Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Why Intermolecular Nitric Oxide (NO) Transfer? Exploring the Factors and Mechanistic Aspects of NO Transfer Reaction

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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 used without further purification unless otherwise indicated. Solvents were dried according to reported literature and distilled under an inert atmosphere before use.[S1] The 12-TMC ligand was prepared by reacting excess amounts of formaldehyde and formic acid with 1,4,7,10-tetraazacyclododecane as reported previously, and BPMEN 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)Cr^{II}(Cl)$_2$] (2-Cr). The preparation of **2-Cr** was carried out under an inert gas atmosphere inside the glove-box. To a suspension of $CrCl_2$ (123 mg, 1 mmol) in 2ml CH_3CN, a solution of BPMEN (270 mg, 1 mmol) ligand in 2ml of CH_3CN (BPMEN= N,N'-bis(2-pyridylmethyl)-1,2-diaminoethane) was added dropwise and kept for stirring for 48 hours at room temperature (298 K). Then excess ether (Et_2O) was added to the resulting solution, which produced a grey color precipitate, and the same was collected by filtration. The grey power was washed with Et_2O multiple times and dried under vacuum. The final product was recrystallized by the solvent diffusion process in a mixture of CH_3OH versus Et_2O at room temperature over a period of 3 to 4 days. [(BPMEN)Cr^{II}(Cl)$_2$] (3) Yield: 350 mg (~ 90 %). UV-Visible spectrum of **2-Cr** in CH_3CN at 298 K: λ_{max} = 350 nm (ε = 1100 $M^{-1}cm^{-1}$). ^{1}H-NMR (400 MHz, Methanol-*d*$_4$) 105.57 (2 H, s), 78.50 (2 H, s), 45.55 (8 H, s), 24.27 (6H, d), -47.86 (4H, s). Magnetic moment, μ_{eff}= 4.30 BM.

Synthesis of [(BPMEN)Cr(NO)(Cl)](Cl) (4-CrNO). The preparation of **4-CrNO** was carried out under an inert gas atmosphere. To the CH_3CN (5 mL) solution of **2-Cr** (98.25 mg, 0.25 mmol), an excess $NO_{(g)}$ was purged for 2 minutes under an Ar atmosphere, which showed a color change from red to dark green. The reaction mixture was purged with Ar gas for 10 min to remove the excess $NO_{(g)}$ from the solution, and then 30 ml Ar saturated Et_2O was added to the solution, which produced a green precipitate. This precipitate was washed multiple times with Et_2O and dried under vacuum. UV-Visible spectrum of **4-CrNO** in CH_3CN at 298 K: λ_{max} = 600 nm (ε = 110 M^{-1} cm^{-1}). FT-IR (in KBr pellet): 1690 cm^{-1} (NO stretching). Mass (*m/z*): Calcd: *m/z* 387.1, Found: *m/z* 387.1 for ([(BPMEN)Cr(NO)(Cl)]$^+$). Magnetic moment, μ_{eff} = 1.68 BM. [(BPMEN)Cr(^{15}NO)(Cl)](Cl) (**4-CrNO-**^{15}NO) was prepared by using the same method with $^{15}NO_{(g)}$. FT-IR (in KBr pellet): 1650 (^{15}NO stretching). ESI-MS: Calcd: *m/z* 388.1, Found: *m/z* 388.1 for ([(BPMEN)Cr(^{15}NO)(Cl)]$^+$).

Synthesis of [(BPMEN)Cr(NO)(Cl)](PF$_6$) (4-CrNO-PF$_6$). The addition of 1 equivalent of $AgPF_6$ (25.2 mg, 0.1 mmol) to a CH_3CN solution (2 mL) of **4-CrNO** (42.3 mg, 0.1 mmol) at 298 K readily starts to form a white color precipitate of AgCl. The Reaction mixture was further stirred for 30 minutes under Ar. The white precipitate was filtered out, and 30 ml of Ar saturated Et_2O was added to the filtrate, which produced a green-color precipitate of **4-CrNO-**PF$_6$. The solid precipitate of **4-CrNO**-PF$_6$ was washed multiple times with Et_2O and dried under vacuum. The suitable green color crystals for X-ray analysis were obtained by layering the CH_3CN solution of **4-CrNO**-PF$_6$ with Et_2O at 243 K for 3 to 4 days.

Synthesis of [(12-TMC)Co^{III}(NO)](BF$_4$)$_2$ (1-CoNO). Complex **1-CoNO** was prepared by the following reported procedure.[S3] An Ar saturated solution of [(12-TMC)Co^{II}](BF$_4$)$_2$ (100 mg, 0.2 mmol) is prepared in 3ml of CH_3CN and purged with excess $NO_{(g)}$ for 10 minutes until the color completely changes from brick red to wine red. Then the reaction mixture was purged with Ar gas for 10 min to remove the excess $NO_{(g)}$. An excess amount of Et_2O was added to the resulting solution to yield the dark pink color powder and collected by filtration. The dark pink powder was washed multiple times with Et_2O. [(12-TMC)Co^{III}(^{15}NO)](BF$_4$)$_2$ (**1-CoNO-**^{15}NO) was prepared by using the same method with $^{15}NO_{(g).}$

Synthesis of [(12-TMC)Cr^{II}(Cl)]Cl (5-Cr). Complex **5-Cr** was prepared by the following already reported procedure.[S4] The preparation of **5-Cr** was carried out under an Ar atmosphere. To a solution of 12-TMC (114 mg, 0.5 mmol) ligand in 4 mL of CH_3CN (12-TMC= 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane), $CrCl_2$ (61.5 mg, 0.5 mmol) was added and kept for stirring for 12 hr at room temperature. Then excess Et_2O was added to the resulting solution, generating a blue color powder of complex **5-Cr** and collected by filtration. The blue powder was washed with Et_2O multiple times and dried in vacuo to yield pure complex **5-Cr**. Yield: 145 mg (~ 82%).

Synthesis of [(12-TMC)Cr^{II}(NO)(Cl)](Cl) (**6-CrNO**)**.** Complex **6-CrNO** was prepared by the following already reported procedure.[S4] The preparation of **6-CrNO** was carried out under an Ar atmosphere. An excess $NO_{(g)}$ was purged to a CH_3CN (5 mL) solution of **5-Cr** (88 mg, 0.25 mmol) for 10 minutes under Ar atmosphere, which showed a color change from blue 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. ESI-MS: Calcd: *m/z* 345.1, Found: *m/z* 345.1 for ([(12-TMC)Cr(NO)(Cl)]$^+$).

Generation of [(BPMEN)Cr(NO)(Cl)]$^+$ (4-CrNO) in the reaction of [(12-TMC)Co^{III}(NO)]$^{2+}$ (1-CoNO) + [(BPMEN)Cr^{II}(Cl)$_2$] (2-Cr). Complex **1-CoNO** was reacted with an equimolar amount of **2-Cr** to determine the product of NO transfer reaction. In this regard, complex **1-CoNO** (25 mg, 0.05 mmol) was reacted with one equivalent of **2-Cr** (20 mg, 0.05 mmol) in CH_3CN at 298 K under Ar atmosphere inside the glove-box. Upon addition of **2-Cr** to the solution of **1-CoNO**changes the color of the reaction mixture from wine-red to bluish-green, indicating the formation of the new products (**4-CrNO** + **3-Co**). The reaction mixture was then stirred for 30 minutes at 298 K. The end products, obtained in the reaction of **1-CoNO** and **2-Cr**, were determined to be [(BPMEN)Cr(NO)(Cl)]$^+$ (**4-CrNO**) and [(12-TMC)Co^{II}]$^{2+}$ (**3-Co**) from various spectroscopic and structural characterization. UV-Visible spectrum: λ_{max} = 600 nm (ε = 110 M^{-1} cm^{-1}). FT-IR (in KBr pellet): 1690 (NO stretching), 1062. Mass (*m/z*): Calcd: *m/z* 387.1, 322.1, 143.6 Found: *m/z* 387.1, 322.1, 143.6 for [(BPMEN)Cr(NO)(Cl)]$^+$, [(12-TMC)Co(Cl)]$^+$, [(12-TMC)Co]$^{2+}$, respectively.

Generation of [(12-TMC)Cr(NO)(Cl)]$^+$ (6-CrNO) in the reaction of [(12-TMC)Co^{III}(NO)]$^{2+}$ (1-CoNO) + [(12-TMC)Cr^{II}(Cl)]$^+$ (5-Cr). Complex **1-CoNO** was reacted with an equimolar amount of **5-Cr** to determine the product of NO transfer reaction. Therefore, complex **1-CoNO** (25 mg, 0.05 mmol) was reacted with an equivalent amount of **5-Cr** (17.5 mg, 0.05 mmol) in CH_3CN at 298 K under an Ar atmosphere inside the glove-box. Upon addition of **5-Cr** to the solution of **1-CoNO** , color of the reaction mixture changed from wine-red to dark-green within 5 minutes, indicating the formation of the new species. The reaction mixture was then stirred for 30 minutes at 298 K. The end products, obtained in the reaction of **1-CoNO** and **5-Cr**, were determined to be [(12-TMC)Co^{II}]$^{2+}$ and [(12-TMC)Cr(NO)(Cl)]$^+$. ESI-MS: Calcd: *m/z* 345.1, 322.1, 143.6 Found: *m/z* 345.1, 322.1, 143.6 for [(12-TMC)Cr(NO)(Cl)]$^+$, [(12-TMC)Co(Cl)]$^+$, [(12-TMC)Co]$^{2+}$, respectively.

