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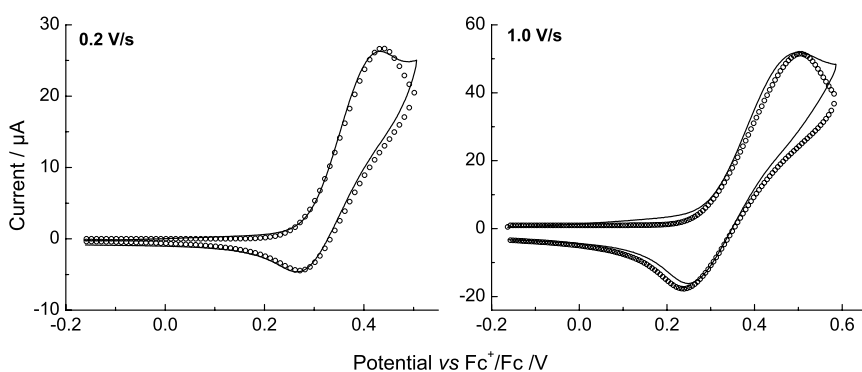


Figure S1. Background-corrected experimental voltammograms of 1.20 mM **4** in THF with 0.1 M Bu₄NPF₆ (black solid line). Simulation based on reactions 1 and 2 (open circles) with parameter values according to Table 1.

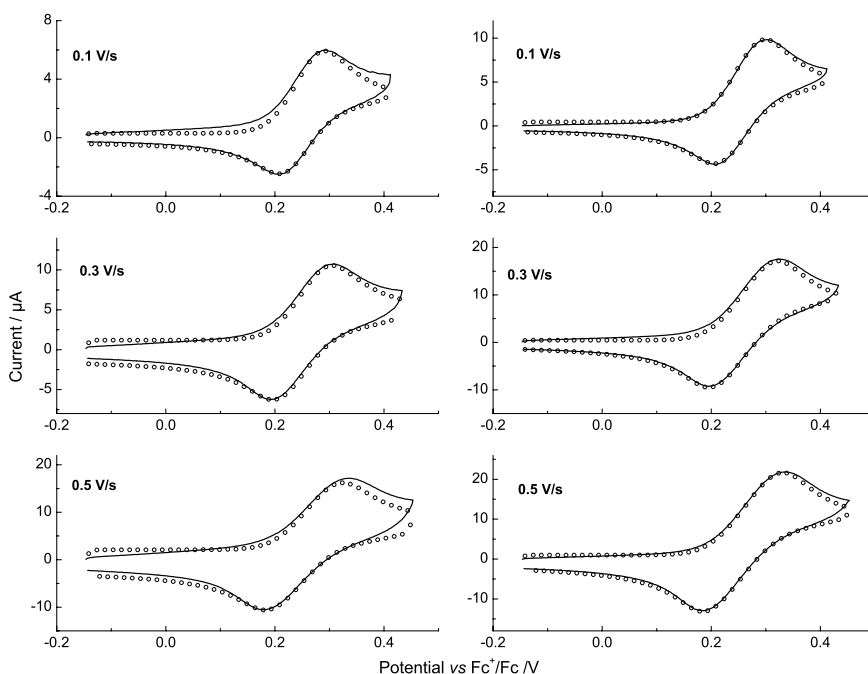


Figure S2. Background-corrected experimental voltammograms of 0.67 mM (left column) and 1.19 mM (right column) **9** in THF with 0.1 M Bu₄NPF₆ (black solid line). Simulation based on reactions 1 and 3 (open circles) with parameter values according to Table 1.

