

Supporting Information

Exploring the Carbonic Anhydrase-Mimetic [(PMDTA)₂Zn^{II}₂(OH⁻)₂]²⁺ for Nitric Oxide Monooxygenation

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Experimental Section

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}

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. ¹H-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 (High-Resolution Bio-QTOF -6545 XT) by infusing samples directly into the source using a manual method. The spray voltage was set at 4 kV and the capillary temperature at 325 °C.

Synthesis of [(PMDTA)₂Zn₂^{II}(OH)₂](ClO₄)₂ (1**).** Perchlorate salts are highly explosive and, thus, should be handled carefully. Necessary precautions should be taken before performing the reaction. To prepare complex **1**, Zn^{II}(ClO₄)₂·6H₂O (372 mg, 1.0 mmol) was dissolved in 30 ml CH₃OH. A solution of PMDTA (173 mg, 1.0 mmol) ligand in 2ml of CH₃OH (PMDTA= N,N,N',N'',N''' pentamethyldiethylenetriamine) was added dropwise to the CH₃OH solution of Zn^{II}(ClO₄)₂·6H₂O and kept for stirring for 15 minutes at room temperature (298 K). After 15 minutes, a solution of KOH (57mg, 1.0 mmol) in 5 ml CH₃OH was added dropwise and stirred for 1 hour at 298 K. After 1 hour, a precipitate of KClO₄ formed at the bottom of the reaction mixture. The solution was filtered to remove the KClO₄, and the filtrate was dried under reduced pressure to yield a white solid. The solid was washed with ether (Et₂O) multiple times and dried to get pure complex **1**. The complex **1** is stable at room temperature for several

months. Yield: 300 mg (~ 85 %). The UV-visible spectrum of **1** in CH₃CN at 298 K: λ_{\max} = 260 nm. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 2.83 – 2.60 (m, 16H), 2.52 (s, 30H). ESI-MS (*m/z*): Calcd: *m/z* 254.12, 611.20 Found: *m/z* 254.12, 611.20 for [(PMDTA)Zn(OH⁻)]⁺ and [(2H)(PMDTA)Zn₂(OH⁻)₂(ClO₄)]⁺ respectively. [(PMDTA)₂Zn^{II}(OD)₂]₂ (ClO₄)₂ was synthesized using a similar method by using KOD. ESI-MS (*m/z*): Calcd: *m/z* 255.12, Found: *m/z* 255.12, for [(PMDTA)Zn(OD⁻)]⁺. Anal. calcd for C₁₈H₄₈Cl₂N₆O₁₀Zn₂: C, 30.44; H, 6.81; N, 11.83; found: C, 30.58; H, 6.72; N, 11.56.

Synthesis of [(PMDTA)₂Zn^{II}(OH)₂](BPh₄)₂ (1-BPh₄**).** To prepare **1-BPh₄**, **1** (72 mg, 0.15 mmol) was dissolved in 10 ml CH₃OH. A methanolic solution of NaBPh₄ (51.3 mg, 0.15 mmol) was added dropwise to **1** at 298 K and stirred for 30 minutes. After 30 minutes, a white colour precipitate of **1-BPh₄** formed at the bottom of the reaction mixture. The precipitate was filtered and washed with CH₃OH multiple times. The solid was then dissolved in 2ml CH₃CN and kept for crystallization with Et₂O. Colourless block-type crystals were obtained by vapor diffusion of Et₂O over 3-4 days at 298 K.

Generation of [(PMDTA)Zn^{II}(NO₂)](ClO₄) (3** or **3b**) in the reaction of **1** + NO.** Perchlorate salts are highly explosive and, thus should be handled carefully. Necessary precautions should be taken before performing the reaction. To determine the NOM product, complex **1** was reacted with NO gas. In this regard, complex **1** (50 mg, 0.07 mmol) was reacted with NO. 50 mg of **1** was dissolved in 3 ml CH₃CN in a 50 ml vial and sealed with rubber septum inside the glove box. The vial was taken out and cooled to 273 K, and equivalent amount of NO was purged to the solution of **1** in CH₃CN under an Ar atmosphere at 273 K. After adding NO, the color of the reaction mixture immediately changed from colorless to yellow. The solution was further stirred for 2 hours at 298 K, and the color of the solution became pale-yellow/colorless from yellow, ensuring the reaction's completion. The reaction

mixture was then purged with Ar and vacuum three times to remove any excess NO is present. Et₂O was added to the reaction mixture to yield a white precipitate of **3**. The reaction mixture was then dissolved in CH₃OH for crystallization with Et₂O. X-ray crystallographic suitable crystals were formed by vapor diffusion of Et₂O within two days at 298 K. The isolated product was characterized to be [(PMDTA)Zn(NO₂⁻)(CH₃OH)](ClO₄) (**3b**) by various spectroscopical techniques. Yield: 21 mg (~ 72 %). FT-IR (in KBr pellet): 1271 (NO₂⁻ stretching), 1084 (ClO₄⁻ stretching). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 2.85 – 2.62 (m, 8H), 2.56 (s, 12H), 2.18 (s, 3H). ESI-MS (*m/z*): Calcd: *m/z* 283.11, Found: *m/z* 283.11 for [(PMDTA)Zn(NO₂⁻)]⁺. [(PMDTA)Zn(¹⁵NO₂⁻)](ClO₄) was synthesized using same method by using ¹⁵NO. FT-IR (in KBr pellet): 1245 (NO₂⁻ stretching), 1084 (ClO₄⁻ stretching). ESI-MS (*m/z*): Calcd: *m/z* 284.11, Found: *m/z* 284.11 for [(PMDTA)Zn(¹⁵NO₂⁻)]⁺. Anal. calcd for C₁₁H₂₆ClN₅O₆Zn: C, 31.07; H, 6.16; N, 16.47; found: C, 30.82; H, 6.32; N, 16.56.

Synthesis of [(PMDTA)Zn^{II}(NO₂)](ClO₄) (3** or **3b**).** Perchlorate salts are highly explosive thus should be handled carefully. Necessary precautions should be taken before performing the reaction. To prepare **3** independently, Zn^{II}(ClO₄)₂·6H₂O (108 mg, 0.29 mmol) dissolved in 5 ml of CH₃OH. A solution of NaNO₂ (20 mg, 0.29 mmol) in 2 ml CH₃OH was added dropwise with continued stirring. The reaction mixture was stirred for 10 minutes. After 10 minutes, a solution of PMDTA ligand (51 mg, 0.29 mmol) in CH₃OH is added dropwise to the reaction mixture and stirred for 30 minutes. After 30 minutes, the solvent was evaporated under reduced pressure to yield a white solid. The solid was then washed multiple times with ether and dried to get pure [(PMDTA)Zn^{II}(NO₂)](ClO₄). The white solid was then dissolved in CH₃OH and kept for crystallization by vapor diffusion of Et₂O. Crystalline yield: 77 mg (~ 70 %). FT-IR (in KBr pellet): 1271 (NO₂⁻ stretching), 1084 (ClO₄⁻ stretching). [(PMDTA)Zn^{II}(¹⁵NO₂)](ClO₄) was prepared using same method by using Na¹⁵NO₂.

