Supporting Information:

Reductive Coupling of Nitrogen Monoxide (•NO) Facilitated by Heme/Copper Complexes

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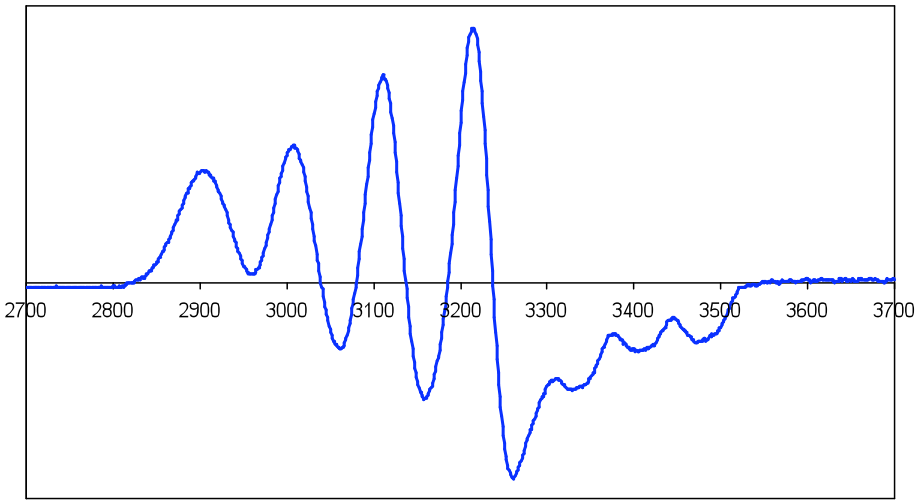

Figure S1. EPR spectrum (77K) of [(tmpa)$Cu^{II}(CH_3CN)](ClO_4)_2$ in acetone ($g_\perp = 2.22$, $g_\parallel = 2.02$, $A_\perp = 105$ G, $A_\parallel = 71$ G).

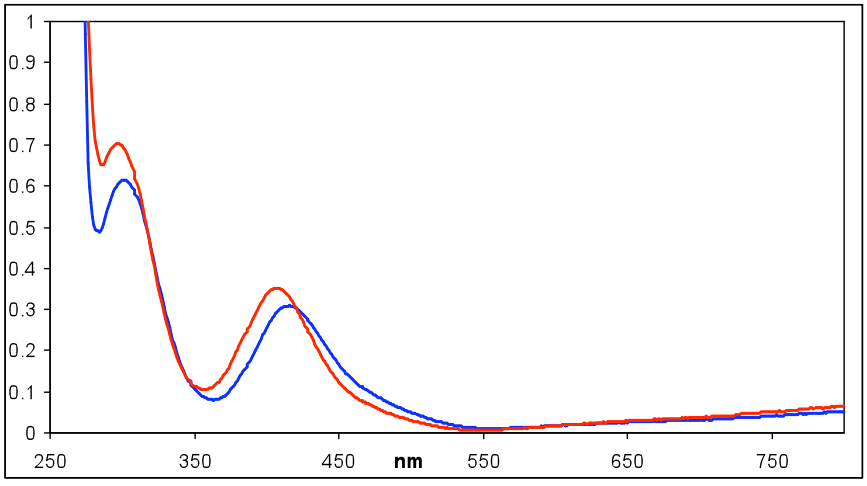

Figure S2. UV-Vis spectrum (RT) of $[(tmpa)Cu(NO_2)]PF_6$ in CH_2Cl_2 (**blue**, $\lambda_{max} = 301, 415$ nm) and in CH_3CN (**red**, $\lambda_{max} = 297, 406$ nm).

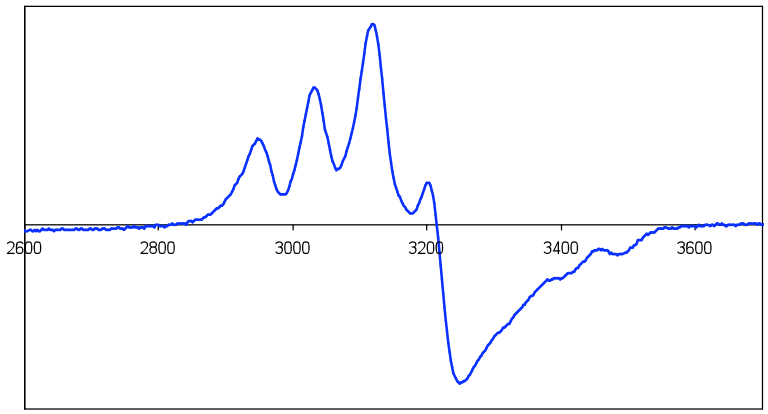

Figure S3. EPR spectrum (77 K) of $[(tmpa)Cu(NO_2)]PF_6$ in CH_2Cl_2 ($g_\perp = 2.21$, $g_\parallel = 2.01$, $A_\perp = 84$ G, $A_\parallel = 80$ G).

