Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information

for

Phenol ring nitration induced by unprecedented reduction of copper(II) centre by nitrogen dioxide

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Experimental

Materials and methods

All reagents and solvents of reagent grade were purchased from commercial sources and used as received except specified. Acetonitrile was distilled from calcium hydride. Deoxygenation of the solvent and solutions was effected by repeated vacuum/purge cycles or bubbling with nitrogen for 30 minutes. NO_2 gas was prepared by the reaction of purified NO with O_2 in a flask fitted with a rubber septum. UV-visible spectra were recorded on a Perkin Elmer Lambda 25 UV-visible spectrophotometer. FT-IR spectra of the solid samples were taken on a Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Solution electrical conductivity was measured using a Systronic 305 conductivity bridge. ^{1}H-NMR spectra were recorded in a 400 MHz Varian FT spectrometer. Chemical shifts (ppm) were referenced either with an internal standard (Me_4Si) or to the residual solvent peaks. The X-band Electron Paramagnetic Resonance (EPR) spectra were recorded on a JES-FA200 ESR spectrometer, at room temperature and 77 K with microwave power, 0.998 mW; microwave frequency, 9.14 GHz and modulation amplitude, 2. Elemental analyses were obtained from a Perkin Elmer Series II Analyzer. The magnetic moment of complexes was measured on a Cambridge Magnetic Balance.

Single crystals were grown by slow diffusion followed by slow evaporation technique. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoK_α radiation (λ = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software. Structures were solved by direct methods using SHELXS-97 and refined with

full-matrix least squares on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Structural illustrations have been drawn with ORTEP-3 for Windows.

Synthesis

Ligand L_1:

N,N-dimethylethylenediamine (880 mg, 0.1 mol) was added in 20 ml of distilled acetone. The mixture was refluxed for 2 h to give corresponding Schiff's base and excess acetone was completely removed under vacuum. Then the imine was dissolved in 50 ml of methanol and was reduced by slow addition of 2.1 equivalent of $NaBH_4$. After removal of methanol under reduced pressure, the crude product was dissolved in water and neutralized with dilute acetic acid. N^1-isopropyl-N^2,N^2-dimethylethane-1,2-diamine was extracted from the aqueous solution by dichloromethane (4 × 50 ml portions). Yield: 780 mg (60%).

N^1-isopropyl-N^2,N^2-dimethylethane-1,2-diamine (1.30 g, 10 mmol), 2,4-di*tert*-butylphenol (2.06 g, 10 mmol) and formalin (2.11 g of 37% solution, 26 mmol) were taken in 10 ml of methanol and the reaction mixture was refluxed for 24 h . Methanol was removed by using rotary evaporator and 100 ml of water was added to the crude mass. Extraction by dichloromethane (3 × 50 ml portions), followed by column chromatographic purification affords the ligand **L_1.** Yield: 1.92 g (55%). Elemental analyses: calcd.(%): C, 62.13; H, 11.57; N, 8.04 ; found(%): C, 62.19; H, 11.56; N, 8.11. FT-IR (in KBr): 2964, 1481, 1460, 1241, 1165 cm^{-1}. ^{1}H-NMR: (400 MHz, $CDCl_3$): δ_{ppm}: 7.174-7.168 (1H, d), 6.808-6.802 (1H, d), 3.756 (2H, s), 3.080-3.014 (1H, m), 2.565-2.528(2H, t), 2.437-2.400(2H, t), 2.166(6H, s), 1.396(9H, s), 1.258(9H, s), 1.061-1.044(6H, d). ^{13}C-NMR: (75 MHz, $CDCl_3$) $\delta_{ppm:}$ 154.57, 140.05, 135.34, 123.41, 122.47, 121.48,

58.29, 54.77, 49.67, 46.41, 45.66, 34.83, 34.05, 31.76, 29.61, 17.22. Mass $(M+H^+)/z$: calcd: 349.31; found: 349.36.

Ligand L_2:

N,N-dimethylethylenediamine (2.19 g, 24.9 mmol), 2,4-di*tert*-butylphenol (8.19 g, 49.9 mmol) and formalin (8.42 g of 37% solution, 104 mmol) were taken in 50 mol of methanol and the mixture was refluxed for 24 h during which a white precipitate was formed. The precipitate was isolated by filtration and washed with cold methanol to obtain the ligand **L_2** as a white powder. It was recrystallized from methanol to obtain pure **L_2**. Yield: 7.8 g (60%). Elemental analyses: calcd.(%): C, 77.81; H, 10.76; N, 5.34; found (%): C, 77.88; H, 10.77; N, 5.43. FT-IR (in KBr): 2959, 1481, 1465, 1361, 1218 cm^{-1}. ^{1}H-NMR: (400 MHz, $CDCl_3$): δ_{ppm}: 9.803(2H, broad s), 7.219-7.208 (2H, d), 6.899-6.888 (2H, d), 3.641-3.628 (4H, d), 2.595-2.577 (4H, m), 2.307 (6H, s), 1.384 (18H, s), 1.266 (18H, s). ^{13}C-NMR: (100 MHz, $CDCl_3$) $\delta_{ppm:}$ 153.50, 140.40, 136.32, 125.03, 123.55, 121.86, 56.81, 56.17, 49.28, 45.07, 35.23, 34.29, 31.94, 29.79. Mass $(M+H^+)/z$: calcd: 525.43; found: 525.25.

Complex 1:

To a stirred solution of $Cu(OAc)_2 \cdot H_2O$ (0.398 g, 2 mmol) in 15 ml methanol was added a solution of ligand **L_1** (0.696 g, 2 mmol) in 10 ml methanol. The reaction mixture was refluxed for 8 h after which it was filtered and the filtrate was reduced under vacuum to obtain the metal complex **1** as a dark brown solid. Yield: 0.90 g (80%) and UV-vis. (methanol): λ_{max}, 673 nm. FT-IR (KBr pellet): 2952, 1580, 1470, 1311, 677 cm^{-1}. The complex **1** behaves as 1:1 electrolyte in methanol solution [Λ_M ($S\,cm^{-1}$), 154]. The observed magnetic moment is found to be 1.60 BM.

Complex 2:

To a stirred solution of $Cu(OAc)_2 \cdot H_2O$ (0.398 g, 2 mmol) in 15 ml methanol was added a solution of ligand **L_2** (1.048 g, 2 mmol) in 10 ml methanol. The reaction mixture was refluxed for 8 h; then the solvent was removed under reduced pressure to obtain a dark solid. The residue was washed with 30 ml CH_3CN to obtain the metal complex **2** as a dark brown solid. Yield: 0.97 g (75%) and UV-vis. (methanol): λ_{max}, 702 nm. FT-IR (KBr pellet): 2952, 1571, 1411, 1240, 1019 cm^{-1}. The complex **2** behaves as 1:1 electrolyte in methanol solution [Λ_M (S cm^{-1}), 146]. The observed magnetic moment is found to be 1.52 BM.

Isolation of modified ligand L_1':

To 30 ml of methanol solution of complex **1** (470 mg), freshly prepared nitrogen dioxide was bubbled for 1 minute. The red color of the solution turned colorless. This solution was allowed to stir for 10 minutes at room temperature. Then the solvent was removed under vacuum using rotavapour. Then equivalent amount of aqueous solution of Na_2S was added to the solution remove copper ion as its sulphide. The precipitate was filtered off and from the filtrate, the modified ligand **L_1'** was extracted with dichloromethane (4 × 50 ml portions). Yield: 235 mg (~70%). Elemental analyses: calcd.(%) C, 64.07; H, 9.26; N, 12.45; found(%): C, 64.11; H, 9.25; N, 12.56. FT-IR (in KBr): 2964, 1589, 1466, 1333, 1167 cm^{-1}. ^{1}H-NMR: (400 MHz, $CDCl_3$): δ_{ppm}: 8.092-8.086 (1H, d), 7.797-7.790 (1H, d), 3.789 (2H, s), 3.034-2.968 (1H, m), 2.590-2.556(2H, t), 2.484-2.450(2H, t), 2.206(6H, s), 1.393(9H, s), 1.061-1.044(6H, d). ^{13}C-NMR: (75 MHz, $CDCl_3$) $\delta_{ppm:}$ 164.54, 138.64, 137.42, 123.01, 122.44, 122.36, 57.14, 53.35, 53.17, 49.70, 45.47, 45.16, 34.89, 28.91, 16.97. Mass $(M+H^+)$/z: calcd: 338.23, found: 338.28.

Isolation of modified ligand L_2':

To 30 ml of methanol solution of complex **2** (645 mg), freshly prepared nitrogen dioxide was bubbled for 1 minute. The red color of the solution turned colorless. This solution was allowed to stir for 10 minutes at room temperature. Then the solvent was removed under vacuum using rotary evaporator. Then equivalent amount of aqueous solution of Na_2S was added to remove the copper ion as its sulphide precipitate. The precipitate was filtered off and from the filtrate, modified ligand $\mathbf{L_2'}$ was extracted with dichloromethane (4 × 50 ml portions). Yield: 175 mg (35%). Elemental analyses: calcd. (%) C, 62.13; H, 7.62; N, 11.15; found(%): C, 62.08; H, 7.62; N, 11.22. FT-IR (in KBr): 2952, 1571, 1465, 1411, 1240 cm^{-1}. ^{1}H-NMR: (400 MHz, $CDCl_3$); δ_{ppm}: 8.132-8.126 (2H, d), 7.887-7.881 (2H, d), 3.691 (4H, s), 2.675 (4H, s), 2.364(6H, s), 1.365(18H, s). ^{13}C-NMR: (75 MHz, $CDCl_3$); $\delta_{ppm:}$ 164.80, 138.90, 137.68, 123.27, 122.70, 122.62, 57.40, 53.61, 49.96, 35.15, 29.17, 16.98. Mass $(M+H^+)/z$: calcd: 503.28; found: 503.09.

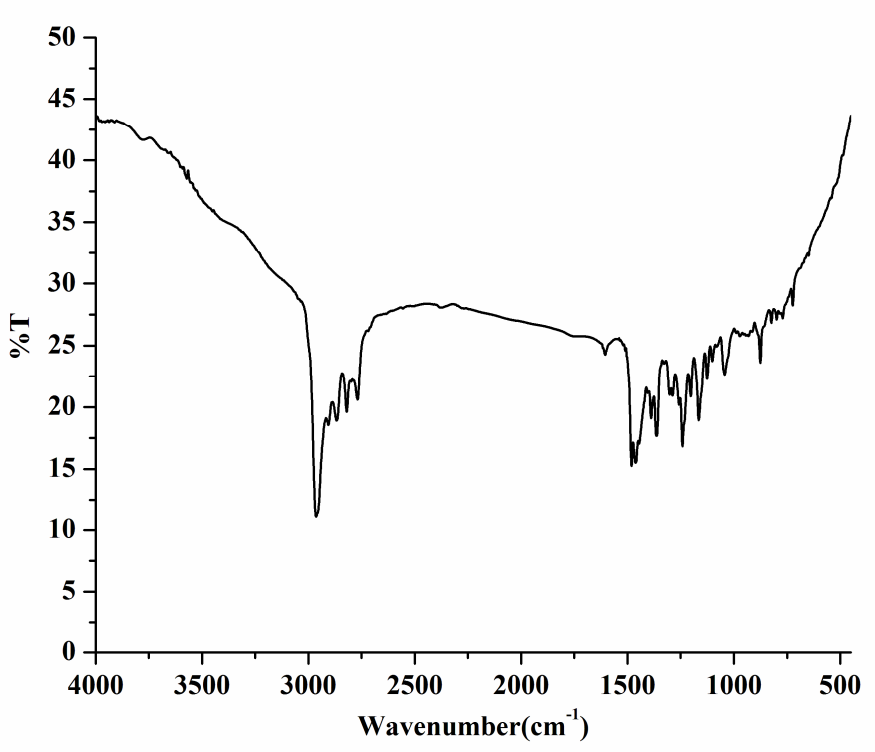

Figure S1: FT-IR spectrum of ligand $\mathbf{L_1}$ in KBr pellet.

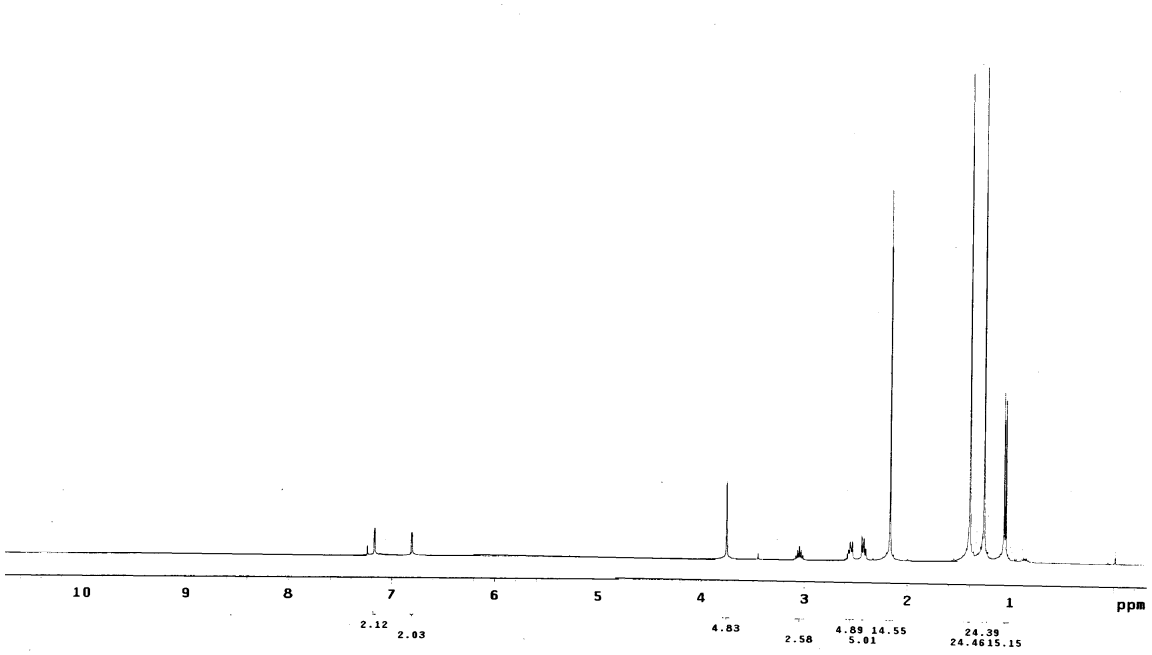

Figure S2: ^{1}H-NMR spectrum of ligand $\mathbf{L_1}$ in $CDCl_3$.

