Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Nickel(II) complexes of 3N ligand as a model for diketone cleaving unusual nickel(II)-dioxygenases enzymes

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Experimental section

Materials

The chemicals 2,6-pyridine-dicarboxylic acid, 1,2-diaminobenzene, poly phosphoric acid (PPA), acetylacetone, 1,3-diphenylpropane-1,3-dione, 2,2,6,6-tetramethyl-3,5-heptanedione, dry triethylamine, nickel(II) chloride, nickel(II) perchlorate and tetrabutylammonium perchlorate (TBAP), 1,1,5,5-tetramethylpentamethylene nitroxide (TEMPO), piperidine, pyridine, $H_2{}^{18}O$ and $^{18}O_2$ were purchased from Sigma-Aldrich and methyl iodide (Alfa Aesar) were used as such without further purification. Anhydrous acetonitrile, potassium hydroxide and acetone were purchased from Merck.

Experimental conditions and physical measurements: All workup were carried out under dry argon using a standard Schlenk line or glove box techniques for the reactions involving air-sensitive synthesis and experiments. All NMR spectra were recorded on Bruker 300 MHz spectrometer. Chemical shift values are given in parts per million (ppm). UV-Vis spectra were recorded on an Agilent 8453 spectrometer with a cooling unit by Unisoku (Osaka, Japan). The electrochemical data were obtained using CH Instrument 660D Electrochemical Workstation. High-resolution mass spectra were obtained from Q-TOF Micro YA263 and HRMS-ESI-Q-TOF LC/MS. Elemental analyses were carried out using a Heraeus Vario Elemental automatic analyzer.

X-ray Structure Determination: A single crystal **2** and **3** of suitable size was selected from the mother liquor, coated with paraffin oil, and mounted on a fiber loop for X-ray diffraction data collection with an Agilent Supernova diffractometer (Cu-Kαradiation) equipped with a Titan CCD detector. The data processing, including face-based absorption correction, was performed with the CrysAlisPro software suite. The structure was solved by direct methods with SHELXS and refined with SHELXL.[1] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were added at calculated positions as riding atoms and refined isotropically. CCDC 1569445 and 1569448 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of 2,6-bis(1-methyl-1H-benzoimidazol-2-yl)pyridine (L)

This compound 2,6-bis(1H-benzoimidazol-2-yl)pyridine was synthesized by a previously reported method.[2] The yield is 52% and characterized by ^{1}H- NMR and ESI-MS Mass. ^{1}H NMR (d_6-DMSO, 300 MHz): δ, 8.31 (d, J = 7.8 Hz, 2H), 7.99 (t, J = 7.8 Hz, 1H), 7.73 (d, J = 7.3 Hz, 2H), 7.60 (d, J = 7.1 Hz, 2H), 7.25 (t, J = 7.8 Hz, 4H) ppm. ESI-MS, m/z: 312.84 for $[C_{19}H_{14}N_5]^+$. To the suspension of above compound (0.2 g, 0.64 mmol) in acetone (10 mL), powdered KOH (0.18 g, 3.2 mmol) was added. The mixture was stirred for 15 minutes at room temperature followed by the addition of methyl iodide (0.26 g, 1.92 mmol) with vigorous stirring. The reaction continued for another 6 hours at room temperature. The reaction mixture was poured into water. The precipitate was filtered and recrystallized from methanol to afford the desired ligand as pale brown, yield = 0.32 g, 52%. ^{1}H NMR (d_6-DMSO, 300 MHz): δ, 8.30 (d, J = 9.6 Hz, 2H), 7.98 (t, J = 8.7 Hz, 1H), 7.69 (d, J = 7.5 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 7.24 (dt, J = 13.3, 6.7 Hz, 4H), 4.18 (s, 6H) ppm. ESI-MS, *m/z*: 340.44 for $[C_{21}H_{18}N_5]^+$.

Synthesis of $[Ni(L)(acac^{Me})(H_2O)]ClO_4$ (1) and $[Ni(L)(acac^{t\text{-}bu})(CH_3CN)]ClO_4$ (2)

These complexes were synthesised by an identical method in a strict inert atmosphere. The nickel salt $Ni(ClO_4)_2.6H_2O$ (0.1 mmol, 0.0365 g) in CH_3CN (2 mL) was added to $acac^x$ 0.1 mmol (X = Me, 10.2 µL; X = *t*-bu, 20.8 µL) and triethyl amine (0.1 mmol, 14 µL) and then stirred to 30 minutes. This solution was then added to ligand (0.1 mmol, 0.034 g) in CH_3CN (2 mL). This solution was stirred for additional 2 hours. To this solution, diethyl ether (8 mL) was added and kept for crystallization in the refrigerator. After 2 days, the complex was precipitated as orange-brown solid. The solvent was removed under vacuum and washed with excess diethyl ether to yield the $[Ni(L)acac^{Me}(CH_3CN)]ClO_4$ **1** (0.0393 g, 75%). HRMS: *m/z,* found, 573.2533 and calculated, 573.1755 for $[Ni(L)acac^{Me}CH_3CN]^+\cdot 2H_2O$. Analytically calculated elements for $C_{28}H_{27}ClN_6NiO_6$: C, 52.74; H, 4.27; N, 13.18%. Found: C, 52.70; H, 4.23; N, 13.16%. However, the complex $[Ni(L)acac^{t\text{-}Bu}(CH_3CN)]ClO_4$ **2**, was obtained as orange-brown single crystals, which are suitable for X-ray diffraction. The yield is 72% (0.0438 g). HRMS: *m/z*, found, 581.2271 and calculated, 581.2295 for $[Ni(L)acac^{t\text{-}But}]^+$. Analytically calculated elements for $C_{32}H_{37}ClN_5NiO_6$: C, 56.37; H, 5.47; N, 10.27%. Found: C, 56.49; H, 5.80; N, 9.84%.

Synthesis of $[Ni(L)(acac^{Ph})(H_2O)]Cl$ (3)

The complex was synthesized by adopting above synthetic procedure. Where $NiCl_2$ (0.1 mmol, 0.0237 g) was used instead of $Ni(ClO_4)_2\cdot 6H_2O$ and substrate $acac^{Ph}$ (0.1 mmol, 0.0224 g) used in the CH_3CN solution. The layering of the solution with diethyl ether afforded an orange-brown single crystal of **3**, which are suitable for X-ray diffraction. The yield is 74 % (0.046 g). HRMS: *m/z,* found, 679.3042 and calculated, 679.1255 for $[Ni(L)acac^{Ph}Cl]$+Na. Analytically calculated elements for $C_{36}H_{30}N_5NiO_3$: C, 67.63; H, 4.73; N, 10.95%. Found: C, 68.01; H, 4.43; N, 10.61%.

Products isolation and identification of 3 with $^{16}O_2$, $^{18}O_2$ and $H_2{}^{18}O$:

In a separate experiment complex, **3** (0.046 g, 0.074 mmol) was dissolved in degassed CH_3CN (10 mL) and triethyl amine (10 µL, 0.074 mmol) was added. The solution was exposed to $^{16}O_2$\$^{18}O_2$ and stirred them for 18 hours at room temperature. For the labelling studies, an excess of $H_2{}^{18}O$ (74 μL, 3.7 mmol) was added and the solution was exposed to $^{16}O_2$. $^{18}O_2$ labelling studies were performed by under identical condition using $^{18}O_2$ instead of $^{16}O_2$. The reaction was quenched with 0.1 mL of dil. HCl (0.1 N) stirred for 30 minutes and solvent was removed by *in vacuo* under nitrogen atmosphere. The products were extracted with ethyl acetate and analysed by GC- MS. The entire similar fraction was combined and then the solvent was removed. Benzoic acid was isolated as major product with the yield of 52% (4.9 mg) and trace of benzil along with some unidentified products.

