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Oxidation of Hydroquinones by a (Salen)ruthenium(VI) Nitrido Complex

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Materials. $[Ru^{VI}(N)(L)(MeOH)](PF_6)$ (**RuN**) and the 50% ^{15}N-labeled complex (**Ru^{15}N**) were prepared by a literature method.[1] Hydroquinone (Sigma-Aldrich, 99%), 2-methylhydroquinone (Sigma-Aldrich, 99%), 2-methoxylhydroquinone (Sigma-Aldrich, 98%), 2-chlorohydroquinone (Sigma-Aldrich, 85%), 2,5-di-tertbutylhydroquinone (Sigma-Aldrich, 99%) and pyridine were purified according to literature procedures.[2] d_6-Hydroquinone (98 atom % D from Cambridge Isotope Laboratories, Inc) was used as received.

Kinetics. The concentrations of hydroquinones (H_2Qs) were at least in 10-fold excess to that of **RuN**. The reaction progress was monitored by observing absorbance changes at 710 nm. Pseudo-first-order rate constants, k_{obs}, were obtained by nonlinear least-square fits of A_t vs t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbance, respectively.

Physical measurements. Electrospray ionization mass spectra (ESI/MS) were obtained on a PE SCIEX API 365 mass spectrometer. The analyte solution was continuously infused with a syringe pump at a constant flow rate of 5 μL min^{-1} into the pneumatically assisted electrospray probe with nitrogen as the nebulising gas. The declustering potential was typically set at 10–20 V. Elemental analyses were done on an Elementar Vario EL analyzer. The kinetics of the reactions were studied by using an Agilent 8453 diode-array spectrophotometer. The temperature of the solutions were maintained with a PolyScience digital temperature controller connected to a circulating water bath. Gas chromatographic analyses of organic products were performed on a HP5890 GC/FID gas chromatograph equipped with a DB-FFAP (30 m × 0.25 mm i.d.) or a HP-5MS (30 m × 0.25 mm i.d.) capillary column. GC/MS measurements were carried out on a HP6890 gas chromatograph interfaced to a HP5975 mass selective detector. N_2 was detected by using GC (Shimadzu GC-17A) equipped with a 5Å molecular sieve column and a thermal conductivity detector (TCD).

X-ray Analysis. Measurements were collected on an Oxford Xcalibur, Sapphire 3, Gemini Ultra diffractometer with a mirror-monochromated Cu-Kα radiation (λ = 1.54178 Å) at 193 K. Details of the intensity data collection and crystal data are given in Table S1. Absorption corrections were done by the multiscan 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.[3,4] All non-hydrogen atoms were refined anisotropically. H atoms were generated by the program SHELXL-97. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times or 1.5 times that of the associated C atoms and 1.2 times that of the associated N atoms, all these were participated in the calculation of final R-indices. All calculations were performed using the teXsan crystallographic software.[5]

DFT Calculations. The structures and energies of all molecular species are calculated at the B3LYP[6] level with the LanL2TZ(f) basis sets[7] for Ru and 6-311G(d,p) basis set for nonmetal atoms. The polarizable continuum model (PCM)[8] is used to account for the solvent effect in dichloromethane. All calculations are performed with Gaussian 09 package of program.[9]

Synthesis of $[Ru^{III}(L)(NH_3)(py)]PF_6 \cdot 2.5CH_3OH$ (1) and $[Ru^{III}(L)(py)_2]PF_6$ (2). An orange solution of **RuN** (41 mg, 0.067 mmol) in $(CH_2Cl)_2$ (50 mL) was slowly added into a mixture containing hydroquinone (220 mg, 2.0 mmol) and py (1.98 g, 25 mmol) in $(CH_2Cl)_2$ (200 mL) with vigorous stirring over a period of 30 min. The mixture was stirred for additional 1 h. The solution was then concentrated to 2 mL under vacuum and excess diethyl ether was added. The resulted precipitate was dissolved in minimum amount of CH_2Cl_2 and loaded onto a silica-gel column (30 × 2 cm). The column was first flushed with CH_2Cl_2 (200 mL) and then eluted with CH_2Cl_2-acetone (v/v, 10:1) to give complex **2** as a green solid (yield 27%). λ_{max} [nm] (ε [$mol^{-1}dm^3cm^{-1}$]) 350 (13000), 382 (15200), 508 (1590), 723 (4170). The synthesis of complex **2** has been previously reported by us.[10] The column was then eluted with CH_2Cl_2-MeOH

(v/v, 20:1) to give complex **1** as a blue solid (yield 55%). Single crystals of **1** suitable for X-ray crystallography were obtained by slow diffusion of Et_2O into a solution of **1** in MeOH at room temperature. (Found: C, 44.23; H, 4.97; N, 7.68. $C_{25}H_{28}N_4O_2PF_6Ru{\cdot}2.5CH_3OH$ requires C, 44.48; H, 5.16; N, 7.54. λ_{max} [nm] (ε [$mol^{-1}dm^3cm^{-1}$]) 348 (9390), 382 (9970), 500 (1270), 702 (3000). ESI/MS in MeOH: *m/z* 518.

Determination of organic products by GC and GC-MS. 10 mL of a $(CH_2Cl)_2$ solution of **RuN** (0.01 mmol) was slowly added to 20 mL of a $(CH_2Cl)_2$ solution of hydroquinone (0.167 mmol) and py (2.8 mmol) with vigorous stirring over a period of 20 min under argon. The solution was stirred for one more hour and was then analyzed by GC using chlorobenzene as internal standard. 8.78 μmol *p*-Benzoquinone was produced.

Determination of N_2. In a typical experiment a degassed solution of **RuN** (0.02 mmol) in 15 mL $(CH_2Cl)_2$ was added to a degassed solution of H_2Q (1.82 mmol) and py (1.98 g, 25 mmol) in 200 mL $(CH_2Cl)_2$. The mixture was stirred for 1.5 h and then analyzed by GC/TCD. 0.0036 mmol N_2 (yield 18% based on **RuN**) was found to be produced.

Determination of pK_a of 1. The pK_a of **1** in CH_3CN was determined by titration using DBU (1,8-Diazabicycloundec-7-ene) according to a literature method.[11] A 3.0 mL solution of **1** (0.128 mM) was titrated with DBU in CH_3CN. 4000 equiv of DBU completely converted **1** to $RuNH_2$. An aliquot of **1** (3.0 mL, 0.128 mM) was firstly titrated with increments of 1.0 equiv (5 μL) of DBU (76.8 mM) until 5.0 equiv. Then the solution was titrated with increments of 10 equiv (5 μL) of DBU (768 mM) until 55 equiv. Following the above procedure, 20 equiv (5μL), 100 equiv (5.8μL), 200

equiv (11.6μL) DBU were further added. UV-vis spectra were recorded for the initial **1** and after each addition of DBU, and the data were analyzed using the absorbance at 686 nm. The plot of $[RuNH_2][DBUH^+]/[\mathbf{1}]$ versus [DBU] yielded a straight line with slope $K_{eq} = (6.74 \pm 0.16) \times 10^{-4}$. The p$K_a$ of **1** is given by pK_a(**1**) = pK_a($DBUH^+$) - log $K_{eq} = 27.5 \pm 0.1$ using the known pK_a of 23.34 for $DBUH^+$.[12]

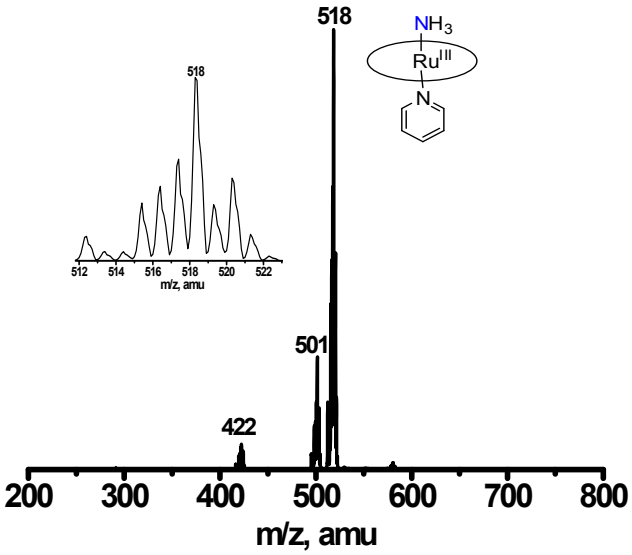


Fig. S1a ESI/MS spectrum of **1**. Inset shows the expanded pattern.

