Efficient Transfer Hydrogenation of Carbonate Salts from Glycerol using Water-Soluble Iridium N-Heterocyclic Carbene Catalysts

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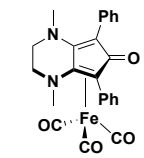
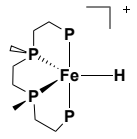
Scheme S1. Summary of reported catalysts for direct hydrogenation of bicarbonate and carbon dioxide, which include work by Renaud *et al.*,[2] Gonsalvi *et al.*,[3] Beller *et al.*,[4] Leitner *et al.*,[5] Nozaki *et al.*[6], Bernskoetter *et al.*[7], Fujita *et al.*,[8] Linehan *et al.*[9] and Beller *et al*. [10]



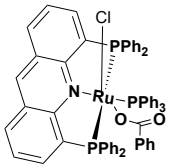
Renaud *et al., 2019*[2]
Na_2CO_3, 20 h,
100°C, H_2 (50 bar)
FA (TOF): 0.85 h^{-1}



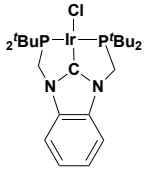
Gonsalvi *et al., 2015*[3]
$NaHCO_3$, 24 h,
80°C, H_2 (60 bar)
FA (TOF): 51 h^{-1}

$[RuCl_2(benzene)_2]_2$
and
dppm

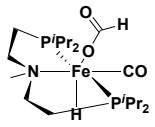
Beller *et al., 2011*[4]
$NaHCO_3$, 2 h,
80°C, H_2 (80 bar)
FA (TOF): 554 h^{-1}



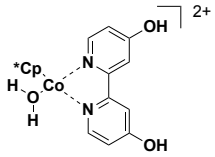
Leitner *et al., 2016*[5]
CO_2 (40 bar), 16 h,
60°C, H_2 (80 bar)
FA (TOF): 260 h^{-1}



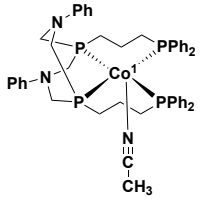
Nozaki *et al., 2018*[6]
CO_2 (25 MPa), 46 h,
120°C, H_2 (25 MPa)
FA (TOF): 5000 h^{-1}



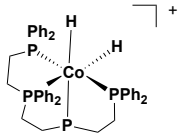
***Bernskoetter et al., 2015*[7]**
CO_2 (34.5 atm),24 h,
80°C, H_2 (34.5 atm)
FA (TOF): 23,190 h^{-1}



Fujita *et al., 2013*[8]
$NaHCO_3$, CO_2 (2 MPa),
1 h, 100°C, H_2 (2 MPa)
FA (TOF): 39 h^{-1}



Linehan *et al., 2017*[9]
CO_2 (0.85 atm), 20 h,
25 °C, H_2 (0.85 atm)
FA (TOF): 150 h^{-1}



Beller *et al., 2012*[10]
CO_2 (30 bar), 20 h,
100°C, H_2 (60 bar)
FA (TOF): 65 h^{-1}

Crystallographic Information

Structure Determination

Diffraction data for crystals of catalyst **7** were collected with a Bruker D8 Quest diffractometer equipped with a Photon II detector using Mo Kα (λ = 0.71073 Å) radiation, operating in shutterless mode. APEX III software was used for unit cell determination and data processing. Reflection data were collected at 100(2)K with 0.5° φ and ω scans. The raw frame data for both compounds were processed using SAINT[11] (integration) and SADABS[12] (absorption correction). The structure was solved *via* intrinsic phasing using ShelXT[13] within the APEX III[14] software package and refined using SHELX2018/3[15] in the WinGX suite[16]. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. Aromatic and methyl hydrogen atoms were placed in idealized positions by utilizing the HFIX43 and HFIX 33 command, respectively, and

allowed to ride on the coordinates of the parent atom with isotropic thermal parameters (U_{iso}) fixed at 1.2 U_{eq}.

PART commands were utilized to model two-part atomic disorder in lattice water molecules and a sodium atom and ligand disorder in a rotating sulfonate group. SIMU, RIGU, and SAME commands were used in conjunction with the PART commands. DFIX commands were used on the disordered sulfonate group to restrain S – O bond lengths and ISOR commands were used on a few atoms where PART commands were not sufficient, or appropriate, in modelling the disorder and achieving refinement convergence.

Alerts in CheckCIF file: The resulting CheckCIF file contains several alerts, the majority of which are directly or indirectly associated with the disorder of the lattice water molecules. The disorder cannot be eliminated as the water molecules have significant positional disorder and the alerts signal the close proximity of two water molecules and/or their lack of H-atoms. The H-atoms could not be identified in the Fourier maps and were thus not modeled, as their position would be arbitrary. Attempts to model this positional disorder using the “PART” commands could not generate improved refinement statistics; furthermore, this method results in over-modeling for limited benefit to the overall structure. The removal of water molecules with the SQUEEZE program in Platon could also not be applied as there is limited ‘void-space’ taken up by those disordered water molecules. The B Alert associated with residual electron density around the Ir atom is relatively common for heavy metal atoms in complexes.

Table S1. Crystallographic data for catalyst ***7***.

Catalyst	***7***
Chemical formula	$Na_2[Ir(CO)_2(C_{10}H_9N_2SO_3)_2]_2 \bullet 6H_2O$
Formula weight	1587.43
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.3801(6)
b (Å)	12.7791(7)
c (Å)	22.1745(12)
α (deg)	92.814(2)
β (deg)	92.689(2)
γ (deg)	104.376(2)
V ($Å^3$)	2840.6(3)
Z	2
T (K)	100(2)
λ (Mo Kα)	0.71073
D_{calc} (Mg cm^{-3})	1.856
μ (mm^{-1})	4.926
R_{int}	0.0442
R1 [I>2σ(I)]	0.0554
wR2 [I>2σ(I)]	0.1275

Table S2. Selected bond distances for catalysts ***7*** with two orientations.

Bonds	**Iridium Metal Center (Å)**	**Imidazole 1 (Å)**	**Imidazole 2 (Å)**	**Carbonyl 1 (Å)**	**Carbonyl 2 (Å)**
Ir1-C1	1.880(10)				
Ir1-C2	1.876(10)				
Ir1-C6	2.093(8)				
Ir1-C16	2.088(8)				
N1-C5		1.396(10)			
N1-C6		1.367(10)			
N2-C4		1.370(11)			
N2-C6		1.342(10)			
C4-C5		1.355(12)			
N3-C15			1.384(10)		
N3-C16			1.361(10)		
N4-C14			1.392(10)		
N4-C16			1.348(10)		
C14-C15			1.351(11)		
C1-O1				1.140(10)	

C2-O2					1.150(11)

Bonds	Iridium Metal Center (Å)	Imidazole 1 (Å)	Imidazole 2 (Å)	Carbonyl 1 (Å)	Carbonyl 2 (Å)
Ir2-C23	1.876(12)				
Ir2-C24	1.898(10)				
Ir2-C28	2.089(9)				
Ir2-C38	2.085(10)				
N5-C27		1.404(16)			
N5-C28		1.24(2)			
N6-C26		1.371(16)			
N6-C28		1.46(2)			
C26-C27		1.31(2)			
N7-C37			1.388(13)		
N7-C38			1.371(11)		
N8-C36			1.366(13)		
N8-C38			1.347(13)		
C36-C37			1.355(14)		
C23-O9				1.151(13)	
C24-O10					1.117(12)

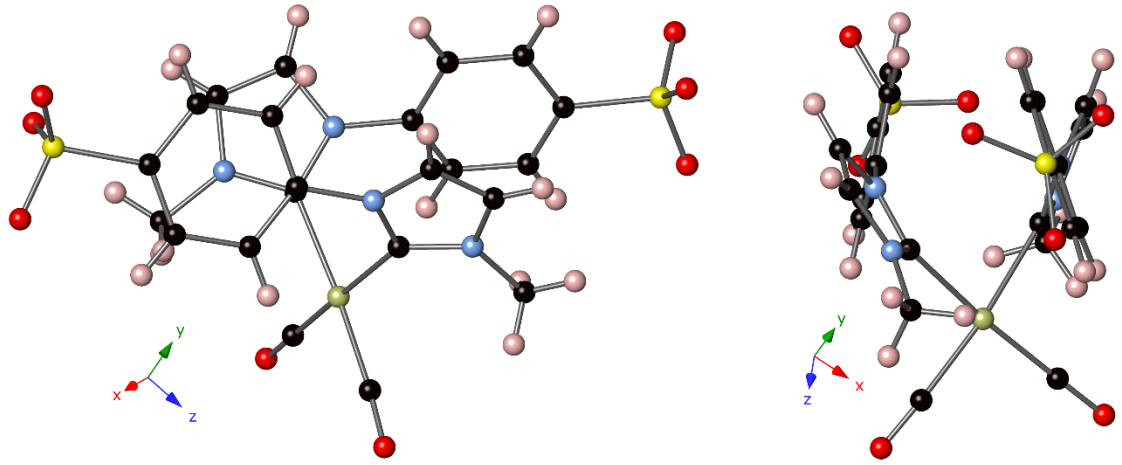


Figure S1. Ball and stick representation of one molecule of ***7*** in two orientations. Disorder around the sulfate and lattice water molecules, as well as lattice sodium cations have been removed for clarity.

