Supplementary Information for

Understanding Electronic Effects on Carboxylate-Assisted C–H Activation at Ruthenium, The Importance of Kinetic and Thermodynamic Control

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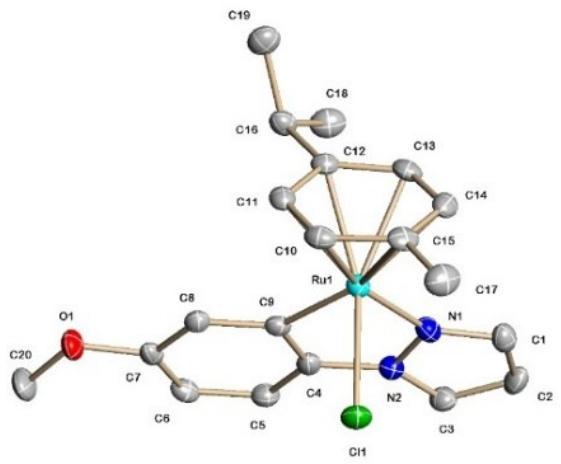
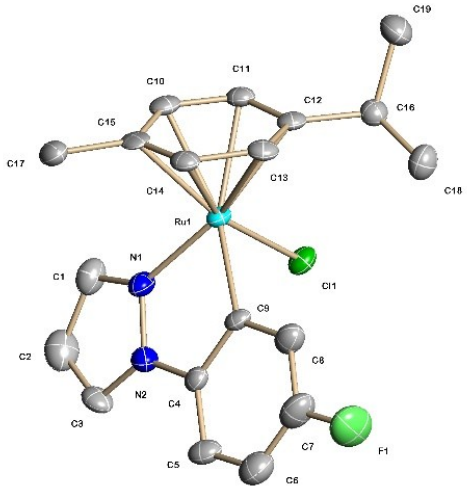
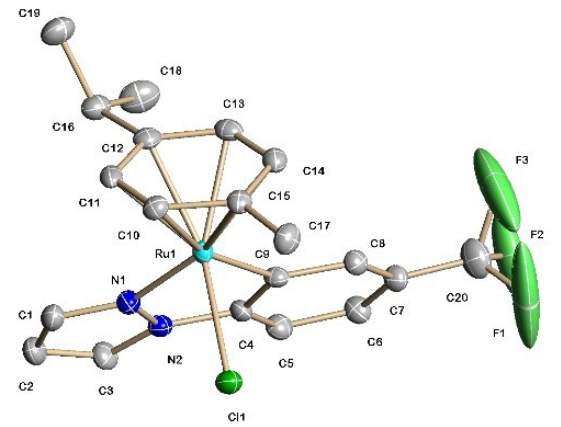
X-ray structures



1-OMe



1-F



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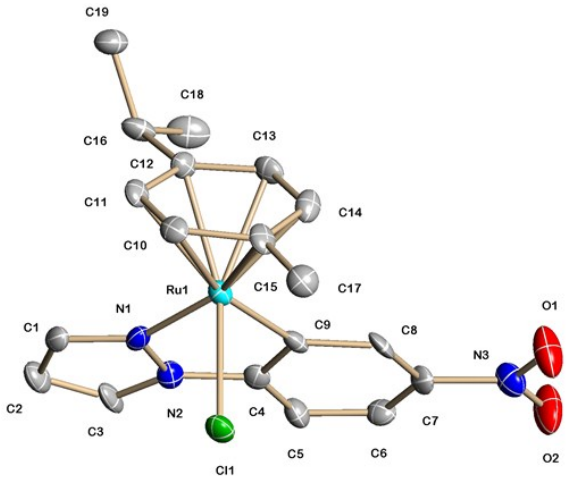

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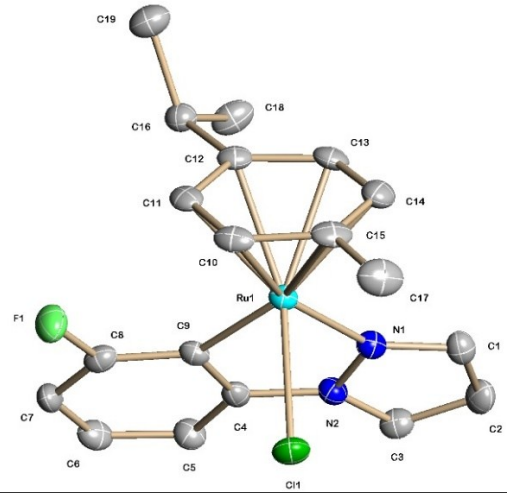


2-F

Fig. S1: Molecular structures of **1-OMe**, **1-F**, **1-CF_3**, **1-NO_2** and **2-F** showing 50% ellipsoids; H atoms are omitted for clarity.

Table S1: Selected bond distances (Å) and bond angles [°] for Ru complexes, **1-H**, **1-OMe**, **1-F**, **1-CF_3**, **1-NO_2** and **2-F**.						
	1-H[a]	**1-OMe**	**1-F**	**1-CF_3**	**1-NO_2**	**2-F**
Ru—C(9)	2.074(3)	2.069(3)	2.067(4)	2.055(6)	2.058(8)	2.082(3)
Ru—N(1)	2.066(3)	2.064(3)	2.061(4)	2.060(5)	2.068(6)	2.071(3)
Ru—Cl(1)	2.420(1)	2.418(1)	2.420 (1)	2.427(1)	2.431(2)	2.4212(9)
Ru—ring	2.165(3) 2.185(3) 2.187(3) 2.203(3) 2.252(3) 2.243(3)	2.164(4) 2.172(3) 2.179(4) 2.184(3) 2.262(3) 2.292(3)	2.166(5) 2.189(5) 2.189(5) 2.205(5) 2.240(5) 2.242(4)	2.147(6) 2.181(6) 2.194(6) 2.225(6) 2.241(6) 2.261(6)	2.172(7) 2.193(7) 2.194(7) 2.220(7) 2.255(7) 2.261(7)	2.165(3) 2.180(3) 2.190(3) 2.196(3) 2.252(3) 2.288(3)
C(9)—Ru—N(1)	77.38(12)	77.56(13)	77.53(17)	77.60(2)	77.2(3)	77.46(11)

a The structure for **1-H** has been published previously[1]

General procedure for the deuteration experiments

An NMR tube was charged with the selected ligand (0.25 mmol) followed by 0.25 ml of a d^4-MeOD solution of $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg.) followed by 0.25 ml of a d^4-MeOD solution of NaOAc (0.05 mmol, 4.1 mg.). The percentage of deuteration was monitored and determined by ^{1}H NMR spectroscopy and the site of deuteration was confirmed by ^{2}H NMR spectroscopy.

For **L1-R** %D in both *ortho* sites. For **L2-R** ratio A:B corresponding to formation of *ortho* cyclometallated isomer and *para* cyclometallated isomer respectively.

Table S2 Results of the deuteration experiments.		
L	Time (Temp.)	%D A:B[b]
L1-NMe_2	16 days (r.t.) 53 days (r.t.)	15:15 32:32
L1-OMe	3 days (r.t.) [c]10 days (r.t.)	N.D N.D
L2-NMe_2	2 h. (r.t.) 5 days (r.t.)	8:50 92:95
L2-OMe	4 h. (r.t.) 6 days (r.t.)	15:15 98:98
L2-Me	7 days (r.t.) 28 days (r.t.)	18:24 33:62

b: % D incorporation refers to each site

c: mixture was not left longer to show further H/D exchange.

d: deuterium exchange experiment was not done.

ND = not detected.

Competition experiments

An oven-dried Schlenk tube equipped with a stirrer bar was degassed three times and left under N2 atmosphere. The reagents and solvent were added in the following order $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 0.0125 mmol), NaOAc (2.1 mg, 0.025 mmol), dry solvent (MeOH 1 ml + DCM 3 ml) and the mixture was stirred for 5 minutes. Then ligand 1 (0.125 mmol) + ligand 2 (0.125 mmol) were dissolved in DCM (1 ml) before adding them to Schlenk tube. The Schlenk tube was then sealed and left stirring at r.t.. The reaction was monitored by integration of appropriate signals in the ^{1}H NMR spectrum and/or by ESI-MS (see below). After some time the reactions were heated to 50 °C and in some cases pivalic acid was added to help establish equilibrium. Alternatively the reaction was repeated on the same scale in TFE (5 ml) with pivalic acid (0.025 mmol) to try and ensure the reaction had reached equilibrium. 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. All the initial ratios were measured after 15 minutes and are taken as indicative of kinetic selectivity. For entries 5 and 6 in **Table S3** and 7 and 8 in **Table S4** the reactions are very slow so the conversion to products is too small to measure at very short reactions times.

Table S3: Results of competition experiments of *meta*- substituted Ru-complexes.

Entry	complex		R_1:R_2 at r.t.[a]	R_1:R_2 at r.t.[b]	R_1:R_2 at 50 °C[c]
	R_1	R_2			
1	H	NMe_2	1:2.3	1:2.1	2.7:1
2	OMe	H	1:1.4	1:1.2	1.2:1
3	H	Me	1:1.3	1:1.2	1.5:1
4	F	H	1:7.8	1:5.7	2.5:1
5	CF_3	F	1:4.7	1:4.7	1.5:1[d]
6	NO_2	CF_3	-	1:3.5	5.8:1[d]

a: DCM:MeOH (4:1) after 15 min except entry 5 after 2 hours.

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

c: DCM:MeOH (4:1) after 3, 5, 4 and 12 days for entries 1, 2, 3 and 4 respectively.

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

Table S4: Results of competition experiments of *para*- substituted Ru-complexes.

Entry	complex		R_1 vs *p*-R_2(o-R_2) at r.t.[a]	R_1 vs *p*-R_2(*o*-R_2) at r.t.[b]	R_1 vs *p*-R_2(o-R_2) at 50 °C[c]
	R_1	R_2			
1	Me	NMe_2	1:8.7	1.3:1	6.0:1
2[e]	Me	NMe_2	1:20	-	-
3	H	OMe	1:1.8(2.3)	1.3:1(2.15)	7.2:1(1.7)
4	H	Me	1:1.3	1:1.1	4.3:1
5	H	F	12:1(3.8)	11:1(4)	3.1:1(42)
6[f]	H	CF_3	10:1	9:1	-
6a[f, g]	H	CF_3	9.6:1	7.8:1	-
7	CF_3	F	-	1:4.0(12)	4.0:1(51)
8	NO_2	CF_3	-	1:2.7	5.0:1[d]

a: DCM:MeOH (4:1) after 15 min.

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

c: DCM:MeOH (4:1) after 7, 4, 3, 11 and 9 days for entries 1, 3, 4, 5 and 7 respectively.

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

e: Different procedure, base (DABCO) was added to inhibit reverse reaction, this is the value used in the Hammett plot.

f: Different conditions, M:**L1-H**:**L-2CF$_3$** (1:1.5:7.5) therefore real ratio **1-H**:**3-CF$_3$** = 48:1. Increased amount of L2-CF3 used otherwise the ratio is too small to measure

g: Ratio according to the ESI-MS.

Due to the high reversibility of reaction with L2-NMe_2 (entry 1 Table S4 above) the reaction was repeated using a base (DABCO) to inhibit the reverse reaction by reacting with the acetic acid formed (entry 2). This did indeed alter the ratio from 1:8.7 (Me:NMe_2) without base to 1:20 with base, hence the latter value was used in the Hammett plot

In the competition reaction between **L1-H** and **L2-CF$_3$**, using the usual conditions only the H product (**1-H)** was observed hence the reaction was repeated with more of **L2-CF$_3$** present (entry 6 **Table S4**) and the ratio was measured by ^{1}H NMR and ESI-MS spectrometry (entry 6a). Reactions with electron withdrawing groups have been heated at 50 °C (DCM/MeOH) or at 90 °C (TFE + pivalic acid) to try and establish the equilibrium ratios.

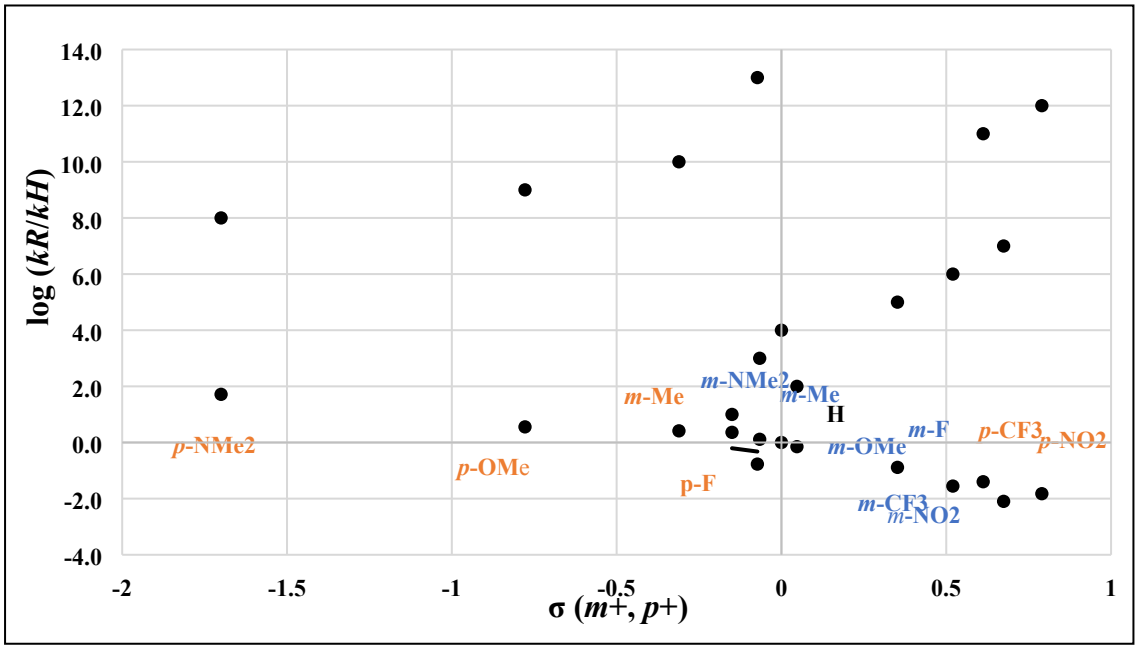


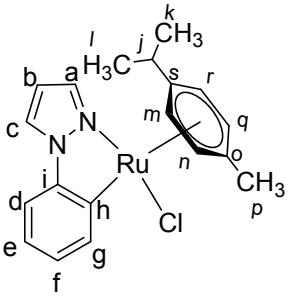
Fig.S2: Hammett plot of log (k_R/k_H) for formation of meta and para-substituted complexes of Ru against $\sigma m^+$and σp^+.

Experimental Procedures and Characterisation Data

General synthesis of cyclometallated complexes

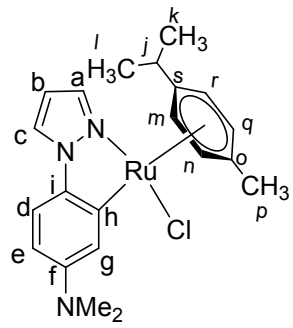
Two equivalents of ligand were added to a solution of one equivalent of $[RuCl_2(p\text{-cymene})]_2$ and two equivalents of NaOAc in dry MeOH or a mixture of dry MeOH and dry DCM in a Schlenk tube and stirred for several hours at room temperature, unless otherwise stated. The reaction was monitored periodically by ^{1}H NMR spectroscopy until completion was reached. The solvent was then evaporated on a rotary evaporator. The crude product was dissolved in DCM or THF and then filtered through Celite. The filtrate was evaporated to dryness and was precipitated from DCM or THF\petroleum ether to give pure cyclometallated products. If necessary, the cyclometallated products were purified by flash chromatography.

Cyclometallation of 2-phenyl pyrazole (L1-H) with $[RuCl_2(p\text{-cymene})]_2$



The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (50 mg., 0.081 mmol), 2-phenyl pyrazole (23.5 mg., 0.163 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml) and the mixture was stirred for 1 hour at room temperature. The product was precipitated from DCM / petroleum ether to give **1-H** (53 mg., 79%) as brown/yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 0.95 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.04 (s, 3H, H^p), 2.43 (sept, 1H, J = 6.9 Hz, H^j), 5.07 (brd, 1H, J = 5.8 Hz, $H^{n/q}$), 5.27 (dd, 1H, J= 0.9, 5.9 Hz, $H^{m/r}$), 5.54 (brd, 2H, J = 6.0 Hz, $H^{m/r/n/q}$), 6.44 (t, 1H, J = 2.5 Hz, H^b), 7.01 (td, 1H, J = 1.3, 7.5 Hz, H^e), 7.09 (td, 1H, J= 1.3, 7.3 Hz, H^f), 7.15 (dd, 1H, J = 1.2, 7.7 Hz, H^d), 7.89 (brd, 1H, J = 2.8 Hz, H^c), 8.04 (dd, 1H, J = 0.3, 2.1 Hz, H^a), 8.13 (dd, 1H, J = 1.2, 7.3 Hz, H^g) . $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.7 (C^p), 21.9 ($C^{k/l}$), 22.3 ($C^{k/l}$), 30.6 (C^j), 82.1 ($C^{n/q}$), 84.0 ($C^{m/r}$), 88.1 ($C^{m/r/n/q}$), 88.5 ($C^{m/r/n/q}$), 100.0 (C^{s+o}), 108.2 (C^b), 111.4 (C^d), 123.1 (C^e), 124.8 (C^c), 125.8 (C^f), 140.1 (C^g), 141.8 (C^i), 142.1 (C^a), 161.8 (C^h) Accurate MS-ESI *m/z* 379.0752 and 420.1014 (calculated), 379.0763 and 420.1015 (found), $[M–Cl]^+$ and $[M–Cl + (MeCN)]^+$ respectively $C_{19}H_{21}N_2{}^{102}Ru$ and $C_{21}H_{24}N_3{}^{102}Ru$.

