Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Mechanistic Insights of Nitric Oxide Oxygenation (NOO) Reactions of $\{CrNO\}^5$ & $\{CoNO\}^8$

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Materials. All reagents and solvents obtained from commercial sources (Sigma Aldrich Chemical Co. and Tokyo Chemical Industry) were of the best available purity and were used without further purification unless otherwise indicated. Solvents were dried according to reported literature and distilled under an inert atmosphere before use.[S1] BPMEN (BPMEN= N, N'-bis(2-pyridylmethyl)-1,2-diaminoethane) ligand was prepared according to reported literature.[S2]

Instrumentation. UV-vis spectra were recorded on an Agilent Cary 8454 diode array spectrometer equipped with a thermostat cell holder (UNISOKU Scientific Instruments) designed for low-temperature experiments. FT-IR spectra in solid form were recorded on the Bruker-Alpha Eco-ATR FTIR spectrometer using the standard KBr disk method. ^{1}H-NMR spectra were measured with a Bruker model Ascend 400 FT-NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were recorded on an Agilent Mass Spectrometer (6200 series TOF/6500 series Q-TOF B.08.00) by infusing samples directly into the source using a manual method. The spray voltage was set at 4.2 kV, and the capillary temperature at 80 °C.

Synthesis of $[(BPMEN)Co^{II}(CH_3CN)_2](BF_4)_2$. The preparation of $[(BPMEN)Co^{II}(CH_3CN)_2](BF_4)_2$ was carried out under an inert gas atmosphere inside the glove box. To a solution of $Co^{II}(BF_4)_2.6H_2O$ (340 mg, 1 mmol) in 5ml CH_3CN, a solution of BPMEN (270 mg, 1 mmol) ligand in 2ml of CH_3CN was added dropwise and kept for stirring for 12 hours at room temperature (298 K) under Argon (Ar) atmosphere. After 12 hours, the color of the solution changed to orange, indicating the completion of the reaction. Then excess ether (Et_2O) was added to the resulting solution, which produced an orangish color precipitate, and the same was collected by filtration. The orange powder was washed with Et_2O multiple times and dried under a vacuum to get pure $[(BPMEN)Co^{II}(CH_3CN)_2](BF_4)_2$. Yield: 479 mg (~ 82%).

Synthesis of $[(BPMEN)Co^{II}(CH_3CN)_2](BPh_4)_2$ (Co-1). $[(BPMEN)Co^{II}(CH_3CN)_2](BF_4)_2$ (372 mg, 0.63 mmol) was dissolved in 10 ml CH_3CN. A solution of $NaBPh_4$ (507 mg, 1.5 mmol) in CH_3CN was added dropwise to the solution of $[(BPMEN)Co^{II}(CH_3CN)_2](BF_4)_2$ at 298 K and stirred for 30 minutes under Ar atmosphere. After 30 minutes, the volume was reduced to 2 ml, and excess ether (Et_2O) was added to yield an orange-colored precipitate of Co-**1** formed at the bottom of the reaction mixture. The precipitate was filtered and again dissolved in CH_3CN and precipitated by adding excess Et_2O. The Et_2O was decanted, and the orange precipitate was washed with Et_2O multiple times. The solid was then dissolved in 2ml CH_3CN and kept for crystallization with Et_2O. Block-type orange crystals suitable for XRD analysis were obtained by vapor diffusion of Et_2O over 3-4 days at 298 K under Ar. Yield: 595 mg (~ 90 %). UV-vis spectrum of Co-**1** in CH_3CN at 298 K: λ_{max} = 465 nm (ε = 59 $M^{-1}cm^{-1}$). ^1H NMR (400 MHz, Acetonitrile-d_3) δ 226.34 (1H, s), 110.62 (2H, s), 93.13(2H, s), 80.18 (2H, s), 72.37 (4H, s), 51.70 (7H, s), 36.28 (4H, s). Anal. Calcd. For $C_{68}H_{68}B_2CoN_6$: C, 77.79; H, 6.53; N, 8.00; Found: C, 77.91; H, 6.48; N, 8.07; Magnetic moment, μ_{eff}= 4.62 BM.

Synthesis of $[(BPMEN)Co(NO)]^{2+}$ (1). Complex Co-**1** (105 mg, 0.1 mmol) was dissolved in 2 ml CH_3CN in a 30 ml vial inside a glove box and, capped with an airtight rubber septum and taken out. The solution was then cooled to 233 K and stirred for 5 minutes at 233 K under an Ar atmosphere. Then, the solution of Co-**1** was purged with excess $NO_{(g)}$ under the Ar atmosphere at 233 K. After purging $NO_{(g)}$, the color of the solution changed from orange to reddish-orange, indicating the formation of the Co-NO complex. The solution was further stirred for 30 minutes under NO pressure at 233K under Ar. After 60 minutes, the excess NO was removed by purging Ar. Precooled Ar-saturated Et_2O at 233 K was added to the reaction mixture using a cannula at 233 K with constant stirring. After adding ether, the solution was stirred for 2 minutes to form a brown precipitate at the bottom of the vial. The excess Et_2O was removed, and the precipitate was washed multiple times with cold Et_2O. The compound was then dried using a standard schlenk line and kept inside the glove box. Yield: 76 mg (~ 76 %). UV-vis spectrum of **1** in CH_3CN at 233 K: λ_{max} = 375 nm (ε = 956 $M^{-1}cm^{-1}$). FT-IR (in Solution IR): 1653 cm^{-1} (NO stretching). Mass (*m/z*): Calcd: *m/z* 376.1, Found: *m/z* 376.1, 364.1, 164.5 for $[(BPMEN)Co(NO)(OH)]^+$, $[(BPMEN)Co(Cl)]^+$, $[(BPMEN)Co]^{2+}$, respectively. **1-BF$_4$** was synthesized using a similar method by using $[(BPMEN)Co^{II}(CH_3CN)_2](BF_4)_2$. ^1H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 9.37 – 8.65 (m, 2H), 8.39 – 8.11 (m, 2H), 8.00 – 7.40 (m, 4H), 5.48 – 3.96 (m, 4H), 3.93 – 2.99 (m, 4H), 2.87 (s, 6H).

Synthesis of [(BPMEN)Cr(NO)(Cl)](Cl) (2). Complex **2** was prepared by the following already reported procedure.[S3] The preparation of **2** was carried out under an Ar atmosphere. An excess $NO_{(g)}$ was purged to a CH_3CN (5 mL) solution of $[(BPMEN)Cr^{II}(Cl)_2]$ (131 mg, 0.33 mmol) for 10 minutes under Ar atmosphere, which showed a color change from greyish to dark green. Then, the reaction mixture was purged with Ar gas for 10 min to remove the excess $NO_{(g)}$. Excess Et_2O was added to the resulting solution to yield the dark green powder and collected by filtration under Ar. Then the green powder was dried under a vacuum. Yield: 125 mg (~ 90%).

Generation of $[(BPMEN)Co^{II}(NO_2^-)_2]$ (3) in the reaction of 1 + KO_2/18-crown-6. To determine the NOM product, complex **1** was reacted with KO_2 in the presence of 18-crown-6. In this regard, complex **1** (100 mg, 0.10 mmol) was reacted with 2 equivalent KO_2/18-crown-6. 100 mg of **1-BF$_4$** was taken in a 50 ml vial and sealed with rubber septum inside the glove box and taken out and cooled to 233 K. To this precooled Ar saturated CH_3CN at 233 K was added and stirred for 5 minutes at 233 K under Ar. After that, 2 equivalent of KO_2/18-crown-6 was added to the solution at 233 K under the Ar atmosphere. The color of the solution immediately changed from reddish-orange to dark red, indicating a reaction of **1** with KO_2. The solution was further stirred for 30 minutes under Ar at 233 K. After 30 minutes, the mixture was warmed to 298 K, and dry Et_2O was added to yield a brown colour precipitate. The residue was washed with Et_2O multiple times and dried under vacuum to yield complex **3**. The complex is then dissolved in 2 ml of Dimethylformamide (DMF) under an Ar atmosphere and then crystallized with Et_2O by vapour diffusion. XRD-suitable crystals were obtained by vapour diffusion of Et_2O to solution **3** in DMF within a week at 298 K under Ar. Crystalline Yield. 31.1 mg (~ 74 %) The isolated product was characterized to be $[(BPMEN)Co^{II}(NO_2^-)_2]$ by various spectroscopical techniques. $\lambda_{max} = 360$ nm ($\varepsilon = 4000$ M^{-1} cm^{-1}). FT-IR (in KBr pellet): 1270 cm^{-1} (NO_2^- stretching). ^1H NMR (400 MHz, DMSO-d_6) δ 195.13 (s, 1H), 142.52 – 131.97 (m, 2H), 82.67 (d, J = 755.9 Hz, 6H), 72.04 – 56.07 (m, 3H), 48.55 (d, J = 240.1 Hz, 2H), 34.85 (s, 2H), 28.09 – 15.60 (m, 6H). Mass (*m/z*): Calcd: *m/z* 375.1, Found: *m/z* 375.1 for $[(BPMEN)Co(NO_2)]^+$. Anal. Calcd. For $C_{16}H_{22}CoN_6O_4$: C, 45.61; H, 5.26; N, 19.95; Found: C, 45.72; H, 5.21; N, 20.01; Magnetic moment, μ_{eff}= 1.77 BM. $[(BPMEN)Co^{II}(^{15}NO_2^-)_2]$ **(3-$^{15}NO_2$)** was prepared in the reaction of **1-^{15}NO** + KO_2. FT-IR (in KBr pellet): 1245 cm^{-1} (NO_2^- stretching) Mass (*m/z*): Calcd: *m/z* 376.1, Found: *m/z* 376.1 for $[(BPMEN)Co(^{15}NO_2)]^+$.

Generation of $[(BPMEN)Cr^{III}(NO_2^-)(Cl)](Cl)$ (4) in the reaction of 2 + KO_2/18-crown-6. To determine the NOM product, complex **2** was reacted with KO_2 in the presence of 18-crown-6. In this regard, complex **2** (97 mg, 0.23 mmol) was reacted with 2 equivalent KO_2/18-crown-6. 97 mg of **2** was dissolved in 10 ml of CH_3CN in a 50 ml vial, sealed with rubber septum inside a glove box, and taken out and cooled to 233 K. After that, 2 equivalent of KO_2/18-crown-6 was added to the solution at 233 K under Ar atmosphere. The color of the solution immediately changed from dark green to dark red, indicating the intermediate species' formation. The color further changes from dark red to brown over a time period of 60 minutes under Ar at 233 K, indicating completion of the reaction. After 60 minutes, the mixture was warmed to 298 K and stirred for 15 minutes. Then, the solution was concentrated at 2 ml. Dry Et_2O was added to the solution to yield a yellowish-brown color precipitate. The precipitate was washed with Et_2O under Ar multiple times and dried under vacuum to yield complex **4**. Yield. 70 mg (~ 70 %) The isolated product was characterized to be $[(BPMEN)Cr^{II}(NO_2^{-})(Cl)]^{+}$ by various spectroscopical techniques. λ_{max} = 370 nm (ε = 715 M^{-1} cm^{-1}). FT-IR (in KBr pellet): 1270 cm^{-1} (NO_2^{-} stretching). Mass (*m/z*): Calcd: *m/z* 403.1, Found: *m/z* 403.1 for $[(BPMEN)Cr(NO_2^{-})(Cl)]^{+}$. Anal. Calcd. For $C_{16}H_{22}Cl_2CrN_5O_2$: C, 43.75; H, 5.05; N, 15.94; Found: C, 43.72; H, 5.10; N, 15.89; Magnetic moment, μ_{eff}= 3.54 BM. $[(BPMEN)Cr^{II}(^{15}NO_2^{-})(Cl)](Cl)$ **(4-^{15} NO_2^{-})** was prepared in the reaction of **2-^{15}NO** + KO_2. FT-IR (in KBr pellet): 1243 cm^{-1} (NO_2^{-} stretching) Mass (*m/z*): Calcd: *m/z* 404.1, Found: *m/z* 404.1 for $[(BPMEN)Cr(^{15}NO_2)(Cl)]^{+}$.

