Electronic Supplementary Material (ESI) for Faraday Discussions.

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Electrocatalytic Benzyl Alcohol Oxidation by a molecular iron complex

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EXPERIMENTAL DETAILS

MATERIALS AND METHODOLOGY.

All reagents were obtained commercially and used without further purification unless otherwise noted. $[Et_4N]_2$ [(bTAML)Fe-Cl] (**1a**), $[Et_4N]$ [(bTAML)Fe-OH_2] (**1b**) (bTAML = biuret-modified tetraamidomacrocyclic ligand) were synthesized by our previously reported method.[1] All the solvents used were purchased and used after distillation over drying agents.[2] Glassy Carbon, Platinum (Pt) wire, Ag/$AgNO_3$ (Non-aqueous) and Ag/AgCl (aqueous) electrodes were purchased from CH Instruments. All the cyclic voltammetry studies were carried out in CHI-660 potentiostat. All the catalytic reactions were performed in an IKA ElectraSyn 2.0 instrument brought from IKA. The ElectraSyn setup consisting of a simple undivided cell (5 ml/ 10 ml), reticulated vitreous carbon (RVC foam) (0.5 cm x 0.5 cm x 3.5 cm) as working electrode, Nickel (Ni foam) (0.8 cm x 0.1 cm x 5 cm) as counter electrode and Ag/$AgNO_3$ (10 mM $AgNO_3$) as the reference electrode. UV−vis spectral studies were carried out using an Agilent diode array cary-8454 spectrophotometer with an attached electrically controlled thermostat. GC-MS was performed on a Thermo Scientific ISQ QD Mass Spectrometer attached with Thermo Scientific TRACE 1300 gas chromatograph using an HP-5 ms capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific) with helium as the carrier gas.

ELECTROCHEMICAL MEASUREMENTS.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiment were carried out in CHI-660 potentiostat instrument. Solutions of **1a** were placed in simple undivided three electrode cells. Glassy Carbon (GC) (3 mm of diameter) was used as working electrode, Ag/$AgNO_3$ (10 mM)/ Ag/AgCl (3M KCl) as reference electrode and Pt wire as counter electrode. Before each measurement, the working electrode was polished with 0.05 μm alumina paste, rinsed with water/acetone, and finally blow-drying. DPVs were obtained with the following parameters: amplitude = 50 mV, step height = 4 mV, pulse width = 0.05 s, pulse period = 0.5 s and sampling width = 0.0167 s. All the CVs were collected under IR compensation mode. For $Fe^{V}(O)$ study, a mixture of (19:1) CH_3CN-H_2O was used as solvent where 0.01 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and Ag/$AgNO_3$ acting as a supporting electrolyte and reference electrode respectively. For $Fe^{IV}(O)$ experiments, a mixture of (1:1) CH_3CN-aqueous phosphate buffer of pH 12 was used as solvent where 0.01

M potassium hexafluorophosphate (KPF_6) and Ag/AgCl acting as a supporting electrolyte and reference electrode respectively.

KINETIC ISOTOPE EFFECT ANALYSIS.

The KIE study for the C-H abstraction of benzyl alcohol was performed by analyzing the CV responses during $PhCH_2OH$ and $PhCD_2OH$ oxidation under similar conditions. During electrochemical oxidation of $PhCH_2OH$ and $PhCD_2OH$ in acetonitrile by [Fe^{III}-bTAML] concentration of both alcohols was kept at 0.47 M.

The kinetic isotope effect (KIE) of Benzyl Alcohol was calculated from the background corrected i_{cat} using the following equation,

$$i_{cat} = n_{cat}FA[Fe](Dk_{\text{cat}})^{0.5} = n_{cat}FA[Fe]\ (Dk_2\ [\text{Benzyl Alcohol}])^{0.5}$$

CONSTANT POTENTIAL ELECTROLYSIS FOR CATALYTIC REACTIONS (IN IKA ELECTRASYN INSTRUMENT) BY $Fe^V(O)$ INTERMEDIATE.

The constant potential electrolysis experiments were performed in an IKA ElectraSyn 2.0 instrument which consisting of a three-electrode undivided electrochemical cell with a RVC working electrode (0.5 cm x 0.5 cm x 3.5 cm), a Ni foam (0.8 cm x 0.1 cm x 5 cm) as counter electrode and an $Ag/AgNO_3$ (10 mM $AgNO_3$ in acetonitrile) as reference electrode. The potential was set at 0.77 V vs Fc^+/Fc throughout the reaction.

REACTION CONDITIONS.

- **Catalyst:** Fe^{III}-bTAML (**1a**) (0.75 mM)
- **Substrate:** Alcohols (15 mM)
- **Solvent:** CH_3CN + Phosphate buffer (4:1 v/v, 5 mM, pH 8)
- **Electrolyte:** $TBAPF_6$ (0.10 M)
- **3-eletrode simple undivided cell**
- **WE:** RVC Foam
- **CE:** Nickel Foam
- **RE:** $Ag/AgNO_3$ (10 mM)
- **Time:** 3-6 hr

- Open Flask, room temperature

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REACTION CONDITIONS.

- **Catalyst:** Fe^{III}-bTAML (**1a**) (0.75 mM)
- **Substrate:** Alcohols (15 mM)
- **Solvent:** CH_3CN + Phosphate buffer (1:1 v/v, 50 mM, pH 12)
- **Electrolyte:** KPF_6 (0.1 M)
- **3-eletrode simple undivided cell**
- **WE:** RVC Foam
- **CE:** Nickel Foam
- **RE:** Ag/AgCl (3 M KCl)
- **Time:** 15-20 hr
- Open Flask, room temperature

PRODUCT IDENTIFICATION AND QUANTIFICATION (IN GC-MS).

The products formed by electrochemical alcohol oxidation reactions were analyzed by gas chromatography–mass spectrometry (GC-MS). After each electrolysis, 1.5 ml solution of the electrolyte solution was taken out from the electrochemical cell and the acetonitrile was evaporated under nitrogen flow. After that the resultant reaction mixture was diluted in 1.5ml dichloromethane and was washed using 500µl of water (For alcohol oxidation using Fe(IV)O 500µl $NaHCO_3$ solution was added). The organic layer was separated and was analyzed by

GC-MS. An internal standard (Bromobenzene) was used for all the reactions. The yields and conversions were estimated using the response factor of authentic substrates and products.

DETERMINATION OF DIFFUSION COEFFICIENT.

The relationship between current and scan rate for a diffusion-based redox event has been described by the Randles-Sevcik equation,

$$i_\mathrm{p} = 0.446 n\mathrm{F}A[\mathrm{Fe}]\sqrt{\frac{n\mathrm{F}\nu D_\mathrm{cat}}{RT}}$$

$$\text{Or, } i_p = 18810.5\ [\mathrm{Fe}]\ \mathrm{D}^{1/2}\,\nu^{1/2}$$

Where, n is the number of electrons transferred, ν the scan rate (V/s), [Fe] is the concentration of catalyst (mol cm^{-3}), *F*, *R*, and *T* are Faraday's constant (C mol^{-1}), the ideal gas constant (J K^{-1} mol^{-1}), and temperature (K) respectively.