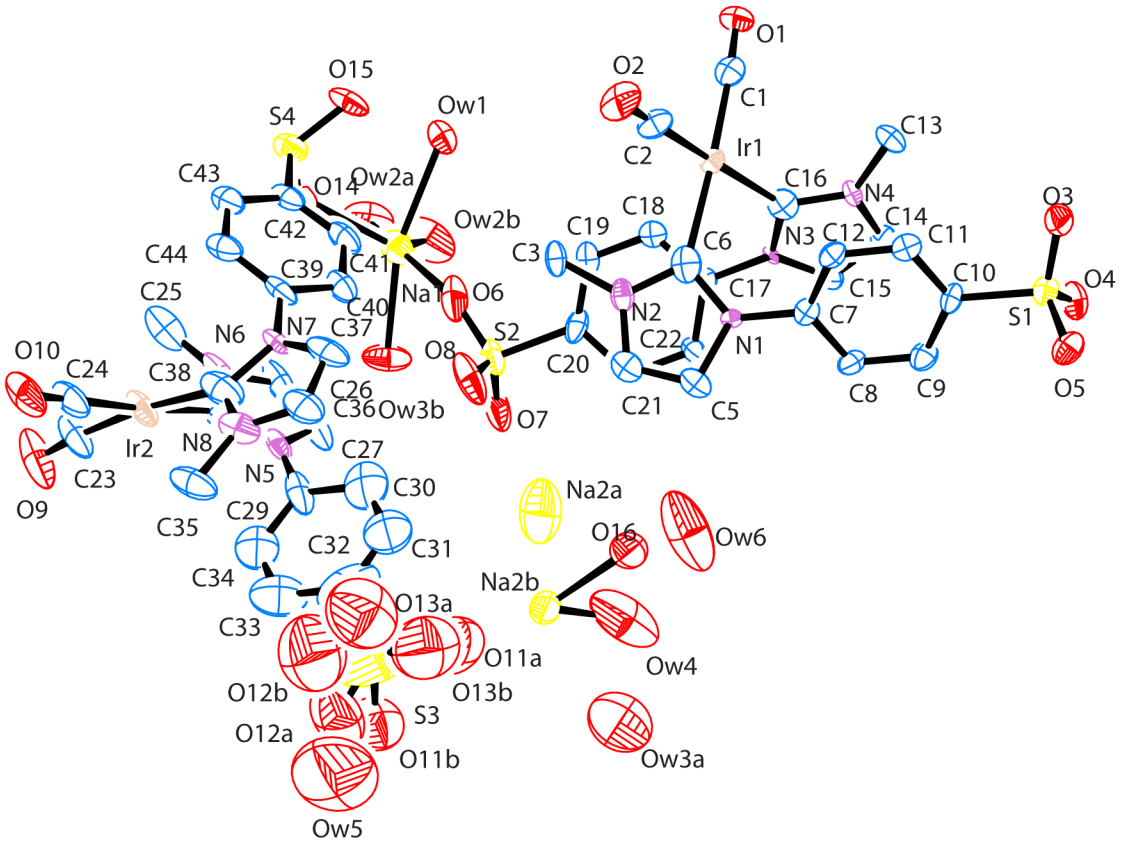


Figure S2. ORETP illustration of the asymmetric unit of catalyst **7**. Ellipsoids are shown at 50% probability level. There is significant disorder associated with the lattice sodium atom and water molecules as well as one of the sulfonate groups.

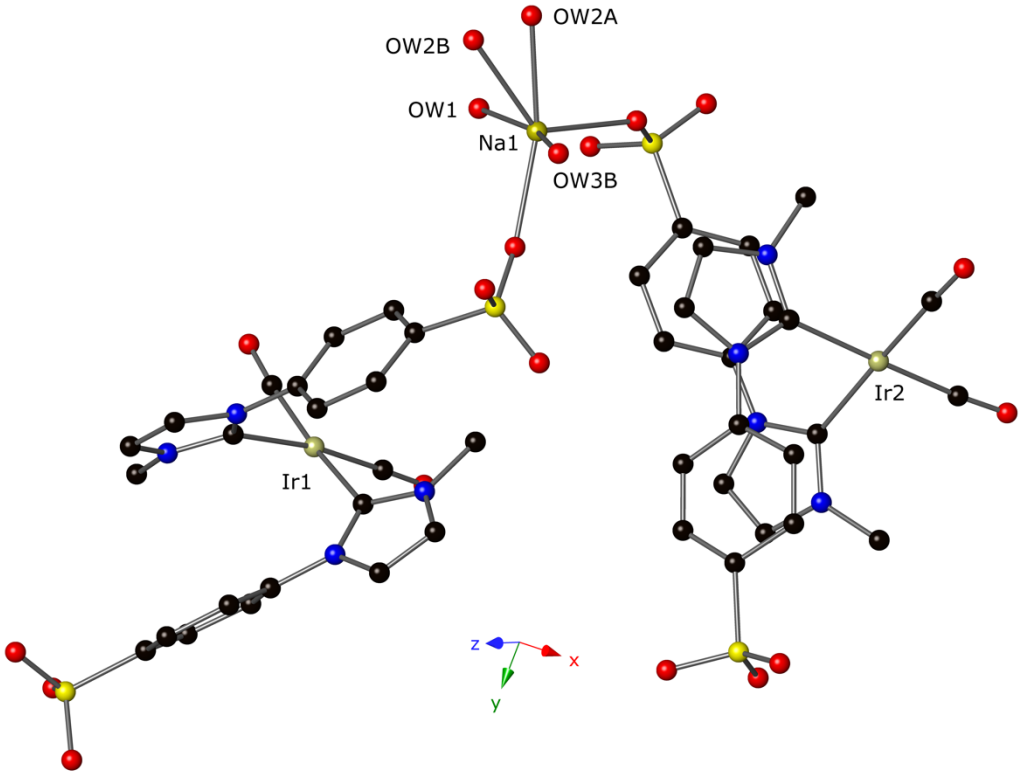
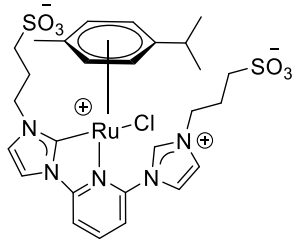


Figure S3. Ball and stick representation of catalyst **7** showing both crystallographically unique Ir centers and a single sodium. Another sodium atom and several water molecules were removed for clarity.

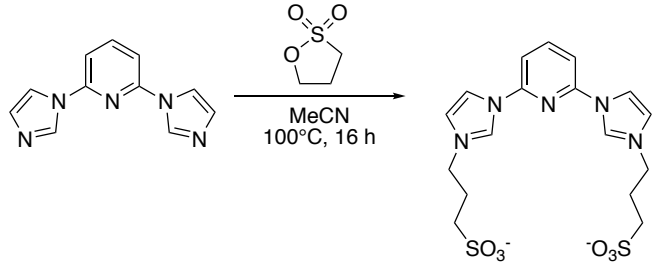
Catalyst Synthesis

Catalyst ***1***



Ligand 1a: 2,6-Bis(1-imidazolyl)pyridine (0.538 g, 2.55 mmol) and 1,3-Propane sultone (1.565 g, 12.8 mmol) were measured into a high pressure Pyrex tube. MeCN (10 mL) was added, and the vial was sealed and heated to 100 °C for 16 hours, according to Scheme S1.

Scheme S2. Synthesis of ligand ***1a*** from 2,6-bis(1-imidazolyl)pyridine.



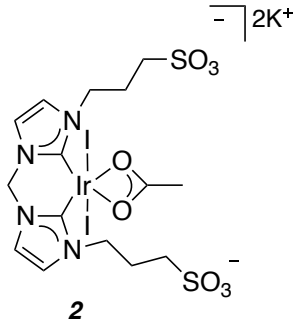
1a

After cooling to room temperature, the white precipitate was collected via filtration and washed with copious amounts of DCM and MeOH. Ligand ***1a*** was collected as a white powder (1.011 g, 0.540 mmol, 87%). **^{1}H NMR** (400 MHz, Deuterium Oxide) δ 9.93 (s, 2H), 8.53 – 8.44 (m, 1H), 8.43 – 8.37 (m, 2H), 8.05 (dt, *J* = 8.2, 1.1 Hz, 2H), 7.88 (dt, *J* = 2.2, 1.3 Hz, 2H), 4.61 (t, *J* = 7.1 Hz, 4H), 3.11 – 3.03 (m, 4H), 2.50 (p, *J* = 7.2 Hz, 4H). [17]

Catalyst 1: The CNC ligand precursor ***1a*** (24 mg, 0.27 mmol) was dissolved in 16 mL MeOH / 3 mL H_2O (solvents degassed) and Ag_2O (63 mg, 0.27 mmol) was added in the darkness. The suspension was stirred at 50°C for 60 min, then NaCl (16 mg, 0.27 mmol) was added and the resulting suspension stirred vigorously for 15 min, after which it was filtered and transferred to a solution of $[Ru(p\text{-cymene})Cl_2]_2$ (98 mg, 0.16 mmol) in 10 mL H_2O. After 1 hour at room temperature the suspension was filtered, and the solvent was removed in vacuo at 50 °C. The resulting dark residue was then extracted with MeOH (3 x 10mL) and filtered. The orange solution was then reduced to a volume of 5 mL and Et_2O added until the precipitation of an orange solid was observed. This procedure was repeated if still some unreacted ligand was visible in crude proton NMR spectroscopy. The solvent was decanted, and the residue washed with Et_2O (3x10 mL) and dried *in vacuo* to yield complex ***1*** as an orange powder (46 mg, 0.063 mmol; 30%). **^{1}H NMR** (d^6-DMSO, 400 MHz): δ = 8.43 (d, J = 0.9 Hz, 1H), 8.35 (t, J = 1.0 Hz, 1H), 8.18 (d, J = 0.8

Hz, 1H), 8.15 (dd, J = 8.5, 1.0 Hz, 1H), 8.05 (d, J = 0.8 Hz, 1H), 7.75 (dd, J = 2.4, 0.8 Hz, 1H), 7.72 (d, J = 6.1 Hz, 1H), 6.12 (brs, 1H), 5.54 (d, J = 6.1 Hz, 1H,), 5.43 (d, J = 6.1 Hz, 1H), 4.75 (brs, 1H), 4.62-4.32 (m, 4H), 2.90-2.68 (m 4H), 2.41-2.18 (m, 4H), 2.10-2.00 (m, 1H), 1.97 (s, 3H), 0.65ppm (d, J = 6.8 Hz, 6H). **^{13}C-NMR** (DMSO, 100 MHz): δ=184.6, 153.9, 150.7, 146.3, 126.6, 126.2, 124.8, 123.0, 119.9, 116.2, 88.1, 50.0/49.3, 48.1/47.5, 30.6, 25.7/25.1, 22.0/21.6, 18.6 ppm.[18]

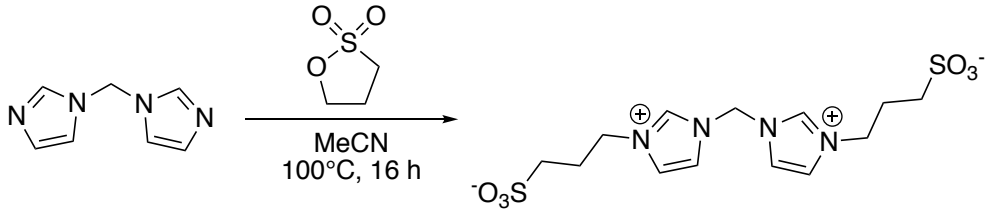
Catalyst ***2***



2

Ligand 2a (methylenebis-[N,N'(propanesulfonate)imidazolium]**:** 1,1'-Methylenebis[imidazole] (0.500 g, 3.38 mmol) and 1,3-Propane sultone (2.083 g g, 17.05 mmol) were measured into a high pressure Pyrex tube. MeCN (10 mL) was added, and the vial was sealed and heated to 100 °C for 16 hours (Scheme S2).

