Supplementary information

Oxidative C-O bond cleavage of dihydroxybenzenes and conversion of coordinated cyanide to carbon monoxide by a luminescent Os(VI) cyanonitrido complex

Jing Xiang,*[a][b] Jiang Zhu,[b]† Miaomiao Zhou,[c]† Lu-Lu Liu,[a] Li-Xin Wang,[a] Min Peng,[a] Bi-Shun Hou,[a] Shek-Man Yiu,[c] Wai-Pong To,[b] Chi-Ming Che,*[b] Kai-Chung Lau,*[c] and Tai-Chu Lau*[c]

[a] College of Chemistry and Environmental Engineering, Yangtze University, Jingzhou 434020, Hubei, China.

[b] State Key Laboratory of Synthetic Chemistry and Department of Chemistry, The University of Hong Kong, Pokfulam Rd., Hong Kong, China.

[c] Department of Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong, China.

Table of Content

Experimental section

Materials: 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. 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. ^{1}H 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. Steady-state emission spectra of samples were recorded on a Horiba Fluorolog-3 spectrophotometer. Solutions for photophysical studies were degassed by using a high vacuum line in a two-compartment cell with five freeze-pump-thaw cycles. The emission lifetime measurements were performed on a Quanta Ray GCR 150-10 pulsed Nd:YAG laser system. Errors for λ values (±1 nm), τ (±10 %), and Φ (± 10 %) were estimated. The measurement of nanosecond time-resolved absorption (ns-TA) was performed on a LP920-KS Laser Flash Photolysis spectrophotometer (Edinburgh Instrument Ltd.) equipped with a Q-switched Nd:YAG laser at room temperature. The transient absorption spectra were recorded with the pump pulse wavelength of 355 nm. The preparation of samples is similar to that for photophysical study. A 450-Watt Xenon arc lamp (probe source) was used for the measurement of ns-TA.

X-ray crystallography. Measurements were collected on an Oxford CCD diffractometer using graphite-monochromated MoK_a radiation (λ = 0.71073 Å) for **1** and **5**. 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 solved by using direct methods with the SHELXS-97 program for

1 and SHELXT-2014 for **5**.[1] The positions of the other non-hydrogen atoms were located after refinement by full matrix least-squares using the SHELXL-2014 for **1** and SHELXL-2016 for **5**, respectively. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated by the program SHELXL-2014 **(1)** and SHELXL-2016 **(5)**.[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 2151718-2151719 for **1** and **5**, respectively.

Computational details

All the calculations were performed with Gaussian 16[3] package. Using implicit polarizable continuum model (PCM)[4] with acetonitrile as solvent, geometric structural optimizations and frequency calculations were conducted with B3LYP-D3(BJ)/def2-SVPD method at 298.15K.[5] Optimized geometries were verified by frequency computations as minima (zero imaginary frequency) or transition state (a single imaginary frequency) at the same level of theory. The transition states (TSs) were also confirmed by examining the normal mode of imaginary vibrational frequency and by intrinsic reaction coordinate (IRC) calculations.[6]

Synthesis of $(PPh_4)[Os^{II}(L)(CN)_2(CO)(o\text{-}NH{=}Ph{=}O)]$ (PPh_4)1, $(^nBu_4N)_2[Os^{II}(L)(CN)_3(NH{=}Ph(OH){=}O)]$ $(^nBu_4N)_2$2, $(PPh_4)[Os^{IV}(L)(CN)_3(N{=}Ph(OH){=}O)]$ (PPh_4)3.

10 Pyrex tubes (15 × 2 cm) each containing **OsN** (5 mg, 5.7 μmol) and catechol (12.5 mg, 114 μmol) in 15 ml MeCN were prepared. Each tube was sealed by a rubber septum, degassed with Ar for 30 min, and then irradiated with blue LED light for 12 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 **OsN)** was eluted by CH_2Cl_2/acetone (v:v, 10:1). The second blue band,

which contains **(PPh$_4$)1** was eluted by CH_2Cl_2/acetone (v:v, 5:1). The third greenish yellow band, which contains compound **(PPh$_4$)3**, was eluted by CH_2Cl_2/acetone (v:v, 5:1~5:3). The fourth blue band, **(^{n}Bu$_4$N)$_2$2**, was eluted by CH_2Cl_2/acetone/MeOH (v:v:v, 5:5:2).

The blue solid obtained from evaporation of the solvent from the second blue band was collected and recrystallization by slow diffusion of diethyl ether into a CH_2Cl_2 solution to give **(PPh$_4$)1.** Yield: 8.3 mg, 15%. Selected IR (KBr disc, cm^{-1}): *v*(N-H) 3168, *v*(C≡N) 2132, 2115; *v*(C≡O) 1961; ESI/MS (-ve mode): *m/z* 634 [*M*]$^-$. Calcd for $C_{46}H_{32}N_5O_6OsP$: C, 56.84; H, 3.32; N, 7.21%. Found: C, 56.88; H, 3.40; N, 7.18%. UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]): 269 (17920), 276 (17760), 293 (17260), 391 (11830), 637 (11090), 696 sh (14010). ^{1}H NMR (600 MHz, $CDCl_3$): δ 14.95 (s, 1H, N-H), 8.94 (d, *J* = 2.9 Hz, 1H, Ar-H), 7.93 (dd, *J* = 9.4, 2.9 Hz, 1H, Ar-H), 7.86 (t, *J* = 7.3 Hz, 4H, PPh$_4$-H), 7.72 (td, *J* = 7.8, 3.5 Hz, 8H, PPh$_4$-H), 7.63 – 7.58 (m, 9H, PPh$_4$-H and Ar-H), 7.50 (d, *J* = 9.3 Hz, 1H, Ar-H), 7.38 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.29 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.18 (t, *J* = 7.8 Hz, 1H, Ar-H), 6.83 (dd, *J* = 8.6, 6.6 Hz, 2H, Ar-H), 6.61 (d, J = 9.4 Hz, 1H, Ar-H). ^{13}C NMR (151 MHz, $CDCl_3$, δ): 194.78 (carbonyl C), 178.29, 177.45, 177.14, 167.52, 159.50, 149.92, 141.41, 141.16, 136.70, 135.74 (PPh$_4$ C), 134.51 (PPh$_4$ C), 130.70 (PPh$_4$ C), 129.25, 128.51, 128.22, 127.82, 126.65, 126.23, 126.18, 123.77, 118.31, 117.82, 117.22, 112.54, 115.18, 111.08.

(^{n}Bu$_4$N)$_2$2 was obtained from the fourth blue band. Yield: 14.2 mg, 22%. ESI/MS (-ve mode): *m/z* 324.1 [*M*]$^{2-}$ and 647.1 [*M*-H]$^-$. Selected IR (KBr disc, cm^{-1}): *v*(C≡N) 2134, 2110; *v*(C=N) 1625; *v*(N=O) 1650. Calcd for $C_{54}H_{84}N_8O_6Os$: C, 57.32; H, 7.48; N, 9.90%. Found: C, 57.30; H, 7.52; N, 9.81%. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε /M^{-1} cm^{-1}): 272 (12530), 335 (9310), 585 (28620). ^{1}H NMR (d^6-acetone): 9.08 (d, *J* = 2.9 Hz, 1H), 8.51 (dd, *J* = 9.6, 2.6 Hz, 1H), 8.38 (dd, *J* = 9.2, 2.9 Hz, 1H), 8.05 – 8.01 (m, 1H), 7.95 – 7.92 (m, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.27 (d, *J* = 9.3 Hz, 1H), 5.20 (d, *J* = 9.6 Hz, 1H); 3.39 (dd, *J* = 16.5, 7.8 Hz, 16H, -CH_2-), 1.88 – 1.67 (m, 16H, -CH_2-), 1.41 (dt, *J* = 14.7, 7.4 Hz, 16H, -CH_2-), 0.96 (t, *J* = 7.4 Hz, 24H, -CH_3).

The third green band gave **(PPh$_4$)3**. Yield: 22.4 mg, 40%. ESI/MS (-ve mode): *m/z* 647

[*M*]$^-$. Selected IR (KBr disc, cm^{-1}): *v*(C≡N) 2130, 2109; *v*(C=N) 1623; *v*(C=O) 1648. Calcd for $C_{46}H_{31}N_6O_6OsP$: C, 56.09; H, 3.17; N, 8.53%. Found: C, 56.12; H, 3.22; N, 8.47%. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε /M^{-1} cm^{-1}): 269 (19690), 277 (20150), 287sh (17200), 332 (14570), 453 (19620). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, *J* = 2.8 Hz, 1H), 8.37 (dd, *J* = 9.6, 2.5 Hz, 1H), 8.13 (dd, *J* = 9.3, 2.9 Hz, 1H), 7.91 (d, *J* = 6.8 Hz, 4H), 7.83-7.75 (m, 8H), 7.76 – 7.72 (m, 2H), 7.71 (d, *J* = 2.5 Hz, 1H), 7.65 (dd, *J* = 12.9, 7.6 Hz, 8H), 7.59 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.02 (d, *J* = 9.3 Hz, 1H), 6.98 (s, 1H).

The fourth blue band was dissolved in acetone/H_2O in the presence of (^{n}Bu$_4$N)Cl and slow evaporation of the blue solution under Ar give blue microcrystalline solid.

Synthesis of (^{n}Bu$_4$N)[Os^{II}(L)(CN)$_3$(*p*-NH=PhOH)] (^{n}Bu$_4$N)5, (PPh$_4$)[Os^{IV}(L)(CN)$_3$(*p*-N=Ph=O)] (PPh$_4$)6 and [Os^{II}(L)(CN)$_2$(CO)(*p*-NH=PhOH)] 7.

10 Pyrex tubes (15 × 2 cm) each containing **OsN** (5 mg, 5.7 μmol) and hydroquinone (12.5 mg, 114 μmol) in 15 ml MeCN were prepared. Each tube was sealed by a rubber septum, degassed with Ar for 30 min, and then irradiated with blue LED light for 12 h, whereby the light-yellow solution turned red. 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 **OsN)** was eluted by CH_2Cl_2/acetone (v:v, 10:1). The second blue band, which contains compound **7**, was eluted by CH_2Cl_2/acetone (v:v, 10:2). The third yellow band, which contains compound **(PPh$_4$)6**, was eluted by CH_2Cl_2/acetone (v:v, 5:3) and the fourth red band, which contains compound **(^{n}Bu$_4$N)5**, was eluted by CH_2Cl_2/acetone/MeOH (v:v, 5:5:1).

(^{n}Bu$_4$N)5. The fourth red band was dissolved in acetone/H_2O in the presence of (^{n}Bu$_4$N)Cl and slow evaporation of the blue solution under Ar give red microcrystalline solid. Yield: 24.9 mg, 50%. Crystals suitable for X-ray determination were obtained by slow diffusion of diethyl ether into a MeOH solution of **(^{n}Bu$_4$N)5**. Selected IR (KBr disc, cm^{-1}): *v*(C≡N) 2127 and 2107; *v*(N=O) 1307. ESI/MS (-ve mode): *m/z* 633 [*M*]$^-$.

Elemental analysis: Calcd for $C_{38}H_{49}N_7O_5Os$: C, 52.22; H, 5.65; N, 11.22%. Found: C, 52.32; H, 5.70; N, 11.18%. UV/vis (CH_2Cl_2): λ_{max} [nm] (ε / M^{-1} cm^{-1}]): 229 (10080), 284sh (10320), 291 (10690), 356 (8650), 432 (4850), 535 (23330). ^{1}H NMR (400 MHz, d^6-acetone): δ 9.03 (d, J = 2.9 Hz, 1H, Ar-H), 8.23 (dd, J = 9.4, 2.9 Hz, 1H, Ar-H), 8.12 (dd, *J* = 9.1, 4.9 Hz, 2H, Ar-H), 7.91 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.67 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.58 (dd, *J* = 12.4, 4.4 Hz, 1H, Ar-H), 7.51 (t, *J* = 7.7 Hz, 1H, Ar-H), 7.28 (d, *J* = 9.4 Hz, 1H, Ar-H), 6.95 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.44 (dd, *J* = 16.5, 7.8 Hz, 8H, -CH_2-), 1.86 – 1.77 (m, 8H, -CH_2-), 1.43 (dt, *J* = 14.7, 7.4 Hz, 8H, -CH_2-), 0.98 (t, *J* = 7.4 Hz, 12H, -CH_3). ^{13}C NMR (151 MHz, $CDCl_3$, δ): 210.42, 209.03 (-CN), 183.36, 172.40, 160.37, 150.27, 145.04, 141.74, 137.37, 128.06, 126.53, 126.24, 125.39, 122.85, 119.51, 111.35, 110.21, 68.40, 58.53, 23.53, 19.49, 15.93, 12.49.

(PPh$_4$)6. This compound was reported recently by us and the yellow band solid was collected with a yield: 5.5 mg, 10%.

7. The second band was collected as neutral blue complex. Yield: 0.4 mg, 1%. Selected IR (KBr disc, cm^{-1}): *v*(N-H) 3155, *v*(C≡N) 2130, 2114; *v*(C≡O) 1960; ESI/MS (-ve mode): *m/z* 634 [*M* - H]$^-$. Elemental analysis: Calcd for $C_{22}H_{13}N_5O_6Os$: C, 41.70; H, 2.07; N, 11.05%. Found: C, 42.12; H, 2.61; N, 11.58%. UV/vis (CH_2Cl_2): λ_{max}[nm] (ε / M^{-1} cm^{-1}): 231 (14710), 293 (10210), 396 (6020), 539 (4080), 666 (7500). ^{1}H NMR (400 MHz, d^6-acetone): 8.92 (d, *J* = 3.0 Hz, 1H), 8.09 (dd, *J* = 9.5, 3.0 Hz, 1H), 8.05 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.88 (dd, *J* = 10.7, 5.3 Hz, 2H), 7.68 (dd, *J* = 10.0, 2.9 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 8.1 Hz, 1H).

Reference:

[1] a) G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, Release 97-2, University of Göttingen, Göttingen, Germany, 1997. b) G. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Crystallographica Section A*, 2015, **71**, 3-8.

[2] G. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallographica Section C*, 2015, **71**, 3-8.

[3] Gaussian 16, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; and Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

[4] S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* 1981, **55**,117–129.

[5] a) A. D. Becke, J. Chem. Phys., 1993, 98, 5648 - 5652; b) A. Schafer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* 1992, **97**, 2571 - 2577; c) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 1372 - 1377; d) A. Schafer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* 1994, **100**, 5829 - 5835; e) S. Grimme, S. Ehrlich and L. J. Goerigk, *Comput. Chem.* 2011, **32**, 1456 – 1465; f) L. Goerigk, S. Grimme, *Phys. Chem. Chem. Phys.* 2011, **13**, 6670-6688; g) S. Ehrlich, J. Moellmann, S. Grimme, *Acc. Chem. Res.* 2013, **46**, 916–926.

[6] C. Gonzalez and H. B. Gonzalez, *J. Phys. Chem.* 1990, **94**, 5523 - 5527.

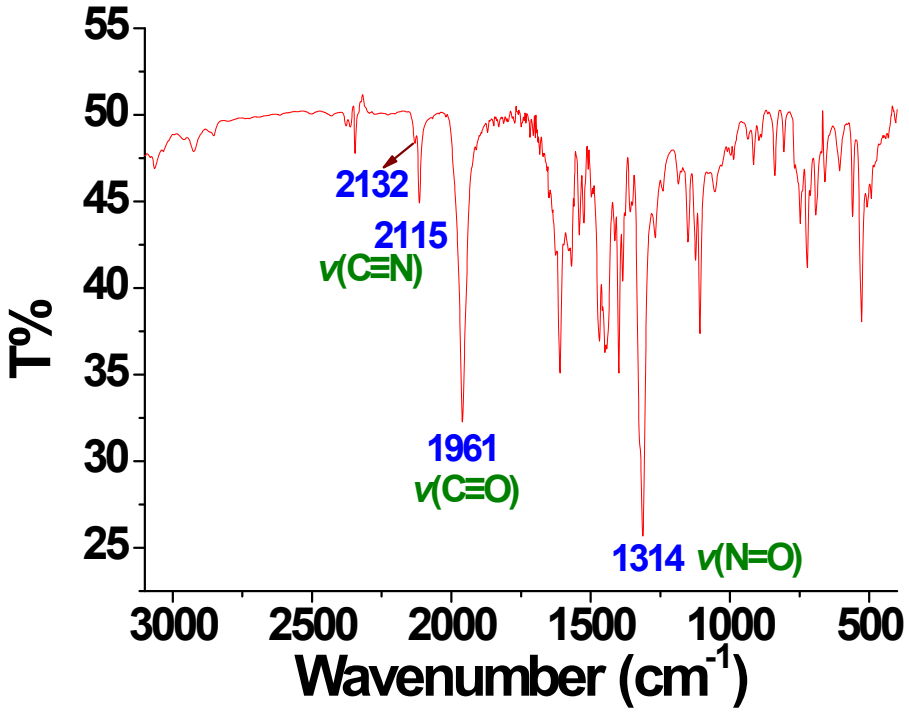


Figure S1. IR spectrum of **(PPh$_4$)1**.

