The Synthesis of Novel Salicylaldimine Ditopic Type Ligands for the Extraction of Transition Metal Salts

Honours Research Project

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Supplementary Information

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1. Experimental

1.1 General Considerations

Solvents and reagents

All chemicals were used as received.

The following chemicals used in these experiments were purchased from Associated Chemical Enterprises:

$Ni(NO_3)_2 \cdot 6H_2O$; $ZnSO_4 \cdot 7H_2O$;

The following chemicals used in these experiments were purchased from Fluka:

$Cd(NO_3)_2 \cdot 4H_2O$; HNO_3; HCl

The following chemicals used in these experiments were purchased from Merck:

Chloroform; ethanol; diethyl ether; DMF; $Co(NO_3)_2 \cdot 6H_2O$; $CuSO_4 \cdot 5H_2O$; $Cu(CH_3COO)_2 \cdot H_2O$; $NaH_2PO_4 \cdot 2H_2O$; Na_2HPO_4

The following chemical used in these experiments was purchased from NT Laboratory Supplies:

CH_3COONa;

The following chemicals used in these experiments were purchased from Riedel-de Haën:

Methanol; 2-propanol; $Zn(NO_3)_2 \cdot 6H_2O$;

The following chemicals used in these experiments were purchased from SAARChem:

K_2CO_3(anhydrous); $Pb(NO_3)_2$; $Cu(NO_3)_2 \cdot 3H_2O$; $Cu(Cl)_2 \cdot 2H_2O$

The following chemicals used in these experiments were purchased from Scienceworld:

N-Hexane; CH_3COOH;

The following chemicals used in these experiments were purchased from Sigma-Aldrich:

Piperidine; 5-tert-butyl-2-hydroxybenzaldehyde; 1,3-diaminopropane; deuterated chloroform; Paraformaldehyde; dihexylamine;

The following chemical used in these experiments was purchased from Unilab:

$NiSO_4 \cdot 7H_2O$;

Instruments

All ^{1}H and ^{13}C nuclear magnetic resonance spectra were obtained using a 300 MHz Varian VNMRS, 400 MHz Varian Unity Inova or 600 MHz Varian Unity Inova NMR instrument using deuterated solvents. Chemical shifts (δ) were recorded using the residual solvent peak or external reference (TMS). All chemical shifts are reported in parts per million and all spectra were obtained at 25 °C. Data was processed using ACD/SpecManager product version 12.01.

Melting points were obtained using a Stuart Scientific Melting Point Apparatus in open capillaries. Infrared spectra were obtained using a Nicolet Avatar 330 FT-IR instrument as neat samples (ATR). High resolution mass spectrometry was performed by CAF (Central Analytical Facility) at Stellenbosch University using a Waters Synapt G2 spectrometer. Metal analysis by ICP-AES was performed by CAF (Central Analytical Facility) at Stellenbosch University using a Thermo Scientific iCAP 6000 Series instrument. Ion chromatography data was obtained on a DIONEX DX-120 instrument. Single crystal data was collected on a Bruker SMART Apex CCD diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The temperature of the crystals was controlled using an Oxford Cryostream Cooler. Data reduction was carried out by means of a standard procedure using the Bruker software package SAINT. [1] Where necessary, systematic errors in the intensity data were corrected by using SADABS. [2,3] File preparation was done with XPrep and structures were solved by direct methods or a combination of Patterson and partial structure expansion using SHELXS-97. [4] In most cases, all non-hydrogen atoms were located using either of these methods. All ordered non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations of F^2 using SHELXL-97 [4] within the X-Seed [5] environment. Where appropriate, the hydrogen atoms were placed in calculated positions using riding models and assigned isotropic thermal parameters 1.2 times those of their parent atoms.

1.2 Procedures and characterisation data

Ligand 1 (L1)

The ligand is prepared by a standard method in which 2 equivalents (3.00 g, 16.8 mmol) of 5-tert-butyl-2-hydroxy-benzaldehyde and 1 equivalent of propylenediamine (0.620 g, 8.42 mmol) are refluxed for 1.5 h in absolute ethanol (50 cm^3). Upon cooling and reduction of the volume a yellow powder (3.19 g, 96.1 %) is obtained. Mp 76.0 – 76.9 °C; IR (neat): 2953 (m, CH), 1632 (m, C=N), 1581 (m, C=C), 1486 (s, CH), 1270 cm^{-1} (s, C-N); ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 1.31 (s, 18 H, $C(CH_3)_3$), 2.07 - 2.14 (quin, *J*=6.64 Hz, 2 H, NCH_2CH_2), 3.69 – 3.73 (t, *J*=6.64 Hz, 4 H, NCH_2CH_2), 6.92 – 6.94 (d, *J*=8.50 Hz, 2 H, Ar*H*), 7.24 – 7.25 (d, *J*=2.28 Hz, 2 H, Ar*H*), 7.35 – 7.38 (dd, *J*=2.49 Hz, 2 H, Ar*H*), 8.39 (s, 2 H, NC*H*), 13.23 (s, 2 H, O*H*); ^{13}C NMR (400 MHz,

CHLOROFORM-*d*) δ ppm 31.08 (C(*C*H_3)$_3$), 31.47 (NCH$_2$*C*H$_2$), 33.60 (*C*(CH$_3$)$_3$), 56.44 (N*C*H$_2$CH$_2$), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 129.21 (C_{Ar}H), 140.94 (C_{Ar}C(CH$_3$)$_3$), 158.40 (C_{Ar}OH), 165.41(Ar*C*N); MS (ES+): *m/z* (%) = 395.3 (30) $[M + H]^+$, 396.3 (10) $[M + 2H]^+$; MS (ES-): *m/z* (%) 393.3 (100) $[M - 2H]^+$; 394.3 (30) $[M - H]^+$;

1-(ethoxymethyl)piperidine

Piperidine (21.3 g, 0.250 mol) was added dropwise to a suspension of paraformaldehyde (30.0 g, 0.313 mol) and anhydrous potassium carbonate (69.1 g, 0.500 mol) in absolute ethanol (150 cm^3) with external cooling in an icebath. The mixture was then stirred vigorously for 48h allowing the temperature to reach ambient gradually. The solid was then filtered off and washed with dried diethyl ether (2 × 35 cm^3). The filtrate was then concentrated *in vacuo* to give a colourless non-viscous liquid which was fractionally distilled through a 30 cm Vigreaux column affording the product (10.1 g, 28.1%). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 1.15 - 1.20 (t, *J*=7.04 Hz, 3 H, OCH$_2$C*H*$_3$), 1.41 – 1.45 (m, 2 H, NCH$_2$CH$_2$C*H*$_2$), 1.52 – 1.58 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$), 2.61 – 2.65 (m, 4 H, NC*H*$_2$CH$_2$CH$_2$), 3.44 – 3.51 (q, *J*=7.04 Hz, 2 H, OC*H*$_2$CH$_3$), 4.04 (s, 2 H, NC*H*$_2$O).

5-tert-butyl-2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde

A mixture of 5-tert-butyl-2-hydroxybenzaldehyde (3.00 g, 16.8 mmol) and 1-(ethoxymethyl)-piperidine (2.68 g, 18.7 mmol) in acetonitrile (70 cm^3) was heated to reflux under a dinitrogen atmosphere for 72h. After cooling to room temperature the solvent was removed *in vacuo* to yield the product (4.38 g, 93.6%) as a yellow powder. ^{1}H NMR (600 MHz, CHLOROFORM-*d*) δ ppm 1.26 (s, 9 H, C(C*H*$_3$)$_3$), 1.50 – 1.53 (m, 2 H, NCH$_2$CH$_2$C*H*$_2$), 1.62 – 1.66 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$), 2.40 – 2.69 (m, 4 H, NC*H*$_2$CH$_2$CH$_2$), 3.69 (s, 2 H, NC*H*$_2$Ar), 7.23 (d, *J*=2.64 Hz, 1 H, Ar*H*), 7.64 (d, *J*=2.64 Hz, 1 H, Ar*H*), 10.4 (s, 1 H, C*H*O), 11.39 (s, 1 H, O*H*); ^{13}C NMR (600 MHz, CHLOROFORM-*d*) δ ppm 24.02 (NCH$_2$CH$_2$*C*H$_2$), 25.89 (NCH$_2$*C*H$_2$CH$_2$), 31.47 (C(*C*H$_3$)$_3$), 34.22 (*C*(CH$_3$)$_3$), 54.06 (N*C*H$_2$CH$_2$CH$_2$), 61.60 (ArN*C*H$_2$), 122.55 (C_{Ar}), 122.99 (C_{Ar}), 123.90 (C_{Ar}H), 132.41 (C_{Ar}H), 141.60 (C_{Ar}C(CH$_3$)$_3$), 160.14 (C_{Ar}OH), 191.22 (Ar*C*HO);

Ligand 2 (L2)

The ligand is prepared by a standard method in which 2 equivalents (3.00 g, 10.9 mmol) of 5-tert-butyl-2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde and 1 equivalent of propylenediamine (0.404 g, 5.45 mol) are refluxed for 1.5 h in absolute ethanol (50 cm^3). Upon cooling and reduction of the

volume a sticky yellow solid (3.08 g, 96.0 %) is obtained. Mp 72.0 – 72.9 °C; IR (neat): 2930 (m, CH), 1629 (s, C=N), 1582 (m, C=C), 1463 (s, CH), 1270 cm^{-1} (s, C-N); ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 1.34 (s, 18 H, C(C*H*$_3$)$_3$), 1.42 – 1.50 (m, 4 H, NCH$_2$CH$_2$C*H*$_2$), 1.60 – 1.67 (m, 8 H, NCH$_2$C*H*$_2$CH$_2$), 2.08 – 2.13 (m, 2 H, NCH$_2$C*H*$_2$), 2.50 (m, 8 H, NC*H*$_2$CH$_2$CH$_2$), 3.63 (s, 4 H, (NC*H*$_2$Ar), 3.69 – 3.74 (t, *J*=6.54 Hz, 4 H, NC*H*$_2$CH$_2$), 7.23 – 7.24 (d, *J*=2.34 Hz, 2 H, Ar*H*), 7.42 – 7.43 (d, *J*=2.49 Hz, 2 H, Ar*H*), 8.44 (s, 2 H, NC*H*), 13.27 (s, 2 H, O*H*); ^{13}C NMR (300 MHz, CHLOROFORM-*d*) δ ppm 24.32 (NCH$_2$CH$_2$*C*H$_2$), 25.95 (NCH$_2$*C*H$_2$CH$_2$), 31.42 (C(*C*H$_3$)$_3$), 31.81(*C*(CH$_3$)$_3$), 33.89 (NCH$_2$*C*H$_2$), 54.41 (N*C*H$_2$CH$_2$CH$_2$), 56.98 (N*C*H$_2$CH$_2$), 57.27 (Ar*C*H$_2$N), 117.99 (*C*$_{Ar}$), 124.78 (*C*$_{Ar}$), 125.89 (*C*$_{Ar}$H), 130.57 (*C*$_{Ar}$H), 140.51 (*C*$_{Ar}$C(CH$_3$)$_3$), 157.21 (*C*$_{Ar}$OH), 165.01 (Ar*C*N); MS (ES+): *m/z* (%) = 589.4 (12) [M + H]$^+$; MS (ES-): *m/z* (%) 587.4 (100) [M - H]$^+$, 588.4 (43) [M]$^+$;

N-(ethoxymethyl)-N-hexylhexan-1-amine

Dihexylamine (23.2 g, 0.125 mol) was added dropwise to a suspension of paraformaldehyde (4.69 g, 0.156 mol) and anhydrous potassium carbonate (34.6 g, 0.250 mol) in absolute ethanol (75 cm^3) with external cooling in an icebath. The mixture was then stirred vigorously for 48h allowing the temperature to reach ambient gradually. The solid was then filtered off and washed with dried diethyl ether (2 × 25 cm^3). The filtrate was then concentrated *in vacuo* to give a colourless oil which was fractionally distilled through a Kugelrohr vacuum distillation apparatus affording the product (18.9 g, 62.2 %). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.86 – 0.91 (m, 6 H, C*H*$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$N), 1.16 – 1.20 (t, *J*=7.16 Hz, 3 H, OCH$_2$C*H*$_3$), 1.26 – 1.34 (m, 12 H, CH$_3$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_2$N), 1.40 – 1.47 (m, 4 H, CH$_3$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$N), 2.59 – 2.64 (m, 4 H, CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$N), 3.41 – 3.48 (q, *J*=7.01 Hz, 2 H, OC*H*$_2$CH$_3$), 4.15 (s, 2 H, OC*H*$_2$N);

5-tert-butyl-3-[(dihexylamino)methyl]-2-hydroxybenzaldehyde

A mixture of 5-tert-butyl-2-hydroxybenzaldehyde (3.49 g, 19.6 mmol) and N-(ethoxymethyl)-N-hexylhexan-1-amine (5.00 g, 20.5 mmol) in acetonitrile (75 cm^3) was heated to reflux under a dinitrogen atmosphere for 72h. After cooling to room temperature the solvent was removed *in vacuo* to yield the product (7.35 g, 99.1 %) as a dark yellow oil. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ ppm 0.83 – 0.86 (m, 6 H, C*H*$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$N), 1.26 (m, 20 H, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$CH$_2$CH$_2$N & C(C*H*$_3$)$_3$), 1.50 – 1.54 (m, 4 H, CH$_3$CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$N) 2.48 – 2.52 (m, 4 H, CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$N), 3.77 (s, 2 H, NC*H*$_2$Ar), 7.24 – 7.25 (d, *J*=2.49 Hz, 1 H, Ar*H*), 7.62 – 7.63 (d, *J*=2.49 Hz, 1 H, Ar*H*), 10.40 (s, 1 H, C*H*O), 11.78 (s, 1 H, O*H*); ^{13}C NMR (400 MHz,

CHLOROFORM-*d*) δ ppm 13.91 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 22.45 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 26.14 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 26.91 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 31.24 ($C(CH_3)_3$), 31.53 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 33.98 ($C(CH_3)_3$), 53.43 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 57.31 ($ArCH_2N$), 122.28 ($C_{Ar}CH_2$), 123.42 ($C_{Ar}$), 123.58 ($C_{Ar}$), 132.06 ($C_{Ar}$), 141.27 ($C_{Ar}C(CH_3)_3$), 160.06 ($C_{Ar}OH$), 191.01 (Ar*C*HO);

Ligand 3 (L3)

