Supporting Information

For

Copper(I)-α-Ketocarboxylate Complexes: Characterization and O_2 Reactions That Yield Copper-Oxygen Intermediates Capable of Hydroxylating Arenes

Sungjun Hong,[†] Stefan Huber,[†] Laura Gagliardi,[§] Christopher C. Cramer,[†,*] and William B. Tolman[†,*]

[†]*Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, USA, and* [§]*Department of Physical Chemistry, Sciences II, University of Geneva, 30 Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland*

E-mail: cramer@chem.umn.edu, tolman@chem.umn.edu

Contents

Experimental

General: All reagents were obtained from commercial sources and used without further purification, unless otherwise noted. The solvents THF, toluene, pentane, and Et_2O were dried over Na/benzophenone and distilled under nitrogen or passed through solvent purification columns (Glass Contour, Laguna, CA). $[Cu_4Mes_4]$ (Mes = mesityl),[1] $[Cu(CH_3CN)_4]O_3SCF_3$,[2] 1-(6'-bromo-pyridin-2'-yl)-ethanone,[3] and 2-bromo-6-(2',6'-dimethylphenyl)pyridine[4] were synthesized following literature procedures. All metal complexes were prepared and stored in a Vacuum Atmospheres inert atmosphere glovebox under a dry nitrogen atmosphere or were manipulated using standard inert atmosphere vacuum and Schlenk techniques. Labeled dioxygen ($^{18}O_2$, 99%) was purchased from Icon Isotopes, Inc and used without further purification.

Physical Methods: NMR spectra were recorded on either Varian VI-300 or VI-500 spectrometers at room temperature. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are reported versus tetramethylsilane and were referenced to residual protium in the deuterated solvent. UV-vis spectra were recorded on an HP8453 (190-1100 nm) diode array spectrophotometer. Beers Law plots have yet to be obtained, so rather than list UV-vis data as $\lambda_{max}(\varepsilon)$ in the text below, the spectra are shown as absorbance vs. wavelength plots in Figure S5. Low temperature spectra were acquired through the use of a Unisoko low temperature UV-vis cell holder. When necessary, UV-vis spectra were corrected for drifting baselines due to minimal frosting of the UV cells caused by the low-temperature device. This was achieved by subtracting the average of a region with no absorbance (i.e., baseline, typically 950-1000 nm) from the entire spectrum. Elemental analyses were performed by Robertson Microlit Lab. ESI-MS (electrospray ionization mass spectra) were recorded on a Bruker BioTOF II instrument.

Ligand Synthesis:

L^H. A solution of 2-dimethylaminoethanol (8.0 mL, 80 mmol) in pentane (100 mL) was treated dropwise with 1.6M *n*BuLi (100 mL, 160 mmol) at 0 °C. After 30 min at 0 °C, a solution of 2-phenylpyridine (5.0 g, 32.0 mmol) in pentane (50 mL) was added dropwise to yield a red-brown species, which was then cooled to -78 °C after 1h at 0 °C. A solution of *N,N*-dimethylacetamide (3.0 mL, 32.0 mmol) in pentane (50 mL) was added carefully at -78 °C. After 1 h at -78 °C, the solution was warmed to room temperature and the reaction mixture was carefully hydrolyzed with H_2O at 0 °C. The aqueous layer was extracted with diethyl ether (2 × 50 mL), dried over Na_2SO_4, and evaporated under vacuum. The crude product, 1-(6'-phenylpyridin-2'-yl)ethanone was directly used to the next step without any further purification. A mixture of the crude 1-(6'-phenylpyridin-2'-yl)ethanone, 2,6-diisopropylaniline (tech 90%, 10.0 g, 51.0 mmol) and formic acid (2 drops) in 100 mL anhydrous MeOH was refluxed for 3 days. The volume of the solvent was reduced to 20 mL under vacuum to yield a yellow microcrytalline material (2.8 g, 7.7 mmol; 25 %) which was isolated by filtration and washing with cold MeOH (2 × 10 mL). Slow evaporation of the mother liquor under ambient temperature overnight gave the second crop of the product (1.2 g, 3.3 mmol; 10 %), for an overall yield of 35 % based on the starting 2-phenylpyridine. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.29-8.32 (m, 1H), 8.12-8.16 (m, 2H), 7.87-7.94 (m, 2H), 7.42-7.54 (m, 3H) 7.06-7.19 (m, 3H), 2.78 (sept, J = 11.5 Hz, 2H), 2.30 (s, 3H), 1.16 (d, J = 11.5 Hz, 6H), 1.14 (d, J = 11.5 Hz, 6H). $^{13}C\{^1H\}$ NMR (75.0 MHz, CD_2Cl_2): δ 167.94, 156.66, 156.33, 147.17, 139.59, 137.79, 136.34, 129.64, 129.27, 127.34, 124.04, 123.50, 121.65, 120.04, 28.79, 23.55, 23.14, 17.58 ppm. Anal. Calcd for $C_{25}H_{28}N_2$: C, 84.23; H, 7.92; N, 7.86. Found: C, 83.98; H, 8.07; N, 7.83.

L^{Me}. A pale yellow solution containing 2-bromo-6-(2',6'-dimethylphenyl)pyridine (6.0 g, 23.0 mmol) in 100 mL THF was cooled to -80 °C using the dry ice/acetone bath. Under nitrogen, a 1.6 M solution of *n*BuLi in hexane (14.5 mL, 23.0 mmol) was added dropwise with syringe to give a dark red solution. After 30 min, dry *N,N*-dimethylacetamide (2.5 mL, 27.0 mmol) was added and the reaction mixture was then warmed to room temperature and carefully quenched with 50 mL of water. The organic phase was separated and the aqueous phase was washed with dichloromethane (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure to yield a dark red oil. This crude product containing 1-{6'-(2'',6''-dimethylphenyl)pyridin-2'-yl}ethanone was directly used in the next step without any further purification. The final product, L^{Me} was synthesized following the same procedure as that described in the synthesis of L^{H}, but with the crude 1-{6'-(2'', 6''-dimethylphenyl)pyridin-2'-yl}ethanone. The overall yield was 57 % based on the starting 2-bromo-6-(2',6'-dimethylphenyl)pyridine. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.29 (d, J = 7.2 Hz, 1H), 7.88 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.25-7.05 (m, 6H), 2.79 (sept, J = 6.9 Hz, 2H), 2.16 (s, 3H), 2.12 (s, 6H), 1.15 (d, J = 6.9 Hz, 12H). ^{13}C{1H} NMR (75.0 MHz, CD_2Cl_2): δ 168.08, 158.98, 156.90, 147.13, 140.98, 137.18, 136.57, 136.39, 128.43, 128.16, 126.29, 124.04, 123.49, 119.60, 28.76, 23.61, 23.13, 20.71, 17.73 ppm. Anal. Calcd for $C_{27}H_{32}N_2$: C, 84.33; H, 8.39; N, 7.28. Found: C, 84.08; H, 8.15; N, 7.19.

$L^{m\text{-}OMe}$. To a mixture of 1-(6'-bromo-pyridin-2'-yl)-ethanone (5.4 g, 27.0 mmol) and $Pd(PPh_3)_4$ in 120 mL toluene was added aqueous Na_2CO_3 (18.0 mL, 2.0 M) and 3-methoxyphenylboronic acid (4.56 g, 30.0 mmol) in 40 mL MeOH under a nitrogen atmosphere and the mixture was refluxed for 8 h. After cooling, dichloromethane (150 mL), aqueous Na_2CO_3 (45.0 mL, 2.0 M) and concentrated ammonium hydroxide (6.0 mL) was added. The organic layer was extracted with dichloromethane (3 × 100 mL), the combined organic layer was dried over magnesium sulfate and the volatile material was removed in vacuo to give crude 1-{6'-(3''-methoxyphenyl)-pyridin-2'-yl}ethanone, which was used directly in the next step without further purification. The final product, $L^{m\text{-}OMe}$ was synthesized following the same procedure as that described in synthesis of L^{H}, but with the crude 1-{6'-(3''-methoxyphenyl)-pyridin-2'-yl}ethanone. The overall yield was 70 % based on the starting 1-(6'-bromo-pyridin-2'-yl)-ethanone. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (dd, J = 6.9 and 1.8 Hz, 1H), 7.93-7.85 (m, 2H), 7.77-7.70 (m, 2H), 7.44 (t, J = 8.1 Hz, 1H), 7.22-7.06 (m, 3H), 7.02 (dd, J = 8.1 and 2.4 Hz, 1H), 3.93 (s, 3H), 2.81 (sept, J = 6.9 Hz, 2H), 2.34 (s, 3H), 1.18 (d, J = 6.9 Hz, 12H). ^{13}C{1H} NMR (75.0 MHz, $CDCl_3$): δ 167.54, 160.25, 156.19, 155.84, 146.70, 140.75, 137.43, 136.03, 130.01, 123.71, 123.17, 121.51, 119.90, 119.47, 114.66, 112.81, 55.56, 28.44, 23.42, 23.14, 17.49 ppm. Anal. Calcd for $C_{26}H_{30}N_2O$: C, 80.79; H, 7.82; N, 7.25. Found: C, 80.58; H, 7.89; N, 7.12.

Synthesis of Copper(I) Complexes:

$[(L^{Me})Cu(O_2CC(O)Mes)]$ (1). A mixture of $[Cu(Mes)]_4$ (47.5 mg, 0.065 mmol) and mesitoylformic acid (50.0 mg, 0.26 mmol) in 3 mL THF was stirred for 30 min and the insoluble material was removed by filtration through a plug of celite. The orange colored filtrate was added to a yellow solution of L^{Me} (100 mg, 0.26 mmol) in 2 mL THF. After 30 min, the solvent was removed under vacuum to give a dark reddish-brown powder (yield 85%). X-ray quality single crystals were grown by slow diffusion of pentane into a concentrated THF solution of the product at -20 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.17 (t, J = 7.5-7.8 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.07-7.22 (m, 6H), 6.72 (s, 2H), 2.82 (sept, J = 6.6-6.9 Hz, 2H), 2.29 (s, 3H), 2.24 (s, 3H), 2.14 (s, 6H), 1.87 (s, 6H), 1.12 (t, J = 5.7-6.6 Hz, 12H). ^{13}C{1H}

NMR (75.0 MHz, CD_2Cl_2): δ 201.65, 168.44, 167.20, 160.75, 151.99, 143.83, 139.48, 138.92, 137.86, 137.41, 136.11, 135.35, 130.00, 129.46, 128.50, 128.25, 126.09, 124.04, 123.25, 28.93, 23.84, 23.55, 21.33, 20.67, 19.63, 17.66 ppm. Anal. Calcd for $C_{38}H_{43}N_2O_3Cu$: C, 71.39; H, 6.78; N, 4.38. Found: C, 71.14; H, 6.59; N, 4.32.

[L^HCu(O_2CC(O)Ph)] (2). A mixture of $[Cu(Mes)]_4$ (51.2 mg, 0.070 mmol) and benzoylformic acid (42.0 mg, 0.28 mmol) in 3 mL THF was stirred for 30 min and the insoluble material was removed by filtration through a plug of celite. The orange colored filtrate was added to a yellow solution of L^H (100 mg, 0.28 mmol) in 2 mL THF. After 30 min, the solvent was removed under vacuum to give a dark reddish-brown powder (yield 80%). X-ray quality single crystals were grown by a slow diffusion of pentane into a concentrated CH_2Cl_2 solution of the product at -20 °C. ^{1}H NMR (300 MHz, d_8-THF): δ 8.17-8.23 (m, 3H), 8.05-8.13 (m, 2H), 7.68 (bd, J = 7.2 Hz, 2H), 7.41-7.53 (m, 4H), 7.33 (t, J = 7.5 Hz, 2H), 7.13-7.23 (m, 3H), 2.96 (sept, J = 6.9 Hz, 2H), 2.34 (s, 3H), 1.17 (d, J = 6.6 Hz, 6H), 1.14 (d, J = 6.9 Hz, 6H). ^{13}C{1H} NMR (75.0 MHz, d_8-THF): δ 192.89, 171.59, 169.96, 158.99, 154.23, 145.65, 140.30, 139.72, 138.19, 133.77, 130.56, 130.42, 129.71, 129.17, 128.91, 127.75, 126.24, 125.98, 124.31, 123.19, 29.34, 24.30, 23.67, 17.74 ppm. Anal. Calcd for $C_{33}H_{33}N_2O_3Cu$: C, 69.64; H, 5.84; N, 4.92. Found: C, 69.91; H, 5.78; N, 4.76.

[(L^{Me})Cu(O_2CC(O)Ph)] (3). A mixture of $[Cu(Mes)]_4$ (47.5 mg, 0.065 mmol) and benzoylformic acid (39.0 mg, 0.26 mmol) in 3 mL THF was stirred for 30 min and the insoluble material was removed by filtration through a plug of celite. The orange colored filtrate was added to a yellow solution of L^{Me} (100 mg, 0.26 mmol) in 2 mL THF. After 30 min, the solvent was removed under vacuum to give a dark reddish-brown powder (yield 80%). X-ray quality single crystals were grown by a slow diffusion of pentane into a concentrated THF solution of the product at -20 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.17 (t, J = 7.8 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.69 (bd, J = 7.2 Hz, 3H), 7.51 (t, J = 7.5-7.8 Hz, 1H), 7.35 (t, J = 7.5, 2H), 7.04-7.24 (m, 6H), 2.85 (sept, J = 6.9 Hz, 2H), 2.30 (s, 3H), 2.13 (s, 6H), 1.17 (d, J = 6.9 Hz, 12H). ^{13}C{1H} NMR (75.0 MHz, CD_2Cl_2): δ 194.16, 169.14, 168.66, 160.82, 152.04, 143.91, 139.72, 139.33, 137.88, 136.14, 134.70, 133.38, 130.47, 129.95, 129.33, 128.54, 128.23, 126.20, 124.14, 123.25, 29.02, 23.92, 23.39, 20.70, 17.57 ppm. Anal. Calcd for $C_{35}H_{37}N_2O_3Cu$: C, 70.39; H, 6.24; N, 4.69. Found: C, 70.32; H, 6.29; N, 4.71.