Reactivity Studies. All UV-vis spectral measurements were performed using a quartz cuvette in CH_3CN at 233 K to 298 K. We performed the reactions under the Ar atmosphere wherever required. All kinetic reactions were run at least three times, and the data reported here are the average outcome for these reactions. We performed all the reactions at 273 K /or 233 K. The formation of complexes **3** and **4** in the above reactions was identified by comparing them with authentic samples.

Solution IR Spectroscopy for Complex 1. The formation of $\{CoNO\}^8$ species was followed by monitoring the characteristic nitrosyl stretching vibration. A CH_3CN solution of Co-**1** (4 mM) was prepared in the glove box, and the liquid demountable cell kit with NaCl solid plate setup was filled with the same solution and air-tightened with parafilm. In a separate sample vial, complex Co-**1** (4 mM in CH_3CN) was prepared, attached with a rubber septum, and cooled to 233 K. First, the FT-IR spectrum of **1** was collected in solution IR. Complex Co-**1** in a separate vial that was purged with $NO_{(g)}$; as soon as the color changed to reddish-orange, the reaction mixture was frozen by dipping in liquid N_2. The vial was purged with Ar and a vacuum to remove excess NO gas. After the removal of excess NO gas, it slowly warmed to

233 K, and as soon it started liquefying, the reaction mixture was taken and injected into the clean demountable cell holding**,** and then the IR spectrum was collected at 298 K. In the following scan, we observed the formation of a new peak at 1686 cm$^{-1,}$ which then decayed to form a peak at 1653 cm$^{-1,}$ corresponding to **1** species.

Labeling (^{14}N & ^{15}N) experiments using FT-IR spectroscopy. We have recorded the FT-IR spectra of the reaction mixtures in their solid state as KBr pellets to follow the N-atom in the NOM reactions. These reactions were executed under an inert atmosphere. 20 mM solutions of **1** and **2** were prepared in CH_3CN in two different vials under an Ar atmosphere and cooled to 233 K. Then, they are reacted to KO_2/18-crown-6 at 233 K in two different reactions. After completion of the reaction, the reaction mixture was warmed to 298 K, and the solvent was evaporated under a vacuum and washed with Et_2O. The FT-IR spectrum of the reaction mixture of **1** with KO_2/18-crown-6 showed a characteristic peak at 1270 cm^{-1} for Co-bound $NO_2^–$. The FT-IR spectrum of the reaction mixture of **2** with KO_2/18-crown-6 showed a characteristic peak at 1270 cm^{-1}, which corresponds to Cr-bound $NO_2^–$. This peak was shifted to 1245 cm^{-1} and 1243 cm^{-1} when the reaction mixture of **1**-^{15}NO + KO_2/18-crown-6 and **2**-^{15}NO + KO_2/18-crown-6 was analyzed, respectively. The change in the IR stretching frequency ($\Delta \sim 30$ cm^{-1}) confirmed that an increase in the reduced mass of N-atom (from ^{14}N to ^{15}N) is responsible for decreasing the IR stretching frequency of the $NO_2^–$ functional group.

^{15}N Labelling experiments using ESI-MS spectrometry. Furthermore, to establish the source of N, complex **1**-^{15}NO and **2**-^{15}NO were reacted with KO_2/18-crown-6 in CH_3CN under Ar at 233 K in two different Experiments. For the above experiments, two cuvettes (4 mL) containing a solution of complex **1**-^{15}NO and **2**-^{15}NO (0.5 mM / 2.5 mL) in CH_3CN sealed with an airtight rubber septum under an Ar atmosphere were taken out from a glovebox and placed in UV cuvette holder attached to a unisoku crystal. The solutions were further cooled to 233 K and reacted with KO_2/18-crown-6 in two separate experiments, and the reactions were monitored by UV-vis spectroscopy. After the completion of the reactions, the ESI-MS spectra of all reaction mixtures were recorded. The ESI-MS spectrum of the reaction mixture obtained in the reaction of **1**-^{15}NO + KO_2/18-crown-6 showed a prominent peak at *m/z* 376.1, whose mass value and isotopic distribution pattern correspond to $[(BPMEN)Co(^{15}NO_2)]^+$ (calcd *m/z* 376.1). Whereas the reaction of **1**-^{15}NO + KO_2/18-crown-6 showed a prominent peak at *m/z* 404.1, whose mass value and isotopic distribution pattern correspond to $[(BPMEN)Cr(^{15}NO_2)(Cl)]^+$. These reactions indicate that NO_2^- moiety in **3** and **4** are derived from the NO moiety of complexes **1** and **2,** respectively.

Detection of $[Co\text{-}PN]^+$ and $[Cr\text{-}PN]^+$ intermediate (Phenol ring nitration test): To confirm the formation of $[Co\text{-}PN]^+$ and $[Cr\text{-}PN]^+$, the phenol ring nitration test performed by trapping $•NO_2$ (produced from the homolysis of PN $\{ONO\text{-}O\}^-$ moiety of M-PN intermediate) using 2,4-di-tert-butylphenol (2,4-DTBP) was performed. In this regard, we have reacted both **1** (1 mM) and **2** (1 mM) with KO_2/18-crown-6 in the presence of 2,4-DTBP (5 mM) in CH_3CN at 233 K under Ar. The reaction mixture was kept for half an hour at 233 K, then warmed to 298 K, and stirred for 30 minutes. GC-MS and HPLC analyzed the reaction mixture for qualitative and quantitative estimation. The yield was calculated using the standard plots of NO_2-2,4-DTBP with 2,4-DTBP-D. In both experiments, we observed the formation of NO_2-2,4-DTBP with 2,4-DTBP-D, suggesting the presence of $[Co\text{-}PN]^+$ and $[Cr\text{-}PN]^+$intermediate. The amount of NO_2-2,4-DTBP formed in the reaction of **1** and $O_2^{•-}$ was found to be ~ 52 (± 2) % and ~ 12 (± 2) % 2,4-DTBP-D. While in the reaction mixture of **2** and $O_2^{•-}$, the amount of NO_2-2,4-DTBP formed in the reaction was found to be ~ 65 (± 3) % and ~ 8 (± 2) % 2,4-DTBP-D.

Single-Crystal XRD Studies: Single-crystal XRD data were collected at 100 K on a Bruker X-ray diffractometer (Photon III-Duo) using monochromated MoKα (lambda = 0.7107 Å) radiation. The collected frames were integrated, scaled, and merged, and absorption correction was performed using the program package APEX4 (Bruker 2022) to determine the unit cell. The structure was solved with SHELXS and refined against F2 by weighted full-matrix least squares using SHELXL.[S4.] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed at calculated positions and refined using a riding model. Detailed crystallographic data and structural refinement parameters are summarized in Table T1 – T2. CCDC-2206431-2206432 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Nitric Oxide Preparation and Purification. Nitric oxide (NO) was prepared and purified by following a detailed procedure, as shown in Figure. S23. First, NO gas was prepared by the reaction of $NaNO_2$ with H_2SO_4 under an Argon (Ar) atmosphere and then passed through two different types of columns. First, pass through a column filled with NaOH beads to remove higher nitrogen oxide impurities. After that, the gas passes through two columns filled with NaOH beads molecular sieves to remove the minor amount of remaining higher nitrogen oxides and moisture impurities. The highly purified NO gas was then collected in a vacuum Schlenk flask fitted with a rubber septum (free from oxygen after several cycles of vacuum and Ar purging). High-pressure NO gas (with pressure >1 atmosphere; the septum bulges outward due to high pressures) then passes through an Ar-saturated (oxygen-free) and dry CH_3CN solution for 15 minutes. The concentration of NO in the NO-saturated CH_3CN solution is ~14 mM.[S5]

Magnetic moment calculation and determination of the number of unpaired electrons in complex Co-**1, 3, and 4**: Evans' method of ^{1}H-NMR was performed to determine the number of unpaired electrons (spin-state) in complex Co-**1**, **3,** and **4** at room temperature[S6-S8].

WILMAD® coaxial insert (with a sealed capillary) tube containing the only CD_3CN solvent (with 1.0 % TMS) was inserted into three different normal NMR tubes containing the complex Co-**1** (4.0 mM in CD_3CN, with 0.1 % TMS), **3** (4.0 mM in CD_3CN, with 0.1 % TMS), and **4** (4.0 mM in CD_3CN, with 0.1 % TMS). We have calculated the chemical shift value of the TMS / solvent peak in the presence of complex Co-**1, 3**, and **4** concerning that of the TMS / solvent peak in the inner NMR tube. The magnetic moment was calculated using the given equation.

Co-**1**

$$\mu_{eff} = 0.0618(\Delta\nu T / 2fM)^{1/2}$$

$$\mu_{eff} = 0.0618 * (60 * 298 / 2 * 400 * 0.004)^{1/2}$$

$$\mu_{eff} = 4.62 \text{ BM}$$

3

$$\mu_{eff} = 0.0618(\Delta\nu T / 2fM)1/2$$

$$\mu_{eff} = 0.0618 * (8.8 * 298 / 2 * 400 * 0.004)$$

$$\mu_{eff} = 1.77 \text{ BM}$$

4

$$\mu_{eff} = 0.0618(\Delta\nu T / 2fM)1/2$$

$$\mu_{eff} = 0.0618 * (35.2 * 298 / 2 * 400 * 0.004)$$

$$\mu_{eff} = 3.54 \text{ BM}$$

Where f = oscillator frequency (MHz) of the superconducting spectrometer, T = absolute temperature, M = molar concentration of the complex, and ν = difference in frequency (Hz) between the two TMS signals[S9]. The calculated magnetic moment of complexes Co-**1, 3**, and **4** were determined to be 4.62 BM, 1.77 BM, and 3.54 BM, respectively, suggesting 3, 1, and 3 unpaired electrons in the metal center of complexes Co-**1, 3**, and **4.**

Equilibrium constant (K_{eq}) calculation: The Equilibrium constant (K_{eq}) for complex **1** was calculated using the following equation[S9]

$$\frac{A_{obs} - A_0}{A_\infty - A_{obs}} = k_{eq}[\mathrm{NO}]$$

A_{obs} = absorbance at a certain NO concentration, A_0 = absorbance at zero NO concentration, A_∞ = Absorbance at ∞ NO concentration, K_{eq} = equilibrium constant, T = Reaction temperature, R = gas constant. The calculated K_{eq} value for **1** was found to be 88 M^{-1} at 298 K.

