Supplementary Information for

Nanometer-size Titanium Dioxide Catalyzed Reactions of Nitric Oxide with Aliphatic Cyclic and Aromatic Amines**

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Contents

** The results have been patented (CN 101230023 A)

1. General information

Reagents were purchased from Shanghai Chemical Reagent Company and used without further purification. Melting points were determined using a capillary apparatus (RDCSY-I) and are reported directly. All of the compounds synthesized except NONOates and cupferrons were purified by column chromatography (CC) on silica gel 60 (200-300 mesh) and thin-layer chromatography (TLC) on silica gel 60 F254 plates (250 μ m; Qingdao Ocean Chemical Company, China). Subsequently, they were routinely analyzed by ^{1}H NMR (Bruker ACF-300Q, 300 MHz), MS (Hewlett-Packard 1100 LC/MSD spectrometer) (except NONOates and cupferrons), and elemental analysis (Elementar Vario EL III instrument). The X-ray diffraction analyses were performed on a Nonius CAD4 diffractometer and incident beam graphite monochromator using a Mo sealed tube source (λ) 0.71073 Å). The nanometer-size titanium dioxide (TiO_2) used in this manuscript is commercially available from Evonik Degussa company. We chose nanometer TiO_2 AEROXIDE® TiO_2 P25, a mixed crystalline, containing 75-85% rutile and 15-25% anatase. It is a kind of dispersed titanium dioxide manufactured according to the AEROSIL®-process with the great specific surface area 50±10 m^2/g and average primary particle size 21nm.

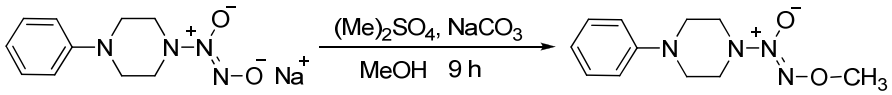
2. General procedure for the preparation of NONOates and cupferrons.

NONOate 2b: A three neck-flask (100 mL) equipped with a gas bag and three-way stopcock, one way of which was attached to a N_2 tank, and the other jointed to a NO tank was used as reaction vessel. Freshly distilled piperidine (**1b**, 5.9 mL, 0.06 mol) and MeONa (3.24 g, 0.06 mol) were dissolved in anhydrous MeOH 50 mL. EROXIDE® TiO_2 P25 (Evonik Degussa) 50 mg was added into the vessel and dispersed with the aid of ultrasound. In order to provide an anaerobic atmosphere, the flask was evacuated and flushed with dry N_2 four times in turn and then evacuated again. NO was introduced bubblly below the layer of the solvent. The pressure in the reaction vessel shown in the reducing valve of NO tank keeps the atmospheric pressure. The excess NO was vented off 48 h later. Ethyl ether 50 mL was added into the reaction mixture. The resulting precipitate was filtered, washed with ethyl ether, and dried under vacuum to give white powder, which was dissolved in MeOH and filtered through microphore film (0.22 μm) to get rid of TiO_2. Finally, ethyl ether was added to the MeOH solution to precipitate sodium 1-(piperidine-1-yl) diazen-1-ium-1,2-diolate **2b**, 9.01 g (90%).

Cupferron 5a: The apparatus is equipped same as that for NONOates. 4-Methoxyl aniline (**4a**,

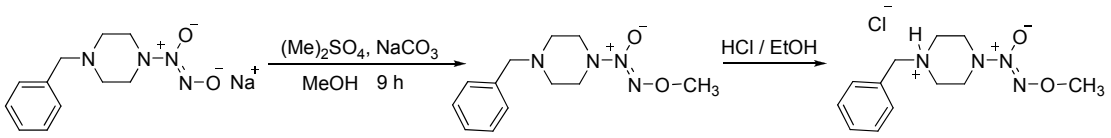
7.38 g, 0.06 mol) and 25% MeONa in MeOH (12.9 mL, 0.02 mol) were dissolved in anhydrous THF 50 mL. AEROXIDE® TiO_2 P25 (Evonik Degussa) 50 mg was added into the flask and then dispersed with the aid of ultrasound. After degassing process performed as above, NO was introduced bubbly below the layer of the solvent. After 48 h, the excess NO was vented off. The precipitate was collected by filtration, and the mother liquid was evaporated to give brown oil, which was isolated on silica gel (200-300 mesh) eluted with 3:1 petroleum ether: ethyl acetate to recover **4a** 3.54 g (48%) as brown oil. The solid was washed with EtOAc, dried under vacuum to give the rude product, which was purified by the same method as that for NONOates, affording brownish yellow powder *N*-nitroso-*N*-oxy-*p*- methoxybenzenamine sodium salt **5a**, 4.50 g (77%, based on the reacted **4a**).

3. The preparation of 3h, 3i and 6a, the recovery of 4 and the isolation of 4-methoxybiphenyl.



2h **3h**

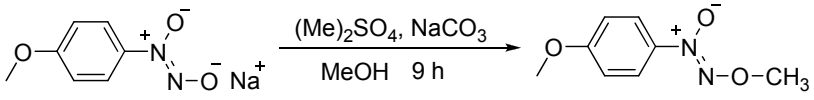
O^2-Methyl 1-(4-Phenylpiperazin-1-yl)diazen-1-ium-1,2-diolate (3h). A slurry of sodium 1-(4-phenylpiperazin-1-yl)diazen-1-ium-1,2-diolate (**2h**, 1.22 g, 0.005 mol) and anhydrous Na_2CO_3 (0.8 g, 0.0075 mol) in anhydrous MeOH 30 mL was cooled to 0 °C under a N_2 atmosphere. To the stirred mixture was added dropwise dimethyl sulfate (0.72 mL, 0.0075 mol). The solution was kept cold for 1 h and then warmed to RT for additional 8 h. To the reaction mixture was added 10 mL of 10% aqueous NaOH, and the solution was stirred for 30 min to decompose any unreacted dimethyl sulfate. Most of the solvent was removed on a rotary evaporator, and the residue was extracted with CH_2Cl_2 (20 mL×3). The solution was dried over sodium sulfate and filtered through magnesium sulfate. The solvent was evaporated to give yellow oil. Purification of the crude material was carried out on silica gel (200-300 mesh) eluted with 4:1 petroleum ether: ethyl acetate to give 779 mg (66 %) of **3h** as white solid. m.p. 86-87 °C. (Found: C, 56.08; H, 6.76; N, 23.72. $C_{11}H_{16}N_4O_2$ requires C, 55.92; H,6.83; N, 23.71); δ_H(300MHz, $CDCl_3$, 25℃, TMS) 3.29-3.34 (4H, m, $2CH_2$), 3.44-3.47 (4H, m, $2CH_2$), 3.93 (3H, s, CH_3), 3.05 (4H, m), 6.82-7.27 (5H, m, ArH); ESI-MS: 236, 237 $[M+H]^+$, 259 $[M+Na]^+$, 495$[2M+Na]^+$.



2i **3i'** **3i**

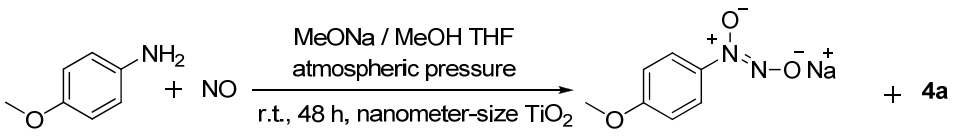
O*^{2}*-Methyl 1-(4-benzylpiperazin-1-yl)diazen-1-ium-1,2-diolate (3i'). The title compound was obtained from sodium 1-(4-benzylpiperazin-1-yl)diazen-1-ium-1,2-diolate **2i** using the same procedure as above. Yellow oil, 60 % yield. δ_H(300MHz, $CDCl_3$, 25℃, TMS) 2.62 (4H, t, ^3J(H,H) = 5.0 Hz, $2CH_2$), 3.44 (t, 4H, ^3J(H,H) = 5.0 Hz, $2CH_2$), 3.54 (2H, s, CH_2), 4.00 (3H, s, CH_3), 7.26-7.33 (5H, m, ArH); ESI-MS: 250 251 $[M+H]^+$.

