catalysts

MDPI

Supplementary Materials

Strong Solvent Effects on Catalytic Transfer Hydrogenation of Ketones with [Ir(cod)(NHC)(PR_3)] Catalysts in 2-Propanol-Water Mixtures

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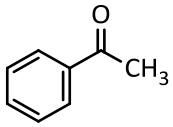
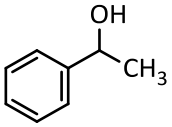
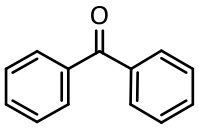
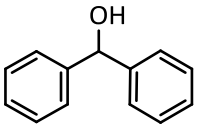
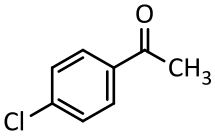
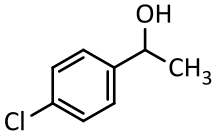
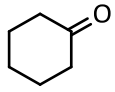
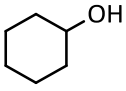
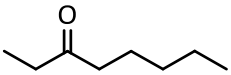
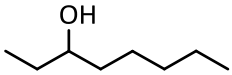
Contents

Table S1. Transfer hydrogenation of ketones catalyzed by complexes **1**–**6** and **9**.

Entry	Substrate	Product	Catalyst	Conversion [a] (%)
1			**1**	87
			2	88
			3	91
			4	48
			5	89
			6	90
			9	93
2			**1**	86
			2	84
			4	63
			5	91
			6	90
3			**1**	94
			2	91
			4	59
			5	92
			6	93
4			**1**	92
			2	84
			4	74
			5	99
			6	100
5			**1**	27
			2	24
			4	8
			5	63
			6	53

Conditions: n(catalyst) = 0.01 mmol, n(acetophenone) = 1.0 mmol, n(*t*-BuOK) = 0.05 mmol, T = 80 °C, t = 30 min, V(2-PrOH) = 1.0 mL; [S]/[C]/[B] = 100/1/5. [a] Determined by gas chromatography.

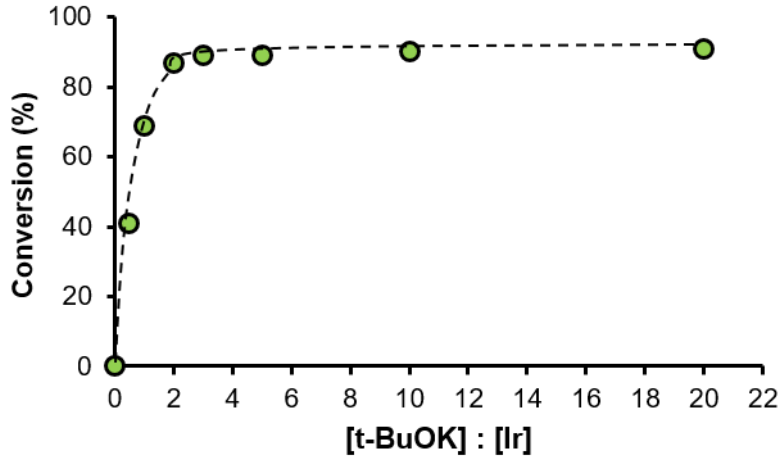


Figure S1. Effect of various bases on the transfer hydrogenation of acetophenone catalysed by [Ir(cod)(emim)(*m*tppms)] (**6**). Conditions: *n*(catalyst) = 0.01 mmol, *n*(acetophenone) = 1 mmol, *T* = 80 °C, *t* = 1 h, *V*(2-PrOH) = 1.0 mL; [S]/[C] = 100/1.

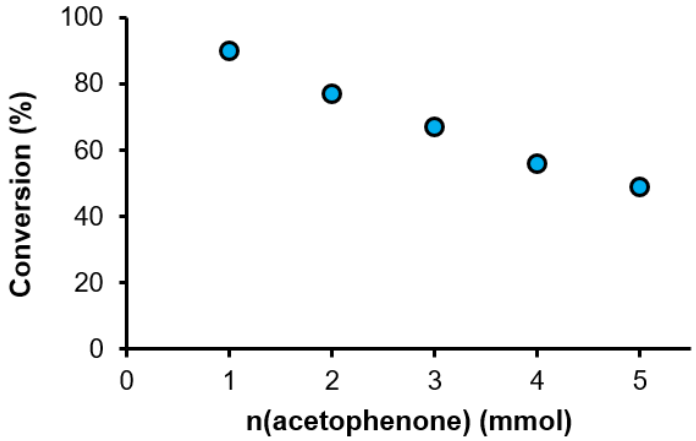


Figure S2. The effect of substrate concentration on the transfer hydrogenation of acetophenone catalyzed by [Ir(cod)(emim)(*m*tppms)] (**6**).

Conditions: *n*(catalyst) = 0.01 mmol, *n*(*t*-BuOK) = 0.05 mmol, *T* = 80 °C, *t* = 30 min, *V*(2-PrOH) = 1.0 mL; [S]/[C] = 100–500, [C]/[B] = 1/5

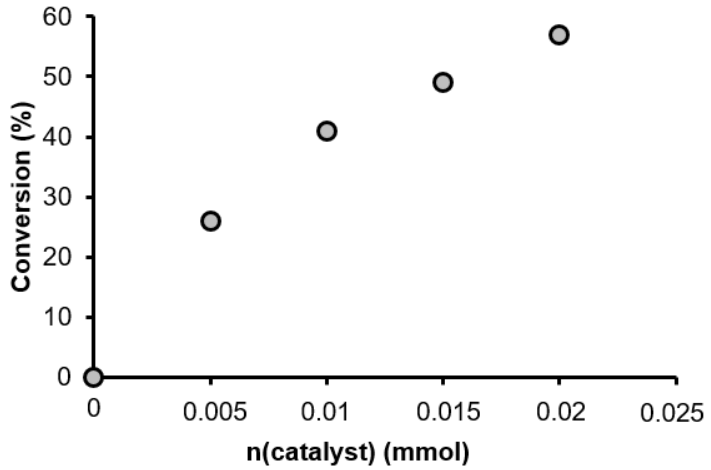


Figure S3. Effect of increasing catalyst amount on the transfer hydrogenation–of acetophenone catalyzed by [Ir(cod)(emim)(*m*tppms)] (**6**).

