revised

Supporting Information

Photochemical reactions of fluorinated pyridines at half-sandwich rhodium complexes: competing pathways of reaction

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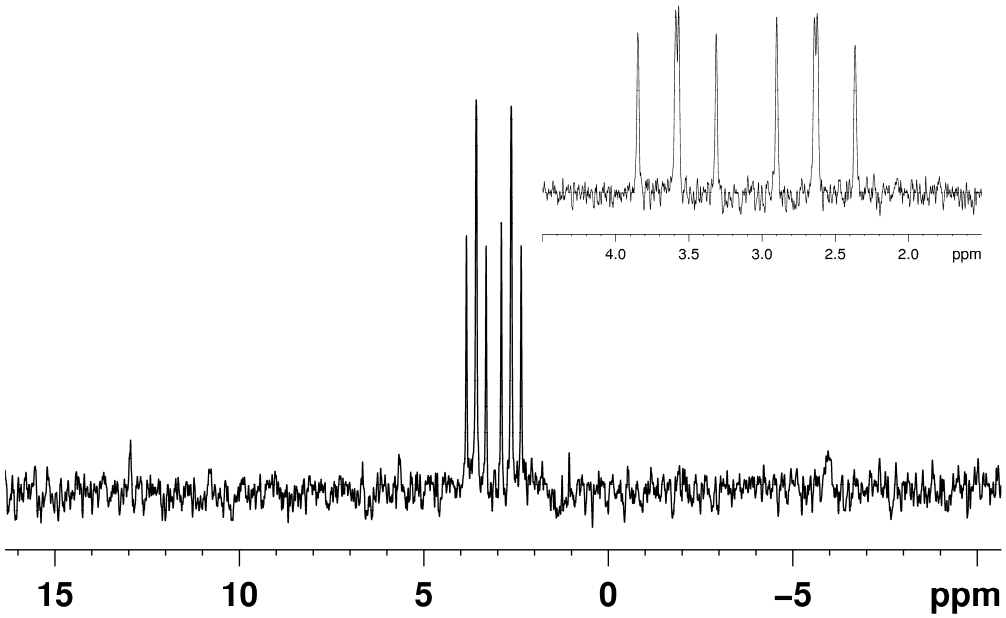
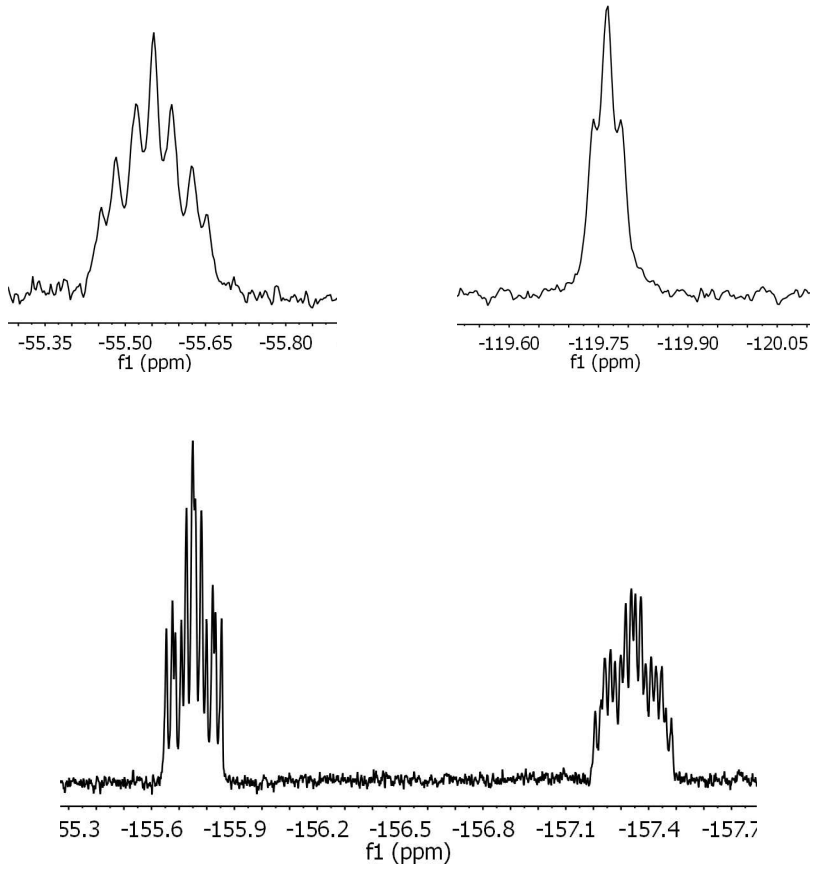


