Electronic Supplementary Information for

Iron(III) Nitrate/TEMPO-Catalyzed Aerobic Alcohol Oxidation: Distinguishing between Serial versus Integrated Redox Cooperativity

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1. General Considerations

Reagents:

Unless noted, all commercial chemicals and solvents were purchased from Millipore-Sigma and were used without further purification. $Fe(OTf)_3$ was purchased from Combi-Blocks. Acetonitrile was obtained from an LC Technology Solutions Inc. solvent purification system.

Instruments and Techniques:

^1H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 and Bruker Avance III 500 spectrometers. Chemical shifts are given in parts per million (ppm) relative to residual solvent peaks. Gas chromatographs were collected on a Shimadzu GC-2010 Gas Chromatograph. High-resolution mass spectra were obtained using a Thermo Q ExactiveTM Plus by the mass spectrometry facility at the University of Wisconsin-Madison. Chromatographic purification of products was accomplished by chromatography on Silicycle P60 silica gel or Biotage Sfär 60µm silica using a Biotage Isolera One flash chromatography system.

Electrochemical measurements were carried out using a Pine WaveNow PGstat potentiostat connected to a BASi RDE-2 Cell Stand. Cyclic voltammetry (CV) experiments were carried out in a three-electrode cell configuration with a glassy carbon (GC) working electrode (3 mm diameter) and a platinum wire counter electrode. Working electrode potentials were measured against Ag/AgCl (3 M KCl) aqueous reference electrode or $Ag/AgNO_3$ (0.1 M NBu_4PF_6 in CH_3CN) reference electrode and were referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple.

Gas uptake experiments were performed in a homemade multi-well reactor system (described below).[1]

2. Electrochemistry of TEMPO

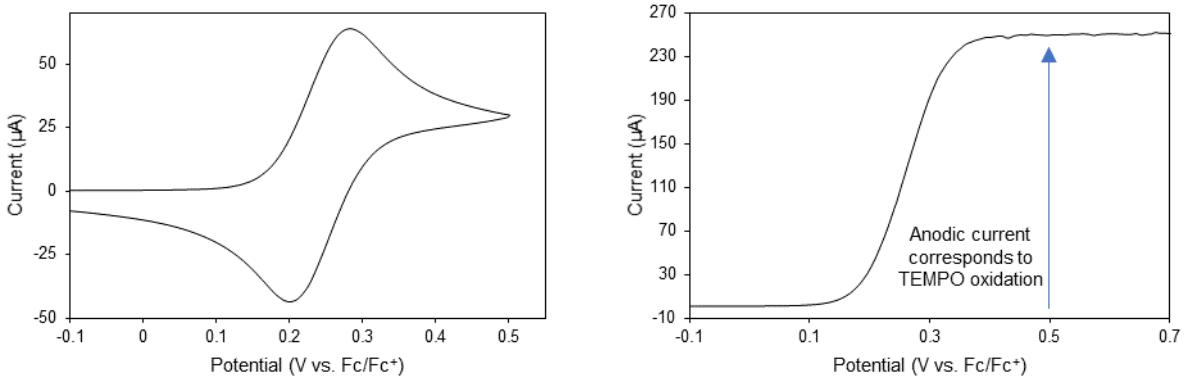


Figure S1. Left: CV of 3 mM TEMPO in 0.1 M NBu_4PF_6 CH_3CN. $E_{1/2}$ = 0.24 V vs. $Fc^{+/0}$. Scan rate = 50 mV/s. Right: LSV of 3 mM TEMPO in 0.1 M NBu_4PF_6 CH_3CN. Scan rate = 50 mV/s, rotation rate = 1000 RPM.

3. Cyclic Step Chronoamperometry–Rotating Disk Electrode Experiments

Aminoxyl speciation in the presence of various reagents was analyzed using cyclic step chronoamperometry (CSCA) at a rotating disk electrode (RDE). For the CSCA experiments, the potential applied at the RDE was alternated at set potentials above and below the nitroxyl/oxoammonium midpoint potential ($E_{1/2}$ = 0.24 V vs. $Fc^{+/0}$, cf. Fig. S1). One potential is applied for 5 s to allow the current measured at the working electrode to stabilize and then the potential is stepped to the other set potential and the electrode potential is held at this potential for 5 s. This cycle is repeated until the end of the experiment. During the CSCA experiment, the working glassy carbon electrode is rotated at 1000 RPM to induce convection at the electrode surface. The currents measured at the applied anodic and cathodic potentials during the CSCA experiment are proportional to the concentration of TEMPO and $TEMPO^+$ in the electrolyte solution, respectively.[2]

3a. TEMPO/HCl/HNO_3

To an electrolysis cell mounted in the three-electrode BASi RDE-2 cell stand was added 10 mL TEMPO solution (3 mM) in supporting electrolyte (0.1 M NBu_4PF_6, CH_3CN). The working electrode was set to rotate at 1000 RPM. The CSCA method was initiated with cycling potentials set to +0.3/+1.0 V vs. Ag/AgCl (–0.18/0.52 V vs. $Fc^{0/+}$). Each potential was held for 5 s before switching to the other. After ca. 1 min, 2.5 µL conc. HCl (3 mM) was added. At ca. 13 min, 2.1 µL conc. HNO_3 (3 mM) was added. After 22 min, the experiment was stopped.

A time course of [TEMPO] and [$TEMPO^+$] in the presence of HCl and HNO_3 was determined using the limiting anodic and cathodic currents measured during the CSCA experiment. The median current measured during the 5 s step period at 1.0 V vs. Ag/AgCl prior to HCl addition (239 µA) was taken as the current proportional to 3 mM TEMPO, $I°_a$. At the end of the CSCA experiment, the median cathodic current was –239 µA.

The limiting anodic current measured after TEMPO and HCl (and then HNO_3) were mixed, I_a, is taken as the median current value measured during the 5 s step period at the anodic potential (*i.e.*, 1.0 V vs. Ag/AgCl). This current can be related to [TEMPO] by eq S1. The limiting cathodic current measured after TEMPO and HCl/HNO_3 have been mixed, I_c, is taken as the median current value measured during the 5 s step period at the cathodic potential (*i.e.*, 0.52 V vs. Fc/Fc^+). This current can be related to [$TEMPO^+$] by eq S2

$$[TEMPO] = \frac{I_a}{I°_a} * 3\ mM \tag{S1}$$

$$[TEMPO^+] = -\frac{I_c}{I°_a} * 3\ mM \tag{S2}$$

The resulting CSCA and concentration time course from this experiment is shown in Fig. 1 of the manuscript.

In a separate experiment, LSV/RDE traces of 3 mM TEMPO and the same solution after mixing 20 min in the presence of HCl and HNO_3 under air were also collected (Fig. S2). These traces show that the cathodic and anodic plateau currents are proportional to the concentrations of TEMPO and $TEMPO^+$ present in the electrolyte.

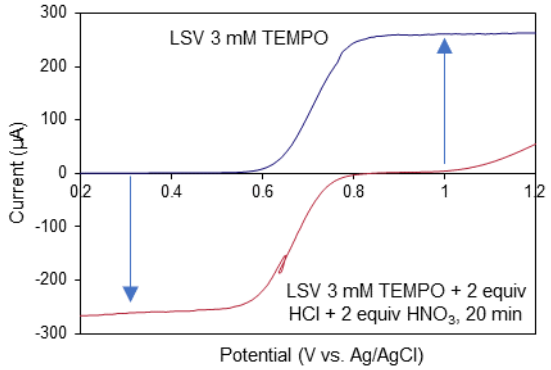


Figure S2. LSV of 3 mM TEMPO (blue) and LSV of a solution of 3 mM TEMPO, 6 mM HCl, and 6 mM HNO_3 after 20 min under air (red). Scan rate = 50 mV/s, rotation rate = 1000 RPM, 0.1 M NBu_4PF_6 CH_3CN.

3b. TEMPO/$Fe(NO_3)_3$ $9H_2O$

Electrochemistry of $Fe(NO_3)_3$ $9H_2O$

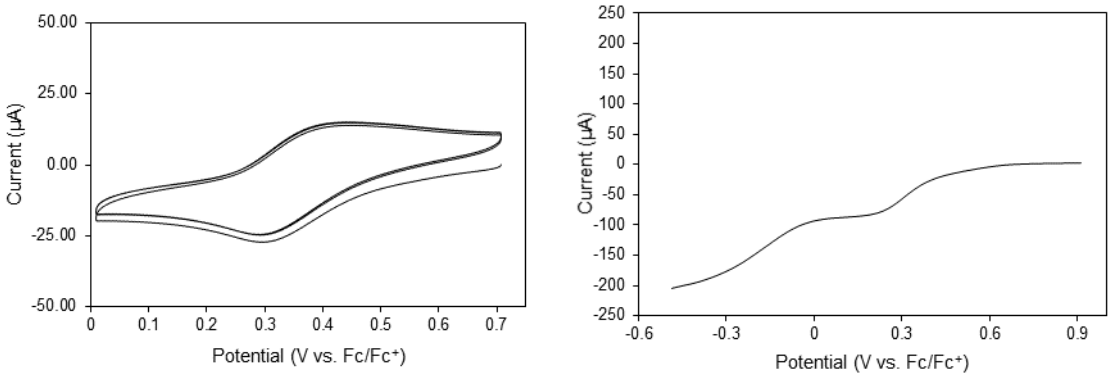


Figure S3. Left: CV of 3 mM $Fe(NO_3)_3 \cdot 9H_2O$ in in 0.1 M NBu_4PF_6 CH_3CN. Scan rate = 200 mV/s. Right: LSV of 6 mM $Fe(NO_3)_3$ $9H_2O$ in 0.1 M NBu_4PF_6 CH_3CN. Scan rate = 50 mV/s, rotation rate = 1000 RPM.

CSCA protocol for TEMPO/$Fe(NO_3)_3 \cdot 9H_2O$

A typical protocol for obtaining the CSCA data and associated time course of TEMPO speciation in the presence of various MX_n additives (cf. Figs. 2 and 3 in the manuscript) is exemplified by the analysis of a solution containing a 1:1 ratio of TEMPO:$Fe(NO_3)_3 \cdot 9H_2O$. To an electrolysis cell mounted in the BASi RDE-2 cell stand is added 5.5 mL TEMPO solution (6 mM) in supporting electrolyte (0.1 M NBu_4PF_6, CH_3CN) under ambient air. The working electrode was set to rotate at 1000 RPM and the CSCA method was then initiated with an anodic potential of +0.64/–0.16 V vs. $Fc/Fc^{+/0}$. The CSCA response of the 6 mM TEMPO solution is monitored for 1 min. This allows the limiting anodic current for a 6 mM solution of TEMPO, $I°_a$, to be established. After ca. 1 min, 5.5 mL of a $Fe(NO_3)_3 \cdot 9H_2O$ solution (6 mM) in supporting electrolyte (0.1 M NBu_4PF_6, CH_3CN) was quickly added via syringe. Fast addition of this solution facilitates mixing of TEMPO and $Fe(NO_3)_3 \cdot 9H_2O$ solutions. The 6 mM $Fe(NO_3)_3 \cdot 9H_2O$ solution was prepared by sonicating $Fe(NO_3)_3 \cdot 9H_2O$ in supporting electrolyte for ca. 1 min. The CSCA experiment was continued for at least 11 min.

The CSCA experiment was then repeated adding 5.5 mL of the 6 mM $Fe(NO_3)_3 \bullet 9H_2O$ solution in electrolyte first, followed by addition of 5.5 mL TEMPO (6 mM, in electrolyte) after 1 min of analysis. By repeating the experiment, the limiting cathodic current, $I°_c$, (from reduction of soluble Fe^{III} species) for a 6 mM solution of $Fe(NO_3)_3 \cdot 9H_2O$ in supporting electrolyte can be determined. Additionally, $I°_a$ and $I°_c$ can be determined from the currents measured during a linear sweep voltammetry experiment of the 6 mM TEMPO or $Fe(NO_3)_3 \cdot 9H_2O$ solutions. After the CSCA experiment was concluded, a cyclic voltammogram of a solution of Fc in 0.1 NBu_4PF_6, CH_3CN was collected.

A time course of [TEMPO] and [$TEMPO^+$] in the presence of $Fe(NO_3)_3 \cdot 9H_2O$ was determined using the limiting anodic and cathodic currents measured during the CSCA experiment. The limiting anodic current measured after TEMPO and $Fe(NO_3)_3 \cdot 9H_2O$ have been mixed, I_a, is taken as the median current value measured during the 5 s step period at the anodic potential. This current can be related to [TEMPO] by eq S3, which takes into account the dilution of the TEMPO stock solution upon addition of the $Fe(NO_3)_3 \cdot 9H_2O$ stock solution. The limiting cathodic current measured after TEMPO and $Fe(NO_3)_3 \cdot 9H_2O$ have been mixed, I_c, is taken as the median current value measured during the 5 s step period at the anodic potential. This

current can be related to [TEMPO$^+$] by eq S4, which takes into account the dilution of the TEMPO stock solution upon addition of the $Fe(NO_3)_3 \cdot 9H_2O$ stock solution *and* the background cathodic current due to the presence of $Fe(NO_3)_3 \cdot 9H_2O$.

$$[TEMPO] = \frac{I_a}{(0.5 * I°_a)} * 3\ mM \tag{S3}$$

$$[TEMPO^+] = -\frac{I_c - (0.5 * I°_c)}{(0.5 * I°_a)} * 3\ mM \tag{S4}$$

For [TEMPO] and [TEMPO$^+$] time courses presented in Figures 2 and 3 in the manuscript, the time axes have been adjusted so that t = 0 s corresponds to addition of the stock solution to the electrochemical cell.

The above protocol was repeated for solutions of TEMPO in the presence of various additives.

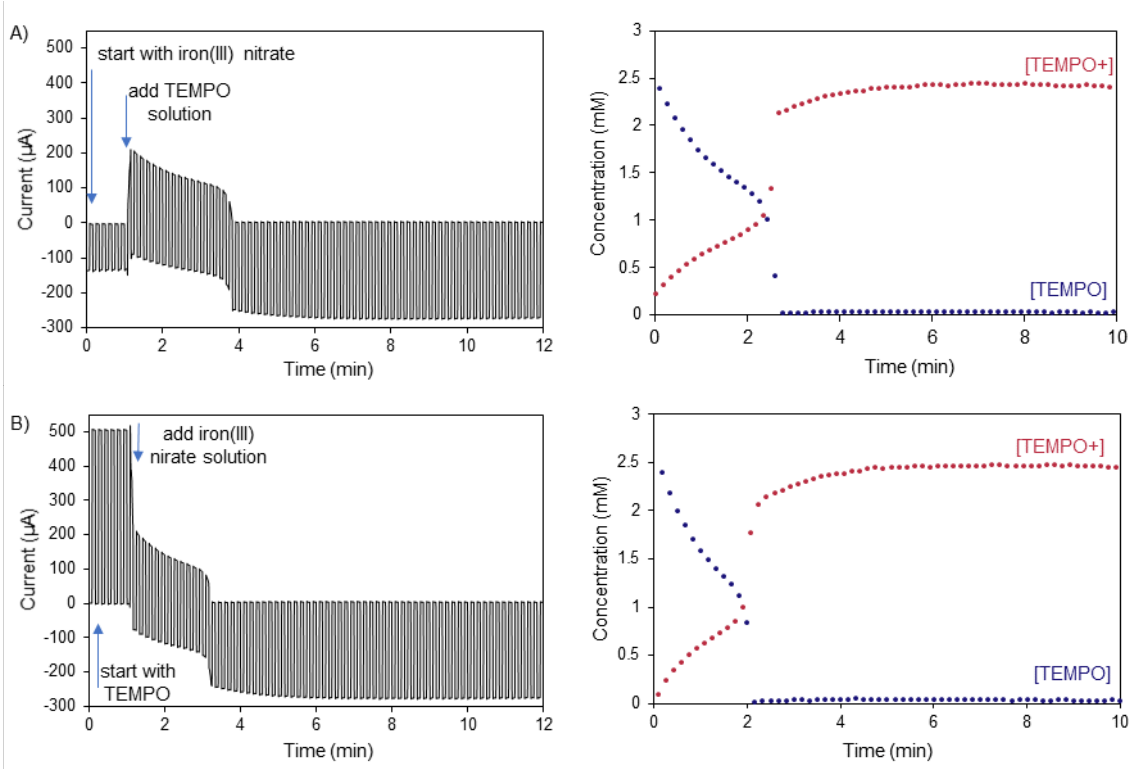


Figure S4. CSCA experiments to analyze a 1:1 solution of TEMPO:$Fe(NO_3)_3 \cdot 9H_2O$. A) Left, CSCA data for a solution of 6 mM $Fe(NO_3)_3 \cdot 9H_2O$ with addition of a solution of 6 mM TEMPO at 1 min. The limiting cathodic current prior to addition of TEMPO is –135 μA. Right, associated [TEMPO] and [TEMPO$^+$] time course derived from the CSCA data. B) Left, CSCA data for a solution of 6 mM TEMPO followed by addition of a solution of 6 mM mM $Fe(NO_3)_3 \cdot 9H_2O$. Right, associated [TEMPO] and [TEMPO$^+$] time course derived from the CSCA data. The limiting anodic current prior to addition of $Fe(NO_3)_3 \cdot 9H_2O$ is +505 μA. The applied anodic and cathodic potentials are +0.64/–0.16 V vs. Fc/Fc^+, respectively.