Hydrochloride salt of O*^{2}*-Methyl 1-(4-benzylpiperazin-1-yl)diazen-1-ium-1,2-diolate (3i). O^2-Methyl 1-(4-benzylpiperazin-1-yl)diazen-1-ium-1,2-diolate (**3i'**, 500 mg, 2.12 mmol) was added into the saturated solution of HCl in ethanol 5 mL with stirring at 0 °C. Several min after the addition precipitate formed. Filtration and then recrystallization of the precipitate from ethanol gave **3i** as needle in 90 %. m.p. 198-200 °C. (Found C, 50.02; H, 6.76; N, 19.30. $C_{12}H_{19}ClN_4O_2$ requires C, 50.26; H, 6.68; N, 19.54); δ_H(300MHz, $CDCl_3$, 25℃, TMS) 3.21-3.43 (4H, m, $2CH_2$), 3.46-3.50 (2H, m, CH_2), 3.90-3.94 (2H, m, CH_2), 3.97 (3H, s, CH_3), 4.35 (2H, s, CH_2), 7.45-7.62 (5H, m, ArH), 11.7 (0.95 H, s, HCl); ESI-MS: 250 251 $[M+H]^+$.



5a **6a**

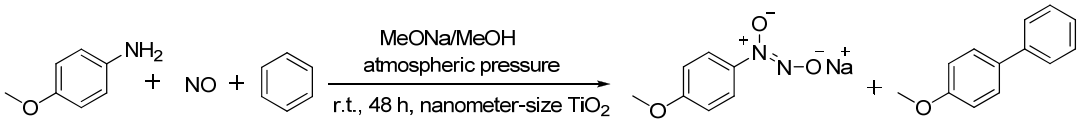
N-Methoxy-N'-p-methoxyphenyldiimide N'-oxide (6a). The title compound was obtained as light yellow solid from N-nitroso-N-oxy-p-methoxybenzenamine sodium salt **5a** using the same procedure as **3h**, 48 %. m.p. 62-63 °C. (Found C 52.90; H 5.62; N 15.45. $C_8H_{10}N_2O_3$ requires 52.74; H 5.53; N 15.38); δ_H(300MHz, $CDCl_3$, 25℃, TMS) 3.87 (3H, s, $NOCH_3$), 4.21 (3H, s, OCH_3), 6.94 (2H, d, ^3J(H,H) = 9.0 Hz, ArH), 7.93 (2H, d, ^3J(H,H) = 9.0 Hz, ArH); ESI-MS: 182, 183 $[M+H]^+$, 205 $[M+Na]^+$, 387 $[2M+Na]^+$.



4a **5a**

The recovery of 4-methoxyl aniline (4a). The reaction was performed as described in experimental section. After N-nitroso-N-oxy-p-methoxybenzenamine sodium salt **5a** was obtained, the mother liquid was evaporated to give brown oil, which was isolated on silica gel (200-300 mesh) eluted with 3:1 petroleum ether: ethyl acetate to recover 4-methoxyl aniline **4a** 3.54 g (48 %) as brown oil. δ_H (300MHz, $CDCl_3$, 25℃, TMS) 3.37 (2H, s, NH2), 3.73 (3H, s), 6.63-6.66 (2H, m, ArH), 6.73-6.75 (2H, m, ArH) .[1]

Compounds **4b-n** were recovered as mentioned for **4a**.



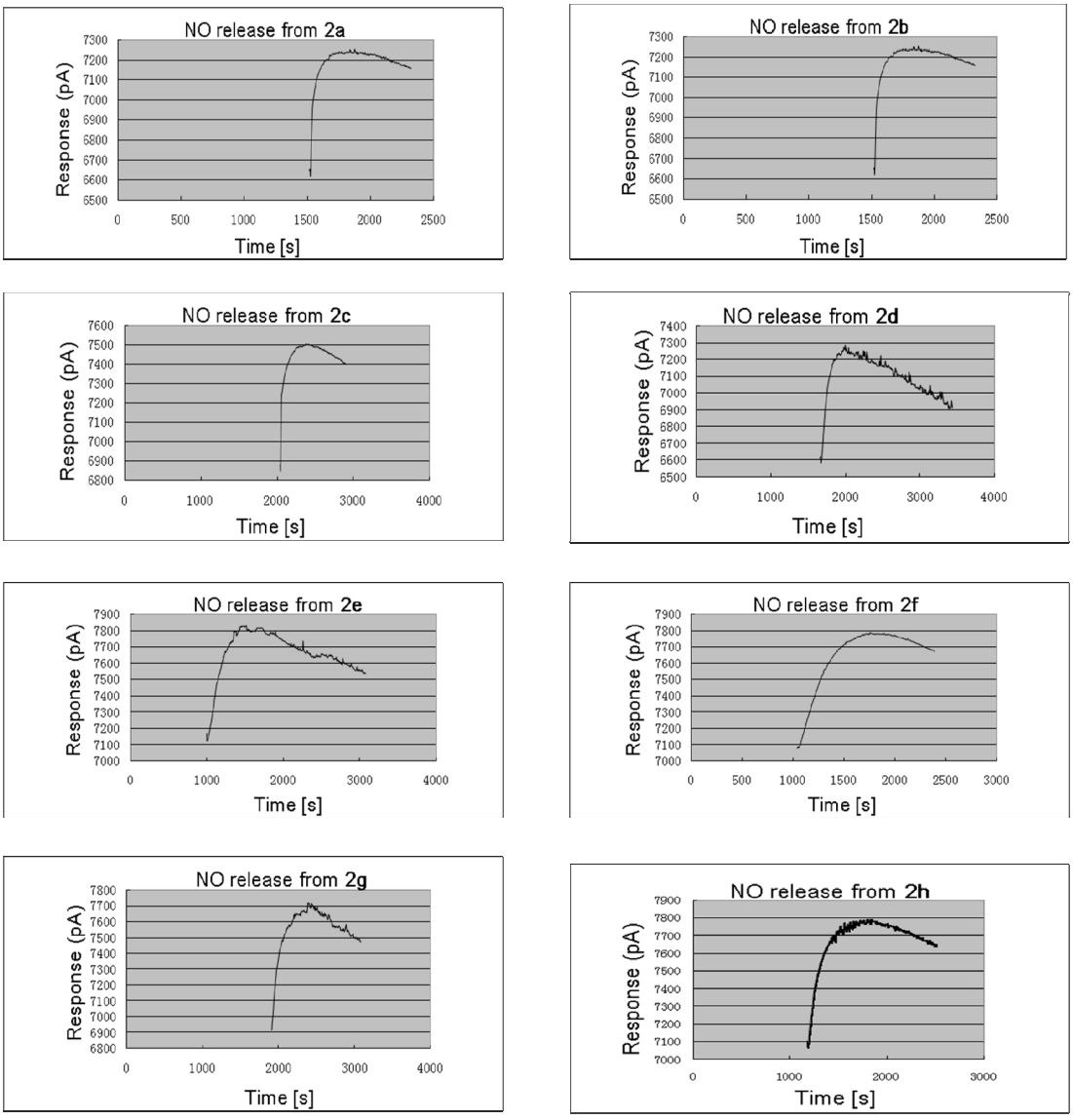
4a **5a** **4-methoxylbiphenyl**

The isolation of the 4-methoxylbiphenyl. 4-methoxylbiphenyl is the key evidence to prove the existence of 4-methoxyl phenyl free radical in the preparation of cupferrons from the reaction of NO with aromatic primary amines at r.t. under atmospheric pressure. The reaction was performed as described in experimental section except using benzene as solvent. After N-nitroso-N-oxy-p-methoxybenzenamine sodium salt **5a** was obtained, the mother liquid was evaporated to give brown oil, subsequently purified on silica gel (200-300 mesh) eluting with n-hexane to offer 230 mg (6.4 %) of 4-methoxylbiphenyl as white solid. m.p. 91-92°C (91-92 °C lit.[2]); δ_H(300MHz, CDCl3, 25℃, TMS) 3.85 (3H, s), 6.99-7.55 (9H, m, 2ArH);[3] ESI-MS: 184 185 $[M+H]^+$.

