Electronic Supplementary Information (ESI) to:

Nitroxide Radical Surfactants Enable Electrocatalytic Oxidation of Fatty Alcohols in Water

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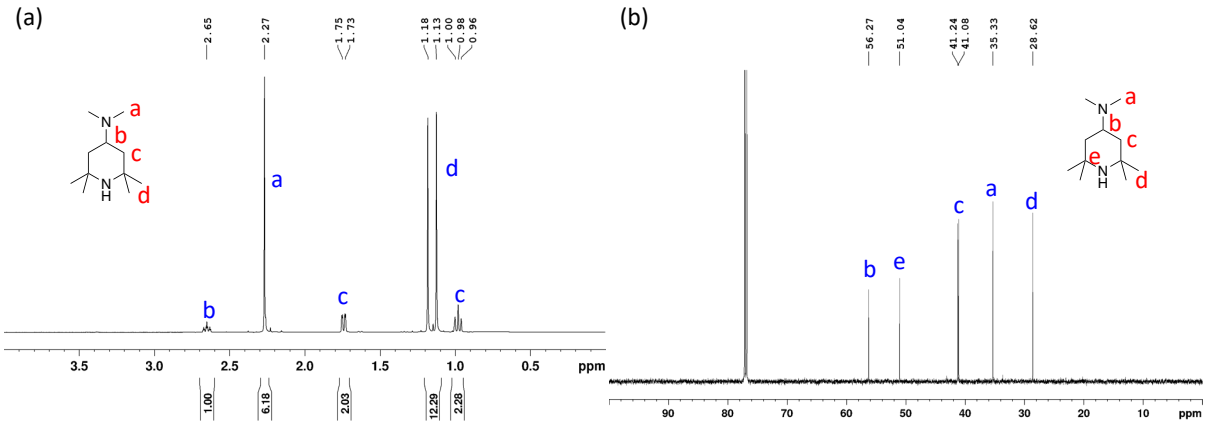

Figure S1. ^{1}H (a) and ^{13}C (b) NMR spectra of 4-dimethylamino-2,2,6,6-tetramethylpiperidine (DMTMP) in $CDCl_3$.

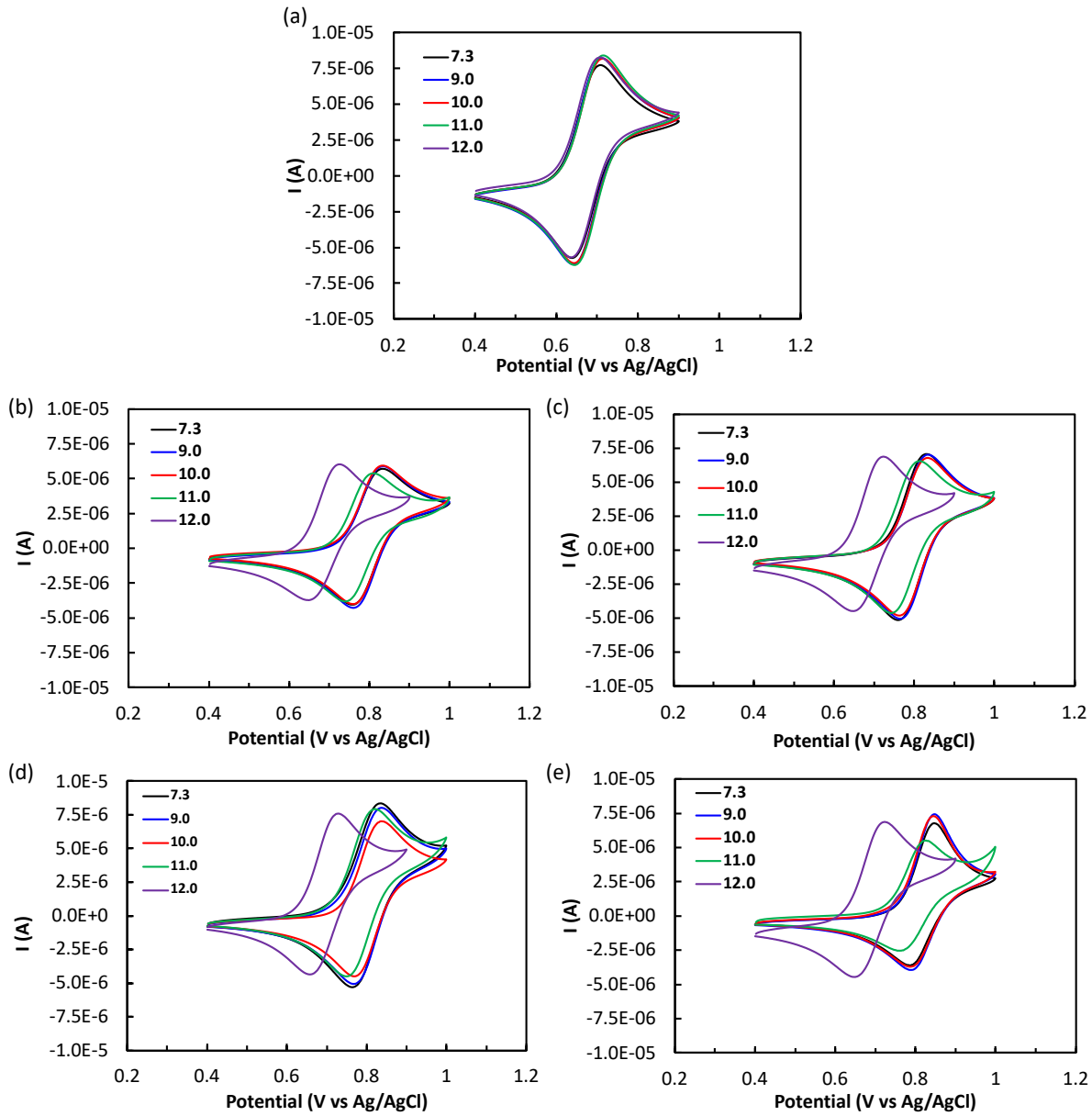

Figure S2. CVs of ACT (a) and TEMPO surfactants with C4 (b), C8 (c), C10 (d), and C14 (e) alkyl chains in different pH buffer solutions. Solution condition: PBS buffer 7.3 and carbonate buffer 9.0. to 12.0 0.1 M with 0.1 M NaCl, TEMPO radicals, 1 mM. Glassy carbon electrode with a scan rate of 50 mV/s.

