

## Electronic Supporting Information (ESI)

### **Chelate ligand driven structural diversity and modeling studies on phenoxazinone synthase-like activity of cobalt (III) complexes**

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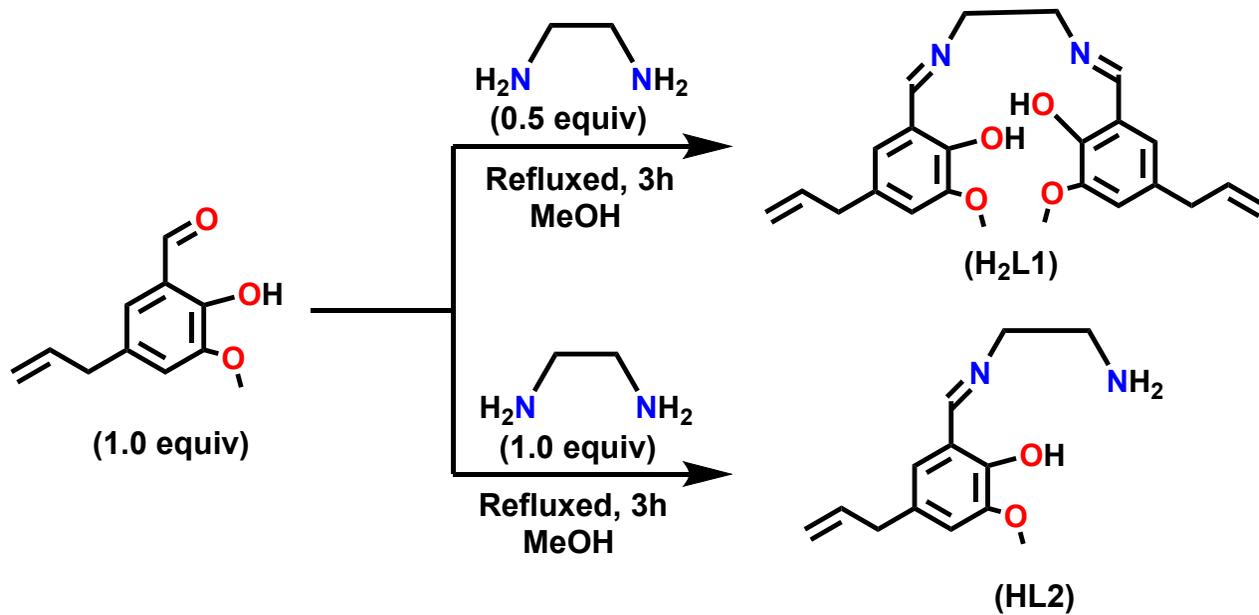
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Scheme S1 Synthesis route of  $\text{H}_2\text{L1}$  and  $\text{HL2}$