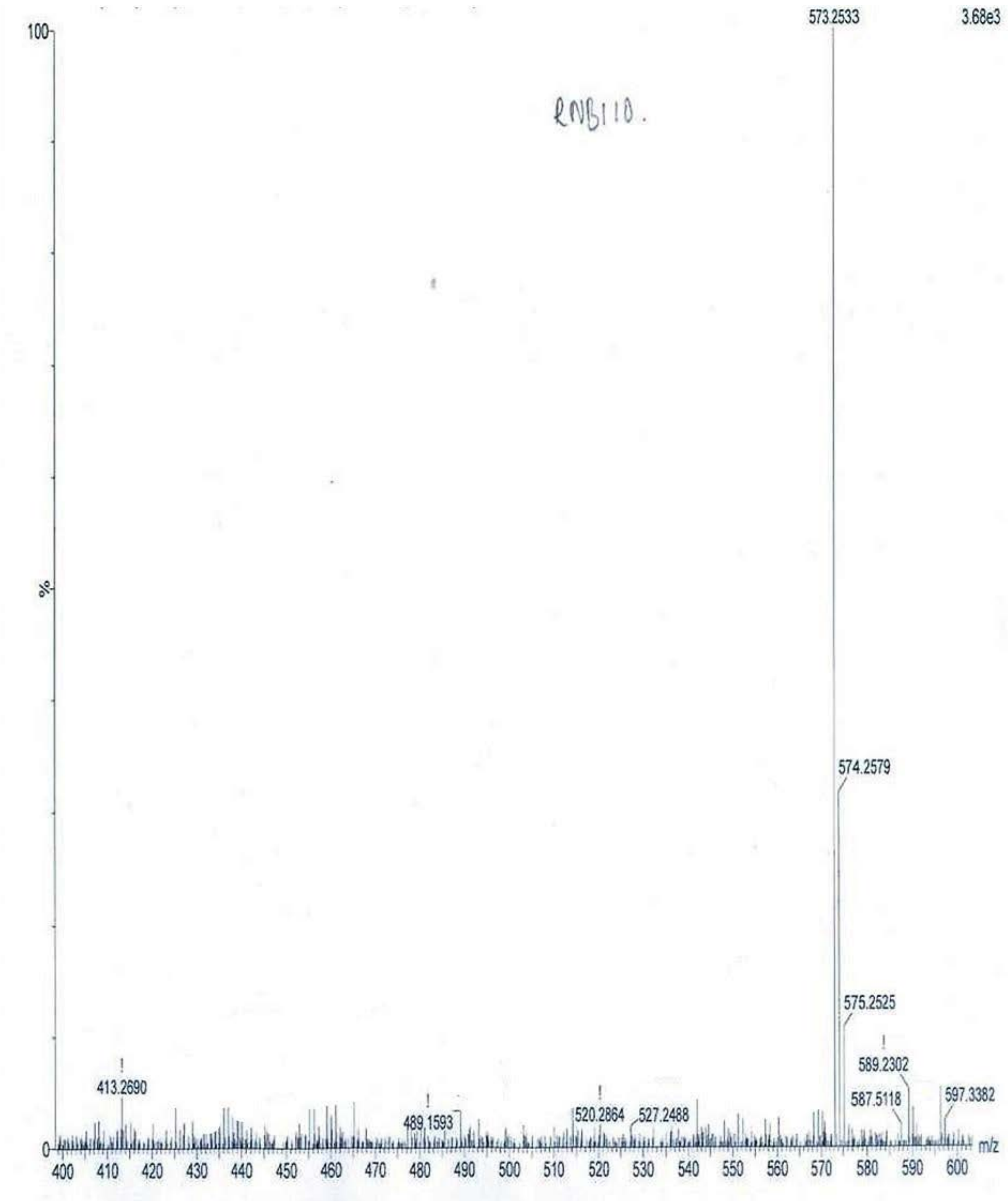
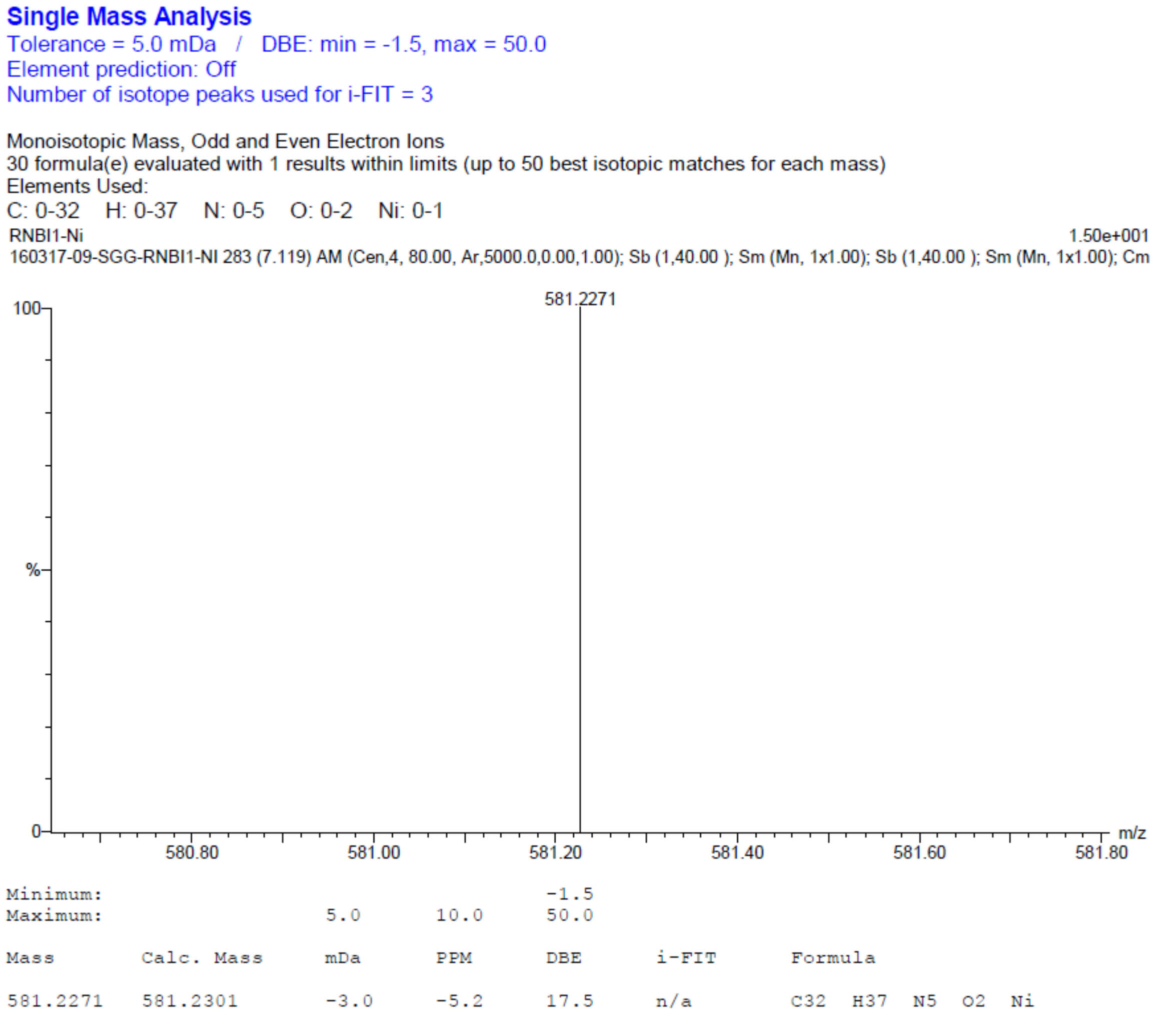


Figure S1: HRMS data of complex 1 $[Ni(L)acac^{Me}CH_3CN]^+ \cdot 2H_2O$ in CH_3CN.



Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-32 H: 0-37 N: 0-5 O: 0-2 Ni: 0-1
RNBI1-Ni 1.50e+001
160317-09-SGG-RNBI1-NI 283 (7.119) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x1.00); Sb (1,40.00); Sm (Mn, 1x1.00); Cm

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Minimum:                                  -1.5
Maximum:                    5.0    10.0   50.0

Mass       Calc. Mass      mDa     PPM     DBE     i-FIT      Formula

581.2271   581.2301       -3.0    -5.2    17.5    n/a        C32  H37  N5  O2  Ni
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Figure S2: HRMS data of complex 2 [Ni(L)acac$^{t\text{-But}}$]$^+$ in CH_3CN.