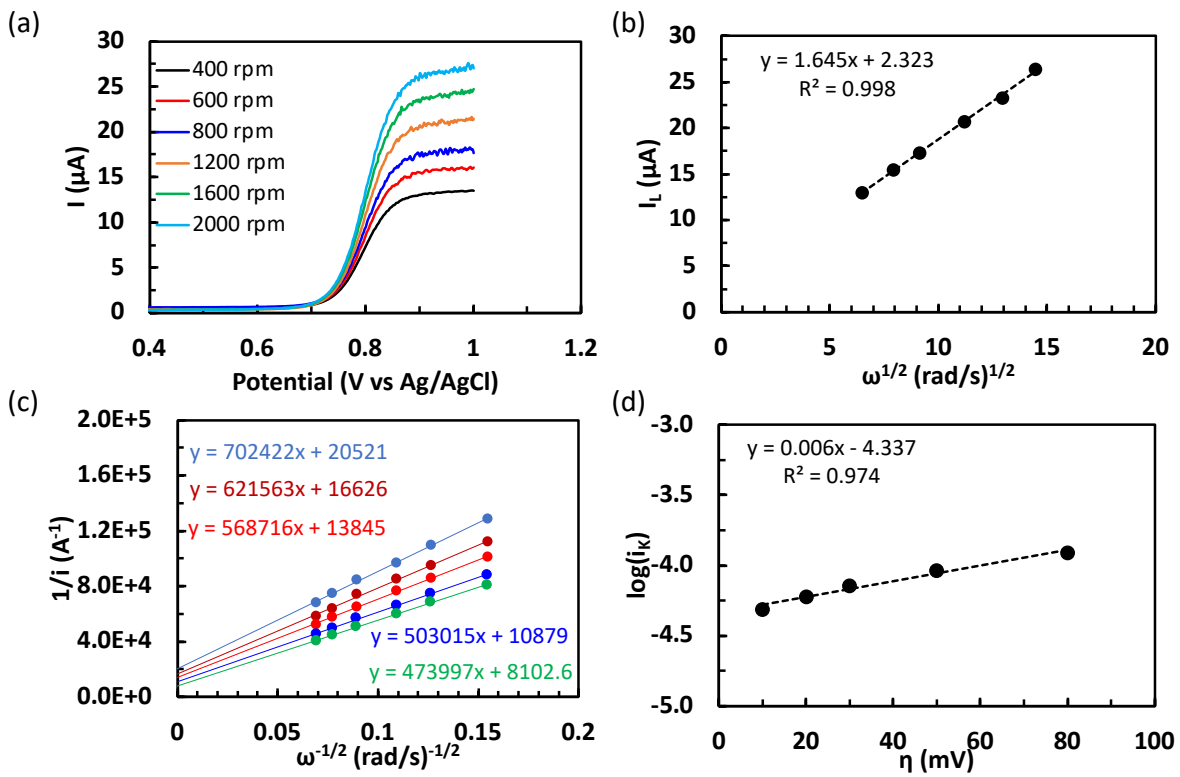

Figure S3. Typical RDE measurements of C8-NO· in a pH 7.3 buffer with 0.1 M NaCl and analysis. (a) Linear scan voltammograms of C8-NO· (1.0 mM) at 10 mV/s at various rotation speeds from 400 rpm to 2000 rpm. (b) The Levich plot of limiting currents (adopted at 0.9 V vs Ag/AgCl) vs the square roots of rotation rates. (c) The Koutecký-Levich plot for different overpotentials (η) to obtain the kinetic current i_k (when $\omega^{-1/2}$ approaching zero). (d) The Tafel plot of kinetic currents i_k vs overpotentials η to obtain the heterogeneous electron transfer rate constant k_0.

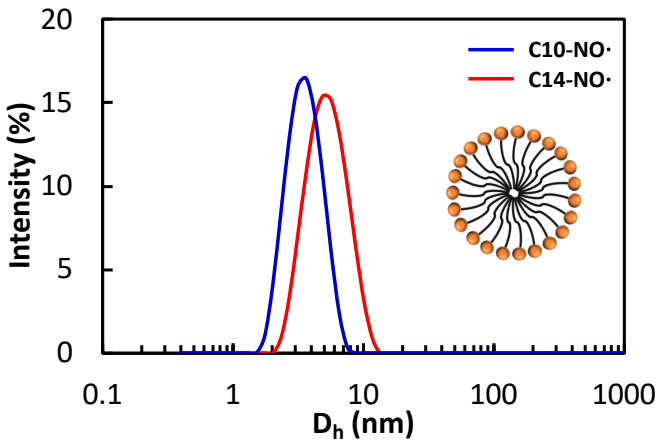

Figure S4. DLS of C10-NO· at 20 mg/mL and C14-NO· at 10 mg/mL in 0.1 M pH 10 buffer with 0.1 M NaCl.

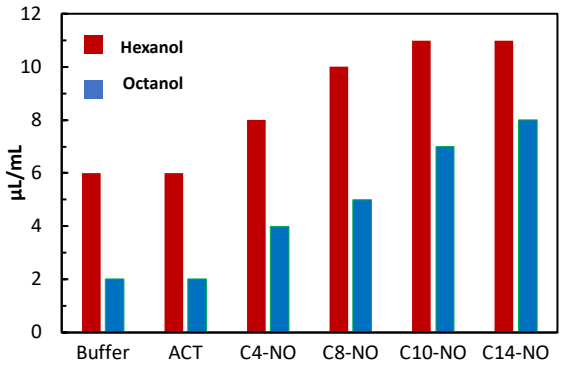

Figure S5. Solubility of hexanol and octanol in buffer 10.0 in the absence or presence of ACT or TEMPO surfactant 1mM.