The ligand is prepared by a standard method in which 2 equivalents (3.50 g, 9.32 mmol) of 5-tert-butyl-3-[(dihexylamino)-methyl]-2-hydroxy-benzaldehyde and 1 equivalent of propylenediamine (0.345 g, 4.66 mmol) are refluxed for 1.5 h in absolute ethanol (50 cm^3). Upon cooling and reduction of the volume an orange oil (3.42 g, 92.9 %) is obtained. IR (neat): 2855 - 2953 (s, CH), 1632 (s, C=N), 1588 (m, C=C), 1462 (s, CH), 1268 cm^{-1} (s, C-N); ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.85 – 0.88 (m, 12 H, $CH_3CH_2CH_2CH_2CH_2CH_2N$), 1.27 – 1.31 (m, 42 H, $CH_3CH_2CH_2CH_2CH_2CH_2N$ & $C(CH_3)_3$), 1.46 – 1.51(m, 8 H, $CH_3CH_2CH_2CH_2CH_2CH_2N$), 2.08 (m, 2 H, NCH_2CH_2), 2.45 – 2.48 (m, 8 H, $CH_3CH_2CH_2CH_2CH_2CH_2N$), 3.65 (s, 4 H, NCH_2C_{Ar}), 3.68 – 3.71 (m, 4 H, NCH_2CH_2), 7.19 (s, 2 H, Ar*H*), 7.52 – 7.53 (m, 2 H, Ar*H*), 8.42 (s, 2 H, NC*H*), 13.25 (s, 2 H, O*H*); ^{13}C NMR (400 MHz, CHLOROFORM-*d*) δ ppm 14.05 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 22.66 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 27.05 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 27.29($CH_3CH_2CH_2CH_2CH_2CH_2N$), 30.13 ($C(CH_3)_3$), 31.44 ($C(CH_3)_3$), 31.85 ($NCH_2CH_2$), 33.98 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 50.14 ($ArCH_2N$), 54.28 ($CH_3CH_2CH_2CH_2CH_2CH_2N$), 57.01 ($NCH_2CH_2$), 116.46 ($C_{Ar}$), 125.39 ($C_{Ar}$), 127.60 ($C_{Ar}H$), 129.96 ($C_{Ar}H$), 140.62 ($C_{Ar}C(CH_3)_3$), 156.98 ($C_{Ar}OH$), 165.68 (Ar*C*N); MS (ES+): *m/z* (%) = 789.7 (100) $[M]^+$; 790.7 (50) $[M + H]^+$;

2. Solvent Extraction – Metal Salt Extraction and Transport

2.1 Solvent extraction of metal ions

A 0.01 M solution of each ligand in chloroform (5 cm^3) was contacted with a buffer solution at pH 5.09 containing a 0.01 M mixture of the Cu(II), Zn(II), Ni(II), Co(II), Pb(II) and Cd(II) metal ions (5 cm^3) and shaken on a labcon-oscillating shaker at 120 rpm for 24 h. Extraction was performed at 25 °C. The aqueous phase was removed and a sample was taken and used for metal ion analysis by ICP-AES. The results are quoted as the average value obtained from duplicate runs. Any apparent extraction of a metal ion of less than 2.0 % was assumed to be within the experimental error of zero and hence ignored in the treatment of results. In all cases the values between any two duplicate runs

did not differ by more than 2 %. Figure S1 shows the colour changes in the different phases before and after metal ion extraction. The results of the extraction are indicated in Figure S2.

(i) (ii)

Figure S1: (i) Before and (ii) after images of solvent extraction using different metal ions for each of the ligands (performed in duplicate).

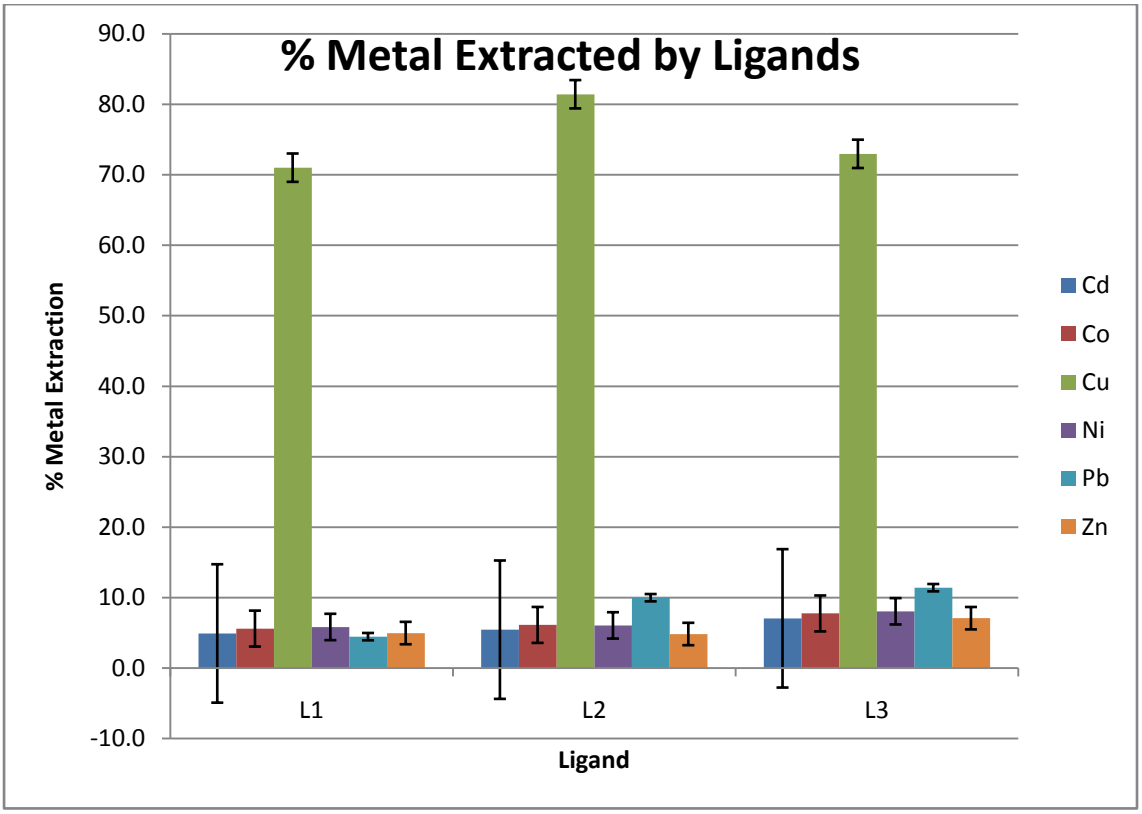
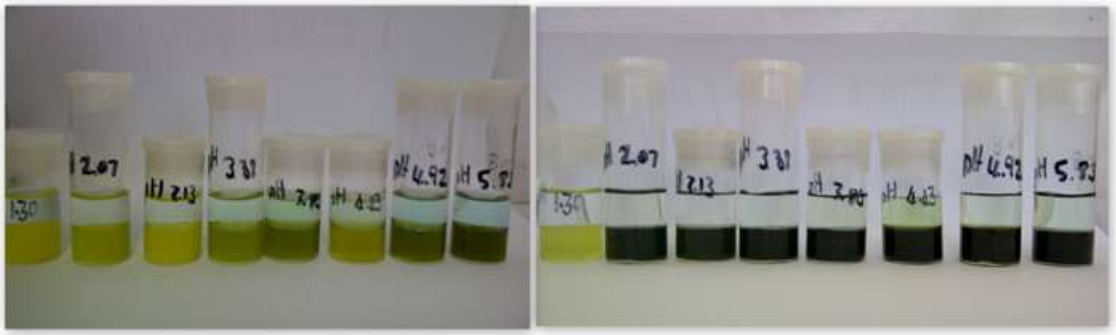


Figure S2: Percentage extraction of Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) by each of the ligands.

2.2 Solvent extraction of Cu(II) at different pH values

A 0.01 M solution of **L2** in chloroform (5 cm^3) was contacted with a 5 cm^3 solution of 0.01 M $Cu(NO_3)_2 \cdot 3H_2O$ at pH 1.30, 2.07, 2.13, 3.38, 3.80, 4.43, 4.92 and 5.83 respectively and shaken on a labcon-oscillating shaker at 120 rpm for 24 h. Extraction was performed at 25 °C. The aqueous phase was removed and a sample was taken and used for metal analysis by ICP-AES.



(i) (ii)

Figure S3: (i) Before and (ii) after images of solvent extraction of Cu(II) at different pH values for **L2**.

Figure S3 shows the colour changes in the different phases before and after metal ion extraction. By measuring the copper(II) ion content of the aqueous phase and plotting the percentage loading values against the equilibrium pH of the aqueous phase, it is possible to determine the metal ion loading S-curve, indicated in Figure S4.

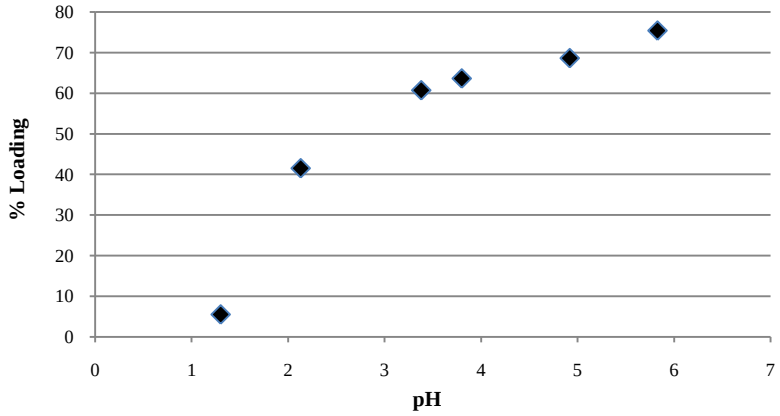
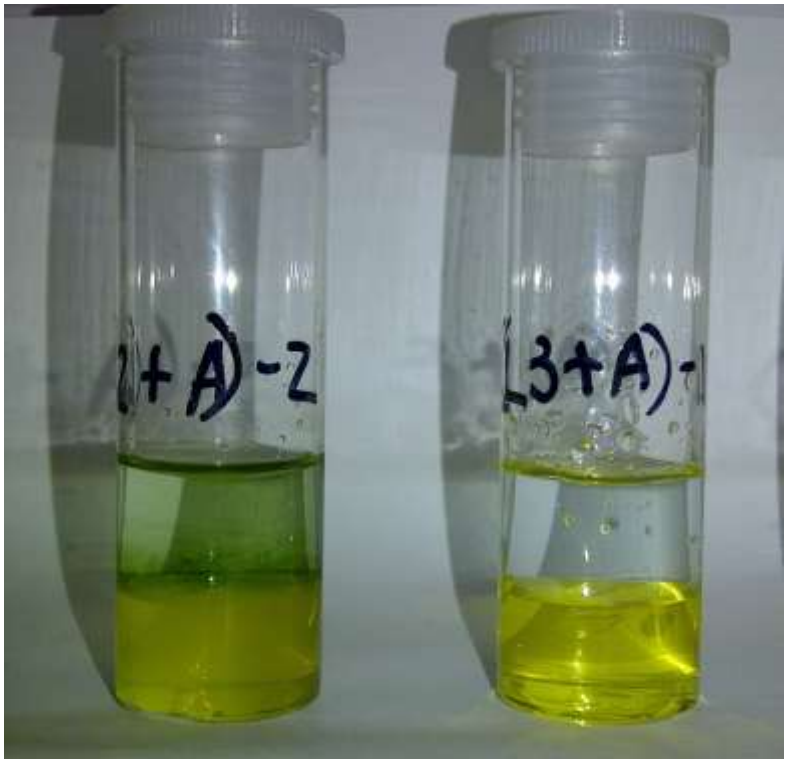


Figure S4: Copper(II) extraction of **L2** as a function of pH.

2.3 Solvent extraction of SO_4^{2-}, NO_3^- or Cl^- by the copper-only complexes

A 0.01 M solution of **L2** and **L3** respectively in chloroform (5 cm^3) was contacted with a solution containing a mixture of 0.01 M $CuSO_4 \cdot 5H_2O$, 0.005 M $Cu(NO_3)_2 \cdot 3H_2O$, and 0.005 M $CuCl_2 \cdot 2H_2O$ at pH 2.51 (5 cm^3) and shaken on a labcon-oscillating shaker at 120 rpm for 24 h. Extraction was performed at 25 °C. The aqueous phase was removed and a sample was taken and used for ion analysis by ion chromatography. The results are quoted as the average value obtained from duplicate runs. Any apparent extraction of an anion of less than 2.0 % was assumed to be within the experimental error of zero and hence ignored in the treatment of results. In all cases the values

between any two duplicate runs did not differ by more than 2 %. Figure S7 shows the phases before solvent extraction. Note that for **L2** extraction has started as soon as the two phases were added together. The results of the experiment are indicated in Table S1.



(i) (ii)

Figure S5: Before image of solvent extraction using different anions for (i) **L2** and (ii) **L3**.

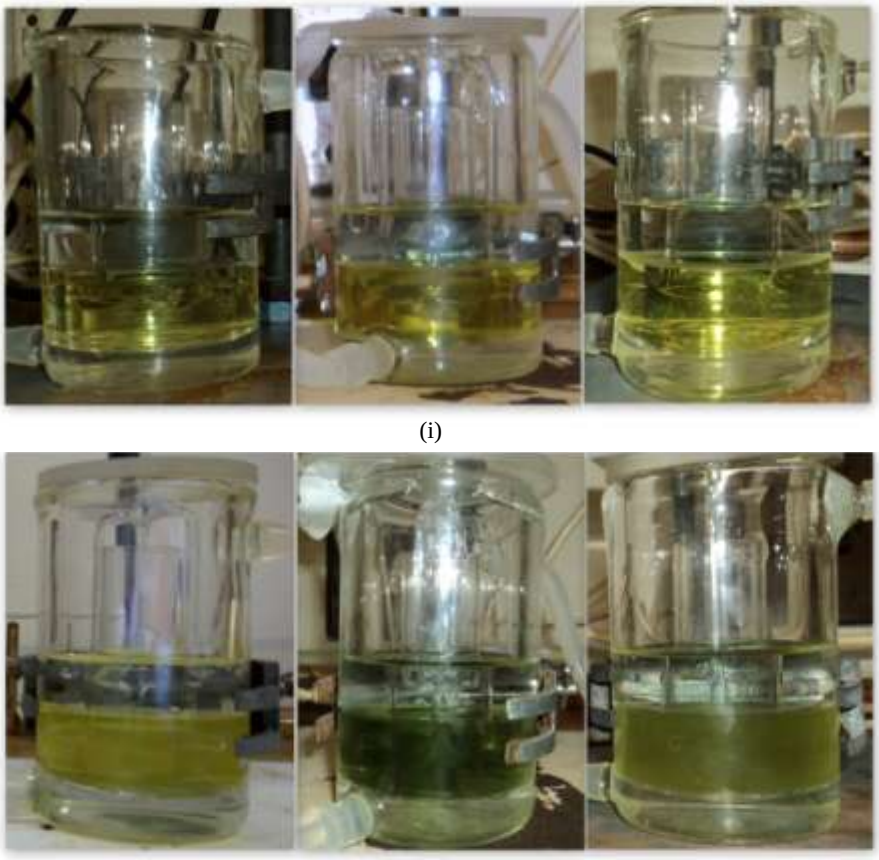
Table S1: Results of the extraction experiments indicating the percentage of anions extracted from the source phase

Ligand	**Phase**	**Cl^-**	**NO_3^-**	**SO_4^{2-}**
L2	Source	74.0	100.0	52.6
L3	Source	75.7	100.0	18.1

2.4 Membrane transport of metal ions:

Each ligand, at a concentration of 0.002M was used separately as a carrier for the transport of metal ions across a $CHCl_3$ (50 cm^3) bulk liquid membrane. Details of the cell design have been reported elsewhere[6]. The source phase consisted of 10 cm^3 of a 0.01 M solution of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) metal ions in a CH_3COONa/CH_3COOH buffer at pH 5.09. The receiving phase consisted of 30 cm^3 of 0.1 M HNO_3 at pH 1.0. All three phases in the transport cell were stirred at 10 rpm at 25° C. Under these conditions, not only was the stirring process consistent, but also the interface between the organic membrane and the two aqueous phases remained flat and well defined. The cells were covered with slips to prevent any evaporation of solvents over the 24 h period.

