Supporting information for

Isolation of Monomeric Copper(II) Phenolate Selenoether Complexes using Chelating *ortho*-Bisphenylselenide-phenolate Ligands and Their Hydrogen Gas Evolution Electrocatalytic Activity

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MS data of **2a**

Display Report

Analysis Info

Analysis Name	D:\Data\new user data 2021\Dec-2021\21 dec\Prof.S.Kumar-AUY-HM-26.d	Acquisition Date	12/21/2021 3:04:58 PM
Method	tune_wide.m	Operator	RUCHI
Sample Name	AUY-HM-26	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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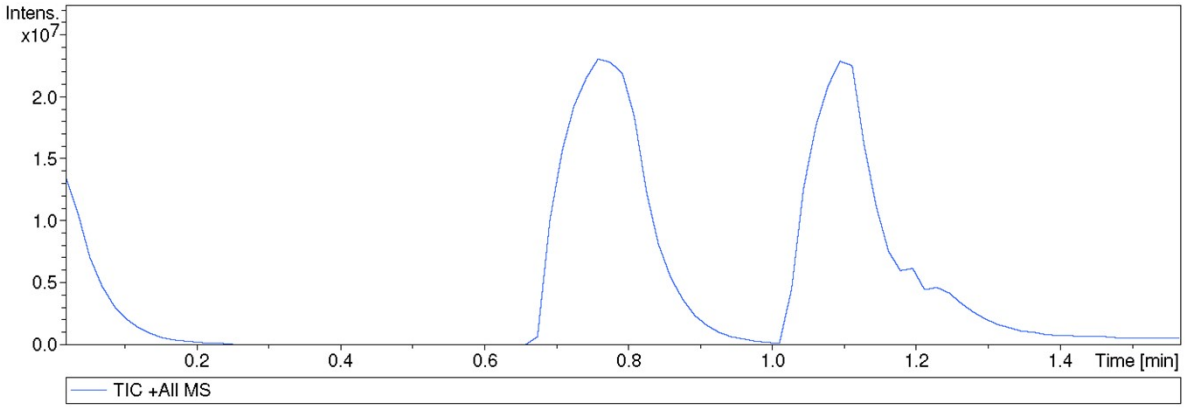

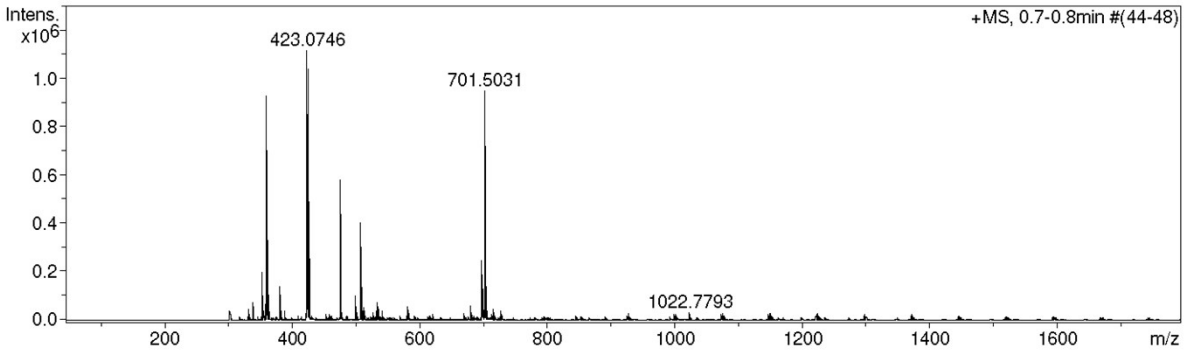

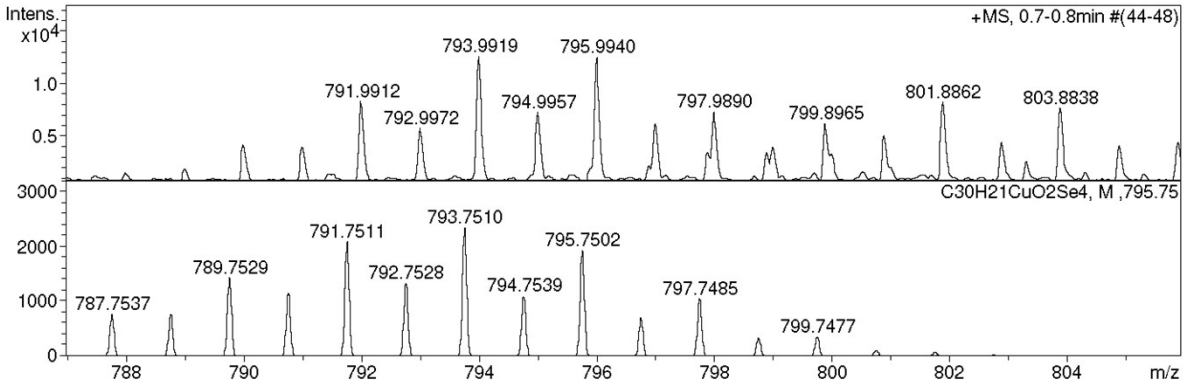

MS data of **2b**

Display Report

Analysis Info

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Sample Name	HM21	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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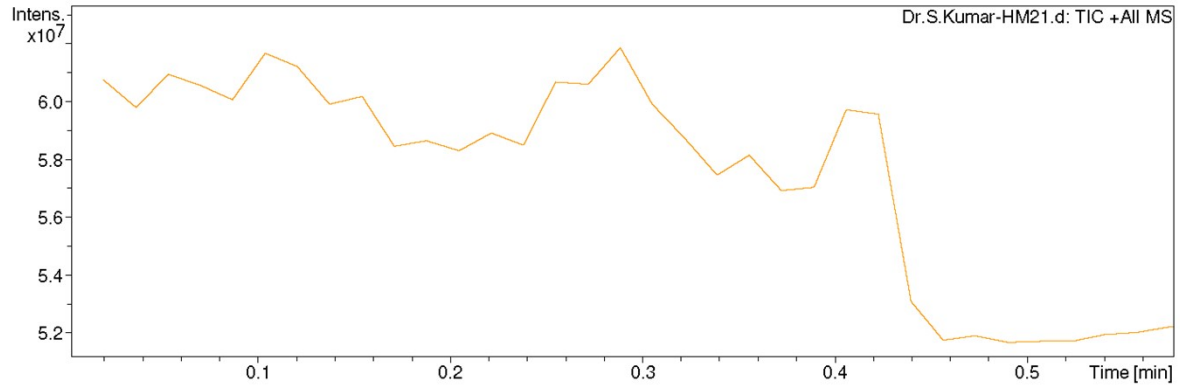

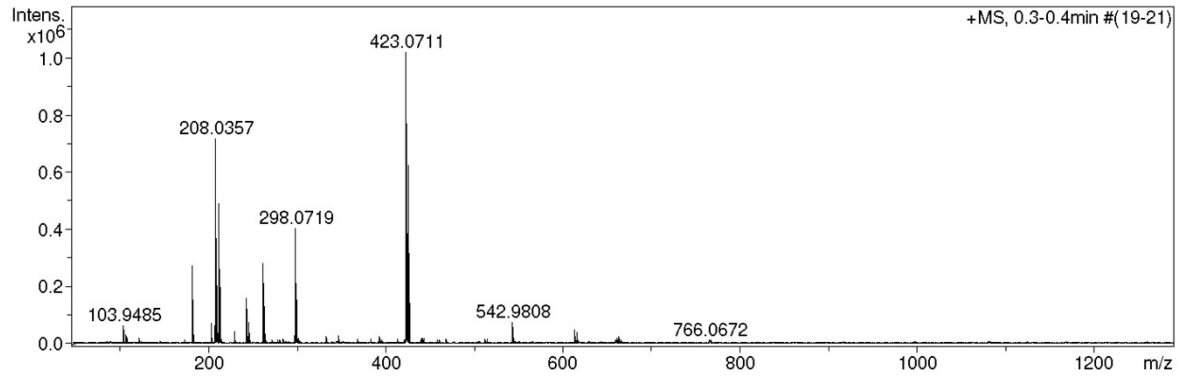

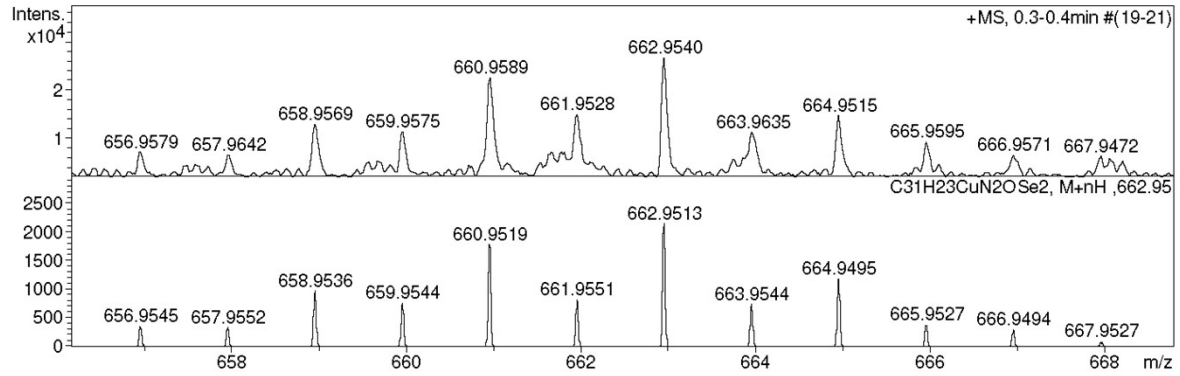

MS data of **2c**

Display Report

Analysis Info

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Method	tune_wide.m	Operator	RUCHI
Sample Name	AUY-328	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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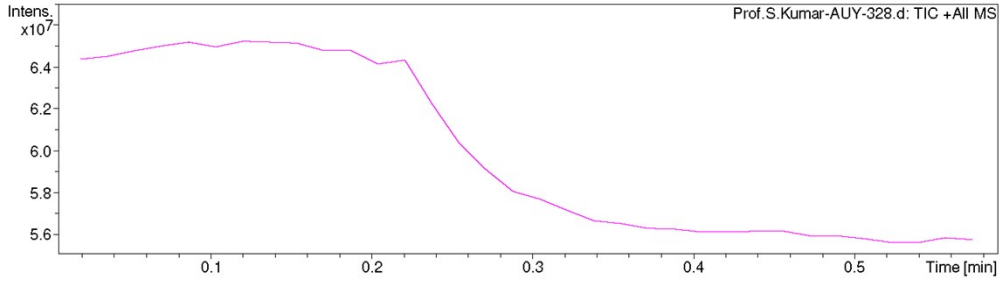
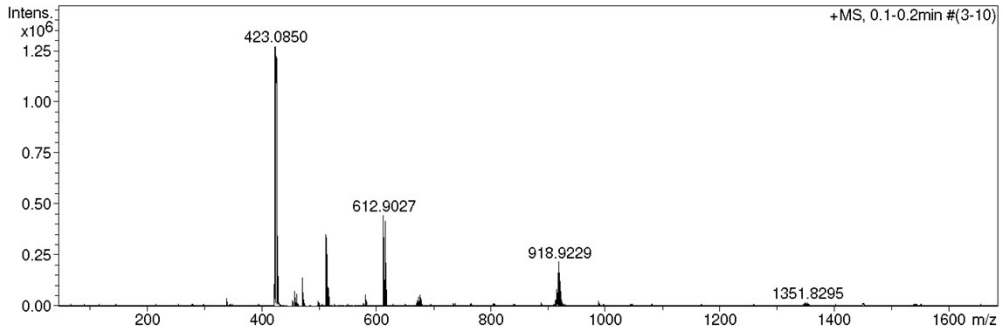
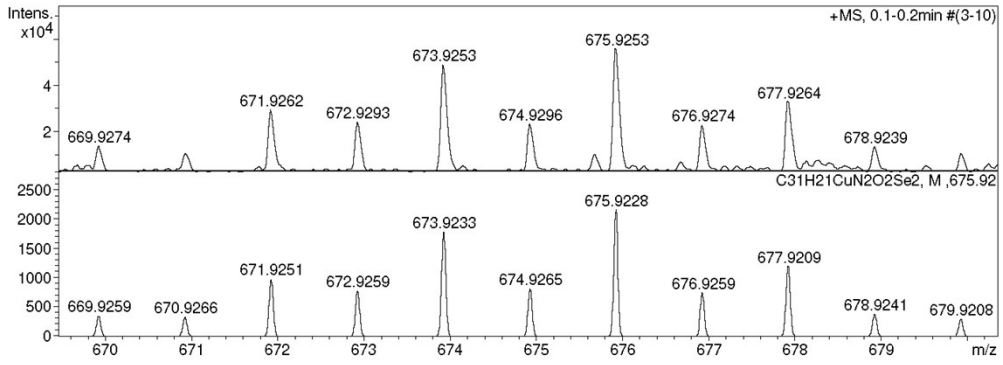
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste







Mass Data of **2d**

Display Report

Analysis Info

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Method	tune_wide _APCI_23.06.m	Operator	RUCHI
Sample Name	AUY-2D	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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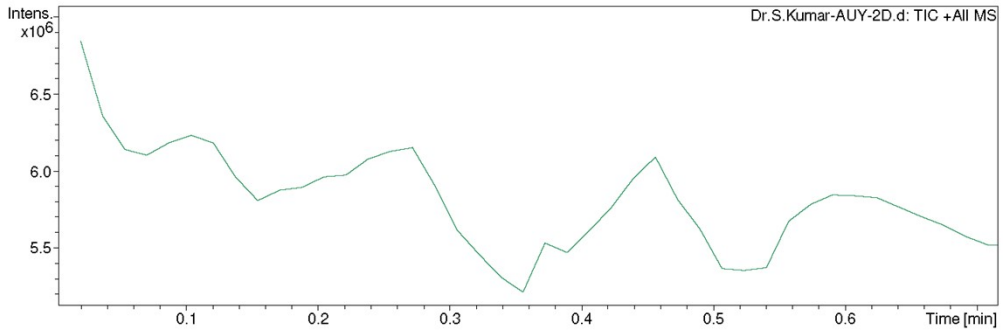
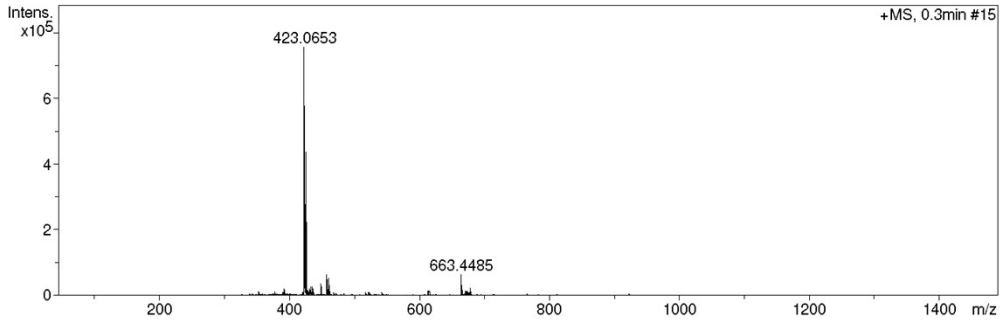
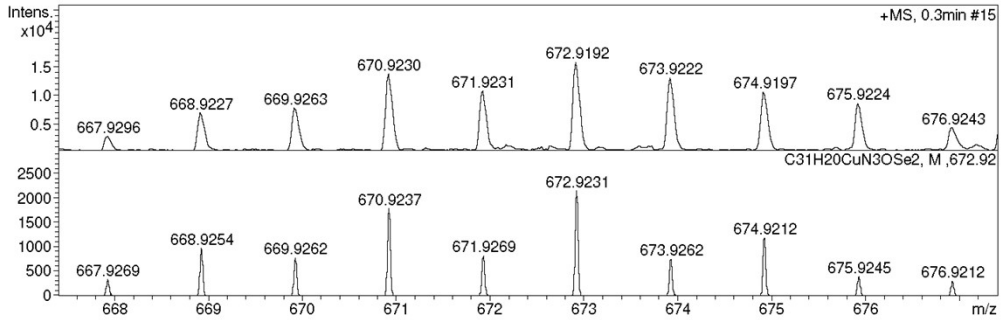
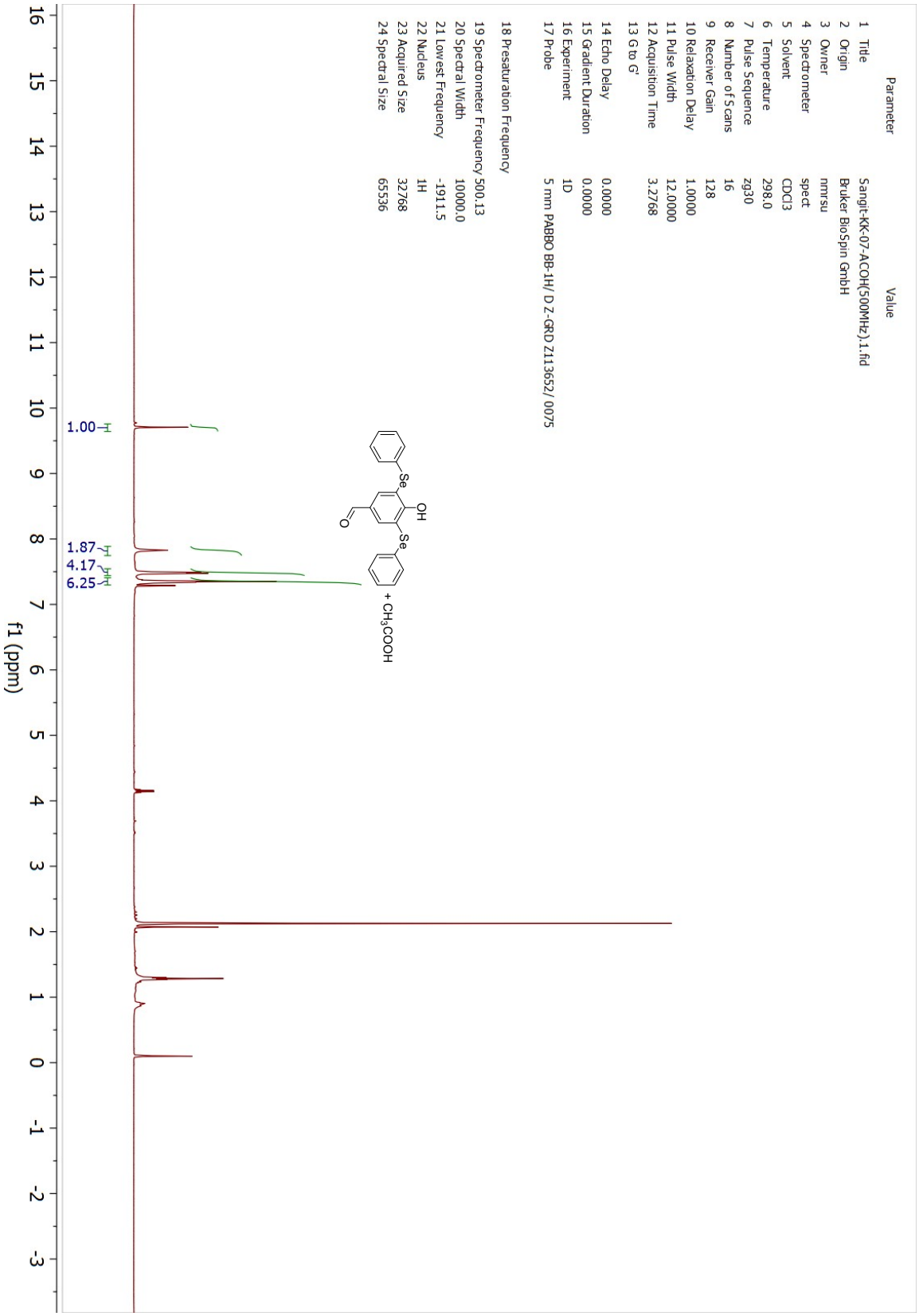