4. The measurement of NO release and half-lives of 2a-i in vitro.

The measurement of NO release [4]**:** NO release was measured by using the Apollo 4000 free-radical analyser system with an ISO-NOP nitric oxide selective sensor built into a multiport measurement chamber by World Precision Instruments Inc., USA. The measurement chamber was tempered with a Lauda M3 circulating thermostat at 37 °C and stirred at 800 r.p.m. All experiments were started after the initial background signal had fallen below 8000 pA in a channel range of 10 nA for the electrode. The apparatus was calibrated daily with 2.0 mL of a 0.1 M KI/0.1 M H_2SO_4 solution in the chamber

and an increasing amount of 50 μM $NaNO_2$ solution to produce nitric oxide by reduction. The nitrite solution was applied with an Eppendorf pipette (10, 20, 30, 40 and 60 μL) to give 249, 493, 728, 952 and 1388 nM solutions of NO, respectively. The dissociation of the diazeniumdiolates was measured by injecting a 100 μM NONOate/0.01 M NaOH solution (20 μL) into phosphate buffer (2.0 mL, pH 6.4) resulting in a 495 nM solution of NONOate. Because 1 mol NONOate produces 2 mol NO, the redox current flow of a 990 nM NO solution was measured. Note that the nitric oxide sensor measurement is not accumulative and only measures the arising current at any given time. For this reason the phosphate buffer at pH 6.4 was used to ensure a sharper signal for slower releasing NONOates. The maximum of the signal was chosen as a parameter with which to compare dissociation rates. Every measurement was carried out at least three times and the mean value with the corresponding standard deviation was calculated. (see Figure 1)



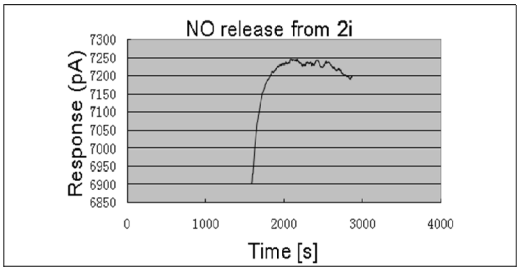


Figure 1. The measurement of NO release for **2a-i** in vitro.

The measurement of half-lives of 2a-i: The half-lives of **2a-i** in the pH 7.4 phosphate buffer at 37 ℃ were detected (Table 1). [5]

Table 1. The measurement of half-lives of **2 a-i**.

Compd.	λ_{max}/nm	λ_{det}/nm	$t_{1/2}$ /s
2a	248	250	5.7
2b	248	250	37
2c	250	250	224
2d	250	250	188
2e	251	250	258
2f	251	250	323
2g	250	250	54
2h	245	245	435
2i	245	245	175

5. The optimization of the TiO_2 loading for the preparation of NONOates.

The optimization of the TiO_2 loading for the preparation of NONOates was studied. Cyclic amine **1d** was used as substrate in five different concentrations of TiO_2 (Table 2). The middle concentration loading was found to be the best. So we selected TiO_2 1.04 mol% for the reactions. Based on this result the TiO_2 loading for the preparation of cupferrons was 1.04 mol% too.

Table 2. The optimization of the TiO_2 loading.[a]

entry	**1d** [mol]	TiO_2 [mol]	Catalyst loading mol%	Yields of **2d** [%][b]
1	0.06	0	0	12
2	0.06	25	5.02	42
3	0.06	50	1.04	53
4	0.06	75	1.56	49
5	0.06	100	2.08	48

[a] The reaction conditions were the same as described in Table 1 in the text

except the reaction time 5 h. [b] Yield of the isolated product.

6. The ^{1}H NMR and elemental analyses data of 2a-i, 5a-d, 5f, 5h and 5i.

Table 3. The ^{1}H NMR data of **2 a-i** (300MHz, D_2O, 25℃, TMS).

2a	δ = 1.78-1.79 (4H, m, $2CH_2$), 3.08-3.12 (4H, m, $2CH_2$).
2b	δ = 1.53-1.59 (6H, m, $3CH_2$), 3.06-3.16 (4H, m, $2CH_2$).
2c	δ = 1.61-1.71(2H, m, CH_2), 1.95-1.98 (2H, m, CH_2), 2.95-3.01 (2H, m, CH_2), 3.11-3.15 (2H, m, CH_2), 3.74-3.75 (1H, m, CH).
2d	δ = 2.50 (2H, t, ^3J(H,H) = 6.0 Hz, $OCH_2\underline{CH_2}N$), 2.61-2.69 (4H, m, $2CH_2$), 3.04-3.07 (4H, m, $2CH_2$), 3.62 (2H, t, ^3J(H,H) = 6.0 Hz, $O\underline{CH_2}CH_2N$), 3.22 (0.39 H, s, OH).
2e	δ = 2.21 (3H, s, CH_3), 2.58-2.63 (4H, m, $2CH_2$), 3.08-3.12 (4H, m, $2CH_2$).
2f	δ = 0.95 (6H, d, ^3J(H,H) = 6.3 Hz, $2CH_3$), 2.57-2.67 (5H, m, CH, $2CH_2$), 3.04-3.07 (4H, m, $2CH_2$).
2g	δ = 1.37 (9H, s, $(CH_3)_3$), 3.00-3.12 (4H, m, $2CH_2$), 3.54-3.56 (4H, m, $2CH_2$).
2h	δ = 3.21-3.22 (4H, m, $2CH_2$), 3.27-3.28 (4H, m, $2CH_2$), 6.97(1H, t, ^3J(H,H) = 7.2 Hz, ArH), 7.06 (2H, d, ^3J(H,H) = 7.8 Hz, ArH), 7.29 (2H, t, ^3J(H,H) = 7.8 Hz, ArH).
2i	δ = 2.61-2.63 (4H, m, $2CH_2$), 3.02-3.04 (4H, m, $2CH_2$), 3.50 (2H, s, CH_2), 7.29 (5H, m, ArH).

Table 4. The elemental analyses results of **2a-i**.

Compd.	Formula	Calculated	Found
2a	$C_4H_8N_3NaO_2$	C, 31.38 H, 5.27 N, 27.44	C, 30.99 H, 5.34 N, 27.00
2b	$C_5H_{10}N_3NaO_2$	C, 35.93 H, 6.03 N, 25.14	C, 35.50 H, 6.34 N, 24.89
2c	$C_5H_{10}N_3NaO_3 \cdot H_2O$	C, 29.85 H, 6.01 N, 20.89	C, 29.45 H, 5.89 N, 20.45
2d	$C_6H_{13}N_4NaO_3 \cdot 0.5H_2O$	C, 32.58 H, 6.38 N, 25.33	C, 32.30 H, 6.56 N, 24.99
2e	$C_5H_{11}N_4NaO_2$	C, 32.97 H, 6.09 N, 30.76	C, 32.67 H, 6.34 N, 30.45
2f	$C_7H_{15}N_4NaO_2$	C, 40.00 H, 7.19 N, 26.65	C, 39.65 H, 7.23 N, 26.34
2g	$C_9H_{17}N_4NaO_2$	C, 40.30 H, 6.39 N, 20.89	C, 39.89 H, 6.30, N, 20.44
2h	$C_{10}H_{13}N_4NaO_2$	C, 49.18 H, 5.37 N, 22.94	C, 48.64 H, 5.37, N, 22.85
2i	$C_{11}H_{15}N_4NaO_2$	C, 51.16 H, 5.85 N, 21.69	C, 50.89 H, 5.99 N, 21.33

Table 5. The ^{1}H NMR data of **5a-d**, **5f**, **5h** and **5i** (300MHz, D_2O, 25℃, TMS).

