Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information: Selective Catalytic Oxidation of Sugar Alcohols to Lactic acid

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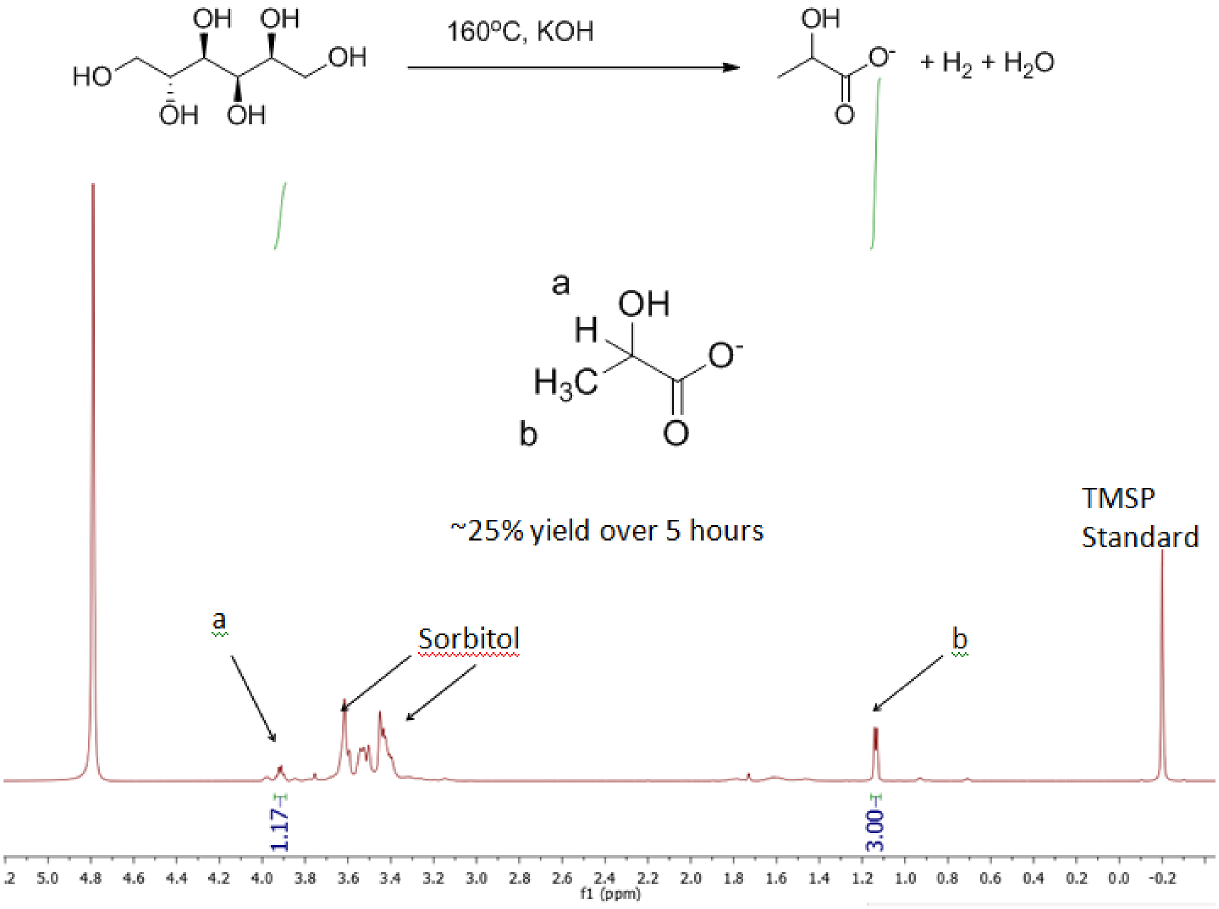
General Methods. The syntheses of the metal complexes were conducted under nitrogen using dry degassed solvents unless otherwise indicated. Solvents were dried and degassed prior to use. $(Et_2Im)BF_4$,[1] $Ag(IBu)_2BF_4$[2] and $[Ir(cod)Cl]_2$[3] were synthesized using literature procedures. All other reagents were commercially available from Airgas, Sigma-Aldrich, Alfa-Aesar and Strem Chemicals and used as received unless otherwise indicated. NMR spectra were recorded at room temperature on a 400 or 500 MHz Bruker or Varian spectrometer. Chemical shifts are reported in ppm with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ NMR spectra. NMR coupling constants (*J*) are given in Hz.

Synthesis of Compound 1. This procedure has been reported in our previous publication.[4] $[Ir(COD)Cl]_2$ (200 mg, 0.298 mmol) and $Ag(IMe)_2BF_4$ (250 mg, 0.648 mmol) were added to a 100 ml round bottom Schlenk flask with a magnetic stir bar. The Schlenk was evacuated and purged with dry nitrogen. Dry dichloromethane (20 mL) was added under nitrogen and the mixture stirred at room temperature for 3 hours in the absence of light. The resulting dark orange solution was run through a short silica plug in air. A bright orange band was collected by flushing the silica with acetone, leaving behind a darker orange/brown band. The solvent of the combined fractions was removed under reduced pressure and the solid taken back up in minimal dichloromethane. $[Ir(COD)(IMe)_2]BF_4$ was precipitated by the addition of diethyl ether and collected by filtration to yield a bright orange powder (252 mg, 73% yield). $[Ir(COD)(IMe)_2]BF_4$ (50 mg, 0.0862 mmol) was added to a 100 ml round bottom Schlenk flask with a magnetic stir bar. The Schlenk was evacuated and purged with carbon monoxide. Dry dichloromethane (2 mL) was added under CO atmosphere and the vessel sealed and stirred at room temperature for 1 hour. The solution visibly turned from orange to yellow within minutes. The solvent was reduced to 5 ml under reduced pressure and diethyl ether was added to precipitate a vibrant yellow powder which was collected by filtration (40 mg, 87% yield) ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.12 (s, 1H), 3.69 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2): δ = 180.60 (s), 124.42 (s), 110.54 (s), 38.58 (s). HRMS (FT-ICR): calcd. for $C_{12}H_{16}IrN_4O_2$ (M^+): 441.0902. Found: m/z = 441.0870. FT-IR (solid): ν (CO) = 1995, 2060 cm^{-1}.