Reactivity Studies. All UV-Visible spectral measurements were performed using a quartz cuvette in CH_3CN at the range of 233 K to 298 K. We have 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 have performed all the reactions either at 298 K /or 273 K as the initial Co^{III}-nitrosyl complex (**1-CoNO**) and the final product, and all reactants are very stable even at 298 K. The formation of complex **4-CrNO** and **6-CrNO** in the above reactions were identified by comparing them with authentic samples.

Labelling (^{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 NO transfer reactions. These reactions were executed under an inert atmosphere. Twenty mM solutions of **1-Co^{14}NO** and **1-Co^{15}NO** were prepared and reacted with **2-Cr** in two different reactions. After completion of the reactions, the solvent was evaporated under a vacuum and washed with Et_2O. The FT-IR spectrum of the reaction mixture of **1-CoNO** and **2-Cr** showed a characteristic peak at 1690 cm^{-1} for Cr-bound nitrosyl. This peak was shifted to 1650 cm^{-1} when the reaction mixture of **1-Co^{15}NO** + **2-Cr** was analyzed. The change in the IR stretching frequency of Cr-bound NO (Δ = 40 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 functional group.

Labelling (^{14}N & ^{15}N) experiments using ESI-MS spectrometry. Furthermore, to establish the source of NO, complex **1-Co^{15}NO** was reacted with one fold of **2-Cr** and **5-Cr** in CH_3CN under Ar at 298 K in two different experiments. For the above experiments, two cuvettes (4 mL) containing a solution of complex **1-Co^{15}NO** (0.5 mM / 2.5 mL), in CH_3CN sealed with a rubber septum under an Ar atmosphere was reacted with one-fold **2-Cr** or **5-Cr** (25 mM / 50 μL) in two separate experiments, and the reactions were monitored by UV-Visible spectroscopy. After the completion of the reactions, the ESI-MS spectra of both reaction mixtures were recorded. The ESI-MS spectrum of the reaction mixture obtained in the reaction of ($[(12\text{-TMC})\mathrm{Co^{III}}(^{15}\mathrm{NO})]^{2+}$ with **2-Cr** or **5-Cr**, showed a prominent peak at *m/z* 388.1, 346.1, respectively whose mass value and isotopic distribution pattern corresponds to $[(\mathrm{BPMEN})\mathrm{Cr}(^{15}\mathrm{NO})(\mathrm{Cl})]^{+}$ (calcd *m/z* 388.1) and $[(12\text{-TMC})\mathrm{Cr}(^{15}\mathrm{NO})(\mathrm{Cl})]^{+}$ (calcd *m/z* 346.1). These reactions indicate clearly that NO in **4-CrNO** and **6-CrNO** are derived from NO moiety of complex **1-CoNO**.

Trapping the μ-NO bridge intermediate by FT-IR spectroscopy. To characterize and witness the nature of the intermediate, the reaction of **1-CoNO** and **2-Cr** was further tracked using FT-IR spectroscopy. A CH_3CN solution of **1-CoNO** (4 mM) was prepared in the glove box, and the liquid demountable cell kit with KBr solid plate setup is filled with the same solution and air-tightened with parafilm. In a separate sample vial, complex **2-Cr** (40 mM in CH_3CN) was prepared, attached with a rubber septum, and equipped with a syringe inside the glove box. First, the FT-IR spectrum of **1-CoNO** was collected, and then **2-Cr** was injected in the demountable cell holding the **1-CoNO,** and then the second IR spectrum was collected at RT. In the following scan, we observed the formation of two new peaks at 1685 cm^{-1} and 1520 cm^{-1}, and the peak at 1703 cm^{-1} for **1-CoNO** disappeared. The peak at 1520 cm^{-1} corresponded to μ-NO bridge intermediate species, which disappeared in the following scan, which shifted to 1491 cm^{-1} when the reaction was performed using **1-Co^{15}NO**. The formation of a peak at 1520 cm^{-1} and its disappearance suggests the formed intermediate is a bridged-NO species.

Trapping the μ-NO bridge intermediate by EPR spectroscopy. To characterize the intermediate formation, the reaction of **2-Cr** and **1-CoNO** was tracked using EPR spectroscopy. A 500 μl CH_3CN solution of **2-Cr** (4mM) was prepared inside the glovebox and sealed inside an EPR tube. The EPR tube was further cooled to 233 K, and a cold solution of one equivalent **1-CoNO was** added to the EPR tube using a syringe, and EPR was recorded at liquid N_2 temperature. After that, the tube again warmed to 233 K, kept for 1 minute, and recorded at liquid N_2 temperature. This process continued until the reaction was completed.

Single-Crystal XRD Studies: Single-crystal XRD data were collected at 296 K on a Bruker X-ray diffractometer (D8 Quest Eco) using monochromated MoKα (lambda = 0.7107 Å) radiation. The collected frames were integrated, scaled, merged, and absorption correction performed using the program package APEX3 (Bruker 2019) to determine the unit cell. The structure was solved with SHELXS and refined against F2 by weighted full-matrix least-squares using SHELXL.[S5] 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. Detail crystallographic data and structural refinement parameters are summarized in Table T1 – T2. CCDC-2076723 ([(BPMEN)Cr(NO)(Cl)](PF_6) 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. S1. 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 pass through a set of 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 passed 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.[S6]

Magnetic moment calculation and determination of the number of unpaired electrons in complex 2-Cr, 4-CrNO, 5-Cr, and 6-CrNO: Evans' method of ^1H-NMR was performed to determine the number of unpaired electrons (spin-state) in complex **2-Cr, 4-CrNO, 5-Cr,** and **6-CrNO** at room temperature[S7-S9]. A WILMAD® coaxial insert (with a sealed capillary) tube containing the only CD_3CN solvent (with 1.0 % TMS) and CD_3OD (for **2-Cr** only, with 1.0 % TMS) was inserted into two normal NMR tubes containing the complex **4-CrNO** (4.0 mM in CD_3CN, with 0.1 % TMS) and **2-Cr** (4.0 mM in CD_3OD, with 0.1 % TMS), **5-Cr** (4.0 mM in CD_3CN, with 0.1 % TMS) and **6-CrNO** (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 **2-Cr, 4-CrNO, 5-Cr,** and **6-CrNO** concerning that of the TMS / solvent peak in the inner NMR tube. The magnetic moment was calculated using the given equation.

4-CrNO

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

$$\mu_{eff} = 0.0618 * (8 * 298 / 2 * 400 * 0.004)^{1/2}$$

$$\mu_{eff} = 1.68 \text{ BM}$$

2-Cr

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

$$\mu_{eff} = 0.0618 * (52 * 298 / 2 * 400 * 0.004)$$

$$\mu_{eff} = 4.30 \text{ BM}$$

5-Cr

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

$$\mu_{eff} = 0.0618 * (49 * 298 / 2 * 400 * 0.004)$$

$$\mu_{eff} = 4.16 \text{ BM}$$

6-CrNO

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

$$\mu_{eff} = 0.0618 * (12 * 298 / 2 * 400 * 0.004)^{1/2}$$

$$\mu_{eff} = 2.06 \text{ BM}$$

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 **4-CrNO, 2-**

Cr, 5-Cr, and **6-CrNO** were determined to be 1.68 BM, 4.30 BM, 4.16 BM, 2.06 BM, respectively, suggesting 1, 4, 4, 1 unpaired electron in the Cr-center of complex **4-CrNO, 2-Cr, 5-Cr, 6-CrNO**.

Activation parameter (ΔG) calculation: The Gibbs free energies and other physical parameters for complexes **1-CoNO**, **4-CrNO**, & **6-CrNO** were calculated using the Eyring equation. 0.5 mM solutions of complexes **3-Co**, **2-Cr**, & **5-Cr** were treated with 10, 15, 20, 25 equivalent of $NO_{(g)}$ and the true second-order rate constants (k_r) of the formation of complexes **1-CoNO**, **4-CrNO**, & **6-CrNO**, respectively were calculated at different temperature $^-$10 °C, -20 °C, -30 °C and -40 °C. Plotting the $\ln(k_r/T)$ as a function of 1/T according to the Eyring equation yielded activation enthalpy and activation entropy.

$$ln\left(\frac{k_r}{T}\right) = -\frac{\Delta H}{RT} + [\frac{\Delta S}{R} + ln\left(\frac{k}{h}\right)]$$

$$\Delta G = \Delta H - T\Delta S$$

T = Reaction temperature, k = Boltzmann constant, h= Plank constant, k_r = True second-order rate constant. The calculated ΔG value for **1-CoNO**, **4-CrNO** and **6-CrNO** were found to be 16.43 ± 0.2 kcal/mol, 15.71 ± 0.3 kcal/mol, 16.17 ± 0.12 kcal/mol at 298 K, respectively.