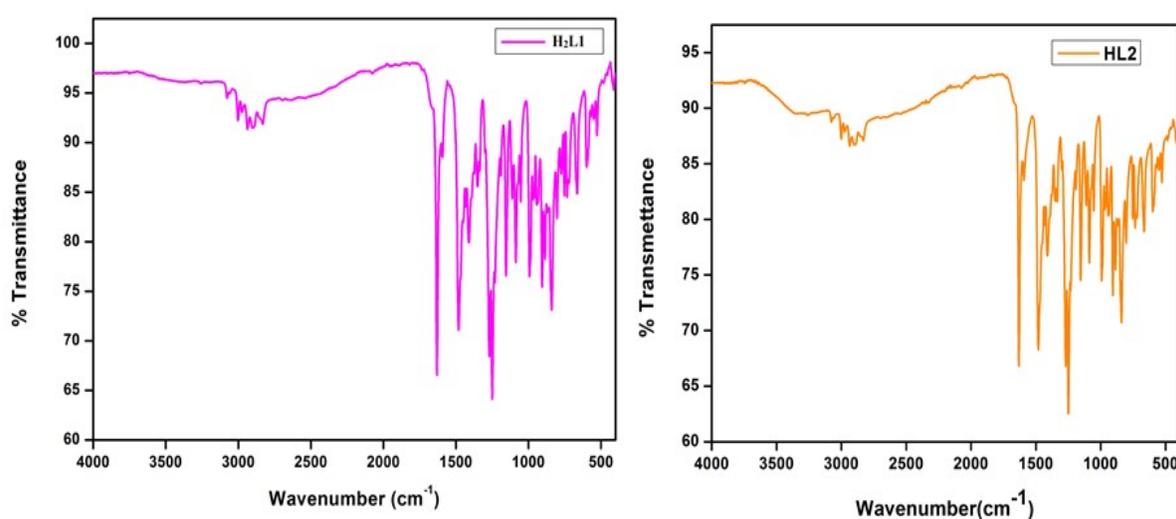


Fig. S1 FT-IR spectra of Ligand  $\text{H}_2\text{L1}$  and  $\text{HL2}$

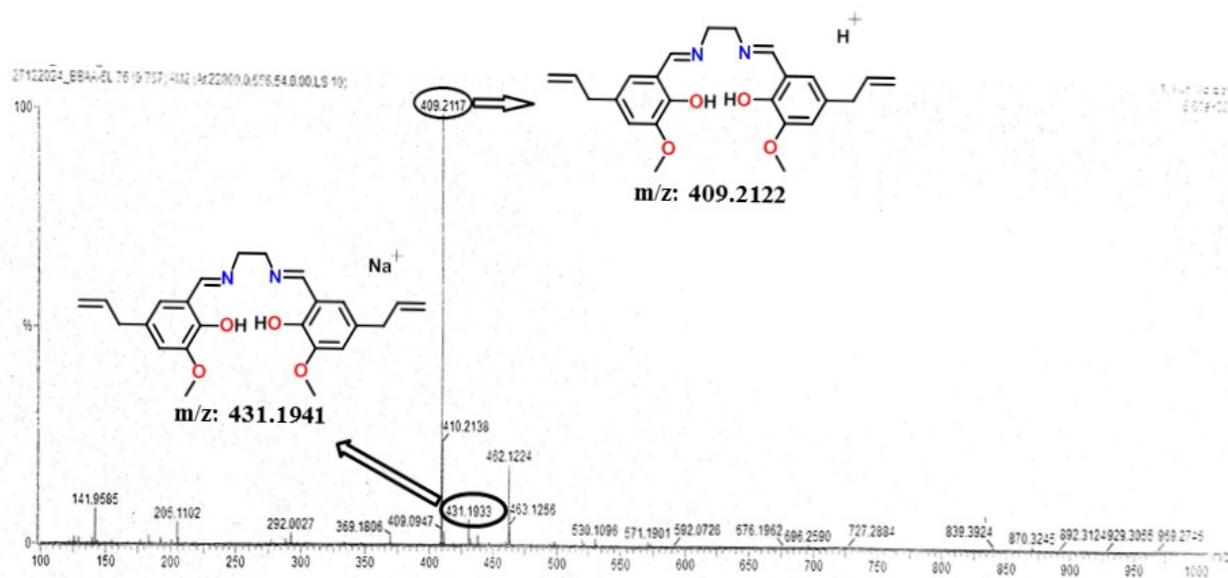
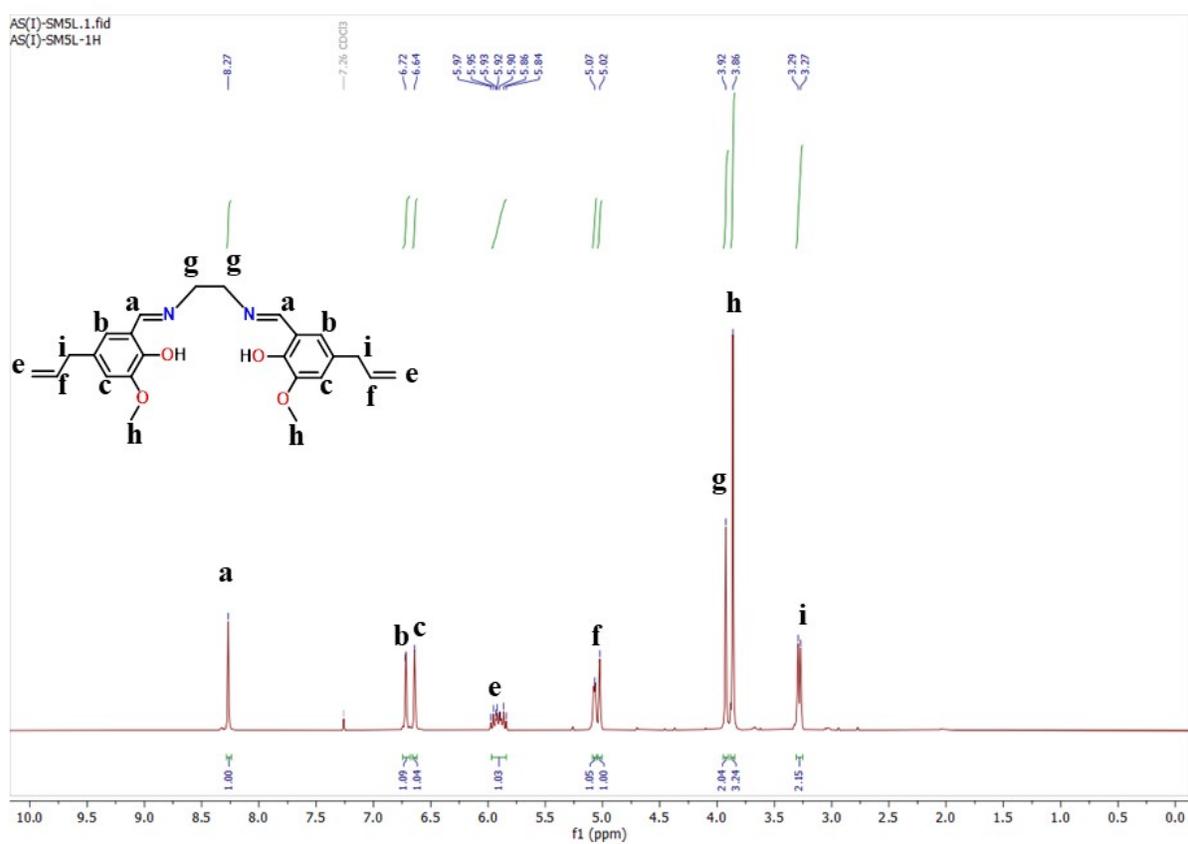
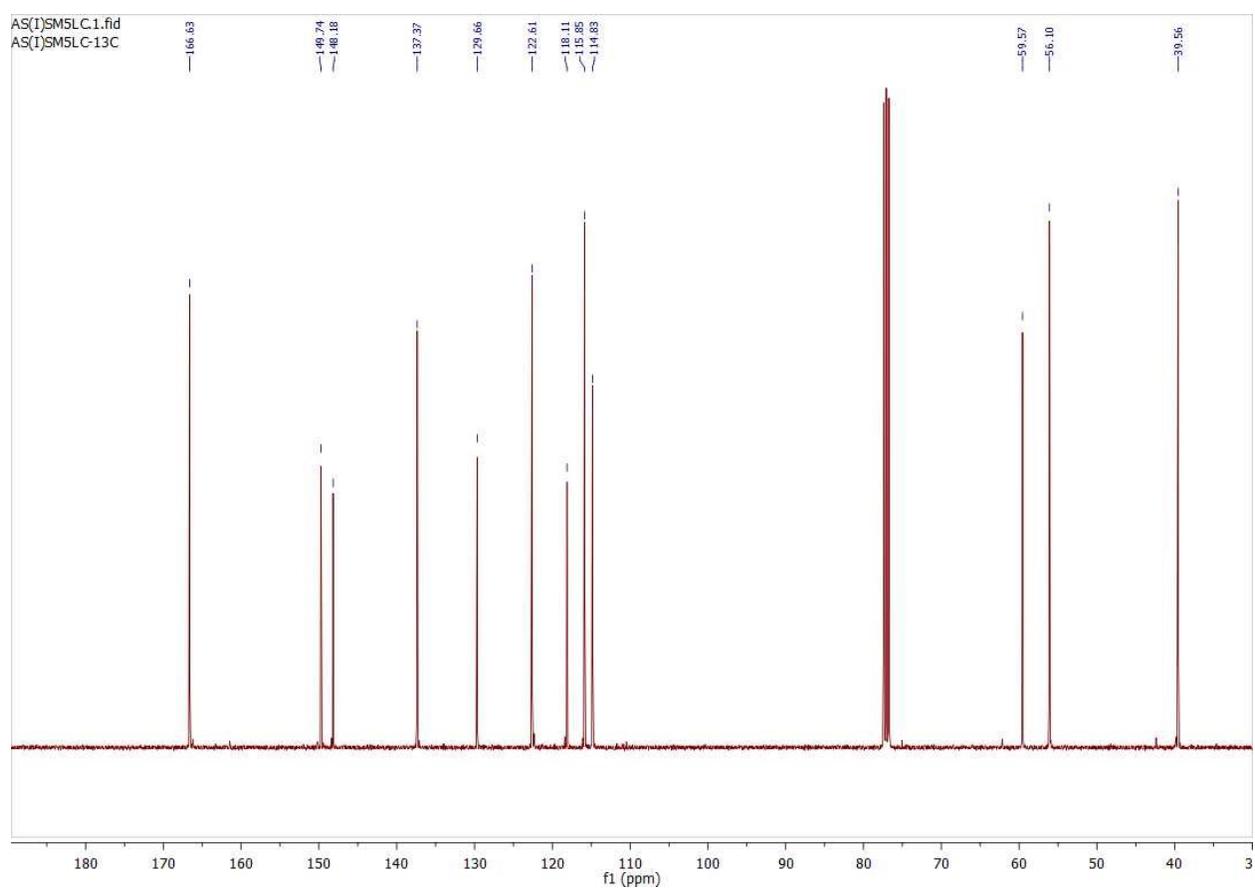


Fig. S2 ESI-mass spectrum of Ligand  $\text{H}_2\text{L1}$  in methanol.



**Fig. S3**  $^1H$  NMR spectra of  $H_2L1$  ligand in  $CDCl_3$  solvent.



**Fig. S4**  $^{13}C$  NMR spectra of  $H_2L1$  ligand in  $CDCl_3$  solvent.

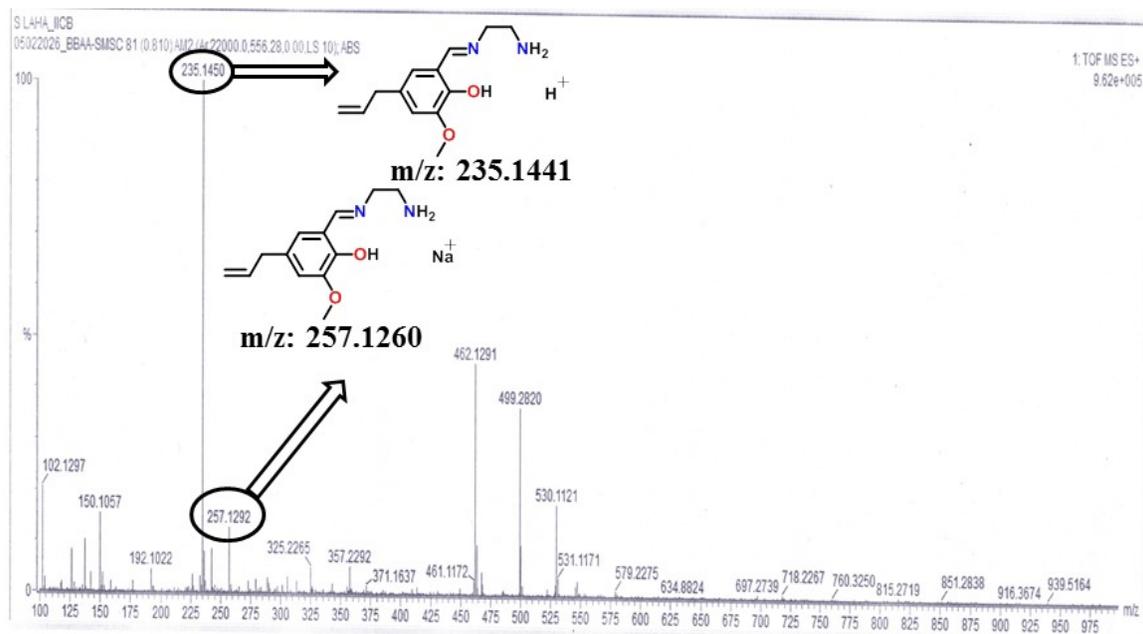


Fig. S5 ESI-mass spectrum of Ligand HL2 in methanol.

