Electronic Supplementary Information (ESI)

Structure and Nitrite Reduction Reactivity Study of Bio-inspired Copper(I)-nitro Complexes in Steric and Electronic Considerations of Tridentate Nitrogen Ligand

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Table S1. Crystallographic details

	1	**2**
empirical formula	$C_{22}H_{34}CuN_7O_2$	$C_{57}H_{64}BCuN_8O_2P_2$
formula weight	492.10	1029.45
T (K)	200(2)	200(2)
cystal size (mm)	0.26 x 0.14 x 0.12	0.40 x 0.35 x 0.25
crystal system	Trigonal	Triclinic
space group	R 3 m	P-1
a (Å)	16.177(5)	13.1118(3)
b (Å)	16.177(5)	13.2532(4)
c (Å)	8.509(3)	18.1725(6)
α (deg)	90	96.0070(10)
β (deg)	90	98.3170(10)
γ (deg)	120	107.554(2)
V (Å^3)	1928.5(14)	2942.15(15)
Z	3	2
D_{calcd} (g cm^{-3})	1.271	1.162
μ (mm^{-1})	0.880	0.471
max./min. transm	0.900 / 0.863	0.8874 / 0.82
reflns mcasd/indep	2696 / 833	20994 / 10105
data/rcstraints/params	833 / 1 /68	10150 / 0 / 628
GOF	1.065	1.181
R_{int}	0.0264	0.0587
R_1 [$I > 2\sigma$] (all data)	0.274 (0.0301)	0.0638 (0.1019)
R_w [$I > 2\sigma$] (all data)	0.0274 (0.0669)	0.1537 (0.1674)
max. pcak/hole (e$^-$/ Å^3)	0.212 / -0.202	1.131 / -0.907

Complex **1** :
PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Cu --N1 . 10.2 s.u.
--- There is no doubt on atom assignments and the high Hirshfeld test difference may resulted from possible minor disordered mode.
PLAT987_ALERT_1_B The Flack x is >> 0 - Do a BASF/TWIN Refinement Please Check
---After trying with TWIN/BASF refinement, the Flack parameter remains as 0.04(1). The acceptable number is 0.03(1). It is not significantly different.
Complex **2**:
PLAT230_ALERT_2_B Hirshfeld Test Diff for O1 -- N1 .. 8.5 s.u.
PLAT230_ALERT_2_B Hirshfeld Test Diff for C2 -- C5 .. 10.8 s.u.
---The O1 N2 C2 C5 are all terminal atoms with large ADP's. The atom assignments are confirmed and the high Hirshfeld test difference may resulted from possible minor disordered mode.
PLAT601_ALERT_2_B Structure Contains Solvent Accessible VOIDS of . 152 Ang3
---The void is rather small. It may due to the unmatched shape of the cation and anion.

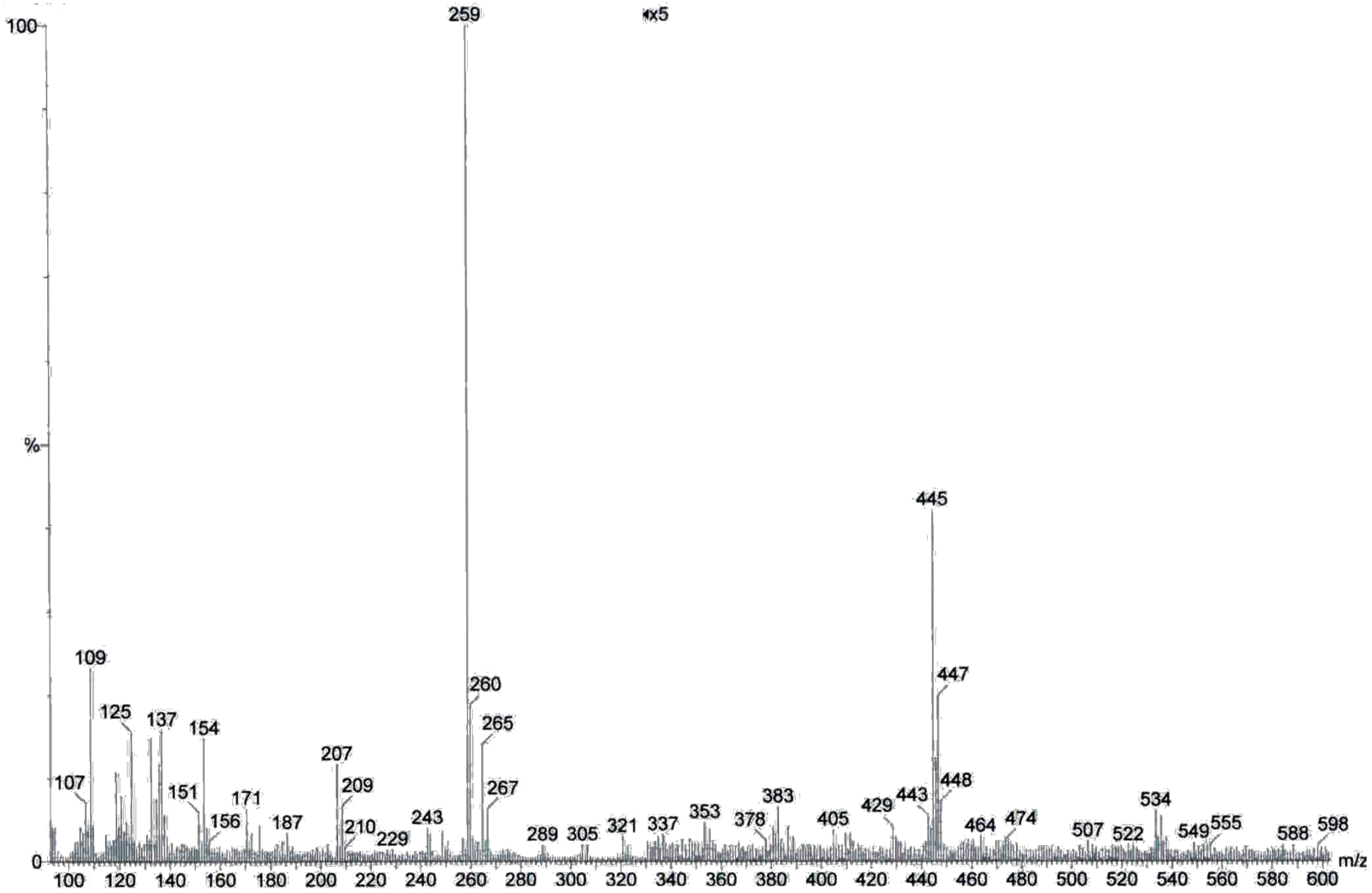

Figure S1. FAB-MS spectrum of **1**.