[($L^{m\text{-}OMe}$)Cu(O_2CC(O)Ph)] (4). A mixture of $[Cu(Mes)]_4$ (47.5 mg, 0.065 mmol) and benzoylformic acid (39.0 mg, 0.26 mmol) in 3 mL THF was stirred for 30 min and the insoluble material was removed by filtration through a plug of celite. The orange colored filtrate was added to a yellow solution of $L^{m\text{-}OMe}$ (100 mg, 0.26 mmol) in 2 mL THF. After 30 min, the solvent was removed under vacuum to give a dark reddish-brown powder (yield 75%). X-ray quality single crystals were grown by a slow diffusion of pentane into a concentrated THF solution of the product at -20 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.13 (t, J = 7.8 Hz, 1H), 8.01 (t, J = 7.5 Hz, 2H), 7.78-7.62 (m, 3H), 7.54-7.48 (m, 2H), 7.42-7.27 (m, 6H), 6.98 (dd, J = 8.1 and 1.8 Hz, 1H), 3.81 (s, 3H) 2.90 (sept, J = 6.9 Hz, 2H), 2.31 (s, 3H), 1.21 (d, J = 6.9 Hz, 6H), 1.16 (d, J = 6.9 Hz, 6H). ^{13}C{1H} NMR (75.0 MHz, CD_2Cl_2): δ 194.07, 170.01, 160.27, 159.35, 143.77, 140.60, 139.74, 138.17, 134.48, 133.53, 130.40, 130.21, 128.70, 127.88, 126.45, 124.27, 123.53, 121.09, 116.50, 113.87, 55.78, 29.02, 24.01, 23.45, 17.84 ppm. Anal. Calcd for $C_{34}H_{35}N_2O_4Cu$: C, 68.15; H, 5.89; N, 4.68. Found: C, 67.92; H, 6.06; N, 4.51.

[L^{Me}Cu(O_3SCF_3)] (5). Upon addition of a yellow solution of a L^{Me} (200 mg, 0.52 mmol) in 3 mL THF to a slurry of a CuCl (26.0 mg, 0.52 mmol) in 2 mL THF, the color of the reaction mixture was immediately changed into dark reddish-brown. After 12 hr, the insoluble material

was removed by a filtration through a plug of celite and the solvent was removed under vacuum to give a purple powder. Pure [L^{Me}CuCl] was isolated by recrystallisation through a slow diffusion of pentane into a concentrated THF solution of the product at -20 °C (yield 80%). ^{1}H NMR (300 MHz, d_8-THF): δ 8.19-8.28 (m, 2H), 7.77 (dd, J = 7.2, 1.2 Hz, 1H), 7.09-7.22 (m, 6H), 2.88 (sept, J = 6.9 Hz, 2H), 2.33 (s, 3H), 2.11 (s, 6H), 1.20 (d, J = 6.9 Hz, 6H), 1.13 (d, J = 6.9 Hz, 6H). ^{13}C{1H} NMR (75.0 MHz, d_8-THF): δ 169.95, 161.40, 152.34, 144.58, 140.49, 140.11, 138.64, 136.55, 130.42, 129.86, 129.00, 126.58, 124.49, 124.24, 29.43, 24.83, 23.77, 21.16, 17.63 ppm. To a dark reddish-brown solution of [L^{Me}CuCl] (150 mg, 0.31 mmol) in 2 mL THF was added a coloress solution of AgO_3SCF_3 (80.0 mg, 0.31 mmol). After 1 h, the insoluble AgCl was removed by filtration through a plug of celite and the filtrate was dried under vacuum to give a purple powder. X-ray quality single crystals were grown by a slow diffusion of pentane into a concentrated THF solution of the product at -20 °C (yield 75%). ^{1}H NMR (300 MHz, d_8-THF): δ 8.26-8.34 (m, 2H), 7.81 (dd, J = 6.6, 2.1 Hz, 1H), 7.10-7.24 (m, 6H), 2.89 (sept, J = 6.6-6.9 Hz, 2H), 2.37 (s, 3H), 2.12 (s, 6H), 1.17 (d, J = 6.6 Hz, 6H), 1.13 (d, J = 6.9 Hz, 6H). ^{13}C{1H} NMR (75.0 MHz, d_8-THF): δ 169.95, 160.58, 152.30, 144.61, 140.63, 140.40 138.76, 136.74, 130.72, 129.52, 128.88, 126.72, 124.96, 124.50, 29.24, 24.09, 23.89, 20.72, 17.91 ppm. Anal. Calcd for $C_{28}H_{32}N_2F_3O_3SCu$: C, 56.32; H, 5.40; N, 4.69. Found: C, 56.32; H, 5.20; N, 4.55.

Oxygenation Experiments. Reactions of complexes **1-4** with O_2 were performed similarly, as described in the following representative example. A 20 mL Schlenk flask containing **4** (60.0 mg, 0.1 mmol) in 10 mL acetone was cooled to -80 °C with an acetone / dry ice bath. The mixture was reacted with O_2 by bubbling the gas through the solution at this temperature for 4 h and then it was gradually warmed to room temperature. An aliquot from the brown solution was removed for analysis by ESI-MS (see Figures S6 and S7). To extract the organic products, the volatile materials were removed from the solution under vacuum. The residue was dissolved in concentrated NH_4OH (2 mL), and the blue mixture was extracted with diethyl ether (3 × 20 mL), dried over anhydrous Na_2SO_4, and dried under vacuum. The residue was analyzed by ESI-MS (Figure S8) and ^{1}H NMR spectroscopy with an internal standard (1,3,5-trimethoxybenzene). The latter indicated that the yield of recovered ligand (starting plus hydroxylated) was > 95 %, with a ratio of $L^{m\text{-OMe}}$ to $L^{m\text{-OMe}}$-OH of 60:40 from analysis of the methyl protons on the methoxy substituent. For the case of the reaction with **2**, the ratio L^{H}:L^{OH} was 87:13. ^{1}H NMR of $L^{m\text{-OMe}}$-OH ($CDCl_3$): δ = 13.81 (s, $L^{m\text{-OMe}}$-O*H*, 1H), 3.88 (s, 3H), 2.77 (sept, J = 6.9 Hz, 2H), 2.29 (s, 3H), 1.17 (d, J = 6.9 Hz, 12H) (other resonances were hidden below those of $L^{m\text{-OMe}}$, Figure S9). The aqueous phase was then acidified to pH = 1 with concentrated HCl. The organic product was extracted with CH_2Cl_2 (3 × 20 mL), dried over anhydrous Na_2SO_4, and dried under vacuum. The brown residue was analyzed by ^{1}H NMR spectroscopy with an internal standard (1,3,5-trimethoxybenzene), which revealed an overall yield (benzoylformic and benzoic acids) of > 98 %, and a ratio of benzoylformic acid (BFH) to benzoic acid (HOBz) of 40:60 based on integrated ratios of the *ortho* protons of benzoylformic acid and benzoic acid. For the case of the reaction with **2**, the ratio was 60:40. ^{1}H NMR ($CDCl_3$): δ = 8.29 (d, J = 7.2 Hz, *ortho* of BFH), 8.14 (d, J = 7.2 Hz, *ortho* of HOBz), 7.71 (t, J = 7.2 Hz, *meta* of BFH), 7.64 (t, J = 7.2 Hz, *meta* of HOBz), 7.58 – 7.45 (m, *para* of BFH and HOBz). The same procedure was used with $^{18}O_2$ instead of $^{16}O_2$ for the reaction of **4**, except instead of bubbling the gas, ~20 mL of $^{18}O_2$ was transferred to the reaction vessel by vacuum transfer. ESI-MS data of the crude product solution and of the isolated mixture of $L^{m\text{-OMe}}$ and $L^{m\text{-OMe}}$-OH are

shown in Figures S7 and S8, respectively. The reaction of **5** with O_2 was performed similarly, but there was no color change at -80 °C, and no attempt was made to analyze the products after warming to room temperature.

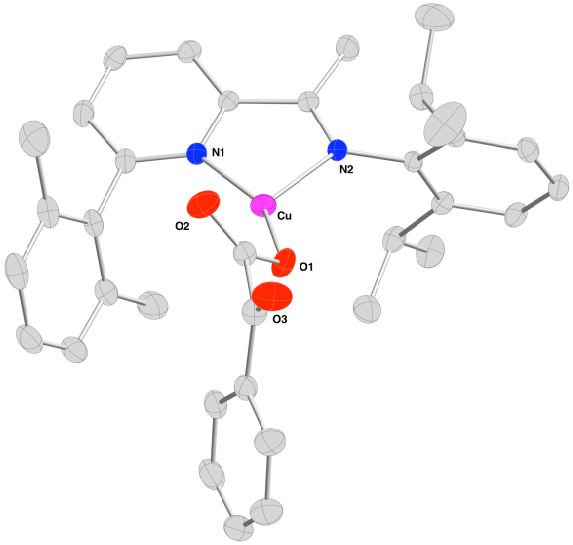


Figure S1. Representation of the X-ray structure of [$L^{Me}Cu(O_2CC(O)Ph)$] (**3**), showing all non-hydrogen atoms as 50 % thermal ellipsoids. Selected bond distances and angles are listed in Table S1 (just below Figure S3).

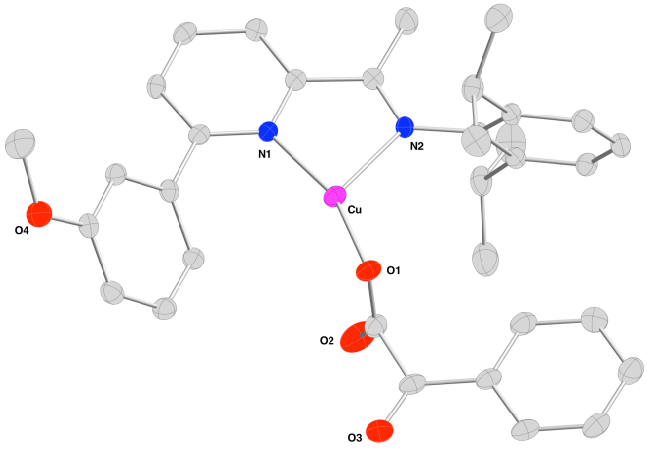


Figure S2. Representation of the X-ray Structure of [$L^{m\text{-}OMe}Cu(O_2CC(O)Ph)$] (**4**), showing all non-hydrogen atoms as 50 % thermal ellipsoids. Selected bond distances and angles are listed in Table S1 (just below Figure S3).

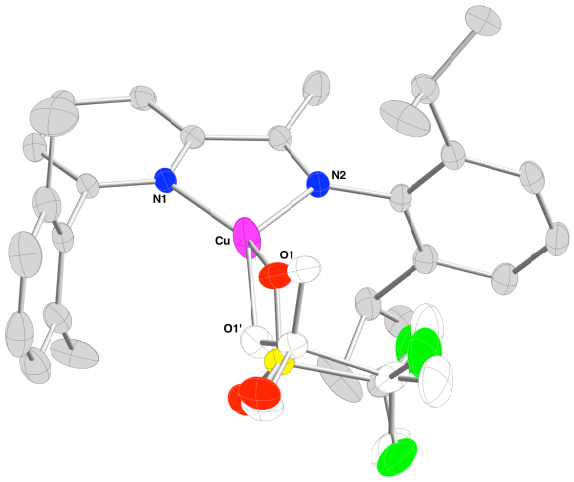


Figure S3. Representation of the X-ray Structure of [$L^{Me}Cu(O_3SCF_3)$] (**5**), showing all non-hydrogen atoms as 50 % thermal ellipsoids. The O_3SCF_3 ligand is disordered over two positions (0.52 to 0.48 occupancy ratio), both of which are shown. Selected bond distances and angles are listed in Table S1 (below).

Table S1. Selected bond lengths (Å) and bond angles (deg) for **3**, **4** and **5**.[a]

	3	**4**	**5**
Cu-N1	1.9804(18)	1.969(2)	1.975(2)
Cu-N2	2.0932(17)	2.140(2)	2.088(2)
Cu-O1	1.8757(17)	1.9010(19)	1.991(4)
N1-Cu-N2	80.55(7)	80.62(9)	80.69(9)
N1-Cu-O1	152.48(6)	158.31(9)	142.95(14)
N2-Cu-O1	126.66(7)	120.90(9)	128.84(14)

[a] Estimated standard deviations are in parentheses.

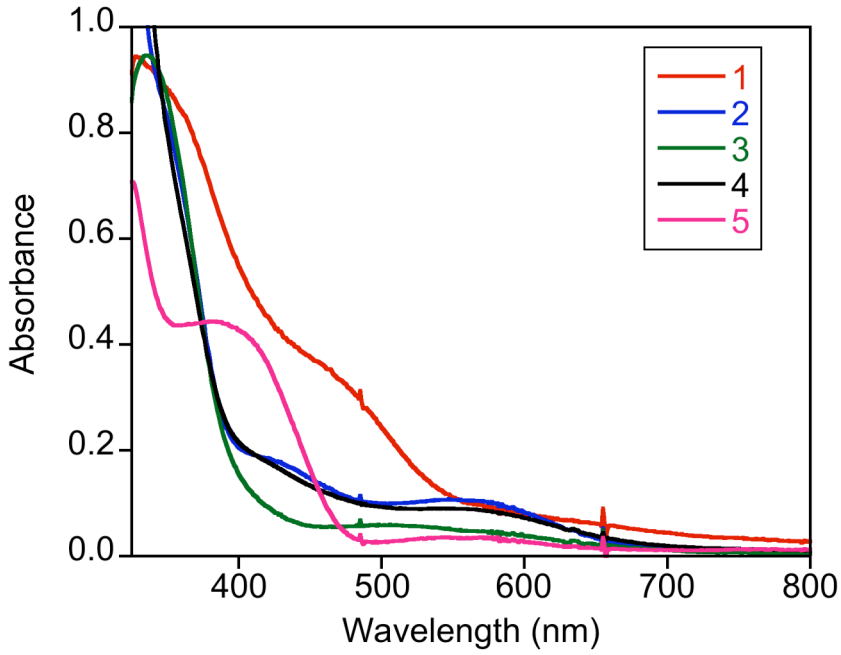


Figure S4. UV-vis spectra of complexes **1-5** (0.25 mM) in acetone at −80 °C.

