

Porous Aromatic Frameworks (PAFs) as efficient supports for *N*-heterocyclic carbene catalysts.

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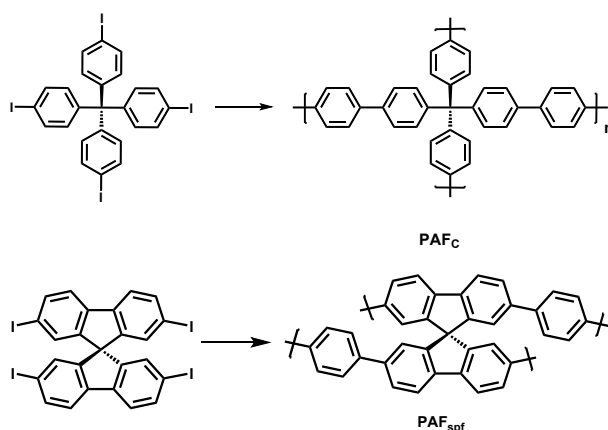
I. General Information.

- ^1H and ^{13}C -NMR spectra of monomers and homogeneous catalysts were recorded in a Bruker Avance 300 MHz spectrometer (Larmor frequencies of 300 MHz for ^1H and 75 MHz for ^{13}C). Solvents used for the NMR spectra were CDCl_3 or DMSO-d_6 . The solid-state ^{13}C NMR spectra were recorded in a Bruker AV-400-WB spectrometer (Larmor frequency of 100 MHz for ^{13}C), using 4-mm MAS probes spinning at a rate of 10 KHz for ^{13}C solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements. The spectra were obtained using a contact time of 3.5 ms and a relaxation time of 4 s with 1024 scans.
- Fourier Transform Infrared Spectra (FTIR) of all compounds and materials were recorded on a Perkin-Elmer RX-1 instrument and are reported in terms of the frequency of absorption (cm^{-1}).
- Microanalyses were made with a Carlo Erba EA1108 elemental analyzer (C, H, N) and the Energy-dispersive X-ray spectroscopy (EDX) measurements of the PAF_S were made in a Philips Model XL30 ESEM.
- Thermogravimetric analysis (TGA) data were obtained on a TA Q-500 analyzer under air atmosphere, using approximately 5 mg of sample under a flow of 60 mL/min. The samples were heated from 40 to 850 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$.
- Specific surface area measurements and porosity analysis were performed using N_2 adsorption isotherms (Micromeritics, ASAP 2020 MICROPOROUS DRY Analyzer) using the BET method for surface area calculation and the BJH method for average pore size and pore volume calculations
- Wide-angle X-ray scattering (WAXS) was carried out using a Bruker D8 Advance diffractometer. Data were collected stepwise over the angular region of $5^\circ \leq 2\theta \leq 65^\circ$, using steps of 0.5 s/step accumulation time, a Vantec detector, and $\text{Cu K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$).
- Scanning electron microscopy (SEM) micrographs were obtained with a Hitachi Model SU-8000 microscope operating at 0.5 kV. The samples were prepared directly by dispersing the powder onto a double-sided adhesive surface.
- Metal contents were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on a Perkin Elmer OPTIMA 2100 DV.
- The reactions were monitored by gas chromatography on HP5890 II and Konik HRGC 4000B GC-MS chromatographs with a cross-linked (95%)-dimethyl-(5%)-

diphenylpolysiloxane (Teknokroma TRB-5MS) column of 30 meters of length; helium as carrier gas.

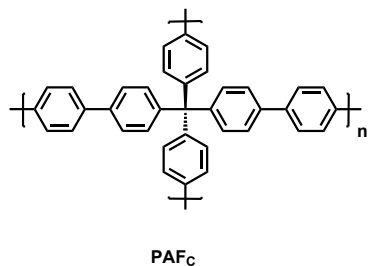
- Mesitylimidazole and 2-(2'-pyridyl)imidazole were synthesized in our laboratory according to the literature procedure.¹

II. Preparation of PAF-NHC-precursors.



Scheme S1: 1,4-phenylenediboronic acid, MW, 12 bar, 145 °C, 10 min.

Microwave assisted synthesis of PAF_c: 200 mg (0.230 mmol) of tetrakis(4-iodophenyl)methane, 2.2 equivalents (84 mg, 0.506 mmol) of the corresponding diboronic acid, triphenylphosphine (30 mg, 0.115 mmol), sodium bicarbonate (85 mg, 1.31 mmol) and palladium acetate (3 mg, 0.015 mmol) were suspended in a mixture of 2 mL DMF and 0.5 mL water. The mixture was degassed by N₂



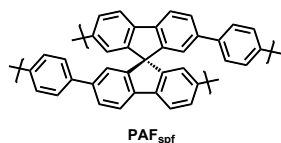
bubbling. Microwave heating was performed in a computer controlled CEM Discover microwave with temperature and pressure control. Initial heating was performed at a power input of 75W. After the pressure has reached approx. 12 bar, the heating was stopped for 1 min. After that period heating was continued to reach the reaction temperature of approx. 145 °C. The reaction was run at that temperature and a pressure of approx. 5-7 bar for 10 min. After cooling to room temperature, the mixture was filtered and the crude product was washed for approx. 1 h with a solution of 50 mL of water, 1 mL of HNO₃ conc. and 1 mL of HCl conc. to remove Pd impurities. The mixture was filtered and the crude product was washed with DMF (3 x 30 mL), THF (3

¹ B. E. Ketz, A. P. Cole and R. M. Waymouth, *Organometallics*, 2004, **23**, 2835.

x 30 mL), water (3x 30 mL), CH₂Cl₂ (3 x 30 mL) and diethyl ether (2 x 20 mL). After drying *in vacuo* a pale yellow powder was obtained. The reaction yield was nearly quantitative based on the molecular weight of the ideal, fully condensed products. Elemental analysis: Calc. for C₃₇H₂₄: C, 94.0; H, 5.2; Found C, 85.1, H, 5.2 %. BET Surface Area (m²·g⁻¹): 393 Pore Volume (cm³·g⁻¹): 0.45, Average Pore Size (nm): 8.5 (Estimated by BHJ method).

PAF_{Ad}: Elemental analysis: Calc. C₄₆H₃₆: C, 93.2; H, 6.8; Found C, 87.04, H, 4.38 %. for BET Surface Area (m²·g⁻¹): 515 Pore Volume (cm³·g⁻¹): 0.42, Average Pore Size (nm): 5.5 (Estimated by BHJ method).

Microwave assisted synthesis of PAF_{spt}. 259 mg (0.316 mmol) of 2,2',7,7'-tetraiodo-9,9'-spirobisfluorene,² 105 mg (0.632 mmol) of 1,4-phenylenediboronic acid, 41 mg (0.158 mmol) of triphenylphosphine, 117 mg (1.39 mmol) of sodium bicarbonate

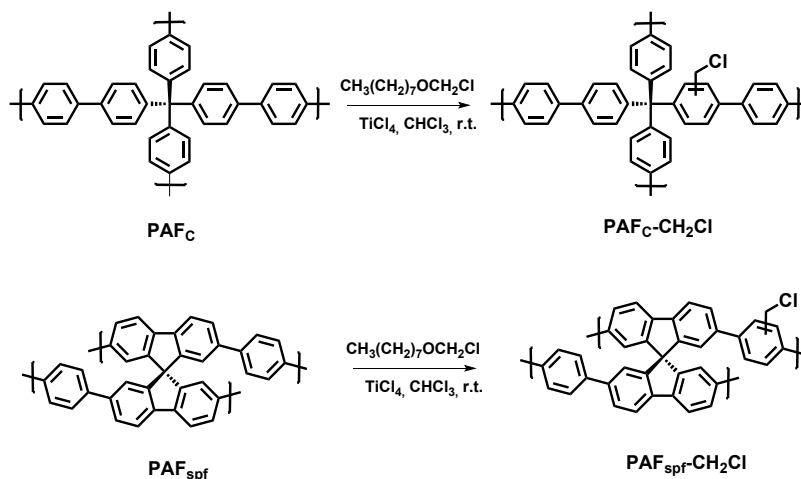


and 3.5 mg (0.016 mmol) of palladium acetate are suspended in a mixture of DMF (2 mL) and water (0.5 mL). The mixture was degassed by argon bubbling. Microwave heating was performed in a computer controlled CEM Discover microwave with temperature and pressure control. Initial heating was performed at a power input of 75 W. After the pressure has reached approx. 10 bars, the heating was stopped until cooled at 60°C and the pressure disappears. After that period heating was continued to reach the reaction temperature of approx. 145°C. The reaction was run at that temperature and a pressure of approx. 7 bars for 5 min. After cooling to room temperature, the mixture was filtrated and the crude product was washed with DMF and water. The solid was suspended in a mixture of water (100 mL), hydrochloric acid (1 mL) and nitric acid (2 mL) and heated to reflux to remove Pd impurities, until to obtain yellow color. Finally, the sample was filtrated and washed with THF and diethyl ether. After drying under *vacuum* a pale yellow powder was obtained.

Elemental analysis: Calc. for C₃₇H₂₀: C, 94.8; H, 5.2; Found C, 87.0 %, H, 5.3 %. FT-IR (KBr): ν = 1709, 1603, 1461, 1400, 1246, 1181, 1111, 1077, 1003, 815, 764, 736, 697 cm⁻¹. BET Surface Area (m²·g⁻¹): 580 Pore Volume (cm³·g⁻¹): 0.42, Average Pore Size (nm): 3 (Estimated by BHJ method).

² J. Salbeck, D. Lupo, US2003/0111107 A1.

Synthesis of the chlorobenzyl material, PAF-CH₂Cl: General method.