5a	δ = 3.76 (3H, s, CH_3), 6.97 (2H, d, ^3J (H,H) = 9.0 Hz, ArH), 7.58 (2H, d, ^3J (H,H) = 9.0 Hz, ArH).
5b	δ = 2.46 (3Hl, s, CH_3), 7.21-7.50 (4H, m, ArH).
5c	δ = 2.40 (3H, s, CH_3), 7.38 (2H, d, ^3J (H,H) = 9.0 Hz, ArH), 7.57(2H, d, ^3J (H,H) = 9.0 Hz, ArH).
5d	δ = 2.34 (3H, s, CH_3), 7.27-7.58 (4H, m, ArH).
5f	δ = 2.28 (3H, s, CH_3), 2.39 (3H, s, CH_3), 7.34-7.65 (3H, m, ArH).
5h	δ = 1.28 (3H, t, ^3J(H,H) = 7.2 Hz, CH_3), 2.75 (2H, q, ^3J(H,H) = 7.2 Hz, CH_2), 7.11-7.65 (4H, m, ArH).

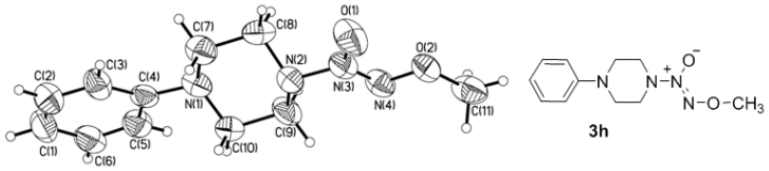
5i	δ = 1.25 (6H, d, ^3J(H,H) = 6.7 Hz, 2CH_3), 2.19-2.22 (1H, m, CH), 6.80-7.70 (4H, m, ArH).

Table 6. The elemental analyses of **5a-d**, **5f**, **5h** and **5i**.

Compd.	Formula	Calculated	Found
5a	$C_7H_7N_2NaO_3$	C, 44.22 H, 3.71 N, 14.73	C, 43.99 H, 3.48 N, 14.82
5b	$C_7H_7N_2NaO_2S$	C, 40.77 H, 3.42 N. 13.59	C, 40.27 H, 3.00 N, 13,45
5c	$C_7H_7N_2NaO_2$	C, 48.28 H, 4.05 N, 16.09	C, 47.88 H, 3.67 N, 15.88
5d	$C_7H_7N_2NaO_2 \cdot 0.3NaNO_2$	C, 43.15 H, 3.62 N, 16.54	C, 43.86 H, 3.42 N, 16.23
5f	$C_8H_9N_2NaO_2 \cdot 0.5NaNO_2$	C, 43.15 H, 4.07 N, 15.73	C, 39.85 H, 4.34 N, 15.35
5h	$C_8H_9N_2NaO_2 \cdot 0.4H_2O$	C, 49.18, H, 5.06 N, 14.34	C, 48.99 H, 5.33 N, 14.28
5i	$C_9H_{11}N_2NaO_2 \cdot 0.75H_2O$	C, 50.11 H, 5.84 N, 12.99	C, 49.79 H, 5.78 N, 13.26

7. crystallographic data of 3h, 3i and 6a.

Table 7a. Crystal data and structure refinement for **3h**.



Empirical formula	$C_{11}H_{16}N_4O_2$
Formula weight	236.28
Temperature	20 □
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 10.638 (2)Å α= 90°
	b = 7.5620 (15)Å β= 90°
	c = 30.221 (6)Å γ= 90°
Volume	2431.1(8) $Å^3$
Z	8
Density (calculated)	1.291 Mg/m^3
Absorption coefficient	0.092 mm^{-1}
F(000)	1008
Crystal size	0.4×0.2×0.1 mm
Theta range for data collection	1.35 to 25.16°
Index range	0≤h≤12, 0≤k≤9, 0≤l≤36
Reflections collected	2169
Independent reflections	2169 [R(int) = 0.0427]
Completeness to thata = 25.16°	99.7 %
Absorption correction	Psi-scan
Goodness-of-fit on F^2	1.035

Final R indices [I>2σ(I)]	$R_1 = 0.0827$, $wR_2 = 0.1771$
R indices (all date)	$R_1 = 0.1502$, $wR_2 = 0.2105$
Largest diff. peak and hole	0.146 and -0.153 e $Å^{-3}$

Table 7b. Atomic coordinates and equivalent isotropic displacement parameters for **3h**.

	x	y	z	U(eq)
N1	1.0073(3)	0.1651(5)	0.13257(11)	0.0859(10)
N2	0.9480(3)	0.4937(4)	0.09331(11)	0.0806(10)
N3	0.9589(4)	0.6360(5)	0.06270(11)	0.0866(10)
N4	1.0574(3)	0.7289(5)	0.06304(11)	0.0878(10)
O1	0.8638(3)	0.6696(5)	0.03826(11)	0.1322(14)
O2	1.0414(3)	0.8626(4)	0.03426(9)	0.0914(9)
C1	1.0159(6)	-0.2692(7)	0.22145(17)	0.1113(16)
C2	0.9101(5)	-0.2365(8)	0.19808(17)	0.1141(16)
C3	0.9068(5)	-0.0992(6)	0.16878(15)	0.0976(13)
C4	1.0063(4)	0.0146(6)	0.16114(13)	0.0787(11)
C5	1.1154(4)	-0.0266(6)	0.18536(15)	0.0923(13)
C6	1.1228(5)	-0.1588(7)	0.21491(15)	0.1062(15)
C7	0.8945(4)	0.1892(7)	0.10436(15)	0.1025(15)
C8	0.9192(4)	0.3337(6)	0.06982(14)	0.0935(14)
C9	1.0635(4)	0.4672(7)	0.11909(14)	0.1004(15)
C10	1.0381(4)	0.3242(6)	0.15337(14)	0.0896(13)
C11	1.1578(4)	0.9723(8)	0.03524(15)	0.1182(18)

Table 7c. Hydrogen coordinates and isotropic displacement parameters for **3h**.

	x	y	z	U(eq)
H1A	1.0188	-0.3624	0.2415	0.134
H2A	0.8395	-0.3076	0.2020	0.137
H3A	0.8330	-0.0809	0.1529	0.117
H5A	1.1867	0.0419	0.1806	0.111
H6A	1.1964	-0.1780	0.2308	0.127
H7A	0.8232	0.2223	0.1226	0.123
H7B	0.8744	0.0789	0.0896	0.123
H8A	0.9891	0.3003	0.0510	0.112
H8B	0.8455	0.3505	0.0514	0.112
H9A	1.0875	0.5764	0.1336	0.121
H9B	1.1316	0.4311	0.0997	0.121
H10A	1.1121	0.3075	0.1717	0.108
H10B	0.9694	0.3607	0.1724	0.108
H11A	1.1478	1.0721	0.0159	0.177
H11B	1.2279	0.9024	0.0256	0.177
H11C	1.1726	1.0130	0.0649	0.177

Table 7d. Anisotropic displacement parameters for **3h**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N1	0.080(2)	0.114(3)	0.0638(19)	-0.001(2)	-0.0008(17)	0.005(2)
O1	0.093(2)	0.194(4)	0.110(3)	0.048(3)	-0.033(2)	-0.017(2)
C1	0.145(4)	0.101(3)	0.089(3)	0.022(3)	0.024(3)	0.005(3)
O2	0.099(2)	0.103(2)	0.0717(17)	0.0113(18)	-0.0061(16)	0.0062(17)
N2	0.082(2)	0.091(2)	0.0685(19)	0.006(2)	0.0018(17)	-0.0004(19)
C2	0.126(4)	0.120(3)	0.095(3)	0.006(3)	0.022(3)	-0.013(3)
N3	0.096(3)	0.093(2)	0.071(2)	0.004(2)	-0.001(2)	0.014(2)
C3	0.102(3)	0.103(3)	0.088(3)	0.011(3)	0.021(3)	0.009(3)
N4	0.076(2)	0.119(3)	0.069(2)	0.009(2)	-0.0043(18)	0.001(2)
C4	0.082(3)	0.097(3)	0.057(2)	-0.016(2)	0.0150(19)	-0.005(2)
C5	0.097(3)	0.096(3)	0.084(3)	-0.004(3)	0.004(2)	0.006(3)
C6	0.123(4)	0.123(4)	0.073(3)	-0.003(3)	0.009(3)	0.004(3)
C7	0.097(3)	0.125(4)	0.085(3)	0.001(3)	-0.004(3)	-0.002(3)
C8	0.102(3)	0.100(3)	0.079(3)	-0.022(3)	-0.019(2)	0.017(3)
C9	0.109(3)	0.125(4)	0.067(2)	0.021(3)	-0.022(2)	-0.011(3)
C10	0.104(3)	0.097(3)	0.068(2)	-0.008(3)	-0.008(2)	-0.008(3)
C11	0.101(3)	0.173(5)	0.080(3)	-0.015(4)	0.009(3)	-0.012(4)

Table 7e. Bond lengths [Å] for **3h**.

