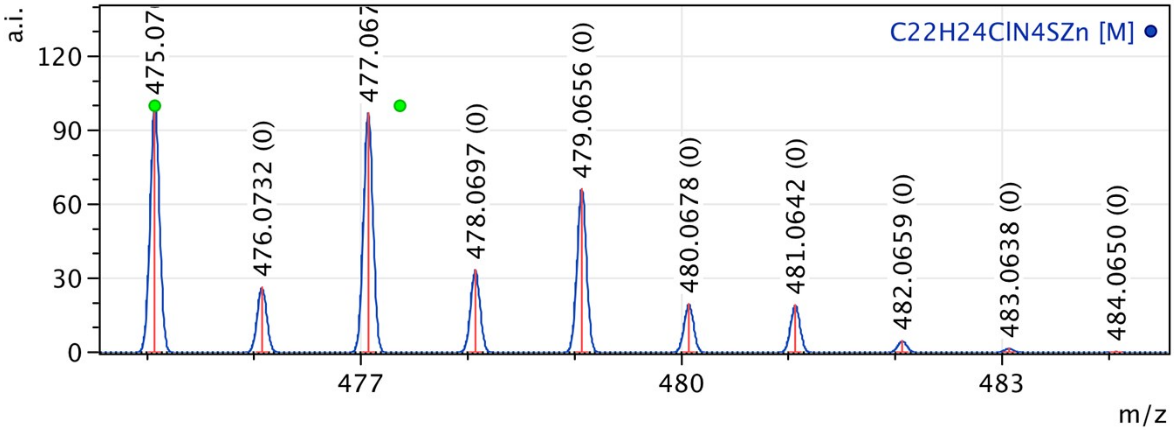
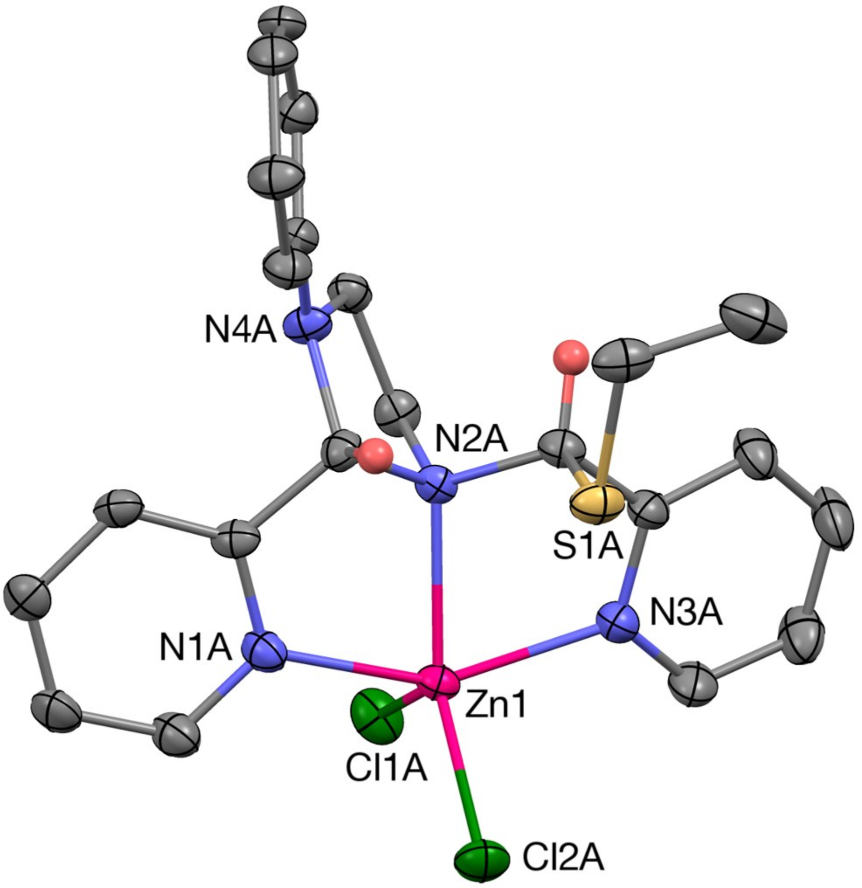


Figure S 15. ORTEP of *anti*-[Zn(L^{Ph}SEt)Cl_2]·CH_3CN.



CCDC-1534800. Solvated acetonitrile and hydrogens except those bound to the stereogenic centres are omitted for clarity. Selected bond distances (Å): Zn(1)-N(1A), 2.127(4); Zn(1)-N(3A), 2.130(4); Zn(1)-N(2A), 2.234(3); Zn(1)-Cl(2A), 2.2694(12); Zn(1)-Cl(1A), 2.2741(11). Selected angles (deg): N(1A)-Zn(1)-N(3A), 150.09(14) = β; N(1A)-Zn(1)-N(2A), 74.96(13); N(3A)-Zn(1)-N(2A), 75.67(13); N(1A)-Zn(1)-Cl(2A), 98.30(10); N(3A)-Zn(1)-Cl(2A), 99.56(10); N(2A)-Zn(1)-Cl(2A), 137.77(9); N(1A)-Zn(1)-Cl(1A), 98.53(10); N(3A)-Zn(1)-Cl(1A), 97.41(10); N(2A)-Zn(1)-Cl(1A), 111.69(9); Cl(2A)-Zn(1)-Cl(1A), 110.53(5) = α; C(15A)-N(4A)-C(6A), 122.4(3); C(15A)-N(4A)-C(14A), 120.7(3); C(6A)-N(4A)-C(14A) 109.1(3) C(15A)-N(4A)-C(6A) 122.4(3); C(15A)-N(4A)-C(14A) 120.7(3); C(6A)-N(4A)-C(14A), 109.1(3); C(15B)-N(4B)-C(6B), 122.3(3); C(15B)-N(4B)-C(14B), 121.2(3); C(6B)-N(4B)-C(14B) 108.8(3). Addison-Reedijk trigonality index,[3] τ = 0.67 (Zn1); 0.65 (Zn2). Angle between Py mean planes, π = 18.65° (Zn1); 21.21° (Zn2).

Table S 2. Crystallographic data of *anti*-$[\mathrm{Zn}(\mathrm{L}^{\mathrm{Ph}}\mathrm{SEt})\mathrm{Cl}_2]\cdot\mathrm{CH}_3\mathrm{CN}$.

Identification code	*anti*-$[\mathrm{Zn}(\mathrm{L}^{\mathrm{Ph}}\mathrm{SEt})\mathrm{Cl}_2]\cdot\mathrm{CH}_3\mathrm{CN}$	CCDC-1534800
Empirical formula	$C_{24}H_{27}Cl_2N_5SZn$	
Formula weight	553.83	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 36.547(7) Å	α= 90°
	b = 10.4667(19) Å	β= 100.796(3)°
	c = 13.743(2) Å	γ = 90°
Volume	5164.0(16) Å^3	
Z	8	
Density (calculated)	1.425 Mg/m^3	
Absorption coefficient	1.261 mm^{-1}	
F(000)	2288	
Crystal size	0.23 x 0.19 x 0.13 mm^3	
Theta range for data collection	2.027 to 28.323°.	
Index ranges	-47<=h<=40, -13<=k<=10, -17<=l<=17	
Reflections collected	30719	
Independent reflections	11932 [R(int) = 0.0490]	
Completeness to theta = 25.500°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.669	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11932 / 12 / 603	
Goodness-of-fit on F^2	1.107	
Final R indices [I>2sigma(I)]	R1 = 0.0557, wR2 = 0.1130	
R indices (all data)	R1 = 0.0833, wR2 = 0.1439	
Largest diff. peak and hole	0.951 and -0.685 e.Å^{-3}	

Figure S 16.^{1}H NMR of *anti*-[Zn(L^{Ph}SCH$_2$CH$_2$OH)Cl$_2$].

