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DAMP (2,6-Bis(dimethyaminomethyl)pyridine). Pyridinedimethanol (25 g) was dissolved in ~300 mL 48% HBr, heated at reflux for 5 h, evaporated to 1/3 its original volume, and chilled in a freezer overnight to yield solid 2,6-Bis(bromomethyl)pyridine•HBr. Approximately 25 g (80 mmol) was carefully dissolved in 200 mL of 40% dimethylamine, and the mixture was heated at reflux for 24 h. The resulting pale yellow solution was chilled in an ice-bath, treated with ~8 g NaOH, and extracted with five 100-mL portions of dichloromethane. Evaporation of the dichloromethane yielded the ligand as a viscous oil. The structure was confirmed by GC-MS.

(DAMP)$RuCl_3$. A mixture of $(DMSO)_4RuCl_2$ (4.85 g, 10 mmol) and DAMP (2.40 g, 12.5 mmol) was suspended in 50 mL absolute ethanol and heated at reflux for 2 h. The reaction was judged complete upon disappearance of the yellow solid to yield a deep red solution. The solvent was removed by rotary evaporation, and the red residue was suspended in 25 mL concentrated HCl. The resulting dark green solution was heated at reflux for ~20 minutes to yield the product as an orange powder that was collected on a medium-porosity frit and dried *in vacuo*. Yield 3.10 g (77%). Anal. Calc. for $C_{11}H_{19}N_3RuCl_3$: C, 32.83; H, 4.73; N, 10.45. Found: C, 32.80; H, 4.89; N, 10.33.

[(DAMP)(bpy)RuCl]PF_6. (DAMP)$RuCl_3$ (50 mg, 125 μmol), bipyridine (24 mg, 150 μmol), and 2 g LiCl were suspended in 40 mL of 3:1 ethanol-water and heated at reflux for 3 h. The solvent volume was reduced to ~10 mL, and the mixture was refrigerated overnight to precipitate [(DAMP)(bpy)RuCl]Cl as a dark brown solid. This solid was suspended in absolute ethanol, and the final product was precipitated by addition of solid NH_4PF_6, collected by suction filtration on a medium-porosity frit, and dried *in vacuo*. Yield 34 mg (43%). Anal. Calc. for $C_{21}H_{27}N_5RuClPF_6$: C, 39.98; H, 4.31; N, 11.10. Found: C, 40.28; H, 4.42; N, 10.90.

[(DAMP)(dppz)RuCl]PF_6•$2H_2O$. This complex was obtained via the method for synthesis of [(DAMP)(bpy)RuCl]PF_6. Yield 63 mg (64%). Anal. Calc. for $C_{29}H_{33}N_7O_2RuClPF_6$: C, 43.92; H, 4.19; N, 12.36. Found: C, 43.82; H, 4.06; N, 12.48.

[(DAMP)(bpy)$RuOH_2$]$(ClO_4)_2$•$2H_2O$. (DAMP)$RuCl_3$ (50 mg, 125 μmol), bipyridine (20 mg, 125 μmol), and 200 mg of zinc dust were suspended in 20 mL of water and heated at reflux for 1 h. The deep red solution was filtered hot, combined with 1 mL saturated $NaClO_4$, and refrigerated overnight to precipitate the product. Glittering red flakes were collected by suction filtration on a medium-porosity frit and dried *in vacuo*. Yield 67 mg (80%). *Caution! Perchlorate salts of DAMP complexes become highly explosive when subjected to rigorous drying conditions. The single crystals of the salt were stored in the mother liquor in a freezer and withdrawn as needed.* Anal. Calc. for $C_{21}H_{35}N_5Cl_2O_{11}Ru$: C, 35.90; H, 4.73; N, 9.96. Found: C, 36.02; H, 4.74; N, 9.96.

[(DAMP)(phen)$RuOH_2$]$(ClO_4)_2$. This complex was prepared as a maroon powder via the method for synthesis of [(DAMP)(bpy)$RuOH_2$]$(ClO_4)_2$•$2H_2O$. Yield 73 mg (84%). Anal. Calc. for $C_{23}H_{29}N_5Cl_2O_9Ru$: C, 39.95; H, 4.23; N, 10.13. Found: C, 39.76; H, 4.18; N, 10.06.

[(DAMP)(bpy)RuO]$(ClO_4)_2$. [(DAMP)(bpy)$RuOH_2$]$(ClO_4)_2$•$2H_2O$ (50 mg, 70 μmol) was dissolved in 3 mL warm distilled water and chilled in an ice bath. $(NH_4)_2Ce(NO_3)_6$ (200 mg) was dissolved in 5 mL ice-cold distilled water and added to the first solution. The resulting yellow-green solution was mixed thoroughly, and the product was precipitated by addition of 2 mL saturated $NaClO_4$. The light green product was collected by suction filtration on a medium-porosity frit and left to dry by suction for 45 min. The solid was

then dissolved in 1 mL acetonitrile, placed in a 2 mL vial inside a scintillation bottle containing diethylether, and refrigerated overnight to yield a crystalline product. Yield 41 mg (88%). Anal. Calc. for $C_{21}H_{27}N_5Cl_2O_9Ru$: C, 37.90; H, 4.09; N, 10.52. Found: C, 38.14; H, 4.03; N, 10.56.