N1-C10	1.396(5)	N1-C4	1.428(5)
N1-C7	1.483(5)	O1-N3	1.278(4)
C1-C2	1.352(7)	C1-C6	1.425(7)
C1-1A	0.9300	O2-N4	1.345(4)
O2-C11	1.490(5)	N2-N3	1.423(4)
N2-C8	1.436(5)	N2-C9	1.469(5)
C2-C3	1.366(6)	C2-H2A	0.9300
N3-N4	1.261(5)	C3-C4	1.384(6)
C3-H3A	0.9300	C4-C5	1.407(6)
C5-C6	1.343(6)	C5-H5A	0.9300
C6-H6A	0.9300	C7-C8	1.534(6)
C7-H7A	0.9700	C7-H7B	0.9700
C8-H8A	0.9700	C8-H8B	0.9700
C9-C10	1.522(5)	C9-H9A	0.9700
C9-H9B	0.9700	C10-H10A	0.9700
C10-H10B	0.9700	C11-H11A	0.9600
C11-H11B	0.9600	C11-H11C	0.9600

Table 7f. Bond angles [°] for **3h**.

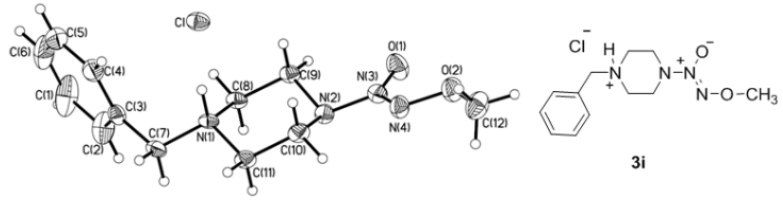
C10-N1-C4	114.6(3)	C10-N1-C7	110.0(4)
C4-N1-C7	116.1(4)	C2-C1-C6	119.0(5)
C2-C1-H1A	120.5	C6-C1-H1A	120.5
N4-O2-C11	107.5(3)	N3-N2-C8	109.4(3)
N3-N2-C9	112.3(3)	C8-N2-C9	109.0(3)
C1-C2-C3	119.9(5)	C1-C2-H2A	120.0
C3-C2-H2A	120.0	N4-N3-O1	123.4(4)
N4-N3-N2	118.9(4)	O1-N3-N2	117.5(4)
C2-C3-C4	124.2(5)	C2-C3-H3A	117.9
C4-C3-H3A	117.9	N3-N4-O2	108.0(3)
C3-C4-C5	114.0(4)	C3-C4-N1	127.0(4)
C5-C4-N1	119.0(4)	C6-C5-C4	124.0(5)
C6-C5-H5A	118.0	C4-C5-H5A	118.0
C5-C6-C1	118.8(5)	C5-C6-H6A	120.6
C1-C6-H6A	120.6	N1-C7-C8	109.9(4)
N1-C7-H7A	109.7	C8-C7-H7A	109.7
N1-C7-H7B	109.7	C8-C7-H7B	109.7
H7A-C7-H7B	108.2	N2-C8-C7	107.5(3)
N2-C8-H8A	110.2	C7-C8-H8A	110.2
N2-C8-H8B	110.2	C7-C8-H8B	110.2
H8A-C8-H8B	108.5	N2-C9-C10	108.0(4)
N2-C9-H9A	110.1	C10-C9-H9A	110.1
N2-C9-H9B	110.1	C10-C9-H9B	110.1
H9A-C9-H9B	108.4	N1-C10-C9	110.3(3)
N1-C10-H10A	109.6	C9-C10-H10A	109.6
N1-C10-H10B	109.6	C9-C10-H10B	109.6
H10A-C10-H10B	108.1	O2-C11-H11A	109.5
O2-C11-H11B	109.5	H11A-C11-H11B	109.5
O2-C11-H11C	109.5	H11A-C11-H11C	109.5
H11B-C11-H11C	109.5		

Table 7g. Torsion angles [°] for **3h**.

C6-C1-C2-C3	-0.1(8)	C8-N2-N3-N4	-126.4(4)
C9-N2-N3-N4	-5.2(5)	C8-N2-N3-O1	58.2(5)
C9-N2-N3-O1	179.4(4)	C1-C2-C3-C4	-0.7(7)
O1-N3-N4-O2	0.3(5)	N2-N3-N4-O2	-174.7(3)
C11-O2-N4-N3	179.5(3)	C2-C3-C4-C5	2.1(6)
C2-C3-C4-N1	-176.9(4)	C10-N1-C4-C3	122.5(5)
C7-N1-C4-C3	-7.6(6)	C10-N1-C4-C5	-56.5(5)
C7-N1-C4-C5	173.4(4)	C3-C4-C5-C6	-2.9(6)

N1-C4-C5-C6	176.2(4)	C4-C5-C6-C1	2.2(7)
C2-C1-C6-C5	-0.6(7)	C10-N1-C7-C8	58.3(4)
C4-N1-C7-C8	-169.5(3)	N3-N2-C8-C7	-174.0(3)
C9-N2-C8-C7	62.8(4)	N1-C7-C8-N2	-59.5(5)
N3-N2-C9-C10	175.0(3)	C8-N2-C9-C10	-63.5(4)
C4-N1-C10-C9	168.0(4)	C7-N1-C10-C9	-59.0(5)
N2-C9-C10-N1	61.6(5)		

Table 8a. Crystal data and structure refinement for **3i**.



Empirical formula	$C_{12}H_{19}ClN_4O_2$
Formula weight	286.76
Temperature	20 □
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.0760 (14)Å α= 90°
	b = 9.0240 (18) Å β= 96.13(3)°
	c = 22.863 (5) Å γ= 90°
Volume	1451.5(5) $Å^3$
Z	4
Density (calculated)	1.312 Mg/m^3
Absorption coefficient	0.268 mm^{-1}
F(000)	608
Crystal size	0.3×0.2×0.1 mm
Theta range for data collection	1.79 to 25.26°
Index range	0⩽h⩽8, 0⩽k⩽10, -27⩽l⩽27
Reflections collected	2633
Independent reflections	2845 [R(int) = 0.0319]
Completeness to thata = 25.26°	99.8 %
Absorption correction	Psi-scan
Goodness-of-fit on F^2	1.003
Final R indices [I>2σ(I)]	R_1 = 0.0537, wR_2 = 0.1401
R indices (all date)	R_1 = 0.0804, wR_2 = 0.1915
Largest diff. peak and hole	0.353 and -0.378 e $Å^{-3}$

Table 8b. Atomic coordinates and equivalent isotropic displacement parameters for **3i**.

