Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Effect of Ligand Substituents on Nickel and Copper [N_4] Complexes: Electronic and Redox Behavior, and Reactivity towards Protons

Pavithra H. A. Kankanamalage,[a],† Danushka M. Ekanayake,[a],† Nirupama Singh,[b],‡ Ana C. P. de Morais,[c],‡ Shivnath Mazumder,[d],* Cláudio N. Verani[a],*, Anusree Mukherjee,[b],* Mauricio Lanznaster,[c],*

[a] Department of Chemistry, Wayne State University, Detroit, MI 48202, USA. E-mail: claudio.verani@wayne.edu
[b] Department of Chemistry, University of Alabama, Huntsville, AL 35899, USA. E-mail: am0095@uah.edu
[c] Instituto de Química, Universidade Federal Fluminense, 24020-141, Niterói, RJ, Brazil. E-mail: ml@id.uff.br
[d] Department of Chemistry, Indian Institute of Technology Jammu, Jammu (J&K) -181221, India
Email: shivnath.mazumder@iitjammu.ac.in

†, ‡ Authors contributed equally to the manuscript

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Supplementary Information

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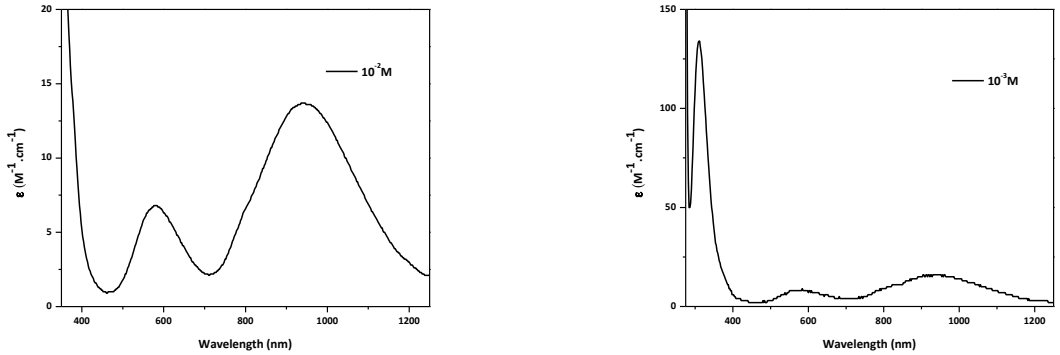


Figure S1. UV-visible absorption spectra of **1** in MeOH.

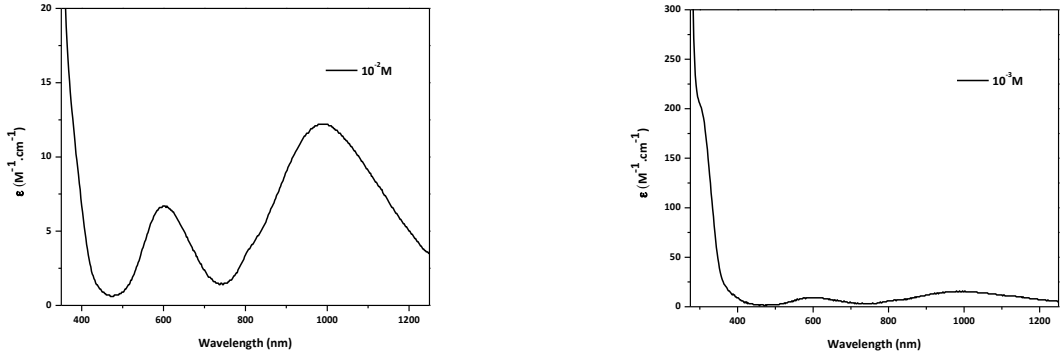


Figure S2. UV-visible absorption spectra of **2** in MeOH.

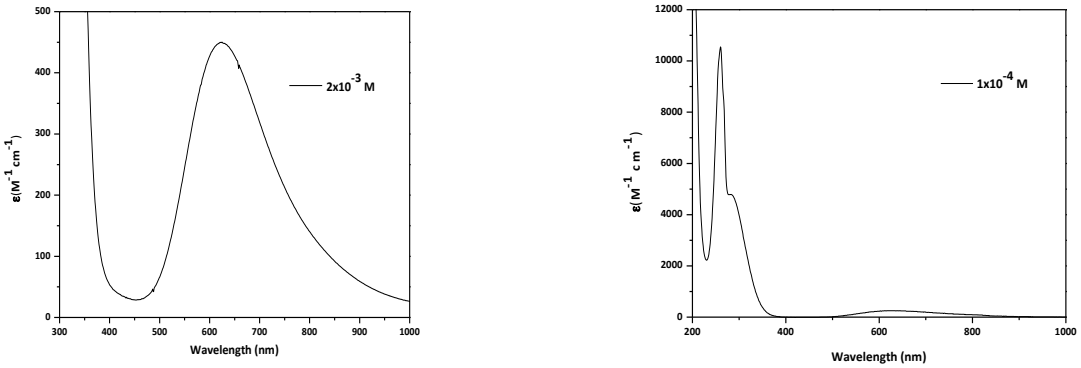
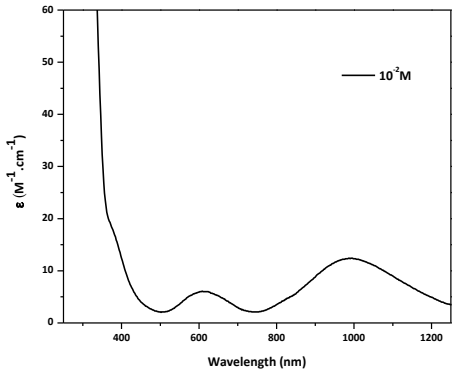


Figure S3. UV-visible absorption spectra of **3** in MeCN.



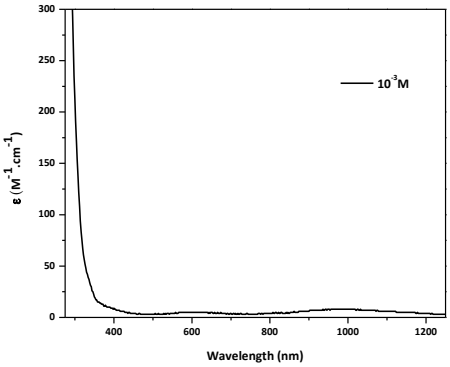
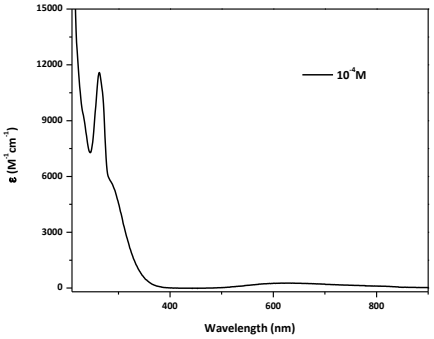


Figure S4. UV-visible absorption spectra of **4** in MeOH.



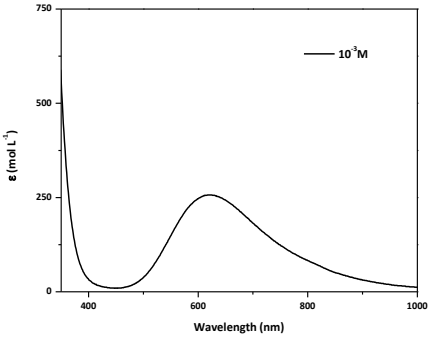


Figure S5. UV-visible absorption spectra of **5** in MeCN.