[(DAMP)(phen)RuO](ClO$_4$)$_2$. This complex was prepared via the method for synthesis of [(DAMP)(bpy)RuO](ClO$_4$)$_2$. Yield 24 mg (51%). Anal. Calc. for $C_{23}H_{27}N_5Cl_2O_9Ru$: C, 40.07; H, 3.95; N, 10.16. Found: C, 39.81; H, 4.04; N, 10.24.

DNA Purification. The synthetic oligonucleotides were obtained from the Oligonucleotide Synthesis Center in the Department of Pathology at UNC. Further purification of the DNA samples was performed using HPLC, with a 15 cm column packed with Self Pack Poros 20 R2 (Perseptive Biosystems). A linear gradient of 0-10% was used (Buffer A, 5% acetonitrile, 50 mM triethylammonium; Buffer B, 100% acetonitrile). The collected DNA solution was lyophilized to dryness, suspended in 1.5 M sodium acetate (60 μL), and precipitated twice with ethanol. The pellets were lyophilized to dryness and dissolved in MilliQ water. The oligomer concentrations were determined from the absorbance at 260 nm and are in terms of nucleotide phosphate. (Maniatis, T., Fritsch, E. F., & Sambrook, J. (1989) *Molecular Cloning: A Laboratory Manual,* 2nd ed., Cold Spring Harbor Press: Cold Spring Harbor, N. Y.).

A small portion of the oligonucleotide solution was purified further and used for 5'-^{32}P-labeling. The DNA was run on a 20% polyacrylamide nondenaturing gel (750 V, 2.5 h). The DNA was visualized by UV-shadowing (254 nm) with the gel placed on top of a TLC F_{254} sheet. The DNA samples were carefully removed from the gel, dissolved in MilliQ water, and filtered to remove the acrylamide using micropure 0.45 M separator (Amicon). The DNA

concentration was determined from the absorbance at 260 nm, as described above.

DNA Reactions. The 5'-^{32}P-labeled oligomers were prepared using T4 polynucleotide kinase and deoxyadenosine 5'-[γ-^{32}P]-triphosphate (Amersham). The ^{32}P-labeled DNA was isolated by ultracentrifugation (0 - 5°C, 45 min) using Centricon-10 (Amicon). The filter was then washed with 1 mL of distilled water, followed by additional centrifugation (35 min). The extent of labeling was determined using a scintillation counter.

Oligonucleotides were annealed by heating to 90°C for 5 min and cooled slowly (2-3 h) to 4°C to ensure hairpin formation, which was then detected by running a native 20% polyacrylamide gel (acrylamide-bisacrylamide = 19:1) at 4°C to prevent any thermal denaturation.

The DNA cleavage reactions were performed in 10 mM sodium phosphate buffer (pH 7.0) with a final DNA concentration of 5 μM and ~3 nCi of the 5'-labeled DNA. The freshly oxidized Ru(IV)O^{2+} complex was immediately added to the DNA solution, and after 1 h, the reactions were quenched with 95% ethanol and lyophilized to dryness. The dried samples were then suspended in 0.7 M piperidine (60 μL) and incubated at 90°C for 30 min. The reaction mixtures were lyophilized, washed with water (10 μL), lyophilized, and resuspended in the gel-loading buffer (5 μL) containing 80% formamide, 0.25% bromophenol blue, and 0.25% xylene cyanol FF.

The DNA fragments were analyzed using 20% polyacrylamide gel electrophoresis under denaturing conditions (7 M urea). Cleavages were visualized using Kodak Biomax MR single-emulsion film at -78°C for 12-18 h. Quantitation of the extent of cleavage was performed by integration of the optical density as a function of the band area using an Apple OneScanner and the Image program from the NIH. Care was taken to ensure that all

quantitated peaks were gaussian and that saturation of the film did not occur. The quantitative cleavages were used to construct the histogram shown in Scheme 2.

Table S1. Crystal Data for [(DAMP)(bpy)RuO](ClO$_4$)$_2$ and [(DAMP)(phen)RuO](ClO$_4$)$_2$

	[(DAMP)(bpy)RuO]$^{2+}$	[(DAMP)(phen)RuO]$^{2+}$
Formula	$C_{21}H_{27}N_5Cl_2O_9Ru$	$C_{23}H_{29}N_5Cl_2O_9Ru$
mol wt, g mol-1	665.44	689.46
crystal size, mm	0.30 x 0.30 x 0.30	0.25 x 0.25 x 0.25
λ(Mo Kα), Å	0.71073	0.71073
a, Å	9.910	9.491
b, Å	11.172	12.081
c, Å	12.879	13.097
α, deg	90.22	74.31
β, deg	108.41	72.66
γ, deg	105.73	70.06
V, Å^3	1295.9	1323.5
space group	P -1	P -1
Z	2	2
D_{calc}, g cm^{-3}	1.705	1.730
F(000), e$^-$	673.98	697.98
no. reflecns measd	4287	3680
R_{int}	0.039	0.058
function minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$	$\Sigma w(\|Fo\| - \|Fc\|)^2$
least-squares weights	$1/[\sigma^2(F) + 0.001F^2]$	$1/[\sigma^2(F) + 0.001F^2]$
no of observns, $I \geq 2.5\sigma(I)$	3063	2838
$R = \Sigma\|\|F_o\| - \|F_c\|\| / \|F_o\|$	0.034	0.042
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.047	0.055
goodness of fit, S	1.78	1.80