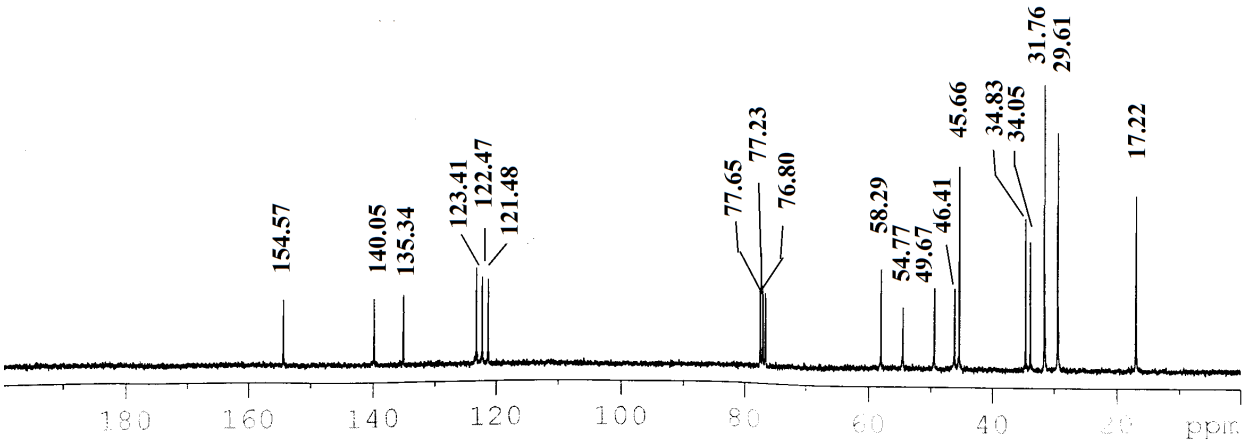

Figure S3: ^{13}C-NMR spectrum of ligand $\mathbf{L_1}$ in $CDCl_3$.

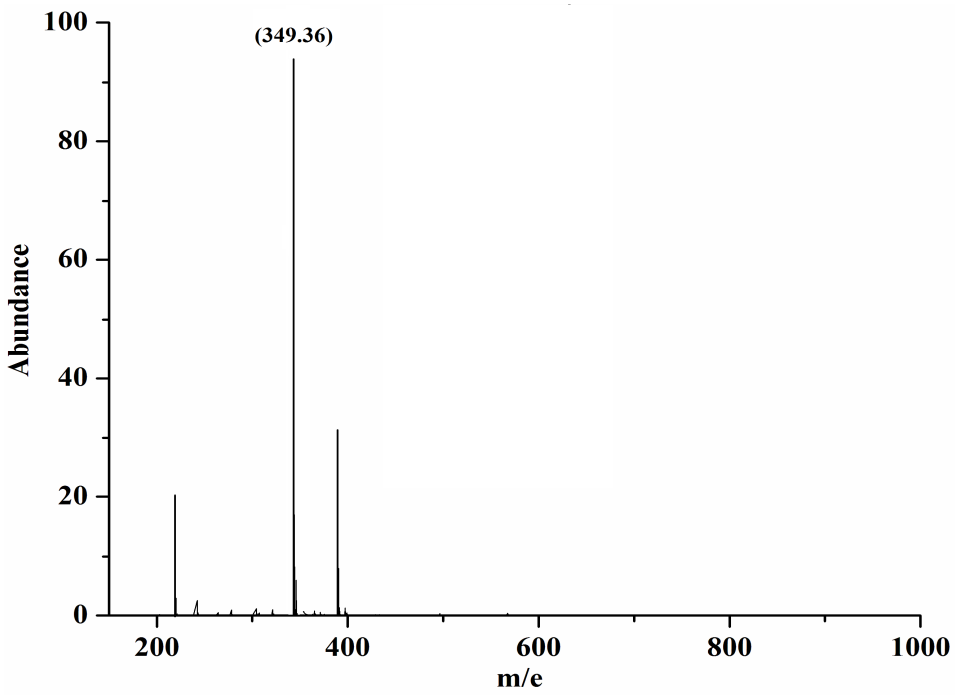

Figure S4: ESI- Mass spectrum of ligand $\mathbf{L_1}$ in methanol.

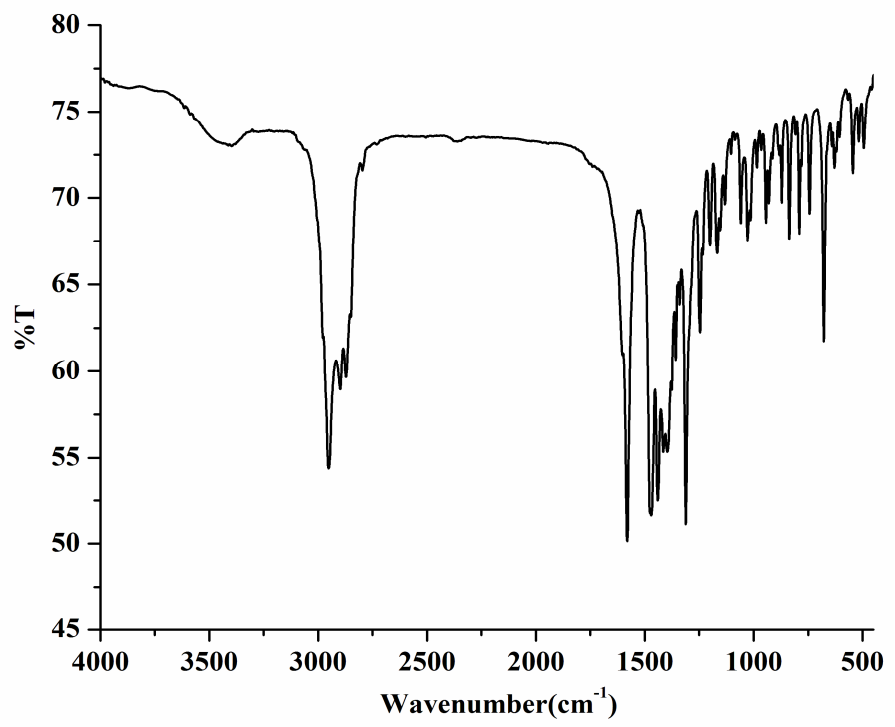

Figure S5: FT-IR spectrum of complex **1** in KBr pellet.

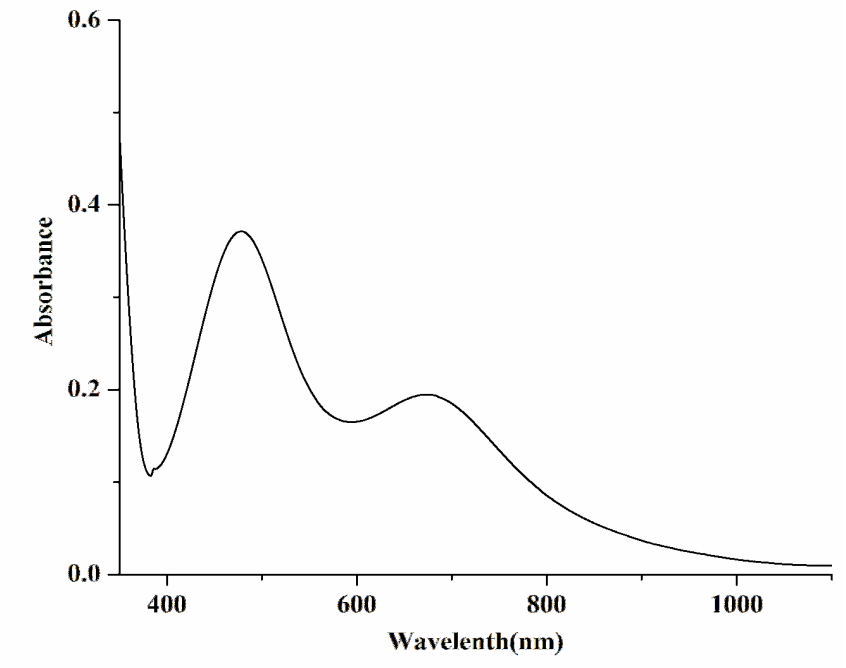

Figure S6: UV-visible spectrum of complex **1** in methanol.

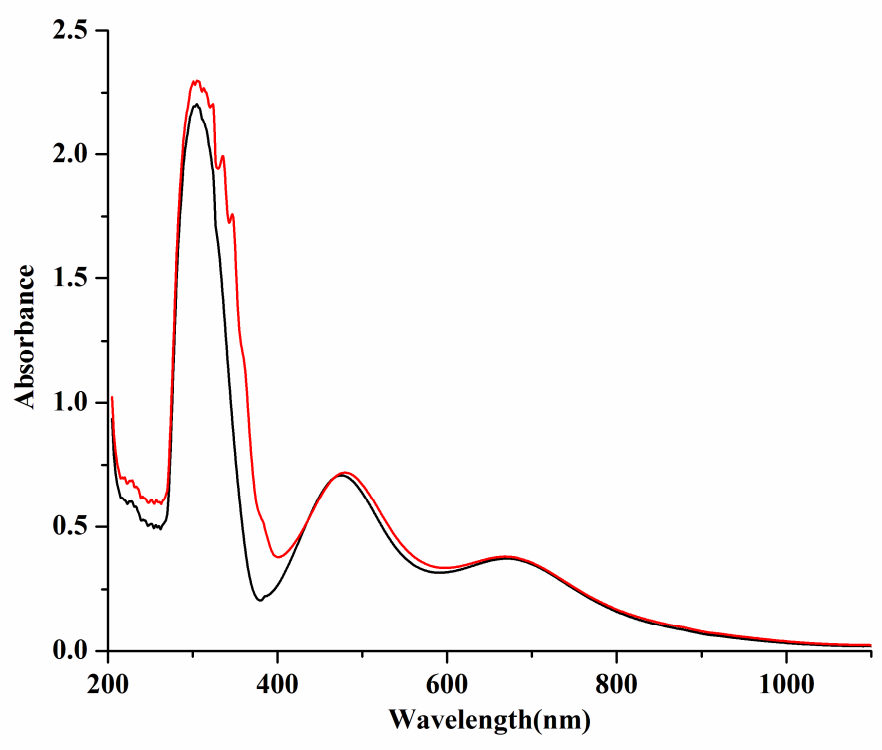

Figure S6: UV-visible spectra of complex **1** before (black trace) and after purging of excess nitric oxide treatment (red trace) in methanol.

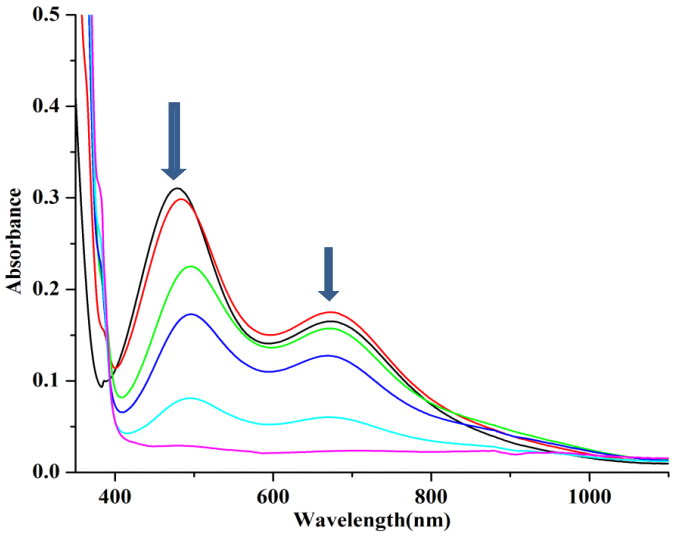

Figure S7: UV-visible spectra of complex **1** before (black trace) and at different times after nitric oxide in presence of air treatment in methanol.

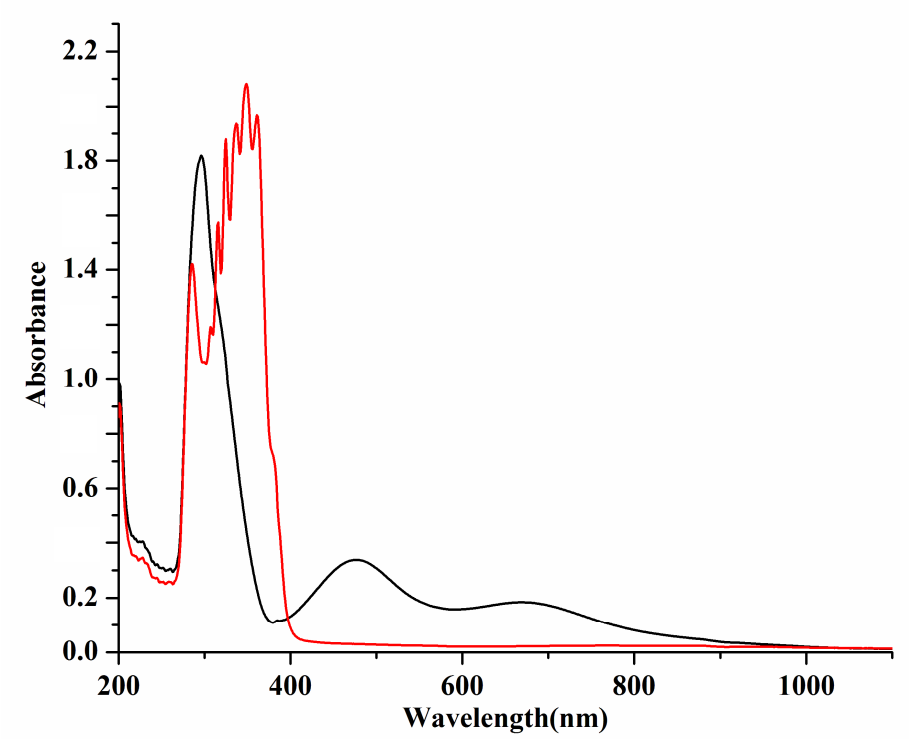

Figure S8: UV-visible spectra of complex **1** before (black trace) and after purging nitrogen dioxide (red trace) in methanol.

