

Supporting information

for

Copper(II) mediated phenol ring nitration by nitrogen dioxide

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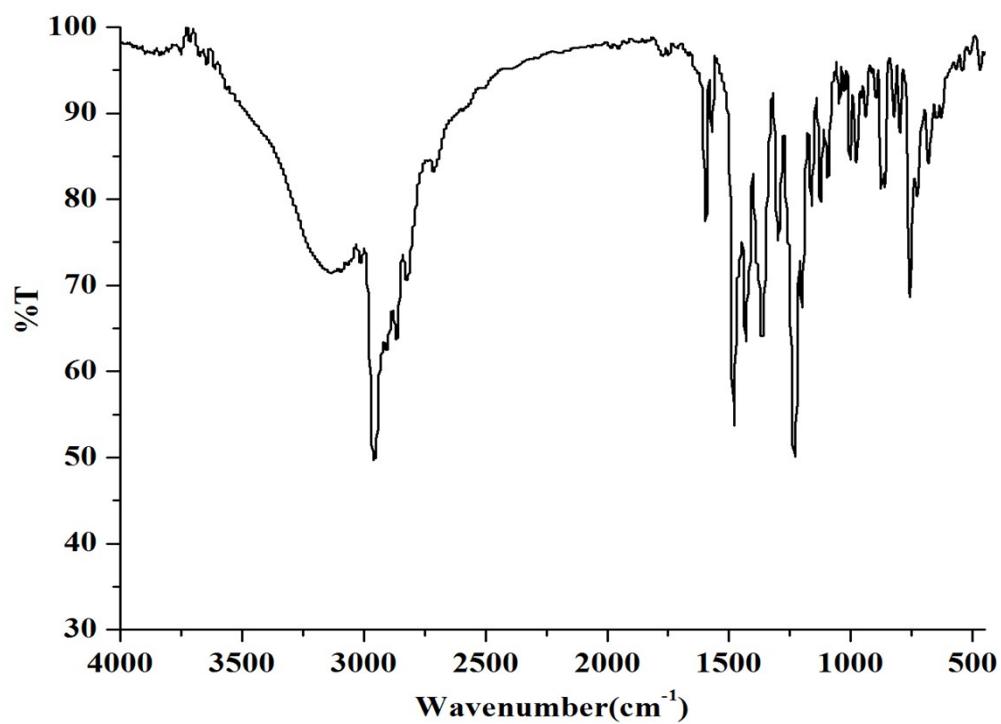


Figure S1: FT-IR spectrum of ligand L¹H₂ in KBr pellet.

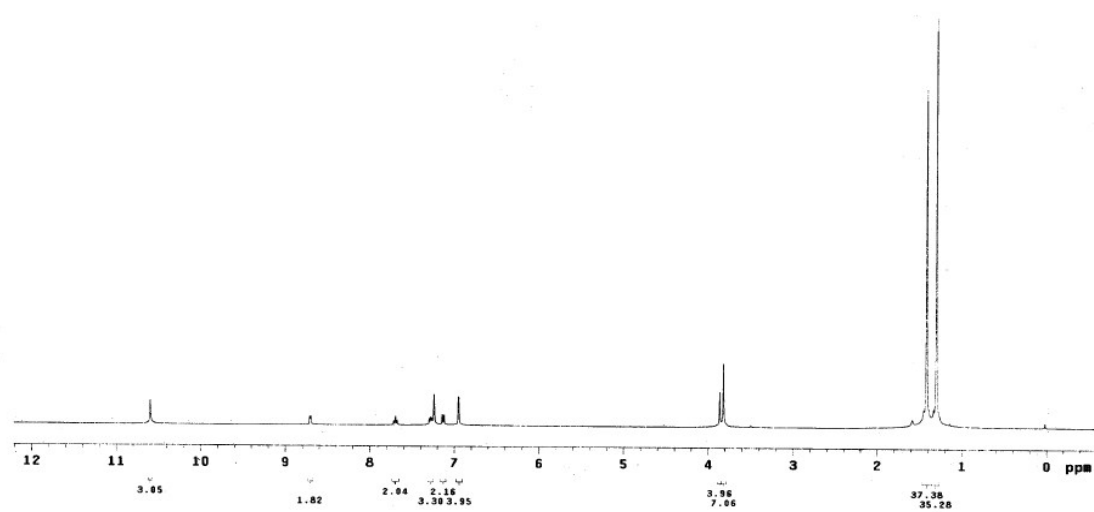


Figure S2: ¹H-NMR spectrum of ligand L¹H₂ in CDCl₃.

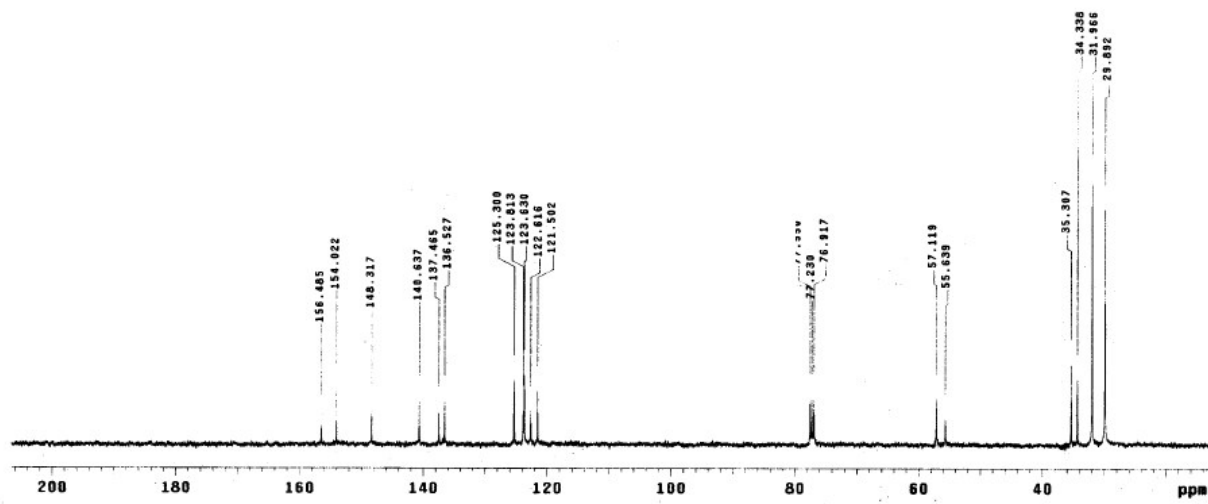


Figure S3: ^{13}C -NMR spectrum of ligand L^1H_2 in CDCl_3 .