Synthesis of [(PMDTA)Zn^{II}(NO₂⁻)(OH⁻)](BPh₄)₂ (4**).** Perchlorate salts are highly explosive thus should be handled carefully. Necessary precautions should be taken before performing the reaction. To prepare **4** [(PMDTA)Zn^{II}(NO₂)](ClO₄) (120 mg, 0.29 mmol) dissolved in 5 ml of CH₃OH. A solution of KOH (34 mg, 0.58 mmol) in 2 ml CH₃OH was added dropwise into [(PMDTA)Zn^{II}(NO₂)](ClO₄) with continued stirring. A white color precipitate starts to form at the bottom of the reaction mixture. The reaction mixture was stirred for a further 1 hour. After 1 hour, the mixture was filtered, and the solvent evaporated under reduced pressure to yield a white product. The white product was further dissolved in 3 ml CH₃OH. A methanolic solution of NaBPh₄ (99 mg, 0.29 mmol) was added dropwise to the reaction mixture at 298 K and stirred for 30 minutes. After 30 minutes, a white precipitate formed. The precipitate was filtered and washed with CH₃OH multiple times and dried under reduced pressure to get a white product **4**. **4** was dissolved in CH₃CN and crystalized using Et₂O. Crystallographically suitable crystal obtained by vapor diffusion of Et₂O to the solution of **4** in CH₃CN over 1 week at 298 K. Crystalline yield: 120 mg (~ 70 %). FT-IR (in KBr pellet): 1268 (NO₂⁻ stretching). Anal. calcd for C₆₆H₈₇B₂N₇O₃Zn₂: C, 67.25; H, 7.44; N, 8.32; found: C, 67.32; H, 7.48; N, 8.29.

Trapping the proposed [Zn₂(ONOH)₂]²⁺ intermediate by Solution IR spectroscopy. To characterize and witness the nature of the intermediate, the reaction of **1** and NO was further tracked using FT-IR spectroscopy. A CH₃CN solution of **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 **1** (4 mM in CH₃CN) was prepared, attached with a rubber septum, and cooled to 233 K. First, the FT-IR spectrum of **1** was collected. Complex **1** in a separate vial was treated with NO, and as soon as the color changed to yellow, it was frozen. The vial was purged with Ar and a vacuum to remove if any excess NO. After the removal of excess NO slowly warmed to 233 K, and as

soon as it started liquefying reaction mixture was taken and injected in the clean demountable cell holding, and the IR spectra were collected at RT. In the following scan, we observed the formation of a new peak at 1260 cm^{-1} and at 1224 cm^{-1} when the reaction was performed with ^{15}NO . The peak at 1260 cm^{-1} and 1224 cm^{-1} corresponded to Zn-nitrous acid intermediate species, which formed with time, disappeared, and shifted to 1273 cm^{-1} and 1247 cm^{-1} , respectively, corresponding to Zn-bound- NO_2^- species.

Reactivity Studies. All UV-Visible 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 have performed all the reactions either at 298 K /or 273 K as the initial $[(\text{PMDTA})_2\text{Zn}_2^{\text{II}}(\text{OH})_2]_2(\text{ClO}_4)_2$ complex (**1**), and the final product, and all reactants are very stable even at 298 K. The formation of complex **3** in the above reactions was identified by comparing them with authentic samples prepared independently.

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 NOM reactions. These reactions were executed under an inert atmosphere. 20 mM solutions of **1** were prepared and reacted with NO and ^{15}NO in two different reactions under an Ar atmosphere at 298 K. 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** and NO showed a characteristic peak at 1271 cm^{-1} for Zn-bound nitrite. This peak was shifted to 1245 cm^{-1} when the reaction mixture of **1** + ^{15}NO was analyzed. The change in the IR stretching frequency of Zn-bound-nitrite ($\Delta = 27\text{ cm}^{-1}$) 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.

Labelling (^{14}N & ^{15}N) experiments using ESI-MS spectrometry. Furthermore, to establish the source of N in the NOM reaction, complex **1** was reacted with NO and ^{15}NO 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** (0.5 mM / 2.5 mL) in CH_3CN sealed with a rubber septum under an Ar atmosphere were reacted with NO and ^{15}NO 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 $[(\text{PMDTA})_2\text{Zn}^{\text{II}}(\text{OH})_2]_2(\text{ClO}_4)_2$ with NO showed a prominent peak at m/z 283.11, whose mass value and isotopic distribution pattern corresponds to $[(\text{PMDTA})\text{Zn}(\text{NO}_2)]^+$ (calcd m/z 283.11). The peak shifted to m/z 284.11 corresponds to $[(\text{PMDTA})\text{Zn}(^{15}\text{NO}_2)]^+$ (calcd m/z 284.11), when the reaction was carried out using ^{15}NO .

Single-Crystal XRD Studies: Single-crystal XRD data were collected at 100 K on a Bruker X-ray diffractometer (D8 Venture) using monochromated $\text{MoK}\alpha$ ($\lambda = 0.7107 \text{ \AA}$) radiation. The collected frames were integrated, scaled, 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 F^2 by weighted full-matrix least squares using SHELXL.^{S2} 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-2242240-2242242 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Hydrogen gas detection and D-labeling experiments by headspace Mass spectrometry. In order to investigate the source of H_2 production in the reaction of Complex **1** with $\text{NO}_{(\text{g})}$, we

carried out two separate experiments of **1** and **1-OD⁻** with NO_(g) in CH₃CN under an Ar atmosphere at 298 K. The mass of the gases produced in each reaction was monitored using an online mass spectrometer with an OmniStar™ Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus. To carry out the experiments, two vials containing Complex **1** (5.0 mM, 2.0 mL) and **1-OD⁻** (5.0 mM, 2.0 mL) in a CH₃CN solution were sealed with a rubber septum and connected to the mass spectrometer via a capillary for real-time measurement. To the solution, NO_(g) was added under an Ar atmosphere using a gas-tight Hamilton syringe. To minimize interference from other gases, all samples were prepared in an ultra-pure Ar (6 grade) atmosphere. The reaction mixture was then stirred at 298 K for 10 minutes prior to the analysis of the gases produced (H₂ or D₂, as appropriate). The expected m/z of the gas was set on the instrument (2 for H₂, 4 for D₂) to track the formation of the gas. Gases produced in each experiment were identified by monitoring the mass of each gas using the mass spectrometer. The formation of H₂ and D₂ gases was observed in similar reaction conditions. These experiments allowed us to investigate the source of H₂ production in the reaction of Complex **1** and **1-OD⁻** with NO_(g) and provided insights into the mechanism of the reaction.

