SUPLEMENTARY MATERIAL

New Mononuclear Cu(I) Compounds Synthesis, Characterization, and Application to the Electroreduction of CO_2.

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Spectroscopic Data for the Obtained Compounds

Compound (**2**), $[(dippe)Cu(PPh_3)NO_3]$.

Compound (**2**). NMR (600 MHz): $^{31}P\{^1H\}$ (THF-d_8), δ=0.45 ppm (br. s., PPh_3), δ=12.14 ppm (br. s., dippe). $^{13}C\{^1H\}$ δ= 20.21 ppm (s, -CH_3), δ= 20.53 ppm (s, -CH_2- bridge), δ= 25.18 ppm (s, -CH-*i*Pr), δ= 129.7 ppm (d, m-PPh_3, $^3J_{C\text{-}P}$= 7.5 Hz), δ= 130.6 ppm (s, p-PPh_3), δ= 135.5 ppm (d, o-C-PPh_3, $^2J_{C\text{-}P}$= 15.09 Hz), δ= 137.81 ppm (s, ^{i}C-PPh_3).

^{1}H, δ=1.20 ppm (s, -CH_3), δ=1.91 ppm (s, -CH2- bridge), δ=2.15 ppm (s, -CH-isopropyl), δ=7.37 ppm (m, H_o y H_m -PPh_3), δ=7.54 ppm (t, H_p -PPh_3). IR (ATR-neat): 3055 cm^{-1} ,2954 cm^{-1} ,2868 cm^{-1} (w, C=C -PPh_3 ring), 1399 cm^{-1}(s, N-O sym), 1299 cm^{-1} (s, N-O asymm.), 700 cm^{-1} (s, -PPh_3 ring). Anal. Calcd. for : $C_{32}H_{47}O_3NP_3Cu$: %C,59.11, %H, 7.3, %N, 2.15. Found: %C, 56.9, %H, 7.5, %N: 2.3. Melting point: 202 ºC (d).

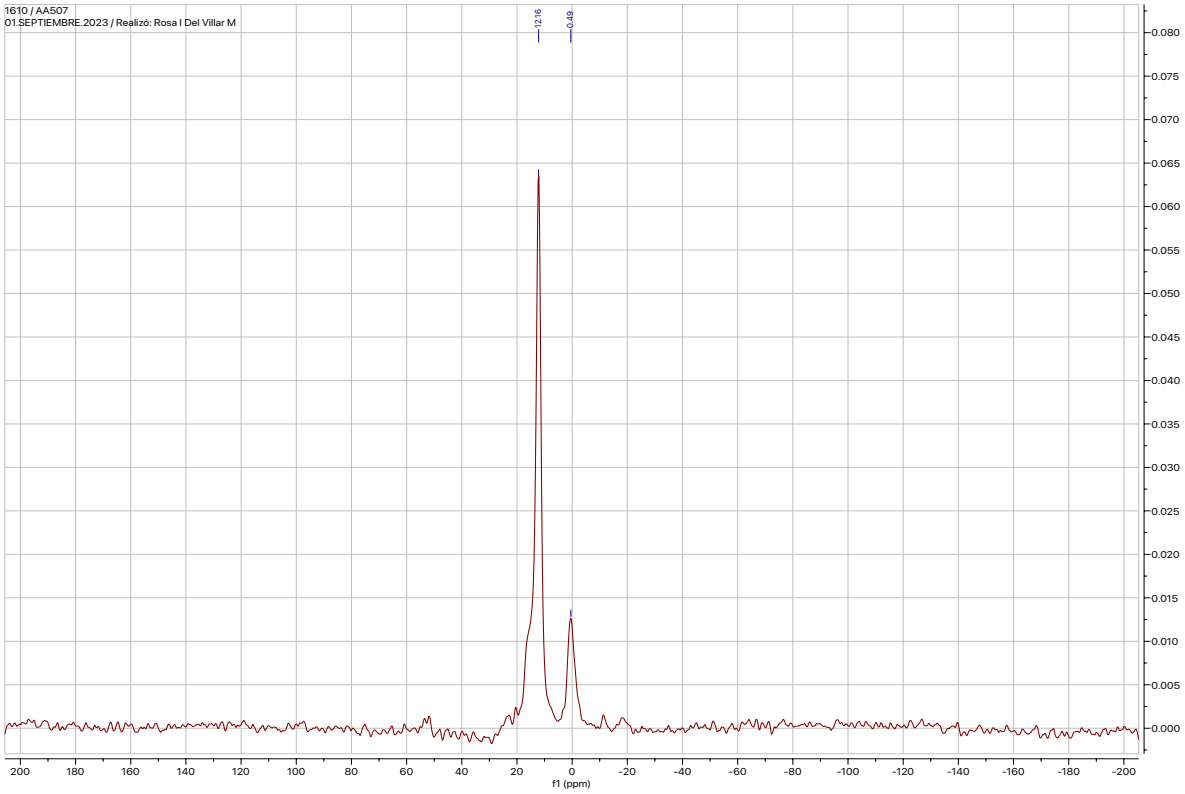


Figure S1. $^{31}P\{^{1}H\}$ (THF-d_8) NMR of Compound (**2**),

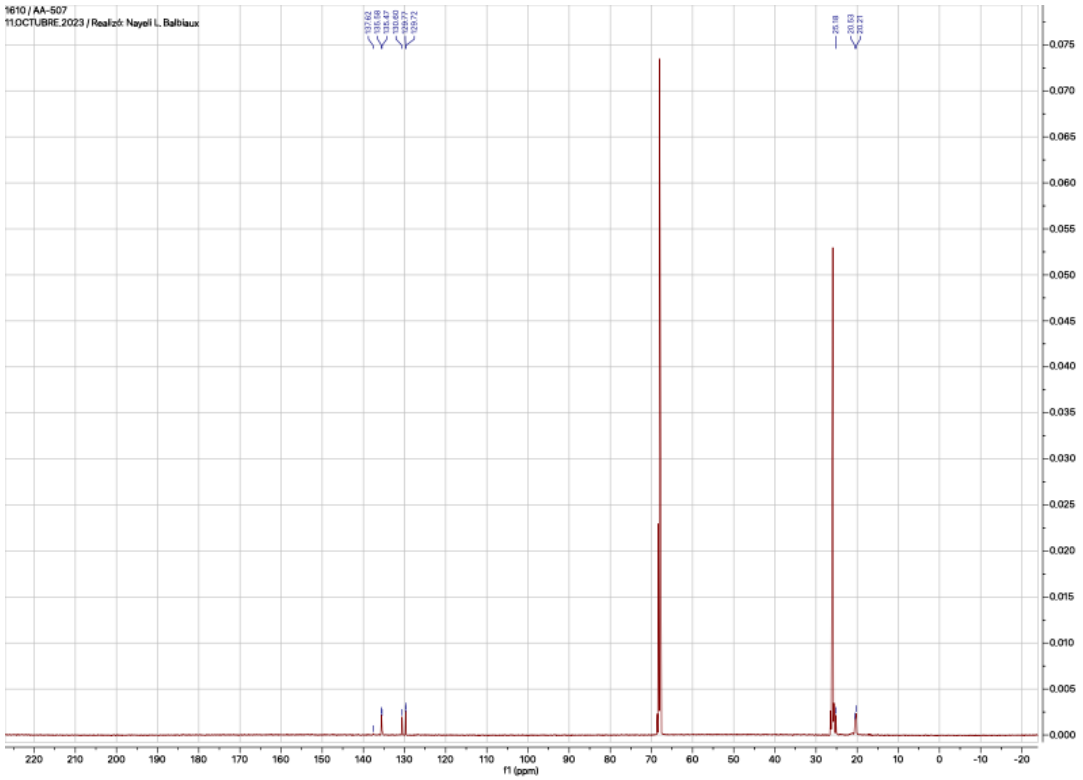


Figure S2. $^{13}C\{^{1}H\}$ (THF-d_8) NMR of Compound (**2**), full spectra.

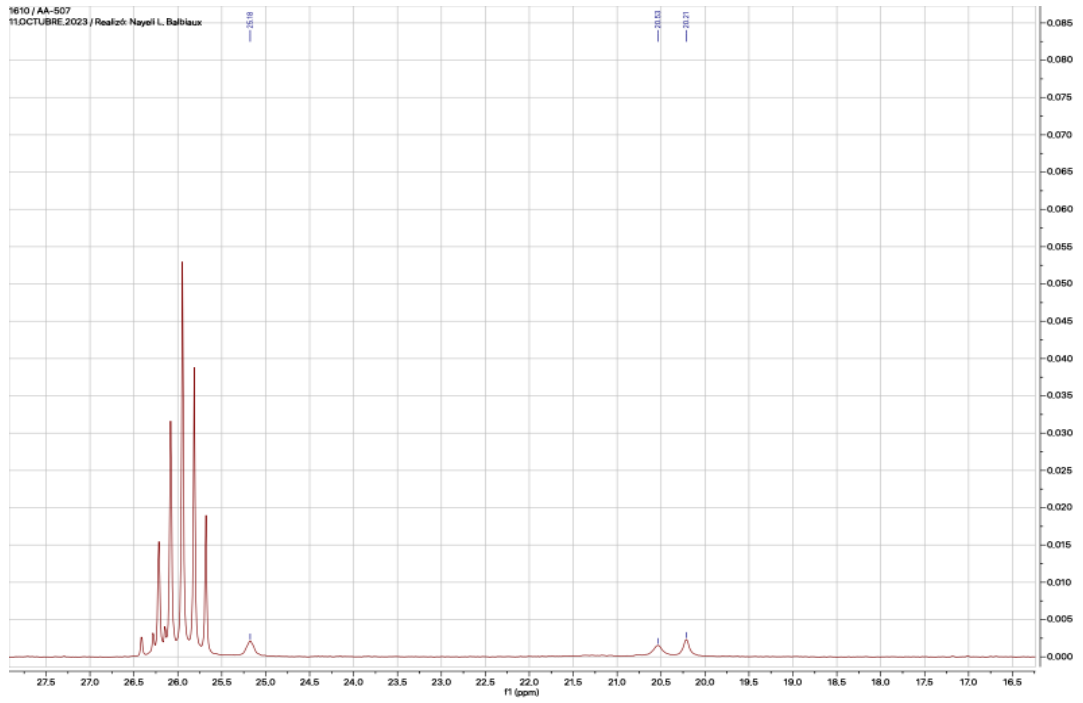


Figure S3. $^{13}C\{^{1}H\}$ (THF-d_8) NMR of Compound (**2**) Aliphatic zone.

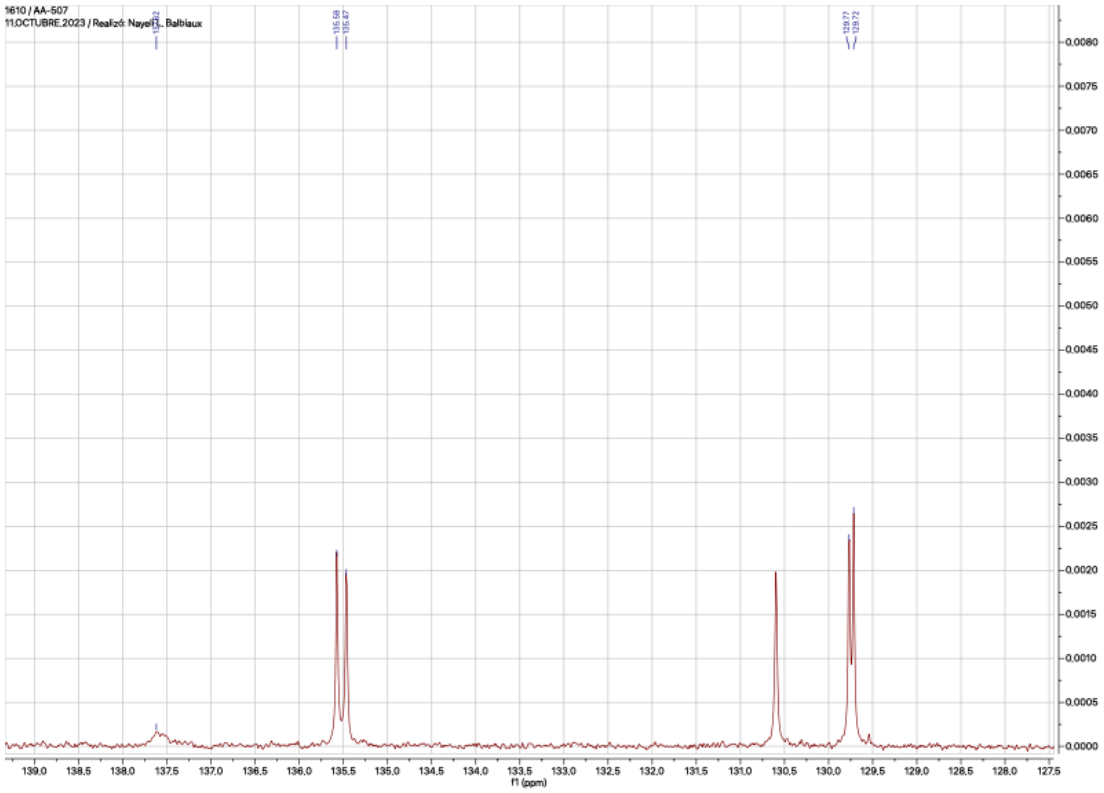


Figure S4. $^{13}C\{^{1}H\}$ (THF-d_8) NMR of Compound (**2**). Aromatic zone-

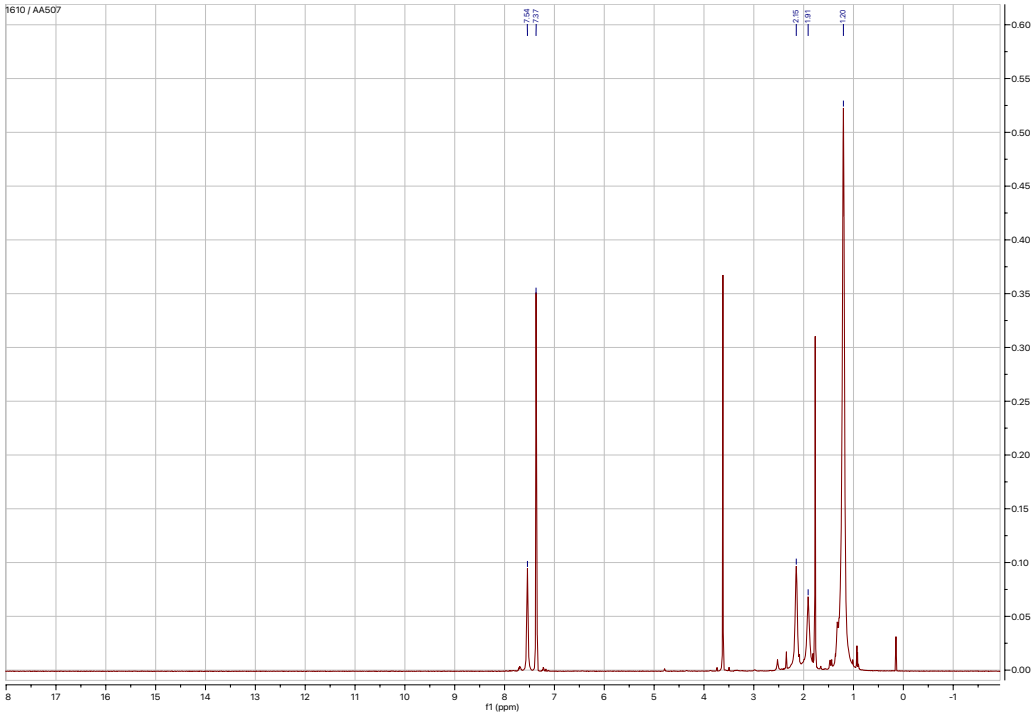


Figure S5. ^{1}H NMR (THF-d_8) NMR of Compound (**2**)

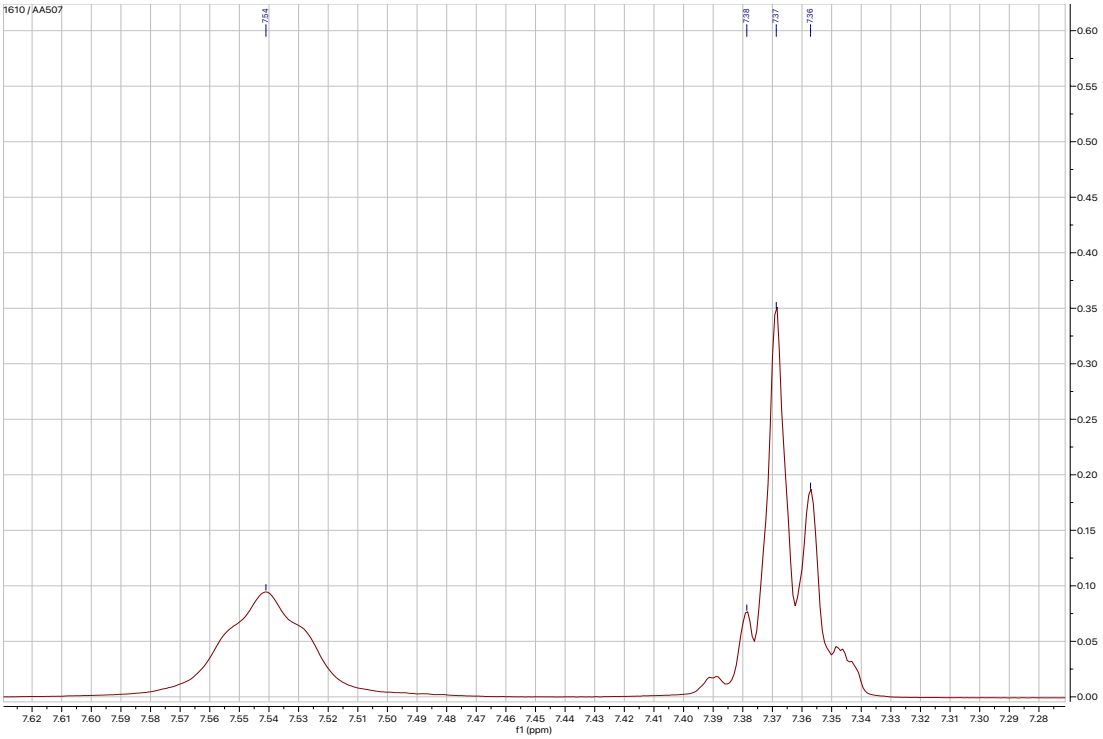


Figure S6. ^{1}H NMR (THF-d_8) NMR of Compound (**2**) Aromatic Zone.

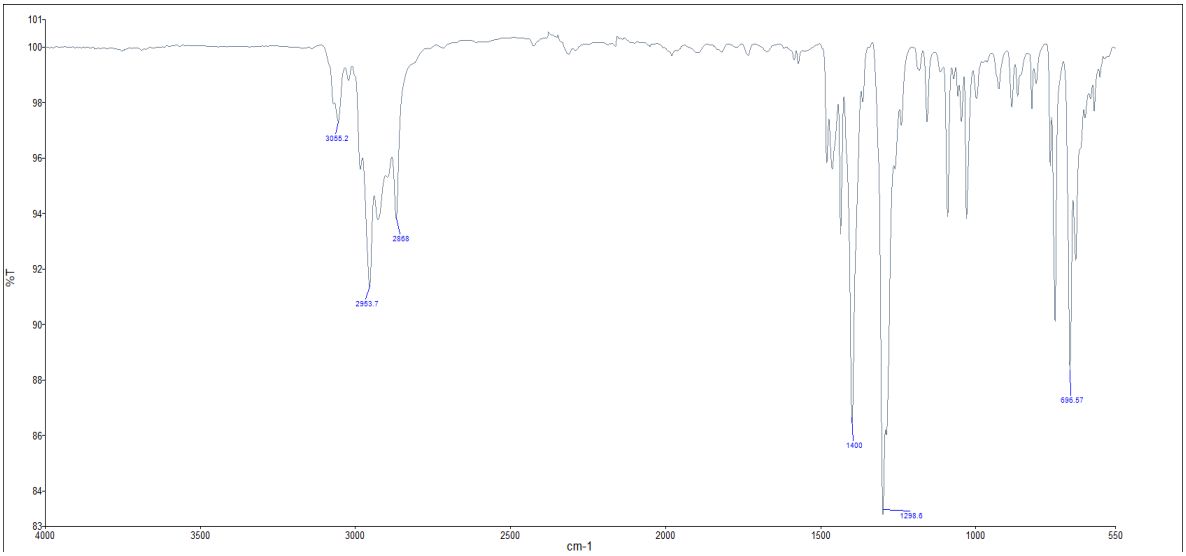
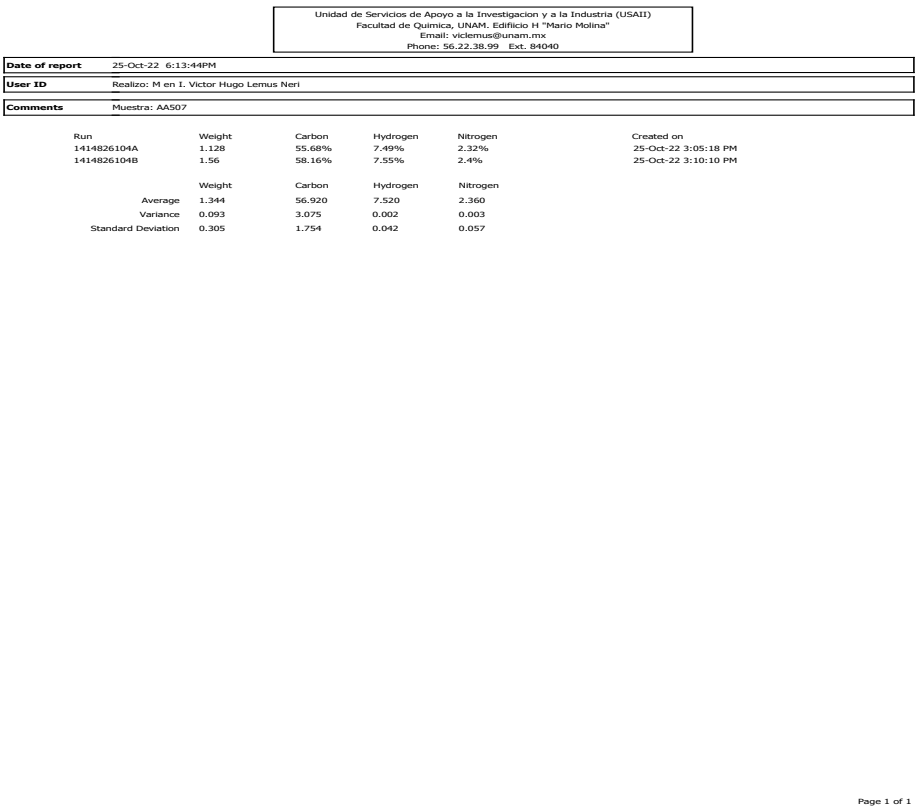


Figure S7. IR-ATR (neat) of Compound (**2**) [(dippe)Cu(PPh_3)NO_3].



