Supporting Information for:

Reinvestigating Catalytic Alcohol Dehydrogenation with an Iridium Dihydroxybipyridine Catalyst

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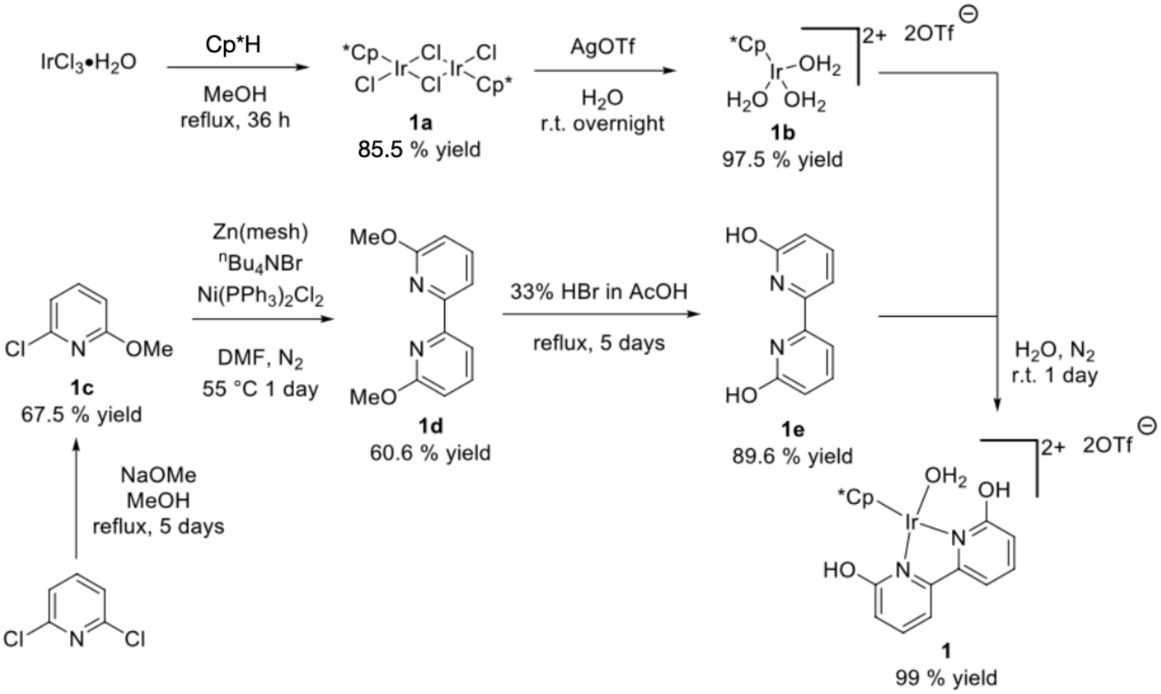
General Considerations: All the syntheses were done as described here using modified literature procedures. Reactions were prepared and performed under an inert atmosphere (N_2) using an MBraun glovebox or Schlenk line techniques in oven dried glassware unless otherwise stated. Work up and purifications were done open to air.

Solvents and Reagents: Dry solvents (either commercial or dried on a glass contour solvent purification system built by Pure Process Technology, LLC) were used for reactions unless described otherwise. Reagent grade solvents were used for work up and purification. All the reagents were used as received from the commercial supplier without further purification.

Instruments and Services: NMR spectra were recorded on a Bruker AVANCE 360 (360 MHz, ^{1}H frequency) or an AVANCE 500 (500MHz, ^{1}H frequency) NMR spectrometer. GC were recorded on an Agilent Technologies 6890N GC system with FID detector. Elemental analysis was performed by Robertson Microlit.

NMR Chemical Shift Reference: ^{1}H and $\{^1H\}^{13}C$ chemical shifts were assigned with respect to the residual peaks from deuterated NMR solvents.[1]

Papish Group Synthesis of [Cp*Ir(6,6'-dhbp)(H_2O)]($OTf)_2$ (1): The synthesis of complex **1** was carried out according to literature procedures as shown in Scheme S1. Each step is described fully below. For the sake of completeness, we include both the Papish group and Brewster group methods of synthesis (p. S13), which give spectroscopically and catalytically identical product.



Scheme S1. The synthesis of the catalyst **1**.

Pentamethylcyclopentadienyl iridium dichloride dimer (1a):[2-3] In a pressure tube, pentamethylcyclopentadiene (Cp*H, 1.44 mL, 9.20 mmol), $IrCl_3 \cdot 3H_2O$ (1.92 g, 5.43 mmol) from Pressure Chemical Co., and dry methanol (40 mL) were added. After purging with N_2, the pressure tube was sealed for heating to reflux with stirring by a magnetic stir bar for 36 h. The reaction was cooled down to room temperature slowly. After isolating the solid by filtration, the red-orange crystalline solid was washed by diethyl ether and dried in vacuum. Yield was 1.85 g (2.32 mmol, 85.5 %)

[Cp*Ir($H_2O)_3$]($OTf)_2$ (1b):[4] In a round bottom flask, **1a** (1.80 g, 2.26 mmol), AgOTf (3.77 g, 14.7 mmol), and H_2O (50 mL) were added. After purging with N_2, the flask was sealed with rubber septum and connected to Schlenk line. The reaction was stirred with a magnetic stir bar at room temperature overnight. The solid was removed by filtration. The solvent of filtrate was evaporated and dried in vacuo. The product was obtained as yellow powder (3.00 g, 4.41 mmol, 97.5 %). ^{1}H-NMR (D_2O, 360 MHz, ppm): δ 1.58 (s, Cp*) ^{19}F-NMR (D_2O, 339 MHz, ppm): δ -78.93.

2-chloro-6-methoxypyridine (1c):[5-7] In a dry round bottom flask, sodium (6.21 g, 270.29 mmol) was added to dry methanol (350 mL) by portions under N_2. 2,6-dichloropyridine (10 g, 67.6 mmol) was then added to the flask. The reaction mixture was heated to reflux for 5 days. After heating, the solution was concentrated under vacuo, and extracted with dichloromethane and H_2O. The organic layer was washed with H_2O and brine. After drying with $MgSO_4$, the solution was concentrated to obtain the product as clear liquid (6.55 g, 45.6 mmol, 67.5 %) ^{1}H-NMR ($CDCl_3$, 360 MHz, ppm): δ 7.51 (t, 1H, J_{HH} = 8 Hz); 6.90 (d, 1H, J_{HH} = 8 Hz); 6.65 (d, 1H, J_{HH} = 8 Hz); 3.94 (s, 3H).

6,6'-dimethoxy-2,2'-bipyridine (1d): [5-7] In a dry round bottom flask, Zn (mesh, 2.29 g, 35.1 mmol), $^nBu_4NBr$ (11.67 g, 42.0 mmol), and $Ni(PPh_3)_2Cl_2$ (6.85 g, 10.5 mmol) were added. The flask was purged with N_2, and dry DMF (100 mL) was added. The reaction was heated at 55 °C for 30 min with stirring with a magnetic stir bar, and 2-chloro-6-methoxypyridine (4.15 mL, 34.8 mmol) was then added. The reaction was heated for another day after addition. After cooling down to room temperature, the solid was removed by filtration. The filtrate was concentrated under vacuo. An extraction was performed with dichloromethane and H_2O, and the organic layer was washed with H_2O and brine. The organic solution was dried over $MgSO_4$. The solvent was removed under vacuo, and the yield was 2.28 g (10.5 mmol, 60.6 %).^{1}H-NMR (DMSO, 360 MHz, ppm): δ 7.98 (d, 2H, J_{HH} = 8 Hz); 7.85 (t, 2H, J_{HH} = 8 Hz); 6.87 (d, 2H, J_{HH} = 8 Hz); 3.96 (s, 6H).