Conditions: *n*(acetophenone) = 5 mmol, *n*(*t*-BuOK) = 0.1 mmol, *T* = 80 °C, *t* = 30 min, *V*(2-PrOH) = 1.0 mL. [S]/[C] = 250–1000

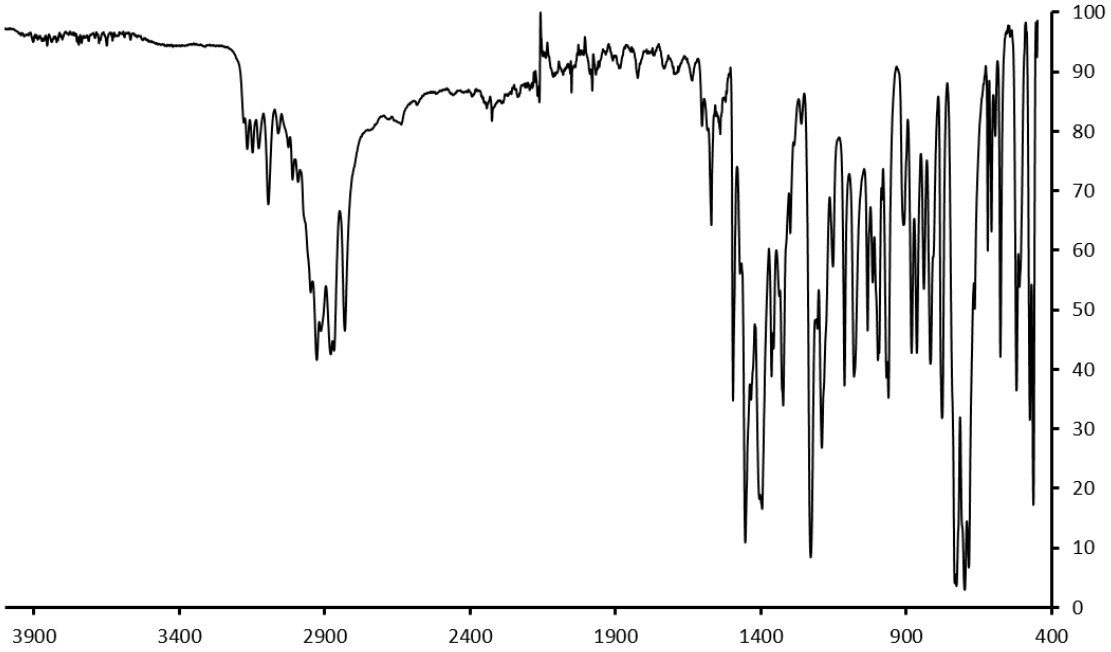


Figure S4. Infrared spectrum of [IrCl(cod)(Bnmim)] (**3**).

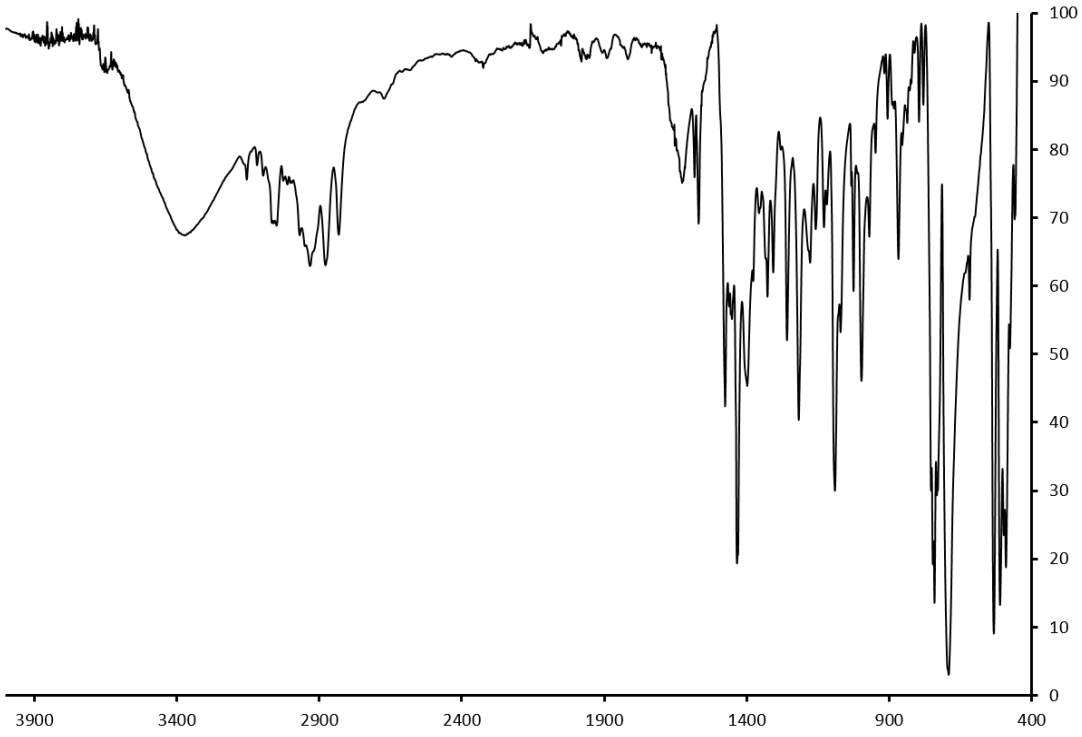


Figure S5. Infrared spectrum of [IrCl(cod)(emim)(PPh_3)] (**5**).