3c. TEMPO/Al(OTf)$_3$

To determine if Lewis acid-promoted TEMPO disproportionation could be observed using the CSCA protocol, we monitored the CSCA response of TEMPO in the presence of $Al(OTf)_3$ following the protocol for CSCA analysis of TEMPO/$Fe(NO_3)_3 \cdot 9H_2O$ described above. CSCA (Fig. S5) and UV-vis analysis (Fig. S6) of TEMPO in the presence of $Al(OTf)_3$ suggests TEMPO undergoes rapid and complete disproportionation in the presence of $Al(OTf)_3$. Solutions for UV-vis analysis were prepared in an N_2-purged glovebox and measured in a quartz cuvette with a 1 cm pathlength.

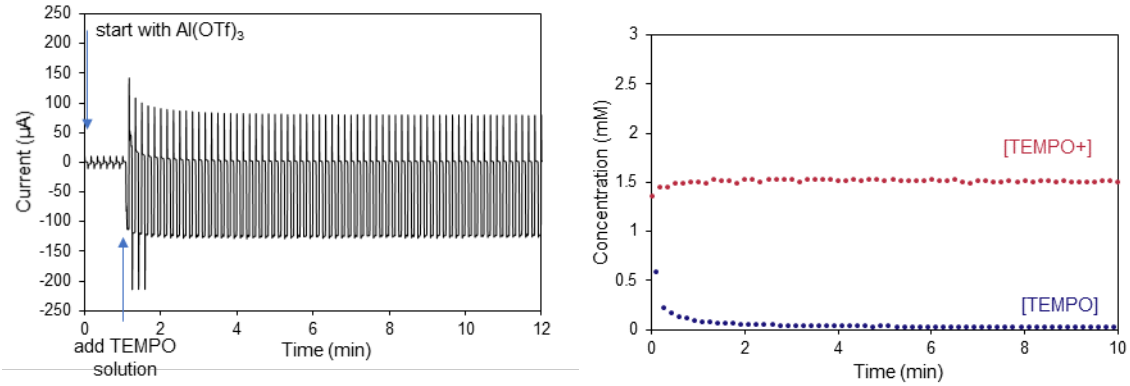


Figure S5. CSCA experiment to analyze a 1:1 solution of TEMPO:$Al(OTF)_3$. Left: CSCA data for the time course of 1 equiv $Al(OTf)_3$ and 1 equiv TEMPO. The CSCA begins with a solution of 6 mM $Al(OTf)_3$ followed by addition of a solution of 6 mM TEMPO. Right, associated [TEMPO], [$TEMPO^+$] time course derived from the CSCA data. The applied anodic and cathodic potentials are +0.66/–0.15 V vs. Fc/Fc^+, respectively. The anodic potential of the 6 mM TEMPO stock solution for this experiment was measured at +491 μA.

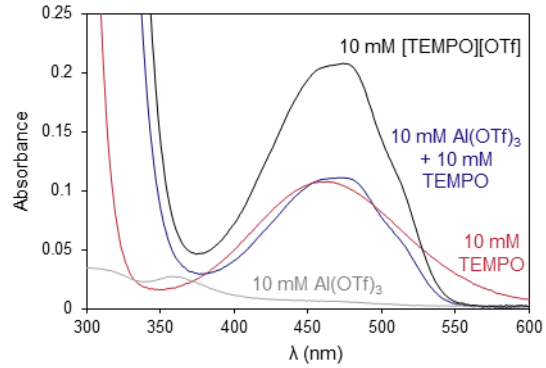


Figure S6. UV-vis absorbance spectra of 10 mM $Al(OTf)_3$ (gray), 10 mM TEMPO (blue), 10 mM TEMPO[OTf], and the spectrum recorded upon mixing 10 mM $Al(OTf)_3$ and 10 mM TEMPO (red) in CH_3CN.

3d. TEMPO/$Zn(NO_3)_2{\cdot}6H_2O$ and TEMPO/$Al(OTf)_3$, NBu_4NO_3

The CSCA protocol was used to examine the reaction of TEMPO with other metal nitrate salts. Zinc nitrate is a redox inactive metal nitrate salt. Under the CSCA analysis conditions, no significant consumption of TEMPO or formation of $TEMPO^+$ was observed in the presence of $Zn(NO_3)_2$ (Fig. S7).

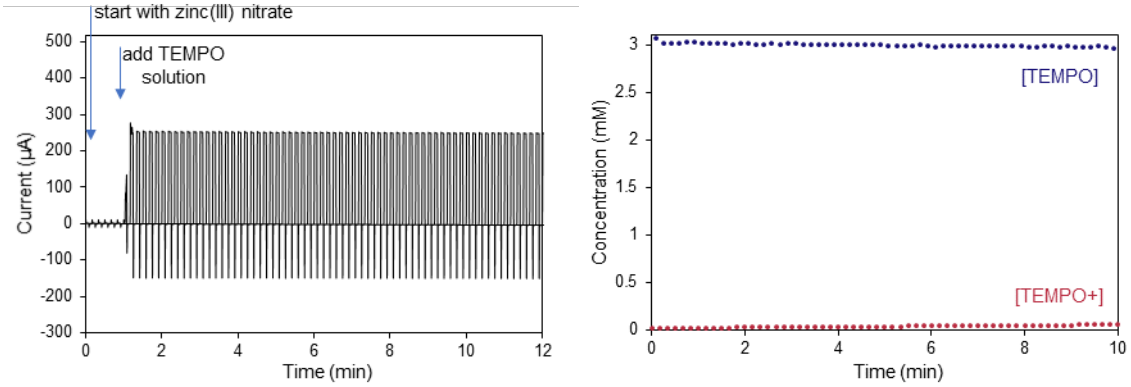


Figure S7. CSCA experiment to analyze a 1:1 solution of TEMPO:$Zn(NO_3)_2{\cdot}6H_2O$. Left: CSCA data for the time course of 1 equiv $Zn(NO_3)_2{\cdot}6H_2O$ and 1 equiv TEMPO. The CSCA begins with 6 mM $Zn(NO_3)_2{\cdot}6H_2O$ followed by addition of a solution of 6 mM TEMPO. Right: Right, associated [TEMPO], [$TEMPO^+$] time course derived from the CSCA data. The applied anodic and cathodic potentials are 0.66/–0.15 V vs. Fc/Fc^+, respectively. The anodic potential of the 6 mM TEMPO stock solution for this experiment was measured at +500 μA.

Aluminum(III) nitrate was not soluble in the CH_3CN electrolyte. Instead, the CSCA protocol was used to analyze a solution of TEMPO in the presence of 1 equivalent of $Al(OTf)_3$ with 3 equivalents of NBu_4NO_3. CSCA analysis (Fig. S8) of this solution suggests TEMPO undergoes slow and incomplete disproportionation in the presence of $Al(OTf)_3$ and NBu_4NO_3 under the time scale of the experiment.

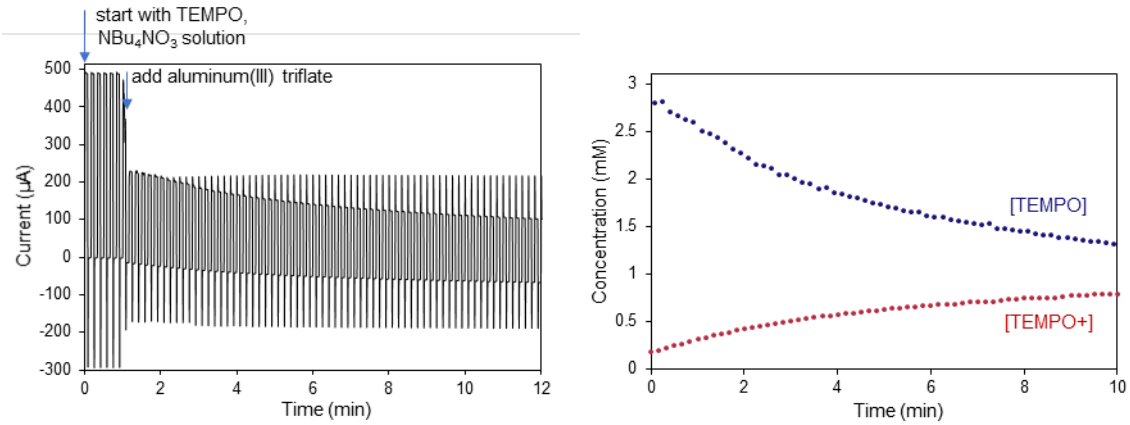


Figure S8. CSCA experiment to analyze a 1:1:3 solution of TEMPO:$Al(OTf)_3$:NBu_4NO_3. Left: CSCA data for the time course of 1 equiv $Al(OTf)_3$, 3 equiv. NBu_4NO_3 and 1 equiv TEMPO. The CSCA begins with a solution of 6 mM TEMPO and 18 mM NBu_4NO_3 followed by addition of a solution of 6 mM $Al(OTf)_3$. Right: associated [TEMPO], [$TEMPO^+$] time course derived from the CSCA data. The applied anodic and cathodic potentials are +0.66/–0.15 V vs. Fc/Fc^+, respectively. The anodic potential of the 6 mM TEMPO stock solution for this experiment was measured at +495 μA.

3e. TEMPO/Fe(OTf)$_3$

The CSCA protocol was used to examine the reaction of TEMPO with other iron(III) species. The CSCA protocol was attempted with iron(III) triflate. At the potentials examined, iron(III) triflate is electrochemically active. Unlike iron(III) nitrate, however, the limiting currents measured for a solution of 6 mM iron(III) triflate under the same CSCA analysis conditions change over time (cf. Fig. S9, 0-3 min). The background current arising from iron(III) triflate at both the anodic and cathodic steps was taken as the median currents measured in the two CSCA steps immediately prior to addition of the TEMPO solution.

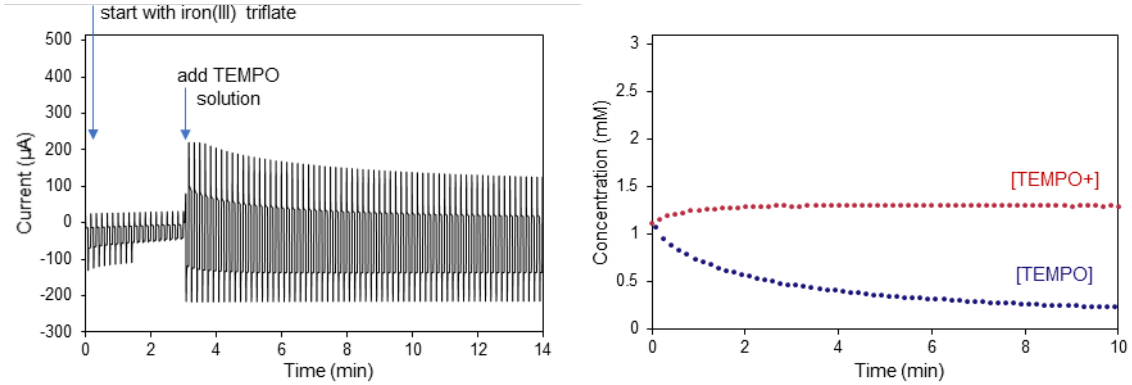


Figure S9. CSCA experiment to analyze a 1:1 solution of TEMPO:Fe(OTf)$_3$. Left: CSCA data for the time course of 1 equiv Fe(OTf)$_3$ and 1 equiv TEMPO. The CSCA begins with 6 mM Fe(OTf)$_3$ followed by addition of a solution of 6 mM TEMPO at ca. 3 min. Right: associated [TEMPO], [TEMPO$^+$] time course derived from the CSCA data. The applied anodic and cathodic potentials are +0.66/–0.15 V vs. Fc/Fc$^+$, respectively. The anodic potential of the 6 mM TEMPO stock solution for this experiment was measured at +537 μA. Prior to addition of the 6 mM TEMPO solution, the measured median current for the 6 mM Fe(OTf)$_3$ solution during the anodic step and cathodic step was –6 μA and –42 μA, respectively.

4. Gas Uptake Protocol

The gas uptake apparatus have been described previously.[1] Reactions were carried out in heavy-walled glass microwave tubes (10 mL volume) with 15 mm oval stir bars. The tubes were capped with a gas-tight manifold containing a gas/vacuum inlet, pressure transducer (Omega Engineering), septum cap, and pressure release valve. The gas vacuum inlet was attached by a T-junction to a diaphragm vacuum pump and a tank of O_2 gas. The individual reactors were placed in an aluminum heating block placed on top of an IKA multi stir plate. The reactor pressure was monitored using a Python based software with RasberriPi centric hardware.

Protocol for gas uptake kinetics of the TEMPO/iron(III) nitrate system

The gas uptake reactor was preheated to 35 °C (minimum stable temperature accessible due to heating effects of the stir plate). To a heavy-walled glass test tube was added a stir bar, 0.05 mmol $Fe(NO_3)_3$ $9H_2O$, 0.05 mmol KCl, and 0.8 mL 1,2-dichloroethane. An evacuation/refill cycle was performed to place the reactor under an O_2 atmosphere of 17 psi. The reactor was then sealed, and the monitored pressure was allowed to stabilize (ca. 25 min). After the pressure stabilized, 0.1 mL of a stock solution of TEMPO in 1,2-dichloroethane (50 mM) was added. After 5 min, 0.1 mL of a stock solution containing substrate (cyclohexanol or cyclohexanemethanol, 1 M) in 1,2-dichloroethane was added. The change in pressure within the reactor was monitored for 20 h. The pressure in an additional reactor containing 1 mL 1,2-dichloroethane was also monitored during the experiment. After the experiment was concluded, the reactors were cooled to ambient temperature. Bromobenzene (8 μL) was added to each reaction solution, which were then diluted with CH_3CN, filtered through a short silica plug, and analyzed by gas chromatography.

Yields of ketone/aldehyde product and recovered starting material were determined compared to the bromobenzene standard.

Protocol for gas uptake kinetics of the TEMPO/Cu(I) system
The gas uptake reactor was preheated to 35 °C (minimum stable temperature accessible due to heating effects of the attached stir plate). To a heavy-walled glass microwave tube was added a stir bar, 0.1 mmol cyclohexanol (or cyclohexanemethanol), and 0.9 mL CH_3CN. An evacuation/refill cycle was performed to place the reactor under an O_2 atmosphere of 17 psi. The reactor was then sealed, and the monitored pressure was allowed to stabilize (ca. 25 min). After the pressure stabilized, 0.1 mL of a freshly prepared stock solution containing 50 mM TEMPO, 50 mM $[Cu(CH_3CN)_4]BF_4$, 50 mM 2,2'-bpy, 100 mM 1-methylimidazole in CH_3CN was added. The change in pressure within the reactor was monitored for 20 h. The pressure in an additional reactor containing 1 mL CH_3CN was also monitored during the experiment. After the experiment was concluded, the reactors were cooled to ambient temperature. Bromobenzene (8 µL) was added to each reaction solution, which were then diluted with CH_3CN, filtered through a short silica plug, and analyzed by gas chromatography. Yields of ketone/aldehyde product and recovered starting material were determined compared to the bromobenzene standard.

The pressure traces shown in Fig. 4 of the manuscript were worked up as follows:
The pressure measured in the reactor containing only solvent was subtracted from the pressure traces of the reactors containing corresponding reactions. The measured absolute pressure values were then converted to the change of O_2 pressure in µmol O_2 (as determined by the ideal gas law).

Gas Chromatography (GC) Time Course of TEMPO/iron(III) nitrate system

TEMPO (0.01 mmol), $Fe(NO_3)_3$ $9H_2O$ (0.01 mmol), and KCl (0.01 mmol) were added to a 1.5-dram vial with a stir bar. To the vial was added $C_2H_4Cl_2$ (0.5 mL). The vial was capped with a septum, which was then pierced with a needle attached to a balloon of O_2. The solution was stirred under O_2 for 5 min, after which 0.5 mL of a stock solution containing 0.2 M cyclohexanol or cyclohexanemethanol (0.1 mmol) and 0.1 M PhBr (0.05 mmol) was added. At given times, 40 µL aliquots of the reaction solution were withdrawn, filtered through a short plug of SiO_2 with added CH_3CN, and analyzed by GC. Conditions: 70 °C, hold 1 min, then 70 °C to 200 °C, 20 deg/min. Retention times: PhBr, 4.3 min; cyclohexanol, 4.6 min; cyclohexanone, 3.9 min; cyclohexanemethanol, 5.6 min; cyclohexane carboxaldehyde, 3.75 min.