Quantification of H₂ gas: To quantify the amount of H₂ gas produced in the reaction, we prepared the H₂ calibration curve with respect to the Ar gas. In this regard, a 20 mL vial with 2 mL CH₃CN was sealed in the glove box with an air-tight rubber septum. In the vial, then 0.2 mL of authentic H₂ gas was purged. The mixture was then analyzed using the Omnistar Online gas mass analyzer. In the next experiment, a mixture of 20 mL Ar and 4 mL H₂ gas was analyzed. The process was repeated with 0.6 mL, 0.8 mL, and 1.0 mL H₂ gas, keeping the volume of Ar constant. Then, the area ratio of Ar/H₂ obtained from the chromatogram was plotted for the amount of the H₂ gas to get a straight calibration curve.

Next, in a 20 ml vial, 15.8 mg (0.022 mmol) of complex **1** was taken, dissolved in 2 ml of CH₃CN, and sealed in the glove box with an air-tight rubber septum. To the solution of **1**, two equivalents of NO (99.9% pure) were added using a gas-tight Hamiltonian syringe. After the addition of NO, the solution immediately turned yellow. The reaction mixture was then further stirred for 1-2 hours until the color of the solution was completely colorless. The reaction mixture was then analyzed using the Omnistar Online gas mass analyzer. Then the area ratio of Ar/H₂ was obtained from the chromatogram, and the amount of H₂ gas was calculated from the calibration curve.

	Experimental H ₂ amount obtained from Calibration Curve	Theoretical Yield	% of yield
Experiment I	0.326 mL	0.5 mL	64%
Experiment I	0.331 mL	0.5 mL	66%
Experiment I	0.292 mL	0.5 mL	58%
Overall Yield \approx 63%			

Nitric Oxide Preparation and Purification. Nitric oxide (NO) was prepared and purified by following a detailed procedure, as shown in Figure. S1. First, NO was prepared by the reaction of NaNO₂ with H₂SO₄ 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 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 CH₃CN solution for 15 minutes. The concentration of NO in the NO-saturated CH₃CN solution is ~14 mM.^{S3}

Table T1 Crystallographic data for **1**, **3**, and **4**.

	1	3	4
Chemical formula	C ₆₆ H ₈₈ B ₂ N ₆ O ₂ Zn ₂	C ₁₀ H ₂₇ ClN ₄ O ₇ Zn	C ₆₈ H ₉₀ B ₂ N _{7.75} O _{3.25} Zn ₂
Formula weight	1149.78	416.17	1220.33
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> , K	100(2)	100	100(2)
<i>a</i> , Å	10.8666(12)	9.6272(4)	13.7304(6)
<i>b</i> , Å	11.7591(13)	11.9853(4)	18.0171(7)
<i>c</i> , Å	13.5100(14)	15.4192(6)	26.2207(11)
α , °	69.809(4)	90	90
β , °	72.122(4)	100.4460(10)	95.764(2)
γ , °	69.657(4)	90	90
<i>V</i> / Å ³	1484.5(3)	1749.39(12)	6453.7(5)
<i>Z</i>	1	4	4
Calculated density, g/cm ³	1.286	1.580	1.256
Abs. Coeff. /mm ⁻¹	1.208	1.595	0.795
Reflections collected	75219	52058	266499
Unique reflections	7330	5294	15979
Refinement method	Least-squares on <i>F</i> ²	Least-squares on <i>F</i> ²	Least-squares on <i>F</i> ²
Data/restraints/parameters	7330/1/360	5294/0/215	15979/132/980
Goodness-of-fit on <i>F</i> ²	1.070	1.072	1.038
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0387, w <i>R</i> 2 = 0.1064	<i>R</i> 1 = 0.0215, w <i>R</i> 2 = 0.0581	<i>R</i> 1 = 0.0543, w <i>R</i> 2 = 0.1408
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0440, w <i>R</i> 2 = 0.1142	<i>R</i> 1 = 0.0227, w <i>R</i> 2 = 0.0587	<i>R</i> 1 = 0.0646, w <i>R</i> 2 = 0.1487

Table T2 Selected bond lengths (Å) and bond angles (°) for **1**, **3** and **4**.

1		3		4	
Zn1 Zn1 ¹	3.1298(5)	Zn1 O1	2.0896(8)	Zn1 O1	1.9525(18)
Zn1 O1	1.9803(15)	Zn1 O2	2.3526(9)	Zn1 N3	2.229(2)
Zn1 O1 ¹	2.0212(15)	Zn1 O3	2.1634(8)	Zn1 N2	2.05(2)
Zn1 N1	2.1173(16)	Zn1 N2	2.1140(8)	Zn1 N4	2.186(3)
Zn1 N2	2.1437(17)	Zn1 N3	2.1779(8)	Zn1 O2	2.053(5)
Zn1 N3	2.2327(17)	Zn1 N4	2.1461(8)	Zn2 O3	2.045(4)
				Zn2 O1	1.9343(18)
				Zn2 N7	2.155(11)
				Zn2 N5	2.152(3)
				Zn2 N6	2.232(3)
O1 ¹ Zn1 Zn1 ¹	38.08(4)	N2 Zn1 O3	92.87(3)	O1 Zn1 N3	95.81(8)
O1 Zn1 Zn1 ¹	39.01(4)	N2 Zn1 O2	89.12(3)	O1 Zn1 N4	127.85(9)
O1 Zn1 O1 ¹	77.09(7)	N2 Zn1 N4	117.07(3)	O1 Zn1 O2	95.8(3)
O1 ¹ Zn1 N1	103.38(6)	N2 Zn1 N3	85.01(3)	O1 Zn1 N2	119.0(6)
O1 Zn1 N1	116.11(7)	O1 Zn1 N2	145.02(3)	N4 Zn1 N3	81.45(9)
O1 Zn1 N2	130.95(7)	O1 Zn1 O3	88.48(3)	O2 Zn1 N3	168.2(3)
O1 ¹ Zn1 N2	98.26(6)	O1 Zn1 O2	55.95(3)	O2 Zn1 N4	93.2(3)
O1 ¹ Zn1 N3	172.75(6)	O1 Zn1 N4	97.66(3)	O2 Zn1 N2	92.4(6)
N3 Zn1 O1	97.14(6)	O1 Zn1 N3	95.31(3)	N2 Zn1 N3	79.9(6)
N1 Zn1 Zn1 ¹	115.33(5)	O3 Zn1 O2	88.85(3)	N2 Zn1 N4	111.7(6)
N1 Zn1 N2	112.48(7)	O3 Zn1 N3	175.84(3)	O3 Zn2 N7	89.6(4)
N1 Zn1 N3	83.04(6)	N4 Zn1 O3	93.93(3)	O3 Zn2 N5	89.70(18)
N2 Zn1 Zn1 ¹	120.49(5)	N4 Zn1 O2	153.43(3)	O3 Zn2 N6	161.42(15)
N2 Zn1 N3	82.12(6)	N4 Zn1 N3	83.88(3)	O1 Zn2 O3	97.33(14)
N3 Zn1 Zn1 ¹	84.45(7)	N3 Zn1 O2	94.69(3)	O1 Zn2 N7	116.1(3)
		O2 N1 O1	112.76(9)	O1 Zn2 N5	117.65(10)
				O1 Zn2 N6	101.18(9)
				N7 Zn2 N6	83.7(4)
				N5 Zn2 N7	125.9(3)
				N5 Zn2 N6	80.37(10)
				Zn2 O1 Zn1	129.50(10)