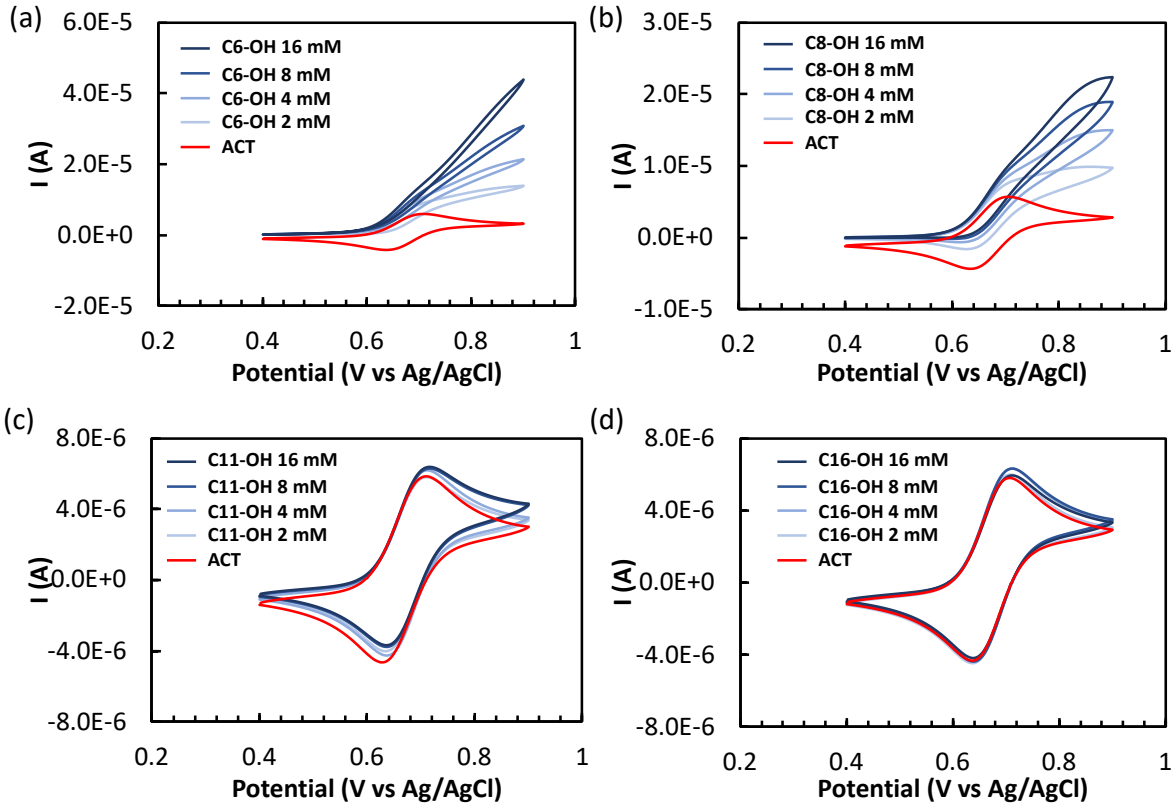

Figure S6. CVs of ACT-mediated electrocatalytic oxidation of (a) C6-OH, (b) C8-OH (c) C11-OH and (d) C16-OH at different alcohol concentrations. Solution conditions: ACT 1 mM, pH 10 buffer $Na_2CO_3/NaHCO_3$ 0.1 M with NaCl 0.1 M, GC working electrode and Ag/AgCl reference electrode, scan rate was 25 mV/s.

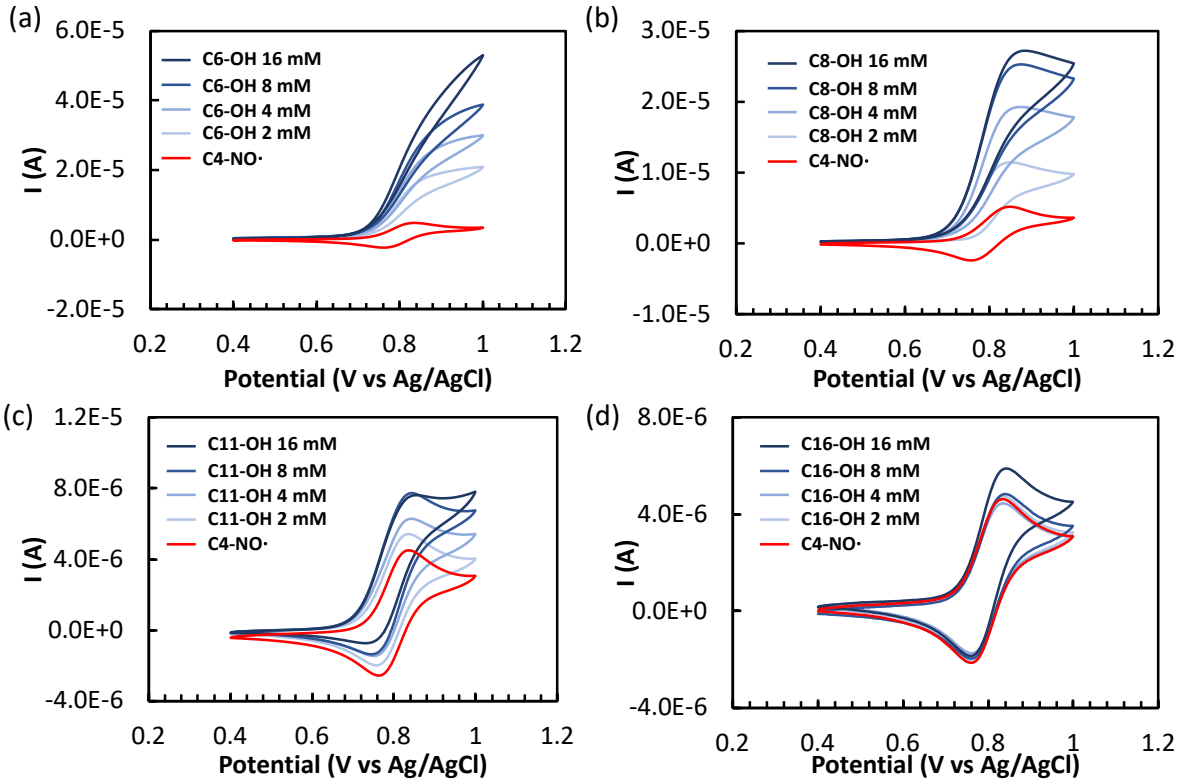

Figure S7. CVs of C4-NO· electrocatalytic oxidation of (a) C6-OH, (b) C8-OH (c) C11-OH and (d) C16-OH at different alcohol concentrations. Solution conditions: C4-NO· 1 mM, pH 10 buffer $Na_2CO_3/NaHCO_3$ 0.1 M with NaCl 0.1 M, GC working electrode and Ag/AgCl reference electrode, scan rate was 25 mV/s.

