Structural and ethylene oligomerization studies of chelating (imino)phenol Fe(II), Co(II) and Ni(II) complexes: Experimental and theoretical approach

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Supplementary Information

1. *Synthesis of Schiff base ligands*

1.1. *2,4-dibromo-6-((pyridin-2-ylimino)methyl)phenol (**L1H**)*

To the ethanolic (10 mL) solution of 2-aminopyridine (0.19 g, 2 mmol), 3,5-dibromosalicylaldehyde (0.56 g, 2 mmol) in ethanol (10 mL) was added dropwise and stirred at room temperature for 24 h. The orange powder formed was filtered, washed with ethanol, and dried to obtain pale orange powder. Yield: 0.61 g (81%). ^{1}H NMR (400 MHz,

CDCl$_3$, δ ppm): 9.42 (s, 1H, imine <u>H</u>C=N-), 8.55 (d, 1H, $^3J_{HH}$ = 9.2 Hz, Py-C<u>H</u>=N), 7.84 (t, 1H, $^3J_{HH}$ = 7.2 Hz, Py-H), 7.80 (s, 1H, Ph-H), 7.60 (s, 1H, Ph-H), 7.34 (t, 1H, $^3J_{HH}$ = 7.2 Hz, Py-H), 7.31 (d, 1H, $^3J_{HH}$ = 9.2 Hz, Py-H); ^{13}C NMR (CDCl$_3$): δ/ppm: 110.22, 113.57, 120.60, 123.45, 124.46, 134.51, 138.79, 138.88, 149.19, 153.84, 159.76, 162.28; IR ν_{max}/ cm^{-1}: 3058 (ν_{OH}), 1606 ($\nu_{C=N}$). ESI-MS: m/z (%) 354.87 (100%) [M-H]$^+$.

1.2. 2,4-dibromo-6-(((4-methylpyridin-2-yl)imino)methyl)phenol (*L2H*)

Ligand **L2H** was synthesized following the same procedure adopted for **L1H** using 2-amino-4-methylpyridine (0.21 g, 2 mmol) and 3,5-dibromosalicylaldehyde (0.56 g, 2 mmol) to give orange powder. Yield: 0.65 g (82%). ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 9.39 (s, 1H, imine <u>H</u>C=N-), 8.39 (d, 1H, $^3J_{HH}$ = 9.2 Hz, Py-C<u>H</u>=N), 7.80 (s, 1H, Ph-H), 7.59 (s, 1H, Ph-H), 7.18 (s, 1H, Py-H), 7.12 (d, 1H, $^3J_{HH}$ = 9.2 Hz, Py-H), 2.45(s, 3H, Py-C<u>H</u>$_3$); ^{13}C {^{1}H} NMR (CDCl$_3$): δ/ppm: 20.99, 110.87, 112.57, 120.38, 121.29, 124.46, 134.43, 138.79, 148.81, 150.32, 155.84, 158.76, 162.08; IR ν_{max}/ cm^{-1}: 3069 (ν_{OH}), 1623 ($\nu_{C=N}$); HRESI-MS: m/z 368.90 (100%) [M-H]$^+$.

1.3. 2,4-dibromo-6-((quinolin-8-ylimino)methyl)phenol (*L3H*)

Ligand **L3**H was synthesized following the same procedure adopted for **L1H** and **L2H**, using 8-aminoquinoline (0.29 g, 2 mmol) and 3,5-dibromosalicylaldehyde (0.56 g, 2 mmol) to give reddish orange powder. The ligand on recrystallization in dichloromethane obtained X-ray quality reddish orange single crystals. Yield: 0.76 g (89%). ^{1}H NMR (400 MHz, CDCl3, δ ppm): 9.03 (d, 1H, $^3J_{HH}$ = 9.2 Hz , quin <u>H</u>C=N-), 8.99 (s, 1H, imine <u>H</u>C=N-), 8.24 (d, 1H, $^3J_{HH}$ = 9.2 Hz, quin-H), 7.82 (d, 1H, $^3J_{HH}$ = 9.2 Hz, quin-H), 7.80 (s, 1H, Ph-H), 7.63 (s, 1H, Ph-H), 7.60 (d, 1H, $^3J_{HH}$ = 9.2 Hz, quin-H), 7.53(t, 2H, $^3J_{HH}$ = 7.2 Hz, quin-H); ^{13}C {^{1}H} NMR (CDCl$_3$): δ/ppm: 109.20, 113.59, 119.37, 120.49, 120.05, 126.49, 127.18, 129.25,

133.59,136.09,138.62, 141.88, 142.37, 150.76, 160.09, 161.76; IR ν_{max}/ cm^{-1}: 3068 (ν_{OH}), 1609 ($\nu_{C=N}$); HRESI-MS: m/z 404.91 (100%) [M-H]$^+$.

Nuclear magnetic resonance spectroscopy characterization of the Schiff base ligands
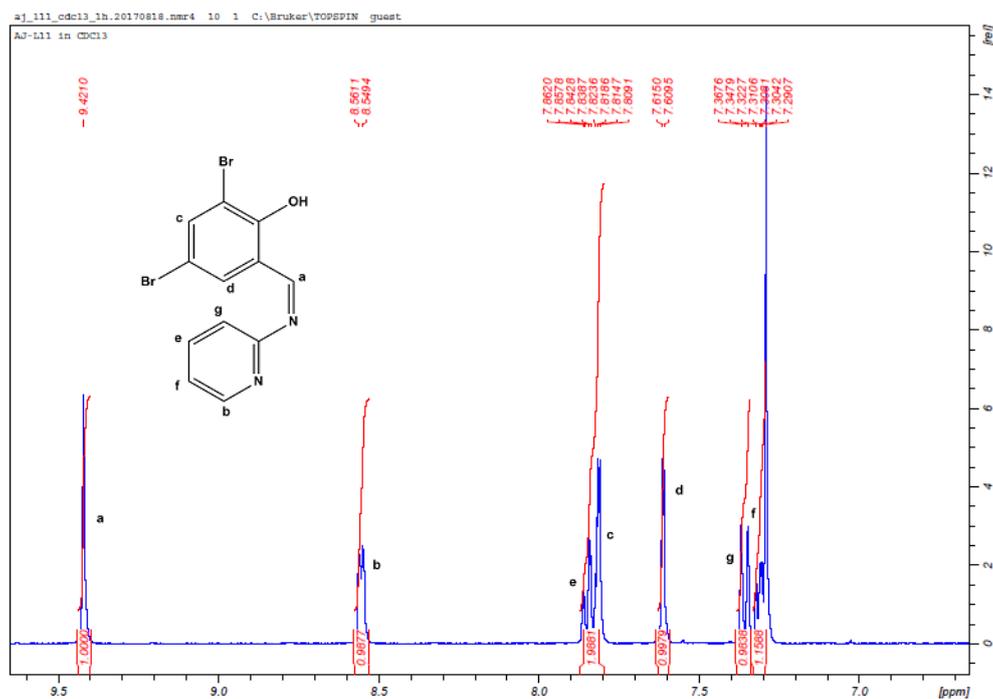
Figure S1: ^{1}H NMR spectrum of ligand **L1H** in CDCl$_3$ showing imine proton signal at 9.42 ppm.
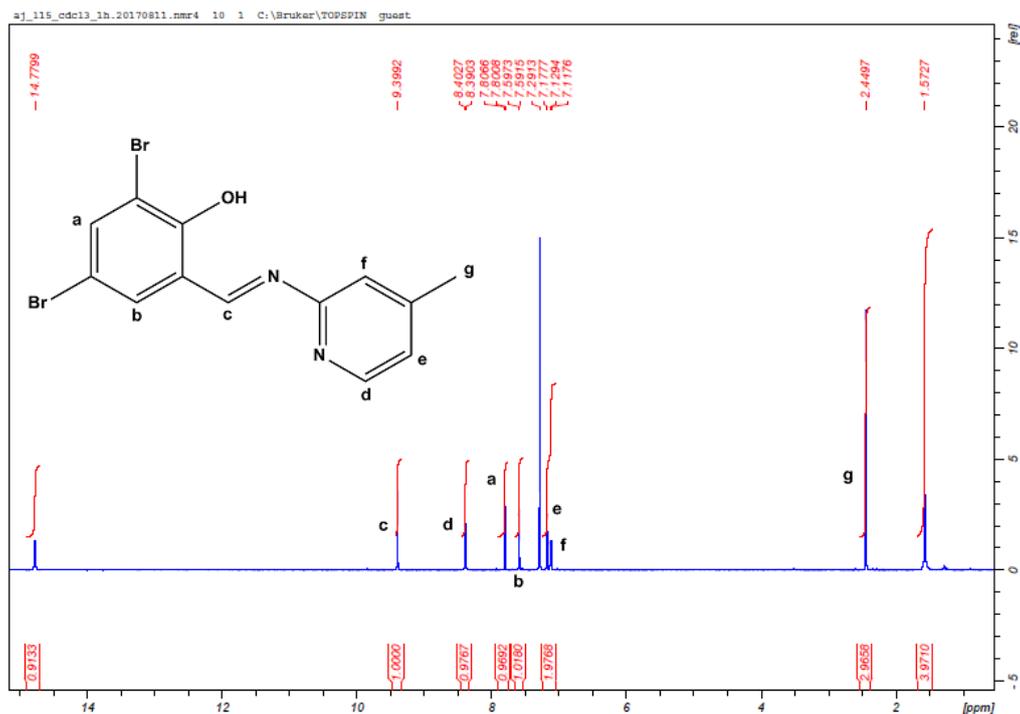
Figure S2: ^{1}H NMR spectrum of ligand **L2H** in CDCl$_3$ displaying the imine proton peak (**c**) at 9.39 ppm.
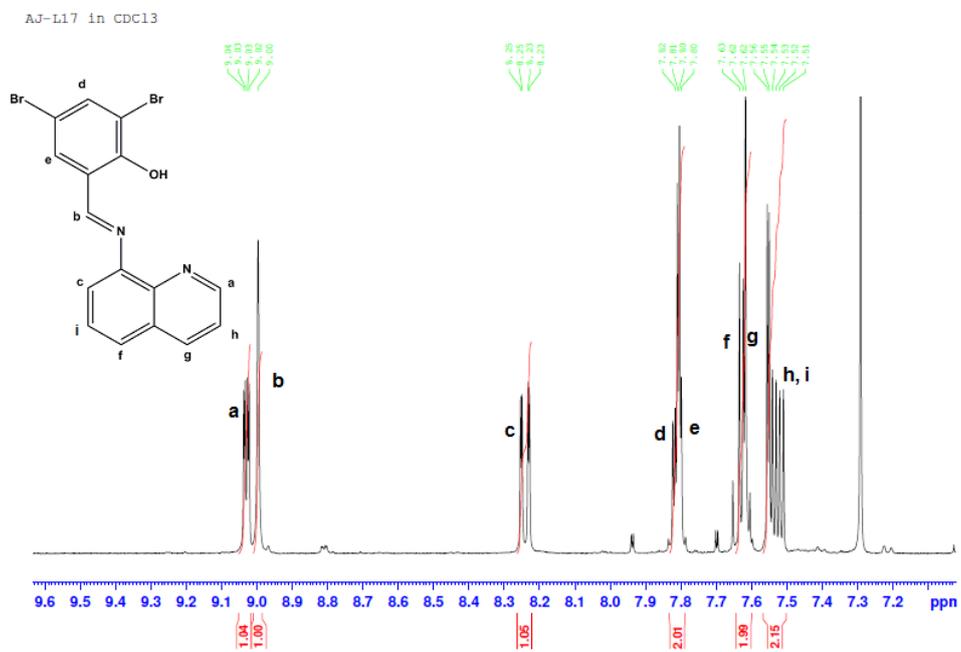
Figure S3: ^{1}H NMR spectrum of ligand **L3H** in CDCl$_3$ showing the presence of the imine (**b**) proton peak at 9.00 ppm.
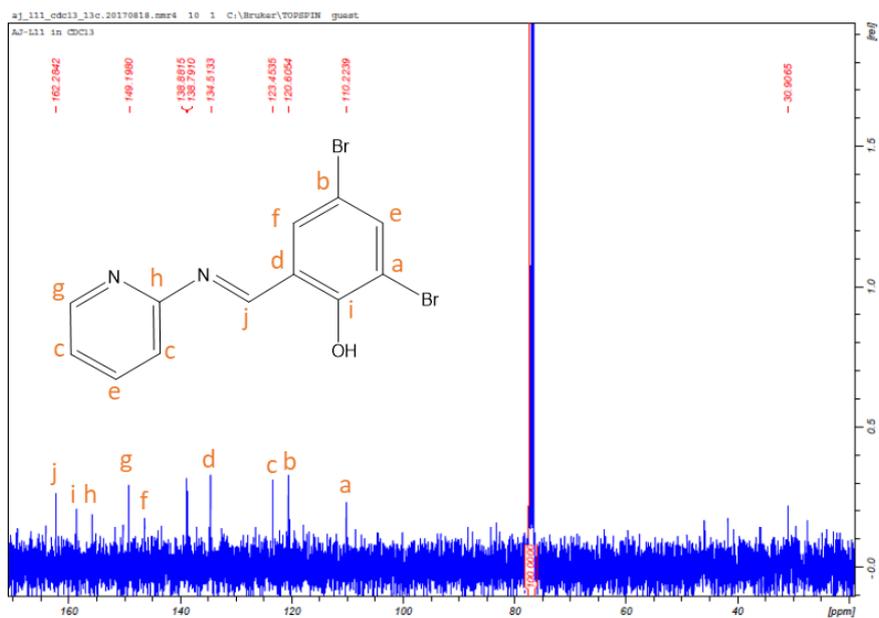
Figure S4: ^{13}C NMR spectrum of ligand **L1H** in CDCl$_3$ showing the presence of all carbons and the imine carbon at 162.3 ppm.
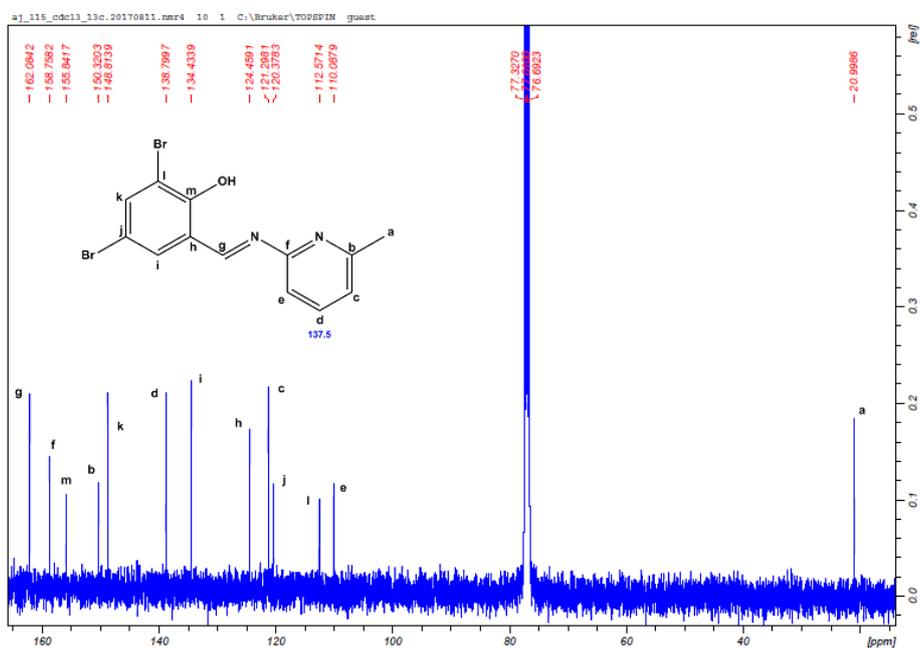
Figure S5: ^{13}C NMR spectrum of ligand **L2H** in CDCl$_3$ showing the imine carbon peak (g) at 162.1 ppm.
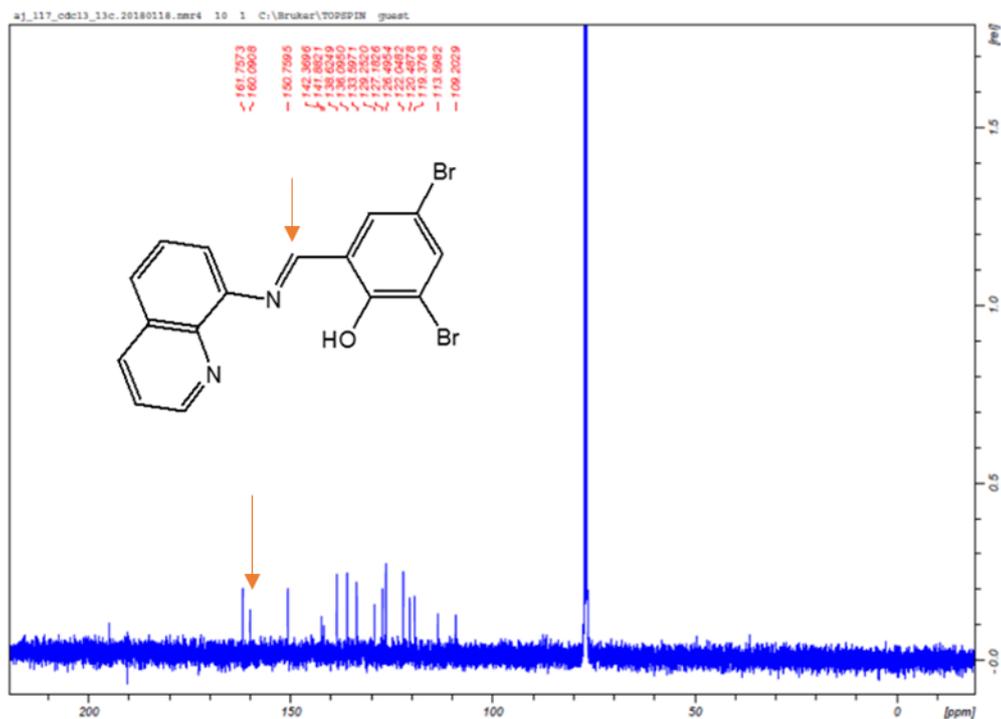
Figure S6: ^{13}C NMR spectrum of ligand **L3H** in CDCl$_3$ showing the diagnostic imine carbon signal at 161.8 ppm.