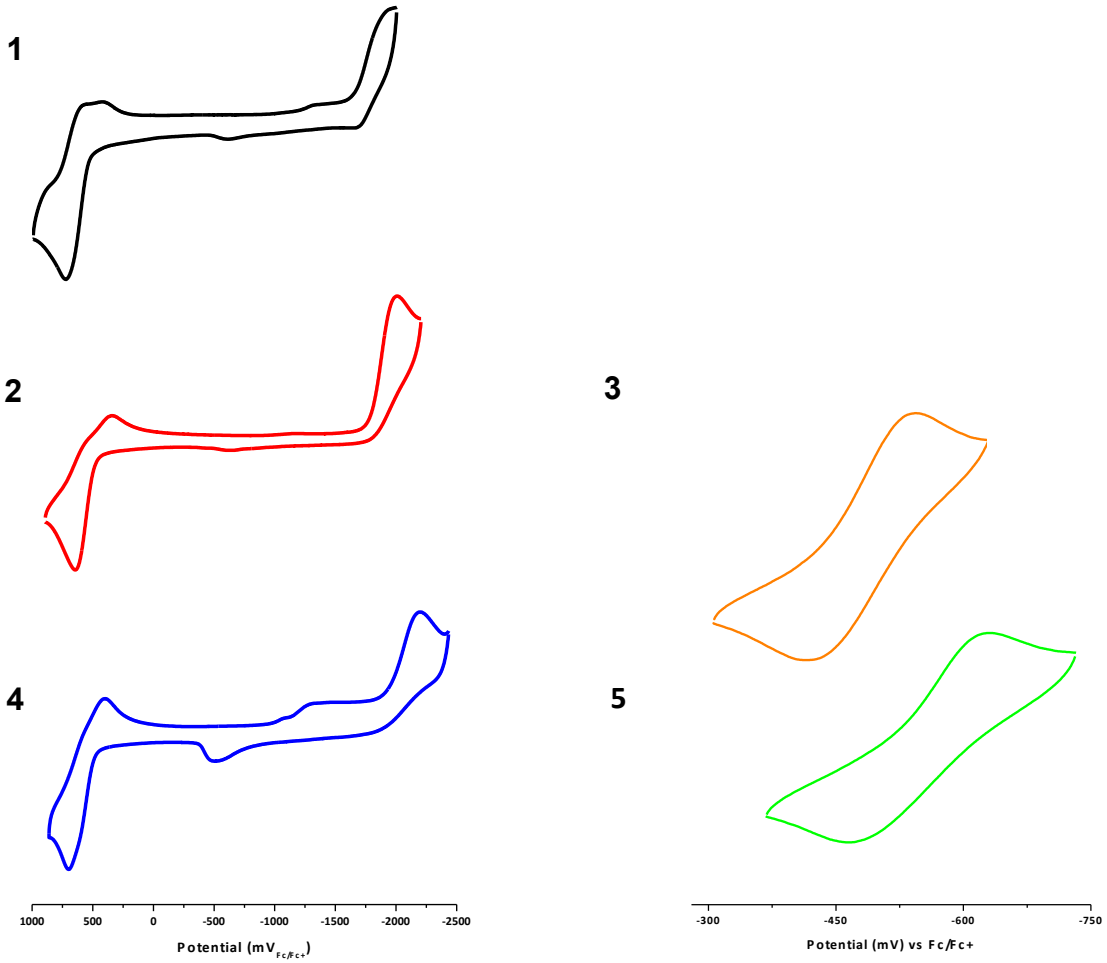


Figure S6. Left: Cyclic voltammograms in acetonitrile for complexes **1** (black), **2** (red) and **4** (blue). Right: Cyclic voltammograms in acetonitrile for complexes **3** (orange) and **5** (green).

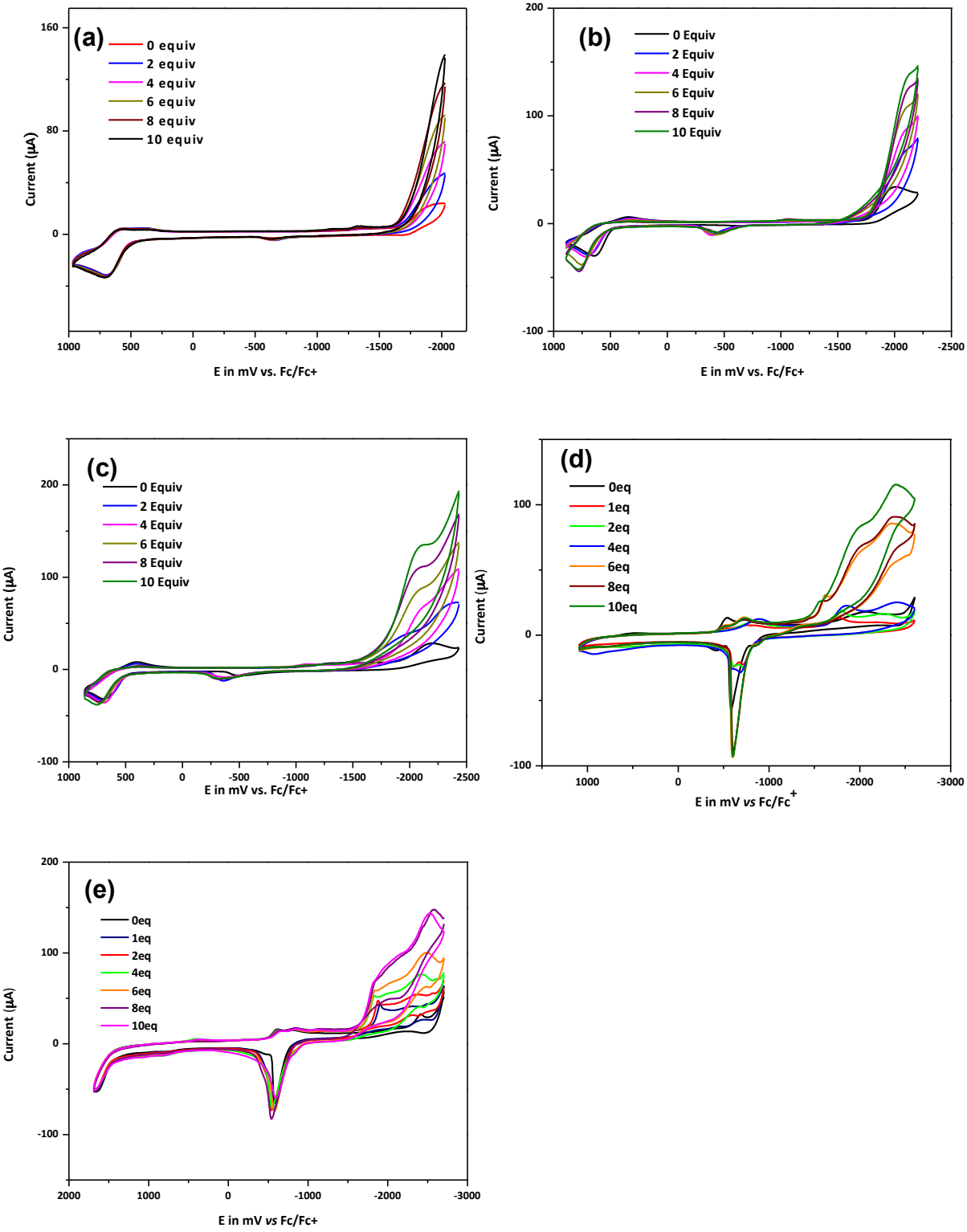


Figure S7. Cyclic voltammograms of **1-5** in MeCN, $TBAPF_6$ (0.1 M) with 0-10 equiv. of acetic acid. (**a**) Complex **1**, (**b**) complex **2**, (**c**) complex **4**, (**d**) complex **3**, (**e**) complex **5**. Electrodes: C_{glassy} (W), Ag/AgCl (R), Pt wire (A). The spike observed at -590mV for complexes **3** and **5** is attributed to Cu^{I}/Cu^{0} couple.[1]

[1] M. Kugler, J. Scholz, A. Kronz, I. Siewert, *Dalton Trans.* 2016, **45**(16), 6974-6982. D. M. Ekanayake, K. M. Kulesa, J. Singh, K. K. Kpogo, S. Mazumder, H. B. Schlegel, C. N. Verani, *Dalton Trans.* 2017, **46**, 16812-16820.

