

Supporting Information for
**Mechanism of Copper/Azodicarboxylate-Catalyzed Aerobic Alcohol Oxidation:
Evidence for Uncooperative Catalysis**

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I. General Considerations

All commercially available compounds were purchased, and used as received unless indicated otherwise. X-band EPR data were collected using a Bruker EleXsys E500 spectrometer; all spectra were acquired at 115 K using a N₂(l) cryostat under nonsaturating conditions. In situ IR data were collected using a Mettler Toledo ReactIR ic10 with an AgX probe. ¹H and ¹³C NMR spectra were recorded on Bruker or Varian 300 MHz spectrometers. Chemical shift values are given in parts per million relative to CDCl₃ (7.26 ppm for ¹H or 77.23 ppm for ¹³C).¹ NMR spectra were plotted with MestReNova v7.1.2 (MestreLab Research S. L. 2012).

General procedure for collection of ReactIR/gas-uptake time course data:

A two-neck flask containing a magnetic stir bar was placed in an oil bath at a controlled temperature of 27 °C. 6.2 mg CuCl (0.063 mmol), 12.4 mg 1,10-phenanthroline (0.069 mmol) and 346 mg K₂CO₃ (2.5 mmol) were added as solids prior to attaching one neck of the flask to a custom-made gas-uptake apparatus to monitor oxygen consumption. The other neck contained a septum equipped with an IR dip probe. The flask was evacuated and backfilled with O₂ five times and then filled to the desired O₂ pressure. 4.5 mL of 13.9 mM DBAD in fluorobenzene was added. After the flask was equilibrated at 27 °C, 0.5 mL of 2.5 M 1-phenylethanol in fluorobenzene was added to initiate the reaction. Burst and catalytic rates were obtained using the method of initial rates by fitting early time points ≤ 10 % conversion for both regions.

General procedure for collection of ReactIR burst time course data:

A two-neck flask containing a magnetic stir bar was placed in an oil bath at a controlled temperature of 27 °C. 6.2 mg CuCl (0.063 mmol), 12.4 mg 1,10-phenanthroline (0.069 mmol) and 346 mg K₂CO₃ (2.5 mmol) were added as solids prior to sealing one neck of the flask with a septum. The other neck contained a septum equipped with an IR dip probe. The flask was evacuated and backfilled with N₂ five times using a large needle that was inserted into a septum and connected to a Schlenk line. The flask was then left under positive N₂ pressure. 4.5 mL of 13.9 mM DBAD in fluorobenzene was added. After the flask was equilibrated at 27 °C, 0.5 mL of 2.5 M 1-phenylethanol in fluorobenzene was added to initiate the reaction. Burst rates were obtained using the method of initial rates by fitting the first 40% of DBAD consumption.

General procedure for collection of ReactIR aerobic time course data:

A two-neck flask containing a magnetic stir bar was placed in an oil bath at a controlled temperature of 27 °C. 6.2 mg CuCl (0.063 mmol), 12.4 mg 1,10-phenanthroline (0.069 mmol) and 346 mg K₂CO₃ (2.5 mmol) were added as solids prior to sealing one neck of the flask with a septum. The other neck contained a septum equipped with an IR dip probe. The flask was evacuated and backfilled with O₂ five times using a large needle that was inserted into a septum and connected to a Schlenk line. 4.5 mL of 13.9 mM DBADH₂ in fluorobenzene was added. After the flask was equilibrated at 27 °C, 0.5 mL of 2.5 M 1-phenylethanol in fluorobenzene was added to initiate the reaction. Burst rates were obtained using the method of initial rates by fitting early time points.

Note: The CuCl remains mostly heterogeneous until substrate is added, at which point it rapidly becomes homogeneous (at concentrations ≤ ~12.5 mM (phen)CuCl). It is important that the solution is stirred by an appropriately sized stir bar to ensure that the Cu is solubilized and that the K₂CO₃ is agitated.

II. Reaction Time Courses and Control Reactions

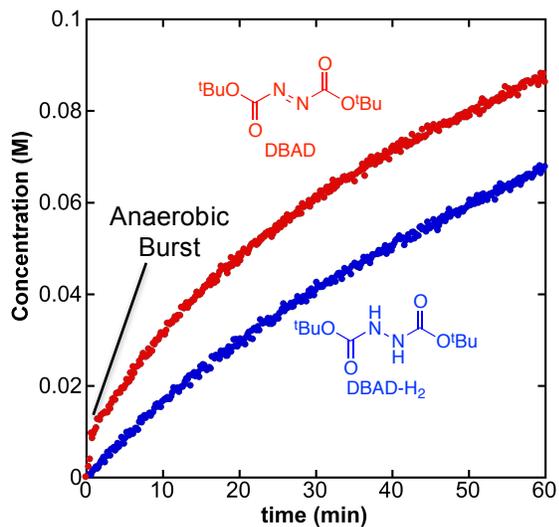


Figure S1. 1-Phenylethanol oxidation time course, monitored by in situ IR, showing the comparison of Cu/DBAD- vs. Cu/DBADH₂-catalyzed aerobic alcohol oxidation reactions. A burst of product formation is evident at the beginning of the time course with DBAD. Standard reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, [(phen)CuCl] = 12.5 mM, [cocatalyst] = 12.5 mM, 2 equiv. K₂CO₃, 650 torr O₂, 27 °C.

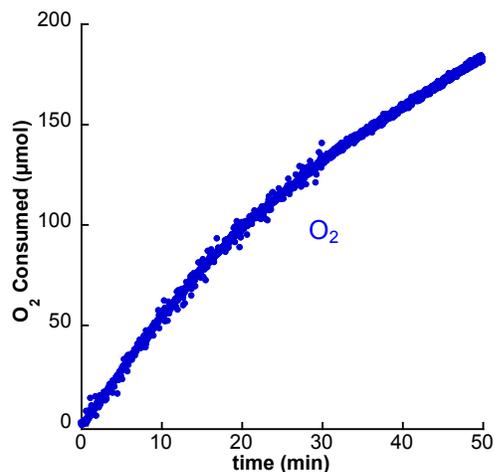


Figure S2. 1-Phenylethanol oxidation data monitored by O₂ uptake using Cu/DBADH₂ catalyst. Standard reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, [(phen)CuCl] = 12.5 mM, [DBADH₂] = 12.5 mM, 2 equiv. K₂CO₃, 650 torr O₂, 27 °C.

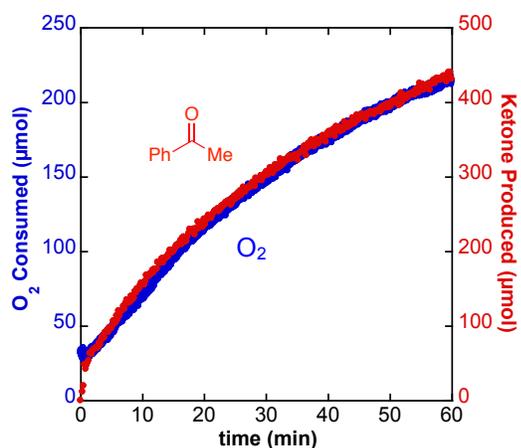


Figure S3. Overlay of product formation (measured by in situ IR) and O₂ consumption (measured by O₂ uptake) for Cu/DBAD-catalyzed oxidation of 1-phenylethanol, which displays a 2:1 product to O₂ stoichiometry. Vertical axis of O₂ consumption offset to account for anaerobic reactivity. Reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, [(phen)CuCl] = 12.5 mM, [DBAD] = 12.5 mM, 2 equiv. K₂CO₃, 650 torr O₂, 27 °C.