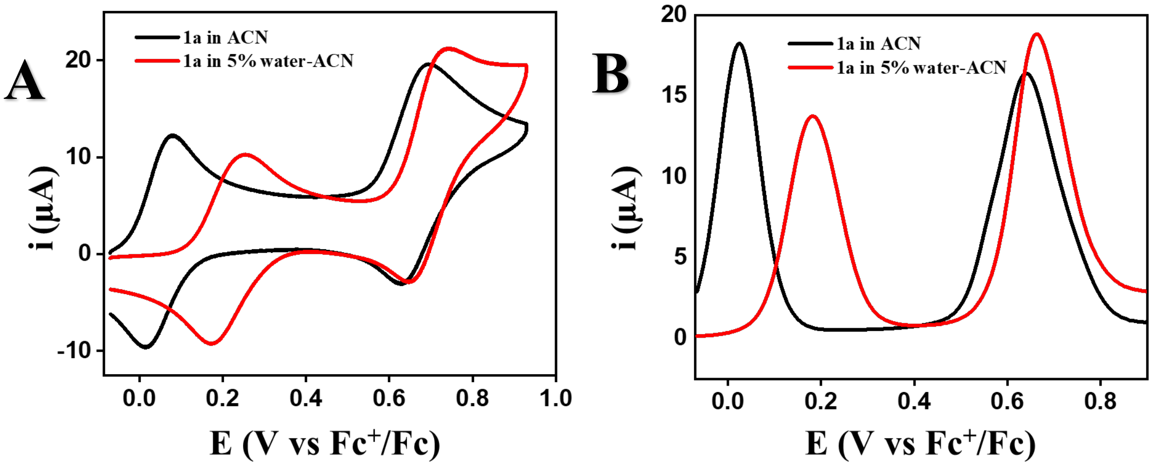

Figure S1.A CVs of **1a** (1 mM) in acetonitrile (black), (19:1) CH_3CN- H_2O (red). Conditions: Scan rate 100 mVs^{-1}, Glassy carbon as working electrode, platinum wire as a counter electrode, Ag/$AgNO_3$ as a reference electrode **B.** DPVs of **1a** (1 mM) in acetonitrile (black), (19:1) CH_3CN- H_2O (red). Conditions: Scan rate 100 mVs^{-1}, Glassy carbon as working electrode, platinum wire as a counter electrode, Ag/$AgNO_3$ as a reference electrode.

REACTION ORDER WITH RESPECT TO CATALYST (Fe-bTAML).

With the variation of concentrations of catalyst, catalytic current (i_{cat}) varies linearly. This shows the first order dependence w.r.t catalyst, [Fe-bTAML].

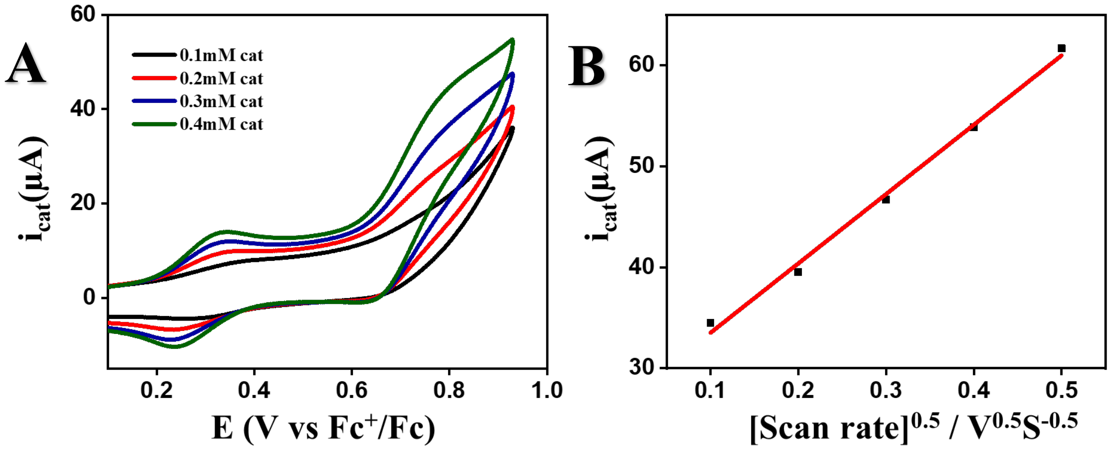

Figure S2. Cyclic voltammogram responses of with varying catalyst (Fe-bTAML) concentration in (19:1) CH_3CN-H_2O (0.1 M $TBAPF_6$) at constant 20 mM concentration of Benzyl Alcohol at 200 mV s^{-1} scan rate (A). A plot of i_{cat} vs [Fe-bTAML] (B).

The rate of Benzyl Alcohol oxidation can be expressed as,

$$\text{rate} = k_2 \times [\text{Fe-bTAML}] \times [\text{Benzyl Alcohol}].$$

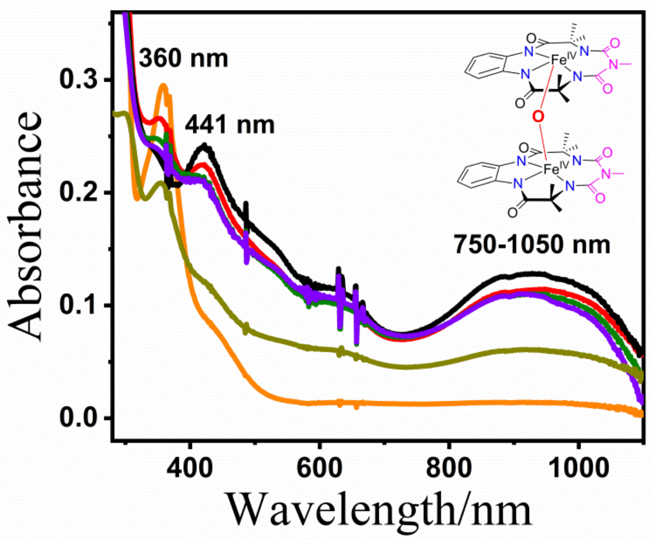

Figure S3. Spectroelectrochemical formation of μ-O-Fe^{IV}_2 species (Dimer) at higher catalyst concentration (> 0.2 mM) in (9:1) CH_3CN-H_2O. [Due to the comproportionation reaction of $Fe^V(O)$ with Fe^{III} in the bulk by the following mechanism][3]

Note: We adopted this plot from our previous report[3] for ease of better understanding.

$$[LFe^{III}\text{-}OH_2]^- \xrightarrow{2H^+/2e^-} [LFe^{V}{=}O]^-$$

$$[LFe^{V}{=}O]^- + [LFe^{III}\text{-}OH_2]^- \xrightarrow[-H_2O]{} [LFe^{IV}\text{-}O\text{-}Fe^{IV}L]^-$$

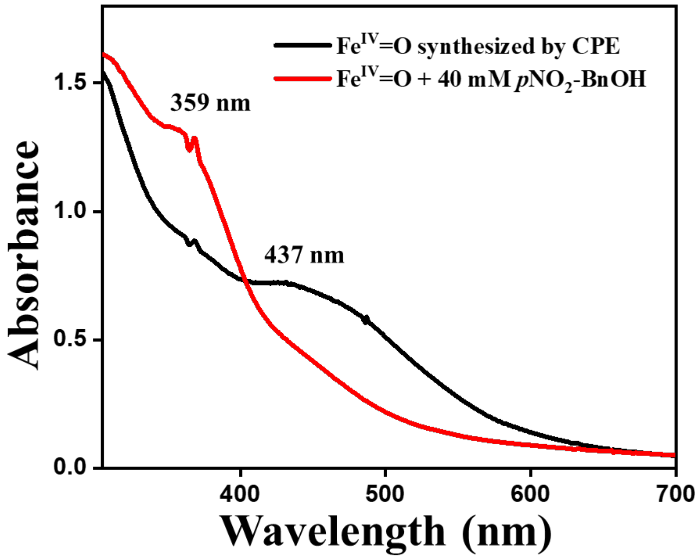

Figure S4. UV-Vis spectra of $Fe^{IV}(O)$ (Black) species prepared from 1a (0.4mM) in 1:1 CH_3CN- H_2O and KPF_6 as a supporting electrolyte at pH~12 using Pt mesh working electrode and Pt wire as a counter electrode during CPE at 0.26 V vs Fc^+/Fc get back to the Fe(III) species (Red) after addition of the p-nitro benzyl alcohol (40mM).