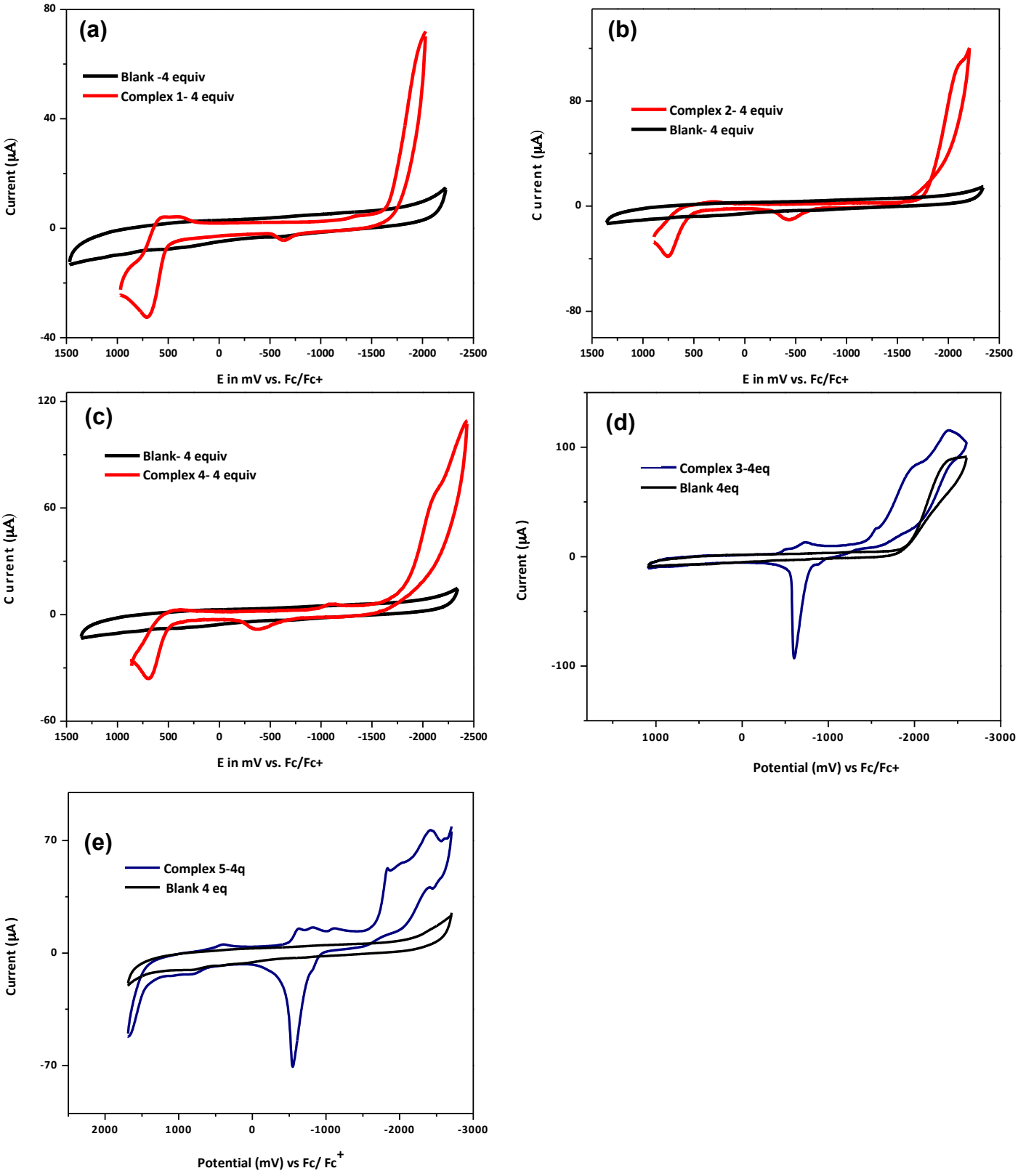


Figure S8. Cyclic Voltammograms of **1-5** in MeCN with and without complexes upon addition of four equivalent of acid. (**a**) Complex **1**, (**b**) complex **2**, (**c**) complex **4**, (**d**) complex **3**, (**e**) complex **5**. Electrodes: C_{glassy} (W), Ag/AgCl (R), Pt wire (A).

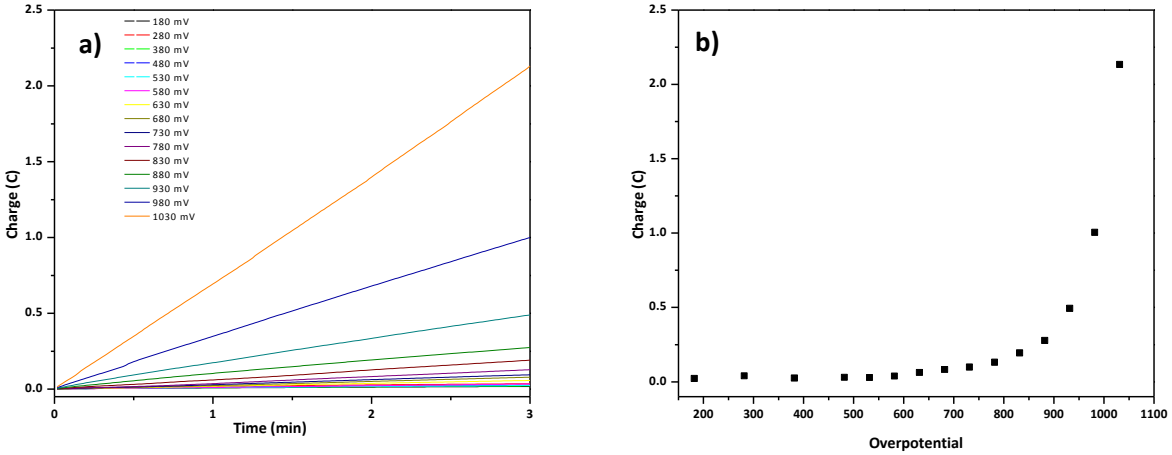


Figure S9. (**a**) Charge *vs*. overpotential plot at various overpotentials over 3 min intervals. (**b**) Charge accumulation (3 min.) *vs*. time plot; 0.1 µmol of **1;** Electrodes: Hg pool (W), Ag/AgCl (R), Pt wire (A). Onset Overpotential = 78 mV.

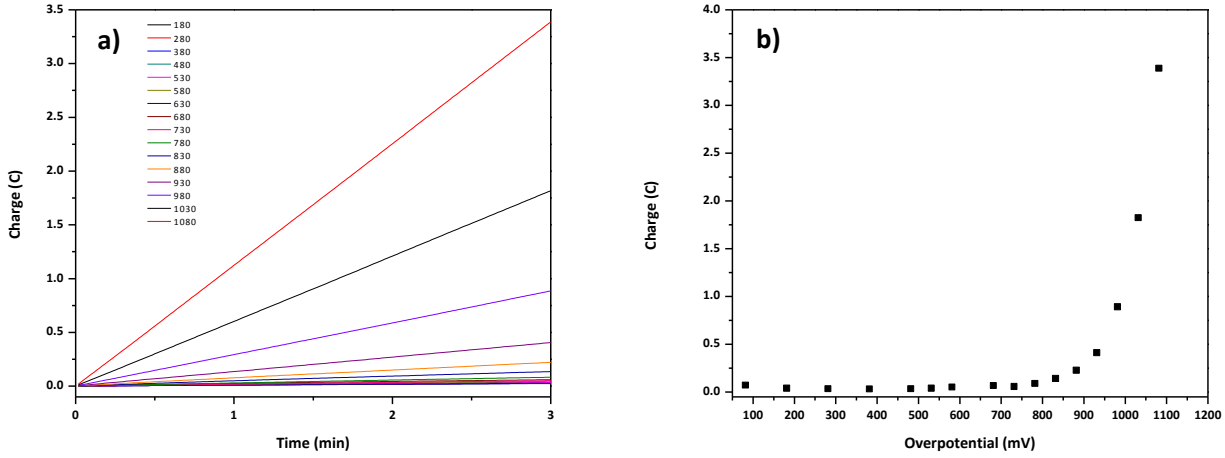


Figure S10. (**a**) Charge *vs*. overpotential plot at various overpotentials over 3 min intervals. (**b**) Charge accumulation (3 min.) *vs*. time plot; 0.1 µmol of **2**; Electrodes: Hg pool (W), Ag/AgCl (R), Pt wire (A). Onset Overpotential = 833 mV.

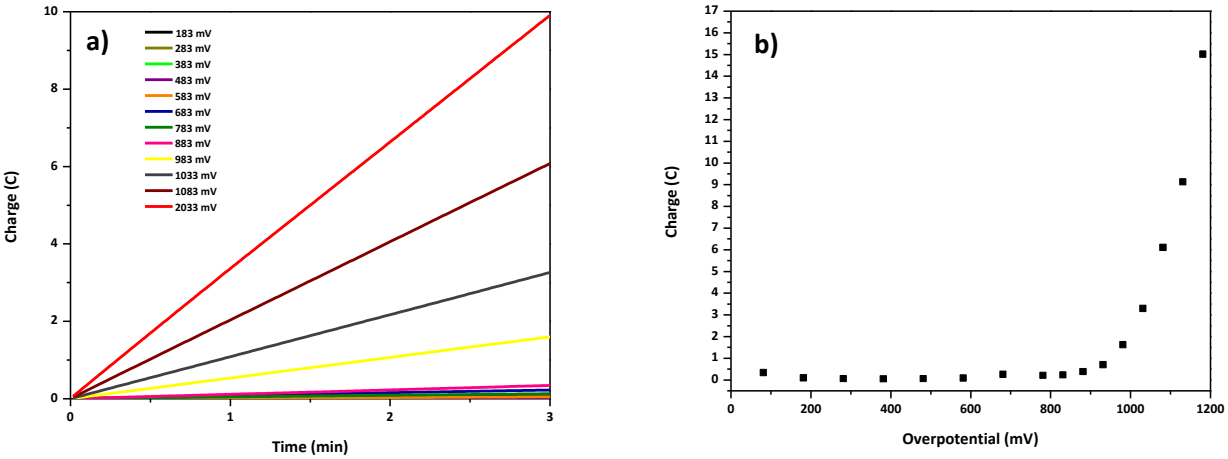


Figure S11. (**a**) Charge *vs*. overpotential plot at various overpotentials over 3 min intervals. (**b**) Charge accumulation (3 min.) *vs*. time plot; 0.1 µmol of **3**; Electrodes: Hg pool (W), Ag/AgCl (R), Pt wire (A). Onset overpotetntial = 883mV.