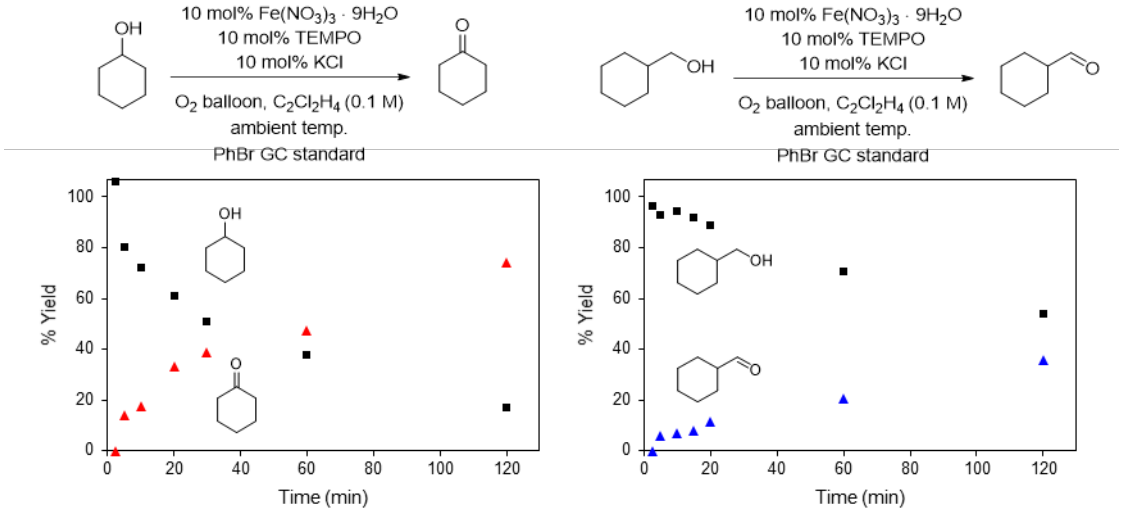
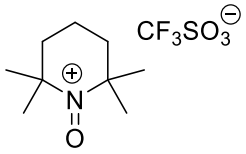


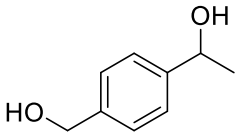
Figure S10. Time courses for the iron(III) nitrate/TEMPO-catalyzed aerobic oxidation of cyclohexanol and cyclohexanemethanol. Monitored by GC with PhBr internal standard.

5. Synthesis of [TEMPO]CF_3SO_3



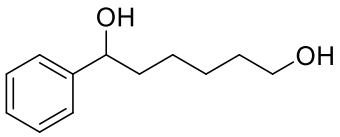
Synthesis of 2,2,6,6-tetramethylpiperidin-1-oxoammonium trifluoromethane sulfonate (TEMPO$^+$ OTf).[3] To a stirred solution of TEMPO (917 mg, 5.9 mmol) in diethyl ether (3 mL) cooled to 0 °C, was added trifluoromethane sulfonic acid (0.5 mL, 5.7 mmol) dropwise. After stirring for 15 min, commercial bleach (4 mL) was added dropwise. The reaction was allowed to stir for an additional 30 min at 0 °C. The orange-yellow precipitate was then collected via vacuum filtration and washed with 5% $NaHCO_3$ (2 mL), H_2O (2 mL), and diethyl ether (10 mL). All washing solutions were chilled in a 0 °C ice bath before washing the orange-yellow precipitate. After washing, the orange-yellow solid (260 mg) was dried under vacuum. Anal. Calcd. For $C_{10}H_{18}F_3NO_4S$▪$0.2H_2O$ C, 38.9; H, 6.00; N, 4.53. Found: C, 38.80; H, 5.86; N, 4.51.

6. Synthesis of Alcohol Substrates



Synthesis of 4-(1'-hydroxyethyl)benzyl alcohol (1).[4] To an oven dried 250 mL round bottom flask, 1.0 g (26 mmol) of $LiAlH_4$ were added under N_2. Dry THF (50 mL) was added and the flask was cooled to 0 °C. To an oven dried 100 mL round bottom flask was added 0.89 g (5 mmol) methyl-4-acetylbenzoate. The flask was placed under an N_2 atmosphere and 30 mL dry THF was added. The flask containing substrate was cooled to 0 °C. The solution of substrate was then transferred dropwise to the flask containing the $LiAlH_4$ suspension via cannula. The reaction was then allowed to warm to room temperature overnight. The reaction was quenched by sequential slow addition of 50 mL EtOAc, 1 mL H_2O, 1 mL 0.1 M $NaOH_{(aq)}$ at 0 °C and then 3 mL H_2O at ambient temperature. The resulting white solids were removed via filtration and the filtrate was transferred to a separatory funnel containing 50 mL H_2O. The aqueous layer was extracted with 3x50 mL EtOAc. The organic layers were combined, dried over $MgSO_4$, filtered, and dried *in vacuo*. The diol product was further purified by flash column chromatography (2:1 EtOAc:Pentane) to give a white solid. Yield 0.486 g (64% yield).

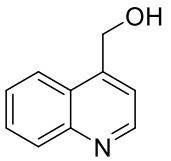
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 5H), 4.90 (q, J = 6.4 Hz, 1H), 4.68 (s, 2H), 1.89 (bs, 1H), 1.77 (bs, 1H), 1.49 (d, J = 6.3 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 145.29, 140.11, 127.20, 125.62, 70.18, 65.10, 25.21. Spectral properties are consistent with literature values.[4]



Synthesis of 1-phenylhexane-1,6 diol (5).[4] To an oven dried 250 mL round bottom flask, 1.0 g (26 mmol) of $LiAlH_4$ were added under N_2. Dry THF (50 mL) was added and the flask was cooled to 0 °C. To an oven dried 100 mL round bottom flask was added 1.0 g (4.8 mmol) 5-benzoylpentanoic acid. The flask was placed under an N_2 atmosphere and 30 mL dry THF was added. The flask containing substrate was cooled to 0 °C. The solution of substrate was then transferred dropwise to the flask containing the $LiAlH_4$ suspension via cannula. The reaction was then allowed to warm to room temperature overnight. The reaction was quenched by sequential slow addition of 50 mL EtOAc, 1 mL H_2O, 1 mL 0.1 M $NaOH_{(aq)}$ at

0 °C and then 3 mL H_2O at ambient temperature. The resulting white solids were removed via filtration and the filtrate was transferred to a separatory funnel containing 50 mL H_2O. The aqueous layer was extracted with 3x30 mL EtOAc. The organic layers were combined, dried over $MgSO_4$, filtered, and dried *in vacuo*. The diol product was further purified by flash column chromatography (1-5% MeOH in CH_2Cl_2) to give a white solid. Yield 0.842 g (90% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 5.5 Hz, 4H), 7.30 – 7.25 (m, 1H), 4.66 (t, *J* = 6.7 Hz, 1H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.03 (bs, 1H), 1.81 (m, 1H), 1.71 (m, 1H), 1.55 (p, *J* = 6.8 Hz, 2H), 1.49 – 1.26 (m, 5H).^{13}C NMR (126 MHz, $CDCl_3$) δ 144.98, 128.58, 127.65, 126.00, 74.67, 62.97, 39.12, 32.73, 25.75, 25.70. Spectral properties are consistent with literature values.[4]



Synthesis of 4-quinoylmethanol (9).[5] To a 100 mL round bottom flask was added 1.572 g (10 mmol) 4-quinoline carboxaldehyde and 40 mL MeOH. To a stirred solution of substrate was added 0.431 g (11.4 mmol) $NaBH_4$ portion-wise over 20 min. The solution was allowed to stir overnight, after which the reaction solution was poured into a separatory funnel containing 100 mL saturated $NH_4Cl_{(aq)}$ solution. The aqueous layer was extracted with 3x50 mL EtOAc. The organic layers were combined, dried over $MgSO_4$, filtered, and dried *in vacuo*. The product was further purified by flash column chromatography (2-10% MeOH in CH_2Cl_2) to give a white solid. Yield 1.241 g 78% yield).

^{1}H NMR (500 MHz, DMSO) δ 8.87 (d, *J* = 4.3 Hz, 1H), 8.04 (t, *J* = 8.2 Hz, 2H), 7.79 – 7.72 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 (d, *J* = 4.3 Hz, 1H), 5.57 (t, *J* = 5.5 Hz, 1H), 5.04 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.40, 147.63, 147.30, 129.47, 129.03, 126.32, 125.43, 123.49, 118.01, 59.63. HRMS (ESI) exact mass calculated for [M+H]+ ($C_{10}H_{10}NO$) requires m/z 160.0757, found m/z 160.0756, difference 0.6 ppm.

7. NMR Yields (0.1 mmol Scale) for Oxidation of 1 and 5

The aerobic oxidation of **1** and **5** by the various TEMPO/co-catalyst systems was first examined at small scale (0.1 mmol) to determine trends in the chemoselectivity. The reaction times and NMR yields for the oxidation of **1** and **5** are reported in Table S1 and Table S2, respectively.

Oxidation of 4-(1'-hydroxyethyl)benzyl alcohol (1, 0.1 mmol) by TEMPO/Cu:
TEMPO (0.005 mmol), $[Cu(CH_3CN)_4]BF_4$ (0.005 mmol), 2,2'-dipyridyl (bpy) (0.005 mmol), and *N*-methyl imidazole (0.01 mmol) were added to a 1.5-dram vial with a stir bar. To the vial was added CH_3CN (1 mL) and **1** (0.1 mmol). The vial was capped with a septum which was pierced with an 18-gauge needle. The reaction was stirred rapidly open to air and was followed by TLC. The reaction was diluted with CH_3CN and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

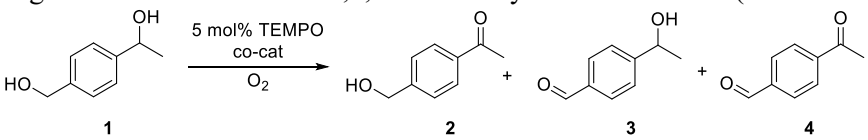
Oxidation of 4-(1'-hydroxyethyl)benzyl alcohol (1, 0.1 mmol) by TEMPO/iron(III) nitrate in CH_3CN:
TEMPO (0.005 mmol) and $Fe(NO_3)_3$ $9H_2O$ (0.005 mmol) were added to a 1.5-dram vial with a stir bar. To the vial was added CH_3CN (1 mL). The solution was stirred rapidly open to air for 5 min, after which **1** (0.1 mmol) was added. The vial was capped with a septum which was pierced with an 18-gauge needle. The reaction was stirred rapidly open to air and was followed by TLC. The reaction was diluted with CH_3CN

and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

Oxidation of 4-(1'-hydroxyethyl)benzyl alcohol (1, 0.1 mmol) by TEMPO/iron(III) nitrate in $C_2H_4Cl_2$: TEMPO (0.005 mmol), $Fe(NO_3)_3$ $9H_2O$ (0.005 mmol), and KCl (0.005mmol) were added to a 1.5-dram vial with a stir bar. To the vial was added $C_2H_4Cl_2$ (1 mL). The solution was stirred rapidly open to air for 5 min, after which **1** (0.1 mmol) was added. The vial was capped with a septum which was pierced with an 18-gauge needle. The reaction was stirred rapidly open to air and was followed by TLC. The reaction was diluted with CH_3CN and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

Oxidation of 4-(1'-hydroxyethyl)benzyl alcohol (1, 0.1 mmol) by TEMPO/NO_x:
TEMPO (0.005 mmol) and $NaNO_2$ (0.01 mmol) were added to a 1.5-dram vial with a stir bar. To the vial was added CH_3CN (1 mL), **1** (0.1 mmol), and then HNO_3 (0.02 mmol). The vial was capped with a septum which was pierced with an 18-gauge needle. The reaction was stirred rapidly open to air and was followed by TLC. The reaction was diluted with CH_3CN and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

Table S1. NMR yields for aerobic oxidation of **1** (0.1 mmol) by TEMPO/cocatalyst systems. Yields determined by integration values relative to 1,3,5-trimethoxybenzene standard (relaxation time =25 sec).



Co-Catalyst	Reaction Time (h)	Mass Balance (%)	**1** (RSM) (% Yield)	**2** (Ketone) (% Yield)	**3** (Ald) (% Yield)	**4** (Ald/Ket) (% Yield)
[Cu]	2	93	<1	<1	**77**	16
$[Fe(NO_3)_3]$, CH_3CN	6	105	31	28	**41**	5
$[Fe(NO_3)_3]$, $C_2H_4Cl_2$	6	91	43	15	**30**	3
NO_x	6	95	32	23	**35**	5

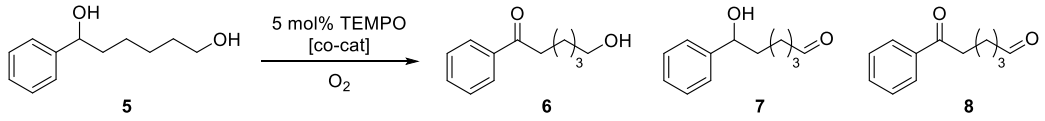
Oxidation of 1-phenylhexane-1,6 diol (5, 0.1 mmol) by TEMPO/Cu:
TEMPO (0.005 mmol), CuBr (0.005 mmol), 2,2'-dipyridyl (0.005 mmol), and **5** (0.1 mmol) were added to a 20 mm culture tube with a stir bar. To the vial was added CH_3CN (1 mL) and *N*-methyl imidazole (0.01 mmol). The reaction was stirred rapidly open to air and was followed by TLC. The reaction was diluted with diethyl ether and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

Oxidation of 1-phenylhexane-1,6 diol (5, 0.1 mmol) by TEMPO/iron(III) nitrate in CH_3CN:
TEMPO (0.005 mmol) and $Fe(NO_3)_3$•$9H_2O$ (0.005 mmol) were added to a 20 mm culture tube with a stir bar. To the tube was added CH_3CN (0.5 mL). The solution was stirred rapidly open to air for 5 min, after which **5** (0.1 mmol) and an additional 0.5 mL CH_3CN was added. The culture tube was capped with an O_2 balloon. The reaction was stirred rapidly and was followed by TLC. The reaction was diluted with diethyl ether and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

Oxidation of 1-phenylhexane-1,6 diol (5, 0.1 mmol) by TEMPO/iron(III) nitrate in $C_2H_4Cl_2$:
TEMPO (0.005 mmol), $Fe(NO_3)_3 \bullet 9H_2O$ (0.005 mmol), and KCl (0.005mmol) were added to a 20 mm culture tube with a stir bar. To the tube was added $C_2H_4Cl_2$ (0.5 mL). The solution was stirred rapidly open to air for 5 min, after which **5** (0.1 mmol) and $C_2H_4Cl_2$ (0.5 mL) was added. The culture tube was capped with an O_2 balloon. The reaction was stirred rapidly and was followed by TLC. The reaction was diluted with diethyl ether and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

Oxidation of 1-phenylhexane-1,6 diol (5, 0.1 mmol) by TEMPO/NO_x:
TEMPO (0.005 mmol), $NaNO_2$ (0.01 mmol), and **5** (0.1 mmol) were added to a 20 mm culture tube with a stir bar. To the vial was added 0.02 M HNO_3 in CH_3CN (1 mL). The culture tube was capped with an O_2 balloon. The reaction was stirred rapidly and was followed by TLC. The reaction was diluted with diethyl ether and passed through a silica plug. To the filtrate was added 1,3,5-trimethoxybenzene. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

Table S2. NMR yields for the oxidation of **5** (4-(1'-hydroxyethyl)benzyl alcohol) (0.1 mmol) by TEMPO/cocatalyst systems. Yields determined by integration values relative to 1,3,5-trimethoxybenzene standard (relaxation delay = 25 s).