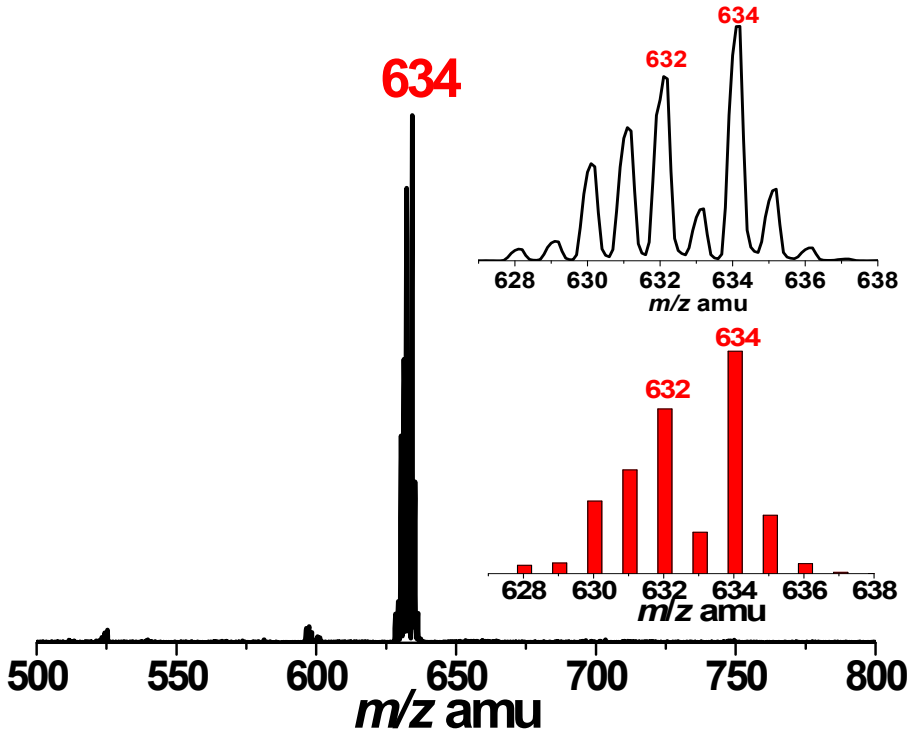


Figure S2. ESI/MS (-ve mode) of **(PPh$_4$)1** in MeOH.

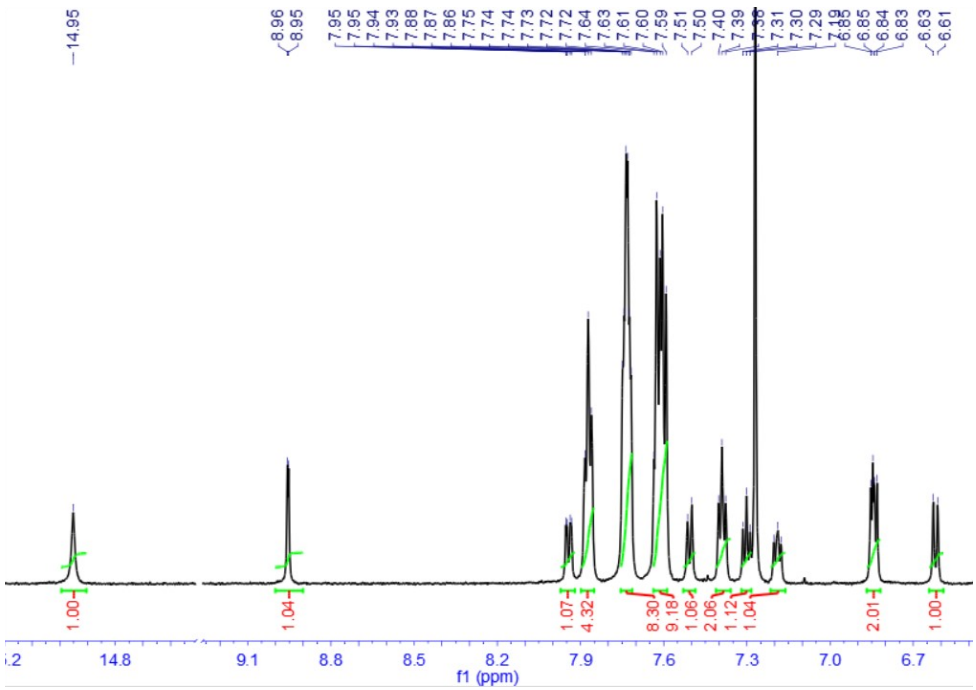


Figure S3. ^{1}H NMR spectrum of **(PPh$_4$)1** in $CDCl_3$.

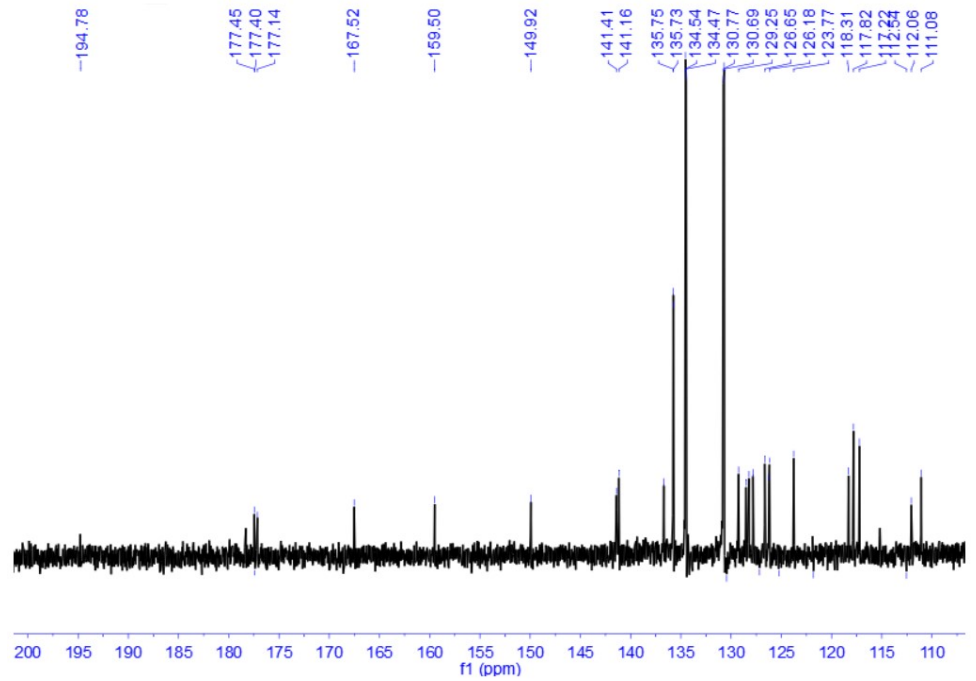
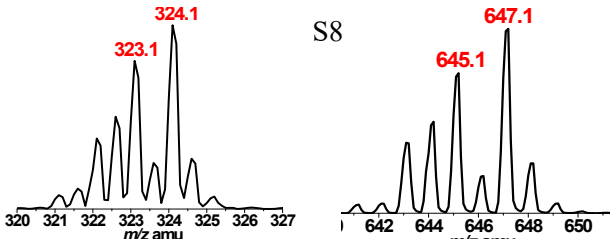


Figure S4. ^{13}C NMR spectrum of **(PPh$_4$)1** in $CDCl_3$.



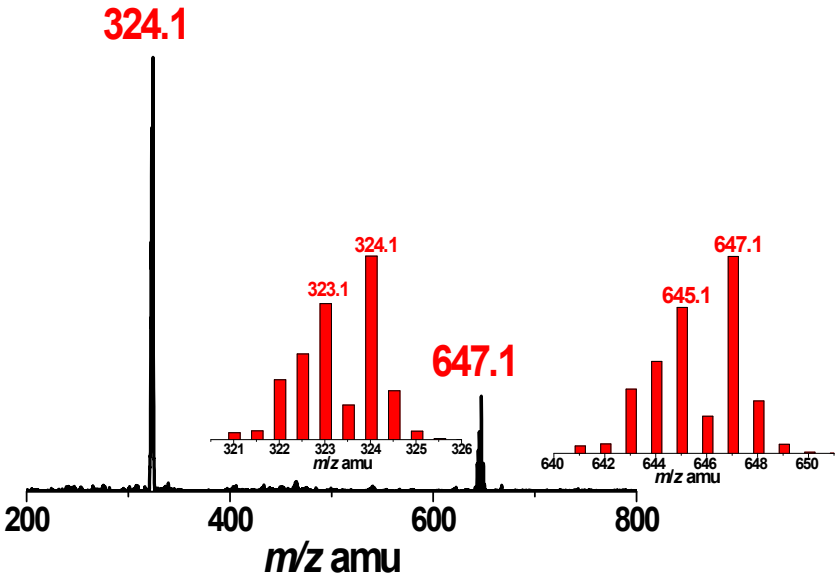


Figure S5. ESI/MS (-ve mode) of **(^{n}Bu$_4$N)$_2$2** in MeOH.

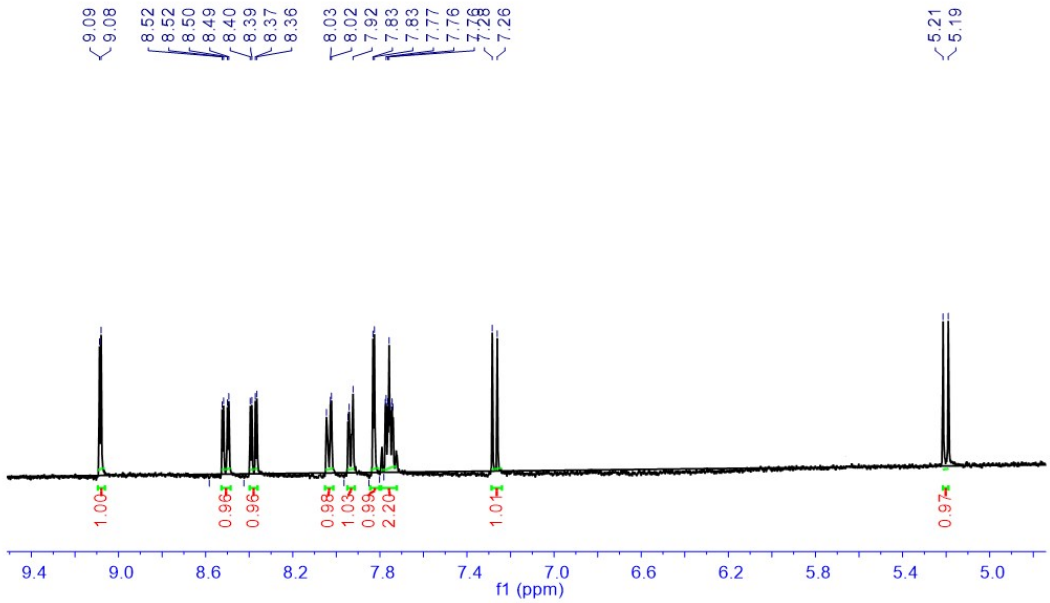


Figure S6. ^{1}H NMR of **(^{n}Bu$_4$N)$_2$2** in d^6-acetone.

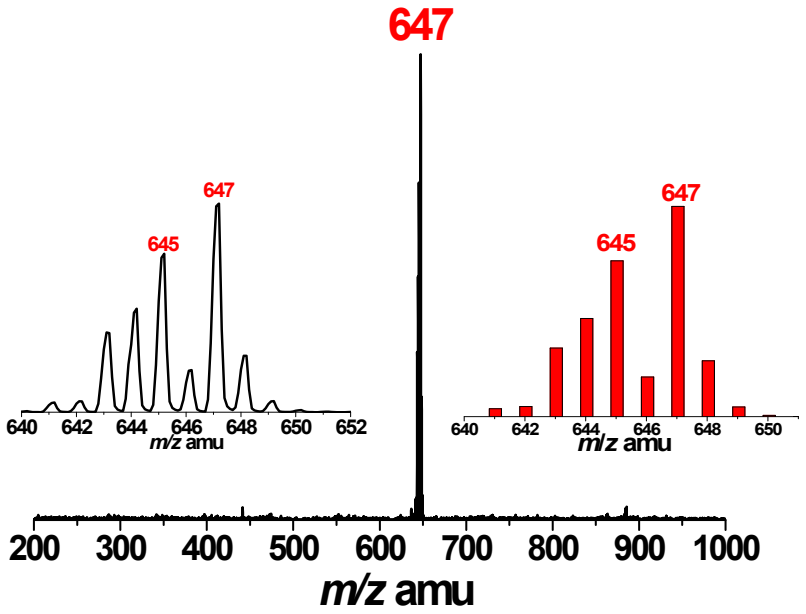


Figure S7. ESI/MS (-ve mode) of **(PPh$_4$)3** in MeOH.

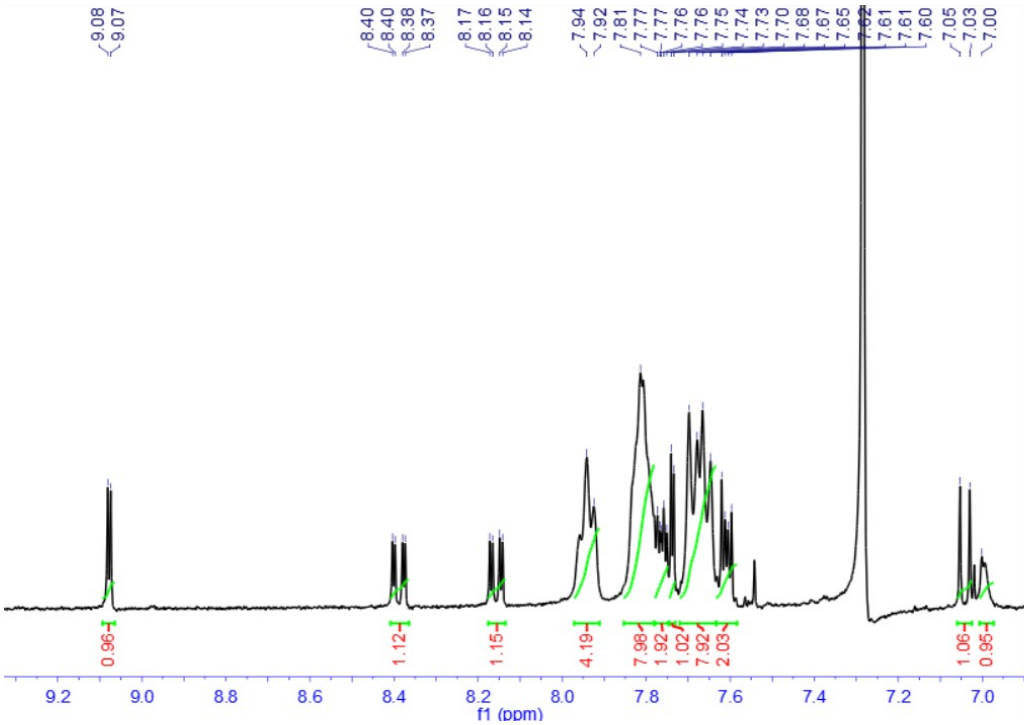


Figure S8. ^{1}H NMR of **(PPh$_4$)3** in $CDCl_3$.

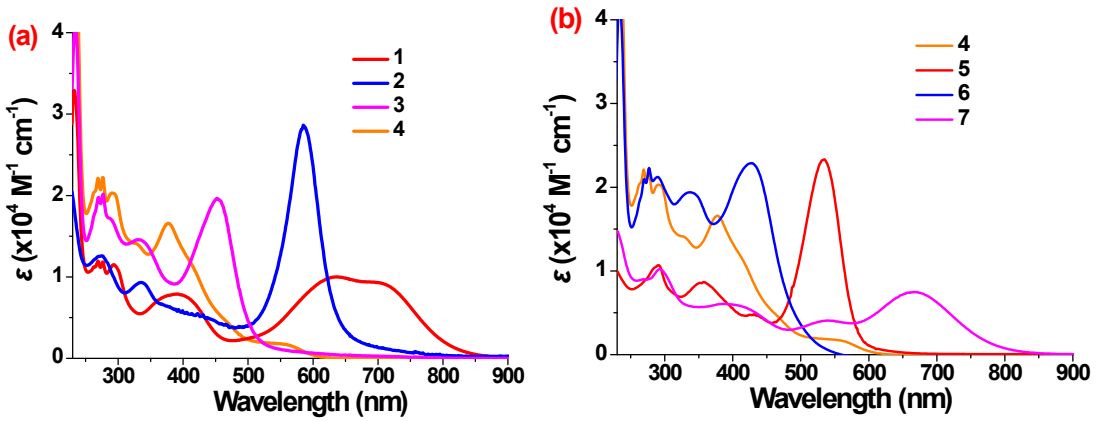


Figure S9. UV/vis spectra (a) for **1-4** and (b) for **4-7** in CH_2Cl_2.