Scheme S3. Synthesis of **(**methylenebis-[N,N'(propanesulfonate)imidazolium] from 1,1'-Methylenebis[imidazole].



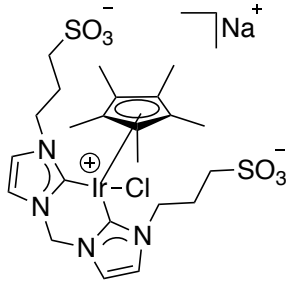
2a

After cooling to room temperature, the white precipitate formed was collected and washed thoroughly with MeOH and DCM before being dried in vacuo at room temperature. Ligand 1a was collected as a dry white powder (0.768 g, 1.96 mmol, 58%) ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.84 (d, *J* = 2.2 Hz, 2H), 7.75 (d, *J* = 2.2 Hz, 2H), 6.75 (s, 2H), 4.49 (t, *J* = 7.2 Hz, 4H), 2.99 (t, *J* = 7.3 Hz, 5H), 2.39 (p, *J* = 7.2 Hz, 4H).[19]

Catalyst 2: A mixture of ***2a*** (78 mg, 0.2 mmol), $[Ir(COD)OMe]_2$ (67mg, 0.1 mmol), KI (100 mg, 0.6 mmol), and NaOAc (65mg, 0.8 mmol) was stirred in MeOH at reflux temperature for 16 h. The suspension was filtered through Celite, and after drying under vacuum; the solid was washed with CH_2Cl_2 (40 mL) and acetone (40 mL). The solid was purified by chromatography. Elution with MeOH/acetone (1:1, 40 mL) afforded the separation of a yellow band that contained the compound. Complex *2* was obtained as a yellow solid by precipitation from MeOH/iPrOH (yield: 134.37 mg, 38%). ^{1}H NMR (CD_3OD, 400 MHz): δ = 7.41 (d, J = 2.2 Hz, 2H), 7.31 (d, J = 2.2 Hz,

2H), 6.26 (s, 2H) 4.56 (t, J = 7.3 Hz, 4H), 2.96 (t, J = 7.3 Hz, 4H), 2.42–2.24 (m, 4H), 1.93 (s, 3H). ^{13}C-NMR (DMSO, 100 MHz): δ= 176.4,123.7,122.1, 120.5, 48.3, 47.8, 26.9, 24.5 ppm.[20]

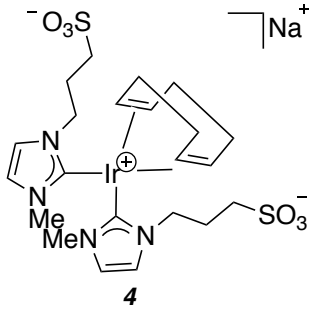
Catalyst ***3*:**



3

Methylenebis-[N,N'(propanesulfonate)imidazolium] (***2a***, 44.6 mg, 0.113 mmol) was dissolved in 10 mL degassed H_2O. Ag_2O (24.8 mg, 0.107 mmol) was added to this solution which was heated at 50 °C for 90 minutes in darkness. A solution of NaCl (7.1 mg, 0.121 mmol) in 0.5 mL degassed H2O was added to the silver solution and stirred for a further 15 minutes. In a 25 mL Schlenk flask, under a nitrogen atmosphere $[IrCp^*Cl_2]_2$ (45.3 mg, 0.057 mmol) was dissolved in 7 mL of degassed H_2O/DMSO (1:1 v:v). Under a flow of nitrogen, the silver solution was transferred to the $[IrCp^*Cl_2]_2$ which immediately became cloudy. After stirring overnight at room temperature, the solvent was removed at 50 °C under vacuum. The orange residue was washed with MeOH (3 x 5 mL) and filtered over Celite. The filtrate was reduced in volume to 3 mL, where addition of Et2O produced a yellow precipitate. Washing 3x more with S-6 Et_2O and drying in vacuo produced catalyst *3* as a yellow solid (69.35 mg, 0.0893 mmol, 79%). ^{1}H NMR (400 MHz, Methanol-d4) δ 7.53 (d, *J* = 2.1 Hz, 2H), 7.49 (d, *J* = 2.1 Hz, 2H), 6.23 (d, *J* = 13.1 Hz, 1H), 5.59 (d, *J* = 13.0 Hz, 1H), 4.36 – 4.23 (m, 5H), 2.92 – 2.85 (m, 5H), 2.43 – 2.29 (m, 3H), 2.17 (ddt, *J* = 14.7, 13.3, 7.2 Hz, 3H), 1.81 (s, 15H). ^{13}C NMR (101 MHz, cd3od) δ 150.94, 121.45, 121.09, 93.18, 61.65, 48.72, 48.39, 26.71, 8.04. [21]

Catalyst 4



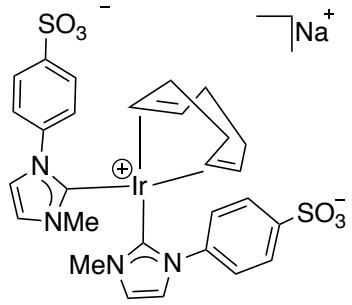
4

Ligand 4a: 1,3-Propane sultone (2.226 g, 18.23 mmol) was added to a 25 mL Schlenk flask under a nitrogen atmosphere. 1-Methylimidazole (1.47 mL, 18.4 mmol) was added slowly at room temperature with constant stirring. After 5 minutes a white solid began to form and excess heat was produced. After 20 minutes the reaction mixture was completely solid. The solid was ground into a fine powder and washed with toluene (3 x 10 mL) and ether (3 x 10 mL) leaving

ligand 6a as a white powder (2.836 g, 13.88 mmol, 76%).[1]H NMR (400 MHz, D_2O) δ 8.79 (s, 1H), 7.56 (s, 1H), 7.48 (s, 1H), 4.40 (t, *J* = 7.1 Hz, 2H), 3.93 (d, *J* = 0.7 Hz, 3H), 2.96 (dd, *J* = 8.2, 6.7 Hz, 2H), 2.41 – 2.30 (m, 2H).

Catalyst 4: Under a nitrogen atmosphere $[Ir(cod)Cl]_2$ (66 mg, 0.098 mmol) was dissolved in 8 mL degassed EtOH (200 proof). A solution of NaH (25 mg, 60 wt% in mineral oil) in 2 mL EtOH was added dropwise, the solution quickly from orange to yellow and was stirred for 30 minutes at 25 °C. A suspension of the imidazolium ligand ***4a*** (0.37 mmol) in 3 mL EtOH and 0.5 mL H_2O, slowly added to the iridium solution via syringe and stirred at 25 °C for 72 hours. The solvent was then removed under reduced pressure and the crude product re-dissolved in a minimum amount of MeOH (3 mL). Addition of Et_2O afforded a precipitate ***4***, which was collected, washed 3x more with Et_2O and dried under vacuum.[1]H NMR (400 MHz, CD_3OD) δ 7.26 (dd, J = 14.0, 2.0 Hz, 2H), 7.17 (dd, J = 10.3, 2.0 Hz, 2H), 4.57−4.45 (m, 2H), 4.24−4.12 (m, 2H), 4.07 (m, 1H), 4.05 (s, 6H), 3.89 (m, 1H), 3.73−3.65 (m, 2H), 2.99−2.89 (m, 4H), 2.50−2.41 (m, 2H), 2.35−2.24 (m, 2H), 2.24−2.14 (m, 4H), 2.05−1.95 (p, J = 7.5 Hz, 2H), 1.91−1.71 (m, 2H). [13]C NMR (101 MHz, CD_3OD) δ 176.60, 161.59, 123.12, 120.66, 109.99, 77.36, 74.54, 49.10, 37.40, 32.01, 29.46, 26.15.

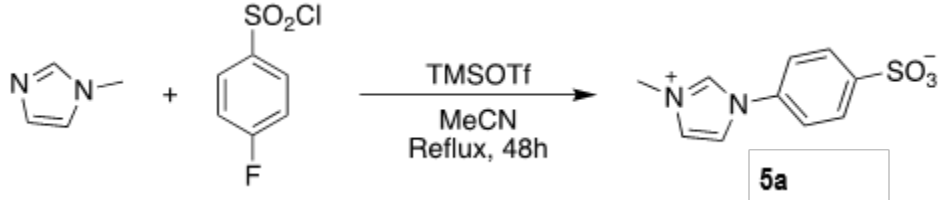
Catalyst ***5***



5

Ligand 5a: In a nitrogen atmosphere, 4-fluorobenzenesulfonyl chloride (1.109 g, 5.7 mmol) was dissolved in 40 mL dry MeCN. 1-Methylimidazole (1.8 mL, 22.5 mmol) and TMSOTf (2 mL, 11.0 mmol) were added via syringe and the mixture was heated to reflux for 48 h under nitrogen, during which the color changed from clear to red and a white precipitate formed.