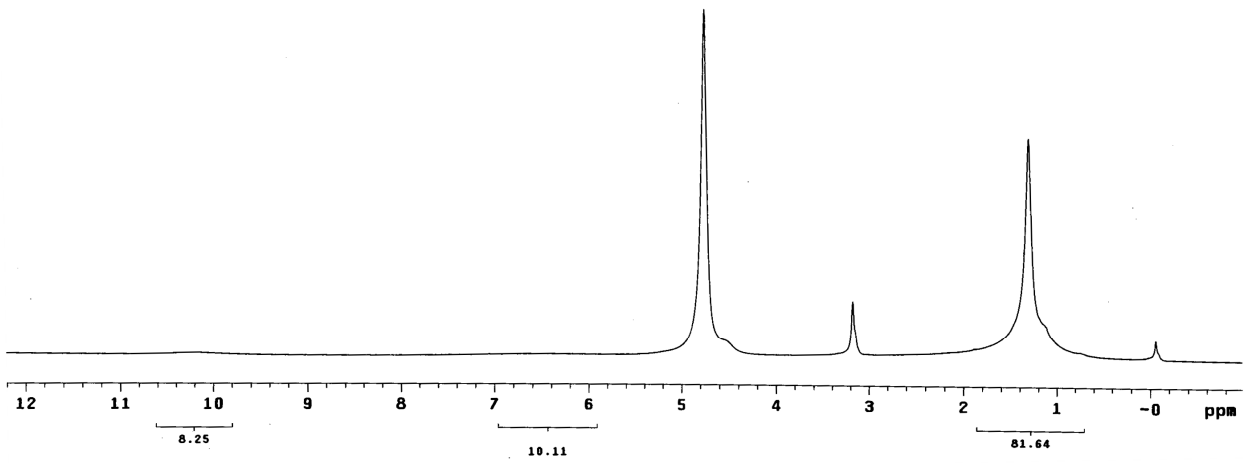

Figure S9: ^{1}H-NMR spectrum of complex **1** in CD_3OD.

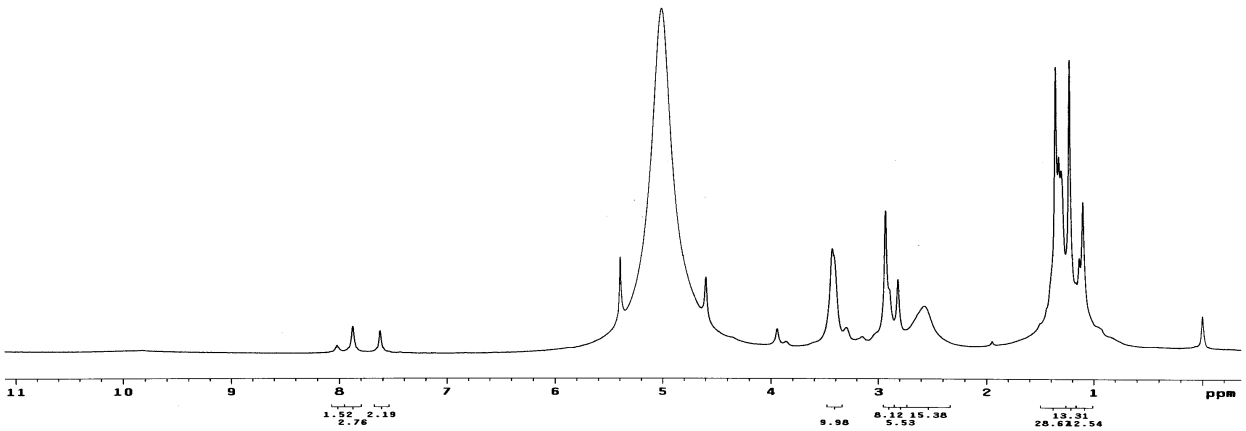

Figure S10: ^{1}H-NMR spectrum of complex **1** after purging nitrogen dioxide in CD_3OD.

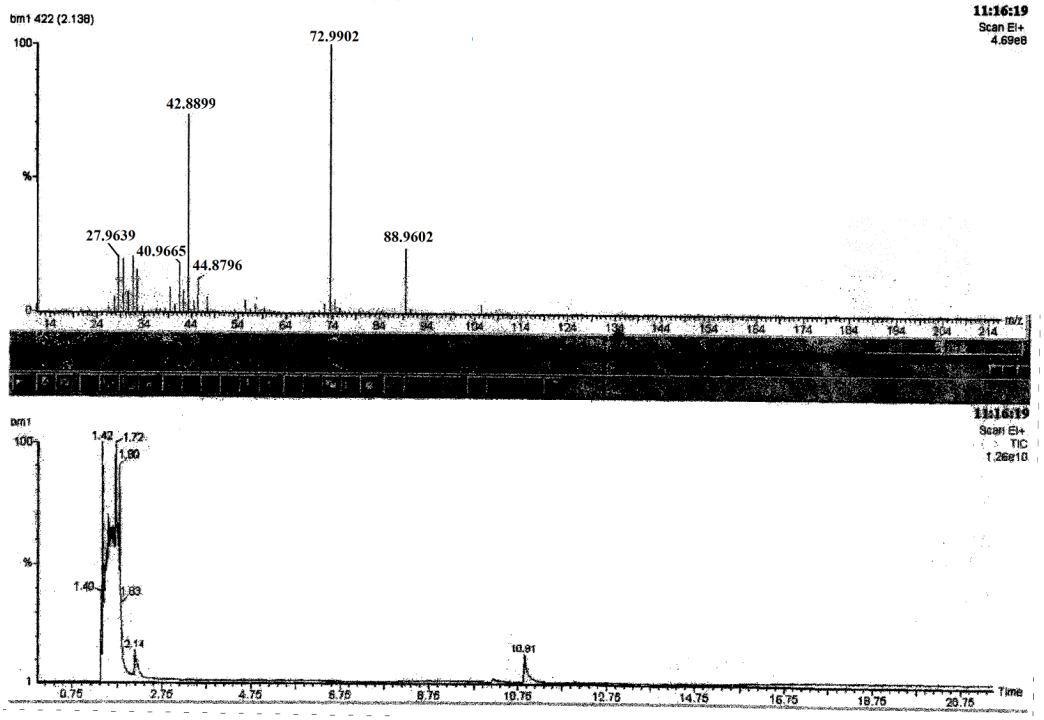

Figure S11: GC**-** Mass spectrum of the reaction mixture after the reaction of complex **1** with nitrogen dioxide in methanol.

Table S1: Crystallographic data for complex **1**.

	Complex **1**
Formulae	C_{24} H_{42} Cu N_2 O_3
Mol. wt.	470.15
Crystal system	monoclinic
Space group	P 21/n
Temperature /K	293(2)
Wavelength /Å	0.71073
a /Å	10.1575(3)
b /Å	24.1596(8)
c /Å	11.0644(3)
α/°	90.00
β/°	103.211(3)
γ/°	90.00
V/ Å^3	2643.36(14)
Z	4
Density/Mgm^{-3}	1.181
Abs. co-eff. /mm^{-1}	0.850
Abs. correction	none
F(000)	1265
Total no. of reflections	4650
Reflections, $I > 2\sigma(I)$	3374
Max. 2θ/°	25
Ranges (h, k, l)	-12≤h ≤11 -28≤ k ≤16 -8≤ l ≤ 13
Complete to 2θ (%)	99.8
Refinement method	Full-matrix least-squares on F^2
Goof (F^2)	0.955
R indices [$I > 2\sigma(I)$]	0.0460
R indices (all data)	0.0677

Table S2: Bond distances (Å) of complex 1.

Atoms	Distances (Å)	Atoms	Distances (Å)
Cu(1) - (O2)	1.973(2)	C(11) - C(10)	1.423(5)
Cu(1) - (O1)	1.863(2)	C(11) - C(12)	1.391(5)
Cu(1) - O(3)	2.565(2)	C(11) - C(15)	1.538(4)
Cu(1) - N(2)	2.045(2)	C(13) - C(12)	1.376(6)
Cu(1) - N(1)	2.046(3)	C(13) - C(14)	1.386(5)
O(2) - C(23)	1.264(4)	C(13) - C(19)	1.538(5)
O(1) - C(10)	1.327(4)	C(5) - C(6)	1.516(5)
O(3) - C(23)	1.228(5)	C(5) - C(7)	1.535(6)
N(2) - C(8)	1.502(4)	C(4) - C(3)	1.508(5)
N(2) - C(5)	1.502(4)	C(15) - C(18)	1.538(5)
N(2) - C(4)	1.482(4)	C(15) - C(17)	1.539(6)
N(1) - C(1)	1.477(5)	C(15) - C(16)	1.535(6)
N(1) - C(3)	1.477(4)	C(19) - C(22)	1.532(7)
N(1) - C(2)	1.490(5)	C(19) - C(20)	1.529(7)
C(9) - C(8)	1.501(4)	C(19) - C(21)	1.480(9)
C(9) - C(10)	1.413(4)	C(23) - C(24)	1.499(5)
C(9) - C(14)	1.388(5)		

Table S3: Bond angles (º) of complex 1.

Atoms	Angles (º)	Atoms	Angles (º)
O(2)-Cu(1)-O(1)	91.6(1)	C(12)-C(11)-C(15)	122.4(3)
O(2)-Cu(1)-O(3)	55.74(9)	N(2)-C(8)-C(9)	113.9(3)
O(2)-Cu(1)-N(2)	169.5(1)	O(1)-C(10)-C(9)	121.3(3)
O(2)-Cu(1)-N(1)	90.2(1)	O(1)-C(10)-C(11)	120.2(3)
O(1)-Cu(1)-O(3)	89.84(9)	C(9)-C(10)-C(11)	118.5(3)
O(1)-Cu(1)-N(2)	94.90(9)	C(12)-C(13)-C(14)	116.8(3)
O(1)-Cu(1)-N(1)	156.8(1)	C(12)-C(13)-C(19)	122.4(3)
O(3)-Cu(1)-N(2)	115.92(9)	C(14)-C(13)-C(19)	120.6(3)
O(3)-Cu(1)-N(1)	110.1(1)	C(11)-C(12)-C(13)	124.6(3)
N(2)-Cu(1)-N(1)	87.0(1)	N(2)-C(5)-C(6)	111.9(3)
Cu(1)-O(2)-C(23)	104.3(2)	N(2)-C(5)-C(7)	113.3(3)
Cu(1)-O(1)-C(10)	128.6(2)	C(6)-C(5)-C(7)	110.8(3)
Cu(1)-O(3)-C(23)	77.4(2)	C(9)-C(14)-C(13)	122.1(3)
Cu(1)-N(2)-C(8)	102.2(2)	N(2)-C(4)-C(3)	110.6(3)
Cu(1)-N(2)-C(5)	114.7(2)	N(1)-C(3)-C(4)	110.3(3)
Cu(1)-N(2)-C(4)	106.7(2)	C(11)-C(15)-C(18)	110.6(3)
C(8)-N(2)-C(5)	111.4(2)	C(11)-C(15)-C(17)	110.5(3)
C(8)-N(2)-C(4)	109.3(2)	C(11)-C(15)-C(16)	111.8(3)
C(5)-N(2)-C(4)	112.0(2)	C(18)-C(15)-C(17)	109.1(3)
Cu(1)-N(1)-C(1)	111.5(2)	C(18)-C(15)-C(16)	107.1(3)
Cu(1)-N(1)-C(3)	103.8(2)	C(17)-C(15)-C(16)	107.7(3)
Cu(1)-N(1)-C(2)	110.8(2)	C(13)-C(19)-C(22)	112.1(4)
C(1)-N(1)-C(3)	112.5(3)	C(13)-C(19)-C(20)	111.3(4)
C(1)-N(1)-C(2)	109.1(3)	C(13)-C(19)-C(21)	110.1(4)
C(3)-N(1)-C(2)	108.9(3)	C(22)-C(19)-C(20)	104.8(4)
C(8)-C(9)-C(10)	120.3(3)	C(22)-C(19)-C(21)	107.9(4)
C(8)-C(9)-C(14)	119.4(3)	C(20)-C(19)-C(21)	110.5(5)
C(10)-C(9)-C(14)	120.2(3)	O(2)-C(23)-O(3)	122.5(3)
C(10)-C(11)-C(12)	117.7(3)	O(2)-C(23)-C(24)	117.6(3)
C(10)-C(11)-C(15)	119.9(3)	O(3)-C(23)-C(24)	119.9(3)

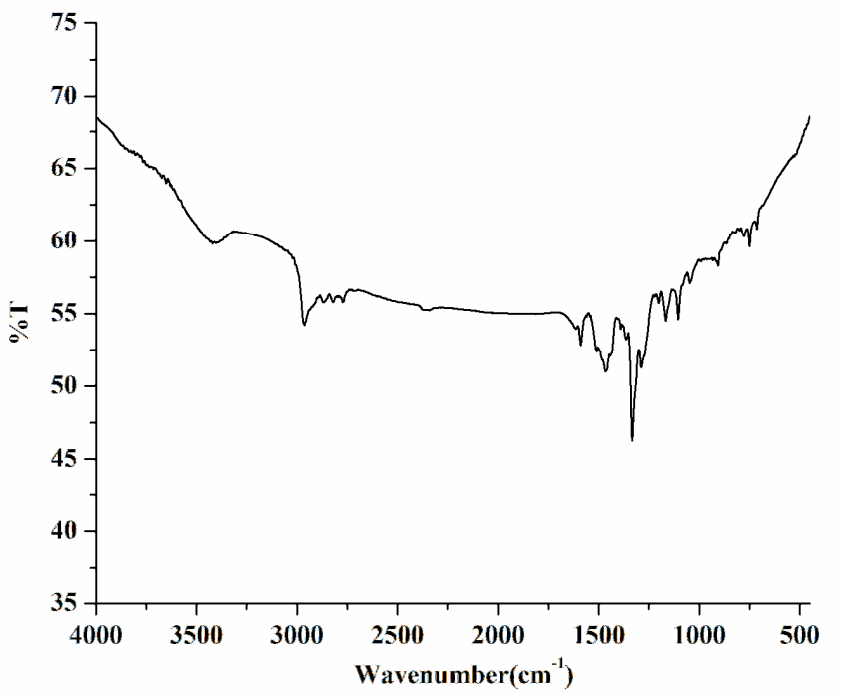

Figure S12: FT-IR spectrum of modified ligand $\mathbf{L_1}'$ in KBr pellet.