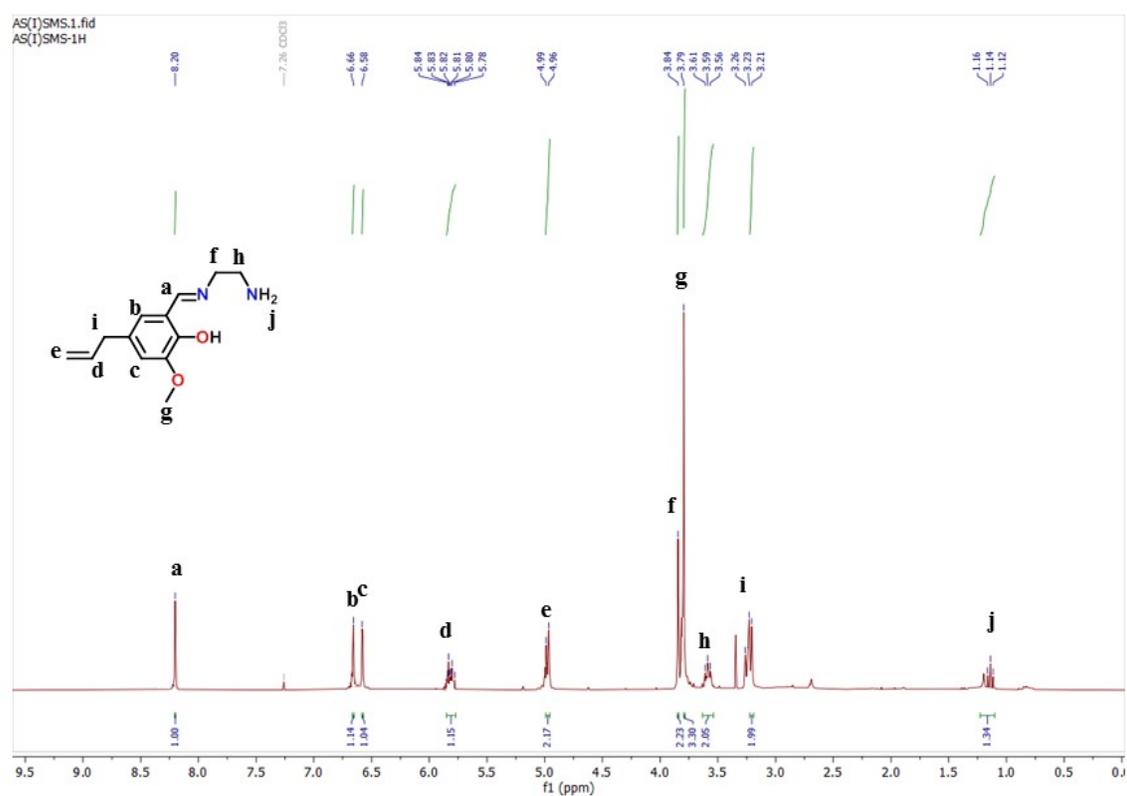


Fig. S6 <sup>1</sup>H NMR of HL2 in CDCl<sub>3</sub> solvent.

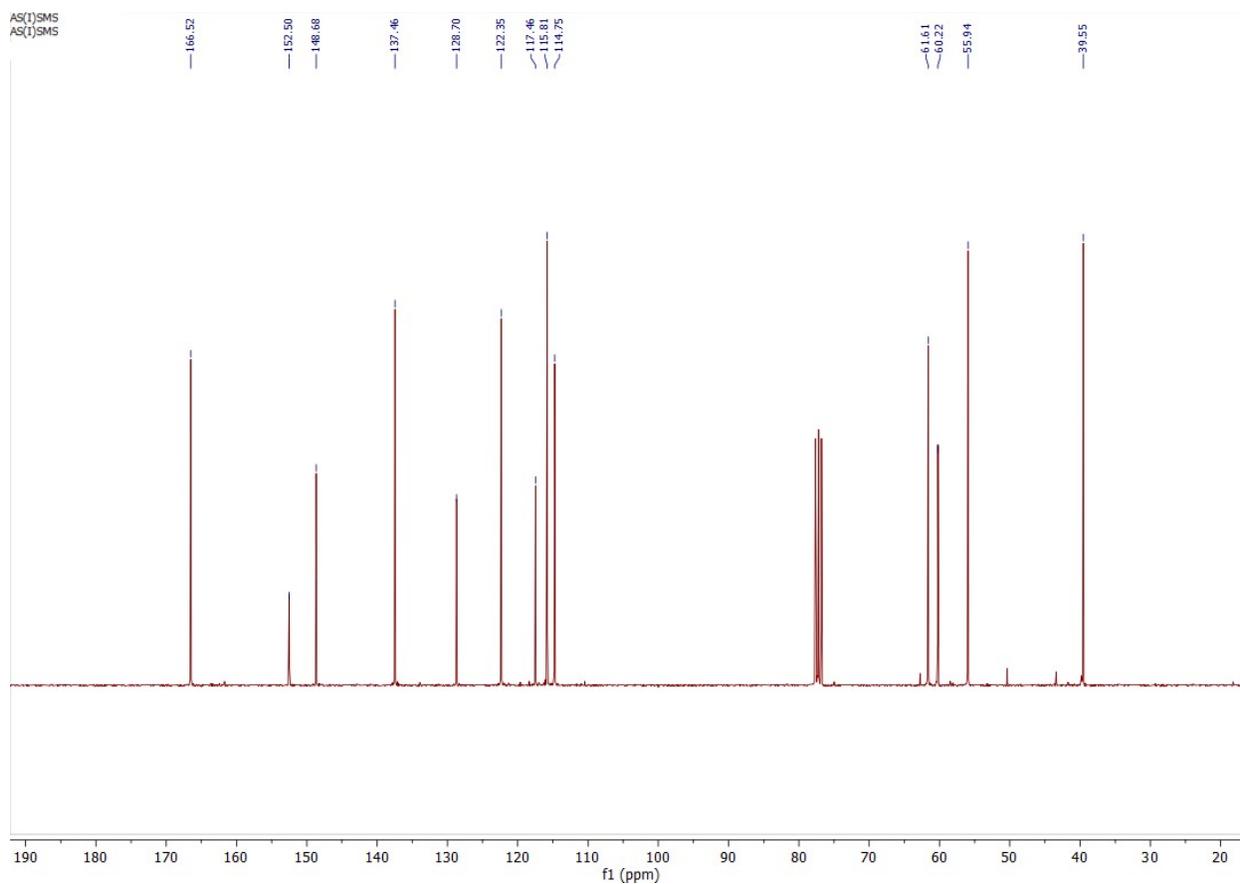


Fig. S7  $^{13}\text{C}$  NMR of HL2 in  $\text{CDCl}_3$  solvent.