	x	y	z	U(eq)
Cl	1.19467(12)	0.42284(10)	0.73602(4)	0.0445(3)
N1	0.7617(4)	0.3954(3)	0.73935(12)	0.0310(6)
N2	0.6733(4)	0.4968(3)	0.62114(12)	0.0388(7)
N3	0.7013(4)	0.5521(3)	0.56470(13)	0.0410(7)
N4	0.7445(5)	0.4546(4)	0.52787(13)	0.0480(8)
O1	0.6773(5)	0.6871(3)	0.55617(13)	0.0621(8)
O2	0.7448(4)	0.5231(4)	0.47435(12)	0.0583(8)
C1	0.6762(10)	0.5947(7)	0.9250(2)	0.094(2)
C2	0.6211(7)	0.5053(6)	0.87668(19)	0.0683(13)
C3	0.7584(5)	0.4342(4)	0.84827(15)	0.0385(8)
C4	0.9473(6)	0.4516(5)	0.86941(17)	0.0532(10)
C5	1.0005(7)	0.5406(6)	0.9180(2)	0.0666(13)
C6	0.8610(10)	0.6124(6)	0.9451(2)	0.0835(18)
C7	0.7018(5)	0.3371(4)	0.79609(15)	0.0400(8)
C8	0.6892(5)	0.5482(3)	0.72571(15)	0.0349(8)
C9	0.7488(5)	0.5998(4)	0.66754(15)	0.0367(8)
C10	0.7516(5)	0.3468(4)	0.63185(16)	0.0413(8)
C11	0.6918(5)	0.2935(4)	0.69025(15)	0.0411(8)
C12	0.7886(7)	0.4128(6)	0.43293(19)	0.0672(13)

Table 8c. Hydrogen coordinates and isotropic displacement parameters for **3i**.

	x	y	z	U(eq)
H1A	0.5838	0.6432	0.9439	0.113
H2A	0.493	0.4934	0.8636	0.082
H4B	1.0403	0.4030	0.8509	0.064
H5A	1.1280	0.5516	0.9321	0.080
H6A	0.8948	0.6733	0.9774	0.100
H7A	0.5647	0.3257	0.7918	0.048
H7B	0.7573	0.2397	0.8035	0.048
H8A	0.7391	0.6155	0.7567	0.042
H8B	0.5516	0.5489	0.7240	0.042
H9A	0.7003	0.6988	0.6587	0.044
H9B	0.8864	0.6030	0.6696	0.044
H10A	0.8892	0.3490	0.6335	0.050
H10B	0.7028	0.2805	0.6004	0.050
H11A	0.5543	0.2876	0.6875	0.049
H11B	0.7423	0.1949	0.6986	0.049
H12A	0.7882	0.4570	0.3947	0.101
H12B	0.6951	0.3354	0.4314	0.101
H12C	0.9119	0.3719	0.4449	0.101
H	0.905(7)	0.397(5)	0.741(2)	0.081

Table 8d. Anisotropic displacement parameters for **3i**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl	0.0322(5)	0.0384(5)	0.0630(6)	0.0045(4)	0.0053(4)	0.0005(3)
O1	0.089(2)	0.0430(17)	0.0550(17)	0.0108(14)	0.0120(15)	0.0047(15)
O2	0.0616(18)	0.069(2)	0.0450(15)	-0.0003(14)	0.0112(13)	-0.0010(15)
N1	0.0262(13)	0.0216(13)	0.0453(16)	-0.0008(11)	0.0051(11)	-0.0011(10)
N2	0.0469(16)	0.0293(15)	0.0396(16)	-0.0008(13)	0.0020(12)	0.0013(13)
N3	0.0396(16)	0.0422(18)	0.0416(17)	0.0013(14)	0.0067(13)	-0.0035(13)
N4	0.057(2)	0.052(2)	0.0356(16)	-0.0013(15)	0.0070(14)	0.0005(16)
C1	0.130(5)	0.100(4)	0.050(3)	-0.014(3)	-0.001(3)	0.069(4)
C2	0.076(3)	0.075(3)	0.054(3)	0.000(2)	0.003(2)	0.039(3)
C3	0.0474(19)	0.0308(17)	0.0373(18)	0.0083(15)	0.0046(15)	0.0038(15)
C4	0.064(3)	0.050(2)	0.046(2)	0.0003(18)	0.0081(18)	-0.006(2)
C5	0.081(3)	0.062(3)	0.054(3)	0.005(2)	-0.006(2)	-0.021(2)
C6	0.147(6)	0.057(3)	0.043(3)	-0.006(2)	-0.008(3)	0.018(3)
C7	0.0392(18)	0.0334(19)	0.048(2)	0.0063(15)	0.0076(15)	-0.0074(15)
C8	0.0347(17)	0.0204(16)	0.050(2)	0.0001(14)	0.0052(14)	0.0016(13)
C9	0.0388(18)	0.0245(16)	0.046(2)	-0.0001(14)	0.0029(15)	0.0001(14)
C10	0.048(2)	0.0265(18)	0.048(2)	-0.0078(15)	0.0014(16)	0.0002(15)
C11	0.047(2)	0.0256(17)	0.050(2)	-0.0042(15)	0.0023(16)	-0.0052(15)
C12	0.067(3)	0.088(4)	0.046(2)	-0.018(2)	0.008(2)	0.007(3)

Table 8e. Bond lengths [Å] for **3i**.

O1-N3	1.242(4)	C4-H4B	0.9300
O2-N4	1.371(4)	C5-C6	1.382(8)
O2-C12	1.431(5)	C5-H5A	0.9300
N1-C8	1.493(4)	C6-H6A	0.9300
N1-C11	1.494(4)	C7-H7A	0.9700
N1-C7	1.502(4)	C7-H7B	0.9700
N1-H	1.01(5)	C8-C9	1.511(5)
N2-N3	1.417(4)	C8-H8A	0.9700
N2-C9	1.468(4)	C8-H8B	0.9700
N2-C10	1.473(4)	C9-H9A	0.9700
N3-N4	1.277(4)	C9-H9B	0.9700
C1-C6	1.349(9)	C10-C11	1.521(5)
C1-C2	1.390(8)	C10-H10A	0.9700
C1-H1A	0.9300	C10-H10B	1.9700
C2-C3	1.383(5)	C11-H11A	2.9700
C2-H2A	0.9300	C11-H11B	3.9700
C3-C4	1.380(6)	C12-H12A	4.9700
C3-C7	1.500(5)	C12-H12B	5.9700

C4-C5	1.390(6)	C12-H12C	6.9700

Table 8f. Bond angles [°] for **3h**.

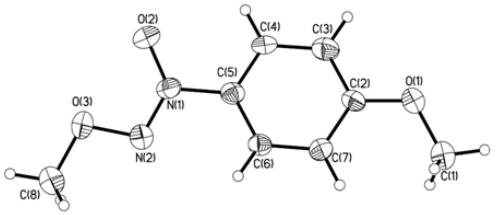
N4-O2-C12	107.3(3)	N1-C7-H7A	108.8
C8-N1-C11	109.5(3)	C3-C7-H7B	108.8
C8-N1-C7	112.4(3)	N1-C7-H7B	108.8
C11-N1-C7	109.4(3)	H7A-C7-H7B	107.7
C8-N1-H	108(3)	N1-C8-C9	110.3(3)
C11-N1-H	107(3)	N1-C8-H8A	109.6
C7-N1-H	110(3)	C9-C8-H8A	109.6
N3-N2-C9	111.1(3)	N1-C8-H8B	109.6
N3-N2-C10	112.8(3)	C9-C8-H8B	109.6
C9-N2-C10	111.1(3)	H8A-C8-H8B	108.1
O1-N3-N4	127.6(3)	N2-C9-C8	109.1(3)
O1-N3-N2	117.2(3)	N2-C9-H9A	109.9
N4-N3-N2	115.1(3)	C8-C9-H9A	109.9
N3-N4-O2	107.5(3)	N2-C9-H9B	109.9
C6-C1-C2	121.3(5)	C8-C9-H9B	109.9
C6-C1-H1A	119.4	H9A-C9-H9B	108.3
C2-C1-H1A	119.4	N2-C10-C11	107.5(3)
C3-C2-C1	119.4(5)	N2-C10-H10A	110.2
C3-C2-H2A	120.3	C11-C10-H10A	110.2
C1-C2-H2A	120.3	N2-C10-H10B	110.2
C4-C3-C2	119.0(4)	C11-C10-H10B	110.2
C4-C3-C7	120.7(3)	H10A-C10-H10B	108.5
C2-C3-C7	120.2(4)	N1-C11-C10	111.3(3)
C3-C4-C5	121.0(4)	N1-C11-H11A	109.4
C3-C4-H4B	119.5	C10-C11-H11A	109.4
C5-C4-H4B	119.5	N1-C11-H11B	109.4
C6-C5-C4	119.0(5)	C10-C11-H11B	109.4
C6-C5-H5A	120.5	H11A-C11-H11B	108
C4-C5-H5A	120.5	O2-C12-H12A	109.5
C1-C6-C5	120.3(5)	O2-C12-H12B	109.5
C1-C6-H6A	119.9	H12A-C12-H12B	109.5
C5-C6-H6A	119.9	O2-C12-H12C	109.5
C3-C7-N1	114.0(3)	H12A-C12-H12C	109.5
C3-C7-H7A	108.8	H12B-C12-H12C	109.5

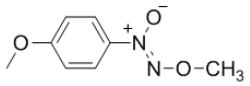
Table 8g. Torsion angles [°]for **3i**.