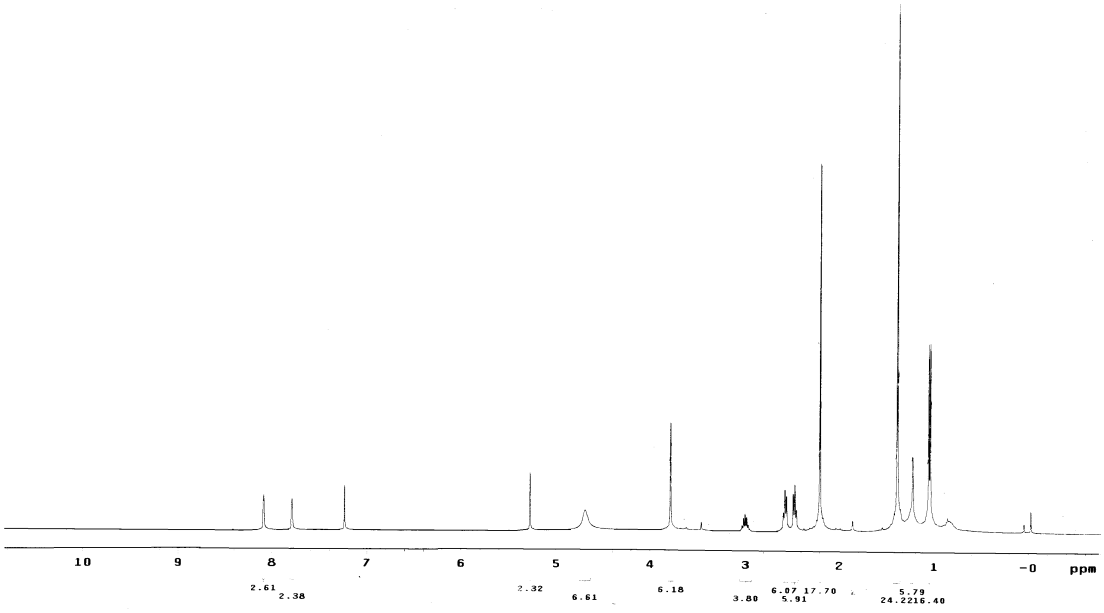

Figure S13: ^{1}H-NMR spectrum of modified ligand $\mathbf{L_1}'$ in $CDCl_3$.

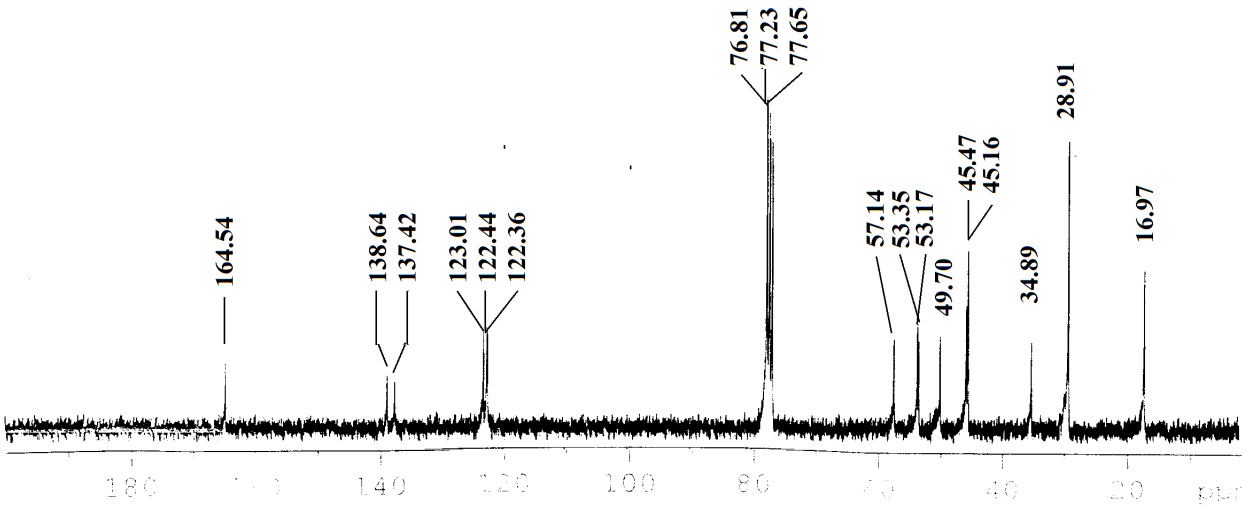

Figure S14: ^{13}C-NMR spectrum of modified ligand $\mathbf{L_1}'$ in $CDCl_3$.

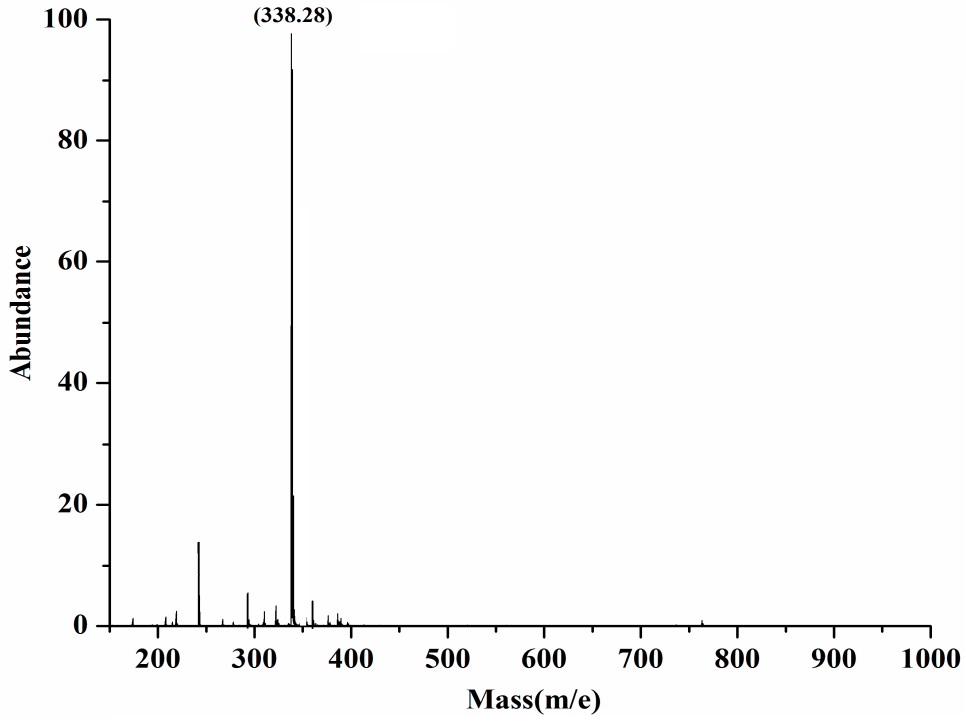

Figure S15: ESI- Mass spectrum of modified ligand $\mathbf{L_1}'$ in methanol.

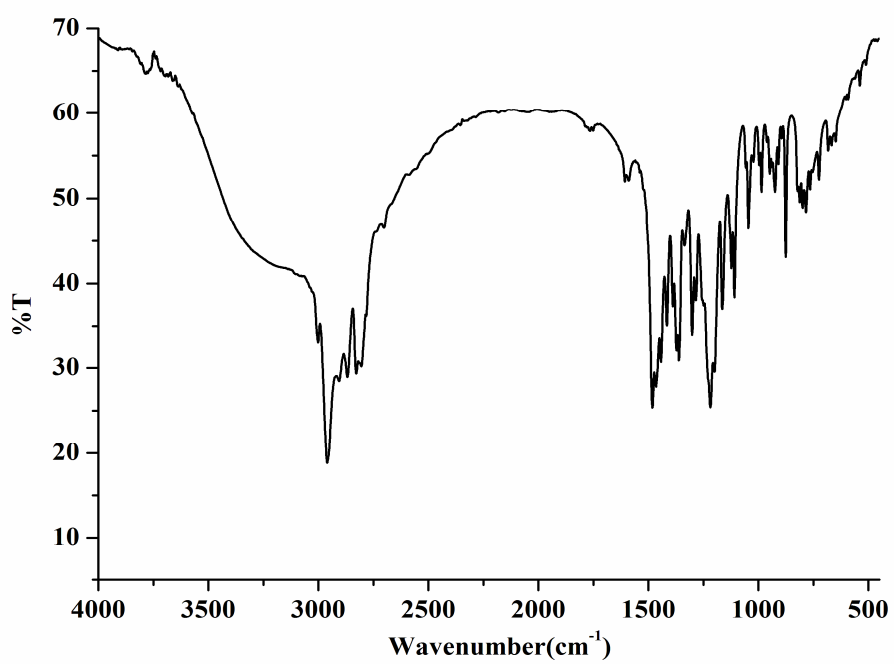

Figure S16: FT-IR spectrum of ligand $\mathbf{L_2}$ in KBr pellet.

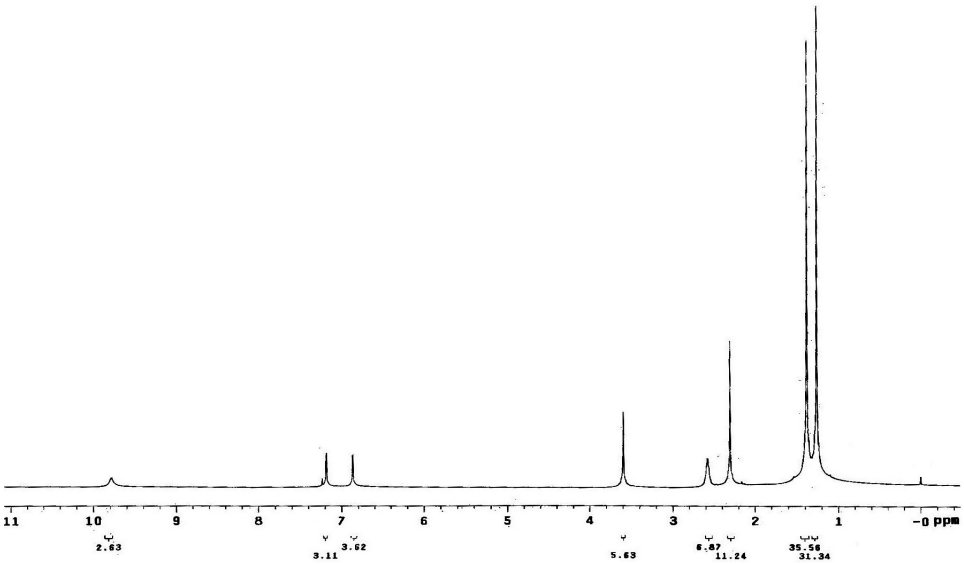

Figure S17: ^{1}H-NMR spectrum of ligand $\mathbf{L_2}$ in $CDCl_3$.

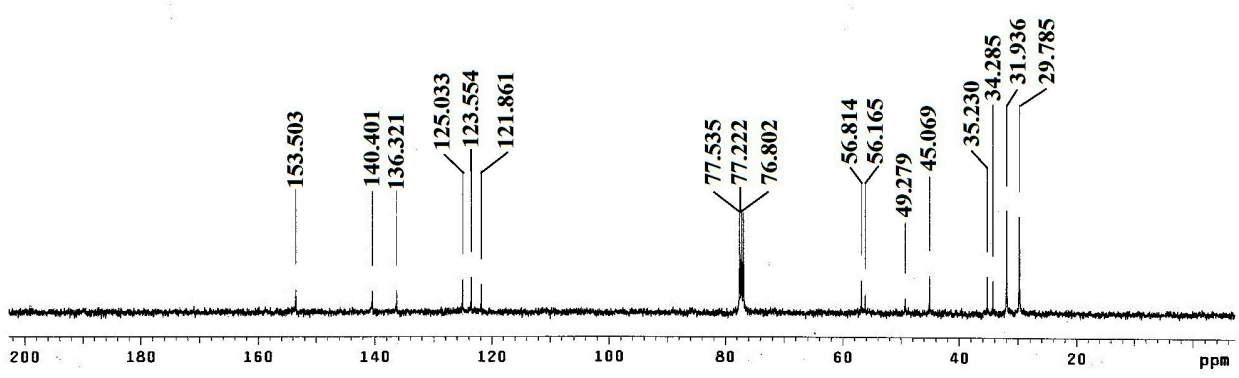

Figure S18: ^{13}C-NMR spectrum of ligand $\mathbf{L_2}$ in $CDCl_3$.

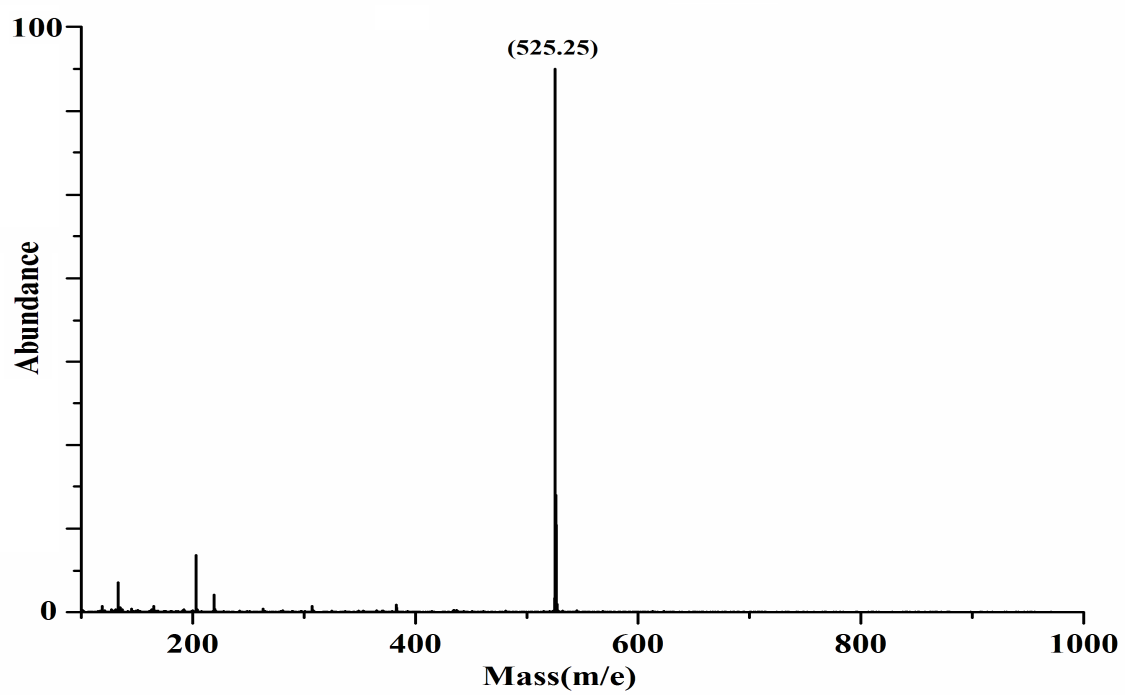

Figure S19: ESI- Mass spectrum of ligand $\mathbf{L_2}$ in methanol.