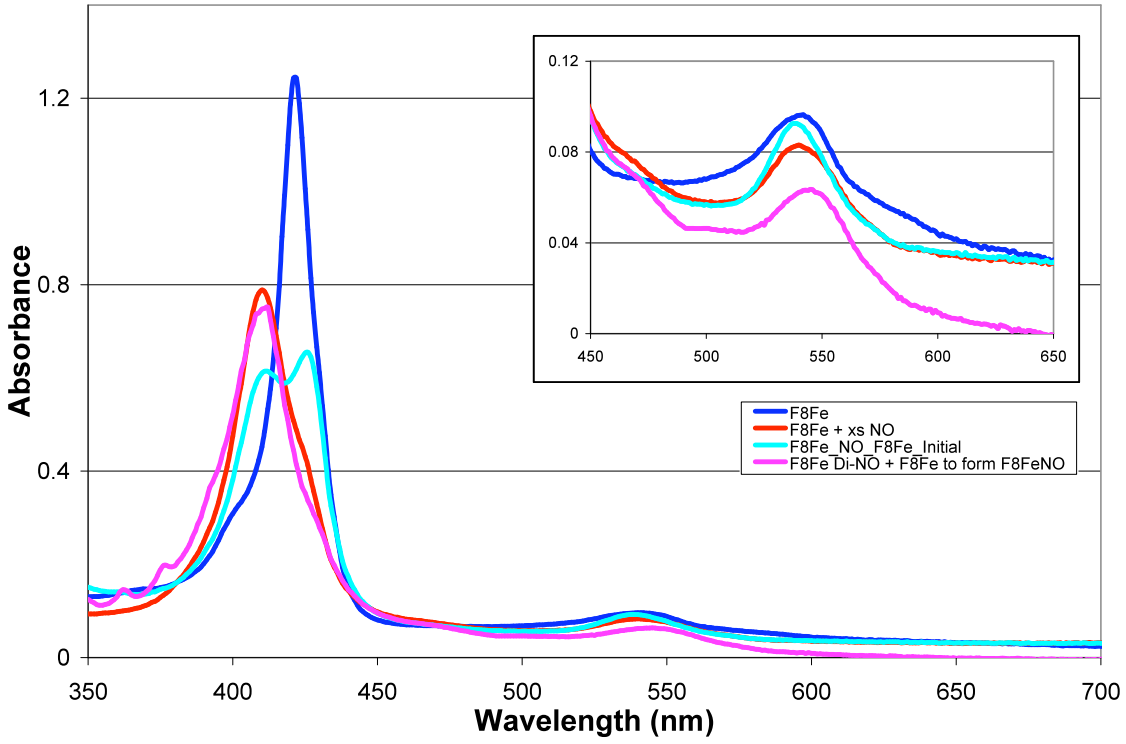

Figure S4. UV-Vis spectrum (in THF) of $(F_8)Fe(NO)_2$ titration with $(F_8)Fe^{II}$ in THF. $(F_8)Fe^{II}$ (**blue**, λ_{max} = 422 nm (Soret), 542 nm) at -78 ºC; $(F_8)Fe(NO)_2$ (**red**, λ_{max} = 410 (Soret), 540 nm) was formed after bubbling excess $\bullet NO_{(g)}$ through the solution and vacuum/purge cycles to remove excess $\bullet NO_{(g)}$ at -78 ºC; the mixture (**light blue**, λ_{max} = 410, 422, 540 nm) after an equal volume solution of $(F_8)Fe^{II}$ was added at -78 ºC; the product (**purple**, λ_{max} = 410 (Soret), 546 nm) after warming to RT and re-cooling to -78 ºC.

Figure S5. Variable-temperature ^{1}H-NMR spectra of $(F_8)Fe(NO)$ in CD_2Cl_2. From top to bottom, the temperatures at which the spectrum was recorded are 20 ºC, -20 ºC, -40 ºC, -60 ºC and -80 ºC.