Calculation of Binding Constant (*k_b*): The binding constants (k_b) *for **1** and **2*** were determined by titrating the complex $[(\mathrm{BPMEN})\mathrm{Co^{II}}]^{2+}$ and $[(\mathrm{BPMEN})\mathrm{Cr^{II}}(\mathrm{Cl})_2]$ concerning the different concentrations of NO, respectively. The stock solutions of $[(\mathrm{BPMEN})\mathrm{Co^{II}}]^{2+}$ (**2** mM) $[(\mathrm{BPMEN})\mathrm{Cr^{II}}(\mathrm{Cl})_2]$ (**1** mM) were prepared in CH_3CN. The UV-vis spectra of $[(\mathrm{BPMEN})\mathrm{Co^{II}}]^{2+}$ and $[(\mathrm{BPMEN})\mathrm{Cr^{II}}(\mathrm{Cl})_2]$ with increasing concentration of the $NO_{(g)}$ were recorded by means to get absorbance values. The binding constants were calculated using the Benesi-Hildebrand equation.[S10 and S11] k_b were calculated from the equation stated below.

$$1/(A-A_o) = 1/\{K_b(A_{max}–A_o)\ [X]_n\} + 1/[A_{max}-A_o]$$

Here, A_o is the absorbance of $[(\mathrm{BPMEN})\mathrm{Co^{II}}]^{2+}$ or $[(\mathrm{BPMEN})\mathrm{Cr^{II}}(\mathrm{Cl})_2]$ in the absence of $NO_{(g)}$, and A is the absorbance in the presence of $NO_{(g)}$ at different concentration, A_{max} is the absorbance in the presence of excess $NO_{(g)}$, and Kb is the binding constant (M^{-1}). The calculated Kb value for **1** and **2** was found to be 83 M^{-1} and 1170 M^{-1} at 298 K, respectively.

Table T1 Crystallographic data for for **Co-1** and **3**.

	Co-1	**3**
Chemical formula	$C_{68}H_{68}B_2CoN_6$	$C_{16}H_{22}CoN_6O_4$
Formula weight	1049.83	421.33
Wavelength /Å	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	Cc	Pbcn
T, K	297.0	101 (2)
a, Å	24.9696(16)	13.350(3)
b, Å	37.384(3)	8.745(2)
c, Å	18.0414(11)	15.324(4)
α, °	90	90
β, °	133.598(2)	90
γ, °	90	90
V/ $Å^3$	12196.1(15)	1789.0(7)
Z	8	4
Calculated density, g/cm^3	1.144	1.564
Abs. Coeff. /mm^{-1}	0.326	0.996
Reflections collected	36861	19799
Unique reflections	13980	1640
Refinement method	Least-squares on F^2	Least-squares on F^2
Data/restraints/parameters	13980/32/1396	1640/0/127
Goodness-of-fit on F^2	1.038	1.013
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0486 wR2 = 0.1328	R1 = 0.0912 wR2 = 0.2346
R indices (all data)	R1 = 0.0588 wR2 = 0.1424	R1 = 0.0990 wR2 = 0.2423

Table T2 Selected bond lengths (Å) and bond angles (°) for **Co-1 and 3**.

Co-1		**3**	
Co1 N1	2.126(7)	Co1 O1^1	2.068(4)
Co1 N2	2.184(7)	Co1 O1	2.068(4)
Co1 N3	2.143(7)	Co1 N2	2.154(4)
Co1 N4	2.156(7)	Co1 N2^1	2.154(4)
Co1 N5	2.168(9)	Co1 N3^1	2.187(5)
Co1 N6	2.129(10)	Co1 N3	2.187(5)
		O1 N4	1.266(7)
		O2 N4	1.218(7)
N1 Co1 N2	102.0(2)	O1^1 Co1 O1	104.5(2)
N1 Co1 N3	176.6(3)	O1 Co1 N2^1	88.26(16)
N1 Co1 N4	77.8(3)	O1 Co1 N2	96.51(16)
N1 Co1 N5	91.9(3)	O1^1 Co1 N2^1	96.51(16)
N1 Co1 N6	87.8(3)	O1^1 Co1 N2	88.26(16)
N3 Co1 N2	77.1(3)	O1 Co1 N3^1	87.41(18)
N3 Co1 N4	98.8(3)	O1 Co1 N3	166.39(18)
N3 Co1 N5	91.3(3)	O1^1 Co1 N3	87.41(18)
N4 Co1 N2	83.3(3)	O1^1 Co1 N3^1	166.39(18)
N4 Co1 N5	166.6(3)	N2^1 Co1 N2	172.2(2)
N5 Co1 N2	90.4(3)	N2 Co1 N3	77.02(17)
N6 Co1 N2	169.5(3)	N2^1 Co1 N3	97.00(17)
N6 Co1N3	92.9(3)	N2 Co1 N3^1	97.00(17)
N6 Co1 N4	95.1(3)	N2^1 Co1 N3^1	77.02(17)
N6 Co1 N5	93.2(3)	N3^1 Co1 N3	81.6(3)
		N4 O1 Co1	118.9(3)
		O2 N4 O1	116.1(5)

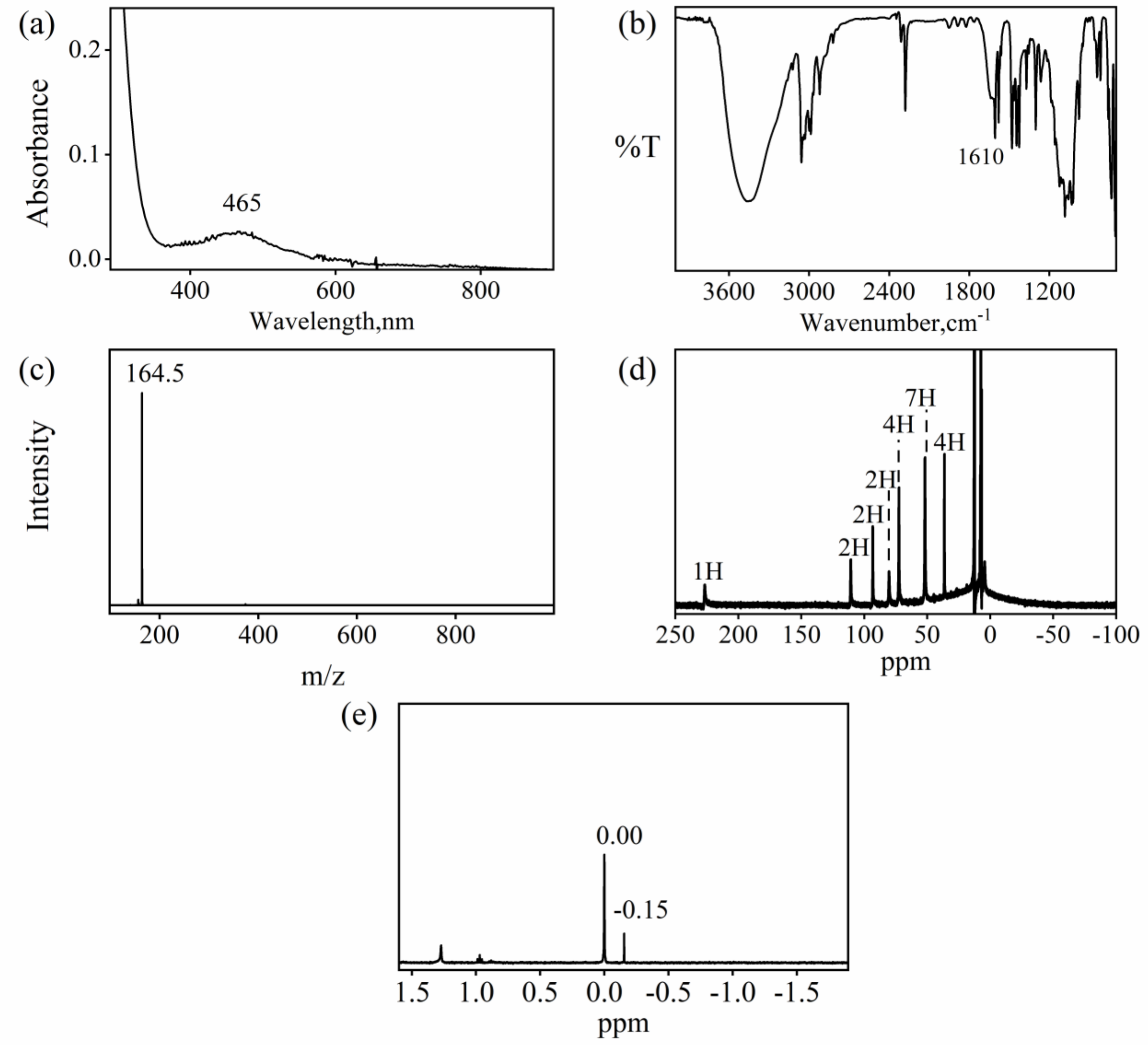

Figure S1. (a) The UV-vis spectrum of Co-**1** (1 mM) in CH_3CN at 298 K under Ar Atmosphere. (b) FT-IR spectrum of Co-**1** recorded in KBr pellet at 298 K. (c) ESI-MS spectrum of Co-**1.** The peak at *m/z* 164.5 assigned to be $[(BPMEN)Co]^{2+}$ (calcd *m/z* 164.5). (d) Long Range ^1H-NMR (400 MHz) spectrum of Co-**1** in CD_3CN. (e) ^1H-NMR (400 MHz) spectrum of Co-**1** (4 mM) in CD_3CN (0.1 % TMS), recorded in a coaxial NMR tube, with inside CD_3CN (1.0 % TMS) at 298 K.