Samples of the source and receiving phases were taken and used for metal analysis by ICP-AES. Figure S6 indicates the phases before and after the transport studies. The results are quoted in Table S4 as the average value obtained from duplicate runs. Any apparent extraction of a metal ion of less than 2.0 % was assumed to be within the experimental error of zero and hence ignored in the treatment of results. In all cases the values between any two duplicate runs did not differ by more than 5 %.



(i)

(ii)

Figure S6:(i) Before and (ii) after images of membrane transport using different metal ions with **L1**, **L2** and **L3** respectively.

Table S2: Results of transport experiments indicating the percentage of metal ions present in the source and receiving phases for each ligand

Ligand	Phase	Cd(II)	Co(II)	Cu(II)	Ni(II)	Pb(II)	Zn(II)
L1	Source	100.0	100.0	90.9	100.0	100.0	100.0
L1	Receiving	0.0	0.0	0.0	0.0	0.0	0.0
L2	Source	100.0	100.0	58.8	100.0	100.0	100.0
L2	Receiving	0.0	0.0	0.0	0.0	0.0	0.0
L3	Source	100.0	100.0	84.6	100.0	100.0	100.0
L3	Receiving	0.0	0.0	0.00	0.0	0.0	0.0

2.5 Membrane transport of anions

L2 and **L3**, each at a concentration of 0.002M were used as carriers for the transport of anions across a $CHCl_3$ (50 cm^3) bulk liquid membrane. Details of the cell design have been reported elsewhere[6]. The source phase contained 10 cm^3 of a 0.01 M solution of 0.01M $CuSO_4$, HNO_3 and HCl at pH 1.91. The receiving phase contained 30 cm^3 NaH_2PO_4/ Na_2HPO_4 buffer at pH 6.95. All three phases in the transport cell were stirred at 10 rpm at 25° C. Under these conditions, not only was the stirring process consistent, but also the interface between the organic membrane and the two aqueous phases remained flat and well defined. The cells were covered with slips to prevent any evaporation of solvents over the 24 h period. Samples of the source phase and the receiving phase were taken and used for ion chromatography. Figure S7 indicates the phases before and after the transport studies. The results are quoted as the average value obtained from duplicate runs in Table S3. Any apparent extraction of a metal ion of less than 2.0% was assumed to be within the experimental error of zero and hence ignored in the treatment of results. In all cases the values between any two duplicate runs did not differ by more than 5 %.

(i) (ii)

Figure S7: After images of membrane transport of anions with **L2** (i) and **L3** (ii).

Table S3: Results of transport experiments indicating the percentage of anions present in the source and receiving phases for **L2** and **L3**

Ligand	Phase	Cl^-	NO_3^-	SO_4^{2-}
L2	Source	26.0	0.0	47.4
L2	Receiving	26.9	24.0	0.0
L3	Source	24.3	0.0	81.9
L3	Receiving	22.8	26.6	0.0

3. Complexes

3.1 Complexes of metal salts

[ZnL^2SO_4]

A solution of $ZnSO_4 \cdot 7H_2O$ (86.3 mg, 0.300 mmol) in methanol (5 cm^3) was added to a stirred solution of **L2** (0.177 g, 0.300 mmol) in methanol (5 cm^3). A colour change due to complexation was rapid and after 12 h water (5 cm^3) was added before the solution was left to evaporate. The sample however did not yet form a powder for IR and NMR analysis.

[CuL^2SO_4]

A solution of $CuSO_4 \cdot 5H_2O$ (74.9 mg, 0.300 mmol) in methanol (5 cm^3) was added to a stirred solution of **L2** (0.177 g, 0.300 mmol) in methanol (5 cm^3). A colour change due to complexation was rapid and after 12 h water (5 cm^3) was added before the solution was left to evaporate. The sample however did not yet form a powder for IR analysis.

[NiL^2SO_4]

A solution of $NiSO_4 \cdot 7H_2O$ (84.3 mg, 0.300 mmol) in methanol (5 cm^3) was added to a stirred solution of **L2** (0.177 g, 0.300 mmol) in methanol (5 cm^3). A colour change due to complexation was rapid and after 12 h water (5 cm^3) was added before the solution was left to evaporate. The sample however did not yet form a powder for IR and NMR analysis.

[ZnL^3SO_4]

A solution of $ZnSO_4 \cdot 7H_2O$ (86.3 mg, 0.300 mmol) in methanol (5 cm^3) was added to a stirred solution of **L3** (0.237 g, 0.300 mmol) in methanol (5 cm^3). Ethanol was added dropwise until the ligand went into solution. A colour change due to complexation was rapid and after 12 h water (5 cm^3) was added before the solution was left to evaporate. The sample however did not yet form a powder for IR and NMR analysis.

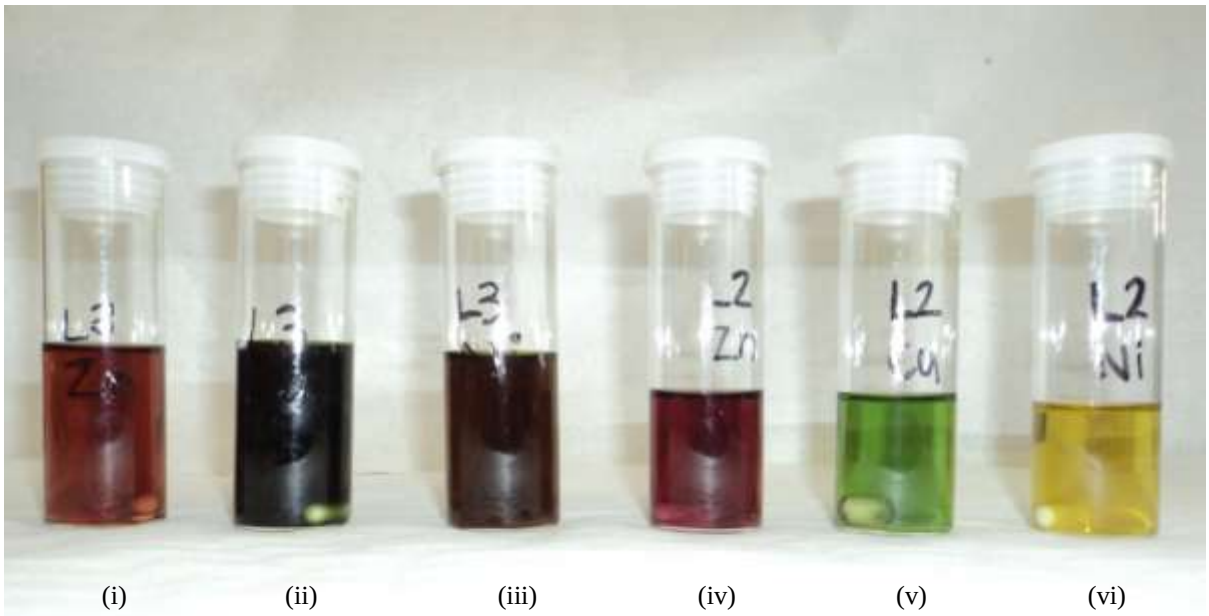
[CuL^3SO_4]

A solution of $CuSO_4 \cdot 5H_2O$ (74.9 mg, 0.300 mmol) in methanol (5 cm^3) was added to a stirred solution of **L3** (0.237 g, 0.300 mmol) in methanol (5 cm^3). Ethanol was added dropwise until the ligand went into solution. A colour change due to complexation was rapid and after 12 h water (5 cm^3) was added before the solution was left to evaporate. The sample however did not yet form a powder for IR analysis.

[NiL^{3}SO$_4$]

A solution of NiSO$_4$·7H$_2$O (84.3 mg, 0.300 mmol) in methanol (5 cm^3) was added to a stirred solution of **L3** (0.237 g, 0.300 mmol) in methanol (5 cm^3). Ethanol was added dropwise until the ligand went into solution. A colour change due to complexation was rapid and after 12 h water (5 cm^3) was added before the solution was left to evaporate. IR (neat): 2857 - 2952 (s, CH), 1680 (s, C=N), 1452 cm^{-1} (s, CH);

Figure S8 shows the colours of the solutions immediately after the metal salt was added to the ligand.



(i) (ii) (iii) (iv) (v) (vi)

Figure S8: Observed colour changes after complex formation for (i) [ZnL^{3}SO$_4$], (ii) [CuL^{3}SO$_4$], (iii) [NiL^{3}SO$_4$], (iv) [ZnL^{2}SO$_4$], (v) [CuL^{2}SO$_4$] and (vi) [NiL^{2}SO$_4$].

3.2 Copper-only complexes

[Cu(L^1-2H)]

A solution of **L1** (0.118 g, 0.300 mmol) in CHCl$_3$ (15 cm^3) and Cu(CH$_3$COO)$_2$·H$_2$O (59.9 mg, 0.300 mmol) in methanol (50 cm^3) was mixed and stirred overnight. The solvent was removed *in vacuo* to yield a dark green oil which was dissolved in CHCl$_3$ (30 cm^3) and washed with a pH 9 ammonia solution (2 × 15 cm^3). The resulting organic phase was dried with anhydrous MgSO$_4$, filtered and then concentrated *in vacuo* to yield the metal complex which was used without further purification. IR (neat): 2952 (m, CH), 1621 (m, C=N), 1472 (s, CH);

[Cu(L^2-2H)]

A solution of **L2** (0.177 g, 0.300 mmol) in CHCl$_3$ (15 cm^3) and Cu(CH$_3$COO)$_2$·H$_2$O (59.9 mg, 0.300 mmol) in methanol (50 cm^3) was mixed and stirred overnight. The solvent was removed *in vacuo* to

yield a dark green oil which was dissolved in $CHCl_3$ (30 cm^3) and washed with a pH 9 ammonia solution (2 × 15 cm^3). The resulting organic phase was dried with anhydrous $MgSO_4$, filtered and then concentrated *in vacuo* to yield the metal complex which was used without further purification. IR (neat): 2939 (m, CH), 1615 (s, C=N), 1261 cm^{-1} (s, C-N);

[Cu(L^3-2H)]

A solution of **L3** (0.237 g, 0.300 mmol) in $CHCl_3$ (15 cm^3) and $Cu(CH_3COO)_2 \cdot H_2O$ (59.9 mg, 0.300 mmol) in methanol (50 cm^3) was mixed and stirred overnight. The solvent was removed *in vacuo* to yield a dark green oil which was dissolved in $CHCl_3$ (30 cm^3) and washed with a pH 9 ammonia solution (2 × 15 cm^3). The resulting organic phase was dried with anhydrous $MgSO_4$, filtered and then concentrated *in vacuo* to yield the metal complex which was used without further purification. IR (neat): 2857 - 2955 (s, CH), 1616 (s, C=N), 1597 (m, C=C), 1456 (s, CH);

Figure S9 shows the colour changes before and after copper acetate has been added to the ligand solution. Complex formation was confirmed by imine shift in the FTIR of the isolated copper(II) complexes, see Table S4.

(i)

(ii)

Figure S9: (i) Before and (ii) after images of complexation of the copper-only complexes with **L1**, **L2** and **L3** respectively.

Table S4: Shifts observed in the imine stretch upon complex formation

	Metal-free ligand	**Complex**
[CuL^1-2H]	1631.62 cm^{-1}	1620.68 cm^{-1}
[CuL^2-2H]	1629.32 cm^{-1}	1615.03 cm^{-1}
[CuL^3-2H]	1631.67 cm^{-1}	1616.29 cm^{-1}

4. Crystal structure

A crystal structure for the copper only complex, [Cu(L^3-2H)] was obtained from a solution of the complex dissolved in methanol, enclosed by diethylether in a sealed container. Crystal data and structure refinement parameters are given in Table S5. Selected bond lengths and angles are given in Table S6.