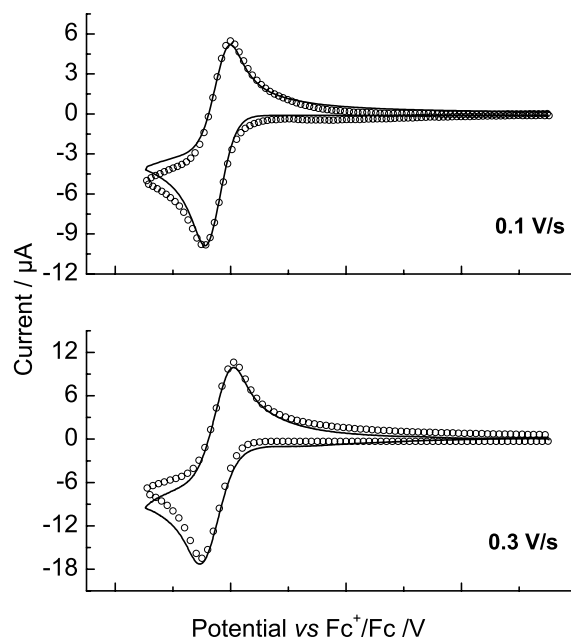


Figure S3. Background-corrected experimental voltammograms of 1.20 mM **9** in THF with 0.1 M Bu₄NPF₆ (black solid line). Simulation based on reactions 4 and 6 (open circles) with parameter values according to Table 2

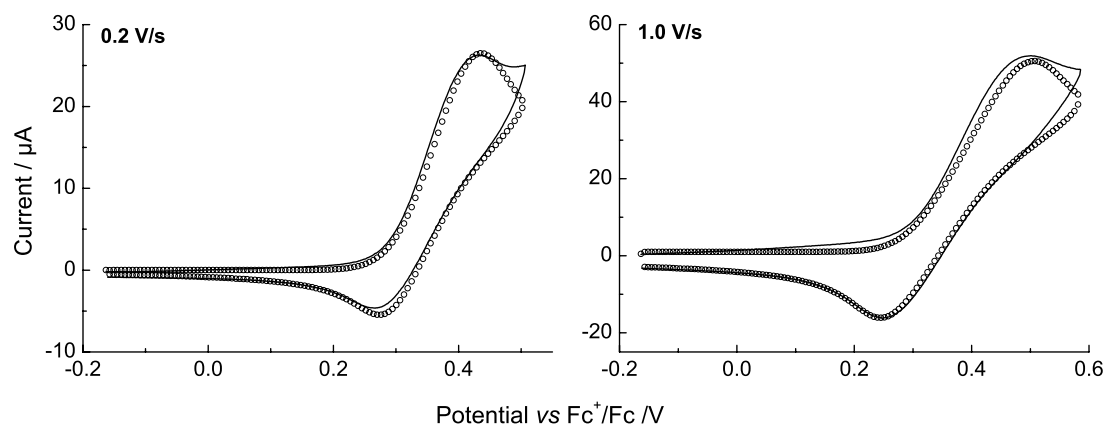


Figure S4. Background-corrected experimental voltammograms of 1.20 mM **4** in THF with 0.1 M Bu₄NPF₆ (black solid line). Simulation based on reactions 1-2, 7 and 8 (open circles) with parameter values according to Table 3.

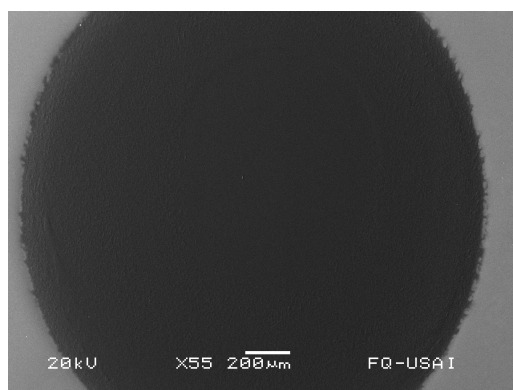


Figure S5. Scanning electron microscopy (SEM) image of a film on a Pt disk electrode obtained after potentiostatic polymerization of 10 mM porphyrin **4** in Bu₄NPF₆ 0.1 M /THF at -5 °C. JEOL JSM-5900-LV SEM instrument.

