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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Department of Chemistry, University of Leicester, Leicester LE1 7RH

Contents

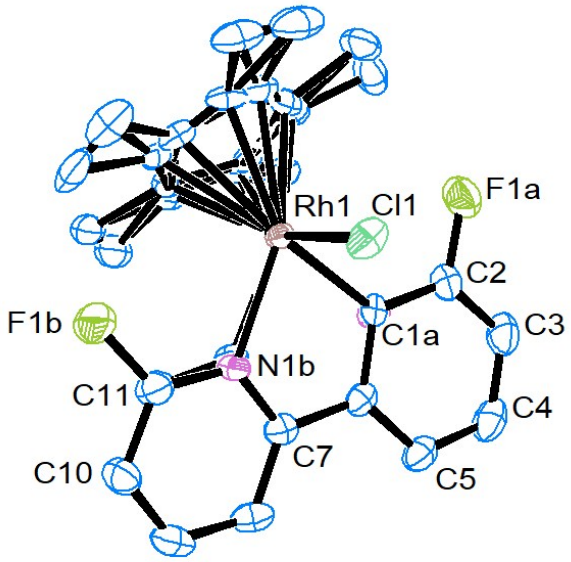


Figure S1 Molecular structure of *ortho* **2b-F** 50% displacement ellipsoids and H atoms have been omitted for clarity. There is a 50:50 C1:N1 and F: H disorder. The methyl's and ring carbon atoms of the Cp* are also disordered each over two sites (50:50).

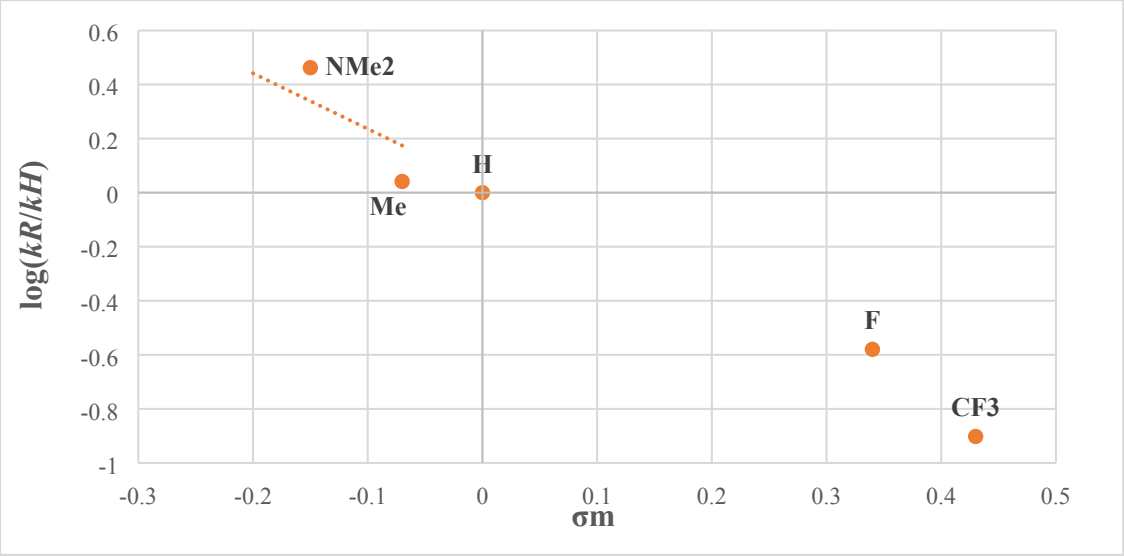


Figure S2 Hammett plot for relative rates of formation of *meta*-cyclometallated complexes of Rh $\log(k_R/k_H)$ against σ_m.

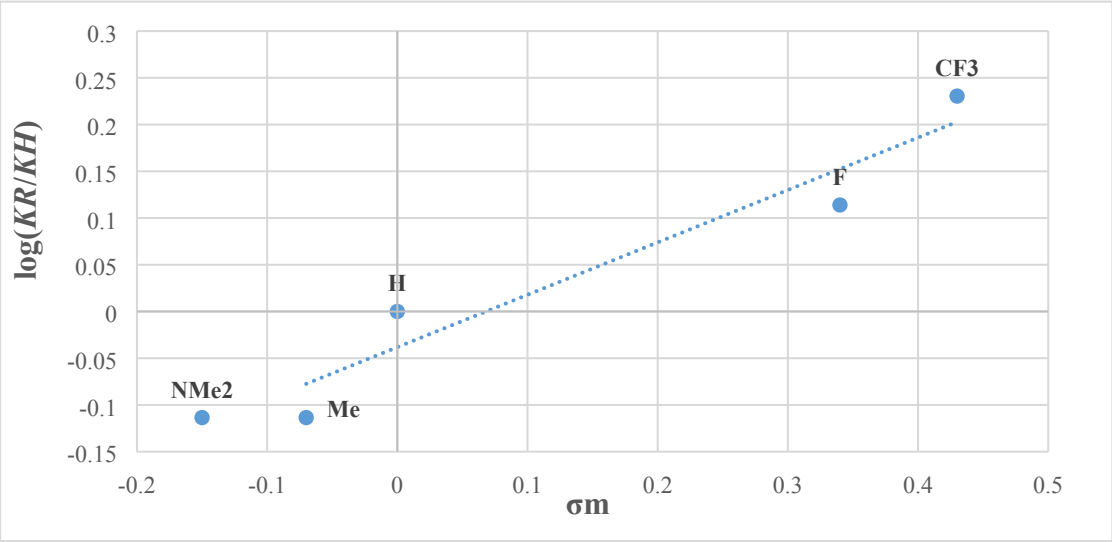


Figure S3 Hammett plot of thermodynamic ratios $\log(K_R/K_H)$ against σ_m for Rh.

Table S1: Deuteration of 2a,b-R in CD_3OD.

Entry	**R**	M	Time	*o:p*	% D in site **5** (*ortho*-isomer)	%D in site **8** (*para*-isomer)
1	**CF_3**	Ir	2 h	*para*-only[a]	-	N.D.
2	**CF_3**	Rh	2 h	*para*-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
[a] No *ortho-isomer* was detected by ^{19}F 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, 60ºC, 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 ºC, 2 hours

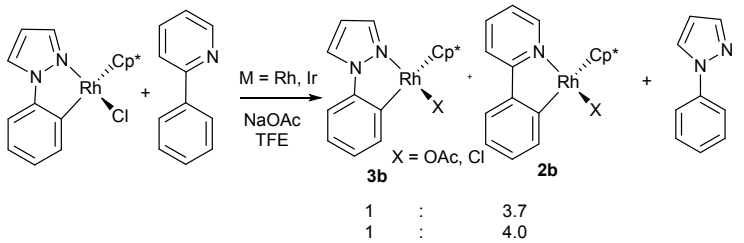
Table S3: Competition experiments to form *meta*-substituted complexes of Rh.

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

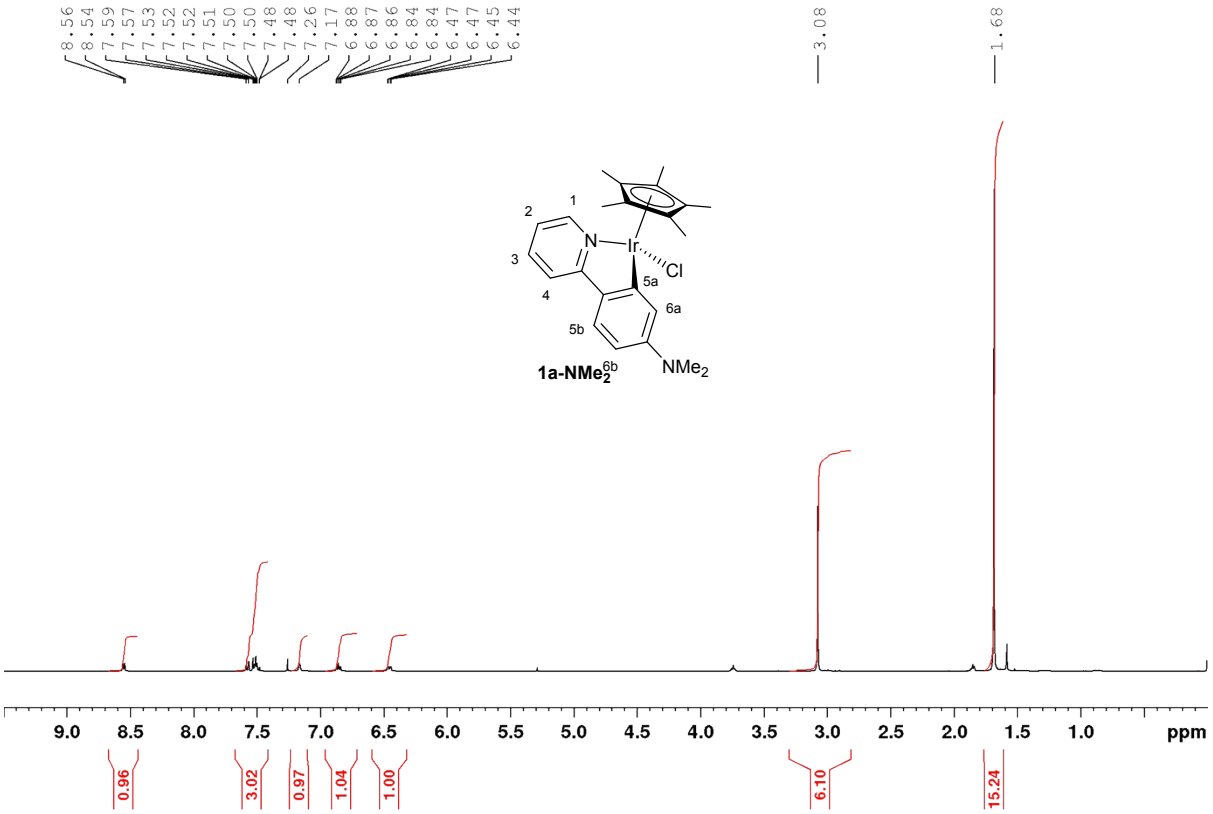
Exchange of phenylpyrazole by 2-phenylpyridine

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.