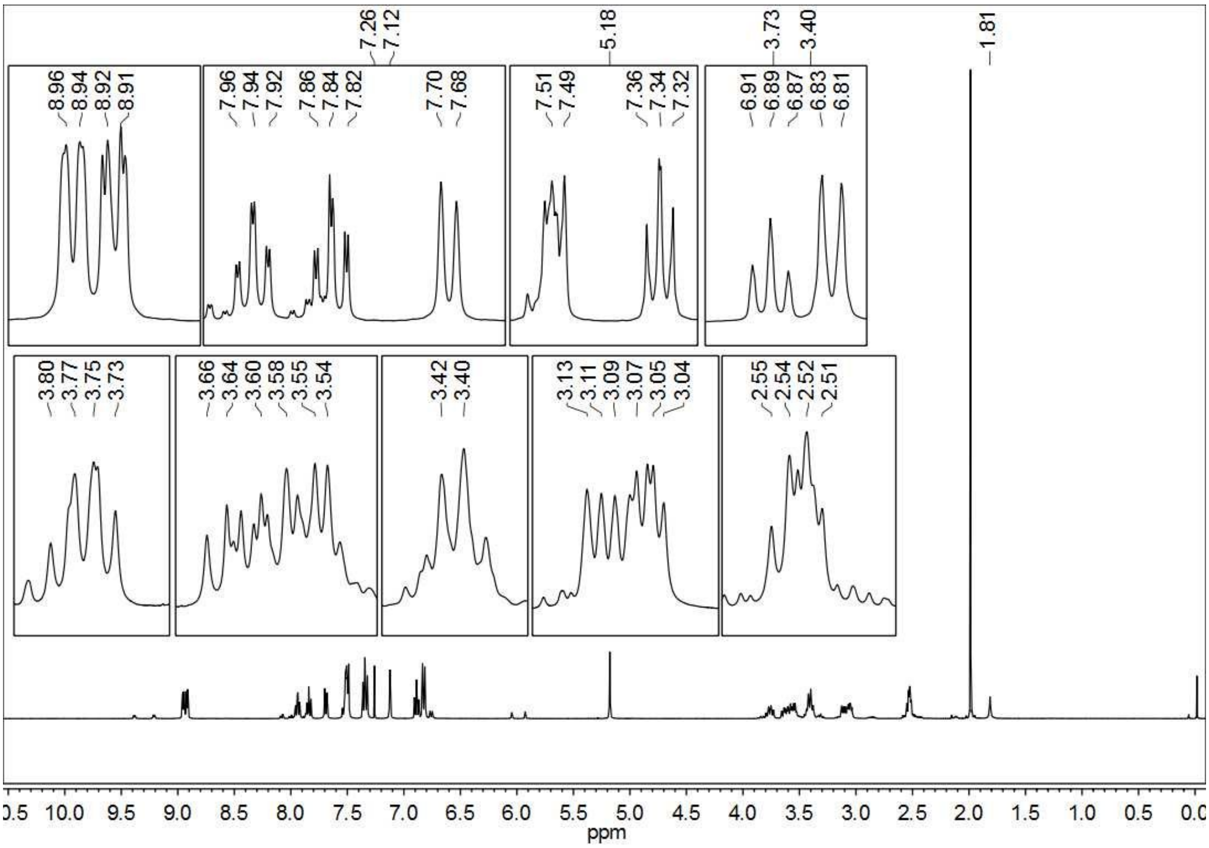
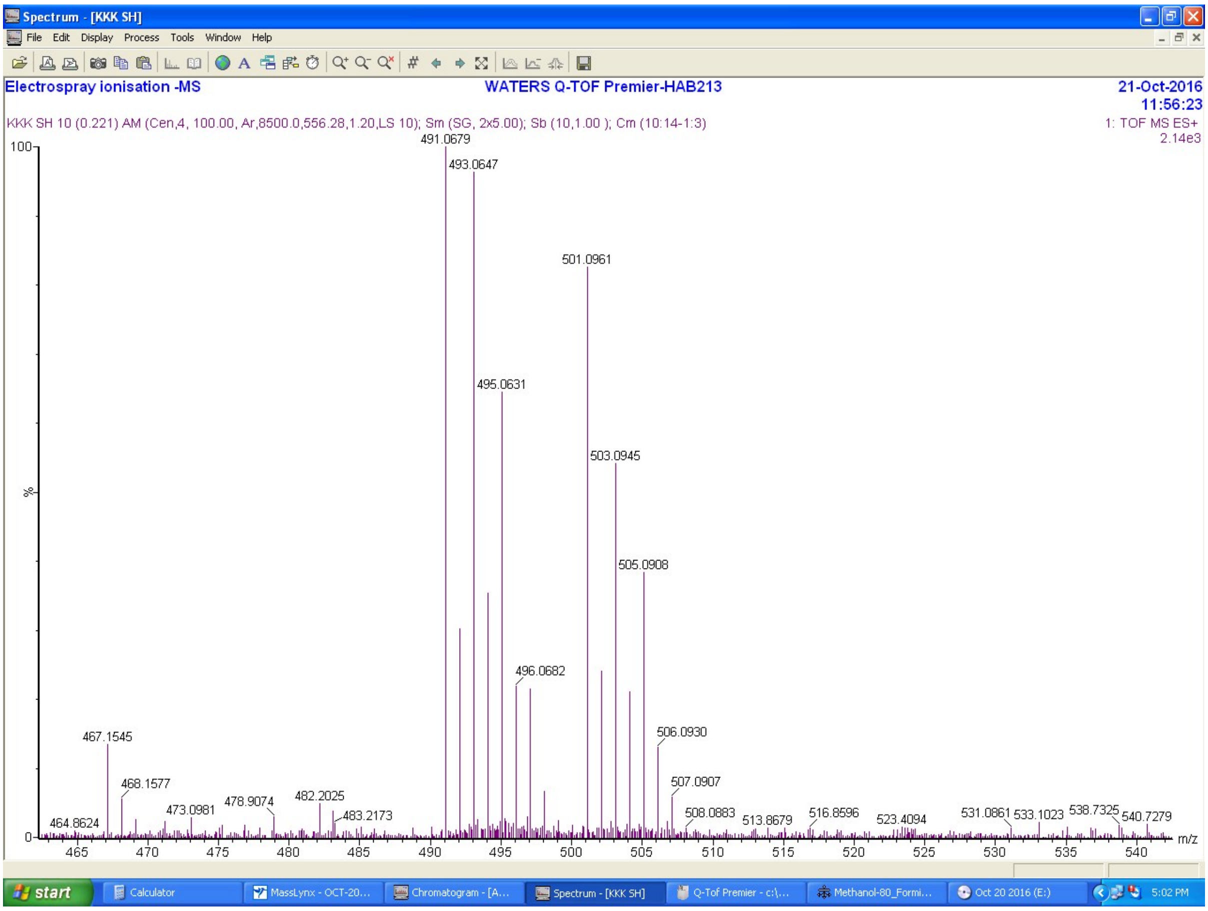


Figure S 17. ESI-MS of *anti*-[Zn($L^{Ph}SCH_2CH_2OH$)Cl_2].