Table S2. Fractional Coordinates of [(DAMP)(bpy)RuO](ClO$_4$)$_2$.

	x	y	z	B_{iso}[a]
Ru1	0.14462 (3)	0.7845 (3)	0.2188 (23)	1.662 (14)
Cl 1	0.26253 (11)	0.20839 (9)	0.52275 (8)	2.45 (5)
Cl 2	0.5589 (12)	0.27599 (9)	0.07241 (8)	2.84 (5)
O 1	0.1299 (3)	0.7705 (3)	0.07569 (21)	2.58 (13)
N 11	0.175 (3)	0.7685 (3)	0.39157 (24)	1.73 (14)
C 12	0.1369 (4)	0.838 (3)	0.4571 (3)	1.94 (19)
C 13	0.1477 (4)	0.8143 (4)	0.5641 (3)	2.22 (18)
C 14	0.2001 (5)	0.7158 (4)	0.6057 (3)	2.67 (20)
C 15	0.2409 (5)	0.6441 (4)	0.539 (3)	2.67 (20)
C 16	0.2285 (4)	0.6725 (3)	0.4329 (3)	1.99 (18)
C 17	0.2711 (4)	0.603 (3)	0.3561 (3)	2.1 (19)
C 18	0.3326 (5)	0.5051 (4)	0.3839 (3)	2.88 (21)
C 19	0.3778 (5)	0.4519 (4)	0.3086 (4)	3.27 (23)
C 20	0.3621 (5)	0.4972 (4)	0.2079 (4)	3.16 (22)
C 21	0.2957 (5)	0.5921 (4)	0.1831 (3)	2.56 (19)
N 22	0.2505 (4)	0.6444 (3)	0.2554 (3)	2.15 (15)
N 23	-0.0852 (4)	0.6745 (3)	0.1852 (3)	2.76 (16)
C 24	-0.155 (5)	0.6306 (5)	0.0652 (4)	3.69 (22)
C 25	-0.1128 (5)	0.5647 (5)	0.2472 (4)	3.9 (24)
C 26	-0.1602 (4)	0.7649 (5)	0.2132 (3)	3.4 (24)
C 27	-0.0972 (5)	0.8939 (5)	0.1886 (3)	3.11 (23)
C 28	-0.1679 (6)	0.9881 (6)	0.1622 (4)	4.9 (3)
C 29	-0.0897 (7)	1.1032 (6)	0.1462 (4)	5.4 (4)
C 30	0.0566 (7)	1.1283 (5)	0.1556 (4)	4.3 (3)
C 31	0.1237 (5)	1.0335 (4)	0.179 (3)	2.91 (22)
N 32	0.0463 (4)	0.9203 (3)	0.1963 (3)	2.27 (16)
C 33	0.2749 (5)	1.0378 (4)	0.1759 (4)	3.08 (22)
N 34	0.3361 (3)	0.943 (3)	0.2437 (3)	2.09 (16)
C 35	0.4079 (4)	0.9962 (4)	0.3603 (4)	2.68 (19)
C 36	0.4535 (5)	0.9182 (4)	0.2042 (4)	3.48 (24)
O 11	0.2308 (4)	0.1132 (3)	0.5928 (3)	4.82 (20)
O 12	0.2307 (4)	0.3179 (3)	0.55605 (25)	3.44 (16)
O 13	0.414 (4)	0.2369 (3)	0.5287 (3)	4.9 (20)
O 14	0.1694 (4)	0.1617 (4)	0.4135 (3)	4.7 (18)
O 21	0.5526 (7)	0.3031 (6)	0.1807 (5)	2.92 (12)
O 22	0.4369 (7)	0.1681 (6)	0.0092 (5)	2.8 (12)
O 23	0.6871 (10)	0.2637 (8)	0.0954 (7)	6.02 (20)
O 24	0.526 (8)	0.3834 (6)	0.0112 (5)	3.53 (14)
O 31	0.5304 (7)	0.1421 (5)	0.0513 (5)	3.89 (12)
O 32	0.5047 (8)	0.328 (7)	-0.0232 (6)	5.57 (16)
O 33	0.7279 (6)	0.3204 (5)	0.091 (4)	2.84 (10)
O 34	0.5136 (6)	0.302 (5)	0.1627 (4)	3.11 (10)

[a]B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table S3. Fractional Coordinates of [(DAMP)(phen)RuO](ClO$_4$)$_2$.

