Supplementary information

Visible light-Induced Oxidative *N*-dealkylation of Alkylamines by a Luminescent Osmium(VI) Nitrido Complex

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Experimental section

Materials: $[^nBu_4N]PF_6$ (Aldrich) for electrochemistry was recrystallized three times from boiling ethanol and dried under vacuum at 120 °C for 24 h. Acetonitrile (Aldrich) for electrochemistry was distilled over calcium hydride. HPLC grade CH_2Cl_2 obtained from RCI Labscan with <0.01% water was used for photochemical experiments. All other chemicals were of reagent grade and used without further purification. All manipulations were performed without precaution to exclude air or moisture unless otherwise stated.

Physical measurements: IR spectra were obtained as KBr discs using a Nicolet 360 FTIR spectrophotometer. UV/vis spectra were recorded using a Perkin–Elmer Lamda 19 spectrophotometer in 1 cm quartz cuvettes. Elemental analysis was performed using an Elementar Vario EL Analyzer. Electrospray ionization mass spectrometry (ESI-MS) was performed using a PE-SCIEX API 365 triple quadruple mass spectrometer. Cyclic voltammogram (CV) was performed using a PAR model 273 potentiostat using a glassy carbon working electrode, a saturated calomel electrode (SCE) reference electrode, and a Pt-wire counter electrode with ferrocene (Cp_2Fe) as the internal standard. ^1H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) are reported relative to tetramethylsilane (Me_4Si). UV/vis spectra were recorded on a Hewlett–Packard 8453 or a Hewlett–Packard 8452A diode-array spectrophotometer. Emission lifetime measurements were conducted using Edinburgh Instruments LP920 laser flash photolysis system using the third harmonic output (355 nm, 6-8 ns fwhm pulse width, 10mJ/pulse) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd:YAG laser as the excitation source. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze pump-thaw cycles. Nanosecond transient absorption was conducted using Edinburgh Instruments LP920 laser flash photolysis system using the third harmonic output (355 nm, 6-8 ns fwhm pulse width, 6mJ/pulse) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd:YAG laser as the excitation source. Solutions were

rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze pump-thaw cycles.

X-ray crystallography: Measurements were collected on an Oxford CCD diffractometer using graphite-monochromated MoK_a radiation (λ = 0.71073 Å) for **2-4**. Details of the intensity data collection and crystal data are given in Supplementary Table S3. Absorption corrections were done by the multi-scan method. The structures were resolved by the heavy-atom Patterson method or direct methods and refined by full-matrix least-squares using SHELX-97 and expanded using Fourier techniques.[1] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated by the program SHELXL-97.[2] The positions of hydrogen atoms were calculated on the basis of riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final R indices. All calculations were performed using the teXsan crystallographic software. CCDC 2083709-2083711 for **2-4**, respectively.

Computational details

The reaction mechanism of *N*-dealkylation by excited triplet state of $[Os^{V}(N)(CN)_3(L)]^{2-}$ has been investigated by the DFT calculations using the Gaussian 16 quantum chemistry software package.[3] All energy profiles for the reaction were calculated at the B3LYP-D3(BJ)/def2-TZVP level.[4–8] The solvent effect of acetonitrile was taken account by the Polarizable Continuum Model (PCM).[9, 10] The nature of all stationary points (minima and transition state structures) was confirmed by vibrational frequencies calculations and the reaction path of transition states was confirmed by intrinsic reaction coordinate calculations.

To ensure the reliability of the calculation results, we have re-optimized the structures and computed the respective $\Delta G_{298}^{\ddagger}$ of TS1 (8.8 kcal/mol) and TS2 (-5.8 kcal/mol) at the *ω*B97x-D/def2-TZVP level, both values are consistent with the above values (9.8 and -1.8 kcal/mol) at the B3LYP-D3(BJ)/def2-TZVP level. The intrinsic reaction coordinate (IRC) path of TS1 is given in Figure S20.

Synthesis of $(PPh_4)_2[Os^{III}(L)(CN)_4]$ [$(PPh_4)_2$1′], $(PPh_4)[Os^{III}(NH{=}DMA_{(-2H)})(L)(CN)_3]$ [(PPh_4)2] and $(^nBu_4N)[Os^{III}(NH{=}DMA_{(-2H)})(L)(CN)_3]$ [$(^nBu_4N)$2].

10 pyrex tubes (15 × 2 cm) each containing **NO_2-OsN** (5 mg, 5.7 μmol) and *N,N*-dimethylaniline (DMA, 7.2 μl, 57 μmol) in 15 ml CH_2Cl_2 were prepared. Each tube was sealed by a rubber septum, degassed with Ar for 30 min, and then irradiated with blue LED light for 24 h, whereby the light-yellow solution turned red. The solutions were combined, and the solvent was removed under reduced pressure. The red residue was extracted by water (150 ml). Excess PPh_4Cl (30 mg) was added to the aqueous extract to give a dark red precipitate, which was recrystallized by slow evaporation of a MeOH/H_2O solution to give $(PPh_4)_2[Os^{III}(L)(CN)_4]$ [$(PPh_4)_2$**1′**]. Yield: 47 mg, 68%. Selected IR (KBr disc, cm^{-1}): *ν*(C≡N) 2085, 2038 and 1995; *ν*(C=N) 1610; *ν*(N=O) 1317. Calcd for $C_{65}H_{47}N_6O_4OsP_2{\cdot}H_2O$: C, 62.64; H, 3.96; N, 6.74. Found: C, 62.67; H, 3.87; N, 6.81. UV/Vis (MeOH): λ_{max}[nm] (ε [M^{-1} cm^{-1}]): 275sh (20460), 284 (20000), 323 (14750), 368 (13180).

The water-insoluble part was dissolved in CH_2Cl_2 and purified by silica gel column chromatography. A red band ((PPh_4)**2**) was eluted with a mixture of CH_2Cl_2/acetone (v:v = 1:1). A dark red band (**NO_2-OsNH_3**)[4a] was eluted by CH_2Cl_2/acetone/MeOH (v:v:v, 20:5:1) and isolated with ~5% yield. Recrystallization of red band by slow diffusion of diethyl ether into a CH_2Cl_2 solution gave the red microcrystalline solid (PPh_4)**2**. Yield: 9 mg, 16%. Selected IR (KBr disc, cm^{-1}): *ν*(C≡N) 2113 and 2088; *ν*(C=N) 1609; *ν*(N=O) 1310. Calcd for $C_{48}H_{37}N_7O_4OsP$: C, 57.82; H, 3.74; N, 9.83. Found: C, 57.75; H, 3.68; N, 9.79. UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]): 228 (40990), 255 (16070), 269 (16210), 276 (16010), 294 (15580), 330sh (12250), 379 (11790), 466sh (5860), 554sh (1880).

$(^nBu_4N)$**2** was obtained by metathesis of (PPh_4)**2** with excess $(^nBu_4N)Cl$ in MeOH/H_2O. Crystals suitable for X-ray determination were obtained by slow diffusion of diethyl ether into a MeOH solution of $(^nBu_4N)$**2**. The IR and ESI/MS are similar to that of (PPh_4)**2.** Calcd for $C_{40}H_{53}N_8O_4Os$: C, 53.37; H, 5.94; N, 12.45. Found: C, 53.40; H, 5.89;

N, 12.52. UV/vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]): 231 (18600), 291 (16020), 324 (13500), 379 (11810), 465sh (5982), 554sh (1910).

Synthesis of $(PPh_4)[Os^{III}(N{\equiv}CCH_3)(L)(CN)_3]$ [(PPh_4)3]. 10 pyrex tubes (15 × 2 cm) each containing **NO_2-OsN** (5 mg, 5.7 μmol) and *N,N*-diethylaniline (DEA, 50 μl, 0.3 mmol) in 15 ml CH_2Cl_2 were prepared. Each tube was sealed by a rubber septum, degassed with Ar for 30 min. and then irradiated with blue LED light for 24 h, whereby the light-yellow solution turned blue. The solutions were combined, and the solvent was removed under reduced pressure. The solid residue was then dissolved in a minimum amount of CH_2Cl_2 and loaded onto a silica gel column. The first yellow band (unreacted **NO_2-OsN)** was eluted by CH_2Cl_2/acetone (v:v, 10:1). The second green band was eluted by CH_2Cl_2/acetone (v:v, 4:1). The green solid was collected. Yield: 41 mg, 80%. Selected IR (KBr disc, cm^{-1}): *v*(C≡N) 2125 and 2102; *v*(N=O) 1310. Calcd for $C_{42}H_{30}N_6O_4OsP$: C, 55.81; H, 3.35; N, 9.30. Found: C, 55.65; H, 3.41; N, 9.27. UV/vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]): 231 (57220), 262sh (20110), 269 (21820), 276 (21850), 291 (19980), 375 (16090), 584 (2270).