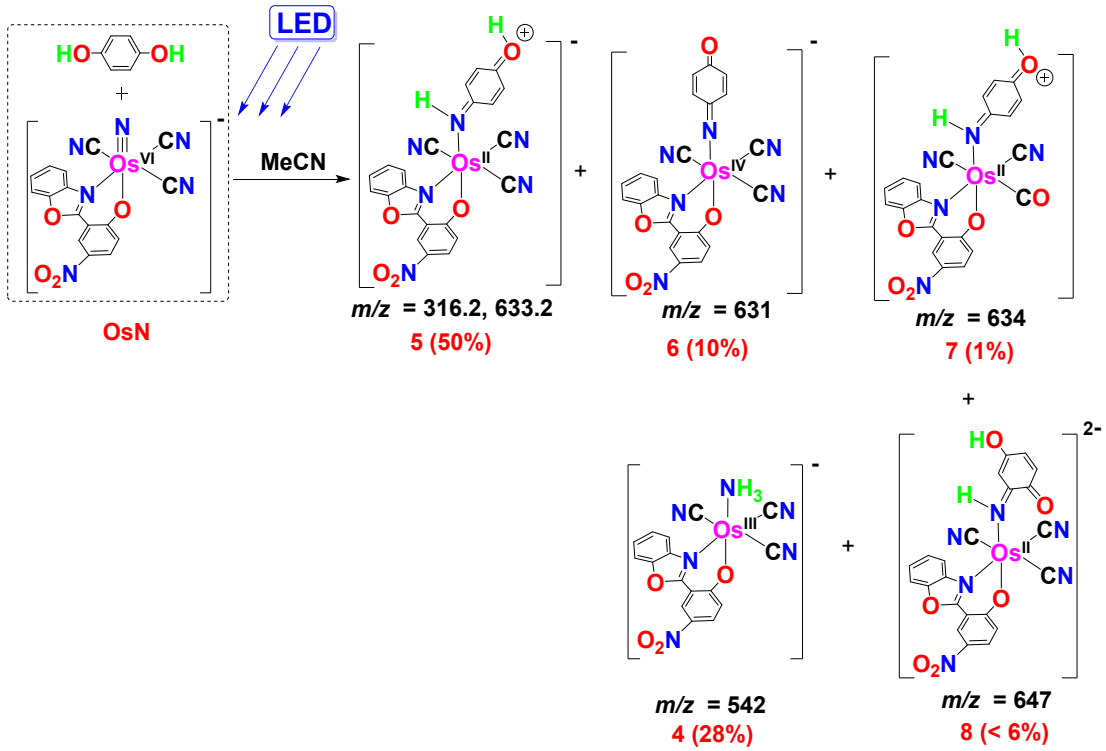


Figure S10. The photoreaction of **OsN** with H_2Q.

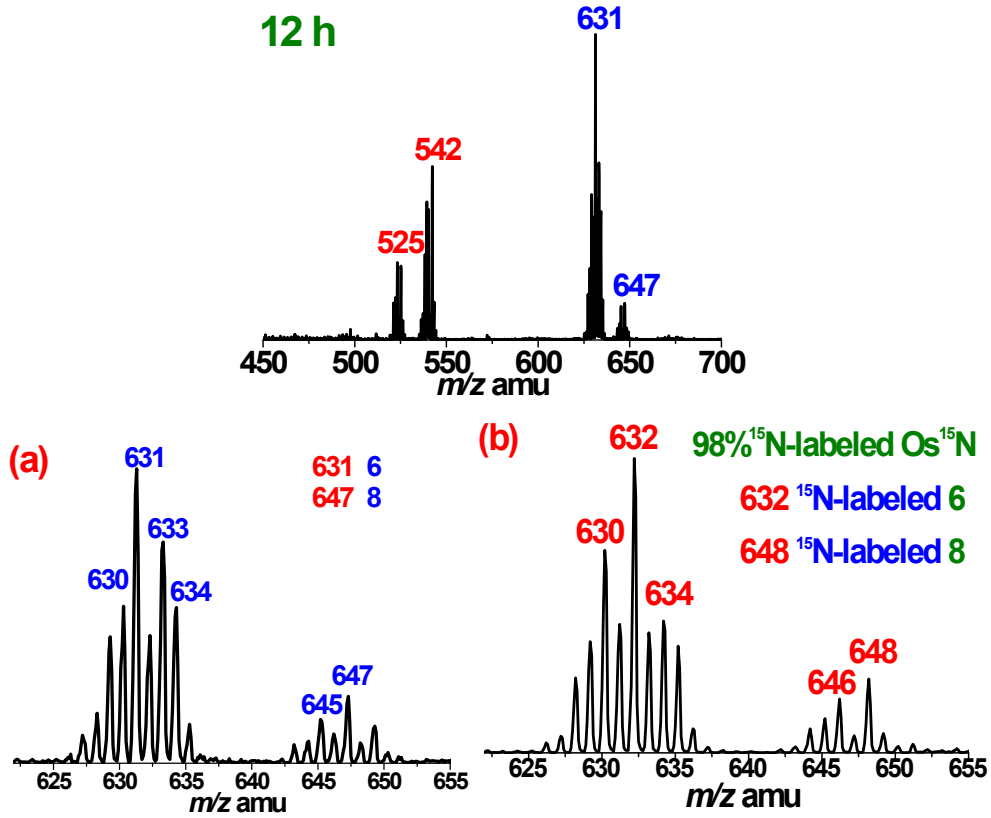


Figure S11. ESI/MS for the photoreaction of **OsN** with H_2Q. (a) The isotopic distributions of *m/z* 631 and 647; (b) ESI/MS for the photoreaction of 98% ^{15}N-labeled **Os^{15}N** with H_2Q.

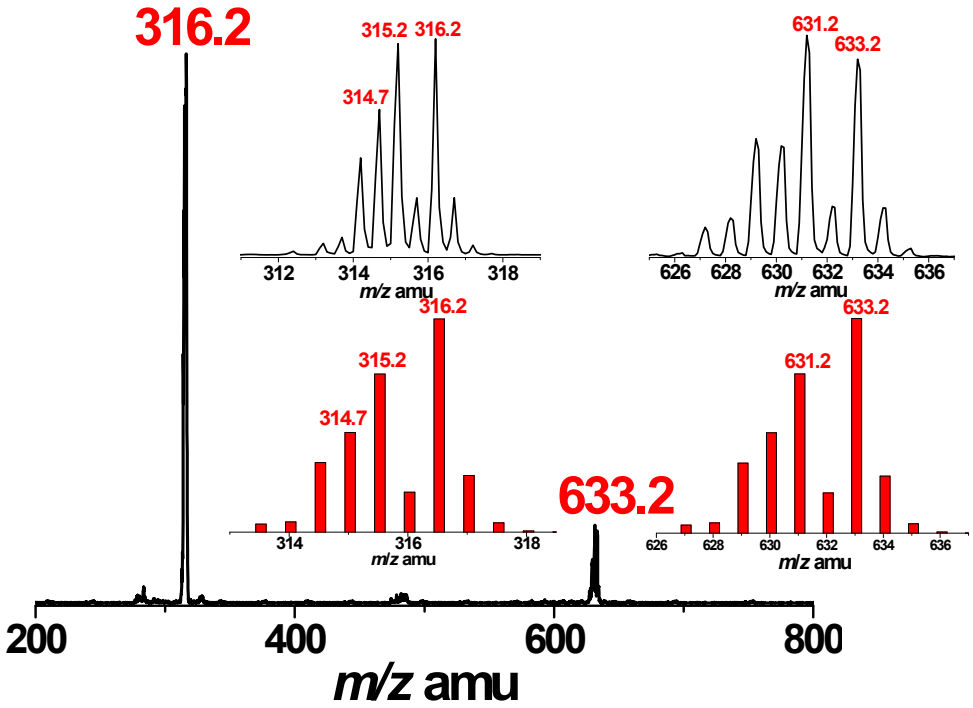


Figure S12. ESI/MS (-ve mode) of **(^{n}Bu$_4$N)5** in MeOH.

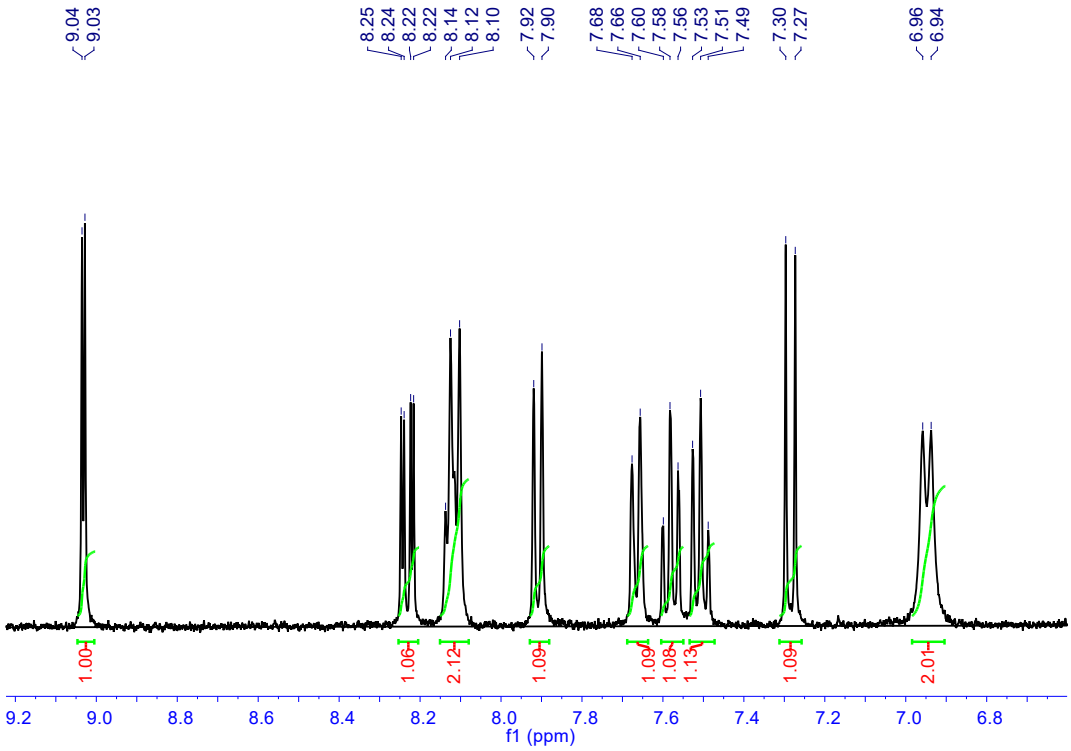


Figure S13. ^{1}H NMR spectrum of **(^{n}Bu$_4$N)5** in d^6-acetone

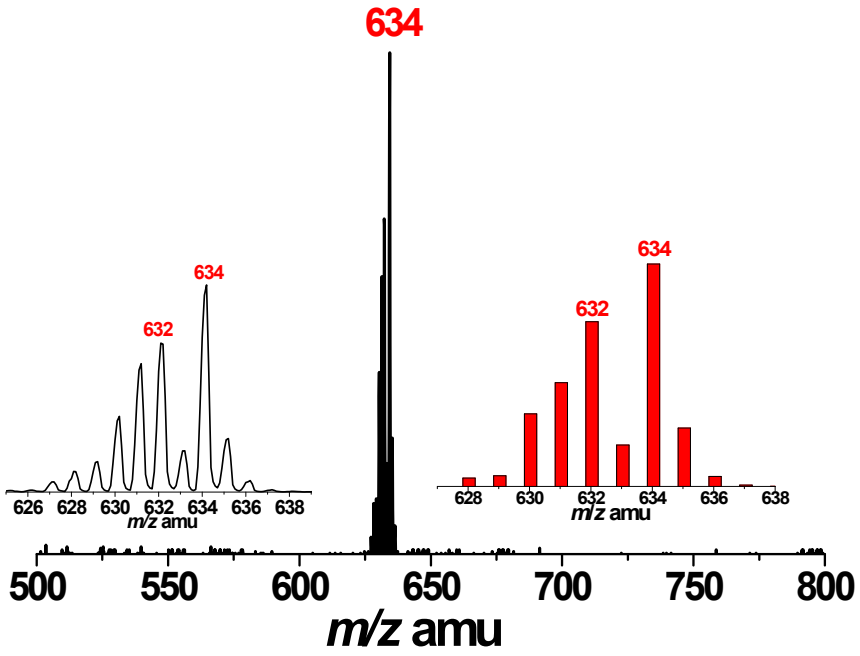


Figure S14. ESI/MS (-ve mode) of **7** in MeOH.

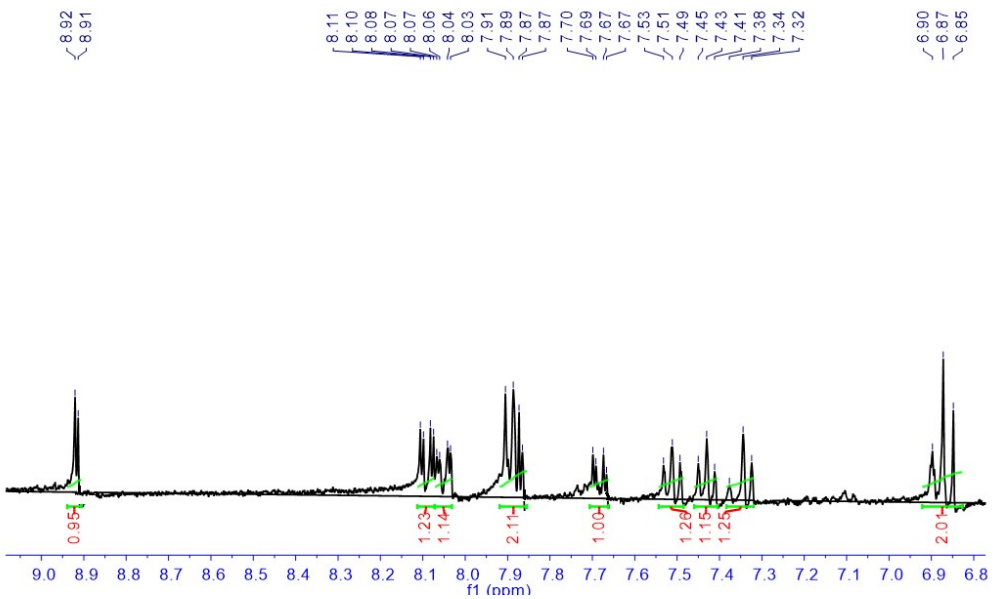


Figure S15. ^{1}H NMR spectrum of **7** in d^{6}-acetone.

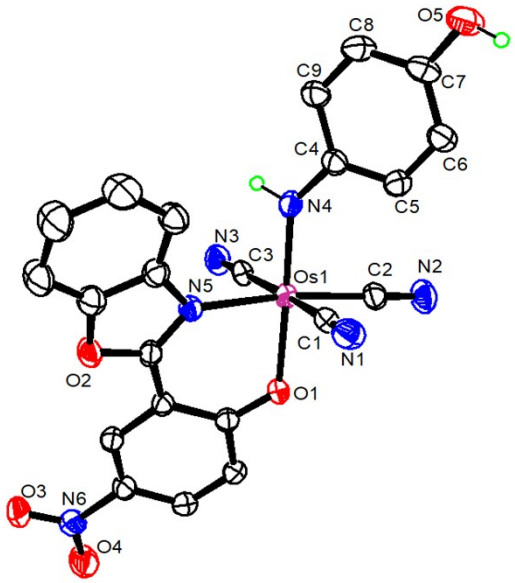


Figure S16. The structure of **5.**

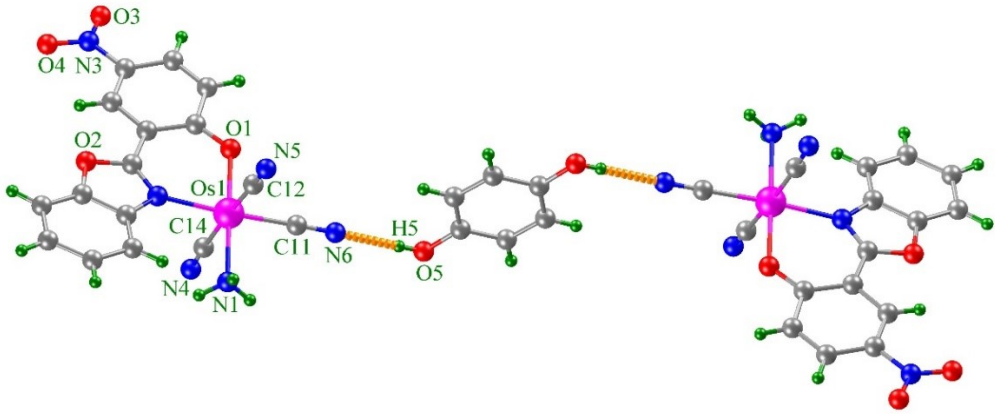


Figure S17. The H-bonding interactions of H_2Q with **4**. ($d_{(O5\cdots N6)}$ = 2.757(8) Å; ∠N6-H5-O5 = 170.9º). selected bond parameters (Å, º) around the Os center (Os1-N1 2.110(3), Os1-N2 2.125(3), Os1-C11 2.007(3), Os1-C12 2.054(4), Os1-C14 2.063(4), Os1-O1 2.036(2), O1-Os1-N1, 176.6(2), O1-Os1-N2, 86.7(2)).

