

Supplementary Information for

Steric and electronic effects on acetate assisted cyclometallation of phenyl pyridines at $[MCl_2Cp^*]_2$ (M = Ir, Rh)

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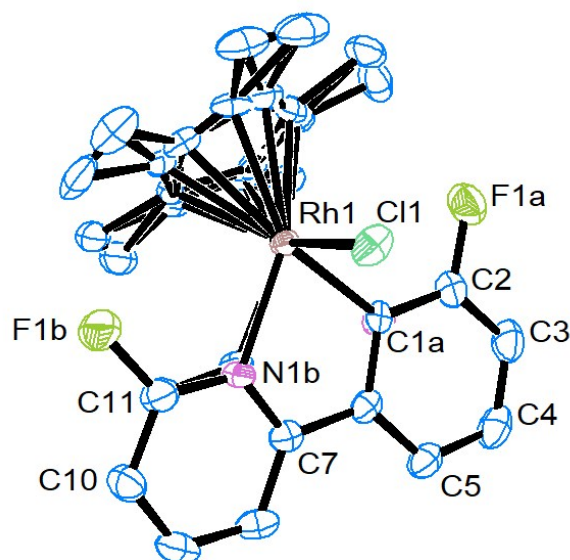


Figure S1 Molecular structure of *ortho* **2b-F** 50% displacement ellipsoids and H atoms have been omitted for clarity. There is a 50:50 C1:N1 and F: H disorder. The methyl's and ring carbon atoms of the Cp* are also disordered each over two sites (50:50).

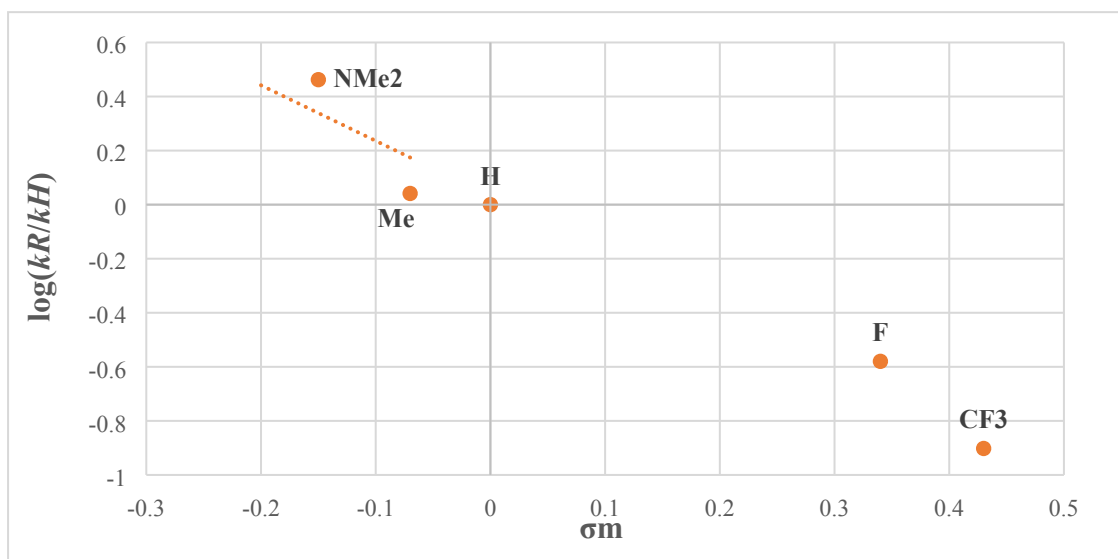


Figure S2 Hammett plot for relative rates of formation of *meta*-cyclometallated complexes of Rh $\log(k_R/k_H)$ against σ_m .

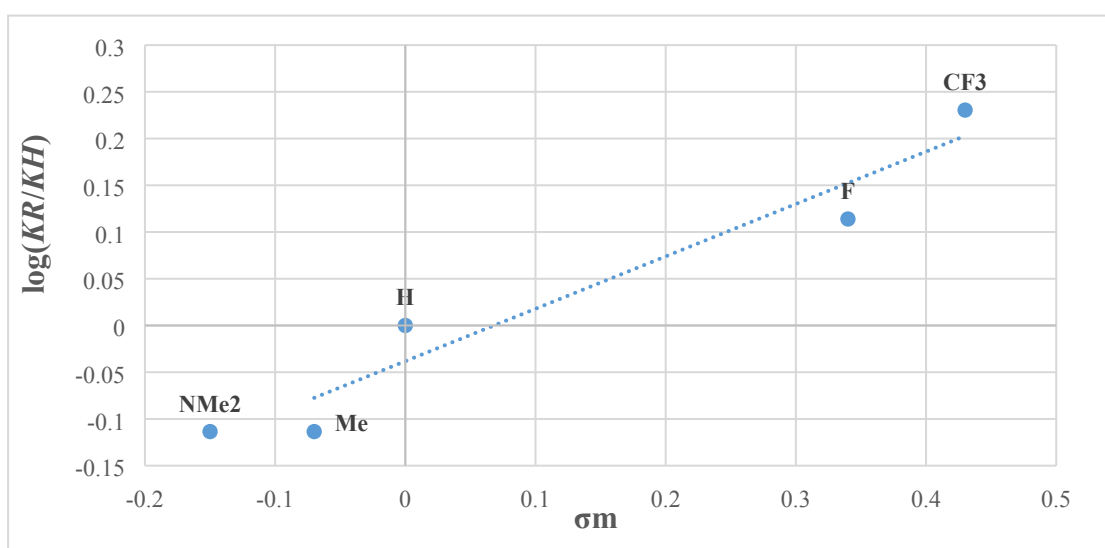


Figure S3 Hammett plot of thermodynamic ratios $\log(K_R/K_H)$ against σ_m for Rh.

Table S1: Deuteration of 2a,b-R in CD₃OD.

Entry	R	M	Time	<i>o:p</i>	% D in site 5 (<i>ortho</i> -isomer)	%D in site 8 (<i>para</i> -isomer)
1	CF ₃	Ir	2 h	<i>para</i> -only ^a	-	N.D.
2	CF ₃	Rh	2 h	<i>para</i> -only ^a	-	N.D.
3	OMe	Ir	2 h	1:1:1	N.D.	N.D.
4	OMe	Rh	15 min.	1:2.2	N.D.	20
5	OMe	Rh	2 h	1:2.5	50	>80

N.D. not detected by ¹H and ²H NMR spectroscopy

^aNo *ortho*-isomer was detected by ¹⁹F NMR spectroscopy

Table S2: Competition experiments to form *meta*-substituted complexes of Ir^a

Entry	R ₁	R ₂	A:B, 15 min, rt, DCM:MeOH	A:B, 15 min, rt, TFE	A:B, 2 h, 60°C, TFE
1	Me	NMe ₂	1:1.4	-	-
2	H	NMe ₂	-	1:1.2	1.3:1
3	H	Me	1:1.3	1.1:1	1.3:1
4	F	H	1:2.9	1:1.3	1.3:1 ^a
5	CF ₃	H	1:5.0	1:1.4	1.7:1 ^a
6	CF ₃	F	1:1.8	-	-

^a 90 °C, 2 hours

Table S3: Competition experiments to form *meta*-substituted complexes of Rh.

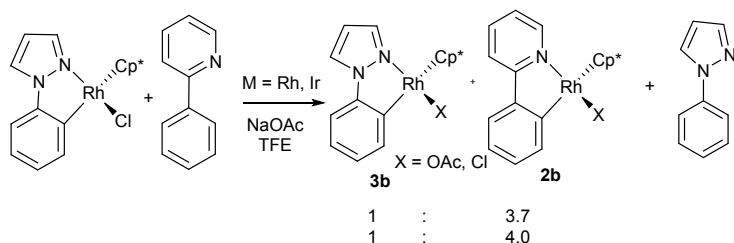
Entry	R ₁	R ₂	DCM:MeOH		TFE	
			A:B, 15 min., rt	A:B, 3 days, 50°C	A:B, 15 min., rt,	A:B, 2h, 60 °C
1	H	NMe ₂	1:2.9	1:1.2 ^a	1.2:1	1.4:1
2	H	Me	1:1.1	1.2:1	1.2:1	1.2:1
3	F	H	1:3.8	1.1:1 ^b	2.8:1	2.8:1
4	CF ₃	F	1:2.1	1:1.7	-	-
5	CF ₃	H	-	-	3.2:1	3.2:1

^a 2 days;

^b 2 hours

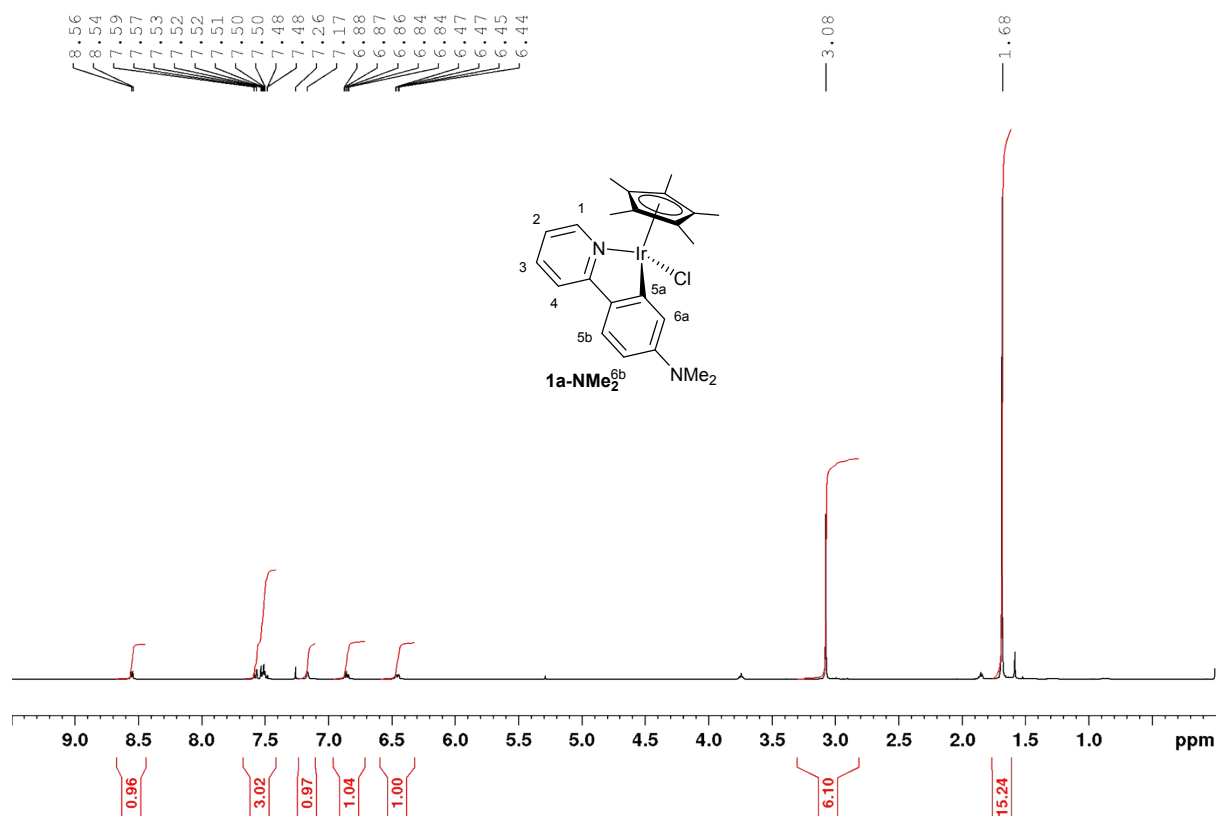
Exchange of phenylpyrazole by 2-phenylpyridine

A Schlenk flask equipped was charged with the Rh phenylpyrazole complex **3b** (0.0395 mmol), NaOAc (0.080 mmol) and TFE (2 mL) and 2-phenylpyridine (0.045 mmol) were added and stirred at rt. The reaction with Rh reached 80% conversion to **2b-H** after 1 hour.

