Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Influence of anionic co-ligands on the structural diversity and catecholase activity of copper(II) complexes with 2-methoxy-6-(8-iminoquinolinylmethyl)phenol

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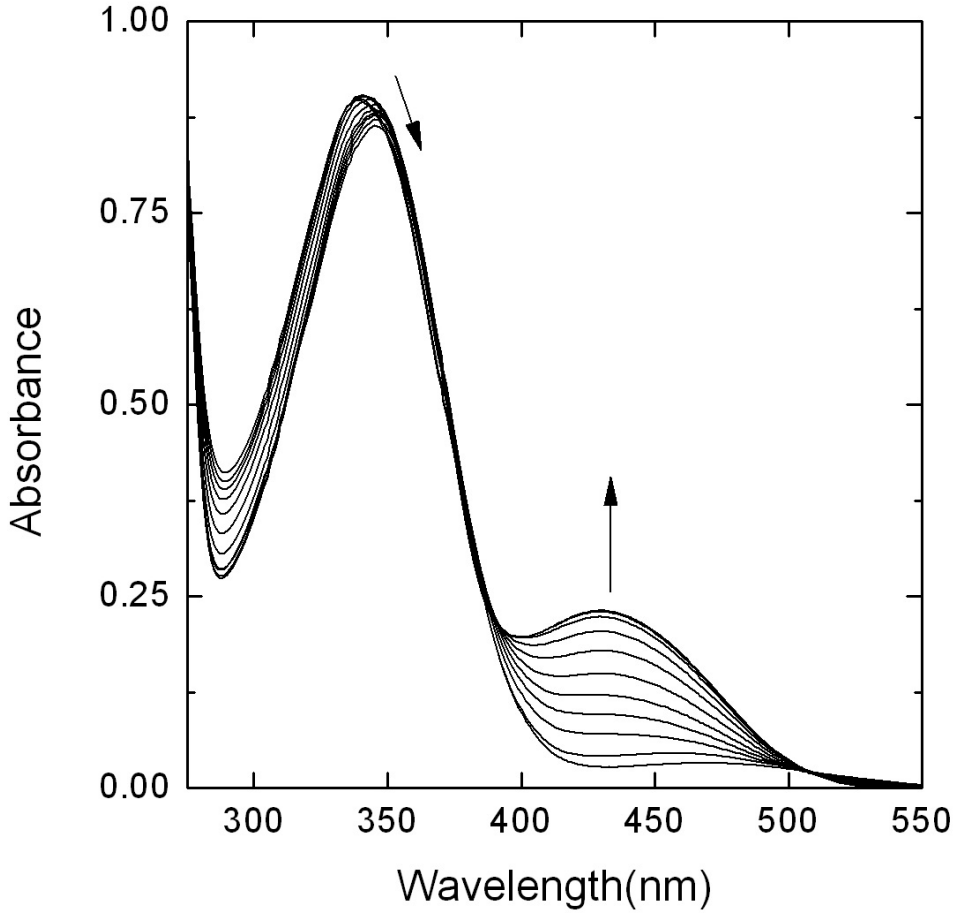

Fig. S1. Absorption spectral titration of 10 μM methanol solution of ligand HL with the incremental addition of 2 μM aqueous solution of NaOH

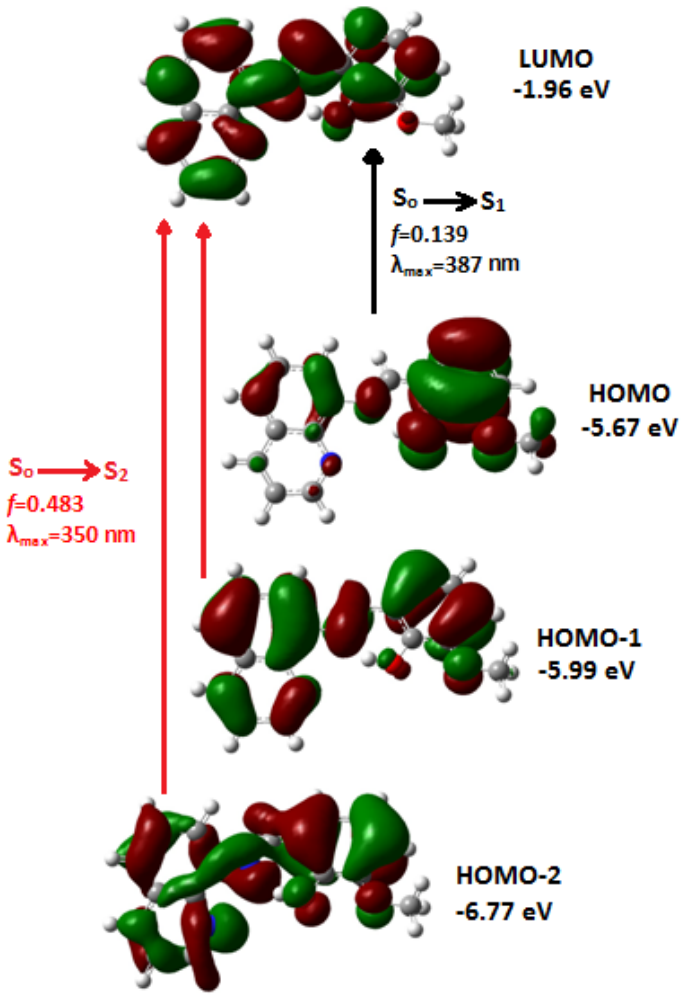

Fig. S2 Frontier molecular orbitals involved in UV-Vis absorption of ligand.

