

Supplementary Information for

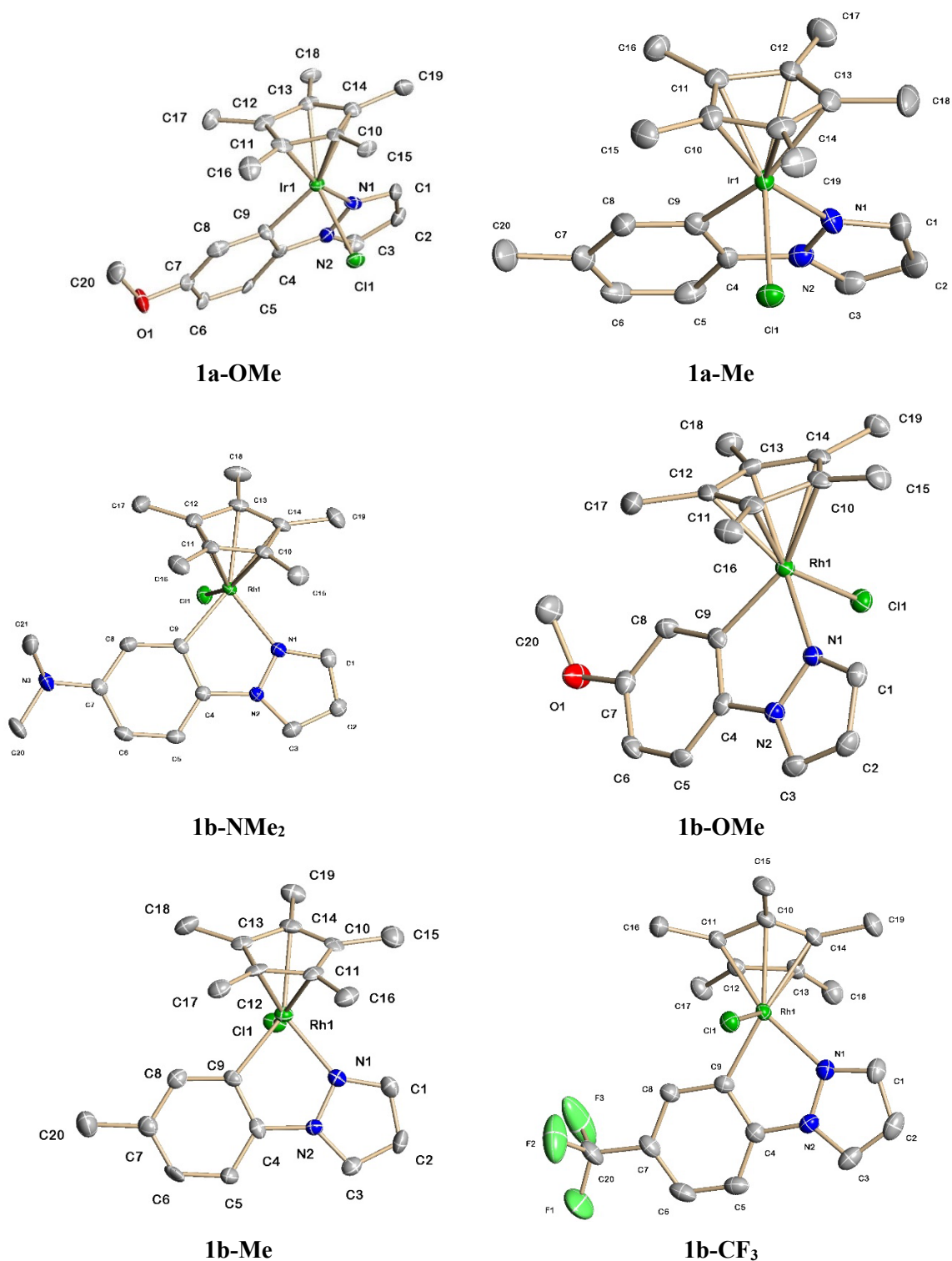
**The Importance of Kinetic and Thermodynamic Control when Assessing Mechanisms of Carboxylate-Assisted C–H Activation.**

Raed A Alharis,<sup>‡,a</sup> Claire L. McMullin<sup>†,b</sup> David L. Davies,<sup>\*,a</sup> Kuldip Singh,<sup>a</sup> and Stuart A. Macgregor. <sup>\*,b</sup>

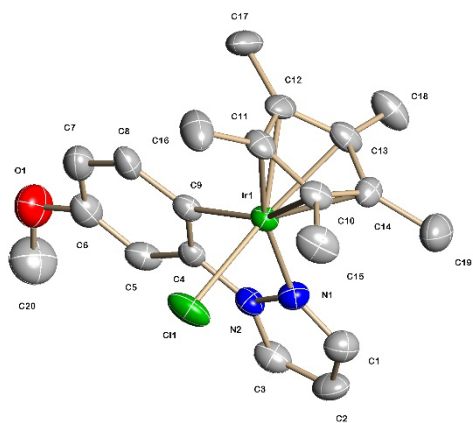
## Contents

	Pages
Fig S1 X-ray structures of selected complexes 1-R	S3
Fig S2 X-ray structures of selected complexes 3-R	S4
Tables S1a-c Selected bond lengths and angles	S5
Deuteration Studies Table S2	S6
Competition experiments Ir Tables S3/4/5	S7-S8
Hammett plot of Ir using $\sigma^+$ values Figure S3	S8
Competition experiments Rh Tables S6-8	S9-S10
Hammett plot of Rh versus $\sigma$ Fig S4, versus $\sigma^+$ Fig S5 and thermodynamic stability Fig S6	S11-12
Experimental Procedures and Characterisation data	S13-S23
NMR spectra	S24-S80

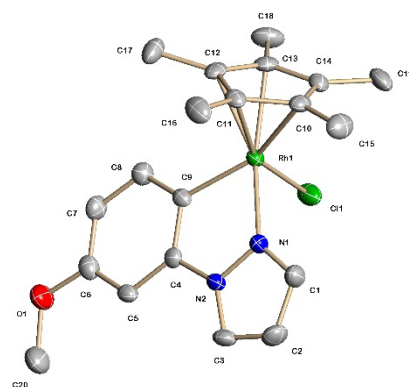
# X-ray structures



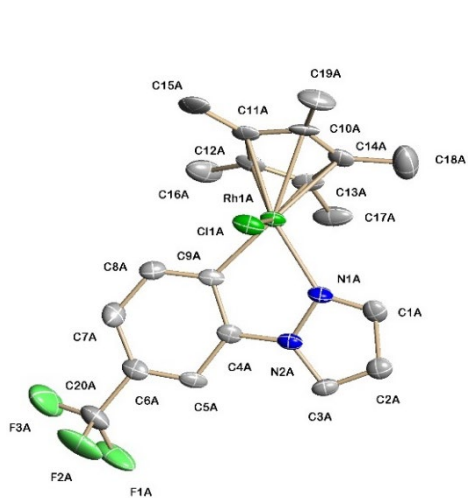
**Fig. S1:** Molecular structures of **1a-OMe**, **1a-Me**, **1b-NMe<sub>2</sub>**, **1b-OMe**, **1b-Me**, **1b-CF<sub>3</sub>** showing 30% ellipsoids; H atoms are omitted for clarity.



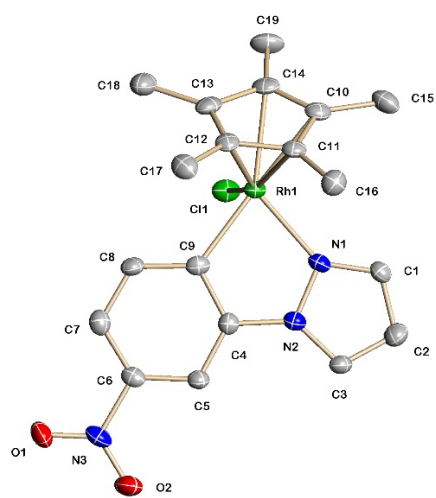
**3a-OMe**



**3b-OMe**



**3b-CF<sub>3</sub>**



**3b-NO<sub>2</sub>**

**Fig. S2:** Molecular structures of **3a-OMe**, **3b-OMe**, **3b-CF<sub>3</sub>** and **3b-NO<sub>2</sub>** showing 30% ellipsoids; H atoms are omitted for clarity.

<b>Table S1a:</b> Selected bond distances (Å) and bond angles [°] for Ir complexes <b>1a-OMe</b> , and <b>1a-Me</b> .			
	<b>1a-OMe</b>	<b>1a-Me</b>	
Ir—C(9)	2.027(9) 2.052(10)	2.043(5)	
Ir—N(1)	2.074(8) 2.073(8)	2.086(4)	
Ir—Cl(1)	2.410(3) 2.409(3)	2.4091(12)	
Ir—Cp*	2.130(9) 2.135(10) 2.152(10) 2.236(10) 2.243(9)	2.150(5) 2.150(5) 2.150(5) 2.230(5) 2.253(5)	
C(9)—Ir—N(1)	77.3(3) 77.4(4)	77.76(18)	

Note for **1a-OMe** there are two unique molecules in the unit cell, data have been given for just one molecule see cif for full data.

<b>Table S1b:</b> Selected bond distances (Å) and bond angles [°] for Rh complexes <b>1b-NMe<sub>2</sub></b> , <b>1b-OMe</b> , <b>1b-Me</b> and <b>1b-CF<sub>3</sub></b> .					
		<b>1b-NMe<sub>2</sub></b>	<b>1b-OMe</b>	<b>1b-Me</b>	<b>1b-CF<sub>3</sub></b>
Rh—C(9)		2.031(3)	2.028(3)	2.056(5)	2.032(3)
Rh—N(1)		2.093(2)	2.090(3)	2.082(5)	2.090(2)
Rh—Cl(1)		2.4065(8)	2.3974(10)	2.4047(15)	2.4019(8)
Rh—Cp*		2.133(3) 2.146(3) 2.158(3) 2.241(3) 2.250(3)	2.132(3) 2.139(3) 2.147(3) 2.263(3) 2.263(3)	2.136(5) 2.152(5) 2.161(5) 2.220(5) 2.245(5)	2.145(3) 2.146(3) 2.163(3) 2.235(3) 2.247(3)
C(9)—Rh—N(1)		78.69(11)	78.27(12)	78.5(2)	78.50(10)

Note for **1b-OMe** and **1b-Me** there are two unique molecules in the unit cell, data have been given for just one molecule see cif for full data.

<b>Table S1c:</b> Selected bond distances (Å) and bond angles [°] for <b>3a-OMe</b> , <b>3b-OMe</b> , <b>3b-CF<sub>3</sub></b> , and <b>3b-NO<sub>2</sub></b> .					
	<b>3a-OMe</b>	<b>3b-OMe</b>	<b>3b-CF<sub>3</sub></b>	<b>3b-NO<sub>2</sub></b>	
M—C(9)	2.062(6)	2.049(3)	2.026(8)	2.039(4)	
M—N(1)	2.075(5)	2.075(3)	2.083(7)	2.092(4)	
M—Cl(1)	2.4042(16)	2.3996(9)	2.389(2)	2.4044(13)	
M—Cp*	2.146(6) 2.151(6) 2.161(5) 2.219(5) 2.229(6)	2.145(3) 2.160(3) 2.175(3) 2.225(3) 2.231(3)	2.106(9) 2.170(8) 2.183(8) 2.201(8) 2.240(8)	2.138(4) 2.151(5) 2.166(4) 2.223(5) 2.238(5)	
C(9)—M—N(1)	77.3(2)	78.12(12)	78.3(3)	78.71(18)	

Note for **3b-CF<sub>3</sub>** there are two unique molecules in the unit cell, data have been given for just one molecule see cif for full data.

## Deuteration Studies

The appropriate ligand was treated with  $[\text{MCl}_2\text{Cp}^*]_2$  (5 mol%) in the presence of NaOAc in  $\text{d}^4$ -methanol. The percentage deuterium incorporation was calculated from the relative integrations of the ortho protons and other signals in the corresponding free ligand. The results are shown in the Table below. For ligands L1-R the two ortho sites are equivalent whilst for L2-R sites A and B are inequivalent with site A corresponding to formation of the ortho isomer and site B the para isomer (see Scheme 4).

Table S2 Deuterium incorporation

Ligand	Ir		Rh	
	Time (Temp)	%D	Time (Temp)	%D
L1-NMe <sub>2</sub>	3 days (50 °C) <sup>a</sup> 22 days (50 °C) <sup>a</sup>	10 55	2 days (r.t.) 60 days (r.t.)	8 76
L1-OMe			3 days (r.t.) 10 days (r.t.)	14 22
		%D A:B		%D A:B
L2-NMe <sub>2</sub>	15min (r.t.) 6 days (r.t.)	76:33 76:39	15 min (r.t.) 24 h. (r.t.)	44:62 95:97
L2-OMe	-	-	30 min (r.t.) 5 days (r.t.)	41:25 100:95
L2-Me	3 days (60 °C) 10 days (60°C)	N.D:20 <sup>b</sup> N.D:40 <sup>b</sup>	12 days (r.t.) 30 days (r.t.)	5:50 50:90
L2-CF <sub>3</sub>	30 days (r.t.)	N.D	30 days (r.t.)	N.D
L2-NO <sub>2</sub>		-	30 days (r.t.)	N.D

<sup>a</sup> No exchange detected at r.t.

<sup>b</sup> For L2-Me the signals for A and B are very close so calculating an accurate ratio is not possible

ND = Not detected

## Competition experiments

Two substrates compete for reaction with a limiting amount of metal (5:5:1 ratio of ligand:ligand:metal) (Scheme 5 in the paper). Five equivalents of ligand are used so that as the reaction progresses there is not a significant change in overall concentration of either ligand. Hence measuring the overall product ratio is a good approximation of the relative rate of the reaction of the two ligands. Using a large excess of ligand can lead to problems since small product peaks may be hidden by large excess ligand peaks, hence not all combinations work well.

**Table S3:** Competition experiments between **L1-R** to form *meta*-substituted complexes of Ir.

Entry	complex		$R_1 : R_2$ at r.t. <sup>a</sup>	$R_1 : R_2$ 50 °C. <sup>b</sup>	$R_1 : R_2$ at 90 °C <sup>d</sup>
	$R_1$	$R_2$			
1	Me	NMe <sub>2</sub>	1:2.3	1:1.5 <sup>c</sup>	-
2	OMe	H	1:2.2	1:2.1	1.2:1
3	H	Me	1:1.2	1:1.3	1.2:1
4	OMe	Me	1:2.0	1:1.9	-
5	F	OMe	1:5.7	1:5.6	2.4:1
6	CF <sub>3</sub>	F	1:2.9	1:3.1	1.5:1
7	NO <sub>2</sub>	CF <sub>3</sub>	1:5.3	1:5.2	5.4:1

a: DCM:MeOH (4:1) after 1 hour except entry 7 after 3 hours.

b: DCM:MeOH (4:1) after 48 hours except entries 2 and 6 after 24 and 96 hours respectively.

c: DCM:MeOH (4:1) after 24 hours at r.t.

d: In TFE (5 ml) + pivalic acid at 90 °C after 24 hours except entry 7 after 66 hours.

**Table S4:** Competition experiments between **L2-R** to form *para*-substituted complexes of Ir.

Entry	complex		$R_1 : p\text{-}R_2 (o\text{-}R_2)$ at r.t. <sup>a</sup>	$R_1$ v.s. $p\text{-}R_2 (o\text{-}R_2)$ at 50 °C <sup>b</sup>	$R_1$ v.s. $p\text{-}R_2 (o\text{-}R_2)$ at 90 °C <sup>c</sup>
	$R_1$	$R_2$			
1	NMe <sub>2</sub>	OMe	15:1(1.3) <sup>e</sup>	1:3.1(2.6)	-
2	H	OMe	1:2.8(3.3)	1:2.0(2.3)	7.1:1(2.2)
3	H	Me	1:1.4(0.14)	1:1.4(0.14)	3.5:1(0)
4 <sup>d</sup>	H	Me	1: 1.5	-	-
5	H	F	9.2:1(3.6)	6.8:1(4.7)	3.1:1(36) <sup>f</sup>
6 <sup>f</sup>	CF <sub>3</sub>	F	1:7.4(31)	1:6.8(35)	11:1(40)
7 <sup>d</sup>	CF <sub>3</sub>	F	1:46	1:36	-
8	CF <sub>3</sub>	H	-	-	2.5:1
9	CF <sub>3</sub>	NO <sub>2</sub>	2.8:1(0.51)	3.4:1(0.44)	1:4.0(trace)

a: DCM:MeOH (4:1) after 15 minutes except entries 1 and 7 after 1 hour.

b: DCM:MeOH (4:1) after 12 days, 1, 48 and 24 hours for entries 1,3, 7 and 9 and after 72 hours for entries 2 and 5.

c: TFE 5 ml + pivalic acid at 90 °C after 24 hours except entry 9 after 96 hours.

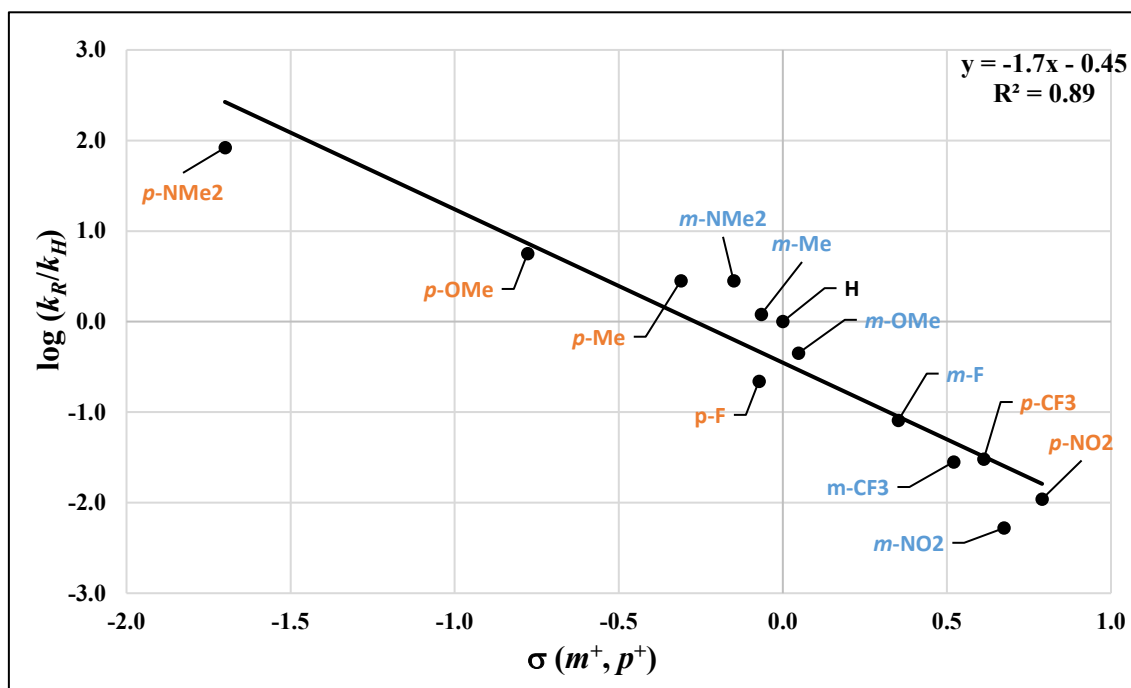
d: ratio monitored by ESI-MS after 15 minutes. Calibration curves for mixtures of the two complexes were measured to establish their relative sensitivity

e: ratio changed over time and reached 8.6:1(1.1) after 24 hours at r.t.

f determined by <sup>19</sup>F NMR spectroscopy. Very similar results were determined by ESI-MS

Table S5: Relative rates of formation of <i>meta</i> and <i>para</i> -substituted complexes of Ir.							
Group	NMe <sub>2</sub>	OMe	Me	H	F	CF <sub>3</sub>	NO <sub>2</sub>
$k_R/k_H$ <i>meta</i> -complexes	2.8	0.45	1.2	1	0.082	0.028	0.0053
$\log k_R/k_H$ <i>meta</i> -complexes	0.45	-0.35	0.08	0	-1.09	-1.55	-2.28
$\sigma_m$	-0.15	0.12	-0.07	0	0.34	0.43	0.71
$2 \times k_R/k_H$ <i>para</i> -complex	84	5.6	2.8	1	0.22	0.030	0.011
$\log (2 k_R/k_H)$ <i>para</i> -complex	1.92	0.75	0.45	0	-0.66	-1.52	-1.96
$\sigma_p$	-0.83	-0.27	-0.17	0	0.06	0.54	0.78

Note for the *para*-substituted complexes the relative rates are multiplied by two, this is due to there being two positions for C–H activation when R = H (unsubstituted ligand) compared with only one position in case of formation of the *para* isomer.



**Fig.S3:** Hammett plot of  $\log (k_R/k_H)$  for formation of *meta* and *para*-substituted complexes of Ir against  $\sigma m^+$  and  $\sigma p^+$ .

$\sigma m^+$ and $\sigma p^+$ values.							
$\sigma$ constant	NMe <sub>2</sub>	OMe	Me	H	F	CF <sub>3</sub>	NO <sub>2</sub>
$\sigma m^+$	-0.15	0.042	-0.066	0	0.352	0.52	0.674
$\sigma p^+$	-1.7	-0.778	-0.311	0	-0.073	0.612	0.790



## Rh competition experiments

All the initial ratios at r.t. in **Tables S6** and **S7** were measured after 15 minutes except entry 7 in both tables after 1 hour and so are taken as indicative of the kinetic selectivity.

<b>Table S6:</b> Results of competition experiments to form <i>meta</i> -substituted complexes of Rh.					
Entry	complex		R <sub>1</sub> :R <sub>2</sub> at r.t. <sup>a</sup>	R <sub>1</sub> :R <sub>2</sub> at r.t. <sup>b</sup>	R <sub>1</sub> :R <sub>2</sub> at 50 °C <sup>d</sup>
	R <sub>1</sub>	R <sub>2</sub>			
1	Me	NMe <sub>2</sub>	1:1.7	2.0:1 <sup>e</sup>	1.8:1
2	OMe	Me	1:1.7	1.1:1	1.7:1
3	H	Me	1:1	1.4:1	1.8:1
4	OMe	H	1:1.5	1:1.1	1.1:1
5	F	H	1:5.0	1:3.3	4.0:1
6	CF <sub>3</sub>	F	1:2.3	1:2.5 <sup>e</sup>	1.3:1 <sup>f</sup>
7	NO <sub>2</sub>	CF <sub>3</sub>	1:3.5	1:3.2 <sup>e</sup>	3.0:1 <sup>f</sup>

a: DCM:MeOH (4:1) after 15 min except entry 7 after 1 hour.

b: DCM:MeOH (4:1) after 24 hours except entry 7 after 48 hours.

c: Ratio did not change with time even after 24 hours.

d: DCM:MeOH (4:1) for 24 hours except entries 1 after 1 hour and 5 after 72 hours.

e: reaction reached equilibrium at r.t. and heating for 24 hours did not change the ratio significantly.

f: DCM:MeOH (4:1) + pivalic acid at 50 °C after 7 days for entry 6 and 9 days for entry 7.

<b>Table S7:</b> Results of competition experiments to form <i>para</i> -substituted complexes of Rh.					
Entry	complex		R <sub>1</sub> vs <i>p</i> -R <sub>2</sub> ( <i>o</i> -R <sub>2</sub> ) at r.t. <sup>a</sup>	R <sub>1</sub> vs <i>p</i> -R <sub>2</sub> ( <i>o</i> -R <sub>2</sub> ) at r.t. <sup>b</sup>	R <sub>1</sub> vs <i>p</i> -R <sub>2</sub> ( <i>o</i> -R <sub>2</sub> ) at 50 °C <sup>d</sup>
	R <sub>1</sub>	R <sub>2</sub>			
1	Me	NMe <sub>2</sub>	1:29	2.2:1	2.2:1 <sup>g</sup>
2	H	OMe	1:3.5(8.9)	6.2:1(1.3)	7.2:1(0.8)
3	H	Me	1:1.20	4.0:1	4.0:1
4	H	F	1:* (2.7) <sup>h</sup>	1:* (4.1) <sup>h</sup>	1:* (8.1) <sup>h</sup>
5 <sup>i</sup>	H	F	1:2.9	1:3.3	1:6.7
6 <sup>i</sup>	CF <sub>3</sub>	H	1:29 <sup>j</sup>	1:23	2.7:1 <sup>e</sup>
7	CF <sub>3</sub>	NO <sub>2</sub>	4.6:1(5.0)	3.0:1(2.3)	1:3.4(0) <sup>f</sup>
7 <sup>i</sup>	CF <sub>3</sub>	NO <sub>2</sub>	1:1.7	1:1.2	-

a: DCM:MeOH (4:1) after 15 min except entry 7 after 1 hour.

b: DCM:MeOH (4:1) after 24 hours.

c: Ratio did not change with time even after 24 hours.

d: DCM:MeOH (4:1) after 24 hours for entries 3 and 5, after 48 hours for entry 4, after 6 and 9 days for 2 and 8 respectively.

e: DCM:MeOH (4:1) + pivalic acid at 50 °C after 7 days.

f: TFE 5 ml + pivalic acid at 90 °C after 24 hours.

g: reaction reached equilibrium at room temperature and heating the mixture for 4 days did not change the ratio significantly.

h: \* trace of *para* isomer, *ortho* isomer is major.

i: Ratio measured by ESI-MS.

j: Only H-product observed by <sup>1</sup>H NMR spectroscopy at 15 minutes so ratio determined by ESI-MS.

Some experiments were also monitored by ESI-MS as mentioned above with Ir. For H versus F (entry

Entry 4 the ratio was measured by <sup>1</sup>H NMR spectroscopy, a separate experiment (entry 5) was

monitored by ESI-MS. For entry 6 (CF<sub>3</sub> versus. H), the ratio from the same experiment was measured by both methods due to the difficulty in integrating small peaks for the CF<sub>3</sub> complex at short reaction time. For entry 7, the ratio was also measured by two methods. In all cases the results obtained by both methods showed reasonable agreement.

<b>Table S8:</b> Relative rates of formation of <i>meta</i> and <i>para</i> -substituted complexes of Rh.							
Group	NMe <sub>2</sub>	OMe	Me	H	F	CF <sub>3</sub>	NO <sub>2</sub>
$k_R/k_H$ <i>m</i> -complexes	1.7	0.66	1	1	0.20	0.087	0.025
log $k_R/k_H$ <i>m</i> -complexes	0.23	-0.18	0	0	-0.7	-1.06	-1.60
$k_R/k_H$ <i>p</i> -complexes	35	3.5	1.2	1	-	0.034	0.0074
$2k_R/k_H$ <i>p</i> -complexes	70	7.0	2.4	1	-	0.068	0.015
log( $2k_R/k_H$ ) <i>p</i> -complexes	1.85	0.85	0.38	0	-	-1.17	-1.82
$\sigma_m$	-0.15	0.12	-0.07	0	0.34	0.43	0.71
$\sigma_p$	-0.83	-0.27	-0.17	0	0.06	0.54	0.78

Note, in the case of *para*-complexes, R = F has been omitted from the order of reactivity because when R = F the *ortho* isomer is strongly favoured over the *para* isomer and only a trace of the *para* isomer is observed.

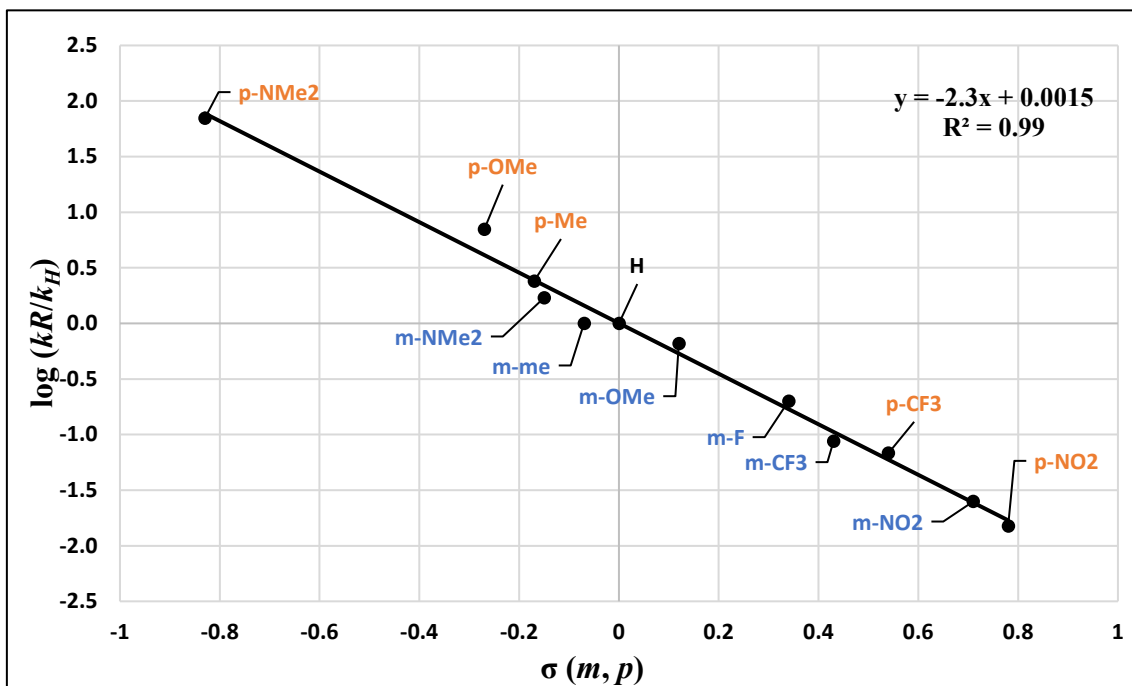


Fig. S4: Hammett plot of  $\log(k_R/k_H)$  for formation of *meta* and *para*-substituted complexes of Rh against  $\sigma_m$  and  $\sigma_p$ .

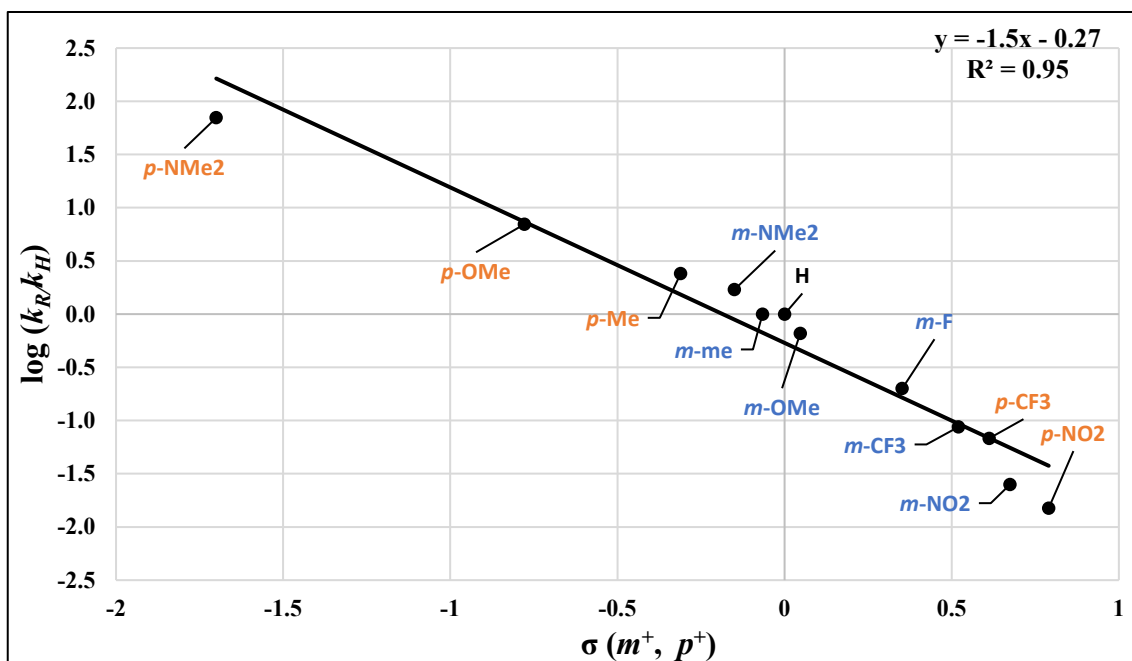
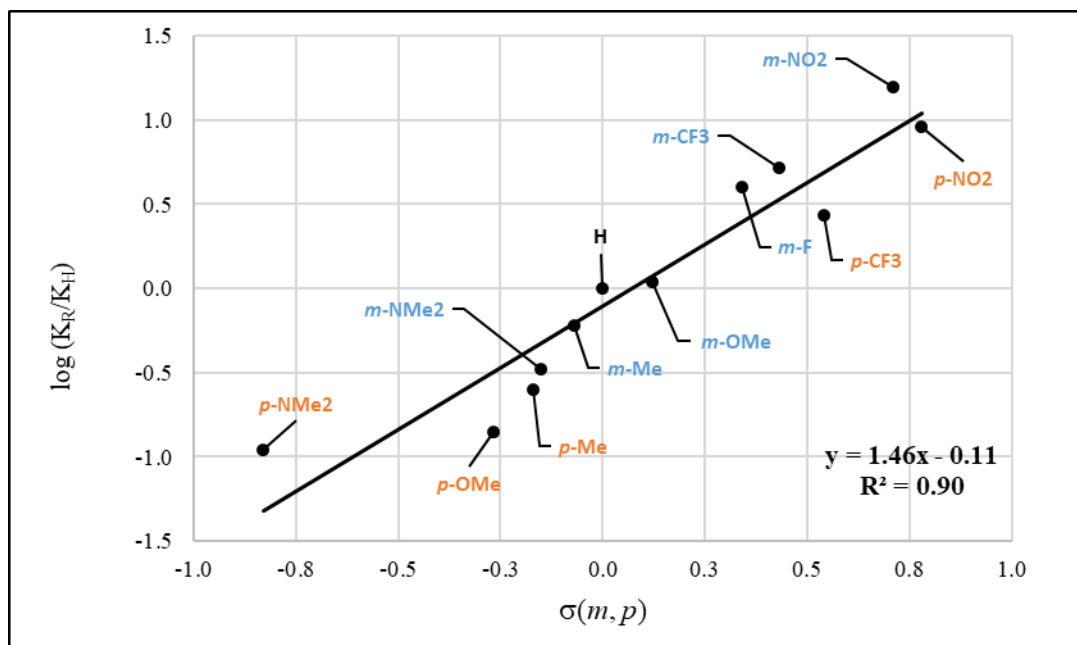


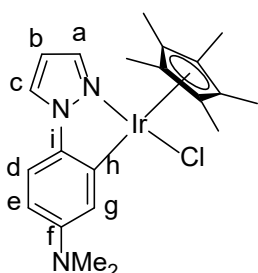
Fig.S5: Hammett plot of  $\log(k_R/k_H)$  for formation of *meta* and *para*-substituted complexes of Rh against  $\sigma_m^+$  and  $\sigma_p^+$ .



**Fig S6** Plot of  $\log(K_R/K_H)$  for formation of *meta*- **1b-R** and *para*-substituted **3b-R** complexes of Rh against  $\sigma_m$  and  $\sigma_p$ .

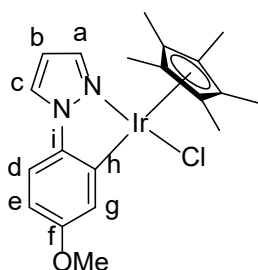
## Experimental Procedures and characterisation Data

### Cyclometallation of 1-(4-N, N dimethylamine)-1*H*-pyrazole (L1-NMe<sub>2</sub>) with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>



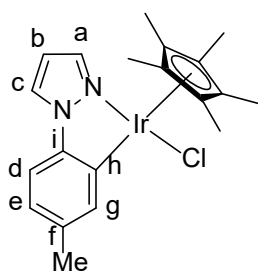
The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.063 mmol), 1-(4-N, N dimethylamine)-1*H*-pyrazole (23.5 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The product was recrystallised from THF / petroleum ether to give **1a-NMe<sub>2</sub>** (54 mg., 78%) as yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.74 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.00 (s, 6H, NMe<sub>2</sub>), 6.42 (dd, 1H, *J* = 2.7, 8.6 Hz, H<sup>e</sup>), 6.45 (t, 1H, *J* = 2.5 Hz, H<sup>b</sup>), 7.15 (d, 1H, *J* = 8.6 Hz, H<sup>d</sup>), 7.17 (d, 1H, *J* = 2.6 Hz, H<sup>g</sup>), 7.64 (dd, 1H, *J* = 0.5, 2.2 Hz, H<sup>a</sup>), 7.75 (dd, 1H, *J* = 0.5, 2.7 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 9.1 (C<sub>5</sub>Me<sub>5</sub>), 41.2 (NMe<sub>2</sub>), 87.9 (C<sub>5</sub>Me<sub>5</sub>), 107.3 (C<sup>b</sup>), 107.6 (C<sup>e</sup>), 111.0 (C<sup>d</sup>), 120.7 (C<sup>g</sup>), 123.6 (C<sup>c</sup>), 134.3 (C<sup>i</sup>), 136.7 (C<sup>a</sup>), 146.6 (C<sup>h</sup>), 149.8 (C<sup>f</sup>). Accurate MS-ESI *m/z* 514.1834 (calculated), 514.1838 (found) [M-Cl]<sup>+</sup> C<sub>21</sub>H<sub>27</sub>N<sub>3</sub><sup>193</sup>Ir.

### Cyclometallation of 1-(4-methoxyphenyl)-1*H*-pyrazole (L1-OMe) with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>



The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.063 mmol), 1-(4-methoxyphenyl)-1*H*-pyrazole (21.8 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The product was recrystallised from DCM / petroleum ether to give **1a-OMe** (53 mg., 79%) as yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.74 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.85 (s, 3H, OMe), 6.47 (t, 1H, *J* = 2.4 Hz, H<sup>b</sup>), 6.55 (dd, 1H, *J* = 2.6, 8.5 Hz, H<sup>e</sup>), 7.19 (d, 1H, *J* = 8.6 Hz, H<sup>d</sup>), 7.30 (d, 1H, *J* = 2.6 Hz, H<sup>g</sup>), 7.64 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.79 (brd, 1H, *J* = 2.6 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 9.0 (C<sub>5</sub>Me<sub>5</sub>), 55.4 (OMe), 88.1 (C<sub>5</sub>Me<sub>5</sub>), 107.6 (C<sup>b/e</sup>), 107.7 (C<sup>b/e</sup>), 111.2 (C<sup>d</sup>), 121.8 (C<sup>g</sup>), 124.4 (C<sup>c</sup>), 136.9 (C<sup>i</sup>), 137.3 (C<sup>a</sup>), 147.3 (C<sup>h</sup>), 158.1 (C<sup>f</sup>). Accurate MS-ESI *m/z* 501.1518 (calculated), 501.1510 (found) [M-Cl]<sup>+</sup> C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sup>193</sup>Ir.