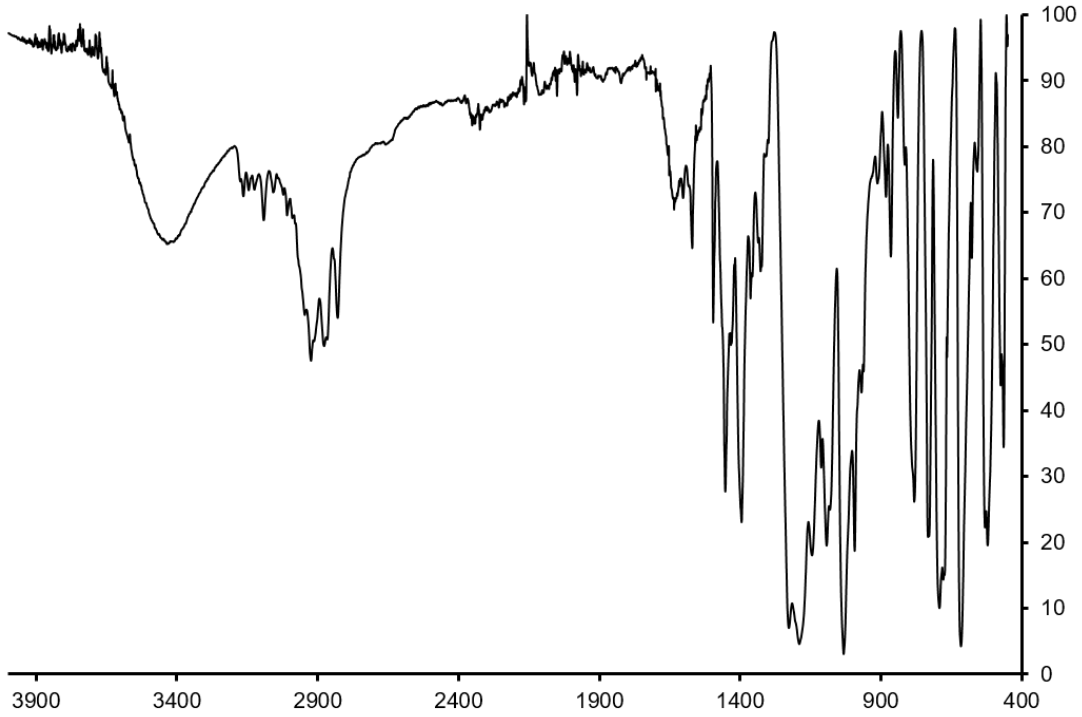


Figure S6. Infrared spectrum of [Ir(cod)(Bnmim)(*m*tppms)] (**9**).

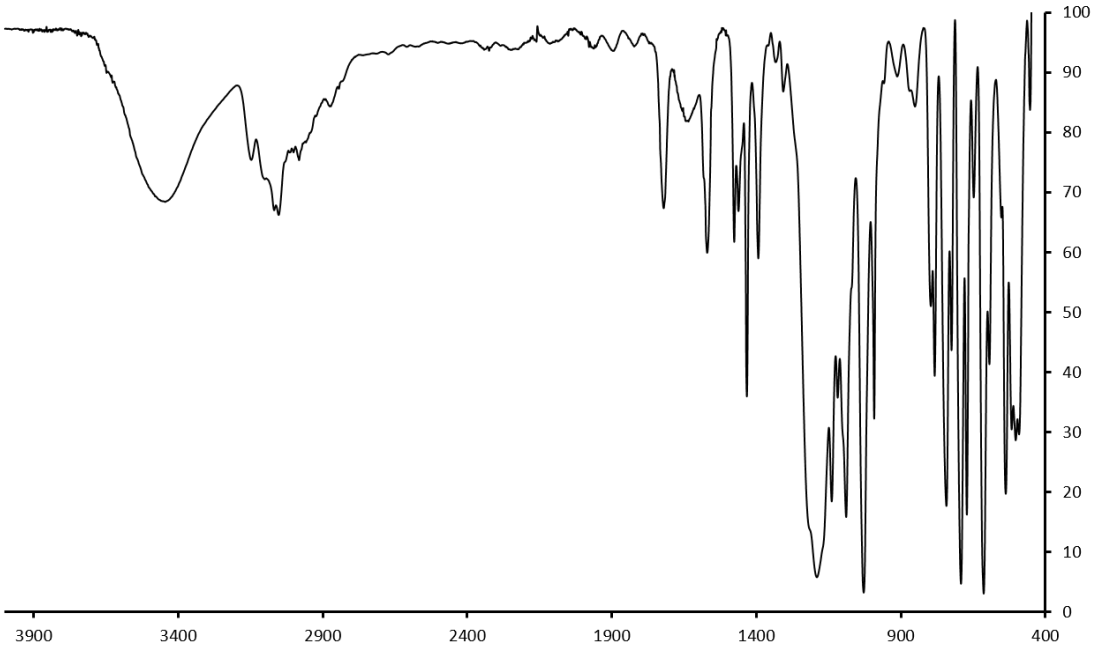


Figure S7. Infrared spectrum of [emimH][*m*tppms].

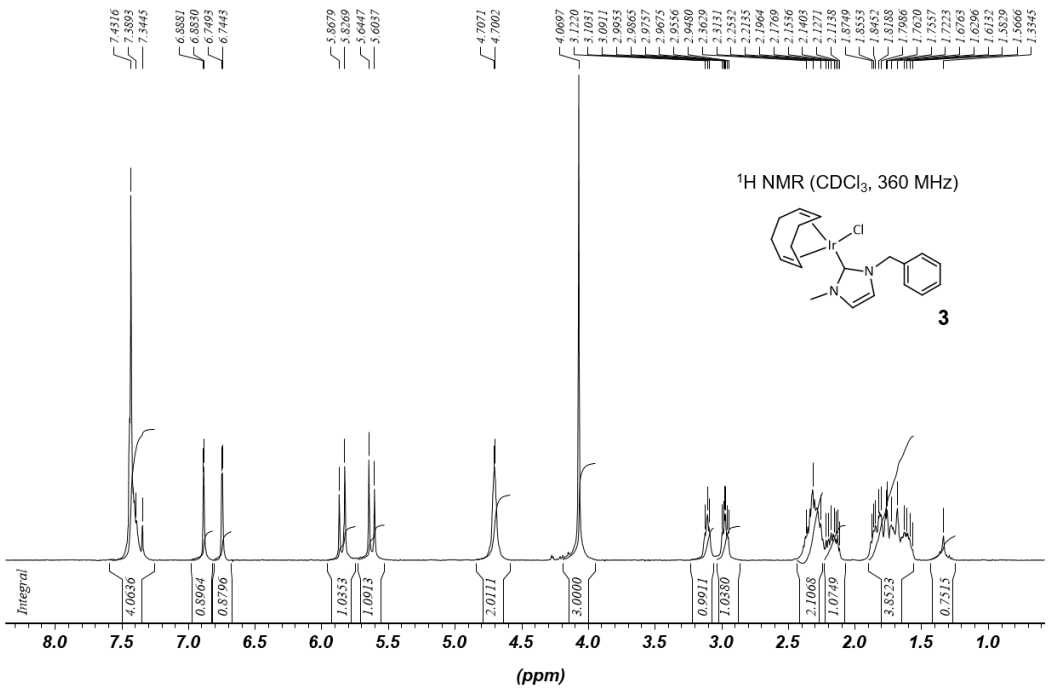


Figure S8. ^{1}H NMR spectrum of [IrCl(cod)(Bnmim)] (**3**).