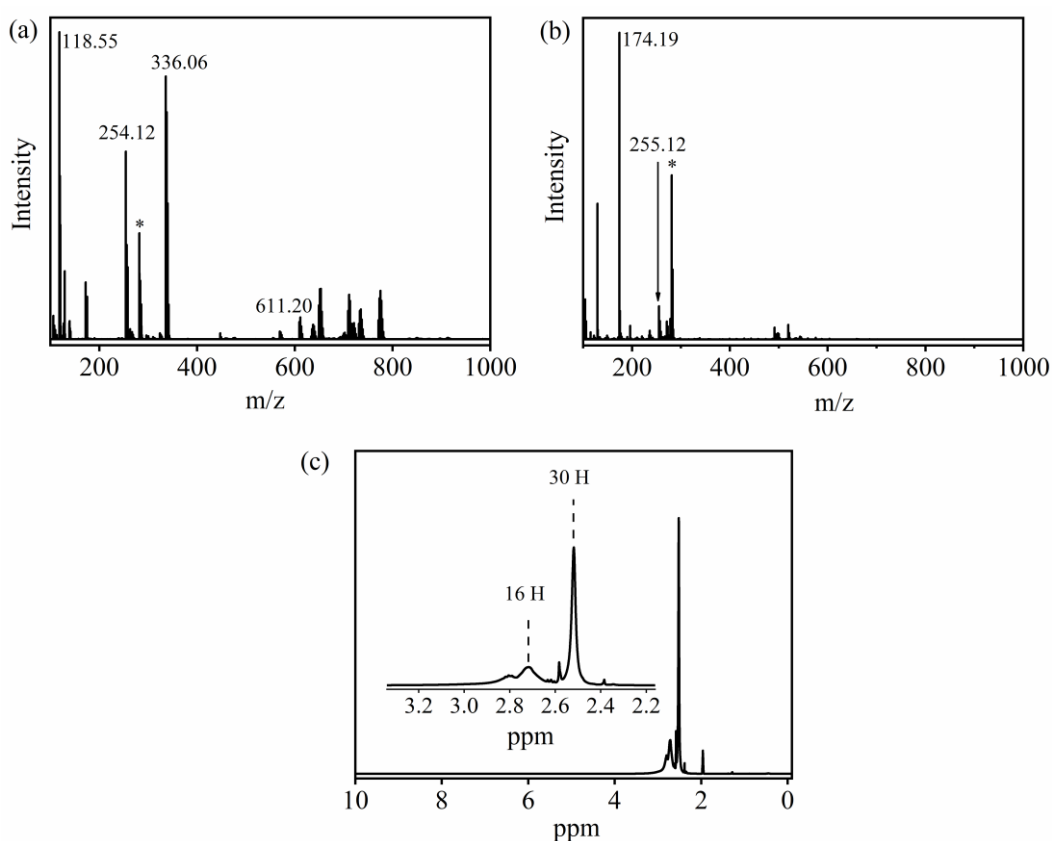


Figure S1. (a) ESI-MS spectrum of **1** in CH₃CN, The peak at m/z 118.55, 254.12, 336.06, are assigned to be [(PMDTA)Zn]²⁺ (calcd. m/z 118.55), [(PMDTA)Zn(OH)]⁺ (calcd. m/z 254.12), [(PMDTA)Zn(ClO₄)]⁺ (calcd. m/z 336.06). The peak at 282.11 marked with an asterisk (*) is assigned to be [(PMDTA)Zn(HCOO⁻)]⁺ (calcd: m/z 282.11), generated due to the formic acid dilution in the mobile phase. (b) ESI-MS spectrum of **1-OD⁻** in CH₃CN, The peak at m/z 174.19, 255.12, are assigned to be [(PMDTA)(H)]⁺ (calcd. m/z 174.19), [(PMDTA)Zn(OD)]⁺ (calcd. m/z 255.12). The peak at 282.11 marked with an asterisk (*) is assigned to be [(PMDTA)Zn(HCOO⁻)]⁺ (calcd: m/z 282.11), generated due to the formic acid dilution in the mobile phase. (c) ¹H-NMR (400 MHz) spectra of complex **1** under Ar in CD₃CN at 298 K.

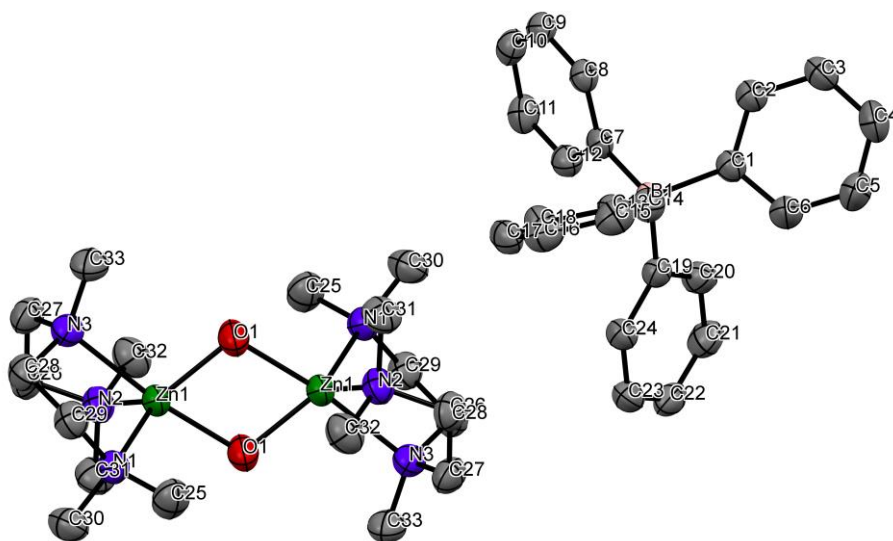


Figure S2. Displacement ellipsoid plots of **1** with 60 % probability at 100 K. The H atoms have been removed for clarity. (Although there is problem with the 100 % occupancy of the OH species in the crystal structure. The Zn-OH species presented in the manuscript is characterized by UV-vis, ^1H NMR, ESI-MS spectrometry, and labeling experiments. In ESI-MS spectroscopy, we observed peaks for both dimeric and monomeric Zn-OH species sensitive to H-labelling. The above results suggested the existence of Zn-OH species. Furthermore, the structural parameter of the presented Zn-OH matches with the previously reported almost similar bridging Zn-OH species by Weiss and co-workers (Present manuscript Zn-O = 1.980, previously reported Zn-O = 1.986)^{S4}. Even the elemental analysis suggested the high purity of the Zn-OH species. Considering all this, we believe that the bridging species are OH^- ions.)