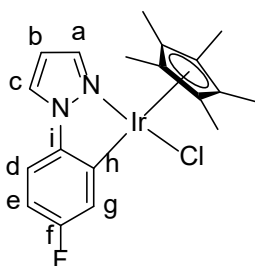
### Cyclometallation of 1-(4-methylphenyl)-1*H*-pyrazole (L1-Me) with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>



The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.063 mmol), 1-(4-methylphenyl)-1*H*-pyrazole (19.8 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The product was recrystallised from DCM / petroleum ether to give **1a-Me** (46 mg., 70%) as yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.73 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.37 (s, 3H, Me), 6.48 (t, 1H, *J* = 2.4 Hz, H<sup>b</sup>), 6.80 (brd, 1H, *J* = 7.9 Hz, H<sup>e</sup>), 7.14 (d, 1H, *J* = 8.0 Hz, H<sup>d</sup>), 7.54 (brs, 1H, H<sup>g</sup>), 7.65 (d, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.83 (d, 1H, *J* = 2.7 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 9.0

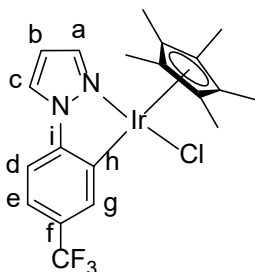
( $C_5Me_5$ ), 21.4 (Me), 88.0 ( $C_5Me_5$ ), 107.8 ( $C^b$ ), 110.4 ( $C^d$ ), 123.4 ( $C^e$ ), 124.7 ( $C^c$ ), 136.2 ( $C^f$ ), 137.2 ( $C^g$ ), 137.5 ( $C^a$ ), 140.5 ( $C^i$ ) 145.4 ( $C^h$ ). Accurate MS-ESI  $m/z$  485.1569 (calculated), 485.1554 (found)  $[M-Cl]^+ C_{20}H_{24}N_2^{193}Ir$ .

#### Cyclometallation of 1-(4-fluoromethylphenyl)-1H-pyrazole (L1-F) with $[IrCl_2Cp^*]_2$



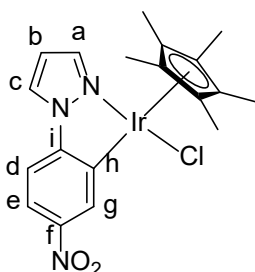
The general procedure was followed using  $[IrCl_2Cp^*]_2$  (50 mg., 0.063 mmol), 1-(4-fluoromethylphenyl)-1H-pyrazole (20.4 mg., 0.125 mmol) and NaOAc (12.8 mg, 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The product was recrystallised from DCM / petroleum ether to give **1a-F** (63 mg., 95%) as yellow crystals.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  1.73 (s, 15H,  $C_5Me_5$ ), 6.48 (t, 1H,  $J = 2.4$  Hz,  $H^b$ ), 6.67 (dt, 1H,  $J_{H-H} = 2.7$ ,  $J_{H-F} = 8.6$  Hz,  $H^e$ ), 7.20 (dd, 1H,  $J_{H-F} = 4.6$ ,  $J_{H-H} = 8.5$  Hz,  $H^d$ ), 7.40 (dd, 1H,  $J_{H-H} = 2.7$ ,  $J_{H-F} = 8.9$  Hz,  $H^g$ ), 7.65 (brd, 1H,  $J = 1.9$  Hz,  $H^a$ ), 7.81 (brd, 1H,  $J = 2.6$  Hz,  $H^c$ ).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  9.1 ( $C_5Me_5$ ), 88.3 ( $C_5Me_5$ ), 108.1 ( $C^b$ ), 109.2 (d,  $^2J_{CF} = 25.1$  Hz,  $C^e$ ), 111.6 (d,  $^3J_{CF} = 8.4$  Hz,  $C^d$ ), 122.4 (d,  $^2J_{CF} = 19.1$  Hz,  $C^g$ ), 125.2 ( $C^c$ ), 137.8 ( $C^a$ ), 139.0 ( $C^i$ ), 148.3 (d,  $^3J_{CF} = 4.8$  Hz,  $C^h$ ), 161.3 (d,  $^1J_{CF} = 247.4$  Hz,  $C^f$ ).  $^{19}F\{^1H\}$  (376 MHz,  $CDCl_3$ ):  $\delta$  -117.5 (s, F). Accurate MS-ESI  $m/z$  489.1318 (calculated), 489.1329 (found)  $[M-Cl]^+ C_{19}H_{21}FN_2^{193}Ir$ .

#### Cyclometallation of 1-(4-trifluoromethylphenyl)-1H-pyrazole (L1-CF<sub>3</sub>) with $[IrCl_2Cp^*]_2$



The general procedure was followed using  $[IrCl_2Cp^*]_2$  (50 mg., 0.063 mmol), 1-(4-trifluoromethylphenyl)-1H-pyrazole (26.5 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The product was recrystallised from DCM / petroleum ether to give **1a-CF<sub>3</sub>** (53 mg., 74%) as yellow crystals.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  1.73 (s, 15H,  $C_5Me_5$ ), 6.51 (t, 1H,  $J = 2.5$  Hz,  $H^b$ ), 7.22 (dd, 1H,  $J = 1.2$ , 8.2 Hz,  $H^e$ ), 7.28 (d, 1H,  $J = 8.2$  Hz,  $H^d$ ), 7.70 (brd, 1H,  $J = 2.0$  Hz,  $H^a$ ), 7.91 (brd, 1H,  $J = 2.8$  Hz,  $H^c$ ), 7.96 (brd, 1H,  $J = 1.3$  Hz,  $H^g$ ).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  9.0 ( $C_5Me_5$ ), 88.5 ( $C_5Me_5$ ), 108.7 ( $C^b$ ), 110.5 ( $C^d$ ), 120.3 (q,  $^3J_{CF} = 3.5$  Hz,  $C^e$ ), 124.6 (q,  $^1J_{CF} = 272.7$  Hz,  $CF_3$ ), 126.0 ( $C^c$ ), 128.1 (q,  $^2J_{CF} = 31.4$  Hz,  $C^f$ ), 133.0 (q,  $^3J_{CF} = 3.1$  Hz,  $C^g$ ), 138.7 ( $C^a$ ), 145.1 ( $C^{h/i}$ ), 145.9 ( $C^{h/i}$ ).  $^{19}F\{^1H\}$  (376 MHz,  $CDCl_3$ ):  $\delta$  -61.6 (s,  $CF_3$ ). Accurate MS-ESI  $m/z$  539.1286 and 580.1552 (calculated), 539.1290 and 580.1565 (found)  $[M-Cl]^+$  and  $[M-Cl + (MeCN)]^+$  respectively  $C_{20}H_{21}F_3N_2^{193}Ir$  and  $C_{22}H_{24}F_3N_3^{193}Ir$ .

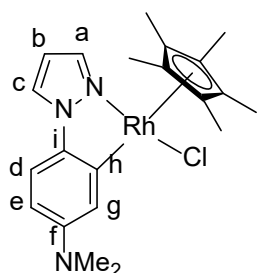
#### Cyclometallation of 1-(4-nitrophenyl)-1H-pyrazole (L1-NO<sub>2</sub>) with $[IrCl_2Cp^*]_2$



The general procedure was followed using  $[IrCl_2Cp^*]_2$  (100 mg., 0.126 mmol), 1-(4-nitrophenyl)-1H-pyrazole (47.4 mg., 0.251 mmol), NaOAc (25.7 mg., 0.313 mmol) in dry MeOH (10 ml). The mixture was stirred for

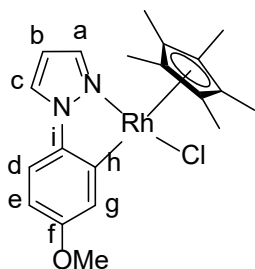
24 hours at room temperature. The product was recrystallised from DCM / petroleum ether to give **1a-NO<sub>2</sub>** (97 mg., 70%) as yellow crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) = δ1.77 (s, 15H, Cp\*), 6.58 (dd, 1H, *J* = 2.4, 2.7 Hz, H<sup>b</sup>), 7.33 (d, 1H, *J* = 8.7 Hz, H<sup>d</sup>), 7.76 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.89 (dd, 1H, *J* = 2.4, 8.7 Hz, H<sup>c</sup>), 7.96 (brd, 1H, *J* = 2.8 Hz, H<sup>e</sup>), 8.58 (d, 1H, *J* = 2.3 Hz, H<sup>g</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz) = δ9.0 (Cp\*), 88.9 (Cp\*), 109.4 (C<sup>b</sup>), 110.8 (C<sup>d</sup>), 119.4 (C<sup>c</sup>), 126.8 (C<sup>e</sup>), 131.2 (C<sup>g</sup>), 139.6 (C<sup>a</sup>), 146.0 (C<sup>i</sup>), 147.1 (C<sup>f/h</sup>), 147.2 (C<sup>f/h</sup>). Accurate MS-ESI *m/z* 516.1263 and 557.1529 (calculated), 516.1260 and 557.1528 (found) [M–Cl]<sup>+</sup> and [M–Cl + (MeCN)]<sup>+</sup> respectively C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub><sup>193</sup>Ir and C<sub>21</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub><sup>193</sup>Ir.

### Cyclometallation of 1-(4-N, N dimethylamine)-1*H*-pyrazole (L1-NMe<sub>2</sub>) with [RhCl<sub>2</sub>Cp\*]<sub>2</sub>



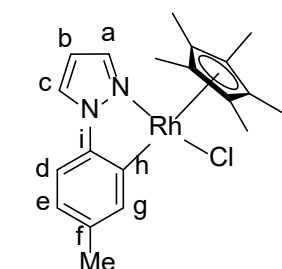
The general procedure was followed using [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (50 mg., 0.081 mmol), 1-(4-N, N dimethylamine)-1*H*-pyrazole (30.3 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 3 hours at room temperature. The product was recrystallised from THF / petroleum ether to give **1b-NMe<sub>2</sub>** (46 mg., 62%) as orange crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) = δ1.68 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.01 (s, 6H, NMe<sub>2</sub>), 6.44 (t, 1H, *J* = 2.4 Hz, H<sup>b</sup>), 6.44(dd, 1H, *J* = 2.6 , 8.6 Hz, H<sup>c</sup>), 7.06 (d, 1H, *J* = 8.6 Hz, H<sup>d</sup>), 7.18 (brd, 1H, *J* = 2.6 Hz, H<sup>e</sup>), 7.73 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.82 (brd, 1H, *J* = 2.5 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) = δ9.3 (C<sub>5</sub>Me<sub>5</sub>), 41.2 (NMe<sub>2</sub>), 95.5 (d, *J* = 6.8 Hz, C<sub>5</sub>Me<sub>5</sub>), 107.3 (C<sup>b/e</sup>), 108.2 (C<sup>b/e</sup>), 111.2 (C<sup>d</sup>), 121.3 (C<sup>g</sup>), 123.7 (C<sup>c</sup>), 133.5 (C<sup>i</sup>), 137.8 (C<sup>a</sup>), 149.5 (C<sup>f</sup>), 160.3 (d, *J*<sub>Rh-C</sub> = 31.9 Hz, C<sup>h</sup>). Accurate MS-ESI *m/z* 424.1260 (calculated), 424.1253 (found) [M–Cl]<sup>+</sup> C<sub>21</sub>H<sub>27</sub>N<sub>3</sub><sup>103</sup>Rh.

### Cyclometallation of 1-(4-methoxyphenyl)-1*H*-pyrazole (L1-OMe) with [RhCl<sub>2</sub>Cp\*]<sub>2</sub>



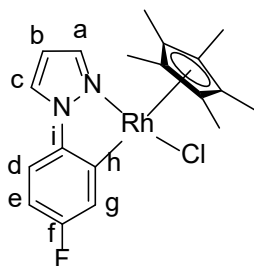
The general procedure was followed using [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (50 mg., 0.081 mmol), 1-(4-methoxyphenyl)-1*H*-pyrazole (28.2 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 24 hours at room temperature. The product was recrystallised from DCM / petroleum ether to give **1b-OMe** (51 mg., 71%) as orange crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) = δ1.68 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.86 (s, 3H, OMe), 6.45 (t, 1H, *J* = 2.4 Hz, H<sup>b</sup>), 6.56 (dd, 1H, *J* = 2.6 , 8.5 Hz, H<sup>c</sup>), 7.11 (d, 1H, *J* = 8.6 Hz, H<sup>d</sup>), 7.32 (d, 1H, *J* = 2.6 Hz, H<sup>e</sup>), 7.75 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.86 (brd, 1H, *J* = 2.6 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) = δ9.2 (C<sub>5</sub>Me<sub>5</sub>), 55.4 (OMe), 95.6 (d, *J* = 6.9 Hz, C<sub>5</sub>Me<sub>5</sub>), 107.7 (C<sup>b</sup>), 108.3 (C<sup>e</sup>), 111.3 (C<sup>d</sup>), 122.6 (C<sup>g</sup>), 124.5 (C<sup>c</sup>), 136.2 (C<sup>i</sup>), 138.3 (C<sup>a</sup>), 157.7 (C<sup>f</sup>), 160.9 (d, *J*<sub>Rh-C</sub> = 32.3 Hz, C<sup>h</sup>). Accurate MS-ESI *m/z* 411.0944 (calculated), 411.0941 (found) [M–Cl]<sup>+</sup> C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sup>103</sup>Rh.

### Cyclometallation of 1-(4-methylphenyl)-1*H*-pyrazole (L1-Me) with [RhCl<sub>2</sub>Cp\*]<sub>2</sub>



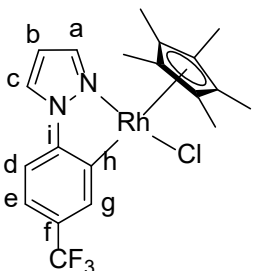
The general procedure was followed using [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (50 mg., 0.081 mmol), 1-(4-methylphenyl)-1*H*-pyrazole (25.6 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162 mmol) dry MeOH (5 ml). The mixture was stirred for 24 hours at room temperature. The product was recrystallised from DCM / petroleum ether to give **1b-Me** (45 mg., 65%) as orange crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) = δ 1.67 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.38 (s, 3H, Me), 6.46 (t, 1H, *J* = 2.4 Hz, H<sup>b</sup>), 6.83 (dd, 1H, *J* = 1.1, 7.9 Hz, H<sup>e</sup>), 7.10 (d, 1H, *J* = 8.0 Hz, H<sup>d</sup>), 7.55 (d, 1H, *J* = 1.0 Hz, H<sup>g</sup>), 7.77 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.90 (brd, 1H, *J* = 2.6 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) = δ 9.2 (C<sub>5</sub>Me<sub>5</sub>), 21.4 (Me), 95.5 (d, *J* = 6.6 Hz, C<sub>5</sub>Me<sub>5</sub>), 107.8 (C<sup>b</sup>), 110.6 (C<sup>d</sup>), 124.0 (C<sup>e</sup>), 124.8 (C<sup>c</sup>), 136.1 (C<sup>f</sup>), 137.9 (C<sup>g</sup>), 138.5 (C<sup>a</sup>), 139.7 (C<sup>i</sup>), 159.0 (d, *J*<sub>Rh-C</sub> = 31.8 Hz, C<sup>h</sup>). Accurate MS-ESI *m/z* 395.0995 (calculated), 395.0992 (found) [M-Cl]<sup>+</sup> C<sub>20</sub>H<sub>24</sub>N<sub>2</sub><sup>103</sup>Rh.

### Cyclometallation of 1-(3-fluoromethylphenyl)-1*H*-pyrazole (L1-F) with [RhCl<sub>2</sub>Cp\*]<sub>2</sub>



The general procedure was followed using [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (50 mg., 0.081 mmol), 1-(3-fluoromethylphenyl)-1*H*-pyrazole (26.2 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 24 hours at room temperature. The product was recrystallised from DCM / petroleum ether to give **1b-F** (49 mg., 69%) as orange crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) = δ 1.68 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.48 (t, 1H, *J* = 2.4 Hz, H<sup>b</sup>), 6.71 (dt, 1H, *J*<sub>H-H</sub> = 2.7, *J*<sub>H-F</sub> = 8.5 Hz, H<sup>c</sup>), 7.13 (dd, 1H, *J*<sub>H-F</sub> = 4.4, *J*<sub>H-H</sub> = 8.6 Hz, H<sup>d</sup>), 7.44 (dd, 1H, *J*<sub>H-H</sub> = 2.6, *J*<sub>H-F</sub> = 8.4 Hz, H<sup>g</sup>), 7.78 (brd, 1H, *J* = 1.9 Hz, H<sup>a</sup>), 7.86 (brd, 1H, *J* = 2.7 Hz, H<sup>e</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz) = δ 9.2 (C<sub>5</sub>Me<sub>5</sub>), 95.8 (d, *J* = 6.5 Hz, C<sub>5</sub>Me<sub>5</sub>), 108.1 (C<sup>b</sup>), 109.9 (d, <sup>2</sup>*J*<sub>CF</sub> = 24.5 Hz, C<sup>e</sup>), 111.6 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.4 Hz, C<sup>d</sup>), 123.3 (d, <sup>2</sup>*J*<sub>CF</sub> = 19.5 Hz, C<sup>g</sup>), 125.1 (C<sup>c</sup>), 138.2 (C<sup>i</sup>), 138.8 (C<sup>a</sup>), 160.8 (d, <sup>1</sup>*J*<sub>CF</sub> = 248.6 Hz, C<sup>f</sup>), 162.0 (dd, <sup>3</sup>*J*<sub>CF</sub> = 4.0, *J*<sub>Rh-C</sub> = 33.1 Hz, C<sup>h</sup>). <sup>19</sup>F{<sup>1</sup>H} (376 MHz, CDCl<sub>3</sub>): δ -117.0 (s, F). Accurate MS-ESI *m/z* 399.0744 (calculated), 399.0756 (found) [M-Cl]<sup>+</sup> C<sub>19</sub>H<sub>21</sub>FN<sub>2</sub><sup>103</sup>Rh.

### Cyclometallation of 1-(4-trifluoromethylphenyl)-1*H*-pyrazole (L1-CF<sub>3</sub>) with [RhCl<sub>2</sub>Cp\*]<sub>2</sub>

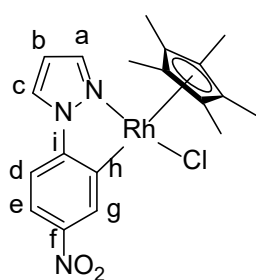


The general procedure was followed using [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (50 mg., 0.081 mmol), 1-(4-trifluoromethylphenyl)-1*H*-pyrazole (34.3 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 72 hours room temperature. The product was recrystallised from DCM / petroleum ether to give **1b-CF<sub>3</sub>** (48 mg., 61%) as orange crystals. <sup>1</sup>H



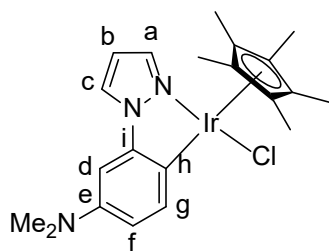
NMR (CDCl<sub>3</sub>, 500 MHz) =  $\delta$  1.67 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.46 (t,  $J$  = 2.4 Hz, 1H, H<sup>b</sup>), 7.19 (d,  $J$  = 8.3 Hz, 1H, H<sup>d</sup>), 7.23 (dd, 1H,  $J$  = 1.2, 8.4 Hz, H<sup>e</sup>), 7.80 (brd, 1H,  $J$  = 2.1 Hz, H<sup>a</sup>), 7.97 (brd, 1H,  $J$  = 2.8 Hz, H<sup>c</sup>), 7.98 (brs, 1H, H<sup>g</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) =  $\delta$  9.20 (C<sub>5</sub>Me<sub>5</sub>), 96.0 (d,  $J$  = 6.6 Hz, C<sub>5</sub>Me<sub>5</sub>), 108.9 (C<sup>b</sup>), 110.8 (C<sup>d</sup>), 121.0 (q, <sup>3</sup> $J_{CF}$  = 3.2 Hz, C<sup>e</sup>), 127.8 (q, <sup>2</sup> $J_{CF}$  = 31.3 Hz, C<sup>f</sup>), 121.9 (q, <sup>1</sup> $J_{CF}$  = 275.0 Hz, CF<sub>3</sub>), 126.1 (C<sup>c</sup>), 133.8 (q, <sup>3</sup> $J_{CF}$  = 3.2 Hz, C<sup>g</sup>), 139.6 (C<sup>a</sup>), 144.3 (C<sup>i</sup>), 159.4 (d,  $J_{Rh-c}$  = 33.6 Hz, C<sup>h</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz) =  $\delta$  -61.4 (s, 3F, CF<sub>3</sub>). Accurate MS-ESI  $m/z$  449.0712 and 490.0977 (calculated), 449.0721 and 490.0987 (found) [M–Cl]<sup>+</sup> and [M–Cl + (MeCN)]<sup>+</sup> respectively C<sub>20</sub>H<sub>21</sub>N<sub>2</sub>F<sub>3</sub><sup>103</sup>Rh and C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>F<sub>3</sub><sup>103</sup>Rh.

### Cyclometallation of 1-(4-nitrophenyl)-1*H*-pyrazole (L75-NO<sub>2</sub>) with [RhCl<sub>2</sub>Cp\*]<sub>2</sub>



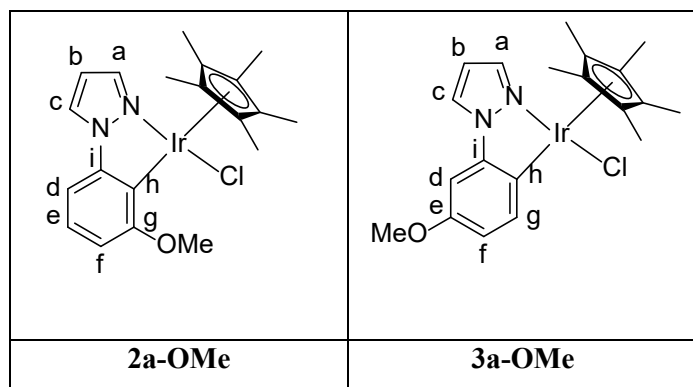
The general procedure was followed using [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (50 mg., 0.081 mmol), 1-(4-nitrophenyl)-1*H*-pyrazole (30.6 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 6 hours at 60 °C. The product was recrystallised from DCM / petroleum ether to give **75b-NO<sub>2</sub>** (46 mg., 61%) as orange crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) =  $\delta$  1.72 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.55 (t, 1H,  $J$  = 2.4 Hz, H<sup>b</sup>), 7.25 (d, 1H,  $J$  = 8.7 Hz, H<sup>d</sup>), 7.88 (brd, 1H,  $J$  = 2.0 Hz, H<sup>a</sup>), 7.90 (dd, 1H,  $J$  = 2.4, 8.7 Hz, H<sup>c</sup>), 8.02 (brd, 1H,  $J$  = 2.8 Hz, H<sup>e</sup>), 8.60 (brd, 1H,  $J$  = 2.4 Hz, H<sup>g</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) =  $\delta$  9.3 (C<sub>5</sub>Me<sub>5</sub>), 96.3 (d,  $J$  = 6.4 Hz, C<sub>5</sub>Me<sub>5</sub>), 109.5 (C<sup>b</sup>), 110.9 (C<sup>d</sup>), 120.1 (C<sup>e</sup>), 126.7 (C<sup>c</sup>), 132.1 (C<sup>g</sup>), 140.5 (C<sup>a</sup>), 145.7 (C<sup>i</sup>), 146.3 (C<sup>f</sup>), 160.7 (d,  $J_{Rh-c}$  = 34.1 Hz, C<sup>h</sup>). Accurate MS-ESI  $m/z$  426.0689 and 467.0954 (calculated), 426.0686 and 467.0956 (found) [M–Cl]<sup>+</sup> and [(M–Cl) + (MeCN)]<sup>+</sup> respectively C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub><sup>103</sup>Rh and C<sub>21</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub><sup>103</sup>Rh.

### Cyclometallation of 1-(3-N, N dimethylamine)-1*H*-pyrazole (L2-NMe<sub>2</sub>) with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>



The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.0627 mmol), 1-(3-methylphenyl)-1*H*-pyrazole (23.5 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The product was recrystallised from THF / petroleum ether to give **3a-NMe<sub>2</sub>** (52 mg., 76%) as yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.74 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.91 (s, 6H, NMe<sub>2</sub>), 6.47 (t, 1H,  $J$  = 2.4 Hz, H<sup>b</sup>), 6.69 (dd, 1H,  $J$  = 2.5, 8.1 Hz, H<sup>f</sup>), 6.71 (d, 1H,  $J$  = 2.3 Hz, H<sup>d</sup>), 7.57 (d, 1H,  $J$  = 8.1 Hz, H<sup>g</sup>), 7.67 (brd, 1H,  $J$  = 2.0 Hz, H<sup>a</sup>), 7.87 (brd, 1H,  $J$  = 2.7 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  9.1 (C<sub>5</sub>Me<sub>5</sub>), 41.5 (NMe<sub>2</sub>), 87.6 (C<sub>5</sub>Me<sub>5</sub>), 97.4 (C<sup>d</sup>), 107.7 (C<sup>b</sup>), 114.0 (C<sup>f</sup>), 124.8 (C<sup>c</sup>), 131.5 (C<sup>h</sup>), 136.3 (C<sup>g</sup>), 137.7 (C<sup>a</sup>), 142.9 (C<sup>i</sup>), 147.9 (C<sup>e</sup>). Accurate MS-ESI  $m/z$  514.1834 (calculated), 514.1838 (found) [M–Cl]<sup>+</sup> C<sub>21</sub>H<sub>27</sub>N<sub>3</sub><sup>193</sup>Ir.

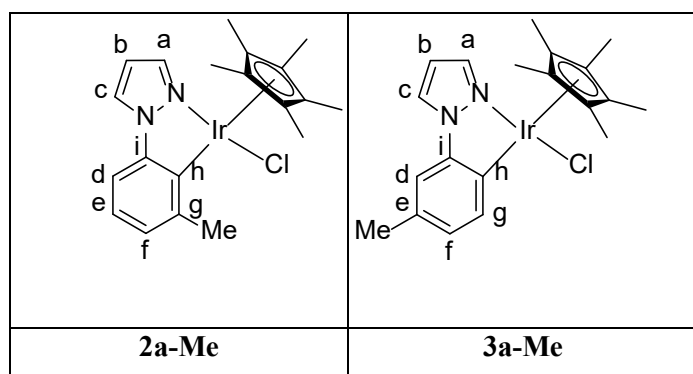
### Cyclometallation of 1-(3-methoxyphenyl)-1*H*-pyrazole (L2-OMe) with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>.



The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.063 mmol), 1-(3-methoxyphenyl)-1*H*-pyrazole (21.8 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.125 mmol) were added in dry MeOH (5ml). The mixture was stirred for 1 hour at room temperature. The product was recrystallised from DCM / petroleum ether

to give **2a-OMe** and **3a-OMe** (40 mg., 60%) as yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): **2a-OMe** δ 1.73 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.84 (s, 3H, OMe), 6.48-6.50 (m, 1H, H<sup>b</sup>), 6.65 (dd, 1H, *J* = 0.7, 7.7 Hz, H<sup>f</sup>), 6.96 (dd, 1H, *J* = 0.8, 7.8 Hz, H<sup>d</sup>), 7.01 (t, 1H, *J* = 7.8 Hz, H<sup>e</sup>), 7.68 (overlapping d, 1H, H<sup>a</sup>), 7.86 (overlapping d, 1H, H<sup>c</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 9.3 (C<sub>5</sub>Me<sub>5</sub>), 56.2 (OMe), 88.5 (C<sub>5</sub>Me<sub>5</sub>), 104.9 (C<sup>d</sup>), 107.7/108.0 (C<sup>a</sup>), 109.4 (C<sup>f</sup>), 124.4 (C<sup>e</sup>), 125.2/125.5 (C<sup>c</sup>), 133.4 (C<sup>h</sup>), 137.6/138.0 (C<sup>a</sup>), 142.8/143.0 (C<sup>i</sup>), 163.8 (C<sup>g</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): **3a-OMe** δ 1.73 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.80 (s, 3H, OMe), 6.48-6.50 (m, 1H, H<sup>b</sup>), 6.77 (dd, 1H, *J* = 2.5, 8.2 Hz, H<sup>f</sup>), 6.87 (d, *J* = 2.4 Hz, H<sup>d</sup>), 7.60 (d, 1H, *J* = 8.2 Hz, H<sup>g</sup>), 7.68 (overlapping d, 1H, H<sup>a</sup>), 7.86 (overlapping d, 1H, H<sup>c</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 9.0 (C<sub>5</sub>Me<sub>5</sub>), 55.6 (OMe), 87.8 (C<sub>5</sub>Me<sub>5</sub>), 98.2 (C<sup>d</sup>), 107.7/108.0 (C<sup>a</sup>), 113.1 (C<sup>f</sup>), 125.2/125.5 (C<sup>c</sup>), 135.1 (C<sup>h</sup>), 136.4 (C<sup>g</sup>), 137.6/138.0 (C<sup>a</sup>), 142.8/143.0 (C<sup>i</sup>), 156.5 (C<sup>e</sup>), Accurate MS-ESI *m/z* 501.1518 (calculated), 501.1520 (found) [M-Cl]<sup>+</sup> C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sup>193</sup>Ir.

### Cyclometallation of 1-(3-methylphenyl)-1*H*-pyrazole (L2-Me) with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>.

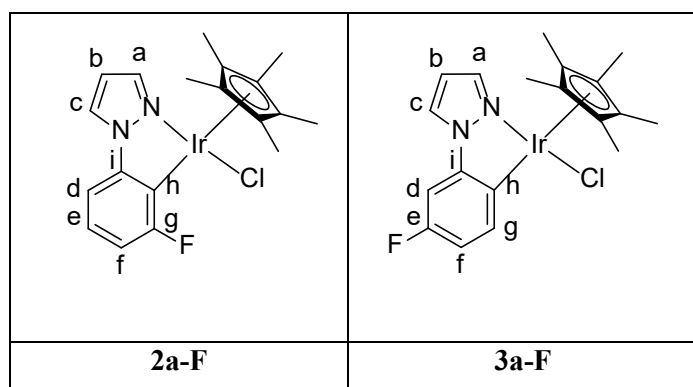


The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.063 mmol), 1-(3-methylphenyl)-1*H*-pyrazole (19.8 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The

product was recrystallised from DCM / petroleum ether to give **2a-Me** and **3a-Me** (57 mg., 88%) as yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): **2a-Me** δ 1.66 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.61 (s, 3H, Me), 6.50 (t, 1H, *J* = 2.5 Hz, H<sup>b</sup>), 6.94 (overlapping t, 1H, H<sup>e</sup>), 7.05 (overlapping d, 2H, H<sup>d+f</sup>), 7.71 (brd, 1H, *J* = 2.1 Hz, H<sup>a</sup>), 7.87 (overlapping d, 1H, H<sup>c</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): Assignment of the <sup>13</sup>C NMR spectra of the *ortho* isomer is difficult due to low

intensity and overlap with the peaks of the *para* isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): **3a-Me**  $\delta$  1.74 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 2.34 (s, 3H, Me), 6.50 (t, 1H,  $J = 2.5$  Hz,  $\text{H}^b$ ), 6.94 (dd,  $J = 0.8$ , 7.5 Hz, 1H,  $\text{H}^f$ ), 7.09 (brs, 1H,  $\text{H}^d$ ), 7.61 (d, 1H,  $J = 7.6$  Hz,  $\text{H}^g$ ), 7.68 (brd, 1H,  $J = 2.1$  Hz,  $\text{H}^a$ ), 7.87 (brd, 1H,  $J = 2.8$  Hz,  $\text{H}^e$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.0 ( $\text{C}_5\text{Me}_5$ ), 21.0 (Me), 87.9 ( $\text{C}_5\text{Me}_5$ ), 107.9 ( $\text{C}^b$ ), 111.7 ( $\text{C}^d$ ), 124.8 ( $\text{C}^e$ ), 128.2 ( $\text{C}^f$ ), 132.3 ( $\text{C}^g$ ), 136.3 ( $\text{C}^g$ ), 137.7 ( $\text{C}^a$ ), 141.4 ( $\text{C}^h$ ), 142.6 ( $\text{C}^i$ ). Accurate MS-ESI  $m/z$  485.1569 (calculated), 485.1567 (found)  $[\text{M}-\text{Cl}]^+ \text{C}_{20}\text{H}_{24}\text{N}_2^{193}\text{Ir}$ .

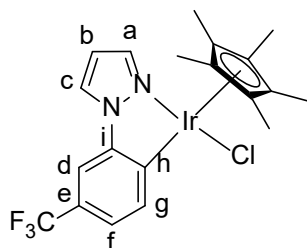
#### Cyclometallation of 1-(3-methoxyphenyl)-1H-pyrazole (L2-F) with $[\text{IrCl}_2\text{Cp}^*]_2$ .



The general procedure was followed using  $[\text{IrCl}_2\text{Cp}^*]_2$  (50 mg., 0.063 mmol), 1-[(3-fluoromethylphenyl)-1H-pyrazole (24.4 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 1 hour at room temperature. The

product was recrystallised from DCM / petroleum ether to give **2a-F** and **3a-F** (51 mg., 77%) as yellow crystals.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): **2a-F**  $\delta$  1.78 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 6.53 (t, 1H,  $J = 2.5$  Hz,  $\text{H}^b$ ), 6.83 (td, 1H,  $J = 0.9$ , 7.8 Hz,  $\text{H}^f$ ), 7.02 – 6.97 (m, 1H,  $\text{H}^e$ ), 7.10 (dd, 1H,  $J = 0.8$ , 7.8 Hz,  $\text{H}^d$ ), 7.71 (brd, 1H,  $J = 1.9$  Hz,  $\text{H}^a$ ), 7.90 (brd, 1H,  $J = 2.7$  Hz,  $\text{H}^c$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.3 (d,  $J_{\text{CF}} = 2.3$  Hz,  $\text{C}_5\text{Me}_5$ ), 88.8 ( $\text{C}_5\text{Me}_5$ ), 107.2 (d,  $^4J_{\text{CF}} = 2.4$  Hz,  $\text{C}^d$ ), 108.1 ( $\text{C}^b$ ), 113.2 (d,  $^2J_{\text{CF}} = 29.5$  Hz,  $\text{C}^f$ ), 124.6 (d,  $^3J_{\text{CF}} = 8.3$  Hz,  $\text{C}^e$ ), 125.8 ( $\text{C}^c$ ), 129.6 (d,  $^2J_{\text{CF}} = 48.2$  Hz,  $\text{C}^h$ ), 138.0 ( $\text{C}^a$ ), 144.1 (d,  $^3J_{\text{CF}} = 18.3$  Hz,  $\text{C}^i$ ), 167.1 (d,  $^1J_{\text{CF}} = 234.2$  Hz,  $\text{C}^g$ ).  $^{19}\text{F}\{^1\text{H}\}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -93.5 (s, F).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): **3a-F**  $\delta$  1.73 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 6.53 (t, 1H,  $J = 2.5$  Hz,  $\text{H}^b$ ), 6.88 (ddd, 1H,  $J = 2.5$ , 8.3, 9.4 Hz,  $\text{H}^f$ ), 6.97 – 7.02 (m, 1H,  $\text{H}^d$ ), 7.64 (dd, 1H,  $J = 6.4$ , 8.2 Hz,  $\text{H}^g$ ), 7.70 (brd, 1H,  $J = 2.2$  Hz,  $\text{H}^a$ ), 7.84 (brd, 1H,  $J = 2.8$  Hz,  $\text{H}^e$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.0 ( $\text{C}_5\text{Me}_5$ ), 88.0 ( $\text{C}_5\text{Me}_5$ ), 99.0 (d,  $^2J_{\text{CF}} = 25.6$  Hz,  $\text{C}^d$ ), 108.4 ( $\text{C}^b$ ), 113.8 (d,  $^2J_{\text{CF}} = 19.3$  Hz,  $\text{C}^f$ ), 125.4 ( $\text{C}^e$ ), 136.7 (d,  $^3J_{\text{CF}} = 7.1$  Hz,  $\text{C}^g$ ), 138.4 ( $\text{C}^a$ ), 139.0 (d,  $^4J_{\text{CF}} = 2.2$  Hz,  $\text{C}^h$ ), 142.5 (d,  $^3J_{\text{CF}} = 9.4$  Hz,  $\text{C}^i$ ), 160.1 (d,  $^1J_{\text{CF}} = 238.4$  Hz,  $\text{C}^e$ ).  $^{19}\text{F}\{^1\text{H}\}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -121.7 (s, F). Accurate MS-ESI  $m/z$  489.1318 (calculated), 489.1333 (found)  $[\text{M}-\text{Cl}]^+ \text{C}_{19}\text{H}_{21}\text{FN}_2^{193}\text{Ir}$ .

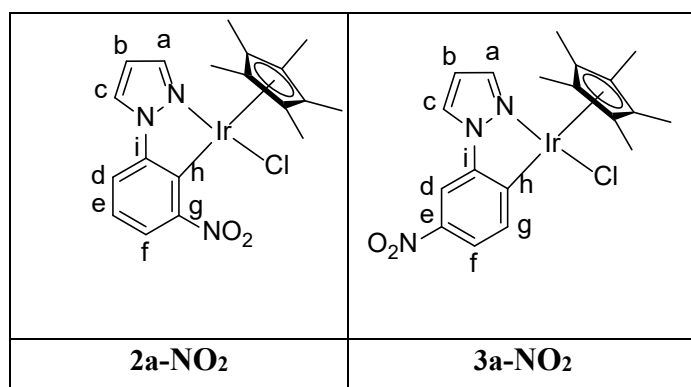
### Cyclometallation of 1-(3-trifluoromethylphenyl)-1*H*-pyrazole **L2-CF<sub>3</sub>** with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>



The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.063 mmol), 1-[(3-trifluoromethylphenyl)-1*H*-pyrazole (26.5 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) in dry MeOH (5 ml). The mixture was stirred for 6 hours at room temperature. The product was recrystallised from DCM / petroleum ether to give **3a-CF<sub>3</sub>** (49 mg., 68%) as yellow crystals. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.74 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.55 (t, 1H, *J* = 2.5 Hz, H<sup>b</sup>), 7.33 (dd, 1H, *J* = 0.9, 7.9 Hz, H<sup>f</sup>),

7.45 (brs, 1H, H<sup>d</sup>), 7.71 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.85 (d, 1H, *J* = 7.8 Hz, H<sup>g</sup>), 7.95 (brd, 1H, *J* = 2.6 Hz, H<sup>c</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 8.0 (C<sub>5</sub>Me<sub>5</sub>), 87.7 (C<sub>5</sub>Me<sub>5</sub>), 106.4 (q, <sup>3</sup>*J*<sub>CF</sub> = 3.8 Hz, C<sup>d</sup>), 107.6 (C<sup>b</sup>), 122.3 (q, <sup>3</sup>*J*<sub>CF</sub> = 3.3 Hz, C<sup>f</sup>), 123.7 (q, <sup>1</sup>*J*<sub>CF</sub> = 271.2 Hz, CF<sub>3</sub>), 124.1 (q, <sup>2</sup>*J*<sub>CF</sub> = 32.5 Hz, C<sup>e</sup>), 124.6 (C<sup>c</sup>), 135.8 (C<sup>g</sup>), 137.5 (C<sup>a</sup>), 141.8 (C<sup>h/i</sup>), 150.8 (C<sup>h/i</sup>). <sup>19</sup>F {<sup>1</sup>H} (376 MHz, CDCl<sub>3</sub>): δ -61.7 (s, CF<sub>3</sub>). Accurate MS-ESI *m/z* 539.1286 and 580.1552 (calculated), 539.1266 and 580.1567 (found) [M-Cl]<sup>+</sup> and [(M-Cl) + (MeCN)]<sup>+</sup> respectively C<sub>20</sub>H<sub>21</sub>F<sub>3</sub>N<sub>2</sub><sup>193</sup>Ir and C<sub>22</sub>H<sub>24</sub>F<sub>3</sub>N<sub>3</sub><sup>193</sup>Ir.