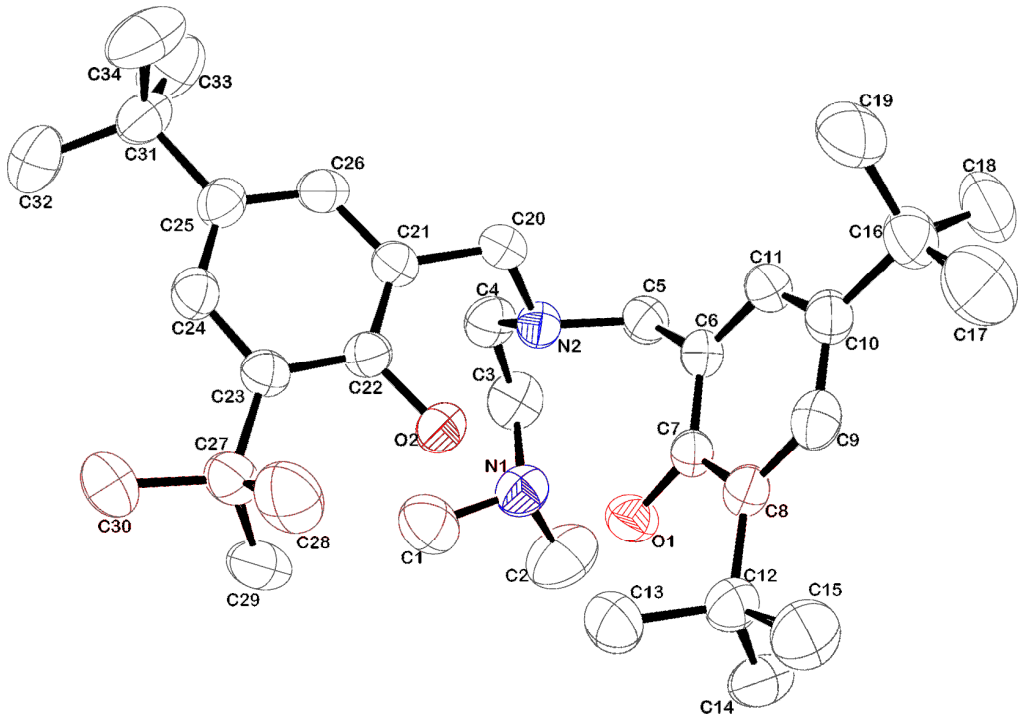

Figure S20: ORTEP diagram of ligand $\mathbf{L_2}$ (50% thermal ellipsoid plot, hydrogen atoms are omitted for clarity).

Table S4: Crystallographic data for ligand $\mathbf{L_2}$.

	$\mathbf{L_2}$
Formulae	$C_{34}\ H_{56}\ N_2\ O_2$
Mol. wt.	524.81
Crystal system	Monoclinic
Space group	P2(1)/c
Temperature /K	293(2)
Wavelength /Å	0.71073
a /Å	15.3347(6)
b /Å	10.3571(7)
c /Å	21.7602(10)
α/°	90.00
β/°	99.939(4)
γ/°	90.00
V/ $Å^3$	3404.2(3)
Z	4
Density/Mgm^{-3}	1.024
Abs. co-eff. /mm^{-1}	0.062
Abs. correction	none
F(000)	1160

Total no. of reflections	5990
Reflections, $I > 2\sigma(I)$	4127
Max. 2θ/°	25.00
Ranges (h, k, l)	-18≤h ≤18 -12≤ k ≤11 -25≤ l ≤ 25
Complete to 2θ (%)	99.8
Refinement method	Full-matrix least-squares on F^2
Goof (F^2)	1.059
R indices [$I > 2\sigma(I)$]	0.0600
R indices (all data)	0.0867

Table S5: Bond distances (Å) for L_2.

Atoms	Distances (Å)	Atoms	Distances (Å)
N(2) - C(20)	1.467(2)	C(25) - C(31)	1.541(3)
N(2) - C(5)	1.481(2)	C(6) - C(11)	1.390(2)
N(1) - C(1)	1.466(3)	C(6) - C(5)	1.504(3)
N(2) - C(4)	1.458(3)	C(9) - C(10)	1.381(3)
N(1) - C(3)	1.463(3)	C(10) - C(11)	1.383(3)
N(1) - C(2)	1.462(3)	C(10) - C(16)	1.539(3)
O(1) - C(7)	1.373(2)	C(27) - C(30)	1.534(3)
O(2) - C(22)	1.366(2)	C(27) - C(28)	1.530(4)
C(26) - C(21)	1.386(3)	C(27) - C(29)	1.538(3)
C(26) - C(25)	1.390(3)	C(12) - C(13)	1.544(3)
C(23) - C(24)	1.393(3)	C(12) - C(14)	1.543(3)
C(23) - C(22)	1.405(3)	C(12) - C(15)	1.536(4)
C(23) - C(27)	1.541(3)	C(4) - C(3)	1.523(3)
C(8) - C(7)	1.401(3)	C(31) - C(33)	1.530(3)
C(8) - C(9)	1.400(2)	C(31) - C(32)	1.531(3)
C(8) - C(12)	1.538(3)	C(31) - C(34)	1.523(4)
C(21) - C(20)	1.512(2)	C(16) - C(19)	1.542(3)
C(21) - C(22)	1.394(3)	C(16) - C(18)	1.534(4)
C(7) - C(6)	1.397(2)	C(16) - C(17)	1.530(4)
C(24) - C(25)	1.386(3)		

Table S6: Bond angles (°) of L_2.

Atoms	Angles (°)	Atoms	Angles (°)
C(20)-N(2)-C(5)	111.0(1)	C(9)-C(10)-C(16)	123.0(2)
C(20)-N(2)-C(4)	111.1(1)	C(11)-C(10)-C(16)	120.1(2)
C(5)-N(2)-C(4)	112.4(1)	C(6)-C(11)-C(10)	121.9(2)
C(3)-N(1)-C(1)	111.0(2)	N(2)-C(5)-C(6)	111.6(2)
C(3)-N(1)-C(2)	110.1(2)	C(23)-C(27)-C(30)	111.8(2)
C(1)-N(1)-C(2)	109.7(2)	C(23)-C(27)-C(28)	109.8(2)
C(21)-C(26)-C(25)	121.5(2)	C(23)-C(27)-C(29)	109.9(2)
C(24)-C(23)-C(22)	116.2(2)	C(30)-C(27)-C(28)	108.1(2)
C(24)-C(23)-C(27)	122.5(2)	C(30)-C(27)-C(29)	106.9(2)
C(22)-C(23)-C(27)	121.2(2)	C(28)-C(27)-C(29)	110.2(2)
C(7)-C(8)-C(9)	116.8(2)	C(8)-C(12)-C(13)	109.4(2)
C(7-C(8)-C(12)	121.8(2)	C(8)-C(12)-C(14)	110.9(2)
C(9)-C(8)-C(12)	121.4(2)	C(8)-C(12)-C(15)	112.0(2)
C(26)-C(21)-C(20)	121.0(2)	C(13)-C(12)-C(14)	109.6(2)
C(26)-C(21)-(C22)	119.5(2)	C(13)-C(12)-C(15)	107.7(2)
C(20)-C(21)-C(22)	119.4(2)	C(14)-C(12)-C(15)	107.1(2)
N(2)-C(20)-C(21)	112.2(1)	N(2)-C(4)-C(3)	114.0(2)
O(1)-C(7)-C(8)	117.9(2)	C(25)-C(31)-C(33)	107.9(2)
O(1)-C(7)-C(6)	121.6(2)	C(25)-C(31)-C(32)	111.7(2)
C(8)-C(7)-C(6)	120.5(2)	C(25)-C(31)-C(34)	111.0(2)
C(23)-C(24)-C(25)	124.4(2)	C(33)-C(31)-C(32)	109.7(2)
C(26)-C(25)-C(24)	117.0(2)	C(33)-C(31)-C(34)	109.3(2)
C(26)-C(25)-C(31)	120.6(2)	C(32)-C(31)-C(34)	107.2(2)
C(24)-C(25)-C(31)	122.3(2)	N(1)-C(3)-C(4)	112.3(2)
C(7)-C(6)-C(11)	119.6(2)	C(10)-C(16)-C(19)	109.6(2)
C(7)-C(6)-C(5)	120.0(2)	C(10)-C(16)-C(18)	108.9(2)
C(11)-C(6)-C(5)	120.4(2)	C(10)-C(16)-C(17)	112.3(2)
C(8)-C(9)-C(10)	124.2(2)	C(19)-C(16)-C(18)	108.9(2)
O(2)-C(22)-C(23)	118.8(2)	C(19)-C(16)-C(17)	108.6(2)
O(2)-C(22)-C(21)	119.8(2)	C(18)-C(16)-C(17)	108.5(2)
C(23)-C(22)-C(21)	121.3(2)	C(9)-C(10)-C(11)	116.9(2)

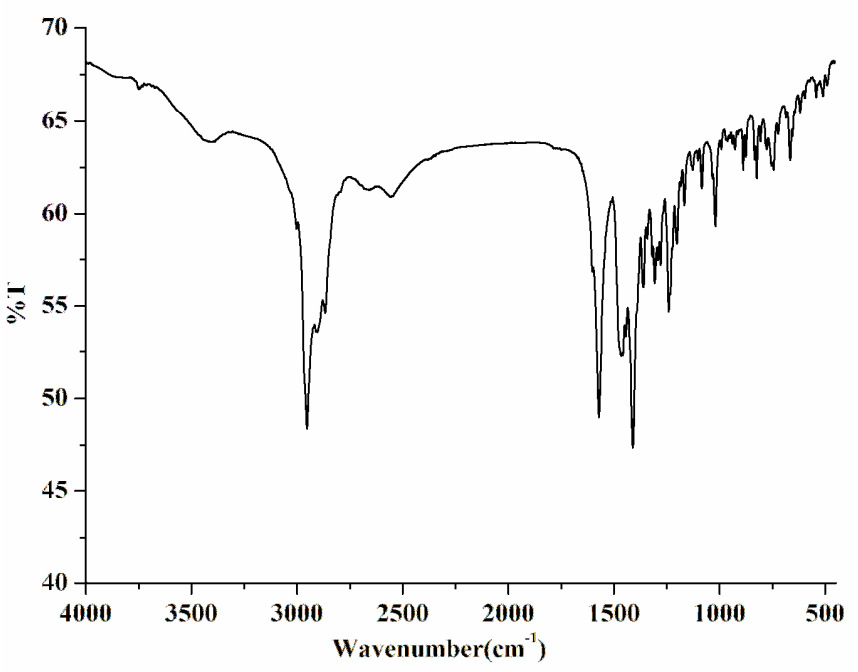

Figure S21: FT-IR spectrum of complex **2** in KBr pellet.

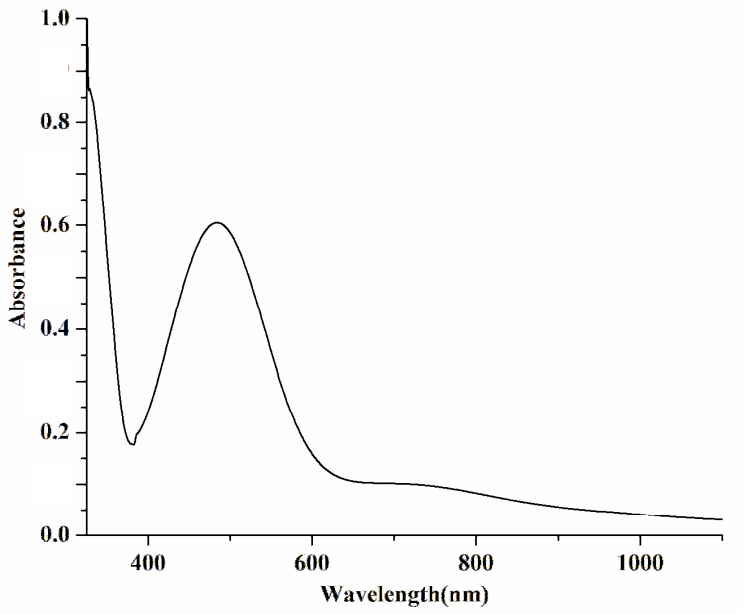

Figure S22: UV-visible spectrum of complex **2** in methanol.

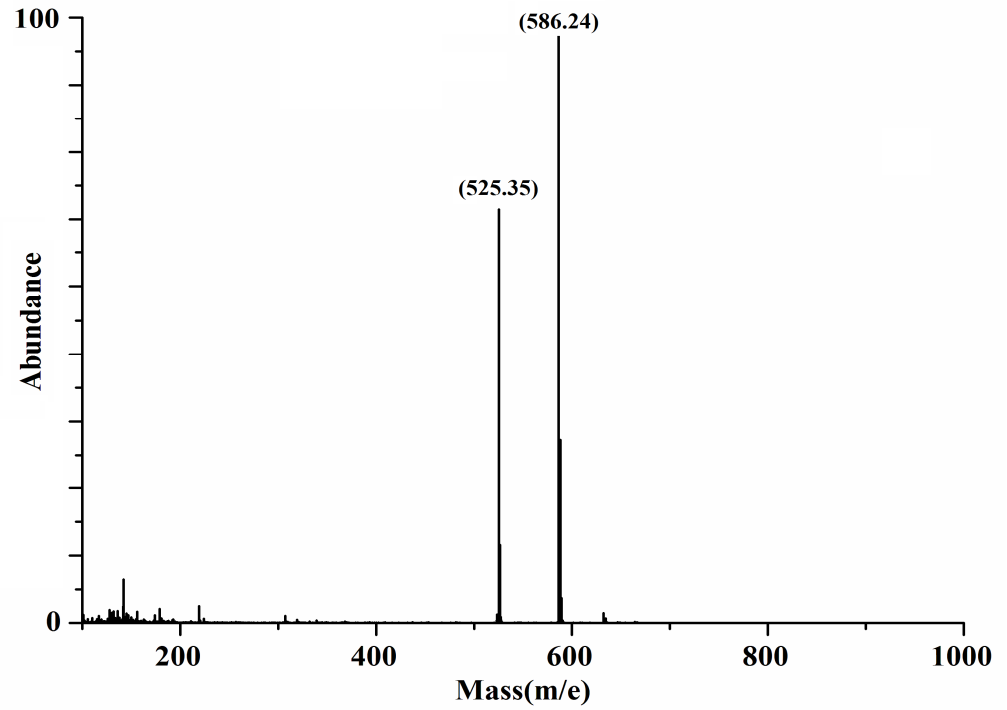

Figure S23: ESI- Mass spectrum of complex **2** in methanol.

