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Electronic Supplementary Information for

Electrochemical C–H oxygenation and alcohol dehydrogenation involving Fe-oxo species using water as the oxygen source

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1. General experimental details

Reagents:
All chemicals and solvents were purchased from commercially available sources and were used without further purification. (TAML)Fe was purchased from GreenOx Catalysts, Inc. and used as received. Acetonitrile was obtained from an LC Technology Solutions Inc. solvent purification system. Purified DI water (18 MΩ) was obtained with a Thermo Scientific Barnstead Nanopure filtration system. Electrolyte solutions were sparged 15-20 minutes with N_2 gas before use.

Instruments and Techniques:
^{1}H 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 in the ^{1}H NMR spectrum. High-resolution mass spectra were obtained using a Thermo Q ExactiveTM Plus by the mass spectrometry facility at the University of Wisconsin-Madison. Gas chromatographs were collected on a Shimadzu GC-2010 Gas Chromatograph. UV-visible spectra were recorded using an Agilent Technologies Cary 60 UV-visible spectrometer fitted with an Agilent Technologies Standard S.S. Absorption Probe. Chromatographic purification of products was accomplished by chromatography on Silicycle P60 silica gel (particle size 40-63 μm, 230-400 mesh) using Teledyne Isco Combiflash R_f or Biotage Isolera One flash chromatography systems.

All cyclic voltammetric and chronoamperometric measurements were carried out using a Pine WaveNow PGstat or BASi Epsilon potentiostat. 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. The potentials were measured against Ag/AgCl (3 M KCl) aqueous reference electrode. Spectroelectrochemical and bulk electrolysis experiments were performed in homemade divided cells with a sintered glass frit (Ace glass, porosity E) (see below). Reticulated vitreous carbon (RVC) or a graphite rod (5 mm diameter) was used for the working electrode material, a platinum wire was used for the counter electrode, and a Ag/AgCl (3 M KCl) was used for the reference electrode. Oxygen evolution measurements were done using a YSI 5331A Clark-type electrode interfaced with a 9 mL volume home-built cell (see below). RDE experiments were conducted using a BASi RDE-2 cell stand interfaced with a Pine WaveDriver 20 bipotentiostat.

Notes on Safety and Potential Hazards
Perchlorate (ClO_4^-) salts are potentially shock sensitive compounds and care must be taken when handling these reagents, particularly when used in the presence of organics,[1] and perchlorate is a potent thyroid hormone disruptor. Thus, the use of perchlorate salts should be minimized or avoided, where possible, and solutions containing perchlorate salts should not be concentrated.

Electrochemical Cells

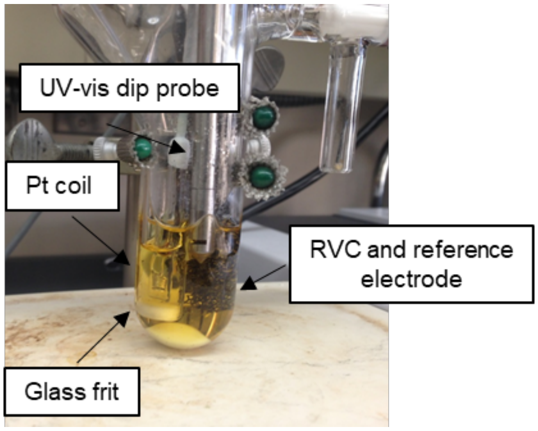


Figure S1. Spectroelectrochemical setup. Electrolysis cell is equipped with a low volume cathodic compartment separated from the anodic compartment with a glass frit.

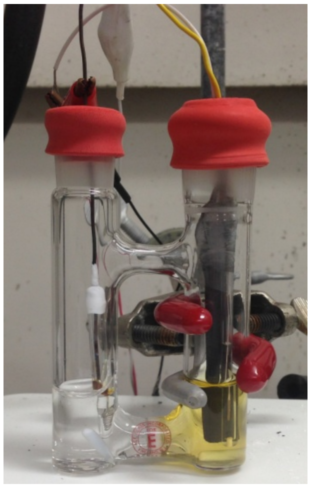


Figure S2. Divided H-type cell used for bulk electrolysis reactions.

Figure S3. Clark-type electrode interfaced with glass electrolysis cell.

2. (dpaq)Fe synthesis and characterization

Ligand synthesis, 2-[Bis(pyridine-2-ylmethyl)amino-*N*-quinolin-8-yl-acetamide (H-dpaq)

Following the reported procedure[2], to an acetonitrile solution (6 mL) of 8-aminoquinoline (302 mg, 2.1 mmol) and sodium carbonate (311 mg, 2.9 mmol), bromoacetyl bromide (508 mg, 2.5 mmol) was added dropwise under nitrogen. The resulting mixture was stirred for 20 min at 0 °C, after which, the solution was filtered through a Celite plug to remove the sodium carbonate. The filtrate was removed *in vacuo* to give a pink powder. To a solution of the powder dissolved in acetonitrile (12 mL) cooled to 0 °C, sodium carbonate (311 mg, 2.9 mmol) and *N*,*N*-dipicoylamine (0.45 mL, 2.5 mmol) were added under nitrogen. The mixture was stirred overnight at 0 °C, after which, the solution was filtered through a Celite plug to remove the sodium carbonate. The filtrate was removed *in vacuo* to give a yellow oil which was purified by flash column chromatography (20% ethyl acetate in pentane to 100% ethyl acetate) to give a yellow powder. Yield 543 mg (67% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.60 (s, 1H), 8.94 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.77 (dd, *J* = 5.8, 3.2 Hz, 1H), 8.52 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 2H), 8.20 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.98 (dt, *J* = 7.8, 1.1 Hz, 2H), 7.65 (td, *J* = 7.7, 1.8 Hz, 2H), 7.58 – 7.48 (m, 3H), 7.15 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 2H), 4.02 (s, 4H), 3.54 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.73, 158.42, 149.30, 148.19, 139.04, 136.74, 136.50, 134.56, 128.27, 127.63, 123.51, 122.51, 121.81, 121.75, 116.76, 61.27, 59.48. Spectra match literature values. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{23}H_{21}N_5O$) requires m/z 384.1819, found m/z 384.1808, difference 2.9 ppm.

Fe complex synthesis, $[Fe^{III}(dpaq)(H_2O)](ClO_4)_2\cdot H_2O$

Following the reported procedure,[2] $Fe^{III}(ClO_4)_3\cdot 6H_2O$ (110 mg, 0.31 mg) and methanol (1 mL) was added to a glass scintillation vial. The resulting yellow solution was then added to a second vial containing H-dpaq (100 mg, 0.26 mmol) in methanol (1 mL) at room temperature. To the mixture was added triethylamine (0.036 mL, 0.26 mmol). The mixture became green and was allowed to stand overnight. The green precipitate was collected and dried by vacuum filtration. Yield 130 mg (75%). UV-vis (CH_3CN): 367 nm, 831 nm. HRMS (ESI) exact mass calculated for $[M + OCH_3 - OH_2]^+$ 469.1201, found m/z 469.1190, difference 2 ppm.

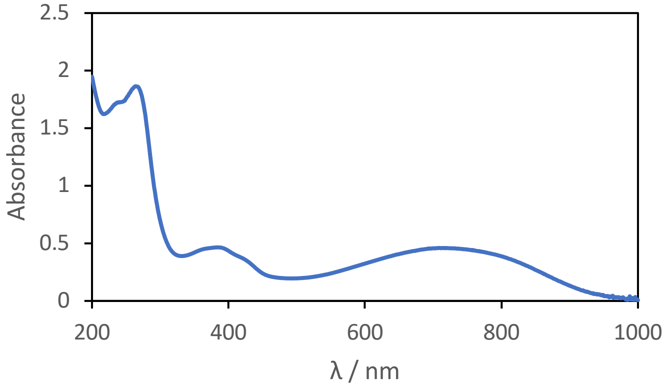


Figure S4. UV-Vis spectrum of synthesized $(dpaq)Fe^{III}H_2O$ in CH_3CN.

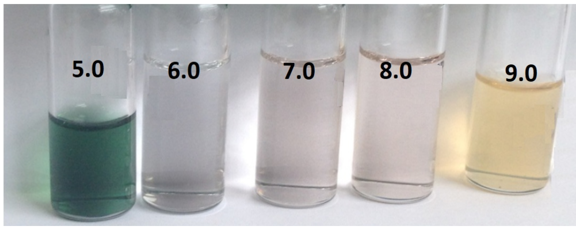


Figure S5. Stability of (dpaq)Fe^{III} at various solution pH, 1:1 H_2O:CH_3CN, 0.1 M phosphate buffer. At pH > 5, the green color of (dpaq)Fe disappears, indicating decomposition of the complex.

3. Clark electrode analysis of (TAML)Fe catalyzed water oxidation

To a homemade glass cell interfaced with a Clark electrode was added (TAML)Fe with the appropriate electrolyte. While the solution was stirring, Clark electrode analysis was initiated with the working electrode set to -800 mV. After the current from the Clark electrode stabilized, the electrolyte solution containing (TAML)Fe was sparged until the Clark electrode current approached 0 µA and stabilized. At that point, the glass cell was fit with a three-electrode setup. A graphite rod was used for the working electrode, a Pt wire housed in a glass cylinder open to the electrolyte solution was used as the counter electrode, and an Ag/AgCl reference electrode was used. Electrolysis at 1250 mV vs. Ag/AgCl was initiated at the three-electrode setup. O_2 evolution was monitored during this electrolysis by the Clark electrode. Figures S6 and S7 demonstrate that O_2 can be detected quantitatively by the Clark electrode in a non-aqueous solvent. Figures S8 and S9 show that no O_2 evolution is observed during the electrolysis of (TAML)Fe under the conditions employed for electrochemical oxidation of organic molecules.

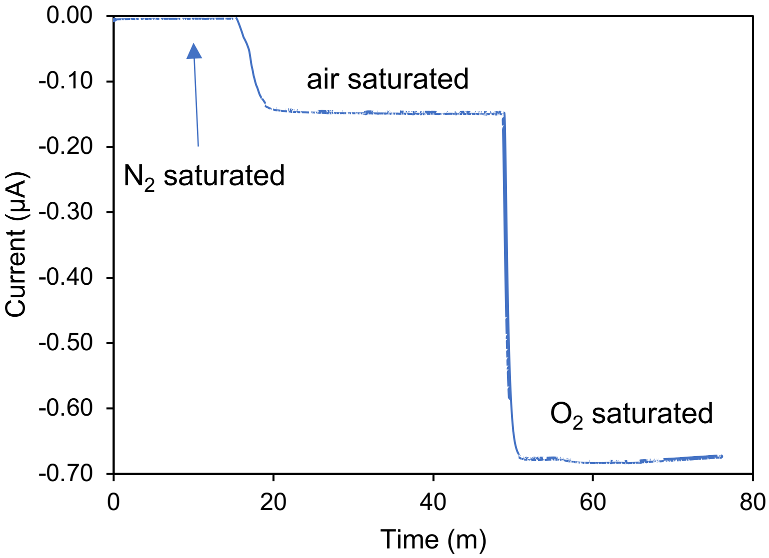


Figure S6. Clark electrode current trace calibrating O_2 content in CH_3CN.

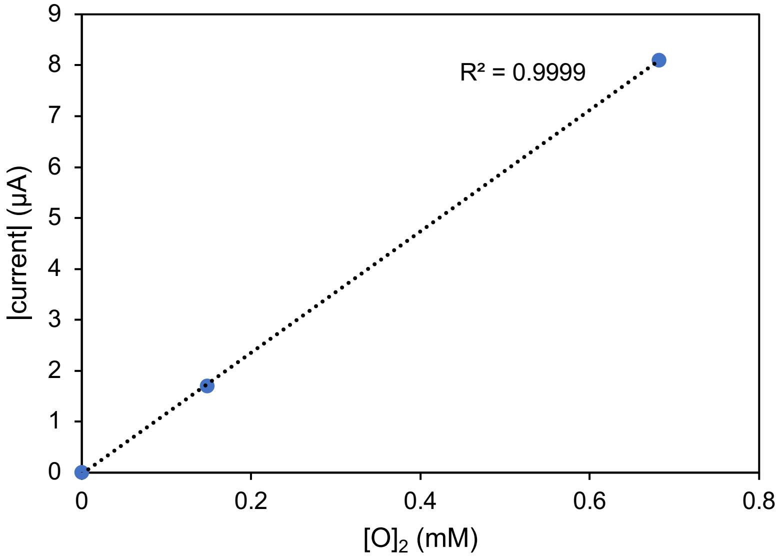


Figure S7. Measured Clark electrode current plotted against concentration of O_2 in N_2 saturated CH_3CN, air saturated CH_3CN, and O_2 saturated CH_3CN.