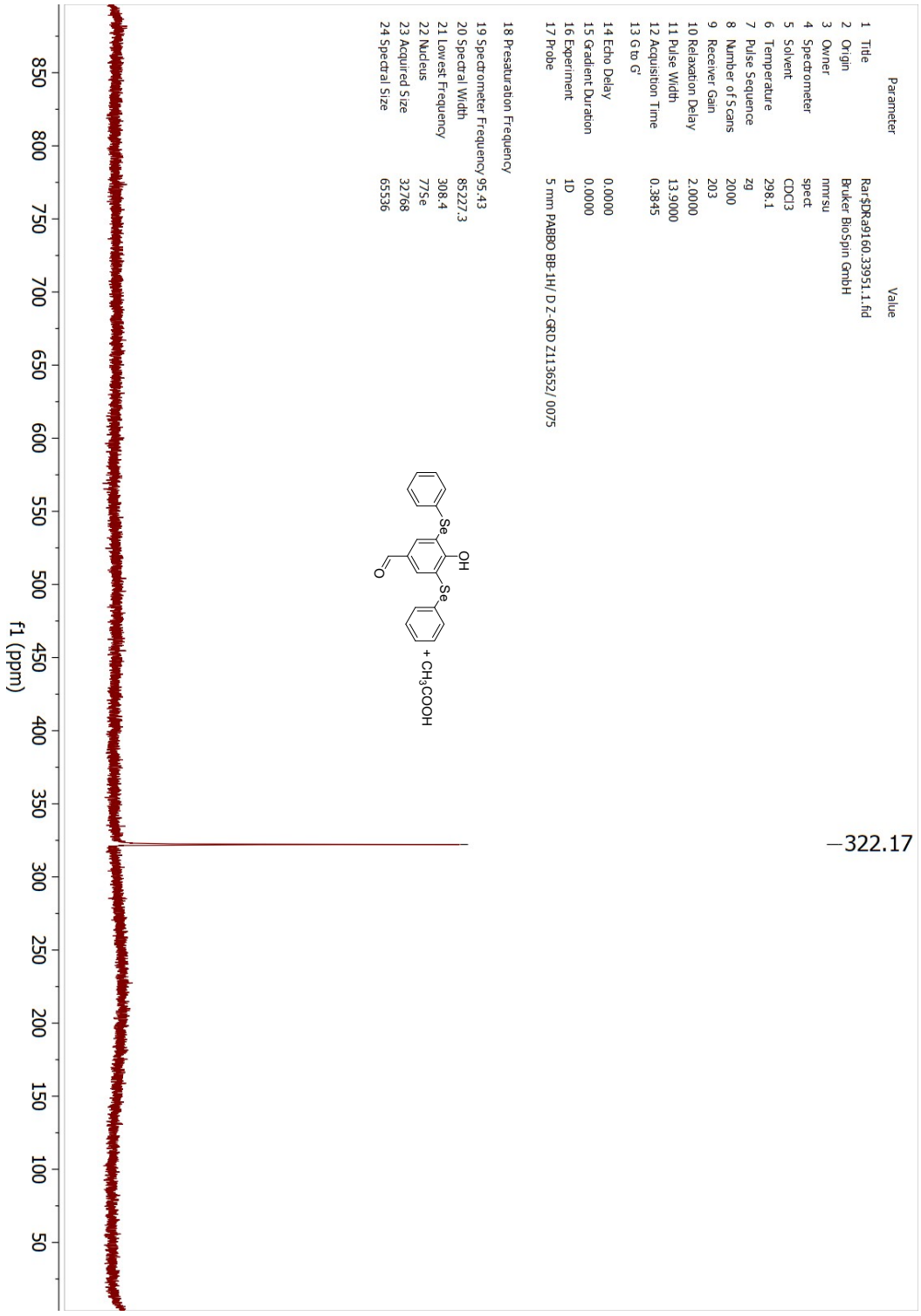




^{1}H NMR of a reaction mixture of ligand **1c** and acetic acid



^{77}Se NMR of a reaction mixture of ligand **1c** and acetic acid



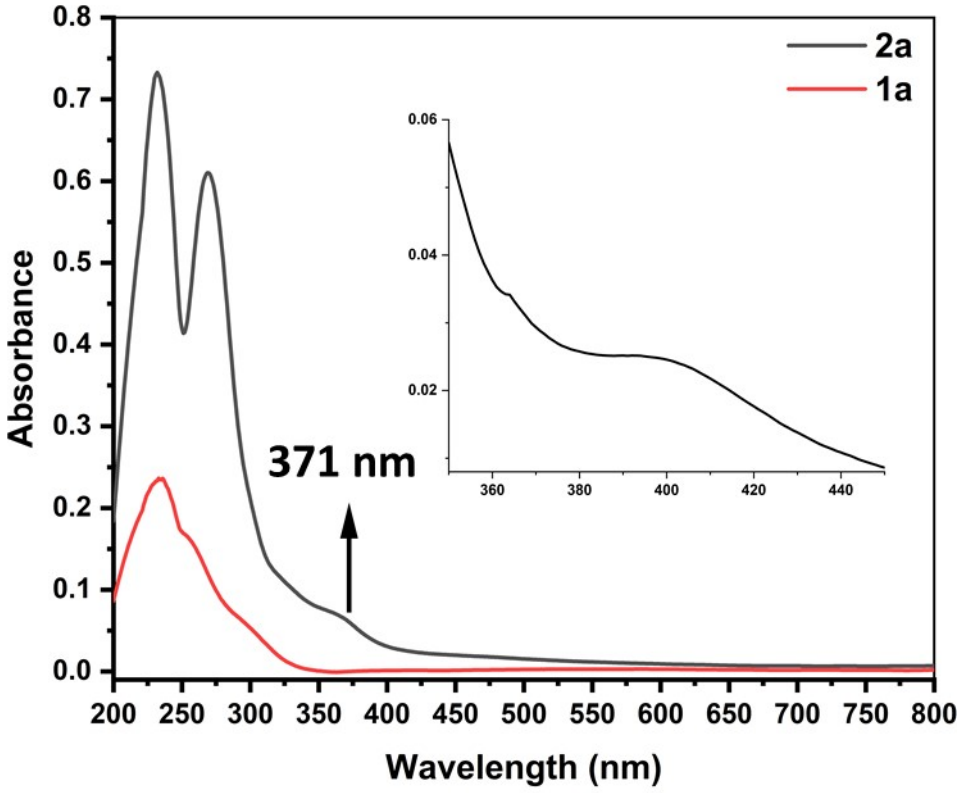


Figure S1. UV-Visible spectra of **2a** and **1a** in CH_2Cl_2 solvent. A zoomed image of LMCT band has been given in the inset of the image.

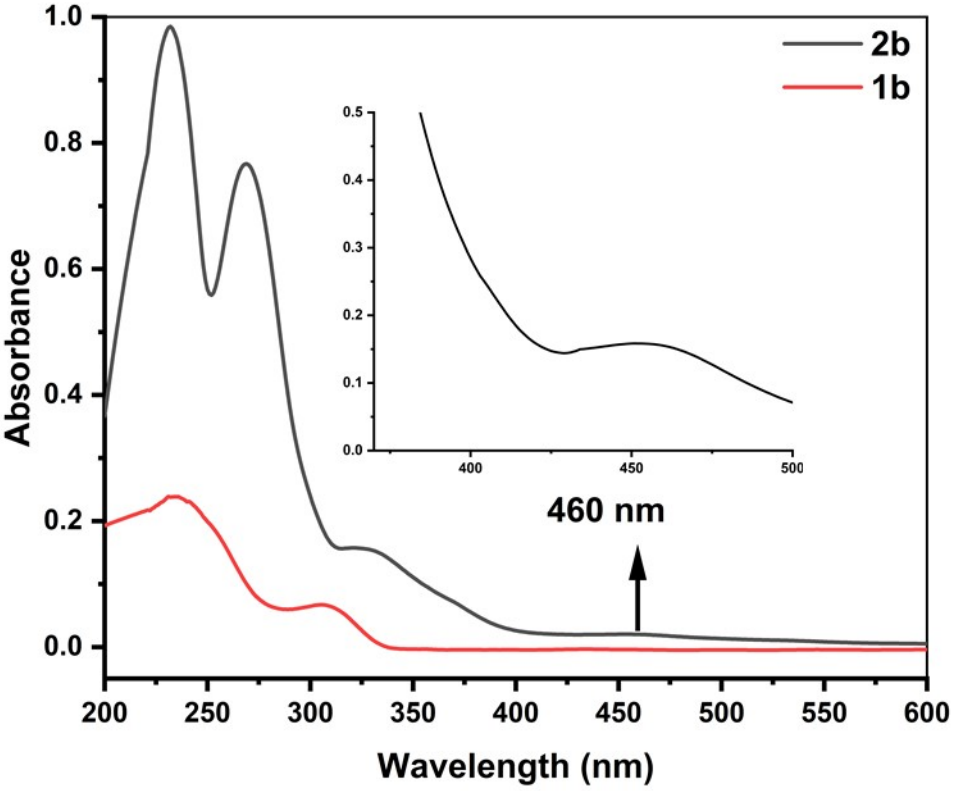


Figure S2. UV-Visible spectra of **2b** and **1b** in CH_2Cl_2 solvent. A zoomed image of LMCT band has been given in the inset of the image.

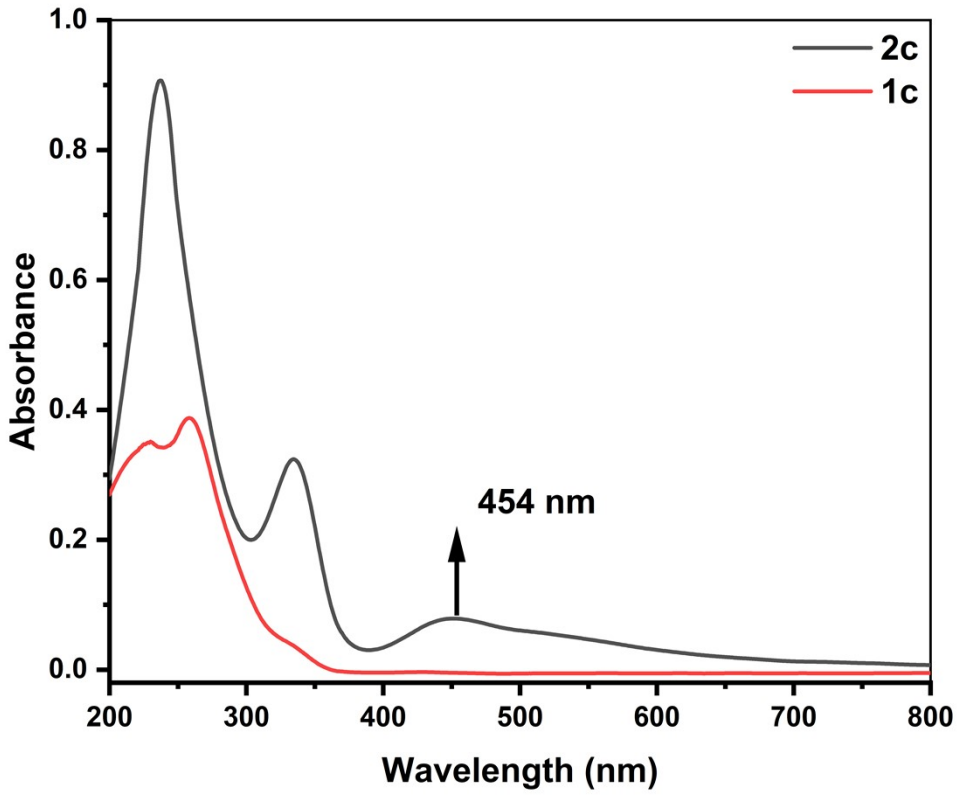


Figure S3. UV-Visible spectra of **2c** and **1c** in CH_2Cl_2 solvent.

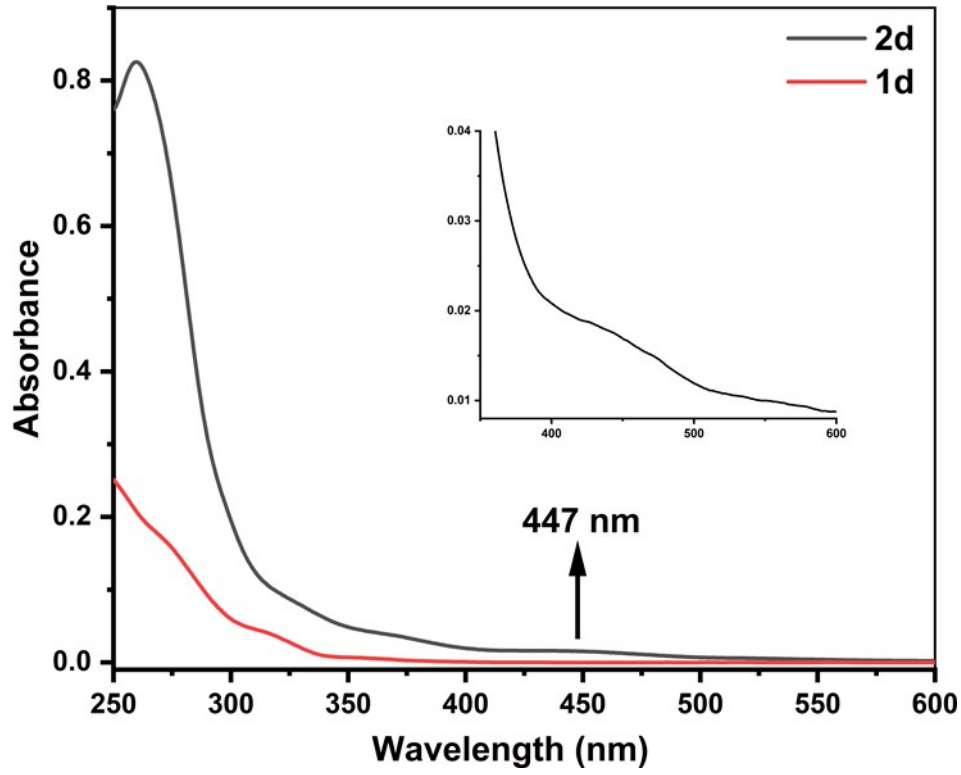


Figure S4. UV-Visible spectra of **2d** and **1d** in CH_2Cl_2 solvent.