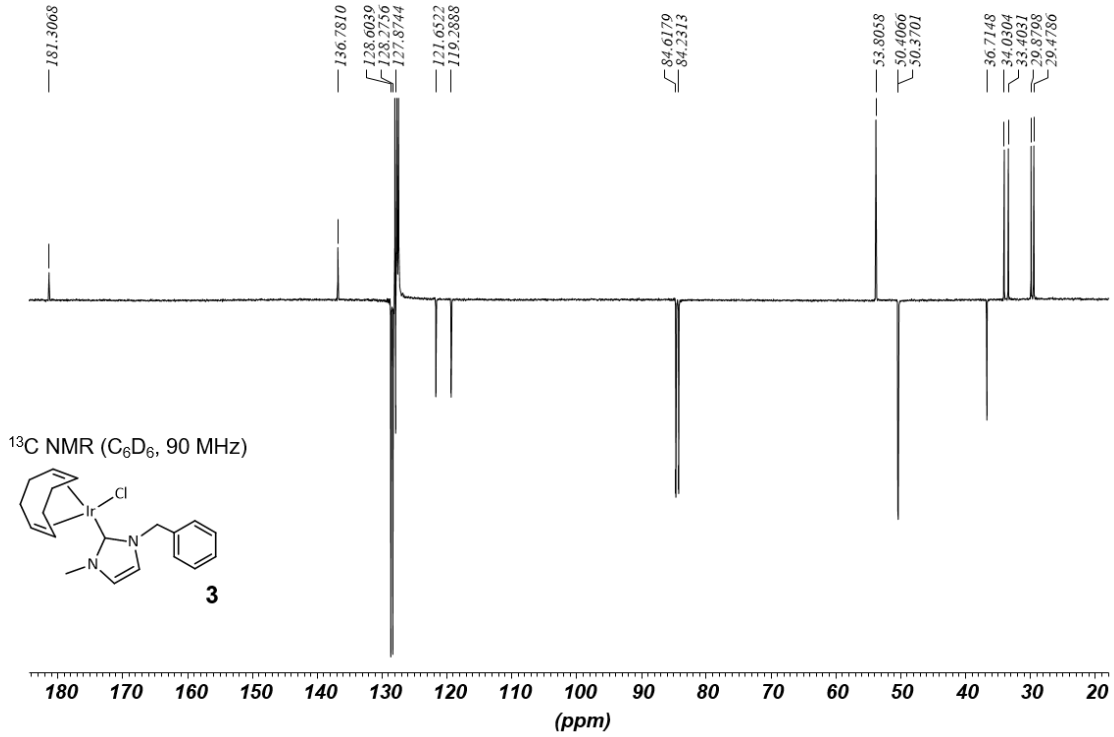


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of [IrCl(cod)(Bnmim)] (**3**).

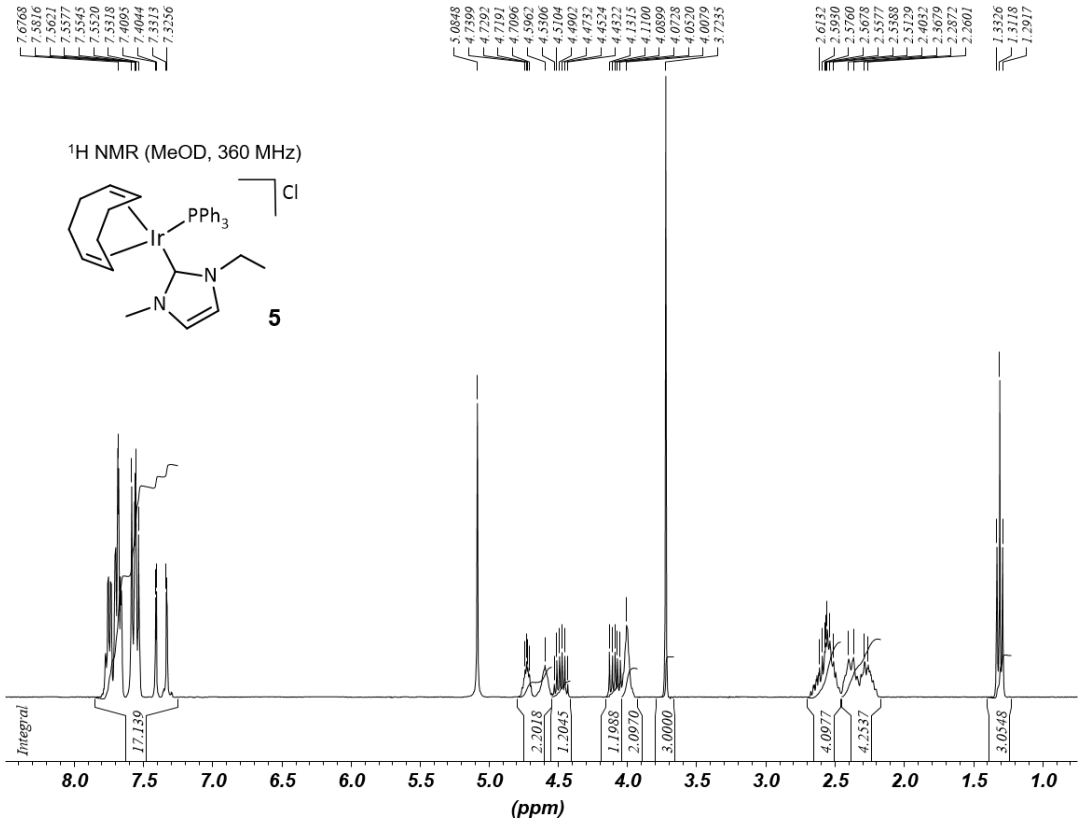


Figure S10. ^{1}H NMR spectrum of [Ir(cod)(emim)(PPh_3)]Cl (**5**).