Co-Catalyst	Reaction Time (h)	Mass Balance (%)	**5** (RSM) (% Yield)	**6** (Ketone) (% Yield)	**7** (Ald) (% Yield)	**8** (Ald/Ket) (% Yield)
[Cu]	3	88	13	4	**59**	12
$[Fe(NO_3)_3]$, CH_3CN	24	90	37	**49**	2	2
$[Fe(NO_3)_3]$, $C_2H_4Cl_2$	24	93	67	**20**	4	2
NO_x	24	99	28	**62**	4	5

8. Alcohol Oxidation Protocols

Oxidation of 4-(1'-hydroxyethyl)benzyl alcohol (1) by TEMPO/Cu:[4]
To a solution of **1** (152 mg, 1 mmol) in CH_3CN (2 mL) in a 20 mm culture tube were added sequentially $[Cu(CH_3CN)_4]BF_4$ (15.7 mg, 0.05 mmol), TEMPO (7.6 mg, 0.05 mmol), 2,2'-dipyridyl (7.8 mg, 0.05 mmol) with 1 mL CH_3CN added after each reagent (5 mL CH_3CN total). *N*-methyl imidazole (8 µL, 0.1 mmol) was immediately added via Hamilton syringe. The solution was stirred rapidly open to air at ambient temperature and was followed by TLC. In order to monitor the chemoselectivity of this oxidation, the reaction was quenched before **1** was fully consumed. After 1 h, the reaction mixture was diluted with 20 mL of diethyl ether and filtered through a short silica plug and rinsed with additional diethyl ether. The solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR spectroscopy with a 25 s relaxation delay in $CDCl_3$ to determine the relative quantity of **1** and oxidation products. The observed ratio of **1**:**2**:**3**:**4** was 34:1:65:1. The residue was then purified by flash column chromatography (30% EtOAc in pentane) to give 89.3 mg of **3** (aldehyde) (60% yield).

Oxidation of 4-(1'-hydroxyethyl)benzyl alcohol (1) by TEMPO/iron(III) nitrate in CH_3CN:[6]

To a 20 mm culture tube, $Fe(NO_3)_3 \bullet 9H_2O$ (20.1 mg, 0.05 mmol) and TEMPO (7.7 mg, 0.05 mmol) were added with CH_3CN (4 mL). The solution was stirred rapidly open to air at ambient temperature for 5 min, after which **1** (152 mg, 1 mmol) was added followed by an additional 1 mL of CH_3CN (5 mL total). The reaction was followed by TLC. After 8 h, the reaction mixture was diluted with 20 mL of diethyl ether and filtered through a short silica plug and rinsed with additional diethyl ether. The solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR spectroscopy with a 25 s relaxation delay in $CDCl_3$ to determine the relative quantity of **1** and oxidation products. The observed ratio of **1**:**2**:**3**:**4** was 1:31:52:17. The residue was then purified by flash column chromatography (20-50% EtOAc in pentane gradient) to give 43.5 mg of **2** (ketone) (29% yield) and 73.6 mg of **3** (aldehyde) (49% yield).

Oxidation of 4-(1'-hydroxyethyl)benzyl alcohol (1) by TEMPO/NO_x:[7]
To a 20 mm culture tube, **1** (152 mg, 1 mmol), TEMPO (7.9 mg, 0.05 mmol), and $NaNO_2$ (6.8 mg, 0.1 mmol) were added followed by CH_3CN (5 mL). Nitric acid (12.6 µL, 0.2 mmol) was added and the reaction was stirred rapidly open to air at ambient temperature and was followed by TLC. After 8 h, the solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR spectroscopy with a 25 s relaxation delay in $CDCl_3$ to determine the relative quantity of **1** and oxidation products. The observed ratio of **1**:**2**:**3**:**4** was 21:29:42:8. The residue was then purified by flash column chromatography (20-50% EtOAc in pentane gradient) to give 38.9 mg of **2** (ketone) (26% yield) and 61.2 mg of **3** (aldehyde) (41% yield).

Oxidation of 1-phenylhexane-1,6 diol (5) by TEMPO/Cu:[4]
To a solution of **5** (195 mg, 1 mmol) in CH_3CN (2 mL) in a 20 mm culture tube were added sequentially CuBr (7.2 mg, 0.05 mmol), TEMPO (7.6 mg, 0.05 mmol), and 2,2'-dipyridyl (7.8 mg, 0.05 mmol) with 1 mL CH_3CN added after each reagent (5 mL CH_3CN total). *N*-methyl imidazole (8 µL, 0.1 mmol) was immediately added via Hamilton syringe. The solution was stirred rapidly open to air at ambient temperature and was followed by TLC. After 3 h, the reaction mixture was diluted with 20 mL of diethyl ether and filtered through a short silica plug and rinsed with additional diethyl ether. The solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR spectroscopy with a 25 s relaxation delay in $CDCl_3$ to determine the relative quantity of **5** and oxidation products. The observed ratio of **5**:**6**:**7**:**8** was 8:5:68:21. The residue was then purified by flash column chromatography (30-100% EtOAc in pentane gradient) to give 108.8 mg of **7** (aldehyde) (56% yield).

Oxidation of 1-phenylhexane-1,6 diol (5) by TEMPO/iron(III) nitrate in CH_3CN:[6]
To a 20 mm culture tube, $Fe(NO_3)_3 \bullet 9H_2O$ (20.0 mg, 0.05 mmol) and TEMPO (7.8 mg, 0.05 mmol) were added with CH_3CN (4 mL). The solution was stirred rapidly open to air at ambient temperature for 5 min, after which **5** (195 mg, 1 mmol) was added followed by an additional 1 mL of CH_3CN (5 mL total). The reaction was capped with a septum and a balloon containing O_2 and was followed by TLC. After 12 h, the reaction mixture was diluted with 20 mL of diethyl ether and filtered through a short silica plug and rinsed with additional diethyl ether. The solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR spectroscopy with a 25 s relaxation delay in $CDCl_3$ to determine the relative quantity of **5** and various oxidation products. The observed ratio of **5**:**6**:**7**:**8** was 36:63:1:1. The residue was then purified by flash column chromatography (30-100% EtOAc in pentane gradient) to give 103 mg of **6** (ketone) (49% yield).

Oxidation of 1-phenylhexane-1,6 diol (5) by TEMPO/NO_x:[7]
To a 20 mm culture tube, **5** (195 mg, 1 mmol), TEMPO (7.7 mg, 0.05 mmol), and $NaNO_2$ (7.1 mg, 0.1 mmol) were added followed by CH_3CN (5 mL). Nitric acid (12.6 µL, 0.2 mmol) was added and the reaction was capped with a septum and a balloon containing O_2. The reaction was stirred rapidly at ambient temperature and was followed by TLC. After 24 h, the solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR spectroscopy with a 25 s relaxation delay in $CDCl_3$ to determine the relative quantity of **5** and oxidation products. The observed ratio of **5**:**6**:**7**:**8** was 60:39:1:1. The residue was then purified by flash column chromatography (30-100% EtOAc in pentane gradient) to give 53.7 mg of **6** (ketone) (28% yield),

Oxidation of 4-quinoylmethanol (9) by TEMPO/Cu:[4]
To a solution of **9** (159 mg, 1 mmol) in CH_3CN (2 mL) in a 20 mm culture tube were added sequentially $[Cu(CH_3CN)_4]BF_4$ (15.6 mg, 0.05 mmol), TEMPO (7.6 mg, 0.05 mmol), and 2,2'-dipyridyl (7.8 mg, 0.05 mmol) with 1 mL CH_3CN added after each reagent (5 mL CH_3CN total). *N*-methyl imidazole (8 µL, 0.1 mmol) was then added via Hamilton syringe. The solution was stirred rapidly open to air at ambient temperature and was followed by TLC. After 3 h, the reaction mixture was diluted with diethyl ether and transferred to a 6-dram vial. The solvent was removed *in vacuo*, and the residue was purified by flash column chromatography (0-10% MeOH in CH_2Cl_2 gradient) to give 138.9 mg of **10** (aldehyde) (88% yield).

Oxidation of 4-quinoylmethanol (9) by TEMPO/iron(III) nitrate in CH_3CN:[6]
To a 20 mm culture tube, $Fe(NO_3)_3 \bullet 9H_2O$ (20.0 mg, 0.05 mmol) and TEMPO (7.8 mg, 0.05 mmol) was added with CH_3CN (4 mL). The solution was stirred rapidly open to air at ambient temperature for 5 min, after which **9** (159 mg, 1 mmol) was added followed by an additional 1 mL of CH_3CN (5 mL total). The reaction was capped with a septum and a balloon containing O_2 and was followed by TLC. After 24 h, no significant oxidation products were observed, and the reaction mixture was diluted with diethyl ether and transferred to a 6-dram vial. The solvent was removed *in vacuo*. The residue was then purified by flash column chromatography (2-10% MeOH in CH_2Cl_2 gradient) to give 128.4 mg of recovered **9** (81% recovery).

Oxidation of 4-quinoylmethanol (9) by TEMPO/iron(III) nitrate in Cl_2C_2H4:[8]
To a 20 mm culture tube, $Fe(NO_3)_3 \bullet 9H_2O$ (20.0 mg, 0.05 mmol), TEMPO (7.8 mg, 0.05 mmol), and KCl (3.9 mg, 0.05 mmol) was added with $C_2H_4Cl_2$ (4 mL). The solution was stirred rapidly open to air at ambient temperature for 5 min, after which **9** (159 mg, 1 mmol) was added followed by an additional 1 mL of $C_2H_4Cl_2$ (5 mL total). The reaction was capped with a septum and a balloon containing O_2 and was followed by TLC. After 24 h, no significant oxidation products were observed, and the reaction mixture was diluted with diethyl ether and transferred to a 6-dram vial. The solvent was removed *in vacuo*. The residue was then purified by flash column chromatography (2-10% MeOH in CH_2Cl_2 gradient) to give 147.9 mg of recovered **9** (93% recovery).

Oxidation of 2-amino benzyl alcohol (11) by TEMPO/Cu:[4]
To a solution of **11** (124 mg, 1 mmol) in CH_3CN (2 mL) in a 20 mm culture tube were added sequentially $[Cu(CH_3CN)_4]BF_4$ (15.7 mg, 0.05 mmol), TEMPO (7.6 mg, 0.05 mmol), 2,2'-dipyridyl (7.8 mg, 0.05 mmol) with 1 mL CH_3CN added after each reagent (5 mL CH_3CN total). *N*-methyl imidazole (8 µL, 0.1 mmol) was immediately added via Hamilton syringe. The solution was stirred rapidly open to air at ambient temperature and was followed by TLC. After 3 h, the reaction mixture was diluted with 20 mL of diethyl ether and filtered through a short silica plug. The solvent was removed *in vacuo* and the residue was then purified by flash column chromatography (20% EtOAc in pentane) to give 113 mg of **12** (aldehyde) (93% yield).

Oxidation of 2-amino benzyl alcohol (11) by TEMPO/iron(III) nitrate in CH_3CN:[6]
To a 20 mm culture tube, $Fe(NO_3)_3 \bullet 9H_2O$ (20.0 mg, 0.05 mmol) and TEMPO (7.8 mg, 0.05 mmol) was added with CH_3CN (4 mL). The solution was stirred rapidly open to air at ambient temperature for 5 min, after which **11** (123 mg, 1 mmol) was added followed by an additional 1 mL of CH_3CN (5 mL total). The reaction was capped with a septum and a balloon containing O_2 and was followed by TLC. After 12 h, the reaction mixture was diluted with 20 mL of diethyl ether and filtered through a short silica plug. The solvent was removed *in vacuo*, and the residue was then purified by flash column chromatography (0-100% EtOAc in pentane gradient) to give 81.9 mg of recovered **11** (67% recovery).

Oxidation of 2-amino benzyl alcohol (11) by TEMPO/iron(III) nitrate in Cl_2C_2H4:[8]
To a 20 mm culture tube, $Fe(NO_3)_3$•$9H_2O$ (20.0 mg, 0.05 mmol), TEMPO (7.8 mg, 0.05 mmol), and KCl (3.9 mg, 0.05 mmol) was added with $C_2H_4Cl_2$ (4 mL). The solution was stirred rapidly open to air at ambient temperature for 5 min, after which **11** (123 mg, 1 mmol) was added followed by an additional 1 mL of $C_2H_4Cl_2$ (5 mL total). The reaction was capped with a septum and a balloon containing O_2 and was followed by TLC. After 24 h, no significant oxidation products were observed, and the reaction mixture was diluted with diethyl ether and transferred to a 6-dram vial. The solvent was removed *in vacuo*. The solvent was removed *in vacuo*, and the residue was then purified by flash column chromatography (0-100% EtOAc in pentane gradient) to give 94.3 mg of recovered **11** (77% recovery).

Oxidation of 4-pentyn-1-ol (13) by TEMPO/Cu:
To a solution of 4-pentyn-1-ol (86 mg, 1 mmol) in CH_3CN (2 mL) in a 20 mm culture tube were added sequentially $[Cu(CH_3CN)_4]BF_4$ (15.7 mg, 0.05 mmol), TEMPO (7.8 mg, 0.05 mmol), and 2,2'-dipyridyl (7.8 mg, 0.05 mmol) with 1 mL CH_3CN added after each reagent (5 mL CH_3CN total). *N*-methyl imidazole (8 μL, 0.1 mmol) was then added via Hamilton syringe. The reaction was capped with a septum and a balloon containing O_2 and was followed by TLC. After 3 h, the reaction mixture was diluted with 20 mL diethyl ether. The solution filtered through a short silica plug. The solvent was removed *in vacuo* at 0 °C, and the unpurified residue was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$, revealing a mixture of 4-pentynal, a dialdehyde product arising from alkyne C–H coupling (confirmed by HRMS), and unreacted starting material in a ratio of ca. 6.5:7.5:1. No acid product is observed. No attempt was made to isolate the product mixture. When the above experiment was repeated under air, **13** underwent conversion. No products derived from **13** could be observed by ^{1}H NMR, however, indicating substrate decomposition, which has been observed previously.[4]

Oxidation of 4-pentyn-1-ol (13) by TEMPO/iron(III) nitrate in Cl_2C_2H4:
To a 20 mm culture tube, $Fe(NO_3)_3$•$9H_2O$ (40.0 mg, 0.1 mmol), TEMPO (15.6 mg, 0.1 mmol), and KCl (6 mg, 0.1 mmol) was added with $C_2H_4Cl_2$ (4 mL). The solution was stirred rapidly open to air at ambient temperature for 5 min, after which 4-pentyn-1-ol **13** (95 μL, 1 mmol) was added via Hamilton syringe followed by an additional 1 mL of $C_2H_4Cl_2$ (5 mL total). The reaction was capped with a septum and a balloon containing O_2 and was followed by TLC. After 24 h the reaction mixture was diluted with 20 mL diethyl passed through a silica plug. The solvent was removed *in vacuo*. The residue was analyzed by ^{1}H NMR which demonstrated < 5% aldehyde product **14** present relative to the acid product **15**. The residue was purified by flash column chromatography (0-9% MeOH in CH_2Cl_2 gradient) to give 70.3 mg of **15** (72% yield).

9. Chemoselectivity of Related $M(NO_3)_x$ Systems

Variations on the $Fe(NO_3)_3$/TEMPO cocatalyst system for aerobic alcohol oxidation have been reported, including a $Fe(NO_3)_3$/2,2'-bipyridine/TEMPO system in acetic acid[9] and a $Cu(NO_3)_2$/TEMPO system.[10] To complement the studies presented in Fig. 4 of the main text, we examined the chemoselectivity of these systems for aerobic alcohol oxidation.

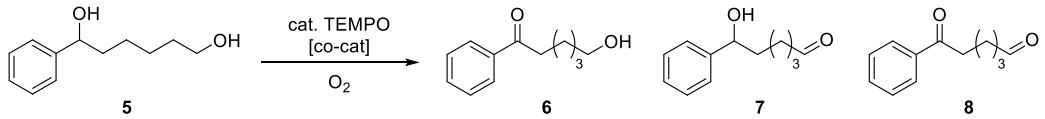
We first examined the aerobic oxidation of **5** under conditions derived from the original reports.[9,10] Results are summarized in Table S3. The TEMPO/$Fe(NO_3)_3$/bpy system showed moderate chemoselectivity for oxidation of the 1° aliphatic alcohol group. The TEMPO/$Cu(NO_3)_2$ system instead showed greater selectivity for oxidation of the 2° benzylic alcohol, albeit with slower overall reactivity.

TEMPO/$Fe(NO_3)_3$/bpy
To a 20 mm culture tube was added TEMPO (0.01 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (0.01 mmol), and 2,2'-bpy (0.01 mmol) with a stir bar. Acetic acid (0.75 mL) was added, and the solution was stirred rapidly (1000 RPM)

open to air for 5 min, after which **5** (0.2 mmol) with an additional 0.25 mL acetic acid to rinse the walls of the tube. The tube was kept open to ambient air during the reaction. After 6 h, the reaction was diluted with ethyl acetate and 1,3,5-trimethoxybenzene was added. The solution was passed through a short silica plug. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR in $CDCl_3$.

TEMPO/Cu(NO$_3$)$_2$
To a 1.5-dram vial was added TEMPO (0.02 mmol), $Cu(NO_3)_2$•2.5(H_2O) (0.02 mmol), and **5** (0.2 mmol) with a stir bar and 1 mL 1,2-dichloroethane or CH_3CN. The vial was capped with a septum pierced with a needle attached to a balloon of O_2. After 24 h, the reaction was diluted with diethyl ether and 1,3,5-trimethoxybenzene was added. The solution was passed through a short silica plug. Solvent was removed *in vacuo* and the residue was analyzed by ^{1}H NMR.