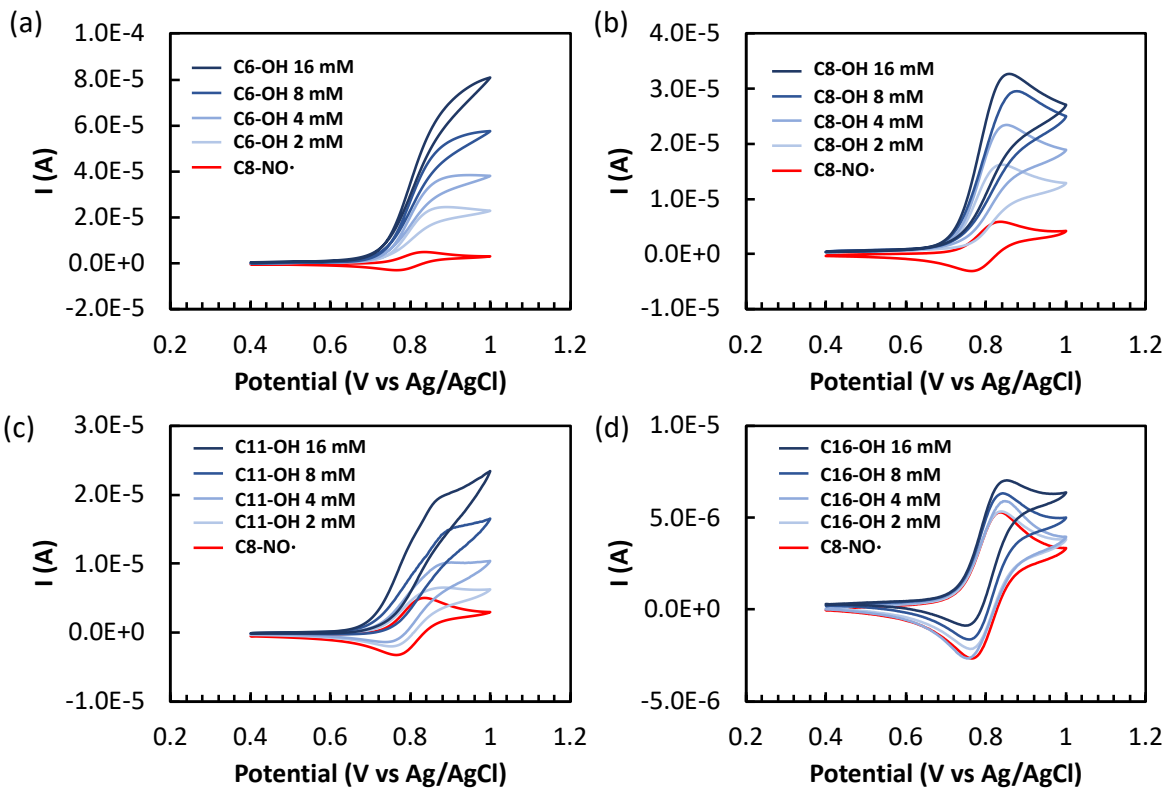

Figure S8. CVs of C8-NO· electrocatalytic oxidation of (a) C6-OH, (b) C8-OH (c) C11-OH and (d) C16-OH at different alcohol concentrations. Solution conditions: C8-NO· 1 mM, pH 10 buffer Na_2CO_3/$NaHCO_3$ 0.1 M with NaCl 0.1 M, GC working electrode and Ag/AgCl reference electrode, scan rate was 25 mV/s.

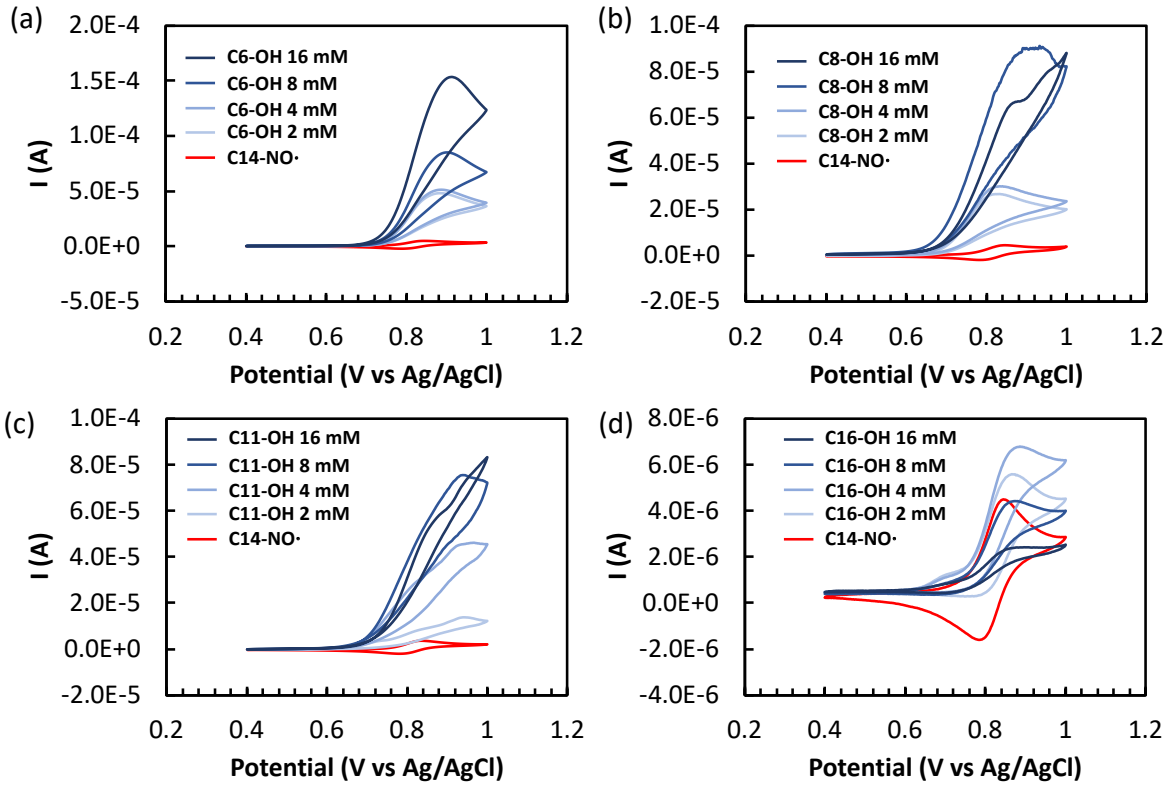

Figure S9. CVs of C14-NO· electrocatalytic oxidation of (a) C6-OH, (b) C8-OH (c) C11-OH and (d) C16-OH at different alcohol concentrations. Solution conditions: C14-NO· 1 mM, pH 10 buffer $Na_2CO_3/NaHCO_3$ 0.1 M with NaCl 0.1 M, GC working electrode and Ag/AgCl reference electrode, scan rate was 25 mV/s.