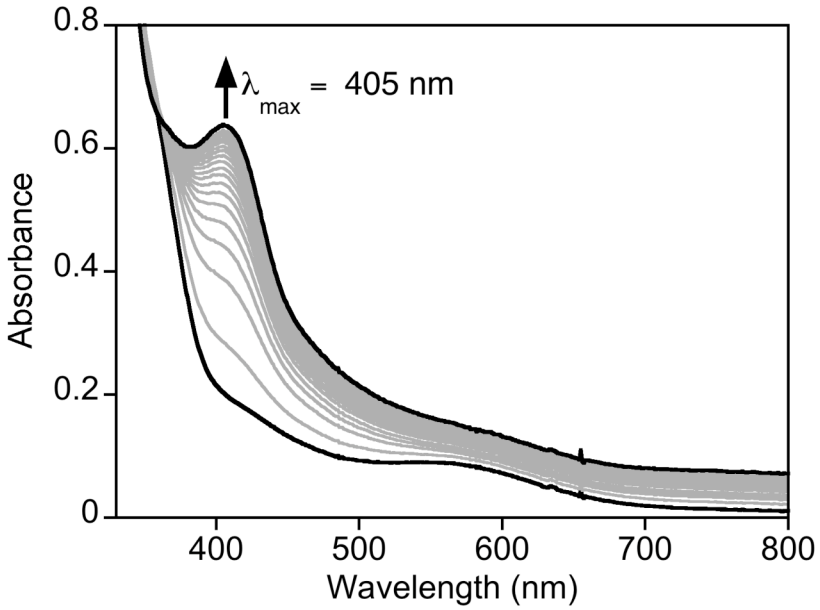


Figure S5. UV-vis spectral changes during the reaction of **4** with O_2 in acetone at - 80 °C (0 → 60 min).

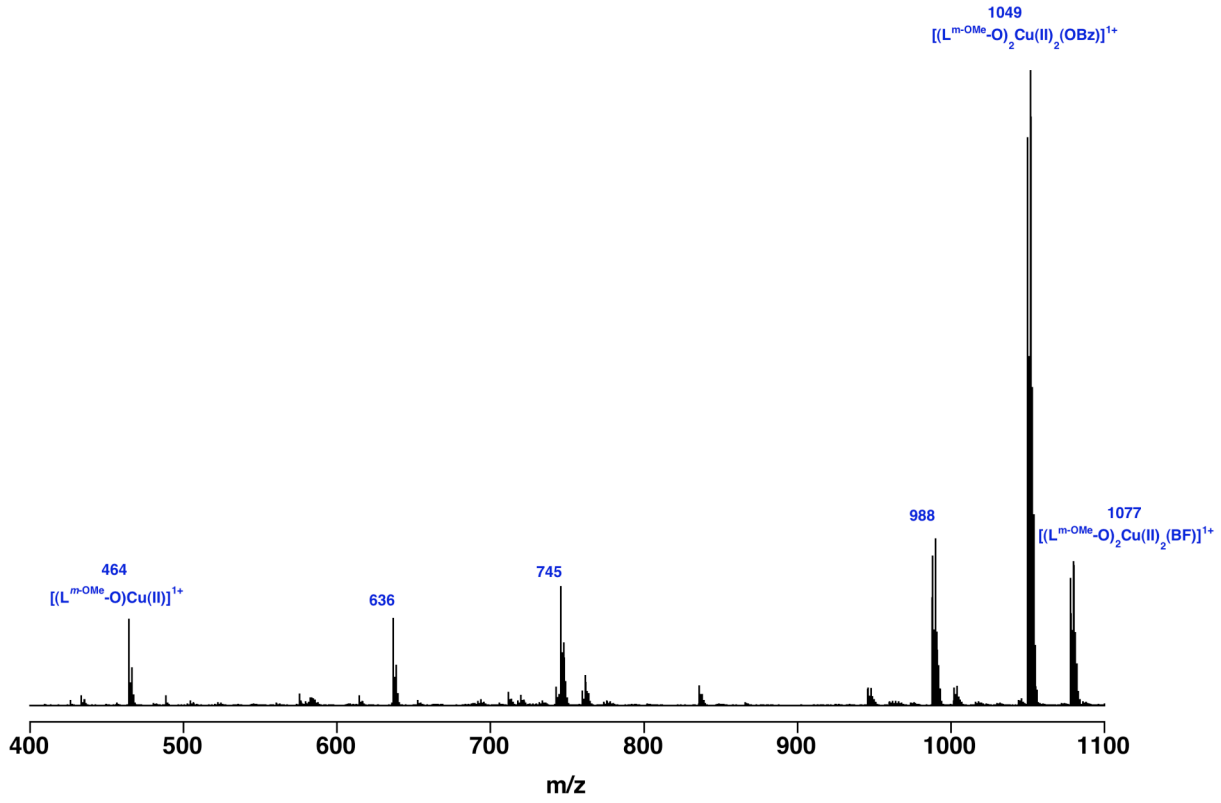


Figure S6. ESI mass spectrum of the brown solution resulting from reaction of **4** with $^{16}O_2$ (OBz = benzoate, BF = benzoylformate, $L^{m\text{-}OMe}$-O = anion of the hydroxylated ligand, see Scheme 4 in the main text). The isotope envelops at m/z 464 and 1049 are shown in detail in Figures S7 and S8.

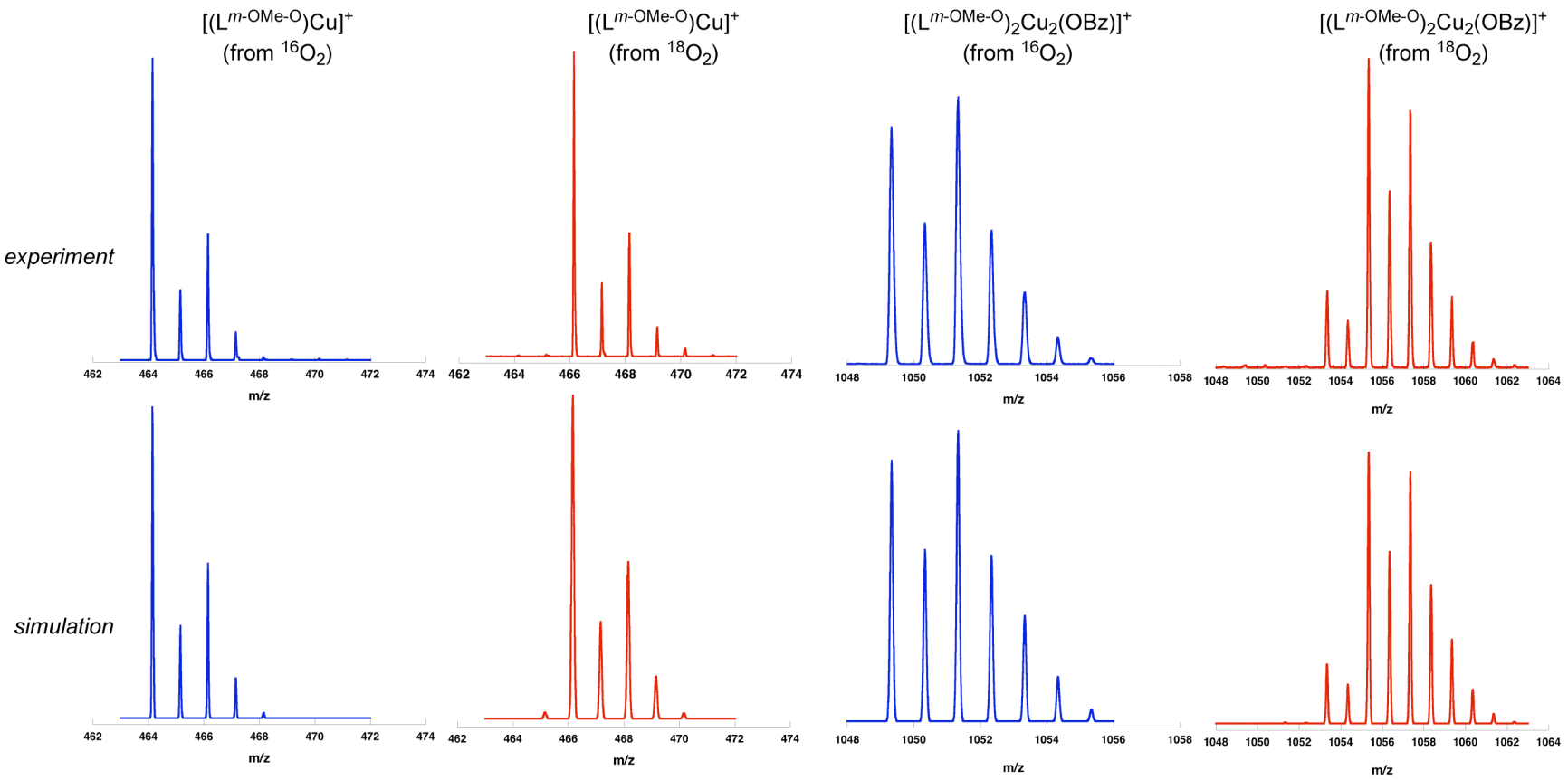


Figure S7. Expanded regions of the ESI mass spectrum of the solution resulting from reaction of **4** with $^{16}O_2$ (in blue) or $^{18}O_2$ (in red), with experimental data (top) and simulations (bottom). For the simulation of $[(L^{m\text{-OMe-O}})Cu]^+$ derived from the reaction with $^{18}O_2$, the simulation is for incorporation of one ^{18}O atom. For the simulation of $[(L^{m\text{-OMe-O}})_2Cu_2(OBz)]^+$ derived from the reaction with $^{18}O_2$, the simulation is for a mixture of the compounds with either three or two ^{18}O atoms (4:1 ratio).

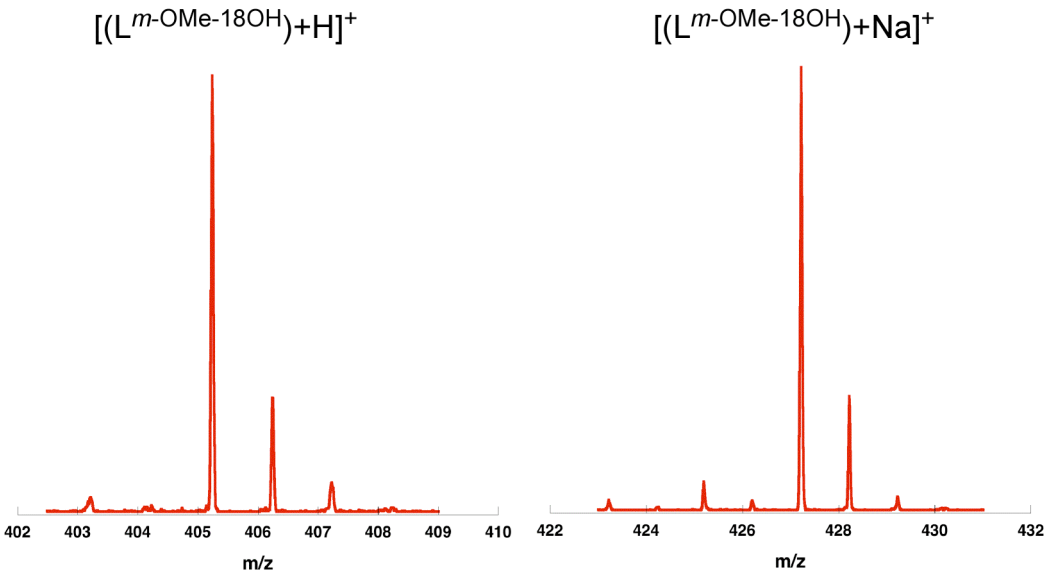


Figure S8. Expanded regions of the ESI mass spectrum of the ligands recovered from the reaction of **4** with $^{18}O_2$ showing the isotope patterns for the ions with one ^{18}O incorporated.

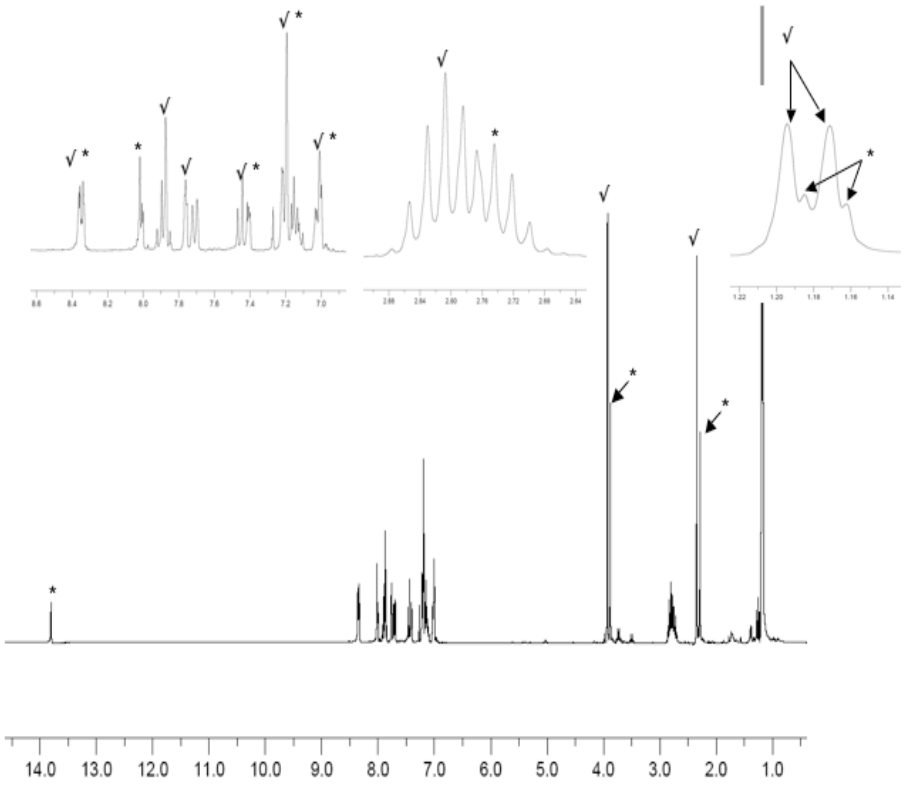


Figure S9. ^1H NMR spectrum showing $L^{m\text{-OMe}}$ (✓) and the product of hydroxylation, $L^{m\text{-OMe}}$-OH (*).

Table S2. Summary of crystallographic data for **1-5**.