Table S5: Crystal data and structure refinement for [Cu(L^3-2H)]

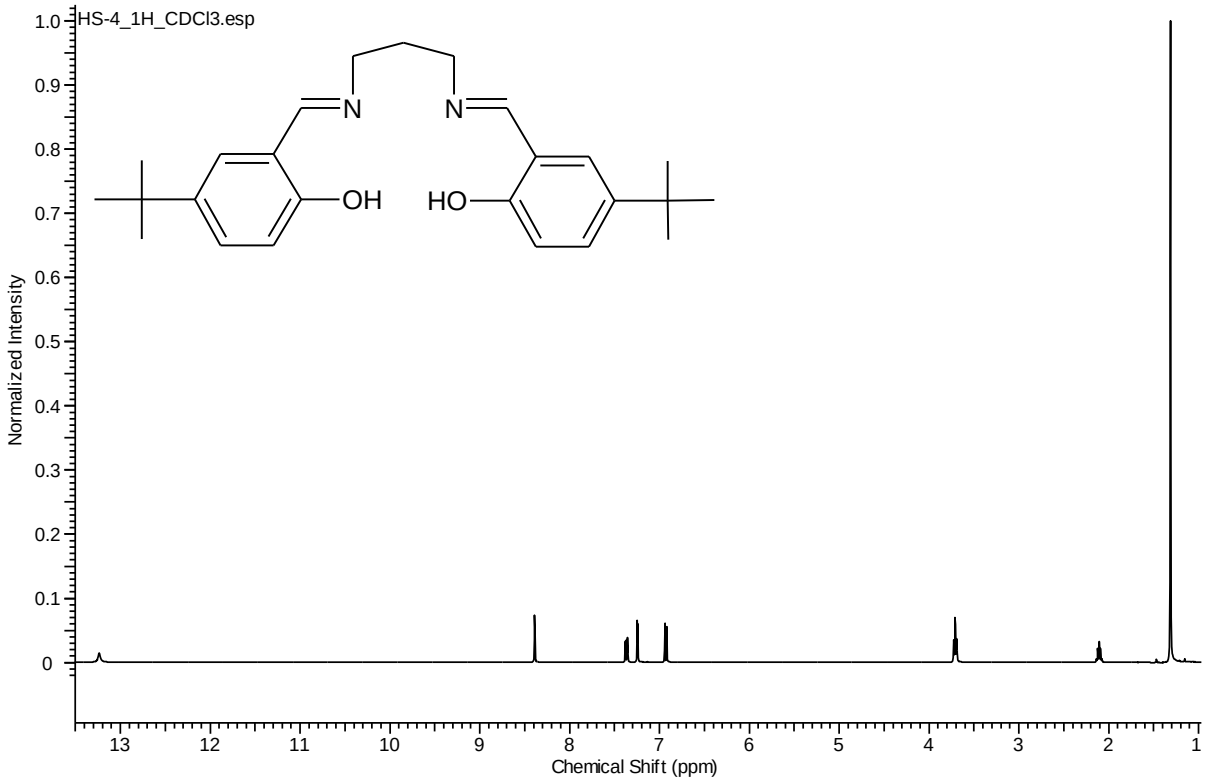
Empirical formula	$C_{25.50}H_{42.12}Cu_{0.50}N_2OS_0$	
Formula weight	424.50	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions (Å, °)	*a* = 42.8482(14)	α = 90.00
	b = 9.1372(3)	β = 128.170(4)
	c = 31.8323(12)	γ = 90.00
Volume (Å^3)	9798.0(6)	
Z	16	
Calculated density (g cm^{-3})	1.151	
Absorption coefficient (mm^{-1})	0.487	
F_{000}	3706	
Crystal size (mm^3)	0.10 × 0.10 × 0.03	
θ range for data collection (□)	1.21 to 26.36	
Miller index ranges	$-53 \le h \le 53$, $-11 \le k \le 11$, $-39 \le l \le 39$	
Reflections collected	114671	
Independent reflections	10009 [R_{int} = 0.1253]	
Completeness to θ_{max} (%)	99.9	
Max. and min. transmission	0.9855 and 0.9529	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10009 / 0 / 543	
Goodness-of-fit on F^2	1.016	
Final *R* indices [$I \geq 2\sigma(I)$]	*R*1 = 0.0480, *wR*2 = 0.1235	
R indices (all data)	*R*1 = 0.0909, *wR*2 = 0.1453	
Largest diff. peak and hole (e Å^{-3})	0.358 and -0.469	

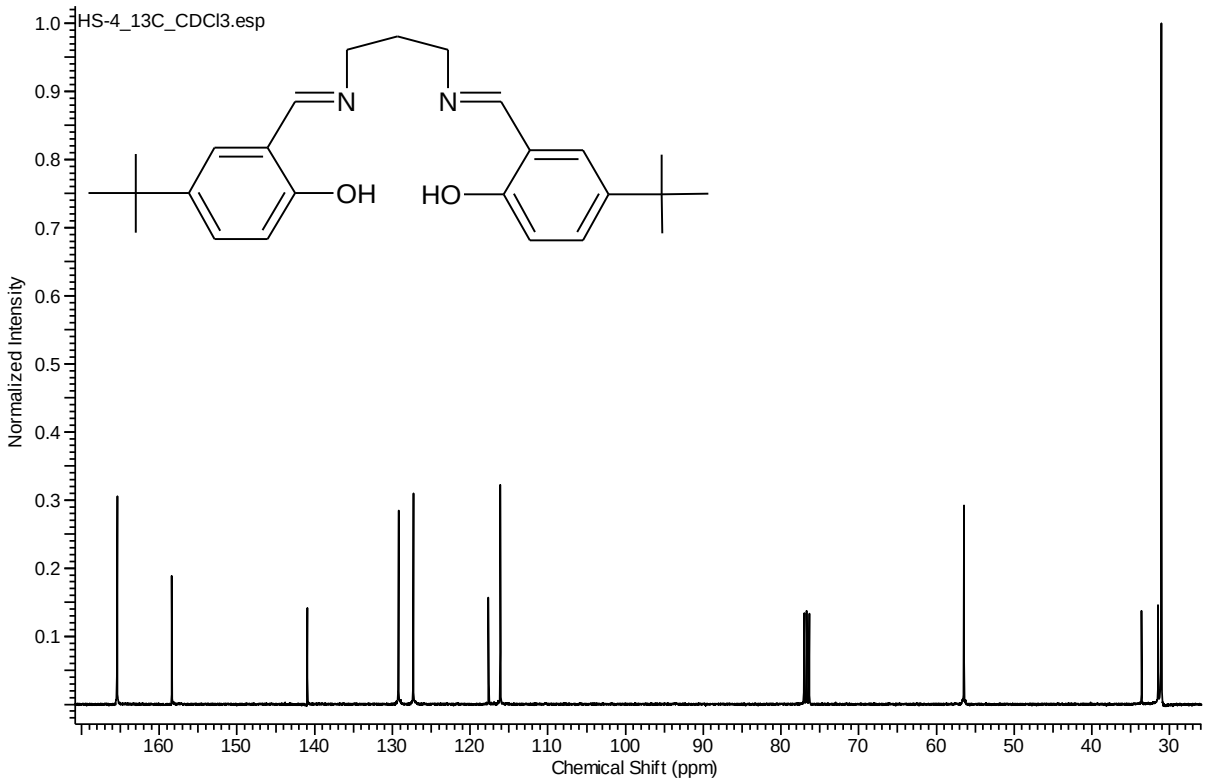
Table S6: Selected bond lengths and angles for [Cu(L^3-2H)]

Bond lengths (Å)	
N(9)-Cu(1)	1.960
N(5)-Cu(1)	1.958
O(1)-Cu(1)	1.902
O(1)-Cu(1)	1.905
Bond angles (°)	
O(1)-Cu(1)-O(2)	85.11
O(1)-Cu(1)-N(9)	93.30
N(9)-Cu(1)-N(5)	96.49
N(5)-Cu(1)-O(2)	93.19

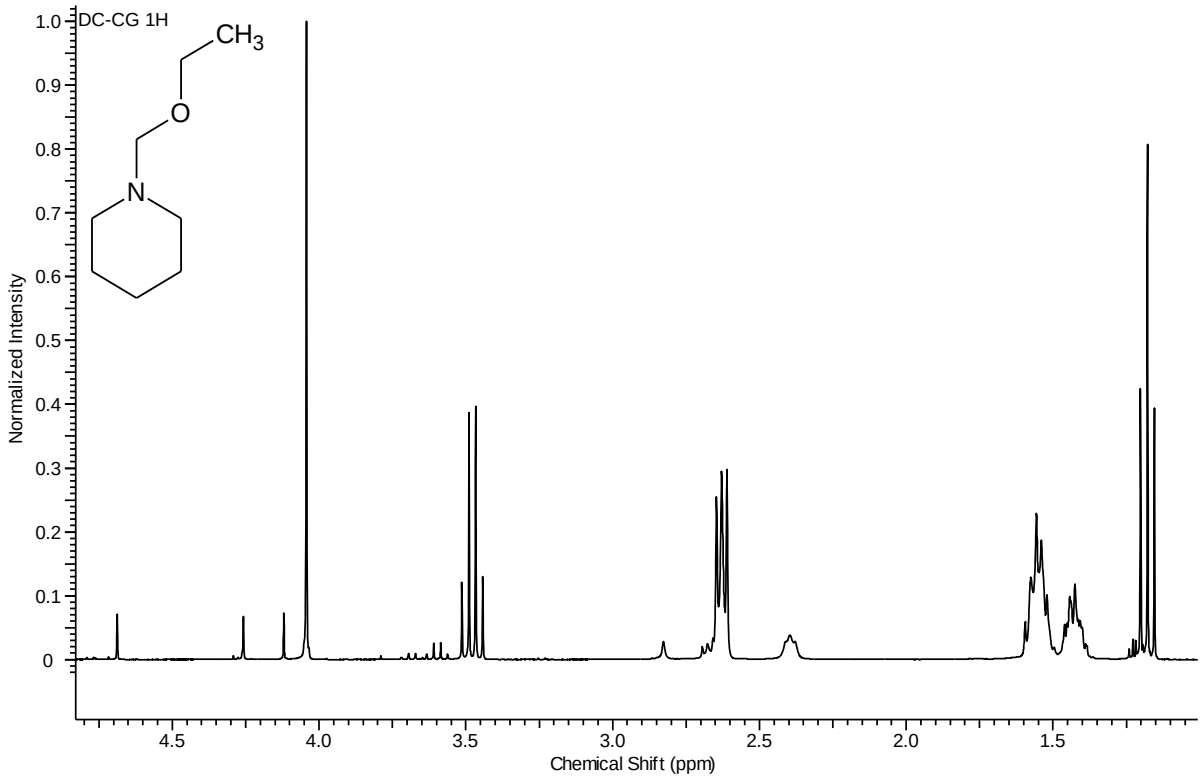
5. NMR spectra for all compounds

Ligand 1 (L1)