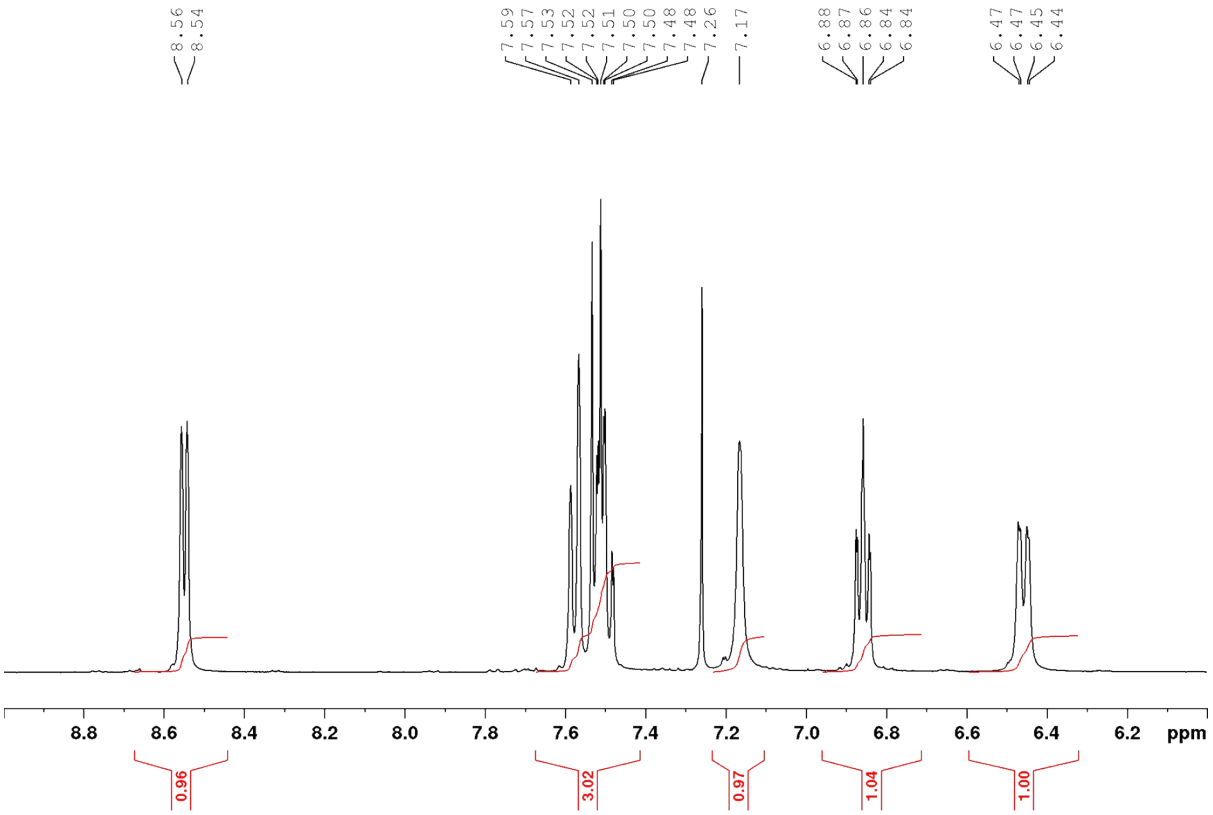


Scheme S1 exchange of phenylpyrazole by 2-phenylpyridine at Cp*Rh

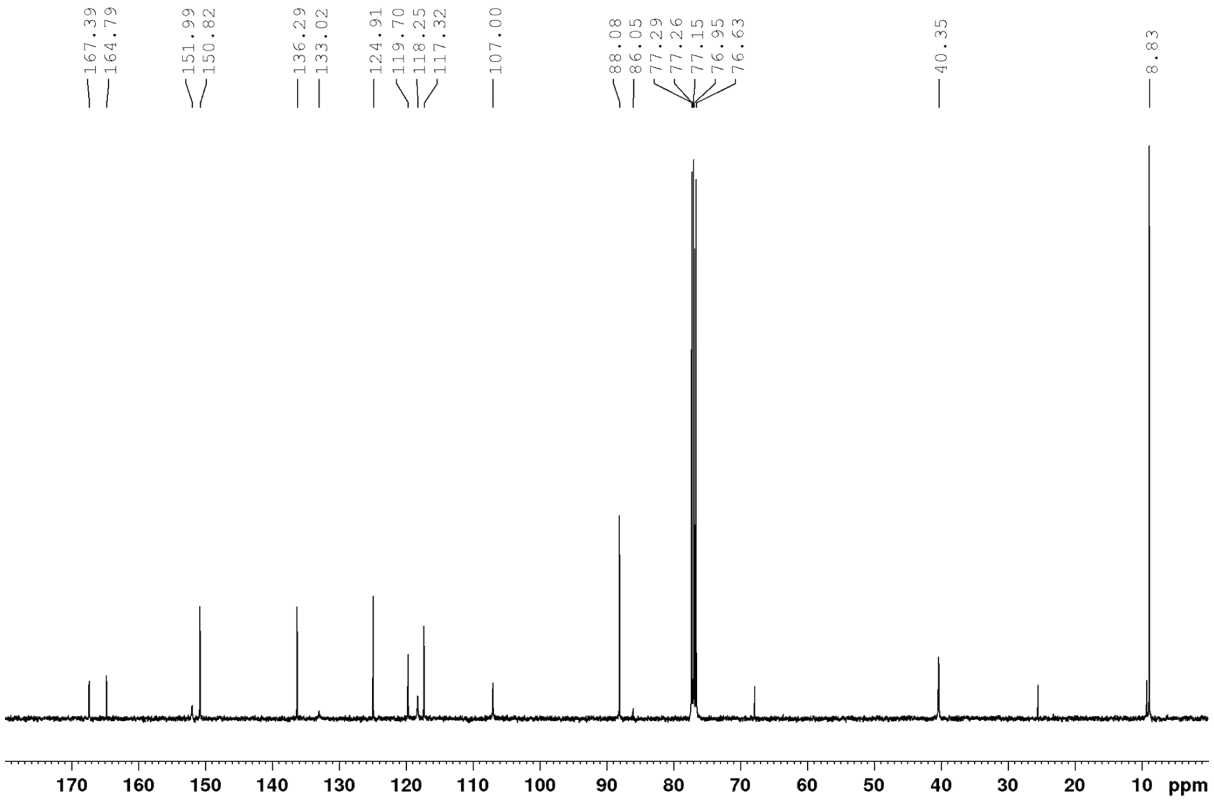
^{1}H NMR 1a-NMe_2



Expansion of ^{1}H NMR



^{13}C NMR 1a-NMe_2



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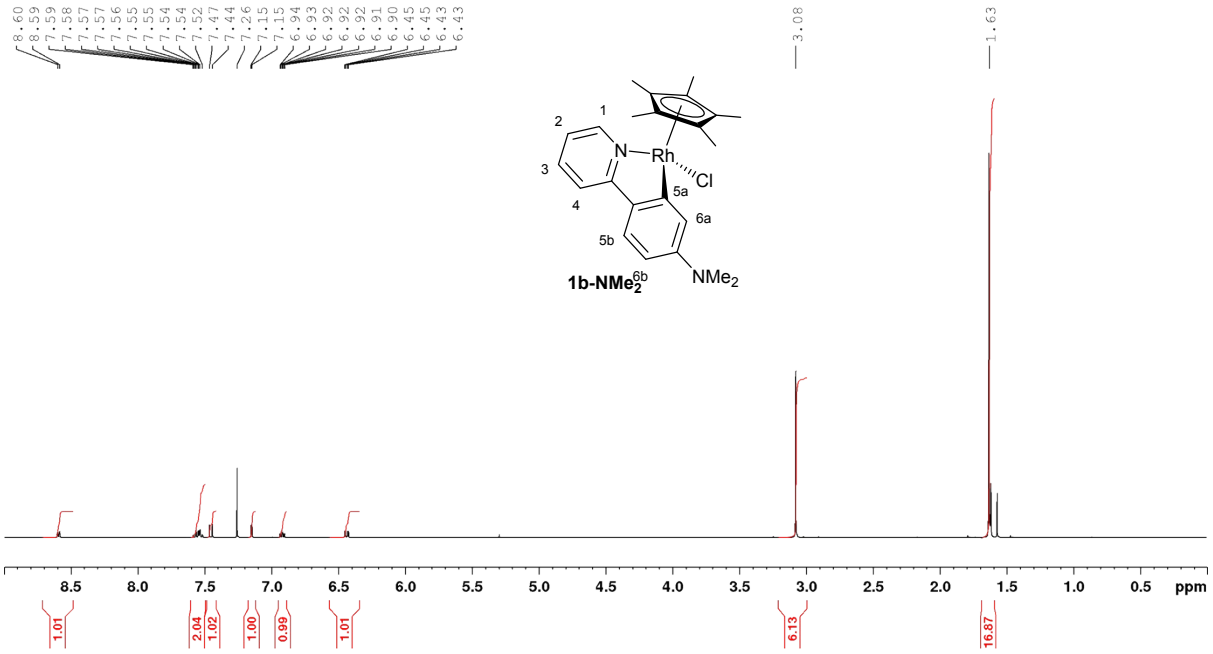
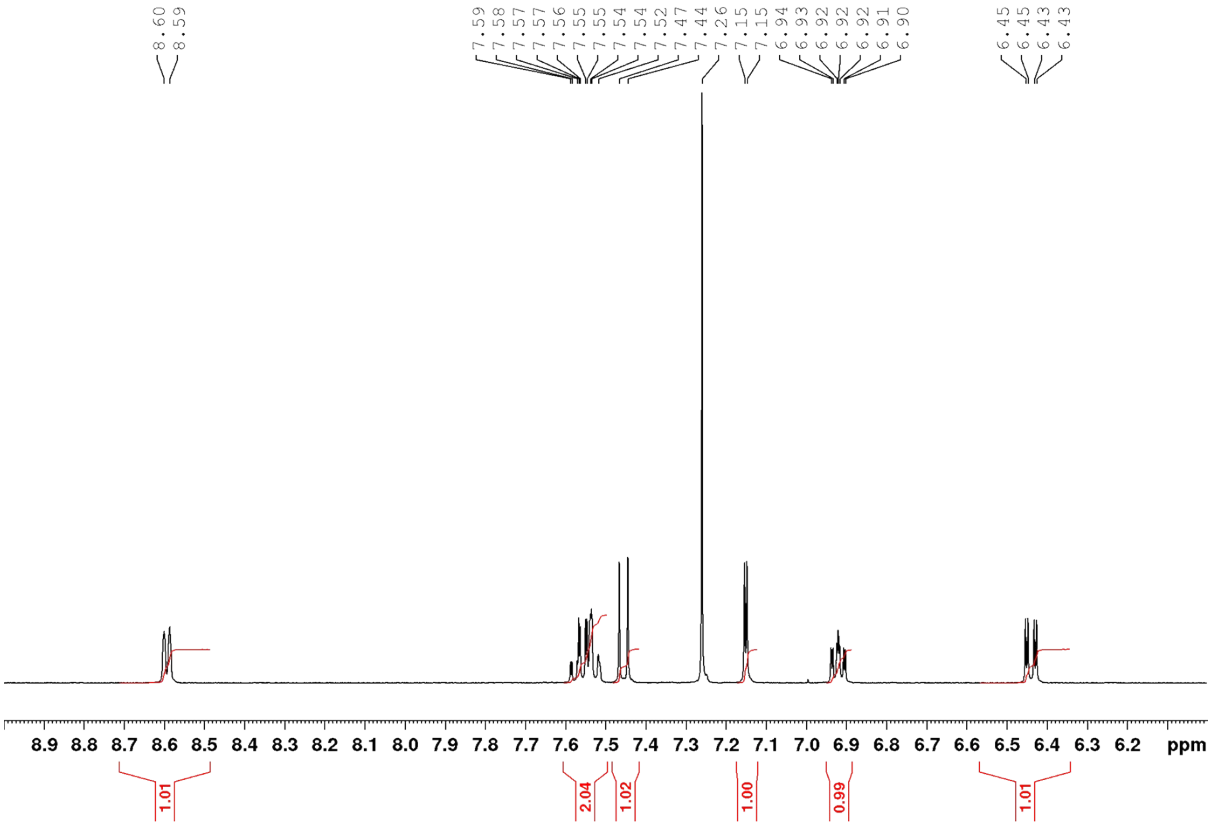
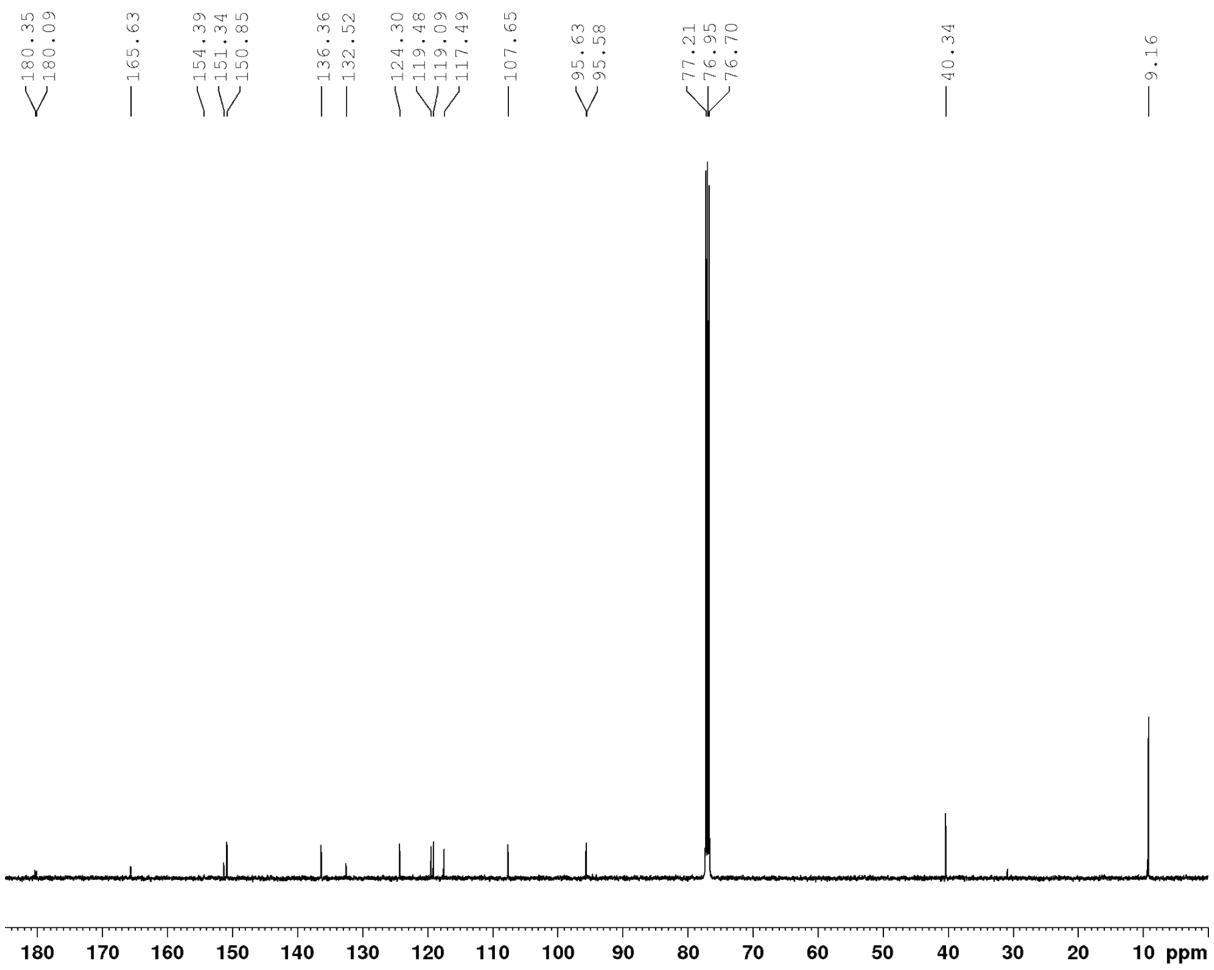


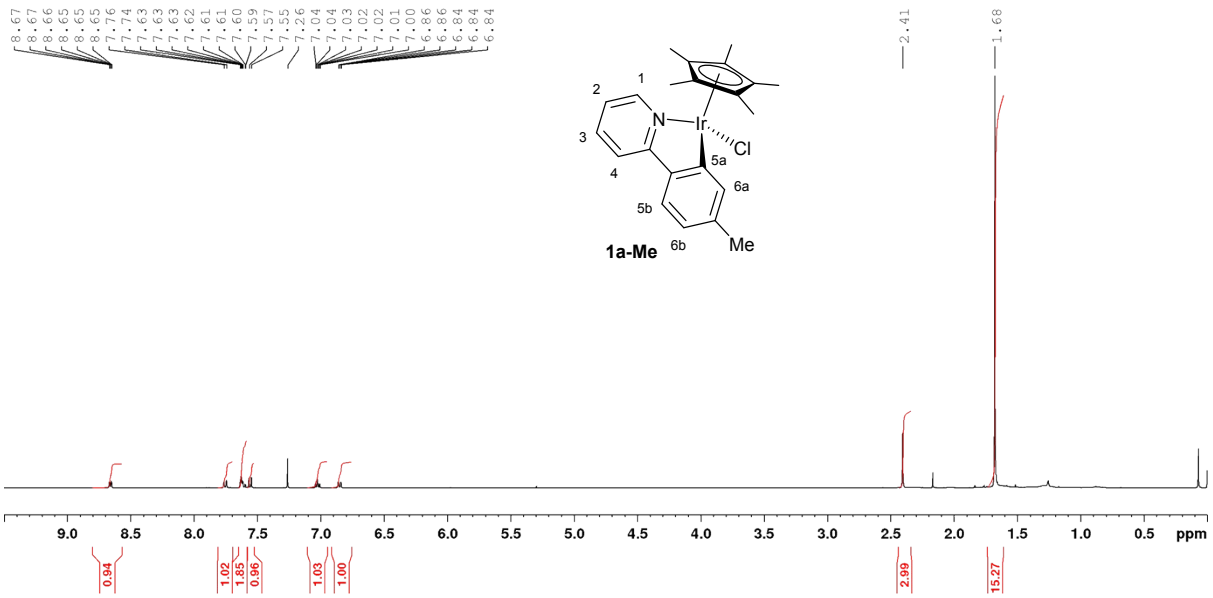
Expansion of ^{1}H NMR



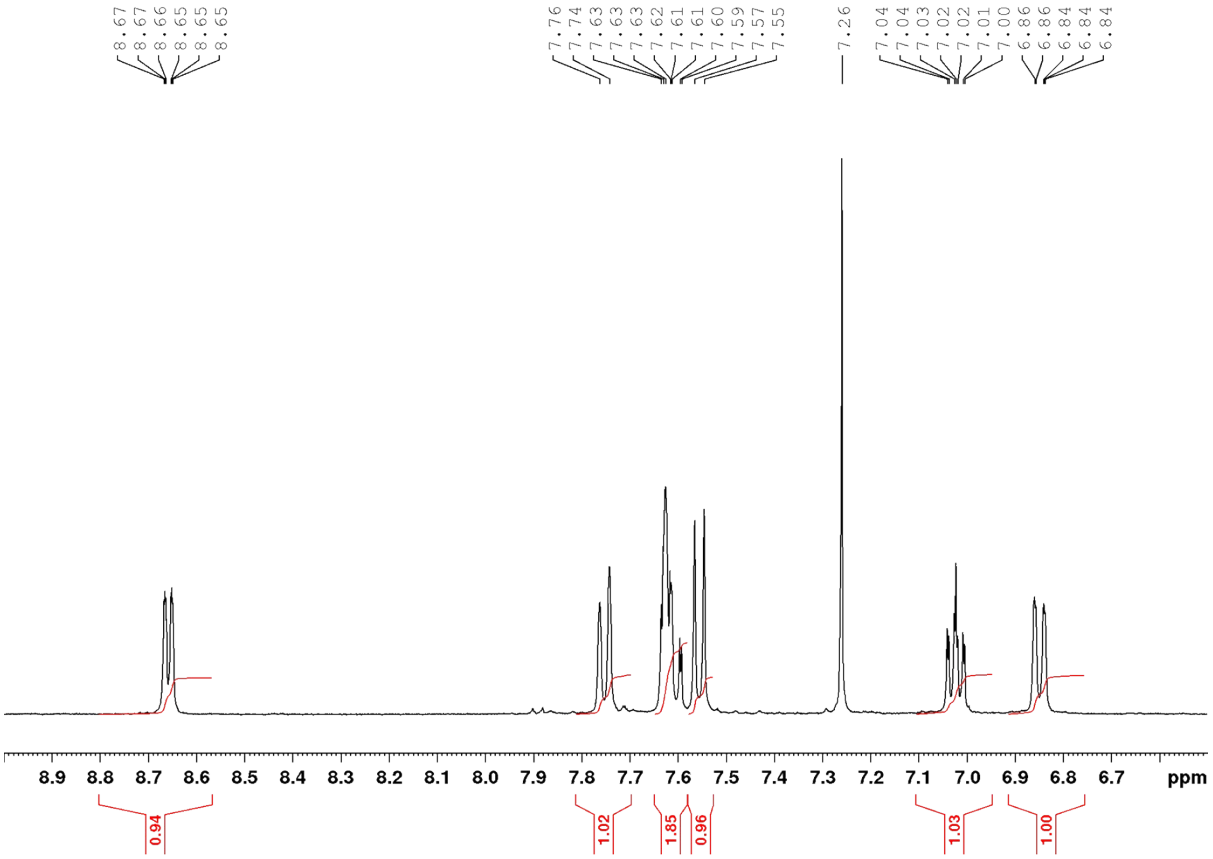
^{13}C NMR 1b-NMe$_2$



^{1}H NMR 1a-Me



Expansion of ^{1}H NMR of 1a-Me



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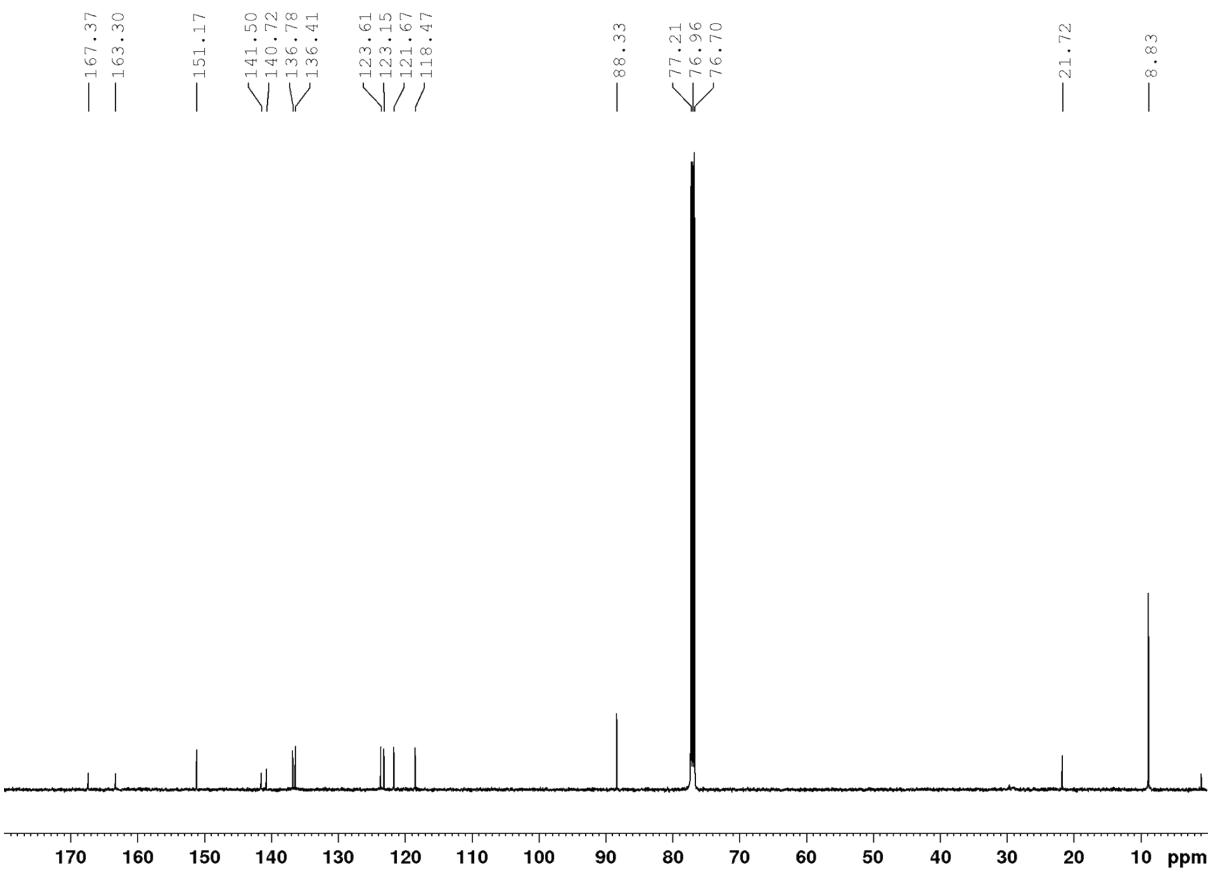

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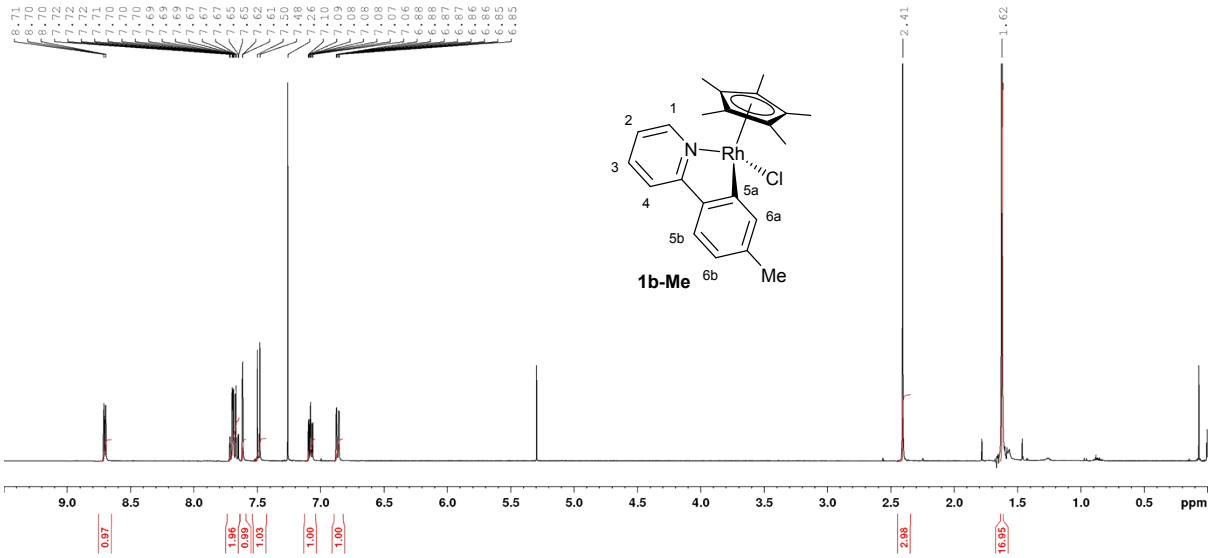