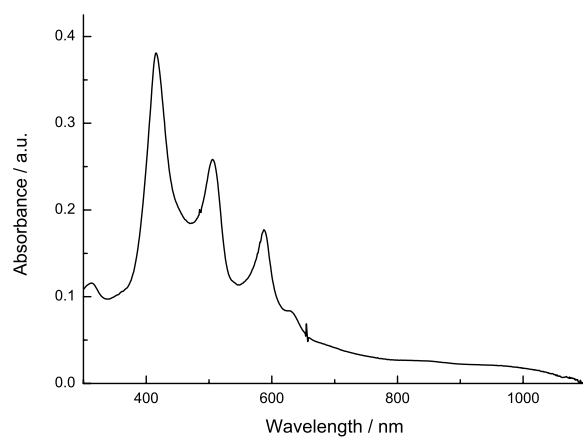


Figure S6. THF absorption spectra after potentiostatic polymerization of porphyrin **4** over a large area Pt electrode.

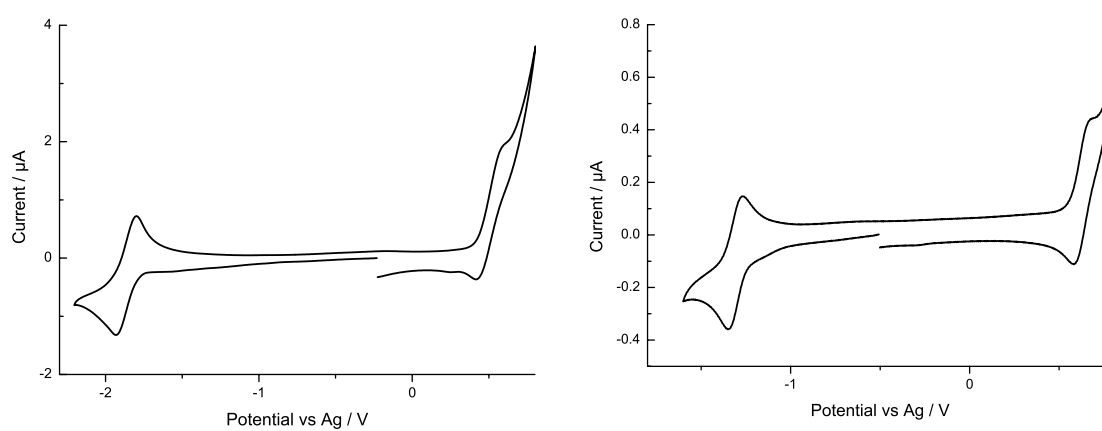


Figure S7. Experimental voltammograms of porphyrin **4** (left) and **9** (right) in ultra anhydrous 0.05 M Bu₄NPF₆/THF at a platinum working electrode.