__FTIR spectroscopic analyses of the Schiff base ligands (L1H-L3H) and their metal complexes__
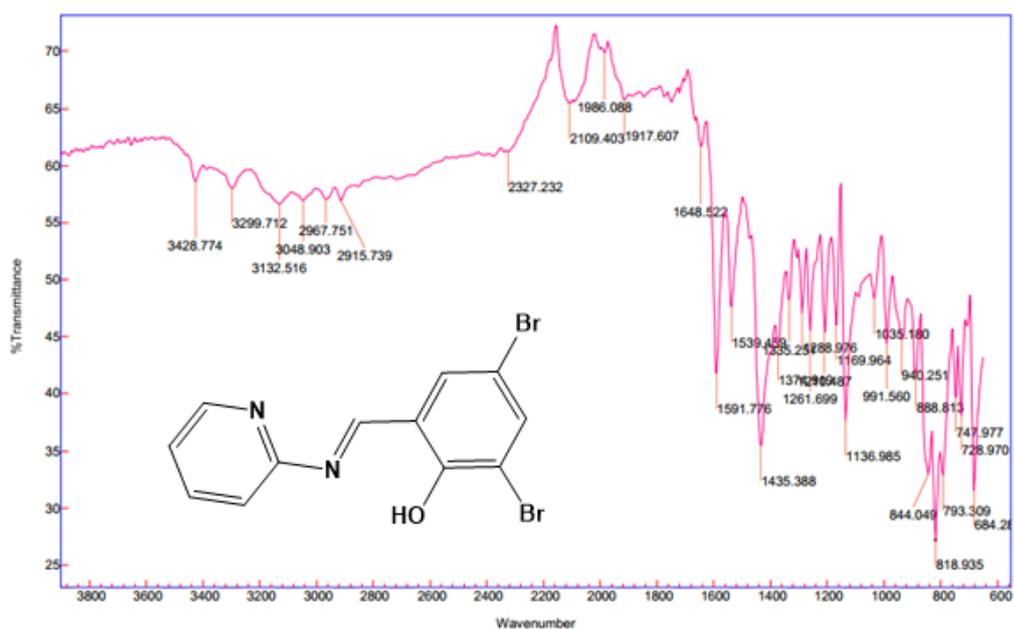
Figure S7: FTIR spectrum of the Schiff base ligand **L1H** showing the presence of $\nu_{(C=N)}$ at 1592 cm^{-1}.
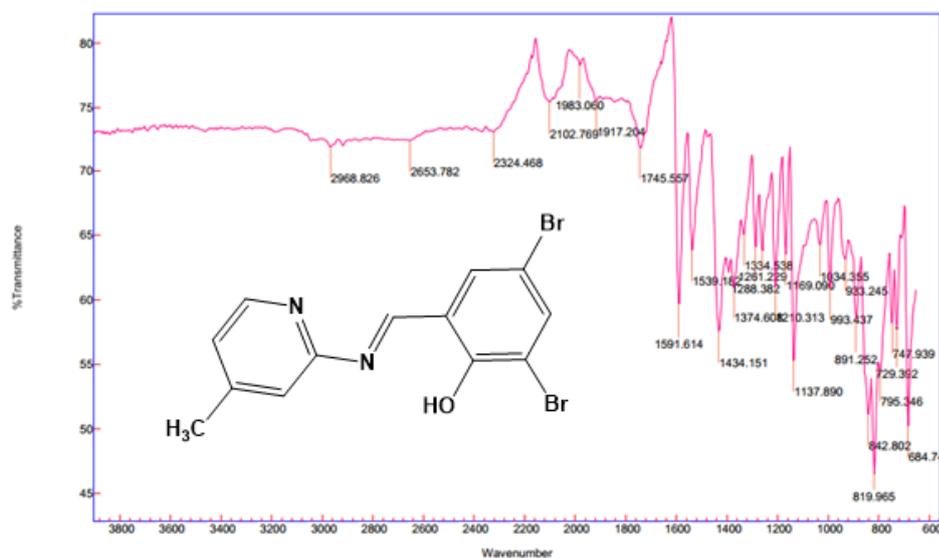
Figure S8: FTIR spectrum of the Schiff base ligand **L2H** showing the presence of $\nu_{(C=N)}$ at 1591 cm^{-1}.
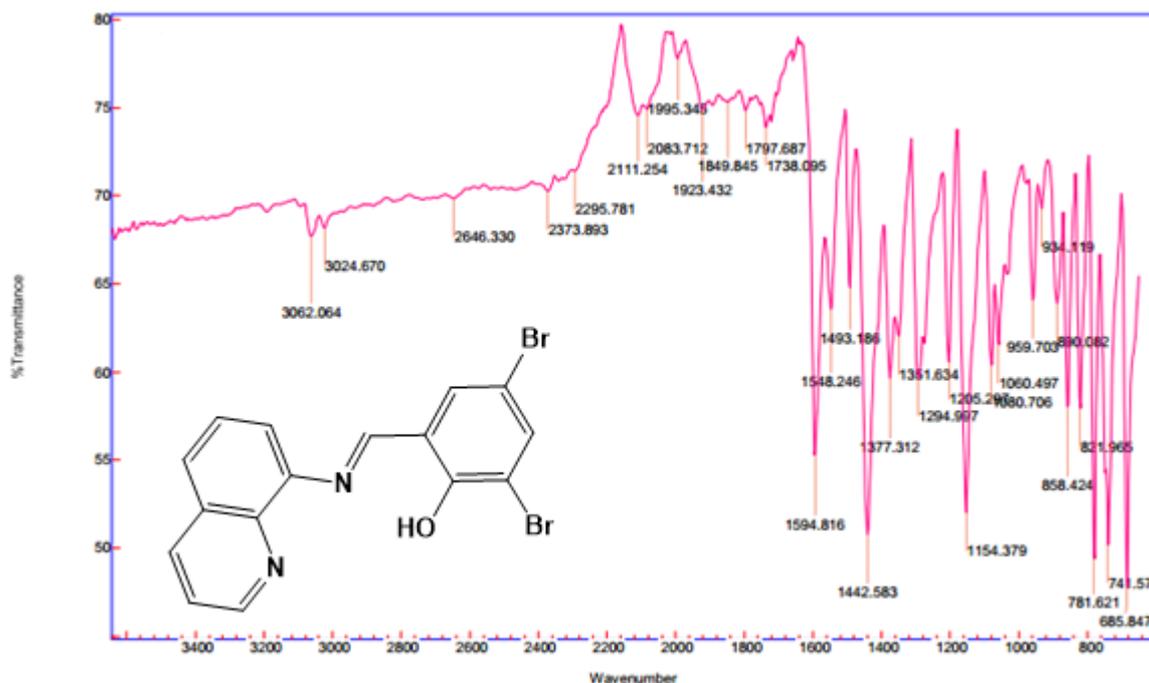
Figure S9: FTIR spectrum of the Schiff base ligand **L3H** showing the presence of $\nu_{(C=N)}$ at and $\nu_{(O-H)}$ and 1594 cm^{-1} and 3062 cm^{-1} respectively.
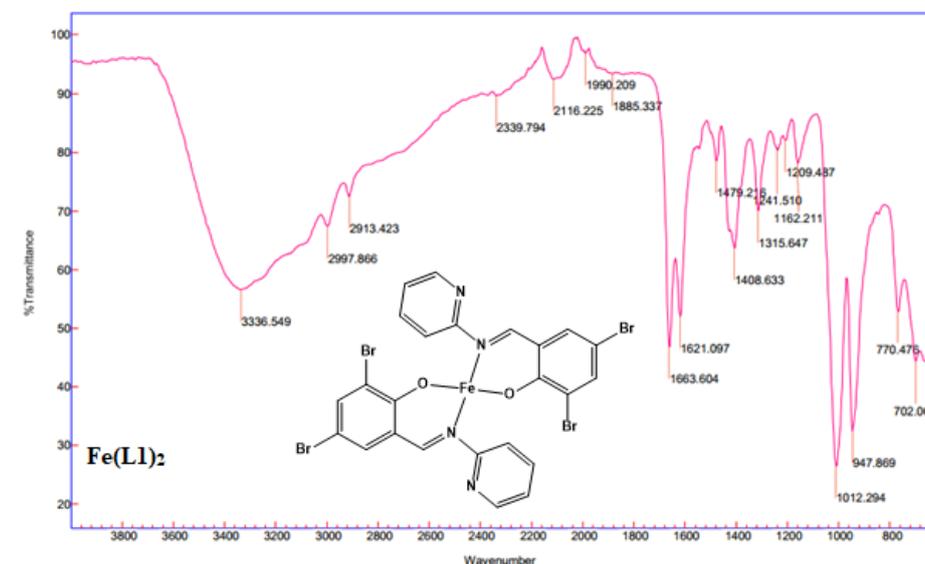
Figure S10: FTIR spectrum of **Fe1** showing the presence of $\nu_{(C=N)}$ at 1663.60 cm^{-1}.
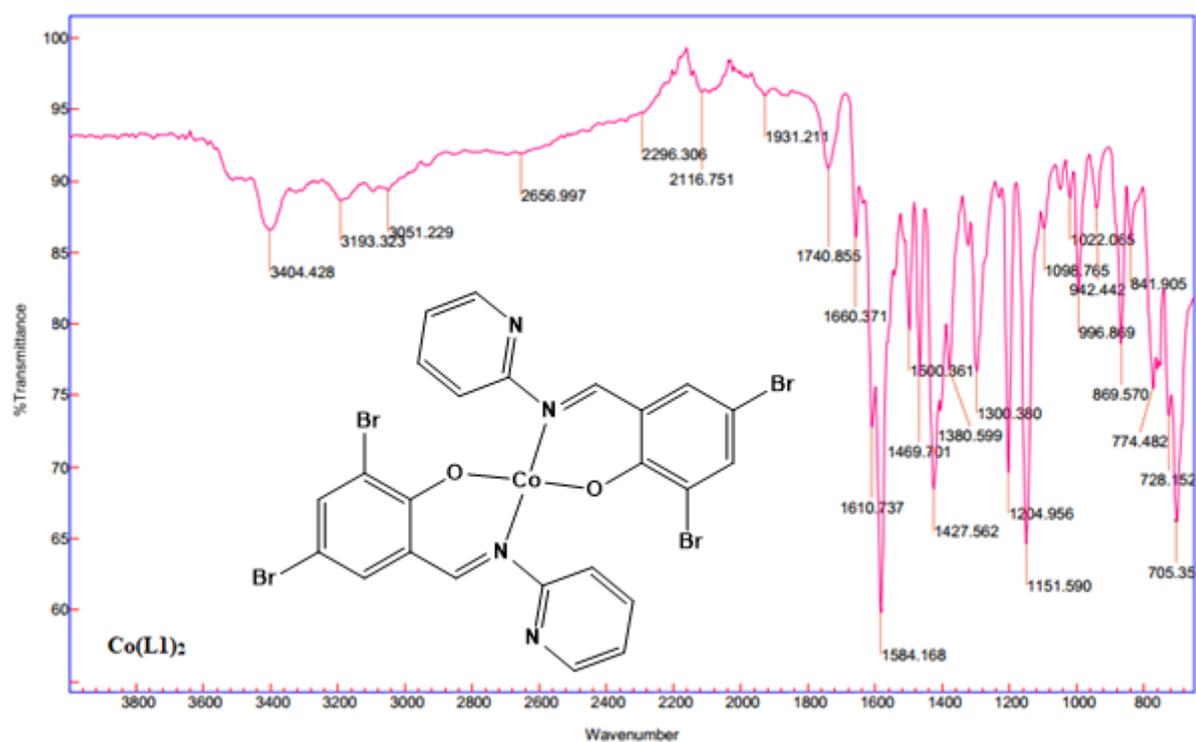
Figure S11: FTIR spectrum of **Co1** showing the $\nu_{(C=N)}$ stretching frequency at 1584 cm^{-1}.
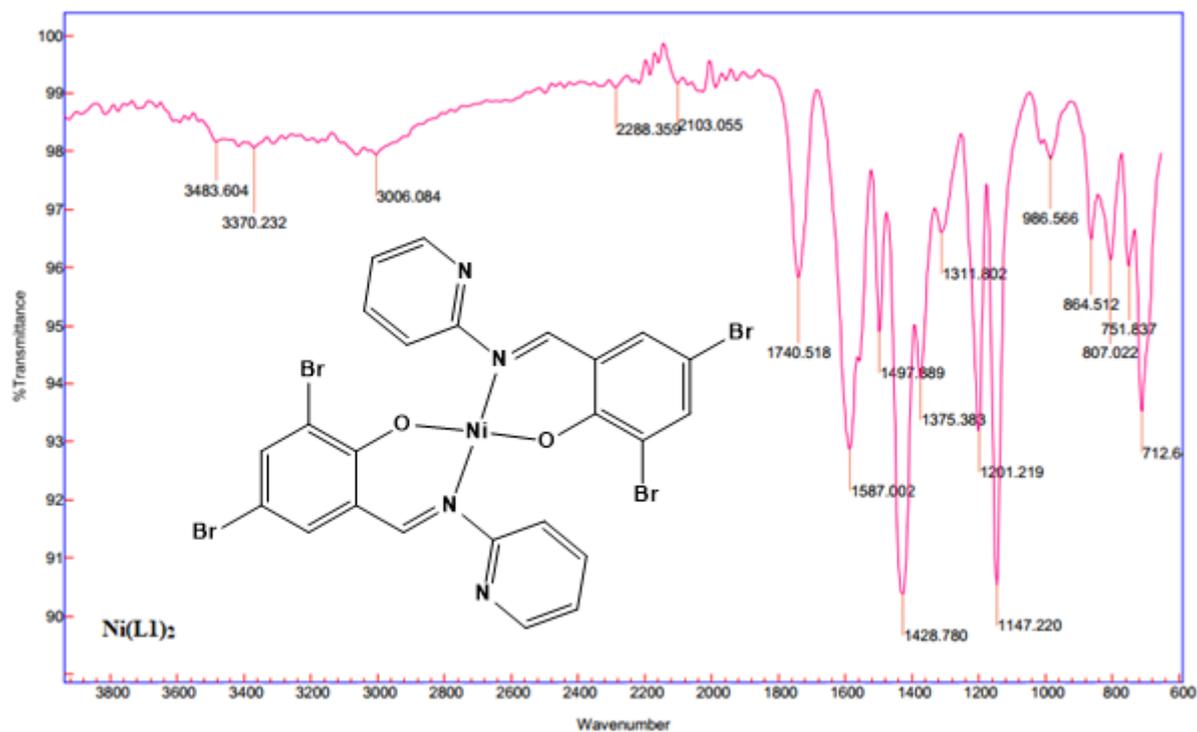
Figure S12: FTIR spectrum of **Ni1** showing the sharp peak at 1587.02 cm^{-1} corresponding to the $\nu_{(C=N)}$ stretching frequency.
