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Supplementary Information

Evidence of Two-State Reactivity in Alkane Hydroxylation by Lewis-acid Bound Copper-Nitrene Complexes

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1. Experimental Section

1.1 Materials. All chemicals were purchased from Sigma Aldrich, Acros, ABCR, TCI and used without further modification. Anhydrous solvents (dichloromethane, acetone, n-hexane) were purchased from Carl Roth GmbH (≥ 99.5%, < 50 ppm H_2O) and degassed by freeze-pump-thaw method prior to use. All the liquid substrates, for reactivity studies, were distilled under argon prior to use.

1.2 Instrumentations and Physical Methods. Preparation and handling of air sensitive materials were performed in a N_2 glove box OMNI-Lab 2 (VAC) with O_2 and H_2O concentrations less than 1 ppm. ^{1}H NMR and ^{13}C NMR spectra were recorded either on a Bruker DPX-300 or on a Bruker AV 400 NMR spectrometer. Elemental analyses were performed with a Leco CHNS-932 elemental analyzer. UV-vis spectra were recorded by Agilent 8453 diode array spectrometer connected with a cryostat from Unisoku Scientific Instruments, Japan. IR spectra of liquids or solutions were recorded in a Bruker Vertex 70 Spectrofotometer with a "golden gate" ATR unit, otherwise a KBR pellet of solid sample was prepared and measured in a Shimadzu FTIR-8400S spectrophotometer.

X-Band EPR derivative spectra were recorded on a Bruker ELEXSYS E500 spectrometer equipped with the Bruker dual mode cavity (ER4116DM) and a Helium flow cryostat (Oxford Instrument ESR 910). Microwave frequencies were calibrated with Hewlett-Packard frequency counter (HP5352B), and field control was calibrated with a Bruker NMR probe (ER035M). The spectrum was simulated with the program GIFT (by Dr. Eckhard Bill).

X-ray absorption spectroscopy was carried out on beamline X3B of the National Synchrotron Lightsource (Brookhaven National Laboratory, Upton, NY, USA). A sagitally focusing Si(111) monochromator was used for energy selection, while a cylindrically-bent nickel-coated mirror located downstream of the monochromator provided vertical focusing and harmonic rejection. Sample temperatures were maintained at approximately 20 K using a He Displex cryostat. A Cu metal foil was used for internal energy calibration, with the first inflection point of the reference foil edge set to 8979.0 eV. XAS data were collected as fluorescence spectra using a 31 element solid state germanium detector (Canberra), over an energy range of 8779 – 9540 eV. A Ni filter of 3 absorption lengths was used to reduce scatter and maintain detector linearity. Samples were monitored for photoreduction during data collection (based upon red-shifts in the absorption edge), and typically only 2 scans were collected at a given position on the sample. Tandem Mossbauer/XAS cups with a sample window og 6 mm x 10 mm were used to provide at least 5 independent beam spots on each sample. Averaging and normalization of the XAS data was performed using Athena, a graphical implementation of the IFEFFIT[1] package. Reference spectra for individual scans were carefully aligned to ensure that the energy scale was

identical for all spectra. Sets of scans at each spot were examined for photoreduction effects. No convincing evidence for photoreduction was observed based upon edge energies, based on both individual scans and sums of first or second scans. Therefore no scans were excluded from averaged data.

1.3 Determination of k_2 by UV-vis spectroscopy. The reactivity studies were done at -90 °C, under inert atmosphere, by injecting the CH_2Cl_2 solution of the substrate to the preformed 1mM CH_2Cl_2 solution of **2**. The pseudo-first order decay of the 560 nm band was monitored by acquiring an UV-vis spectrum every 1 second. The pseudo-first order fitting of the decay curves yielded the rate constants (k_{obs}) which were found to be linearly increasing with the increment of substrate concentration. The slope of the rate constant k_{obs} vs. substrate concentration fitting plot provided the second order rate constants (k_2).

Product analysis was done by passing the reaction mixtures through celite to remove undissolved particles prior to the NMR measurements. For the quantification of products by ^{1}H- NMR, 2 µl of nitromethane was used as internal standard. For the qualitative product analysis by GC, the reaction mixtures were passed through the silica layer to remove the metal complex and eluted with ethylacetate.

1.4 Syntheses and Characterizations.

1.4.1 [Cu(L_1)][BF_4] (L1=3,3'-iminobis(N,N,-dimethylpropylamine). The complex was prepared by following a previously reported procedure[2]. A solution of ligand L1 (0.345 g, 1.84 mmol) in dry CH2Cl2 (5 mL) was added to [Cu(MeCN)4][BF4] (0.579 9, 1.84 mmmol), and the resultant solution was stirred under inert atmosphere for 30 minutes. nN-Hexane (25 mL) were added to the resultant colorless, clear solution to produce a cloudy solution that was kept at -35 °C for 2 hours. After that, the solvent was decanted and the resultant colorless, clear oil was dried in *vacuo* to yield a white solid. Yield: 509 mg (1.51 mmol, 82%). Elemental analysis calculated for $C_{10}H_{25}N_3BCuF_4$: C, 35.57; H, 7.46; N, 12.44. Found: C, 35,81; H, 7.53; N, 12.3. IR (KBr pellet): $\tilde{\nu}$ (cm^{-1}) = 3289 s, 2924 s, 2844 s, 2794 s, 1480 s, 1466 s, 1429 s, 1387 m, 1345 m, 1324 m, 1293 m, 1263 m, 1239 m, 1203 m, 1139 s, 1107 s, 1054 s, 978 s, 950 m, 919 w, 899 m, 859 s, 851 s, 771 s, 756 w, 523 m, 492 w, 458 w.

1.4.2 Mesitylazide. 2,4,6-trimethylaniline (1,01 g, 7.5 mmol) was added to a mixture of concentrated HCl (10 mL) and H_2O (10 mL) at 0 °C. In small portions, sodium nitrite (0.62 g, 9.0 mmol) was added; the reaction mixture was stirred for 2 hours keeping the temperature constant at 0 °C. A solution of sodium acetate (12.3 g, 150 mmol) in H_2O (33 mL) was then added, followed by the addition of sodium azide (0.97 g, 15 mmol) in small portions. The reaction mixture was stirred for 30 min at RT, and then extracted with n-Pentan (3 times). The organic phase was washed with a concentrated NaCl solution and dried with $MgSO_4$. After vacuum removal of

the solvent, red oil was obtained which was further purified with a chromatographic column using n-Hexane as eluent to get yellow oil as the pure product. Yield: 1.00 g (6.2 mmol, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.83 (s, 2H), 2.32 (s, 6H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ [ppm] = 135.5 (1C), 134.5 (1C), 132.0 (2C), 129.6 (2C), 20.8 (1C), 18.2 (2C). IR (KBr pellet): $\tilde{\nu}$ (cm^{-1}) = 2920 vw, 2115 vs, 2089 m, 2058 w, 1479 w, 1316 w, 1279 m, 853 m.