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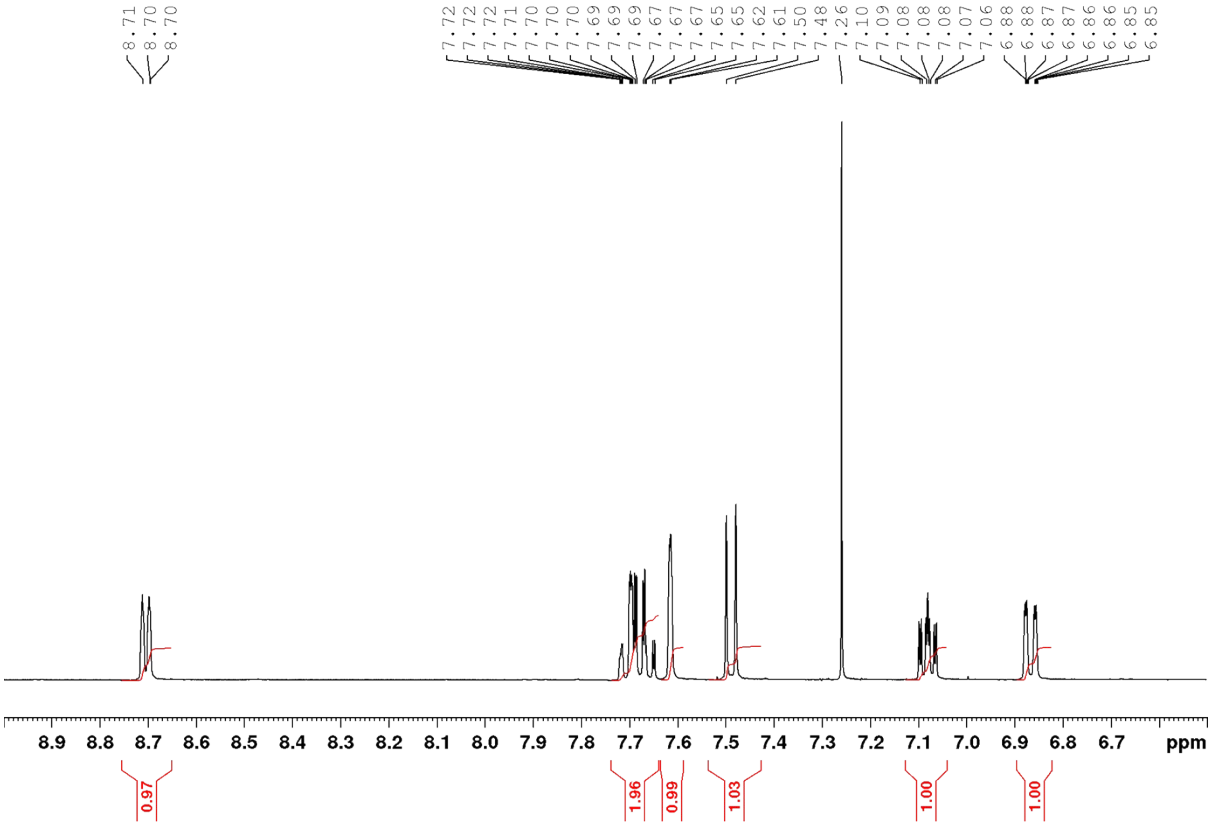

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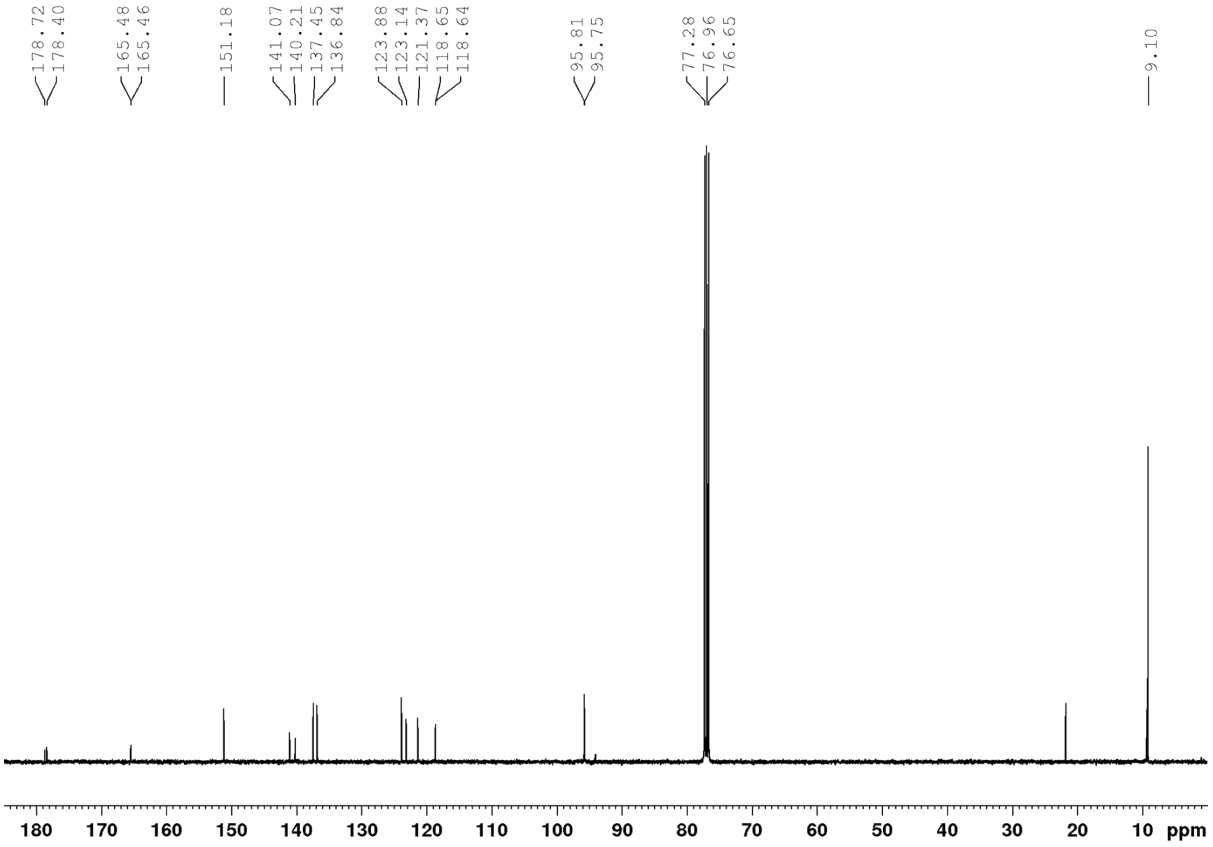

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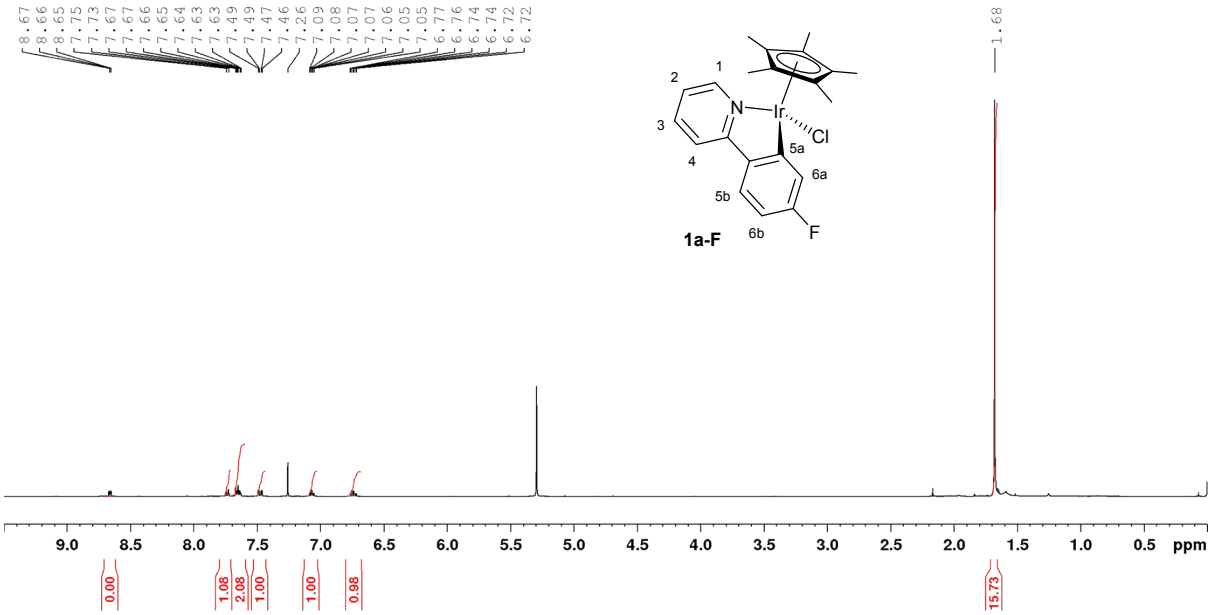
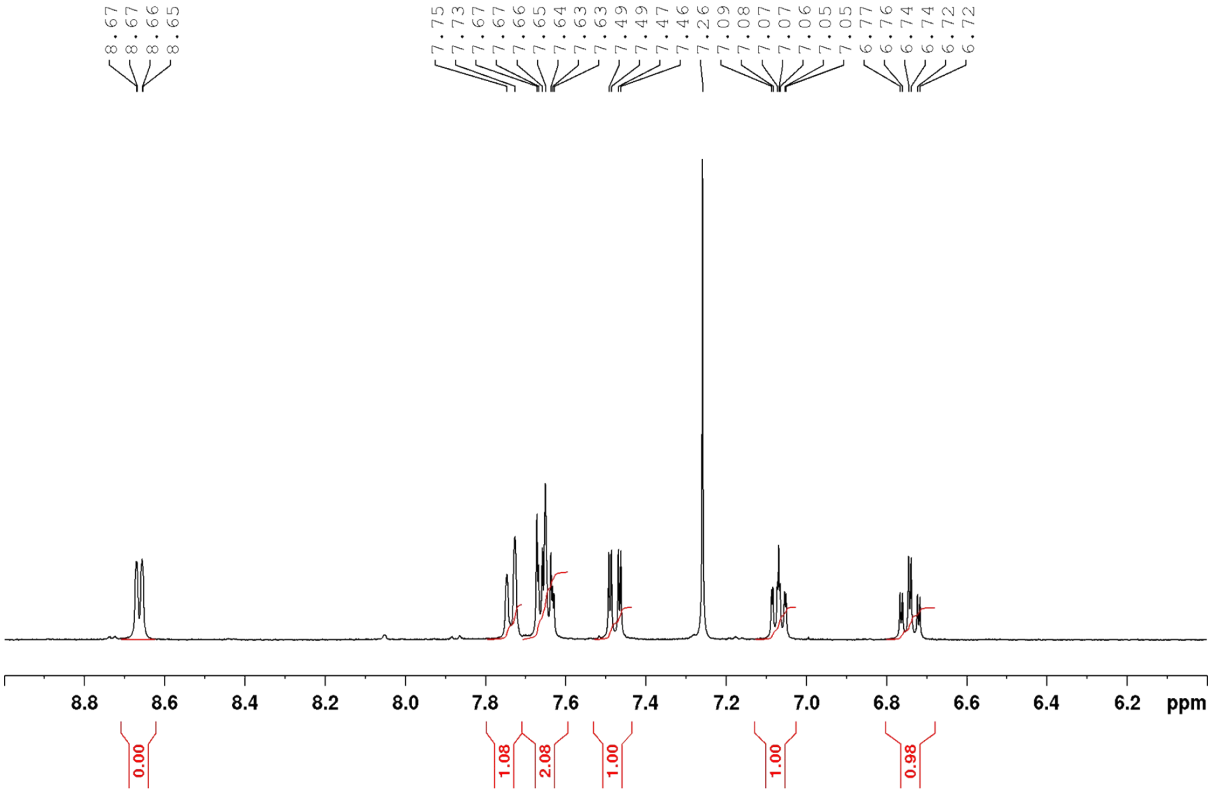
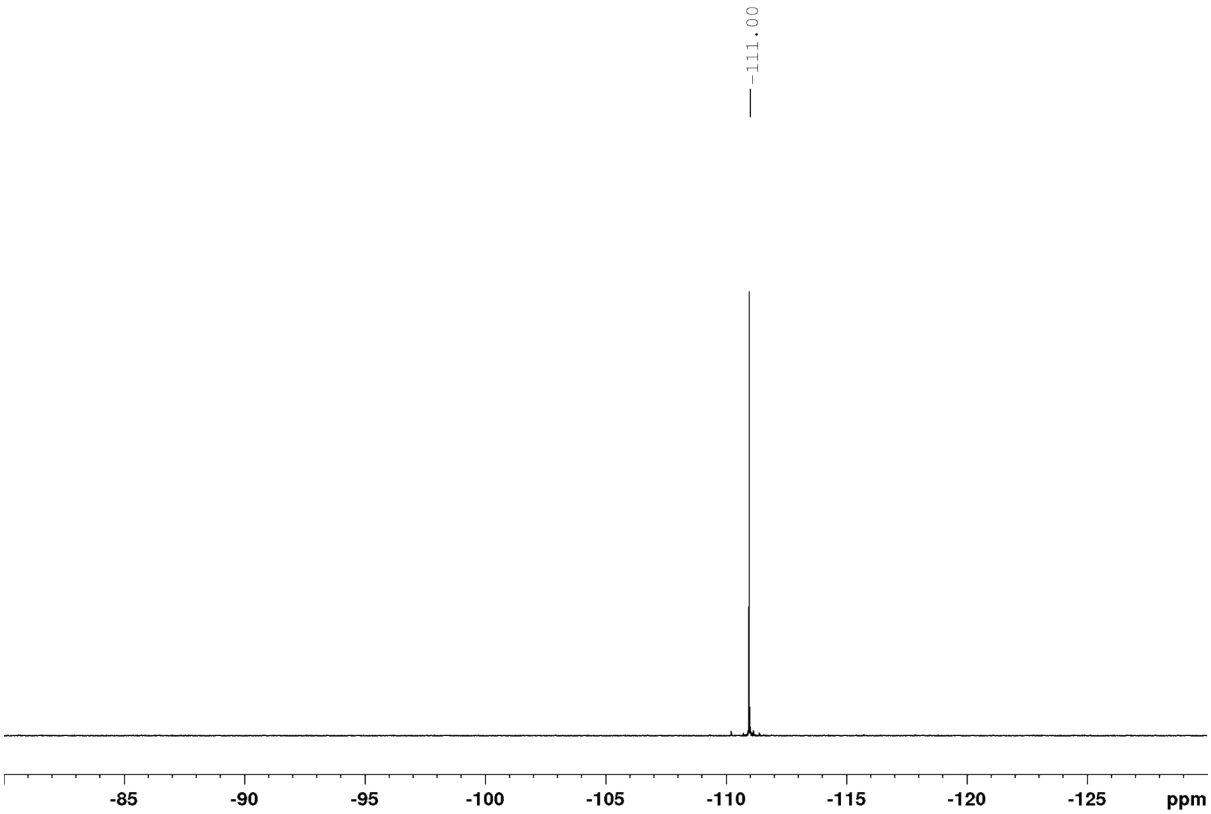


Expansion of ^{1}H NMR 1a-F



^{19}F NMR of 1a-F



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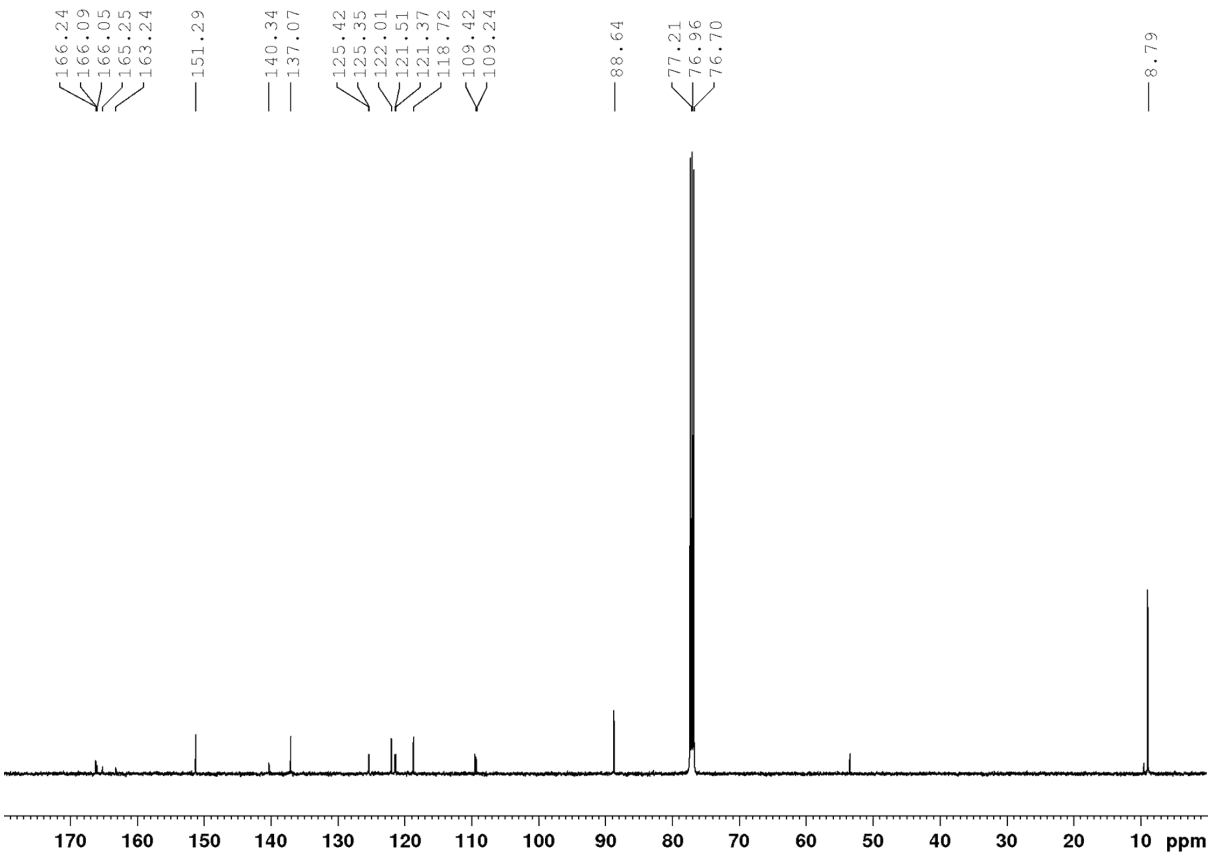