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Date of report	25-Oct-22 6:13:44PM
User ID	Realizo: M en I. Victor Hugo Lemus Neri
Comments	Muestra: AA507

Run	Weight	Carbon	Hydrogen	Nitrogen	Created on
1414826104A	1.128	55.68%	7.49%	2.32%	25-Oct-22 3:05:18 PM
1414826104B	1.56	58.16%	7.55%	2.4%	25-Oct-22 3:10:10 PM

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.344	56.920	7.520	2.360
Variance	0.093	3.075	0.002	0.003
Standard Deviation	0.305	1.754	0.042	0.057

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Figure S8. Elemental Analysis for Compound (**2**)

Compound (**3**). [(depe)Cu(PPh_3)NO_3]

Compound (**3**). NMR (600MHz): $^{31}P\{^1H\}$ (THF-d_8): δ=-6.47 (d, P-bridge), δ= 2.78 ppm (m, -PPh_3). ^1H: δ= 0.95 ppm (m, -CH_3), δ= 1.60 ppm (s, -CH_2), δ=2.52 ppm (m,-CH_2 bridge), δ= 7.3 ppm (2H, -PPh_3), δ= 7.37 ppm (2H, -PPh_3), δ= 7.51 ppm (H, PPh_3). IR (ATR-neat): 3053-2875 cm-1(-CH_3 and -CH_2-, str.), 1434 cm^{-1}(N-O asym), 1337 cm^{-1} (C-H felx.), 1090-1028 cm^{-1} (C-H arom.), 694 cm^{-1} (C-H arom.). Anal. Calcd. for $C_{28}H_{39}O_3NP_3Cu$: %C, 56.7, %H, 6.62, %N, 2.3. Found: %C, 62, %H, 6.6, %N, 2.02. Melting point: 257 ºC (d).

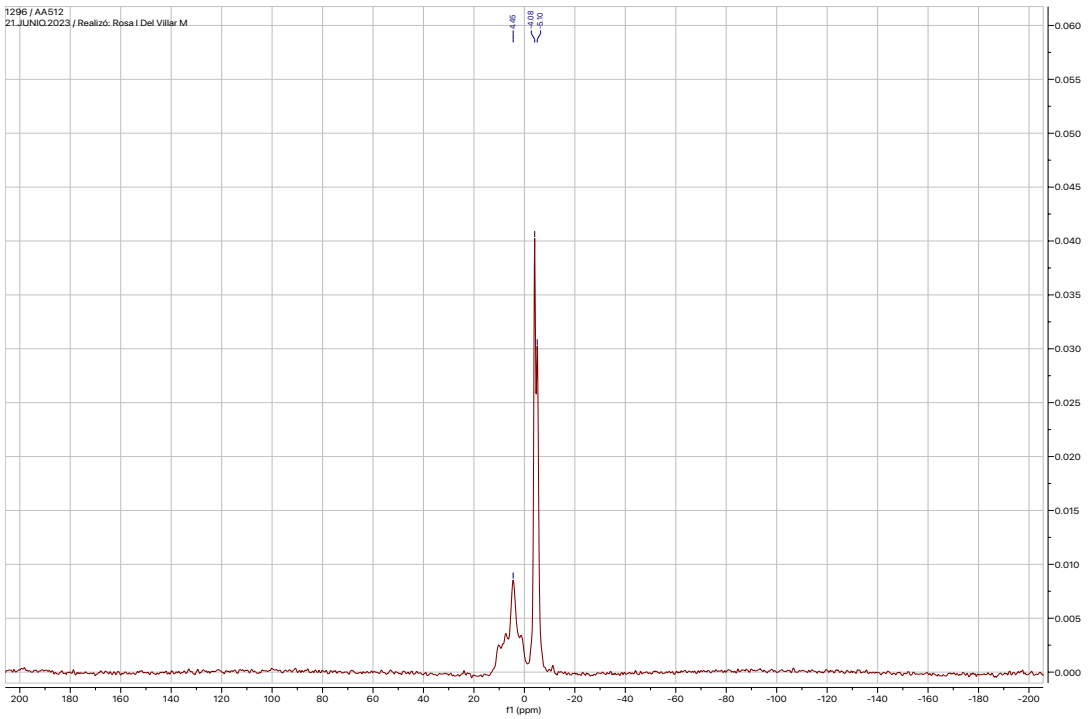


Figure S9. $^{31}P\{^{1}H\}$ (THF-d_8) NMR of Compound (**3**) [(depe)Cu(PPh_3)NO_3].

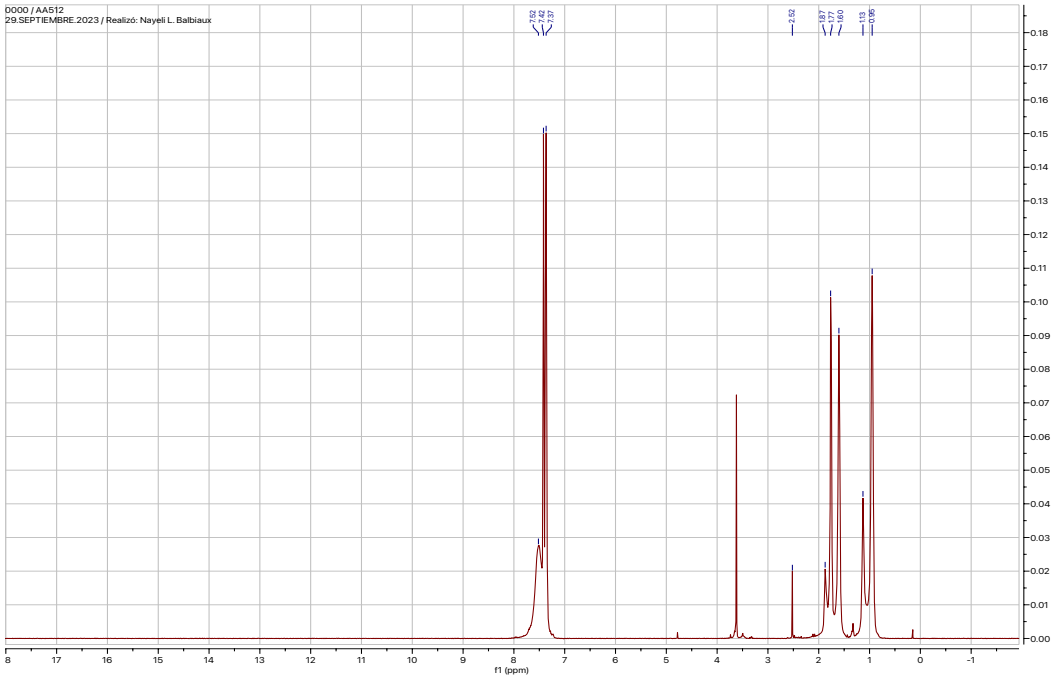


Figure S10. ^{1}H (THF-d_8) NMR of Compound (**3**) [(depe)Cu(PPh_3)NO_3].

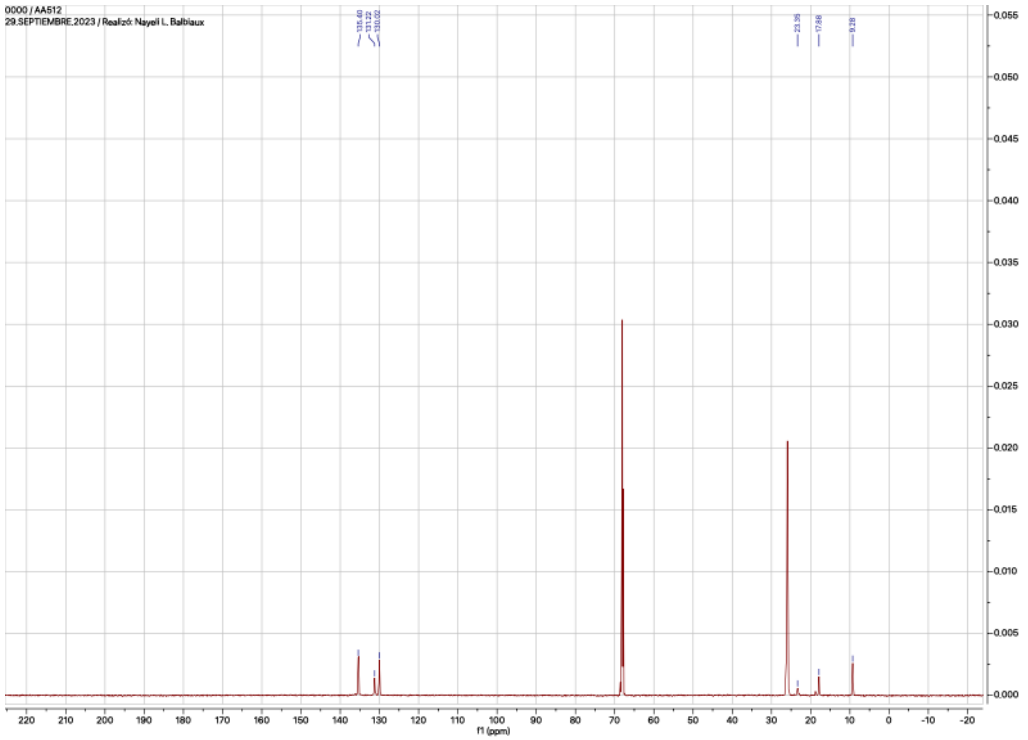


Figure S11. ^{13}C {^{1}H} (THF-d_8) NMR of Compound (**3**). Full spectra.

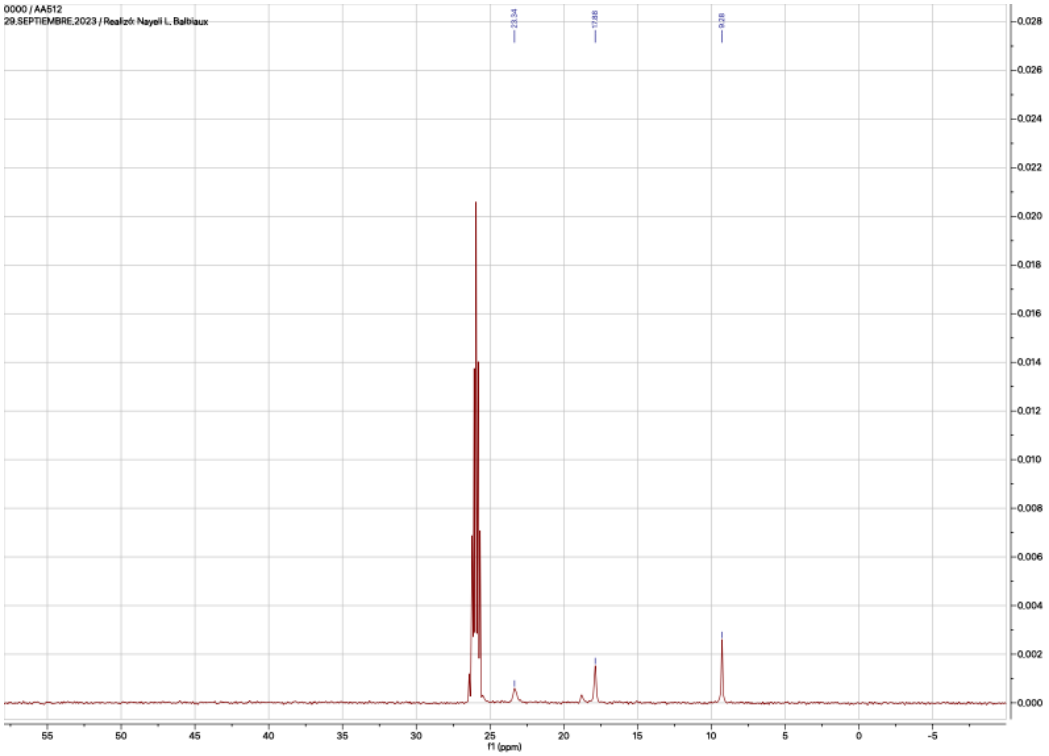


Figure S12. ^{13}C {^{1}H} (THF-d_8) NMR of Compound (**3**) Alifatic zone.

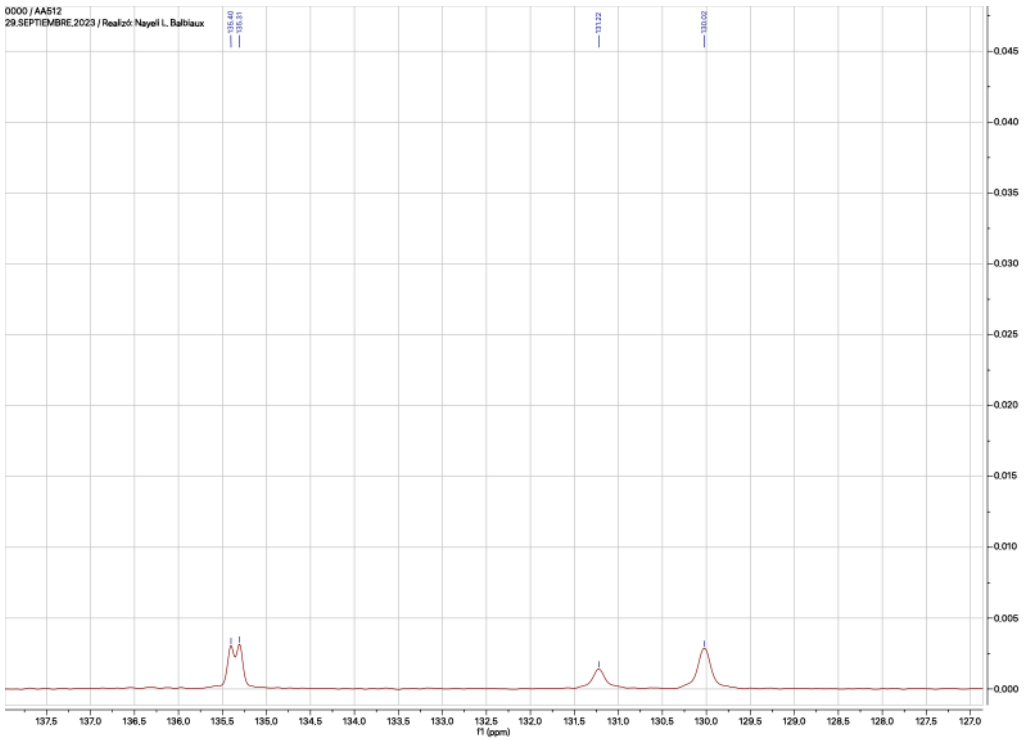


Figure S13. ^{13}C {^{1}H} (THF-d_8) NMR of Compound (**3**) Aromatic zone.

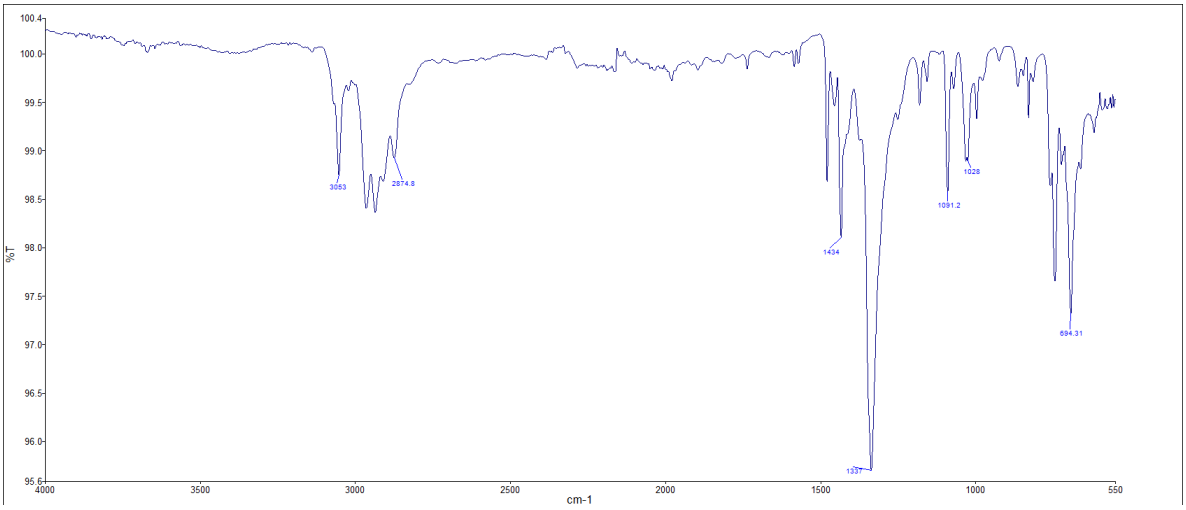
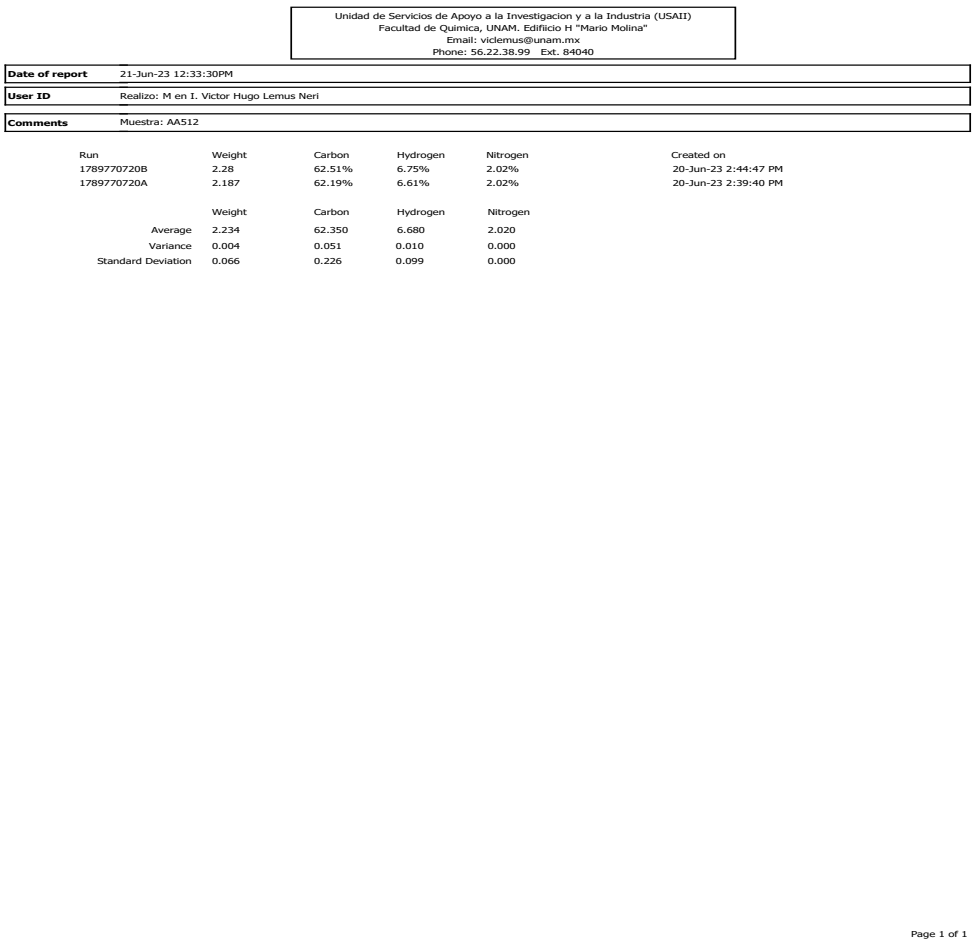


Figure S14. IR-ATR (neat) of Compound (**3**) [(depe)Cu(PPh_3)NO_3].



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Date of report	21-Jun-23 12:33:30PM
User ID	Realizo: M en I. Victor Hugo Lemus Neri
Comments	Muestra: AA512

Run	Weight	Carbon	Hydrogen	Nitrogen	Created on
1789770720B	2.28	62.51%	6.75%	2.02%	20-Jun-23 2:44:47 PM
1789770720A	2.187	62.19%	6.61%	2.02%	20-Jun-23 2:39:40 PM

	Weight	Carbon	Hydrogen	Nitrogen
Average	2.234	62.350	6.680	2.020
Variance	0.004	0.051	0.010	0.000
Standard Deviation	0.066	0.226	0.099	0.000

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Figure S15. Elemental Analysis of Compound (**3**)

Compound (**4**). [(dppe)Cu(PPh_3)NO_3].

Compound (**4**). NMR (600MHz): $^{31}P\{^1H\}$ (THF-d_8): δ=-6.22 ppm (s, P-bridge), δ=2.91 ppm (m, -PPh_3). ^1H: δ= 2.42 ppm (m, -CH bridge), δ= 7.3 ppm (m, aromatic phosphines).IR (ATR-neat): 3052 cm^{-1} (C-H str. Arom.), 1434 cm-1 (N-O asym), 1274 cm^{-1} (N-O sym), 1096-1022 cm^{-1} (C-H arom.), 692 cm^{-1} (C-H arom.). Anal. Calcd. for $C_{44}H_{43}O_3NP_3Cu$: %C, 66.8, %H, 5.4, %N, 1.8. Found: %C, 66.8, %H, 5.1, %N, 2.6. Melting ppoint: 256 ºC (d).