Synthesis of $(PPh_4)[Os^{IV}(N{=}C(CH_3)_2)(L)(CN)_3]$ [(PPh_4)4]. The procedure is similar to that for **3** except that *N,N*-diisopropylaniline (DIA, 50 μl, 0.26 mmol) was used instead of DEA. The reactants in CH_2Cl_2 solution were irradiated with blue light for 24 h and complex **4** was isolated as PPh_4^+ salt by silica gel column chromatography and recrystallized by slow diffusion of diethyl ether into a CH_2Cl_2 solution of (PPh_4)**4**. Yield for (PPh_4)**4**: 43 mg, 82%. Selected IR (KBr disc, cm^{-1}): *v*(C≡N) 2142 and 2119; *v*(C=N) 1611; *v*(N=O) 1316. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (d, *J* = 2.9 Hz, 1H, L-H), 7.96-7.89 (m, 5H, Ar-H), 7.82-7.76 (m, 8H, Ar-H), 7.75 – 7.71 (t, *J* = 4.0 Hz, 1H, L-H), 7.70-7.61 (m, 9H, Ar-H), 7.51 (dd, *J* = 6.4, 2.8 Hz, 2H, L-H), 6.75 (d, *J* = 9.4 Hz, 1H, L-H), 4.68 (s, 6H, -CH_3). Calcd for $C_{43}H_{33}N_6O_4OsP$: C, 56.20; H, 3.62; N, 9.15. Found: C, 56.12; H, 3.55; N, 9.08. UV/vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]): 227 (78880), 261sh (21640), 269 (21800), 276 (21110), 289 (18160), 328 (22150), 378sh (16320), 418sh (11910).

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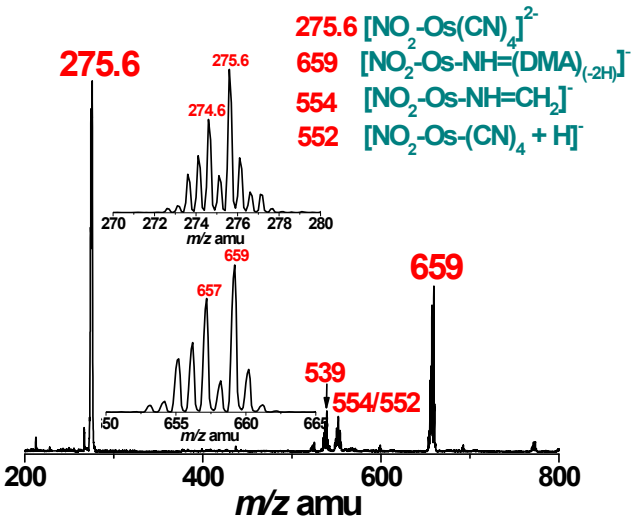

Figure S1. ESI/MS for the photoreaction of **NO_2-OsN** with 10 equiv. *N,N*-dimethylaniline (DMA) (insets show the experimental and simulated isotopic distribution patterns of m/z 275.6).

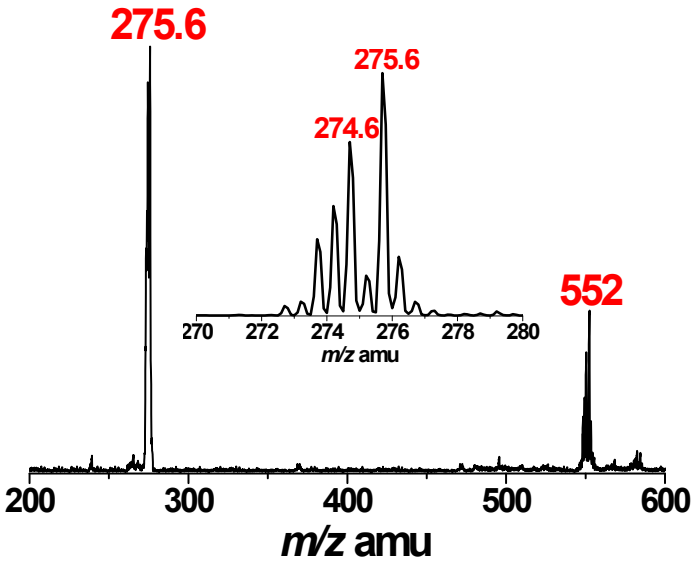

Figure S2. ESI/MS of $(PPh_4)_2$**1′** (-ve mode) in MeOH.

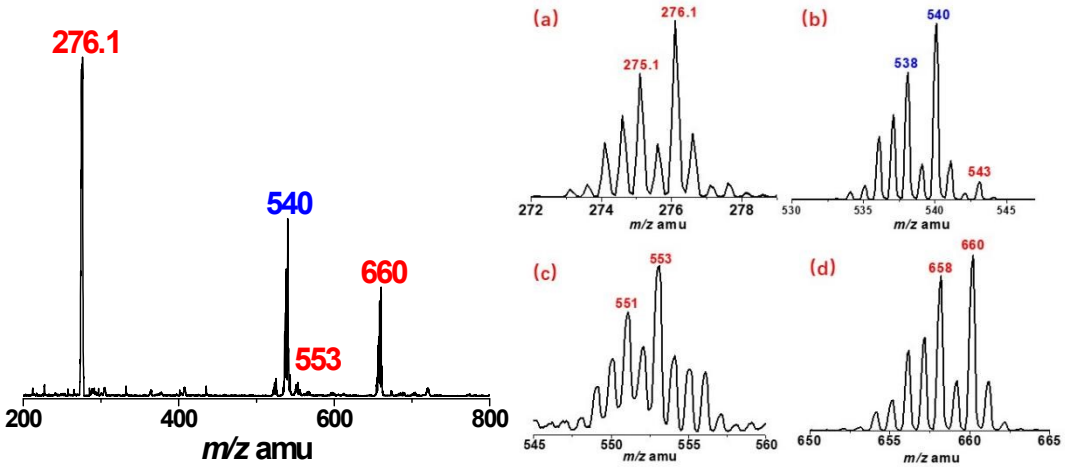

Figure S3. ESI/MS for the photoreaction of ^{15}N-labelling **NO_2-Os^{15}N** with 10 equiv. DMA.

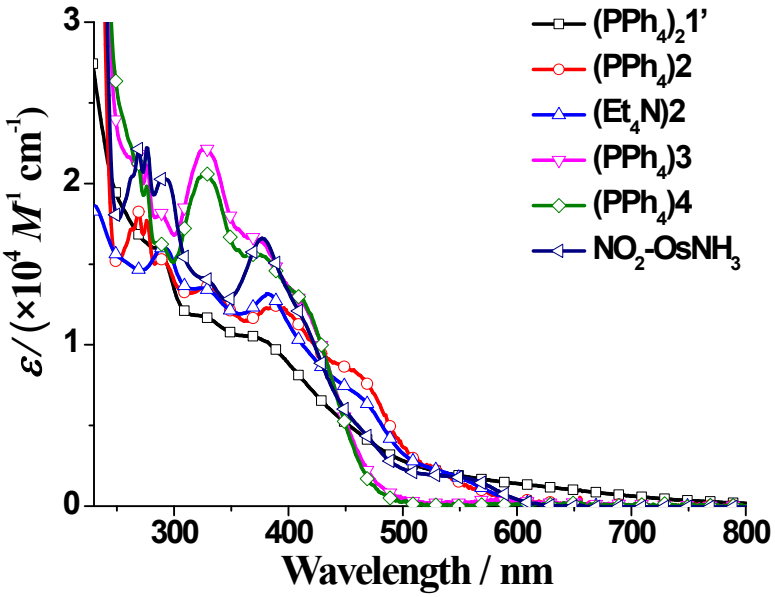

Figure S4. The UV/vis spectra of $(PPh_4)_2$**1'**, (PPh_4)**2**, $(^nBu_4N)$**2**, PPh_4)**3**, (PPh_4)**4** in CH_2Cl_2 and **NO_2-OsNH$_3$** in MeOH.

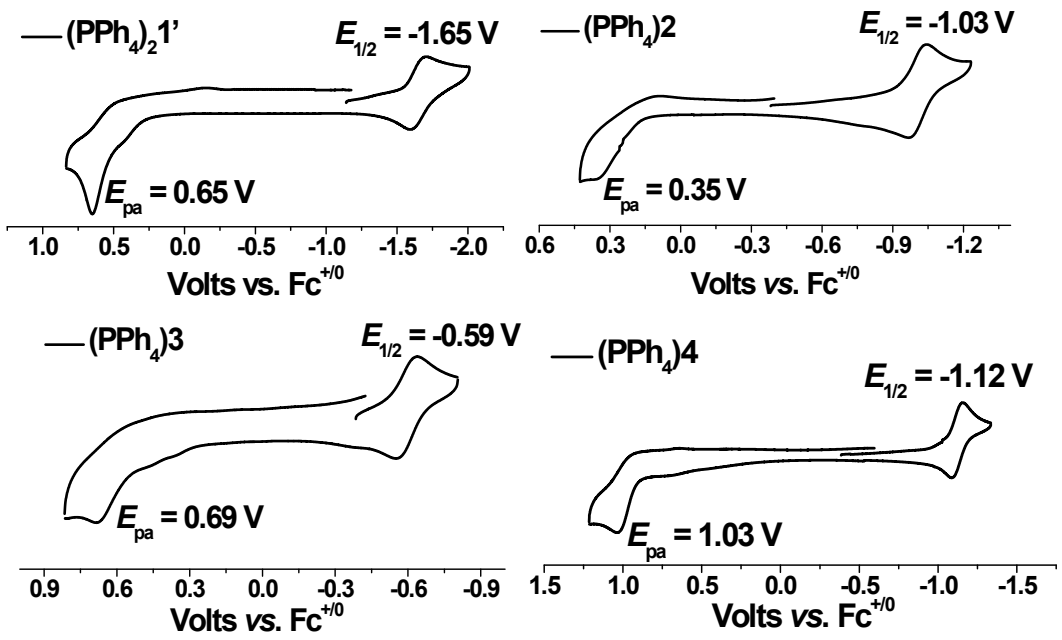

Figure S5. Cyclic voltammetry (CV) of **1**-**4** in MeCN containing 0.1 *M* $[^{n}Bu_4N]PF_6$ as supporting electrolyte (Scan rate = 0.1 V·s $^{-1}$).