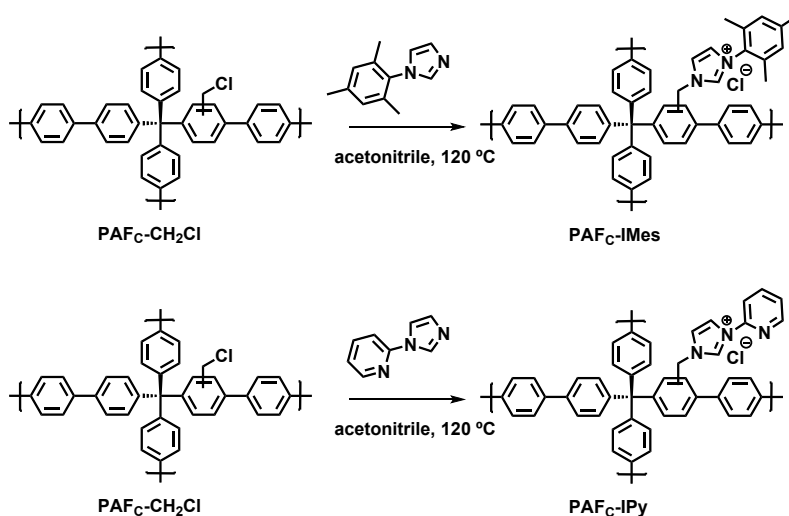
PAF_s were suspended on chloroform and reacted with CH₃(CH₂)₇OCH₂Cl in presence of TiCl₄ at room temperature for 24 h, after filtration and drying at 135 °C under vacuum (10–5 mm Hg), PAF-CH₂Cl was obtained as a white or yellow solid (98%).

PAF_c-CH₂Cl: ¹³C CP-MAS solid state NMR: 146.11, 139.40, 128.93, 65.04, 44.33 ppm. Elemental analysis: C, 77.5 %, H, 5.0 %, Cl, 1.8 %.

PAF_{spf}-CH₂Cl: ¹³C CP-MAS solid state NMR: 147.70, 140.88, 127.76, 67.02, 43.99 ppm. Elemental analysis: C, 60.4 %, H, 4.1, Cl, 4.0 %.

PAF_{Ad}-CH₂Cl: Elemental analysis: C, 78.05%, H, 4.18, Cl, 4.0 %.

Synthesis of PAF_c-Im: General method.



PAF_c-CH₂Cl (0.5 g, 1.00 mmol) was treated with mesitylimidazole or 2-(2'-pyridyl)imidazole (1.5 mmol) in acetonitrile (30 mL), and the reaction mixture was heated to reflux for 24 h. After filtration, the solid was washed successively with tetrahydrofuran and diethyl ether. Then it was dried under vacuum overnight (135 °C, 10–5 mm Hg) (71-75 %).

PAF_c-IMes: ¹³C CP-MAS solid state NMR (125.7 MHz): 146.11, 138.91, 130.34, 128.94, 65.04 ppm. Elemental analysis: C, 65.9 %, H, 4.4 %, N, 1.3 %.

PAF_c-IPy: ¹³C CP-MAS solid state NMR (125.7 MHz): 145.86, 139.07, 131.14, 127.48, 64.77 ppm. Elemental analysis: C, 66.6 %, H, 4.5 %, N, 2.4 %.

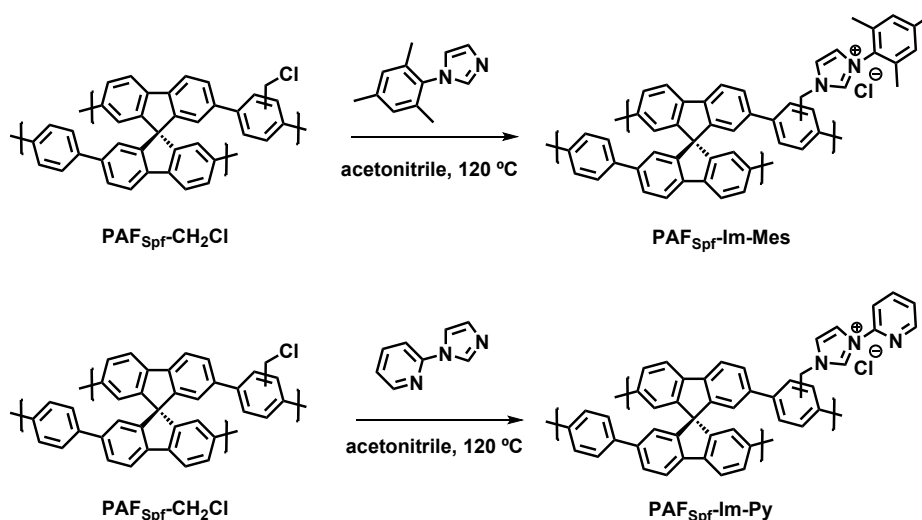
PAF_{Ad}-IMes: ¹³C CP-MAS solid state NMR (125.7 MHz): 157.5, 149.2, 138.9, 134.8, 128.2, 48.6, 39.8, 18.9 ppm. Elemental analysis: C, 71.3 %, H, 6.0 %, N, 2.90 %.

Synthesis of PAF_{spf}-Im: General method.

These compounds were prepared as described above, from **PAF_{spf}-CH₂Cl**.

PAF_{spf}-IMes: ¹³C CP-MAS solid state NMR (125.7 MHz): 148.14, 140.72, 128.14, 124.57, 67.03 ppm. Elemental analysis: C, 61.1 %, H, 4.8 %, N, 2.9 %.

PAF_{spf}-IPy: ¹³C CP-MAS solid state NMR (125.7 MHz): 147.38, 140.03, 127.18, 123.48, 66.58 ppm. Elemental analysis: C, 58.9 %, H, 4.5 %, N, 4.4 %.



III. Preparation of PAF-(NHC)M

PAFs-IMesIr and PAFs-IPyIr.

To a suspension of **PAF-Im** (0.10 mmol) in CH₂Cl₂ (3 mL), was added Ir(acac)(COD) (0.10 mmol) dissolved in CH₂Cl₂ (2.0 mL). After stirring for 3 h the reaction mixture

was heated at 40 °C for additional 24 h. The solid was filtered and washed with CH₂Cl₂, THF until the filtrate was colorless and dried in vacuum.

PAF_c-IMesIr: ¹³C CP-MAS solid state NMR (125.7 MHz): 145.37, 138.69, 130.61, 127.95, 64.83 ppm. Elemental analysis: C, 62.5 %, H, 4.6 %, N, 1.2 %. Ir: 3.8 % (0.197 mmol/g).

PAF_{sp}-IMesIr: Elemental analysis: C, 55.5 %, H, 4.3 %, N, 1.7 %. Ir: 2.6 % (0.133 mmol/g).

PAF_c-IPyIr: Elemental analysis: C, 60.0 %, H, 4.4 %, N, 1.8 %. Ir: 4.5 % (0.226 mmol/g).

PAF_{sp}-IPyIr: Elemental analysis: C, 58.3 %, H, 4.3 %, N, 2.6 %. Ir: 4.30% (0.224 mmol/g).

PAFs-IMesRu and PAFs-IPyRu.

To a suspension of **PAF-Im** (0.10 mmol) in toluene (2.0 mL) a solution of potassium *bis*(trimethylsilyl)amide ([[(CH₃)₃Si]₂NK, 20 mg, 0.10 mmol) in toluene was dropwise added at 0 °C and the mixture stirred for 1 h at room temperature under N₂ and then, [Ru(*p*-cymene)Cl₂]₂ (45 mg, 0.07 mmol) in toluene (2.0 mL) was added. After stirring for 48 h at 60 °C, the reaction mixture was filtered, and the solid was washed several times with dichloromethane and THF until the filtrate was colorless and finally dried under vacuum.

PAF_c-IMesRu: ¹³C CP-MAS solid state NMR (125.7 MHz): 143.99, 139.47, 129.67, 65.55 ppm. Elemental analysis: C: 60.9 %; H: 4.5 %; N: 2.0 %; Ru: 1.22 % (0.122 mmol/g).

PAF_{sp}-IMesRu: Elemental analysis: C: 53.6 %; H: 4.0 %; N: 2.2 %; Ru: 1.97 % (0.195 mmol/g).

PAF_c-IPyRu: Elemental analysis: C: 57.3 %; H: 4.1 %; N: 2.1 %; Ru: 2.34 % (0.231 mmol/g).

PAF_{Ad}-IMesRu: ¹³C CP-MAS solid state NMR (125.7 MHz): 49, 127, 134, 141 ppm. Elemental analysis: C: 59.7%; H: 4.9%; N: 1.8%; Ru: 1.0% (0.1 mmol/g)

IV. Characterization Data.

Table S1. Elemental analyses of the **PAF**-NHC-precursors.^[a]

Compound	Funct. (%) ^[b]	C [wt%]	H [wt%]	Cl [wt%]	N [wt%]
		calc./found	calc./found	calc./found	calc./found
PAF _c (C ₃₇ H ₂₄)		94.0/85.10	5.2/5.18	-	-
PAF _c -CH ₂ Cl	30	91.96/77.46	5.86/4.96	2.18/1.8	-
PAF _c -IMes	30	90.37/65.94	6.15/4.41	-	1.53/1.34
PAF _c -IPy	30	89.76/66.62	5.89/4.51	-	2.36/2.39
PAF _{Ad} (C ₄₆ H ₃₆)		93.2/87.04	6.80/4.38	-	
PAF _{Ad} -CH ₂ Cl	70	89.49/78.05	6.55/4.18	3.96/4.0	-
PAF _{Ad} -IMes	70	87.22/71.30	7.02/6.0	-	2.54/2.90
PAF _{Ad} -IPy	60	86.89/66.04	6.66/4.50	-	3.49/3.23
PAF _{spf} (C ₃₇ H ₂₀)		94.8/87.0	5.2/5.3	-	-
PAF _{spf} -CH ₂ Cl	60	90.74/60.44	4.98/4.07	4.27/4.0	-
PAF _{spf} -IMes	60	88.29/61.12	5.46/4.79	-	2.76/2.93
PAF _{spf} -IPy	60	87.09/58.94	4.96/4.45	-	4.31/4.39

^[a] It is very well known that in conjugated porous polymers lead to bad combustion and incorrect values of carbon and carbon-hydrogen ratio.³ ^[b] Related to parent material.

Table S2. Analytical data of the **PAF**-(NHC)M.