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum for complex **2** in C_6D_6 showing a doublet of doublets of doublets due to coupling of ^{31}P to ^{103}Rh and two inequivalent fluorines.



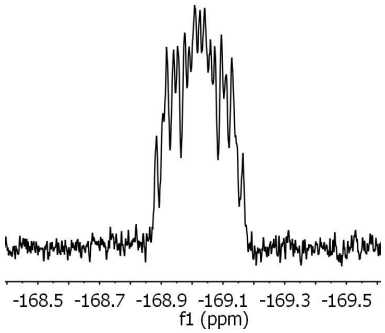


Figure S2. Enlargement of the five resonances from ^{19}F NMR spectrum in C_6D_6 belonging to the five inequivalent fluorines on the pyridyl ring.

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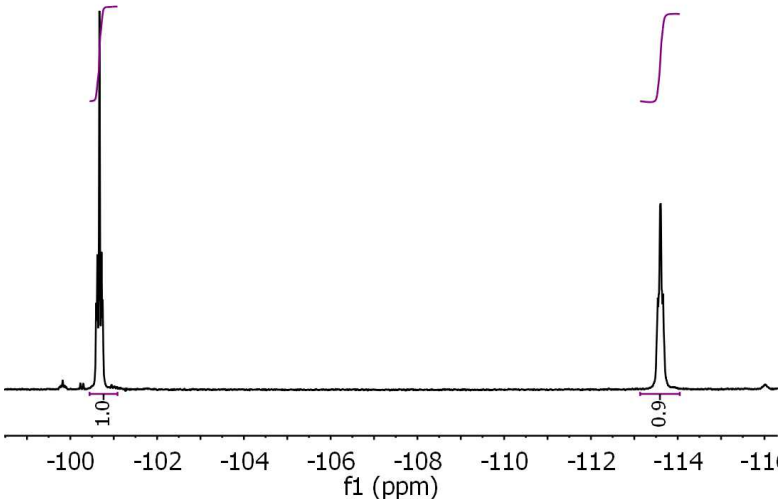

Figure S3. ^{19}F spectrum in C_6D_6 for complex **3**. The two resonances belong to the two sets of inequivalent fluorines.