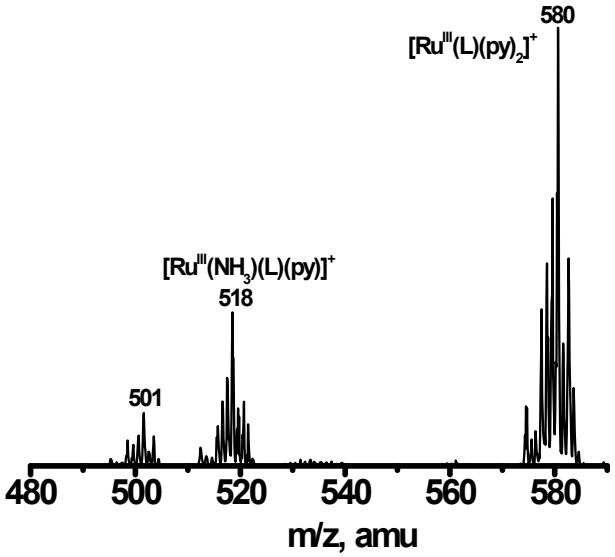


Fig. S1b ESI/MS spectrum of a solution containing $[Ru(L)(NH_3)(py)]^+$ (4.2×10^{-4} M) and $[Ru(L)(py)_2]^+$ (2.1×10^{-4} M) in $(CH_2Cl)_2$. The sensitivity of $[Ru(L)(NH_3)(py)]^+$ is relatively lower than that of $[Ru(L)(py)_2]^+$ under our experimental conditions.

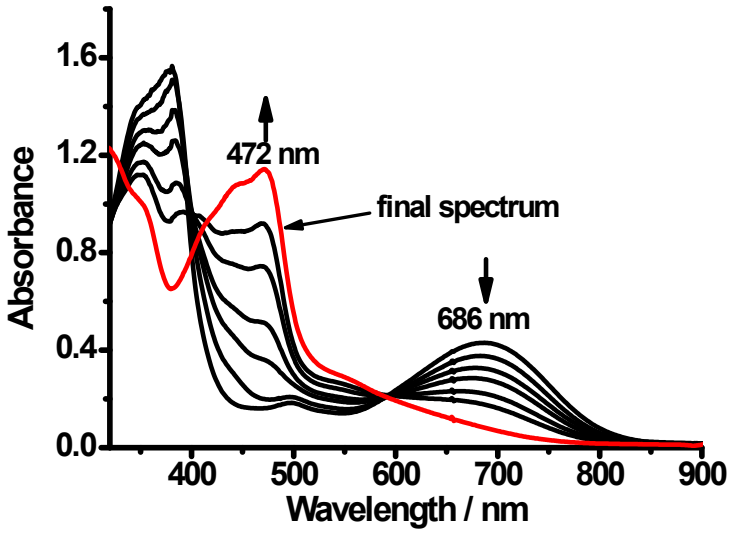


Fig. S2 UV-vis titration plot of **1** using DBU in CH_3CN.

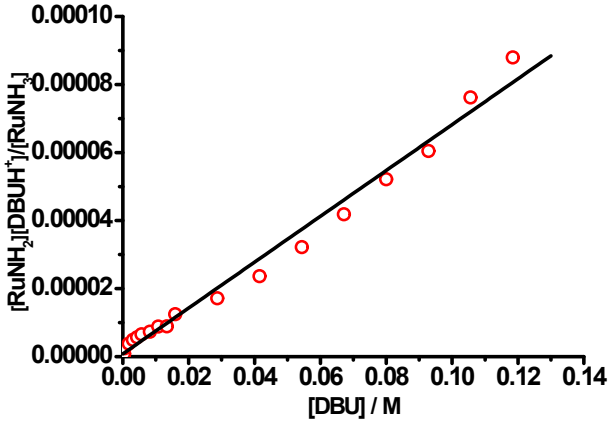


Fig. S3 Plot of $[RuNH_2][DBUH^+]/[\mathbf{1}]$ vs. [DBU] for the equilibrium titration: **1** + DBU ⇌ $RuNH_2$ + $DBUH^+$ in CH_3CN. The slope of the linear plot ($R^2 = 0.99$) is the equilibrium constant $K_{eq} = (6.74 \pm 0.16) \times 10^{-4}$.

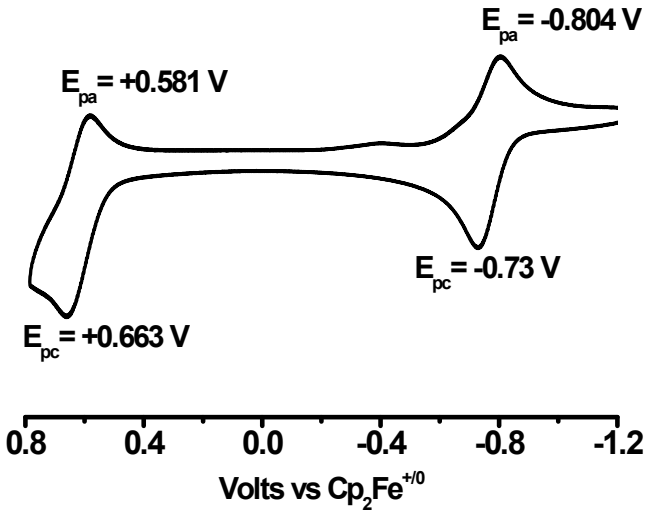


Fig. S4 Cyclic voltammogram of **1** in CH_3CN.

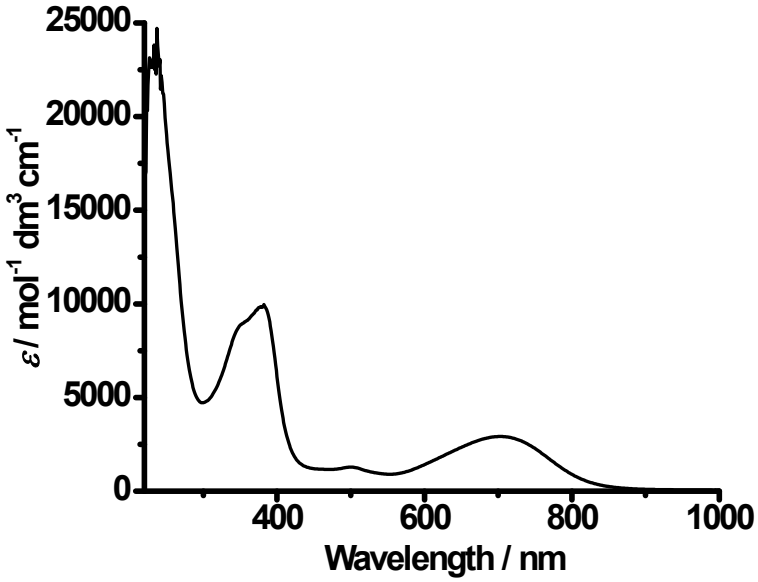


Fig. S5 UV–vis spectrum of **1** in $(CH_2Cl)_2$.

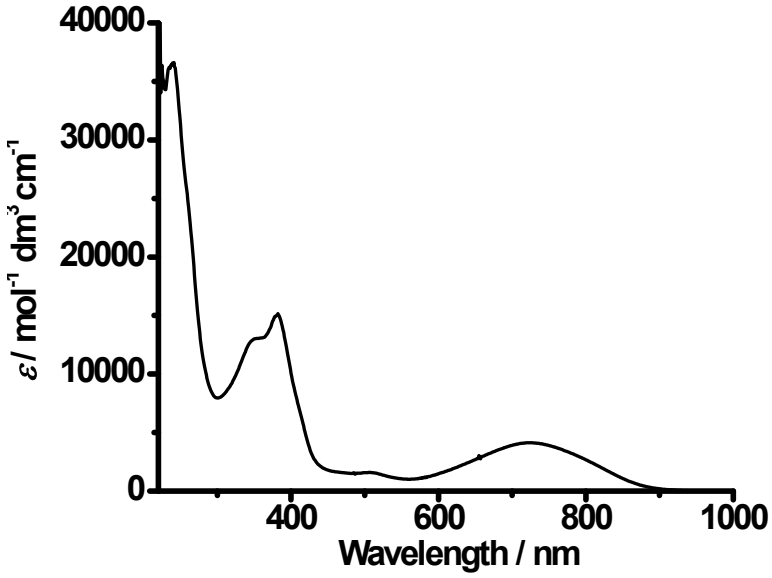


Fig. S6 UV–vis spectrum of **2** in $(CH_2Cl)_2$.