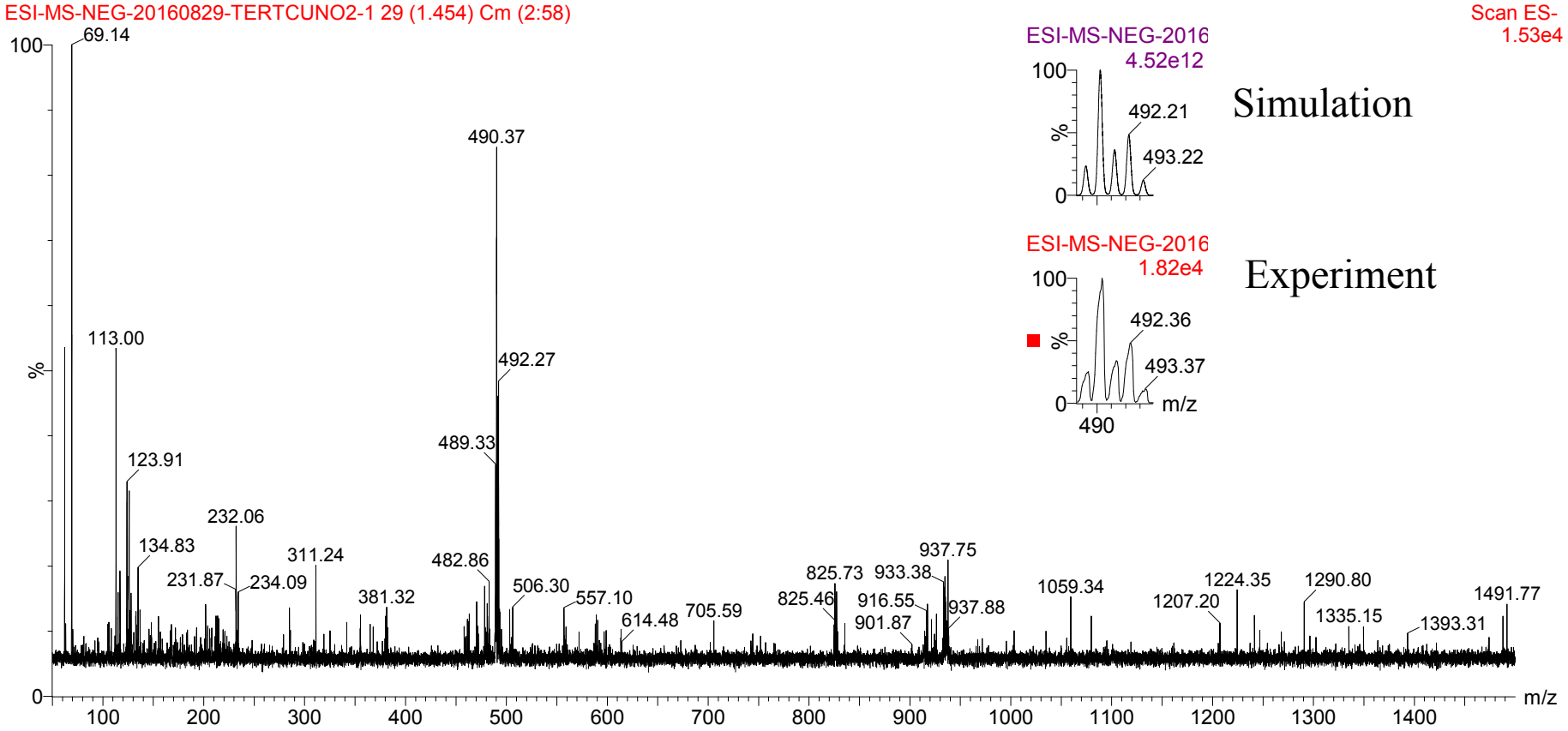

Figure S2. ESI-MS spectrum of **2**.

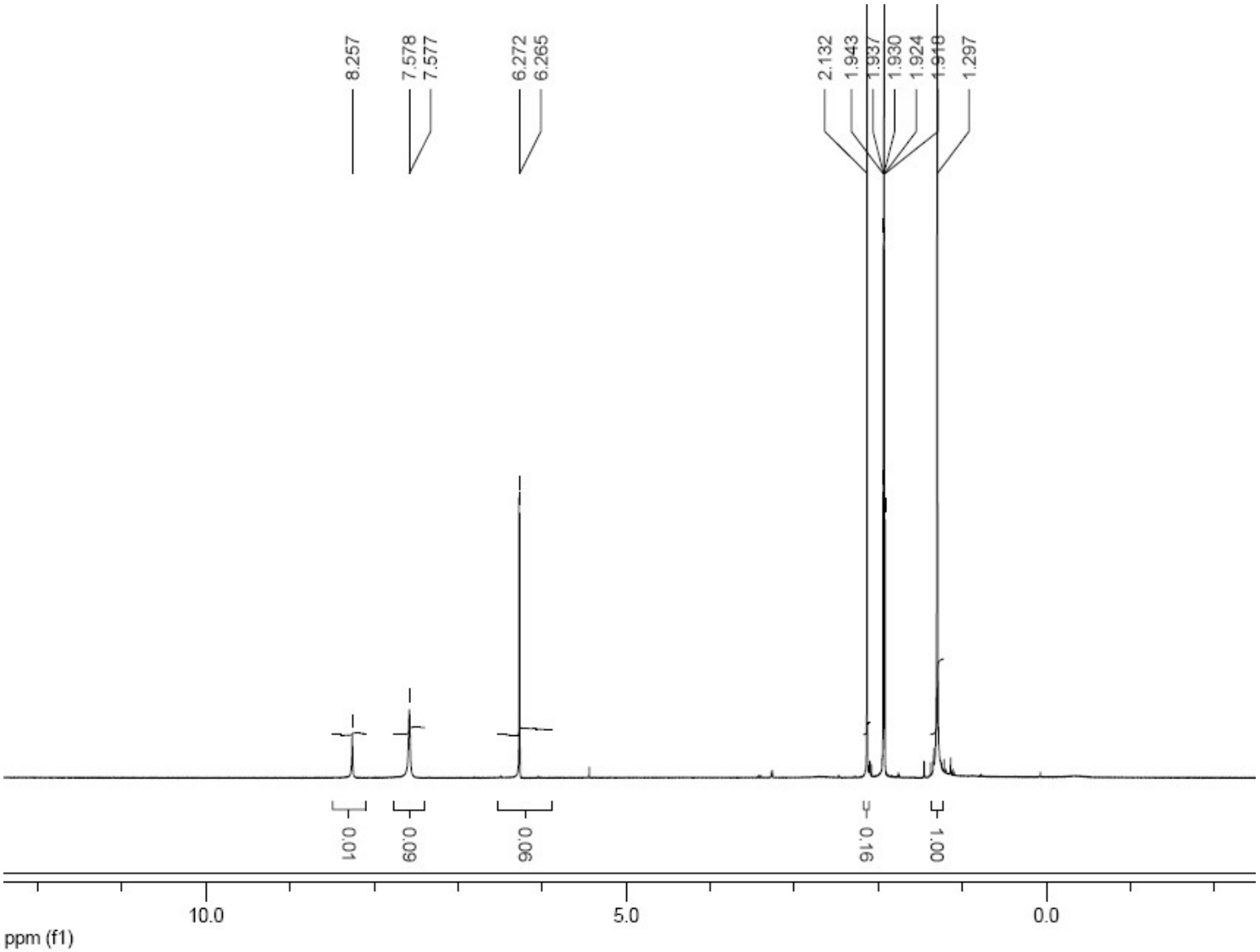

Figure S3. ^{1}H NMR spectrum of **1** in acetonitrile-d^{3}.