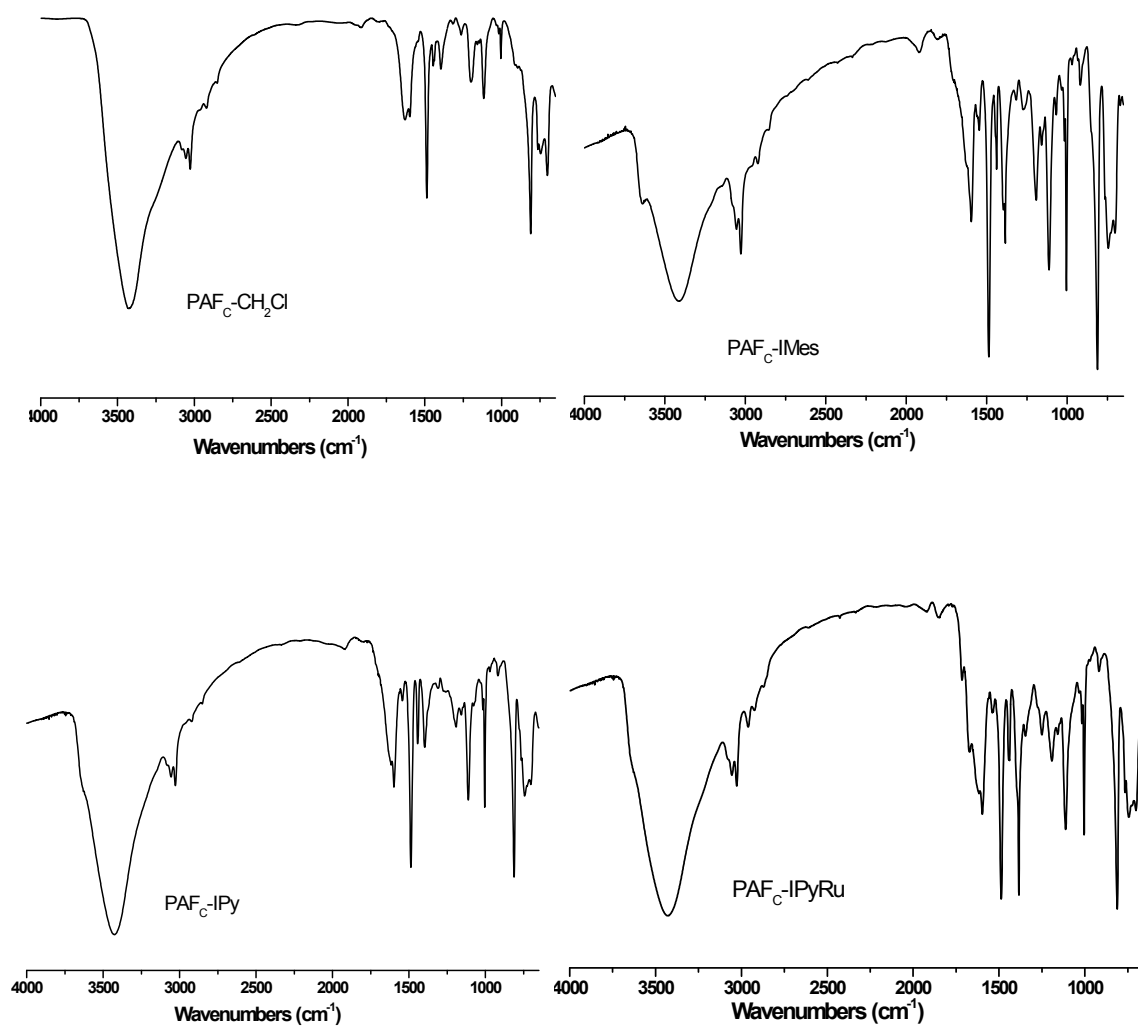
Compound	C [wt%] ^[a]	H [wt%] ^[a]	N [wt%] ^[a]	Metal loading ^[b]		Funct. (%) ^[c]
	calc./found	calc./found	calc./found (mmol/g)	[wt%] calc./found	[mmol/g]	
PAF _c -IMesIr	87.34/62.51	6.02/4.59	1.46/1.15 (0.82)	3.34/3.78	0.197	33
PAF _c -IPyIr	85.02/60.02	5.71/4.36	2.17/1.80 (1.26)	4.97/4.50	0.226	50
PAF _c -IMesRu	88.21/60.90	6.08/4.53	1.47/2.03 (1.44)	1.76/1.22	0.122	33
PAF _c -IPyRu	86.30/57.34	5.81/4.14	2.19/2.05 (1.47)	2.63/2.34	0.231	50
PAF _{spf} -IMesIr	85.65/55.48	5.39/4.26	2.63/1.70 (1.22)	3.01/2.56	0.133	17
PAF _{spf} -IPyIr	83.75/58.32	4.92/4.29	3.43/2.65 (1.89)	4.71/4.30	0.224	30
PAF _{spf} -IMesRu	86.41/53.64	5.46/3.96	2.64/2.17 (1.54)	1.59/1.97	0.195	17

^[a] Determined by elemental analyses.

^[b] Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

^[c] Related to imidazolium groups.

FTIR spectra

Figure S1. FTIR spectra of PAF_c-materials

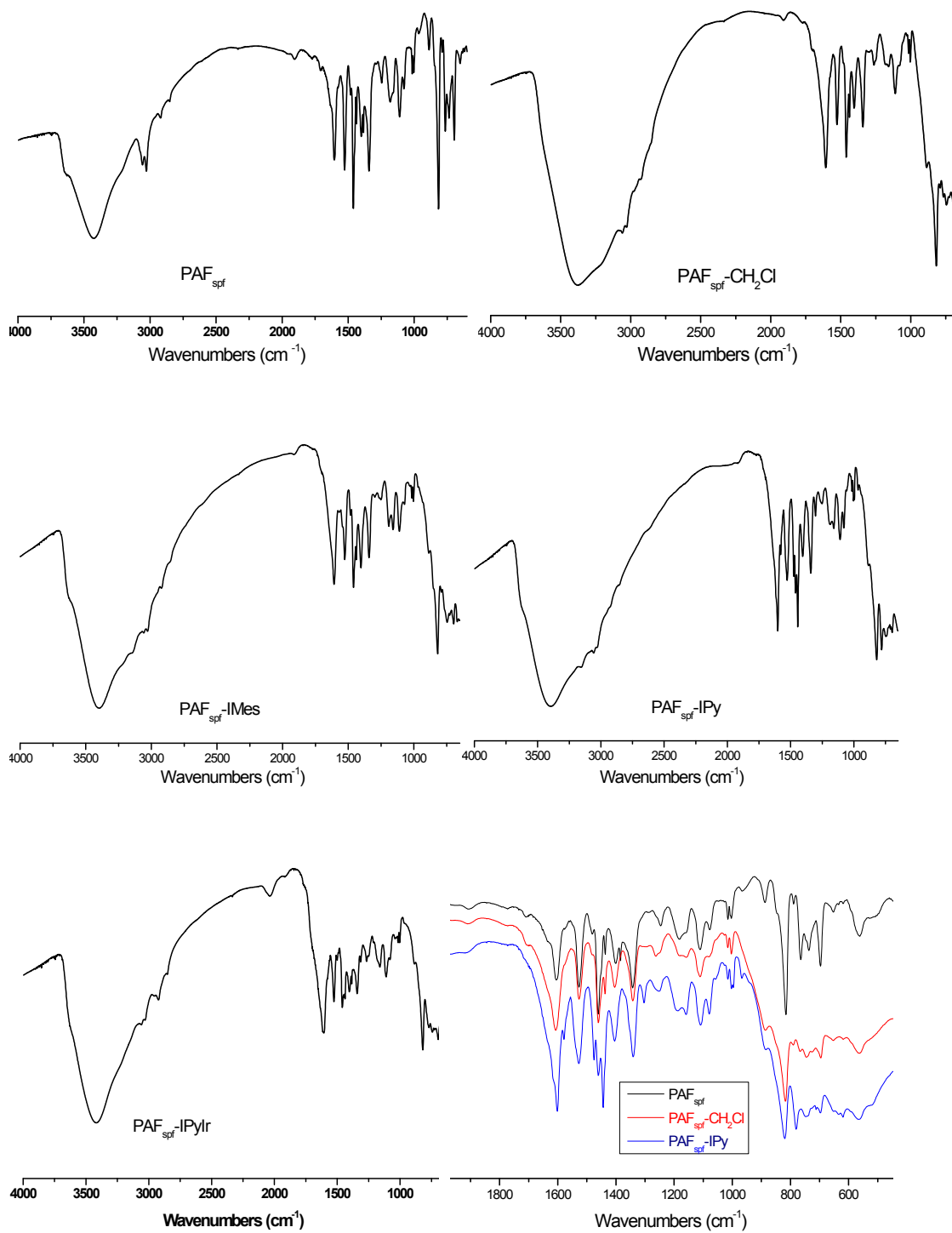
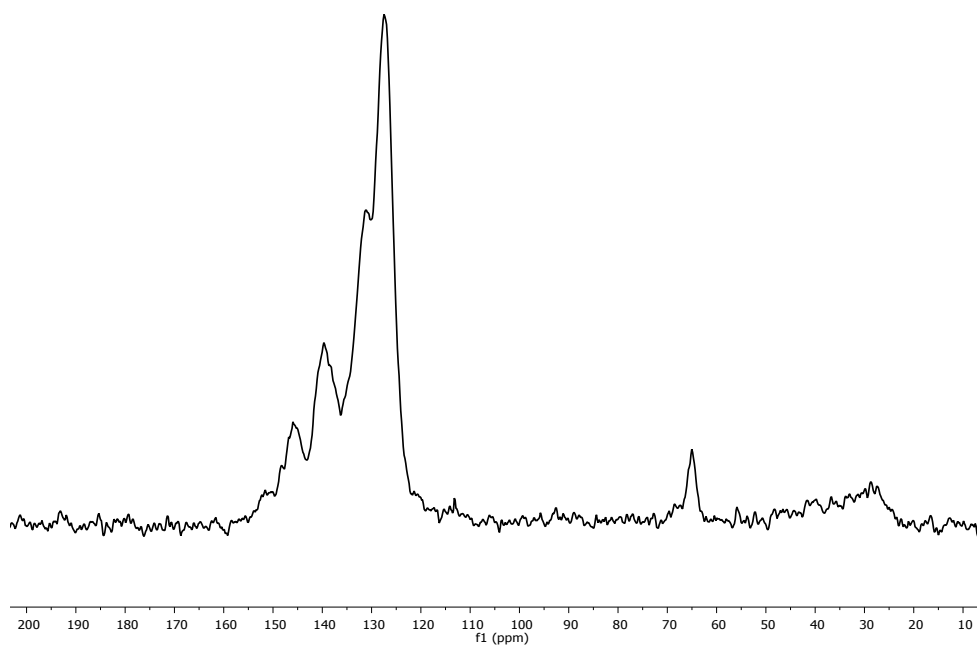
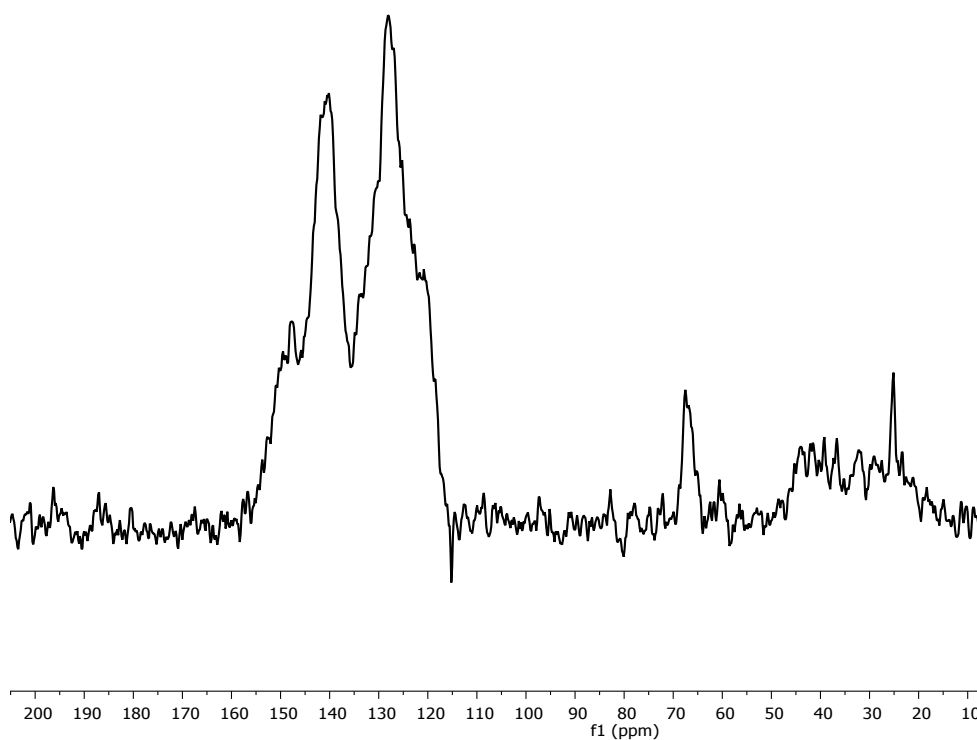