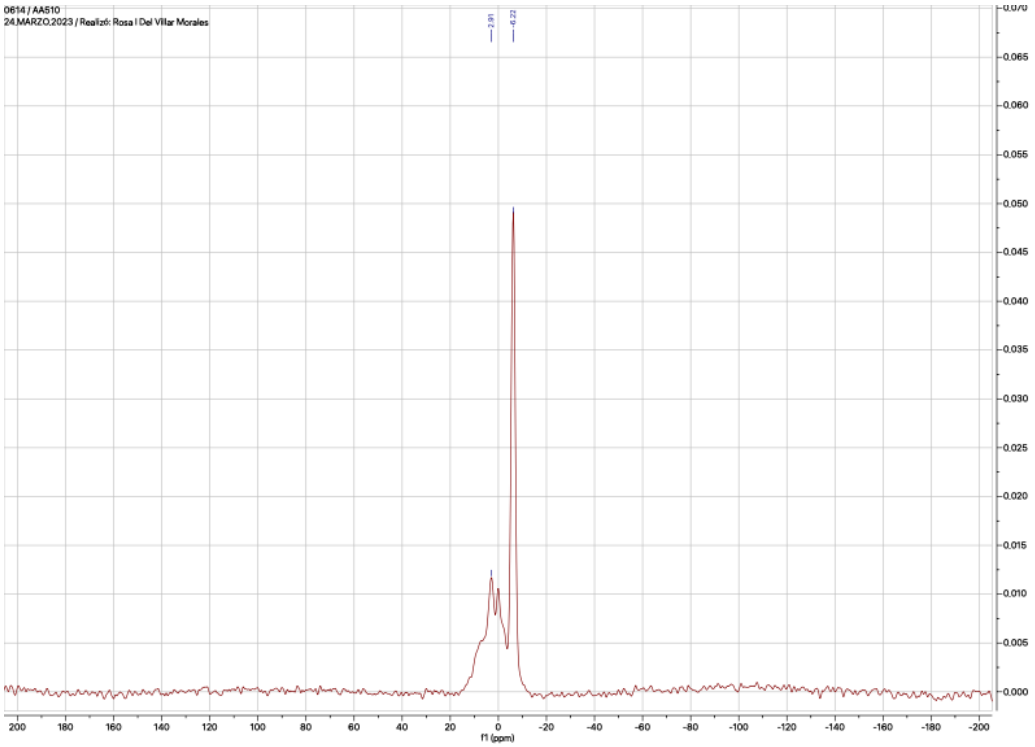

Figure S16 $^{31}P\{^{1}H\}$ (THF-d_8): NMR of Compound (**4**)

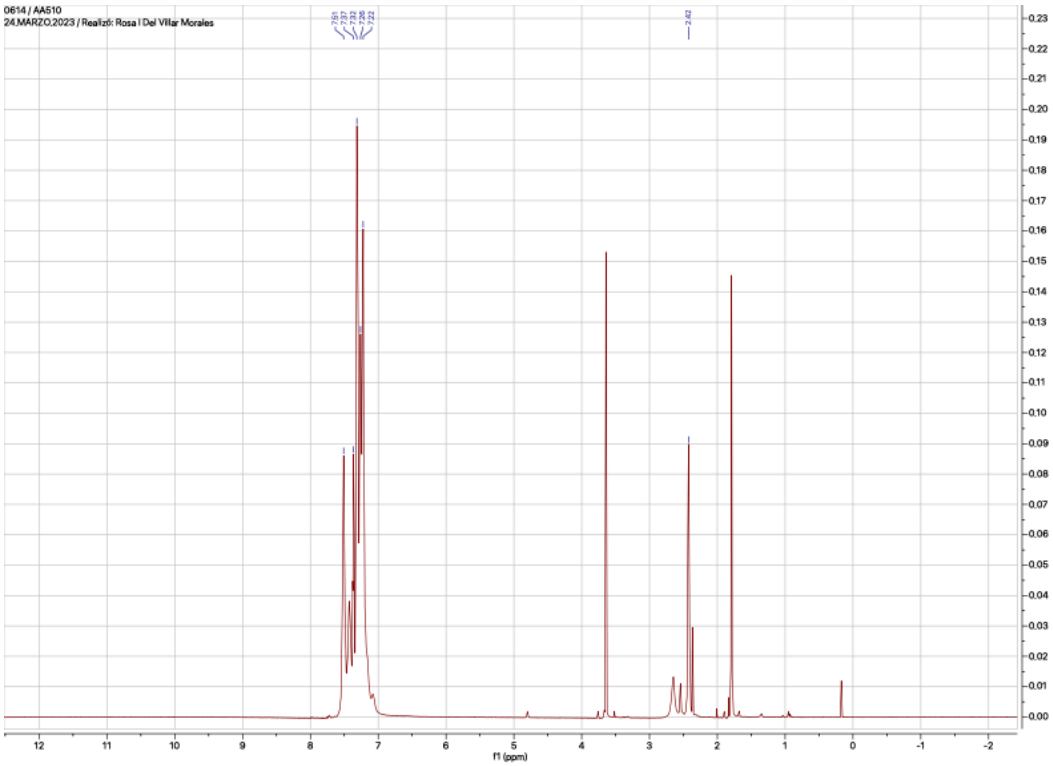

Figure S17. ^{1}H (THF-d_8): NMR of Compound (**4**)

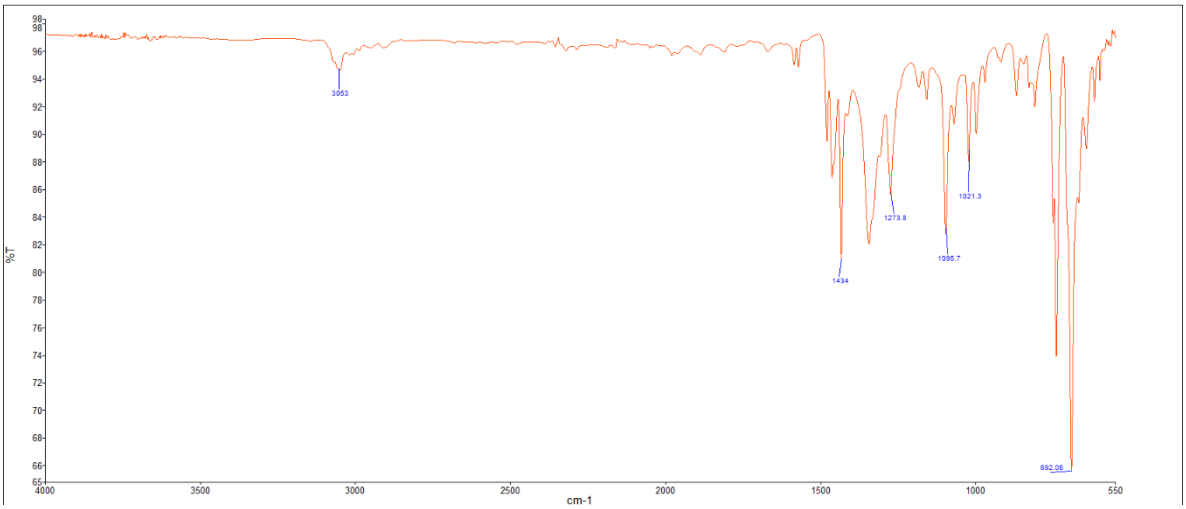

Figure S18. IR-ATR (neat) of Compound (**4**)

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Date of report	22-May-23 7:04:52PM
User ID	Realizo: M en I. Victor Hugo Lemus Neri
Comments	Muestra: AA510

Run	Weight	Carbon	Hydrogen	Nitrogen	Created on
7734833569B	1.227	66.79%	5.14%	2.72%	22-May-23 4:39:04 PM
7734833569A	1.499	66.85%	5.1%	2.59%	22-May-23 4:34:00 PM

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.363	66.820	5.120	2.655
Variance	0.037	0.002	0.001	0.008
Standard Deviation	0.192	0.042	0.028	0.092

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Figure S19. Elemental Analysis of Compound (**4**).

Compound (**5**) [(dipf)$CuNO_3$].

Compound (**5**). NMR (600 MHz): $^{31}P\{^1H\}$ (THF-d_8), δ= 3.13 ppm (s). ^1H, δ= 1.30 ppm (m, -CH_3), δ= 2.29 ppm (m, -CH-), δ= 4.44 (s, -CH, Fc), δ= 4.53 ppm (s, -CH, Fc). $^{13}C\{^1H\}$, δ= 20.59 ppm (m, -CH_3), δ= 21.44 ppm (-CH-), δ= 72.48 ppm (-CH-, Fc), δ= 75.19 ppm (-CH-, Fc). IR (ATR-neat): 2958-2866 cm^{-1} (-C-H alkyl), 1431 cm^{-1} (N-O asym), 1286 cm^{-1} (N-O sym), 1024 cm^{-1}(Fc), 820 cm^{-1} (Fc). Anal. Calcd. for $C_{22}H_{36}O_3NP_2FeCu$: %C,48.59, %H, 6.67, %N, 2.58. Found: %C, 50.22, %H, 6.81, %N, 3.11 Melting Point: 183 ºC (d).

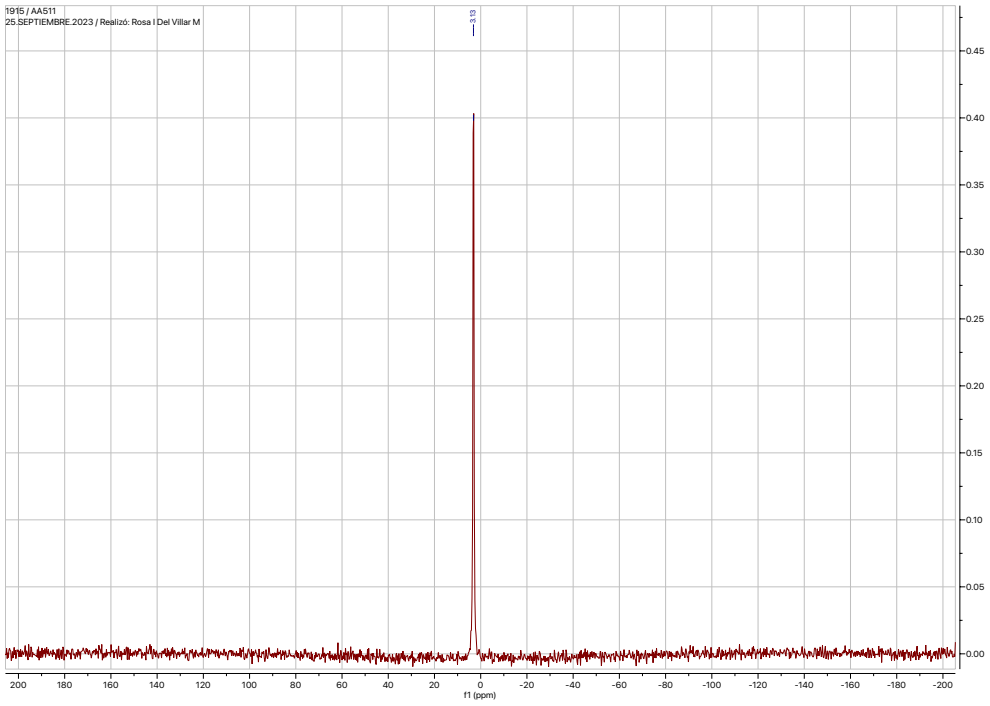

Figure S20. $^{31}P\{^1H\}$ (THF-d_8) NMR of Compound (**5**).

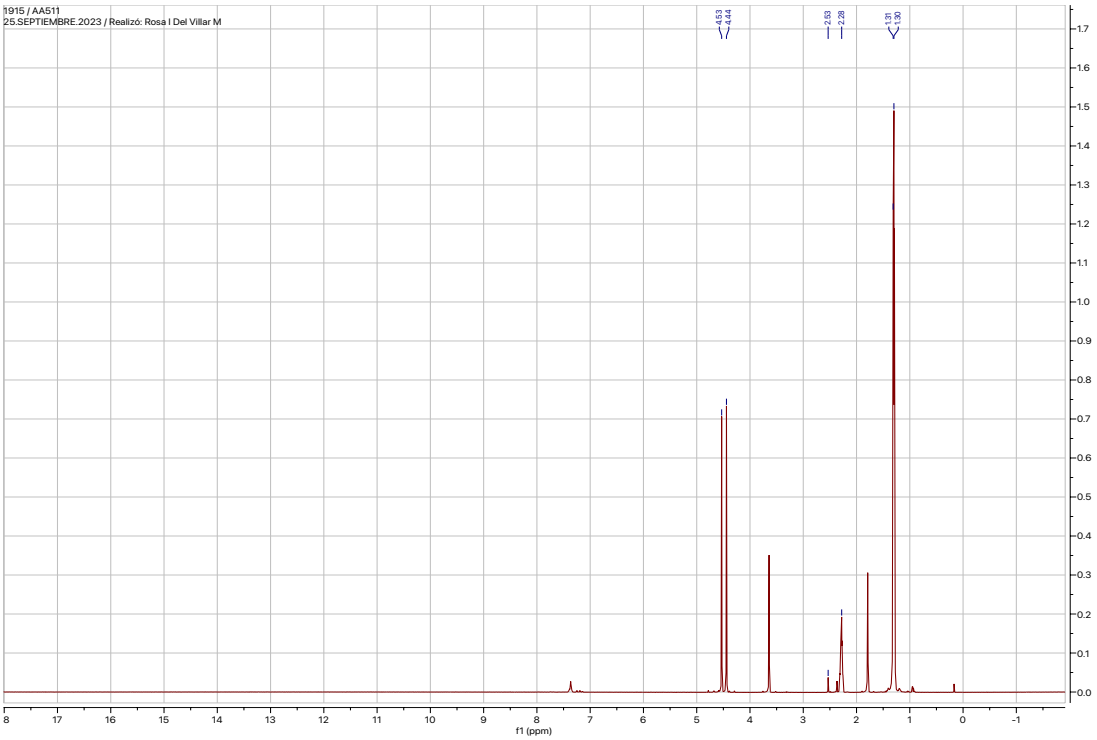

Figure S21. ^{1}H (THF-d_8) NMR of Compound (**5**.,

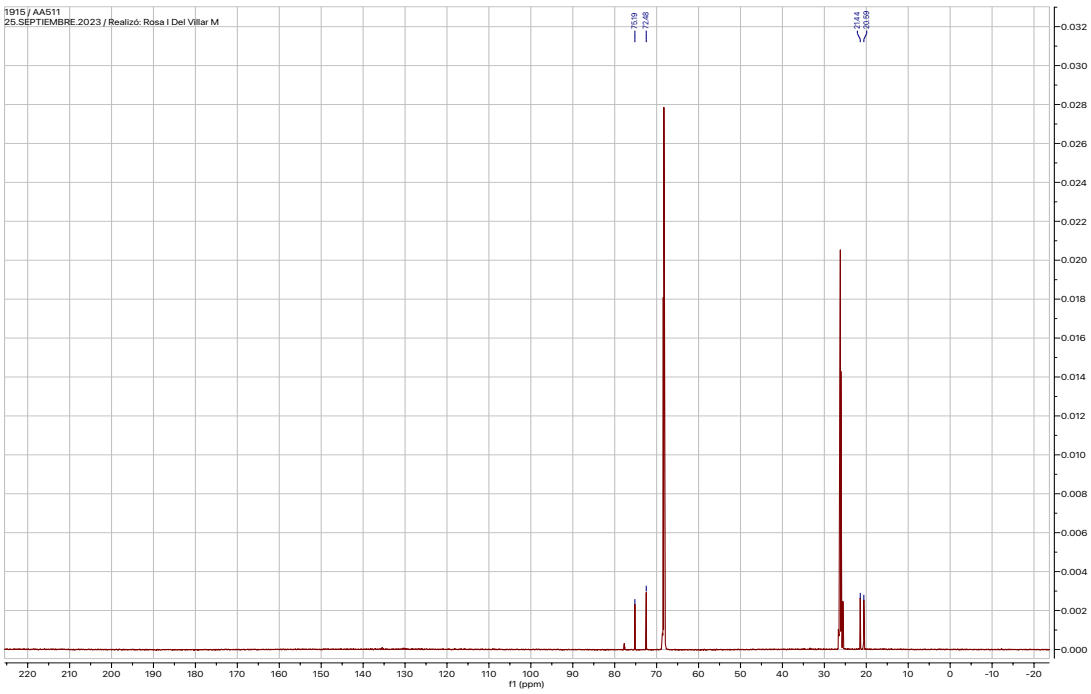

Figure S22. $^{13}C\{^{1}H\}$ (THF-d_8) NMR of Compound (**5**).

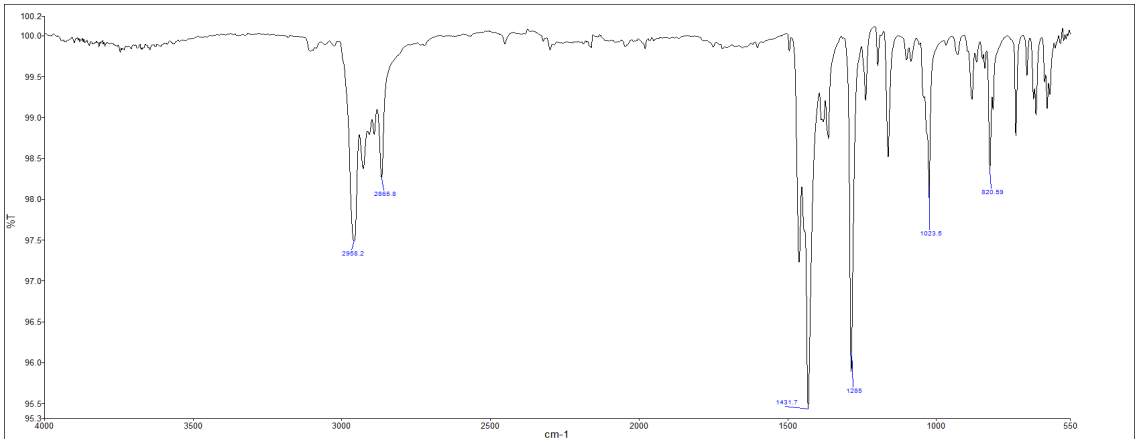

Figure S23. IR-ATR (neat) of Compound (**5**).

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User ID	Realizo: M en I. Victor Hugo Lemus Neri
Comments	Muestra: AA511

22-May-23

Run	Weight (mg)	Carbon	Hydrogen	Nitrogen
2846988985A	1.439	50.22%	6.81%	3.11%

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Figure S24 Elemental Analysis for Compound (**5**).

XRD data for Cu(I) compounds

Table S1. Crystal data and structure refinement for (**2**) [(dippe)Cu(PPh_3)(NO_3)]

Identification code	**2**	
Empirical formula	C_{32} H_{47} Cu N O_3 P_3	
Formula weight	650.15	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.7674(5) Å	α= 90°.
	b = 17.7058(7) Å	β= 105.218(4)°.
	c = 15.0682(6) Å	γ = 90°.
Volume	3286.8(2) $Å^3$	
Z	4	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.843 mm^{-1}	
F(000)	1376	
Crystal size	0.400 x 0.370 x 0.270 mm^3	
Theta range for data collection	3.434 to 29.596°.	
Index ranges	-17<=h<=12, -24<=k<=15, -17<=l<=19	
Reflections collected	16174	
Independent reflections	7717 [R(int) = 0.0278]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7717 / 0 / 369	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1289	
R indices (all data)	R1 = 0.0722, wR2 = 0.1436	
Largest diff. peak and hole	1.857 and -0.896 $e.Å^{-3}$	

Table S2. Selected bond lengths [Å] and angles [°] for (**2**) [(dippe)Cu(PPh_3)(NO_3)]

C(1)-C(2)	1.510(5)	O(1)-Cu(1)-P(3)	97.27(7)
C(1)-P(1)	1.842(4)	O(1)-Cu(1)-P(2)	111.01(7)
C(3)-C(5)	1.500(6)	P(3)-Cu(1)-P(2)	124.54(3)
C(3)-C(4)	1.517(6)	O(1)-Cu(1)-P(1)	108.62(7)
C(3)-P(1)	1.868(4)	P(3)-Cu(1)-P(1)	125.08(3)
C(15)-C(16)	1.386(5)	P(2)-Cu(1)-P(1)	90.25(3)
C(15)-P(3)	1.828(3)	O(3)-N(1)-O(2)	119.8(3)
Cu(1)-O(1)	2.146(2)	O(3)-N(1)-O(1)	119.2(3)
Cu(1)-P(3)	2.2688(9)	O(2)-N(1)-O(1)	121.0(3)
Cu(1)-P(2)	2.2904(9)	C(1)-P(1)-C(6)	104.7(2)
Cu(1)-P(1)	2.2944(9)	C(15)-P(3)-Cu(1)	116.01(11)
N(1)-O(3)	1.251(4)		
N(1)-O(2)	1.253(4)		
N(1)-O(1)	1.254(4)		

Table S3. Crystal data and structure refinement for (**3**) [(depe)Cu(PPh_3)(NO_3)]

Identification code	(**3**)	
Empirical formula	C_{28} H_{39} Cu N O_3 P_3	
Formula weight	594.05	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.4119(11) Å	α= 90°.
	b = 15.363(2) Å	β= 90°.
	c = 18.5644(17) Å	γ = 90°.
Volume	2969.5(6) $Å^3$	
Z	4	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	0.926 mm^{-1}	
F(000)	1248	
Crystal size	0.290 x 0.190 x 0.060 mm^3	
Theta range for data collection	3.474 to 29.616°.	
Index ranges	-14<=h<=14, -21<=k<=19, -22<=l<=24	
Reflections collected	16522	
Independent reflections	7018 [R(int) = 0.0646]	
Completeness to theta = 25.242°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7018 / 0 / 329	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.0674	
R indices (all data)	R1 = 0.0934, wR2 = 0.0821	
Absolute structure parameter	-0.017(13)	
Largest diff. peak and hole	0.585 and -0.637 e.$Å^{-3}$	

Table S4. Selected bond lengths [Å] and angles [°] for (**3**) [(depe)Cu(PPh_3)(NO_3)]

C(1)-C(2)	1.537(7)	O(1)-Cu(1)-P(3)	99.13(10)
C(1)-P(1)	1.828(6)	O(1)-Cu(1)-P(2)	109.20(11)
C(3)-C(4)	1.532(7)	P(3)-Cu(1)-P(2)	129.28(6)
C(3)-P(1)	1.841(5)	O(1)-Cu(1)-P(1)	112.16(11)
C(15)-C(16)	1.391(7)	P(3)-Cu(1)-P(1)	116.47(6)
C(15)-P(3)	1.822(5)	P(2)-Cu(1)-P(1)	90.84(5)
Cu(1)-O(1)	2.090(3)	O(2)-N(1)-O(3)	120.9(5)
Cu(1)-P(3)	2.2323(13)	O(2)-N(1)-O(1)	120.7(5)
Cu(1)-P(2)	2.2593(16)	O(3)-N(1)-O(1)	118.4(5)
Cu(1)-P(1)	2.2759(16)	C(1)-P(1)-C(3)	104.4(3)
N(1)-O(2)	1.230(5)	C(6)-P(1)-C(3)	104.0(3)
N(1)-O(3)	1.237(5)	C(12)-P(2)-C(2)	102.0(3)
N(1)-O(1)	1.273(5)	C(12)-P(2)-C(9)	105.1(3)
		C(15)-P(3)-C(21)	102.6(2)

Table S5. Crystal data and structure refinement for (**5**) [(dipf)Cu(NO_3)]