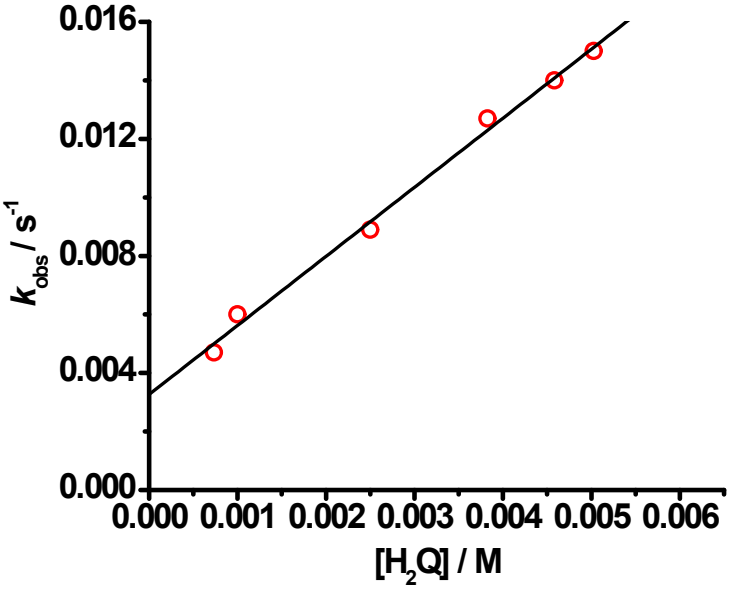


Fig. S7 Plot of k_{obs} vs [H_2Q] for the reaction between **RuN** (5.00×10^{-5} M) and H_2Q in the presence of py (0.1 M) in $(CH_2Cl_2)_2$ at 25 °C [slope = (2.36 ± 0.09); *y*-intercept = $(3.27 \pm 0.29) \times 10^{-3}$; $r^2 = 0.993$].

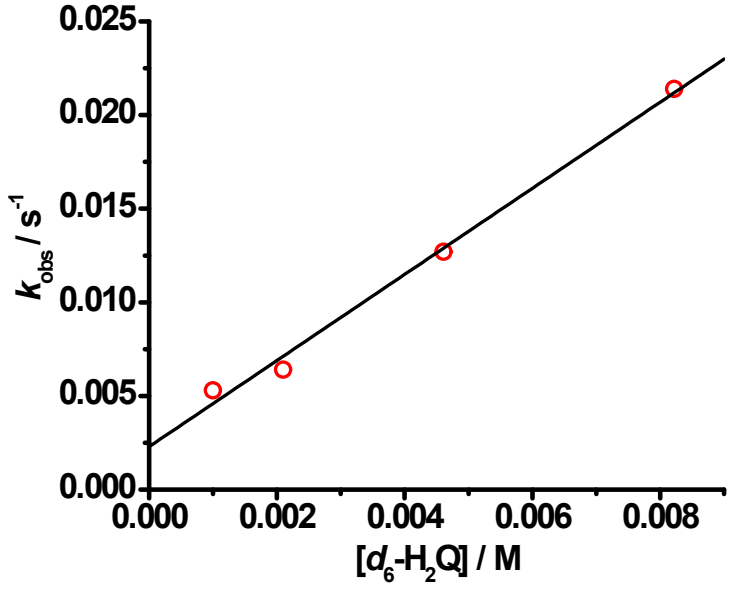


Fig. S8 Plot of k_{obs} vs [d_6-H_2Q] for the reaction between **RuN** (5.00×10^{-5} M) and d_6-H_2Q in the presence of py (0.1 M) in $(CH_2Cl_2)_2$ at 25 °C [slope = (2.30 ± 0.13); *y*-intercept = $(2.29 \pm 0.65) \times 10^{-3}$; $r^2 = 0.990$].

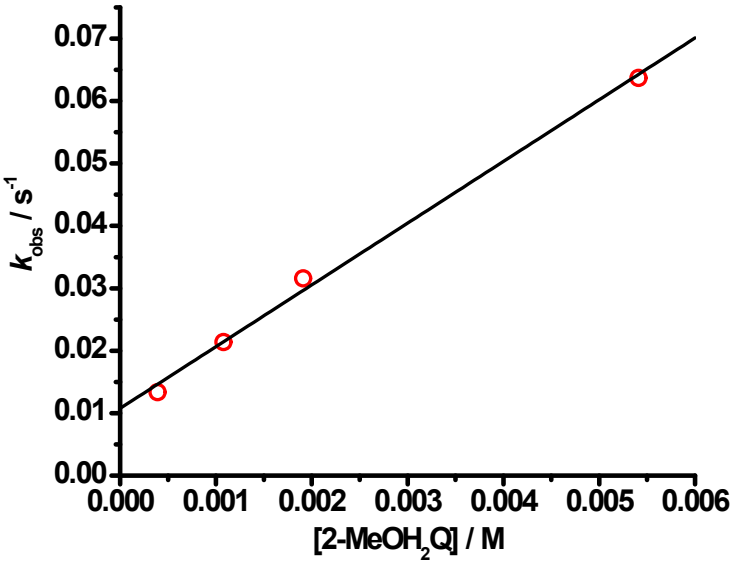


Fig. S9 Plot of k_{obs} vs [2-MeOH$_2$Q] for the reaction between **RuN** (6.85×10^{-5} M) and 2-MeOH$_2$Q in the presence of py (0.1 M) in $(CH_2Cl_2)_2$ at 25 °C [slope = (9.89 ± 0.44); *y*-intercept = $(1.08 \pm 0.13) \times 10^{-2}$; $r^2 = 0.994$].

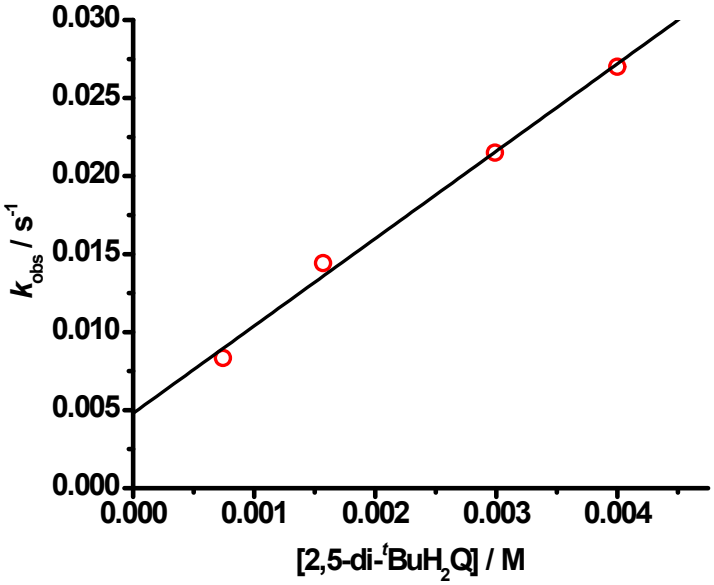


Fig. S10 Plot of k_{obs} vs [2,5-di-^{t}BuH$_2$Q] for the reaction between **RuN** (6.85×10^{-5} M) and 2,5-di-^{t}BuH$_2$Q in the presence of py (0.1 M) in $(CH_2Cl_2)_2$ at 25 °C [slope = (5.60 ± 0.30); *y*-intercept = $(4.80 \pm 0.78) \times 10^{-3}$; $r^2 = 0.992$].