	1	**2**	**3**	**4**	**5**
empirical formula	C38 H43 Cu N2 O3	C33 H33 Cu N2 O3 • CH_2Cl_2	C35 H37 Cu N2 O3	C34 H35 Cu N2 O4	C28 H32 Cu F3 N2 O3 S
formula weight (g/mol)	639.28	654.08	597.21	599.18	597.16
crystal habit, color	red, block	brown, Plate	red-brown, Plate	red-brown, block	red, block
crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P_{2/1}$/n	$P\bar{1}$	$P_{2/1}$/c
a (Å)	8.958(3)	10.2026(12)	13.812(10)	10.1018(11)	13.4571(11)
b (Å)	11.008(4) Å	12.1789(14)	14.651(9)	11.7821(13)	13.8773(10)
c (Å)	19.141(11) Å	15.2420(18)	15.986(9)	12.8840(14)	15.4330(12)
α (deg)	78.74(4)	67.379(2)	90°	86.043(2)	90°
β (deg)	78.76(4)	85.964(2)	109.14(3)	73.753(2)	99.702(2)
γ (deg)	66.24(4)	65.239(2)	90°	88.886(2)	90°
V ($Å^3$)	1679.9(13)	1578.2(3)	3056(3)	1468.7(3)	2840.9(4)
Z	2	2	4	2	4
D_{calc} (g/cm^3)	1.264	1.376	1.298	1.355	1.396
temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Absorption (cm^{-1})	6.88	8.98	7.52	7.85	8.93
θ range (deg)	1.09 to 25.11	1.46 to 25.06	1.94 to 25.06	1.65 to 25.06	1.99 to 25.03
hkl ranges	-10 to 10, -13 to 13, -22 to 22	-12 to 12, -14 to 14, -18 to 17	-16 to 16, -17 to 17, -19 to 19	-12 to 12, -14 to 14, -15 to 15	-14 to 16, -16 to 15, -18 to 18
no. of reflections collected	13556	13378	28455	14194	18007
no. of unique reflections	5878 (R_{int} = 0.0280)	5581 (R_{int} = 0.0305)	5404 (R_{int} = 0.0358)	5179 (R_{int} = 0.0376)	5015 (R_{int} = 0.0228)
Observed reflections ($I > 2\sigma(I)$)[a]	4702	4599	4529	4047	4477
Completeness to θ = 25.11°	98.3 %	99.4 %	99.7 %	99.5 %	100.0 %
Data / restraints / parameters	5878 / 5 / 397	5581 / 0 / 379	5404 / 4 / 377	5179 / 0 / 375	5015 / 20 / 368
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0356 / 0.0893	0.0378 / 0.0799	0.0303 / 0.0779	0.0451 / 0.1067	0.0509 / 0.1118
R1/wR2 (all data)	0.0513 / 0.1013	0.0518 / 0.0853	0.0415 / 0.0866	0.0644 / 0.1143	0.0567 / 0.1157
Goodness-of-fit on F^2 [a]	1.059	1.043	1.062	1.061	1.053
Max/min peak ($e.Å^{-3}$)	0.386 / -0.347	0.695 / -0.517	0.303 / -0.293	1.017 / -0.627	0.744 / -1.724

[a] $R1 = \Sigma||F_0|-|F_c||/\Sigma|F_0||$. $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma w(F_0^2)^2]]^{1/2}$ where $w = q / [\sigma^2 (F_0^2) + (a \times P)^2 + b \times P + d + e \times sin(\theta)$. $GooF = S = [\Sigma[w(F_0^2-F_c^2)^2] / (n-p)]^{1/2}$

Electronic Structure Calculations:

All geometries were fully optimized at the M06L level of density functional theory[5] using the Stuttgart [8s7p6d | 6s5p3d] ECP10MWB contracted pseudopotential basis set on Cu[6] and the 6-31G(d) basis set[7] on all other atoms. In addition, 3 uncontracted f functions having exponents 5.100, 1.275, and 0.320 were placed on Cu. The grid=ultrafine option (in Gaussian 03) was chosen for integral evaluation and an automatically generated density-fitting basis set was used within the resolution-of-the-identity approximation for the evaluation of Coulomb integrals. All singlet geometries other than those for the peracid complex, the peracid transition-state (TS) structure leading to ring oxidation, and the starting complexes were obtained using broken-spin-symmetry calculations; the peracid and starting complexes were predicted to have stable restricted Kohn-Sham wave functions, and the wave function for the peracid TS structure inevitably returned to restricted solutions during geometry optimizations, although later checks did not necessarily confirm restricted stability. The nature of all stationary points was verified by analytic computation of vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions (with all frequencies below 50 cm^{-1} replaced by 50 cm^{-1} when computing free energies), and for determining the reactants and products associated with each transition-state structure (by following the normal modes associated with imaginary frequencies). Partition functions were used in the computation of 298 K thermal contributions to free energy employing the usual rigid-rotator harmonic oscillator approximation.

In order to correct for biradical character in some of the singlet structures, multireference second-order perturbation theory (CASPT2)[8] computations were also performed. Singlet energies were computed by taking M06L *triplet* energies and adjusting them by singlet-triplet splittings computed at the CASPT2 level for structures otherwise identical to broken-symmetry singlets computed at the M06L level but with truncated ligands (for details see Figure S10) and the Stuttgart basis set on Cu and MIDI! basis set[9] on all other atoms. Orbital active spaces were chosen to include the most important copper d orbitals and oxygen valence orbitals, and these spaces were systematically expanded to ensure convergence with respect to active space size. Typically, space of 8 electrons in 8 orbitals, 10 electrons in 10 orbitals, and 12 electrons in 12 orbitals were evaluated, and good convergence was obtained by the (10,10) level. For structures that were predicted to be triplet ground states, free energies were computed based exclusively on the DFT energies and partition functions. For those structures predicted to be ground-state singlets, free energies were computed by combining DFT *triplet* electronic energies with CASPT2 singlet-triplet splittings and thermal contributions from the broken-symmetry DFT frequencies. Solvation effects (e.g., as modeled with a continuum solvent approximation) were not included; we note that all species are uncharged so that gas phase results are likely to be of good qualitative, and perhaps quantitative, utility. The latter point will be explored in future work.

Spin-orbit effects on the Cu atom were estimated using the Complete Active Space State Interaction (CASSI) method, in which an effective one-electron spin-orbit (SO) Hamiltonian based on the atomic mean field approximation of the two-electron part is employed.[10] CASSCF singlet and triplet wave functions based on all-electron calculations replacing the ECP10MWB basis set on Cu with the ANO-RCC relativistic basis set[11] (contracted to 5s4p3d2f) were used as basis functions to set up the SO Hamiltonian, and CASPT2 energies were used in the diagonal elements.

All DFT computations were performed with MN-GFM,[12] a locally modified version of Gaussian 03.[13] All CASPT2 calculations were performed with MOLCAS.[14] Selected free energies of activation and reaction free energies are presented in Figure S11. CASPT2 singlet-triplet splittings, calculated with the respective truncated (broken-spin-symmetry) DFT-singlet

geometries, are shown in Table S3. An illustration of the singlet and triplet reaction coordinates on a common energy scale is provided as Figure S12.

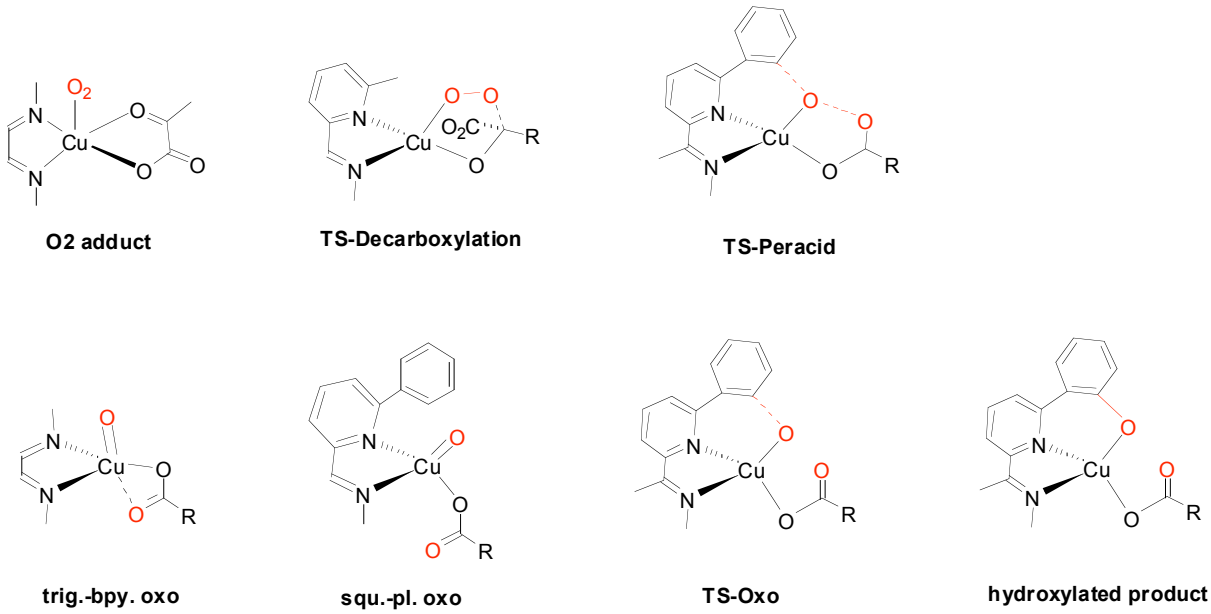


Figure S10. Truncated ligand systems used for the CASPT2 calculations on the respective (mentioned) structure of the reaction mechanism (cf. Scheme 4 and Figures S11 and S12).

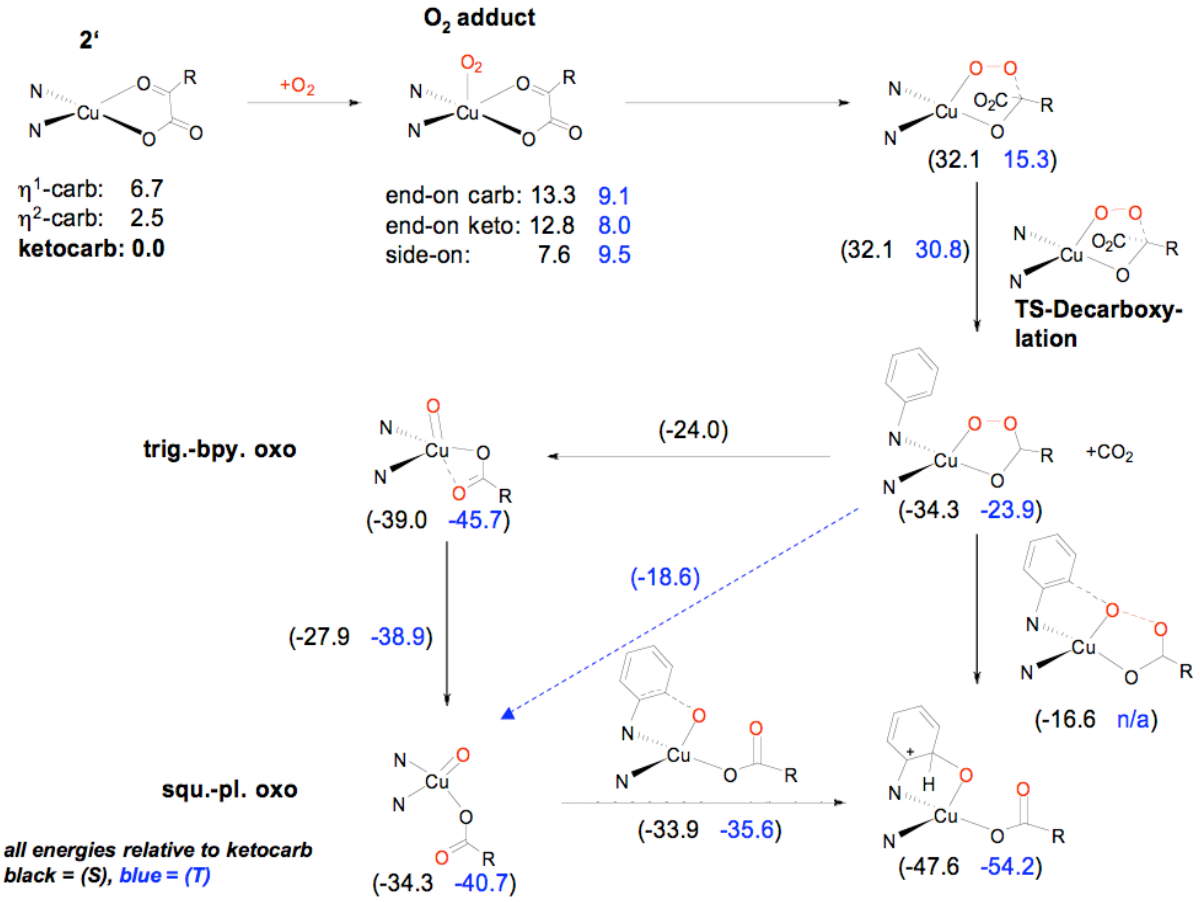


Figure S11. Free energies relative to lowest-energy ketocarboxylate for singlet (black) and triplet (blue) intermediates and TS structures in oxidation reaction mechanisms (see also Figure S12). The nomenclature is identical with that used in Scheme 4. For ease of viewing, reduced ligand schemes are used in the figure although DFT computations employed complete representations. Ball-and-stick structures and cartesian coordinates for all species may be found later in this Supporting Information.