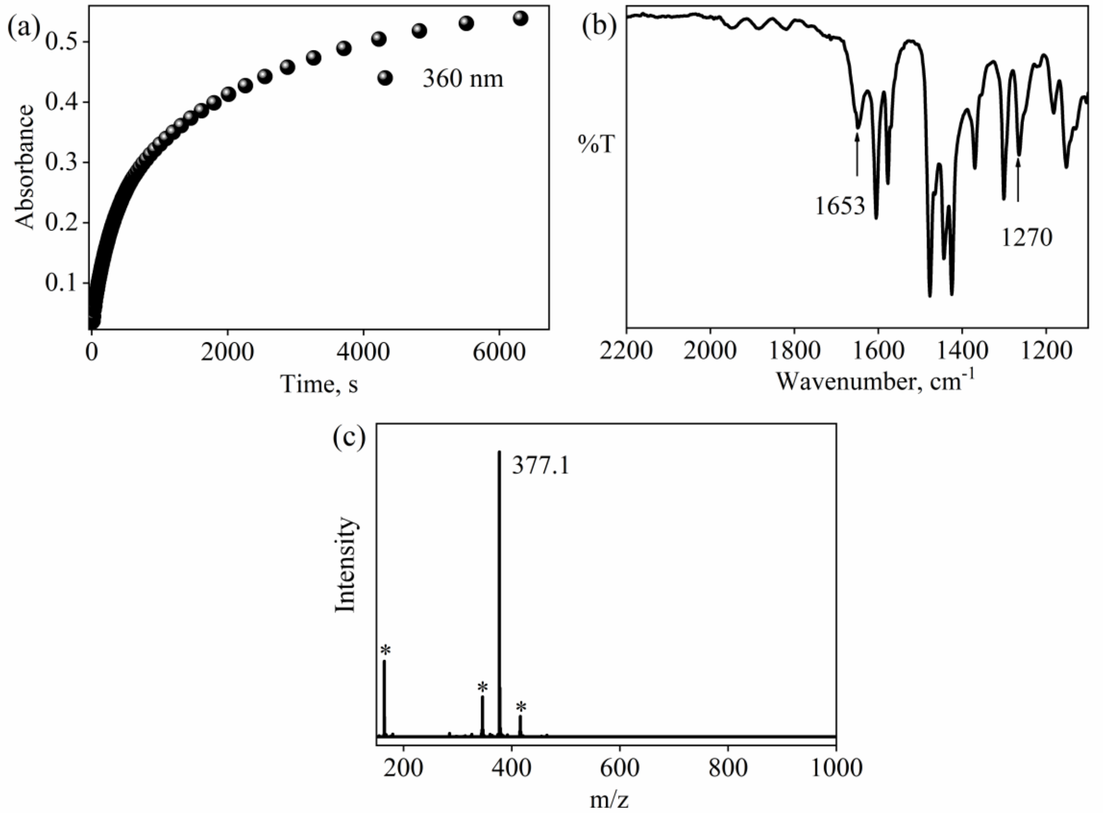

Figure S2. (a) The time course of formation of **1** was monitored at 375 nm upon addition of $NO_{(g)}$ to a solution of Co-**1** (0.5 mM) in CH_3CN at 233 K under Ar (b) FT-IR (liquid) spectrum of **1** recorded at 233 K. (c) ESI-MS spectrum of complex **1-^{15}NO** in CH_3CN. The peak at *m/z* 377.1 is assigned to be $[(BPMEN)Co(^{15}NO)(OH)]^+$ (calcd: *m/z* 377.1). The peaks at 164.5, 346.1, and 416.1 marked with an asterisk are assigned to be $[(BPMEN)Co]^{2+}$ (calcd: *m/z* 164.5), $[(BPMEN)Co(OH)]^+$ (calcd: *m/z* 346.1) and $[(BPMEN)Co(BF_4)]^+$ (calcd: *m/z* 416.1) respectively.

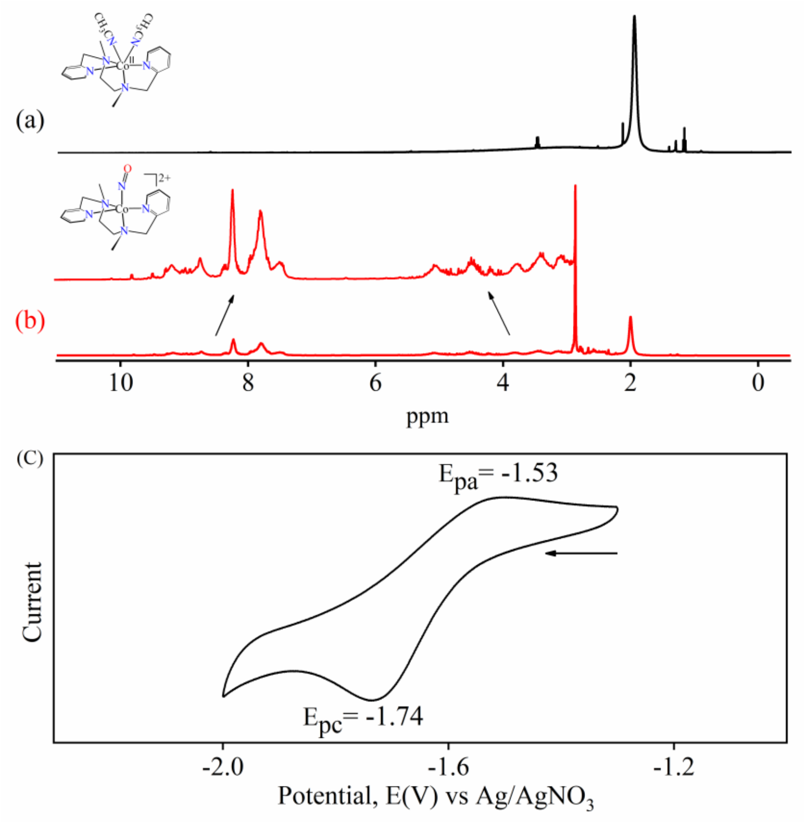

Figure S3. ^{1}H-NMR (400 MHz) spectrum of (a) Co-**1** (b) $[(BPMEN)Co(NO)]^{2+}$ in CD_3CN at 298 K under Ar atmosphere. (c) Cyclic voltammogram of **1** (1 mM) in CH_3CN containing n-Bu_4NPF_6 (0.25 M) as a supporting electrolyte (scan rate = 0.08 V/s) at 233 K.

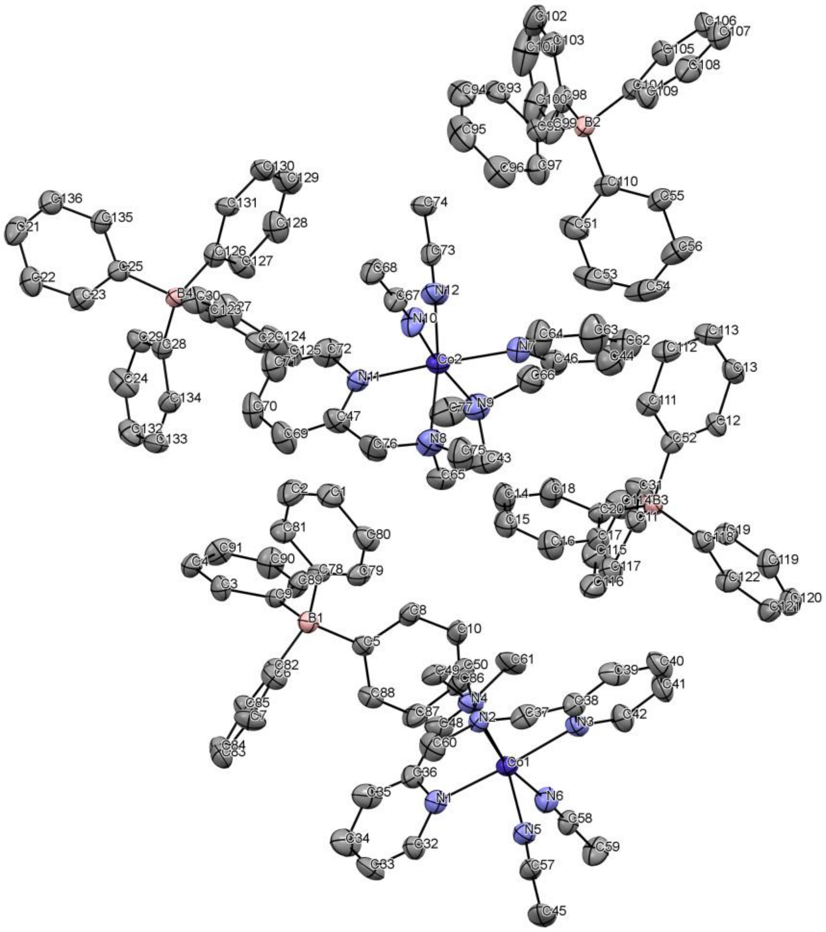

Figure S4. Displacement ellipsoid plot (30 % probability) of Co-**1** at 298 K. H-atoms have been removed for clarity.

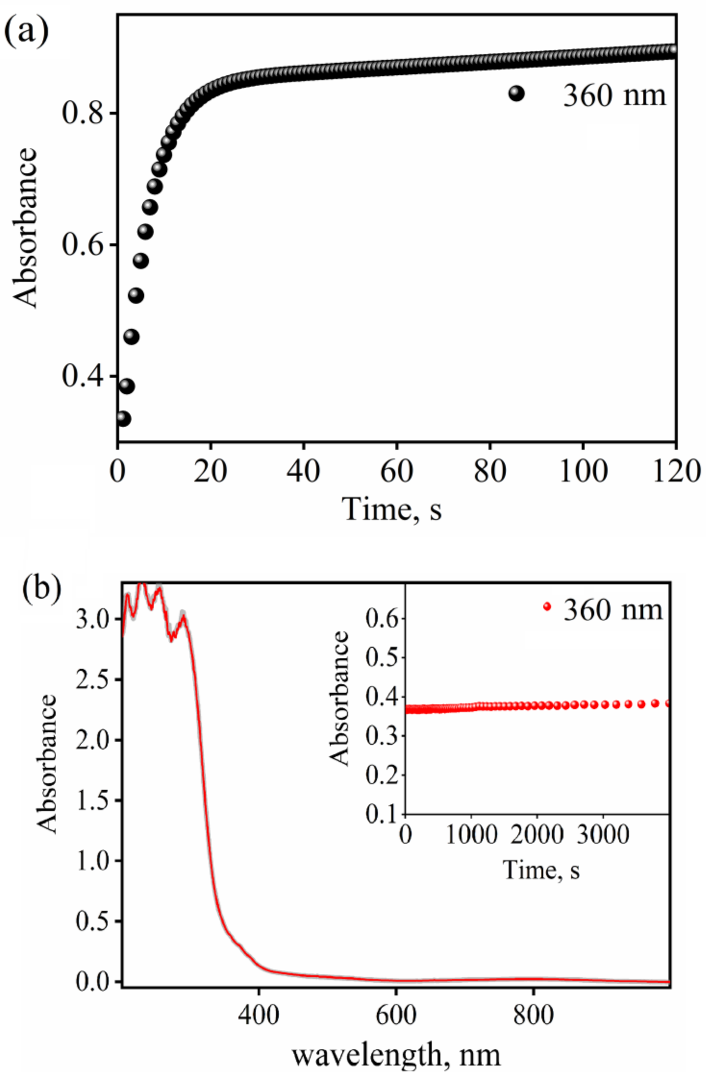

Figure S5. (a) The time course of the formation of **3** was monitored at 360 nm upon the addition of KO_2/18-crown-6 to a solution of **1** (0.25 mM) in CH_3CN at 233 K. (b) The UV-vis spectra of **1** (0.5 mM) in CH_3CN at 233 K under Ar atmosphere. Inset: time trace of **1** followed at 360 nm.