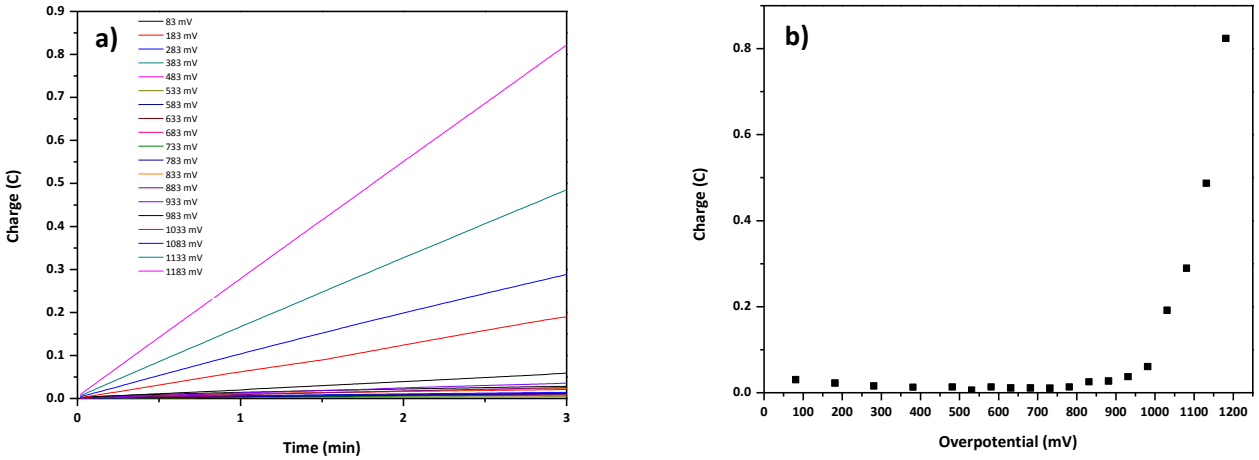


Figure S12. (**a**) Charge *vs*. overpotential plot at various overpotentials over 3 min intervals. (**b**) Charge accumulation (3 min.) *vs*. time plot; 0.1 μmol of **4** Electrodes: Hg pool (W), Ag/AgCl (R), Pt wire (A). Onset Overpotential = 983 mV.

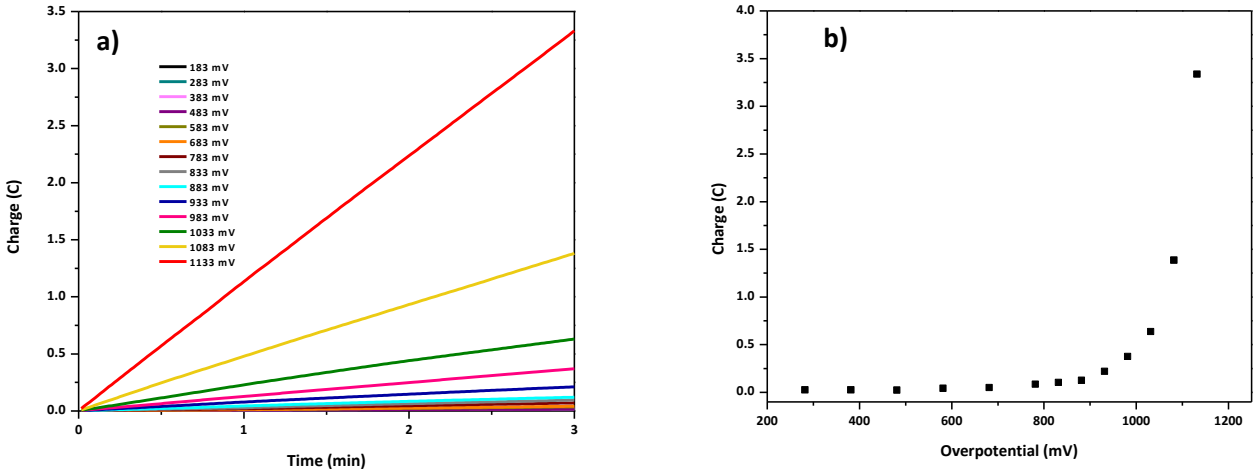


Figure S13. (**a**) Charge *vs*. overpotential plot at various overpotentials over 3 min intervals. (**b**) Charge accumulation (3 min.) *vs*. time plot; 0.1 μmol of **5**; Electrodes: Hg pool (W), Ag/AgCl (R), Pt wire (A). Onset Overpotential = 933 mV.

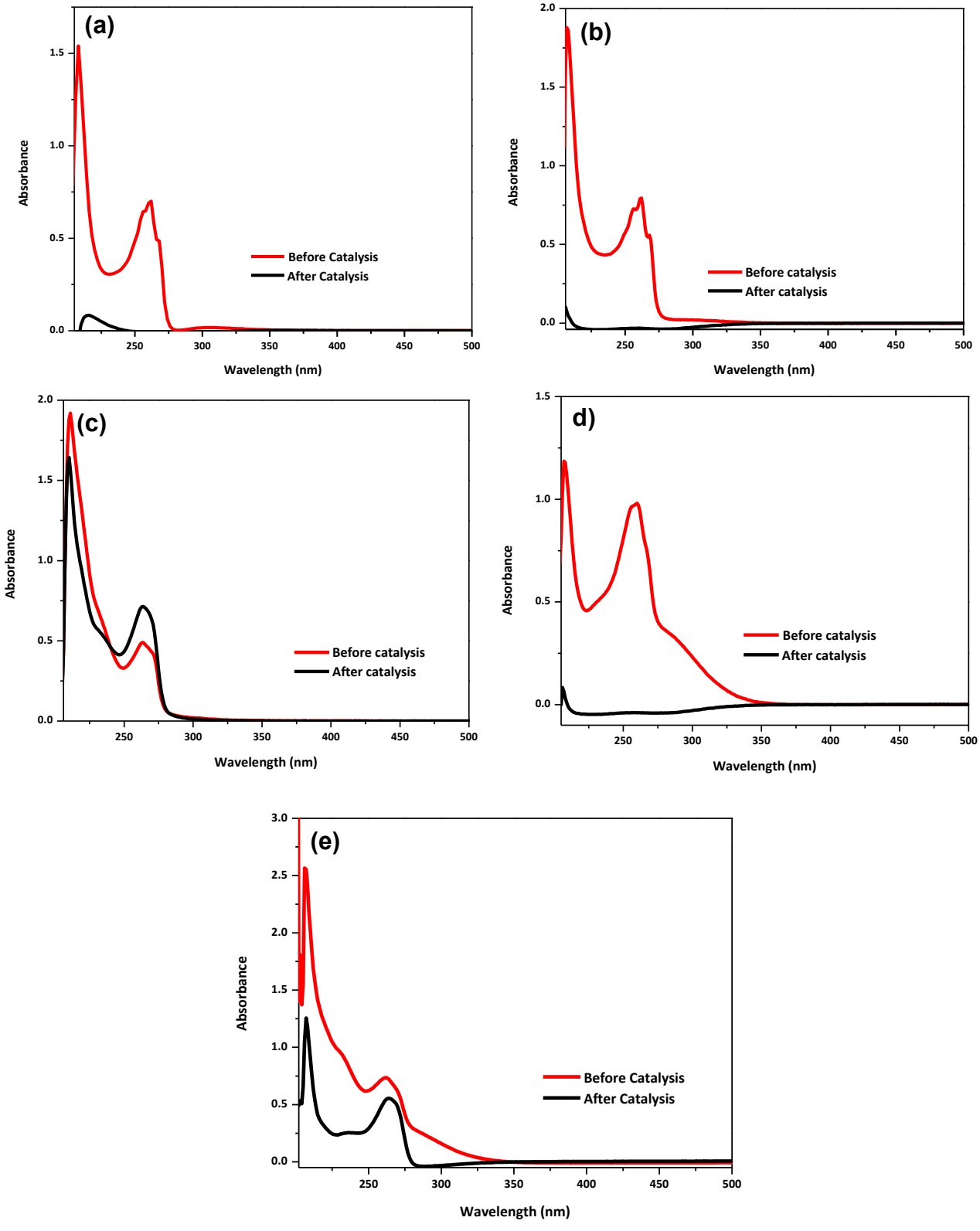


Figure S14. UV-Visible spectra for complex **1**-**5** before and after catalysis: (**a**) Complex **1**, (**b**) complex **2**, (**c**) complex **4**, (**d**) complex **3**,(**e**) complex **5**.

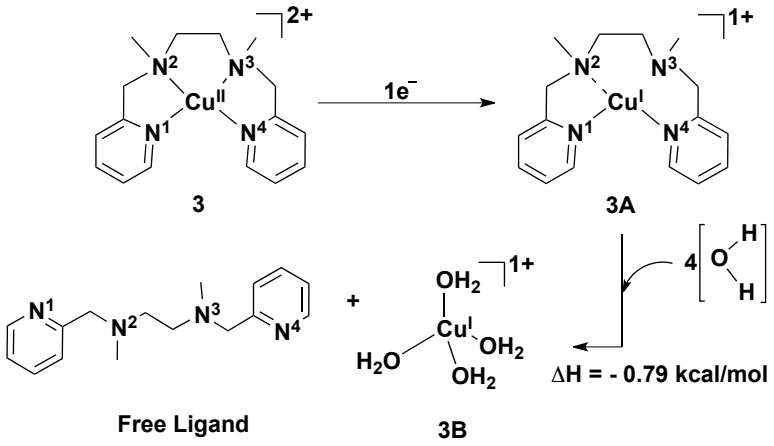


Figure S15. DFT calculated mechanistic pathway for the decomposition of Cu catalyst **3** in water. The formation of 3B has been calculated from four monomeric water molecules. The ΔG for this process is calculated to be +20.57 kcal/mol. However, in solution, it is expected that the four water molecules will not be monomeric. Rather they are known to form a single tetramer complex, $(H_2O)_4$. Therefore, it is more appropriate that the formation of 3B should be considered from a single tetrameric complex, $(H_2O)_4$, rather than four monomeric water molecules, $4H_2O$. When considered the formation of 3B from $(H_2O)_4$, the process will not be considerably affected by entropy. Therefore, the DFT-calculated ΔG (= +20.57 kcal/mol) is only an upper limit for the formation of 3B and, in actual case, ΔG will be considerably less than this value.