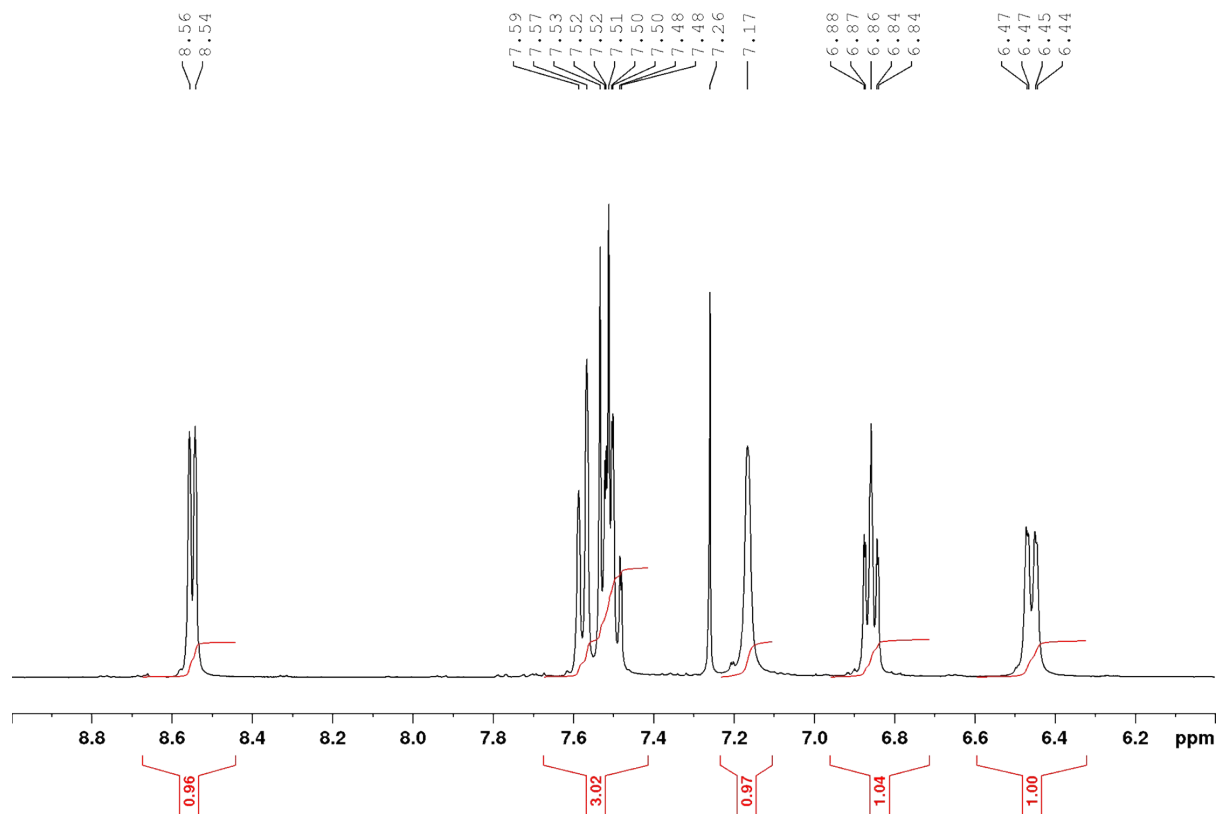


Scheme S1 exchange of phenylpyrazole by 2-phenylpyridine at Cp*Rh

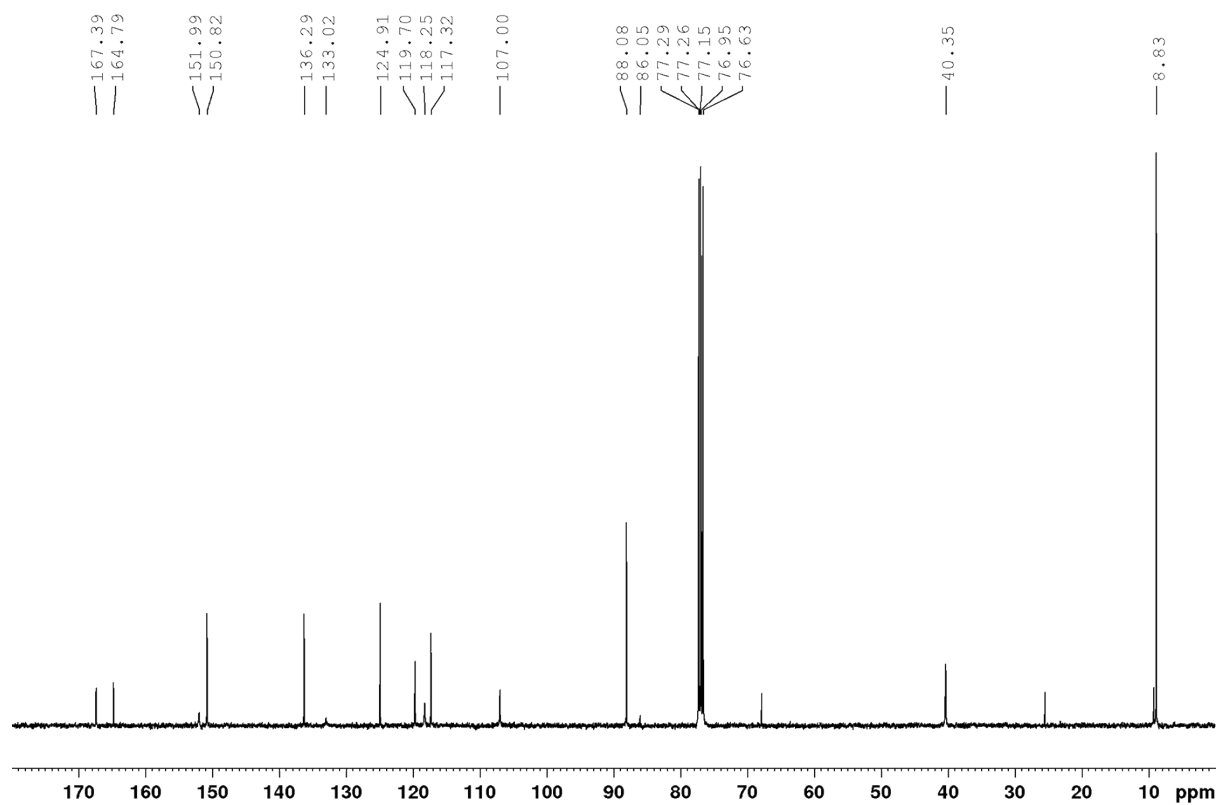
¹H NMR 1a-NMe₂



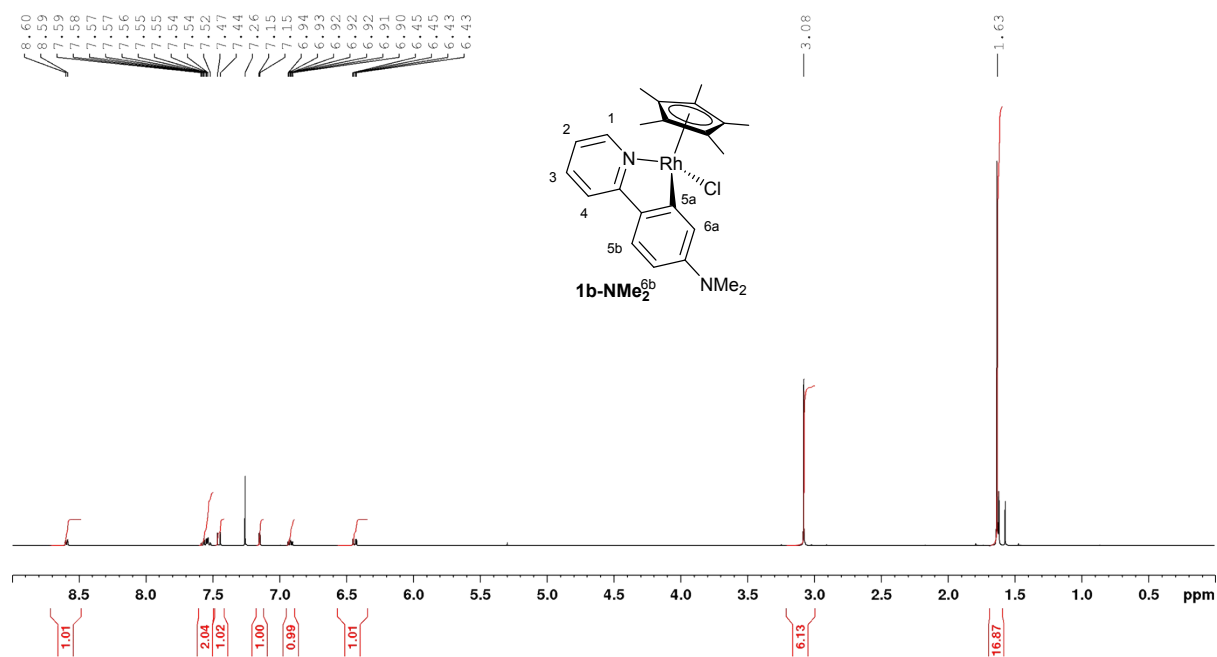
Expansion of ¹H NMR



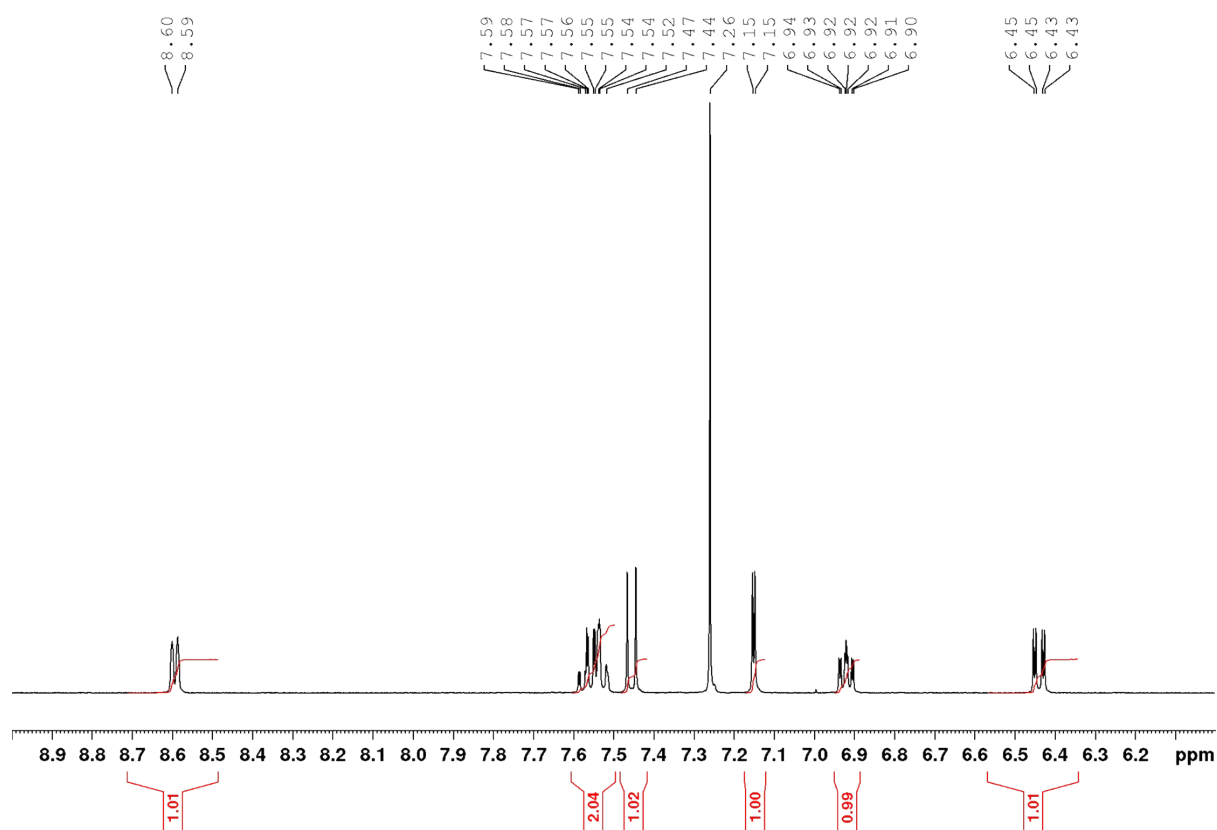
^{13}C NMR 1a-NMe₂



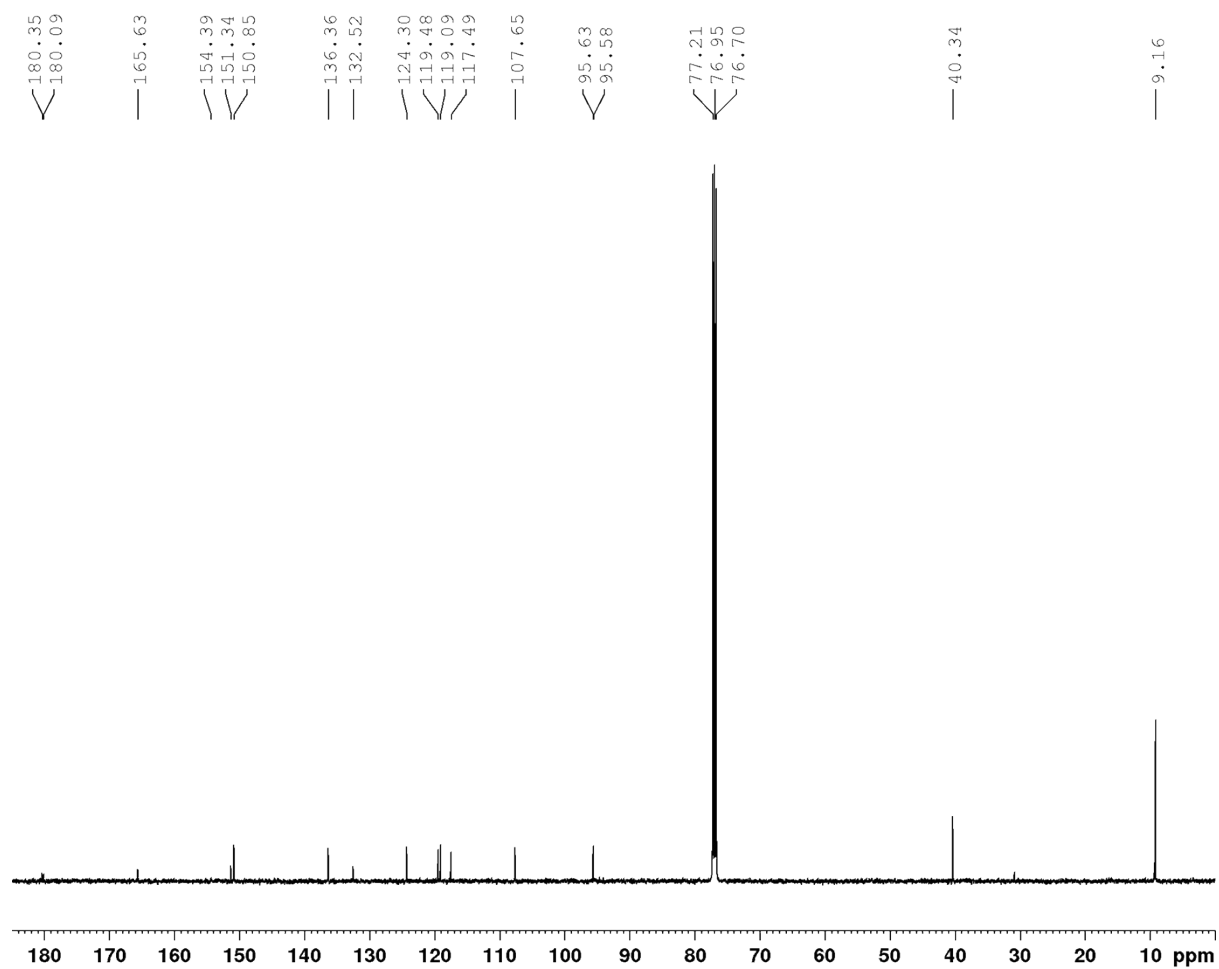
¹H NMR 1b-NMe₂



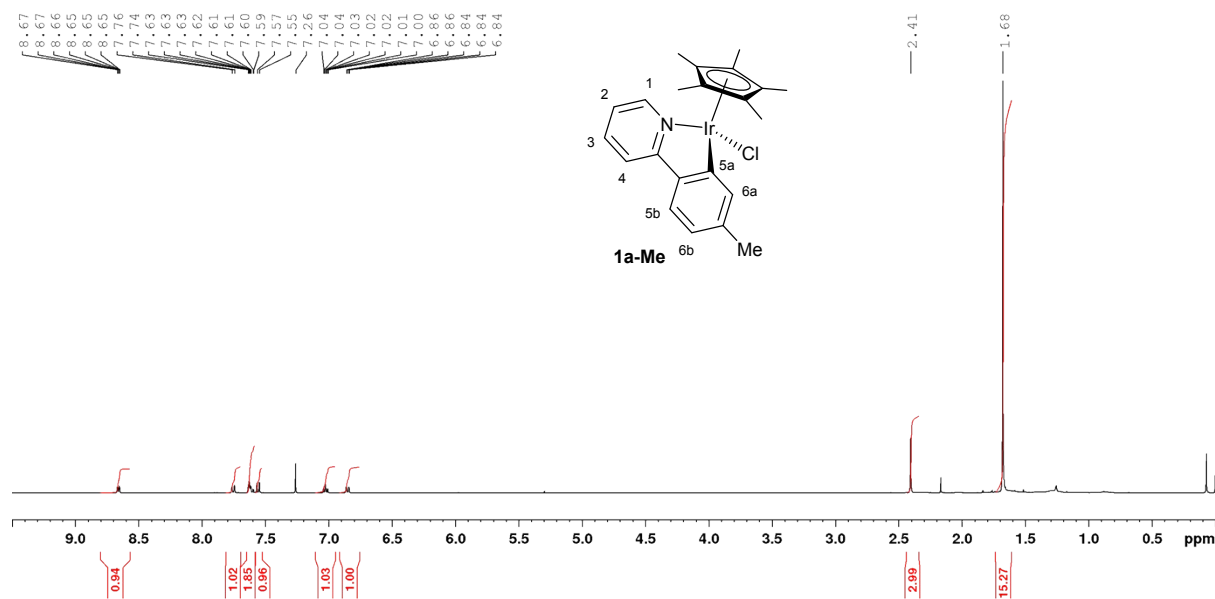
Expansion of ¹H NMR



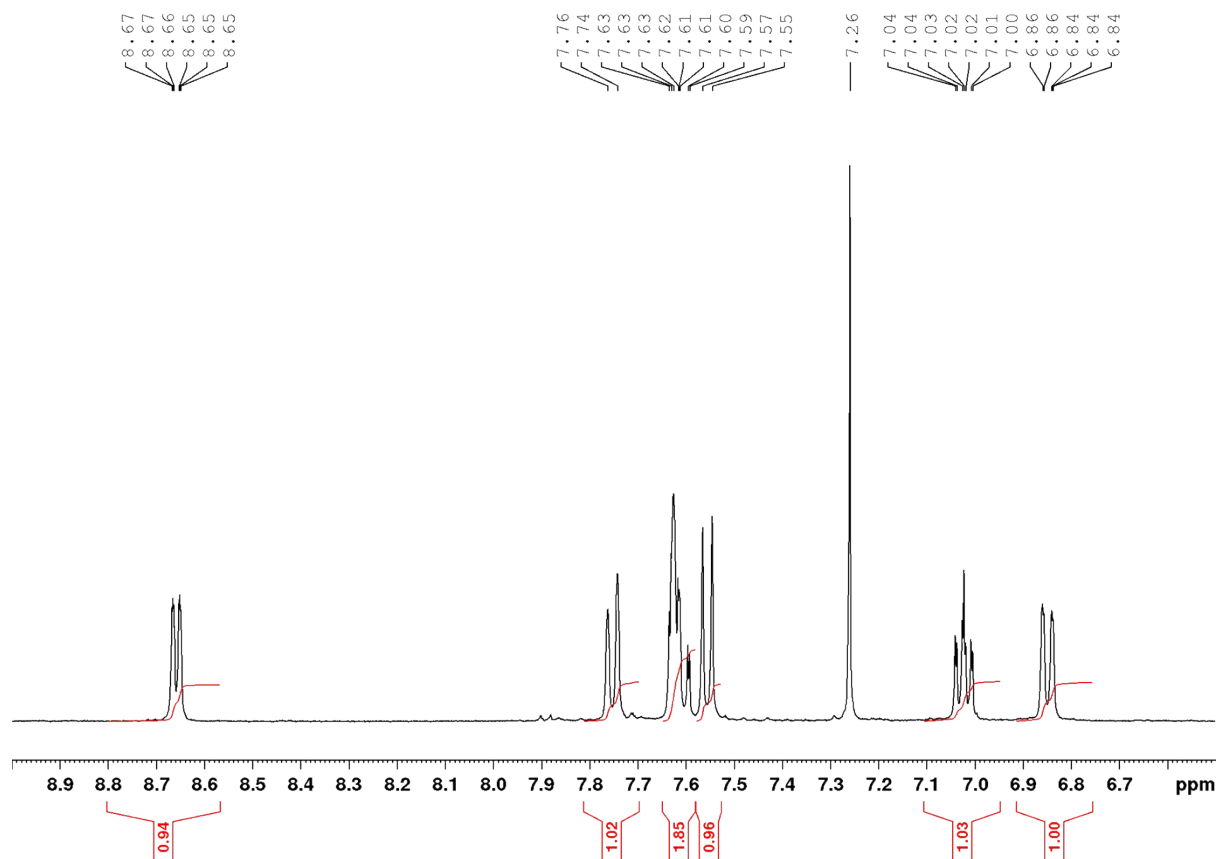
^{13}C NMR 1b-NMe₂



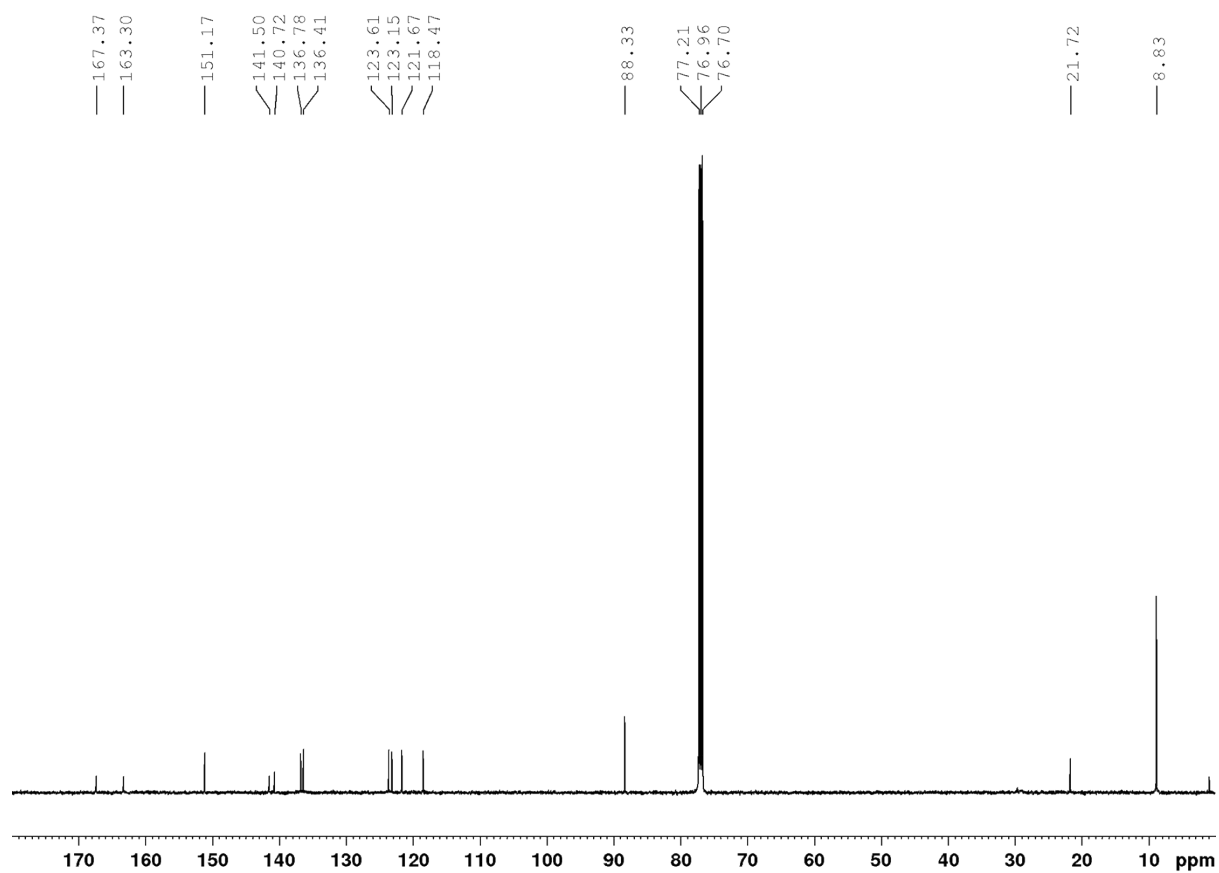
¹H NMR 1a-Me



Expansion of ¹H NMR of 1a-Me



^{13}C NMR of 1a-Me



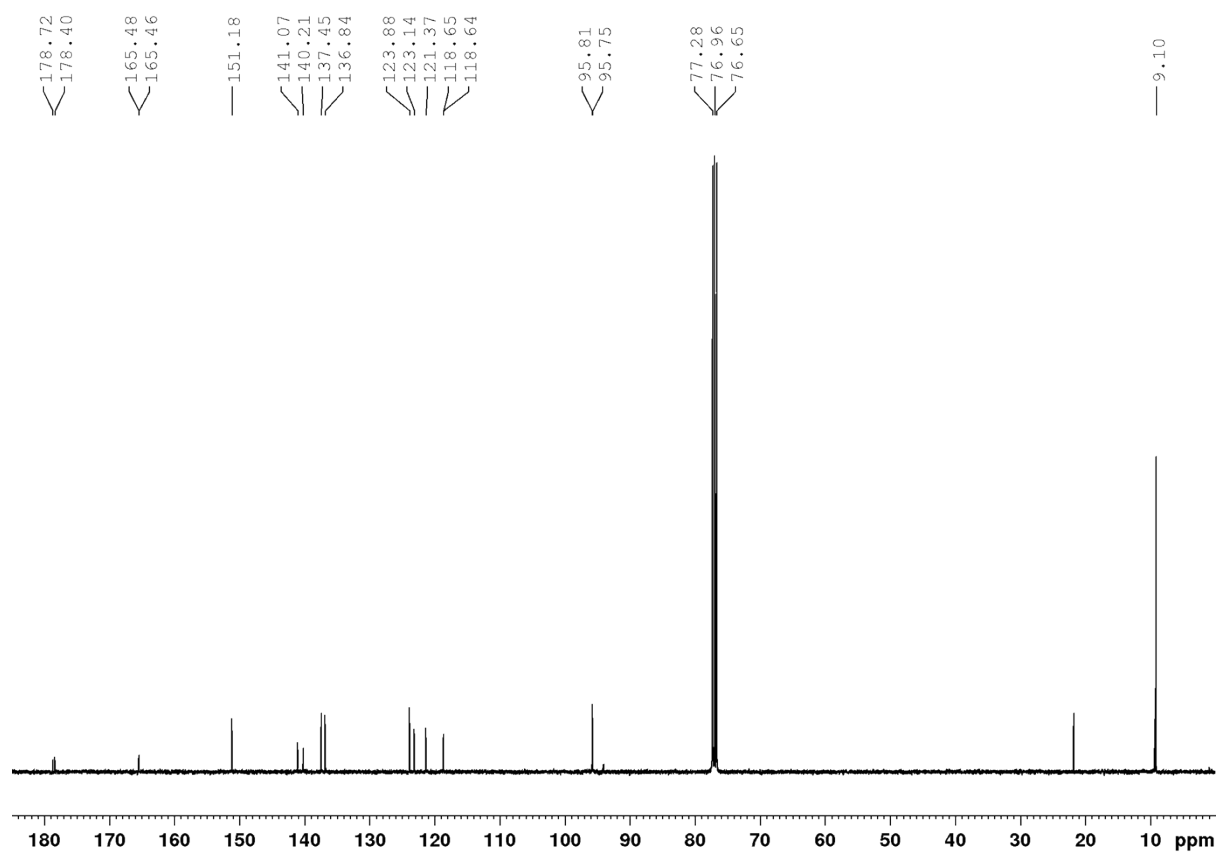
1b-Me

Chemical structure of **1b-Me** is shown as an inset. It features a rhodium (Rh) center coordinated by a 1-methyl-2-phenylpyrrolidine ligand (labeled 5a) and a 1-methyl-2-phenylpyrrolidine