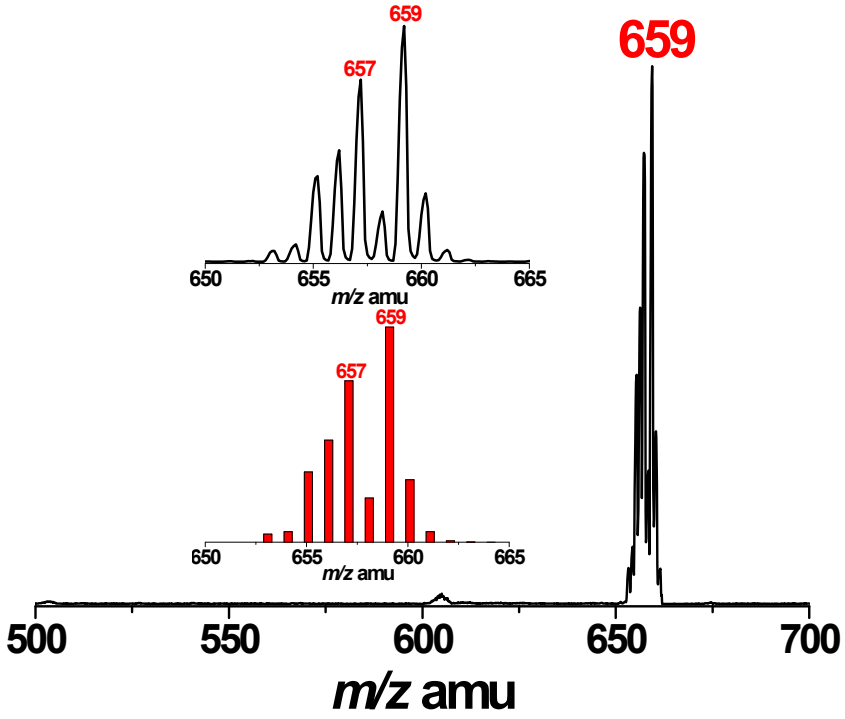

Figure S6. ESI/MS (-ve mode) of (PPh_4)**2** in MeOH.

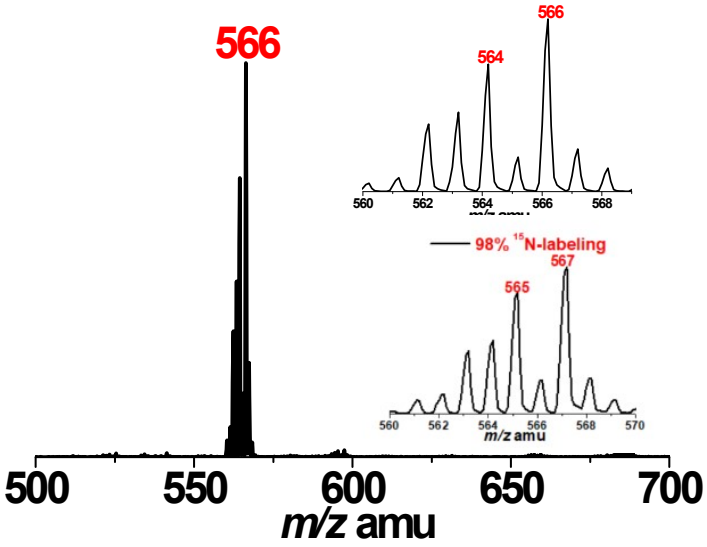

Figure S7. ESI/MS (-ve mode) of $[Os^{III}(L)(CN)_3(N{\equiv}CCH_3)]^-$ (**3**) (inset shows the isotopic distribution of *m/z* 566 and the corresponding *m/z* 567 species for ^{15}N-labelling $[Os^{III}(L)(CN)_3(^{15}N{\equiv}CCH_3)]^-$.

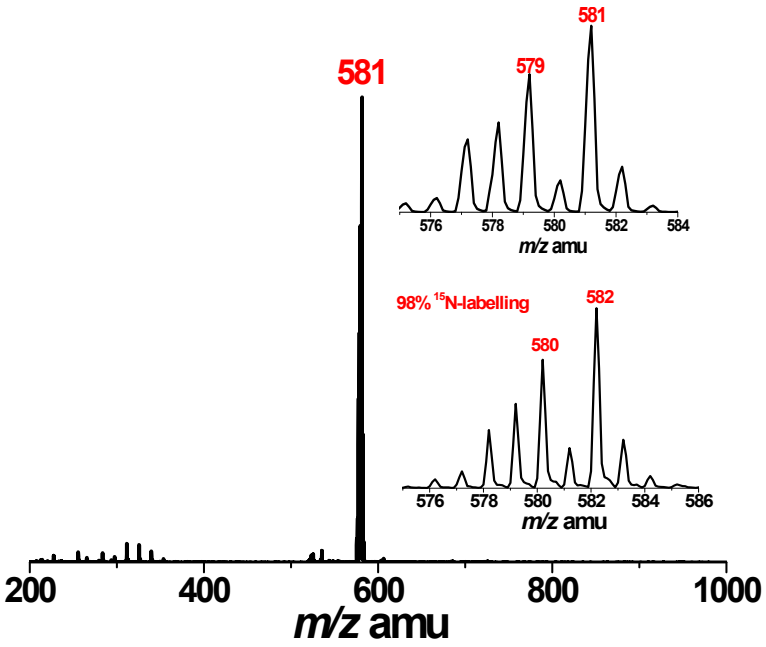

Figure S8. ESI/MS (-ve mode) of $[Os^{IV}(L)(CN)_3\{N{=}C(CH_3)_2\}]^-$ (**4**) (inset shows the isotopic distribution of *m/z* 581 and the corresponding *m/z* 582 species for ^{15}N-labelling $[Os^{IV}(L)(CN)_3\{^{15}N{=}C(CH_3)_2\}]^-$.

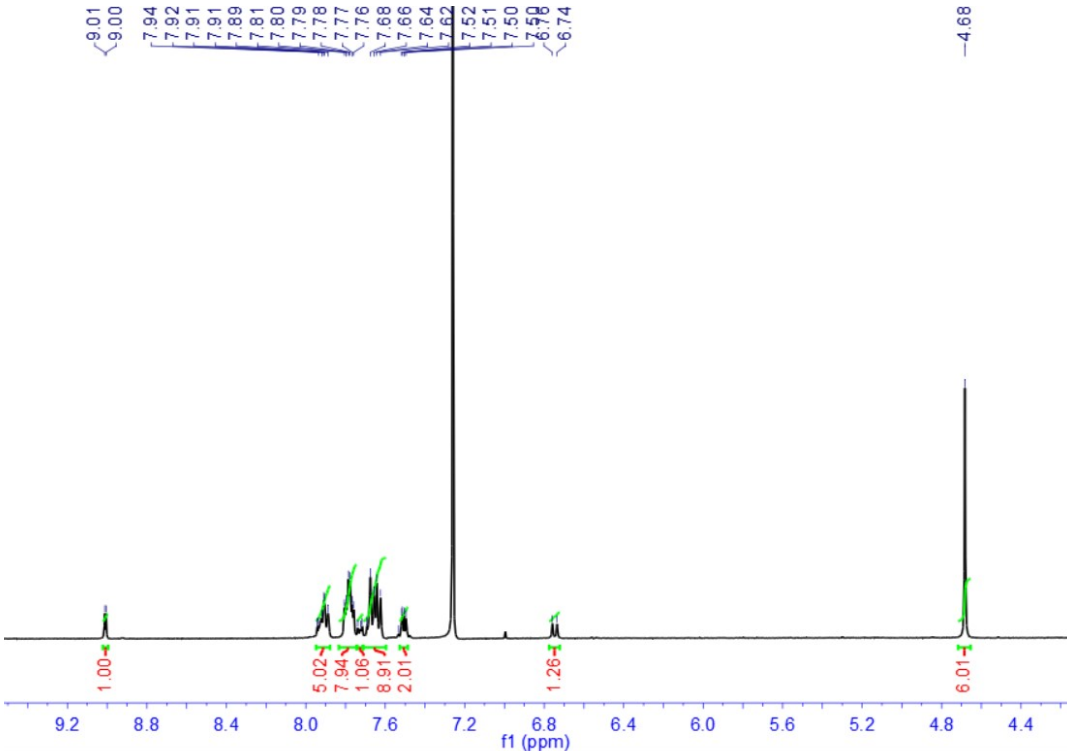

Figure S9. ^{1}H NMR spectrum of (PPh_4)**4** in $CDCl_3$.