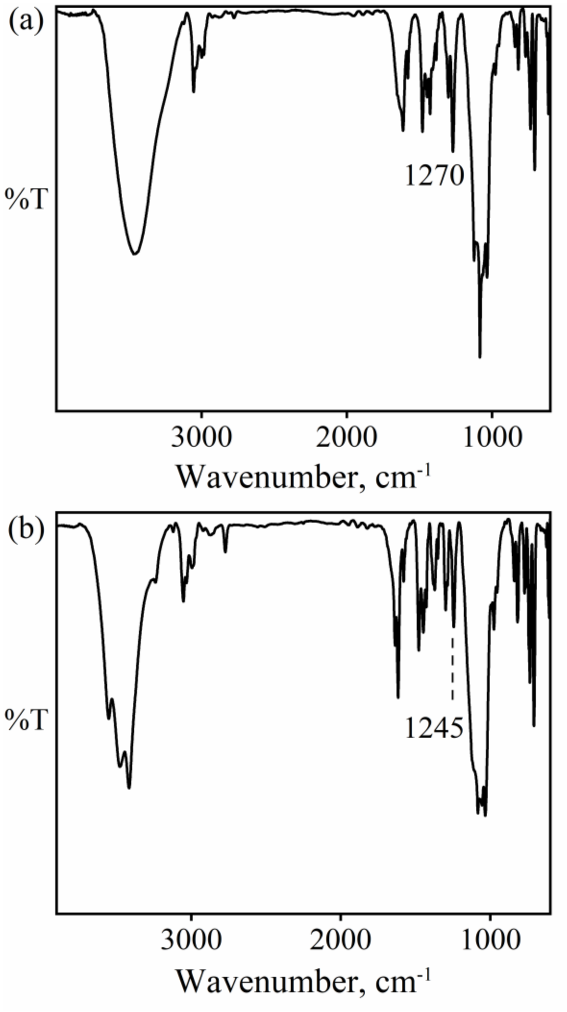

Figure S6. FT-IR spectrum of isolated product, obtained in the reaction of (a) **1** + KO_2/18-crown-6 (b) **1-^{15}NO** + KO_2/18-crown-6 recorded in KBr pellet at 298 K. The spectrum showed the peaks for [Co-$^{14}NO_2^-$] (1270 cm^{-1}), and [Co-$^{15}NO_2^-$] (1243 cm^{-1}), respectively.

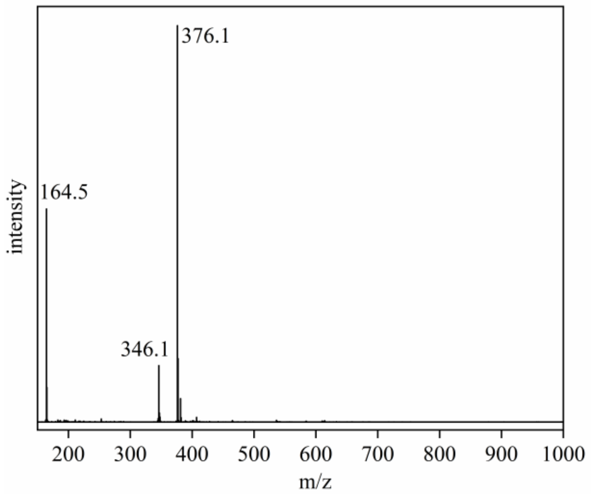

Figure S7. ESI-MS spectrum of isolated complex **3-^{15}**NO_2^-, formed in the reaction of $[(BPMEN)Co(^{15}NO)]^{2+}$ with KO_2/18-crown-6 recorded in CH_3CN. The peak at *m/z* 376.1 is assigned to be $[(BPMEN)Co(^{15}NO_2)]^+$ (calcd: *m/z* 376.1). The peaks at 164.5 and 346.1 are assigned to be $[(BPMEN)Co]^{2+}$ (calcd: *m/z* 164.5) and $[(BPMEN)Co(OH)]^+$ (calcd: *m/z* 346.1), respectively.

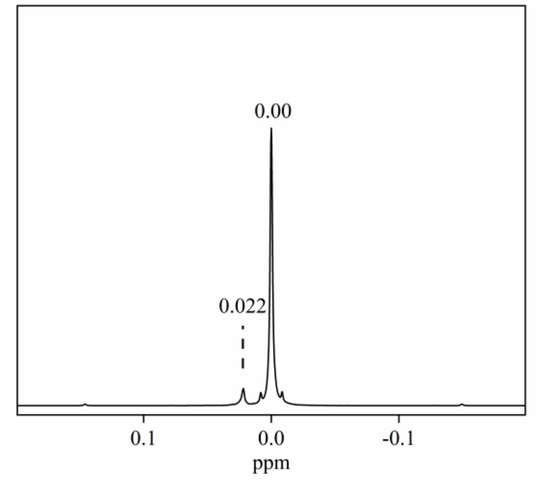

Figure S8. ^{1}H-NMR (400 MHz) spectrum of **3** (4 mM) in CD_3CN (0.1 % TMS) , recorded in a coaxial NMR tube, with inside CD_3CN (1.0 % TMS) at 298 K.

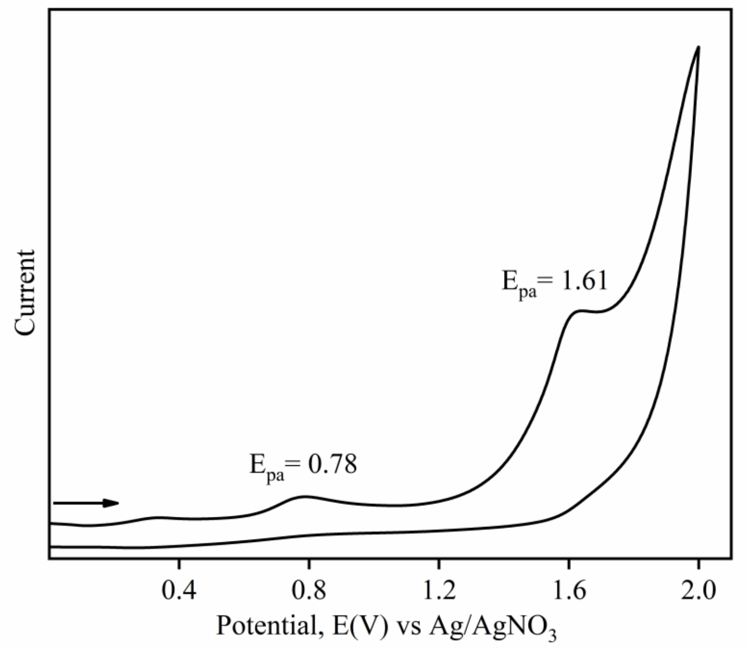

Figure S9. Cyclic voltammogram of **3** (1 mM) in CH_3CN containing n-Bu_4NPF_6 (0.25 M) as a supporting electrolyte (scan rate = 0.1 V/s) at 298 K.

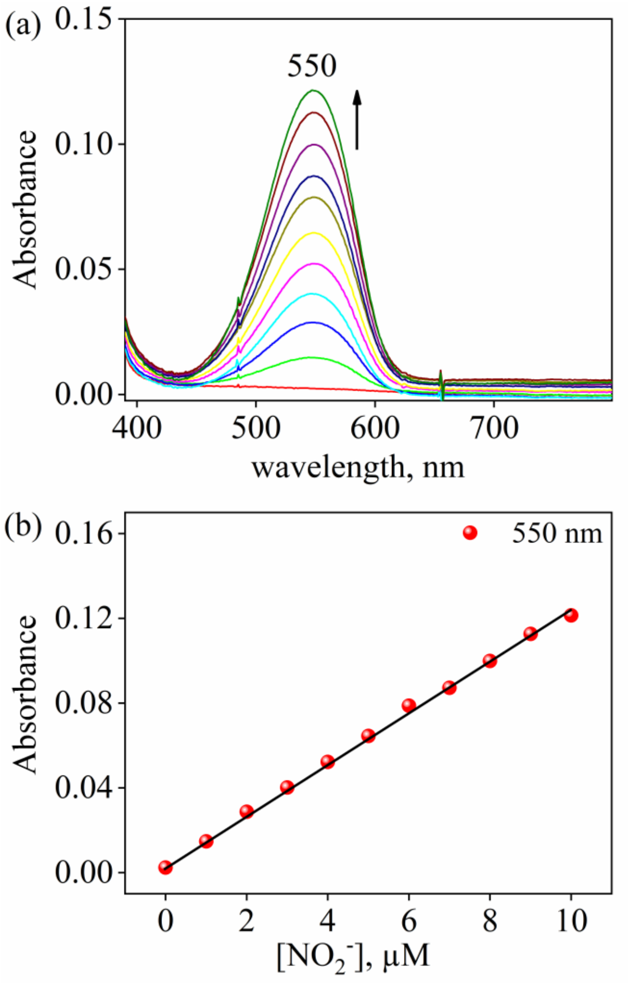

Figure S10. a) UV-vis spectral changes showing the increase in the absorbance at 550 nm (due to the formation of azo dye) upon the addition of $NaNO_2$ solutions in various concentrations (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10 μM) to Griess reagent at 298 K. (b) Spectral calibration curve for the formation of the peak at 550 nm as a function of the concentration of $NaNO_2$ (μM) in increments of 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.