ligand (labeled 6a). The structure also includes a 1-methyl-2-phenylpyrrolidine ligand (labeled 1b-Me) and a 1-methyl-2-phenylpyrrolidine ligand (labeled 6b).

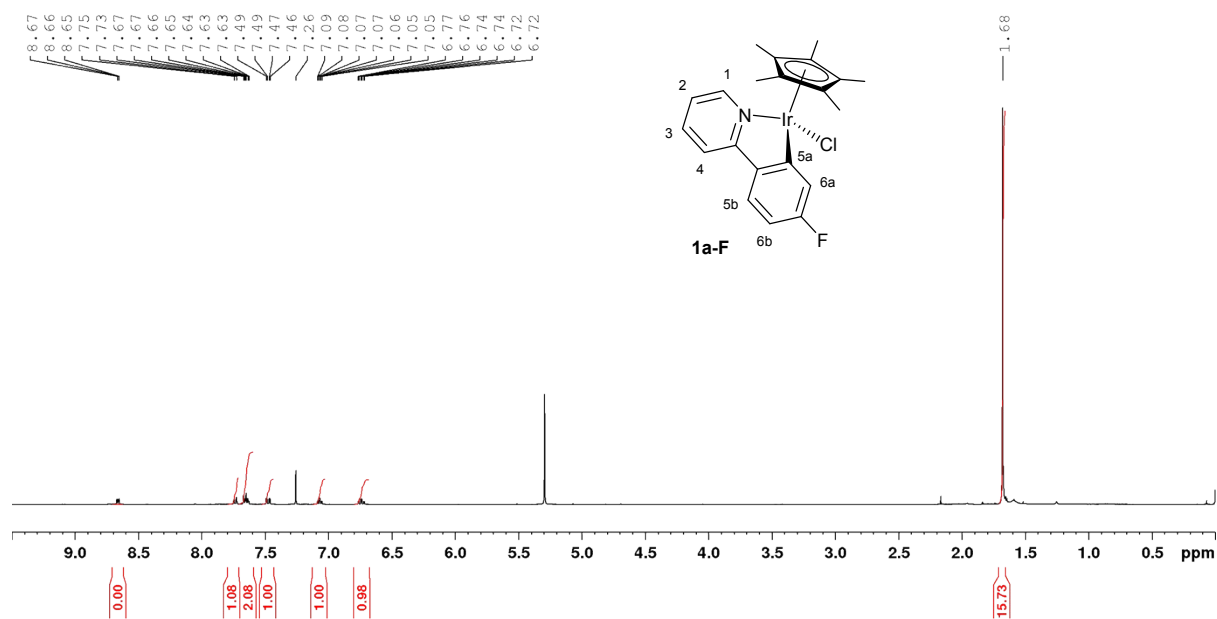
The ^1H NMR spectrum (CDCl₃) shows the following peaks and integrations:

- Aromatic and heterocyclic protons: 6.5–8.8 ppm (integrations: 0.97, 1.04, 0.99, 1.03, 1.00, 1.00).
- Methyl group (CH₃): 2.41 ppm (integration: 2.98).
- Reference peak (TMS): 0 ppm.

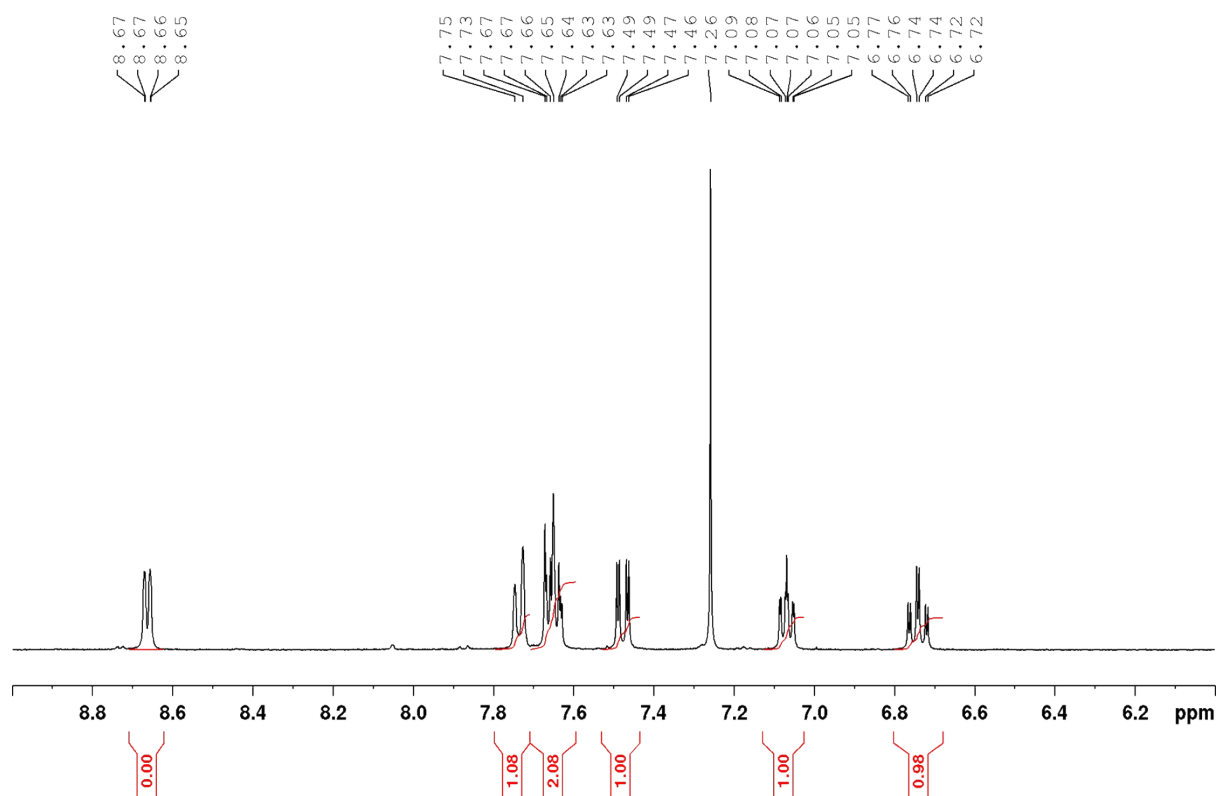
^{13}C NMR of 1b-Me



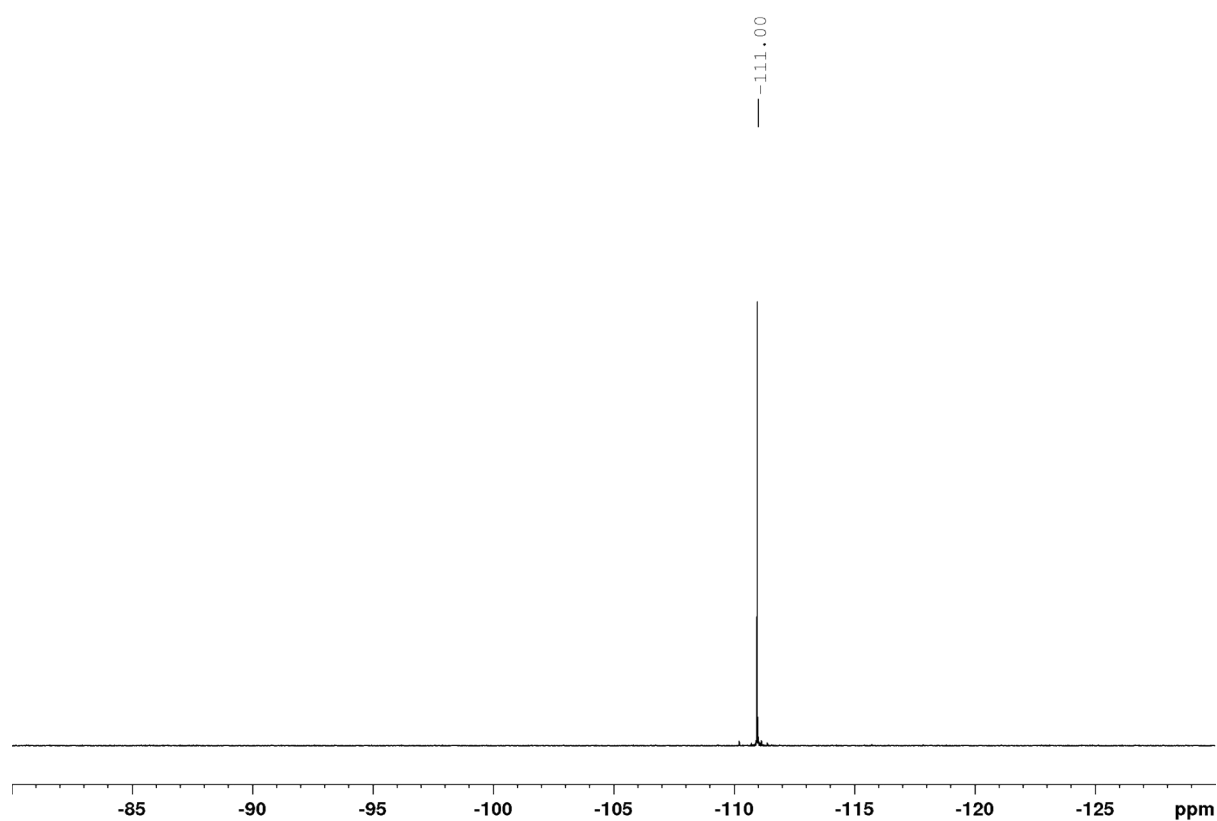
¹H NMR 1a-F



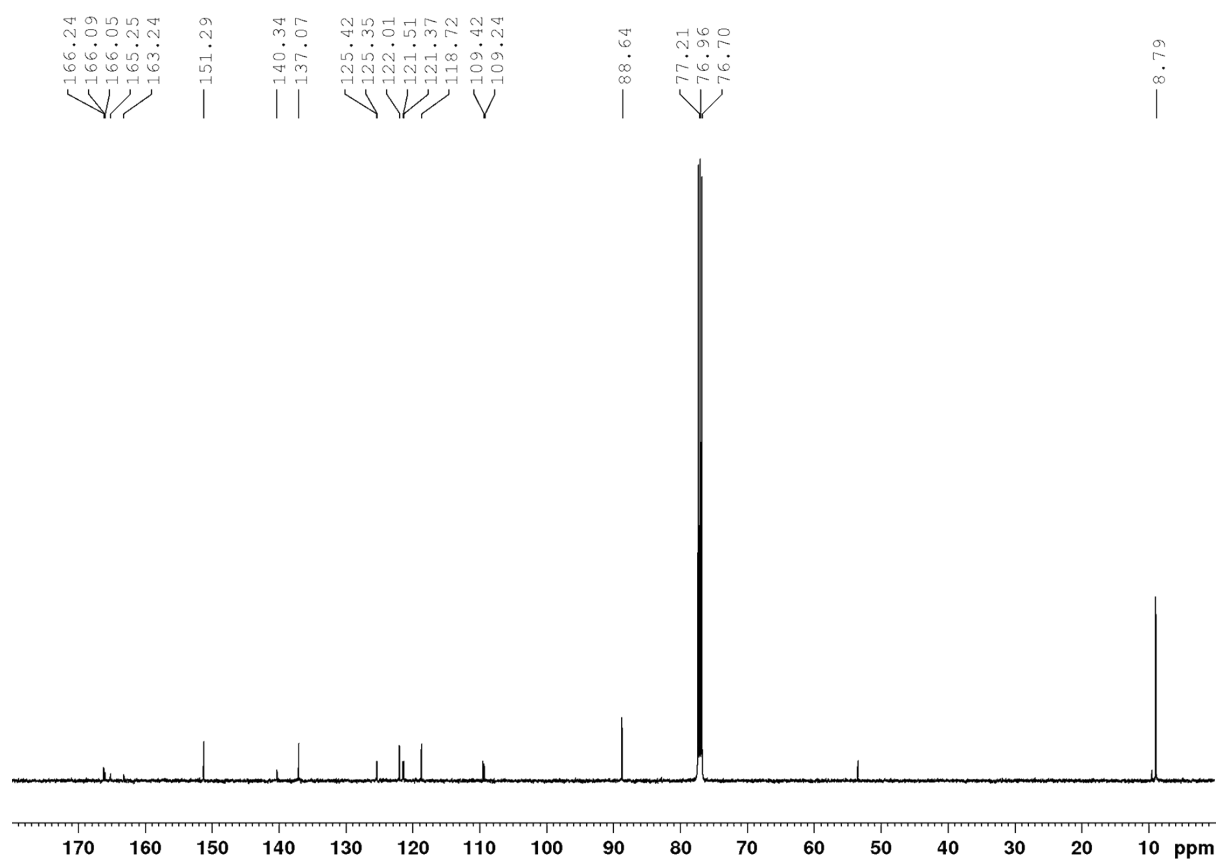
Expansion of ¹H NMR 1a-F



^{19}F NMR of 1a-F



^{13}C NMR of 1a-F

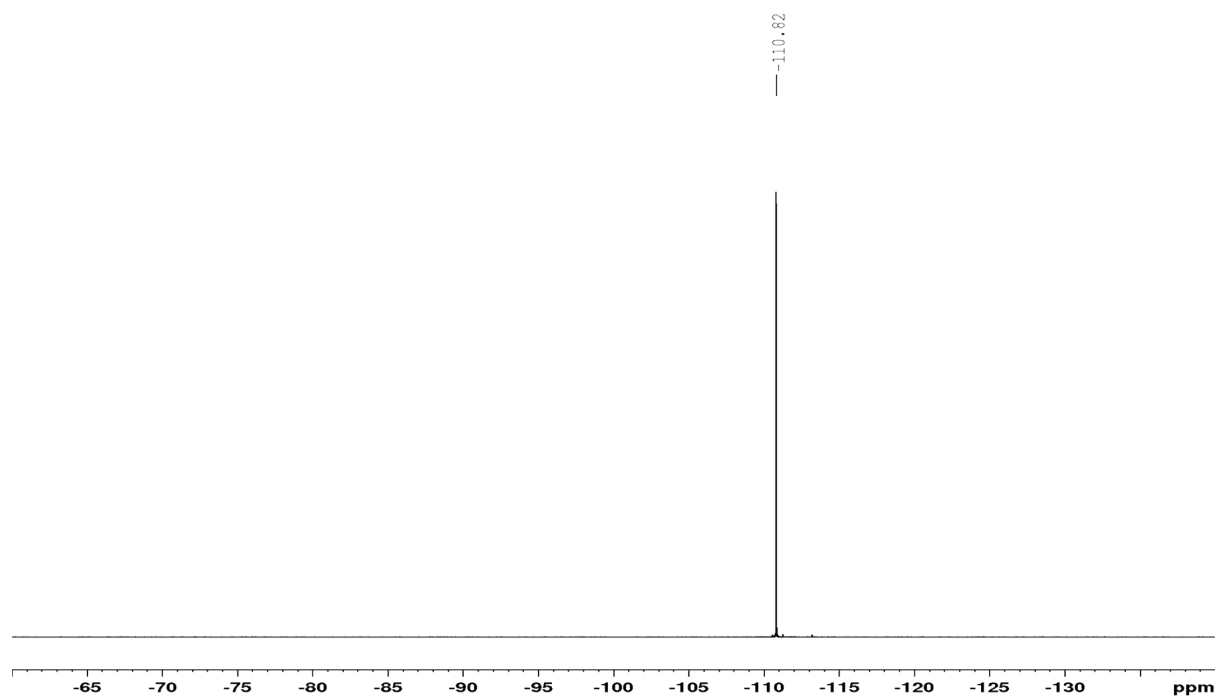


Chemical structure of 1a-F: Fc1ccc(cc1[C@H]2C=CC=C2N2C=CC=CC=C2)[Rh](Cl)(C3=CC=CC=C3)C4=CC=CC=C4