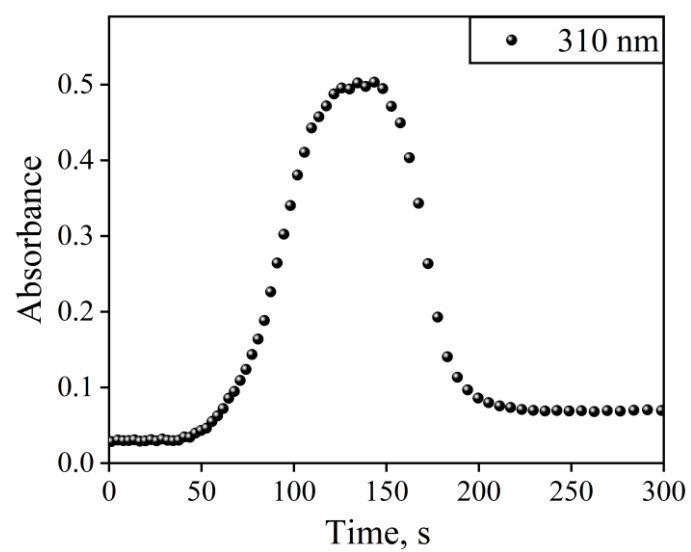


Figure S3. The Time course of formation and the decay of **2** were monitored at 310 nm upon the addition of NO to a solution of **1** (0.5 mM) under Ar in CH₃CN at 273 K.

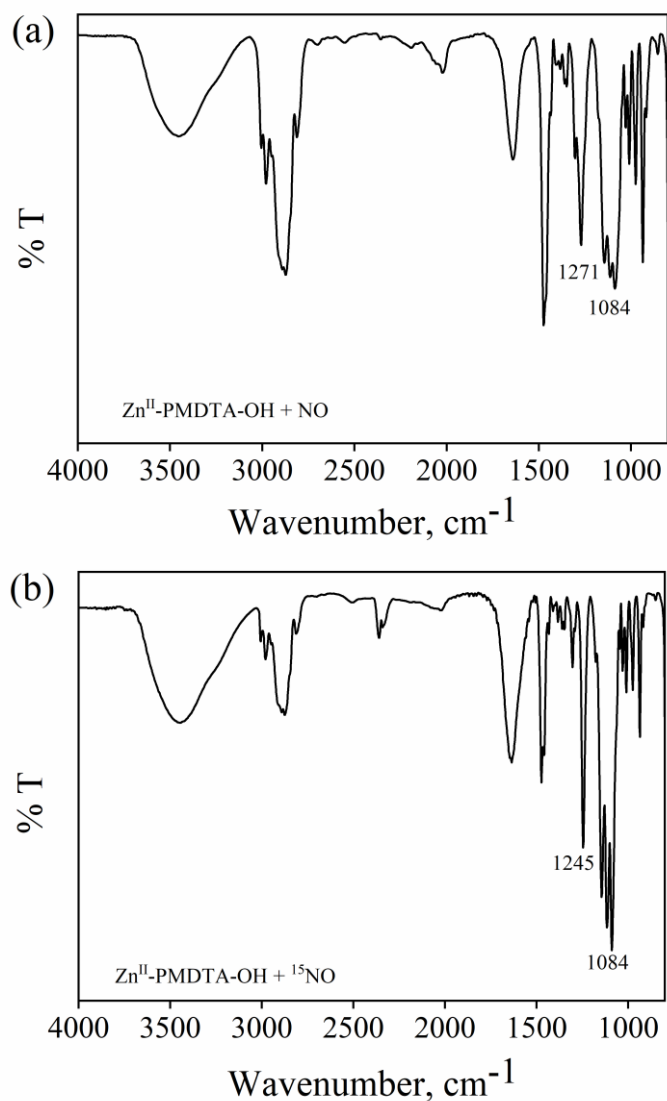


Figure S4. FT-IR spectrum of (a) isolated product, obtained in the reaction of **1** + ¹⁴NO recorded in KBr pellet at 298 K. The spectrum showed the peaks for [Zn-¹⁴NO₂] (1271 cm⁻¹) and an additional peak for ClO₄⁻ (1084 cm⁻¹). (b) The isolated product obtained in the reaction of **1** + ¹⁵NO was recorded in a KBr pellet at 298 K. The spectrum showed the peaks [Zn-¹⁵NO₂] (1245 cm⁻¹) and an additional peak for ClO₄⁻ (1084 cm⁻¹).

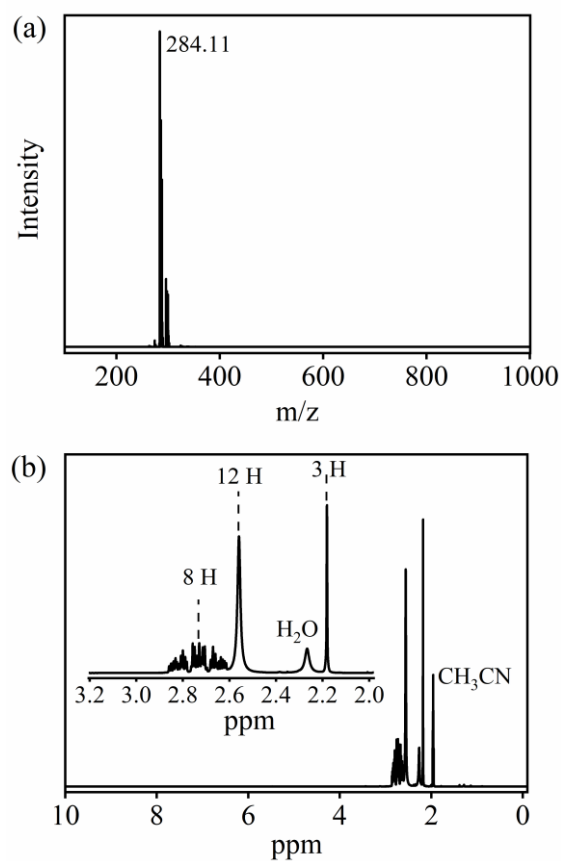


Figure S5. (a) ESI-MS spectrum of **3**-¹⁵NO₂, formed in the reaction of **1** + ¹⁵NO, recorded in CH₃CN. The peak at *m/z* 284.11 assigned to be [(PMDTA)Zn(¹⁵NO₂)]⁺ (calcd: *m/z* 284.11) (b) ¹H-NMR (400 MHz) spectra of isolated complex **3** prepared in the reaction of **1** + NO under Ar in CD₃CN at 298 K.

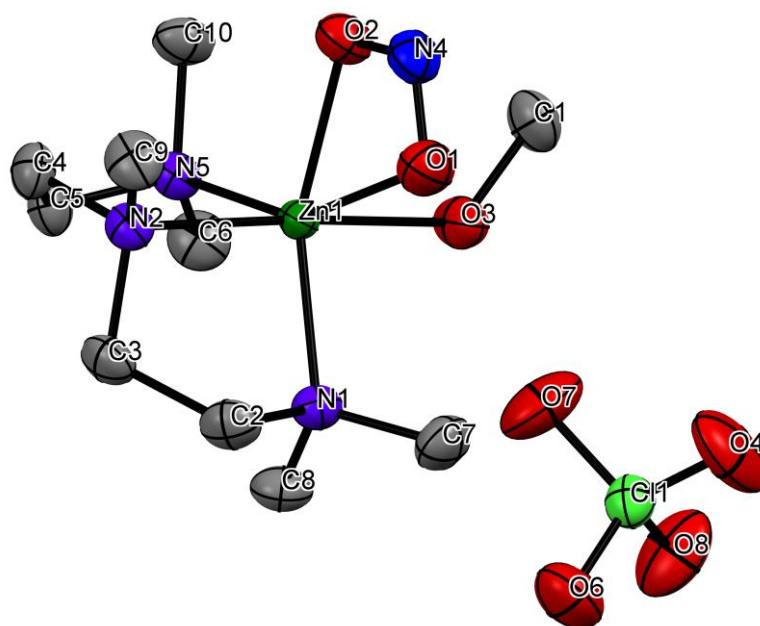


Figure S6. Displacement ellipsoid plots of **3** with 60 % probability at 273 K. The H atoms have been removed for clarity.

