Table S1. ^{1}H and ^{13}C NMR chemical shifts of free ligands and ruthenium(II) complexes in $(CD_3)_2SO$

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^{1}H NMR data

Free ligands : δ (multiplicity, integration, assignment)

pdto : δ 8.487 (d, 2H, H_a), 7.209 (t, 2H, H_b), 7.687 (t, 2H, H_c), 7.301 (d, 2H, H_d), 3.367 (t, 4H, H_e), 2.974 (m, 4H, H_f), 2.922 (t, 4H, H_g).

bbdo : δ 7.472 (dd, 4H, H_a and H_d), 7.115 (dd, 4H, H_b and H_c), 3.086 (t, 4H, H_d), 3.003 (t, 4H, H_f), 2.749 (s, 4H, H_g).

bpy : δ 8.500 (d, 2H, H_3), 7.996 (t, 2H, H_4), 7.497 (t, 2H, H_5), 8.771 (d, 2H, H_6).

dpa : δ 7.737 (d, 2H, H_3), 7.636 (t, 2H, H_4), 6.847 (t, 2H, H_5), 8.213 (d, 2H, H_6), 9.632 (s, 1H, NH).

terpy : δ 8.444 (d, 2H, H_3), 8.008 (t, 2H, H_4), 7.493 (t, 2H, H_5), 8.725 (d, 2H, H_6), 8.636 (d, 2H, $H_{3'}$), 8.097 (t, 1H, $H_{4'}$).

Ruthenium(II) complexes : δ (multiplicity, integration, assignment, J/Hz, coordination-induced shifts: c.i.s., $\delta_{complex} - \delta_{ligand}$)

$[Ru(pdto)Cl]_2(ClO_4)_2$ 1 : Isomer **A**, δ 7.978 (d, 2H, H_a, 7.8, -0.509), 7.526 (t, 2H, H_b, 7.3, 0.317), 7.579 (t, 2H, H_c, 6.6, -0.108), 9.552 (d, 2H, H_d, 5.4, 2.251), 2.229 (t, 2H, H_e, 9.8, -1.138), 4.197 (t, 2H, $H_{e'}$, 13.9, 0.830), 3.282 (d, 2H, H_f, 5.9, 0.308), 3.413 (t, 2H, $H_{f'}$, 13.2, 0.439), 2.113 (t, 2H, H_g, 9.8, -0.809), 2.947 (t, 2H, $H_{g'}$, 11.7, 0.025). Isomer **B**, δ 7.938 (d, 2H, H_a, 7.8, -0.549), 7.474 (t, 2H, H_b, 6.8, 0.265), 7.526 (t, 2H, H_c, 7.3, -0.161), 9.219 (d, 2H, H_d, 4.9, 1.918), 2.169 (t, 2H, H_e, 12.7, -1.198), 3.482 (t, 2H, $H_{e'}$, 13.7, 0.115), 3.247 (d, 2H, H_f, 5.4, 0.273), 3.413 (t, 2H, $H_{f'}$, 13.2, 0.439), 1.811 (t, 2H, H_g, 9.5, -1.111), 2.947 (t, 2H, $H_{g'}$, 11.7, 0.025).

$[Ru(bbdo)Cl]_2(ClO_4)_2$ 2 : Isomer **A**, δ 7.983 (d, 2H, H_a, 8.0, 0.511), 7.592 (t, 2H, H_b, 6.0, 0.477), 7.476 (t, 2H, H_c, 6.8, 0.361), 9.556 (d, 2H, H_d, 5.2, 2.084), 2.247 (t, 2H, H_e, 13.4, -0.839), 4.201 (t, 2H, $H_{e'}$, 14.0, 1.115), 3.272 (d, 2H, H_f, 5.2, 0.269), 3.408 (t, 2H, $H_{f'}$, 10.8, 0.405), 2.126 (t, 2H, H_g, 10.4, -0.623), 2.951 (t, 2H, $H_{g'}$, 13.6, 0.202). Isomer **A'**, δ 7.944 (d, 2H, H_a, 8.0, 0.472), 7.535 (t, 2H, H_b, 7.4, 0.420), 7.535 (t, 2H, H_c, 7.4, 0.420), 9.223 (d, 2H, H_d, 5.2, 1.751), 2.182 (t, 2H, H_e, 12.2, -0.904), 3.470 (t, 2H, $H_{e'}$, 13.9, 0.419), 3.237 (d, 2H, H_f, 4.8, 0.234), 3.408 (t, 2H, $H_{f'}$, 10.8, 0.405), 1.820 (t, 2H, H_g, 14.0, -0.929), 2.951 (t, 2H, $H_{g'}$, 13.6, 0.202). Isomer **B**, δ 7.236 (d, 2H, H_a, 7.6, -0.236), 7.535 (t, 2H, H_b, 7.4, 0.420), 6.773 (t, 2H, H_c, 6.4, -0.342), 8.915 (d, 2H, H_d, 5.2, 1.443), 1.724 (t, 2H, H_e, 12.8, -1.362), 3.441 (t, 2H, $H_{e'}$, 11.0, 0.419), 3.068 (d, 2H, H_f, 4.4, 0.065), 3.097 (d, 2H, $H_{f'}$, 4.0, 0.094), 1.411 (d, 2H, H_g, 9.6, -1.338), 2.612 (d, 2H, $H_{g'}$, 9.6, -0.137).

$[Ru(pdto)(bpy)](ClO_4)_2$ 3 : δ 7.349 (d, 2H, H_a, 7.8, -1.138), 7.227 (t, 2H, H_b, 6.4, 0.018), 8.031 (t, 2H, H_c, 6.4, 0.326), 8.609 (d, 2H, H_d, 6.4, 1.308), 2.382 (t, 2H, H_e, 12.7, -0.985), 3.662 (d, 2H, $H_{e'}$, 9.8, 0.295), 3.237 (d, 2H, H_f, 10.8, 0.263), 3.377 (d, 2H, $H_{f'}$, 16.6,

0.403), 2.247 (d, 2H, H_g, 9.8, -0.675), 3.188 (d, 2H, $H_{g'}$, 8.3, 0.266), 10.058 (d, 2H, H_3, 4.9, 1.558), 8.286 (t, 2H, H_4, 7.8, 0.290), 7.736 (t, 2H, H_5, 7.6, 0.239), 8.609 (d, 2H, H_6, 6.4, -0.162).

