Supporting Information

Unveiling the role of ancillary ligands in acceptorless benzyl alcohol dehydrogenation and etherification mediated by mesoionic carbene iridium complexes

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CONTENT:

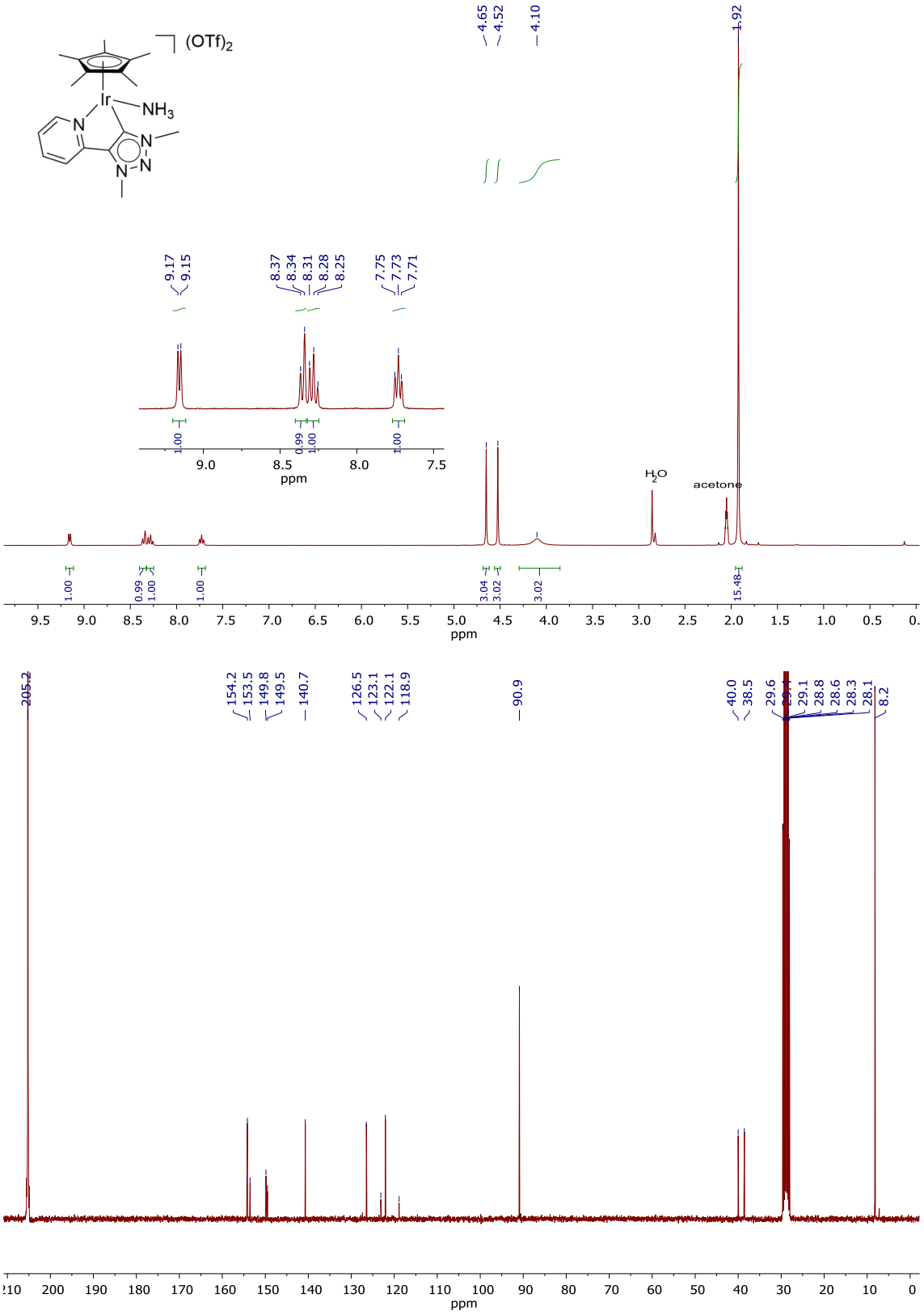


Figure S1. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of complex **3** (acetone-d_6, 300 and 75 MHz).