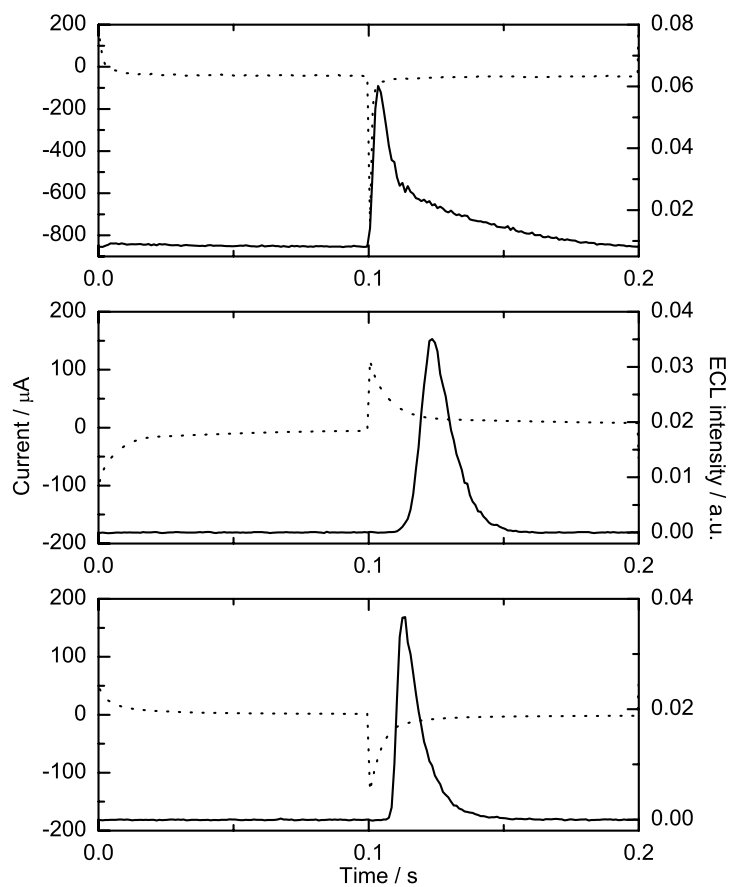