1.4.3 [(L1)Cu(NMes)][Sc^{3+}][BF_4] (2). 2mL of a 1 mM solution of the Cu^{I} complex in CH_2Cl_2 were cooled to -90 °C. 1.5 equivalents of $Sc(OTf)_3$ in acetone (0.1 mL) and 1.5 equivalents of Mesitylazide in CH_2Cl_2 (0.1 mL) were added in that order to yield a deep purple intermediate. The generation of this species was monitored following the growth of the 560 nm band in the UV-vis spectrum.

2. DFT calculations.

The DFT Calcualtions were performed using the ORCA[3] package. The structures were optimized using the BP86 exchange functional[4,5] and Default-Basis-2,3,4[6–9] increasing stepwise for the optimization process. The Default-Basis set 2 and higher are including the Ahlrichs polarization functions, which were obtained from the TurboMole basis set library under ftp.chemie.uni-karlsruhe.de/pub/basen. Broken symmetry[10,11] calculations were performed on the optimized structures from the BP86/Default-Basis-4 calculations.

Final single point energies (FSPEs) on the optimized structures were calculated with the B3LYP[12–15] correlation functional and the Dafault-Basis-4[6,7].

All calculations are including the COSMO solvation model with the built-in parameters for dichloromethane[3] and an empirical dispersion correction using the Becke-Johnson damping.[16,17]

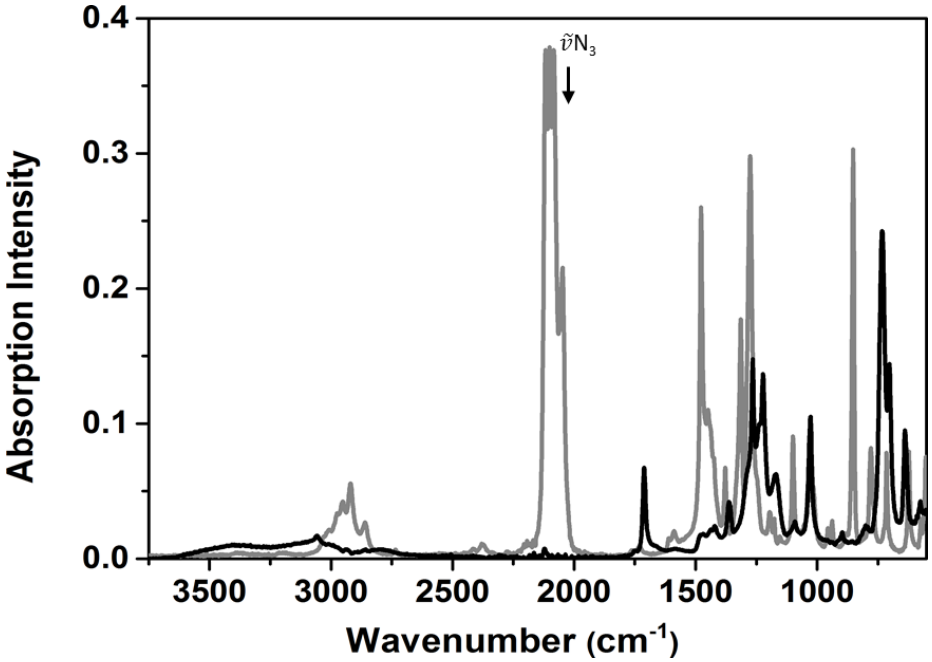

Figure S1: IR spectra of the Mesityl azide (gray) and of **2** (black). The signal assigned to the vibration of azide disappears completely, indicating its complete transformation towards forming **2**.

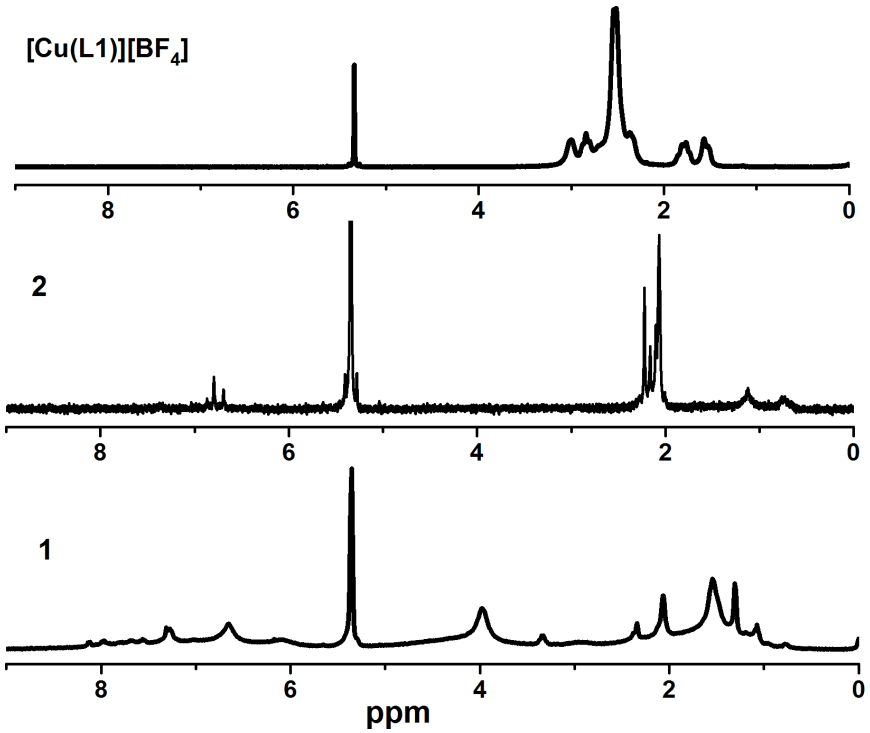

Figure S2: ^{1}H-NMR spectra recorded in CH_2Cl_2 at -90°C of for [Cu(L1)][BF_4], **1**, and **2.**