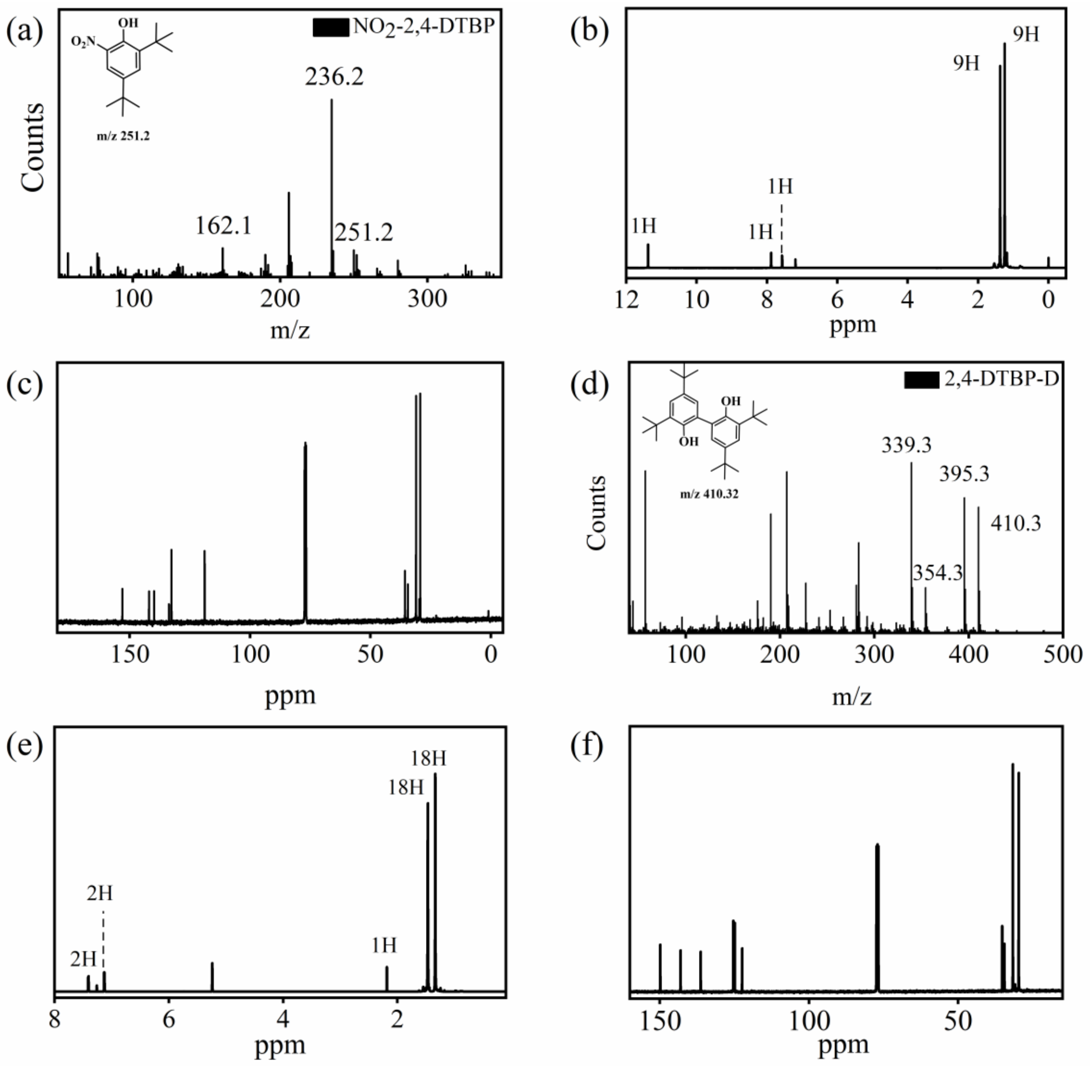

Figure S11. (a) GC-MS characterization of nitro-2,4-DTBP (NO_2-2,4-DTBP): The peaks at *m/z* 251.2 and 236.2 are assigned to be nitro-2,4-DTBP and loss of CH_3 from nitro-2,4-DTBP. (b) ^1H NMR (400 MHz) spectra of NO_2-2,4-DTBP in $CDCl_3$ at 298 K (c) ^{13}C NMR (100 MHz) spectra of NO_2-2,4-DTBP in $CDCl_3$ at 298 K (d) GC-MS characterization of 2,4-DTBP-dimer (2,4-DTBP-D); the peaks at *m/z* 410.3, 395.3, 339.3, and 190.2 are assigned to be 2,4-DTBP-D, loss of CH_3 from 2,4-DTBP-D, loss of C_4H_8 and CH_3 from 2,4-DTBP-D and loss of CH_3 from monomer 2,4-DTBP. The peaks were compared with the NIST standard library. (e) ^1H NMR (400 MHz) spectra of 2,4-DTBP-D in $CDCl_3$ at 298 K (f) ^{13}C NMR (100 MHz) spectra of 2,4-DTBP-D in $CDCl_3$ at 298 K

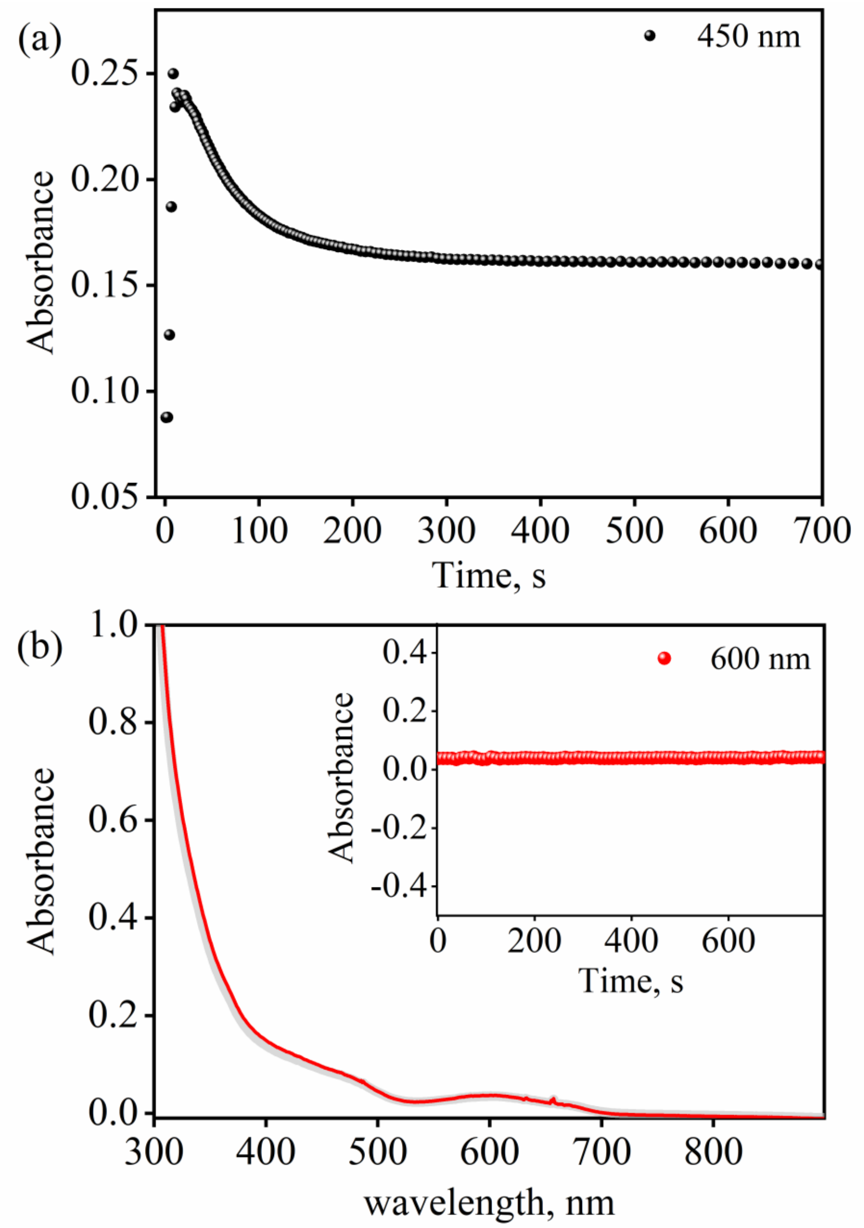

Figure S12. (a) The time course of the decay of **2** (black-circles) on reaction with KO_2 monitored at 450 nm in CH_3CN at 298 K. (b) UV-vis spectral changes of **2** (1 mM) in CH_3CN under Ar at 298 K. The Inset shows the time course of the decay of **2** (red-circles) monitored at 600 nm in CH_3CN at 298 K.

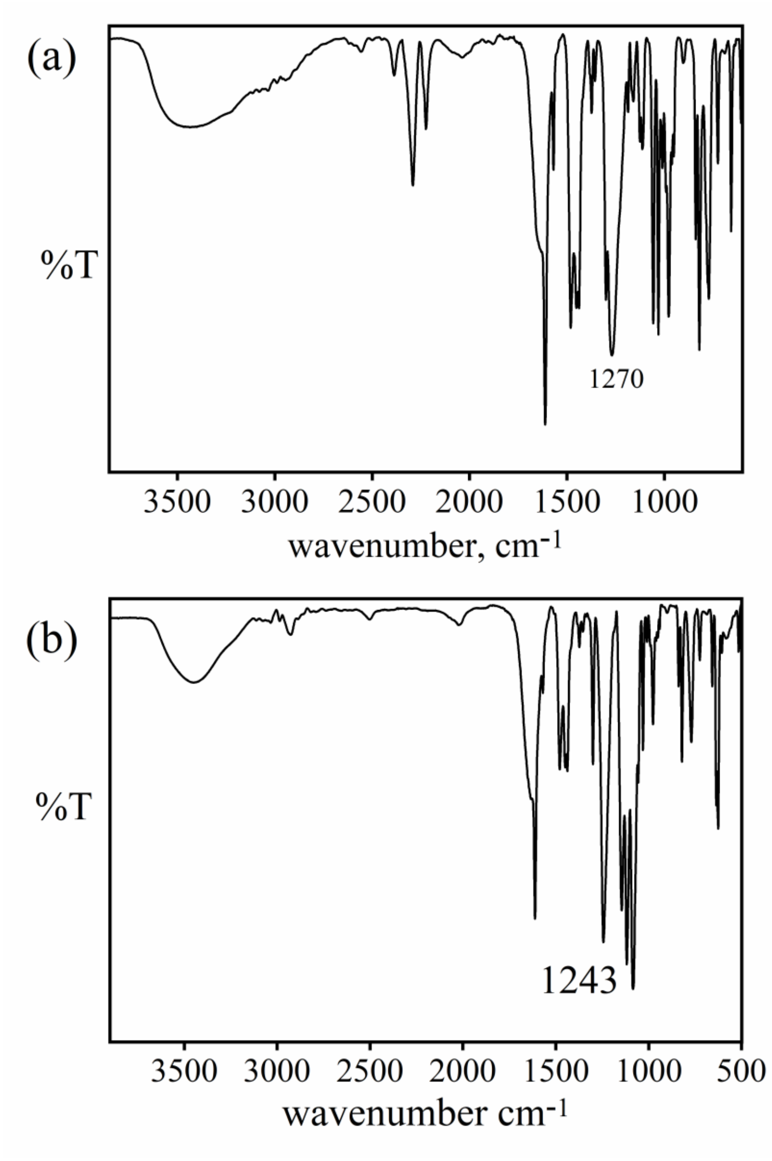

Figure S13. FT-IR (Solution) spectra of (a) **2** + KO_2/18-crown-6 (b) **2-^{15}NO** + KO_2/18-crown-6 recorded in KBr pellet at 298 K. The spectrum showed the peaks for [Cr-$^{14}NO_2^-$] (1270 cm^{-1}), [Cr-$^{15}NO_2^-$] (1243 cm^{-1}), respectively.

