Electronic Supplementary Information for:

Second Sphere Ligand Modifications Enable a Recyclable Catalyst for Oxidant-Free Alcohol Oxidation to Carboxylates

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Experimental Details

General Considerations: All commercially-available reagents were used as received without further purification. All liquid alcohol substrates were distilled from CaH_2 and stored over 3Å molecular sieves prior to use. 6,6"-bis(2,4,6-trimethylphenylamino)terpyridine (H_2Tpy^{NMes})[1], complex **2**[2] and complex **3**[3], $Ru(PPh_3)_3Cl_2$[4] were prepared as previously described. KOH, NaOH, and LiOH were dried under vacuum at 150°C overnight and powered using a mortar and pestle or automated grinder before use. All manipulations were carried out under an atmosphere of nitrogen in an Innovative Technologies Pure LabHE GP-1 glovebox or using Schlenk techniques, unless otherwise specified. Degassed, anhydrous solvents were obtained by a SG Water USA solvent purification system or by drying overnight with CaH_2 followed by distillation. NMR spectra were collected on a Varian MR400, Varian vnmrs 500 or Varian vnmrs 700 and were referenced to residual solvent peaks. ^{31}P NMR spectra were referenced to their respective ^{1}H spectrum. IR spectra were collected on a Nicolet is10 spectrometer using a diamond attenuated total reflectance (ATR) accessory. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, Ga.

General Procedure for GC-FID Analysis: Gas chromatography was performed on a Shimadzu GC-2014 equipped with an FID detector and a Shimadzu SH-Rxi-5ms (15 m, 0.25 mm ID, 0.25 μm df) column. H_2 gas was used as the carrier gas. All GC experiments were collected using the following method: 80°C hold for first 2 min, ramp to 300°C at 30°C/min and hold for 2 min. The injector temperature was set to 260°C and the detector was set to 300°C. GC calibration curves were obtained by plotting the response ratios of the areas of $A_{sample}/A_{standard}$ against the known concentrations.

Synthesis of $Ru(H_2Tpy^{NMes})(PPh_3)Cl_2$ (1): To a 100 mL Schlenk flask, 1.0996 g (1.147 mmol) $Ru(PPh_3)_3Cl_2$ and 0.6012 g (1.204 mmol) H_2Tpy^{NMes} was added. The flask was then subjected to multiple vacuum/refill cycles with N_2. 60 mL of bench top toluene (not dry) was then sparged for 6 minutes with N_2 and added to the flask. A reflux condenser was affixed to the flask and the reaction was heated to reflux for 20 hours. Upon cooling to room temperature a purple precipitate formed in the flask. 50 mL of N_2-sparged hexane was added to the flask and the flask was placed in a -25 °C freezer for 16 h. The product was collected on a glass frit in the air, washed with pentane (3 x 10 mL), and dried *in vacuo.* The product was further purified in an N_2-filled glovebox by dissolution in minimal CH_2Cl_2 followed by precipitation with diethyl ether. The product was isolated by filtration on a glass frit, washed with diethyl ether (2 x 10 mL) and dried *in vacuo* for 16 h to yield 820.8 mg (77% yield) of a purple powder. Purple crystals suitable for X-ray diffraction were grown from a concentrated benzene solution at room temperature. ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.56 (s, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.20 (dd, *J* = 7.4, 8.5 Hz, 2H), 7.17 (m, 9H), 7.00 (m, 6H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.88 (s, 2H), 6.84 (s, 2H), 5.98 (d, *J* = 8.5 Hz, 2H), 2.29 (s, 6H), 2.26 (s, 6H), 1.96 (s, 6H). ^{31}P NMR (283 MHz, $CDCl_3$) δ 44.2 (s, PPh_3). IR (powder, cm^{-1}): 1614, 1567, 1515, 1467, 1421, 1253, 778. HRMS (ESI-TOF) m/z: [**1** – Cl]$^+$ Calcd for $C_{51}H_{48}ClN_5PRu$: 898.2379; Found: 898.2383.

Synthesis of [Ru(H_2Tpy^{NMes})(PPh_3)$_2$H]PF_6 (1-H): In the air, a 100 mL Schlenk flask was charged with 500.0 mg (0.5354 mmol) **1**, 280.8 mg (1.071 mmol) triphenylphosphine, and 174.6 mg (1.071 mmol) ammonium hexafluorophosphate. The flask was then subjected to multiple vacuum/refill cycles with N_2. 75 mL of N_2-sparged benchtop (not dry) methanol was added to the flask and the solution was allowed to stir at room temperature for 20 hours. The orange product, [Ru(H_2Tpy^{NMes})(PPh_3)$_2$Cl]PF_6, was then converted in one-pot to **1-H** by addition of 202.5 mg (5.354 mmol) sodium borohydride to the reaction flask, causing gas evolution from the dark red reaction solution. After stirring at room temperature for an additional 24 hours the methanol was removed by rotary evaporation to afford a red powder. The solid was brought into a nitrogen-filled glovebox, washed with pentane (3 x 10 mL), dissolved in ~50 mL CH_2Cl_2 and filtered over Celite. The CH_2Cl_2 was concentrated to ~10 mL and ~50 mL diethyl ether was used to precipitate the product as a red solid. The precipitate was filtered, washed with diethyl ether (2 x 10 mL), and dried *in vacuo* overnight affording 456 mg (67 % yield) of **1-H**. Red crystals suitable for X-ray diffraction were grown from toluene. ^{1}H NMR (700 MHz, CD_2Cl_2) δ 8.99 (s, 2H), 7.71 (t, *J* = 8.0 Hz 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 7.4, 8.3 Hz, 2H), 7.20 (m, 12H), 7.05 (d, *J* = 7.4 Hz, 2H), 6.95 (m, 16H), 6.73 (s, 4H), 5.68 (d, *J* = 8.3 Hz, 2H), 2.23 (s, 6H), 1.28 (s, 12H), -6.76 (t, J_{HP} = 21.2 Hz, 1H). ^{31}P NMR (283 MHz, $CDCl_3$) δ 41.5 (s, PPh_3), -144.5 (quint, PF_6). IR (powder, cm^{-1}): 1819 (Ru-H), 1605, 1564, 1497, 1479, 1432, 1418, 1247, 833 (PF_6). HRMS (ESI-TOF) m/z: [**1-H**]$^+$ Anal. calcd for $C_{69}H_{64}F_6N_5P_3Ru$: 1126.3680 Found: 1126.3691.