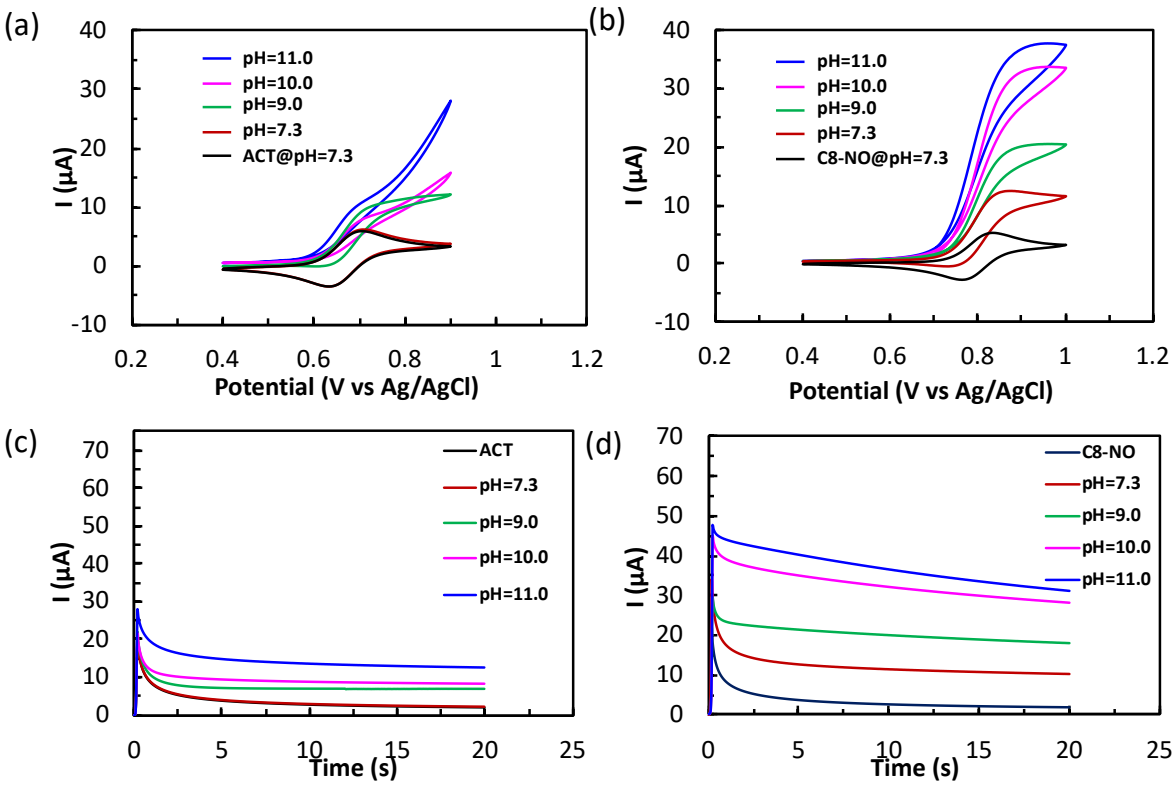

Figure S10: pH-dependent catalytic oxidation of C6-OH by (a, c) ACT and (b, d) C8-NO·, (a) and (b) were CVs and (c) and (d) were CAs. Solution conditions: catalyst 1 mM, GC working electrode and Ag/AgCl reference electrode; scan rates for all CVs were 25 mV/s. The applied potentials for CA were 0.8 V for ACT and 0.9 V for C8-NO·

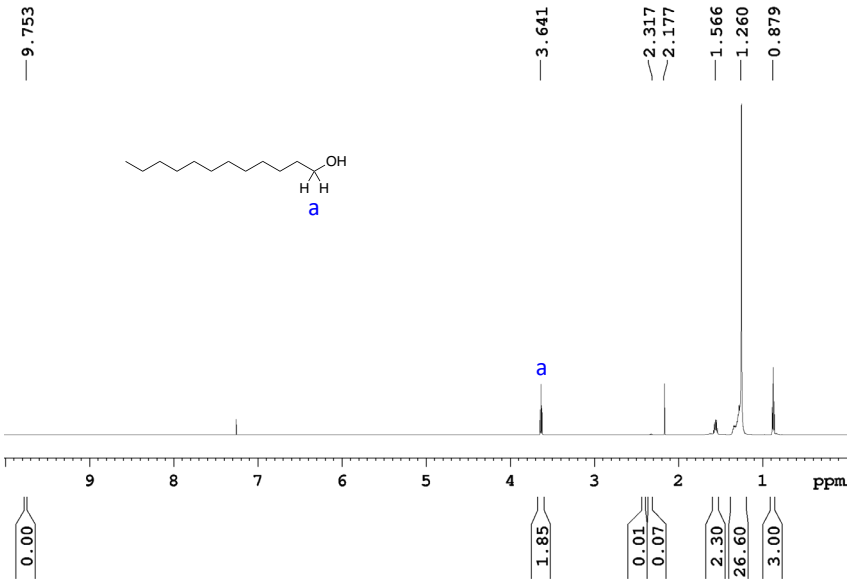

Figure S11. ^{1}H NMR of the crude product oxidized from C12-OH (20 mM) by ACT (1 mM) in pH 10 buffer. Applied potential 0.8 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 35 °C.

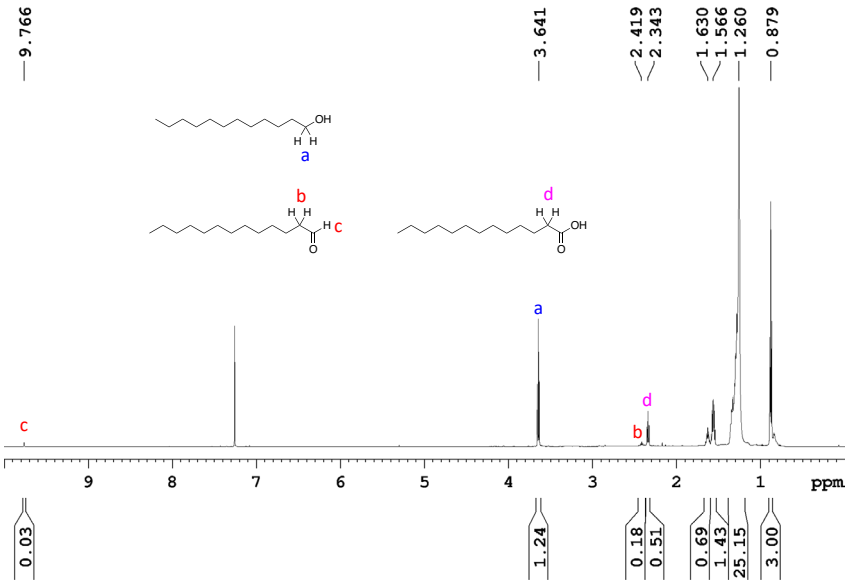

Figure S12. ^{1}H NMR of the crude product oxidized from C12-OH (20 mM) by C10-NO· (1 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 35 °C.