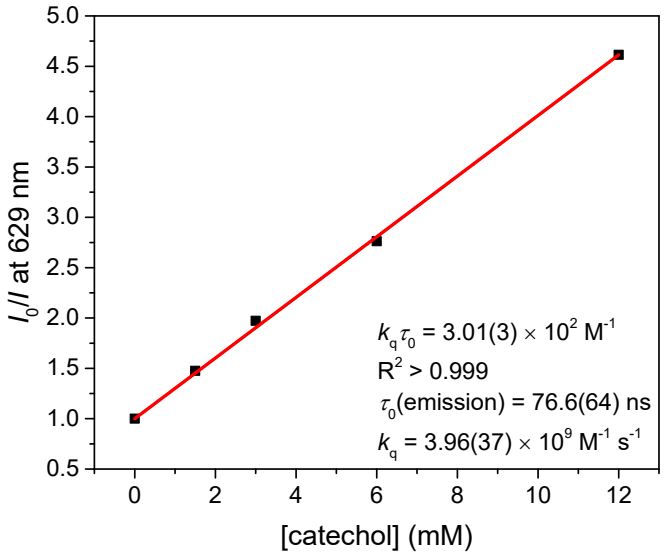


Figure S18. Kinetic quenching rate constant determined by Stern-Volmer experiment for steady-state emission intensity with addition of different amounts of H_2Cat (excited at 365 nm, determined with slit = 5 nm, each curve was treated by averaging three parallel experiments)

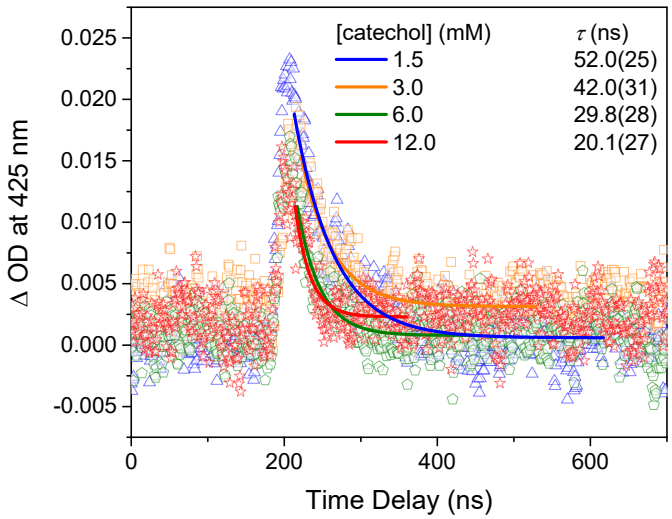


Figure S19. Decay curve of TA signal at 425 nm fitted with function of first exponential decay in the different [H_2Cat] (band width: 2.0 nm; probe offset: 430(20) mV; each curve was treated by averaging five parallel experiments).

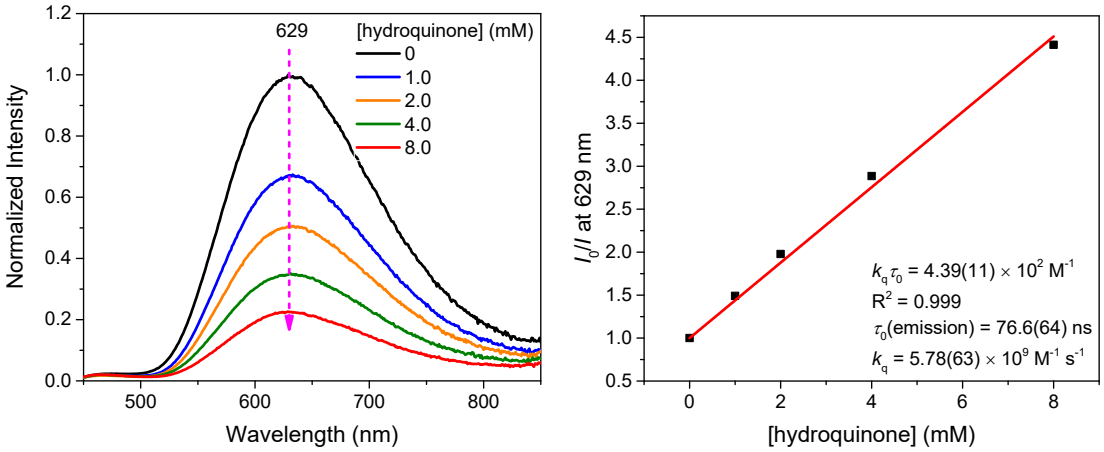


Figure S20. Left: steady-state emission spectra of **OsN** (4.6×10^{-5} M) in MeCN with different concentrations of H_2Q (excited at 365 nm, determined with slit = 5 nm, each curve was treated by averaging three parallel experiments). Right: kinetic quenching rate constant determined by Stern-Volmer experiment for steady-state emission intensity.

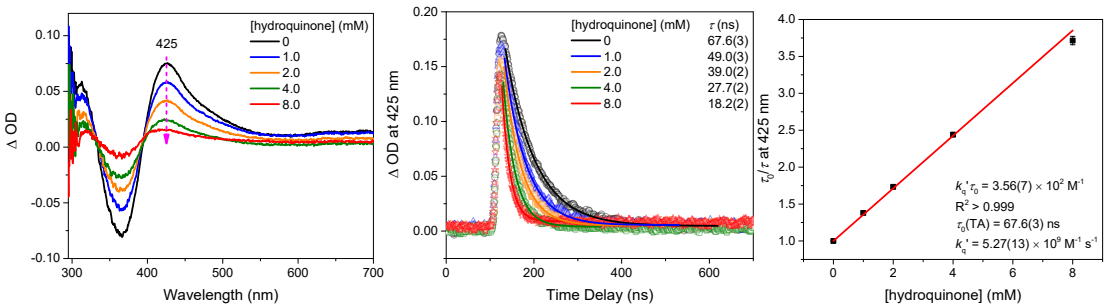


Figure S21. Left: TA spectra of **OsN*** (4.6×10^{-5} M) in MeCN with different concentrations of H_2Q (time zero t_0 = 35 ns; gate width 120 ns; band width = 3.5 nm; gain = 70(1); each curve was treated by averaging five parallel experiments). Middle: Decay curve of TA signal at 425 nm fitted with function of first exponential decay (band width: 2.0 nm; probe offset: 430(20) mV; each curve was treated by averaging five parallel experiments); Right: Kinetic quenching rate constant determined by Stern-Volmer plot.

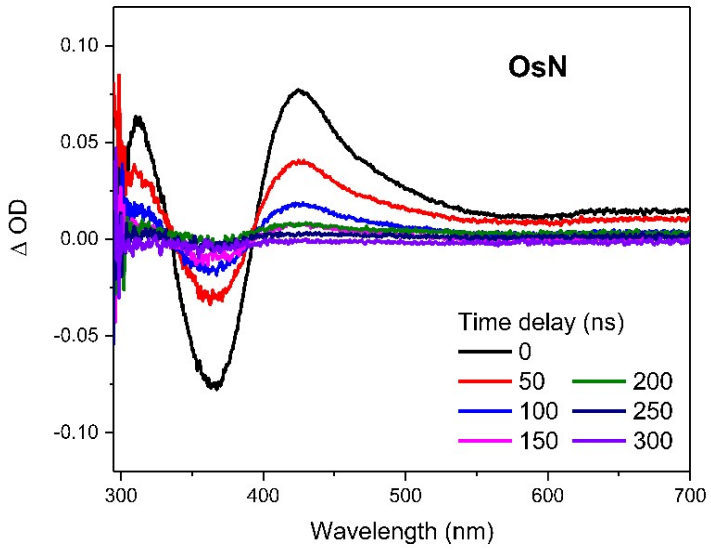


Figure S22. Map of the TA spectra for **OsN***.

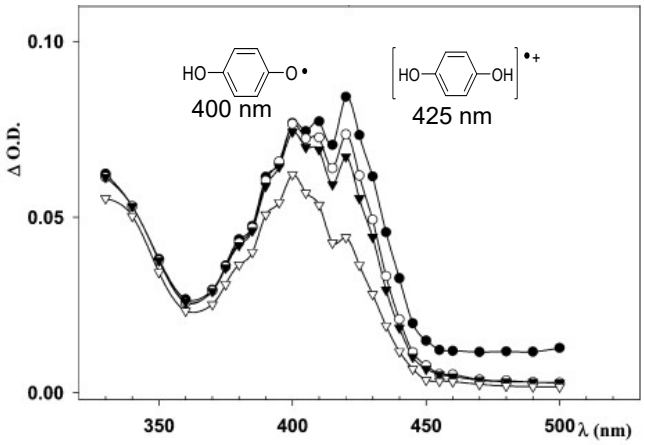


Figure S23. Transient spectra of the pulse radiolysis of a N_2-purged solution of 10^{-2} mol dm^{-3} hydroquinone in 1,2-dichloroethane taken (●) immediately after the pulse and after (○) 50, (▼) 100 and (▽) 550 ns, retrieved from the report of Naumov and co-workers.

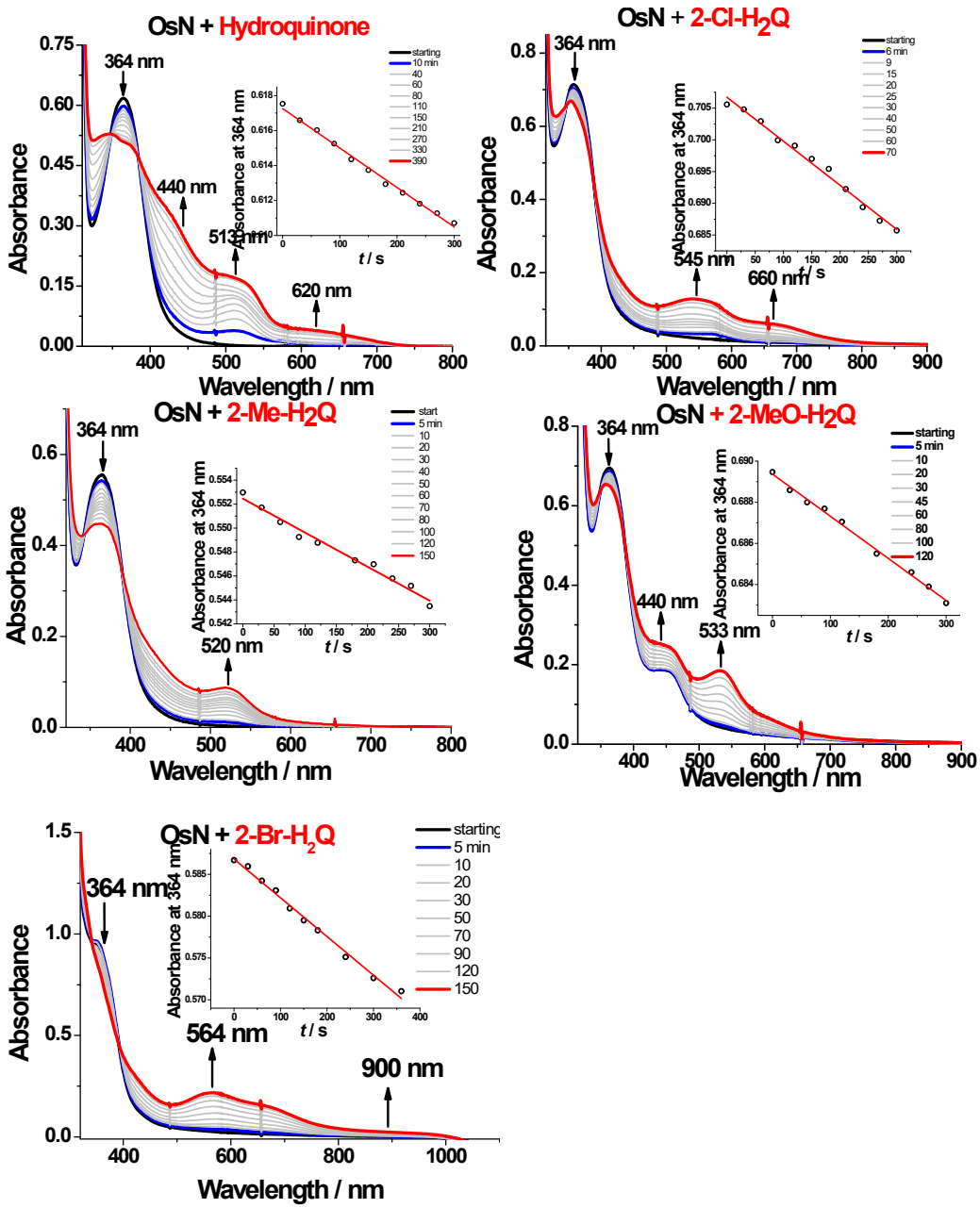


Figure S24. UV/vis spectral changes for the photoreaction of **OsN** (3.3×10^{-5} mol/L) with 100 equiv. of 2-X-H_2Qs in MeCN; The inset shows the time-trace of absorbance at 364 nm for the photoreactions of **OsN** with 2-X-H_2Qs. (All the spectra were collected in the same experimental conditons except that different 2-X-H_2Qs were used (blue LED light ($\lambda > 460$ nm), and instrument (Hewlett–Packard 8453)).

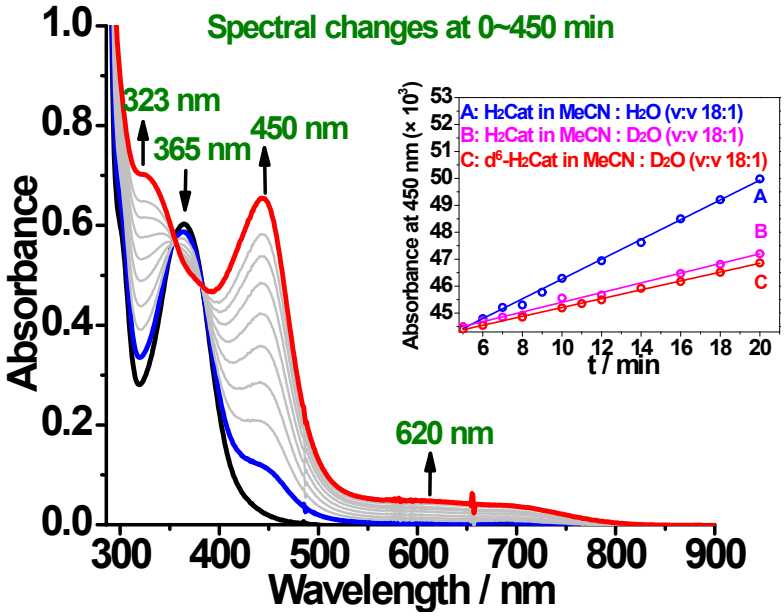


Figure S25. UV/vis spectral changes for the photoreaction of **OsN** (3.42×10^{-5} M) with H_2Cat (3.42×10^{-3} M) in MeCN. The inset shows the time-trace of absorbance at 450 nm for the photoreactions of **OsN** with H_2Cat in MeCN/H_2O and MeCN/D_2O (v:v = 18:1), and the observed KIE is 2.5±0.1.

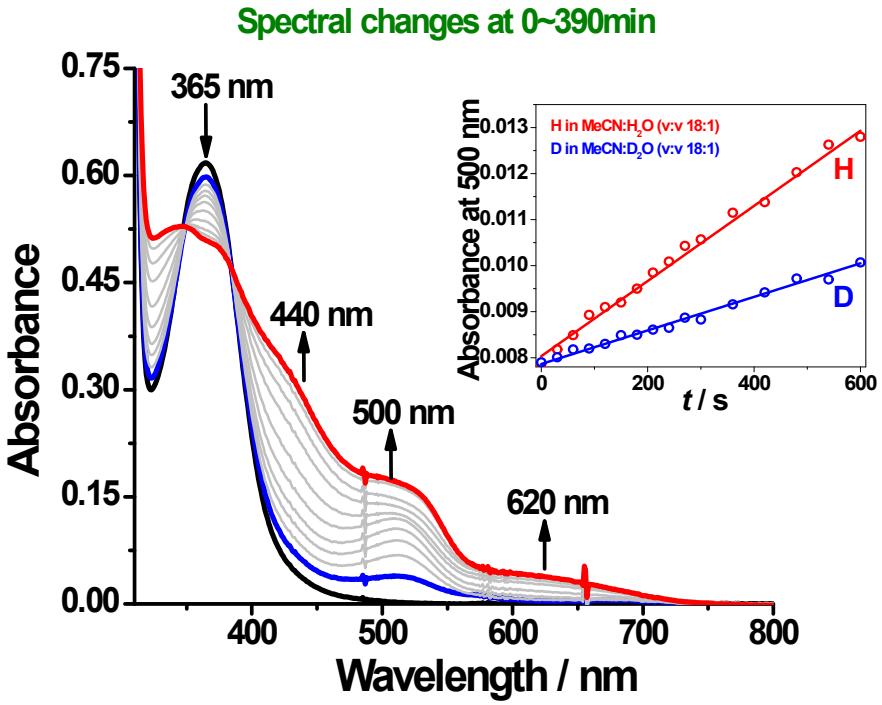


Figure S26. The UV/vis spectral changes for the photoreaction of **OsN** (3.45×10^{-5} M) with 100 equiv. of H_2Q (3.45×10^{-3} M) in MeCN. The inset shows the time-trace of the

absorbance at 365 nm for the photoreactions of **OsN** with H_2Q and d^6-H_2Q in MeCN/D_2O (v:v 18:1), and the observed KIE is $R_{obs}(H) / R_{obs}(D) = 2.3\pm0.1$.