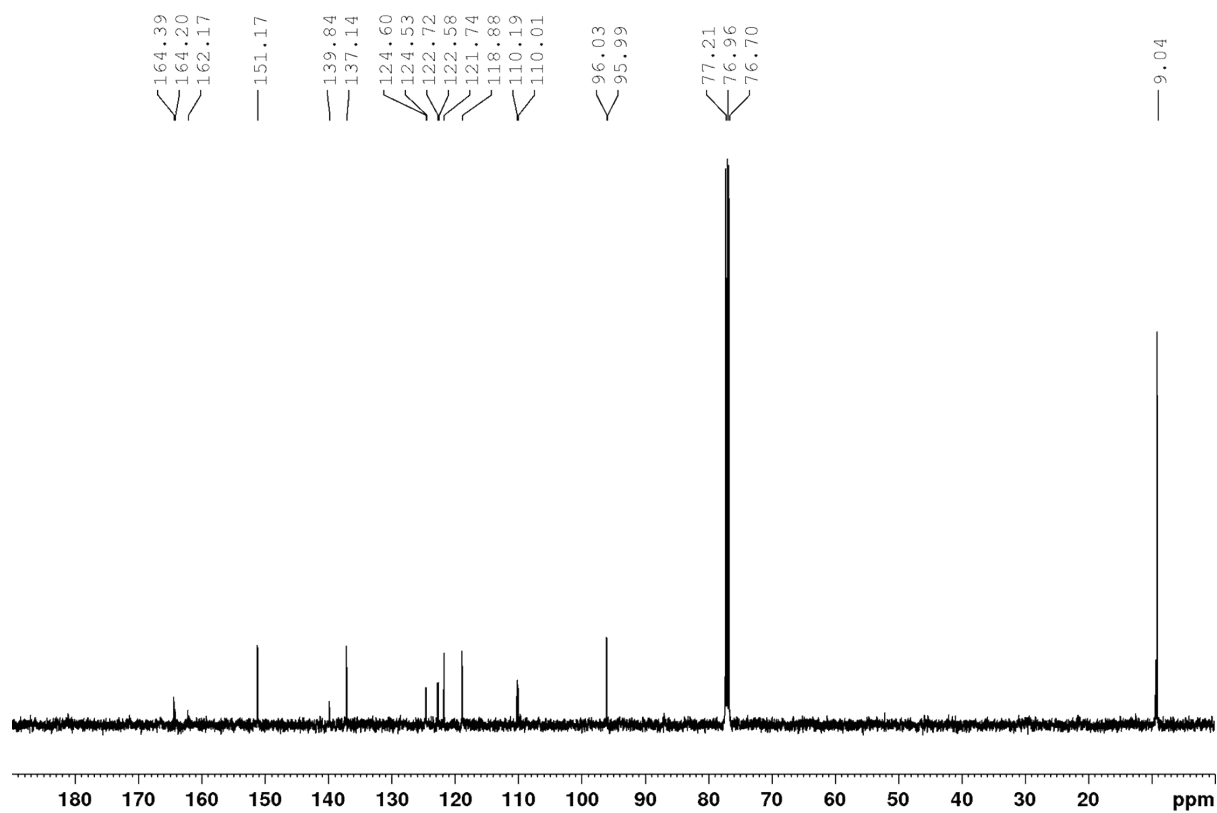
¹H NMR spectrum (CDCl₃):

Chemical Shift (ppm)	Integration
8.70, 8.69, 7.72, 7.72, 7.70, 7.69, 7.68, 7.67, 7.60, 7.58, 7.56, 7.51, 7.51, 7.51, 7.49, 7.49, 7.26, 7.26, 7.13, 7.13, 7.12, 7.11, 7.10, 7.10, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72	1.03, 2.07, 1.03, 1.00, 1.02, 1.00
1.63	15.34