NMR Data:

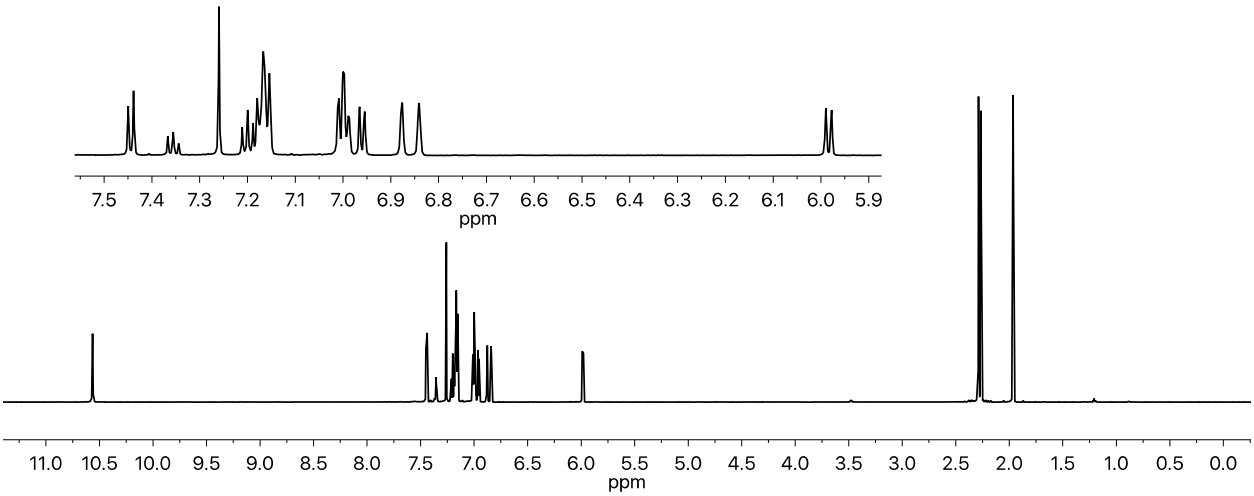


Figure S1: 700 MHz ^{1}H NMR spectrum of **1** collected at 25°C in $CDCl_3$.