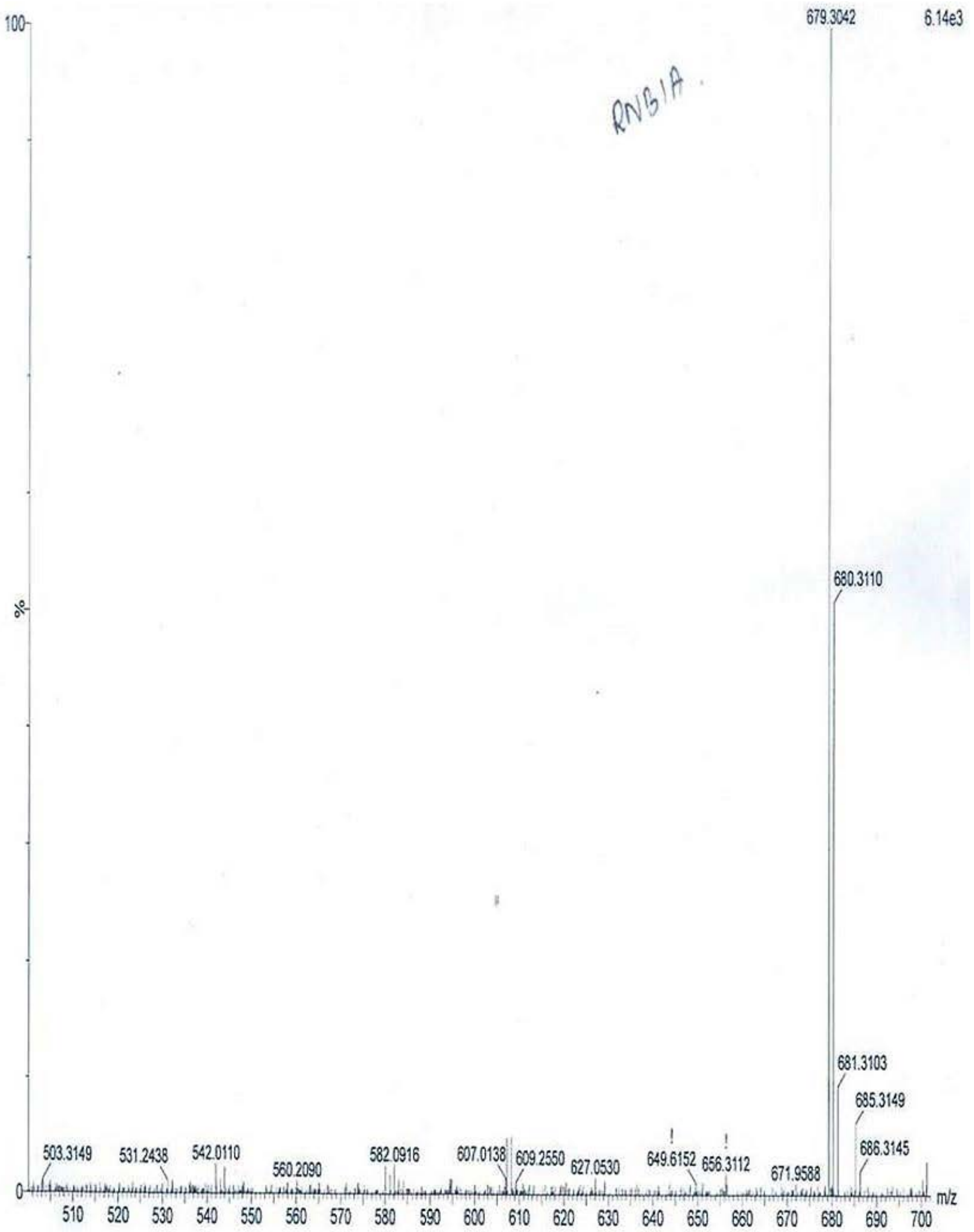

Figure S3: HRMS data of complex [Ni(L)acac^{Ph}Cl]+Na in CH_3CN.

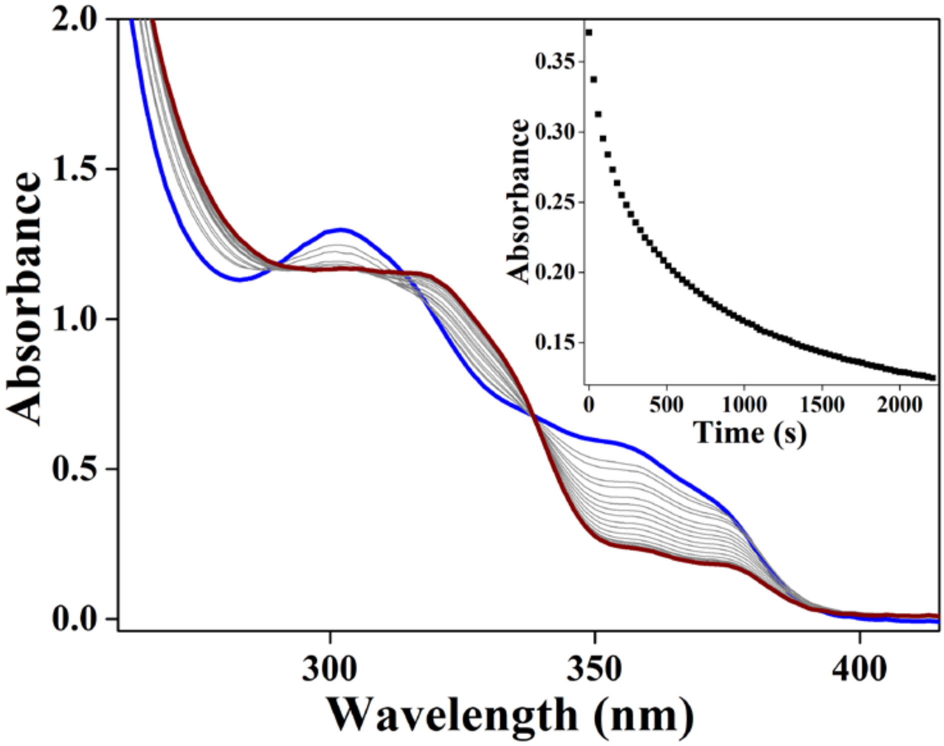

Figure S4: UV- Visible spectral changes for the reaction of **1** (6×10^{-4} M) with saturated O_2 in acetonitrile at 25˚C. The monitored disappearance of acac to $Ni^{(II)}$ LMCT band at 371 nm with 30 seconds time interval.

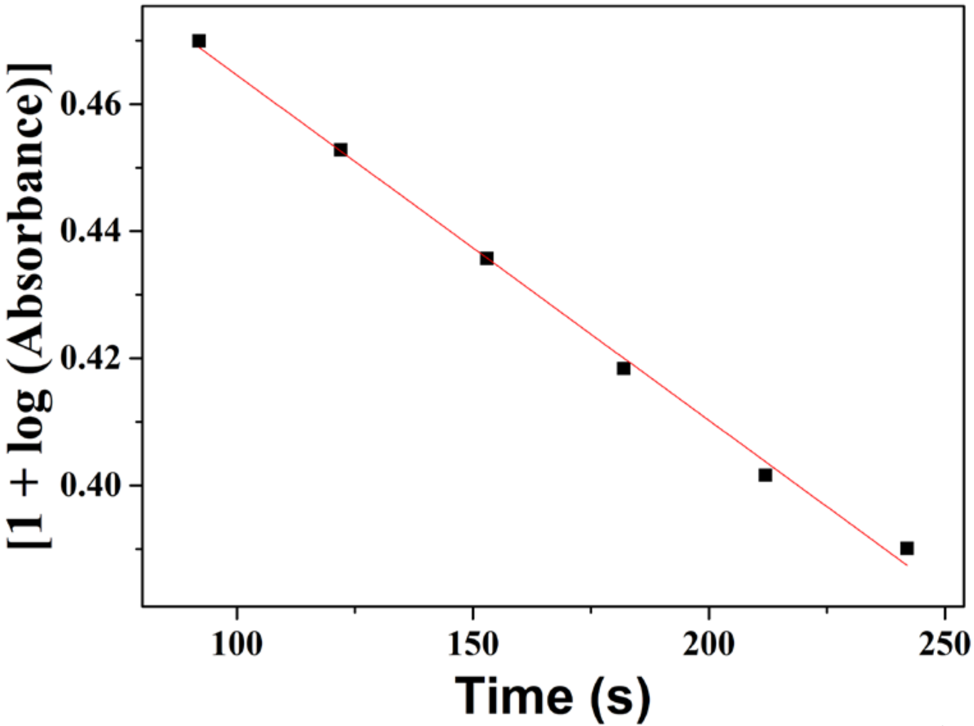

Figure S5: Plot of [1 +log (Absorbance)] vs time the reaction of **1** (6×10^{-4} M) with saturated O_2 in acetonitrile at 25˚C.