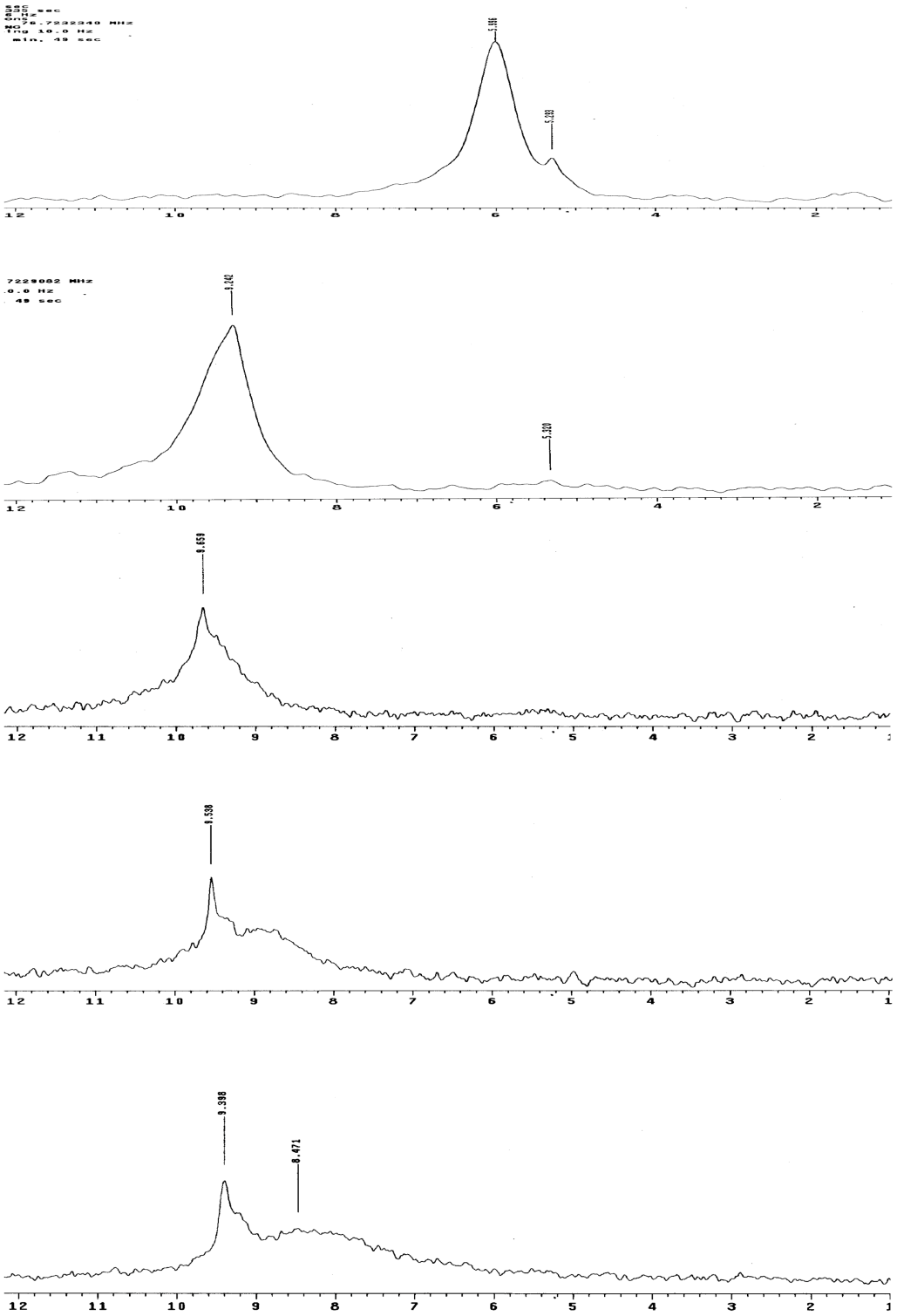

Figure S6. Variable-temperature ^{2}H-NMR spectra of (F_8-d_8)Fe(NO) in CH_2Cl_2. The temperatures at which the spectrum was recorded are 20 ºC, -20 ºC, -40 ºC, -60 ºC and -80 ºC, from top to bottom.