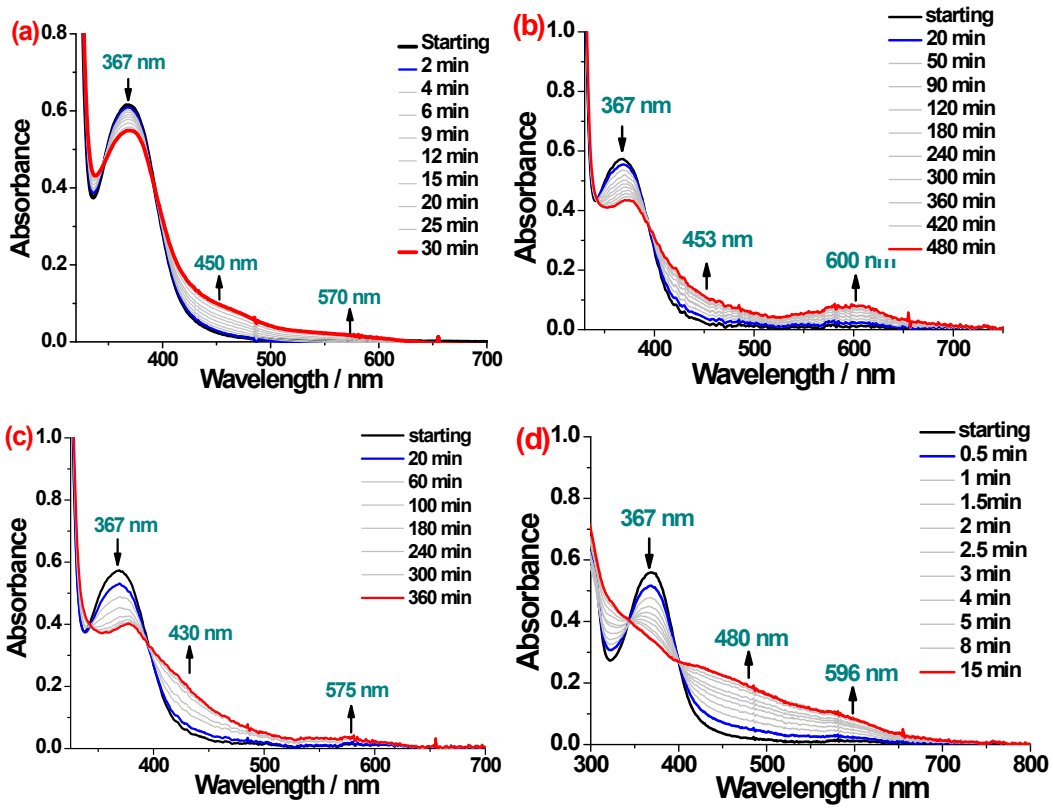

Figure S10. UV/vis spectra collected at various time intervals for the photoreaction of **NO_2-OsN** (3.45×10^{-5} M) with 100 equiv. of (a) *N,N*-dimethylaniline, (b) *N,N*-diethylaniline, (c) *N,N*-diisopropylaniline, and (d) triethylamine in $C_2H_4Cl_2$.

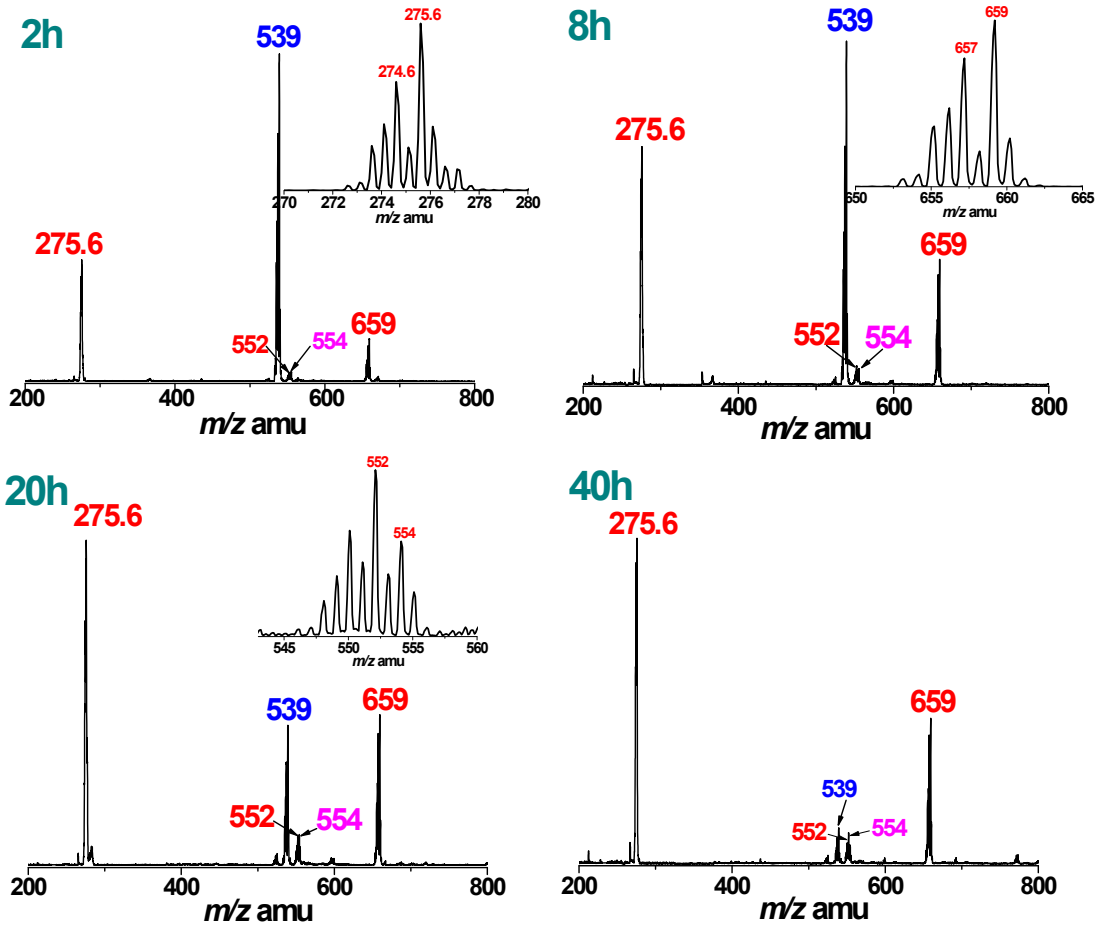

Figure S11. ESI/MS collected at various time intervals for the photoreaction of **NO_2-OsN** with 10 equiv. *N,N*-dimethylaniline (DMA) in CH_2Cl_2.

Table S1. Products from the reaction of various amines with **NO_2-OsN***.

Entry	Substrates	Organic Products	yield	Os-amidine	**NO_2-$OsNH_3$**	Other Os products (isolated yield)
1			71%	16%	5%	**NO_2-$Os(CN)_4$** (68%)
2			87%	< 2%	<1%	**NO_2-Os-N≡CCH_3** (80%)
3			91%	/	<1%	**NO_2-Os-N=$C(CH_3)_2$** (82%)
4			72%	< 2%	<2%	**NO_2-Os-N≡CCH_3** (65%)
5			48%	/	30%	**NO_2-Os-N=$C(CH_3)_2$** (42%)

Table S2. Hammett constant (σ_p) and redox potential of 4-X-*N,N*-dimethylanilines, pK_a values of 4-X-N,N-dimethylaniline radical cations.

X	Hammett constant (σ_p)	*E*° *vs*. NHE (V) [a]	pK_a radical cation [b]
Br	0.232	1.15	9.4
Cl	0.227	1.11	10.1
H	0	1.0	12.4
Me	-0.170	0.94	13.0
MeO	-0.268	0.84	15.4

[a] data estimated in water (ref 11b); [b] data estimated in water (refs 11b, 11e-g)