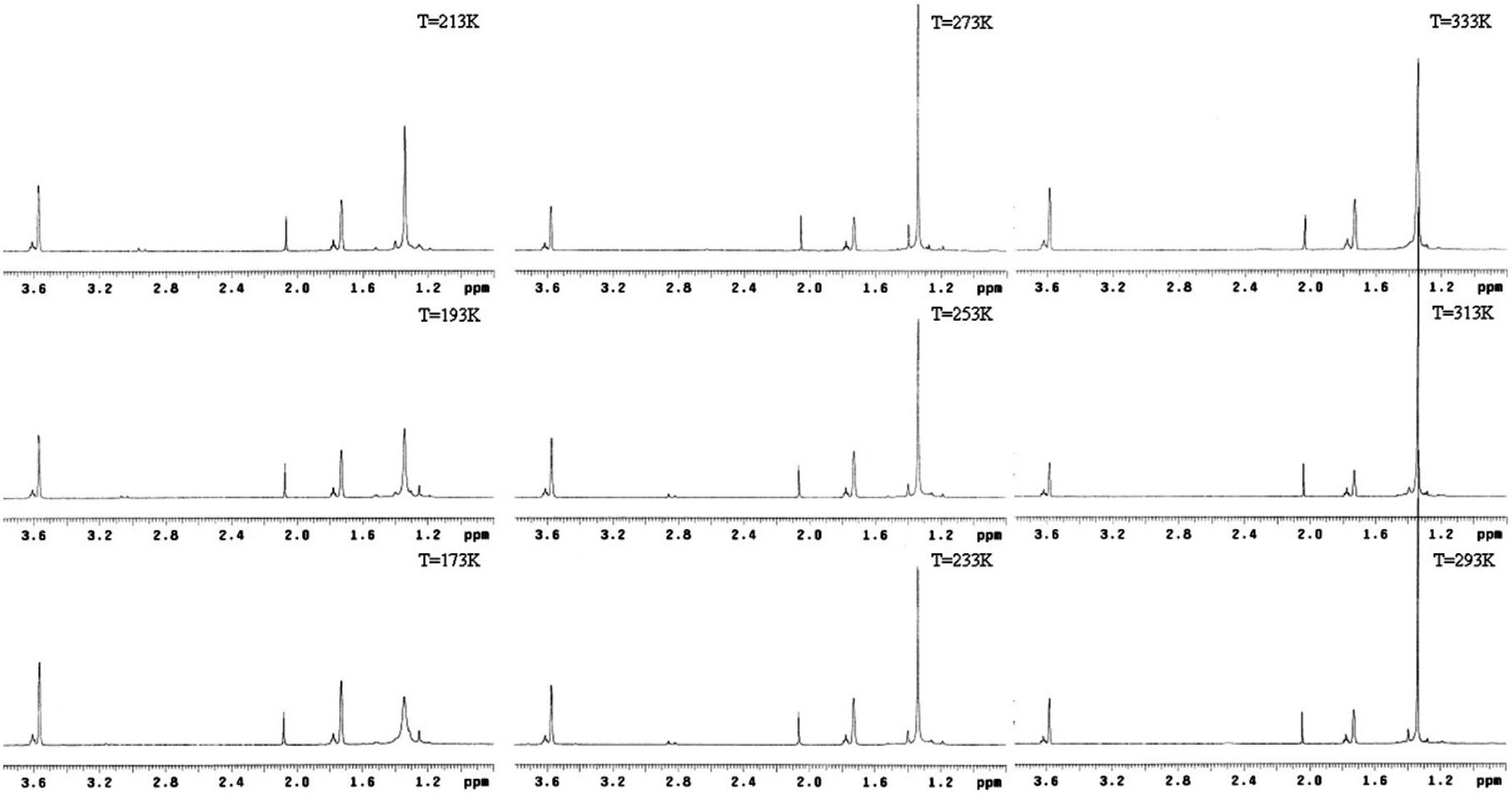

Figure S4. ^{1}H NMR spectrum (1.0~3.8ppm) of **2** in THF-d^{8}.

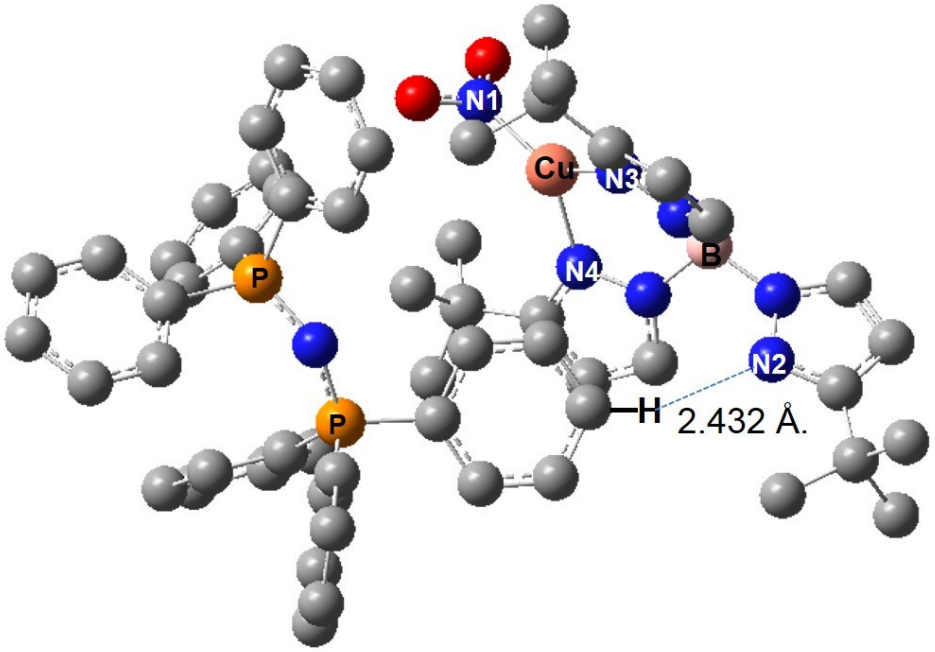

Figure S5. (a) Optimized structure of **2** (in gas phase). The shortest distance between $[Tp^{Me2}Cu(NO_2)]^-$ and $[(Ph_3P)_2N]^+$ was found to be 2.432 Å