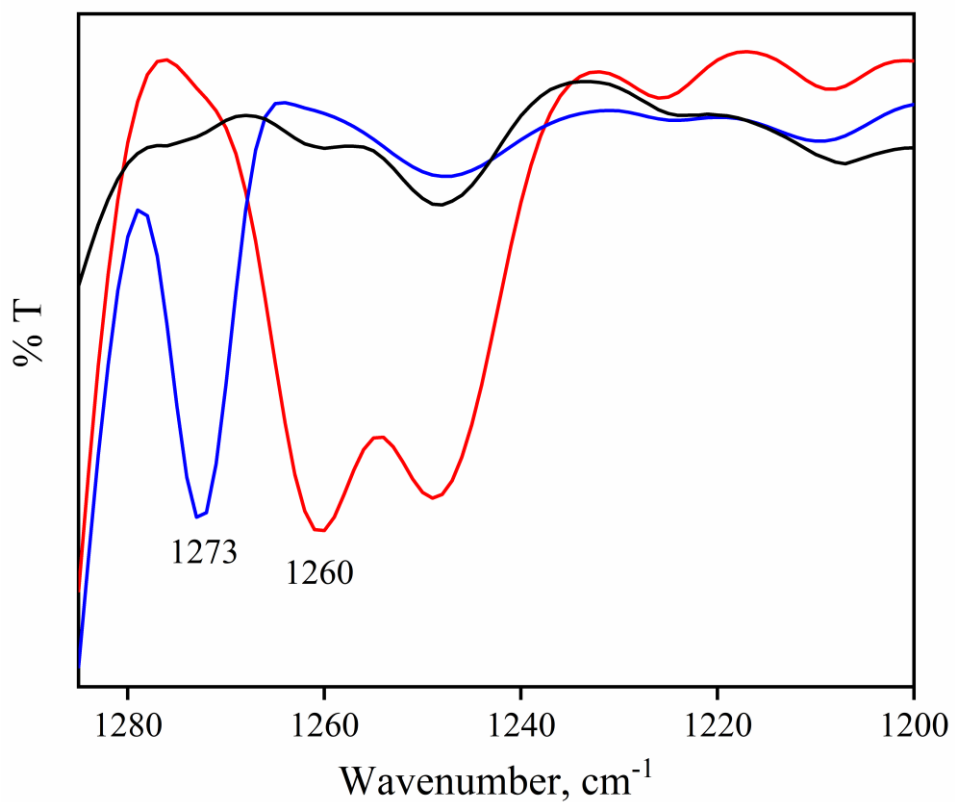


Figure S7. The solution IR spectra of **1** (Black line) and the $[\text{Zn}_2(\text{ONOH})_2]^{2+}$ intermediate (**2**) formed in the reaction of **1** + NO (Red line). The intermediate further changed to a blue line, which corresponds to **3**.

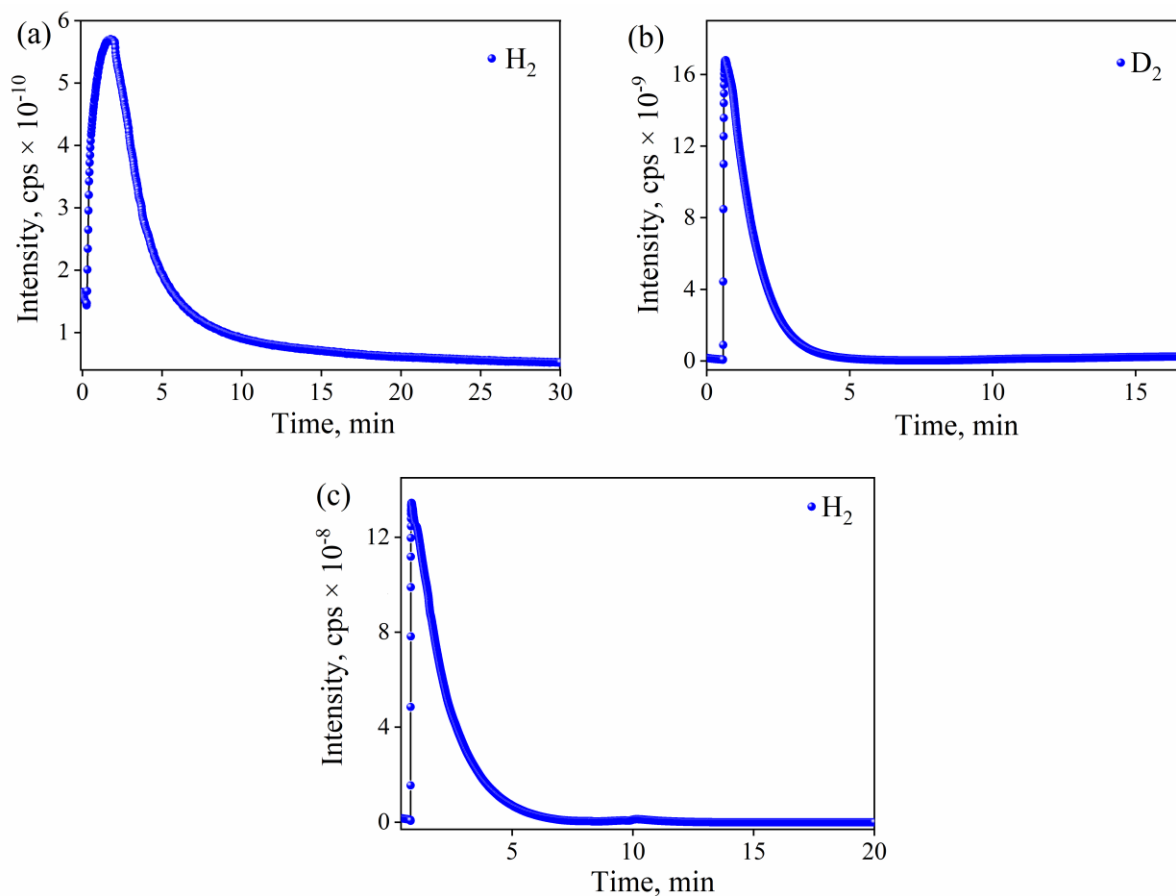


Figure S8. Time profile of Mass spectra monitoring (a) H₂ isotopes [two (¹H-¹H)] produced in the reaction of **1** (5.0 mM) with NO, (b) D₂ isotopes [four (²D-²D)] in the reaction of **1-OD** (5.0 mM) with NO (c) H₂ isotopes [two (¹H-¹H)] produced in the reaction of **1** (5.0 mM) with NO in presence of 2,4 DTBP.