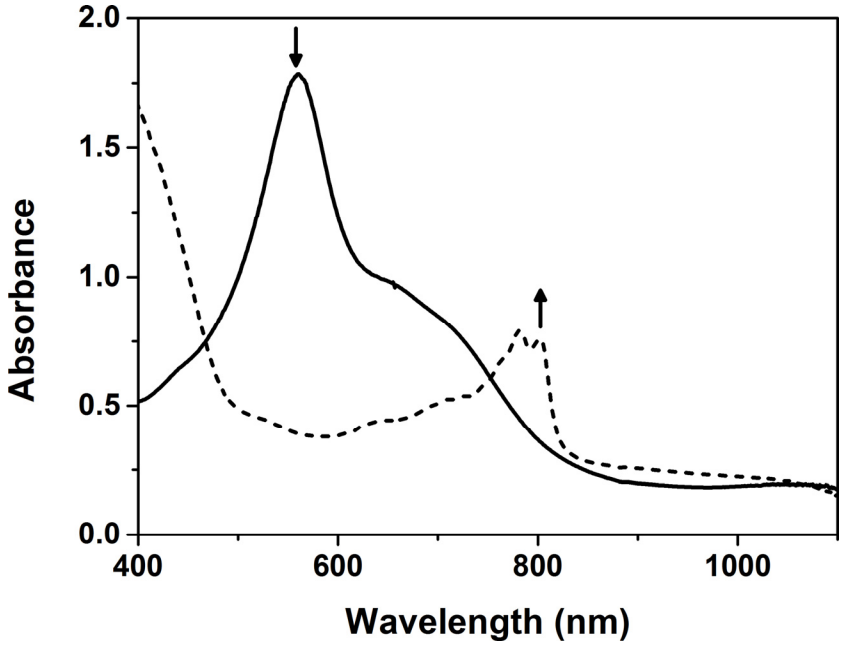

Figure S3: Absorption spectra of **2** (solid line) (1 mM) and the product of its reaction with decamethylferrocene ($Me_{10}Fc$) (30 equiv) (dashed line) in CH_2Cl_2 at −90 °C. The yield of $Me_{10}Fc^+$ (183%) was determined on the basis of the extinction coefficient of the 780 nm band in CH_2Cl_2 at −90 °C ($\varepsilon = 520\ M^{-1}\ cm^{-1}$) determined via the full conversion of $Me_{10}Fc$ with trifluoroacetic acid and O_2.

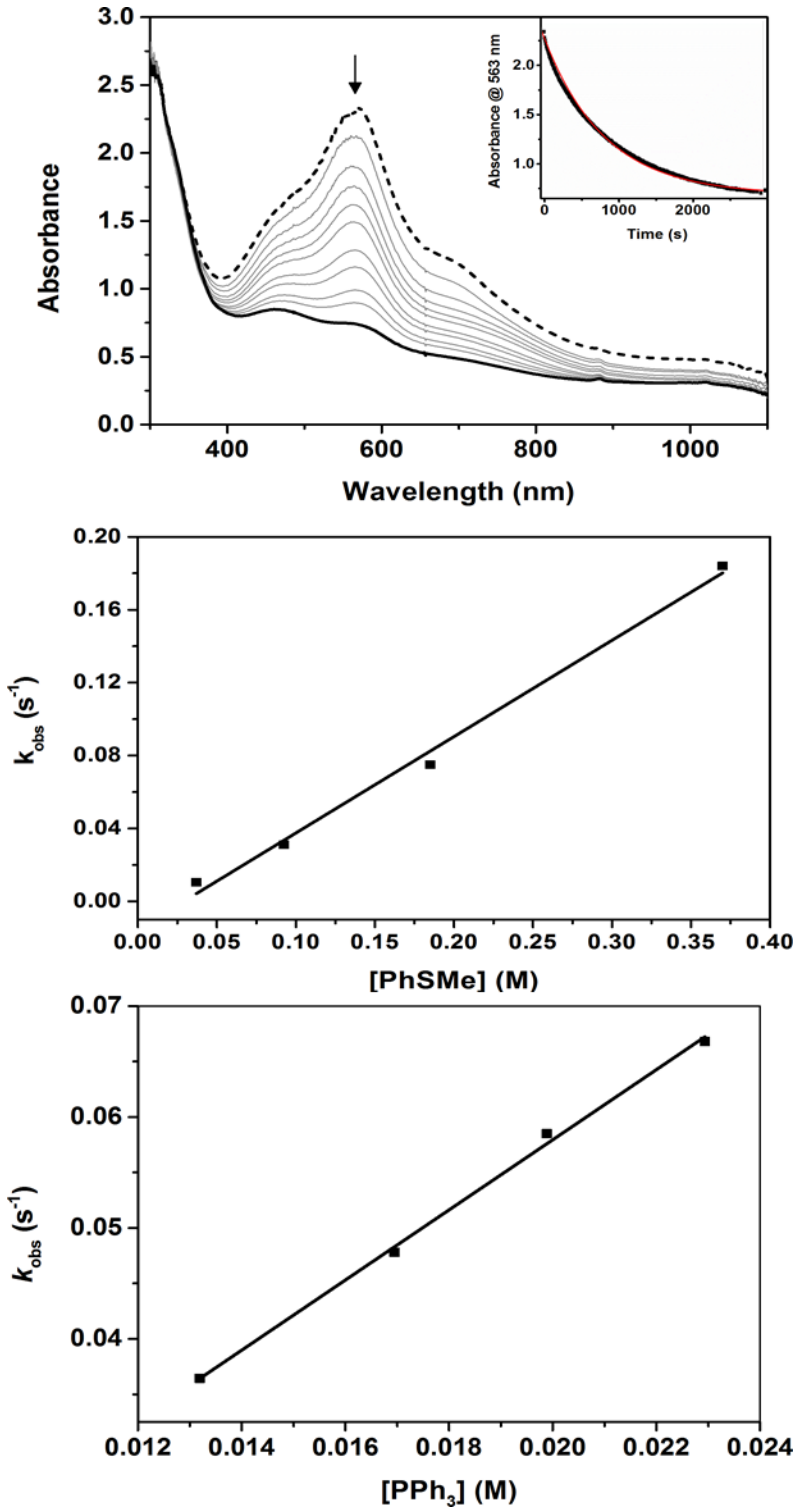

Figure S4: Top: Changes in the absorption spectra associated with the reaction of **2** (1 mM) with Thioanisole at -90 °C. **Inset**: The Pseudo-first order decay of the absorption band at 563 nm as a function of time. **Middle**: Linear dependence of k_{obs} on the concentration of thioanisole. **Bottom**: Linear dependence of k_{obs} on the concentration of triphenylphosphine.