Synthesis of $Ag(IEt)_2BF_4$.

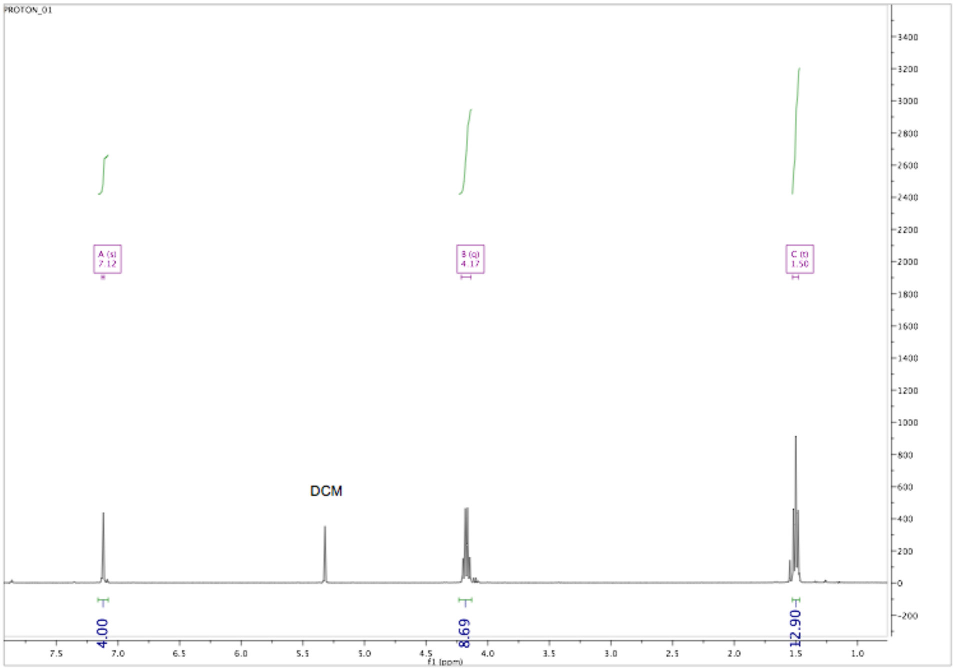
This compound was prepared using an adaptation of a previously published procedure.[2] $(Et_2Im)BF_4$ (860 mg, 4.06 mmol) and Ag_2O (1.08 g, 4.66 mmol) were dissolved in CH_2Cl_2 (65 mL) and 20 mL of an aqueous solution of NaOH (270 mg, 6.75 mmol) was added. The biphasic mixture was stirred under N_2 with exclusion of light for 15 hours. The resulting suspension was filtered, the aqueous layer was extracted three times with CH_2Cl_2, and the organics were combined. Removal of the solvent *in vacuo* gave $Ag(IEt_2)BF_4$ (420 mg, 47%) as a white powder. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): ∂ = 7.12 (s, 4H, CH_{Ar}), 4.17 (q, $^3J_{H\text{-}H}$=7.2 Hz, 8H, NCH_2 (α)) 1.50 (t, 12H, $^3J_{H\text{-}H}$=7.2, CH_3 (ß)). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C): ∂ = 179.2 (d, $^1J_{Ag\text{-}C}$=43 Hz, Ag=C), 121.5 (CH_{Ar}), 47.6 (NCH_2(α)), 17.4 (CH_3 (ß)). HRMS (FT-ICR): calcd. for $C_{14}H_{24}AgN_4$ ($[M]^+$): 355.1052. Found: m/z =355.1042.