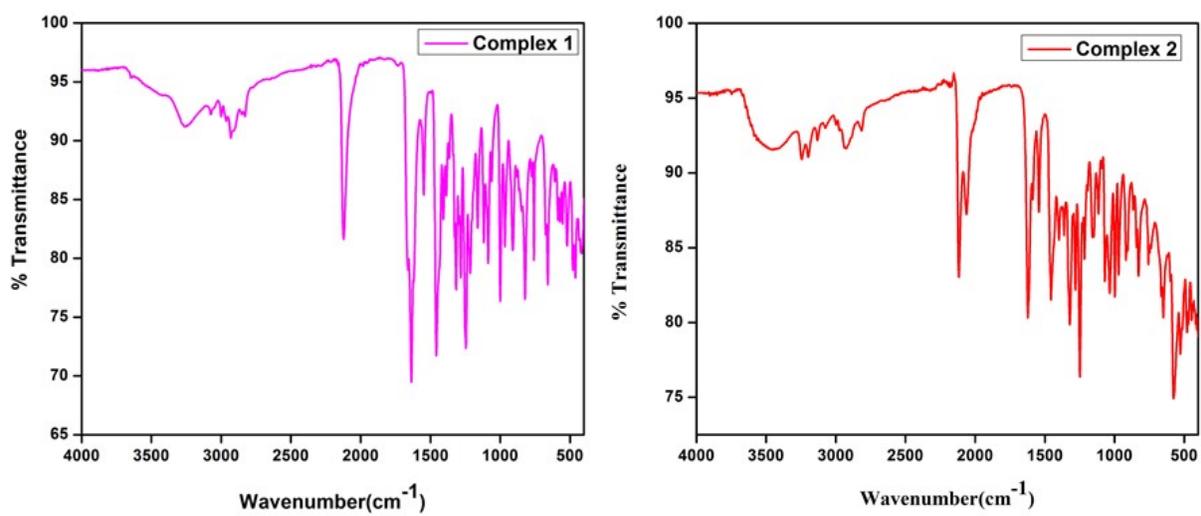


Fig. S8 IR of Complex 1 and 2

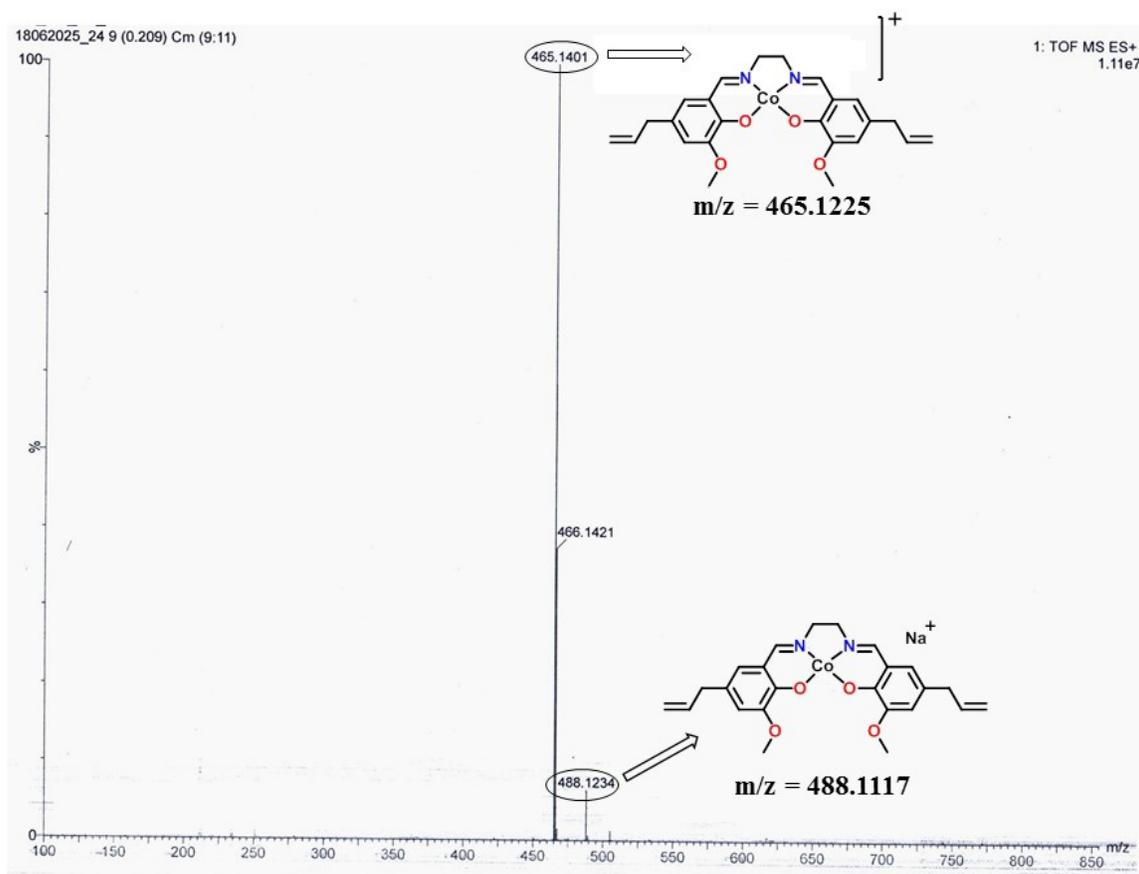


Fig. S9 ESI mass spectrum of complex 1

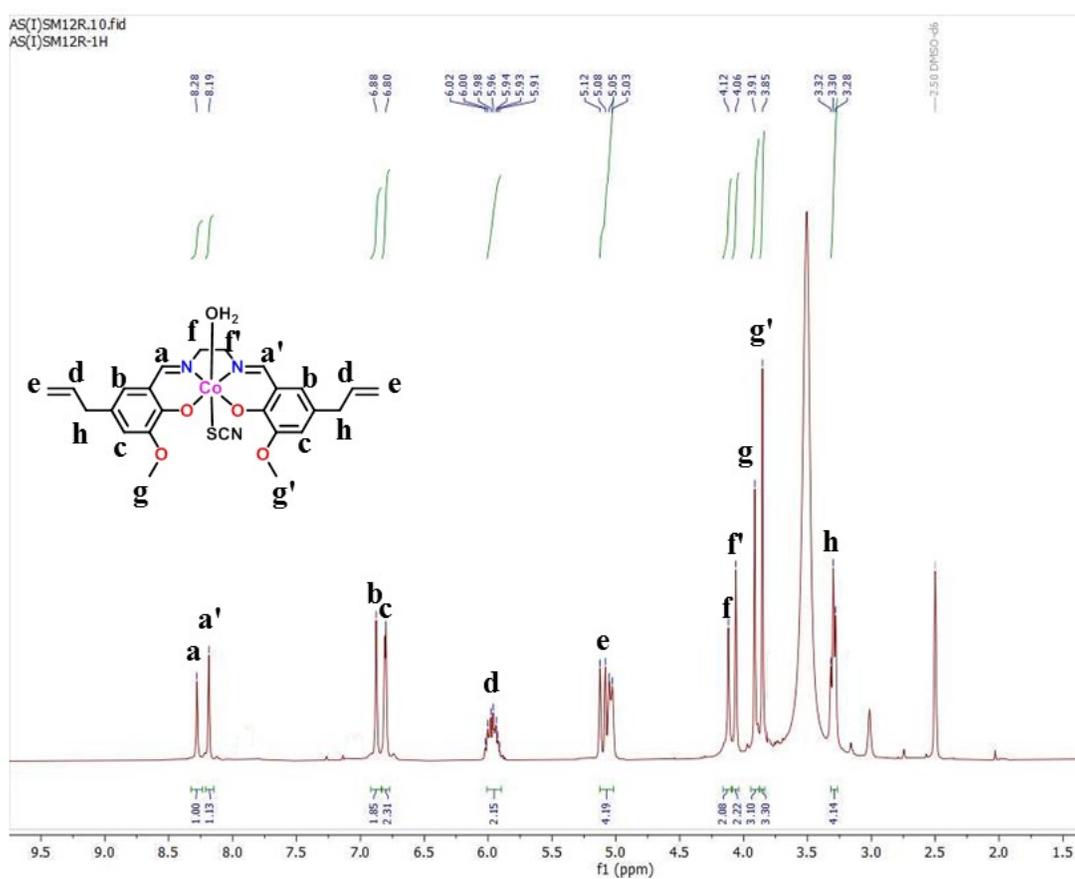


Fig. S10 <sup>1</sup>H NMR of Complex 1 in DMSO-d<sub>6</sub>