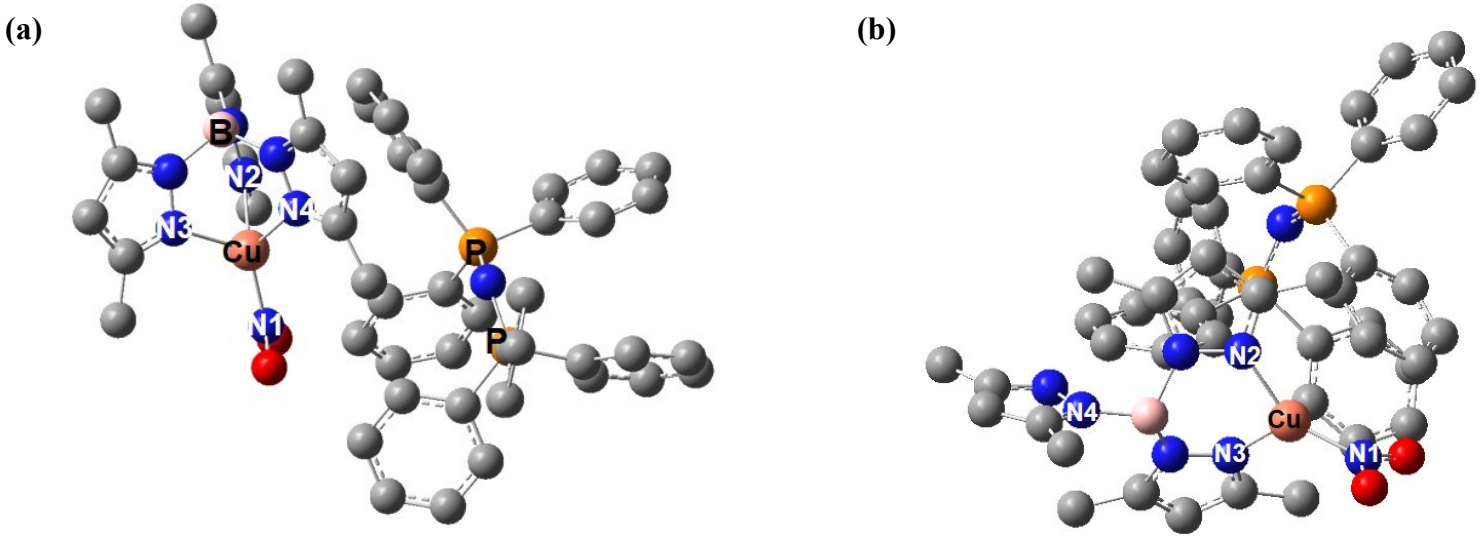

Figure S6. (a) Optimized structures of **$[(Ph_3P)_2N][Tp^{Me2}Cu(NO_2)]$** (in gas phase): (a) a tetra-coordinated geometry, relative E = 0 kcal/mol; (b) a tri-coordinated geometry, relative E = 18.7 kcal/mol.

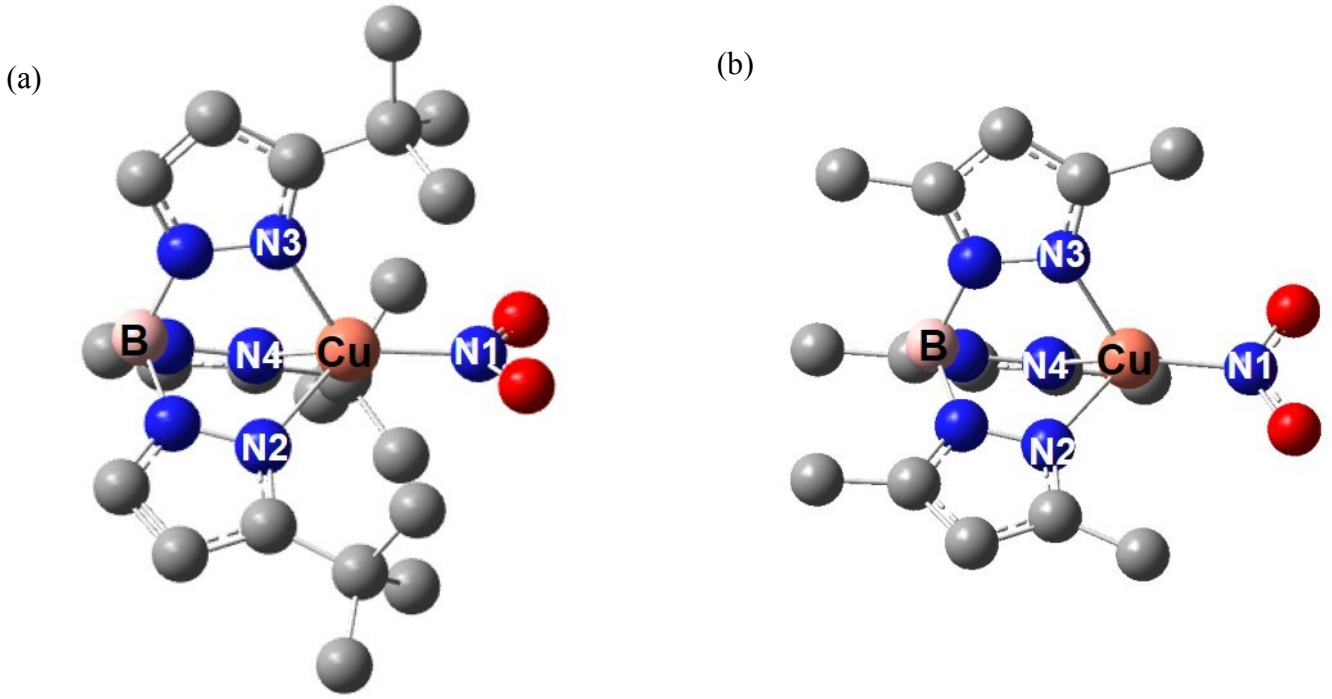

Figure S7. (a) Optimized structure of **[Tp$^{3\text{-}t\text{Bu}}$Cu(NO$_2$)]$^-$** (in gas phase). Selected bond lengths (Å) and bond angles (°): Cu–N1 1.902, Cu–N2 2.156, Cu–N3 2.123, Cu–N4 2.045, N2–Cu–N3 88.03, N3–Cu–N4 92.55, N2–Cu–N4 91.98 (2) Optimized structure of **[Tp^{Me2}Cu(NO$_2$)]$^-$** (in gas phase). Selected bond lengths (Å) and bond angles (°): Cu–N1 1.886, Cu–N2 2.103, Cu–N3 2.023, Cu–N4 2.017, N2–Cu–N3 90.45, N3–Cu–N4 92.41, N2–Cu–N4 90.79.

