Supporting Information

for

Chiral CNN Pincer Ir(III)-H complexes. Transient Ligand and Counterion Influences in the Asymmetric Hydrogenation of Imines and Quinolines

by

Yisong Wen,[a,b] Albert Cabré,[a] Jordi Benet-Buchholz,[c] Antoni Riera,[a,b] Xavier Verdaguer*[a,b]*

[a] Institute for Research in Biomedicine (IRB Barcelona), The Barcelona Institute of Science and Technology, Baldiri Reixac 10, Barcelona E-08028, Spain.
[b] Departament de Química Inorgànica i Orgànica, Secció de Química Orgànica. Universitat de Barcelona, Martí i Franquès 1, Barcelona E-08028, Spain.
[c] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain.

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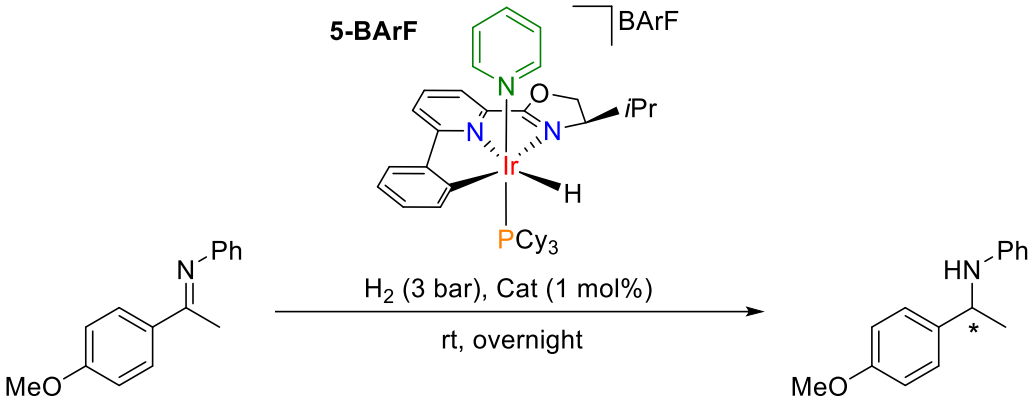
Solvent comparison.

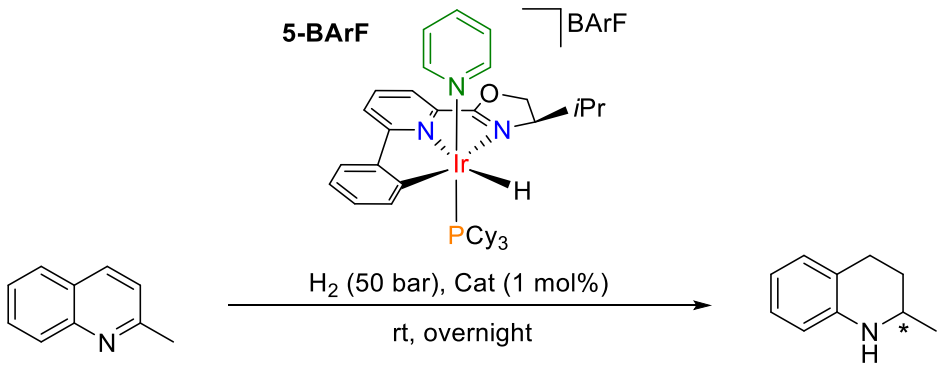
Dichloromethane, tetrahydrofuran and toluene were compared in the asymmetric hydrogenation of 1-(4-methoxyphenyl)-*N*-phenylethan-1-imine catalyzed by **5-BArF**, at 1 mol% of catalyst loading, under 3 bar of hydrogen pressure at room temperature.



Solvent	Conversion (%)	ee (%)*
Dichloromethane	60	48
Tetrahydrofuran	6	N.D.
Toluene	54	20

*N.D.: not determined.

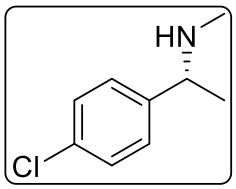
These solvents were also compared in the asymmetric hydrogenation of 2-methylquinoline, at 1 mol% of catalyst loading, under 50 bar of hydrogen pressure at room temperature.



Solvent	Conversion (%)	ee (%)*
Dichloromethane	43	N.D.
Tetrahydrofuran	< 5	N.D.
Toluene	25	N.D.

Hydrogenated substrates.

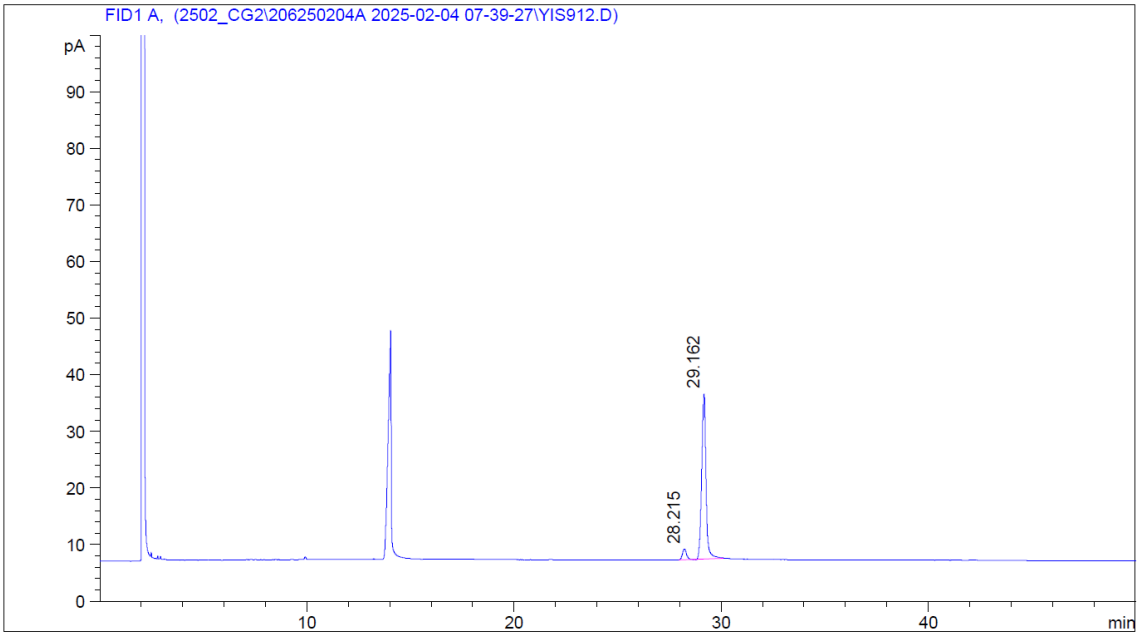
(*R*)-1-(4-chlorophenyl)-*N*-methylethan-1-amine.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.20 (m, 4H), 3.63 (q, *J* = 6.6 Hz, 1H), 2.29 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 3H) ppm.

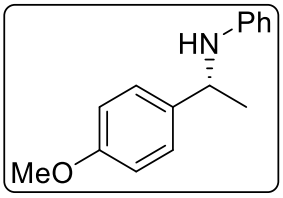
The product amine was derivatized via trifluoroacetylation prior to chiral GC analysis: the corresponding amine was placed in a 4 mL septum vial, together with 1 mL of CH_2Cl_2. 4 equiv. of triethylamine was added, followed by 2 equiv. of trifluoroacetic anhydride. The mixture was stirred at room temperature for 1 hour, and 1 mL of MeOH was added and stirred for 5 min before removing the solvent under reduced pressure. The crude was purified with a short silica column (Hexanes – EtOAc 90:10).

Chiral GC (derivatized as trifluoroacetamide): GAMMA-DEX (30 m), T_{col} = 140 ºC, T_{det} = 300 ºC, T_{inj} = 220 ºC, Split 50:1, 1 mL/ min, Carrier: He.



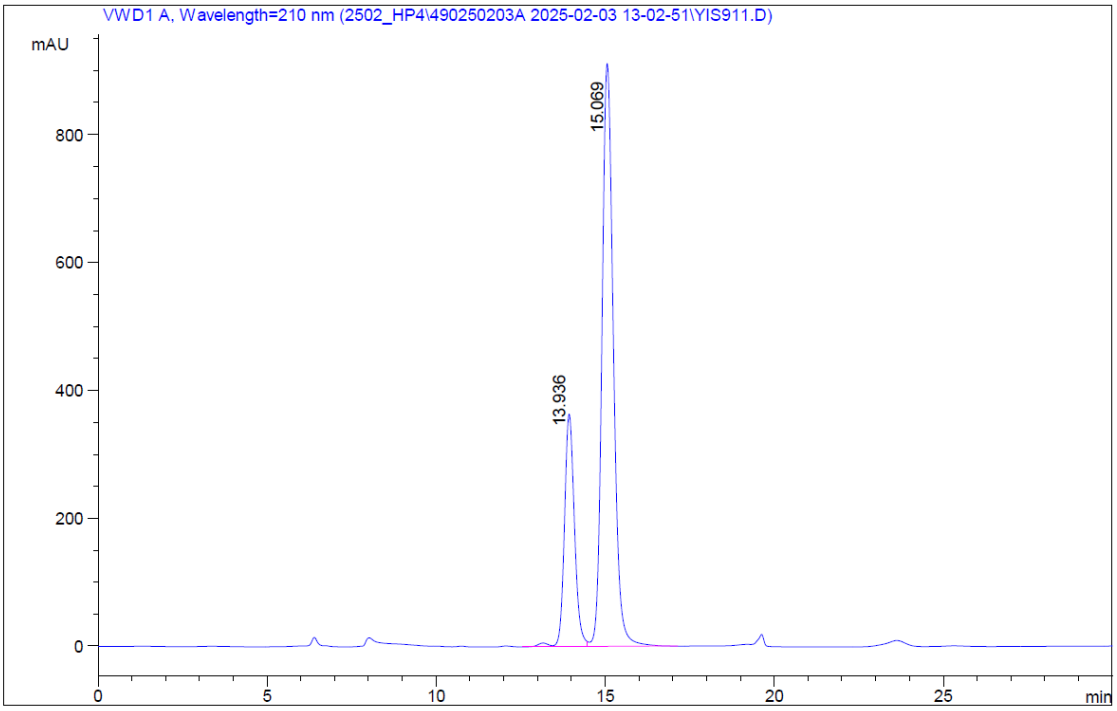
#	Meas. R	Pea	Width	Area	Height	Area %
1	28.215	MM	0.224	25.704	1.915	5.714
2	29.162	MM	0.241	424.162	29.292	94.286

(*R*)-*N*-(1-(4-methoxyphenyl)ethyl)aniline.