Scheme S4. Synthesis of ligand ***5a*** from 1-Methylimidazole and 4-fluorobenzenesulfonyl chloride

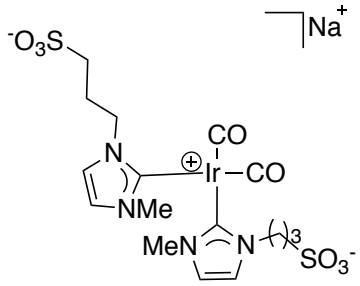


After cooling to room temperature, the precipitate was collected, washed with MeCN (3 x 10 mL) and DCM (3 x 10 mL) and dried *in vacuo,* affording ligand ***5a*** a as a white powder (205 mg, 0.862

mmol, 15%).[1]H NMR (400 MHz, Deuterium Oxide) δ 9.32 (s, 1H), 8.07 – 8.00 (m, 2H), 7.96 (t, *J* = 1.9 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.68 (t, *J* = 1.9 Hz, 1H), 4.06 (s, 3H).[22]

Catalyst 5: Under a nitrogen atmosphere $[Ir(cod)Cl]_2$ (66 mg, 0.098 mmol) was dissolved in 8 mL degassed EtOH (200 proof). A solution of NaH (25 mg, 60 wt% in mineral oil) in 2 mL EtOH was added dropwise, the solution quickly from orange to yellow and was stirred for 30 minutes at 25 °C. A suspension of the imidazolium ligand ***5a*** (0.37 mmol) in 3 mL EtOH and 0.5 mL H_2O, slowly added to the iridium solution via syringe and stirred at 25 °C for 72 hours. The solvent was then removed under reduced pressure and the crude product re-dissolved in a minimum amount of MeOH (3 mL). Addition of Et_2O afforded a precipitate, which was collected, washed 3x more with Et_2O and dried under vacuum. Catalyst ***5*** was recovered as a bright red solid (69 mg, 0.086 mmol, 53% yield). [1]H NMR (400 MHz, CD_3OD) δ 8.02 – 7.97 (m, 4H), 7.37 – 7.32 (m, 4H), 7.24 (d, *J* = 2.0 Hz, 2H), 7.14 (d, *J* = 2.0 Hz, 2H), 4.78 – 4.70 (m, 2H), 3.61 (q, *J* = 7.7 Hz, 2H), 3.22 (s, 6H), 2.51 – 2.38 (m, 2H), 2.28 (dd, *J* = 15.2, 7.8 Hz, 2H), 2.17 – 2.05 (m, 2H), 1.69 (td, *J* = 14.4, 7.3 Hz, 2H). [13]C NMR (101 MHz, CD_3OD) δ 177.58, 147.47, 142.61, 128.28, 127.14, 124.30, 124.25, 80.73, 73.91, 38.00, 35.94, 28.26.[23]

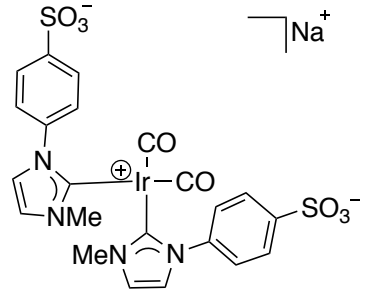
Catalyst ***6***



6

Complex ***4*** (69 mg, 0.086 mmol) was dissolved in 10 mL degassed MeOH, and the system was flushed with N_2 for 10 minutes. CO(g) was bubbled through the solution at room temperature for 90 minutes, and a solution changed from red/orange to an orange/yellow color. The solvent was reduced to about 2 mL *in vacuo,* after which Et_2O was added until a yellow precipitate was formed. The solid was washed 3 times with Et_2O and dried *in vacuo* to yield complex ***7*** as a yellow solid. [1]H NMR (400 MHz, CD_3OD) δ 7.45 (d, J = 2.0 Hz, 2H), 7.41 (d, J = 2.0 Hz, 2H), 4.06 (t, J = 7.6 Hz, 4H), 3.98 (s, 6H), 2.78 (t, J = 7.2 Hz, 4H), 2.13 (m, 4H). [13]C NMR (101 MHz, CD_3OD) δ 179.88, 166.83, 124.26, 122.46, 49.33, 47.71, 37.74, 26.28.

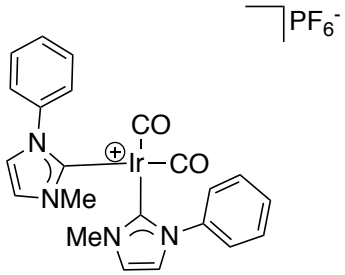
Catalyst ***7***



7

Complex ***5*** (69 mg, 0.086 mmol) was dissolved in 10 mL degassed MeOH, and the system was flushed with N_2 for 10 minutes. CO(g) was bubbled through the solution at room temperature for 90 minutes, and a solution changed from red/orange to an orange/yellow color. The solvent was reduced to about 2 mL *in vacuo,* after which Et_2O was added until a yellow precipitate was formed. The solid was washed 3 times with Et_2O and dried *in vacuo* to yield complex ***7*** as a yellow solid (36 mg, 0.047 mmol, 54% yield). ^{1}H NMR (400 MHz, D_2O) δ 7.90 – 7.85 (m, 4H), 7.50 – 7.46 (m, 4H), 7.24 (d, *J* = 2.0 Hz, 2H), 7.00 (d, *J* = 2.0 Hz, 2H), 3.44 (s, 6H). ^{13}C NMR (101 MHz, D_2O) δ 179.49, 168.73, 163.16, 142.84, 140.92, 126.64, 125.27, 123.95, 122.39, 38.31. [23]

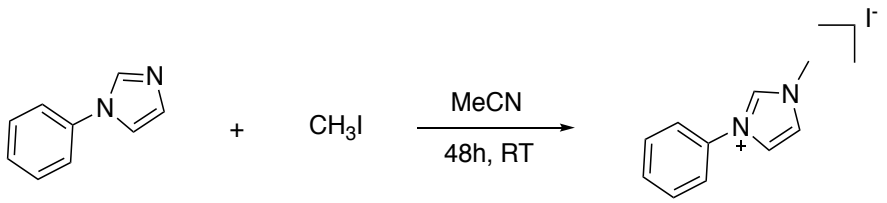
Catalyst ***8***



8

Ligand 8a:[24] 1-phenyl-1H-imidazole (870 mg, 6.03 mmol) and MeI (3.42 g, 24.1 mmol) were added to acetonitrile (10 mL) and the mixture was stirred in a sealed vial refluxing for 48 h. The solvent was removed in vacuo, the crude product was dissolved in the minimum amount of ethanol and added dropwise to a flask of stirring diethyl ether (40 mL) where a pale yellow solid precipitated. The precipitate was filtered and dried in vacuo yielding ***8a*** as a pale yellow solid. (Scheme S5). ^{1}H NMR (400 MHz, DMSO-d6): δ 9.72 (m, 1H, NCHN), 8.28 (dd, 1H, ImH), 7.93 (dd, 1H, ImH), 7.77 (m, 2H, ArH), 7.67 (m, 2H, ArH), 7.59 (m, 1H, p-ArH) 3.95 (s, 3H).

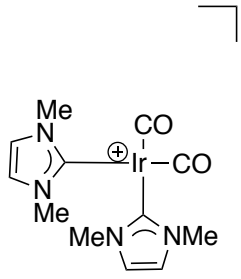
Scheme S5. Synthesis of 1-methyl-3-phenyl-1H-imidazolium iodide from 1-phenyl-1H-imidazole.



8a

Under a nitrogen atmosphere $[Ir(cod)Cl]_2$ (73 mg, 0.11 mmol) was dissolved in 8 mL degassed EtOH (200 proof). A solution of NaH (25 mg, 60 wt% in mineral oil) in 2 mL EtOH was added dropwise, the solution quickly from orange to yellow and was stirred for 30 minutes at 25 °C. A suspension of the imidazolium ligand ***8a*** (0.44 mmol) in 3 mL EtOH and 0.5 mL H_2O, slowly added to the iridium solution via syringe and stirred at 25 °C for 72 hours. The solvent was then removed under reduced pressure and the crude product re-dissolved in a minimum amount of MeOH (3 mL). Addition of Et_2O afforded a precipitate, which was collected, washed 3x more with Et_2O and dried under vacuum. A bright red solid was obtained. The bright red solid was then dissolved in 10 mL degassed CH_2Cl_2, and the system was flushed with N_2 for 10 minutes. CO(g) was bubbled through the solution at room temperature for 90 minutes, and a solution changed from red/orange to an orange/yellow color. The solvent was reduced to about 2 mL *in vacuo,* after which it was was loaded onto a silica column conditioned with acetone. Elution of a yellow band was achieved with acetone/KPF_6. The yellow band was collected and solvent was removed under vacuum, leaving a yellow residue with excess KPF_6. Washing with CH_2Cl_2 and filtration over Celite leaves **8** in solution, which can be dried under vacuum to a yellow powder (68% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 6H), 7.27 (m, 2H), 7.19 (d, 2H), 7.02 (d, 2H), 3.23 (s, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.47, 167.38, 138.66, 129.91, 129.67, 125.10, 123.97, 123.76, 38.26. HRMS(ESI/Q-TOF) m/z: $[M\text{-}PF_6]^+$ Calculated for $C_{28}H_{39}N_4Ir$ 617.2256; Found 617.2244.

Catalyst ***9***



9

The *cod* precursor to ***9***, (η^4-1,5-cyclooctadiene)(bis-1,3-dimethylimidazole-2-ylidene)iridium(I) acetate, was prepared as previously reported from the dimethyl imidazolium carboxylate.[25] Briefly, a 10-mL Schlenk flask was charged with $[Ir(cod)Cl]_2$ (110 mg, 486.6 μmol), *N*,*N*'-dimethyl imidazolium-2-carboxylate (276 mg, 1.94 mmol) and sodium acetate (0.100g). Acetonitrile (10 mL) was added under an inert atmosphere and the reaction was heated to reflux for 2 hours, over

which time it turned to a bright orange color. The solution was cooled and filtered through Celite and the filtrate was concentrated to dryness *in vacuo* and washed with ether (2 x 10 mL). The crude solid was found to be analytically pure without further purification. It was recrystallized from 1:4 CH_2Cl_2/diethyl ether to yield bright orange needles (180 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10 (s, 4H, NCH), 3.89 (s, 6H, CH_3), 3.72 (br m, 4H, COD CH), 2.10 (br m, 4H, COD CH_2), 1.89 (br m, 4H, COD CH_2). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 178.88 (s, NCN), 124.70 (s, NCH), 77.22, 39.22 (s, COD) 35.87 (s, NCH_3). Characterization data is consistent with that previously reported. [25]

Catalyst ***9*** was synthesized from (η^4-1,5-cyclooctadiene)(bis-1,3-dimethylimidazole-2-ylidene)iridium(I) acetate by dissolving 177 mg (0.324 mmol) in 10 mL degassed, dry dichloromethane. The reaction vessel was flushed with N_2 for 10 minutes. CO(g) was bubbled through the solution at room temperature for 90 minutes, and a solution changed from red/orange to an orange/yellow color. The solvent was reduced to about 2 mL *in vacuo,* after which Et_2O was added until a yellow precipitate was formed. The solid was washed 3 times with Et_2O and dried *in vacuo* to yield complex ***9*** as a yellow solid (106 mg, 0.181 mmol, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 3.70 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 180.65 (s), 124.91 (s), 110.50 (s), 38.54 (s). Characterization data is consistent with that previously reported. [26]

Calculation of free energies of reaction (ΔG_{rxn})

All calculations were carried out using the G3B3 (or G3//B3LYP) method as implemented in the GAUSSIAN 16 software package.[27] This method is a variant of G3 theory, in which geometries are determined using the B3LYP/6-31G(d) method; energies are calculated at the MP4/6-31(d) level and corrected to QCISD(T)(full)/G3Large level using several additivity approximations at MP2 and MP4 levels. Geometries were fully optimized; all minima were verified to have no imaginary vibrational frequencies. Free energies were evaluated at 298 K. To estimate solvent effects, the self-consistent reaction-field (SCRF) continuum approach was employed using the IEF version of the polarizable continuum model (PCM) with parameters for toluene in single-point calculations on gas-phase geometries.