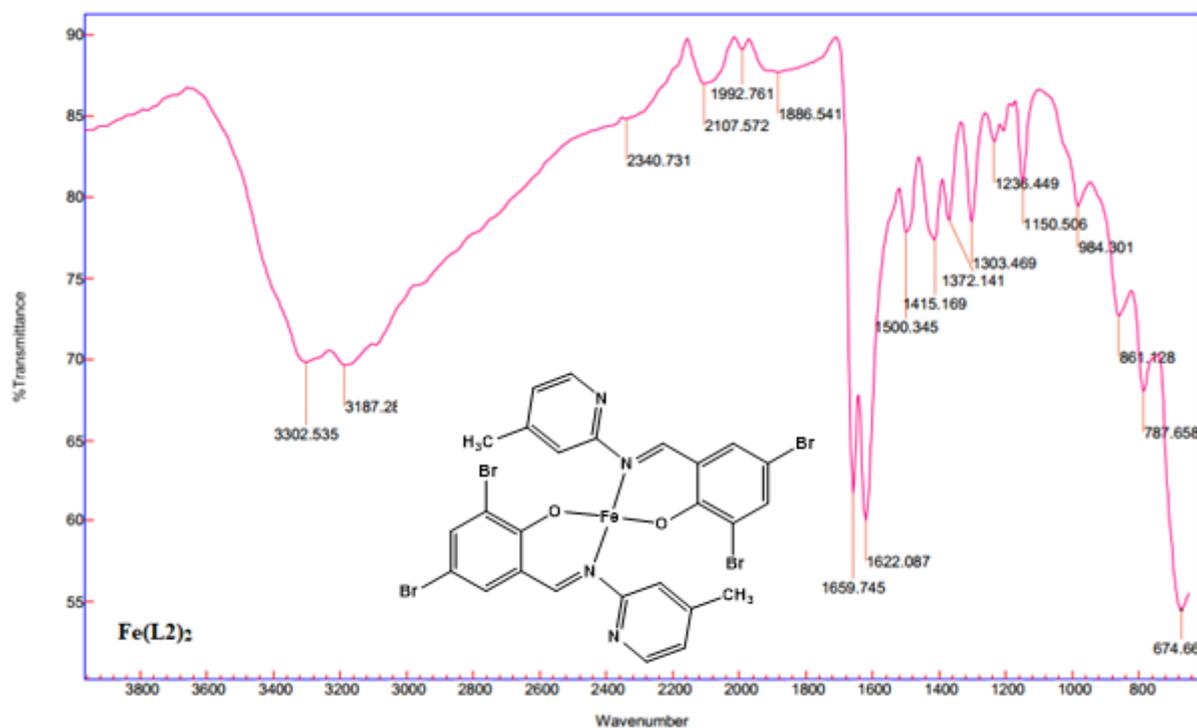
Figure S13: FTIR spectrum of **Fe2** showing the $\nu_{(C=N)}$ stretching frequency at 1659.74 cm^{-1}.
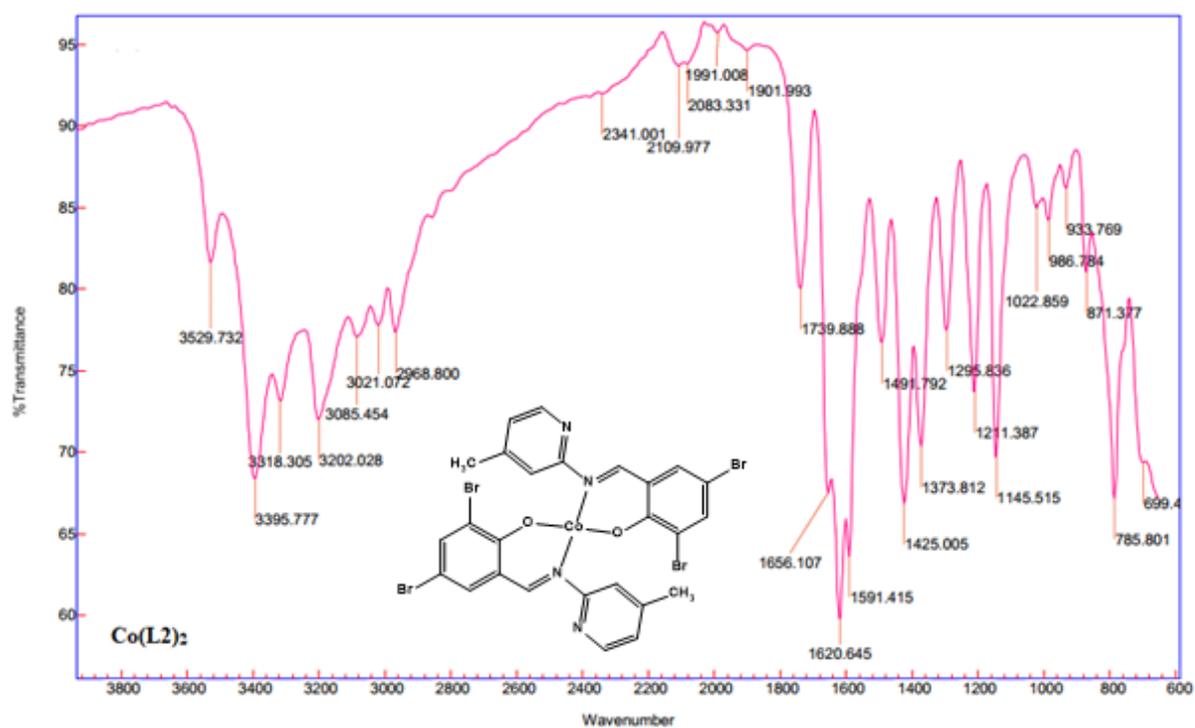
Figure S14: FTIR spectrum of **Co2** showing the $\nu_{(C=N)}$ stretching frequency at 1620.64 cm^{-1}.
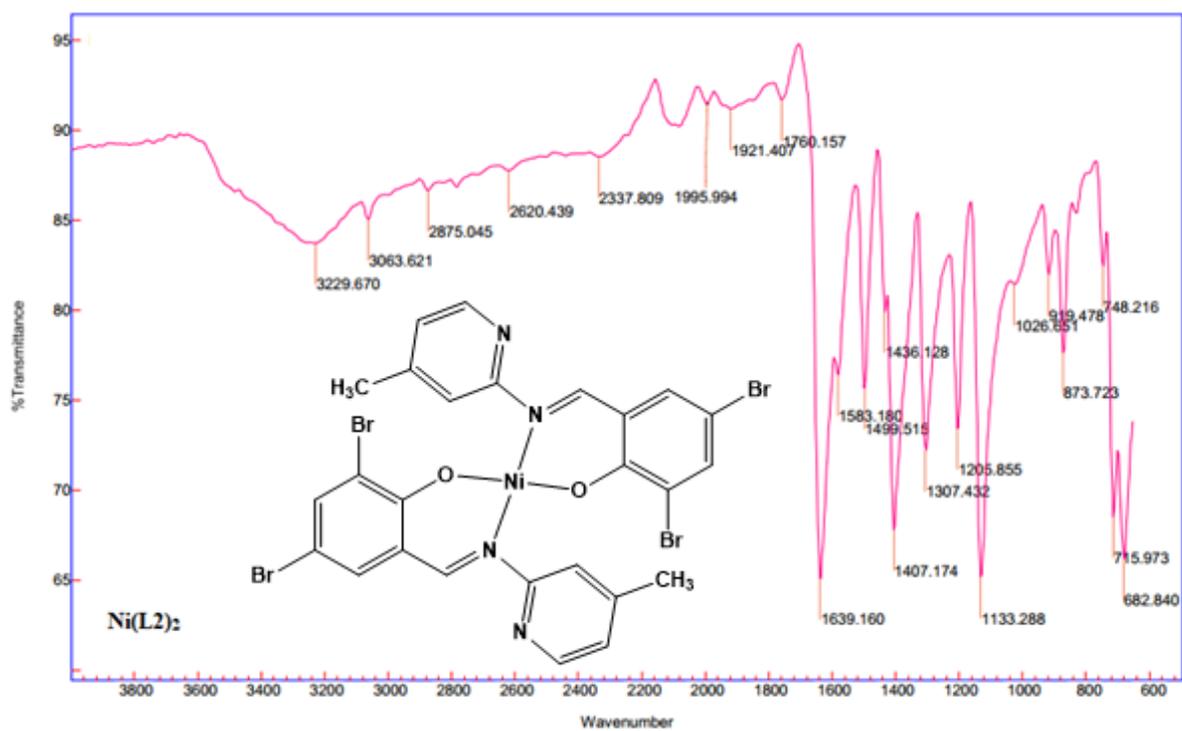
Figure S15: FTIR spectrum of **Ni2** showing a long and sharp peak at 1639.16 cm^{-1} which is a diagnostic peak of $v_{(C=N)}$ stretching frequency.
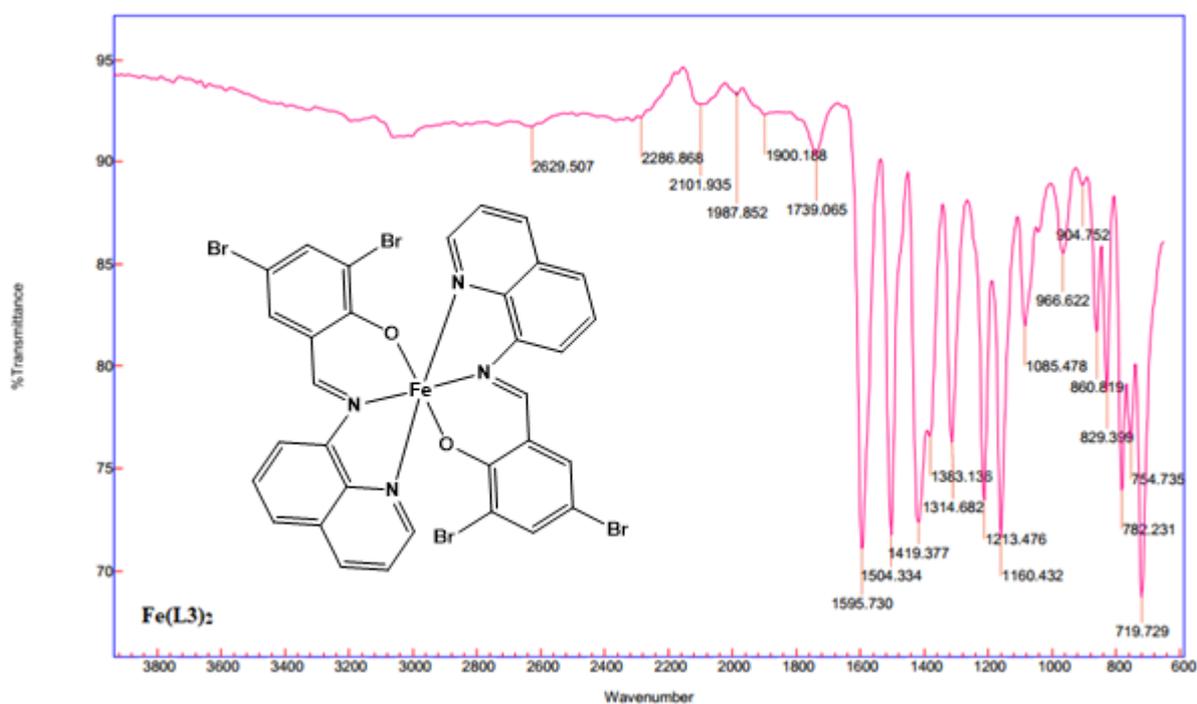
Figure S16: FTIR spectrum of **Fe3** showing the $v_{(C=N)}$ stretching frequency at 1595 cm^{-1}.
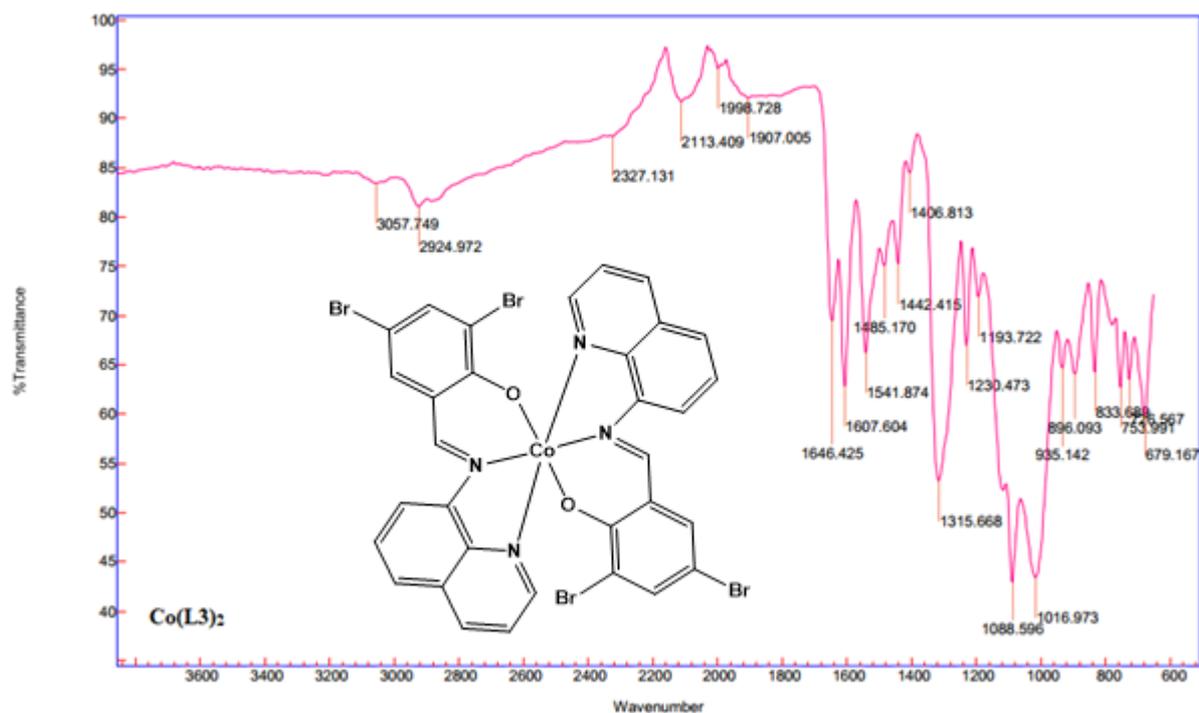
Figure S17: FTIR spectrum of **Co3** showing the $v_{(C=N)}$ stretching frequency at a higher wavenumber of 1646.43 cm^{-1}.
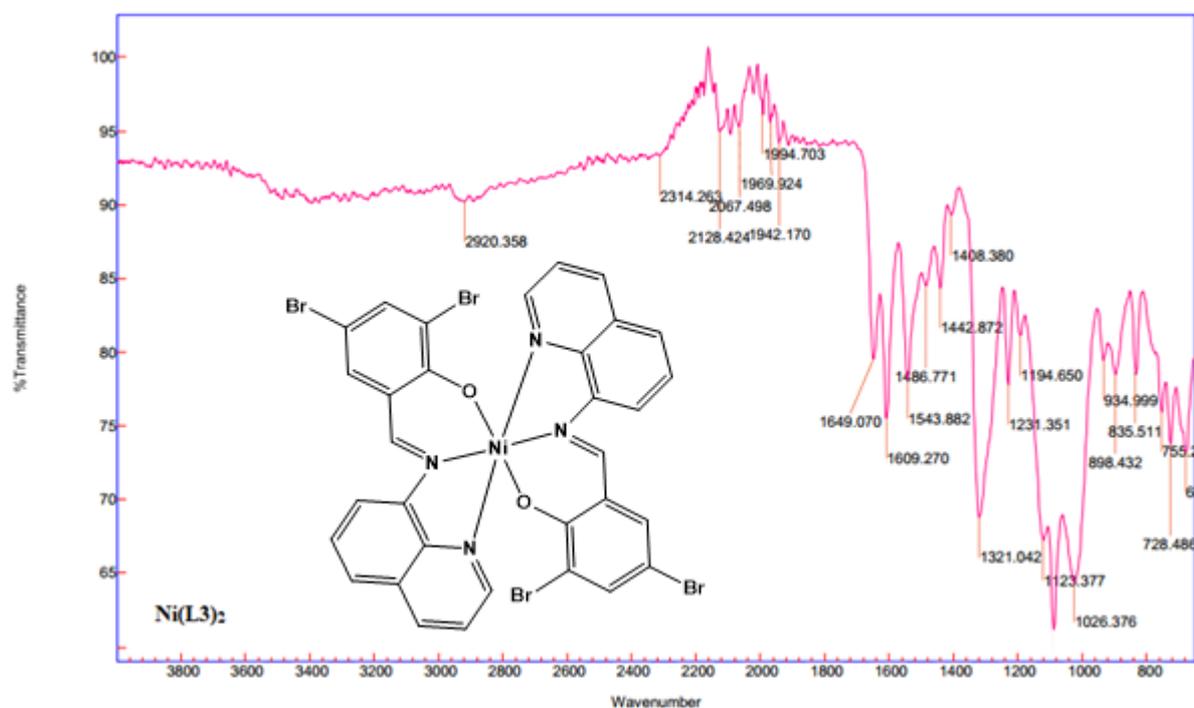
Figure S18: FTIR spectrum of **Ni3** revealing the presence of the $v_{(C=N)}$ stretching frequency at 1609.27 cm^{-1} and the absence of the O-H proton upon complexation.