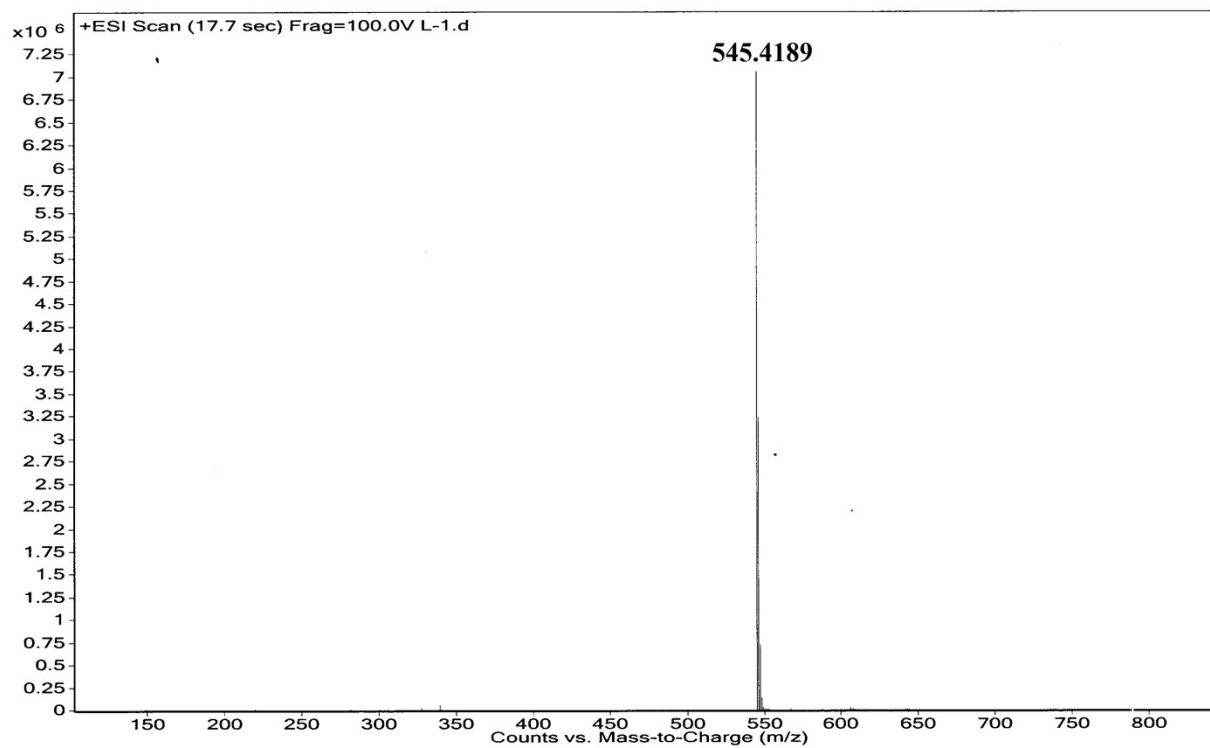


Figure S4: ESI mass spectrum of ligand L^1H_2 in methanol.

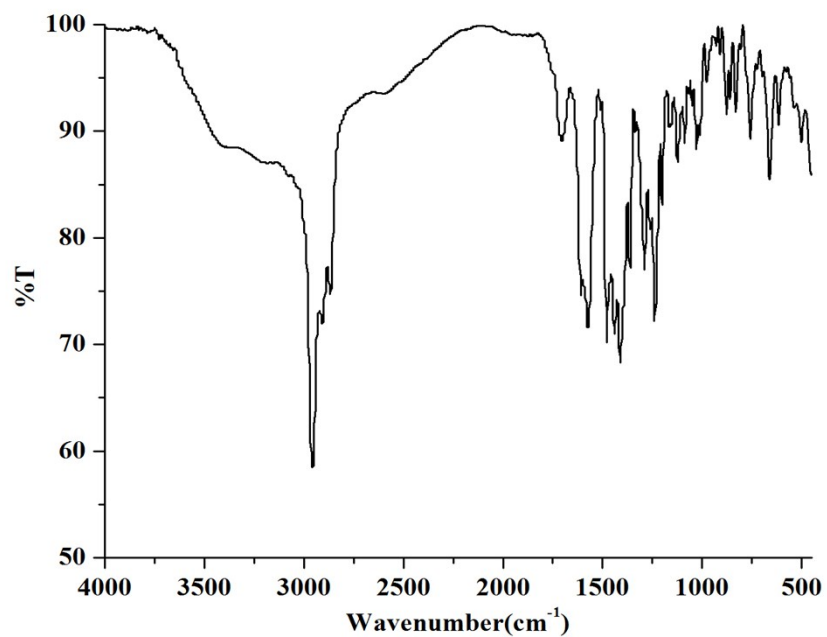


Figure S5: FT-IR spectrum of complex 1 in KBr pellet.

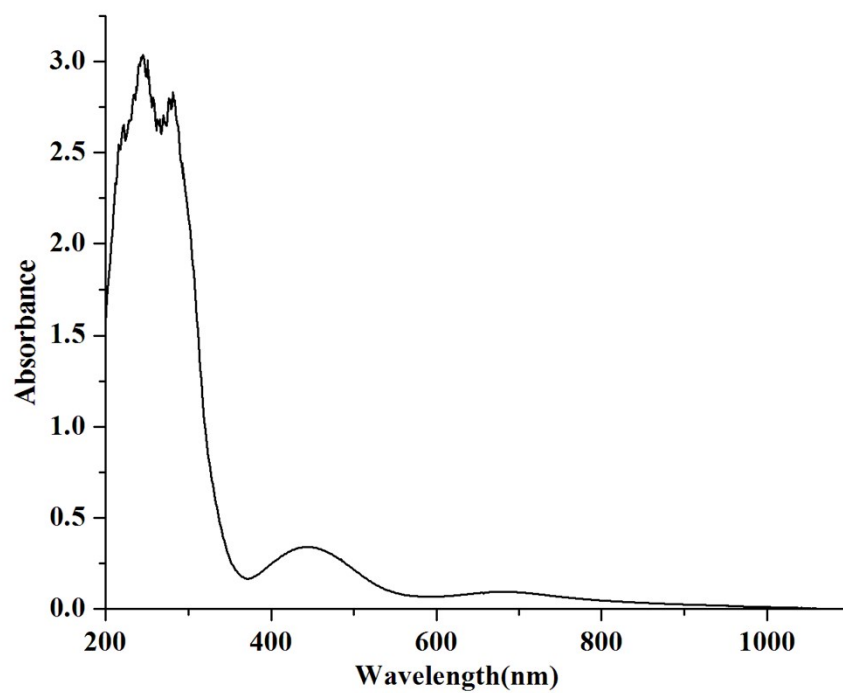


Figure S6: UV-visible spectrum of complex 1 in methanol.

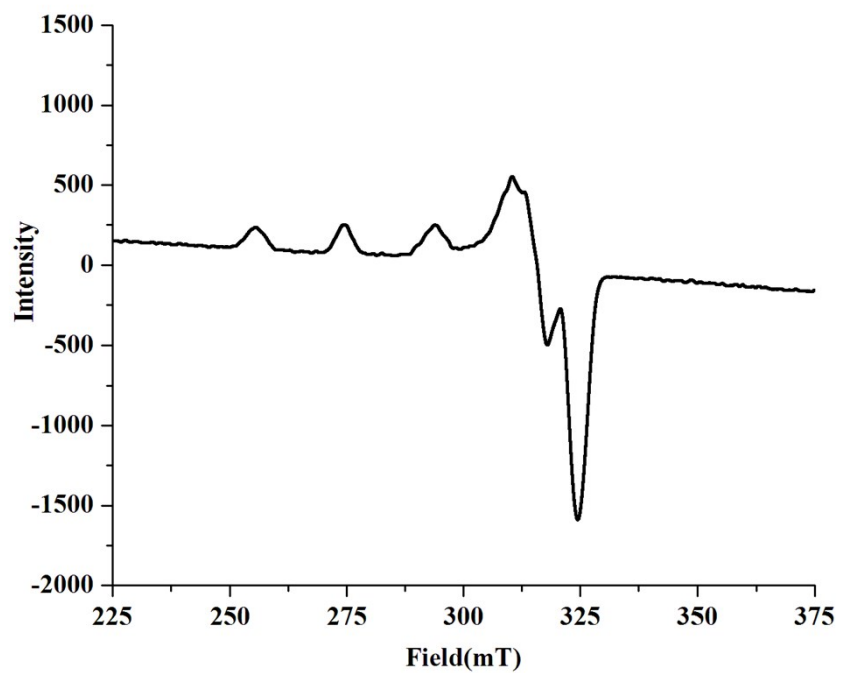


Figure S7: X-Band EPR spectrum of complex **1** in THF at 77 K.

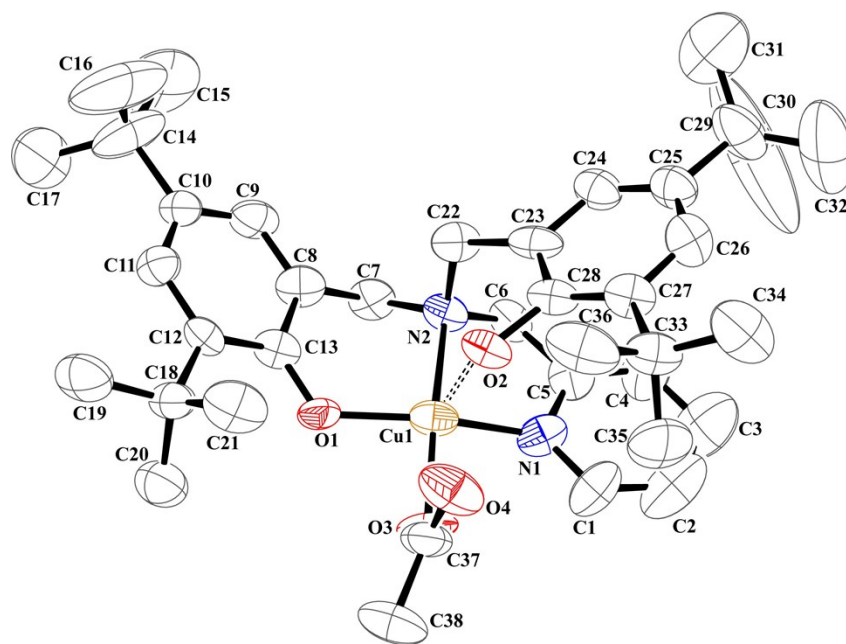


Figure S8: ORTEP diagram of complex **1** (50% thermal ellipsoid plot, hydrogen atoms and solvent molecules are omitted for clarity).