Synthesis of [(phen)Cu(OH)]₂Cl₂

The procedure was adapted from literature syntheses.² To a mixture of CuCl₂ (268.8 mg, 2.0 mmol) and 1,10-phenanthroline monohydrate (396.6 mg, 2.0 mmol) in H₂O (6 mL) was added aq. NaOH (1 M, 2 mL). The resulting solution was stirred at 60 °C under air for 2 h. The precipitate was filtered and washed with 95% EtOH (2 x 10 mL), Et₂O (2 x 10 mL). The resulting light blue solid was dried under reduced pressure (532.6 mg, 73%). Mp = 217 °C (black decomposition), Lit = 218-220 °C (black decomp.).^{2b}

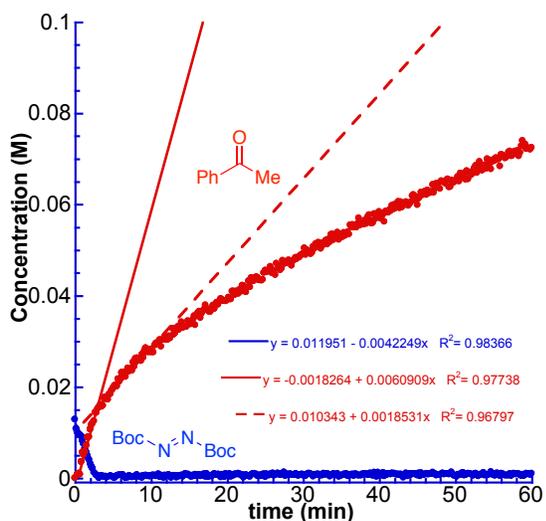


Figure S4. Reaction time course for CuCl₂/DBAD-catalyzed aerobic oxidation of 1-phenylethanol monitored by in situ IR spectroscopy. Red trace = [acetophenone]; Blue trace = [DBAD]. Reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, [(phen)CuCl₂] = 12.5 mM, [DBAD] = 12.5 mM, 2 equiv. K₂CO₃, 650 torr O₂, 27 °C.

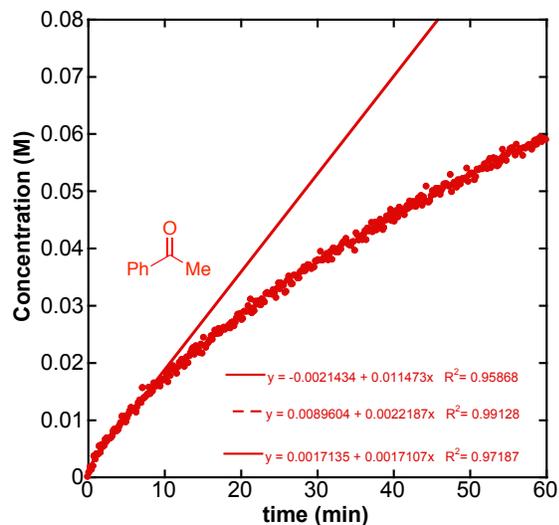


Figure S5. Reaction time course for acetophenone formation $[(\text{phen})\text{Cu}(\text{OH})_2\text{Cl}_2/\text{DBADH}_2]$ -catalyzed aerobic oxidation of 1-phenylethanol monitored by in situ IR spectroscopy. Reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, $[(\text{phen})\text{Cu}(\text{OH})_2\text{Cl}_2] = 6.25$ mM (12.5 mM Cu), $[\text{DBAD}] = 12.5$ mM, 2 equiv. K_2CO_3 , 650 torr O_2 , 27 °C.

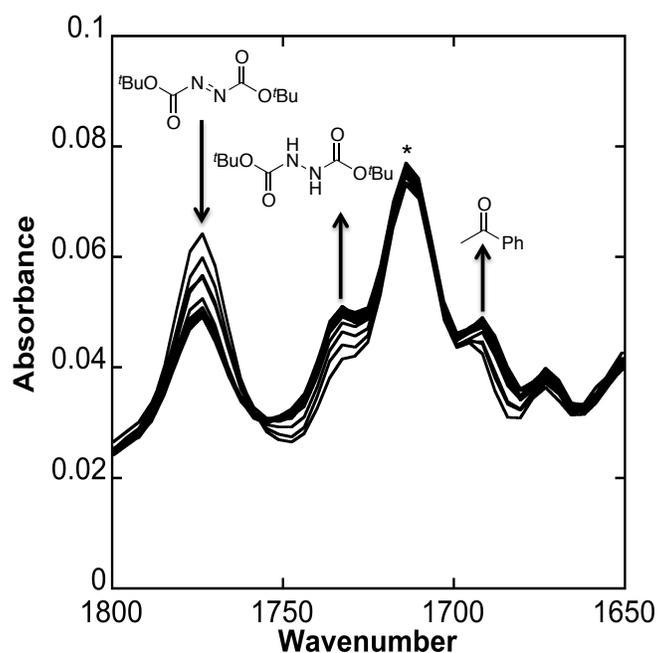


Figure S6. Representative absorbance data obtained during the anaerobic burst phase in Cu/DBAD-catalyzed oxidation of 1-phenylethanol (see Figure S1 for full reaction conditions). Concentration data were generated by conversion of absorbance data.

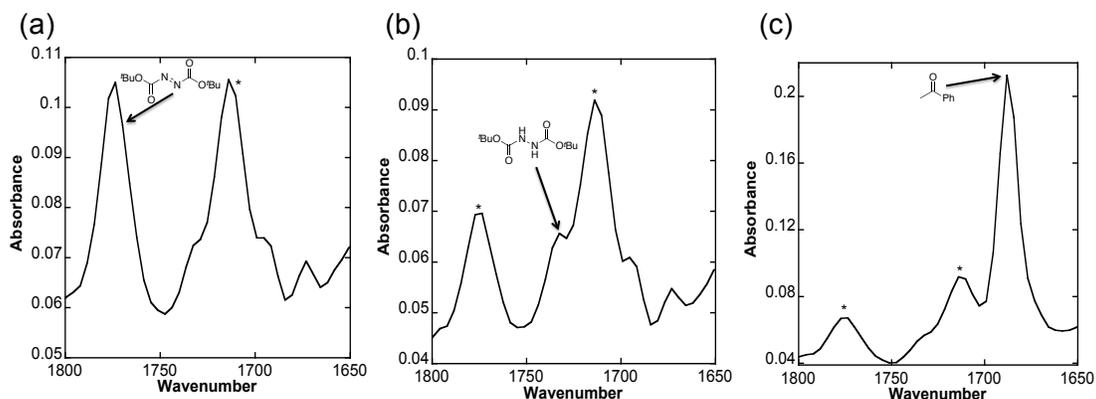


Figure S7. Solution-phase (fluorobenzene) IR spectra of (a) pure DBAD (12.5 mM), $\nu = 1773 \text{ cm}^{-1}$, (b) DBADH₂ (12.5 mM), $\nu = 1734 \text{ cm}^{-1}$, and (c) acetophenone (0.25 M), $\nu = 1686 \text{ cm}^{-1}$. The "*" designates absorption peaks associated with the fluorobenzene solvent. Samples were prepared in a volumetric flask and transferred into a sample vial. The measurement was made by placing the IR dip probe directly into the solution.