Figure S19: Mass spectrum of ligand **L1H** showing the ligand's $[M]^+$ molecular ion peak at

354.34 amu and its predicted isotopic distribution inserted.
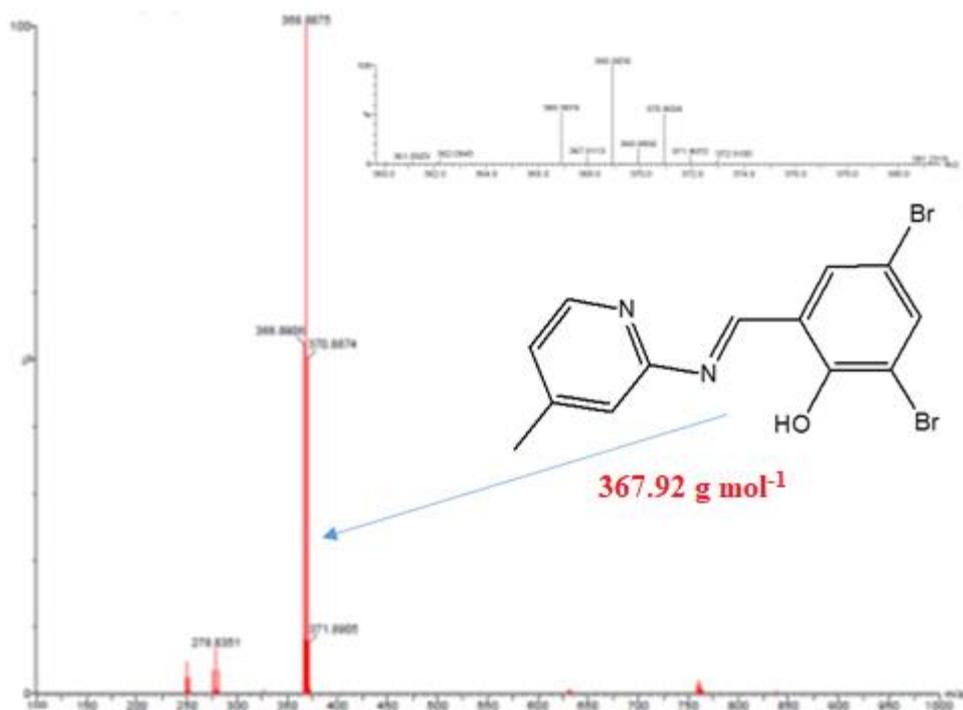
Figure S20: Mass spectrum of ligand **L2H** (HR-MS inserted) illustrating the ligand's molecular ion peak [M]$^+$ at 368.04 amu.
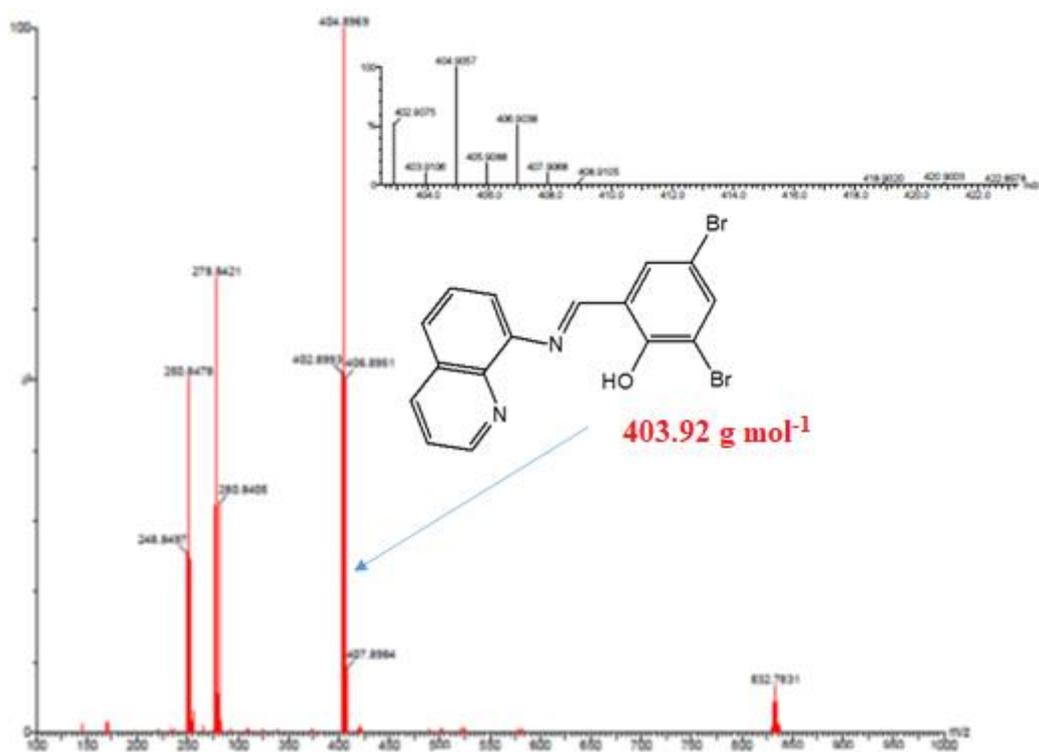
Figure S21: Mass spectrum of ligand **L3H** (HR-MS inserted) showing the ligand's base peak [M]$^+$ at 404.84 amu.
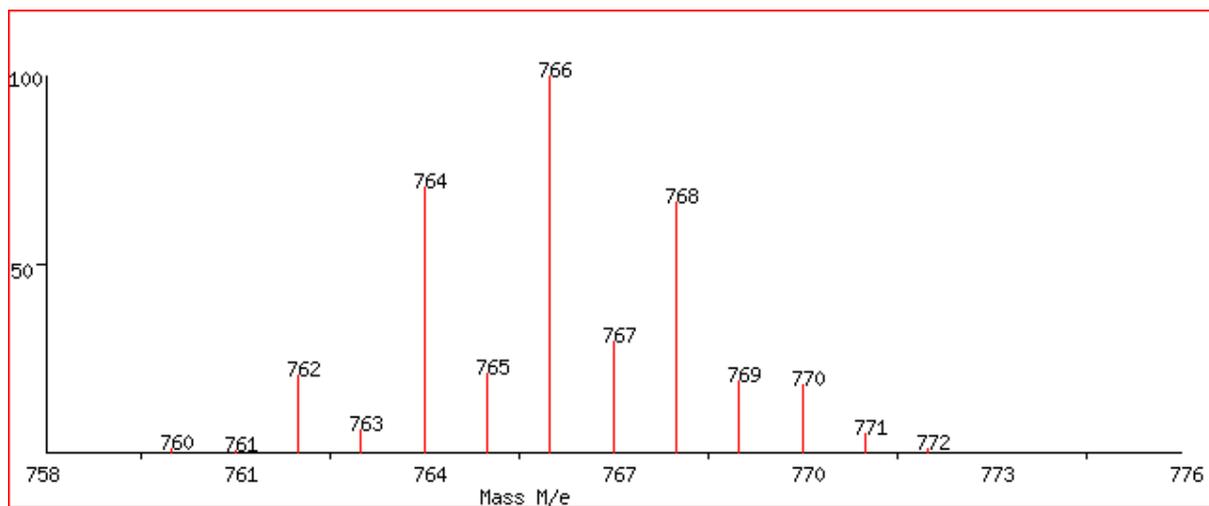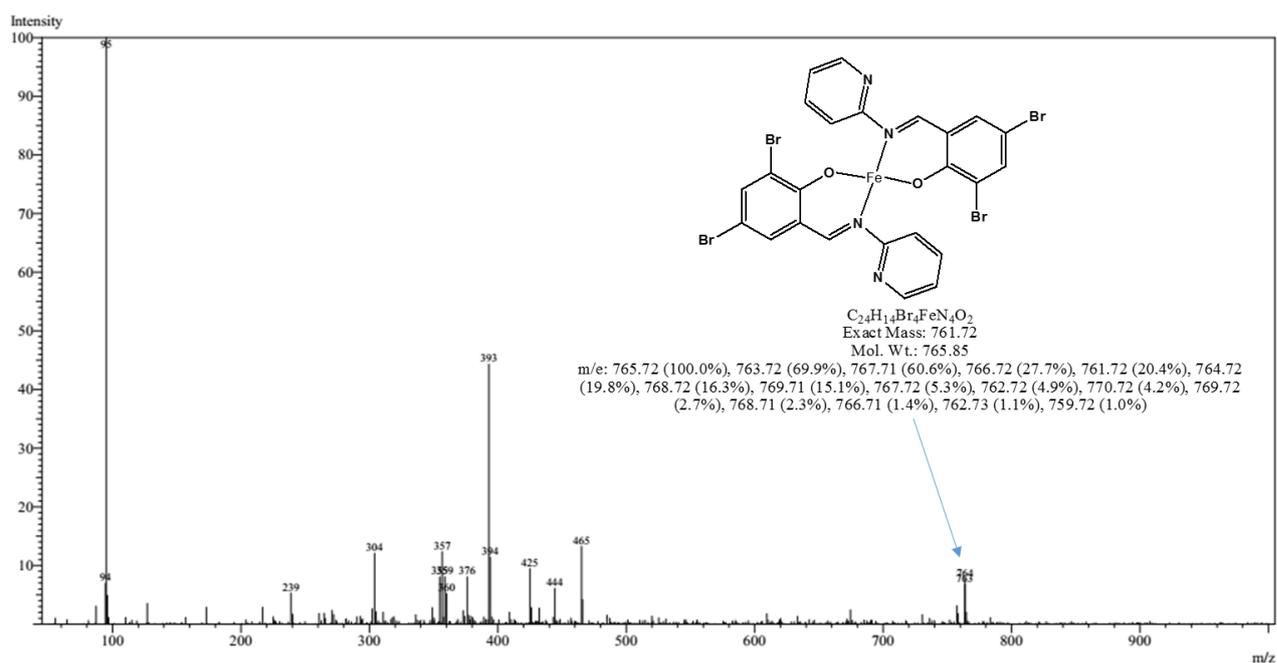
Figure S22: Mass spectrum of complex **Fe1** showing the formation of the *bis*-chelated complex

by the peak at 364.00 (10 %) and its predicted isotopic distribution at m/z = 765 amu.
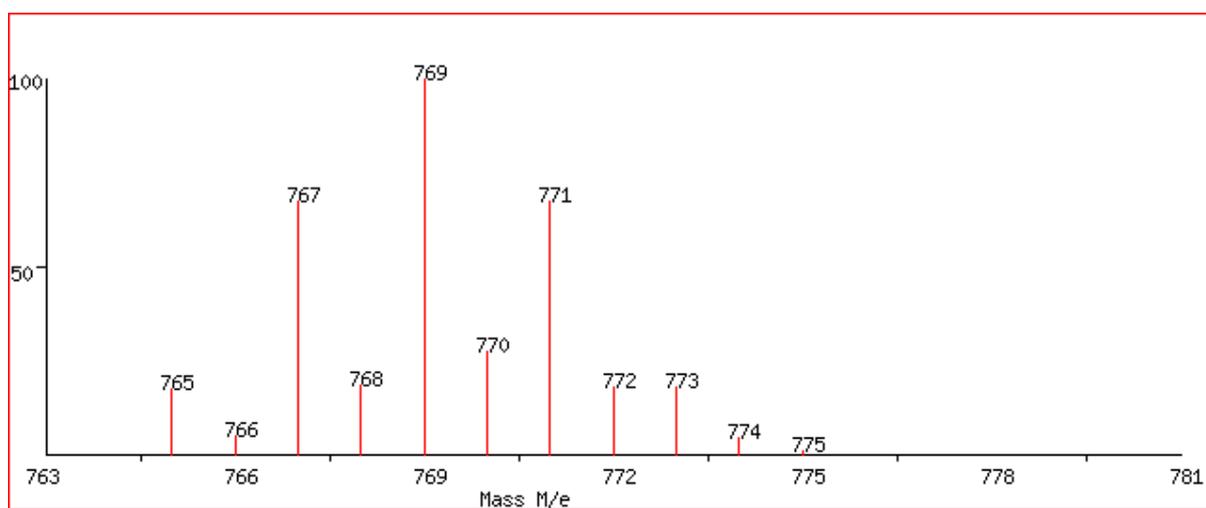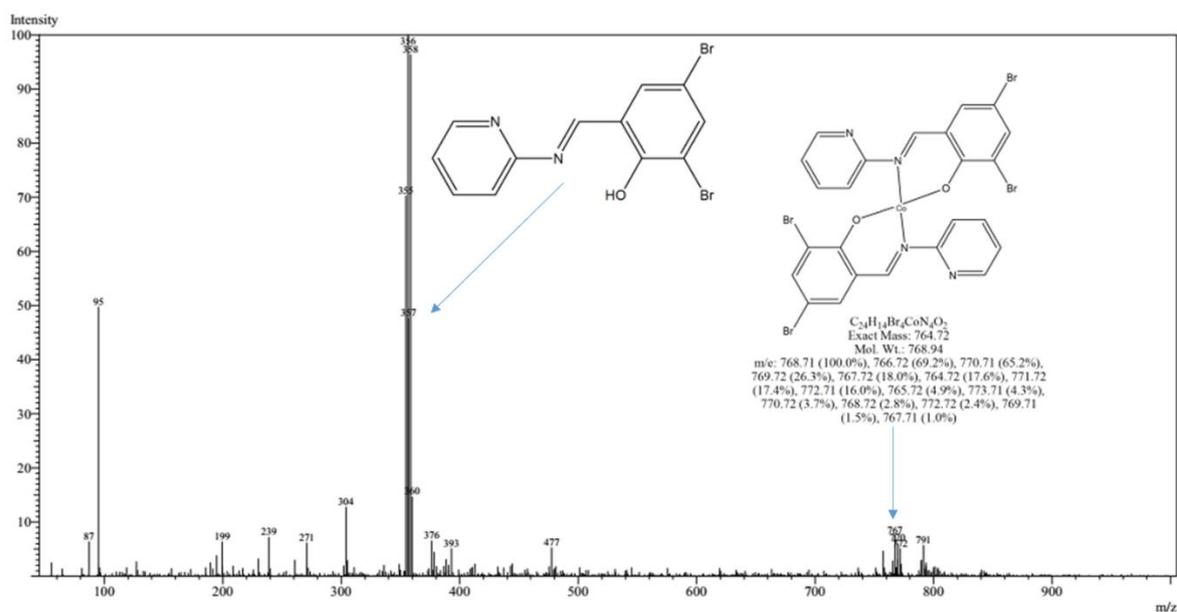
Figure S23: ESI Mass spectrum of complex **Co1** showing a peak at 767.00 amu corresponding

to [Co(**L1**)$_2$]$^+$ fragment and its simulated isotopic distribution at m/z = 769 amu.
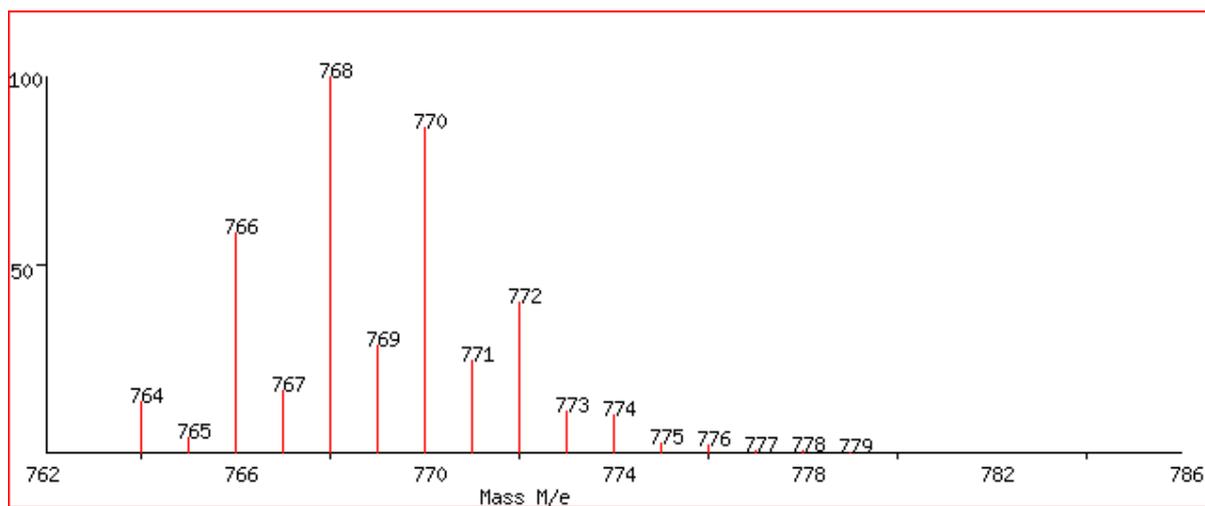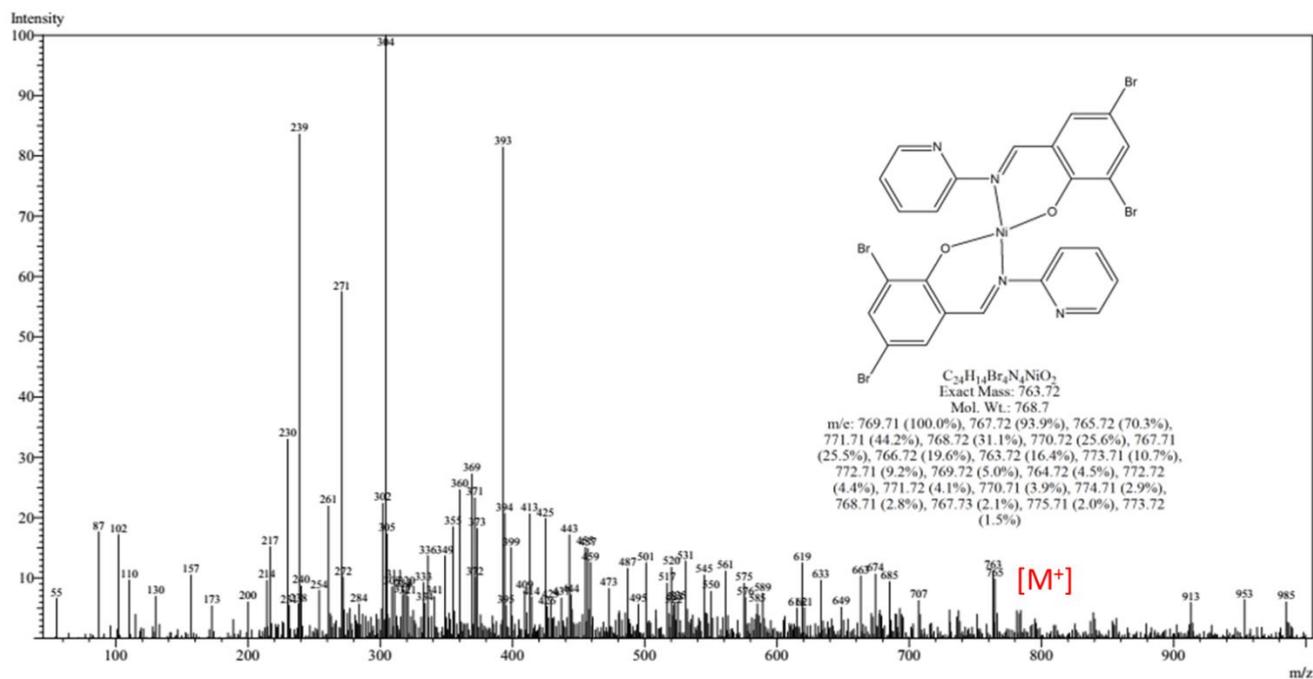
Figure S24: Mass spectrum of complex **Ni1** showing the peak [Ni(**L1**)$_2$]$^+$ fragment at 763.00 amu and its predicted isotopic distribution at m/z = 768 amu.