Figure S2. FTIR spectra of PAF_{spf} -materials.

^{13}C solid state CP-MAS NMRFigure S3a. ^{13}C solid state CP-MAS NMR spectrum of **PAF_c-CH₂Cl**.Figure S3b. ^{13}C solid state CP-MAS NMR spectrum of **PAF_{spf}-CH₂Cl**.

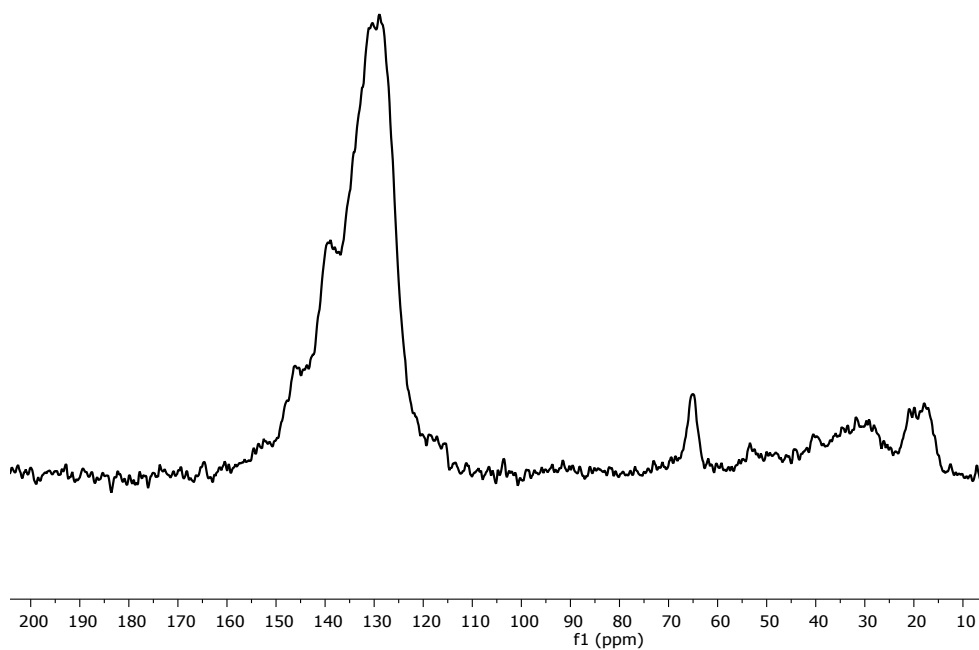


Figure S3c. ^{13}C solid state CP-MAS NMR spectrum of $\text{PAF}_c\text{-IMes}$.

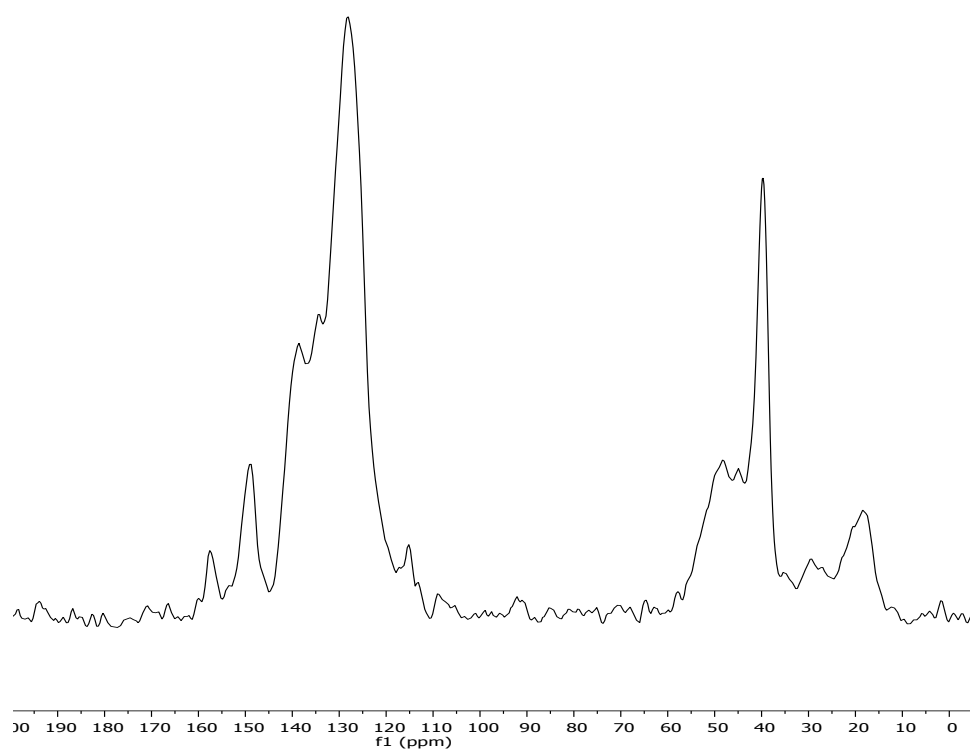


Figure S3d. ^{13}C solid state CP-MAS NMR spectrum of $\text{PAF}_{\text{Ad}}\text{-IMes}$.

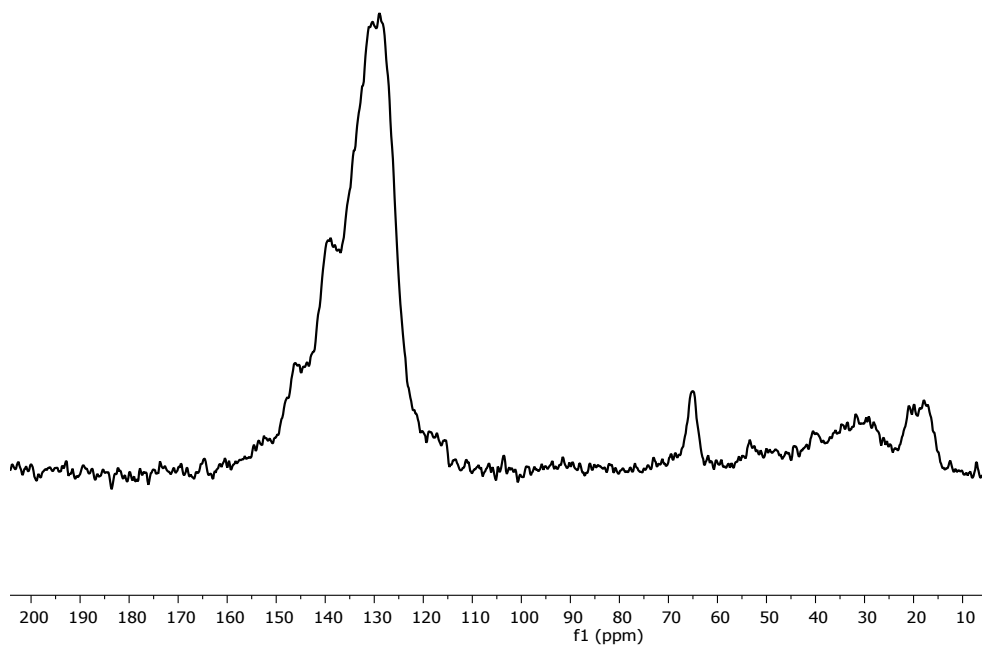


Figure S3e. ^{13}C solid state CP-MAS NMR spectrum of $\text{PAF}_{\text{spf}}\text{-IMes}$.