### Cyclometallation of 1-(3-methoxyphenyl)-1*H*-pyrazole (**L2-NO<sub>2</sub>**) with [IrCl<sub>2</sub>Cp\*]<sub>2</sub>.

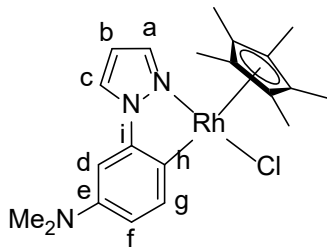


The general procedure was followed using [IrCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.063 mmol), 1-(3-nitrophenyl)-1*H*-pyrazole (23.7 mg., 0.125 mmol) and NaOAc (12.8 mg., 0.156 mmol) were added in dry MeOH (5ml). The mixture was stirred for 24 hours at room

temperature. The product was recrystallised from DCM / petroleum ether to give **2a-NO<sub>2</sub>** and **3a-NO<sub>2</sub>** (40 mg., 58%) as yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): **2a-NO<sub>2</sub>** δ 1.63 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.60 (dd, 1H, *J* = 2.3, 2.8 Hz, H<sup>b</sup>), 7.10 (t, 1H, *J* = 7.9 Hz, H<sup>c</sup>), 7.42 (dd, 1H, *J* = 1.1, 7.8 Hz, H<sup>d</sup>), 7.61 (dd, 1H, *J* = 1.1, 8.0 Hz, H<sup>f</sup>), 7.71 (dd, 1H, *J* = 0.5, 2.2, H<sup>a</sup>), 7.95 (dd, 1H, *J* = 0.5, 2.9 Hz, H<sup>c</sup>), <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 9.00 (C<sub>5</sub>Me<sub>5</sub>), 89.4 (C<sub>5</sub>Me<sub>5</sub>), 109.1 (C<sup>b</sup>), 114.0 (C<sup>d</sup>), 122.7 (C<sup>f</sup>), 123.8 (C<sup>e</sup>), 126.4 (C<sup>c</sup>), 137.8 (C<sup>h</sup>), 139.2 (C<sup>a</sup>), 144.8 (C<sup>i</sup>), 158.7 (C<sup>g</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): **3a-NO<sub>2</sub>** δ 1.75 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.63 (dd, 1H, *J* = 2.3, 2.8 Hz, H<sup>b</sup>), 7.74 (dd, 1H, *J* = 0.5, 2.2 Hz, H<sup>a</sup>), 7.90 (d, 1H, *J* = 8.3 Hz, H<sup>g</sup>), 7.97 (dd, 1H, *J* = 2.2, 8.3 Hz, H<sup>f</sup>), 8.05 (dd, 1H, *J* = 0.5, 2.8 Hz, H<sup>c</sup>), 8.11 (d, 1H, *J* = 2.2 Hz, H<sup>d</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 9.00 (C<sub>5</sub>Me<sub>5</sub>), 89.3 (C<sub>5</sub>Me<sub>5</sub>), 105.6 (C<sup>d</sup>), 109.2 (C<sup>b</sup>), 121.4 (C<sup>f</sup>), 126.2 (C<sup>c</sup>), 136.8 (C<sup>g</sup>), 139.0 (C<sup>a</sup>), 143.1 (C<sup>h</sup>), 144.3 (C<sup>i</sup>), 159.8 (C<sup>e</sup>). Accurate MS-ESI *m/z*

516.1263 and 557.1529 (calculated), 516.1270 and 557.1532 (found)  $[M-Cl]^+$  and  $[(M-Cl) + (MeCN)]^+$  respectively  $C_{19}H_{21}N_3O^{193}Ir$  and  $C_{21}H_{24}N_4O^{193}Ir$ .

#### Cyclometallation of 1-(3-N, N dimethylamine)-1*H*-pyrazole (L2-NMe<sub>2</sub>) with $[RhCl_2Cp^*]_2$

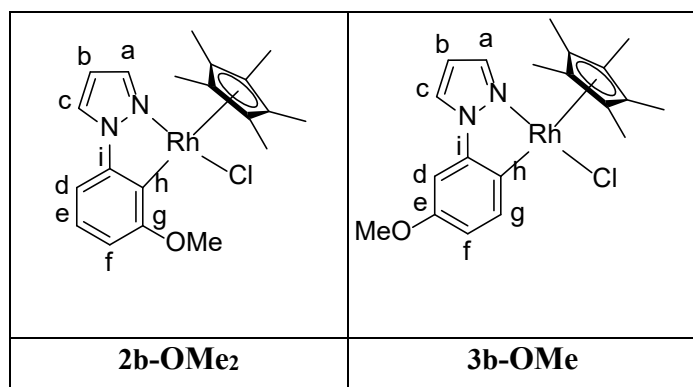


The general procedure was followed using  $[Cp^*RhCl_2]_2$  (50 mg., 0.081 mmol), 1-(3-N, N dimethylamine)-1*H*-pyrazole (30.3 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162mmol) in dry MeOH (5 ml).

The mixture was stirred for 4 hours at room temperature. The product was recrystallised from THF / petroleum ether to give **3b-NMe<sub>2</sub>** (34 mg., 46%) orange crystals.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.67 (s,

15H,  $C_5Me_5$ ), 2.91 (s, 6H,  $NMe_2$ ), 6.45 (t, 1H,  $J = 2.4$  Hz,  $H^b$ ), 6.63 (d, 1H,  $J = 2.4$  Hz,  $H^d$ ), 6.72 (dd, 1H,  $J = 2.5, 8.3$  Hz,  $H^f$ ), 7.57 (d, 1H,  $J = 8.3$  Hz,  $H^g$ ), 7.78 (brd, 1H,  $J = 2.0$  Hz,  $H^a$ ), 7.94 (brd, 1H,  $J = 2.6$  Hz,  $H^c$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz) =  $\delta$  9.3 ( $C_5Me_5$ ), 41.4 ( $NMe_2$ ), 95.2 (d,  $J = 6.6$  Hz,  $C_5Me_5$ ), 97.6 ( $C^d$ ), 107.7 ( $C^b$ ), 113.8 ( $C^f$ ), 124.8 ( $C^e$ ), 137.0 ( $C^g$ ), 138.8 ( $C^a$ ), 141.9 ( $C^i$ ), 144.2 (d,  $J_{Rh-C} = 33.1$  Hz,  $C^h$ ), 148.3 ( $C^c$ ). Accurate MS-ESI  $m/z$  424.1260 (calculated), 424.1244 (found)  $[M-Cl]^+$   $C_{21}H_{27}N_3^{103}Rh$ .

#### Cyclometallation of 1-(3-methoxyphenyl)-1*H*-pyrazole (L2-OMe) with $[RhCl_2Cp^*]_2$ .

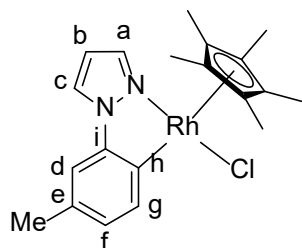


The general procedure was followed using  $[Cp^*RhCl_2]_2$  (50 mg., 0.081 mmol), 1-(3-methoxyphenyl)-1*H*-pyrazole (28.2 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162mmol) in dry MeOH (5 ml). The mixture was stirred for 20 hours at room temperature and

**2b-OMe** and **3b-OMe** were observed. The product was recrystallised from DCM / petroleum ether to give only **3b-OMe** (44 mg., 61%) orange crystals. The  $^1H$  NMR signals for the *ortho* isomer **2b-OMe** have been assigned from the crude mixture.  $^1H$  NMR ( $CDCl_3$ , 400 MHz) **2b-OMe**  $\delta$  1.68 (s, 15H,  $C_5Me_5$ ), 3.88 (s, 3H, OMe), 6.52-6.50 (m, 1H,  $H^b$ ), 6.70 (brd, 1H,  $J = 7.8$ , Hz,  $H^d$ ), 6.92 (dd, 1H,  $J = 0.8, 7.8$  Hz,  $H^f$ ), 7.07 (t, 1H,  $J = 7.9$  Hz,  $H^c$ ), 7.84 (overlapping d, 1H,  $H^a$ ), 7.96 (brd, 1H,  $J = 2.6$  Hz,  $H^e$ ). This isomer was not characterised by  $^{13}C$  NMR.  $^1H$  NMR ( $CDCl_3$ , 500 MHz) : **3b-OMe**  $\delta$  1.67 (s, 15H,  $C_5Me_5$ ), 3.79 (s, 3H, OMe), 6.46 (t, 1H,  $J = 2.5$  Hz,  $H^b$ ), 6.79 (d, 1H,  $J = 2.4$ , Hz,  $H^d$ ), 6.81 (dd, 1H,  $J = 2.5, 8.1$  Hz,  $H^f$ ), 7.61 (d, 1H,  $J = 8.0$  Hz,  $H^g$ ), 7.79 (brd, 1H,  $J = 2.1$  Hz,  $H^a$ ), 7.93 (brd, 1H,  $J = 2.6$  Hz,  $H^c$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz) :  $\delta$  9.2 ( $C_5Me_5$ ), 55.6 (OMe), 95.4 (d,  $J = 6.5$  Hz,

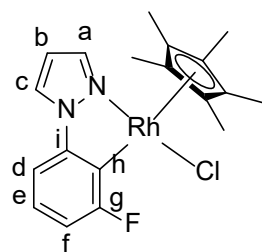
$C_5Me_5$ ), 98.5 ( $C^d$ ), 108.1 ( $C^b$ ), 113.0 ( $C^f$ ), 125.2 ( $C^e$ ), 137.2 ( $C^g$ ), 139.0 ( $C^a$ ), 141.8( $C^i$ ), 147.9 ( $d$ ,  $J_{Rh-C} = 32.8$  Hz,  $C^h$ ), 157.0 ( $C^e$ ). Accurate MS-ESI  $m/z$  411.0944 (calculated), 411.0946 (found)  $[M-Cl]^+ C_{20}H_{24}N_2O^{103}Rh$ .

#### Cyclometallation of 1-(3-methylphenyl)-1*H*-pyrazole (L2-Me) with $[RhCl_2Cp^*]_2$



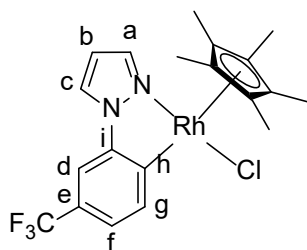
The general procedure was followed using  $[Cp^*RhCl_2]_2$  (50 mg., 0.081 mmol), 1-(3-methylphenyl)-1*H*-pyrazole (25.6 mg., 0.162 mmol), NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 4 hours at room temperature. The product was recrystallised from DCM / petroleum ether to give **86b-Me** (40 mg., 62%) as orange crystals.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.68 (s, 15H,  $C_5Me_5$ ), 2.34 (s, 3H, Me), 6.48 (t, 1H,  $J = 2.4$  Hz,  $H^b$ ), 6.99 (brd, 1H,  $J = 7.7$  Hz,  $H^f$ ), 7.02 (brs, 1H,  $H^d$ ), 7.63 (d, 1H,  $J = 7.6$  Hz,  $H^g$ ), 7.80 (brd, 1H,  $J = 1.9$  Hz,  $H^a$ ), 7.94 (brd, 1H,  $J = 2.6$  Hz,  $H^e$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  9.2 ( $C_5Me_5$ ), 21.0 (Me), 95.5 ( $d$ ,  $J = 6.9$  Hz,  $C_5Me_5$ ), 107.9 ( $C^b$ ), 112.0 ( $C^d$ ), 124.9 ( $C^e$ ), 128.1 ( $C^f$ ), 132.9 ( $C^e$ ), 137.0( $C^g$ ), 138.8 ( $C^a$ ), 141.7 ( $C^i$ ), 154.8 ( $d$ ,  $J_{Rh-C} = 32.0$  Hz,  $C^h$ ). Accurate MS-ESI  $m/z$  395.0995 (calculated), 395.0993 (found)  $[M-Cl]^+ C_{20}H_{24}N_2^{103}Rh$ .

#### Cyclometallation of 1-(3-fluoromethylphenyl)-1*H*-pyrazole (L2-F) with $[RhCl_2Cp^*]_2$



The general procedure was followed using  $[RhCl_2Cp^*]_2$  (50 mg., 0.081 mmol), 1-[(3-fluoromethylphenyl)-1*H*-pyrazole (26.2 mg., 0.162 mmol) and NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 2 hours at room temperature. The product was recrystallised from DCM / petroleum ether to give **2b-F** (51 mg., 73%) as orange crystals.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  1.73 (s, 15H,  $C_5Me_5$ ), 6.53 (t, 1H,  $J = 2.5$  Hz,  $H^b$ ), 6.83 – 6.89 (m, 1H,  $H^f$ ), 7.07 – 7.01 (m, 2H,  $H^{d/e}$ ), 7.83 (brd, 1H,  $J = 2.1$  Hz,  $H^a$ ), 7.97(brd, 1H,  $J = 2.7$  Hz,  $H^e$ ).  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  9.5 ( $d$ ,  $J = 2.2$  Hz,  $C_5Me_5$ ), 96.4 ( $d$ ,  $J = 6.8$  Hz,  $C_5Me_5$ ), 107.5 ( $d$ ,  $^4J_{CF} = 2.1$  Hz,  $C^d$ ), 108.2 ( $C^b$ ), 113.4 ( $d$ ,  $^2J_{CF} = 29.7$  Hz,  $C^f$ ), 125.1 ( $d$ ,  $^3J_{CF} = 8.1$  Hz,  $C^e$ ) 125.7 ( $C^e$ ), 139.1 ( $C^a$ ), 141.4 (dd,  $^2J_{CF} = 35.2$ ,  $J_{Rh-C} = 50.3$  Hz,  $C^h$ ), 143.5 ( $d$ ,  $^3J_{CF} = 19.4$  Hz,  $C^i$ ), 167.8 ( $d$ ,  $^1J_{CF} = 233.6$ Hz,  $C^g$ ).  $^{19}F\{^1H\}$  (376 MHz,  $CDCl_3$ ):  $\delta$  -92.7 (s, F). Accurate MS-ESI  $m/z$  399.0744 (calculated), 399.0727 (found),  $[M-Cl]^+ C_{19}H_{21}FN_2^{103}Rh$ .

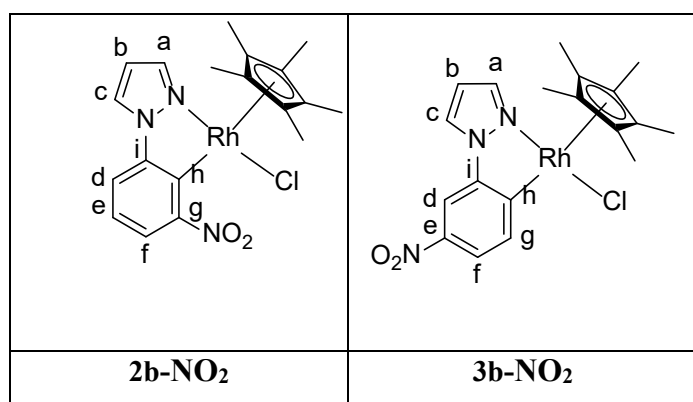
#### Cyclometallation of 1-(3-trifluoromethylphenyl)-1*H*-pyrazole (L2-CF<sub>3</sub>) with $[RhCl_2Cp^*]_2$



The general procedure was followed using  $[Cp^*RhCl_2]_2$  (50 mg., 0.081 mmol), 1-(3-trifluoromethylphenyl)-1*H*-pyrazole (34.3 mg., 0.162mmol), NaOAc (13.3 mg., 0.162 mmol) in dry MeOH (5 ml). The mixture was stirred for 18 hours at 60 °C. The product was recrystallised from DCM /

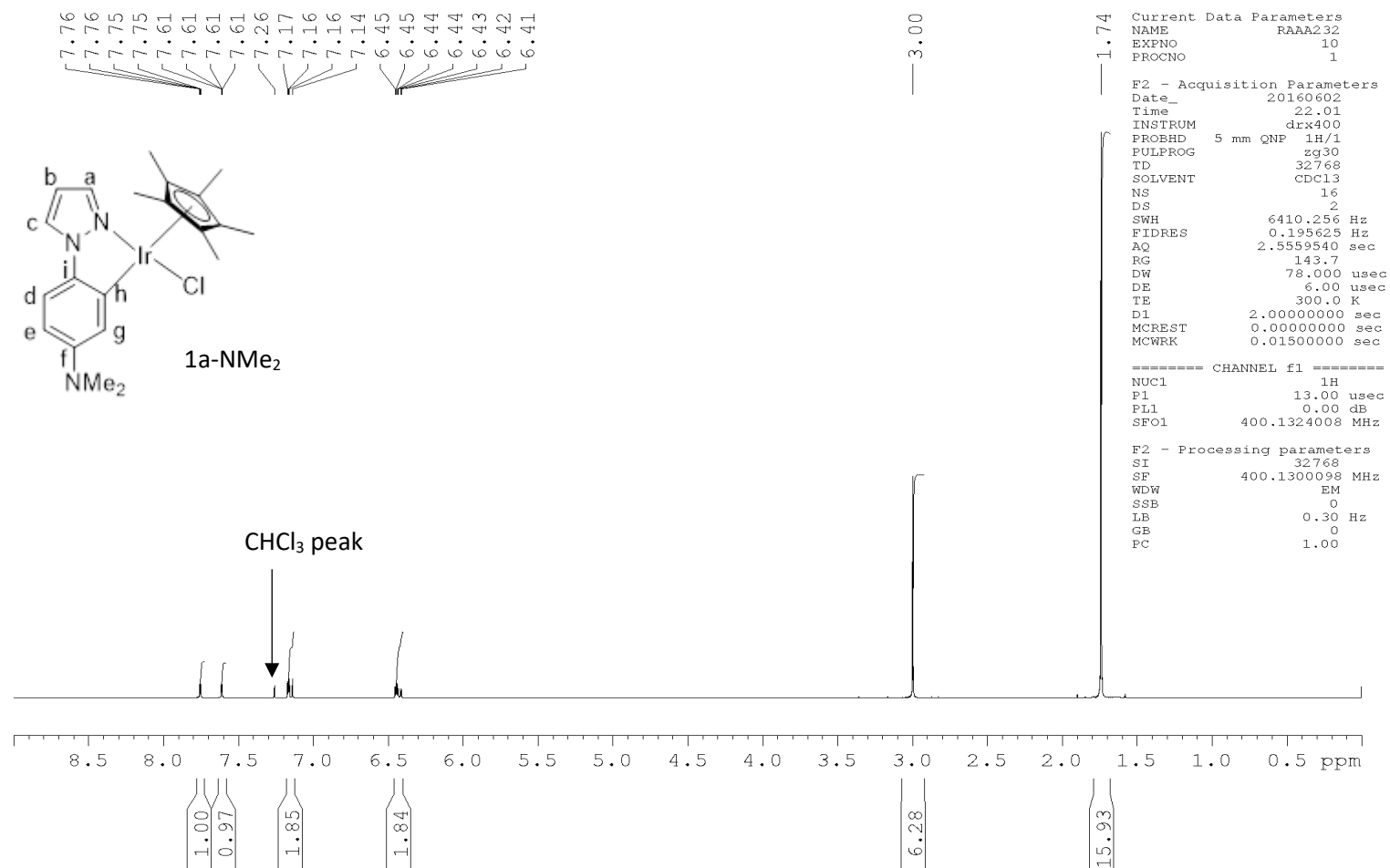
petroleum ether to give **3b**-CF<sub>3</sub> (42 mg., 54%) as orange crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.69 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.55 (t, *J* = 2.4 Hz, 1H, H<sup>b</sup>), 7.38 (s, 1H, H<sup>d</sup>), 7.39 (brd, 1H, *J* = 7.8 Hz, H<sup>f</sup>), 7.84 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.88 (d, 1H, *J* = 7.6 Hz, H<sup>g</sup>), 8.02 (brd, 1H, *J* = 2.7 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz): δ 9.2 (C<sub>5</sub>Me<sub>5</sub>), 96.1 (d, *J* = 6.7 Hz, C<sub>5</sub>Me<sub>5</sub>), 107.5 (q, <sup>3</sup>*J*<sub>CF</sub> = 3.6 Hz, C<sup>d</sup>), 108.7 (C<sup>b</sup>), 123.0 (q, <sup>3</sup>*J*<sub>CF</sub> = 3.1 Hz, C<sup>f</sup>), 125.6 (C<sup>c</sup>), 124.6 (q, <sup>1</sup>*J*<sub>CF</sub> = 271.5 Hz, CF<sub>3</sub>), 125.9 (q, <sup>2</sup>*J*<sub>CF</sub> = 32.5 Hz, C<sup>e</sup>), 137.7 (C<sup>g</sup>), 139.5 (C<sup>a</sup>, CH), 141.9 (C<sup>i</sup>), 165.8 (d, *J*<sub>Rh-C</sub> = 33.1 Hz, C<sup>h</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz) = δ -61.8 (s, 3F, CF<sub>3</sub>). Accurate MS-ESI *m/z* 449.0712 and 490.0977 (calculated), 449.0711 and 490.0975 (found) [M-Cl]<sup>+</sup> and [M-Cl + (MeCN)]<sup>+</sup> respectively C<sub>20</sub>H<sub>21</sub>N<sub>2</sub>F<sub>3</sub><sup>103</sup>Rh and C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>F<sub>3</sub><sup>103</sup>Rh.

### Cyclometallation of 1-(3-methoxyphenyl)-1*H*-pyrazole (L2-NO<sub>2</sub>) with [RhCl<sub>2</sub>Cp\*]<sub>2</sub>.

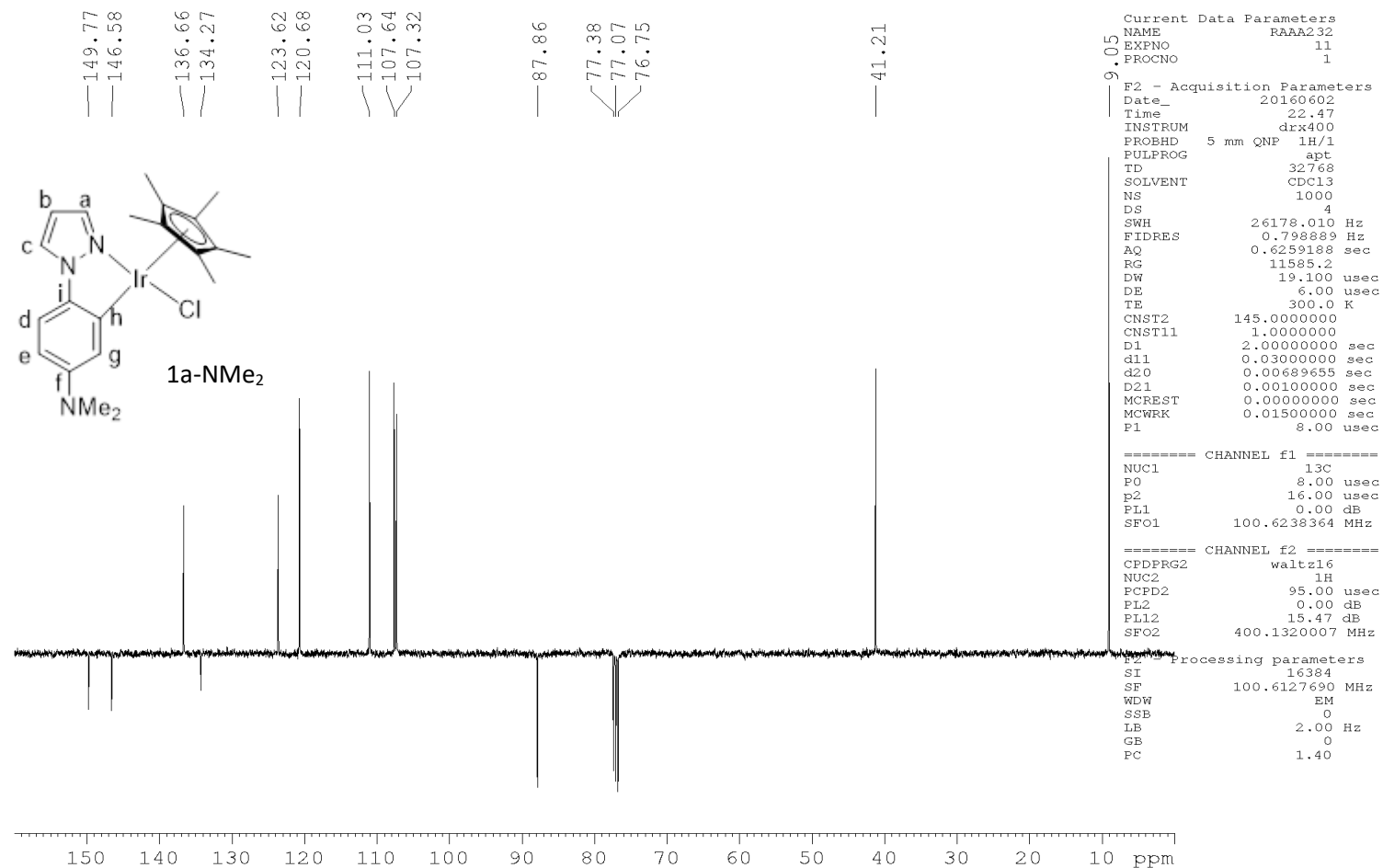


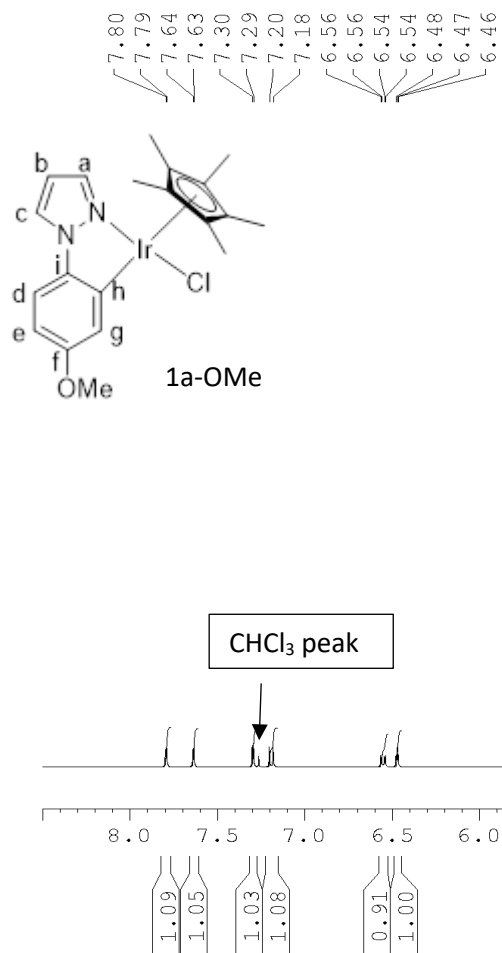
The general procedure was followed using [RhCl<sub>2</sub>Cp\*]<sub>2</sub> (50 mg., 0.081 mmol), 1-(3-nitrophenyl)-1*H*-pyrazole (46.0 mg., 0.243 mmol) and NaOAc (13.3 mg., 0.162 mmol) were added in dry MeOH (5ml). The mixture was stirred for 96 hours at room temperature. The product was

recrystallised from DCM / petroleum ether to give **2b**-NO<sub>2</sub> and **3b**-NO<sub>2</sub> (44 mg., 58%) as orange crystals. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): **2b**-NO<sub>2</sub> δ 1.59 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.54 (t, 1H, *J* = 2.5 Hz, H<sup>b</sup>), 7.14 (t, 1H, *J* = 7.9 Hz, H<sup>c</sup>), 7.38 (dd, 1H, *J* = 1.0, 7.8 Hz, H<sup>d</sup>), 7.73 (dd, 1H, *J* = 1.0, 8.0 Hz, H<sup>f</sup>), 7.84 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 8.04 (brd, 1H, *J* = 2.8 Hz, H<sup>e</sup>), <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 9.3 (C<sub>5</sub>Me<sub>5</sub>), 89.3/89.4 (C<sub>5</sub>Me<sub>5</sub>), 109.3 (C<sup>b</sup>), 114.7 (C<sup>d</sup>), 123.1 (C<sup>f</sup>), 124.6 (C<sup>e</sup>), 126.6 (C<sup>c</sup>), 140.5 (C<sup>a</sup>), 144.2 (C<sup>i</sup>), 152.2 (d, *J*<sub>Rh-C</sub> = 37.7 Hz, C<sup>h</sup>), 159.5 (C<sup>g</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): **3b**-NO<sub>2</sub> δ 1.70 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 6.61 (t, 1H, *J* = 2.5 Hz, H<sup>b</sup>), 7.86 (brd, 1H, *J* = 2.0 Hz, H<sup>a</sup>), 7.94 (dd, 1H, *J* = 1.2, 7.3 Hz, H<sup>f</sup>), 8.02 – 8.0 (m, 2H, H<sup>d+g</sup>), 8.11 (d, 1H, *J* = 2.75 Hz, H<sup>c</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 9.2 (C<sub>5</sub>Me<sub>5</sub>), 89.3/89.4 (C<sub>5</sub>Me<sub>5</sub>), 105.5 (C<sup>d/g</sup>), 109.3 (C<sup>b</sup>), 120.7 (C<sup>d/g</sup>), 126.2 (C<sup>c</sup>), 137.6 (C<sup>f</sup>), 139.9 (C<sup>a</sup>), 142.2 (C<sup>e/i</sup>), 145.1 (C<sup>e/i</sup>), 174.1 (d, *J*<sub>Rh-C</sub> = 34.0 Hz, C<sup>h</sup>). Accurate MS-ESI *m/z* 426.0689 and 467.0954 (calculated), 426.692 and 467.0957 (found) [M-Cl]<sup>+</sup> and [M-Cl + (MeCN)]<sup>+</sup> respectively C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub><sup>103</sup>Rh and C<sub>21</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub><sup>103</sup>Rh.







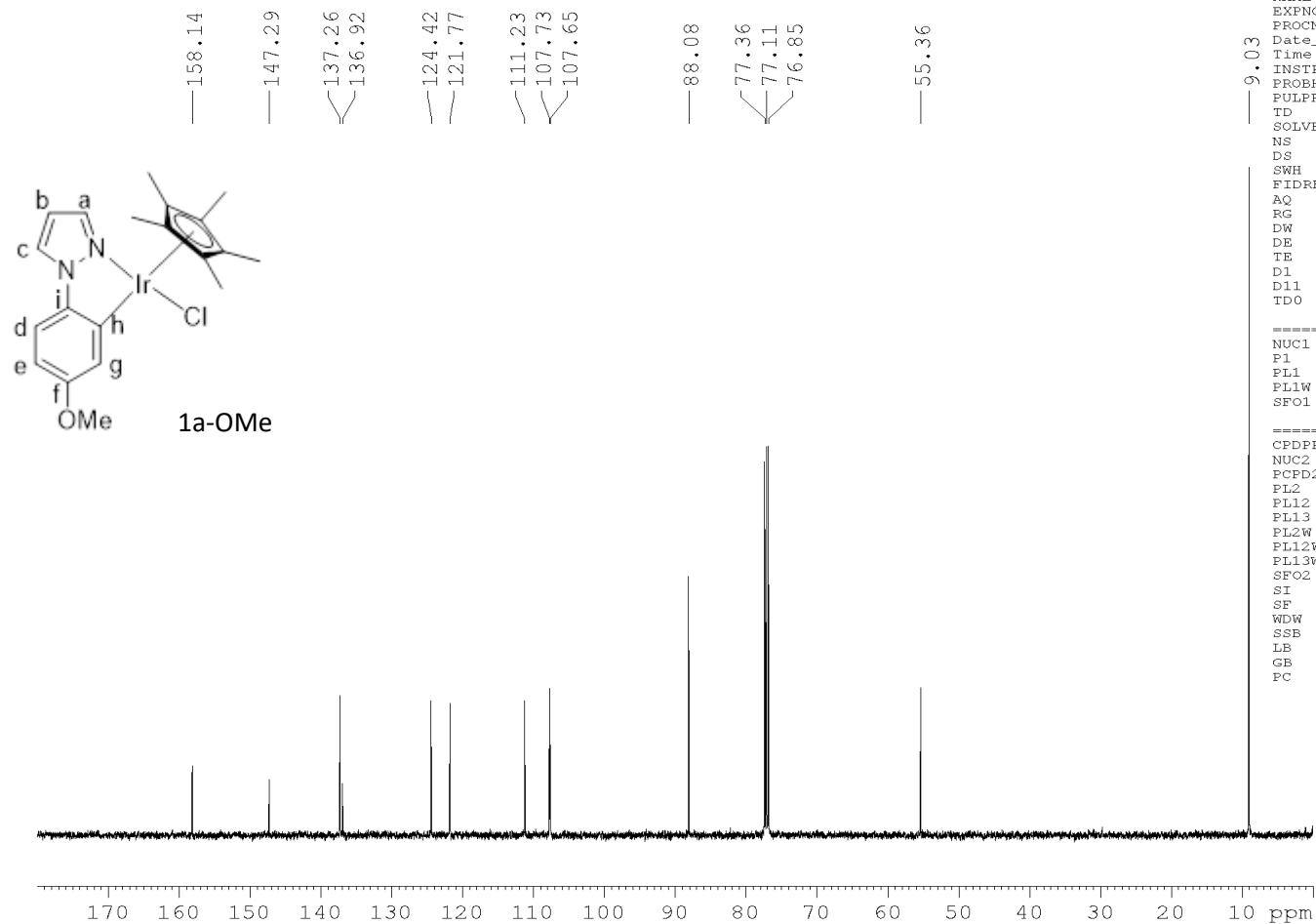


```

NAME          RAAA20_2
EXPNO         2
PROCNO        1
Date_         20140701
Time          9.30
INSTRUM       drx400
PROBHD        5 mm QNP 1H/1
PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            2
SWH           6410.256 Hz
FIDRES        0.195625 Hz
AQ            2.5559540 sec
RG            114
DW            78.000 usec
DE            6.00 usec
TE            300.0 K
D1            2.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            13.00 usec
PL1           0.00 dB
SFO1          400.1324008 MHz
SI            32768
SF            400.1300083 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