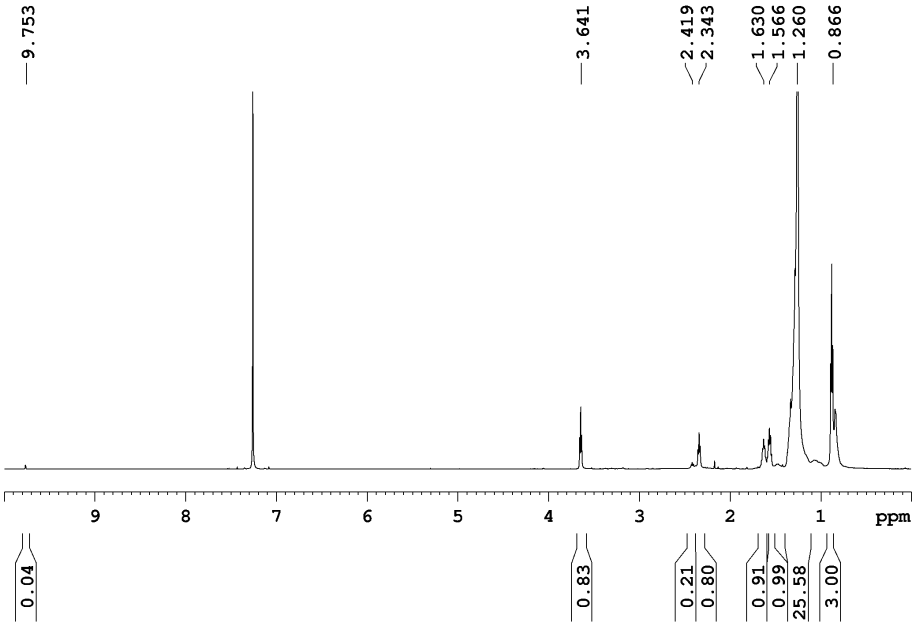

Figure S13. ^{1}H NMR of the crude product oxidized from C12-OH (20 mM) by C14-NO· (1 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 35 ^{o}C.

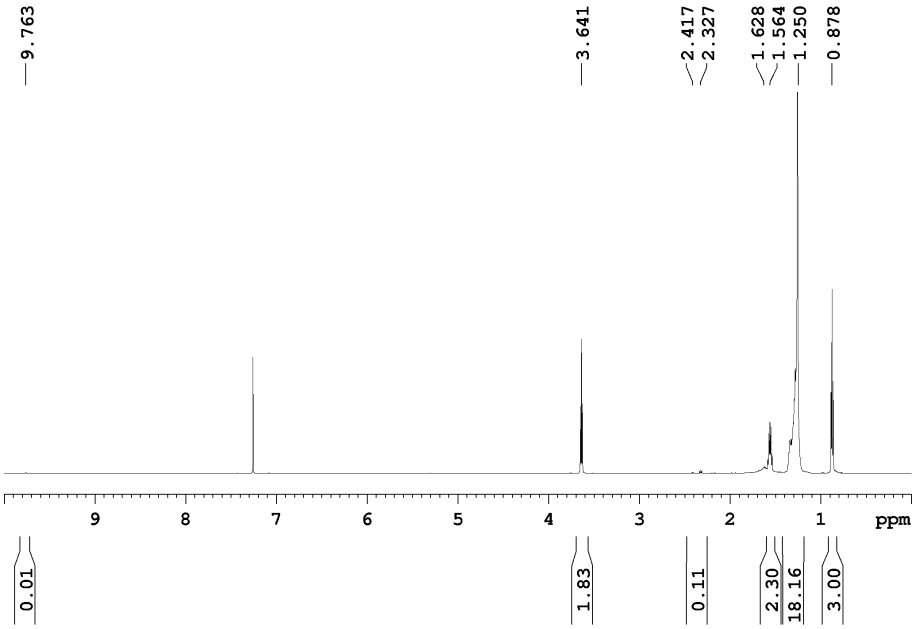

Figure S14. ^{1}H NMR of the crude product oxidized from C16-OH (20 mM) by ACT (1 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 60 ^{o}C.

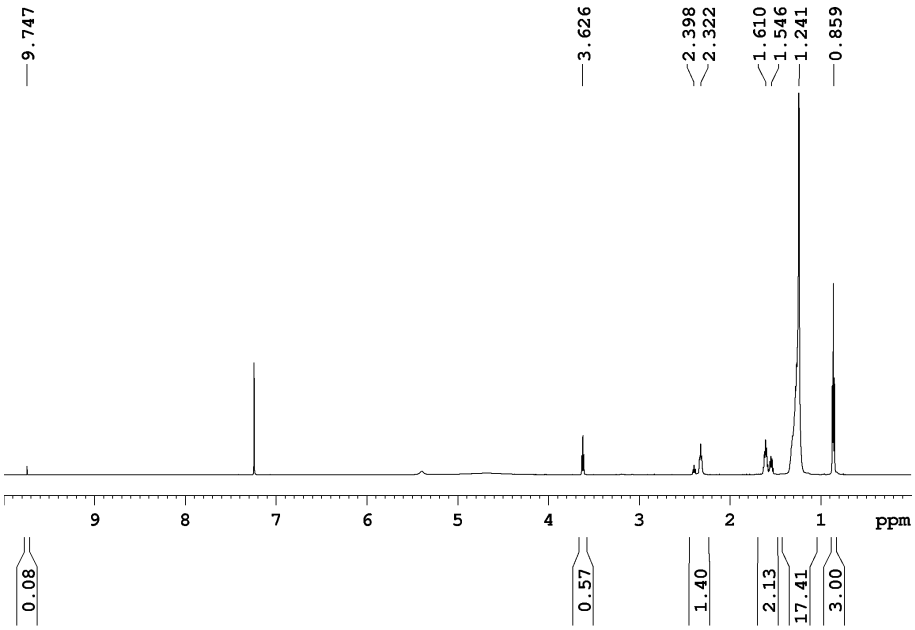

Figure S15. ^{1}H NMR of the crude product oxidized from C16-OH (20 mM) by C10-NO· (1 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 60 ^{o}C.