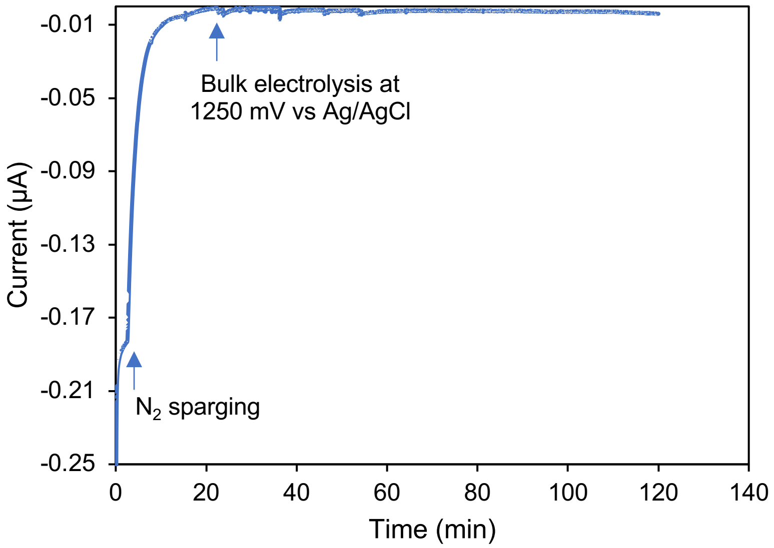


Figure S8. Clark electrode current trace during bulk electrolysis of 1 mM (TAML)Fe. Electrolyte 0.1 M K_2HPO_4, 1:1 CH_3CN:H_2O. No O_2 evolution was observed under reaction conditions, indicating that under conditions used for electrocatalytic C–H oxygenation (see below), (TAML)Fe does not catalyze background water oxidation.

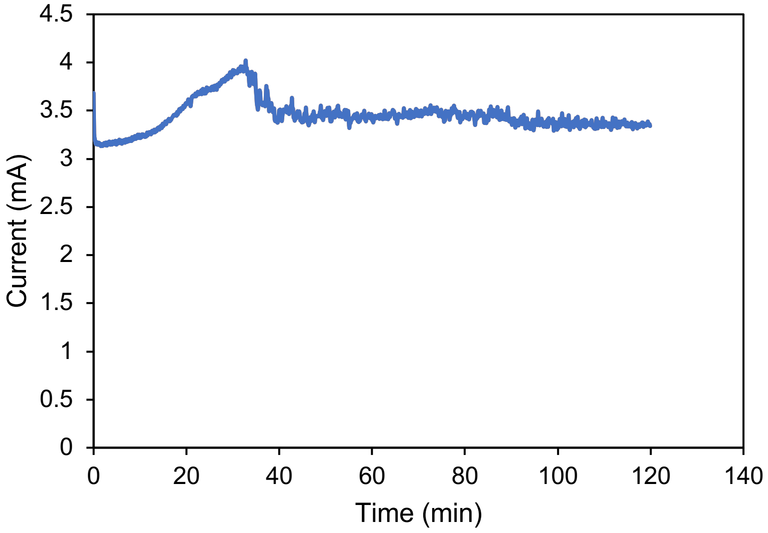


Figure S9. Graphite working electrode current trace during bulk electrolysis of 1 mM (TAML)Fe for Clark electrode analysis. Electrolyte 0.1 M K_2HPO_4, 1:1 CH_3CN:H_2O.

4. Stability of (TAML)Fe at varied pH

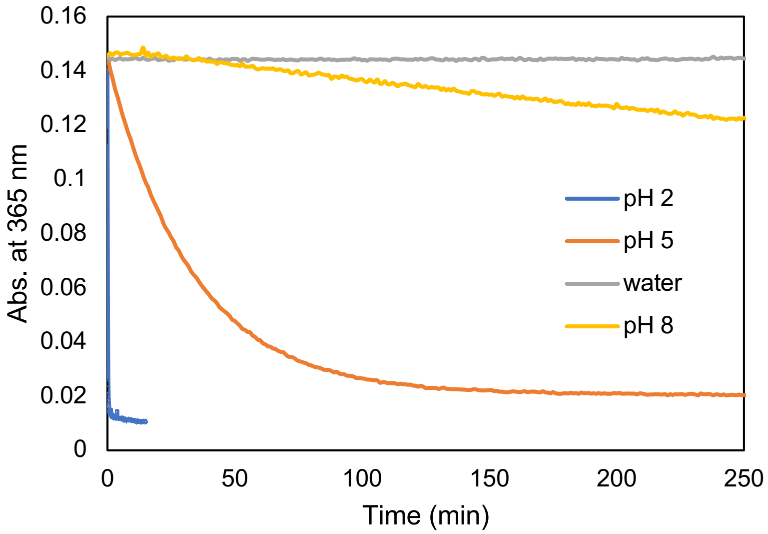


Figure S10. Measured absorbance at 365 nm vs. time for 1 mM (TAML)Fe in aqueous solutions of varied pH. Solutions consist of 10 mM $HClO_4$ (pH 2), 0.1 M NaOAc (pH 5), and 0.1 M K_2HPO_4 (pH 8). These data show that (TAML)Fe has moderate stability in a pH 8 buffer, but quickly decomposes at lower pH.[3]

5. CV analysis of (TAML)Fe with titrated CH_3CN and CD_3CN

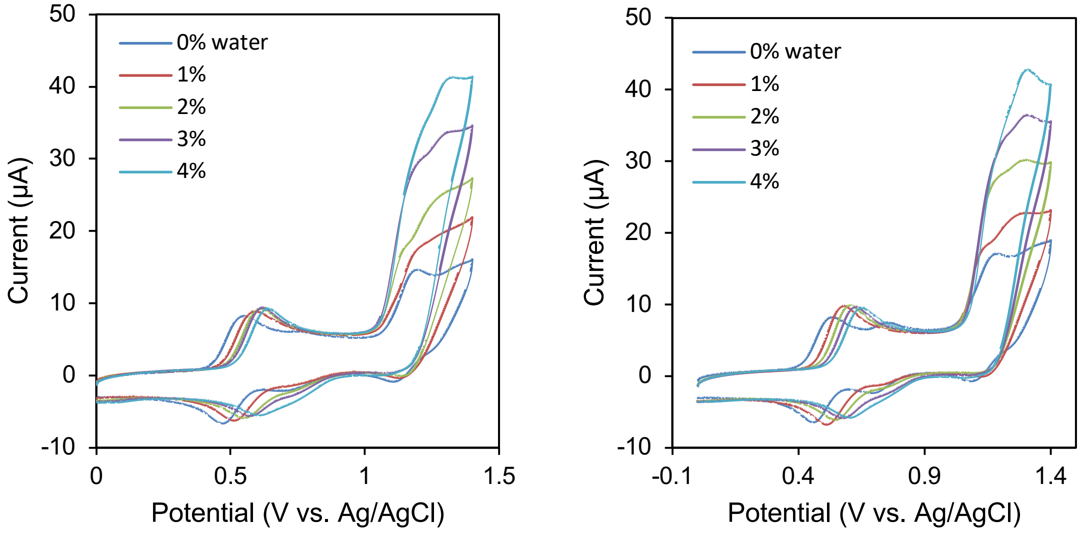


Figure S11. Left: CVs of 0.5 mM (TAML)Fe in 50 mM *n*$Bu_4N[PF_6]$ CH_3CN. Right: CVs of 0.5 mM (TAML)Fe in 50 mM *n*$Bu_4N[PF_6]$ CD_3CN. To the solution of (TAML)Fe, aliquots of water were added to give reported volume. Scan rate = 50 mV/s. Upon addition of water, the redox feature at ca. 0.5 V shifts to higher potentials, indicating a less facile redox process in the precense of water. The redox feature at ca. 1.2 V instead shifts to lower potentials upon addition of water, indicating that the corresponding redox process becomes easier in the presene of water. The similar currents observed in CH_3CN and CD_3CN for the high potential redox feature further indicates that acetonitrile is not oxidized by high valent (TAML)Fe species.[4]

6. CV analysis of (TAML)Fe with titrated phosphate

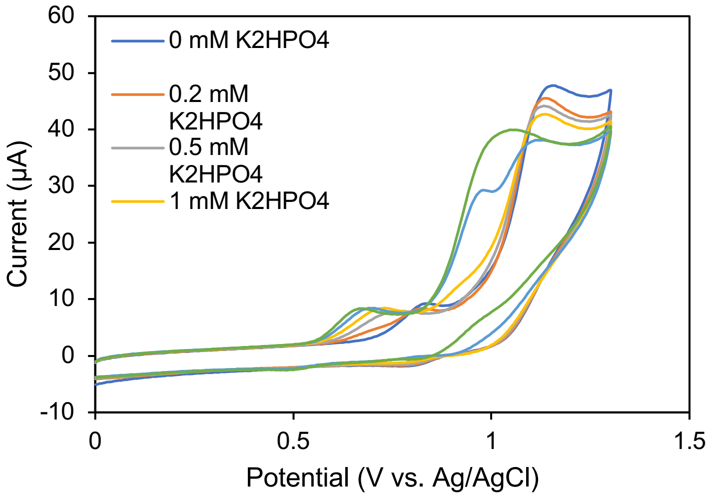


Figure S12. CVs of 0.5 mM (TAML)Fe in 0.1 M $NaClO_4$, H_2O. To the solution of (TAML)Fe was added aliquots of 0.1 M K_2HPO_4 to give the reported concentration. A third peak at ca. 980 mV grows in upon addition of K_2HPO_4, indicating that the redox feature at 980 mV is likely due to redox of a phosphate-coordinated (TAML)Fe species.[3] Scan rate = 50 mV/s.

7. CV analysis of (TAML)Fe in aqueous solution with titrated CH_3CN

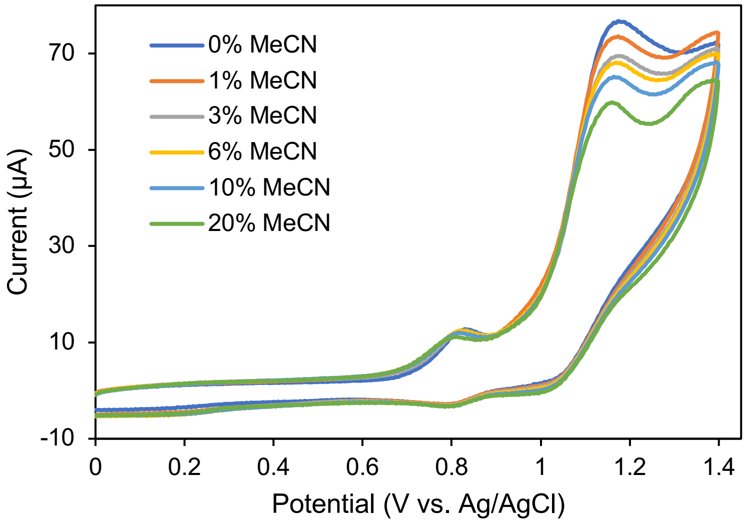


Figure S13. CVs of 1 mM (TAML)Fe in 0.1 M KPF_6, H_2O. To the solution of (TAML)Fe was added aliquots of CH_3CN to give the reported volume percentages. No new redox features appear following addition of CH_3CN, indicating that the redox feature at 980 mV in Figure S14 does not arise from a CH_3CN-coordinated (TAML)Fe species. Scan rate = 50 mV/s.