```



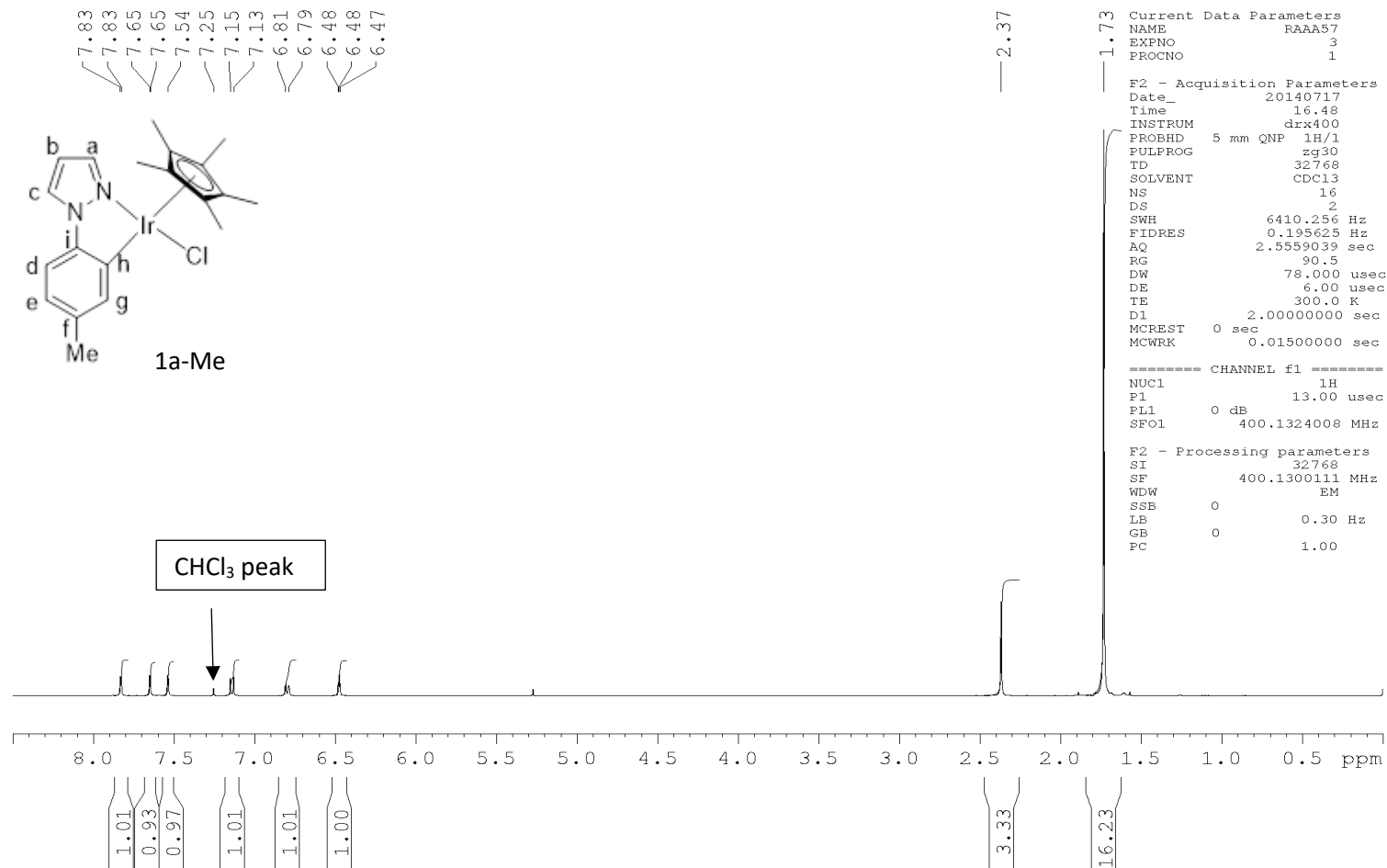
```

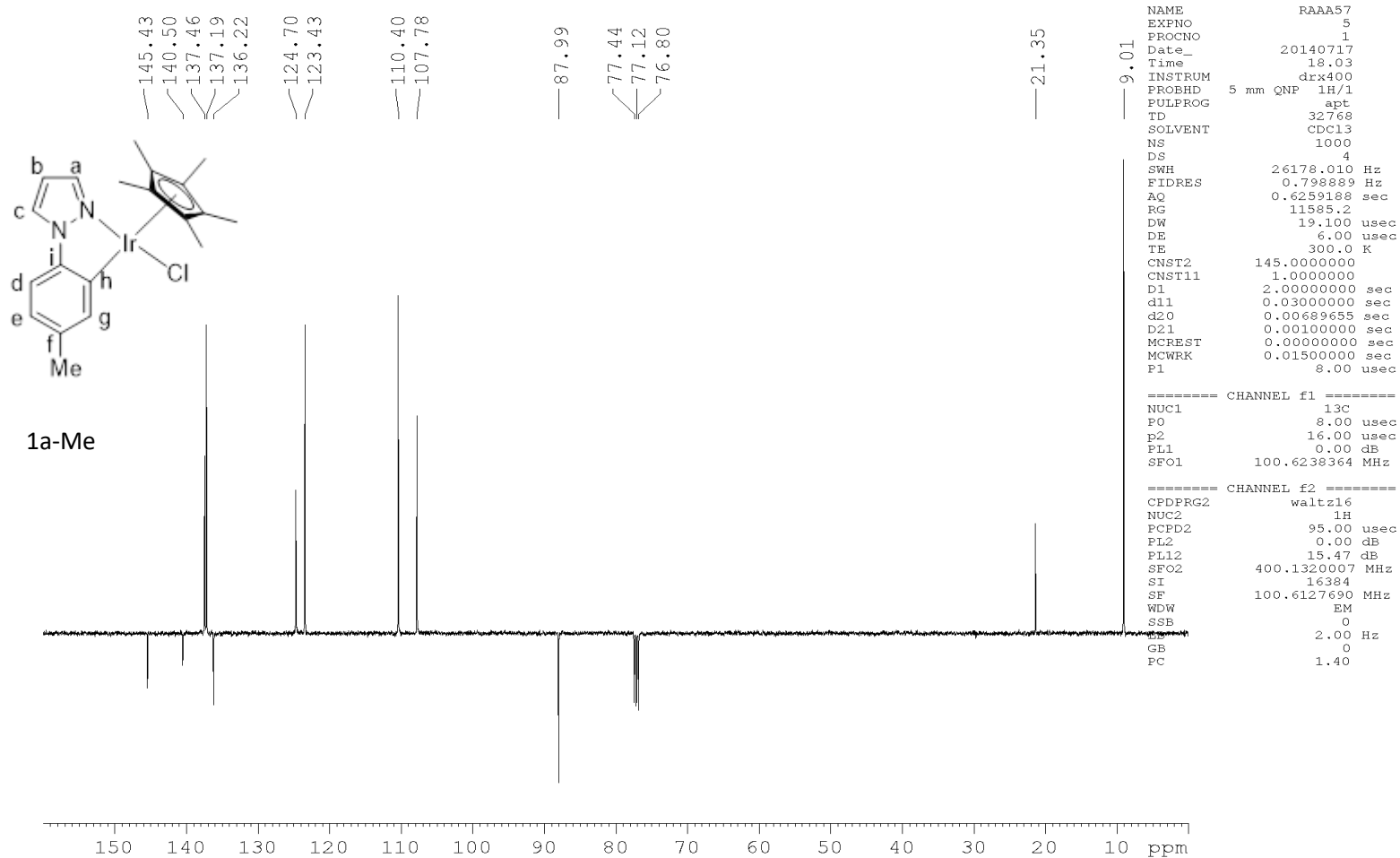
NAME          raaa20
EXPNO         2
PROCNO        1
Date_         20140701
Time          15.11
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            32768
SOLVENT       CDC13
NS            128
DS            2
SWH           32894.738 Hz
FIDRES        1.003868 Hz
AQ            0.4981236 sec
RG            2050
DW            15.200 usec
DE            6.50 usec
TE            298.0 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0           1

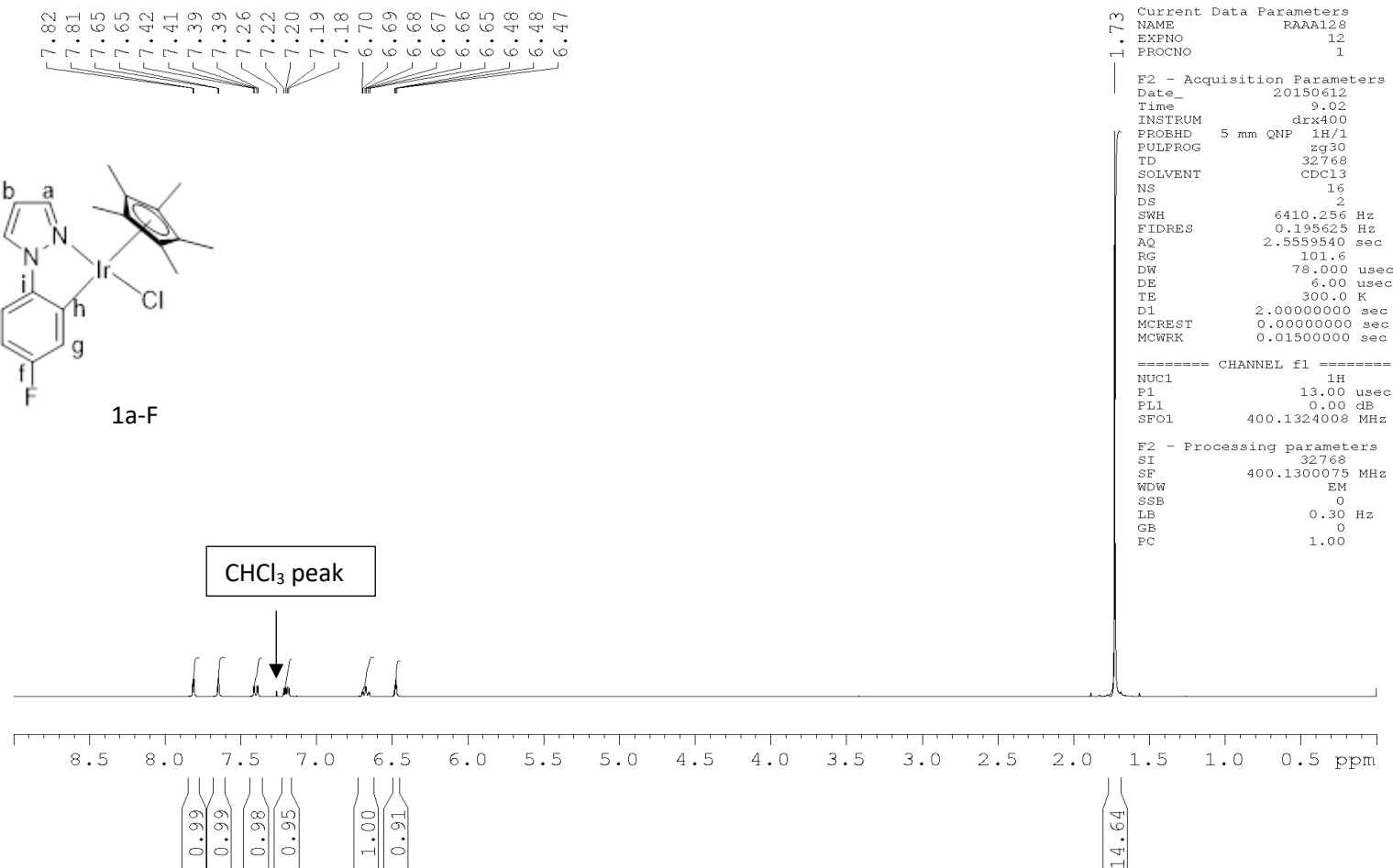
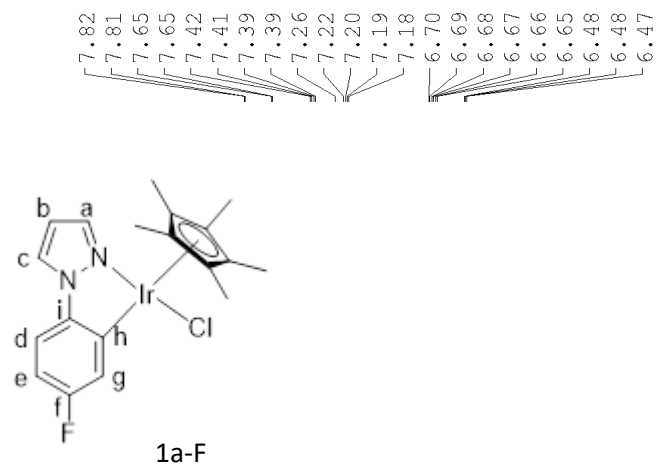
===== CHANNEL f1 =====
NUC1          13C
P1            8.50 usec
PL1           1.00 dB
PL1W          58.06213379 W
SFO1          125.7716224 MHz

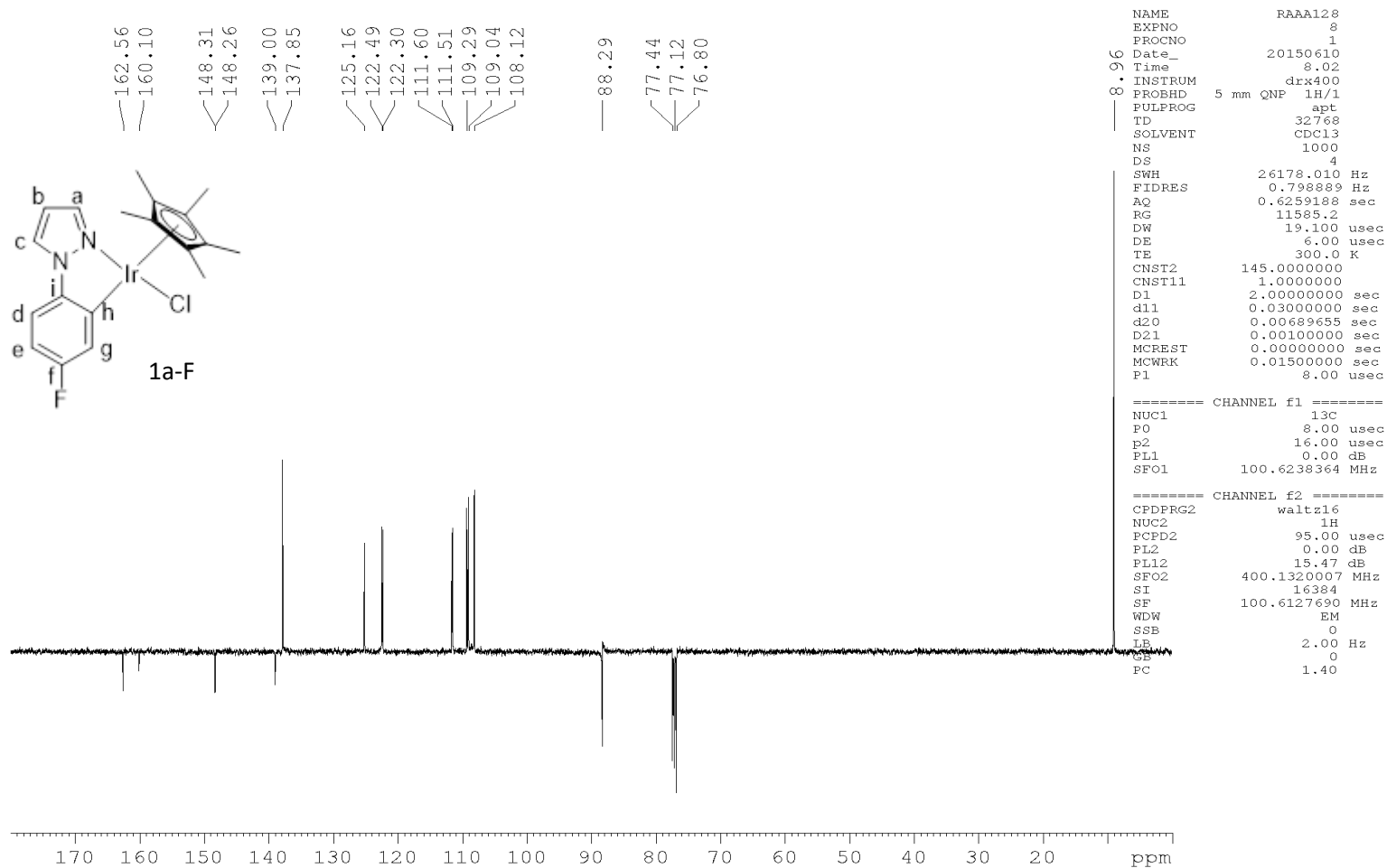
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           0.00 dB
PL12          17.00 dB
PL13          17.00 dB
PL2W          22.85816574 W
PL12W         0.45608038 W
PL13W         0.45608038 W
SFO2          500.1320005 MHz
SI            32768
SF            125.7577890 MHz
WDW           EM
SSB           0
LB            2.00 Hz
GB            0
PC            1.40

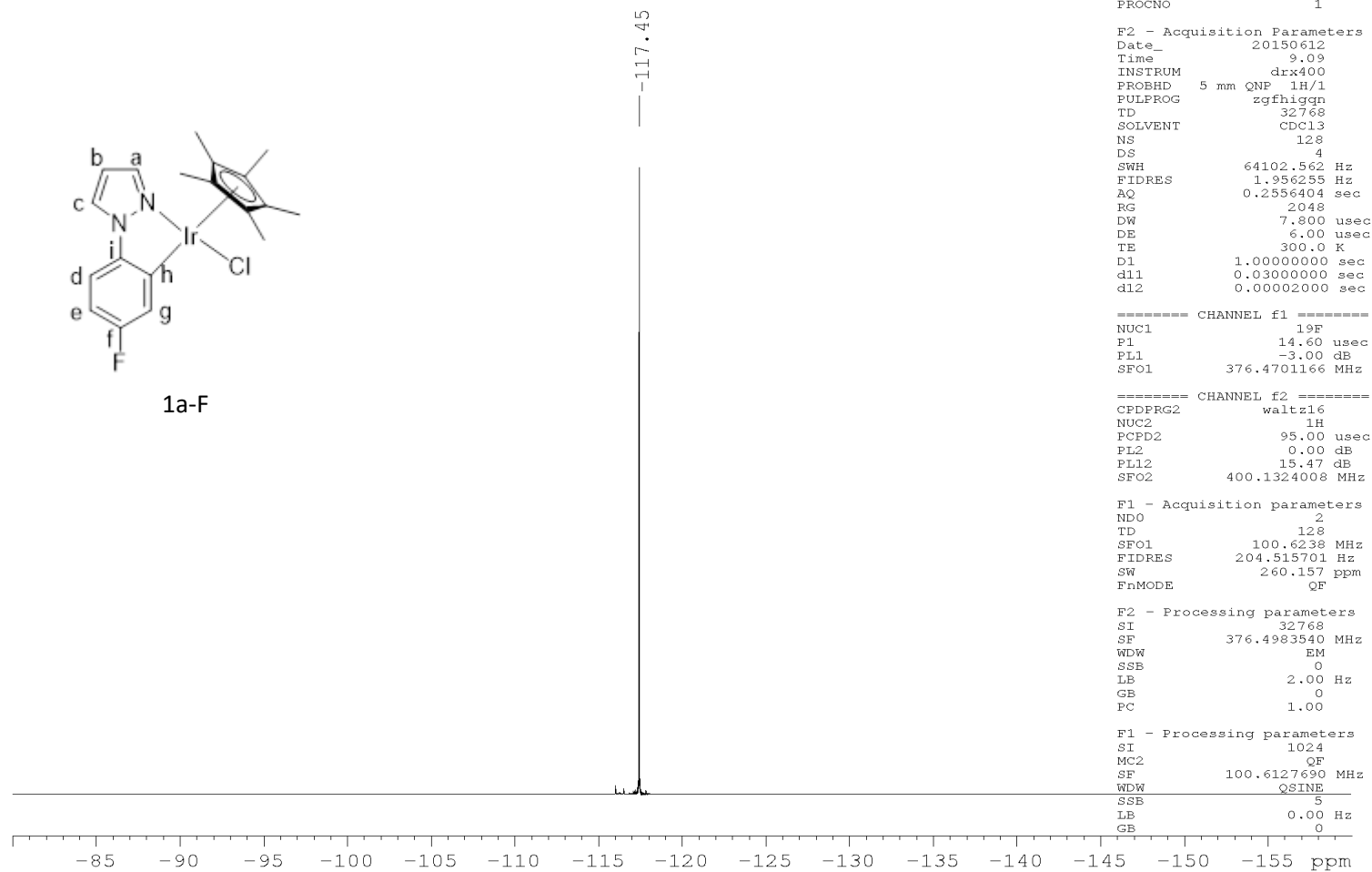
```





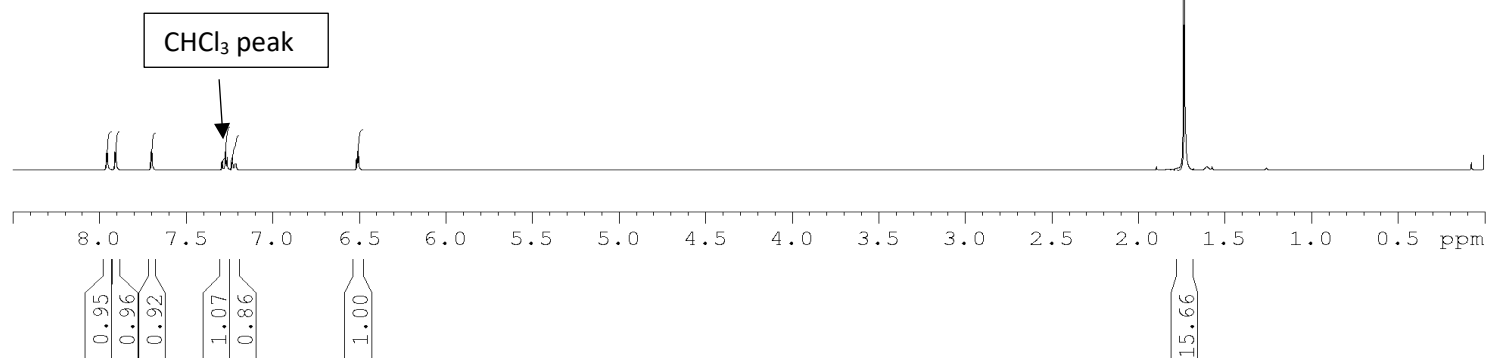
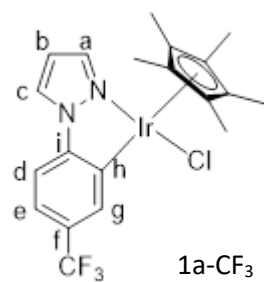






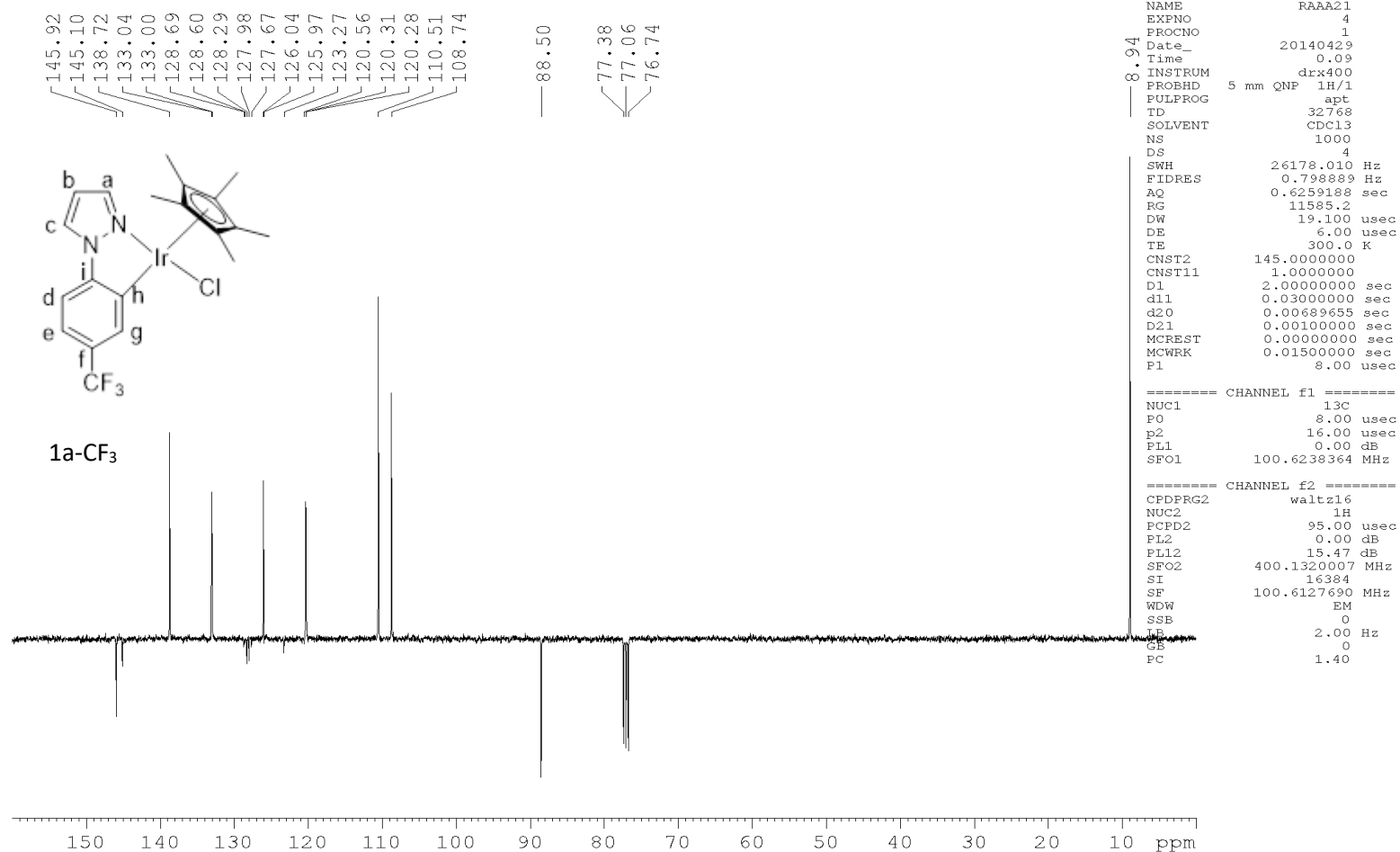


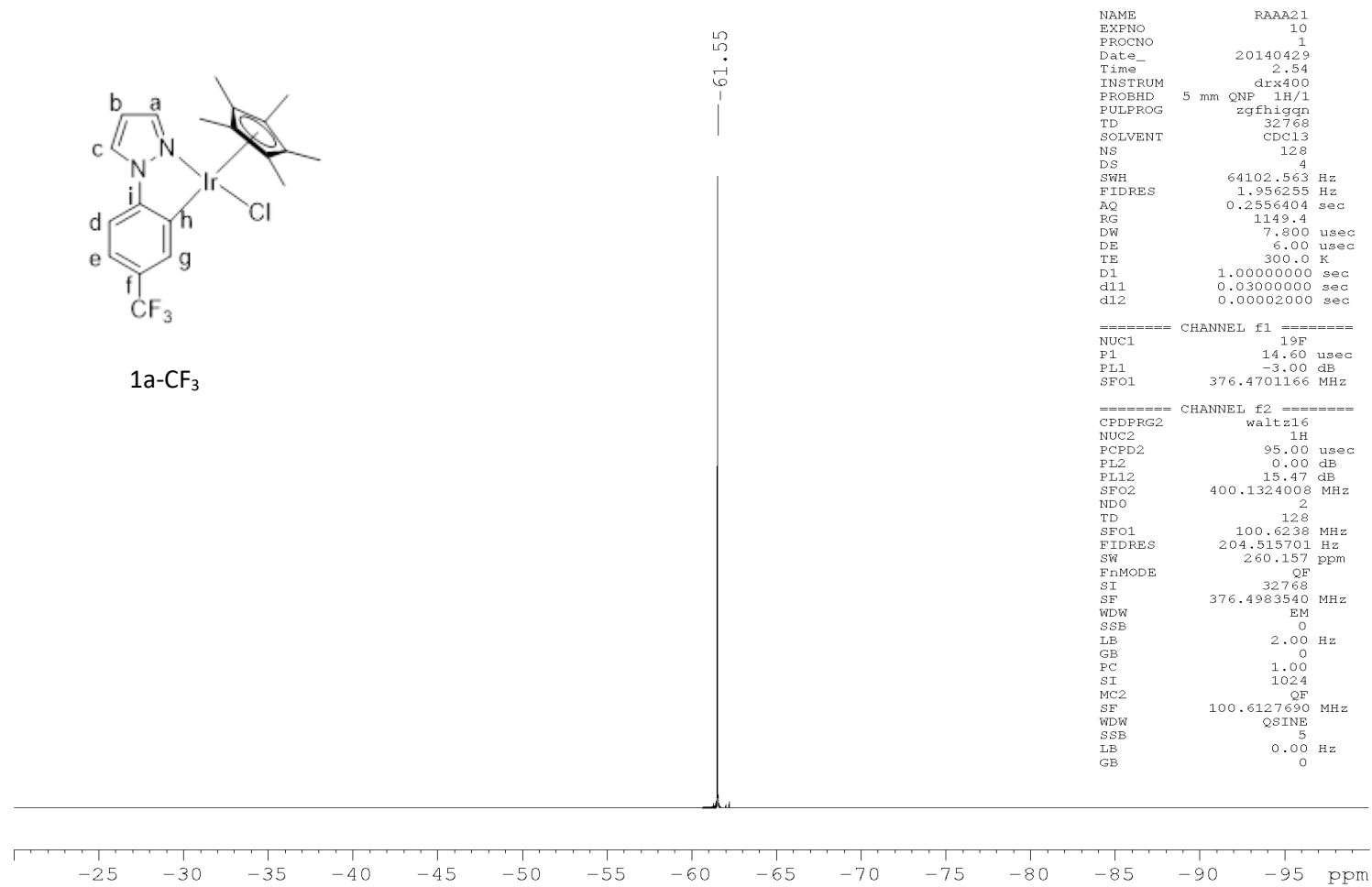
7.96  
7.96  
7.91  
7.90  
7.70  
7.70  
7.29  
7.27  
7.23  
7.23  
7.21  
7.21  
6.51  
6.51  
6.50

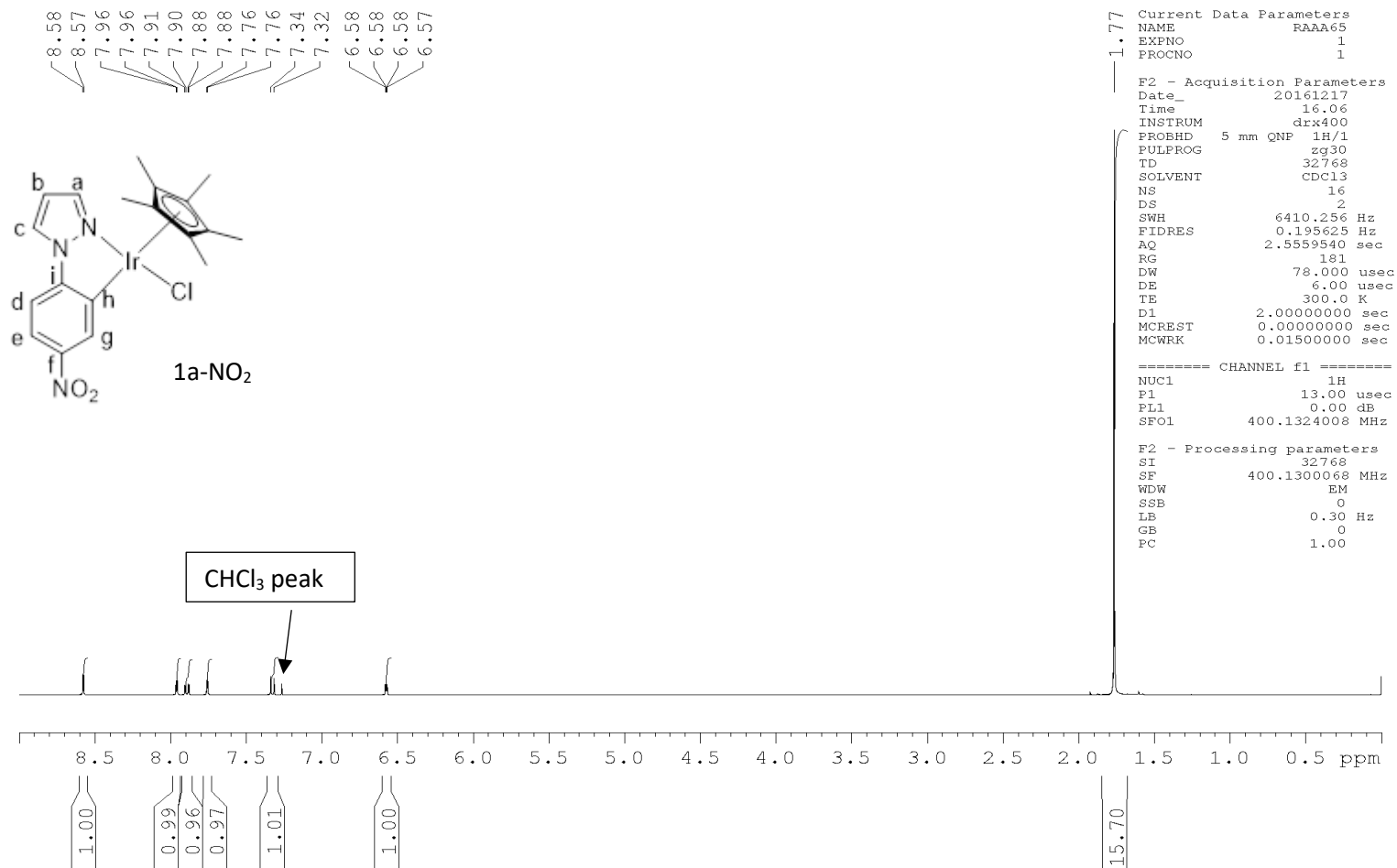


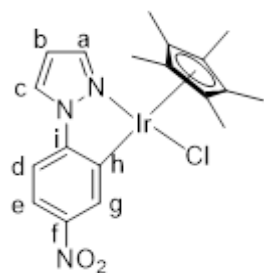
NAME RAAA21  
EXPNO 11  
PROCNO 1  
Date\_ 20140626  
Time 13.44  
INSTRUM drx400  
PROBHD 5 mm QNP 1H/1  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 6410.256 Hz  
FIDRES 0.195625 Hz  
AQ 2.5559540 sec  
RG 143.7  
DW 78.000 usec  
DE 6.00 usec  
TE 300.0 K  
D1 2.00000000 sec  
MCREST 0.00000000 sec  
MCWRK 0.01500000 sec

===== CHANNEL f1 =====  
NUC1 1H  
P1 13.00 usec  
PL1 0.00 dB  
SFO1 400.1324008 MHz  
SI 32768  
SF 400.1300085 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