6,6'-dihydroxy-2,2'-bipyridine (6,6'-dhbp, 1e):[5-7] In a round bottom flask, 6,6'-dimethoxy-2,2'-bipyridine (2.000 g, 9.249 mmol), and 33 % HBr in acetic acid (140 mL) were added. The flask was connected to a condenser with a base trap. The reaction was heated to reflux for 5 days with stirring by a magnetic stir bar. After cooling down the reaction to room temperature, the solid was isolated by filtration. The solid was then added to 200 mL H_2O and the pH was adjusted to 10 with a 5 M NaOH solution. After filtration to remove any undissolved impurities, the product was recovered by adjusting the pH to 7.5 with 5 M acetic acid solution and 0.1 M acetic acid solution. The product was isolated by filtration and dried in air as white solid (1.56 g, 8.29 mmol, 89.6 %).^{1}H-NMR (DMSO, 500 MHz, ppm): δ 7.57 (t, 2H, J_{HH} = 8 Hz); 7.14 (d, 2H, J_{HH} = 8 Hz); 6.50 (d, 2H, J_{HH} = 8 Hz); 1.77 (s, 2H)

[Cp*Ir(6,6'-dhbp)(H_2O)]($OTf)_2$ (1):[8] The preparation of catalyst **1** followed the literature method, and **1** was characterized using ^{1}H NMR and ^{19}F NMR. The yield was 366.8 mg prior to recrystallization (99 %) A sample was recrystallized by dissolving **1** in acetone and adding Et_2O to precipitate out a solid. The isolated solid was dissolved in acetone and recrystallized by diffusion of Et_2O into the solution. The resulting yellow crystals were analyzed by single crystal X-Ray diffraction (p. S20) which showed the structure as [Cp*Ir(6,6'-dhbp)(H_2O)]($OTf)_2(H_2O)_2$, in agreement with the published structure (collected at a different temperature)[8] and the elemental analysis. ^{1}H-NMR (D_2O, 360 MHz, ppm): δ 7.97 (t, 2H, J_{HH} = 8 Hz); 7.78 (d, 2H, J_{HH} = 8 Hz);

7.14 (d, 2H, J_{HH} = 8 Hz); 1.52 (s, 15H). ^{19}F-NMR (D_2O, 339 MHz, ppm): δ -78.92. Elemental Analysis for [**1** + $2H_2O$]: Calcd: C 30.45, H 3.37, N 3.23; Obsd: C 30.54, H 3.21, N 3.04.

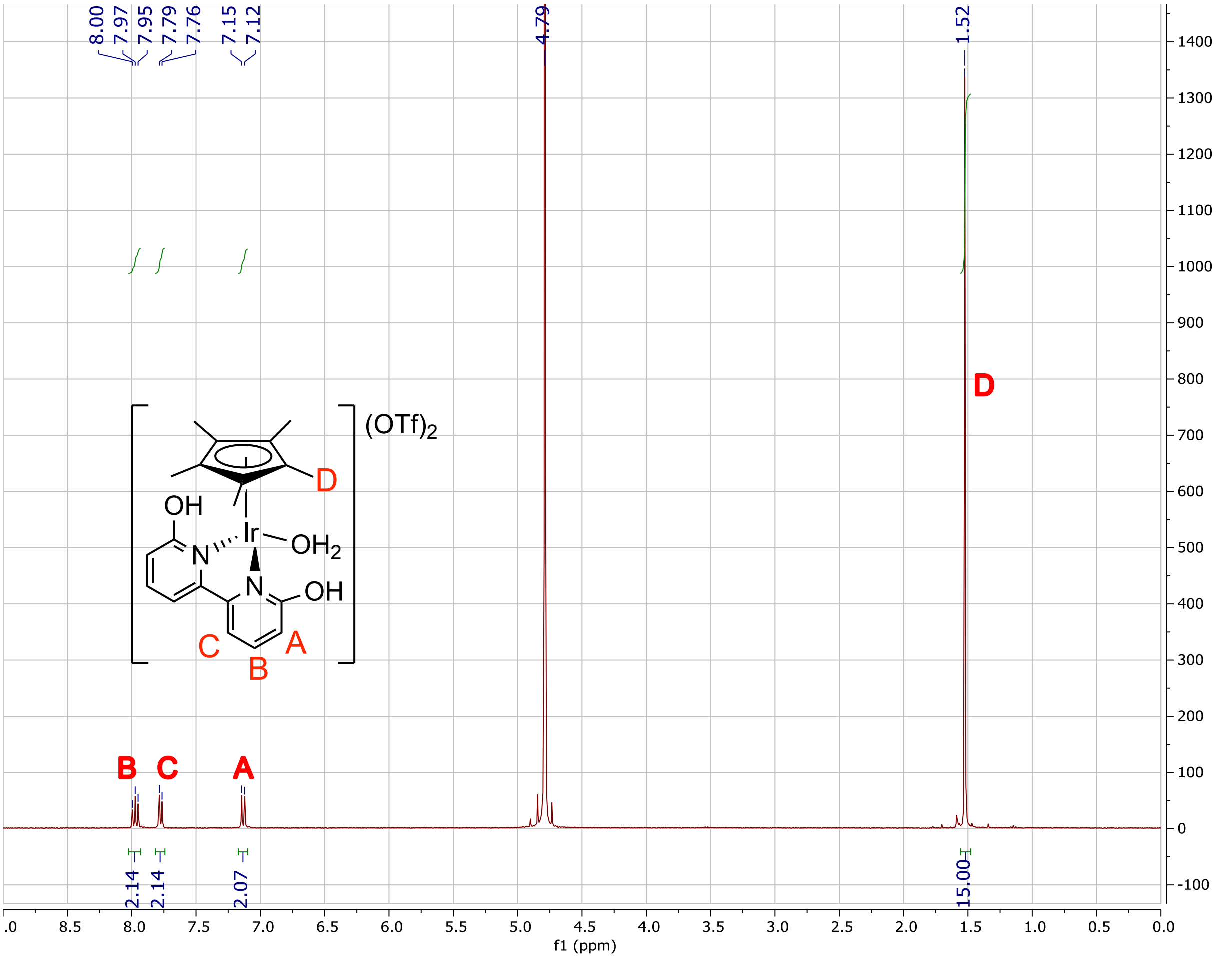


Figure S1. ^{1}H-NMR spectrum of [Cp*Ir(6,6'-dihydroxy-2,2'-bipyridine)(H_2O)]$(OTf)_2$ (**1**) in D_2O.