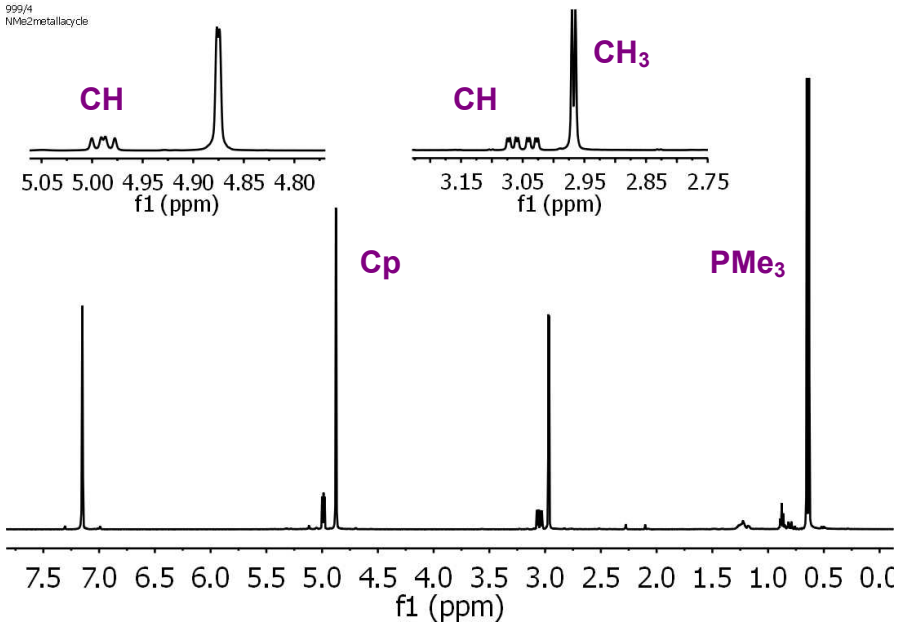

Figure S4. ^{1}H NMR spectrum of complex **4** in C_6D_6.

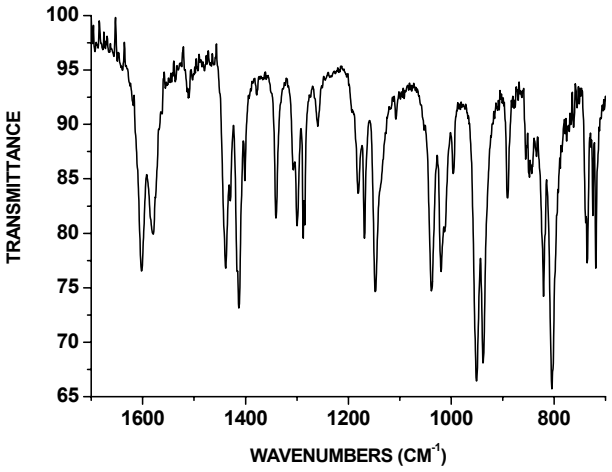

Figure S5. Solid state IR spectrum (ATR) of **4**.

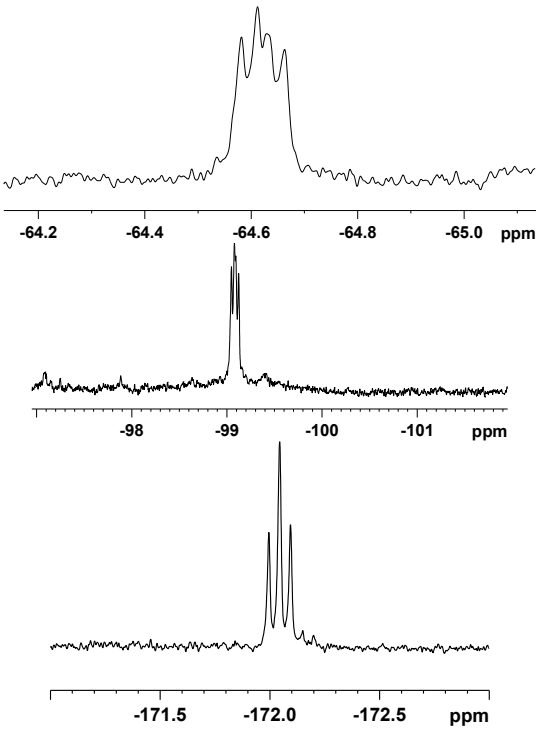

Figure S6. Three ^{19}F resonances for complex **5** in C_6D_6.

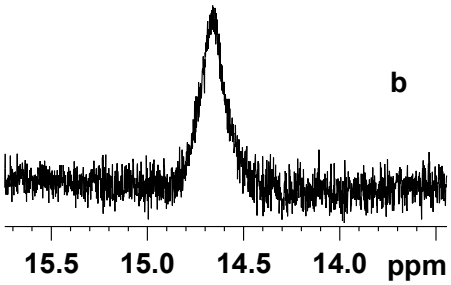

Figure S7. Broad peak at low field in the ^{1}H NMR spectrum assigned to HF.

Preparation of $C_5F_4N(OCD_3)$.

Na (68 mg, 2.96 mmol) was slowly add to a solution of deuterated methanol (5 ml). Upon complete reaction of Na was reacted, 500 mg of C_5F_5N (2.96 mmol) was added on drop-wise, the solution was stirred and heated under reflux for 30 min. The product was treated with water (15 ml) and extracted with ether (3 × 10 ml). The organic extract was dried over $MgSO_4$ and the solvent removed by rotary evaporator giving a colourless oil.