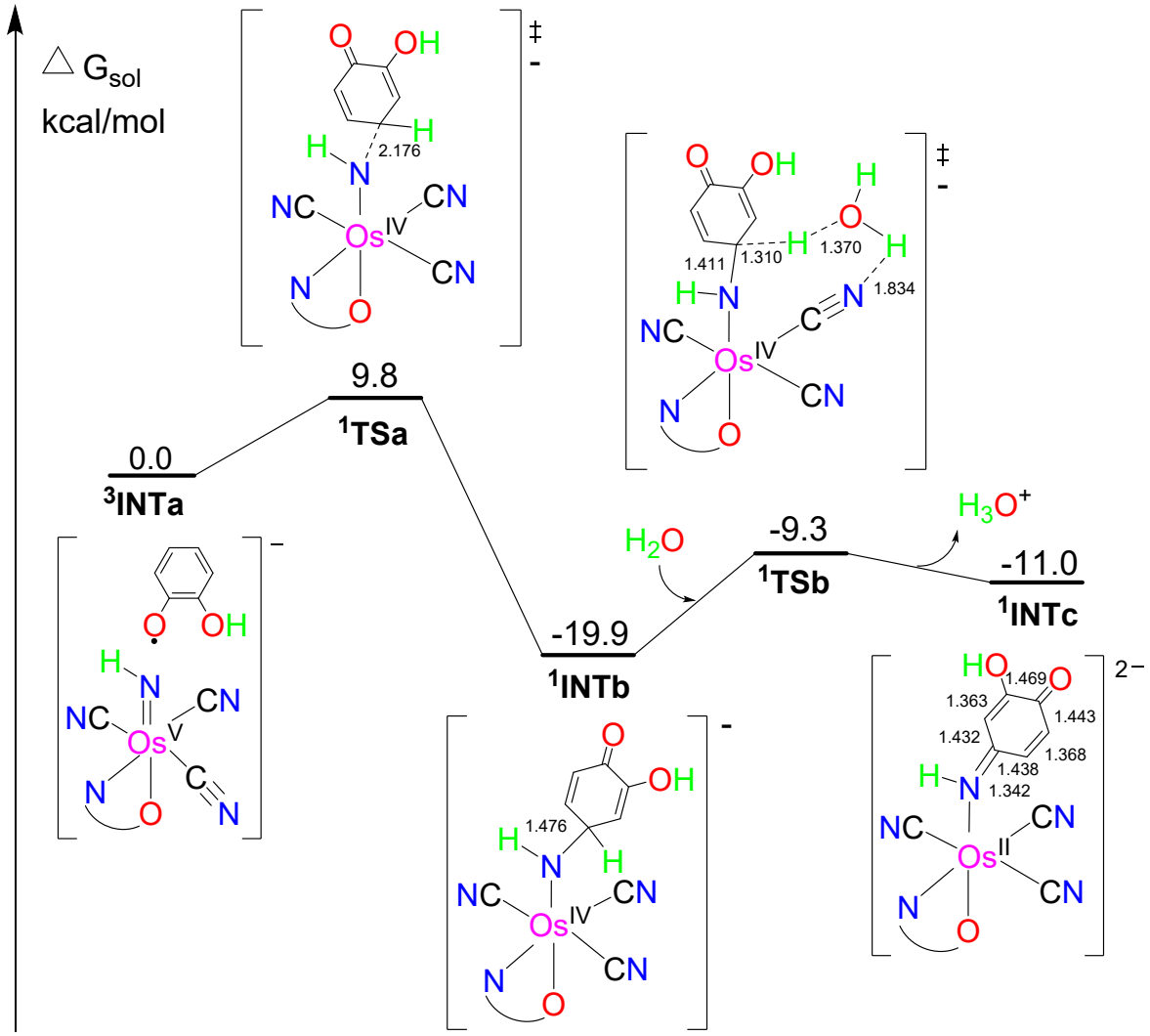


Figure S27. The potential energy surface for reaction of semiquinone radical and $[Os^{V}(NH)(CN)_3(L)]^-$ in MeCN via **Pathway B**.

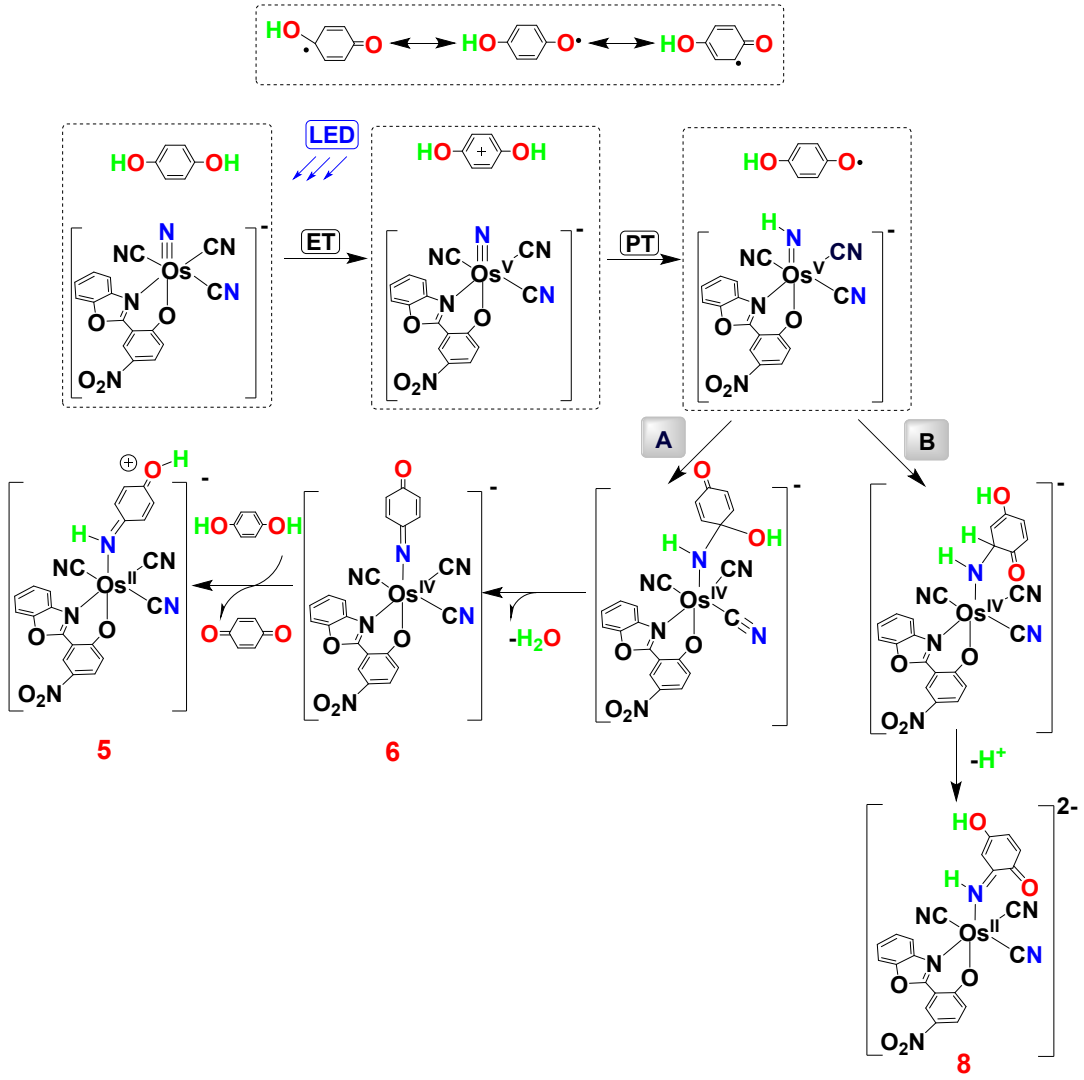


Figure S28. Proposed oxidative pathways (A and B) of H_2Q by **OsN*.**

Table S1. Bond dissociation energy (BDE), pK_{a1}, oxidation potentials and the observed initial reaction rates of various 2-substituted H_2Qs.

X	BDE / kcal mol^{-1}	pK_{a1}	E^{ox}_{NHE}	R_x
Cl	84.7	14.5	1.730	6.95×10^{-5}
H	83.4	19.1	1.607	2.26×10^{-5}
MeO	84.0	20.0	1.400	2.05×10^{-5}
Me	81.5	18.3	1.543	2.84×10^{-5}
Br	83.3	16.5	1.730	4.63×10^{-5}

Table S2. Selected bond parameters (Å, °) for **1** and **5.**

	1	**5**
Os1—C1	2.025 (8)	2.057 (6)
Os1—C2	1.895 (9)	2.025 (5)
Os1—C3	2.098 (9)	2.059 (5)
Os1—N4	2.117 (6)	1.912 (4)
Os1—N5	1.974 (6)	2.120 (4)
Os1—O1	2.069 (5)	2.052 (3)
N5—Os1—O1	171.7 (2)	\
N4—Os1—O1	\	177.83(14)
C4—N5—Os1	136.3 (6)	\
C4—N4—Os1	\	135.7(3)

Table S3. Crystal data and structure refinement details for compounds **1** and **5**.

	1	**5**
Formula	$C_{47}H_{34}Cl_2N_5O_6OsP$	$C_{39}H_{53}N_7O_6Os$
Mr	1056.86	906.08
T /K	100.0(1)	173(2)
Crystal syst	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a/Å	13.9692(7)	33.5994(16)
b/Å	13.1008(5)	12.6388(5)
c/Å	23.5542(10)	26.0050(12)
α, (°)	90	90
β, (°)	105.841 (5)	126.456 (1)
γ, (°)	90	90
V/ Å^3	4146.9 (3)	8882.2 (7)
Z	4	8
ρ_{calcd}, Mg m^{-3}	1.693	1.355
F(000)	2096	3680
Collected refl.	17922	66109
Unique refl.	7314	9119
Final *R* indices, *I*	0.055	0.036
> 2σ(I)	0.140	0.095
GOF	1.04	1.04
No. of par.	559	484

]

Table S4. Cartesian coordinates of all the compounds optimized in this study

H_2O

$G_{acetonitrile}$= -76.38393 a.u.

$E_{acetonitrile}$ = -76.38740917 a.u.

O	0.00000000	0.00000000	0.11786800
H	0.00000000	0.76503900	-0.47147100
H	0.00000000	-0.76503900	-0.47147100

H_3O^+

$G_{acetonitrile}$= -76.757788 a.u.

$E_{acetonitrile}$ = -76.77401702 a.u.

H	0.00000000	0.93324600	-0.21860000
H	-0.80821500	-0.46662300	-0.21860000
H	0.80821500	-0.46662300	-0.21860000
O	0.00000000	0.00000000	0.08197500

NH_3

$G_{acetonitrile}$= -56.515352 a.u.

$E_{acetonitrile}$ = -56.53106613 a.u.

N	0.00000000	0.00000000	0.11629500
H	0.00000000	0.94345400	-0.27135500
H	-0.81705600	-0.47172700	-0.27135500
H	0.81705600	-0.47172700	-0.27135500

INT1

$G_{acetonitrile}$= -1715.613375 a.u.

$E_{acetonitrile}$ = -1715.866304 a.u.

C	-0.58390200	1.71552700	1.11639400
C	0.68343600	2.08472400	1.58525900
C	0.97555400	3.32496100	2.13093600
C	-0.09284800	4.22316500	2.18640600
C	-1.37475300	3.87581600	1.71617000
C	-1.64719800	2.61902900	1.17428800
H	1.97313000	3.57748000	2.48333000
H	0.07105500	5.21865600	2.59774800
H	-2.17598500	4.61166600	1.77542800
H	-2.63548900	2.34969800	0.81251500
O	1.52002100	1.01132100	1.40849900
N	-0.47171400	0.40250900	0.64641300
C	0.77629300	0.03267600	0.84246100
C	1.40952600	-1.23412600	0.56230900
C	2.80658700	-1.29936000	0.55594400
C	0.62788000	-2.42224100	0.35374800
C	3.44351700	-2.51410300	0.33395400

H	3.39700400	-0.40408900	0.72265500
C	1.32763400	-3.64521200	0.15278900
C	2.70413200	-3.69654300	0.13349300
H	0.73367100	-4.54475800	0.00063700
H	3.22720200	-4.63457900	-0.03603200
O	-0.66703500	-2.43519300	0.37092200
N	4.88720200	-2.55665000	0.30923000
O	5.43712800	-3.64314800	0.12863400
O	5.51206400	-1.50755800	0.46846000
Os	-2.02427500	-0.90000200	-0.14404800
C	-2.68404700	-1.13479200	1.82215800
C	-3.33440100	-2.32065900	-0.76595000
C	-0.98315300	-1.06539600	-1.94531100
N	-0.37099900	-1.18964600	-2.92857800
N	-4.08012300	-3.14535600	-1.11736100
N	-3.02872600	-1.26272900	2.92762600
N	-3.08852900	0.39671700	-0.66633800
H	-3.99415600	0.47328100	-1.14470300
C	0.62831500	2.66233300	-1.77295500
C	1.50720000	1.58967600	-1.89723400
C	2.82072600	1.75000600	-1.46039900
C	3.27464900	2.97185500	-0.88999500
C	2.42645100	4.04498100	-0.76173100
C	1.05802000	3.94731600	-1.20760100
H	3.51644700	0.91659800	-1.55300800
H	2.75226900	4.98941800	-0.32703800
O	-0.63961900	2.58891900	-2.16805700
H	-1.04204900	3.45872200	-1.96614300
H	4.30809700	3.04667900	-0.55226300
O	0.21365400	4.87547500	-1.14997300
H	1.15646200	0.65111200	-2.32109600

INT2

$G_{acetonitrile}$= -1715.628475 a.u.

$E_{acetonitrile}$ = -1715.889853 a.u.

C	0.07933600	2.41767200	-0.29668900
C	1.20626900	3.24423100	-0.18603500
C	1.15267600	4.62864100	-0.17925200
C	-0.12669700	5.18137800	-0.29825800
C	-1.27177700	4.37044800	-0.41655200
C	-1.19512300	2.97615300	-0.41958100
H	2.04882900	5.23988600	-0.08952300
H	-0.23863000	6.26554400	-0.30211600
H	-2.24822500	4.84472700	-0.51253100

H	-2.08294600	2.36001500	-0.52234000
O	2.31056500	2.43254100	-0.09215800
N	0.54123000	1.09738800	-0.23446900
C	1.85425700	1.16151100	-0.13213100
C	2.81047800	0.08193100	-0.10989300
C	4.13638800	0.33999800	0.25759900
C	2.43059900	-1.22644600	-0.55310100
C	5.07456500	-0.68257500	0.20559300
H	4.43215700	1.33166600	0.58669600
C	3.42828300	-2.23373600	-0.61321700
C	4.72718500	-1.97596700	-0.22982200
H	3.13147400	-3.22258200	-0.95823600
H	5.48543800	-2.75456000	-0.25975500
O	1.22134300	-1.50874900	-0.94545200
N	6.44046900	-0.40623300	0.60550000
O	7.26065000	-1.32021500	0.54505000
O	6.72379200	0.72770800	0.98720400
Os	-0.52761300	-0.78628900	-0.17600700
C	-1.26589200	-0.53205000	-2.10498800
C	0.27661100	-0.98877400	1.73879200
N	0.74610600	-1.07695800	2.80428600
N	-1.76681000	-0.33935600	-3.14411600
C	-1.17992200	-2.70554300	-0.24930100
N	-1.50220900	-3.82700100	-0.29026000
H	-2.03061600	0.46516200	1.43350800
N	-2.10860000	-0.07806600	0.56879000
C	-6.00589300	-1.19306600	1.01053400
C	-5.64108600	-0.01570900	1.57618200
C	-4.35475000	0.57912500	1.26343400
C	-3.50903300	-0.03925200	0.10569300
C	-3.99861600	-1.38077800	-0.37288500
C	-5.17247000	-1.88774000	0.03947900
H	-5.53079800	-2.83187400	-0.36970500
O	-3.65865900	0.90714800	-0.94413100
H	-3.22124300	0.55923100	-1.74367000
H	-6.25784000	0.48809100	2.31937200
H	-6.95583800	-1.65106100	1.29044300
H	-3.39525900	-1.88646200	-1.12119600
O	-3.88538200	1.54219800	1.85497000

INT3

$G_{acetonitrile}$= -1715.613443 a.u.

$E_{acetonitrile}$ = -1715.877301 a.u.