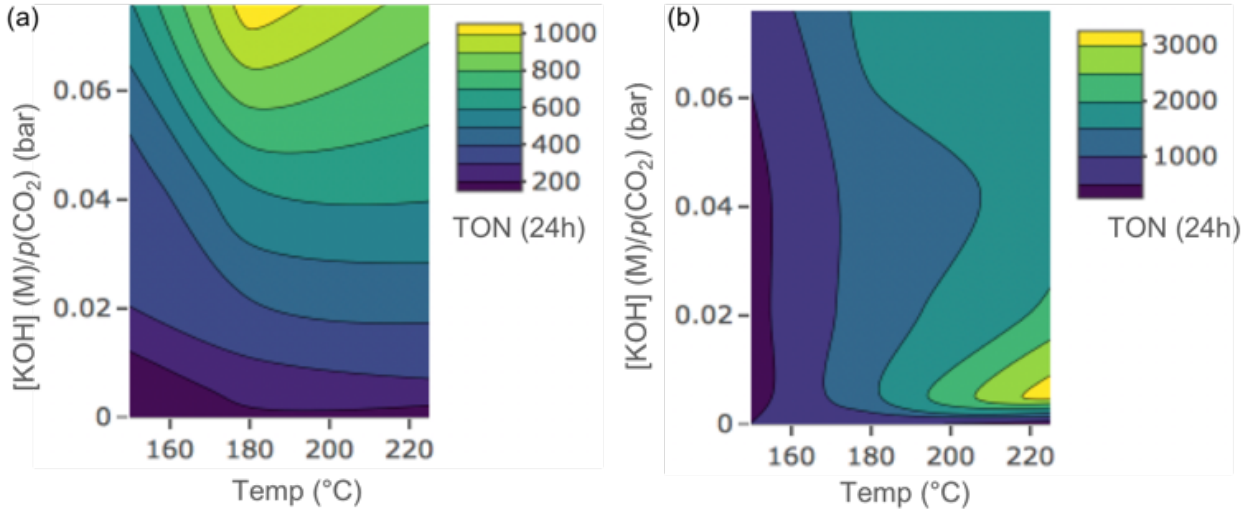


Figure S4. Contour plot showing TONs of (a) formate and (b) lactate in 24 h using catalyst ***1***. Figure reproduced from Heltzel *et al*.[1]

Table S3. Calculated free energies of reaction ($\Delta G°_{aq}$) for the CO_2 direct hydrogenation and transfer hydrogenation (Gaussian16, G3B3, PCM water, room temperature).

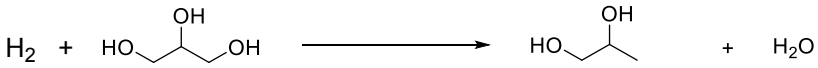
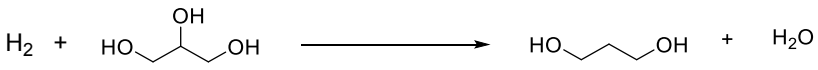
Entry		***$\Delta G°_{aq}$ (kcal/mol)***
1		-20.0
2		-14.6

Table S4. Table summarizing activity of Ir and Ru NHC catalysts ***1*** – ***9*** for transfer hydrogenation of K_2CO_3 from glycerol, based on observed turnover numbers (TON) and turnover frequencies (TOF) of for FA, LA and 1,2-PDO (data graphically represented in Figure2). Relative excess terms are defined as follows:

$$excess_{AD/TH} = \frac{[LA] - ([FA] + [1,2\text{-PDO}])}{[FA] + [1,2\text{-PDO}]} \times 100$$

and

$$excess_{AD/FA} = \frac{[LA] - [FA]}{[FA]} \times 100$$

Carbonate	TON			TOF			Relative $excess_{AD/TH}$	*Relative $excess_{AD/FA}$
	LA	FA	1,2-PDO	LA	FA	1,2-PDO		
1	2750	506	0	459	84	0	444	444
2	5190	1360	0	865	226	0	283	283
3	5350	886	0	891	148	0	503	503
4	1270	0	0	212	0	0	N/A	N/A
5	2075	508	0	346	85	0	308	308
6	2780	810	0	463	135	0	244	244
7	15400	8120	4080	2564	1353	680	26	89
8	3780	644	0	630	107	0	487	487
9	2060	918	0	343	153	0	124	124

Conditions: 1: 1 water: glycerol (6.84 M), K_2CO_3 (2.7M), 0.001 mol% catalyst, 150 °C, 6 h. * Note that $excess_{AD/TH}$ and $excess_{AD/FA}$ only differ for catalyst ***7***.

Table S5. Literature values for aqueous solubility of carbonate salts.[28]

Carbonate salt	**Solubility (g/mL)**
Li_2CO_3	3.11 g/100 mL (25°C)
Na_2CO_3	34.07 g/100 mL (27.8°C)
K_2CO_3	112 g/100 mL (20 °C)
Cs_2CO_3	2605 g/L (15 °C)

Table S6. Effect of carbonate source on the TONs of formic acid (FA), lactic acid (LA) and 1,2-propanediol (1,2-PDO) using catalyst **7**.

Entry	Carbonate	TON			Selectivity			Conv.%[a]
		LA	FA	1,2-PDO	Relative $excess_{AD/TH}$	Relative $excess_{AD/FA}$	Selectivity FA:1,2PDO	Glycerol
1	**Li_2CO_3**	2530	146	0	1636	1636	100	NA
2	**Na_2CO_3**	13760	7060	736	76	95	91	NA
3	**K_2CO_3**	15400	8120	4080	26	89	67	16
4	**Cs_2CO_3**	27850	13350	14490	0	108	48	26
5	**$CaCO_3$**	354	0	0	-	-	-	NA
6	**Cs_2CO_3: K_2CO_3 (1:9)**	22200	12660	8780	4	75	59	21
7	**Li_2CO_3:K_2CO_3 (1:9)**	12630	7620	2240	28	66	77	NA

[a] Conversion of glycerol from HPLC data with refractive index detector; NA indicates "not available". Conditions: 1: 1 water: glycerol (6.84 M), carbonate salt (2.7M), 0.001 mol% **7**, 150 °C, 6 h.

Table S7. Comparison of lactic and formic acid TONs obtained with microwave heating and conventional heating after 6 h using catalyst **7**.

	Microwave heating	Conventional heating
Lactic acid	15,380	27,760
Formic acid	8,120	16,630

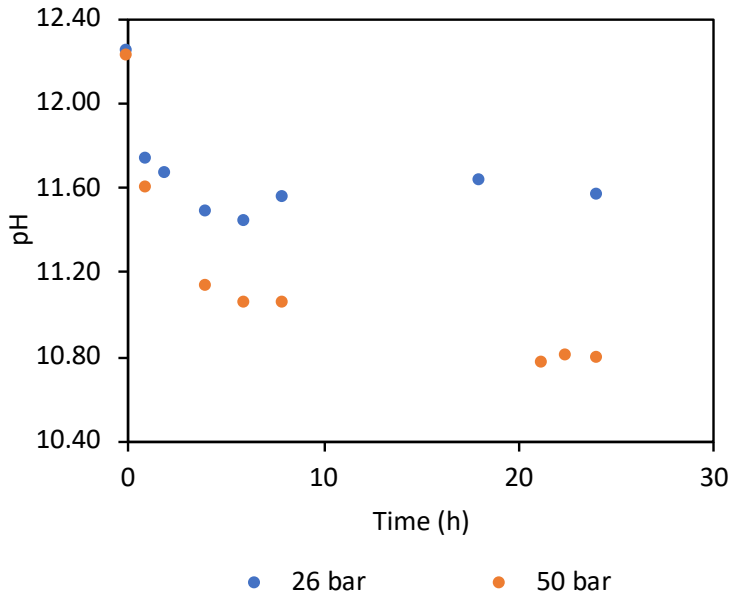
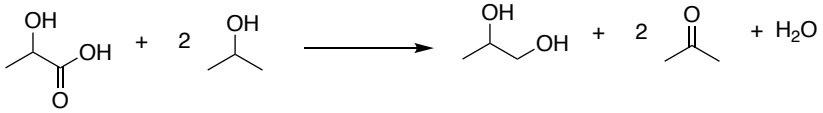
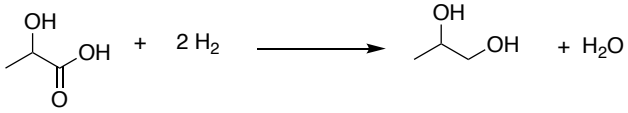


Figure S5. Comparison of changes in pH observed in the reaction of glycerol using catalyst ***7,*** 6.85 M aqueous glycerol, 2.70 M K_2CO_3, 0.001 mol% ***7***, 150 °C, N_2 pressure of 26 bar and 50 bar.

Table S8. Calculated free energies of reaction ($\Delta G°_{aq}$) for direct hydrogenation and transfer hydrogenation of lactic acid (Gaussian16, G3B3, PCM water, 150 °C).