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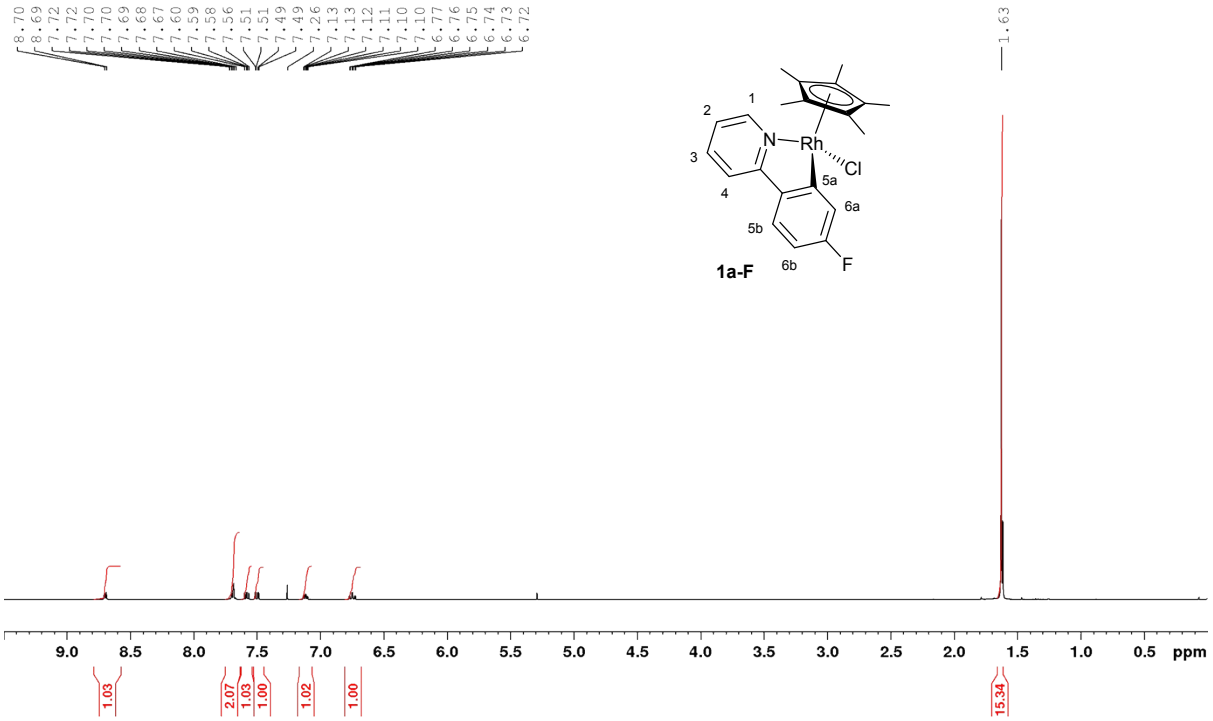
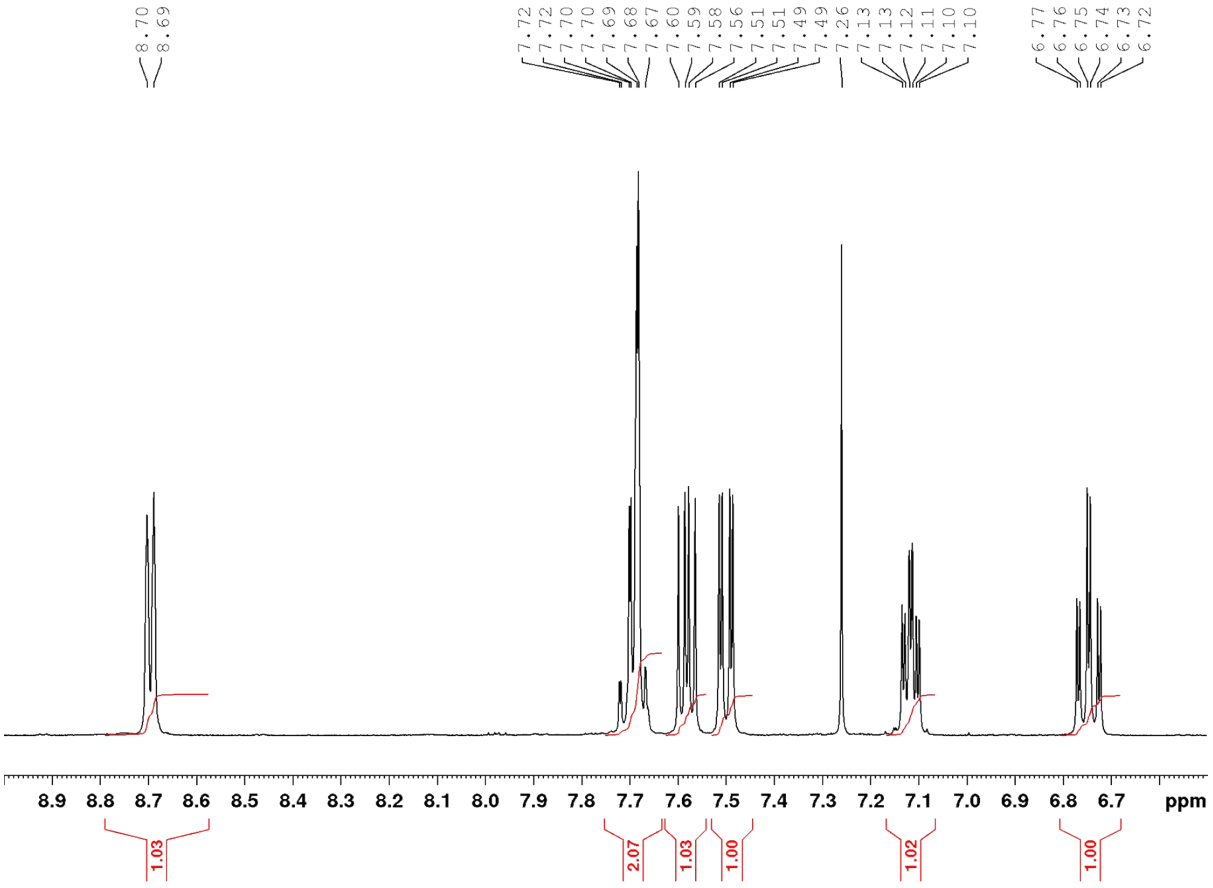


Expansion of ^{1}H NMR 1b-F



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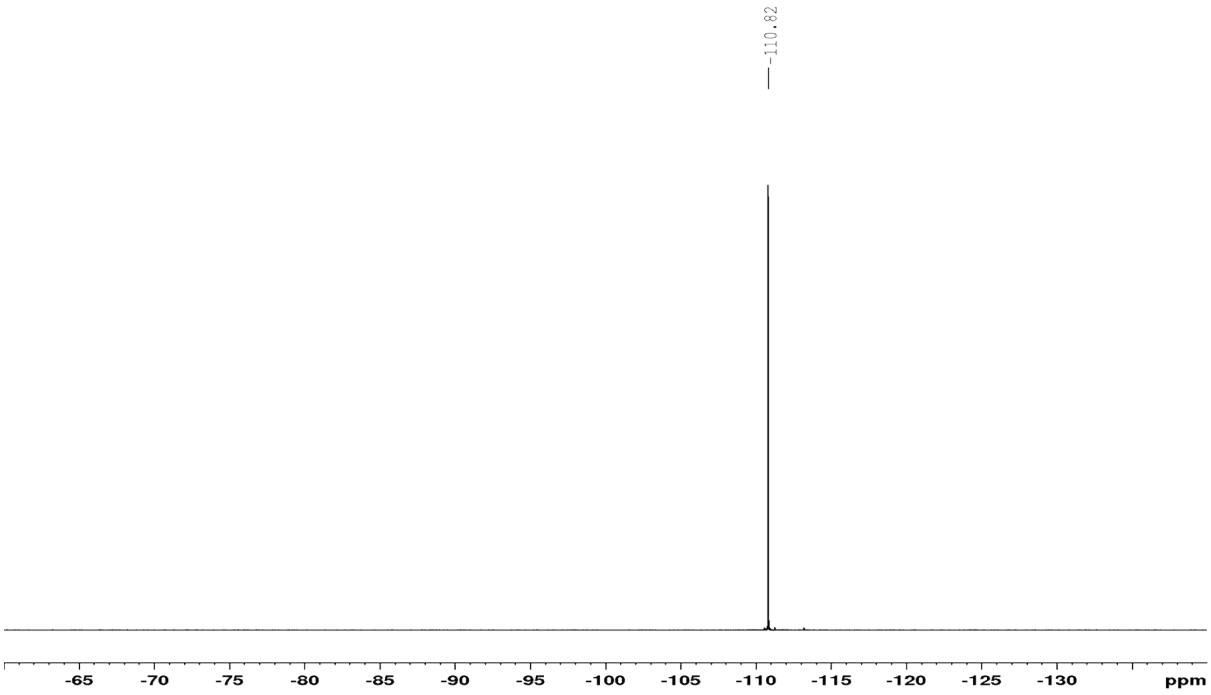

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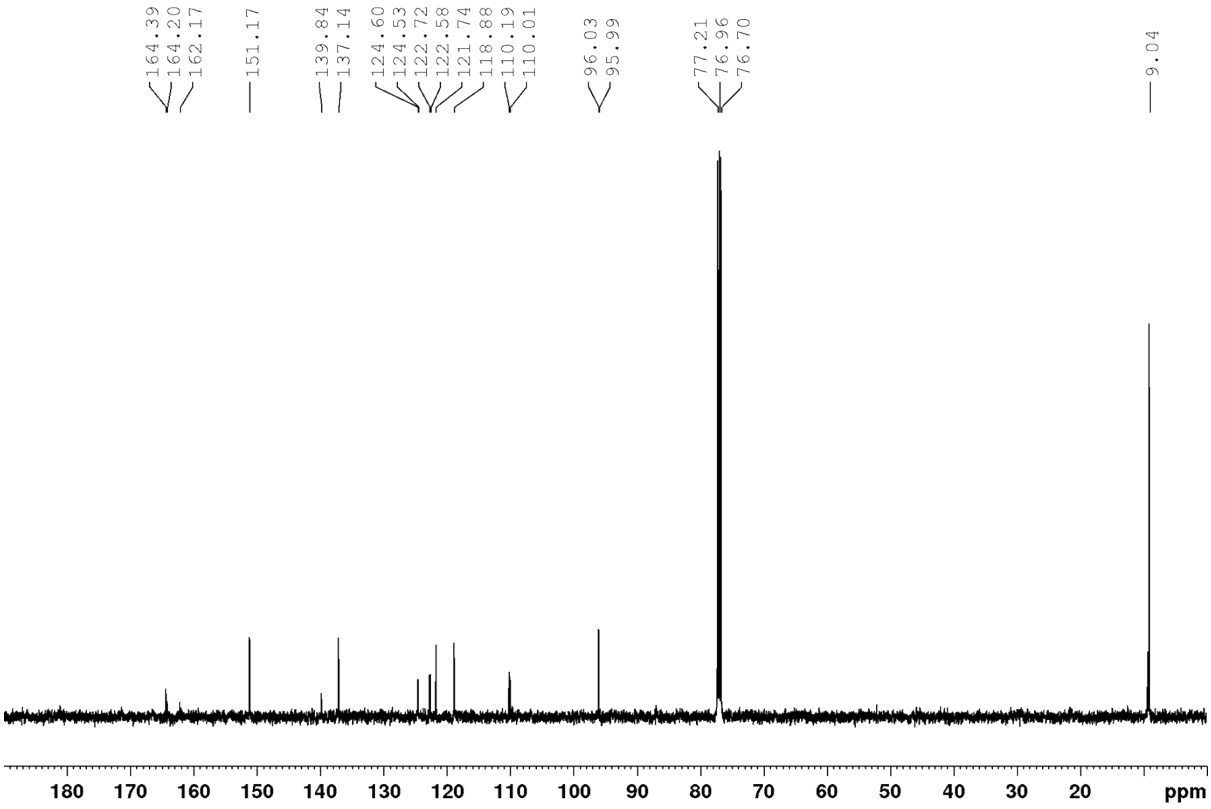
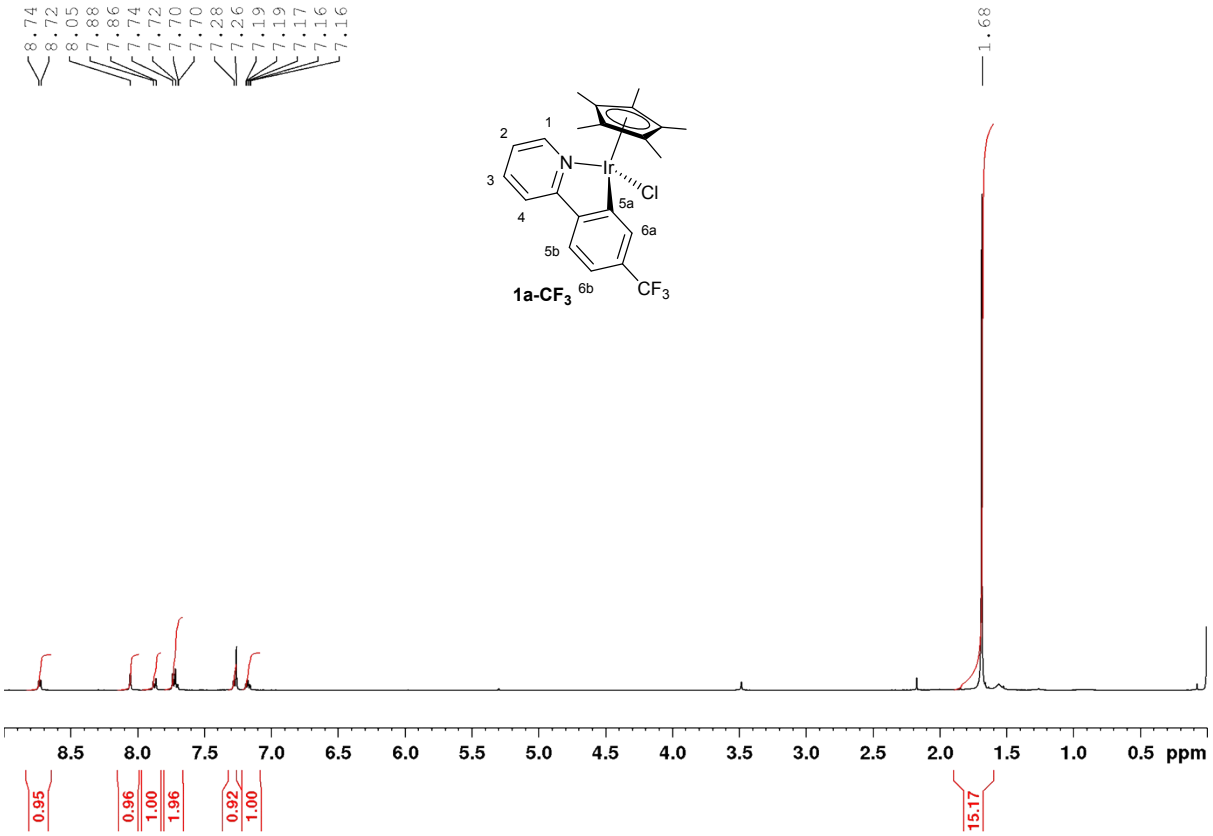


^{1}H NMR of 1a-CF_3



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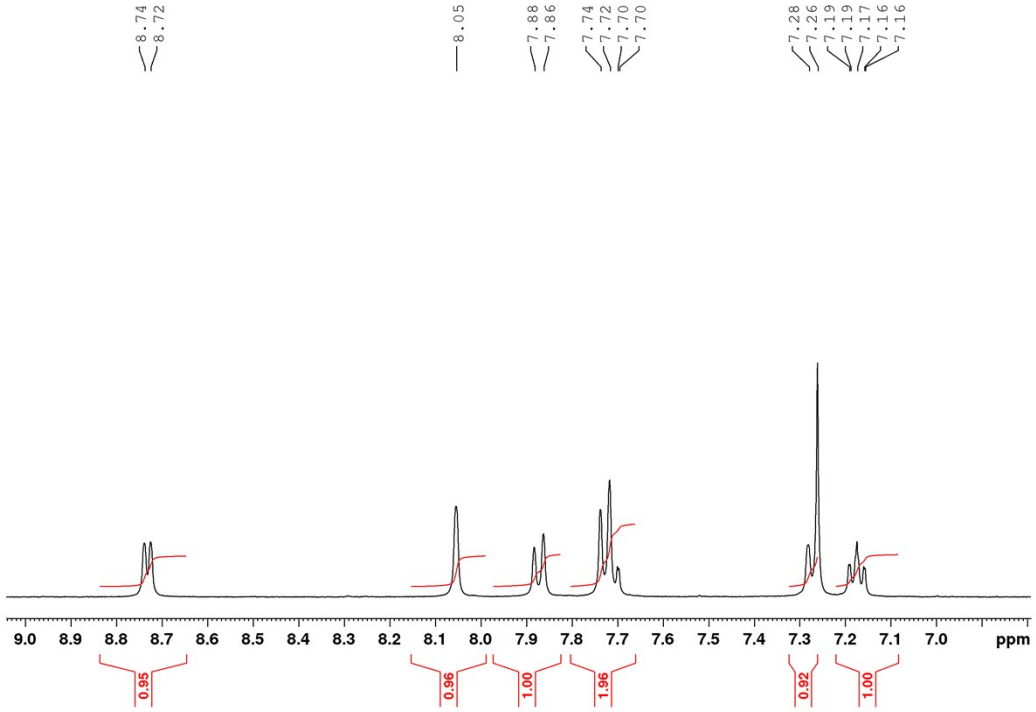

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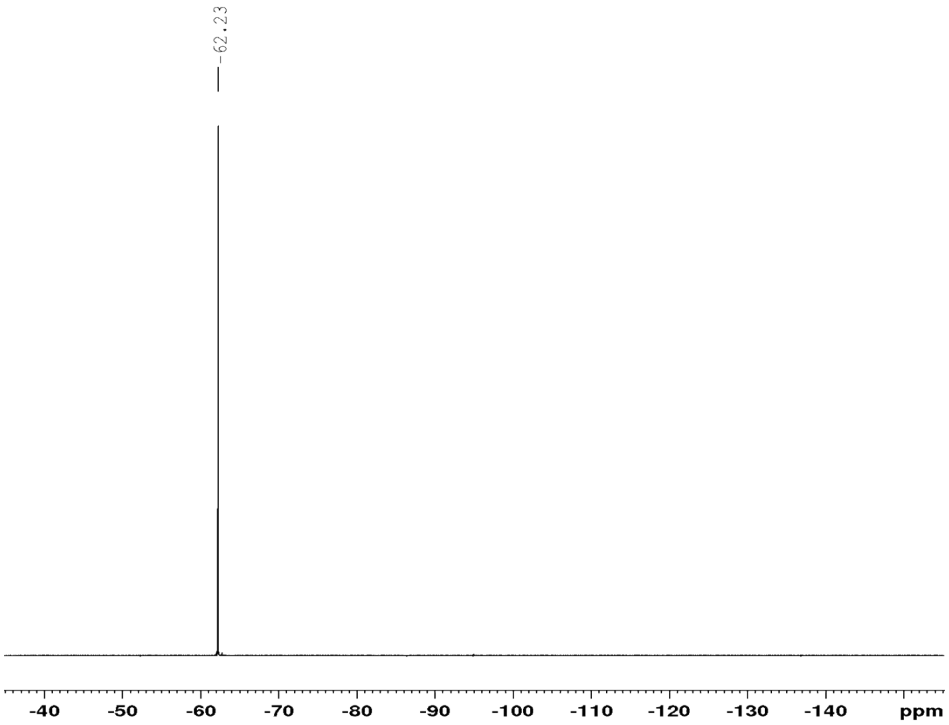

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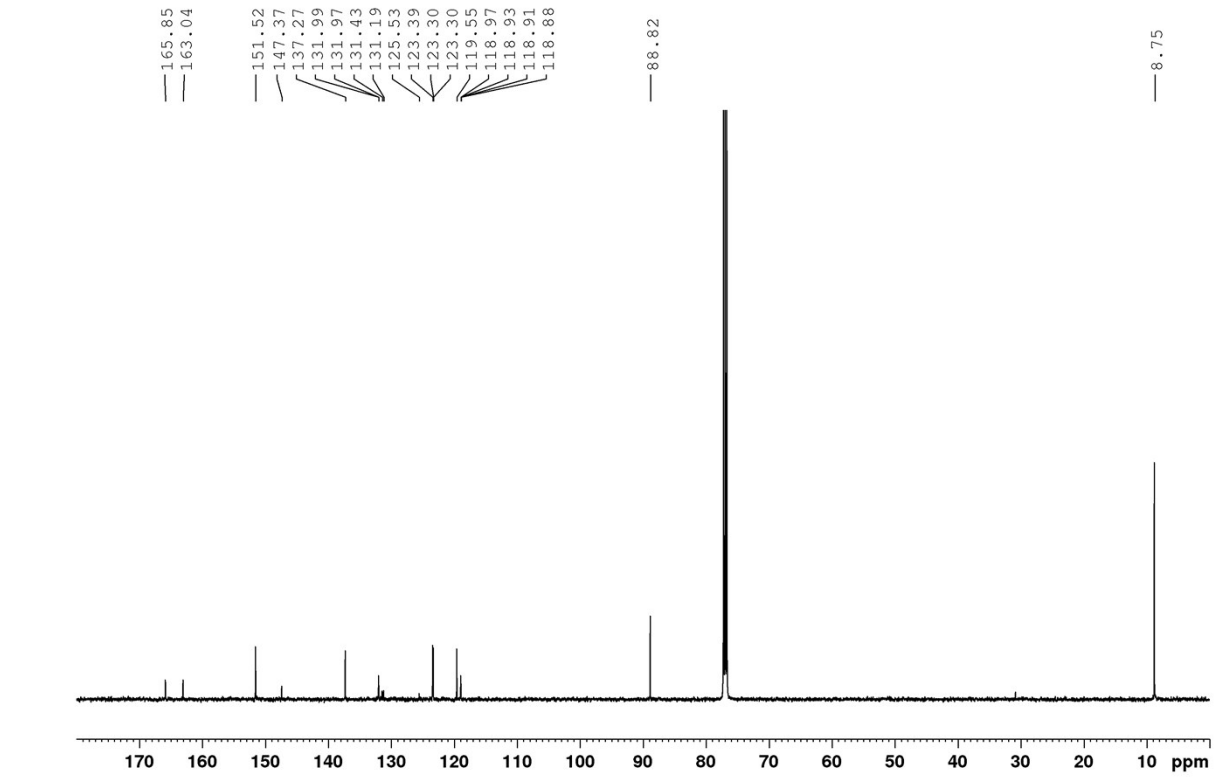