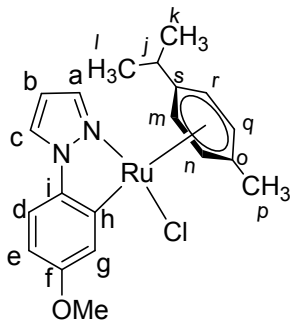
Cyclometallation of 1-(4-N,N-dimethylamine)-1*H*-pyrazole (L1-NMe_2) with $[RuCl_2(p\text{-cymene})]_2$



The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (50 mg., 0.081 mmol), 1-(4-N,N-dimethylamine)-1*H*-pyrazole (30.5 mg., 0.163 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml) and the mixture was stirred for 3 hours at room temperature. The product was precipitated from THF / petroleum ether to give **1-NMe_2** (47 mg., 62%) as brown/yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 0.97 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.01 (s, 3H, H^p), 2.46 (sept, 1H, J =

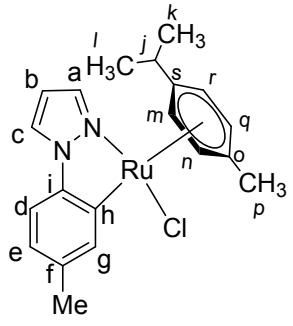
6.9 Hz, H^{j}), 3.01 (s, 6H, NMe_2), 5.06 (brd, 1H, *J* = 5.7 Hz, $H^{n/q}$), 5.26 (brd, 1H, *J*= 5.7 Hz, $H^{m/r}$), 5.47 (brd, 1H, *J* = 5.8 Hz, $H^{n/q}$), 5.53 (brd, 1H, *J* = 5.8 Hz, $H^{m/r}$), 6.37 (t, 1H, *J* = 2.3 Hz, H^{b}), 6.41 (dd, 1H, *J* = 2.5, 8.6 Hz, H^{e}), 7.04 (d, 1H, *J*= 8.6 Hz, H^{d}), 7.55 (d, 1H, *J* = 2.6 Hz, H^{g}), 7.75 (brd, 1H, *J* = 2.5 Hz, H^{c}), 7.96 (brd, 1H, *J* = 1.9 Hz, H^{a}). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 18.8 (C^{p}), 21.8 ($C^{k/l}$), 22.5 ($C^{k/l}$), 30.6 (C^{j}), 41.3 (NMe_2), 82.4 ($C^{n/q}$), 84.0 ($C^{m/r}$), 87.9 ($C^{n/q}$), 88.4 ($C^{m/r}$), 9.3 (C^{s}), 99.8 (C^{o}), 107.6 (C^{b}), 108.1 (C^{e}), 111.6 (C^{d}), 123.6 (C^{c}), 123.8 (C^{g}), 133.6 (C^{i}), 141.0 (C^{a}), 148.7 (C^{f}), 162.8 (C^{h}) Accurate MS-ESI *m/z* 422.1170 and 463.1436 (calculated), 422.1163 and 463.1431 (found), $[M–Cl]^+$ and $[M–Cl + (MeCN)]^+$ respectively $C_{21}H_{26}N_3{}^{102}Ru$ and $C_{23}H_{29}N_4{}^{102}Ru$.

Cyclometallation of 1-(4-methoxyphenyl)-1*H*-pyrazole (L1-OMe) with $[RuCl_2(p\text{-cymene})]_2$



The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (100 mg., 0.163 mmol), 1-(4-methoxyphenyl)-1*H*-pyrazole (56.9 mg., 0.327 mmol) and NaOAc (26.8 mg., 0.327 mmol) in dry MeOH (10 ml) and the mixture was stirred for 24 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **1-OMe** (89 mg., 61%) as brown/yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 0.95 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 2.03 (s, 3H, H^{p}), 2.43 (sept, 1H, *J* = 6.9 Hz, H^{j}), 3.86 (s, 3H, OMe), 5.07 (brd, 1H, *J* = 5.9 Hz, $H^{n/q}$), 5.28 (brd, 1H, *J*= 5.7 Hz, $H^{m/r}$), 5.52 (brd, 2H, *J* = 5.9 Hz, $H^{m/r/n/q}$), 6.40 (t, 1H, *J* = 2.4 Hz, H^{b}), 6.53 (dd, 1H, *J* = 2.6, 8.5 Hz, H^{e}), 7.08 (d, 1H, *J*= 8.5 Hz, H^{d}), 7.69 (d, 1H, *J* = 2.8 Hz, H^{g}), 7.80 (brd, 1H, *J* = 2.6 Hz, H^{c}), 7.99 (brd, 1H, *J* = 2.0 Hz, H^{a}). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 18.8 (C^{p}), 21.9 ($C^{k/l}$), 22.4 ($C^{k/l}$), 30.6 (C^{j}), 55.5 (OMe), 82.3 ($C^{n/q}$), 84.2 ($C^{m/r}$), 88.1 ($C^{m/r/n/q}$), 88.5 ($C^{m/r/n/q}$), 99.9 (C^{s}), 100.0 (C^{o}), 108.0 ($C^{b/e}$), 108.0 ($C^{b/e}$), 111.7 (C^{d}), 124.3 (C^{c}), 125.4 (C^{g}), 136.2 (C^{i}), 141.6 (C^{a}), 156.9 (C^{f}), 163.5 (C^{h}). Accurate MS-ESI *m/z* 409.0845, 450.1119 and 398.0555 (calculated), 409.0860, 450.1126 and 398.0526 (found), $[M–Cl]^+$, $[M–Cl + (MeCN)]^+$ and $[M–Cl – (p\text{-cymene}) + 3(MeCN)]^+$respectively $C_{20}H_{23}N_2O^{102}Ru$, $C_{22}H_{26}N_3O^{102}Ru$ and $C_{16}H_{18}N_5O^{102}Ru$.

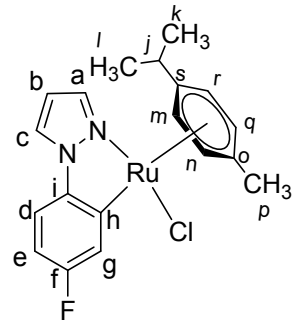
Cyclometallation of 1-(4-methylphenyl)-1*H*-pyrazole (L1-Me) with $[RuCl_2(p\text{-cymene})]_2$.



The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (50 mg., 0.081 mmol), 1-(4-methylphenyl)-1*H*-pyrazole (26.0 mg., 0.164 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml) and the mixture was stirred for 5 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **1-Me** (37 mg., 53%) as brown/yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 0.94 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 2.05 (s, 3H, H^{p}), 2.39 (s, 3H, Me), 2.42 (sept, 1H, *J* = 6.9 Hz, H^{j}), 5.09 (dd, 1H, *J* = 0.9, 5.8, $H^{n/q}$), 5.31 (dd, 1H, *J* = 1.0, 6.1, $H^{m/r}$), 5.54 (overlapping d, 2H, $H^{m/r/n/q}$), 6.45 (t, 1H, *J* = 2.5 Hz, H^{b}), 6.82 (dd, 1H, *J* = 1.1, 7.9 Hz, H^{e}), 7.06 (d, 1H, *J* = 7.9 Hz,

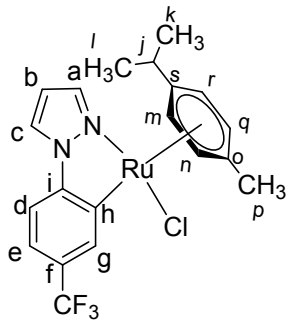
H^d), 7.86 (dd, 1H, J = 0.5, 2.7 Hz, H^c), 7.94 (brd, 1H, J= 1.0, H^g), 8.03 (dd, 1H, J = 0.5, 2.2 Hz, H^a). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.8 (C^p), 21.4 (Me) 22.0 ($C^{k/l}$), 22.3 ($C^{k/l}$), 30.7 (C^j), 82.0 ($C^{n/q}$), 84.3 ($C^{m/r}$), 87.8 ($C^{m/r/n/q}$), 88.8 ($C^{m/r/n/q}$), 99.8 (C^{s+o}), 108.0 (C^b), 111.0 (C^d), 123.9 (C^e), 124.5 (C^c), 135.2 (C^f), 139.6 (C^i), 140.6 (C^g), 141.8 (C^a), 161.6 (C^h). Accurate MS-ESI *m/z* 393.0905, 434.1170 and 382.0606 (calculated), 393.0911, 434.1178 and 382.0602 (found), $[M–Cl]^+$, $[M–Cl + (MeCN)]^+$ and $[M–Cl – (p\text{-cymene}) + 3(MeCN)]^+$ respectively $C_{20}H_{23}N_2{}^{102}Ru$, $C_{22}H_{26}N_3{}^{102}Ru$ and $C_{16}H_8N_5{}^{102}Ru$.

Cyclometallation of 1-(4-fluoromethylphenyl)-1*H*-pyrazole (L1-F) with $[RuCl_2(p\text{-cymene})]_2$



The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (50 mg., 0.081 mmol), 1-(4-fluoromethylphenyl)-1H-pyrazole mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml) and the mixture was stirred for 21 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **1-F** (47 mg., 66%) as brown/yellow crystals. ^1H NMR (500 MHz, $CDCl_3$): δ 0.91 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 0.94 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.05 (s, 3H, H^p), 2.42 (sept, 1H, J = 6.9 Hz, H^j), 5.07 (brd, 1H, J = 5.7 Hz, $H^{n/q}$), 5.29 (brd, 1H, J= 5.7 Hz, $H^{m/r}$), 5.53 (brd, 1H, J= 6.0 Hz, $H^{m/r/n/q}$), 5.55 (brd, 1H, J= 6.0 Hz, $H^{m/r/n/q}$), 6.42 (t, 1H, J = 2.4 Hz, H^b), 6.67 (dt, 1H, $J_{H\text{-}H}$ = 2.7, $J_{H\text{-}F}$ = 8.6 Hz, H^e), 7.09 (dd, 1H, $J_{H\text{-}F}$ = 4.5, $J_{H\text{-}H}$ = 8.5 Hz, H^d), 7.80 (brd, 1H, J = 2.7 Hz, H^c), 7.82 (overlapping d, 1H, H^g), 8.01 (brd, 1H, J = 2.1 Hz, H^a). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.8 (C^p), 21.9 ($C^{k/l}$), 22.3 ($C^{k/l}$), 30.6 (C^j), 82.2 ($C^{n/q}$), 84.5 ($C^{m/r}$), 88.1 ($C^{m/r/n/q}$), 88.7 ($C^{m/r/n/q}$), 100.3 (C^s), 100.7 (C^s), 108.0 (C^b), 109.7 (d, $^2J_{CF}$ = 24.4 Hz, C^e), 112 (d, $^3J_{CF}$ = 8.5 Hz, C^d), 125.1 (C^c), 125.9 (d, $^2J_{CF}$ = 19.0 Hz, C^g), 138.2 (C^i), 142.2 (C^a), 160.0 (d, $^1J_{CF}$ = 247.6 Hz, C^f), 164.7 (d, $^3J_{CF}$ = 3.8 Hz, C^h). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -117.7 (s, F). ^{19}F NMR (376 MHz, $CDCl_3$): Accurate MS-ESI *m/z* 397.0654 and 438.0920 (calculated), 397.0661 and 438.0920 (found), $[M–Cl]^+$ and $[M–Cl + (MeCN)]^+$ respectively $C_{19}H_{20}FN_2{}^{102}Ru$ and $C_{21}H_{23}FN_3{}^{102}Ru$.

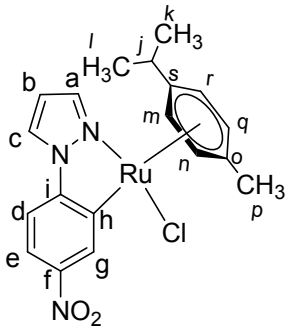
Cyclometallation of 1-(4-trifluoromethylphenyl)-1*H*-pyrazole (L1-CF_3) with $[RuCl_2(p\text{-cymene})]_2$



The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (50 mg., 0.081 mmol), 1-(4-trifluoromethylphenyl)-1*H*-pyrazole (34.7 gm., 0.164 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml) and the mixture was stirred for 79 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **1-CF_3** (42 mg., 54%) as brown/yellow crystals.^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 0.96 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.07 (s, 3H, H^p), 2.42 (sept, 1H, J =6.9 Hz, H^j), 5.10 (brd, 1H, J = 5.8 Hz, $H^{n/q}$), 5.32 (brd, 1H, J = 6.0 Hz, $H^{m/r}$), 5.58 (overlapping d, 2H, $H^{m/r/n/q}$), 6.50 (t, 1H, J = 2.4 Hz, H^b), 7.20 (d, 1H, J = 8.2 Hz, H^d), 7.27 (brd, 1H, J = 8.2 Hz, H^e), 7.94 (brd, 1H, J = 2.7 Hz, H^c), 8.08 (brd, 1H, J = 1.9 Hz, H^a), 8.35 (brs, 1H, H^g). $^{13}C\{^1H\}$ NMR (125

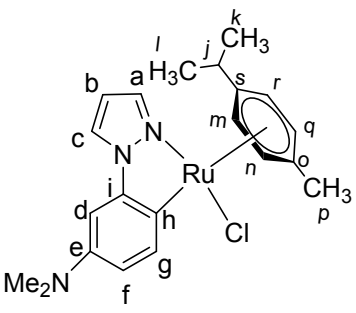
MHz, $CDCl_3$): δ 18.8 (C^p), 22.0 ($C^{k/l}$), 22.3 ($C^{k/l}$), 30.7 (C^j), 82.0 ($C^{n/q}$), 84.5 ($C^{m/r}$), 88.2 ($C^{m/r/n/q}$), 88.8 ($C^{m/r/n/q}$), 100.8 (C^s), 101.0 (C^o), 109.0 (C^b), 111.0(C^d), 120.8 (q, $^3J_{CF}$ = 3.8 Hz, C^e), 122.5 (q, $^1J_{CF}$ = 275.9 Hz, CF_3), 125.7 (C^c), 127.2 (q, $^2J_{CF}$ = 31.4 Hz, C^f), 136.4 (q, $^3J_{CF}$ = 3.3 Hz, C^g), 143.0 (C^a), 144.3 (C^i), 162.3 (C^h). ^{19}F {^1H} NMR (376 MHz, CDCl3): δ -61.4 (s, CF_3). Accurate MS-ESI *m/z* 447.0622, 488.0888 and 436.0323 (calculated), 447.0652, 488.0907 and 436.0322 (found), $[M–Cl]^+$, $[M–Cl + (MeCN0)]^+$ and $[M–Cl – (p\text{-cymene}) + 3(MeCN)]^+$ respectively $C_{20}H_{20}F_3N_2{}^{102}Ru$, $C_{22}H_{23}F_3N_3{}^{102}Ru$ and $C_{16}H_{15}F_3N_5{}^{102}Ru$.