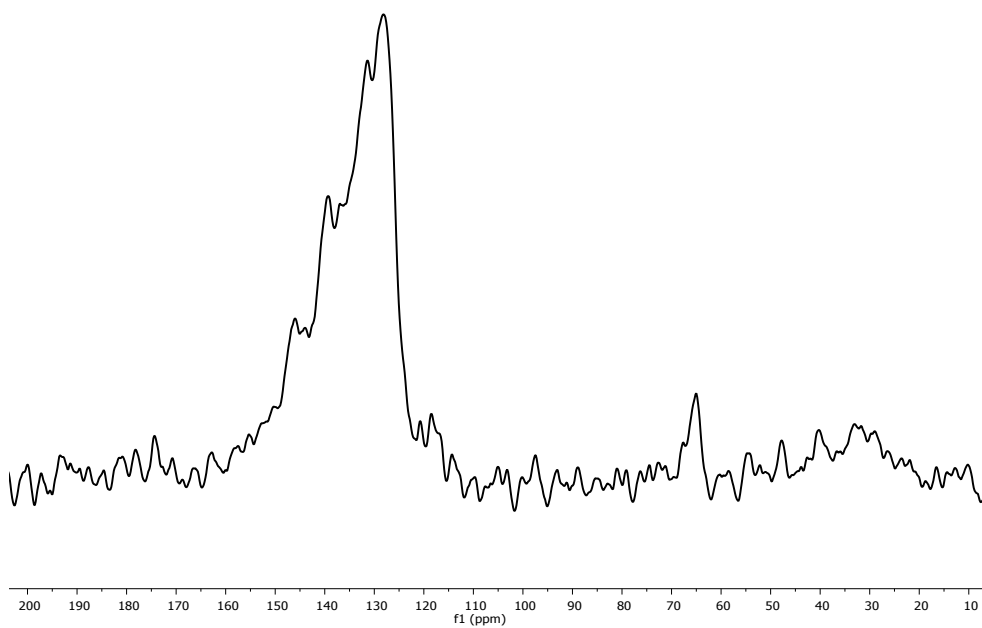


Figure S3f. ^{13}C solid state CP-MAS NMR spectrum of $\text{PAF}_{\text{c}}\text{-IPy}$.

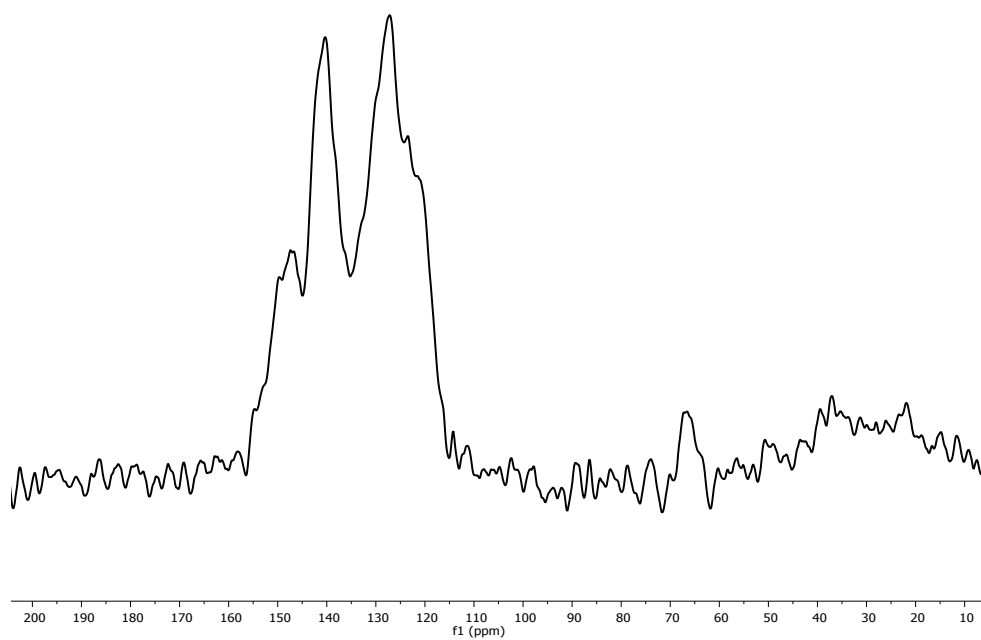


Figure S3g. ^{13}C solid state CP-MAS NMR spectrum of $\text{PAF}_{\text{sp}}\text{-IPy}$.

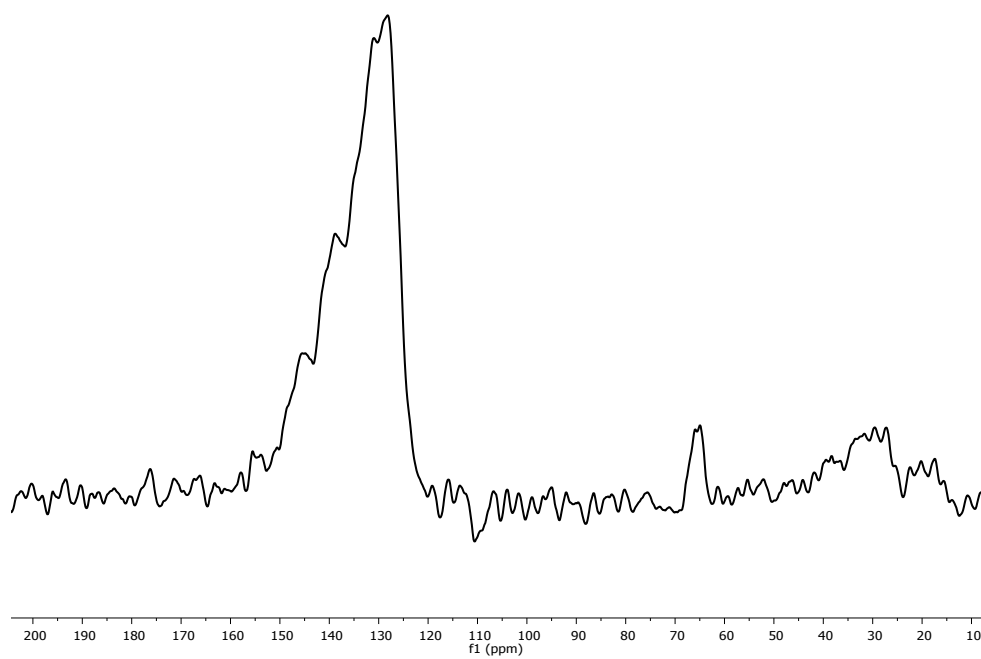


Figure S3h. ^{13}C solid state CP-MAS NMR spectrum of $\text{PAF}_{\text{c}}\text{-IMesIr}$.

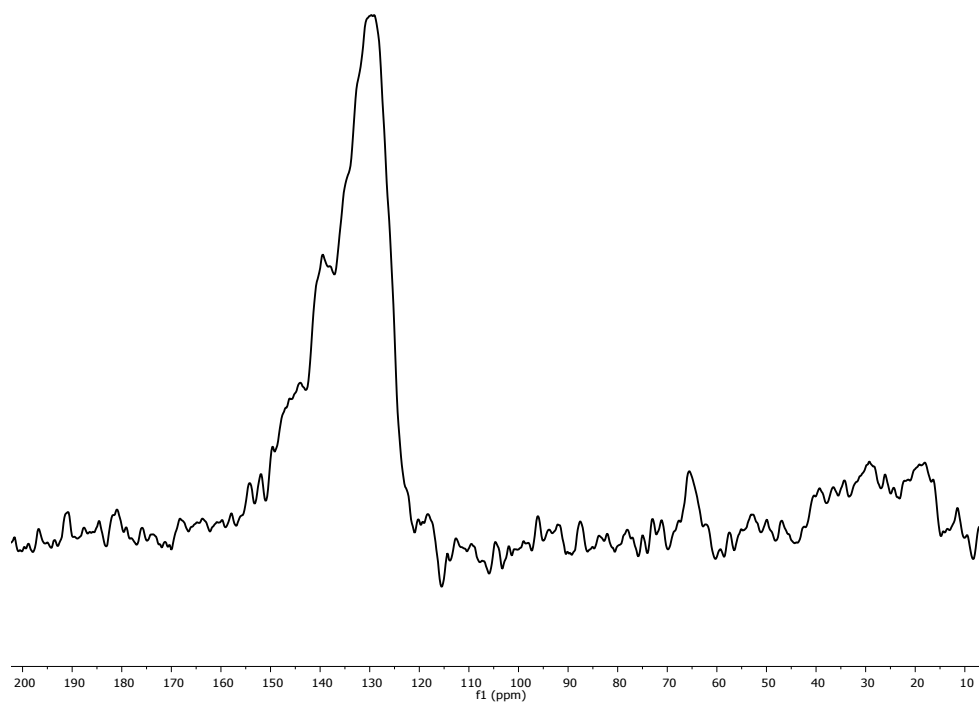


Figure S3i. ^{13}C solid state CP MAS NMR spectrum of $\text{PAF}_c\text{-IPyRu}$.

Thermogravimetric analyses

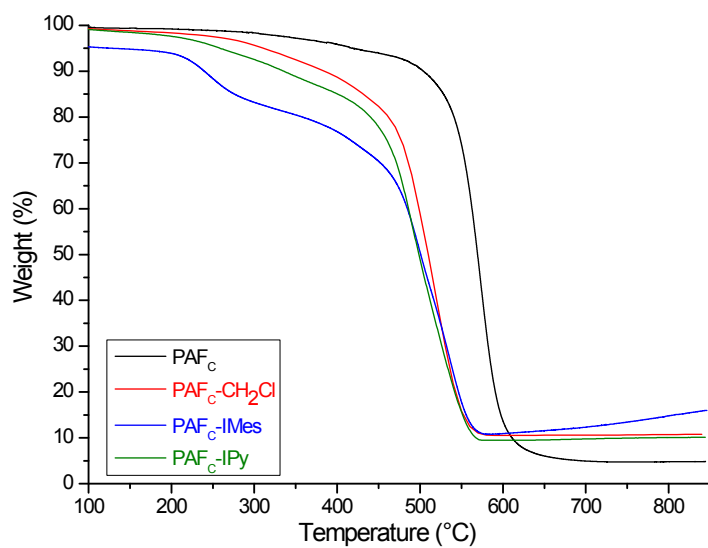


Figure S4a. TGAs of PAF_C, PAF_C-CH₂Cl, PAF_C-IMes and PAF_C-IPy.