Equilibrium constant (k_{eq}) calculation: The Equilibrium constant (keq) and standard gibbs free energy (ΔG^0) for complexes **1-CoNO**, **4-CrNO**, & **6-CrNO** were calculated using the following equation

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

$$\Delta G^0 = -RTlnk_{eq}$$

A_{obs} = Absorbance at certain NO concentration, A_0 = Absorbance at 0 NO concentration, A_∞ = Absorbance at ∞ NO concentration, k_{eq} = equilibrium constant, ΔG^0 = standard gibbs free energy T = Reaction temperature, R = gas constant. The calculated k_{eq} and ΔG^0 value for **1-CoNO**, **4-CrNO** and **6-CrNO** were found to be 8.9×10^2 M^{-1}, 2.27×10^3 M^{-1}, 1.48×10^3 M^{-1} and -4.02 kcal/mol, -4.57 kcal/mol, -4.32 kcal/mol at 298 K, respectively.

Computational Details: All calculations have been done using density functional theory (DFT) method with Gaussian09 software [S10] The molecular geometries have been optimised in the gas phase using the UB3LYP functional[S11] and def2-SVP basis set.[S12] Frequency calculations have been performed at the optimized geometry to confirm the saddle points. While the minima (reactant, intermediate, and product) have no imaginary frequency, each transition state (the maxima) has one. Further single point calculations have been performed at the previously optimised geometries with def2-TZVP basis set retaining the functional at 233 K temperature. The solvent effect have been taken into account using the continuum solvent model of SMD in acetonitrile.[S13] The thermochemistry study provides free energies including Gibbs free energy correction obtained from the vibrational analysis. This approach follows a similar approach which has been used in previous literatures on the same topic.[S14]

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Table T1 Crystallographic data for **2**.

Chemical formula	$C_{16}H_{22}ClCrF_6N_5OP$
Formula weight	532.81
Wavelength /Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
T, K	296
a, Å	9.2977 (4)
b, Å	18.0900
c, Å	12.9340 (6)
α, °	90
β, °	96.379(2)
γ, °	90
V/ Å^3	2161.97 (17)
Z	4
Calculated density, g/cm^3	1.637
Abs. Coeff. /mm^{-1}	0.797
Reflections collected	32063
Unique reflections	5365
Refinement method	Least-squares on F^2
Data/restraints/parameters	5365/0/282
Goodness-of-fit on F^2	1.10
Final R indices [$I > 2\sigma(I)$]	R_1=0.094, WR_2= 0.2085
R indices (all data)	R_1= 0.1302, WR_2= 0.2279

Table T2 Selected bond lengths (Å) and bond angles (°) for **2**.

Cr1 N5	1.883 (7)
Cr1 N4	2.077 (4)
Cr1 N1	2.092 (4)
Cr1 N2	2.123 (4)
Cr1 N3	2.169 (4)
Cr1 Cl1	2.3130 (17)
O1 N5	0.826 (9)
N5 Cr1 N4	95.2 (3)
N5 Cr1 N1	91.9 (2)
N4 Cr1 N1	170.54 (17)
N5 Cr1 N2	93.5 (3)
N4 Cr1 N2	95.73 (17)
N1 Cr1 N2	77.57 (16)
N5 Cr1 N3	171.0 (3)
N4 Cr1 N3	77.15 (18)
N1 Cr1 N3	95.22 (17)
N2 Cr1 N3	82.73 (17)
N5 Cr1 Cl1	95.7 (2)
N4 Cr1 Cl1	91.52 (13)
N1 Cr1 Cl1	93.99 (12)
N2 Cr1 Cl1	167.72 (14)
N3 Cr1 Cl1	89.27 (13)
O1 N5 Cr1	174.0 (11)

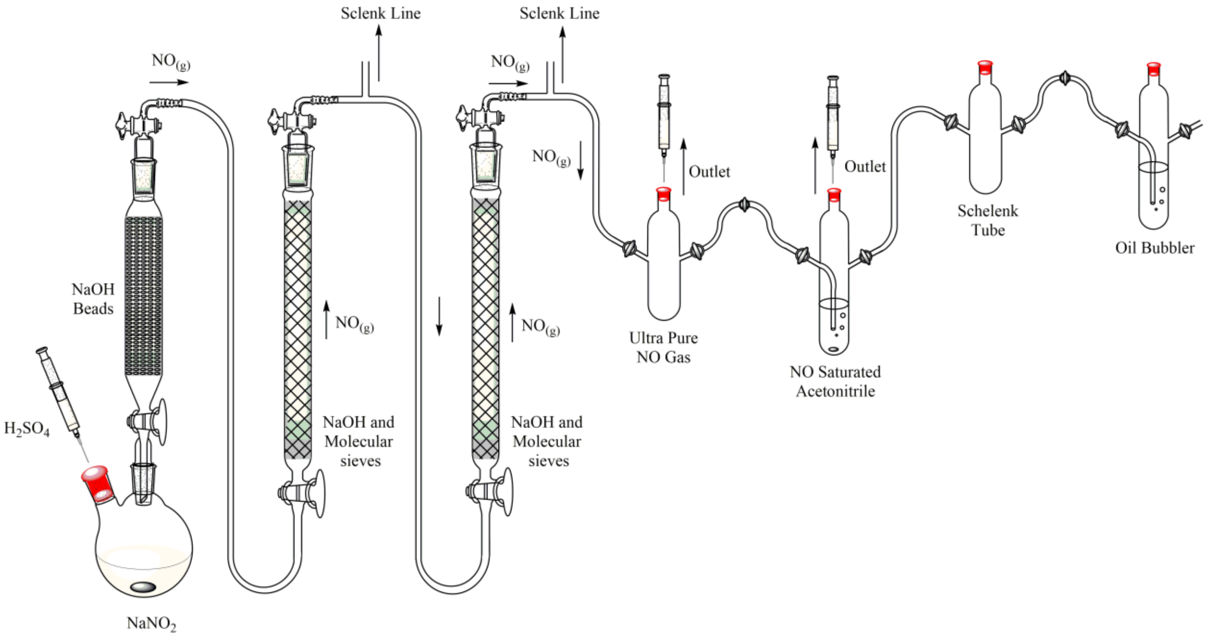

Figure. S1. Schematic diagram showing the generation and purification setup for NO.