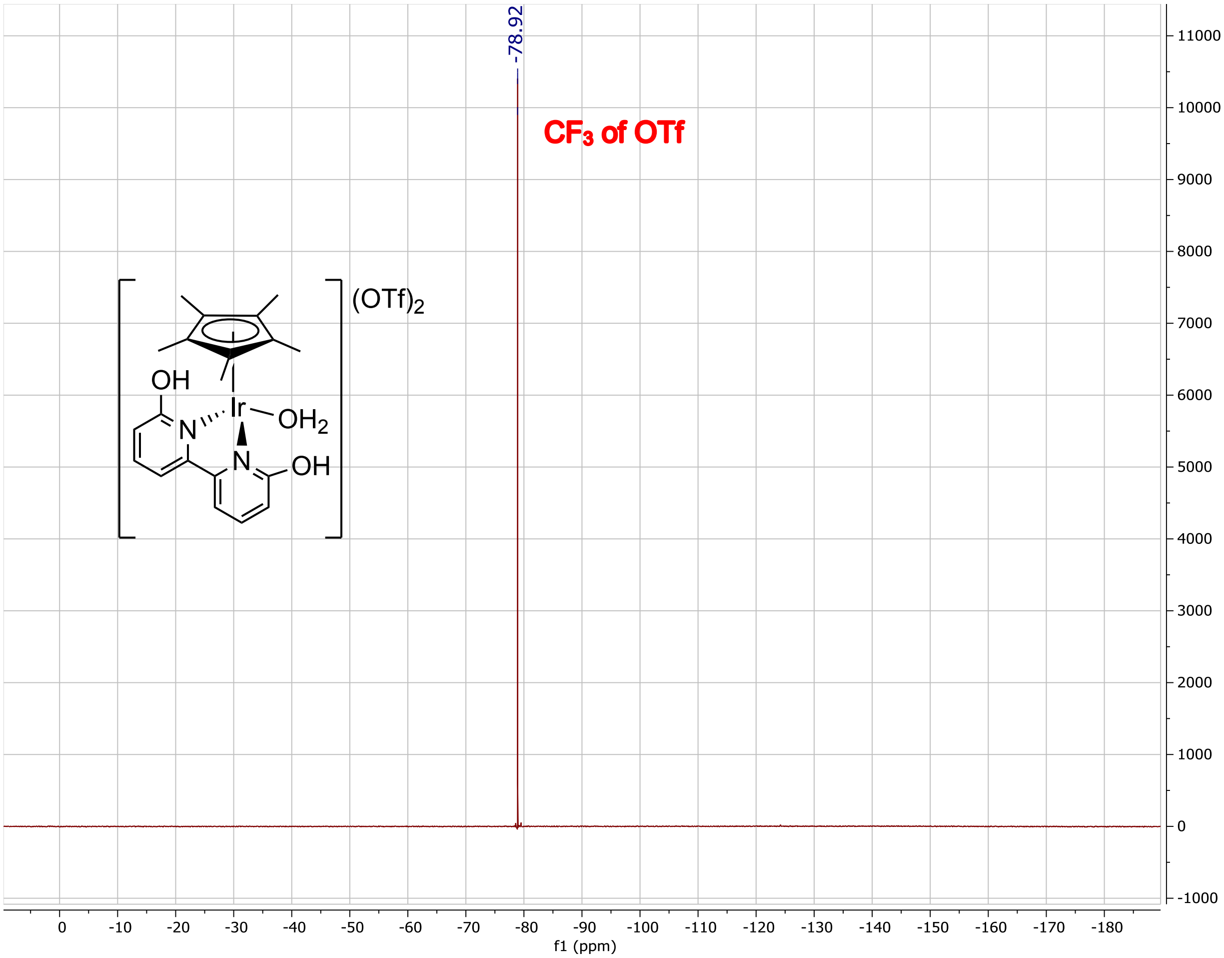


Figure S2. ^{19}F-NMR spectrum of [Cp*Ir(6,6’-dihydroxy-2,2’-bipyridine)(H_2O)]$(OTf)_2$ (**1**) in D_2O.

General Procedure for Dehydrogenative Oxidation of Benzyl Alcohol: Procedure for entry 7 of Table 1: To a 10 mL Schlenk flask, H_2O (5 mL), catalyst **1** (3.1 mg, 0.0037 mmol), and benzyl alcohol (25.9 µL, 0.250 mmol) were added. The reaction system was purged with Ar after connecting the reflux condenser, which is connected to a bubbler. The reaction mixture was then heated in an oil bath with stirring at 130 °C (oil bath temperature) for 20 h. The reaction was cooled down to room temperature after heating. Isopropanol (5 mL) was then added to the reaction mixture by syringe, followed by addition of biphenyl solution (100 µL, 0.01781 mmol biphenyl in 100 µL iPrOH solution) with a micro pipette. A sample was taken for GC analysis after stirring the mixture for 3 min.

Notes: In most cases (Table 1), the pH was not adjusted and the catalyst **1** produced an acidic solution. As indicated in Table 1, for some entries an alternate temperature was used for the oil bath or an alternate gas (N_2 or air) for purging was used. For the data in Table S2, the pH was adjusted with NaOH solution in certain cases, when a particular pH was desired.

Procedures for Dehydrogenative Oxidation of Benzyl Alcohol in Sealed Tube (Evidence for Benzene Formation): In a sealed reaction tube benzyl alcohol (BnOH) (16.6 µL, 0.1603 mmol), catalyst **1 (**2 mg, 0.002404 mmol, 1.5 mol%), and H_2O (5mL) were added. The reaction container was purged with N_2, and sealed for heating with stirring by a magnetic stir bar. After heating the reaction for 20 h, the reaction was cooled down to room temperature and extracted with 1 mL $CDCl_3$. A sample was taken for ^{1}H-NMR (Figure S3). Benzene can be observed at δ 7.36 ppm.