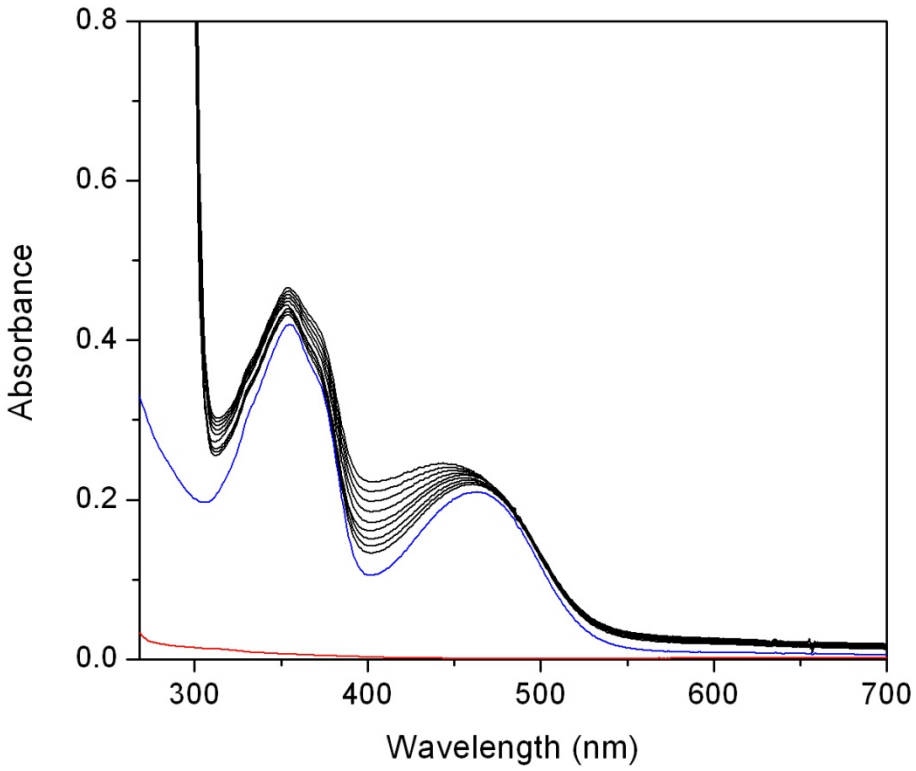

Fig. S3 UV-vis spectral profile after the addition of 200-fold 3,5-DTBCH$_2$ to a solution containing complex **1** (2×10^{-5} M) in dioxygen saturated MeOH/DMF (50:1) at 25 °C. The spectra were recorded for the period of 2h.

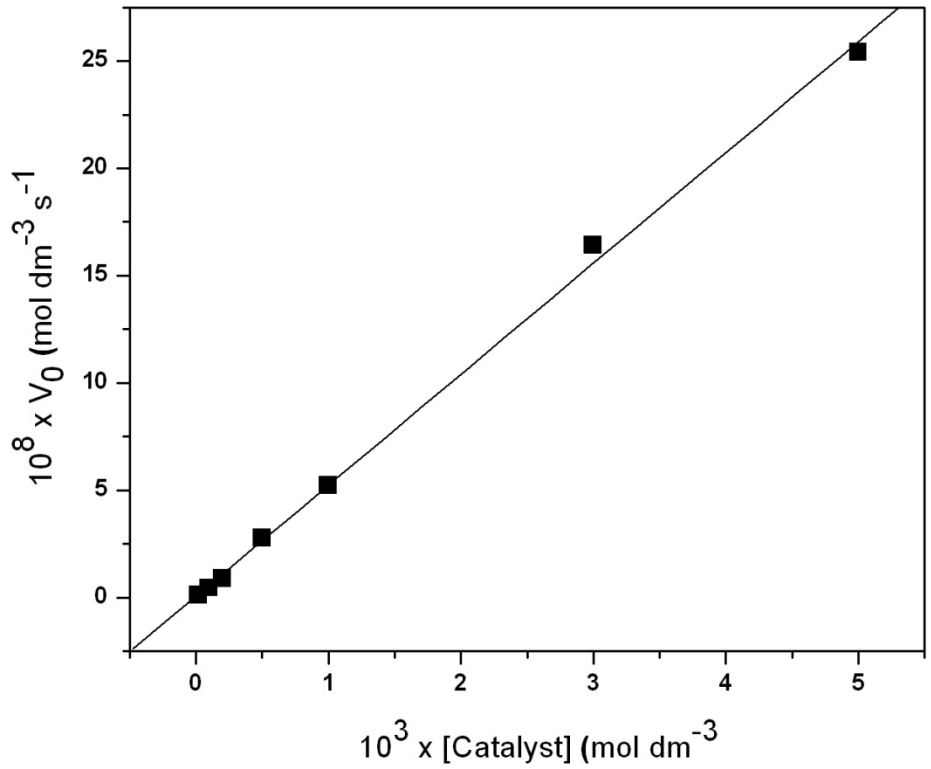

Fig. S4 Plot of initial rate verses catalyst concentration for the oxidation of 3,5-DTBCH_2 catalyzed by **2** in methanol/DMF. Symbols and solid lines represent the experimental and simulated profiles, respectively.