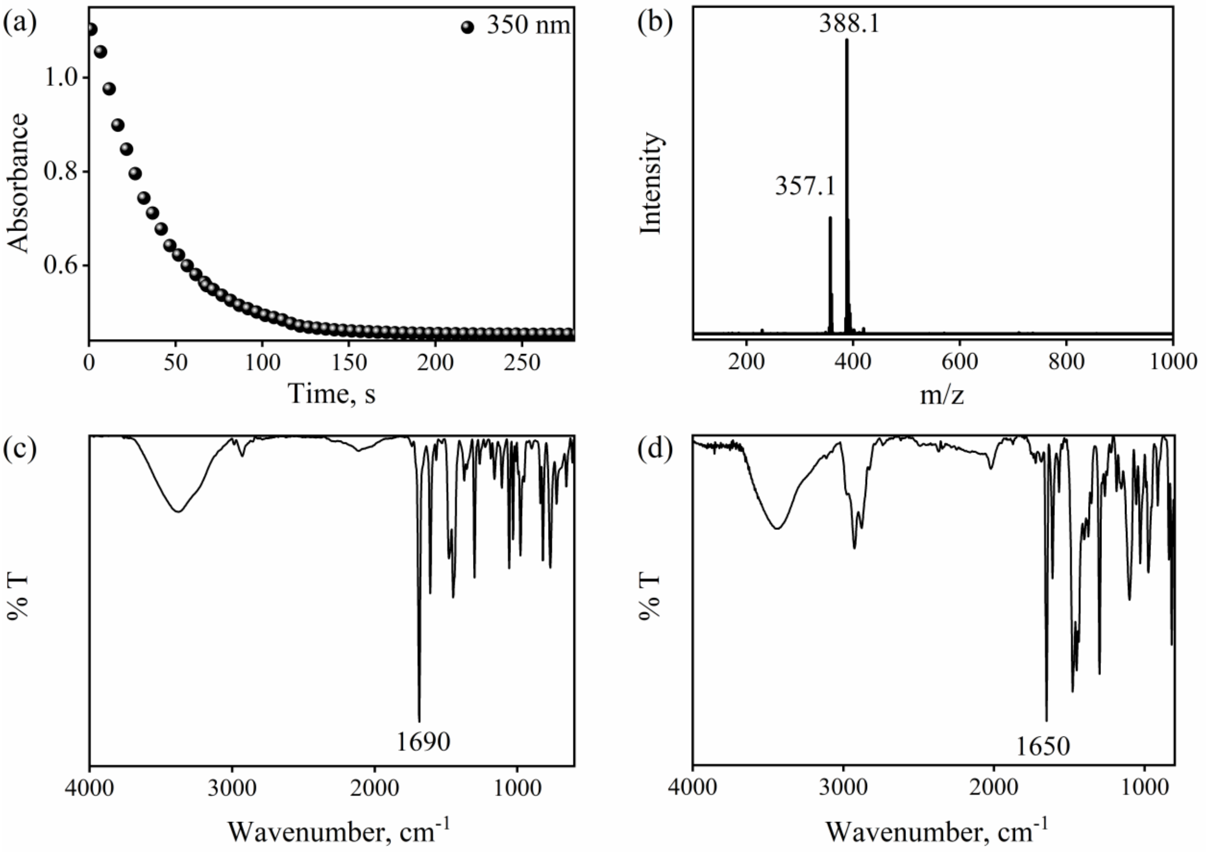

Figure. S2. (a) Time course of the decay of **2-Cr** monitored at 350 nm upon addition $NO_{(g)}$ to a solution of **2-Cr** (1 mM) in CH_3CN at 298 K (b) ESI-MS spectrum of **4-CrNO**-^{15}NO. The peaks at *m/z* 388.1 and *m/z* 357.1 are assigned to be [(BPMEN)Cr(^{15}NO)(Cl)]$^+$ (calcd *m/z* 388.1) and [(BPMEN)Cr(Cl)]$^+$ (calcd *m/z* 357.1). FT-IR spectrum of (c) **4-CrNO** (d) **4-Cr^{15}NO** recorded in KBr pellet at 298 K.

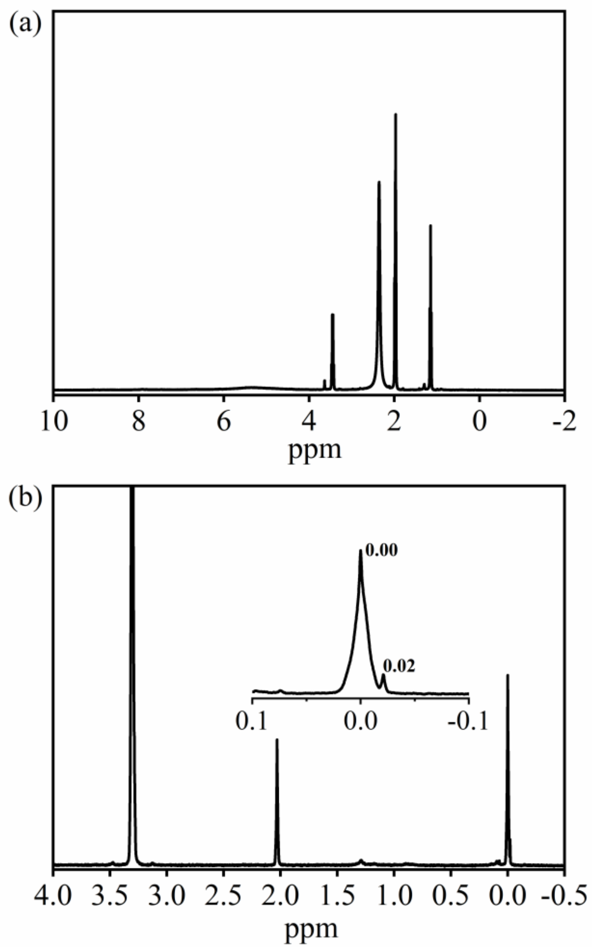

Figure S3. (a) ^{1}H-NMR (400 MHz) spectrum of **4-CrNO** in CD_3CN (b) ^{1}H-NMR (400 MHz) spectrum of **4-CrNO** (4 mM) in CD_3CN (0.1 % TMS), recorded in a coaxial NMR tube, with inside CD_3CN (1.0 % TMS) at RT.

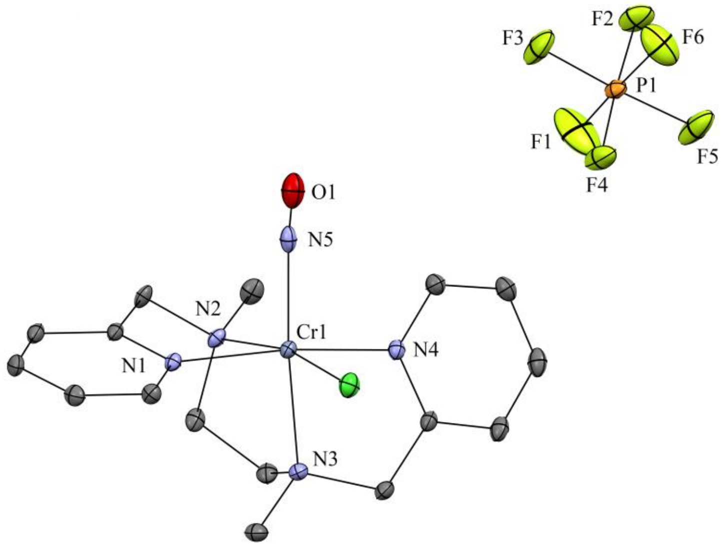

Figure. S4. Displacement ellipsoid plot (20 % probability) of **4-CrNO** at 296 K. Disorder in N-atom of NO ligand is refined; H-atoms have been removed for clarity.

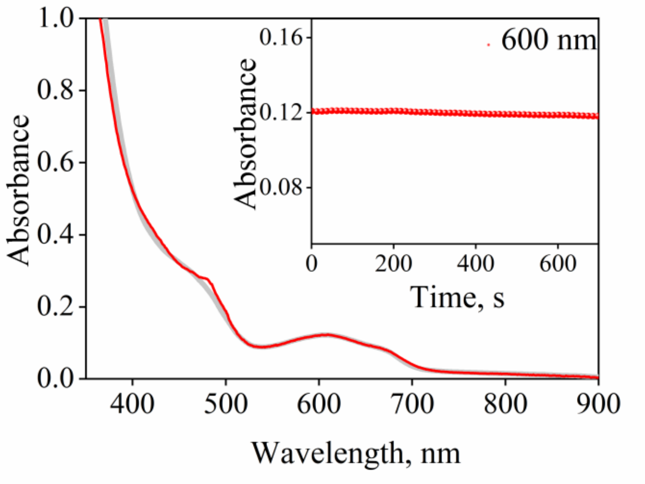

Figure. S5. UV-Visible spectral changes of **4-CrNO** (1 mM, Grey line) upon addition of 1 equivalent of **3-Co** in CH_3CN under Ar at 298 K (Red line). The Inset shows the time course of the decay of **4-CrNO** (red circles) monitored at 600 nm upon addition **3-Co** (1 equivalent) to a solution of **4-CrNO** (1 mM) in CH_3CN at 298 K.

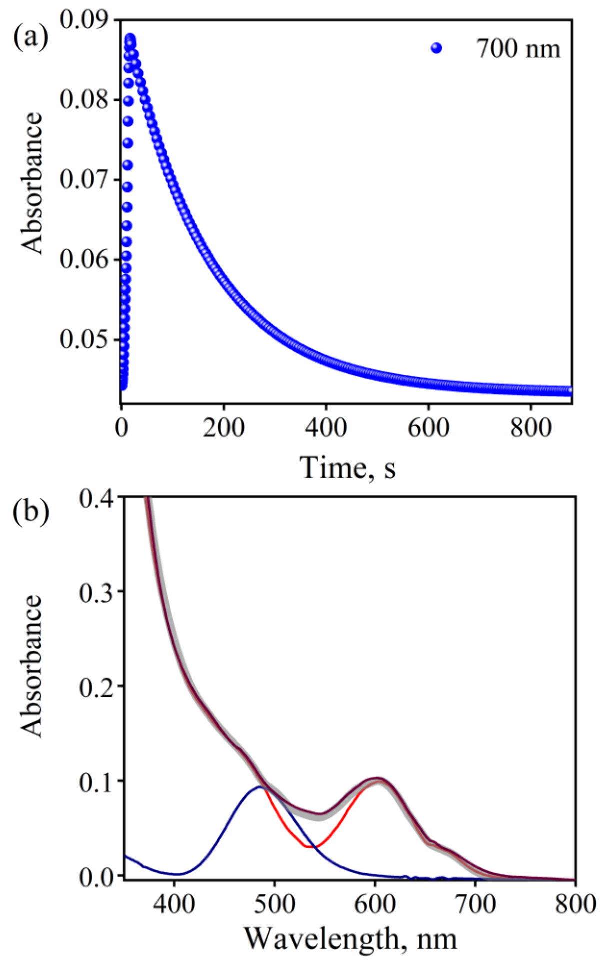

Figure. S6: (a) Time course of the generation & decomposition of intermediate species in the reaction of **1-CoNO** and **2-Cr** monitored at 700 nm (b) UV-Visible spectra of complex **3-Co** (1 mm, navy blue line), **4-CrNO** (1 mM, red line), summation of the spectra of complex **4-CrNO** + **3-Co** (1 mM, grey line), mixture obtained after completion of the reaction of **1-CoNO** + **2-Cr** (1 mM, brown line).