Table S1: Crystallographic table for complex 1.

	Complex 1
Formulae	C ₃₉ H ₅₇ N ₂ O ₅ Cu
Mol. wt.	697.41
Crystal system	Monoclinic
Space group	P21/n
Temperature /K	296(2)
Wavelength /Å	0.71073
<i>a</i> /Å	26.8261(11)
<i>b</i> /Å	10.7728(4)
<i>c</i> /Å	27.9227(17)
α /°	90.00
β /°	96.304(4)
γ /°	90.00
<i>V</i> / Å ³	8020.6(7)
<i>Z</i>	8
Density/Mgm ⁻³	1.155
Abs. co-eff. /mm ⁻¹	0.585
Abs. correction	multi-scan
F(000)	2992
Total no. of reflections	18185
Reflections, <i>I</i> > 2σ(<i>I</i>)	7961
Max. 2θ/°	28.75
Ranges (h, k, l)	-34 ≤ h ≤ 35 -14 ≤ k ≤ 13 -37 ≤ l ≤ 33
Complete to 2θ (%)	87.2
Refinement method	Full-matrix least-squares on <i>F</i> ²
Goof (<i>F</i> ²)	1.270
R indices [<i>I</i> > 2σ(<i>I</i>)]	0.1204
R indices (all data)	0.2014

Table S2: Selected bond angles (°) for complex 1.

Atoms	Angles (°)	Atoms	Angles (°)
N1 - Cu1 - N2	83.7(2)	O2 - Cu1 - O3	95.1(2)
N1 - Cu1 - O1	162.8(2)	Cu1 - N1 - C5	115.3(4)
N1 - Cu1 - O2	90.9(2)	Cu1 - N1 - C1	126.3(5)

N1 - Cu1 - O3	93.8(2)	Cu1 - N2 - C7	107.8(4)
N2 - Cu1 - O1	94.5(2)	Cu1 - N2 - C22	111.8(4)
N2 - Cu1 - O2	86.7(2)	Cu1 - O1 - C13	127.9(4)
N2 - Cu1 - O3	177.0(2)	Cu1 - O3 - C37	126.3(5)
O1 - Cu1 - O2	106.1(2)	Cu1 - N2 - C6	106.8(4)
O1 - Cu1 - O3	87.4(2)	-	-

Table S3: Selected bond distances (Å) for complex **1** and **5**.

Atoms	Distances (Å)	Atoms	Distances (Å)
Cu1 - N1	1.993(5)	O3 - C37	1.25(1)
Cu1 - N2	2.047(4)	N1 - C1	1.340(9)
Cu1 - O1	1.900(4)	N2 - C7	1.498(8)
Cu1 - O2	2.404(5)	N2 - C6	1.485(8)
Cu1 - O3	1.959(4)	N2 - C22	1.47(1)
N1 - C5	1.342(8)	O1 - C13	1.335(8)
C8 - C7	1.506(9)	O2 - C28	1.348(9)

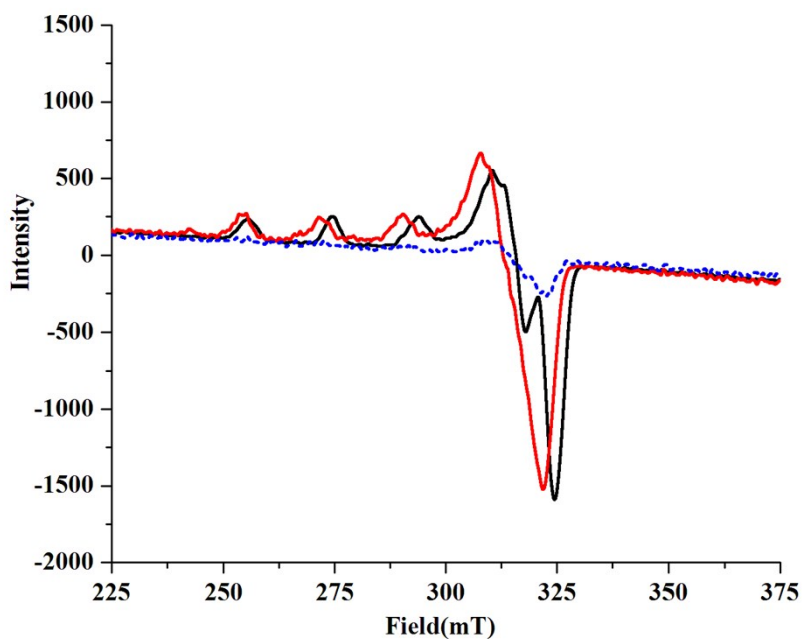


Figure S9: X-Band EPR spectrum of complex **1** (black trace), phenoxyl radical intermediate (blue trace) and complex **3** (red trace) in THF at 77 K.

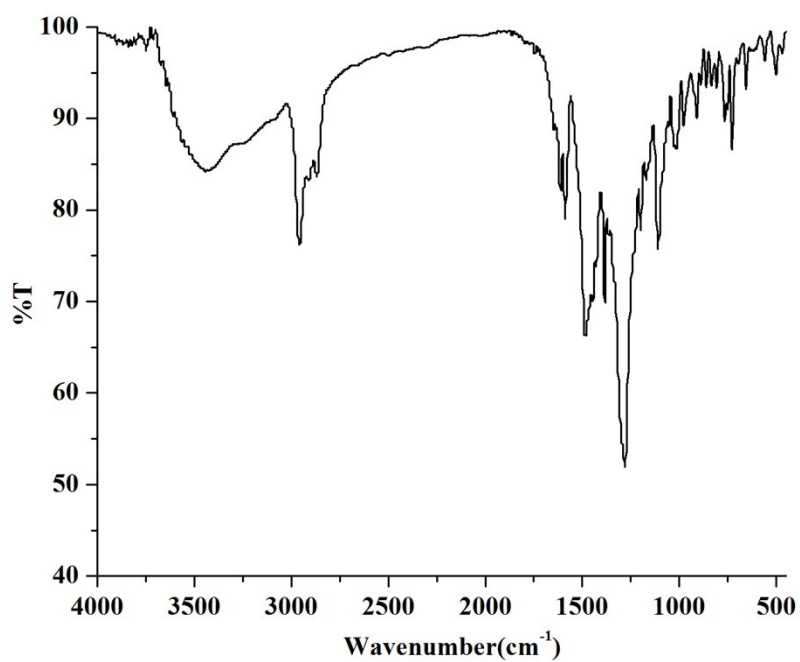


Figure S10: FT-IR spectrum of complex **3** in KBr pellet.