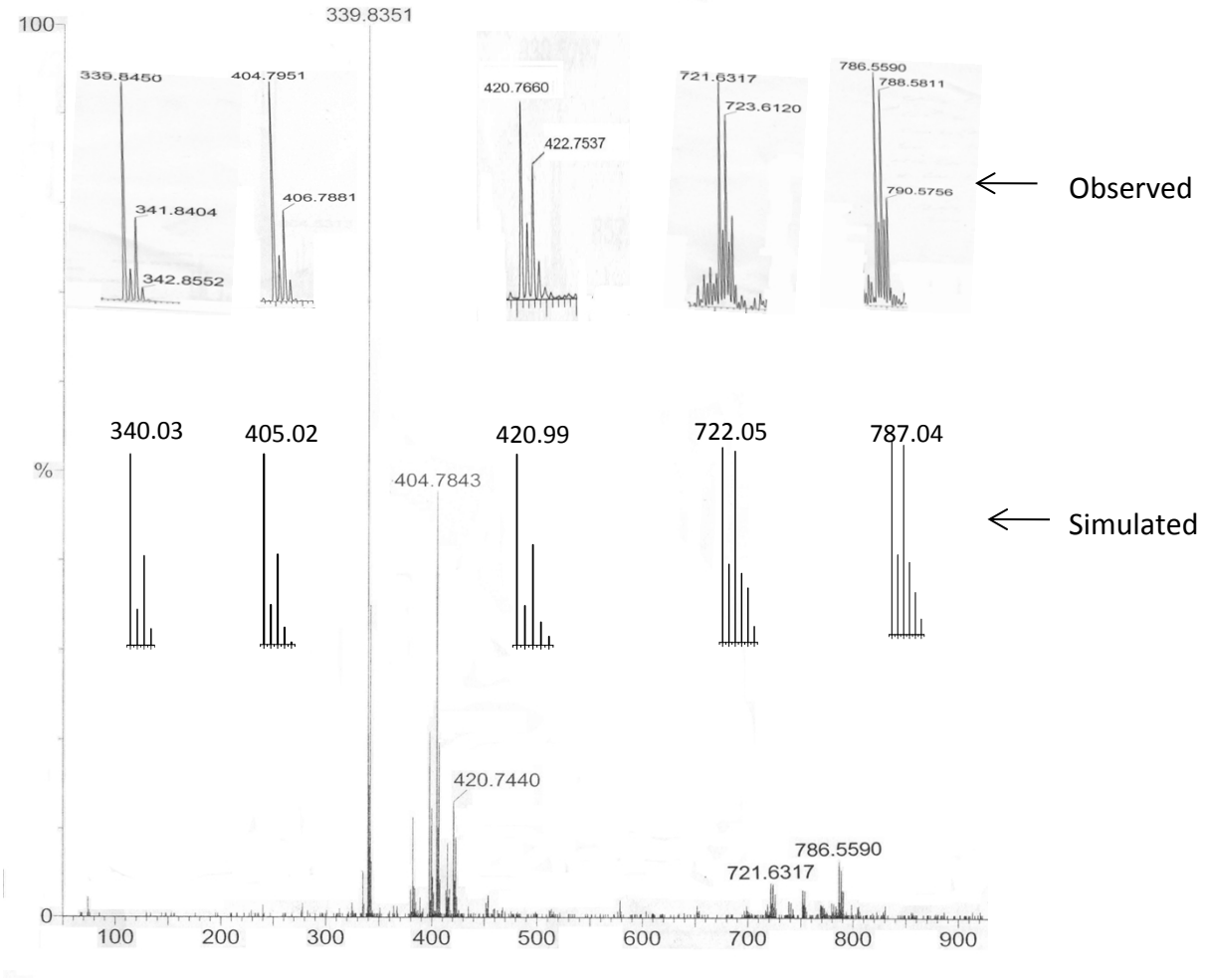

Fig. S5 Electrospray ionization mass spectrum (ESI-MS positive) of [CuL(NCO)](**2**) in MeOH/DMF showing observed and simulated isotopic distribution pattern.