Calculated *m/z* for [Zn($L^{Ph}SCH_2CH_2OH$)Cl]$^+$ = 491.0651; Observed *m/z* is 491.0679. Calculated *m/z* for [Zn($L^{Ph}SCH_2CH_2OH$)(HCOO)]$^+$ = 501.0939; Observed *m/z* is 501.0961. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

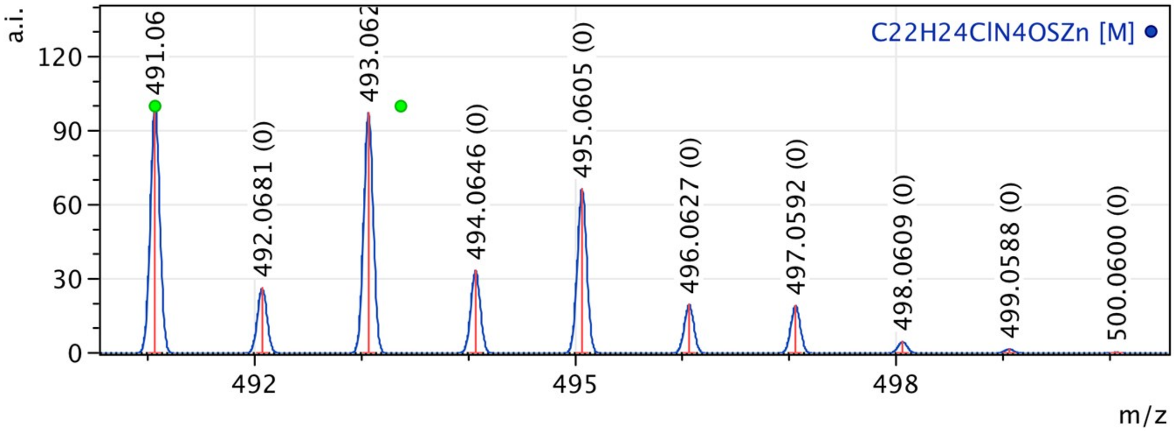
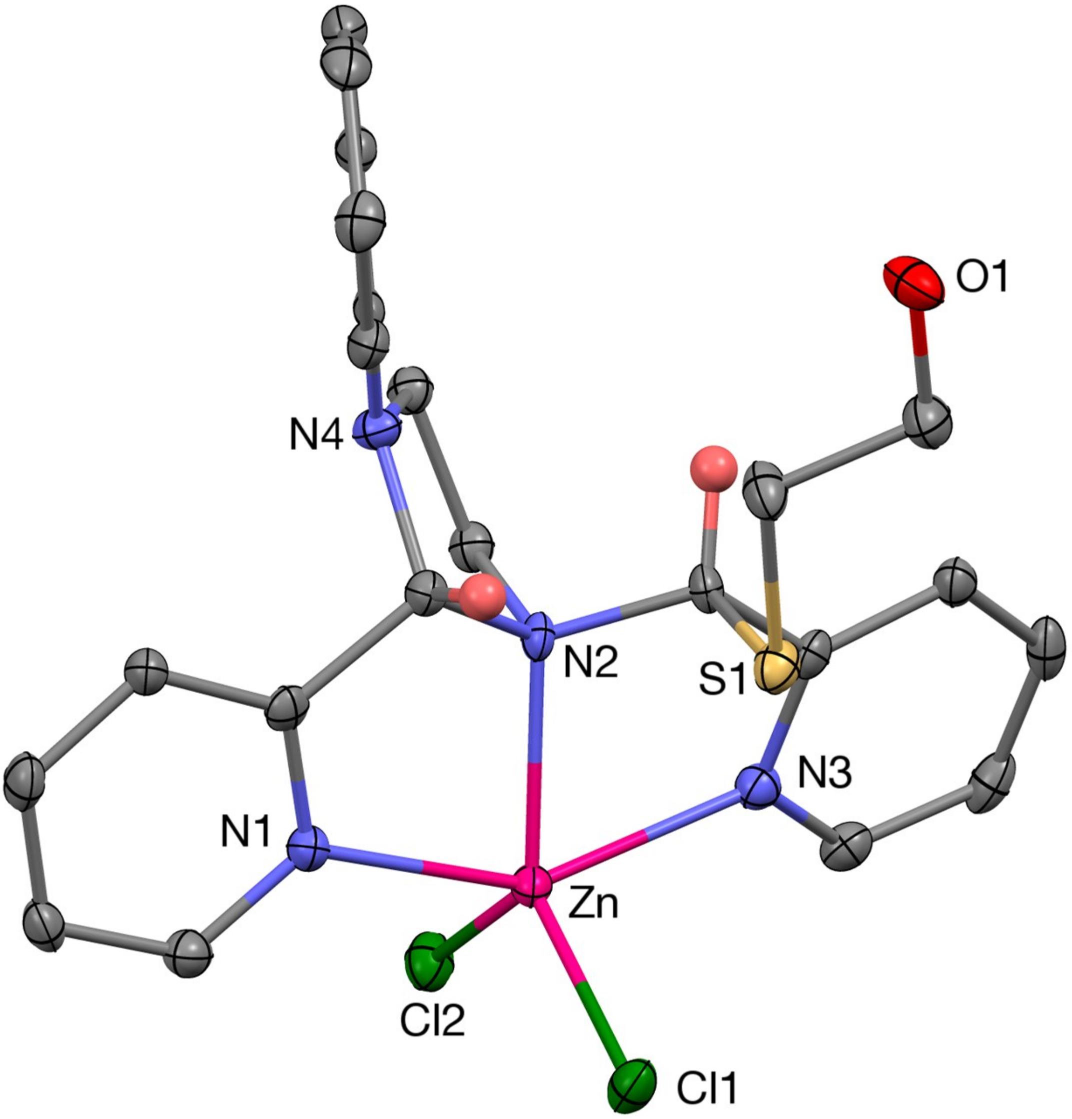


Figure S 18. ORTEP of *anti*-[Zn(L^{Ph}SCH$_2$CH$_2$OH)Cl$_2$]·CH$_3$CN.



CCDC-1534799. Solvated acetonitrile and hydrogens except those bound to the stereogenic centres are omitted for clarity. Selected bond distances (Å): Zn-N(1), 2.177(2); Zn-N(2), 2.171(2); Zn-N(3), 2.217(2); Zn-Cl(1), 2.2705(7); Zn-Cl(2), 2.2591(7). Selected angles (deg): N(2)-Zn-N(1), 75.18(7); N(2)-Zn-N(3), 73.98(8); N(1)-Zn-N(3), 149.12(8) = β; N(2)-Zn-Cl(2), 122.27(6); N(1)-Zn-Cl(2), 98.64(6); N(3)-Zn-Cl(2), 96.42(6); N(2)-Zn-Cl(1), 122.54(6) = α; N(1)-Zn-Cl(1), 98.46(6); N(3)-Zn-Cl(1), 99.24(6); Cl(2)-Zn-Cl(1), 115.17(3); C(15)-N(4)-C(6), 123.7(2); C(15)-N(4)-C(14), 121.0(2); C(6)-N(4)-C(14), 109.8(2). Addison-Reedijk trigonality index,[3] τ = 0.44. Angle between Py mean planes, π = 15.40°.

Table S 3. Crystallographic data of *anti*-$[Zn(L^{Ph}SCH_2CH_2OH)Cl_2]\cdot CH_3CN$.

Identification code	*anti*-$[Zn(L^{Ph}SCH_2CH_2OH)Cl_2]\cdot CH_3CN$	CCDC-1534799
Empirical formula	$C_{24}H_{27}Cl_2N_5OSZn$	
Formula weight	569.83	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.0819(5) Å	α = 105.8220(10)°
	b = 11.9997(6) Å	β = 92.123(2)°
	c = 12.4935(6) Å	γ = 108.5890(10)°
Volume	1230.09(11) $Å^3$	
Z	2	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	1.329 mm^{-1}	
F(000)	588	
Crystal size	0.32 x 0.17 x 0.09 mm^3	
Theta range for data collection	2.388 to 28.340°.	
Index ranges	-12<=h<=12, -16<=k<=16, -16<=l<=16	
Reflections collected	18510	
Independent reflections	6108 [R(int) = 0.0505]	
Completeness to theta = 25.500°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6467	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6108 / 0 / 313	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.0897	
R indices (all data)	R1 = 0.0767, wR2 = 0.1001	
Largest diff. peak and hole	0.691 and -0.387 $e.Å^{-3}$	

Figure S 19. ^{1}H NMR of *anti*-[Cd(L^{Ph}SCH$_2$CH$_2$OH)Cl$_2$]