NMR of standard 5hr sorbitol dehydrogenation reaction under optimized conditions

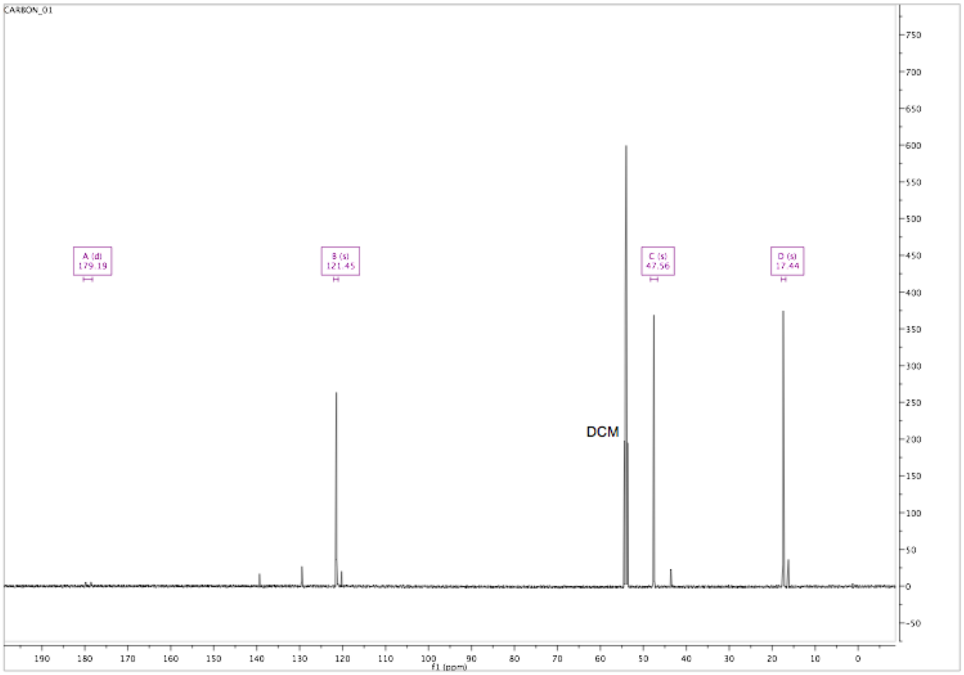


NMR data for $Ag(IEt_2)BF_4$

^1H NMR

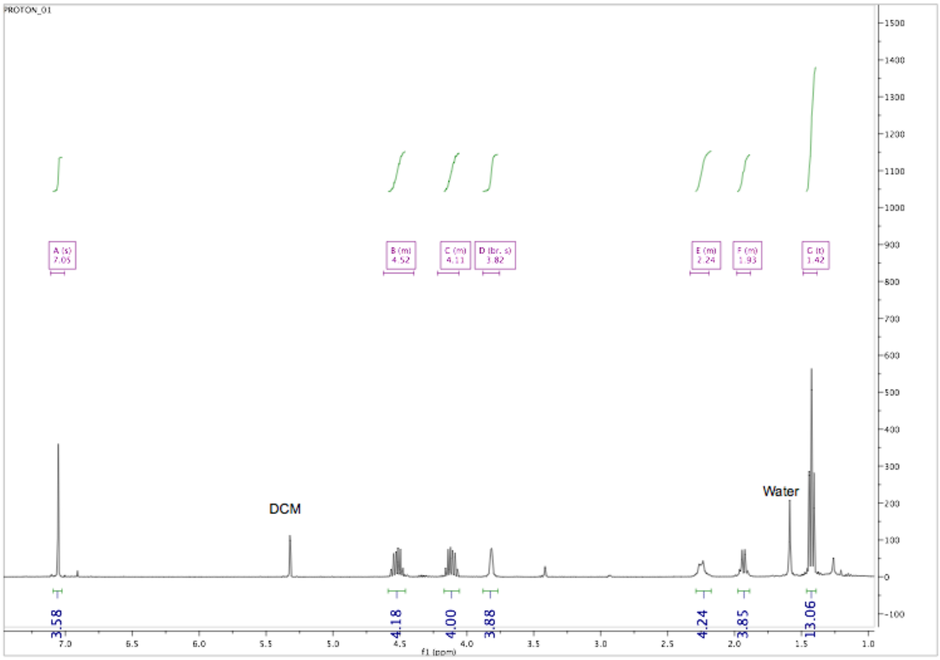


$^{13}C\{^1H\}$ NMR

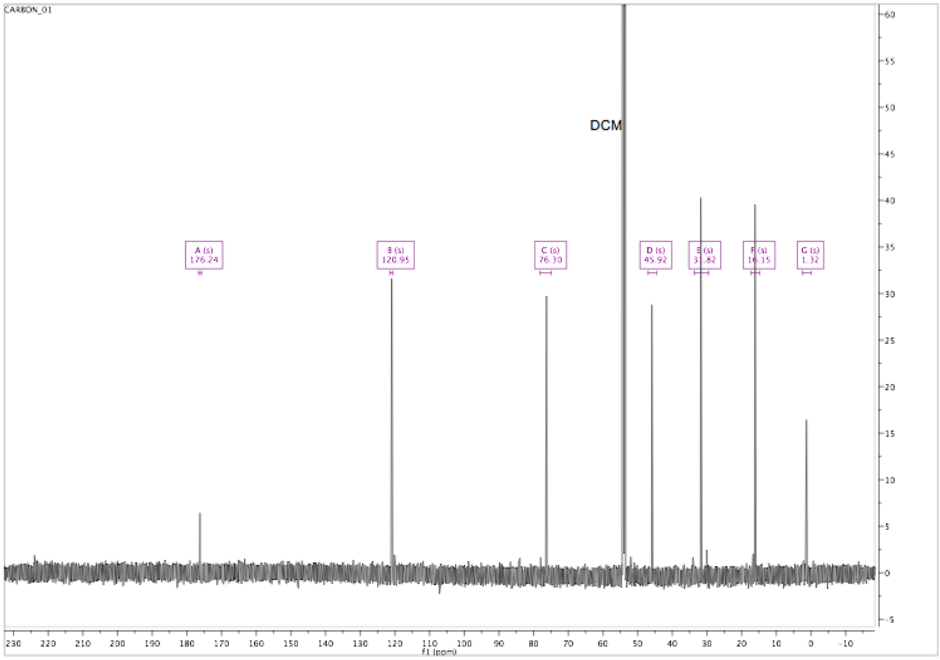


NMR data for Ir(IEt)$_2$(cod)BF$_4$ (2)