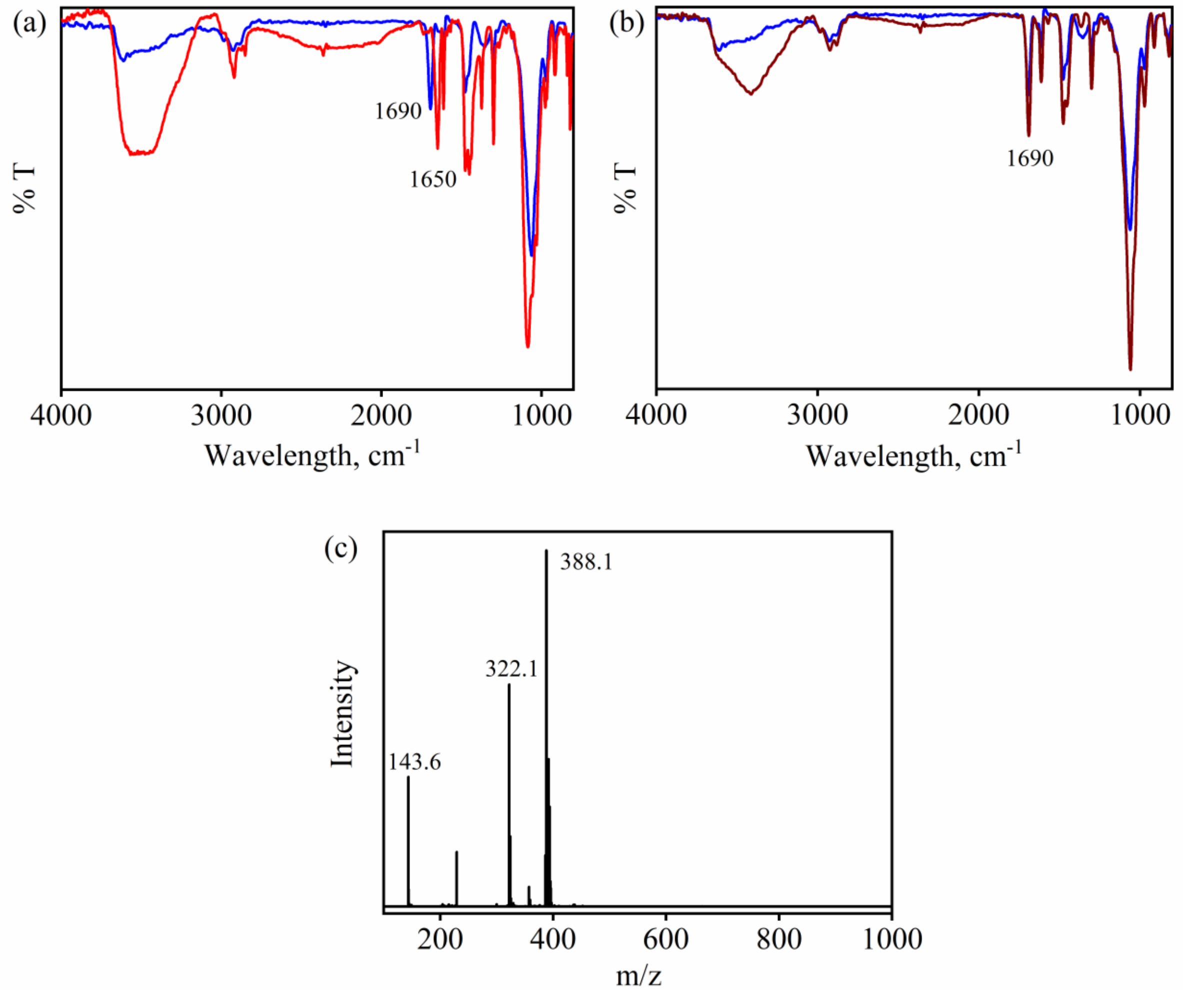

Figure. S7. (a) FT-IR spectra of reaction mixture of **1-CoNO** and **2-Cr** (blue spectra) and reaction mixture of **1-Co^{15}NO** and **2-Cr** (b) FT-IR spectra of reaction mixture of **1-CoNO** and **2-Cr** (blue spectra) and mixture of independently prepared **4-CrNO** and **3-Co** (brown line) (c) ESI-MS spectrum of reaction mixture, **1-Co^{15}NO** + **2-Cr**, The peak at *m/z* 388.1, 322.1, 143.6 are assigned to be [(BPMEN)Cr(^{15}NO)(Cl)]$^{+}$ (calcd *m/z* 388.1), [(12-TMC)Co(Cl)]$^{+}$ (calcd *m/z* 322.1) and [(12-TMC)Co]$^{2+}$(calcd *m/z* 143.6).

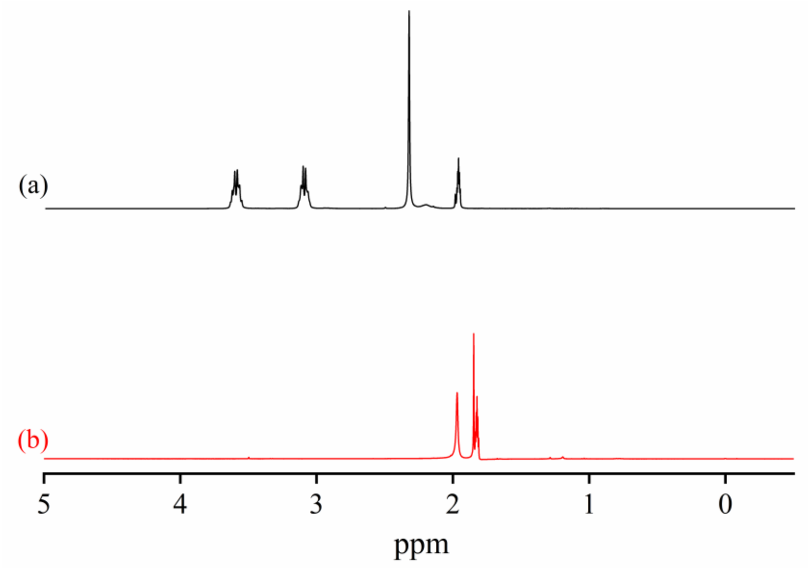

Figure. S8. ^{1}H-NMR (400 MHz) spectra of (a) complex **1-CoNO** (b) Reaction mixture obtained in the reaction of **1-CoNO** with **2-Cr** under Ar in CD_3CN at RT.

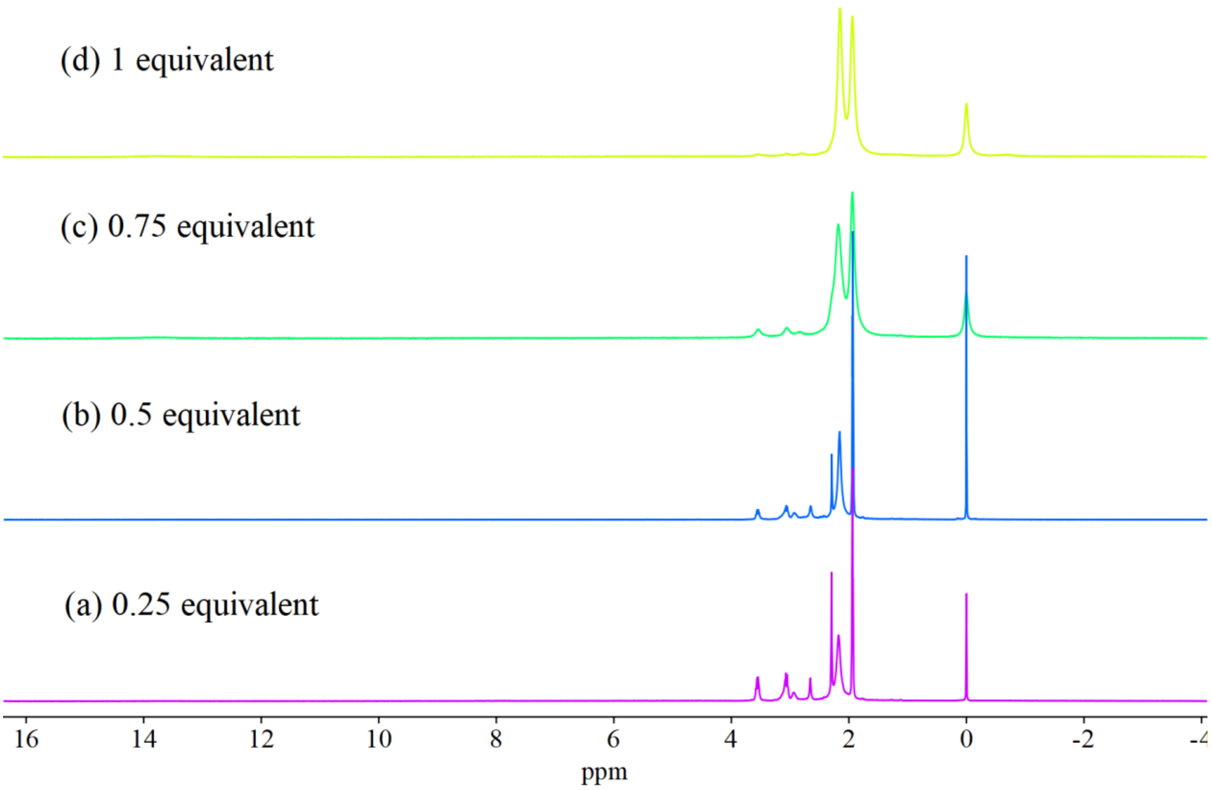

Figure. S9. ^{1}H-NMR (400 MHz) spectral changes of the 12-TMC ligand of **1-CoNO** observed in the addition (a) 0.25 equivalent (b) 0.5 equivalent (c) 0.75 equivalent (d) 1 equivalent of **2-Cr** in CD_3CN under Ar at 298 K.