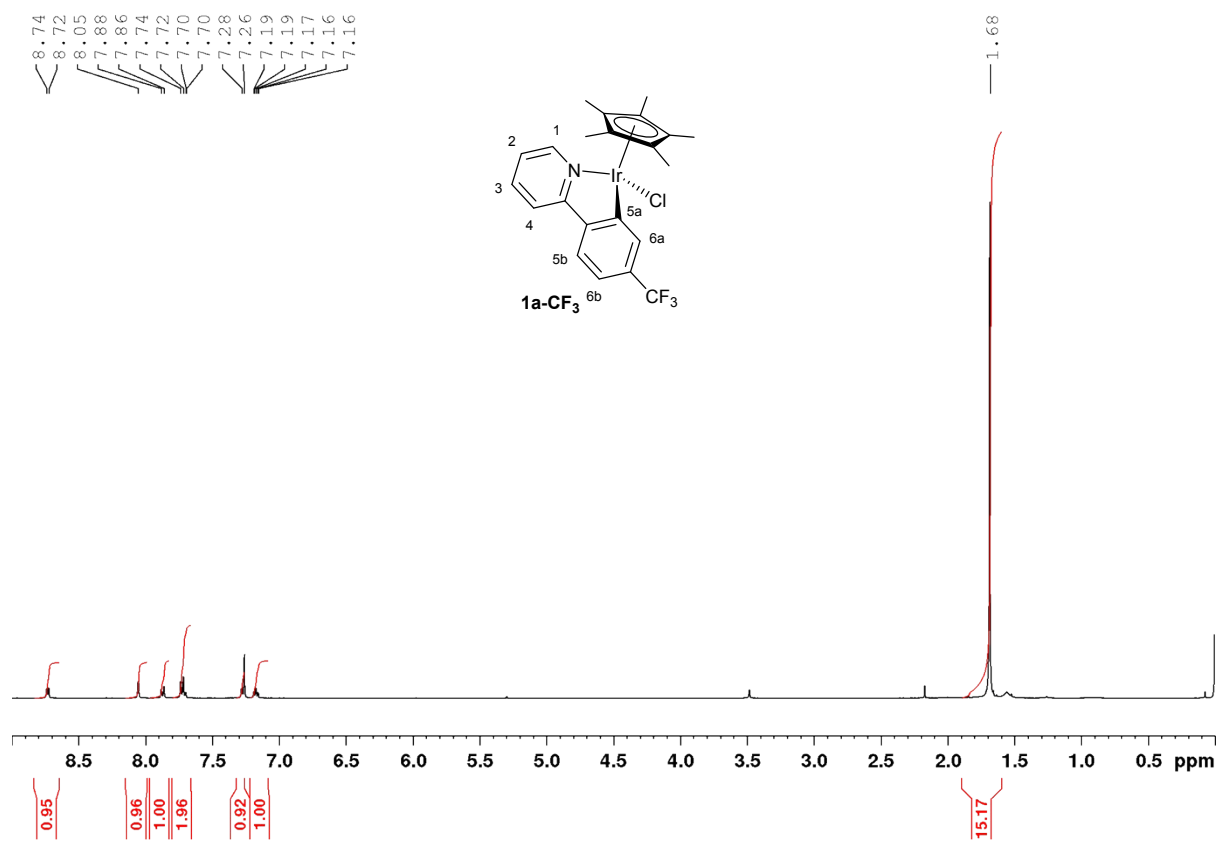
^{19}F NMR of 1b-F



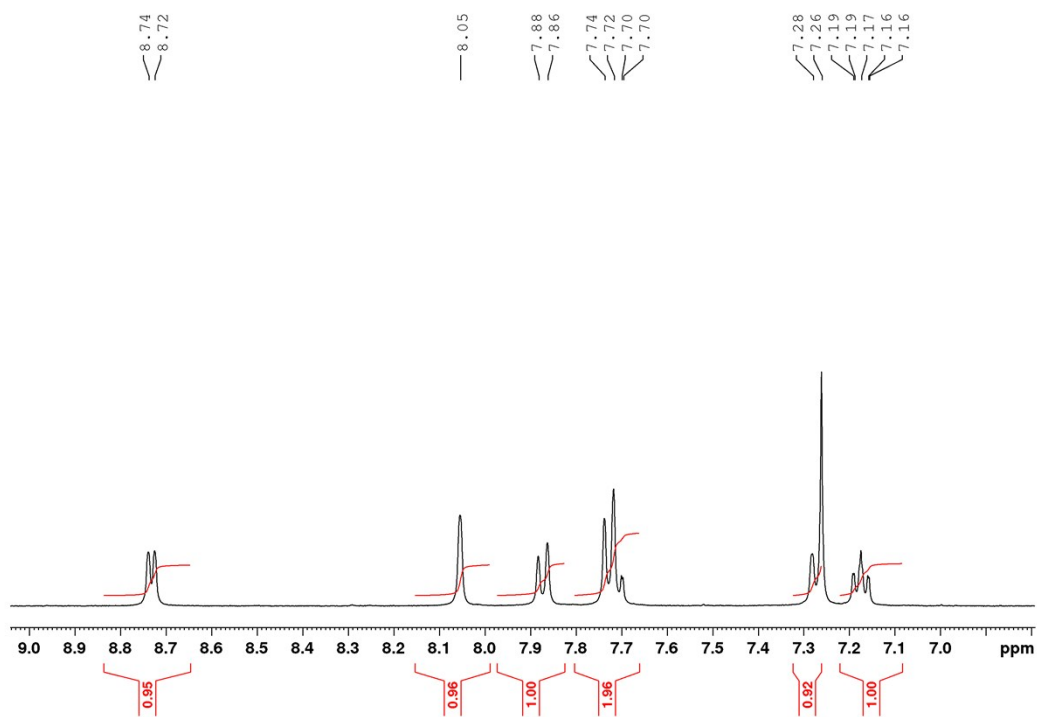
^{13}C NMR of 1b-F



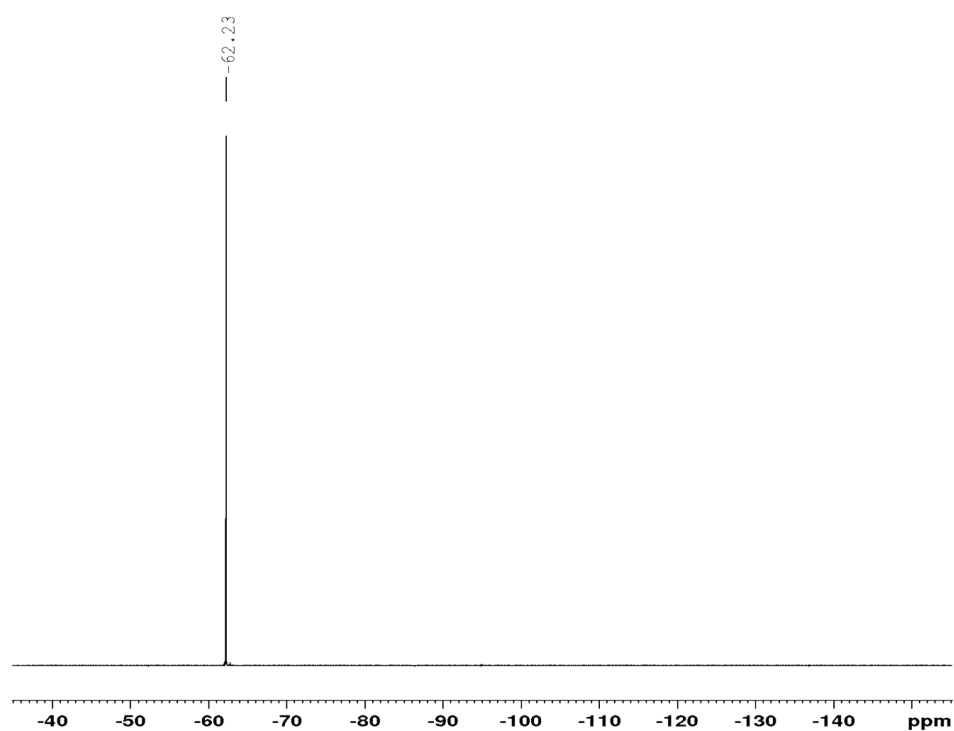
¹H NMR of 1a-CF₃



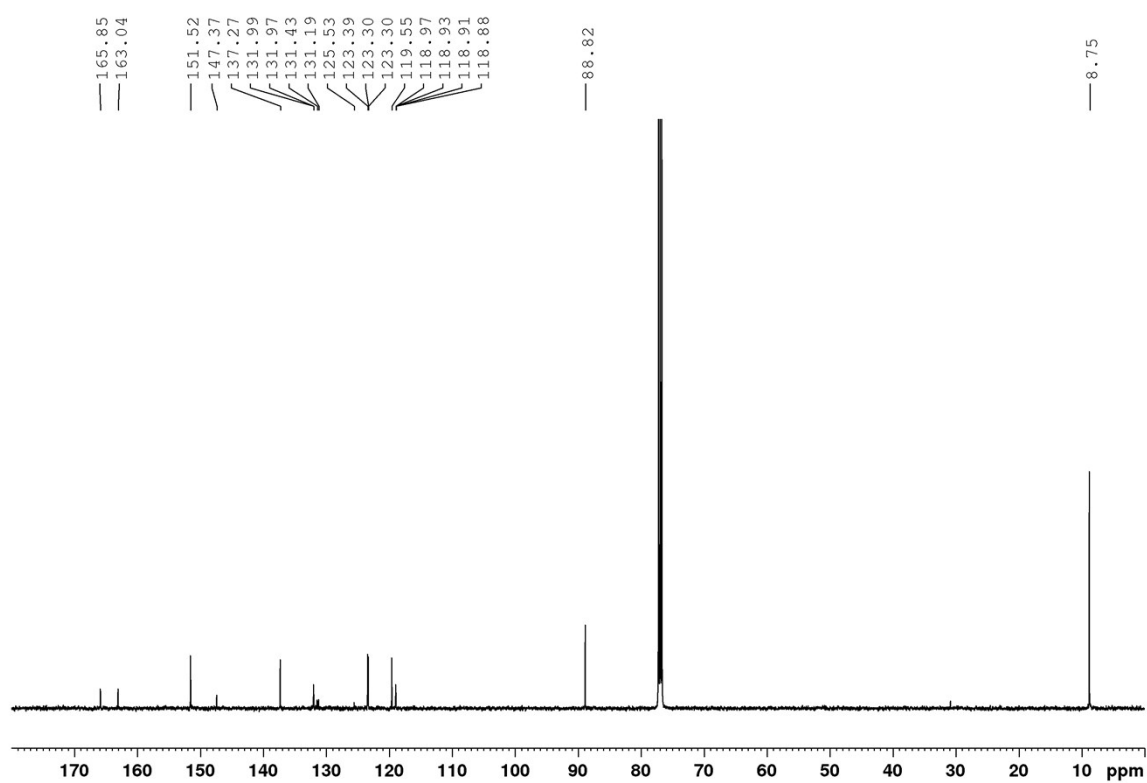
Expansion of ¹H NMR of 1a-CF₃



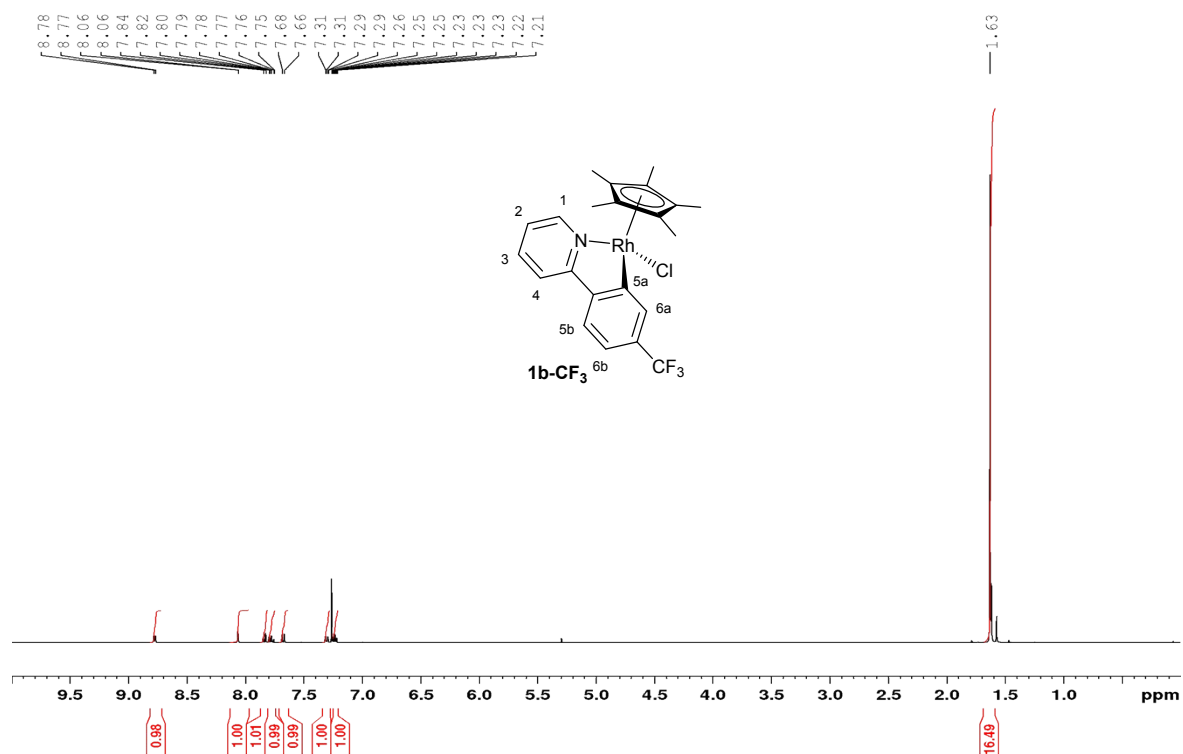
^{19}F NMR of 1a-CF₃



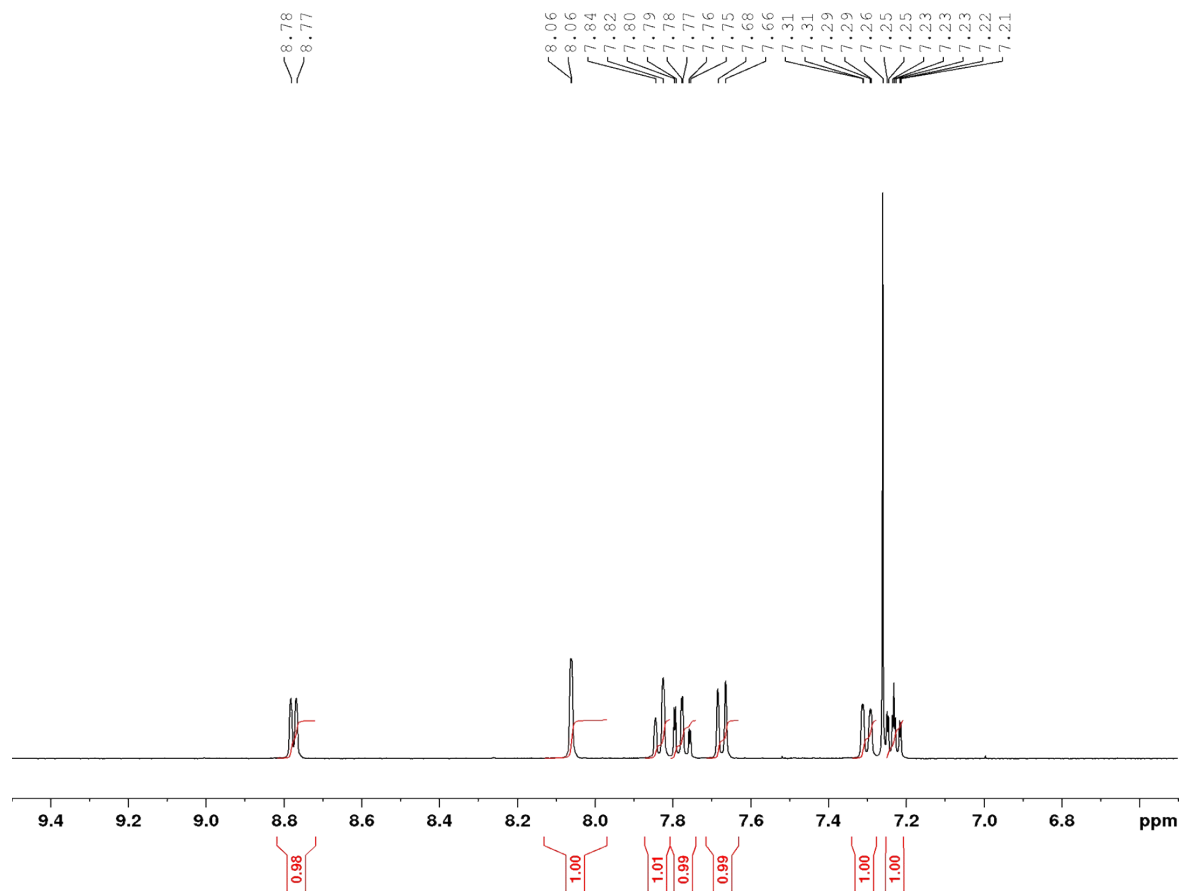
^{13}C NMR of 1a-CF₃



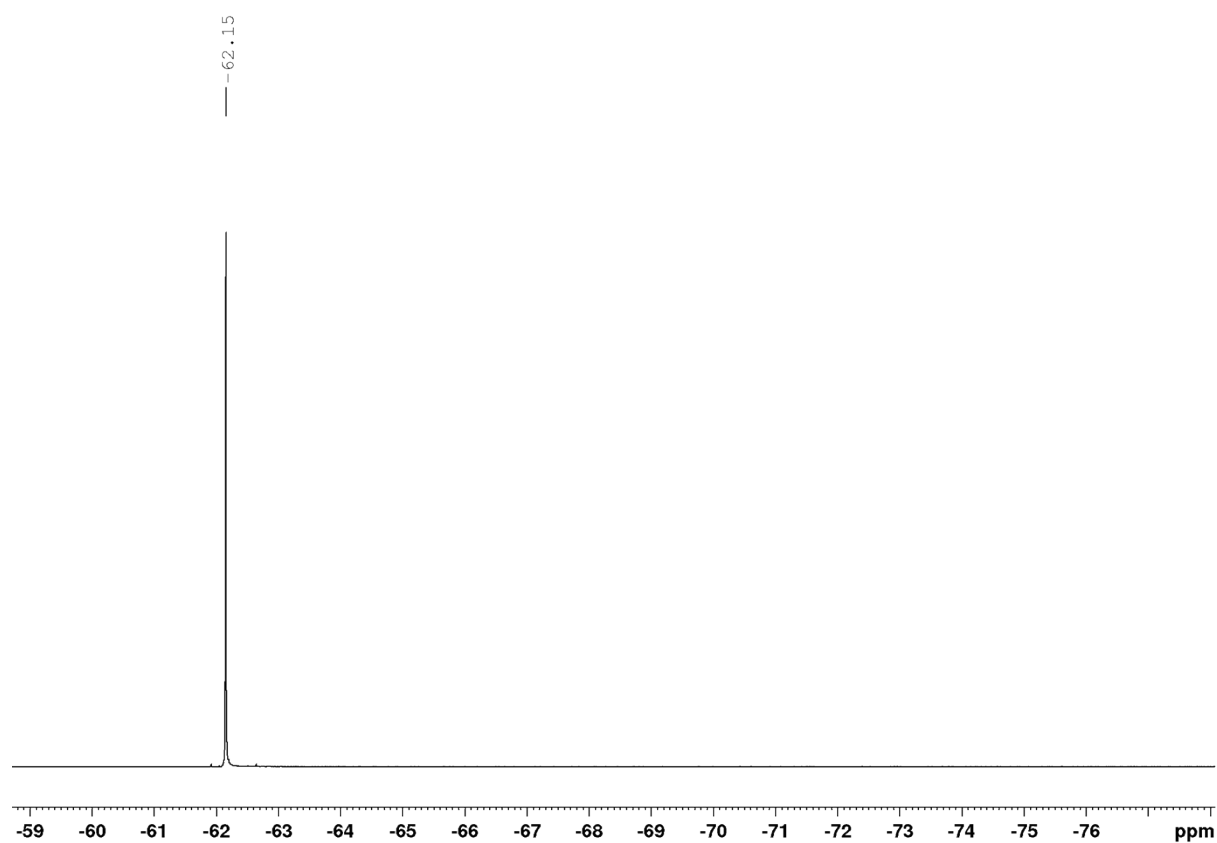
¹H NMR of 1b-CF₃



Expansion of ¹H NMR of 1b-CF₃



^{19}F NMR of 1b-CF₃



^{13}C NMR of 1b-CF₃

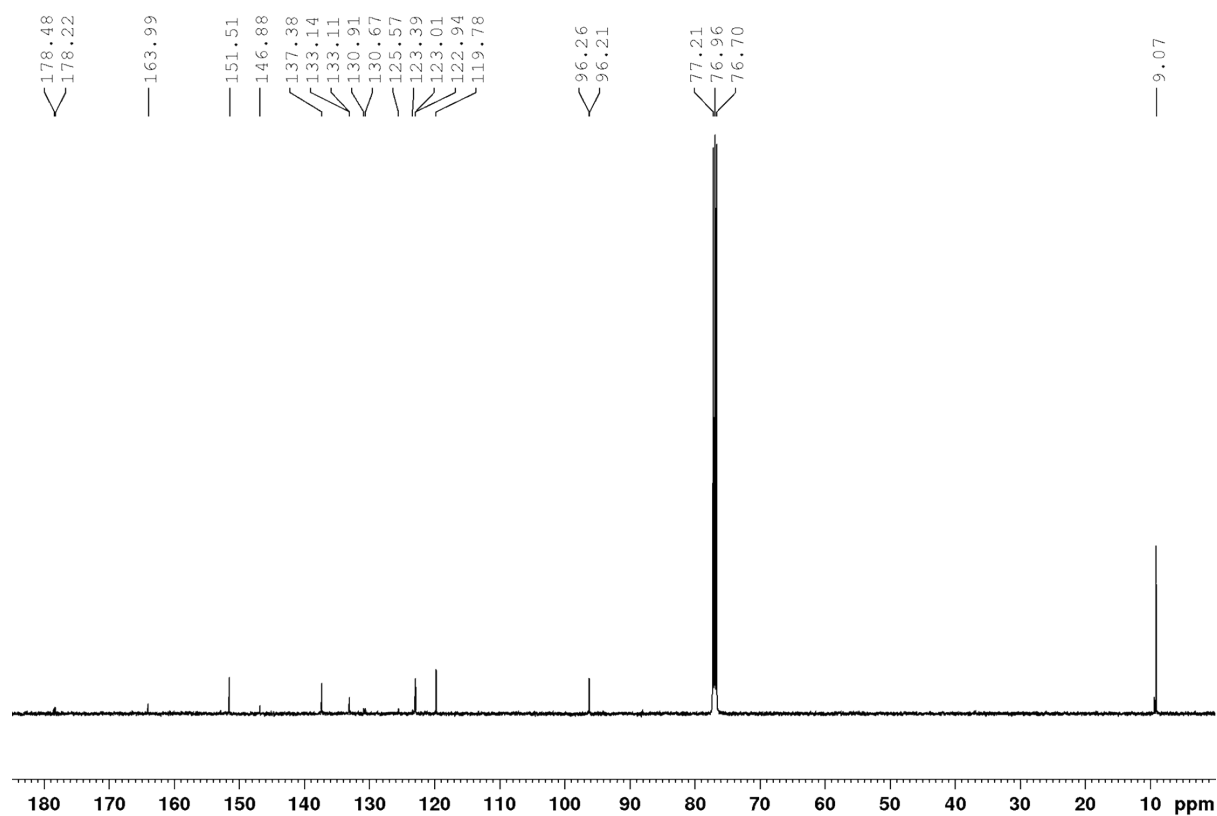
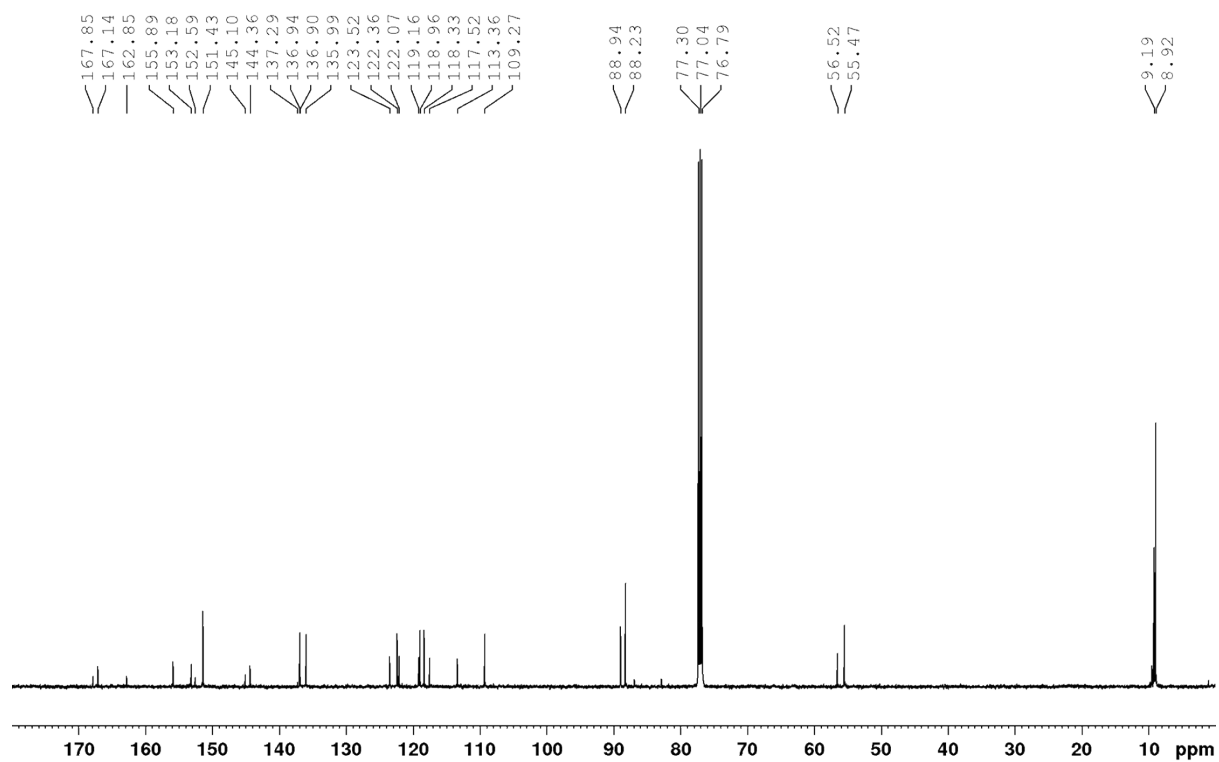


Figure S10 displays the ^1H NMR spectrum of compound 2a-OMe in CDCl_3 . The spectrum shows peaks corresponding to the protons of the molecule, with integration values provided below the baseline. The chemical structures of the *ortho* and *para* isomers of 2a-OMe are shown above the spectrum, with protons labeled 1 through 8. The *ortho* isomer has a methoxy group at the 2-position, and the *para* isomer has a methoxy group at the 4-position. The integration values are: 2.31, 2.42, 3.70, 1.13, 1.27, 3.48, 1.26, 1.00, 6.98, 20.77, 16.29, 1.68, 1.68.

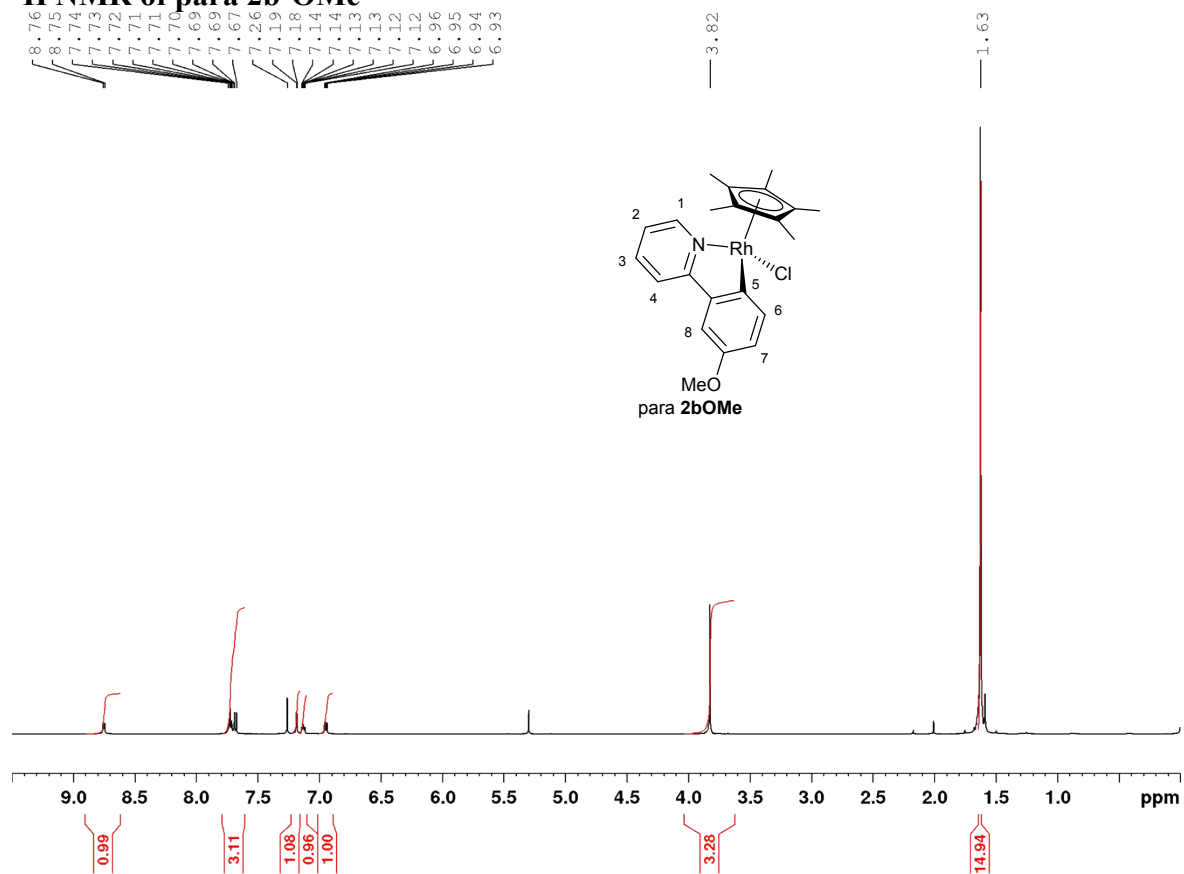
¹H NMR spectrum (CDCl₃) of compound 1. The x-axis represents the chemical shift in ppm, ranging from 6.7 to 8.9. The spectrum shows several multiplets and a sharp singlet at 7.26 ppm. Integration values are provided below the peaks, and chemical shifts are listed above the peaks.