		x	y	z	B_{iso}[a]
Ru	1	0.20428 (10)	0.2226 (8)	0.20631 (7)	1.78 (4)
Cl	1	0.12659 (17)	0.73054 (13)	0.08883 (12)	2.11 (7)
Cl	2	0.61791 (17)	0.21442 (14)	0.48478 (13)	2.46 (8)
O	1	0.1854 (5)	0.2522 (4)	0.0669 (3)	2.94 (25)
N	2	0.0962 (6)	0.0825 (4)	0.2424 (4)	2.06 (24)
C	3	0.2032 (8)	-0.0029 (6)	0.1691 (6)	3.0 (3)
C	4	0.3683 (8)	-0.0169 (6)	0.1681 (5)	2.6 (3)
C	5	0.4943 (8)	-0.113 (6)	0.1456 (5)	2.9 (4)
C	6	0.6393 (8)	-0.104 (6)	0.1317 (6)	3.3 (4)
C	7	0.6577 (7)	0.0026 (6)	0.1412 (5)	2.7 (3)
C	8	0.5297 (7)	0.0961 (6)	0.168 (5)	2.1 (3)
N	9	0.3893 (6)	0.0834 (4)	0.1811 (4)	2.1 (3)
C	10	0.5249 (7)	0.2149 (6)	0.1889 (5)	2.3 (3)
N	11	0.3842 (6)	0.3108 (4)	0.1629 (4)	1.8 (24)
C	12	0.0819 (7)	0.016 (6)	0.3575 (5)	2.5 (3)
C	13	-0.0597 (8)	0.1229 (7)	0.2165 (6)	3.2 (4)
C	14	0.4141 (7)	0.3605 (6)	0.0449 (5)	2.4 (3)
C	15	0.3553 (8)	0.4096 (6)	0.2218 (5)	2.5 (3)
N	21	0.0075 (6)	0.365 (4)	0.242 (4)	1.99 (25)
C	22	-0.082 (8)	0.4359 (6)	0.1749 (5)	2.09 (4)
C	23	-0.2152 (8)	0.5249 (7)	0.209 (6)	3.5 (4)
C	24	-0.258 (8)	0.5408 (6)	0.3133 (6)	3.2 (4)
C	25	-0.1665 (7)	0.4681 (6)	0.3877 (5)	2.4 (3)
C	26	-0.0354 (7)	0.3811 (5)	0.3484 (5)	1.8 (3)
C	27	-0.2056 (7)	0.4743 (6)	0.5009 (6)	2.7 (3)
C	28	-0.1138 (7)	0.4009 (6)	0.5672 (5)	2.4 (3)
C	29	0.0221 (7)	0.3123 (5)	0.5292 (5)	1.9 (3)
C	30	0.0603 (6)	0.3023 (5)	0.4193 (4)	1.5 (3)
C	31	0.1231 (7)	0.2331 (6)	0.5948 (5)	2.1 (3)
C	32	0.2484 (7)	0.1512 (5)	0.551 (5)	2.0 (3)
C	33	0.2758 (7)	0.1437 (5)	0.4423 (5)	1.8 (3)
N	34	0.187 (5)	0.2168 (4)	0.377 (4)	1.48 (22)
O	11	0.1869 (6)	0.6673 (4)	0.0002 (4)	3.8 (3)
O	12	0.0213 (7)	0.6716 (6)	0.1678 (4)	5.6 (3)
O	13	0.0485 (7)	0.8509 (5)	0.0561 (5)	5.5 (4)
O	14	0.245 (6)	0.7205 (5)	0.1394 (5)	4.4 (3)
O	21	0.5373 (6)	0.3254 (5)	0.4316 (5)	5.6 (3)
O	22	0.5462 (6)	0.1915 (7)	0.597 (4)	6.2 (4)
O	23	0.7731 (5)	0.2134 (4)	0.473 (4)	3.3 (3)
O	24	0.6188 (6)	0.1223 (4)	0.4347 (4)	3.8 (3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table S4. Electronic Absorption of Aquaruthenium(II), Hydroxoruthenium(III), and Oxoruthenium(IV) Complexes

Complex	λ (nm) (ε (M^{-1} cm^{-1}))
$[(DAMP)(bpy)RuOH_2]^{2+}$	200 (27900), 246 (17700), 294 (38800), 368 (11900), 486 (6900)
$[(DAMP)(bpy)RuOH]^{2+}$	200 (33500), 250 (15200), 294 (14800), 370 (5300), 486 (620)
$[(DAMP)(bpy)RuO]^{2+}$	200 (36300), 246 (17100), 268(13100), 300 (14200), 308(13300), 348 (3800), 368 (2070)
$[(DAMP)(phen)RuOH_2]^{2+}$	208 (33100), 224 (31500), 268 (36000), 360 (5990), 438 (5590), 486 (4400)
$[(DAMP)(phen)RuOH]^{2+}$	208 (31900), 224 (27500), 268 (27500), 366 (5600), 486 (1600)
$[(DAMP)(phen)RuO]^{2+}$	208 (34000), 226 (30500), 272 (28200), 358 (4400)
$[(DAMP)(dppz)RuOH_2]^{2+}$	208 (37300), 276 (58200), 318 (16000), 358 (18600), 372 (18200), 434 (10100)
$[(DAMP)(dppz)RuO]^{2+}$	206 (45100), 280 (57000), 364 (13900), 384 (13500)

Table S5. Yields of acetophenone from oxidation of sec-phenylethanol by [(DAMP)(bpy)RuO]$^{2+}$.

[RuO^{2+}] (mM)	[sec-phenylethanol] (mM)	Yield based on Ru (%)
5	1.25	29 ± 2
5	2.5	18 ± 1
5	5	17 ± 1
5	10	19 ± 1
5	25	35 ± 2
5	50	40 ± 2
5	100	91 ± 5

Table S6. Rate Constants for Oxidation of Sec-phenylethanol by 100 μM [(DAMP)(bpy)RuO]$^{2+}$.