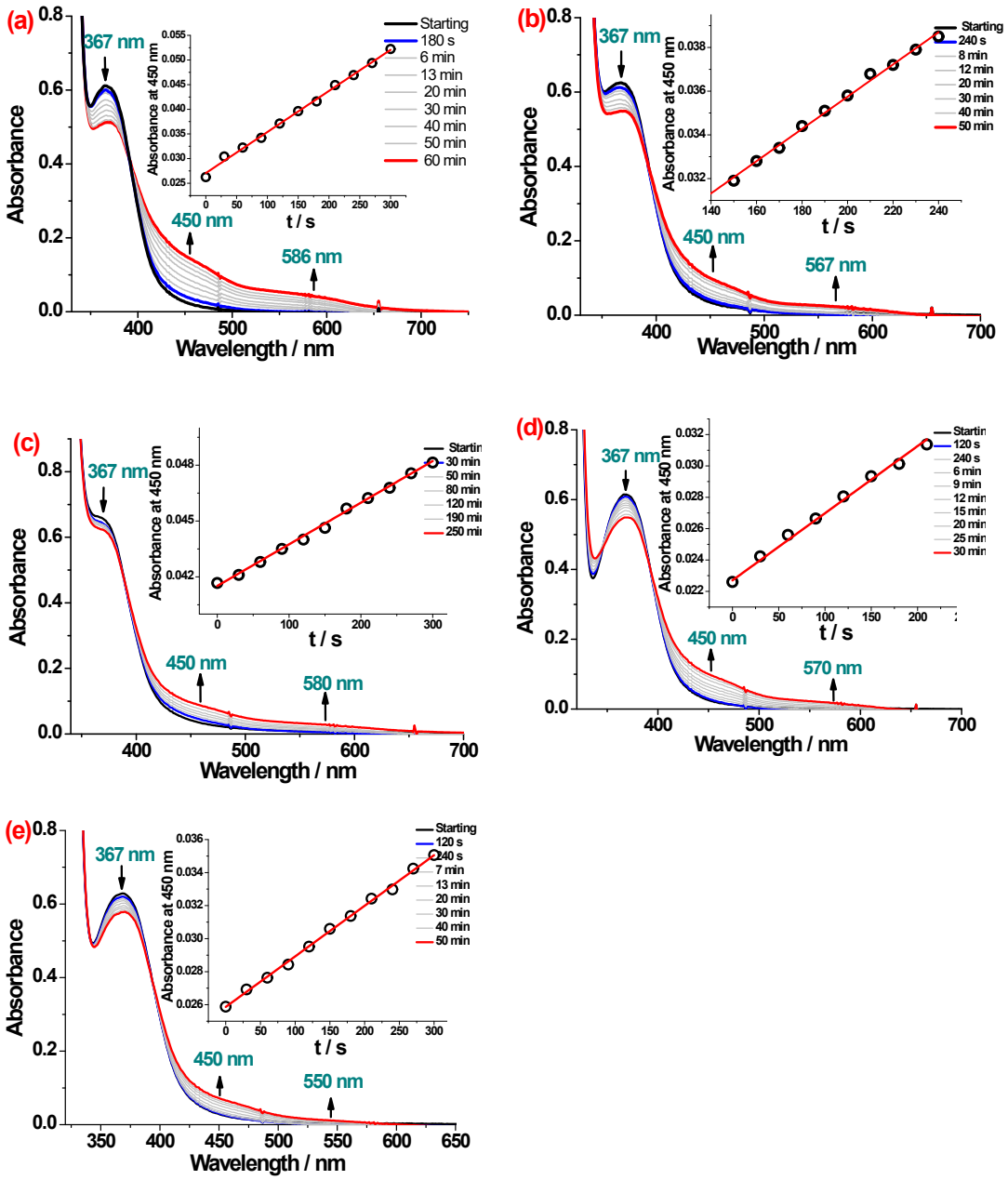

Figure S12. The UV/vis spectra collected at various time intervals for the photoreaction of **NO_2-OsN** (3.38×10^{-5} M) with 100 equiv. of (a) 4-chloro-*N,N*-dimethylaniline; (b) 4-bromo-*N,N*-dimethylaniline; (c) 4-methoxyl-*N,N*-dimethylaniline; (d) *N,N*-dimethylaniline; (e) *4*, *N,N*-trimethylaniline in $C_2H_4Cl_2$. (Insets shows the initial time trace of absorbance at 450 nm).

Figure S13. The photoreaction of **NO_2-OsN** with *N*-ethyl-*N*-methylaniline giving two dealkylation products.

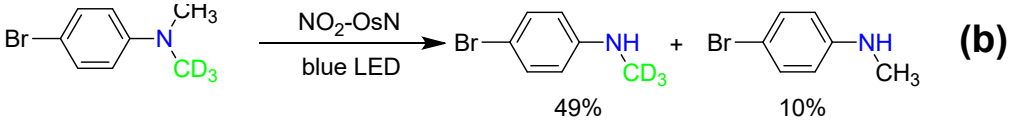

Figure S14. (a) The inter-molecular KIE value obtained from the competition experiment of **NO_2-OsN*** with equimolar *N,N*-dimethylaniline ($C_6H_5N(CH_3)_2$) and d^6 *N,N*-dimethylaniline ($C_6H_5N(CD_3)_2$). (b) The intra-molecular KIE value obtained from the reaction of **NO_2-OsN*** with 4-bromo-*N*-methyl-*N*-(trideuteromethyl)aniline.

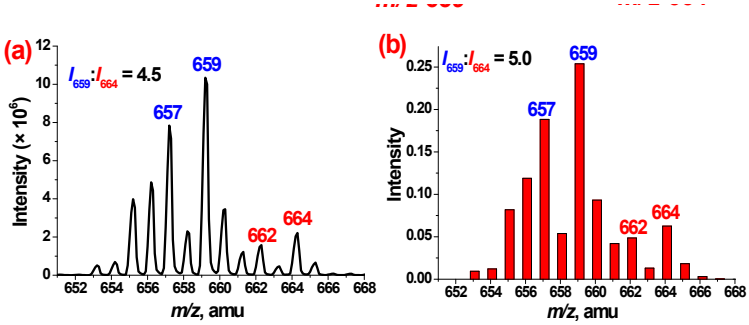

Figure S15. The photoreaction of **NO_2-OsN** with equimolar $C_6H_5N(CH_3)_2$ and $C_6H_5N(CD_3)_2$, and the experimental (a) and simulated (b) isotropic distribution patterns.

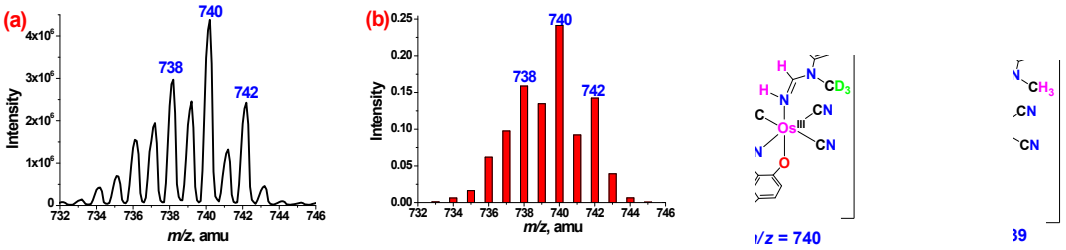

Figure S16. The experimental (a) and simulated (b) isotopic distribution for the photoreaction of **NO_2-OsN** with d^3 *N*-methylaniline ($C_6H_5NHCD_3$) and ratio of *m/z* 740:739 of ~5:1.

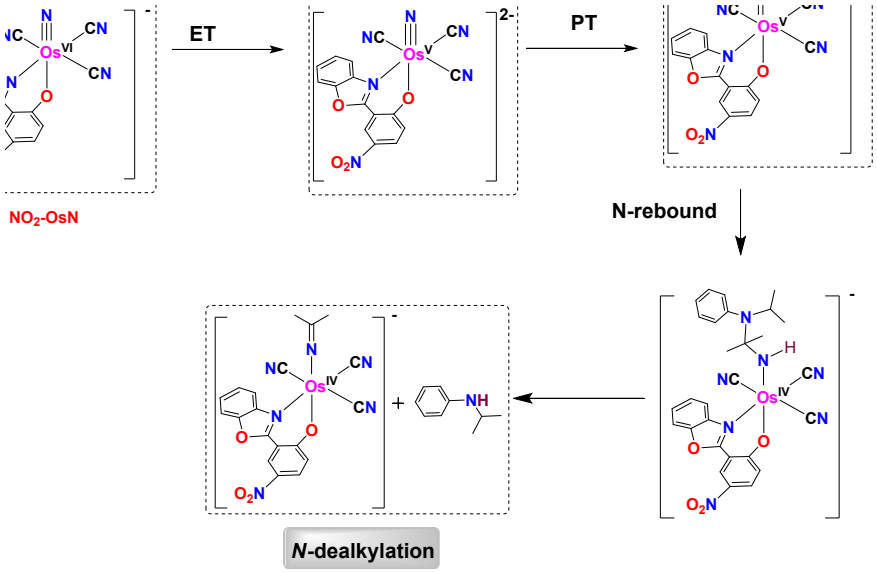

Figure S17. The proposed reaction mechanism of **NO_2-OsN*** with *N,N*-diisopropylaniline.

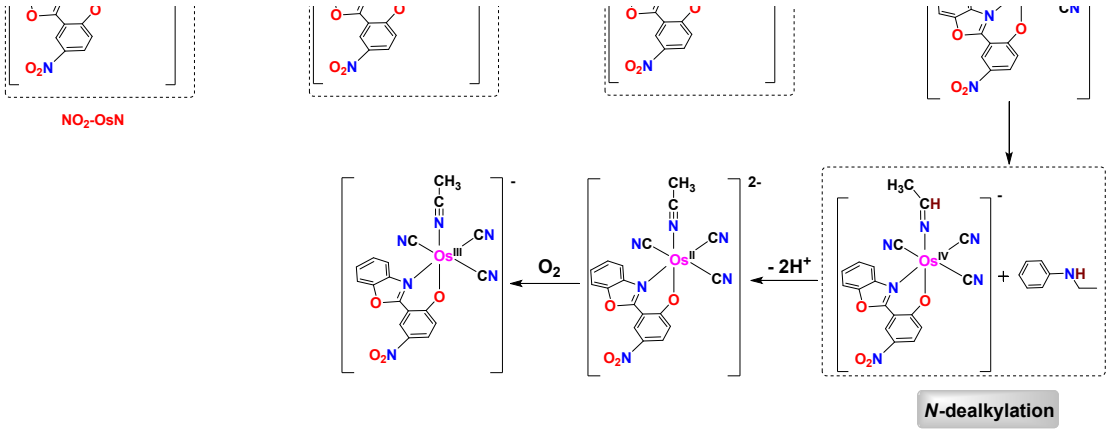

Figure S18. The proposed reaction mechanism of **NO_2-OsN*** with *N,N*-diethylaniline (DEA).