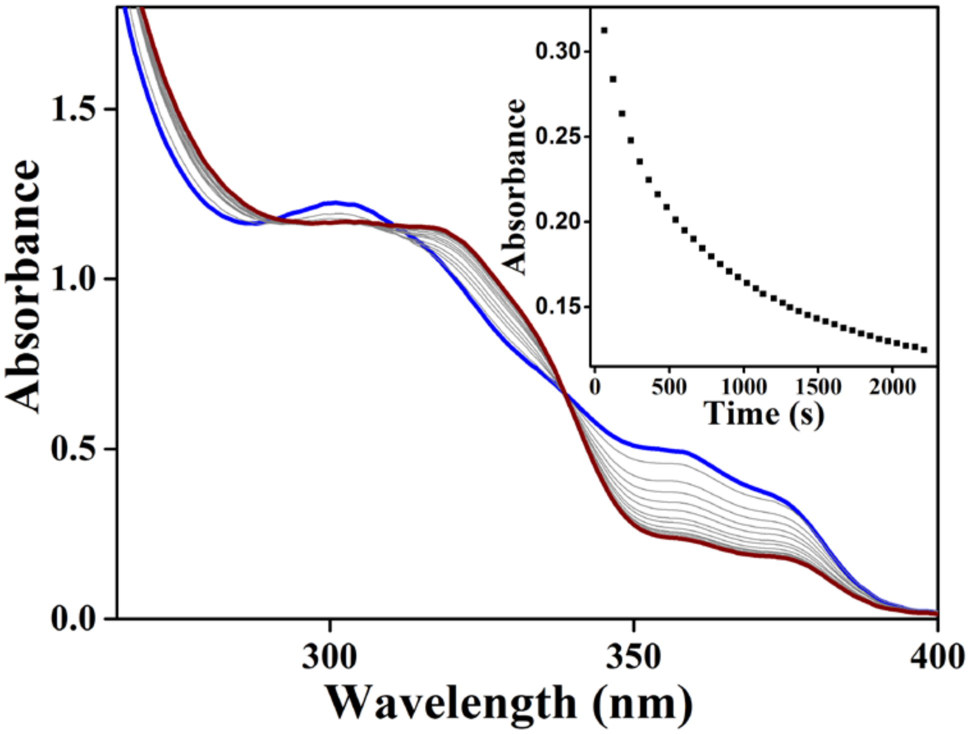

Figure S6: UV- Visible spectral changes for the reaction of **1** (6×10^{-4} M) with saturated O_2 in acetonitrile (10% H_2O) at 25˚C. The monitored disappearance of acac to Ni$^{(II)}$ LMCT band at 371 nm with 30 seconds time interval.

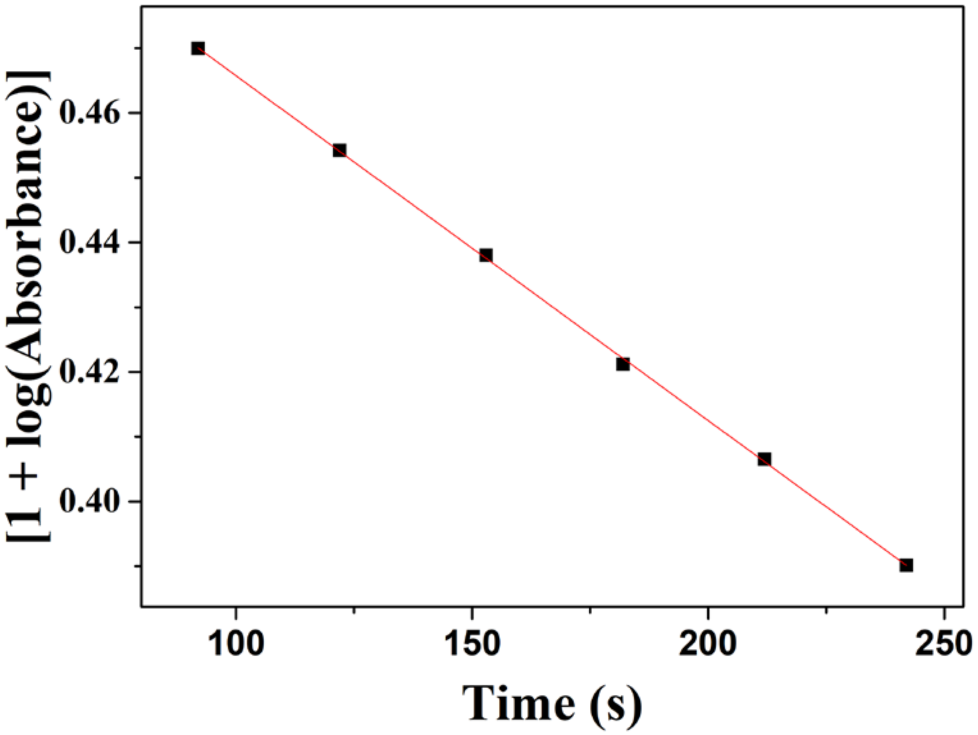

Figure S7: Plot of [1 +log(Absorbance)] vs Time the reaction of **1** (6×10^{-4} M) with saturated O_2 in acetonitrile (10% H_2O) at 25˚C.

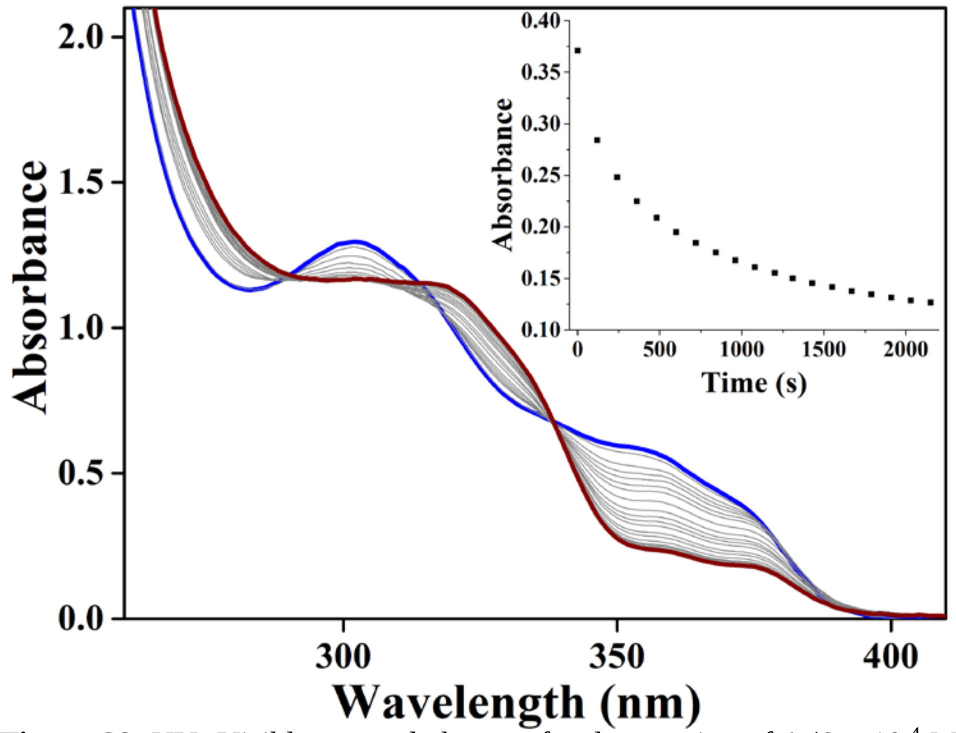

Figure S8: UV- Visible spectral changes for the reaction of **1** (6×10^{-4} M) with saturated O_2 in acetonitrile in presences of 1 equivalent of piperidine at 25˚C. The monitored disappearance of acac to $Ni^{(II)}$ LMCT band at 371 nm with 120 seconds time interval.

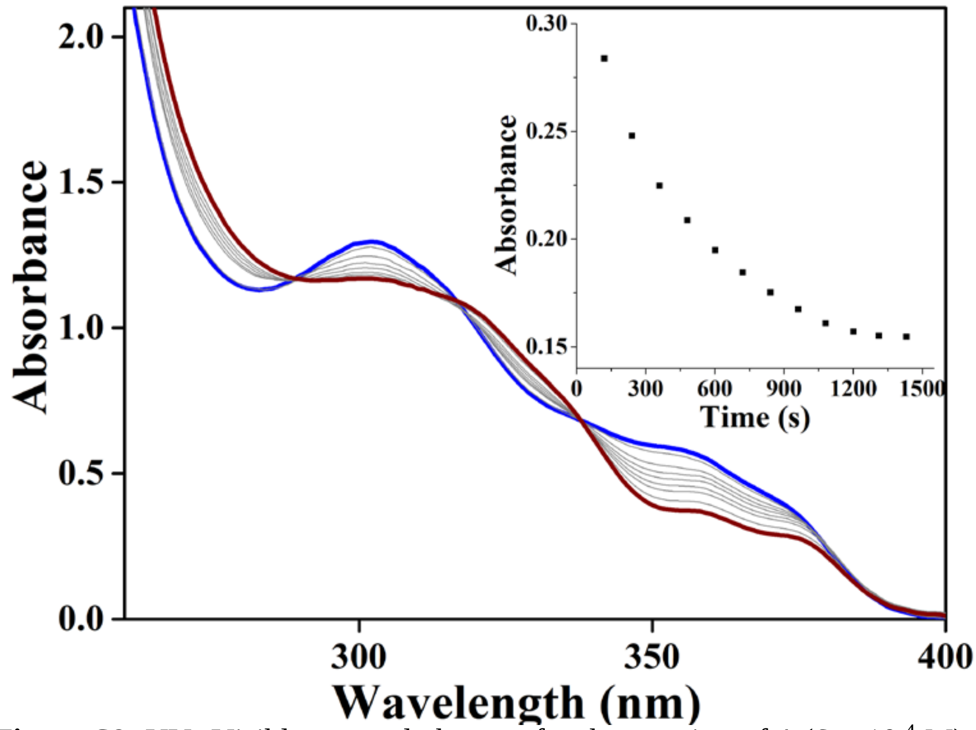

Figure S9: UV- Visible spectral changes for the reaction of **1** (6×10^{-4} M) with saturated O_2 in acetonitrile in presences of 1 equivalent of pyridine at 25˚C. The monitored disappearance of acac to $Ni^{(II)}$ LMCT band at 371 nm with 120 seconds time interval.