[RuO] (mM)	$k_{1,obs}$ (s^{-1})	k_2 (M^{-1} s^{-1})	k_3 (M^{-1} s^{-1})	k_2/k_3
5	1.3×10^{-4}	2.3×10^{5}	0.98×10^{3}	230
15	2.5×10^{-4}	4.0×10^{5}	1.7×10^{3}	240
25	3.9×10^{-4}	5.6×10^{5}	2.5×10^{3}	220
45	6.9×10^{-4}	2.3×10^{5}	1.0×10^{3}	230

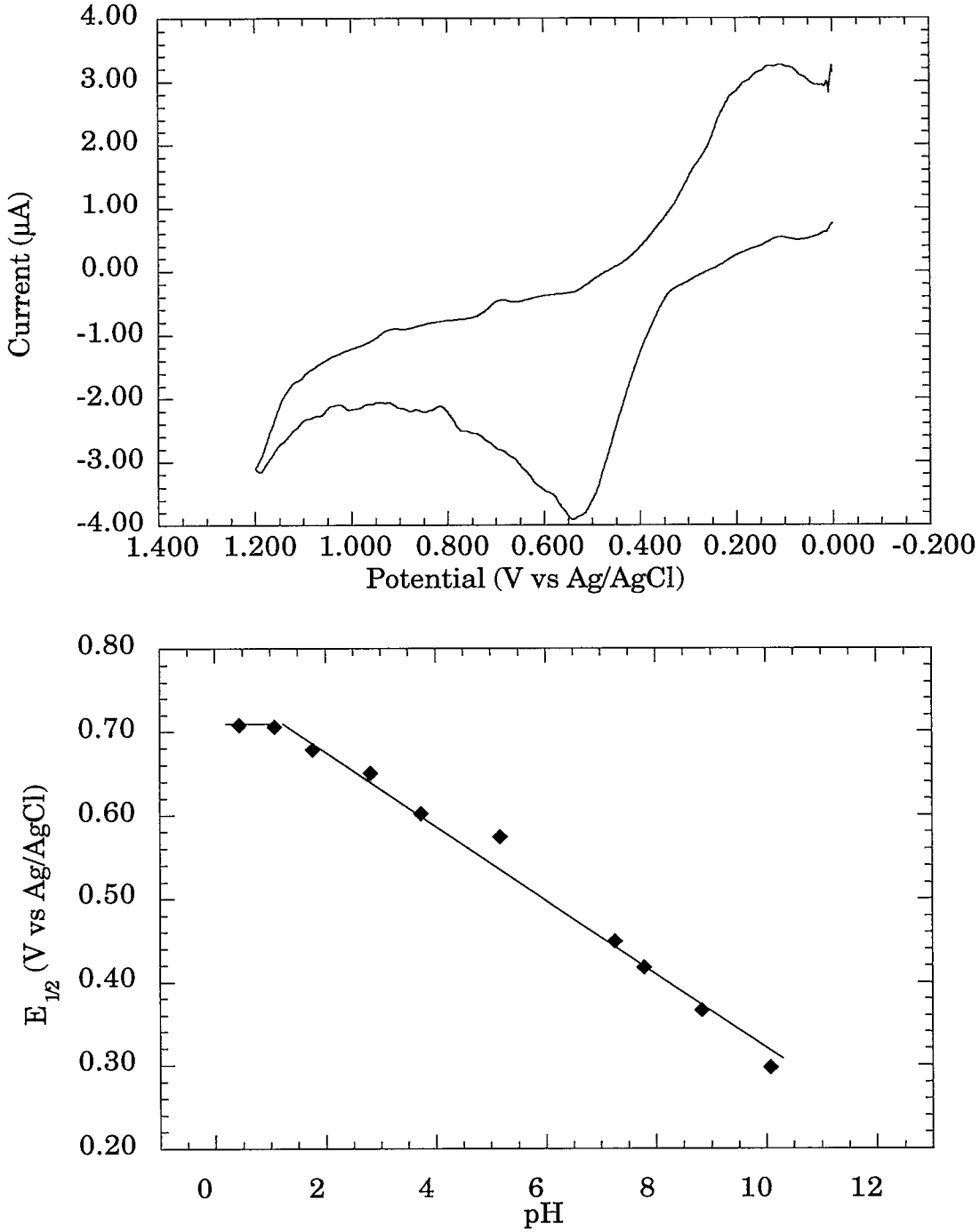

Figure S1. Cyclic voltammetry of a 100 μM solution of $[(DAMP)(dppz)RuOH_2]^{2+}$ (top) and Pourbaix Diagram (bottom). Conditions: EOPG working electrode, Pt Auxillary, Ag/AgCl reference, 2 mV s^{-1} scan rate.