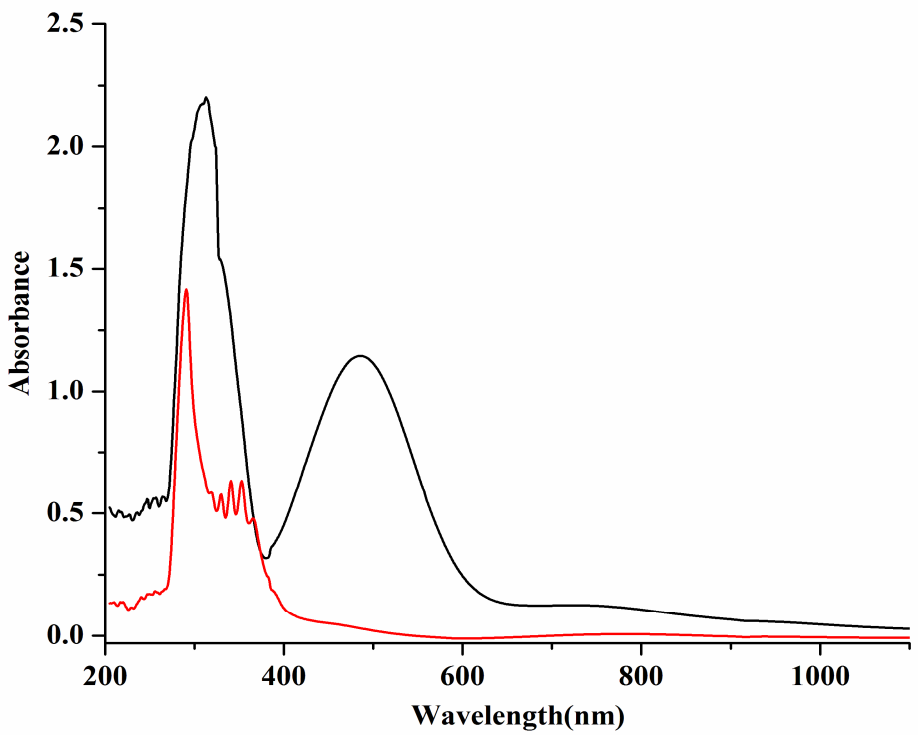

Figure 24: UV-visible spectra of complex **2** before (black trace) and after purging nitrogen dioxide (red trace) in methanol.

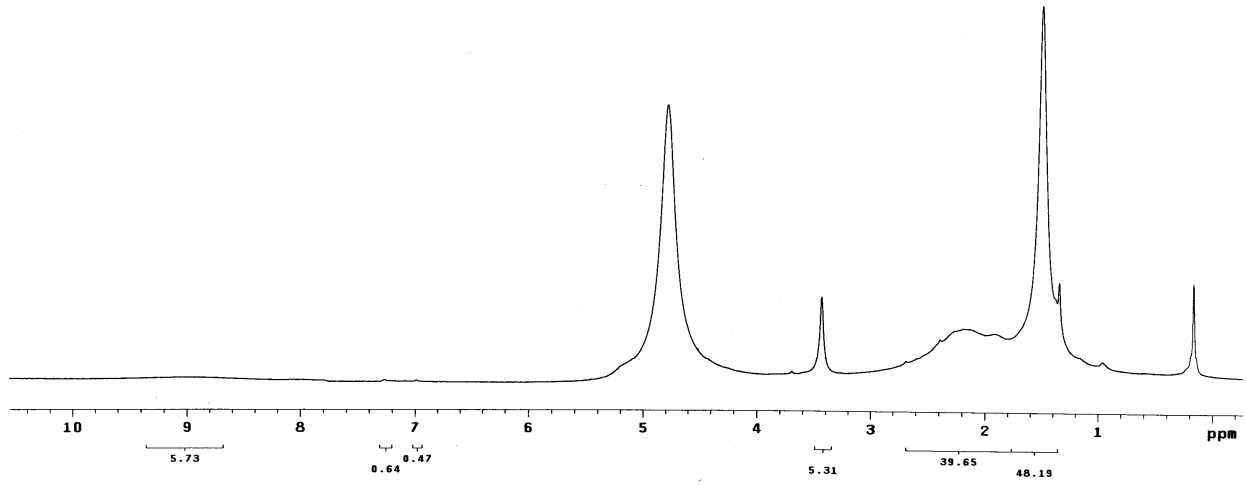

Figure S25: ^{1}H-NMR spectrum of complex **2** in CD_3OD.

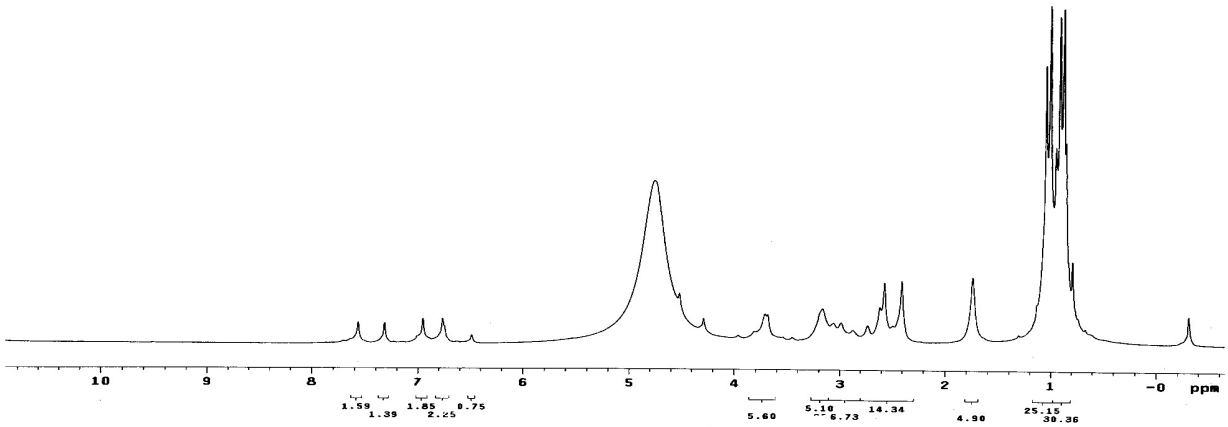

Figure S26: ^{1}H-NMR spectrum of complex **2** after purging nitrogen dioxide in CD_3OD.

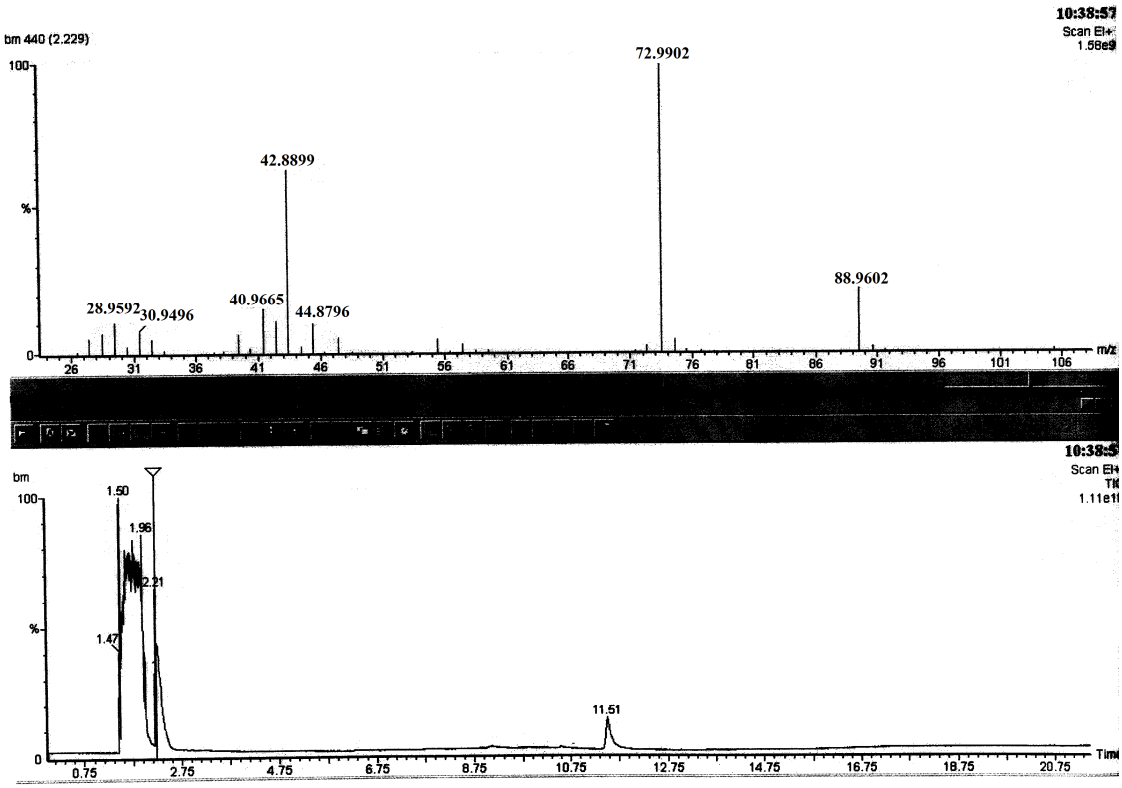

Figure S27: GC- mass spectrum of the reaction mixture after the reaction of complex **2** with nitrogen dioxide in methanol.

Table S7: Crystallographic data for complex **2**.

	Complex **2**
Formulae	$C_{36}\ H_{58}\ Cu_1\ N_2\ O_4$
Mol. wt.	646.38
Crystal system	Triclinic
Space group	P-1
Temperature /K	296(2)
Wavelength /Å	0.71073
a /Å	9.8751(13)
b /Å	13.671(2)
c /Å	14.078(2)
α/°	98.778(8)
β/°	104.531(8)
γ/°	96.777(8)
V/ Å^3	1793.8(4)
Z	2

Density/Mgm^{-3}	1.197
Abs. co-eff. /mm^{-1}	0.647
Abs. correction	None
F(000)	698
Total no. of reflections	6345
Reflections, $I > 2\sigma(I)$	4341
Max. 2θ/°	25.24
Ranges (h, k, l)	-11≤h ≤11 -16≤ k ≤14 -15≤ l ≤ 16
Complete to 2θ (%)	97.9
Refinement method	Full-matrix least-squares on F^2
Goof (F^2)	0.986
R indices [$I > 2\sigma(I)$]	0.0477
R indices (all data)	0.0671

Table S8: Bond distances (Å) of complex **2**.

	Distances (Å)		Distances (Å)
Cu(1) - O(1)	1.893(2)	C(10) - C(16)	1.544(5)
Cu(1) - O(2)	1.922(3)	C(12) - C(13)	1.536(5)
Cu(1) - N(1)	2.059(3)	C(12) - C(14)	1.526(5)
Cu(1) - N(2)	2.026(3)	C(12) - C(15)	1.530(5)
O(1) - C(7)	1.329(4)	C(16) - C(17)	1.483(8)
O(2) - C(20)	1.267(4)	C(16) - C(18)	1.479(7)
O(3) - C(20)	1.235(5)	C(16) - C(19)	1.472(9)
O(4) - C(24)	1.377(5)	C(20) - C(21)	1.510(7)
N(1) - C(1)	1.478(5)	C(22) - C(23)	1.510(3)
N(1) - C(2)	1.469(5)	C(23) - C(24)	1.399(4)
N(1) - C(3)	1.489(6)	C(23) - C(28)	1.389(4)
N(2) - C(4)	1.488(5)	C(24) - C(25)	1.405(5)
N(2) - C(5)	1.496(3)	C(25) - C(26)	1.382(6)
N(2) - C(22)	1.506(4)	C(25) - C(29)	1.544(5)
C(3) - C(4)	1.502(4)	C(26) - C(27)	1.411(5)
C(5) - C(6)	1.504(4)	C(27) - C(2)	1.377(4)
C(6) - C(7)	1.403(5)	C(27) - C(33)	1.532(6)
C(6) - C(11)	1.384(4)	C(29) - C(30)	1.531(6)
C(7) - C(8)	1.426(4)	C(29) - C(31)	1.527(6)
C(8) - C(9)	1.389(4)	C(29) - C(32)	1.537(6)
C(8) - C(12)	1.539(5)	C(33) - C(34)	1.534(6)
C(9) - C(10)	1.394(5)	C(33) - C(35)	1.519(6)
C(10) - C(11)	1.379(4)	C(33) - C(36)	1.530(5)

Table S9: Bond angles (°) of complex **2**.