^{1}H NMR



^{13}C{^{1}H} NMR



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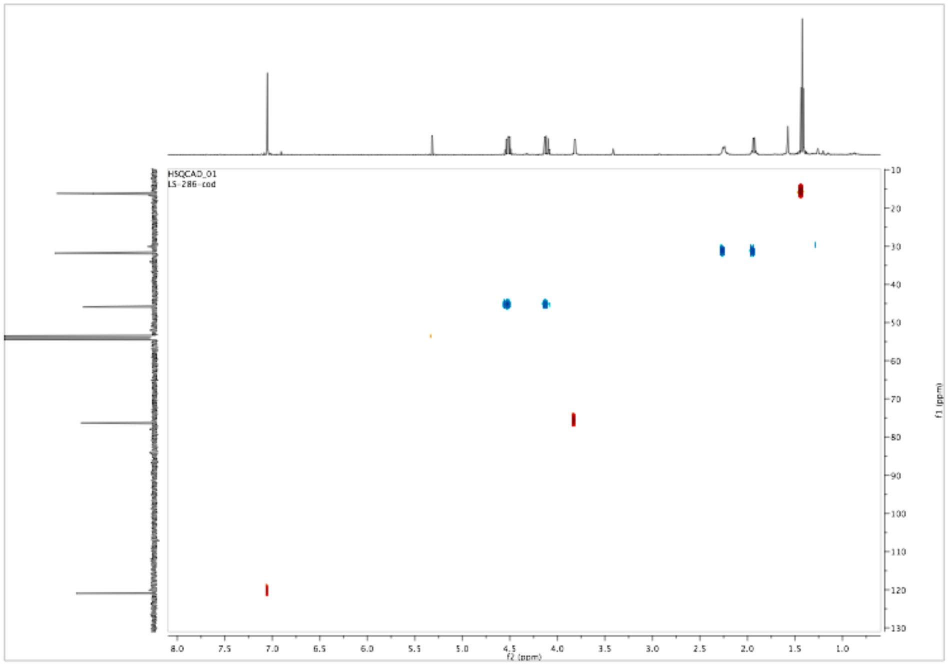
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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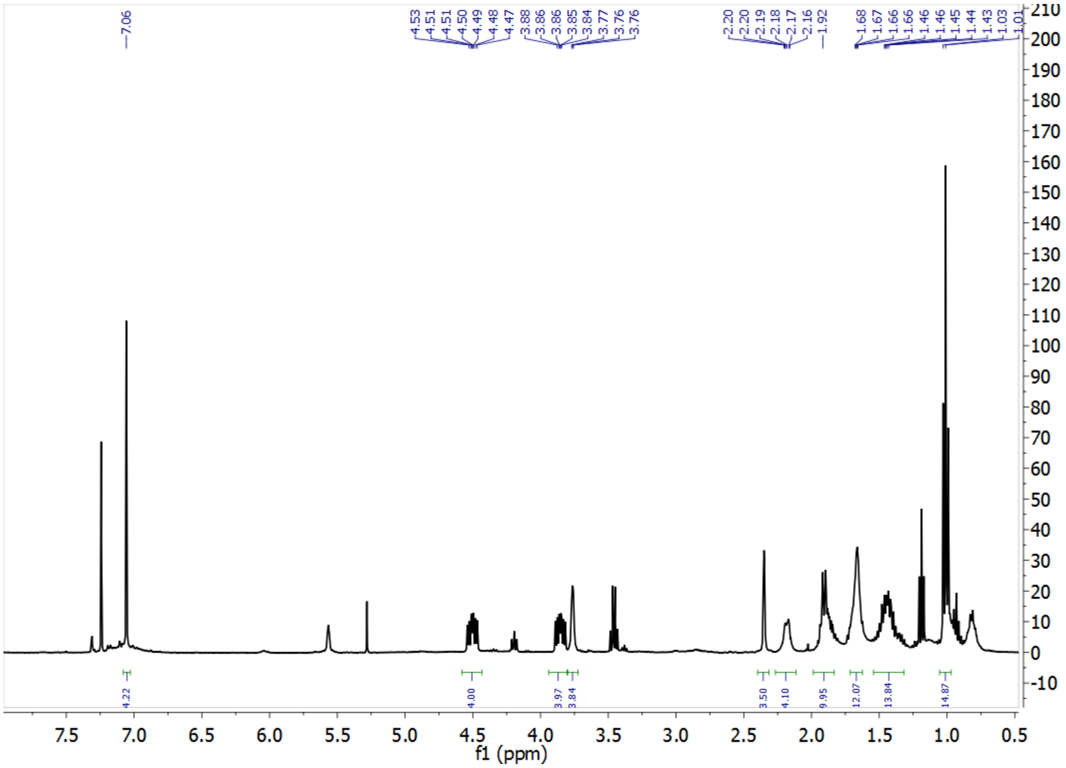
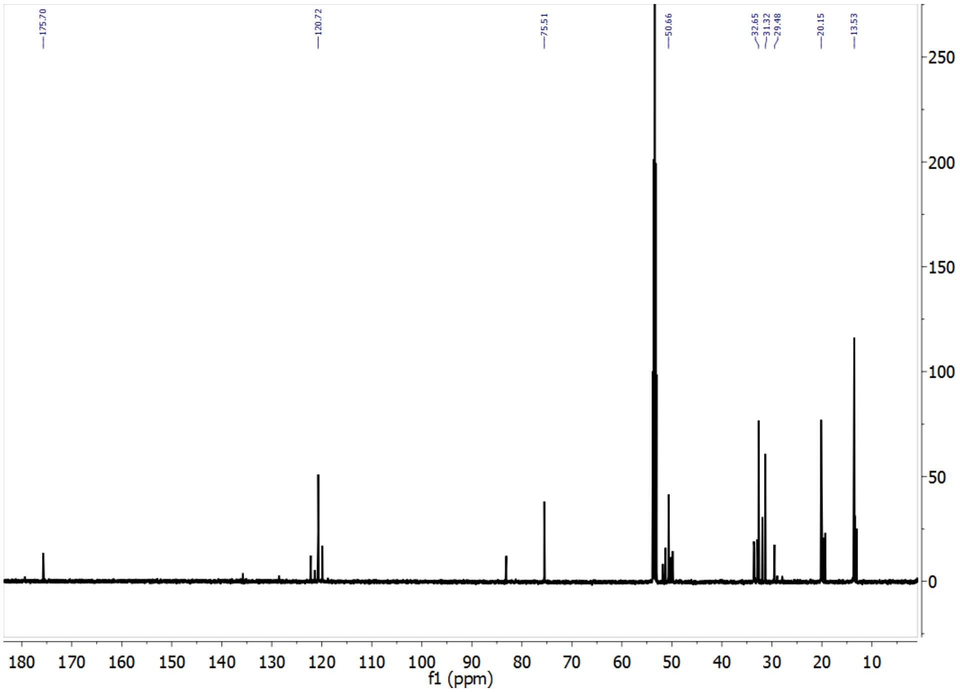
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)