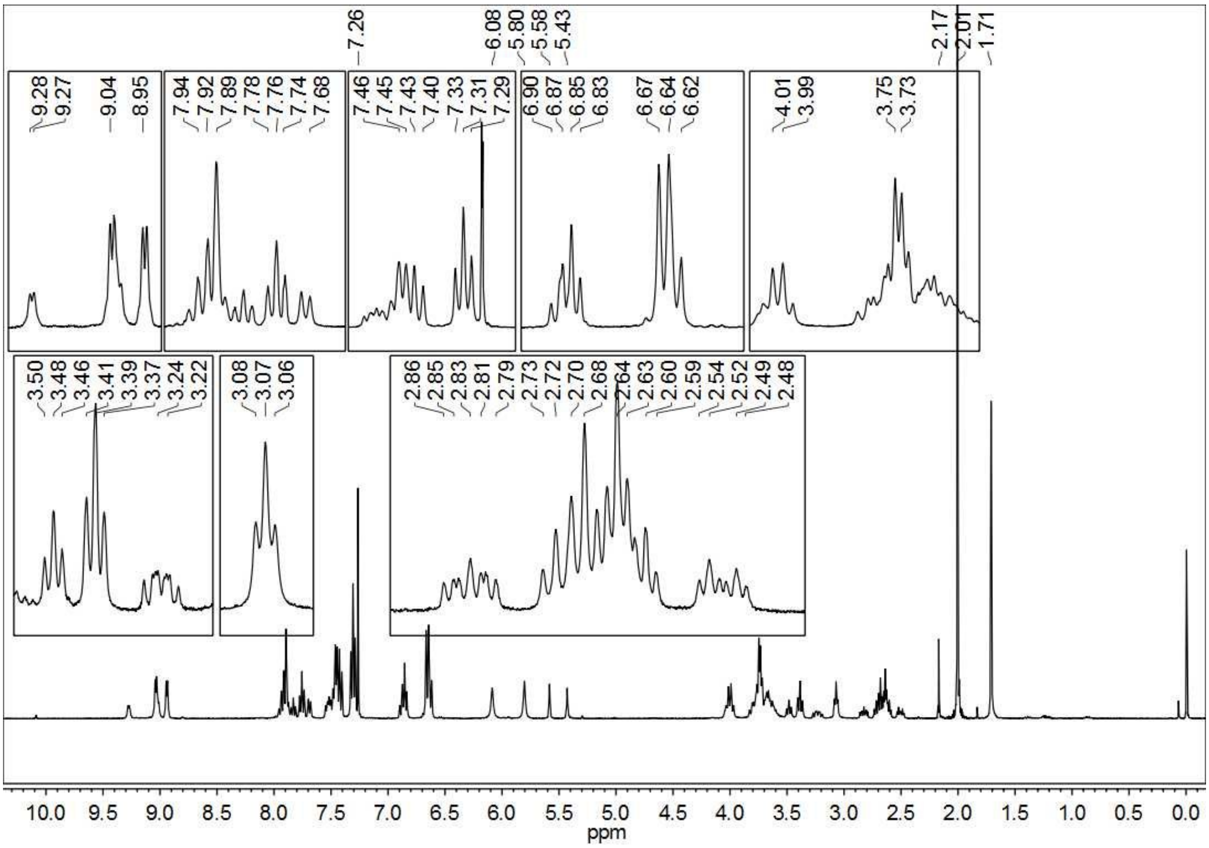
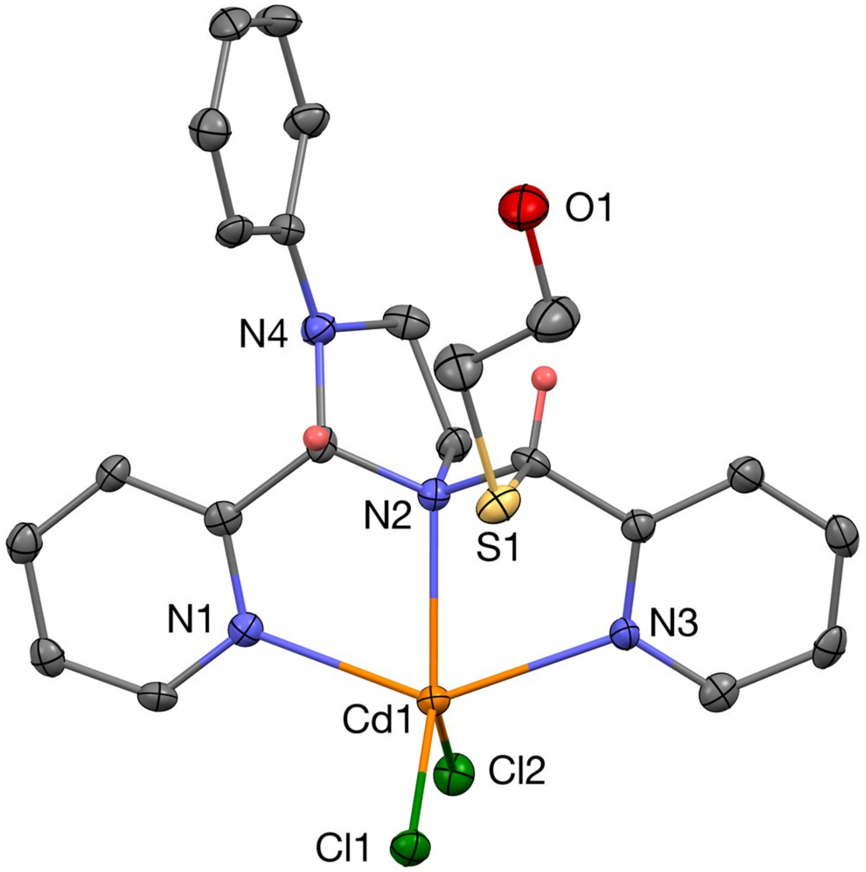