C9-N2-N3-O1	-39.6(4)
C10-N2-N3-O1	-165.2(3)
C9-N2-N3-N4	142.0(3)

C10-N2-N3-N4	16.5(4)
O1-N3-N4-O2	-5.0(5)
N2-N3-N4-O2	173.2(3)
C12-O2-N4-N3	-178.6(3)
C6-C1-C2-C3	-0.6(9)
C1-C2-C3-C4	1.3(7)
C1-C2-C3-C7	179.9(4)
C2-C3-C4-C5	-0.9(6)
C7-C3-C4-C5	-179.5(4)
C3-C4-C5-C6	-0.1(7)
C2-C1-C6-C5	-0.4(9)
C4-C5-C6-C1	0.8(8)
C4-C3-C7-N1	-67.8(4)
C2-C3-C7-N1	113.6(4)
C8-N1-C7-C3	-56.0(4)
C11-N1-C7-C3	-177.9(3)
C11-N1-C8-C9	-56.7(3)
C7-N1-C8-C9	-178.5(3)
N3-N2-C9-C8	171.3(3)
C10-N2-C9-C8	-62.2(4)
N1-C8-C9-N2	59.0(3)
N3-N2-C10-C11	-173.3(3)
C9-N2-C10-C11	61.2(4)
C8-N1-C11-C10	57.2(4)
C7-N1-C11-C10	-179.2(3)
N2-C10-C11-N1	-58.7(4)

Table 9a. Crystal data and structure refinement for **6a**.





6a

Empirical formula	$C_{16}H_{20}N_4O_6$
Formula weight	364.36
Temperature	20 □
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna21
Unit cell dimensions	a = 11.553 (2)Å α= 90°
	b =21.960 (4) Å β= 90°
	c = 6.9610 (14) Å γ= 90°
Volume	1766.0 (6) $Å^3$

Z	4
Density (calculated)	1.370 Mg/m^3
Absorption coefficient	0.106 mm^{-1}
F(000)	768
Crystal size	0.2×0.2×0.05 mm
Theta range for data collection	1.85 to 25.30°
Index range	0⩽h⩽13, -26⩽k⩽26, 0⩽l⩽8
Reflections collected	1747
Independent reflections	3441 [R(int) = 0.0393]
Completeness to thata = 25.30°	100.00 %
Absorption correction	Psi-scan
Goodness-of-fit on F^2	1.000
Final R indices [I>2σ(I)]	R_1 = 0.0541, wR_2 = 0.1298
R indices (all date)	R_1 = 0.1142, wR_2 = 0.1620
Largest diff. peak and hole	0.279 and -0.201 e $Å^{-3}$

Table 9b. Atomic coordinates and equivalent isotropic displacement parameters for **6a**.

	x	y	z	U(eq)
O1	0.6309(3)	0.90781(16)	0.9391(8)	0.0672(17)
O2	0.5072(3)	0.63183(16)	0.9898(11)	0.0931(18)
O3	0.6786(3)	0.56556(15)	0.9881(10)	0.0703(13)
N1	0.6066(4)	0.6550(2)	0.9791(11)	0.0550(15)
N2	0.7018(4)	0.62664(18)	0.9777(9)	0.0594(14)
C1	0.7381(5)	0.9386(2)	0.9740(17)	0.079(2)
C2	0.6310(5)	0.8461(3)	0.9519(10)	0.0462(18)
C3	0.5303(5)	0.8170(3)	0.8988(10)	0.0584(17)
C4	0.5222(6)	0.7538(2)	0.9085(12)	0.0460(17)
C5	0.6165(4)	0.7208(2)	0.9708(10)	0.0457(15)
C6	0.7170(6)	0.7493(2)	1.0290(11)	0.0435(17)
C7	0.7265(4)	0.8123(2)	1.0129(11)	0.0510(16)
C8	0.7872(5)	0.5338(2)	0.9789(16)	0.085(2)
O4	0.6207(3)	0.09438(16)	0.9664(10)	0.0670(14)
O5	0.7463(3)	0.37166(15)	0.9825(10)	0.0773(15)
O6	0.5727(3)	0.43613(15)	0.9927(12)	0.0729(14)
N3	0.6469(4)	0.3473(2)	0.9804(9)	0.0504(14)
N4	0.5515(4)	0.3748(2)	0.9890(11)	0.0647(15)
C9	0.5138(5)	0.0648(2)	0.9360(14)	0.085(3)
C10	0.6236(5)	0.1569(2)	0.9636(12)	0.0477(18)
C11	0.7237(4)	0.1839(2)	1.0183(12)	0.0526(17)
C12	0.7330(6)	0.2467(2)	1.0248(13)	0.0508(19)
C13	0.6388(4)	0.2805(2)	0.9712(10)	0.0459(15)
C14	0.5377(6)	0.2548(2)	0.9098(12)	0.0474(18)

C15	0.5287(5)	0.1915(2)	0.9046(10)	0.0502(16)
C16	0.4626(5)	0.4669(3)	0.9956(18)	0.092(3)

Table 9c. Hydrogen coordinates and isotropic displacement parameters for **6a**.

	x	y	z	U(eq)
H1A	0.727	0.9817	0.9603	0.118
H1B	0.7949	0.9249	0.8832	0.118
H1C	0.7641	0.9297	1.1019	0.118
H3A	0.4674	0.8397	0.8562	0.07
H4A	0.4541	0.7342	0.8734	0.055
H6A	0.778	0.7266	1.0786	0.052
H7A	0.7958	0.8317	1.0425	0.061
H8A	0.7737	0.4908	0.9869	0.127
H8B	0.8354	0.5464	1.0841	0.127
H8C	0.8251	0.5431	0.8597	0.127
H9A	0.5248	0.0215	0.9426	0.127
H9B	0.4843	0.0755	0.8116	0.127
H9C	0.4597	0.0772	1.0330	0.127
H11A	0.7869	0.16	1.052	0.063
H12A	0.8012	0.2654	1.0643	0.061
H14A	0.4758	0.2791	0.872	0.057
H15A	0.461	0.1728	0.8628	0.06
H16A	0.4748	0.5101	0.9968	0.138
H16B	0.4204	0.4551	1.1085	0.138
H16C	0.419	0.4559	0.8834	0.138

Table 9d. Anisotropic displacement parameters for **6a**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	0.057(2)	0.047(2)	0.097(5)	0.002(3)	0.000(3)	0.007(2)
O2	0.044(2)	0.066(3)	0.170(6)	0.002(5)	0.006(4)	-0.0121(19)
O3	0.067(3)	0.042(2)	0.102(4)	-0.004(3)	-0.002(4)	-0.006(2)
N1	0.038(2)	0.055(3)	0.072(4)	-0.008(4)	0.003(3)	-0.006(2)
N2	0.054(3)	0.049(3)	0.075(4)	0.003(4)	0.001(4)	0.001(2)
C1	0.071(4)	0.052(3)	0.113(6)	0.002(5)	-0.004(6)	0.004(3)
C2	0.039(3)	0.051(3)	0.049(5)	0.003(3)	-0.001(3)	0.008(3)
C3	0.046(3)	0.069(4)	0.060(4)	0.004(4)	-0.007(3)	0.005(3)
C4	0.029(3)	0.060(4)	0.049(4)	0.000(3)	0.000(4)	-0.004(2)
C5	0.042(3)	0.052(3)	0.043(4)	-0.006(4)	0.007(4)	0.001(3)
C6	0.040(4)	0.050(3)	0.040(5)	0.003(3)	-0.009(4)	0.002(2)
C7	0.044(3)	0.049(3)	0.060(5)	-0.003(4)	-0.007(3)	-0.004(2)
C8	0.069(4)	0.057(4)	0.128(7)	-0.006(6)	-0.005(6)	0.007(3)
O4	0.050(2)	0.053(2)	0.098(4)	-0.002(3)	-0.003(3)	0.0016(19)