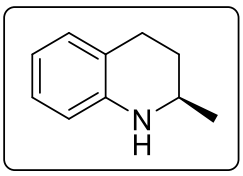
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 2H), 7.12 – 7.06 (m, 2H), 6.88 – 6.83 (m, 2H), 6.67 – 6.61 (m, 1H), 6.53 – 6.48 (m, 2H), 4.45 (q, *J* = 6.7 Hz, 1H), 3.78 (s, 3H), 1.49 (d, *J* = 6.7 Hz, 3H) ppm.

Chiral HPLC: CHIRALPAK IA, Heptane/EtOH 98:2, 0.5 mL/min, λ = 210 nm.



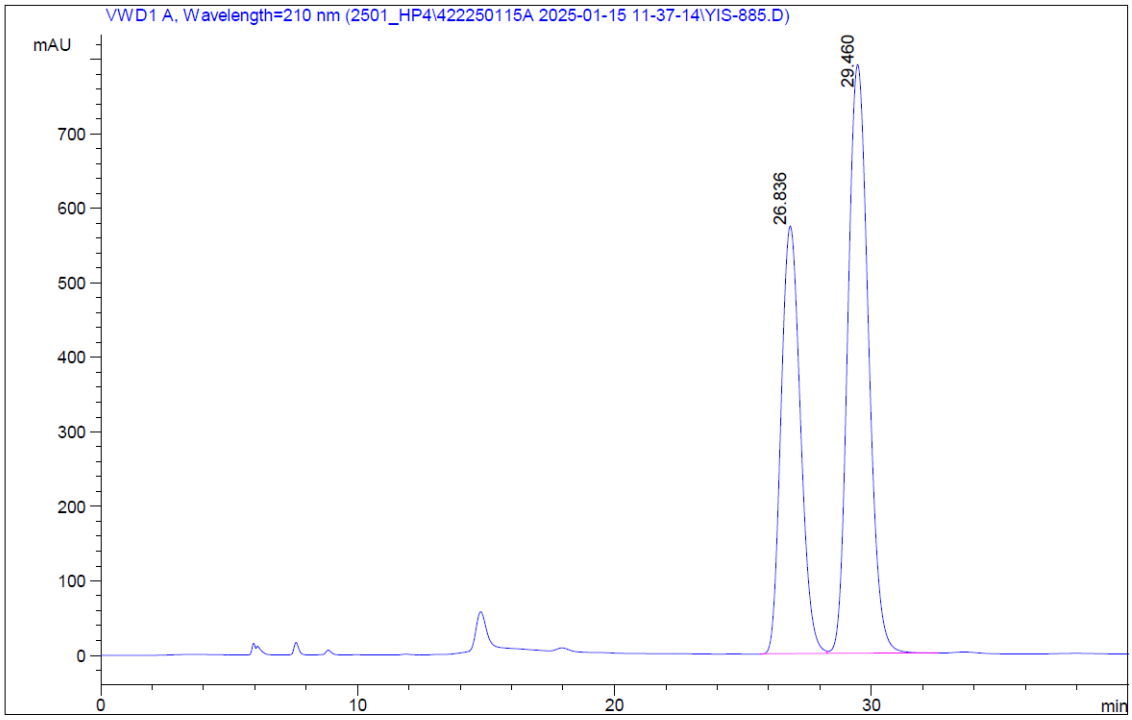
#	Meas. R	Pea	Width	Area	Height	Area %
1	13.936	BV	0.401	7540.383	337.131	26.047
2	15.069	VB	0.407	21408.775	794.705	73.953

(*R*)-2-methyl-1,2,3,4-tetrahydroquinoline



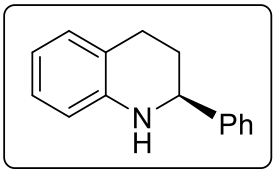
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 – 6.92 (m, 2H), 6.60 (td, *J* = 7.4, 1.2 Hz, 1H), 6.47 (dd, *J* = 8.3, 1.2 Hz, 1H), 3.40 (dqd, *J* = 10.0, 6.3, 2.8 Hz, 1H), 3.68 (broad s, 1H), 2.84 (dddt, *J* = 17.3, 11.5, 5.6, 1.1 Hz, 1H), 2.72 (ddd, *J* = 16.4, 5.4, 3.5 Hz, 1H), 1.93 (dddd, *J* = 12.9, 5.7, 3.5, 2.9 Hz, 1H), 1.59 (dddd, *J* = 12.9, 11.5, 9.9, 5.4 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H) ppm.

Chiral HPLC: CHIRALCEL OJ, Heptane/*i*PrOH 95:5, 0.5 mL/min, λ = 210 nm.



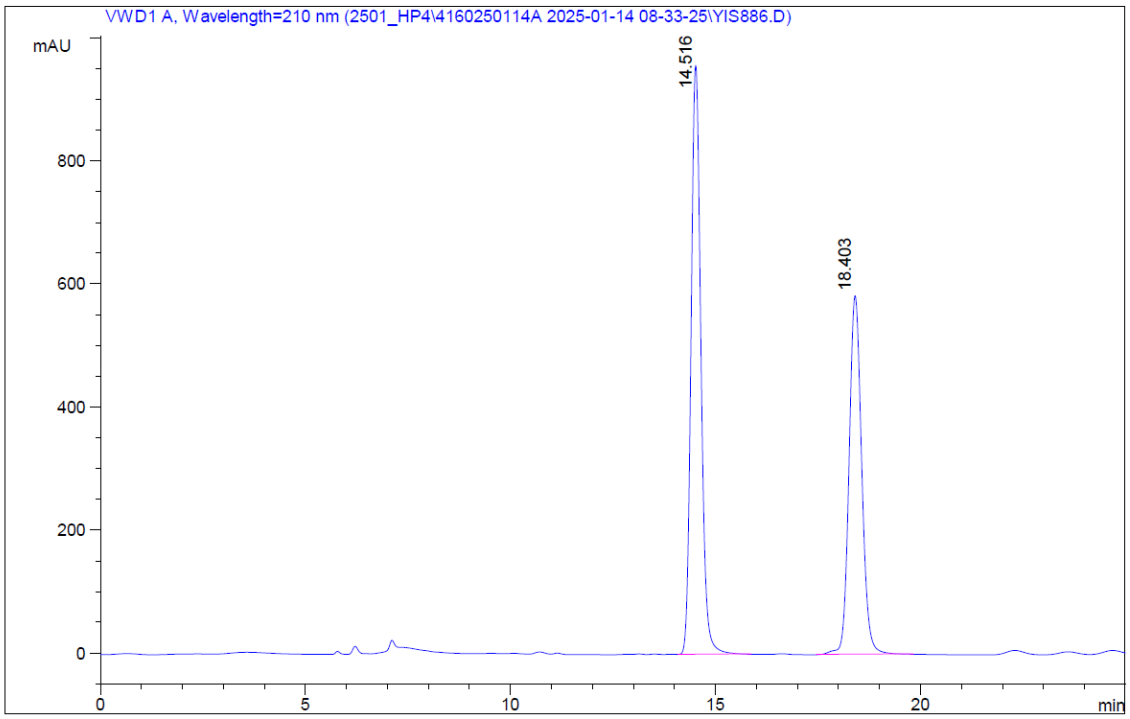
#	Meas. R	Pea	Width	Area	Height	Area %
1	26.836	BV	0.849	30062.744	569.671	40.617
2	29.460	VB	0.886	43952.219	785.475	59.383

(*S*)-2-phenyl-1,2,3,4-tetrahydroquinoline



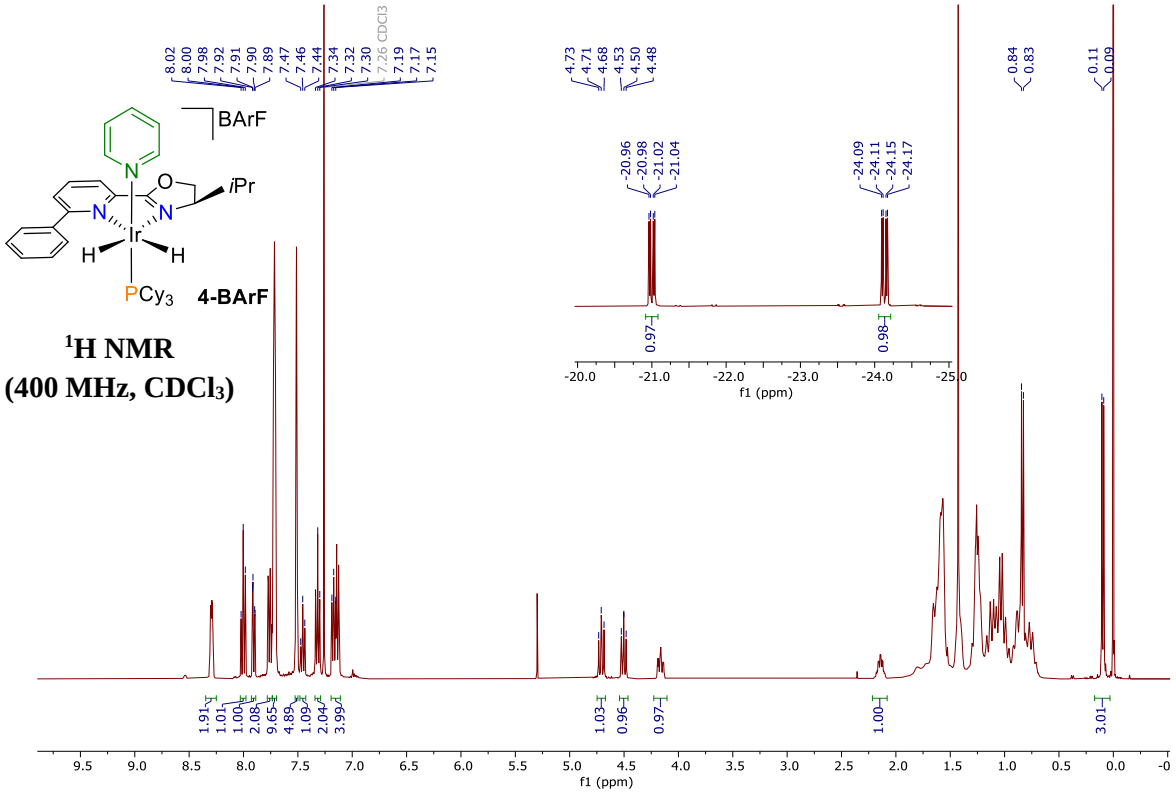
^{1}H NMR (400 MHz, CD_3OD): δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.27 – 7.20 (m, 1H), 6.95 – 6.86 (m, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.53 (t, *J* = 7.4 Hz, 1H), 4.41 (dd, *J* = 8.7, 3.4 Hz, 1H), 2.85 (ddd, *J* = 15.6, 9.8, 5.4 Hz, 1H), 2.64 (dt, *J* = 16.2, 5.3 Hz, 1H), 2.13 – 2.03 (m, 1H), 2.00 – 1.88 (m, 1H)