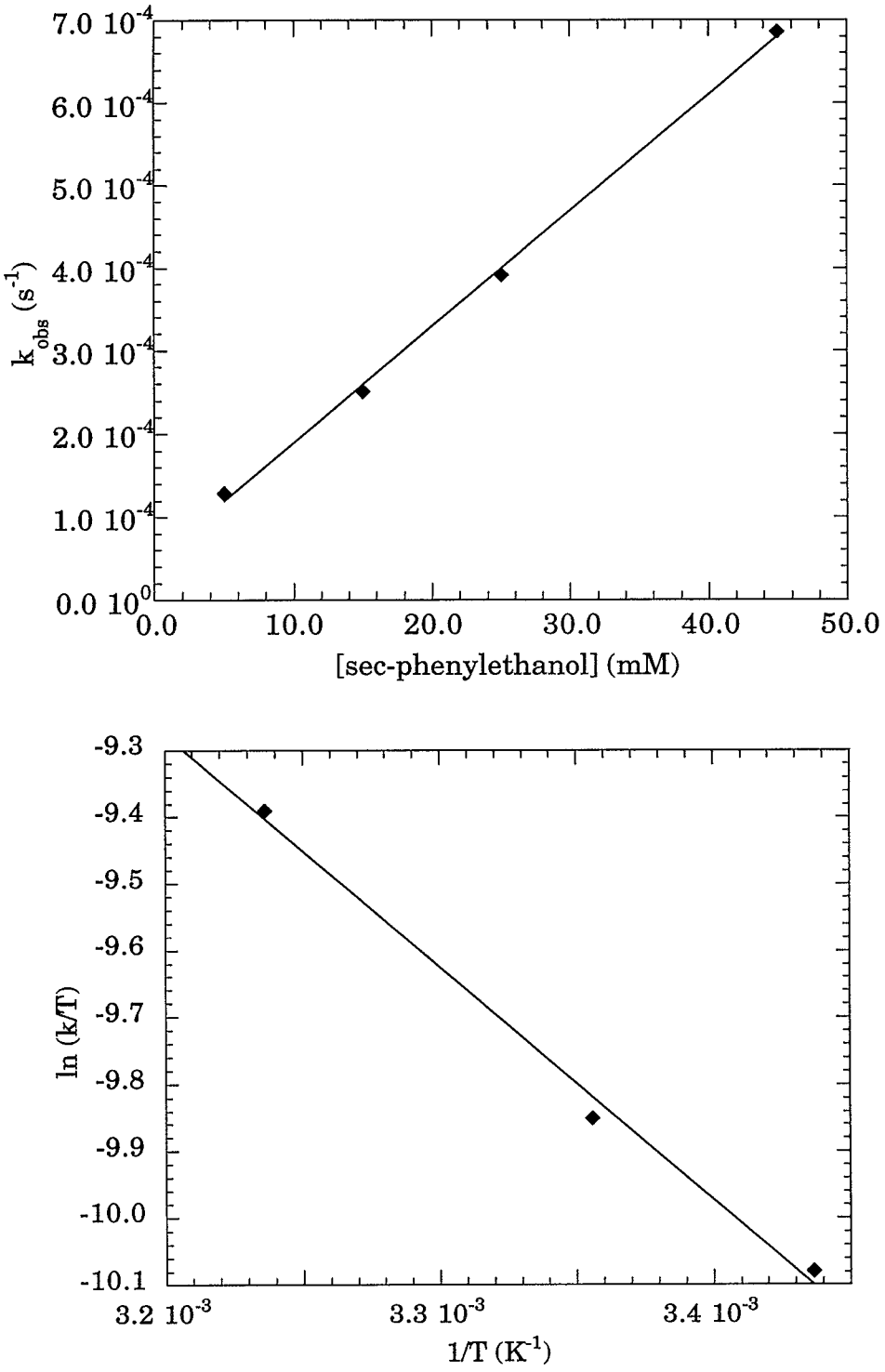

Figure S2. Plot of k_{obs} vs [sec-phenylethanol] (top) and Eyring plot (bottom) for oxidation of 25 mM sec-phenylethanol by 100 μM $[(DAMP)(bpy)RuO]^{2+}$.