[Ru(bbdo)(bpy)](ClO$_4$)$_2$ 4 : δ 5.620 (d, 2H, H_a, 8.3, -1.852), 5.754 (t, 2H, H_b, 7.8, -1.361), 6.044 (t, 2H, H_c, 8.1, -1.071), 7.417 (d, 2H, H_d, 7.8, -0.055), 1.466 (d, 2H, H_e, 10.7, -1.620), 2.525 (t, 2H, $H_{e'}$, 6.9, -0.561), 2.184 (d, 2H, H_f, 9.3, -0.819), 2.212 (t, 2H, $H_{f'}$, 6.4, -0.791), 1.449 (d, 2H, H_g, 10.7, -1.300), 1.784 (t, 2H, $H_{g'}$, 9.3, -0.965), 12.167 (br, 2H, NH_{bzim}), 8.853 (d, 2H, H_3, 5.4, 0.353), 7.105 (t, 2H, H_4, 7.3, -0.891), 6.695 (t, 2H, H_5, 6.1, -0.802), 6.335 (d, 2H, H_6, 7.8, -2.436).

[Ru(pdto)(dpa)](ClO$_4$)$_2$ 5 : δ 7.364 (d, 2H, H_a, 7.1, -1.123), 7.091 (t, 2H, H_b, 6.2, -0.118), 7.822 (t, 2H, H_c, 6.7, 0.135), 7.841 (d, 2H,H_d, 6.3, 0.540), 3.510 (t, 2H, H_e, 8.4, 0.143), 3.510 (t, 2H, $H_{e'}$, 8.4, 0.143), 3.225 (t, 2H, H_f, 6.8, 0.251), 3.225 (t, 2H, $H_{f'}$, 6.8, 0.251), 2.816 (t, 2H, H_g, 8.3, -0.106), 2.816 (t, 2H, $H_{g'}$, 8.3, -0.106), 8.040 (d, 2H, H_3, 6.8, 0.303), 7.796 (t, 2H, H_4, 7.0, 0.160), 7.091 (t, 2H, H_5, 6.4, -0.406), 7.364 (d, 2H, H_6, 5.8, -1.407), 10.921 (s, 1H, NH_{dpa}, 1.289).

[Ru(bbdo)(dpa)](ClO$_4$)$_2$ 6 : δ 6.583 (d, 2H, H_a, 8.1, -0.889), 6.823 (t, 2H, H_b, 7.1, -0.292), 7.803 (t, 2H, H_c, 7.3, 0.688), 8.393 (d, 2H, H_d, 7.1, 0.921), 3.592 (t, 2H, H_e, 8.2, 0.506), 3.592 (t, 2H, $H_{e'}$, 8.2, 0.506), 3.102 (t, 2H, H_f, 6.9, 0.099), 3.102 (t, 2H, $H_{f'}$, 6.9, 0.099), 2.612 (t, 2H, H_g, 8.4, -0.137), 2.612 (t, 2H, $H_{g'}$, 8.4, -0.137), 11.992 (br, 2H, NH_{bzim}), 8.866 (d, 2H, H_3, 6.9, 1.129), 8.102 (t, 2H, H_4, 7.2, 0.466), 7.139 (t, 2H, H_5, 6.2, -0.358), 7.517 (d, 2H, H_6, 6.6, -1.254), 10.720 (s, 1H, NH_{dpa}, 1.088).

[Ru(pdto)(terpy)](ClO$_4$)$_2$ 7 : δ 7.351 (d, 2H, H_a, 7.9, -1.136), 7.324 (t, 2H, H_b, 7.6, 0.115), 7.785 (t, 2H, H_c, 7.2, 0.098), 8.659 (d, 2H, H_d, 4.9, 1.358), 1.901 (t, 2H, H_e, 12.3, -1.466), 3.300 (t, 2H, $H_{e'}$, 8.1, -0.067), 2.929 (d, 2H, H_f, 9.7, -0.045), 3.101 (t, 2H, $H_{f'}$, 13.7, 0.127), 1.818 (d, 2H, H_g, 9.5, -1.104), 2.222 (d, 2H, $H_{g'}$, 9.6, -0.700), 10.677 (s, 2H, H_3, 2.233), 7.785 (t, 2H, H_4, 7.2, -0.223), 7.477 (t, 2H, H_5, 7.6, -0.016), 8.659 (d, 2H, H_6, 4.9, -0.066), 10.677 (s, 2H, $H_{3'}$, 2.041), 10.166 (s, 1H, $H_{4'}$, 2.069).

[Ru(bbdo)(terpy)](ClO$_4$)$_2$ 8 : δ 7.184 (d, 2H, H_a, 6.2, -0.288), 7.075 (t, 2H, H_b, 4.8, -0.040), 7.470 (t, 2H, H_c, 6.2, 0.355), 8.445 (d, 2H, H_d, 7.7, 0.973), 1.590 (t, 2H, H_e, 12.2, -1.496), 3.205 (t, 2H, $H_{e'}$, 8.6, -0.119), 2.800 (d, 2H, H_f, 9.2, -0.203), 2.198 (d, 2H, $H_{f'}$, 12.8, -0.085), 1.343 (d, 2H, H_g, 8.0, -1.406), 2.386 (d, 2H, $H_{g'}$, 8.1, -0.363), 11.752 (br, 2H, NH_{bzim}), 8.634 (d, 2H, H_3, 6.6, 0.190), 8.056 (t, 2H, H_4, 7.1, 0.051), 7.470 (t, 2H, H_5, 6.2, -0.027), 8.412 (d, 2H, H_6, 8.2, -0.313), 8.724 (s, 2H, $H_{3'}$, 0.088), 8.113 (t, 1H, $H_{4'}$, 7.6, 0.016).

^{13}C NMR data

Free ligands : δ (assignment)

pdto : δ 159.56 (C_{a*}), 148.92 (C_a), 123.03 (C_b), 136.29 (C_c), 121.43 (C_d), 37.61 (C_e), 31.22 (C_f), 30.50 (C_g).

bbdo : δ 157.73 (C_{c*}), 142.90 (C_{b*} and C_{a*}), 118.79 (C_a and C_d), 125.58 (C_b and C_c), 35.44 (C_e), 33.73 (C_f), 33.44 (C_g).

bpy : δ 155.36 (C_2), 120.52 (C_3), 124.15 (C_4), 137.23 (C_5), 149.29 (C_6).

Ruthenium(II) complexes : δ (assignment, coordination-induced shifts: c.i.s., $\delta_{complex}$ - δ_{ligand})

[Ru(pdto)Cl]$_2$(ClO$_4$)$_2$ 1 : Isomer **A**, δ 165.53 (C_{a*}, 5.97), 138.88 (C_a, -10.04), 123.85 (C_b, 0.82), 127.61 (C_c, -8.68), 157.67 (C_d, 36.24), 34.45 (C_e, -3.16), 33.70 (C_f, 2.48), 26.52 (C_g, -3.98). Isomer **B**, δ 163.68 (C_{a*}, 4.12), 138.77 (C_a, -10.15), 123.44 (C_b, 0.41), 127.05 (C_c, -9.24), 156.96 (C_d, 35.53), 34.23 (C_e, -3.38), 31.93 (C_f, 0.71), 24.88 (C_g, -5.62).