SCHEME 1. CONTROL REACTION FOR BULK ELECTROLYSIS:

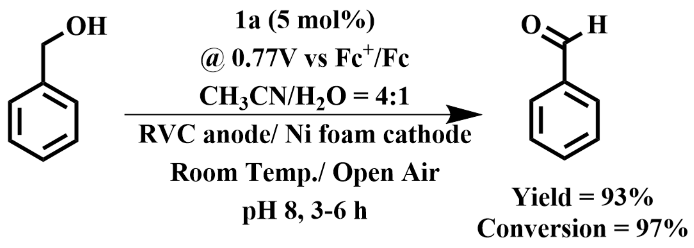

TABLE S1. OPTIMIZATION TABLE:

Entry	Condition	% conversion	% yield
1	No catalyst	—	—
2	No water	—	—
3	@0.47V	—	—
4	@0.77 V	99%	96%
5	Under Argon	No change	
6	Fe_2O_3	—	—

'-' denotes no conv. / no yield / trace amount of product found after the reactions.

Table S2. CALCULATION OF FARADAIC EFFICIENCY:

Charge (after 4 hr) = 6.5 F/mol

Benzyl Alcohol substrate = 0.045 mmol

Total charge (Q) passed for 0.045 mmol Benzyl Alcohol = 6.5 x 0.045 x 10-3 x 96485 C = 28.22 C

Hence, number of moles of product (n) = Q/zF = 28.22/ 2*96485 = 0.000146 mol = 0.146 mmol (According to electrochemistry)

Where, the number of electrons transferred during the reaction, z = 2 and F = 96485 C/mol

Whereas, number of moles of product formed in the reaction (bulk electrolysis) is given by, 0.93 x 0.045 mmol = 0.04185 mmol

(According to 93% yield after 4 hr of Benzyl Alcohol oxidation)

Faradaic efficiency = 0.04185 (*100)/0.146 = 28.7 %

GC-MS TRACES OF THE ELECTROCHEMICAL OXYGENATION REACTION FOR ALCOHOLS.

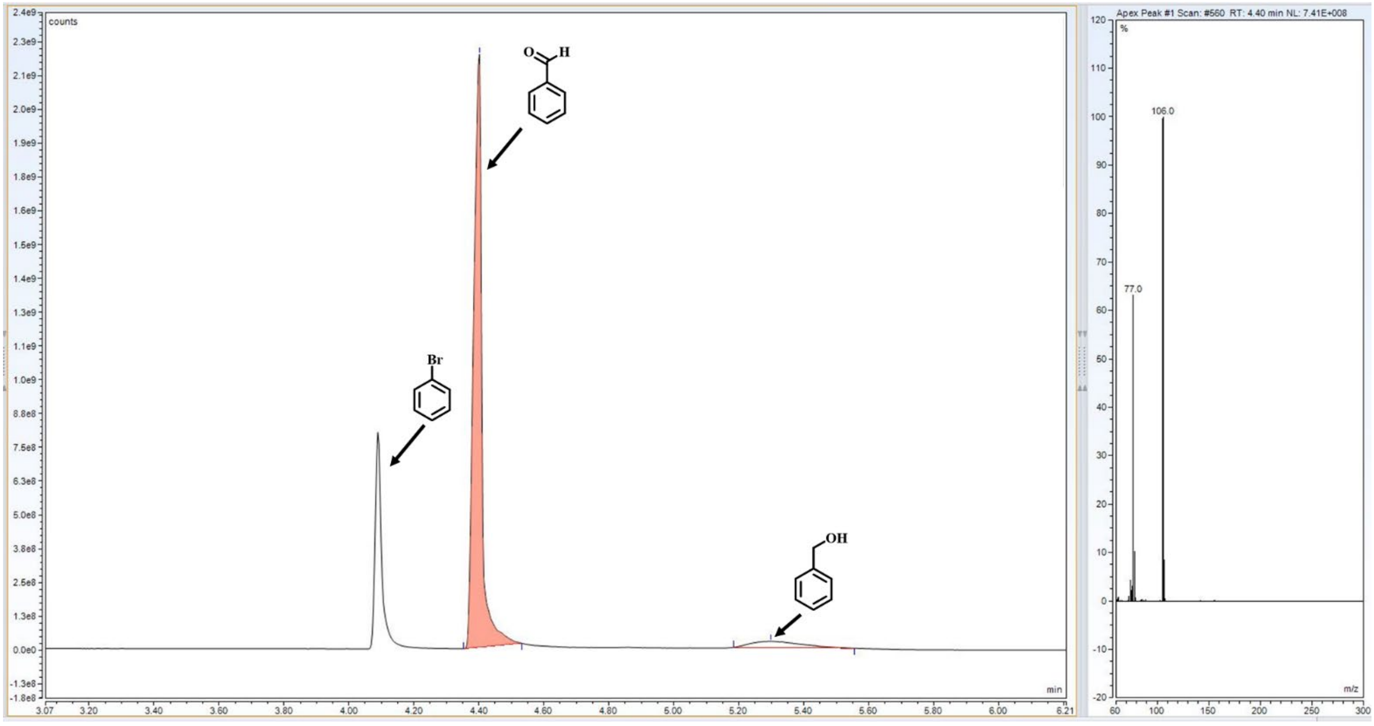

Figure S5: GC-MS traces for electrochemical oxidation of Benzyl Alcohol (yield 93%)