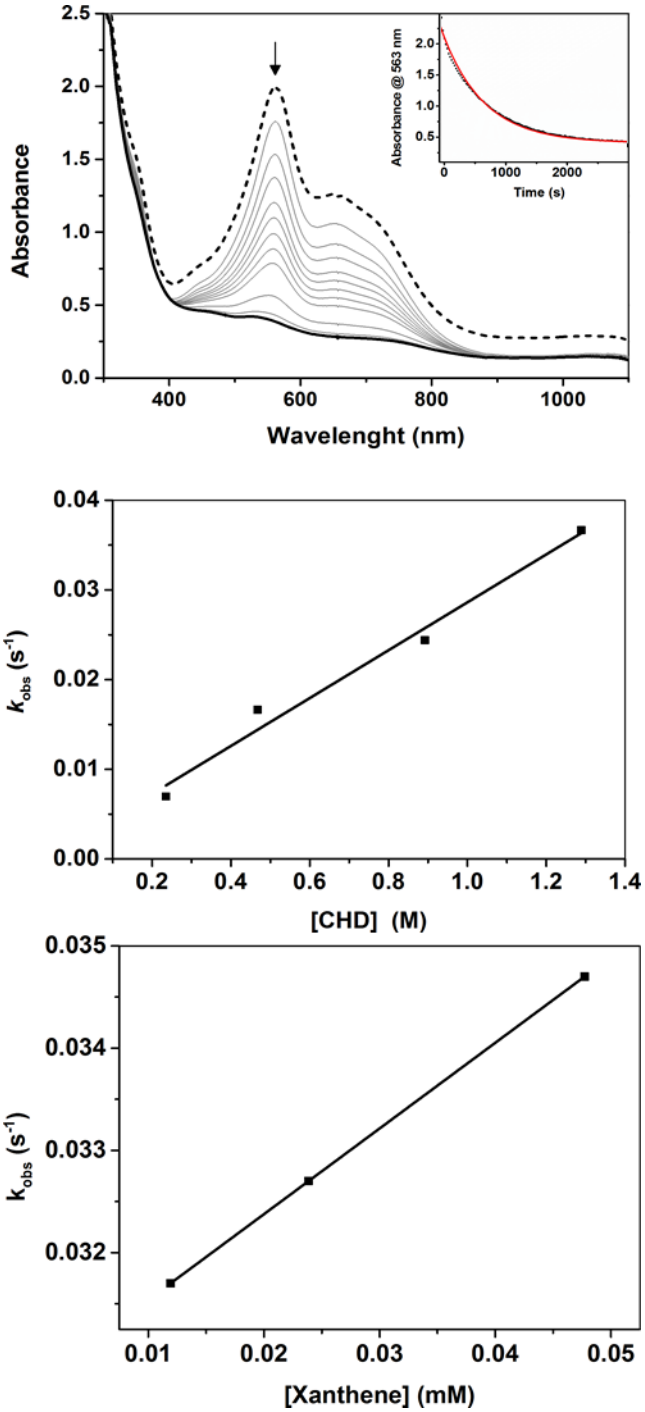

Figure S5: Top: Changes in the absorption spectra associated with the reaction of **2** (1 mM) with Cyclohexadiene at -90 °C. **Inset**: The Pseudo-first order decay of the absorption band at 563 nm as a function of time. **Middle**: Linear dependence of k_{obs} on the concentration of cyclohexadiene. **Bottom**: Linear dependence of k_{obs} on the concentration of xanthene.

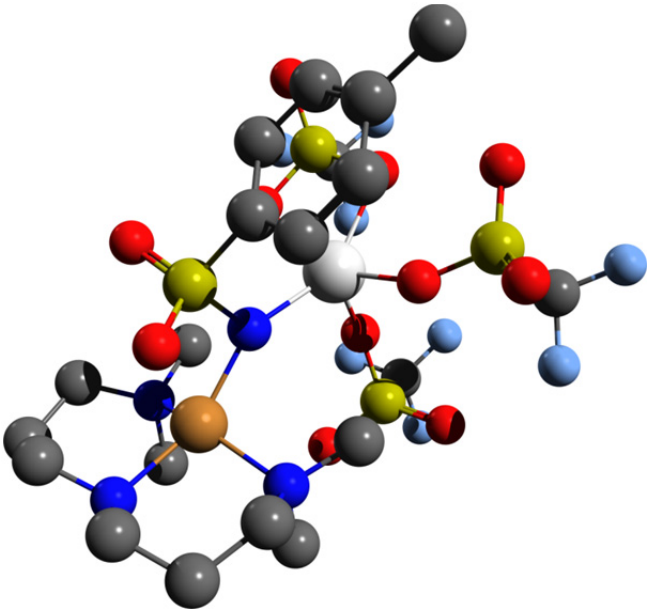

Figure S6. DFT energy minimized structure for the singlet state of **1**. The Hydrogen Atoms are removed for clarity. Gray: Carbon, blue: Nitrogen, red: Oxygen, yellow: Sulfur, orange: Cu, light blue: Fluorine and white: Scandium.

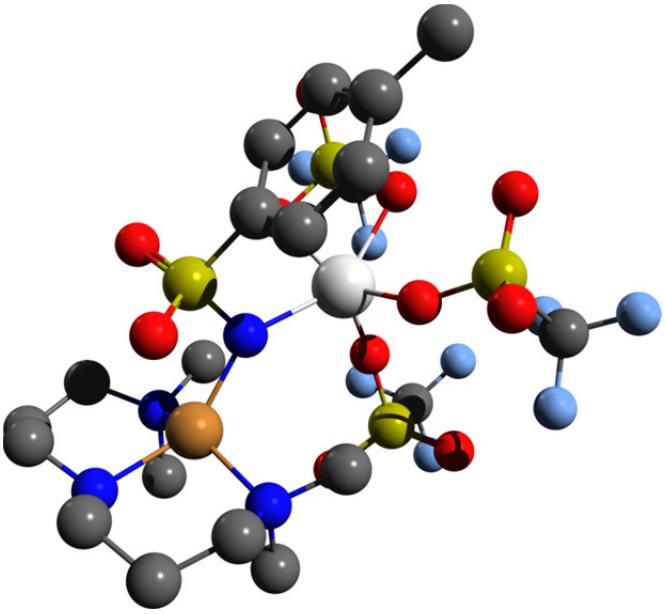

Figure S7. DFT energy minimized structure for the triplet state of **1** (**1**^{3}). The Hydrogen Atoms are removed for clarity. Gray: Carbon, blue: Nitrogen, red: Oxygen, yellow: Sulfur, orange: Cu, light blue: Fluorine and white: Scandium.

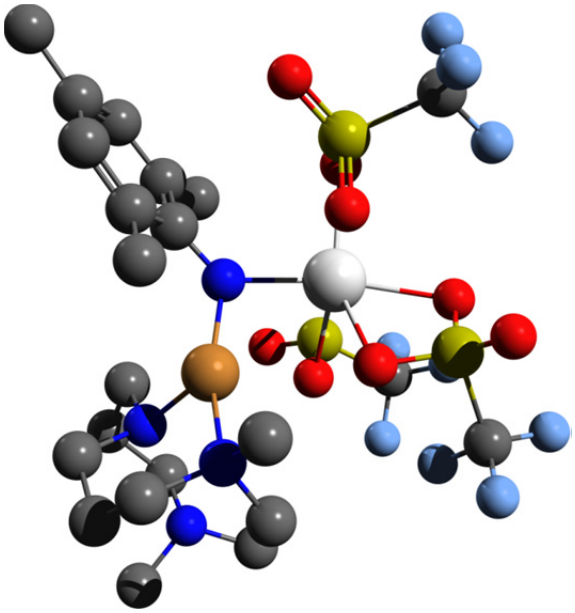

Figure S8. DFT energy minimized structure for the singlet state of **2**. The Hydrogen Atoms are removed for clarity. Gray: Carbon, blue: Nitrogen, red: Oxygen, yellow: Sulfur, orange: Cu, light blue: Fluorine and white: Scandium.