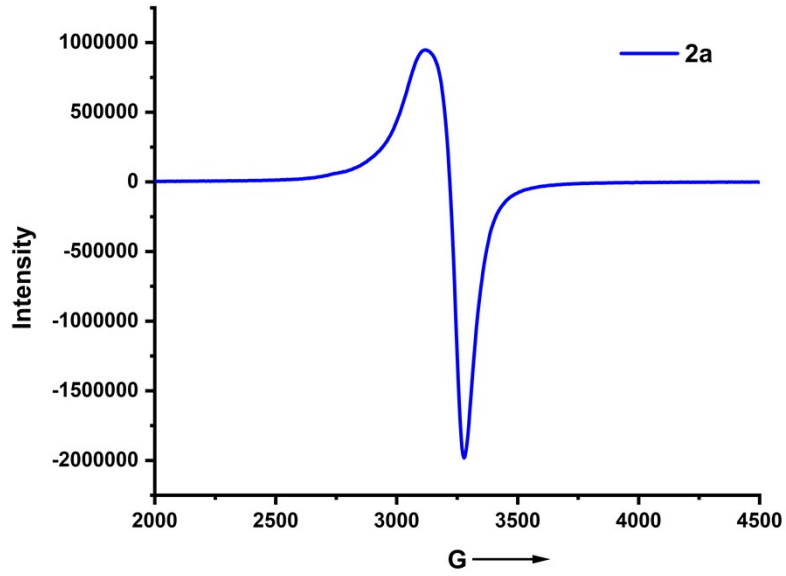


Figure S5. EPR spectra of **2a**.

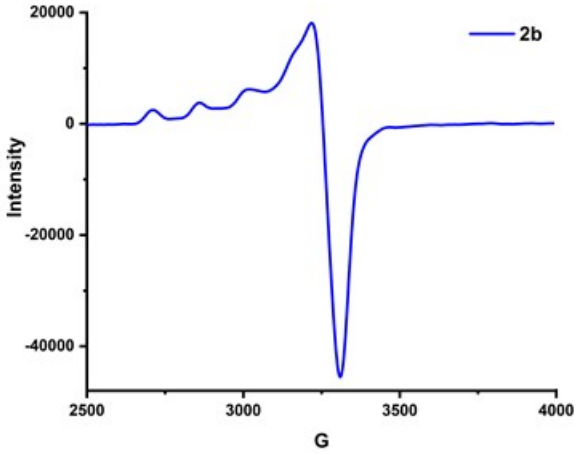


Figure S6. EPR spectra of **2b**.

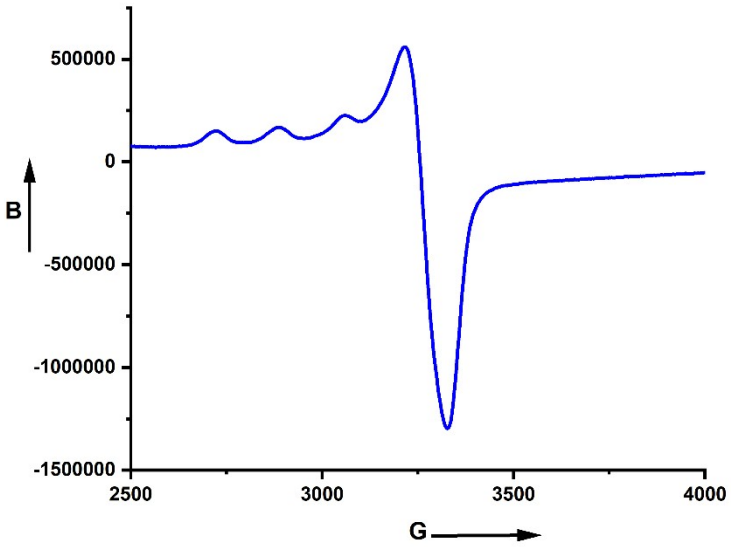


Figure S7. EPR spectra of **2c**.

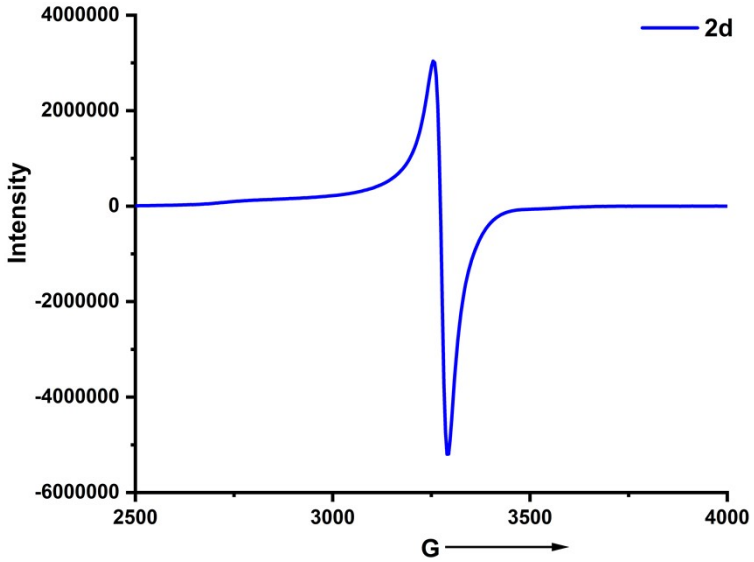


Figure S8. EPR spectra of **2d**.

SHAPE analysis:

The coordination geometry of copper(II) selenoether complexes around copper metal ion is carefully analyzed by SHAPE 2.1[2] using respective CIF file.

Table S1. Summary of SHAPE analysis of **2b**

Entry	Geometry	Point group	CShM
1	Square Planar	D4h	0.567
2	Tetrahedral	Td	28.550

Table S2. Summary of SHAPE analysis of **2c**

Entry	Geometry	Point group	CShM
1	Pentagon	D5h	23.697
2	Vacant Octahedron	C4v	6.417
3	Trigonal Bipyramid	D3h	8.053
4	Spherical Square Pyramid	C4v	4.886

Table S3. Summary of SHAPE analysis of **2d**

Entry	Geometry	Point group	CShM
1	Hexagon	D6h	33.151
2	Pentagonal Pyramid	C5v	23.012
3	Octahedron	Oh	5.376
4	Trigonal Prism	D3h	11.227
5	Johnson Pentagonal Pyramid	C5v	24.791

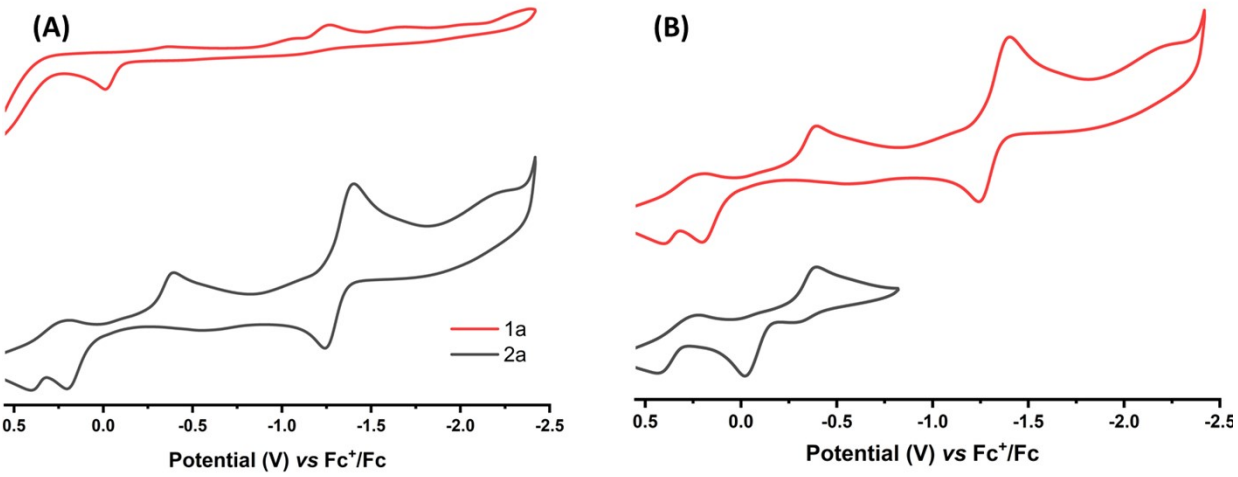


Figure S9 A-B. (A) Comparison of CV of **2a** and **1a,** and (B) CV of **2a** in DMF solvent using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte at 0.1V/s scan rate.

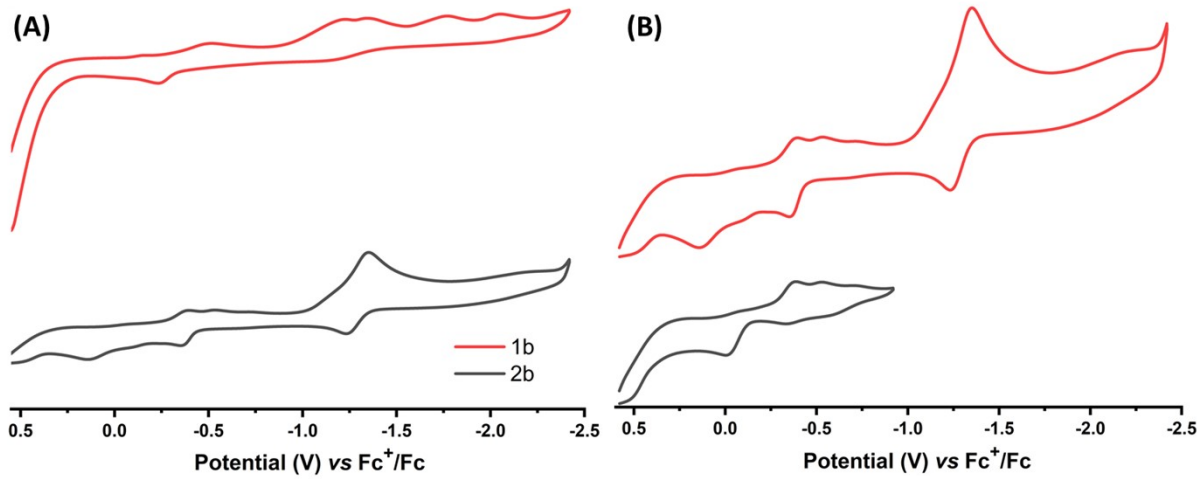


Figure S10 A-B. (A) Comparison of CV of **2b** and **1b,** and (B) CV of **2b** in DMF solvent using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte at 0.1V/s scan rate.

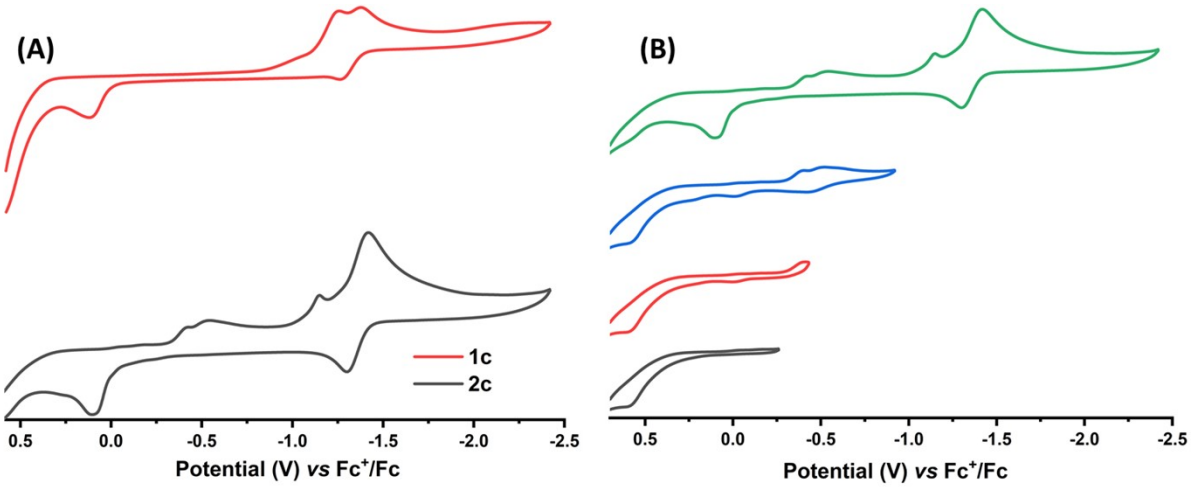


Figure S11 A-B. (A) Comparison of CV of **2c** and **1c,** and (B) CV of **2c** in DMF solvent using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte at 0.1V/s scan rate.

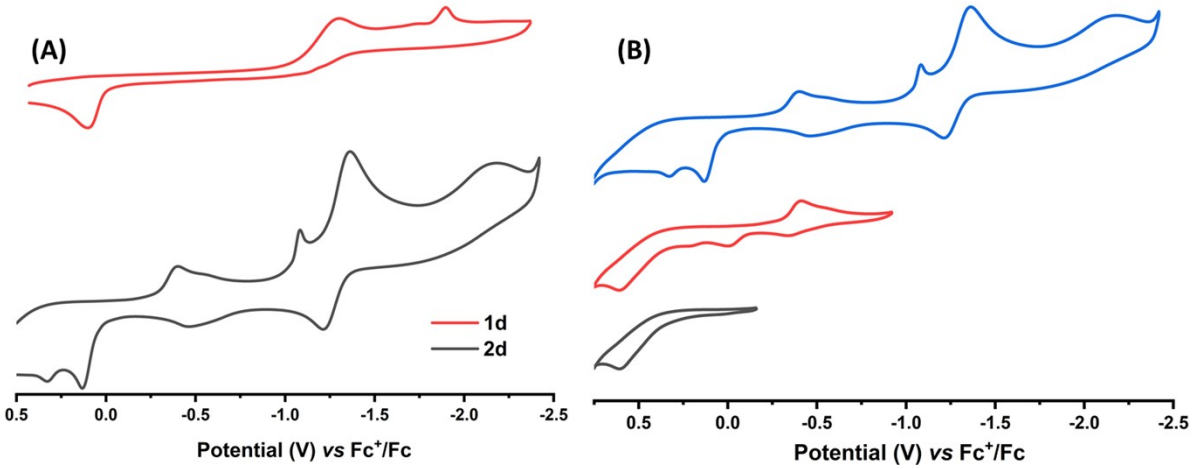


Figure S12 A-B. (A) Comparison of CV of **2d** and **1d,** and (B) CV of **2d** in DMF solvent using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte at 0.1V/s scan rate.

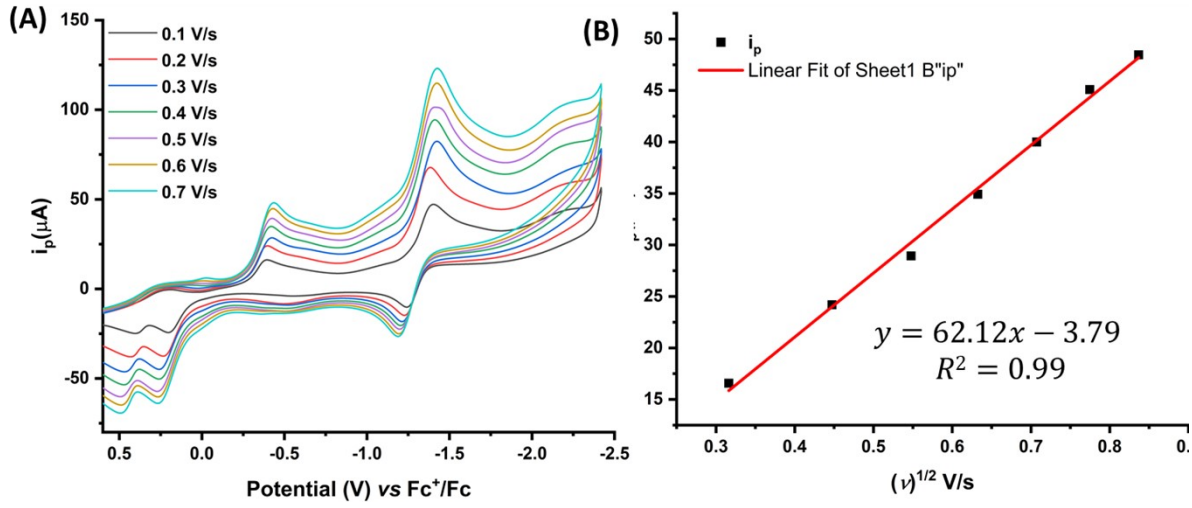


Figure S13 A-B. **(A)** CV study of **2a** at various scan rates. **(B)** Corresponding graph of i_{pc} *vs* square root of scan rate for Cu^{II}/Cu^{I} reduction using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte in DMF solvent.