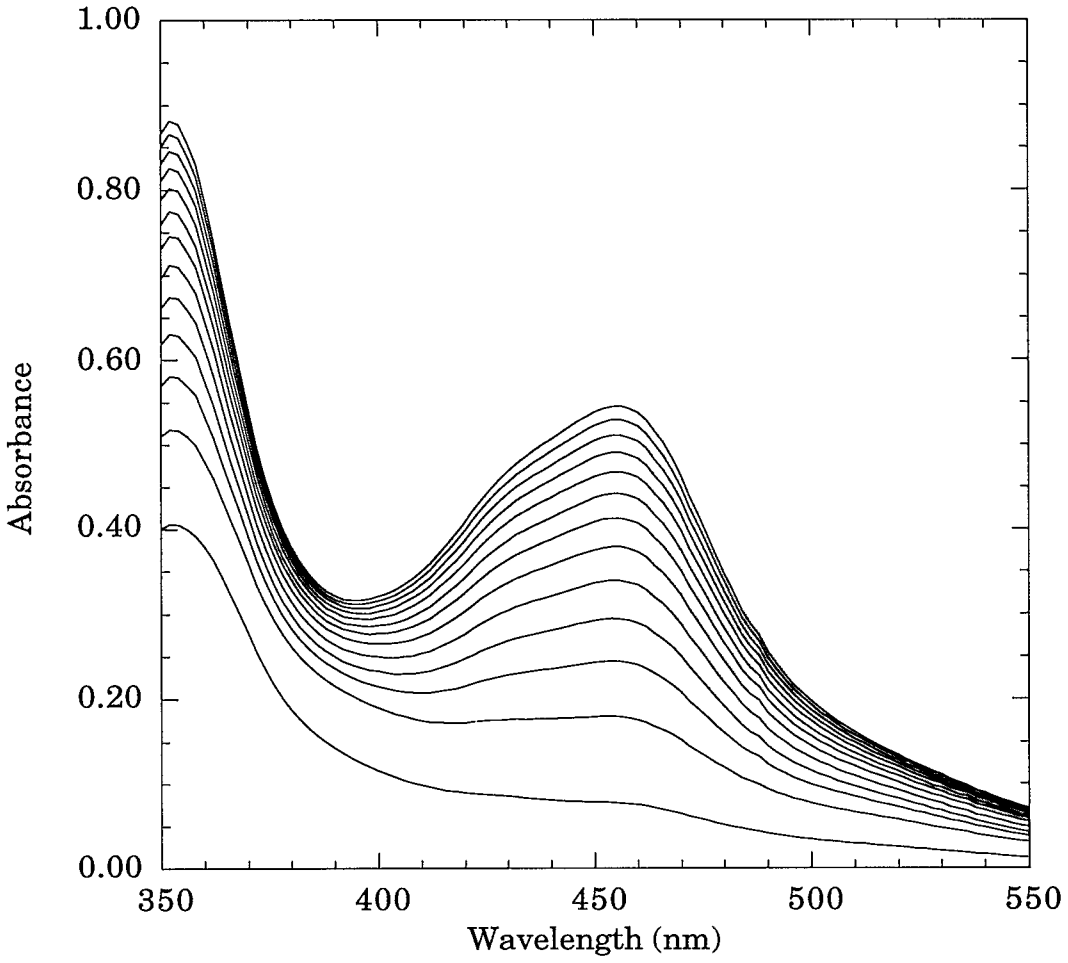

Figure S3. UV-visible spectral changes at 1200 s intervals during the reaction of 100 μM $[(DAMP)(bpy)RuO]^{2+}$ with 100 mM trans-stilbene in acetonitrile.

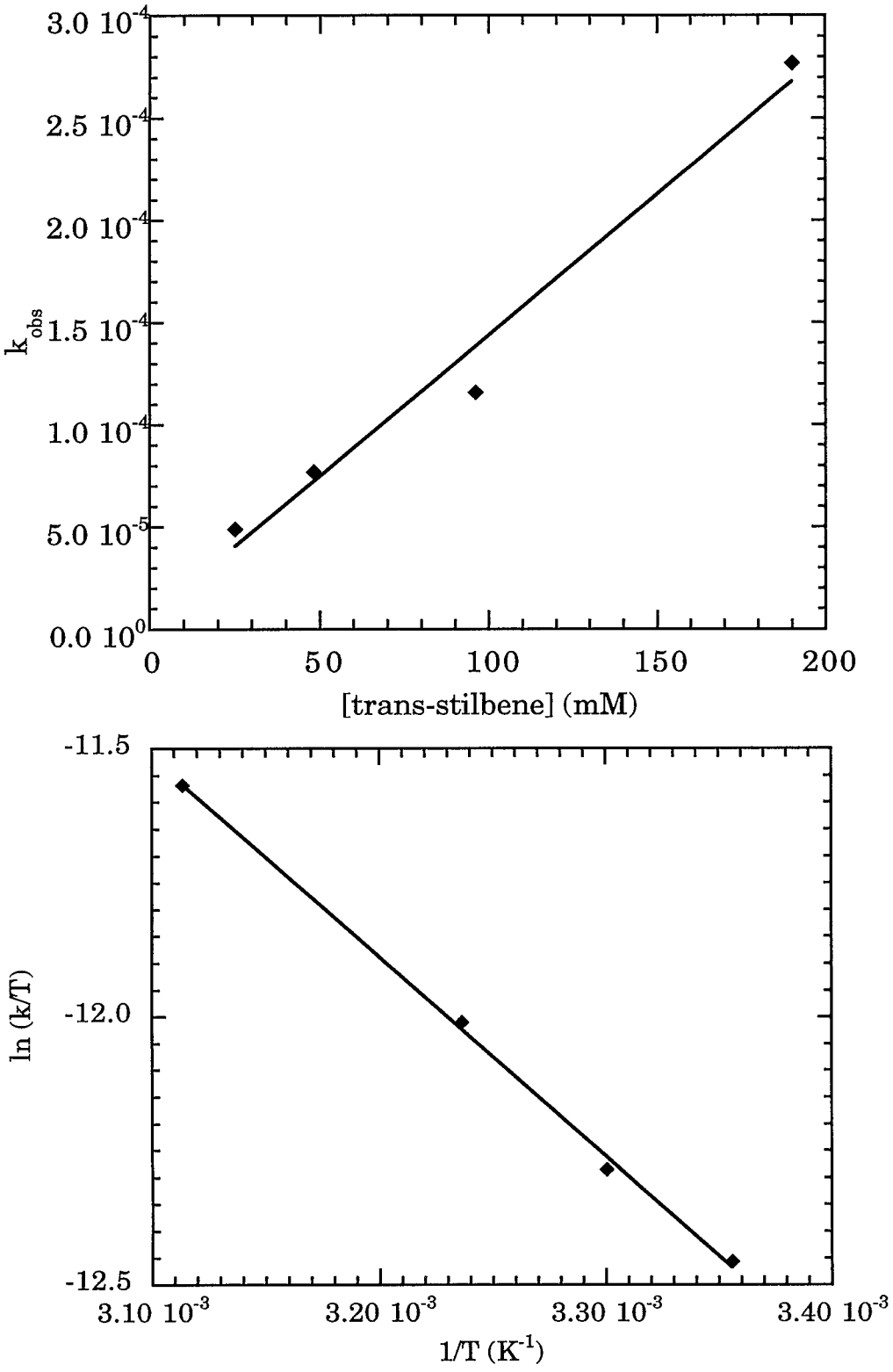

Figure S4. Plot of k_{obs} vs [trans-stilbene] (top) and Eyring plot (bottom) for oxidation of 100 mM trans-stilbene by 100 μM $[(DAMP)(bpy)RuO]^{2+}$ in acetonitrile.