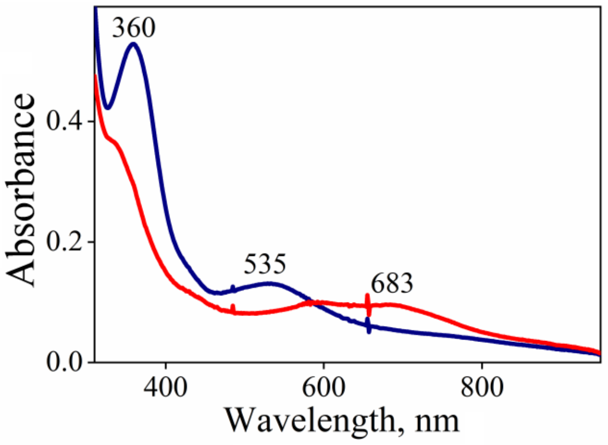

Figure. S10. Sum of the UV-Vis spectra of **1-CoNO** and **2-Cr** (navy blue line) and the red line is the intermediate spectrum obtained upon addition of **1-CoNO** (0.50 mM) to a solution of **2-Cr** (0.50 mM) under an Ar atmosphere in CH_3CN at 273 K.

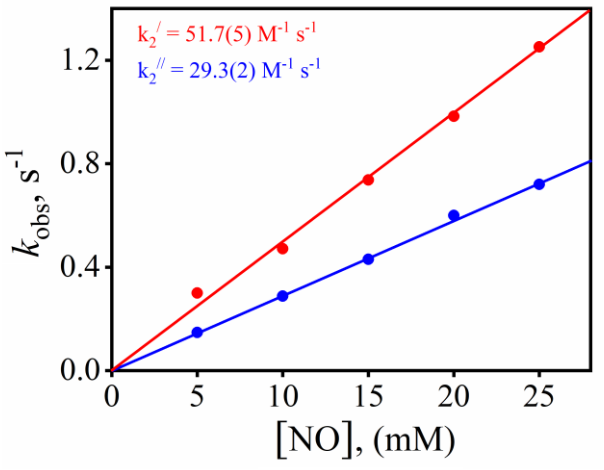

Figure. S11. Plots of pseudo-first-order rate constants (k_{obs}) for the formation of **4-CrNO** (red circles) and **6-CrNO** (blue circles) against the NO concentration to determine the second-order rate constants (k_2) in the reaction of [(BPMEN)Cr^{II}(Cl)$_2$] and [(12-TMC)Cr^{II}(Cl)]$^+$ with NO$_{(g)}$, respectively.

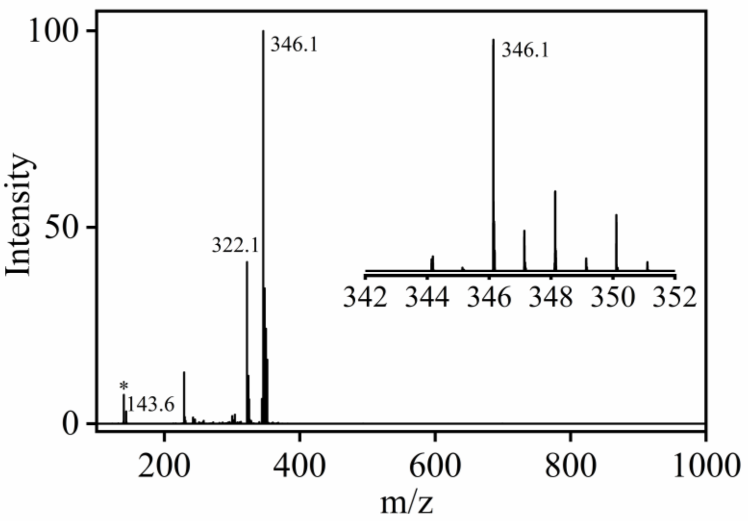

Figure. S12. ESI-MS spectrum of reaction mixture, **1-Co^{15}NO** + **5-Cr**, The peak at *m/z* 346.1, 322.1, 143.6 are assigned to be [(12-TMC)Cr(^{15}NO)(Cl)]$^{+}$ (calcd *m/z* 346.1), [(12-TMC)Co(Cl)]$^{+}$ (calcd *m/z* 322.1) and [(12-TMC)Co]$^{2+}$ (calcd *m/z* 143.6). The peak at *m/z* 140.1 marked with asterisk is assigned to [(12-TMC)Cr]$^{2+}$, which is the starting Cr^{II} complex.

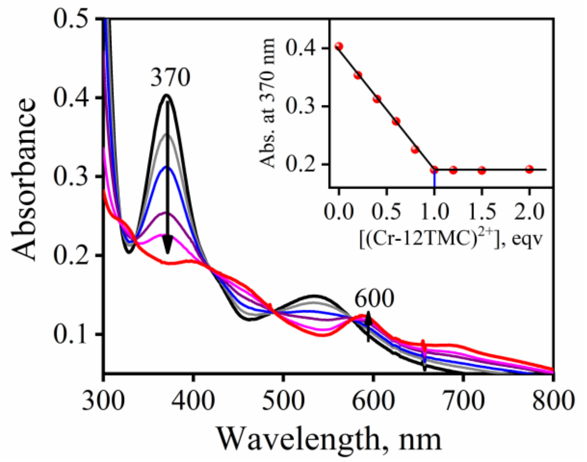

Figure S13. UV-vis spectral changes observed in the reaction **1-CoNO** with **5-Cr** (in the increments of 0, 0.20, 0.40, 0.60, 0.80, 1.0, 1.2, 1.5, 2.0 equivalent) in CH_3CN under Ar at 298 K.

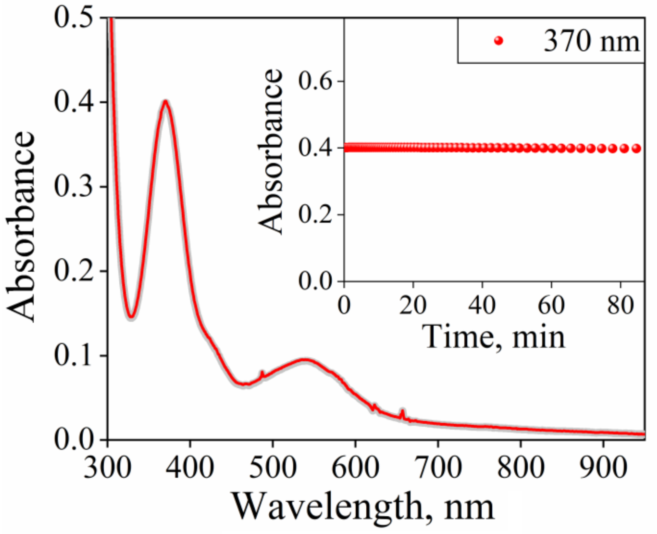

Figure S14. UV-vis spectral changes of **1-CoNO** (0.50 mM, Grey-line to red-line) in CH_3CN under Ar at 298 K. The Inset shows the time course of the decay of **1-CoNO** (red-circles) monitored at 370 nm in CH_3CN at 298 K

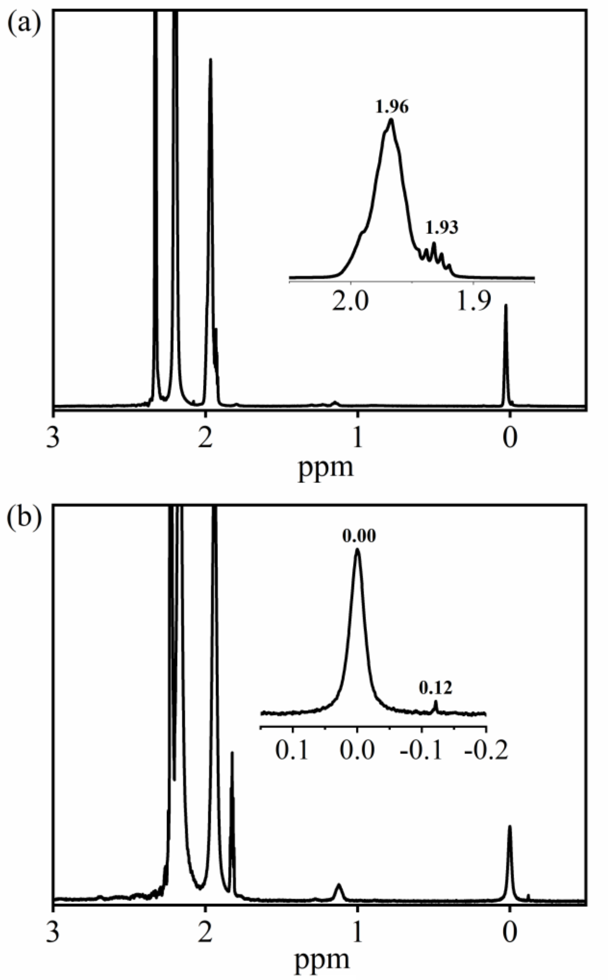

Figure S15. (a) ^{1}H-NMR (400 MHz) spectrum of **6-CrNO** (4 mM) in CD_3CN (0.1 % TMS) (b) ^{1}H-NMR (400 MHz) spectrum of **5-Cr** (4 mM) in CD_3CN (0.1 % TMS), recorded in a coaxial NMR tube, with inside CD_3CN (1.0 % TMS) at RT.