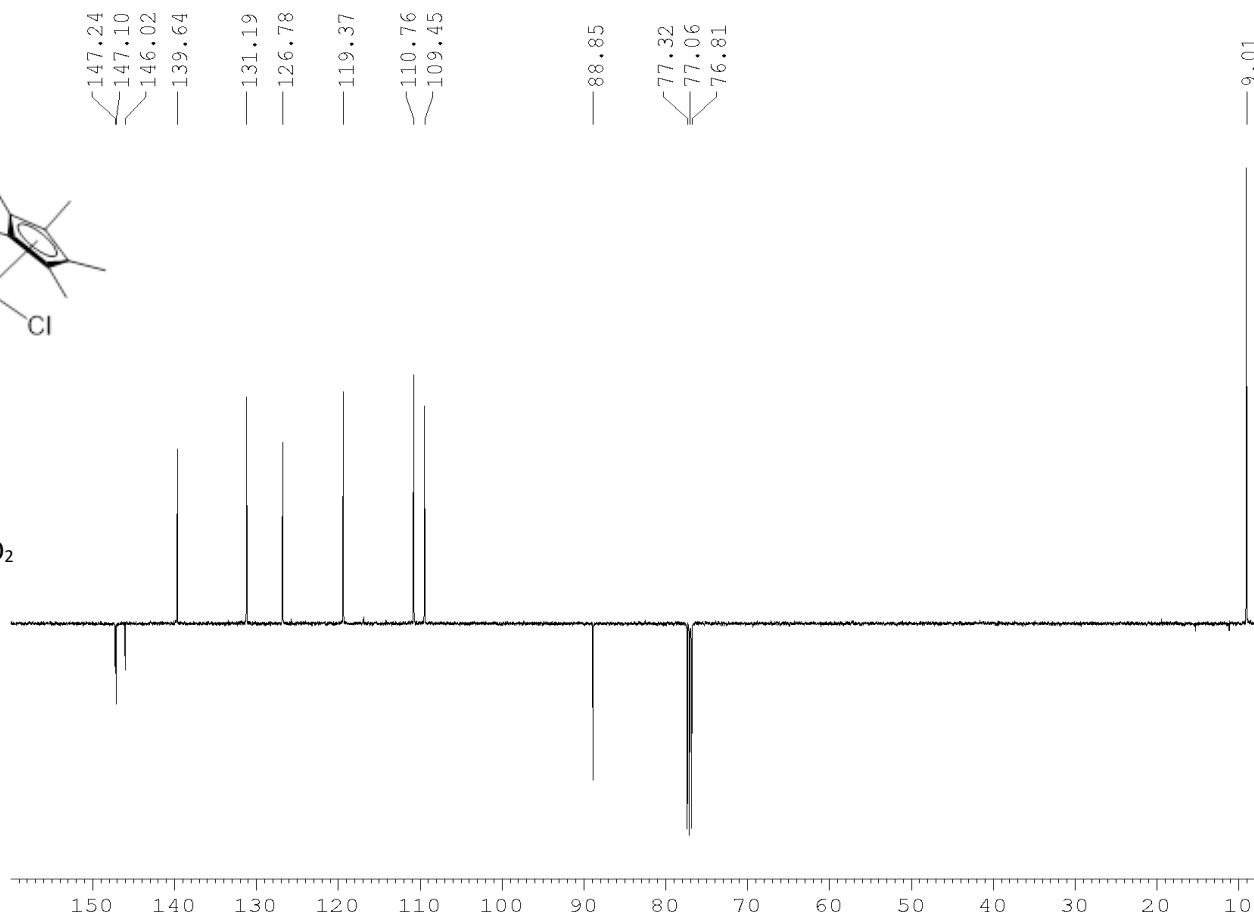








1a-NO<sub>2</sub>



```

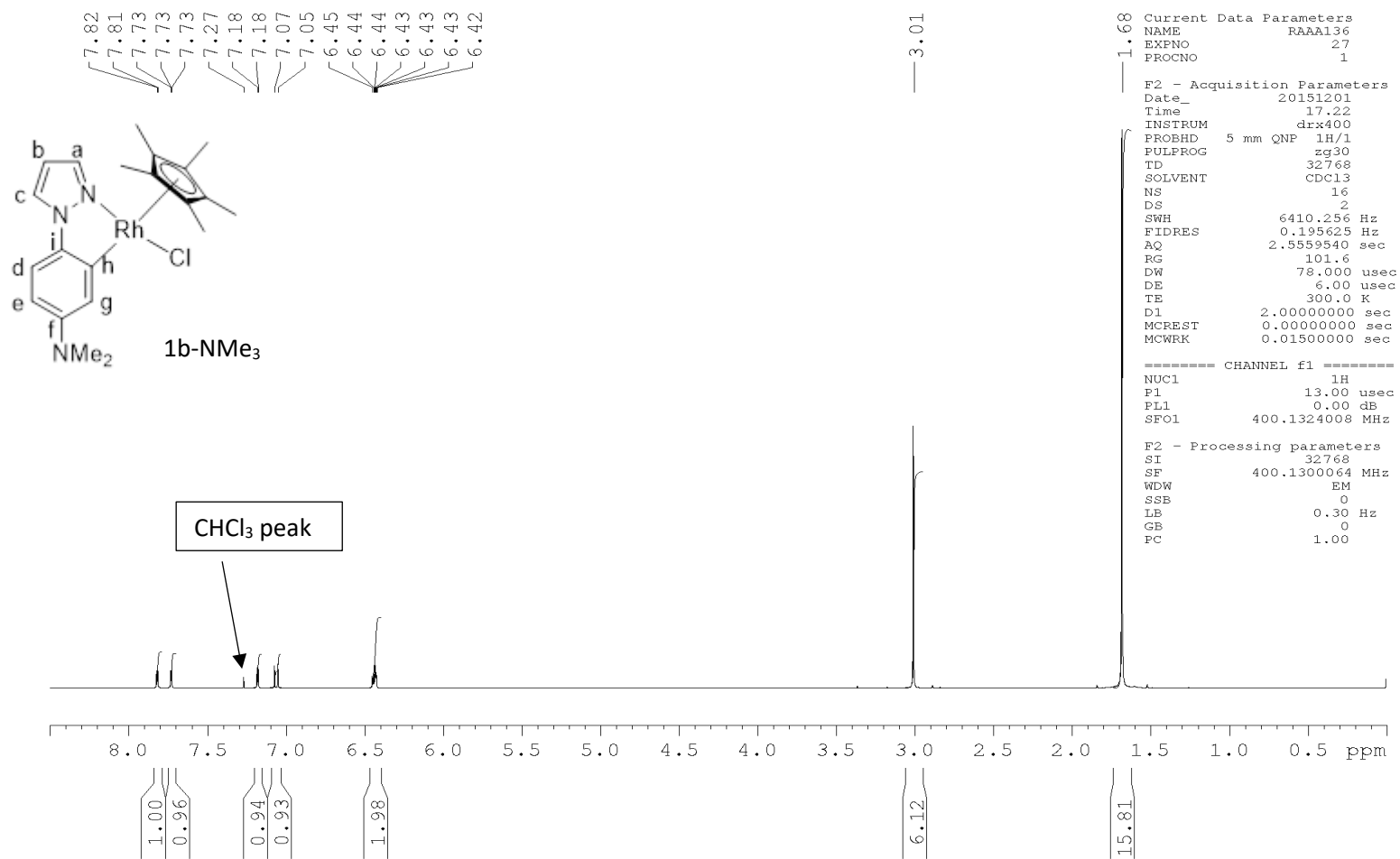
NAME          RAAA65
EXPNO         2
PROCNO        1
Date_         20161217
Time          23.41
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       deptqgpgp
TD            32768
SOLVENT       CDC13
NS            1000
DS            8
SWH           32894.738 Hz
FIDRES        1.003868 Hz
AQ            0.4981236 sec
RG            2050
DW            15.200 usec
DE            6.50 usec
TE            298.0 K
CNST2         145.0000000
CNST12        1.5000000
D1            4.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
D16           0.00020000 sec
TD0           1

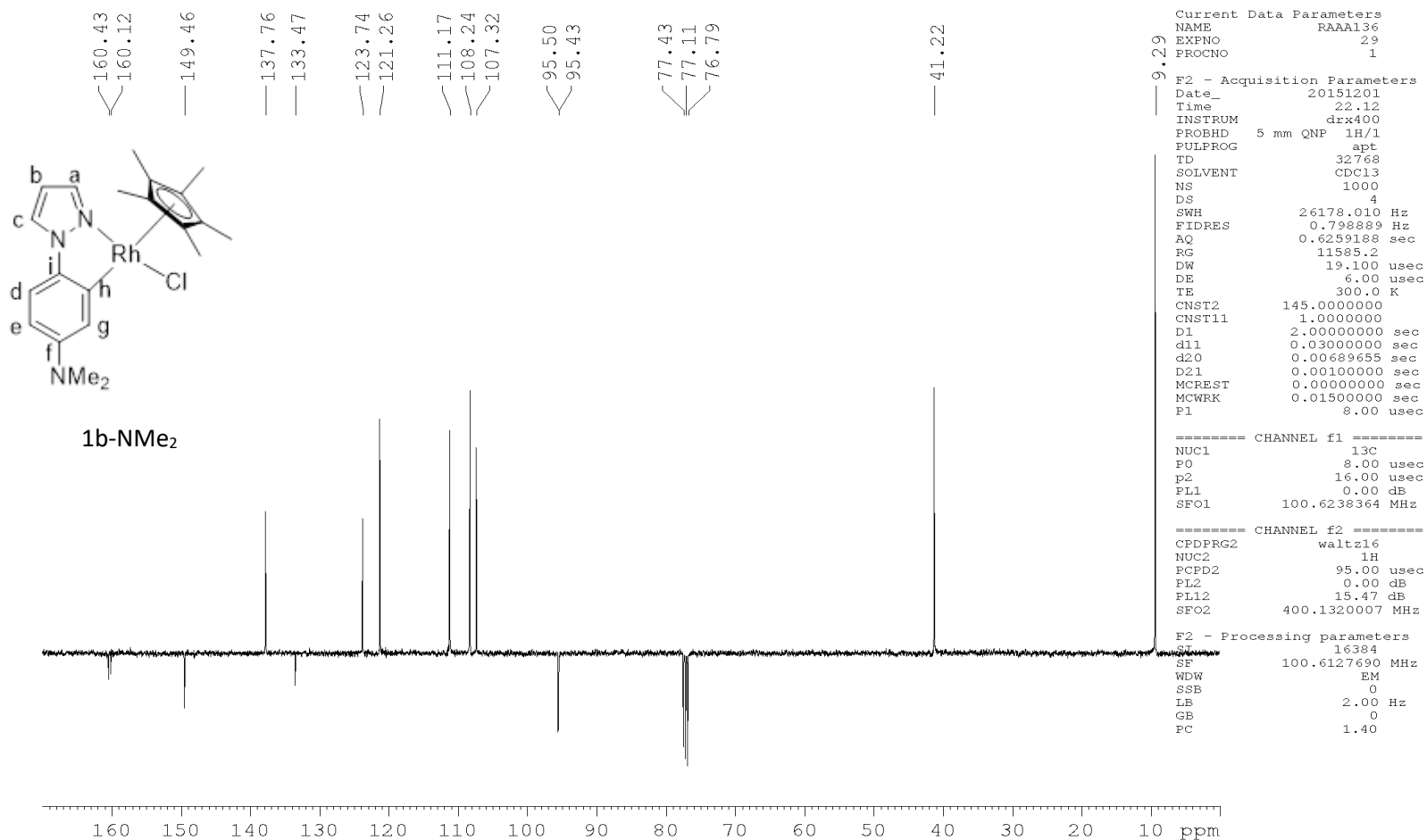
===== CHANNEL f1 =====
NUC1           13C
P1             8.50 usec
P12            2000.00 usec
PL0            120.00 dB
PL1            1.00 dB
PL0W           0.00000000 W
PL1W           58.06213379 W
SFO1           125.7716224 MHz
SP2            10.57 dB
SPNAM2         Crp60comp.4
SFOAL2         0.500
SPOFFS2        0.00 Hz

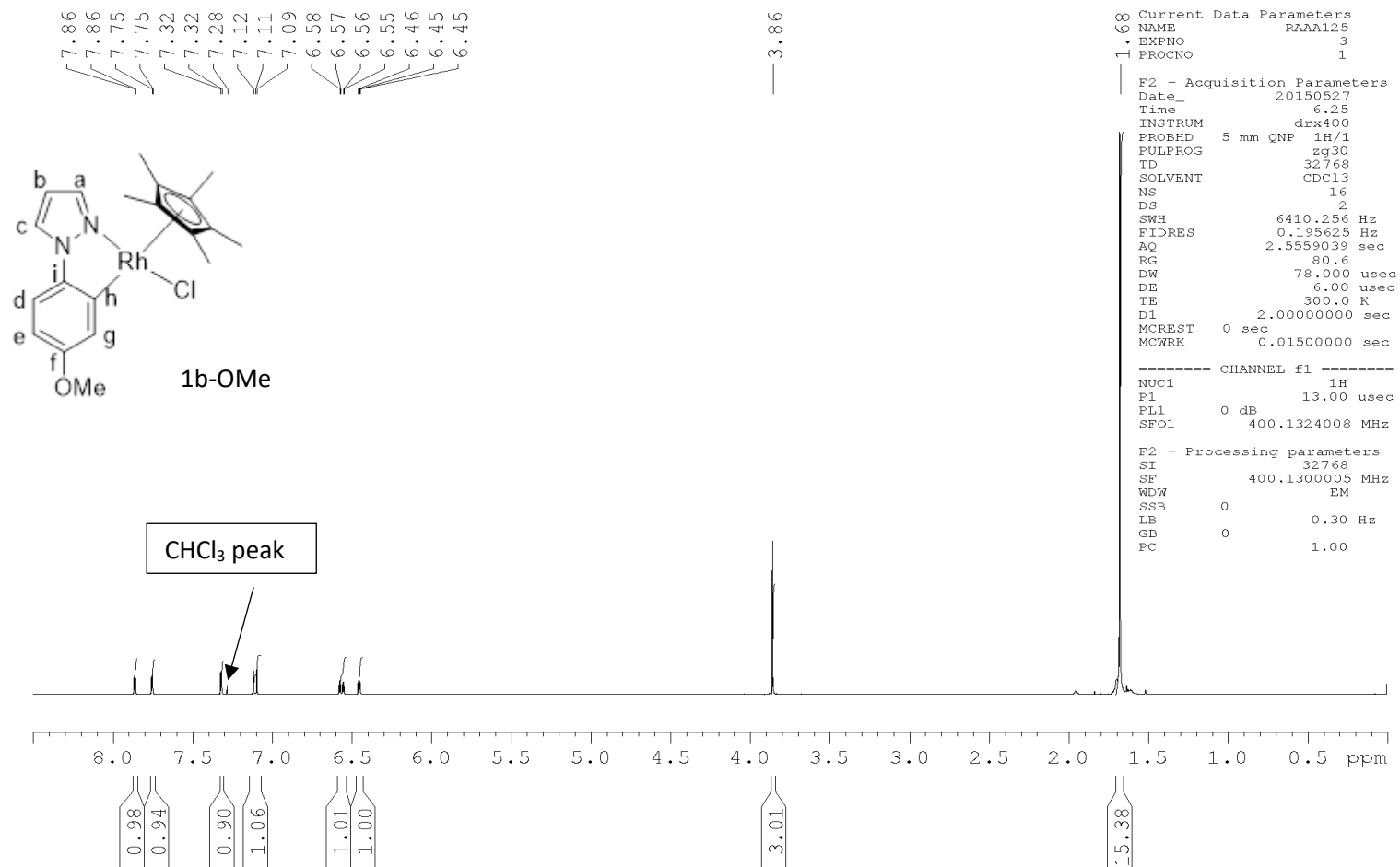
===== CHANNEL f2 =====
CPDPRG2        waltz16
NUC2            1H
P0             15.00 usec
P1             10.00 usec
P4             20.00 usec
PCPD2          80.00 usec
PL2            0.00 dB
PL12           17.00 dB
PL2W           22.85816574 W
PL12W          0.45608038 W
SFO2           500.1330008 MHz

===== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPNAM3         SINE.100
GPZ1           31.00 %
GPZ2           31.00 %
GPZ3           31.00 %
P16            1000.00 usec
SI             32768
SF             125.7577890 MHz
WDW            EM
SSB            0
LB             2.00 Hz
GB             0
PC             1.40

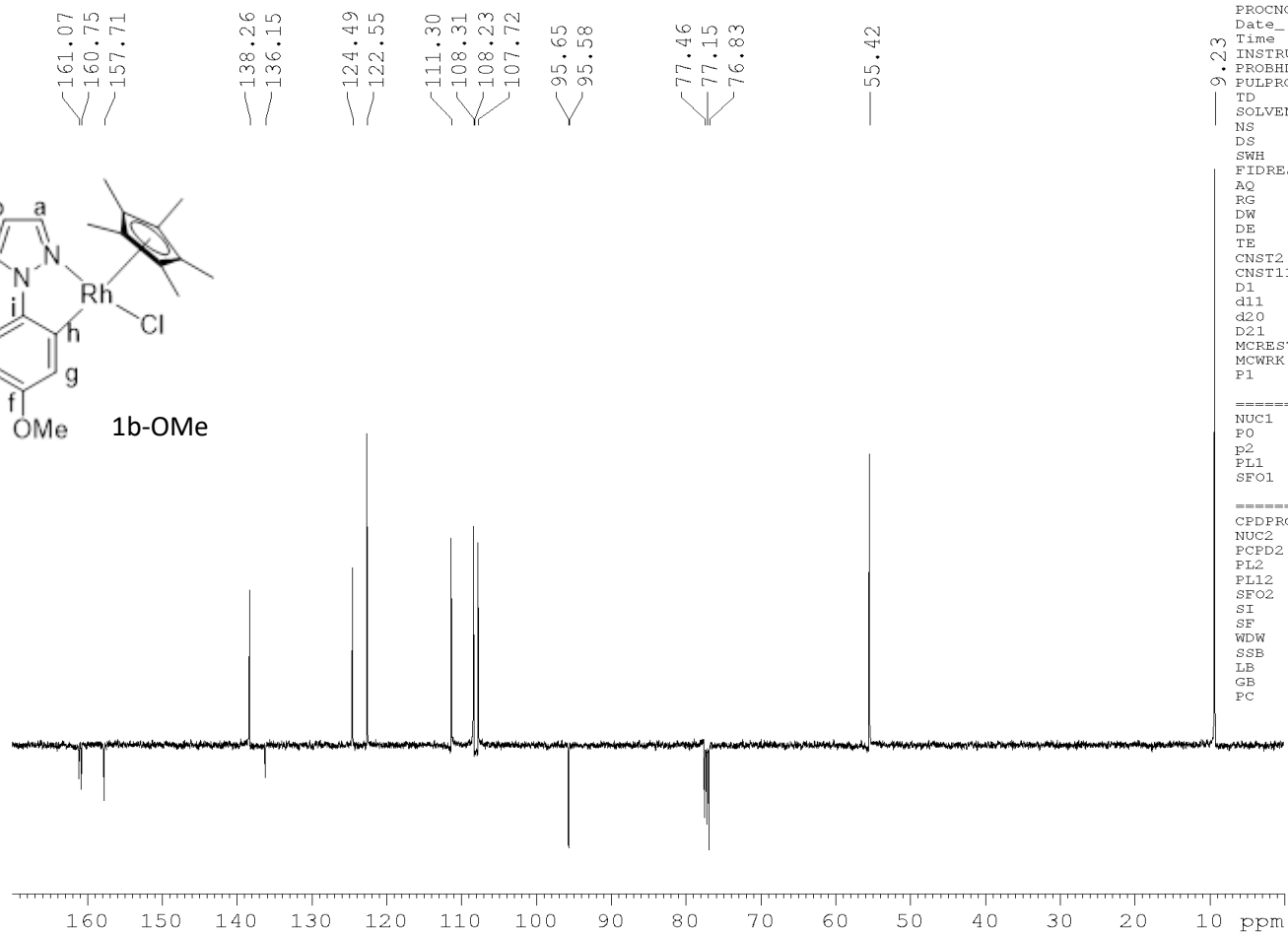
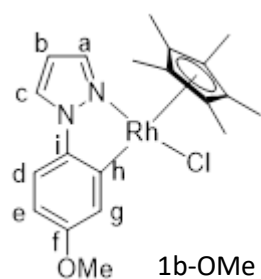
```











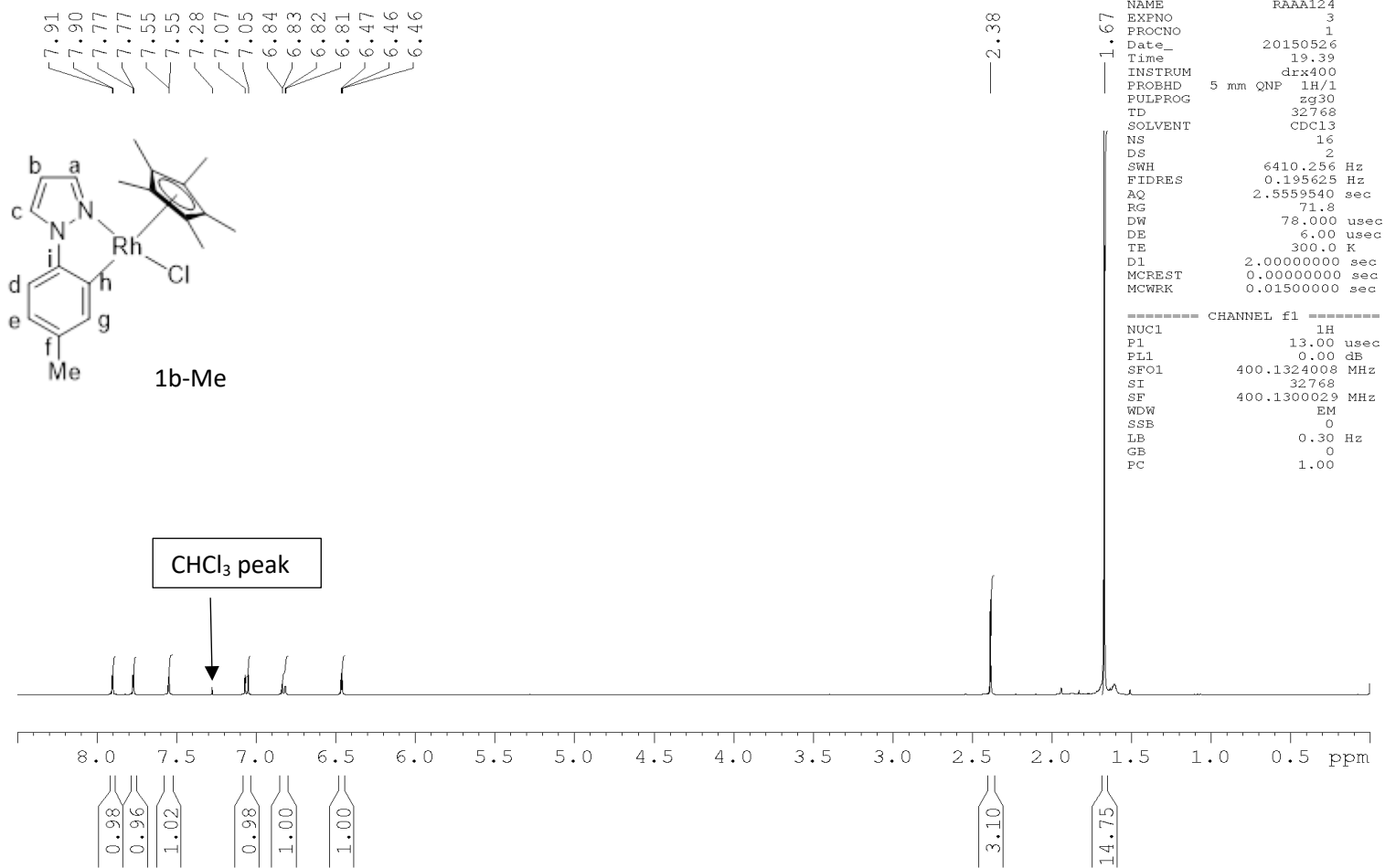
```

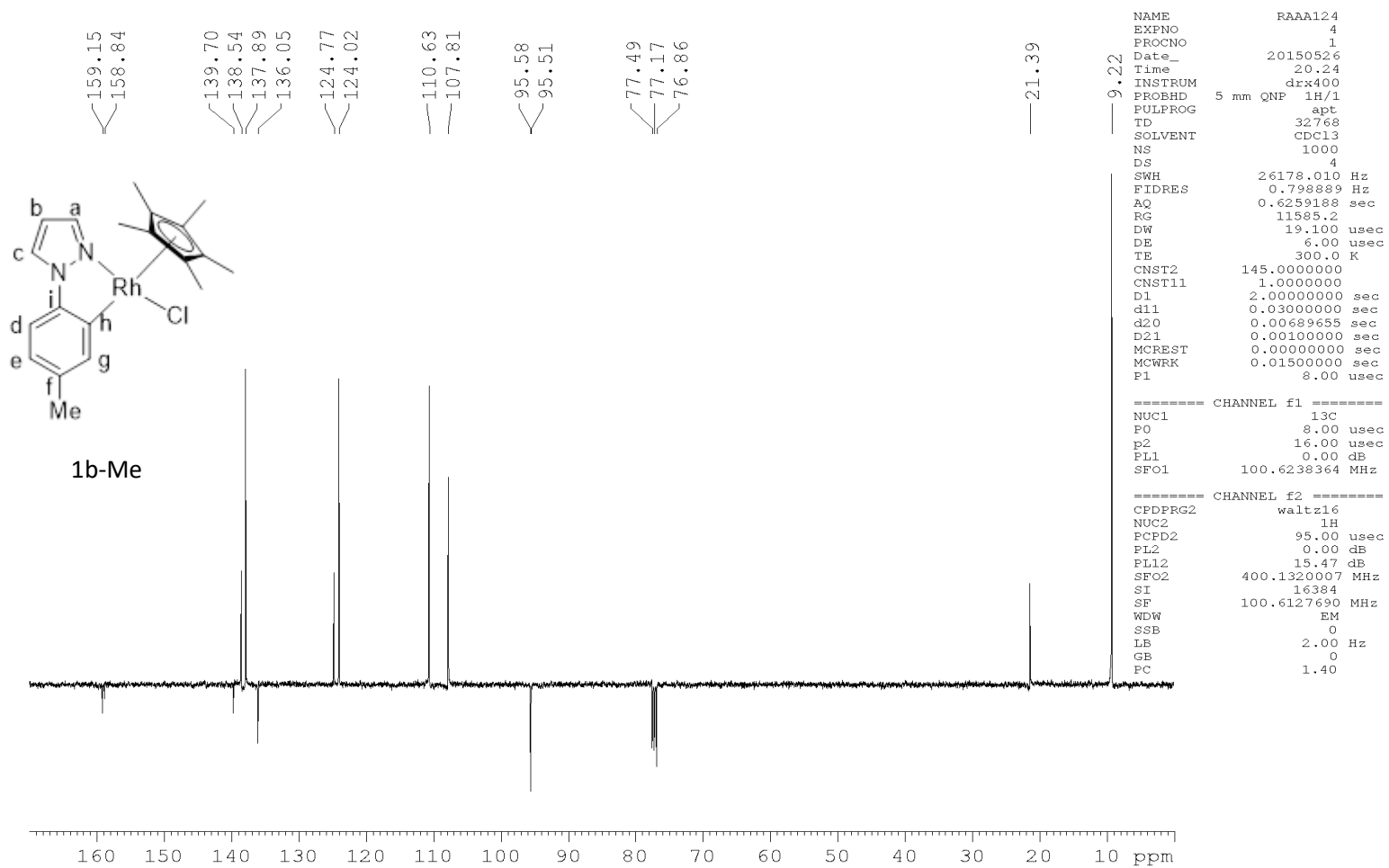
NAME          RAAA125
EXPNO         4
PROCNO        1
Date_         20150527
Time          7.11
INSTRUM       drx400
PROBHD        5 mm QNP 1H/1
PULPROG       apt
TD            32768
SOLVENT       CDCl3
NS            1000
DS            4
SWH           26178.010 Hz
FIDRES        0.798889 Hz
AQ            0.6259188 sec
RG            11585.2
DW            19.100 usec
DE            6.00 usec
TE            300.0 K
CNST2         145.0000000
CNST11        1.0000000
D1            2.000000000 sec
d11           0.030000000 sec
d20           0.00689655 sec
d21           0.001000000 sec
MCREST        0.00000000 sec
MCWRK         0.015000000 sec
F1            8.00 usec

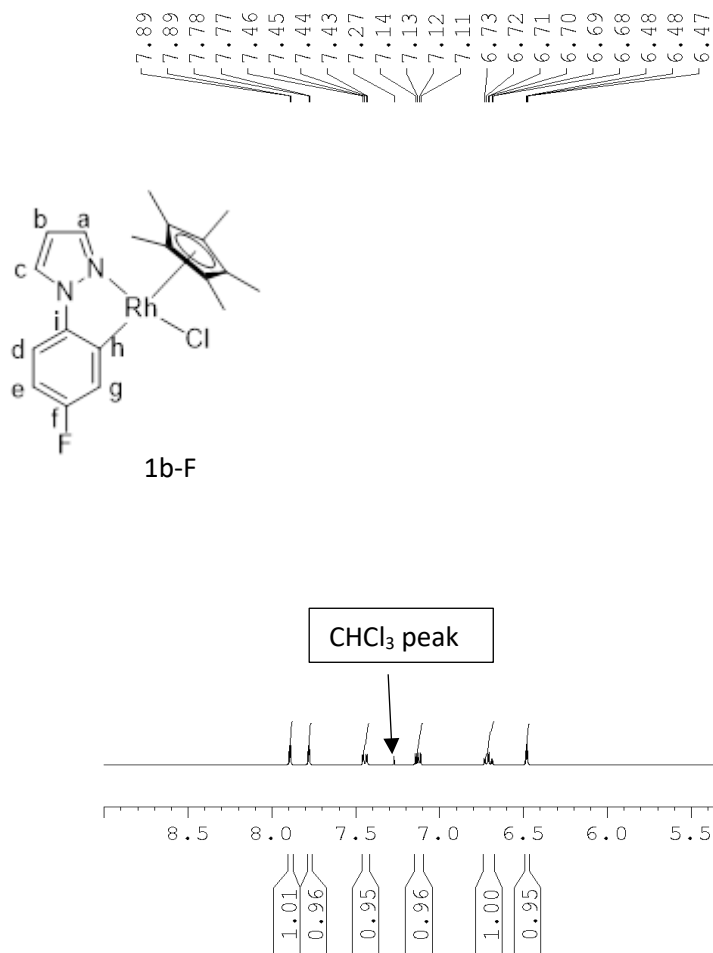
===== CHANNEL f1 =====
NUC1          13C
P0            8.00 usec
p2            16.00 usec
PL1           0.00 dB
SFO1          100.6238364 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         95.00 usec
PL2           0.00 dB
PL12          15.47 dB
SFO2          400.1320007 MHz
SI            16384
SF            100.6127690 MHz
WDW           EM
SSB           0
LB            2.00 Hz
GB            0
PC            1.40

```







```

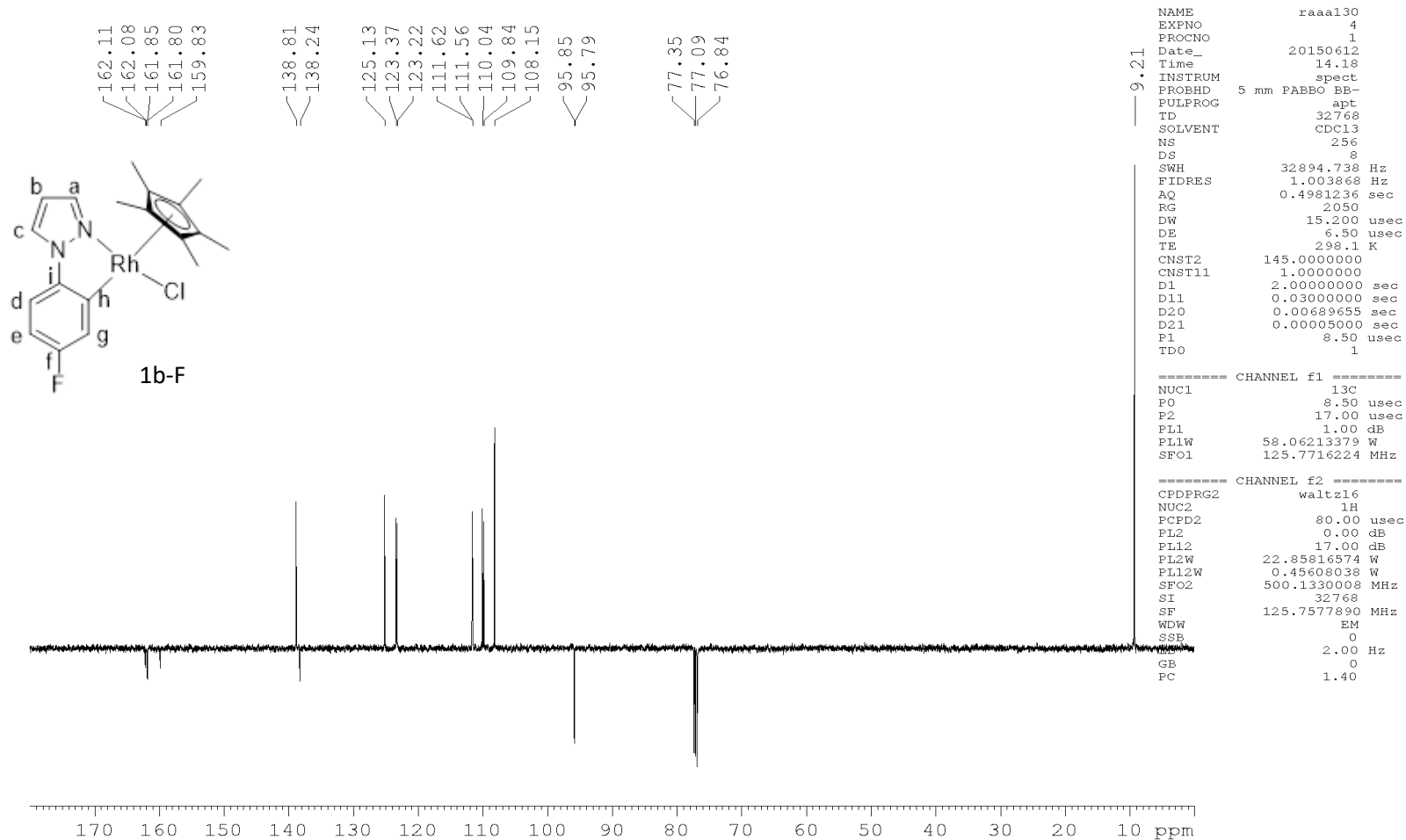
1.68 Current Data Parameters
NAME      RAAAL30
EXPNO     12
PROCNO    1

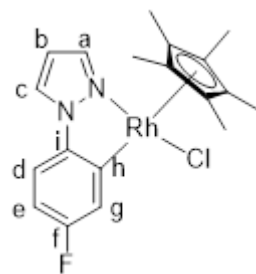
F2 - Acquisition Parameters
Date_     20150612
Time      8.46
INSTRUM   drx400
PROBHD    5 mm QNP 1H/1
PULPROG   zg30
TD        32768
SOLVENT   CDCl3
NS         16
DS         2
SWH        6410.256 Hz
FIDRES     0.195625 Hz
AQ         2.5559540 sec
RG         128
DW         78.000 usec
DE         6.00 usec
TE         300.0 K
D1         2.00000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

===== CHANNEL f1 =====
NUC1       1H
P1         13.00 usec
PL1        0.00 dB
SFO1       400.1324008 MHz

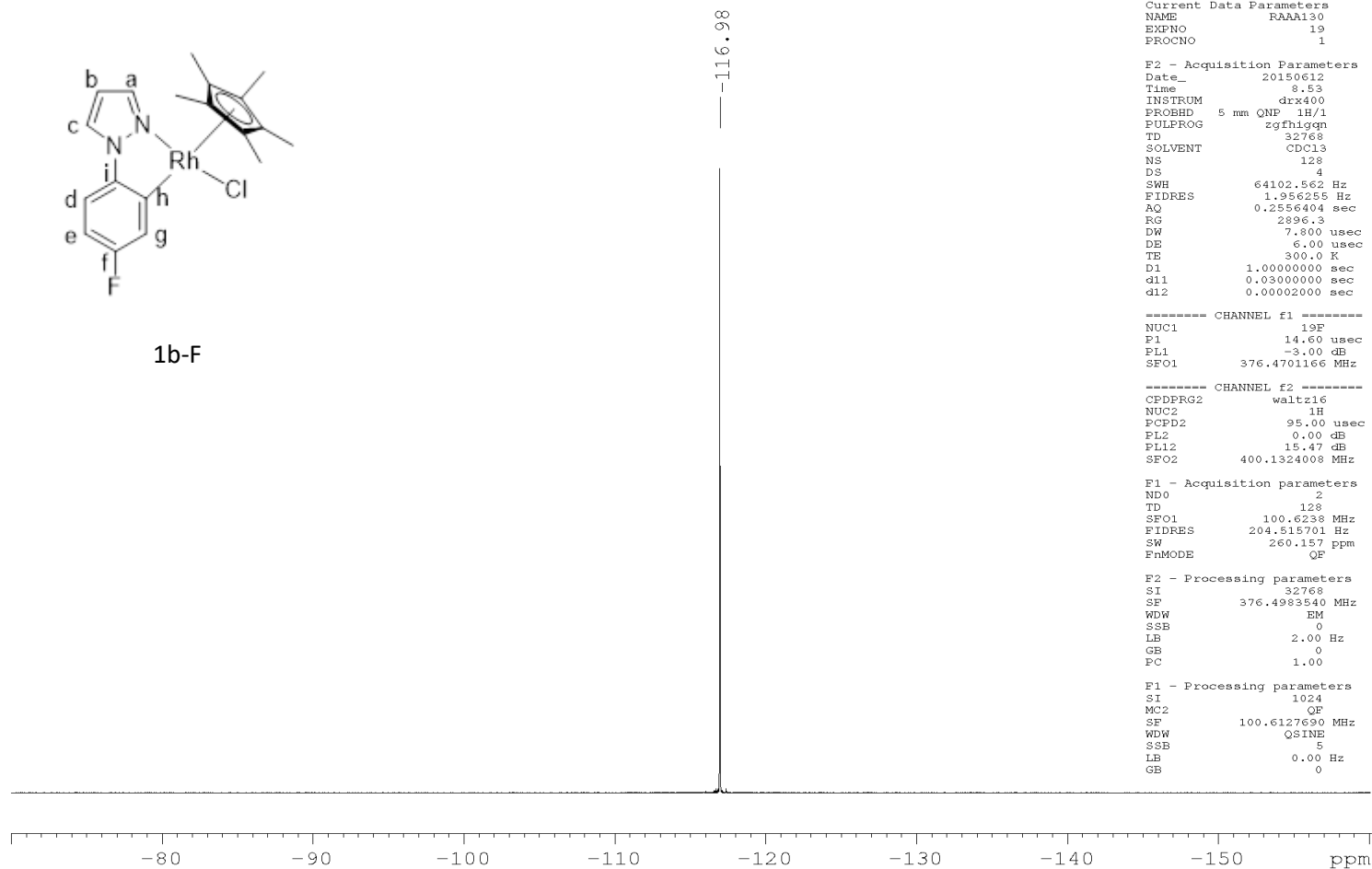
F2 - Processing parameters
SI         32768
SF         400.1300056 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```





1b-F



Current Data Parameters  
NAME RAAA130  
EXPNO 19  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20150612  
Time 8.53  
INSTRUM drx400  
PROBHD 5 mm QNP 1H/1  
PULPROG zgfhigqn  
TD 32768  
SOLVENT CDCl3  
NS 128  
DS 4  
SWH 64102.562 Hz  
FIDRES 1.956255 Hz  
AQ 0.2556404 sec  
RG 2896.3  
DW 7.800 usec  
DE 6.00 usec  
TE 300.0 K  
D1 1.00000000 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

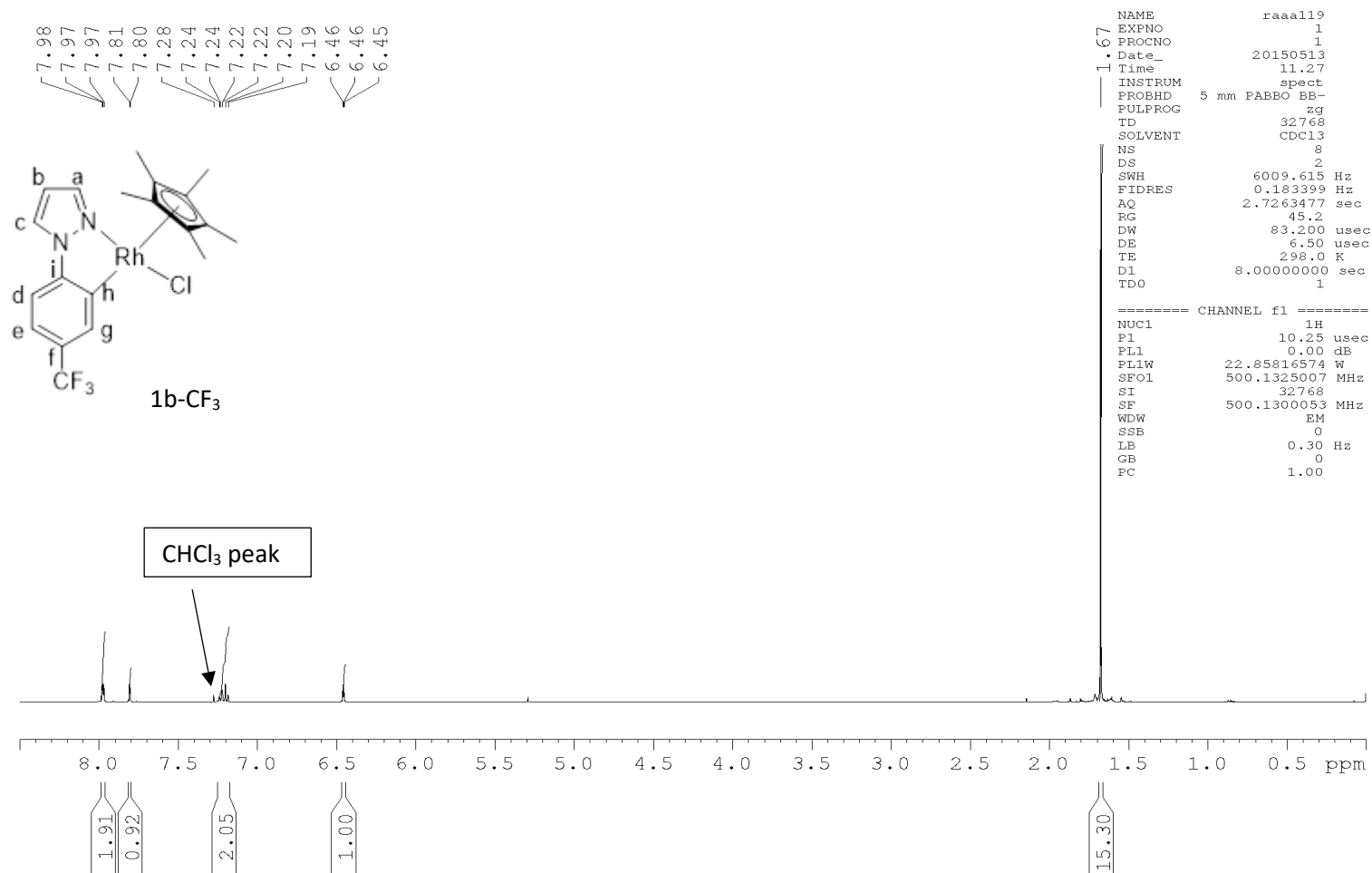
===== CHANNEL f1 =====  
NUC1 19F  
P1 14.60 usec  
PL1 -3.00 dB  
SFO1 376.4701166 MHz

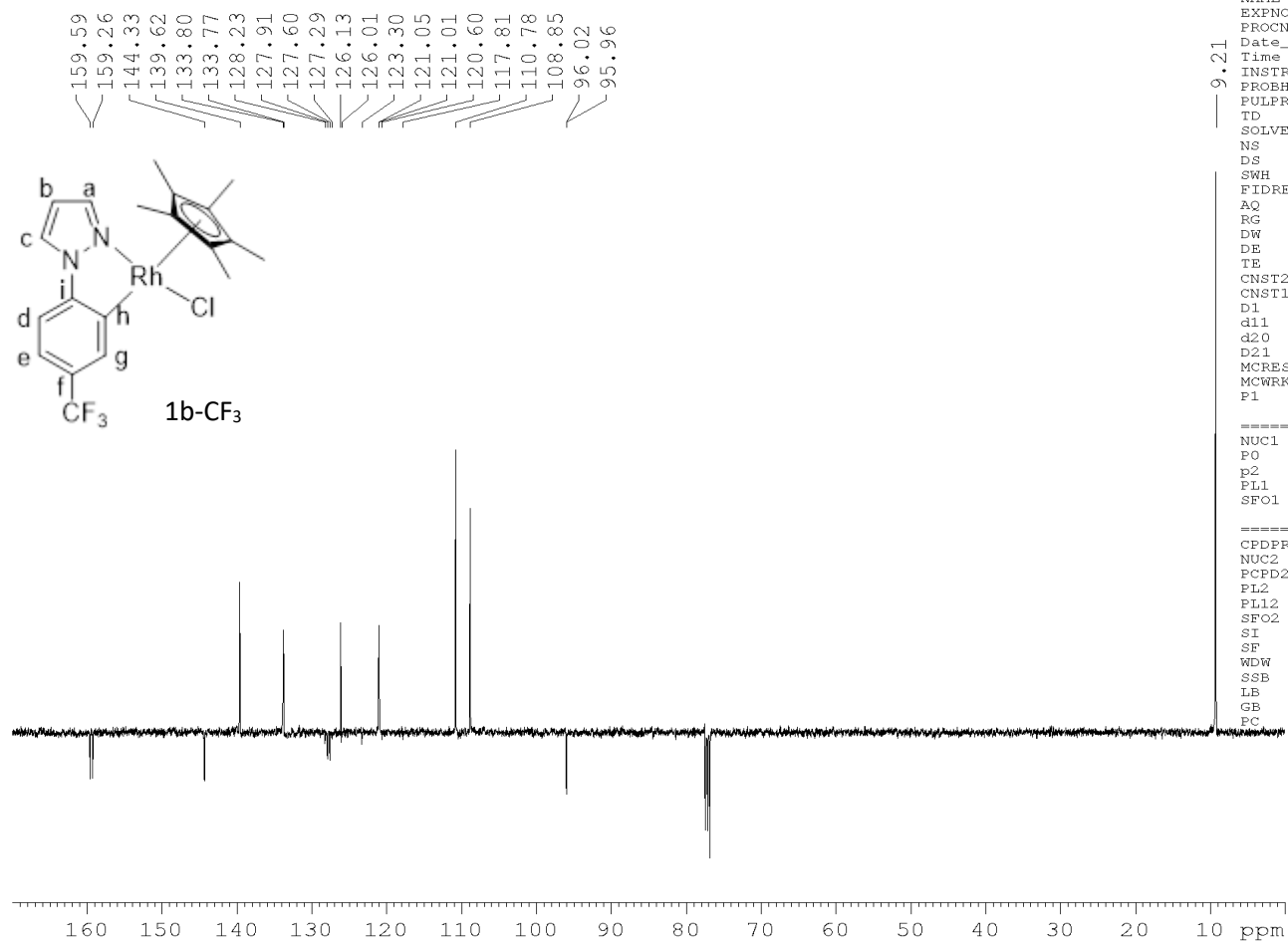
===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 95.00 usec  
PL2 0.00 dB  
PL12 15.47 dB  
SFO2 400.1324008 MHz

F1 - Acquisition parameters  
ND0 2  
TD 128  
SFO1 100.6238 MHz  
FIDRES 204.515701 Hz  
SW 260.157 ppm  
FnMODE QF

F2 - Processing parameters  
SI 32768  
SF 376.4983540 MHz  
WDW EM  
SSB 0  
LB 2.00 Hz  
GB 0  
PC 1.00

F1 - Processing parameters  
SI 1024  
MC2 QF  
SF 100.6127690 MHz  
WDW QSINE  
SSB 5  
LB 0.00 Hz  
GB 0