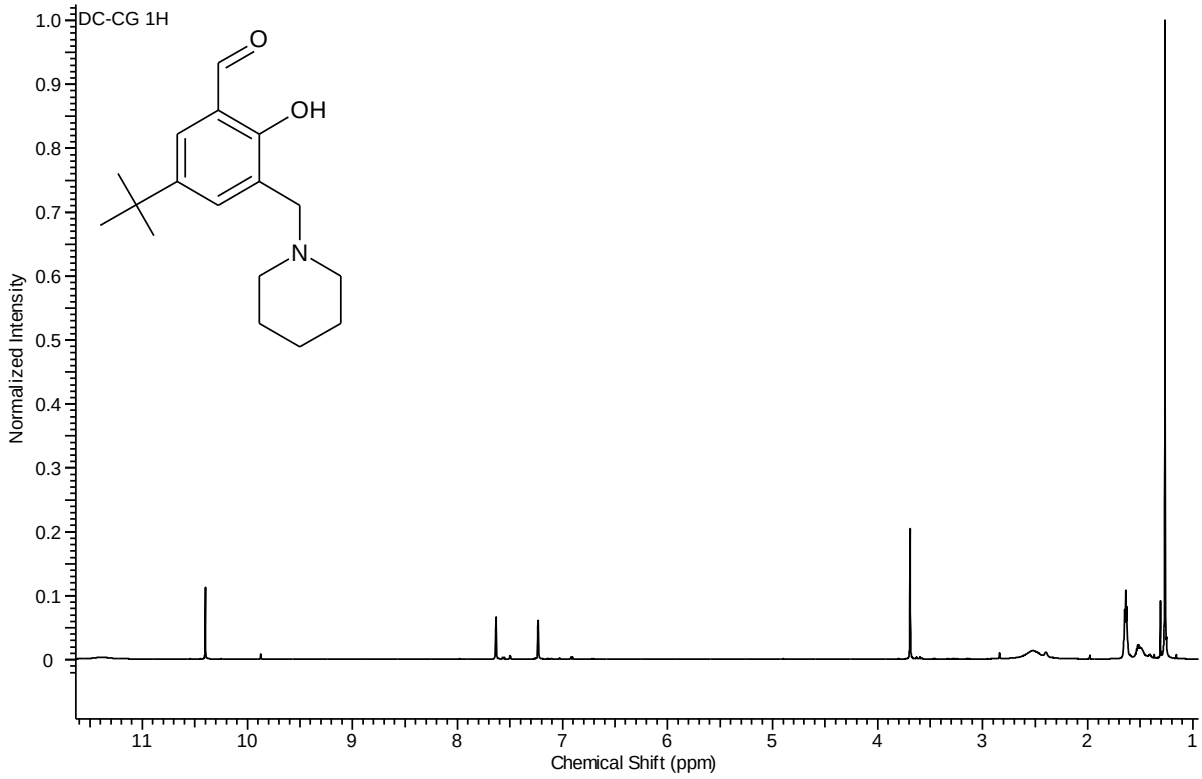


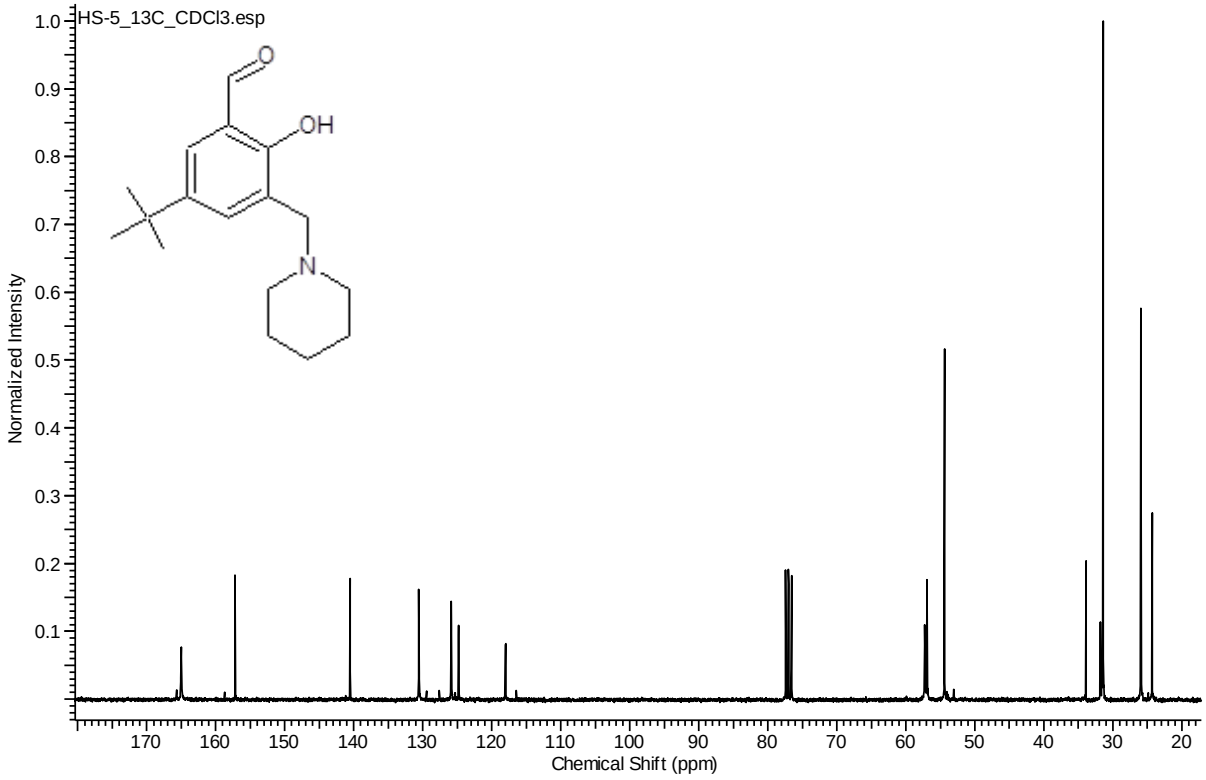


1-(ethoxymethyl)piperidine

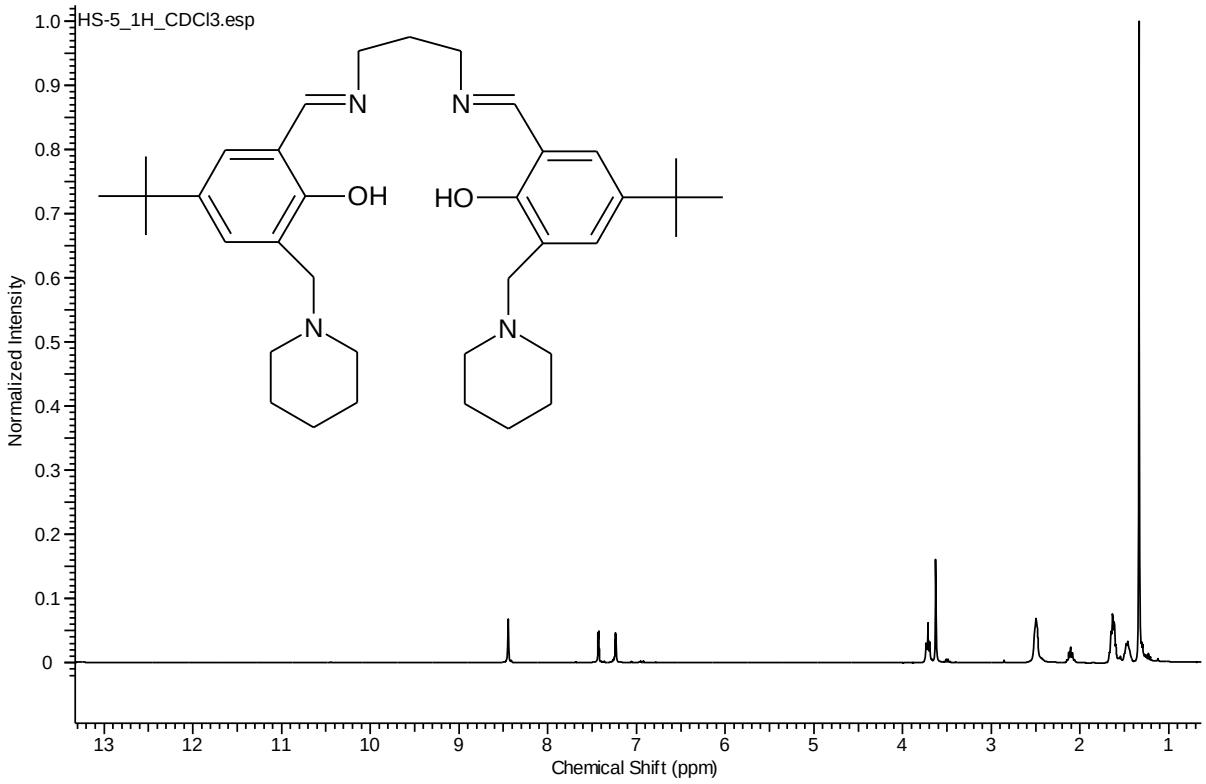


5-tert-butyl-2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde





Ligand 2 (L2)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Normalized Intensity
Chemical Shift (ppm)
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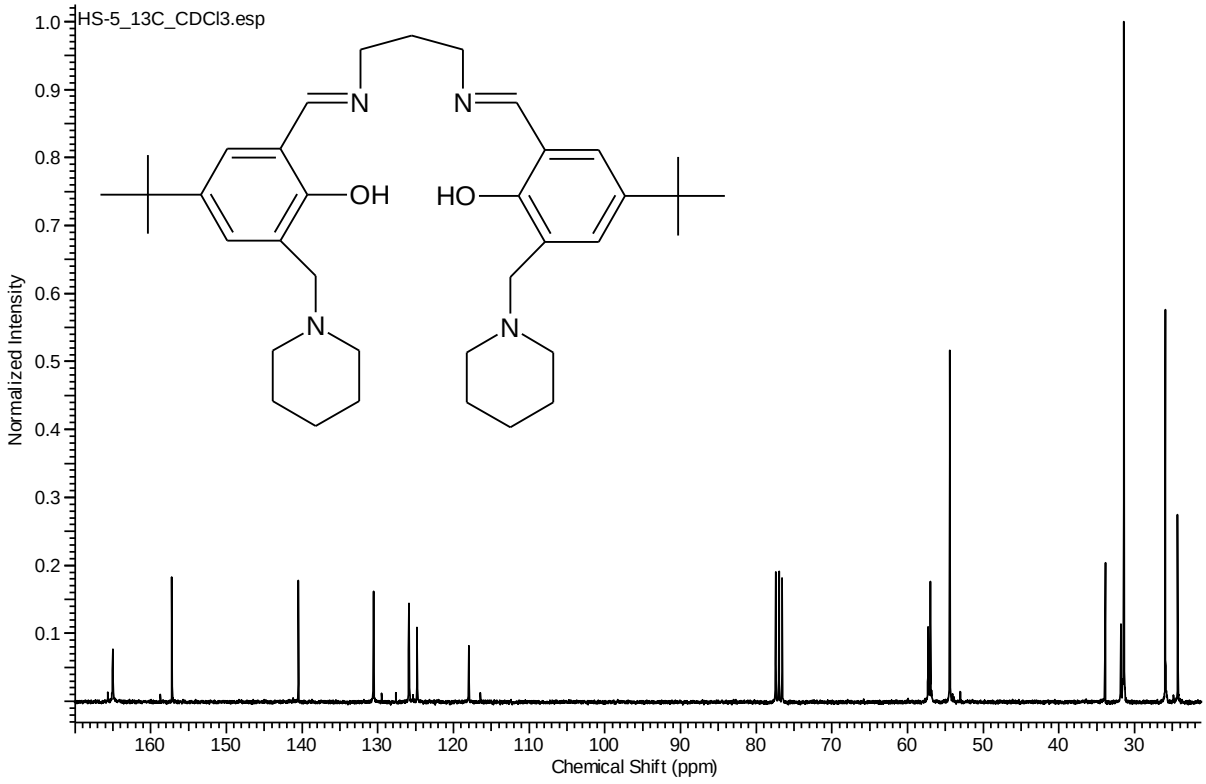
N
OH
HO
N
N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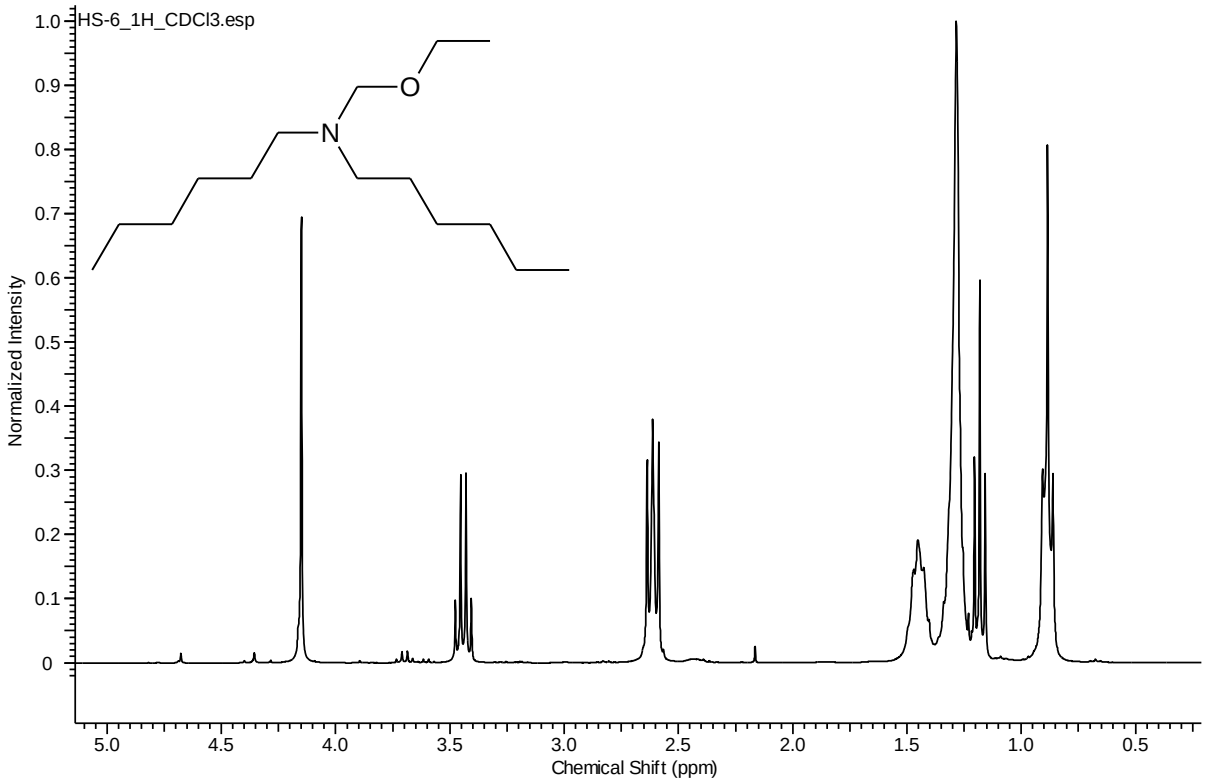
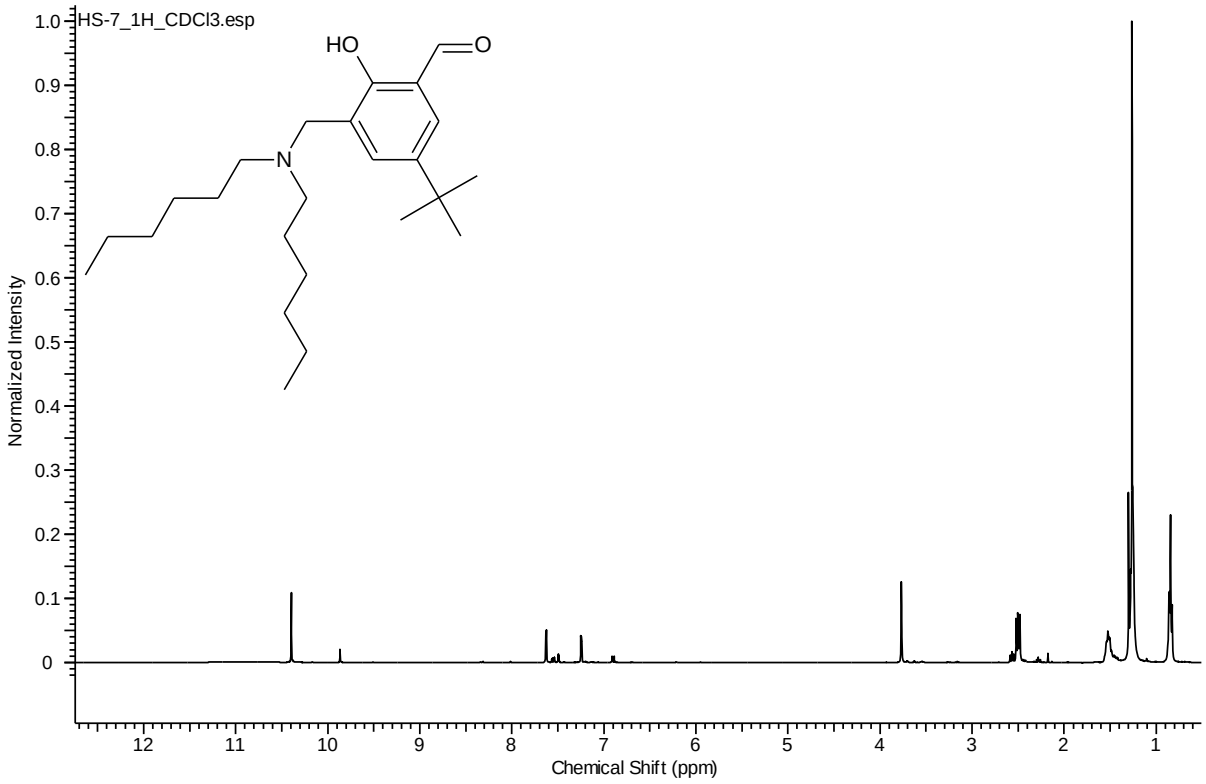
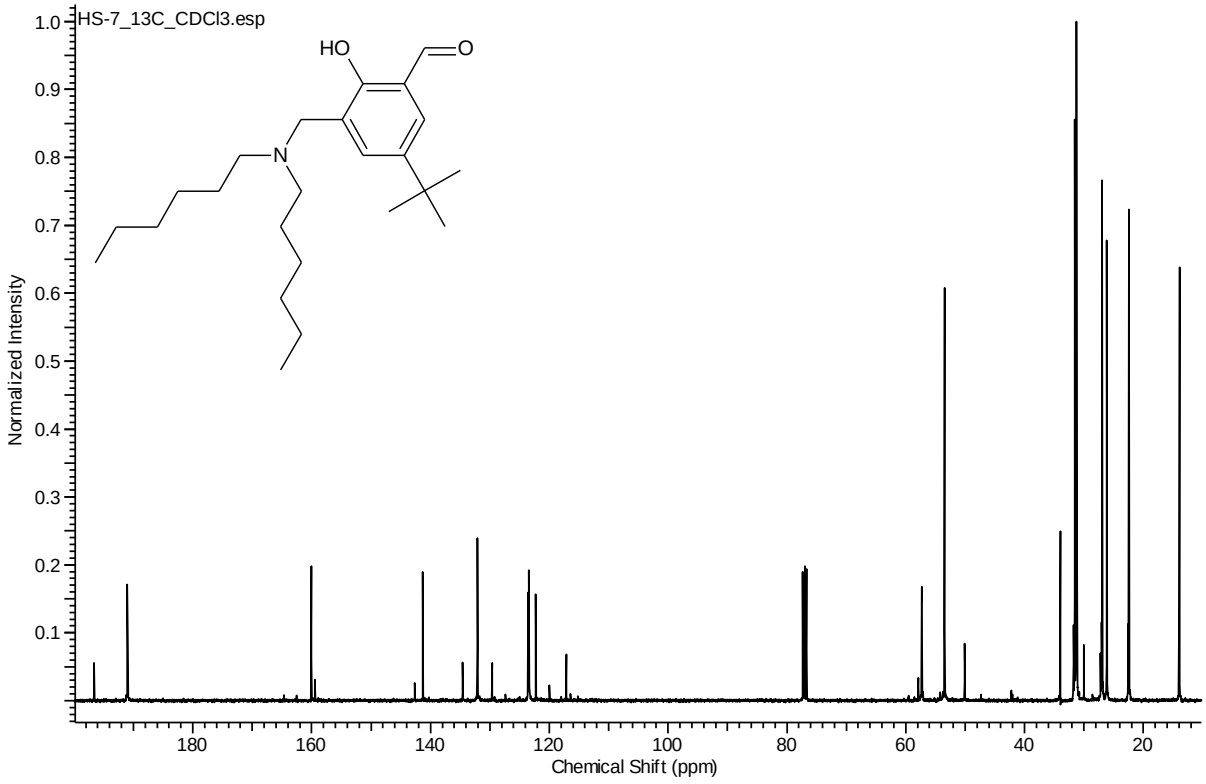
Chemical Shift (ppm)
N
N
OH
HO
N
N