8. Rotating Disk Voltammetry of (TAML)Fe under bulk electrolysis conditions

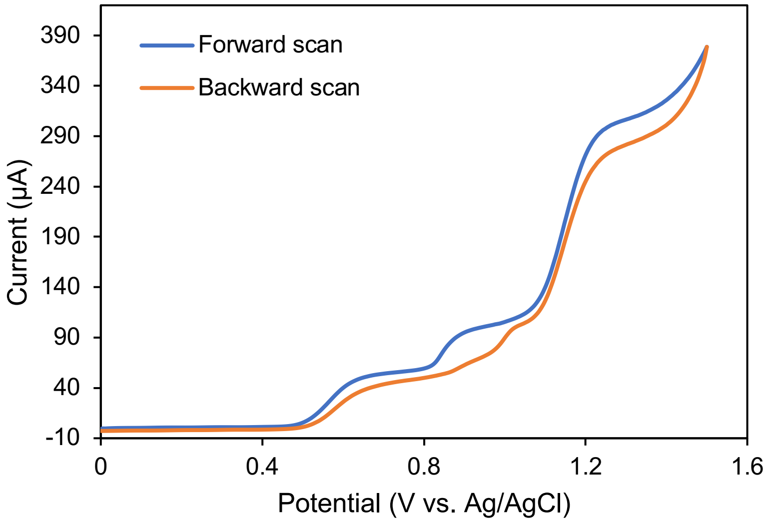


Figure S14. Rotating disk voltammograms of 2 mM (TAML)Fe in 0.1 M K_2HPO_4, 1:1 CH_3CN:H_2O. The potential for the forward scan was scanned from 0 to 1500 mV, while the potential for the reverse scan was scanned from 1500 to 0 mV. The electrode rotor speed was set to 1000 RPM. Scan rate = 50 mV/s. The absence of a redox feature in the reverse scan at ca. 0.9 V indicates that the species involved with this redox feature are not required intermediates for the regeneration of the (TAML)Fe^{III}–OH_2 from the species generated at potentials > 1.1 V.

9. Spectroelectrochemistry of (TAML)Fe under bulk electrolysis conditions

To a homemade divided cell, 12 mL of a solution of (TAML)Fe (0.5 mM) in 0.1 M K_2HPO_4, 1:1 CH_3CN:H_2O and a Teflon-coated stir bar were added to the anodic compartment. A solution of 0.1 M K_2HPO_4, 1:1 CH_3CN:H_2O was added to the cathodic compartment such that the electrolyte level for the anodic and cathodic compartments were level. A rubber septum fitted with a RVC working electrode, Pt coil counter electrode, and Ag/AgCl (3 M NaCl) reference electrode was inserted into the cell. The solution in the cell was sparged with bubbling N_2 for 20 minutes through a side arm in the electrolysis cell. After the cell was sparged, the dip probe apparatus was inserted into the cell (see Fig. S1). While the solution was stirring, controlled potential electrolysis was initiated at the reported potential. Immediately after commencing electrolysis, UV-vis analysis was initiated. The experiment was conducted for 30 minutes total. After the experiment, the cell, electrodes, and probe were rinsed by water and acetone and was then air dried. The same RVC electrode and stock solution of (TAML)Fe were used for the spectroelectrochemical experiment to ensure the identical electrode surface area and [(TAML)Fe].

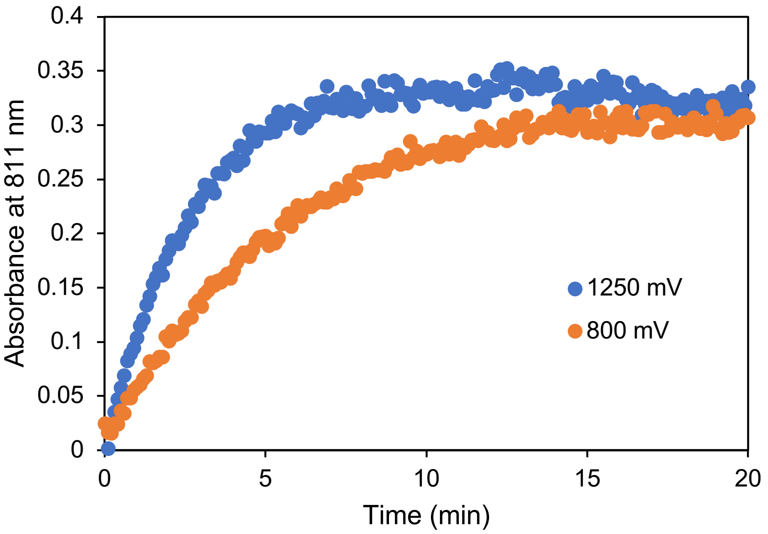


Figure S15. Measured absorbance at 811 nm vs. time for the spectroelectrochemical oxidation of (TAML)Fe in 0.1 M K_2HPO_4, 1:1 CH_3CN: H_2O.

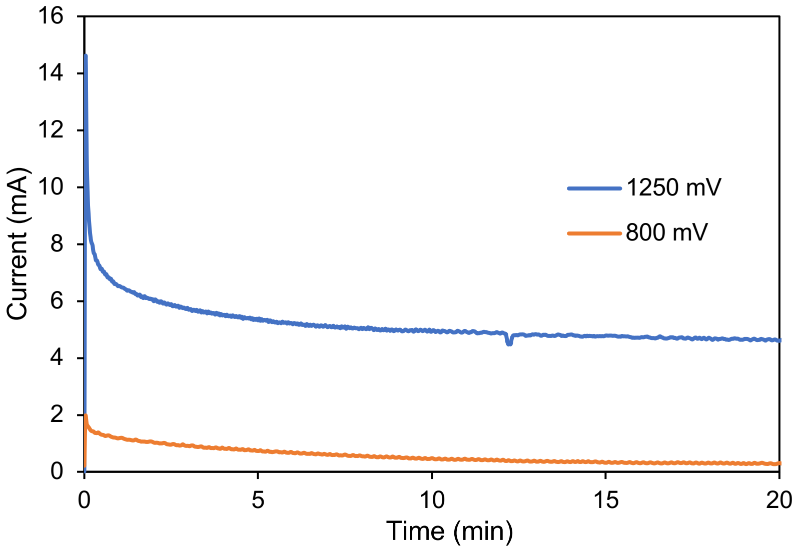


Figure S16. Bulk electrolysis traces for the spectroelectrochemical oxidation of (TAML)Fe in 0.1 M K_2HPO_4, 1:1 CH_3CN: H_2O.

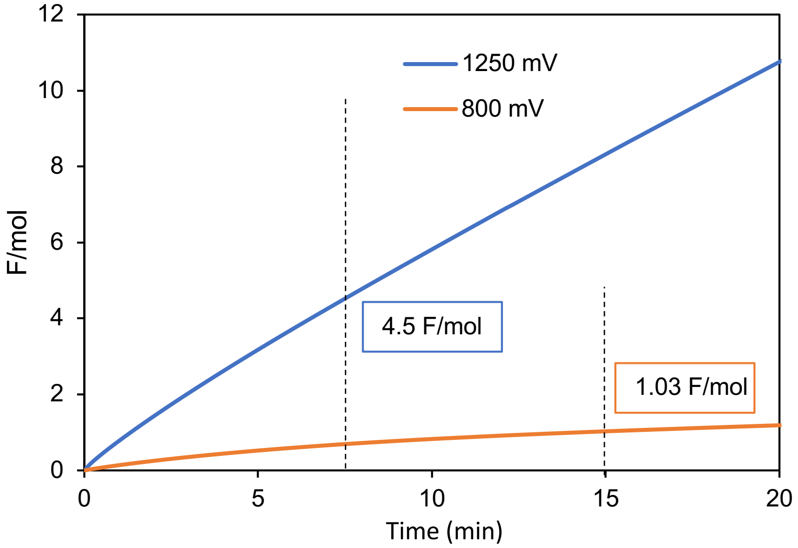


Figure S17. Charge passed (determined for 1 equiv of electrons relative to (TAML)Fe) for the spectroelectrochemical oxidation of (TAML)Fe in 0.1 M K_2HPO_4, 1:1 CH_3CN:H_2O. After 15 minutes at an applied potential of 800 mV, sufficient charge has passed (1 F/mol) to convert $[(TAML)Fe^{III}(OH_2)]^-$ to $[(TAML)Fe^{IV}(OH)]^-$ and the current begins to decrease. After 7.5 min of electrolysis at 1250 mV, the measured absorbance at 811 nm reaches a maximum value. At this time, the 4.5 F/mol of charge has passed, exceeding the charge required to convert $[(TAML)Fe^{III}(OH_2)]^-$ to $[(TAML)Fe^{IV}(OH)]^-$ (1 F/mol) or a $(TAML)Fe^V$ species (2 F/mol). This excess charge is attributed to background oxidation reactions (e.g. ligand oxidation) that involve catalytic regeneration of Fe^V.

10. Oxidative decomposition of (TAML)Fe during bulk electrolysis

To determine if (TAML)Fe undergoes oxidative decomposition during electrolysis, a solution of (TAML)Fe was subjected to bulk electrolysis conditions in the absence of substrate. The resulting organic-soluble fraction of the electrolysis solution was analyzed by ^{1}H NMR spectroscopy and compared to the organic-soluble fraction of a solution of (TAML)Fe that was not subjected to bulk electrolysis.

To the anodic compartment of an H-type divided cell was added a magnetic stir bar and 0.016 mmol (TAML)Fe. A septum fitted with an RVC electrode and Ag/AgCl reference electrode was inserted into the anodic compartment. A septum fitted with a platinum wire electrode was inserted into the anodic compartment. The cell was purged with N_2. A solution of 1:1 CH_3CN:H_2O with 0.1 M K_2HPO_4 was sparged with bubbling N_2 for 30 min. To the anodic and cathodic cells were added 8 mL of the degassed solvent. The reaction was stirred at 700 RPM. Constant potential electrolysis was performed at 1250 mV (vs. Ag/AgCl) for 10 hours (current decays to ~10% original current). When the electrolysis was stopped, the anolyte was acidified with conc. HCl (~ 10 drops) and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and filtered through a glass wool plug. The solvent was then removed *in vacuo*. The resulting residue was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR spectroscopy. No aromatic residues corresponding to the TAML ligand were observed (Fig. S18A), indicating oxidative decomposition of the TAML ligand.

To a 12 mL vial was added a magnetic stir bar and 0.016 mmol (TAML)Fe. A solution of 1:1 CH_3CN:H_2O with 0.1 M K_2HPO_4 was sparged with bubbling N_2 for 30 min. To the vial was added 8 mL of the degassed solvent. The reaction was stirred at 700 RPM. After 12 h, the solution was acidified with conc. HCl (~ 10 drops) and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and filtered through a glass wool plug. The solvent was then removed *in vacuo*. The resulting residue was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR. Peaks corresponding to TAML ligand were observed (Fig. S18B). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (s, 2H), 7.74 (s, 2H), 7.46 (dd, J = 6.0, 3.6 Hz, 2H), 7.16 (dd, J = 6.1, 3.5 Hz, 2H), 1.47 (s, 12H), 1.44 (s, 6H).[5]

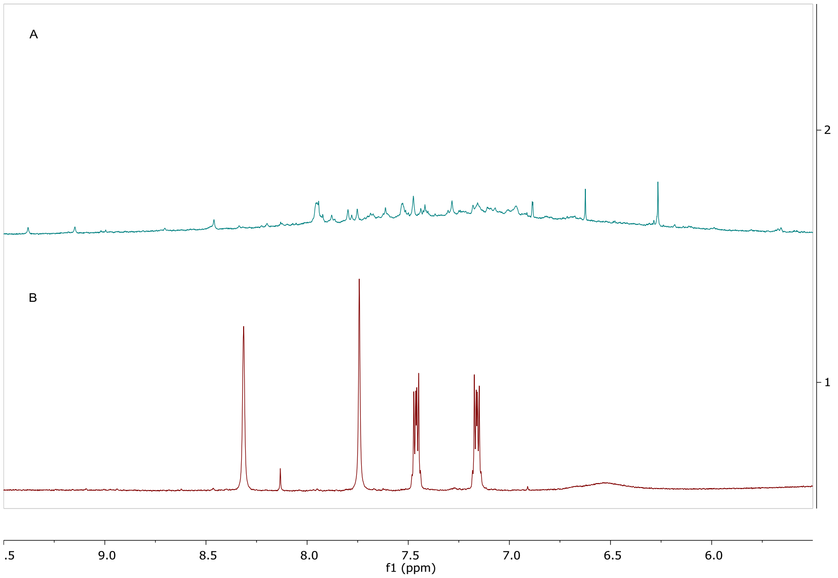
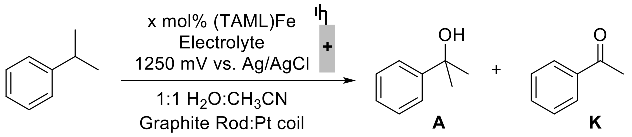


Figure S18. A) Aromatic region in the ^{1}H NMR spectrum of the organic soluble fractions for the (TAML)Fe solution subjected to bulk electrochemical oxidation at 1250 mV, and B) Corresponding aromatic region in the NMR spectrum of the organic soluble fractions for the (TAML)Fe solution that was not subjected to bulk electrochemical oxidation.