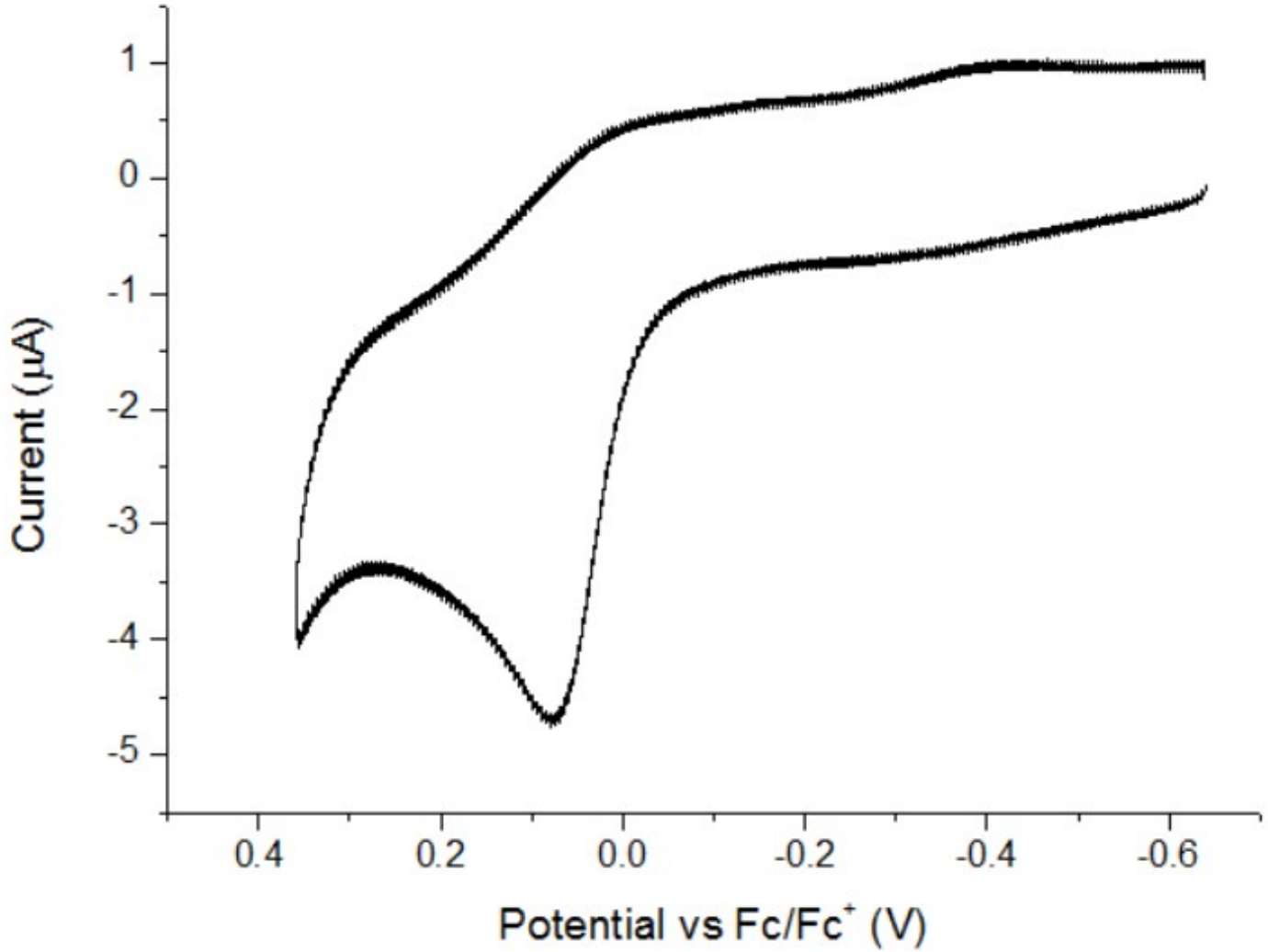

Figure S8. Cyclic voltammetry of **2** where the measured E_{pa} is 0.08 V vs. Fc. Cyclic voltammetry measurements were taken in 10^{-4} M MeCN solutions using 0.1 M $(Bu_4N)(PF_6)$ as supporting electrolyte and referenced to $Fc^{+/0}$.

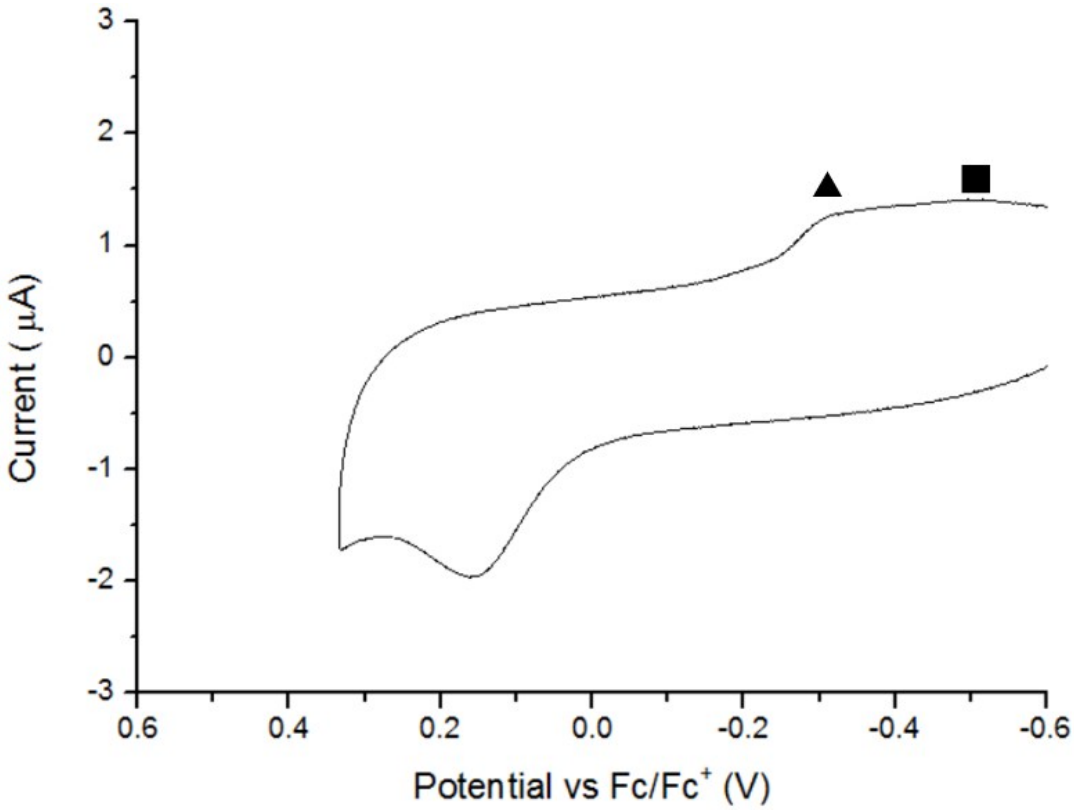

Figure S9. Cyclic voltammetry of **1** where the measured E_{pa} is 0.16 V vs. Fc. Cyclic voltammetry measurements were taken in 10^{-4} M MeCN solutions using 0.1 M $(Bu_4N)(PF_6)$ as supporting electrolyte and referenced to $Fc^{+/0}$. The waves at E_{pc} = -0.32 V (▲) and -0.50 V (■) may be tentatively assigned to $[Tpm^{3\text{-}t\text{Bu}}Cu(NO_2)]^{+/0}$ and $[Tpm^{3\text{-}t\text{Bu}}Cu(ONO)]^{+/0}$, respectively. The assignments of redox potentials for $Tpm^{3\text{-}t\text{Bu}}Cu^{I/II}$ couples nitro and nitrito isomers are according to literature precedent complex $TPACu^{II}(NO_2)$ (TPA = Tris(2-pyridylmethyl)amine).[1]

1. K. Nobutoshi, N. Hirotaka, K. Yoshinori, A. Gin-ya, S. Masatatsu, U. Akira and T. Koji, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 581-589.