C	-0.60783300	2.09744900	0.85217500

C	0.28012300	3.14785300	0.59083900
C	-0.06977500	4.48639500	0.66729500
C	-1.39267900	4.74285900	1.04435100
C	-2.29557700	3.70027000	1.33176900
C	-1.92084500	2.35902800	1.24395200
H	0.64079000	5.28217400	0.45131200
H	-1.73004900	5.77609000	1.12525400
H	-3.31264900	3.94856100	1.63370800
H	-2.61351700	1.55711100	1.48215900
O	1.49715800	2.59423000	0.26189800
N	0.09504600	0.91393600	0.61532000
C	1.32959400	1.25389200	0.30570500
C	2.46131100	0.38152800	0.12829100
C	3.64645900	0.87305400	-0.42616500
C	2.39779600	-0.96379000	0.63843400
C	4.76412100	0.05015100	-0.50072300
H	3.69550100	1.89098200	-0.80210100
C	3.57763500	-1.75571700	0.56659700
C	4.73380700	-1.26883100	-0.00261700
H	3.53185700	-2.76997400	0.95939500
H	5.62451600	-1.88820800	-0.07500500
O	1.32973600	-1.44627400	1.18786100
N	5.97737100	0.56101400	-1.09572300
O	6.96113100	-0.17791200	-1.14416500
O	5.98292600	1.71301200	-1.53048500
Os	-0.63407700	-1.08875300	0.61078400
C	-0.23170900	-1.27053800	-1.44287900
C	-1.23100800	-0.84563900	2.63108300
N	-1.61152700	-0.68911500	3.72619000
N	0.76724100	-1.56538100	-2.17502700
C	-0.90426400	-3.10177000	0.77679100
N	-1.03929000	-4.25744500	0.87555900
H	-3.20178400	-0.66813800	0.46863500
N	-2.32631800	-0.72725300	-0.05639100
C	-5.09115900	0.67646000	-1.77612600
C	-4.95805700	-0.76966300	-1.93380200
C	-3.75706400	-1.37007700	-1.87271300
C	-2.52149300	-0.58355900	-1.51996400
C	-2.66672200	0.96219400	-1.75436600
C	-4.02116000	1.50321400	-1.67676200
H	-6.09660000	1.09959300	-1.78522900
H	-5.85791900	-1.35568400	-2.11852100
H	-4.12734000	2.58695600	-1.64742600
O	-1.41118800	-1.06469900	-2.19546600

H	1.58973300	-1.74434200	-1.60301300
O	-1.67174900	1.63120900	-1.95219300
H	-3.62343100	-2.44531700	-1.98483500

INT4

$G_{acetonitrile}$= -1792.393548 a.u.

$E_{acetonitrile}$ = -1792.691809 a.u.

C	-0.45494800	2.36493600	0.65564100
C	0.46547900	3.31651800	0.19914900
C	0.16583000	4.65952300	0.04024500
C	-1.14025100	5.02922600	0.38038700
C	-2.07549800	4.09023200	0.85800600
C	-1.75115100	2.74106200	1.00828400
H	0.89978300	5.37569900	-0.32453800
H	-1.43900400	6.07237700	0.27858200
H	-3.07770100	4.42729200	1.12065000
H	-2.46884200	2.02378100	1.39644300
O	1.65101700	2.66307200	-0.05476000
N	0.19828100	1.13210000	0.61486200
C	1.43471000	1.36019800	0.21741800
C	2.51915400	0.41461700	0.13695100
C	3.70795200	0.76508000	-0.51220900
C	2.41134400	-0.84681800	0.81977600
C	4.77710800	-0.12094600	-0.50917000
H	3.79484300	1.72069000	-1.02111600
C	3.54050400	-1.70694700	0.81742900
C	4.69935600	-1.36073500	0.15530600
H	3.45713600	-2.65810900	1.34003500
H	5.55439000	-2.03212700	0.13784800
O	1.33653800	-1.18848100	1.46549500
N	5.99609200	0.24271200	-1.20290800
O	6.93502900	-0.55111300	-1.18426000
O	6.04271700	1.32724500	-1.78048900
Os	-0.59638300	-0.81749900	0.87462600
C	-0.25009800	-1.27582800	-1.14579400
C	-1.13326500	-0.34005600	2.85908800
N	-1.47943700	-0.05106700	3.93743700
C	-0.98649300	-2.80985800	1.03905900
N	-1.26788500	-3.92829700	0.83685900
H	-3.13816600	-0.24215700	0.76146200
N	-2.30043800	-0.45720700	0.21638500
C	-4.86748100	1.04265700	-1.85250300
C	-4.99518100	-0.39796100	-1.64905000
C	-3.92450400	-1.17427300	-1.41298600

C	-2.56242200	-0.56576700	-1.23661200
C	-2.43320300	0.89917400	-1.79489800
C	-3.66677200	1.66806300	-1.90812800
H	-5.78143500	1.61937100	-1.99910700
H	-5.98916100	-0.84119700	-1.69649900
H	-3.57358300	2.72943600	-2.13310000
O	-1.56121800	-1.36560900	-1.81210800
N	0.67213900	-1.65844000	-1.91530900
H	1.57084800	-1.67675100	-1.43636700
O	-1.32891700	1.32118600	-2.07298600
H	-4.01774600	-2.24383200	-1.23276200
H	-1.51233300	-4.11631100	-0.70444600
H	-2.39191400	-4.45671600	-2.09012500
H	-1.71187800	-2.96206700	-1.89855800
O	-1.63297000	-3.96638200	-1.73258300

INT5

$G_{acetonitrile}$= -1792.451162 a.u.

$E_{acetonitrile}$ = -1792.751334 a.u.

C	0.39977600	2.52734500	-0.63601000
C	-0.63198200	3.39275300	-0.25484600
C	-0.49132000	4.76713700	-0.15651100
C	0.77709900	5.26548300	-0.47043300
C	1.82546900	4.41508900	-0.87149400
C	1.65703500	3.03298400	-0.96826900
H	-1.31713500	5.41115500	0.13964900
H	0.95488500	6.33904800	-0.41293800
H	2.79335300	4.84812000	-1.12146400
H	2.46423200	2.39003400	-1.30504600
O	-1.75679200	2.62893500	-0.03443800
N	-0.14067800	1.23476900	-0.60483300
C	-1.41241100	1.34946200	-0.26505500
C	-2.41195200	0.32084300	-0.15159700
C	-3.66336600	0.64535900	0.38777700
C	-2.16551400	-0.99505200	-0.67317600
C	-4.67089500	-0.30802100	0.41763500
H	-3.84928900	1.64071000	0.77984200
C	-3.24313200	-1.92555800	-0.65030300
C	-4.46615400	-1.59938400	-0.10967900
H	-3.06794200	-2.91498500	-1.06942500
H	-5.27597600	-2.32448700	-0.08325300
O	-1.03625200	-1.36578800	-1.19011700
N	-5.95298000	0.03699200	0.99108100
O	-6.83830800	-0.81736200	0.99428000

O	-6.10800600	1.16726100	1.45204100
Os	0.87671900	-0.63651400	-0.73917500
C	1.05004700	-2.57374600	0.27997900
C	0.95644700	-0.04395400	-2.68913900
N	0.97679800	0.39589800	-3.76680300
C	1.88781900	-2.05778000	-1.80179400
N	2.49947400	-2.81667800	-2.43989100
H	3.44602300	0.12234900	-0.73532800
N	2.61406300	0.06260100	-0.14529400
C	2.69576600	1.23036100	3.78419200
C	3.87643300	1.44499200	2.99170900
C	3.92024500	1.06882000	1.67814100
C	2.75642800	0.46745200	1.10864300
C	1.56401400	0.23034700	1.92014700
C	1.56112700	0.64228400	3.27730400
H	2.71022600	1.54509300	4.82796800
H	4.74117000	1.91745500	3.45548300
H	0.67215900	0.47479000	3.88230400
O	2.17564800	-2.65838300	0.96875700
N	0.12982000	-3.43842000	0.30901800
H	2.16903200	-3.51314300	1.48770900
O	1.54452800	-4.97715700	2.08980500
H	-0.65109300	-3.22266400	-0.30525500
H	1.95990400	-5.78116000	1.75211800
H	0.78927300	-4.78077100	1.48729000
O	0.58380900	-0.36666900	1.35124400
H	4.80215600	1.22741900	1.05877500

INT6

$G_{acetonitrile}$= -1792.48171 a.u.

$E_{acetonitrile}$ = -1792.782697 a.u.

C	-0.65432800	1.87853600	-1.11832700
C	0.30581700	2.89253800	-1.20368700
C	0.02378300	4.20341300	-1.55167100
C	-1.32031300	4.47776900	-1.81911200
C	-2.30438000	3.47323700	-1.74523900
C	-1.99340500	2.15783300	-1.39971800
H	0.80126400	4.96250700	-1.61193600
H	-1.61180800	5.49042800	-2.09664700
H	-3.33960200	3.72699300	-1.97028100
H	-2.75736300	1.39045800	-1.37315100
O	1.52682900	2.33846400	-0.89606200
N	0.03582300	0.71493100	-0.73883700
C	1.31442100	1.03967200	-0.62200600

C	2.44326800	0.22472300	-0.24632000
C	3.68545900	0.84552200	-0.05562900
C	2.32496700	-1.20015200	-0.12175500
C	4.80129600	0.08031800	0.25095500
H	3.78113100	1.92270100	-0.14900300
C	3.50061500	-1.94264200	0.17570800
C	4.71478100	-1.32193100	0.36584100
H	3.40427800	-3.02355600	0.26056900
H	5.60566300	-1.89699100	0.60645100
O	1.21340500	-1.84348900	-0.30805400
N	6.07381000	0.73867300	0.45144300
O	7.05424800	0.04300700	0.71286700
O	6.12614400	1.96397900	0.35282100
Os	-0.72650500	-1.12884900	0.04840300
C	-0.94971300	-1.19986800	-2.15755000
C	-0.73967100	-2.52551000	1.53078400
N	-0.67830300	-3.26186900	2.43019400
C	-1.63332000	-2.78442300	-0.68860100
N	-2.19352100	-3.73971900	-1.05244400
H	-3.34780600	-0.56035000	-0.02732600
N	-2.47775800	-0.35560200	0.50337800
C	-2.40937100	2.38507200	3.54986900
C	-1.25244700	1.71900200	3.22324500
C	-1.29292200	0.76329700	2.17278200
C	-2.56292000	0.53229100	1.47714100
C	-3.74508500	1.24608200	1.85530300
C	-3.65751700	2.15429400	2.87118100
H	-2.38924300	3.11895200	4.35612500
H	-0.31295800	1.89895900	3.74287200
H	-4.53533700	2.72007500	3.17997600
O	-1.93785100	-0.71807500	-2.68784700
N	0.11279700	-1.67421600	-2.80319200
H	0.11177700	-1.70194800	-3.81598600
O	-4.37836500	-0.82842300	-1.46029500
H	0.88822900	-2.06992600	-2.28503100
H	-3.61624400	-0.80737300	-2.07686000
H	-5.02921700	-0.20461400	-1.80256100
O	-0.28774500	0.07174300	1.79524900
H	-4.67573100	1.05875900	1.32178100

INT7

$G_{acetonitrile}$= -1792.47909 a.u.

$E_{acetonitrile}$ = -1792.773434 a.u.

C	0.44998200	2.39996600	-0.22600200

C	-0.54349900	3.30908800	0.15982900
C	-0.30791600	4.64918200	0.42276900
C	1.01775600	5.06790300	0.27230300
C	2.03155200	4.17599600	-0.12865100
C	1.76890000	2.83058100	-0.38886700
H	-1.10572500	5.32705500	0.72036900
H	1.27058700	6.11080500	0.46245400
H	3.04915100	4.54752100	-0.24618600
H	2.55535000	2.16037500	-0.71536700
O	-1.73413700	2.62653300	0.20323300
N	-0.17868000	1.16040400	-0.38635300
C	-1.45804600	1.34888700	-0.13973100
C	-2.55219500	0.40787300	-0.21042600
C	-3.81613700	0.80729800	0.24115600
C	-2.37750900	-0.89491200	-0.78145400
C	-4.89567700	-0.06049600	0.13882900
H	-3.95704700	1.79381700	0.67141500
C	-3.51283600	-1.74176500	-0.87787400
C	-4.75187900	-1.34143800	-0.42547000
H	-3.36923100	-2.72728300	-1.31709300
H	-5.61402200	-2.00013200	-0.49506800
O	-1.24085900	-1.34444000	-1.23073300
N	-6.19251000	0.36801300	0.62198100
O	-7.13836200	-0.41106500	0.51856800
O	-6.29588000	1.48967100	1.11561700
Os	0.69120300	-0.76297200	-0.84445600
C	0.07381700	-1.43470900	1.10635200
C	0.73699200	-0.18796600	-2.85861500
N	0.75357600	0.14423100	-3.97569700
C	1.26101200	-2.65180000	-1.31722400
N	1.53519200	-3.76674400	-1.52588600
N	2.32631800	-0.39134000	-0.29795200
C	5.92047800	0.18956500	1.57309700
C	5.74842100	0.59218700	0.19617500
C	4.56617500	0.39472600	-0.44053400
C	3.46264500	-0.22221100	0.26937500
C	3.61777200	-0.67289900	1.71160500
C	4.92650800	-0.40496000	2.28849700
H	6.88657500	0.36843900	2.04698600
H	6.58304400	1.05266700	-0.33131800
H	5.07073800	-0.70950500	3.32500900
O	-0.31662500	-0.54715700	1.97481200
H	-0.62642900	-0.94906400	2.83813800
O	-1.06810600	-1.90239100	4.09702500

H	-0.53300800	-1.89847900	4.90227600
H	-1.99190800	-1.92595600	4.38093500
H	4.41126900	0.67863400	-1.48010700
O	2.69630900	-1.21484000	2.31633600
N	-0.02785500	-2.70740200	1.40597600
H	0.28324700	-3.40520700	0.73966600
H	-0.37289300	-3.01897100	2.31237700

INT8

$G_{acetonitrile}$= -1716.092143 a.u.

$E_{acetonitrile}$ = -1716.366821 a.u.

C	-0.29929700	2.24378900	-0.29793400
C	0.70982100	3.20871500	-0.18418700
C	0.48275800	4.57449500	-0.23897900
C	-0.84877000	4.95522300	-0.43357600
C	-1.87625500	4.00206000	-0.57409500
C	-1.62325600	2.63111000	-0.51372600
H	1.29063200	5.29765000	-0.14460300
H	-1.09528800	6.01535100	-0.48847300
H	-2.89693100	4.34347600	-0.74414900
H	-2.41721200	1.90780400	-0.66261000
O	1.90381500	2.54450300	-0.03696500
N	0.32357500	0.99663200	-0.17845300
C	1.61521600	1.22646700	-0.05175000
C	2.70132600	0.27769700	0.01485700
C	3.98977200	0.73515200	0.31812600
C	2.49037500	-1.10001400	-0.31168700
C	5.05676000	-0.15287200	0.30202900
H	4.15802100	1.77948800	0.56259600
C	3.61262000	-1.96552000	-0.33526400
C	4.87730600	-1.50840600	-0.02776400
H	3.44107800	-3.00960500	-0.59031400
H	5.73271100	-2.17938300	-0.03386400
O	1.32064100	-1.59898100	-0.60489600
N	6.38427300	0.33488600	0.62906400
O	7.31923700	-0.46180900	0.59829500
O	6.51783200	1.52085400	0.92179400
Os	-0.54369800	-0.97881600	-0.09249500
C	-0.82396100	-0.89056600	-2.19560800
C	0.24521400	-1.12398100	1.86076400
N	0.70391200	-1.17902500	2.92988800
C	-1.12151800	-2.93085200	-0.13611700
N	-1.47024900	-4.04069000	-0.21103800
N	-2.16330200	-0.51768200	0.41861600

C	-5.89331100	0.44658800	1.77069200
C	-4.90745200	-0.04785200	2.69742700
C	-3.66363600	-0.38441400	2.26549800
C	-3.33943300	-0.23490200	0.86303600
C	-4.35712700	0.24852400	-0.12296900
C	-5.63897700	0.59345200	0.43549600
H	-6.87932200	0.70946500	2.15599100
H	-5.16724900	-0.14682800	3.75059900
H	-6.39679300	0.96452100	-0.25371600
O	-0.04880000	-0.66449800	-3.07384600
H	-2.51544300	-2.14502300	-2.43560300
H	-2.34625100	-1.04477500	-3.67832500
N	-2.27182200	-1.17425300	-2.66408100
H	-2.96687900	-0.54820800	-2.15792300
O	-4.08851600	0.33959900	-1.33897400
H	-2.88743600	-0.75372300	2.93316200

INT9

$G_{acetonitrile}$= -1659.57805 a.u.

$E_{acetonitrile}$ = -1659.811878 a.u.