$[M^+-4Br^-+Na] = 478.33$ g/mol

$C_{26}H_{18}Br_4FeN_4O_2$
Exact Mass: 789.75
Mol. Wt.: 793.91
m/e: 793.75 (100.0%), 791.75 (71.2%), 795.75 (67.9%), 794.75 (30.4%), 792.75 (20.9%), 789.75 (20.9%), 796.75 (19.5%), 797.74 (15.2%), 790.75 (5.4%), 798.75 (4.5%), 797.75 (3.4%), 793.76 (2.8%), 792.76 (2.0%), 794.74 (1.4%), 790.76 (1.2%), 787.76 (1.1%), 791.76 (1.0%)
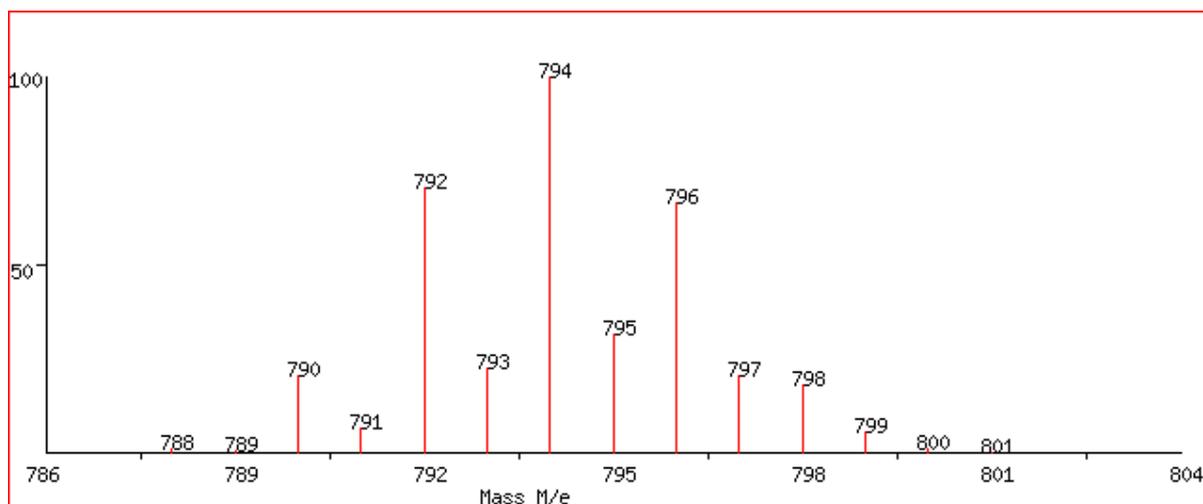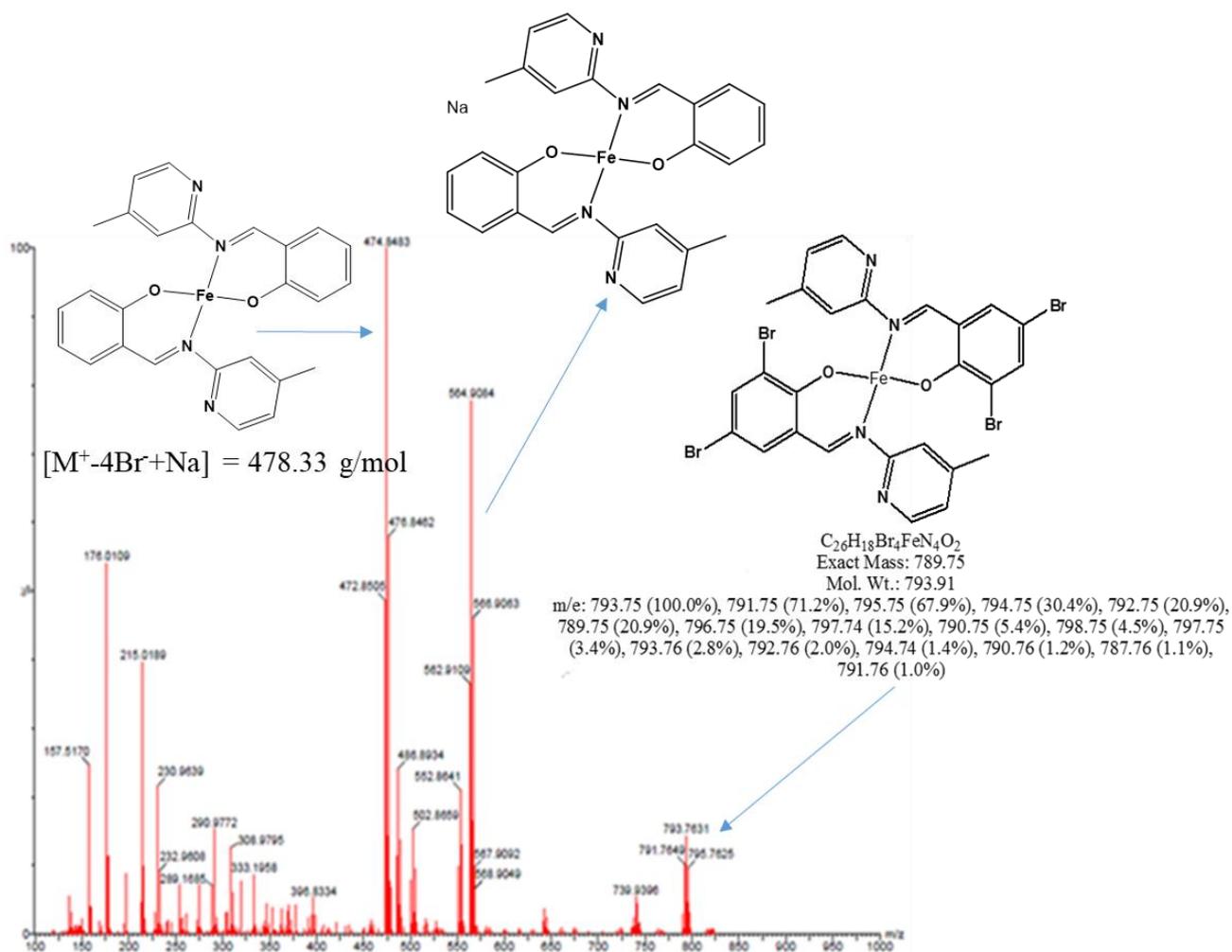
Figure S25: ESI Mass spectrum of complex **Fe2** showing the [M+] peak at 793.76 amu and base peak at 474.14 amu corresponding to [Fe(**L2**)$_2$ – 4Br$^-$]$^+$ fragment. Its predicted isotopic distribution at m/z = 794 amu is also illustrated.

[M⁺-4Br+Na] = 504.41 g/mol

$C_{26}H_{18}Br_4CoN_4NaO_2$
Exact Mass: 815.74
Mol. Wt.: 819.99
m/e: 819.74 (100.0%), 817.74 (66.6%), 821.73 (62.9%), 820.74 (27.6%), 818.74 (18.9%), 822.74 (18.0%), 815.74 (17.1%), 823.73 (15.6%), 816.74 (5.1%), 821.74 (4.6%), 824.73 (4.5%), 823.74 (2.7%), 820.73 (1.4%)

[M⁺+ Na]
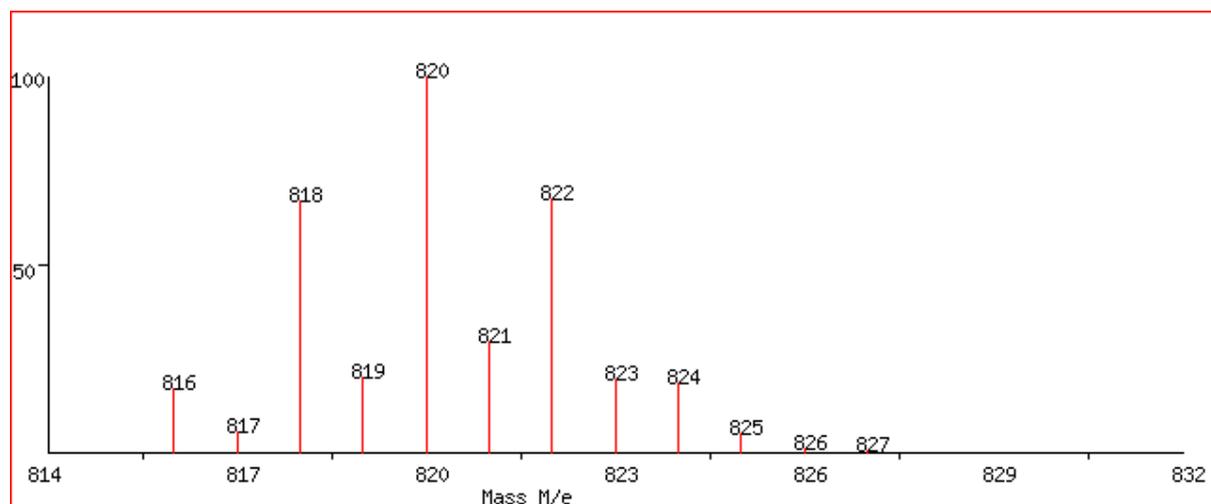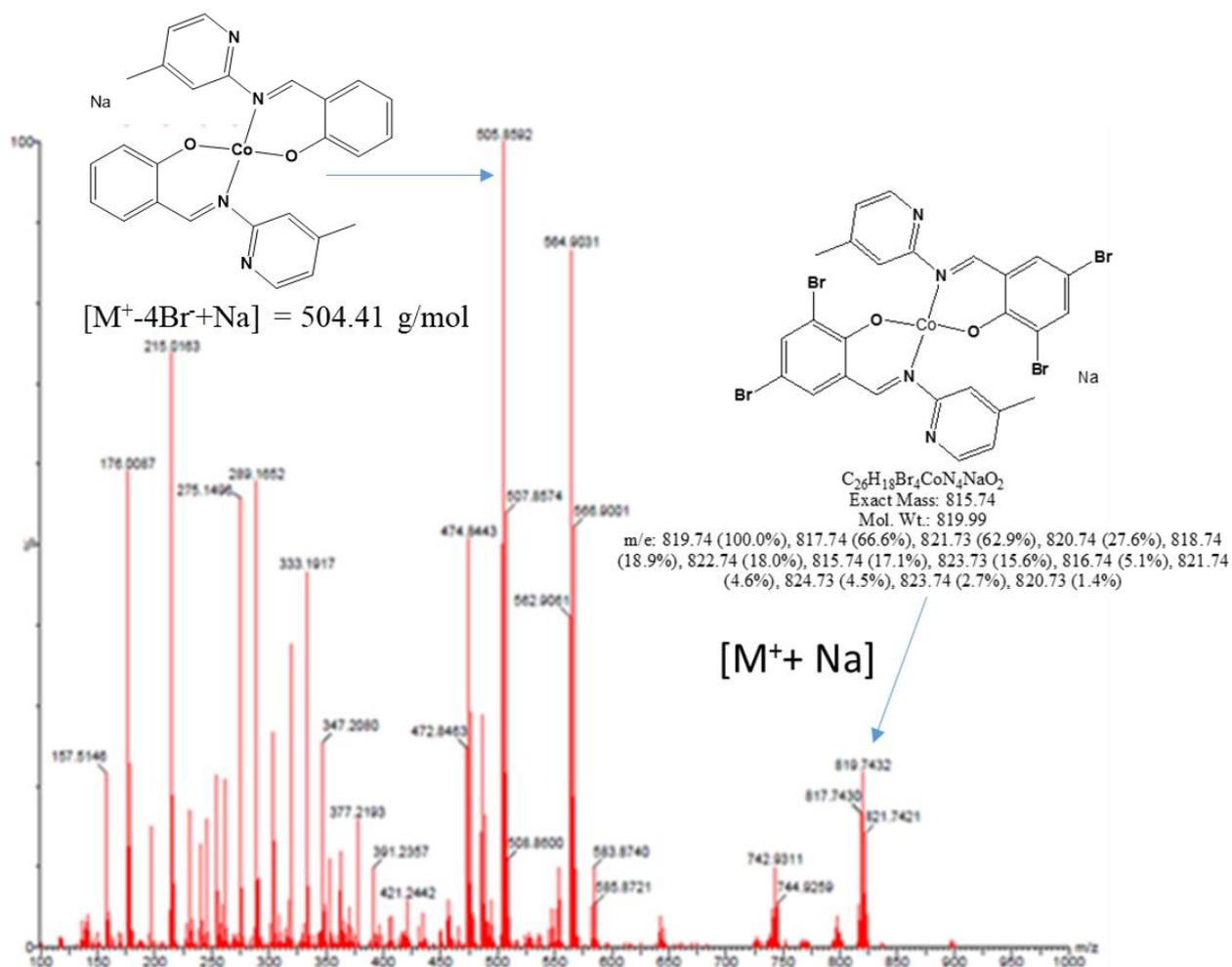
Figure S26: ESI Mass spectrum of complex **Co2** showing the [M⁺] peak at 819.74 amu (25 %) and its predicted isotopic distribution at m/z = 820 amu.
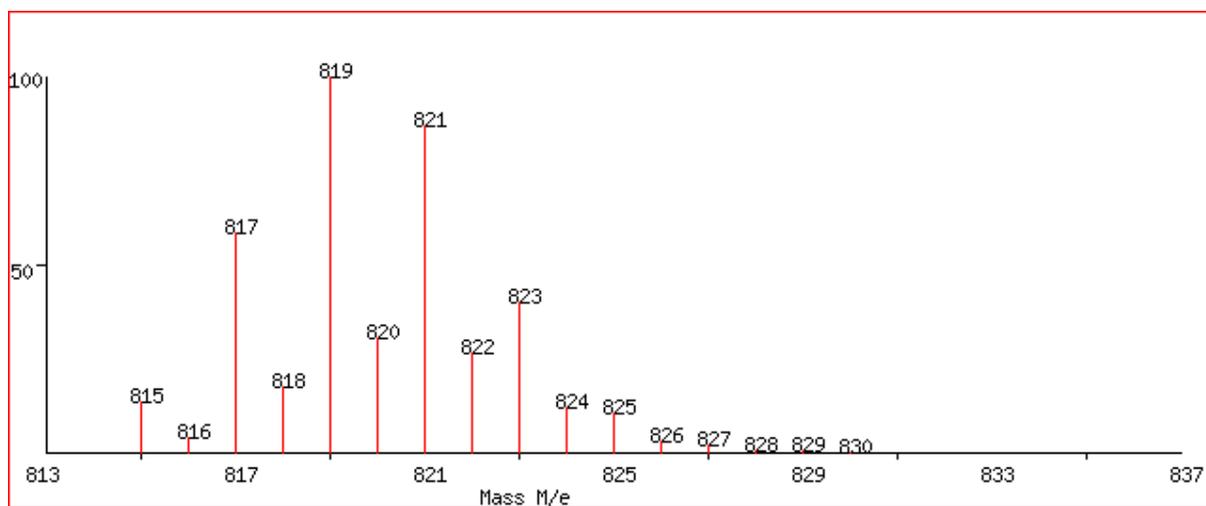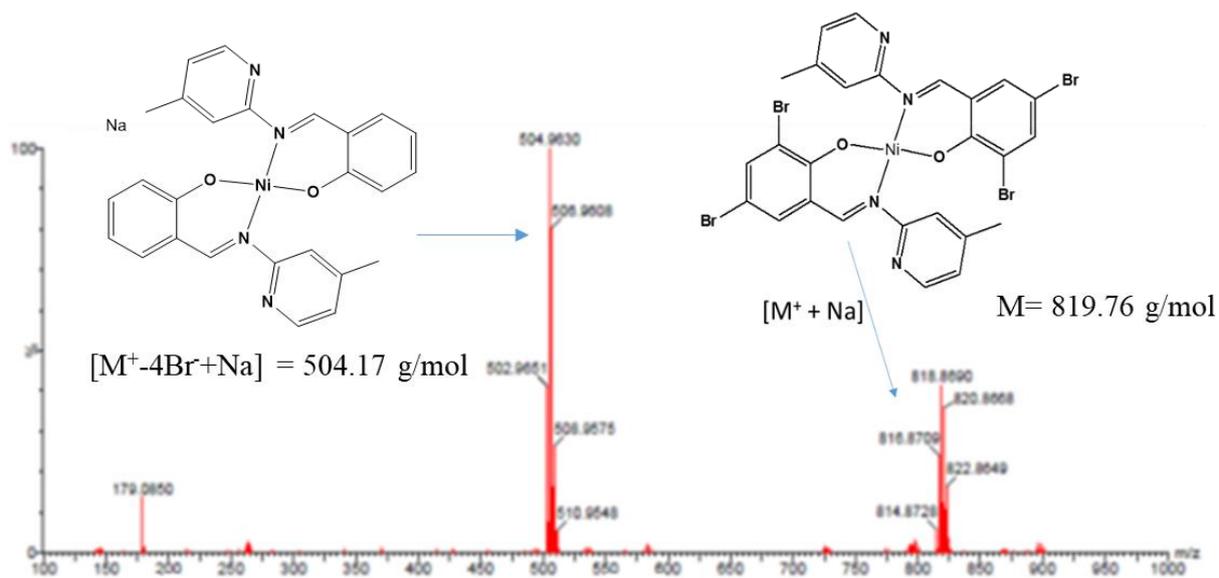
Figure S27: Mass spectrum of complex **Ni2** showing the [Ni(**L2**)$_2$]$^+$ fragment at 818.86 amu (30 %) and its predicted isotopic distribution at m/z = 819 amu. The peak at m/z = 504.17 amu corresponds to [Ni(**L2**)$_2$ + Na – 4Br$^-$]$^+$ molecular ion peak.