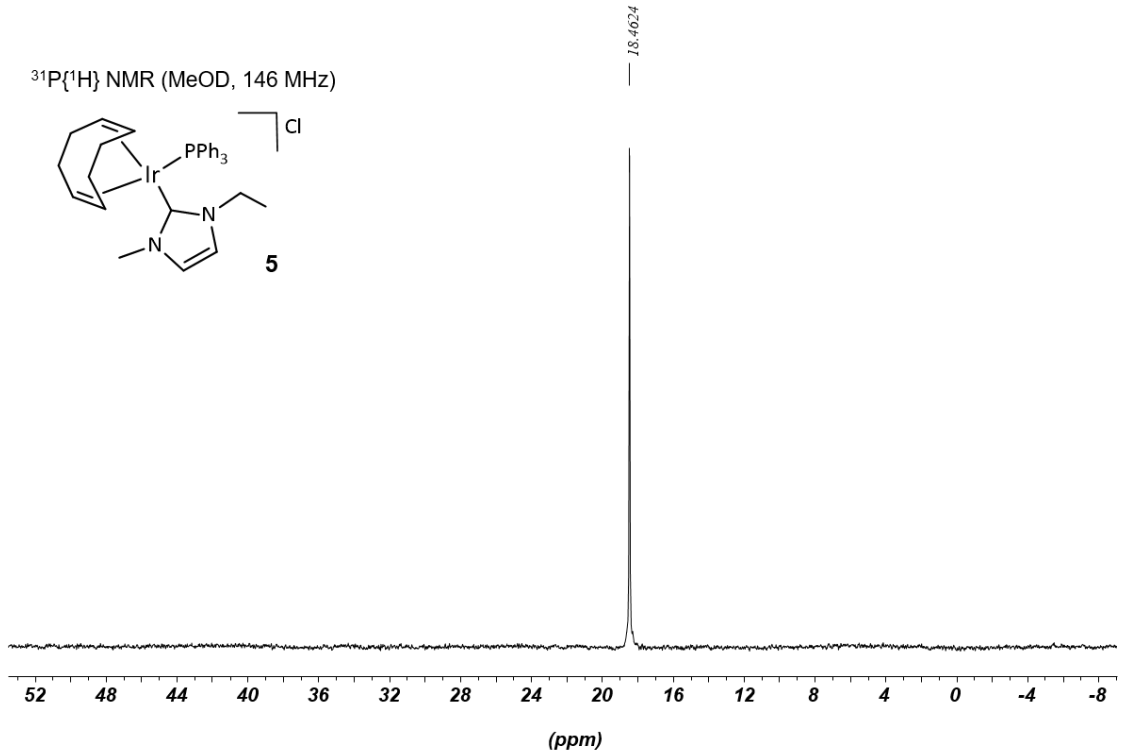


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of [Ir(cod)(emim)(PPh_3)]Cl (**5**).

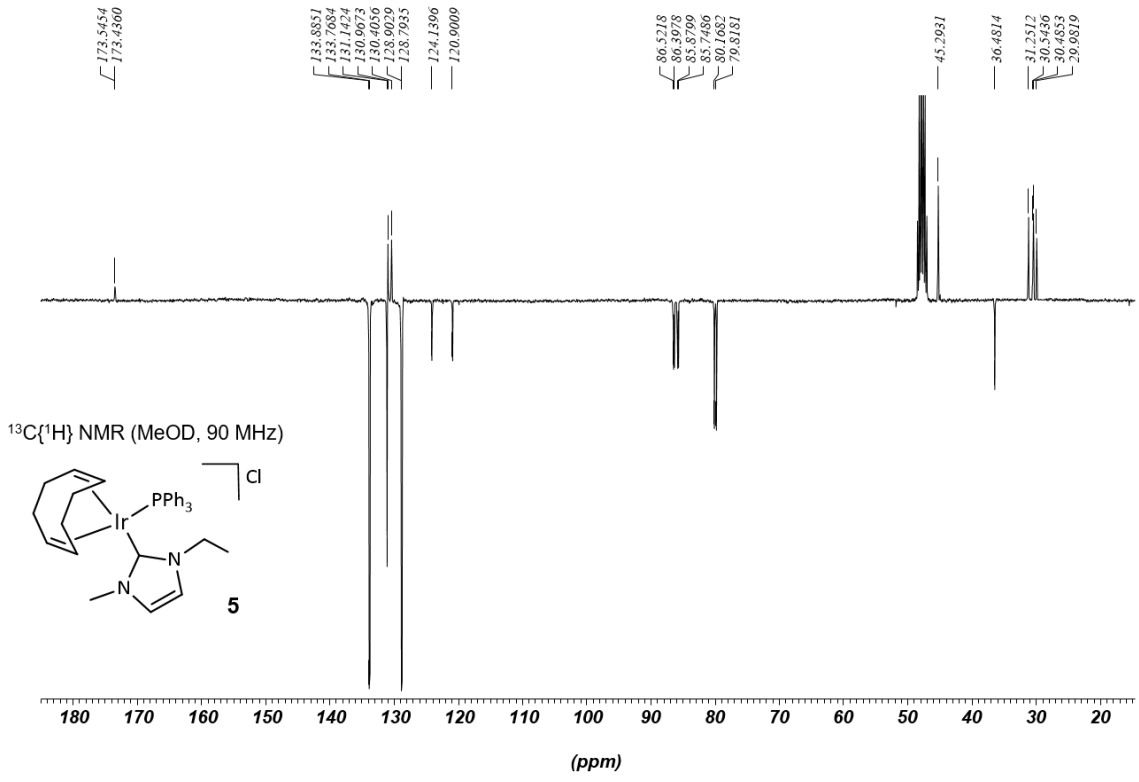


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of [Ir(cod)(emim)(PPh_3)]Cl (**5**).

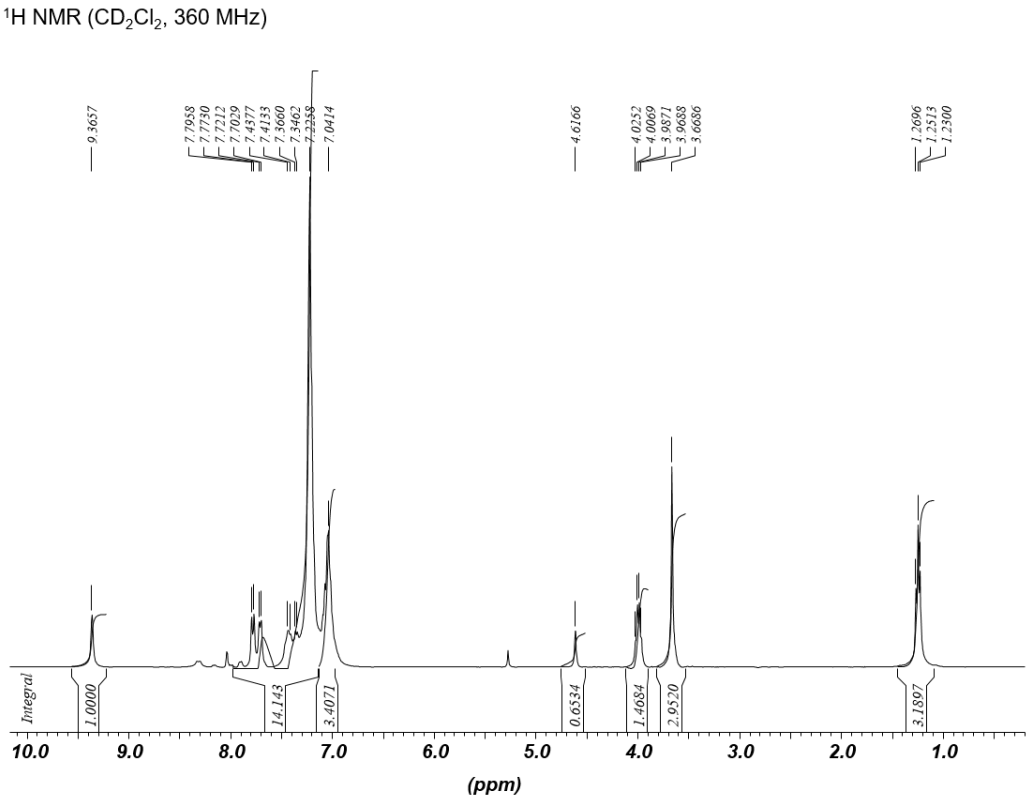


Figure S13. ^{1}H NMR spectrum of [emimH][*m*tppms].