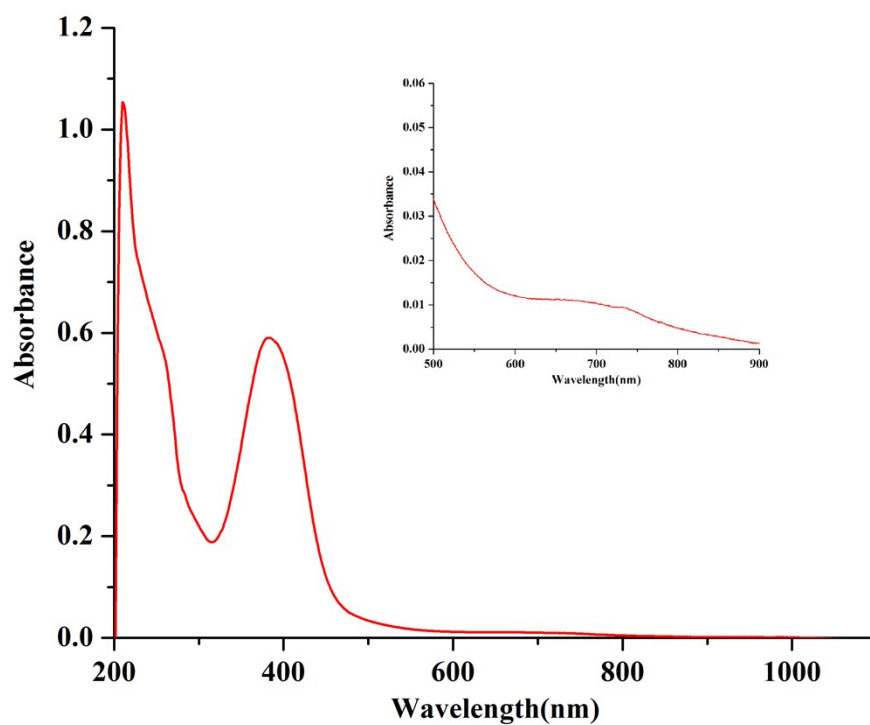


Figure S11: UV-visible spectrum of complex **3** in methanol at room temperature.

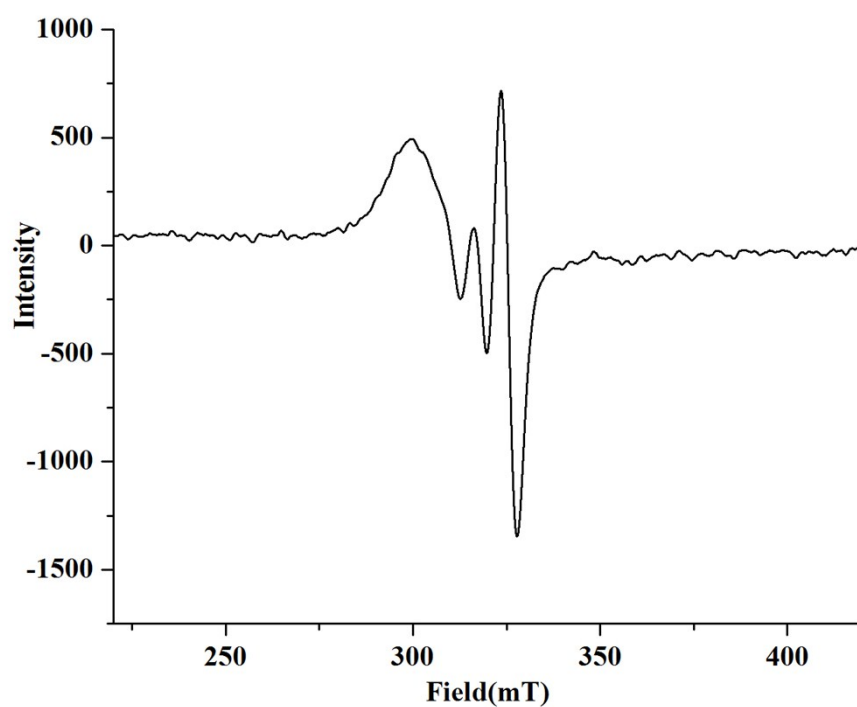


Figure S12: X-Band EPR spectrum of complex **5** in methanol at room temperature.

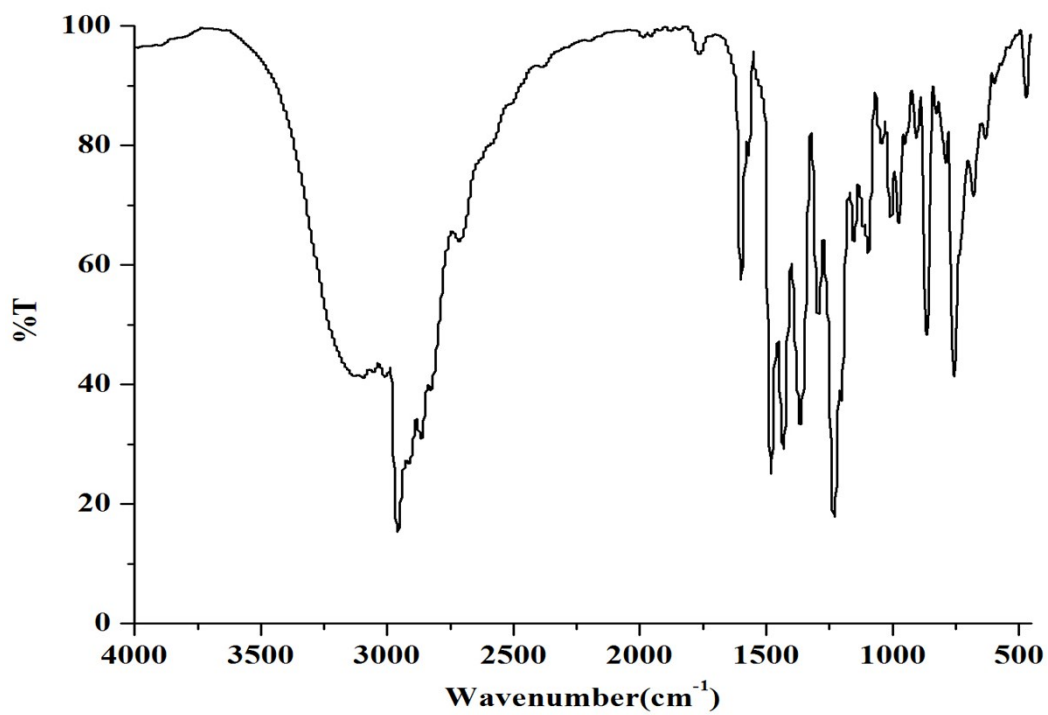


Figure S13: FT-IR spectrum of ligand **L²H₂** in KBr pellet.

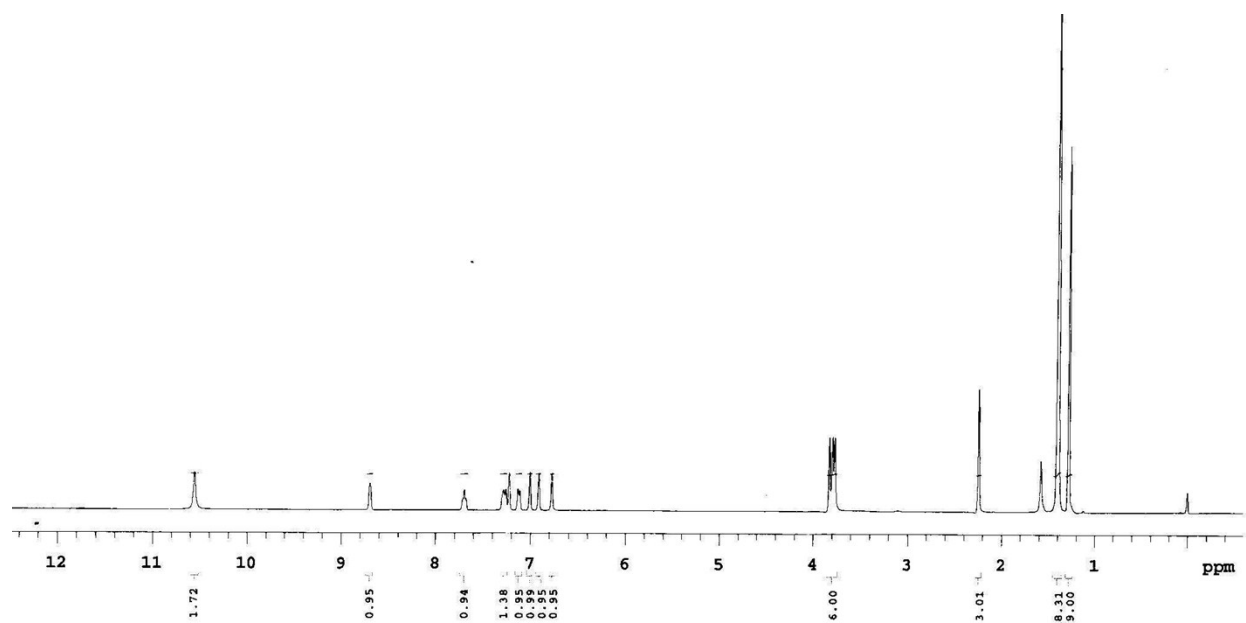


Figure S14: $^1\text{H-NMR}$ spectrum of ligand L^2H_2 in CDCl_3 .