^{2}D NMR ($CHCl_3$, 300 K): δ 3.28 (CD_3).

^{19}F NMR: δ - 91.9 (2 F,m) δ - 160.9 (2 F,m).

EI mass-spec.: m/z 184.0336 (M^+) 100%, (calculated 184.0339).

IR (liquid film) ν(CD) / cm^{-1} 2082 (s), ν(CF) / cm^{-1} 900-1000 (s), ν(CN) / cm^{-1} 1648 (s), ν(ring vibration) 1480 (s).

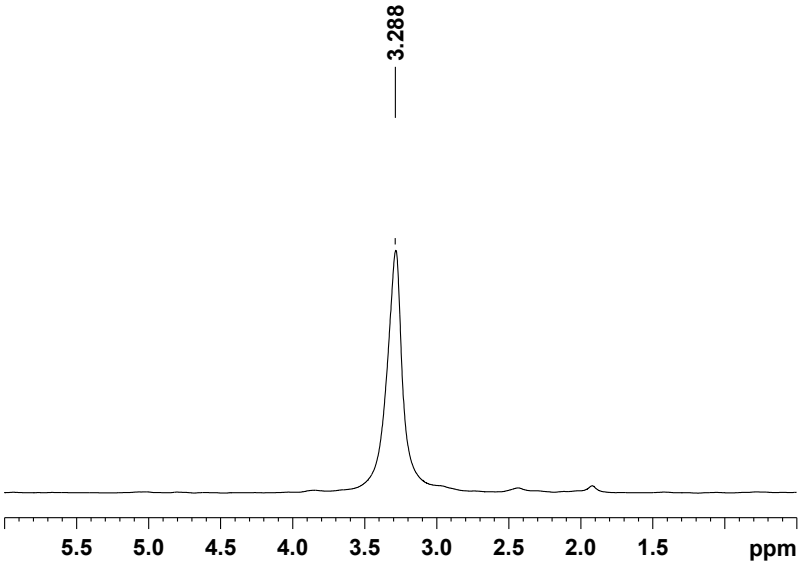

Figure S8. ^{2}H NMR spectrum of $C_5F_4N(OCD_3)$. in $CDCl_3$.

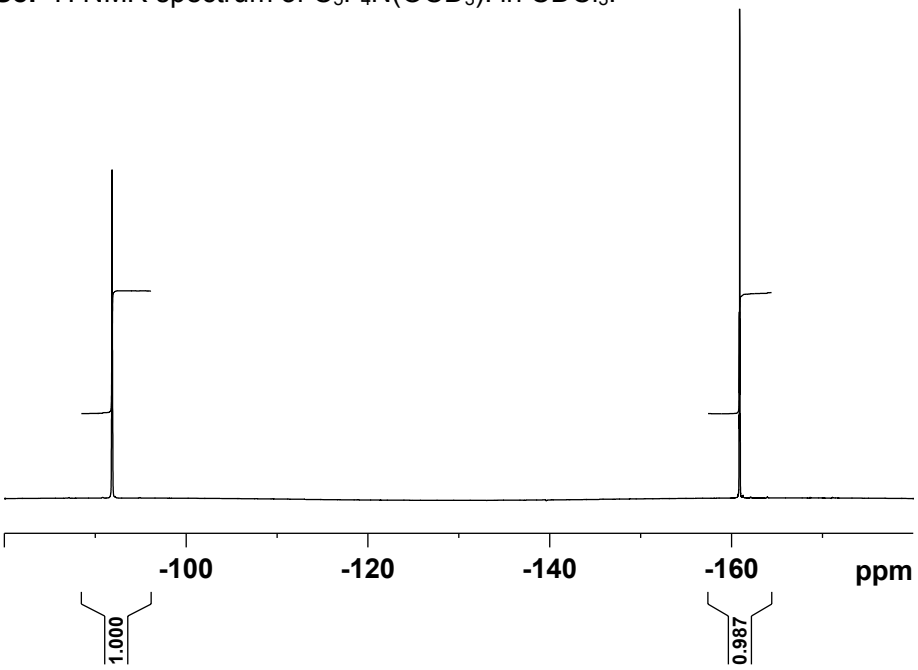

Figure S9. ^{19}F spectrum in $CDCl_3$ for $C_5F_4N(OCD_3)$. The two resonances belong to the two sets of inequivalent fluorines.