Table S3. NMR yields for the oxidation of **5** (4-(1'-hydroxyethyl)benzyl alcohol) (0.2 mmol) by TEMPO/$Fe(NO_3)_3$/bpy and TEMPO/$Cu(NO_3)_2$ systems. Yields determined by integration values relative to 1,3,5-trimethoxybenzene standard (relaxation delay = 25 s).



Co-Catalyst	Reaction Time (h)	Mass Balance (%)	**5** (RSM) (% Yield)	**6** (Ketone) (% Yield)	**7** (Ald) (% Yield)	**8** (Ald/Ket) (% Yield)
$Cu(NO_3)_2$, CH_3CN	24	87	70	15	2	trace
$Cu(NO_3)_2$, DCE	24	85	68	15	2	trace
$Fe(NO_3)_3$/bpy	6	86	34	14	27	11

We also followed the aerobic oxidation of cyclohexane (2° aliphatic alcohol) and cyclohexylmethanol (1° aliphatic alcohol) by these systems.

TEMPO/Fe(NO$_3$)$_3$/bpy
To a 1.5-dram vial was added $Fe(NO_3)_3 \cdot 9H_2O$ (0.01 mmol) with a stir bar. To the vial was added 0.5 mL of a stock solution containing TEMPO (20 mM) and 2,2'-bpy (20 mM) in acetic acid. The solution was stirred open to air. After 5 min, 0.5 mL of a stock solution containing cyclohexanol (200 mM) or cyclohexylmethanol (200 mM) with a known amount of PhBr in acetic acid was added. The vial was capped with a septum pierced with a needle attached to a balloon of O_2. At given times, 40 μL aliquots were withdrawn from the reaction solution, filtered through a short SiO_2 plug, rinsed with ca. 2 mL CH_3CN, and analyzed by GC. For the cyclohexanol reaction, the peak in the GC associated with cyclohexanol was obscured by acetic acid, but the peaks for cyclohexanone and PhBr were well resolved. Conditions: 60 °C, hold 1 min, then 60 °C to 200 °C, 20 deg/min. Retention times: PhBr, 4.7 min; cyclohexanol, 5.1 min; cyclohexanone, 4.4 min; cyclohexylmethanol, 6.1 min; cyclohexane carboxaldehyde, 4.2 min.

For the oxidation of cyclohexylmethanol, a 3 h induction period is observed during which the rate of cyclohexanemethanol conversion is approximately equal to the conversion of cyclohexanol over the same time (Fig. S11). However, after this induction period, the rate of cyclohexanemethanol conversion increases while that of cyclohexanol is unchanged.

TEMPO/Cu(NO$_3$)$_2$
To a 1.5-dram vial was added TEMPO (0.01 mmol), $Cu(NO_3)_2 \cdot 2.5(H_2O)$ (0.01 mmol), a stir bar and 1 mL of a stock solution containing cyclohexanol (100 mM) or cyclohexylmethanol (100 mM) with a known

amount of PhBr in DCE. The vial was capped with a septum pierced with a needle attached to a balloon of O_2. At given times, 40 µL aliquots were withdrawn from the reaction solution, filtered through a short SiO_2 plug, rinsed with ca. 2 mL CH_3CN, and analyzed by GC.

In this system, conversion of cyclohexanol is observed to be more rapid than conversion of cyclohexanemethanol (Fig. S12).

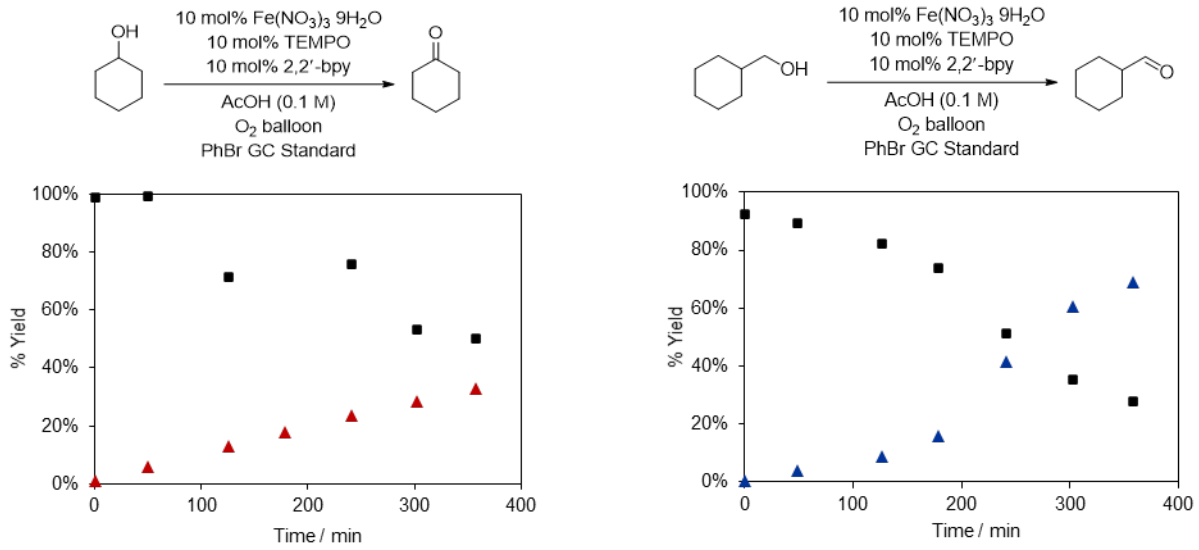


Figure S11. Time courses for the $Fe(NO_3)_3$/bpy/TEMPO cocatalyzed aerobic oxidation of cyclohexanol and cyclohexylmethanol. Monitored by GC with PhBr internal standard.

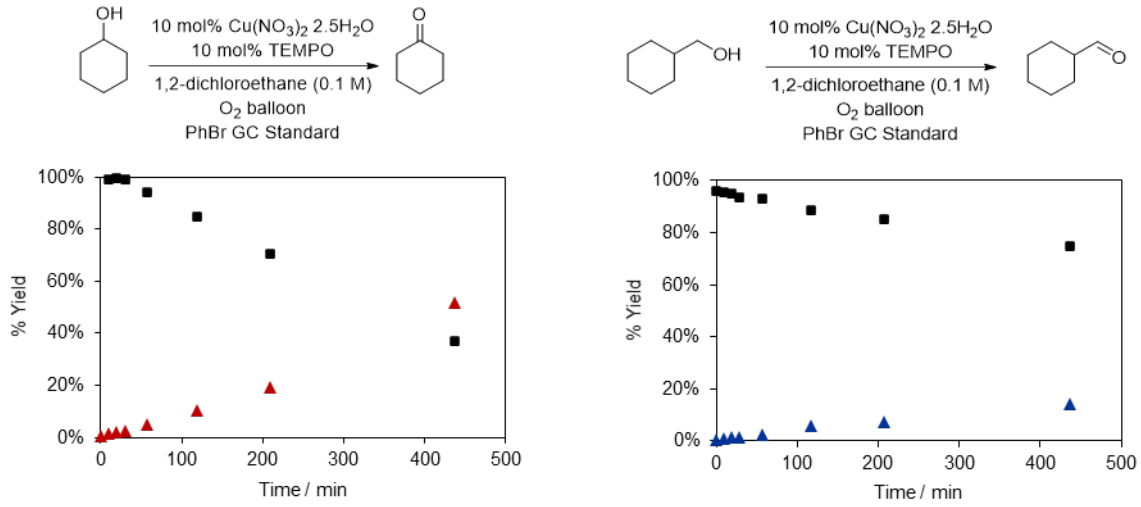
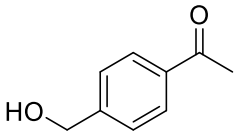
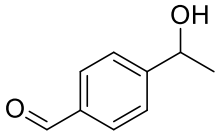


Figure S12. Time courses for the $Cu(NO_3)_2$/TEMPO cocatalyzed aerobic oxidation of cyclohexanol and cyclohexylmethanol. Monitored by GC with PhBr internal standard.

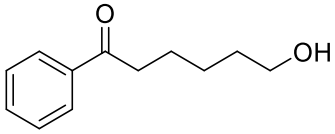
10. Characterization of Alcohol Oxidation Products



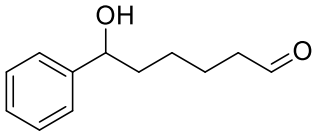
4-(Hydroxymethyl)acetophenone (2). Colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 4.76 (s, 2H), 2.58 (s, 3H), 2.26 (bs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.13, 146.42, 136.42, 128.73, 126.73, 64.68, 26.75. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_{11}O_2$) requires m/z 151.0754, found m/z 151.0753, difference 0.7 ppm. Spectral properties are consistent with literature values.[11]



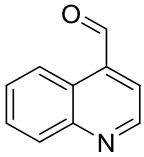
4-(1-hydroxyethyl)benzaldehyde (3). Colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.96 (d, *J* = 3.0 Hz, 1H), 7.84 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.52 (dd, *J* = 8.0, 1.3 Hz, 2H), 4.97 (q, *J* = 6.5 Hz, 1H), 2.35 (b, 1H), 1.50 (dd, *J* = 6.5, 1.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.16, 152.89, 135.68, 130.15, 126.03, 70.00, 25.47. Spectral properties are consistent with literature values.[4,12]



5-Hydroxypentyl phenyl ketone (6). Colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.98 (t, *J* = 7.3 Hz, 2H), 1.77 (p, *J* = 7.4 Hz, 2H), 1.63 (m, 3H), 1.52 – 1.42 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.52, 137.12, 133.07, 128.68, 128.14, 62.75, 38.56, 32.61, 25.58, 24.03. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}O_2$) requires m/z 193.1223, found m/z 193.1222, difference 0.5 ppm. Spectral properties are consistent with literature values.[13]

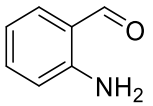


6-Hydroxy-6-phenyl-hexanal (7). Colorless syrup. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.73 (s, 1H), 7.39 – 7.26 (m, 5H), 4.66 (t, *J* = 6.6 Hz, 1H), 2.41 (t, *J* = 7.3 Hz, 2H), 2.06 (bs, 1H), 1.88 – 1.77 (m, 1H), 1.77 – 1.60 (m, 3H), 1.46 (s, 1H), 1.33 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.70, 144.76, 128.62, 127.74, 125.95, 74.46, 43.91, 38.84, 25.49, 22.03. Spectral properties are consistent with literature values.[4]

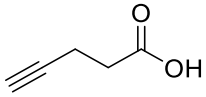


Quinoline-4-carboxaldehyde (10). Peach-colored solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.52 (s, 1H), 9.20 (d, *J* = 4.1 Hz, 1H), 9.02 (d, *J* = 9.3 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 4.2 Hz, 1H), 7.74 (t, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.99, 150.59, 149.43,

136.90, 130.32, 130.20, 129.53, 125.94, 124.56, 124.03. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_8NO$) requires m/z 158.0600, found m/z 158.0599, difference 0.6 ppm. Spectral properties are consistent with literature values.[14]

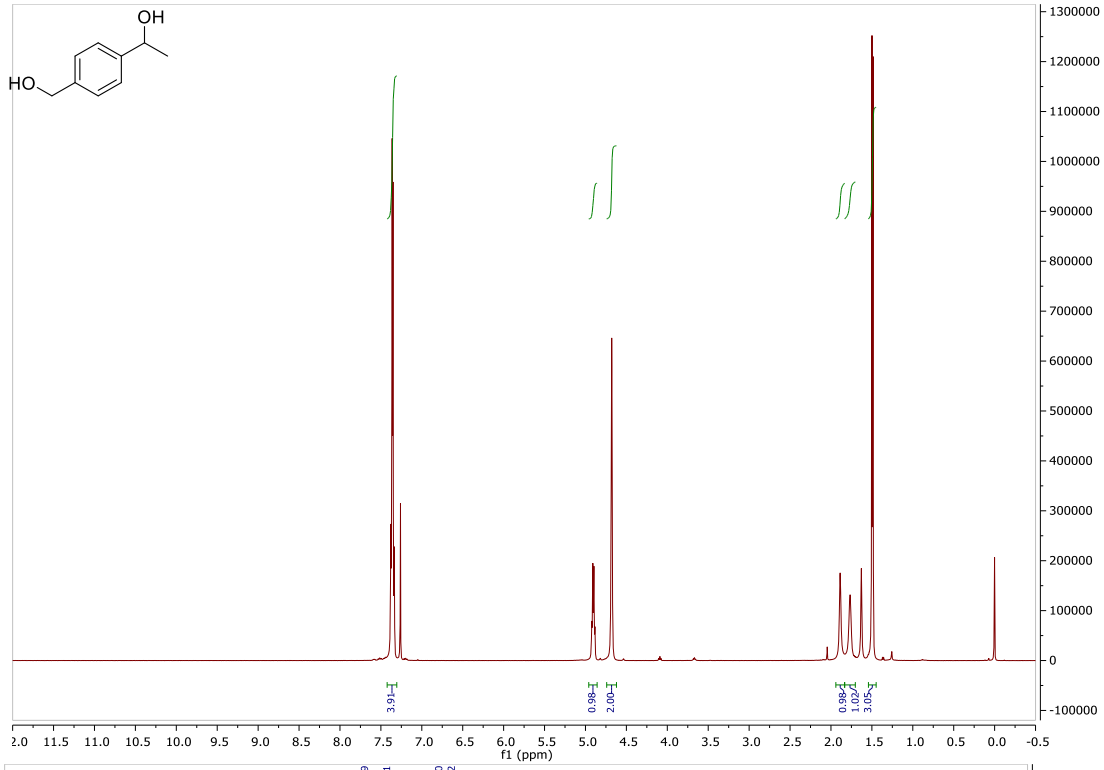


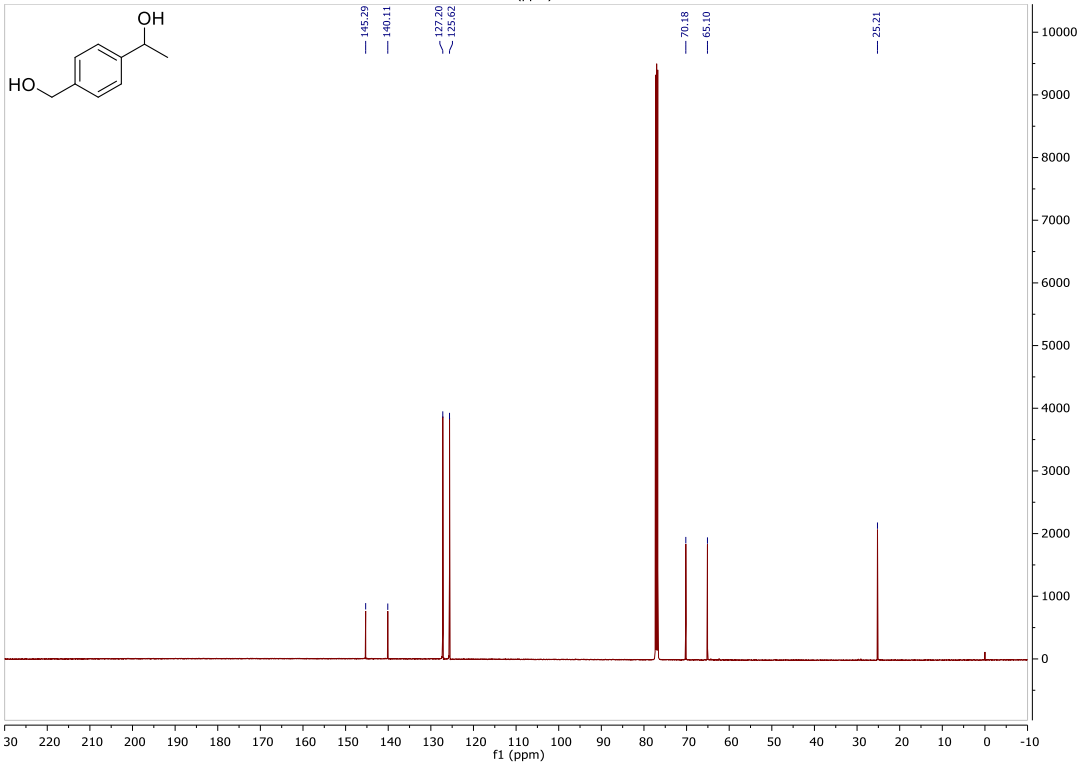
2-Aminobenaldehyde (12). Yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.87 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 8.5 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.11 (bs, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.19, 150.01, 135.85, 135.32, 119.02, 116.53, 116.15. HRMS (ESI) exact mass calculated for $[M+H]^+$ (C_7H_8NO) requires m/z 122.0600, found m/z 122.0599, difference 0.9 ppm. Spectral properties are consistent with literature values.[4]