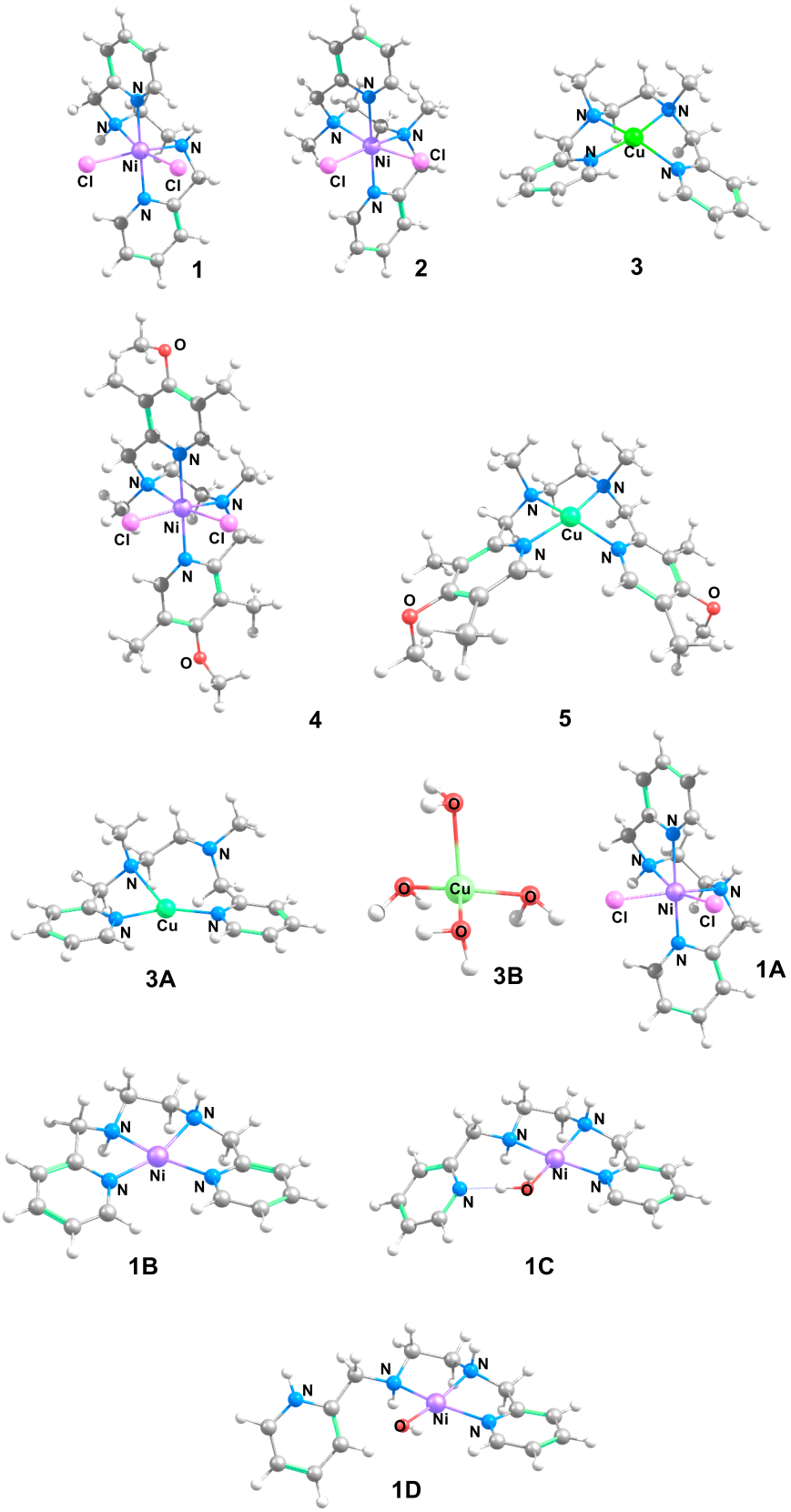


Figure S16. DFT calculated optimized geometries of the intermediates and catalytic complexes.

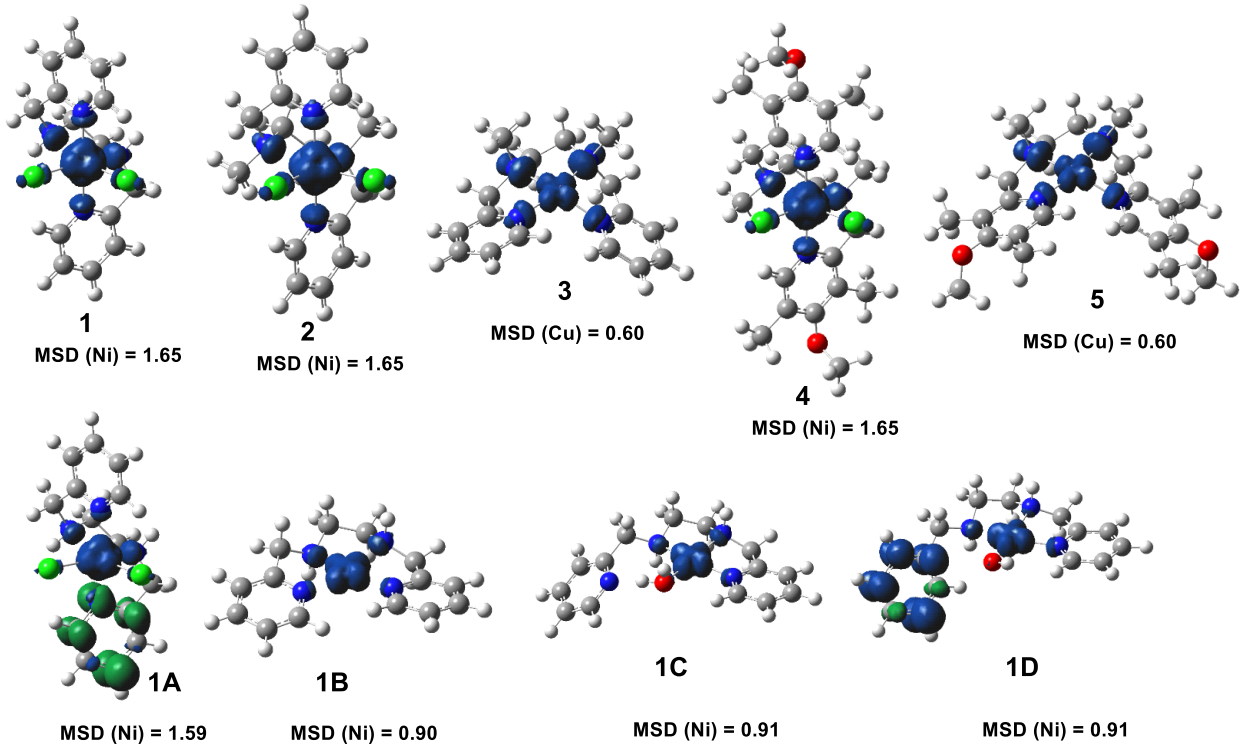
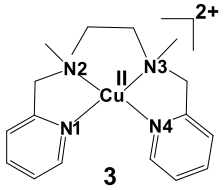


Figure S17. DFT calculated spin density plots (isodensity = 0.004 au) with Mulliken Spin Density (MSD) values on the metal atoms of the intermediates and catalytic complexes.