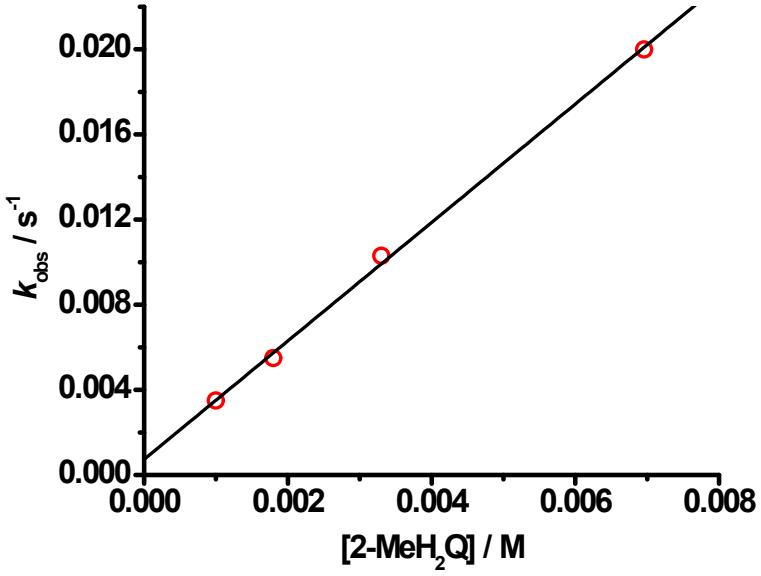


Fig. S11 Plot of k_{obs} vs [2-MeH$_2$Q] for the reaction between **RuN** (6.85 × 10^{-5} M) and 2-MeH$_2$Q in the presence of py (0.1 M) in $(CH_2Cl_2)_2$ at 25 °C [slope = (2.78 ± 0.07); *y*-intercept = (7.33 ± 2.91) × 10^{-4}; r^2 = 0.998].

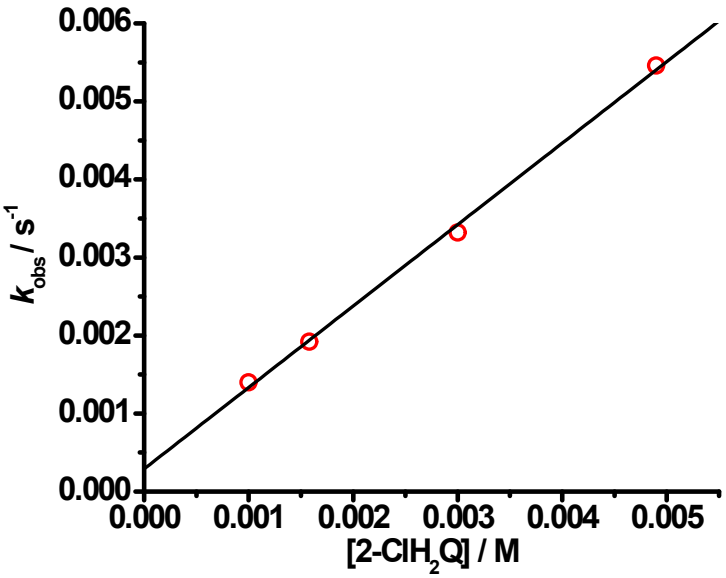


Fig. S12 Plot of k_{obs} vs [2-ClH$_2$Q] for the reaction between **RuN** (6.85 × 10^{-5} M) and 2-ClH$_2$Q in the presence of py (0.1 M) in $(CH_2Cl_2)_2$ at 25 °C [slope = (1.04 ± 0.03); *y*-intercept = (2.90 ± 0.96) × 10^{-4}; r^2 = 0.997].

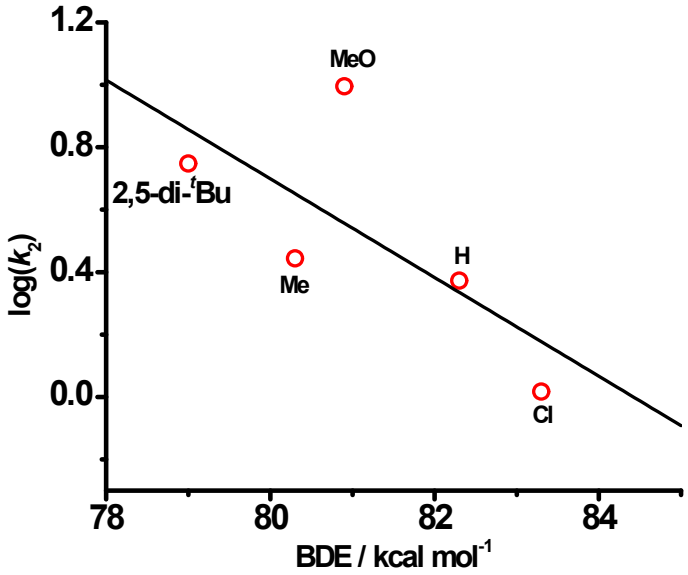
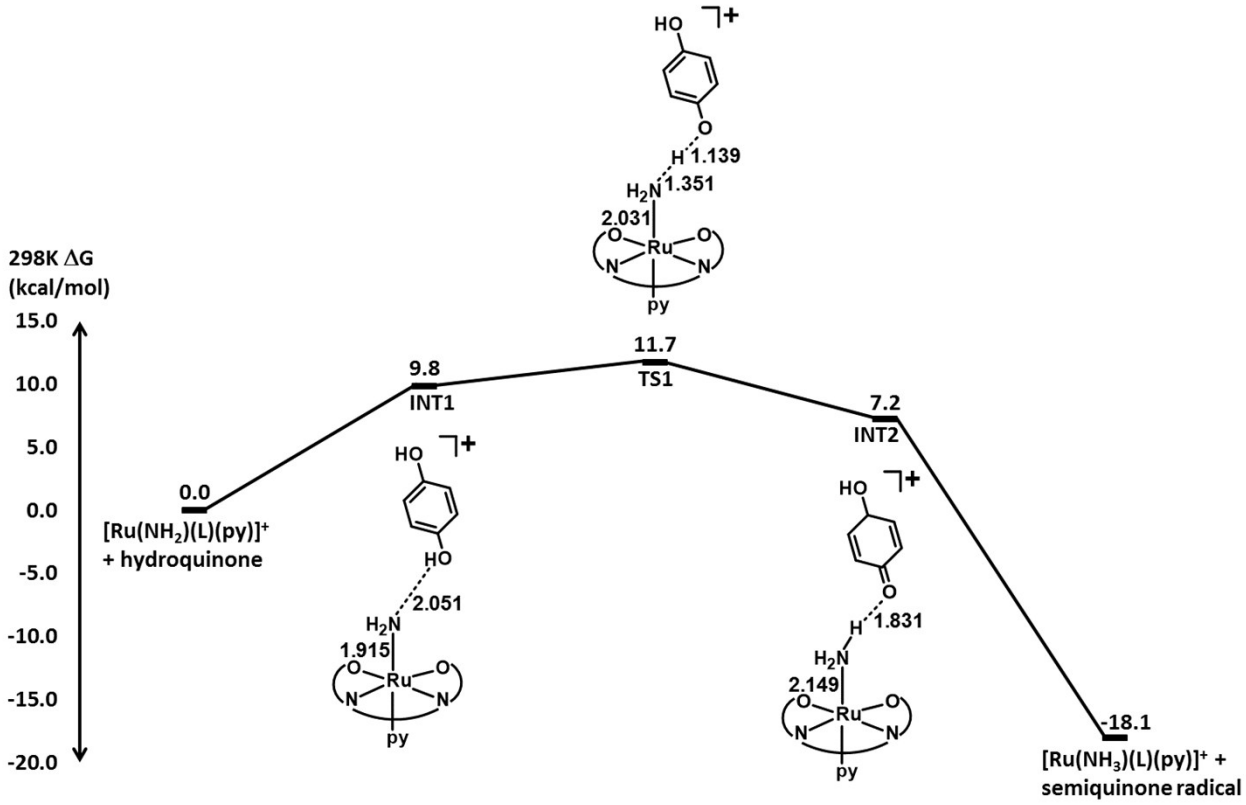


Fig. S13 Plot of log k_2 vs O-H BDE for the oxidation of H_2Qs by **RuN** in $(CH_2Cl_2)_2$ in the presence of 0.1 M py at 25 °C.