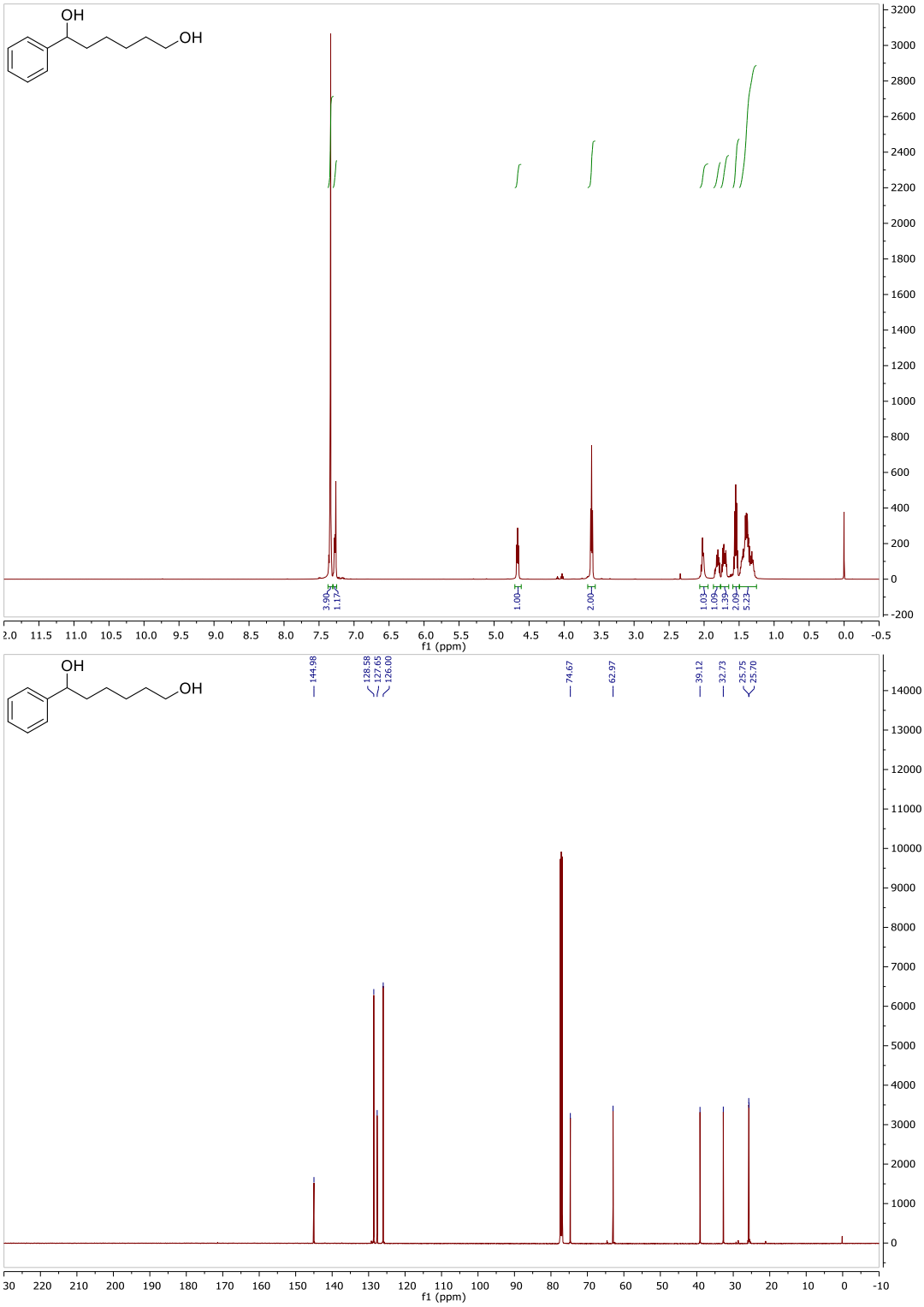


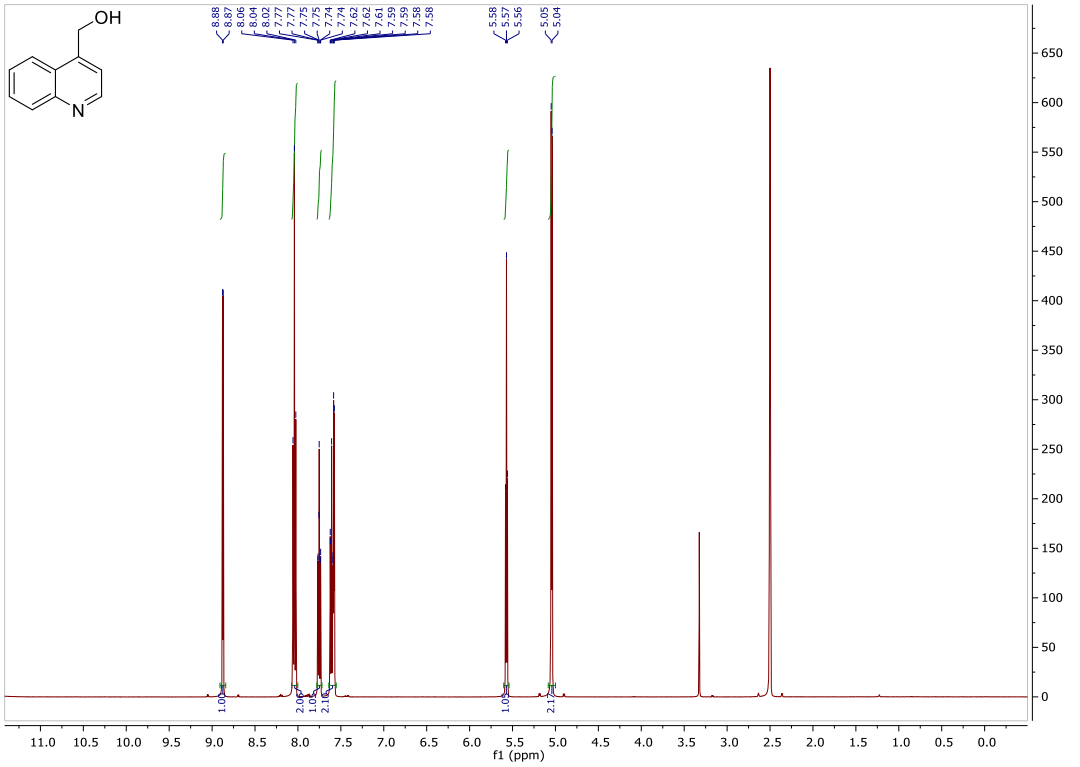
4-Pentynoic acid (15). White powder. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.42 (bs), 2.62 (t, *J* = 6.9 Hz, 2H), 2.52 (td, *J* = 7.7, 2.6 Hz, 2H), 2.00 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.76, 82.25, 69.38, 33.27, 14.25. RMS (ESI) exact mass calculated for $[M-H]^-$ ($C_5H_5O_2$) requires m/z 97.0295, found m/z 97.0296, difference 1.0 ppm.

11. ^{1}H and ^{13}C NMR Spectra of Alcohol Substrates






OH
OH
3.90
1.17
1.00
2.00
1.03
1.09
1.39
2.09
5.23
f1 (ppm)
OH
OH
144.98
128.58
127.65
126.00
74.67
62.97
39.12
32.73
25.75
25.70
f1 (ppm)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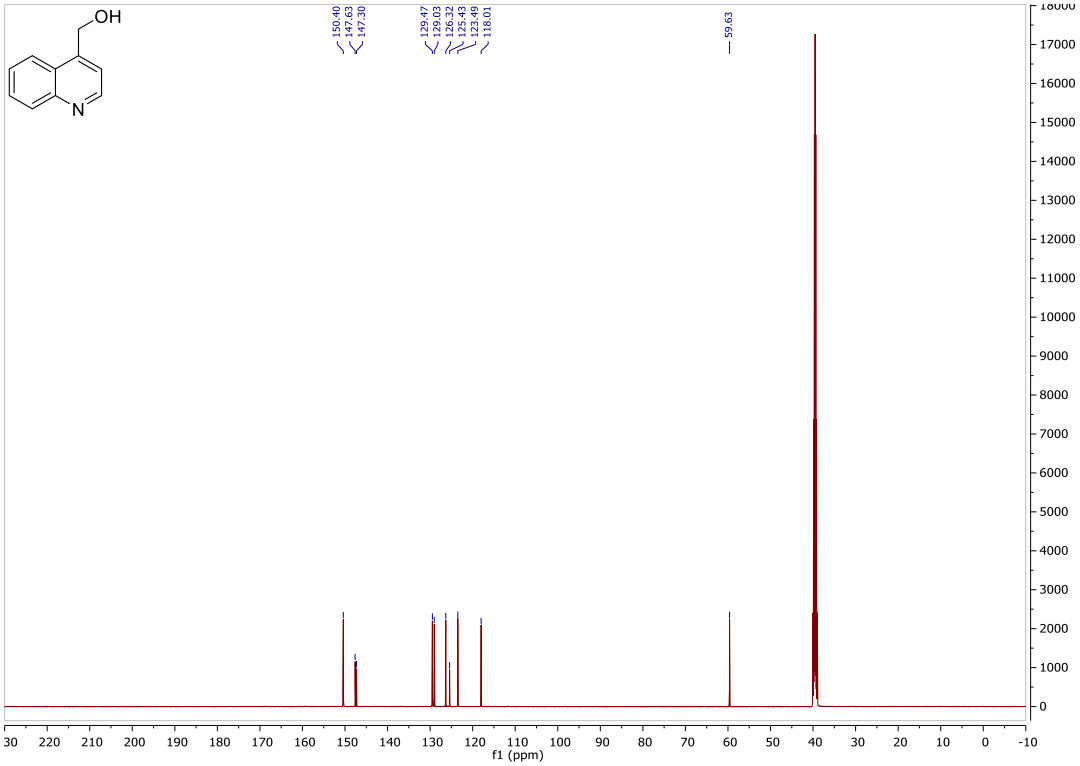
8.87
8.06
8.04
8.02
7.77
7.75
7.74
7.62
7.61
7.59
7.58
5.58
5.57
5.56
5.05
5.04
1.00
2.05
1.01
2.16
1.03
2.17
f1 (ppm)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147.63
147.30
129.47
129.03
126.32
125.43
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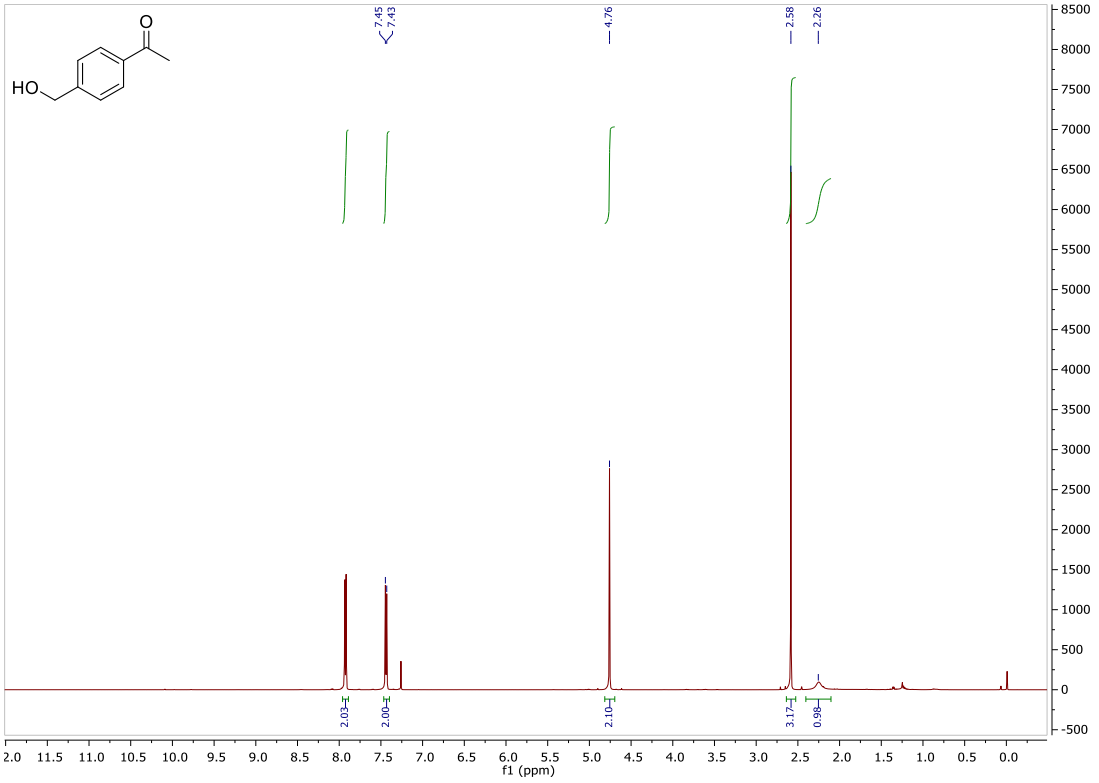
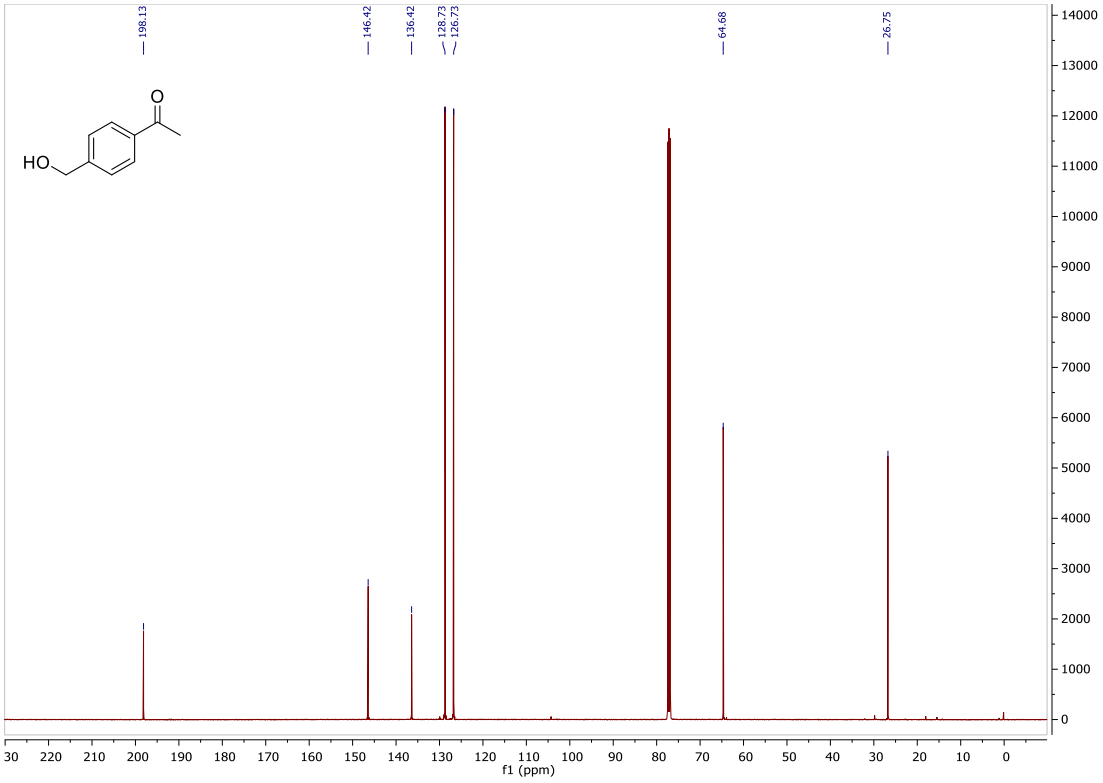
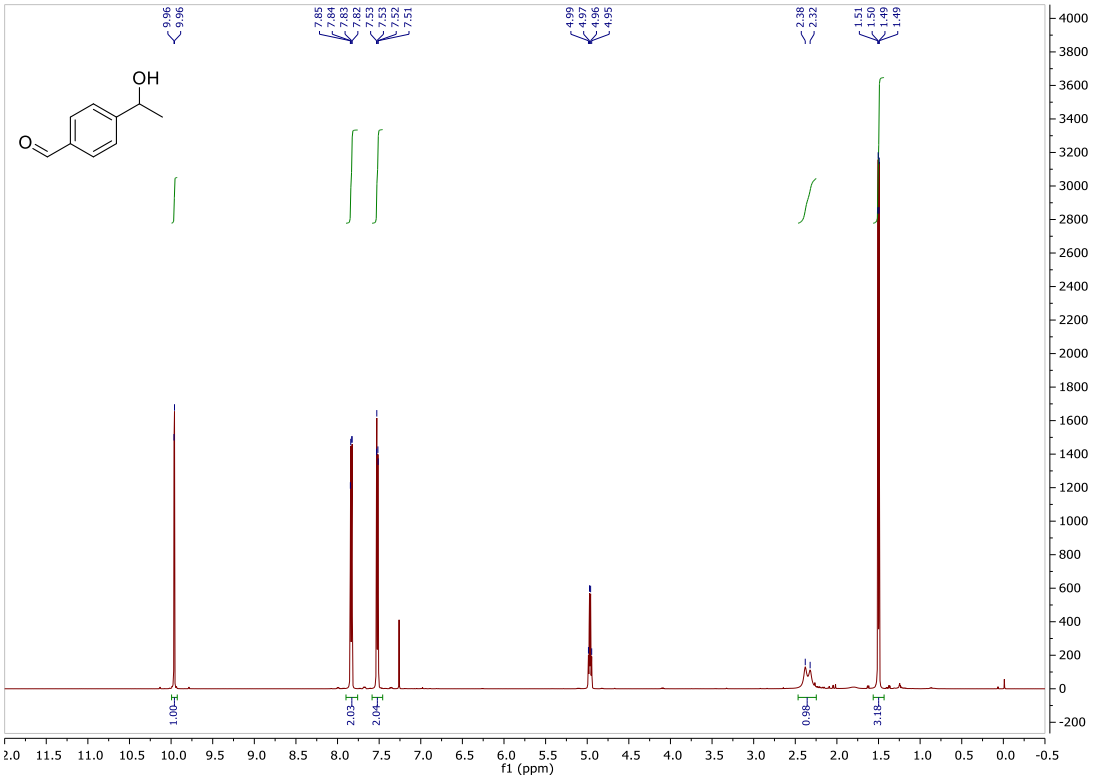
118.01
59.63
f1 (ppm)