Identification code	(**5**)	
Empirical formula	C_{22} H_{36} Cu Fe N O_3 P_2	
Formula weight	543.85	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6246(7) Å	α= 91.601(5)°.
	b = 9.3841(6) Å	β= 97.997(6)°.
	c = 17.1248(10) Å	γ = 100.216(6)°.
Volume	1348.77(16) $Å^3$	
Z	2	
Density (calculated)	1.339 Mg/m^3	
Absorption coefficient	1.465 mm^{-1}	
F(000)	568	
Crystal size	0.160 x 0.130 x 0.080 mm^3	
Theta range for data collection	3.568 to 29.590°.	
Index ranges	-11<=h<=11, -13<=k<=12, -23<=l<=23	
Reflections collected	29144	
Independent reflections	6766 [R(int) = 0.0493]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6766 / 0 / 279	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0646	
R indices (all data)	R1 = 0.0512, wR2 = 0.0722	
Largest diff. peak and hole	0.493 and -0.370 $e.Å^{-3}$	

Table S6. Selected bond lengths [Å] and angles [°] for (**5**) [(dipf)Cu(NO_3)]

C(3)-C(5)	1.534(3)	O(1)-Cu(1)-P(1)	122.00(5)
C(3)-C(4)	1.537(3)	O(1)-Cu(1)-P(2)	113.29(4)
C(6)-P(1)	1.852(2)	P(1)-Cu(1)-P(2)	117.96(2)
C(9)-P(2)	1.8553(19)	O(1)-Cu(1)-O(2)	58.44(6)
C(12)-P(2)	1.859(2)	P(1)-Cu(1)-O(2)	117.31(4)
C(15)-C(16)	1.436(3)	P(2)-Cu(1)-O(2)	114.09(5)
C(15)-P(2)	1.816(2)	C(19)-Fe(1)-C(23)	140.20(8)
C(20)-C(21)	1.444(3)	C(19)-Fe(1)-C(21)	139.37(8)
C(20)-P(1)	1.812(2)	C(15)-Fe(1)-C(16)	40.79(8)
Cu(1)-O(1)	2.1598(15)	O(3)-N(1)-O(2)	122.0(2)
Cu(1)-P(1)	2.2305(6)	O(3)-N(1)-O(1)	121.3(2)
Cu(1)-P(2)	2.2383(6)	O(2)-N(1)-O(1)	116.70(18)
Cu(1)-O(2)	2.2580(16)	C(6)-P(1)-C(3)	106.05(9)
N(1)-O(3)	1.239(2)	C(9)-P(2)-C(12)	103.59(9)
N(1)-O(2)	1.264(2)		
N(1)-O(1)	1.271(2)		

Table S7. Overpotential values (η) for the Cu(I) compounds-

Compound	η_{NHE} (V)
Cu-1	0.348
Cu-2	0.39
Cu-3	0.35
Cu-4	0.30
Cu-5	0.43

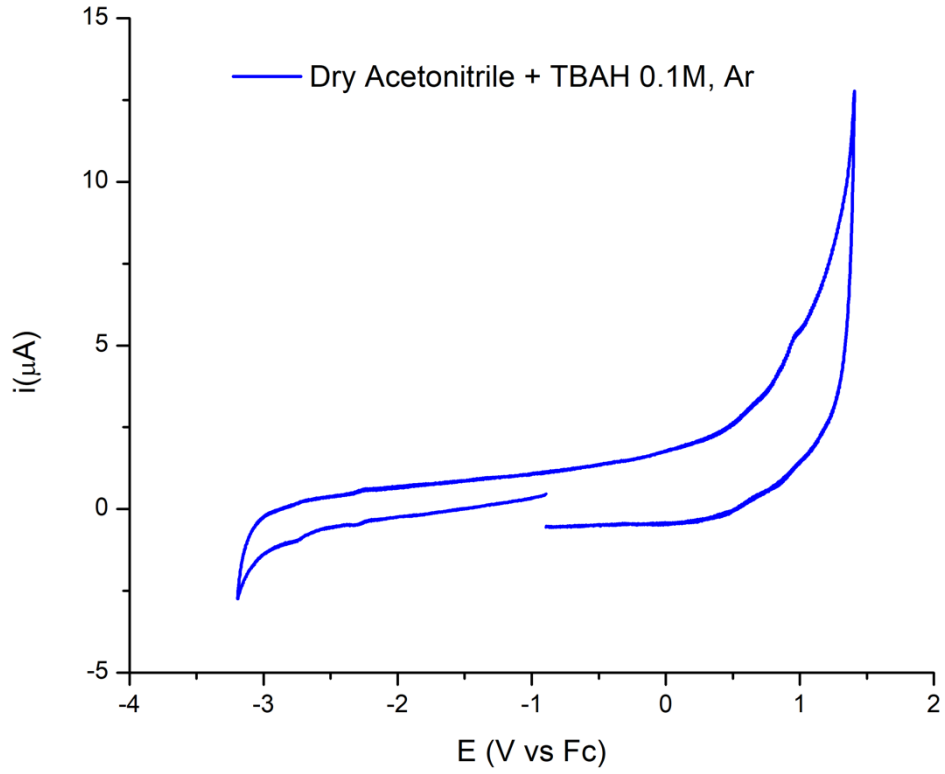

Figure S25. CV trace for dry acetonitrile.

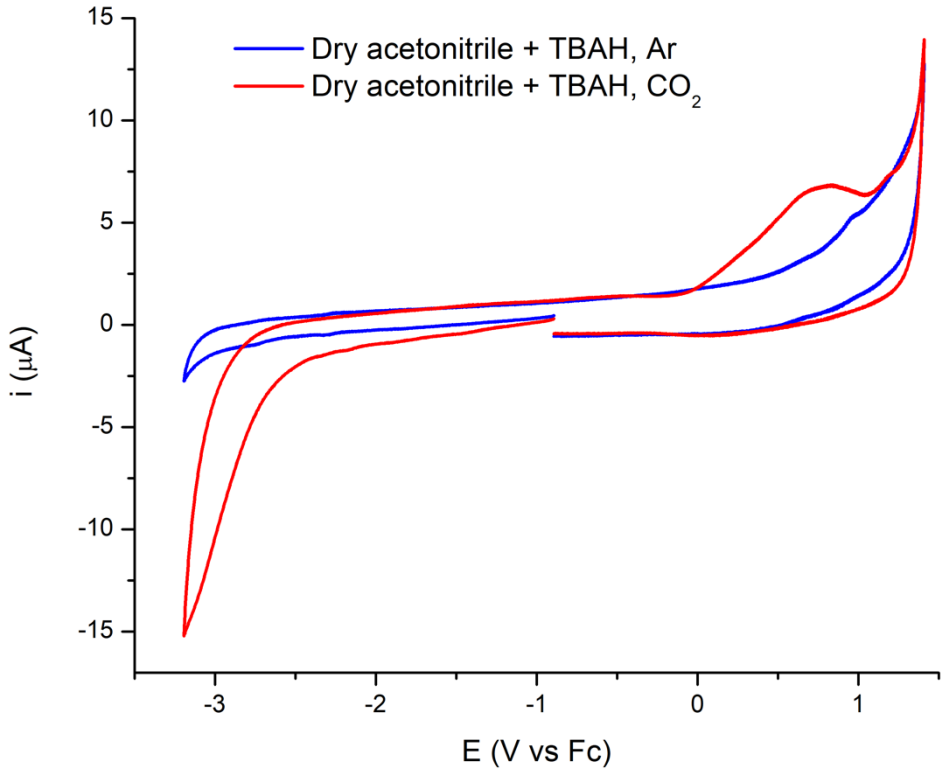

Figure S26. CV trace for dry acetonitrile and CO_2.

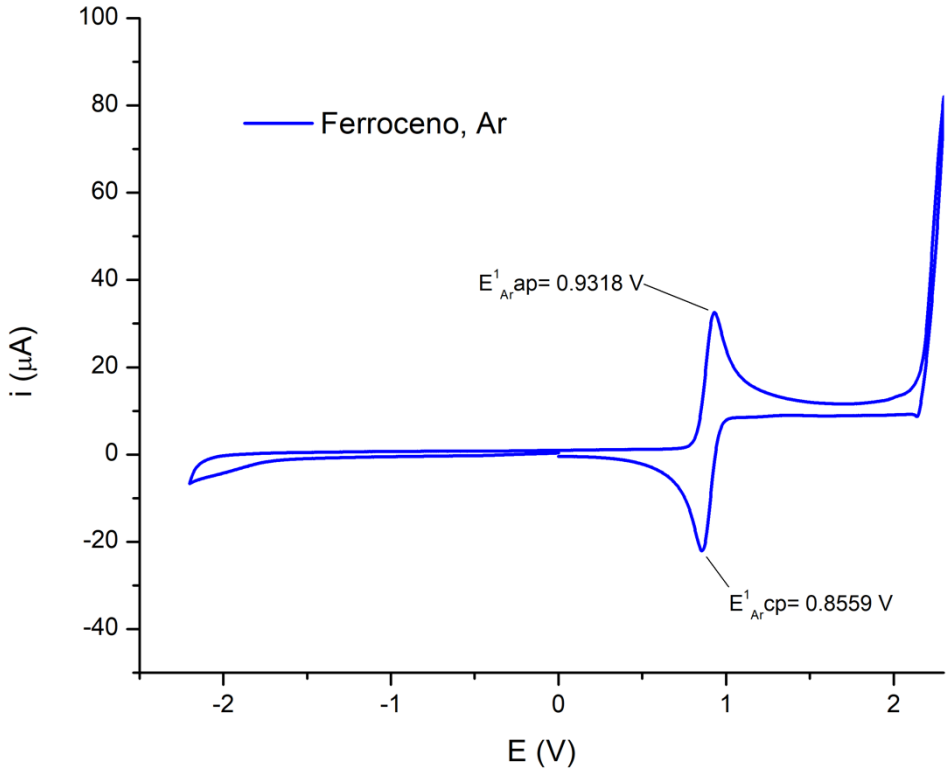

Figure S27. CV trace for ferrocene/ferrocinium pair.

Electrochemical Data for Cu(I) compounds.

ANODIC PEAKS ASSIGNMENT OF PHOSPHINES FOR Cu(I) COMPOUNDS

For compound (**2**), anodic peaks L1 were assigned to the oxidation process corresponding to dippe ligand while anodic peak L2 corresponds to the sum of PPh_3 oxidation and to the second oxidation process for dippe ligand.

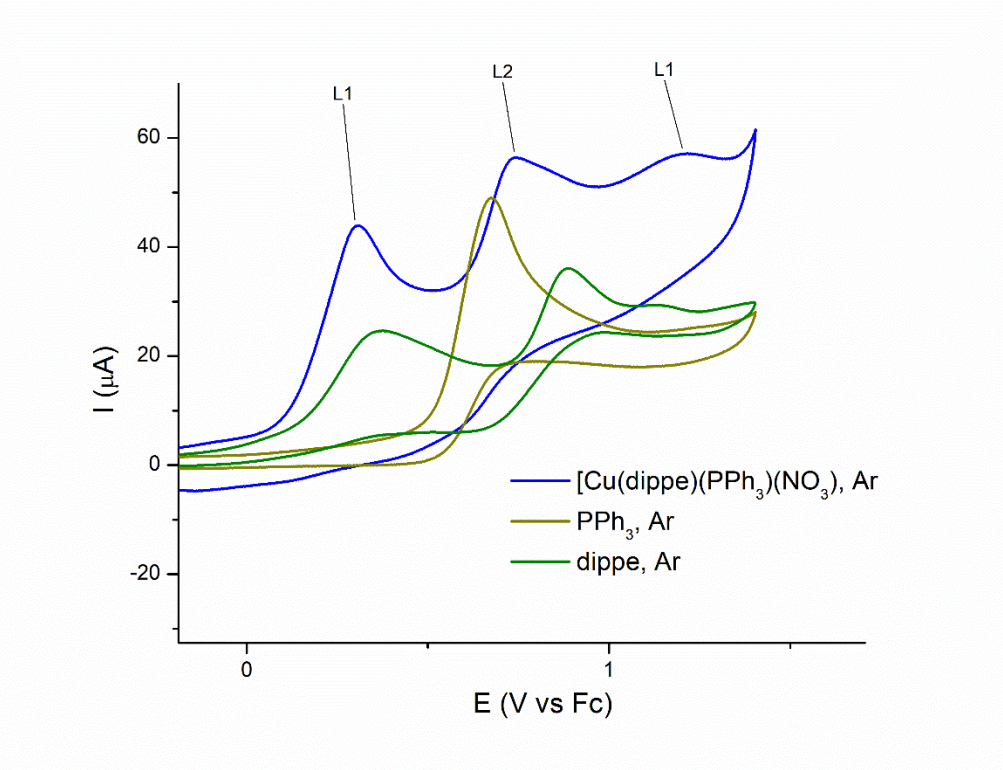

Figure S28. Anodic peaks assignments corresponding to phosphine ligands in compound (**2**)

For compound (3), L5 peak was assigned to the first oxidation of depe ligand. Anodic peak L2 + L5 corresponds to the sum of oxidation processes for PPh3 and depe second oxidation process.

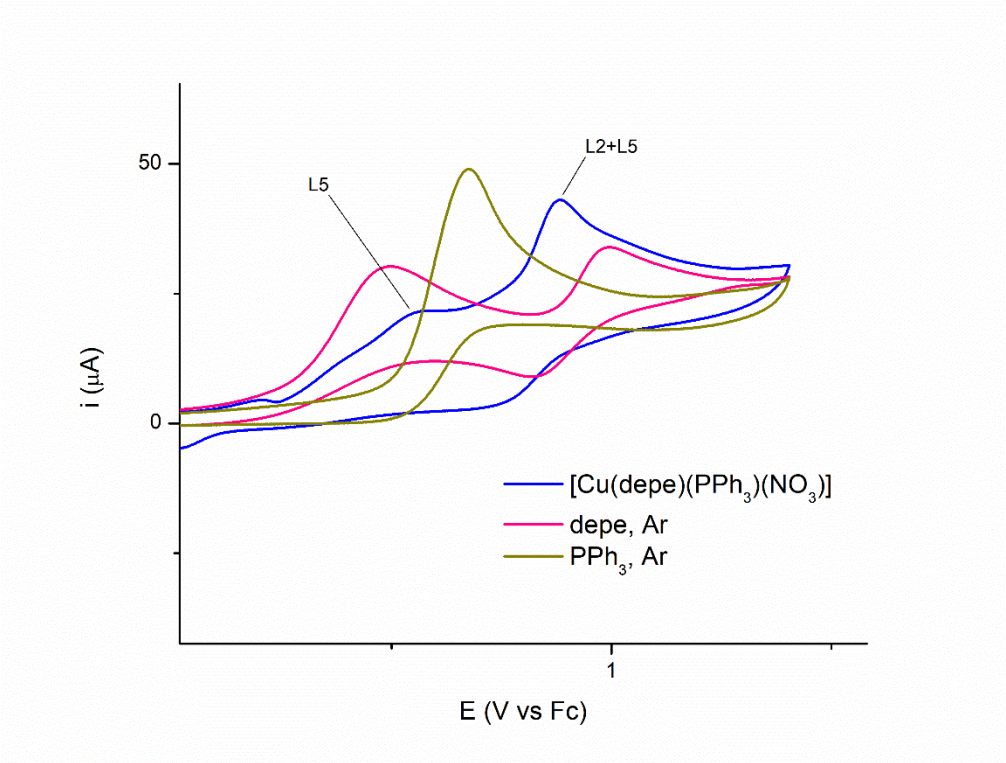

Figure S29. Assignment of anodic peaks of the phosphine ligands for compound (**3**)

For compound (4), L2 peak was assigned to the oxidation processes for PPh_3 and L3 peak corresponds to the oxidation of DIPHOS.

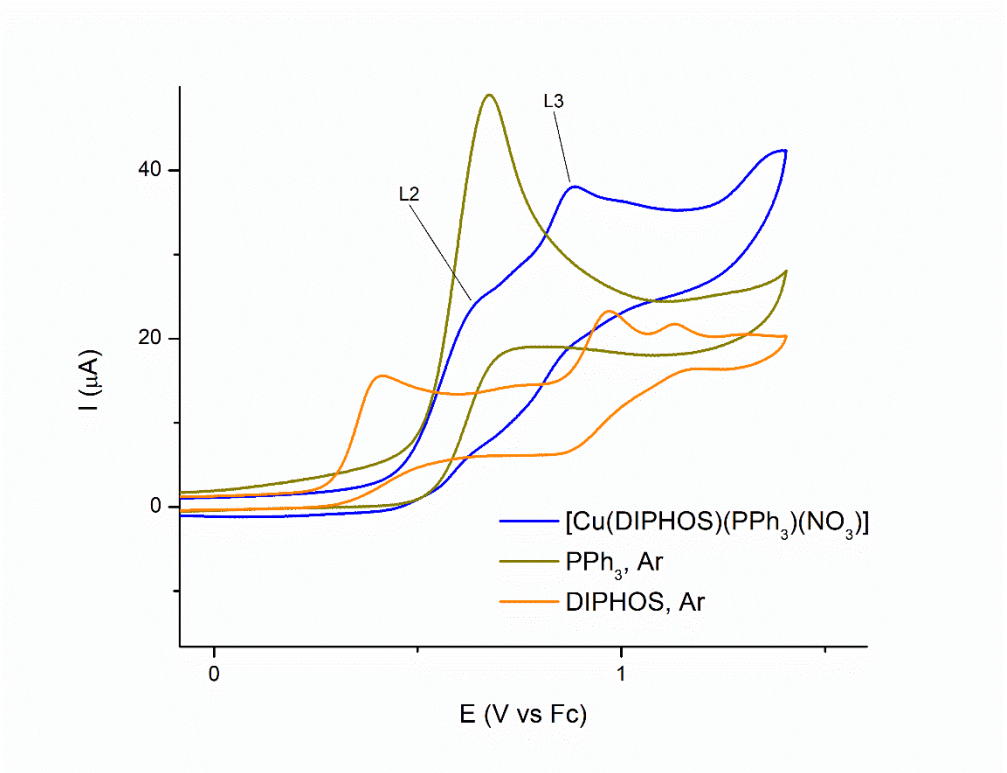

Figure S30. Assignment of anodic peaks of the phosphine ligands for compound (**4**)

Compound [Cu(dipf)NO_3] (**5**).

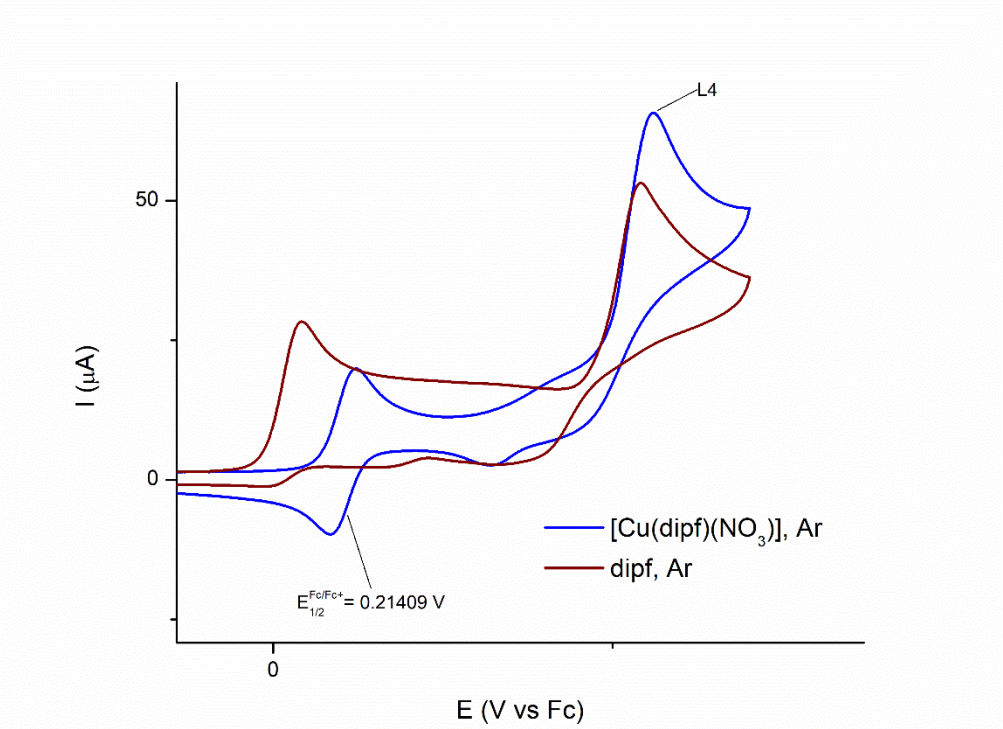

Figure S31. Assignment of anodic peaks of the phosphine ligands for compound (**5**)

L4 peak corresponds to the oxidation of dipf ligand, in Compound (**5**),

COMPOUND (2) BEHAVIOR UNDER Ar AND CO_2 ATMOSPHERE AND DIFFERENT PROTIC MEDIA.