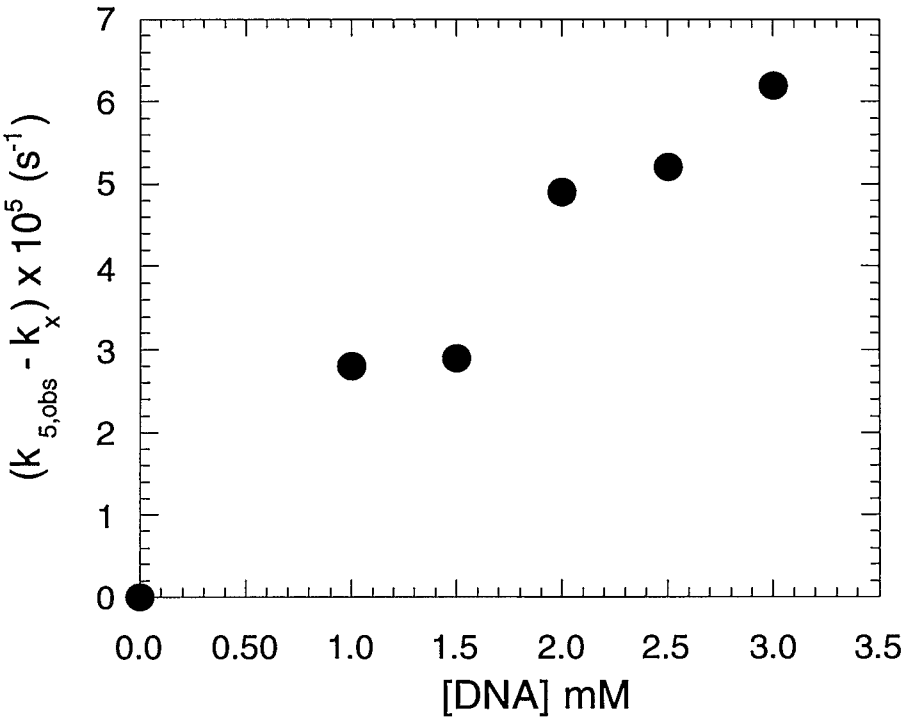

Figure S5. Plot of enhancement in pseudo first-order oxidation rate constant as a function of DNA concentration for 100 μM $[(DAMP)(bpy)RuO]^{2+}$.

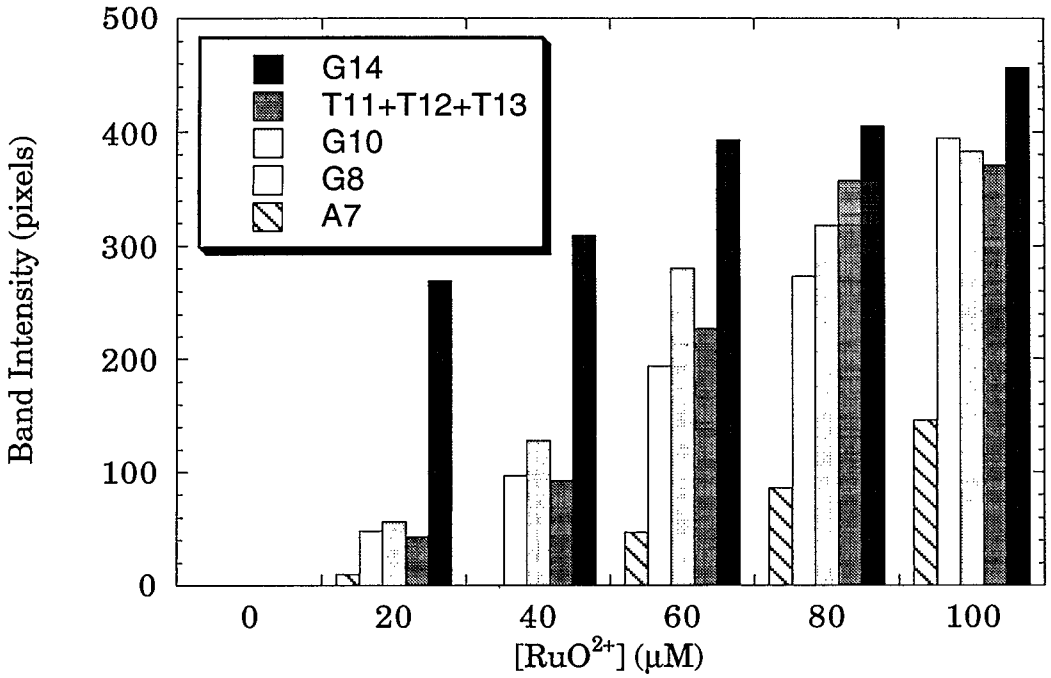

Figure S6. Histogram depicting relative yields of piperidine-labile lesions on the hairpin structure shown in Scheme 2 following reaction of 4 μM strand with $[(DAMP)(bpy)RuO]^{2+}$.