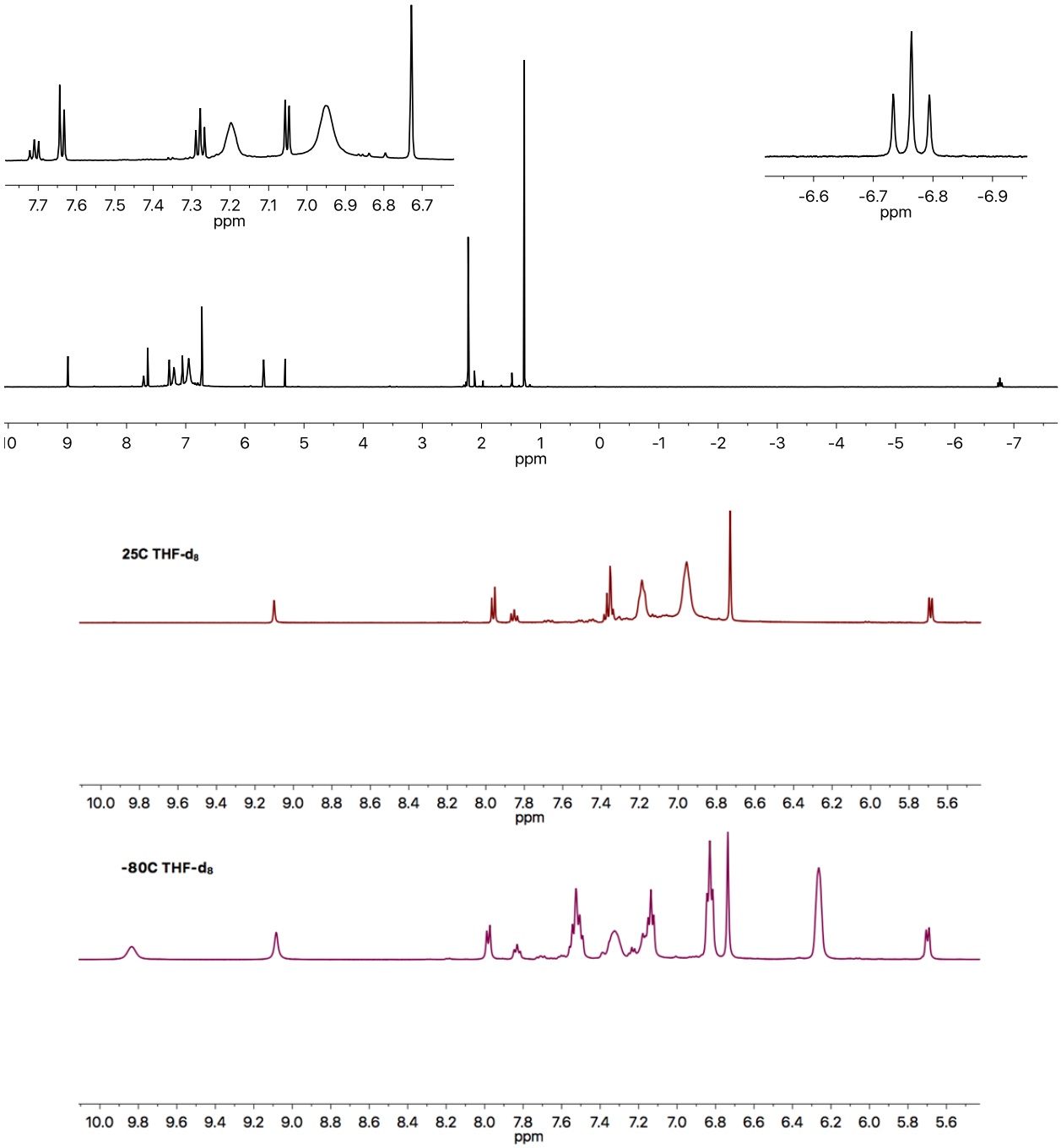


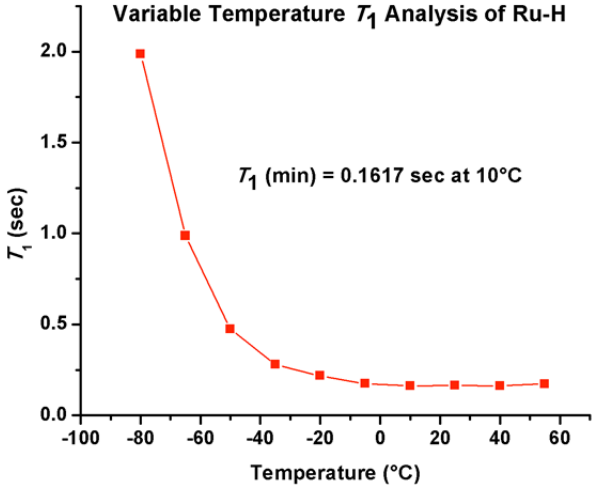
Figure S2: (Top) 700 MHz ^{1}H NMR spectrum of **1-H** collected at 25°C in CD_2Cl_2. (Bottom) Overlay of the ^{1}H NMR spectrum collected at 25°C and -80°C in THF-d_8. We ascribe the broadening of the PPh_3 resonances in the 25°C spectrum to H-H coupling between multiple rotating aryl CH protons with the Ru-H. The ortho-CH protons of the PPh_3 ligand are in close contact with the Ru-H (see crystal structure), and these are resolved in the -80°C spectrum at 9.83 ppm consistent with similar systems.[5]

Details of H–H distance calculation:

The average intramolecular H–H distance between the Ru-hydride and the pendent ligand mesitylamino group in solution was determined by evaluating through-space dipole–dipole induced nuclear spin relaxation contributions.[6] For a detailed example of this analysis from our lab see the supporting information in reference 7. The T_1(min) for **1-H** was estimated by obtaining a T_1 value at variable temperatures (-80°C to 55°C in THF). Although the boiling point of THF limited the maximum temperature that could be reached (and the complete temperature/T_1 profile), we used the temperature T_1 of 10 °C, with a value of 0.1617. The T_1(min) value was then used for the interatomic distance calculation based on the relationship between dipole-dipole relaxation and interatomic distance. Using the crystal structure, the net contribution to the T_1(min) from *all* the atoms, except the pendent mesitylamine protons, was calculated based on distance to the hydride. The remaining relaxation time contribution was used to calculate the interatomic hydride-NH distance.

Interaction	**$1/T_1$(min)**
^{1}H–H1	1.1206
^{13}C–H1	0.00003887
^{14,15}N–H1	0.01005
^{31}P–H1	0.05882
^{101}Ru–H1	0.03639

Observed T_1(min) = 0.1617 sec
Corrected T_1(min) = 0.2064 sec
Calculated H–H distance = 1.782 Å



Details of H/D exchange experiment:

D_2O was added to NMR samples of **1-H** and H_2Tpy^{NMes} in THF and the progress of H/D exchange was monitored by ^1H NMR spectroscopy against a trimethyl(phenyl)silane internal standard.