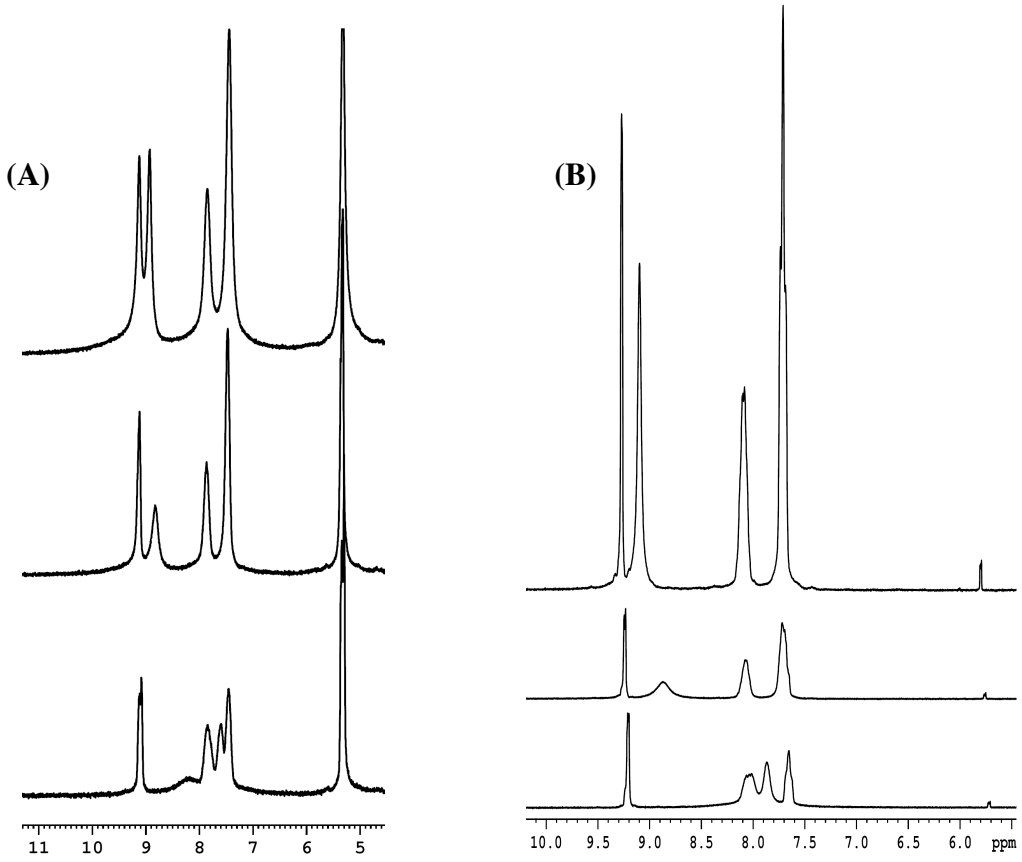

Figure S7. ^{1}H-NMR spectra of $(F_8)Fe(NO)_2$. (**A**) in CD_2Cl_2, **Top**: at -80 ºC; **Middle**: after warming to -60 ºC; **Bottom**: after warming to -40 ºC. (**B**) in acetone- d_8, **Top**: at -80 ºC; **Middle**: after warming to -60 ºC; **Bottom**: after warming to -40 ºC.

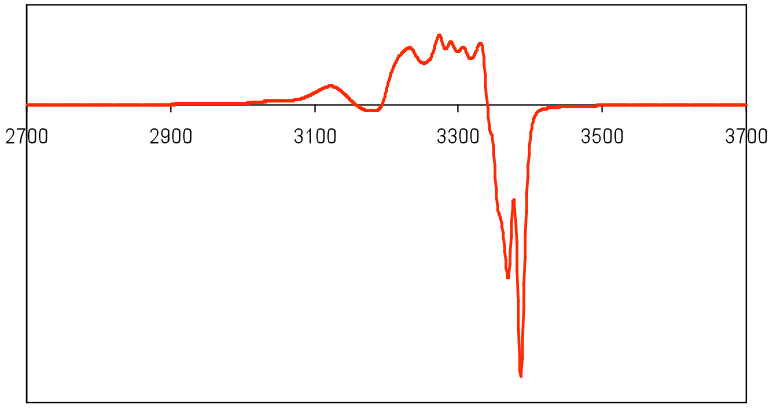

Figure S8. Expanded view of the EPR spectrum of the product mixture from the reaction of $(F_8)Fe(NO)_2$ + $[(tmpa)Cu^{I}(MeCN)]^+$, i.e. complexes $(F_8)FeNO$, 1/3 $[(tmpa)Cu^{II}(NO_2)]^+$ and unreacted 2/3 $[(tmpa)Cu^{I}(solvent)]^+$.