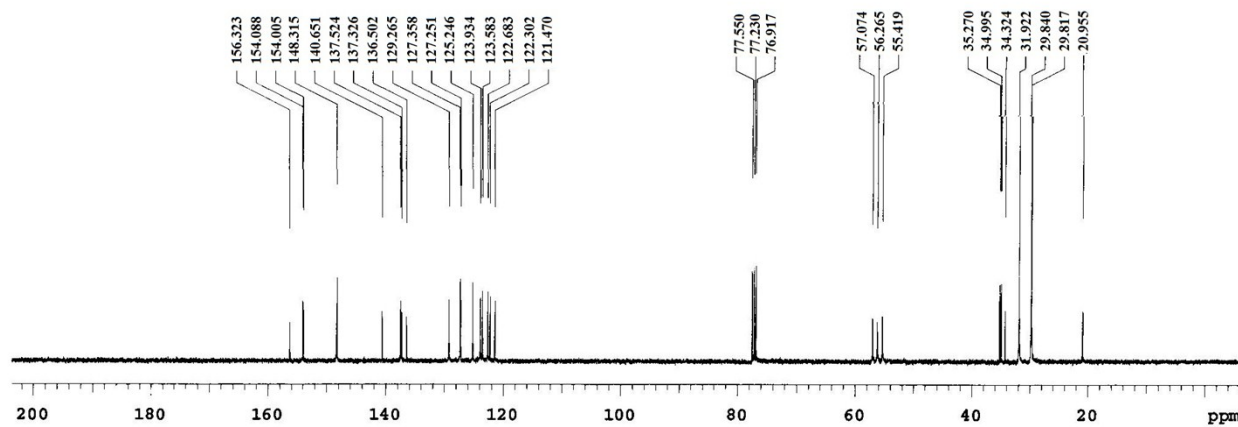


Figure S15: $^{13}\text{C-NMR}$ spectrum of ligand L^2H_2 in CDCl_3 .

Sample Name	L-2	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	L-2.d	ACQ Method		Comment		Acquired Time	12/9/2014 3:34:49 PM

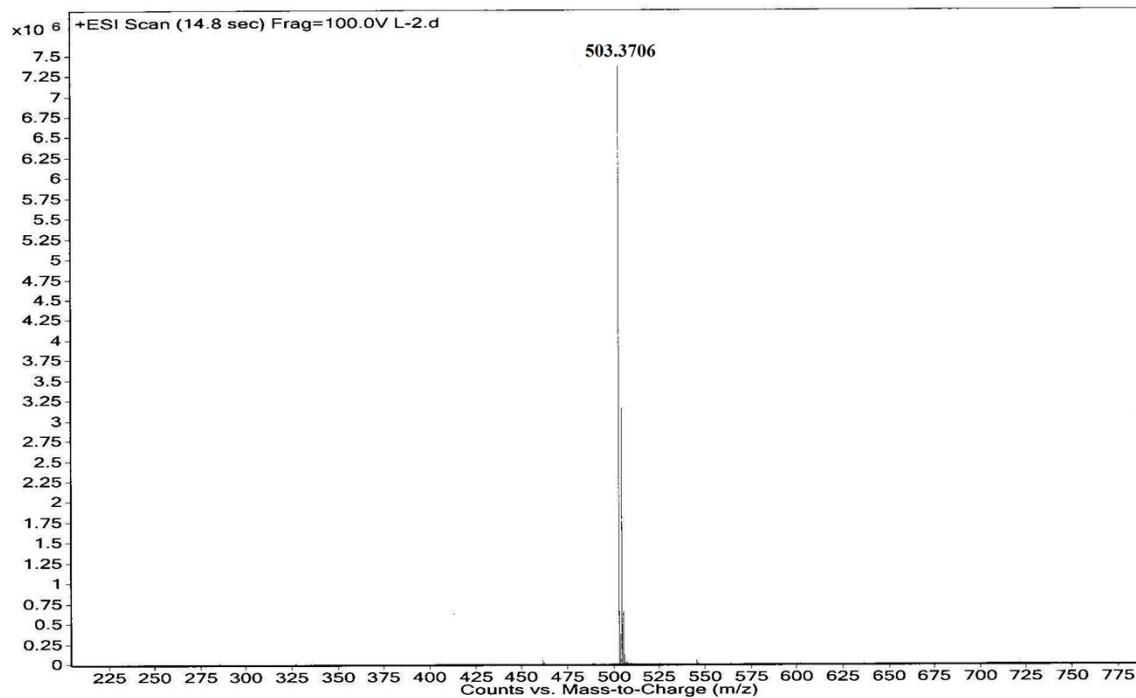


Figure S16: ESI mass spectrum of ligand L^2H_2 in methanol.

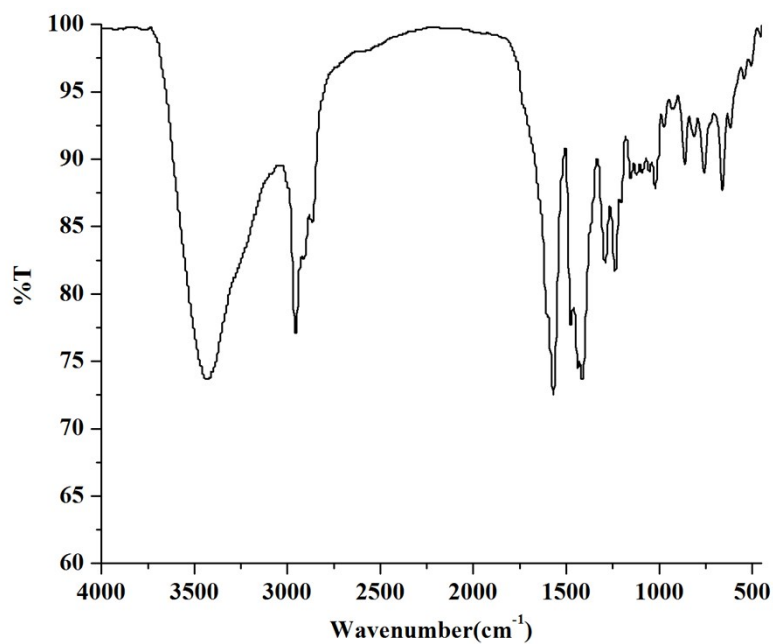


Figure S17: FT-IR spectrum of complex **2** in KBr pellet.

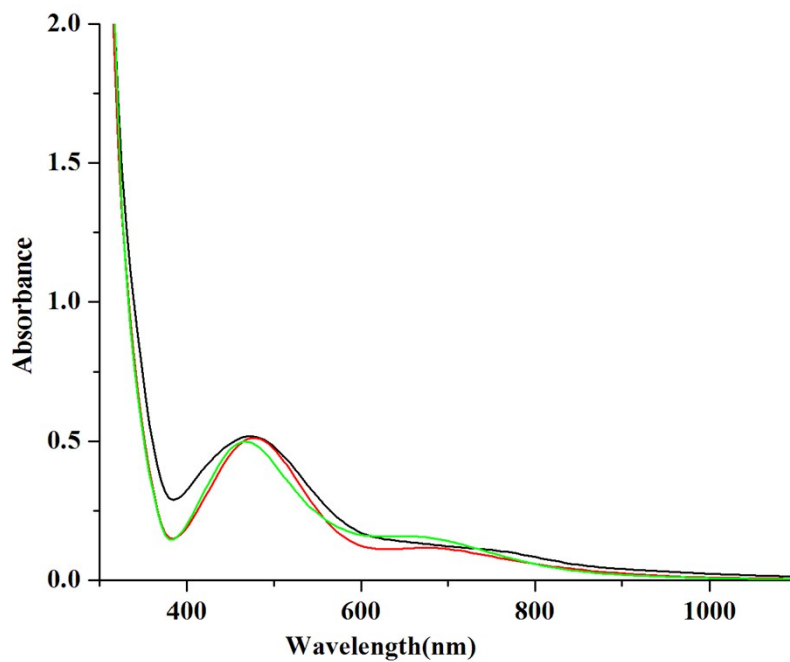


Figure S18: UV-visible spectra of complex **2** in different solvents.