Table S1. Comparison of DFT and crystallographic structures of catalyst **3.**

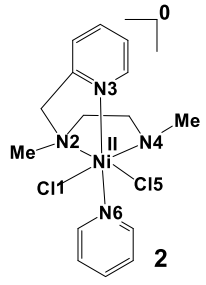
Bond	Bond Distance (Å) DFT	Bond Distance (Å) Crystal	Difference (Å)
Cu-N1	2.041	2.000	0.041
Cu-N2	2.063	2.028	0.035
Cu-N3	2.059	2.031	0.028
Cu-N4	2.060	2.000	0.060



3

Table S2. Comparison of DFT and crystallographic structures of catalyst **2.**

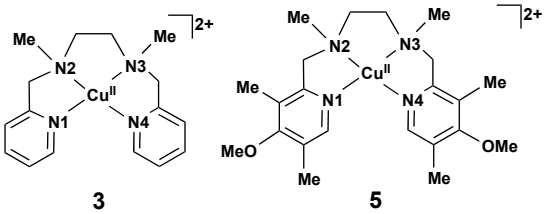
Bond	Bond Distance (Å) DFT	Bond Distance (Å) Crystal	Difference (Å)
Ni-Cl1	2.484	2.433	0.051
Ni-N2	2.225	2.160	0.065
Ni-N3	2.141	2.094	0.047
Ni-N4	2.226	2.160	0.066
Ni-Cl5	2.487	2.433	0.054
Ni-N6	2.142	2.094	0.048



2

Table S3. Comparison of DFT-calculated structures of **3** and **5.**

Bond	Bond Distance (Å) Complex 3	Bond Distance (Å) Complex 5
Cu-N1	2.041	2.038
Cu-N2	2.063	2.058
Cu-N3	2.059	2.055
Cu-N4	2.060	2.056

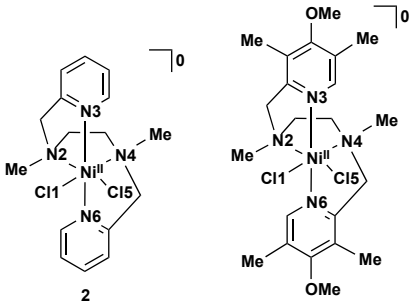


3 **5**

***** Comparison of the structures of **3** and **5** shows that ligand L3 in complex **5** has better coordination ability compared to the parent ligand L2 in complex **3**. The metal-ligand bond distances in case of L3 are shorter than the distances in case of L2 (Table S3). However, the differences in the metal-ligand bond distances are not very prominent between L3 and L2. Ligand L3 has larger steric impedance than L2, this factor tends to increase the metal-ligand bond distances in case of L3 than L2. On the other hand, L3 being electron richer has better coordination ability than L2, this factor tends to decrease the metal-ligand bond distances in case L3 than L2. Therefore, overall there is only a slight decrease of the metal-ligand bond distances from L2 to L3.

Table S4. Comparison of DFT-calculated structures of **2** and **4.**

Bond	Bond Distance (Å) Complex 3	Bond Distance (Å) Complex 5
Ni-N2	2.225	2.208
Ni-N3	2.141	2.143
Ni-N4	2.226	2.213
Ni-N6	2.142	2.139



2 **4**

Table S5. Coordinates of the DFT-calculated geometries.

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1

C	0.477230000	0.166811000	-2.170048000
C	-0.670328000	1.103127000	-1.835470000
C	1.421932000	-3.794648000	-1.466510000
C	0.557966000	-4.863799000	-1.241252000
C	2.044830000	-1.363113000	-1.066050000
C	1.132435000	-2.555064000	-0.894588000
C	-0.578441000	-4.659671000	-0.457718000
C	-0.802065000	-3.393342000	0.072627000
C	-2.269219000	1.554647000	-0.029829000
C	-1.378305000	2.331148000	0.912562000
C	-1.679583000	3.636393000	1.304639000
C	-0.835898000	4.287114000	2.201773000
C	0.529536000	2.319346000	2.232782000
C	0.294038000	3.617507000	2.673112000
H	1.103670000	0.596809000	-2.960780000
H	-1.281308000	1.292429000	-2.726173000
H	0.079906000	-0.780894000	-2.546261000
H	2.310252000	-3.908426000	-2.079281000
H	2.577722000	-1.431246000	-2.022746000
H	0.763603000	-5.836960000	-1.676400000
H	-0.273193000	2.066034000	-1.499343000
H	-2.770497000	2.240740000	-0.724243000
H	-1.282363000	-5.460948000	-0.261370000
H	2.785791000	-1.367791000	-0.261221000
H	-1.662863000	-3.173822000	0.695614000
H	-3.037907000	1.041137000	0.554982000
H	-2.561638000	4.126855000	0.905894000
H	-1.051776000	5.302042000	2.521059000
H	1.384820000	1.743417000	2.570948000
H	0.982692000	4.087214000	3.366829000
Cl	-2.017919000	-1.026358000	2.178069000
Cl	1.734842000	-0.857555000	2.281639000
N	1.265779000	-0.120014000	-0.948920000
N	-1.480368000	0.531188000	-0.734363000
N	0.034516000	-2.361558000	-0.137252000
N	-0.289334000	1.685556000	1.374711000
Ni	-0.124904000	-0.372030000	0.711767000
H	1.899450000	0.654091000	-0.762108000
H	-2.108850000	-0.177700000	-1.106119000

==========

1A

C	0.392775000	0.199806000	-2.218498000
C	-0.720854000	1.170713000	-1.859579000
C	1.537771000	-3.808946000	-1.334652000
C	0.750742000	-4.964017000	-1.055424000
C	1.990994000	-1.336520000	-1.151812000
C	1.105480000	-2.553761000	-0.970894000
C	-0.472531000	-4.730437000	-0.371675000
C	-0.862519000	-3.448994000	-0.055949000
C	-2.284877000	1.638418000	-0.026012000
C	-1.359099000	2.360280000	0.928096000
C	-1.601372000	3.676445000	1.329687000
C	-0.736105000	4.278753000	2.240143000
C	0.528948000	2.245634000	2.262865000
C	0.354655000	3.550009000	2.716236000
H	1.006180000	0.612966000	-3.030637000
H	-1.320824000	1.409996000	-2.747785000
H	-0.037288000	-0.739618000	-2.576548000
H	2.499891000	-3.904038000	-1.835937000
H	2.524027000	-1.383120000	-2.113275000
H	1.080544000	-5.960693000	-1.327200000
H	-0.282462000	2.109576000	-1.504330000
H	-2.779987000	2.365086000	-0.685037000
H	-1.127914000	-5.557574000	-0.105358000
H	2.744263000	-1.307035000	-0.357517000
H	-1.799813000	-3.254215000	0.456347000
H	-3.056838000	1.130299000	0.560152000
H	-2.454514000	4.213088000	0.926599000
H	-0.905325000	5.300711000	2.565745000
H	1.353721000	1.626088000	2.602290000
H	1.059313000	3.979444000	3.420412000
Cl	-2.198085000	-1.044809000	2.106862000
Cl	1.636752000	-0.997309000	2.278774000
N	1.203868000	-0.099529000	-1.021707000
N	-1.548135000	0.611785000	-0.771004000
N	-0.126479000	-2.308337000	-0.368160000
N	-0.308186000	1.658062000	1.391029000
Ni	-0.189825000	-0.475599000	0.650880000
H	1.832537000	0.680069000	-0.844829000
H	-2.205179000	-0.064009000	-1.151336000

==========

1B

C	0.015121000	0.302423000	-3.257205000
C	-0.134705000	1.730566000	-2.723765000
C	1.352572000	-3.895802000	-0.878935000
C	1.599377000	-4.441280000	0.379302000
C	0.538879000	-1.970845000	-2.320715000
C	0.851506000	-2.598502000	-0.976703000
C	1.352406000	-3.661190000	1.508851000
C	0.858283000	-2.373883000	1.333179000
C	-0.750984000	2.836988000	-0.548431000
C	-1.108613000	2.424745000	0.865881000
C	-1.677236000	3.324902000	1.765562000
C	-1.962697000	2.907509000	3.064136000
C	-1.119976000	0.746889000	2.469082000
C	-1.680636000	1.589375000	3.421987000
H	0.550021000	0.309838000	-4.215170000
H	-0.636873000	2.362145000	-3.467541000
H	-0.974537000	-0.133536000	-3.430365000
H	1.548506000	-4.462151000	-1.783713000
H	-0.507824000	-2.177986000	-2.574351000
H	1.988747000	-5.449944000	0.475206000
H	0.854690000	2.159896000	-2.533064000
H	0.292079000	3.175393000	-0.566564000
H	1.541208000	-4.034728000	2.509253000
H	1.158105000	-2.430986000	-3.100728000
H	0.669732000	-1.732415000	2.186822000
H	-1.371691000	3.686513000	-0.859393000
H	-1.894686000	4.337653000	1.442242000
H	-2.405911000	3.594422000	3.778212000
H	-0.903621000	-0.288760000	2.706887000

H	-1.894761000	1.211803000	4.415748000
N	0.701939000	-0.512905000	-2.235224000
N	-0.864800000	1.676417000	-1.442097000
N	0.598815000	-1.844002000	0.120343000
N	-0.826856000	1.145132000	1.214220000
Ni	-0.094143000	0.038419000	-0.363825000
H	1.697140000	-0.291262000	-2.255755000
H	-1.851249000	1.501728000	-1.632116000