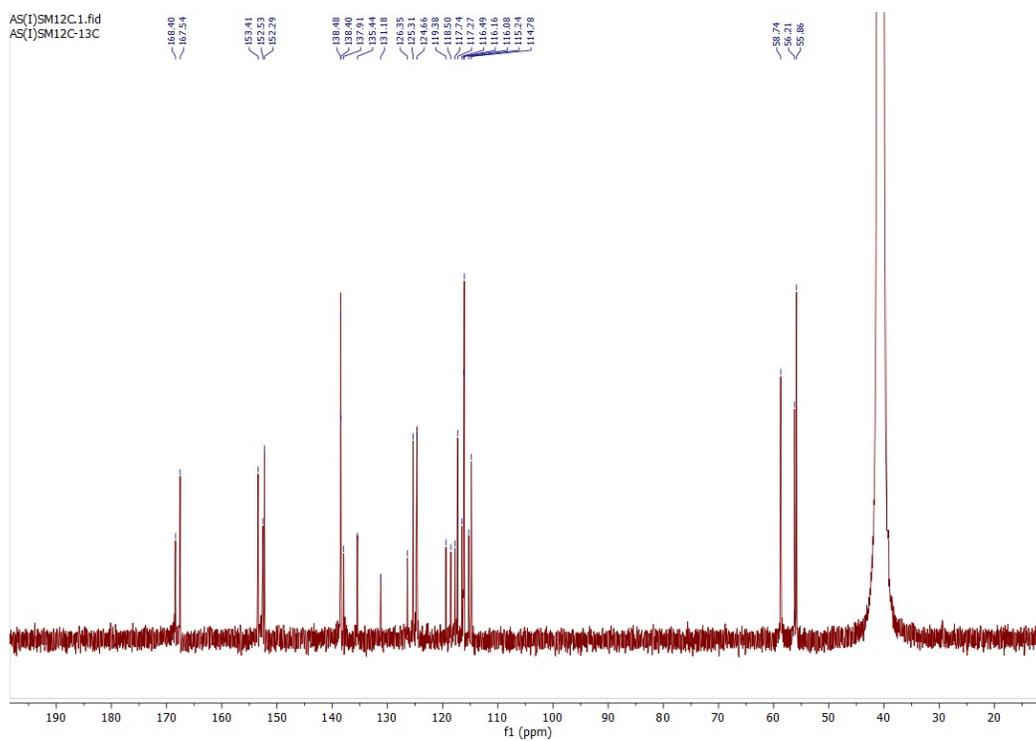


Fig. S11  $^{13}\text{C}$  NMR of Complex 1 in  $\text{DMSO-d}_6$

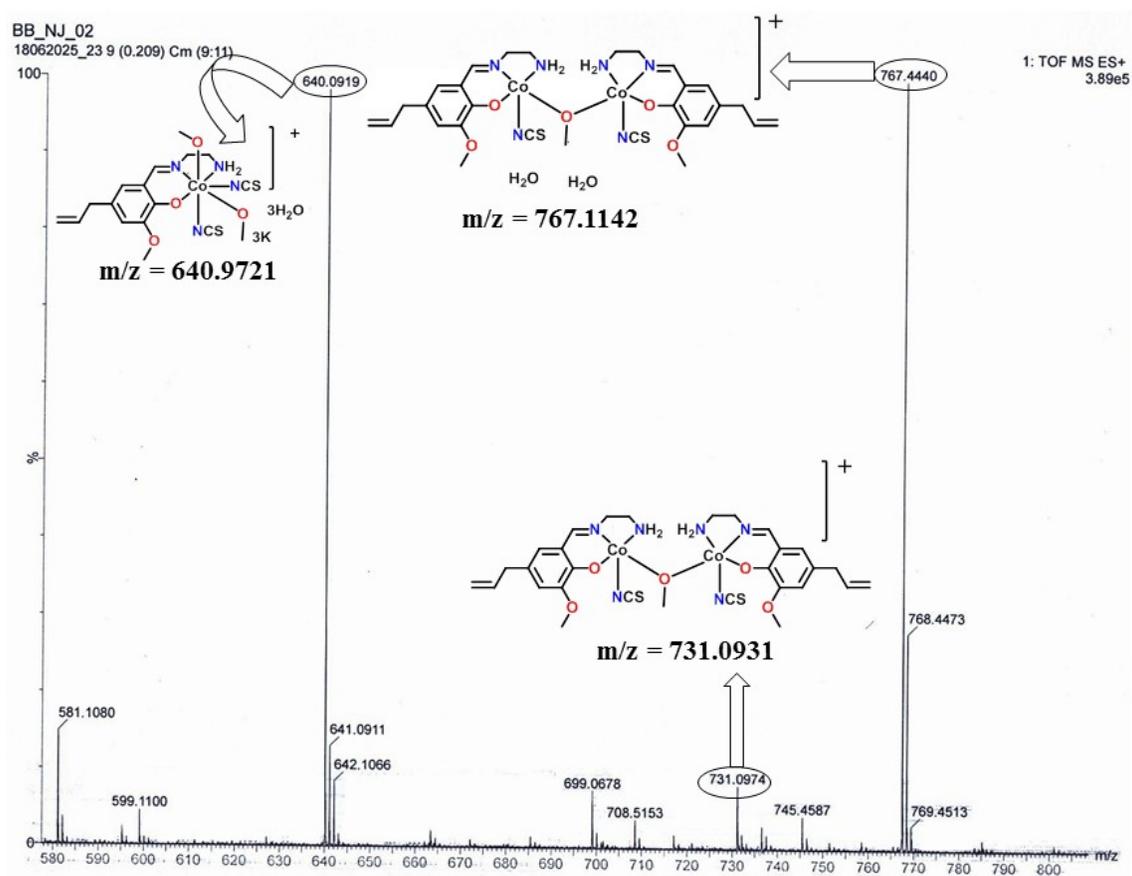


Fig. S12 ESI mass spectrum of complex 2

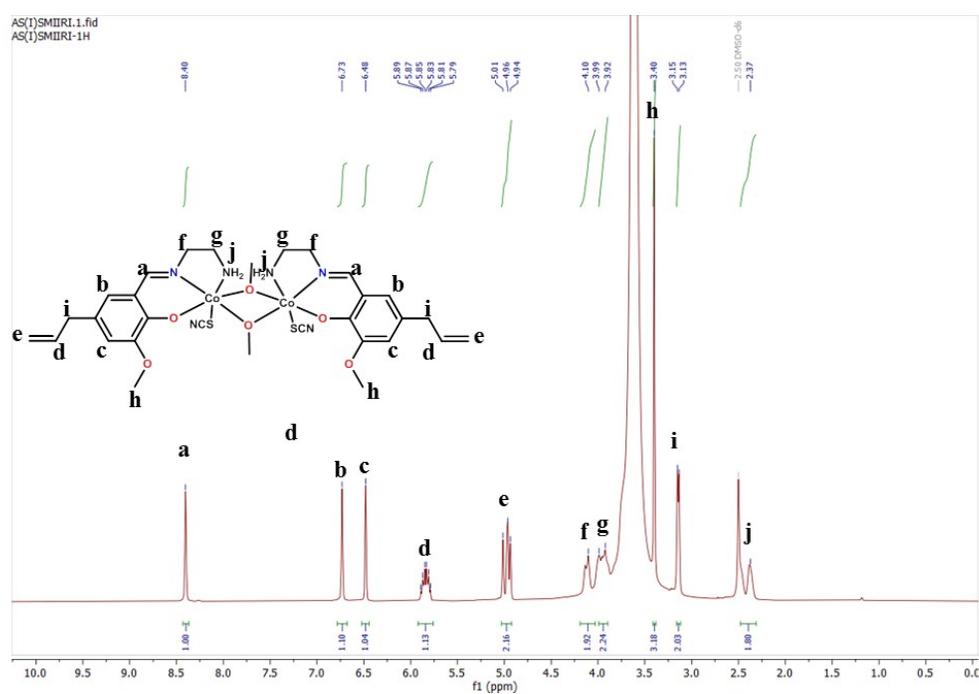