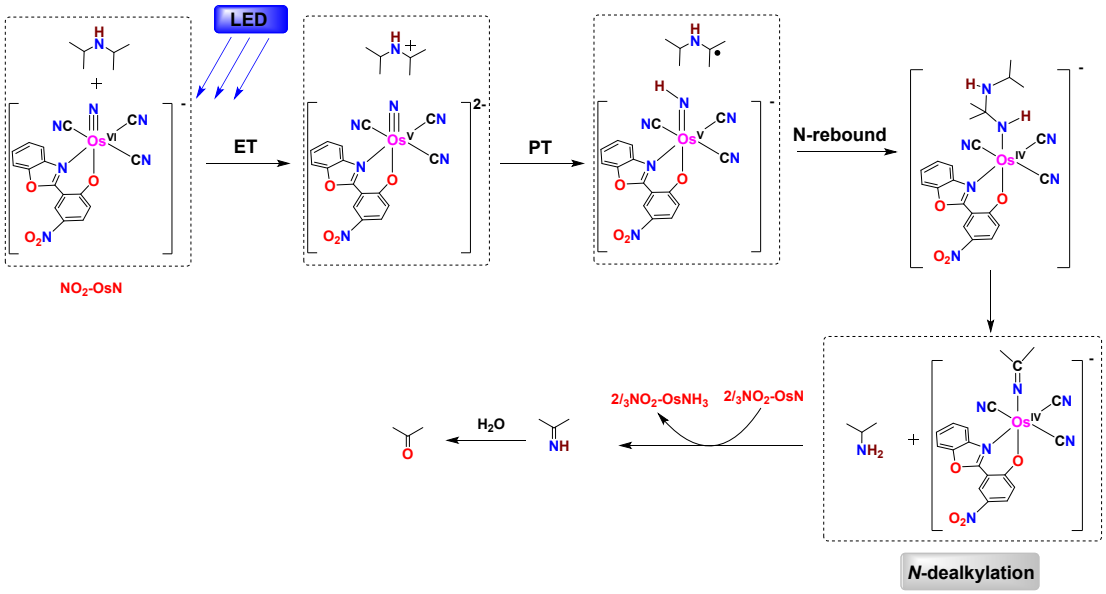

Figure S19. The proposed reaction mechanism of **NO_2-OsN*** with diisopropylamine.

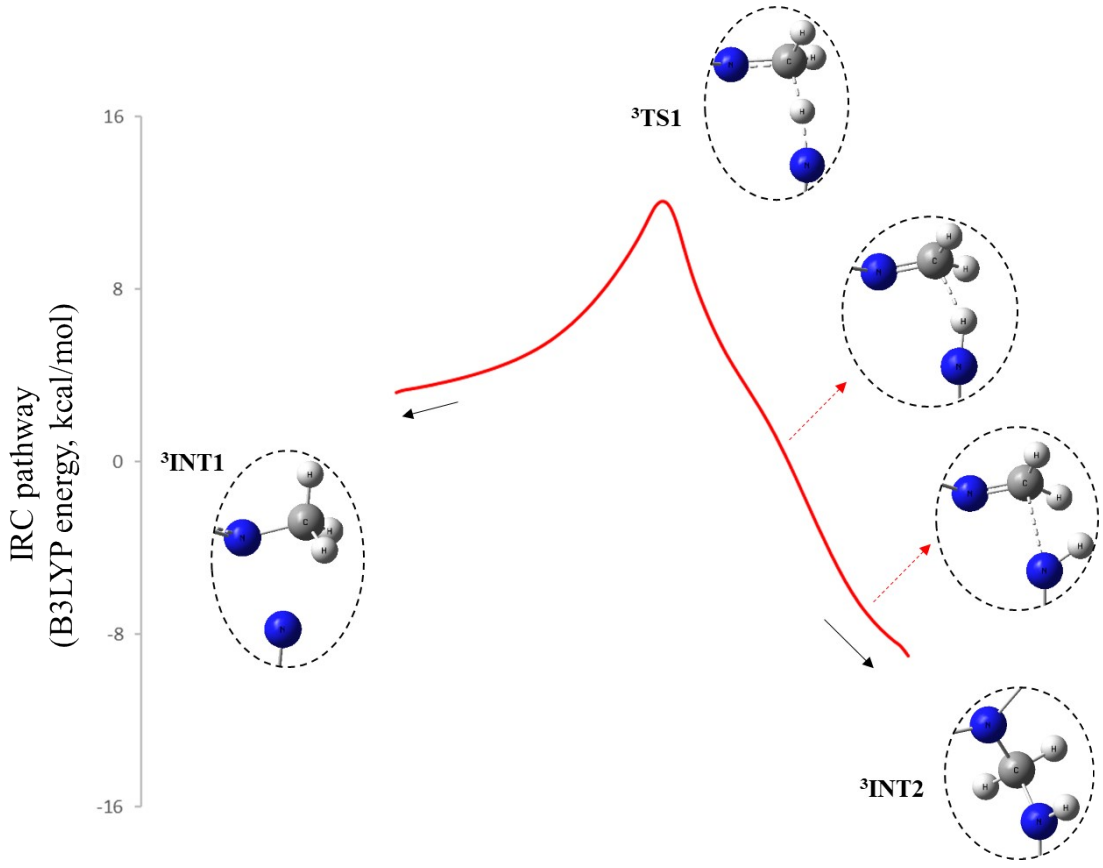

Figure S20. Forward and reverse IRC pathway for ^{3}TS1 at B3LYP-D3(BJ)/def2-TZVP level with the PCM solvent effect. The zero point is set to the B3LYP energy of ^{3}INT1. The proton-transfer and *N*-rebound step occurs simultaneously from ^{3}TS1 to ^{3}INT2. Not all the atoms are shown for simplicity.

Table S3. Crystal data and structure refinement details for compounds **2-4**.

	2	**3**	**4**
Formula	$C_{41}H_{57}Cl_2N_8O_5Os$	$C_{42}H_{30}N_6O_4OsP$	$C_{43}H_{33}N_6O_4OsP{\cdot}CH_3CN$
Mr	1003.04	903.89	959.98
T /K	243 (2)	293 (2)	296 (2)
Crystal syst	triclinic	Monoclinic	Triclinic
Space group	*P*-1	*I*2/*a*	*P*-1
a/Å	9.9670(6)	31.9083 (16)	7.541 (4)
b/Å	12.1691(6)	7.4874 (3)	16.410 (9)
c/Å	19.6141(10)	32.0080 (15)	17.308 (10)
α, (°)	99.995(2)	/	108.857 (10)
β, (°)	100.207(2)	94.356 (3)	93.523 (10)
γ, (°)	92.367(2)	/	91.599 (9)
V/ Å^3	2299.4(2)	7624.9 (6)	2020.3 (19)
Z	2	8	2
ρ_{calcd}, Mg m^{-3}	1.449	1.575	1.578
F(000)	1018	3576	956
Collected refl.	26919	29627	12353
Unique refl.	9982	6712	6801
Final *R* indices, *I* > 2σ(I)	R_1(obs) = 0.039 *w*R(all) = 0.098	R_1(obs) = 0.035 *w*R(all) = 0.092	R_1(obs) = 0.046 *w*R(all) = 0.182
GOF	1.019	0.73	1.18
No. of par.	541	488	526

Table S4. Cartesian coordinates for the optimized geometries of ^{3}INT1, ^{3}TS1, ^{3}INT2, ^{3}TS2, ^{3}INT3, ^{3}TS3, ^{3}INT4 at B3LYP-D3(BJ)/def2-TZVP level.

^{3}INT1

Os	-0.35893800	-0.98222300	-0.34836100
C	0.85112600	-1.42791500	-1.98431700
C	-1.06521200	-2.86525600	-0.31854100
C	-1.08905800	-0.66135100	1.56982800
N	1.55860600	-1.66499900	-2.87207500
N	-1.46553500	-3.95676100	-0.27896600
N	-1.46720300	-0.47814400	2.65097400
N	-1.70406600	-0.36731400	-1.26267000
C	0.03704900	2.23562700	-0.29266500
C	1.05766000	3.17132800	-0.14974500
C	0.86046500	4.53599800	-0.18800300
C	-0.45643000	4.94792600	-0.37724500
C	-1.50035700	4.02326100	-0.51392500
C	-1.27615100	2.65241300	-0.47387700
C	1.90087300	1.16086000	0.01414800