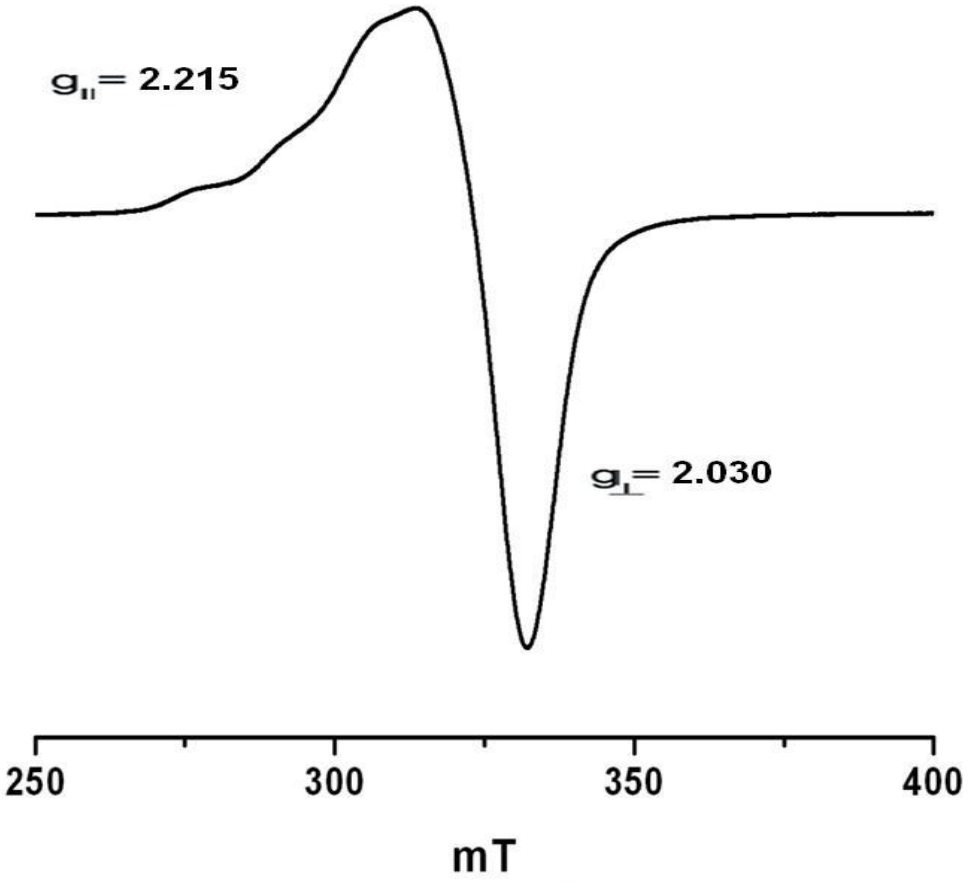

Fig. S6. X-band EPR spectra of complex **2** at 77 K in acetonitrile/DMF (4:1, v/v).

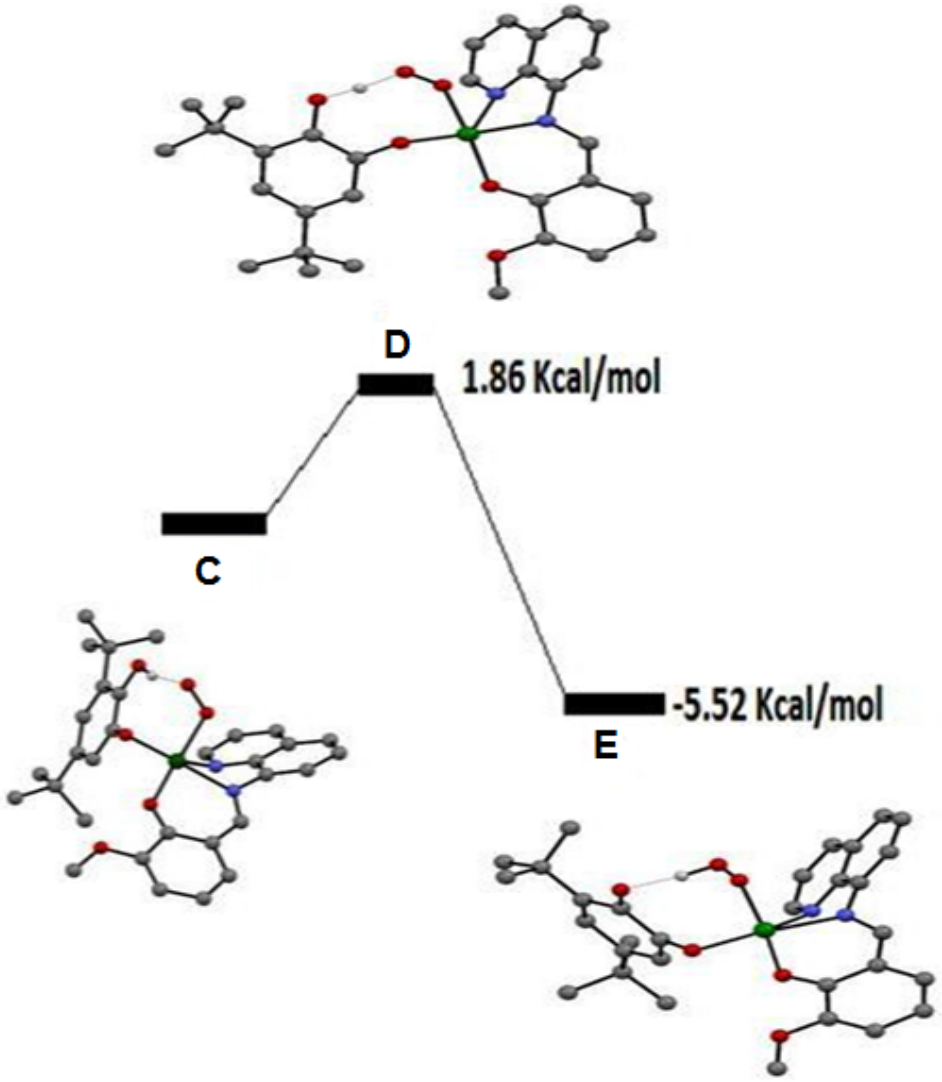

Fig. S7 Computed free energy profile diagram along with the DFT optimized structures of intermediates. Relative energies of **D** and **E** are shown considering energy of **C** state is zero kcal/mole.