[Ru(bbdo)Cl]$_2$(ClO$_4$)$_2$ 2 : Isomer **A**, δ 134.16 (C_{a*}, -8.74), 142.18 (C_{b*}, -0.72), 154.77 (C_{c*}, -2.96),121.91 (C_a, 3.12), 112.10 (C_b, -13.48), 119.70 (C_c, -5.88), 126.21 (C_d, 7.42), 32.28 (C_e, -3.16), 27.02 (C_f, -6.71), 24.01 (C_g, -9.43). Isomer **A'**, δ 132.32 (C_{a*}, -10.58), 139.01 (C_{b*}, -3.89), 152.28 (C_{c*}, -5.45), 120.68 (C_a, 1.89), 110.23 (C_b, -15.35), 117.31 (C_c, -8.27), 124.11 (C_d, 5.32), 30.12 (C_e, -5.32), 26.48 (C_f, -7.25), 22.63 (C_g, -10.81). Isomer **B**, δ 130.21 (C_{a*}, -12.69), 137.89 (C_{b*}, -5.01), 150.85 (C_{c*}, -6.88), 120.09 (C_a, 1.30), 108.14 (C_b, -17.44), 115.28 (C_c, -10.30), 122.43 (C_d, 3.64), 28.29 (C_e, -7.15), 24.68 (C_f, -9.05), 21.09 (C_g, -12.35).

[Ru(pdto)(bpy)](ClO$_4$)$_2$ 3 : δ 163.62 (C_{a*}, 4.07), 124.06 (C_a, -24.86), 123.60 (C_b, 0.57), 128.45 (C_c, -5.42), 153.11 (C_d, 31.68), 33.88 (C_e, -3.93), 31.68 (C_f, 0.46), 26.08 (C_g, -4.42), 163.62 (C_2, 8.26), 156.94 (C_3, 36.42), 138.40 (C_4, 14.25), 127.35 (C_5, -9.88), 139.42 (C_6, -9.87).

[Ru(bbdo)(bpy)](ClO$_4$)$_2$ 4 : δ 132.45 (C_{a*}, -10.45), 143.03 (C_{b*}, 0.13), 154.52 (C_{c*}, -3.21), 112.34 (C_a, -6.45), 115.91 (C_b, -9.67), 121.95 (C_c, -3.63), 138.90 (C_d, 20.11), 35.50 (C_e, 0.06), 27.40 (C_f, -6.33), 25.96 (C_g, -7.48), 154.52 (C_2, -0.84), 157.60 (C_3, 37.08), 126.61 (C_4, 2.46), 124.01 (C_5, -13.22), 123.13 (C_6, -26.16).

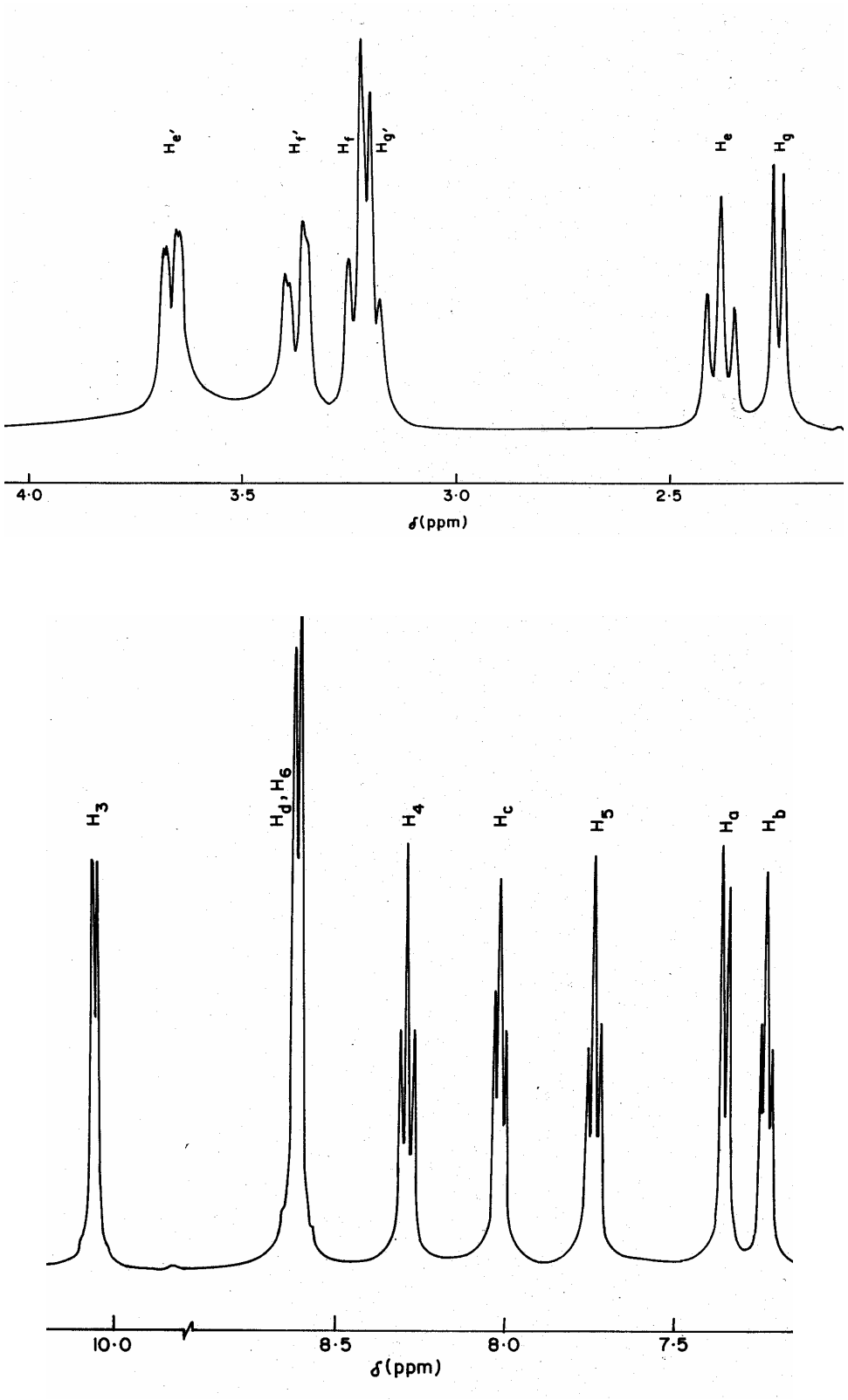

Fig. S1. ^{1}H NMR spectrum of [Ru(pdto)(bipy)]$(ClO_4)_2$ **3** in $(CD_3)_2SO$.