III. Kinetic Data for Determination of Rate Laws

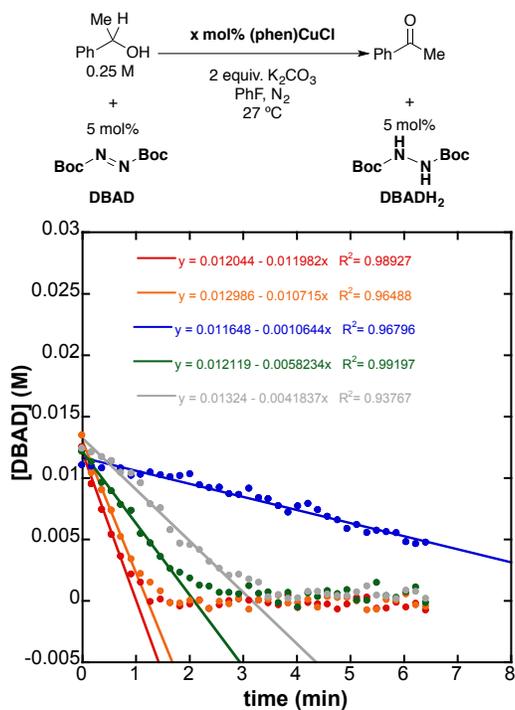


Figure S8. Assessment of the kinetic dependence on [(phen)CuCl] during the burst by in situ IR spectroscopy. Kinetic data in Figure 3A were generated from a linear fit of the first 40% of consumed DBAD. Standard reaction conditions: 12.5 mM [DBAD], 0.25 M [1-phenylethanol], 650 torr O₂, [(phen)CuCl] = (•) 1.3 mM, (◐) 3.8 mM, (◑) 8.3 mM, (◒) 12.3 mM, (◓) 16.3 mM.

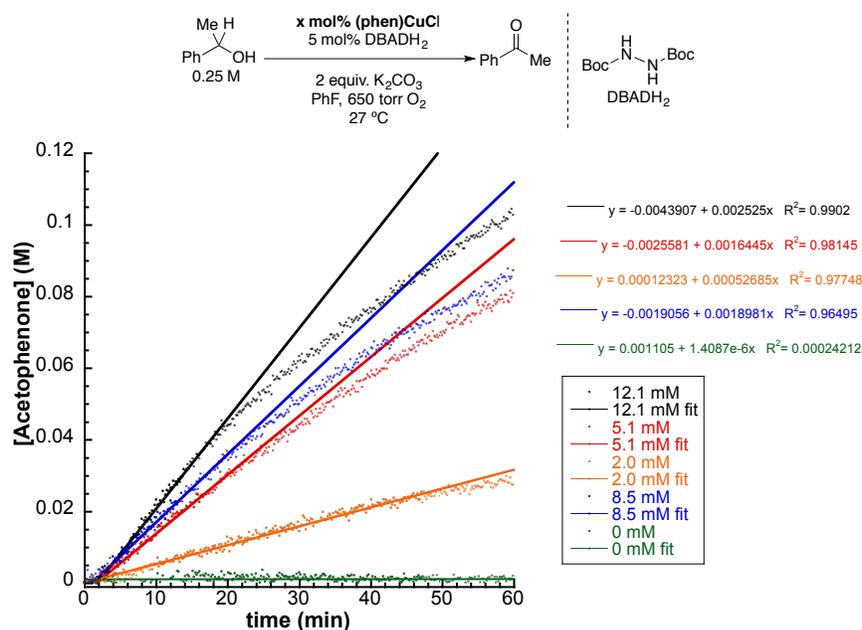


Figure S9. Assessment of the kinetic dependence on $[(\text{phen})\text{CuCl}]$ during aerobic catalysis by in situ IR spectroscopy. Kinetic data in Figure 4A were generated from a linear fit from 2% to 10% acetophenone produced. Standard reaction conditions: 12.5 mM $[\text{DBADH}_2]$, 0.25 M $[\text{1-phenylethanol}]$, 1 atm O_2 , (a) $[(\text{phen})\text{CuCl}] = (\bullet)$ 0.0 mM (\circ) 2.0 mM, (\circ) 5.1 mM, (\bullet) 8.5 mM, (\circ) 12.1 mM.

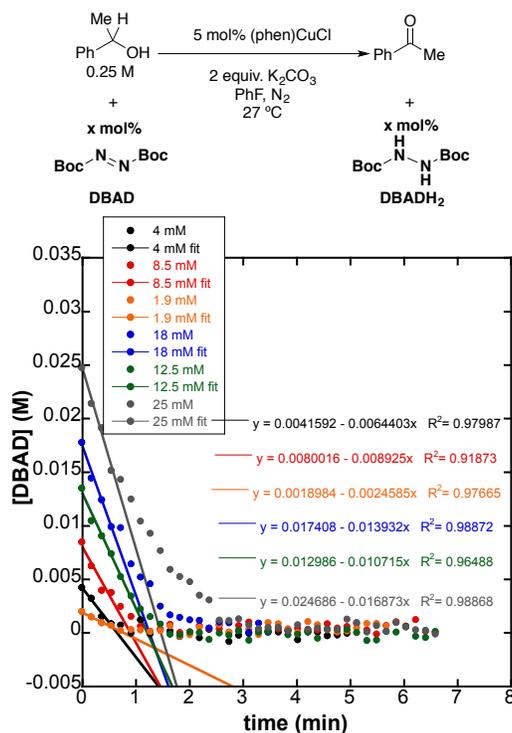


Figure S10. Assessment of the kinetic dependence on $[\text{DBAD}]$ during the burst by in situ IR spectroscopy. Kinetic data in Figure 3B were generated from a linear fit of the first 40% of consumed DBAD. Standard reaction conditions: 12.5 mM $[(\text{phen})\text{CuCl}]$, 650 torr O_2 , $[\text{alcohol}] = 0.25$, $[\text{DBAD}] = (\bullet)$ 1.9 mM, (\bullet) 4.0 mM, (\circ) 8.5 mM, (\bullet) 12.5 mM, (\bullet) 18 mM, (\circ) 25 mM.