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1C

C	0.218446000	0.452648000	-3.039746000
C	0.057708000	1.799272000	-2.345627000
C	1.433839000	-4.049248000	-1.218141000
C	1.529118000	-4.785882000	-0.038764000
C	0.765980000	-1.912511000	-2.423168000
C	0.949114000	-2.742926000	-1.169298000
C	1.140488000	-4.189014000	1.161466000
C	0.675245000	-2.879491000	1.132285000
C	-0.794341000	2.940864000	-0.358258000
C	-2.009309000	3.060193000	0.532364000
C	-3.037105000	3.954954000	0.221397000
C	-4.138933000	4.054258000	1.070687000
C	-3.127639000	2.381071000	2.446567000
C	-4.187351000	3.252655000	2.209610000
H	0.784353000	0.577902000	-3.971983000
H	-0.409606000	2.519718000	-3.029925000
H	-0.764902000	0.045421000	-3.298649000
H	1.731838000	-4.475025000	-2.170868000
H	-0.240739000	-2.096705000	-2.817806000
H	1.903841000	-5.804467000	-0.055598000
H	1.041182000	2.195544000	-2.069512000
H	0.117645000	3.033763000	0.239707000
H	1.200012000	-4.721298000	2.104431000
H	1.478560000	-2.230050000	-3.194053000
H	0.366643000	-2.373171000	2.041119000
H	-0.810975000	3.777427000	-1.067349000
H	-2.967290000	4.564426000	-0.673307000
H	-4.944234000	4.746305000	0.844857000
H	-3.122993000	1.732521000	3.318611000
H	-5.022584000	3.295540000	2.900012000
N	0.868751000	-0.481190000	-2.103020000
N	-0.739223000	1.647469000	-1.099120000
N	0.576764000	-2.162641000	-0.005300000
N	-2.062922000	2.287287000	1.635203000
Ni	0.021542000	-0.188018000	-0.221188000
H	1.854853000	-0.231999000	-2.025994000
H	-1.693659000	1.428332000	-1.390136000
O	-0.504595000	0.113102000	1.774762000
H	0.319353000	0.282098000	2.255528000
H	-1.024412000	0.976166000	1.803048000

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1D

C	0.286989000	0.448174000	-2.993493000
C	0.097740000	1.806099000	-2.331109000
C	1.515477000	-4.073730000	-1.273121000
C	1.642203000	-4.855038000	-0.126047000
C	0.780226000	-1.910290000	-2.380693000
C	0.999466000	-2.782217000	-1.164282000
C	1.252471000	-4.315458000	1.100572000
C	0.756168000	-3.017006000	1.126743000
C	-0.914418000	2.952914000	-0.436855000
C	-2.095596000	3.024729000	0.491532000
C	-3.073573000	2.084390000	0.671886000
C	-4.171019000	2.309176000	1.555851000
C	-3.268166000	4.503165000	2.035684000
C	-4.244843000	3.564838000	2.216489000
H	0.911906000	0.550464000	-3.890363000
H	-0.316348000	2.517883000	-3.059866000
H	-0.684407000	0.051324000	-3.308947000
H	1.812097000	-4.453264000	-2.245796000
H	-0.230346000	-2.095455000	-2.765797000
H	2.040641000	-5.862941000	-0.187712000
H	1.066001000	2.200960000	-2.002484000
H	0.008129000	3.136521000	0.130867000
H	1.333505000	-4.883170000	2.021170000
H	1.484272000	-2.186248000	-3.175963000
H	0.443596000	-2.561241000	2.061453000
H	-0.996364000	3.788739000	-1.155366000
H	-3.005814000	1.145757000	0.131863000
H	-4.939783000	1.556931000	1.686412000
H	-3.269100000	5.479105000	2.503798000
H	-5.078166000	3.801671000	2.871331000
N	0.865760000	-0.488827000	-2.012544000
N	-0.773333000	1.670358000	-1.144312000
N	0.627538000	-2.255244000	0.023030000
N	-2.158074000	4.218164000	1.231358000
Ni	0.034577000	-0.202846000	-0.121332000
H	1.850558000	-0.250922000	-1.890670000
H	-1.695532000	1.402738000	-1.489447000
O	-0.428869000	0.217049000	1.730734000
H	0.060070000	-0.408552000	2.280666000
H	-1.559387000	4.984339000	0.953253000

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3

Cu	1.512700000	3.265475000	9.993328000
N	1.110789000	4.714558000	8.586019000
C	0.031708000	5.507345000	8.443463000
H	-0.788501000	5.342625000	9.131722000
C	-0.035323000	6.495025000	7.469153000
H	-0.922441000	7.112688000	7.389774000
C	1.051200000	6.665206000	6.610501000
H	1.029303000	7.425542000	5.836343000
C	2.164873000	5.840847000	6.753370000
H	3.025326000	5.935330000	6.099921000
C	2.166277000	4.874464000	7.756136000
C	3.359376000	3.984834000	8.010439000
H	3.919154000	3.811260000	7.084205000
H	4.031241000	4.487830000	8.713933000
N	2.931632000	2.698329000	8.613114000
C	4.041136000	2.015142000	9.351543000
H	5.004668000	2.230986000	8.878506000
H	3.876348000	0.939597000	9.273461000
C	4.058850000	2.454230000	10.812054000
H	4.787953000	1.861827000	11.378351000
H	4.343246000	3.507175000	10.885431000
N	2.694599000	2.316436000	11.392782000
C	2.496852000	3.106943000	12.631498000
H	3.083333000	4.027844000	12.550881000
H	2.853181000	2.560458000	13.511961000
C	1.036850000	3.468071000	12.780120000
C	0.437072000	3.677697000	14.018737000
H	1.018219000	3.546460000	14.924949000
C	-0.904347000	4.052163000	14.066180000
H	-1.389637000	4.225249000	15.021349000
C	-1.617254000	4.188163000	12.874283000
H	-2.664940000	4.465524000	12.868497000
C	-0.958057000	3.956179000	11.673876000
H	-1.471678000	4.034858000	10.722650000

N	0.342969000	3.614458000	11.628725000
C	2.343283000	1.803095000	7.585871000
H	3.112120000	1.486895000	6.870833000
H	1.552353000	2.326224000	7.045920000
H	1.918210000	0.924358000	8.073986000
C	2.310174000	0.900491000	11.612920000
H	3.016762000	0.421875000	12.301649000
H	2.300713000	0.355152000	10.669043000
H	1.308417000	0.858423000	12.043423000

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3A

Cu	0.875505000	4.227930000	10.329342000
N	0.998824000	4.950476000	8.510997000
C	-0.081280000	5.595949000	8.018531000
H	-0.940632000	5.661326000	8.676265000
C	-0.110130000	6.161198000	6.749393000
H	-1.004406000	6.670200000	6.408013000
C	1.027282000	6.063135000	5.951096000
H	1.047081000	6.495494000	4.955744000
C	2.143660000	5.397158000	6.454324000
H	3.048993000	5.301530000	5.864837000
C	2.106397000	4.842535000	7.733876000
C	3.290514000	4.106855000	8.313925000
H	4.198015000	4.381839000	7.751001000
H	3.423717000	4.462355000	9.337013000
N	3.085862000	2.649816000	8.336001000
C	3.940376000	1.979002000	9.326141000
H	5.012919000	2.109865000	9.088259000
H	3.742746000	0.905919000	9.242487000
C	3.772361000	2.425382000	10.781149000
H	4.408296000	1.754841000	11.386539000
H	4.180304000	3.431386000	10.916329000
N	2.391728000	2.440092000	11.297138000
C	2.377579000	2.993126000	12.658675000
H	3.018010000	3.883632000	12.670576000
H	2.793214000	2.289424000	13.397056000
C	0.993764000	3.415798000	13.097493000
C	0.546305000	3.211074000	14.402477000
H	1.184083000	2.688382000	15.107381000
C	-0.710710000	3.678654000	14.779957000
H	-1.071731000	3.527625000	15.792386000
C	-1.497013000	4.337168000	13.834907000
H	-2.482500000	4.717239000	14.079353000
C	-0.992158000	4.501308000	12.551274000
H	-1.567450000	5.007183000	11.783888000
N	0.228153000	4.054882000	12.184755000
C	3.323322000	2.077302000	7.008877000
H	4.362139000	2.221935000	6.663005000
H	2.654784000	2.535573000	6.274881000
H	3.115103000	1.003495000	7.028071000
C	1.795594000	1.095842000	11.299137000
H	2.387925000	0.383932000	11.898141000
H	1.715146000	0.709510000	10.281504000
H	0.787014000	1.139968000	11.718707000

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3B

Cu	-2.787319000	-0.868968000	-1.381709000
O	-2.388734000	-0.032251000	-3.244540000
H	-2.540183000	0.922817000	-3.183658000
O	-5.045850000	-0.910283000	-1.379096000
H	-5.285053000	-0.768526000	-0.451429000
O	-2.438130000	-0.220351000	0.655045000
H	-1.816653000	-0.859821000	1.033925000
O	-2.064121000	-2.910754000	-0.950921000
H	-1.644059000	-3.241681000	-1.758204000
H	-1.436724000	-0.114582000	-3.403555000
H	-5.288534000	-0.079143000	-1.812797000
H	-1.325226000	-2.772109000	-0.339461000
H	-1.934712000	0.605813000	0.613148000