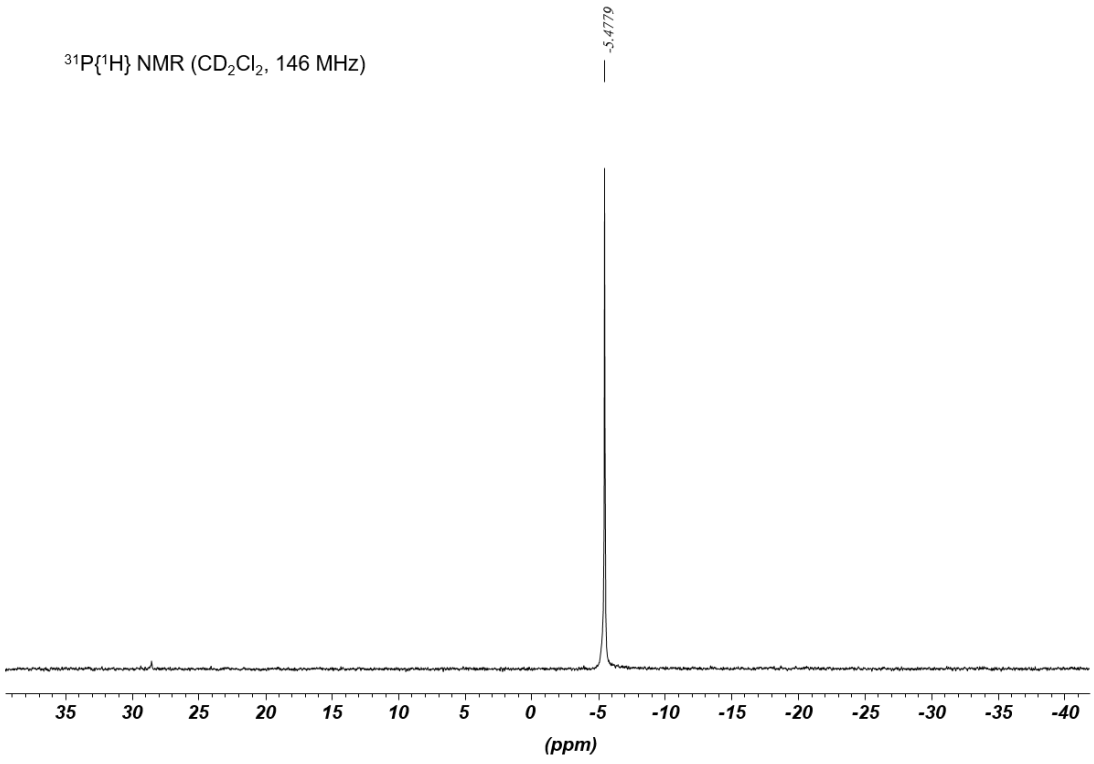


Figure S14. ^{31}P{^{1}H} NMR spectrum of [emimH][*m*tppms].

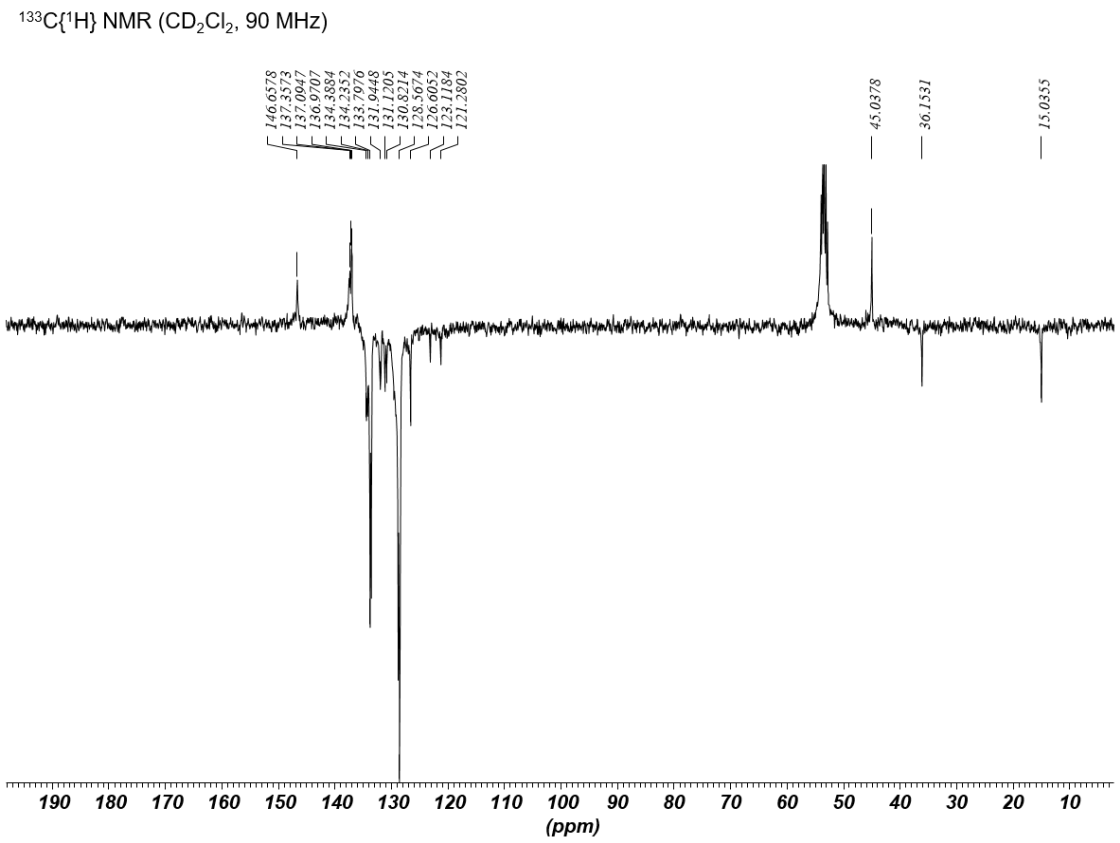


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of [emimH][*m*tppms].