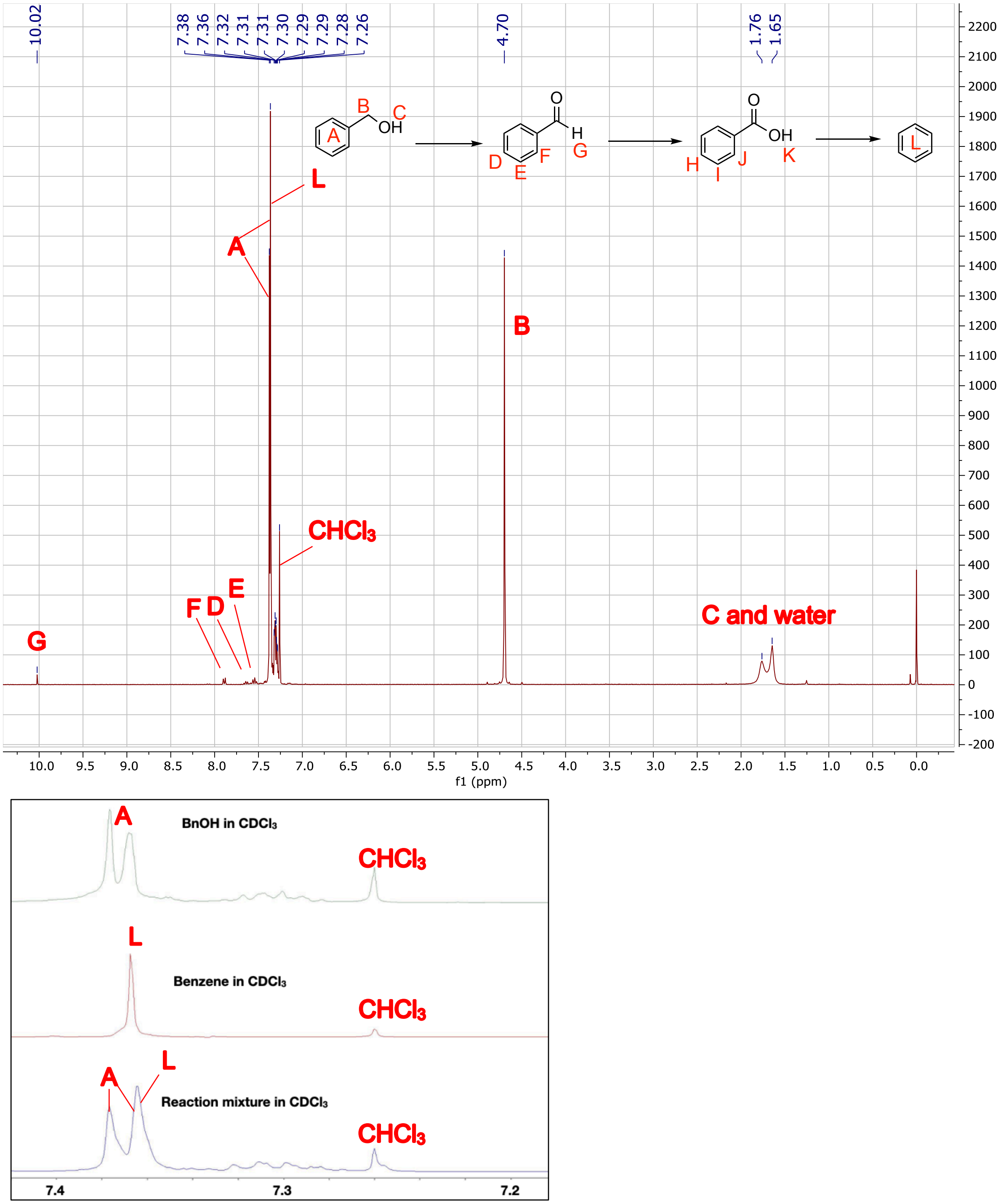
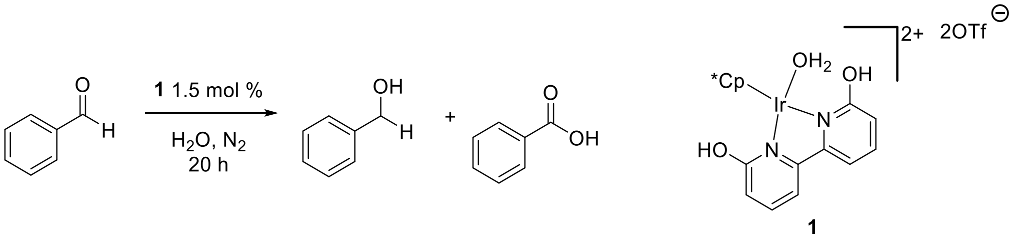


Figure S3. Top: ^{1}H NMR in CDCl$_3$ for the isolated organic compounds from the dehydrogenative oxidation of benzyl alcohol (BnOH) in water in a sealed tube. Benzene is present in this sample at 7.36 ppm, along with BnOH and other products (benzaldehyde). Benzoic acid is not observed here. **Bottom**: Stacked plot showing the zoomed in region at 7.2 to 7.4 ppm as compare to benzene and BnOH. Although the peaks of interest overlap, it is clear that the peak height and the peak width suggests that benzene may be present, with further evidence from the GC.

General Procedure for Benzaldehyde Reactions: To a 10 mL Schlenk flask, H_2O (5 mL), catalyst **1** (2.0 mg, 0.0024 mmol), and benzaldehyde (16.3 μL, 0.160 mmol) were added. The reaction system was purged with N_2 (Ar was used instead in some cases as indicated in the text) after connecting the reflux condenser, which is connected to Schlenk line with a bubbler. The reaction mixture was then heated in an oil bath with stirring at 130 °C (oil bath temperature) for 20 h. The reaction was cooled down to room temperature after heating. Isopropanol (5 mL) was then added to the reaction mixture by syringe, followed by addition of biphenyl solution (100 μL, 0.01781 mmol biphenyl in 100 μL iPrOH solution) with a micro pipette. A sample was taken for GC analysis after stirring the mixture for 3 min.

Table S1. Reactions of benzaldehyde with **1** in water at different temperatures.[a]



Entry	T of oil bath (°C)	% conv.	% sel. for alcohol	% sel. for acid
1	80	12.7(3)	98(1)	2(1)
2	95	17.8(9)	97.4(6)	2.6(6)
3	110	21.1(9)	95.7(7)	4.3(7)
4	130	23(4)	96.9(5)	3.1(5)

[a] All reactions were carried out with 0.16 mmol of benzaldehyde and 1.5 mol % of **1** in water for 20 h. All yields were determined via GC analysis with biphenyl as an internal standard. Reactions were conducted under nitrogen. All experiments were done in triplicate or with more than 3 replicates.

To study the effect of temperature on this reaction, various temperatures were tested in the above Table. However, there was no significantly influence on conversion and selectivity according data in Table S1. The interesting result from this group of data is that the selectivity favored alcohol formation over acid. If the disproportionation reaction occurred, benzoic acid would be formed in equal amounts to benzyl alcohol. The observed results may be caused by decomposition of the generated benzoic acid. After benzoic acid formed, it further decomposed to benzene and CO_2. We note that percent conversion is not really a true percent conversion to all products, because benzene and CO_2 are not quantified. The % conversion here is 100*(moles of alcohol + moles of acid)/(moles of benzaldehyde at the start of the reaction).

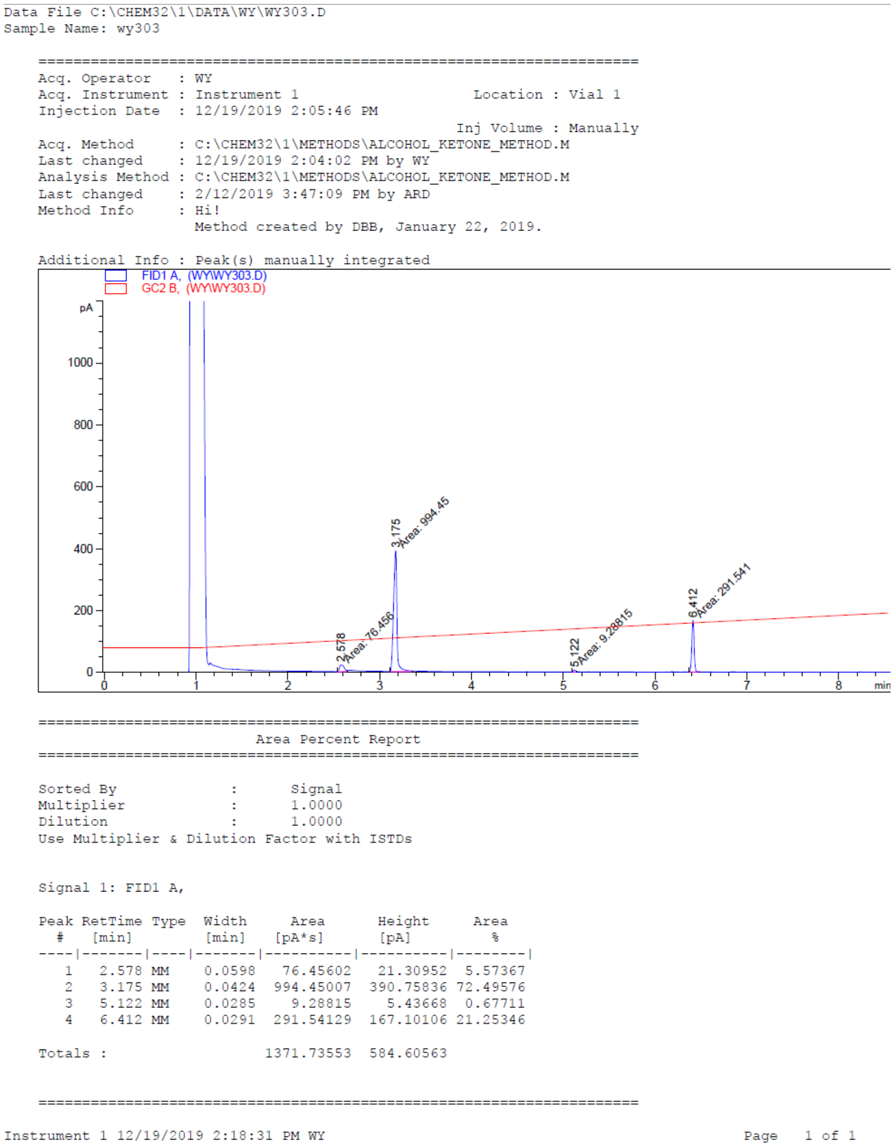
Table S2. Effect of pH on the Dehydrogenative Oxidation of Benzyl Alcohol with catalyst **1**.[a]