O5	0.048(2)	0.059(2)	0.125(4)	-0.013(4)	-0.007(3)	-0.0076(19)
O6	0.057(3)	0.043(2)	0.119(4)	0.000(3)	0.003(4)	-0.0031(19)
N3	0.042(3)	0.049(2)	0.060(4)	0.000(3)	0.002(4)	-0.003(2)
N4	0.052(3)	0.052(3)	0.091(4)	-0.004(4)	0.007(4)	0.003(2)
C9	0.069(5)	0.051(3)	0.135(10)	-0.004(5)	0.003(5)	-0.011(3)
C10	0.049(4)	0.040(3)	0.054(5)	0.000(4)	0.003(3)	0.003(2)
C11	0.041(3)	0.049(3)	0.067(5)	0.001(4)	0.000(3)	0.005(3)
C12	0.036(4)	0.062(4)	0.055(5)	0.004(4)	-0.006(4)	-0.005(2)
C13	0.041(3)	0.052(3)	0.045(4)	0.000(4)	0.000(4)	-0.004(3)
C14	0.035(4)	0.051(3)	0.056(5)	-0.004(3)	0.002(4)	0.006(2)
C15	0.043(3)	0.051(3)	0.056(4)	-0.008(3)	-0.002(3)	-0.003(3)
C16	0.064(4)	0.060(4)	0.151(8)	0.005(6)	0.008(6)	0.011(3)

Table 9e. Bond lengths [Å] for **6a**.

O1-C2	1.358(6)	O4-C10	1.373(6)
O1-C1	1.431(7)	O4-C9	1.412(6)
O2-N1	1.259(5)	O5-N3	1.266(5)
O3-N2	1.370(5)	O6-N4	1.369(5)
O3-C8	1.437(6)	O6-C16	1.440(6)
N1-N2	1.264(6)	N3-N4	1.259(5)
N1-C5	1.451(6)	N3-C13	1.471(6)
C1-H1A	0.9600	C9-H9A	0.9600
C1-H1B	0.9600	C9-H9B	0.9600
C1-H1C	0.9600	C9-H9C	0.9600
C2-C3	1.378(8)	C10-C11	1.355(8)
C2-C7	1.396(7)	C10-C15	1.396(8)
C3-C4	1.392(7)	C11-C12	1.383(7)
C3-H3A	0.9300	C11-H11A	0.9300
C4-C5	1.378(8)	C12-C13	1.369(8)
C4-H4A	0.9300	C12-H12A	0.9300
C5-C6	1.380(8)	C13-C14	1.367(8)
C6-C7	1.392(6)	C14-C15	1.393(7)
C6-H6A	0.9300	C14-H14A	0.9300
C7-H7A	0.9300	C15-H15A	0.9300
C8-H8A	0.9300	C16-H16A	0.9300
C8-H8B	0.9300	C16-H16B	0.9300
C8-H8C	0.9300	C16-H16C	0.9300

Table 9f. Bond angles [°] for **6a**.

C2-O1-C1	117.4(5)	C10-O4-C9	118.6(5)
N2-O3-C8	107.5(4)	N4-O6-C16	107.7(4)
O2-N1-N2	126.6(5)	N4-N3-O5	126.2(4)

O2-N1-C5	118.5(5)	N4-N3-C13	115.1(4)
N2-N1-C5	115.0(4)	O5-N3-C13	118.7(4)
N1-N2-O3	108.1(4)	N3-N4-O6	108.5(4)
O1-C1-H1A	109.5	O4-C9-H9A	109.5
O1-C1-H1B	109.5	O4-C9-H9B	109.5
H1A-C1-H1B	109.5	H9A-C9-H9B	109.5
O1-C1-H1C	109.5	O4-C9-H9C	109.5
H1A-C1-H1C	109.5	H9A-C9-H9C	109.5
H1B-C1-H1C	109.5	H9B-C9-H9C	109.5
O1-C2-C3	116.5(5)	C11-C10-O4	117.1(5)
O1-C2-C7	123.4(5)	C11-C10-C15	120.9(5)
C3-C2-C7	120.1(5)	O4-C10-C15	122.0(5)
C2-C3-C4	120.5(6)	C10-C11-C12	120.8(5)
C2-C3-H3A	119.8	C10-C11-H11A	119.6
C4-C3-H3A	119.8	C12-C11-H11A	119.6
C5-C4-C3	119.0(6)	C13-C12-C11	118.0(6)
C5-C4-H4A	120.5	C13-C12-H12A	121
C3-C4-H4A	120.5	C11-C12--H12A	121
C4-C5-C6	121.3(5)	C14-C13-C12	122.7(5)
C4-C5-N1	118.3(5)	C14-C13-N3	118.8(5)
C6-C5-N1	120.4(5)	C12-C13-N3	118.6(5)
C5-C6-C7	119.5(5)	C13-C14-C15	119.0(6)
C5-C6-H6A	120.2	C13-C14-H14A	120.5
C7-C6-H6A	120.2	C15-C14-H14A	120.5
C6-C7-C2	119.4(5)	C14-C15-C10	118.5(5)
C6-C7-H7A	120.3	C14-C15-H15A	120.7
C2-C7-H7A	120.3	C10-C15-H15A	120.7
O3-C8-H8A	109.5	O6-C16-H16A	109.5
O3-C8-H8B	109.5	O6-C16-H16B	109.5
H8A-C8-H8B	109.5	H16A-C16-H16B	109.5
O3-C8-H8C	109.5	O6-C16-H16C	109.5
H8A-C8-H8C	109.5	H16A-C16-H16C	109.5
H8B-C8-H8C	109.5	H16B-C16-H16C	109.5

Table 9g. Torsion angles [°] for **6a**.

O2-N1-N2-O3	0.6(12)	O5-N3-N4-O6	2.6(11)
C5-N1-N2-O3	179.4(7)	C13-N3-N4-O6	-178.8(7)
C8-O3-N2-N1	177.8(8)	C16-O6-N4-N3	178.0(8)
C1-O1-C2-C3	-173.6(7)	C9-O4-C10-C11	171.5(7)
C1-O1-C2-C7	5.7(12)	C9-O4-C10-C15	-9.5(14)
O1-C2-C3-C4	-179.6(6)	O4-C10-C11-C12	-178.2(8)
C7-C2-C3-C4	1.1(11)	C15-C10-C11-C12	2.7(13)
C2-C3-C4-C5	-0.4(11)	C10-C11-C12-C13	-1.1(12)

C3-C4-C5-C6	2.0(11)	C11-C12-C13-C14	-0.9(13)
C3-C4-C5-N1	-179.7(7)	C11-C12-C13-N3	179.1(7)
O2-N1-C5-C4	-22.3(11)	N4-N3-C13-C14	21.4(10)
N2-N1-C5-C4	158.8(7)	O5-N3-C13-C14	-159.9(7)
O2-N1-C5-C6	156.0(8)	N4-N3-C13-C12	-158.6(7)
N2-N1-C5-C6	-22.9(11)	O5-N3-C13-C12	20.1(11)
C4-C5-C6-C7	-4.3(11)	C12-C13-C14-C15	1.3(12)
N1-C5-C6-C7	177.5(7)	N3-C13-C14-C15	-178.7(6)
C5-C6-C7-C2	4.9(11)	C13-C14-C15-C10	0.3(11)
O1-C2-C7-C6	177.4(7)	C11-C10-C15-C14	-2.3(11)
C3-C2-C7-C6	-3.3(11)	O4-C10-C15-C14	178.7(7)

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