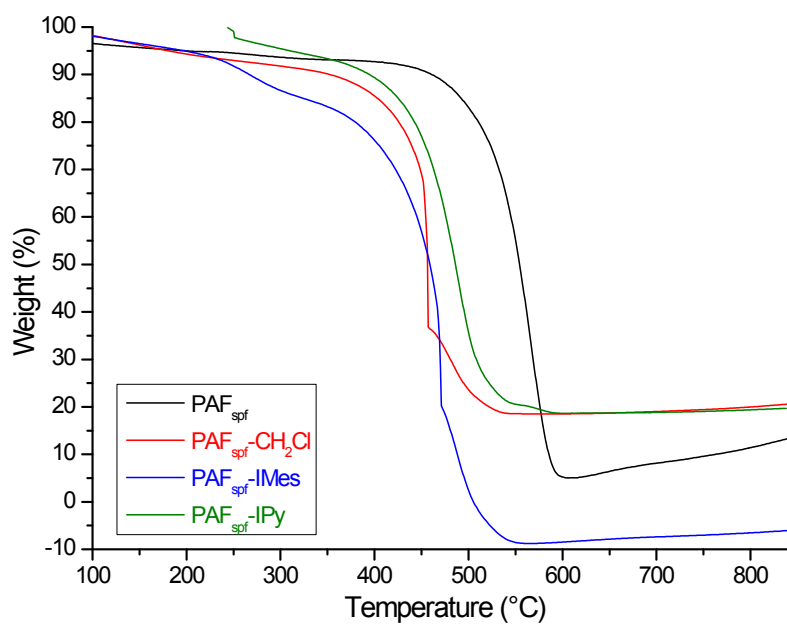
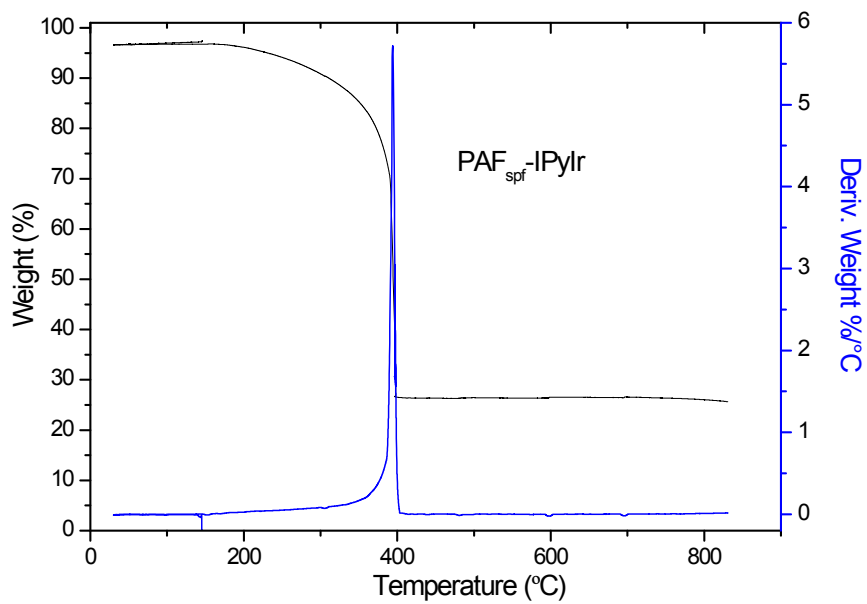
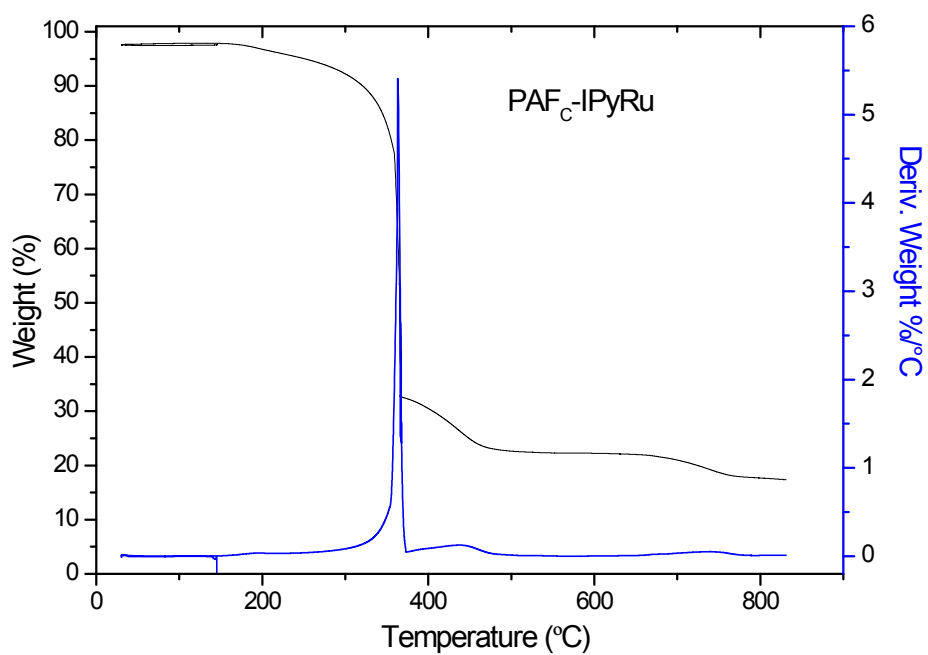
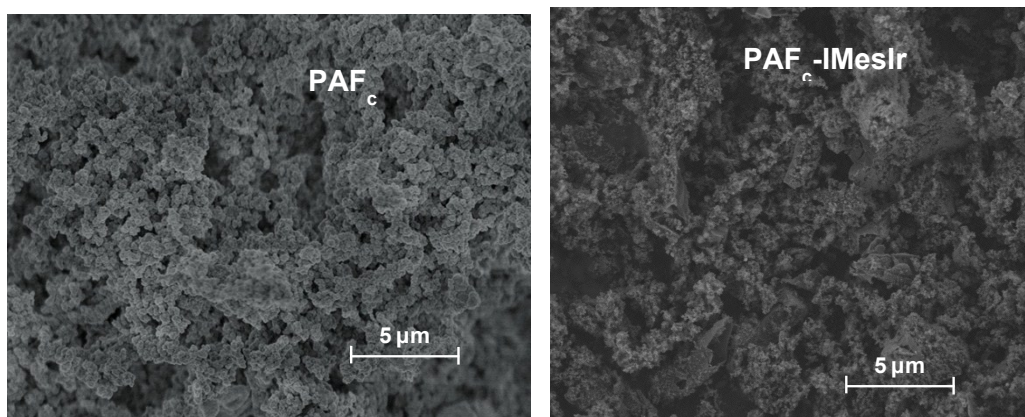
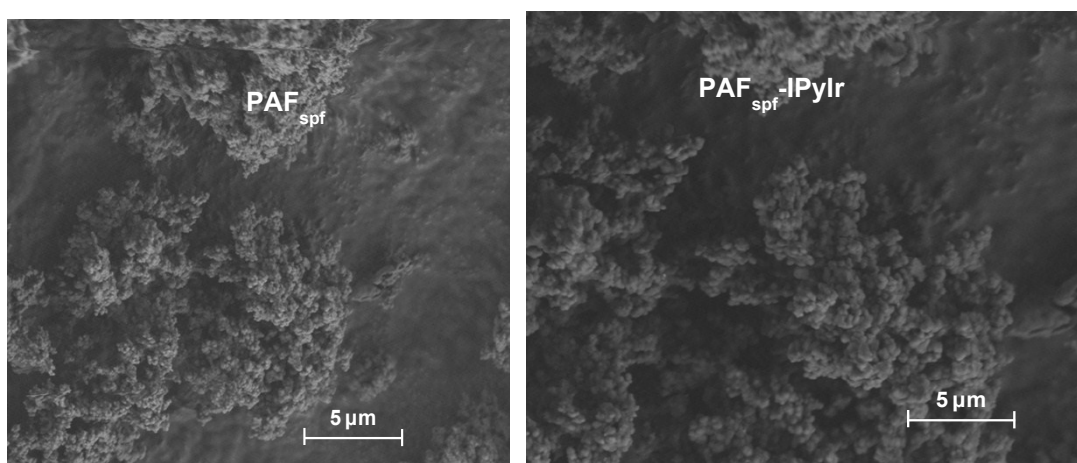
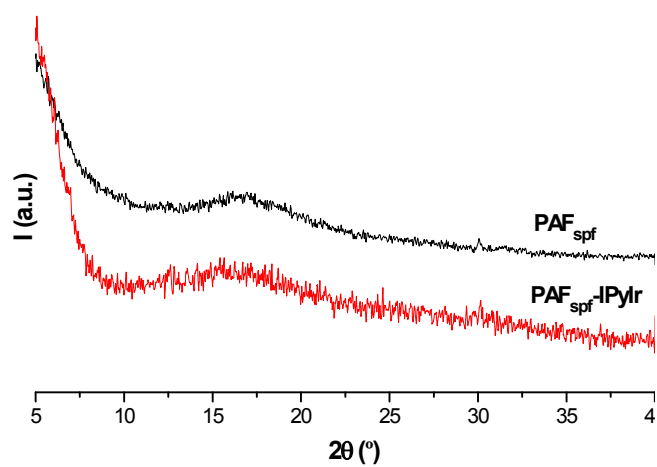


Figure S4b. TGAs of PAF_{spf}-derivatives

Figure S4c. TGAs of PAF_{spf}-IPyIr.Figure S4d. TGAs of PAF_C-IPyRu.

SEM images

Figure S5a. SEM image of PAF_c and $\text{PAF}_c\text{-IMesIr}$.Figure S5b. SEM image of PAF_{spf} and $\text{PAF}_{\text{spf}}\text{-IPyIr}$.Figure S6. PXRD of PAF_{spf} and $\text{PAF}_{\text{spf}}\text{-IPyIr}$.

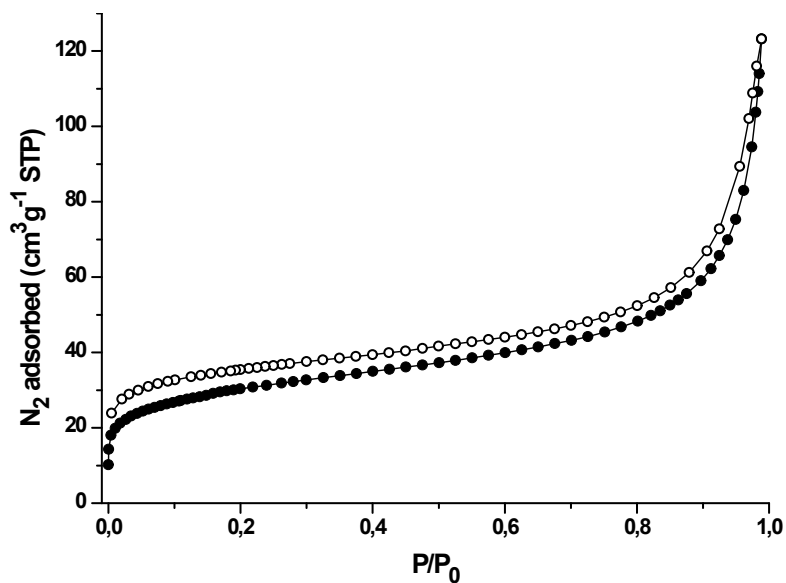
Textural studies

Figure S7a. Nitrogen sorption isotherms (filled circles: adsorption; open circles: desorption) of PAF_C-IMes at 77 K.