11. Time course studies for electrochemical (TAML)Fe-catalyzed ethylbenzene and 1-phenylethanol oxidation (cf. Figure 4)

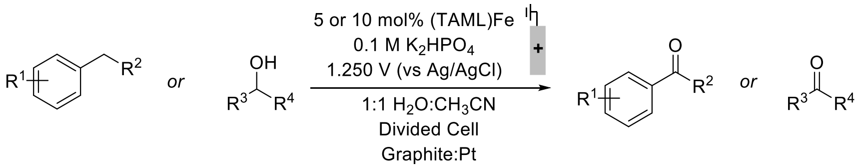
To the anodic compartment of an H-type divided cell was added a magnetic stir bar and 0.012 mmol (TAML)Fe. A septum fitted with an RVC electrode and Ag/AgCl reference electrode was inserted into the anodic compartment. A septum fitted with a platinum wire electrode was inserted into the anodic compartment. The cell was purged with N_2. A solution of 1:1 $CH_3CN:H_2O$ with 0.1 M K_2HPO_4 was sparged with bubbling N_2 for 30 min. To the anodic and cathodic cells were added 6 mL of the degassed solvent. Ethylbenzene (0.12 mmol, 20 mM) or 1-phenylethanol (0.12 mmol, 20 mM) was added via syringe followed by addition of bromobenzene (internal standard). The reaction was stirred at 700 RPM. Constant potential electrolysis was performed at 1250 mV or 800 mV (vs. Ag/AgCl) for 10 hours (current decays to ~10% original current). At given time points, 30-40 µL aliquots of the anolyte were removed from the anodic chamber with a syringe. The aliquots were transferred to a dram vial containing 1:1 ethyl acetate:brine. The organic layer was removed for analysis by GC. After 10 h electrolysis at 1250 mV, 73% aceteophenone and 1% 1-phenylethanol were detected relative to ethylbenzene (93% conversion). After 10 h of electrolysis at 800 mV, 11% acetophenone and 11% 1-phenylethanol were detected relative to ethylbenzene (28% conversion). For the oxidation of 1-phenylethanol, quantitative conversion to acetophenone was observed after 10 h electrolysis at both 1250 mV and 800 mV.

12. Optimization for electrochemical (TAML)Fe catalyzed C–H oxidation



Entry	x	Cell Type	Electrolyte	MB (%)	A:K	Yield (A+K) (%)
1	5	Undivided	0.1 M Phosphate Buffer, pH 7	85	-	n.d.
2	5	Divided	0.1 M Phosphate Buffer, pH 7	60	4:1	10
3	5	Divided	0.1 M Phosphate Buffer, pH 8	65	2:1	30
4	5	Divided	0.1 M K_3PO_4	60	4:1	23
5	5	Divided	0.1 M K_2HPO_4	67	4:1	52
6	10	Divided	0.1 M K_2HPO_4	70	4:1	63
7	0	Divided	0.1 M K_2HPO_4	80	-	n.d.

13. Bulk electrolysis procedure for (TAML)Fe catalyzed C–H oxidation and alcohol dehydrogenation and characterization of relevant products



For substrates with a low boiling point:

To the anodic compartment of an H-type divided cell was added a magnetic stir bar and (TAML)Fe. For C–H oxidation reactions, 0.1 mmol (TAML)Fe was used; for alcohol dehydrogenation reactions, 0.05 mmol (TAML)Fe was used. A septum fitted with a graphite rod electrode and a Ag/AgCl reference electrode was inserted to the anodic compartment. A septum fitted with a platinum wire electrode was inserted into the cathodic compartment. The cell was purged with N_2. A solution of 1:1 $CH_3CN:H_2O$ with 0.1 M K_2HPO_4

was sparged with bubbling N_2 for 30 min. To the anodic and cathodic cells were added 5 mL of the degassed solvent. Substrate (0.1 mmol, 20 mM) was added via syringe followed by addition of bromobenzene (internal standard). The reaction was stirred at 700 RPM. Constant potential electrolysis was performed at 1250 mV (vs. Ag/AgCl) for 10 hours (current decays to ~10% original current).

Following electrolysis, the anolyte was transferred to a dram vial. The anolyte was extracted with 3 mL ethyl acetate. A portion of the organic layer was removed and analyzed by GC.

For substrates with a high boiling point:
To the anodic compartment of an H-type divided cell was added a magnetic stir bar, (TAML)Fe, and substrate (0.1 mmol). For C–H oxygenation reactions, 0.1 mmol (TAML)Fe was used; for alcohol dehydrogenation reactions, 0.05 mmol (TAML)Fe was used. A septum fitted with a graphite rod electrode and a Ag/AgCl reference electrode was inserted to the anodic compartment. A septum fitted with a platinum wire electrode was inserted into the cathodic compartment. The cell was purged with N_2. A solution of 1:1 CH_3CN:H_2O with 0.1 M K_2HPO_4 was sparged with bubbling N_2 for 30 min. To the anodic and cathodic cells were added 5 mL of the degassed solvent. The reaction was stirred at 700 RPM. Constant potential electrolysis was performed at 1250 mV (vs. Ag/AgCl) for 10 hours (current decays to ~10% original current).

Following electrolysis, the anolyte was transferred to a dram vial containing 1,3,5-trimethoxybenzene as the internal standard. The anodic cell was rinsed with ethyl acetate, and the rinsing solution was added to the anolyte. The anolyte was extracted with 3 mL ethyl acetate. The organic layer was dried over $MgSO_4$ and filtered through a glass wool plug. The solvent was then removed *in vacuo*. The resulting residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy.

The product identity for the C–H oxidation or alcohol dehydrogenation reaction was confirmed via product isolation. Following electrolysis, the anolyte was transferred to a separatory funnel. The aqueous portion was extracted with ethyl acetate (3x15 mL). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo*. If the resulting material was not of sufficient purity, the dried material was purified by flash column chromatography. The chromatography conditions are specified for the characterized products.

14. Typical bulk electrolysis trace for (TAML)Fe catalyzed C–H oxidation

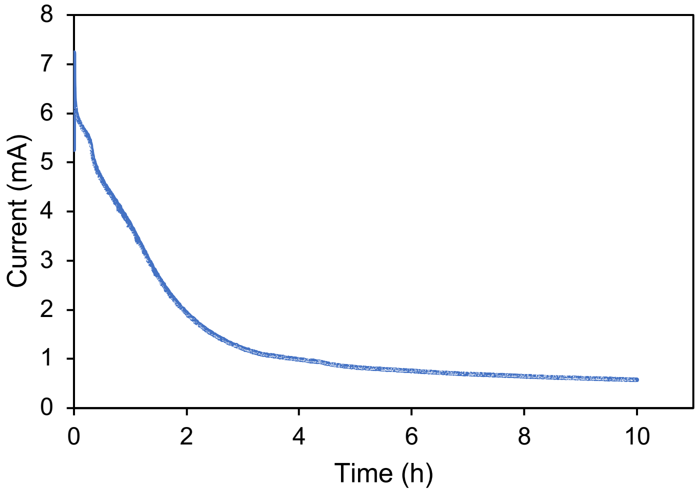


Figure S19. Typical bulk electrolysis traces for C-H oxidation reaction.

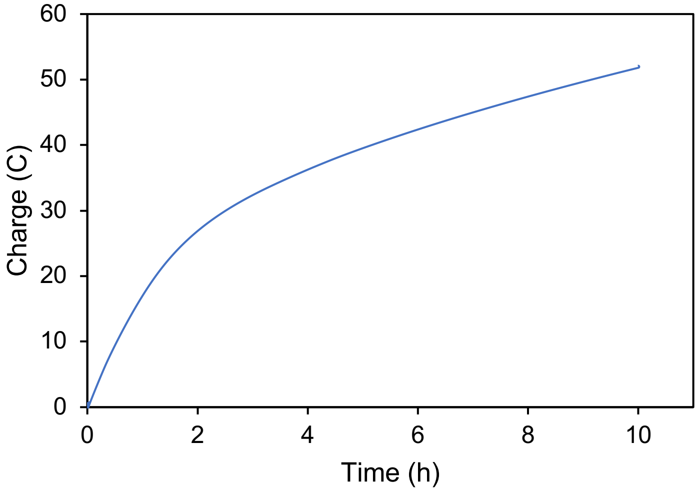


Figure S20. Charge passed during bulk electrolysis experiment in Fig. S19.

15. CVs of electron-rich substrates

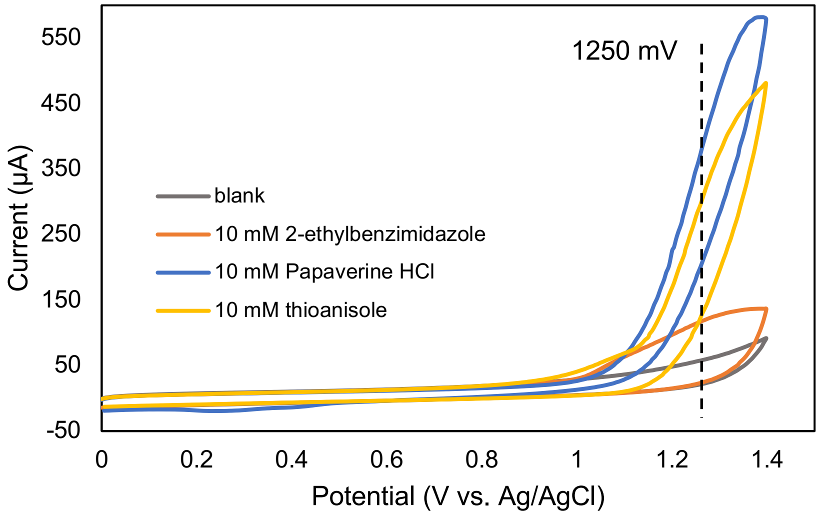
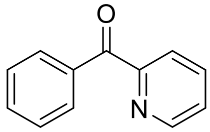
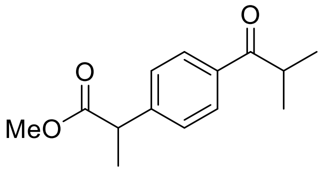


Figure S21. CVs of 2-ethylbenzimidazole, papaverine HCl, and thioanisole in 0.1 M K_2HPO_4, 1:1 CH_3CN:H_2O. The applied potential for the (TAML)Fe-catalyzed bulk electrolysis procedure (1250 mV vs. Ag/AgCl) is marked. These substrates would undergo undesired direct electrochemical oxidation at the potentials required to oxidize the (TAML)Fe catalyst. Scan rate = 100 mV/s.