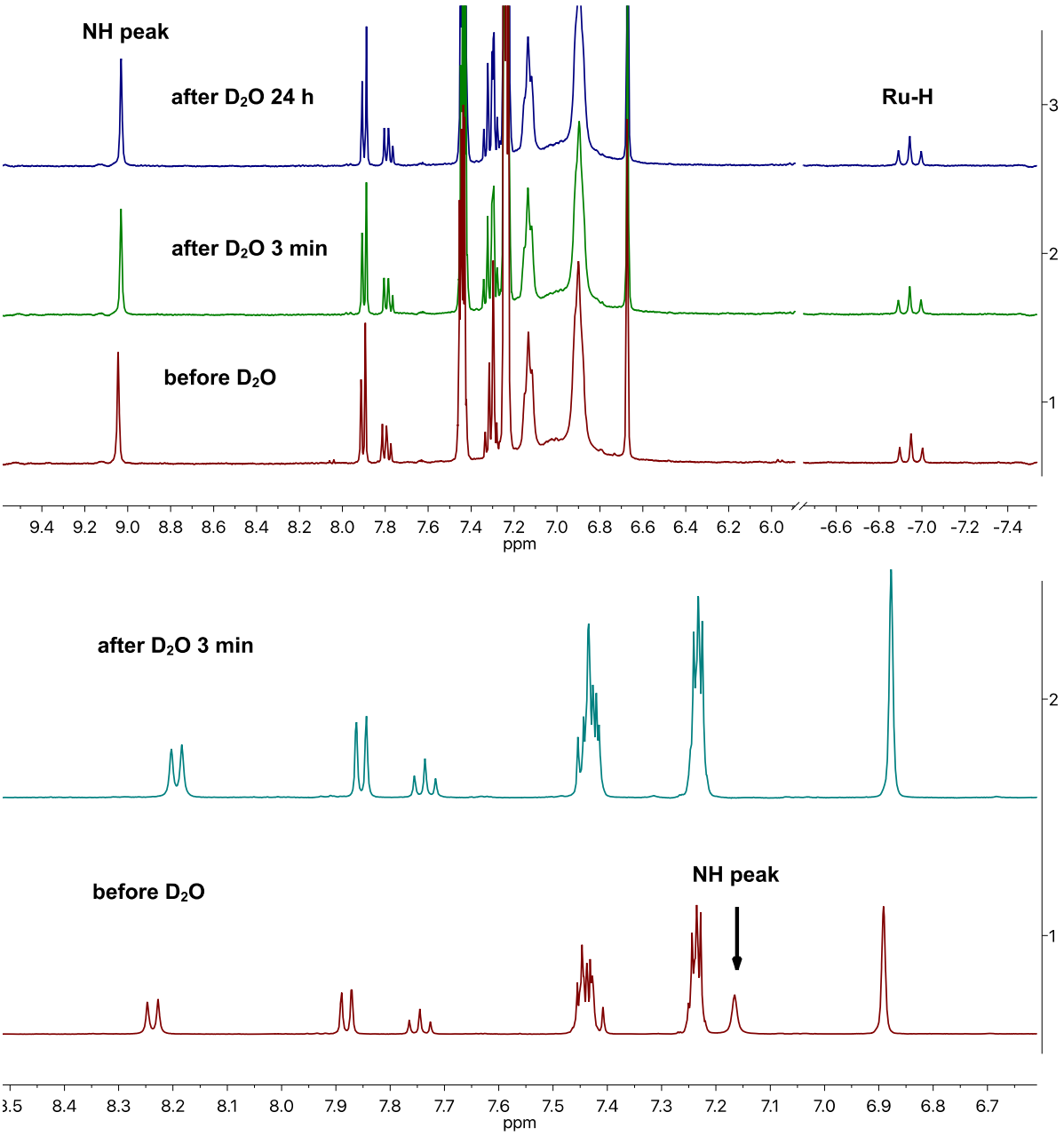
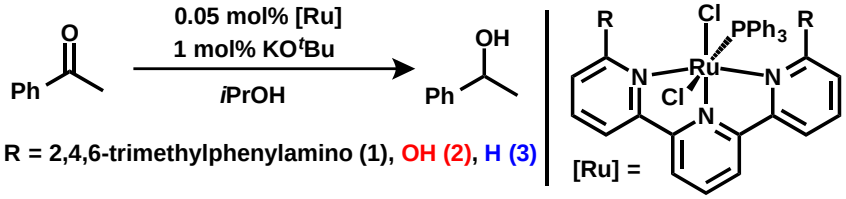


Figure S3: H/D exchange ^1H NMR spectra of **1-H** (top) and H_2Tpy^{NMes} (bottom) collected at 25°C in THF before and after adding D_2O at the specified times.

Details of transfer hydrogenation reactions:

Transfer hydrogenation reactions were carried out in NMR tubes using 0.05 mmol acetophenone, 0.0005 mmol KO^{t}Bu, 0.000025 mmol [Ru], and 0.5 mL *i*PrOH. 1.25 mM stock solutions of **1**-**3** with KO^{t}Bu were prepared and stirred for 10 min to dissolve the catalysts of which 20 µL was added to the respective NMR tube. 5 µL of trimethyl(phenyl)silane (PhTMS) was added to each tube as an internal standard. For each sample, the ^{1}H NMR spectrum was obtained prior to being placed in pre-heated oil bath for the allotted time. Reaction yield was determined by the consumption of the acetophenone resonance against the PhTMS peak. 25µL degassed H_2O (5% w/v) was added to tubes for water stability tests.

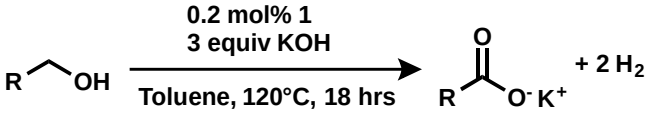


Entry	Catalyst	Temp. (°C)	Time	% Yield	Turnover Number
1	**1**	40	24	95%	1900
2	**2**	40	24	0%	0
3	**3**	40	24	17%	340
4	**1**	80	12	69%	1380
5	**2**	80	12	34%	680
6[a]	**1**	80	12	56%	1120
7[a]	**2**	80	12	2%	40

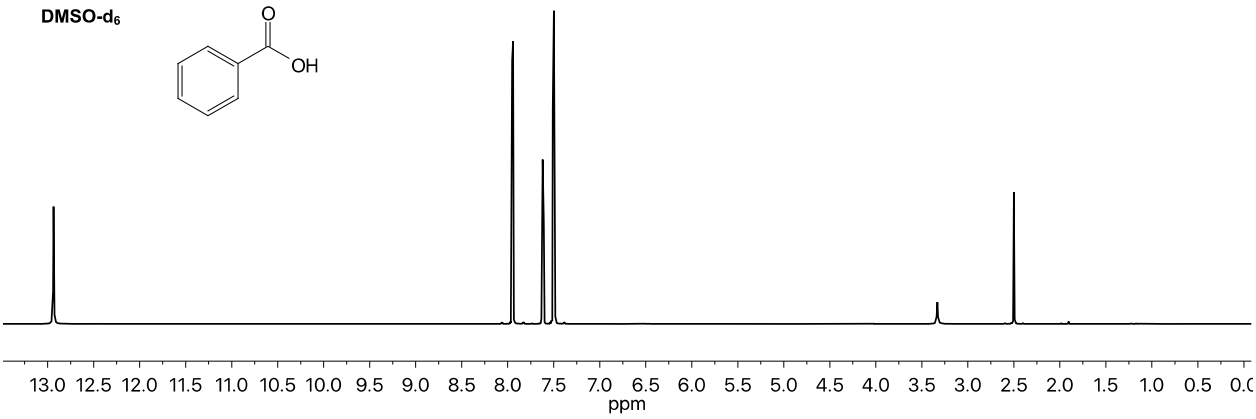
[a] 25 µL H_2O added.