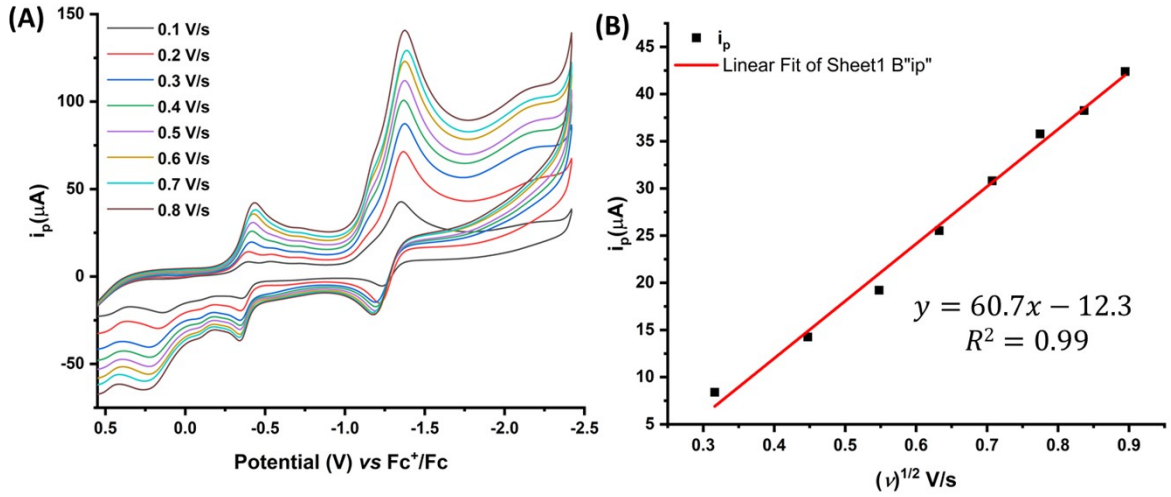


Figure S14 A-B. **(A)** CV study of **2b** at various scan rates. **(B)** Corresponding graph of i_{pc} *vs* square root of scan rate for Cu^{II}/Cu^{I} reduction using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte in DMF solvent.

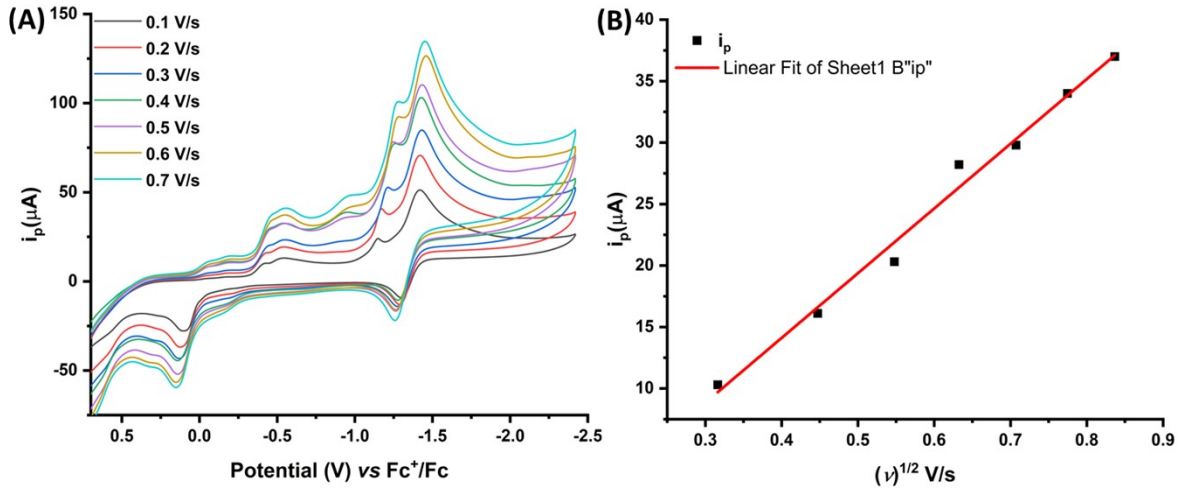


Figure S15 A-B. **(A)** CV study of **2c** at various scan rates. **(B)** Corresponding graph of i_{pc} *vs* square root of scan rate for Cu^{II}/Cu^{I} reduction using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte in DMF solvent.

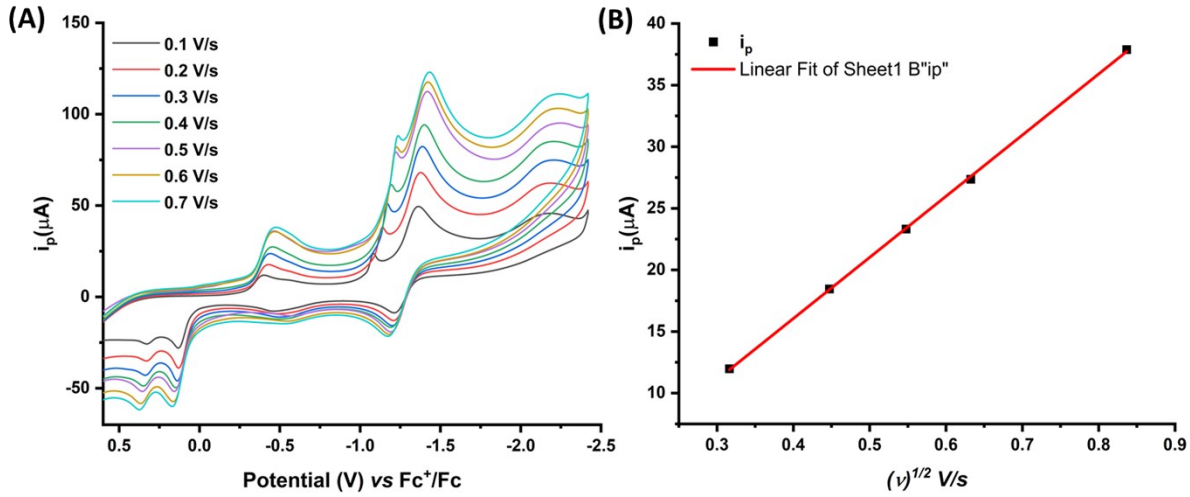


Figure S16 A-B. **(A)** CV study of **2d** at various scan rates. **(B)** Corresponding graph of i_{pc} *vs* square root of scan rate for Cu^{II}/Cu^{I} reduction using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte in DMF solvent.

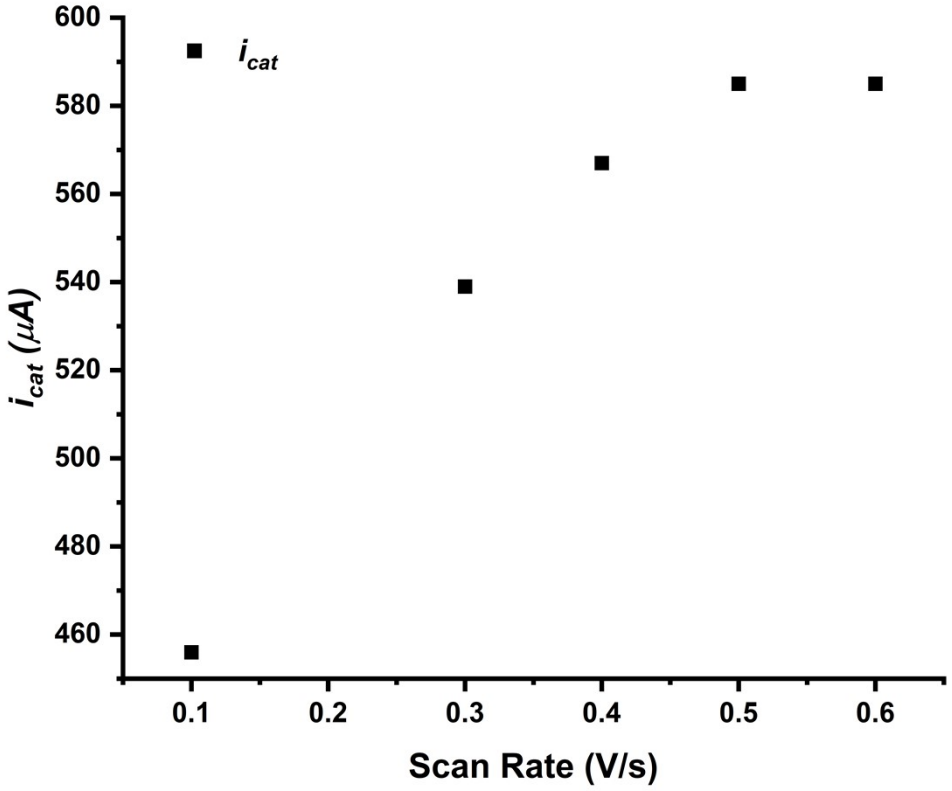


Figure S17. i_{cat} *vs* scan rate study of catalyst **2a** (0.5mM) at 28mM acetic acid concentration.

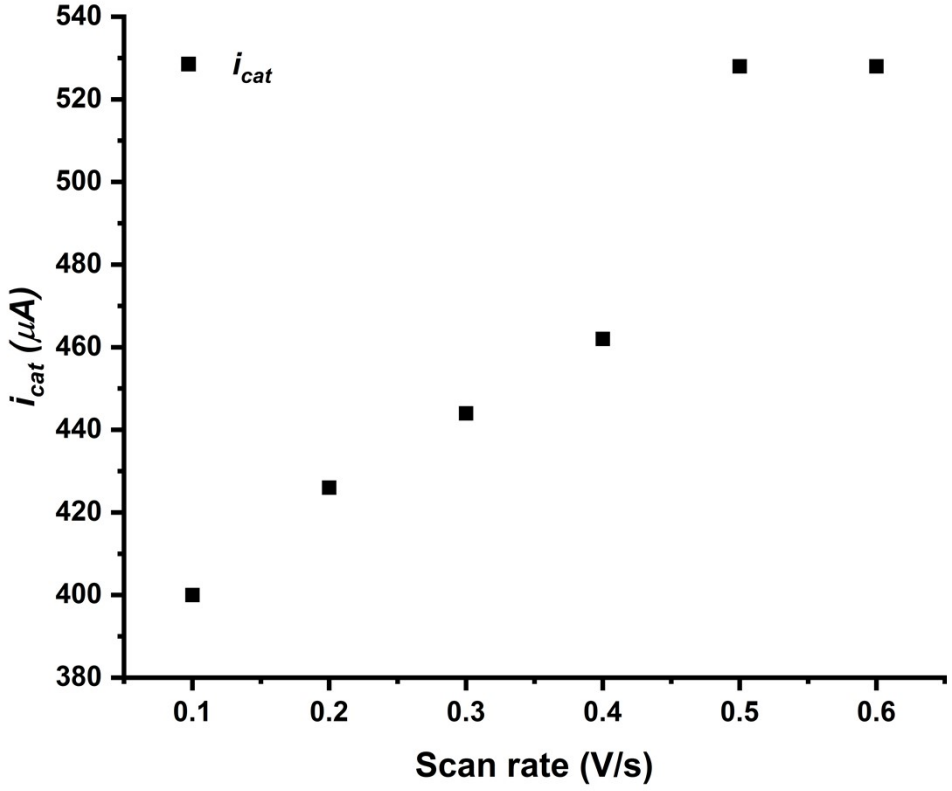


Figure S18. i_{cat} *vs* scan rate study of catalyst **2b** (0.5mM) at 22mM acetic acid concentration.

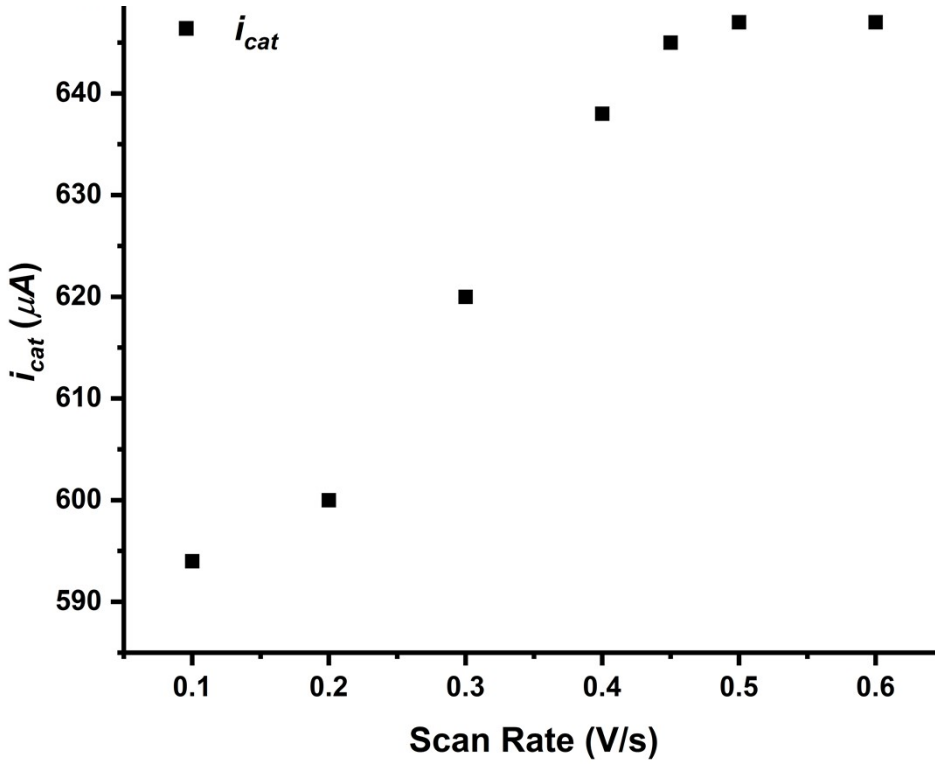


Figure S19. i_{cat} *vs* scan rate study of catalyst **2c** (0.5mM) at 44mM acetic acid concentration.

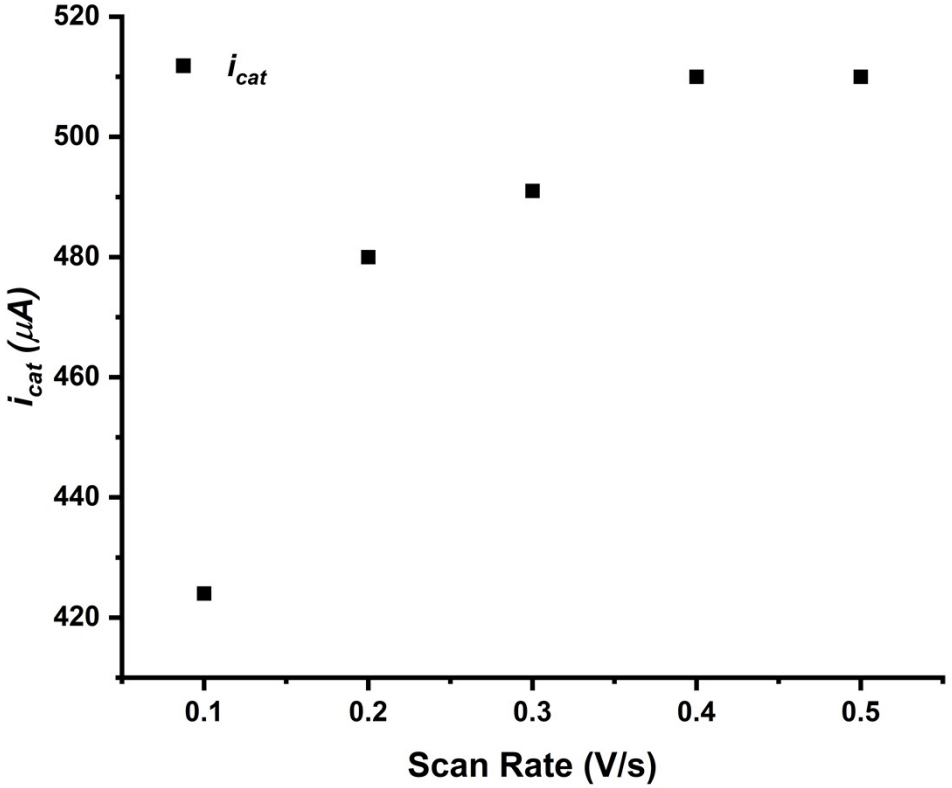


Figure S20. i_{cat} *vs* scan rate study of catalyst **2d** (0.5mM) at 28mM acetic acid concentration.