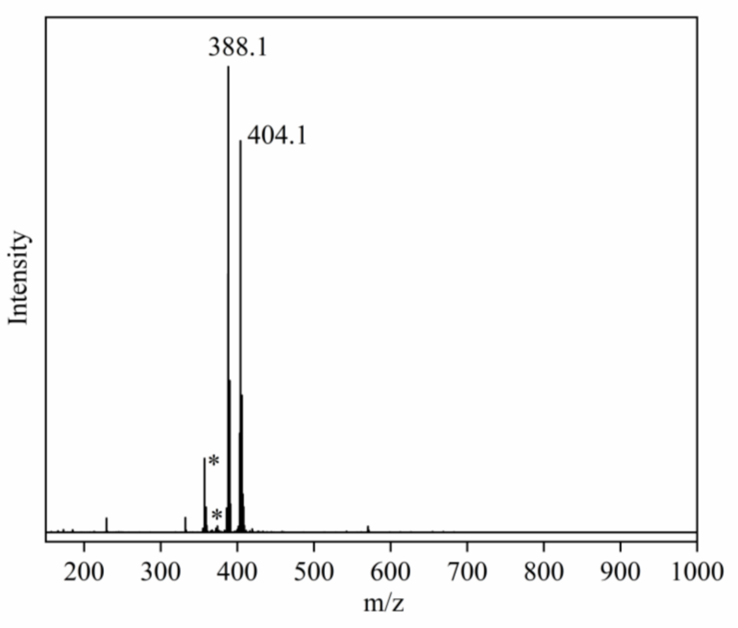

Figure S14. ESI-MS spectrum of isolated complex **4-^{15}NO$_2$**, formed in the reaction of [(BPMEN)Cr(^{15}NO)]$^{2+}$ with KO$_2$/18-crown-6 recorded in CH$_3$CN. The peak at *m/z* and 404.1 is assigned to be [(BPMEN)Cr(^{15}NO$_2$)(Cl)]$^+$ (calcd: *m/z* 404.1 and) respectively. The peaks at 388.1, 357.1, and 374.1 marked with asterisks are assigned to be[(BPMEN)Cr(^{15}NO)(Cl)]$^+$ (calcd: *m/z* 388.1), [(BPMEN)Cr(Cl)]$^+$ (calcd: *m/z* 357.1) and [(BPMEN)Cr(OH)(Cl)]$^+$ (calcd: *m/z* 374.1), respectively.

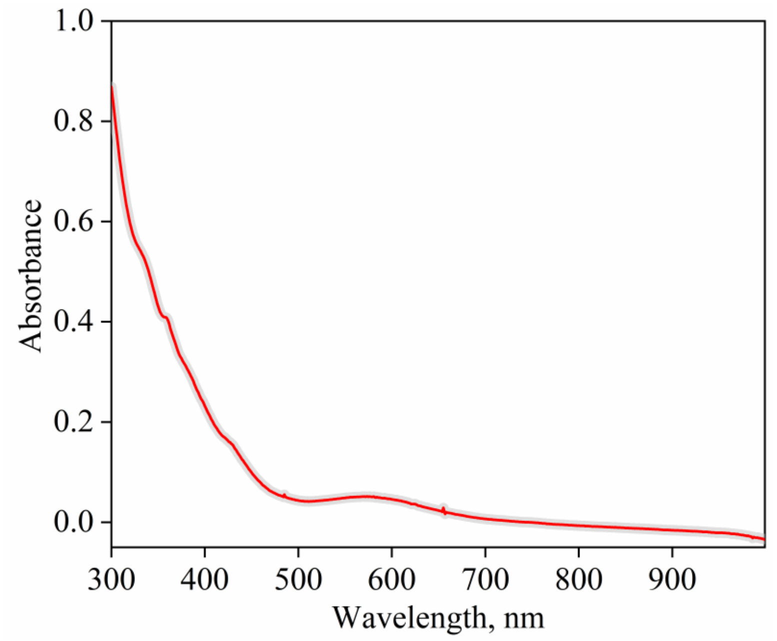

Figure. S15 UV-vis spectral comparison of authentic **4** (1 mM) prepared in the reaction of [(BPMEN)$CrCl_3$] + $AgNO_2$ (Grey Line) and complex **4** (1 mM) isolated from the reaction of **2** + KO_2/18-crown-6 (Red line) in CH_3CN at 298 K under Ar atmosphere.

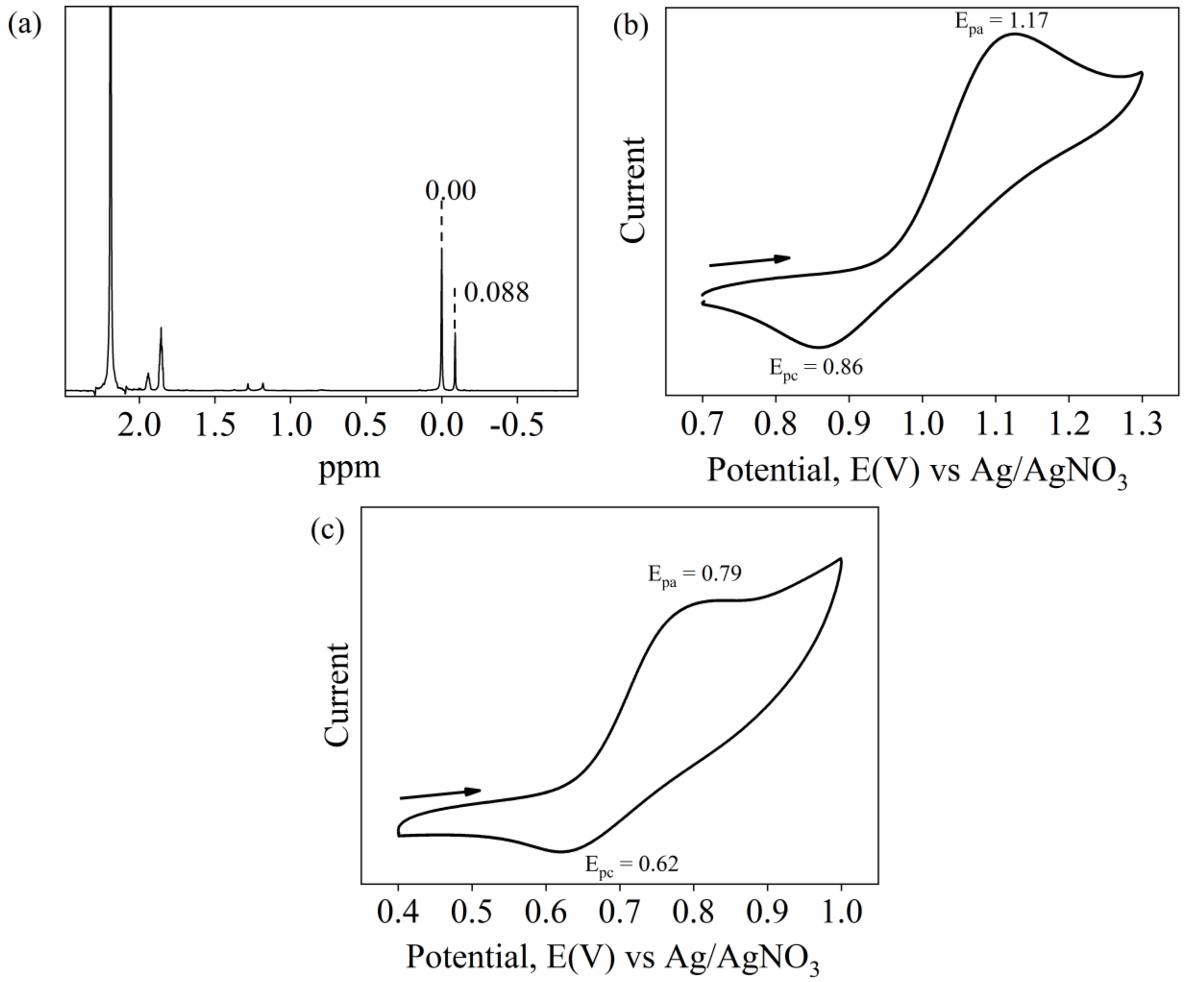

Figure S16. (a) ^{1}H-NMR (400 MHz) spectrum of isolated complex **4** (4 mM) in CD_3CN (0.1 % TMS) recorded in a coaxial NMR tube, with inside CD_3CN (1.0 % TMS) at 298 K. (b) Cyclic voltammogram of **2** (1 mM) in CH_3CN containing n-Bu_4NPF_6 (0.25 M) as a supporting electrolyte (scan rate = 0.1 V/s) at 298 K. (c) Cyclic voltammogram of **4** (1 mM) in CH_3CN containing n-Bu_4NPF_6 (0.25 M) as a supporting electrolyte (scan rate = 0.1 V/s) at 298 K.

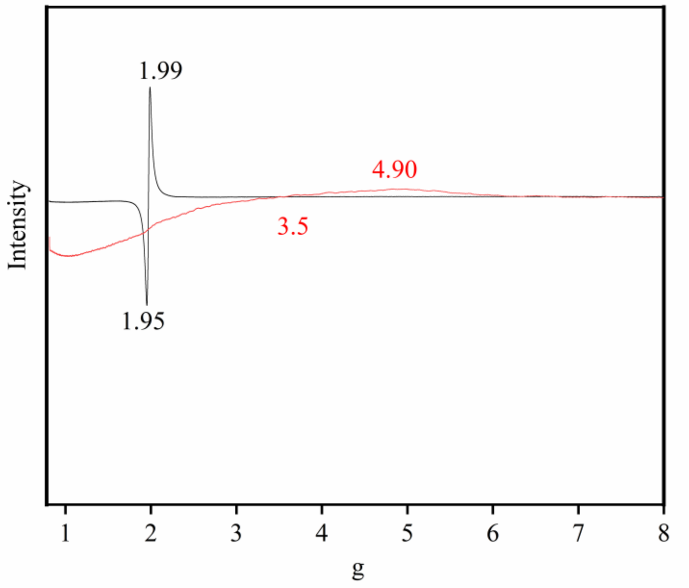

Figure S17. EPR spectrum of **2** (4 mM) (black line) and **4** (red line) isolated from the reaction mixture of **2** with KO_2 (4 mM) in CH_3CN at liquid N_2 temprature.

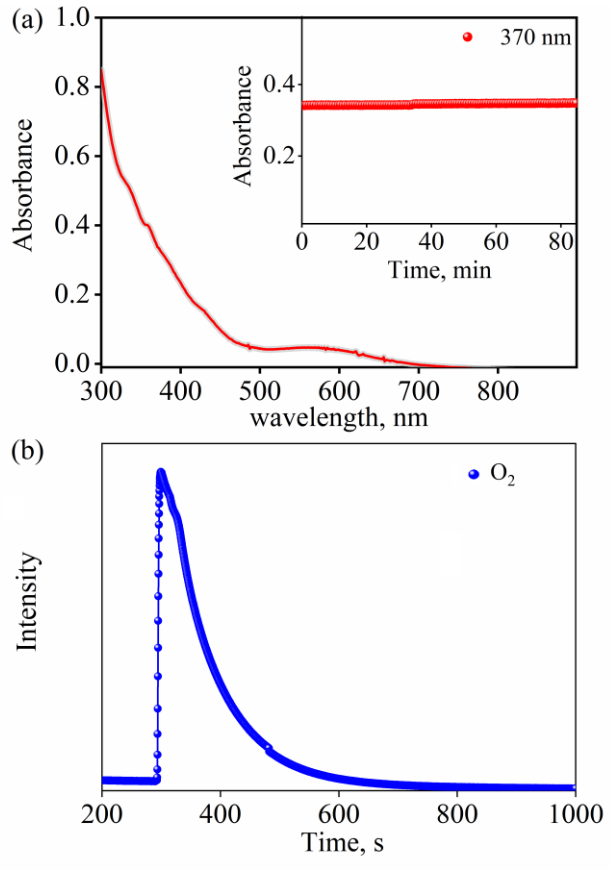

Figure S18. (a) UV-vis spectral changes of **4** (1 mM) in CH_3CN under Ar at 298 K. The Inset shows the time course of the decay of **4** (red-circles) monitored at 370 nm in CH_3CN at 298 K. (b) Head-space gas mass spectrum of formation of O_2 in the reaction of **2** (30.0 mM) with KO_2/18-crown-6.