NMR data for Ir(IBu)$_2$(cod)BF$_4$ (3)

^{1}H NMR

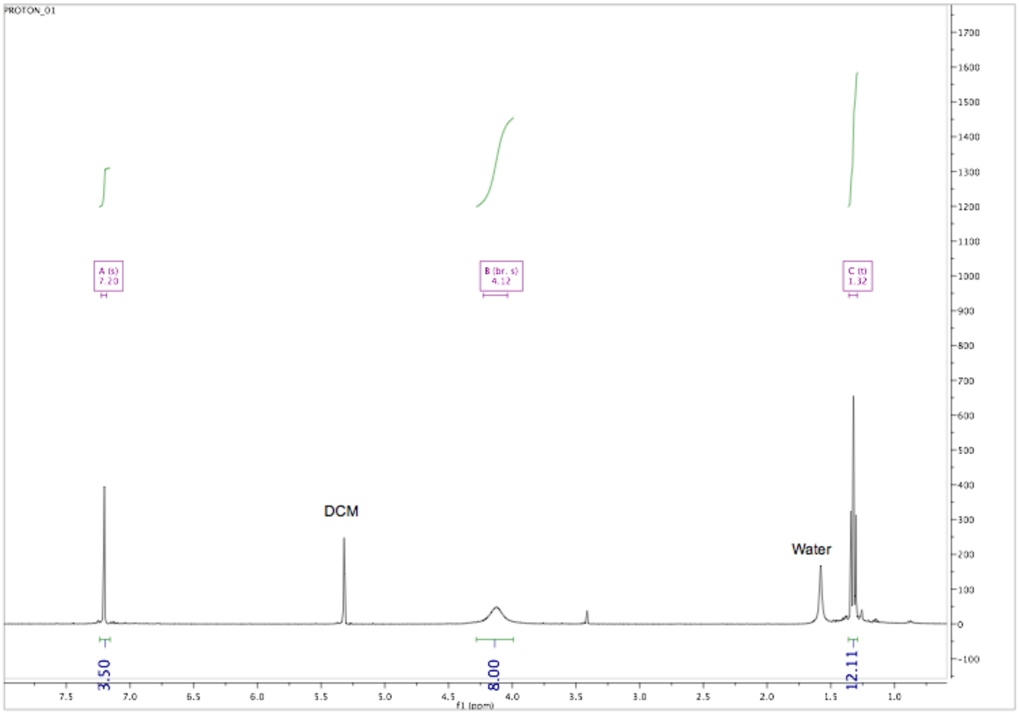


^{13}C{^{1}H} NMR



NMR data for Ir(IEt)$_2$(CO)$_2$BF$_4$ (4)