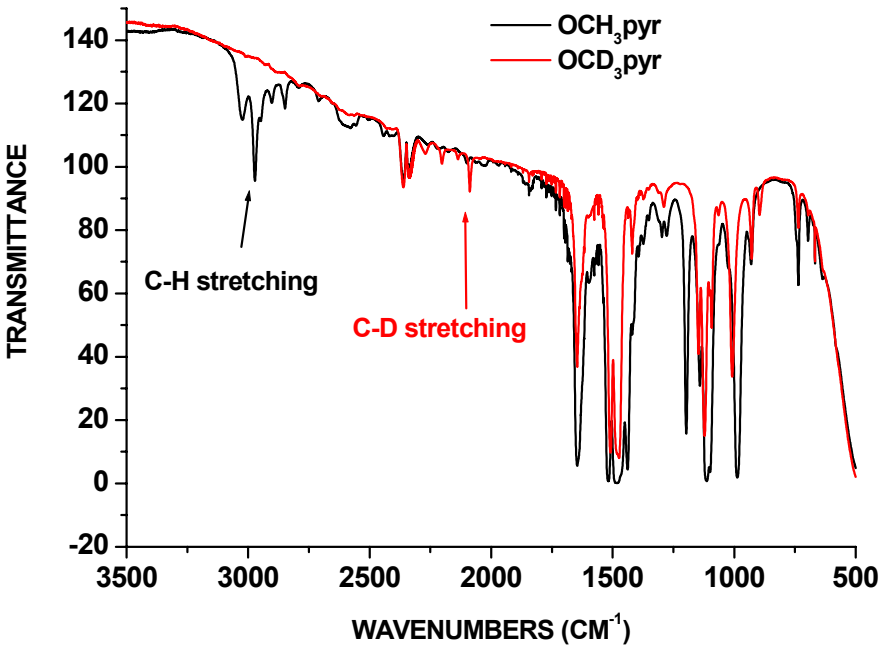

Figure S10. Liquid film IR spectrum of $C_5F_4N(OCD_3)$, red, and of $C_5F_4N(OCH_3)$ black.

Table S1. Crystallographic data and refinement data for **2**, **3**, and **4**

	2	**3**	**4**
Formula	$C_{13}H_{14}F_5NPRh$	$C_{13}H_{15}F_4NPRh$	$C_{15}H_{19}F_3N_2PRh$
M	413.13	395.14	418.20
a/Å	10.0121(13)	10.54836(14)	8.4609(14)
b/Å	12.8944(16)	8.63903(11)	16.312(3)
c/Å	10.9517(14)	16.43266(19)	11.9985(19)
β/deg	90.00	106.8831(13)	100.907(3)
V/ Å^3	1413.9(3)	1432.93(3)	1626.1(5)
T/K	110(2)	110(2)	110(2)
Space group	*P*na21	$P2_1/n$	*P*2(1)/c
Z	4	4	4
μ(Mo Kα)/mm^{-1}	0.71073	1.336	0.71073
Reflns measd	14753	13834	16531
Reflns indep	4060	4625	4045
R_{int}	0.0660	0.0248	0.0362
Final *R* [I> 2σ(I)]	R_1 = 0.0393	R_1 = 0.0255	R_1 = 0.0312
	wR_2 = 0.0922	wR_2 = 0.0560	wR_2 = 0.0770
Final *R* (all data)	R_1 = 0.0439	R_1 = 0.0323	R_1 = 0.0398
	wR_2 = 0.0953	wR_2 = 0.0601	wR_2 = 0.0809
GooF on F^2	1.034	1.064	1.055
Largest diff. peak and hole (e Å^{-3})	2.245 and -0.732	1.58 and -0.73	1.796 and -0.469