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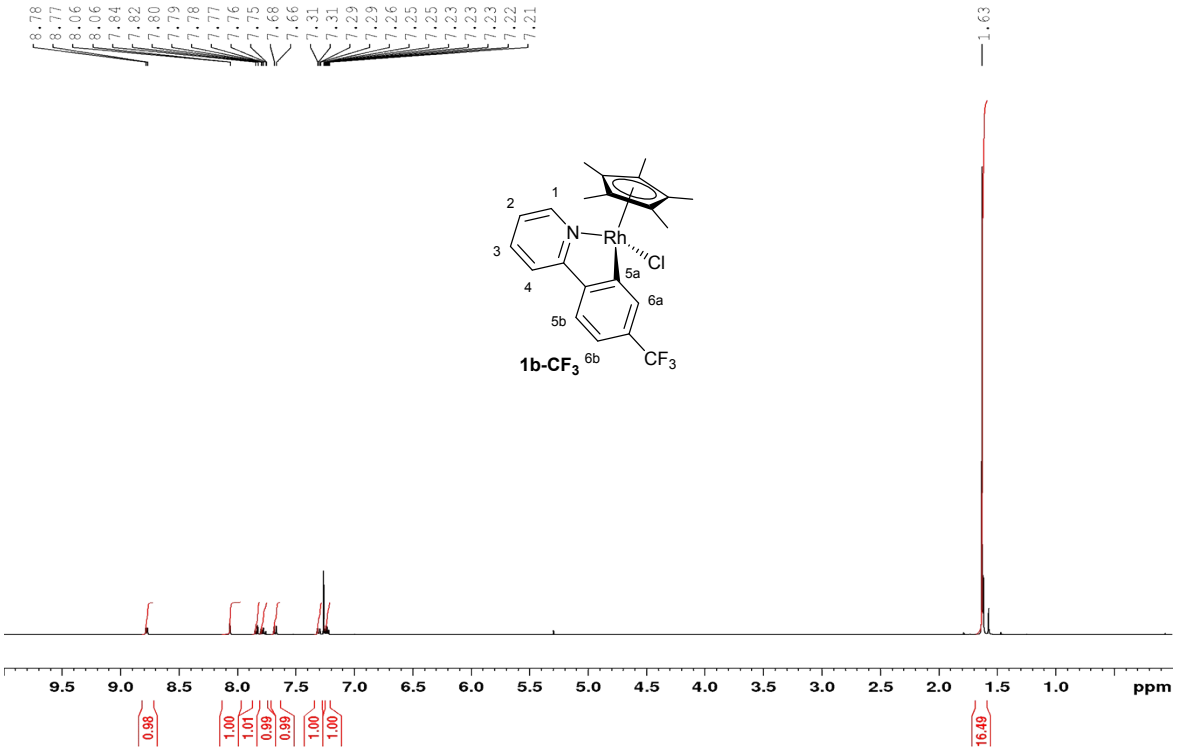

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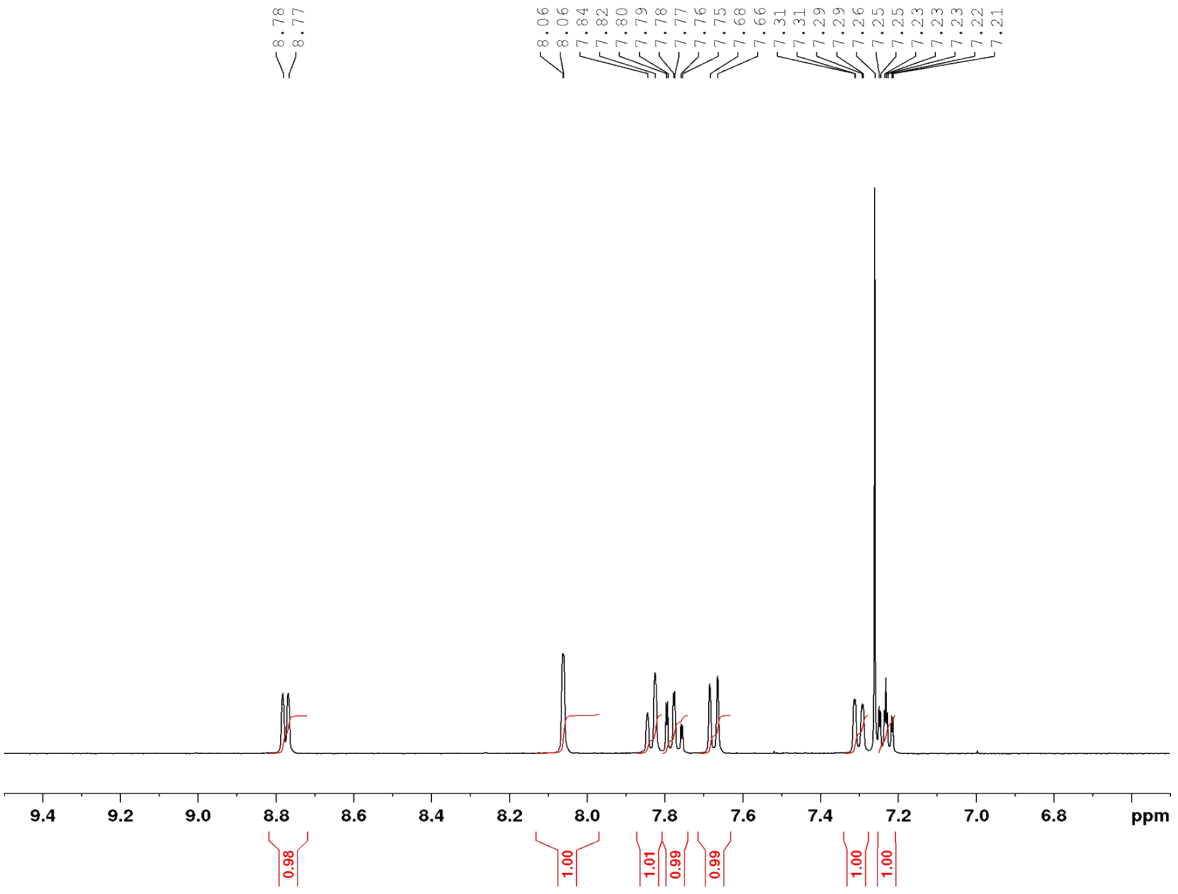

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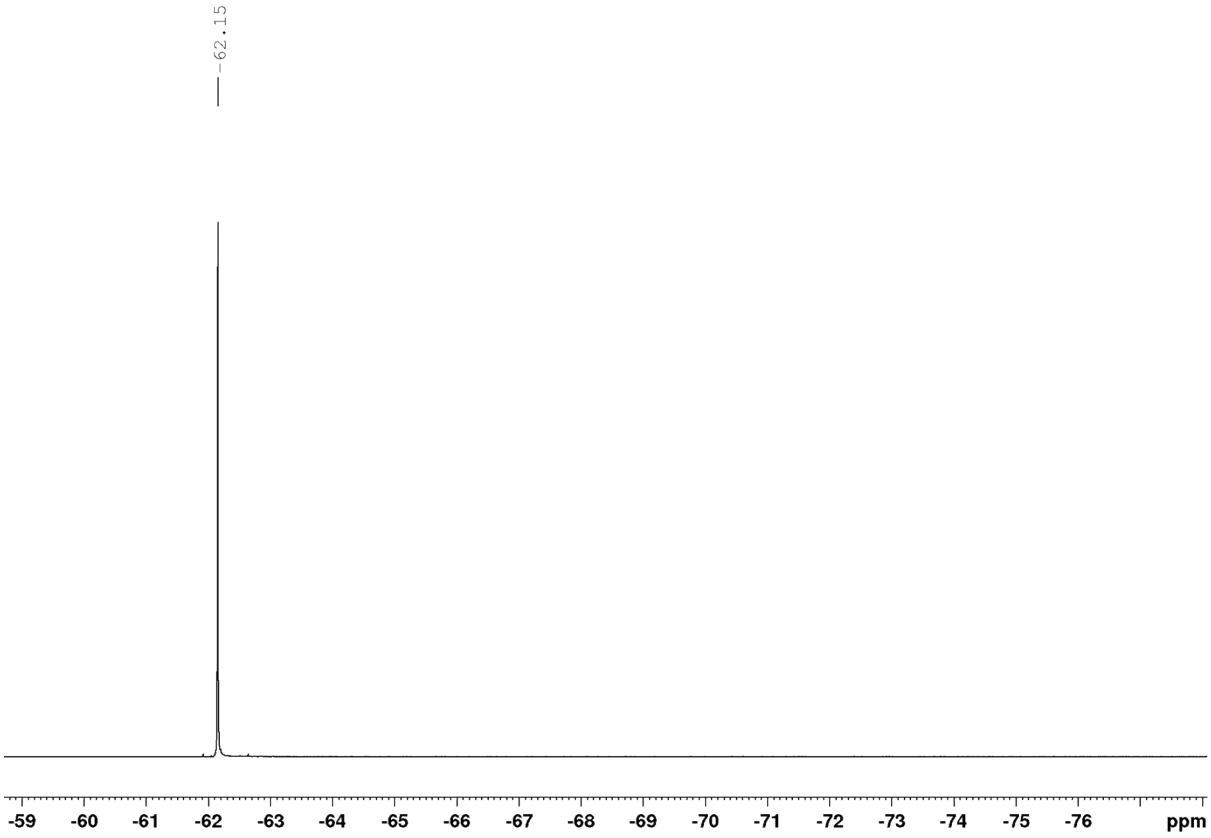

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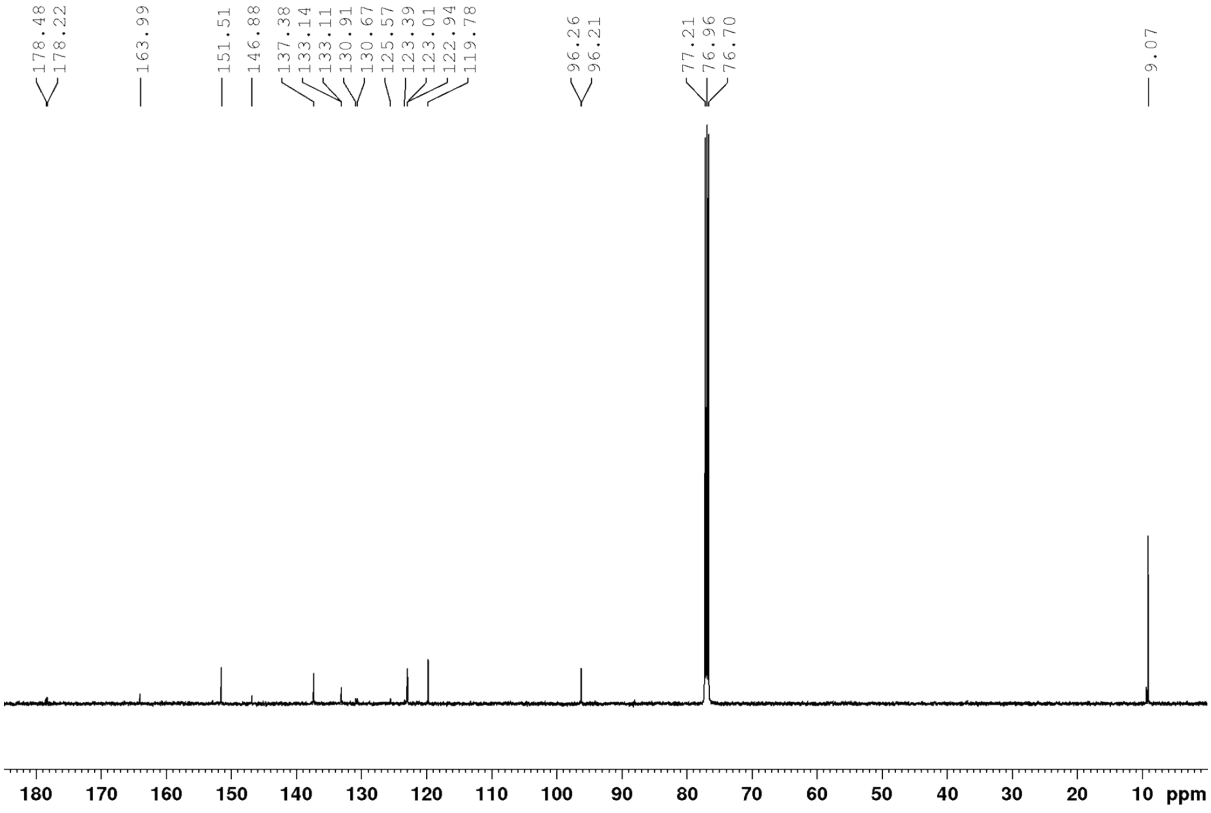
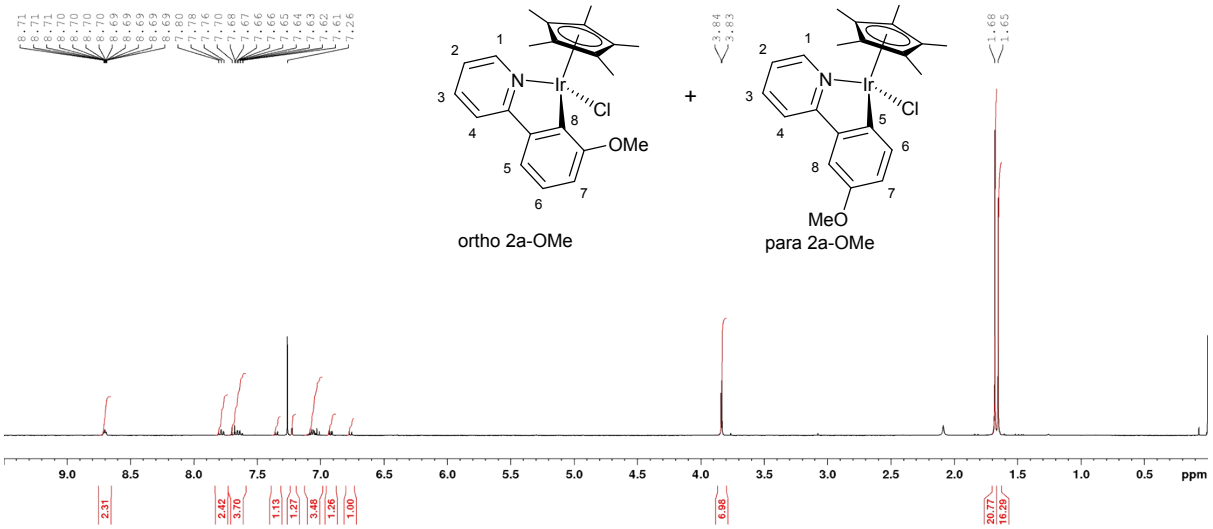
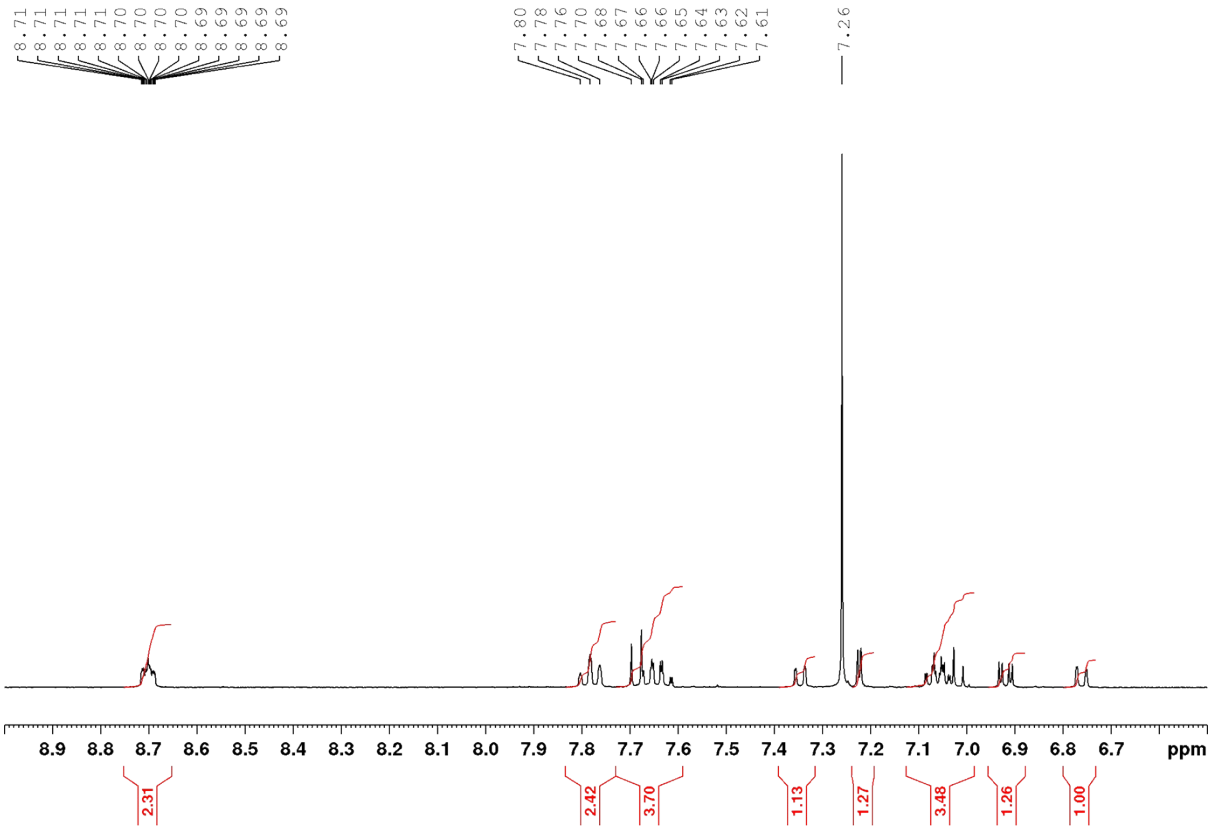