Quantitative estimation of evolved hydrogen by GC thermal detector

Vial# : 1
Sample Name : sks -ma-h2 pure1
Sample ID : 1.5ml
Sample Type : Unknown
Injection Volume :
ISTD Amount :

Data Name : D:\test\MA\08.06.2019\sks -ma-h2 pure1.gcd
Method Name : D:\test\MA\h2 and co2.gcm

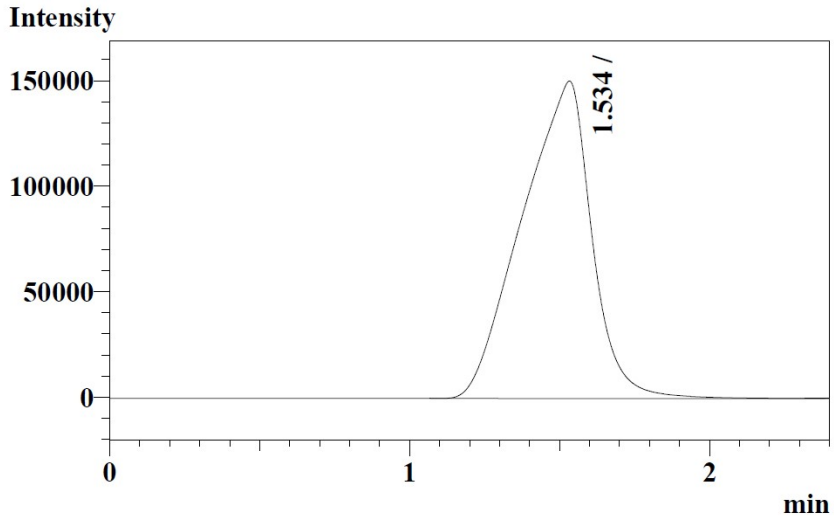


Figure S21. GC-TCD scan of pure hydrogen gas injected by Hamilton gas tight syringe.

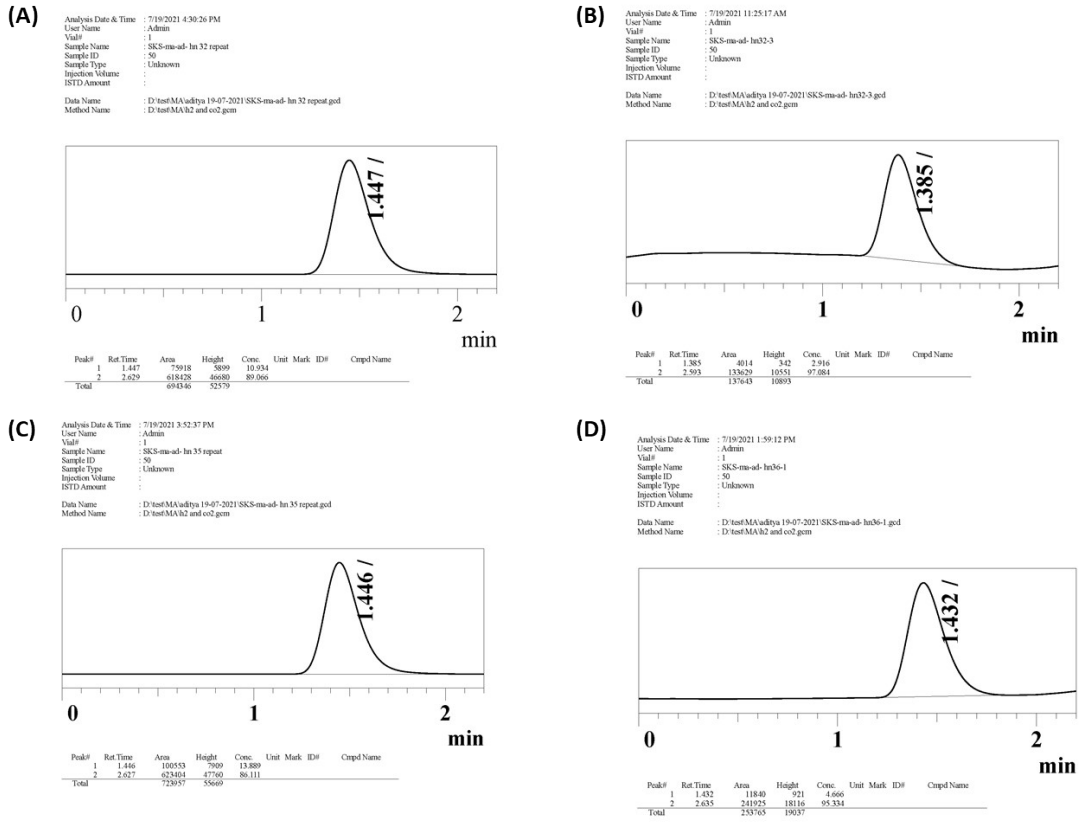


Figure S22 A-D. GC TCD readout of catalysts **(A)** 2a, **(B)** 2b, **(C)** 2c, and **(D)** 2d during electrolysis

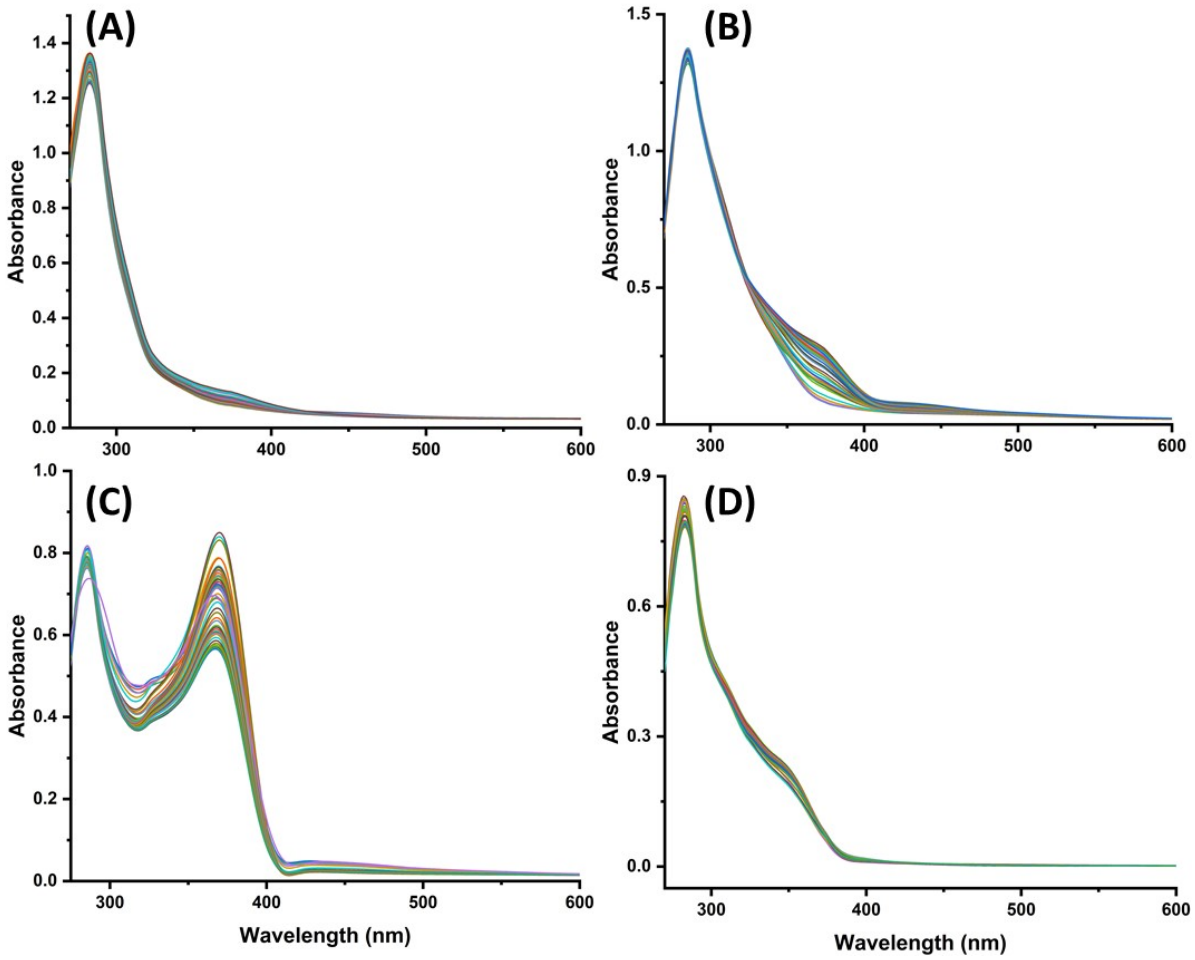


Figure S23. UV-visible spectra of electrocatalytic solution during the constant potential electrolysis (CPE) study at -2.2 V *vs* Fc^{+}/Fc of catalyst **2a** (A), catalyst **2b** (B), catalyst **2c** (C), and catalyst **2d** (D), in DMF solvent using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte.

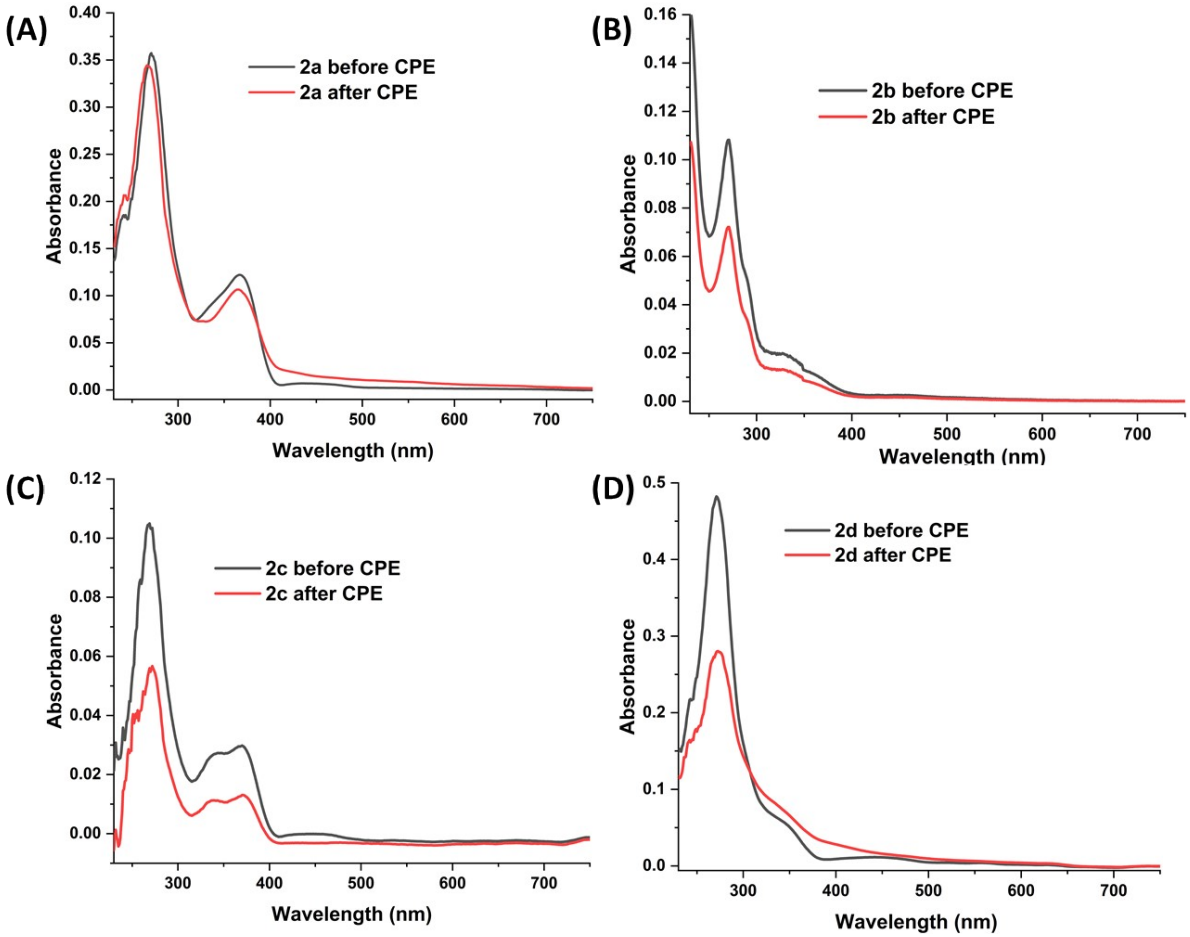


Figure 24. UV-visible comparison of electrocatalytic solution before and after the constant potential electrolysis (CPE) study of catalyst **2a** (A), catalyst **2b** (B), catalyst **2c** (C), and catalyst **2d** (D), in DMF solvent using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte.

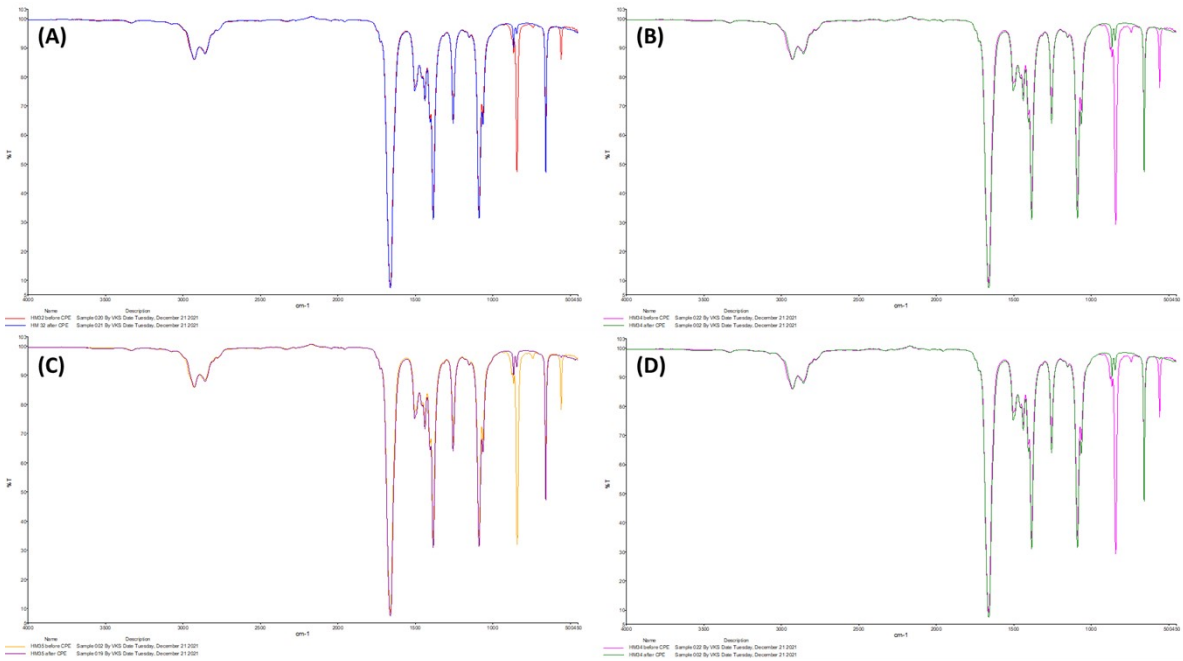


Figure 25. IR comparison of electrocatalytic solution of acetic acid and catalyst **2a** (A), catalyst **2b** (B), catalyst **2c** (C), and catalyst **2d** (D), in DMF solvent using 0.1M $^{n}Bu_4NPF_6$ as a supporting electrolyte.

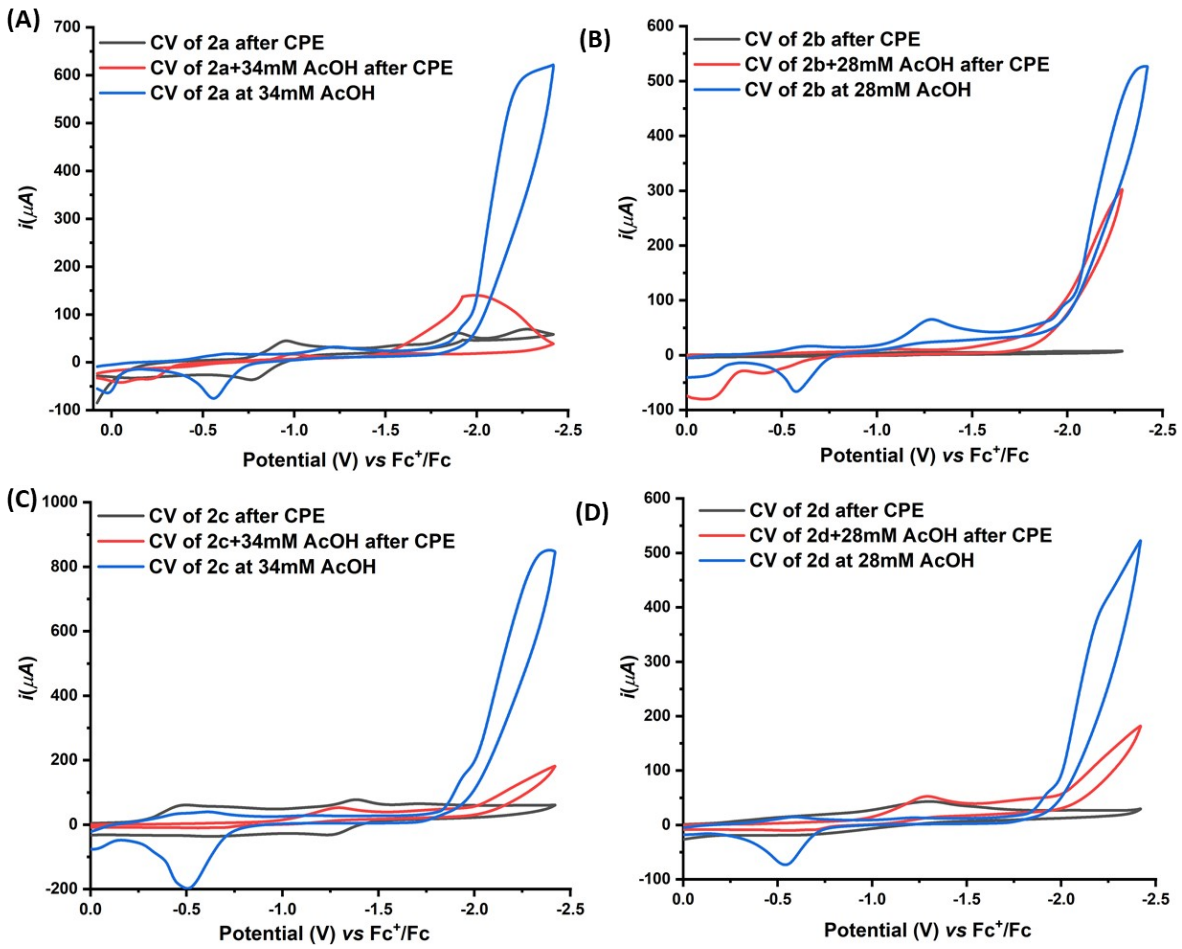


Figure 26. CV of catalysts before and after CPE using 0.1mM **2a-2d** at corresponding saturated acetic acid concentration.