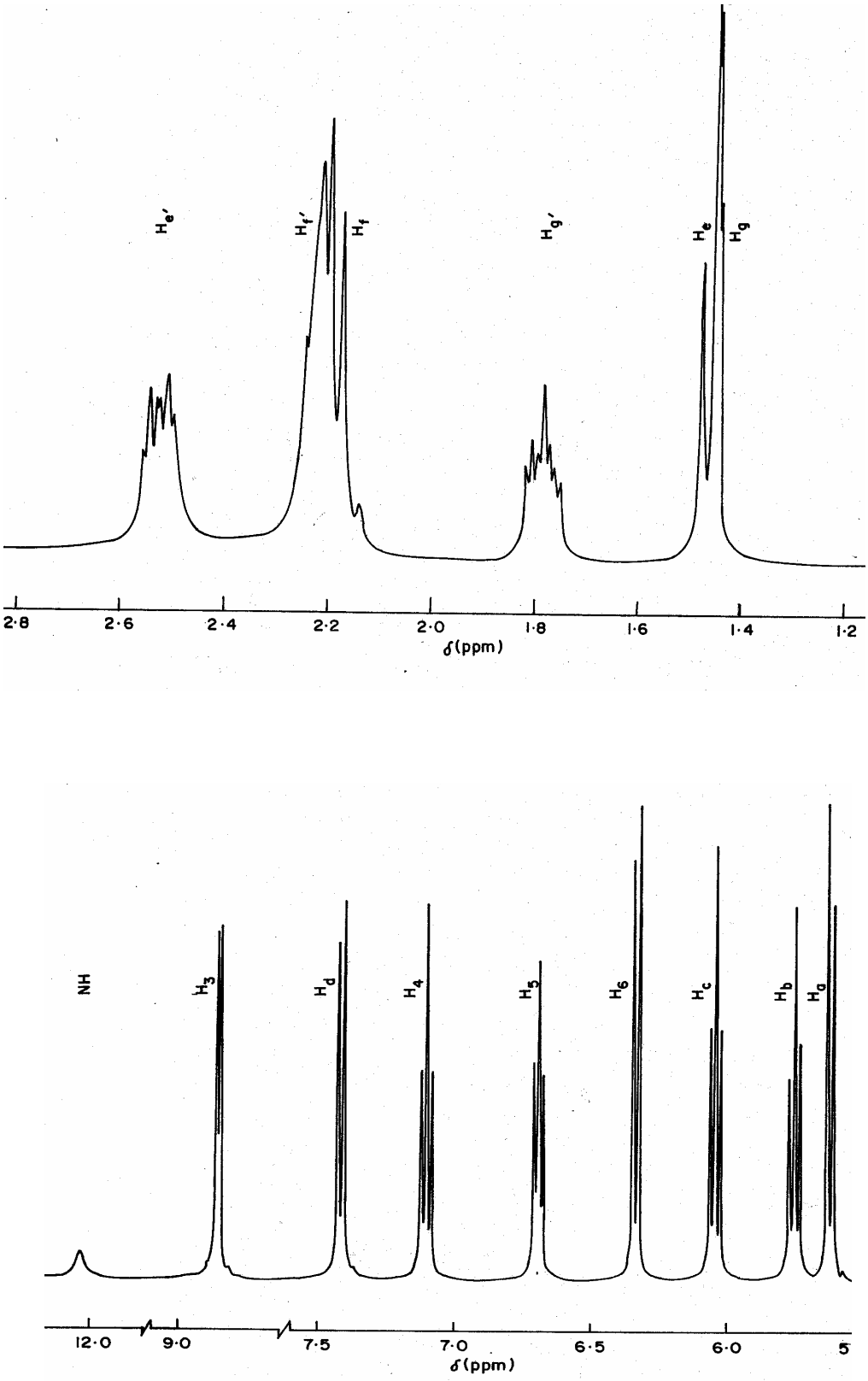

Fig. S2. ^{1}H NMR spectrum of [Ru(bbdo)(bipy)]$(ClO_4)_2$ **4** in $(CD_3)_2SO$.

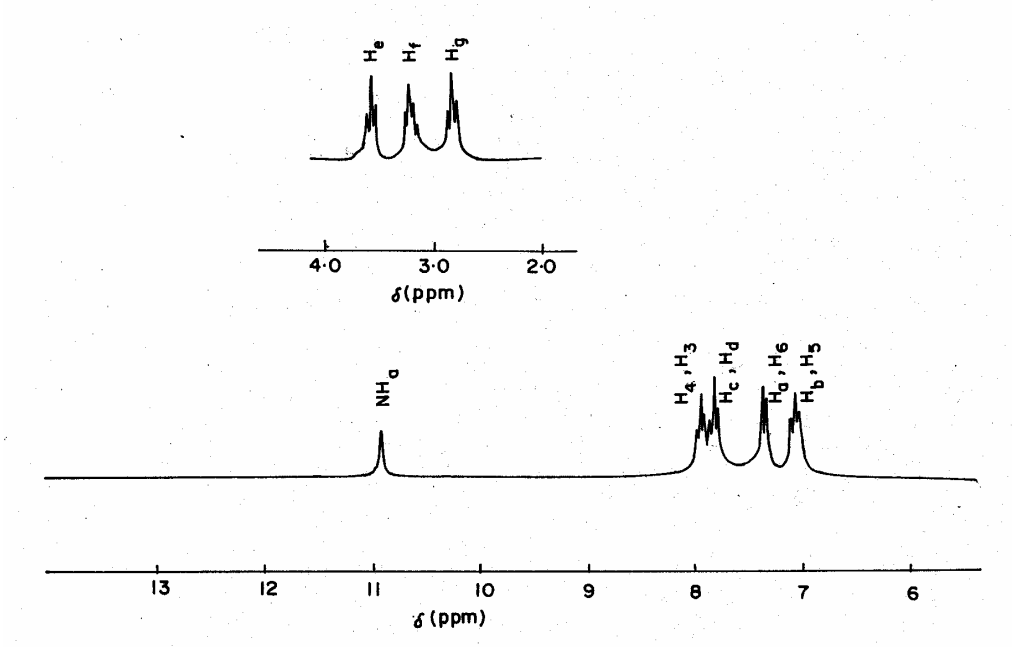

Fig. S3. ^{1}H NMR spectrum of [Ru(pdto)(dpa)]$(ClO_4)_2$ **5** in $(CD_3)_2SO$.