Entry	**T of oil bath (°C)**	**pH at start**	**pH at end**	**% conv.**	**% sel. for aldehyde**	**% sel. for acid**
1	110	7.1	4.2	3(1)	100	0
2	110	10.1	5	5(2)	97(3)	3(3)

[a] A water solution of **1** (1.5 mol %) was combined with benzyl alcohol and heated following the protocol on page S8. In these experiments, the pH was adjusted with NaOH solution at the start of the experiment. These experiments were performed in triplicate.

Method for gas chromatography: 1 μL of sample was injected into the inlet at 250 °C with pressure 27.8 psi. One tenth of the sample was split into the column with a flow rate 3.0 mL/min and pressure 27.8 psi. The column was kept at 80 °C for 1 min, then heated to 200 °C with heating ramp rate of 15 °C/min. The temperature was held for 2 min after reaching 200 °C. Biphenyl was used as an internal standard. Conversion was calculated by using the equation below. Figure S4 shows a sample GC trace.

$$\frac{\text{molar amount of products}}{\text{molar amount of starting material at start of the reaction}} \times 100\%$$



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                                                   Inj Volume : Manually
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    Last changed    : 12/19/2019 2:04:02 PM by WY
    Analysis Method : C:\CHEM32\1\METHODS\ALCOHOL_KETONE_METHOD.M
    Last changed    : 2/12/2019 3:47:09 PM by ARD
    Method Info     : Hi!
                      Method created by DBB, January 22, 2019.

    Additional Info : Peak(s) manually integrated

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.578 MM    0.0598   76.45602   21.30952  5.57367
       2   3.175 MM    0.0424  994.45007  390.75836 72.49576
       3   5.122 MM    0.0285    9.28815    5.43668  0.67711
       4   6.412 MM    0.0291  291.54129  167.10106 21.25346

    Totals :                   1371.73553  584.60563

    =====================================================================
Instrument 1 12/19/2019 2:18:31 PM WY                               Page    1 of 1
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Figure S4. Example of GC trace.

Brewster Lab Experimental Details and Results

Synthesis of [Cp*Ir(6,6'-dhbp)OH_2][OTf_2] (1). This complex was synthesized in a modified form of the method reported from Papish.[9] 212 mg (0.266 mmol) [Cp*$IrCl_2$]$_2$ (prepared as described using pentamethylcyclopentadiene purchased from Sigma Aldrich and $IrCl_3 \cdot 3H_2O$ purchased from Pressure Chemical[2]) and 102 mg (0.543 mmol) 6,6'-dihydroxy-2,2'-bipyridine (purchased from TCI) were weighed to a 25 mL Schlenk flask fit with a reflux condenser. 10 mL methanol was then added. The flask was sparged three times with argon, then refluxed for 24 h under argon atmosphere. The resulting yellow suspension was dried using a rotary evaporator to yield a yellow solid. Without further purification, 258 mg (1.01 mmol) AgOTf was added to the flask. 10 mL H_2O was then added and the resulting mixture was stirred at room temperature for 2 hours in the absence of light. The resulting yellow suspension was filtered through Celite to remove AgCl and the filtrate dried *in vacuo* to yield a yellow solid. Further purification was done by recrystallization. A solution of **1** in acetone was layered with diethyl ether. Spectral characteristics are consistent with those previously reported. Yield (combined over 2 steps): 292 mg (65%). Elemental Analysis on recrystallized and dried sample: Calculated for **1**: C 31.77, H 3.03, N 3.37; Measured: C 31.48, H 3.31, N 3.35.

Synthesis of [Cp*Ir(bpy)OH_2][OTf_2] (2). This complex was synthesized using the method reported by Goldberg.[10] 201 mg (0.253 mmol) [Cp*$IrCl_2$]$_2$ (prepared as described[2]) and 79 mg (0.506 mmol) 2,2'-bipyridine (purchased from Sigma Aldrich) were weighed to a 25 mL Schlenk flask fit with a reflux condenser. 10 mL methanol was then added. The flask was sparged three times with argon, then stirred at room temperature for 1 hour. The resulting yellow suspension was dried using a rotary evaporator to yield a yellow solid. Without further purification, 258 mg (1.01 mmol) AgOTf was added to the flask. 10 mL H_2O was then added and the resulting mixture was stirred at room temperature for 3 hours in the absence of light. The resulting yellow suspension was filtered through Celite to remove AgCl and the filtrate dried *in vacuo* to yield a yellow solid. Further purification was done by redissolving the solid in water and filtering through a 2 micron Nylon syringe filter. Spectral characteristics are consistent with those previously reported. Yield (combined over 2 steps): 198 mg (49%). Elemental Analysis: Calculated: C 33.04, H 3.15, N 3.50; Measured: C 33.19, H 2.89, N 3.44.