[M+-4Br-+Na] = 573.39 g/mol
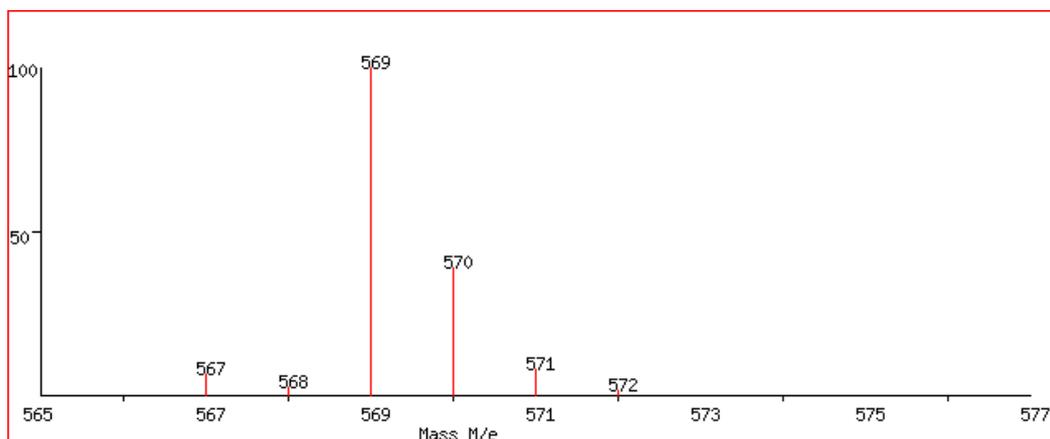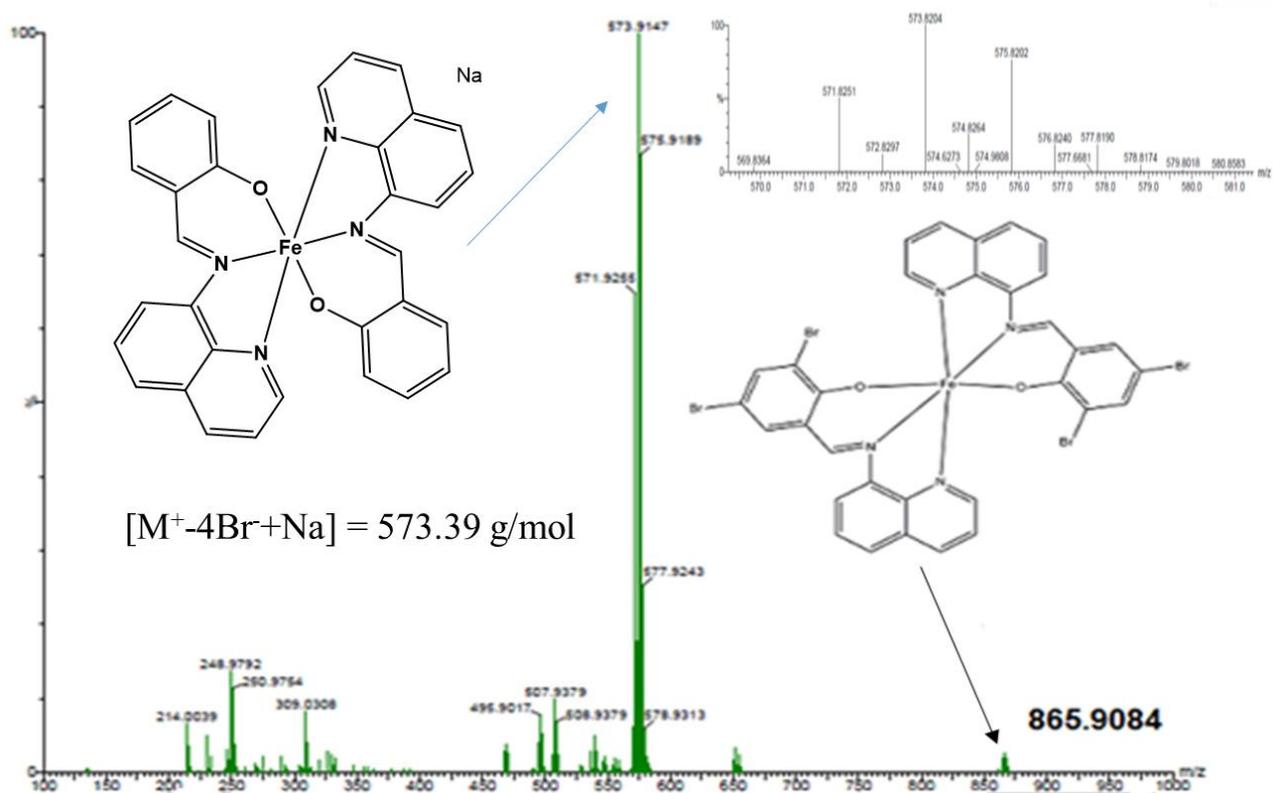
Figure S28: LR-MS and HR-MS ESI (inserted) mass spectra of complex **Fe3** showing the base peak at 573.91 amu (100 %) corresponding to [Fe(**L3**)$_2$ + Na – 4Br$^-$]$^+$ fragment and the isotopic distribution of the molecular ion peak at m/z = 569 amu.
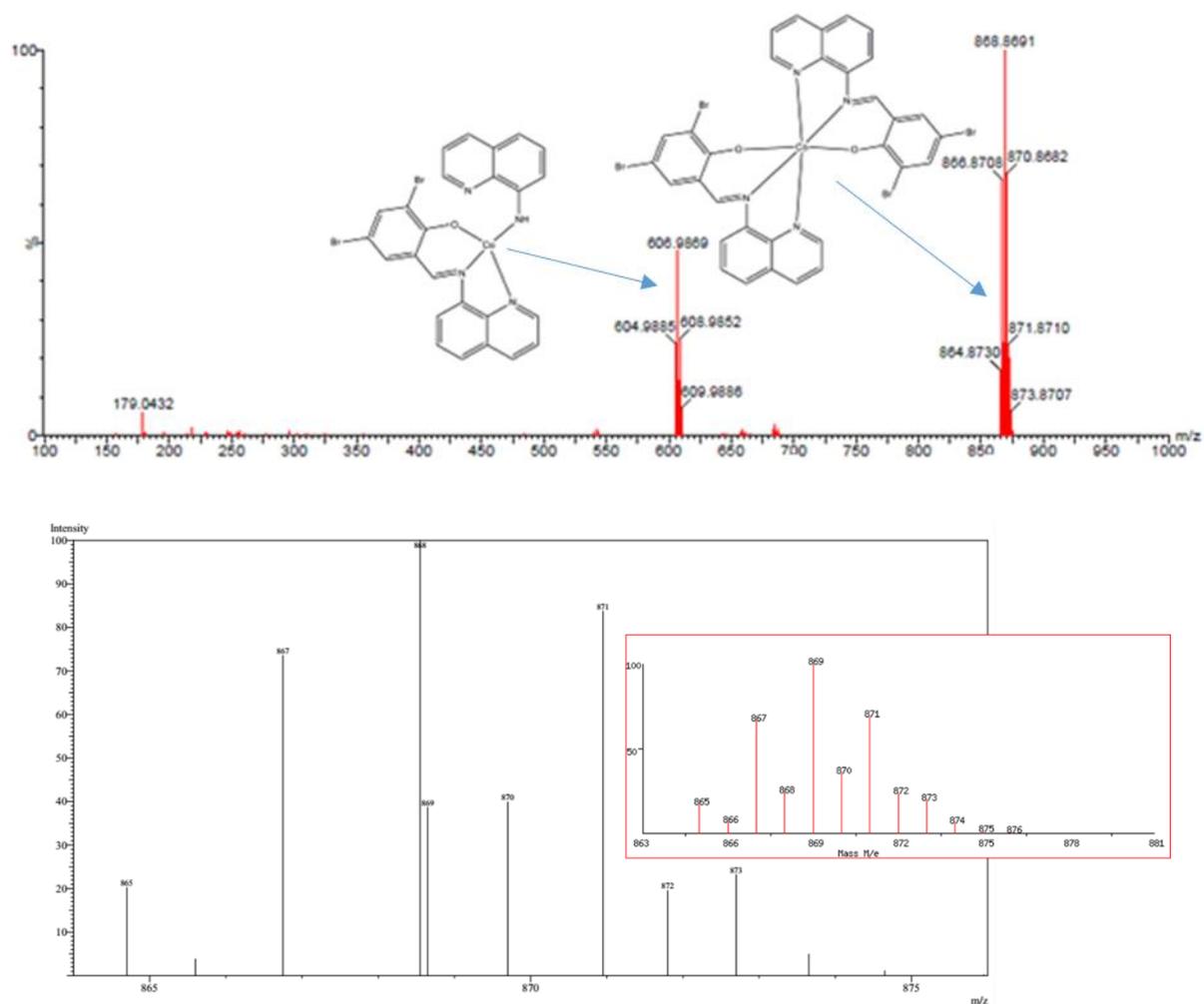
Figure S29: Mass spectrum of complex **Co3** showing the formation of a *bis*-chelated cobalt complex at 868.87 amu and the combination of experimental and the predicted isotopic distribution of the molecular ion peak of the complex.
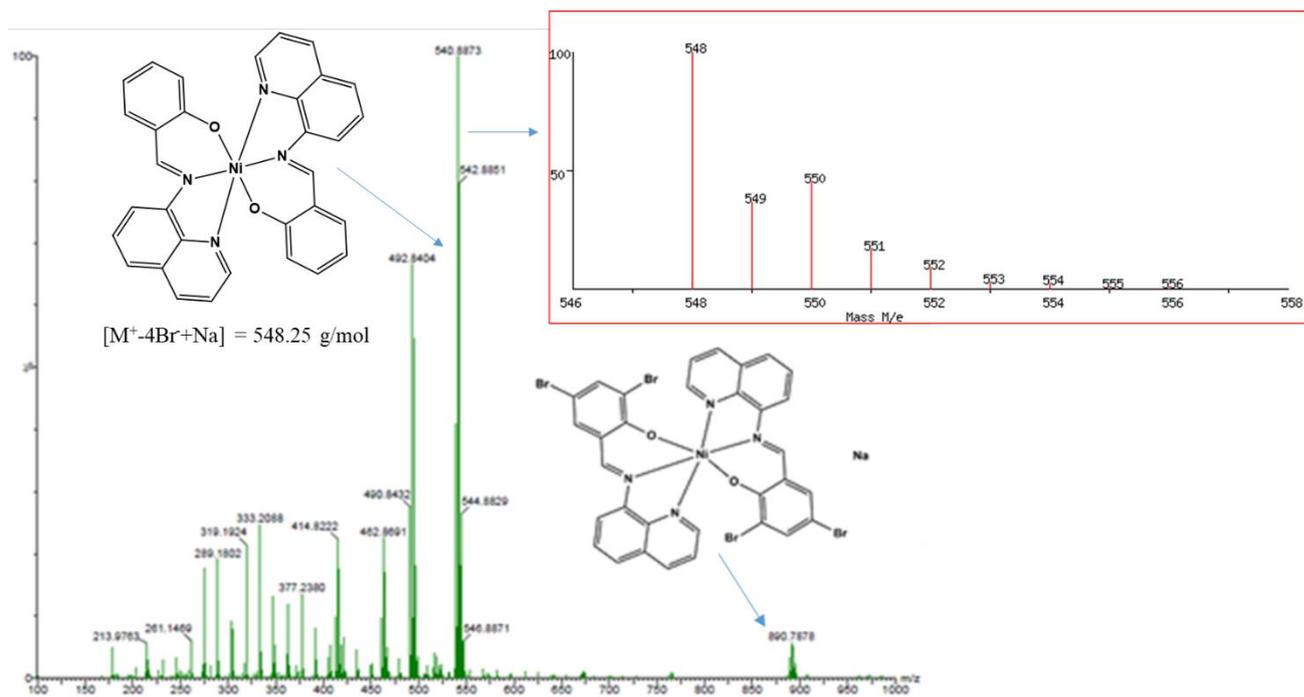
Figure S30: Mass spectrum of complex **Ni3**, showing the $[Ni(\mathbf{L3})_2 + Na - 4Br^-]^+$ molecular

ion peak at m/z of 890.7878 amu and the isotopic distribution of the molecular ion peak at

m/z = 548 amu inserted.

UV-vis studies of the late transition metal complexes
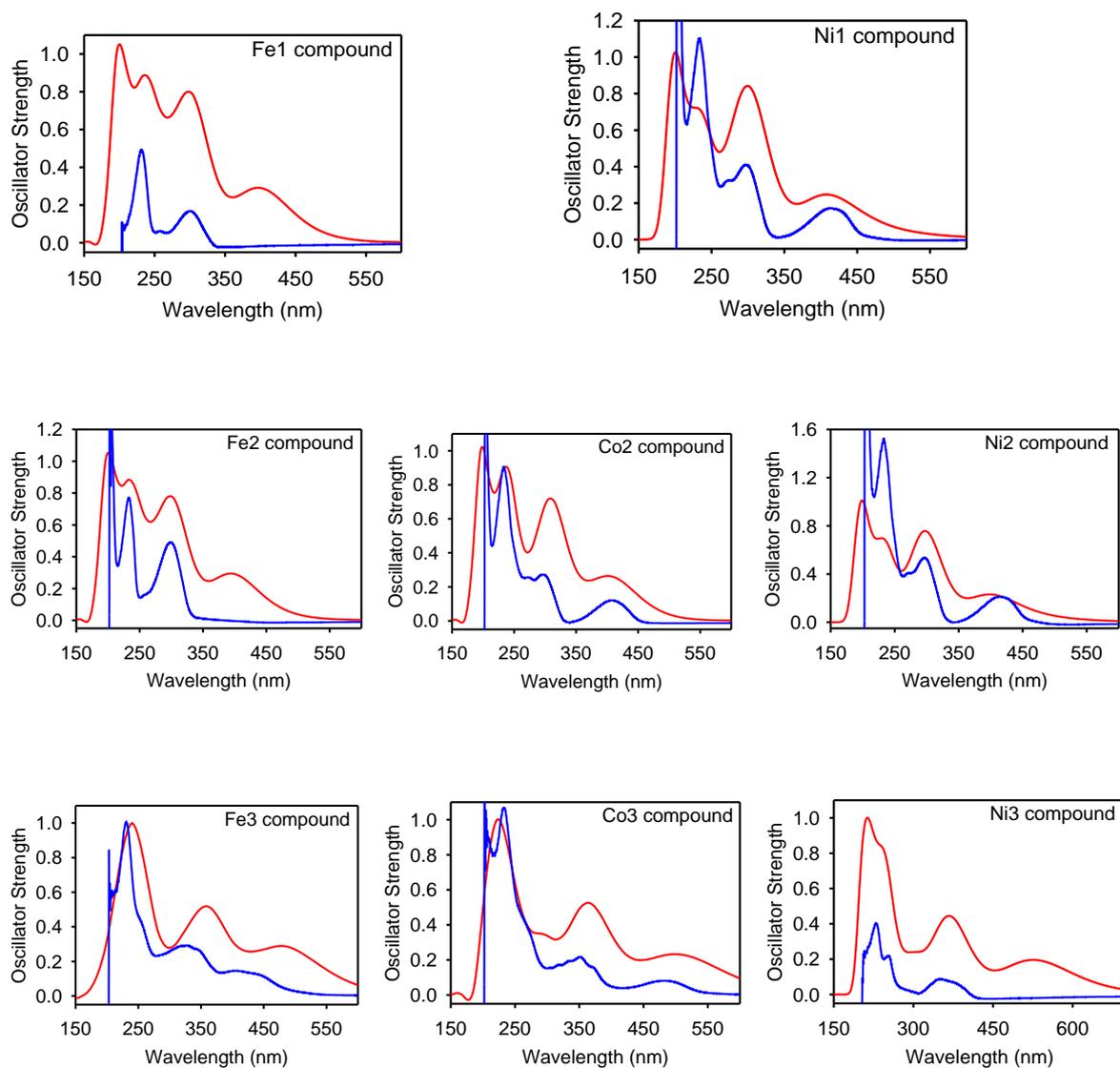
Figure S31: Absorption spectra of the metal complexes. The red curve shows the absorption spectra generated theoretically by using B3LYP functional whereas the black curve shows the absorption spectra generated experimentally.