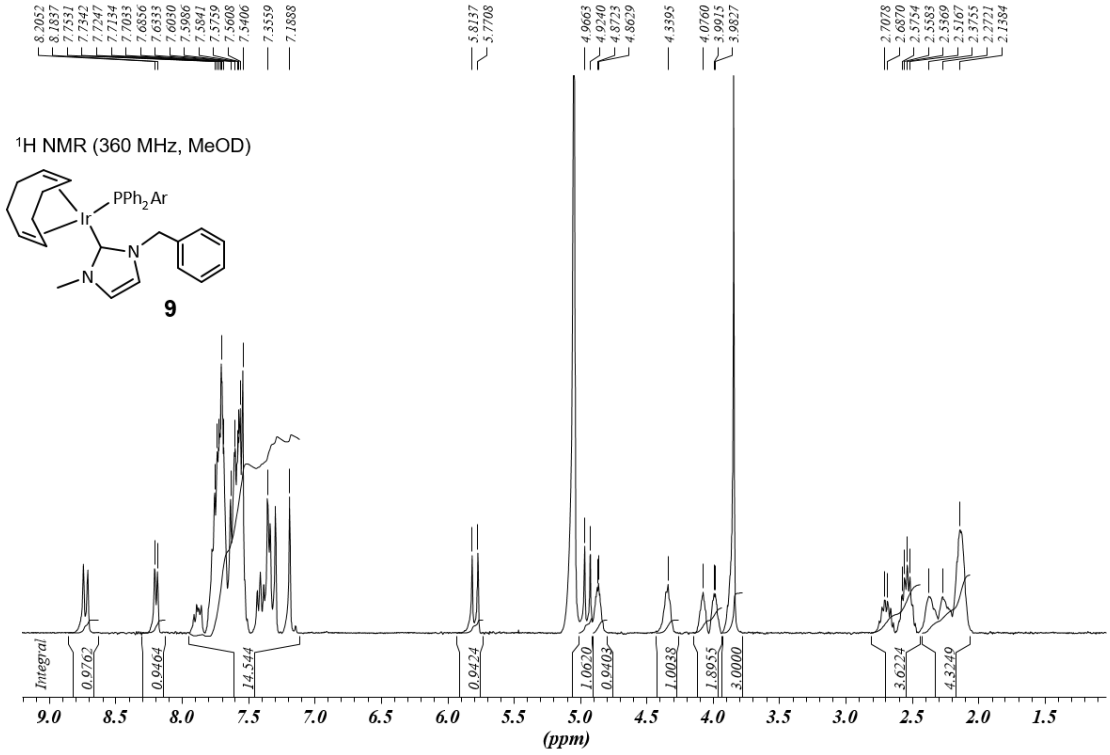


Figure S16. ^{1}H NMR spectrum of [Ir(cod)(Bnmim)(*m*tppms)] (**9**; Ar=C_6H_4-*m*-SO_3^-).

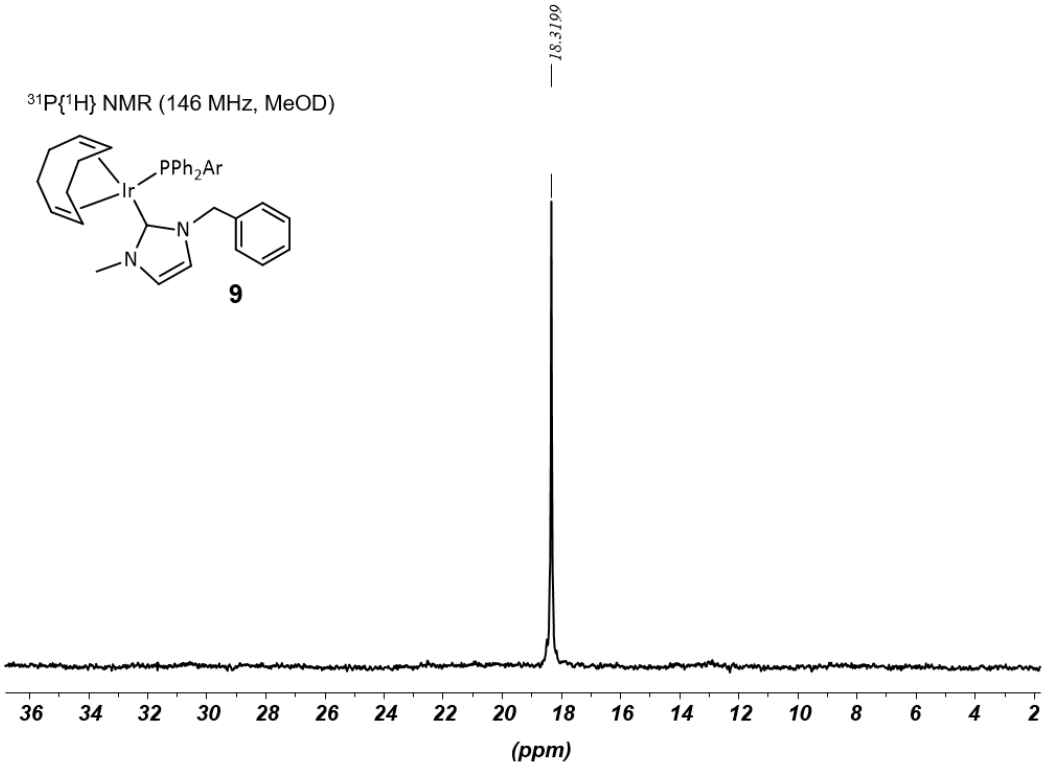


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of [Ir(cod)(Bnmim)(*m*tppms)] (**9**; Ar=C_6H_4-*m*-SO_3^-).