Chemical Shift (ppm)	Integration
8.71	2.31
8.70	
8.69	
8.68	
8.67	
8.66	
8.65	
8.64	
8.63	
8.62	
8.61	
7.80	
7.78	
7.76	
7.70	
7.68	
7.67	
7.66	
7.65	
7.64	
7.63	
7.62	
7.61	
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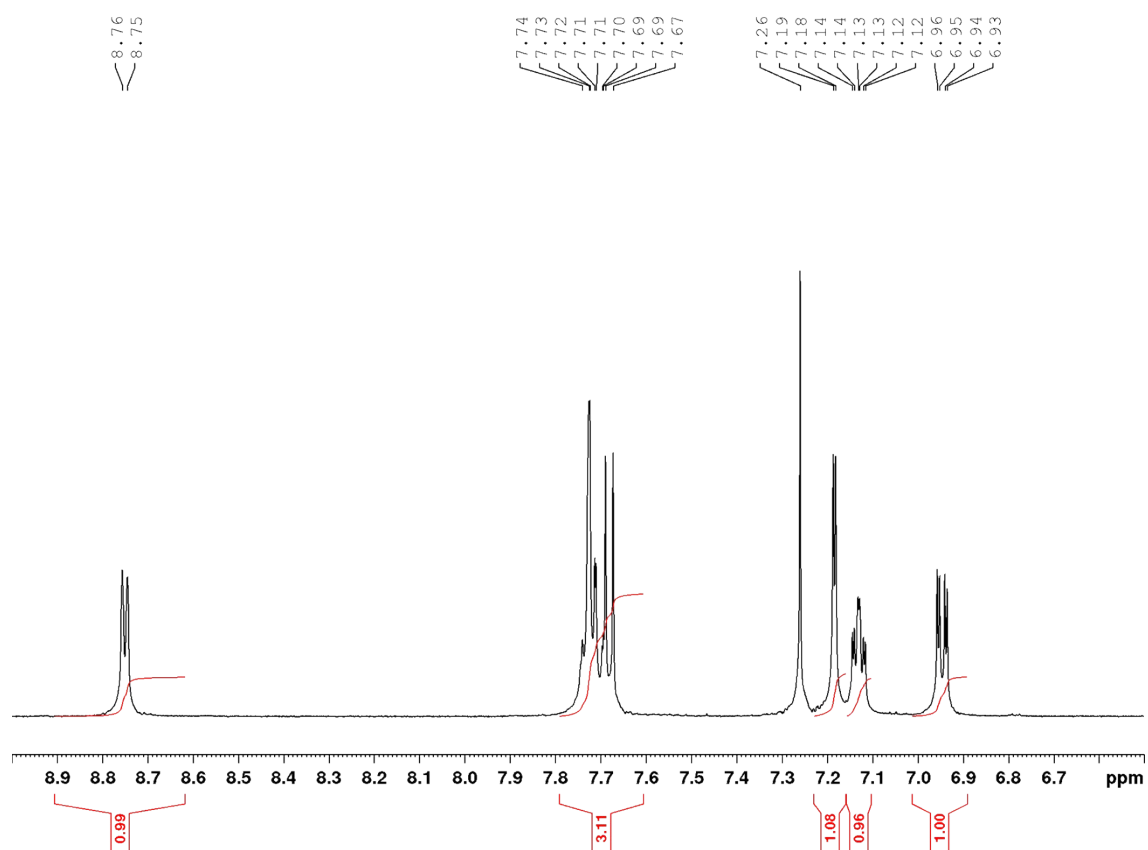
^{13}C NMR of a mixture of ortho and para 2a-OMe