Chiral HPLC: CHIRALCEL ODH, Heptane/*i*PrOH 80:20, 0.5 mL/min, λ = 210 nm.

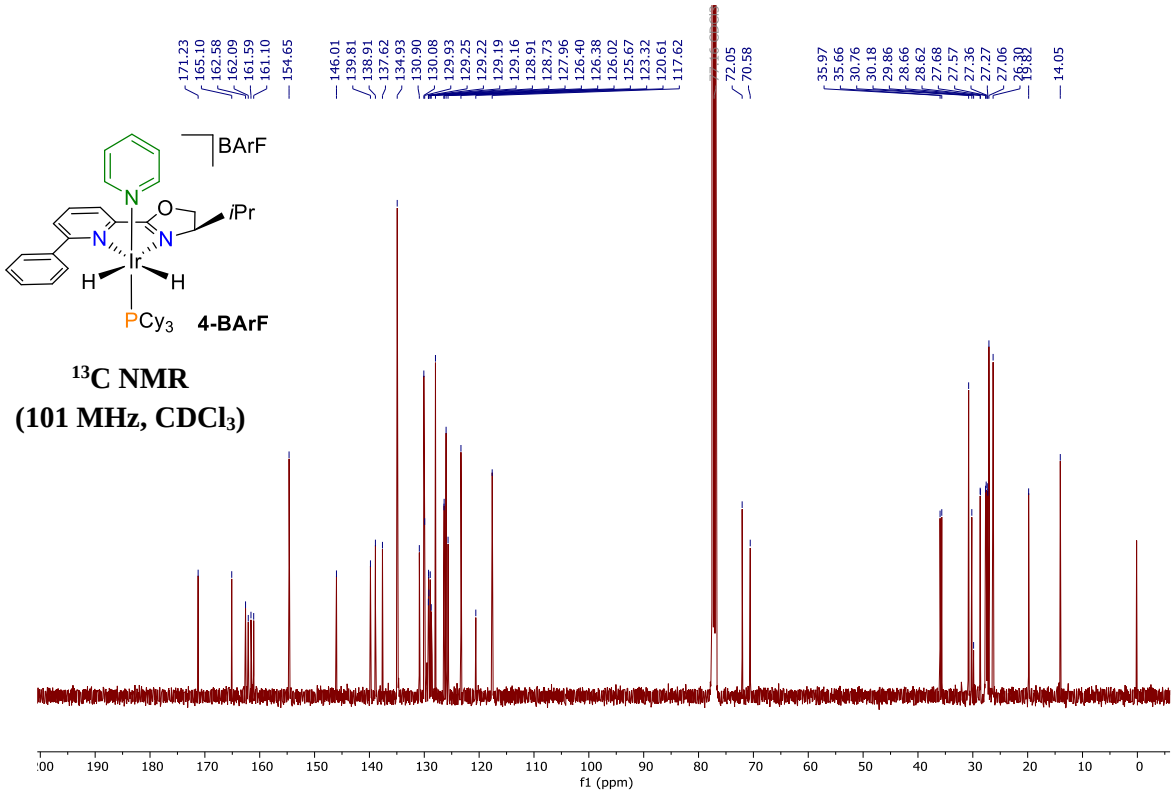


#	Meas. R	Pea	Width	Area	Height	Area %
1	14.516	BB	0.257	15977.420	957.274	56.044
2	18.403	BB	0.331	12531.508	583.184	43.956

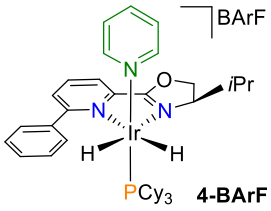
NMR spectra



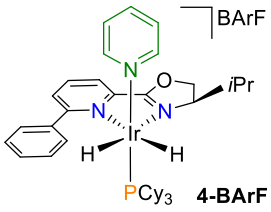
^{1}H NMR
(400 MHz, $CDCl_3$)



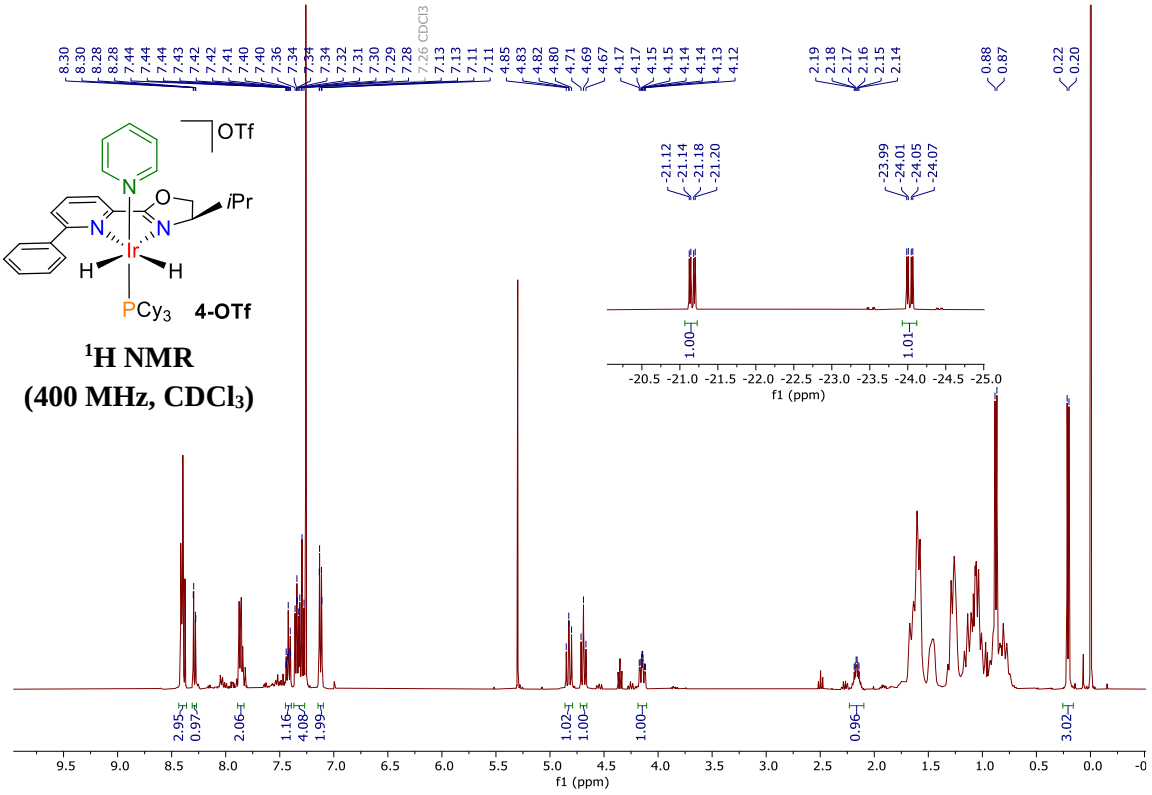
^{13}C NMR
(101 MHz, $CDCl_3$)



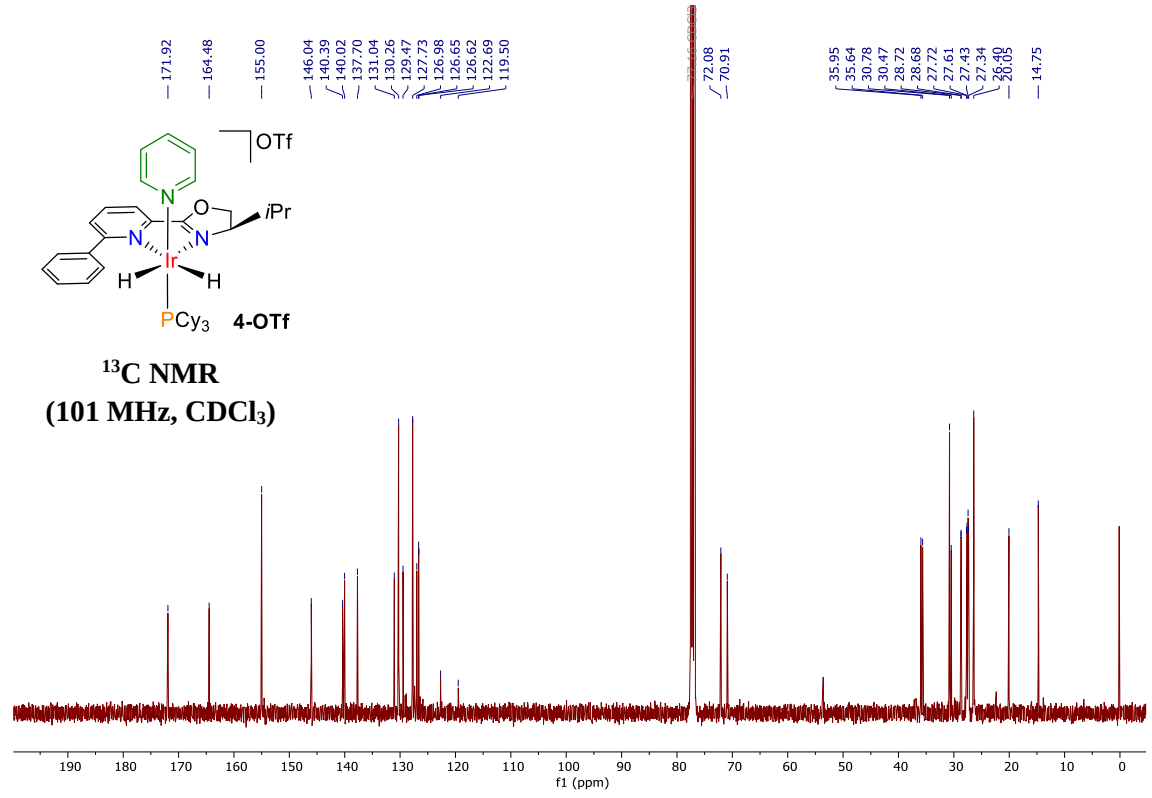
^{31}P NMR
(162 MHz, $CDCl_3$)