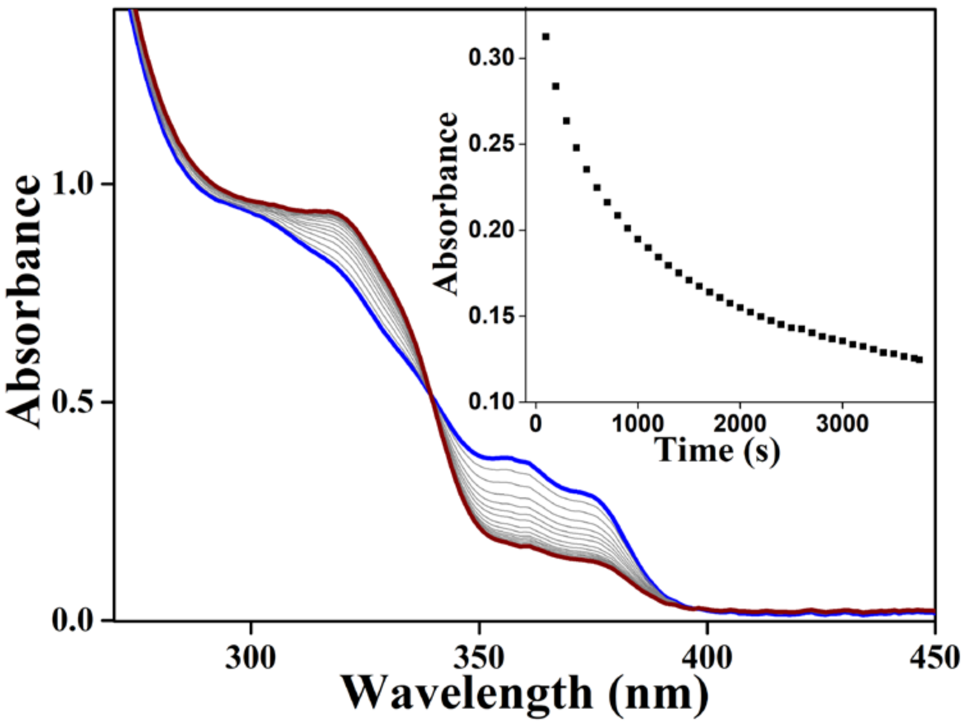

Figure S10: UV- Visible spectral changes for the reaction of **2** (6 × 10^{-4} M) with saturated O_2 in acetonitrile (10% H_2O) at 25˚C. The monitored disappearance of acac to Ni$^{(II)}$ LMCT band at 373 nm with 50 seconds time interval.

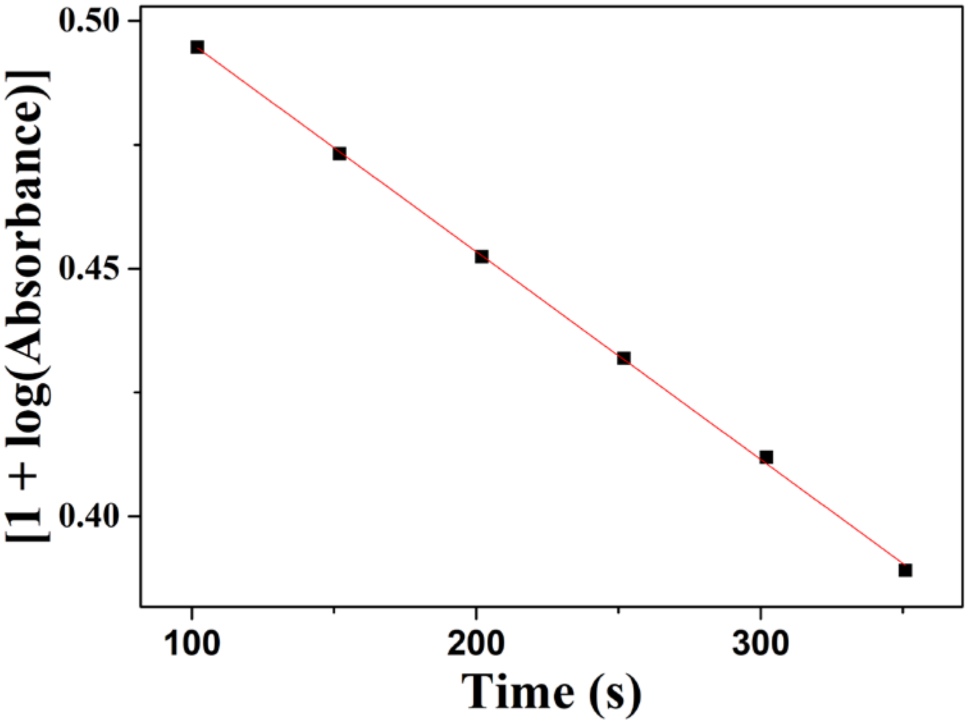

Figure S11: Plot of [1 +log(Absorbance)] vs Time the reaction of **2** (6 × 10^{-4} M) with saturated O_2 in acetonitrile (10% H_2O) at 25˚C.

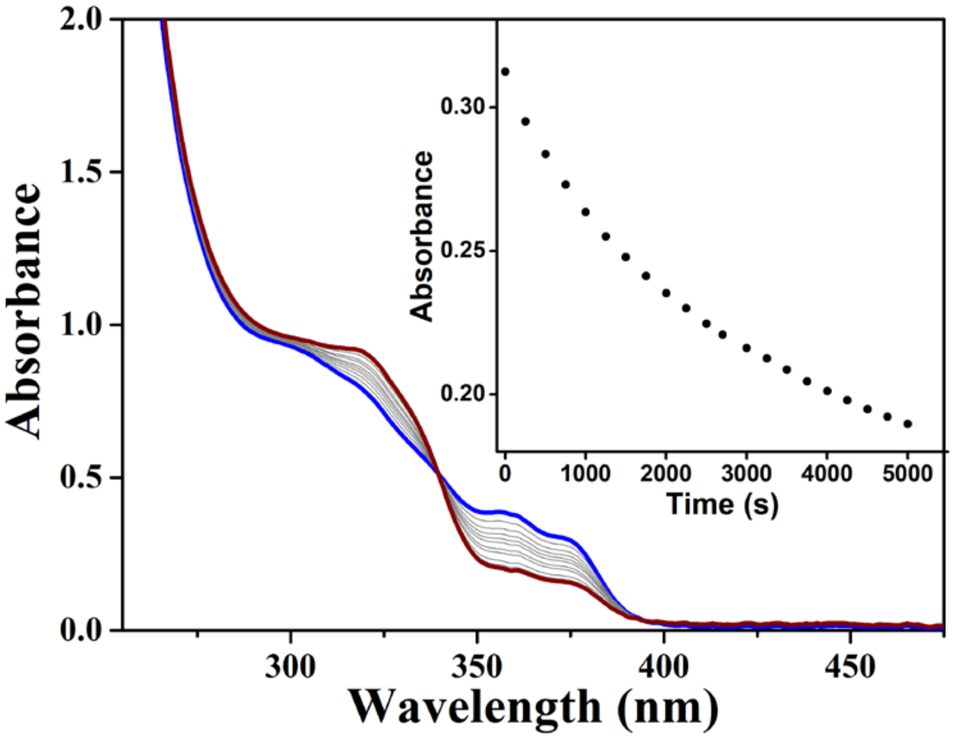

Figure S12: UV- Visible spectral changes for the reaction of **3** (6×10^{-4} M) with saturated O_2 in acetonitrile at 25˚C. The monitored disappearance of acac to $Ni^{(II)}$ LMCT band at 377 nm with 250 seconds time interval.