Ethylene oligomerization reactions
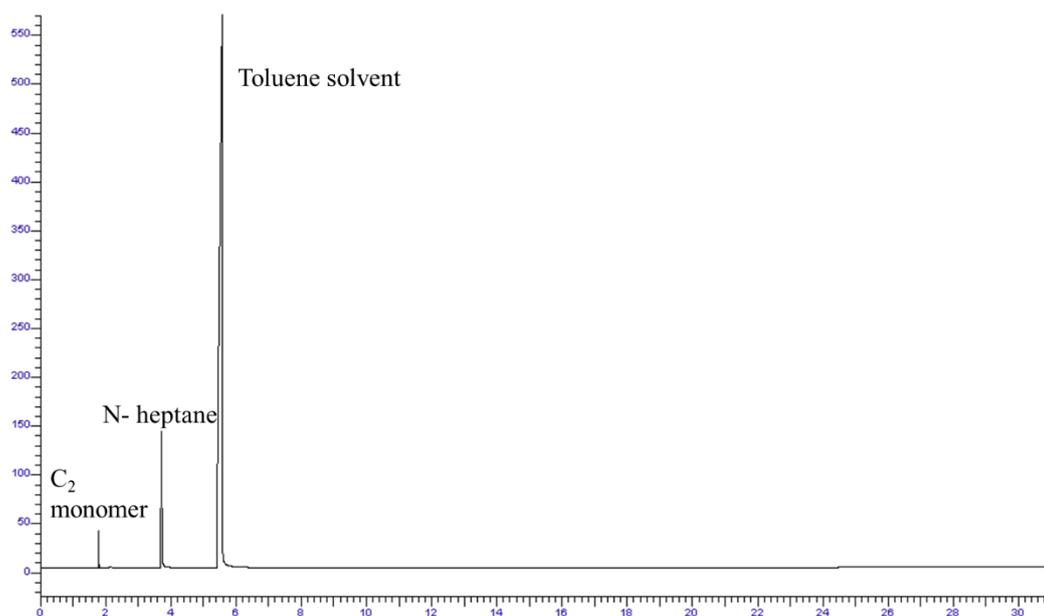
Figure S32: The GC-FID chromatogram showing no activity or formation of products when the Ni(II) complex **Ni1** is activated with MMAO-12 co-catalyst/toluene and used to catalyze the oligomerization of ethylene monomer in toluene solvent (Table 2, entry 10).
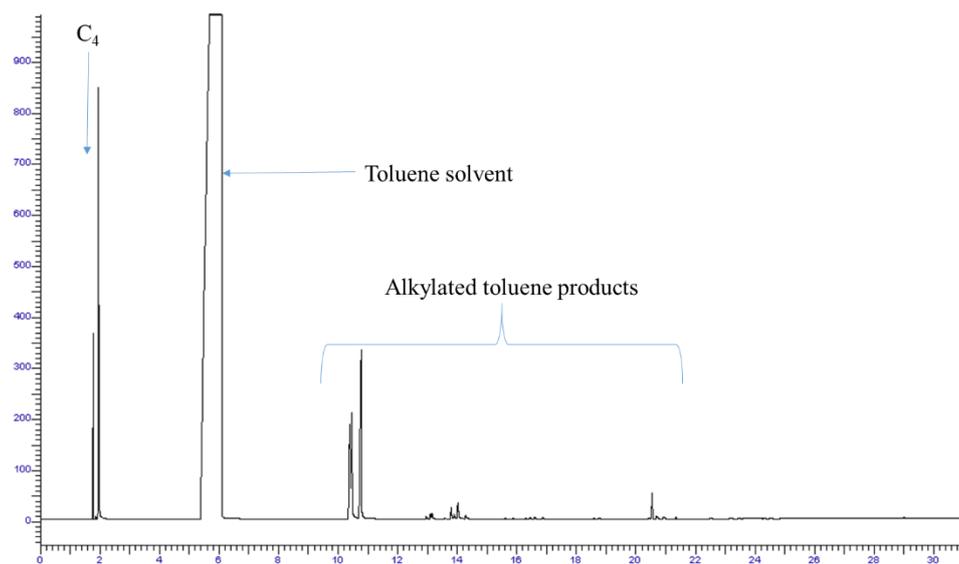
Figure S33: The GC-FID chromatogram showing the formation of C_4 oligomers and alkylated toluene products when the Ni(II) complex **Ni1** is activated by $EtAlCl_2$ co-catalyst/toluene and used to catalyse the oligomerization of ethylene monomer in toluene solvent (Table 2, entry 11).
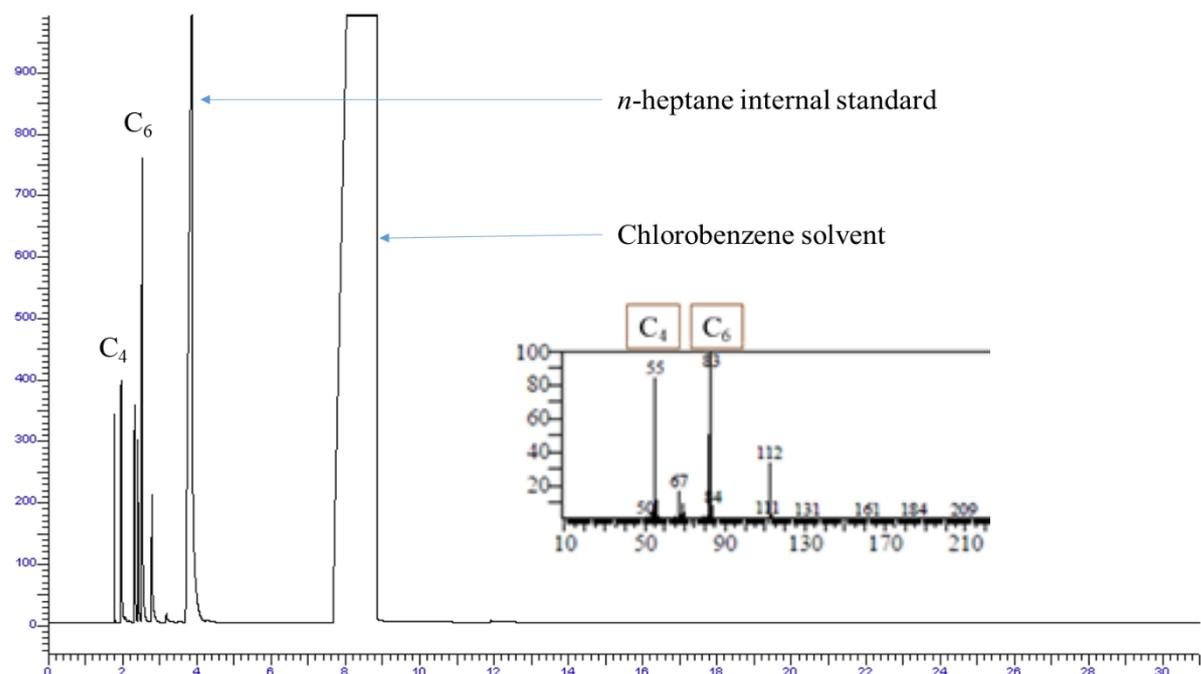
Figure S34: The GC-FID chromatogram showing the C4 and C6 oligomers obtained from **Fe1**/EtAlCl$_2$ system in chlorobenzene solvent (Table 2, entry 1). **Inset:** The GC-MS showing the molar masses C$_4$ and C$_6$ at 55 and 83 respectively.
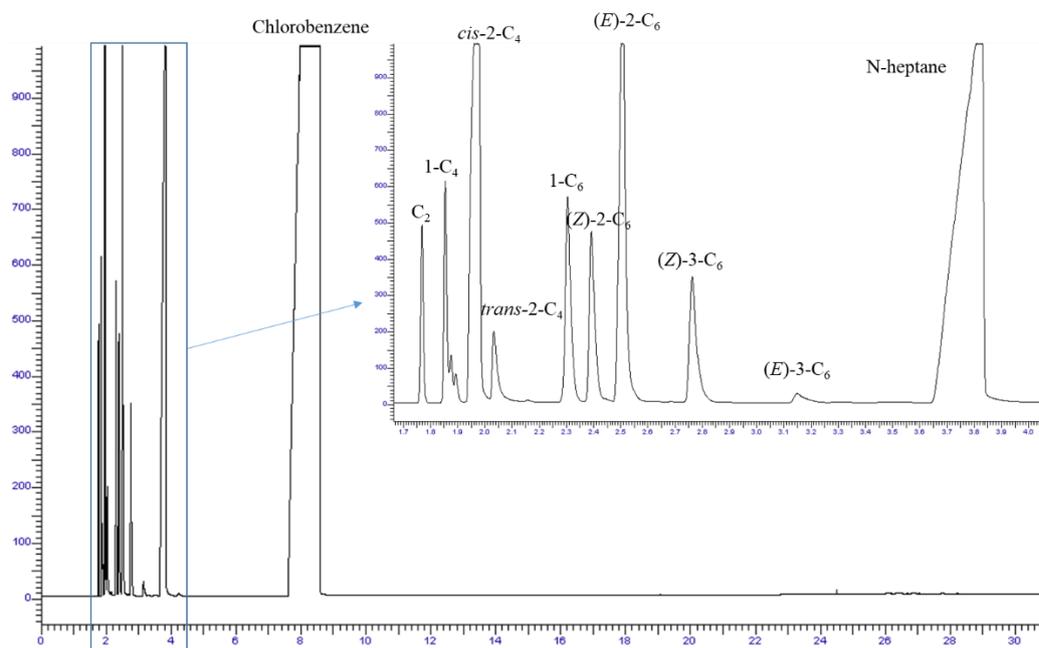
Figure S35: The GC-FID of **Ni1**/EtAlCl$_2$ system showing temperature effect on product distribution (Table 3, entry 10; T= 50 ˚C). Drastic drop in the composition of C$_4$ oligomer fractions from 60 % to 49 % was recorded.

Density functional theory studies of the complexes
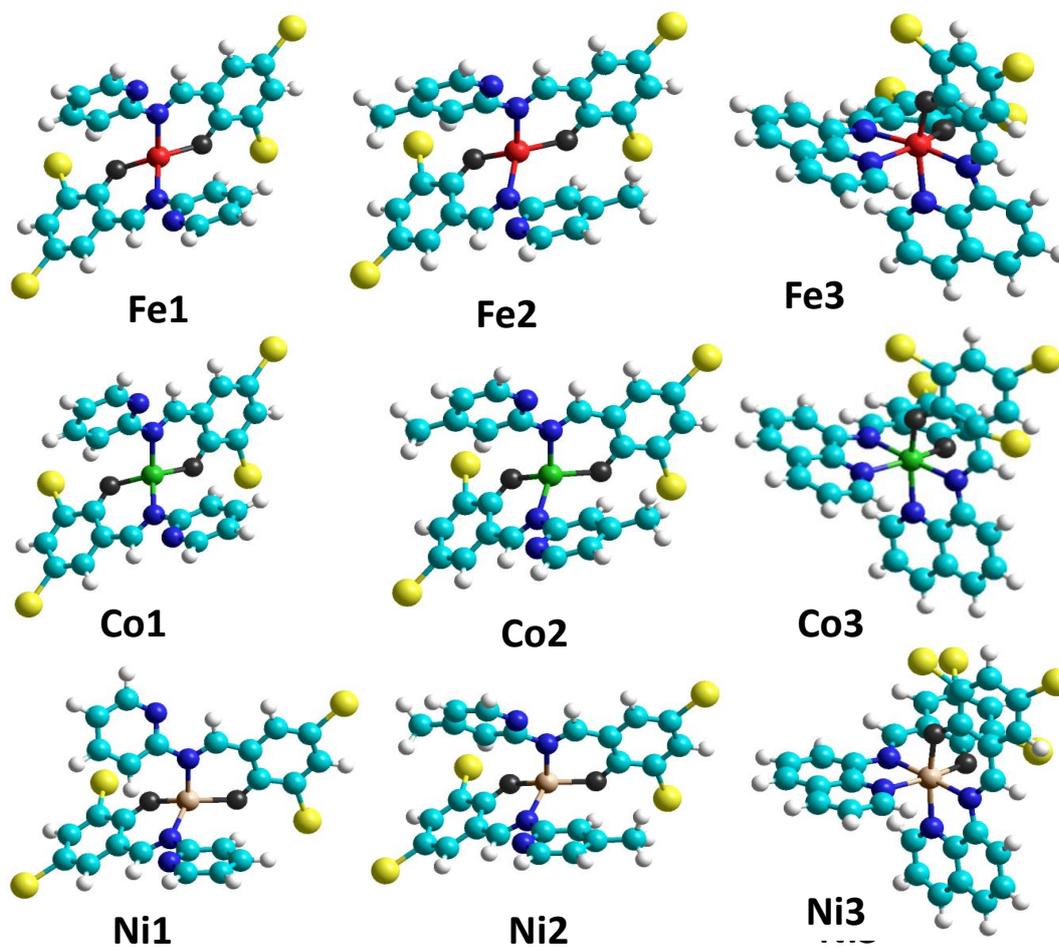
Figure S36: B3LYP optimized geometries of the metal complexes using Lanl2dz basis set for metal cation and 6-311G(dp) basis set for the remaining atoms.
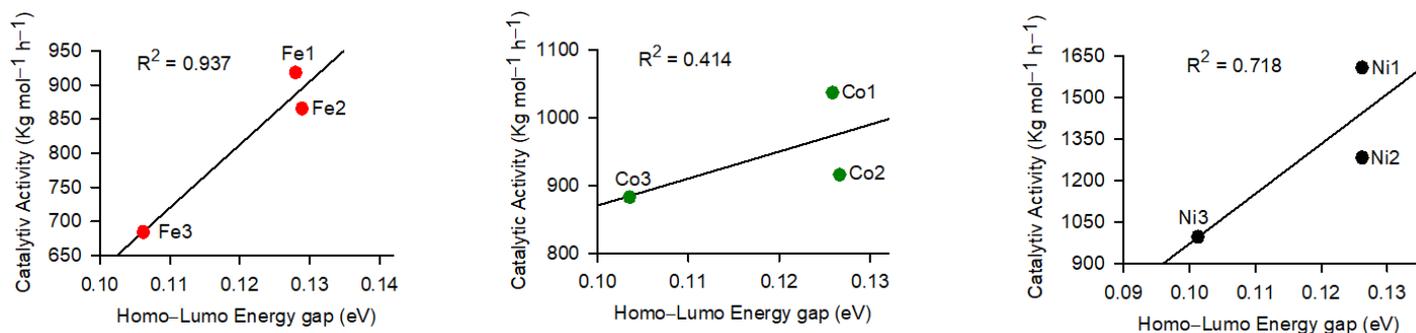
Figure S37: Dependence of catalytic activities in ethylene oligomerization of the metal complexes on their frontier orbitals.
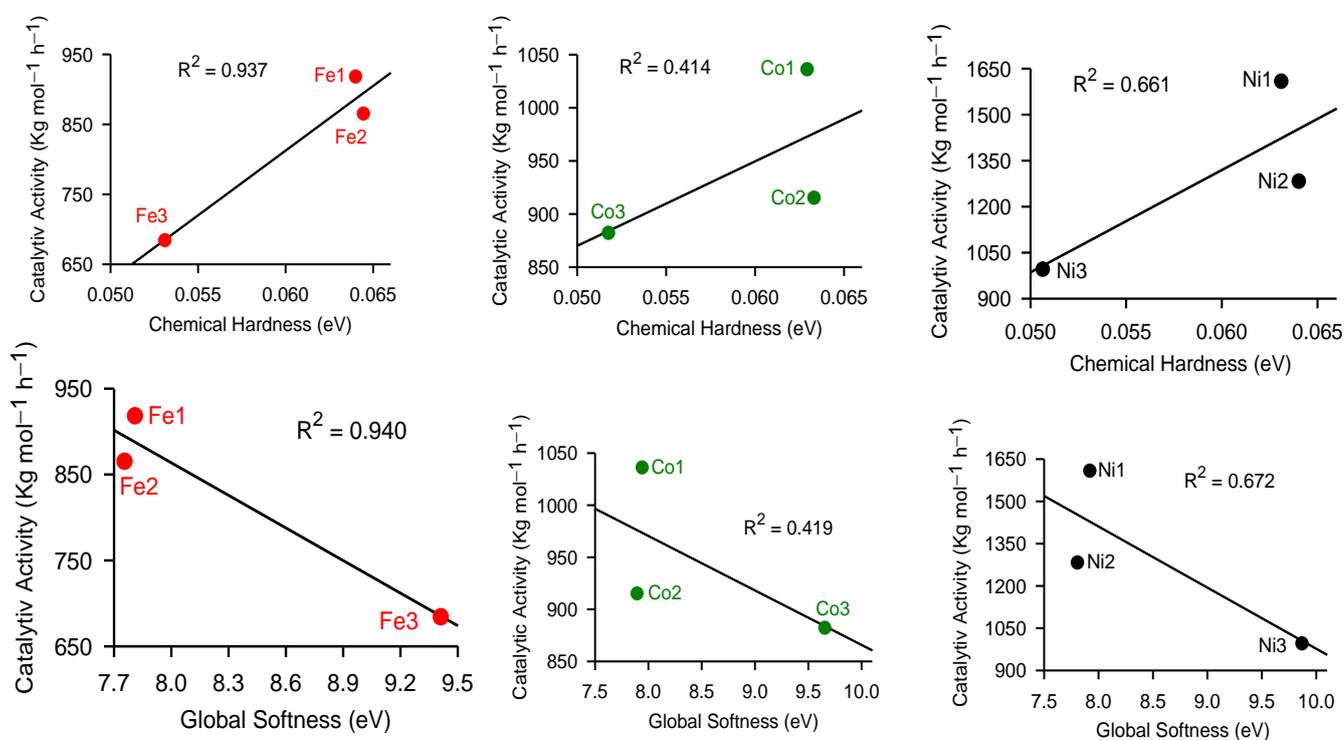
Figure S38: Dependence of catalytic activities in ethylene oligomerization on the global softness and chemical hardness of the metal complexes.
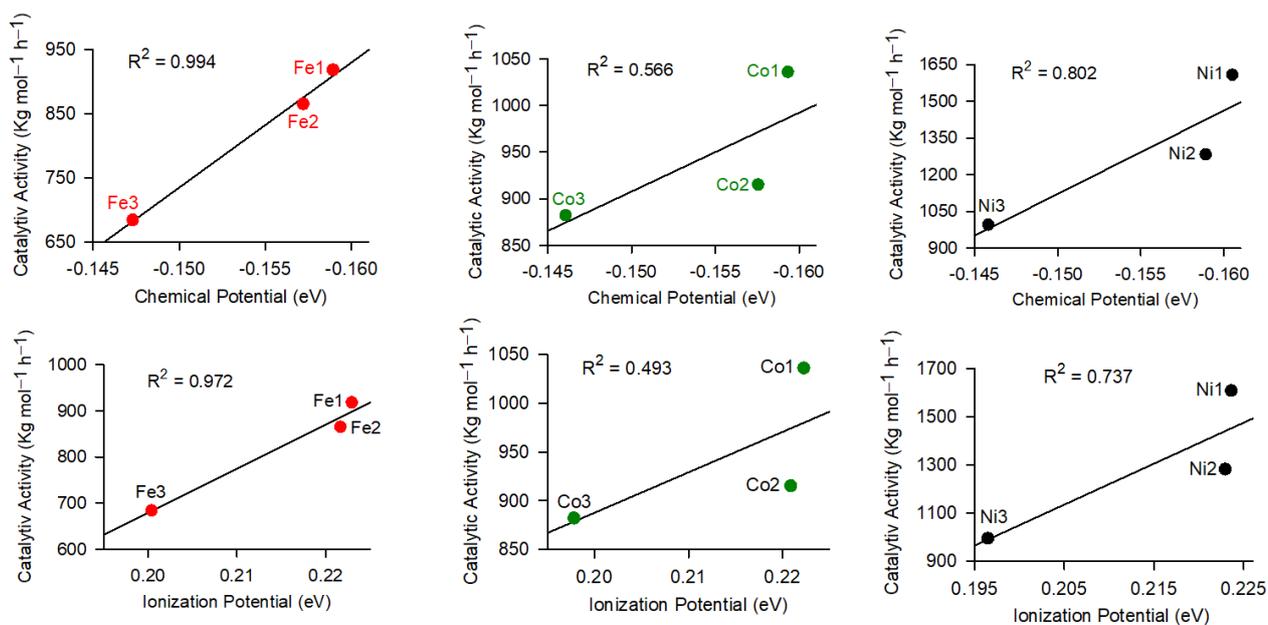
Figure S39: Dependence of catalytic activities on chemical and ionization potentials of the metal complexes. The more negative complexes were more activity, consistent with enhanced stability.