Post electrolysis Dip test: The constant pulse electrolysis (CPE) study was performed on **2a-2d** (1mM) using $^{n}Bu_4NPF_6$ (0.1M) electrolyte and acetic acid (12mM) for 2h. The electrode was then removed, rinsed with DI water and placed in a new cell containing acetic acid and 0.1M $^{n}Bu_4NPF_6$ in the absence of catalysts **2a-2d** and CPE studies were performed for 2h. In the presence of complexes **2a-2d**, an appreciable charge was produced in the CPE study. By using the same electrode after rinsing with DI water and in the absence of catalysts **2a-2d**, no significant charge was observed in the CPE study. Next, the post electrolysis dip test for **2a-2d** suggests that electrocatalytically active film is not generated over the time of electrolysis. Therefore, catalysis under this condition seems attributed to homogeneous catalysis.

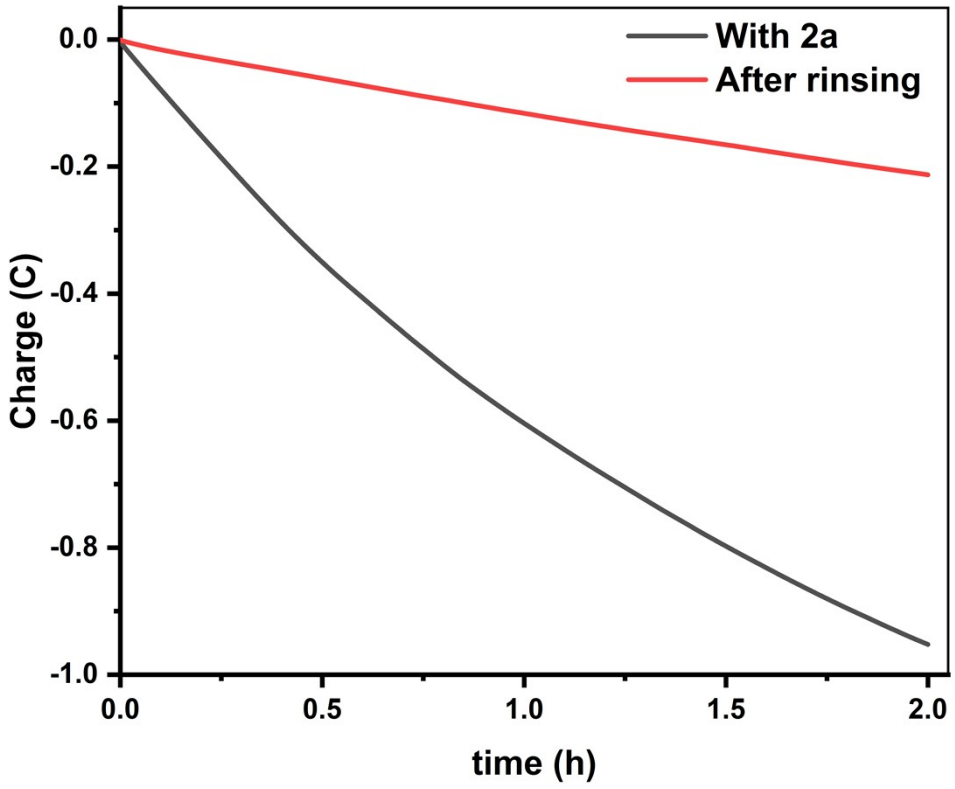


Figure S27. Post electrolysis rinse test for **2a**.

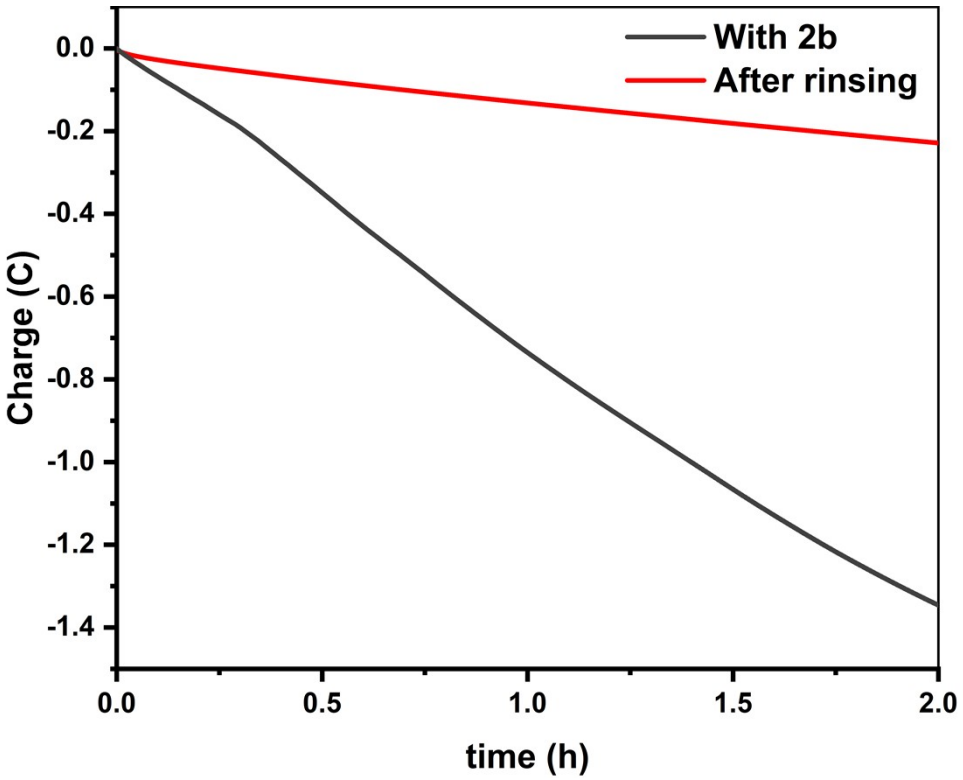


Figure S28. Post electrolysis rinse test for **2b**.

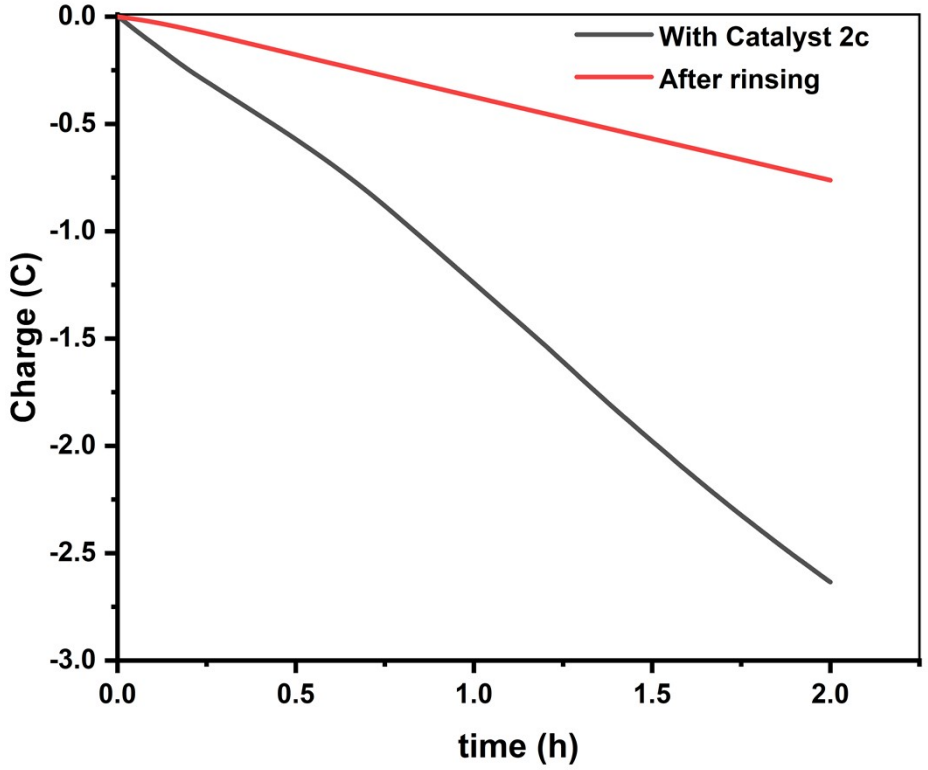


Figure S29. Post electrolysis rinse test for **2c**.

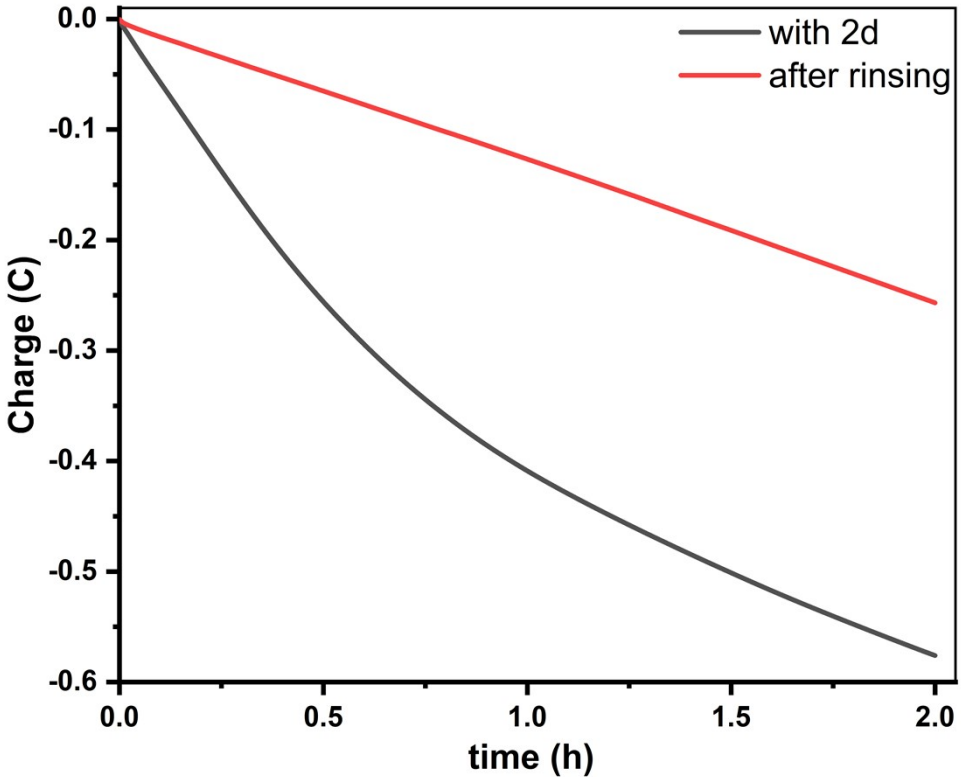


Figure S30. Post electrolysis rinse test for **2d**.

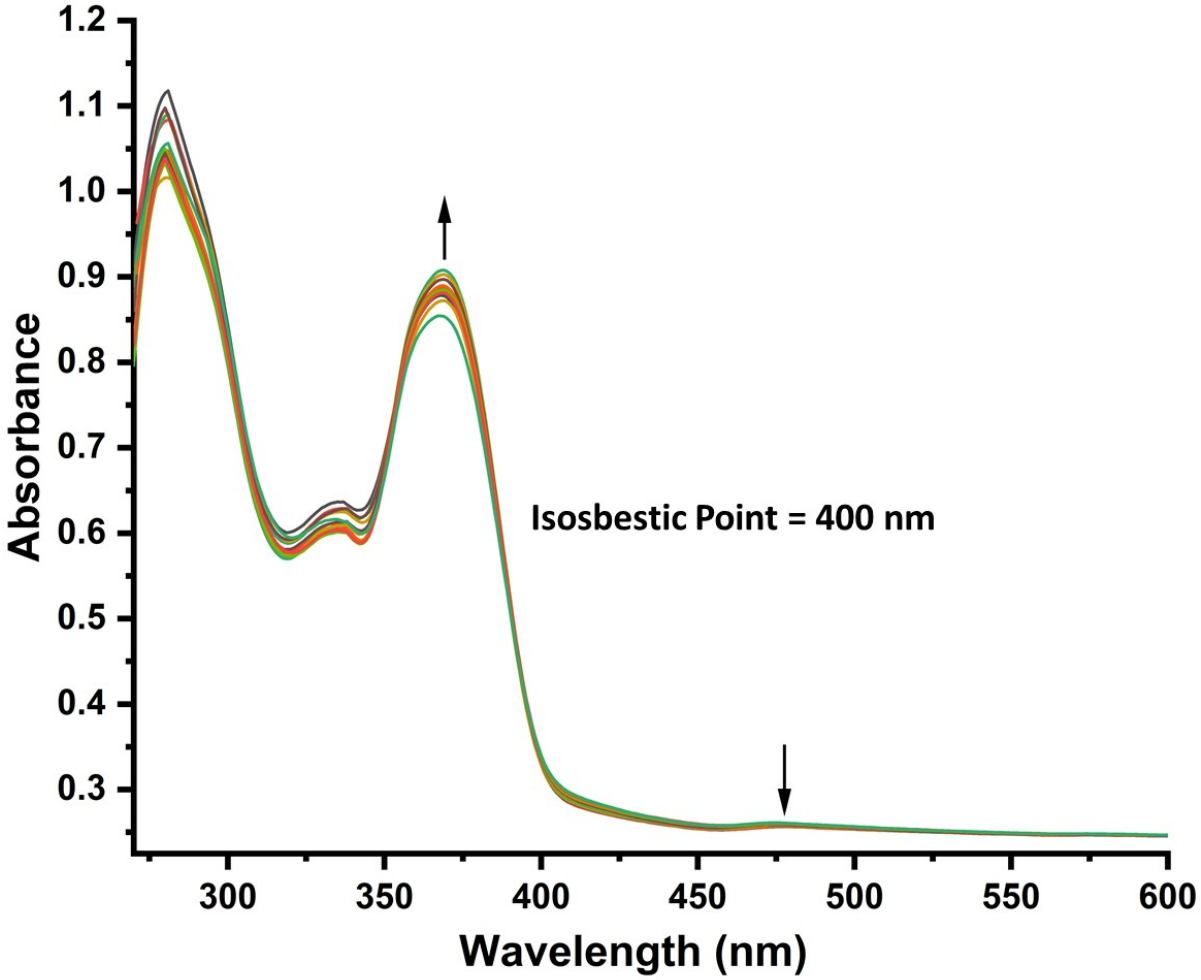


Figure S31. UV analysis of reaction mixture at -2.2 V *vs* Fc^{+}/Fc containing catalyst **2c** (0.03mM), acetic acid (15mM) in DMF solvent by using $TBAPF_6$ (0.1 M) as a supporting electrolyte.