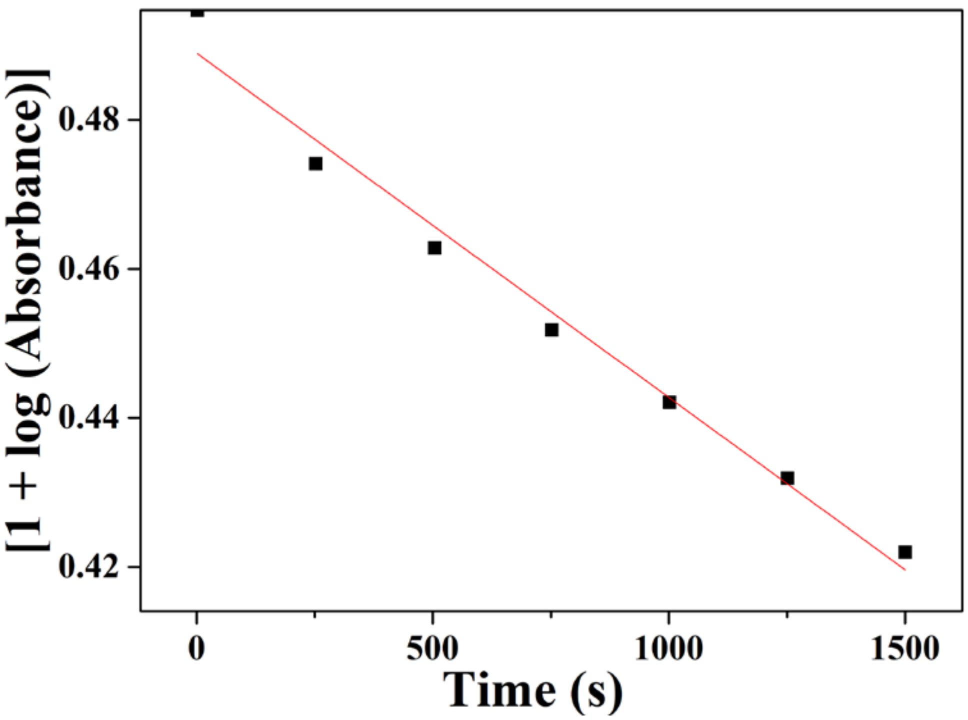

Figure S13: Plot of [1 +log(Absorbance)] vs time the reaction of **3** (6×10^{-4} M) with saturated O_2 in acetonitrile at 25˚C.

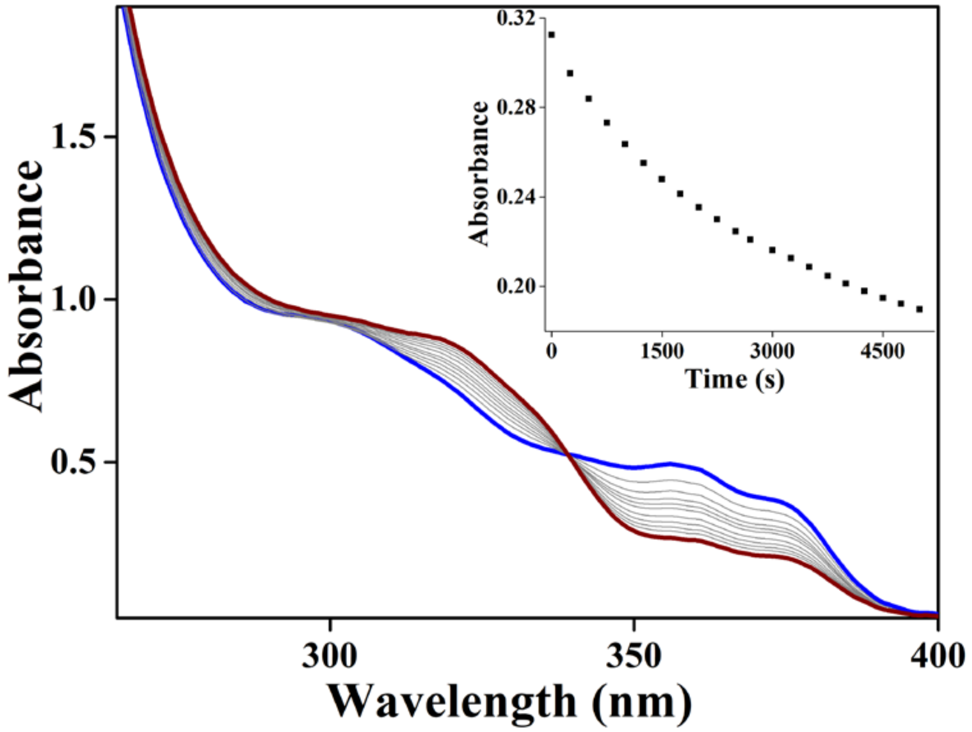

Figure S14: UV- Visible spectral changes for the reaction of **3** (6×10^{-4} M) with saturated O_2 in acetonitrile (10% H_2O) at 25˚C. The monitored disappearance of acac to $Ni^{(II)}$ LMCT band at 377 nm with 250 seconds time interval.

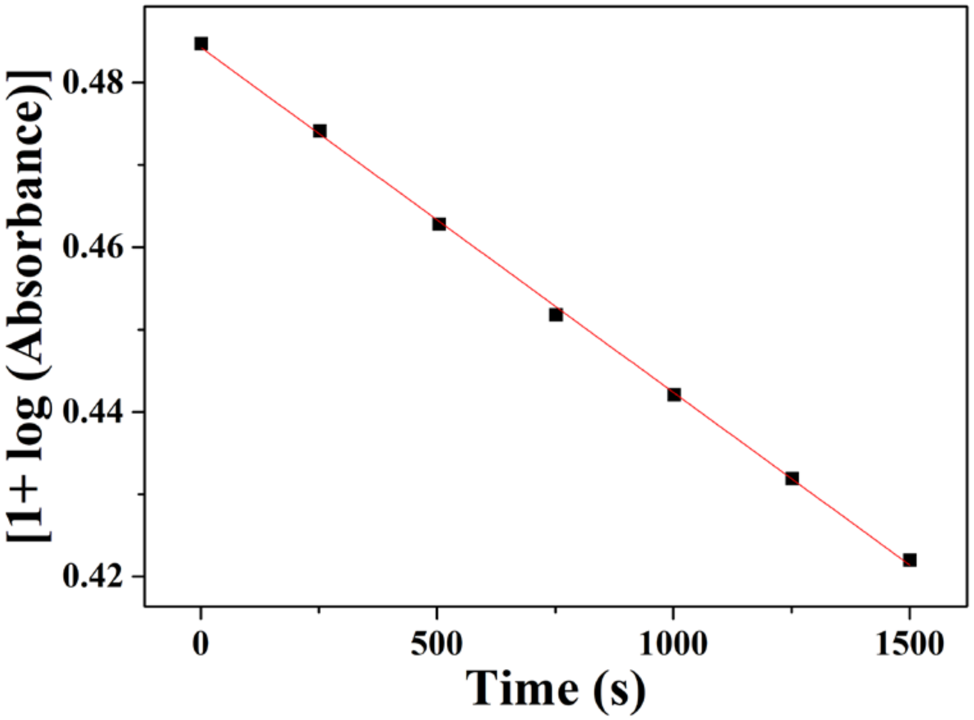

Figure S15: Plot of [1 +log(Absorbance)] vs time the reaction of **3** (6×10^{-4} M) with saturated O_2 in acetonitrile (10% H_2O) at 25˚C.

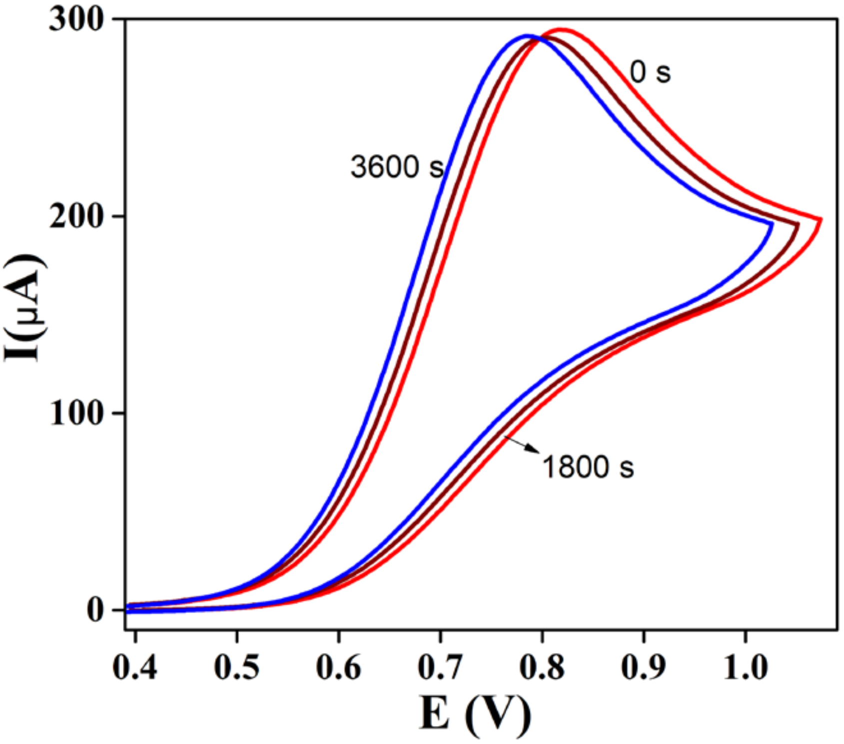

Figure S16: Time-dependent cyclic voltammetry (1×10^{-3} M) of **3** with O_2.