Table S1: X-ray crystallographic data and structure refinement for the **Fe3a** and **Ni3** complexes.

Compound	Fe3a	Ni3
Formula	$C_{32}H_{18}Br_4ClFeN_4O_2$	$C_{32}H_{18}Br_4N_4NiO_2$
$D_{calc.}$/ g cm^{-3}	1.630	1.981
μ/mm^{-1}	4.867	6.193
Formula Weight	901.44	868.85
Colour	orange	green
Shape	block	rod
Size/mm^3	0.23×0.15×0.11	0.31×0.22×0.14
T/K	100(2)	100(2)
Crystal System	monoclinic	monoclinic
Space Group	$C2/c$	$P2_1/c$
a/Å	33.700(4)	21.712(4)
b/Å	9.2687(11)	10.1595(17)
c/Å	24.484(3)	13.621(2)
$\alpha/^\circ$	90	90
$\beta/^\circ$	106.157(2)	104.217(8)
$\gamma/^\circ$	90	90
V/Å^3	7345.6(16)	2912.5(8)
Z	8	4
Z'	1	1
Wavelength/Å	0.71073	0.71073
Radiation type	MoK$_a$	MoK$_a$
$\Theta_{min}/^\circ$	1.258	1.935
$\Theta_{max}/^\circ$	27.495	25.998
Measured Refl.	60212	30407
Independent Refl.	8417	5655
Reflections Used	6346	4594
R_{int}	0.0556	0.0631
Parameters	461	401
Restraints	200	25
Largest Peak	3.076	4.520
Deepest Hole	-1.224	-1.323
GooF	1.069	1.140
wR_2 (all data)	0.1498	0.1792
wR_2	0.1412	0.1728
R_1 (all data)	0.0788	0.0955
R_1	0.0572	0.0787

Table S2: Theoretical and experimental electronic transitions, oscillator strengths and assignments for metal compounds.

Metal Compound	B3LYP/6-311G(d,p)			Experimental	Assignments
	λ (nm)	(*f*)	*E* (eV)	λ (nm)	
Fe2	390	0.1025	3.1798	294	$d \rightarrow d$
	302	0.2319	4.0988	257	$n \rightarrow \pi^*$
	234	0.0747	5.2897	232	$\pi \rightarrow \pi^*$
	197	0.0804	6.2926	204	$n \rightarrow \sigma^*$
Co2	403	0.1123	3.0792	407	$d \rightarrow d$
	310	0.4242	4.0008	295	$n \rightarrow \pi^*$
	242	0.1523	5.1237	272	$\pi \rightarrow \pi^*$
	198	0.1337	6.2715	234	$n \rightarrow \sigma^*$
Ni2	402	0.0794	3.0874	414	$d \rightarrow d$
	308	0.2743	4.0254	296	$n \rightarrow \pi^*$
	236	0.1940	5.2622	274	$\pi \rightarrow \pi^*$
	200	0.1070	6.1924	233	$n \rightarrow \sigma^*$
Fe3	474	0.1287	2.6176	347	$d \rightarrow d$
	358	0.2238	3.4629	256	$n \rightarrow \pi^*$
	250	0.0985	4.9664	231	$\pi \rightarrow \pi^*$
Co3	503	0.1260	2.4660	–	$d \rightarrow d$
	361	0.2107	3.4359	353	$n \rightarrow \pi^*$
	305	0.0463	4.0713	271	$\pi \rightarrow \pi^*$
	239	0.0775	5.1789	233	$n \rightarrow \sigma^*$
Ni3	527	0.1329	2.3507	–	$d \rightarrow d$
	364	0.2520	3.3955	354	$n \rightarrow \pi^*$
	306	0.0516	4.0548	291	$\pi \rightarrow \pi^*$
	251	0.2574	4.9398	254	$\pi \rightarrow \pi^*$
	222	0.1510	5.5750	229	$n \rightarrow \sigma^*$

Table S3. The optimized DFT HOMO and LUMO frontier molecular orbitals of the **Fe1**,

Co1, and **Ni1** metal complexes.

Metal Complex	HOMO Map	LUMO Map
Fe1		
Co1		
Ni1		

Table S3. The optimized DFT HOMO and LUMO frontier molecular orbitals of the **Fe2**, **Co2**, and **Ni2** metal complexes (*continued*).

Metal Complex	HOMO Map	LUMO Map
Fe2		
Co2		
Ni2		
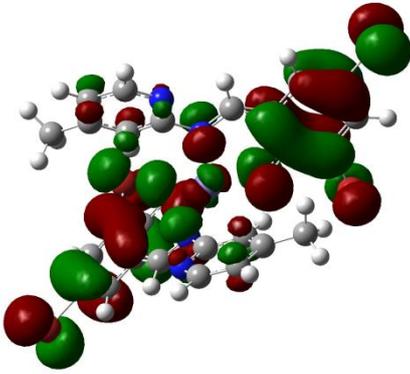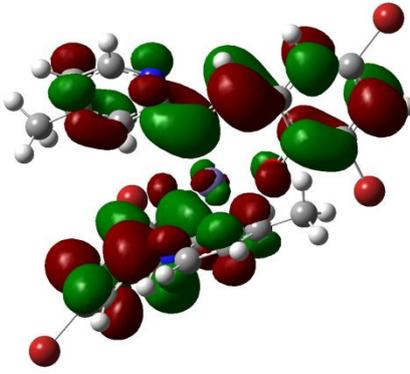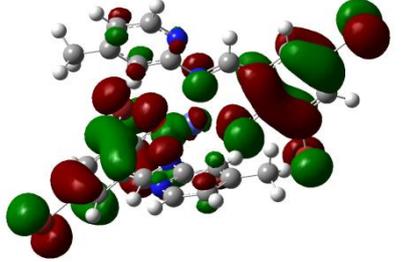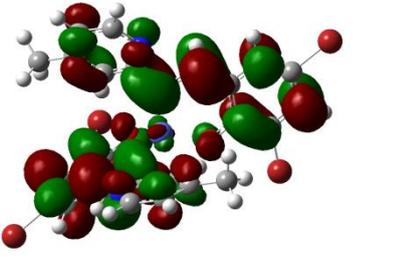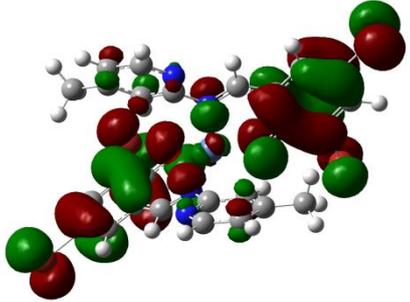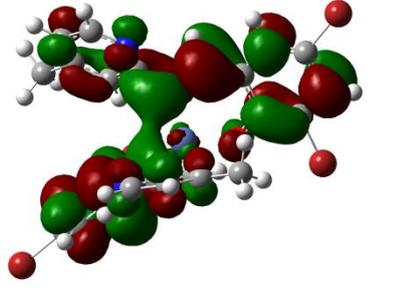
Table S3. The optimized DFT HOMO and LUMO frontier molecular orbitals of the **Fe3**, **Co3**, and **Ni3** metal complexes (*continued*).

Metal Complex	HOMO Map	LUMO Map
Fe3		
Co3		
Ni3		

Table S4: Optimization of the reaction conditions in ethylene oligomerization reactions using **Ni1**/EtAlCl$_2$ system.

Entry	Al/M	Time (h)	Pressure	Yield (g)[b]	Activity (kg mol^{-1} h^{-1})	Product Distribution (%)[c]	
						C$_4$ (α-C$_4$)	C$_6$ (α-C$_6$)
1	**100**	1	10	2.23	223	40 (98)	60 (19)
2	**150**	1	10	4.59	459	46 (95)	54 (18)
3	**200**	1	10	8.66	866	54 (92)	46 (15)
4	**250**	1	10	16.08	1608	60 (95)	40 (17)
5	**300**	1	10	4.18	418	35 (97)	65 (13)
6	**250**	0.5	10	6.09	1218	75 (98)	25 (31)
7	**250**	2	10	18.50	925	52 (88)	48 (13)
8	**250**	1	5	15.50	1550	55 (92)	45 (17)
9	**250**	1	20	10.25	1025	46 (92)	54 (20)
10[d]	**250**	1	10	9.96	996	49 (79)	51 (11)
11[e]	**250**	1	10	6.60	660	52 (64)	48 (9)

[a]Reaction conditions: complex, 10 µmol; solvent, chlorobenzene, 30 mL; temperature, 30 ˚C; time, 1 h; pressure, 10 bar; EtAlCl$_2$: Al/M=200; [b]Determined using GC and n-heptane served as an internal standard. [c]Determined by GC and GC-MS. [d]T=50 ˚C, [e]T=70 ˚C. The optimized conditions were obtained as temperature, 30 ºC, time, 1 h, Al/Ni, 250 and pressure of 10 bar (entry 4).
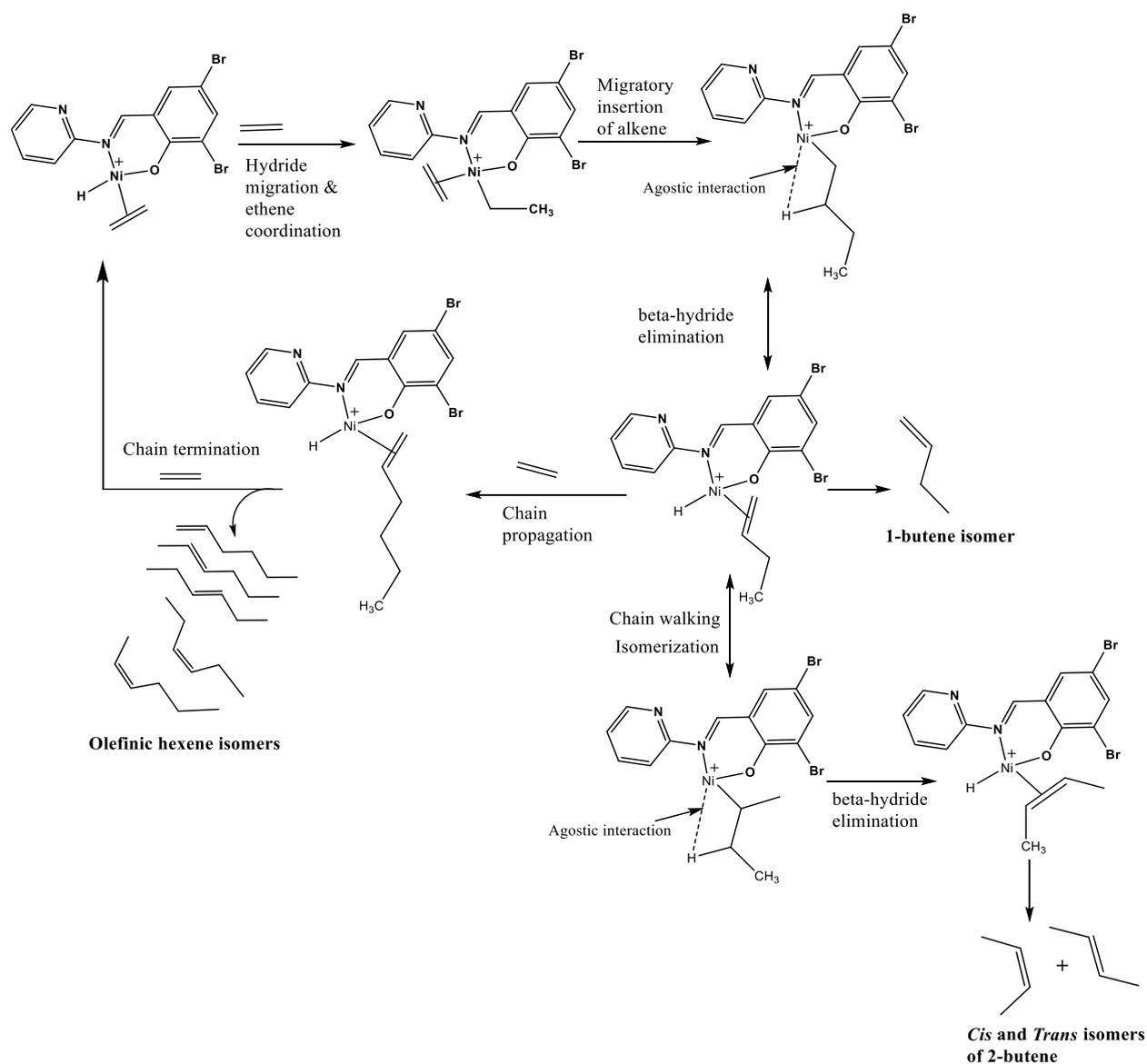
Scheme S1: The proposed mechanism for the formation of 1-butene, *cis* and *trans* isomers of 2-butene and the favoured production of internal hexene oligomers by the Fe(II), Co(II) and Ni(II) complexes. The absence of C_8 oligomers implies that after the formation of C_6 oligomer, chain isomerism and termination was more favoured than chain propagation to form long chain C_{8+} oligomers.