Entry		***ΔG°aq (kcal/mol)***
1		-74.7
2		-59.4

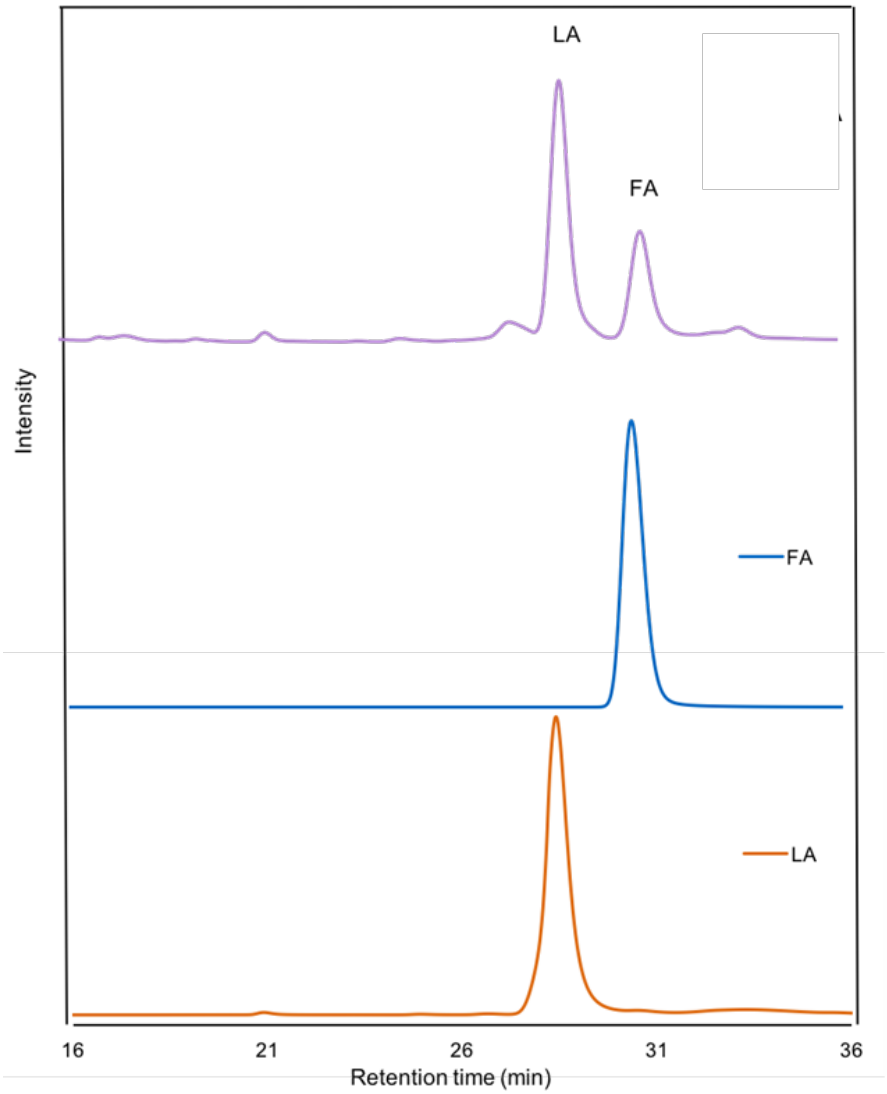
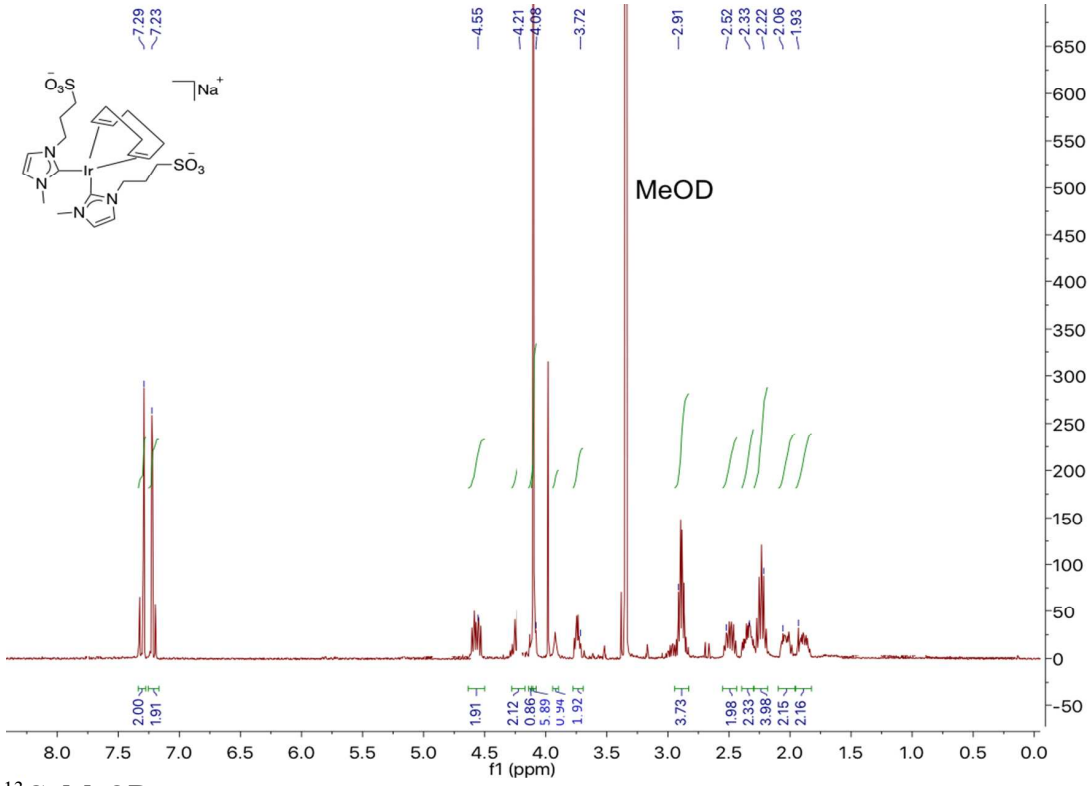


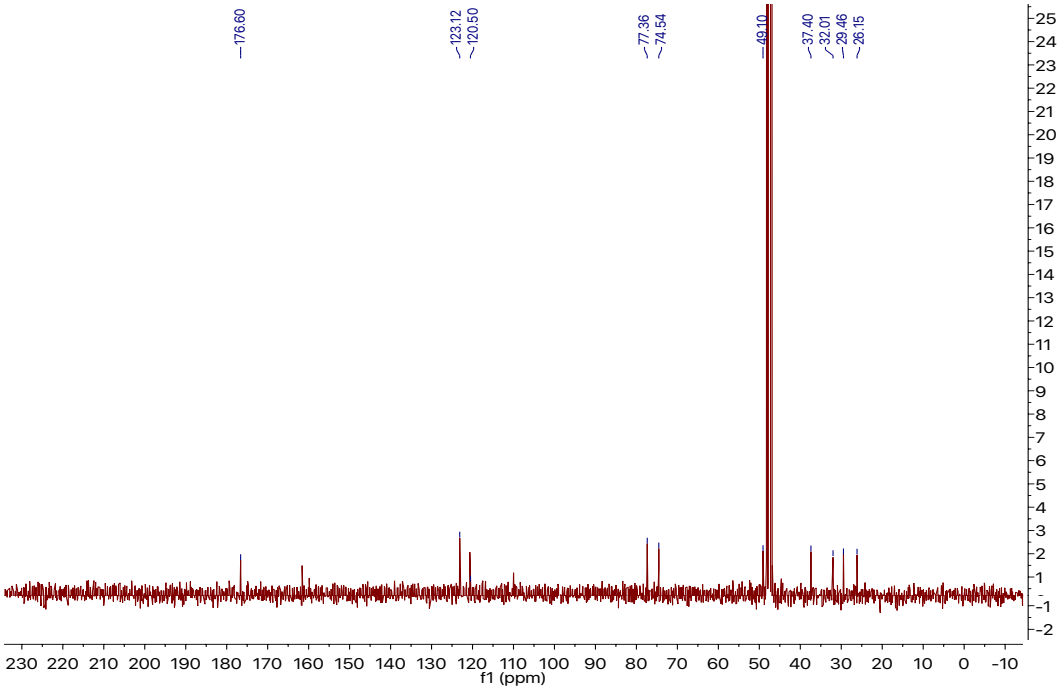
Figure S6. Typical HPLC chromatogram at 218 nm wavelength against authentic formic acid (FA), lactic acid (LA).

NMR spectra of select catalysts
Spectra have been previously by our group.[22]