Fig. S13 <sup>1</sup>H NMR of Complex 2 in DMSO-d<sub>6</sub>

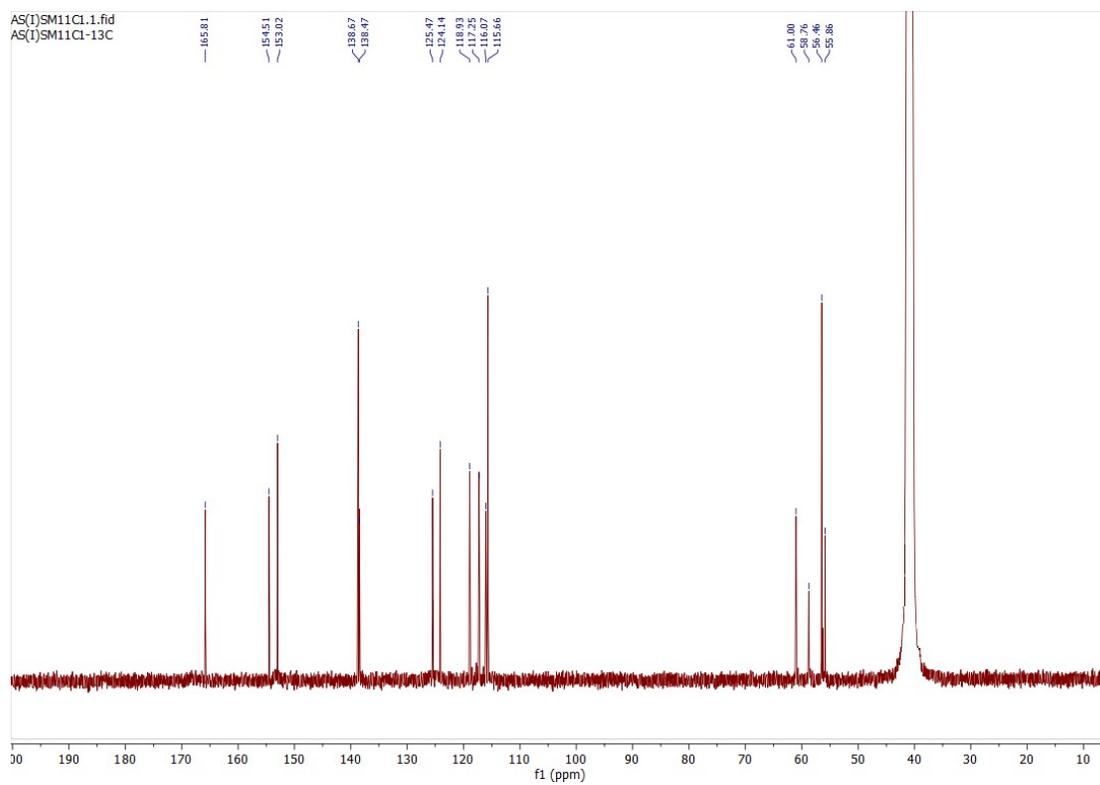
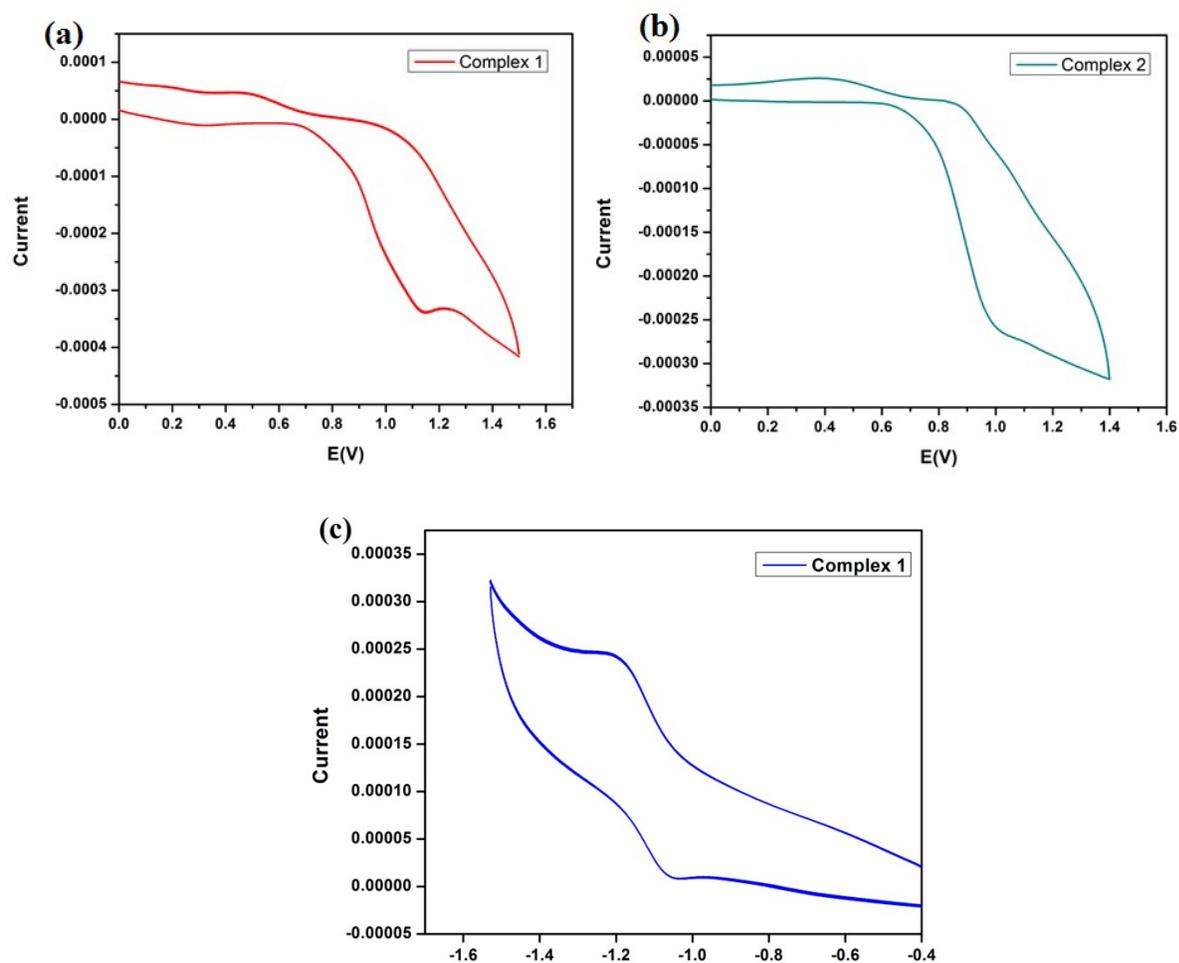
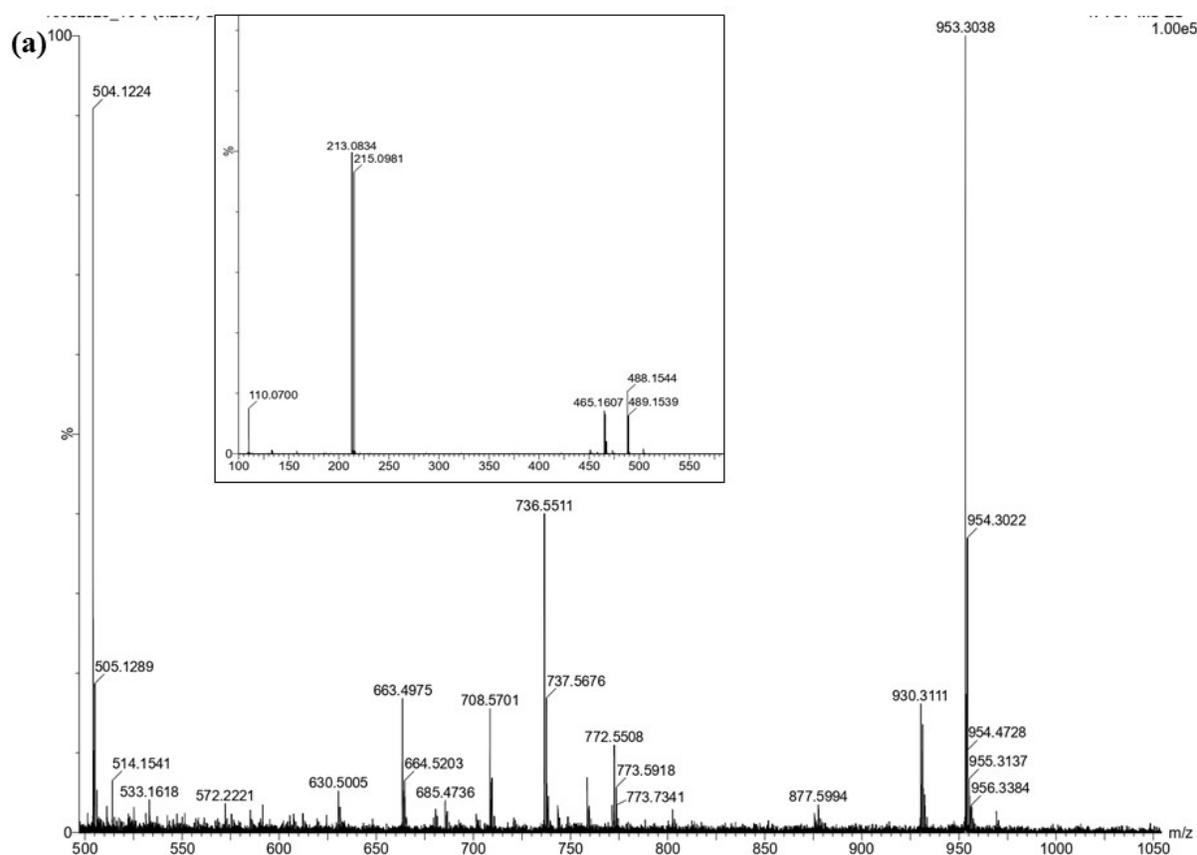
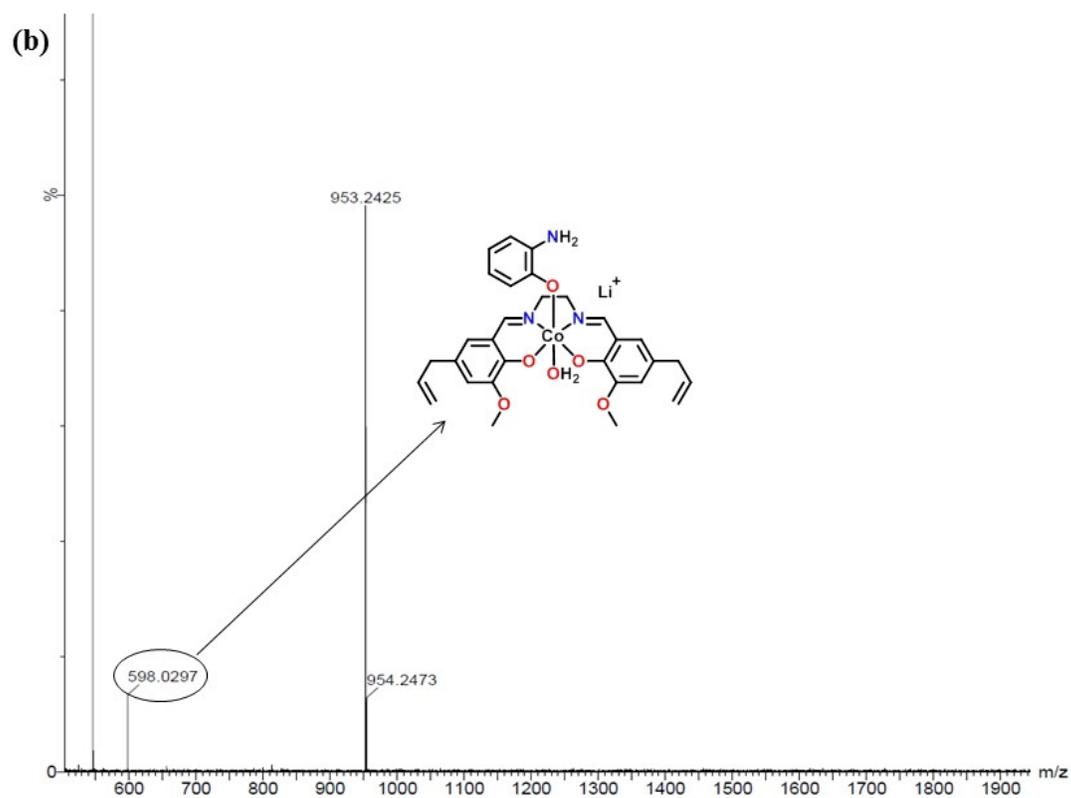