Table S1 Crystal data and structure refinement details for $[Ru(L)(NH_3)(py)]PF_6$

	$[Ru(NH_3)(L)(py)]PF_6$
Formula	$C_{25}H_{28}F_6N_4O_2PRu$
M_r	662.55
Crystal system	Monoclinic
Space group	C 1 2/c 1
a/Å	30.6243(5)
b/Å	19.9078(3)
c/Å	11.5863(2)
β(°)	102.8133(16)
V/ Å^3	6887.8(2)
Z	8
ρ_c/Mg m^{-3}	1.276
F(000)	2680
Collected refl.	15986
Unique refl.	5451
R(int)	0.045
Final R indices, $I > 2\sigma(I)$ R^a	R_1(obs) = 0.0407, wR(all) = 0.1120
GOF	1.046
No. of parameters	356

Scheme S1 Potential energy surface for the reaction of hydroquinone with $[Ru(NH_2)(L)(py)]^+$ at the B3LYP level using LanL2DZ basis set (Ru) and 6-311G(d,p) basis set (non-metals). Relative 298K Gibbs free energies in dichloromethane are given in kcal/mol and selected bond lengths are in Å.



Optimized geometries at the B3LYP level using LanL2DZ basis set (Ru) and 6-311G(d,p) basis set (non-metals).

INT1

Ru	1.02512200	-0.17350500	-0.36853200
N	0.77791800	-0.99498900	-1.74616900
N	2.43095700	-1.35780000	0.54672600
N	2.70232700	0.84710800	-0.94685000
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O	-0.15891700	1.44804700	-0.62415300
C	3.83190400	-0.88156800	0.35471800
C	4.90435600	-1.97747900	0.33516700
C	3.87847400	-0.05792600	-0.94806800
H	4.03662800	-0.20351900	1.19038000
C	6.29253200	-1.35391200	0.11130400
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H	4.91176300	-2.52649700	1.27865200
C	5.24703000	0.59566900	-1.14502000
H	3.70301700	-0.75098300	-1.78058600
C	6.33970500	-0.48693700	-1.15076100
H	7.03599000	-2.15225000	0.04815300
H	6.55848300	-0.74612500	0.98377300
H	5.27212100	1.13857300	-2.09278400
H	5.43877700	1.32017800	-0.34524700
H	7.31805500	-0.00977500	-1.24534900
H	6.21118700	-1.12022800	-2.03588500
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C	-1.60034800	-2.66237300	1.85037000
C	0.75924400	-4.04534000	2.39062700
C	-1.62600600	-3.86439200	2.52981000
H	-2.51502100	-2.13204300	1.61753800
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H	1.68409700	-4.57116900	2.60040700
H	-2.57988700	-4.26979800	2.84827500
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C	-0.75601800	3.60637400	-1.23593100
C	1.85094700	4.25769900	-1.95690200
C	-0.45324100	4.86316200	-1.72111900
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H	2.87155300	4.50030500	-2.23180500

H	-1.24521900	5.59761900	-1.81618400
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C	2.13117900	-2.36512400	1.30651000
H	2.95794100	-2.93284400	1.72695200
H	3.65767800	2.49128700	-1.68224200
C	0.28259600	1.37035800	2.61843600
C	0.22236000	2.15566700	3.76440600
C	1.34677600	2.88309200	4.14180400
C	2.48834200	2.79764800	3.35127500
C	2.45726700	1.98748100	2.22174500
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H	3.33011700	1.91605200	1.58463400
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C	-1.73343600	-2.31864100	-3.32108200
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C	-3.14219900	-0.98339200	-1.87090100
C	-3.65110800	-2.14005100	-1.27312400
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H	-1.89246200	-4.44339700	-3.07459800
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C	-5.76837100	2.12394400	2.02027100
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H	-7.86998900	2.62444700	-0.59409000
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N	2.41648000	0.91570900	-0.77549700
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C	3.46579500	-0.79463600	0.63360100
C	4.57493000	-1.84859400	0.73089900
C	3.59297700	0.01893600	-0.67657800
H	3.57623500	-0.09414800	1.47016500
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H	4.51647200	-2.37599200	1.68532900
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H	3.47801500	-0.69057600	-1.50682600
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H	6.72877200	-1.96657300	0.63467200
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H	5.05716800	1.20404800	-1.74584800
H	5.08315000	1.43520400	0.00150900
H	7.05480700	0.13237000	-0.71613500
H	6.03784300	-1.03336400	-1.54692600
C	-0.78318900	-2.19906900	1.27984600
C	0.43189900	-2.91238300	1.55982800
C	-2.00564400	-2.83899900	1.60566500
C	0.35414800	-4.19891200	2.15185200
C	-2.03835700	-4.10117500	2.16274300
H	-2.92162200	-2.30996200	1.37638400
C	-0.85036600	-4.79787600	2.44520000
H	1.28159000	-4.71724000	2.37169300
H	-2.99664800	-4.55776500	2.38539500
H	-0.88225800	-5.78532600	2.88799500
C	-0.06249200	2.63176400	-1.24346600
C	1.30720900	2.95078600	-1.54873100
C	-1.03907400	3.62284900	-1.52546400
C	1.60591900	4.21405100	-2.12352100
C	-0.70535700	4.83724400	-2.08660800
H	-2.06776200	3.38315000	-1.28504000
C	0.63162700	5.14713700	-2.39545500
H	2.64292000	4.43807000	-2.35116400
H	-1.48706000	5.56094200	-2.29073400
H	0.88892300	6.10181500	-2.83640700
C	2.43730300	2.09064600	-1.31339400
C	1.75858400	-2.39764800	1.34595800

H	2.55975400	-2.99761900	1.77255900
H	3.39913400	2.49812900	-1.61928300
C	-0.11208100	1.12307900	2.79391800
C	-0.18300100	1.85486100	3.97330400
C	0.82756900	2.76627200	4.26291000
C	1.87107600	2.90973600	3.35440100
C	1.86415600	2.13713300	2.19917300
N	0.89584800	1.25185200	1.91427500
H	0.80198500	3.35228100	5.17379700
H	-0.87763900	0.40664300	2.52793400
H	-1.01760800	1.70608900	4.64654400
H	2.67971100	3.60789600	3.52856700
H	2.65990700	2.23673400	1.47346800
C	-1.49448700	-3.43201100	-3.13394300
C	-0.59593700	-2.37520200	-3.23267500
C	-0.87513700	-1.10670200	-2.58621400
C	-2.12658600	-0.97171500	-1.88263800
C	-2.99805400	-2.03080300	-1.77927300
C	-2.66958200	-3.25522400	-2.42476100
H	-1.25520100	-4.38055100	-3.59706700
H	-0.60125400	-0.22438400	-3.16689000
H	-2.35166500	-0.01094600	-1.44376800
H	-3.37449600	-4.07376600	-2.33526700
O	0.57038600	-2.55338000	-3.84985600
H	1.17084300	-1.83685600	-3.57649600
O	-4.17129500	-1.99924500	-1.11904500
H	-4.34278300	-1.10553000	-0.69615300
C	-3.96456800	1.02331200	0.89683000
C	-4.34461300	2.16841100	1.58961400
C	-5.64639300	2.63913500	1.44071500
C	-6.51901700	1.94845600	0.60371500
C	-6.05384900	0.81306300	-0.05056500
N	-4.80222200	0.35519200	0.09045400
H	-5.97505700	3.52797400	1.96629800
H	-2.95900100	0.62343000	0.97749000
H	-3.63250200	2.67612200	2.22783500
H	-7.53958400	2.27900900	0.45792900
H	-6.70136100	0.24631800	-0.71140000

INT2

Ru	-0.74477800	0.00600600	-0.03350500
N	-0.58175600	0.98054200	-1.58437900
N	-2.14403100	1.28083100	0.71833400
N	-2.37648300	-0.94144500	-0.78704200