General procedure for dehydrogenative oxidation reactions:

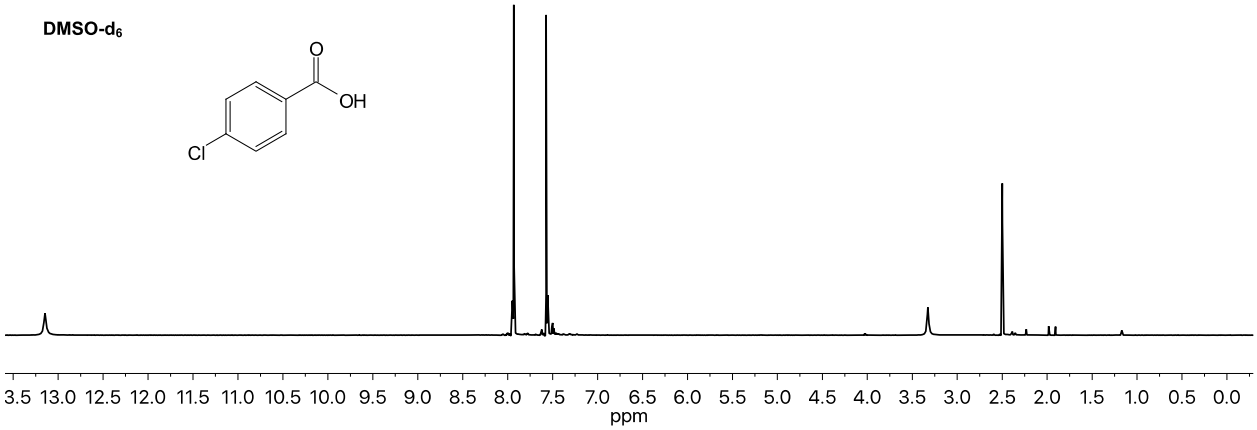
In a nitrogen-filled glovebox, a 20 mL glass scintillation vial was charged with KOH (84.1 mg, 1.5 mmol), primary alcohol substrate (0.5 mmol), and a Teflon stir bar. A 2 mL aliquot of a 0.5 mM solution of **1** in toluene was then added to the vial (0.001 mmol, 0.2 mol% **1**). The vial was then sealed with a Teflon-lined cap and placed on a pre-heated aluminum block at 120°C for 18 h while stirring at 1000 rpm. After cooling to room temperature, the vial was removed from the glovebox and H_2O (5 mL) was added to the reaction solution. *Note: the vial may be under positive pressure due to hydrogen gas evolved during acceptorless dehydrogenation.* The organic layer was extracted with ethyl acetate (3 x 5 mL) and discarded. 0.4 mL of a 6 M HCl solution was added to the aqueous layer and the product was extracted with ethyl acetate (3 x 5 mL). The organic fractions were combined, dried over Na_2SO_4, and filtered through a pipette fitted with glass filter paper. The ethyl acetate was removed by rotary evaporation to yield the product carboxylic acid.



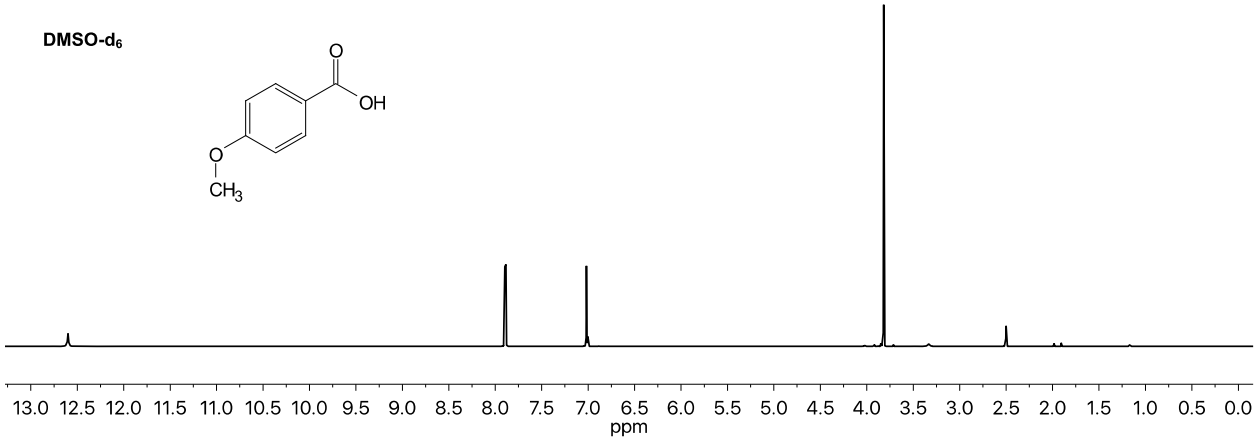
Benzoic acid: ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.50 (dd, J = 7.3, 8.4 Hz, 2H).



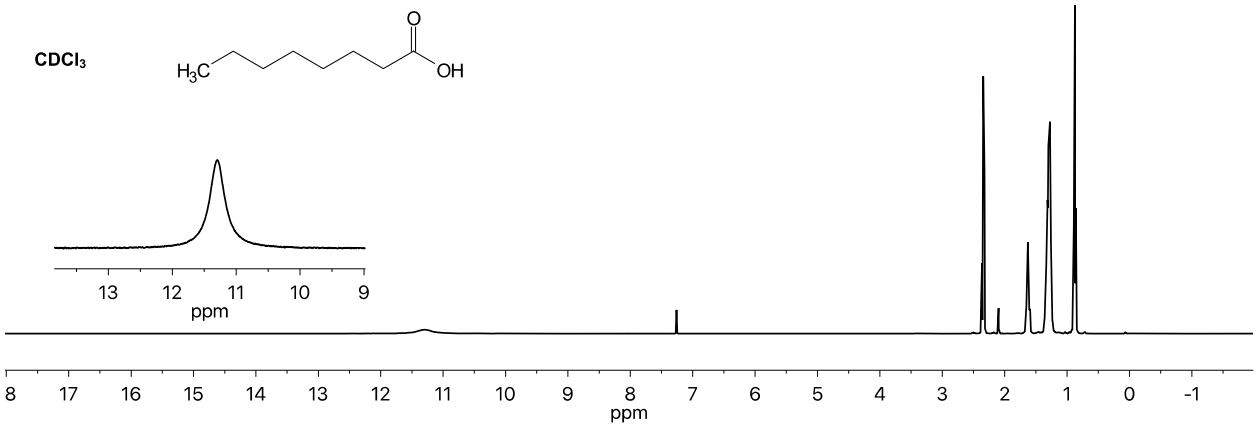
4-chloro benzoic acid: ^{1}H NMR (700 MHz, DMSO-d_6) δ 13.15 (s, 1H), 7.94 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H).