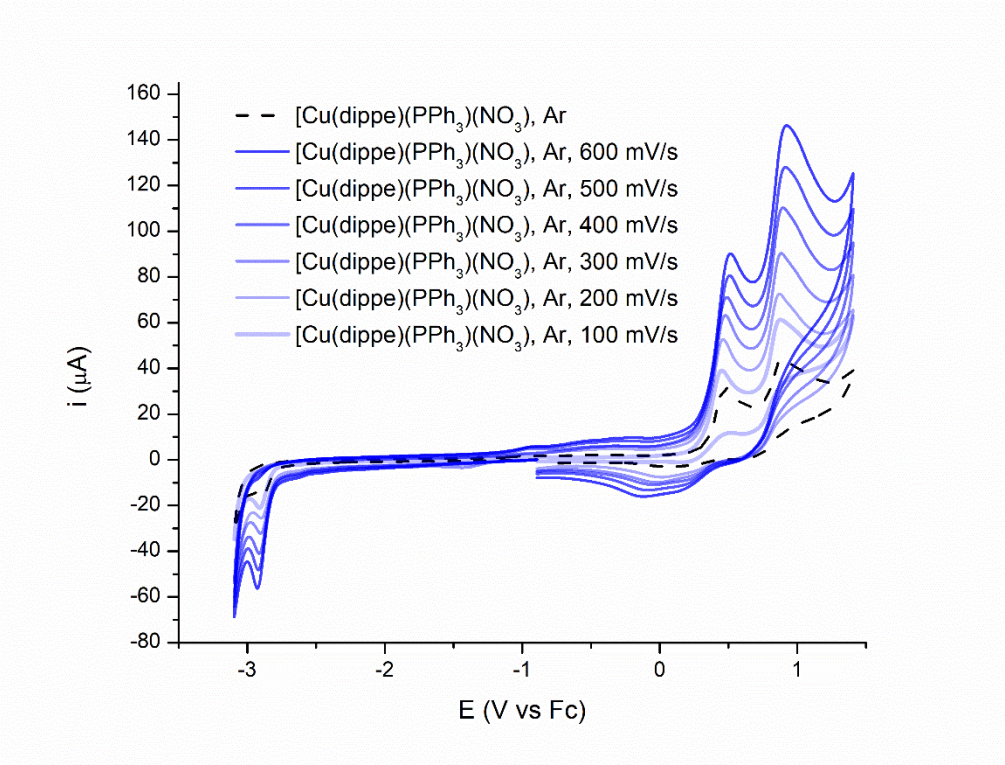

Figure S32. Compound (**2**) behavior with different scanning speeds in Ar atmosphere

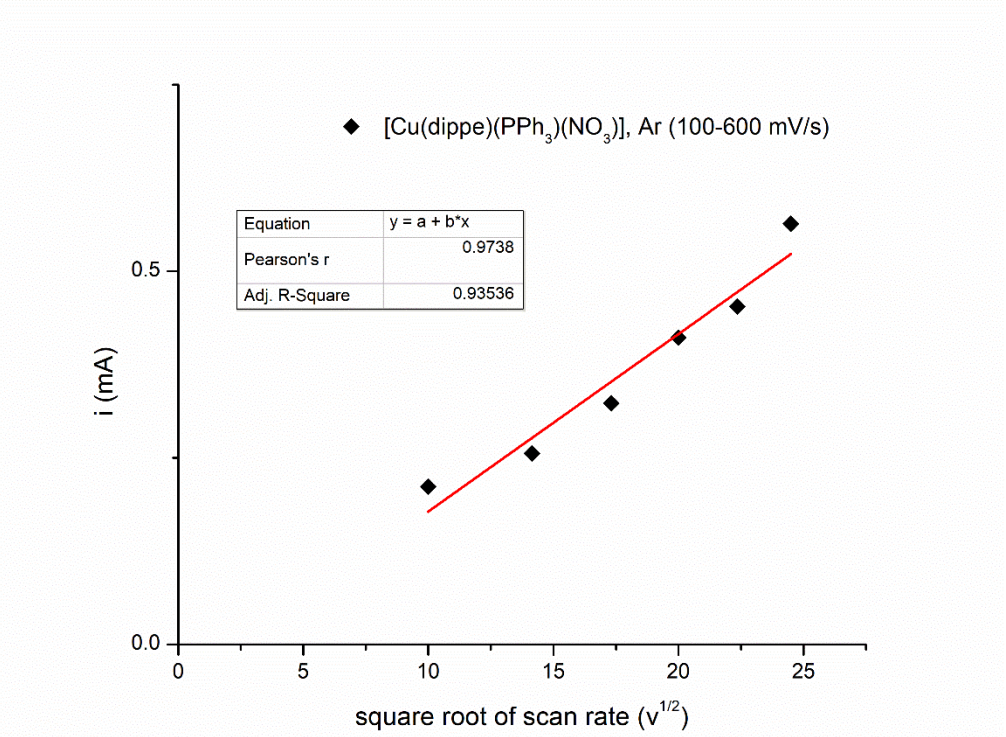

Figure S33. Pseudo-first-order behavior of the cathodic process of Compound (**2**)

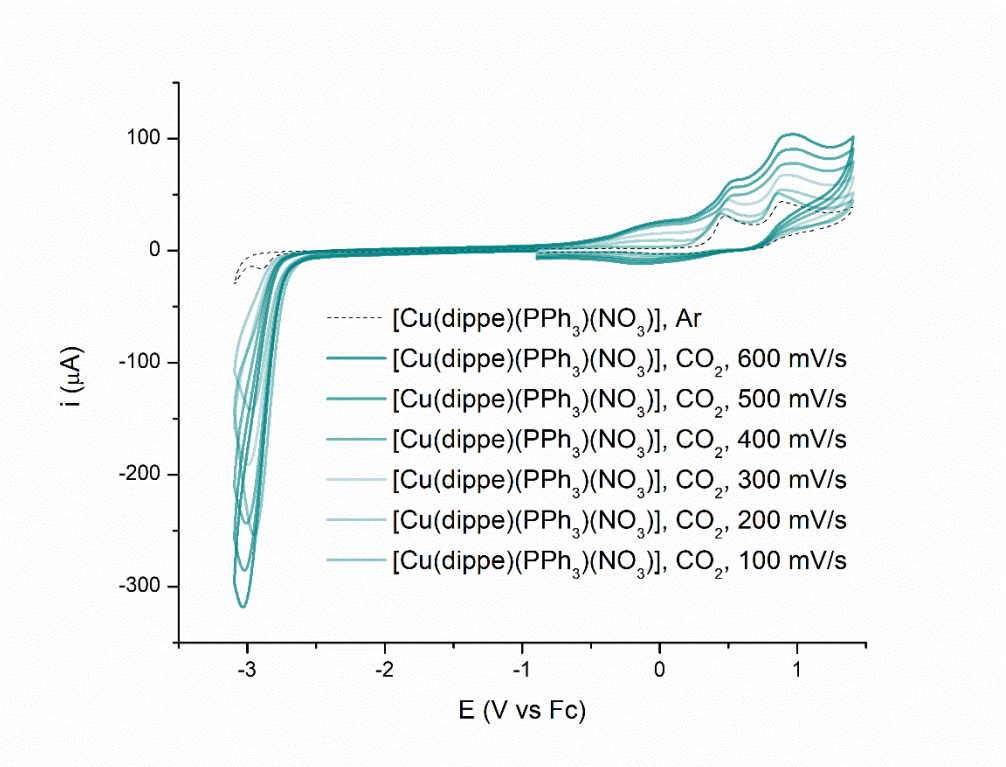

Figure S34. Compound (**2**) behavior with different scanning speeds in CO_2 atmosphere

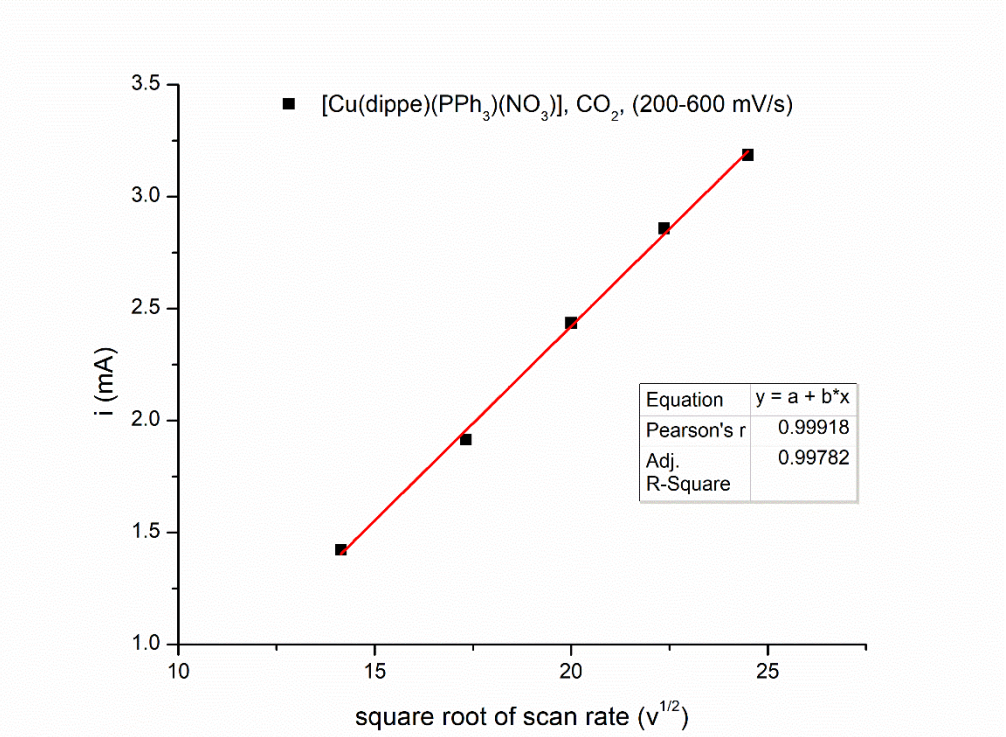

Figure S35. Pseudo-first-order behavior of the cathodic process of Compound (**2**) with CO_2.

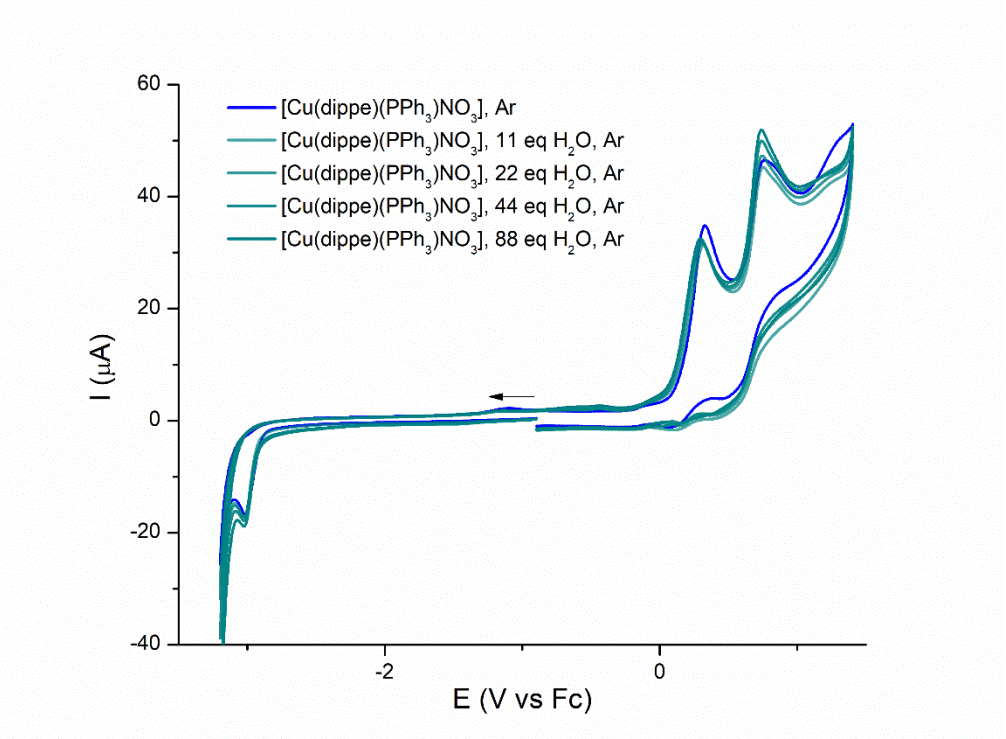

Figure S36. Compound (**2**) behavior with variable water equivalents under Ar atmosphere.

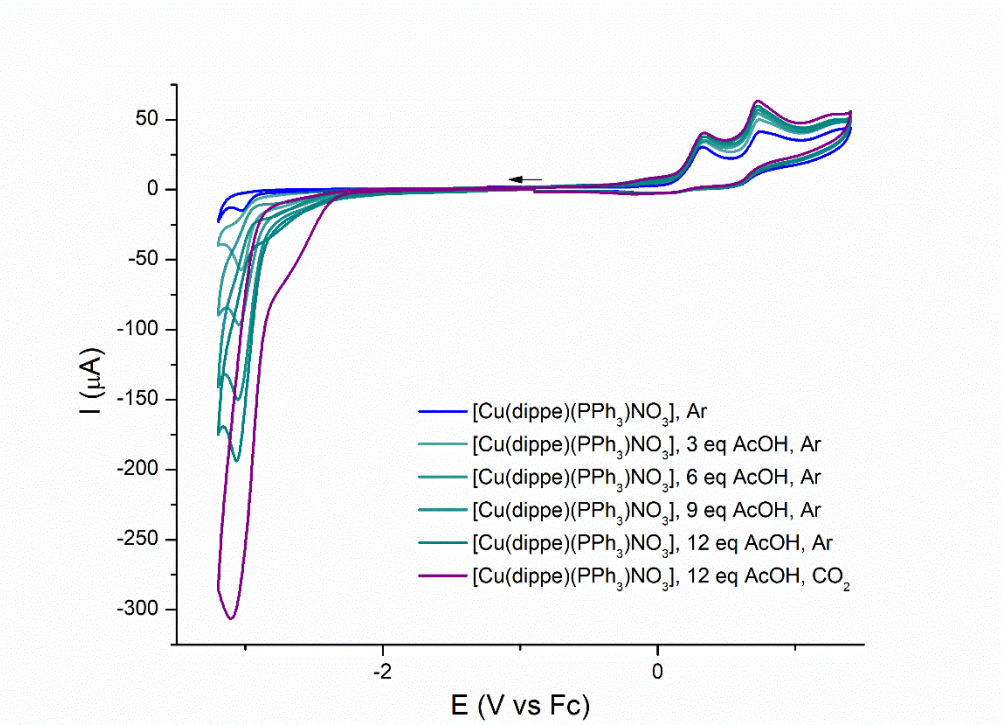

Figure S37. Compound (**2**) behavior with variable acetic acid equivalents under Ar and CO_2 atmosphere.

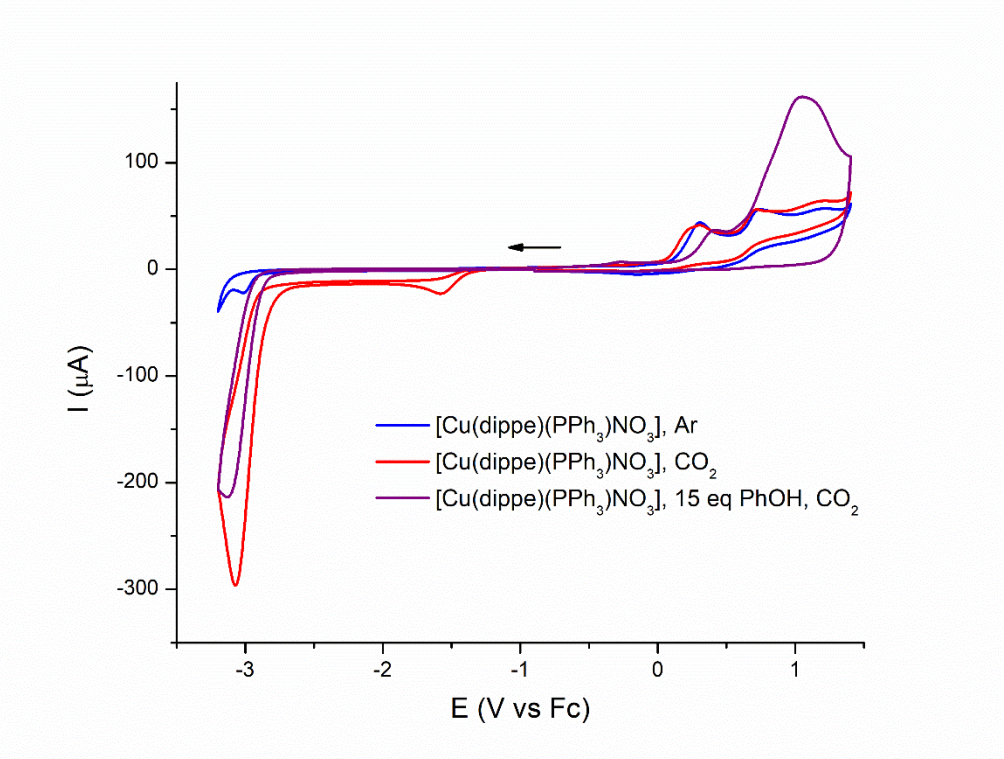

Figure S38. Compound (**2**) behavior with variable phenol equivalents and inhibition of the CO_2RR process.

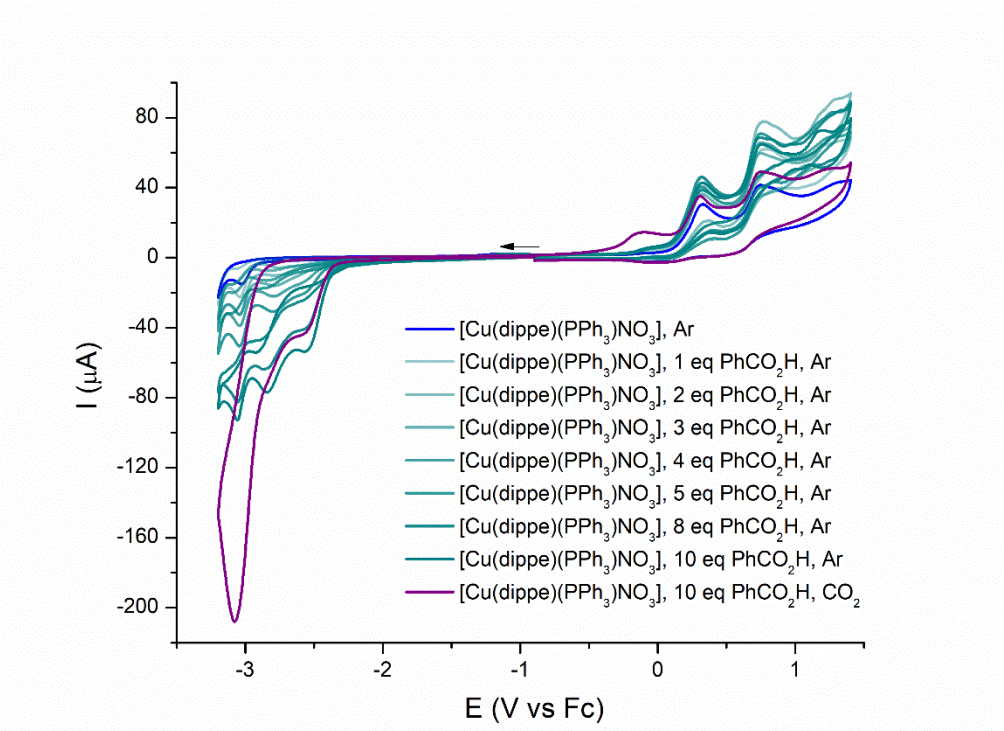

Figure S39. Compound (**2**) behavior with variable benzoic acid equivalents under Ar and CO_2 atmosphere.

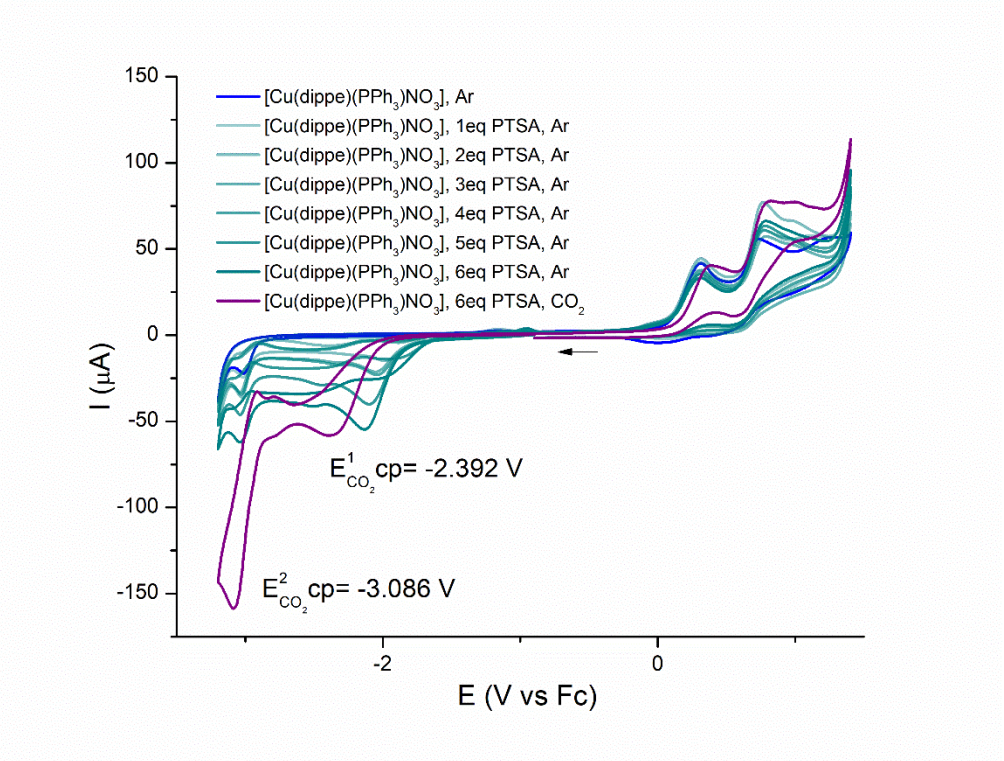

Figure S40. Compound (**2**) behavior with PTSA equivalents under Ar and CO_2 atmosphere.

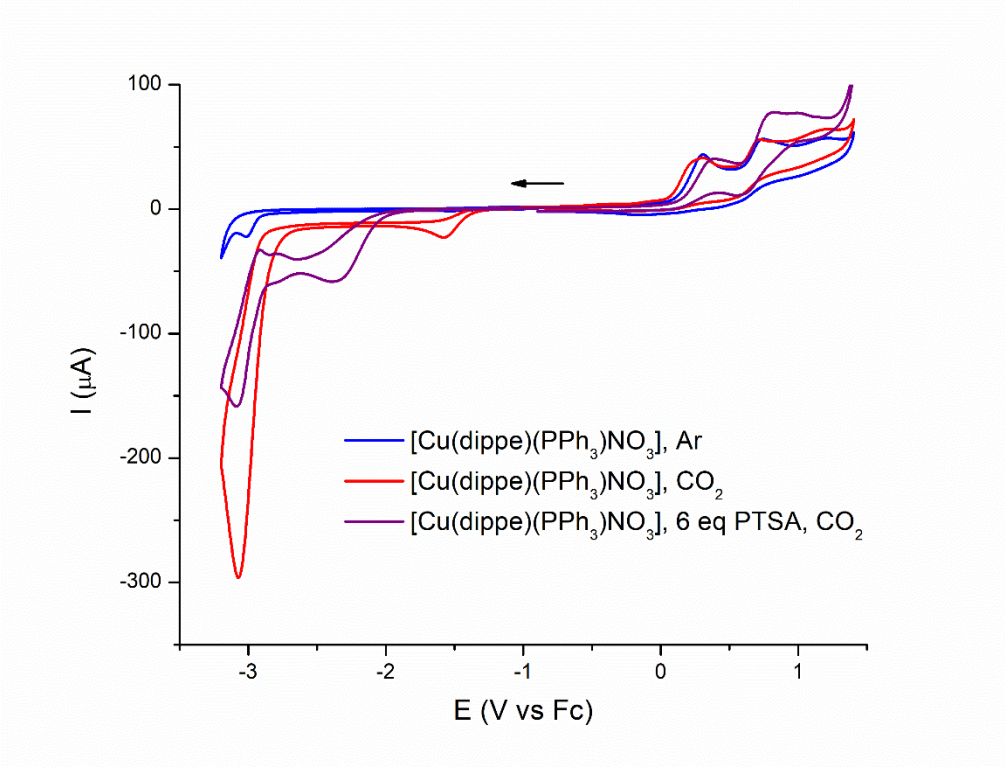

Figure S41. Compound (**2**) behavior with PTSA equivalents and inhibition of the CO_2RR process.