Cyclometallation of 1-(4-nitrophenyl)-1*H*-pyrazole (L1-NO_2) with [$RuCl_2$(*p*-cymene)]$_2$



The general procedure was followed using [$RuCl_2$(*p*-cymene)]$_2$ (50 mg., 0.081 mmol), 1-(4-nitrophenyl)-1*H*-pyrazole (30.8 mg., 0.163) and NaOAc (13.7 mg., 0.167 mmol) in mixture of in dry MeOH (5 ml) and dry DCM (3 ml). The mixture was stirred for 96 hours at 40 ˚C. The product was precipitated from DCM / petroleum ether to give **1-NO_2** (38 mg., 51%) as brown/yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 0.96 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 2.11 (s, 3H, H^p), 2.43 (sept, 1H, *J* = 6.9 Hz, H^j), 5.19 (dd, 1H, *J* = 0.7, 5.8 Hz, $H^{n/q}$), 5.38 (dd, 1H, *J* = 0.7, 6.0 Hz, $H^{m/r}$), 5.62 (brd, 1H, *J* = 6.3 Hz, $H^{m/r/n/q}$), 5.65 (brd, 1H, *J* = 6.2 Hz, $H^{m/r/n/q}$), 6.56 (t, 1H, *J* = 2.4 Hz, H^b), 7.24 (d, 1H, *J* = 8.6 Hz, H^d) 7.93 (dd, 1H, *J* = 2.4, 8.6 Hz, H^e), 7.98 (brd, 1H, *J* = 2.7 Hz, H^c), 8.14 (brd, 1H, *J* = 2.0 Hz, H^a), 8.96 (d, 1H, *J* = 2.4 Hz, H^g). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 18.8 (C^p), 22.0 ($C^{k/l}$), 22.3 ($C^{k/l}$), 30.7 (C^j), 82.4 ($C^{n/q}$), 84.9 ($C^{m/r}$), 88.2 ($C^{m/r/n/q}$), 89.1 ($C^{m/r/n/q}$), 101.1 ($C^{s/o}$), 101.5 ($C^{s/o}$), 109.8 (C^b), 111.0 (C^d), 119.9 (C^e), 126.4 (C^c), 134.6 (C^g), 143.8 (C^a), 144.9 (C^i), 146.4 (C^f), 163.5 (C^h). Accurate MS-ESI *m/z* 424.0599, 465.0864 and 413.0300 (calculated), 424.0585, 465.0865 and 413.0261 (found), $[M–Cl]^+$, $[M–Cl + (MeCN)]^+$ and $[M–Cl – (p\text{-cymene}) + 3(MeCN)]^+$ respectively $C_{19}H_{20}N_3O_2{}^{102}Ru$, $C_{21}H_{23}N_4O_2{}^{102}Ru$ and $C_{15}H_{15}N_6O_2{}^{102}Ru$.

Cyclometallation of 1-(3-N,N-dimethylamine)-1*H*-pyrazole (L2-NMe_2) with [$RuCl_2$(*p*-cymene)]$_2$

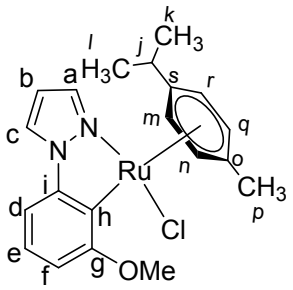


The general procedure was followed using [$RuCl_2$(*p*-cymene)]$_2$ (50 mg., 0.081 mmol), 1-(3-N,N- dimethylamine)-1H-pyrazole (30.5 mg., 0.163 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml). The mixture was stirred for 5 hours at room temperature. The product was precipitated from THF / petroleum ether to give **3-NMe_2** (45 mg., 60%) as brown/yellow crystals. ^1H NMR (400 MHz, $CDCl_3$) : δ 0.93 (d, 3H, *J* = 6.9, $H^{k/l}$), 0.97 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 2.02 (s, 3H, H^p), 2.45 (sept, 1H, *J* = 6.9 Hz, H^j), 2.90 (s, 6H, NMe_2), 5.04 (brd, 1H, *J* = 5.7 Hz, $H^{n/q}$), 5.25 (brd, 1H, *J* = 5.8 Hz, $H^{m/r}$), 5.5 (d, 1H, *J* = 5.8 Hz $H^{n/q}$), 5.53 (d, 1H, *J* = 5.7 Hz $H^{m/r}$), 6.43 (t, 1H, *J* = 2.4 Hz, H^b), 6.63 (d, 1H, *J* = 2.4 Hz, H^d), 6.67 (dd, 1H, *J* = 2.4, 8.5 Hz, H^f), 7.89 (d, 1H, *J* = 2.7 Hz, H^c), 7.94 (d,

1H, J = 8.2 Hz, H^g), 8.04 (d, 1H, J = 2.0 Hz, H^a). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.8 (C^p), 21.9 ($C^{k/l}$), 22.5 ($C^{k/l}$), 30.7 (C^j), 41.4 (NMe_2), 81.8 ($C^{n/q}$), 83.5 ($C^{m/r}$), 87.9 ($C^{m/r/n/q}$), 88.0 ($C^{m/r/n/q}$), 98.0 (C^d), 99.2 (C^s), 99.6 (C^o), 107.9 (C^b), 112.9 (C^f), 124.7 (C^c), 139.7 (C^g), 142.0 (C^a), 142.0 ($C^{h/i}$), 147.2 ($C^{h/i}$), 148.2 (C^e). Accurate MS-ESI *m/z* 422.1170 (calculated), 422.1156 (found), $[M–Cl]^+$ $C_{21}H_{26}N_3{}^{102}Ru$.

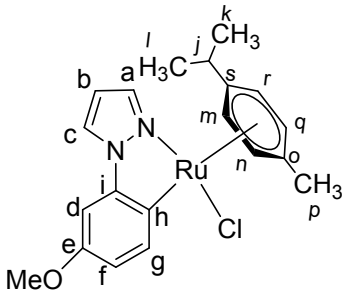
Cyclometallation of 1-(3-methoxyphenyl)-1*H*-pyrazole (L2-OMe) with $[RuCl_2(p\text{-cymene})]_2$

Isomer 2-OMe (ortho)



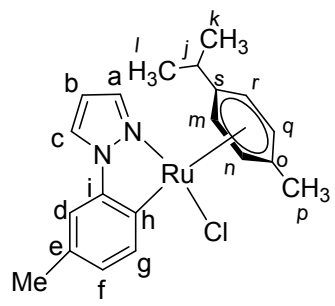
The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (50 mg., 0.081 mmol), 1-(3-methoxyphenyl)-1H-pyrazole (28.6 mg., 0.164 mmol) and NaOAc (13.7 mg., 0.167 mmol) were added in dry MeOH (10 ml). The mixture was stirred for 21 hours at room temperature. The product was precipitated from DCM / petroleum ether to give a mixture of **2-OMe** and **3-OMe** (41 mg., 56%) as brown/yellow crystals.^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 0.84 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.11 (s, 3H, H^p), 2.24 (sept, 1H, J = 6.9 Hz, H^j), 3.93 (s, 3H, OMe), 5.24 (dd, 1H, J = 1.2, 5.7 Hz, $H^{m/r/n/q}$), 5.39 (dd, 1H, J = 1.0, 6.0 Hz, $H^{m/r}$), 5.80 (dd, 1H, J = 1.0, 6.0 Hz, $H^{n/q}$), 5.95 (dd, 1H, J = 1.1, 5.7 Hz, $H^{m/r}$), 6.43 - 6.44 (m, 1H, H^b), 6.72 (dd, J = 0.8, 8.0 Hz, 1H, H^f), 6.90 (dd. J = 0.9,7.8 Hz, 1H, H^d), 7.03 (t, 1H, J = 7.9 Hz, H^e), 7.88 (dd, 1H, J = 0.3, 2.7 Hz, H^c), 8.04 (overlapping d, H^a). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 19.0 (C^p), 22.2($C^{k/l}$), 22.3 ($C^{k/l}$), 30.8 (C^j), 56.8 (OMe), 79.6 ($C^{m/r/n/q}$), 85.6($C^{m/r}$), 86.1($C^{m/r}$), 88.7 ($C^{n/q}$), 98.1 (C^s), 103.1 (C^o), 105.7 (C^d), 108.2 (C^b), 109.1 (C^f), 124.5 (C^e), 125.3 (C^c), 142.2 (C^a), 143.0 ($C^{h/i}$), 148.4 ($C^{h/i}$), 165.8 (C^g). Accurate MS-ESI *m/z* 409.0845 and 450.1119 (calculated), 409.0849 and 450.1125 (found), $[M–Cl]^+$ and $[M–Cl + (MeCN)]^+$ respectively $C_{20}H_{23}N_2O^{102}Ru$ and $C_{22}H_{26}N_3O^{102}Ru$.

Isomer 3-OMe (para)



^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 0.96 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.04 (s, 3H, H^p), 2.43 (sept, 1H, J = 6.9 Hz, H^j), 3.78 (s, 3H, OMe), 5.03 (dd, 1H, J = 0.8, 5.9 Hz, $H^{n/q}$), 5.24 (dd, 1H, J = 1.2, 5.7 Hz, $H^{m/r/n/q}$), 5.53 (overlapping d, 2H, $H^{m/r/n/q}$), 6.43 - 6.44 (m, 1H, H^b), 6.75 (dd, 1H, J = 2.5Hz, 8.0, H^f), 6.77 (d, 1H, J = 2.4 H^d), 7.86 (brd, 1H, J = 2.6 Hz, H^c), 7.98 (d, 1H, J = 8.0 Hz, H^g), 8.04 (overlapping d, H^a). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.8 (C^p), 21.9 ($C^{k/l}$), 22.4 ($C^{k/l}$), 30.7 (C^j), 55.6 (OMe), 81.7 ($C^{n/q}$), 83.6 ($C^{m/r/n/q}$), 87.9 ($C^{m/r/n/q}$), 88.3 ($C^{m/r/n/q}$), 98.9 ($C^{d/f}$), 99.8(C^s), 99.9 (C^o), 108.3 (C^b), 112.1 ($C^{d/f}$), 125.1 (C^c), 139.9 (C^g isomer A), 141.8 ($C^{h/i}$), 142.3 (C^a), 150.7 ($C^{h/i}$), 156.8 (C^e). Accurate MS-ESI *m/z* 409.0845 and 450.1119 (calculated), 409.0849 and 450.1125 (found), $[M–Cl]^+$ and $[M–Cl + (MeCN)]^+$ respectively $C_{20}H_{23}N_2O^{102}Ru$ and $C_{22}H_{26}N_3O^{102}Ru$.

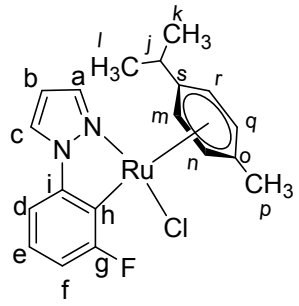
Cyclometallation of 1-(3-methylphenyl)-1*H*-pyrazole (L2-Me) with [$RuCl_2$(*p*-cymene)]$_2$



The general procedure was followed using [$RuCl_2$(*p*-cymene)]$_2$ (50 mg., 0.081 mmol), 1-(3-methylphenyl)-1H-pyrazole (26.0 mg., 0.164 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml). The mixture was stirred for 24 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **3-Me** (39 mg., 55%) as brown/yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.92 (d, 3H, J = 6.9, $H^{k/l}$), 0.97 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.03 (s, 3H, H^p), 2.33(s, 3H, Me), 2.44 (sept, 1H, J = 7.0 Hz, H^j), 5.06 (brd, 1H, J = 5.4 Hz, $H^{n/q}$), 5.26 (brd, 1H, J = 5.8 Hz, $H^{m/r}$), 5.53 (overlapping d, 2H, $H^{m/r/n/q}$), 6.44 (t, 1H, J = 2.4 Hz, H^b), 6.93 (dd, 1H, J = 0.8, 7.5 Hz, H^f), 6.99 (brs, 1H, H^d), 7.88 (brd, 1H, J = 2.7 Hz, H^c), 7.99 (d, 1H, J = 7.6 Hz, H^g), 8.03 (brd, 1H, J = 2.0 Hz, H^a). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 18.8 (C^p), 21.04 (Me), 21.9 ($C^{k/l}$), 22.4 ($C^{k/l}$), 30.7 (C^j), 82.1 ($C^{n/q}$), 83.8 ($C^{m/r}$), 88.1 ($C^{m/r/n/q}$), 88.3 ($C^{m/r/n/q}$), 99.5 (C^s), 100.1 (C^o), 108.1(C^b), 112.3 (C^d), 124.7 (C^c), 127.1 (C^f), 132.7 (C^e), 139.7 (C^g), 141.7 (C^i), 142.0 (C^a), 157.4 (C^h). Accurate MS-ESI *m/z* 393.0905 and 434.1170 (calculated), 393.0912 and 434.1178 (found), $[M–Cl]^+$ and $[M–Cl + (MeCN)]^+$ respectively $C_{20}H_{23}N_2{}^{102}Ru$ and $C_{22}H_{26}N_3{}^{102}Ru$.

Cyclometallation of 1-(3-fluoromethylphenyl)-1*H*-pyrazole (L2-F) with [$RuCl_2$ (*p*-cymene)]$_2$

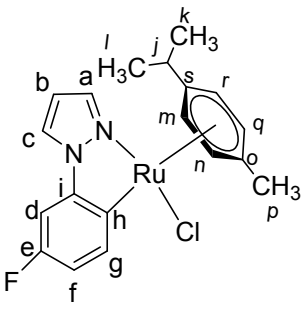
Isomer 2-F (ortho)



The general procedure was followed using [$RuCl_2$(*p*-cymene)]$_2$(50 mg., 0.081 mmol), 1-[(3-fluoromethyl]phenyl)-1*H*-pyrazole (26.4 mg., 0.163 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml) . The mixture was stirred for 5 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **2-F** and **3-F** (59 mg., 84%) as brown/yellow crystals. Recrystallisation gave a sample of pure **2-F**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (d, 3H, J = 6.8 Hz, $H^{k/l}$), 0.89 (d, 3H, J = 6.8 Hz, $H^{k/l}$), 2.12 (s, 3H, H^p), 2.33 (sept, 1H, J = 6.9 Hz, H^j), 5.32 (brd, 1H, J = 5.8 Hz, $H^{n/q}$), 5.47 (brd, 1H, J = 6.0 Hz, $H^{m/r}$), 5.79 (brd, 1H, J = 5.9 $H^{n/q}$), 5.88 (brd, 1H, J = 5.8 $H^{m/r}$), 6.47 (t, 1H, J = 2.5 Hz, H^b), 6.83 – 6.90 (m, 1H, J = Hz, H^f), 6.97 – 7.02 (m, 2H, $H^{d/e}$), 7.90 (brd, 1H, J = 2.7 Hz, H^c), 8.05 (brd, 1H, J = 2.0 Hz, H^a). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 19.0 (C^p), 22.1 ($C^{k/l}$), 22.3 ($C^{k/l}$), 30.8 (C^j), 79.8 (d, J_{CF} = 2.8 Hz, $C^{n/q}$), 85.5 ($C^{m/r}$), 85.7 (d, J_{CF} = 3.8 Hz, $C^{m/r}$), 88.7 ($C^{n/q}$), 99.6 (C^s), 102.5 (C^o), 107.7 (C^d), 108.6 (C^b), 112.3 (d, $^2J_{CF}$ = 30.5 Hz, C^f), 124.7 (d, $^3J_{CF}$ = 8.7 Hz, C^e), 125.6 (C^c), 142.5 (C^a), 143.6 (d, $^2J_{CF}$ = 50.2, Hz, C^h), 144.0 (d, $^3J_{CF}$ = 19.4 Hz, C^i), 169.0 (d, $^1J_{CF}$ = 232 Hz, C^g). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -91.5 (s, F). Accurate MS-ESI *m/z* 397.0654, 432.0343, 303.9824 and 345.0089 (calculated), 397.0670, 432.0364, 303.9826 and 345.0081 (found), $[M–Cl]^+$,

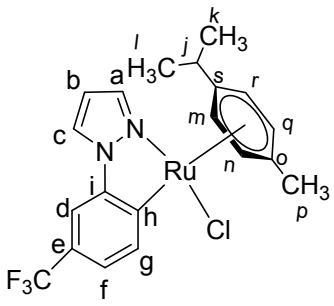
$[M]^+$, [M–Cl – (*p*-cymene) + (MeCN)] and [M–Cl – (*p*-cymene) + 2(MeCN)]$C_{19}H_{20}FN_2{}^{102}Ru$, $C_{19}H_{20}FN_2{}^{102}RuCl$, $C_{11}H_9FN_3{}^{102}Ru$ and $C_{13}H_{12}FN_4{}^{102}Ru$.