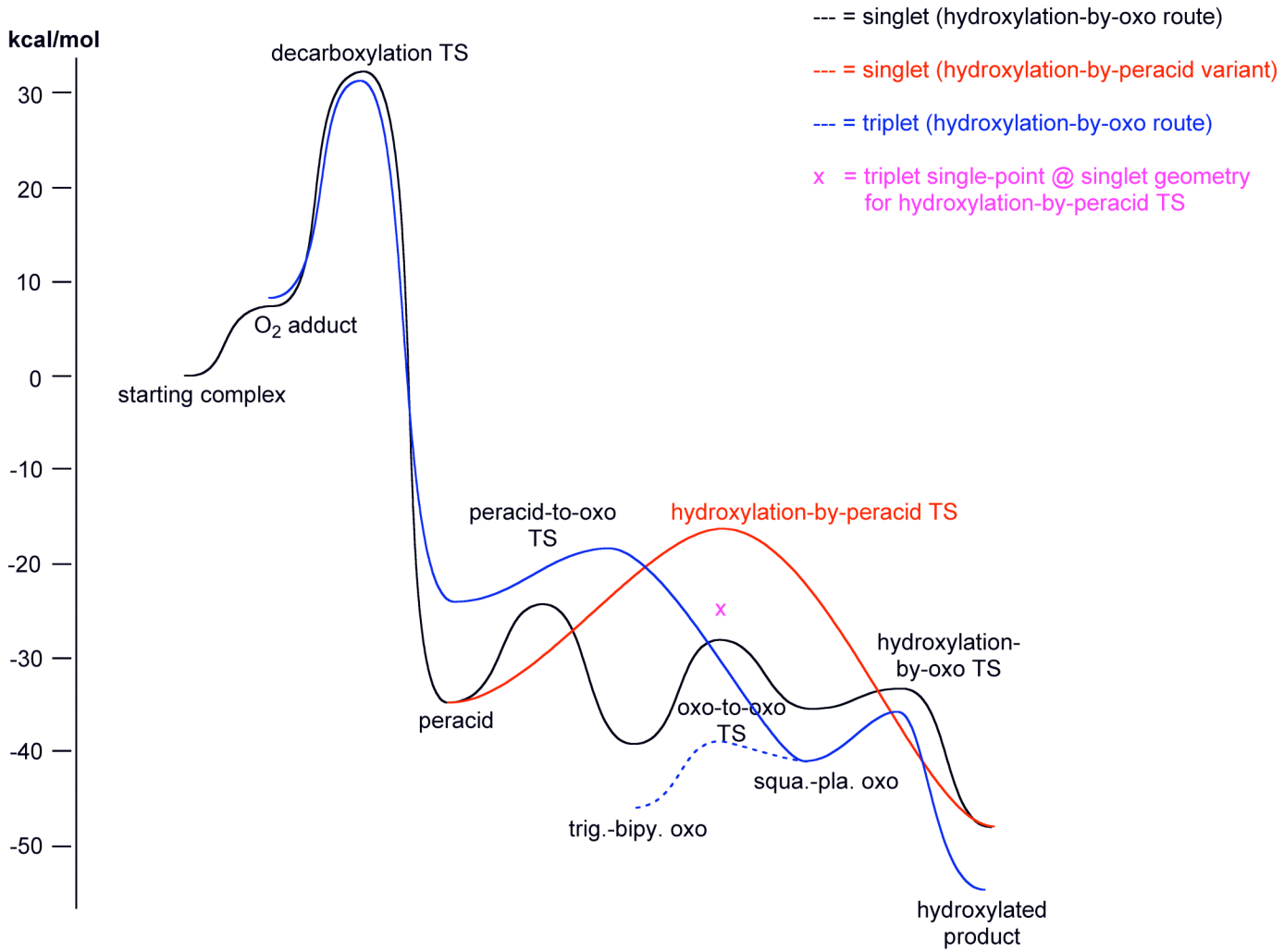


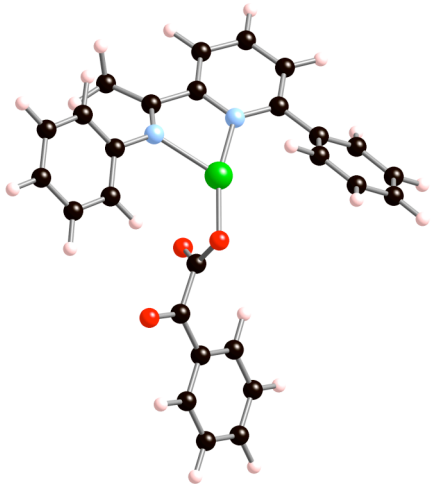
Figure S12. Corresponding singlet and triplet surfaces for various oxidation reaction mechanisms. All stationary points represent optimized structures that are qualitatively similar, but not exactly identical. No triplet structure analogous to the singlet hydroxylation by peracid TS structure could be found (all attempts led to other triplet TS structures) but the triplet single point energy for this species is shown. Note that the reaction could, in principle, take place entirely on the triplet surface. If, however, spin crossing to the singlet surface occurs, either a recrossing event is required or intersystem crossing in the final structure is required to reach the triplet ground state of the product. Relatively low-energy pathways are available for all possibilities.

Table S3: CASPT2 singlet triplet splittings in kcal/mol (singlet compared to triplet).

Side-on	- 9
End-on keto	+ 3
End-on carb	+ 3
TS-Decarboxylation	0
TS-Peracid	- 7
Trig.-bpy. Oxo	+ 5
Squ.-pl. Oxo	+ 5
TS-Oxo	+ 1
Hydroxylated product	- 2

The coordinates of the structures (minima and transition state structures) are presented below, labeled according to Figure S11:

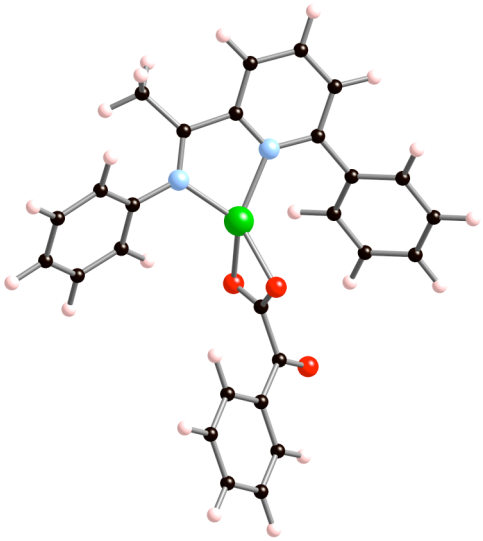
"η^1-carb" starting complex (2')



Cu	-0.73195500	-0.06704200	-0.50123400
O	1.08515000	-0.19811000	-1.06188400
C	1.16689400	4.23929700	-1.30756100
H	2.19021600	4.16106700	-1.66967300
C	0.51148000	3.08401100	-0.90412100
C	-0.79585700	3.15544500	-0.39975800
C	-0.79747100	5.54316800	-0.81566600
H	-1.32403700	6.49628100	-0.80724500
C	0.51968000	5.47345000	-1.26488100
H	1.03213300	6.37446200	-1.59677500
N	-1.43877700	1.96225000	-0.03866000
C	-2.42648100	2.87911900	2.06745500
H	-1.63490900	3.63254500	2.04587800
H	-2.42974500	2.40449100	3.05559300
H	-3.38432000	3.40622700	1.96043700
N	-2.44106300	-0.46387200	0.37430600
O	1.35449100	0.03897100	1.16377500
C	-2.21553400	1.85190200	0.99579700
O	3.54301100	1.30752100	-0.86783600
C	4.28528400	-0.57634200	0.37441900
C	3.25480400	0.29963600	-0.23205200
C	4.95111400	-2.49174500	1.69081000

H	4.68765300	-3.34520900	2.31345700
C	6.28944500	-2.21169900	1.42203700
H	7.07131100	-2.85033300	1.83113200
C	6.62999800	-1.11397300	0.63035900
H	7.67634200	-0.89698100	0.42090400
C	3.95011400	-1.67927100	1.16952800
H	2.90433700	-1.87905800	1.39472500
C	-1.45153200	4.39824400	-0.37647600
C	1.78409100	-0.01409200	0.00120200
C	5.63302500	-0.30122600	0.11013600
H	5.86591800	0.56108200	-0.51221400
C	-4.19163800	-1.86984600	1.20093100
H	-4.69228100	-2.83492100	1.18141100
C	-2.53493000	-2.71571400	-0.48093000
C	-4.00928800	0.38866100	1.97648400
H	-4.36449500	1.21820900	2.58247800
C	-3.07462100	-1.65726200	0.38447300
C	-2.91180900	0.55805700	1.13309600
C	-2.57744400	-4.05771900	-0.08081200
C	-1.95222400	-2.39735600	-1.71719900
C	-1.41227100	-3.39440400	-2.52221700
H	-0.96598100	-3.13055500	-3.47860900
C	-2.03367500	-5.05261800	-0.88470500
H	-2.05619000	-6.08836000	-0.55136200
C	-4.65547800	-0.84215700	2.00867000
H	-5.52417000	-0.99122900	2.64651100
C	-1.44688200	-4.72255200	-2.10508400
H	-1.01794300	-5.50200500	-2.73208500
H	-3.00162200	-4.31693500	0.88878900
H	-1.96225100	-1.36341600	-2.06579500
H	1.01200900	2.12239400	-0.98177300
H	-2.49037400	4.45268500	-0.05557600

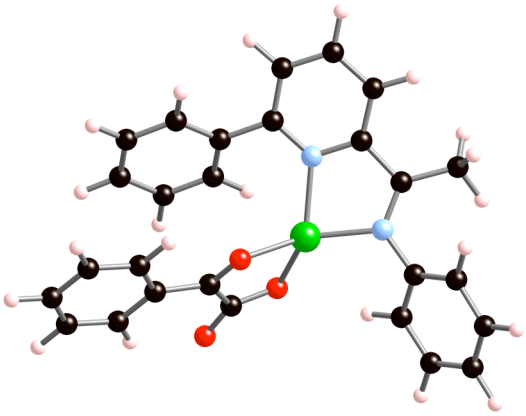
"η^2-carb" starting complex



C	2.17219200	2.53868500	-0.21167500
C	3.17475700	1.46368700	-0.14429600
Cu	0.64002900	0.14062400	0.02393800
N	2.68189900	0.20102600	-0.07532600
N	0.94126700	2.16481100	-0.01514200
O	-0.86990200	-0.71212900	-1.29486500
O	-0.81582600	-1.03902800	0.90212700
C	-1.32307700	-1.23650600	-0.23937400
C	3.53479300	-0.84430600	-0.00235500
C	4.92151900	-0.64252600	0.00625700
H	5.58537300	-1.50380800	0.02828500
C	5.42965900	0.64770000	-0.05028700
H	6.50420600	0.81859400	-0.04326500
C	4.54730400	1.71867100	-0.12882200
H	4.91699700	2.74067200	-0.16220000
C	2.62233900	3.92654300	-0.54760300
H	3.37430300	3.90674000	-1.34482700
H	1.78359100	4.54508800	-0.87790500
H	3.08340100	4.43049600	0.31303700
C	-2.52302300	-2.15619700	-0.35203100
O	-2.37409900	-3.32121600	-0.69816500
C	-3.84893400	-1.56535700	-0.05416600
C	-4.99803100	-2.34284600	-0.24059400
C	-3.97240100	-0.24236700	0.38773100
C	-6.25261200	-1.80461600	0.00807300
H	-4.87293300	-3.36786700	-0.58555800
C	-5.23032100	0.29517400	0.63650100
H	-3.07904400	0.36053100	0.55289800
C	-6.36988000	-0.48425300	0.44579000
H	-7.14544700	-2.41021800	-0.13888700
H	-5.32204000	1.32295400	0.98477000
H	-7.35503300	-0.06255900	0.64040000
C	2.95212500	-2.19409200	0.07291700
C	3.54903600	-3.17930500	0.87099000
C	1.77629600	-2.50706700	-0.62332400
C	2.96459900	-4.43470600	0.99394100
H	4.45147200	-2.94325900	1.43513600
C	1.18646500	-3.75952900	-0.49257300
H	1.32272300	-1.77018600	-1.28507000
C	1.77797900	-4.72290100	0.32162600
H	3.42647800	-5.18426200	1.63416300
H	0.25174000	-3.96746900	-1.01077300
H	1.31165300	-5.69994700	0.43521800
C	-0.15877600	3.03743600	0.01868800
C	-0.15926100	4.23599300	0.74709900
C	-1.33905500	2.61763500	-0.61519200
C	-1.31553600	5.00623200	0.82048800
H	0.73384300	4.53519600	1.29290400
C	-2.47867300	3.40864200	-0.55745100
H	-1.33950700	1.66328900	-1.14494200
C	-2.47425300	4.60525500	0.16043400

H	-1.30919000	5.92528000	1.40415500
H	-3.38364200	3.07676700	-1.06442400
H	-3.37469900	5.21351900	0.21843000

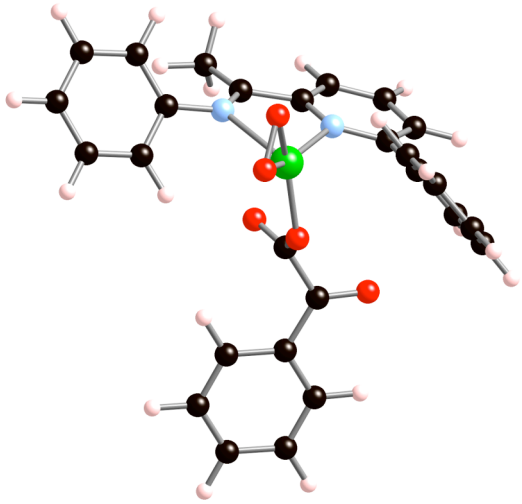
“ketocarb” starting complex



Cu	0.79078800	-0.17435500	-0.15705000
N	0.94420200	1.88093200	-0.15727400
O	0.06437200	-1.49902600	-1.43700900
C	-1.67241600	-1.37633800	0.16598300
O	-1.80040300	-2.68372300	-1.86682700
C	-1.11901700	-1.92316000	-1.17662800
C	-2.54362900	2.74310300	0.17912000
O	-0.88384500	-0.72080500	0.87686400
C	-4.76518200	-0.93797700	2.23436900
H	-5.06028000	-0.40149300	3.13488600
C	-0.06778700	2.77490300	-0.14097300
C	-3.05945400	-1.55367700	0.62077700
C	-5.70575400	-1.68902200	1.52694800
C	-1.41045700	2.28482800	-0.50380100
C	-5.32418100	-2.37458400	0.37578800
H	-6.05616100	-2.96445100	-0.17343500
C	-3.95514900	1.31219000	-1.15491700
H	-4.94061400	0.91200900	-1.38816100
N	2.76748000	0.02274600	0.14727800
C	-4.01257300	-2.31199900	-0.08179000
C	-2.83537400	0.86198700	-1.85392100
H	-2.94043800	0.11410000	-2.63854100
C	-3.80693200	2.25467100	-0.14108000
H	-4.67621000	2.59625100	0.41842300
C	-1.57122000	1.34375500	-1.53067200
C	-3.45528700	-0.87349200	1.78752900
C	2.49109700	3.62981400	0.42556800
H	3.51041200	3.93452000	0.65202700
C	4.66924200	1.64205600	0.03743400
H	5.28646200	0.81385700	-0.32139400
H	5.07394000	1.94922300	1.01192600
H	4.79707600	2.49227600	-0.64236100
C	2.20600900	2.29511000	0.12364600