```

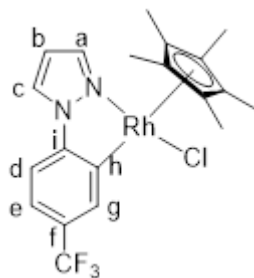
NAME          RAAA119
EXPNO         2
PROCNO        1
Date_         20150513
Time          1.46
INSTRUM       drx400
PROBHD        5 mm QNP 1H/1
PULPROG       apt
TD            32768
SOLVENT       CDCl3
NS            1000
DS            4
SWH           26178.010 Hz
FIDRES        0.798889 Hz
AQ            0.6259188 sec
RG            11585.2
DW            19.100 usec
DE            6.00 usec
TE            290.6 K
CNST2         145.0000000
CNST11        1.0000000
D1            2.00000000 sec
d11           0.03000000 sec
d20           0.00689655 sec
D21           0.00100000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P1            8.00 usec

===== CHANNEL f1 =====
NUC1          13C
P0            8.00 usec
p2            16.00 usec
PL1           0.00 dB
SFO1          100.6238364 MHz

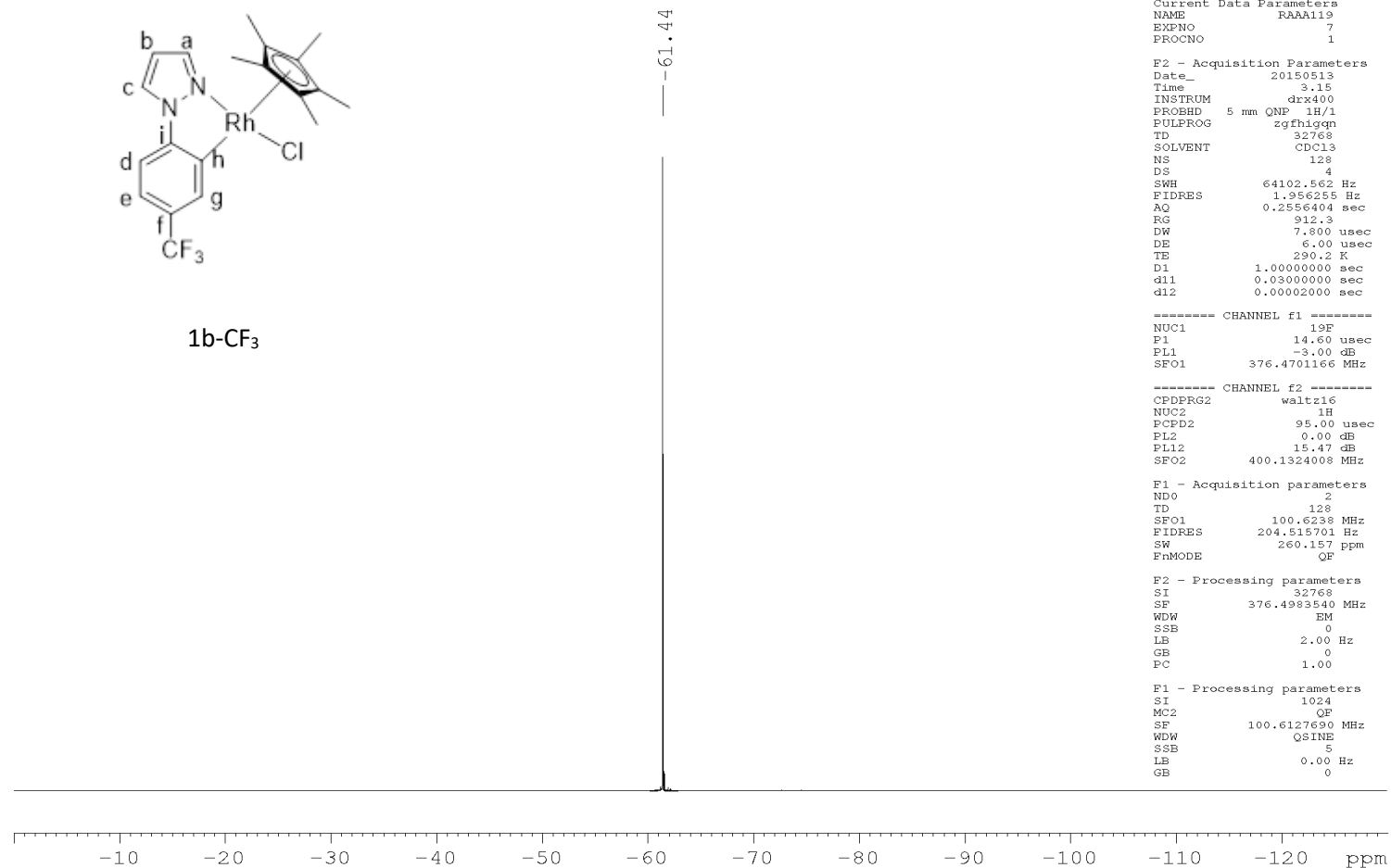
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         95.00 usec
PL2           0.00 dB
PL12          15.47 dB
SFO2          400.1320007 MHz
SI            16384
SF            100.6127690 MHz
WDW           EM
SSB           0
LB            2.00 Hz
GB            0
PC            1.40

```





1b-CF<sub>3</sub>



```

Current Data Parameters
NAME      RAAA119
EXPNO     7
PROCNO    1

F2 - Acquisition Parameters
Date_     20150513
Time      3.15
INSTRUM   drx400
PROBHD    5 mm QNP 1H/1
PULPROG   zgfhigqn
TD         32768
SOLVENT   CDCl3
NS         128
DS         4
SWH        64102.562 Hz
FIDRES     1.956255 Hz
AQ         0.2556404 sec
RG         912.3
DW         7.800 usec
DE         6.00 usec
TE         290.2 K
D1         1.00000000 sec
d11        0.03000000 sec
d12        0.00002000 sec

===== CHANNEL f1 =====
NUC1       19F
P1         14.60 usec
PL1        -3.00 dB
SFO1       376.4701166 MHz

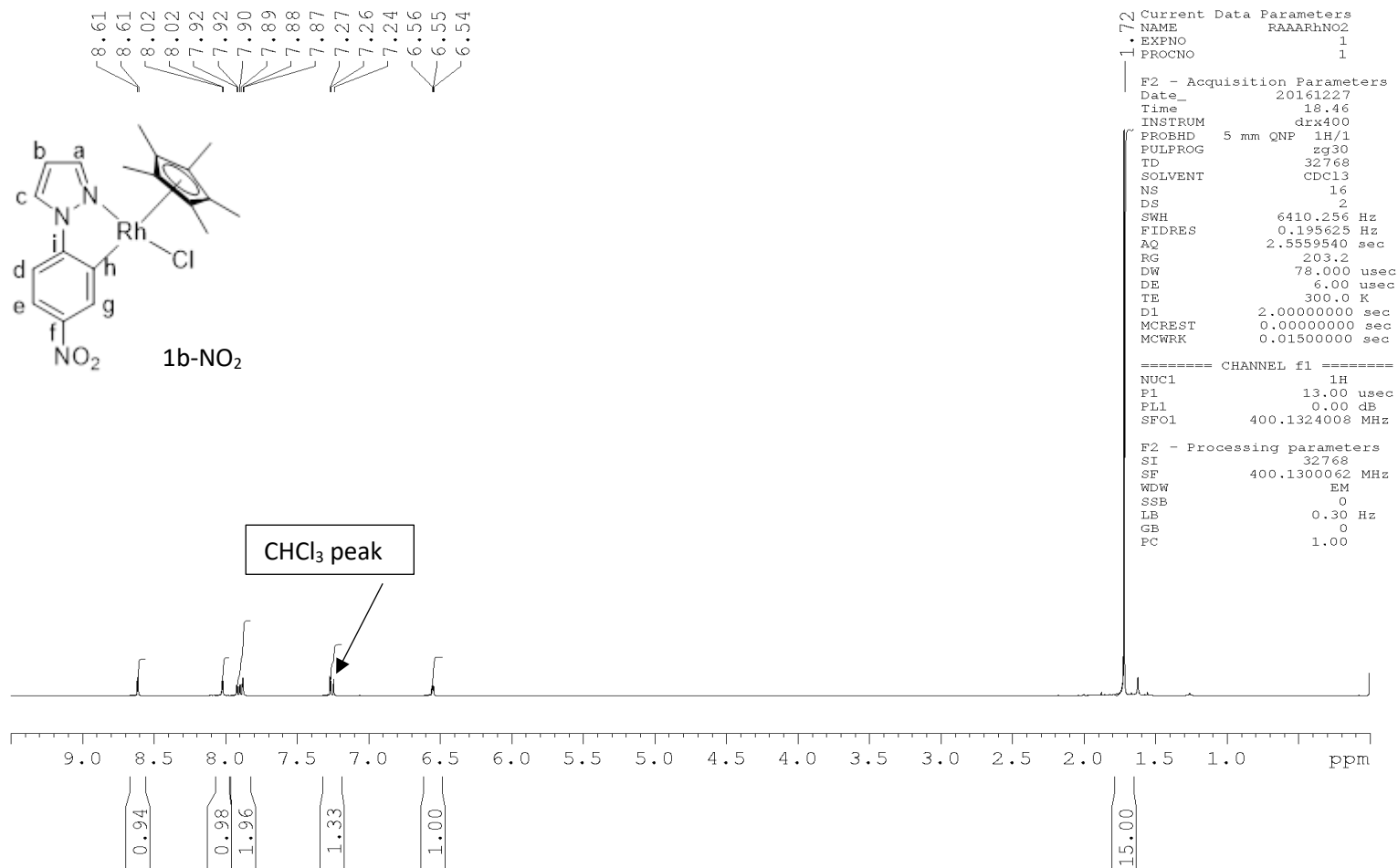
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      95.00 usec
PL2        0.00 dB
PL12       15.47 dB
SFO2       400.1324008 MHz

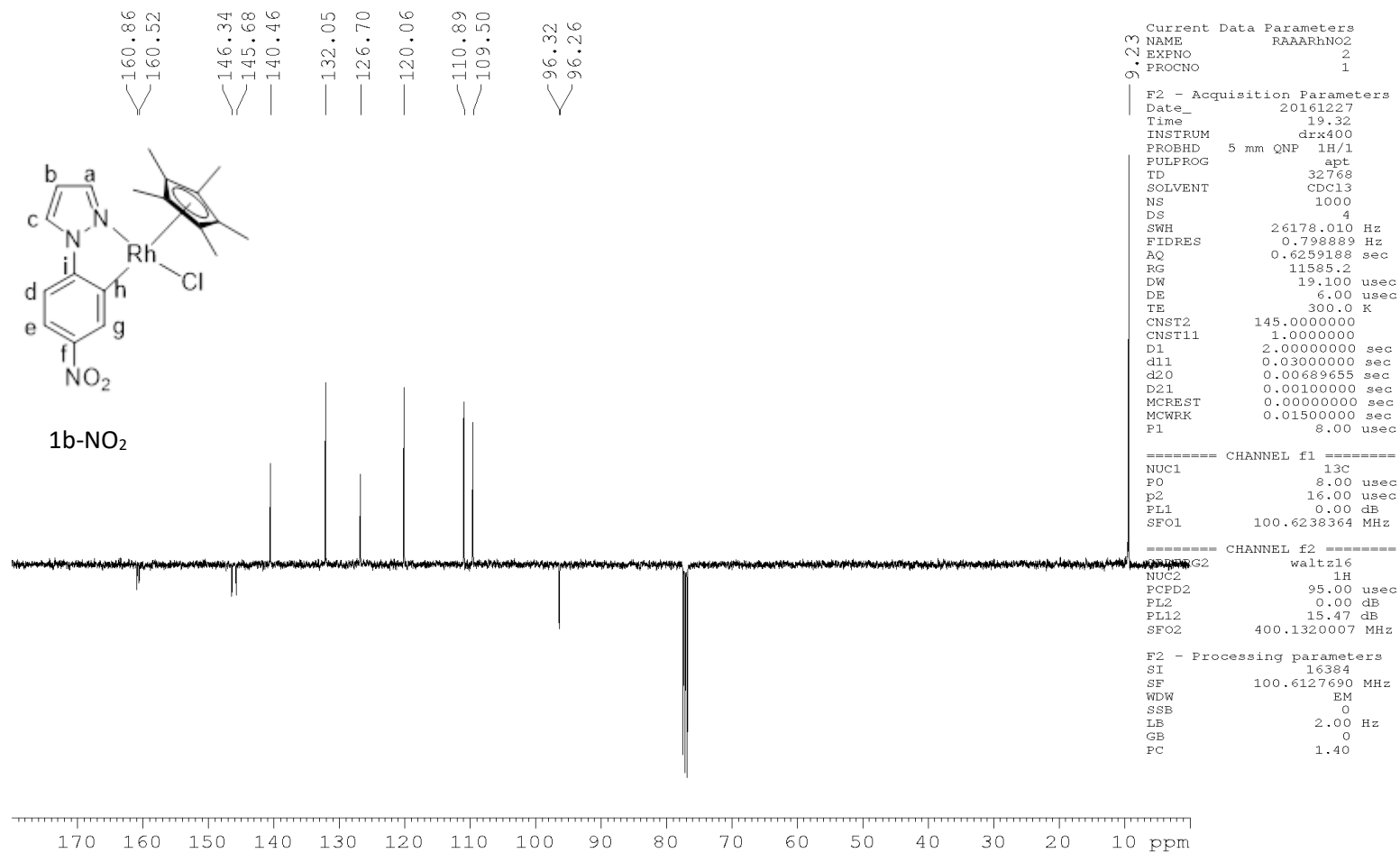
F1 - Acquisition parameters
ND0        2
TD         128
SFO1       100.6238 MHz
FIDRES     204.515701 Hz
SW         260.157 ppm
FnMODE     QF

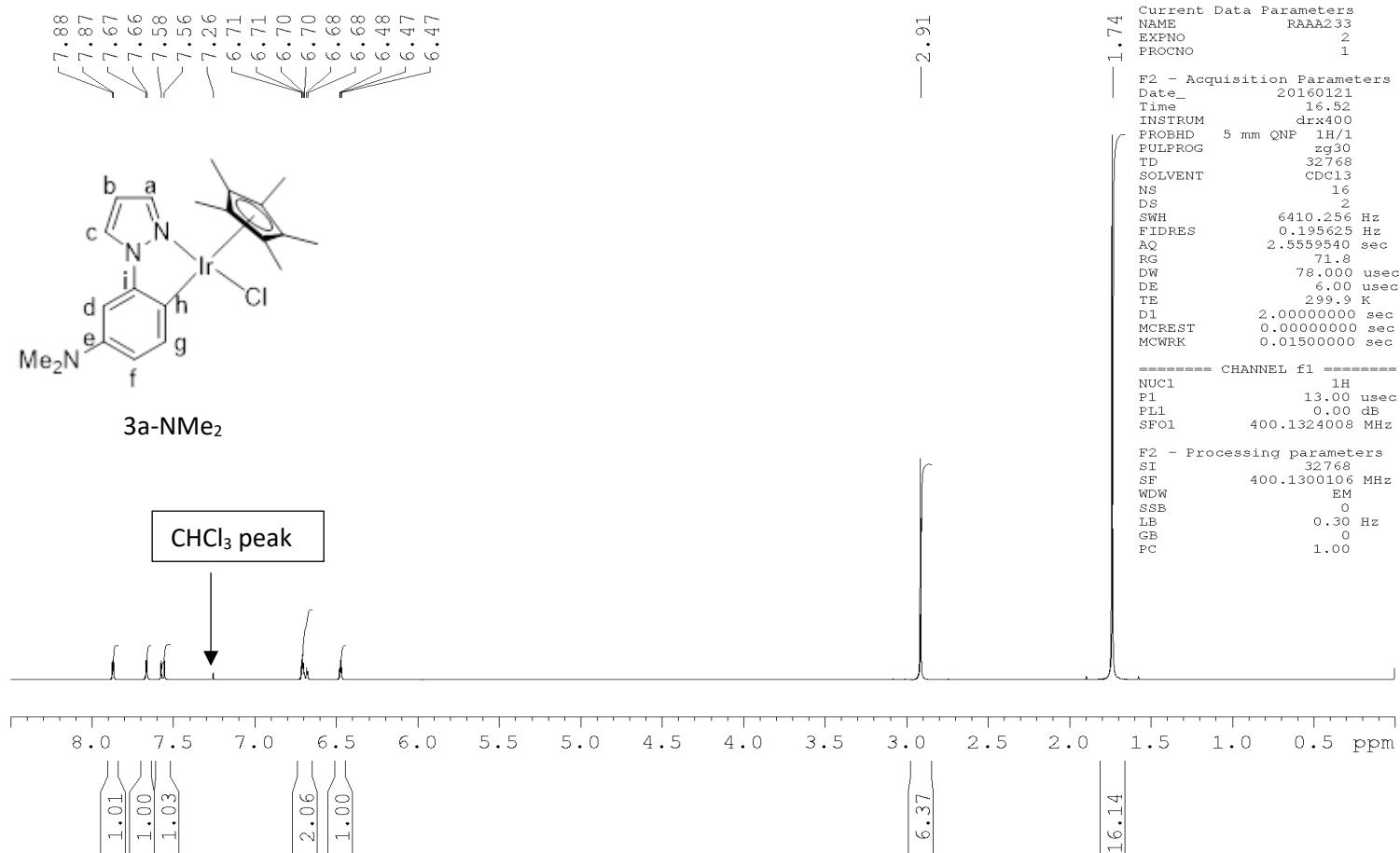
F2 - Processing parameters
SI         32768
SF         376.4983540 MHz
WDW        EM
SSB        0
LB         2.00 Hz
GB         0
PC         1.00

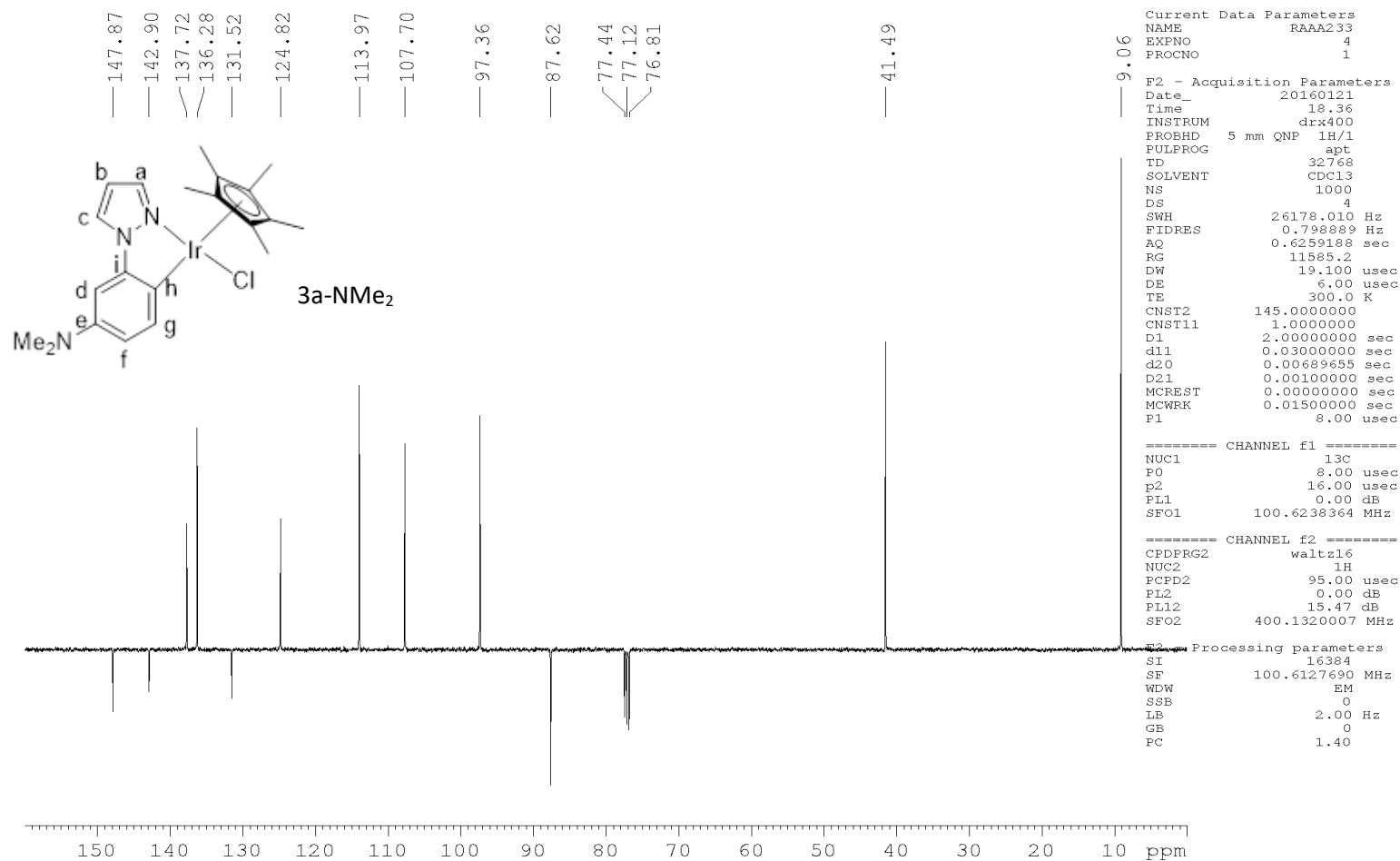
F1 - Processing parameters
SI         1024
MC2        QF
SF         100.6127690 MHz
WDW        QSINE
SSB        5
LB         0.00 Hz
GB         0