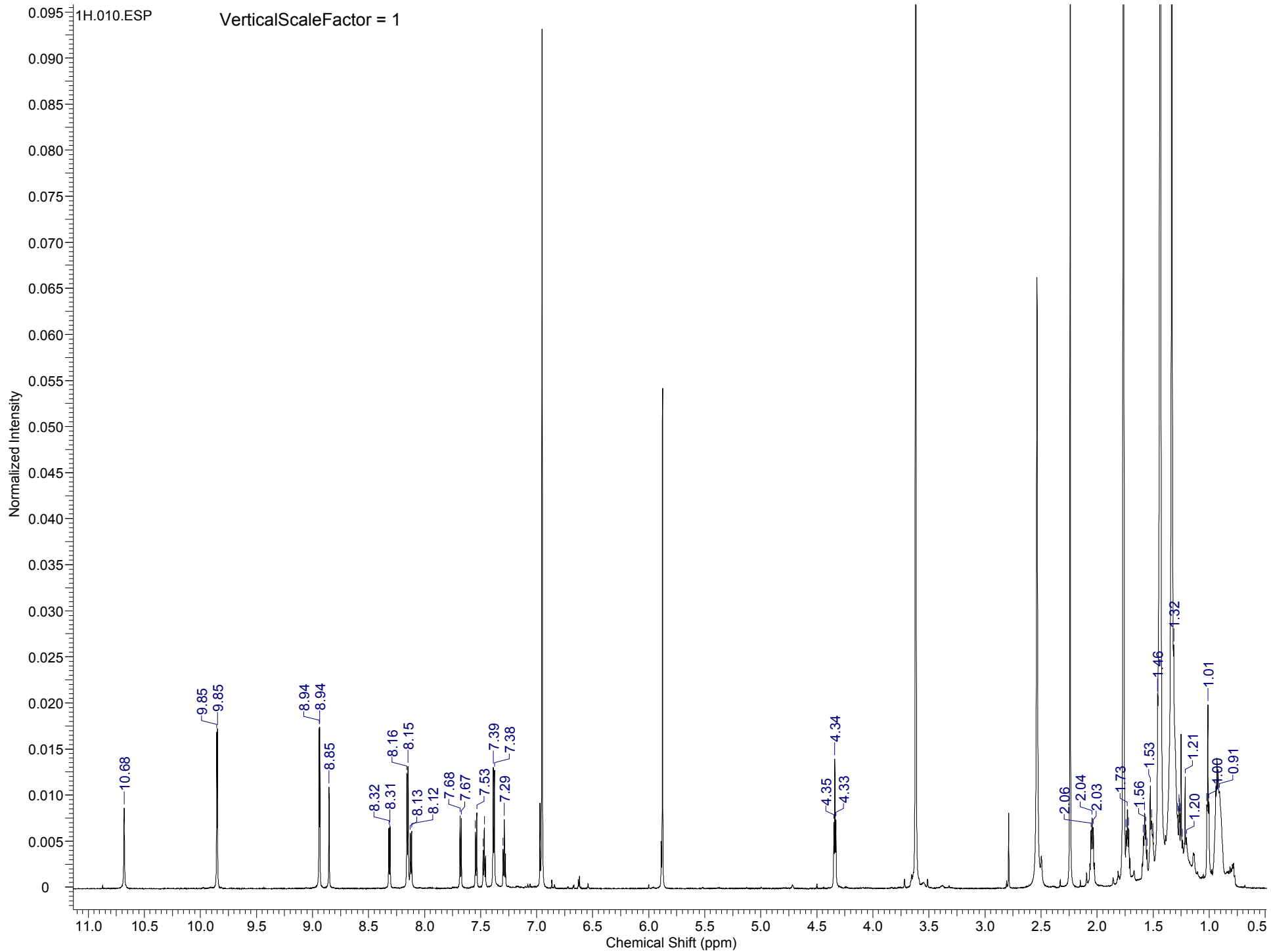
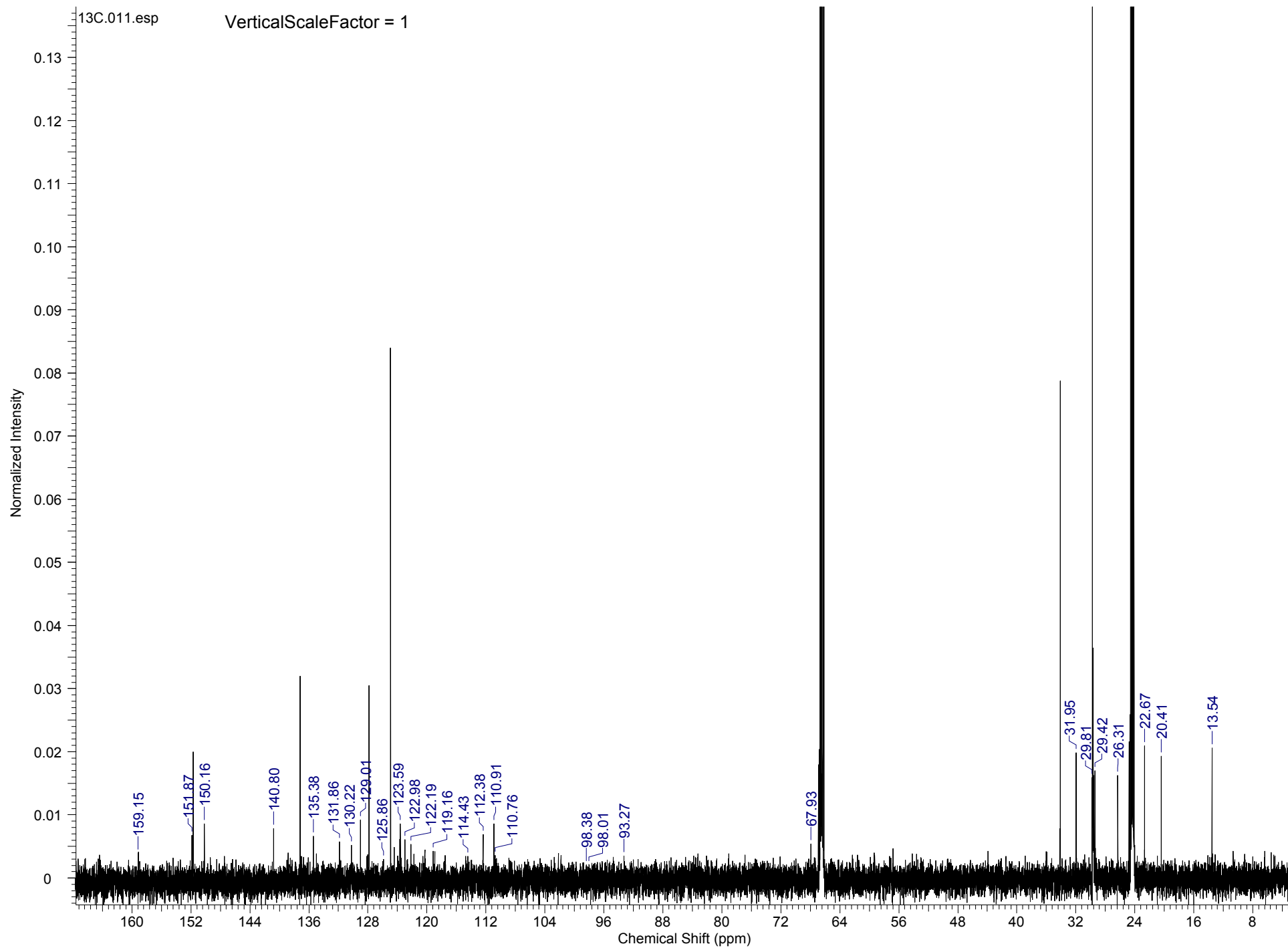