Figure S 20. ORTEP of *anti*-[Cd($L^{Ph}SCH_2CH_2OH$)Cl_2]·CH_3CN

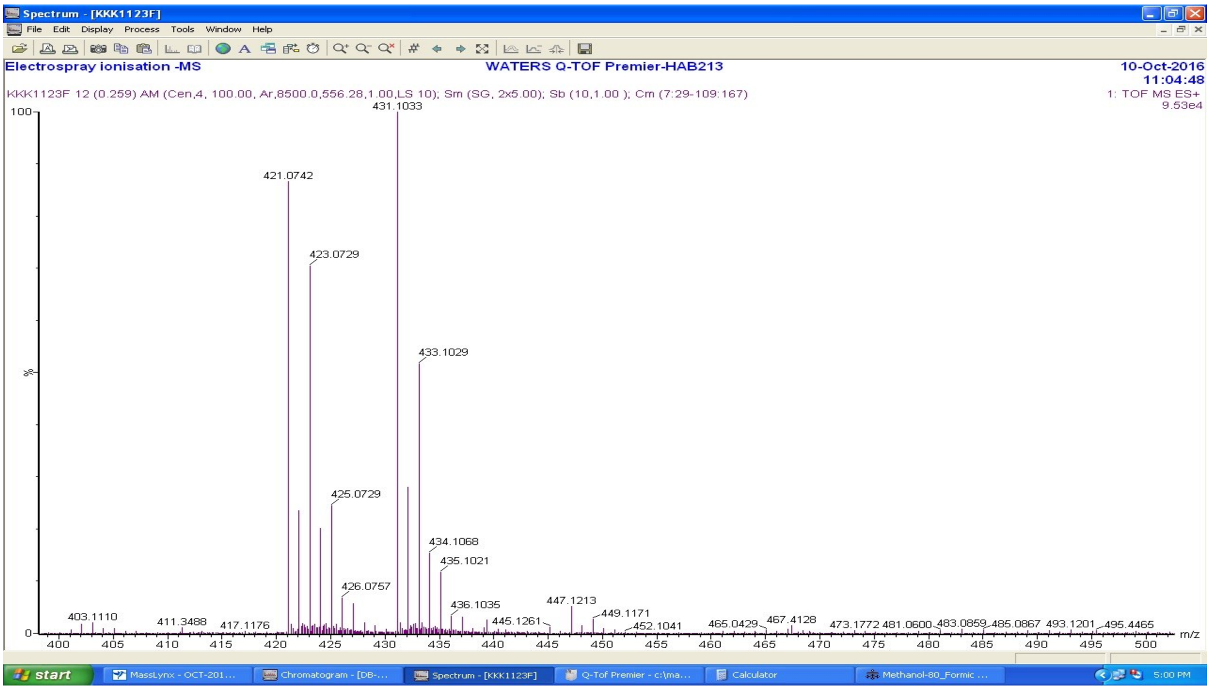


CCDC-1534798. Solvated acetonitrile and hydrogens except those bound to the stereogenic centres are omitted for clarity. Selected bond distances (Å): Cd(1)-N(1), 2.332(4); Cd(1)-N(3), 2.356(4); Cd(1)-N(2), 2.400(4); Cd(1)-Cl(2), 2.4319(13); Cd(1)-Cl(1), 2.4727(13). Selected angles (deg): N(1)-Cd(1)-N(3), 140.10(14); N(1)-Cd(1)-N(2), 70.05(14); N(3)-Cd(1)-N(2), 70.11(14); N(1)-Cd(1)-Cl(2), 101.54(11); N(3)-Cd(1)-Cl(2), 104.58(10); N(2)-Cd(1)-Cl(2), 128.38(11); N(1)-Cd(1)-Cl(1), 97.92(11); N(3)-Cd(1)-Cl(1), 97.59(10); N(2)-Cd(1)-Cl(1), 116.36(10); Cl(2)-Cd(1)-Cl(1), 115.23(5). Addison-Reedijk trigonality index,[3] $\tau = 0.42$. Angle between Py mean planes, $\pi = 16.40°$.

Table S 4. Crystallographic data for *anti*-$[Cd(L^{Ph}SCH_2CH_2OH)Cl_2]\cdot CH_3CN$

Identification code	*anti*-$[Cd(L^{Ph}SCH_2CH_2OH)Cl_2]\cdot CH_3CN$	CCDC-1534798
Empirical formula	C24 H27 Cd Cl2 N5 O S	
Formula weight	616.87	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.5375(12) Å	α= 90°.
	b = 14.0018(12) Å	β= 109.974(3)°.
	c = 15.3625(15) Å	γ = 90°.
Volume	2534.6(4) Å^3	
Z	4	
Density (calculated)	1.617 Mg/m^3	
Absorption coefficient	1.182 mm^{-1}	
F(000)	1248	
Crystal size	0.22 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.03 to 25.11°.	
Index ranges	-14<=h<=14, -16<=k<=16, -18<=l<=18	
Reflections collected	19979	
Independent reflections	4501 [R(int) = 0.0748]	
Completeness to theta = 25.11°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4501 / 0 / 309	
Goodness-of-fit on F^2	0.834	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1031	
R indices (all data)	R1 = 0.0775, wR2 = 0.1286	
Largest diff. peak and hole	0.758 and -0.512 e.Å^{-3}	

Figure S 21. ESI-MS of [Ni(L^{Et}SEt)Cl_2]



Calculated *m/z* for [Ni(L^{Et}SEt)Cl]$^+$ = 421.0764; Observed *m/z* is 421.0742;. Calculated *m/z* for [Ni(L^{Et}SEt)(HCOO)]$^+$ = 431.1052; Observed *m/z* is 431.1033. Formate must have originated from the acetonitrile solution (with 0.1% HCOOH) used to infuse the sample.

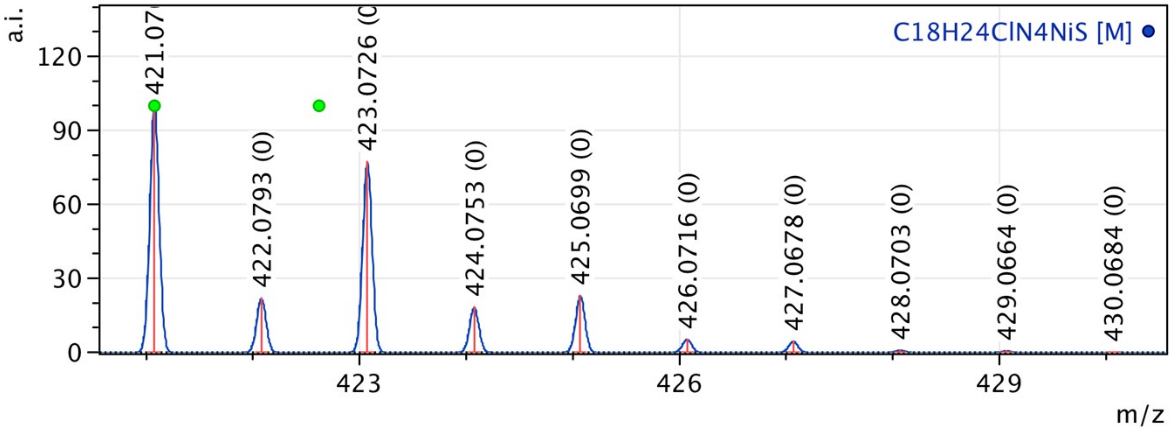
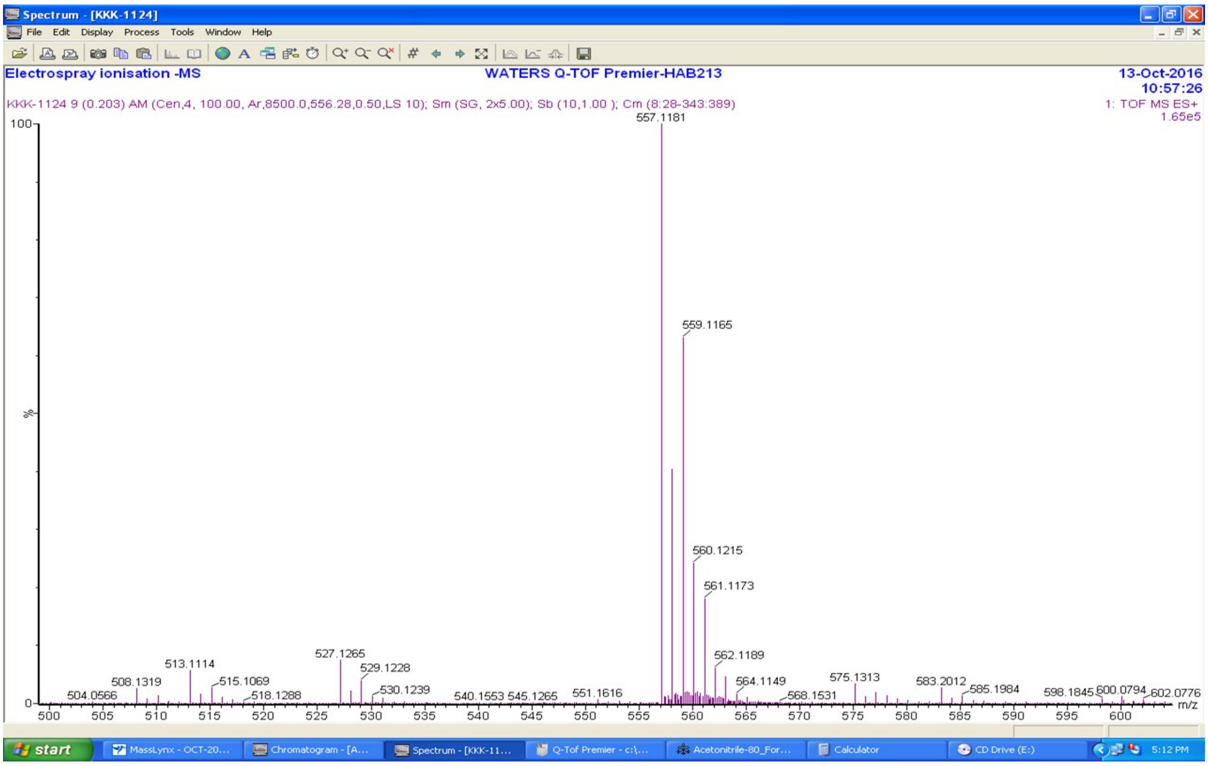


Figure S 22. ESI-MS of [Ni(L^{Et}SEt)(OTs)$_2$]



Spectrum - [KKK-1124]

Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

13-Oct-2016
10:57:26

KKK-1124 9 (0.203) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.50,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (8:28-343:389)

1: TOF MS ES+
1.65e5

Calculated *m/z* for [Ni(L^{Et}SEt)(OTs)]$^+$ = 557.1191; Observed *m/z* is 557.1181.