^{1}H NMR



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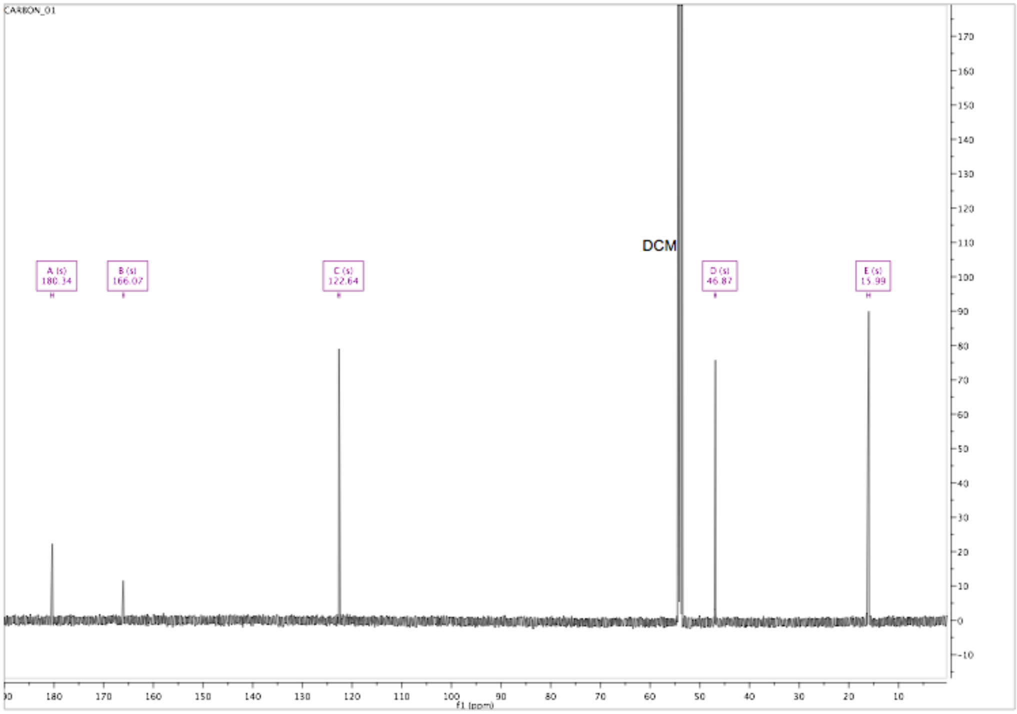
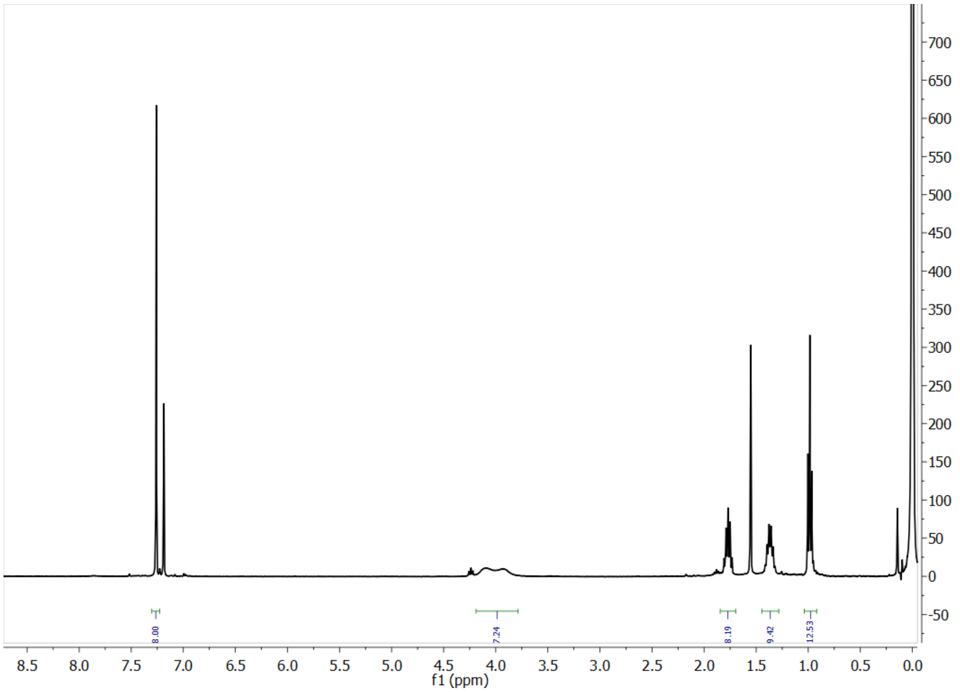
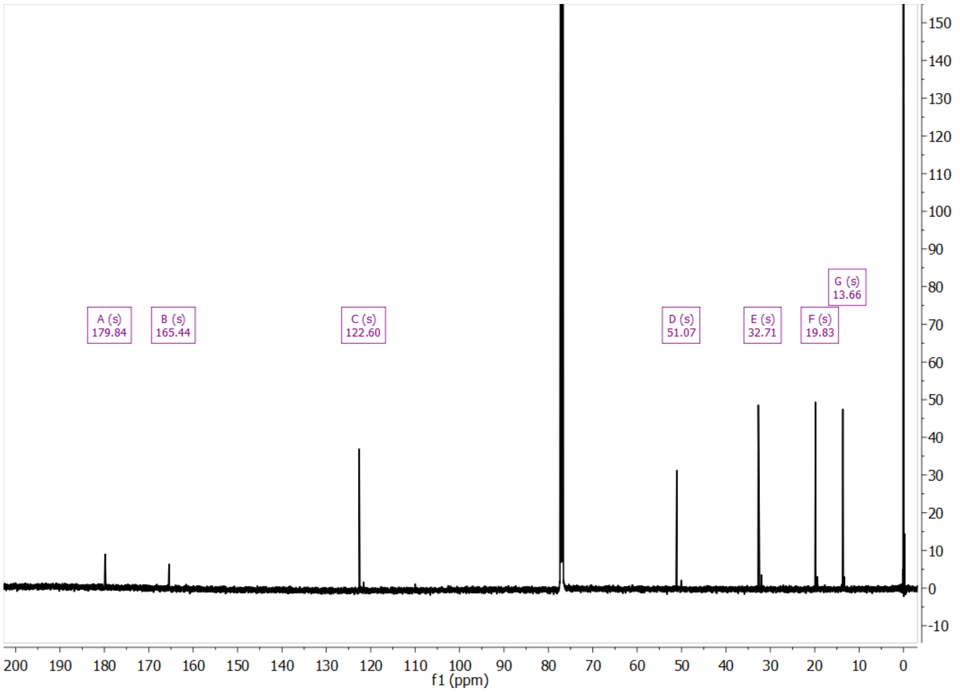


NMR data for $Ir(IBu)_2(CO)_2BF_4$ (5)