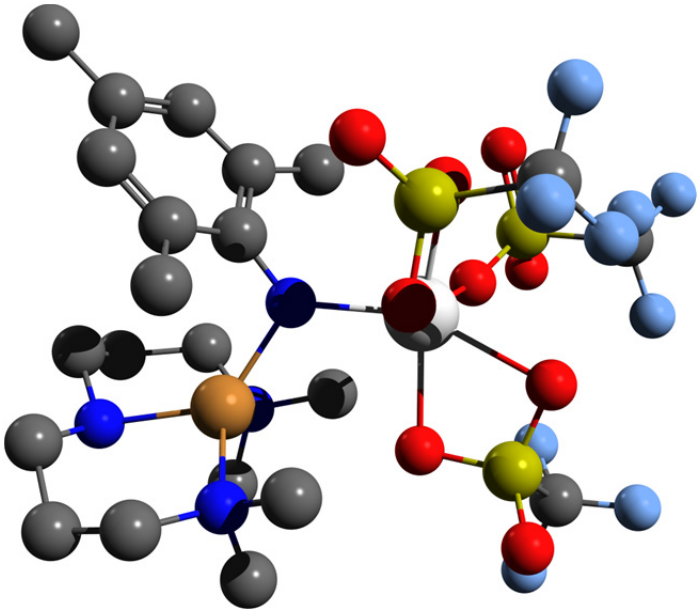

Figure S9. DFT energy minimized structure for the triplet state of **2** (**2**^{3}). The Hydrogen Atoms are removed for clarity. Gray: Carbon, blue: Nitrogen, red: Oxygen, yellow: Sulfur, orange: Cu, light blue: Fluorine and white: Scandium.

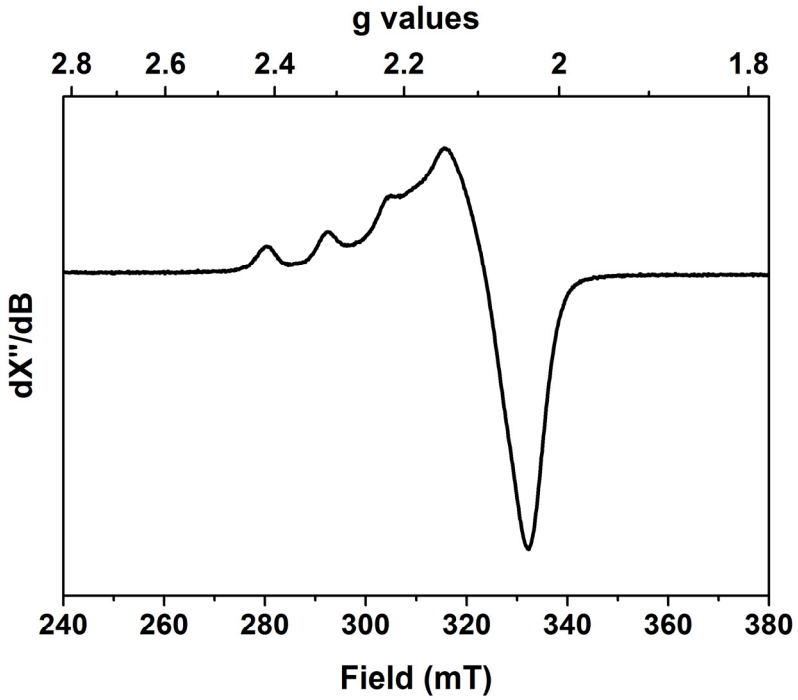

Figure S10: X-band EPR spectrum of the reaction mixture of $[(L1)Cu]BF_4$ with mesityl azide in CH_2Cl_2 at -90 °C.

Table S1 Summary of the calculated energies

structure	S	distance: Cu-N_{Nit} Å	Cu-Sc Å	energy: FSPE Eh		ΔE kcal
1	1	1.946	3.853	-6742.9917	[§]	2.92
1^3	3	1.946	3.847	-6742.9871	[§]	
2	1	1.841	3.040	-6272.9285	[§]	14.22
2^3	3	1.994	3.510	-6272.9058	[§]	

[§]broken symmetry calculations

Table S2 Cartesian coordinates (Å) for the DFT energy minimized structure for the singlet state of **1**.

C	0.57782730159061	8.30502791882486	7.21523704931429
C	-0.41968756501818	7.97767801377301	8.15101362864597
C	-0.99356347039316	6.71026400582492	8.17416633195353
C	-0.57868113985388	5.76341233689774	7.22310097978488

C	0.41422530679659	6.06159146686416	6.27715433706367
C	0.99446504053589	7.32022638252332	6.29371496816573
S	-1.39784416548836	4.19089237639542	7.16984474955676
O	-0.48243393529991	3.13373666111008	6.60528019654188
C	1.16867859817967	9.67878439638929	7.17214817644833
O	-1.92943109384649	3.89513412604223	8.52057777536752
N	-2.53067319294138	4.44629831503620	6.03459220133974
Cu	-2.54841621180505	2.62957518275930	5.33670300458923
N	-4.24955376695506	2.11156665153199	6.39612263670191
C	-3.94404784916648	1.26839878627262	7.58681940148267
C	-3.22950660228992	-0.02961946350203	7.27180944776734
C	-1.85555923448385	0.16407844938230	6.66678799621117
N	-1.86090845038231	0.71901867130003	5.27591735747290
C	-0.46939775515481	0.60390008161010	4.74263075888107
C	-0.28052031710513	1.13283148458543	3.33761984379653
C	-0.43389922184586	2.63604952393568	3.23393501035403
N	-1.81360552546889	3.14484563621108	3.46813752065190
C	-1.79805853297667	4.60444896339322	3.21291314074709
C	-2.81492073883413	2.51102734435492	2.56623204745646
C	-5.05299895365815	1.38612711783693	5.37220709520968
C	-5.03527299384837	3.28568178703635	6.85913213629744
H	-2.47738991645213	0.14070912293588	4.69277808486686
H	0.73162831721053	5.30718099908169	5.55862432410798
H	1.77641780457613	7.55887845248226	5.57286987217137
H	-0.74019906455984	8.72206350350349	8.88019206314052
H	-1.72645390437118	6.43668819906057	8.93200515380943
H	0.65243312832570	10.26845510810694	6.39718022226701
H	2.23375052349782	9.64821816823086	6.90654473569124
H	1.04479746509637	10.20153902422788	8.12852252737295
H	0.21740874790383	3.14307080469559	3.95920538423755
H	-0.14057450497534	2.97040158457058	2.22474056631083
H	-0.92644744770338	0.60586391665178	2.62092210728720
H	0.75098859028176	0.89583293475511	3.04132650326568
H	-0.20722438629002	-0.46448062821502	4.77350834136702
H	0.18194920253487	1.13392478761123	5.44863925550101
H	-1.24125145125554	0.84362086460433	7.27377890053533
H	-1.33722279733947	-0.80586629276402	6.62132480075720
H	-3.84485542669829	-0.69333199128709	6.64689014836321
H	-3.09201109540534	-0.55730816594157	8.22592567700853
H	-4.90845247419115	1.05515395057332	8.07720457325862
H	-3.34900177999174	1.89198812113419	8.26824617702673
H	-5.31518716743041	2.08104543705232	4.56877596982794