C	0.14474200	2.45557800	0.26608800
C	-0.93196600	3.29965800	-0.03548700
C	-0.82410500	4.67633500	-0.14126300
C	0.45561200	5.19527800	0.08225200
C	1.55058600	4.36251700	0.38595700
C	1.42007900	2.97606800	0.48375700
H	-1.67878300	5.30628200	-0.38018600
H	0.60895300	6.27227900	0.01710700
H	2.52931700	4.81360700	0.54683600
H	2.27569700	2.33813600	0.68749400
O	-2.04911300	2.51032000	-0.19296900
N	-0.35961700	1.15068300	0.25856600
C	-1.65430800	1.24063800	0.00276300
C	-2.63304300	0.18361400	-0.01993200
C	-3.89536400	0.41278300	-0.58213000
C	-2.35075500	-1.06220700	0.62210800
C	-4.85400100	-0.58836400	-0.52612000
H	-4.12153700	1.36011800	-1.06271900
C	-3.36400500	-2.04691000	0.67439400
C	-4.59911400	-1.82185700	0.10001600
H	-3.13773200	-2.98927400	1.16954600
H	-5.37520600	-2.58280000	0.12442400
O	-1.20489400	-1.29288600	1.21787200
N	-6.15765100	-0.34951300	-1.12938400

O	-6.99796600	-1.24118400	-1.06076900
O	-6.35774500	0.73023100	-1.67731400
Os	0.62103500	-0.72707700	0.56100000
C	1.18252600	-0.32177100	2.45539500
C	-0.02343500	-1.20957700	-1.35602300
N	-0.38348100	-1.47178900	-2.43101000
C	1.12574700	-2.68317000	0.93057700
N	1.39842900	-3.79685600	1.12836300
N	2.27989100	-0.47774200	-0.12365300
C	5.78524300	-0.87679500	-2.19948800
C	4.90050900	-2.01316400	-2.01188100
C	3.75544000	-1.90499700	-1.30189200
C	3.38992600	-0.61566500	-0.71712900
C	4.35711600	0.57574400	-0.82414500
C	5.53103400	0.33936500	-1.65444000
H	6.68719000	-1.02066200	-2.79539300
H	5.16673600	-2.96667800	-2.46756000
H	6.20717200	1.18365800	-1.78604300
O	1.50217100	-0.14020400	3.52776700
O	4.14700500	1.61602700	-0.22100400
H	3.07009800	-2.73733900	-1.15865400

INTa

$G_{acetonitrile}$= -1715.613375 a.u.

$E_{acetonitrile}$ = -1715.866304 a.u.

C	-0.58390200	1.71552700	1.11639400
C	0.68343600	2.08472400	1.58525900
C	0.97555400	3.32496100	2.13093600
C	-0.09284800	4.22316500	2.18640600
C	-1.37475300	3.87581600	1.71617000
C	-1.64719800	2.61902900	1.17428800
H	1.97313000	3.57748000	2.48333000
H	0.07105500	5.21865600	2.59774800
H	-2.17598500	4.61166600	1.77542800
H	-2.63548900	2.34969800	0.81251500
O	1.52002100	1.01132100	1.40849900
N	-0.47171400	0.40250900	0.64641300
C	0.77629300	0.03267600	0.84246100
C	1.40952600	-1.23412600	0.56230900
C	2.80658700	-1.29936000	0.55594400
C	0.62788000	-2.42224100	0.35374800
C	3.44351700	-2.51410300	0.33395400
H	3.39700400	-0.40408900	0.72265500
C	1.32763400	-3.64521200	0.15278900

C	2.70413200	-3.69654300	0.13349300
H	0.73367100	-4.54475800	0.00063700
H	3.22720200	-4.63457900	-0.03603200
O	-0.66703500	-2.43519300	0.37092200
N	4.88720200	-2.55665000	0.30923000
O	5.43712800	-3.64314800	0.12863400
O	5.51206400	-1.50755800	0.46846000
Os	-2.02427500	-0.90000200	-0.14404800
C	-2.68404700	-1.13479200	1.82215800
C	-3.33440100	-2.32065900	-0.76595000
C	-0.98315300	-1.06539600	-1.94531100
N	-0.37099900	-1.18964600	-2.92857800
N	-4.08012300	-3.14535600	-1.11736100
N	-3.02872600	-1.26272900	2.92762600
N	-3.08852900	0.39671700	-0.66633800
H	-3.99415600	0.47328100	-1.14470300
C	0.62831500	2.66233300	-1.77295500
C	1.50720000	1.58967600	-1.89723400
C	2.82072600	1.75000600	-1.46039900
C	3.27464900	2.97185500	-0.88999500
C	2.42645100	4.04498100	-0.76173100
C	1.05802000	3.94731600	-1.20760100
H	3.51644700	0.91659800	-1.55300800
H	2.75226900	4.98941800	-0.32703800
O	-0.63961900	2.58891900	-2.16805700
H	-1.04204900	3.45872200	-1.96614300
H	4.30809700	3.04667900	-0.55226300
O	0.21365400	4.87547500	-1.14997300
H	1.15646200	0.65111200	-2.32109600

INTb

$G_{acetonitrile}$= -1715.645065 a.u.

$E_{acetonitrile}$ = -1715.905821 a.u.

C	0.01039500	2.30111600	0.24544200
C	1.04591400	3.22904100	0.06743500
C	0.85406600	4.60055600	0.02154700
C	-0.46872800	5.02997100	0.17359100
C	-1.52430200	4.11705700	0.36163400
C	-1.30639600	2.73921100	0.40415800
H	1.68089600	5.29403700	-0.12054300
H	-0.68640900	6.09761400	0.14974300
H	-2.53846400	4.49643000	0.48325800
H	-2.12435500	2.04603000	0.56686900
O	2.21952600	2.52450500	-0.04365000

N	0.59387700	1.03176200	0.20467800
C	1.88926100	1.21538400	0.05270800
C	2.94254000	0.22956400	0.02182000
C	4.22525200	0.61583600	-0.38653500
C	2.70932200	-1.10974100	0.48202700
C	5.26567900	-0.30328200	-0.35813400
H	4.40913000	1.62990700	-0.72837900
C	3.81001300	-2.00742100	0.51112700
C	5.06489000	-1.62262500	0.09147200
H	3.62521900	-3.01949800	0.86692800
H	5.89878200	-2.32016200	0.10319000
O	1.55415700	-1.52886000	0.91048900
N	6.58298800	0.11013400	-0.79749200
O	7.49512400	-0.71385400	-0.75776300
O	6.73726400	1.26514000	-1.19093100
Os	-0.30523100	-0.92921800	0.28574100
C	0.40113000	-1.15579800	-1.66973200
C	-0.83726000	-0.65579300	2.28561000
N	-1.13693000	-0.47526100	3.39992400
N	0.82766300	-1.25258200	-2.75233500
C	-0.92141000	-2.84878100	0.49064800
N	-1.27480300	-3.95592900	0.61214100
H	-2.07142400	0.19703800	-1.16400200
N	-1.99350400	-0.41708600	-0.34880700
C	-3.91244900	0.24163800	0.97625600
C	-3.33330200	-0.83794000	0.10485300
C	-4.16594300	-1.21881600	-1.07789400
C	-5.33291900	-0.60193800	-1.34709900
C	-5.86537100	0.47944100	-0.47355500
C	-5.08134900	0.84721100	0.70730100
H	-3.32642700	0.50229400	1.85706000
H	-3.18016400	-1.72279200	0.74261900
H	-5.49033900	1.62074800	1.35685000
O	-6.11106600	-0.90970000	-2.39986000
H	-6.89005000	-0.32294000	-2.35582700
O	-6.93630900	1.00545800	-0.77878200
H	-3.78765700	-2.01025000	-1.72493500

INTc

$G_{acetonitrile}$= -1715.253395 a.u.

$E_{acetonitrile}$ = -1715.504317 a.u.

C	-0.73025900	1.37628100	1.43140000
C	-0.02307200	2.58172900	1.52472800
C	-0.55142600	3.74573900	2.06277200

C	-1.86450500	3.65097500	2.53646000
C	-2.58494600	2.44136400	2.47592800
C	-2.03264600	1.28335500	1.92703200
H	0.02372500	4.66840700	2.11864700
H	-2.33705700	4.53161000	2.97172600
H	-3.60035200	2.40942300	2.87054300
H	-2.58407200	0.34922100	1.89013100
O	1.23526500	2.36532100	1.02002100
N	0.11653600	0.45194500	0.81160700
C	1.26524100	1.06261900	0.62291600
C	2.51383500	0.51522900	0.14562800
C	3.54659700	1.39173800	-0.19541600
C	2.73886000	-0.91493300	0.13573500
C	4.80065600	0.90137700	-0.55204200
H	3.37687500	2.46420200	-0.17966500
C	4.05519800	-1.36147000	-0.20676100
C	5.05768400	-0.48809600	-0.55232000
H	4.22985900	-2.43643800	-0.20371500
H	6.04493500	-0.84961900	-0.82998500
O	1.84903300	-1.79044000	0.43602500
N	5.84012500	1.82065800	-0.91285000
O	6.95112300	1.36956800	-1.21222000
O	5.59564500	3.03197200	-0.91350000
Os	-0.24649200	-1.58013700	0.17754200
C	0.19976000	-1.00954800	-1.76592200
C	-0.55788800	-2.11974700	2.16121500
N	-0.72628400	-2.41035800	3.28421100
N	0.48857500	-0.68501600	-2.85455200
C	-0.38942800	-3.52341400	-0.33799800
N	-0.45565600	-4.65832000	-0.62883300
H	-2.72811400	-2.14161500	0.32387700
N	-2.17351600	-1.38664900	-0.08179000
C	-4.39785300	-0.64901300	-0.55642500
C	-2.97441700	-0.47095500	-0.64937900
C	-2.46254600	0.70648700	-1.28552300
C	-3.33033500	1.64074300	-1.76787500
C	-4.78817000	1.48841600	-1.67306100
C	-5.27219400	0.28488600	-1.04151600
H	-4.77064800	-1.55229100	-0.07010300
H	-6.35038700	0.14624100	-0.96119600
O	-2.91739600	2.77955000	-2.36491800
H	-3.73895800	3.25467800	-2.60403200
O	-5.51096500	2.40236100	-2.14129000
H	-1.39139500	0.85151900	-1.37436000

TS1

$G_{acetonitrile}$= -1715.599859 a.u.

$E_{acetonitrile}$ = -1715.855799 a.u.

C	-0.08987600	2.30934700	-0.18580000
C	0.96403000	3.22444500	-0.06530100
C	0.78902600	4.59760200	-0.00998100
C	-0.53690000	5.03832900	-0.08704000
C	-1.60961700	4.13451800	-0.21116900
C	-1.41042000	2.75362800	-0.26504700
H	1.62912300	5.28295000	0.08640800
H	-0.74312300	6.10796300	-0.05122300
H	-2.62647700	4.52104400	-0.26931700
H	-2.24561300	2.07013900	-0.37381500
O	2.13601500	2.50567700	-0.01641100
N	0.48626700	1.03467900	-0.18344000
C	1.79170200	1.20218300	-0.09288800
C	2.82967900	0.20184600	-0.10656000
C	4.13925900	0.55143200	0.23684600
C	2.52786000	-1.12876400	-0.55648100
C	5.14984600	-0.39894400	0.14752700
H	4.36969000	1.55789800	0.57356600
C	3.59783100	-2.06044800	-0.65021400
C	4.88277200	-1.70970500	-0.29896300
H	3.36683300	-3.06617700	-0.99711300
H	5.69489400	-2.43030400	-0.35805100
O	1.33434000	-1.47460900	-0.91572300
N	6.49710500	-0.03130700	0.51747300
O	7.38246900	-0.88155900	0.42132500
O	6.70974400	1.11516200	0.91314900
Os	-0.51118200	-0.87180800	-0.15382700
C	-1.20294100	-0.60488300	-2.10831300
C	0.31460000	-1.19520100	1.73581700
N	0.80131500	-1.36623400	2.78178700
N	-1.67587300	-0.50093200	-3.17202900
C	-1.05834500	-2.83307400	-0.27253500
N	-1.37177100	-3.95361700	-0.34015500
H	-2.32121900	-0.43512100	1.59807500
N	-2.02891000	-0.34662000	0.61741300
C	-4.99365400	-1.22824100	1.94830600
C	-4.95969300	0.13994400	1.91165000
C	-4.55946300	0.85483600	0.71462500
C	-4.09379100	0.00606600	-0.41693400
C	-4.21048100	-1.41182300	-0.35701900

C	-4.63149600	-2.01373000	0.80576300
H	-4.68393000	-3.10007800	0.86214400
O	-3.79096100	0.66817300	-1.51915100
H	-3.32614000	0.11843100	-2.18382500
H	-5.26271100	0.74170800	2.76818800
H	-5.31362100	-1.73956200	2.85647900
H	-3.91796600	-2.00202000	-1.22436100
O	-4.58490600	2.09247900	0.61164000

TS2

$G_{acetonitrile}$= -1791.981192 a.u.

$E_{acetonitrile}$ = -1792.259962 a.u.

C	0.54400500	2.09179000	-0.86171500
C	-0.32907900	3.15278000	-0.58985500
C	0.04072100	4.48702300	-0.64122900
C	1.36902800	4.73086600	-1.00728600
C	2.25598000	3.67989600	-1.30993500
C	1.86068700	2.34321300	-1.24643500
H	-0.66054600	5.28879800	-0.41740400
H	1.72244000	5.75999900	-1.06863400
H	3.27818800	3.91589100	-1.60347700
H	2.54596700	1.54103400	-1.50026600
O	-1.56005100	2.61441200	-0.29076600
N	-0.18544900	0.91581200	-0.66562900
C	-1.41850800	1.27342800	-0.36603000
C	-2.57229900	0.42277100	-0.21932300
C	-3.74704100	0.92253700	0.34973700
C	-2.53997200	-0.90074000	-0.78353300
C	-4.88721300	0.12819700	0.37857300
H	-3.77171400	1.92462200	0.76834800
C	-3.74129100	-1.66136500	-0.76067700
C	-4.88887600	-1.16650400	-0.18128500
H	-3.72000400	-2.65833100	-1.19741800
H	-5.79782900	-1.76225100	-0.14570500
O	-1.47573500	-1.38260100	-1.34179900
N	-6.09105200	0.64465100	0.98733700
O	-7.09640400	-0.06618000	0.99050700
O	-6.06762200	1.77341100	1.47887900
Os	0.48474500	-1.12446200	-0.66187300
C	-0.19247200	-1.27099700	1.22766800
C	1.14294000	-0.87250300	-2.63323600
N	1.52912100	-0.70387300	-3.72238400
N	-0.66957900	-1.26096600	2.30468500
C	0.68205900	-3.14670600	-0.82649300

N	0.77165000	-4.30500000	-0.93333700
H	2.93390700	-0.59498700	-0.85116500
N	2.24180200	-0.77508600	-0.11742100
C	5.18506300	1.11350700	0.91198100
C	5.36600300	-0.32747900	0.80432100
C	4.32984000	-1.17053600	0.95928500
C	2.90969700	-0.69799200	1.24369100
C	2.82958400	0.86669100	1.54026800
C	4.00171000	1.68403700	1.24932800
H	6.36939000	-0.71126500	0.61792000
H	3.90065500	2.76005700	1.38751100
O	2.33186100	-1.41815400	2.19112600
H	-0.13034600	-1.04437700	3.27641000
H	4.44465900	-2.25335900	0.90101400
O	1.79765600	1.31872500	2.00655200
H	6.05460200	1.75138700	0.74435200
O	0.94756600	-0.76530500	4.13653000
H	1.62453000	-0.94303300	3.34277100
H	0.96845800	0.19021700	4.28016300

TS3

$G_{acetonitrile}$= -1792.376236 a.u.

$E_{acetonitrile}$ = -1792.671168 a.u.

C	0.51835800	2.20601000	-0.73103700
C	-0.38559900	3.21632800	-0.38349900
C	-0.05403800	4.56044100	-0.33239700
C	1.27218100	4.86304200	-0.65971400
C	2.19599900	3.86152700	-1.02079900
C	1.83890000	2.51403000	-1.06522600
H	-0.77788000	5.32535100	-0.05791900
H	1.59780200	5.90296000	-0.63950400
H	3.21639300	4.14858300	-1.27218800
H	2.54452700	1.73754200	-1.34624800
O	-1.59678800	2.61882500	-0.11652400
N	-0.16899900	0.99412800	-0.62741600
C	-1.41097600	1.29364400	-0.28943900
C	-2.52573800	0.39800900	-0.14621700
C	-3.73893300	0.88826000	0.36242900
C	-2.44013800	-0.96567900	-0.57029200
C	-4.82893100	0.04010300	0.46783900
H	-3.82289500	1.92360300	0.67790300
C	-3.58308800	-1.79150000	-0.45130400
C	-4.76699800	-1.30450000	0.06564400
H	-3.49671400	-2.82551300	-0.77972400

H	-5.64280400	-1.94075800	0.16320300
O	-1.35860300	-1.51163000	-1.09021300
N	-6.07889300	0.56565100	1.01404100
O	-7.03209900	-0.19940700	1.10430700
O	-6.11449800	1.74245200	1.35453900
Os	0.53859300	-0.97829800	-0.92446000
C	0.56910800	-1.66894800	1.10113300
C	1.31912400	-0.38423000	-2.73009300
N	1.75110500	-0.07192700	-3.76887700
C	1.01803000	-2.88527400	-1.42725300
N	1.28337400	-3.98204900	-1.72932200
H	3.15424400	-1.29954100	-0.84542400
N	2.47958700	-0.71532900	-0.35904900
C	4.67321600	1.39365300	1.95872900
C	5.08800200	0.01345200	1.71292200
C	4.21916800	-0.91539500	1.27719500
C	2.82208900	-0.52956000	0.94759300
C	2.33681700	0.79394000	1.59562800
C	3.38022600	1.78138600	1.86909100
H	5.43659400	2.11377900	2.25467700
H	6.13380600	-0.24988800	1.86810900
H	3.05267200	2.78926700	2.11787800
O	1.81068400	-1.64898300	1.72031000
N	-0.38124500	-2.11958300	1.81591300
H	1.70480500	-1.72429800	2.78380900
O	1.10085400	-1.91578300	4.04726200
H	-1.28047700	-2.16447800	1.34739300
H	1.40122300	-2.69704000	4.53283200
H	0.24672300	-2.15251600	3.60094500
O	1.16358800	0.96866100	1.86554500
H	4.51859400	-1.93812000	1.04881900

TS4

$G_{acetonitrile}$= -1792.439225 a.u.