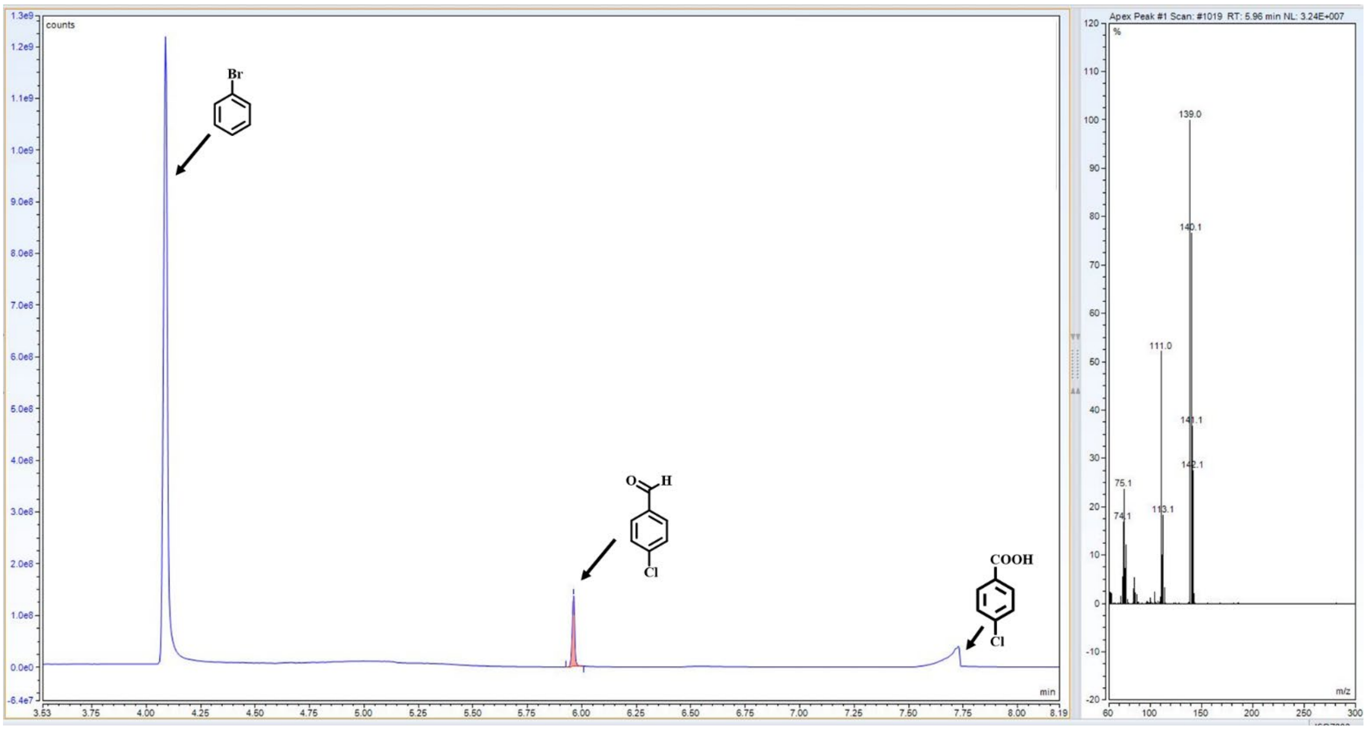

Figure S6: GC-MS traces for electrochemical oxidation of p-Cl Benzyl Alcohol (yield 96%)

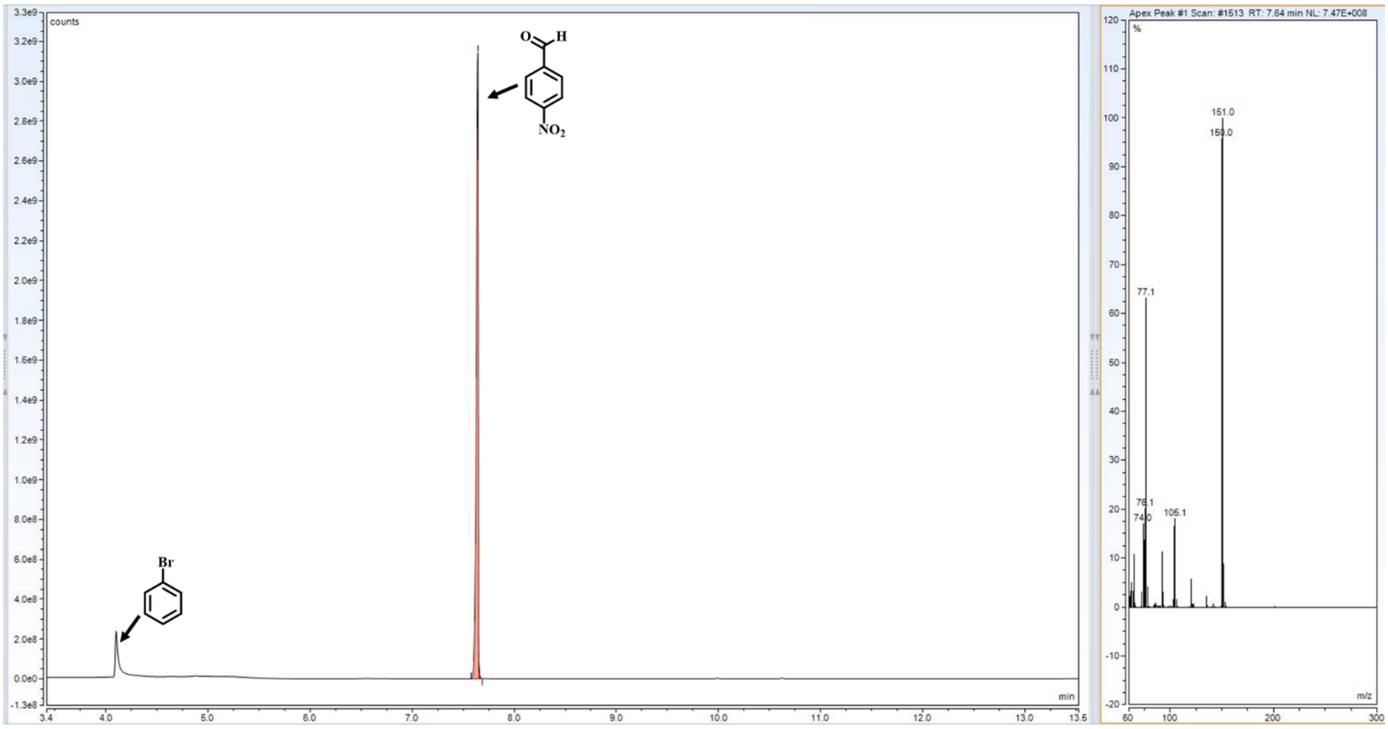

Figure S7: GC-MS traces for electrochemical oxidation of p-NO_2 Benzyl Alcohol. (Yield 99%)

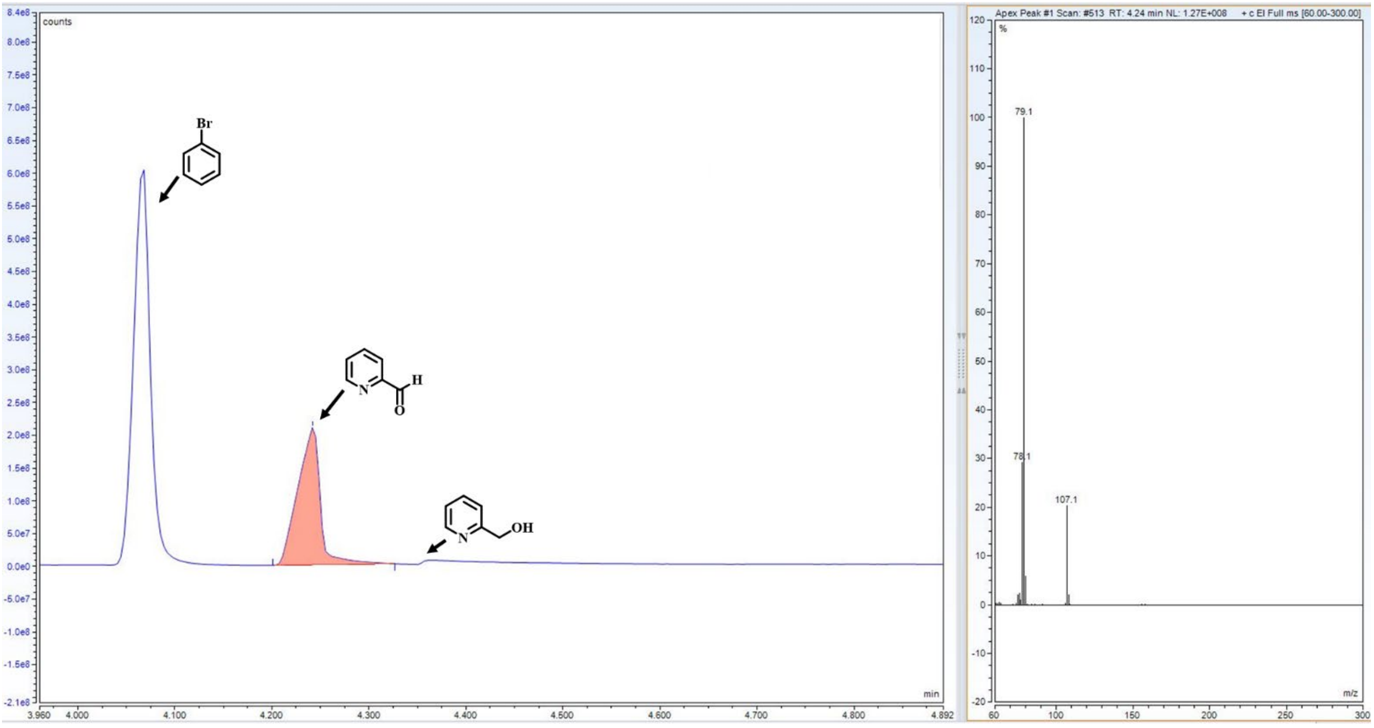

Figure S8: GC-MS traces for electrochemical oxidation of 2-Pyridinemethanol. (Yield 96%).