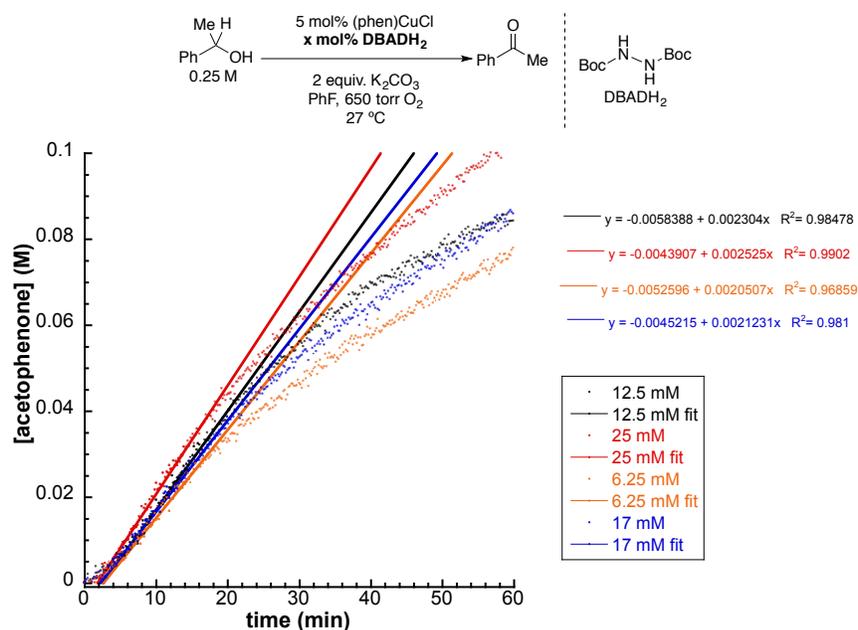


Figure S11. Assessment of the kinetic dependence on [DBADH₂] during aerobic catalysis by in situ IR spectroscopy. Kinetic data in Figure 4B were generated from a linear fit from 2% to 10% acetophenone produced. Standard reaction conditions: 12.5 mM [(phen)CuCl], 1 atm O₂, [alcohol] = 0.25, [DBADH₂] = (•) 6.25 mM, (●) 12.5 mM, (◐) 17 mM, (◑) 25 mM.

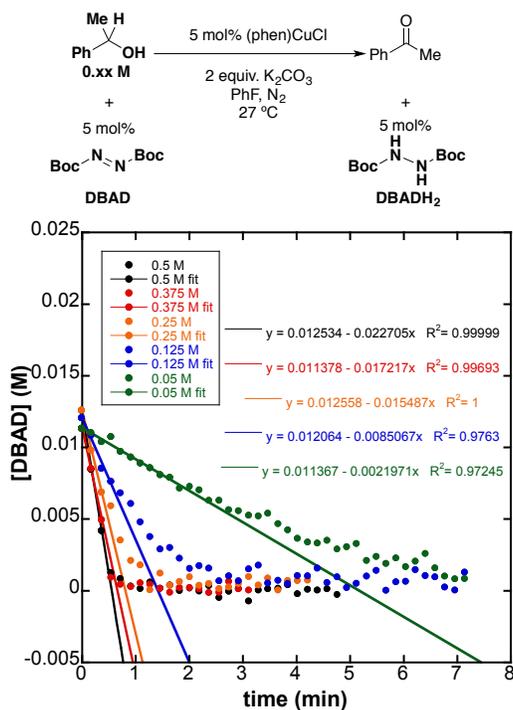


Figure S12. Assessment of the kinetic dependence on [alcohol] during the burst by in situ IR spectroscopy. Kinetic data in Figure 3C were generated from a linear fit of the first 40% of consumed DBAD. Standard reaction conditions: 12.5 mM [(phen)CuCl], 12.5 mM [DBAD], 1 atm N₂, [alcohol] = (•) 0.05 M, (◐) 0.125 M, (◑) 0.25 M, (◒) 0.375 M, (◓) 0.50 M.

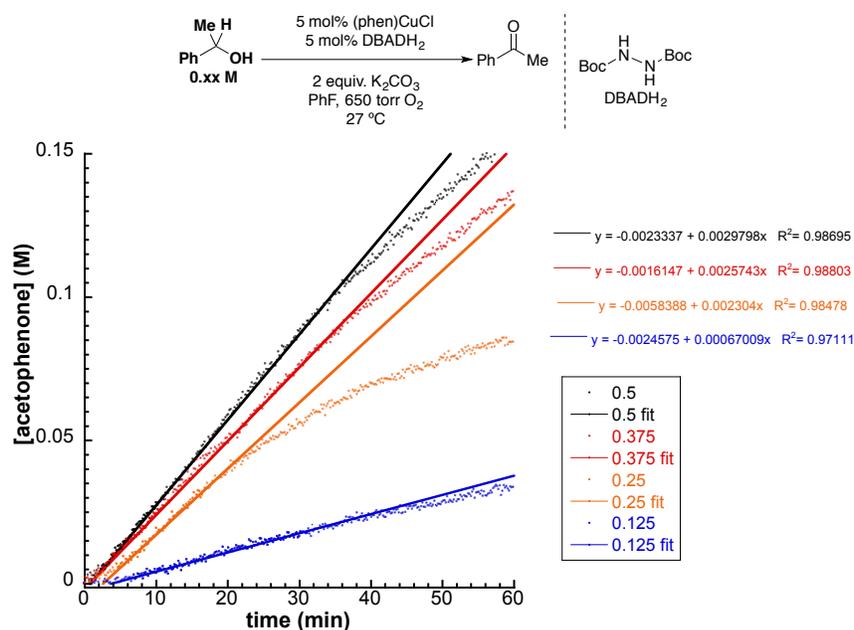


Figure S13. Assessment of the kinetic dependence on [alcohol] during aerobic catalysis by in situ IR spectroscopy. Kinetic data in Figure 4C were generated from a linear fit from 2% to 10% acetophenone produced. Standard reaction conditions: 12.5 mM [(phen)CuCl], 12.5 mM [DBADH₂], 1 atm O₂, [alcohol] = (•) 0.5 M, (◐) 0.25 M, (◑) 0.25 M, (◒) 0.125 M.

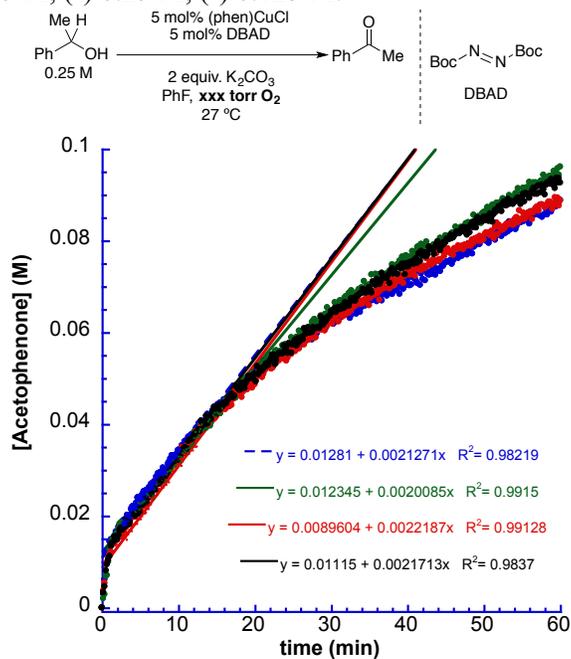


Figure S14. Time course data for kinetic dependence on pO_2 during aerobic catalysis. Standard reaction conditions: 12.5 mM [(phen)CuCl], 12.5 mM [DBAD], [alcohol] = 0.25 M, pO_2 = (◐) 450 torr, (◑) 550 torr, (◒) 650 torr, (◓) 750 torr. Slopes from early time points were used to construct Figure S17.