C	0.15813200	4.11760900	0.17955300
H	-0.67274900	4.81952200	0.15754400
C	3.22776400	1.24621400	0.12213200
C	1.44979900	4.54694200	0.46589400
H	1.64298800	5.58995200	0.70816800
C	4.67709300	-1.22633500	1.08204400
C	5.41028900	-2.40681600	1.14201000
H	6.23865900	-2.48690500	1.84403000
C	3.99982600	-3.37640600	-0.55306500
H	3.72594400	-4.21685300	-1.18808400
C	3.59375600	-1.11637800	0.19843900
C	3.24307200	-2.21327800	-0.60301400
C	5.08557300	-3.48019600	0.31661600
H	5.66417400	-4.40065600	0.36350500
H	-0.69760400	0.98145400	-2.07084600
H	-2.42659300	3.45720200	0.99460000
H	4.91279400	-0.40080900	1.75125400
H	2.36832300	-2.13710000	-1.25004000
H	-3.69998400	-2.83337800	-0.98134800
H	-2.71285200	-0.28133600	2.31772700
H	-6.73634500	-1.73954900	1.87638500

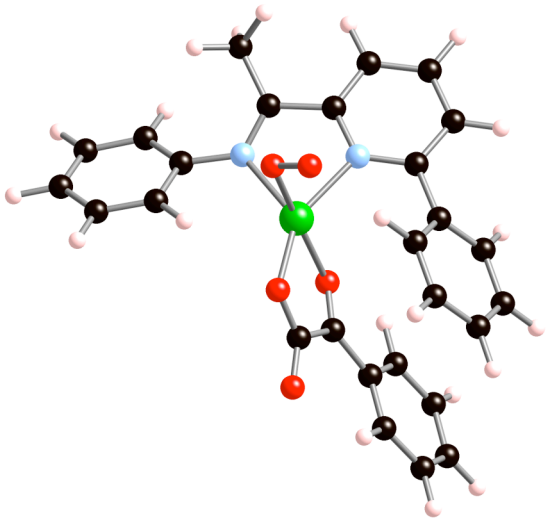
“side-on” O_2 adduct



Cu	-0.93405800	-0.79338000	-0.80860100
O	0.79001600	0.04387600	-0.97550800
C	-4.00076500	2.71013900	-1.69400600
H	-3.72353400	3.32227800	-2.55015700
C	-3.05133300	1.88535800	-1.10734500
C	-3.39120900	1.10626200	0.00747300
C	-5.65781200	1.93832100	-0.12294900
H	-6.68128000	1.93841100	0.24850200
C	-5.30718700	2.73917700	-1.20697200
H	-6.05376000	3.37317400	-1.68141100
N	-2.40242600	0.26474500	0.52745700
C	-2.66678600	0.99277700	2.88480100
H	-3.32598800	1.77425800	2.50125100

H	-1.84619300	1.47471800	3.43037500
H	-3.23144000	0.39200900	3.60951800
N	-0.48523600	-1.47881200	1.06861500
C	-2.10756300	0.15972700	1.77479400
C	-4.70695400	1.12966000	0.49016600
C	1.11531500	-2.46363600	2.53869500
H	1.96119500	-3.13359800	2.67159100
C	1.11922600	-2.98951600	0.08605000
C	-0.53798600	-0.95814500	3.39807900
H	-0.98803500	-0.41636200	4.22502100
C	0.56921100	-2.29384700	1.25883000
C	-1.02270700	-0.79698900	2.10231900
C	2.50294600	-3.16164500	-0.04381800
C	0.27157300	-3.46473100	-0.92399600
C	0.80005100	-4.09056500	-2.04676100
H	0.12974500	-4.45076100	-2.82479900
C	3.02596500	-3.78753500	-1.16831900
H	4.10405900	-3.89463300	-1.27179100
C	0.54991600	-1.79890000	3.61245600
H	0.95410800	-1.92788400	4.61443900
C	2.17788700	-4.25283300	-2.17131500
H	2.59243200	-4.73619900	-3.05450400
H	3.16928500	-2.73933700	0.70565000
H	-0.80858000	-3.35572800	-0.82586400
H	-2.03075500	1.83775600	-1.48632400
H	-4.98331800	0.48296000	1.32201100
O	-2.37272500	-1.70852700	-1.76783400
O	-1.63596700	-0.94005300	-2.55974700
C	1.13059600	0.85420200	-0.03943100
C	2.63975000	0.96152600	0.18806300
O	0.40845700	1.47729100	0.74451600
O	3.23098200	-0.00859700	0.64690800
C	3.30504500	2.25988500	-0.05976100
C	2.58923500	3.38667400	-0.48233200
C	4.69232300	2.34764500	0.11292800
C	3.25385500	4.58332200	-0.72425400
H	1.50861500	3.32564400	-0.59745300
C	5.35382300	3.54207900	-0.13240200
H	5.22625600	1.45643400	0.43829700
C	4.63410600	4.66236400	-0.55035000
H	2.69379200	5.45963600	-1.04575700
H	6.43271300	3.60629000	-0.00023000
H	5.15276100	5.60084500	-0.74197300

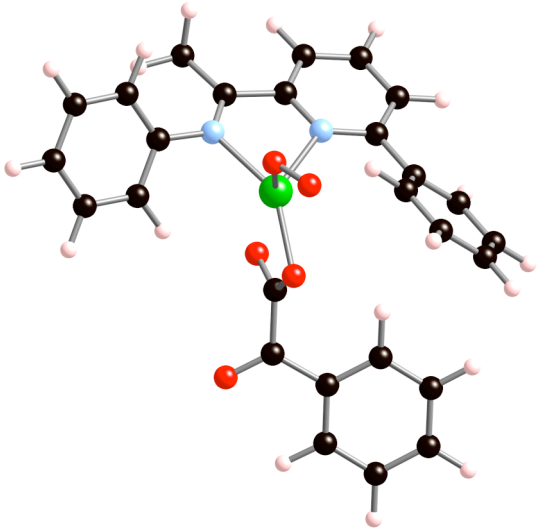
“end-on keto” O_2 adduct



Cu	-0.72368600	-0.13352500	0.57273200
N	-0.70817400	1.85245300	-0.06521800
O	0.10834400	-1.59974800	1.54867700
C	1.64176100	-1.39135600	-0.25479900
O	1.89555300	-2.96515000	1.55553000
C	1.21102400	-2.06138500	1.07824400
C	2.83531100	2.30491300	-0.17095400
O	0.79638600	-0.69012100	-0.83699400
C	4.46599300	-1.00950000	-2.69030300
H	4.63199100	-0.55367000	-3.66517400
C	0.37356400	2.65198300	-0.07308500
C	2.97927200	-1.55109800	-0.85081800
C	5.51694700	-1.64395700	-2.02578200
C	1.62000200	2.11034000	0.49737200
C	5.30091400	-2.23019800	-0.78060900
H	6.12003400	-2.72746200	-0.26411800
C	3.97322700	0.94961200	1.46618500
H	4.88492000	0.47900500	1.83071500
N	-2.61774900	0.05172800	-0.47404800
C	4.04167500	-2.19258500	-0.19286800
C	2.77170800	0.76511800	2.14800600
H	2.73785700	0.15824100	3.05103400
C	4.00469300	1.72521800	0.30991900
H	4.93763800	1.85476000	-0.23640700
C	1.59999800	1.34630200	1.67324200
C	3.21077300	-0.95915900	-2.10529300
C	-1.99990500	3.55436000	-1.14508700
H	-2.94496100	3.87771400	-1.57490100
C	-4.36422700	1.79056100	-0.85190500
H	-5.10133700	1.05965600	-0.50843700
H	-4.57787000	2.00197500	-1.90844400
H	-4.51505100	2.72599200	-0.30099800
C	-1.86930100	2.27478800	-0.60467400
C	0.30800700	3.94031900	-0.62337700
H	1.18863300	4.57829800	-0.59724600
C	-2.96967500	1.28352500	-0.64861800

C	-0.89014600	4.39362400	-1.15283300
H	-0.96366800	5.39625800	-1.56960400
C	-4.46753500	-1.20280200	-1.52379000
C	-5.25303900	-2.34993900	-1.55150300
H	-5.99459200	-2.47189000	-2.33921300
C	-4.11428700	-3.18760100	0.40013500
H	-3.96828300	-3.96222500	1.15014000
C	-3.49315600	-1.04260200	-0.52727700
C	-3.30231900	-2.06226300	0.41832900
C	-5.09207000	-3.33747800	-0.58270100
H	-5.71393300	-4.23015100	-0.60461400
H	0.66903100	1.21526500	2.22778600
H	2.85299100	2.87622500	-1.09967200
H	-4.57576900	-0.44701400	-2.29963000
H	-2.51788200	-1.95290700	1.16768400
H	3.85730100	-2.65426700	0.77205800
H	2.38191300	-0.45706600	-2.59984600
H	6.50519800	-1.68240500	-2.48277300
O	-1.94121000	0.35095300	2.21686300
O	-1.34170600	0.93483800	3.16672000

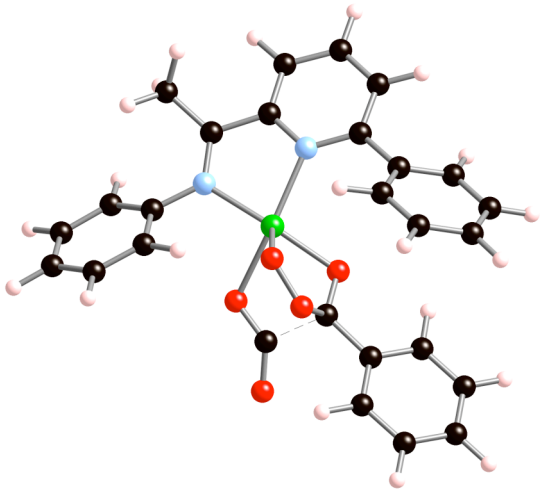
“end-on carb” O_2 adduct



Cu	-0.80893000	-0.06177200	0.52574300
O	0.83522600	-1.23353000	0.80563300
C	-3.83458800	-3.41194900	0.10101000
H	-3.40646400	-4.40618200	-0.00871900
C	-3.04634900	-2.29902300	-0.15579200
C	-3.59394700	-1.01442300	-0.03558300
C	-5.69311500	-1.98156900	0.66355300
H	-6.71792100	-1.85456100	1.00835200
C	-5.15803100	-3.25841100	0.51433700
H	-5.76605700	-4.13323300	0.73553000
N	-2.73265400	0.07531300	-0.25178800
C	-4.24775800	1.25387800	-1.81755500
H	-4.82564900	0.32754300	-1.84788800
H	-3.98583800	1.52930900	-2.84561800

H	-4.90029700	2.04723400	-1.42985600
N	-0.85841900	1.95026600	-0.33033900
O	0.10472900	-1.02648700	-1.28138000
C	-3.01129600	1.09926500	-0.98816800
O	1.57382600	-3.59993700	-1.31752500
C	3.37418400	-2.15488200	-0.75273000
C	1.94379800	-2.51996400	-0.87906400
C	5.13819200	-0.61819800	-0.15058400
H	5.45404400	0.33866600	0.26293900
C	6.08845400	-1.53287500	-0.59904000
H	7.14845900	-1.28911100	-0.53909500
C	5.68532000	-2.76133100	-1.12513700
H	6.42937200	-3.47486400	-1.47573400
C	3.78381300	-0.92427100	-0.22452500
H	3.04242100	-0.21644700	0.14588600
C	-4.92116600	-0.85892000	0.38378200
C	0.89850200	-1.50929200	-0.43583500
C	4.33527500	-3.06902700	-1.20298300
H	3.98597400	-4.01597900	-1.61092300
C	0.04942300	3.99547200	-1.17815400
H	0.86635200	4.71348300	-1.18321600
C	1.35338700	2.56513000	0.41191000
C	-2.13523500	3.29213600	-1.85437000
H	-3.04855200	3.44819100	-2.42207400
C	0.14801900	2.83863100	-0.38738400
C	-1.97473300	2.15652700	-1.05928300
C	2.61705600	2.97203500	-0.03878700
C	1.25589100	1.89696200	1.63867700
C	2.39239000	1.62321500	2.38959400
H	2.29104300	1.08910000	3.33221500
C	3.75237600	2.70698900	0.71729300
H	4.72899800	3.01883400	0.35002900
C	-1.10378300	4.22426100	-1.90810000
H	-1.20514700	5.12256600	-2.51379400
C	3.64332600	2.03096300	1.93247800
H	4.53554600	1.81520400	2.51841200
H	2.71456000	3.46716300	-1.00469300
H	0.27939400	1.61056200	2.02192900
H	-2.00792200	-2.39785700	-0.47406300
H	-5.32569400	0.14155600	0.53036000
O	-1.55730400	-0.04516200	2.38999900
O	-0.72229900	-0.05948600	3.34340000