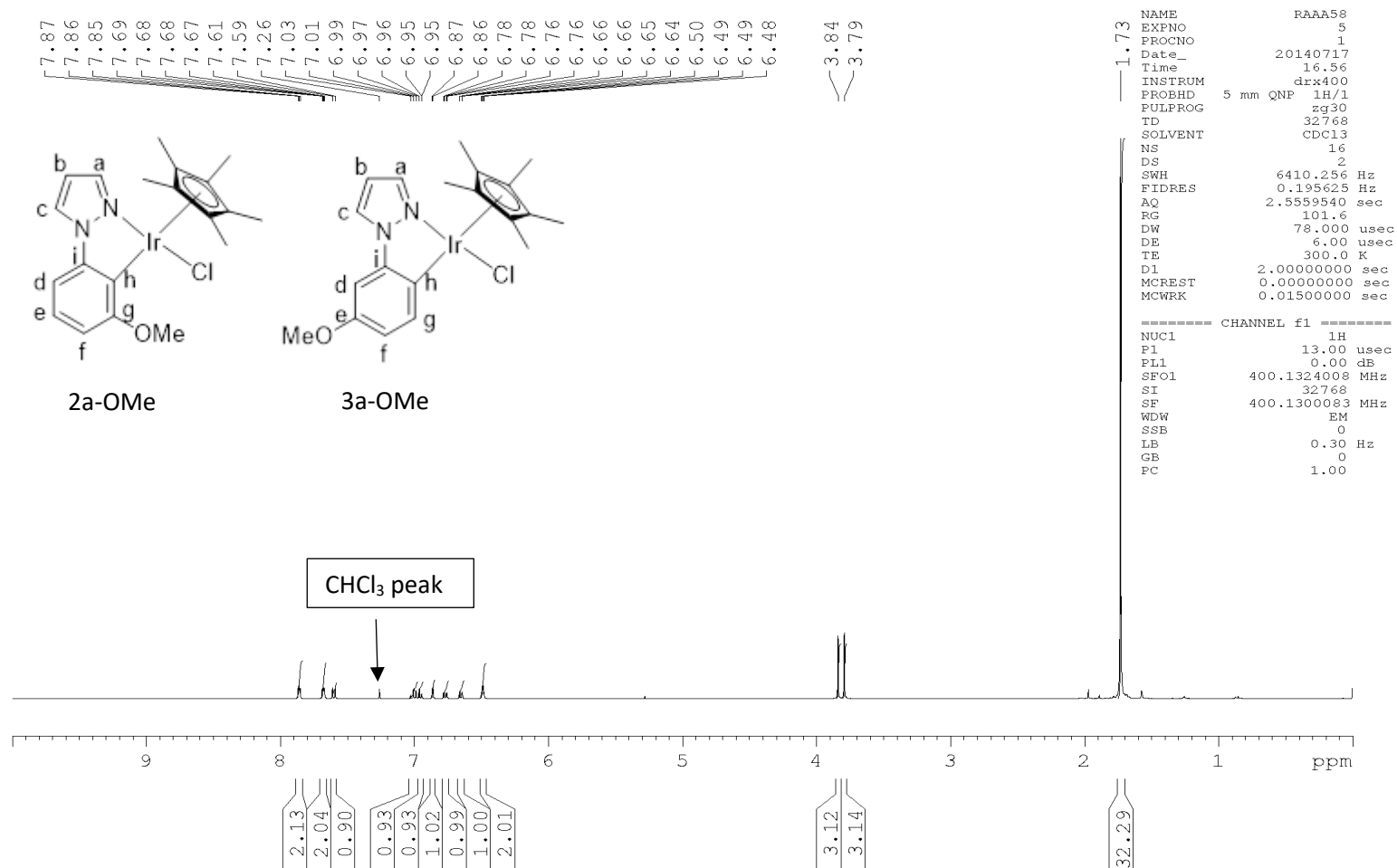
```

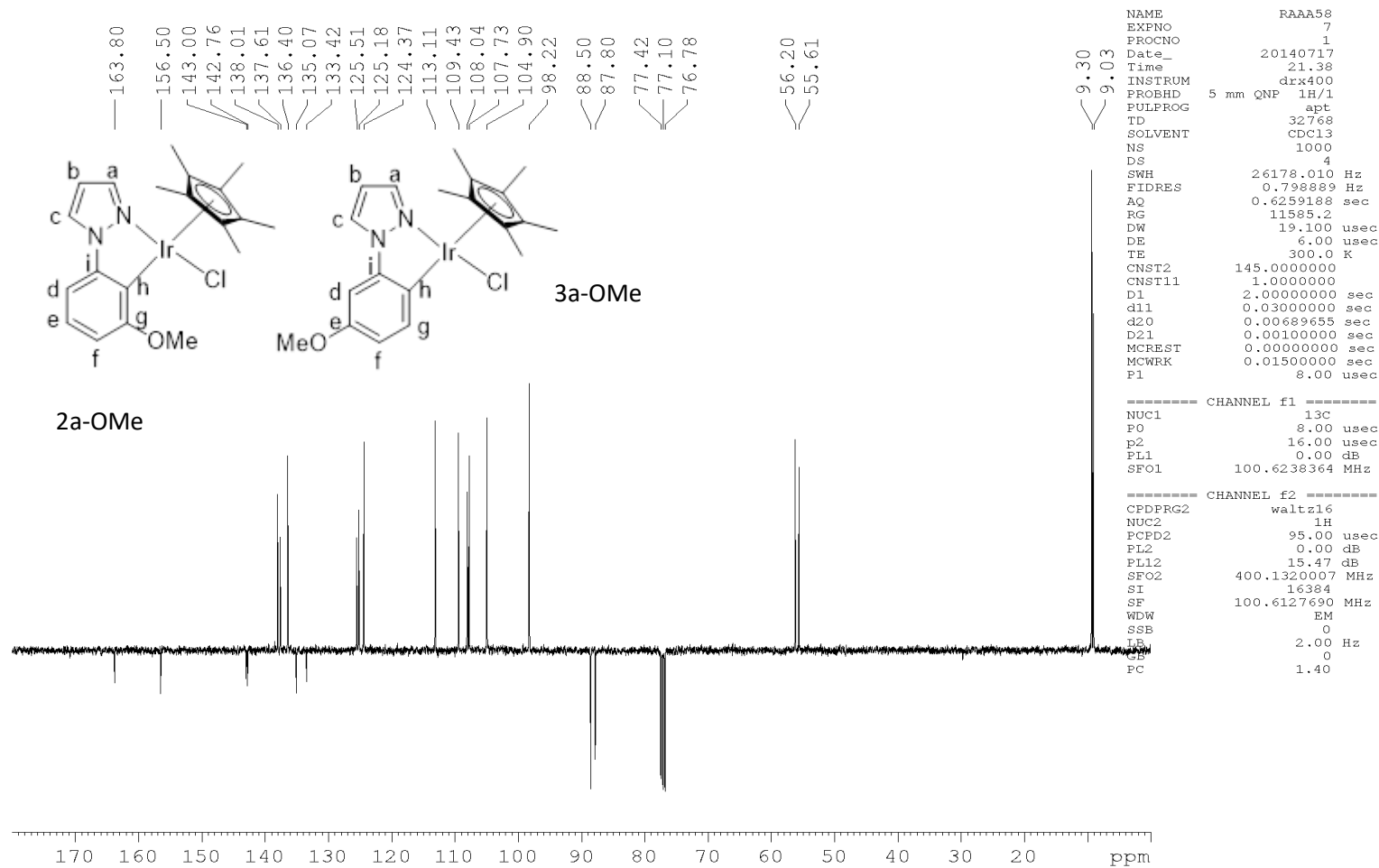


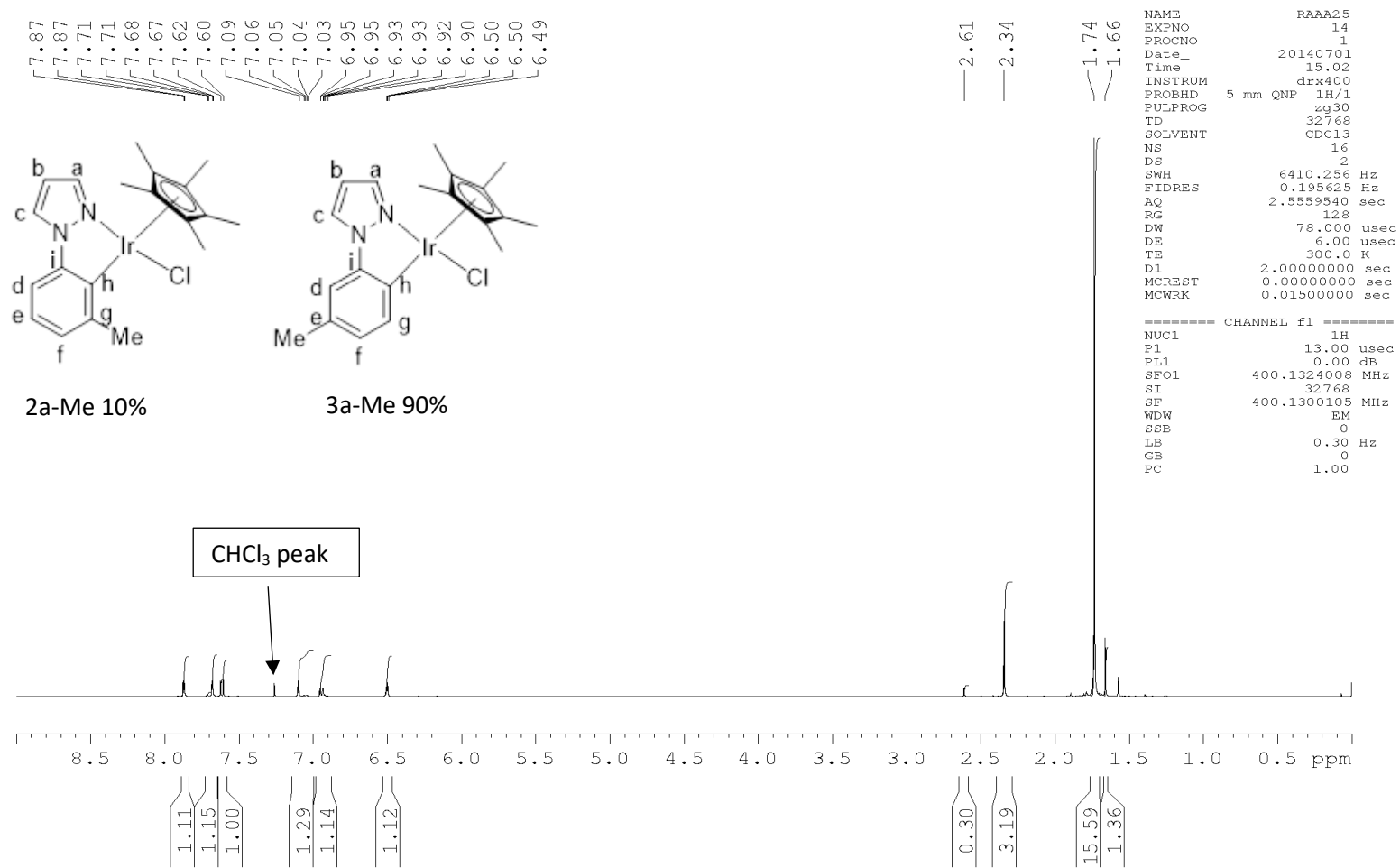




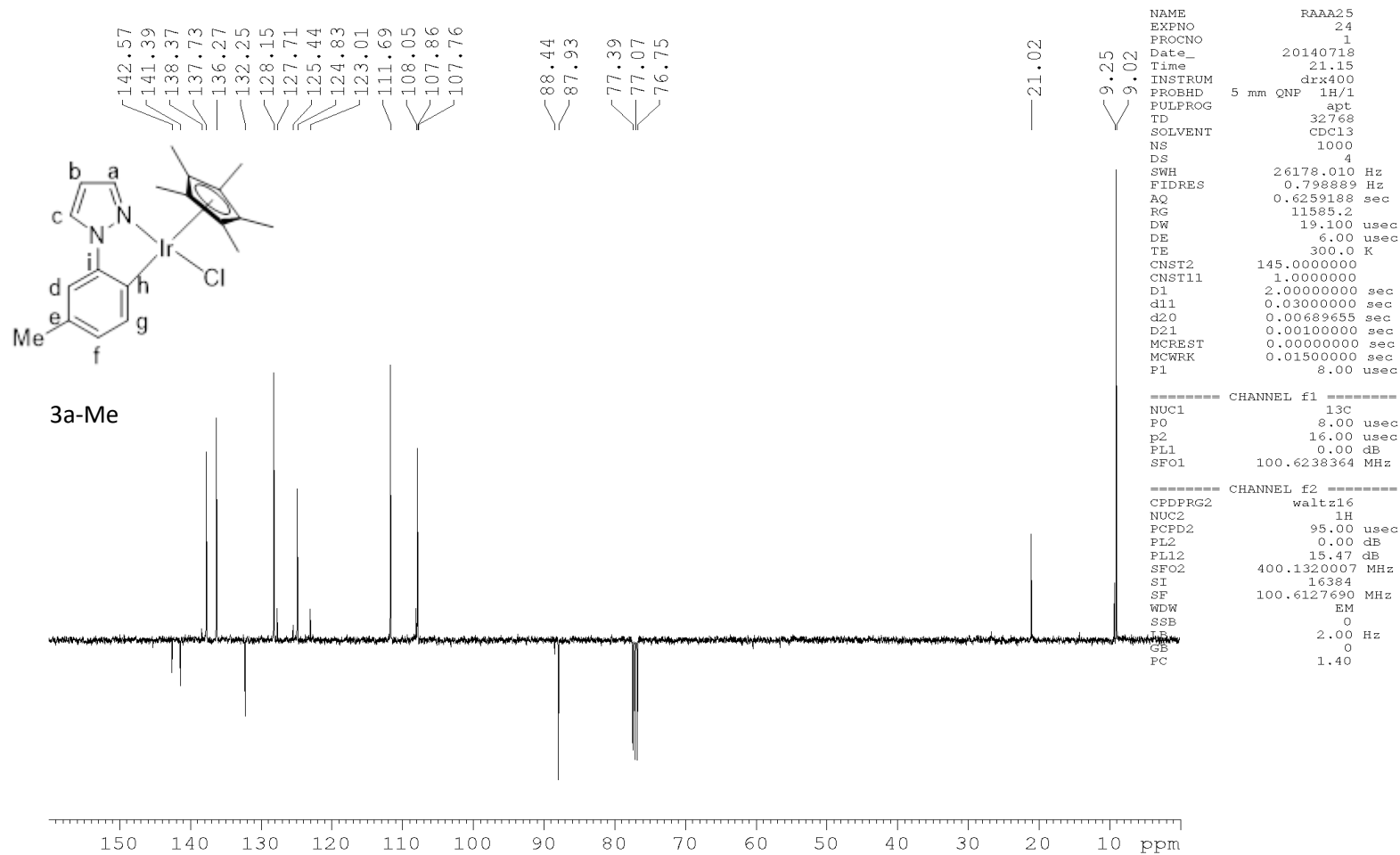


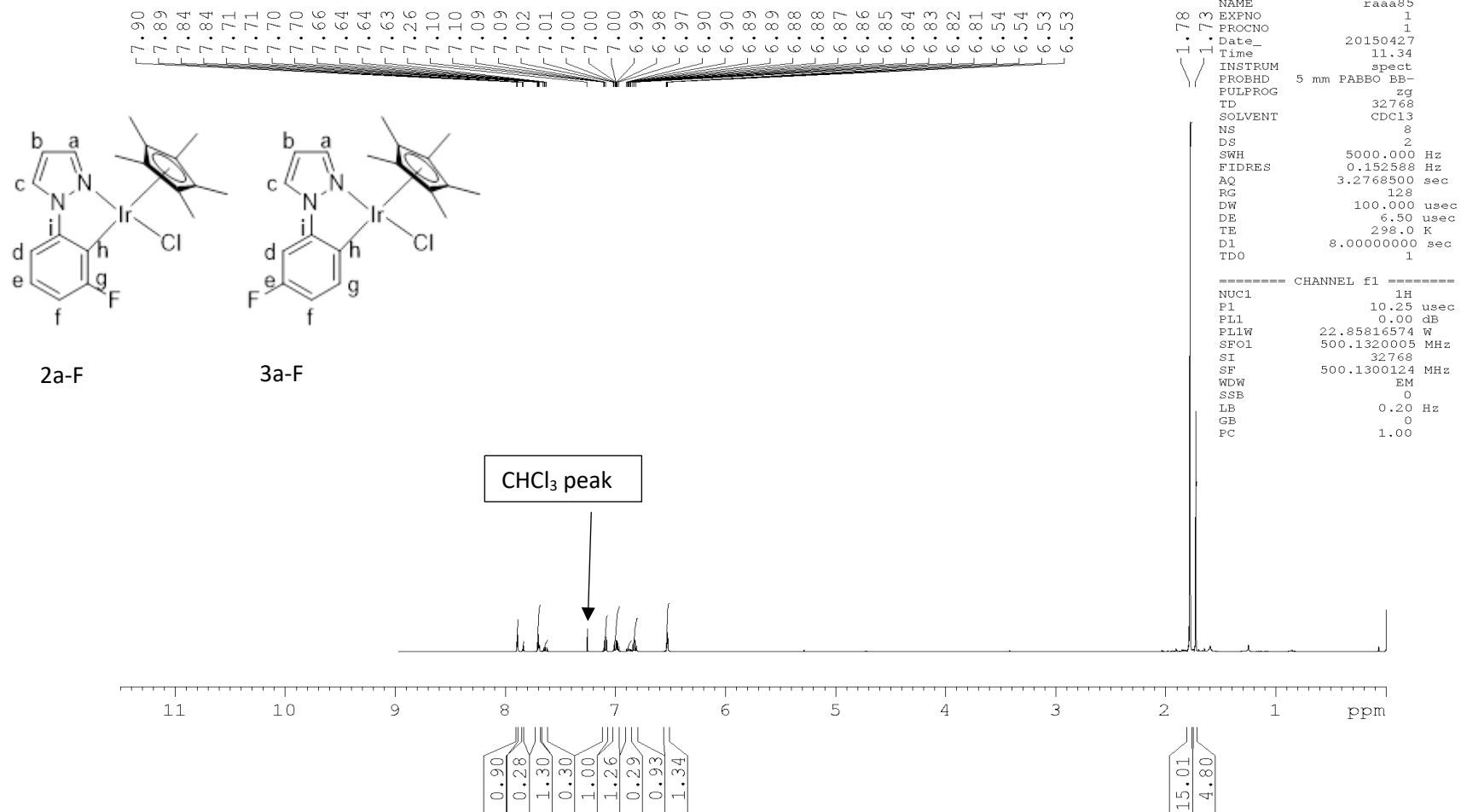


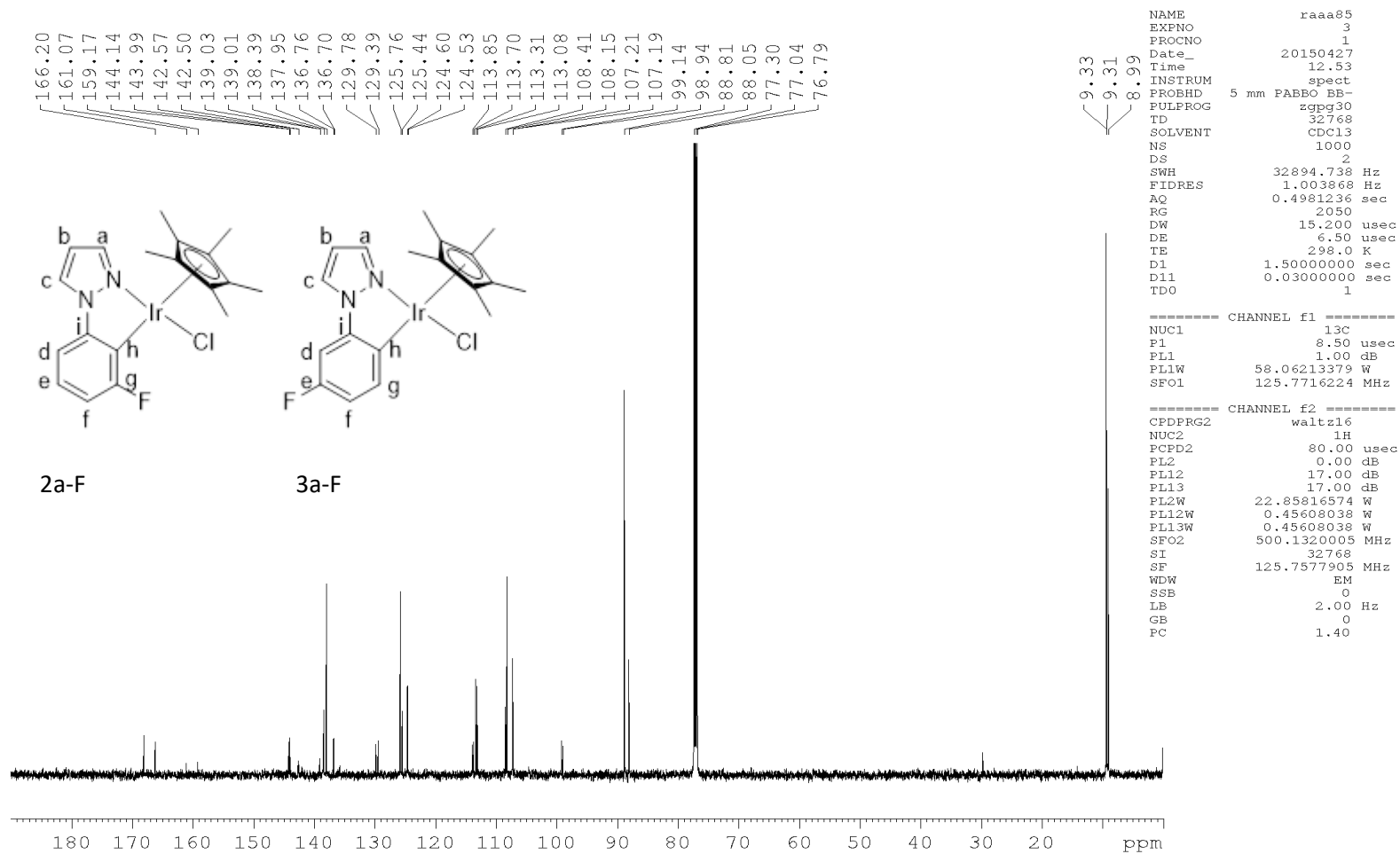


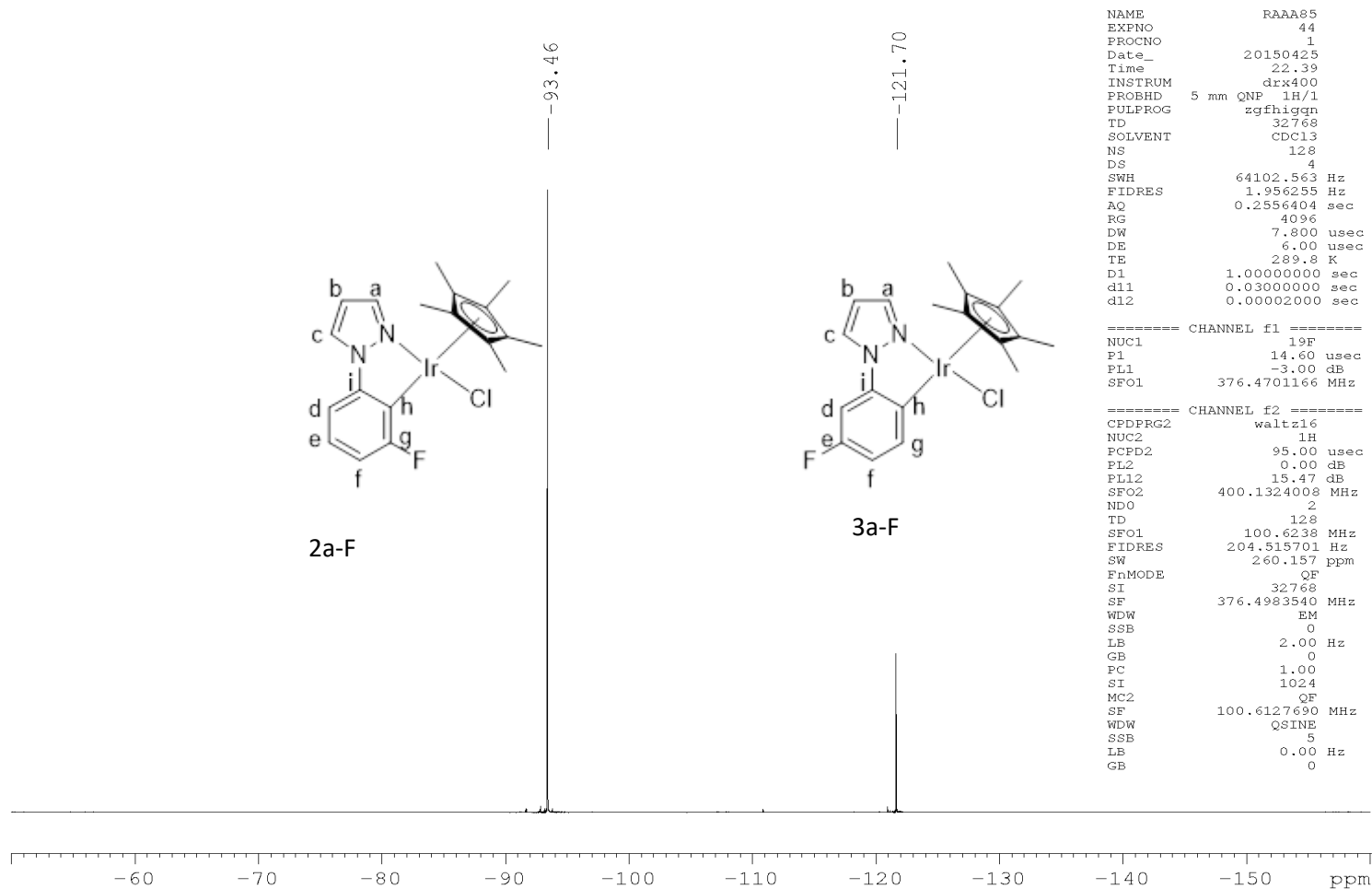


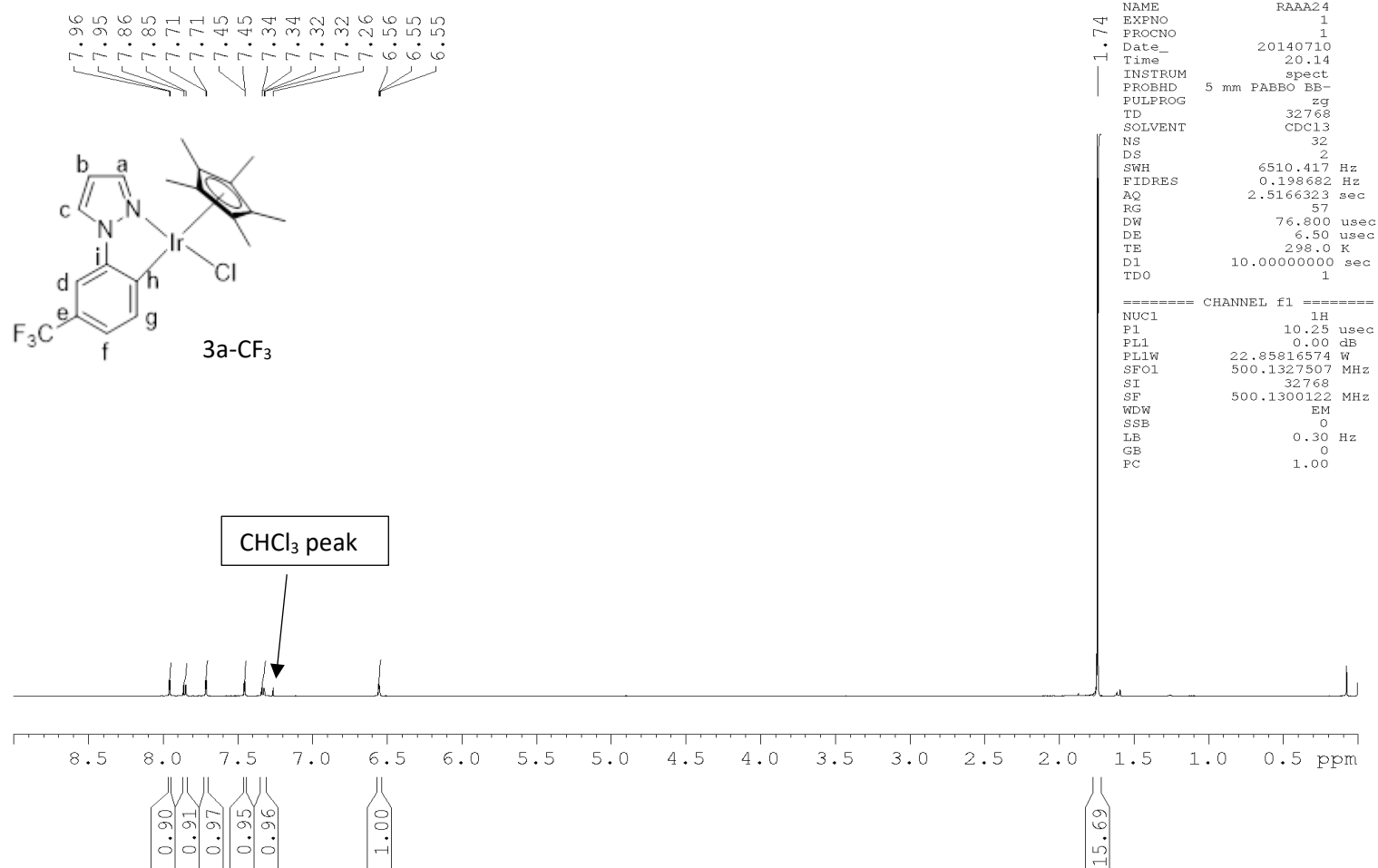


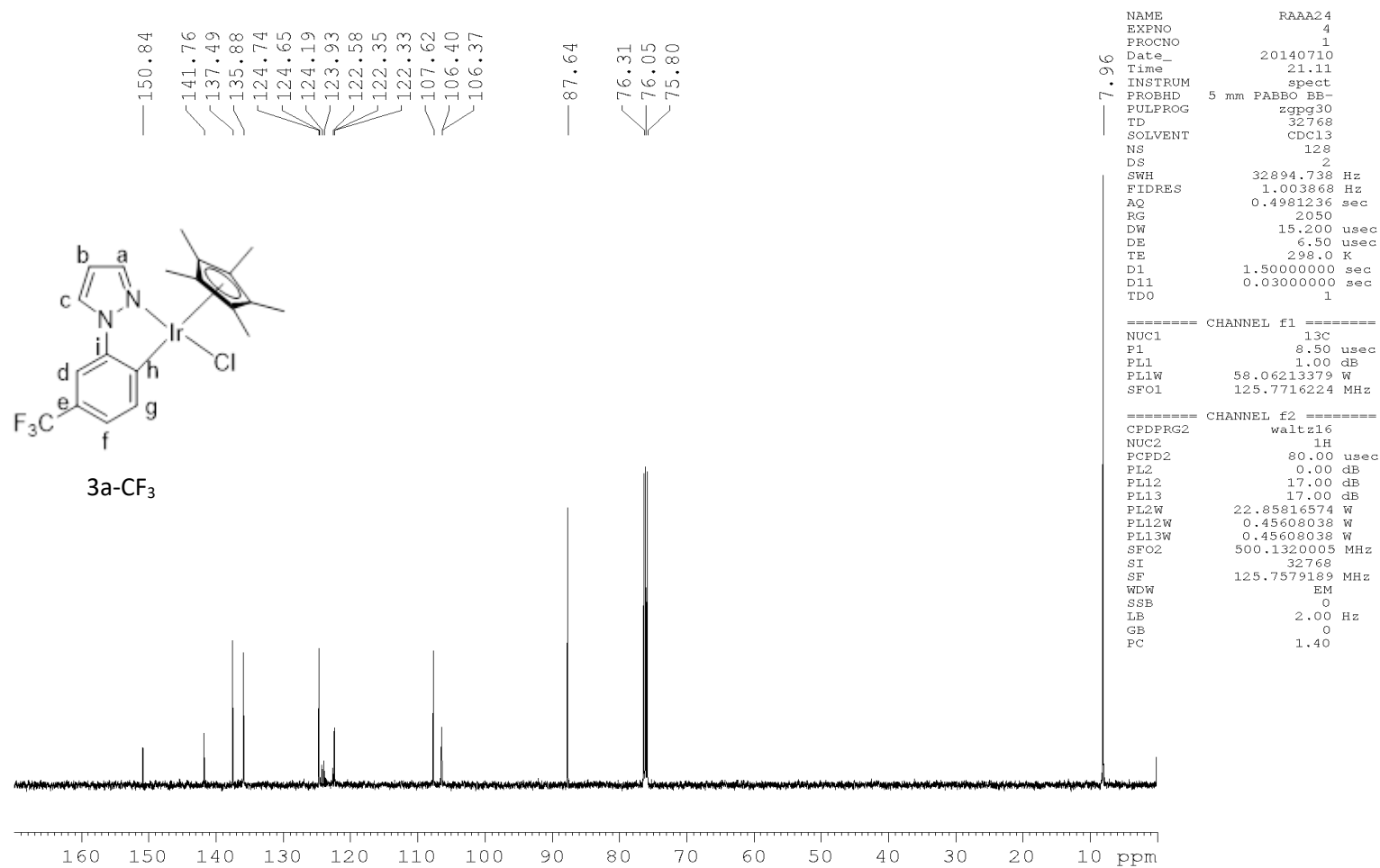


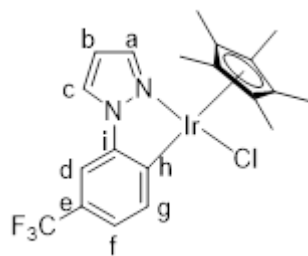




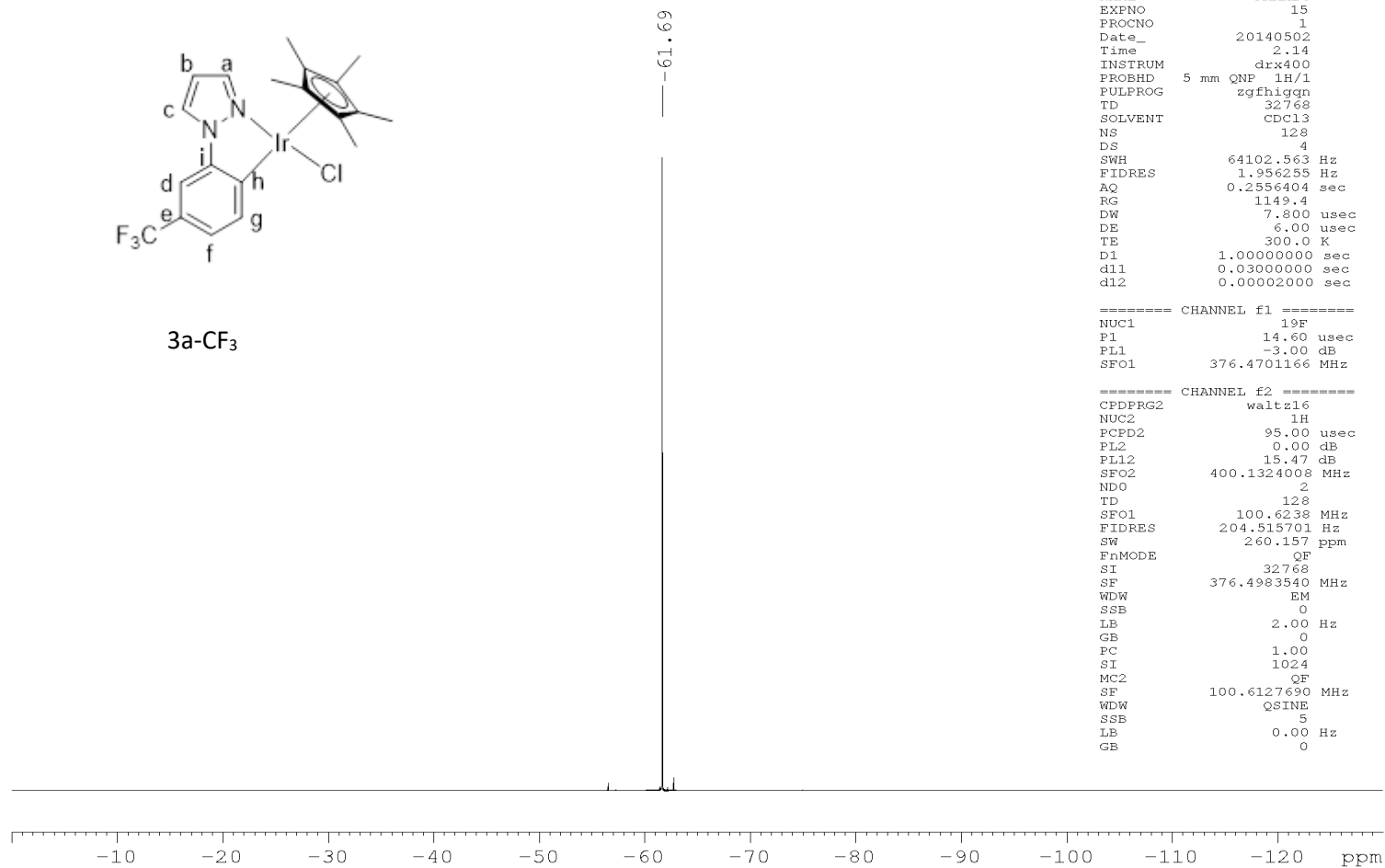








3a-CF<sub>3</sub>



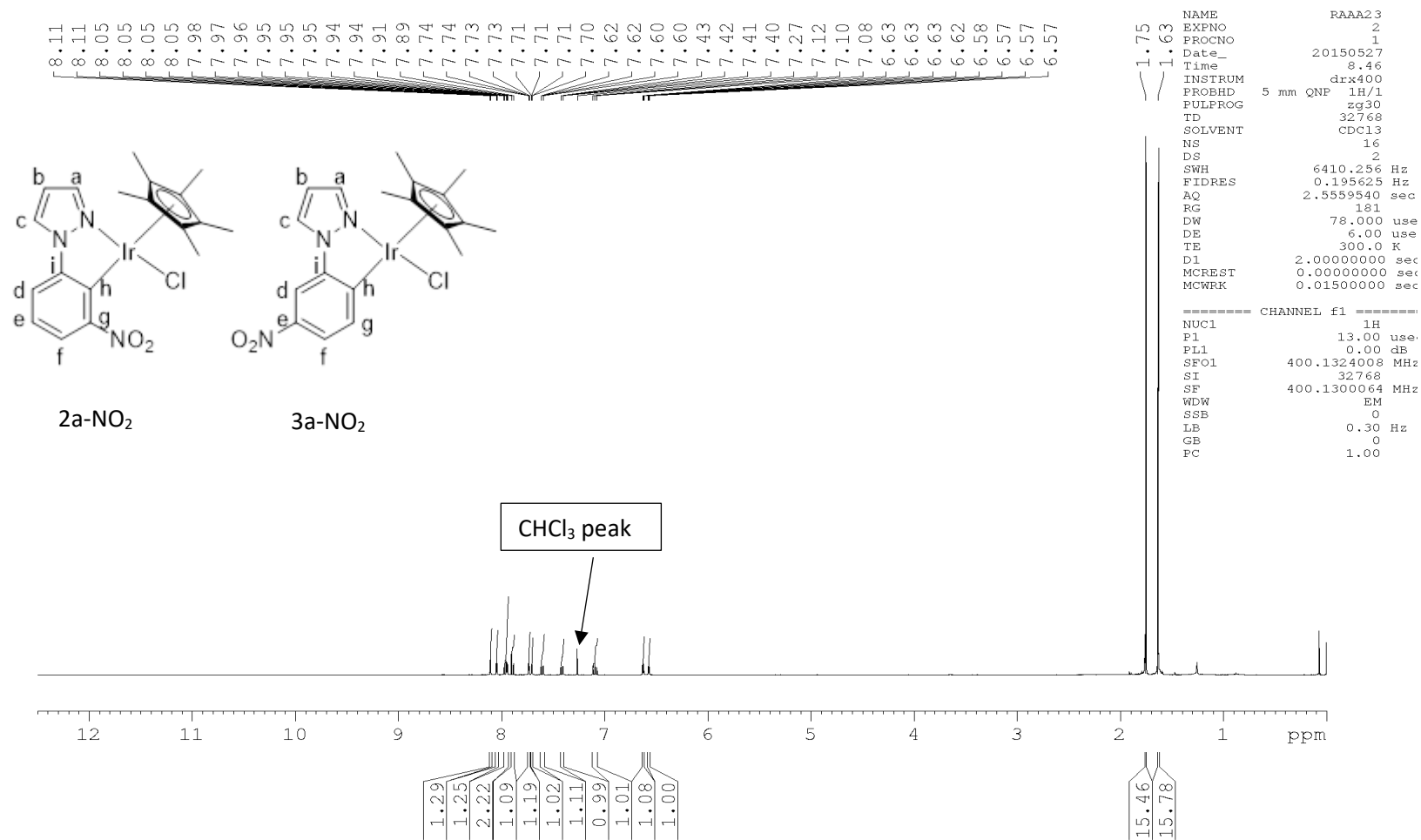
```

NAME          RAAA24
EXPNO         15
PROCNO        1
Date_         20140502
Time          2.14
INSTRUM       drx400
PROBHD        5 mm QNP 1H/1
PULPROG       zgfhigqn
TD            32768
SOLVENT       CDC13
NS            128
DS            4
SWH           64102.563 Hz
FIDRES        1.956255 Hz
AQ            0.2556404 sec
RG            1149.4
DW            7.800 usec
DE            6.00 usec
TE            300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

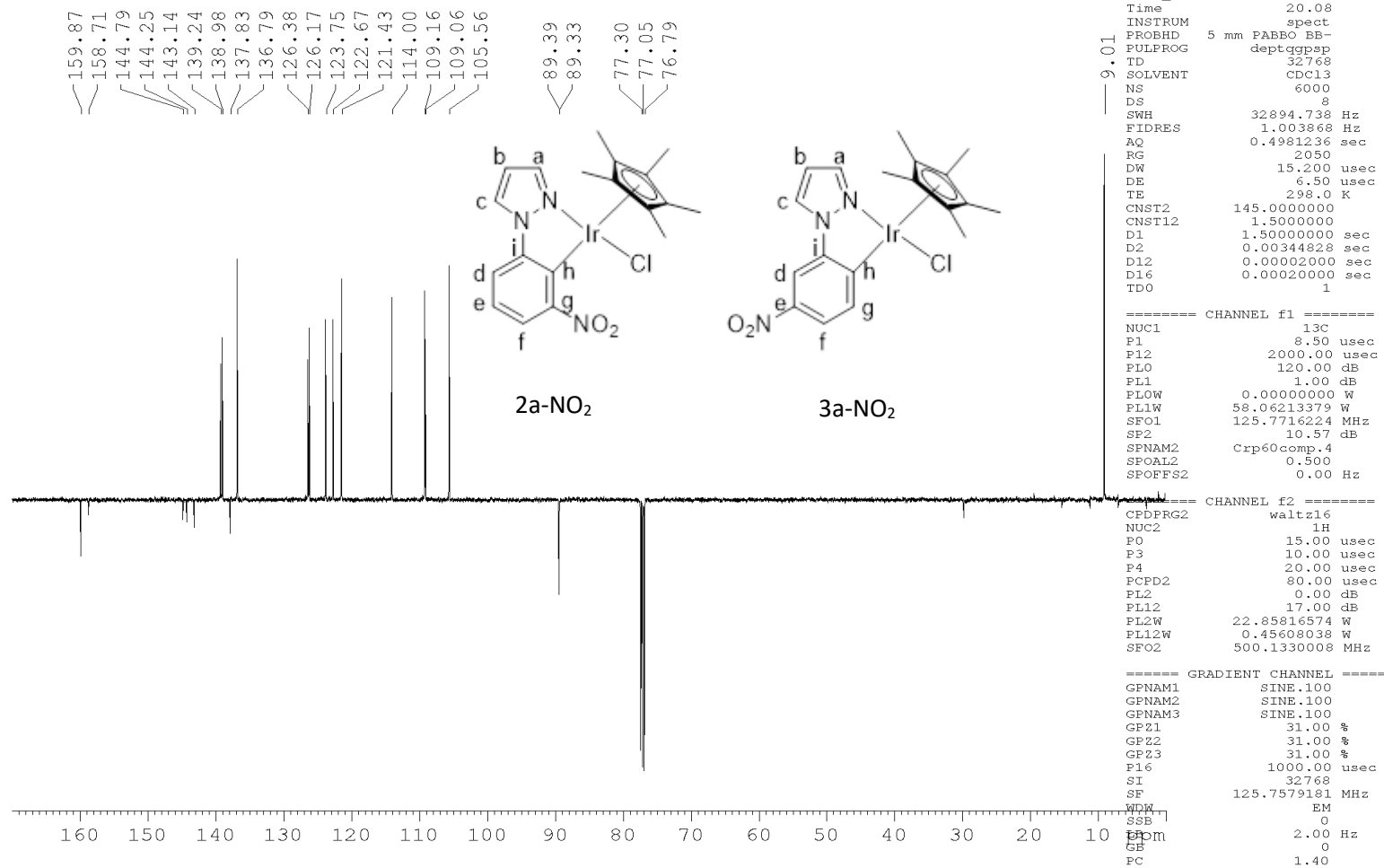
===== CHANNEL f1 =====
NUC1          19F
P1            14.60 usec
PL1           -3.00 dB
SFO1          376.4701166 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         95.00 usec
PL2           0.00 dB
PL12          15.47 dB
SFO2          400.1324008 MHz
ND0           2
TD            128
SFO1          100.6238 MHz
FIDRES        204.515701 Hz
SW            260.157 ppm
F0MODE        QF
SI            32768
SF            376.4983540 MHz
WDW           EM
SSB           0
LB            2.00 Hz
GB            0
PC            1.00
SI            1024
MC2           QF
SF            100.6127690 MHz
WDW           QSINE
SSB           5
LB            0.00 Hz
GB            0