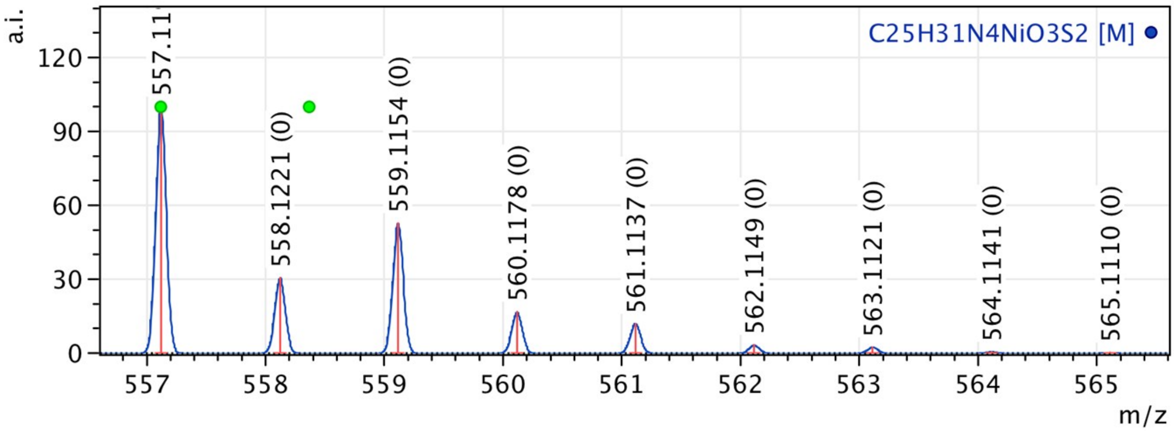


Figure S 23. DFT optimised[4] structure of *syn-equatorial*-[Ni(L^{Et}SEt)Cl](Cl)(H_2O).

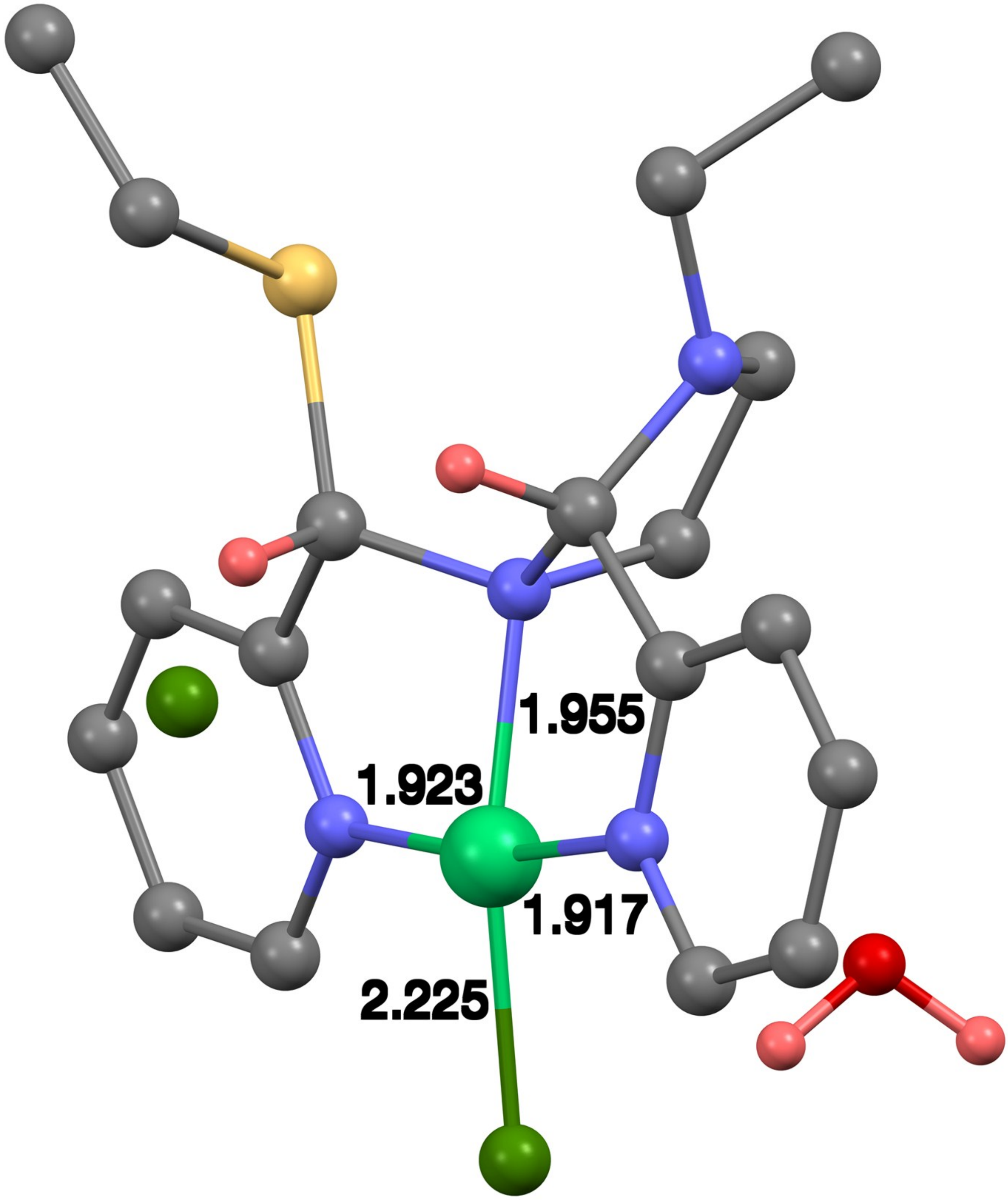


Table S 5. Cartesian coordinates of the optimized[4] *syn-equatorial*-[Ni(L^{Et}SEt)Cl$_2$].