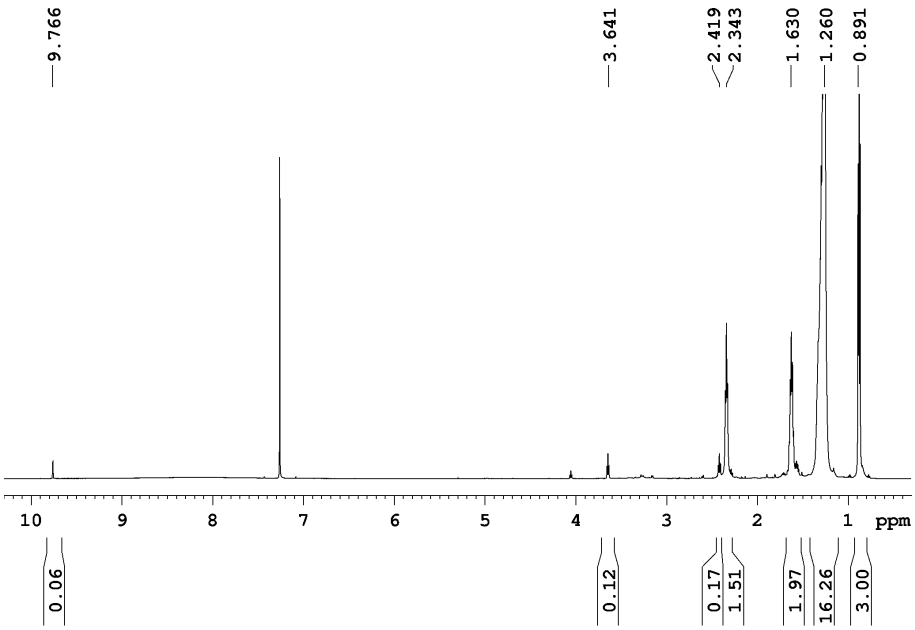

Figure S16. ^{1}H NMR of the crude product oxidized from C16-OH (20 mM) by C14-NO· (1 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 60 ^{o}C.

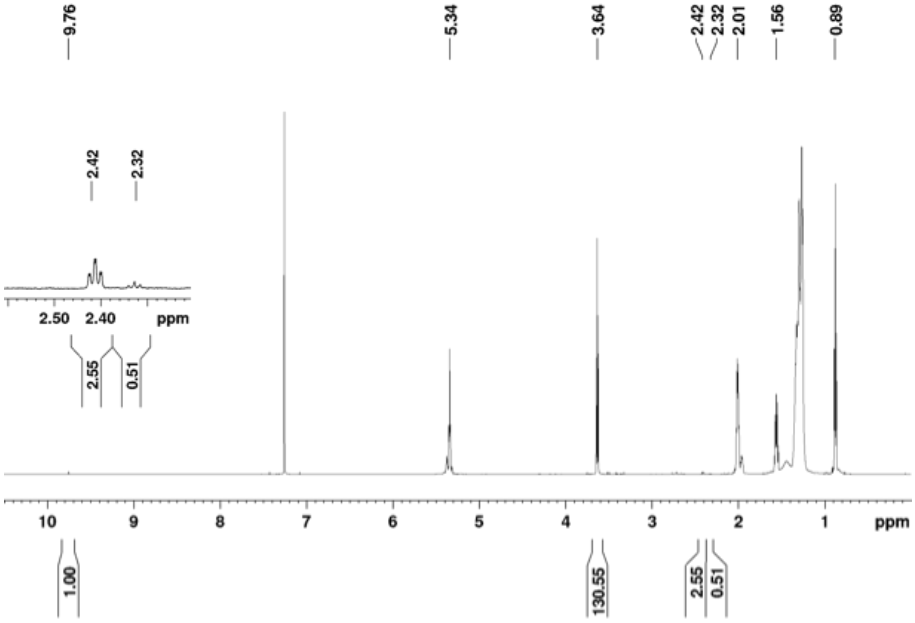

Figure S17. ^{1}H NMR of the crude product oxidized from oleyl alcohol (C18-OH) (20 mM) by ACT (1 mM) in pH 10 buffer. Applied potential 0.8 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 25 ^{o}C.

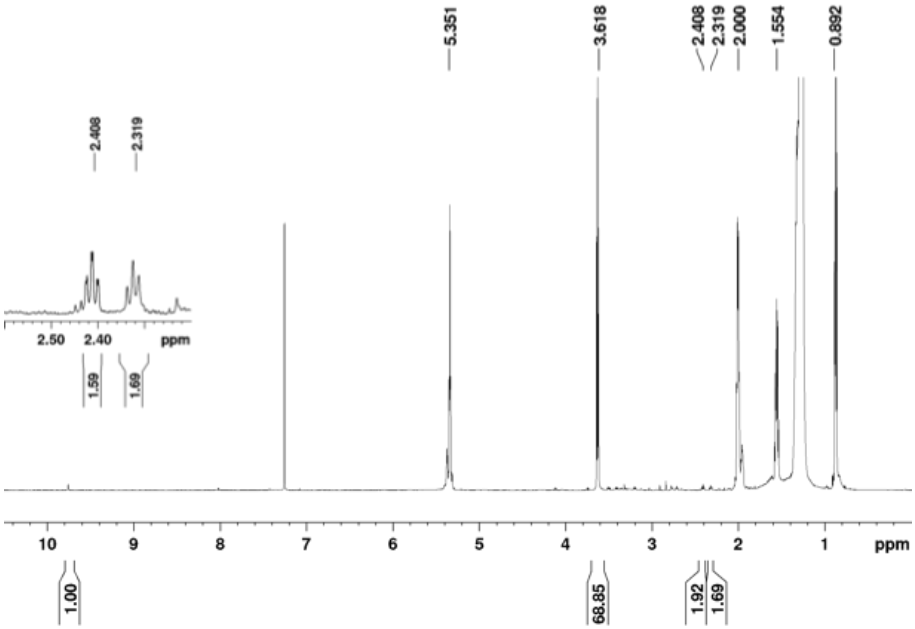

Figure S18. ^{1}H NMR of the crude product oxidized from oleyl alcohol (C18-OH) (20 mM) by C10-NO· (1 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 25 ^{o}C.

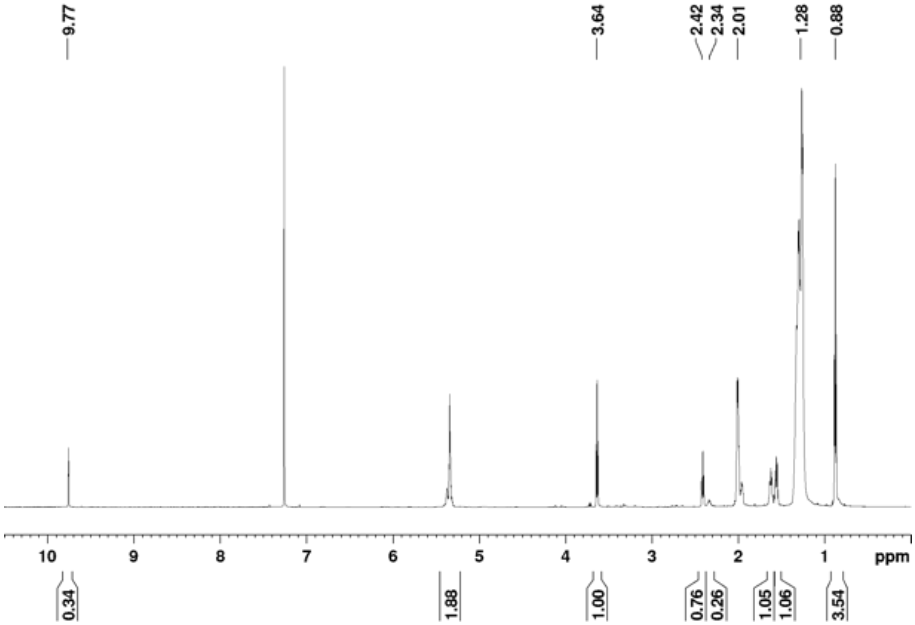

Figure S19. ^{1}H NMR of the crude product oxidized from oleyl alcohol (C18-OH) (20 mM) by C14-NO· (1 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 25 °C.