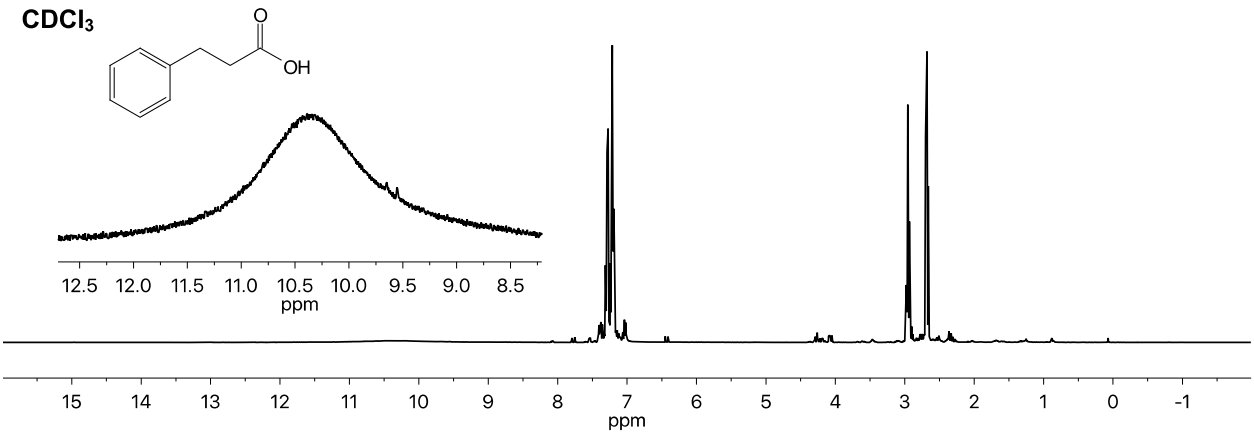
4-methoxy benzoic acid: ^{1}H NMR (700 MHz, DMSO-d_6) δ 12.60 (s, 1H), 7.89 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H).



Octanoic acid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 2.34 (t, J = 7.5 Hz, 2H), 1.63 (quint, J = 7.5 Hz, 2H), 1.29 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H).



3-phenylpropionic acid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 7.30 (dd, *J* = 6.8, 7.2 Hz 2H), 7.23 (t, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H).



General procedure for dehydrogenative oxidation recyclability study:

In a nitrogen-filled glovebox, an 8 mL glass vial was charged with KOH (42.1 mg, 0.75 mmol), benzyl alcohol (25.9 μL, 0.25 mmol), and a Teflon stir bar. A 1 mL sample of a 0.25 mM solution of **1**, **2**, or **3** in toluene was then added to the vial (0.00025 mmol, 0.1 mol% **1**). The vial was then sealed with a Teflon-lined cap and placed on a pre-heated aluminum block at 120°C for 18 h while stirring at 1000 rpm. After cooling to room temperature, the reaction solution was filtered through a pipette filter into a new 8 mL vial containing fresh KOH (42.1 mg, 0.75 mmol), benzyl alcohol (25.9 μL, 0.25 mmol), and a Teflon stir bar. The vial was sealed and placed on a pre-heated aluminum block at 120°C for 18 h. This process was then repeated a second time. Samples from the first two cycles were quenched by passage of, through the respective filter pipette, into the reaction vial. Samples from the final cycle did not require filtration, therefore, 1 mL H_2O was added directly to the reaction vial after cooling. 0.2 mL of a 6 M HCl solution was added to each vial followed by 1 mL of a 0.1 M hexamethylbenzene solution in ethyl acetate (measured by Hamilton syringe). The vials were then sealed and vortexed for 5 seconds. Samples for GC analysis were prepared from a ~30 μL aliquot of the organic layer added to ~1 mL ethyl acetate in a GC vial. Yields for benzoic acid were calculated based on the hexamethylbenzene internal standard.

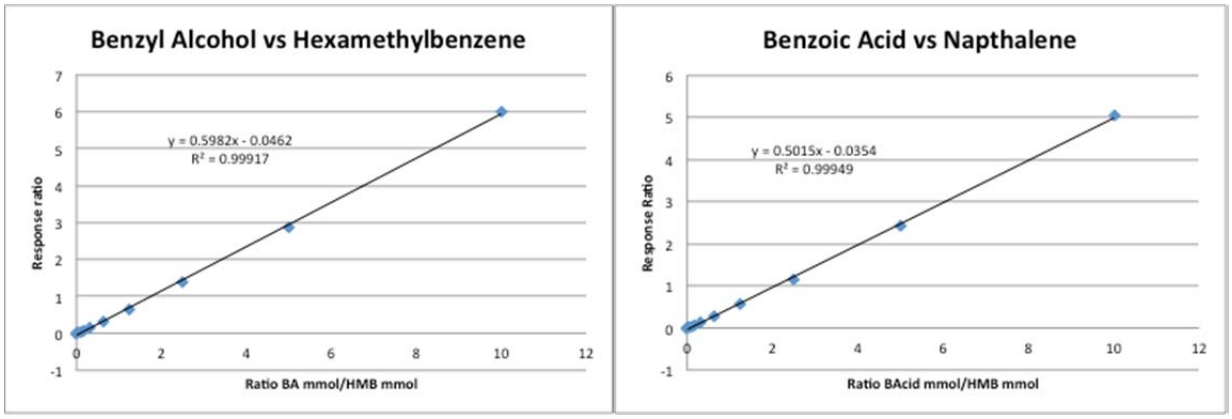


Figure S4: Plot of calibration curves for benzyl alcohol and benzoic acid against a hexamethylbenzene internal standard.