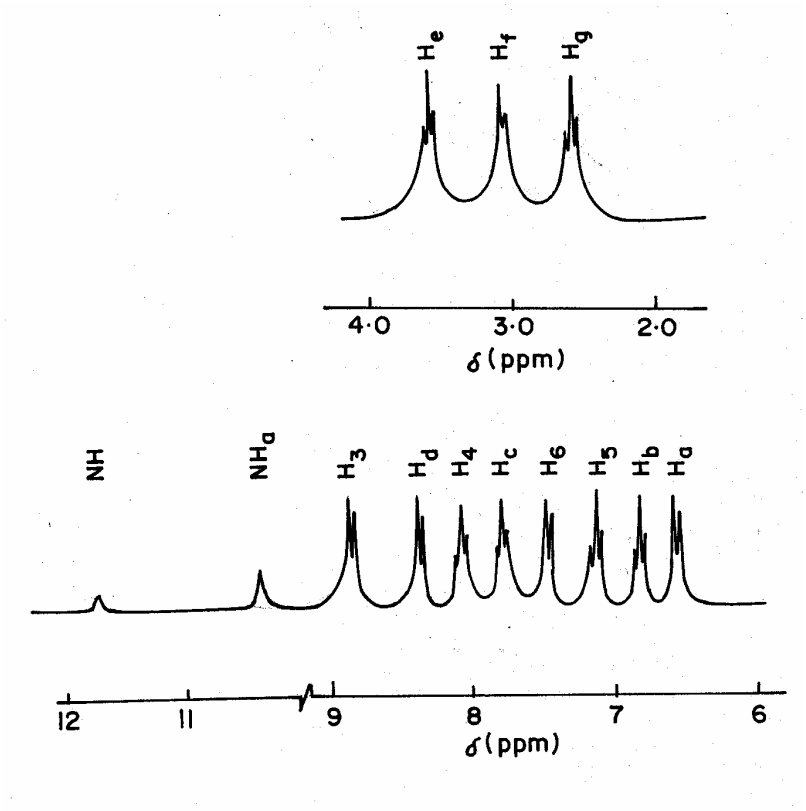

Fig. S4. ^{1}H NMR spectrum of [Ru(bbdo)(dpa)]$(ClO_4)_2$ **6** in $(CD_3)_2SO$.

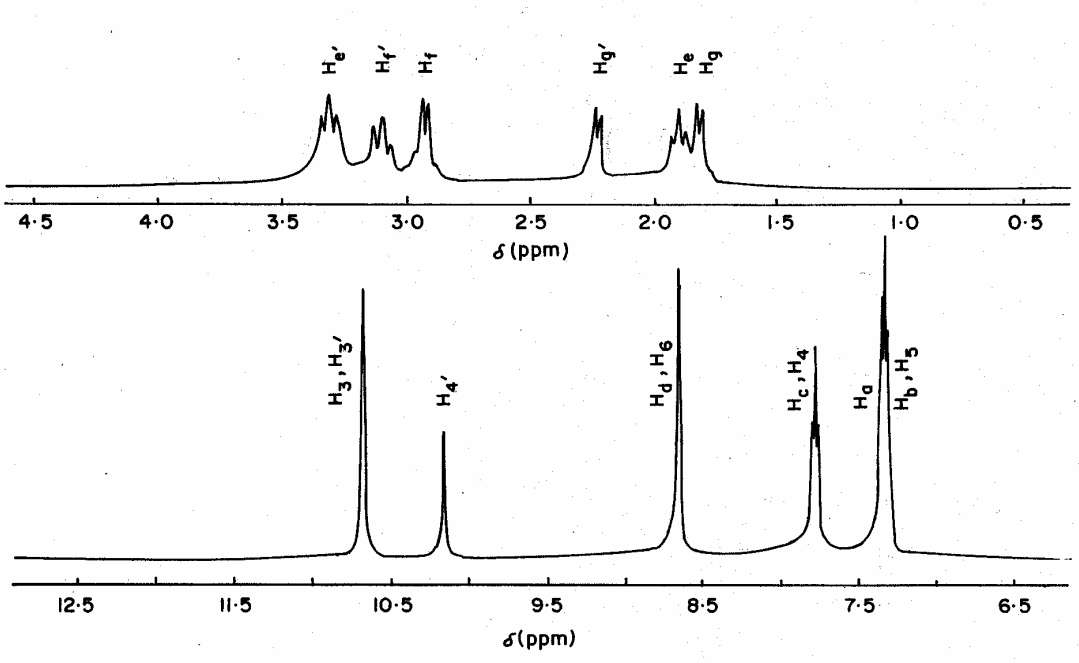

Fig. S5. ^{1}H NMR spectrum of [Ru(pdto)(terpy)]$(ClO_4)_2$ **7** in $(CD_3)_2SO$.

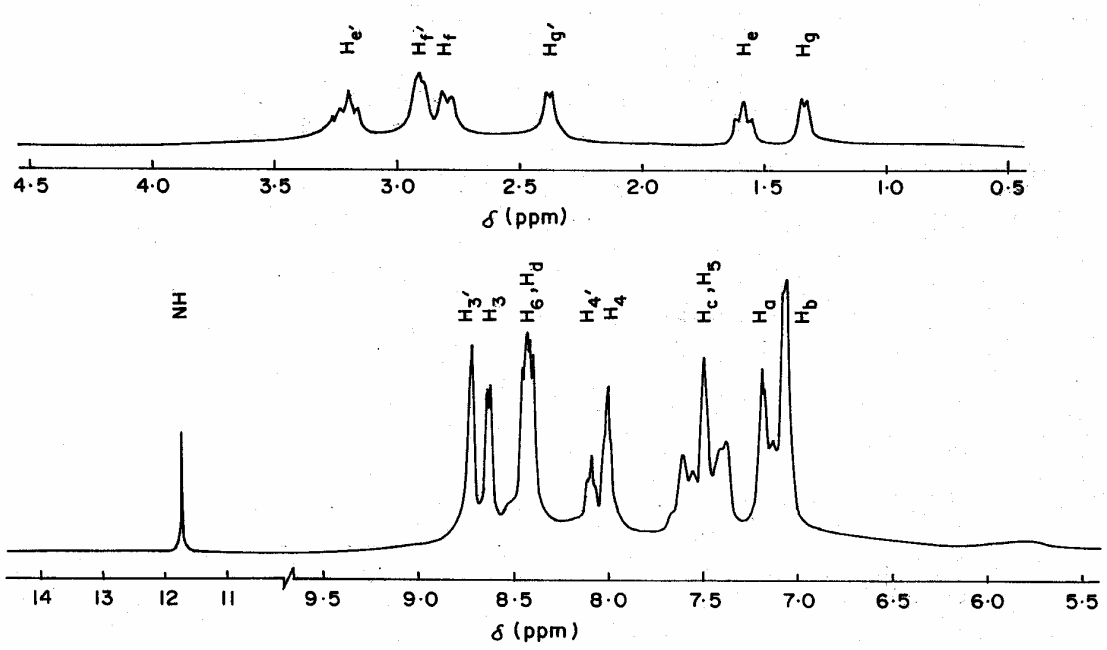

Fig. S6. ^{1}H NMR spectrum of [Ru(bbdo)(terpy)]$(ClO_4)_2$ **8** in $(CD_3)_2SO$.