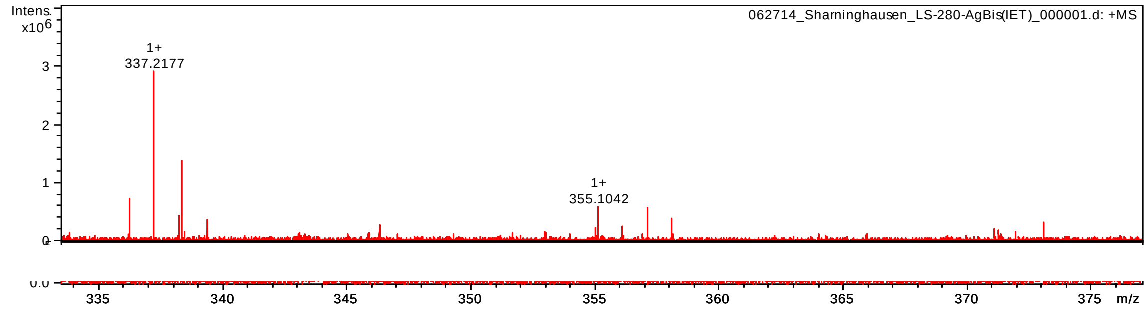
^{1}H NMR



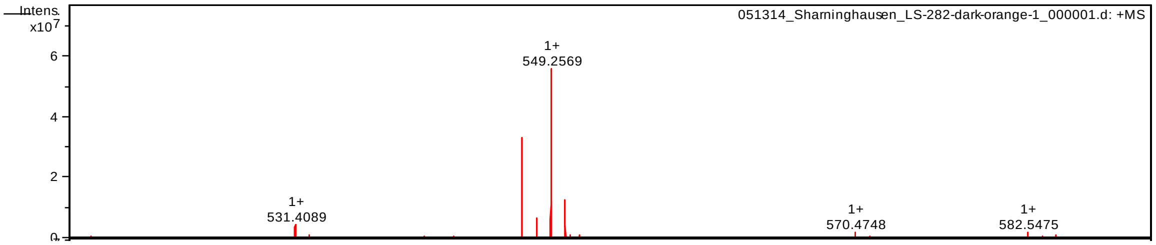
^{13}C{^{1}H} NMR



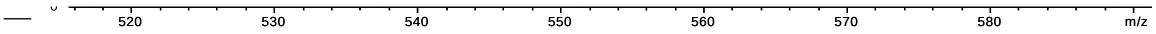
HRMS data for $Ag(IEt_2)BF_4$

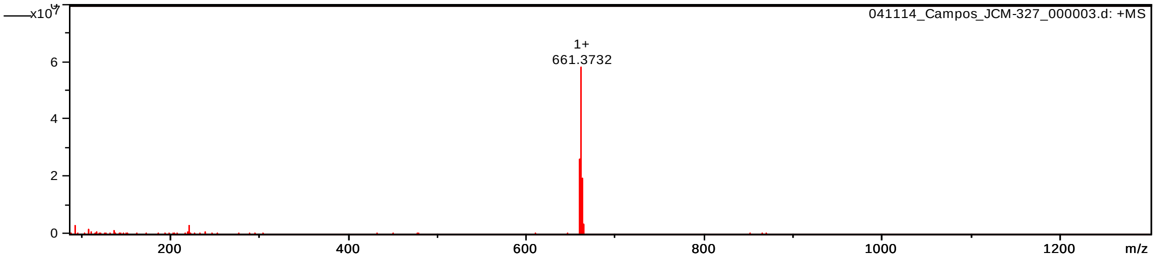


HRMS data for $Ir(IEt)_2(cod)BF_4$ (2)

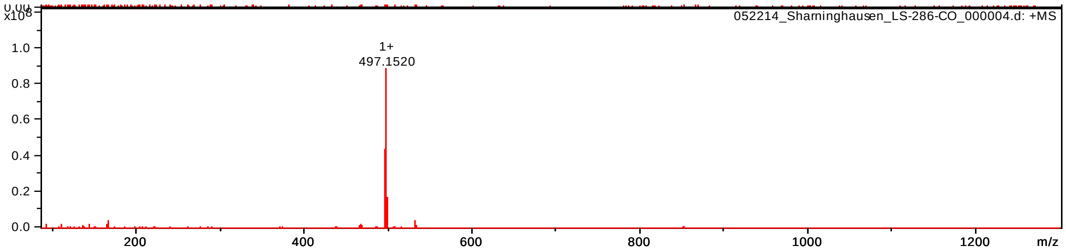


HRMS data for $Ir(IBu)_2(cod)BF_4$ (3)

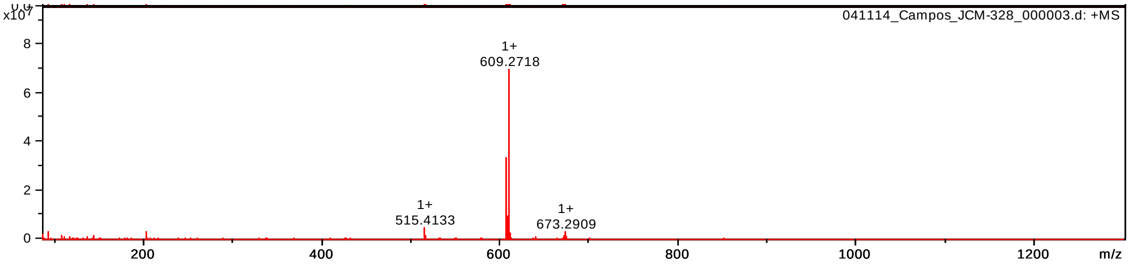




HRMS data for Ir(IEt)$_2$(CO)$_2$BF$_4$ (4)