N-(ethoxymethyl)-N-hexylhexan-1-amine



5-tert-butyl-3-[(dihexylamino)methyl]-2-hydroxybenzaldehyde





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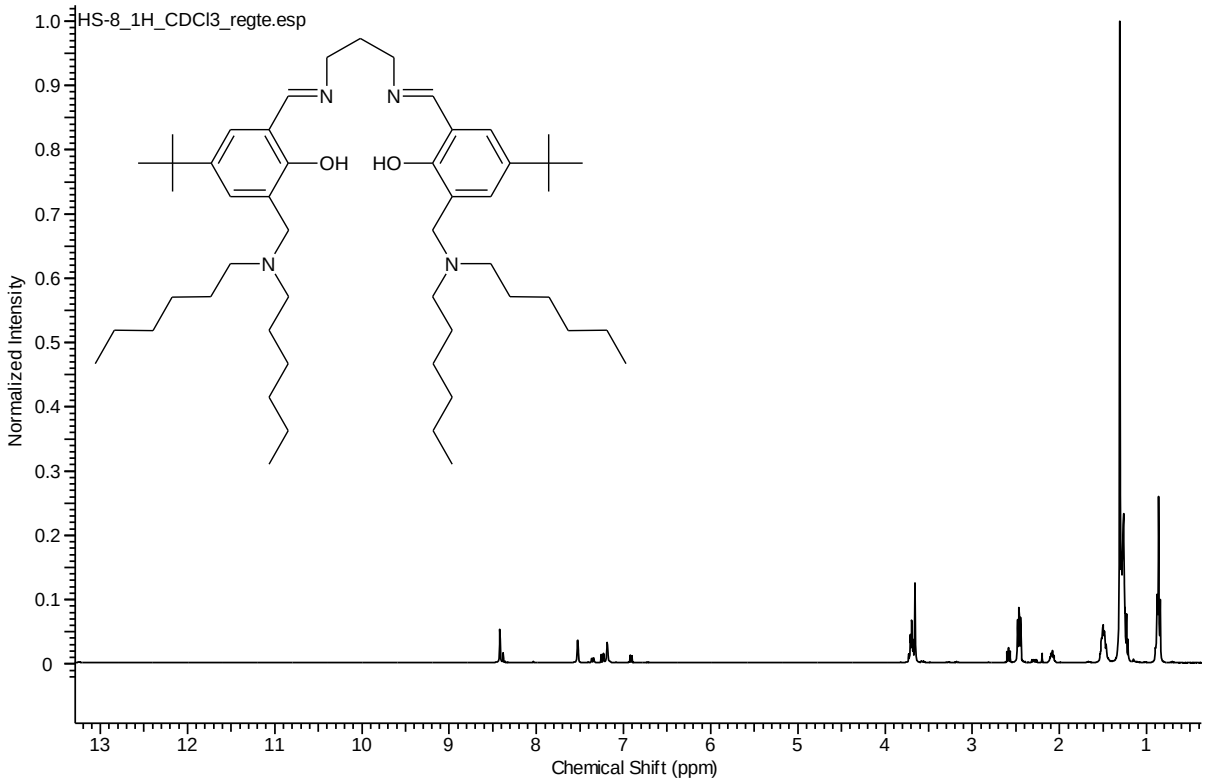
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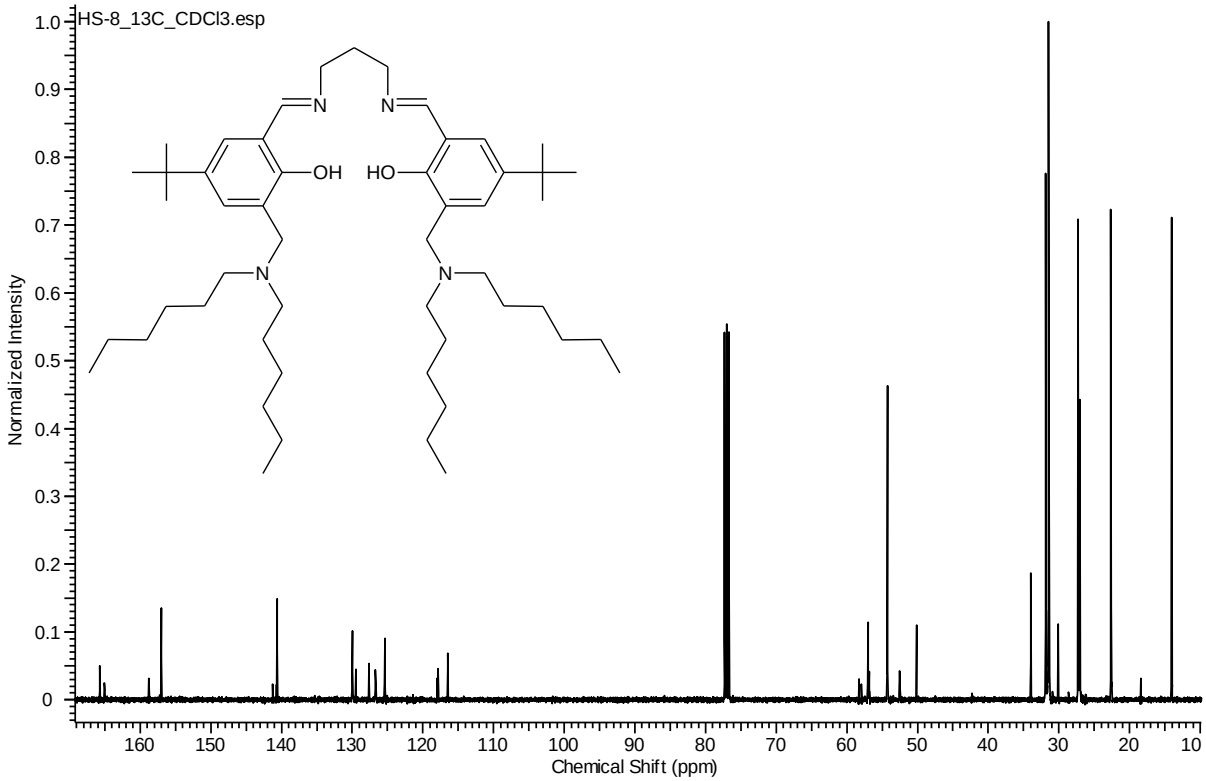
Normalized Intensity
Chemical Shift (ppm)
OH
HO
N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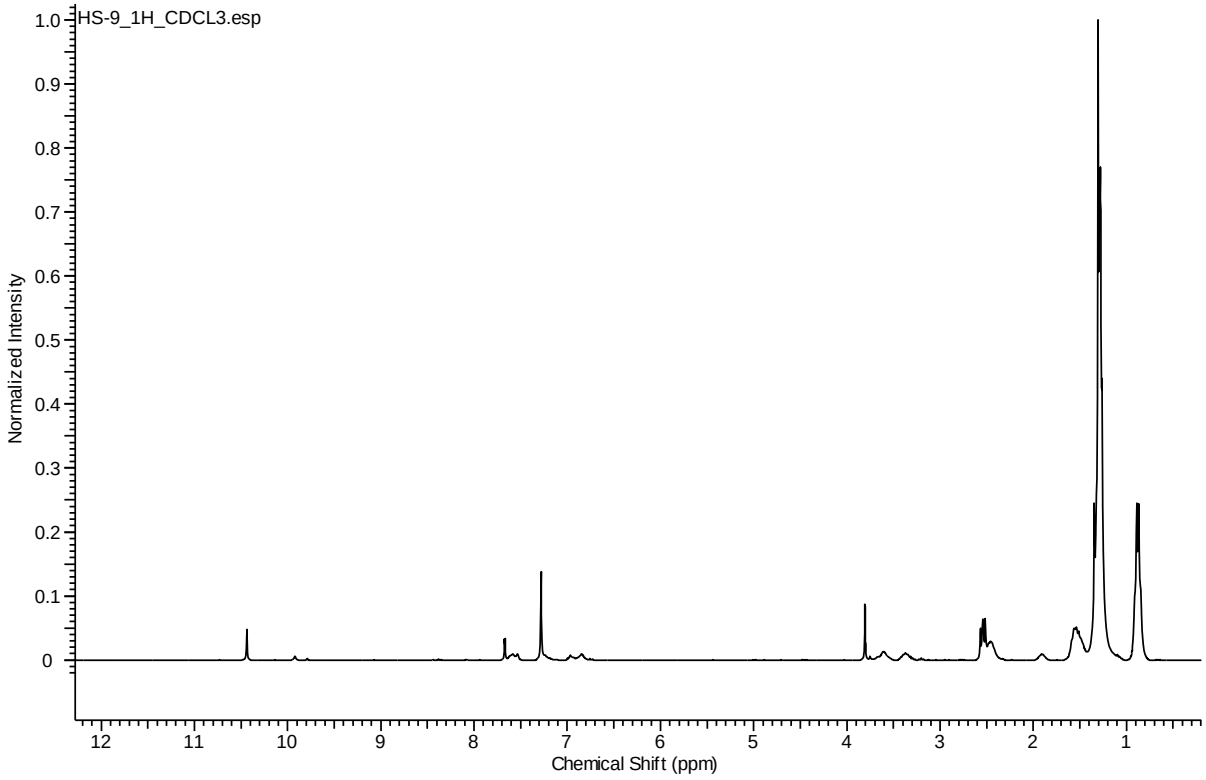
Normalized Intensity
Chemical Shift (ppm)
OH
HO
N

[NiL^{3}SO$_4$]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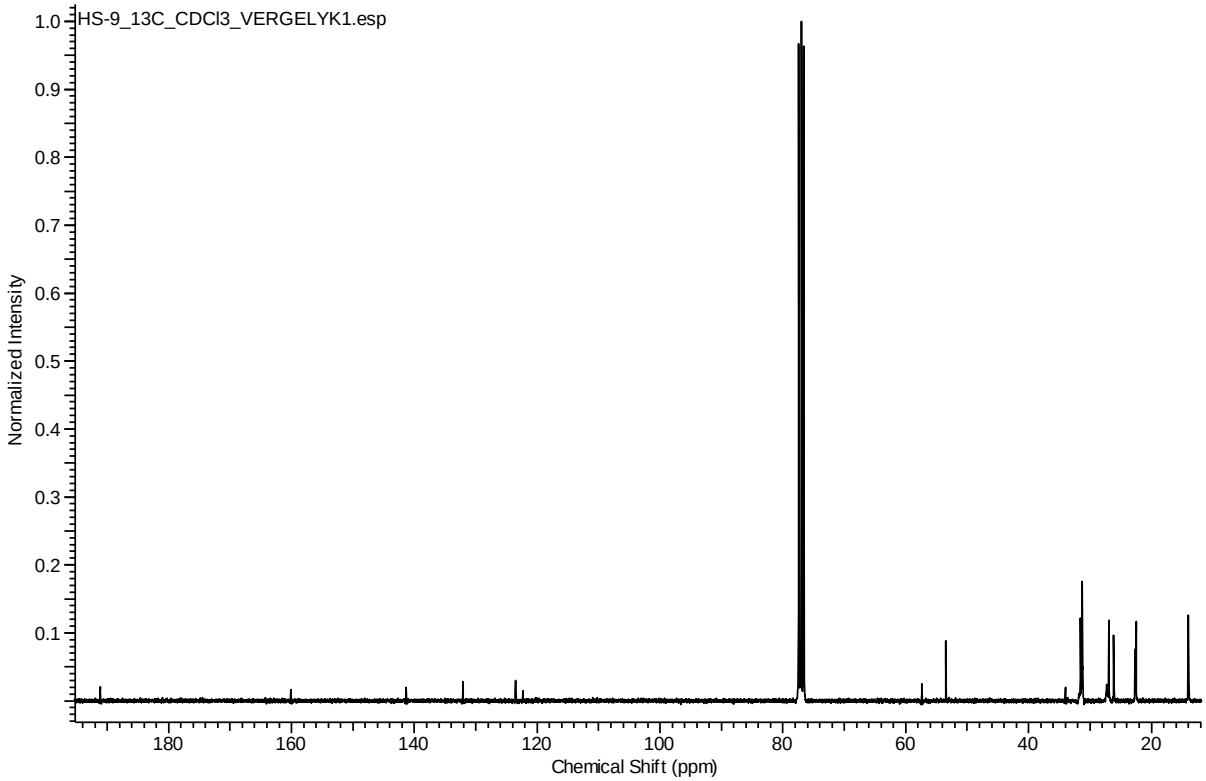
Chemical Shift (ppm)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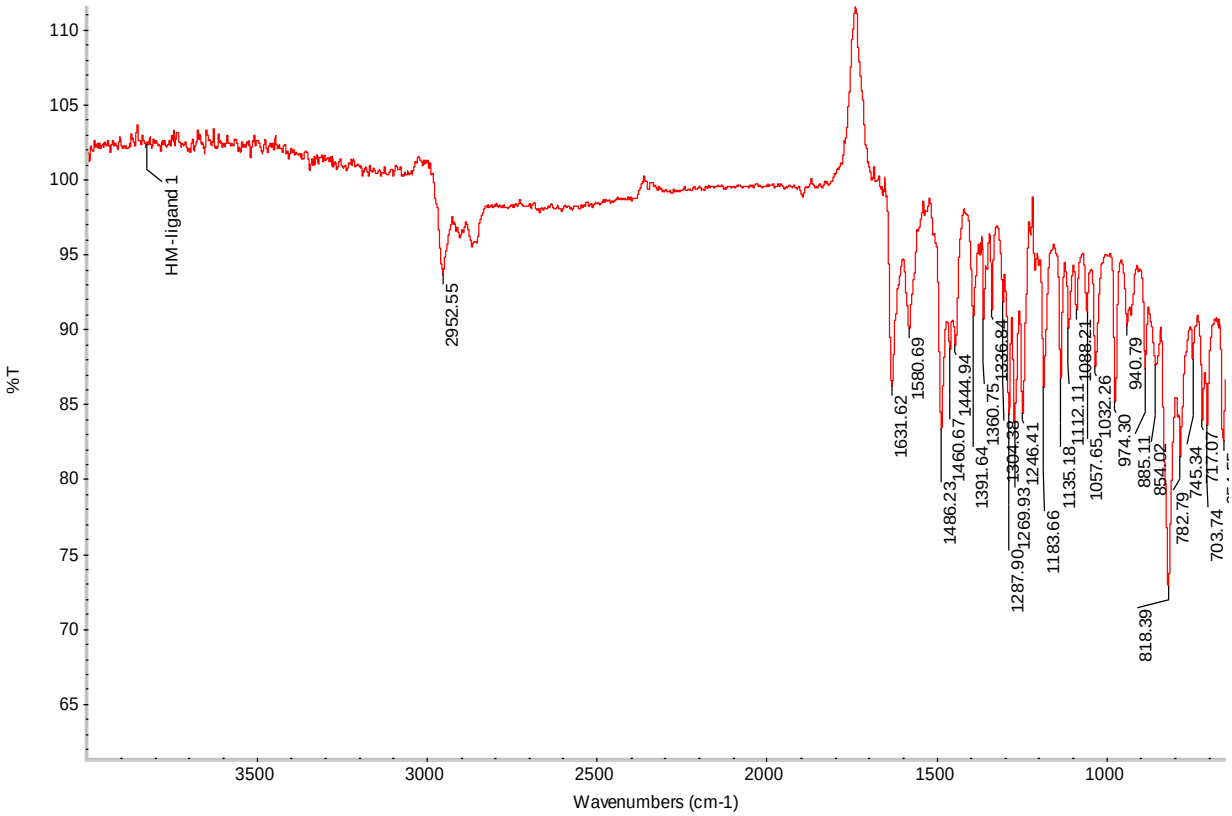
Chemical Shift (ppm)