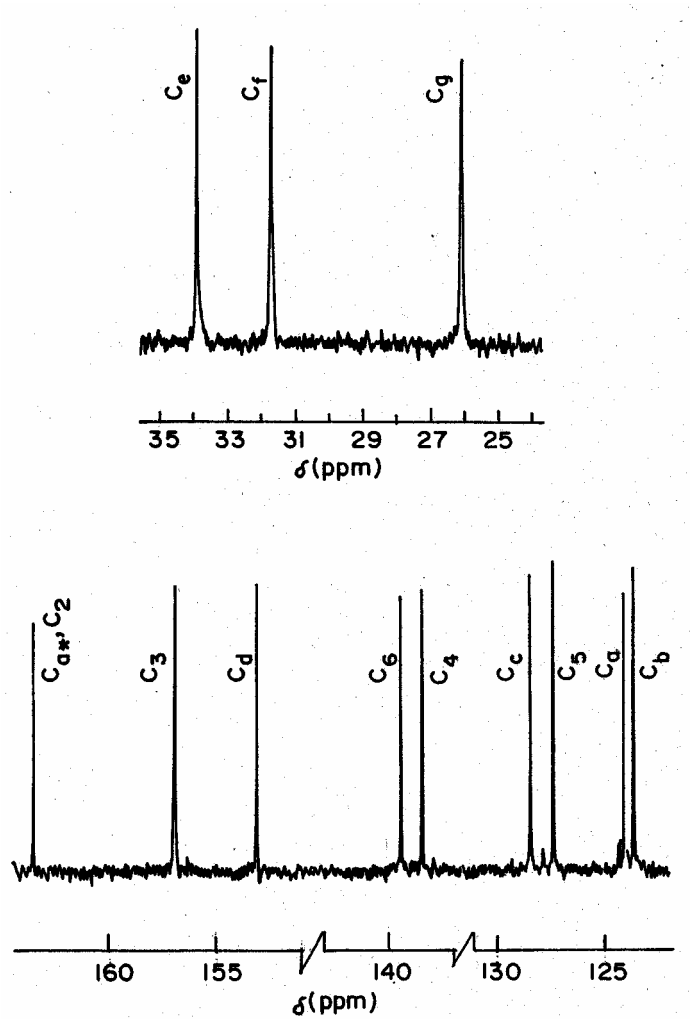

Fig. S7. ^{13}C NMR spectrum of $[Ru(pdto)(bipy)](ClO_4)_2$ **3** in $(CD_3)_2SO$.

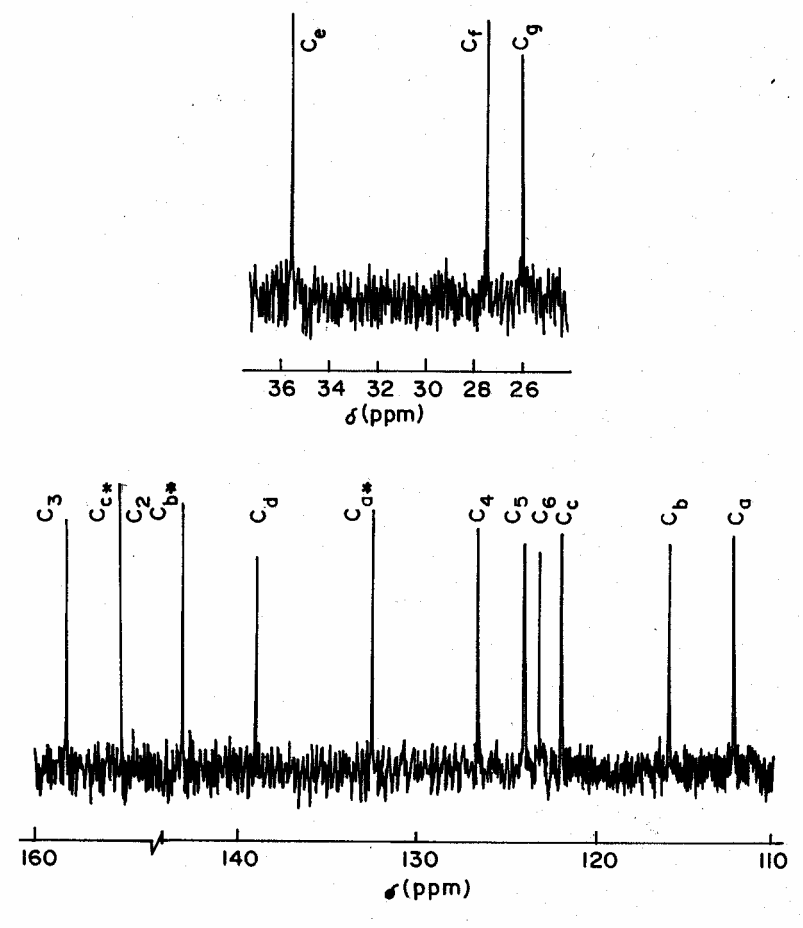

Fig. S8. ^{13}C NMR spectrum of [Ru(bbdo)(bipy)]$(ClO_4)_2$ **4** in $(CD_3)_2SO$.