syn-equatorial : Total Energy = -3822.768700 Ha			
17	-3.539060000	1.208721000	0.316341000
17	0.205365000	0.031235000	2.947126000
7	-1.823546000	-1.337264000	0.453085000
7	0.322730000	-0.099192000	-0.463389000
7	-0.703518000	2.268017000	-0.154961000
7	1.294638000	-2.202489000	-1.063279000
6	-3.011922000	-1.857894000	0.822551000
6	-3.182573000	-3.217875000	1.046228000
6	-2.097043000	-4.075299000	0.864469000
6	-0.874346000	-3.534421000	0.480938000
6	-0.763245000	-2.156964000	0.303081000
6	0.578394000	-1.507000000	-0.001433000
6	1.264854000	0.927631000	0.112119000
6	0.654174000	2.275452000	-0.174039000
6	1.365006000	3.462550000	-0.347178000
6	0.666232000	4.658147000	-0.502906000
6	-0.727503000	4.638307000	-0.484550000
6	-1.378602000	3.422669000	-0.309335000
6	0.326593000	-0.217353000	-1.968478000
6	1.274721000	-1.385532000	-2.285393000
6	3.774184000	0.340090000	1.329583000
6	5.252906000	0.719952000	1.352687000
1	-3.821005000	-1.148967000	0.934852000
1	-0.004416000	-4.159069000	0.317528000
1	1.127784000	-1.464823000	0.944993000
1	1.163070000	0.763360000	1.214116000
1	2.447146000	3.430201000	-0.357790000
1	1.205899000	5.590721000	-0.637124000
1	-1.312092000	5.544177000	-0.599747000
1	-2.457270000	3.341769000	-0.276146000
1	0.643150000	0.728171000	-2.411121000
1	-0.694229000	-0.419228000	-2.300787000
1	0.909484000	-1.952561000	-3.149533000
1	2.285643000	-1.022005000	-2.514165000
1	3.644309000	-0.732700000	1.492838000
1	3.211539000	0.863500000	2.105483000
1	5.688836000	0.425087000	2.313154000
1	5.389097000	1.799269000	1.233256000
1	5.817703000	0.215917000	0.560806000
1	-4.154047000	-3.588078000	1.354007000
1	-2.201572000	-5.144621000	1.021951000
16	3.042260000	0.793796000	-0.312846000
28	-1.432536000	0.513869000	0.142153000
1	-3.333682000	0.555326000	-1.952512000
1	-3.750819000	0.034137000	-3.348189000
8	-2.980460000	0.230617000	-2.801737000
6	2.577660000	-2.831381000	-0.736309000
1	3.397464000	-2.093615000	-0.756233000
1	2.510395000	-3.216710000	0.286484000
6	2.905019000	-3.983695000	-1.689074000
1	3.855239000	-4.449564000	-1.406114000
1	2.120491000	-4.747153000	-1.665668000
1	3.004051000	-3.633607000	-2.722095000

Figure S 24. DFT optimised[4] structure of *anti-facial*-[Ni(L^{Et}SEt)Cl$_2$].

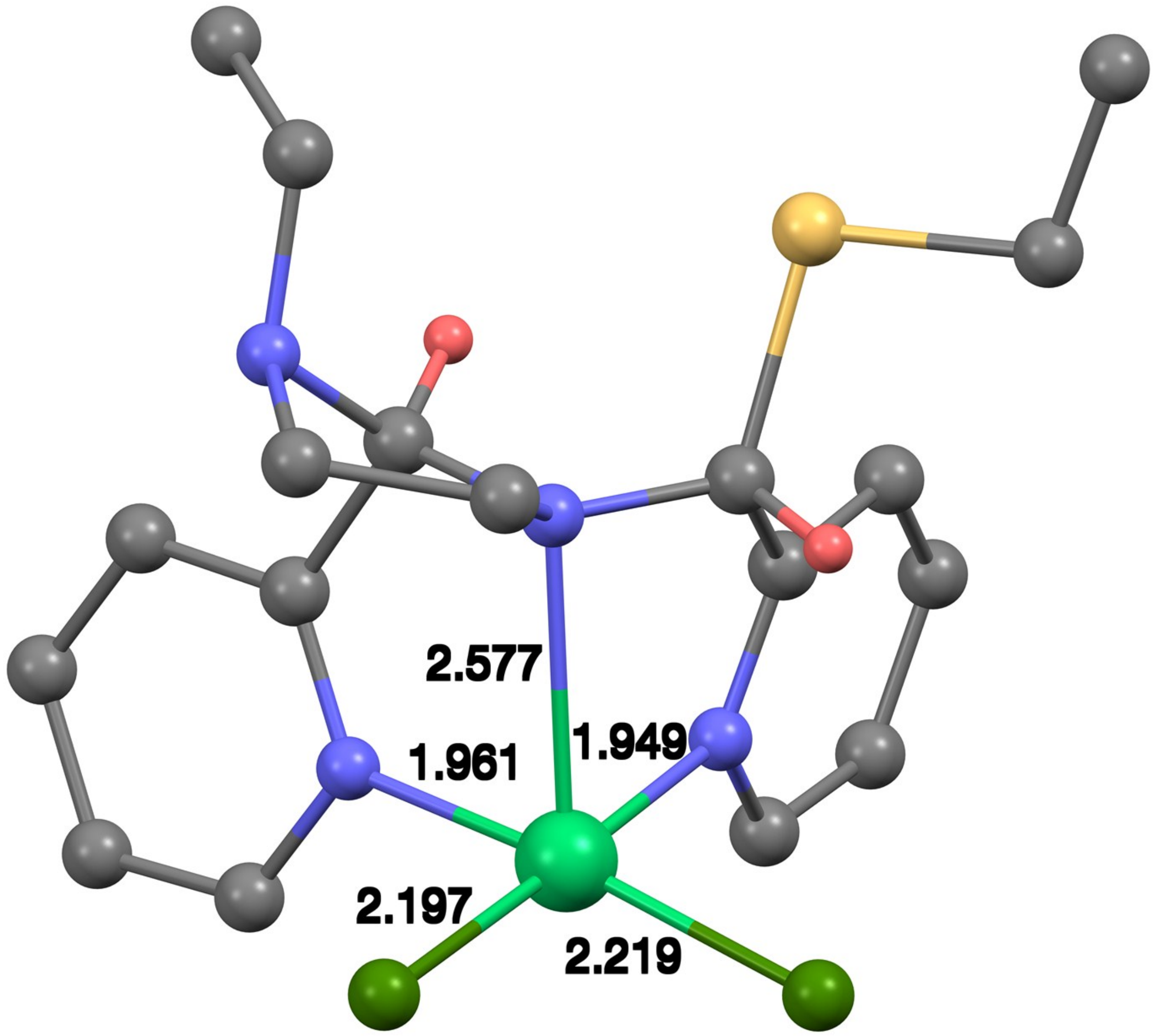


Table S 6. Cartesian coordinates of the optimized[4] *anti-facial*-[Ni(L^{Et}SEt)Cl$_2$].

anti-facial : Total Energy = -3822.767625 Ha			
8	-2.570315000	-2.307549000	-2.197461000
1	4.379286000	2.921697000	1.947955000
1	2.020630000	3.392421000	1.259489000
1	-0.291616000	2.041726000	1.005078000
1	-1.834848000	-0.852630000	-0.621214000
1	-2.580417000	-0.333146000	2.633817000
1	-1.669265000	-1.710860000	4.514342000
1	0.499093000	-2.947874000	4.159348000
1	1.635790000	-2.720280000	1.945988000
1	-0.380716000	0.177094000	-2.661553000
1	-1.695553000	1.293641000	-2.180223000
1	-0.849031000	4.447191000	-1.597885000
1	-1.817037000	3.325341000	-0.636700000
1	-1.494653000	5.471649000	0.562599000
1	-0.674302000	4.200613000	1.464354000
1	0.271262000	5.310809000	0.450553000
1	-4.074697000	-0.876693000	-0.820510000
1	-4.412272000	-1.001026000	0.913395000
7	2.209714000	0.196899000	0.264032000
7	-0.439824000	0.640865000	-0.591994000
7	0.216101000	-1.448424000	1.157452000
7	0.281368000	2.885139000	-0.844396000
6	3.500071000	-0.050363000	0.585323000
6	4.310897000	0.891633000	1.199595000
6	3.775779000	2.153283000	1.474266000
6	2.462008000	2.414353000	1.108374000
6	1.691323000	1.413341000	0.501446000
6	0.244860000	1.754591000	0.092712000
6	-1.490557000	-0.078858000	0.074104000
6	-0.960958000	-0.800610000	1.314858000
6	-1.652526000	-0.880824000	2.526324000
6	-1.136056000	-1.645811000	3.570663000
6	0.064639000	-2.328221000	3.382773000
6	0.707342000	-2.201176000	2.156708000
6	-0.648601000	1.010127000	-2.006550000
6	0.301390000	2.206493000	-2.160254000
6	-0.841492000	3.834246000	-0.690703000
6	-0.668893000	4.753584000	0.518016000
6	-4.362895000	-0.307943000	0.067278000
17	0.308876000	-3.234220000	-1.138749000
17	2.415583000	-1.117819000	-2.340777000
1	-2.579033000	-2.328179000	-3.162187000
1	-1.718695000	-2.719927000	-1.942380000
1	3.873082000	-1.030452000	0.312623000
1	5.338028000	0.641917000	1.441666000
1	1.315735000	1.849576000	-2.365725000
1	0.008468000	2.897257000	-2.953174000
28	1.230456000	-1.319281000	-0.501537000
16	-3.044450000	0.948111000	0.390596000
6	-5.707923000	0.389793000	-0.130192000
1	-5.680621000	1.065933000	-0.990319000
1	-6.487448000	-0.358771000	-0.310002000
1	-5.997960000	0.970944000	0.751699000