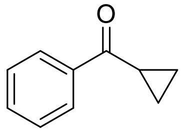
16. Characterization of compounds assayed by NMR spectroscopy



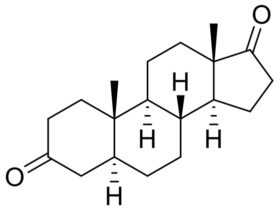
Phenyl(pyridine-2-yl)methanone.[6] Chromatography with 5% ethyl acetate in pentane to 20% ethyl acetate in pentane gradient to give a colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.73 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1H), 8.10 – 8.01 (m, 3H), 7.91 (td, *J* = 7.7, 1.8 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.53 – 7.45 (m, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 194.03, 155.23, 148.69, 137.19, 136.39, 133.06, 131.11, 128.30, 126.29, 124.77. HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{12}H_9NO$) requires m/z 184.0757, found m/z 184.0757, difference < 0.1 ppm.



Methyl-2-[4-(2-methylpropanoyl)phenyl]propanoate.[7] Chromatography with 5% ethyl acetate in pentane to 60% ethyl acetate in pentane gradient to give a colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 3.79 (q, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 3.53 (hept, *J* = 6.8 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 204.09, 174.45, 145.58, 135.26, 128.90, 127.94, 52.35, 45.54, 35.48, 19.29, 18.56. HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{14}H_{19}O_3$) requires m/z 235.1329, found m/z 235.1328, difference 0.4 ppm.



Cyclopropyl phenyl ketone.[8] Chromatography with 30% ethyl acetate in pentane to give a colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.0 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 0H), 7.48 (t, *J* = 7.6 Hz, 1H), 2.68 (m, 1H), 1.28 – 1.22 (m, 2H), 1.05 (m, 2H).^{13}C NMR (126 MHz, CDCl$_3$) δ 200.80, 138.14, 132.85, 128.63, 128.14, 17.28, 11.81. HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{10}H_{11}O$) requires m/z 147.0804, found m/z 147.0803, difference 0.7 ppm.



Androstanedione.[9] Chromatography with 5% ethyl acetate in pentane to 30% ethyl acetate in pentane gradient to give a colorless solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.49 – 2.23 (m, 4H), 2.15 – 1.91 (m, 4H), 1.83 (dq, *J* = 13.8, 3.8 Hz, 2H), 1.70 (dq, *J* = 9.3, 3.4 Hz, 1H), 1.65 – 1.49 (m, 3H), 1.45 – 1.22 (m, 6H), 1.03 (s, 3H), 1.06 – 0.96 (dq, *J* = 12.4, 5.0 Hz, 1H), 0.88 (s, 3H), 0.80 (td, *J* = 11.7, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 221.06, 211.74, 54.02, 51.37, 47.87, 46.74, 44.73, 38.58, 38.22, 35.96, 35.95, 35.09, 31.62, 30.67, 28.75, 21.93, 20.85, 13.95, 11.61. HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{19}H_{29}O_2$) requires m/z 289.2162, found m/z 289.2158, difference 1.2 ppm.

17. References

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5. Horwitz, C. P.; Ghosh, A. Synthesis of macrocyclic tetraamido compounds and new metal insertion process. U.S. Patent 7,060,818, June 13, 2006.
6. De Houwer, J.; Abbaspour Tehrani, K.; Maes, B. U. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 2745–2748.
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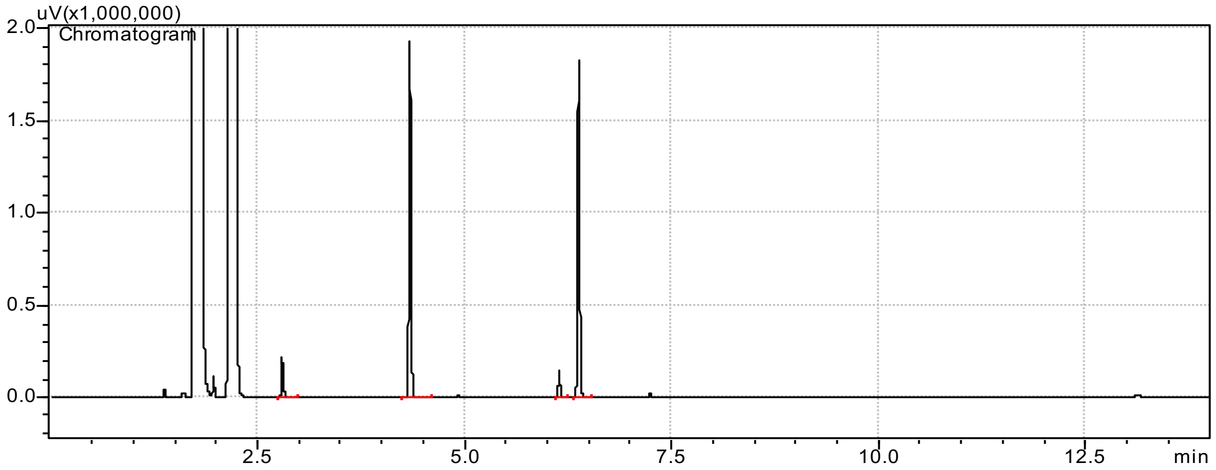
9. Kamijo, S.; Tao, K.; Takao, G.; Tonoda, H.; Murafuji, T. *Org. Lett*. **2015**, *17*, 3326–3329.

18. GC traces

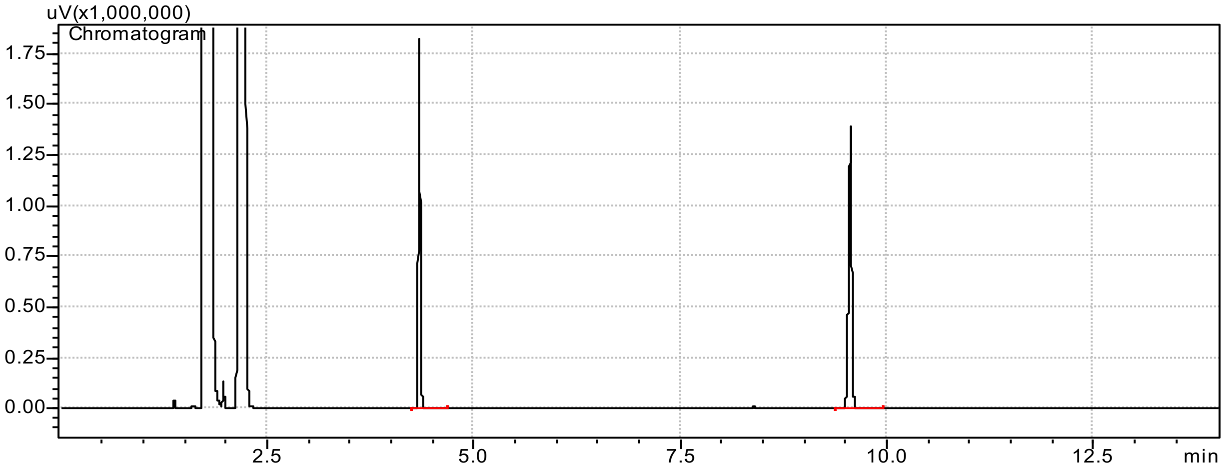
a. Ethylbenzene oxidation



	RT (min)	Response Factor
Ethylbenzene	2.8	1.23
Acetophenone	6.3	1.37
1-Phenylethanol	7.2	1.13
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
2.795	372921.1	217200.7	5.5022
4.339	3140830.5	1903957.3	46.3406
6.143	226137.5	141815.4	3.3365
6.378	3037819.3	1806129	44.8207
7.246	21543	10501.2	0.681

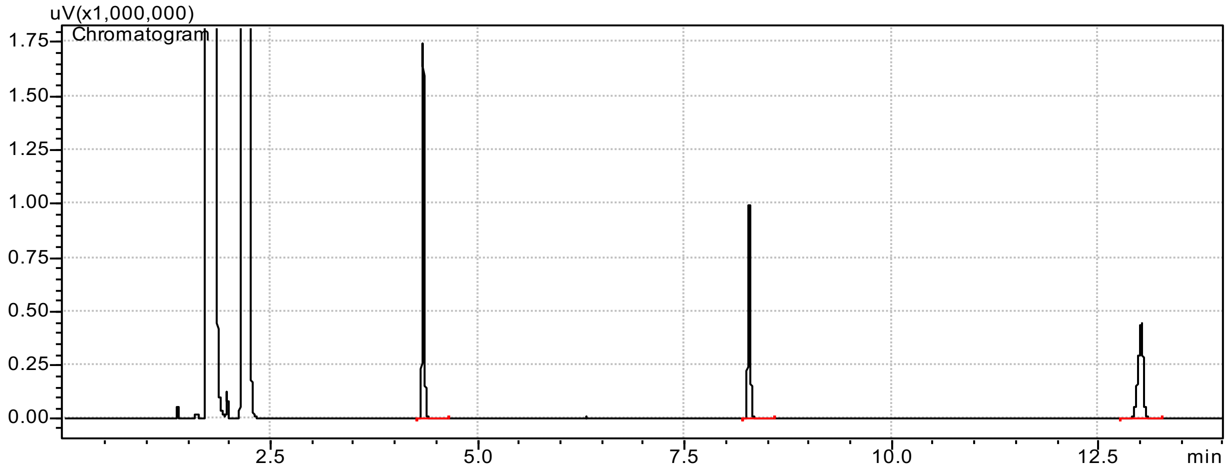
b. 4-Ethylanisole oxidation



	RT (min)	Response Factor
4-Ethylanisole	5.6	1.45
4-Methoxyacetophenone	9.6	1.41
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
4.341	2929670	1771729.8	44.2775
9.559	3686944.7	1382394.7	55.7225

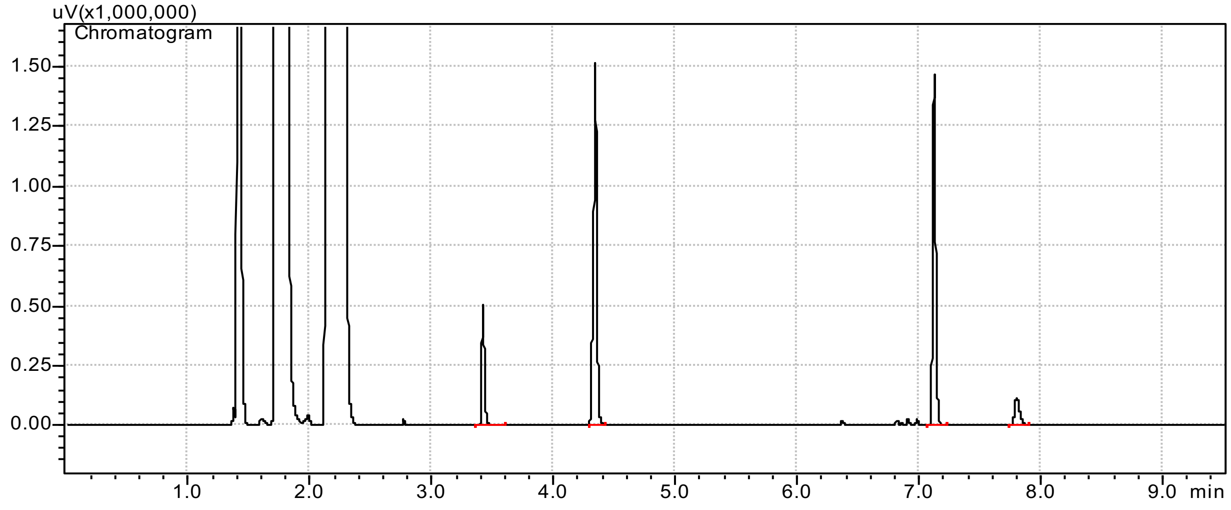
c. *1-Ethyl-4-nitrobenzene oxidation*



	RT (min)	Response Factor
1-Ethyl-4-nitrobenzene	8.3	1.53
4-Nitroacetophenone	13.0	1.40
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
4.341	2792867.7	1689248.7	42.113
8.279	1925669.5	973492.9	29.0368
13.016	1913297.1	440913.9	28.8502