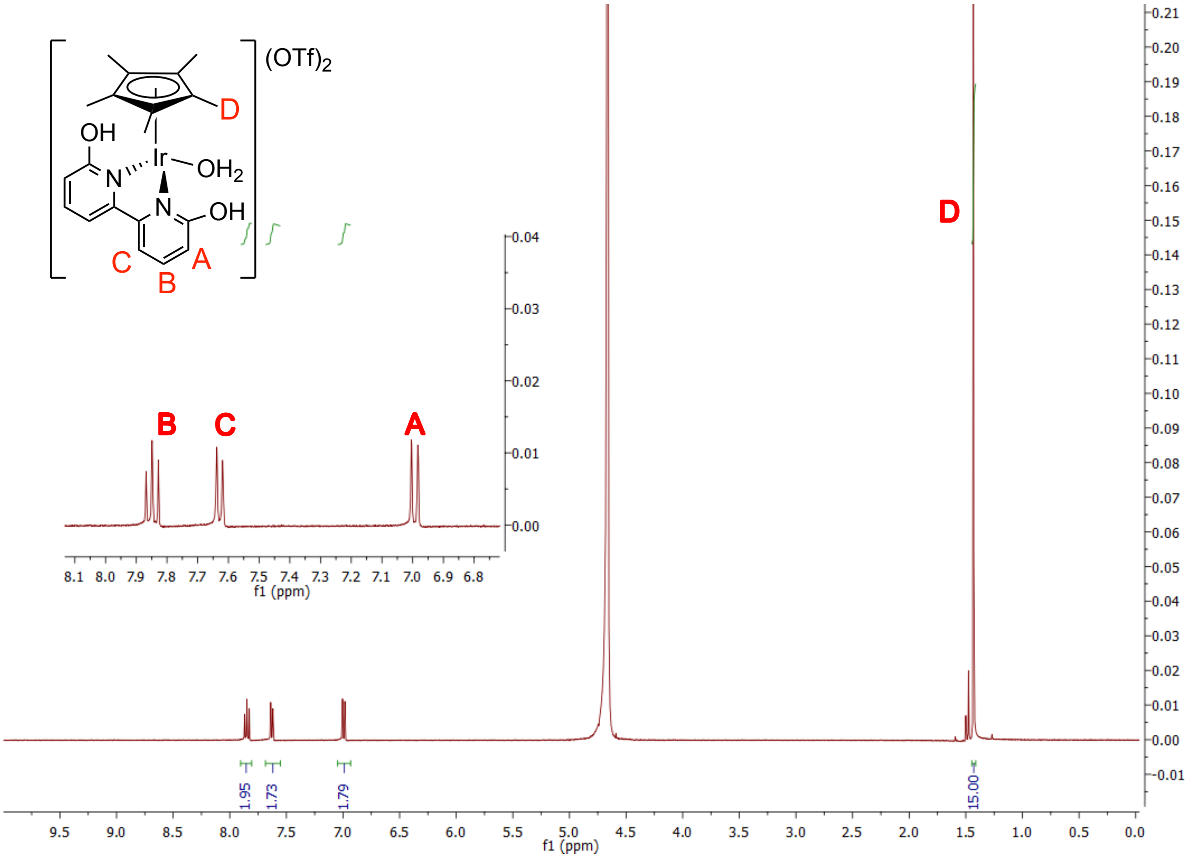

Figure S5. ^{1}H NMR spectrum in D_2O of [Cp*Ir(6,6'-dhbp)OH_2][OTf_2] (**1**) as prepared in the Brewster laboratory.

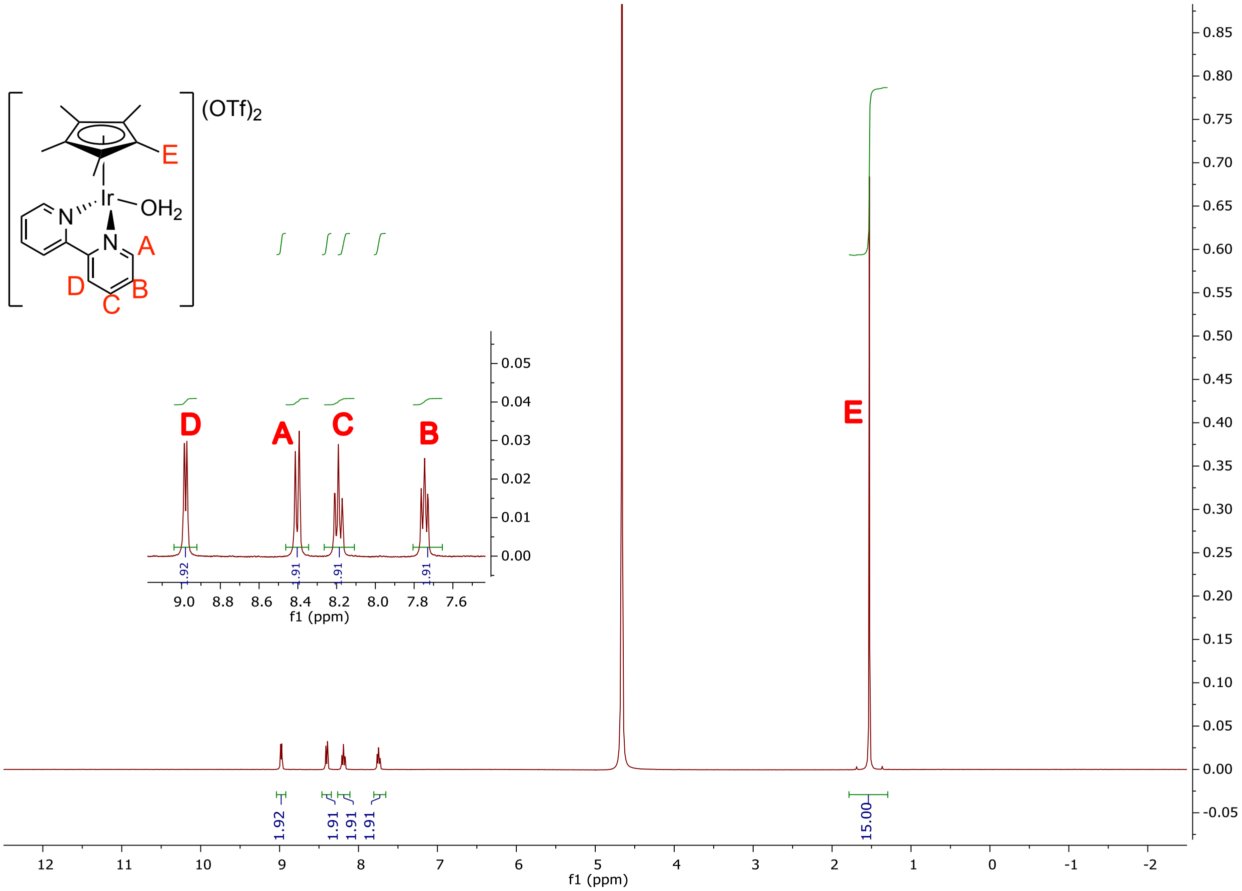

Figure S6. ^{1}H NMR spectrum in D_2O of [Cp*Ir(bpy)OH_2][OTf_2] (**2**) as prepared in the Brewster laboratory.

Procedure for Benzyl Alcohol Dehydrogenation in Brewster Laboratory 9 mg of **1** was weighed into a 20 mL beaker. 15 mL of deionized H_2O and 78 µL benzyl alcohol were added via syringe. 5 mL aliquots of the resulting solution were taken and added to a 10 mL Schlenk flask. The solution was sparged three times with argon. The resulting solutions were then heated to the specified temperature for 22 h under a positive pressure of argon. After the reaction time was complete, the reactions were cooled to room temperature. The crude mixtures were transferred, with isopropanol washing, to clean 50 mL round-bottom flasks and diluted with 25 mL of isopropanol. Approximately 23 mg of bibenzyl was added as an internal GC standard. Product yield was determined using GC/FID on an Agilent 5890 gas chromatograph fit with an HP-5 column. Peak integrations were standardized relative to bibenzyl using authentic samples from commercial suppliers.

Procedure for Hydrogenation of Alternative Substrates in Brewster Laboratory 0.25 mmol of substrate was weighed to a 10 mL Schlenk flask. The appropriate amount of catalyst (mol % determined by Fujita paper)[8] was weighed to a beaker and dissolved in 15 mL deionized H_2O. The catalyst solution was divided in 5 mL aliquots among the three Schlenk flasks. The resulting solutions were then heated to the specified temperature for 22 h under a positive pressure of argon. After the reaction time was complete, the reactions were cooled to room temperature. The crude mixtures were transferred, with isopropanol washing, to clean 50 mL round-bottom flasks and diluted with 25 mL of isopropanol. Approximately 23 mg of bibenzyl was added as an internal GC standard. Product yield was determined using GC/FID on an Agilent 5890 gas chromatograph fit with an HP-5 column. Peak integrations were standardized relative to bibenzyl using authentic samples from commercial suppliers. For NMR analysis, a 200 microliter aliquot of the product mixture was removed prior to dilution with isopropanol. This aliquot was transferred to an NMR tube, diluted with 20 microliters of D_2O (for NMR lock), then analyzed on a 400 MHz JEOL spectrometer using the WATERGATE pulse sequence. Peaks were identified by comparison with commercially available materials.

