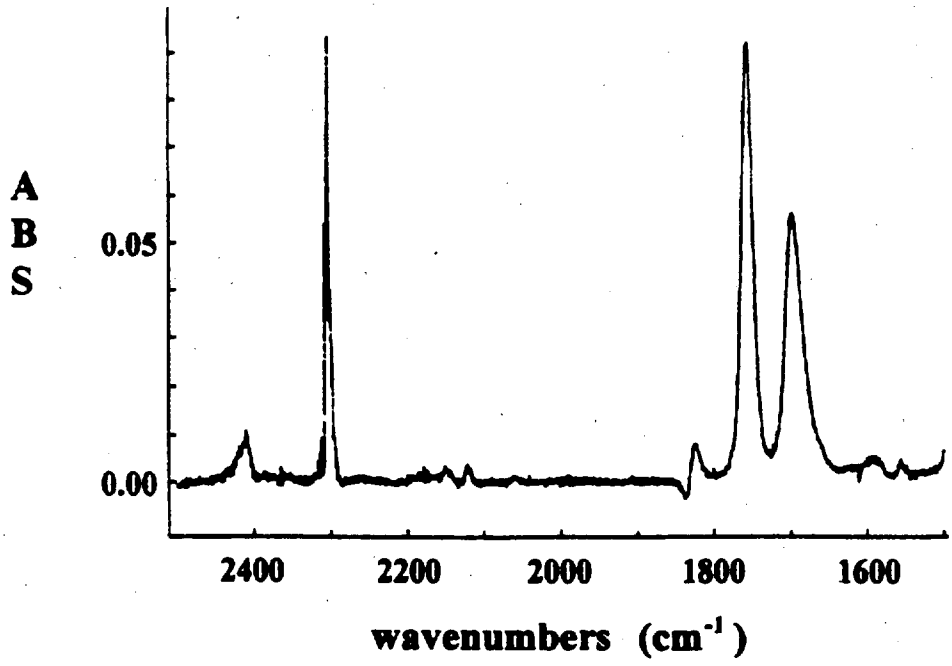
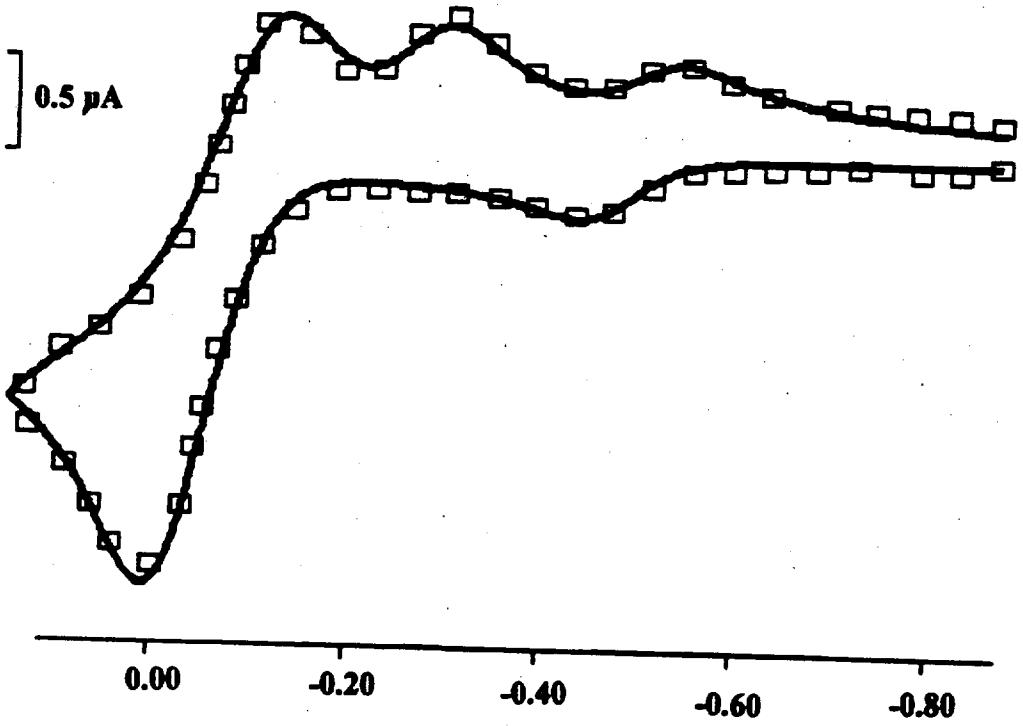
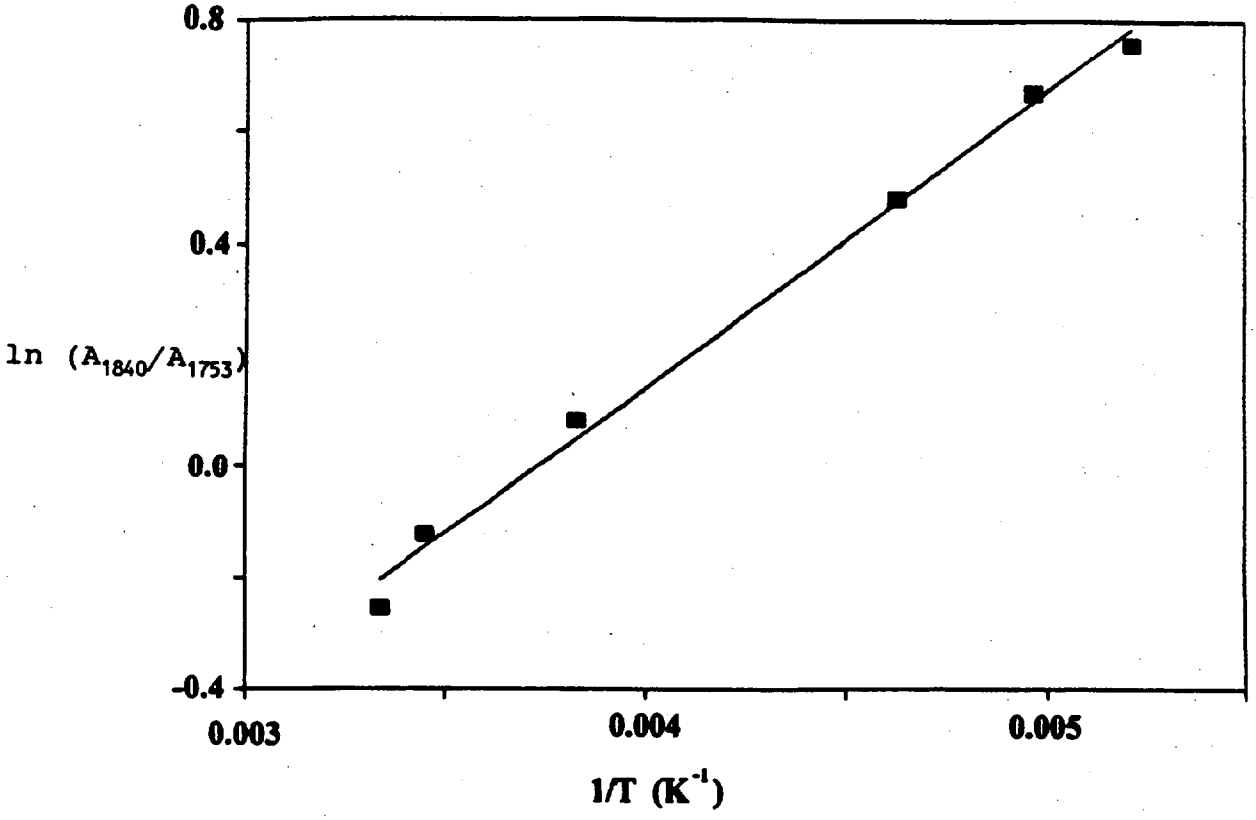