Atoms	Angles (°)	Atoms	Angles (°)
O(1)-Cu(1)-O(2)	90.0(1)	C(13)-C(12)-C(14)	107.9(3)
O(1)-Cu(1)-N(1)	160.0(1)	C(13)-C(12)-C(15)	107.1(3)
O(1)-Cu(1)-N(2)	94.3(1)	C(14)-C(12)-C(15)	109.8(3)
O(2)-Cu(1)-N(1)	94.6(1)	C(10)-C(16)-C(17)	111.2(4)
O(2)-Cu(1)-N(2)	162.1(1)	C(10)-C(16)-C(18)	109.3(4)
N(1)-Cu(1)-N(2)	87.2(1)	C(10)-C(16)-C(19)	112.6(4)
Cu(1)-O(1)-C(7)	126.6(2)	C(17)-C(16)-C(18)	107.3(5)
Cu(1)-O(2)-C(20)	124.8(2)	C(17)-C(16)-C(19)	107.6(5)
Cu(1)-N(1)-C(1)	106.1(2)	C(18)-C(16)-C(19)	108.7(5)
Cu(1)-N(1)-C(2)	114.7(2)	O(2)-C(20)-O(3)	124.6(4)
Cu(1)-N(1)-C(3)	107.0(2)	O(2)-C(20)-C(21)	114.6(3)
C(1)-N(1)-C(2)	109.4(3)	O(3)-C(20)-C(21)	120.7(4)
C(1)-N(1)-C(3)	109.9(3)	N(2)-C(22)-C(23)	114.7(2)
C(2)-N(1)-C(3)	109.6(3)	C(22)-C(23)-C(24)	121.5(3)
Cu(1)-N(2)-C(4)	105.3(2)	C(22)-C(23)-C(28)	119.4(3)
Cu(1)-N(2)-C(5)	109.5(2)	C(24)-C(23)-C(28)	119.2(3)
Cu(1)-N(2)-C(22)	112.9(2)	O(4)-C(24)-C(23)	118.6(3)
C(4)-N(2)-C(5)	107.7(2)	O(4)-C(24)-C(25)	120.3(3)
C(4)-N(2)-C(22)	112.4(2)	C(23)-C(24)-C(25)	121.0(3)
C(5)-N(2)-C(22)	108.9(2)	C(24)-C(25)-C(26)	116.7(3)
N(1)-C(3)-C(4)	110.7(3)	C(24)-C(25)-C(29)	122.2(3)
N(2)-C(4)-C(3)	111.9(3)	C(26)-C(25)-C(29)	121.1(3)
N(2)-C(5)-C(6)	113.4(2)	C(25)-C(26)-C(27)	124.4(3)
C(5)-C(6)-C(7)	118.6(2)	C(26)-C(27)-C(28)	116.2(3)
C(5)-C(6)-C(11)	119.9(3)	C(26)-C(27)-C(33)	119.5(3)
C(7)-C(6)-C(11)	121.3(3)	C(28)-C(27)-C(33)	124.4(3)
O(1)-C(7)-C(6)	120.7(3)	C(23)-C(28)-C(27)	122.5(3)
O(1)-C(7)-C(8)	120.7(3)	C(25)-C(29)-C(30)	108.5(3)
C(6)-C(7)-C(8)	118.5(3)	C(25)-C(29)-C(31)	111.0(3)
C(7)-C(8)-C(9)	117.3(3)	C(25)-C(29)-C(32)	111.8(3)
C(7)-C(8)-C(12)	121.0(3)	C(30)-C(29)-C(31)	110.0(3)
C(9)-C(8)-C(12)	121.7(3)	C(30)-C(29)-C(32)	107.4(3)
C(8)-C(9)-C(10)	124.6(3)	C(31)-C(29)-C(32)	108.0(3)
C(9)-C10-C(11)	116.7(3)	C(27)-C(33)-C(34)	112.1(3)
C(9)-C(10)-C(16)	121.5(3)	C(27)-C(33)-C(35)	109.4(3)
C(11)-C(10)-C(16)	121.8(3)	C(27)-C(33)-C(36)	110.2(3)
C(6)-C(11)-C(10)	121.6(3)	C(34)-C(33)-C(35)	107.6(4)
C(8)-C(12)-C(13)	111.9(3)	C(34)-C(33)-C(36)	107.2(3)
C(8)-C(12)-C(14)	110.2(3)	C(35)-C(33)-C(36)	110.4(4)
C(8)-C(12)-C(15)	109.9(3)		

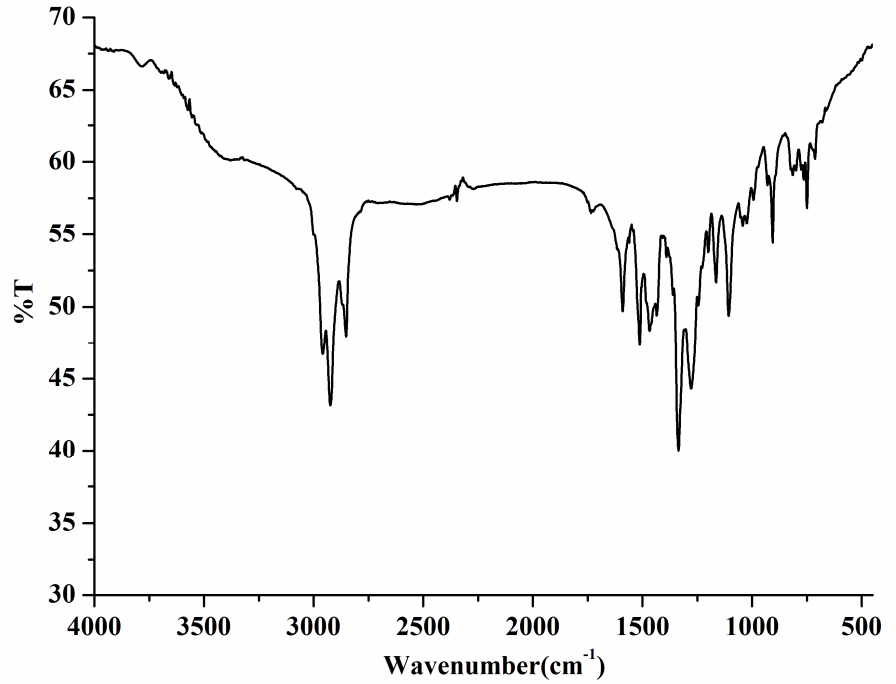

Figure S28: FT-IR spectrum of $\mathbf{L_2'}$ in KBr pellet.

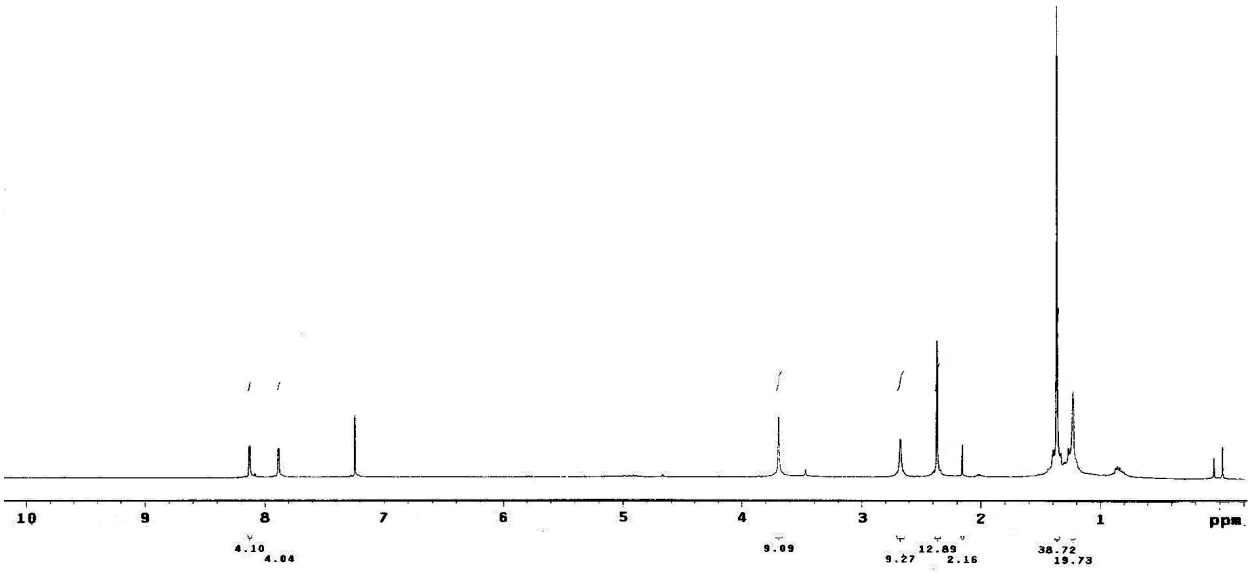

Figure S29: ^{1}H-NMR spectrum of $\mathbf{L_2'}$ in $CDCl_3$.

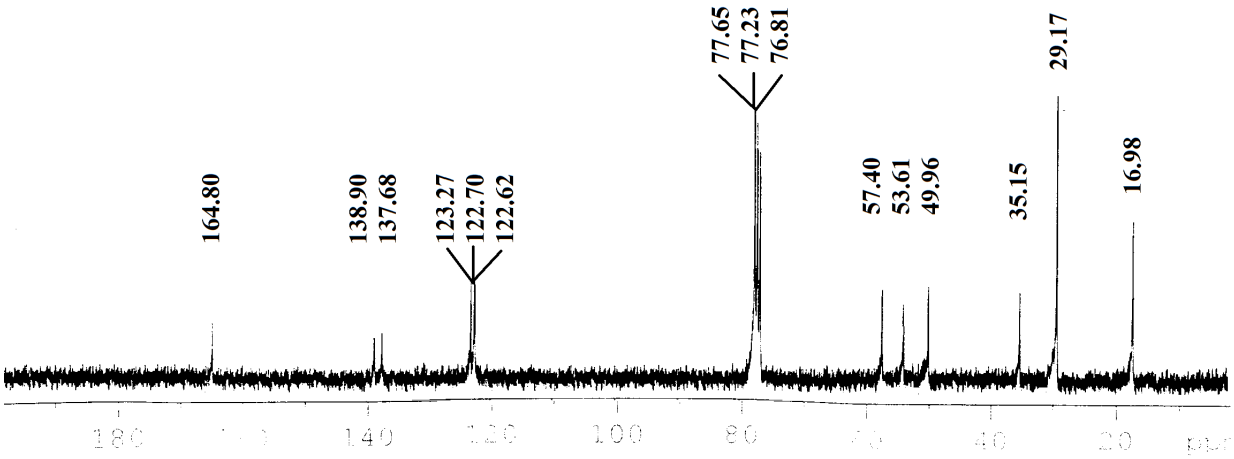

Figure S30: ^{13}C-NMR spectrum of $\mathbf{L_2'}$ in $CDCl_3$.

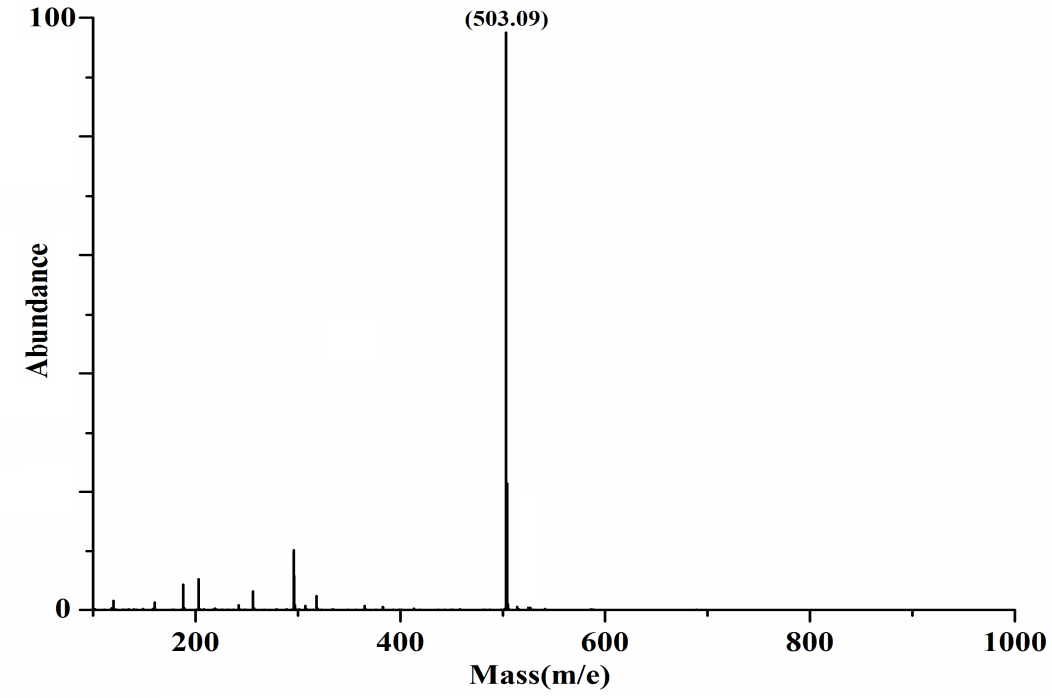

Figure S31: ESI- Mass spectrum of $\mathbf{L_2'}$ in methanol.

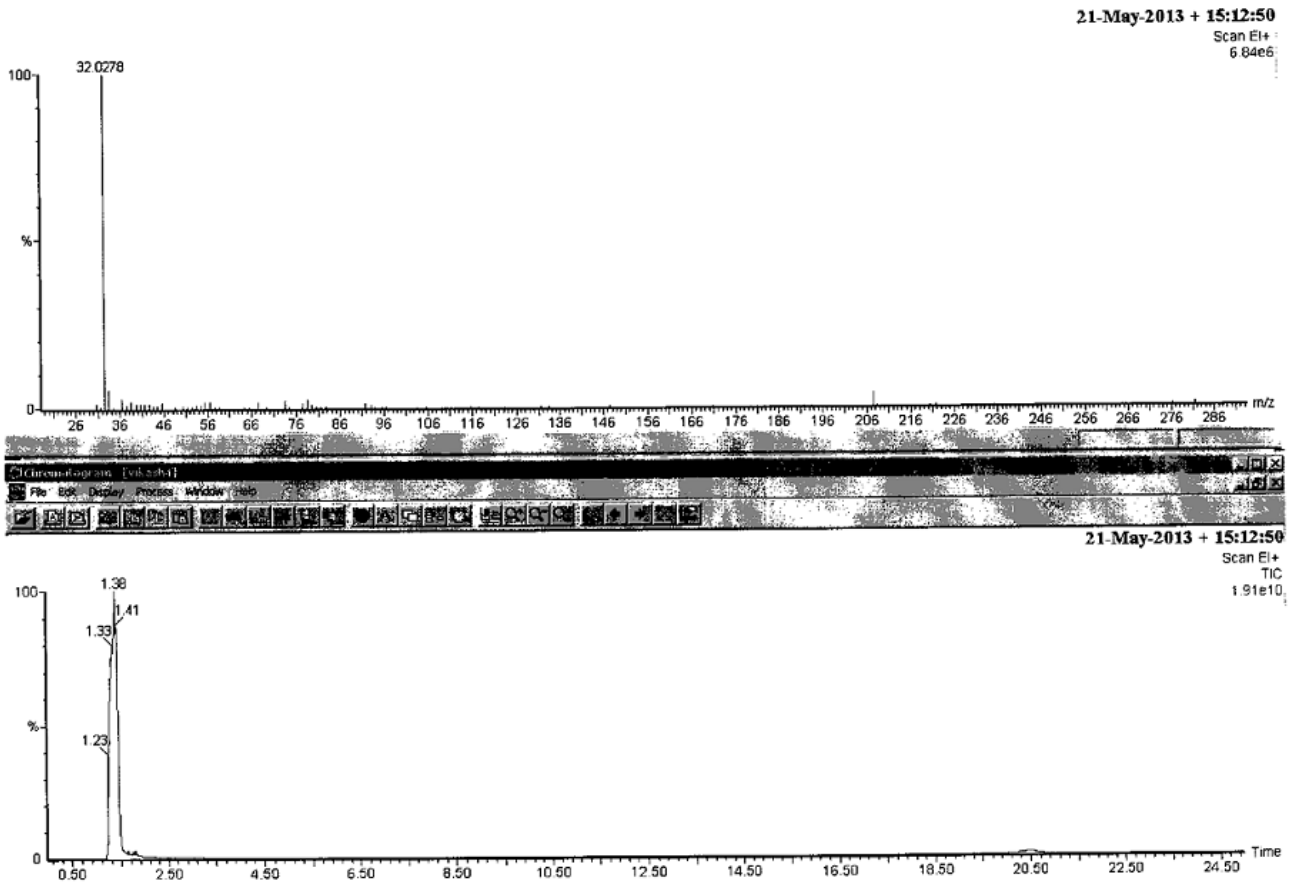

Figure S32: GC- Mass spectrum of dry methanol before purging nitrogen dioxide.