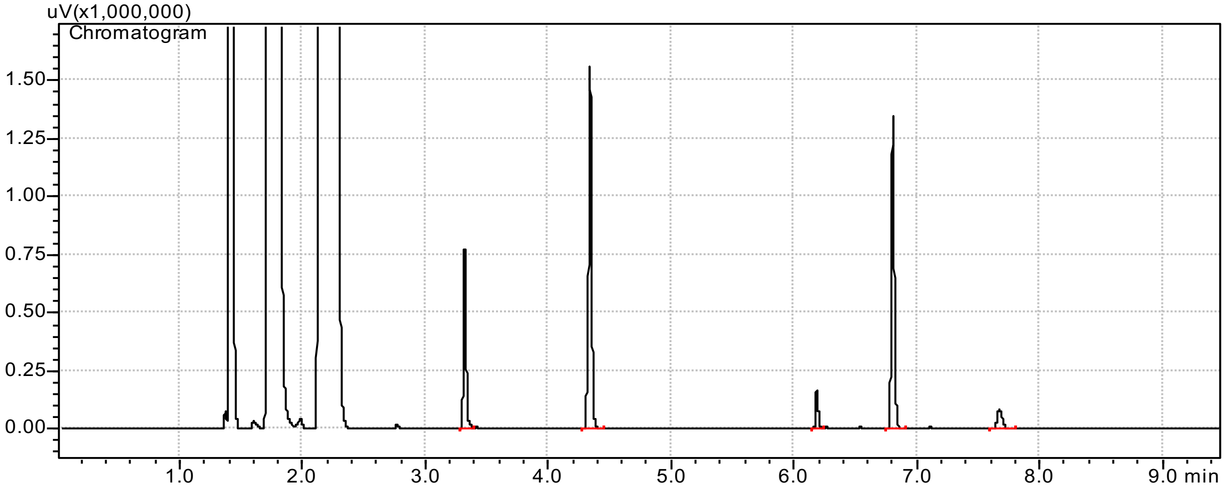
d. *4-Ethyltoluene oxidation*



	RT (min)	Response Factor
4-Ethyltoluene	3.5	1.4312
4'-Methylacetophenone	7.1	1.2137
1-(*p*-tolyl)-ethanol	7.8	1.2205
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
3.42	764328	498587.1	11.9831
4.342	2831908.7	1490760.9	44.3984
7.124	2442402.8	1450799.9	38.2917
7.801	339769.4	117410.4	5.3269

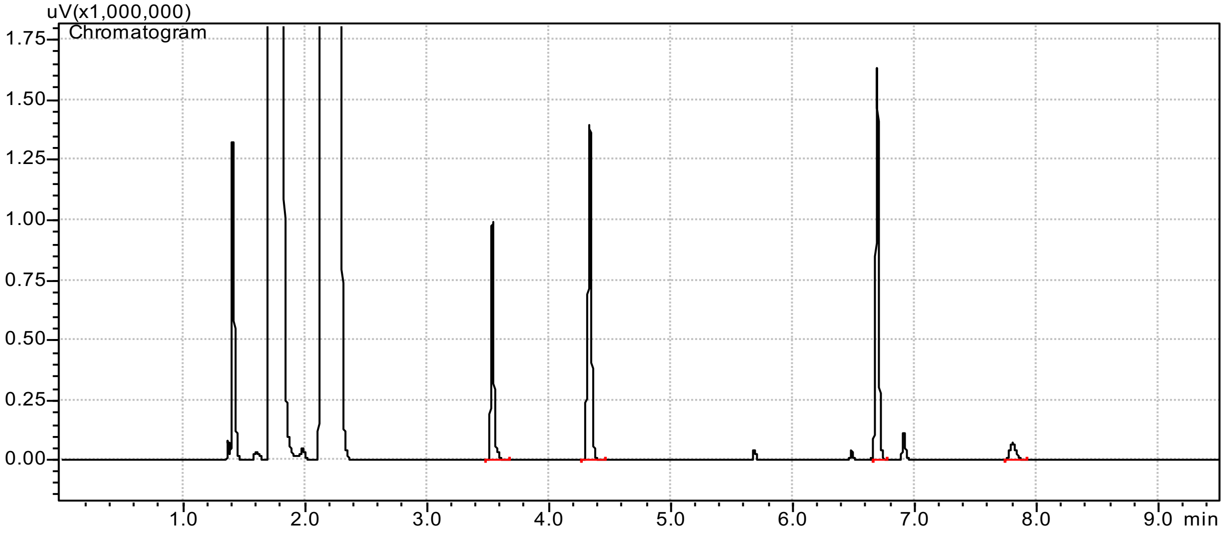
e. Propylbenzene oxidation



	RT (min)	Response Factor
Propylbenzene	3.4	1.4882
Propiophenone	6.8	1.2286
1-Phenyl-1-propanol	7.7	1.2038
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
3.32	1142047	757659.3	17.6383
4.341	2635563.2	1510047.1	40.7049
6.186	251589.1	165994.2	3.8857
6.806	2186849	1320067.1	33.7748
7.673	258749.6	83233.7	3.9963

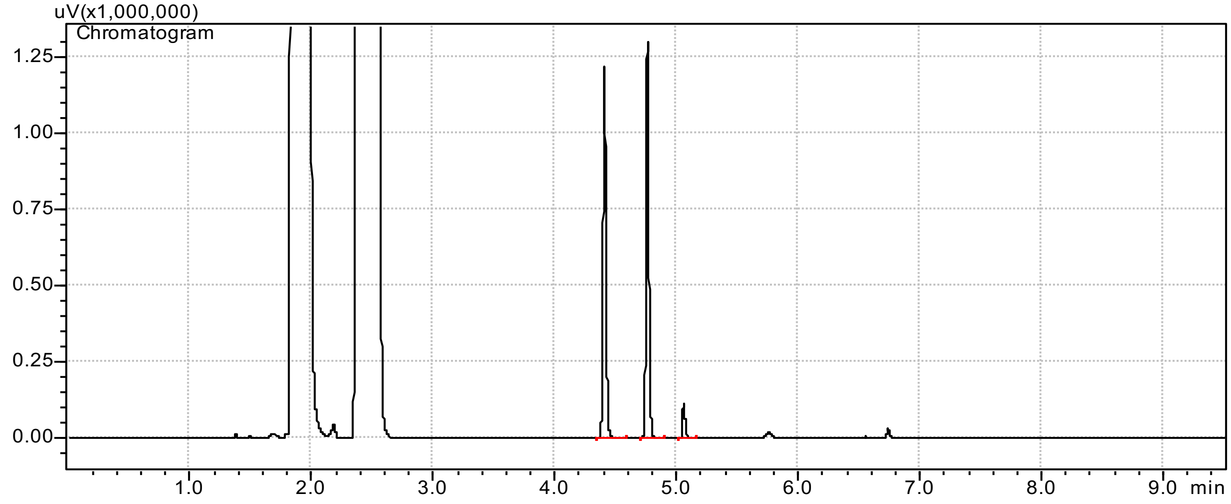
f. Isobutylbenzene oxidation



	RT (min)	Response Factor
Isobutylbenzene	3.6	1.4005
Isobutyrophenone	6.7	1.179
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
3.539	1556257.5	962707.3	21.5191
4.339	2709634.1	1375179.8	37.4673
6.695	2707059.7	1607834.3	37.4317
7.805	259044.5	71799.2	3.5819

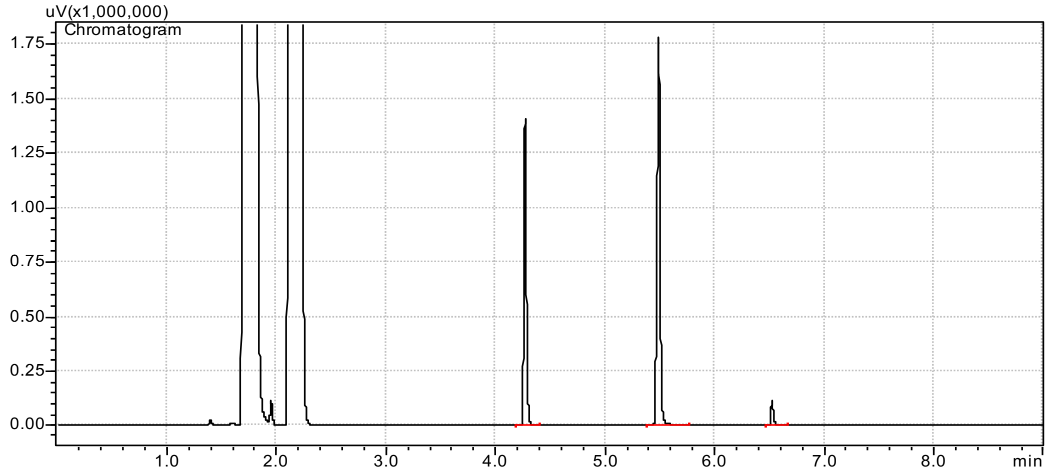
g. Cyclohexanol oxidation



	RT (min)	Response Factor
Cyclohexanol	5.06	0.8828
Cyclohexanone	4.40	0.8643
Bromobenzene	4.76	-

RT (min)	Area	Height	Area %
4.407	1996757.8	1192447.7	47.5439
4.76	2024773.6	1268857.9	48.211
5.058	178284	113108.7	4.245

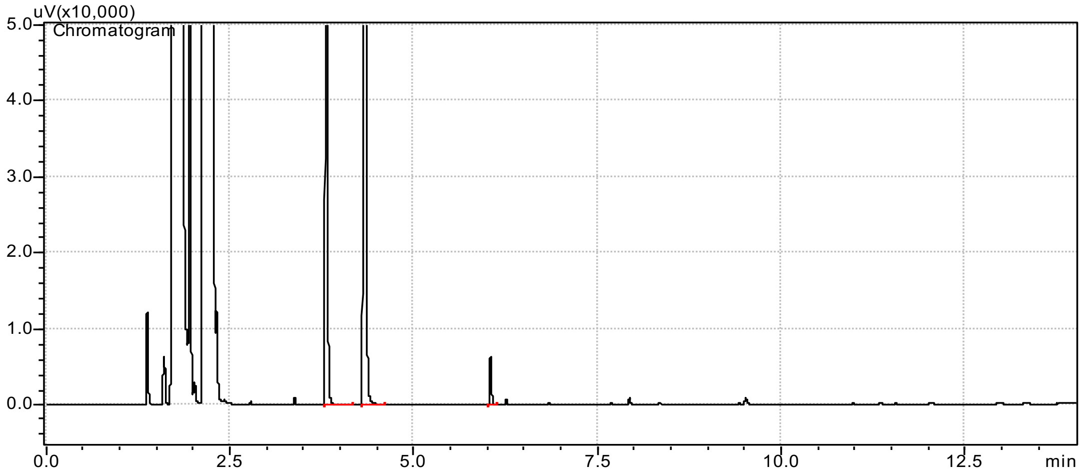
h. Borneol Oxidation



	RT (min)	Response Factor
Borneol	6.5	1.51
Camphor	5.49	1.54
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
4.269	2218261	1390073	38.6128
5.488	3338654	1737582	58.1152
6.523	187975	114449	3.272