Compound (**1**), $[Cu(PPh_3)_2NO_3]$.

COMPOUND (1) BEHAVIOR UNDER Ar AND CO_2 ATMOSPHERE AND DIFFERENT PROTIC MEDIA.

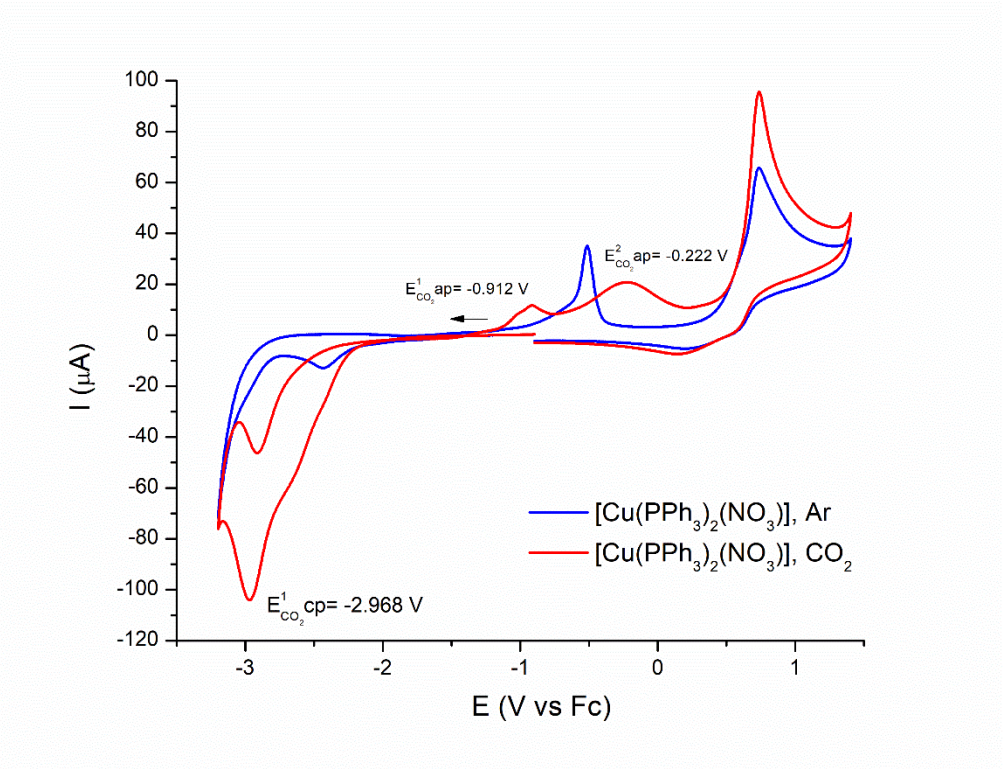

Figure S42. Compound (**1**) under Ar and CO_2 atmosphere.

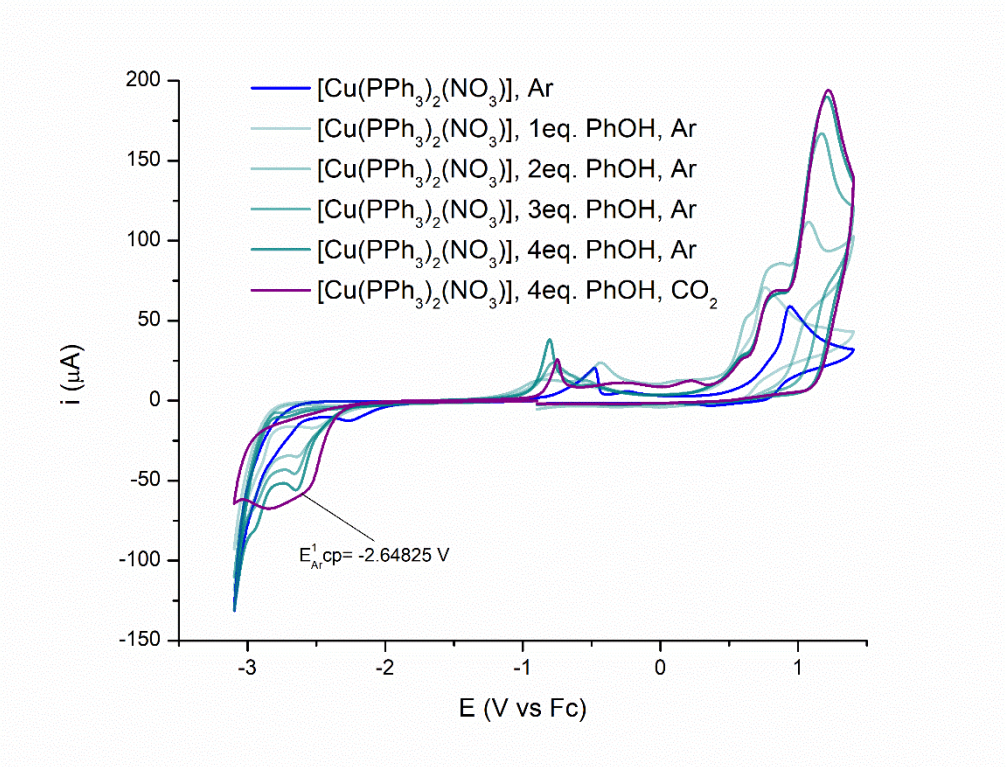

Figure S43. Compound (**1**) behavior with variable phenol equivalents under Ar and CO_2 atmosphere.

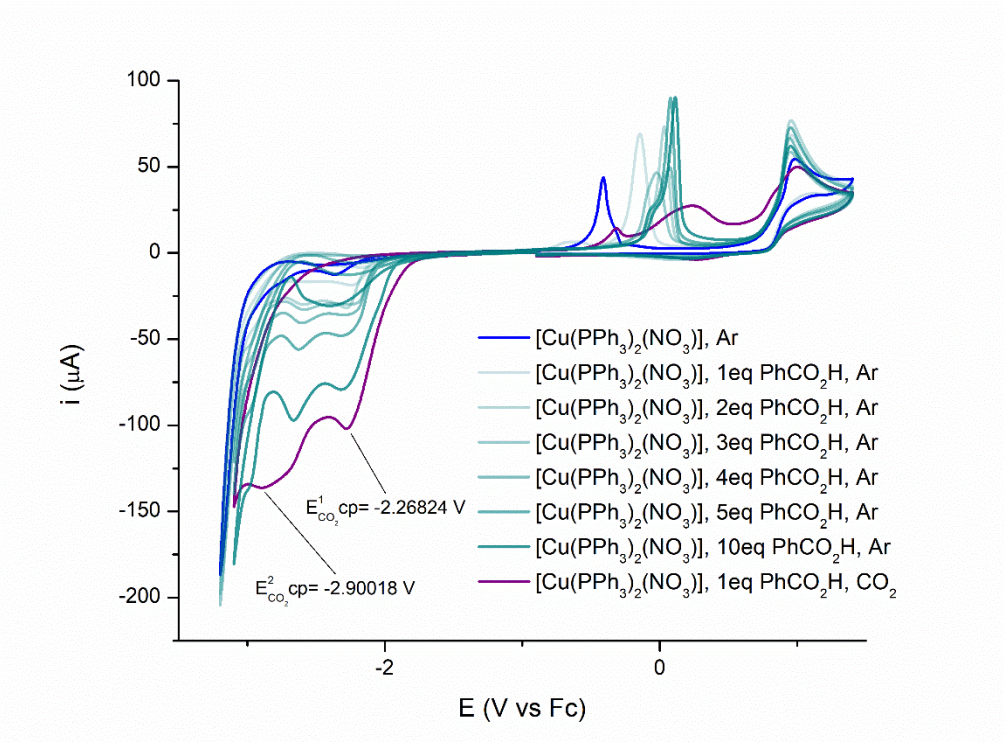

Figure S44. Compound (**1**) behavior with variable benzoic acid equivalents under Ar and CO_2 atmosphere.

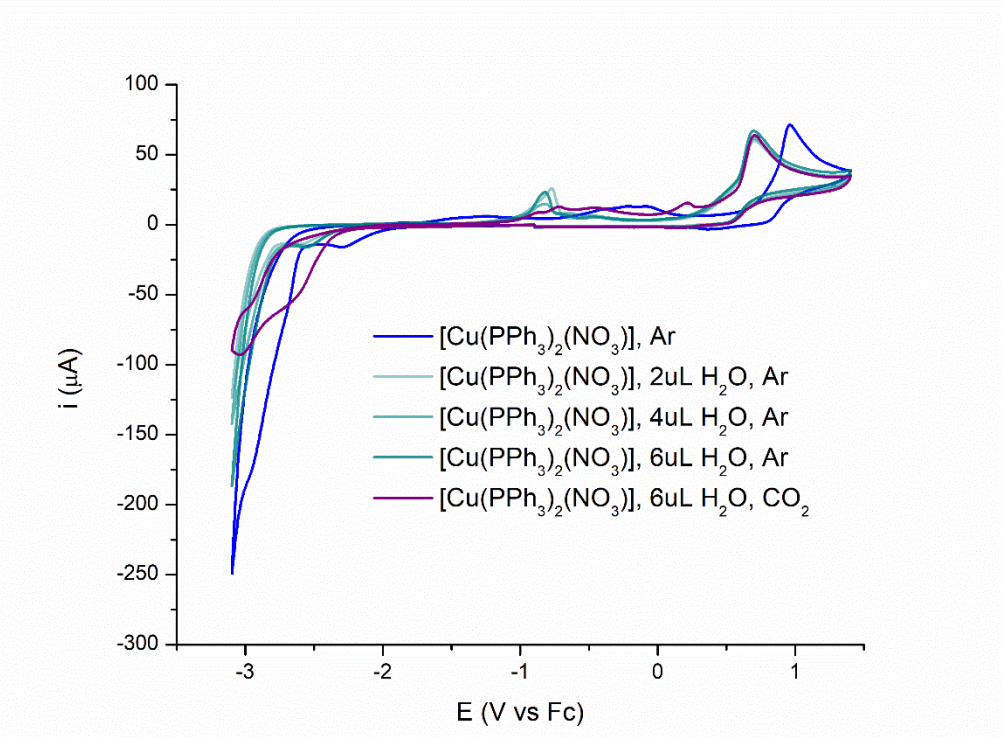

Figure S45. Compound (**1**) behavior with variable water equivalents under Ar and CO_2 atmosphere.

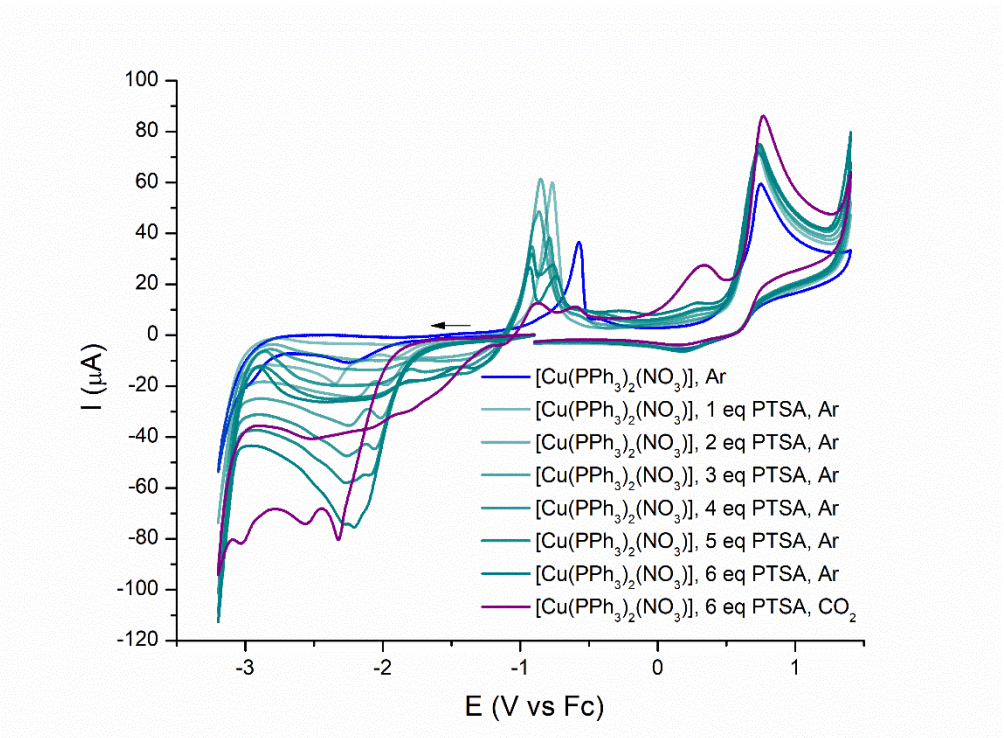

Figure S46. Compound (**1**) behavior with variable PTSA equivalents under Ar and CO_2 atmosphere.

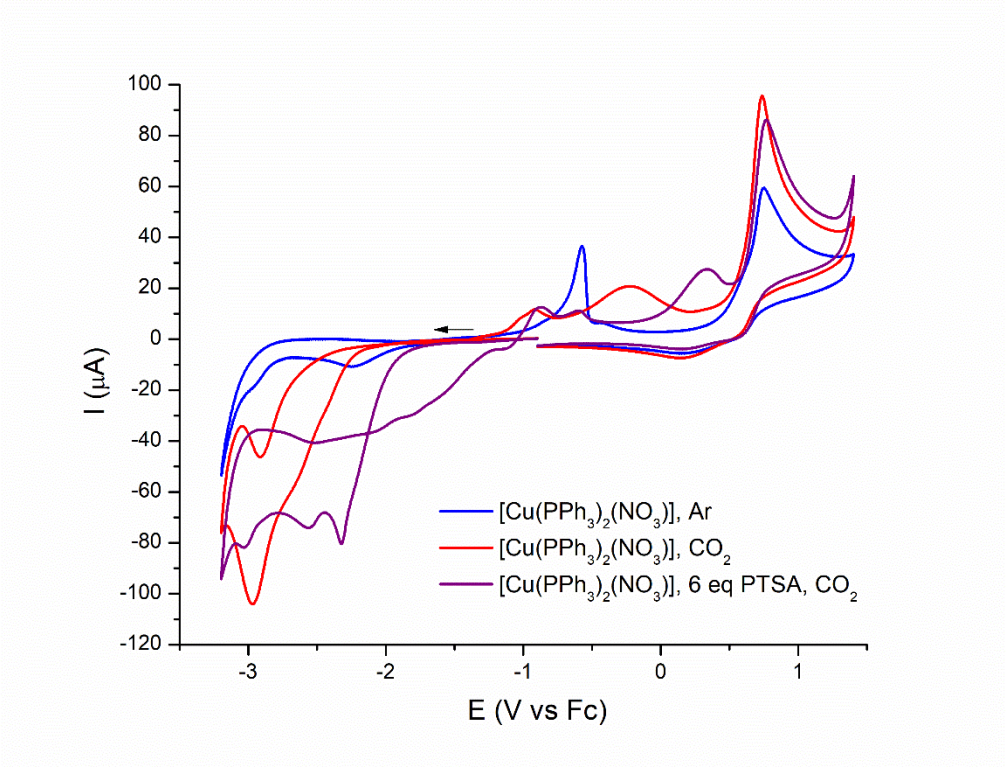

Figure S47. Compound (**1**) behavior with variable PTSA equivalents and inhibition of the CO_2RR process.

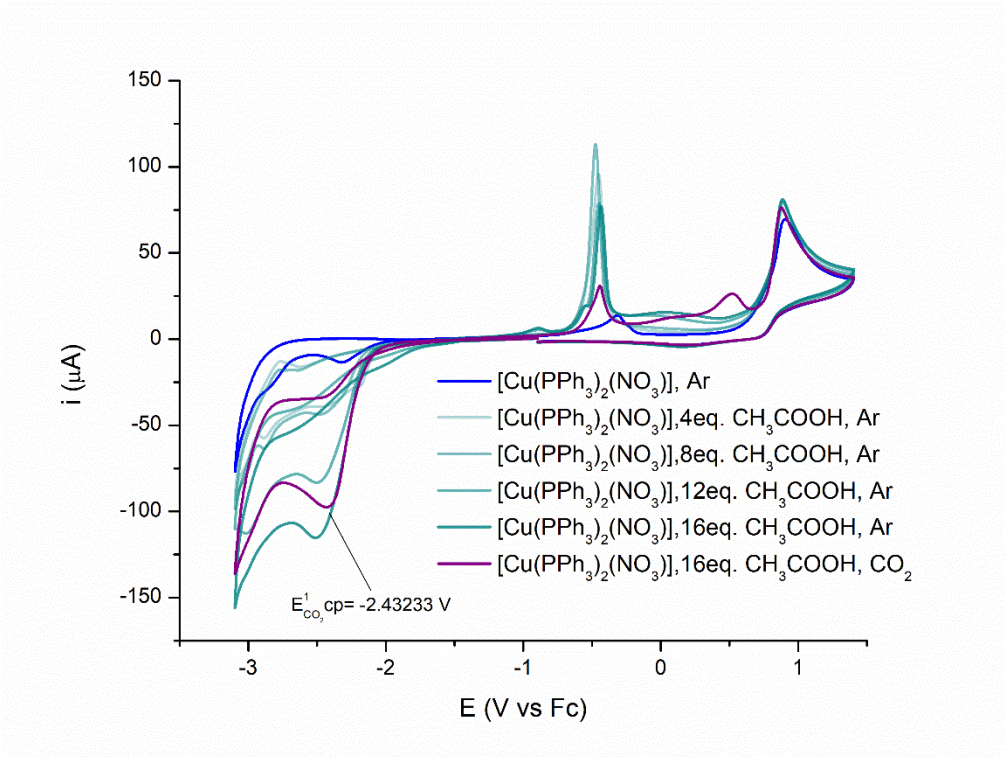

Figure S48. Compound (**1**) behavior with variable acetic acid equivalents under Ar and CO_2 atmosphere.

Compound (**3**), [Cu(depe)(PPh_3)(NO_3)].

COMPOUND (3) BEHAVIOR UNDER Ar AND CO_2 ATMOSPHERE, AND DIFFERENT PROTIC MEDIA.

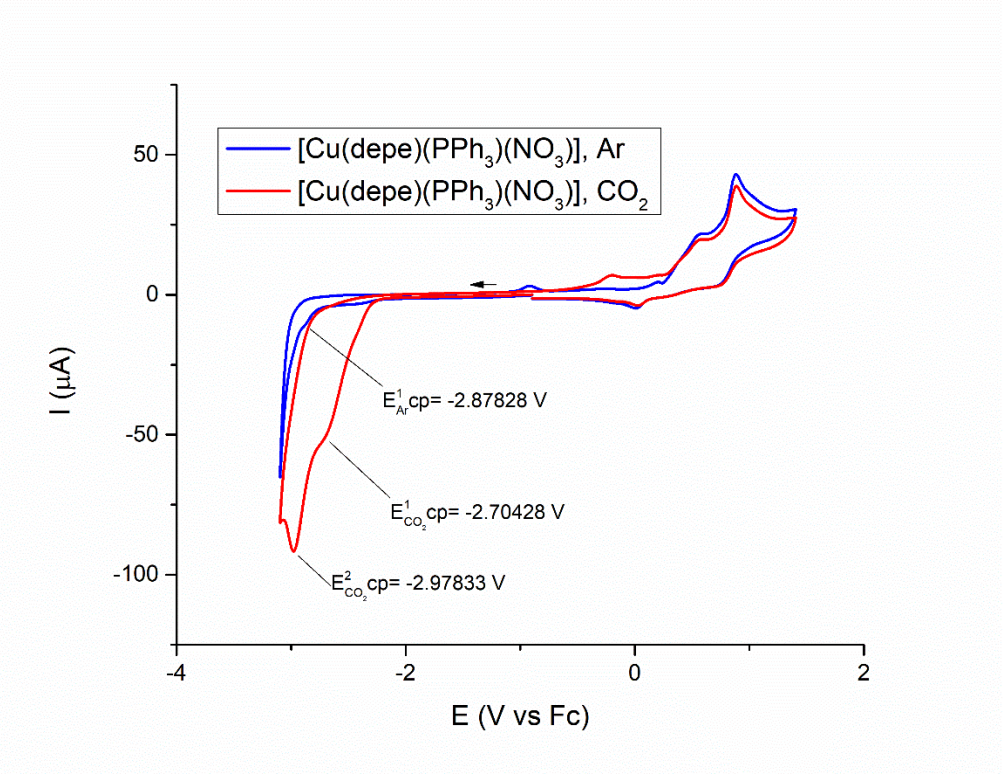

Figure S49. Compound (**3**) under Ar and CO_2 atmosphere.