H	1.67438700	5.23716600	-0.07306100
H	-0.67690100	6.00609700	-0.41443400
H	-2.50883200	4.38822900	-0.65431500
H	-2.07216100	1.93509900	-0.58563000
C	4.27476600	0.65176100	0.15127600
C	5.32930100	-0.20231500	0.42460400
C	5.09177600	-1.52985300	0.82184200
C	3.80701300	-1.97884800	0.92892900
C	2.67810700	-1.15166700	0.63805800
C	2.95907100	0.20898300	0.24476400
H	4.48373500	1.66959400	-0.13667000
H	5.92798000	-2.17867700	1.03414400
H	3.60055300	-2.99633600	1.23140400
N	0.62185900	0.96929200	-0.19953100
O	2.23025100	2.48472300	0.04498900
O	1.50590300	-1.63877100	0.75528500
N	6.67493300	0.27743400	0.30545400
O	6.86517200	1.44345700	-0.05109200
O	7.60112000	-0.49563800	0.56525000
C	-4.85643500	1.99460500	-0.67256400
C	-4.67536300	0.63897100	-0.79714500
C	-4.49653000	-0.16891300	0.36223900
C	-4.49882800	0.46035900	1.63835600
C	-4.67887300	1.81889000	1.73621600
C	-4.86034900	2.59726100	0.58942600
H	-4.98353200	2.59850200	-1.55998800
H	-4.64862800	0.19317300	-1.77652900
H	-4.36211800	-0.12150900	2.53330900
H	-4.67935000	2.28575300	2.71102300
H	-4.99912600	3.66579900	0.67795500
N	-4.34030900	-1.50495900	0.24171200
C	-4.42890400	-2.15704900	-1.06198700
H	-4.38113800	-3.22878700	-0.91572000
H	-5.36386200	-1.89231600	-1.55234100
H	-3.57963300	-1.83488400	-1.66779400
C	-4.09956400	-2.37798000	1.38438000
H	-3.53409700	-1.86243100	2.15086200
H	-5.05743300	-2.72305000	1.78220700
H	-3.51904900	-3.22703100	1.03691100

^{3}TS1

Os	-0.15807300	-1.01194300	-0.28769900

C	1.03131700	-1.36079100	-1.96507300
C	-0.63684300	-2.98442200	-0.15361400
C	-1.16187700	-0.65480600	1.50105400
N	1.73054900	-1.53931500	-2.87399000
N	-0.92447800	-4.10451600	-0.06683700
N	-1.70774900	-0.45166800	2.50498200
N	-1.57709100	-0.60763700	-1.25828200
C	-0.00859400	2.16398700	-0.24857800
C	0.94388300	3.17446900	-0.15797300
C	0.64207800	4.51749700	-0.23228100
C	-0.70744900	4.82142500	-0.39785000
C	-1.68210300	3.81832100	-0.48055800
C	-1.35325900	2.47004100	-0.40793900
C	1.94490900	1.24159200	0.03017000
H	1.40224600	5.28182900	-0.16211200
H	-1.00856500	5.85827300	-0.45872600
H	-2.71915500	4.10120900	-0.59906600
H	-2.10101500	1.69386400	-0.46316000
C	4.34689500	0.82486600	0.16569200
C	5.41285200	-0.00156300	0.46906800
C	5.20188500	-1.31862900	0.91199600
C	3.92602200	-1.79358300	1.03764200
C	2.79275000	-0.99581300	0.71493600
C	3.04338900	0.35031700	0.27531700
H	4.53214800	1.83714000	-0.15721200
H	6.05166900	-1.94182900	1.14529100
H	3.74149900	-2.80321000	1.37739100
N	0.67709000	0.95087700	-0.14708600
O	2.17219400	2.57990000	0.02268900
O	1.61364700	-1.47955900	0.86058300
N	6.75483100	0.49956200	0.33429100
O	6.92090700	1.65410800	-0.06222600
O	7.69098100	-0.24767800	0.62224000
C	-5.25753700	2.06597400	-0.40758800
C	-4.77386500	0.81963400	-0.76141500
C	-4.86318900	-0.25368800	0.14260200
C	-5.44669200	-0.03867900	1.40149700
C	-5.92850500	1.21438200	1.73834200
C	-5.83700500	2.27417800	0.84125700
H	-5.17112900	2.88400600	-1.10984400
H	-4.30149900	0.69437200	-1.72253300
H	-5.53095200	-0.84553700	2.11197100
H	-6.37727200	1.36344900	2.71103000
H	-6.20883400	3.25257900	1.11300200

N	-4.36484500	-1.51124000	-0.19311800
C	-3.88509800	-1.78405100	-1.45954000
H	-3.65152500	-2.82835100	-1.61540500
H	-4.42802600	-1.31301300	-2.27190600
H	-2.73938100	-1.13413100	-1.49700300
C	-4.15648400	-2.50818700	0.85658200
H	-3.64213900	-2.05370400	1.70023400
H	-5.11715600	-2.91328300	1.17756600
H	-3.54222600	-3.30740900	0.45713100

^{3}INT2

Os	-0.11364300	-1.60142300	-0.23562700
C	-0.41847000	-1.99025800	-2.25343100
C	-0.15928600	-3.57959500	0.18627400
C	0.15624000	-1.14590600	1.77024700
N	-0.60553500	-2.18072400	-3.38275600
N	-0.16989900	-4.71349800	0.43265700
N	0.35066300	-0.85376900	2.87659300
N	-2.06364500	-1.48624700	-0.04326900
C	-0.68785300	1.46374300	-1.16055600
C	0.01058200	2.66714700	-1.19960700
C	-0.54138400	3.86969800	-1.58806000
C	-1.88016100	3.81961900	-1.96091000
C	-2.60169200	2.61911300	-1.93957700
C	-2.02282100	1.42286900	-1.54303200
C	1.35685900	1.09340700	-0.52201800
H	0.03117600	4.78555300	-1.60118200
H	-2.37522800	4.72943600	-2.27147900
H	-3.64296800	2.62632000	-2.22887300
H	-2.59000500	0.50917100	-1.51754600
C	3.68742100	1.38937600	0.14546700
C	4.93377200	0.87064100	0.43305400
C	5.17019800	-0.50910000	0.42434500
C	4.13651200	-1.36146700	0.13471700
C	2.83611900	-0.87887800	-0.14061300
C	2.62603200	0.53233700	-0.14357800
H	3.54049500	2.45730500	0.14238800
H	6.15634800	-0.88538000	0.64816000
H	4.28458600	-2.43183900	0.12375300
N	0.20531000	0.48818400	-0.70013500
O	1.30166900	2.41815400	-0.79786700
O	1.90475600	-1.75194200	-0.38836600

N	6.02117100	1.77961900	0.74386900
O	5.79183900	2.98552200	0.75587600
O	7.12600700	1.30037100	0.98165800
C	-4.67373000	2.96265300	1.02071500
C	-4.86082100	1.59300700	0.88533200
C	-3.84414700	0.68926300	1.23673800
C	-2.63630400	1.22202900	1.72200300
C	-2.46479400	2.59038200	1.84875400
C	-3.47713500	3.47831100	1.49984000
H	-5.47606300	3.63055000	0.73262900
H	-5.79969700	1.23441900	0.49291900
H	-1.81315500	0.57673100	1.98203100
H	-1.51532500	2.96475800	2.21072200
H	-3.33032200	4.54632700	1.58724400
N	-4.03494500	-0.68556900	1.10986500
C	-5.23059500	-1.17480100	0.44377200
H	-5.21712400	-2.26192800	0.45535800
H	-6.12818600	-0.84513800	0.96856700
H	-5.30402800	-0.83884500	-0.59752600
C	-2.90136300	-1.57224700	1.15306700
H	-2.61892000	-1.61178200	-0.88216300
H	-2.28297700	-1.36520000	2.02013200
H	-3.27683900	-2.59318300	1.25670400

^{3}TS2

Os	0.07767700	-1.44334700	-0.28796200
C	-0.33893900	-1.46487300	-2.32497000
C	-0.03283300	-3.45706000	-0.18939200
C	0.60211300	-1.34991700	1.72608400
N	-0.56590900	-1.45401800	-3.46388700
N	-0.07624700	-4.61701100	-0.13758800
N	0.91093600	-1.26460600	2.84159100
N	-1.74019500	-1.21791700	0.22878300
C	-0.47171400	1.72866000	-0.61055000
C	0.23132400	2.92181600	-0.46514000
C	-0.34635100	4.16997500	-0.56285500
C	-1.71292300	4.18016600	-0.83246500
C	-2.43546100	2.99260100	-1.00615600
C	-1.82869700	1.74722600	-0.90620800
C	1.61127900	1.24797800	-0.22762600
H	0.22577400	5.07830300	-0.44165100

H	-2.22476300	5.12894900	-0.91831400
H	-3.49315500	3.04376500	-1.22327500
H	-2.37678000	0.83297200	-1.05862300
C	3.99085000	1.41704400	0.28016000
C	5.25331000	0.86218600	0.36837900
C	5.46486100	-0.49857500	0.10238400
C	4.40016100	-1.28906500	-0.23564300
C	3.07963600	-0.77442500	-0.31670900
C	2.89726000	0.62442200	-0.06117300
H	3.85860800	2.46983900	0.47119300
H	6.46087400	-0.90787400	0.17330300
H	4.53424700	-2.34207600	-0.43927200
N	0.44264900	0.68821800	-0.42555200
O	1.54883000	2.60573800	-0.23187700
O	2.12701200	-1.58771300	-0.62761800
N	6.36913600	1.70117300	0.73195000
O	6.16219000	2.89037700	0.97106900
O	7.48799500	1.19209500	0.78839300
C	-5.48141000	2.26470600	1.45316100
C	-4.72905900	1.12150800	1.69394300
C	-4.59876600	0.16635600	0.69306900
C	-5.22263200	0.33897900	-0.53594700
C	-5.97757500	1.48196800	-0.76843000
C	-6.10574900	2.44721100	0.22422200
H	-5.57799400	3.01265000	2.22866000
H	-4.24819900	0.97982300	2.65225800
H	-5.10623000	-0.41285000	-1.30538700
H	-6.45538800	1.62102500	-1.72884400
H	-6.68654600	3.34087900	0.03924100
N	-3.81185200	-1.03060300	0.89844100
C	-4.56506600	-2.14827200	1.50170200
H	-3.93195000	-3.03328700	1.50531300
H	-4.86275700	-1.90120700	2.52127300
H	-5.45072600	-2.33614500	0.90012400
C	-2.41225900	-0.83953200	1.44292700
H	-3.03631800	-1.35843400	-0.09992700
H	-2.23990700	0.19409300	1.74668500
H	-2.22825800	-1.50320100	2.28986200