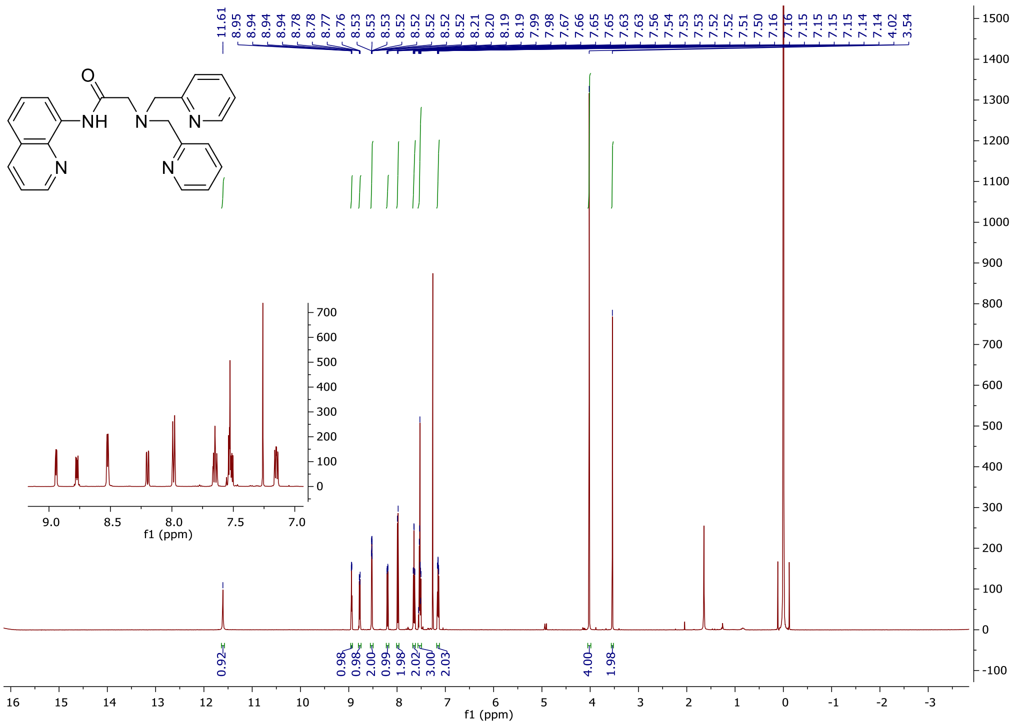
i. 2-Ethylpyridine Oxidation

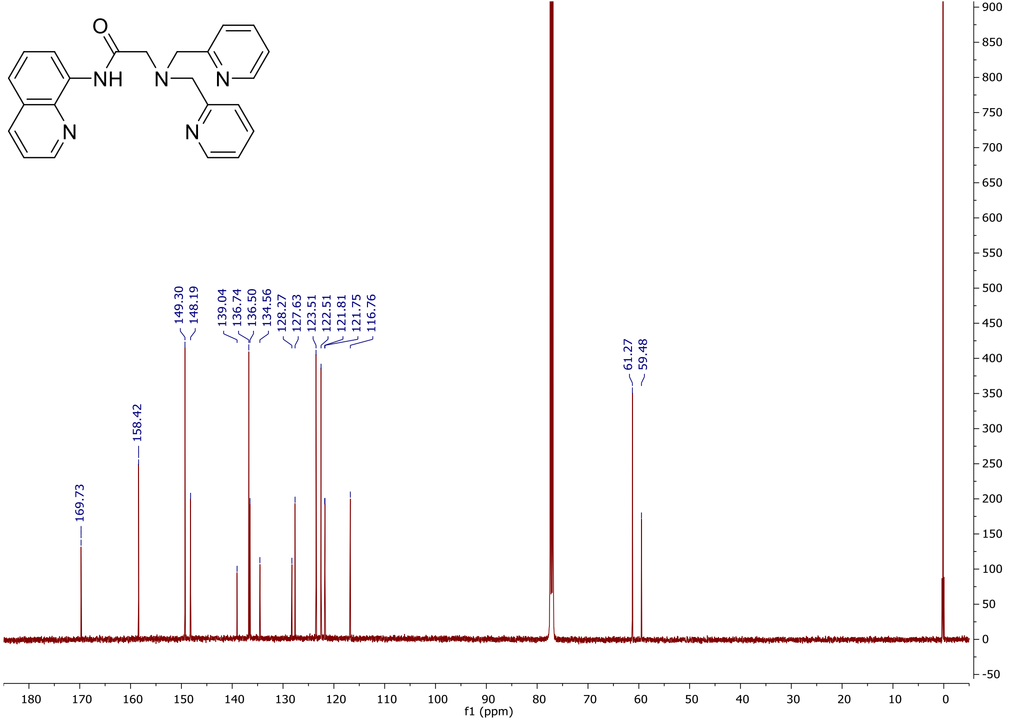


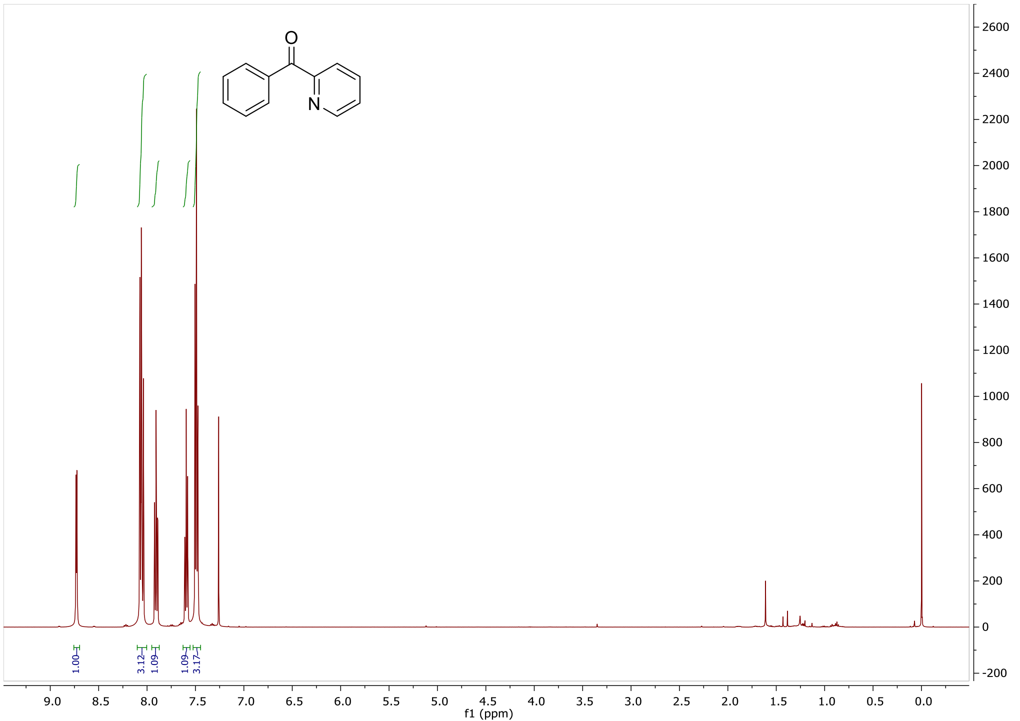
	RT (min)	Response Factor
2-Ethylpyridine	3.8	1.0181
2-Acetylpyridine	6.0	1.0689
Bromobenzene	4.3	-

RT (min)	Area	Height	Area %
3.812	801050	546287.2	35.9955
4.33	1327408	880134.7	59.6476
6.047	96957.3	61375.6	4.3568

19. NMR spectra







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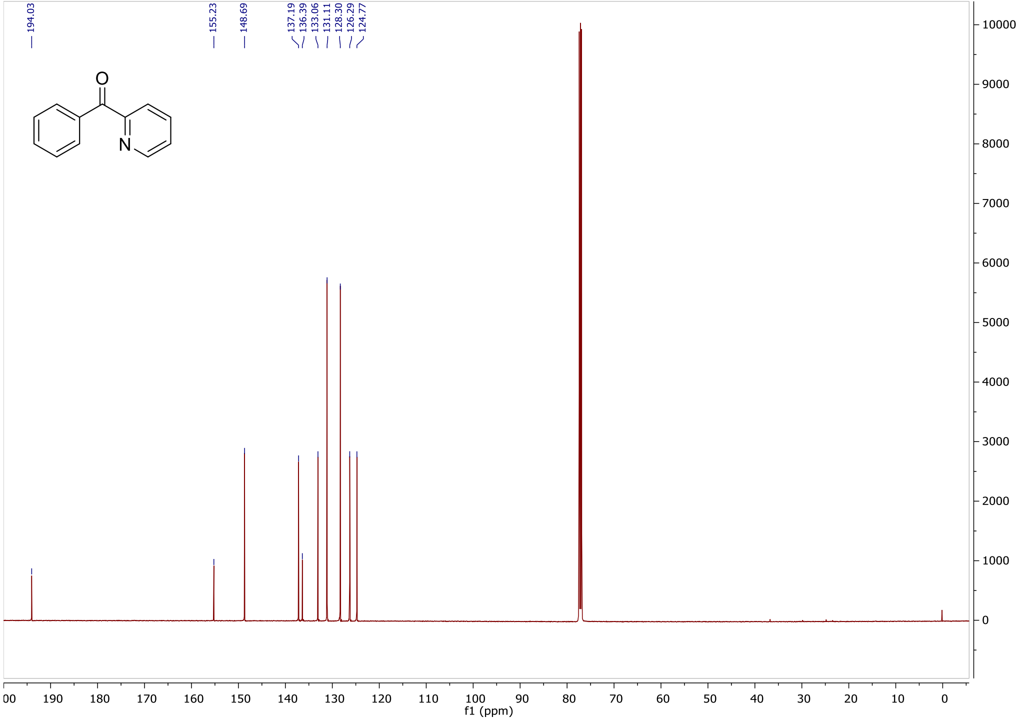