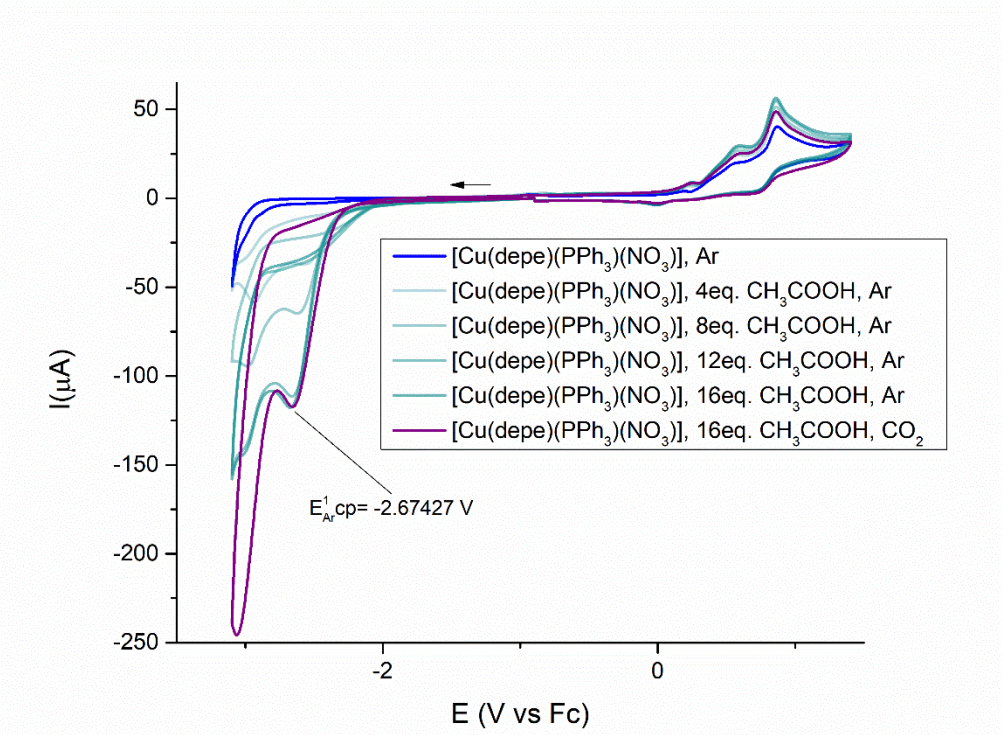

Figure S50. Compound (**3**) behavior with variable acetic acid equivalents under Ar and CO_2 atmosphere.

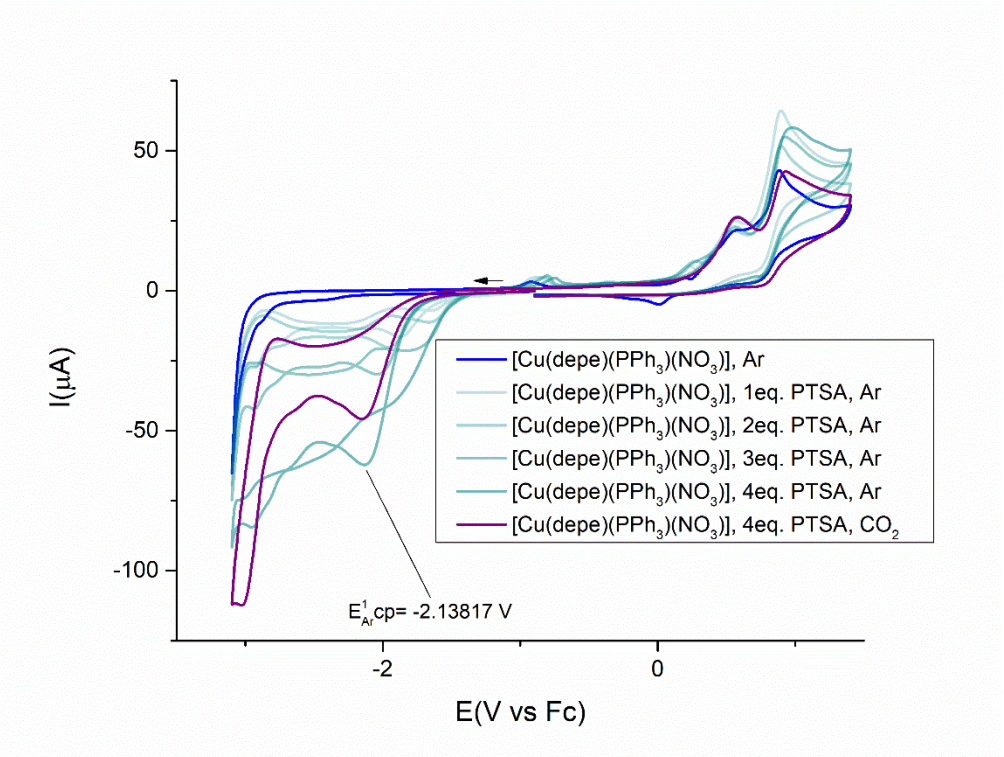

Figure S51. Compound (**3**) behavior with variable PTSA equivalents under Ar and CO_2 atmosphere.

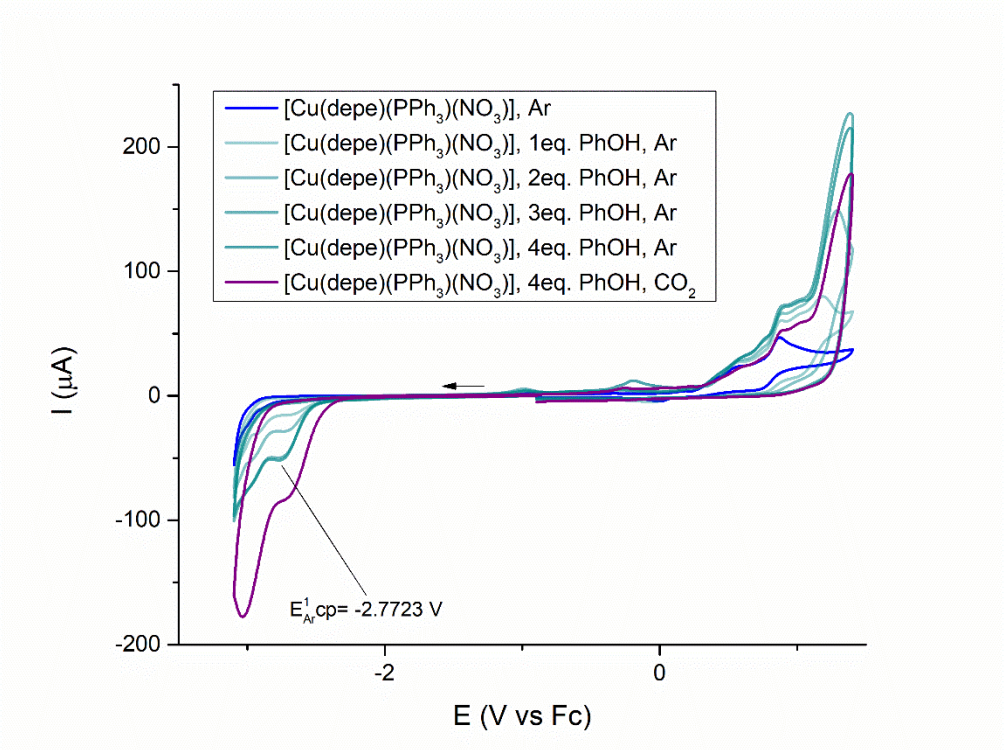

Figure S52. Compound (**3**) behavior with variable phenol equivalents under Ar and CO_2 atmosphere.

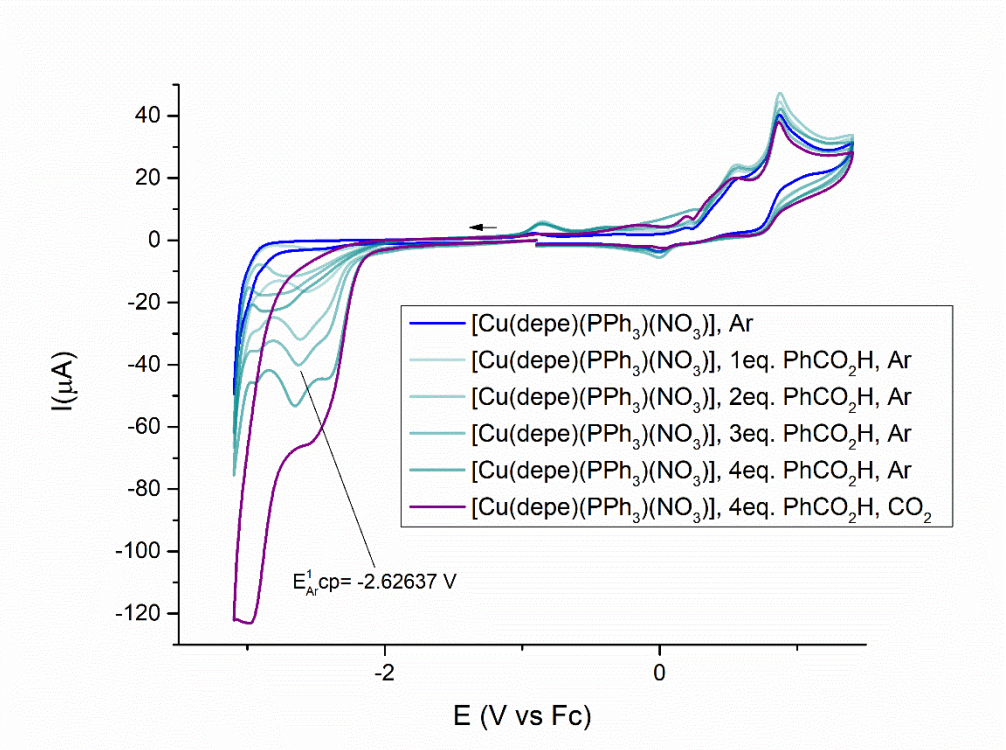

Figure S53. Compound (**3**) behavior with variable benzoic acid equivalents under Ar and CO_2 atmosphere.

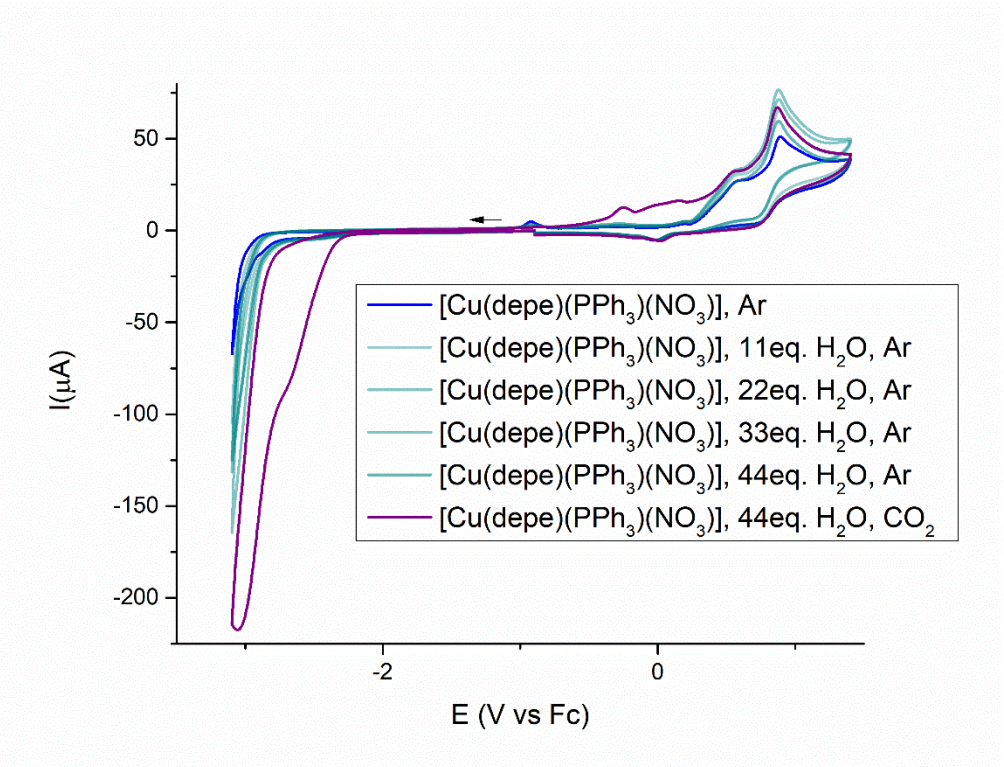

Figure S54. Compound (**3**) behavior with variable water equivalents under Ar and CO_2 atmosphere.

Compound (**4**), [Cu(dppe)(PPh_3)(NO_3)].

COMPOUND (4) BEHAVIOR UNDER Ar AND CO_2 ATMOSPHERE, AND DIFFERENT PROTIC MEDIA.

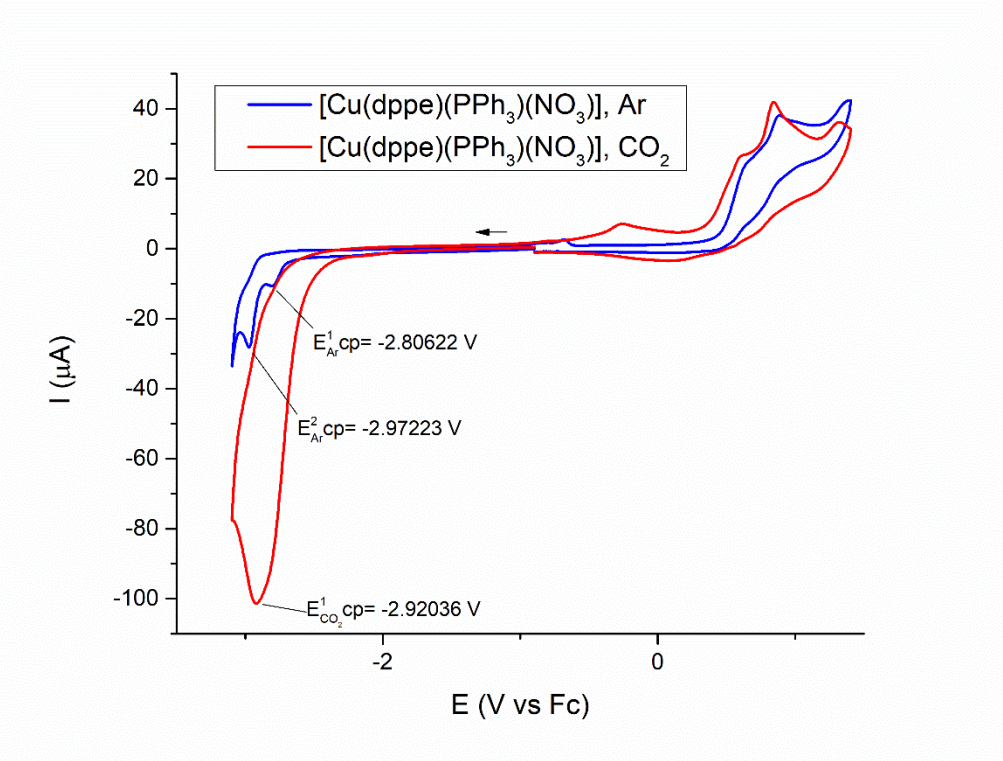

Figure S55. Compound (**4**) under Ar and CO_2 atmosphere.

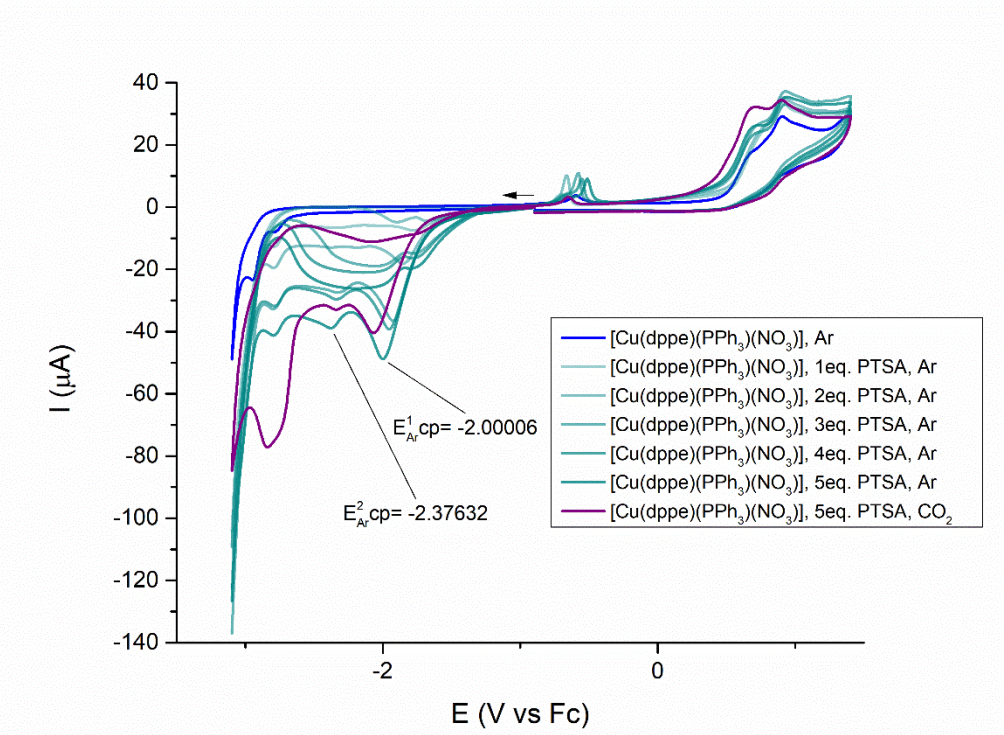

Figure S56. Compound (**4**) behavior with variable PTSA equivalents under Ar and CO_2 atmosphere.

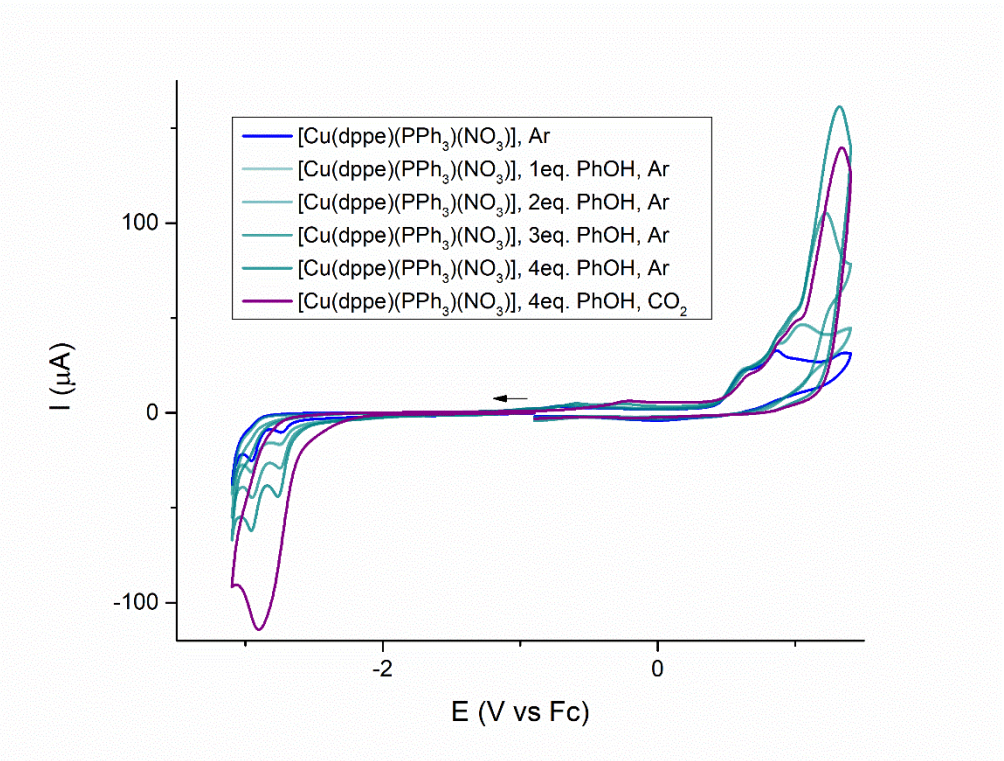

Figure S57. Compound (**4**) behavior with variable phenol equivalents under Ar and CO_2 atmosphere.

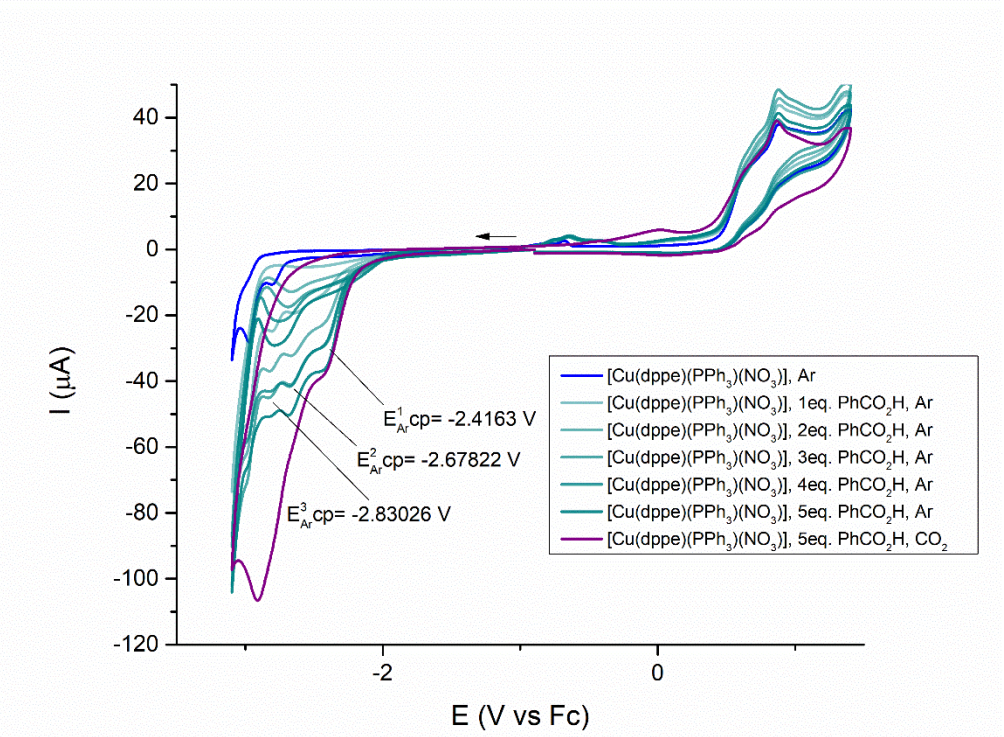

Figure S58. Compound (**4**) behavior with variable benzoic acid equivalents under Ar and CO_2 atmosphere.