12. ^{1}H and ^{13}C NMR Spectra of Alcohol Oxidation Products



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9.96
7.85
7.84
7.83
7.82
7.53
7.52
7.51
4.99
4.97
4.96
4.95
2.38
2.32
1.51
1.50
1.49
1.49
OH
O
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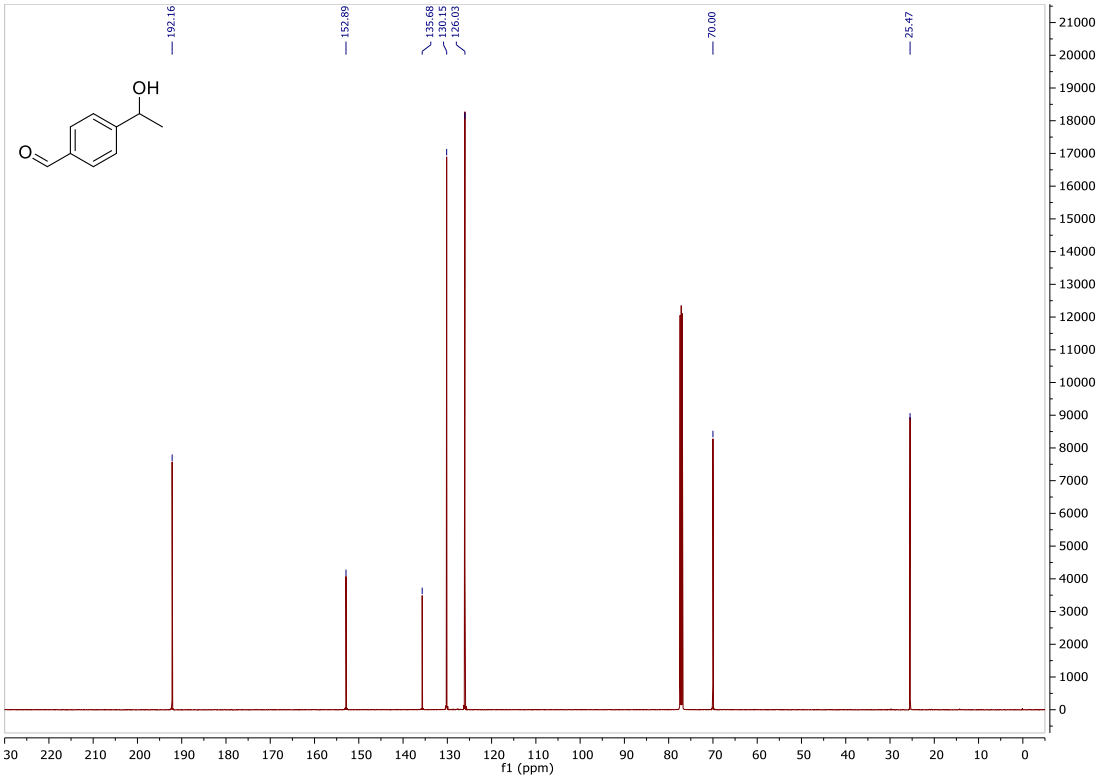
2.04
0.98
3.18
f1 (ppm)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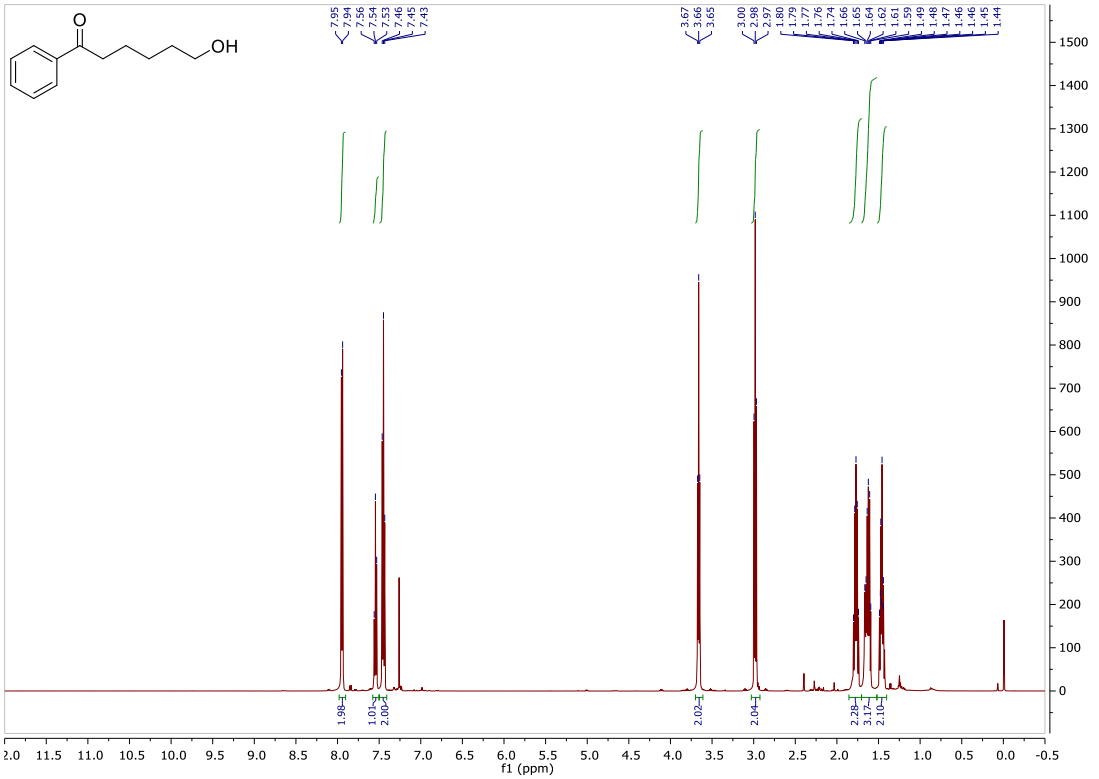
126.03
70.00
25.47
OH
O
f1 (ppm)


O
OH
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7.94
7.56
7.54
7.53
7.46
7.45
7.43
3.67
3.66
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2.98
2.97
1.80
1.79
1.77
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1.74
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1.61
1.59
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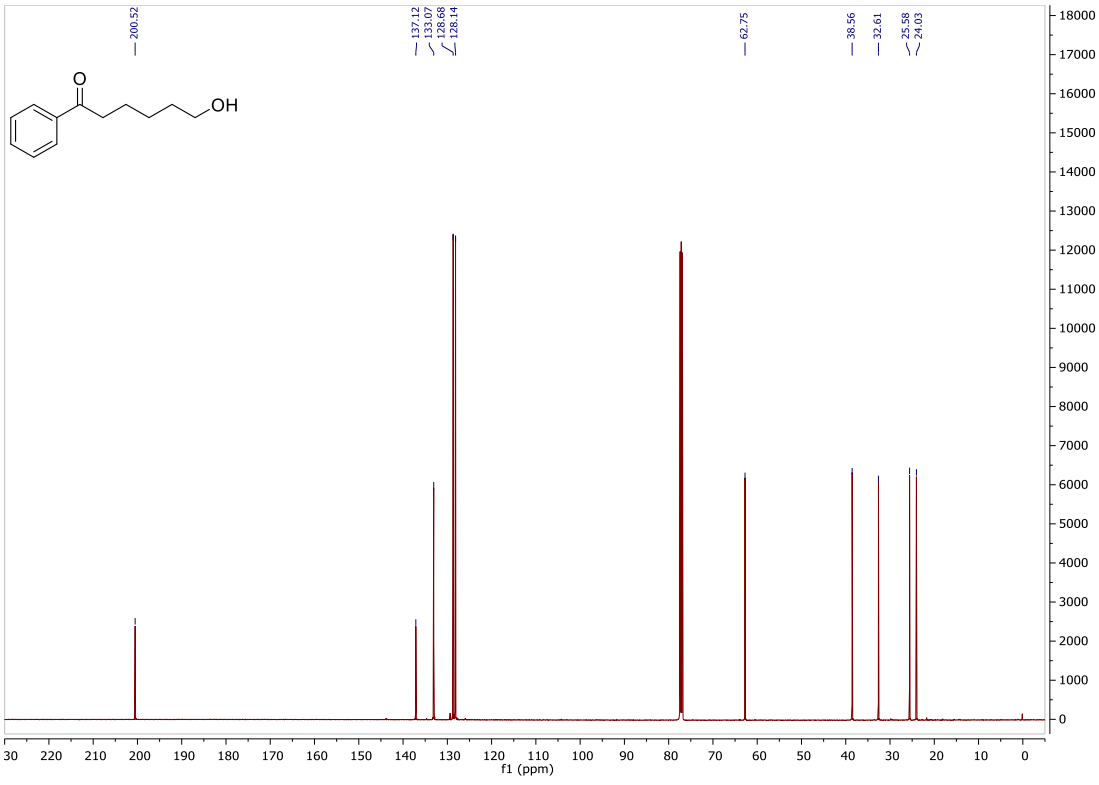
2.10
f1 (ppm)