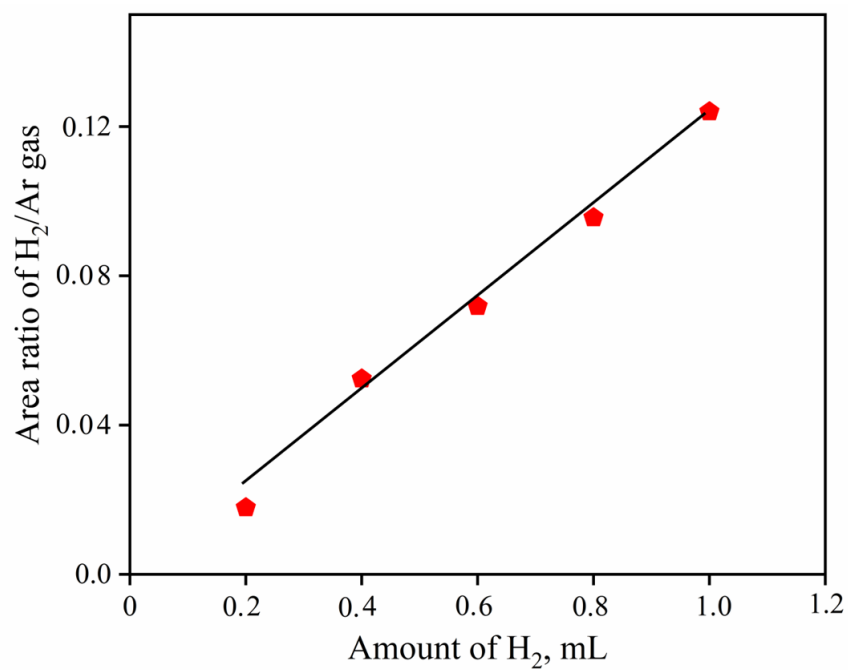


Figure S9. The gas-mass analyzer calibration plot for H₂ was made with respect to the internal standard Ar gas.

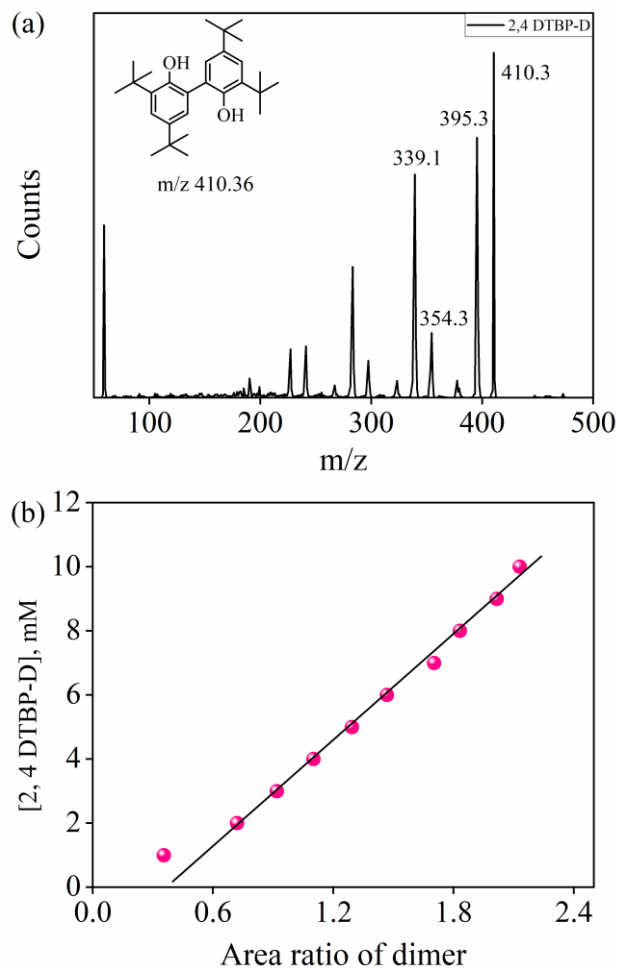


Figure S10. GC-MS characterization of (a) 2,4-DTBP-dimer (2,4-DTBP-D); the peaks at m/z 410.3, 395.3, 354.3 339.3, and 190.2 are assigned to be 2,4-DTBP-D, loss of CH_3 , loss of C_4H_9 , loss of C_5H_{11} from 2,4-DTBP-D and loss of CH_3 from monomer 2,4-DTBP (b) GC-MS Calibration plot for 2,4-DTBP-D.

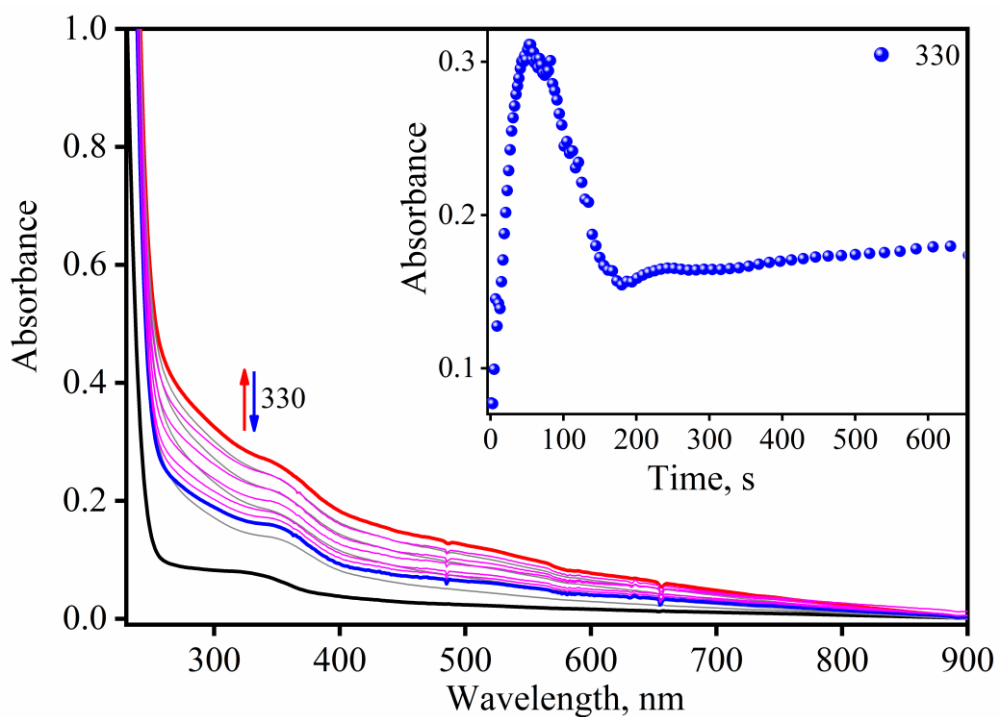


Figure S11. UV-Visible spectral changes were observed when **3** (1 mM, black line) reacted with two equivalents of KOH (blue line) under Ar in CH₃CN at 273 K. Inset shows the time course of absorption at 330 nm.