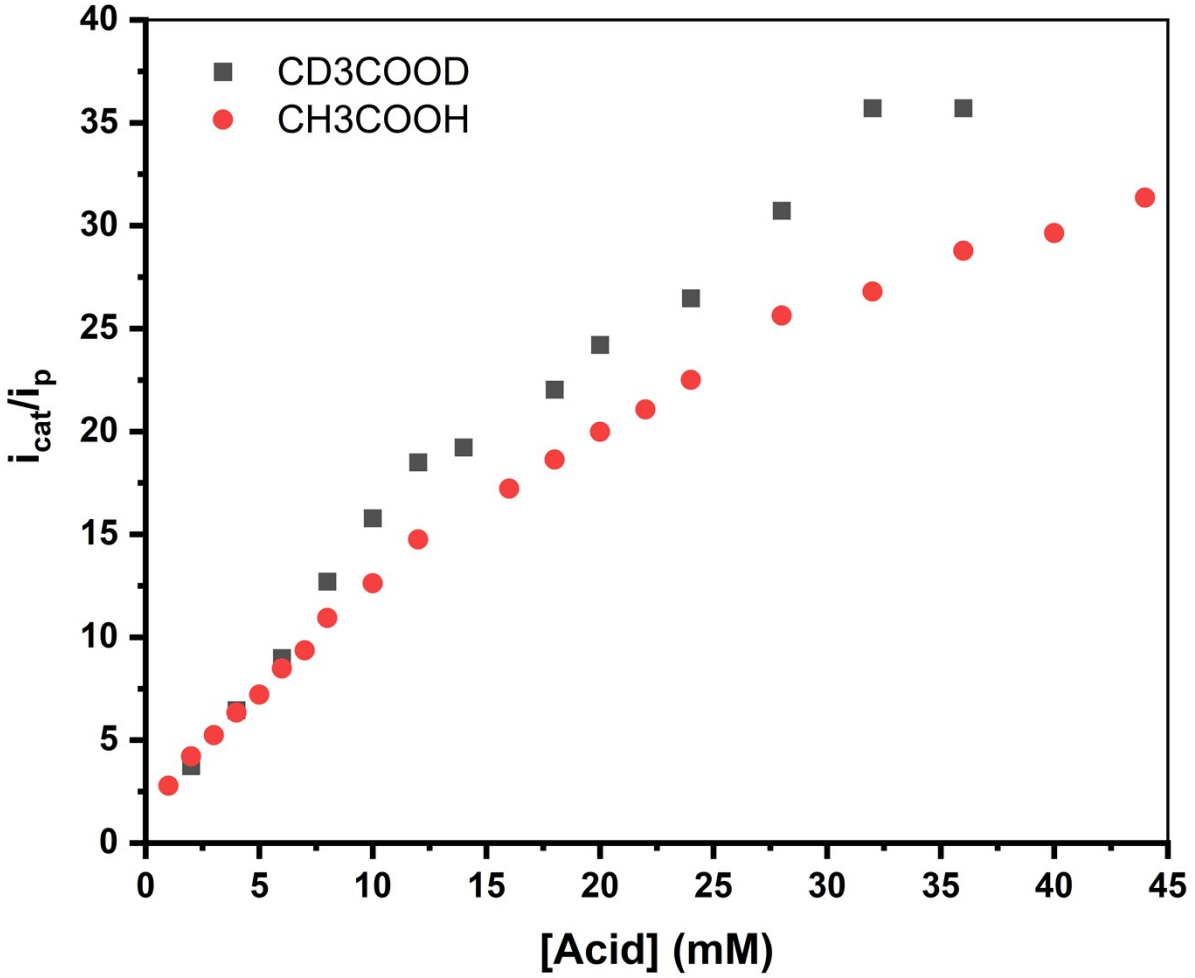


Figure S32. The comparison graph of i_{cat}/i_p *vs* concentration of acetic acid and deuterated acetic acid of **2c**.

$$KIE = \left(\frac{Slope_{CH3COOH}}{Slope_{CD3COOD}}\right)^2$$

i_{cat}/i_p *vs* [Acid]

$Slope_{CH3COOH}$ = 0.83, R^2 = 0.98

$Slope_{CD3COOD}$= 0.98, R^2 = 0.98

$$KIE = \left(\frac{0.83}{0.93}\right)^2 KIE = 0.69$$

DFT Calculations:

All computational studies were performed with the Gaussian 09 Revision A.02 program suite with the DFT method of Becke's three parameter hybrid Hartree-Fock procedure with the Lee-Yang-Parr correlation function (B3LYP). The geometry optimization and energy calculations of the reactants, intermediates, and transition state in this study were fully optimized by DFT/B3LYP method with the 6-31+g(d) basis set in gas phase.

Table S4. Comparison of bond lengths and bond angles of experimentally obtained structure of copper(II) selenolate complex **2c** (see Table S5) and calculated structure using DFT/B3LYP/6-31+g(d). In experiment, copper(II) selenolate complex **2c** crystallizes with CH_2Cl_2: hexane. Relative error presented here are calculated as (|calculated – experimental|/ experimental) × 100.

Bond Distance	**Experimental**	**Calculated**	**%Error**
Cu-N1	1.969	2.025	2.8
Cu-N2	2.004	2.037	1.6
Cu-O1	1.924	1.924	0
Cu-O2	1.928	1.926	0.1
Cu-Se1	3.042	2.752	9.5
Cu-Se2	3.106	3.074	1.0
Bond Angle			
N1-Cu-N2	82.21	81.25	1.1
Se1-Cu-Se2	137.11	139.04	1.4
O1-Cu-N2	171.69	168.32	1.9

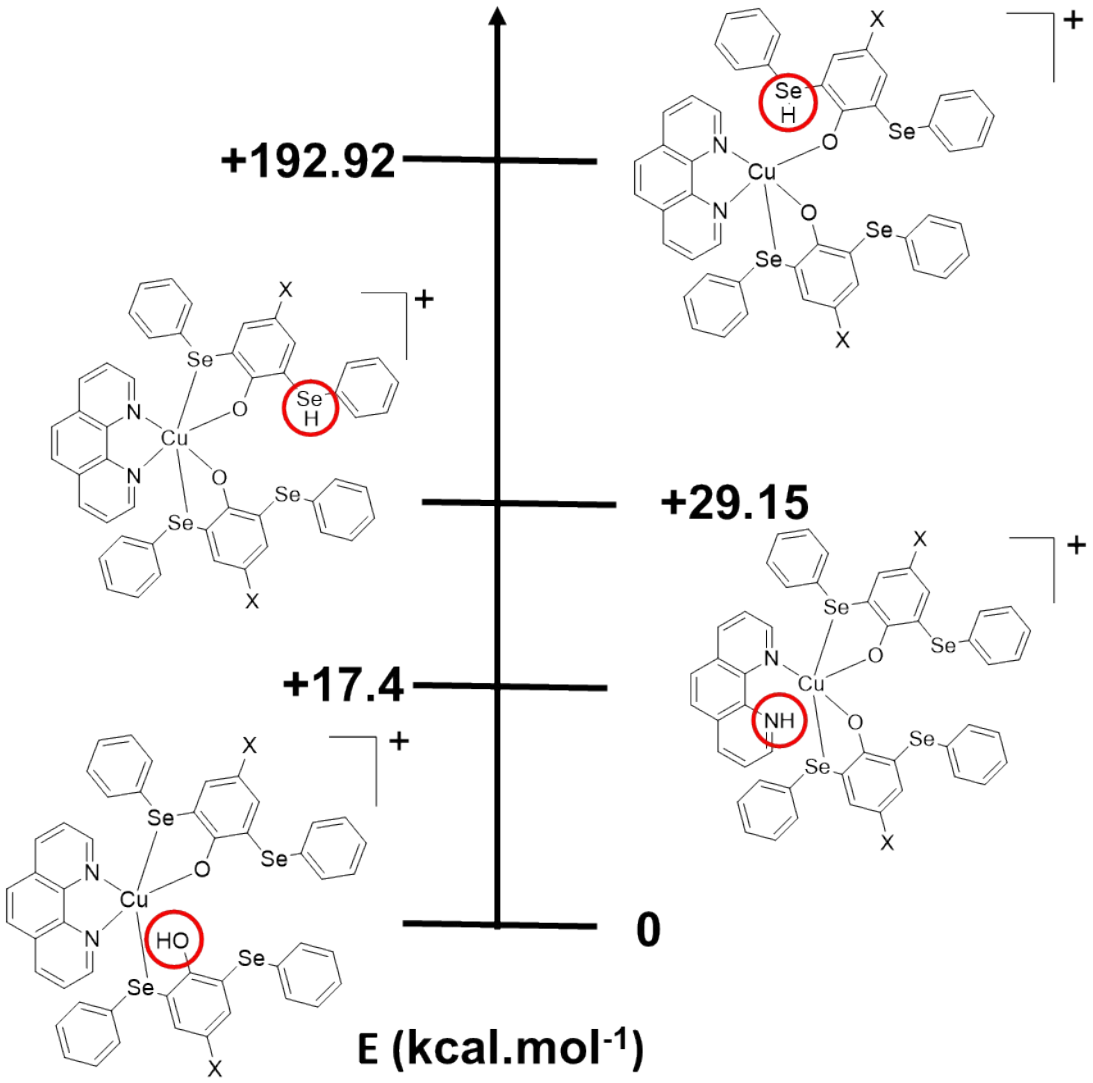


Figure S33. Energetic stability of the protonated species of **2c** (X=CHO) in the singlet (S = 1) electronic states using B3LYP/6-31+g(d) basis set in gas phase.

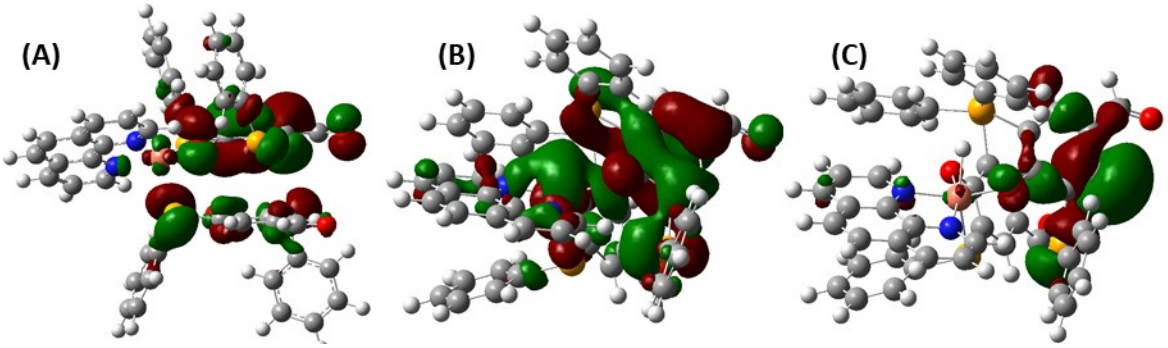
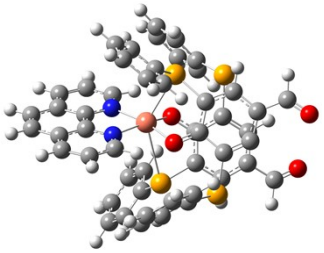


Figure S34 A-C: SOMO picture of radical cation intermediate **II** in the scheme 2, main manuscript (A); HOMO-1 picture (B) and HOMO picture (C) of copper hydride intermediate **III** in the scheme 2.

Cartesian Coordinates of the optimized structures:

2c



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C	-1.32364	-1.52766	-0.39072
O	-6.17926	2.085342	2.01027
C	-2.46582	-2.06254	0.340167
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C	-1.46406	1.165294	1.801054
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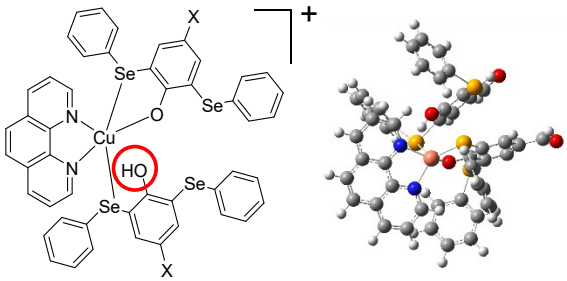

Symbol	X	Y	Z
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H	5.902085	3.7542	3.033957
C	-4.21695	-4.8034	-1.39822
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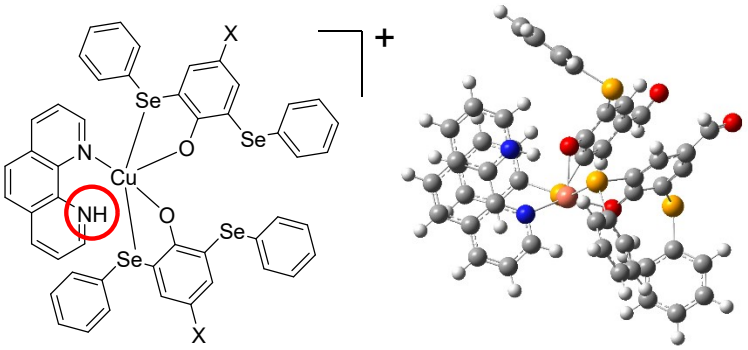

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Cu	-0.22775	-1.23768	-0.11652
O	-1.0587	0.744338	0.305239
O	1.743911	-0.72138	-0.47601
N	-1.55841	-2.83461	0.153461
N	-3.32856	-0.57157	0.453819
C	2.256555	0.128898	0.305536
O	1.604448	5.735323	-2.73453
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C	-0.54109	1.641591	-0.48281
C	-0.19652	2.946894	-0.00349
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H	-0.62571	-6.0701	-0.15304
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C	-3.09813	0.71868	-3.08146
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C	-6.03755	-0.92054	0.599524
H	-7.11289	-1.07132	0.645953
C	6.162911	-3.19538	-2.11946
H	6.648109	-4.16484	-2.19561
C	1.308719	4.599745	-3.06602
H	1.49353	4.249635	-4.10512
C	4.03831	3.162562	2.984627
H	3.635267	3.120254	4.017145
C	-5.11147	4.058388	2.15387
H	-6.17502	4.258685	2.255583
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H	-5.0196	1.541039	-3.59527
C	-4.93443	-0.57807	-3.99772
H	-5.95026	-0.63095	-4.37956
C	-4.45171	4.345159	0.952966
H	-5.00167	4.768454	0.115715
C	-4.38496	3.543888	3.233218
H	-4.88427	3.328423	4.174689
C	6.911119	-2.06757	-1.76765
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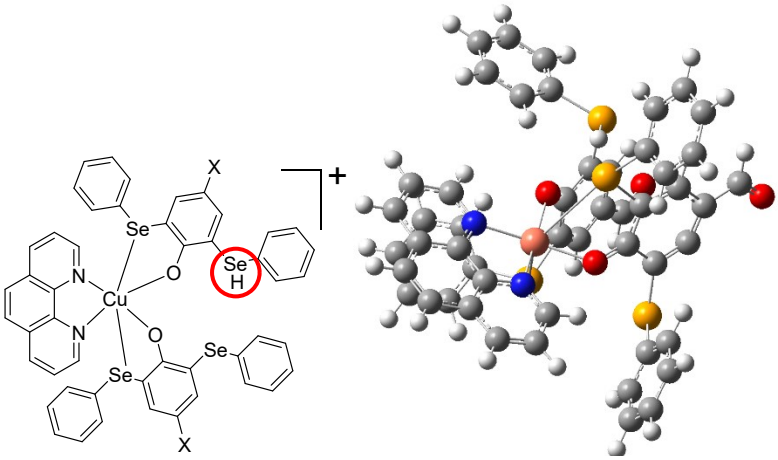

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Se	1.913804	0.240212	-2.109055
Se	-2.685762	-2.62983	-0.12787
Cu	1.342419	0.100167	0.575018
O	0.082029	-1.34055	-0.069074
O	-0.029602	1.597913	0.152713
N	2.500108	1.502665	1.557877
N	2.794678	-1.175292	1.493484
C	-1.265357	1.503751	-0.103541
O	-3.22489	-1.800989	-5.528665
C	-1.818141	2.141539	-1.297484
C	-0.401267	-1.285792	-1.265819
C	-1.680006	-1.856573	-1.559784
C	0.246046	-0.667603	-2.38002
C	3.713078	-0.461768	2.192264
O	-6.032731	1.668987	-2.194546
C	-3.120014	2.000192	-1.528806
C	-3.599279	0.875776	0.427821
H	-4.309867	0.374349	1.085515
C	3.555204	0.971477	2.226687
C	-2.257423	-1.854074	-2.816724
H	-3.235052	-2.292465	-3.002968
C	-0.330004	-0.66529	-3.64276
H	0.200244	-0.189607	-4.465116
C	-2.254762	0.885752	0.744615
C	-1.718636	-4.232883	0.380264
C	-4.121721	1.43594	-0.784469
C	-0.134339	4.603926	-1.530558
C	4.481554	1.765189	2.945262
C	-1.576057	-1.263669	-3.891518
C	-3.050701	0.280198	3.53296
C	2.322107	2.818928	1.569957
H	1.460156	3.187875	1.022069
C	-4.151064	1.730384	5.119878
H	-4.212595	2.682008	5.640712

C	-0.753006	5.04198	-0.35678
H	-1.645169	4.543327	0.008827
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H	-5.890255	0.90464	6.093467
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C	4.799118	-1.064994	2.873012
C	2.91611	-2.495672	1.439541
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H	-0.426977	-3.250302	1.803726
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C	5.326312	-1.835813	-3.367756
H	6.299601	-1.550908	-3.758629
C	-2.103512	-5.428304	-0.230602
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C	-3.123025	1.506186	4.201932
H	-2.386388	2.2783	4.000415
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H	4.954495	3.812093	3.485261
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H	1.46597	4.937457	-2.951366
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C	5.725102	-0.233123	3.591166
H	6.555158	-0.70611	4.109211
C	3.190206	3.688769	2.258433
H	3.000813	4.756969	2.235356
C	3.958615	-3.189237	2.085751
H	4.015603	-4.270341	2.006833
C	2.811184	-2.550315	-2.373179
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H	-1.568753	-0.7457	-6.020922
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H	0.02608	-7.517312	1.407909
C	3.731749	-3.537401	-2.735923
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C	4.993933	-3.185737	-3.223508
H	5.70671	-3.956824	-3.502154