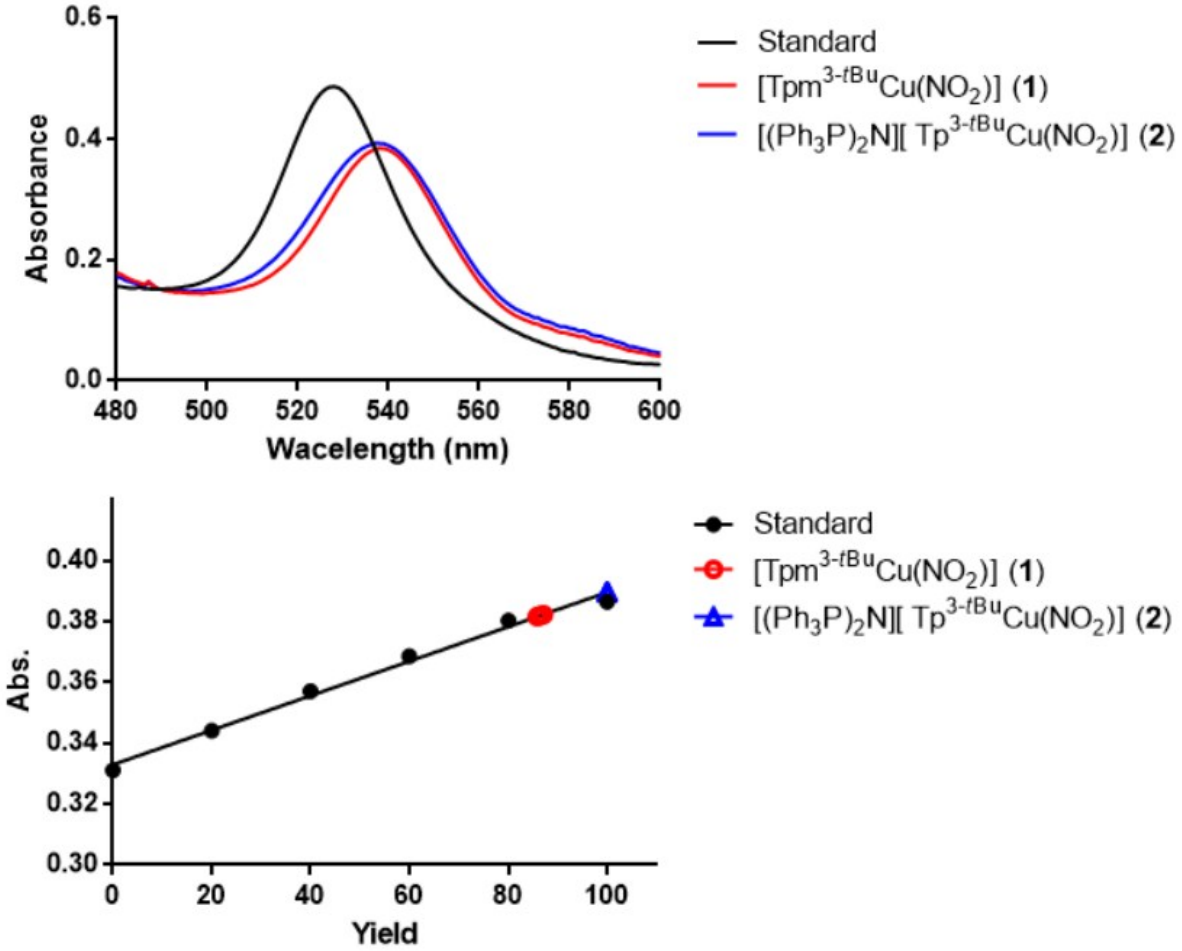

Figure S10. NO generation experiments for **1** and **2**. NO concentration was performed by calibrating curve response with known concentrations of NO mixed with N_2 (120ppm, 100ppm, 80ppm, 60ppm and 40ppm of NO in N_2); molar quantities were calculated using the ideal gas equation.