Fig. S14 <sup>13</sup>C NMR of Complex 2 in DMSO-d<sub>6</sub>

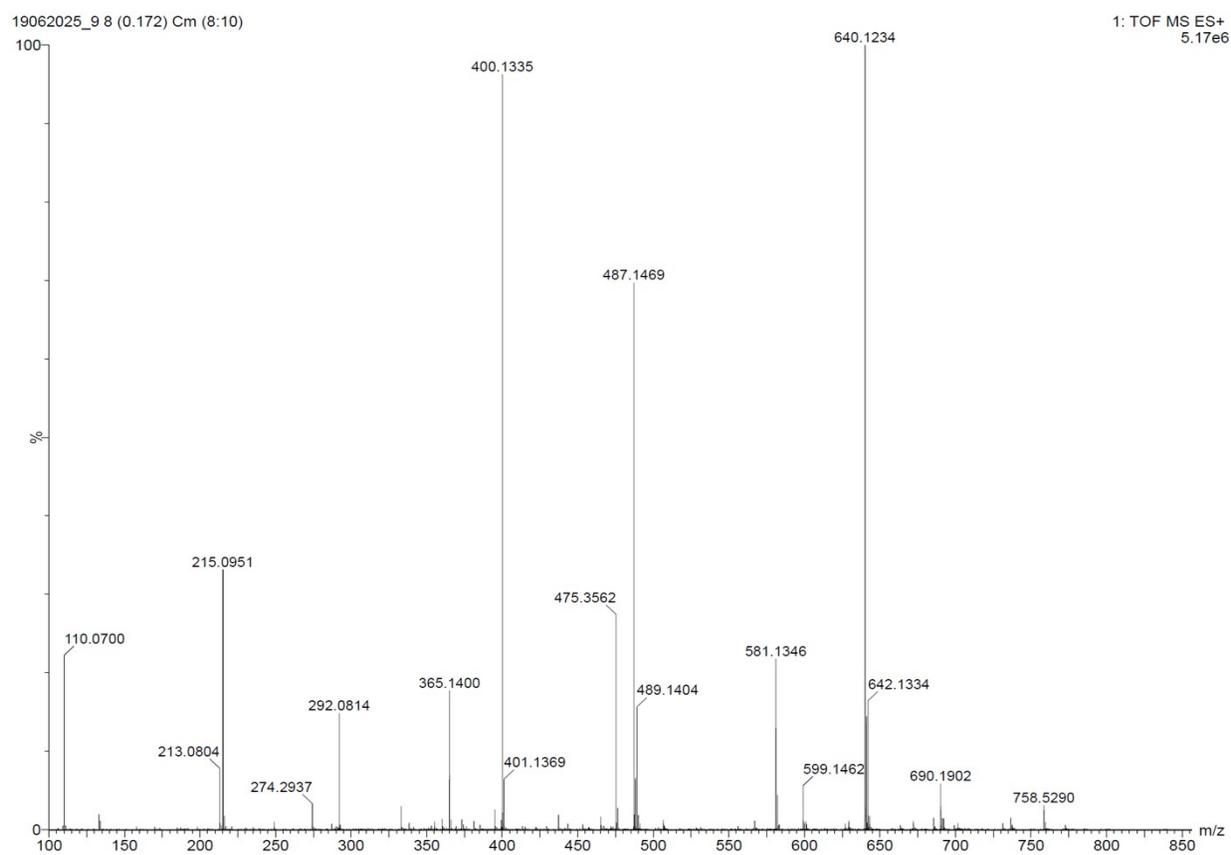


**Fig. S15** Cyclic voltammograms of **1** and **2**, (a) anodic scan of **1**, (b) anodic scan of **2** and (c) cathodic scan of **1**, in acetonitrile using a platinum working electrode in the presence of TBHP as a supporting electrolyte at room temperature with a scan rate of  $50 \text{ mV s}^{-1}$ .





**Fig. S16** ESI mass spectrum of complex 1 (a, b) in the presence of excess o-aminophenol



**Fig. S17** ESI mass spectrum of complex 2 in the presence of excess o-aminophenol.

**Table S1** Crystallographic data of Complex **1** and **2**

Complex	<b>1</b>	<b>2</b>
CCDC	2466985	2466976
Empirical formula	C <sub>25</sub> H <sub>28</sub> CoN <sub>3</sub> O <sub>5</sub> S	C <sub>15</sub> H <sub>20</sub> CoN <sub>3</sub> O <sub>3</sub> S
Formula weight	541.49	381.33
Temperature (K)	100.00(10)	100.00(10)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2/c</i>
<i>a</i> (Å)	12.0785(5)	11.1748(8)
<i>b</i> (Å)	14.3615(5)	8.1368(4)
<i>c</i> (Å)	14.9258(6)	18.3700(13)
$\alpha$ (°)	90	90
$\beta$ (°)	103.188(4)	107.570(7)
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> )	2520.83(18)	1592.41(19)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.427	1.591
Absorption coefficient (mm <sup>-1</sup> )	0.804	1.227
<i>F</i> (000)	1128.0	792.0
2 $\theta$ Range for data collection (°)	6.902 – 61.074	6.858 – 61.052
Reflections collected	20672	11787
Independent reflection / <i>R</i> <sub>int</sub>	6057 / 0.0715	3715 / 0.0365
Data / restraints / parameters	6057 / 1 / 321	3715 / 0 / 210
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.122	1.052
Final indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.1041, <i>wR</i> <sub>2</sub> = 0.2069	<i>R</i> <sub>1</sub> = 0.0353, <i>wR</i> <sub>2</sub> = 0.0903
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1673, <i>wR</i> <sub>2</sub> = 0.2435	<i>R</i> <sub>1</sub> = 0.0439, <i>wR</i> <sub>2</sub> = 0.0952
Largest diff. peak / deepest hole (e Å <sup>-3</sup> )	1.86 / -1.01	0.64 / -0.33

**Table S2** Selected Bond lengths (Å) and Bond angles (°) for complex **1** and **2**

<b>1</b>		<b>2</b>	
<b>Atoms</b>	<b>Distance (Å)</b>	<b>Atoms</b>	<b>Distance (Å)</b>
Co1–O1	1.886(5)	Co1–O1	1.8791(15)
Co1–O3	1.899(5)	Co1–N1	1.8857(17)
Co1–N2	1.890(6)	Co1–N2	1.9631(18)
Co1–N1	1.888(6)	Co1–O3 <sup>1</sup>	1.9043(13)
Co1–O5	1.951(5)	Co1–N3	1.9058(17)
Co1–N3	1.883(6)	Co1–O3	1.9306(13)
<b>Atoms</b>	<b>Angle (°)</b>	<b>Atoms</b>	<b>Angle (°)</b>
N1–Co1–N2	85.3(2)	N1–Co1–N2	85.85(7)
O1–Co1–N1	93.6(2)	O1–Co1–N1	92.91(7)
O1–Co1–O3	86.8(2)	O1–Co1–O3	86.33(6)
N2–Co1–O3	94.3(2)	O1–Co1–O3 <sup>1</sup>	89.86(6)
N3–Co1–O5	177.8(3)	N3–Co1–N2	90.61(7)
N2–Co1–O5	90.5(2)	N3–Co1–N1	91.79(7)
N1–Co1–O5	88.5(2)	Co1–O5–Co1 <sup>1</sup>	98.38(6)
O1–Co1–O5	89.3(2)	O1–Co1–N2	176.60(7)
O3–Co1–O5	89.69(19)	N1–Co1–O3	174.92(7)