Isomer 3-F



^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 0.96 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 2.05 (s, 3H, H^p), 2.43 (sept, 1H, *J* = 6.9 Hz, H^j), 5.04 (dd, 1H, *J* = 0.8, 5.8 Hz, $H^{n/q}$), 5.26(dd, 1H, *J* = 0.8, 5.8 Hz, $H^{m/r}$), 5.55 (overlapping d, 2H, $H^{n/q/m/r}$), 6.46 – 6.48 (m, 1H, H^b), 6.83 – 6.93 (m, 2H, *J* = Hz, H^{d+f}), 7.85 (brd, 1H, *J* = 2.5 Hz, H^c), 8.20 (dd, 1H, $J_{H\text{-}F}$ = 6.4, $J_{H\text{-}H}$ = 8.2, Hz, H^g), 8.05 (overlapping d, 1H, H^a). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.8 (C^p), 21.9 ($C^{k/l}$), 30.7 (C^j), 81.7 ($C^{n/q}$), 83.9 ($C^{m/r}$), 88.0 ($C^{n/q/m/r}$), 88.5 ($C^{n/q/m/r}$), 99.6 (d, $^2J_{CF}$ = 25.6 $C^{d/f}$), 102.2 ($C^{s/o}$), 100.5 ($C^{s/o}$), 108.7 (C^b), 112.8 (d, $^2J_{CF}$ = 19.1 Hz, $C^{d/f}$), 125.3 (C^c), 142.7 (C^a), 143.9 (d, $^3J_{CF}$ = 19.1 Hz, C^i), $C^{k/l}$, C^e, C^g and C^h signals are difficult to see due to hidden under major *ortho* isomer (**2-F**). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -121.3 (s, F). Accurate MS-ESI *m/z* 397.0654, 432.0343, 303.9824 and 345.0089 (calculated), 397.0670, 432.0364, 303.9826 and 345.0081 (found), $[M–Cl]^+$, $[M]^+$, [M–Cl – *p*-cymene + MeCN] and [M–Cl – (*p*-cymene) + 2(MeCN)] $C_{19}H_{20}FN_2{}^{102}Ru$, $C_{19}H_{20}FN_2{}^{102}RuCl$, $C_{11}H_9FN_3{}^{102}Ru$ and $C_{13}H_{12}FN_4{}^{102}Ru$.

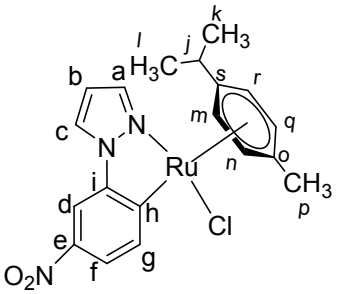
Cyclometallation of 1-(3-trifluoromethylphenyl)-1*H*-pyrazole (L2-CF_3) with [$RuCl_2$ (*p*-cymene)]$_2$



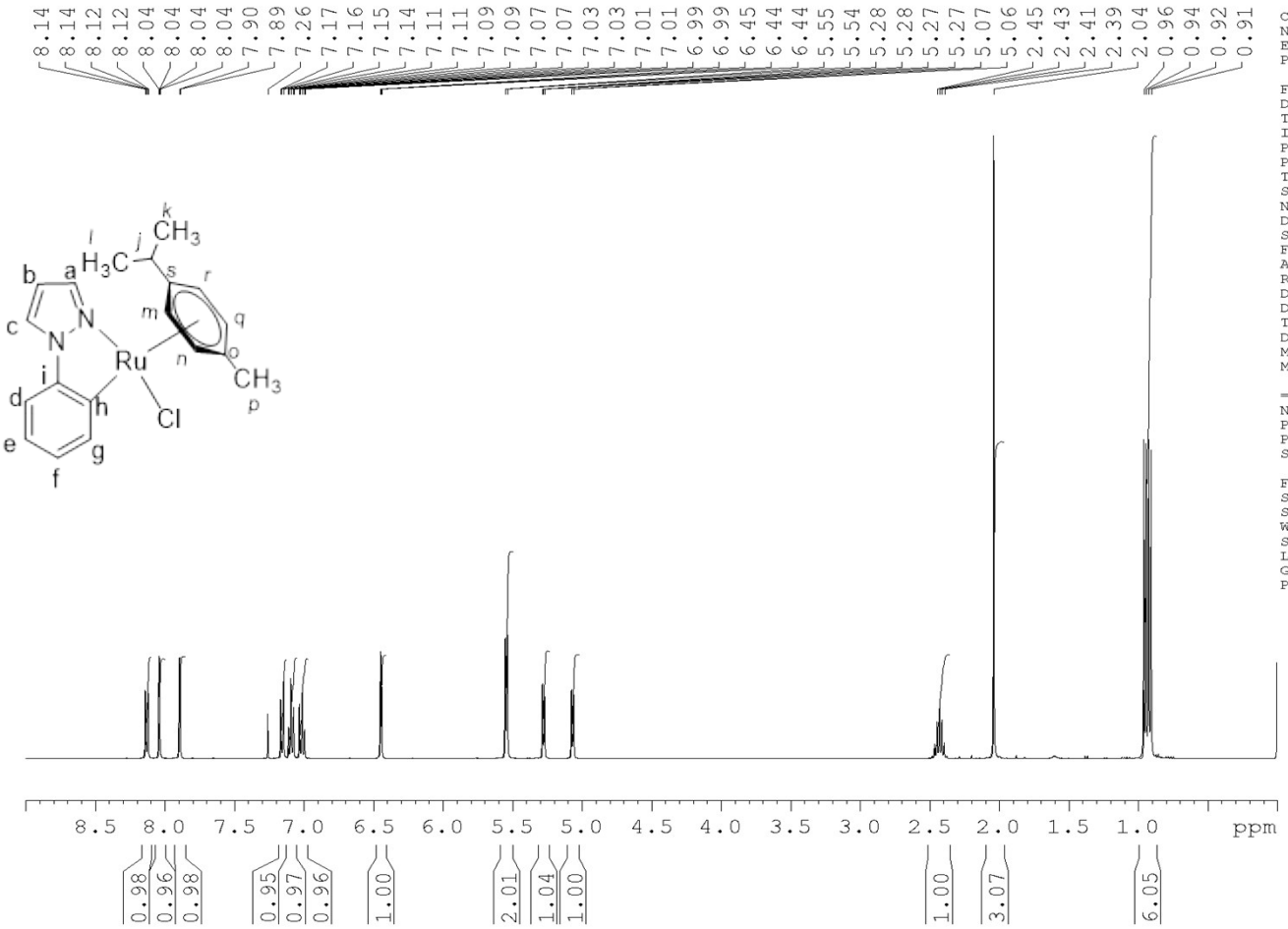
The general procedure was followed using [$RuCl_2$(*p*-cymene)]$_2$ (50 mg., 0.081 mmol), 1-[(3 trifluoromethyl]phenyl)-1*H*-pyrazole (34.7 mg., 0.163 mmol) and NaOAc (16.4 mg., 0.2 mmol) in dry MeOH (5 ml). The mixture was stirred for 85 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **3-CF_3** (41 mg., 52%) as brown/yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 0.97 (d, 3H, *J* = 6.9 Hz, $H^{k/l}$), 2.06 (s, 3H, H^p), 2.44 (sept, 1H, *J* = 6.9 Hz, H^j), 5.10 (brd, 1H, *J* = 5.8 Hz, $H^{n/q}$), 5.32 (brd, 1H, *J* = 5.8 Hz, $H^{m/r}$), 5.58 (overlapping d, 2H, *J* = 5.1, 5.4 $H^{m/r/n/q}$), 6.52 (t, 1H, *J* = 2.3 Hz, H^b), 7.32 (brd, 1H, *J* = 8.2 Hz, H^f), 7.35 (brs, 1H, H^d), 7.97 (brd, 1H, *J* = 2.7 Hz, H^c), 8.08 (brd, 1H, *J* = 2.0 Hz, H^a), 8.24 (d, 1H, *J* = 7.7, H^g). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.7 (C^p), 21.9 ($C^{k/l}$), 22.3 ($C^{k/l}$), 30.6 (C^j), 82.5 ($C^{n/q}$), 84.6 ($C^{m/r}$), 88.2 ($C^{m/r/n/q}$), 88.9 ($C^{m/r/n/q}$), 100.7 (C^s), 101.1 (C^o), 107.7 (q, $^3J_{CF}$ = 3.7 Hz, C^d), 108.9 (C^b), 122.0 (q, $^3J_{CF}$ = 3.3 Hz, C^f), 124.7 (q, $^1J_{CF}$ = 271.4 Hz, CF_3), 125.5 (q, $^2J_{CF}$ = 32.4 Hz, C^e), 125.5 (C^c), 141.9 (C^i), 140.4 (C^g), 142.9 (C^a), 168.7 (C^h). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -61.7 (s, CF_3). Accurate MS-ESI *m/z* 447.0622, 488.0888 and 436.0323(calculated), 447.0653, 488.0915

and 436.0331 (found), $[M–Cl]^+$, $[M–Cl + (MeCN)]^+$ and $[M–Cl – p\text{-cymene} + 3xMeCN]^+$ respectively $C_{20}H_{20}F_3N_2{}^{102}Ru$, $C_{22}H_{23}F_3N_3{}^{102}Ru$ and $C_{16}H_{15}F_3N_5{}^{102}Ru$.

Cyclometallation of 1-(3-nitrophenyl)-1*H*-pyrazole (L2-NO_2) with $[RuCl_2(p\text{-cymene})]_2$



The general procedure was followed using $[RuCl_2(p\text{-cymene})]_2$ (50 mg., 0.081 mmol), 1-[(3-nitrophenyl)-1*H*-pyrazole (31.0 mg., 0.163 mmol) and NaOAc (13.7 mg., 0.167 mmol) in dry MeOH (5 ml). The mixture was stirred for 85 hours at room temperature. The product was precipitated from DCM / petroleum ether to give **3-NO_2** (39 mg., 52%) as brown/yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 0.97 (d, 3H, J = 6.9 Hz, $H^{k/l}$), 2.09 (s, 3H, H^p), 2.44 (sept, 1H, J = 6.9 Hz, H^j), 5.14 (brd, 1H, J = 5.8 Hz, $H^{n/q}$), 5.35 (brd, 1H, J =5.9 Hz, $H^{m/r}$), 5.60 (brd, 1H, J = 5.9 Hz, $H^{m/r}$), 5.64 (brd, 1H, J = 6.0 Hz, $H^{n/q}$), 6.58 (t, 1H, J = 2.4 Hz, H^b), 7.95 (dd, 1H, J = 2.1, 8.2 Hz, H^f), 8.00 (d, 1H, J = 2.2 Hz, H^d), 8.06 (brd, 1H, J = 2.8 Hz, H^c), 8.10 (brd, 1H, J = 2.1 Hz, H^a), 8.30 (d, 1H, J = 8.2 Hz, H^g). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.8 (C^p), 22.0 ($C^{k/l}$), 22.3($C^{k/l}$), 30.7 (C^j), 82.8 ($C^{n/q}$), 85.1 ($C^{m/r}$), 88.6 ($C^{m/r}$), 89.5 ($C^{n/q}$), 101.9 (C^s), 101.9 (C^o), 105.6 (C^d), 109.4 (C^b), 119.8 (C^f), 126.0 (C^c), 140.3 (C^g), 142.2 ($C^{e/i}$), 143.3 (C^a), 144.8 ($C^{e/i}$), 177.6 (C^h). Accurate MS-ESI *m/z* in MeCN 413.0300 (calculated), 413.0299 (found), $[M–Cl – (p\text{-cymene}) + 3(MeCN)]^+$ $C_{15}H_{15}N_6O_2{}^{102}Ru$ whilst in MeOH 424.0599 (calculated), 424.0606 (found), $[M–Cl]^+$ $C_{19}H_{20}N_3O_2{}^{102}Ru$.



Current Data Parameters

NAME	RAAA172
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

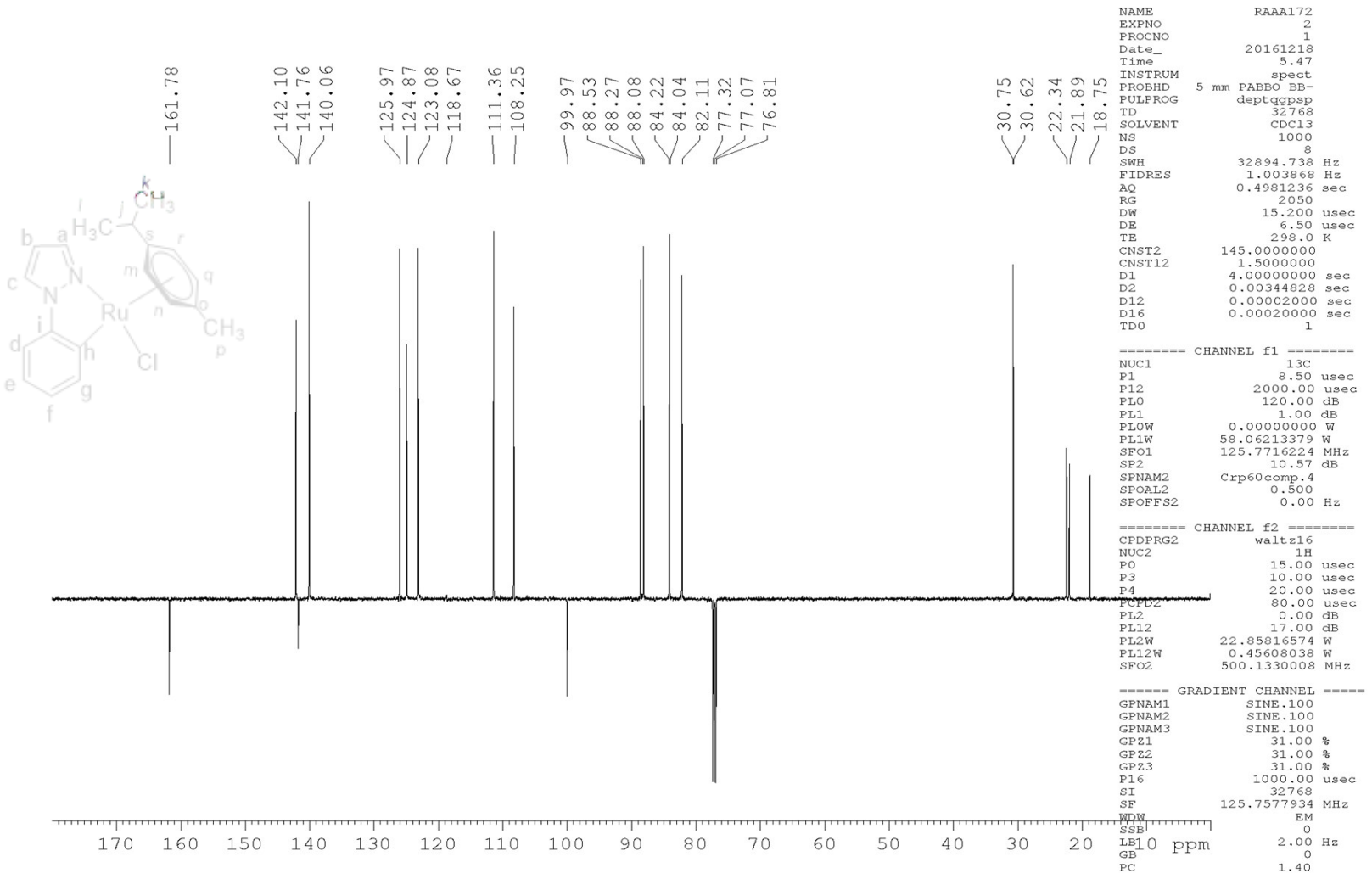
Date_	20161217
Time	16.49
INSTRUM	drx400
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	32768
SOLVENT	CDC13
NS	16
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 sec
RG	161.3
DW	78.000 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