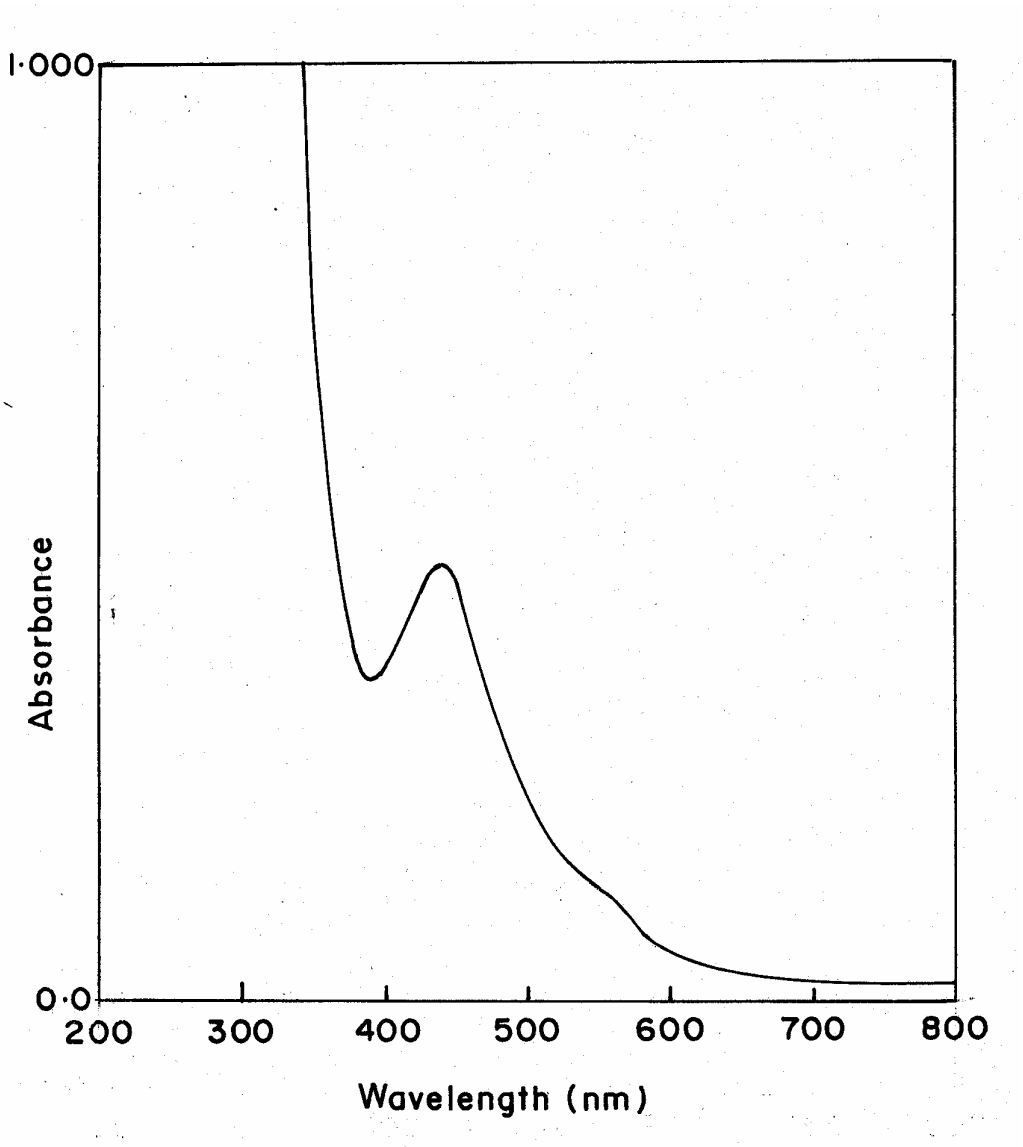

Fig. S9. Electronic spectrum of the complex [Ru(bbdo)(terpy)]$(ClO_4)_2$ **8** in acetonitrile solution.

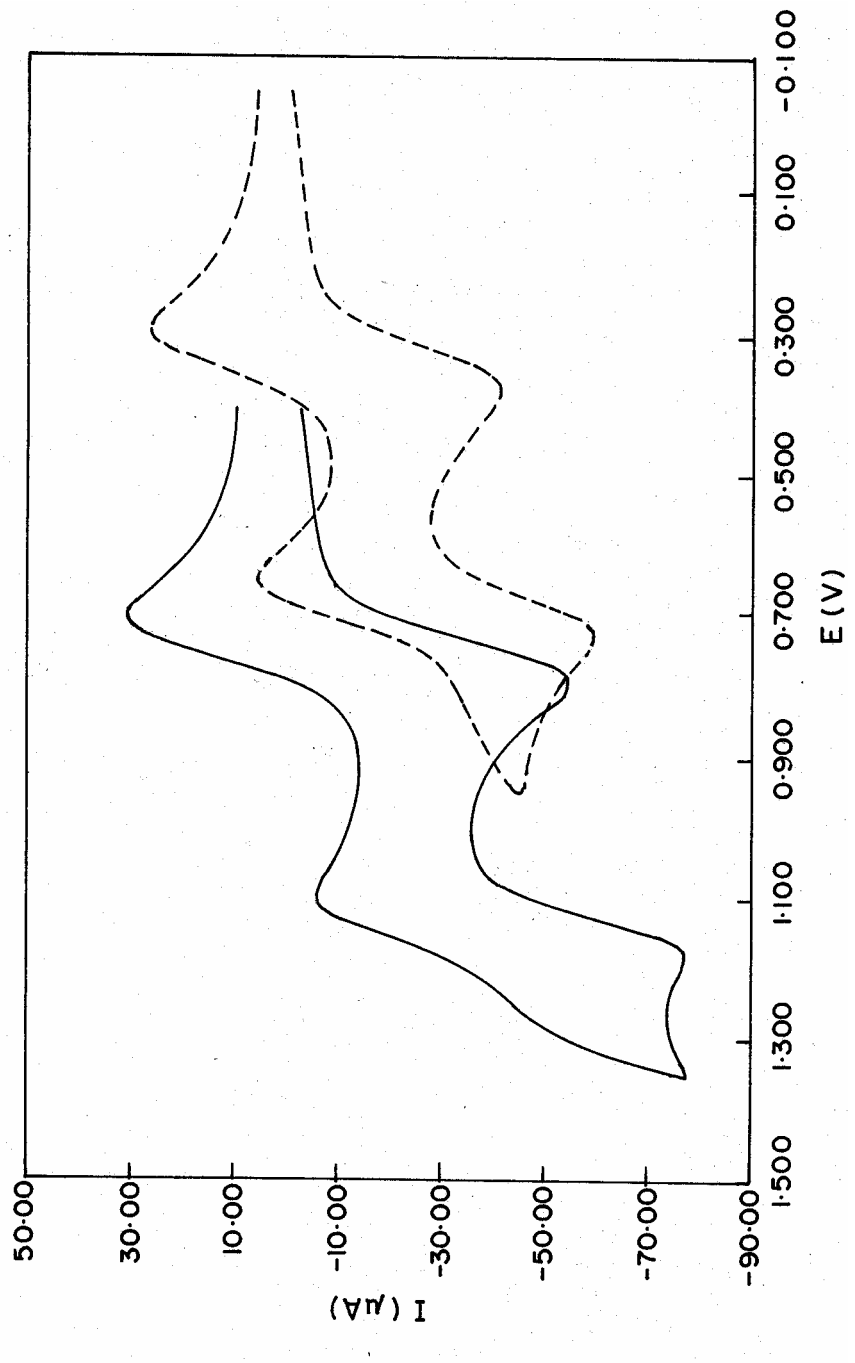

Fig. S10. Cyclic voltammograms of 0.001 M complexes $[Ru(pdto)(\mu\text{-}Cl)]_2(ClO_4)_2$ **1** (—) and $[Ru(bbdo)(\mu\text{-}Cl)]_2(ClO_4)_2$ **2** (----) in CH_3CN at 25 °C at 0.05 Vs-1 scan rate.