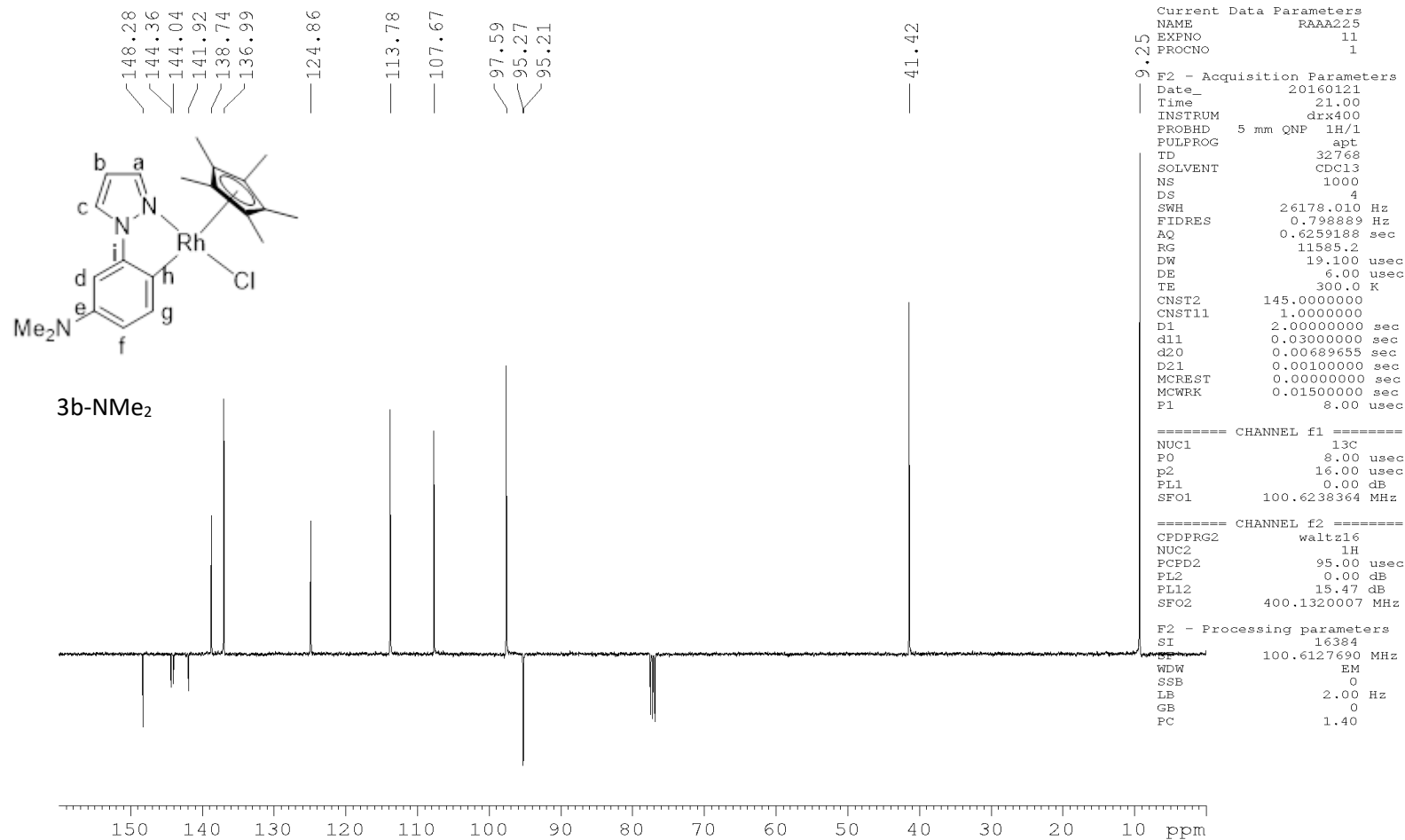
```

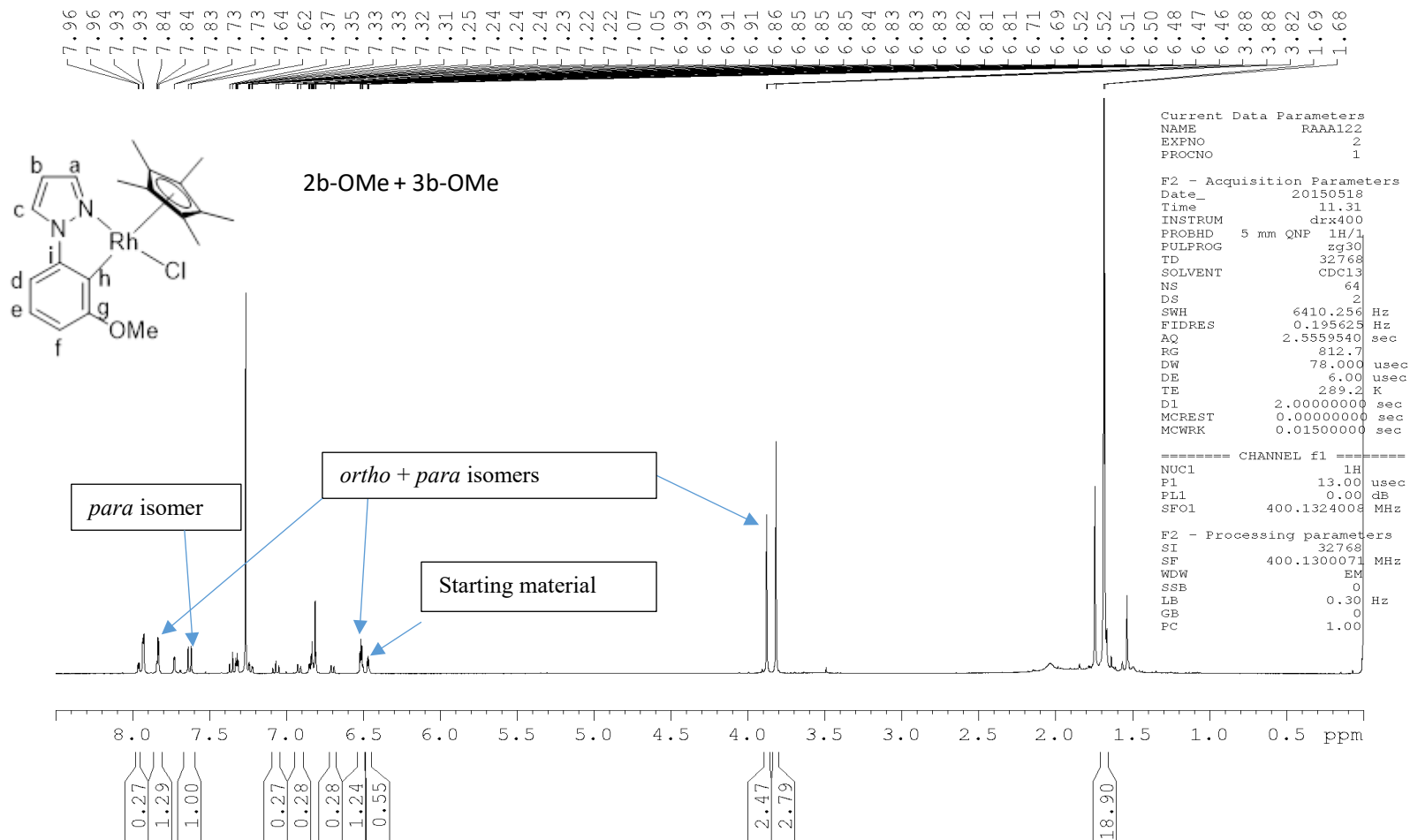


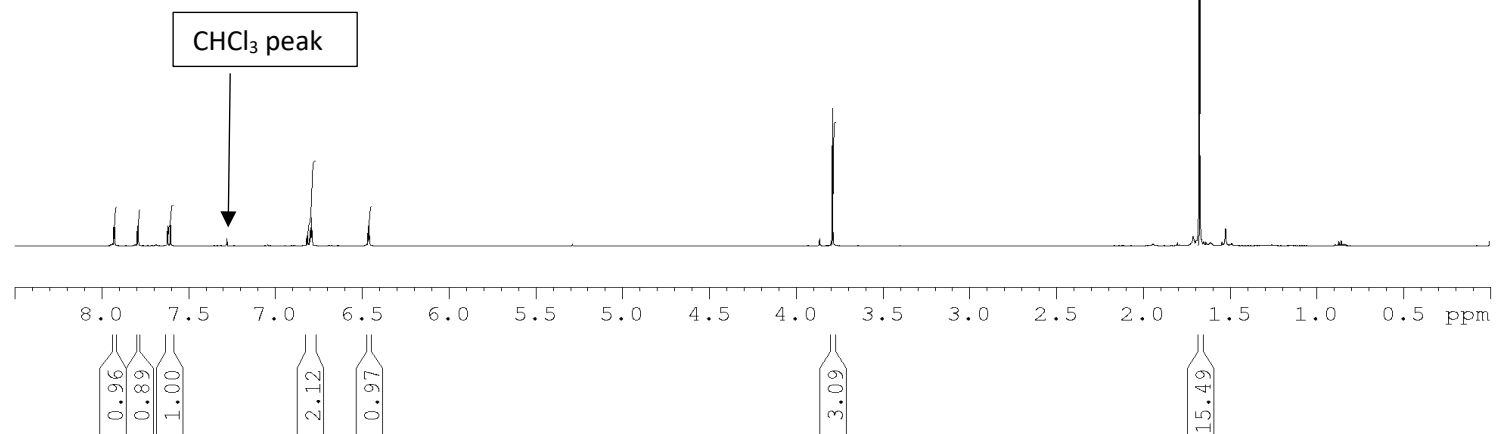
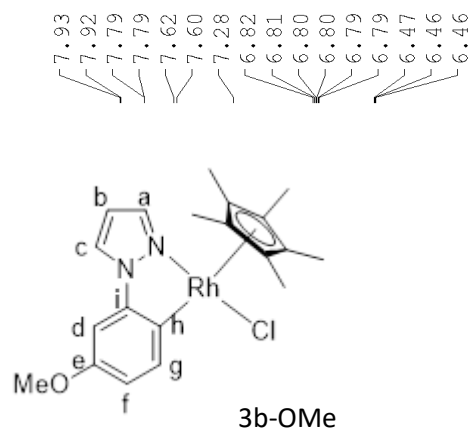






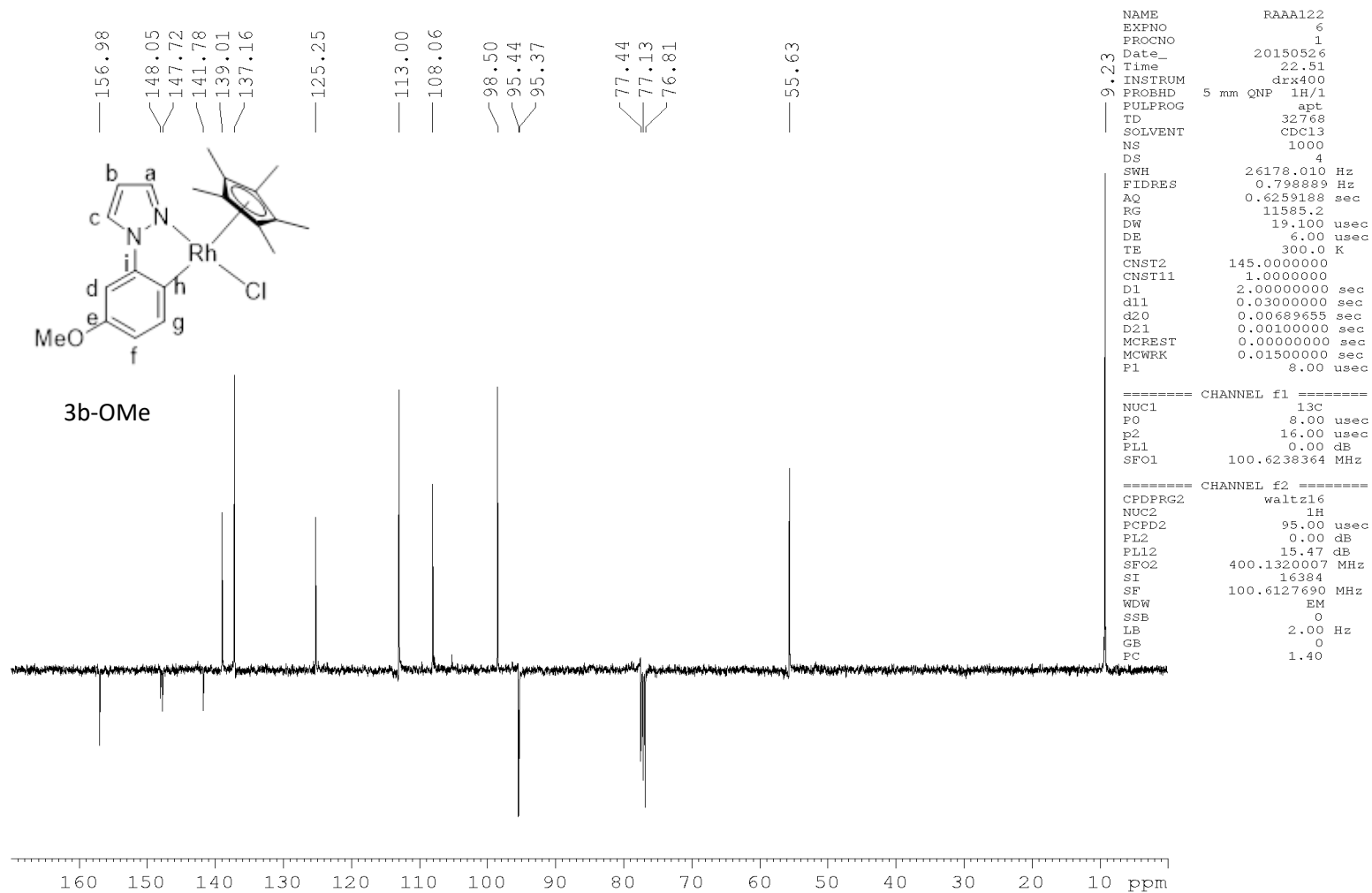


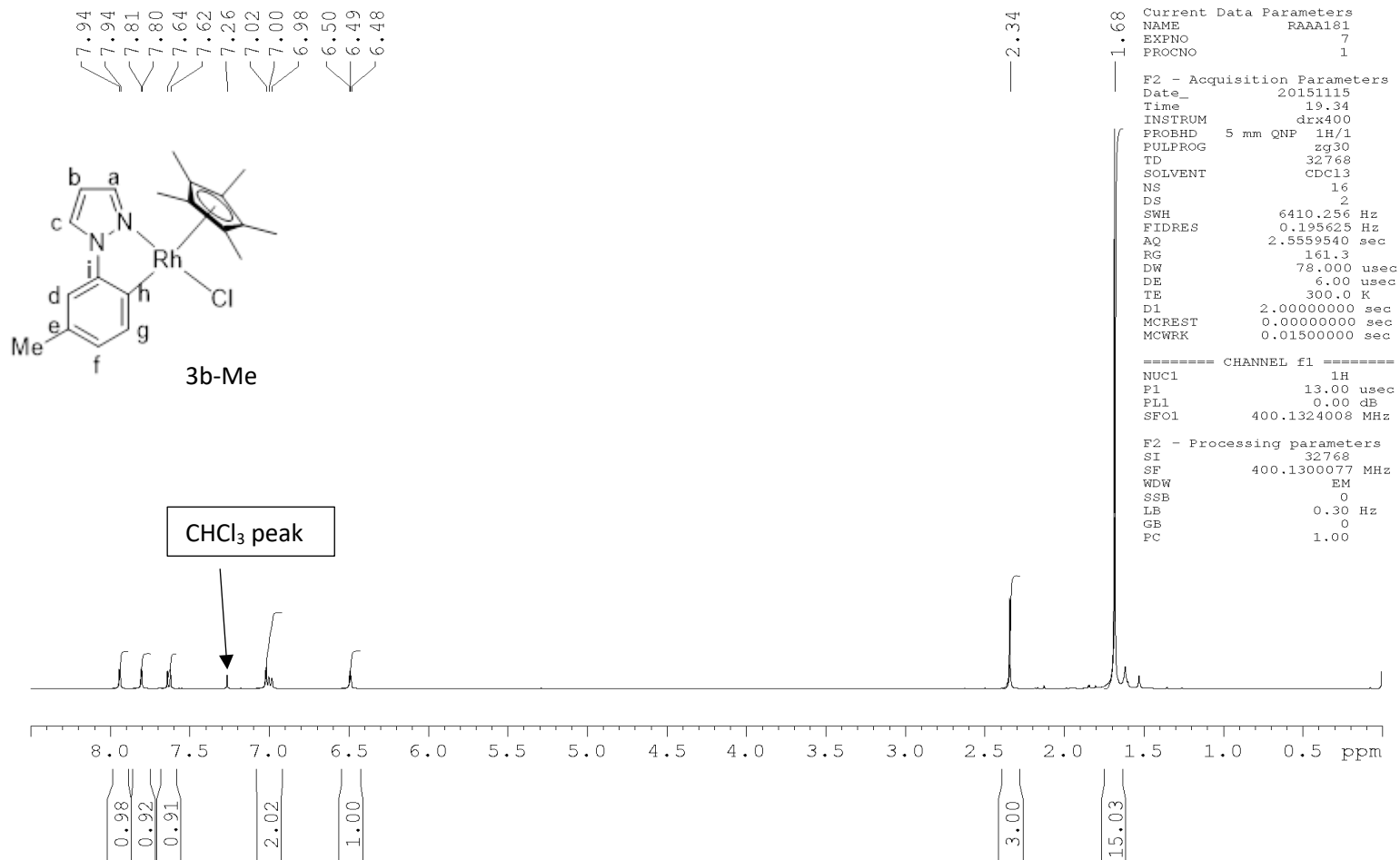


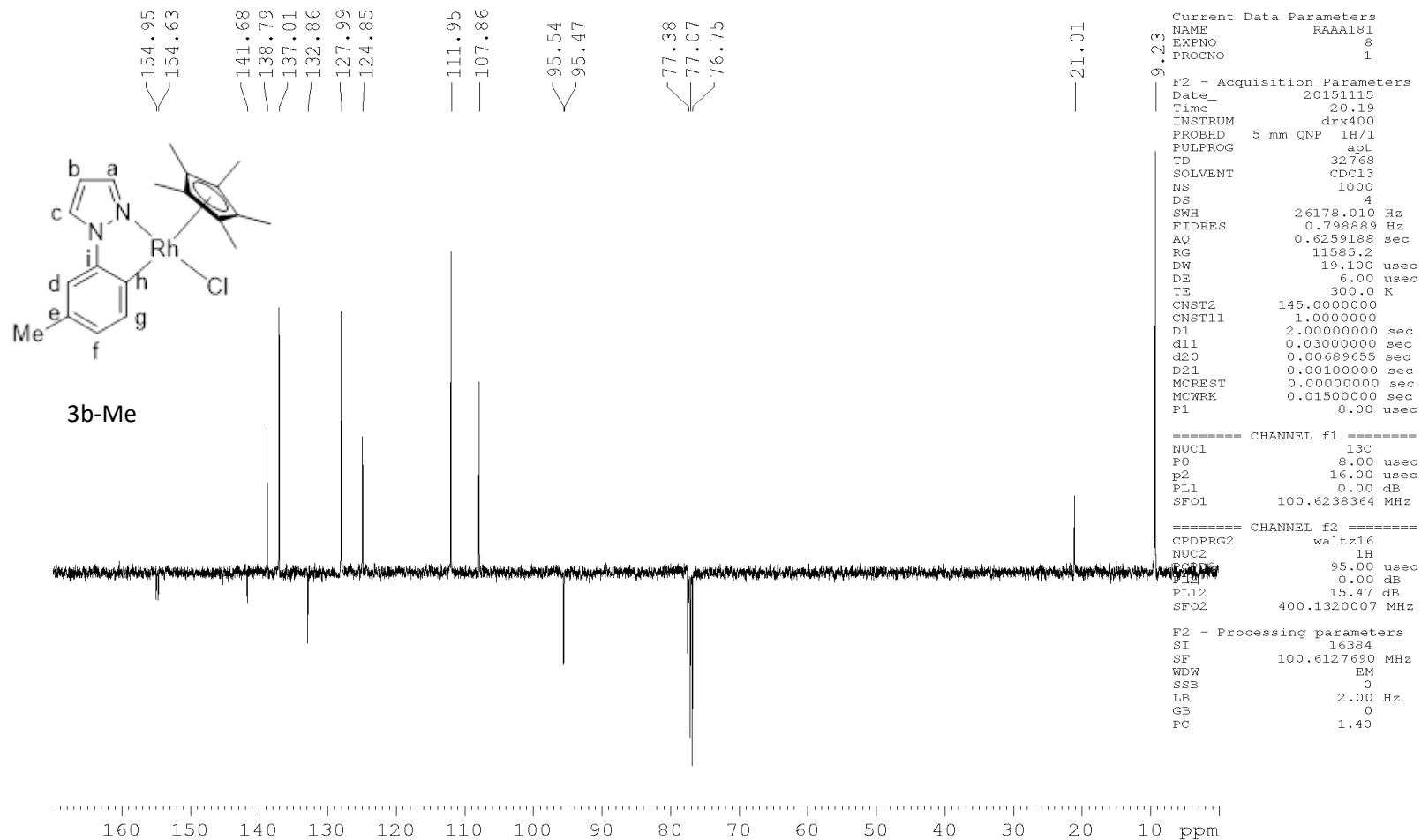


```

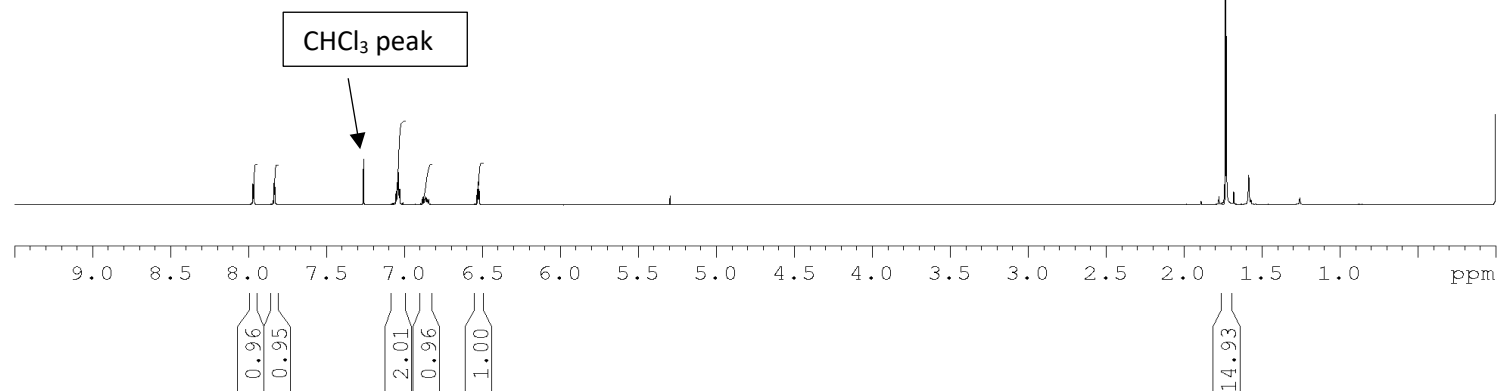
NAME          raaa122
EXPNO         1
PROCNO        1
Date_         20150527
Time          9.54
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg
TD            32768
SOLVENT       CDCl3
NS            8
DS            2
SWH           5000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            36
DW            100.000 usec
DE            6.50 usec
TE            298.0 K
D1            5.00000000 sec
TD0           1
===== CHANNEL f1 =====
NUC1          1H
P1            10.25 usec
PL1           0.00 dB
PL1W          22.85816574 W
SFO1          500.1322506 MHz
SI            32768
SF            500.1300049 MHz
WDW           EM
SSB           0
LB            0.20 Hz
GB            0
PC            1.00
  
```









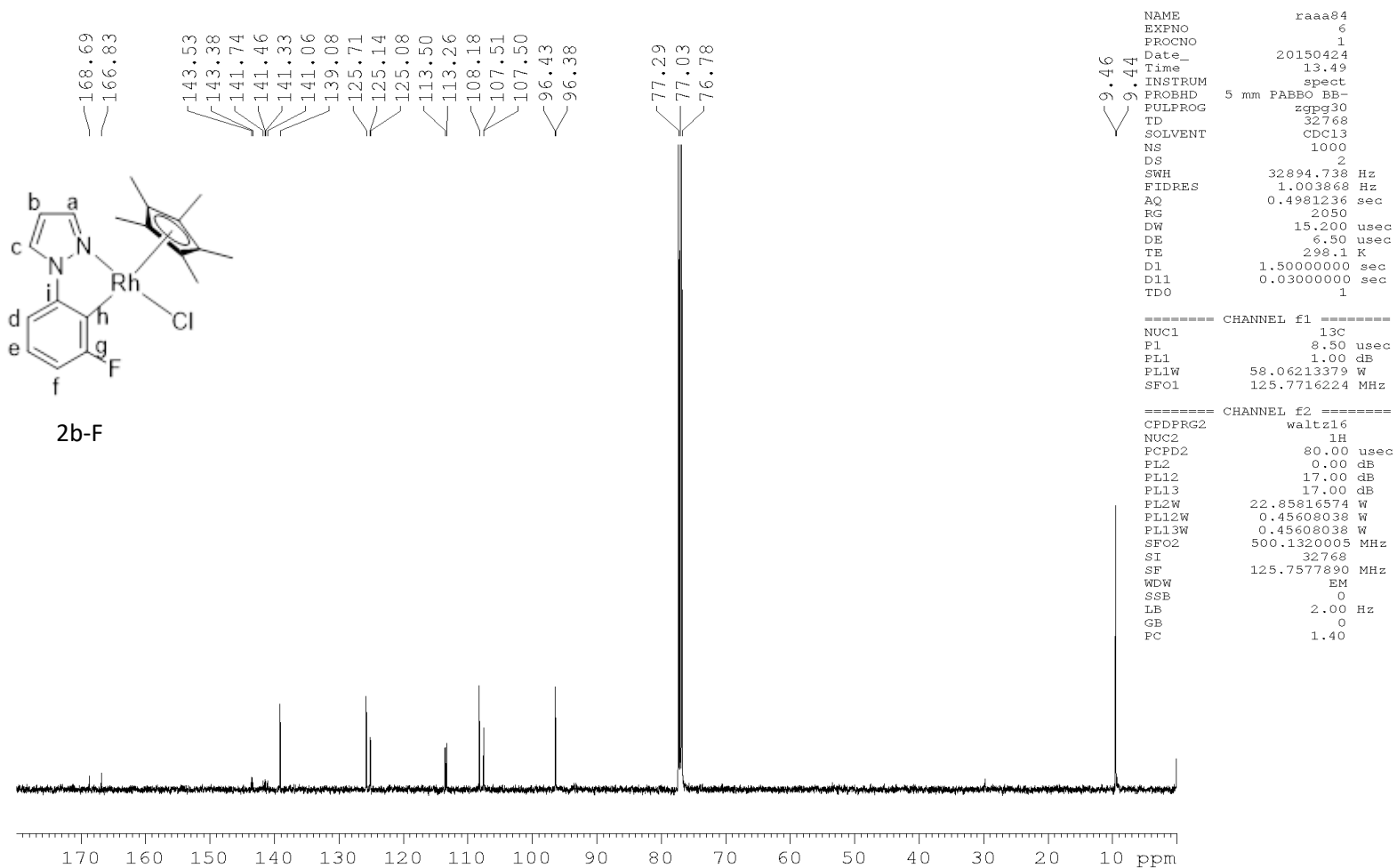


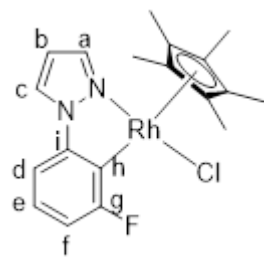
```

NAME                               RAAA84
EXPNO                             34
PROCNO                            1
Date_                              20150424
Time_                             2.57
INSTRUM                          drx4000
PROBHD          5 mm QNP   1H/1
PULPRQG                         zg30
TD                                32768
SOLVENT                        CDC13
NS                                 16
DS                                 2
SWH                      6410.256 Hz
FIDRES                   0.195625 Hz
AQ             2.5559540 sec
RG              322.5
DW               78.000    usec
DE               6.00     usec
TE                300.0 K
D1           2.000000000 sec
MCREST        0.00000000 sec
MCWCRK        0.01500000 sec

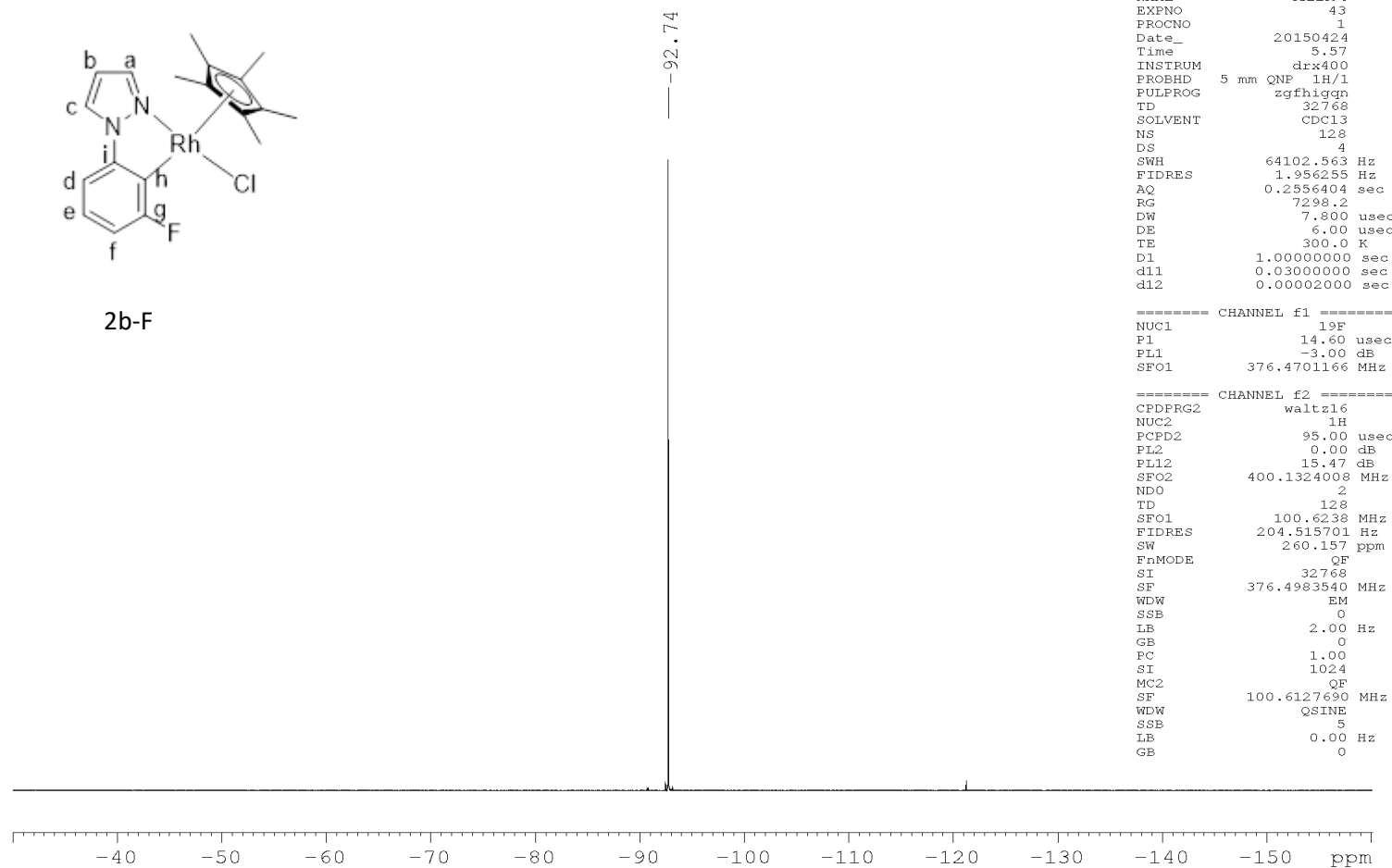
===== CHANNEL f1 =====
NUC1                  1H
P1                    13.00 usec
PL1                   0.00 dB
SF01                 400.1324008 MHz
SI                     32768
SF                   400.1300084 MHz
WDW                    EM
SSB                     0
LB                    0.30 Hz
GB                     0
PC                     1.00

```





2b-F



```

NAME          RAAA84
EXPNO         43
PROCNO        1
Date_         20150424
Time          5.57
INSTRUM       drx400
PROBHD        5 mm QNP 1H/1
PULPROG       zgfhigqn
TD            32768
SOLVENT       CDCl3
NS            128
DS            4
SWH           64102.563 Hz
FIDRES        1.956255 Hz
AQ            0.2556404 sec
RG            7298.2
DW            7.800 usec
DE            6.00 usec
TE            300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

```

```

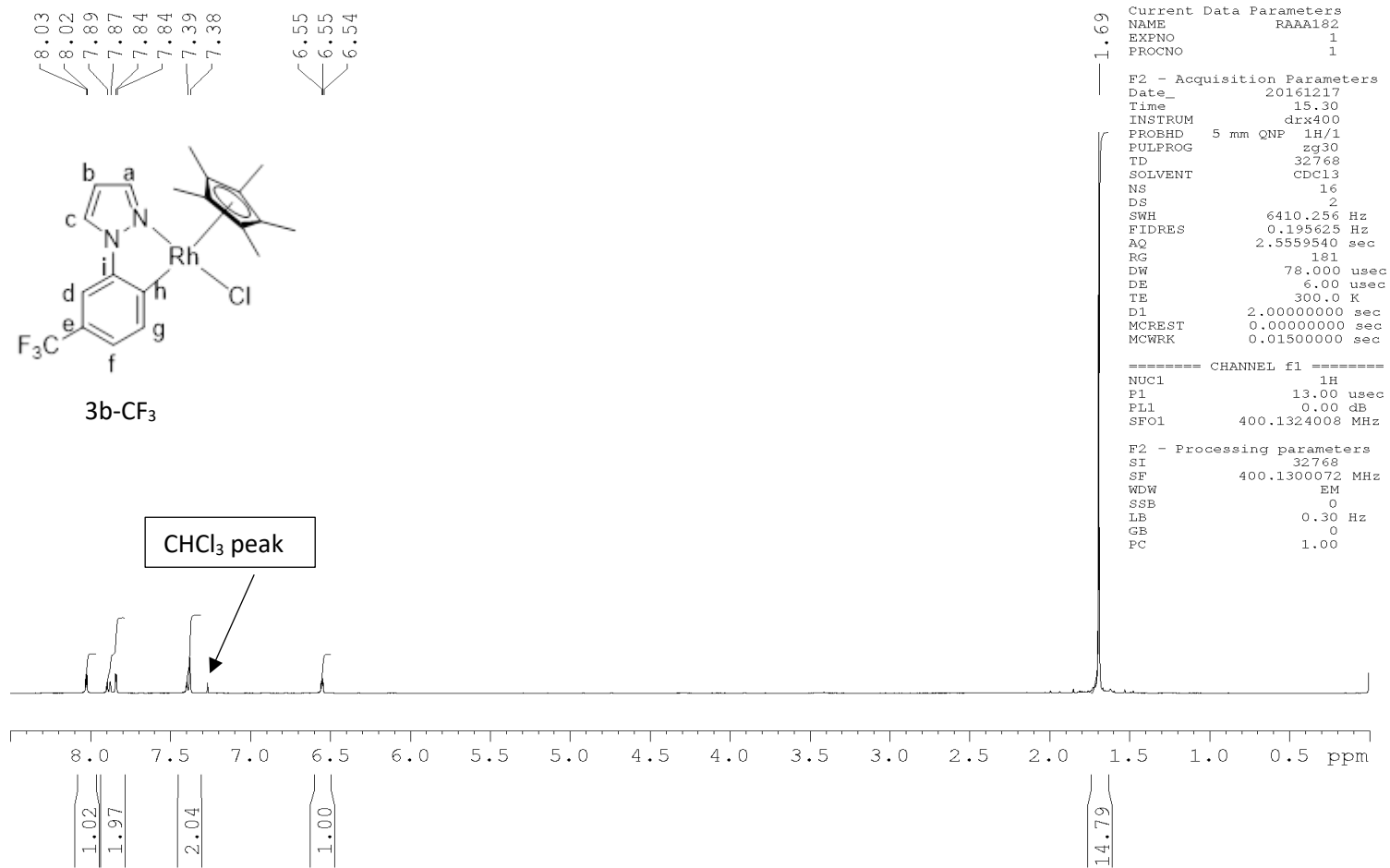
===== CHANNEL f1 =====
NUC1          19F
P1            14.60 usec
PL1           -3.00 dB
SFO1          376.4701166 MHz

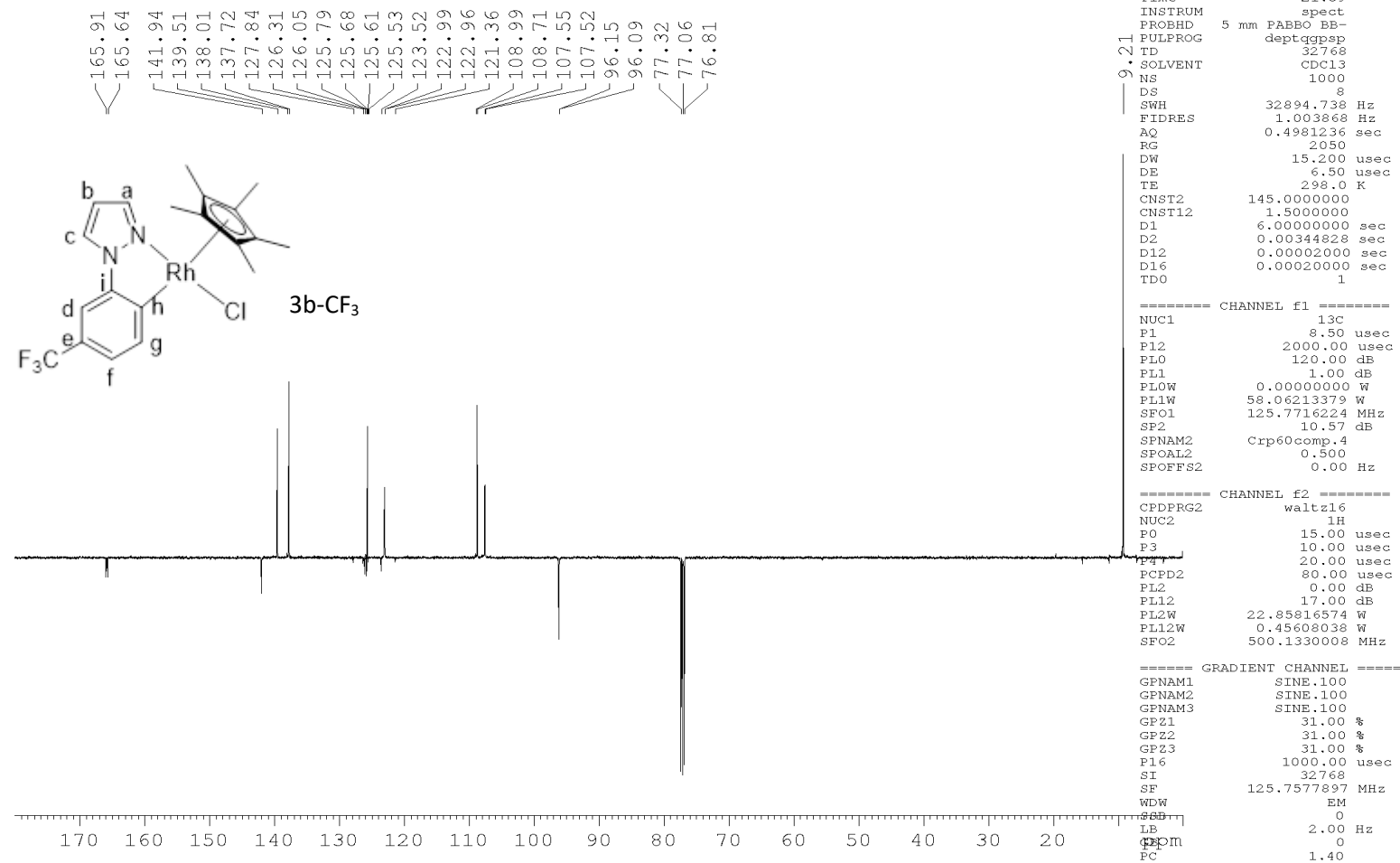
```

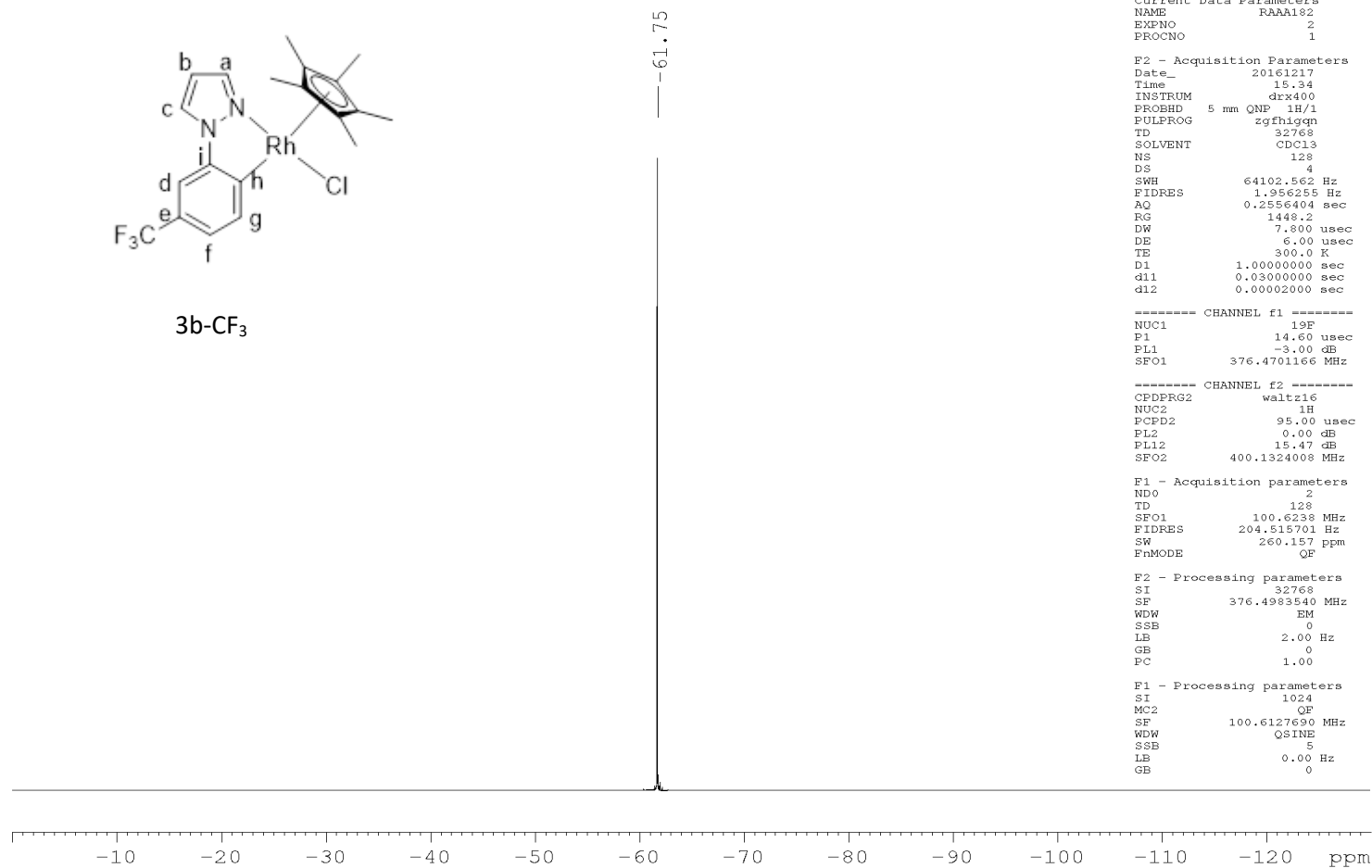
```

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         95.00 usec
PL2           0.00 dB
PL12          15.47 dB
SFO2          400.1324008 MHz
ND0           2
TD            128
SFO1          100.6238 MHz
FIDRES        204.515701 Hz
SW            260.157 ppm
FnMODE        QF
SI            32768
SF            376.4983540 MHz
WDW           EM
SSB           0
LB            2.00 Hz
GB            0
PC            1.00
SI            1024
MC2           QF
SF            100.6127690 MHz
WDW           QSINE
SSB           5
LB            0.00 Hz
GB            0

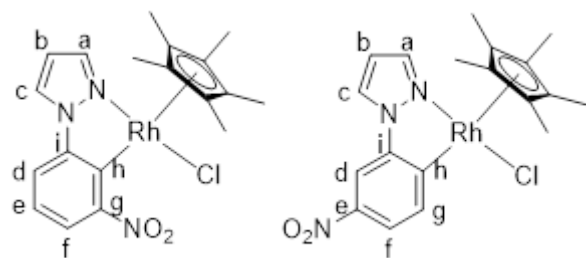
```





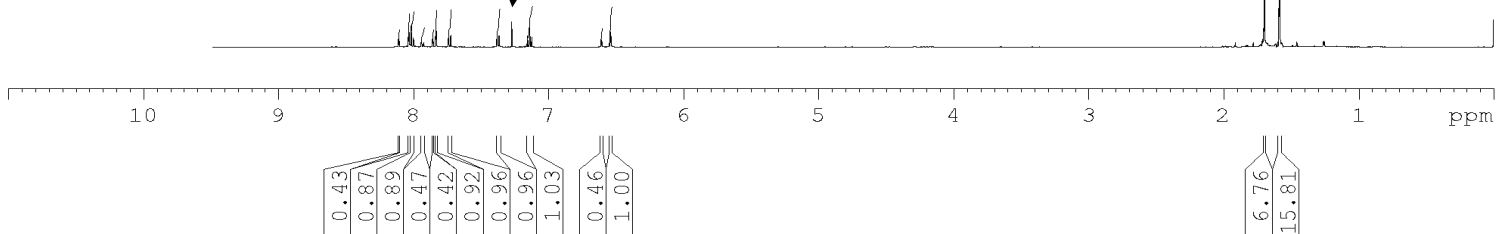


8.11  
8.11  
8.04  
8.03  
8.03  
8.02  
8.02  
8.01  
8.00  
7.94  
7.94  
7.93  
7.93  
7.86  
7.86  
7.84  
7.83  
7.74  
7.74  
7.73  
7.72  
7.38  
7.38  
7.37  
7.37  
7.27  
7.16  
7.14  
7.13  
6.61  
6.61  
6.61  
6.55  
6.54  
6.54



2b-NO<sub>2</sub> + 3b- NO<sub>2</sub>

CHCl<sub>3</sub> peak



NAME raaa123  
EXPNO 1  
PROCNO 1  
Date\_ 20150601  
Time 9.27  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg  
TD 32768  
SOLVENT CDCl3  
NS 8  
DS 2  
SWH 5000.000 Hz  
FIDRES 0.152588 Hz  
AQ 3.2768500 sec  
RG 80.6  
DW 100.000 usec  
DE 6.50 usec  
TE 298.0 K  
D1 7.00000000 sec  
TD0 1

----- CHANNEL f1 -----  
NUC1 1H  
P1 10.25 usec  
PL1 0.00 dB  
PL1W 22.85816574 W  
SFO1 500.1322506 MHz  
SI 32768  
SF 500.1300060 MHz  
WDW EM  
SSB 0  
LB 0.20 Hz  
GB 0  
PC 1.00