Catalyst *4* - *Na[Ir(NHC-nPrSO$_3$)$_2$(cod)]*
^{1}H: MeOD

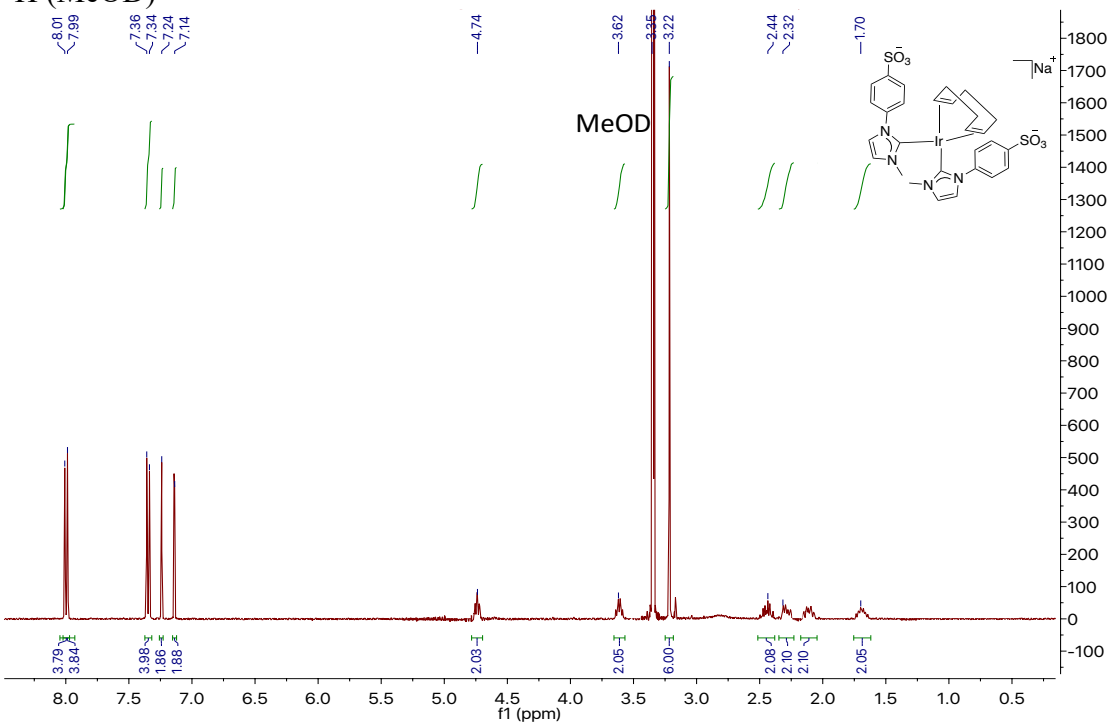


^{13}C: MeOD

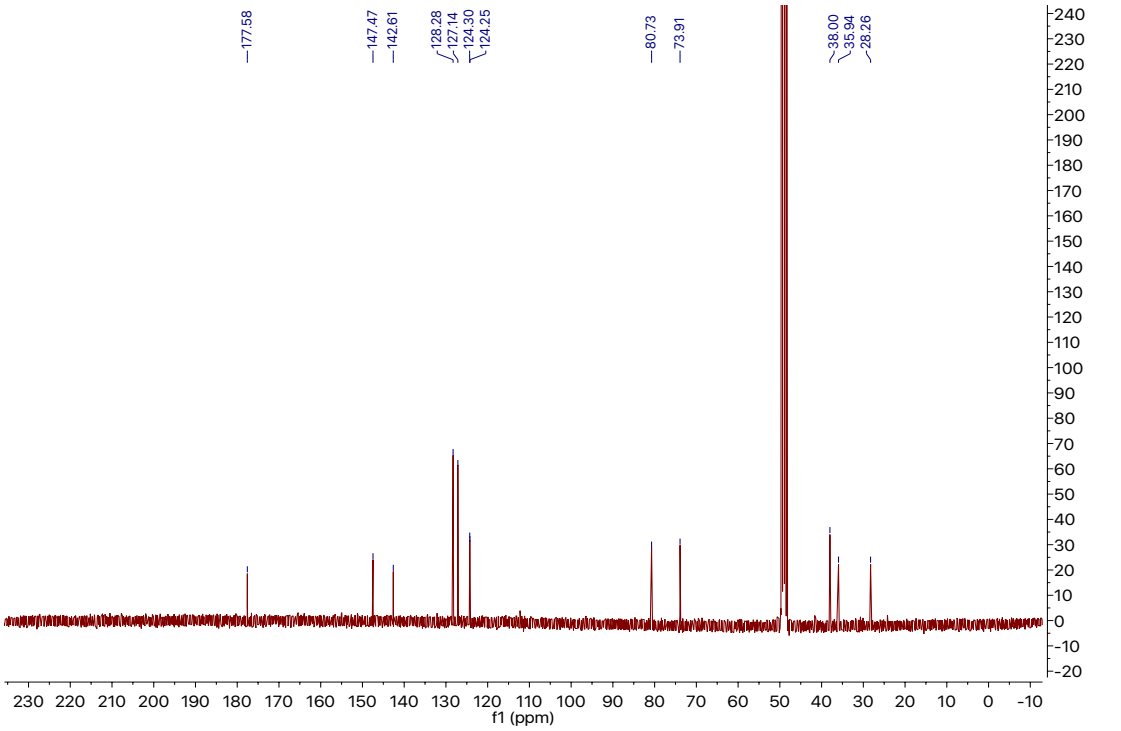


Catalyst *5* - *Na[Ir(NHC-PhSO$_3$)$_2$(cod)]*

^{1}H (MeOD)