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

F2 - Processing parameters

SI	32768
SF	400.1300100 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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EXPNO	2
PROCNO	1
Date_	20161218
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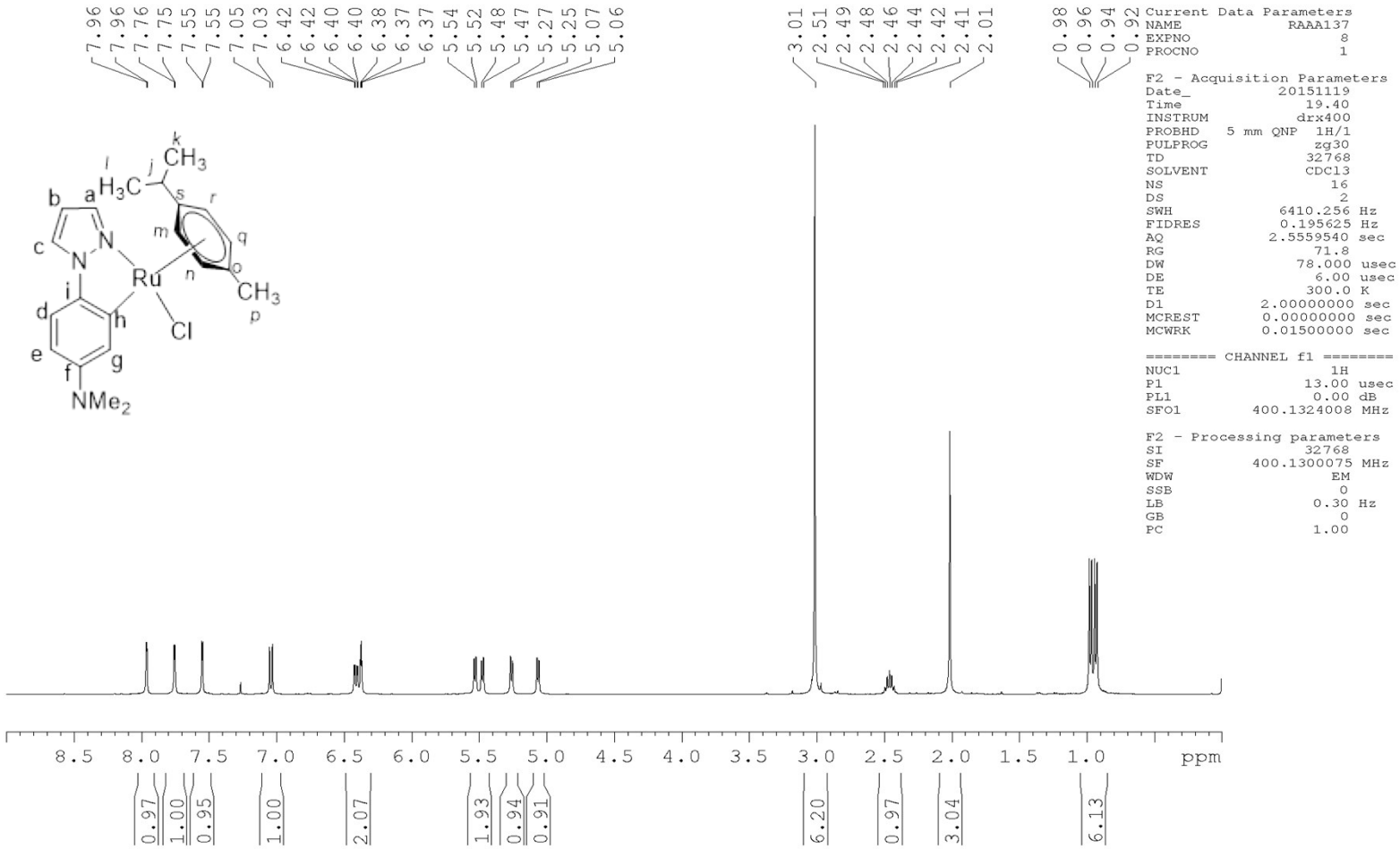
PULPROG	deptqgpsp
TD	32768
SOLVENT	CDCl3
NS	1000
DS	8
SWH	32894.738 Hz
FIDRES	1.003868 Hz
AQ	0.4981236 sec
RG	2050
DW	15.200 usec
DE	6.50 usec
TE	298.0 K
CNST2	145.0000000
CNST12	1.5000000
D1	4.00000000 sec
D2	0.00344828 sec
D12	0.00002000 sec
D16	0.00020000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	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
SPOAL2	0.500
SPOFFS2	0.00 Hz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
P0	15.00 usec
P3	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	125.7577934 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40

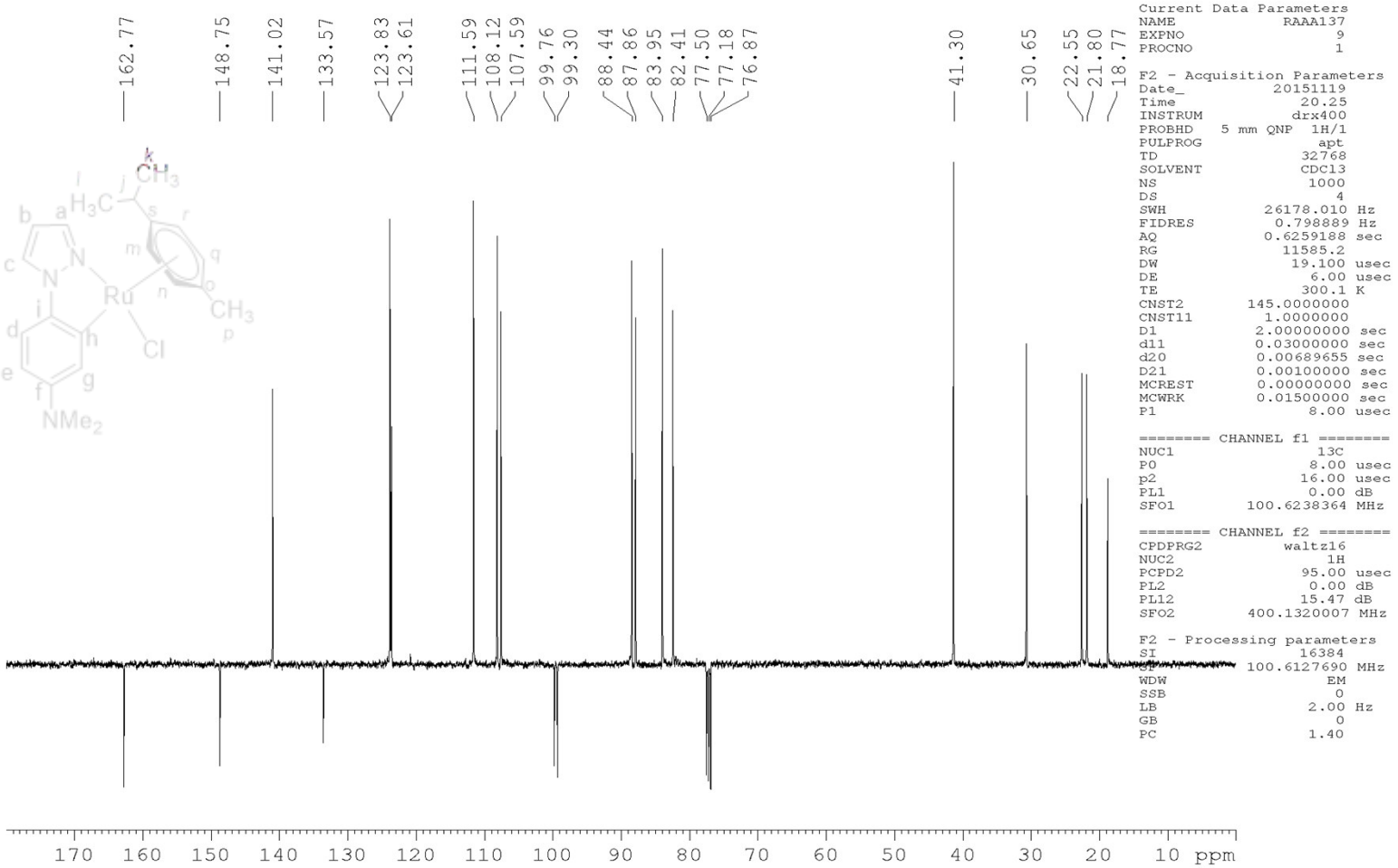


Current Data Parameters
NAME RAAA137
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151119
Time 19.40
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 71.8
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 400.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


162.77
148.75
141.02
133.57
123.83
123.61
111.59
108.12
107.59
99.76
99.30
88.44
87.86
83.95
82.41
77.50
77.18
76.87
41.30
30.65
22.55
21.80
18.77
Current Data Parameters
NAME RAAA137
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151119
Time 20.25
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 300.1 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
F2 - Processing parameters
SI 16384
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
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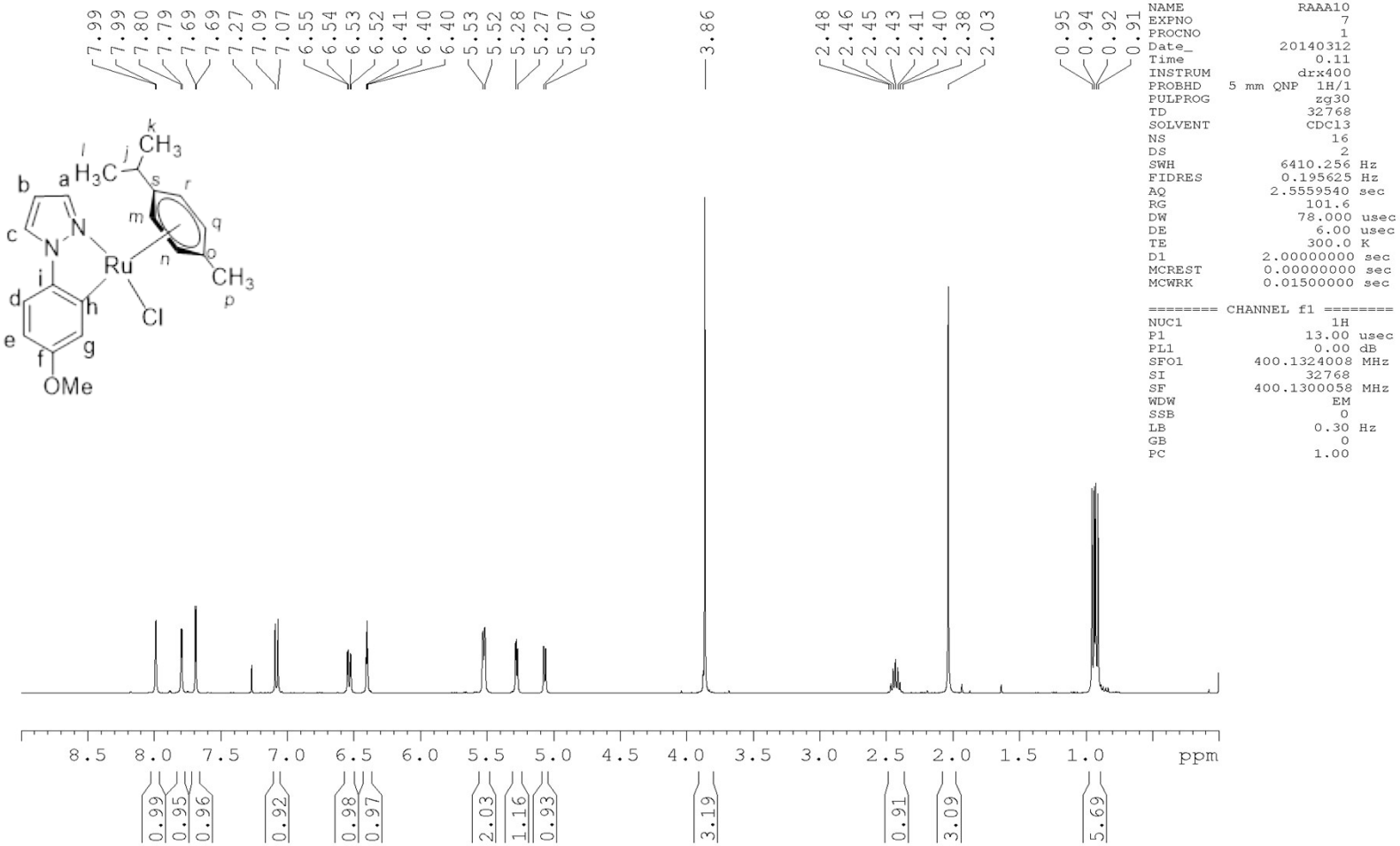
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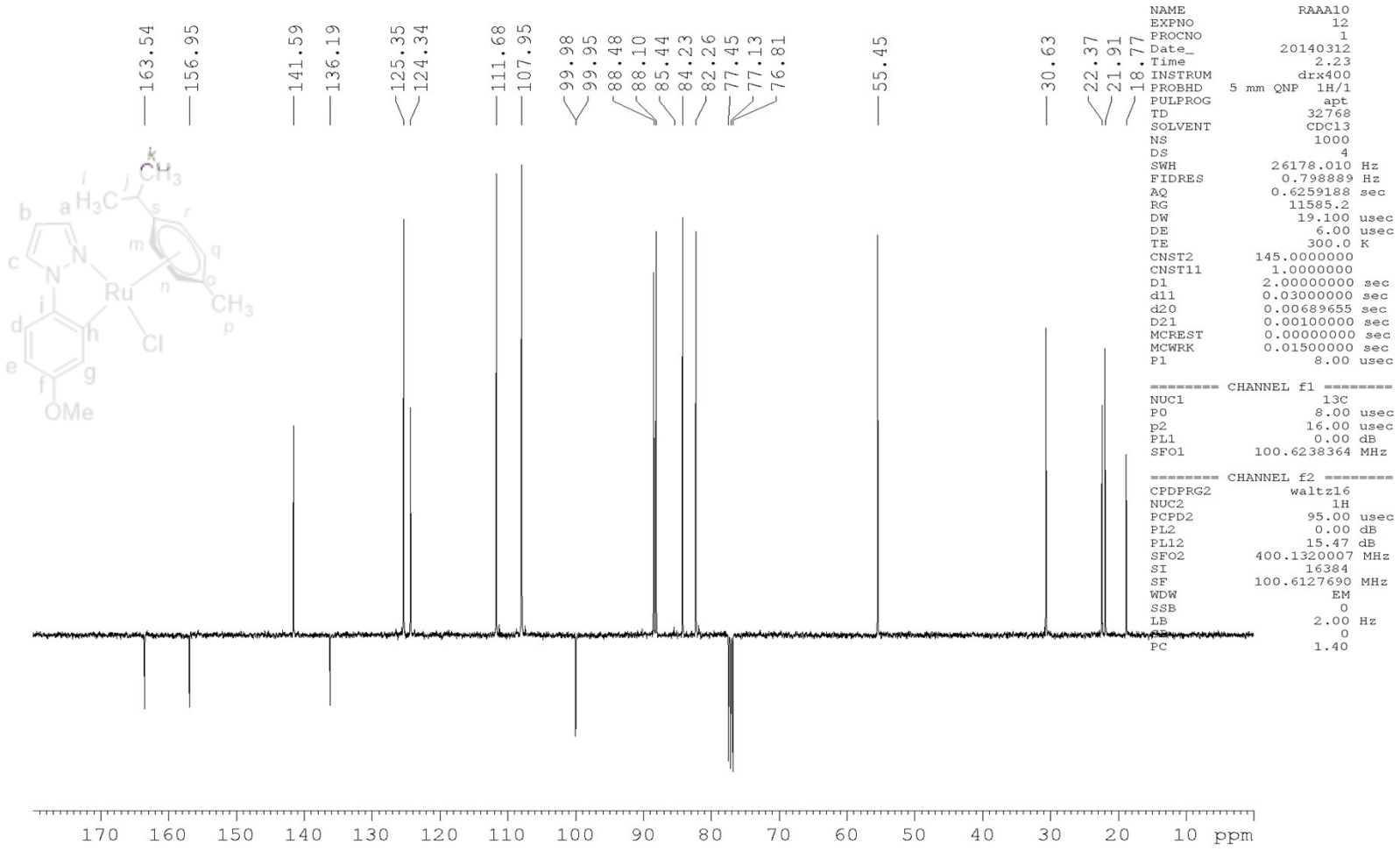
7.99
7.80
7.79
7.69
7.69
7.27
7.09
7.07
6.55
6.54
6.53
6.52
6.41
6.40
6.40
5.53
5.52
5.28
5.27
5.07
5.06
3.86
2.48
2.46
2.45
2.43
2.41
2.40
2.38
2.03
0.95
0.94
0.92
0.91
NAME RAAA10
EXPNO 7
PROCNO 1
Date_ 20140312
Time 0.11
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 101.6
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 400.1300058 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ru
Cl
OMe
ppm
0.99
0.95
0.96
0.92
0.98
0.97
2.03
1.16
0.93
3.19
0.91
3.09
5.69