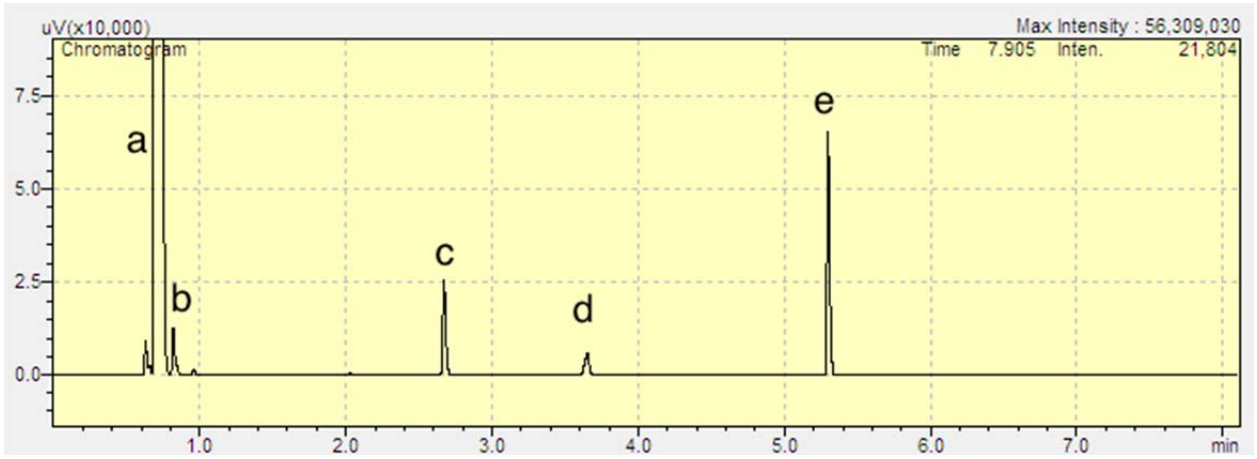


Figure S5: Representative GC chromatogram of conversion of benzyl alcohol to benzoic acid. Peaks: a) Ethyl acetate; b) toluene; c) benzyl alcohol; d) benzoic acid; e) hexamethylbenzene.

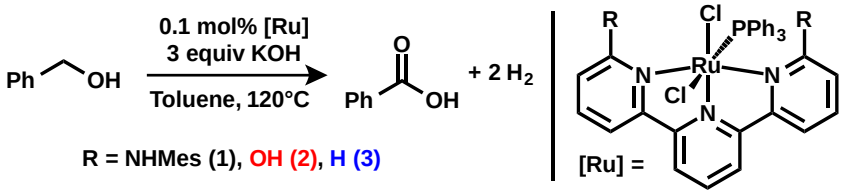


Table S1: GC data from catalyst recycling experiment

Cycle	Catalyst	Trial	% Yield Benzoic Acid	Avg % Yield	Total TON
1	**1**	1	83%	84%	840
		2	85%		
	2	1	82%	82%	820
		2	82%		
	3	1	52%	50%	500
		2	48%		
2	**1**	1	86%	81%	1650
		2	77%		
	2	1	23%	21%	1030
		2	18%		
	3	1	18%	20%	700
		2	22%		
3	**1**	1	94%	85%	2500
		2	76%		
	2	1	10%	9%	1120
		2	7%		
	3	1	11%	10%	790
		2	8%		

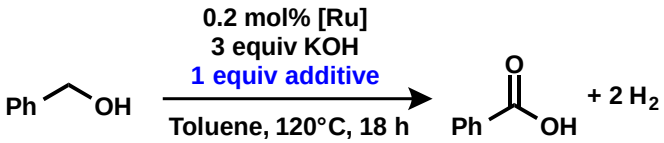
General procedure for dehydrogenative oxidation reaction screening:

In a nitrogen-filled glovebox, an 8 mL glass vial was charged with KOH (42.1 mg, 0.75 mmol), benzyl alcohol (25.9 µL, 0.25 mmol), any additional additive (0.25 mmol) and a Teflon stir bar. A 1 mL sample of a 0.5 mM solution of **1** in toluene was then added to the vial (0.0005 mmol, 0.2 mol% **1**). The vial was then sealed with a teflon-lined cap and placed on a pre-heated aluminum block at 120°C for 18 h while stirring at 1000 rpm. After cooling to room temperature, the vial was removed from the glovebox and H_2O (1 mL) was added to the reaction solution. *Note: the vial may be under positive pressure due to hydrogen gas evolved during acceptorless dehydrogenation.* 0.2 mL of a 6 M HCl solution was added to the vial followed by 1 mL of a 0.1 M hexamethylbenzene solution in ethyl acetate (measured by Hamilton syringe). The vial was then sealed and vortexed for 5 seconds. Samples for GC analysis were prepared from a ~30 µL aliquot of the organic layer added to ~1 mL ethyl acetate in a GC vial. Yields for benzoic acid were calculated based on the hexamethylbenzene internal standard.