O
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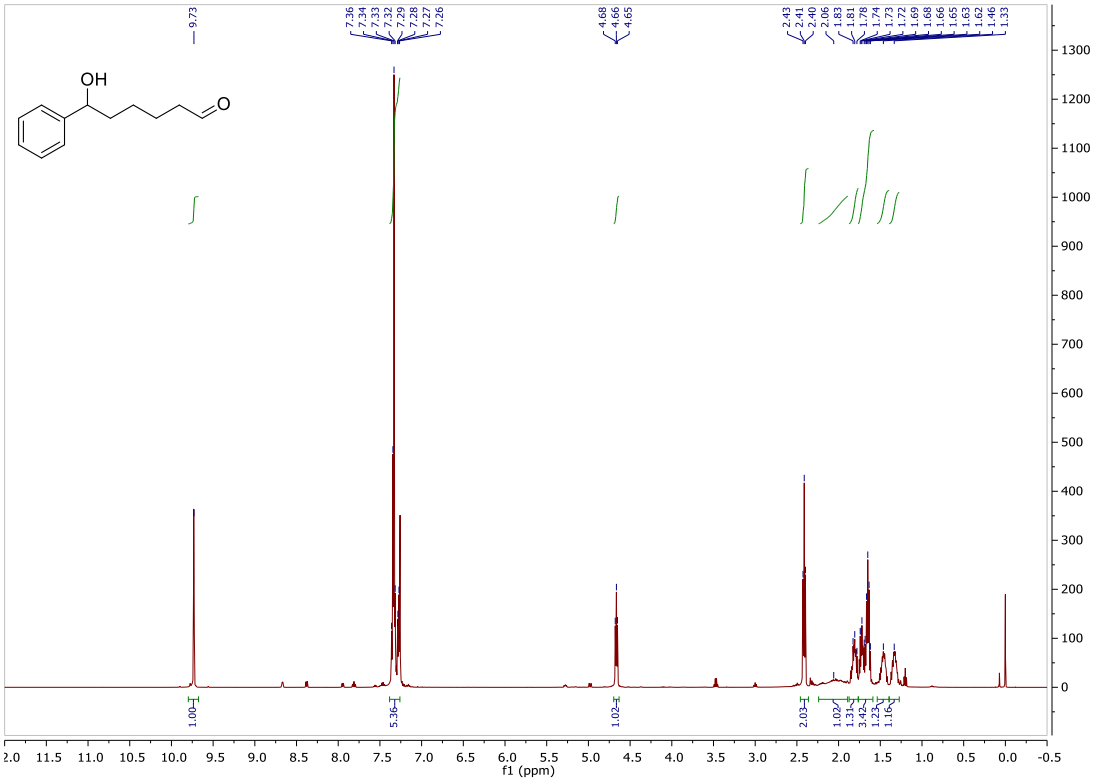
128.14
62.75
38.56
32.61
25.58
24.03
f1 (ppm)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7.33
7.32
7.29
7.28
7.27
7.26
4.68
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2.40
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1.81
1.78
1.74
1.73
1.72
1.69
1.68
1.66
1.65
1.63
1.62
1.46
1.33
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2.03
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3.42
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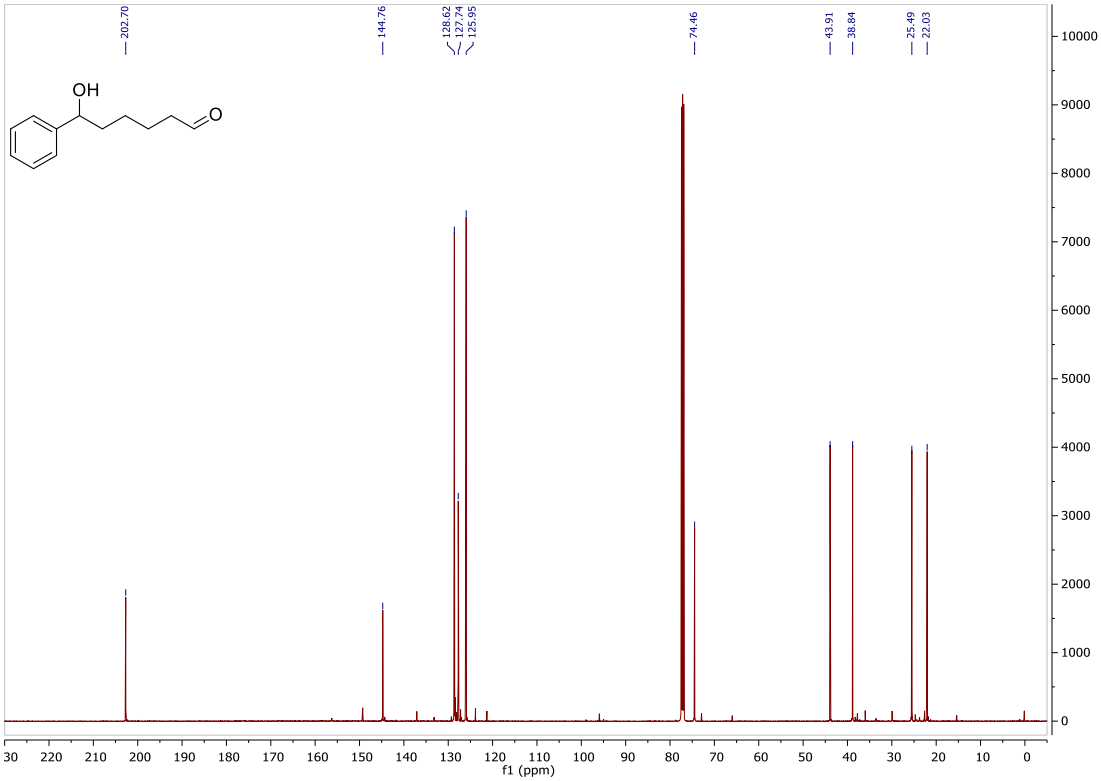
1.16
f1 (ppm)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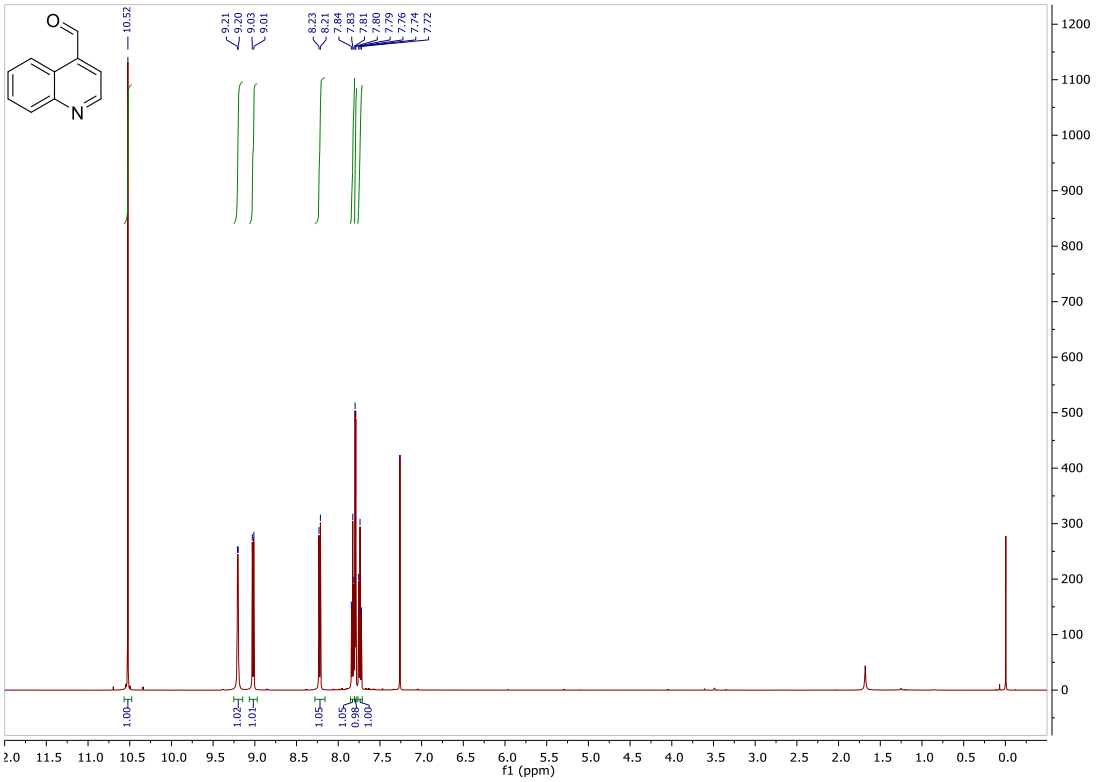
22.03
OH
O
f1 (ppm)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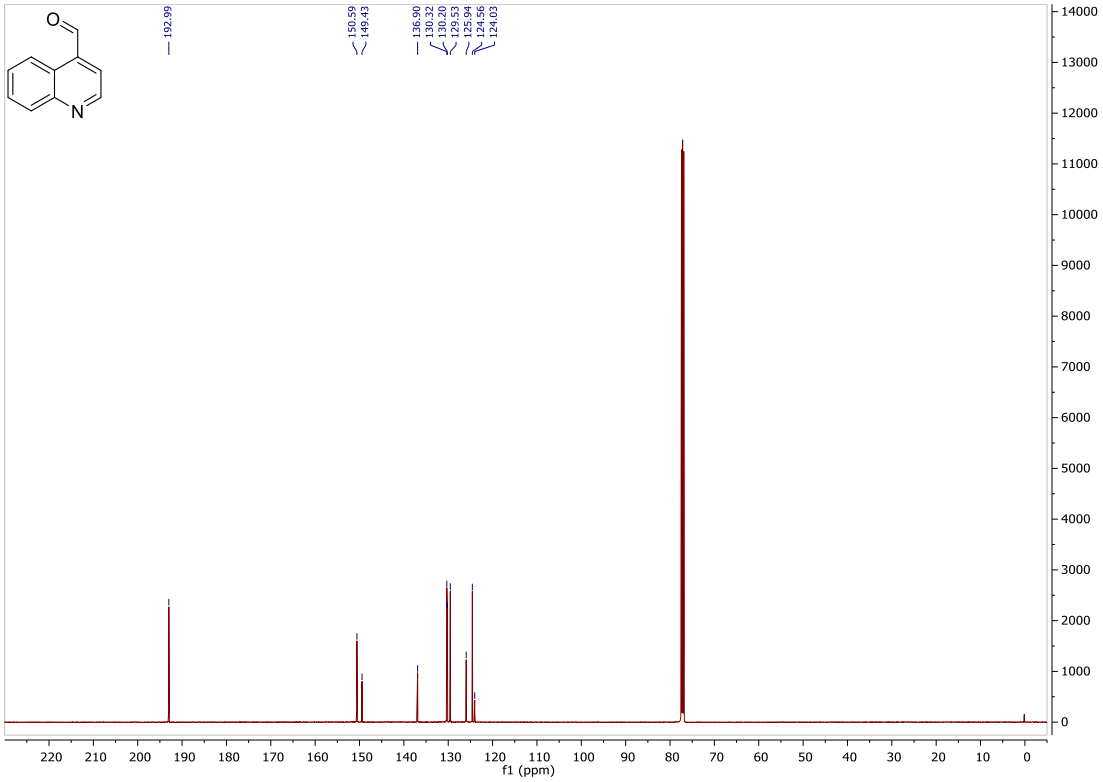
9.21
9.20
9.03
9.01
8.23
8.21
7.84
7.83
7.81
7.80
7.79
7.76
7.74
7.72
1.00
1.02
1.01
1.05
1.05
0.98
1.00
f1 (ppm)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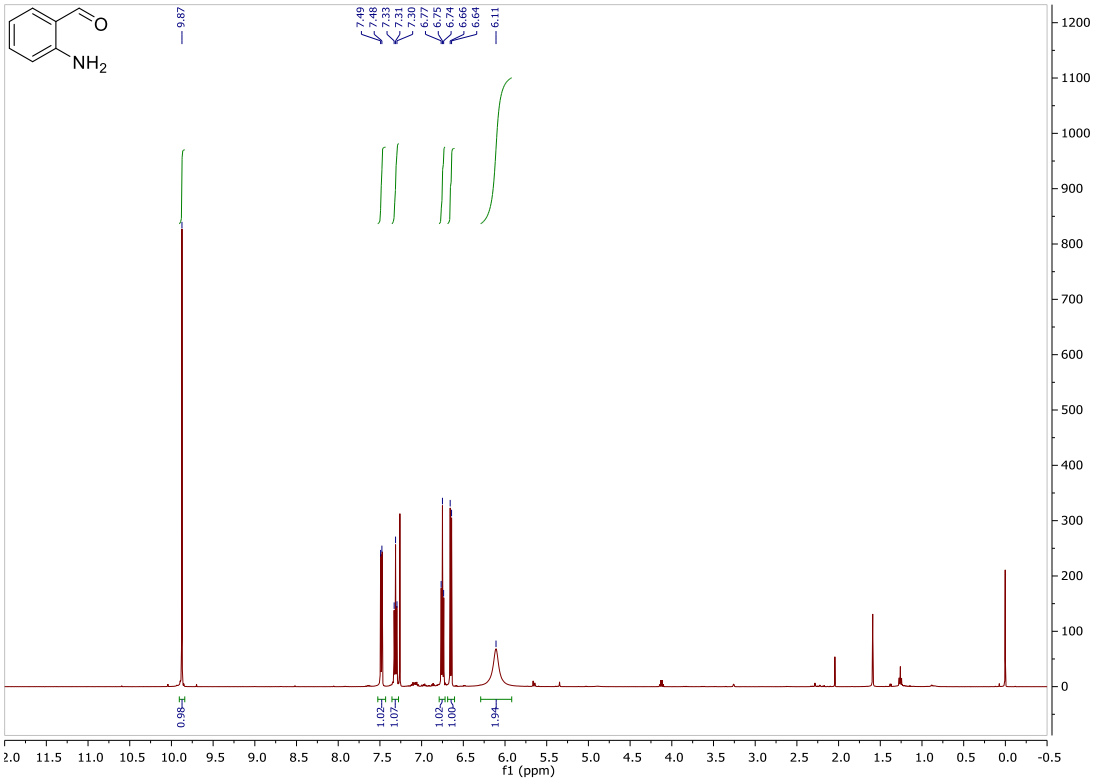
130.20
129.53
125.94
124.56
124.03
f1 (ppm)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7.30
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6.64
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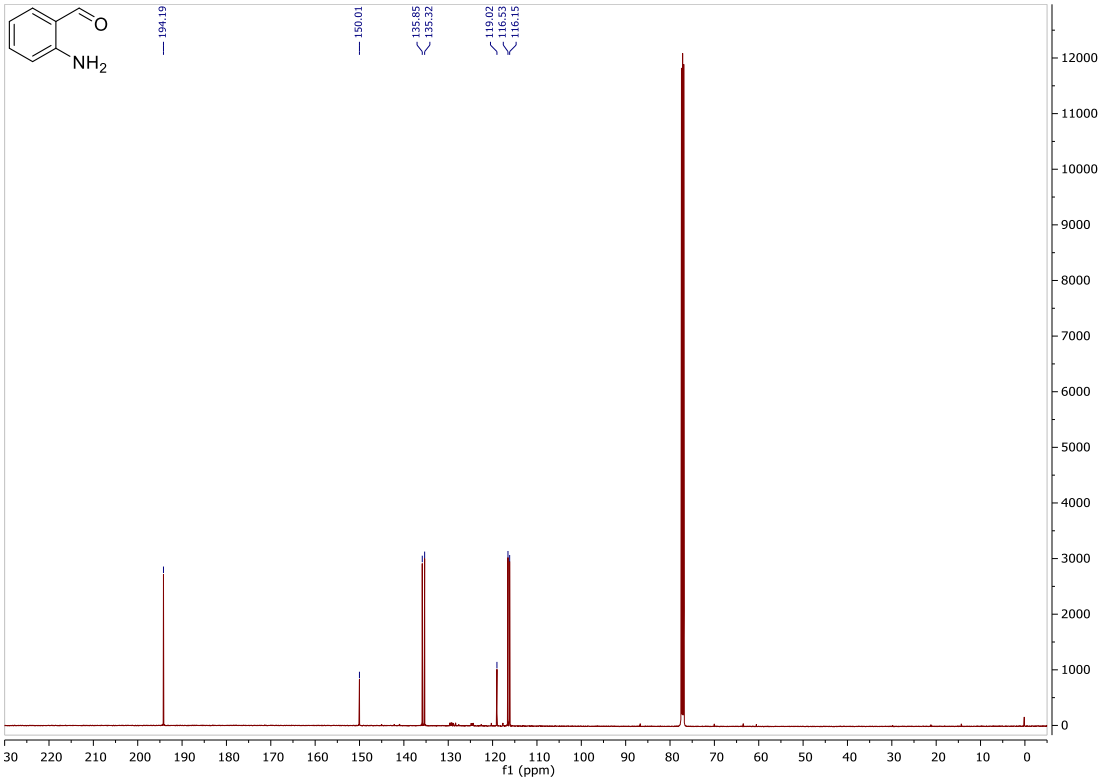
1.07
1.02
1.00
1.94
f1 (ppm)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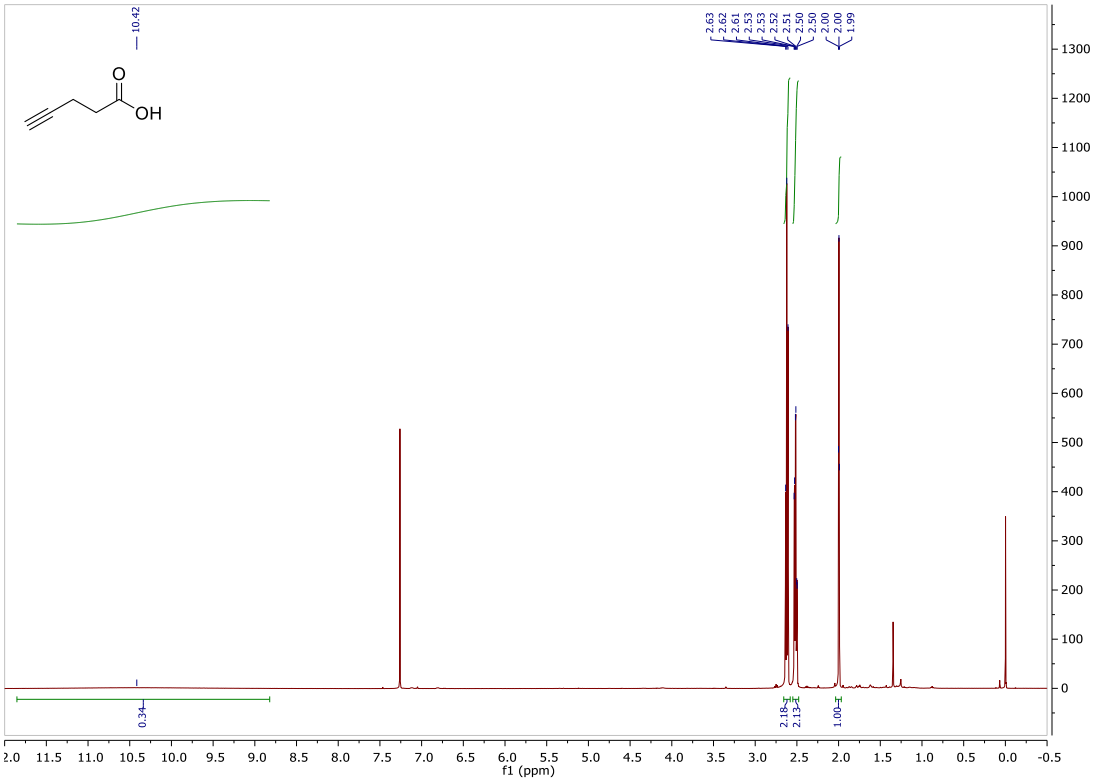
116.15
f1 (ppm)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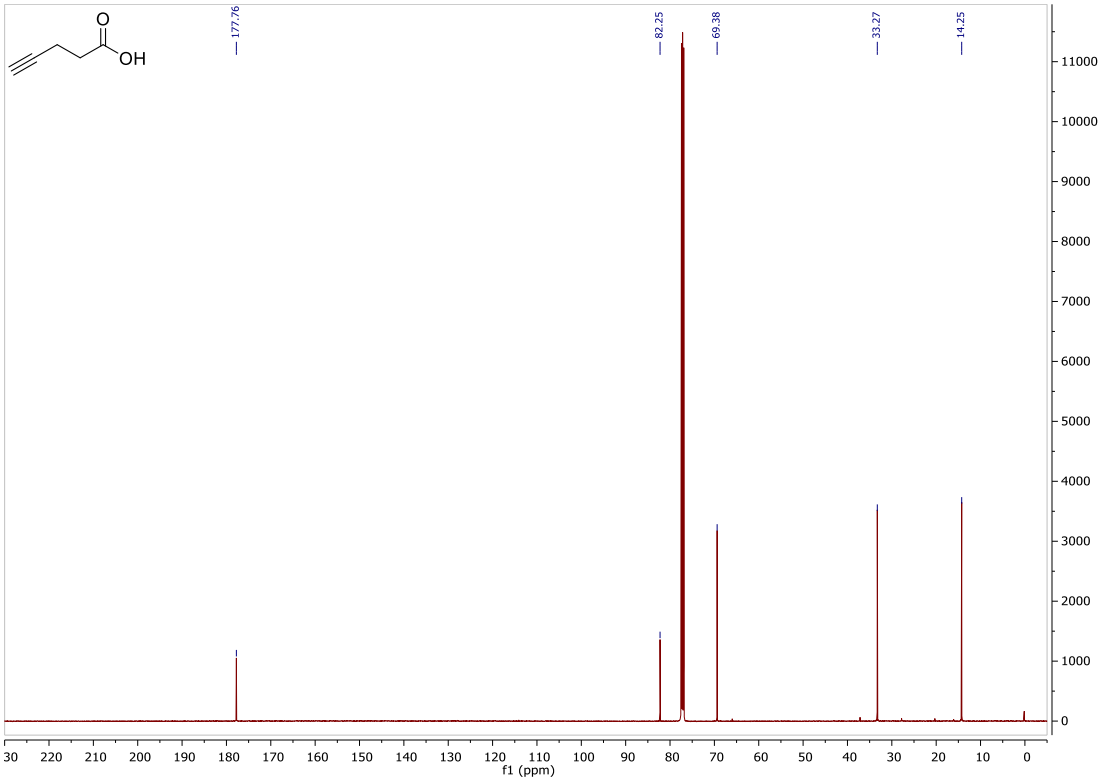
2.53
2.53
2.52
2.51
2.50
2.50
2.00
2.00
1.99
O
OH
0.34
2.18
2.13
1.00
f1 (ppm)


177.76
82.25
69.38
33.27
14.25
O
OH
f1 (ppm)

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