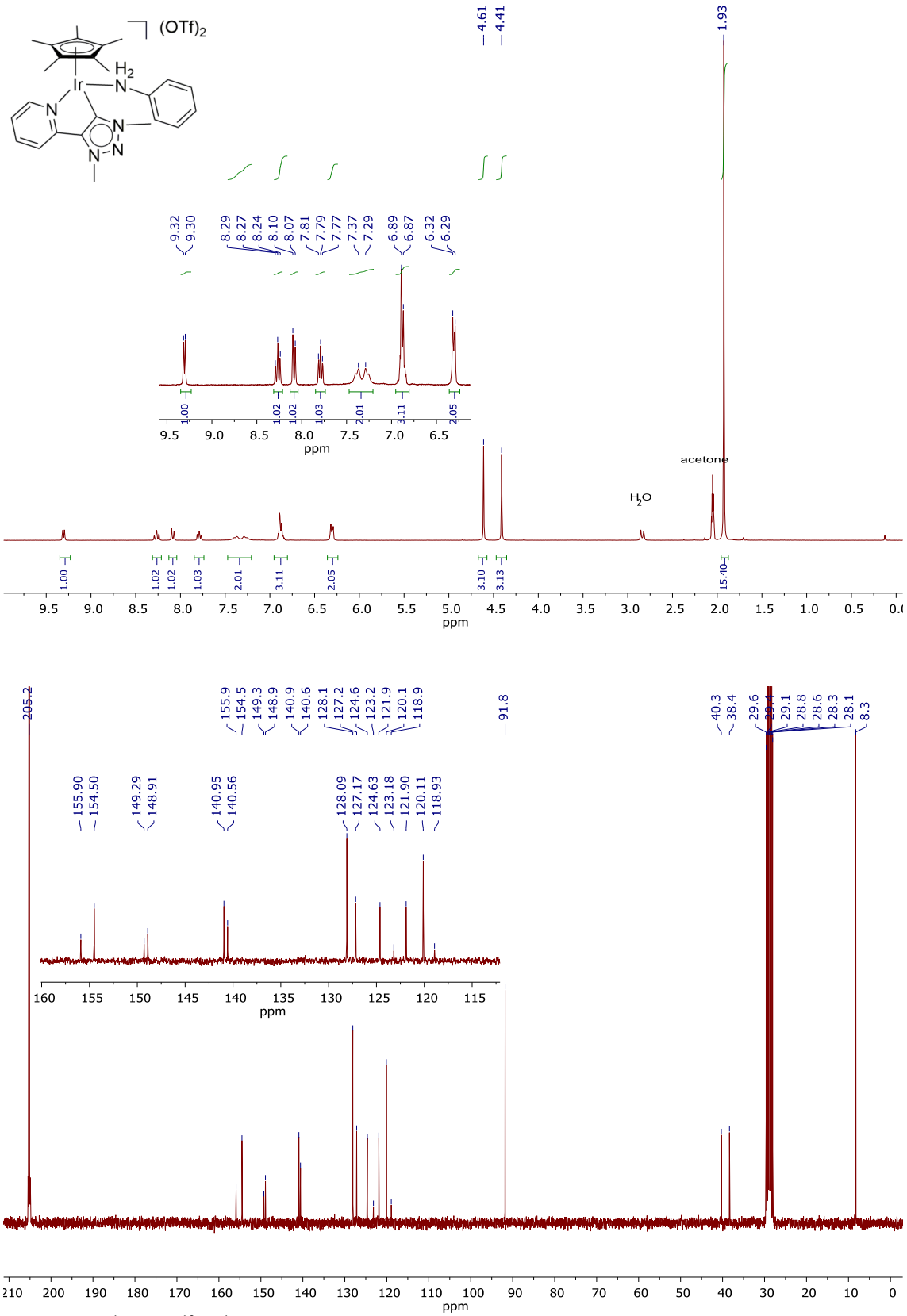
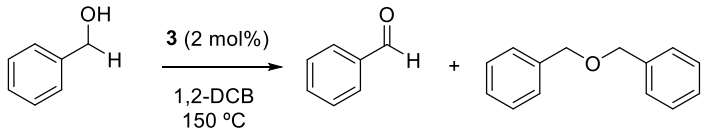
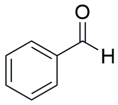
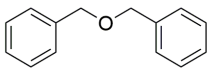


Figure S2. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of complex **4** (acetone-d_6, 300 and 75 MHz).

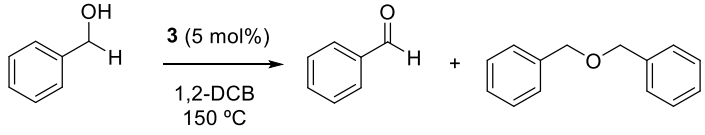
Table S1. BnOH oxidation catalysed by iridium complex **3**.[a]



Entry	Time (h)	Conversion[b]			Ratio BnCHO/Bn_2O
1	0.25	25	25	-	
2	0.5	46	40	6	6.7
3	1	61	49	12	6.1
4	2	71	53	18	2.9
5	4	72	57	25	2.3
6	6	78	59	27	2.2
7	24	97	62	35	1.8

[a] Conditions: alcohol (0.4 mmol), catalyst **3** (6.5 mg, 0.008 mmol), 1,2-DCB (2 mL), 150 ºC, sealed tube.
[b] Determined by ^{1}H NMR spectroscopic analysis in $CDCl_3$. Note that the % given for the symmetric ether refers to the % of alcohol converted in ether.