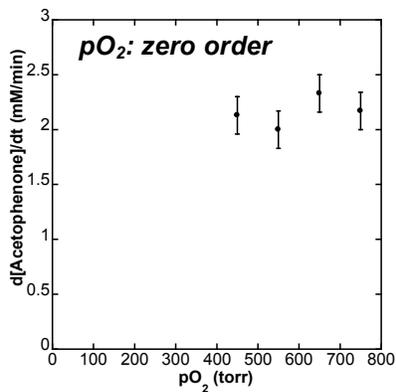


Figure S15. The pO_2 -dependence of steady-state aerobic oxidation of 1-phenylethanol oxidation catalyzed by (phen)CuCl/DBAD. Rates were obtained by monitoring product formation using in situ IR spectroscopy. Error bars correspond to $\pm\sigma$ of three repetitions of standard reaction conditions. Standard reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, [(phen)CuCl] = 12.5 mM, [DBAD] = 12.5 mM, 2 equiv. K_2CO_3 , 27 °C.

IV. Synthesis/Characterization of Deuterated Alcohols for KIE Experiments

1-phenylethanol-1- d_1 This procedure was adapted from a literature procedure.³ 363 mg (3.03 mmol) of freshly recrystallized acetophenone (recrystallized from hexanes at $-20\text{ }^\circ\text{C}$) was massed into a 100 mL round-bottom flask equipped with a Teflon™ stirbar. 8 mL of MeOD was added and the solution was cooled in an ice bath. 0.159 g NaBD_4 was added portion-wise over ~ 10 min as solid. The reaction was monitored by TLC until all of the starting material was consumed. The reaction was quenched with 25 mL saturated NH_4Cl . The resulting solution was extracted with EtOAc (3 x 10 mL) and dried over MgSO_4 . The solvent was removed under reduced pressure and the resulting oil was purified by silica gel column chromatography (3:1 hexane:ethyl acetate). The solvent was removed under reduced pressure, giving a clear and colorless oil (0.177 g, 48%). The deuterium incorporation was determined to be $> 99\%$ by ^1H NMR.

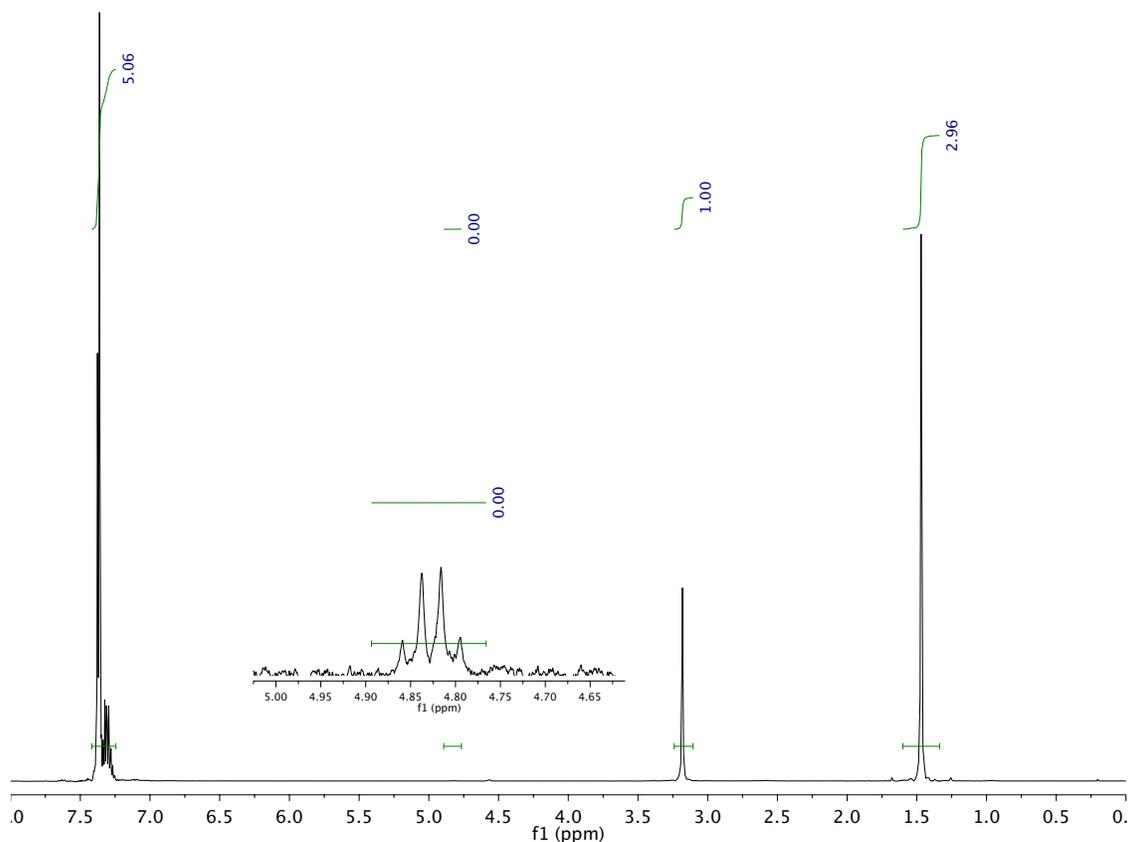


Figure S16. ^1H NMR spectrum of 1-phenylethanol-1- d_1 used in independent rate KIE measurements.

Benzylalcohol-*d*₁ This procedure was adapted based upon literature procedure.³ 1.5 g (12.3 mmol) of freshly distilled benzaldehyde was massed into a 250 mL round-bottom flask equipped with a Teflon™ stirbar. 25 mL of MeOD was added and the solution was cooled in an ice bath. 0.642 g NaBD₄ (15.3 mmol) was added portion-wise over ~10 min as solid. The reaction was monitored by TLC until all of the starting material was consumed. The reaction was quenched with 100 mL saturated NH₄Cl. The resulting solution was extracted with EtOAc (3 x 50 mL) and dried over MgSO₄. The solvent was removed under reduced pressure and the resulting oil was purified by silica gel column chromatography (3:1 hexane:ethyl acetate). The solvent was removed under reduced pressure, giving a clear and colorless oil (2.73 g, 55%). The deuterium incorporation was determined to be > 98% by ¹H NMR.