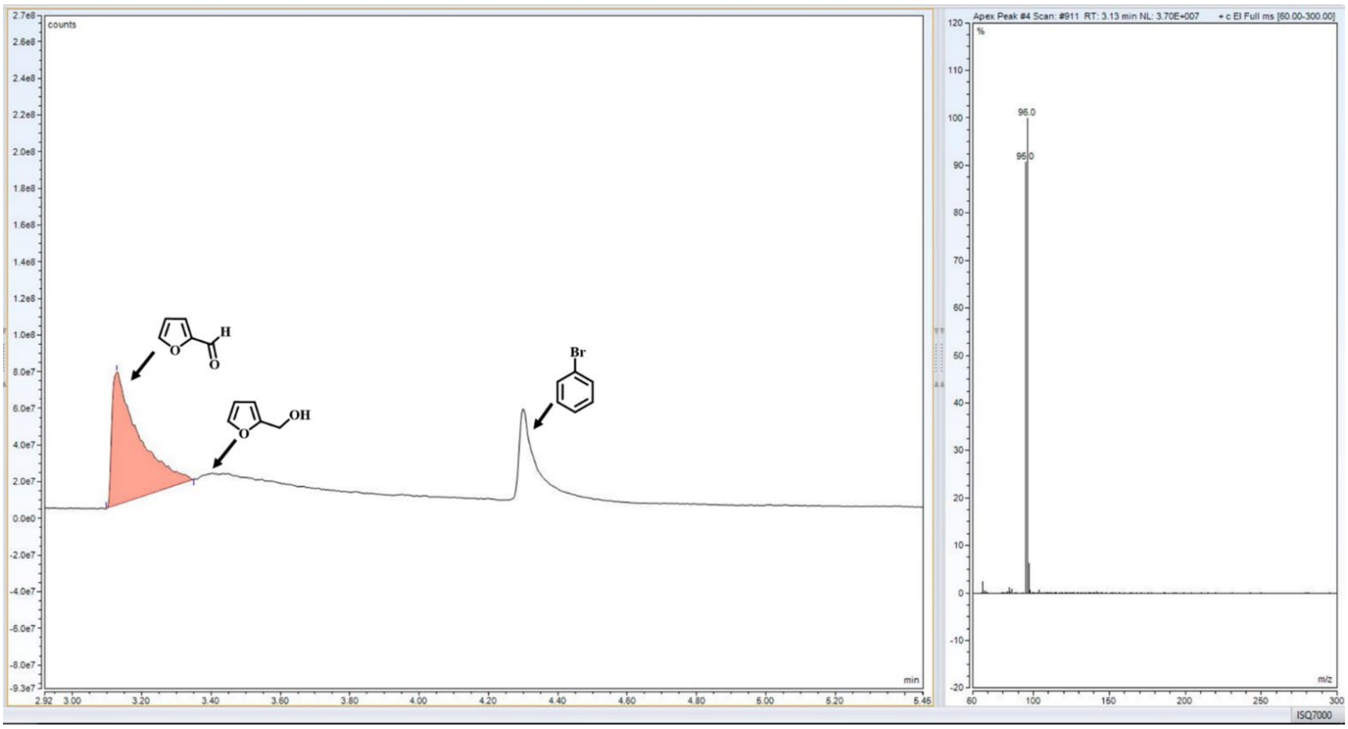

Figure S9: GC-MS traces for electrochemical oxidation of Furfuryl Alcohol. (Yield 95%)

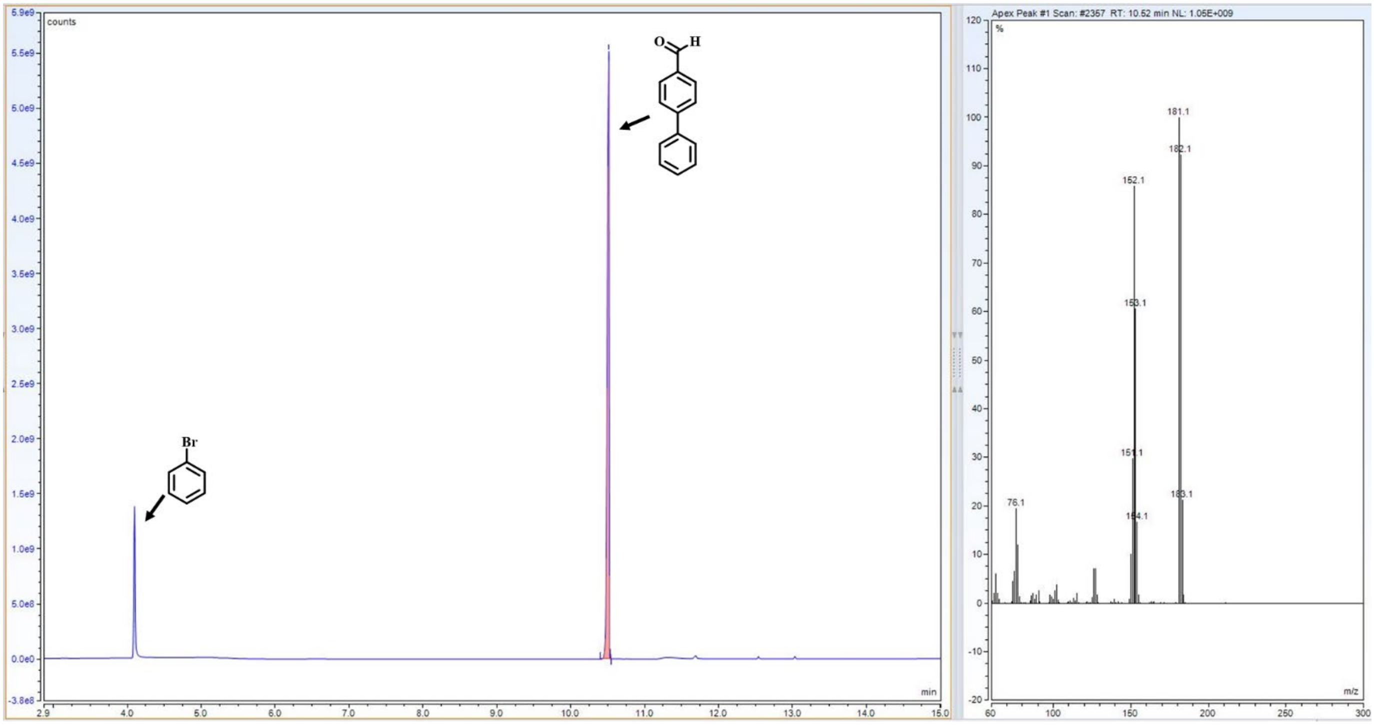

Figure S10: GC-MS traces for electrochemical oxidation of Biphenyl-4-methanol (Yield 96%)