163.54
156.95
141.59
136.19
125.35
124.34
111.68
107.95
99.98
99.95
88.48
88.10
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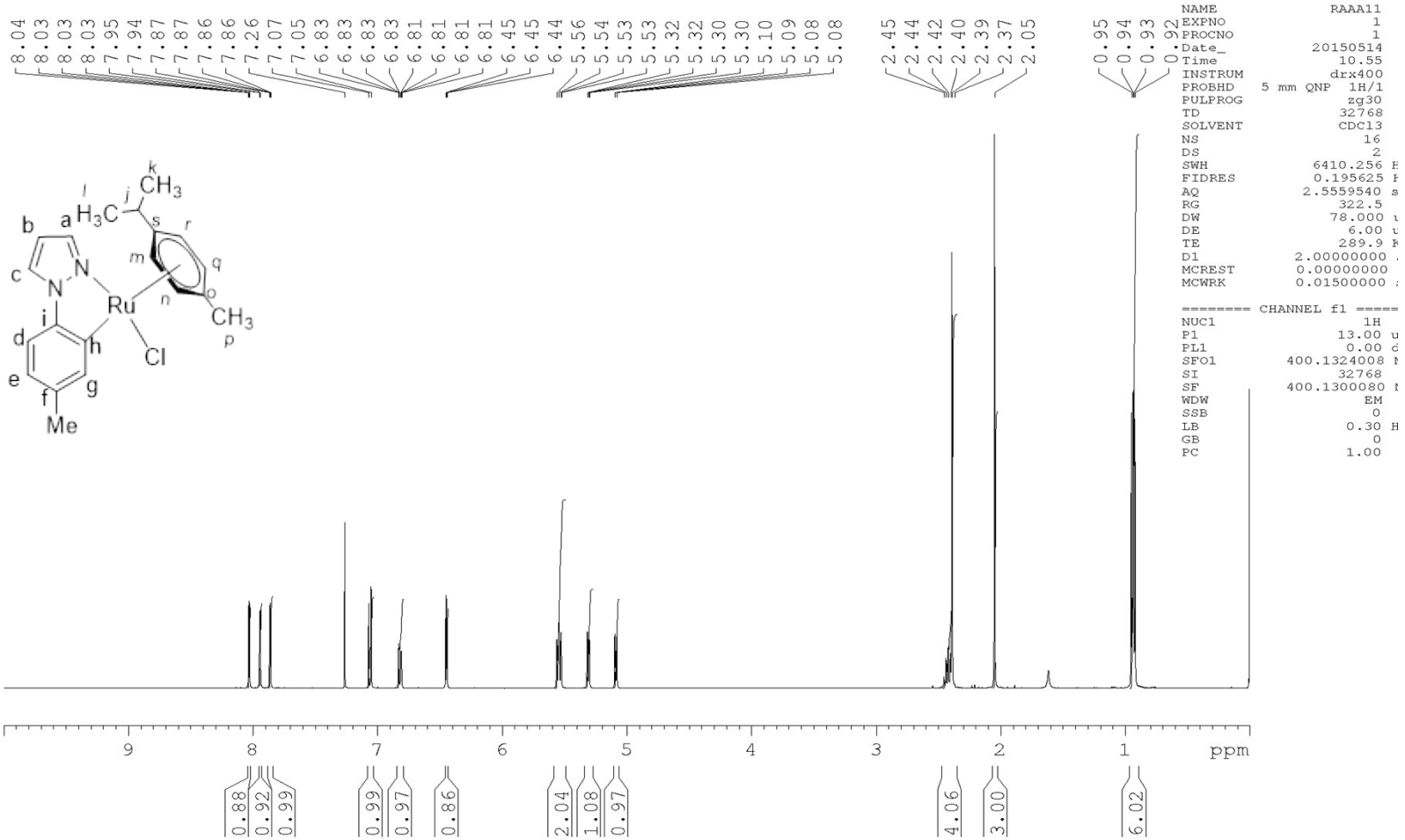
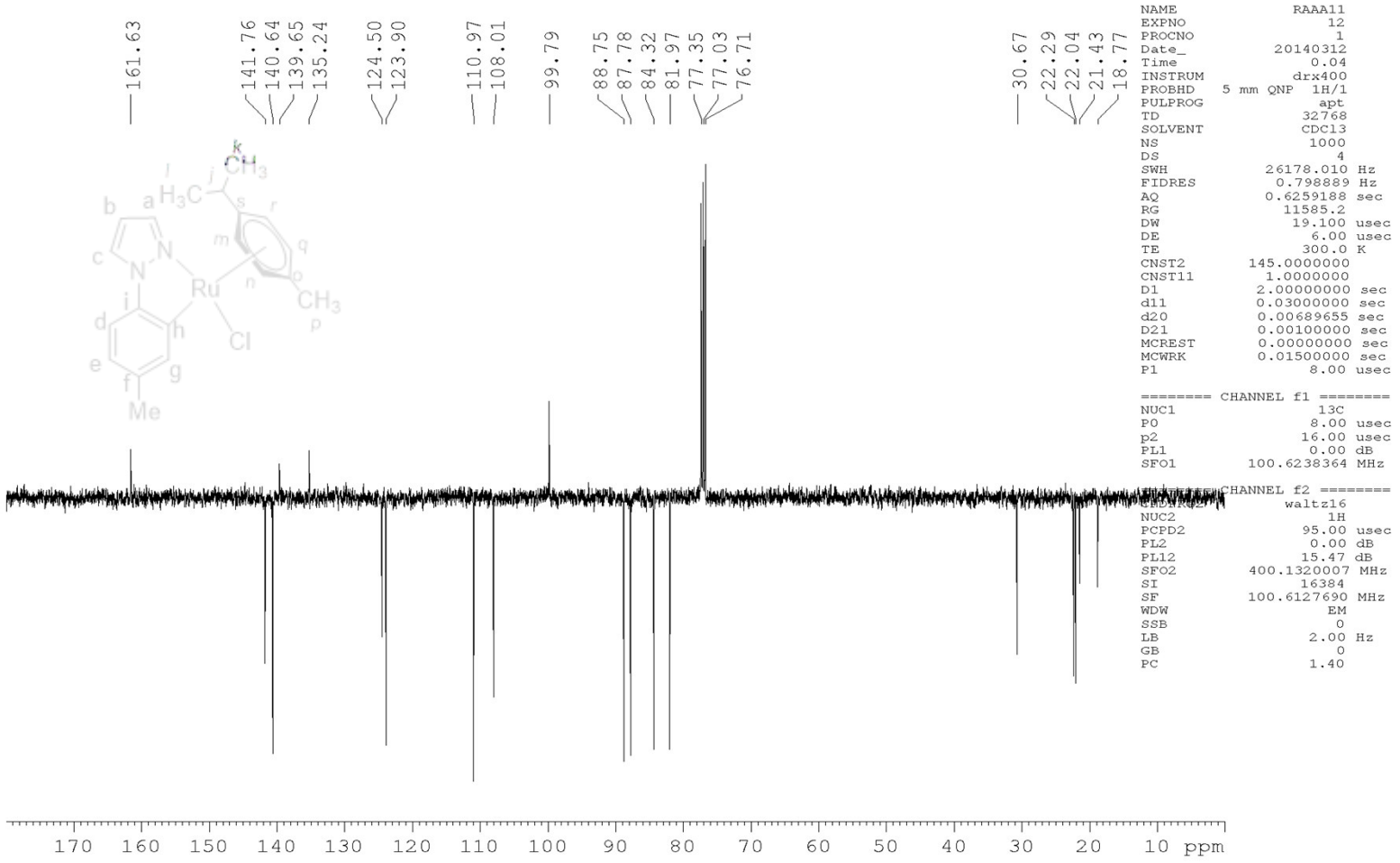
84.23
82.26
77.45
77.13
76.81
55.45
30.63
22.37
21.91
18.77
NAME RAAA10
EXPNO 12
PROCNO 1
Date_ 20140312
Time 2.23
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG apt
TD 32768
SOLVENT CDCl3
NS 1000
DS 4
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 11585.2
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 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
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.04 8.03 8.03 8.03 7.95 7.94 7.87 7.87 7.86 7.86 7.26 7.07 7.05 6.83 6.83 6.83 6.81 6.81 6.81 6.81 6.45 6.45 6.44 5.56 5.54 5.53 5.53 5.32 5.32 5.30 5.30 5.10 5.09 5.08 5.08
2.45 2.44 2.42 2.40 2.39 2.37 2.05
0.95 0.94 0.93 0.92
NAME RAAA11
EXPNO 1
PROCNO 1
Date_ 20150514
Time 10.55
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256
FIDRES 0.195625
AQ 2.5559540
RG 322.5
DW 78.000
DE 6.00
TE 289.9
D1 2.00000000
MCREST 0.00000000
MCWRK 0.01500000
======== CHANNEL f1 ======
NUC1 1H
P1 13.00
PL1 0.00
SFO1 400.1324008
SI 32768
SF 400.1300080
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
Ru
Cl
CH3
Me
9 8 7 6 5 4 3 2 1 ppm
0.88 0.92 0.99 0.99 0.97 0.86 2.04 1.08 0.97 4.06 3.00 6.02



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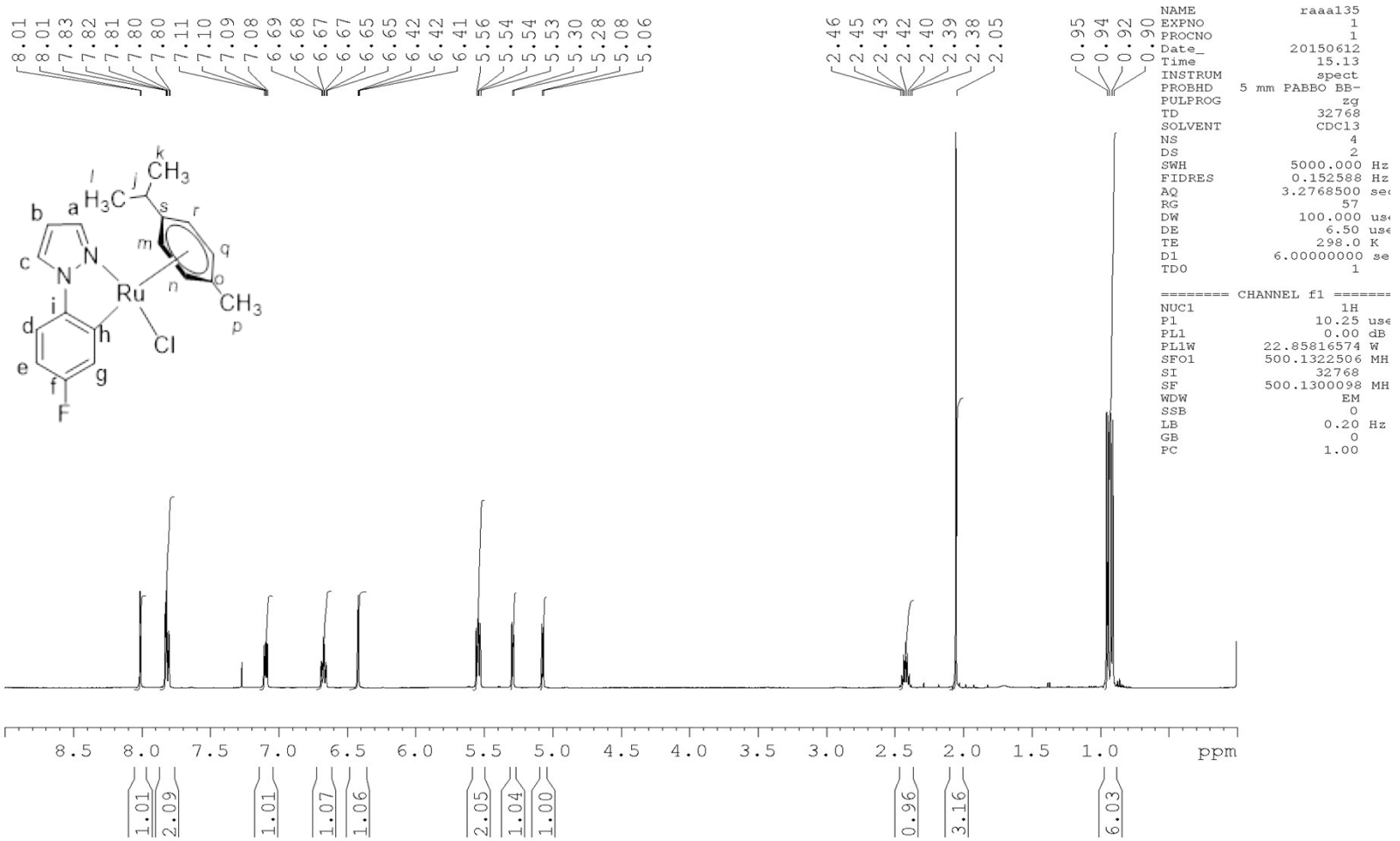
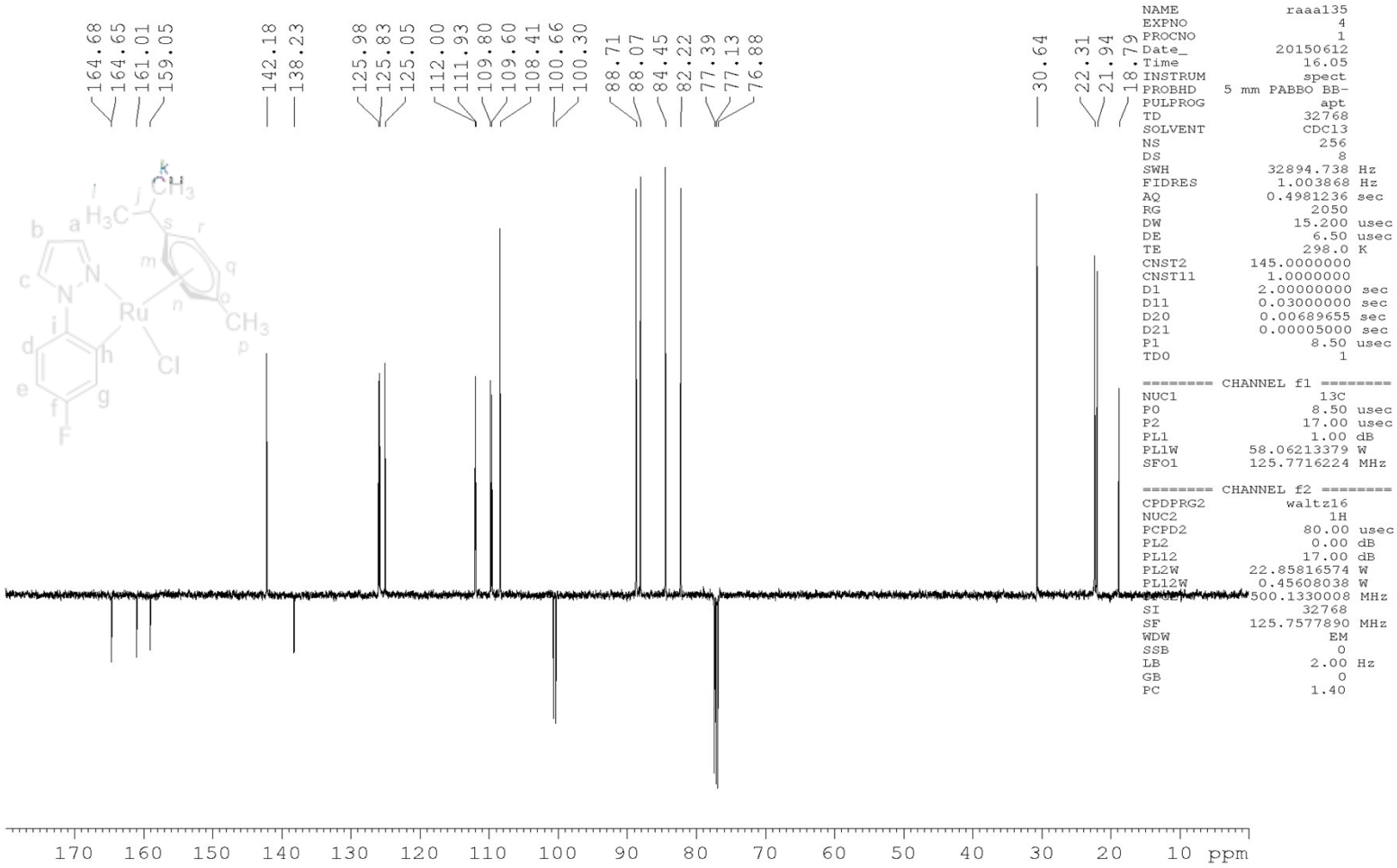
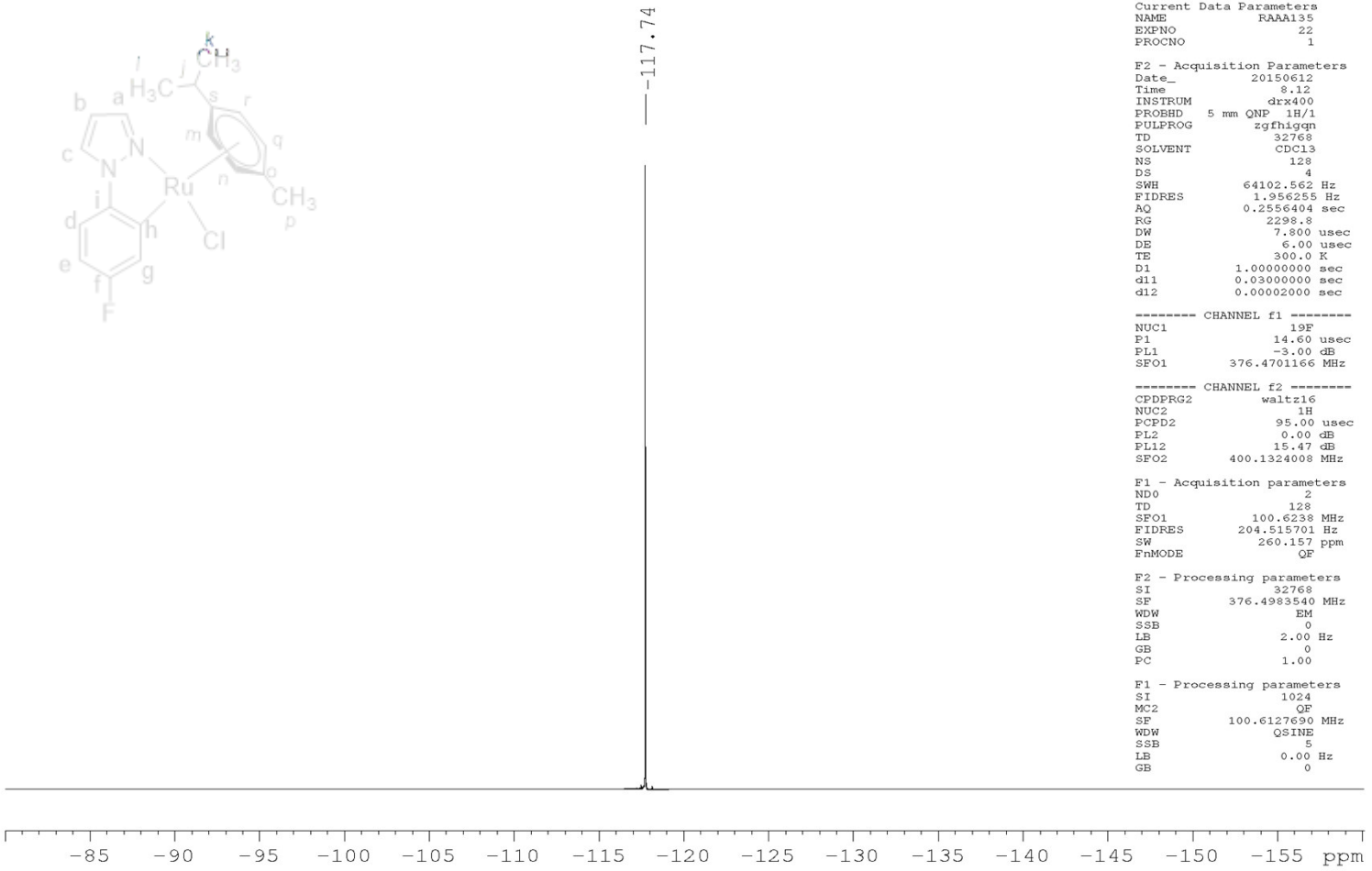
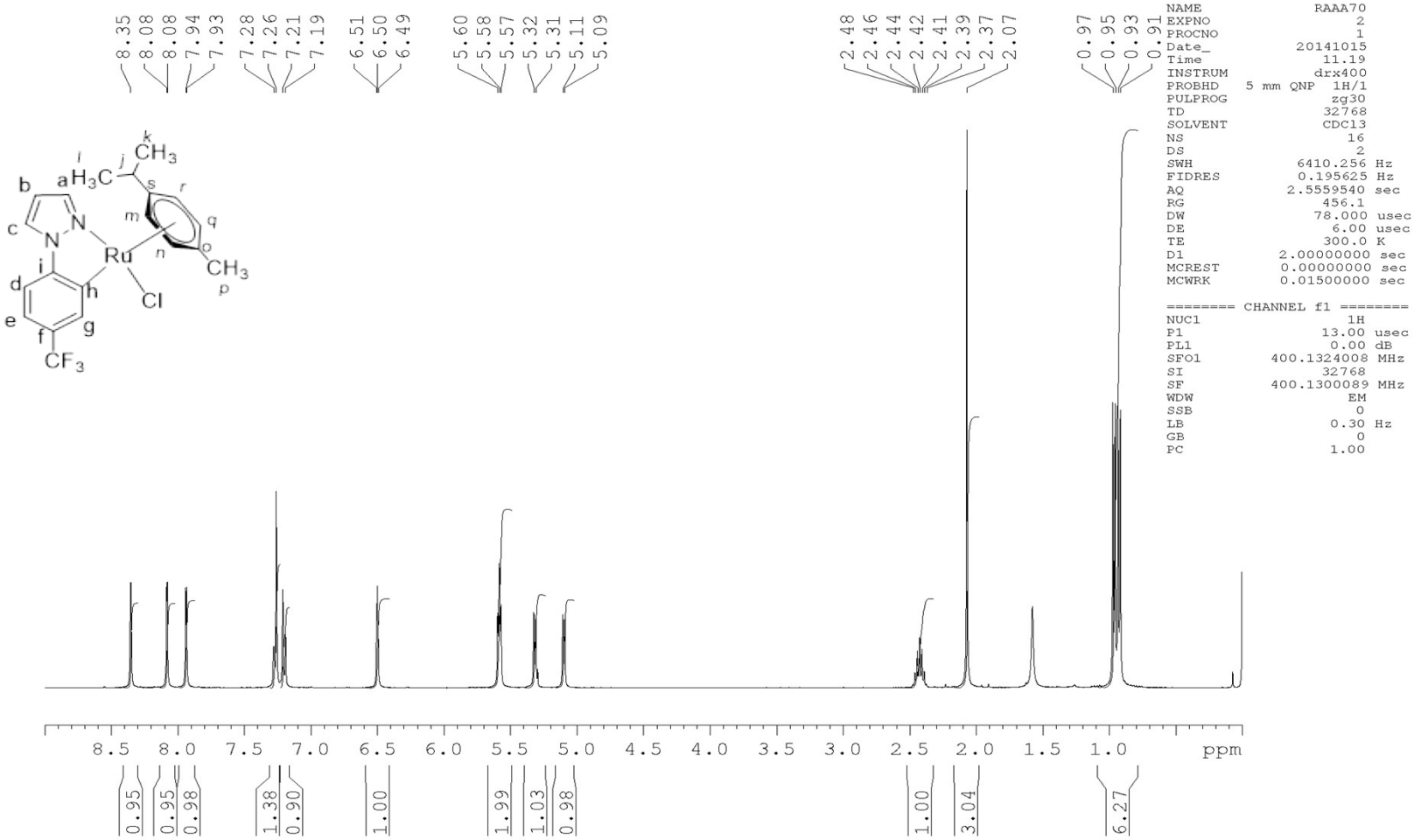
EXPNO	12
PROCNO	1
Date_	20140312
Time	0.04
INSTRUM	drx400
PROBHD	5 mm QNP 1H/1
PULPROG	apt
TD	32768
SOLVENT	CDCl3
NS	1000
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	11585.2
DW	19.100 usec
DE	6.00 usec
TE	300.0 K
CNST2	145.0000000
CNST11	1.0000000
D1	2.00000000 sec
d11	0.03000000 sec
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 ========	
[illegible]	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