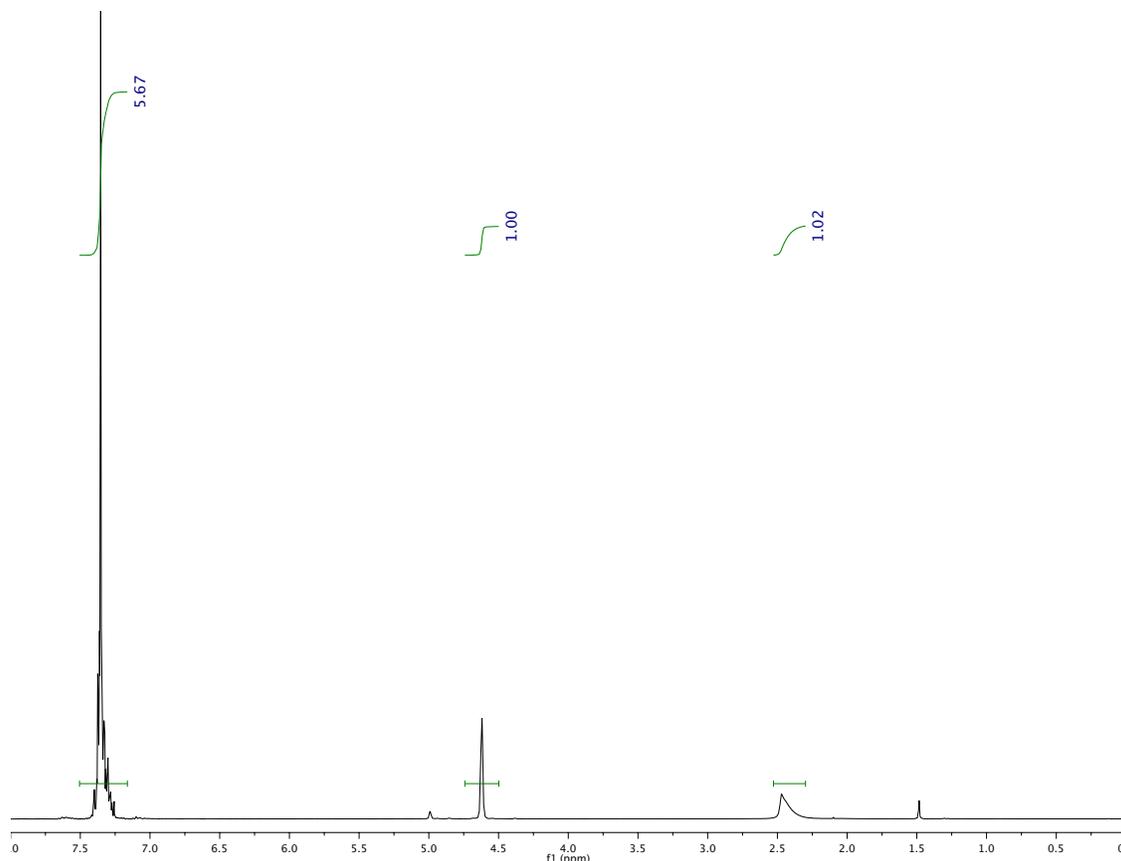


Figure S17. ¹H NMR spectrum of benzylalcohol-*d*₁ used in intramolecular competition KIE measurements.

V. Methods and Data for Determination of KIE Values

KIE values were determined by using quantitative ¹H NMR analysis. The intramolecular competition KIE was determined by comparing the integration of the *HCO* (δ 10.1) and the *ortho CH* in benzaldehyde using the equation:

$$\text{KIE} = \text{int}(\delta 7.9)/2 - \text{int}(\delta 10.1).$$

Full analysis is presented below, showing the yield of *H*- and *D*-aldehyde, remaining starting material, and mass balance.

(A) Cu-Only Catalytic Intramolecular KIE A 25 mL round-bottom flask containing a magnetic stir bar was placed in an oil bath at a controlled temperature of 27 °C. 6.2 mg CuCl (0.063 mmol), 12.4 mg 1,10-phenanthroline (0.069 mmol) and 346 mg K₂CO₃ (2.5 mmol) were added as solids prior to the flask being plugged with a septum. The closed system was purged with O₂ for 15 minutes and then 4.5 mL of fluorobenzene was added. The slurry was allowed to stir for 5 minutes, followed by the injection of 0.5 mL of 2.5 M benzylalcohol-*d*₁. The reaction was allowed to stir for 1-2 hours and was quenched by addition of ~2 g of silica. 10 mL of EtOAc was added and the resulting slurry was filtered through a medium porosity glass frit. The filtrate was concentrated under vacuum (some solvent remained in certain cases to prevent product evaporation). The resulting oil was subjected to ¹H NMR analysis (20 s delay time).

Table S1. ¹H NMR integrations used to determine intramolecular competition KIE for Cu-only aerobic alcohol oxidation.

a	Relative Integration				yield H ald	yield D ald	RSM	KIE
	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)				
	1.00	6.84	118.55	19.42	4.2%	10.2%	81.9%	2.4
					Mass balance: 96.3%			
b	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	yield H ald	yield D ald	RSM	KIE
	1.00	7.13	49.19	5.90	10.2%	26.1%	60.0%	2.6
					Mass balance: 96.2%			
c	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	yield H ald	yield D ald	RSM	KIE
	1.00	7.0	175.39	30.7	2.9%	7.1%	87.5%	2.5
					Mass balance: 97.5%			

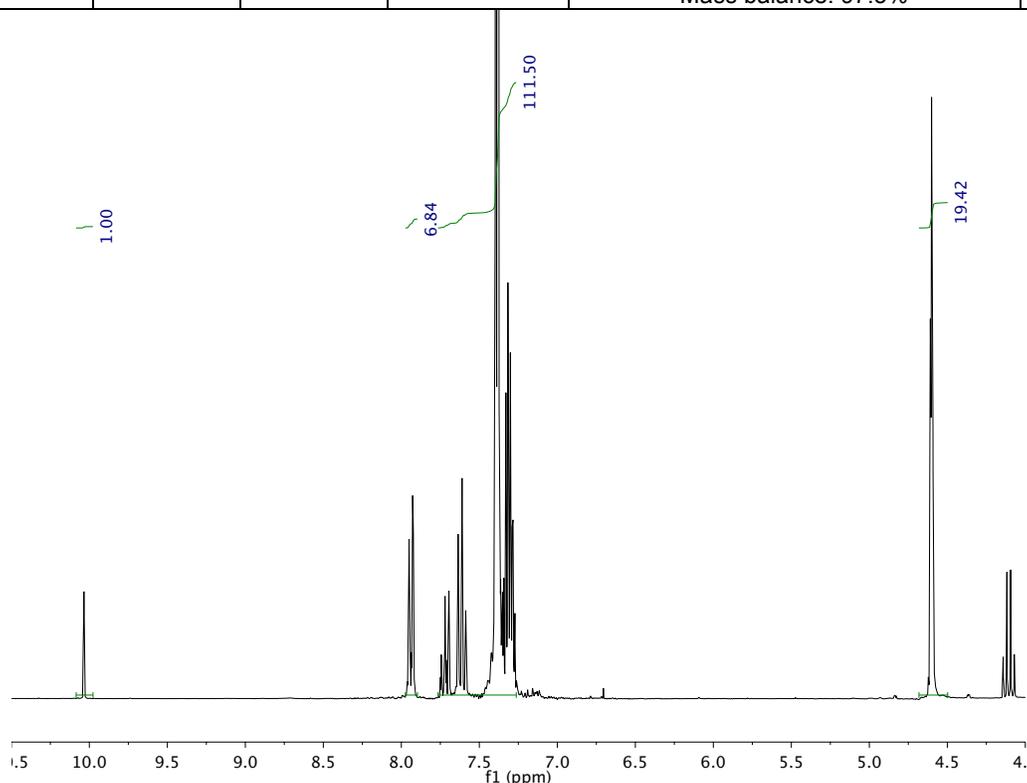


Figure S18. Representative ¹H NMR spectrum used to generate data in Table S1.