H	-5.97880804819162	1.01987475644301	5.84361704520096
H	-4.51185738633085	0.52693738650769	4.96845893282324
H	-5.98517839952659	2.91102624914530	7.27037417502269
H	-5.24935213427681	3.94209712282129	6.01334143401545
H	-4.48172171244659	3.81771721585337	7.63434288757735
H	-2.51238343855363	2.67389620141924	1.51934196624114
H	-3.79276611407830	2.97675385865072	2.73054592324335
H	-2.88267102479362	1.43446001315165	2.74559679150628
H	-1.49115540386570	4.77273069202766	2.16960249419426
H	-1.09733715289383	5.09868834996717	3.88689803539086
H	-2.79925752028166	5.01854625330656	3.34244764679792
Sc	-3.36848083200037	6.35404157723690	5.88706742634831
O	-4.99023786806996	6.03940609527366	4.76257736494042
S	-5.55614329537611	5.48917478583744	3.42745141598400
F	-7.93465972257075	5.68296213609721	4.61868049046516
F	-7.98665298746000	5.79409540432184	2.42913010927867
F	-7.28556461788968	7.51229858264812	3.59762697474551
C	-7.32218494802953	6.17487496975381	3.53034238788944
O	-5.67772135025700	4.02219799835849	3.49324065880532
O	-4.91356894331247	6.09513952991911	2.26111376405067
O	-2.10194298194474	7.27981663997510	4.63146370575301
S	-1.50330058392865	8.62433941249932	4.14078857222655
F	-2.76804425945039	8.24816199803256	1.81328818723760
F	-2.52854556548074	10.34615565018696	2.39800426962630
F	-4.02815710712432	9.09626823912514	3.39791234162359
C	-2.80097498339615	9.10739183955877	2.84388902520610
O	-0.25860065633738	8.38257185701277	3.40419997112616
O	-1.55113049919985	9.66794724714786	5.16799676810376
O	-3.77272028274323	8.32053138904858	6.82918658263747
S	-4.36341330693267	7.73742011755383	8.10167754790671
F	-6.84163031196471	7.50271863014603	9.02550162912753
F	-6.41072595601845	9.42782505375216	8.06496139243520
F	-6.70840979007466	7.63302657874432	6.84081203707627
C	-6.22617102305727	8.10472147076288	7.99985198458492
O	-3.89525939363976	8.26420022867958	9.37559780555110
O	-4.25805829155155	6.22805035157440	7.89065707528058

Table S3 Cartesian coordinates (Å) for the DFT energy minimized structure for the triplet state of **1** (**1**^{3}).

C	0.53390610535205	8.46597404111537	7.34578041317790
C	-0.45992808001233	8.04687502142126	8.24922010133519

C	-0.95709512734323	6.74750515102018	8.21849782738166
C	-0.46065278255896	5.86089401716778	7.25063841463340
C	0.53946440418214	6.24354472519994	6.34457371847500
C	1.03192427913752	7.53929015540807	6.40784745382184
S	-1.15376175332122	4.23369289211799	7.13626819069241
O	-0.14834968050141	3.32545948297002	6.53157129230735
C	1.03810506768645	9.87461468689051	7.35890661461461
O	-1.74868421282486	3.84195056905015	8.43669552123285
N	-2.40896396202456	4.41911872207274	6.08051089187906
Cu	-2.60067828314029	2.65791680005987	5.27596344471803
N	-4.35940460260629	2.08993555770480	6.29645788022163
C	-4.05044481091879	1.30345462783573	7.52536201804473
C	-3.25538228408575	0.03080971587975	7.29588911598425
C	-1.85519425344721	0.25338031851235	6.75451938040384
N	-1.84143867395536	0.73453539438217	5.34117757112824
C	-0.45824519380403	0.62057436462654	4.79730307424191
C	-0.34281658362647	1.04270160437606	3.34491550766142
C	-0.52941675393472	2.53216759908332	3.11577175663464
N	-1.91299454633706	3.04422928221949	3.33733363372426
C	-1.89722897411277	4.49854016586350	3.04489622595777
C	-2.90025582365044	2.38185234922467	2.44557861754287
C	-5.14910972856098	1.31123672961219	5.30974490801192
C	-5.14871882916185	3.27775526326986	6.70978925873023
H	-2.44093670189805	0.10890257589227	4.79078812157678
H	0.92135165465860	5.53331365009931	5.61274897345589
H	1.81055928465381	7.84850145655439	5.71072275345930
H	-0.83662510916915	8.74340367452511	8.99843656933591
H	-1.68201795429566	6.40393795916721	8.95469959684592
H	0.52401366783380	10.44806330329541	6.57050654034524
H	2.11421794719501	9.91571652453946	7.14346934156229
H	0.83893755301890	10.36683402181919	8.31859008002375
H	0.12963264695205	3.10209687683152	3.78575099951345
H	-0.25414580204734	2.78699173310261	2.07757933727054
H	-1.01491809798759	0.44762043695509	2.70872000970887
H	0.67591879050169	0.79656089805446	3.01290350256750
H	-0.14179686984127	-0.42890795010918	4.90677809461876
H	0.18930219482197	1.23695863089494	5.43357927408983
H	-1.30605960741449	0.99116205764345	7.35700225356126
H	-1.29136962419761	-0.69231973403014	6.79509480041861
H	-3.80453413867156	-0.68034573623539	6.66005140999740
H	-3.15624569819792	-0.45987204275750	8.27456300199129
H	-5.01431302258049	1.05948190349279	8.00500164551835
H	-3.50249477926620	1.97756472482886	8.19855948773438