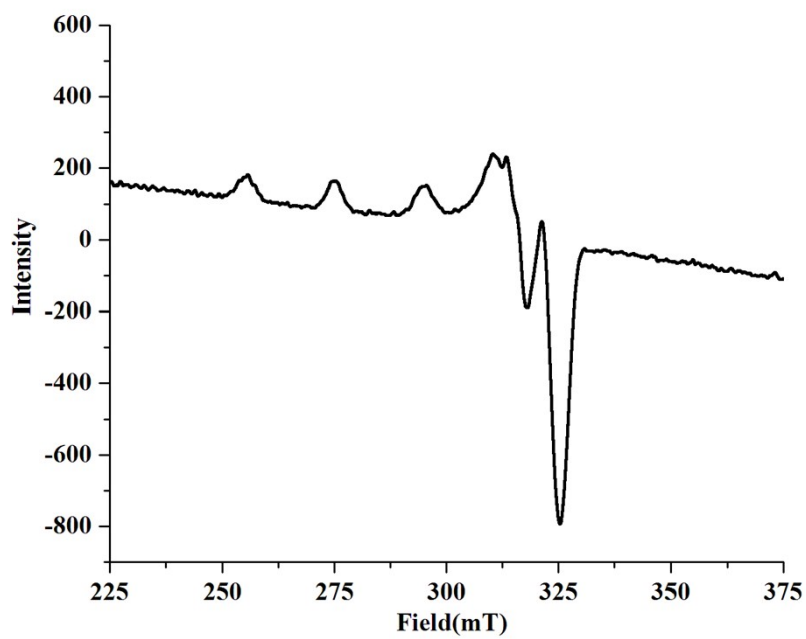


Figure S19: X-Band EPR spectrum of complex **2** in THF at 77 K.

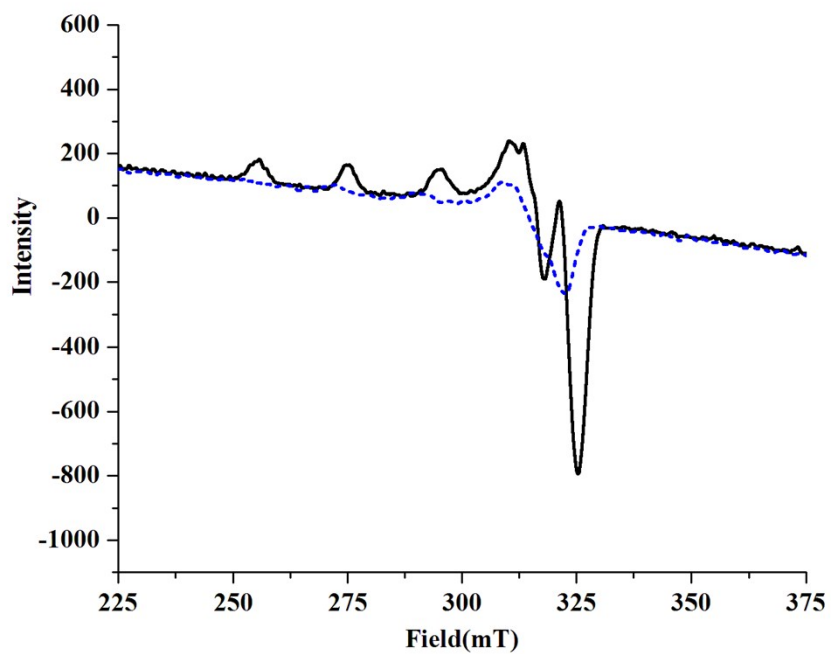


Figure S20: X-Band EPR spectrum of complex **2** (black trace) and phenoxyl radical intermediate (blue trace) in THF at 77 K.

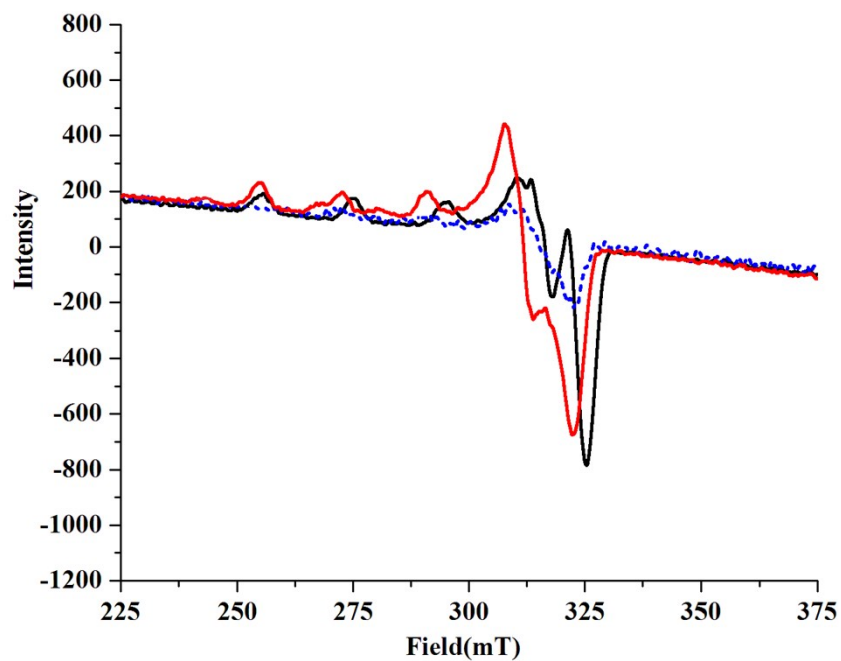


Figure S21: X-Band EPR spectrum of complex **2** (black trace), phenoxyl radical intermediate (blue trace) and complex **4** (red trace) in THF at 77 K.

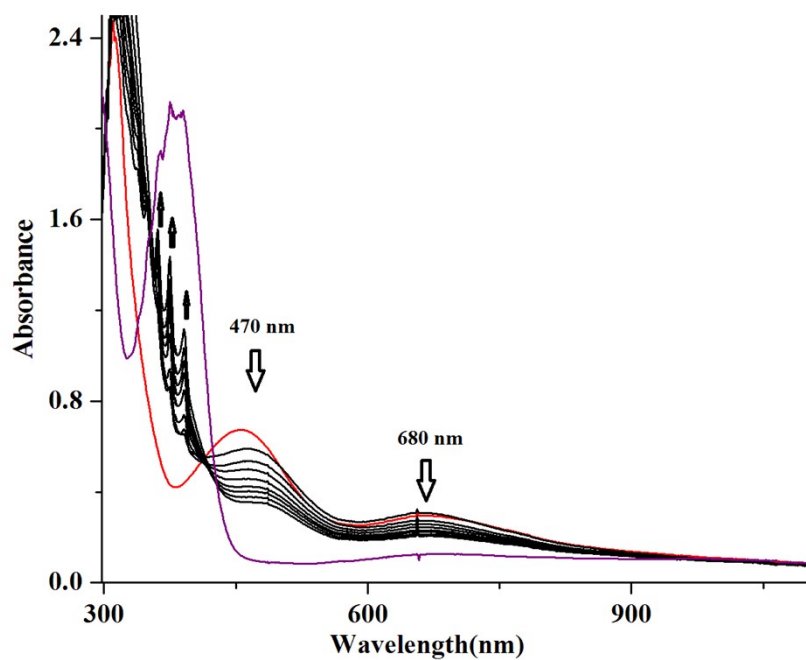


Figure S22: UV-visible spectra of complex **2** (red trace), phenoxyl radical (black traces) and final decomposition product (violet trace) in THF at -80 °C.