^{1}H NMR of a mixture of ortho and para 2a-OMe



Expansion of ^{1}H NMR of para 2a-OMe



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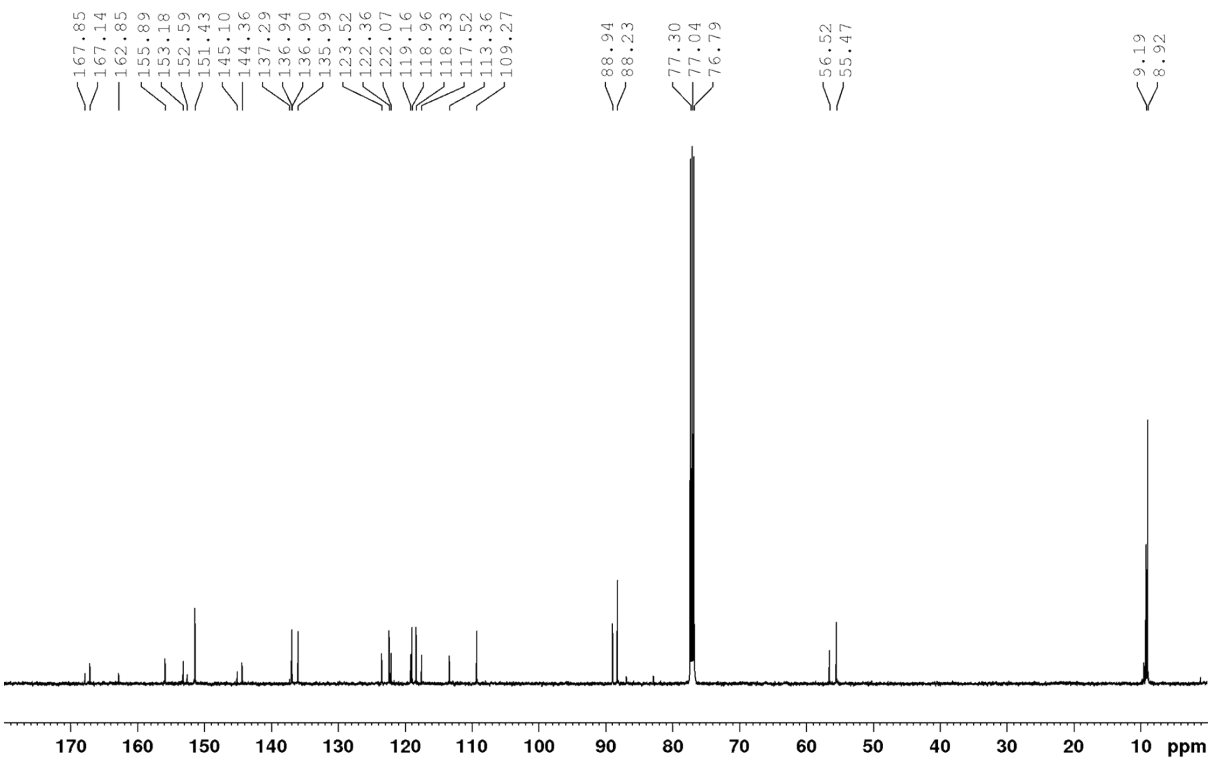

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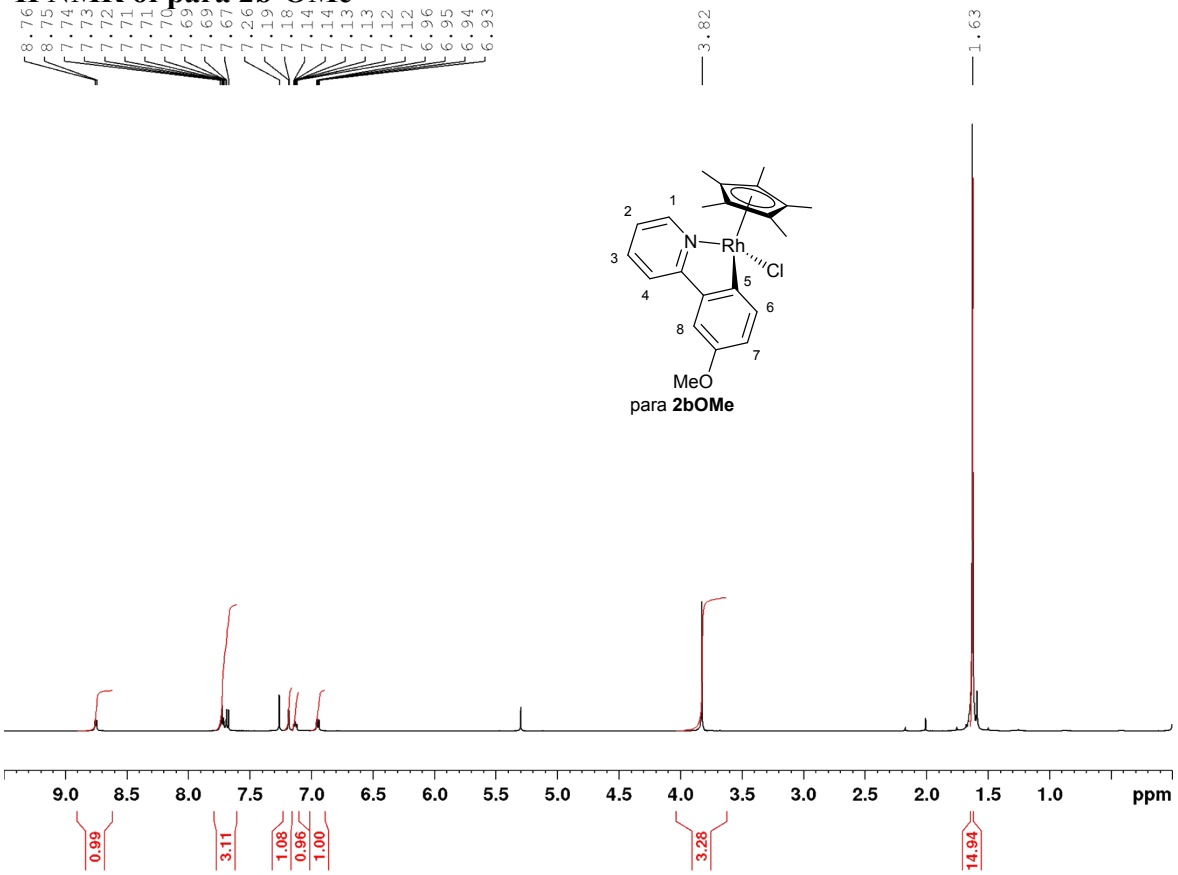

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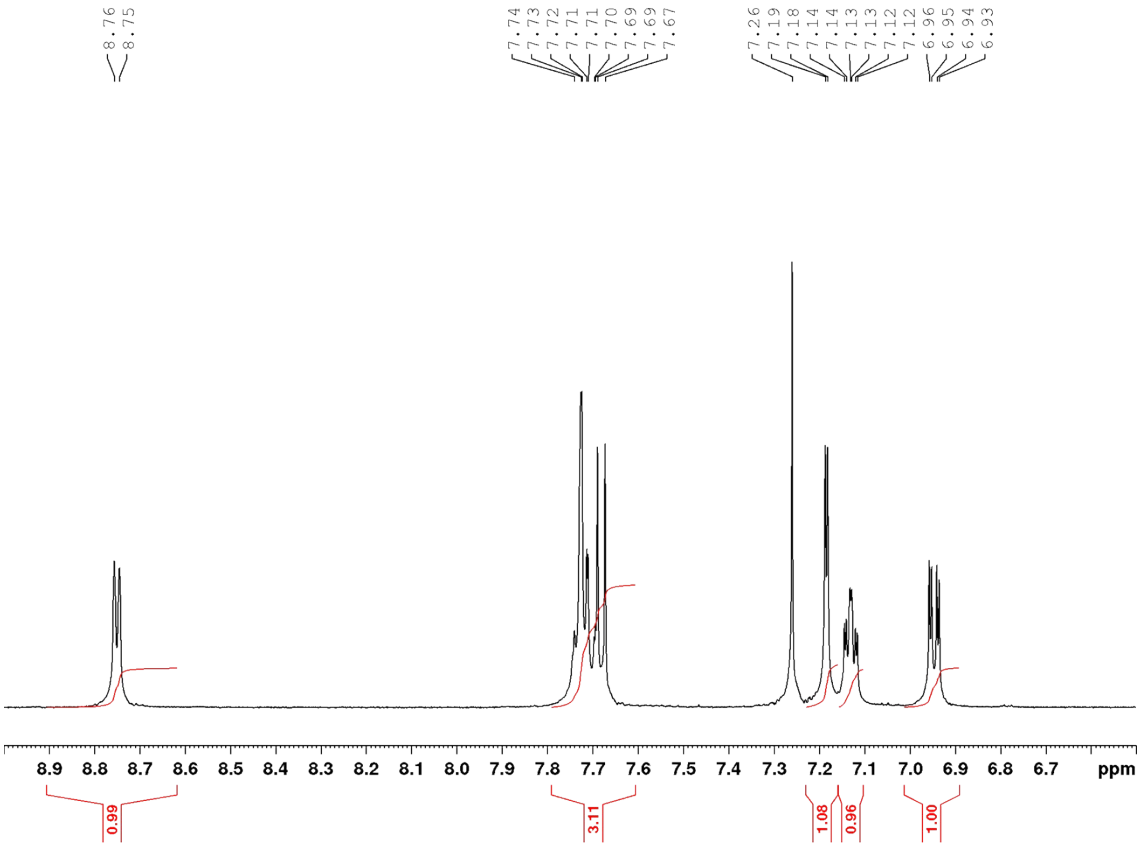

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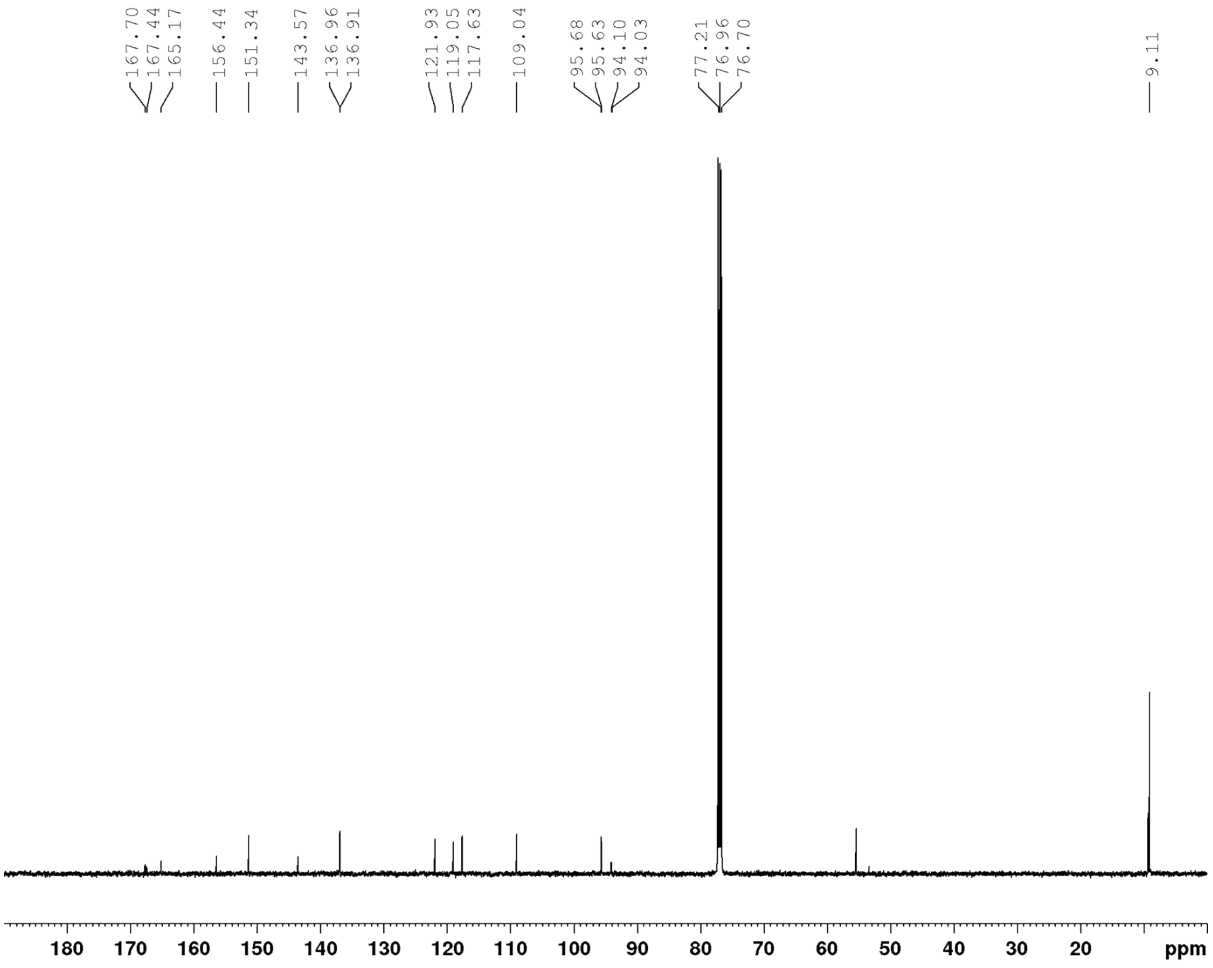

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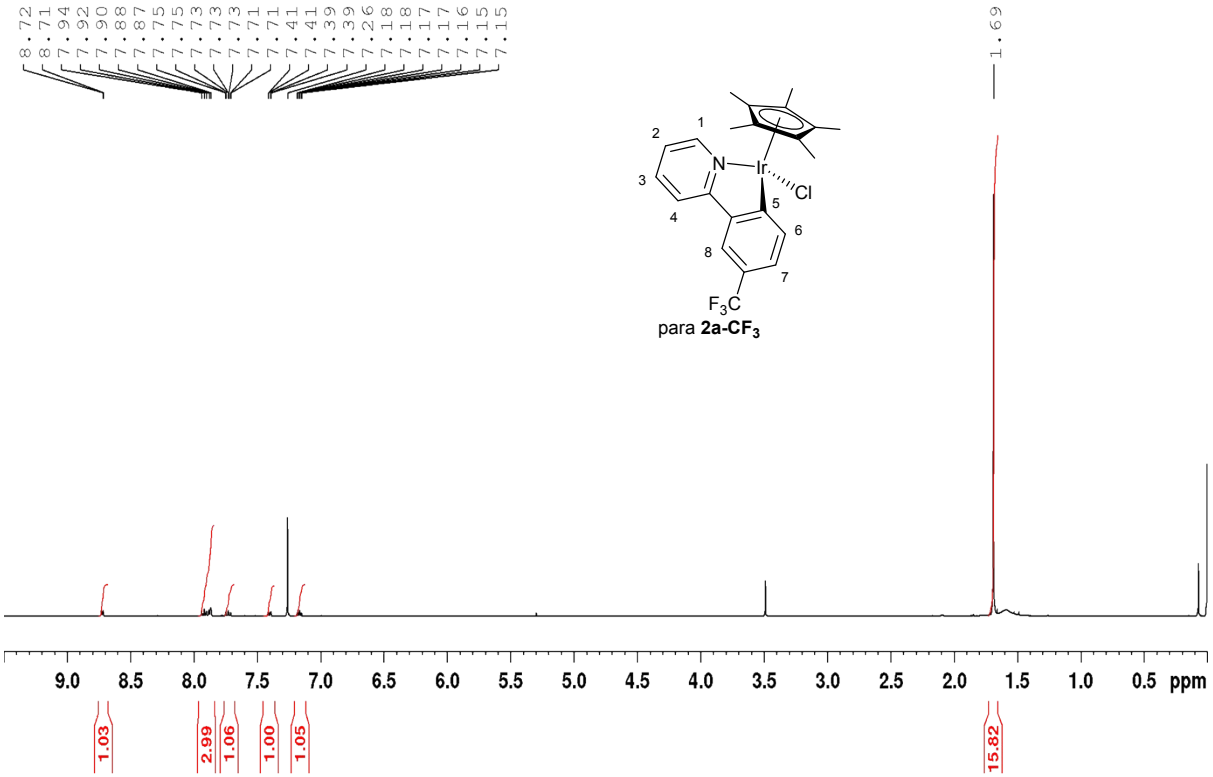

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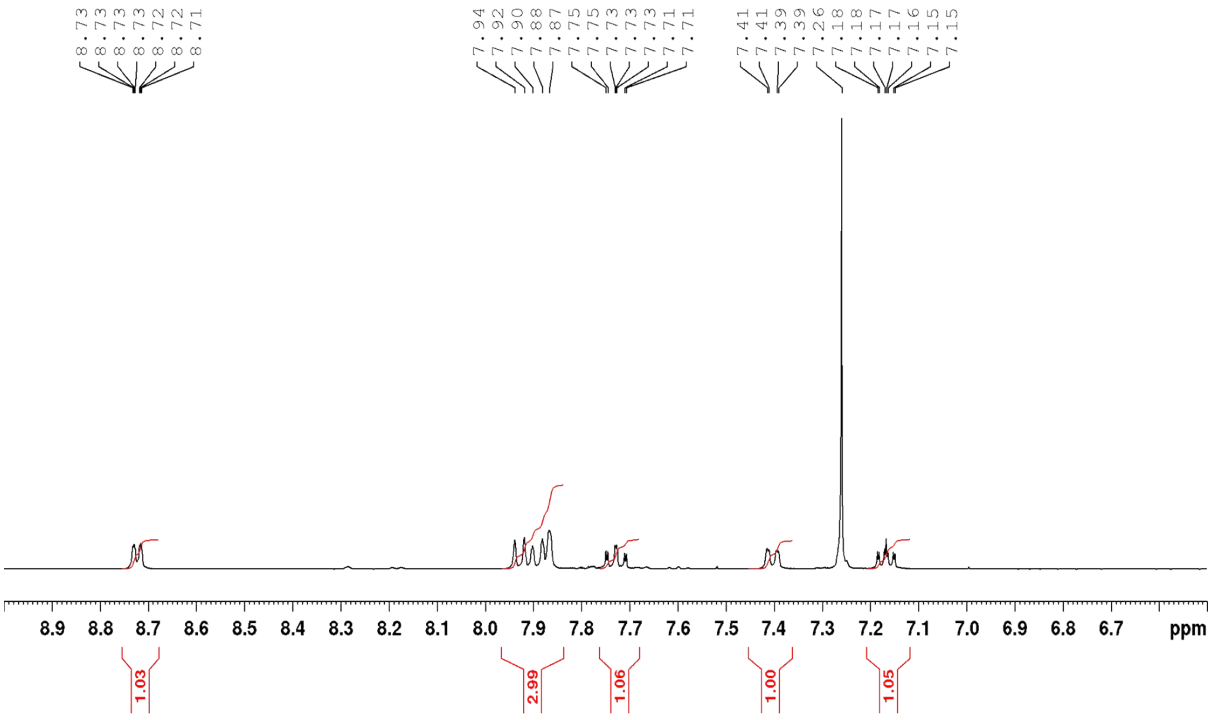
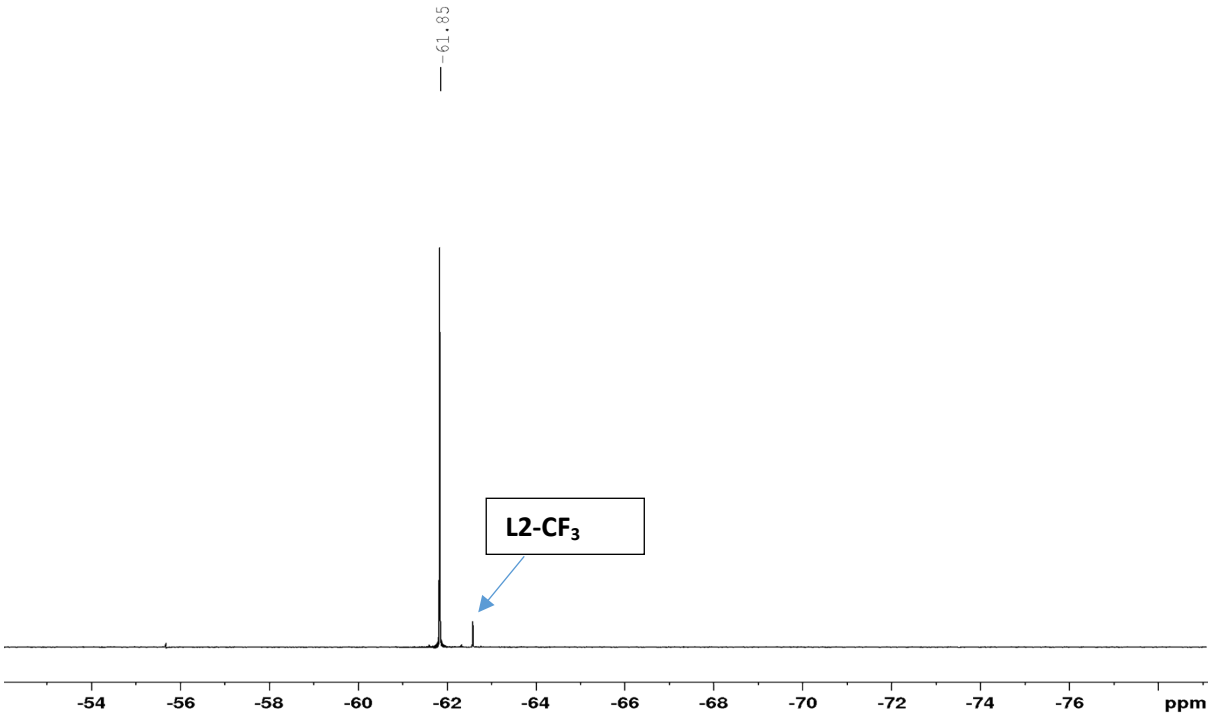