H	-5.41607272949043	1.96413398347566	4.47239623394221
H	-6.07375380390411	0.94319062920544	5.78453955953590
H	-4.58356396358849	0.45007734127192	4.94155601643659
H	-6.10898701417364	2.94278356681078	7.13292360332257
H	-5.34545307506724	3.90685313976580	5.83926104536575
H	-4.59601598505277	3.83346045653841	7.47225319569851
H	-2.58709143207698	2.49647714048544	1.39463204537070
H	-3.87867734420008	2.85556698566766	2.57993274336413
H	-2.97628558525008	1.31439670422376	2.67490858503064
H	-1.61780255429048	4.65977482048832	1.99211265002763
H	-1.17195404847697	4.99927442258190	3.69189055978512
H	-2.89244988307229	4.92167511225238	3.20034592700271
Sc	-3.30255758718490	6.38870790627712	5.89898518890340
O	-4.91162341717917	6.05363855380432	4.78504731242457
S	-5.54483487619014	5.56219847508226	3.45000837100131
F	-7.85322988050704	5.63490795796607	4.78313697704100
F	-8.03269283317189	5.87154969252660	2.61047415780357
F	-7.29856974362611	7.53464261428269	3.83653710697474
C	-7.31484650571618	6.20305703169481	3.69274457509955
O	-5.63099953262999	4.09276377744794	3.44934938821405
O	-4.98127641116918	6.24866309664186	2.28922865090370
O	-2.04027339874057	7.24408148078888	4.63215296896900
S	-1.37562902092847	8.54605735115334	4.08430648671429
F	-2.61734079335167	8.06831382522803	1.76703115003954
F	-2.28152447508251	10.18770032677007	2.21043917844370
F	-3.85880996992770	9.08766202214423	3.26447224078715
C	-2.62757706993139	8.99949576171307	2.73167110082080
O	-0.12382283495602	8.21562932071206	3.40032131964870
O	-1.42256993393320	9.63193546953299	5.06517663259409
O	-3.75017226052116	8.29970957950776	6.85015626852581
S	-4.28772388381020	7.69597381456860	8.14347930172466
F	-6.72666574321744	7.38007136124750	9.13568807114856
F	-6.39081953736186	9.31340005018436	8.15409655690860
F	-6.65923883932495	7.50200146538535	6.94782902493619
C	-6.16606973704557	7.99811386753101	8.09066175715969
O	-3.80000859665194	8.24006917246633	9.40075058599936
O	-4.13159694969495	6.19100752092726	7.91933483617905

Table S4 Cartesian coordinates (Å) for the DFT energy minimized structure for the singlet state of **2**.

C	2.37784890382662	6.76496416076791	7.41766803988768
C	1.31357531225792	6.83231414300436	8.33715387823974
C	0.03818100259292	6.39973566541282	8.02147009098034

C	-0.20939525856225	5.84305771760288	6.69906899380890
C	0.91347407249506	5.70759862929985	5.77980115975264
C	2.15040318747976	6.19397934411710	6.14596682688634
C	3.72452462719476	7.30080457026207	7.77024443251885
N	-1.45223676230715	5.52988798571445	6.31685719143301
Cu	-1.83417443257992	4.06774156562710	5.26541723806713
N	-4.05881491415904	1.03855783606600	7.20097940521652
C	-3.69492835668878	1.44155993170493	8.58142814619620
C	-2.18511839347524	1.60830410962868	8.76885407920962
C	-1.62414603505379	2.73972451108084	7.89879343791610
N	-1.83634710051754	2.46376428938315	6.44422505639164
C	-0.86763324546866	1.47114043032034	5.90962787500541
C	-1.30893441565677	0.91104617052714	4.56391610666116
C	-1.30349246010073	1.90484600493640	3.41030630258054
N	-2.23619187640534	3.06635774978774	3.55794336927842
C	-2.05804710782132	3.94309373893391	2.36513252576576
C	-3.65171492263317	2.61121373626457	3.60536126552685
C	-3.83462832034873	-0.39426103243126	6.97538985663037
C	-5.43877758032029	1.41705624372555	6.87510281666375
H	-2.80483994692460	2.02032611951458	6.41303506325315
C	0.70129579451501	5.12777181159889	4.42079509256259
H	2.97826658846440	6.13974832855744	5.43665842599672
H	1.50353121691681	7.23944585111014	9.33193474748160
C	-1.05210904778320	6.49289099830286	9.03821638253201
H	3.82954644551734	8.32040913427658	7.35876139869759
H	4.52709241348588	6.69723758065399	7.32475033766511
H	3.86605469306637	7.36739839339546	8.85577152721102
H	-0.29406948643004	2.32257845986032	3.28135013661672
H	-1.56103495082979	1.38378706950646	2.47240334586034
H	-2.29349266927044	0.43062492140782	4.66259781903643
H	-0.61164663516657	0.10647732602282	4.29039910463321
H	-0.76364760625691	0.64383865589493	6.62924055831055
H	0.12008486229964	1.95305474415066	5.84158380373026
H	-2.15464663206354	3.66819197495861	8.13407539488439
H	-0.55228137152144	2.90275092815515	8.07776441994196
H	-1.65508881542673	0.66224091145551	8.58370845055470
H	-1.98999068433574	1.86373659270363	9.82067068968724
H	-4.09519334570723	0.71003089545339	9.30906947365286
H	-4.18430857590129	2.40334805252154	8.78489356871669
H	-4.04574096936054	-0.64120099441961	5.92663957164138
H	-4.48796109781125	-1.01268603312703	7.61995144176215
H	-2.79130987086896	-0.65606860892399	7.19319345078416

H	-6.16866251739539	0.95437644070113	7.56607812111506
H	-5.67765558942744	1.08974218906926	5.85457410403636
H	-5.53945762137688	2.50781296304529	6.92769507549702
H	-3.89349025505538	2.03092204377109	2.70085933966605
H	-4.29959066895793	3.49059347297840	3.66137512728264
H	-3.82564734473627	1.98686167510576	4.48732716781257
H	-2.33839992043753	3.38950087630730	1.45433125992101
H	-1.00768925807806	4.24312342040181	2.28598470771974
H	-2.69036777356071	4.82913167084185	2.46566576712896
Sc	-3.17986184614578	6.68241942548086	6.03576347501848
O	-3.87269460804049	5.85005725005950	4.08772897261770
H	-0.63046509467259	6.65487891584815	10.03721477291466
H	-1.67627777427198	5.59283940049308	9.05859860108215
H	-1.71751149832985	7.33981436278216	8.81575214664625
H	1.59039294615731	5.25184535405828	3.79203708906958
H	-0.15392581349795	5.61226702436246	3.92339015999458
H	0.49300795515376	4.04471505146561	4.47770941341580
S	-4.99641412766668	6.86235600256703	3.88497983131250
O	-5.04253006185575	7.64852235820650	5.17732539739472
O	-4.99374402383738	7.60663620013303	2.63183121961364
C	-6.57868691765505	5.80564801640580	3.84562998961767
F	-7.64385254910526	6.60878803286748	3.95386411324304
F	-6.61626678747122	5.15129294738535	2.67335733023809
F	-6.57659821186411	4.91446898093804	4.84746875106161
O	-4.33430531742311	4.88492406419427	6.78967352094454
S	-4.63514011431870	5.51037926689913	8.14294759172177
F	-7.09026899340428	4.50478092830284	8.02164739979636
F	-6.85335763428338	6.16365318094806	9.43774501895581
F	-6.94483694828866	6.56697371786571	7.28848581553781
C	-6.52728734969086	5.70746202558194	8.22244639384480
O	-4.09344681213659	6.92242667432569	8.04637178562756
O	-4.26956658108986	4.73044453494738	9.32322034104130
O	-2.28075839463604	8.54652095848866	6.77112518639591
S	-1.50759740550014	8.89157314308232	5.50164526073288
F	-1.78192581519770	10.79642157109919	3.67748063595179
F	-3.63565776800606	10.32303519545150	4.74720049421014
F	-2.06162338444409	11.47730551156290	5.74498850526372
C	-2.31443420514334	10.49317567106953	4.87050141905794
O	-1.91636893846785	7.81834937903396	4.51355156313846
O	-0.08479120819617	9.17348948710488	5.65045483452960