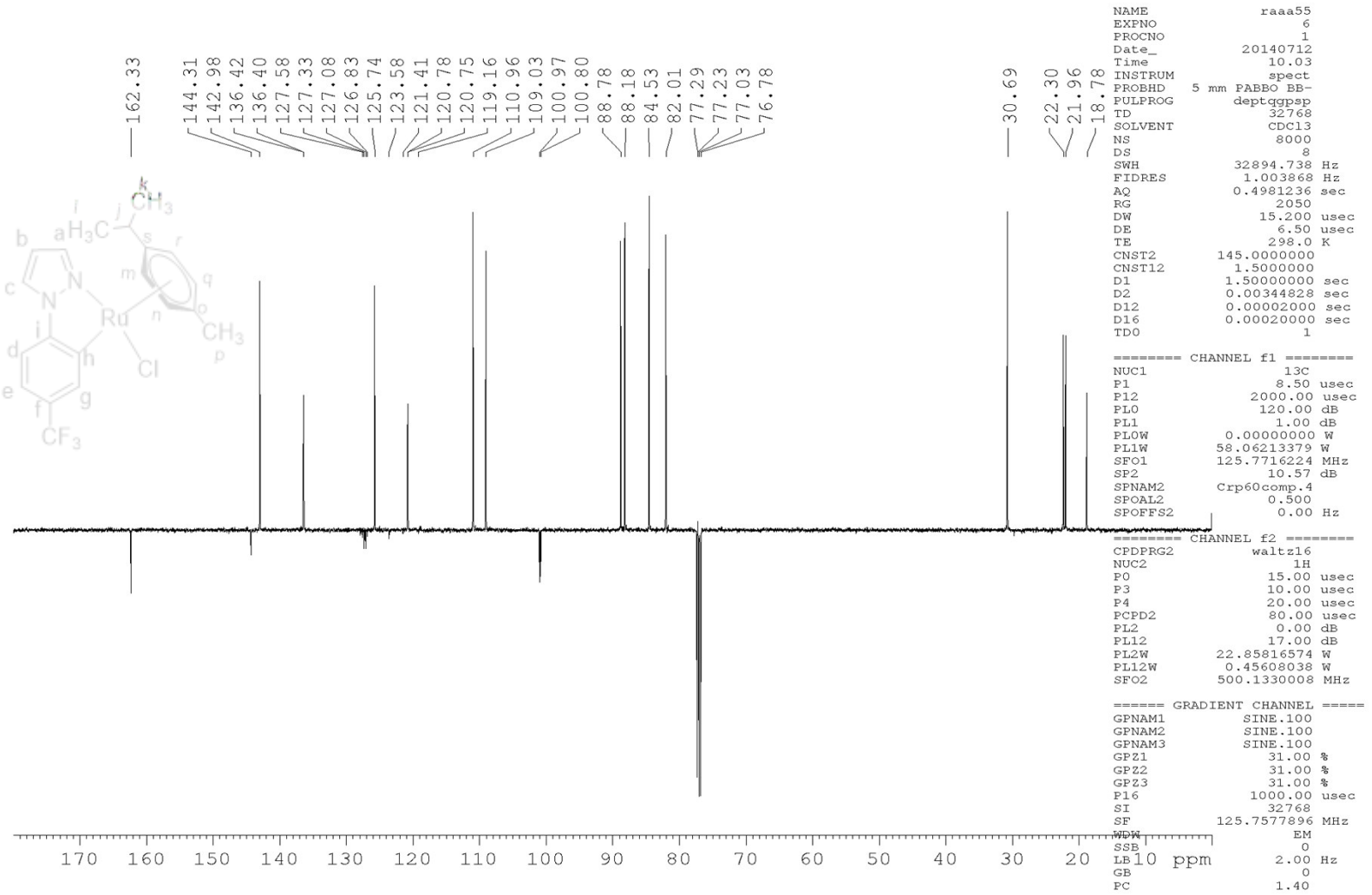

8.01 8.01 7.83 7.82 7.81 7.80 7.80 7.11 7.10 7.09 7.08 6.69 6.68 6.67 6.67 6.65 6.65 6.42 6.42 6.41 5.56 5.54 5.54 5.53 5.30 5.28 5.08 5.06
2.46 2.45 2.43 2.42 2.40 2.39 2.38 2.05
0.95 0.94 0.92 0.90
NAME raaa135
EXPNO 1
PROCNO 1
Date_ 20150612
Time 15.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDC13
NS 4
DS 2
SWH 5000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 se
RG 57
DW 100.000 us
DE 6.50 us
TE 298.0 K
D1 6.00000000 se
TD0 1
======== CHANNEL f1 =======
NUC1 1H
P1 10.25 us
PL1 0.00 dB
PL1W 22.85816574 W
SFO1 500.1322506 MH
SI 32768
SF 500.1300098 MH
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
Ru
Cl
F
ppm
1.01 2.09 1.01 1.07 1.06 2.05 1.04 1.00 0.96 3.16 6.03


164.68
164.65
161.01
159.05
142.18
138.23
125.98
125.83
125.05
112.00
111.93
109.80
109.60
108.41
100.66
100.30
88.71
88.07
84.45
82.22
77.39
77.13
76.88
30.64
22.31
21.94
18.79
NAME raaa135
EXPNO 4
PROCNO 1
Date_ 20150612
Time 16.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG apt
TD 32768
SOLVENT CDCl3
NS 256
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
CNST11 1.0000000
D1 2.00000000 sec
D11 0.03000000 sec
D20 0.00689655 sec
D21 0.00005000 sec
P1 8.50 usec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P0 8.50 usec
P2 17.00 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
PL2W 22.85816574 W
PL12W 0.45608038 W
SFO2 500.1330008 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

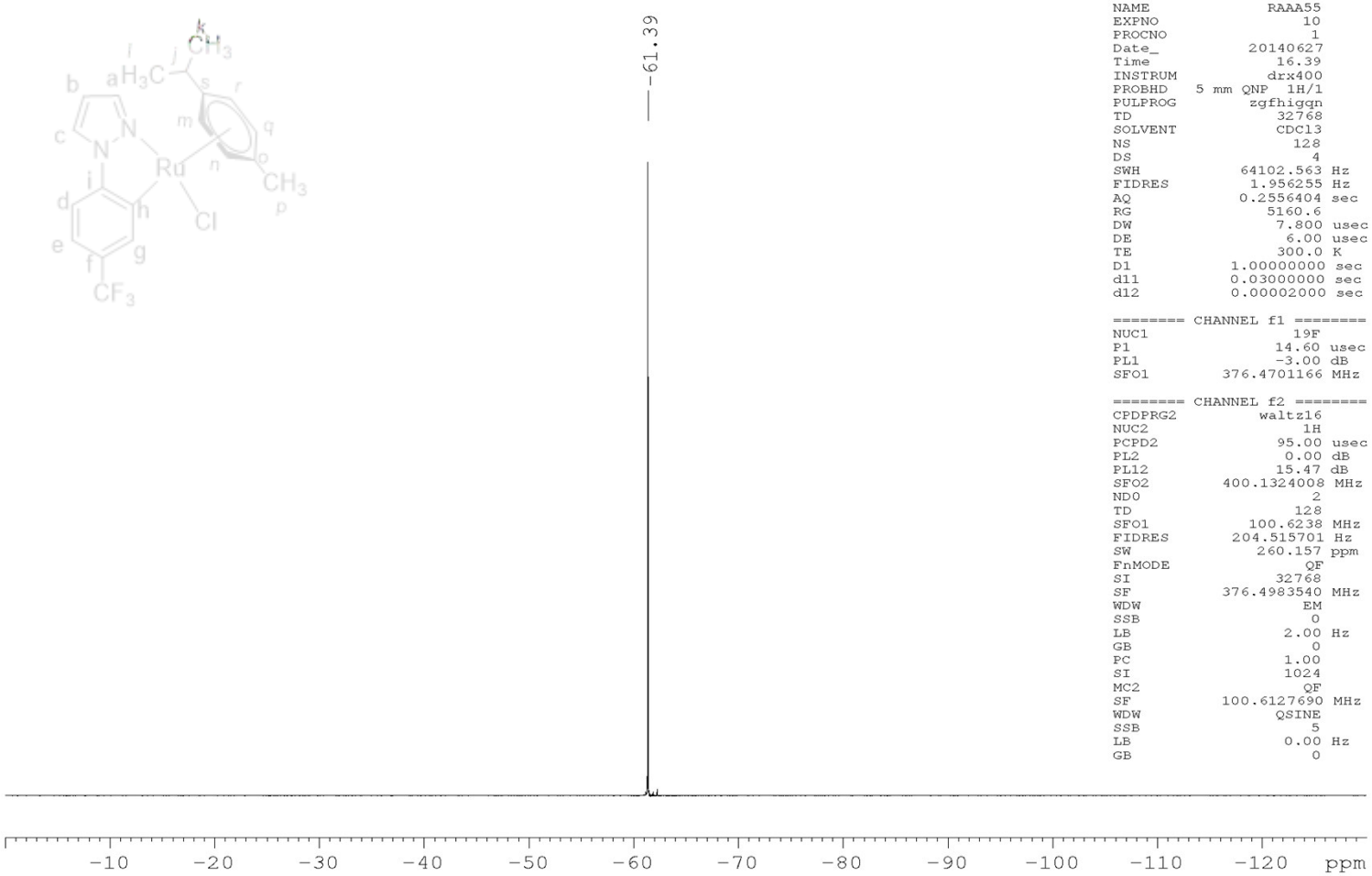



```
Current Data Parameters
NAME                  RAAA135
EXPNO                      22
PROCNO                      1

F2 - Acquisition Parameters
Date_               20150612
Time                    8.12
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                    2298.8
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
```