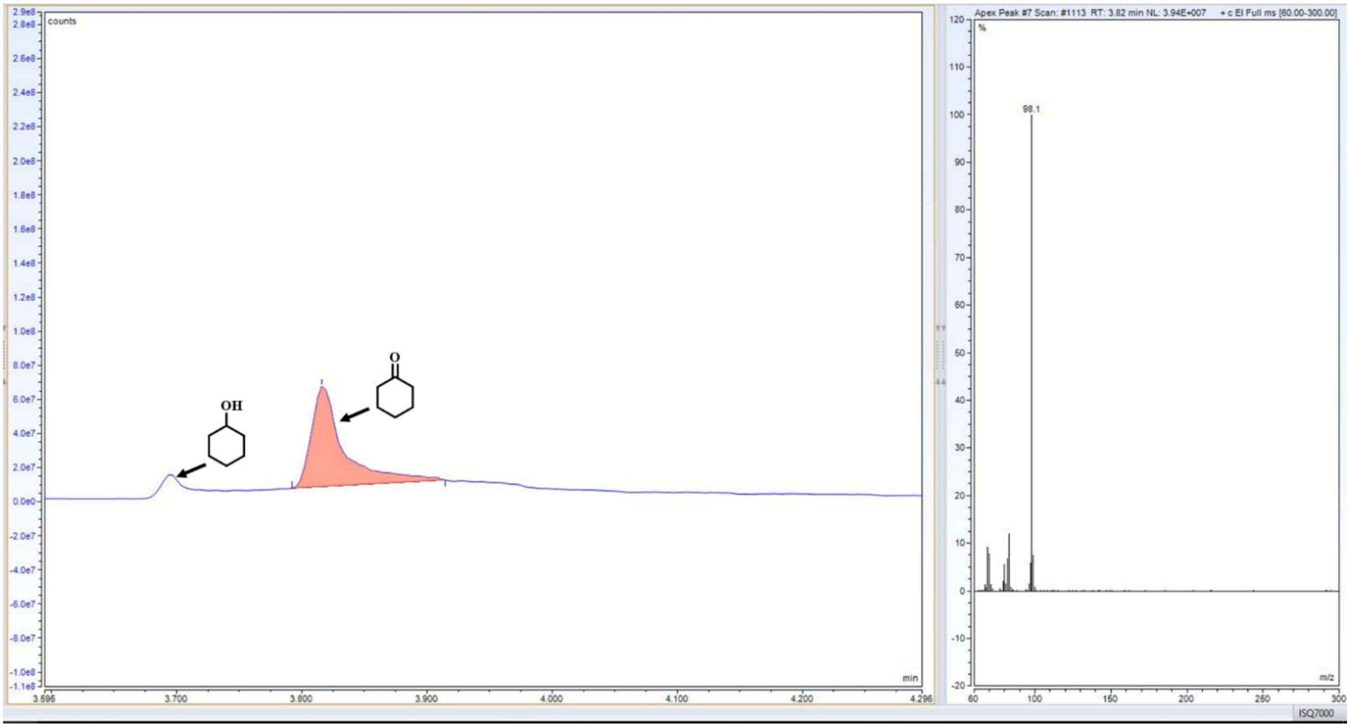

Figure S11: GC-MS traces for electrochemical oxidation of Cyclohexanol. (Yield 75%)

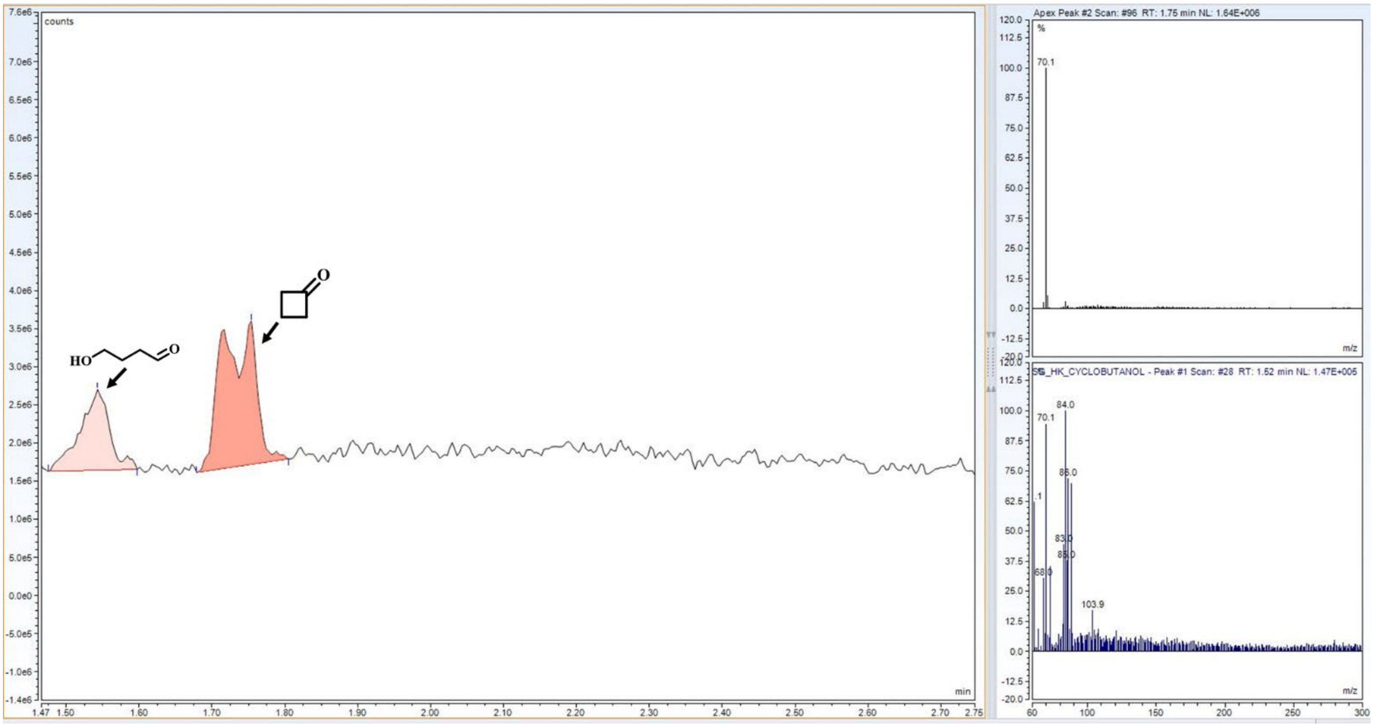

Figure S12: GC-MS traces for electrochemical oxidation of Cyclobutanol.