^{19}F NMR of para 2a-CF_3



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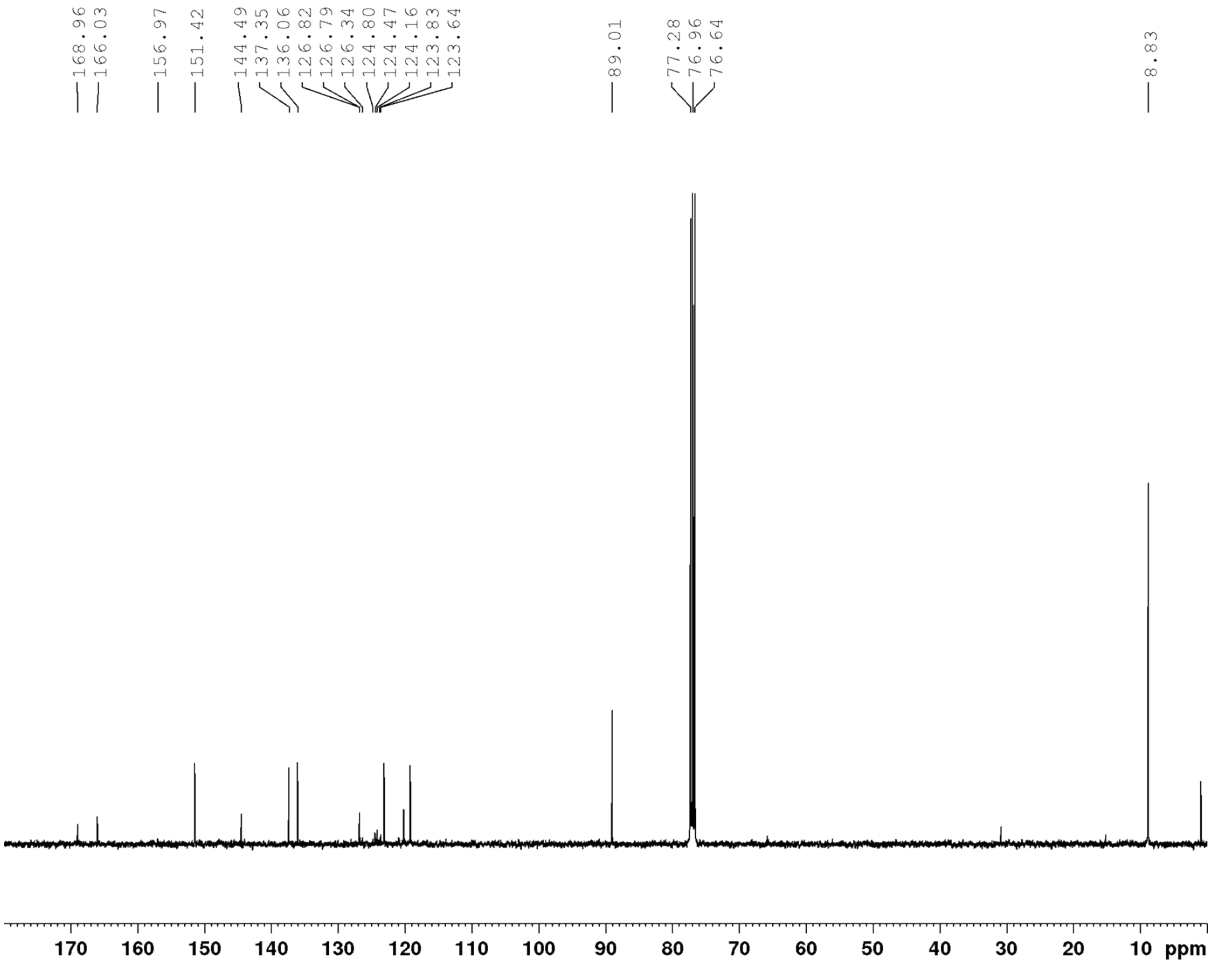
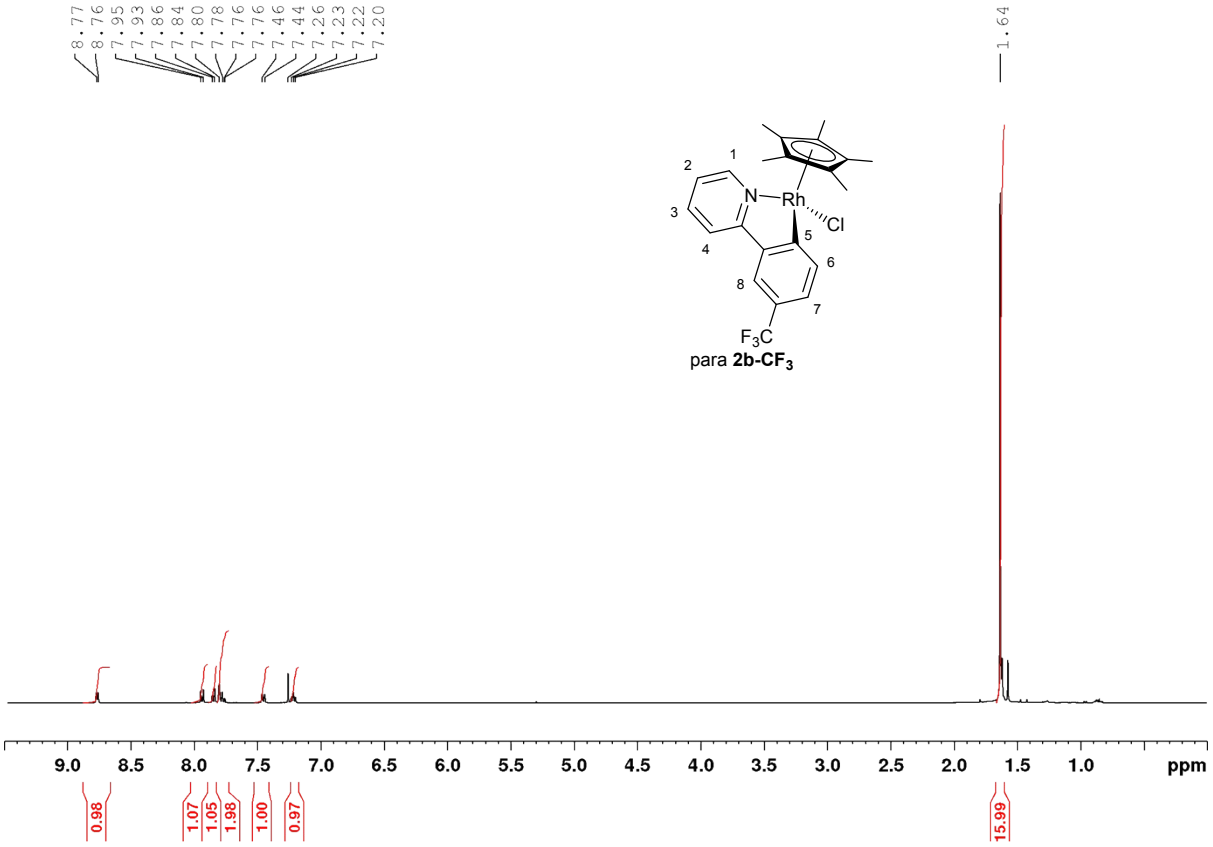
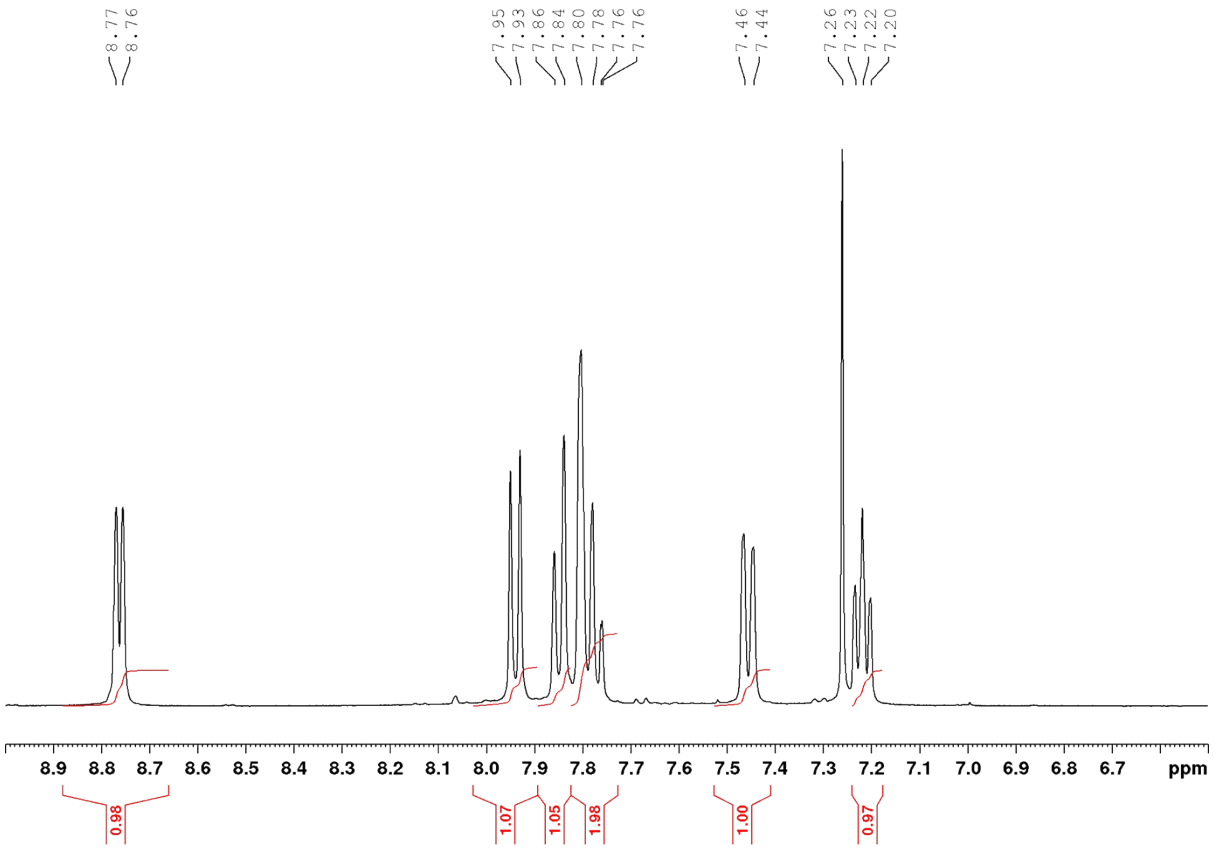


Expansion of ^{1}H NMR of para 2b-CF_3



Expansion of ^{1}H NMR of para 2b-CF_3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8.76
7.95
7.93
7.86
7.84
7.80
7.78
7.76
7.76
7.46
7.44
7.26
7.23
7.22
7.20
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
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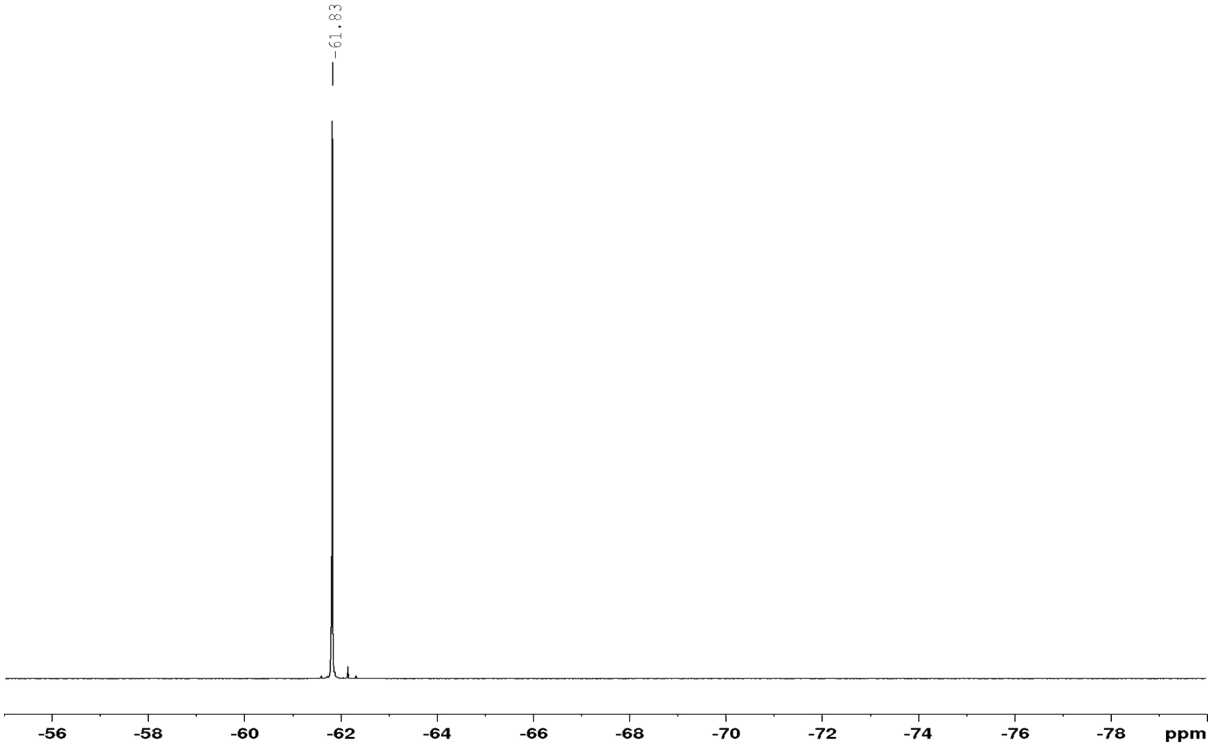
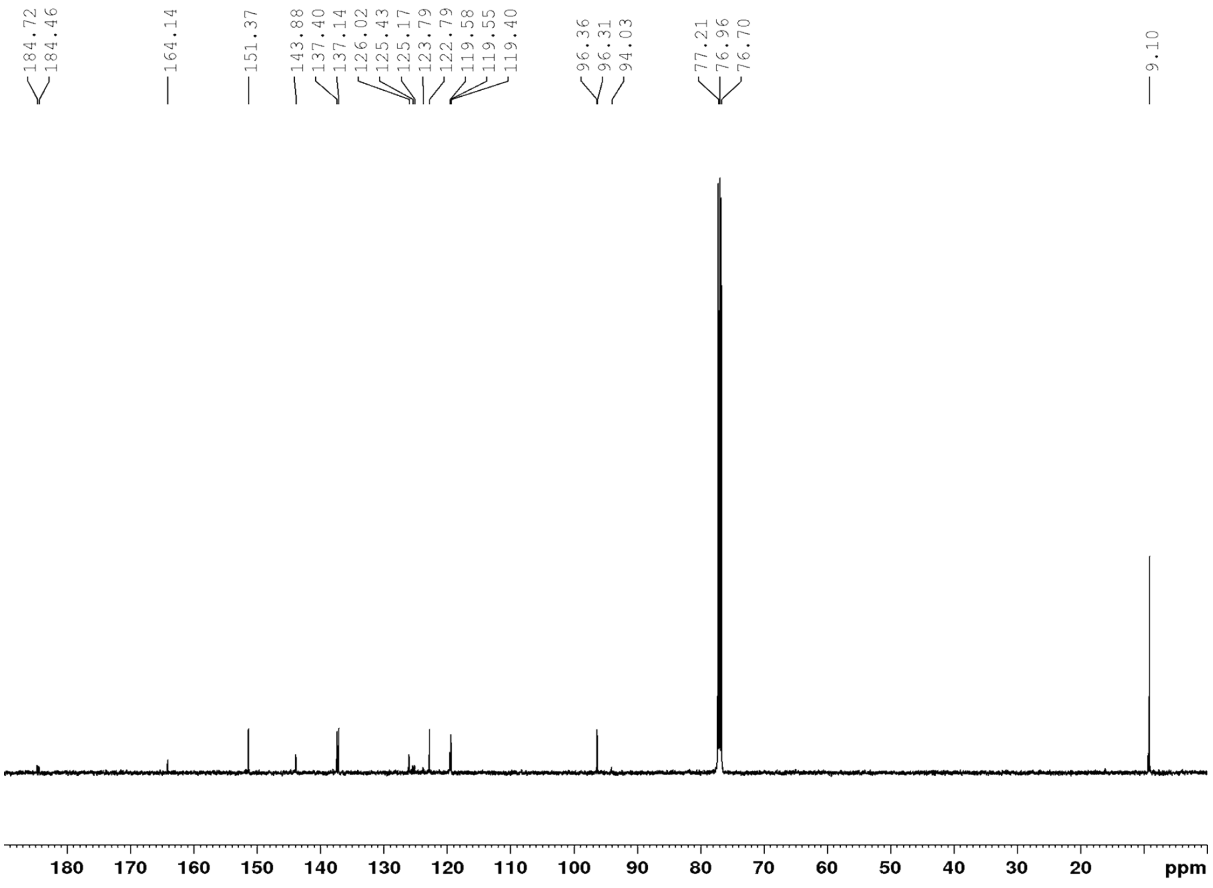
1.98
1.00
0.97