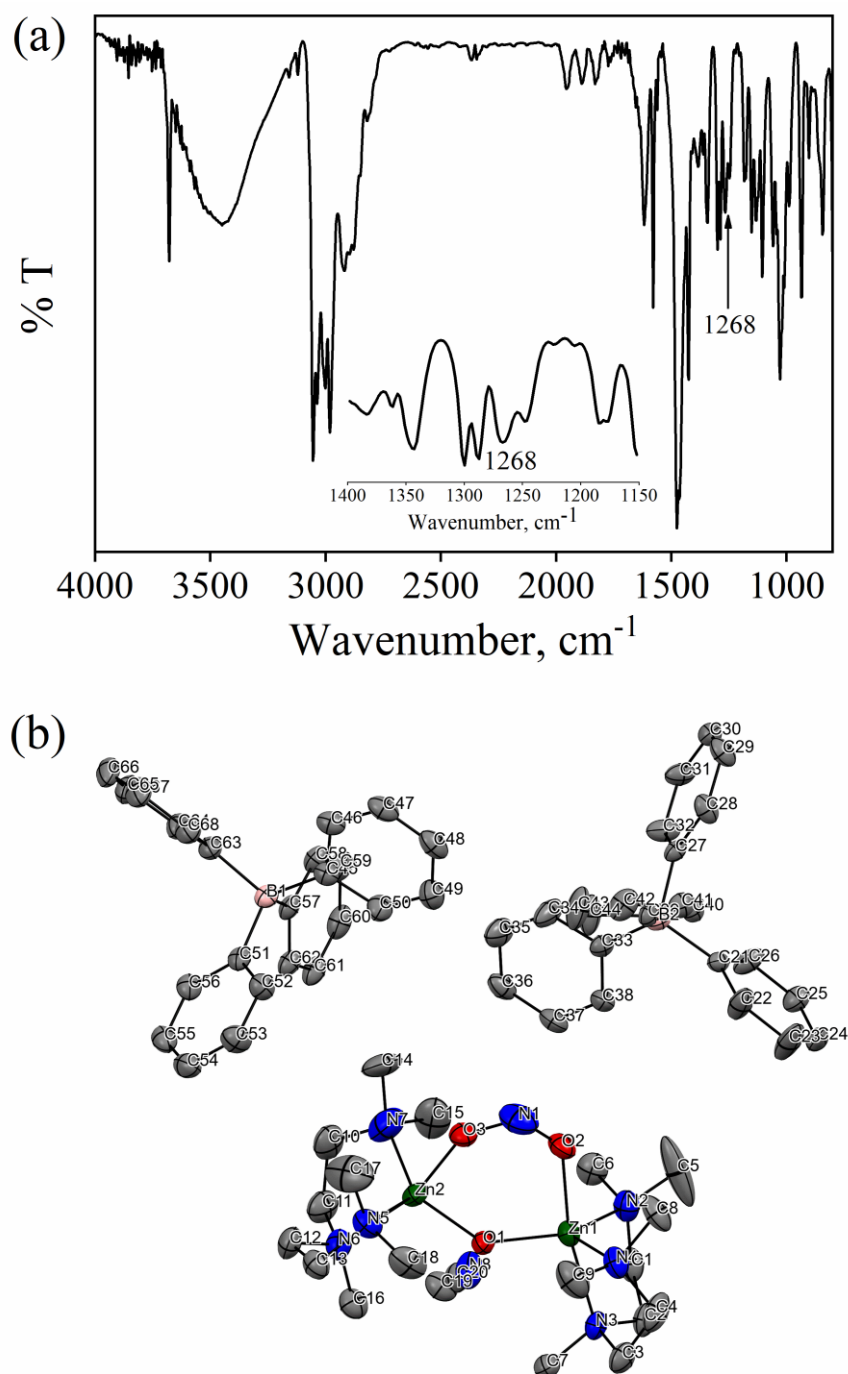


Figure S12. (a) FT-IR spectrum of isolated product **4**, obtained in the reaction of **3** + KOH recorded in KBr pellet at 298 K. (b) Displacement ellipsoid plots of **4** with 60 % probability at 100 K. Disordered C atoms, and H atoms have been removed for clarity.

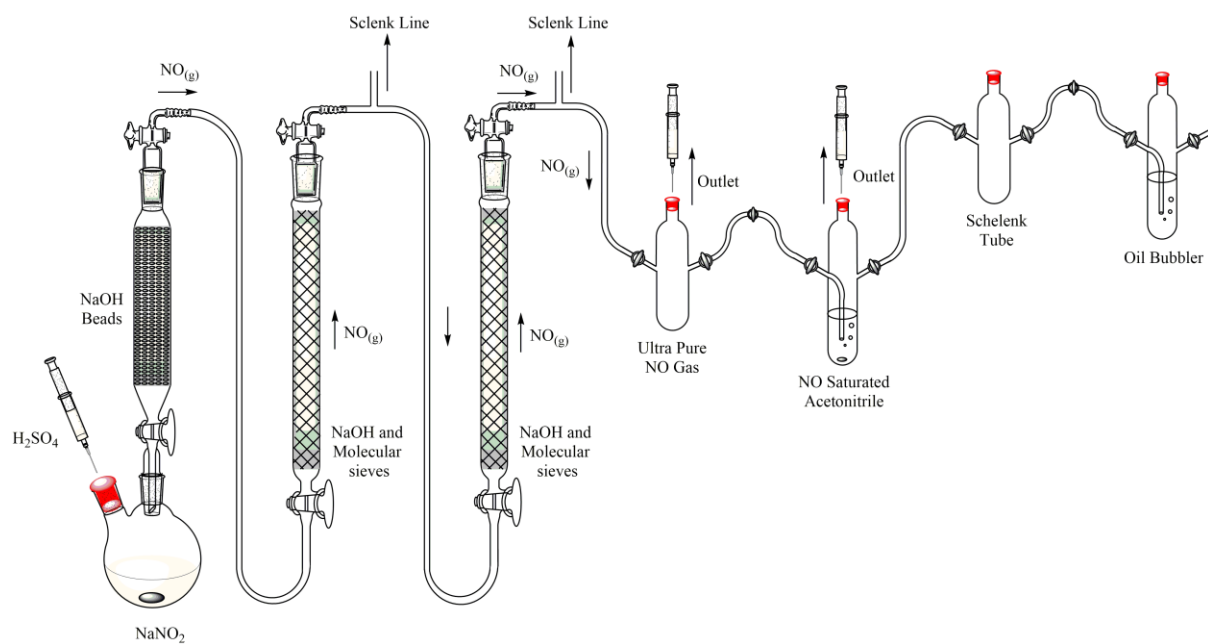


Figure S13. Schematic diagram showing the generation and purification setup for NO.

References

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