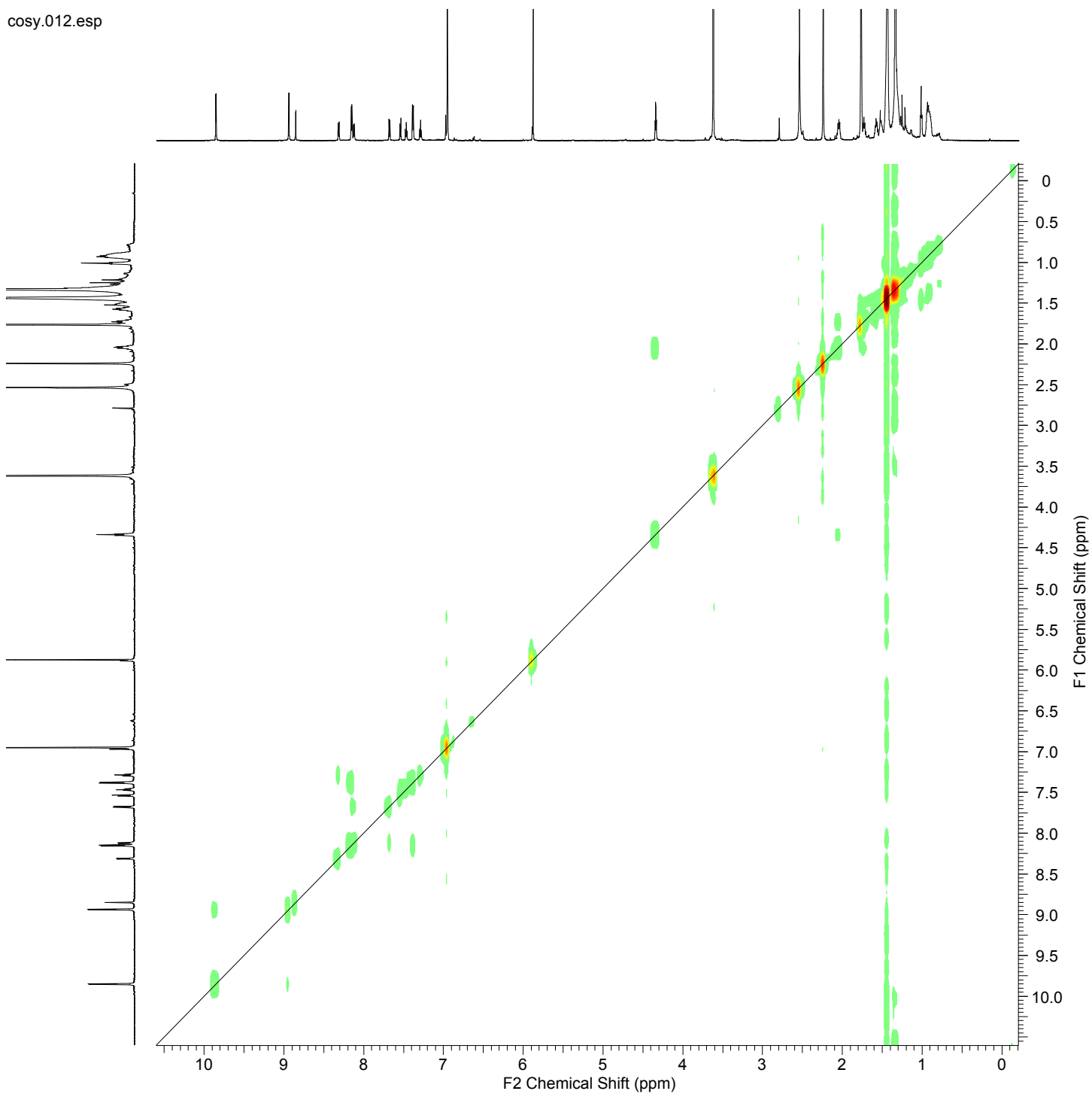