**Table S3** List of hydrogen bonding/ $\pi\cdots\pi$  interactions studied in the complex **1**

Complex 1	Distance H $\cdots$ O/ $\pi\cdots\pi$ (Å)	O-H (Å)	O $\cdots$ O (Å)	Angle of <O-H $\cdots$ O> (°)
O5-H35B $\cdots$ O1	1.984	0.869	2.767	149.24
O5-H35B $\cdots$ O2	2.337	0.869	2.916	124.27
O5-H35A $\cdots$ O3	2.128	0.870	2.850	140.05
O5-H35A $\cdots$ O4	2.172	0.870	2.908	142.08
$\pi$ (C17-C22) $\cdots$ $\pi$ (C5-C10)	3.643			

**Table S4** List of hydrogen bonding, C-H $\cdots\pi$  interactions studied in the complex **2**

Complex 2	Distance H $\cdots$ O/ H $\cdots$ S (Å)	N-H/ N-H (Å)	N $\cdots$ O/C $\cdots$ S (Å)	Angle of <N-H $\cdots$ O>/ <C-H $\cdots$ S> (°)
N2-H2A $\cdots$ O2	2.775	0.910	3.565	145.75
N2-H2A $\cdots$ O1	2.155	0.910	2.862	133.90
C3-H3B $\cdots$ S1	2.898	0.980	3.622	131.48
C11-H11 $\cdots$ S1	2.933	0.950	3.862	166.22
C4-H4 $\cdots\pi$	3.562			
C3-H3A $\cdots\pi$	2.749			
C6-H6B $\cdots\pi$	2.618			

**Table S5** Cyclic Voltammetric Data <sup>a</sup>

<sup>a</sup> Experiments were carried out in CH<sub>3</sub>CN at 298 K with TBHP as supporting electrolyte. The

Complex	Oxidation $E_{1/2}$ (V)	Reduction $E_{1/2}$ (V)
<b>1</b>	+1.15 <sup>b</sup>	-1.20, -1.05 <sup>c</sup>
<b>2</b>	+1.01 <sup>b</sup>	-1.5 <sup>d</sup>

reported data correspond to a scan rate of 50 mV s<sup>-1</sup>. <sup>b</sup> Irreversible anodic response. <sup>c</sup> Quasireversible cathodic response. <sup>d</sup> Irreversible cathodic response.

**Table S6** Comparison of catalytic performances in the oxidation of o-aminophenol

Compounds	$V_{\max}(\text{M}^{-1} \text{s}^{-1})$	$K_{\text{cat}}(\text{h}^{-1})$	References
[Co(Hdmg) <sub>2</sub> (AsPh <sub>3</sub> )]		56.16	22. <i>Coord. Chem. Rev.</i> , 2003, <b>245</b> , 85-93.
[Co <sub>2</sub> (amp) <sub>2</sub> (μ-imp) <sub>2</sub> Cl <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	1.91 x 10 <sup>-7</sup>	13.752	23. <i>Dalton Trans.</i> , 2013, <b>42</b> , 5068-5075.
[Co <sub>3</sub> L <sub>2</sub> <sup>R</sup> (μ <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> ]. (CH <sub>3</sub> CN) <sub>2</sub>	2.13 x 10 <sup>-4</sup>	153.60	24. <i>Polyhedron</i> , 2017, <b>134</b> , 99-106.
[Co(L)(N <sub>3</sub> ) <sub>2</sub> ]	(1.31 ± 0.02) x 10 <sup>-7</sup>	47.36	25. <i>Inorg. Chim. Acta</i> , 2019, <b>490</b> , 163-172.
[Co(L)(NCS) <sub>2</sub> ]	(1.32 ± 0.03) x 10 <sup>-7</sup>	47.60	25. <i>Inorg. Chim. Acta</i> , 2019, <b>490</b> , 163-172.
[Co(L)(sal)] <sub>2</sub> [Co(NCS) <sub>2</sub> ]	(4.57 ± 0.04) x 10 <sup>-8</sup>	16.46	25. <i>Inorg. Chim. Acta</i> , 2019, <b>490</b> , 163-172.
[Co(L) <sub>2</sub> ] <sub>2</sub> [Co <sub>0.5</sub> (NCS) <sub>2</sub> ][Co <sub>0.25</sub> (NCS)]Cl <sub>0.5</sub>	(2.87 ± 0.04) x 10 <sup>-8</sup>	10.34	25. <i>Inorg. Chim. Acta</i> , 2019, <b>490</b> , 163-172.
[Co(HL <sub>1</sub> )(N <sub>3</sub> ) <sub>4</sub> ]	(1.72 ± 0.03) x 10 <sup>-7</sup>	61.92	26. <i>New J. Chem.</i> , 2020, <b>44</b> , 11527-11536.
[Co(L <sub>2</sub> )(N <sub>3</sub> ) <sub>3</sub> ]	(1.12 ± 0.03) x 10 <sup>-7</sup>	40.34	26. <i>New J. Chem.</i> , 2020, <b>44</b> , 11527-11536.
[Co(L <sub>3</sub> )(N <sub>3</sub> ) <sub>3</sub> ]	(1.18 ± 0.03) x 10 <sup>-7</sup>	42.63	26. <i>New J. Chem.</i> , 2020, <b>44</b> , 11527-11536.
[Co(L <sub>4</sub> )(imz) <sub>2</sub> ]ClO <sub>4</sub> ·H <sub>2</sub> O·MeOH	(8.81 ± 0.22) x 10 <sup>-8</sup>	31.71	27. <i>New J. Chem.</i> , 2024, <b>48</b> , 2389-2402.

$[\text{Co}(\text{L}_4)(\text{pyz})_2]\text{ClO}_4 \cdot 1.5\text{H}_2\text{O}$	$(8.08 \pm 0.25) \times 10^{-8}$	29.07	27. <i>New J. Chem.</i> , 2024, <b>48</b> , 2389-2402.
$[\text{Co}(\text{L}_4)(\text{py})_2]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$	$(1.15 \pm 0.04) \times 10^{-7}$	41.38	27. <i>New J. Chem.</i> , 2024, <b>48</b> , 2389-2402.
$[\text{Co}(\text{L}_4)(\text{mpy})_2]\text{ClO}_4 \cdot 0.5\text{mpy} \cdot 1.5\text{H}_2\text{O}$	$(1.03 \pm 0.03) \times 10^{-7}$	37.05	27. <i>New J. Chem.</i> , 2024, <b>48</b> , 2389-2402.
$[\text{Co}_2(\text{L}_4)_2(4\text{-O-py})(4\text{-OH-py})_3]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$	$(1.08 \pm 0.03) \times 10^{-7}$	38.80	27. <i>New J. Chem.</i> , 2024, <b>48</b> , 2389-2402.
$[\text{Co}(\text{L}_4)(4\text{-NH}_2\text{-py})_2]\text{ClO}_4$	$(1.01 \pm 0.03) \times 10^{-7}$	36.43	27. <i>New J. Chem.</i> , 2024, <b>48</b> , 2389-2402.
<b>Complex 1</b>	$(9.84 \pm 0.25) \times 10^{-8}$	35.45	<b>This work</b>
<b>Complex 2</b>	$(6.18 \pm 0.17) \times 10^{-8}$	22.25	<b>This work</b>

Where,  $\text{H}_2\text{dmg}$  = dimethylglyoxime;  $\text{amp}$  = 2-aminomethylpyridine;  $\text{imp}$  = 2-iminomethylpyridine anion; ( $\text{H}_2\text{L}^{\text{R}}$  = N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine;  $\text{SalH}$  = salicylaldehyde; Schiff base ligand  $\text{HL}$  = derive from salicylaldehyde ( $\text{SalH}$ ) and N,N-dimethyldipropylenetriamine;  $\text{L}_1$  = N,N-dimethyldipropylenetriamine;  $\text{L}_2$  = N<sup>1</sup>-isopropyl-diethylenetriamine and  $\text{L}_3$  = N,N-diethyldiethylenetriamine;  $\text{H}_2\text{L}_4$  = N,N'-bis(3-methoxy-5-methylsalicylidene)-ethane-1,2-diamine ;  $\text{imz}$  = imidazole;  $\text{pyz}$  = pyrazole;  $\text{py}$  = pyridine;  $\text{mpy}$  = 4-methylpyridine; 4-OH-py = 4-hydroxypyridine; 4-NH<sub>2</sub>-py = 4-aminopyridine.