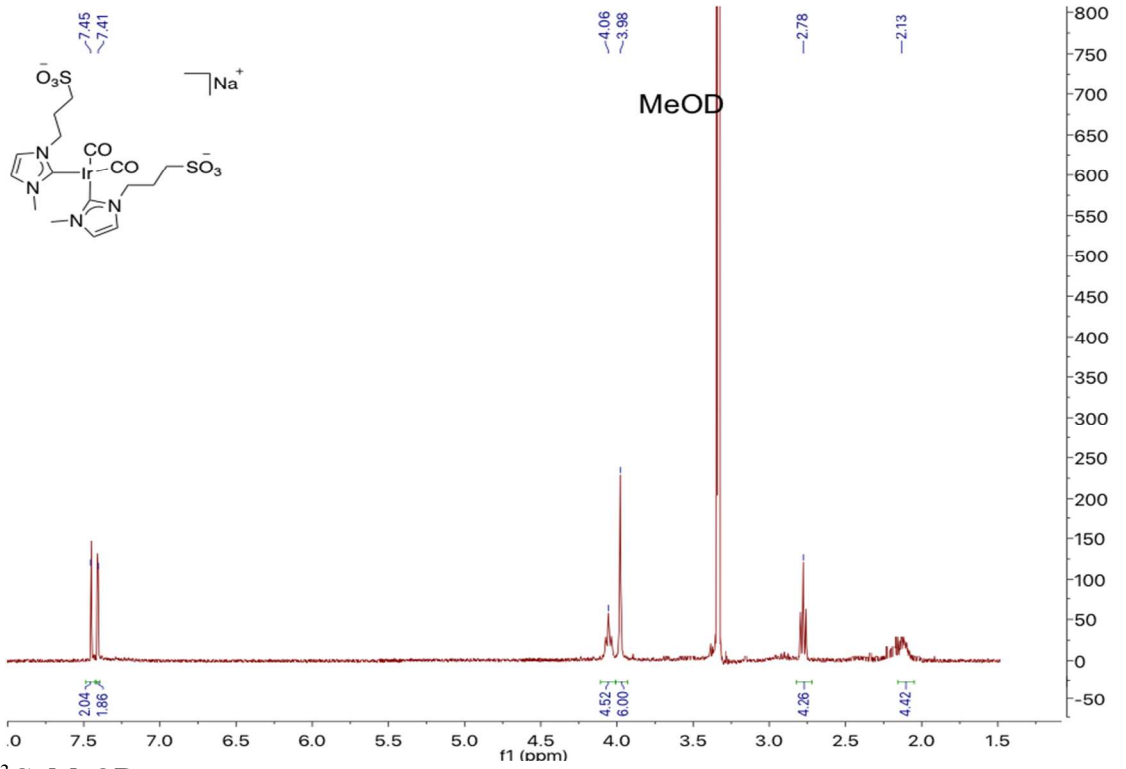


^{13}C: MeOD

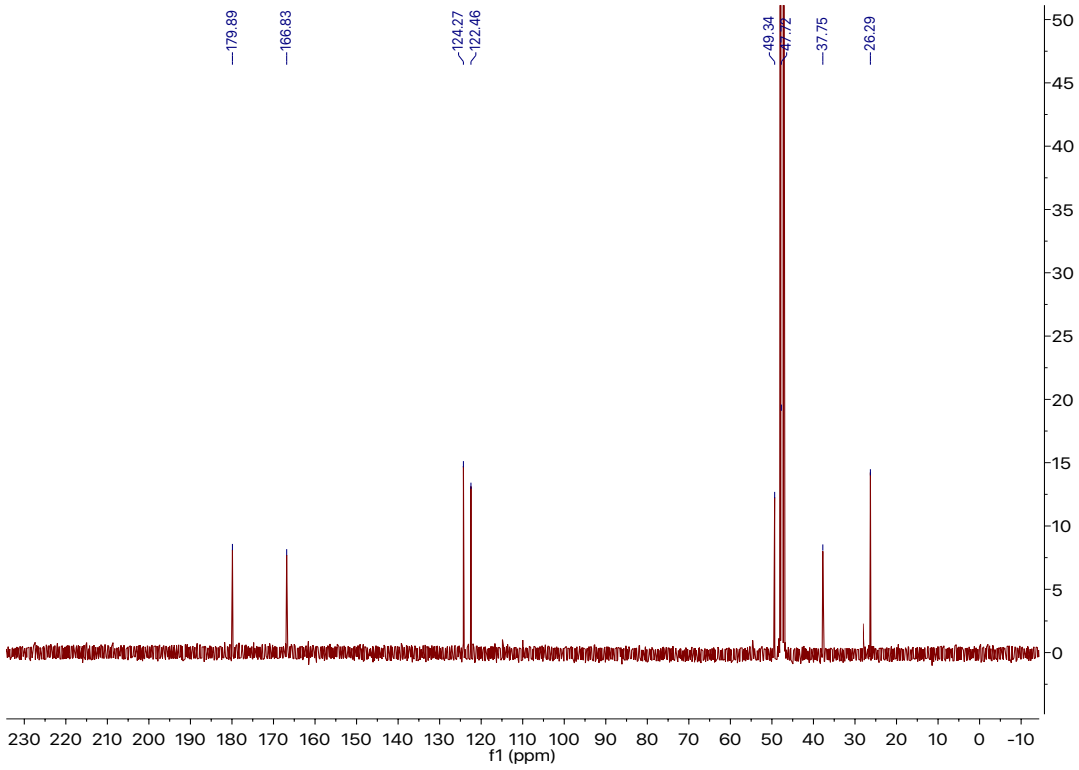


Catalyst *6* - *Ir(NHC-nPrSO₃)(CO)₂*

^{1}H: MeOD

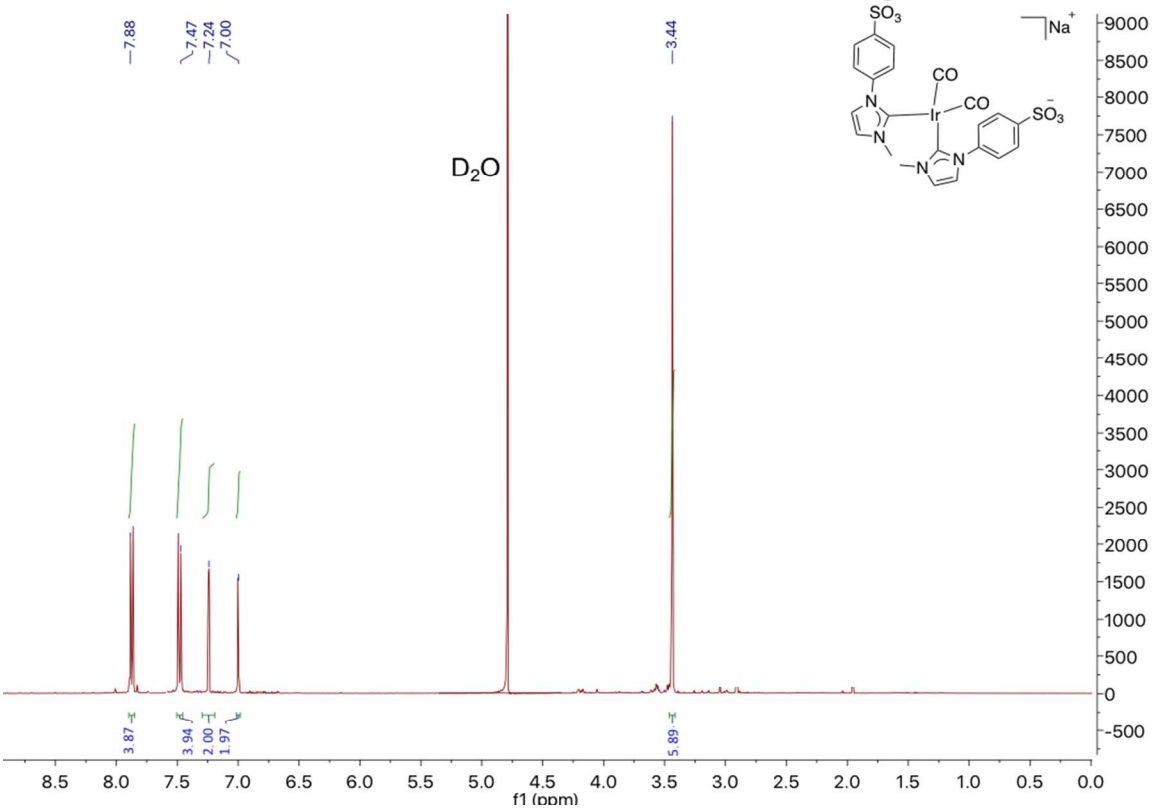


^{13}C: MeOD

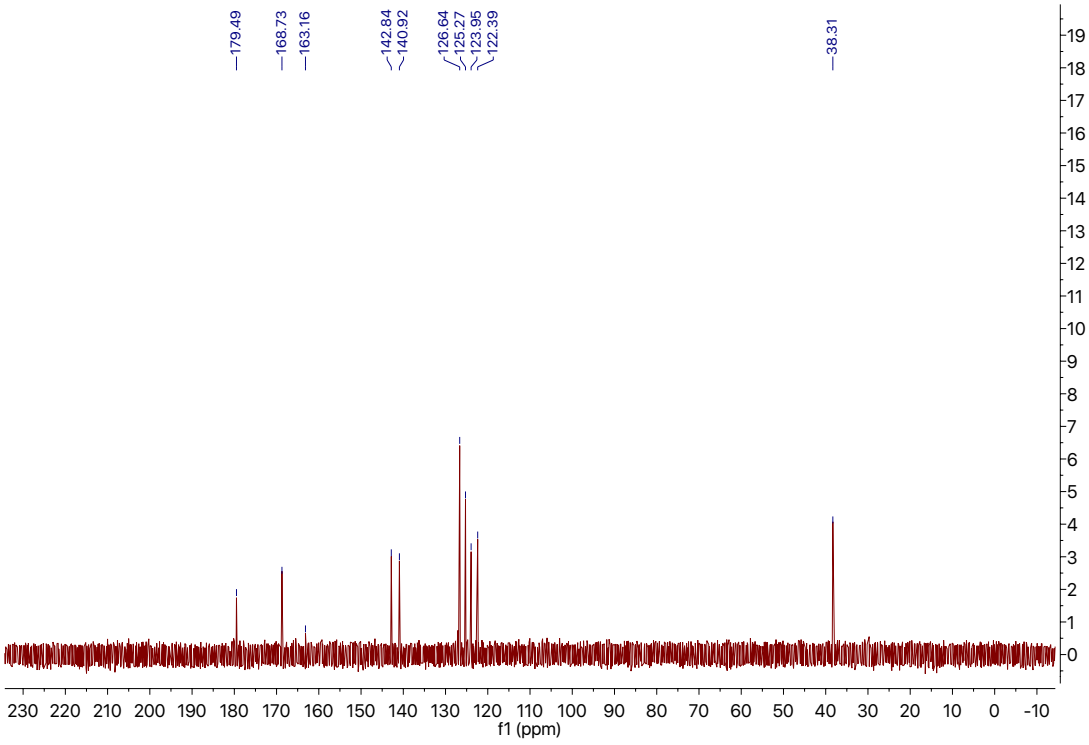


Catalyst *7* - *Ir(NHC-PhSO$_3$)$_2$(CO)$_2$*

^{1}H: D_2O

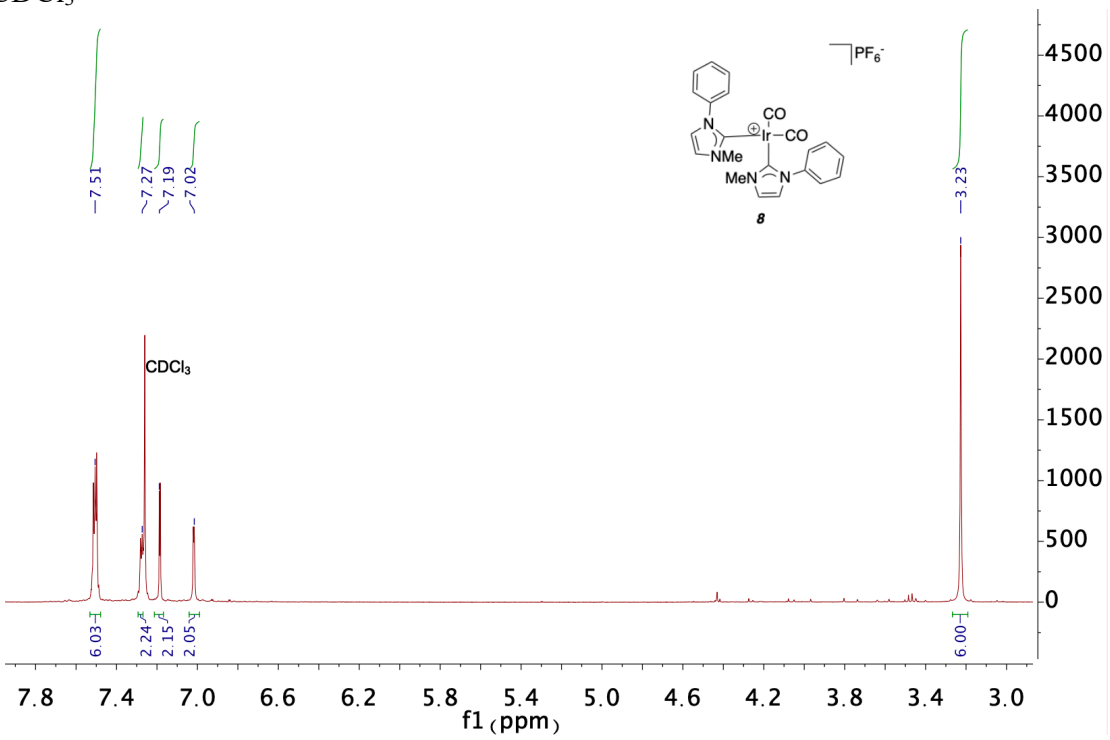


^{13}C: D_2O

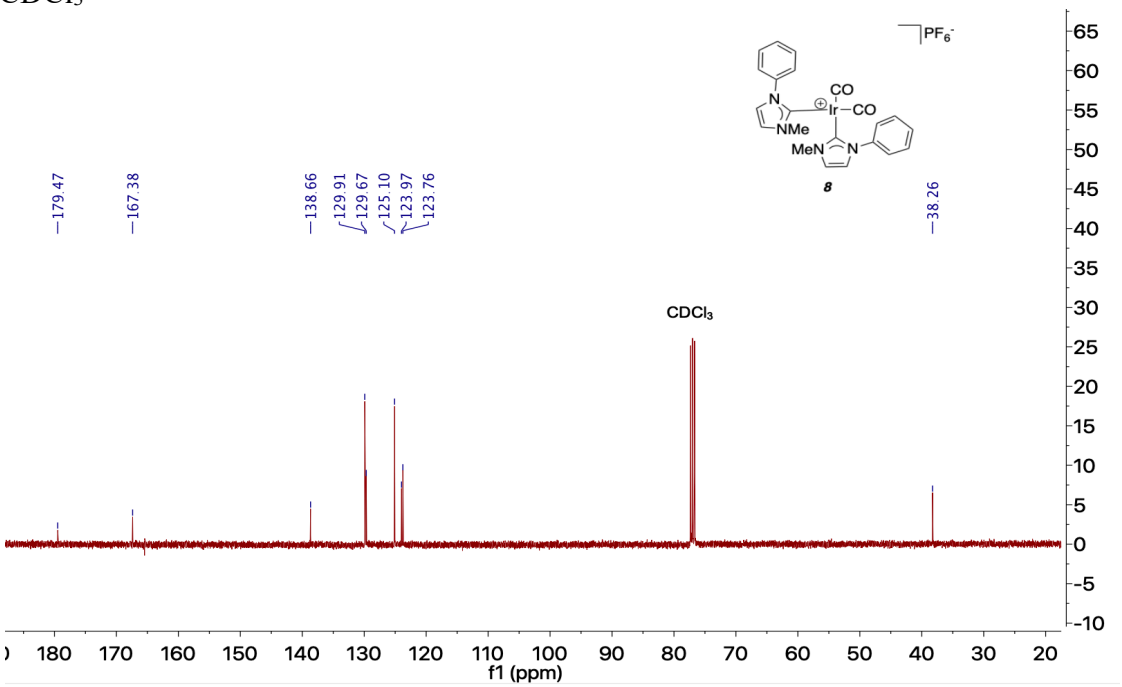


Catalyst *8* - *Ir(NHC-Ph)$_2$(CO)$_2$*

^{1}H: $CDCl_3$



^{13}C: $CDCl_3$



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