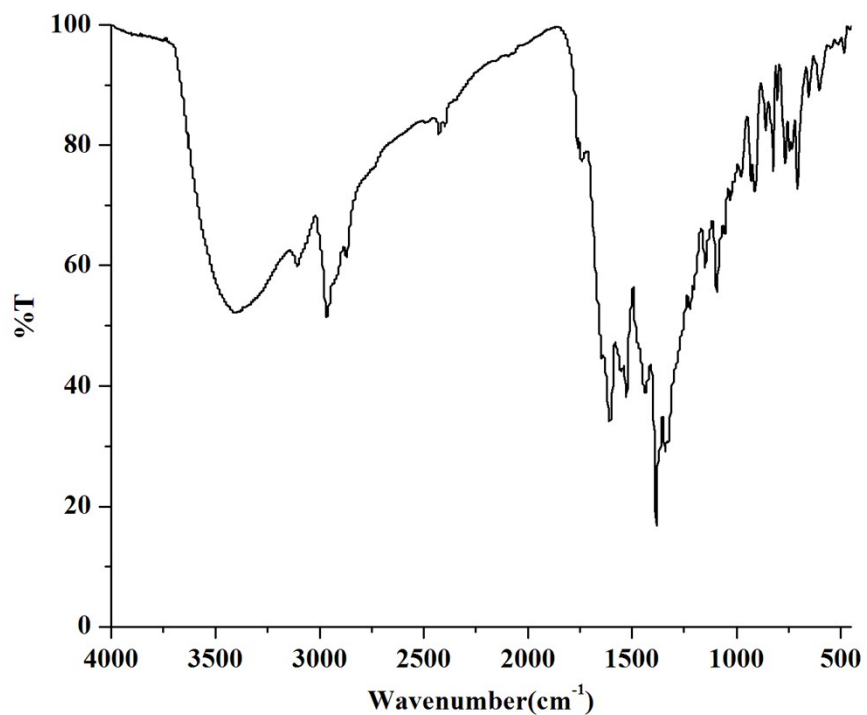


Figure S23: FT-IR spectrum of complex **4** in KBr pellet.

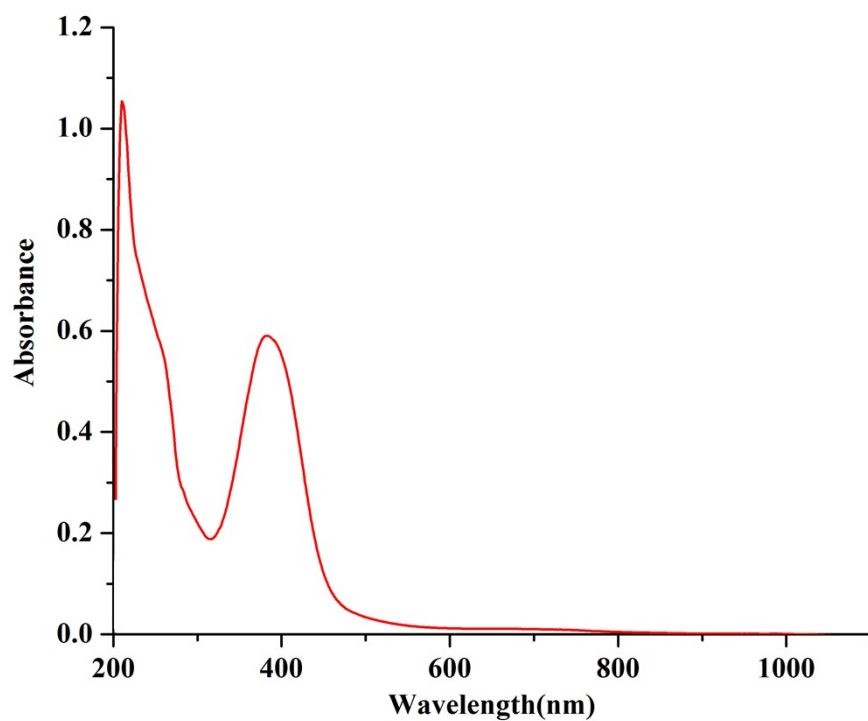


Figure S24: UV-visible spectrum of complex **4** in methanol at room temperature.

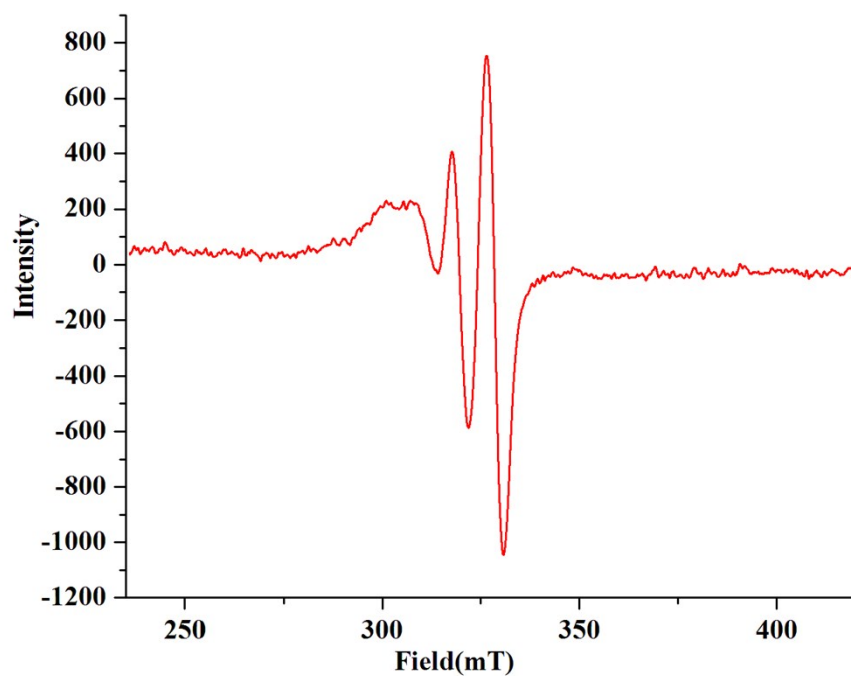


Figure S25: X-Band EPR spectrum of complex **4** in methanol at room temperature.

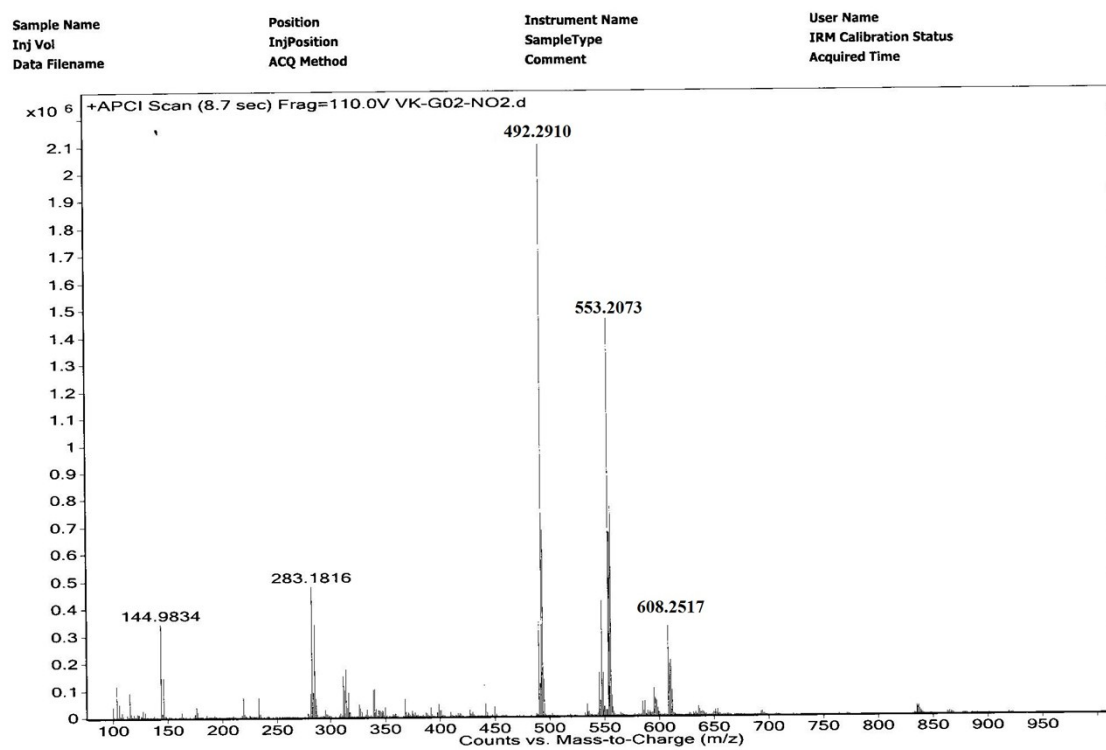


Figure S26: ESI mass spectrum of complex 4 in methanol.