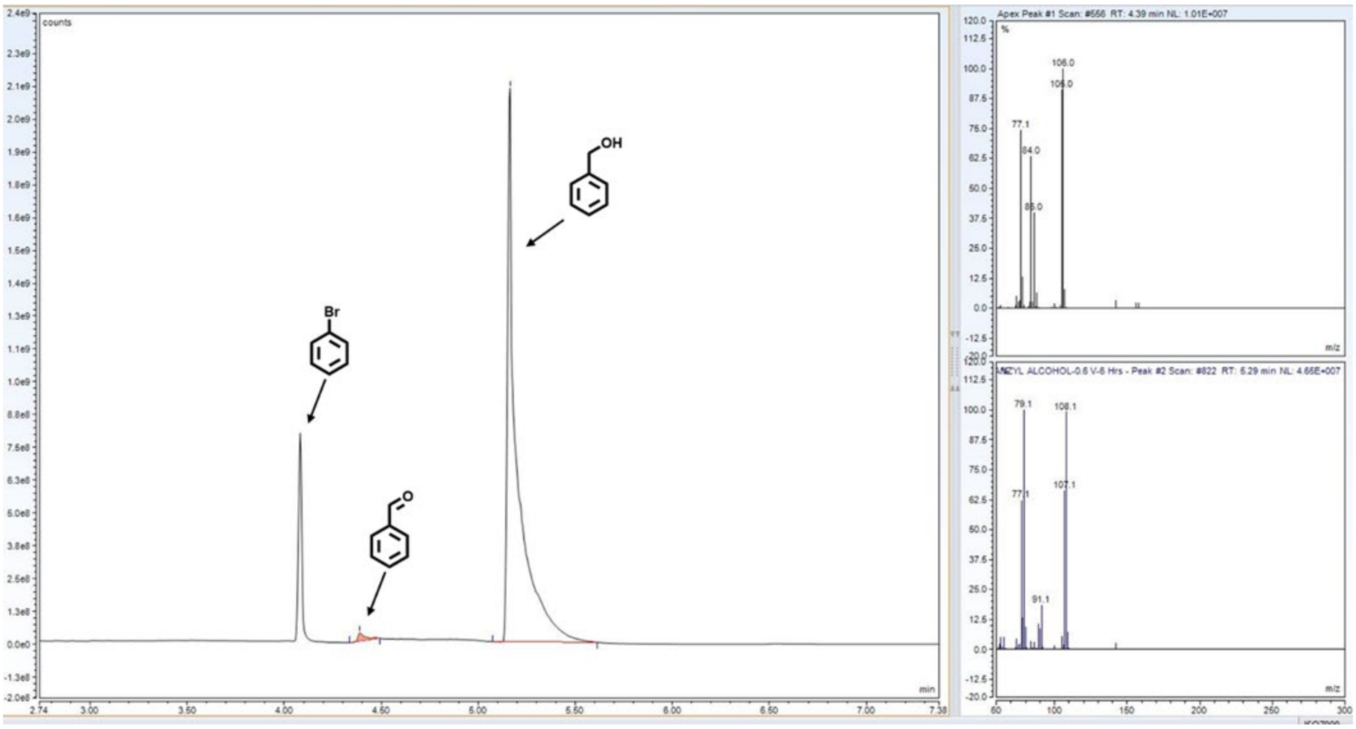

Figure S13: GC-MS traces for electrochemical oxidation of benzyl alcohol at a constant potential of 0.47 V vs Fc^+/Fc and at pH 8. (Trace amount of product)

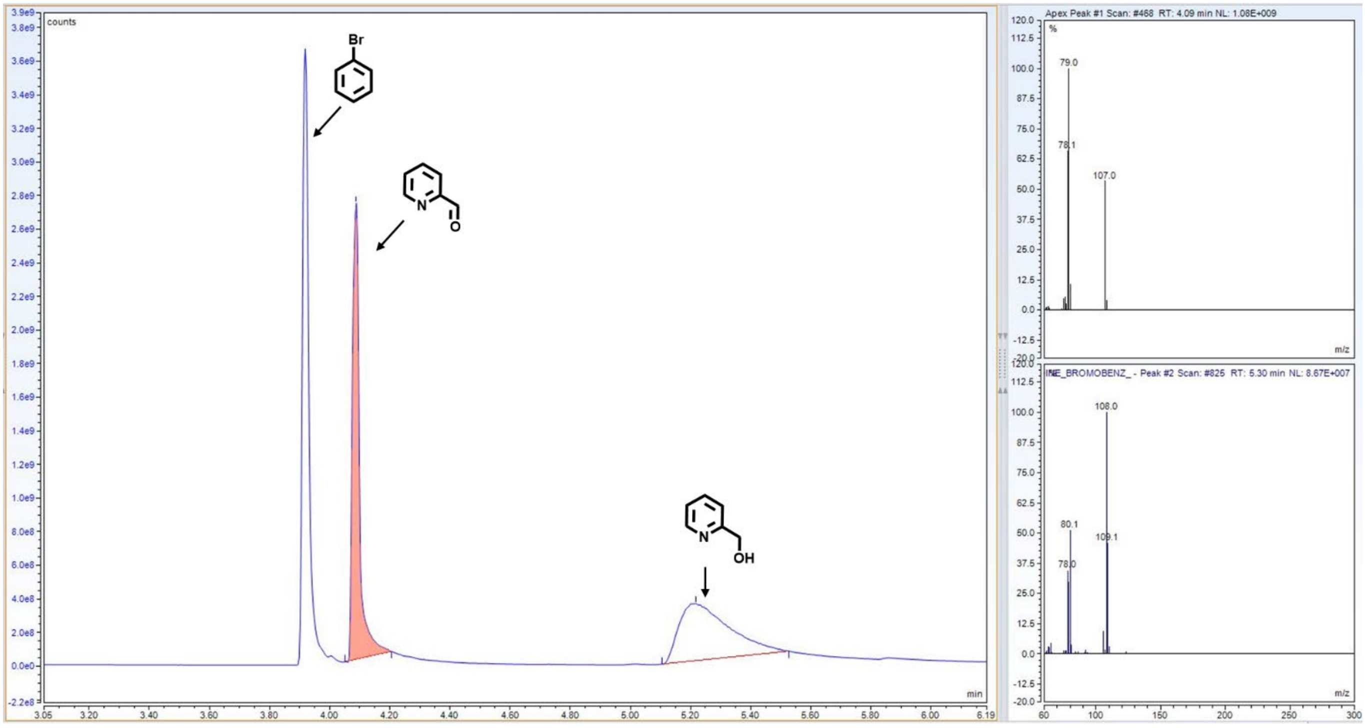

Figure S14: GC-MS traces for electrochemical oxidation of 2-pyridine methanol at a constant potential of 0.26 V vs Fc^+/Fc and at pH 12. (Yield 58%)

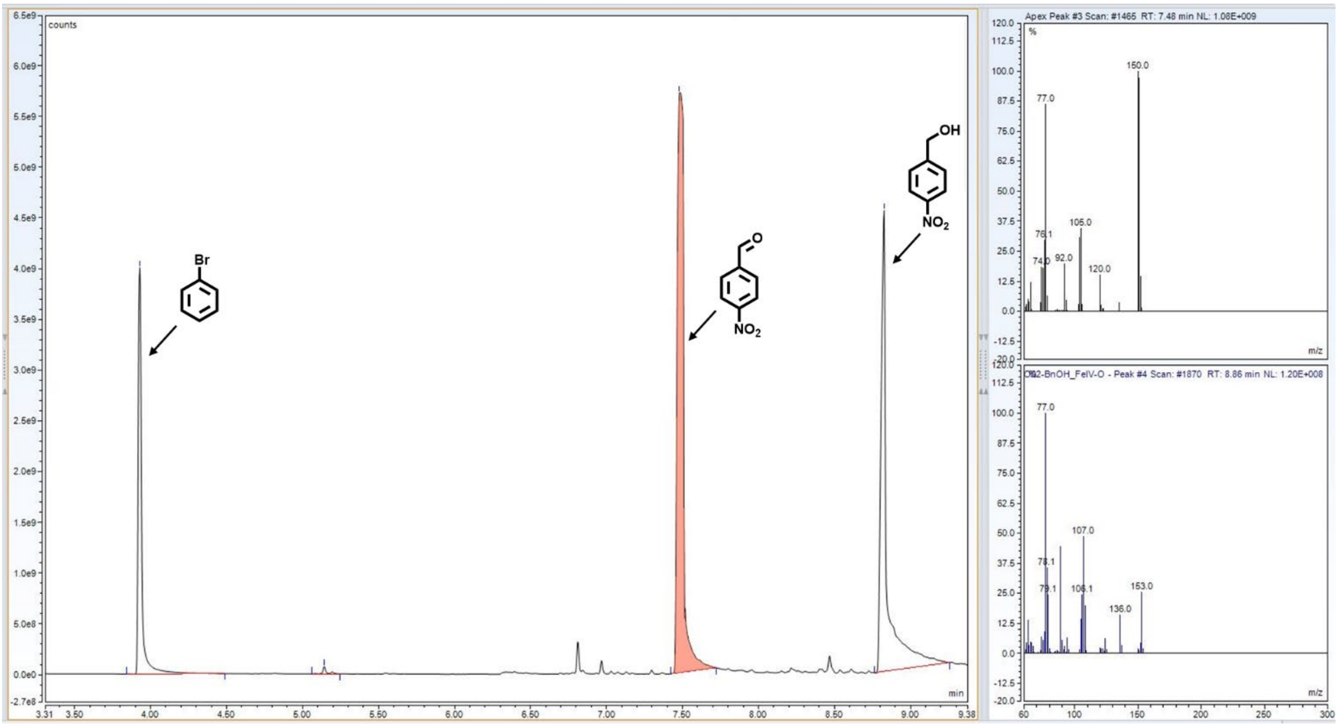

Figure S15: GC-MS traces for electrochemical oxidation of *p*-NO_2 benzyl alcohol at a constant potential of 0.26 V vs Fc^+/Fc and at pH 12. (Yield 51%)