^{3}INT3

Os	0.34574900	-1.57429800	-0.47177000
C	0.00578600	-1.31540600	1.55431500

C	0.55275600	-3.56003100	-0.17673500
C	0.51338200	-1.82008000	-2.53134000
N	-0.08974400	-1.14809500	2.70211100
N	0.66388000	-4.70377600	0.00312100
N	0.57847700	-1.94317500	-3.68494700
N	2.17333800	-1.29406700	-0.18394700
C	0.71917000	1.50956100	-1.33206800
C	-0.02673800	2.68477300	-1.34361600
C	0.46474000	3.90016300	-1.77011500
C	1.78555400	3.89097900	-2.21101600
C	2.55068600	2.71773300	-2.21257900
C	2.03546400	1.50512400	-1.77359000
C	-1.27350200	1.05547100	-0.59424800
H	-0.13665300	4.79761200	-1.76386000
H	2.23072000	4.81382700	-2.55715500
H	3.57521500	2.76105700	-2.55611000
H	2.62050900	0.59906200	-1.75306300
C	-3.54093500	1.24522200	0.27900600
C	-4.75677000	0.68959700	0.63428000
C	-4.96666200	-0.69660900	0.54741900
C	-3.95126300	-1.50495800	0.11838200
C	-2.67088700	-0.99094200	-0.23348400
C	-2.49414100	0.43510200	-0.15076600
H	-3.41011900	2.31424000	0.33390600
H	-5.92514500	-1.10795400	0.82490600
H	-4.08899500	-2.57488700	0.04593600
N	-0.10888400	0.50377100	-0.82836400
O	-1.28609700	2.38796200	-0.87481700
O	-1.76477800	-1.81208600	-0.62685600
N	-5.81803900	1.54569400	1.08928700
O	-5.61196100	2.75836300	1.16882600
O	-6.89961600	1.03352900	1.38415500
C	4.31899700	2.69620600	0.92529800
C	4.24270400	1.34598000	1.23662000
C	3.04034900	0.83047200	1.69750300
C	1.92105500	1.63147400	1.84958100
C	2.00820200	2.98180900	1.53283900
C	3.20389000	3.51433100	1.07151600
H	5.25034900	3.10590100	0.55902800
H	5.11152200	0.71443300	1.11541100
H	0.99176000	1.20467000	2.19879900
H	1.13477100	3.61035500	1.63731300
H	3.26596900	4.56271700	0.81447100
N	2.93875200	-0.59249300	2.03977400

C	3.84454500	-0.99956000	3.15314500
H	3.61782100	-2.02726900	3.42223000
H	4.87615600	-0.92025500	2.82397800
H	3.67123500	-0.34122000	3.99925800
C	3.12229500	-1.53605800	0.78454000
H	1.96946900	-0.76393200	2.34337900
H	4.14339900	-1.33843400	0.44949600
H	3.06818800	-2.54255900	1.21757900

^{3}TS3

Os	-0.31905500	-1.60484900	0.45966800
C	-0.02154100	-1.31818500	-1.57410900
C	-0.50532100	-3.58825600	0.12838600
C	-0.43807300	-1.88668200	2.51866600
N	0.07517400	-1.14692700	-2.71946100
N	-0.60696200	-4.72884200	-0.06948800
N	-0.47807000	-2.03120000	3.67017000
N	-2.15004400	-1.33665100	0.20948000
C	-0.72363000	1.45749400	1.38440000
C	0.01086300	2.63915400	1.41965900
C	-0.48905500	3.83985500	1.87655700
C	-1.80792000	3.80897200	2.32103000
C	-2.56298500	2.62934500	2.29737800
C	-2.03847100	1.43154300	1.83021800
C	1.26750900	1.04434300	0.61662000
H	0.10421800	4.74259500	1.88706600
H	-2.26020100	4.71969300	2.68920700
H	-3.58650400	2.65549100	2.64554600
H	-2.61651600	0.52159300	1.79519200
C	3.52432000	1.27800900	-0.27795600
C	4.73755400	0.73885600	-0.66422100
C	4.95650400	-0.64699500	-0.62092200
C	3.95061800	-1.47417800	-0.20263000
C	2.67545900	-0.97554600	0.17950500
C	2.48836700	0.44831800	0.14155800
H	3.38632300	2.34727000	-0.30082200
H	5.91341500	-1.04456500	-0.92270100
H	4.09459700	-2.54489600	-0.16346300
N	0.11166600	0.47344000	0.84935600
O	1.26885200	2.36715400	0.93146200
O	1.77559400	-1.81364500	0.56208200
N	5.78987300	1.61509900	-1.10874400
O	5.57560400	2.82735000	-1.14837800

O	6.86847700	1.11716700	-1.43349700
C	-4.29606800	2.81968500	-0.97571200
C	-4.28001400	1.48678300	-1.36155400
C	-3.08475600	0.91062200	-1.78276700
C	-1.91305700	1.65880900	-1.80814400
C	-1.94041800	2.99196700	-1.42116300
C	-3.12892200	3.57569600	-1.00376700
H	-5.22424200	3.26586000	-0.64446600
H	-5.19204000	0.90742000	-1.33000300
H	-0.98941200	1.19688000	-2.12652900
H	-1.02634000	3.56956500	-1.43778300
H	-3.14535900	4.61058000	-0.69094500
N	-3.03467700	-0.47317300	-2.15282200
C	-4.04649100	-0.94042700	-3.11617600
H	-3.81707300	-1.96779800	-3.38717300
H	-5.03484000	-0.90378200	-2.66526400
H	-4.03298500	-0.31504300	-4.00778900
C	-3.13839800	-1.57869600	-0.62634000
H	-2.09672200	-0.70179700	-2.48493100
H	-4.13573500	-1.25582100	-0.32593800
H	-3.12581900	-2.52407100	-1.17784000

^{3}INT4

Os	-2.06718900	-0.89834000	-0.06033100
C	-1.49991400	-0.52825400	-2.02543100
C	-2.94482400	-2.63423200	-0.61381000
C	-2.68034600	-1.19720300	1.90425300
N	-1.14465800	-0.28272400	-3.10282200
N	-3.45142600	-3.62883200	-0.93091900
N	-3.01194700	-1.34549700	3.00607100
N	-3.72337300	0.01546100	-0.40367400
C	-1.32482300	2.15584700	0.67897000
C	-0.21772600	2.87858700	1.11720300
C	-0.21986800	4.23895000	1.33650400
C	-1.42656200	4.88500800	1.08652100
C	-2.55436900	4.18137100	0.64343900
C	-2.52752600	2.80874800	0.43273300
C	0.34717700	0.78509000	0.90737100
H	0.66106700	4.76569500	1.67309900
H	-1.49344600	5.95381600	1.23631300
H	-3.47231200	4.72282800	0.45974000
H	-3.39416300	2.26708300	0.09095800

C	2.58459300	-0.09667500	1.29043500
C	3.48038200	-1.14271800	1.31220000
C	3.08532700	-2.45209500	1.01033300
C	1.77999900	-2.69302600	0.67843600
C	0.82769400	-1.64712300	0.62139800
C	1.25020500	-0.32721400	0.95039300
H	2.92251300	0.89964400	1.51969100
H	3.81151400	-3.24947200	1.03375300
H	1.44159200	-3.68926400	0.43224000
N	-0.92342100	0.81866000	0.56919600
O	0.82690500	2.00171000	1.26271700
O	-0.38044300	-1.95807000	0.26148400
N	4.86651300	-0.87355000	1.64010300
O	5.18307300	0.26796000	1.95958900
O	5.66576700	-1.80385400	1.58181200
C	4.80910200	0.95110200	-1.46678900
C	3.60682300	1.64219500	-1.56672700
C	2.42822400	0.96809700	-1.92414500
C	2.50563400	-0.41269300	-2.18869200
C	3.70991500	-1.08388100	-2.08876900
C	4.87679400	-0.41218500	-1.72365800
H	5.70211100	1.49098800	-1.17754900
H	3.58271100	2.70170100	-1.35571700
H	1.60264900	-0.94504900	-2.45854500
H	3.73844400	-2.14816100	-2.28576000
H	5.81414000	-0.94450900	-1.63588400
N	1.20809200	1.60101100	-1.97196500
C	1.08920200	3.04069500	-2.04837700
H	0.03438800	3.29649800	-2.12512100
H	1.48144300	3.51714100	-1.14886700
H	1.61715900	3.46401000	-2.91195500
C	-4.91677000	-0.06014300	-0.76582800
H	0.46694900	1.07611600	-2.41464500
H	-5.54980800	0.82896300	-0.81565700
H	-5.37151200	-1.01736700	-1.04545100