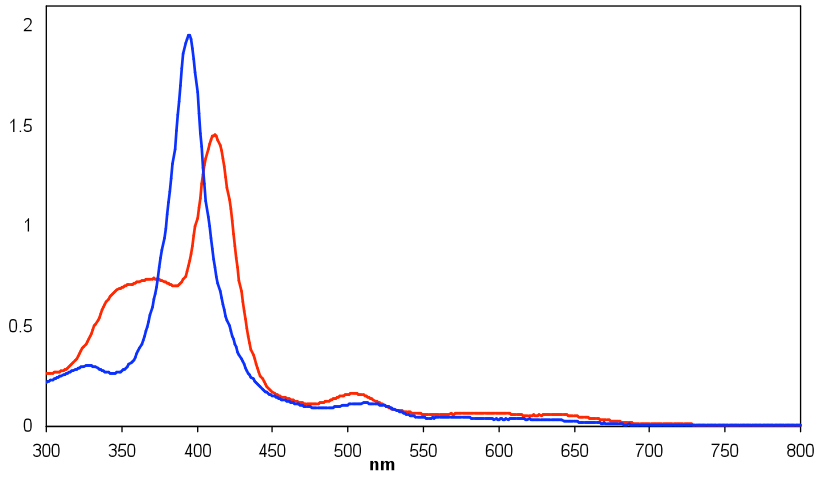

Figure S9. UV-Vis Spectrum (RT) of $[(F_8)Fe^{III}]SbF_6$ (**blue**, λ_{max}= 394 (Soret), 512 nm) and $(F_8)Fe^{III}Cl$ (**red**, λ_{max}= 370, 411 (Soret), 503, 639 nm) in CH_2Cl_2.