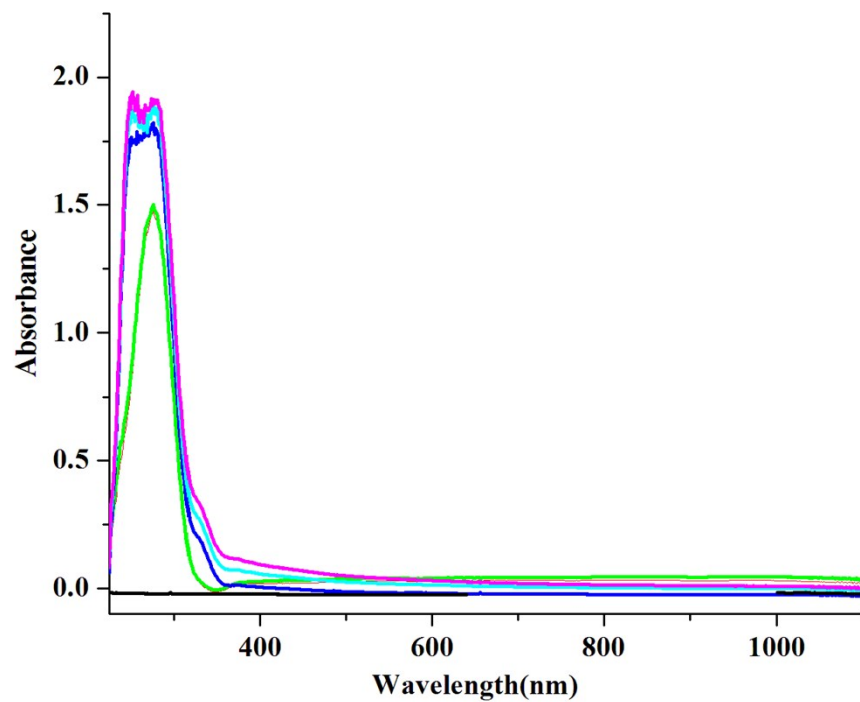


Figure S27: UV-visible spectra of NO₂ purged in THF at -80 °C at various time after purging.

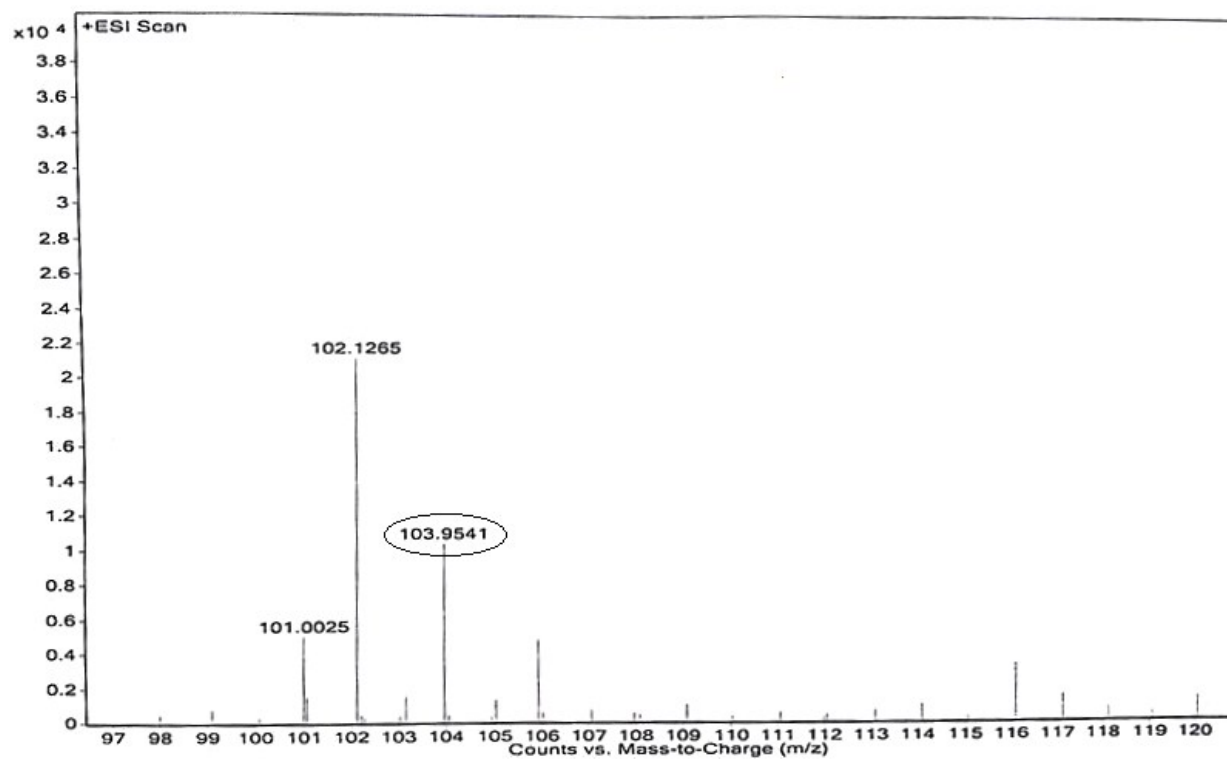


Figure S28: ESI-Mass of $(\text{CH}_3)_3\text{NO}_2$ from the reaction of complex **1** with NO_2 .

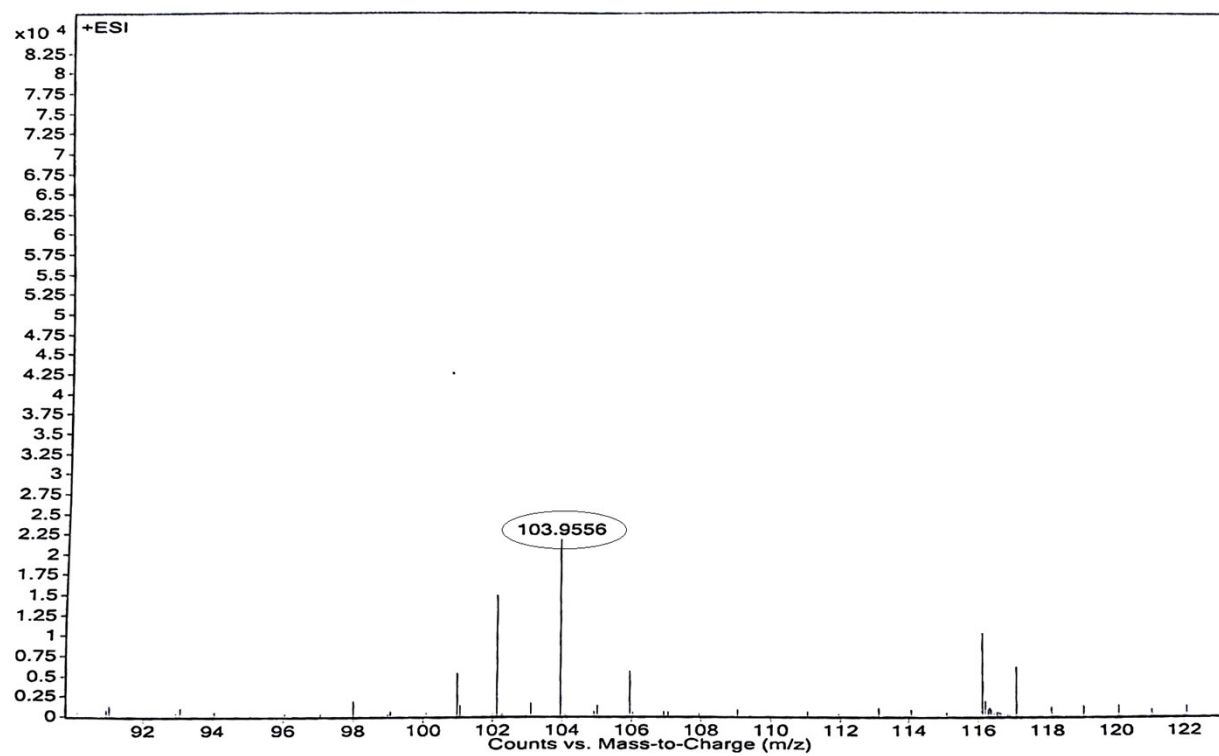


Figure S29: ESI-Mass of $(\text{CH}_3)_3\text{NO}_2$ from the reaction of complex **2** with NO_2 .