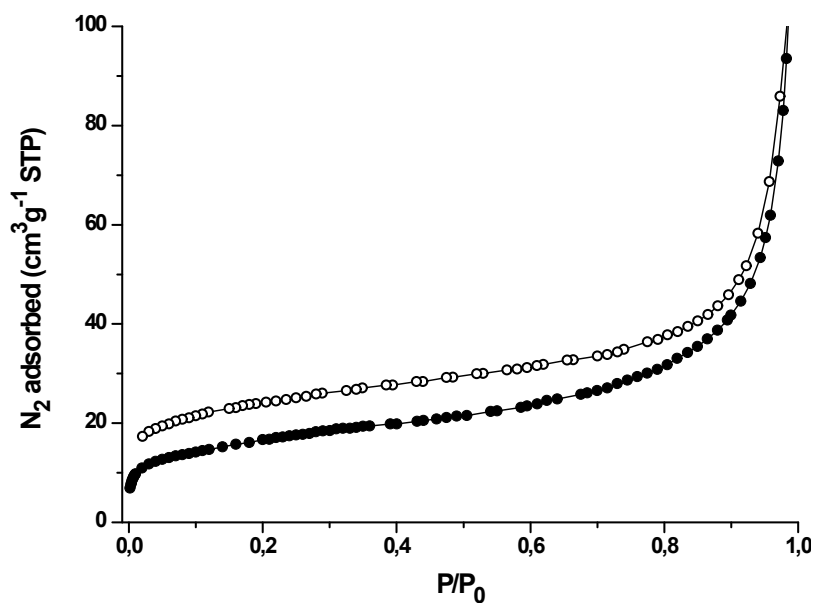


Figure S7b. Nitrogen sorption isotherms (filled circles: adsorption; open circles: desorption) of PAF_{Ad}-IMes at 77 K.

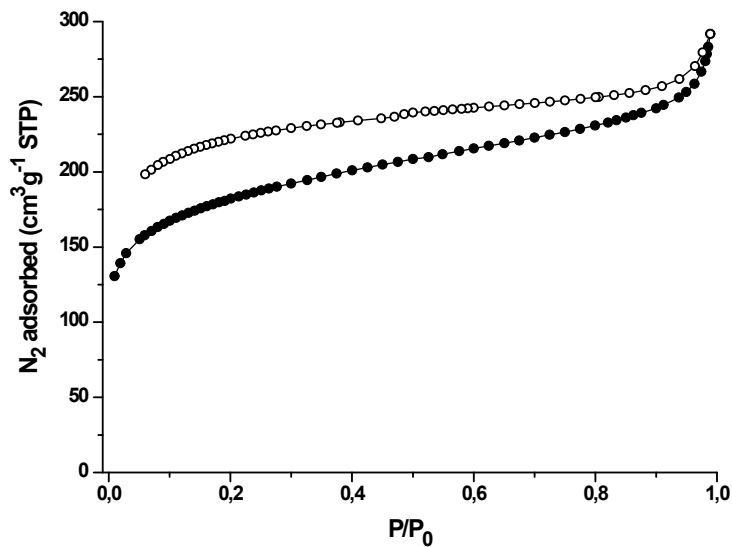


Figure S7c. Nitrogen sorption isotherms (filled circles: adsorption; open circles: desorption) of PAF_{spf} at 77 K.

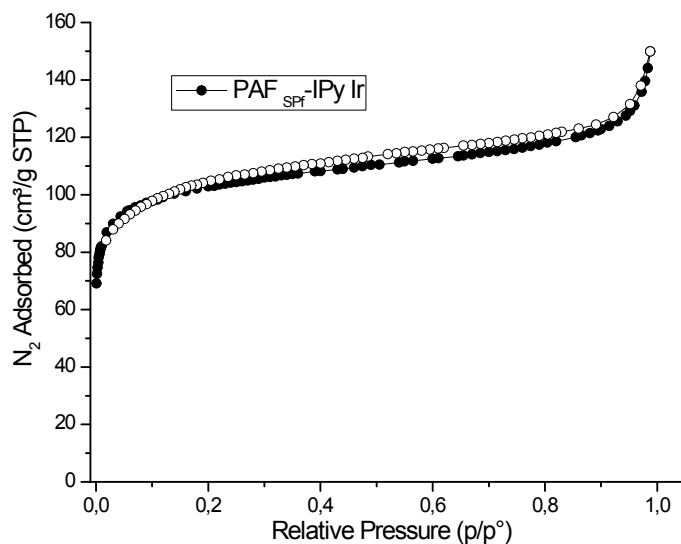


Figure S7d. Nitrogen sorption isotherms (filled circles: adsorption; open circles: desorption) of $\text{PAF}_{\text{spf-IPyIr}}$ at 77 K.

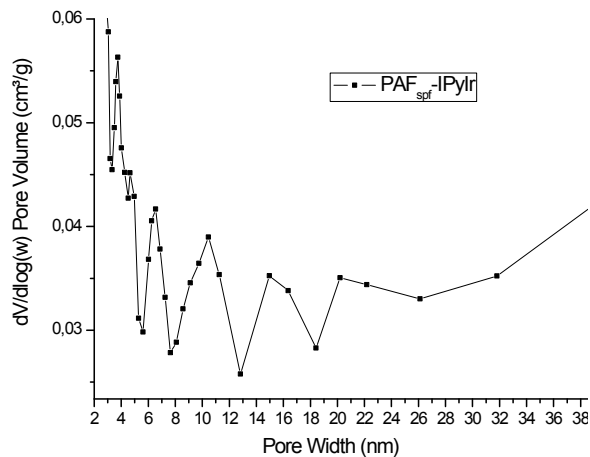


Figure S7e. Pore size distribution for $\text{PAF}_{\text{spf-IPyIr}}$.

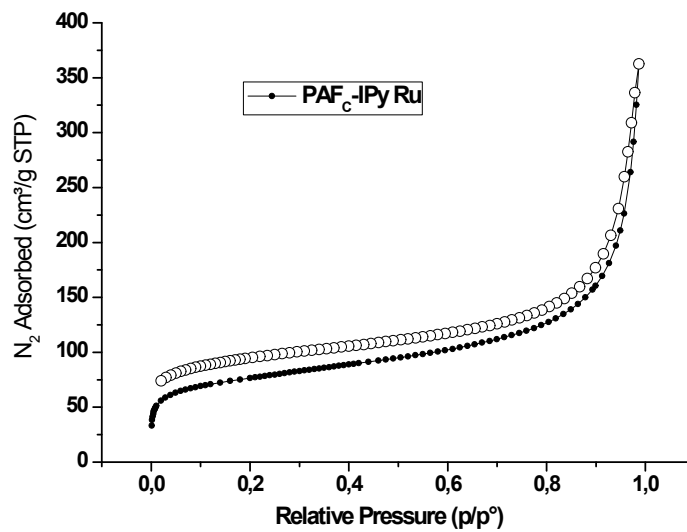


Figure S7f. Nitrogen sorption isotherms (filled circles: adsorption; open circles: desorption) of PAF_c-IPyRu at 77 K.

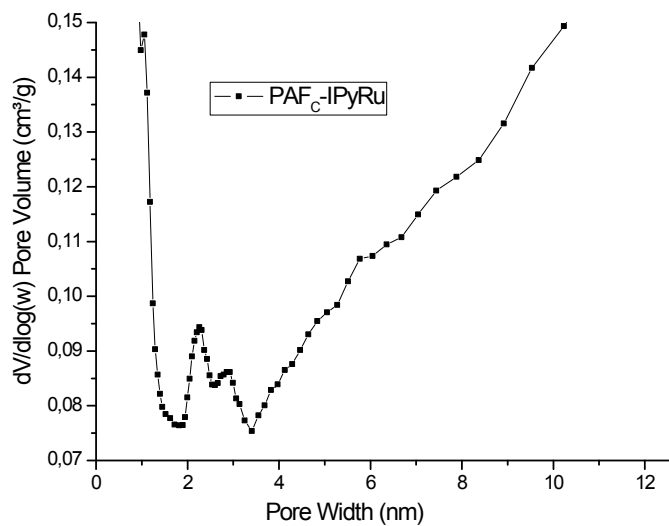


Figure S7g. Pore size distribution for PAF_c-IPyRu

Catalytic activity

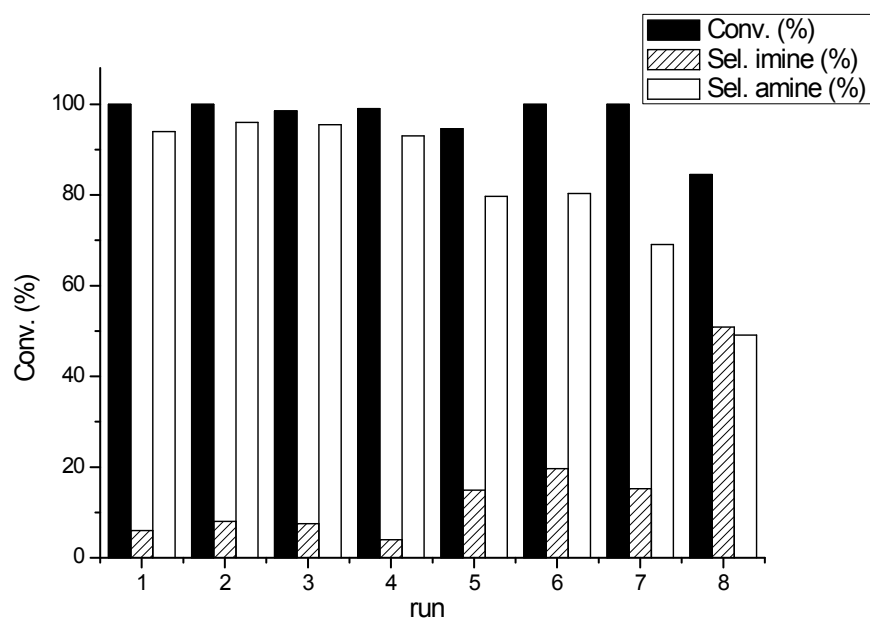


Figure S8. Recycling experiments of PAF_{sp}Ir in the *N*-alkylation of *p*-methoxy aniline with benzyl alcohol.