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131.11
128.30
126.29
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N
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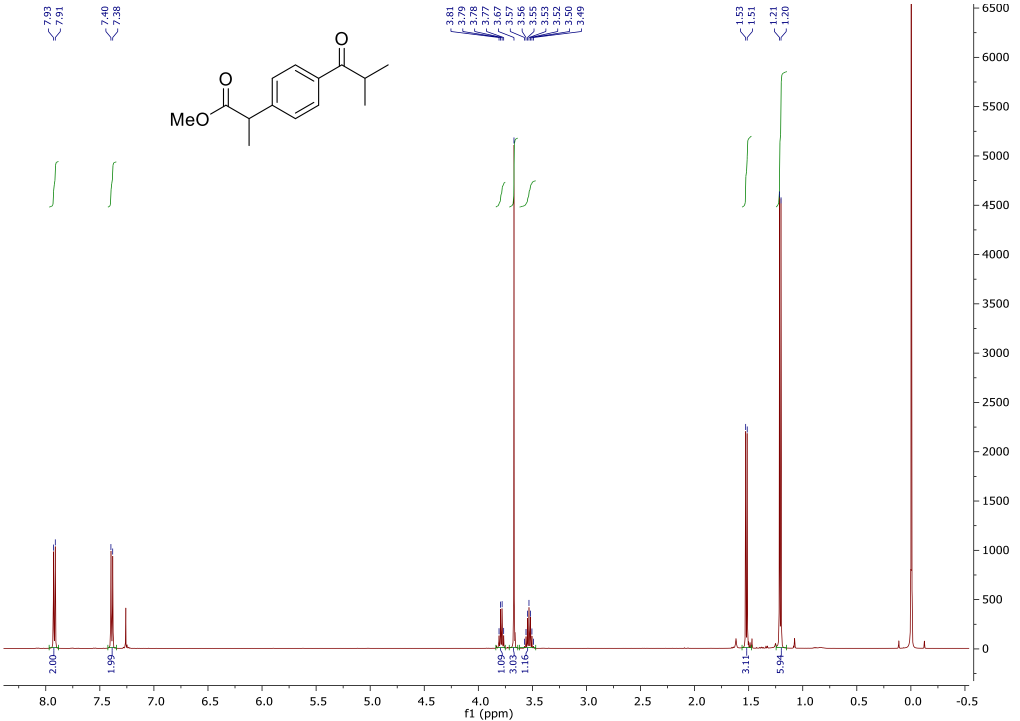
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3.52
3.50
3.49
1.53
1.51
1.21
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O
MeO
2.00
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3.03
1.16
3.11
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7.5
7.0
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2.0
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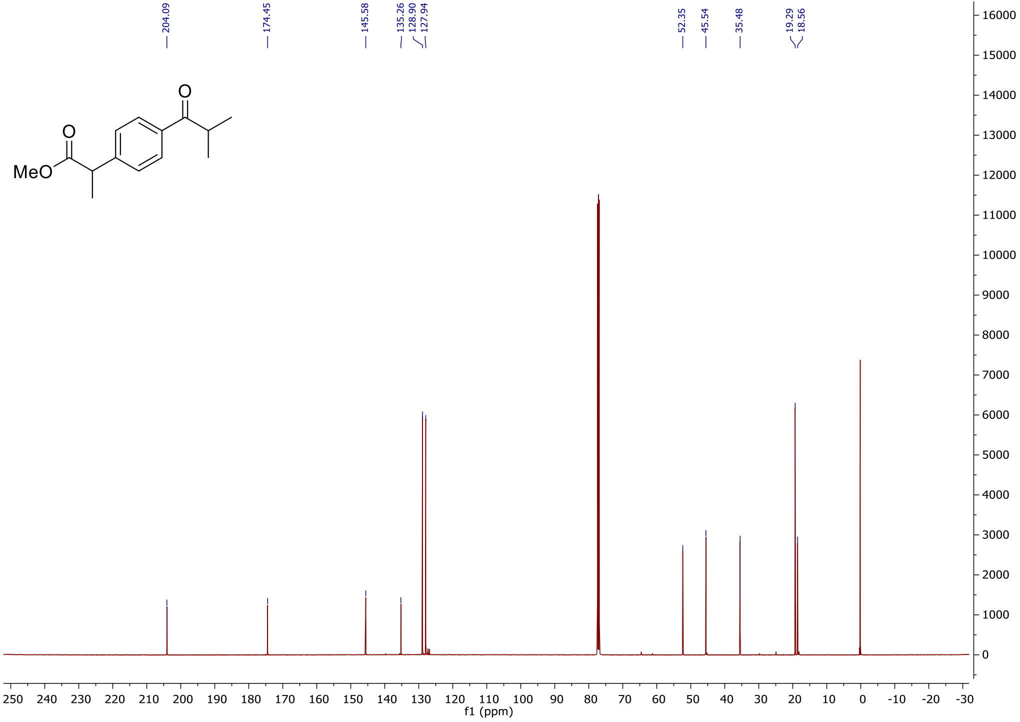
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f1 (ppm)
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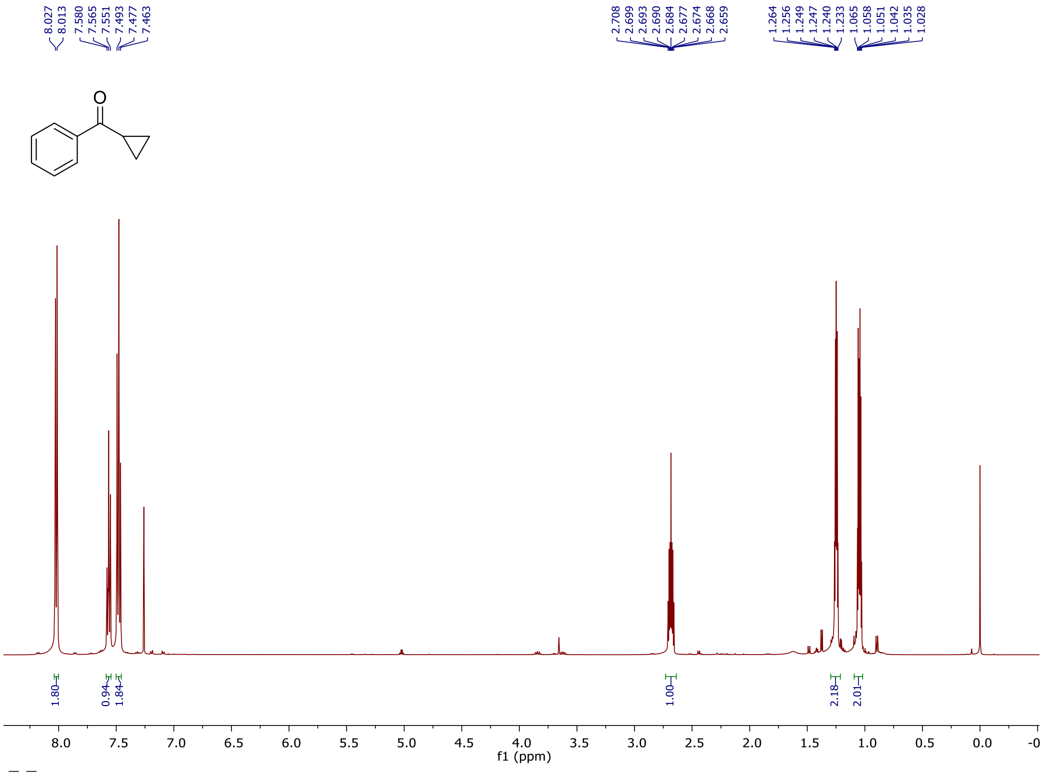
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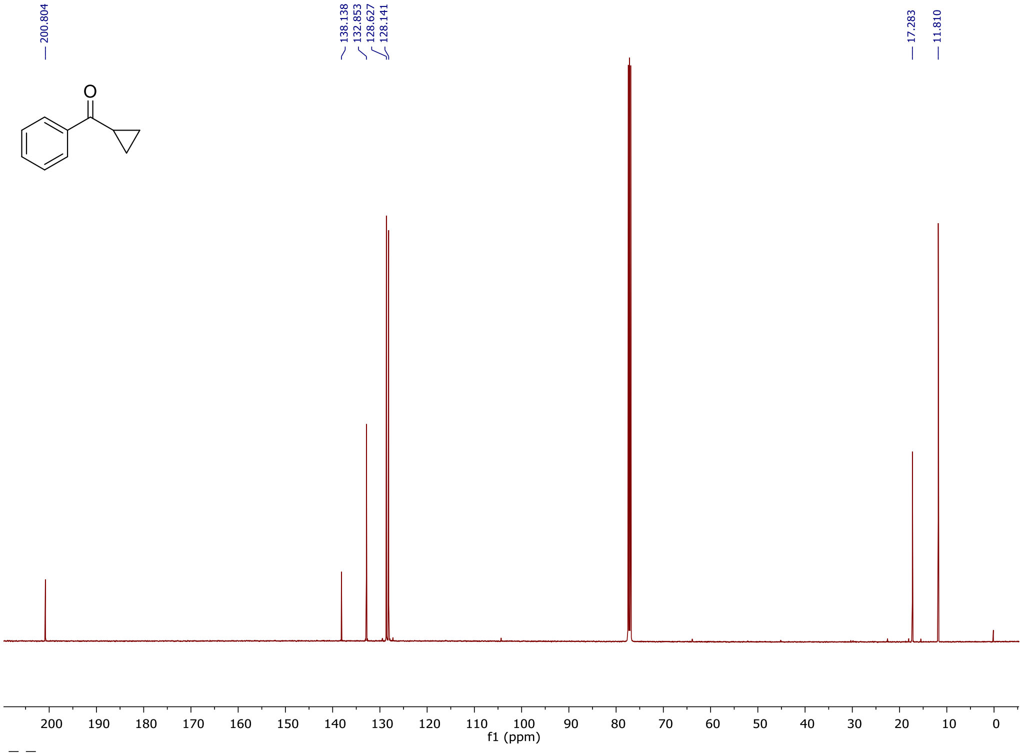
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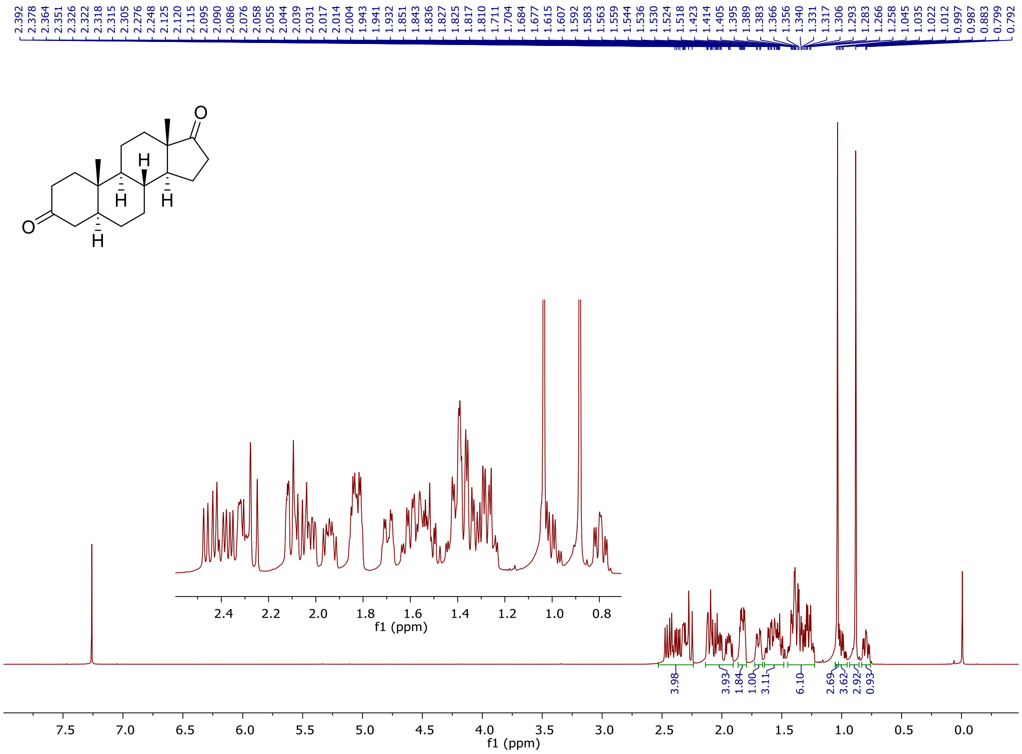
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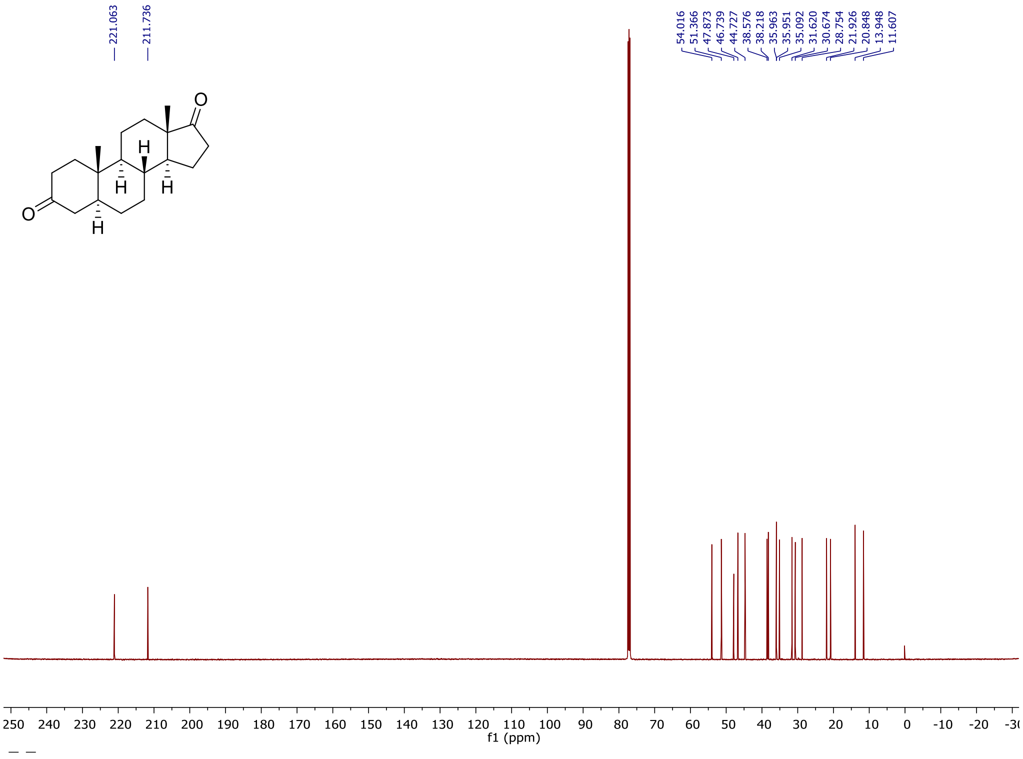
f1 (ppm)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150
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110
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90
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50
40
30
20
10
0
-10
-20
-30
f1 (ppm)