Table S1.Cartesian Coordinates for Ground State Optimized Structures and their Energies in

Hartrees: B3LYP/6-31+g(d) for H,C,N,O and LANL2DZ for Cu

Ligand_HL

	Coordinates (Angstroms)		
Atom	X	Y	Z
O	-4.14907500	1.66846100	0.51333200
N	0.38872600	-0.51759100	0.14676000
O	-1.56996000	1.16126100	0.53710000
N	2.18275100	1.50021600	-0.34220100
C	-0.47542800	-1.38079600	-0.27574300
H	-0.16636700	-2.35971800	-0.66189900
C	-1.89827300	-1.09482500	-0.28447100
C	-2.80713000	-2.08600300	-0.72018800
H	-2.41916300	-3.05073700	-1.03608800
C	-4.16508900	-1.83030100	-0.73777600
H	-4.86606600	-2.59047800	-1.06800600
C	-4.65152300	-0.57577600	-0.32675100
H	-5.71920300	-0.39000500	-0.34741100
C	-3.77898400	0.42210200	0.10017600
C	-5.53805300	1.98401600	0.51402300
H	-5.96344300	1.92316700	-0.49526900
H	-5.60938800	3.01068500	0.87600500
H	-6.09918700	1.32142400	1.18443600
C	-2.38311900	0.17117800	0.12595000
C	1.75750800	-0.80907600	0.20955900
C	2.67876700	0.26879900	-0.02996900
C	3.04346400	2.47592300	-0.56855800
H	2.61765200	3.44970300	-0.80814800
C	4.45042700	2.32486500	-0.51685400
H	5.09470500	3.17415200	-0.72069000
C	4.96580600	1.08978000	-0.20274600
H	6.03890800	0.92509500	-0.14864400
C	4.08382300	0.00837500	0.05656800
C	4.54470000	-1.29197700	0.39161400
H	5.61415800	-1.47284200	0.45795000
C	3.64060000	-2.30088000	0.63874900
H	3.98883600	-3.29277800	0.91171300
C	2.25151300	-2.06021600	0.55258900
H	1.55807300	-2.86181700	0.78833800
H	-0.63162500	0.80688100	0.47531000

b3lyp/6-31g(d)=-916.19191936 Hartree

Complex-2

	Coordinates (Angstroms)		
Atom	X	Y	Z
O	4.30124800	0.76419300	0.03657900
N	-0.58968600	-1.10996900	0.00350400
O	1.70082800	0.56985100	0.02706500
N	-2.24935200	0.94827300	-0.01627100
C	0.33231300	-2.04094400	-0.02136600

H	0.01191000	-3.08355700	-0.04273400
C	1.74186600	-1.85198200	-0.02401100
C	2.55508000	-3.02617600	-0.05149600
H	2.06548800	-3.99630200	-0.07321400
C	3.92343900	-2.93382900	-0.04943700
H	4.54138700	-3.82584800	-0.07005600
C	4.54408800	-1.65994300	-0.01953300
H	5.62706700	-1.60588800	-0.01806800
C	3.79147600	-0.50021000	0.00695600
C	5.71651400	0.90919400	0.04284300
H	6.16406000	0.43788800	0.92709600
H	5.90710400	1.98311300	0.06893700
H	6.16751600	0.48077400	-0.86123100
C	2.34801700	-0.55336500	0.00415600
C	-1.96747600	-1.42066200	0.01445500
C	-2.83223900	-0.28544100	-0.00074400
C	-3.00057400	2.03843000	-0.03164900
H	-2.46036800	2.97947500	-0.04176600
C	-4.41018700	1.97772100	-0.03327800
H	-4.98360700	2.89778100	-0.04701200
C	-5.02809400	0.74604100	-0.01558300
H	-6.11156700	0.66754000	-0.01453700
C	-4.24744700	-0.43868500	0.00263900
C	-4.79237900	-1.74781000	0.02581400
H	-5.87039900	-1.87632300	0.02904800
C	-3.94747900	-2.83738400	0.04687600
H	-4.35902700	-3.84166200	0.06807400
C	-2.54244300	-2.68321500	0.04272100
H	-1.92930700	-3.57712300	0.06442600
Cu	-0.20342900	0.85804200	0.00144900
N	-0.02827000	2.81175700	-0.00813000
C	0.91973800	3.55365700	-0.00406200
O	1.81980700	4.34771600	-0.00070500

ub3lyp/6-31g(d),Lanl2dz =-1279.88911326 Hartree

Active Catalyst_B

Coordinates (Angstroms)

Atom	X	Y	Z
Cu	-1.22377500	0.08711900	0.44287800
O	-3.89986900	3.81032600	0.38066400
N	-2.82630700	-1.30929900	0.21212900
O	-2.82126600	1.43406400	0.76438000
N	-0.34121400	-1.76899500	1.13769500
C	-3.84780000	-0.97859600	-0.54830900
H	-4.32559900	-1.75862300	-1.16112900
C	-4.39346600	0.32345400	-0.68915500
C	-5.51995200	0.48274700	-1.55267500
H	-5.91479600	-0.40319600	-2.04915300
C	-6.10441400	1.70522700	-1.75414300
H	-6.96766400	1.81185300	-2.40603800
C	-5.57406200	2.85694600	-1.10438700
H	-6.04877600	3.81820900	-1.27766600