HRMS data for Ir(IBu)$_2$(CO)$_2$BF$_4$ (5)



Crystallographic details

General. Low-temperature diffraction data (ω scans) were collected on a Rigaku Mercury275R CCD (SCX mini) detector using filtered Mo Kα radiation ($\lambda = 0.71073$ Å) at 223K. The data frames were processed and scaled using the Rigaku *CrystalClear*[5] software. The data were corrected for Lorentz and polarization effects. All structures were solved by direct methods using SHELXS[6] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[7] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Complete details of the X-ray analyses reported herein have been deposited at The Cambridge Crystallographic Data Centre CCDC 1021458

Crystallographic details for compound 5. The rotational disorder of the BF_4 counterion was modeled over two positions with occupancies of 56:46 and their anisotropic displacement parameters restrained using SIMU and DELU instructions. Similarity restrains (SADI) to the distances and angles of the ^{n}Bu chains of one of the NHCs were applied due to their high thermal motion. SIMU and DELU commands were also applied to these hydrocarbon chains.

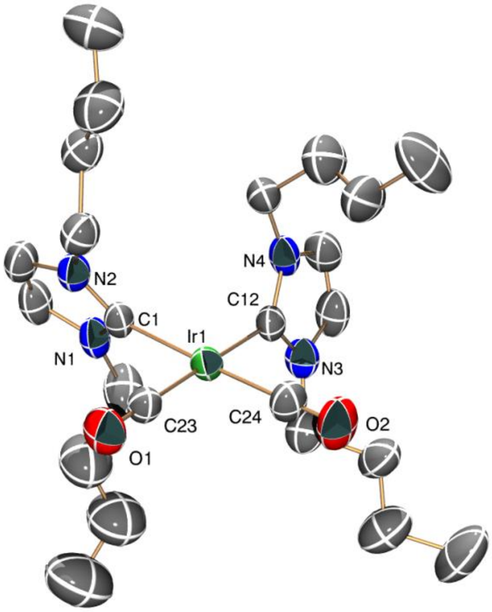


Figure S1. ORTEP diagram of the cationic portion of compound **5**. 50% thermal ellipsoids are shown. Hydrogen atoms and BF_4 counterions have been omitted for clarity.

Crystal data

$C_{24}H_{40}BF_4IrN_4O_2$	$Z = 2$
$M_r = 695.61$	$F(000) = 692$
Triclinic, $P\overline{1}$	$D_x = 1.495$ Mg m^{-3}
$a = 10.1442$ (16) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.7709$ (18) Å	Cell parameters from 16343 reflections
$c = 15.044$ (2) Å	$\theta = 3.2$–$27.5°$
$\alpha = 109.125$ (8)°	$\mu = 4.37$ mm^{-1}
$\beta = 97.344$ (7)°	$T = 496$ K
$\gamma = 109.259$ (8)°	Prism, yellow
$V = 1545.2$ (4) Å^3	0.30 × 0.10 × 0.10 mm

Data collection

Rigaku Mercury275R CCD diffractometer

Radiation source: fine-focus sealed tube

graphite

Detector resolution: 6.8 pixels mm^{-1}

ω scans

Absorption correction: multi-scan Jacobson, R. (1998) Private Communication

$T_{\min} = 0.475$, $T_{\max} = 0.475$

19692 measured reflections

5570 independent reflections

4175 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.059$

$\theta_{\max} = 25.3°$, $\theta_{\min} = 3.2°$

$h = -12\rightarrow12$

$k = -14\rightarrow14$

$l = -18\rightarrow18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.117$

$S = 1.03$

5570 reflections

357 parameters

31 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.6729P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.043$

$\Delta\rho_{\max} = 0.83$ e Å^{-3}

$\Delta\rho_{\min} = -0.45$ e Å^{-3}

Selected geometric parameters (Å, º)

Ir1—C23	1.874 (9)	C23—O1	1.141 (10)
Ir1—C24	1.885 (10)	C24—O2	1.111 (10)
Ir1—C12	2.084 (8)	C12—N3	1.345 (11)

Ir1—C1	2.105 (8)	C12—N4	1.362 (11)
C1—N2	1.333 (10)	C15—N3	1.468 (13)
C1—N1	1.352 (11)	C15—C16	1.548 (14)

C23—Ir1—C24	91.5 (4)	N2—C1—N1	105.7 (7)
C23—Ir1—C12	177.0 (4)	N2—C1—Ir1	126.7 (7)
C24—Ir1—C12	89.8 (4)	N1—C1—Ir1	127.4 (7)
C23—Ir1—C1	89.0 (3)	O1—C23—Ir1	179.5 (9)
C24—Ir1—C1	178.4 (4)	O2—C24—Ir1	178.5 (11)
C12—Ir1—C1	89.8 (3)	N4—C12—Ir1	127.3 (7)
N3—C12—Ir1	127.4 (6)		

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[2] Hintermair, U., Englert, U. and Leitner, W. *Organometallics* **2011**, *30*, 3726-3731.

[3] Crabtree , R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-khan, *Synth. React. Inorg. Met.-Org. Chem.*, **1982**, *12*, 407-413.

[4] Campos, J.; Sharninghausen, L. S.; Crabtree, R. H.; Balcells, D. *Angew. Chem. Int. Ed.* **2014**, *in press*.

[5] *CrystalClear* and *CrystalStructure*; Rigaku/MSC: The Woodlands, TX, **2005**.

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[7] Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112-122.