FT-IR spectra

Ligand 1 (L1)



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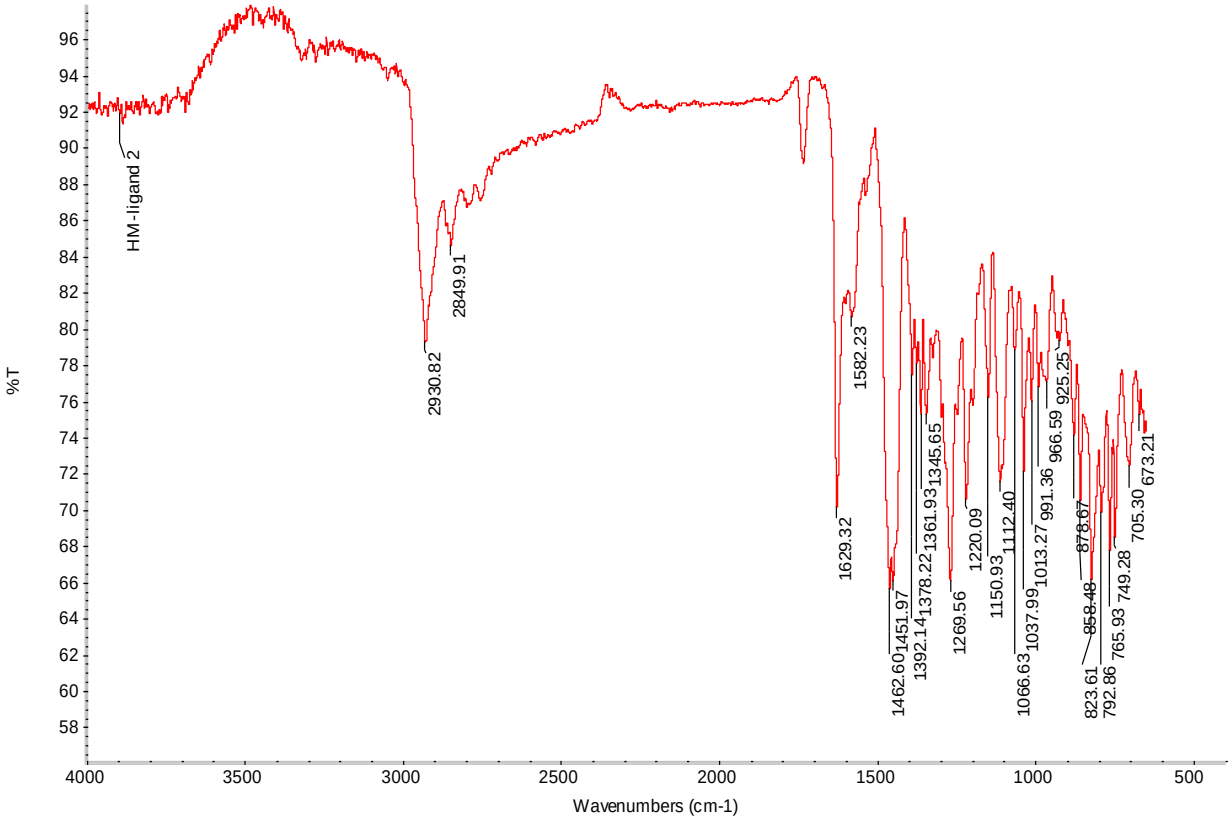
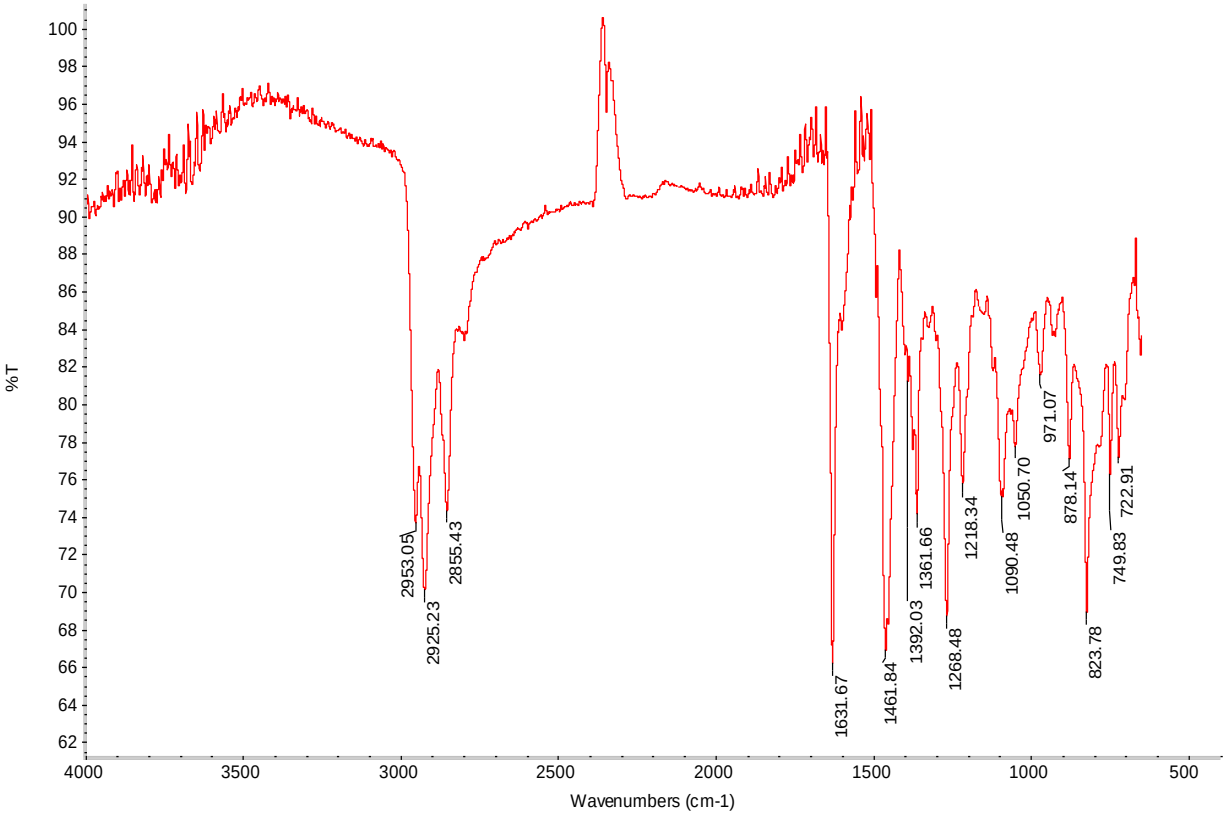
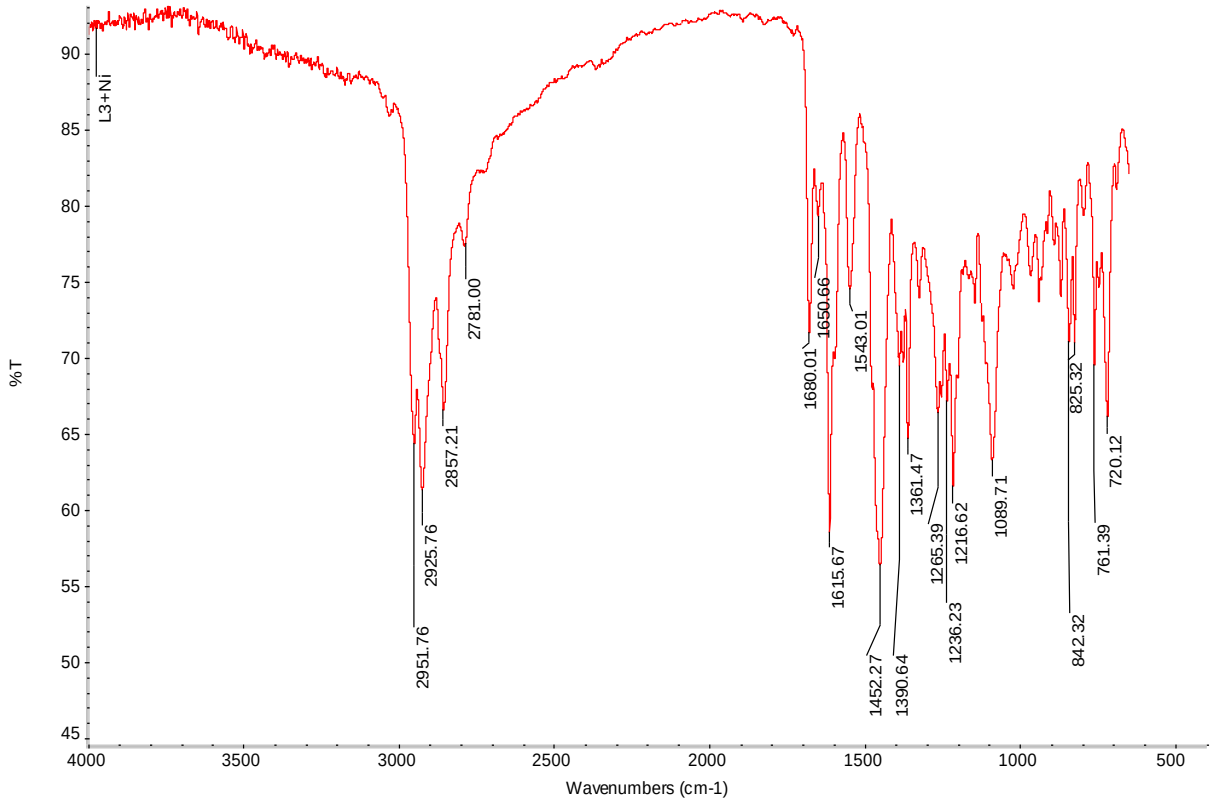


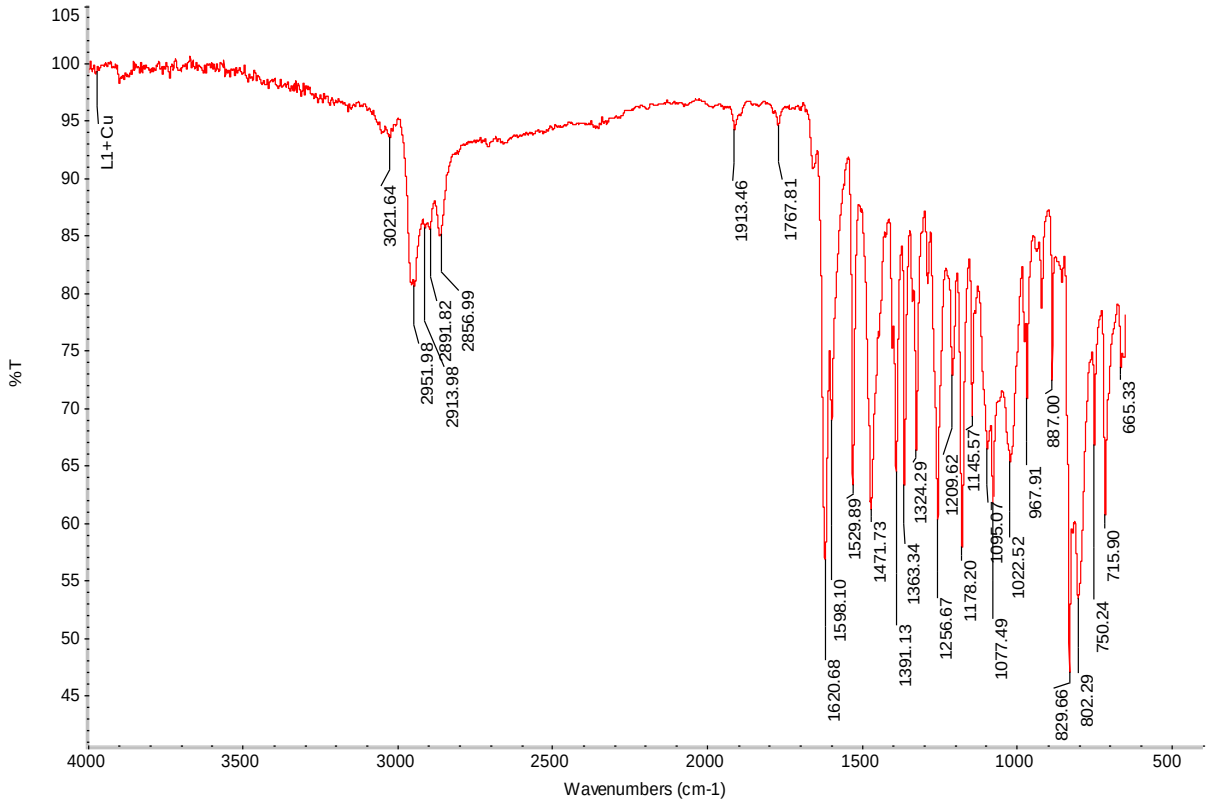
Ligand 3 (L3)