C	-4.47781400	2.75841700	-0.27821700
C	-4.43142400	5.09260100	0.15425000
H	-4.37865500	5.37769600	-0.90778400
H	-3.82196900	5.78432700	0.74150500
H	-5.48031700	5.16913700	0.48225000
C	-3.82293900	1.47710600	-0.00808900
C	-2.47699200	-2.62252500	0.43215900
C	-1.13147900	-2.85540800	0.90351500
C	0.91418100	-1.95116500	1.52729800
H	1.50203000	-1.05429200	1.69593200
C	1.47455000	-3.23174900	1.72227500
H	2.51007300	-3.32033200	2.03781400
C	0.68291100	-4.34372100	1.53544500
H	1.07551700	-5.34516000	1.70004300
C	-0.66693300	-4.19044300	1.12421100
C	-1.55212000	-5.28074900	0.92442800
H	-1.19316700	-6.29449100	1.08518200
C	-2.85607700	-5.03736300	0.53707100
H	-3.54291900	-5.87101300	0.40484200
C	-3.32224500	-3.73161400	0.29888900
H	-4.35926500	-3.58108200	0.01627200
C	1.51079400	0.97740500	-0.34061300
C	2.44703900	1.83125600	0.31812400
C	2.01378800	-0.07693300	-1.12185300
C	3.39559200	-0.28549000	-1.25961200
C	3.82892600	1.65806000	0.20428000
C	4.27404800	0.58134500	-0.59397600
H	5.34105700	0.42014800	-0.69823100
H	1.28747100	-0.71544400	-1.61337900
O	0.23826500	1.27348600	-0.15511300
O	1.86326700	2.83022700	1.05588800
H	0.90181000	2.65065100	0.88313200
C	4.80647700	2.60932800	0.92277100
C	3.97068800	-1.44186500	-2.10555800
C	4.58540200	4.05722700	0.42052800
H	4.79676500	4.12673200	-0.65386800
H	3.55335200	4.37343000	0.58705300
H	5.25569700	4.75412600	0.94404100
C	6.28207000	2.24457700	0.66810800
H	6.93188600	2.95215500	1.19922000
H	6.52223700	1.23725200	1.02869000
H	6.53706500	2.29393200	-0.39710300
C	4.56408500	2.55267400	2.45079800
H	3.53168500	2.81513900	2.69181300
H	4.76097600	1.54296000	2.83278800
H	5.23468000	3.24912000	2.97441100
C	4.79266100	-2.39163200	-1.20135900
H	5.22445700	-3.21635600	-1.78643600
H	5.61331600	-1.86368500	-0.70421000
H	4.15510700	-2.82461700	-0.42140900
C	4.89075200	-0.87754600	-3.21422200
H	5.31531900	-1.68943900	-3.82194200
H	4.32924700	-0.21072300	-3.87895900
H	5.72223800	-0.30162200	-2.79452500

C	2.87077500	-2.27806900	-2.78769000
H	2.20043000	-2.73997200	-2.05464600
H	2.26132400	-1.66803100	-3.46372000
H	3.32621700	-3.08302000	-3.37933300

b3lyp/6-31g(d),Lanl2dz=-1808.43213442Hartree

Intermediate_C

Coordinates (Angstroms)

Atom	X	Y	Z
Cu	1.17790000	-0.23050000	-0.88120000
O	4.13970000	3.32180000	-0.93690000
N	2.36410000	-1.52180000	0.19520000
O	2.62500000	1.19220000	-0.70130000
N	-0.17710000	-1.55050000	1.21170000
C	3.59980000	-1.29140000	0.55040000
H	4.11490000	-2.07880000	1.11660000
C	4.37090000	-0.11100000	0.33490000
C	5.71910000	-0.12380000	0.79960000
H	6.09670000	-1.03730000	1.25720000
C	6.53090000	0.97470000	0.67800000
H	7.55880000	0.95340000	1.02960000
C	6.01710000	2.16090000	0.08740000
H	6.66810000	3.02530000	-0.00130000
C	4.71600000	2.22240000	-0.36260000
C	4.93240000	4.47520000	-1.08300000
H	5.28270000	4.86020000	-0.11270000
H	4.29390000	5.22500000	-1.55650000
H	5.81010000	4.29300000	-1.72230000
C	3.81470000	1.07760000	-0.26950000
C	1.78090000	-2.75650000	0.51860000
C	0.43850000	-2.74960000	1.03430000
C	-1.41880000	-1.53650000	1.65320000
H	-1.88530000	-0.55820000	1.74920000
C	-2.14290000	-2.71060000	1.98200000
H	-3.16550000	-2.63060000	2.33930000
C	-1.52810000	-3.93090000	1.83370000
H	-2.04760000	-4.85630000	2.07530000
C	-0.19720000	-3.99230000	1.34450000
C	0.50570000	-5.21060000	1.15520000
H	0.01190000	-6.15020000	1.39320000
C	1.78970000	-5.19210000	0.65700000
H	2.32410000	-6.12460000	0.49200000
C	2.42270000	-3.97170000	0.33160000
H	3.41650000	-3.98140000	-0.10650000
C	-1.34700000	1.09620000	-0.88710000
C	-2.52840000	0.40980000	-1.33220000
C	-1.45720000	1.97980000	0.20460000
C	-3.77450000	0.65270000	-0.71690000
C	-2.67590000	2.22450000	0.84560000
H	-0.53990000	2.47640000	0.51090000
C	-3.81260000	1.55360000	0.36460000
H	-4.76460000	1.73850000	0.84250000