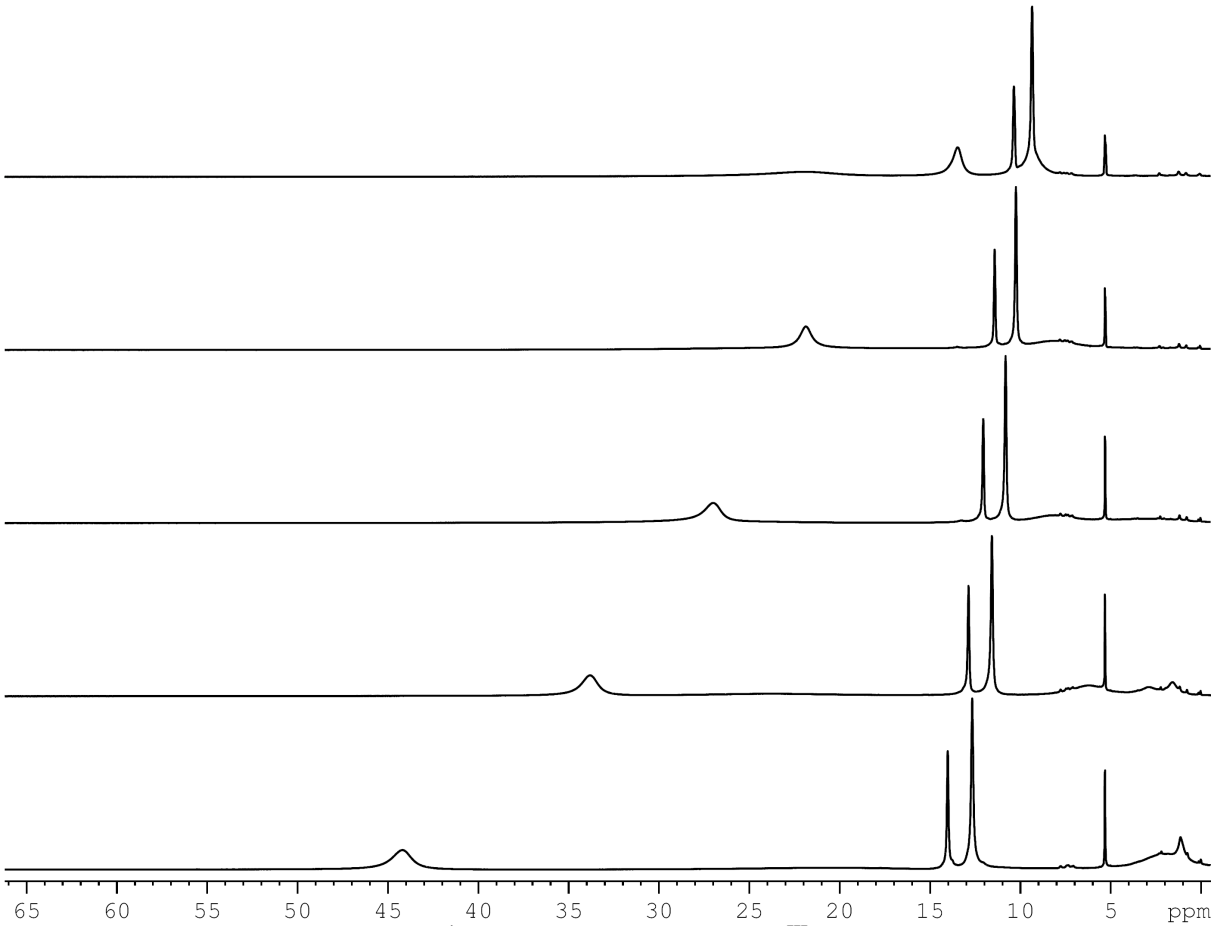

Figure S10. Variable-temperature ^{1}H-NMR spectra of $(F_8)Fe^{III}SbF_6$ in CD_2Cl_2. From top to bottom, the temperatures at which the spectrum was recorded are 20 ºC, -20 ºC, -40 ºC, -60 ºC and -80 ºC.

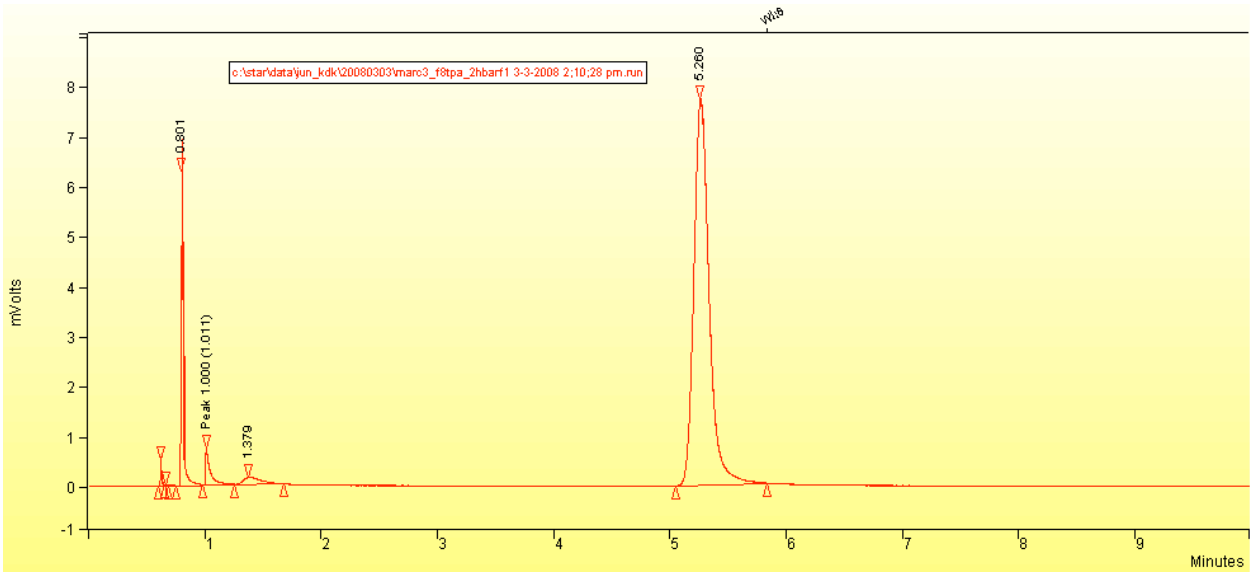

Figure S11. Gas chromatography (GC) of the head space of the product mixture, obtained from the reaction of $(F_8)Fe(NO)_2$ with $[(tmpa)Cu^{I}(MeCN)]^{+}$ plus Acid. It was performed on a Varian CP-3800 instrument equipped with a 1041 manual injector, electron conductivity detector, and a 25 m 5 Å molecular sieve capillary column. When the oven temperature is 200 ºC and the flow rate equals to 8 mL/min, the retention time (min) are 5.260 for N_2O, 0.801 for small amount of air in the syringe needle that was used for gas injection, 1.000 and 1.379 for trace impurities.