(B) Cu/DBAD-H₂ Catalytic Intramolecular Competition KIE A 25 mL round-bottom flask containing a magnetic stir bar was placed in an oil bath at a controlled temperature of 27 °C. 6.2 mg CuCl (0.063 mmol), 12.4 mg 1,10-phenanthroline (0.069 mmol), 14.5 mg DBADH₂ and 346 mg K₂CO₃ (2.5 mmol) were added as solids prior to the flask being plugged with a septum. The closed system was purged with O₂ for 15 minutes and then 4.5 mL of fluorobenzene was added. The slurry was allowed to stir for 5 minutes, followed by the injection of 0.5 mL of 2.5 M benzylalcohol-*d*₁. The reaction was allowed to stir for 1-2 hours and was quenched by addition of ~2 g of silica. 10 mL of EtOAc was added and the resulting slurry was filtered through a medium porosity glass frit. The filtrate was concentrated under vacuum (some solvent remained in certain cases to prevent product evaporation). The resulting oil was subjected to ¹H NMR analysis (20 s delay time).

Table S2. ¹H NMR integrations used to determine intramolecular competition KIE for Cu/DBAD-H₂ aerobic alcohol oxidation.

a	Relative Integration				yield H ald	yield D ald	RSM	KIE
	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	6.2%	24.0%	66.2%	3.9
	1.00	9.71	80.29	10.63	Mass balance: 96.4%			
b	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	yield H ald	yield D ald	RSM	KIE
	1.00	9.87	50.26	4.78	10.0%	39.2%	47.6%	3.9
					Mass balance: 96.7%			
c	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	yield H ald	yield D ald	RSM	KIE
	1.00	9.53	81.52	10.56	6.1%	23.1%	64.8%	3.8
					Mass balance: 94.0%			

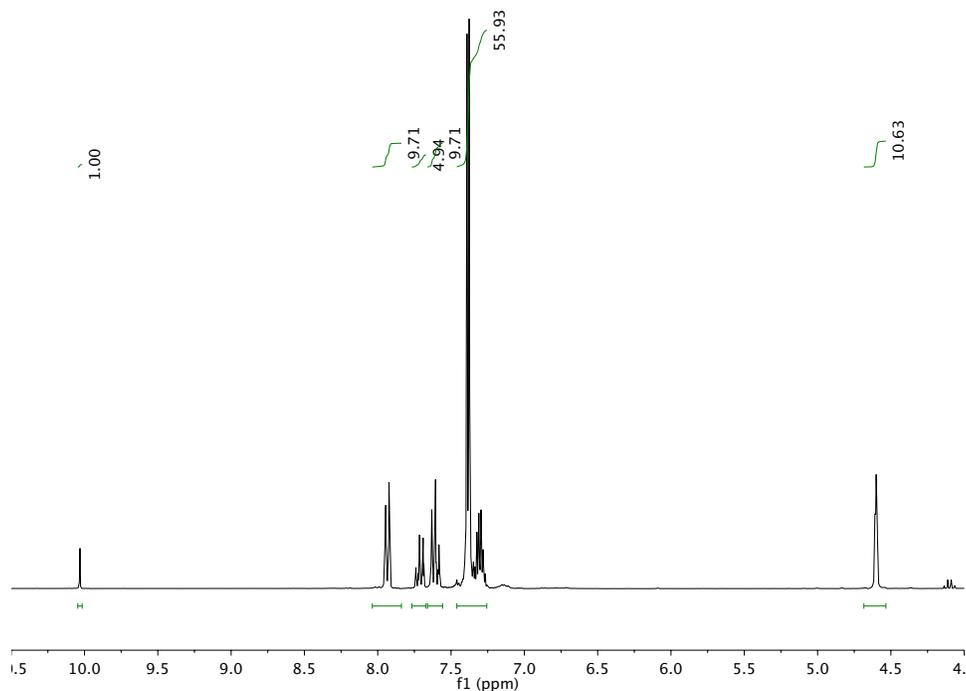


Figure S19. Representative ¹H NMR spectrum used to generate data in Table S2.

(C) Cu/DBAD Anaerobic Intramolecular Competition KIE A 25 mL round-bottom flask containing a magnetic stir bar was placed in an oil bath at a controlled temperature of 27 °C. 6.2 mg CuCl (0.063 mmol), 12.4 mg 1,10-phenanthroline (0.069 mmol) and 346 mg K₂CO₃ (2.5 mmol) were added as solids prior to the flask being plugged with a septum. The closed system was purged with N₂ for 15 minutes and then 4.5 mL of 27.6 mM DBAD in fluorobenzene was added. The slurry was allowed to stir for 5 minutes, followed by the injection of 0.5 mL of 2.5 M benzylalcohol-*d*₁. The reaction was allowed to stir for 1 hour and was quenched by addition of ~2 g of silica. 10 mL of EtOAc was added and the resulting slurry was filtered through a medium porosity glass frit. The filtrate was concentrated under vacuum (some solvent remained in certain cases to prevent product evaporation). The resulting oil was subjected to ¹H NMR analysis (20 s delay time).

Table S3. ¹H NMR integrations used to determine intramolecular competition KIE for Cu/DBAD anaerobic alcohol oxidation.

a	Relative Integration				yield H ald	yield D ald	RSM	KIE
	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	1.2%	6.4%	88.2%	5.2
	1.00	12.43	406.15	71.61	Mass balance: 96.4%			
b	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	yield H ald	yield D ald	RSM	KIE
	1	13.07	319.88	61.82	1.6%	8.7%	96.6%	5.5
					Mass balance: 106.8%			
c	Ald (δ 10.1)	Ald (δ 7.9)	Ar tot	CHD (δ 4.7)	yield H ald	yield D ald	RSM	KIE
	1.00	12.67	213.99	35.75	2.3%	12.5%	83.53%	5.3
					Mass balance: 98.3%			