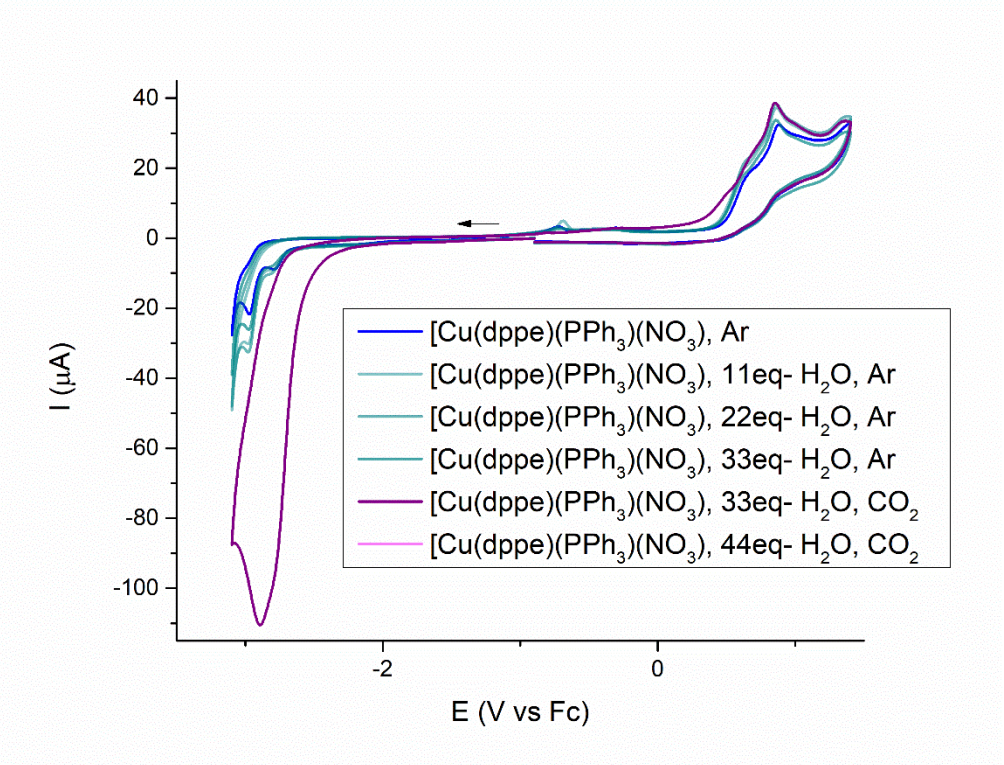

Figure S59. Compound (**4**) behavior with variable water equivalents under Ar and CO_2 atmosphere.

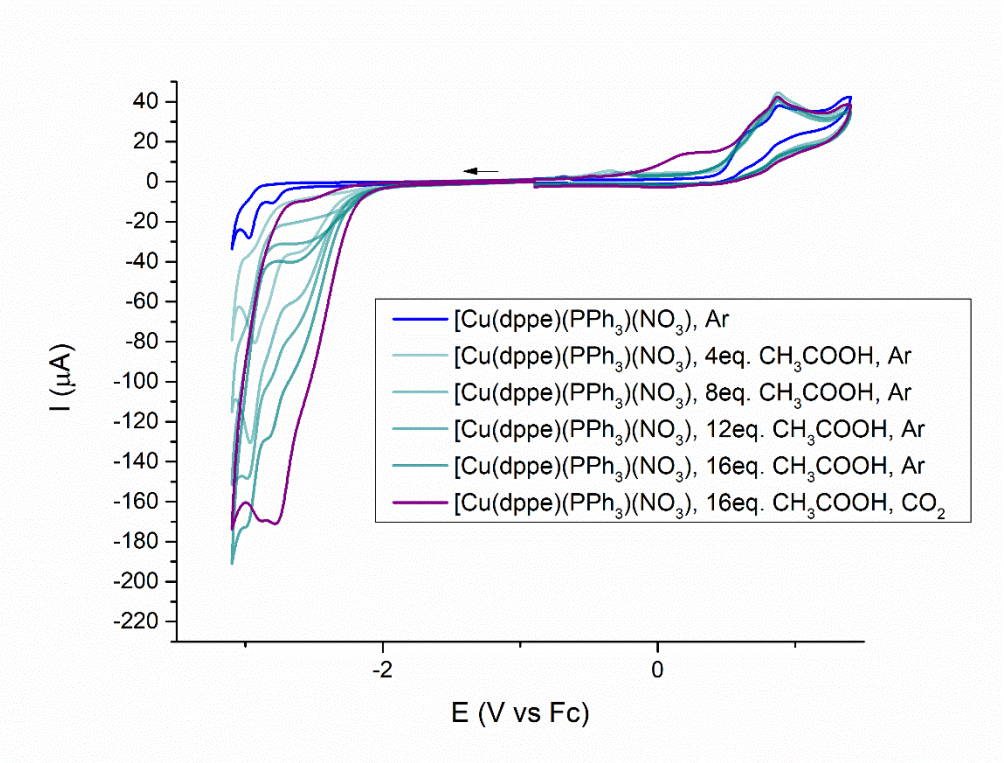

Figure S60. Compound (**4**) behavior with variable acetic acid equivalents under Ar and CO_2 atmosphere.

Compound (**5**), [Cu(dipf)NO_3].

COMPOUND (5) BEHAVIOR UNDER Ar AND CO_2 ATMOSPHERE, AND DIFFERENT PROTIC MEDIA.

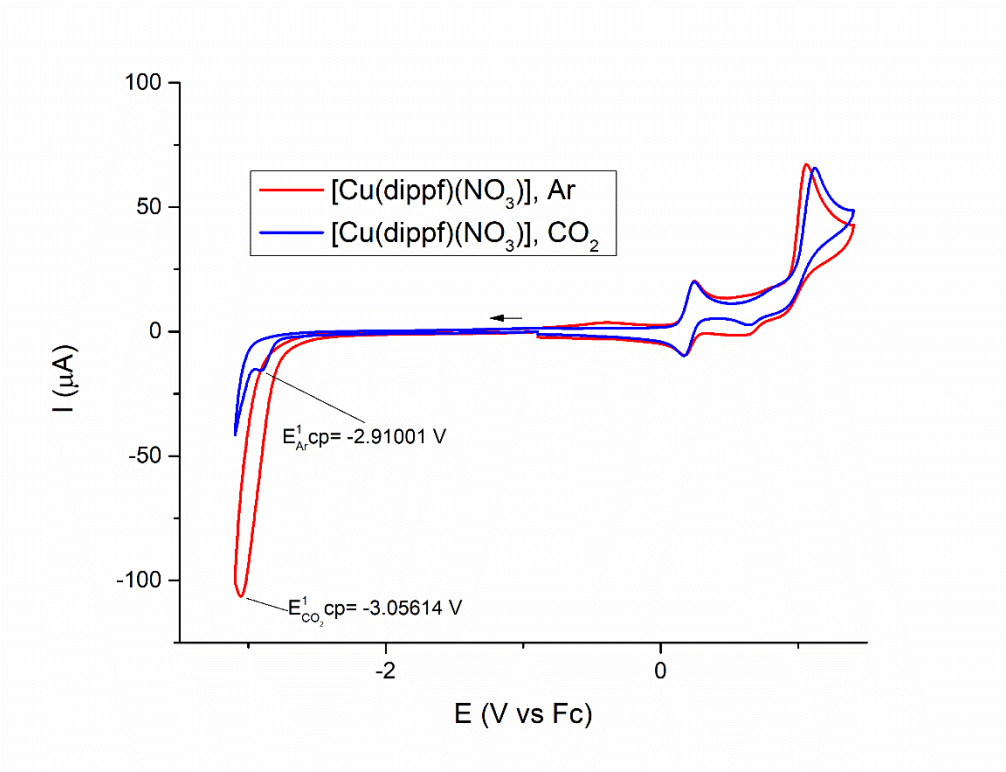

Figure S61. Compound (**5**) under Ar and CO_2 atmosphere.

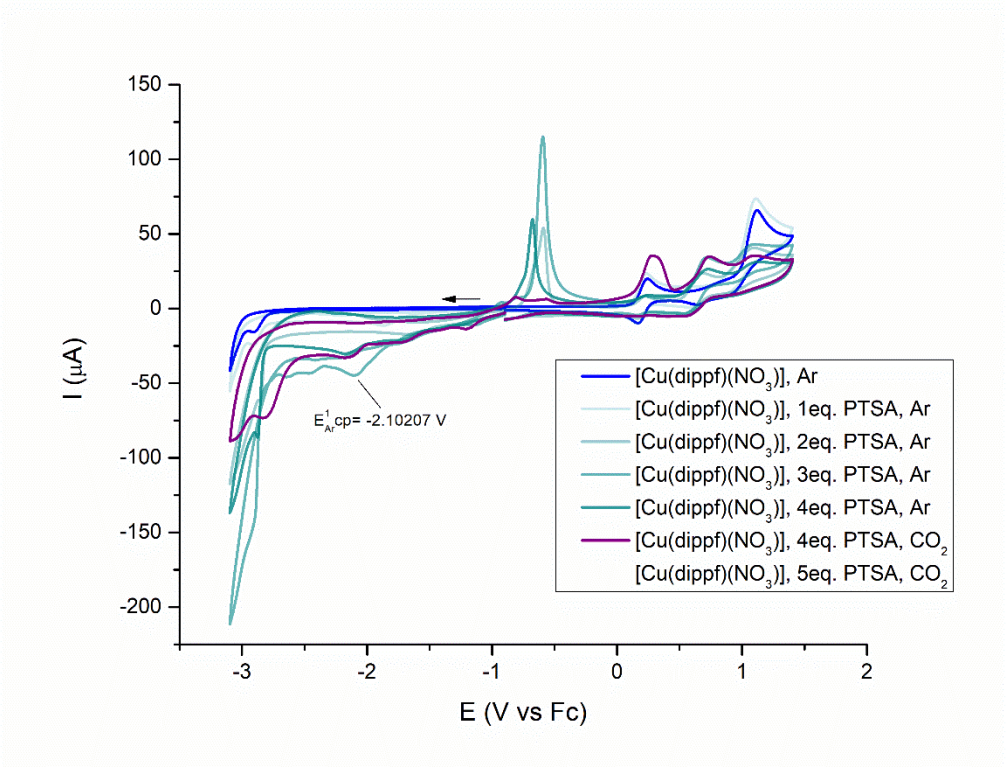

Figure S62. Compound (**5**) behavior with variable PTSA equivalents under Ar and CO_2 atmosphere.

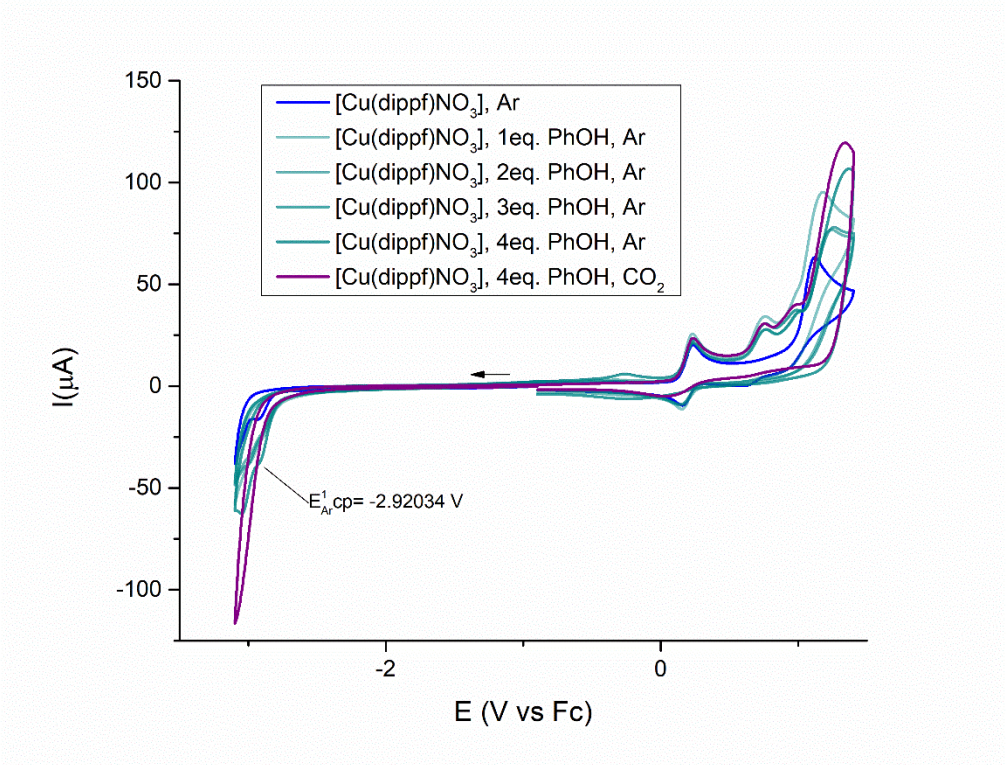

Figure S63. Compound (**5**) behavior with variable phenol equivalents under Ar and CO_2 atmosphere.

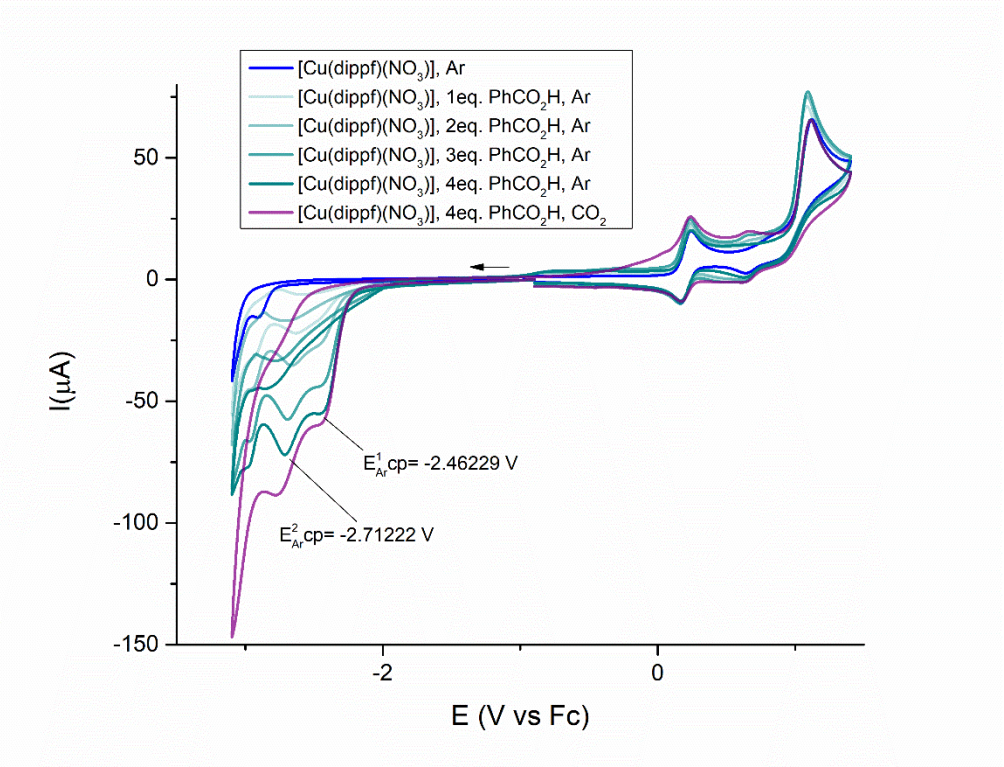

Figure S64. Compound (**5**) behavior with variable benzoic acid equivalents under Ar and CO_2 atmosphere.

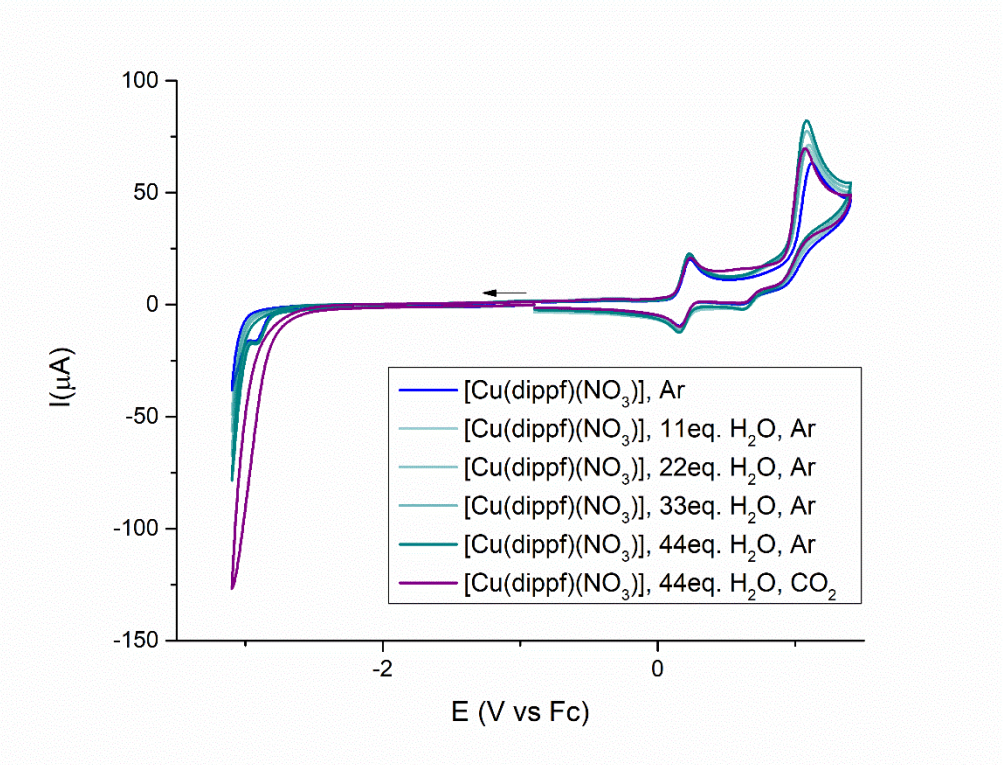

Figure S65. Compound (**5**) behavior with variable water equivalents under Ar and CO_2 atmosphere.

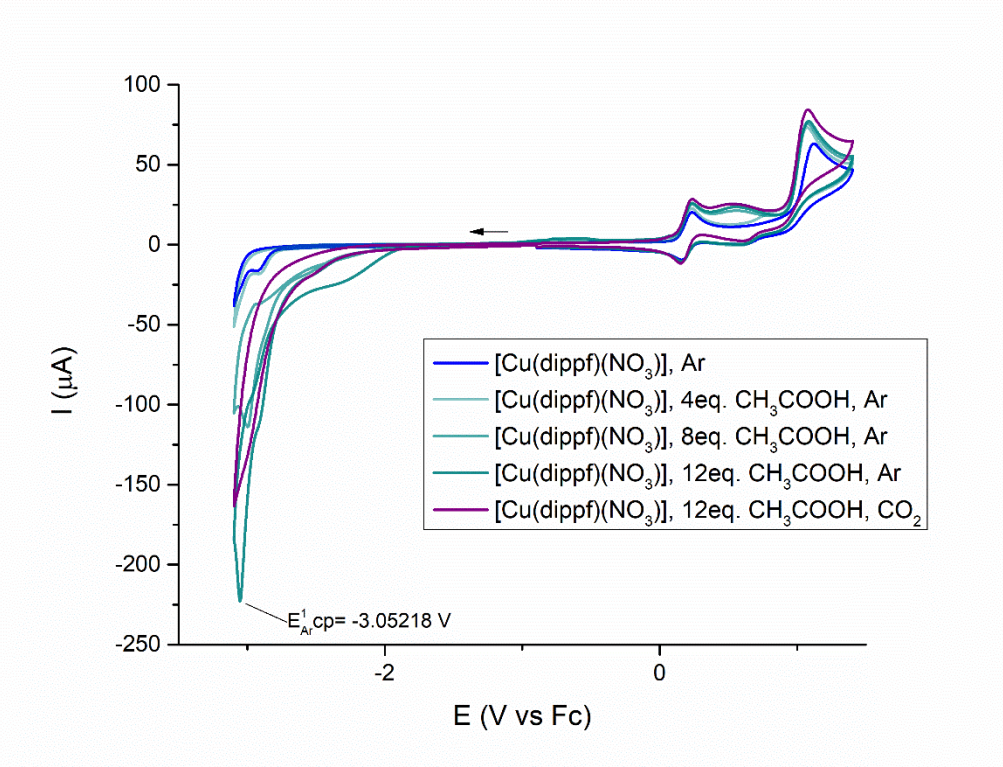

Figure S66. Compound (**5**) behavior with variable acetic acid equivalents under Ar and CO_2 atmosphere.

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Date of report	22-May-23 7:05:48PM
User ID	Realizo: M en I. Victor Hugo Lemus Neri
Comments	Muestra: AA507CPCW

Run	Weight	Carbon	Hydrogen	Nitrogen	Created on
4423055320B	1.655	67.81%	5.21%	1.38%	22-May-23 4:49:12 PM
4423055320A	1.341	67.75%	5.26%	1.56%	22-May-23 4:44:08 PM

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.498	67.780	5.235	1.470
Variance	0.049	0.002	0.001	0.016
Standard Deviation	0.222	0.042	0.035	0.127

Figure S67. Elemental Analysis for [$Rh(PPh_3)_3Cl(NO)$].

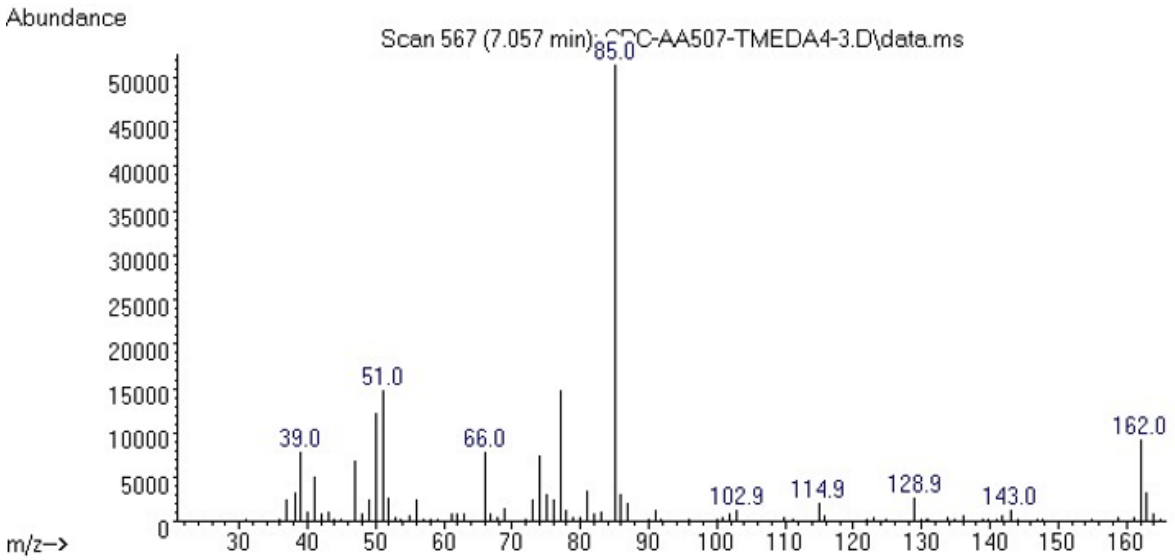

Figure S68. MS spectra of hydrolyzed product (d).
(m/z)= 162, 115 (2H, CO_2), 85 (-HNMe).