O	0.77996100	0.99494500	0.95926200
O	0.53572400	-1.50715100	-0.64148000
C	-3.52287600	0.75514600	0.55876200
C	-4.64796300	1.79522600	0.60239800
C	-3.56521000	-0.05651800	-0.75787400
H	-3.67254700	0.05000300	1.38578200
C	-6.01463400	1.12425100	0.39481300
H	-4.47772300	2.54836800	-0.17559100
H	-4.64789700	2.31483500	1.56328800
C	-4.92622500	-0.73162500	-0.95398900
H	-3.40562900	0.65655500	-1.57789800
C	-6.05605600	0.30854500	-0.90041900
H	-6.79511300	1.88963100	0.38625400
H	-6.22812700	0.46838100	1.24717400
H	-4.95835300	-1.24575900	-1.91751100
H	-5.08068200	-1.48887000	-0.17641400
H	-7.01971700	-0.19790700	-0.99973300
H	-5.96586700	0.98333600	-1.75978600
C	0.66859200	2.21572800	1.42584800
C	-0.56754700	2.93193200	1.58729900
C	1.86073700	2.87421100	1.82808500
C	-0.53501400	4.24191300	2.12951900
C	1.85017600	4.15646300	2.33534800
H	2.79184100	2.33417000	1.70655400
C	0.64187500	4.85915900	2.49072900
H	-1.47721000	4.76488600	2.25715100
H	2.78677100	4.62494000	2.61785200
H	0.63659400	5.86424500	2.89341000
C	0.14677700	-2.61839000	-1.20275800
C	-1.20772500	-2.93990700	-1.57891100
C	1.14376200	-3.59901900	-1.46746200
C	-1.46689100	-4.18947800	-2.20329200
C	0.84625100	-4.79875800	-2.07441200
H	2.15871800	-3.35765800	-1.17471000
C	-0.47447600	-5.10834800	-2.45387100
H	-2.49012300	-4.41404000	-2.48694200
H	1.64146800	-5.51246800	-2.26168200
H	-0.70353200	-6.05229500	-2.93227600
C	-2.35391600	-2.09411300	-1.37751400
C	-1.87767700	2.39778000	1.30930300
H	-2.70670800	3.01403800	1.65094400
H	-3.29087900	-2.49142700	-1.76318400
C	0.04001100	-1.18565900	2.84205000
C	0.06365500	-1.94598000	4.00440000

C	-0.96338300	-2.85484600	4.23845600
C	-1.97683000	-2.96708500	3.29252000
C	-1.92666700	-2.16713000	2.15778600
N	-0.94098300	-1.28367500	1.92749300
H	-0.97276400	-3.46281000	5.13511700
H	0.81787900	-0.46880600	2.61708700
H	0.87652700	-1.82120500	4.70836800
H	-2.79636500	-3.66214800	3.42215200
H	-2.69621000	-2.24142600	1.40227600
C	1.56552000	3.04602400	-3.70731700
C	0.47861000	2.31791600	-3.22102300
C	0.67949900	1.15417300	-2.29448400
C	2.03138400	1.04336200	-1.68206800
C	3.05919500	1.81280100	-2.14369900
C	2.80575700	2.78925500	-3.16778300
H	1.41261900	3.84183700	-4.42421000
H	0.67526900	0.29660400	-3.01393600
H	2.17503500	0.25551900	-0.96002000
H	3.66082300	3.36434700	-3.50655000
O	-0.75758400	2.58948500	-3.49833900
H	-1.25464400	2.00134500	-2.82615000
O	4.33201000	1.75410400	-1.71579200
H	4.46928000	1.02603300	-1.03469100
C	4.19414800	-0.64063300	1.08629100
C	4.64152700	-1.61714600	1.97010700
C	5.90360400	-2.17039600	1.77249200
C	6.67014000	-1.72777400	0.69767200
C	6.14332700	-0.74764800	-0.13594700
N	4.92982800	-0.20999200	0.05127500
H	6.28269400	-2.93279400	2.44269200
H	3.21417900	-0.18845900	1.20239700
H	4.01099000	-1.93430800	2.79090800
H	7.65625600	-2.13095600	0.50537800
H	6.70772800	-0.37553600	-0.98455800

TS2

Ru	0.78171400	-0.02373900	0.00907000
N	0.55163900	-0.93253800	-1.57799700
N	2.18944400	-1.33610300	0.67288000
N	2.39861600	0.93313300	-0.76075000
O	-0.71121700	-0.99697400	1.04539300
O	-0.51212900	1.50171600	-0.54824400
C	3.57366300	-0.84151700	0.45865200
C	4.66859300	-1.91237000	0.38487900

C	3.57311900	0.03191500	-0.81810700
H	3.79400500	-0.18575500	1.30999500
C	6.04139000	-1.26373100	0.14612100
H	4.43675200	-2.61432400	-0.42441900
H	4.70399500	-2.48670100	1.31308100
C	4.93675800	0.69320500	-1.03990100
H	3.37151600	-0.64018200	-1.66284900
C	6.04333400	-0.37185100	-1.09879400
H	6.79888900	-2.04631600	0.05245000
H	6.31482500	-0.66653600	1.02404000
H	4.93533500	1.25950600	-1.97406100
H	5.14243600	1.40382700	-0.23059200
H	7.01347900	0.11891900	-1.21229800
H	5.89817800	-0.99103000	-1.99196100
C	-0.60111100	-2.21412700	1.52009000
C	0.62468800	-2.95887800	1.61451100
C	-1.78259400	-2.83887700	1.99952900
C	0.59179600	-4.26640400	2.16256500
C	-1.77381100	-4.11916200	2.51139300
H	-2.70474300	-2.27440900	1.93521800
C	-0.57660600	-4.85246700	2.59564900
H	1.52668200	-4.81227500	2.23669100
H	-2.70287700	-4.56220100	2.85338000
H	-0.57271800	-5.85628400	3.00144700
C	-0.12233900	2.64352500	-1.04339100
C	1.23032900	2.98167400	-1.41298400
C	-1.11710500	3.64233600	-1.24067500
C	1.49008800	4.26637400	-1.96147100
C	-0.81868200	4.87660600	-1.77308400
H	-2.13090300	3.38705300	-0.95579200
C	0.50046600	5.20399100	-2.14347900
H	2.51163100	4.50271600	-2.24154500
H	-1.61190100	5.60415900	-1.90828100
H	0.73002100	6.17522500	-2.56341900
C	2.37232200	2.11656600	-1.28690200
C	1.92869600	-2.45362700	1.26675900
H	2.76045000	-3.09084700	1.55960900
H	3.30259300	2.52485900	-1.67726900
C	-0.03148000	1.31089800	2.77379100
C	-0.04502400	2.08442600	3.92705200
C	1.07836300	2.84032000	4.24725800
C	2.17511600	2.79293000	3.39312700
C	2.10706800	1.99336300	2.25937600
N	1.02858600	1.25596600	1.94771500

H	1.09792300	3.45393200	5.13988100
H	-0.87804400	0.70192800	2.48804800
H	-0.92461600	2.08807200	4.55791400
H	3.07177500	3.36543400	3.59230600
H	2.93986000	1.94879900	1.57172800
C	-1.54861700	-2.64447500	-4.02184700
C	-0.47434500	-1.99886200	-3.39428800
C	-0.71079200	-0.99489000	-2.29713700
C	-2.05981800	-1.03315900	-1.66718900
C	-3.06717000	-1.71993900	-2.27450500
C	-2.79174900	-2.49813700	-3.45843500
H	-1.37692300	-3.30587300	-4.86066100
H	-0.73472800	-0.03124000	-2.86361400
H	-2.22002100	-0.40145300	-0.80760000
H	-3.63885700	-3.01444900	-3.89731600
O	0.76942800	-2.21009100	-3.63823000
H	1.18834200	-1.70389300	-2.79122400
O	-4.34676500	-1.76193300	-1.86328100
H	-4.52633600	-1.11043800	-1.11899900
C	-4.45805000	0.48135400	1.10014500
C	-5.01087400	1.40856700	1.97715600
C	-6.28053700	1.91061100	1.70478800
C	-6.94759800	1.46784100	0.56570700
C	-6.31788200	0.53872200	-0.25494700
N	-5.09688700	0.05011600	0.00372800
H	-6.74125600	2.63385900	2.36713700
H	-3.46874800	0.07103800	1.27500500
H	-4.45548100	1.72661600	2.85029600
H	-7.93548800	1.83226500	0.31422600
H	-6.80238400	0.16827700	-1.15225700

INT3

Ru	-0.75634400	-0.01077500	0.02901600
N	-0.47061500	1.00657900	-1.53206600
N	-2.14335500	1.28335200	0.74435000
N	-2.37139300	-0.88660200	-0.82292100
O	0.72428900	0.89056700	1.11742300
O	0.51509100	-1.50950100	-0.58854800
C	-3.53239200	0.80426400	0.52548600
C	-4.62920100	1.87471600	0.54132300
C	-3.55476100	0.01044400	-0.80290100
H	-3.73357600	0.09635600	1.33838400
C	-6.00483100	1.23613600	0.29012100
H	-4.41651200	2.62756800	-0.22615700