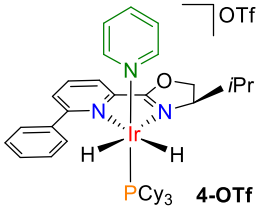
^{19}F NMR
(376 MHz, $CDCl_3$)



^{1}H NMR
(400 MHz, $CDCl_3$)

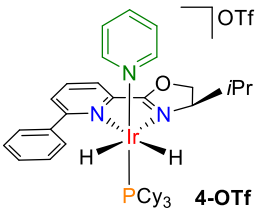


^{13}C NMR
(101 MHz, $CDCl_3$)



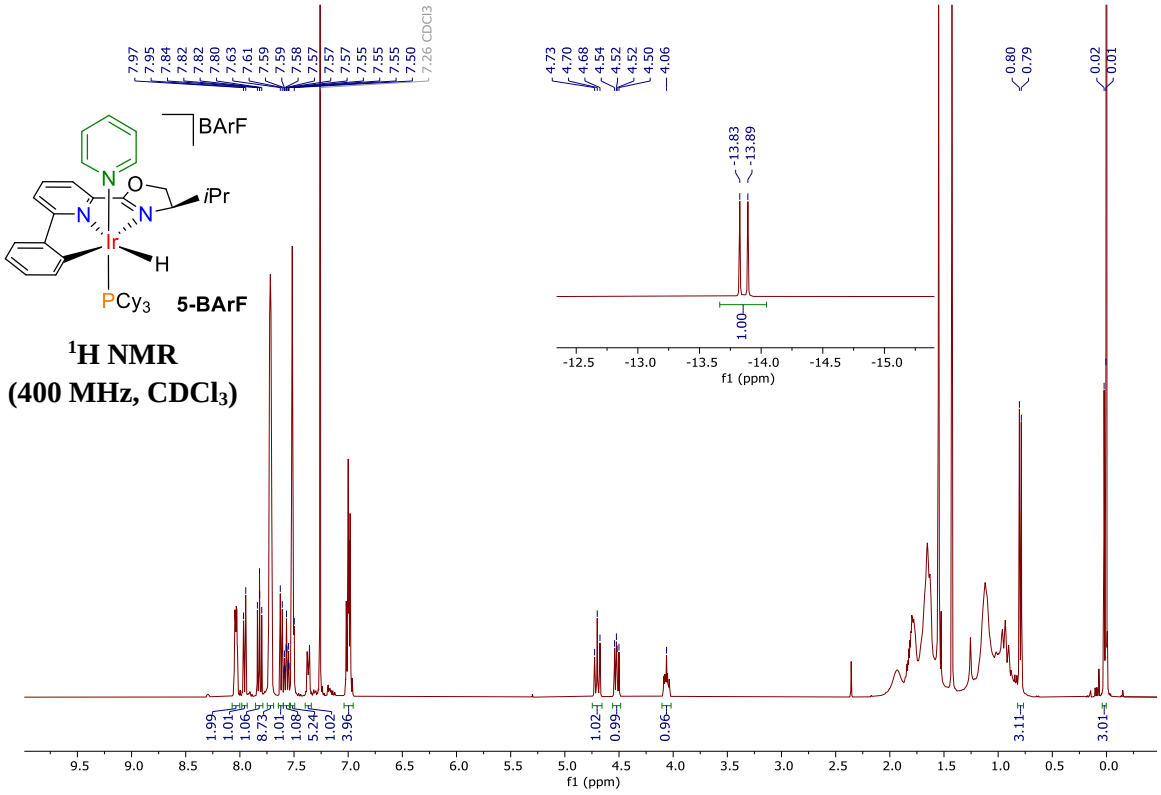
4-OTf

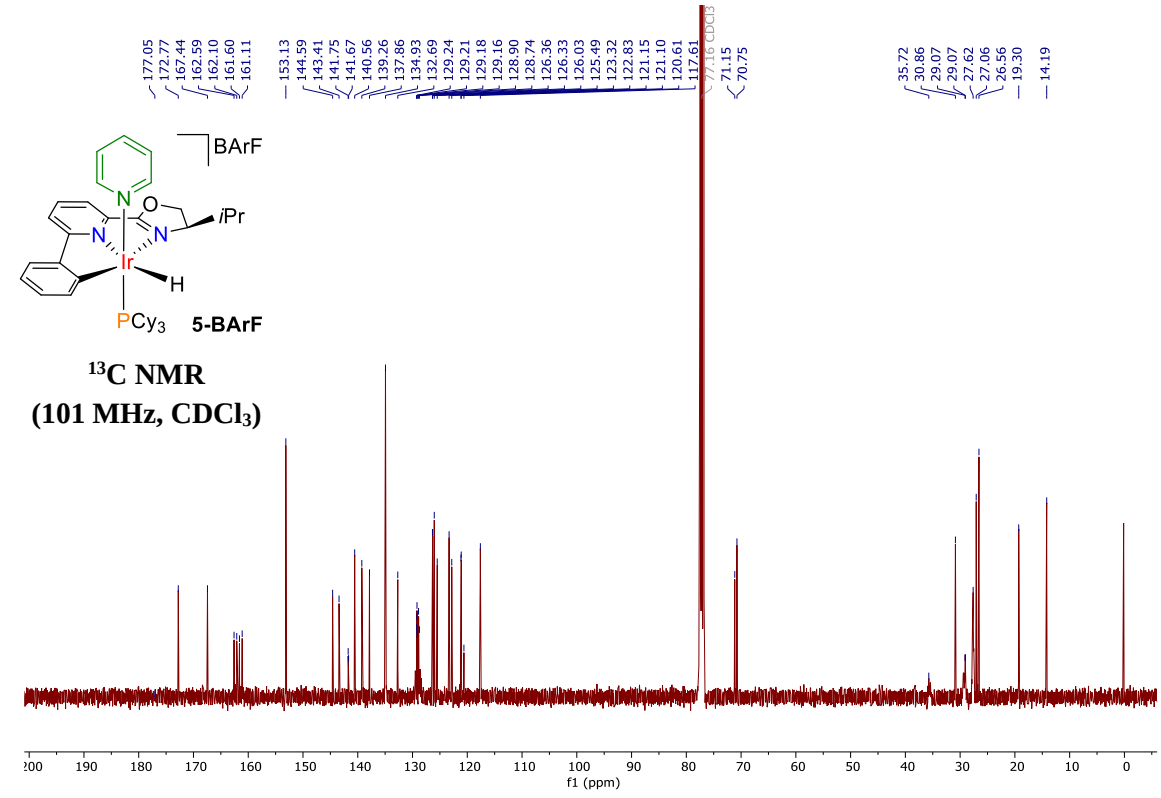
^{31}P NMR
(162 MHz, $CDCl_3$)

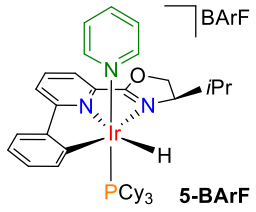


4-OTf

^{19}F NMR
(376 MHz, $CDCl_3$)

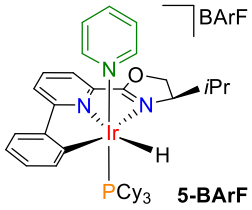

BArF
iPr
PCy3
5-BArF
1H NMR
(400 MHz, CDCl3)
f1 (ppm)


BArF
iPr
PCy3
5-BArF
13C NMR
(101 MHz, CDCl3)
f1 (ppm)