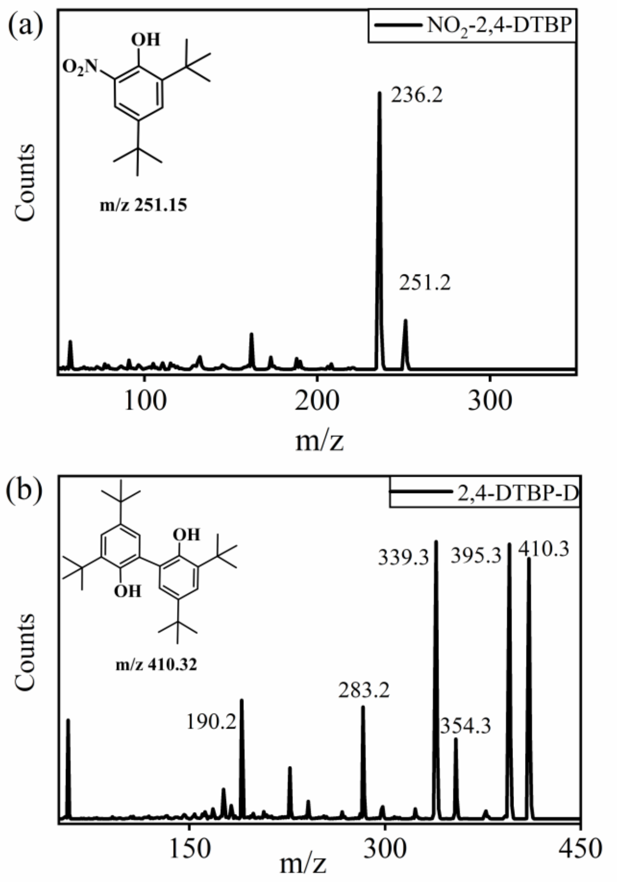

Figure S19. GC-MS characterization of (a) nitro-2,4-DTBP (NO$_2$-2,4-DTBP): The peaks at *m/z* 251.2 and 236.2 are assigned to be nitro-2,4-DTBP and loss of CH$_3$ from nitro-2,4-DTBP. (b) 2,4-DTBP-dimer (2,4-DTBP-D); the peaks at *m/z* 410.3, 395.3, 339.3 and 190.2 are assigned to be 2,4-DTBP-D, loss of CH$_3$ from 2,4-DTBP-D, loss of C$_4$H$_8$ and CH$_3$ from 2,4-DTBP-D and loss of CH$_3$ from monomer 2,4-DTBP. The peaks were compared with the NIST standard library.

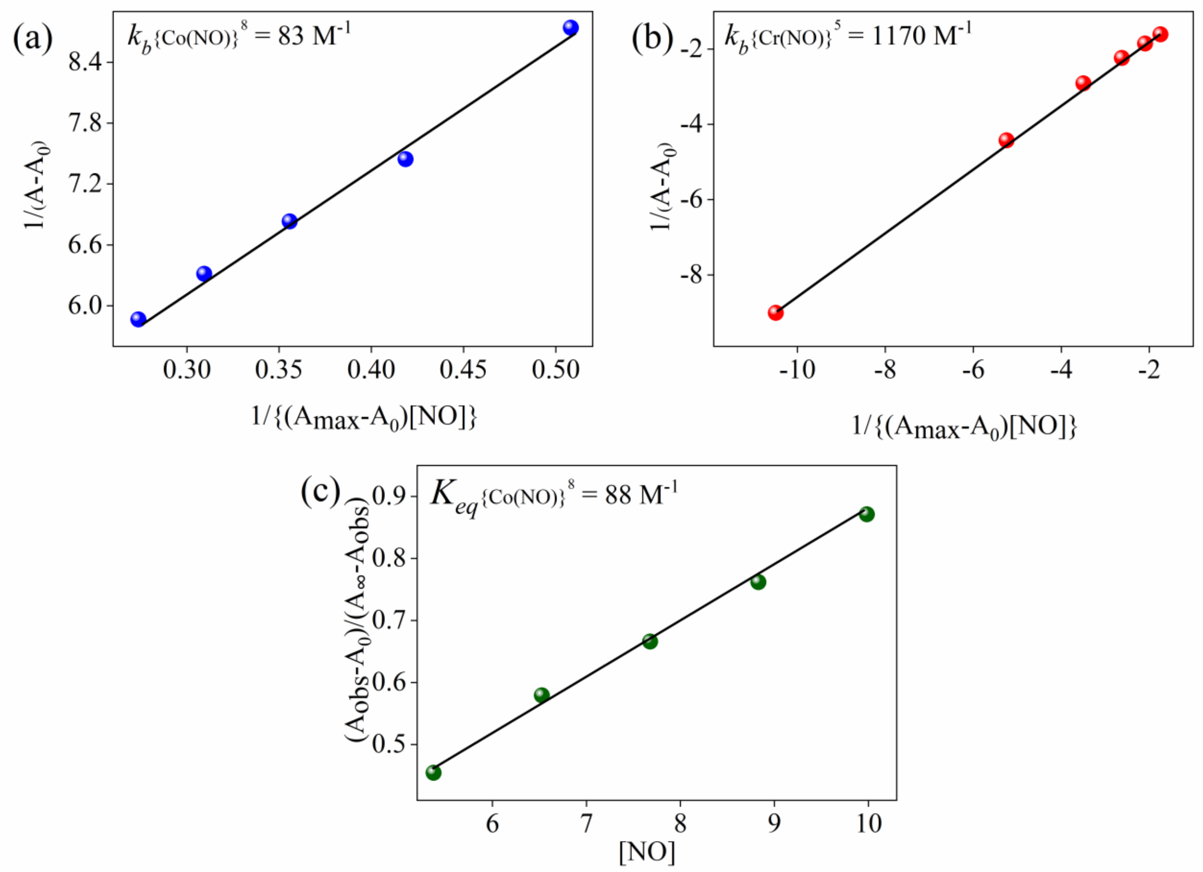

Figure S20. Binding constants of complex (a) **1**, (b) **2**. calculated from the Benesi-Hildebrand equation (c) Equilibrium constant calculation of **1.**

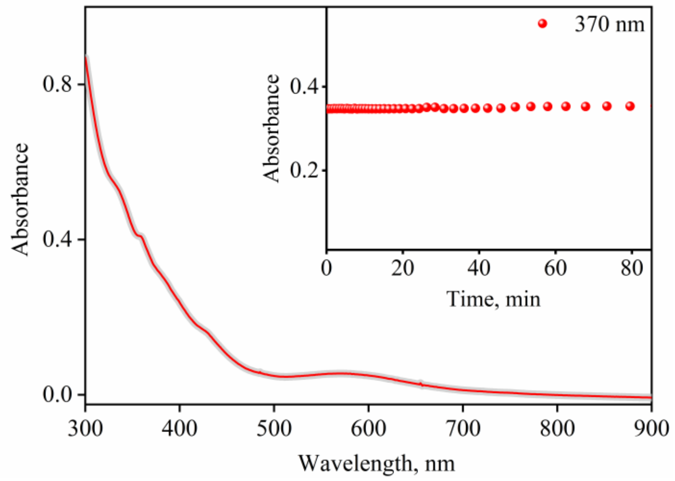

Figure S21. UV-vis spectral changes of **4** (1 mM, Grey-line to red-line) upon addition of NO in CH_3CN under Ar at 298 K. The Inset shows the time course of the decay of **4** (red-circles) monitored at 370 nm in CH_3CN at 298 K.

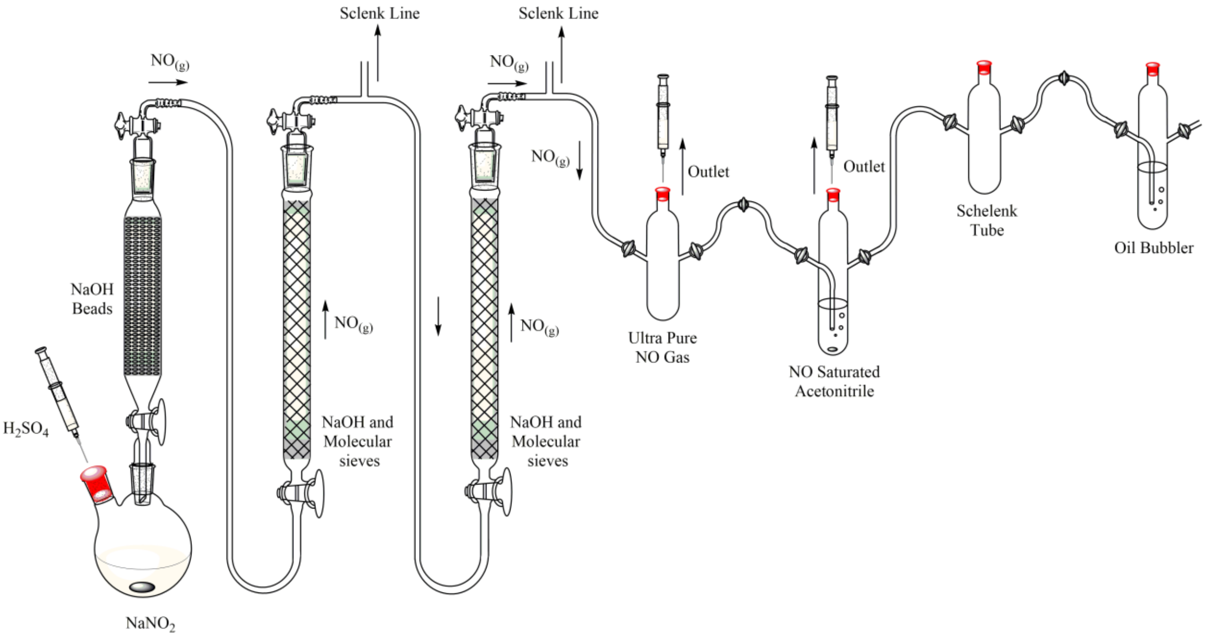

Figure S22. Schematic diagram showing the generation and purification setup for NO

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