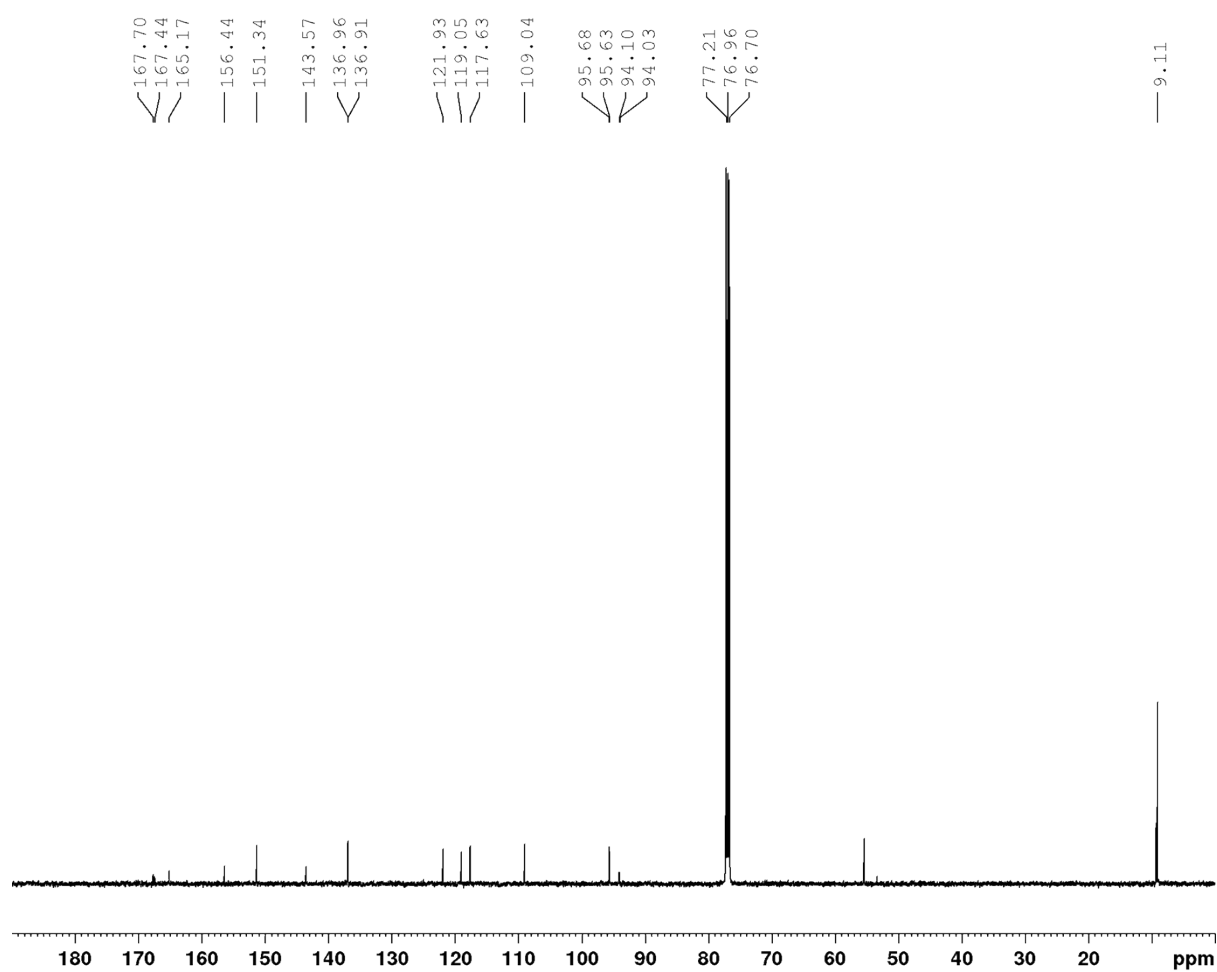
¹H NMR of para 2b-OMe



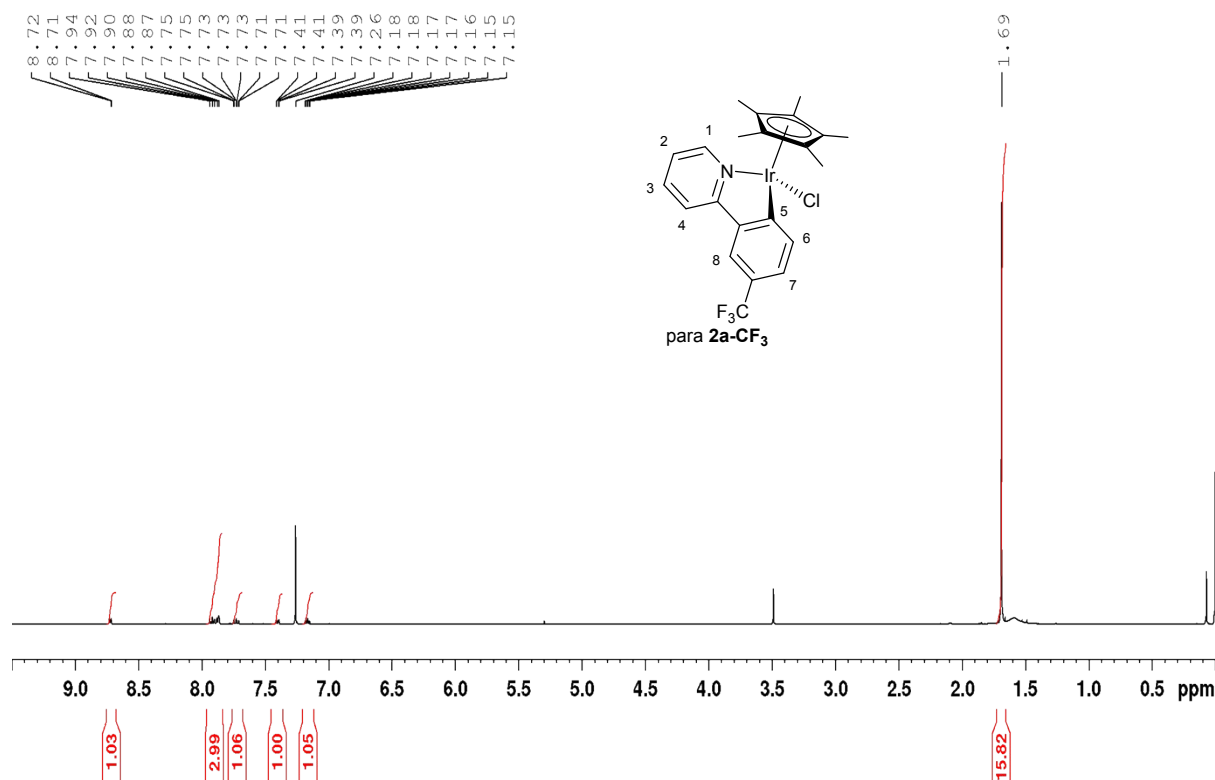
Expansion of ¹H NMR of para 2b-OMe



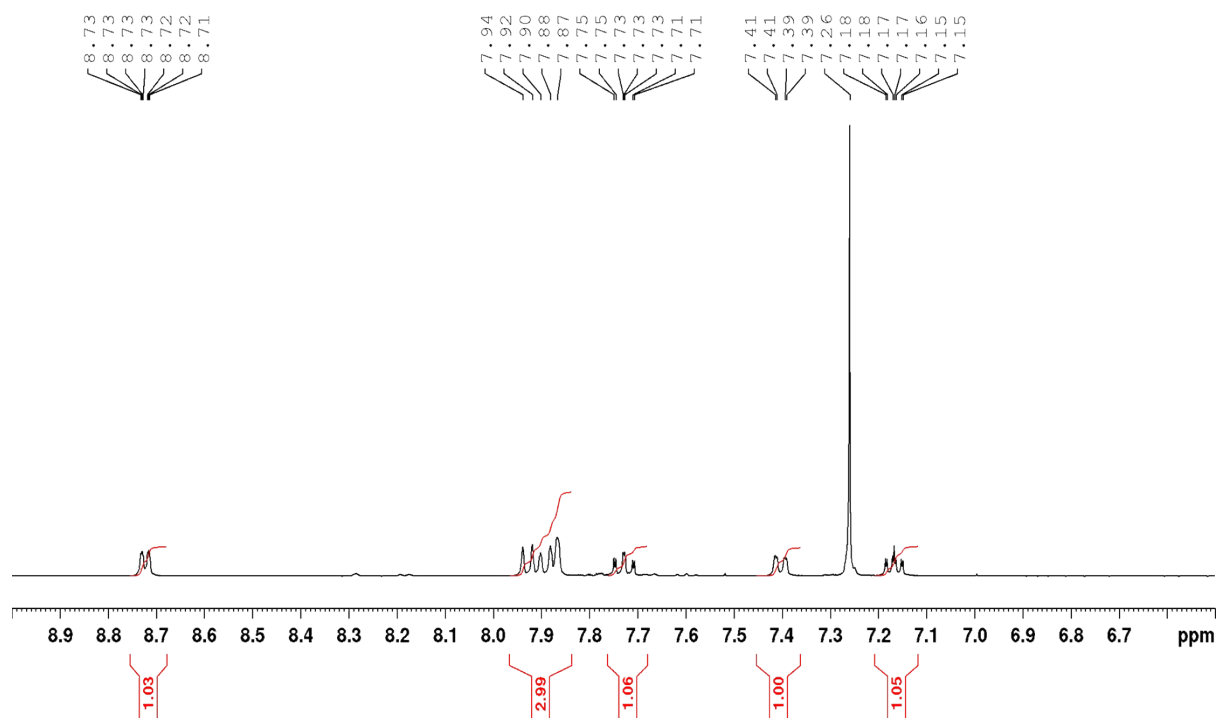
^{13}C NMR of para 2b-OMe



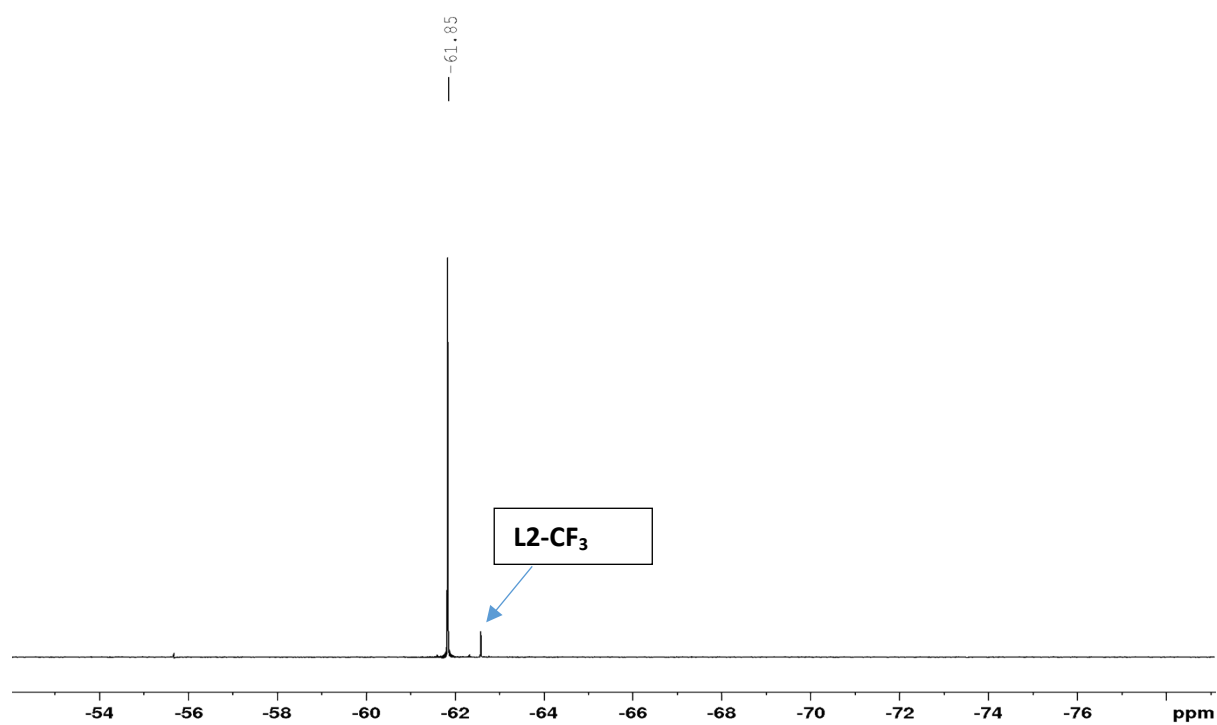
¹H NMR of para 2a-CF₃



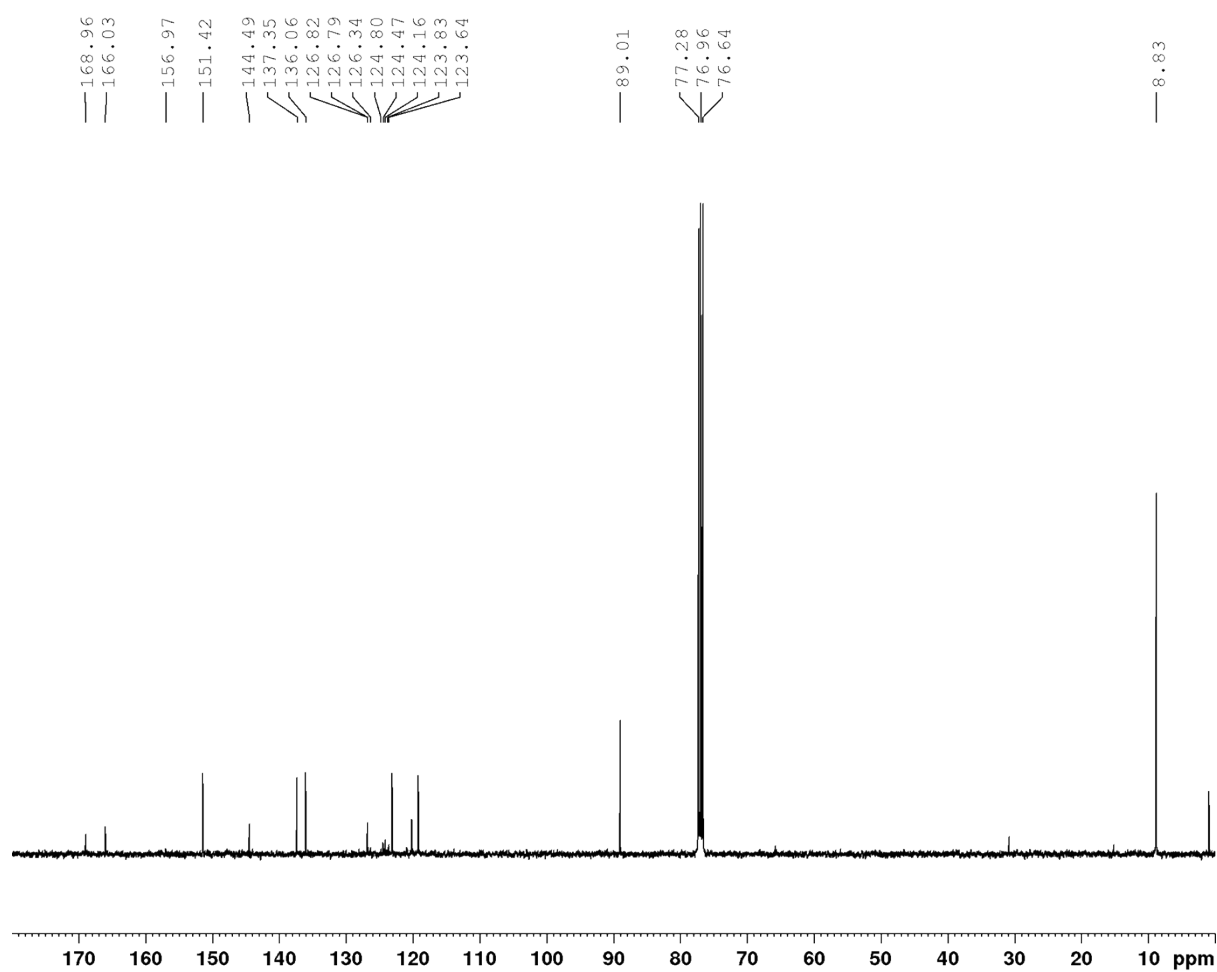
Expansion of ¹H NMR of para 2a-CF₃



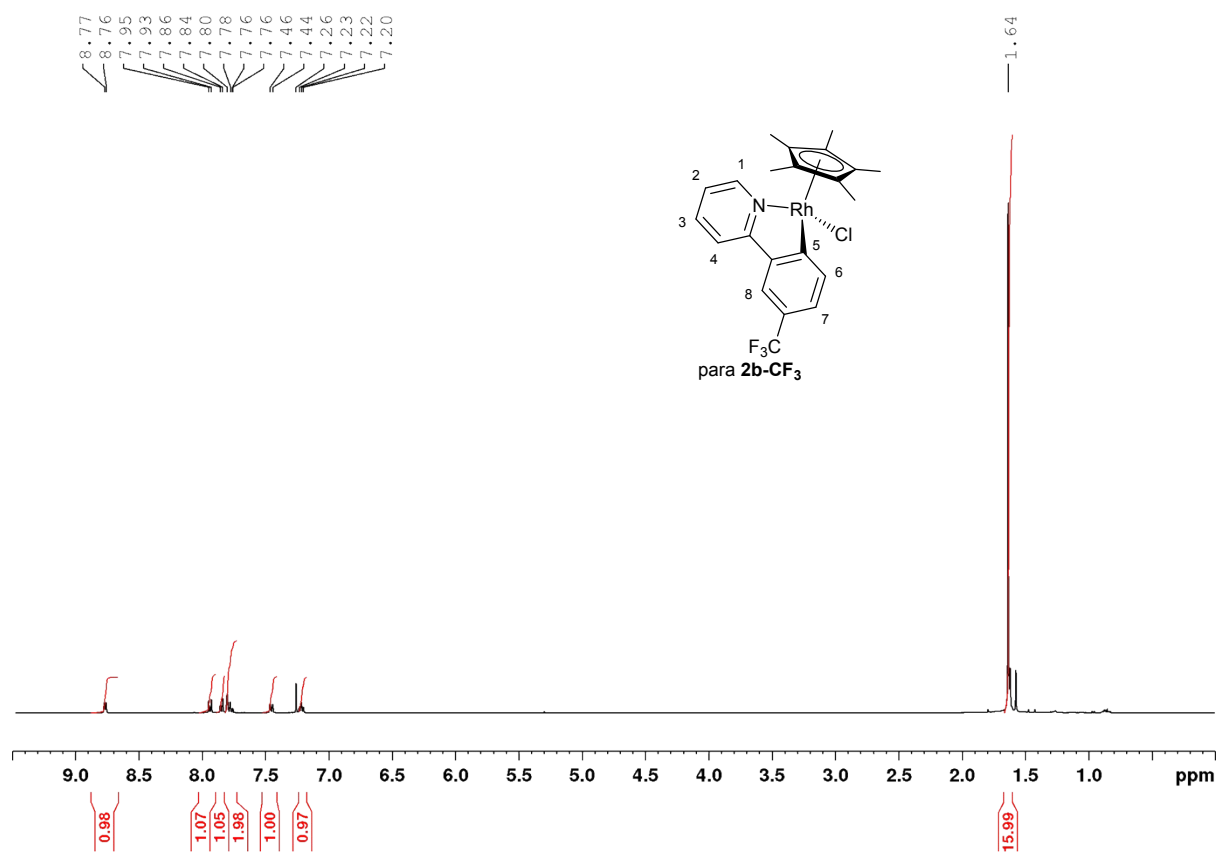
^{19}F NMR of para 2a- CF_3



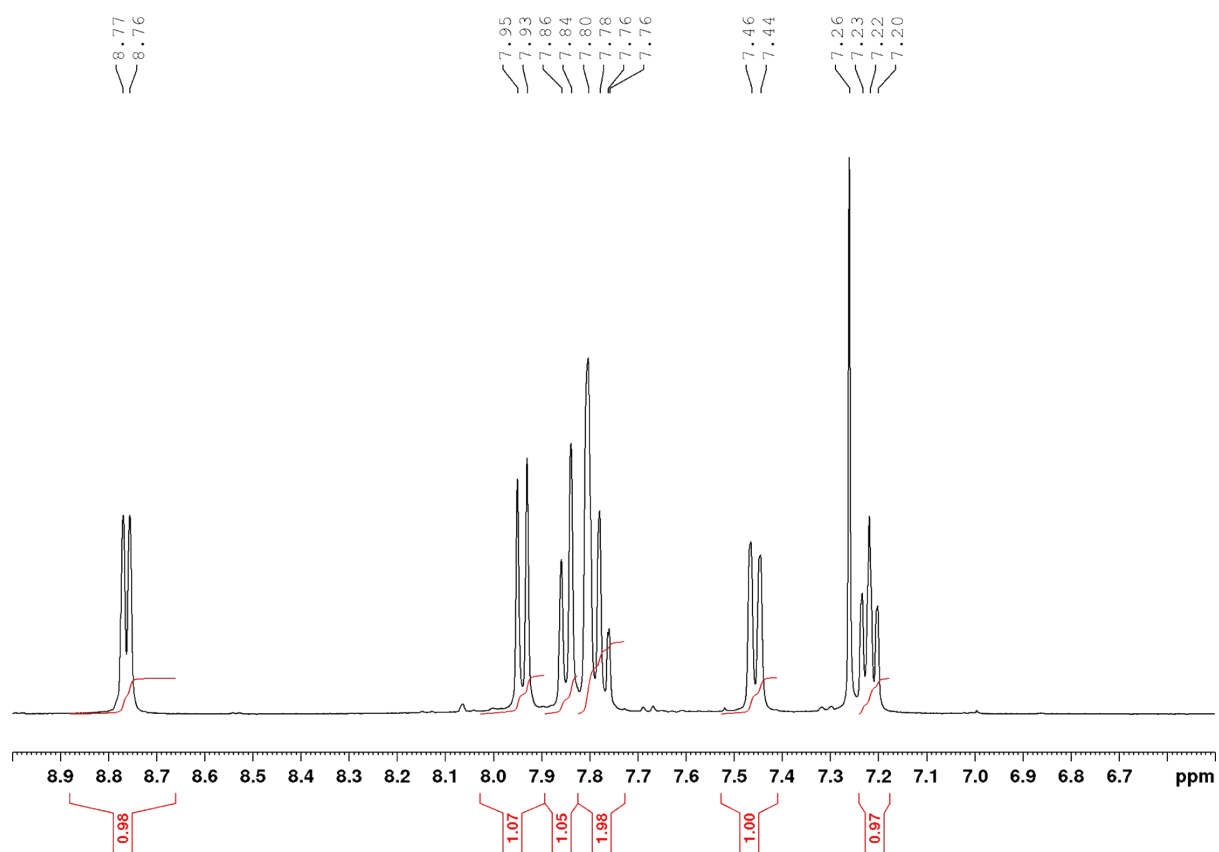
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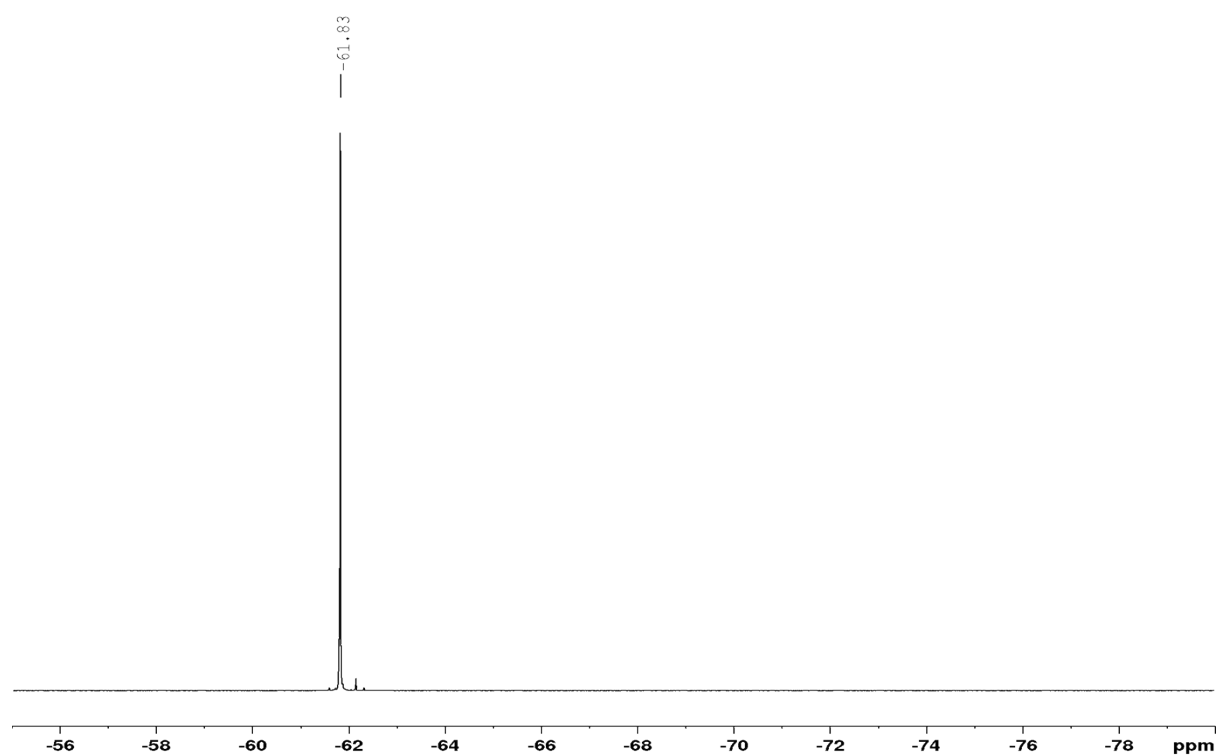
Expansion of ^1H NMR of para 2b- CF_3