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2

C	0.424851000	0.242565000	-2.140379000
C	-0.732575000	1.128498000	-1.709031000
C	1.508362000	-3.610915000	-1.428724000
C	2.166868000	-1.169693000	-1.197277000
C	0.704914000	-4.678612000	-1.035246000
C	2.369626000	1.229669000	-1.040615000
C	-2.405283000	-0.438956000	-0.863855000
C	1.301442000	-2.356460000	-0.852835000
C	-0.289582000	-4.459555000	-0.081626000
C	-2.053197000	1.665353000	0.264425000
C	-0.438818000	-3.179947000	0.442450000
C	-1.035129000	2.531270000	0.964181000
C	-1.276561000	3.878903000	1.236208000
C	-0.318116000	4.612877000	1.931068000
C	1.033670000	2.636896000	2.009568000
C	0.860820000	3.980175000	2.326378000
H	0.897631000	0.656882000	-3.041283000
H	-1.451821000	1.232098000	-2.532877000
H	0.052834000	-0.750790000	-2.402017000
H	2.574470000	-1.276589000	-2.211987000
H	2.285836000	-3.737533000	-2.174803000
H	2.978140000	1.241543000	-1.956198000
H	0.848363000	-5.662820000	-1.470117000
H	-0.366390000	2.131720000	-1.477791000
H	-3.230504000	0.006924000	-1.437083000
H	-1.942807000	-1.219029000	-1.470594000
H	1.825483000	2.173042000	-0.974377000
H	3.008446000	-1.140624000	-0.498015000
H	-2.696110000	2.278653000	-0.382069000
H	3.026133000	1.141919000	-0.173330000
H	-2.801695000	-0.892589000	0.046075000
H	-0.941932000	-5.259469000	0.250632000
H	-2.687375000	1.197387000	1.023774000
H	-2.201835000	4.336743000	0.902598000
H	-1.188859000	-2.947777000	1.190882000
H	-0.485889000	5.661873000	2.154182000
H	1.926336000	2.089601000	2.292985000
H	1.637005000	4.512738000	2.864669000
Cl	2.298541000	-0.506142000	2.158258000
Cl	-1.386285000	-0.743796000	2.607744000
N	1.422544000	0.097534000	-1.046935000
N	-1.402177000	0.580620000	-0.498106000
N	0.340800000	-2.150089000	0.069514000
N	0.105623000	1.924421000	1.347102000
Ni	0.236931000	-0.147298000	0.820187000

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4

C	0.493523000	0.164745000	-2.090661000
C	-0.697926000	1.060062000	-1.792518000
C	1.414630000	-3.792089000	-1.438407000
C	0.509349000	-4.839072000	-1.207722000
C	2.033238000	-1.360214000	-0.992672000
C	1.108761000	-2.548195000	-0.859718000
C	-0.659707000	-4.638995000	-0.456373000
C	-0.857009000	-3.364495000	0.065488000
C	-2.309463000	1.524345000	-0.031883000
C	-1.409218000	2.304695000	0.898423000
C	-1.700018000	3.628408000	1.270998000
C	-0.817087000	4.243904000	2.171707000
C	0.498935000	2.262032000	2.218913000
C	0.315737000	3.570060000	2.656178000
H	1.117578000	0.619634000	-2.871950000
H	-1.273083000	1.233147000	-2.712320000
H	0.146581000	-0.796655000	-2.475945000
H	2.581485000	-1.390955000	-1.942476000
H	-0.350310000	2.034506000	-1.441702000
H	-2.804844000	2.189916000	-0.749890000
H	2.769826000	-1.403701000	-0.183849000
H	-1.726452000	-3.135701000	0.673443000
H	-3.090359000	1.043072000	0.565575000
H	1.340862000	1.669221000	2.561973000
Cl	-2.075274000	-1.043564000	2.230642000
Cl	1.636378000	-0.934484000	2.379738000
N	1.296866000	-0.085056000	-0.863149000
N	-1.564554000	0.462343000	-0.740543000
N	0.004500000	-2.350769000	-0.117108000
N	-0.341983000	1.640018000	1.376716000
Ni	-0.175479000	-0.398985000	0.751666000
C	2.253876000	1.014611000	-0.628810000
H	2.751857000	0.858072000	0.329435000
H	3.008006000	1.057297000	-1.427657000
H	1.726082000	1.968641000	-0.597918000
C	-2.517973000	-0.497526000	-1.330575000
H	-1.981076000	-1.258889000	-1.898269000
H	-3.074291000	-0.986695000	-0.529517000
H	-3.222704000	0.009942000	-2.004861000
C	-2.901504000	4.358746000	0.727072000
H	-2.898060000	4.365303000	-0.368131000
H	-3.836154000	3.883785000	1.044867000
H	-2.910577000	5.393804000	1.068736000
C	1.297624000	4.227193000	3.587899000
H	0.841337000	4.459147000	4.556355000
H	2.152611000	3.570513000	3.766590000
H	1.667098000	5.170505000	3.173083000
C	-1.659649000	-5.741479000	-0.237533000
H	-2.016997000	-6.145126000	-1.190620000
H	-1.222544000	-6.576174000	0.320700000
H	-2.521578000	-5.371968000	0.323468000
C	2.654385000	-3.996861000	-2.271060000
H	3.563661000	-3.887354000	-1.669883000
H	2.659025000	-4.991171000	-2.717872000
H	2.713292000	-3.263662000	-3.082281000
O	-1.018999000	5.558091000	2.546982000
C	-1.836604000	5.726562000	3.722812000
H	-2.846856000	5.337651000	3.557839000
H	-1.391043000	5.223165000	4.587006000
H	-1.884015000	6.800519000	3.910133000
O	0.723921000	-6.080418000	-1.774478000
C	1.541377000	-6.966233000	-0.982942000
H	2.546521000	-6.554805000	-0.843048000
H	1.085359000	-7.151279000	-0.004645000
H	1.604919000	-7.902288000	-1.540095000

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5

Cu	1.509262000	3.220961000	9.979976000
N	1.107679000	4.667675000	8.574273000
C	0.017031000	5.445371000	8.450456000
H	-0.805338000	5.243278000	9.126346000
C	-0.077357000	6.472614000	7.519899000
C	1.034888000	6.677181000	6.685624000
C	2.175492000	5.862735000	6.774226000
C	2.163346000	4.860440000	7.754607000
C	3.357660000	3.965523000	7.999290000
H	3.913952000	3.777904000	7.075178000
H	4.040151000	4.468775000	8.693103000
N	2.936751000	2.677619000	8.604668000
C	4.051721000	2.004136000	9.343680000
H	5.014830000	2.235855000	8.877361000
H	3.902064000	0.926876000	9.258878000
C	4.055884000	2.435360000	10.806476000
H	4.788546000	1.848819000	11.374485000
H	4.327526000	3.491298000	10.885935000
N	2.689663000	2.280355000	11.378466000
C	2.485658000	3.050118000	12.629453000
H	3.092720000	3.960518000	12.582648000
H	2.830976000	2.472610000	13.493086000
C	1.029112000	3.438602000	12.771534000
C	0.445130000	3.713766000	14.015641000
C	-0.899847000	4.117839000	14.009713000
C	-1.637336000	4.197331000	12.815301000
C	-0.960093000	3.895279000	11.640896000
H	-1.471796000	3.928837000	10.685438000
N	0.339615000	3.549292000	11.616386000
C	2.360719000	1.778213000	7.574062000
H	3.134964000	1.471622000	6.860558000
H	1.566193000	2.294676000	7.033095000
H	1.943659000	0.893711000	8.058735000
C	2.314719000	0.858938000	11.579508000
H	3.025233000	0.374913000	12.260507000
H	2.306845000	0.326164000	10.628419000
H	1.313996000	0.805469000	12.011039000
C	-1.316109000	7.316005000	7.403259000
H	-2.065637000	7.000999000	8.132943000
H	-1.094435000	8.374654000	7.572651000
H	-1.752703000	7.234447000	6.402587000
C	3.353969000	6.055805000	5.855712000
H	4.229368000	6.426380000	6.400167000
H	3.641530000	5.111709000	5.382447000
H	3.114505000	6.768182000	5.066391000
C	1.222266000	3.575720000	15.298539000
H	1.650946000	2.572181000	15.389807000
H	2.051794000	4.289561000	15.341953000
H	0.577408000	3.744150000	16.160840000
C	-3.091352000	4.578674000	12.809498000
H	-3.685057000	3.872476000	13.398942000
H	-3.243091000	5.570709000	13.246953000
H	-3.481680000	4.591247000	11.789137000
O	-1.546388000	4.383429000	15.194206000
O	0.959565000	7.663407000	5.729792000
C	-1.393991000	5.738913000	15.670302000
H	-1.785588000	6.453929000	14.939841000
H	-1.971862000	5.802106000	16.593276000
H	-0.343522000	5.965598000	15.878550000
C	1.545376000	8.925920000	6.116548000
H	2.619193000	8.821911000	6.301272000
H	1.381248000	9.604611000	5.278602000
H	1.056666000	9.321107000	7.012685000

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