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H	0.66938	-5.376969	2.494435
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H	-0.720539	6.488202	1.235264
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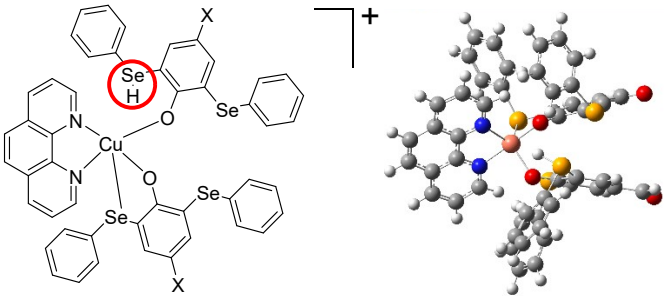

Symbol	X	Y	Z
Se	0.720441	1.17974	-2.4267
Se	1.739369	-3.52032	0.783035
Se	-0.38283	-1.8613	2.703722
Se	-2.51105	0.014268	-2.25161
Cu	0.250991	1.160588	0.021473
O	-1.37622	0.157199	0.680752
O	1.236297	-0.5027	0.066508
N	1.665374	2.218696	1.158398
N	-0.72134	2.906829	0.181533
C	1.195382	-1.23879	-0.99
O	-3.62654	-5.34245	-1.68392
C	1.398875	-2.67478	-0.90137
C	-1.71773	-1.03665	0.32697
C	-2.36665	-1.34661	-0.91413
C	-1.46953	-2.16806	1.165297
C	-0.03013	3.864788	0.847077
O	0.96915	-4.96783	-4.54649
C	1.326001	-3.34926	-2.05612
C	1.026149	-1.49403	-3.43623
H	0.851162	-1.03838	-4.41138
C	1.266393	3.502349	1.350936
C	-2.7764	-2.63566	-1.21098
H	-3.27488	-2.8467	-2.15219
C	-1.86739	-3.46311	0.86632
H	-1.63993	-4.28638	1.540653
C	1.047887	-0.70359	-2.30291
C	-4.24192	0.787204	-1.87164
C	1.131984	-2.90837	-3.34421

C	3.392616	-2.65408	1.276505
C	2.055699	4.467005	2.017448
C	-2.55141	-3.70868	-0.3268
C	2.528637	1.837824	-2.68169
C	2.869296	1.856113	1.585717
H	3.14957	0.822662	1.405975
C	4.904191	1.790901	-2.27147
H	5.767042	1.332153	-1.79643
C	4.532691	-2.84165	0.488594
H	4.469663	-3.43391	-0.41905
C	5.07145	2.906888	-3.09523
H	6.063134	3.317317	-3.26143
C	-1.59969	-1.04471	3.992756
C	-0.53748	5.166961	1.055648
C	-1.93813	3.178922	-0.27709
H	-2.41978	2.368332	-0.81219
C	-4.65555	1.826794	-2.71478
H	-4.02082	2.150633	-3.53645
C	2.689228	2.951611	-3.5114
H	1.83055	3.390534	-4.01229
C	-2.48178	-1.11843	6.233196
H	-2.5119	-1.57438	7.218094
C	-5.06691	0.363206	-0.82808
H	-4.75732	-0.44563	-0.17473
C	3.634278	1.255847	-2.05442
H	3.513594	0.391012	-1.41009
C	1.525973	5.79028	2.199949
H	2.136987	6.526526	2.714298
C	3.329074	4.049955	2.468546
H	3.975855	4.755044	2.983641
C	3.471637	-1.91875	2.46279
H	2.585972	-1.77125	3.073565
C	3.962316	3.488663	-3.71066
H	4.085745	4.350346	-4.36037
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H	-0.99807	-2.4926	5.48618
C	0.2821	6.123254	1.747144
H	-0.10711	7.125739	1.900366
C	3.735568	2.747525	2.247057
H	4.707667	2.398161	2.578355
C	-2.53353	4.441361	-0.10153
H	-3.52926	4.61517	-0.49498
C	-2.40729	0.051261	3.679909
H	-2.37933	0.491414	2.688823
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H	-2.26765	6.422525	0.694133
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H	6.783419	-1.12855	2.38287

C	-3.01244	-5.07001	-0.67204
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H	0.718853	-3.17859	-5.46912
C	-6.72042	2.020192	-1.46602
H	-7.68599	2.492491	-1.31138
C	-3.25225	0.559573	4.666492
H	-3.88721	1.411237	4.44004
C	-3.29093	-0.02144	5.937262
H	-3.95505	0.380183	6.696913
C	-6.30318	0.982497	-0.63123
H	-6.94532	0.643596	0.17734
C	-5.89165	2.439971	-2.50917
H	-6.20987	3.23816	-3.17433
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H	6.629797	-2.42111	0.263883
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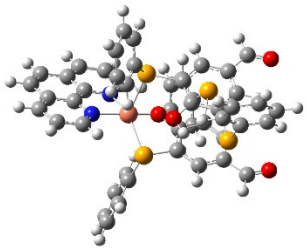
Intermediate II



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Se	-4.3401	0.165353	1.358312
Cu	1.68989	-0.69134	0.254249
O	-1.8688	-1.45532	0.589135
O	1.163473	1.082093	-0.11625
N	3.378447	-0.29463	-0.84424
N	2.701453	-2.4028	0.632141
C	0.144842	1.628349	0.489572
O	-4.13496	2.919604	-3.50057
C	-0.52437	2.75608	-0.07893
C	-2.21498	-0.60653	-0.40908
C	-3.34791	0.228648	-0.29467
C	-1.41311	-0.53452	-1.55907
C	3.904299	-2.4493	-0.00655
O	-3.93195	4.331111	2.030056
C	-1.57388	3.276665	0.613755

C	-1.44134	1.702868	2.37353
H	-1.80156	1.278012	3.308879
C	4.265799	-1.316	-0.80836
C	-3.6604	1.120593	-1.3088
H	-4.51007	1.789379	-1.21648
C	-1.74646	0.35704	-2.57576
H	-1.11423	0.423896	-3.45682
C	-0.35139	1.13705	1.723571
C	-5.83191	-0.91725	0.755547
C	-2.09663	2.821244	1.822008
C	1.595931	4.255272	-1.54127
C	5.492222	-1.29568	-1.50631
C	-2.86645	1.188425	-2.46307
C	1.851864	0.271599	3.513346
C	3.644351	0.778662	-1.5814
H	2.88137	1.551381	-1.59097
C	3.727176	1.734595	3.897587
H	4.429822	2.479068	3.53429
C	1.899581	4.891739	-0.33449
H	1.190769	4.872291	0.487302
C	3.796	1.29478	5.222498
H	4.553136	1.696828	5.889222
C	-0.34427	-3.34503	-1.78044
C	4.778536	-3.55682	0.078535
C	2.335519	-3.44518	1.373858
H	1.373481	-3.37339	1.870577
C	-5.72579	-2.3087	0.681022
H	-4.79944	-2.80488	0.954645
C	1.908497	-0.16794	4.837147
H	1.191802	-0.89635	5.205652
C	-0.87841	-5.26613	-3.14508
H	-0.99248	-5.71915	-4.12557
C	-7.02375	-0.27649	0.407429
H	-7.09933	0.804667	0.471126
C	2.757919	1.223904	3.034639
H	2.701956	1.571422	2.007311
C	6.365175	-2.431	-1.3972
H	7.309458	-2.41488	-1.93358
C	5.767623	-0.13767	-2.27137
H	6.700124	-0.06794	-2.82474
C	2.507363	4.308263	-2.60396
H	2.270806	3.822515	-3.54779
C	2.888818	0.344207	5.690874
H	2.932677	0.006479	6.722189
C	-0.48882	-3.92987	-3.04183
H	-0.29473	-3.34794	-3.93762
C	6.023249	-3.51268	-0.638
H	6.691834	-4.36528	-0.56499

C	4.845832	0.892029	-2.30812
H	5.029055	1.79265	-2.88365
C	3.139163	-4.5878	1.520586
H	2.791731	-5.40758	2.139642
C	-0.59129	-4.08755	-0.62297
H	-0.5023	-3.62053	0.350069
C	4.360481	-4.6457	0.875418
H	4.999558	-5.5187	0.974384
C	4.023015	5.623692	-1.24927
H	4.959637	6.161898	-1.1364
C	-3.18269	2.168402	-3.52966
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C	-3.28978	3.402941	2.473201
H	-3.57046	2.908753	3.430148
C	-8.01465	-2.4254	-0.09436
H	-8.86639	-3.01395	-0.42294
C	-0.97949	-5.42345	-0.73392
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C	-1.1236	-6.01298	-1.99169
H	-1.42847	-7.05233	-2.07285
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H	-6.74066	-4.14262	0.193918
C	3.114749	5.563067	-0.19011
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C	3.711528	5.000867	-2.45942
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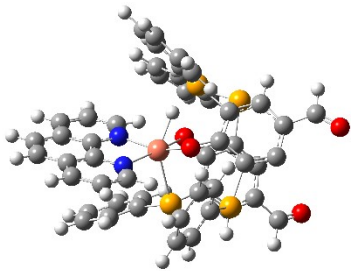
Intermediate III



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Se	-0.5018	0.196117	-2.41813
Se	4.023781	0.307861	1.073397
Cu	-1.01567	0.377107	0.077702
O	1.253937	0.980602	-0.01116
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C	1.935242	0.366498	-0.8954
C	3.321284	0.026348	-0.68495
C	1.382262	-0.03597	-2.16053
C	-2.77991	2.611623	0.390769
O	3.895959	-5.71632	1.139655
C	1.646125	-4.06183	0.0294
C	2.253973	-2.6246	1.965933
H	2.957093	-2.35465	2.755831
C	-3.73995	1.559092	0.183218
C	4.07801	-0.58315	-1.66192
H	5.122783	-0.82089	-1.48598
C	2.148267	-0.66832	-3.12419
H	1.687954	-0.96952	-4.06293
C	1.138118	-1.81787	1.724569
C	3.995187	2.243026	1.123134
C	2.450314	-3.77027	1.184626
C	-2.12196	-3.66994	-1.54259
C	-5.12935	1.843063	0.229897
C	3.510863	-0.93333	-2.90811
C	-0.48811	-0.55998	3.942182
C	-4.09832	-0.68473	-0.21573
H	-3.6548	-1.65948	-0.39226
C	-2.1096	-2.0108	4.975674
H	-2.5926	-2.98231	5.043118
C	-2.4976	-4.27406	-0.33257
H	-1.74244	-4.44156	0.428955
C	-2.49864	-0.97569	5.829028
H	-3.28081	-1.14073	6.565811
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C	-3.23094	3.944638	0.560594
C	-0.55684	3.249864	0.526747
H	0.479152	2.931044	0.481155
C	3.067832	2.919326	1.922138
H	2.306386	2.351085	2.444845
C	-0.87461	0.481629	4.788659
H	-0.38882	1.452995	4.72067
C	-1.97208	3.945497	-3.55862
H	-2.96262	4.348835	-3.75772
C	4.943973	2.9724	0.400467
H	5.660305	2.441263	-0.21948
C	-1.10518	-1.80641	4.028138
H	-0.80471	-2.60419	3.356331
C	-5.55414	3.197458	0.438266

H	-6.62039	3.410012	0.467448
C	-6.01081	0.75496	0.050358
H	-7.08493	0.925253	0.078382
C	-3.10736	-3.47505	-2.52632
H	-2.83381	-3.00842	-3.46987
C	-1.87992	0.272442	5.734164
H	-2.1776	1.083497	6.394391
C	-1.83533	2.608437	-3.18705
H	-2.72047	1.983155	-3.08846
C	-4.64421	4.203615	0.581162
H	-4.97608	5.22958	0.7222
C	-5.49586	-0.51183	-0.15964
H	-6.14176	-1.37211	-0.3021
C	-0.91573	4.597804	0.668296
H	-0.13209	5.343855	0.753667
C	0.558805	2.888434	-3.03682
H	1.543598	2.484526	-2.82599
C	-2.25383	4.950661	0.706095
H	-2.5603	5.985802	0.835825
C	-4.79843	-4.45153	-1.0905
H	-5.82729	-4.7583	-0.91597
C	4.316322	-1.54442	-3.95817
H	3.734961	-1.82355	-4.86906
C	3.562646	-4.64031	1.606649
H	4.136343	-4.22577	2.4806
C	4.052962	5.039557	1.287432
H	4.078668	6.124646	1.35589
C	0.416889	4.225731	-3.41269
H	1.302288	4.852029	-3.49741
C	-0.84467	4.762047	-3.67704
H	-0.94939	5.803707	-3.9705
C	4.968928	4.36617	0.475899
H	5.709182	4.924895	-0.09219
C	3.104488	4.312827	2.010971
H	2.383614	4.830866	2.640127
C	-3.82131	-4.6506	-0.10879
H	-4.09091	-5.11401	0.838377
C	-4.42847	-3.86545	-2.3046
H	-5.17187	-3.70667	-3.0838
H	-0.12179	0.342489	1.55516

Electrochemical Studies

Overpotential Calculation

Calculations of $E^{T}_{1/2}$ (= E_{ref}) and η using $E^{o}_{H^+/H_2}$, pK_a, ε_D and $C^{o}_{H_2}$ using Fourmond's approach. +3 Values for $E^{o}_{H^+/H_2}$, pK_a, ε_D and $C^{o}_{H_2}$ were obtained from the same reference.

$$E_{1/2}{}^{T} = E^{0}_{\frac{H^+}{H_2}} - 2.303\frac{RT}{F}pK_a + \varepsilon_D - \frac{RT}{2F}ln\frac{C_0}{C^{0}_{H_2}} \quad (1)$$

2a with 14mM acetic acid in DMF

$$E_{1/2}{}^{T} = (-0.62) - 2.303 \times \frac{8.314 \times 298}{96485} \times 13.5 + 0.040 - \frac{8.314 \times 298}{2 \times 96485} ln \frac{26mM}{1.9mM}$$

$$E_{\frac{1}{2}}{}^{T} = -1.41\ V\ vs\ Fc^{+}/Fc$$

Overpotential (η) = $E_{ref} - E_{cat/2}$ = − 1.41 − (− 2.01) = **0.60 V** $vs\ Fc^{+}/Fc$

2b with 22mM acetic acid in DMF

$$E_{1/2}{}^{T} = (-0.62) - 2.303 \times \frac{8.314 \times 298}{96485} \times 13.5 + 0.040 - \frac{8.314 \times 298}{2 \times 96485} ln \frac{22mM}{1.9mM}$$

$$E_{1/2}{}^{T} = -1.41\ V\ vs\ Fc^{+}/Fc$$

Overpotential (η) = $E_{ref} - E_{cat/2}$ = − 1.41 − (− 2.09) = **0.68 V** $vs\ Fc^{+}/Fc$

2c with 44mM acetic acid in DMF

$$E_{1/2}{}^{T} = (-0.62) - 2.303 \times \frac{8.314 \times 298}{96485} \times 13.5 + 0.040 - \frac{8.314 \times 298}{2 \times 96485} ln \frac{44mM}{1.9mM}$$

$$E_{1/2}{}^{T} = -1.42\ V\ vs\ Fc^{+}/Fc$$

Overpotential (η) = $E_{ref} - E_{cat/2}$ = − 1.42 − (− 2.03) = **0.61 V** $vs\ Fc^{+}/Fc$

2d with 20mM acetic acid in DMF

$$E_{1/2}{}^{T} = (-0.62) - 2.303 \times \frac{8.314 \times 298}{96485} \times 13.5 + 0.040 - \frac{8.314 \times 298}{2 \times 96485} ln \frac{28mM}{1.9mM}$$

$$E_{1/2}{}^{T} = -1.41\ V\ vs\ Fc^{+}/Fc$$

Overpotential (η) = E_{ref} − $E_{cat/2}$ = − 1.41 − (− 2.12) = **0.71 V** $vs\ Fc^{+}/Fc$

Turn over frequency (TOF) calculation:

Table S5. Experimental results from acetic acid titration under cathodic direction

Catalyst	i_{cat} *µA*	i_p *µA*	i_{cat}/i_p	*Scan rate (V/s)*	*TOF* (s^{-1})
2a	695	35	19.8	0.5	382
2b	528	25	21	0.5	427
2c	1043	30	35	0.5	1188
2d	651	27	24	0.5	564

Calculation of Faradaic Efficiency (F.E.):

Table S6. Experimental results from controlled-potential coulometry experiment

Catalyst	*Coulombs (C)**	*Exp. moles of* H_2 *(*$\times 10^{-3}$ *moles)**	*% Faradaic Efficiency*
2a	9.1	0.040	84
2b	2.2	0.0053	47
2c	12.1	0.056	89
2d	3.5	0.091	50

* Values are obtained after subtracting the background charge and moles.

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