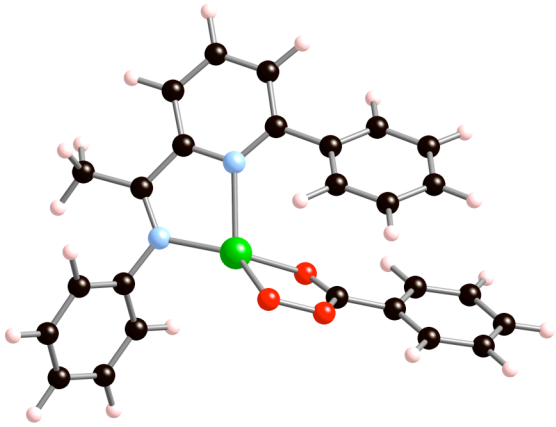
TS-Decarboxylation



Cu	-0.68601400	0.02737500	-0.02711000
N	-0.96180700	2.09384600	-0.05969700
O	-0.68540700	-1.86176300	-1.01648300
C	1.55059900	-1.23133200	-0.05331200
O	0.90689800	-3.50319600	-1.20568000
C	0.41480400	-2.43831300	-0.92656500
C	2.42749000	3.38576800	-0.30197200
O	1.15106700	-0.06966600	-0.50621000
C	5.14569200	-1.05206300	-1.16933000
H	5.79179700	-0.36331600	-1.71283500
C	-0.03550900	3.07534000	-0.08114200
C	2.97394600	-1.60562200	-0.26969400
C	5.65886900	-2.24925100	-0.67543500
C	1.34091100	2.77153900	0.33413700
C	4.82634900	-3.12568900	0.01928800
H	5.22146700	-4.06530500	0.40228600
C	3.95662100	2.19905500	1.13444800
H	4.97607900	1.95577200	1.42941600
N	-2.67435200	0.09678200	0.03046900
C	3.48788000	-2.80997900	0.22011900
C	2.88087700	1.60025200	1.78634300
H	3.05058000	0.88305800	2.58736900
C	3.72845600	3.09396200	0.09079400
H	4.56640400	3.55576400	-0.42823000
C	1.58072700	1.88218700	1.38990100
C	3.80694300	-0.73082700	-0.97153500
C	-2.68290200	3.68445800	-0.59752500
H	-3.73272800	3.89923900	-0.77836700
C	-4.67558100	1.57075300	-0.06701100
H	-5.22473400	0.75804600	0.41501500
H	-5.10541700	1.70996200	-1.06798300
H	-4.85953200	2.49467200	0.49214100
C	-2.26995700	2.39334900	-0.26689200
C	-0.39990500	4.38479300	-0.43733100
H	0.36372300	5.15891200	-0.44932700
C	-3.21053200	1.27638700	-0.11880600
C	-1.72363300	4.68407500	-0.71426500

H	-2.01481700	5.69634000	-0.98708600
C	-4.50524300	-1.40191400	-0.66790400
C	-5.14322300	-2.63004100	-0.54493000
H	-5.99285000	-2.85931100	-1.18529200
C	-3.57027900	-3.28416500	1.16184800
H	-3.19076900	-4.02537400	1.86207200
C	-3.39671500	-1.10770200	0.13901500
C	-2.91013300	-2.07041200	1.03451600
C	-4.68889500	-3.56757900	0.38033000
H	-5.19186600	-4.52823300	0.47324400
H	0.74760100	1.37965800	1.87882200
H	2.25242600	4.06083100	-1.13997300
H	-4.83346100	-0.68833700	-1.42108700
H	-1.99684100	-1.86085200	1.59388800
H	2.82928500	-3.49574300	0.74784300
H	3.39333600	0.20588500	-1.34019800
H	6.70624200	-2.50253600	-0.83503900
O	-0.02290300	-0.94876400	1.65573900
O	1.17355100	-1.57655700	1.25908400

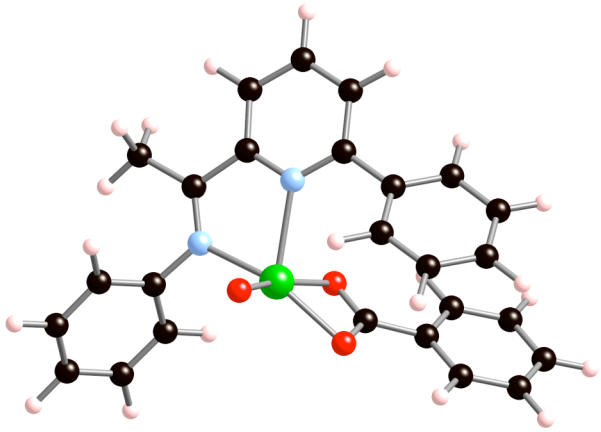
Peracid



Cu	-0.84917500	-0.41712500	0.24785700
C	-4.16333900	-3.27134900	-0.92327400
H	-3.95781600	-4.11948600	-1.57378400
C	-3.32716000	-2.16306100	-0.96066100
C	-3.58552900	-1.06101200	-0.13727300
C	-5.48858600	-2.22534500	0.79471100
H	-6.31884600	-2.25360300	1.49839700
C	-5.24625400	-3.30899900	-0.04535300
H	-5.88895700	-4.18613200	-0.00593300
N	-2.67940800	0.02654500	-0.16547000
C	-4.48968200	1.66892000	-0.63617400
H	-5.13066600	0.80465200	-0.82173300
H	-4.51975300	2.30691500	-1.52787600
H	-4.93788600	2.25019600	0.18137400
N	-0.80165000	1.87114900	0.06341000
C	-3.08134400	1.26300000	-0.33027200

O	0.83608400	-0.92830000	-0.79433400
C	3.03230600	-1.76768700	-0.38743200
C	1.63654900	-1.47569600	-0.01420500
C	5.22921000	-2.64592900	0.09748000
H	5.90488400	-3.17869800	0.76446700
C	5.69349900	-2.16045800	-1.12494900
H	6.73320400	-2.31218400	-1.41109400
C	4.82651200	-1.48243400	-1.97990800
H	5.18783300	-1.10163600	-2.93369200
C	3.90518700	-2.45065000	0.46938400
H	3.53760800	-2.81856900	1.42453800
C	-4.66995500	-1.10149900	0.74751200
C	3.50001800	-1.28755200	-1.61526900
H	2.80827900	-0.74967300	-2.25981700
C	0.02941700	4.08788100	-0.31659300
H	0.87052800	4.77730800	-0.29153900
C	1.55792300	2.25718100	0.42887100
C	-2.29747900	3.62627700	-0.62982500
H	-3.30326100	3.95024500	-0.88453900
C	0.22033500	2.74485300	0.04135800
C	-2.03822600	2.29193700	-0.28985400
C	2.70425700	2.76245100	-0.20025700
C	1.70658800	1.29105300	1.43152800
C	2.97306000	0.84398800	1.79260900
H	3.06676300	0.08068100	2.56325300
C	3.96803700	2.30259600	0.15320000
H	4.84665100	2.68544200	-0.36344500
C	-1.24513500	4.53042600	-0.64309100
H	-1.41852400	5.57356100	-0.90095500
C	4.10602600	1.34255700	1.15310600
H	5.09358900	0.96878700	1.42021400
H	2.59961600	3.49389500	-1.00176400
H	0.82525200	0.87009900	1.91490200
H	-2.45996400	-2.13302500	-1.61938000
H	-4.84253900	-0.26105100	1.41835100
O	0.00812200	-1.45264000	1.65178300
O	1.35080200	-1.80701800	1.22810000

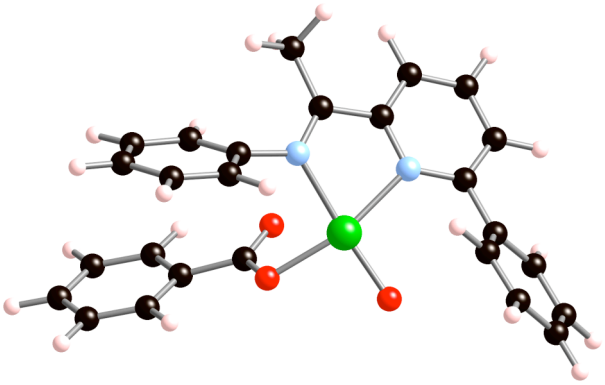
Trig.-bpy. oxo



Cu	-0.70321700	-0.40403500	0.65495400
C	-4.19519400	-3.10199000	-0.67198600
H	-3.99054100	-4.05531100	-1.15550700
C	-3.26481600	-2.07469300	-0.76413800
C	-3.52904100	-0.84097200	-0.15787000
C	-5.61696200	-1.70743700	0.68672300
H	-6.52072200	-1.57054200	1.27776400
C	-5.37302400	-2.92317100	0.05240800
H	-6.09043800	-3.73683400	0.13782900
N	-2.53345800	0.15175800	-0.23267500
C	-4.04524800	1.87509300	-1.16005700
H	-4.78531900	1.07796300	-1.25341800
H	-3.89748000	2.32331400	-2.14956000
H	-4.46312700	2.65887000	-0.51540200
N	-0.47900300	1.82306700	0.01829100
C	-2.74530000	1.36351700	-0.62029200
O	0.47411300	-0.80465300	-1.00727800
C	2.62583200	-1.79649200	-0.65999300
C	1.26430800	-1.41907100	-0.21798000
C	4.79590900	-2.73618900	-0.16819900
H	5.47305800	-3.23675100	0.52228000
C	5.23387400	-2.38739600	-1.44520700
H	6.25398700	-2.61584300	-1.75138800
C	4.36857400	-1.74648000	-2.33127200
H	4.71304600	-1.47462000	-3.32792700
C	3.49598900	-2.44013300	0.22517000
H	3.13521800	-2.68738600	1.22175900
C	-4.70387600	-0.66393500	0.58110100
C	3.06736900	-1.45246300	-1.94081500
H	2.37655900	-0.94325100	-2.60992200
C	0.68811700	3.81003000	-0.61373100
H	1.60649300	4.39288100	-0.58920500
C	1.83772600	1.96432400	0.64539300
C	-1.61764400	3.53989400	-1.20414900
H	-2.52361600	3.90840800	-1.67784900
C	0.64819700	2.54712000	0.00250400
C	-1.58138300	2.28516300	-0.59205200
C	3.10750800	2.15519700	0.08181400
C	1.71073600	1.18520200	1.80285100

C	2.83636300	0.60079300	2.37364800
H	2.72147600	-0.01802700	3.26145000
C	4.22652400	1.55966000	0.65048200
H	5.20278600	1.68556600	0.18557800
C	-0.45822700	4.31027000	-1.20733700
H	-0.45478500	5.29425100	-1.67235000
C	4.09208200	0.78260900	1.79997600
H	4.96721900	0.30514200	2.23829700
H	3.20835900	2.73288000	-0.83727900
H	0.72558300	1.02532700	2.24672200
H	-2.32749100	-2.20527300	-1.30394000
H	-4.86791600	0.27622000	1.10525200
O	-1.39636500	-0.21494700	2.31134200
O	0.89823000	-1.65220300	0.97992200

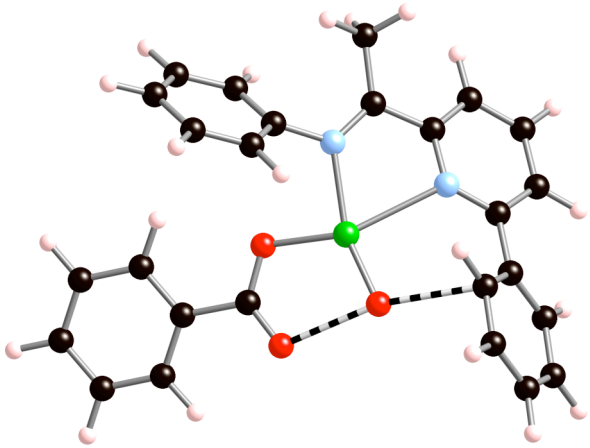
Squ.-pl.oxo



Cu	0.66504400	-0.45863100	0.39084400
C	-4.09482900	1.50967100	0.85490000
H	-4.93611800	1.72788100	0.19910900
C	-2.79846800	1.63383800	0.36791400
C	-1.71223600	1.30448700	1.18698500
C	-3.23207500	0.73505900	2.96930300
H	-3.40041300	0.37128900	3.98126800
C	-4.31522700	1.07477100	2.15854900
H	-5.33102100	0.97432300	2.53602900
N	-0.39128100	1.32047400	0.69474000
C	-0.52221600	3.68249600	-0.05686200
H	-1.38185500	3.78906200	0.60859700
H	-0.87818200	3.83540600	-1.08432000
H	0.19209600	4.48525900	0.15893000
N	2.08954400	0.98265900	-0.12444300
C	0.12508200	2.34310100	0.09705400
O	-0.94723100	-0.28514500	-1.54425000
C	-2.98515700	-1.40377200	-1.02956100
C	-1.55977700	-1.03961500	-0.75724600
C	-5.08510900	-2.37619300	-0.33243400
H	-5.66823600	-2.93708300	0.39712300
C	-5.69250000	-1.90508800	-1.49541200
H	-6.74953400	-2.09881700	-1.67551800

C	-4.94571200	-1.18811300	-2.42950300
H	-5.41806400	-0.82329000	-3.34110300
C	-3.73604500	-2.12881800	-0.10053300
H	-3.24755900	-2.47692700	0.80729000
C	-1.93554500	0.82574900	2.48187800
C	-3.59855900	-0.93755300	-2.19564500
H	-2.99319900	-0.36954600	-2.89986600
C	3.98890900	1.64274300	-1.41623700
H	5.00130200	1.42360500	-1.74746400
C	4.03709400	-0.45935000	-0.07002100
C	2.08753400	3.08759200	-1.27985200
H	1.57163000	4.00717200	-1.54259100
C	3.34068800	0.73792300	-0.55913600
C	1.47979200	2.14621900	-0.45252000
C	4.88425000	-1.18571500	-0.91650300
C	3.90654800	-0.85273500	1.26859900
C	4.60878000	-1.95165900	1.74702000
H	4.49923900	-2.24916200	2.78788100
C	5.56568100	-2.29733300	-0.44072200
H	6.19846100	-2.87337200	-1.11309100
C	3.35305800	2.81393100	-1.78866900
H	3.84476800	3.52281200	-2.45182100
C	5.43225100	-2.67893900	0.89353700
H	5.97036000	-3.54879700	1.26625600
H	4.96992700	-0.90143900	-1.96516500
H	3.25607700	-0.28339700	1.93009800
H	-2.61476500	1.90936400	-0.66939200
H	-1.08394700	0.52280000	3.08839100
O	1.68643600	-1.93341600	0.34778200
O	-1.05825000	-1.48455900	0.34315300

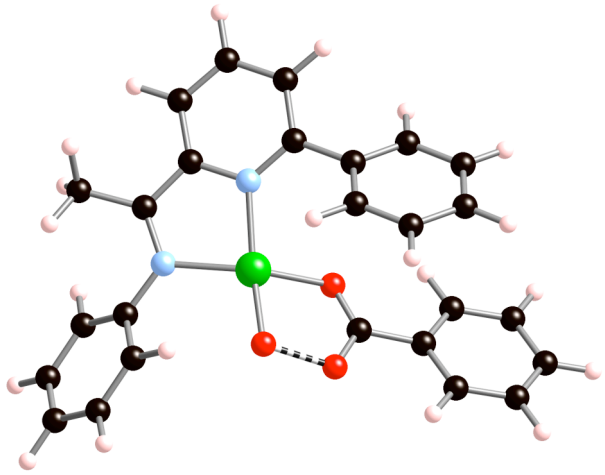
TS-Peracid



Cu	0.33301600	-0.18494900	0.30770100
C	-3.42576500	3.26466700	0.19054300
H	-4.06120700	3.85346700	-0.46859100
C	-2.11732100	2.98335900	-0.19092800
C	-1.29854300	2.21319500	0.63972100