H	-4.64662700	2.38738000	1.50548400
C	-4.92064300	-0.64424200	-1.03237200
H	-3.38766200	0.73305200	-1.61348000
C	-6.02964400	0.41986800	-1.00539300
H	-6.76464300	2.02103900	0.25722200
H	-6.26045300	0.58760200	1.13624800
H	-4.93989900	-1.15552800	-1.99727500
H	-5.10626600	-1.39848000	-0.25890300
H	-7.00020400	-0.06742900	-1.12770000
H	-5.90441100	1.09054900	-1.86340100
C	0.64723500	2.09965000	1.60984800
C	-0.56221000	2.87309500	1.70561900
C	1.84351600	2.68191300	2.10624800
C	-0.50071100	4.17221700	2.27101000
C	1.86218300	3.95568400	2.62997200
H	2.75004000	2.09405800	2.03667200
C	0.68158000	4.71865000	2.71516600
H	-1.42079600	4.74152900	2.34780300
H	2.79904300	4.37371500	2.98106000
H	0.70336000	5.71752900	3.13207100
C	0.13344700	-2.59666900	-1.19547200
C	-1.21090500	-2.88004100	-1.63743000
C	1.12716600	-3.58344200	-1.44814400
C	-1.46412200	-4.10343100	-2.31464900
C	0.83470200	-4.75574000	-2.10627700
H	2.13198500	-3.36735000	-1.10623900
C	-0.47500400	-5.02820600	-2.55147900
H	-2.47686100	-4.30139300	-2.64950500
H	1.62389200	-5.47785100	-2.28486900
H	-0.69720500	-5.95190100	-3.07058700
C	-2.34465700	-2.02063600	-1.45460100
C	-1.86948200	2.39230400	1.35507700
H	-2.69519900	3.03268000	1.65570600
H	-3.27268000	-2.38189400	-1.89204600
C	-0.01019900	-1.44629600	2.71576100
C	-0.03553400	-2.28321300	3.82239900
C	-1.15419200	-3.07998100	4.04437800
C	-2.20759900	-3.00941800	3.13941400
C	-2.10521100	-2.14783200	2.05574800
N	-1.03111500	-1.36800600	1.84111000
H	-1.20238900	-3.74242700	4.90006600
H	0.83555600	-0.80634100	2.50904600
H	0.81224000	-2.30190000	4.49485100
H	-3.09810200	-3.61235500	3.25955000

H	-2.90142300	-2.08962700	1.32849900
C	1.63779900	3.21790500	-3.63724400
C	0.46084300	2.46114600	-3.24404700
C	0.70664900	1.21969500	-2.34765600
C	2.03478900	1.14541600	-1.66129700
C	3.04598000	1.95302800	-2.04250100
C	2.83225000	2.98309000	-3.05367000
H	1.49478300	4.02299700	-4.34775700
H	0.70424500	0.40441800	-3.10535700
H	2.17123000	0.36222600	-0.93121000
H	3.69721300	3.58420500	-3.31377300
O	-0.67851700	2.73548700	-3.59298100
H	-1.26454300	1.44224200	-2.00907400
O	4.30528100	1.92744900	-1.55737600
H	4.44587300	1.16346600	-0.92803900
C	4.27334800	-0.75960900	1.03921900
C	4.77578900	-1.80676000	1.80510000
C	6.06317400	-2.26781400	1.54323100
C	6.79760000	-1.66540900	0.52528400
C	6.21430700	-0.62453400	-0.18918600
N	4.97671800	-0.17498200	0.05969300
H	6.48596100	-3.08136400	2.12080200
H	3.27289200	-0.37419800	1.20802400
H	4.16877600	-2.24757500	2.58575600
H	7.80177300	-1.99191400	0.28621200
H	6.75251400	-0.12909700	-0.99058800

TS3

Ru	-0.64584900	0.02327500	-0.14544800
N	-0.42787600	0.87229400	-1.74989300
N	-2.09167500	1.26375500	0.55937000
N	-2.23663100	-1.01494300	-0.86127500
O	0.86473400	1.19540800	0.74021000
O	0.63580600	-1.53278900	-0.45917400
C	-3.43331500	0.63418700	0.50178600
C	-4.63066800	1.58569800	0.58662900
C	-3.49328500	-0.22315100	-0.78442800
H	-3.47610100	-0.05565700	1.35358800
C	-5.94817900	0.79904200	0.50296400
H	-4.57703300	2.31652300	-0.22859700
H	-4.60560300	2.14281700	1.52618400
C	-4.80093800	-1.01779700	-0.85423800
H	-3.46186800	0.46889500	-1.63645500
C	-6.01027800	-0.07456600	-0.75341000

H	-6.78835600	1.49808300	0.52012400
H	-6.04751600	0.16694600	1.39324600
H	-4.86002600	-1.57357800	-1.79259400
H	-4.82585100	-1.75027900	-0.03895500
H	-6.93031800	-0.66483300	-0.75977400
H	-6.04244300	0.56612800	-1.64245500
C	0.68757300	2.44209300	1.06597500
C	-0.59631600	3.08734200	1.21397600
C	1.84129000	3.23189500	1.34039900
C	-0.64166800	4.44730900	1.62493600
C	1.74916900	4.55174600	1.72120800
H	2.80625300	2.75614300	1.21498900
C	0.49585800	5.17949100	1.86877400
H	-1.61557600	4.91175100	1.74136900
H	2.65705300	5.11567000	1.90772900
H	0.43161000	6.21727600	2.17060800
C	0.32375700	-2.64214000	-1.08686700
C	-0.97924700	-2.97760200	-1.59293300
C	1.35997000	-3.59419000	-1.26977500
C	-1.15536600	-4.21381400	-2.26353200
C	1.14891800	-4.78275500	-1.93782800
H	2.33617500	-3.34308700	-0.87305800
C	-0.12058800	-5.10495900	-2.44785900
H	-2.14462800	-4.45396300	-2.63931200
H	1.97407400	-5.47456500	-2.06793900
H	-0.28418800	-6.03905300	-2.97029300
C	-2.16667600	-2.17240600	-1.43222300
C	-1.86965600	2.44614000	1.04168800
H	-2.72777200	3.03642500	1.35681700
H	-3.08005900	-2.61716800	-1.82086500
C	-0.49965000	-0.33135700	3.09686600
C	-0.57059700	-0.89481100	4.36542100
C	-1.03876800	-2.19851500	4.49759000
C	-1.41848500	-2.88798400	3.35002900
C	-1.31986500	-2.24860100	2.12049500
N	-0.86995400	-0.99022900	1.98671700
H	-1.10593300	-2.66665800	5.47229000
H	-0.12923300	0.67431400	2.95545800
H	-0.26172400	-0.31645200	5.22674000
H	-1.78710600	-3.90453100	3.39802900
H	-1.60950100	-2.75898500	1.21177700
C	1.62158000	3.25242500	-3.06565300
C	0.81918100	2.11627500	-3.55721000
C	1.17152900	0.77148200	-3.00217200

C	2.37773800	0.56887500	-2.35432200
C	3.15167600	1.67600500	-1.91926800
C	2.72103700	3.03570700	-2.32778000
H	1.31618800	4.24356100	-3.38119400
H	0.68067100	-0.06067200	-3.49652700
H	2.67943500	-0.42920000	-2.06620600
H	3.35120700	3.85021000	-1.98804800
O	-0.07246400	2.25612300	-4.38279100
H	-1.21722300	0.85071100	-2.41462600
O	4.18347200	1.58473700	-1.19745500
H	4.40649100	0.33965800	-0.27802500
C	5.67706500	-1.11376400	0.52512900
C	5.83767800	-2.11324800	1.46593700
C	4.77830000	-2.40180700	2.32685900
C	3.58747100	-1.68717300	2.22393800
C	3.47610700	-0.69448100	1.26415800
N	4.51630400	-0.43905900	0.45119500
H	4.88307400	-3.18054200	3.07218700
H	6.44699700	-0.82690100	-0.17760500
H	6.77332300	-2.65185900	1.52209700
H	2.75039300	-1.89199200	2.87674500
H	2.58479400	-0.09334700	1.11161600