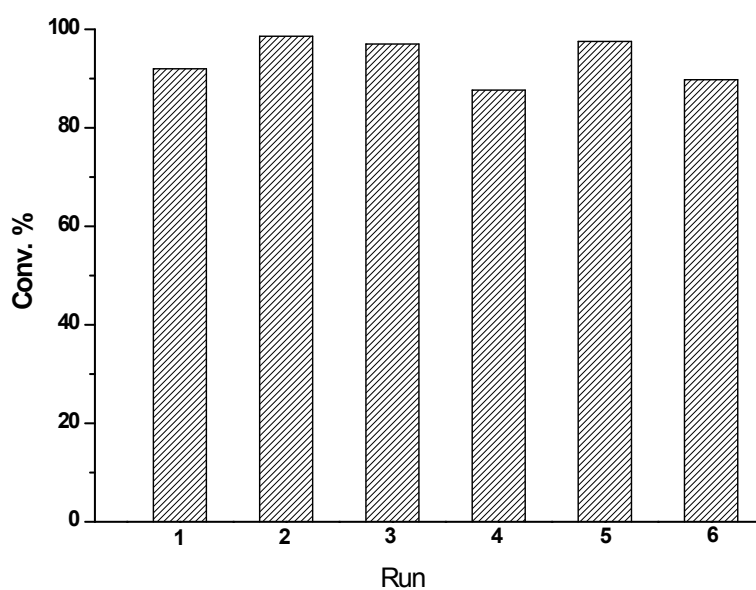
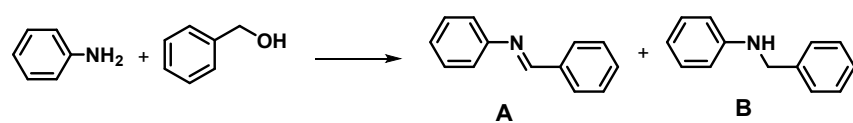
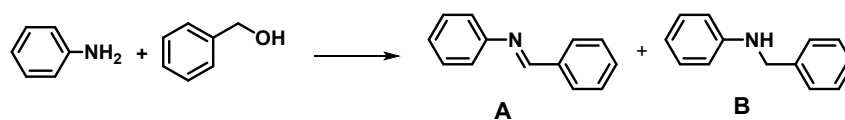


Figure S9. Recycling of PAF_c-IPyRu in transfer hydrogen from 2-Propanol to acetophenone.

Table S3. Alkylation of aniline with benzyl alcohol using PAFs-(NHC)Ir.^a

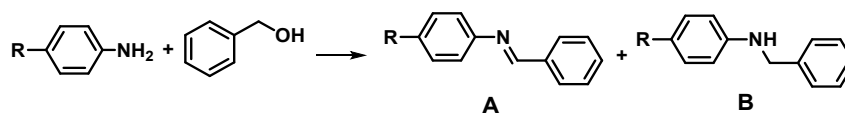
entry	catalyst	Base	catalyst ^b [mol %]	t (h)	yield ^c [%]	
					A	B
1	PAF _{spf} -IPyIr	---	2.0	24	7.3	---
2	PAF _{spf} -IPyIr	KOH	1.0	4	15.4	84.6
3	PAF _{spf} -IPyIr	KOH	0.5	4	49.2	50.8
				24	4.1	95.9
4	PAF _{spf} -IPyIr	KOH	0.2	4	73.5	17.0
				24	55.6	44.4
5	PAF _c -IMesIr	KOH	2.0	4	9.13	89.9

^aReaction conditions: aniline (0.104 mmol), benzyl alcohol (0.208), KOH (1.3 eq.), toluene (0.3 mL), 130 °C. ^bbased on iridium. ^cYields determined via GC and GC-MS.

Table S4. Alkylation of aniline with benzyl alcohol using **PAFs**-(NHC)M.^a

entry	catalyst	t (h)	Conv. ^b [%]	Sel. [%]	
				A	B
1	PAF _{spF} -IPyIr	4	100	49.2	50.8
2		24	100	4.1	95.9
3	PAF _{spF} -IMesIr	4	93.1	52.9	47.9
4		24	100	14.1	85.9
5	PAF _{spF} -IMesRu	4	66.6	61.9	38.1
6		24	91.7	33.8	66.2
7	PAF _c -IPyIr	4	82.4	73.3	26.7
8		24	100	22.1	77.9
9	PAF _c -IMesIr	4	92.4	52.4	47.6
10		24	100	20.8	79.2
11	PAF _c -IMesRu	4	72.7	56.9	8.1
12		24	100	94.3	5.7

^aReaction conditions: aniline (0.104 mmol), benzyl alcohol (0.208 mmol), KOH (1.3 eq.), toluene (0.3 mL), 130 °C, 0.5 mol(%) based on iridium. ^bYields determined via GC and GC-MS.

Table S5. Alkylation of anilines with benzyl alcohol using **PAFs**-(NHC)M in water.^a

entry	catalyst	mmol (%) ^b	Base	R	Selec. [%]	
					A	B
1		0.5	KOH	H	40.0 (24h)	-
2	PAF _{spf} -IPyIr	2.0	KOH	H	14.6 (24h)	16.1
3		0.5	K ₂ CO ₃	H	10.2 (24h)	4.9
4		0.5	(Et) ₃ N	H	-	-
5		0.5	(<i>i</i> Pr) ₂ NH	H	23.30 (48h)	
6	PAF _c -IMesIr	3.0	KO ^{<i>t</i>} Bu	H	51.23 (24h)	6.1
7		3.0	KOH	H	64.1 (24h)	3.4
8		3.0	KOH	CH ₃	91.3 (24h)	-
9		3.0	KOH	Cl	95.6 (24h)	-
10		3.0	KOH	OCH ₃	62.3 (24h)	37.7

^aReaction conditions: aniline (0.104 mmol), benzyl alcohol (0.208 mmol), 100 °C. ^bbased on iridium. ^cYields determined via GC and GC-MS.

Table S6. Recycling experiments for the coupling reaction of benzyl alcohol and 4-chloroaniline in water.^a

entry	time (h)	Conv. ^b [%]	Selec. [%]	
			A	B
1	4	10.7	10.7	---
	24	95.6	95.6	---
2	4	47.8	47.8	---
	24	100	54.65	--
3	4	9.25	9.25	---
	24	58.1	58.1	---
4	4	11.4	11.4	---
	24	57.4	57.4	---

^a Reaction conditions: 4-chloroaniline (0.104 mmol), benzyl alcohol (0.208 mmol), KOH (1.3 eq.), 130 °C, 0.3 mL water, 3.0 % mol (%) based on iridium. ^b Determined by GC and GC-MS analysis.

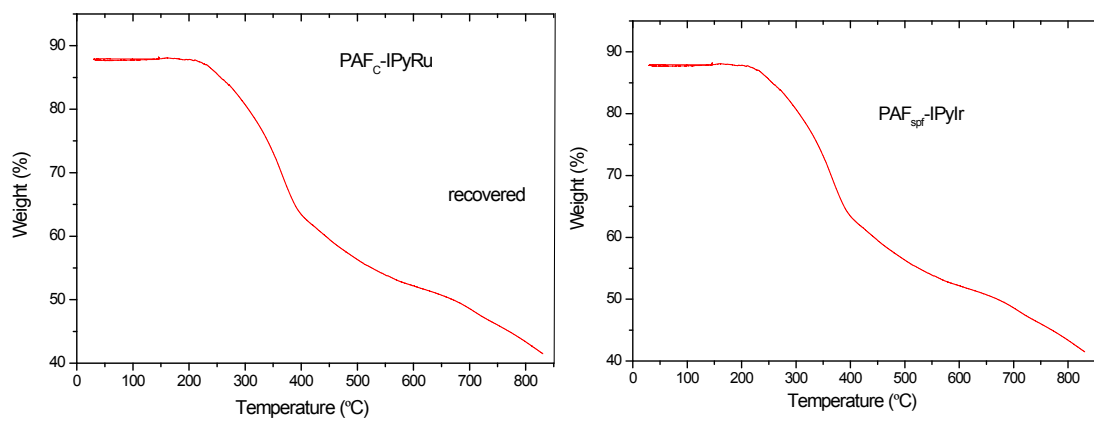


Figure S10. TGAs of recovered catalysts after four cycles.

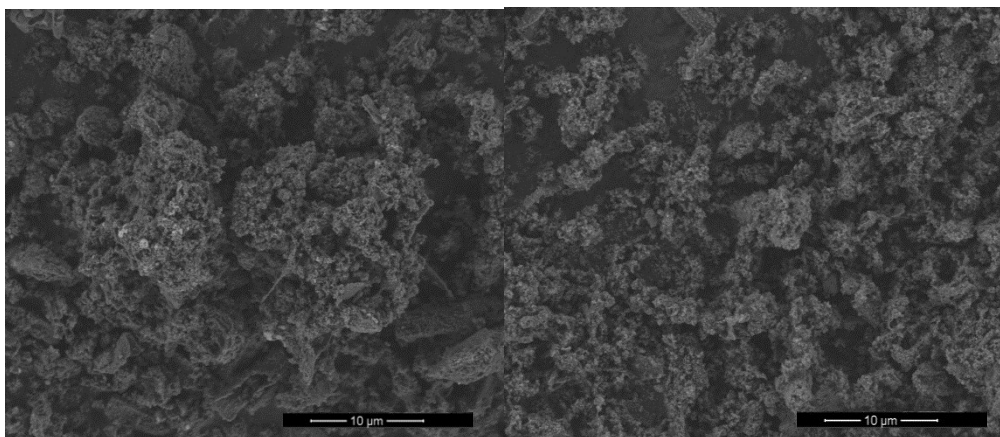


Figure S11. SEM image of $\text{PAF}_C\text{-IMesIr}$ and $\text{PAF}_{\text{spr}}\text{-IPyIr}$ recovered after recycling.