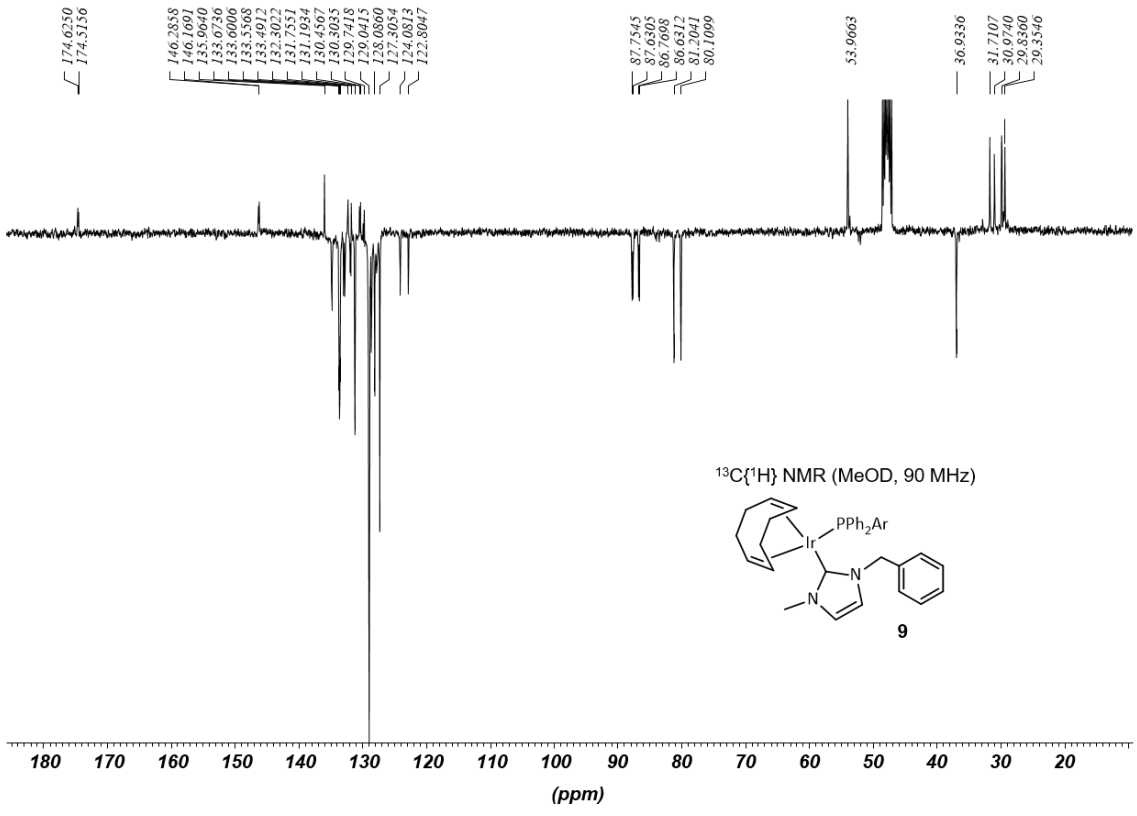


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of [Ir(cod)(Bnmim)(*m*tppms)] (**9**; Ar=C_6H_4-*m*-SO_3^-).

Experimental details for solid state structure determinations of 1, 3, and 6 by single crystal X-ray diffraction

Suitable crystals were mounted on Mitegen loops and fixed with high density paraffin oil. X-ray diffraction data were collected using a Bruker-D8 Venture diffractometer equipped with INCOATEC IμS 3.0 dual (Cu and Mo) sealed tube microsources and Photon II Charge-integrating Pixel Array detector. Mo Kα (λ = 0.7107 Å) radiation was used for all compounds. Diffraction data collection and integration of the frames were performed by APEX3 packages [S1]. Using the Olex² [S2] and WinGX suites [S3], the structures were solved with the SIR-2014 [S4] or the SHELXT [S5] structure solution programs and refined by full-matrix least-squares method of F^2. Non-hydrogen atoms were refined with anisotropic thermal parameters using the SHELXL package [S6] and hydrogen atoms were placed into their geometric positions. [Ir(cod)(emim)(*m*tppms)], **6** contains two disordered $CHCl_3$ molecules. The publication materials (figures) were prepared by the WINGX [S3], PublCIF4 [S7] and the Mercury [S8] programs.

The *crystallographic data* (excluding the structure factors) for the **1**,**3**,**6** structures were *deposited* at the *Cambridge Crystallographic Data Centre*, CCDC-1967347, CCDC-1967348, CCDC-1967349

Table S2. Summary of crystallographic data.

	[IrCl(cod)(emim)], **1**	[IrCl(cod)(Bnmim)], **3**	[Ir(cod)(emim)(*m*tppms)], **6**
Chemical formula	$C_{14}H_{22}ClIrN_2$	$C_{38}H_{48}Cl_2Ir_2N_4$	$C_{17.50}H_{18}C_{l4.25}Ir_{0.50}NO_2P_{0.50}\ S_{0.50}$
FW (g mol^{-1})	445.98	1016.1	552.61
T (K)	295(2)	273(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	0.073×0.109×0.141	0.4×0.073×0.064	0.113×0.119×0.138
Crystal habit, colour	prism, yellow	needle, yellow	block, orange
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	P-1
a (Å)	7.2744(3)	17.9759(11)	10.2957(11)
b (Å)	17.9521(7)	11.1446(6)	10.7135(12)
c (Å)	11.6308(5)	19.6327(10)	20.585(2)
α (°)	90	90	78.888(6)
β (°)	103.313(2)	111.922(2)	83.008(5)
γ (°)	90	90	88.625(6)
V ($Å^3$)	1478.06(11)	3648.7(4)	2207.4(5)
Z	4	4	4
ρ_{calc} (g/cm^3)	2.004	1.850	1.663
μ (mm^{-1})	9.199	7.466	3.660
Θ range	2.90-25.69	2.20-25.40	2.34-26.11
Index range	$-8 \le h \le 8$	$-21 \le h \le 20$	$-12 \le h \le 12$
	$-22 \le k \le 22$	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-14 \le l \le 14$	$-23 \le l \le 23$	$-25 \le l \le 25$
Reflns collected	16544	38714	142890
Independent reflns	2884 [R_{int}=0.0578]	6688 [R_{int}=0.1925]	7229 [R_{int}=0.1151]
Data / restraints / parameters	2884/0/174	6688/0/418	7229/0/526

Goodness-of fit on $\mathbf{F}^2$	1.064	1.028	1.268
R_1 [I>2σ(I)]	0.0283	0.0542	0.0878
wR_2 [all data]	0.0471	0.1330	0.2203
CSD	1967347	1967348	1967349

Reference:

[S1] APEX3 v2017.3-0, Bruker AXS Inc., 2017.

[S2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann *J. Appl. Cryst.* **1999**, *42*, 339-341.

[S3] L. J. Farrugia: WinGX suite for small-molecule single-crystal crystallography, *J. Appl. Crystallogr.* **1999**, *32*, 837-838.

[S4] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna, *J. Appl. Cryst.* **2007**, *40*, 609-613.

[S5] G. M. Sheldrick: SHELXT - Integrated space-group and crystal-structure determination *Acta Cryst.* **2015**, *A71*, 3-8.

[S6] G. M. Sheldrick: A short history of SHELX, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112-122.

[S7] S. P. Westrip: PublCIF: Software for editing, validating and formatting crystallographic information files, *J. Appl. Crystallogr.* **2010**, *43*, 920-925.

[S8] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.* **2008**, *41*, 466-470.