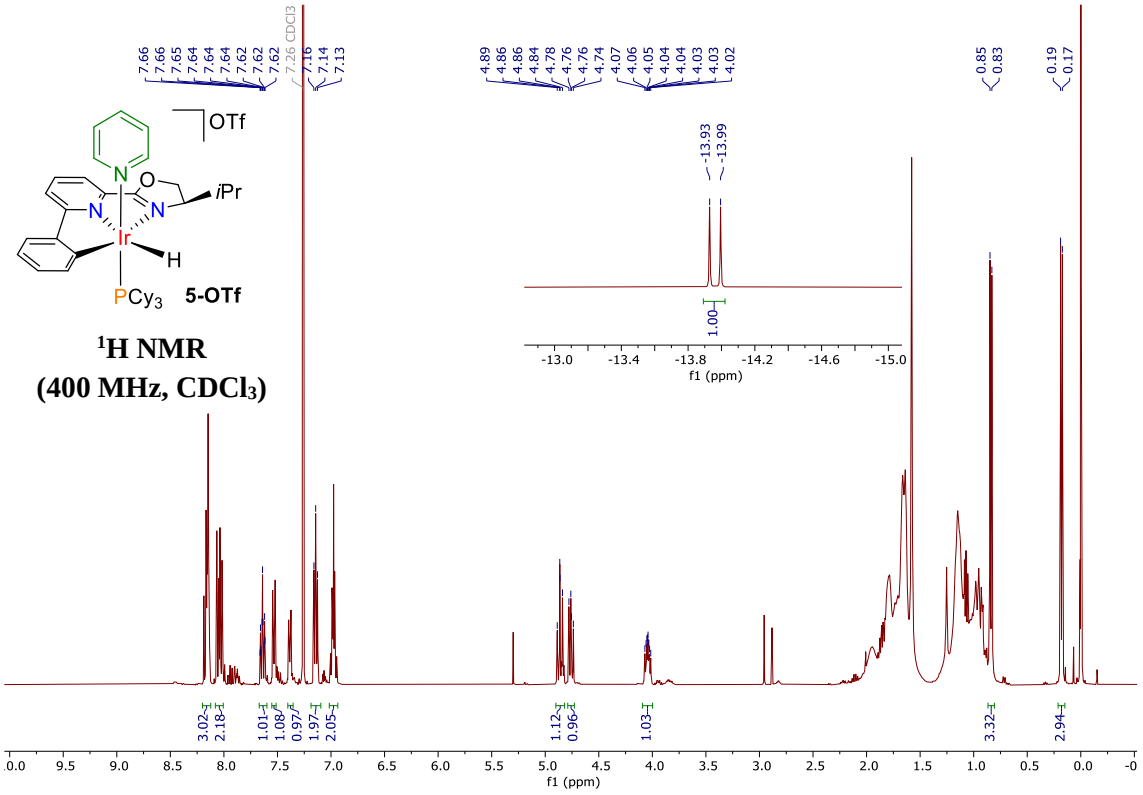
5-BArF

^{31}P NMR
(162 MHz, $CDCl_3$)

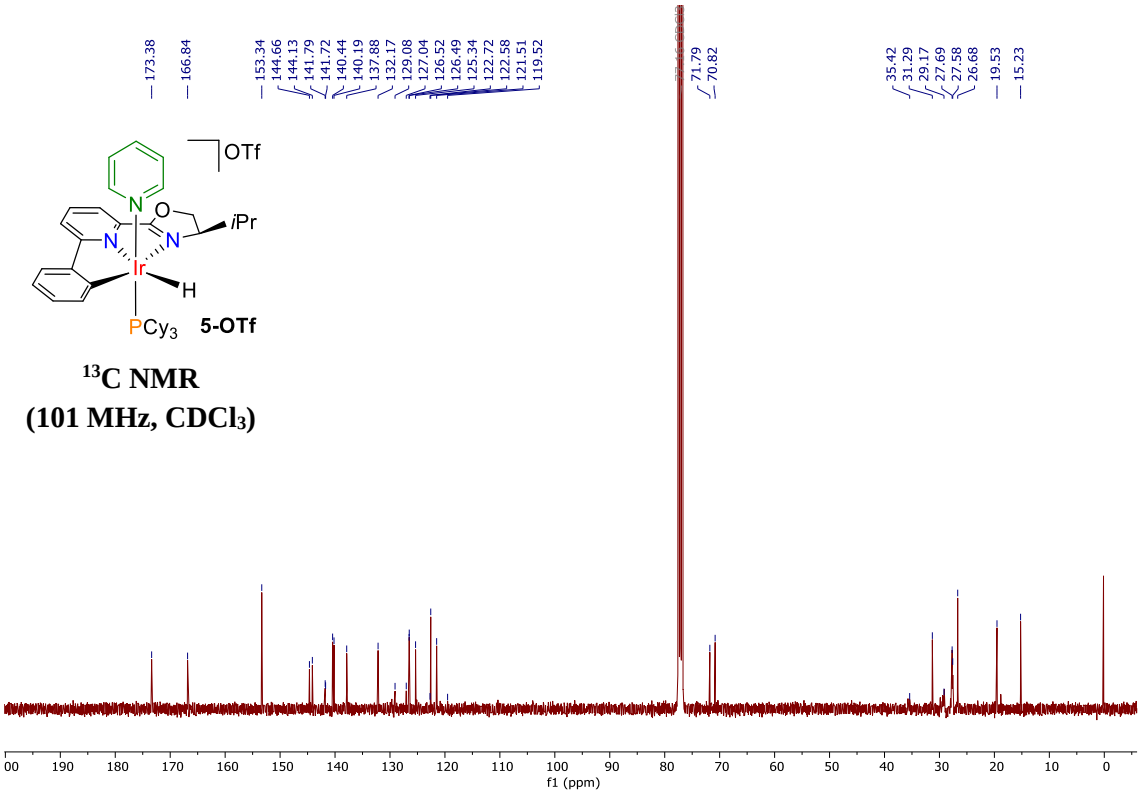


5-BArF

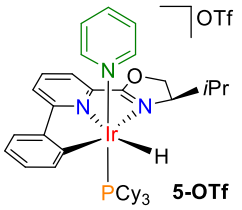
^{19}F NMR
(376 MHz, $CDCl_3$)



^{1}H NMR
(400 MHz, $CDCl_3$)

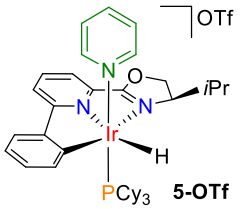


^{13}C NMR
(101 MHz, $CDCl_3$)



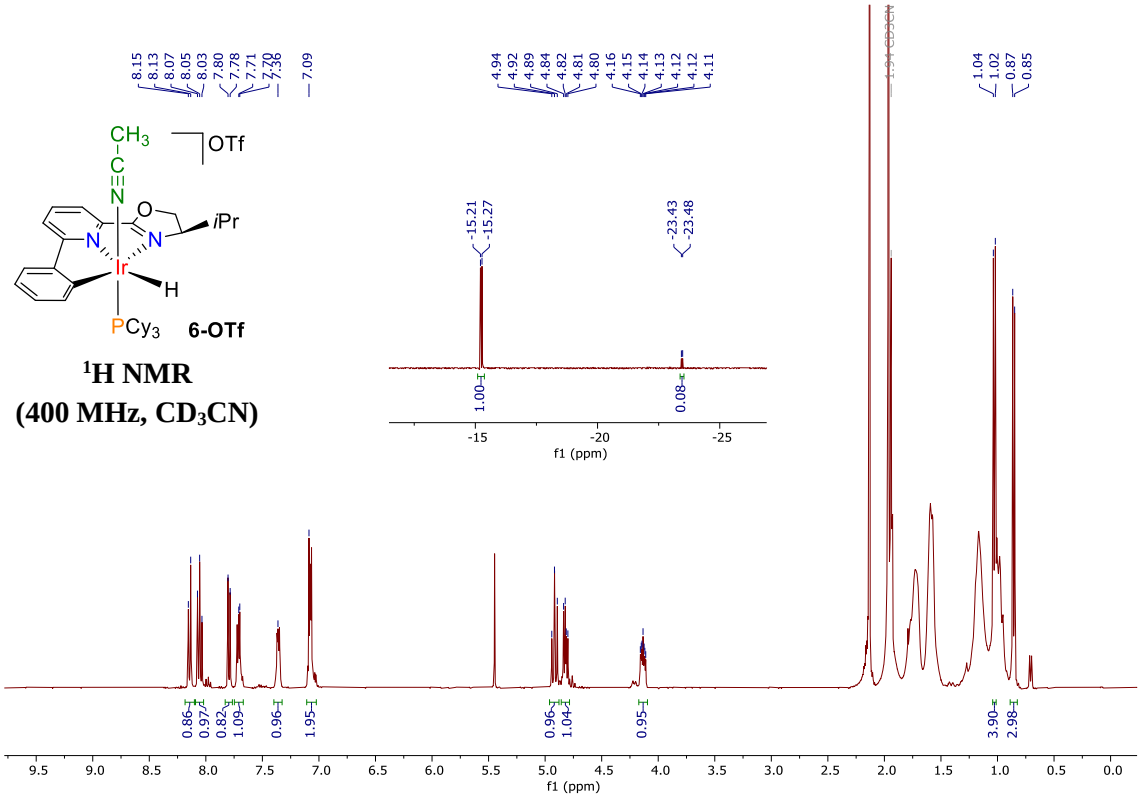
5-OTf

^{31}P NMR
(162 MHz, $CDCl_3$)