Table S2. Catalyst reuse and stability during consecutive additions of benzyl alcohol.[a]



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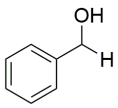
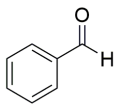
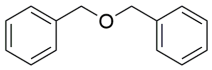
Entry		Conversion (%)[b]		
1	0.4 mmol	100	82	18
2	+0.4 mmol	100	18	82
3	+0.4 mmol	100	17	83
4	+0.4 mmol	96	19	77
5	+0.4 mmol	91	37	54

[a] Conditions: benzyl alcohol (41 µL, 0.4 mmol), complex **3** (16 mg, 0.02 mmol, 5 mol%), 1,2-dichlorobenzene (2 mL), 150 ºC, sealed tube; 24 h interval before addition of the next portion of substrate.
[b] Conversion of each run independently.

Table S3. Crystal data and structure refinement for **3**.

Identification code	1583136	
Empirical formula	$C_{21}\ H_{30}\ N_5\ O_7\ F_6\ S_2\ Ir$	
Molecular formula	$[C_{19}\ H_{28}\ N_5\ Ir]^{2+}\{[C\ O_3\ F_3\ S]^-\}_2\ x\ H_2\ O$	
Formula weight	834.82	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 11.7545(2) Å	α= 90°.
	b = 15.1242(2) Å	β= 106.402(2)°.
	c = 16.9226(3) Å	γ = 90°.
Volume	2886.02(8) $Å^3$	
Z	4	
Density (calculated)	1.921 Mg/m^3	
Absorption coefficient	4.859 mm^{-1}	
F(000)	1640	
Crystal size	0.0904 x 0.0694 x 0.0379 mm^3	
Theta range for data collection	2.85 to 29.63°.	
Index ranges	–16<=h<=15, –19<=k<=19, –22<=l<=23	
Reflections collected	50428	
Independent reflections	7408 [R(int) = 0.0327]	
Completeness to theta = 28.00°	98.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.877 and 0.755	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7408 / 21 / 428 [a)]	
Goodness–of–fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0438	
R indices (all data)	R1 = 0.0274, wR2 = 0.0457	
Largest diff. peak and hole	0.948 and –0.726 e.$Å^{-3}$	

[a)] The two disorder parts were restrained to have similar shapes using SAME.

Table S4. Crystal data and structure refinement for **4**.

Identification code	1583137	
Empirical formula	$C_{27}\ H_{32}\ N_5\ O_6\ F_6\ S_2\ Ir$	
Molecular formula	$[C_{25}\ H_{32}\ N_5\ Ir]^{2+}\{[C\ O_3\ F_3\ S]^-\}_2$	
Formula weight	892.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P–1 (#2)	
Unit cell dimensions	a = 11.5139(1) Å	α= 82.8016(7)°.
	b = 12.1655(1) Å	β= 85.3357(7)°.
	c = 12.3732(1) Å	γ = 68.0905(8)°.
Volume	1594.17(2) $Å^3$	
Z	2	
Density (calculated)	1.860 Mg/m^3	
Absorption coefficient	4.403 mm^{-1}	
F(000)	880	
Crystal size	0.2676 x 0.2169 x 0.1534 mm^3	
Theta range for data collection	2.83 to 29.73°.	
Index ranges	–15<=h<=15, –16<=k<=16, –17<=l<=17	
Reflections collected	15710	
Independent reflections	7946 [R(int) = 0.0550] [a]	
Completeness to theta = 28.00°	99.7 %	
Absorption correction	Analytical	
Max. and min. transmission	0.626 and 0.405	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7946 / 46 / 579 [b]	
Goodness–of–fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0792	
R indices (all data)	R1 = 0.0351, wR2 = 0.0811	
Largest diff. peak and hole	2.464 and –1.440 $e.Å^{-3}$	

[a] The crystal is a non–merohedral twin and was refined on an HKLF5 reflection file. This forces the treatment of all reflections as unique, so these two numbers cannot be determined from that file. They are taken from the corresponding HKLF4 file, lacking the overlapped reflections, and are thus approximations. [b] The two disordered ligands are restrained to have the same shape using SAME. The disordered CF_3 groups are restrained to have the ideal shape using DFIX.