B3LYP/def2-SVP optimized Cartesian coordinates:

Reactant-quintate

Cr	-2.358243	-0.048487	-0.051813
C	-1.685635	-2.889014	1.020502
H	-1.057299	-2.273671	1.670574
N	-2.426599	-2.212170	0.123491
Cl	-0.939284	-0.140369	-2.026456
Cl	-0.481956	0.230952	1.933734
C	-1.719256	-4.277713	1.125057
H	-1.106725	-4.782958	1.873994
N	-4.444569	-0.791681	-1.229055
N	-2.699357	2.071516	-0.213910
C	-3.330937	-4.290001	-0.655888
H	-4.008307	-4.814134	-1.333220
N	-3.984066	0.335589	1.512458
C	-2.557993	-4.993211	0.268215
H	-2.619419	-6.082679	0.325143
C	-5.439884	-0.866541	-0.147829
H	-5.307864	-1.816310	0.391451
H	-6.473134	-0.882105	-0.546522
C	-4.861117	0.084333	-2.327954
H	-4.018251	0.231121	-3.018578
H	-5.157633	1.069418	-1.941265
H	-5.718461	-0.332845	-2.892306
C	-4.024833	-2.100413	-1.730888
H	-3.359665	-1.922450	-2.593027
H	-4.876696	-2.706794	-2.098519
C	-3.241792	-2.894938	-0.709451
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H	-5.438289	1.246864	0.286235
H	-6.118078	0.253592	1.578335
C	-3.949922	-0.595749	2.658280
H	-2.934597	-0.616141	3.076359
H	-4.214882	-1.609156	2.331520
H	-4.663699	-0.285777	3.443761
C	-3.661048	1.701199	1.982178
H	-2.754299	1.622580	2.605041
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H	-4.227545	4.400026	1.697725
C	-3.342672	4.781009	-0.246095
H	-3.602754	5.842218	-0.257819
C	-2.674402	4.197770	-1.325442
H	-2.399700	4.781680	-2.205863
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N	4.699398	-1.438768	-0.077258
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H	5.180365	-0.288890	-3.282098
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H	2.650581	-1.014767	2.984677
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H	3.275883	3.659858	1.130615
H	2.133659	2.547862	1.899964
C	5.728095	-0.830981	0.823051
H	6.151340	0.050939	0.317253
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C	5.098083	-0.437855	2.149444
H	4.824894	-1.333152	2.721828
H	5.817448	0.119861	2.771772
C	5.201517	-1.502005	-1.486473
H	4.691056	-2.333768	-1.988239
H	6.279163	-1.737073	-1.508182
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H	0.848048	1.697963	-1.213379
H	1.026764	3.324346	-0.454261
H	0.598809	1.857592	0.514930

TS_1-quintet

Cr	-2.459133	-0.039988	-0.075046
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C	-1.702453	-4.200397	1.264988
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C	-3.307865	2.689872	0.770433
C	-3.610181	4.053804	0.748469
H	-4.088038	4.520285	1.612354
C	-3.301695	4.800675	-0.390321
H	-3.534790	5.867418	-0.430313
C	-2.706767	4.158939	-1.479249
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C	-2.437622	2.794723	-1.387639
H	-1.979593	2.232412	-2.205800
Co	3.263058	-0.027030	0.022828
N	3.290428	-0.592695	-1.981887
N	4.077285	0.982303	1.653854
N	2.710921	1.891687	-0.676509
N	4.844512	-1.390876	0.268682
N	1.064322	-0.760030	0.403422
C	4.735417	-0.915062	-2.166477
H	5.306162	0.024899	-2.127044
H	4.910653	-1.346463	-3.168853
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H	3.679249	1.796119	3.594628
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H	3.671212	3.781553	-0.308576
H	2.544128	3.233290	0.932104
C	5.891778	-0.537683	0.893056
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H	6.746619	-1.149627	1.234462
C	4.474492	2.278844	1.027805
H	4.828259	2.985316	1.800647
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C	3.321326	1.893059	-2.032814
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H	2.993693	2.778428	-2.607918
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H	4.780806	-2.863033	-1.238747
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H	1.850061	0.596385	-2.951141
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C	1.249910	2.156560	-0.774693
H	0.747768	1.412857	-1.403943
H	1.085260	3.165720	-1.192442
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Intermediate-triplet

Cr	-2.198587	0.041903	-0.309929
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N	-2.198751	-2.018381	-0.077395
Cl	-1.320633	-0.035878	-2.462485
Cl	0.183961	-0.589018	3.338110
C	-1.431937	-4.088915	0.831959
H	-0.768901	-4.610714	1.524247

N	-4.155648	-0.455324	-1.072088
N	-2.322121	2.145957	-0.238972
C	-3.216217	-4.064785	-0.787929
H	-3.967775	-4.575166	-1.393616
N	-3.255476	0.360177	1.564193
C	-2.353143	-4.783183	0.044580
H	-2.417617	-5.872921	0.092724
C	-5.058211	-0.512842	0.121582
H	-4.973551	-1.509028	0.576328
H	-6.108637	-0.392258	-0.191490
C	-4.684658	0.495435	-2.081697
H	-3.956244	0.602042	-2.894364
H	-4.855114	1.476646	-1.620700
H	-5.641762	0.127399	-2.488453
C	-3.991441	-1.803010	-1.687610
H	-3.504073	-1.661780	-2.664444
H	-4.974377	-2.273456	-1.862007
C	-3.114659	-2.674516	-0.824546
C	-4.672726	0.553840	1.133064
H	-4.783031	1.554345	0.691337
H	-5.344639	0.513105	2.007358
C	-3.182649	-0.684034	2.624391
H	-2.133558	-0.832089	2.930101
H	-3.610723	-1.625849	2.262669
H	-3.763316	-0.350523	3.501409
C	-2.662308	1.612914	2.102331
H	-1.677093	1.338307	2.528560
H	-3.277788	2.012784	2.927119
C	-2.501819	2.635648	1.010001
C	-2.516289	4.011676	1.252946
H	-2.673810	4.381600	2.268090
C	-2.339379	4.893671	0.185861
H	-2.355943	5.973187	0.354071
C	-2.154565	4.375604	-1.100055
H	-2.023546	5.030346	-1.963441
C	-2.149477	2.994792	-1.271657
H	-1.994505	2.531340	-2.248518
Co	2.883611	0.016763	-0.158074
N	3.009445	1.725817	-1.265753
N	3.589193	-1.612972	0.852296
N	3.301739	1.157468	1.459295
N	3.204997	-1.035952	-1.862996
N	-0.068145	0.269707	0.485683
C	3.922093	1.282864	-2.360178
H	4.933817	1.176786	-1.938424
H	3.991383	2.052416	-3.150238
O	0.809780	-0.363536	-0.031700
C	2.603366	-2.407145	1.632378
H	2.027812	-1.776136	2.328220
H	3.119135	-3.211193	2.185785
H	1.882448	-2.854409	0.936601
C	3.926194	0.236654	2.459813
H	4.664646	0.773281	3.080693
H	3.118463	-0.102166	3.124780
C	4.462122	-1.742481	-1.476830
H	5.262449	-0.991176	-1.382282
H	4.781021	-2.442358	-2.270846
C	4.572619	-0.951425	1.762116
H	4.956109	-1.669746	2.508637
H	5.439656	-0.633824	1.159986
C	4.292460	2.076661	0.830034
H	5.180960	1.494177	0.536695
H	4.640410	2.837373	1.552257
C	1.727356	2.233967	-1.806040
H	1.212368	1.456421	-2.382189
H	1.894124	3.119211	-2.444301
H	1.066547	2.503687	-0.973137
C	2.147921	-1.988765	-2.279574
H	1.959147	-2.721154	-1.487033
H	2.449697	-2.525110	-3.195891
H	1.213101	-1.442426	-2.457829
C	4.269035	-2.485610	-0.158222
H	3.644866	-3.373896	-0.315599
H	5.237276	-2.853004	0.220176
C	3.443888	-0.037771	-2.947020
H	2.494704	0.106708	-3.479318
H	4.167811	-0.420110	-3.687399
C	3.669302	2.749384	-0.390521
H	2.907151	3.472361	-0.075642
H	4.427769	3.319612	-0.951742
C	2.214134	1.926392	2.118891
H	1.686722	2.550648	1.388214
H	2.640287	2.576888	2.902672
H	1.493250	1.223432	2.568684