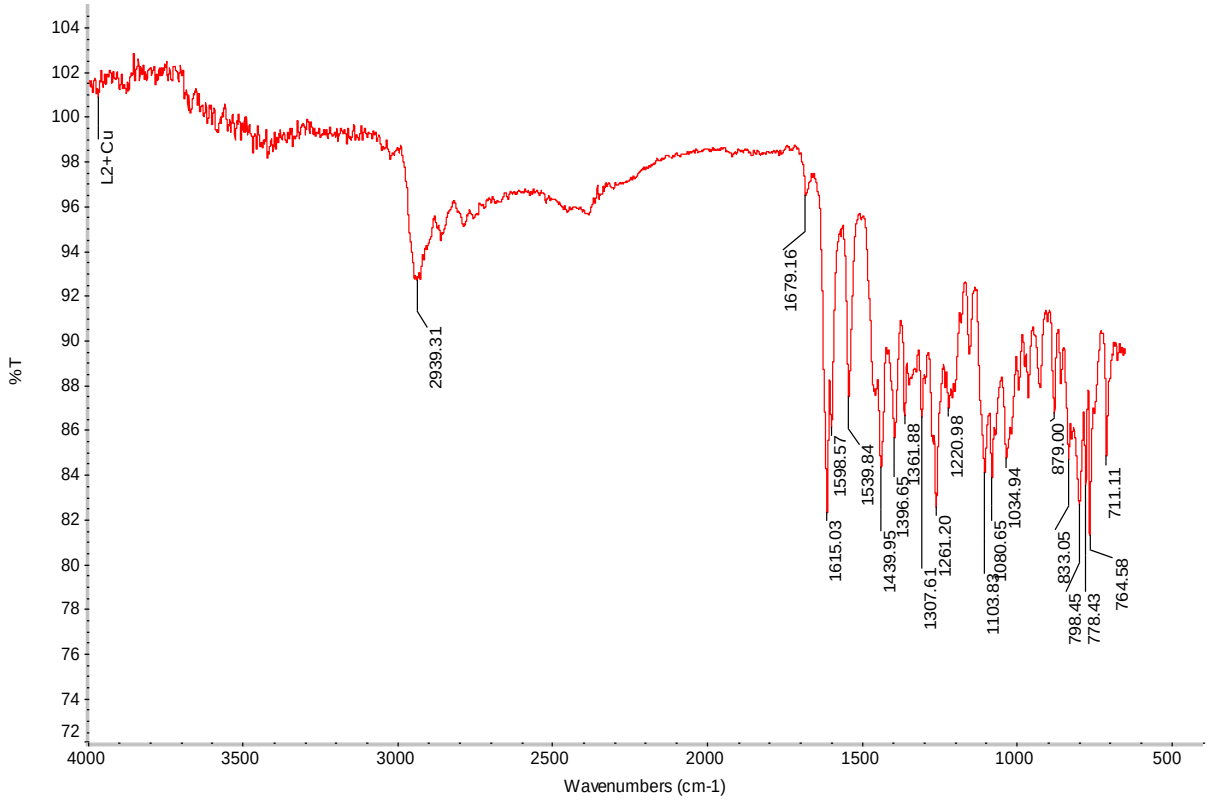
[NiL^{3}SO$_4$]



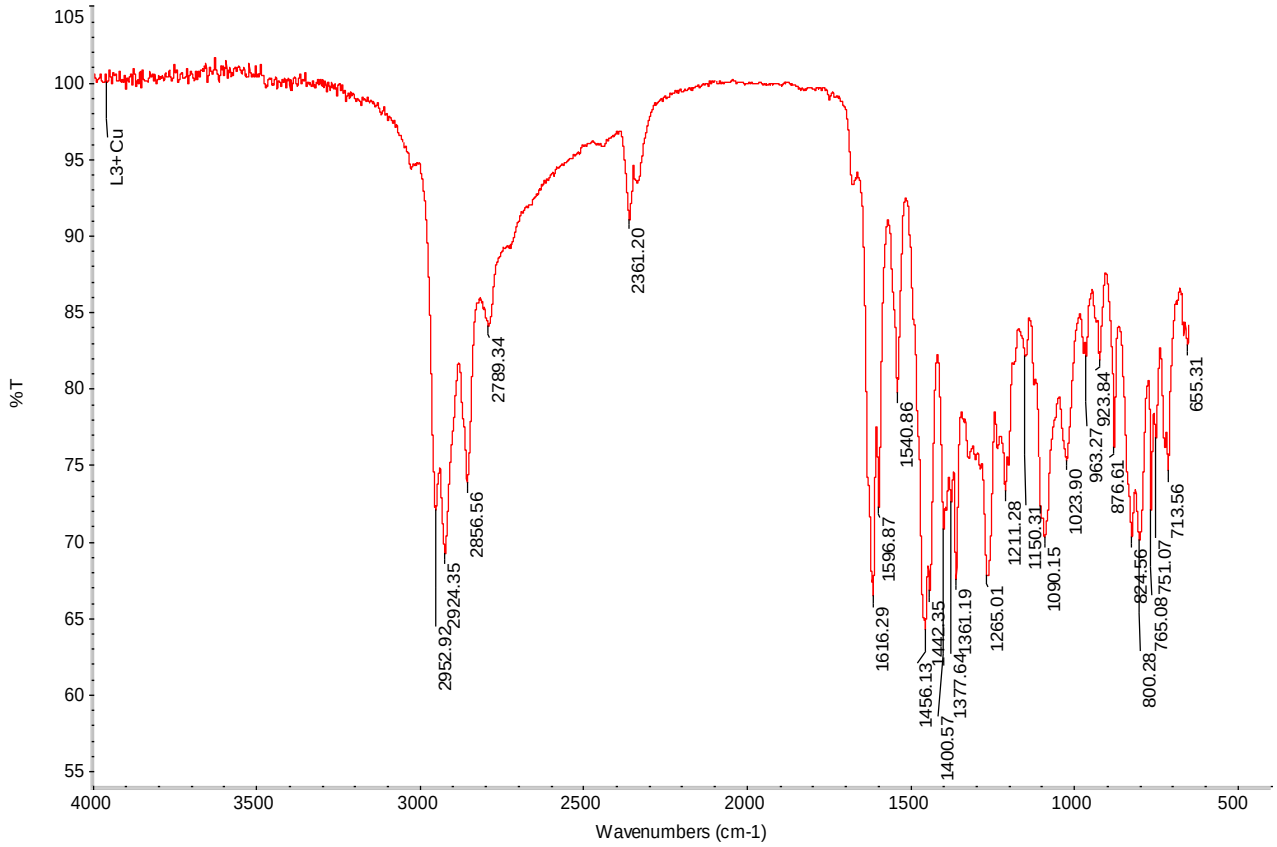
[Cu(L^1-2H)]



[Cu(L^2-2H)]

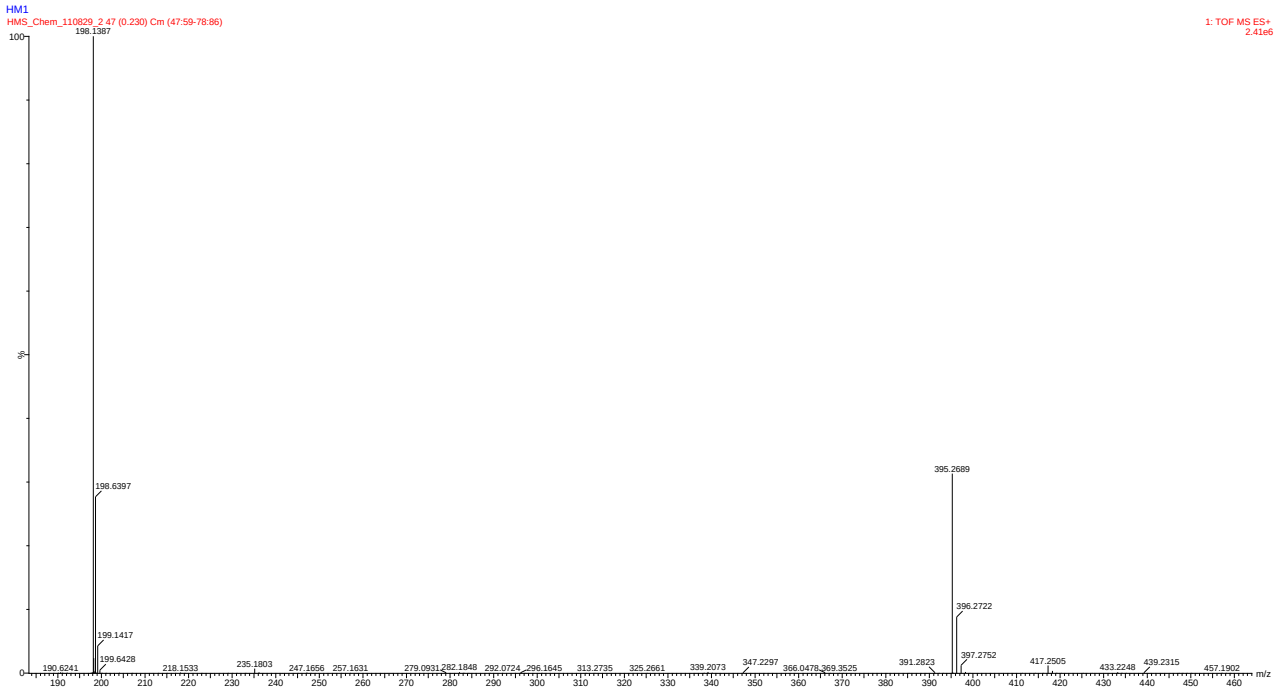


[Cu(L^3-2H)]



MS

Ligand 1 (L1)



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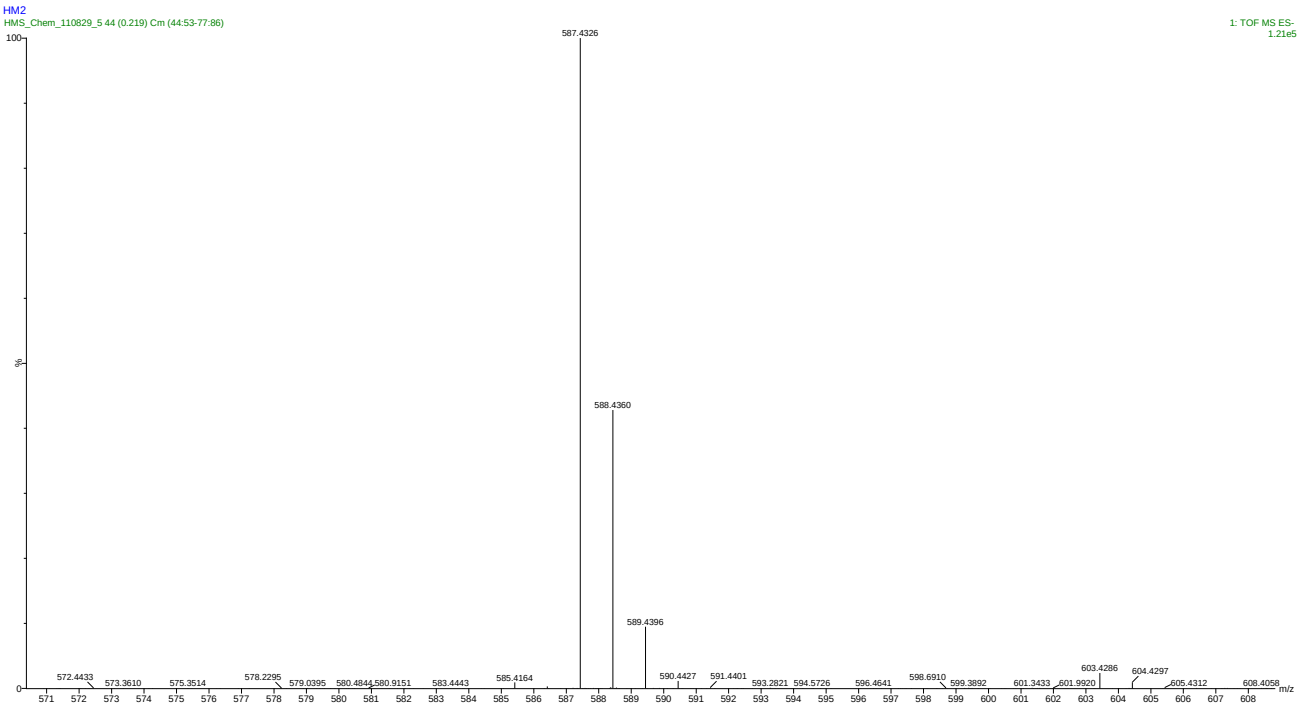

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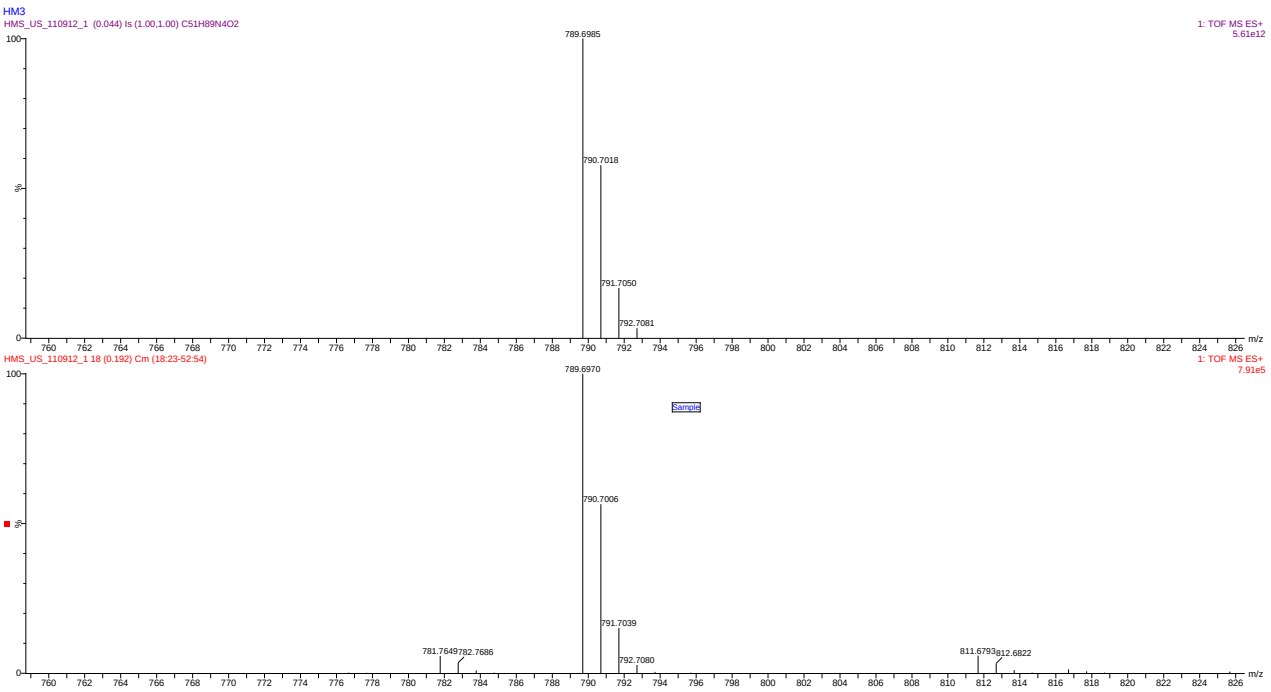

6. References

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