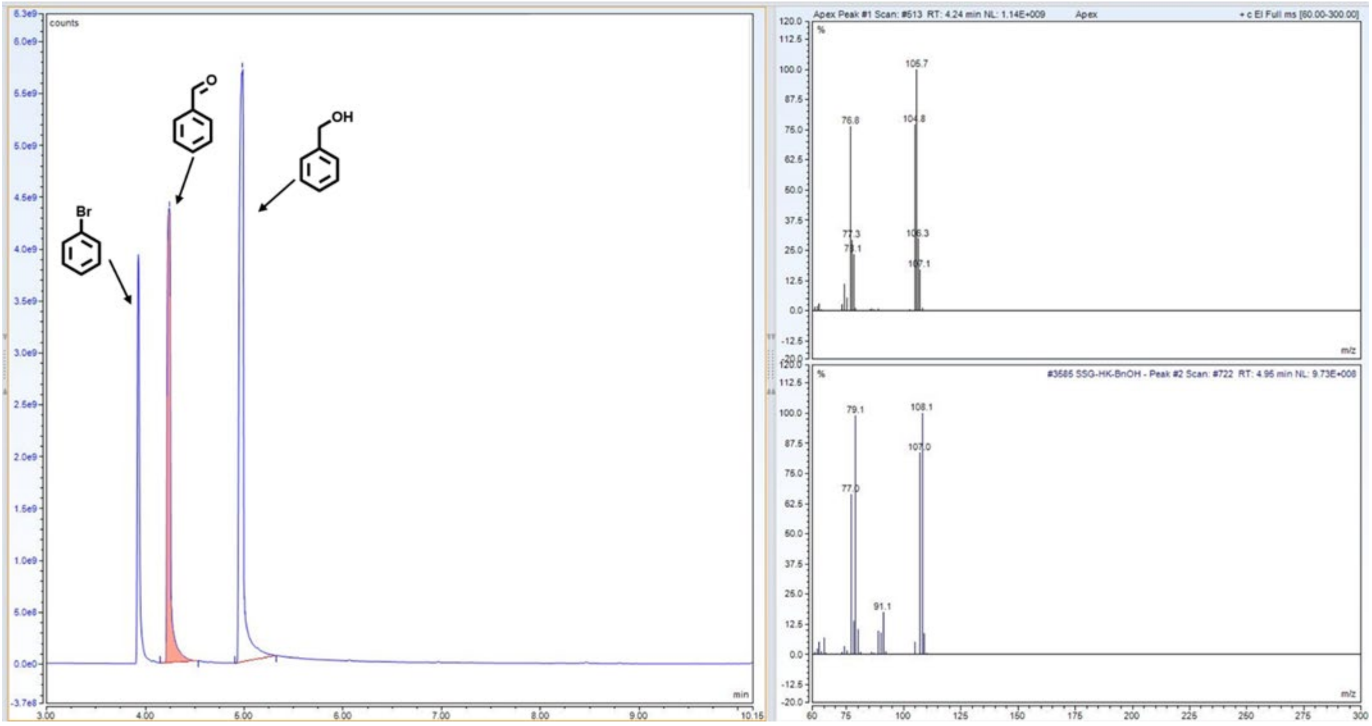

Figure S16: GC-MS traces for electrochemical oxidation of benzyl alcohol at a constant potential of 0.26 V vs Fc$^+$/Fc and at pH 12. (Yield 46%)

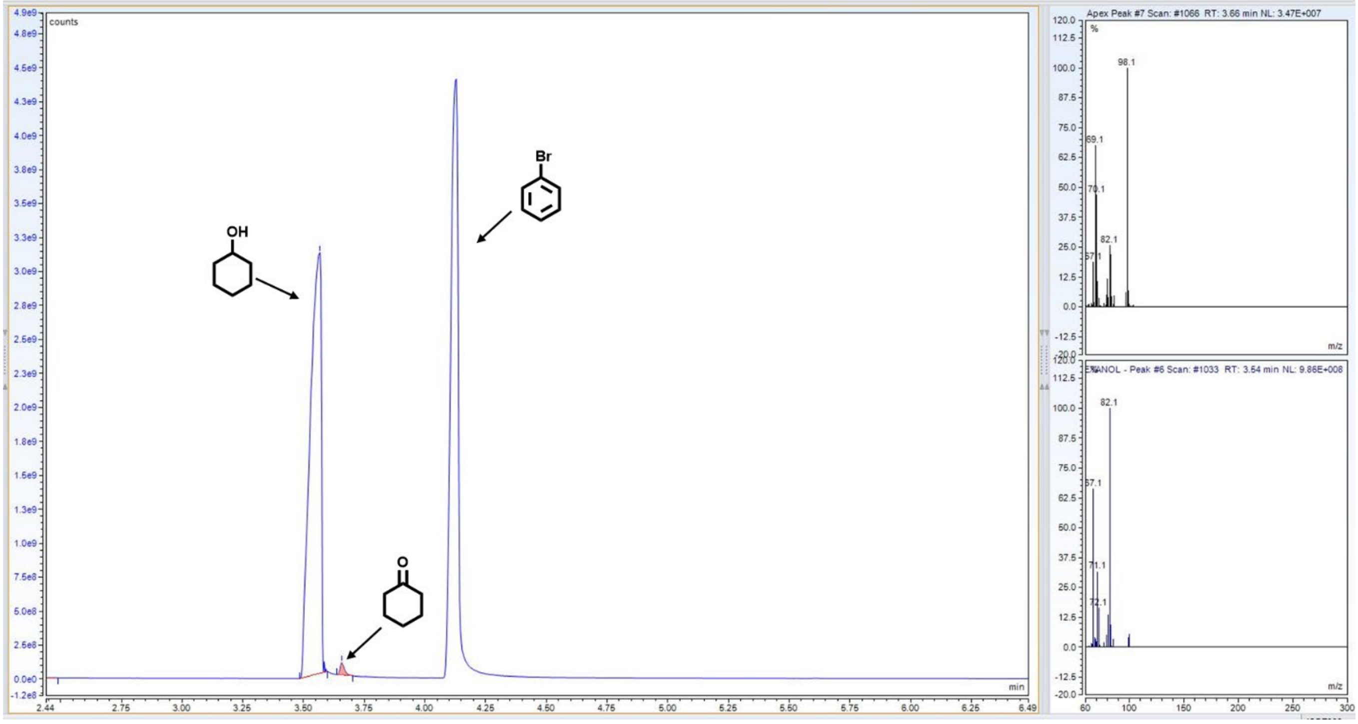

Figure S17: GC-MS traces for electrochemical oxidation of cyclohexanol at a constant potential of 0.26 V vs Fc$^+$/Fc and at pH 12. (Trace amount of product)

REFERENCES.

1. C. Panda, M. Ghosh, T. Panda, R. Banerjee, S. Sen Gupta, *Chem. Commun.* **2011**, *47*, 8016–8018.

2. W. L. F. Armarego, *Purif. Lab. Chem.* **2017**, 1–1176.
3. B. Chandra, Hellan K. M., S. Pattanayak and S. Sen Gupta, *Chem. Sci.*, 2020, **11**, 11877-11885.