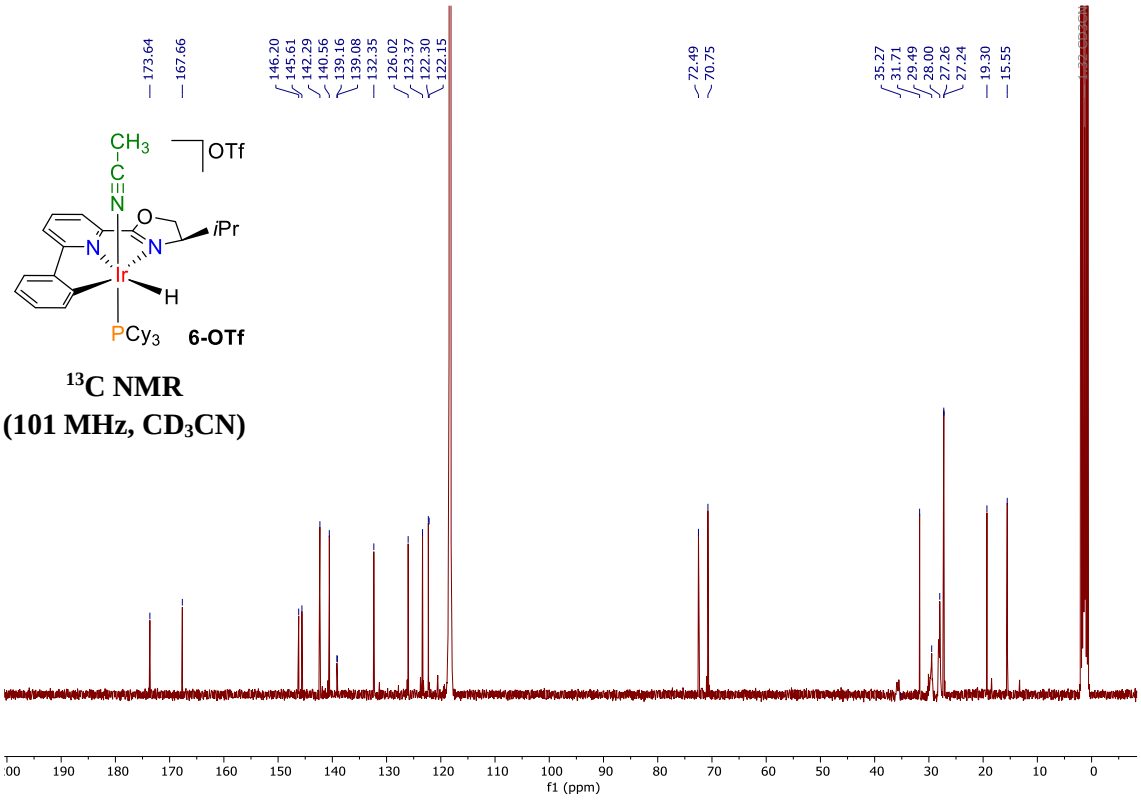


5-OTf

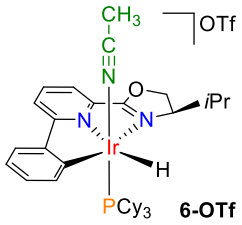
^{19}F NMR
(376 MHz, $CDCl_3$)



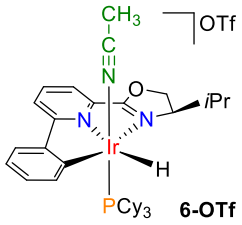
^{1}H NMR
(400 MHz, CD_3CN)



^{13}C NMR
(101 MHz, CD_3CN)

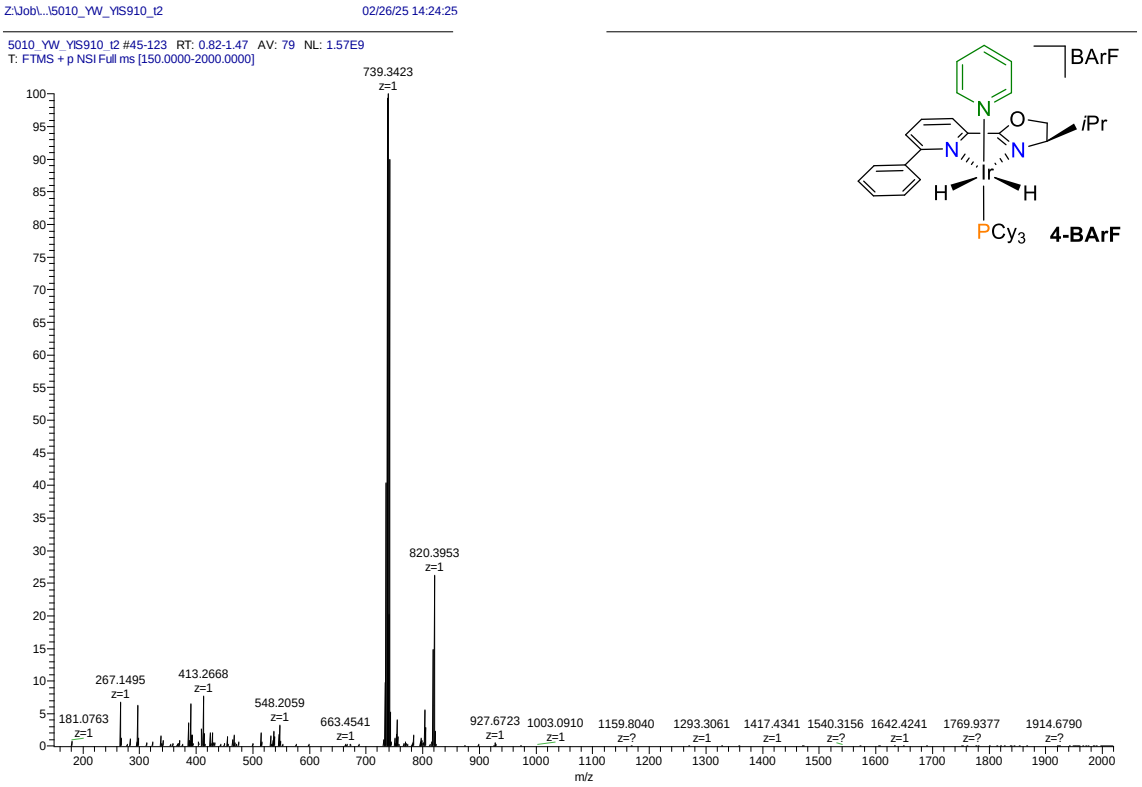


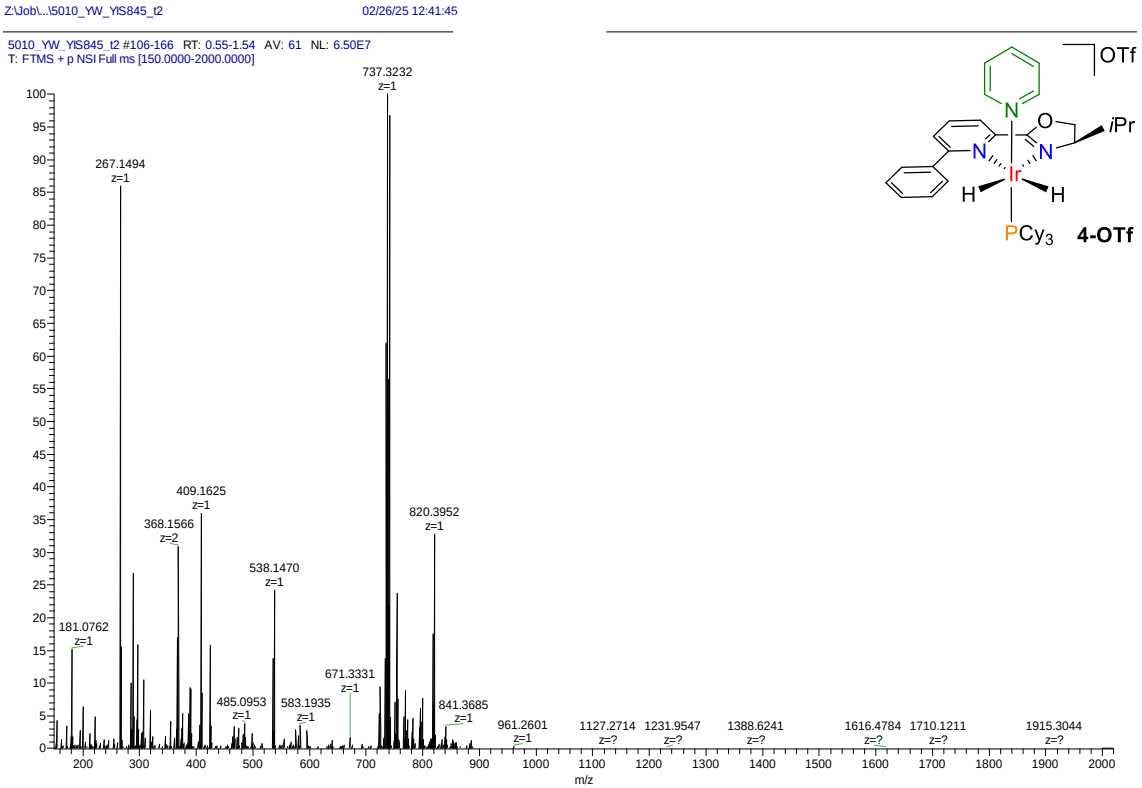
^{31}P NMR
(162 MHz, CD_3CN)



^{19}F NMR
(376 MHz, CD_3CN)

HRMS spectra





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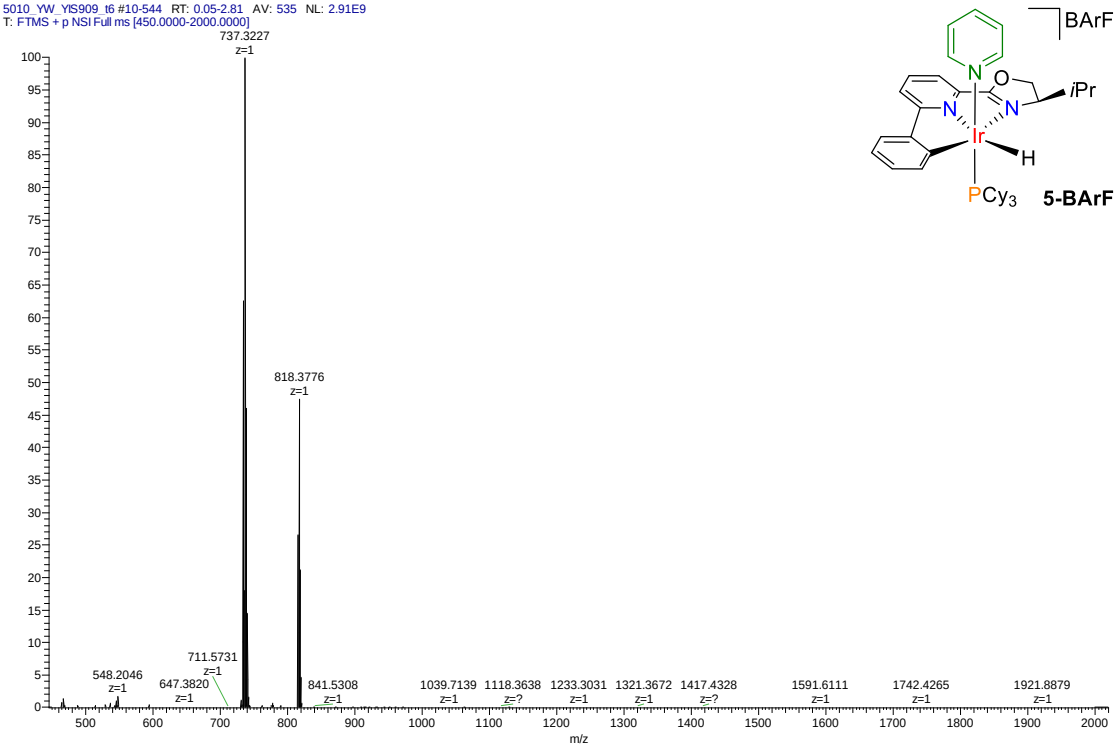