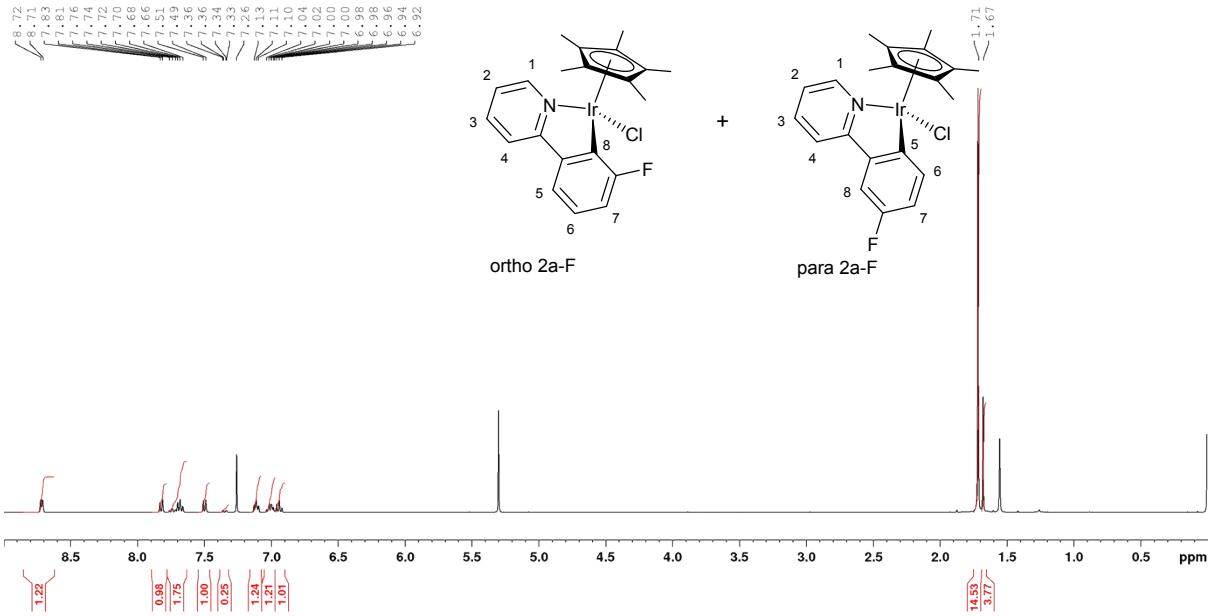
^{19}F NMR of para 2b-CF_3



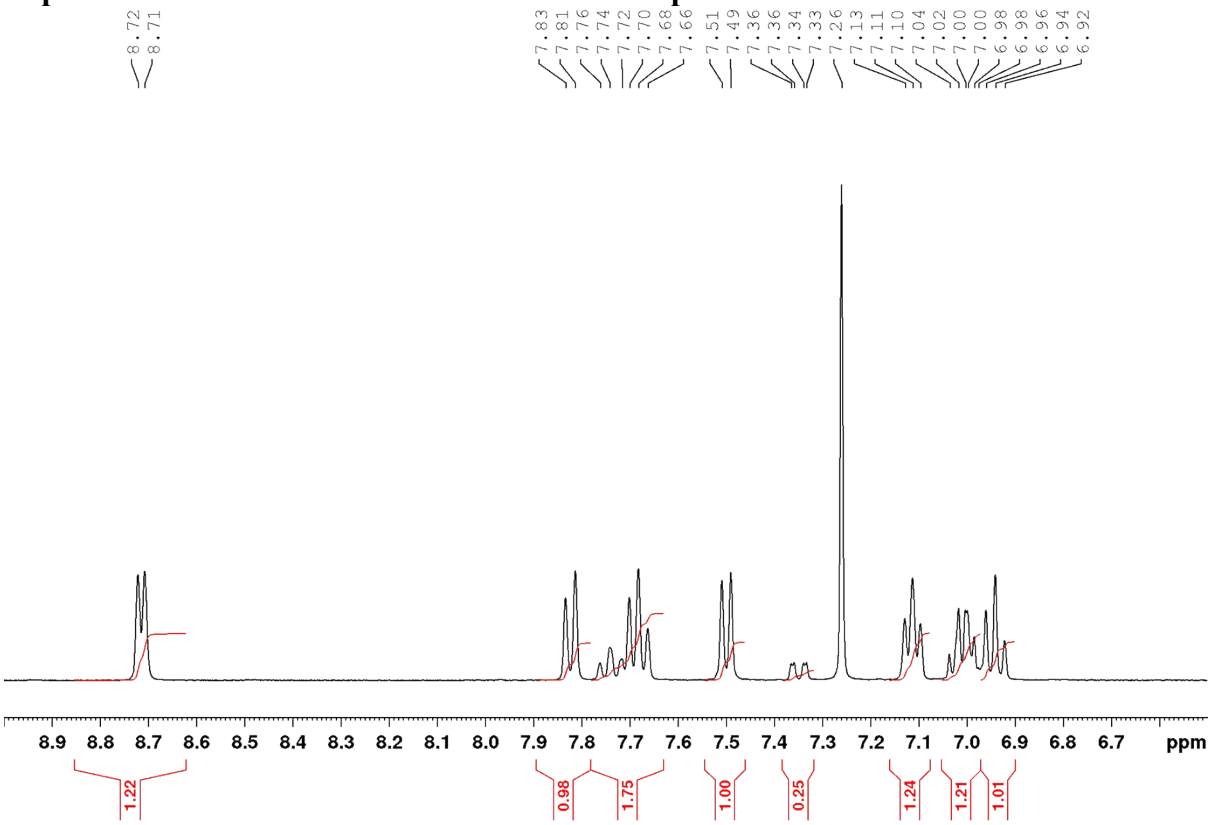
^{13}H NMR of para 2b-CF_3



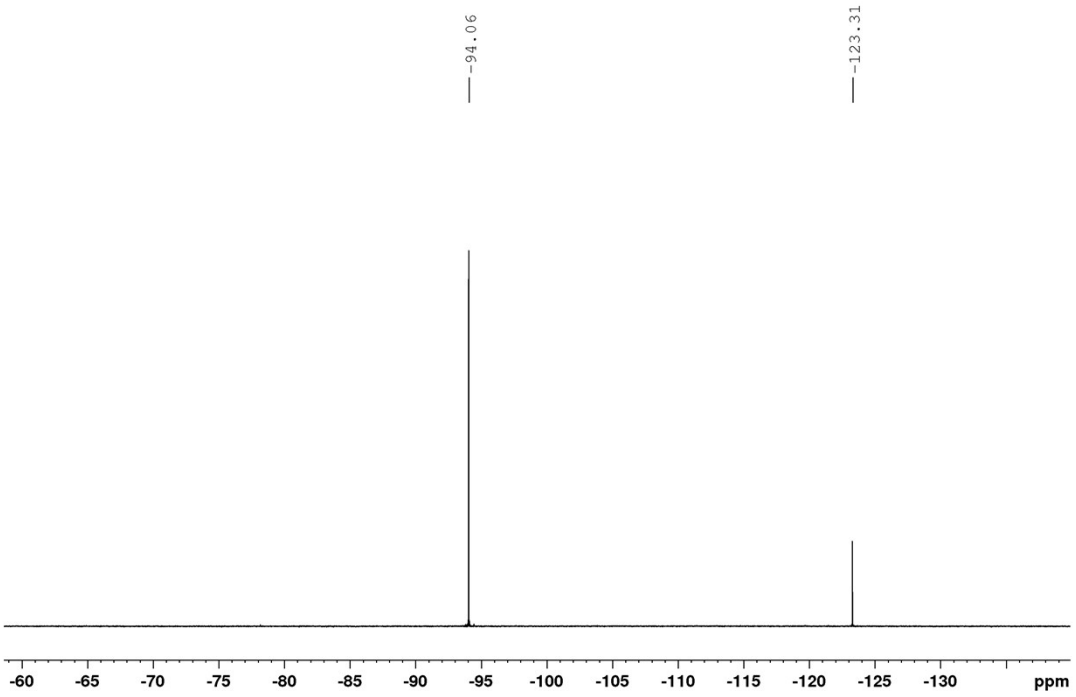
^{1}H NMR of a mixture of ortho and para 2a-F



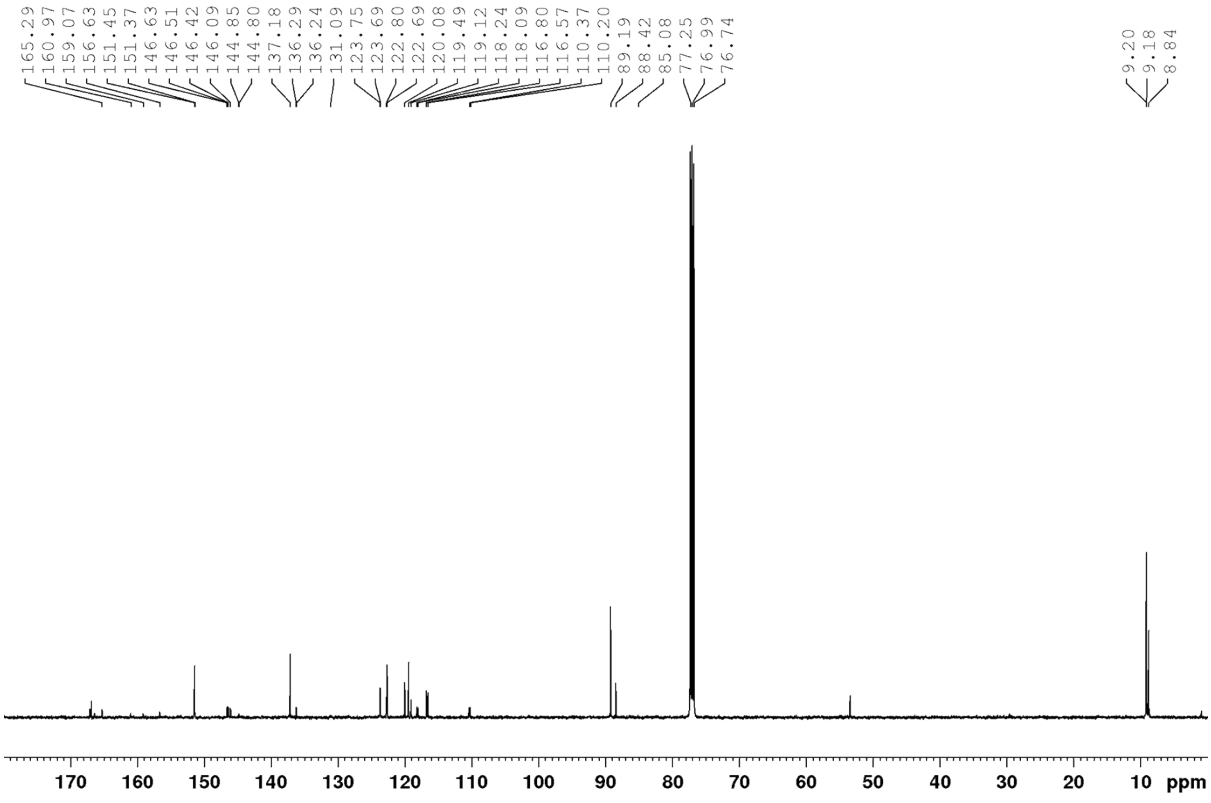
Expansion of ^{1}H NMR of a mixture of ortho and para 2a-F



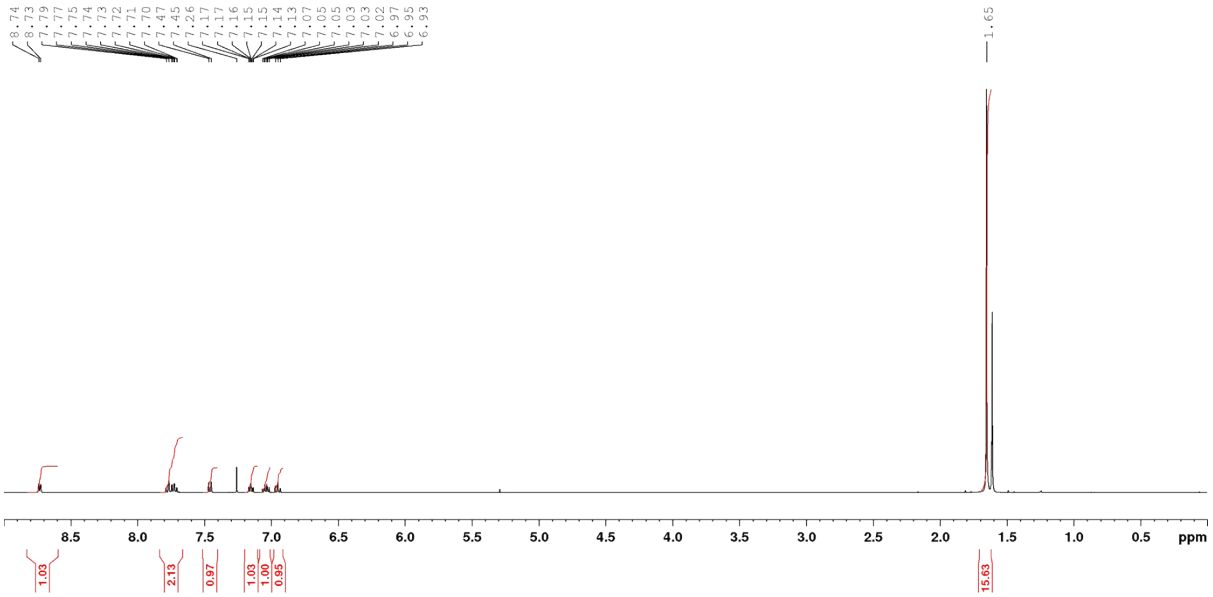
^{19}F NMR of a mixture of ortho and para 2a-F



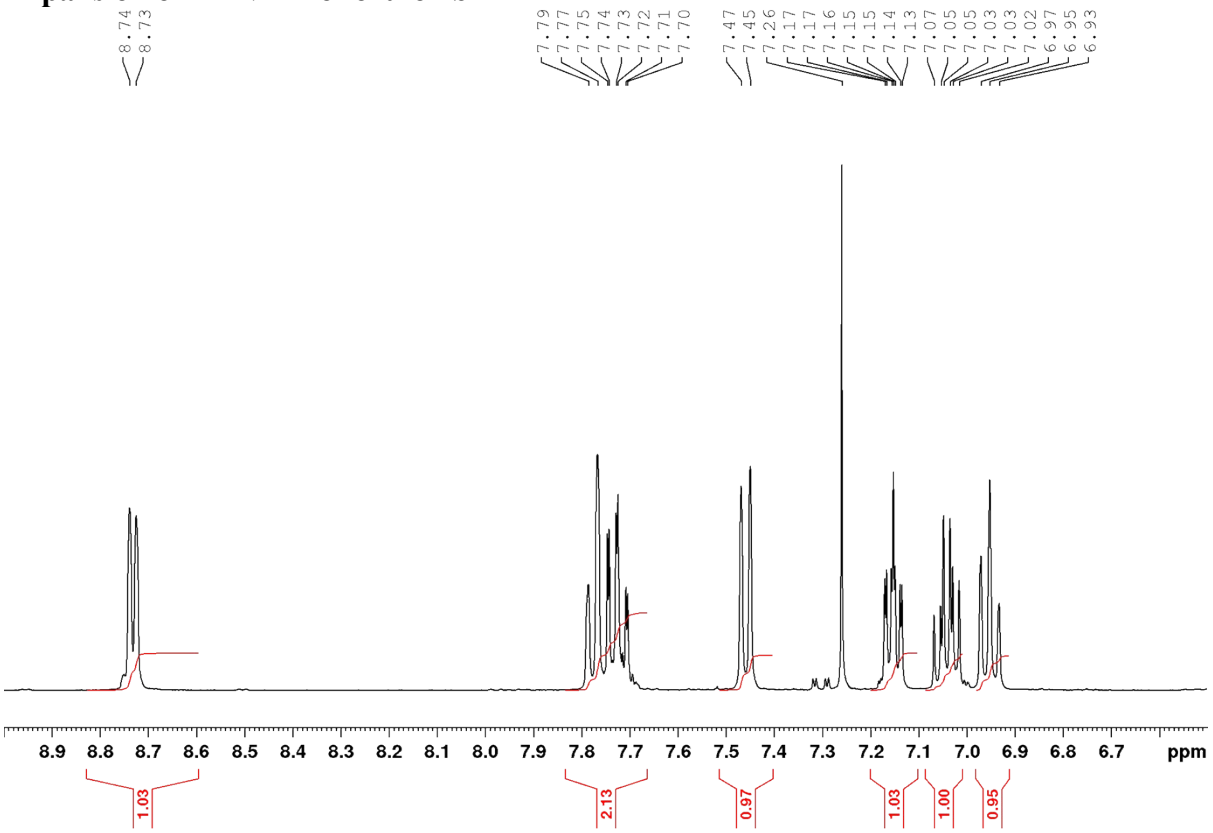
^{13}C NMR of a mixture of ortho and para 2a-F



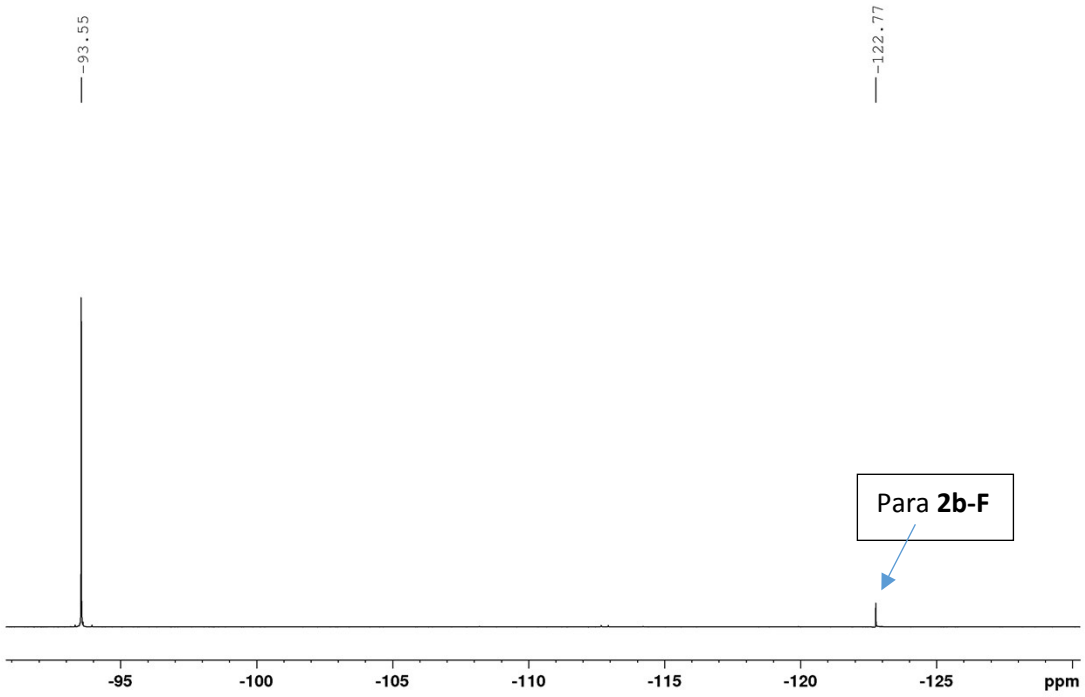
^{1}H NMR of ortho 2b-F



Expansion of ^{1}H NMR of ortho 2b-F



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



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