C	-3.10920800	2.00704700	2.22200200
H	-3.49687000	1.61240700	3.15897700
C	-3.92272800	2.78647600	1.40002600
H	-4.94723700	3.00475400	1.69448300
N	0.01037400	1.82871000	0.25699400
C	0.69801000	4.17552000	-0.17305900
H	-0.13503200	4.48722100	0.46182200
H	0.48149200	4.52731100	-1.19065600
H	1.60989400	4.68827000	0.15220600
N	2.51012200	0.93873300	-0.09729500
C	0.89590100	2.69161300	-0.13726300
O	-1.46676600	-0.43285300	-0.28683400
C	-3.29371800	-1.87467500	-0.57972100
C	-1.84761300	-1.67052000	-0.22562800
C	-5.13634200	-3.39064100	-0.96293900
H	-5.52344400	-4.40689800	-1.02161300
C	-5.98218700	-2.30699900	-1.19445200
H	-7.03134300	-2.47572700	-1.43426300
C	-5.48446400	-1.00753900	-1.11653800
H	-6.14481200	-0.15940500	-1.29372800
C	-3.79822700	-3.17605900	-0.65303600
H	-3.11910000	-4.00359100	-0.45991200
C	-1.80878000	1.70717200	1.83946800
C	-4.14452200	-0.78950100	-0.81274600
H	-3.74105000	0.21892600	-0.74718700
C	4.52264800	0.97633300	-1.39068400
H	5.44502100	0.48360700	-1.69090000
C	3.90779800	-0.99033200	0.06677300
C	3.04643600	2.86630300	-1.42580700
H	2.78363800	3.86249200	-1.77507400
C	3.64641500	0.34095200	-0.49116000
C	2.20671700	2.15857300	-0.56471900
C	4.67485100	-1.93380500	-0.62437100
C	3.32511000	-1.35237900	1.29434900
C	3.50144400	-2.63742400	1.80472300
H	3.02420400	-2.90780900	2.74345700
C	4.84932200	-3.21399000	-0.10936700
H	5.43529900	-3.94360600	-0.66530900
C	4.22137100	2.24717500	-1.85006800
H	4.89734000	2.76116200	-2.53066100
C	4.25745200	-3.56900400	1.10239700
H	4.38284500	-4.57683000	1.49387300
H	5.10220700	-1.68276200	-1.59486400
H	2.78860700	-0.60087900	1.86368200
H	-1.73781100	3.32298000	-1.15311000
H	-1.17635300	1.06796000	2.45456000
O	1.06693400	-1.69943300	0.64158300
O	-1.15536200	-2.63955400	0.09731300

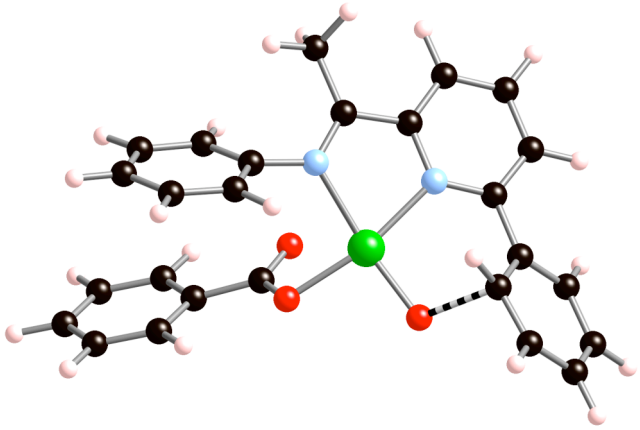
TS-O-O cleavage



Cu	0.78340600	-0.26066500	-0.54204700
C	5.36060500	-2.27262000	1.20585500
H	6.11661400	-2.35212200	1.98516600
C	4.55999600	-1.13757000	1.14406000
C	3.56800300	-1.02941500	0.15836200
C	4.19416400	-3.20576400	-0.68387700
H	4.03957800	-4.01658300	-1.39319100
C	5.19233300	-3.30366600	0.28473100
H	5.82315300	-4.18902000	0.33446200
N	2.68332200	0.06449100	0.09665900
C	4.47491600	1.78884100	0.29967800
H	5.17338300	1.02469400	-0.05132500
H	4.76912900	2.05483200	1.32414600
H	4.60536500	2.68896900	-0.31216000
N	0.75421600	1.84098600	-0.12563900
C	3.05924200	1.30598500	0.22391700
O	-0.76047300	-0.82222500	0.63818800
C	-2.92229800	-1.77365400	0.51155600
C	-1.56621000	-1.50175500	-0.06328600
C	-5.15363800	-2.67602200	0.30000400
H	-5.89345900	-3.23650300	-0.26956400
C	-5.48885000	-2.13919600	1.54227400
H	-6.49176900	-2.27908900	1.94361300
C	-4.53948000	-1.42508700	2.27125600
H	-4.80001000	-1.00619800	3.24227900
C	-3.87549800	-2.49358400	-0.21557300
H	-3.59918700	-2.89376900	-1.18866900
C	3.37195600	-2.08813100	-0.74072900
C	-3.25941000	-1.24307000	1.75964800
H	-2.50699700	-0.67870500	2.30551000
C	-0.16410200	3.99493400	0.36808100
H	-1.03316400	4.64883000	0.37799500
C	-1.62920800	2.14904700	-0.46352000
C	2.17956500	3.61295600	0.66274300
H	3.17073600	3.95001600	0.95643500
C	-0.30873600	2.66757600	-0.06158600
C	1.97445100	2.29572800	0.24303800

C	-2.77412900	2.53662500	0.24650700
C	-1.76682400	1.26488800	-1.54087900
C	-3.01892000	0.76877100	-1.88607200
H	-3.09977200	0.05879500	-2.70688700
C	-4.02354900	2.03290300	-0.09633000
H	-4.89922600	2.31711200	0.48470700
C	1.08889500	4.46975300	0.72848300
H	1.21589800	5.50035500	1.05399100
C	-4.14841100	1.14547300	-1.16276300
H	-5.12297900	0.73123700	-1.41655600
H	-2.67489000	3.20210200	1.10425100
H	-0.88931600	0.94194500	-2.10002900
H	4.66986500	-0.34898700	1.88621400
H	2.55834800	-2.02037100	-1.46499400
O	0.35002700	-1.27372300	-1.95178400
O	-1.36730500	-1.94658400	-1.23473100

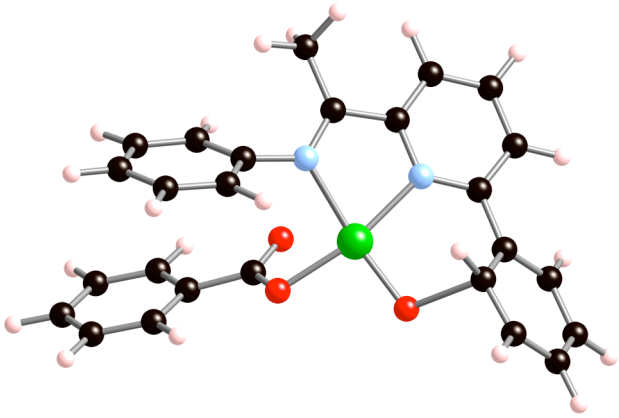
TS-Oxo



Cu	0.69106700	-0.37947600	0.34169000
C	-4.06286200	1.74610900	0.39625200
H	-4.82267200	2.05036900	-0.32128500
C	-2.71852700	1.86180700	0.06031900
C	-1.73527400	1.42913700	0.95803200
C	-3.45519600	0.77063200	2.51585900
H	-3.74116100	0.32856400	3.46838800
C	-4.43486400	1.21335300	1.62734200
H	-5.48807800	1.11464900	1.88278500
N	-0.37053300	1.42848700	0.60769100
C	-0.33532800	3.84496500	0.03884700
H	-1.27303800	3.92636700	0.59314900
H	-0.54242400	4.11002200	-1.00626500
H	0.36873700	4.59109600	0.42510200
N	2.13926300	1.01739900	-0.04983300
C	0.24278600	2.46934300	0.14756100
O	-0.94128700	-0.34774100	-1.50932700
C	-2.96177100	-1.44627700	-0.88324500
C	-1.53475000	-1.06032900	-0.66780900
C	-5.02257200	-2.43052000	-0.09093600

H	-5.57396800	-2.97599800	0.67401200
C	-5.67099000	-2.01275300	-1.25200500
H	-6.72870900	-2.23182700	-1.39455200
C	-4.96418300	-1.31763100	-2.23313600
H	-5.46939400	-0.99528800	-3.14293800
C	-3.67246700	-2.14974400	0.09287000
H	-3.14951900	-2.45810400	0.99578900
C	-2.11154200	0.85347400	2.17633500
C	-3.61571300	-1.03526500	-2.04819200
H	-3.04116000	-0.48399000	-2.79062900
C	4.19209000	1.67363700	-1.08005500
H	5.21460800	1.42229100	-1.35037400
C	3.93391800	-0.59537700	-0.06320100
C	2.38467100	3.23811000	-0.92155200
H	1.95815700	4.21897300	-1.11172200
C	3.40346100	0.71545900	-0.41523600
C	1.63865700	2.25228600	-0.28089500
C	4.89748100	-1.22068100	-0.86555100
C	3.46587900	-1.25368900	1.11300200
C	4.11204300	-2.44997100	1.51919300
H	3.80800500	-2.91363200	2.45475200
C	5.44285000	-2.44035600	-0.49664100
H	6.17625200	-2.92386900	-1.13866400
C	3.67800100	2.93009300	-1.33930600
H	4.28282200	3.67769500	-1.84857800
C	5.05367300	-3.04693600	0.71124900
H	5.51041700	-3.98810900	1.01291300
H	5.19438400	-0.75857400	-1.80681500
H	2.95987400	-0.65753700	1.86859900
H	-2.41831000	2.21592000	-0.92445800
H	-1.33966200	0.46368200	2.83691700
O	1.78664900	-1.85189400	0.38091700
O	-0.99586600	-1.43565600	0.44031800

Hydroxylated product



Cu	0.67380400	-0.33301200	0.33238700
C	-4.05053900	1.81837600	0.25522400
H	-4.78424800	2.13066200	-0.48563800

C	-2.69518900	1.91968700	-0.03823100
C	-1.74543300	1.47847000	0.89061500
C	-3.51999100	0.84008800	2.39399600
H	-3.84026300	0.40168000	3.33727700
C	-4.46664500	1.29006500	1.47411500
H	-5.52835000	1.20061200	1.69560800
N	-0.37083200	1.46187200	0.57951800
C	-0.28183200	3.88348000	0.05436900
H	-1.24102100	3.96266100	0.57073700
H	-0.43987800	4.17857700	-0.99111600
H	0.41336900	4.60984500	0.49071500
N	2.14215200	1.00545800	-0.06414900
C	0.27435200	2.49776100	0.15170700
O	-0.98596200	-1.40617600	0.48679600
C	-2.95708500	-1.46948800	-0.83237400
C	-1.53268500	-1.07182000	-0.63009000
C	-4.96407000	-1.38345200	-2.17844800
H	-5.47441200	-1.08365000	-3.09304100
C	-5.66285900	-2.06300200	-1.18082300
H	-6.71933100	-2.29273000	-1.31563100
C	-5.00833600	-2.45149400	-0.01301500
H	-5.55360000	-2.98489600	0.76472300
C	-3.61698300	-1.08825800	-2.00399900
H	-3.04847000	-0.54905100	-2.75983900
C	-2.16521100	0.90994000	2.09777000
C	-3.65999500	-2.15654300	0.16097400
H	-3.13217200	-2.44148300	1.06881100
C	4.24313000	1.67750700	-0.98814600
H	5.27198600	1.43616600	-1.23866700
C	3.91058100	-0.63945800	-0.10762000
C	2.46009000	3.26615700	-0.80627800
H	2.06050200	4.26502500	-0.95541000
C	3.41697100	0.68359900	-0.41106600
C	1.67679000	2.26380200	-0.24587700
C	5.08603000	-1.12234300	-0.67176300
C	3.12160600	-1.48915800	0.87243300
C	3.80989700	-2.77453500	1.21923200
H	3.26097400	-3.41481400	1.90735400
C	5.62386900	-2.35664800	-0.31022300
H	6.53509600	-2.70480800	-0.79343100
C	3.76639600	2.95403600	-1.18983500
H	4.40709400	3.71665200	-1.62780100
C	4.97892900	-3.17433900	0.65493400
H	5.41224600	-4.14085500	0.90899900
H	5.59509300	-0.55030500	-1.44792200
H	3.08158700	-0.89531600	1.82426800
H	-2.35994900	2.27174600	-1.01245100
H	-1.41864300	0.51358400	2.78284800
O	1.84013200	-1.79729500	0.43456400
O	-0.94015700	-0.38375900	-1.49419700

(1) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192-194.
(2) Kubas, G. J. *Inorg. Synth*. **1979**, *19*, 90-92; **1990**, *28*, 68-70.
(3) Scott, N. M.; Schareina, T.; Tok, O.; Kempe, R. *Eur. J. Inorg. Chem.* **2004**, 3297-3304.
(4) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci. F. *Organometallics.* **2003**, *22*, 2545-2547.
(5) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* in press.
(6) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866-872.
(7) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(8) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218-1226.
(9) Easton, R. E.; Giesen, D. J.; Welch, A.; Cramer, C. J.; Truhlar, D. G. *Theor. Chim. Acta* **1996**, *93*, 281-301.
(10) Roos, B. O.; Malmqvist, P. A. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2919-2927.
(11) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575-6579.
(12) Zhao, Y.; Truhlar, D. G. *MN-GFM (version 3.0)*, University of Minnesota, Minneapolis, MN, 2007.
(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.
(14) Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P. O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. *Comp. Mat. Sci.* **2003**, *28*, 222-239.