5-BArF

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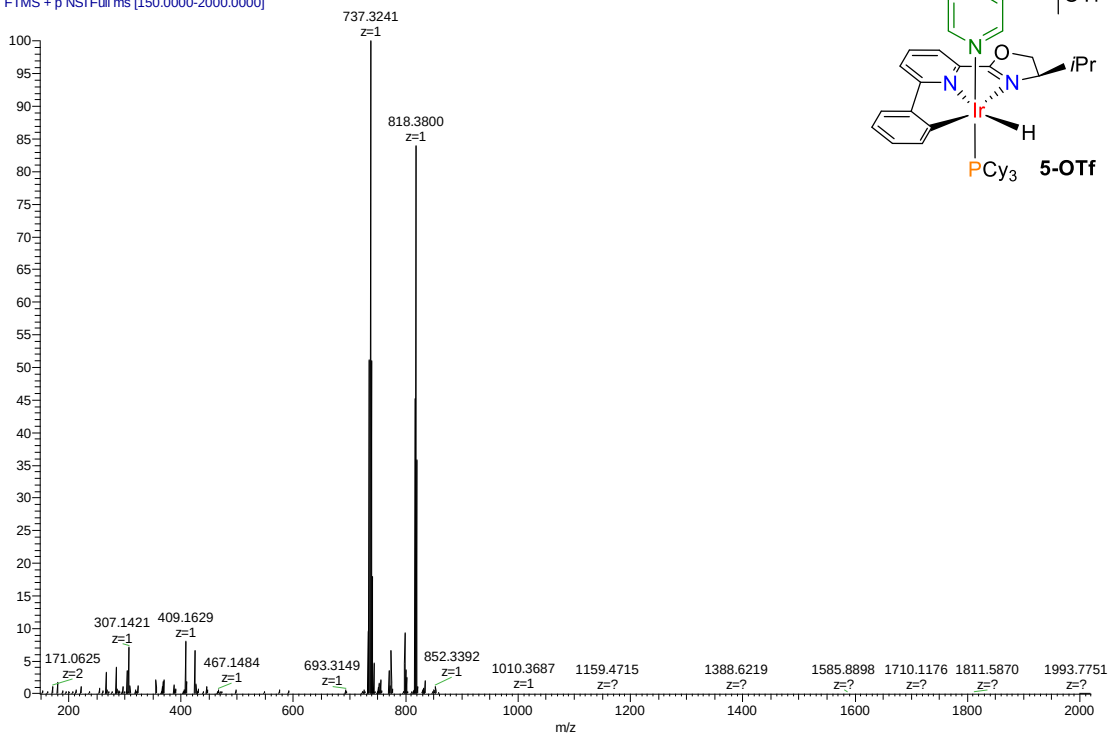
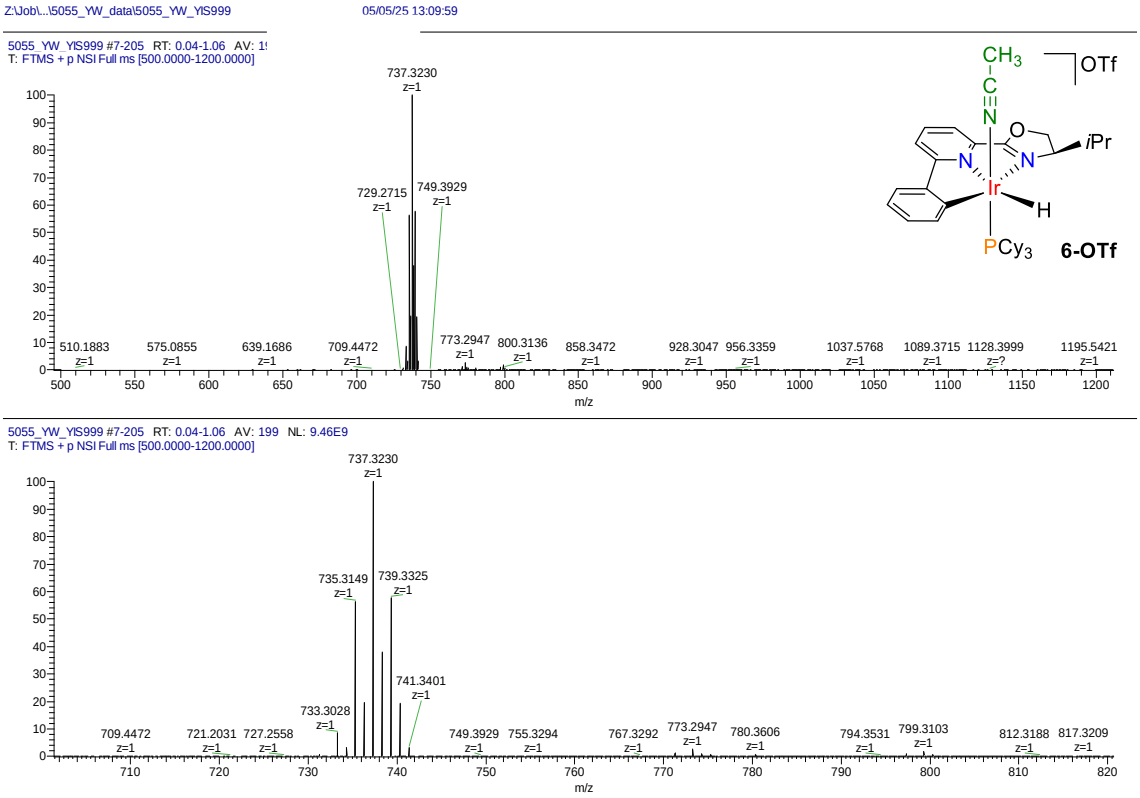


5-OTf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C
N
OTf
O
N
N
iPr
Ir
H
PCy3
6-OTf

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812.3188 z=1
817.3209 z=1
m/z

Crystallographic data

Figure S1. ORTEP drawing (50 %) showing the molecules in the asymmetric unit for compound **4-BARF**.

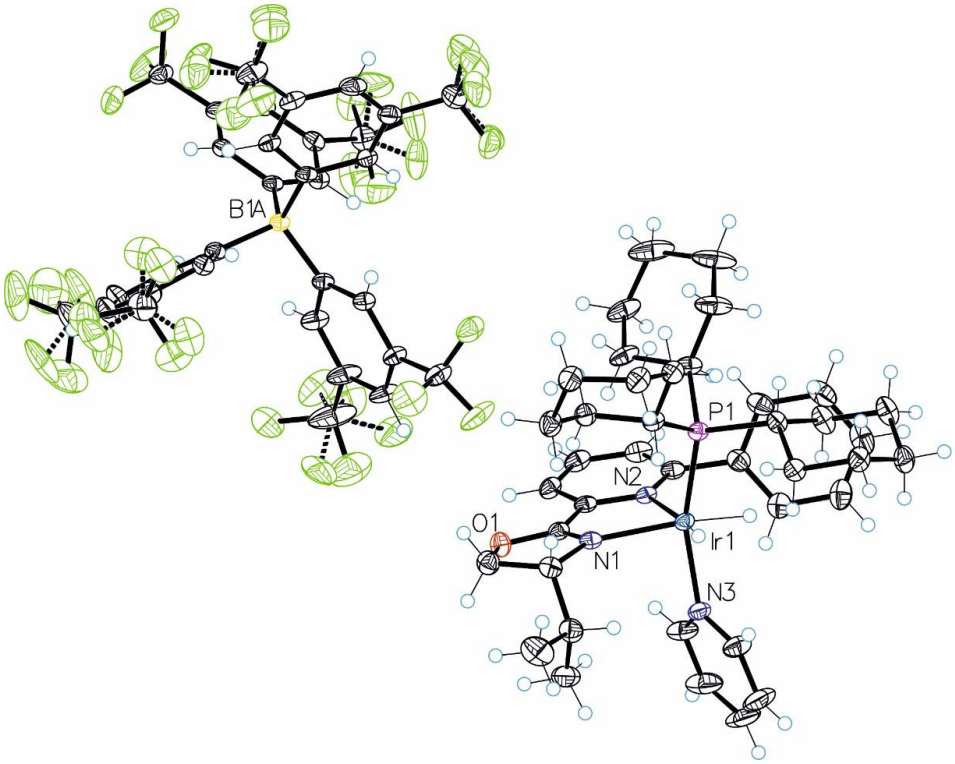

Figure S2. ORTEP drawing (50 %) showing the cationic part of compound **4-BARF**.

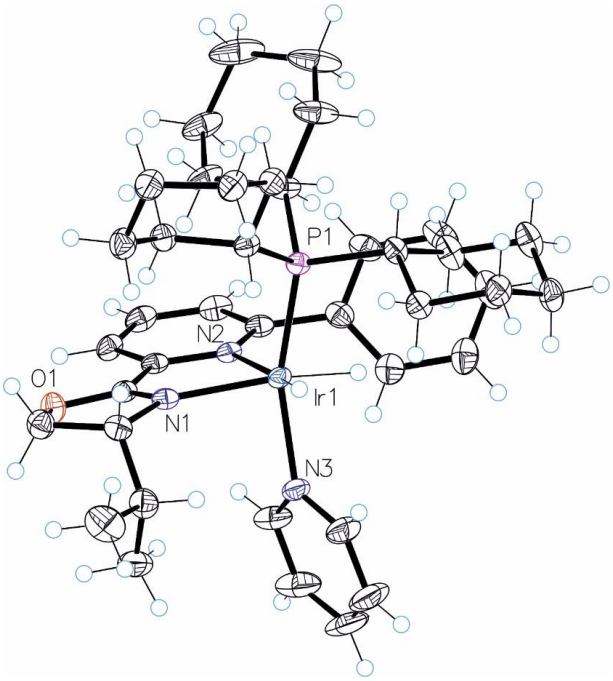

Table S1. Crystal data and structure refinement for 4-BArF.