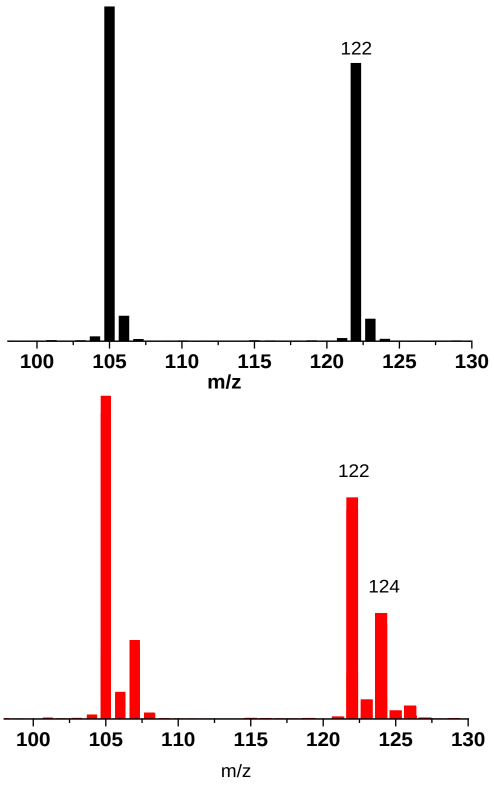

Figure S17: Oxygen isotopic studies for the reaction **3** using $^{16}O_2$ (top) and with $^{18}O_2$ (bottom)

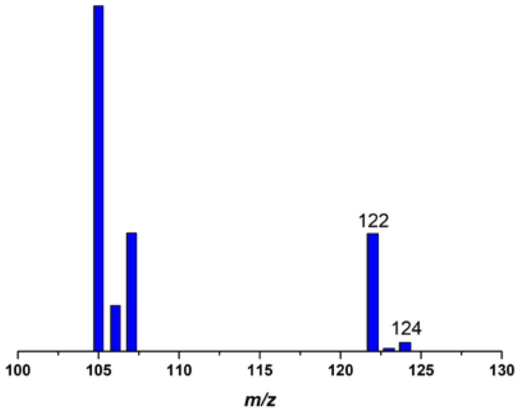

Figure S18: The dioxygen reaction of **3** using $H_2{}^{18}O$ in presence of $^{16}O_2$.

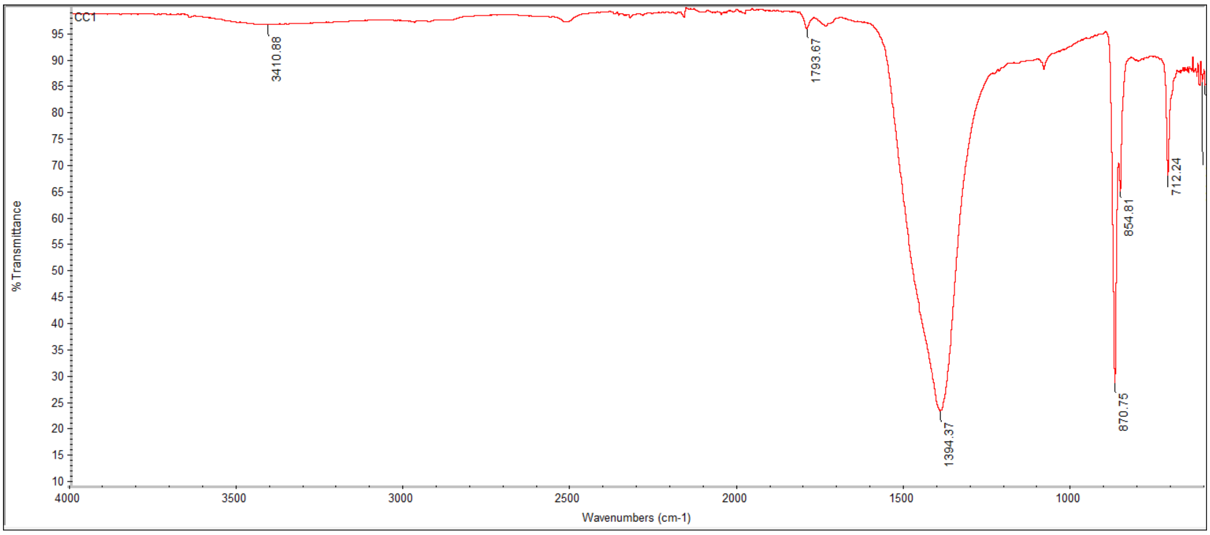

Figure S19: FT-IR spectra of $CaCO_3$ generated by purging a headspace gas evolved into a saturated solution of $Ca(OH)_2$ from the reaction of **3** with dioxygen.

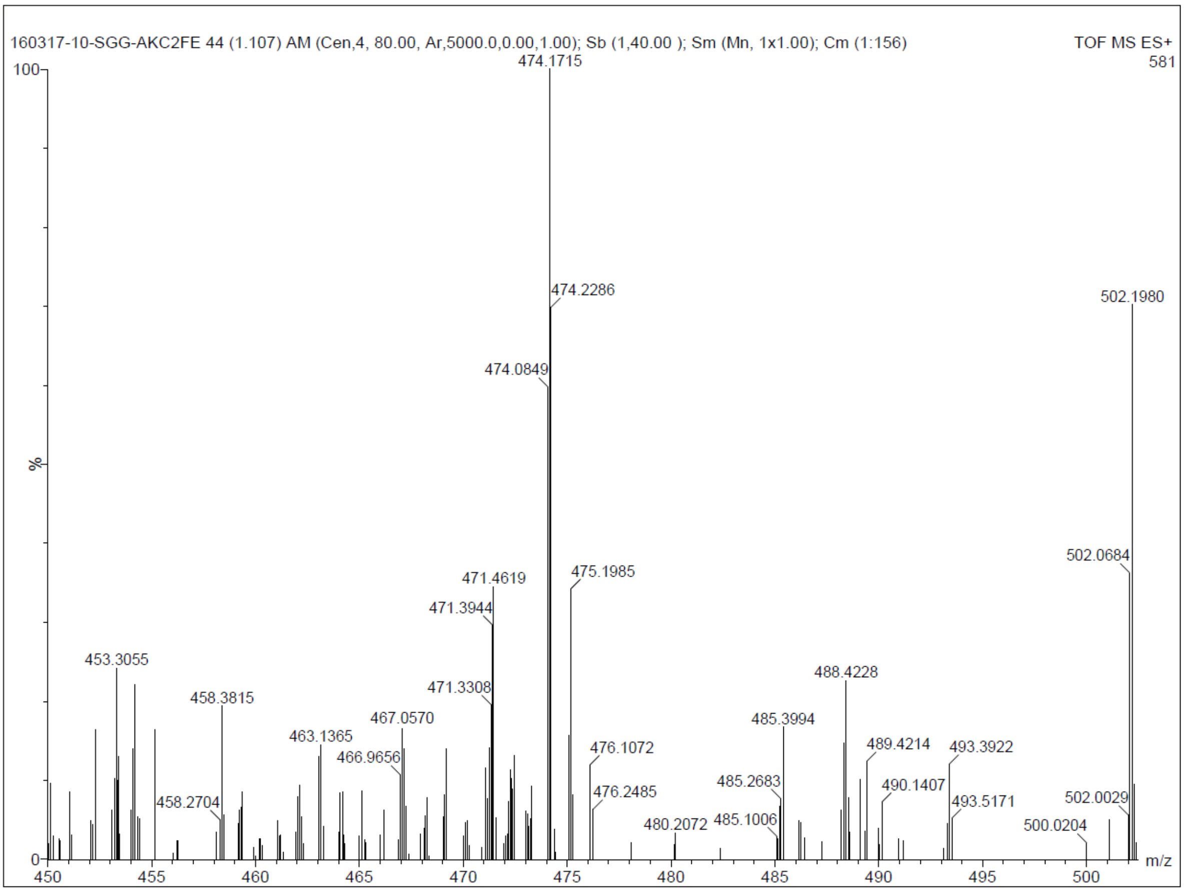

Figure S20: ESI-MS data for the dioxygenated reaction mixture of **1** in ACN {m/z, 474.1715 corresponds to [Ni^{II}(L)(CH$_3$COO).H$_2$O]; m/z, 502.1980 corresponds to [Ni^{II}(L)(CH$_3$CN)$_2$] + Na}