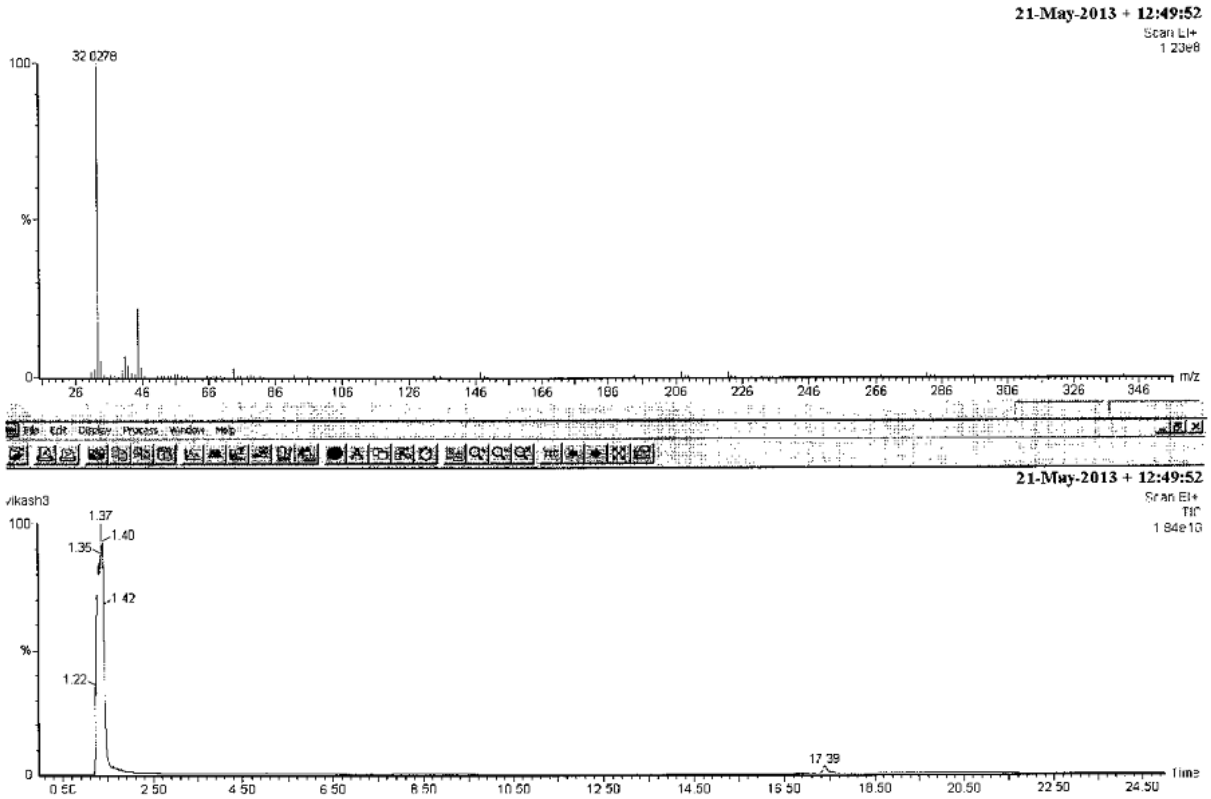

Figure S33: GC- Mass spectrum of dry methanol after purging nitrogen dioxide.

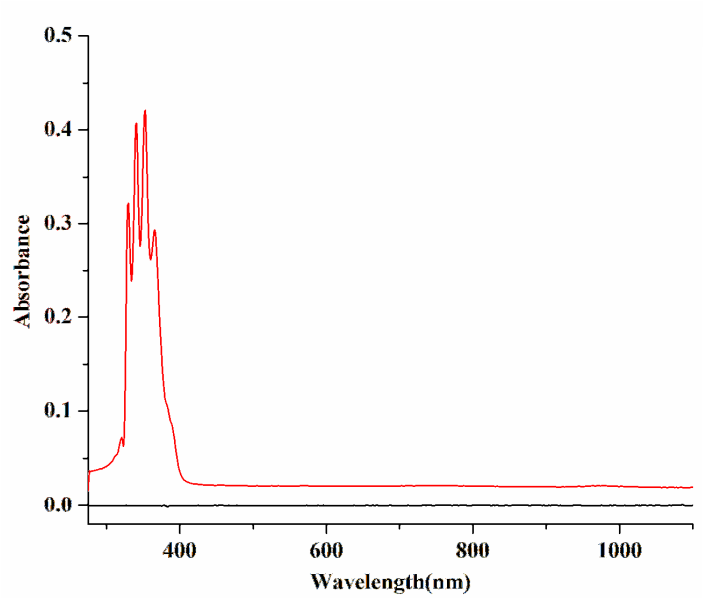

Figure S34: UV-VIS spectra of methanol before (black trace) and after (red trace) purging NO_2 .

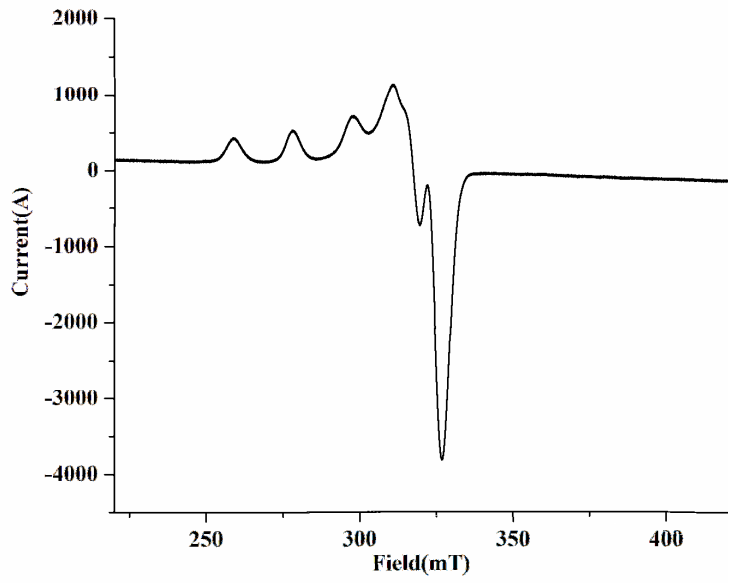

Figure S35: X-band EPR spectrum of complex **1** in methanol at 77 K.

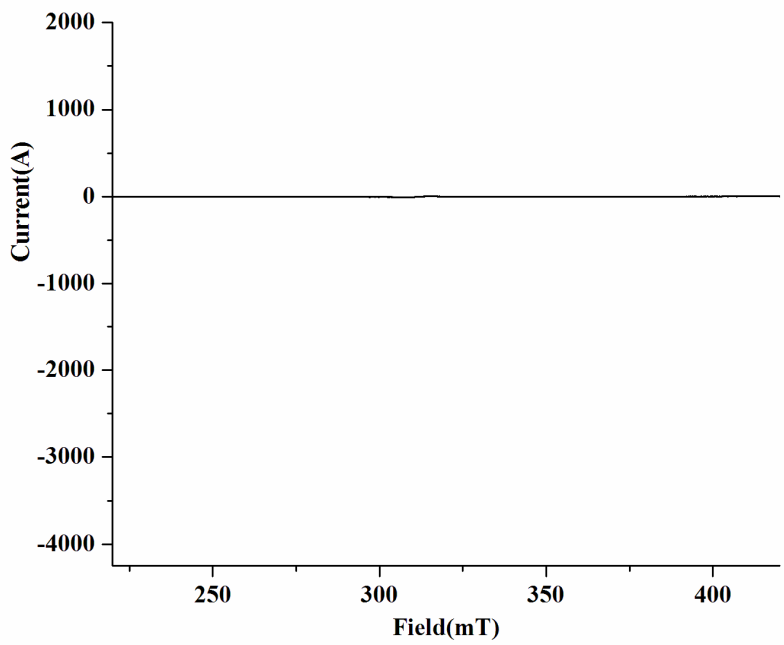

Figure S36: X-band EPR spectrum of complex **1** after purging NO_2 in methanol at 77 K.

Table S10: Crystallographic data for $\mathbf{L_2'}$.

	$\mathbf{L_2'}$
Formulae	$C_{26}\ H_{38}\ N_4\ O_6$
Mol. wt.	502.60
Crystal system	Monoclinic
Space group	P2(1)/c
Temperature /K	293(2)
Wavelength /Å	0.71073
a /Å	15.5224(11)
b /Å	9.7342(9)
c /Å	19.2871(12)
α/°	90.00
β/°	105.076(7)
γ/°	90.00
V/ Å^3	2813.9(4)
Z	4
Density/Mgm^{-3}	1.186
Abs. co-eff. /mm^{-1}	0.085
Abs. correction	none
F(000)	1080
Total no. of reflections	4824
Reflections, $I > 2\sigma(I)$	2465
Max. 2θ/°	25.00
Ranges (h, k, l)	-18≤h ≤14 -11≤ k ≤8 -22≤ l ≤ 22
Complete to 2θ (%)	97.3
Refinement method	Full-matrix least-squares on F^2
Goof (F^2)	1.434
R indices [$I > 2\sigma(I)$]	0.0895
R indices (all data)	0.1532

Table S11: Bond distances (Å) of $\mathbf{L_2'}$.

Atoms	Distances (Å)	Atoms	Distances (Å)
N(2) - C(16)	1.478(5)	C(8) - C(12)	1.510(6)
N(2) - C(5)	1.493(5)	C(11) - C(10)	1.376(5)
N(2) - C(4)	1.470(6)	C(21) - C(22)	1.364(6)
N(4) - O(6)	1.224(5)	C(21) - C(20)	1.370(6)
N(4) - O(5)	1.228(5)	C(9) - C(10)	1.381(5)
N(4) - C(21)	1.462(5)	C(18) - C(17)	1.409(6)
N(3) - O(3)	1.237(5)	C(18) - C(19)	1.412(7)
N(3) - O(4)	1.220(5)	C(22) - C(17)	1.376(5)
N(3) - C(10)	1.470(6)	C(17) - C(16)	1.487(7)
N(1) - C(3)	1.412(7)	C(12) - C(13)	1.567(7)
N(1) - C(1)	1.448(8)	C(12) - C(14)	1.546(6)
N(1) - C(2)	1.451(6)	C(12) - C(15)	1.553(6)
O(1) - C(7)	1.356(5)	C(19) - C(20)	1.391(5)
O(2) - C(18)	1.371(5)	C(19) - C(23)	1.531(6)
C(6) - C(7)	1.407(4)	C(4) - C(3)	1.492(6)
C(6) - C(11)	1.369(5)	C(23) - C(26)	1.522(9)
C(6) - C(5)	1.503(5)	C(23) - C(25)	1.545(8)
C(8) - C(7)	1.413(5)	C(23) - C(24)	1.538(8)
C(8) - C(9)	1.392(7)		

Table S12: Bond angles (Å) of $\mathbf{L_2'}$.

Atoms	Angles (Å)	Atoms	Angles (Å)
C(16)-N(2)-C(5)	109.5(3)	C(11)-C(10)-C(9)	122.3(3)
C(16)-N(2)-C(4)	112.0(3)	O(2)-C(18)-C(17)	120.3(4)
C(5)-N(2)-C(4)	112.6(3)	O(2)-C(18)-C(19)	117.1(4)
O(6)-N(4)-O(5)	123.4(4)	C(17)-C(18)-C(19)	122.5(4)
O(6)-N(4)-C(21)	118.5(4)	C(21)-C(22)-C(17)	119.4(4)
O(5)-N(4)-C(21)	118.1(4)	C(18)-C(17)-C(22)	118.4(4)
O(3)-N(3)-O(4)	124.1(4)	C(18)-C(17)-C(16)	120.8(4)
O(3)-N(3)-C(10)	117.4(4)	C(22)-C(17)-C(16)	120.7(4)
O(4)-N(3)-C(10)	118.5(4)	C(8)-C(12)-C(13)	110.5(3)
C(3)-N(1)-C(1)	111.5(4)	C(8)-C(12)-C(14)	110.0(4)
C(3)-N(1)-C(2)	111.3(4)	C(8)-C(12)-C(15)	112.2(4)
C(1)-N(1)-C(2)	107.0(4)	C(13)-C(12)-C(14)	109.7(4)
C(7)-C(6)-C(11)	119.6(3)	C(13)-C(12)-C(15)	105.8(3)
C(7)-C(6)-C(5)	119.4(3)	C(14)-C(12)-C(15)	108.6(4)
C(11)-C(6)-C(5)	121.0(3)	C(18)-C(19)-C(20)	115.9(4)
C(7)-C(8)-C(9)	115.9(4)	C(18)-C(19)-C(23)	122.7(4)
C(7)-C(8)-C(12)	122.6(4)	C(20)-C(19)-C(23)	121.3(4)
C(9)-C(8)-C(12)	121.3(4)	N(2)-C(16)-C(17)	112.2(3)
O(1)-C(7)-C(6)	118.9(3)	N(2)-C(5)-C(6)	111.6(3)
O(1)-C(7)-C(8)	118.9(3)	C(21)-C(20)-C(19)	121.1(4)
C(6)-C(7)-C(8)	122.2(3)	N(2)-C(4)-C(3)	110.7(4)
C(6)-C(11)-C(10)	118.8(3)	N(1)-C(3)-C(4)	116.5(4)
N(4)-C(21)-C(22)	119.0(4)	C(19)-C(23)-C(26)	112.1(4)
N(4)-C(21)-C(20)	118.3(4)	C(19)-C(23)-C(25)	107.5(4)
C(22)-C(21)-C(20)	122.6(4)	C(19)-C(23)-C(24)	110.1(4)
C(8)-C(9)-C(10)	121.2(4)	C(26)-C(23)-C(25)	108.9(5)
N(3)-C(10)-C(11)	118.7(3)	C(26)-C(23)-C(24)	108.2(5)
N(3)-C(10)-C(9)	118.9(3)	C(25)-C(23)-C(24)	110.0(5)