Figure S 25. DFT optimised[4] structure of *anti-equatorial*-[Ni(L^{Et}SEt)Cl_2].

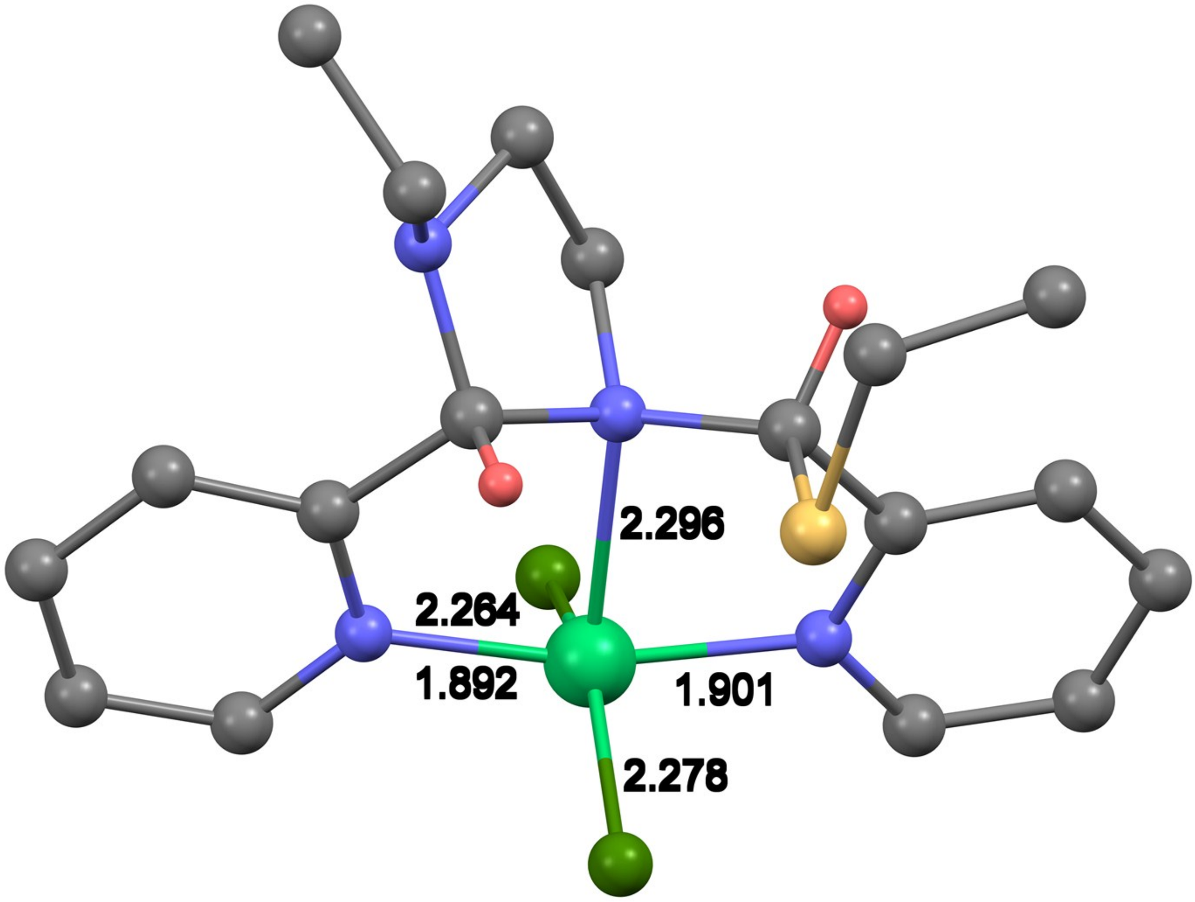


Table S 7. Cartesian coordinates of the optimized[4] *anti-equatorial*-$[\mathrm{Ni}(\mathrm{L}^{\mathrm{Et}}\mathrm{SEt})\mathrm{Cl}_2]$.

anti-equatorial : Total Energy = -3822.760305 Ha			
17	0.533169000	-1.401489000	2.336379000
17	0.393265000	-2.853301000	-1.816532000
16	1.162114000	1.959378000	1.401523000
7	-1.530364000	-1.672816000	0.168580000
7	-0.032510000	0.503794000	-0.734755000
7	2.170091000	-1.084015000	-0.161870000
7	-2.038644000	1.740031000	-1.060923000
6	-2.219075000	-2.813074000	0.353179000
6	-3.606740000	-2.837785000	0.371446000
6	-4.295869000	-1.641024000	0.169229000
6	-3.573978000	-0.469732000	-0.037571000
6	-2.178362000	-0.504670000	-0.022477000
6	-1.353146000	0.794476000	-0.152606000
6	1.203579000	1.197016000	-0.290419000
6	2.389642000	0.231758000	-0.364595000
6	3.680478000	0.701157000	-0.625566000
6	4.747524000	-0.191169000	-0.652302000
6	4.503247000	-1.545516000	-0.417802000
6	3.196027000	-1.952440000	-0.183680000
6	-0.275243000	0.648019000	-2.189470000
6	-1.225575000	1.851850000	-2.279756000
6	1.147902000	3.755931000	0.987944000
6	2.486471000	4.346343000	0.545838000
1	-1.622289000	-3.708926000	0.473018000
1	-4.126693000	-3.775890000	0.530435000
1	-5.381565000	-1.621699000	0.168796000
1	-4.070032000	0.474485000	-0.220265000
1	-1.242583000	1.205475000	0.856259000
1	1.429810000	2.035023000	-0.961891000
1	3.839304000	1.760781000	-0.793810000
1	5.753381000	0.163815000	-0.854881000
1	5.302236000	-2.278249000	-0.427609000
1	2.933750000	-2.991268000	-0.025281000
1	-0.742227000	-0.271456000	-2.555068000
1	0.661071000	0.778522000	-2.735473000
1	-0.657445000	2.800954000	-2.284743000
1	-1.836877000	1.826265000	-3.188222000
1	0.364243000	3.949023000	0.249246000
1	0.819415000	4.221369000	1.923306000
1	2.393859000	5.431247000	0.414551000
1	2.819358000	3.930474000	-0.411400000
1	3.266416000	4.154150000	1.288516000
6	-2.491457000	3.002567000	-0.479827000
1	-1.650791000	3.710583000	-0.342338000
1	-2.891516000	2.790183000	0.516792000
6	-3.569476000	3.678450000	-1.329439000
1	-4.433396000	3.018302000	-1.458272000
1	-3.906484000	4.603321000	-0.848864000
1	-3.193770000	3.939460000	-2.324494000
28	0.358023000	-1.608836000	0.074857000
1	-1.978792000	0.705908000	4.019206000
1	-1.271838000	-0.164337000	2.961767000
8	-2.040010000	0.427421000	3.097874000

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