$E_{acetonitrile}$ = -1792.733325 a.u.

C	0.27924800	2.43663000	-0.19901500
C	-0.76520800	3.35227000	-0.02757000
C	-0.58269300	4.72049700	0.08627500
C	0.74417600	5.15826000	0.00948900
C	1.80894500	4.25745500	-0.18248000
C	1.59906900	2.88152000	-0.29516100
H	-1.41806300	5.40518700	0.22010200
H	0.95663000	6.22408300	0.09058700
H	2.82489500	4.64468800	-0.25235000

H	2.42112400	2.19607900	-0.47154500
O	-1.94393100	2.64075000	-0.01921300
N	-0.30767600	1.16676000	-0.25942900
C	-1.61684600	1.34203900	-0.17701000
C	-2.67179400	0.36543800	-0.26093200
C	-3.97826600	0.76389700	0.05613500
C	-2.41981100	-0.97121300	-0.74044100
C	-5.03334600	-0.12503000	-0.08689900
H	-4.16947500	1.77063400	0.41494100
C	-3.54654100	-1.83477200	-0.89733400
C	-4.81982300	-1.43411500	-0.57245600
H	-3.35470900	-2.83963900	-1.26960500
H	-5.66408800	-2.11088200	-0.67978000
O	-1.25529200	-1.42841000	-1.05420300
N	-6.36669200	0.30035100	0.26387000
O	-7.29131200	-0.50103500	0.12211600
O	-6.53141700	1.44370600	0.69154300
Os	0.59070000	-0.75671600	-0.34237500
C	0.32076800	-2.09046000	1.25481800
C	1.27205700	-0.26568100	-2.17345500
N	1.63589700	0.08755100	-3.22373900
C	1.43148800	-2.50534500	-0.96112800
N	1.88568700	-3.52417900	-1.30236100
H	2.06816500	0.32121200	1.49707700
N	2.25702600	-0.13072800	0.58962400
C	6.36768700	-0.12687000	0.22569000
C	5.55544400	-0.70756600	-0.82742000
C	4.19975500	-0.73092900	-0.74903600
C	3.54784400	-0.16790000	0.40687200
C	4.37871600	0.44950100	1.51654500
C	5.82134000	0.42418700	1.34161000
H	7.45170600	-0.13966700	0.10520600
H	6.05670300	-1.13366200	-1.69596800
H	6.43234500	0.85990800	2.13128400
O	-0.25762600	-1.01376100	1.66371800
N	0.38986700	-3.25544000	1.70573000
H	-1.42507100	-1.44911500	2.26727500
O	-2.17386000	-2.08937400	2.70715100
H	0.86405800	-3.91292000	1.08793600
H	-2.44849400	-1.78412600	3.59033400
H	-1.75370000	-2.97359400	2.77924900
H	3.59497700	-1.16690100	-1.53694900
O	3.81066200	0.94037700	2.49442200

TS5

$G_{acetonitrile}$= -1792.460148 a.u.

$E_{acetonitrile}$ = -1792.757763 a.u.

C	0.63216800	1.92256700	1.10243000
C	-0.35251800	2.91000600	1.21080600
C	-0.09959900	4.22415300	1.56841400
C	1.24051600	4.53118000	1.82120900
C	2.24966400	3.55456600	1.72109800
C	1.96665200	2.23613000	1.36323900
H	-0.89542700	4.96230400	1.64661300
H	1.50913500	5.54833900	2.10524300
H	3.28170500	3.83363900	1.92992800
H	2.75153900	1.49408800	1.29509500
O	-1.56162700	2.32581700	0.91567600
N	-0.03041200	0.74228100	0.72834300
C	-1.32057500	1.03320500	0.63186200
C	-2.43759100	0.19830300	0.26632600
C	-3.68282000	0.80345100	0.04702900
C	-2.30405600	-1.23009400	0.18063700
C	-4.78890200	0.02210800	-0.25481200
H	-3.78857400	1.88179900	0.11183900
C	-3.47212200	-1.98820200	-0.11755700
C	-4.68805800	-1.38269100	-0.33681300
H	-3.36622000	-3.07007100	-0.17599200
H	-5.57113000	-1.97049500	-0.57559200
O	-1.19087200	-1.85107600	0.40178700
N	-6.06279300	0.66363600	-0.48598400
O	-7.03464900	-0.04606100	-0.74501900
O	-6.12860000	1.89089600	-0.41502700
Os	0.77193100	-1.09574500	-0.01915600
C	1.02056800	-1.21180100	2.13424700
C	0.73266700	-2.48948200	-1.50667400
N	0.63727600	-3.23486100	-2.39558900
C	1.74215700	-2.76413700	0.61706600
N	2.31824400	-3.71466200	0.96675400
H	3.62202300	-0.54777200	0.50111600
N	2.51579900	-0.31212600	-0.49322500
C	2.31132000	2.29617100	-3.65756600
C	1.17120200	1.62045000	-3.28344200
C	1.25523300	0.70691200	-2.20202700
C	2.53288000	0.51601100	-1.51321400
C	3.69235300	1.24836100	-1.94969700
C	3.57427500	2.11702100	-2.99745700
H	2.25917000	2.99822600	-4.49081100

H	0.21959900	1.76675600	-3.79219000
H	4.43500300	2.68729100	-3.34436200
O	2.06249500	-0.82758800	2.74163900
N	-0.02366000	-1.60411200	2.83370000
H	0.02194800	-1.64844700	3.84596900
O	4.08099100	-0.76149700	1.43775300
H	-0.85459700	-1.92186000	2.34406100
H	3.08494300	-0.76569800	2.14457100
H	4.73312800	-0.08488900	1.66307100
O	0.26251900	0.01846600	-1.77120500
H	4.63531500	1.09552000	-1.42615600

TS6

$G_{acetonitrile}$= -1792.442382 a.u.

$E_{acetonitrile}$ = -1792.737648 a.u.

C	0.51937800	2.40431000	-0.21002100
C	-0.45548300	3.33562700	0.16969000
C	-0.19650200	4.67618800	0.40737400
C	1.13333800	5.07239000	0.23417200
C	2.12803900	4.15870600	-0.16523900
C	1.84204200	2.81302300	-0.39881300
H	-0.98054600	5.37101800	0.70250400
H	1.40407900	6.11432900	0.40390000
H	3.14922700	4.51292300	-0.30348100
H	2.61350600	2.12609200	-0.72652500
O	-1.65623900	2.67379800	0.23351300
N	-0.13046900	1.17182800	-0.34299000
C	-1.40489700	1.38539200	-0.09161200
C	-2.52115000	0.46919700	-0.14618900
C	-3.77726300	0.91504400	0.28045900
C	-2.37199200	-0.86169600	-0.65896900
C	-4.87760800	0.06883800	0.21406800
H	-3.89720200	1.92187000	0.66765900
C	-3.52803400	-1.68740800	-0.71738300
C	-4.75912300	-1.24051600	-0.28853300
H	-3.40550100	-2.69492300	-1.11089700
H	-5.63494500	-1.88329300	-0.33131800
O	-1.25024700	-1.35951000	-1.08267200
N	-6.16344300	0.54692800	0.67150700
O	-7.12545200	-0.21829000	0.61062200
O	-6.24657100	1.69615500	1.10371900
Os	0.71577600	-0.76156300	-0.81021600
C	0.13924200	-1.41849500	1.15541000
C	0.57689000	-0.21829700	-2.83420600

N	0.51039100	0.10612200	-3.95197000
C	1.27925800	-2.64574300	-1.30618700
N	1.57725700	-3.75149600	-1.53213900
N	2.35245000	-0.39514100	-0.27016500
C	5.89998900	0.21446500	1.68175700
C	5.79141600	0.51132200	0.27322000
C	4.62301100	0.30474100	-0.38755700
C	3.47481200	-0.21322800	0.32773900
C	3.55986800	-0.53660700	1.80410400
C	4.85725500	-0.28052700	2.40589300
H	6.85597900	0.39326600	2.17588900
H	6.66030700	0.89809000	-0.25808200
H	4.95414500	-0.50337700	3.46831800
O	-0.55773900	-0.73130900	1.90165000
H	-1.55715400	-1.72126700	2.69090200
O	-1.81914300	-2.70475400	2.82196700
H	-2.69225300	-2.88272600	2.42935500
H	-1.03568000	-3.10069000	2.23874800
H	4.51240500	0.51046800	-1.45106400
O	2.58998100	-0.97610100	2.42385000
N	0.39376100	-2.75157600	1.57638100
H	0.87555500	-3.31818000	0.88143200
H	0.92781100	-2.75176200	2.44847800

TS7

$G_{acetonitrile}$= -1716.081619 a.u.

$E_{acetonitrile}$ = -1716.351759 a.u.

C	-0.40737700	2.22538000	0.67274300
C	0.55723000	3.21693800	0.45539700
C	0.29851400	4.57421700	0.55422300
C	-1.01199900	4.90954700	0.91097700
C	-1.99069900	3.92541400	1.15409500
C	-1.70924900	2.56420800	1.03949700
H	1.06690800	5.32392200	0.37588400
H	-1.28007100	5.96102800	1.01236500
H	-2.99441900	4.23669100	1.44143300
H	-2.46006600	1.80589100	1.23975400
O	1.74855700	2.58512100	0.16439700
N	0.23212300	1.00100200	0.45699400
C	1.50063800	1.26387500	0.20113000
C	2.57927600	0.31692700	0.08082500
C	3.80403800	0.70416500	-0.47677000
C	2.43240800	-0.97970600	0.67796300
C	4.86881300	-0.18483900	-0.45992300

H	3.92074400	1.68966900	-0.91875200
C	3.55710500	-1.84014900	0.70181600
C	4.75418700	-1.45749900	0.13270300
H	3.44358200	-2.81826900	1.16528700
H	5.61071100	-2.12726500	0.13116300
O	1.31235100	-1.35644000	1.23440400
N	6.12923300	0.21293600	-1.06113600
O	7.06780400	-0.57827500	-1.01756300
O	6.20327500	1.32093800	-1.58671600
Os	-0.57164100	-0.97000900	0.52415500
C	0.20563700	-1.45020100	-1.34718100
C	-1.19635300	-0.58030700	2.45713300
N	-1.54238900	-0.35480200	3.54621900
C	-0.92512600	-2.96157800	0.84736500
N	-1.11657600	-4.09430700	1.03513300
N	-2.18585200	-0.66823100	-0.16438000
C	-5.91868800	-0.11613600	-1.72705200
C	-5.53326400	-1.40581900	-1.19278900
C	-4.28530800	-1.61884900	-0.71111800
C	-3.32475400	-0.52523300	-0.71677000
C	-3.66970400	0.80219000	-1.38172100
C	-5.05181800	0.92886500	-1.80760900
H	-6.94092600	0.00749300	-2.08624000
H	-6.26891900	-2.20915800	-1.16987500
H	-5.34434100	1.88876400	-2.23205700
O	0.77416100	-2.13062900	-2.07046100
H	-0.66934000	-0.06389700	-3.49654200
H	0.51074200	0.85787100	-2.81288300
N	-0.33084400	0.32010700	-2.61700600
H	-1.04714200	0.94232200	-2.23551900
O	-2.81008600	1.66048400	-1.56482300
H	-3.97217800	-2.56941100	-0.28408100

TSa

$G_{acetonitrile}$= -1715.597795 a.u.

$E_{acetonitrile}$ = -1715.85539 a.u.

C	0.18911800	2.19804500	-0.48140200
C	-0.78062800	3.19359100	-0.30481200
C	-0.50715900	4.55119100	-0.35553800
C	0.82696800	4.88772400	-0.61018900
C	1.81487400	3.90267700	-0.80515700
C	1.51568700	2.54065100	-0.74853500
H	-1.28168000	5.30218900	-0.21112700
H	1.10732200	5.93954100	-0.66435400

H	2.83927300	4.21186800	-1.01066200
H	2.27434500	1.78365300	-0.91665500
O	-1.98468600	2.56543600	-0.09369400
N	-0.46111900	0.97035700	-0.33710300
C	-1.73452700	1.23617700	-0.13279400
C	-2.83739300	0.31447400	-0.00205600
C	-4.07952200	0.79274000	0.43162000
C	-2.69240300	-1.05899500	-0.39263600
C	-5.16775600	-0.06813500	0.49318200
H	-4.19566700	1.83276700	0.72126400
C	-3.83850800	-1.89544700	-0.32867500
C	-5.05438500	-1.41878700	0.11205100
H	-3.72140800	-2.93484600	-0.63025500
H	-5.92379200	-2.06898200	0.17036200
O	-1.57719500	-1.56395600	-0.83268600
N	-6.44293300	0.43995300	0.95595800
O	-7.39766000	-0.33431400	0.99812200
O	-6.52115100	1.62193000	1.28698500
Os	0.35401900	-1.02681600	-0.36017500
C	-0.30585900	-1.19333400	1.62479500
C	0.77149100	-0.84395900	-2.39598700
N	1.02418500	-0.72583300	-3.52915300
N	-0.70539400	-1.26177100	2.71837600
C	0.87408100	-2.98449800	-0.49704200
N	1.18130100	-4.10846700	-0.56875100
H	2.31107000	0.09225000	0.93679200
N	2.00454000	-0.57705500	0.21788800
C	5.02905100	0.81678800	0.48752800
C	5.00419900	-0.06286100	1.68919300
C	4.40933300	-1.32230600	1.71130700
C	3.78990000	-1.77548700	0.55068400
C	3.72318500	-0.92832400	-0.62190200
C	4.38817400	0.31520500	-0.66524000
H	3.34320500	-2.76611900	0.50385100
H	3.36062400	-1.36789100	-1.54821700
H	4.42237300	-1.92096600	2.62068700
O	5.62513700	1.91648100	0.63980600
O	5.60865900	0.46149000	2.72988900
H	5.92607900	1.34435100	2.40005000
H	4.37641500	0.91060200	-1.57666400

TSb

$G_{acetonitrile}$= -1792.012161 a.u.

$E_{acetonitrile}$ = -1792.29155 a.u.

C	-0.20340200	2.35003000	-0.17357200
C	-1.26446400	3.26031500	-0.07218900
C	-1.09596900	4.63535300	-0.04293700
C	0.22727700	5.08284300	-0.13293300
C	1.30654300	4.18576200	-0.25031800
C	1.11404700	2.80314100	-0.27794600
H	-1.93882500	5.31913900	0.03982000
H	0.42632700	6.15434100	-0.11841900
H	2.31858700	4.58160100	-0.32988700
H	1.94577100	2.11384200	-0.39235400
O	-2.43124200	2.53460200	-0.02154000
N	-0.76611100	1.07303000	-0.14438300
C	-2.07062400	1.22922700	-0.07913800
C	-3.09378900	0.21312100	-0.11505800
C	-4.41048100	0.56221200	0.20670900
C	-2.78840300	-1.12177200	-0.56103800
C	-5.42373200	-0.38311200	0.10839000
H	-4.64353600	1.57063400	0.53559000
C	-3.86646700	-2.04618900	-0.66352900
C	-5.15521800	-1.69608000	-0.32942900
H	-3.63279900	-3.05282600	-1.00631600
H	-5.96712000	-2.41606100	-0.39750500
O	-1.60254300	-1.51009100	-0.91304500
N	-6.77435900	-0.00800400	0.45858700
O	-7.66147800	-0.85570800	0.35602600
O	-6.98839700	1.14145200	0.84471100
Os	0.20319900	-0.83686800	-0.16029400
C	-0.60928100	-1.13803400	1.74259000
C	0.81662900	-0.46981200	-2.11219600
N	1.11436100	-0.23834000	-3.21881200
N	-1.09563500	-1.27616000	2.79605300
C	0.97710100	-2.69551100	-0.27460900
N	1.51821200	-3.73506400	-0.24746200
H	1.64270400	0.29176000	1.54193600
N	1.79804000	-0.21081400	0.66474700
C	5.89258400	0.15726600	-0.34449400
C	5.35278100	0.66899000	0.92926800
C	4.06603300	0.45481200	1.29666700
C	3.18496900	-0.37742800	0.46712500
C	3.68642100	-0.78630400	-0.84302200
C	4.97993300	-0.57606200	-1.19969700
H	3.36331400	-1.54632500	1.03206500
H	3.01268900	-1.32612200	-1.50062000
H	3.68888600	0.84451100	2.24324400

O	7.08688900	0.38712900	-0.61084600
O	6.23009300	1.36485300	1.68126100
H	7.06852300	1.36300200	1.17834900
H	5.36355800	-0.94031600	-2.15253900
O	3.42579500	-2.80653400	1.56540000
H	4.31747900	-3.17654000	1.48209700
H	2.82195800	-3.33345900	0.97817400