Figure S8. Chronoamperometry (solid line) and ECL (dashed) curves of 0.5 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ (top), **4** (middle), and **9** (bottom) in 0.05 M $\text{Bu}_4\text{NPF}_6/\text{THF}$. Working electrode platinum disk ($D = 2$ mm). PMT bias 750V.

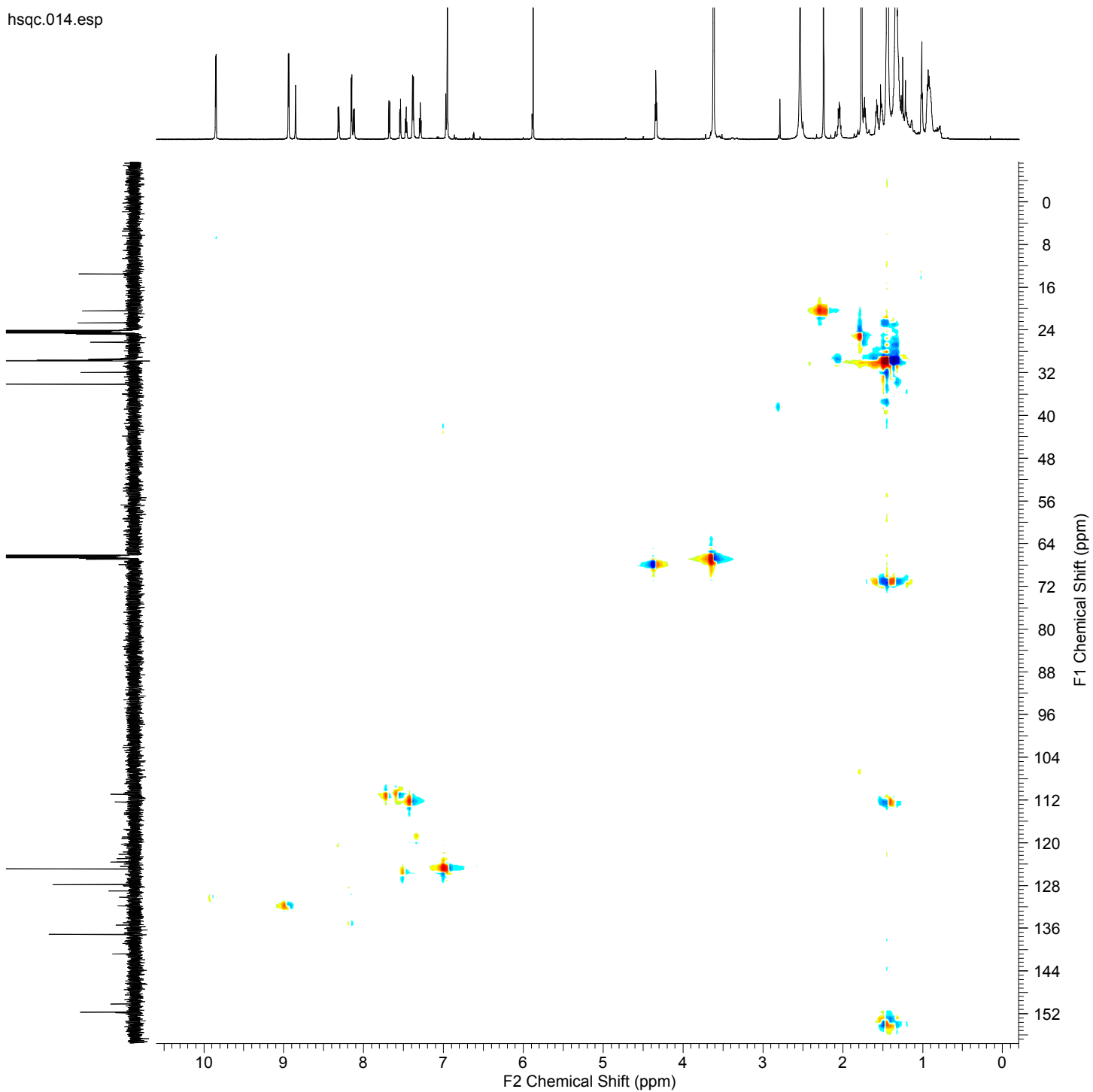




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