O	-0.22270000	0.91300000	-1.54220000
O	-2.43650000	-0.44260000	-2.37380000
H	-1.47810000	-0.63550000	-2.61740000
C	-2.73340000	3.22520000	2.01710000
C	-5.05250000	-0.05650000	-1.21710000
C	-6.30420000	0.33880000	-0.40720000
H	-6.51210000	1.41380000	-0.46820000
H	-7.17830000	-0.19090000	-0.80720000
H	-6.21070000	0.06980000	0.65190000
C	-5.31810000	0.32340000	-2.69500000
H	-5.48610000	1.40370000	-2.78950000
H	-4.46960000	0.05110000	-3.32530000
H	-6.21430000	-0.19260000	-3.06840000
C	-4.89190000	-1.59220000	-1.10070000
H	-4.02710000	-1.93720000	-1.66980000
H	-4.75350000	-1.88620000	-0.05250000
H	-5.79090000	-2.10060000	-1.47790000
C	-4.14900000	3.37000000	2.60920000
H	-4.86550000	3.73350000	1.86340000
H	-4.52400000	2.41780000	3.00270000
H	-4.13540000	4.09070000	3.43690000
C	-2.28010000	4.62140000	1.52690000
H	-1.26390000	4.59240000	1.12150000
H	-2.94290000	4.98640000	0.73330000
H	-2.29690000	5.34990000	2.35000000
C	-1.79030000	2.76060000	3.15230000
H	-2.10370000	1.78430000	3.54140000
H	-0.75840000	2.66040000	2.80180000
H	-1.79800000	3.47740000	3.98560000
O	0.29370000	-1.71870000	-1.75860000
O	-0.05540000	-1.45300000	-2.99550000

ub3lyp/6-31g(d),Lanl2dz=-1958.72656293Hartree

Transition_state_D

Coordinates (Angstroms)

Atom	X	Y	Z
Cu	-0.96214300	0.13714100	0.83658100
O	0.79695000	4.31920800	0.08420000
N	-2.88556000	0.53863200	0.22653300
O	-0.43795200	2.01797300	0.35954300
N	-2.64136500	-1.45918300	-1.68071500
C	-3.33429200	1.73442700	-0.03733800
H	-4.40298000	1.82396700	-0.27183300
C	-2.60518600	2.96254000	-0.09795400

C	-3.34193300	4.14355000	-0.40027300
H	-4.41984200	4.05955800	-0.53137900
C	-2.72183900	5.36139200	-0.52769100
H	-3.29098600	6.25863900	-0.75454500
C	-1.31351500	5.44782500	-0.36705400
H	-0.83315500	6.41544000	-0.47476200
C	-0.56236100	4.32736900	-0.08152600
C	1.47983400	5.54633700	-0.03290600
H	1.35673900	5.99053500	-1.03228300
H	2.53610400	5.32231900	0.13164900
H	1.14110300	6.27530400	0.71890700
C	-1.17729900	3.01708400	0.08072700
C	-3.80714700	-0.53000700	0.20572200
C	-3.63685900	-1.57646400	-0.76112500
C	-2.48638700	-2.42979700	-2.55700700
H	-1.67326700	-2.30802400	-3.27222000
C	-3.30217700	-3.58691200	-2.61056400
H	-3.11113900	-4.35221400	-3.35774000
C	-4.33041100	-3.70728200	-1.70569900
H	-4.98911900	-4.57355400	-1.71347700
C	-4.53816900	-2.68893900	-0.74110000
C	-5.59215300	-2.72933100	0.20914800
H	-6.26733100	-3.58220100	0.21497900
C	-5.74602700	-1.69863600	1.10773000
H	-6.55038700	-1.72625600	1.83876700
C	-4.85410900	-0.60150700	1.10738200
H	-4.95992700	0.18492800	1.84915200
C	1.78536300	-0.41527200	1.02990500
C	2.21022100	-1.78274600	0.81309400
C	2.57182500	0.64950200	0.54073600
C	3.45938500	-2.01676300	0.16385700
C	3.76992200	0.42642600	-0.12915300
H	2.16891900	1.64569700	0.69533700
C	4.18944400	-0.91248900	-0.29028300
H	5.12562200	-1.09628200	-0.80081100
O	0.68982600	-0.20448900	1.72064800
O	1.46383900	-2.78044600	1.24091400
H	0.41859100	-2.52403600	1.65862700
C	4.57415100	1.62539700	-0.66855400
C	3.96292400	-3.45994800	-0.04860600
C	5.32853500	-3.51303800	-0.76300800
H	6.11044800	-2.99472200	-0.19452700
H	5.63989600	-4.55957900	-0.87688600
H	5.28711500	-3.07014700	-1.76562400
C	4.12629800	-4.16474800	1.32067900
H	4.88114200	-3.65104100	1.92976700
H	3.18109700	-4.16368600	1.86626800
H	4.45521100	-5.20463300	1.18062000
C	2.95233900	-4.25003300	-0.91645600
H	1.96797200	-4.25941000	-0.44538500
H	2.85856200	-3.79128600	-1.90903900
H	3.29223900	-5.28692900	-1.05330300
C	5.87392900	1.20226400	-1.37987700
H	6.54953100	0.66159800	-0.70633600