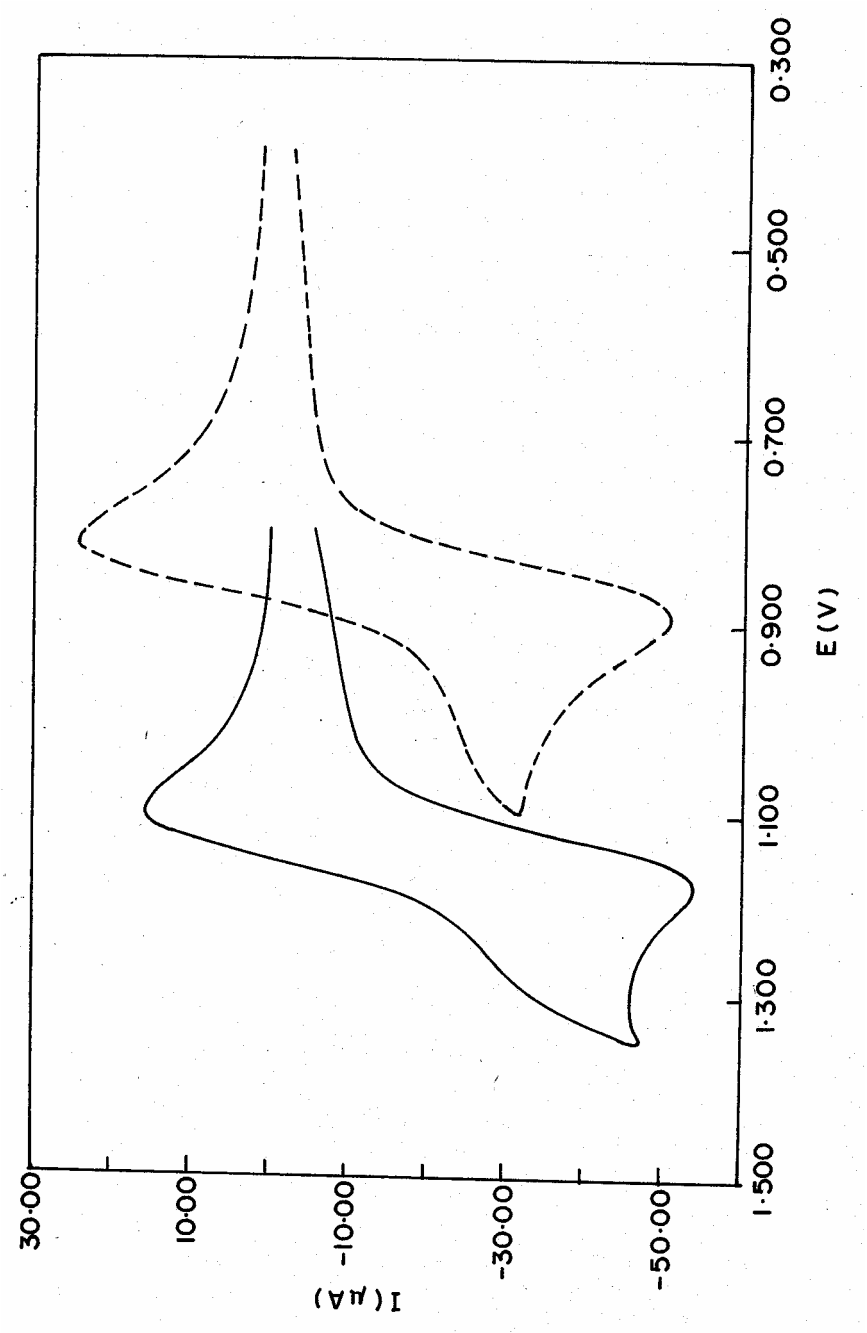

Fig. S11. Cyclic voltammograms of 0.001 M complexes [Ru(pdto)(bipy)]$(ClO_4)_2$ **3** (—) and [Ru(bbdo)(bipy)]$(ClO_4)_2$ **4** (----) in CH_3CN at 25 °C at 0.05 Vs-1 scan rate.

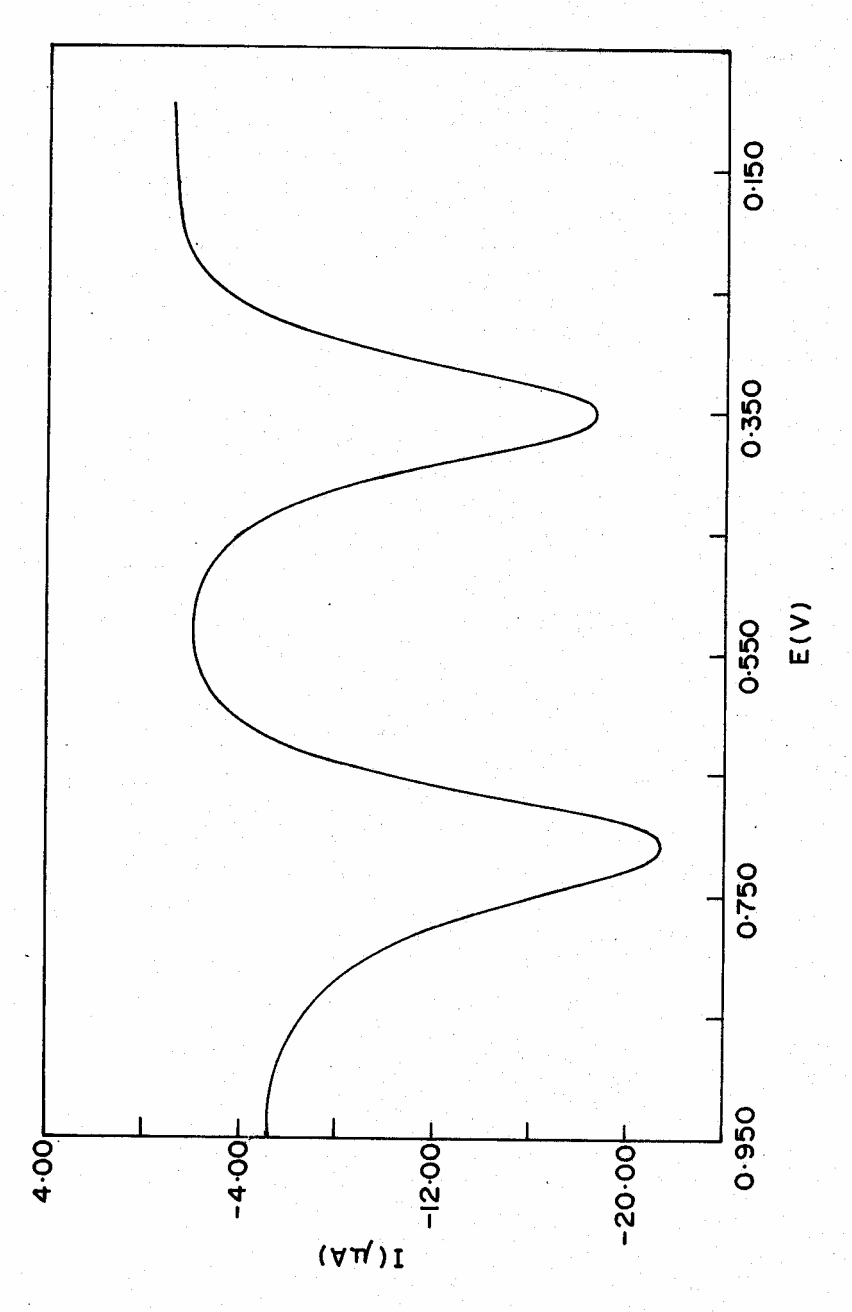

Fig. S12. Differential pulse voltammogram of 0.001 M complex [Ru(bbdo)(terpy)]$(ClO_4)_2$ **8** in CH_3CN at 25 °C at 0.05 Vs-1 scan rate.