TS_2-triplet

Cr	2.111924	-0.058537	-0.274081
C	1.641155	2.804498	0.730557
H	0.875202	2.299706	1.328051
N	2.404289	2.016517	-0.052316
Cl	1.350987	0.130731	-2.473610
Cl	-0.256848	0.348657	3.235753
C	1.847156	4.179348	0.811181
H	1.217507	4.784983	1.465330
N	4.250654	0.244122	-0.977814
N	2.093990	-2.185643	-0.273147
C	3.683635	3.925907	-0.724311
H	4.515127	4.336227	-1.300941
N	3.160113	-0.543775	1.617228
C	2.879021	4.751798	0.062224

H	3.068847	5.826970	0.105251
C	5.089513	0.211564	0.249926
H	5.064975	1.204221	0.720692
H	6.145055	0.008649	-0.003115
C	4.715368	-0.751319	-1.967849
H	4.008671	-0.786456	-2.806582
H	4.766372	-1.746936	-1.508279
H	5.719910	-0.491393	-2.346319
C	4.234154	1.592486	-1.590054
H	3.761112	1.501196	-2.580262
H	5.258589	1.977533	-1.742336
C	3.421839	2.554132	-0.759345
C	4.569992	-0.835231	1.221497
H	4.613042	-1.830545	0.757028
H	5.211369	-0.876891	2.118983
C	3.140088	0.469910	2.703951
H	2.100382	0.694577	2.981832
H	3.651112	1.383977	2.379386
H	3.665636	0.074317	3.590569
C	2.472683	-1.772004	2.087966
H	1.495777	-1.454915	2.501907
H	3.039320	-2.250615	2.906526
C	2.267253	-2.736397	0.951084
C	2.236119	-4.121863	1.132400
H	2.392747	-4.541474	2.128178
C	2.016804	-4.950222	0.030402
H	1.997256	-6.036009	0.151478
C	1.839273	-4.369740	-1.228551
H	1.679226	-4.980153	-2.119140
C	1.884404	-2.982050	-1.338689
H	1.747405	-2.470263	-2.294109
Co	-2.899817	0.081677	-0.139369
N	-3.161753	-1.574136	-1.322847
N	-3.487992	1.735069	0.905531
N	-3.456956	-1.075343	1.408181
N	-3.073786	1.219330	-1.811620
N	0.318027	-0.033917	0.484409
C	-3.980962	-0.999366	-2.430623
H	-4.993664	-0.805775	-2.043524
H	-4.095376	-1.728411	-3.252889
O	-0.731428	0.030352	-0.118840
C	-2.460991	2.445326	1.713105
H	-1.944794	1.761148	2.402950
H	-2.927285	3.275638	2.271081
H	-1.700261	2.853770	1.035315
C	-3.995851	-0.139491	2.444133
H	-4.781350	-0.628771	3.045881
H	-3.160935	0.100713	3.118174
C	-4.292239	1.997064	-1.438585
H	-5.143789	1.299340	-1.392063
H	-4.538508	2.741700	-2.217299
C	-4.529948	1.127753	1.791238
H	-4.849750	1.849265	2.563678
H	-5.419780	0.912355	1.177702
C	-4.527815	-1.862086	0.730045
H	-5.345538	-1.178917	0.447897
H	-4.964845	-2.607335	1.419105
C	-1.926494	-2.202949	-1.849538
H	-1.297016	-1.461460	-2.356130
H	-2.174446	-3.020697	-2.548212
H	-1.340827	-2.606290	-1.015109
C	-1.938376	2.109301	-2.157529
H	-1.717713	2.789351	-1.327295
H	-2.178447	2.708859	-3.052593
H	-1.041189	1.505147	-2.344984
C	-4.089978	2.681858	-0.091223
H	-3.410427	3.535570	-0.201986
H	-5.043300	3.093067	0.278774
C	-3.346958	0.284967	-2.943569
H	-2.387874	0.067762	-3.431827
H	-3.990859	0.760872	-3.703401
C	-3.958333	-2.550771	-0.508359
H	-3.297447	-3.374575	-0.212907
H	-4.765833	-2.999758	-1.109250
C	-2.450425	-1.976044	2.027819
H	-1.978381	-2.604951	1.264122
H	-2.938956	-2.626373	2.773980
H	-1.672696	-1.364569	2.512843

Product-triplet

Cr	-2.107702	-0.040055	0.248742
C	-1.467940	2.758677	-0.771736
H	-0.763541	2.198499	-1.399827
N	-2.256711	2.029543	0.043396
Cl	-1.394175	0.054881	2.509240
Cl	0.241437	0.380432	-3.181656
C	-1.584882	4.144203	-0.850066
H	-0.941468	4.703822	-1.531322
N	-4.170081	0.381051	1.001695
N	-2.277902	-2.159007	0.237433
C	-3.378825	4.021453	0.752185
H	-4.160137	4.489326	1.354487
N	-3.197004	-0.422087	-1.612329
C	-2.547318	4.787647	-0.066595
H	-2.664964	5.873163	-0.108558
C	-5.043308	0.428680	-0.207292
H	-4.961815	1.424705	-0.663736
H	-6.101956	0.295672	0.074597
C	-4.703486	-0.584605	1.990010
H	-3.992247	-0.684363	2.818855
H	-4.843596	-1.566544	1.520292

H	-5.677689	-0.242886	2.380667
C	-4.062392	1.723186	1.628173
H	-3.576622	1.593933	2.607761
H	-5.060473	2.163440	1.800490
C	-3.211637	2.634935	0.782238
C	-4.618844	-0.632535	-1.204717
H	-4.721075	-1.631122	-0.757608
H	-5.272969	-0.611952	-2.093232
C	-3.129611	0.601244	-2.690109
H	-2.080482	0.760988	-2.982208
H	-3.578551	1.541550	-2.349559
H	-3.693540	0.244765	-3.569303
C	-2.591602	-1.682128	-2.115372
H	-1.595842	-1.415367	-2.522594
H	-3.189667	-2.100326	-2.944252
C	-2.458672	-2.680025	-0.997599
C	-2.502723	-4.061949	-1.201353
H	-2.664205	-4.456850	-2.206388
C	-2.348135	-4.916997	-0.108977
H	-2.386048	-6.000289	-0.246534
C	-2.157646	-4.366074	1.161410
H	-2.043370	-4.997693	2.044190
C	-2.126106	-2.979934	1.293377
H	-1.970353	-2.489538	2.256899
Co	2.913233	0.023515	0.141901
N	3.225131	-1.672570	1.253491
N	3.446572	1.741291	-0.830792
N	3.511788	-1.044439	-1.455756
N	3.028336	1.094455	1.854033
N	-0.438150	-0.188022	-0.162804
C	4.015491	-1.111597	2.389426
H	5.022086	-0.862388	2.018411
H	4.154615	-1.868319	3.182241
O	0.734667	-0.391766	-0.086405
C	2.407934	2.455826	-1.620198
H	1.905297	1.783405	-2.333865
H	2.860918	3.313325	-2.147303
H	1.637974	2.828585	-0.932344
C	4.019785	-0.045792	-2.446869
H	4.820547	-0.481574	-3.069206
H	3.176541	0.196978	-3.109862
C	4.224609	1.927116	1.527742
H	5.098449	1.259379	1.461367
H	4.438004	2.644054	2.341211
C	4.512613	1.205301	-1.735019
H	4.814079	1.971002	-2.471182
H	5.405038	0.989267	-1.125323
C	4.607620	-1.822709	-0.808458
H	5.402978	-1.125512	-0.497375
H	5.069670	-2.524423	-1.526289
C	2.022180	-2.383007	1.753057
H	1.361639	-1.697181	2.297216
H	2.313721	-3.217406	2.413875
H	1.452690	-2.775387	0.902905
C	1.861903	1.934364	2.222920
H	1.626558	2.638358	1.416478
H	2.075934	2.509221	3.140578
H	0.981477	1.298475	2.387675
C	4.014512	2.662232	0.208649
H	3.312771	3.493626	0.347184
H	4.959947	3.112258	-0.135174
C	3.325655	0.123853	2.949680
H	2.370674	-0.150903	3.416653
H	3.942156	0.592515	3.736140
C	4.061968	-2.581623	0.399435
H	3.432512	-3.415896	0.067450
H	4.884460	-3.024790	0.984147
C	2.538841	-1.947959	-2.125217
H	2.097031	-2.640127	-1.399546
H	3.052651	-2.531223	-2.908710
H	1.733197	-1.340222	-2.570222