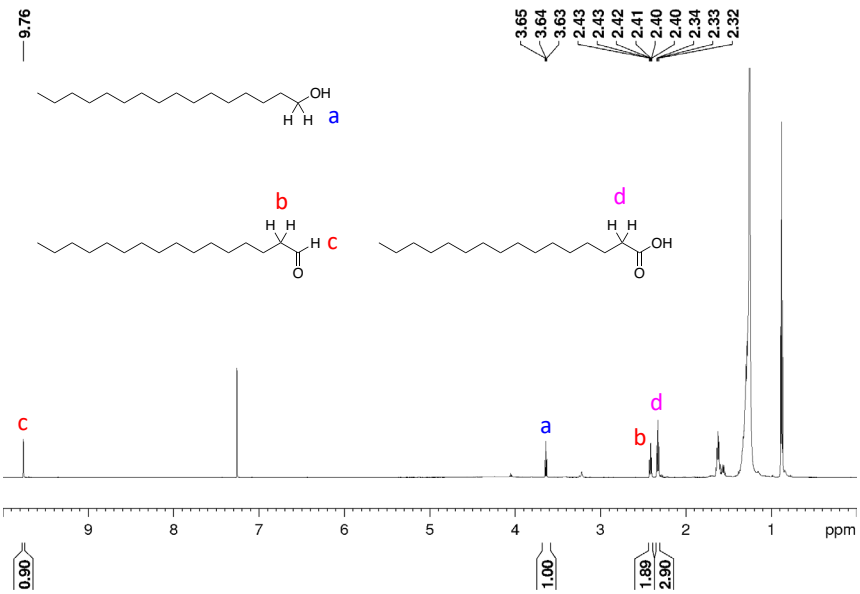

Figure S20. ^{1}H NMR of the crude product oxidized from C16-OH (100 mM) by C14-NO· (5 mM) in pH 10 buffer. Applied potential 0.9 V vs Ag/AgCl. Carbon felt 20 cm^{2} as the working electrode, Pt wire 16 cm as the counter electrode, Ag/AgCl as the reference electrode, and temperature 60 °C for 15 h.

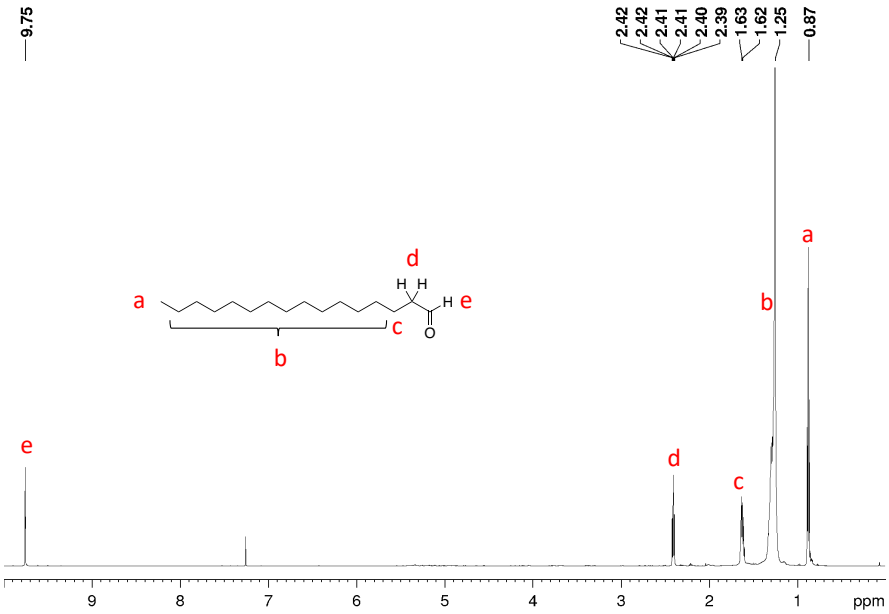

Figure S21. ^{1}H NMR of the purified hexadecanal (aldehyde from C16-OH) in $CDCl_3$.

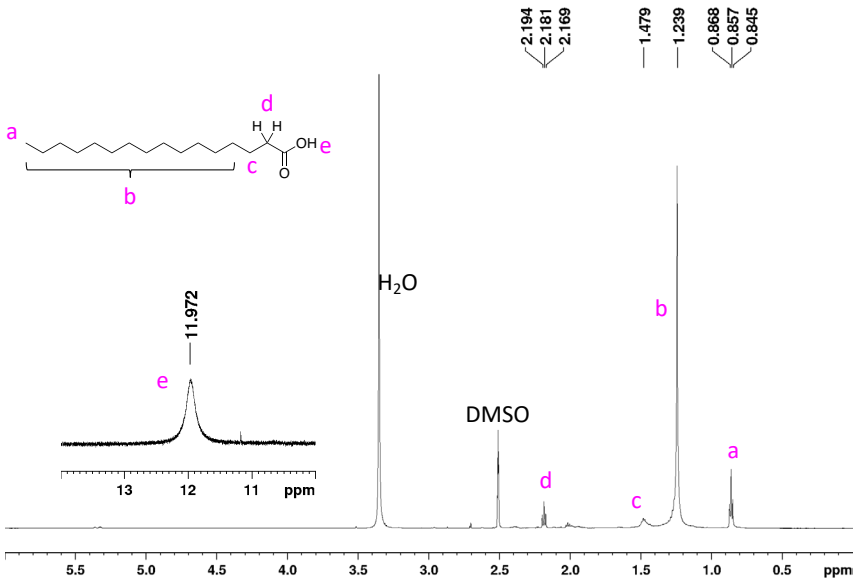

Figure S22. ^{1}H NMR of the purified hexadecanoic acid (carboxylic acid from C16-OH) in DMSO-d_6.