INT4

Ru	0.98461500	0.01053300	-0.09335900
N	0.55989500	-0.57248700	-1.75240000
N	2.43766400	-1.35457400	0.30508100
N	2.55591000	1.08991600	-0.79880600
O	-0.51114500	-1.22546400	0.74289100
O	-0.21998600	1.66684300	0.02097600
C	3.80457300	-0.80257100	0.12439900
C	4.91621300	-1.82936900	-0.12101000
C	3.74181000	0.22654200	-1.02896200
H	4.03850300	-0.25294800	1.04474100
C	6.26738500	-1.12544600	-0.32211800
H	4.66885100	-2.42896100	-1.00483300
H	4.99491800	-2.51559800	0.72525100
C	5.08514400	0.93754500	-1.21434400
H	3.52261200	-0.33645800	-1.94601600
C	6.20713400	-0.08689900	-1.44605500
H	7.03590600	-1.87267800	-0.53696600
H	6.56045800	-0.63429500	0.61338100
H	5.03872000	1.61844400	-2.06758100
H	5.30890500	1.54153500	-0.32716900

H	7.16348900	0.43586100	-1.53128900
H	6.04012700	-0.59397200	-2.40367700
C	-0.33524300	-2.48499500	0.98824000
C	0.93771500	-3.17028100	0.98703500
C	-1.48239000	-3.26513000	1.32660900
C	0.97780200	-4.55279000	1.32014400
C	-1.39624100	-4.60420100	1.62989600
H	-2.43851500	-2.75531200	1.32085100
C	-0.15259800	-5.27010000	1.62993900
H	1.94417700	-5.04709300	1.32280600
H	-2.29946400	-5.15447300	1.87283500
H	-0.09113500	-6.32362800	1.87235000
C	0.12082700	2.86417300	-0.38470800
C	1.39276200	3.23265300	-0.94500100
C	-0.85077300	3.89193400	-0.25161300
C	1.60145900	4.57496800	-1.34830500
C	-0.60996300	5.18634600	-0.66424500
H	-1.80397100	3.61311800	0.18203200
C	0.62872000	5.54364500	-1.22392800
H	2.56746900	4.83624200	-1.76844500
H	-1.38758700	5.93454000	-0.55231900
H	0.81731800	6.56015200	-1.54588300
C	2.52152700	2.34543600	-1.10164100
C	2.20891300	-2.56197600	0.72002600
H	3.06724200	-3.20916300	0.88925700
H	3.42260400	2.81149000	-1.49492500
C	0.55064800	0.31530600	3.15700300
C	0.64876100	0.73280600	4.47955500
C	1.66388800	1.61650000	4.83314100
C	2.53969200	2.05289800	3.84385900
C	2.36973500	1.58320300	2.54641900
N	1.39899300	0.72430300	2.20057600
H	1.76784400	1.96090200	5.85524300
H	-0.22949100	-0.36024900	2.83082300
H	-0.06087300	0.36892100	5.21187600
H	3.34089000	2.74651200	4.06512800
H	3.02829600	1.91271900	1.75280800
C	-1.39635500	-2.44901700	-3.07306400
C	-1.06905900	-1.12146600	-3.64896600
C	-1.86709600	0.02847900	-3.15449700
C	-2.92101400	-0.14497200	-2.34115700
C	-3.27287900	-1.47705800	-1.83847900
C	-2.45373100	-2.61871300	-2.26485900
H	-0.77504400	-3.27711000	-3.39394400

H	-1.58759400	1.00368600	-3.53568700
H	-3.52601300	0.68988800	-2.00736500
H	-2.73186200	-3.58665500	-1.86584200
O	-0.27938600	-1.00118000	-4.57785000
H	1.29845300	-0.43854500	-2.46750000
O	-4.22358600	-1.65451200	-1.05864100
H	-5.22778000	-0.55998700	-0.32225800
C	-7.18484800	0.09970400	-0.25124600
C	-8.10729000	0.89999100	0.39607100
C	-7.69402300	1.65085500	1.49567400
C	-6.36869900	1.58516500	1.92317500
C	-5.48547600	0.76953400	1.24089300
N	-5.91304300	0.05697300	0.18346100
H	-8.40134000	2.28375400	2.01660300
H	-7.42168900	-0.51393100	-1.10887300
H	-9.12849400	0.93115900	0.04326200
H	-6.02133400	2.15648300	2.77242100
H	-4.44296400	0.66160000	1.50501100

INT5

Ru	1.68319900	-0.03945400	0.05554300
N	-0.13294600	0.33369700	0.21872500
N	1.87516100	0.56957300	-1.85557300
N	2.14637800	1.90075200	0.45669500
O	1.18878200	-1.98818100	-0.51077500
O	2.05840200	-0.62401100	1.94405700
C	2.45419400	1.93453100	-1.97356800
C	2.15394900	2.68409000	-3.27652800
C	1.97875500	2.75285200	-0.74929800
H	3.54051200	1.81332600	-1.89282200
C	2.79838600	4.07971600	-3.24978100
H	1.06921000	2.77115300	-3.40766300
H	2.54320300	2.13015600	-4.13348800
C	2.64146400	4.13271000	-0.71299400
H	0.89675300	2.89649200	-0.86156400
C	2.36586900	4.88838300	-2.02300600
H	2.53619000	4.61392700	-4.16652600
H	3.88937300	3.97218000	-3.25081800
H	2.25550400	4.71718600	0.12528900
H	3.72157400	4.02180200	-0.56305700
H	2.88510500	5.84982700	-2.00128000
H	1.29478500	5.11188500	-2.09068100
C	0.89001600	-2.33311300	-1.72563600
C	1.03904800	-1.48980100	-2.89040000

C	0.40648800	-3.65695000	-1.93832100
C	0.69400900	-2.01538800	-4.16851600
C	0.07955700	-4.11716200	-3.19120200
H	0.30420900	-4.28984900	-1.06551600
C	0.21869800	-3.29223200	-4.32923600
H	0.81534400	-1.37218200	-5.03358100
H	-0.29005100	-5.13032000	-3.30641900
H	-0.04203300	-3.66501300	-5.31159000
C	2.41348200	0.17033900	2.92998200
C	2.57438600	1.59355600	2.83719400
C	2.65399100	-0.44251700	4.18388700
C	2.93340700	2.31528100	4.00035600
C	2.99273400	0.29885900	5.29795600
H	2.54378600	-1.51858600	4.23816300
C	3.13423600	1.69380100	5.21526700
H	3.05387800	3.39039700	3.91987400
H	3.15350700	-0.20507900	6.24444800
H	3.40409300	2.27206800	6.08984600
C	2.44322000	2.36498200	1.62431400
C	1.55201400	-0.15700900	-2.88638700
H	1.67320200	0.28910200	-3.87067600
H	2.63544900	3.43039200	1.72789200
C	4.16578400	-1.97340400	-0.22918400
C	5.46428000	-2.46337900	-0.26693000
C	6.52715500	-1.56815200	-0.19988800
C	6.24661600	-0.21019100	-0.08816200
C	4.92041200	0.19944500	-0.05726300
N	3.89053900	-0.66037600	-0.13575300
H	7.55100300	-1.92091400	-0.22721500
H	3.30875300	-2.63161500	-0.26514700
H	5.62986000	-3.53000900	-0.34537400
H	7.03624100	0.52667800	-0.02027200
H	4.67255500	1.24616200	0.04865800
C	-10.04262800	0.57505800	0.38517100
C	-9.98459200	1.80361400	-0.44657100
C	-8.64007900	2.31913300	-0.80914400
C	-7.52457400	1.70006100	-0.40296500
C	-7.58474800	0.47130900	0.42622400
C	-8.92702200	-0.04441100	0.79083200
H	-11.03364700	0.21662700	0.63887400
H	-8.62083500	3.21714200	-1.41592000
H	-6.53371900	2.05939000	-0.65608100
H	-8.94770800	-0.94196500	1.39822200
O	-11.00161600	2.36784700	-0.81780400

H	-0.52945500	1.27090700	0.21322200
O	-6.56537700	-0.09477100	0.79509000
H	-0.84217700	-0.40734100	0.37798500
C	-3.48986800	-1.52768400	1.05042400
C	-4.34327800	-2.48632400	1.58973000
C	-3.80037900	-3.69520500	2.01620500
C	-2.42876400	-3.89707100	1.88401000
C	-1.65529300	-2.88052900	1.33096000
N	-2.16953100	-1.71291500	0.91967200
H	-4.43290000	-4.46515700	2.44284400
H	-3.88827000	-0.57737300	0.71137700
H	-5.40137500	-2.27241600	1.66577000
H	-1.96290200	-4.82177900	2.20176700
H	-0.58403500	-2.99660100	

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