Table S2: GC data from reaction screening

Entry	Catalyst	Cat. Loading	Time	Base	Additive	% Yield Benzoic Acid	TON
1	**1**	0.2 mol%	18 h	KOH	None	83%	445
2	**1**	0.2 mol%	18 h	KOH (anhydrous)	None	28%	140
3	**1**	0.2 mol%	18 h	KOH	1 equiv H2O	16%	80
4	**1**	0.2 mol%	18 h	NaOH	None	7%	35
5	**1**	0.2 mol%	18 h	LiOH	None	3%	15

Table S3: Functional group robustness screen



Additive	Additive Remaining	Yield of Benzoic Acid	Starting Material Remaining
3,5-lutidine	85%	51%	22%
Octylamine	0%	34%	34%
2,3-benzofuran	80%	31%	35%
n-butylthiophene	82%	62%	19%
N-benzylpyrrole	83%	57%	0%
Acetanilide	0%	0%	57%
2-chloroquinoline	5%	0%	3%
1-dodecene	46%	62%	12%
1-decyne	0%	3%	77%
4-octyne	55%	36%	11%

Crystallographic Details:

Crystals were mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer with a low temperature apparatus and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). Samples were measured at 85(2)K. The data were processed with CrystalClear 2.0[8] and corrected for absorption. Structures were solved in Olex2[9] using the XL refinement program[10].

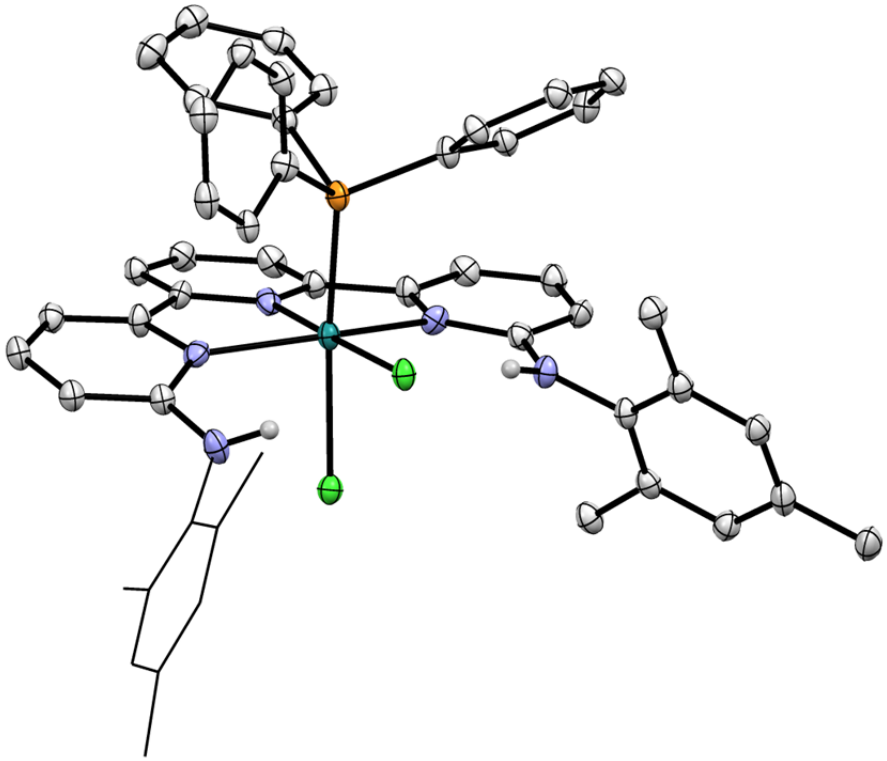


Figure S6: ORTEP X-ray crystal structure of **1**. (Ellipsoids at 30% probability. Some mesityl carbon atoms displayed in wireframe for clarity.)

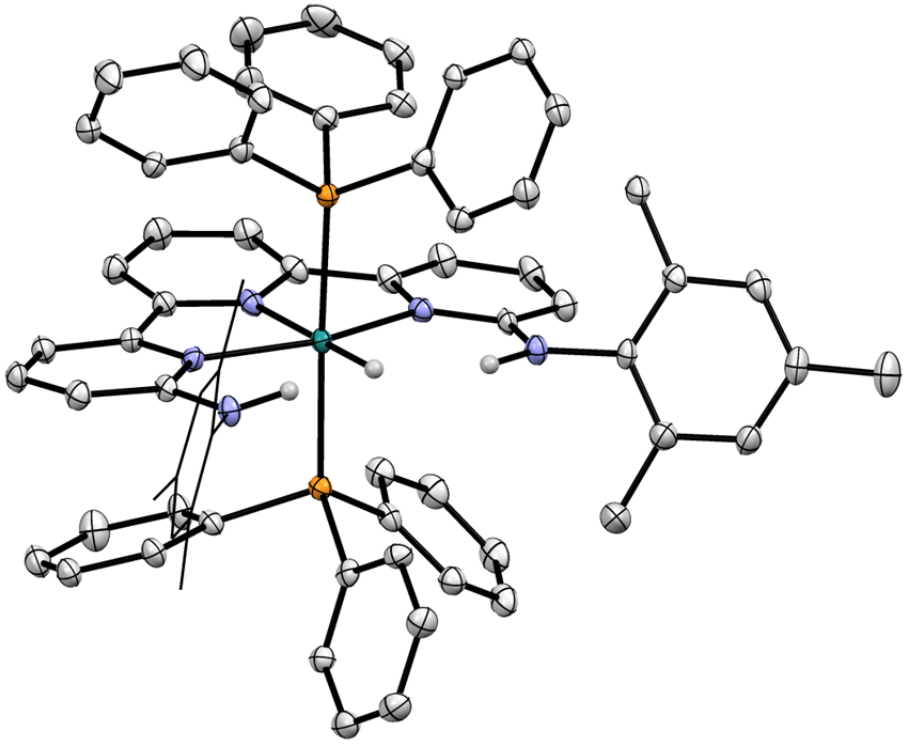


Figure S7: ORTEP X-ray crystal structure of **1-H**. (Ellipsoids at 30% probability. Some mesityl carbon atoms displayed in wireframe for clarity.)

References:

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