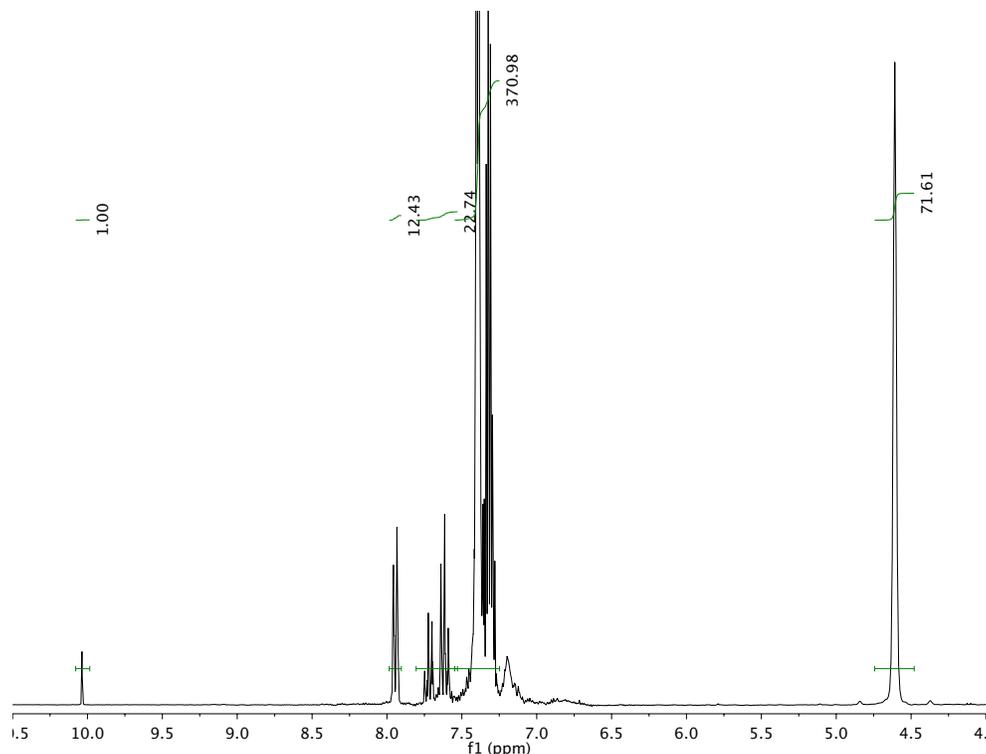


Figure S20. Representative ¹H NMR spectrum used to generate data in Table S3.

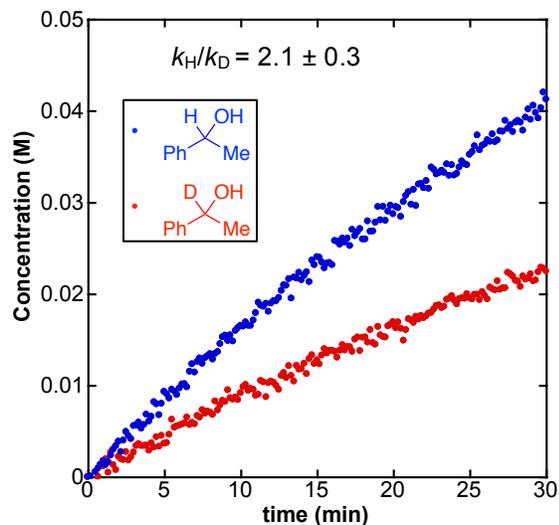


Figure S21. Independent rate kinetic isotope effect experiment for Cu/DBADH₂-catalyzed aerobic alcohol oxidation. Standard reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, [(phen)CuCl] = 12.5 mM, [cocatalyst] = 12.5 mM, 2 equiv. K₂CO₃, 650 torr O₂, 27 °C.

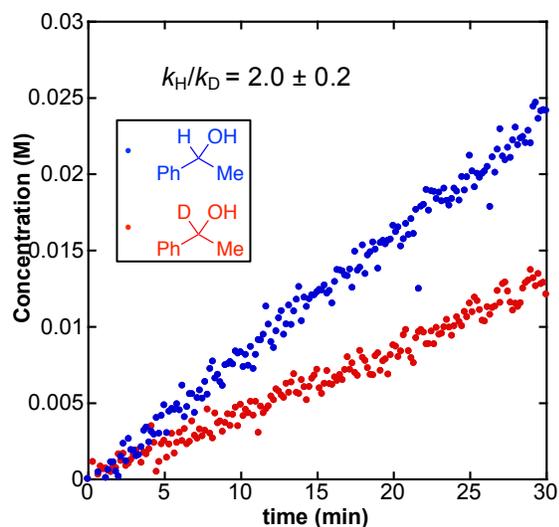


Figure S22. Independent rate kinetic isotope effect experiment for Cu-catalyzed aerobic alcohol oxidation. Standard reaction conditions: 0.25 M 1-phenylethanol in 5 mL fluorobenzene, [(phen)CuCl] = 12.5 mM, 2 equiv. K₂CO₃, 650 torr O₂, 27 °C.

VI. EPR Spectroscopic Studies

A 25 mL round-bottom flask containing a magnetic stir bar was placed in an oil bath at a controlled temperature of 27 °C. 9.9 mg CuCl (0.1 mmol), 18.0 mg 1,10-phenanthroline (0.1 mmol), 23.0 mg DBAD (0.1 mmol) and 3.5 g K₂CO₃ (25 mmol) were added as solids prior to the flask being plugged with a septum. The closed system was purged with O₂ for 15 minutes and then 10 mL of 1.0 M 1-phenylethanol in fluorobenzene was added. The reaction was allowed to stir for 1 hour and a 0.4 mL aliquot was removed and immediately flash-frozen at 77 K to prevent further reactivity. EPR simulations were performed using the Easy Spin program.⁴ Spin quantitation was performed by double-integration of the spectra and comparison to an external calibration curve generated using Cu^{II}(OTf)₂ in *N*-methylimidazole/fluorobenzene solution.

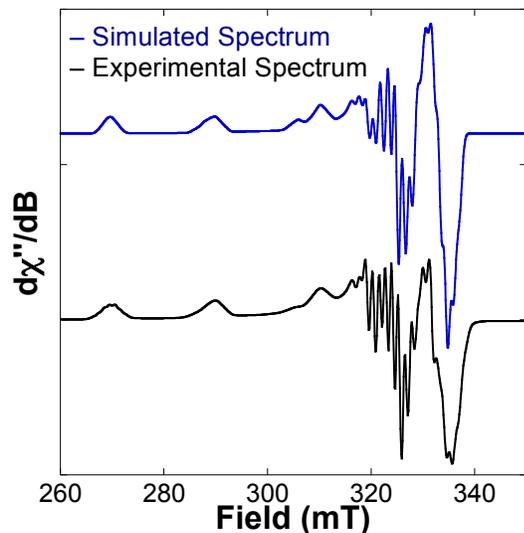


Figure S23. Experimental and simulated EPR spectra.

Simulation parameters:

Species 1 [Cu, ¹⁴N, ¹⁴N]:

Weight: 64 %

$g_x, g_y = 2.055; g_z = 2.21$

$A_{x,y}(\text{Cu}) = 60 \text{ MHz}; A_z(\text{Cu}) = 600 \text{ MHz}$

$A_{x,y}(\text{N}) = 36.5 \text{ MHz}; A_z(\text{N}) = 30 \text{ MHz}$

Species 2 [Cu, ¹⁴N, ¹⁴N]:

Weight: 36 %

$g_x, g_y = 2.052; g_z = 2.23$

$A_{x,y}(\text{Cu}) = 60 \text{ MHz}; A_z(\text{Cu}) = 582 \text{ MHz}$

$A_{x,y}(\text{N}) = 36.5 \text{ MHz}; A_z(\text{N}) = 30 \text{ MHz}$

IX. References.

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