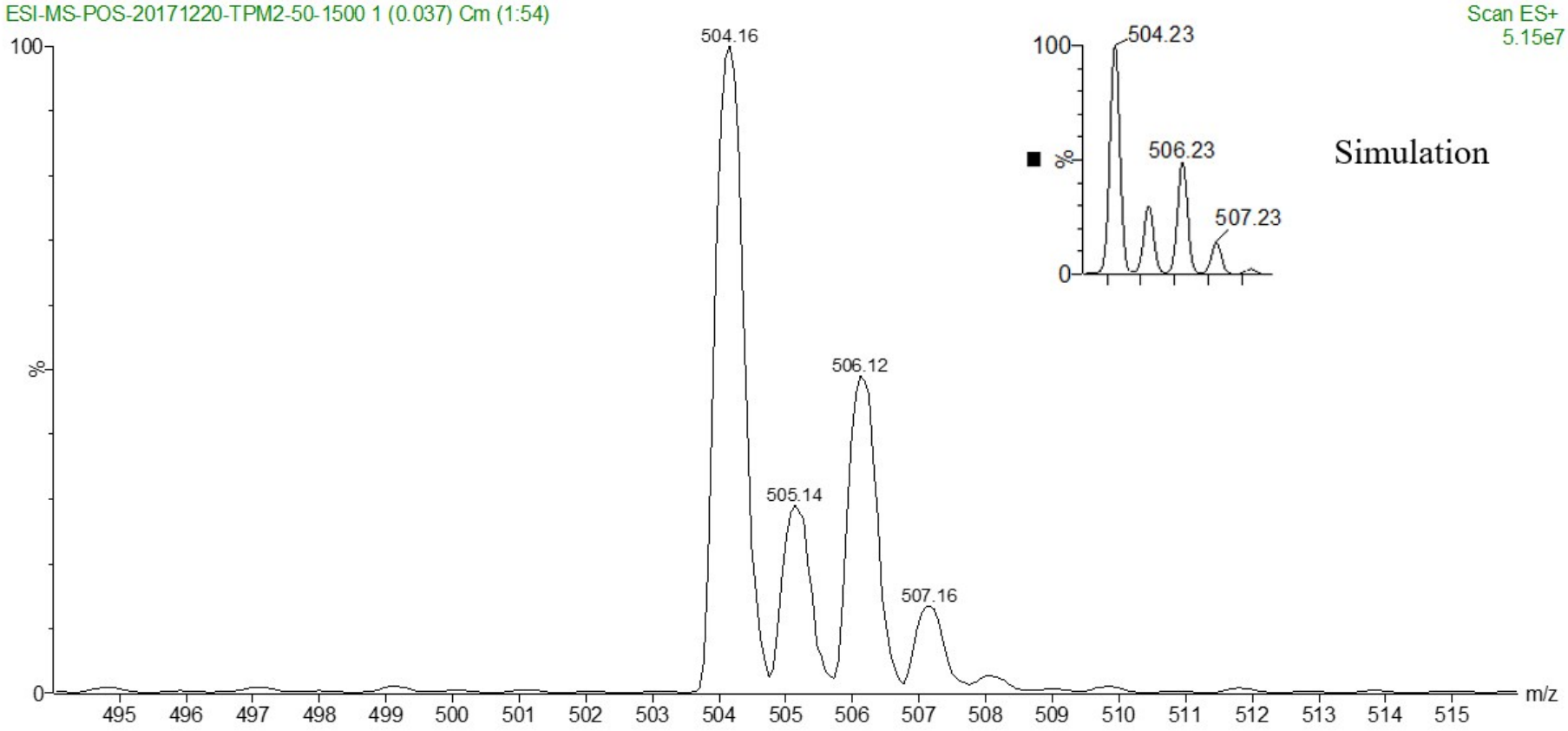

Figure S11. ESI-Mass spectrum of **3** : m/z = 504.16 [Tpm^{3tBu}Cu(OAc)]$^{+}$.

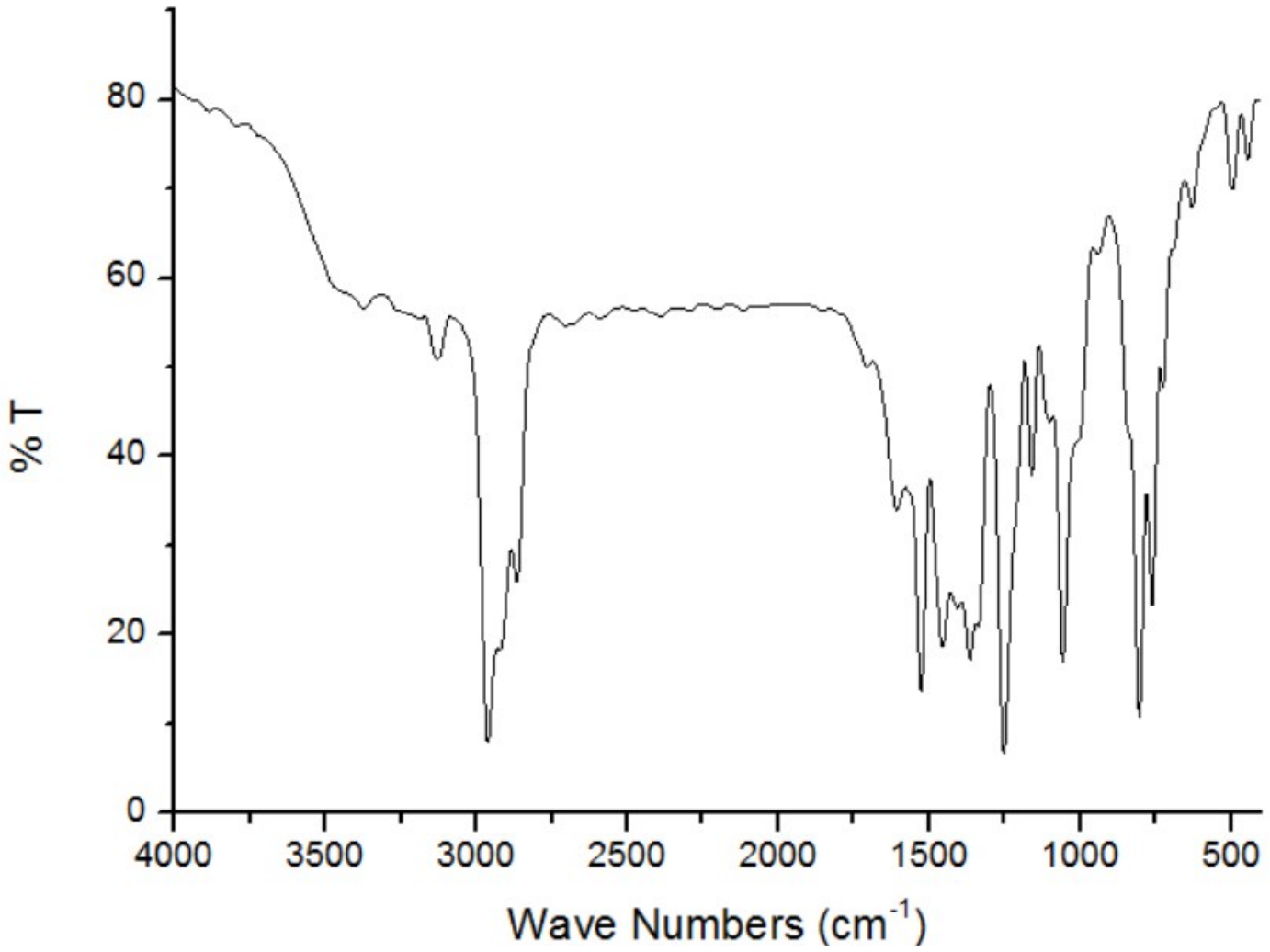

Figure S12. FTIR spectrum of **3** in KBr disk (400 cm^{-1} - 4000 cm^{-1}).