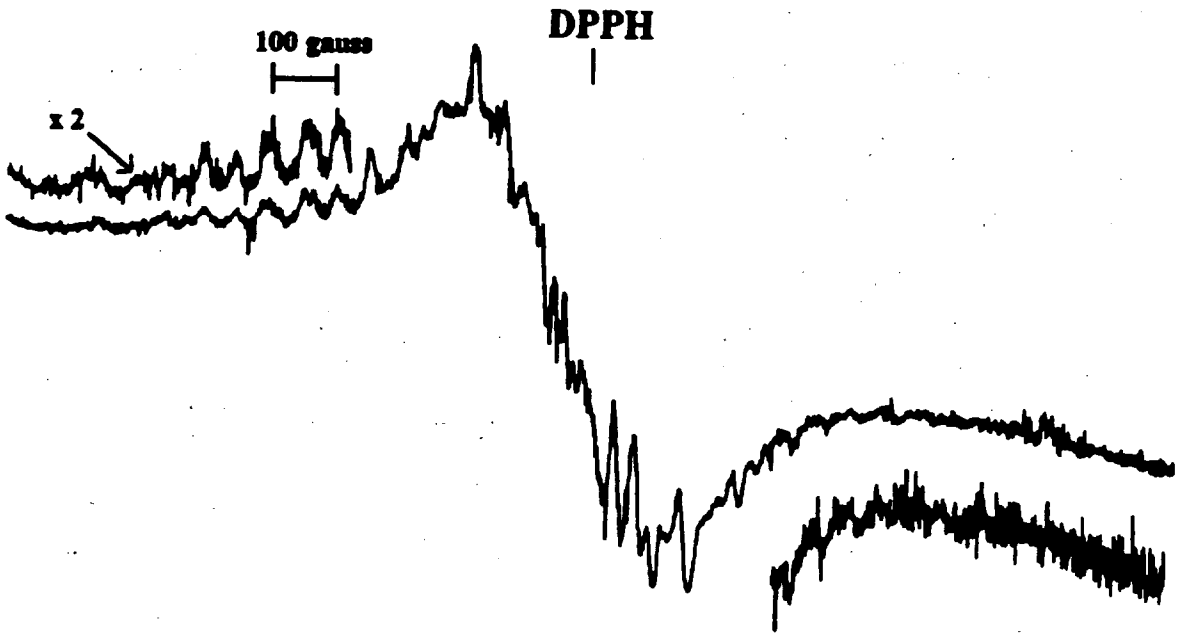
Supplementary Figure 1. IR spectrum of **1B**$^-$ obtained after a cathodic electrolysis of 1 mM **1B** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at 223 K in an IRTTLE cell.



Supplementary Figure 2. Comparison of experimental CV curve (open boxes) with that calculated (solid line) for **1B** in CH_2Cl_2; T = 223 K, v = 0.6 V/s. $E_{1/2}$ (**1B**) = 0.29 V, $E_{1/2}$ (**1T/1F**) = 0.11 V, k(**1B**$^+$ $\longrightarrow$ **1T**$^+$) = 1.6 s^{-1}. In this experiment an oxidizable impurity was present having an $E_{1/2}$ of -0.13 V. The simulation therefore included a second species with a concentration of 14 % relative to that of **1B**.



Supplementary Figure 3. Plot of ln (A_{1840}/A_{1753}) vs 1/T to obtain ΔH for the equilibrium of Eq 3.



Supplementary Figure 4. Frozen solution (77 K) EPR spectrum of **1F**$^{\cdot}$ produced by the cathodic reduction of a 1 mM solution of **1T/1F** at 223 K in 1:1 CH_2Cl_2:$C_2H_4Cl_2$.