Table S5 Cartesian coordinates (Å) for the DFT energy minimized structure for the triplet state of **2** (**2**^{3}).

C	1.63795047617372	5.59604327899035	8.26566323727265
C	0.42239905513688	5.78194120004065	8.94770300864239
C	-0.81107180975673	5.70143956464672	8.31892477236488
C	-0.86542644137136	5.31399523717389	6.91836996019591
C	0.39155169182904	5.23848054505242	6.19338838291047
C	1.58663417922165	5.36437412797228	6.87641268202707
C	2.95029048066911	5.70982856591427	8.97428774418983
N	-2.05753456543421	5.00830807739591	6.35401151023040
Cu	-1.98301425356290	3.18224445217515	5.55721039422527
N	-3.15423710015751	2.31106107526044	7.18585326735469
C	-2.27689262555430	2.23179939944557	8.39157031511906
C	-1.04778408168973	1.34382631602487	8.25848016698682
C	-0.05031722220226	1.75133629784685	7.18478195086735
N	-0.62808115431788	1.62405147522929	5.81592220642405
C	0.41790792555512	1.53691137474544	4.76867537965918
C	-0.19741230402549	1.25343333022809	3.40764556631275
C	-0.86798133990896	2.44943194319106	2.75271080547552
N	-2.07741710938285	3.00501211747951	3.43820247611881
C	-2.43809493564432	4.24962276530492	2.70881337698630
C	-3.21281838962011	2.04793431598446	3.33772061247586
C	-3.66909737520391	0.97634904546565	6.79470011042426
C	-4.32281537378947	3.14735296354202	7.53563665076804
H	-1.13673179215459	0.73388324233246	5.78283678555669
C	0.39367112318940	5.14962842944263	4.70211455766363
H	2.52082062977452	5.29962381848296	6.31429797676376
H	0.44563776242698	6.00711664253525	10.01594360616292
C	-2.05174401495215	6.00581549091419	9.09498136635816
H	3.39501504972305	6.70225258810163	8.78833866635656
H	3.66914852589124	4.96613514536663	8.60243404492835
H	2.83564085228065	5.59415089984509	10.05904791570526
H	-0.14396893911052	3.27009554322704	2.66519232125650
H	-1.17635628662714	2.18481849457483	1.72673665852970
H	-0.88142848228812	0.39266699706570	3.47740269288111
H	0.60670207857386	0.93833932851669	2.72749767011389
H	1.11815050927517	0.73055378820672	5.04111276882012
H	0.98600076846026	2.47720939310571	4.76586427897650
H	0.28973327403527	2.78886472749706	7.31811779342516
H	0.83961979709541	1.10437323097386	7.25149103551655
H	-1.33618138929578	0.29110827460965	8.11451845793874

H	-0.52844605931903	1.37870714031960	9.22682903301172
H	-2.89189694119284	1.87436227398633	9.23621912194189
H	-1.96868423628865	3.25961283601453	8.62415603385591
H	-4.36829192146024	1.09150167926610	5.95954555677851
H	-4.20303075737876	0.51474225283316	7.64205428471154
H	-2.86492397881731	0.29887190184722	6.49397941917244
H	-4.87305653037745	2.69682717531725	8.37771606639387
H	-4.98970728190686	3.23421711914953	6.67430769626576
H	-3.98482451538798	4.14117927350705	7.84061148488006
H	-3.43054609034030	1.83129498106803	2.27864603081803
H	-4.10034408421242	2.49800109085353	3.79635773459931
H	-2.96784003688730	1.10744446537072	3.84306902151369
H	-2.53191462563932	4.02934324595756	1.63348109039168
H	-1.66433109876886	5.00859954552519	2.85371011496639
H	-3.39181253292418	4.62343169908648	3.07631805924811
Sc	-3.70045390399248	6.22104995357377	5.92322185935687
O	-4.75818576877502	4.64368165394800	4.84073332002016
H	-1.81601537677303	6.15045527243515	10.15546529070414
H	-2.81526932497760	5.22287003527098	9.01936205088455
H	-2.51247444649188	6.93637443005968	8.73301046132672
H	1.38090294373868	4.86692328260067	4.31911048558110
H	0.12152004288564	6.12297949067914	4.26720681908370
H	-0.35141364099719	4.43199378485618	4.34534668741726
S	-5.83214043305523	5.52178196270703	4.17650681739190
O	-5.55047398629876	6.91033574644145	4.67958507986237
O	-6.01100933662592	5.32119055557665	2.74315348831505
C	-7.44310248857203	4.93431787059085	5.00125200875429
F	-8.43532609735583	5.75955364121276	4.65137316429612
F	-7.70460805817236	3.69140854501709	4.56582005223699
F	-7.30214774351826	4.92099223738289	6.33181094468283
O	-4.89227955162303	6.39023676398057	7.53457304010007
S	-5.57495920816561	7.18791476169594	8.67277016326934
F	-7.55069790748948	7.83137288559391	6.96980578240319
F	-7.19001660064541	9.28518282874311	8.56770372546050
F	-5.80414394685214	9.15314982774940	6.87324875453923
C	-6.60379953703712	8.44871853554647	7.69415996205396
O	-4.60804048159205	7.98756101858729	9.43319594281471
O	-6.53090865143810	6.33400606360162	9.38339838192261
O	-2.74057193071141	8.12300532220526	6.39897616568028
S	-2.06011411431822	8.28922696293242	5.04331641837687
F	-2.41259568673527	9.97344591011270	3.02768029438035
F	-4.22094448333835	9.61773422258324	4.21479472373965
F	-2.61868116284426	10.88178287778190	5.01490718745643

C	-2.89889432717415	9.80867673379068	4.26491761954097
O	-2.55338768910911	7.10118322988542	4.23124127253044
O	-0.62640360430453	8.54929340884753	5.04493811328327

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