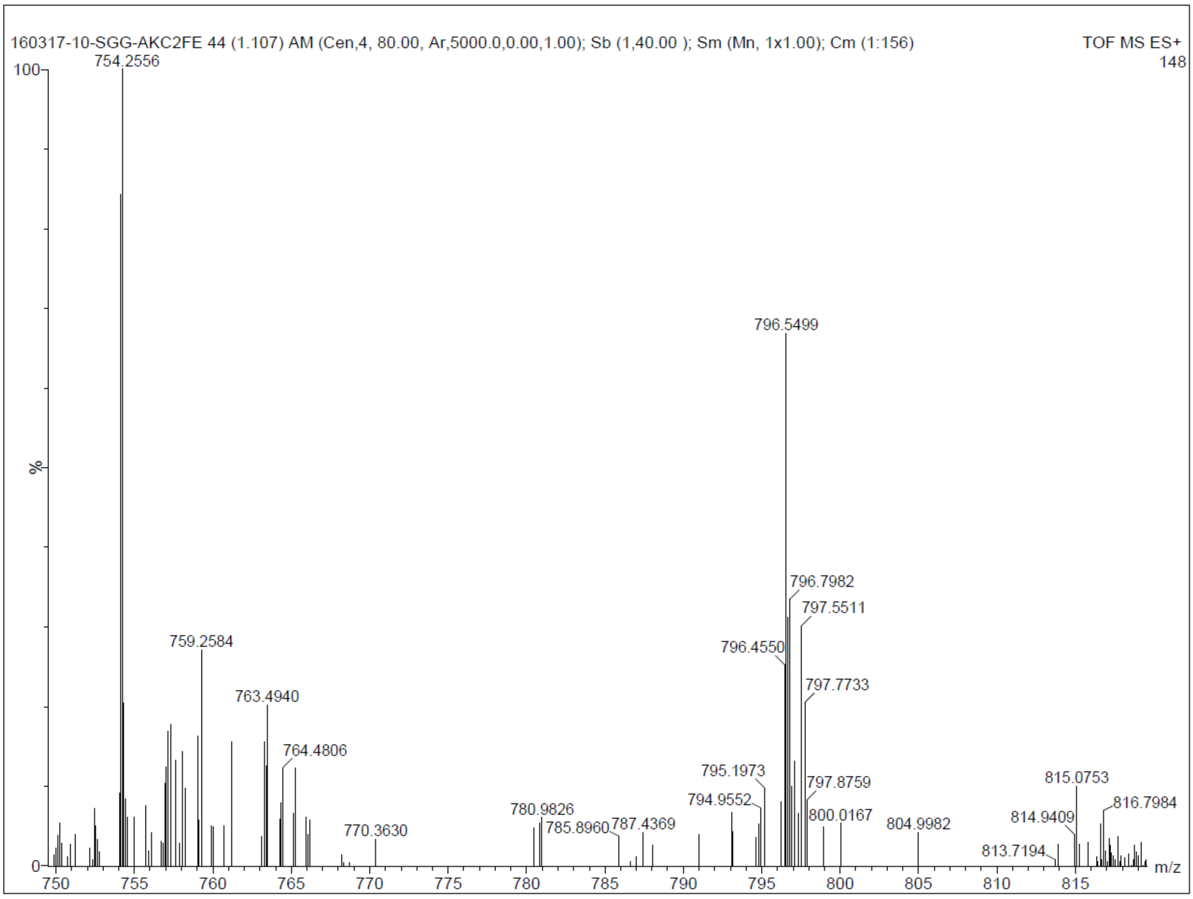

Figure S21: ESI-MS data for the dioxygenated reaction mixture of **2** in ACN {m/z, 754.2556 corresponds to [$Ni^{II}(L)_2$].H_2O; m/z, 796.5499 corresponds to [$Ni^{II}(L)_2$].H_2O + CH_3CN}

Table S1. Crystal data and structure refinement for $[Ni(L)(acac^{t\text{-}Bu})(CH_3CN)]ClO_4$ **2** and $[Ni(L)(acac^{Ph})(H_2O)]Cl$ **3**

	2	**3**
Empirical formula	$C_{34}H_{39}ClN_6NiO_6$	$C_{36}H_{30}ClN_5NiO_3$
Formula weight	721.87	674.81
Temperature	293(2) K	293(2) K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 21/c
Unit cell dimensions	a = 9.5304(4) Å	a = 9.1764(4) Å
	b = 10.1589(4) Å	b = 13.0535(6) Å
	c = 19.4742(7) Å	c = 26.4288(9) Å
Volume	1779.24(13) Å^3	3134.6(2) Å^3
Z	2	4
Density (mg/m^3)	1.347	1.430
μ(mm^{-1})	1.905	2.046
F(000)	756	1400
No. of reflections collected	12699	12384
Goodness-of-fit on F^2	1.041	1.133
R1[a]	0.0674	0.0678
wR2[b]	0.2156	0.2238

[a] $R1=\sum||F_o|-|Fc||/\sum|F_o|$, [b] $R_2=\sum w[(F_o- F_c)^2/\sum w[(F_o^2)^2]^{1/2}$

Table S2. Crystal data and structure refinement for [Ni(L)(acac$^{t\text{-}Bu}$)(CH_3CN)]ClO_4 **2** and [Ni(L)(acac^{Ph})(H_2O)]Cl **3**

	2	**3**
Ni(1)-N(1)	2.089(3)	2.088(4)
Ni(1)-N(3)	2.068(3)	2.050(3)
Ni(1)-N(4)	2.103(3)	2.107(3)
Ni(1)-N(6) /O(3)[a]	2.131(3)	2.039(3)
Ni(1)-O(1)	1.994(2)	2.004(3)
Ni(1)-O(2)	2.009(2)	2.057(3)
O(1)-Ni(1)-O(2)	90.61(9)	89.99(11)
O(1)-Ni(1)-N(3)	178.29(10)	86.94(12)
O(2)-Ni(1)-N(3)	90.72(10)	175.63(13)
O(1)-Ni(1)-N(1)	101.76(11)	96.00(14)
O(2)-Ni(1)-N(1)	91.92(11)	99.45(13)
N(3)-Ni(1)-N(1)	77.13(11)	77.80(13)
O(1)-Ni(1)-N(4)	104.26(11)	87.72(13)
O(2)-Ni(1)-N(4)	89.51(11)	105.78(13)
N(3)-Ni(1)-N(4)	76.82(11)	77.22(13)
N(1)-Ni(1)-N(4)	153.92(12)	154.51(13)
O(1)-Ni(1)-N(6)/O(3)[a]	88.81(11)	177.99(12)
O(2)-Ni(1)-N(6)/O(3)[a]	177.42(11)	88.60(12)
N(3)-Ni(1)-N(6)/O(3)[a]	89.91(12)	94.54(12
N(1)-Ni(1)-N(6)/O(3)[a]	90.66(12)	85.64(13)
N(4)-Ni(1)-N(6)/O(3)[a]	88.20(12)	91.29(13)

O(3) [a] belongs to coordinated H_2O of [NiL1(acac^{Ph})(H_2O)]Cl **3**

Table S3. Electronic spectral, redox and kinetic data for the complexes **1–3** in acetonitrile

Complexes	λ_{max}, nm (ε,M^{-1} cm^{-1})	Ep_a (V)	Ep_c (V)	ΔE(mV)	$E_{1/2}$ (V)
1	371 (3201) 355 (5553) 302 (127.8 $\times 10^2$) 255 (346.2 $\times 10^2$)	0.927	0.819	108	0.873
2	373 (3707) 358 (4882) 300 (9340) 257 (283.6$\times 10^2$) 240 (331.4$\times 10^2$)	0.899	0.782	117	0.84
3	377 (3992) 361 (4717) 301 (9219) 253 (263.6$\times 10^2$) 237 (321.4$\times 10^2$)	0.837	0.705	132	0.771

[a] Concentration of nickel(II) complexes, 1 × 10^{-4} M;

[b] Electrochemistry: concentration of complexes:1 ×10^{-3} M; TBAP (0. 1 M) as supporting electrolyte in acetonitrile. Potential measured versus Ag(s)/Ag^+ (0.01 M, 0.10 M TBAP); add 0.681 V to convert to NHE. Pt-disc and Pt-wire were used as working and counter electrodes respectively. Scan rate: 100 mV s^{-1}.

Reference:

1. (a) R. Blessing, *Acta Crystallogr. Sect. A*, 1995, **51**, 33-38; (b) L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786-790; (c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

2. I. Mathew and W. Sun, *Dalton Trans*, 2010, **39**, 5885–98.