H	5.67213000	0.55865300	-2.24413000
H	6.40660400	2.09035100	-1.74423500
C	4.95611300	2.56455000	0.50060500
H	4.06661800	2.92195400	1.02918600
H	5.58703300	2.04172100	1.22969100
H	5.51107800	3.44031200	0.13418600
C	3.70753100	2.41254100	-1.68194100
H	3.44450800	1.77900400	-2.53757600
H	2.77310000	2.75879100	-1.22910900
H	4.25309800	3.28874000	-2.06217800
O	-1.38631800	-1.71745000	1.10121400
O	-0.77427100	-2.39110900	2.08471400

ub3lyp/6-31g(d), Lanl2dz = -1958.72359375Hartree
Calculated frequency along the bond O_{74}•••H_{46}•••O_{45} is = -1121.6

Intermediate_E

Coordinates (Angstroms)

Atom	X	Y	Z
Cu	1.17097800	0.22363200	-0.43837500
O	3.89468200	3.84315200	0.20717900
N	2.61588600	-1.26623200	-0.15766700
O	2.56159600	1.60657500	-0.07110500
N	0.44174900	-2.12724200	1.30634100
C	3.88458500	-1.03200900	0.03089800
H	4.54720500	-1.90105200	0.14594800
C	4.53682800	0.23403600	0.14409700
C	5.94744600	0.21898000	0.34700300
H	6.45110800	-0.74609400	0.38355300
C	6.66546700	1.37918300	0.49151500
H	7.74154900	1.35731500	0.64088500
C	5.98932900	2.62728900	0.44616000
H	6.56623800	3.53973400	0.56163100
C	4.62429000	2.68757000	0.26134700
C	4.58670400	5.06107900	0.33708800
H	5.09573500	5.14483700	1.31007500
H	3.83331900	5.84869900	0.25829400
H	5.33501800	5.19633200	-0.45930800
C	3.81806800	1.48371300	0.09503800
C	2.18737500	-2.59537500	-0.27980800
C	1.03497200	-3.01830000	0.46868600
C	-0.62792800	-2.51046600	1.97271100
H	-1.08909300	-1.76140900	2.61497900
C	-1.18823100	-3.80800800	1.88831800
H	-2.07521900	-4.05520800	2.46508300
C	-0.58466500	-4.73046200	1.06612300
H	-0.97646100	-5.74140700	0.97098700
C	0.56250400	-4.36109000	0.31949600
C	1.24167200	-5.25966700	-0.54557800
H	0.86984700	-6.27642600	-0.65131900
C	2.34627500	-4.83169600	-1.24585900
H	2.86140500	-5.51100500	-1.92098700

C	2.81501600	-3.50465100	-1.11821600
H	3.65615400	-3.17064500	-1.71847200
C	-1.50027100	1.30482000	-0.12259000
C	-2.40380900	1.19946600	-1.29345900
C	-2.03876300	1.17621300	1.19678400
C	-3.38771600	1.02973000	1.42654700
C	-3.83234900	1.02943800	-1.02311700
C	-4.25540900	0.95787300	0.28646400
H	-5.31506600	0.82848400	0.48043500
H	-1.31502900	1.24421200	2.00273900
O	-0.25595800	1.57041200	-0.29101200
O	-1.94297000	1.27560200	-2.47006000
H	-0.59152100	0.32632700	-2.68009500
C	-4.80946000	0.90667100	-2.20718500
C	-4.00214300	0.94296400	2.83403400
C	-4.74359800	2.18517900	-3.07933700
H	-5.05337500	3.06472400	-2.50007600
H	-3.72692800	2.34601800	-3.44123000
H	-5.41959200	2.09295600	-3.94119500
C	-6.27093900	0.72610900	-1.75181300
H	-6.92003100	0.64639200	-2.63306600
H	-6.40698100	-0.18651000	-1.15861600
H	-6.62536700	1.57659000	-1.15598900
C	-4.42844900	-0.32412300	-3.06745200
H	-3.39906200	-0.24122900	-3.41942100
H	-4.52045900	-1.24688800	-2.48120300
H	-5.09865500	-0.40456800	-3.93519300
C	-4.74681100	-0.40443200	2.99899900
H	-5.19014500	-0.48370600	4.00134600
H	-5.55383900	-0.51614900	2.26709400
H	-4.05766600	-1.24577400	2.86157400
C	-5.00546500	2.10382900	3.04155100
H	-5.46744300	2.04545800	4.03691800
H	-4.49840800	3.07191400	2.95638300
H	-5.80913900	2.08341800	2.29781400
C	-2.93744600	1.03600700	3.94317500
H	-2.20726000	0.22173800	3.87420600
H	-2.38757400	1.98240600	3.89674600
H	-3.41669200	0.97315400	4.92851600
O	-0.06998900	-0.89622000	-1.35378900
O	0.05503100	-0.43612900	-2.69079000

ub3lyp/6-31g(d),Lanl2dz =-1958.73536226 Hartree

Table S2. DFT optimized selected data for different intermediates.[#]

Distance	**B**	**C**	**D**	**E**
O1-O2		1.324	1.347	1.416
Cu-O1		1.932	1.928	1.944
O2-H		1.596	1.305	0.992
O2-O3		2.599	2.413	2.687
C-O3	1.365	1.350	1.321	1.261
C-O4	1.323	1.306	1.298	1.275
Mulliken Charge				
Cu	0.211	0.452	0.448	0.421
O1		-0.259	-0.297	-0.385
O2		-0.297	-0.355	-0.436
O3		-0.697	-0.681	-0.567
O4		-0.596	-0.569	-0.51
H		0.484	0.507	0.464

[#]O1 and O2 stands for molecular dioxygen while O3 and O4 represent catecholase oxygen atoms; Proton transfer takes place O3 to O2.