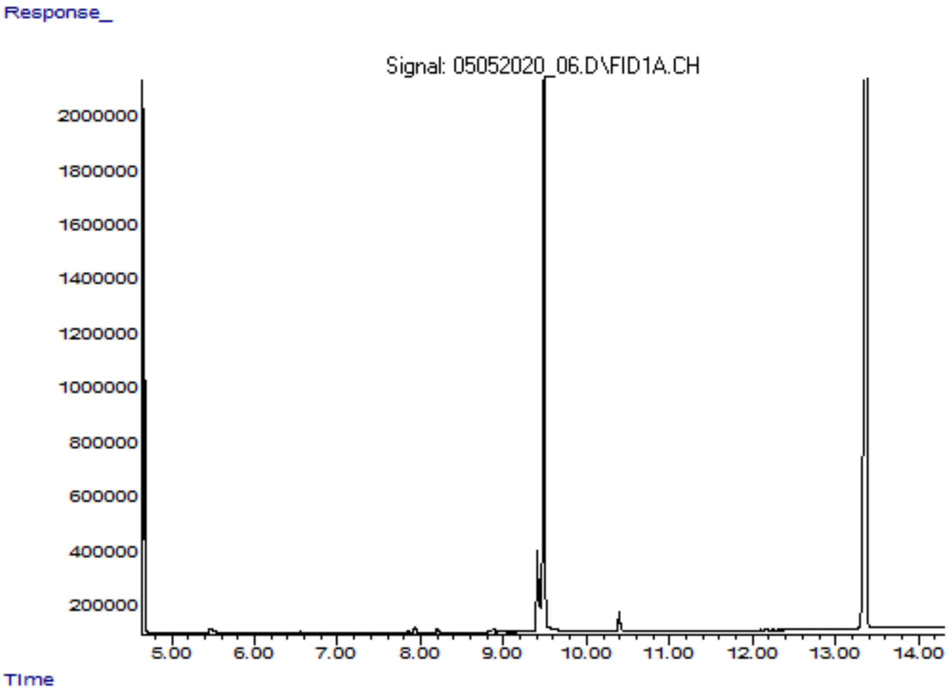

Figure S7. Representative GC/FID chromatogram from reaction at 120°C in the Brewster laboratory. Retention times for peaks of interest: 4.17 min – isopropanol solvent; 8.890 minutes: benzaldehyde; 9.48 minutes: benzyl alcohol; 10.49 minutes: benzoic acid; 13.36 minutes: bibenzyl internal standard. The peak at 5.54 minutes is benzene (see Figure S7 below).

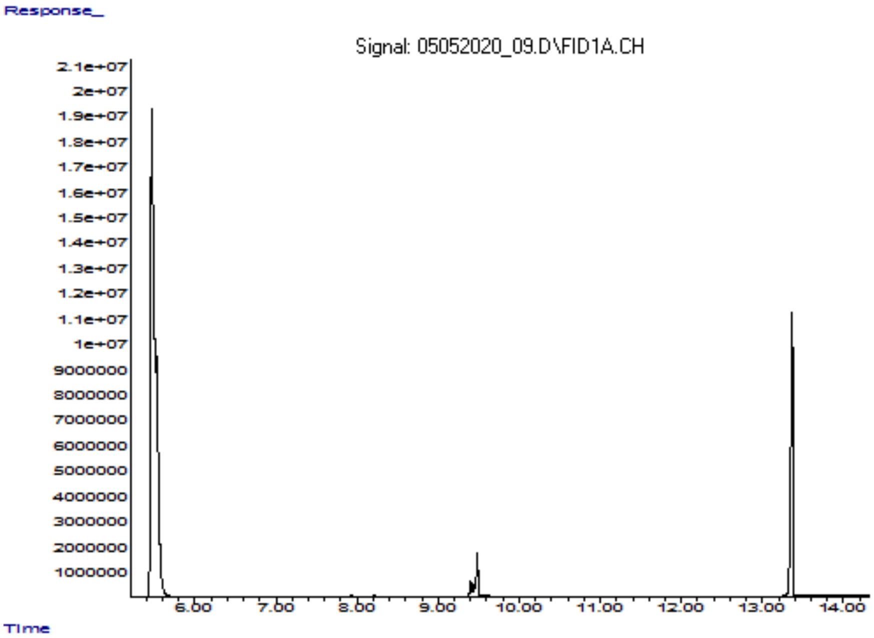

Figure S8. Representative GC/FID chromatogram from reaction at 120°C in Brewster laboratory. Sample was spiked with benzene.

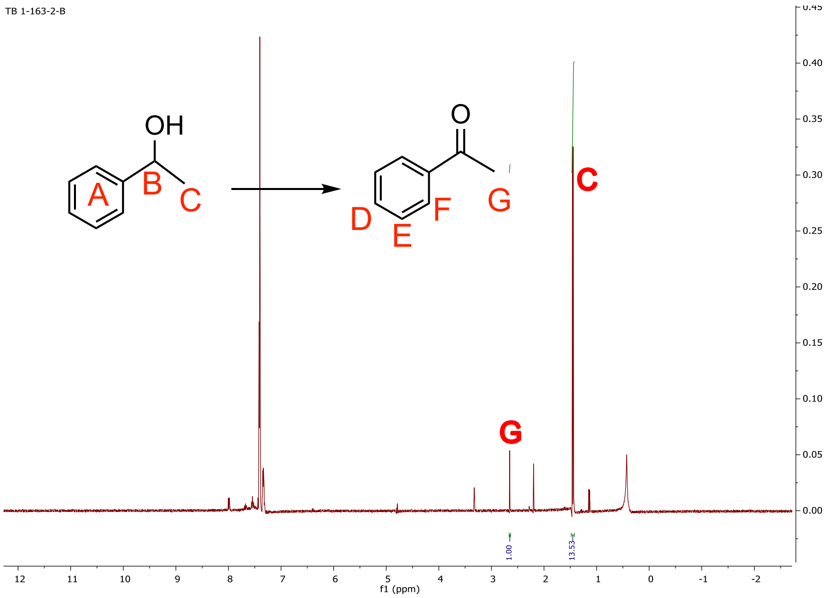

Figure S9. ^{1}H NMR spectrum in H_2O/D_2O of product mixture from dehydrogenation of 1-phenylethanol catalyzed by **1**. Spectrum acquired using WATERGATE pulse sequence.