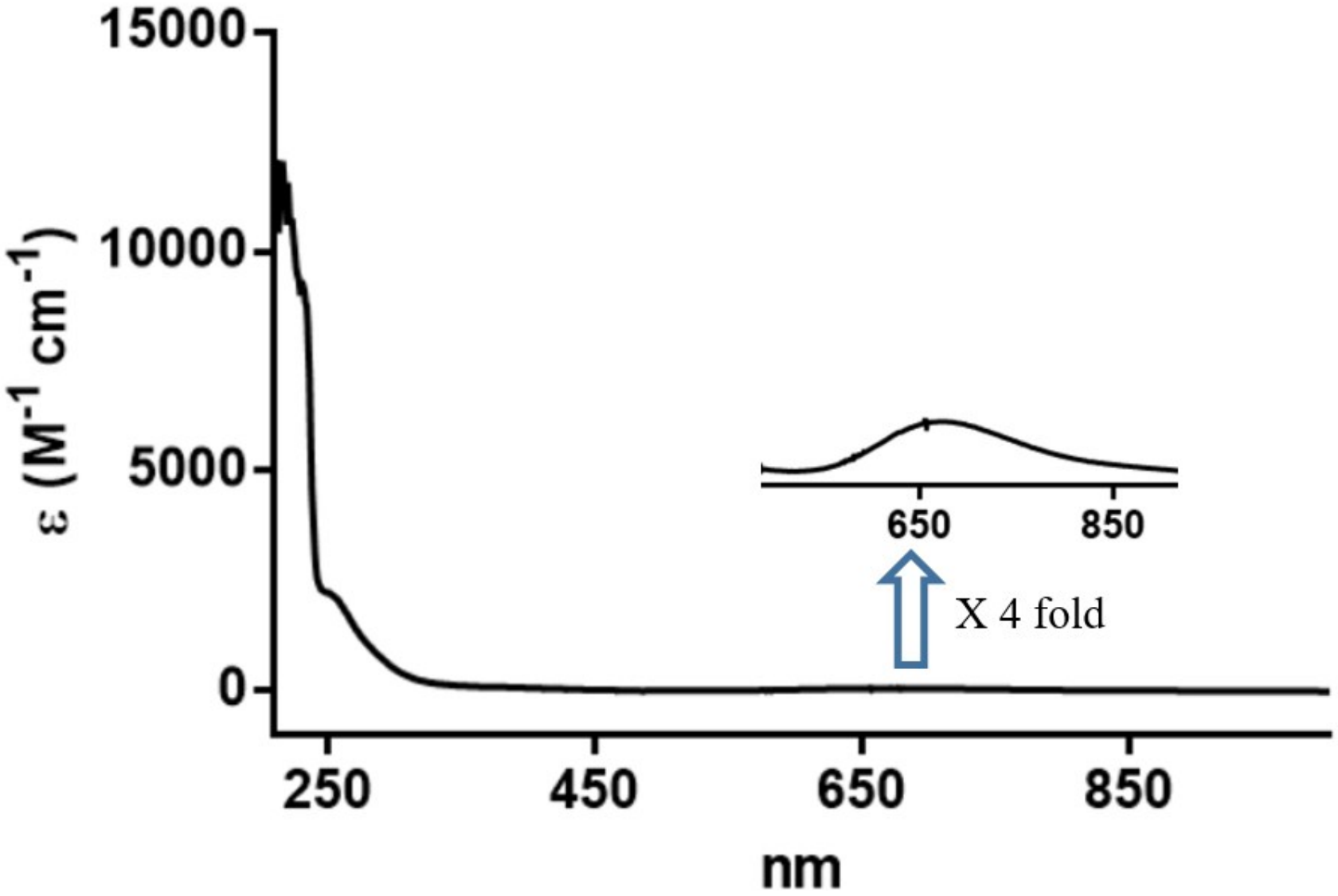

Figure S13. Absorption spectra of **3** in CH_3CN at room temperature.

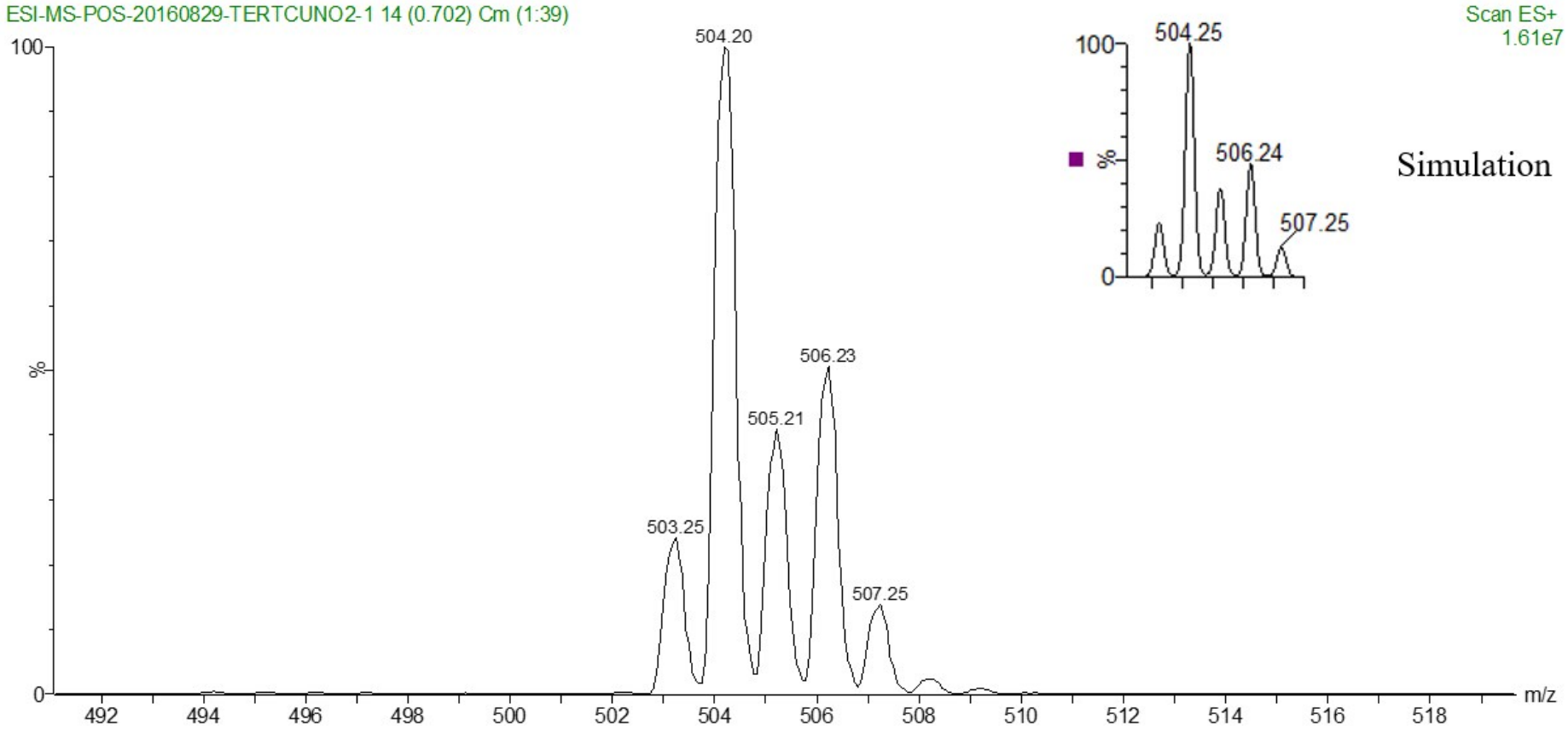

Figure S14. ESI-Mass spectrum of **4** in MeOH : m/z = 504.20 $[Tp^{3tBu}Cu(OAc) + H^+]^+$.