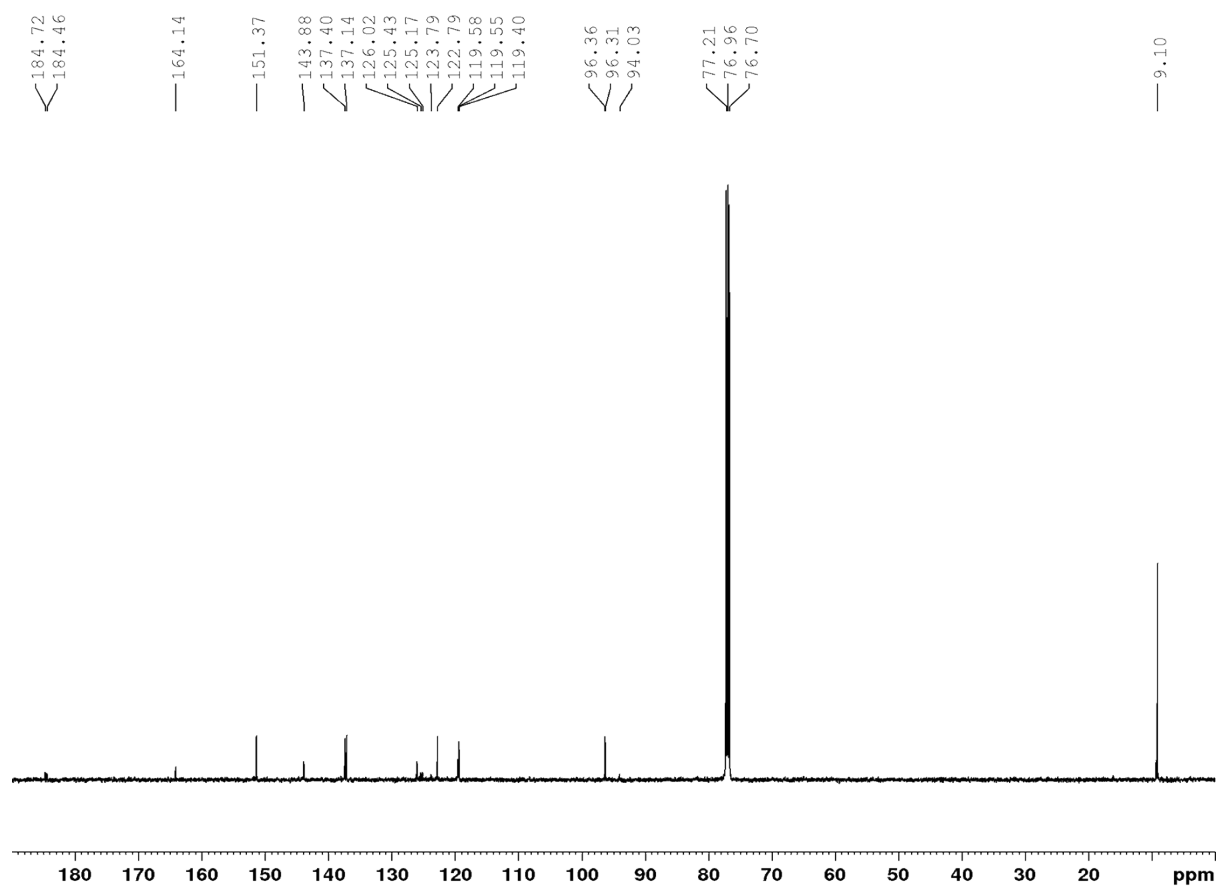
Expansion of ^1H NMR of para 2b- CF_3



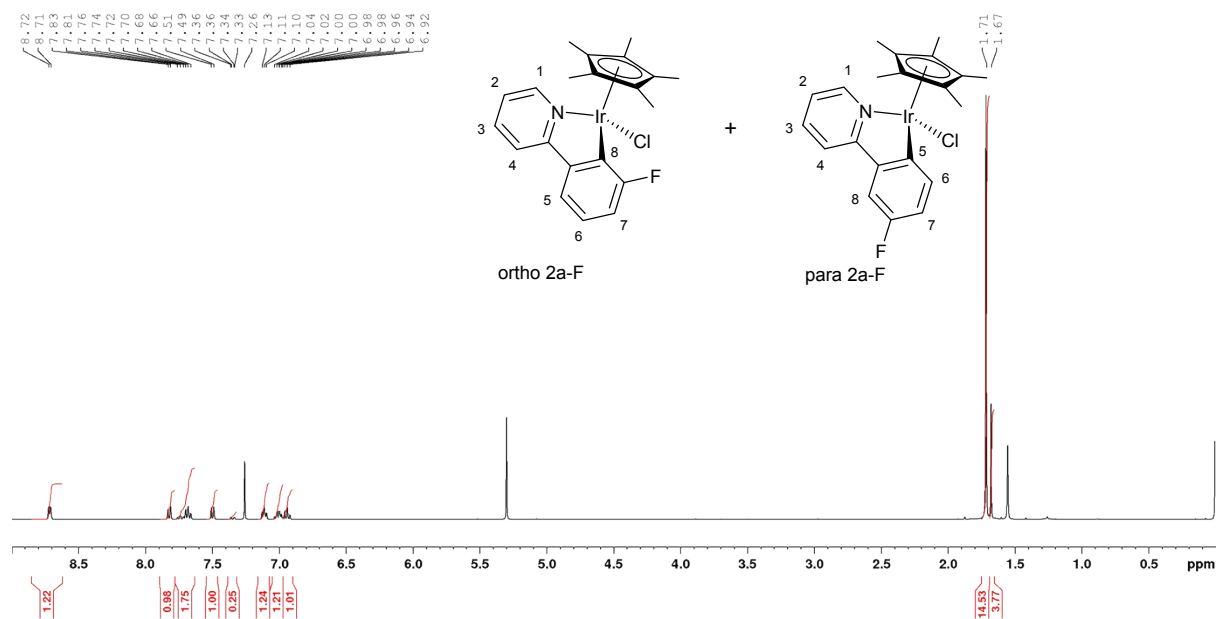
^{19}F NMR of para 2b- CF_3



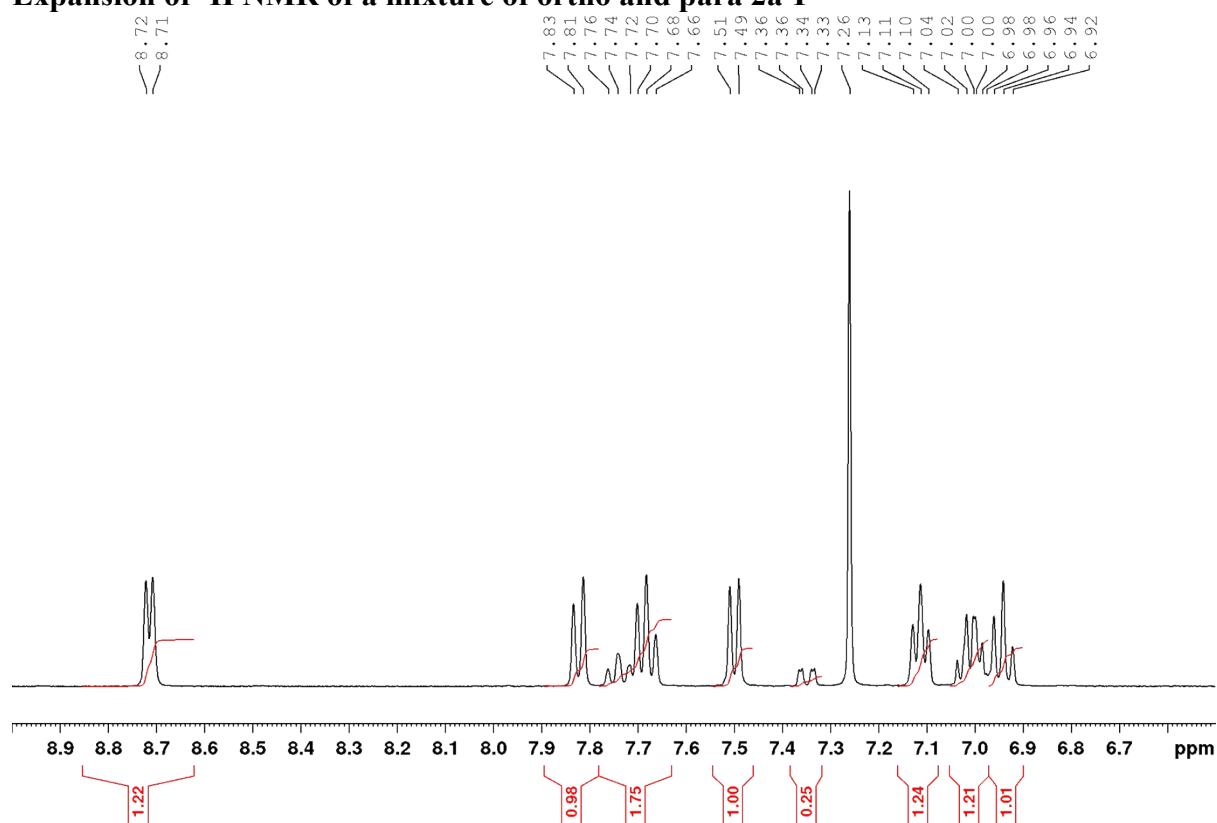
^{13}C NMR of para 2b- CF_3



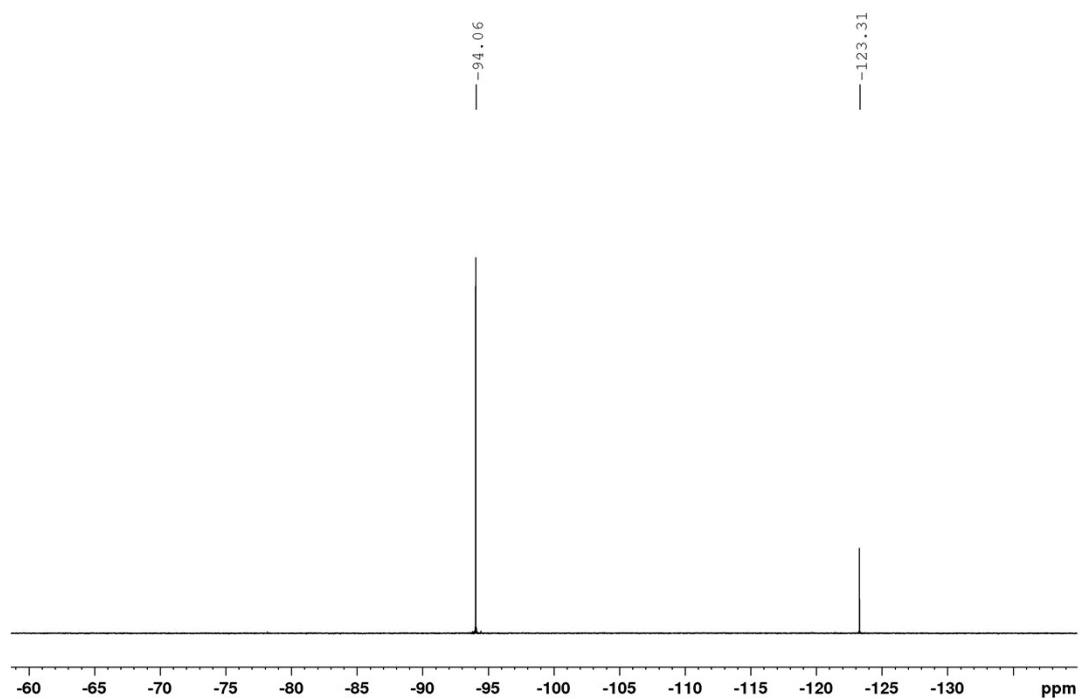
^1H NMR of a mixture of ortho and para 2a-F



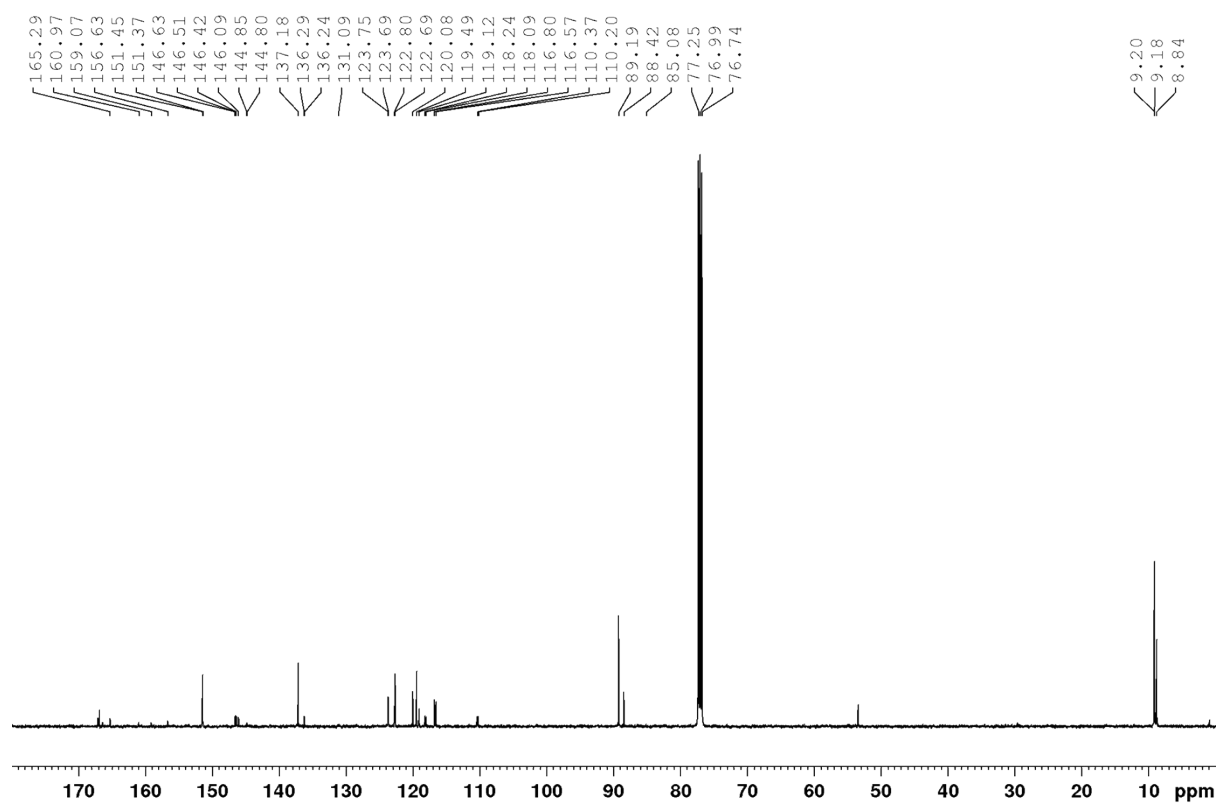
Expansion of ^1H NMR of a mixture of ortho and para 2a-F



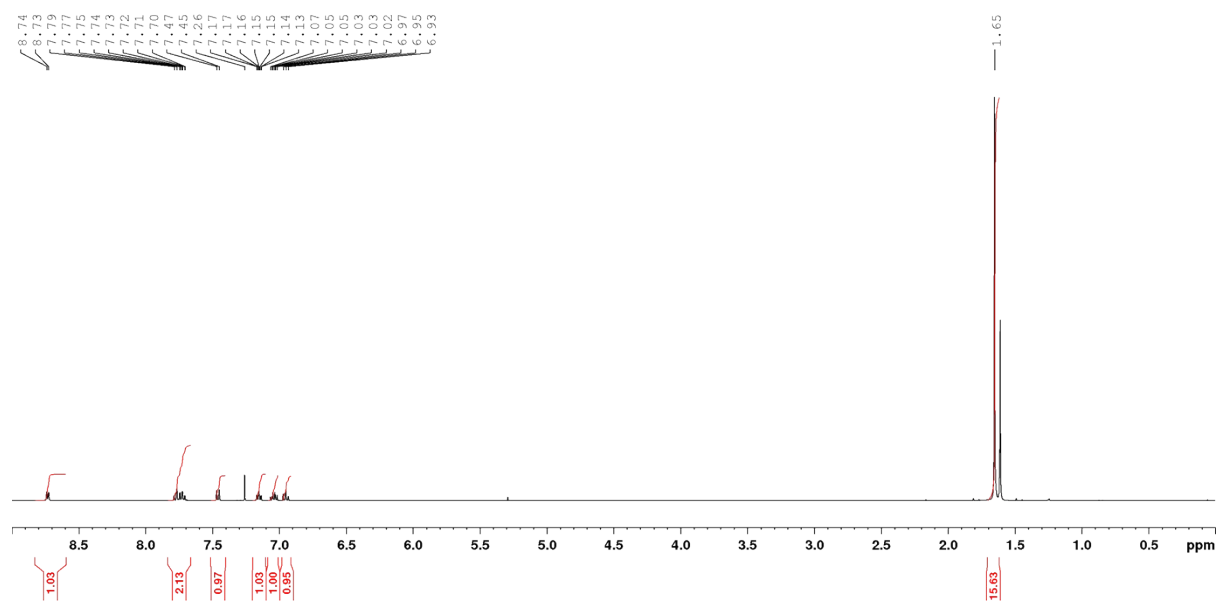
^{19}F NMR of a mixture of ortho and para 2a-F



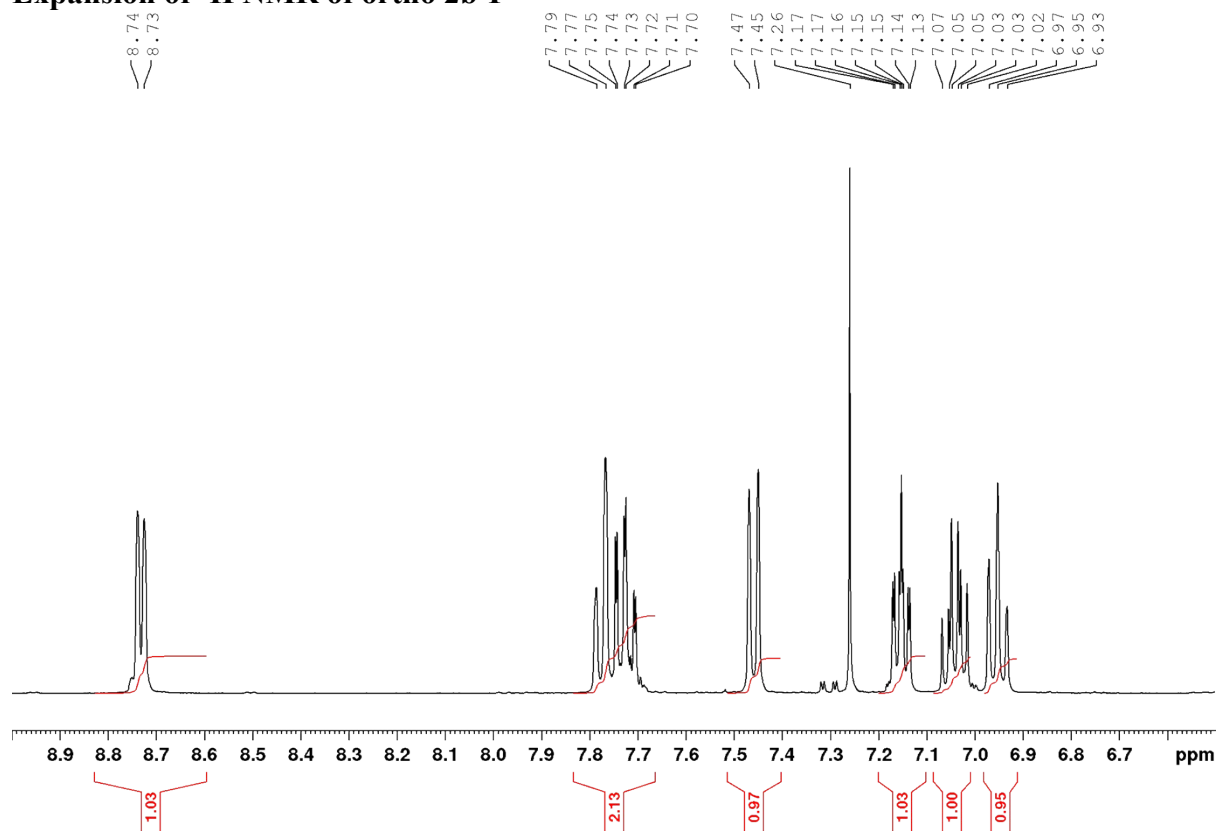
^{13}C NMR of a mixture of ortho and para 2a-F



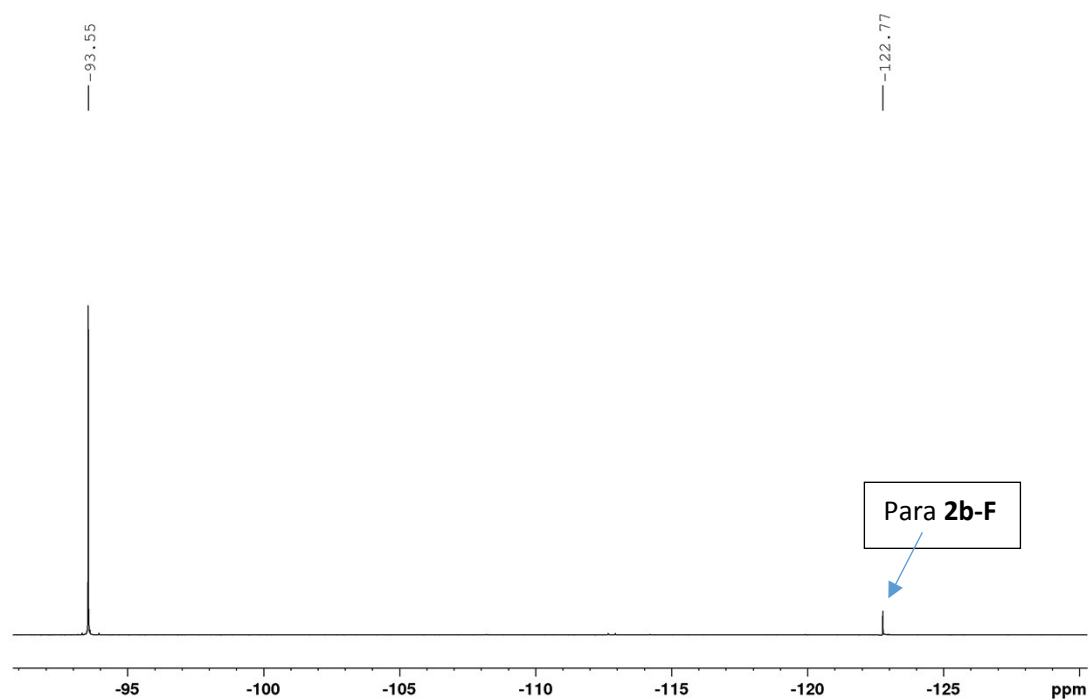
¹H NMR of ortho 2b-F



Expansion of ¹H NMR of ortho 2b-F



^{19}F NMR of ortho 2b-F



^{13}C NMR of ortho 2b-F