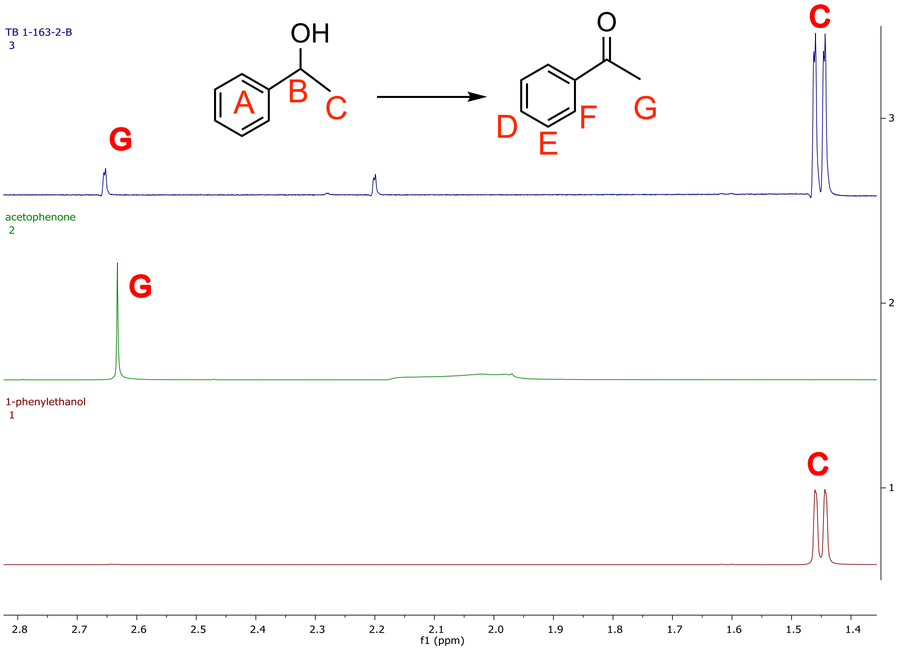

Figure S10. Stacked spectra for product identification. Bottom: Truncated ^{1}H NMR spectrum of 1-phenylethanol in D_2O. Run as saturated solution using commercially available material (Sigma Aldrich). Middle: Truncated ^{1}H NMR spectrum of acetophenone in H_2O/D_2O. Run as saturated solution using commercially available material (Sigma Aldrich). Top: Truncated ^{1}H NMR spectrum in H_2O/D_2O of product mixture from dehydrogenation of 1-phenylethanol catalyzed by **1**. Spectrum acquired using WATERGATE pulse sequence.

Single Crystal X-Ray Diffraction on 1

Experimental. Single clear yellow plate crystals of 1 were used as supplied. A suitable crystal with dimensions 0.21 × 0.09 × 0.07 mm^3 was selected and mounted on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at a steady T = 100.0(3) K during data collection. The structure was solved with the ShelXT[11] solution program using dual methods and by using Olex2[12] as the graphical interface. The model was refined with ShelXL 2018/3[13] using full matrix least squares minimisation on F^2. This data has been deposited in the CCDC database under deposit number 2025971.

Crystal Data. $C_{22}H_{29}F_6IrN_2O_{11}S_2$, M_r = 867.79, triclinic, P-1 (No. 2), a = 11.2579(4) Å, b = 11.4851(4) Å, c = 14.2451(5) Å, α = 105.902(3)°, β = 95.039(3)°, γ = 117.496(4)°, V = 1520.89(11) Å^3, T = 100.0(3) K, Z = 2, Z' = 1, μ(Mo K$_\alpha$) = 4.621, 9628 reflections measured, 9628 unique which were used in all calculations. The final wR_2 was 0.1301 (all data) and R_1 was 0.0403 ($I \geq 2\sigma(I)$).

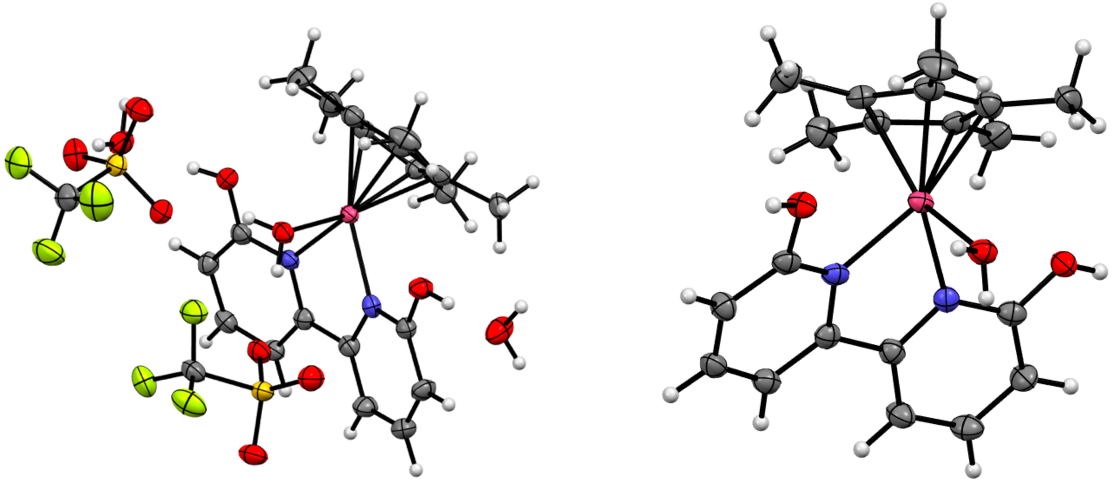

Figure S11. Molecular Diagram for **1** (crystallized as $[Cp^*Ir(OH_2)(6,6'\text{-dhbp})](OTf)_2(H_2O)_2)$ showing all atoms (left) and with the OTf anions and water molecules hidden (right). Ellipsoids are shown at 50% probability. Grey = C, Blue = N, Red = O, Pink = Ir, Yellow = S, Green = F.

Table S3. Crystal Data for **1**.

Compound	**1**
Formula	$C_{22}H_{29}F_6IrN_2O_{11}S_2$
$D_{calc.}$/ g cm^{-3}	1.895
μ/mm^{-1}	4.621
Formula Weight	867.79
Colour	clear yellow
Shape	plate
Size/mm^3	0.21×0.09×0.07
T/K	100.0(3)
Crystal System	triclinic
Space Group	P-1
a/Å	11.2579(4)
b/Å	11.4851(4)
c/Å	14.2451(5)
α/°	105.902(3)
β/°	95.039(3)
γ/°	117.496(4)
V/Å^3	1520.89(11)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	2.107
Θ_{max}/°	30.033
Measured Refl's.	9628
Indep't Refl's	9628
Refl's I≥2 σ(I)	9069
R_{int}	N/A
Parameters	411
Restraints	0
Largest Peak	2.445
Deepest Hole	-2.074
GooF	1.113
wR_2 (all data)	0.1301
wR_2	0.1282
R_1 (all data)	0.0433
R_1	0.0403

Structure Quality Indicators

Reflections:	d min (Mo) 0.71	I/σ(I) 88.7	Rint n/a	complete 100%
Refinement:	Shift 0.000	Max Peak 2.4	Min Peak -2.1	GooF 1.113

A clear yellow plate-shaped crystal with dimensions 0.21 × 0.09 × 0.07 mm^3 was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix diffractometer operating at T = 100.0(3) K.

Data were measured using ω scans using Mo K$_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.80a, 2020). The maximum resolution that was achieved was Θ = 30.033° (0.71 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.80a, 2020). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.80a, 2020) on 12149 reflections, 126% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.80a, 2020). The final completeness is 100.00 % out to 30.033° in Θ. A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.80a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this material is 4.621 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.739 and 1.000.

The structure was solved and the space group P-1 (# 2) determined by the ShelXT[11] structure solution program using using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of ShelXL 2018/3.[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_*refine_special_details*: Refined as a 3-component non-merohedral twins.

_*exptl_absorpt_process_details*: CrysAlisPro 1.171.40.80a (Rigaku Oxford Diffraction, 2020) using spherical harmonicsas implemented in SCALE3 ABSPACK.

_*twin_special_details*: Component 2 rotated by 0.9261° around [-0.03 0.93 -0.38] (reciprocal) or [0.41 0.91 0.04] (direct). Component 3 rotated by 0.8101° around [-0.41 -0.91 0.06] (reciprocal) or [-0.60 -0.78 -0.20] (direct).

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

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