Empirical formula	C9.29 H9.03 B0.13 F3.10 Ir0.13 N0.39 O0.13 P0.13	
Formula weight	217.20	
Temperature	293(2)K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 13.1050(2)Å	a= 90°.
	b = 20.1498(3)Å	b = 90°.
	c = 27.2687(3)Å	g = 90°.
Volume	7200.66(17) Å3	
Z	31	
Density (calculated)	1.553 Mg/m3	
Absorption coefficient	1.984 mm-1	
F(000)	3376	
Crystal size	? x ? x ? mm3	
Theta range for data collection	2.381 to 31.977°.	
Index ranges	-19<=h<=19,-29<=k<=29,-40<=l<=39	
Reflections collected	64017	
Independent reflections	22797[R(int) = 0.0268]	
Completeness to theta =31.977°	95.1%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00 and 0.58	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	22797/ 441/ 1098	
Goodness-of-fit on F2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0661	
R indices (all data)	R1 = 0.0323, wR2 = 0.0673	
Largest diff. peak and hole	2.157 and -0.838 e.Å-3	

Figure S3. ORTEP drawing (50 %) showing the molecules in the asymmetric unit for compound **5-BARF**.

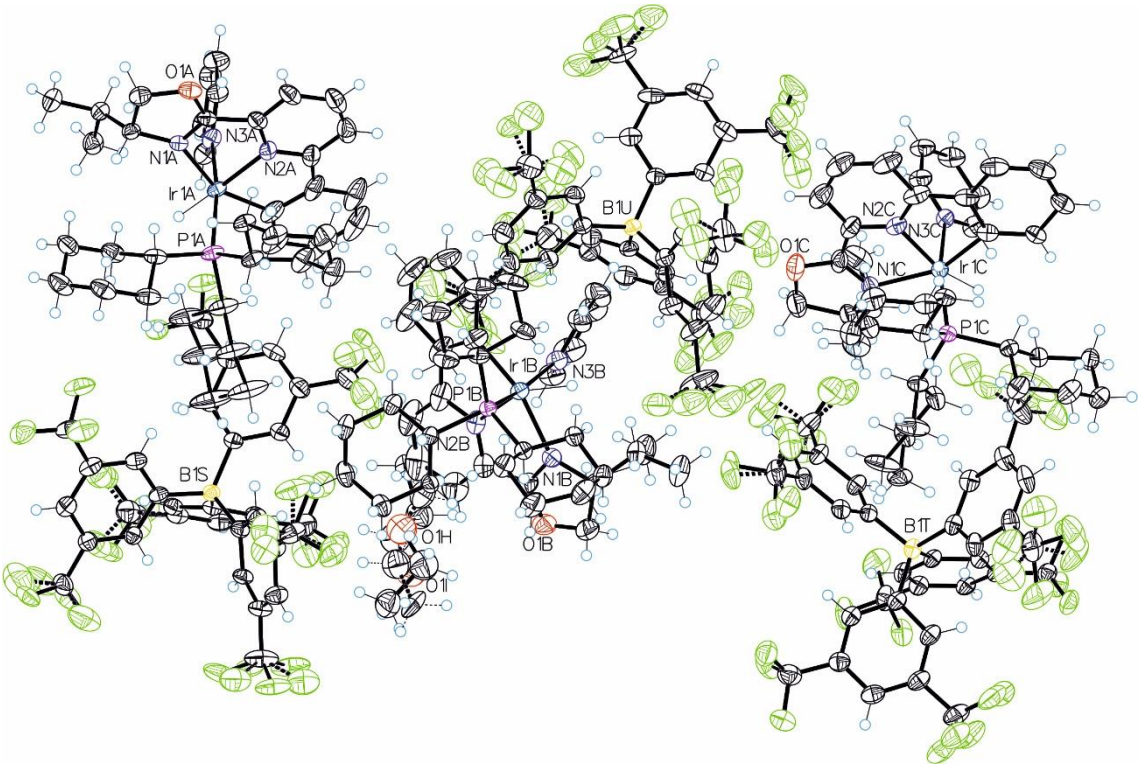

Figure S4. ORTEP drawing (50 %) showing compound **5-BARF**.

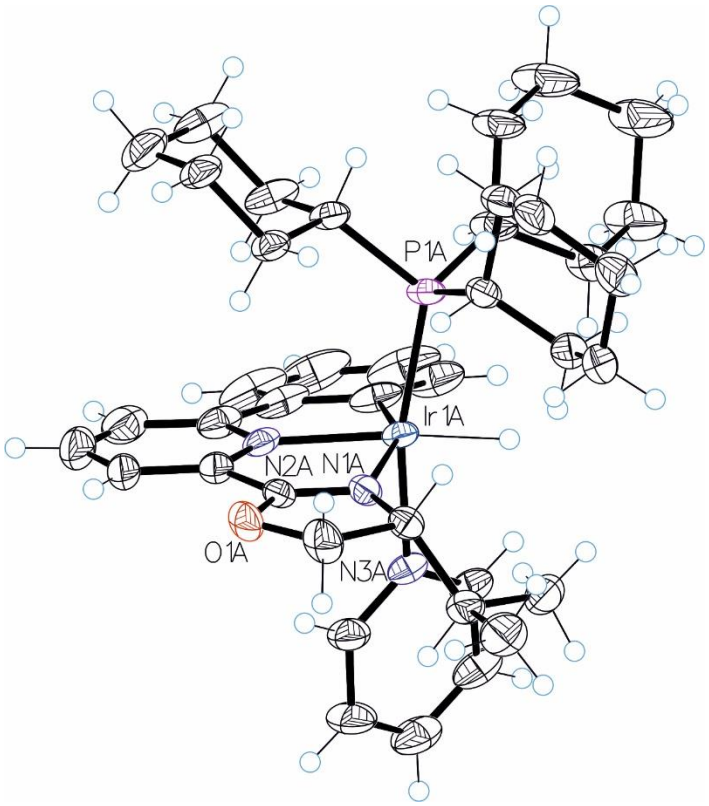

Table S2. Crystal data and structure refinement for 5-BArF.

Empirical formula	C218 H209 B3 F72 Ir3 N9 O3.50 P3	
Formula weight	5080.87	
Temperature	293(2)K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P 1	
Unit cell dimensions	a = 13.50600(10)Å	a= 99.8810(10)°.
	b = 14.15850(10)Å	b = 90.4460(10)°.
	c = 28.9101(2)Å	g = 93.7400(10)°.
Volume	5433.71(7) Å3	
Z	1	
Density (calculated)	1.553 Mg/m3	
Absorption coefficient	1.973 mm-1	
F(000)	2547	
Crystal size	? x ? x ? mm3	
Theta range for data collection	2.174 to 34.311°.	
Index ranges	-21<=h<=20,-22<=k<=22,-45<=l<=45	
Reflections collected	197046	
Independent reflections	83919[R(int) = 0.0454]	
Completeness to theta =34.311°	95.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00 and 0.82	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	83919/ 1920/ 3400	
Goodness-of-fit on F2	0.988	
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.0969	
R indices (all data)	R1 = 0.0515, wR2 = 0.0992	
Largest diff. peak and hole	3.115 and -1.328 e.Å-3	

Data collection: The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.
Crystal structure determination for compound **4-BARF** and **5-BARF** was carried out using a Rigaku diffractometer equipped with a Pilatus 200K area detector, a Rigaku MicroMax-007HF microfocus rotating anode with MoK_α radiation, Confocal Max Flux optics and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = -173 °C). Full-sphere data collection was used with ω and φ scans. *Programs used:* Data collection data reduction with CrysAlisPro[1] and absorption correction with Scale3 Abspack scaling algorithm[2].

Structure Solution and Refinement: Crystal structure solution was achieved using the computer program SHELXT[3]. Visualization and processing was performed with the program OLEX2[4]. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXL 2015[5]. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Comments to the structures: Compound 4-BARF: The asymmetric unit contains one molecule of the cationic Iridium metal complex and a Barf anion. Some of the CF_3-groups in the Barf anion show rotational disorder. The structure is of excellent quality and the two hydrogen atoms attached to the Iridium atom could be localized experimentally from the residual electron density. Geometry and distances corroborate the presence of these hydrogen atoms. The structure does not have any A- or B-alert.

Compound 5-BARF: The asymmetric unit contains three independent molecules of the cationic Iridium metal complex, three Barf anions and a half molecule of diethyl ether. Most of the CF_3-groups in the Barf anion show rotational disorder. The diethyl ether molecule is also disordered in two orientations with an occupancy of 0.25:0.25. Although the structure shows high disorder and some residual electron densities close to the metal atoms, at each metal complex an electron density could be localized which should correspond to hydrogen atoms. Geometry and distances correspond with the position expected for these hydrogen atoms. The presence of this hydrogen atoms was confirmed by H^1-NMR. For this compound alerts related to high densities located close

[1] Data reduction with CrysAlisPro 1.171.44.110 (Rigaku OD, 2018).
[2] Empirical absorption correction using spherical harmonics implemented in Scale3 Abspack scaling algorithm, CrysAlisPro 1.171.44.110 (Rigaku OD, 2018).
[3] SHELXT; V2018/2. Sheldrick, G.M. *Acta Cryst*. **2015** A71, 3-8.
[4] OLEX2 Version 1.5-ac7-014. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.
[5] SHELXL; SHELXL-2018/3. Sheldrick, G.M. *Acta Cryst*. **2015** C71, 3-8.

to the Iridium atoms were commented in the CIF-file: “The residual densities observed were attributed to the presence of the Iridium atoms. The structure was checked for unaccounted twinning, wrongly assigned atom types and other model errors and seems to be sound. Modifying the integration of the data (smaller boxes) and choosing the strong absorber option in the absorption correction, improved the data, but not enough to completely reduce the observed density. This structure was considered suitable for publication.