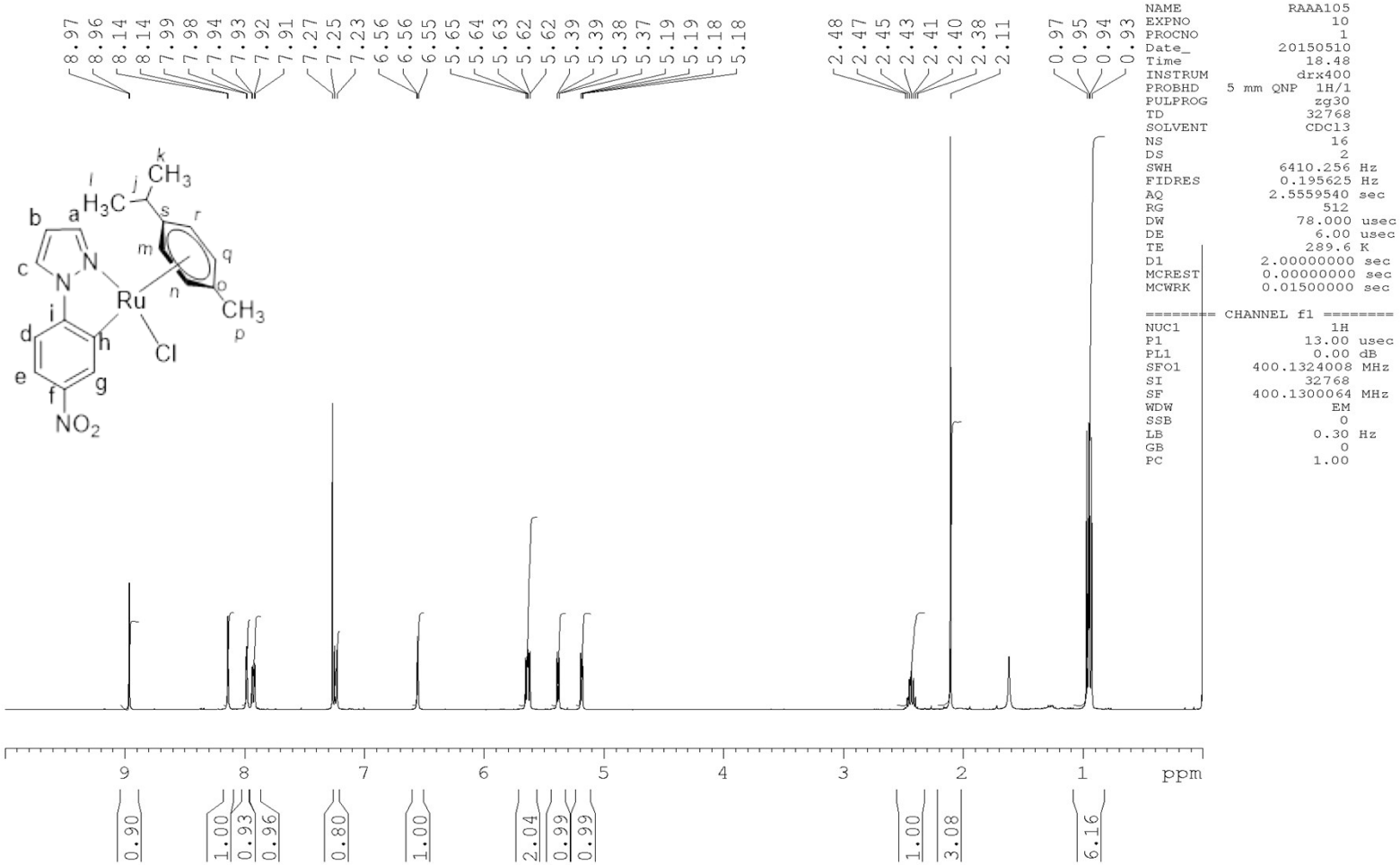

8.35
8.08
8.08
7.94
7.93
7.28
7.26
7.21
7.19
6.51
6.50
6.49
5.60
5.58
5.57
5.32
5.31
5.11
5.09
2.48
2.46
2.44
2.42
2.41
2.39
2.37
2.07
0.97
0.95
0.93
0.91
NAME RAAA70
EXPNO 2
PROCNO 1
Date_ 20141015
Time 11.19
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 456.1
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 400.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ru
Cl
CH3
CF3
ppm
0.95
0.95
0.98
1.38
0.90
1.00
1.99
1.03
0.98
1.00
3.04
6.27

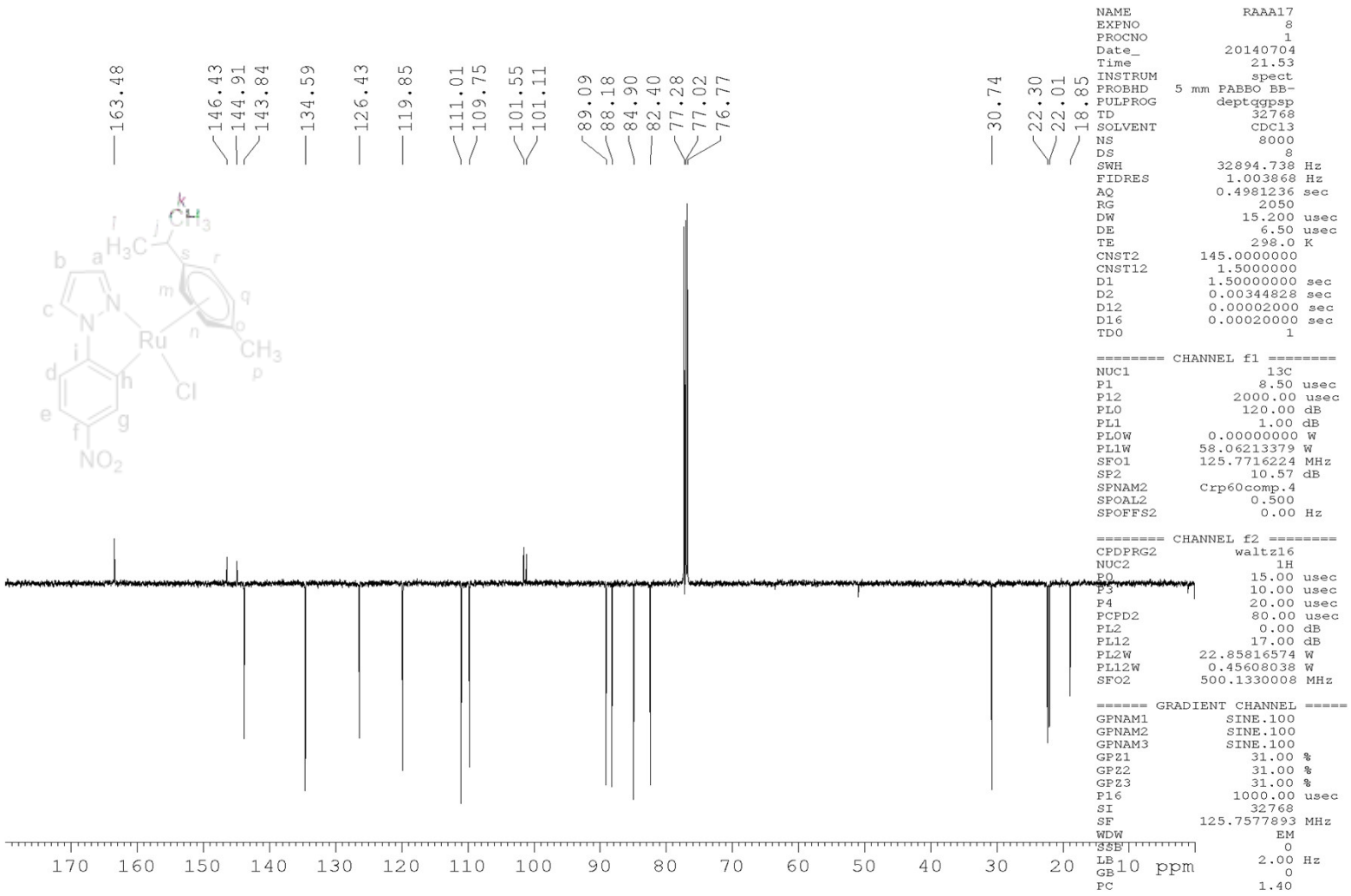


NAME	raaa55
EXPNO	6
PROCNO	1
Date_	20140712
Time	10.03
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	deptqgpsp
TD	32768
SOLVENT	CDCl3
NS	8000
DS	8
SWH	32894.738 Hz
FIDRES	1.003868 Hz
AQ	0.4981236 sec
RG	2050
DW	15.200 usec
DE	6.50 usec
TE	298.0 K
CNST2	145.0000000
CNST12	1.5000000
D1	1.50000000 sec
D2	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
SPOAL2	0.500
SPOFFS2	0.00 Hz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
P0	15.00 usec
P3	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	125.7577896 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40

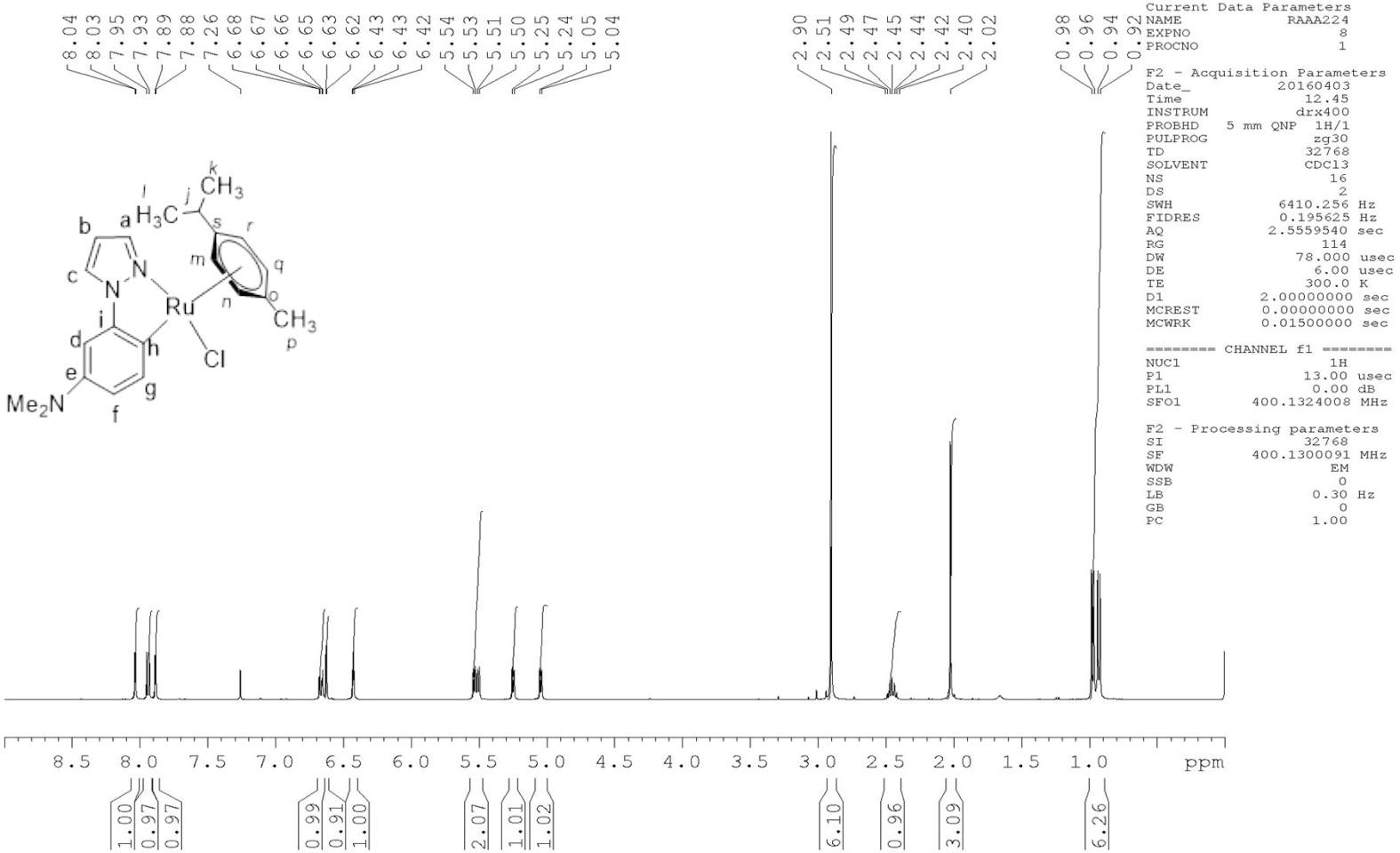


NAME	RAAA55
EXPNO	10
PROCNO	1
Date_	20140627
Time	16.39
INSTRUM	drx400
PROBHD	5 mm QNP 1H/1
PULPROG	zgfhigqn
TD	32768
SOLVENT	CDCl3
NS	128
DS	4
SWH	64102.563 Hz
FIDRES	1.956255 Hz
AQ	0.2556404 sec
RG	5160.6
DW	7.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
======== 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


8.97
8.96
8.14
8.14
7.99
7.98
7.94
7.93
7.92
7.91
7.27
7.25
7.23
6.56
6.56
6.55
5.65
5.64
5.63
5.62
5.62
5.39
5.39
5.38
5.37
5.19
5.19
5.18
5.18
2.48
2.47
2.45
2.43
2.41
2.40
2.38
2.11
0.97
0.95
0.94
0.93
NAME RAAA105
EXPNO 10
PROCNO 1
Date_ 20150510
Time 18.48
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 512
DW 78.000 usec
DE 6.00 usec
TE 289.6 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 400.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ru
Cl
CH3
NO2
ppm
0.90
1.00
0.93
0.96
0.80
1.00
2.04
0.99
0.99
1.00
3.08
6.16



NAME	RAAA17
EXPNO	8
PROCNO	1
Date_	20140704
Time	21.53
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	deptqgpsp
TD	32768
SOLVENT	CDCl3
NS	8000
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	1.50000000 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
SPOAL2	0.500
SPOFFS2	0.00 Hz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
P0	15.00 usec
P3	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	125.7577893 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40



Current Data Parameters

NAME	RAAA224
EXPNO	8
PROCNO	1

F2 - Acquisition Parameters

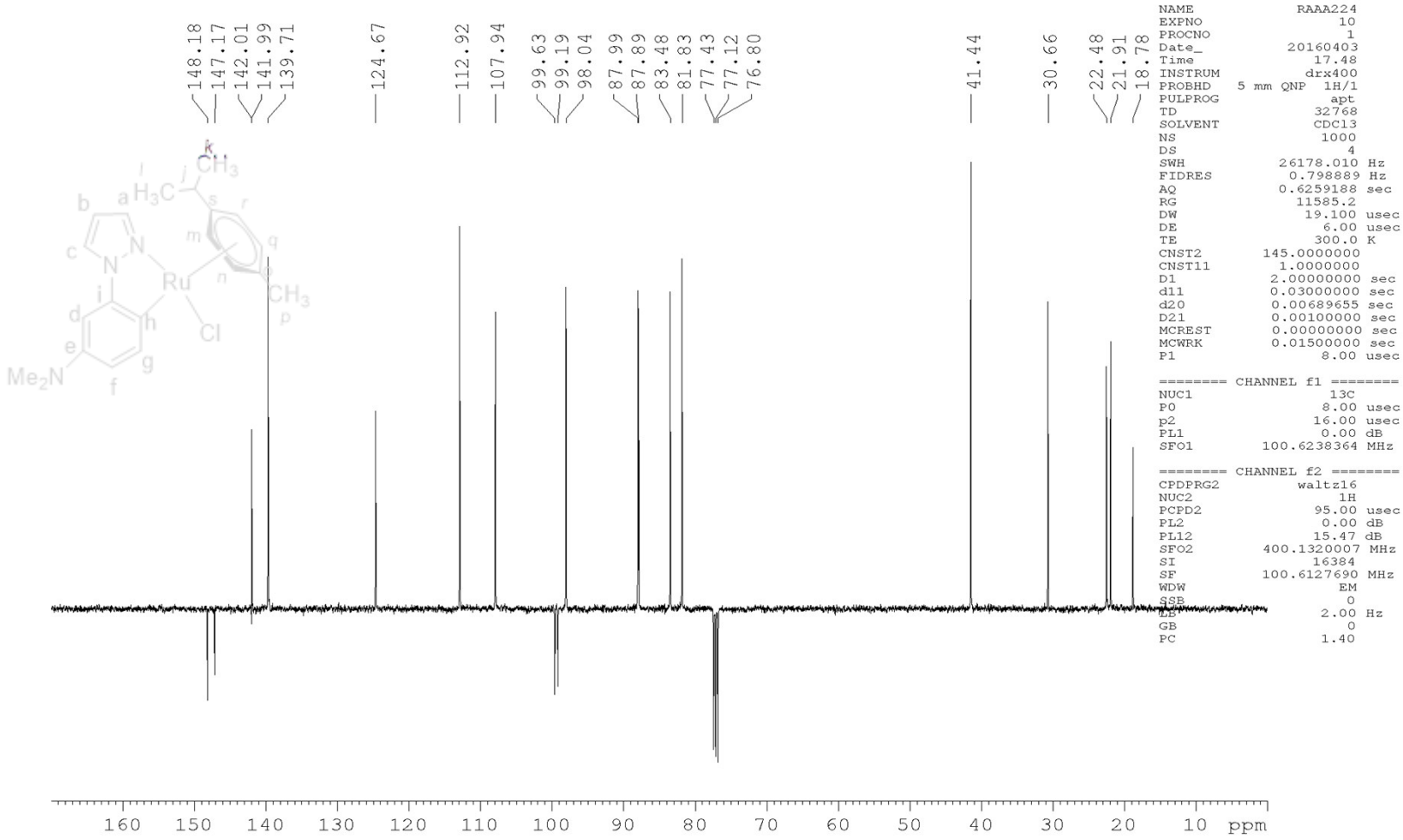
Date_	20160403
Time	12.45
INSTRUM	drx400
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 sec
RG	114
DW	78.000 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

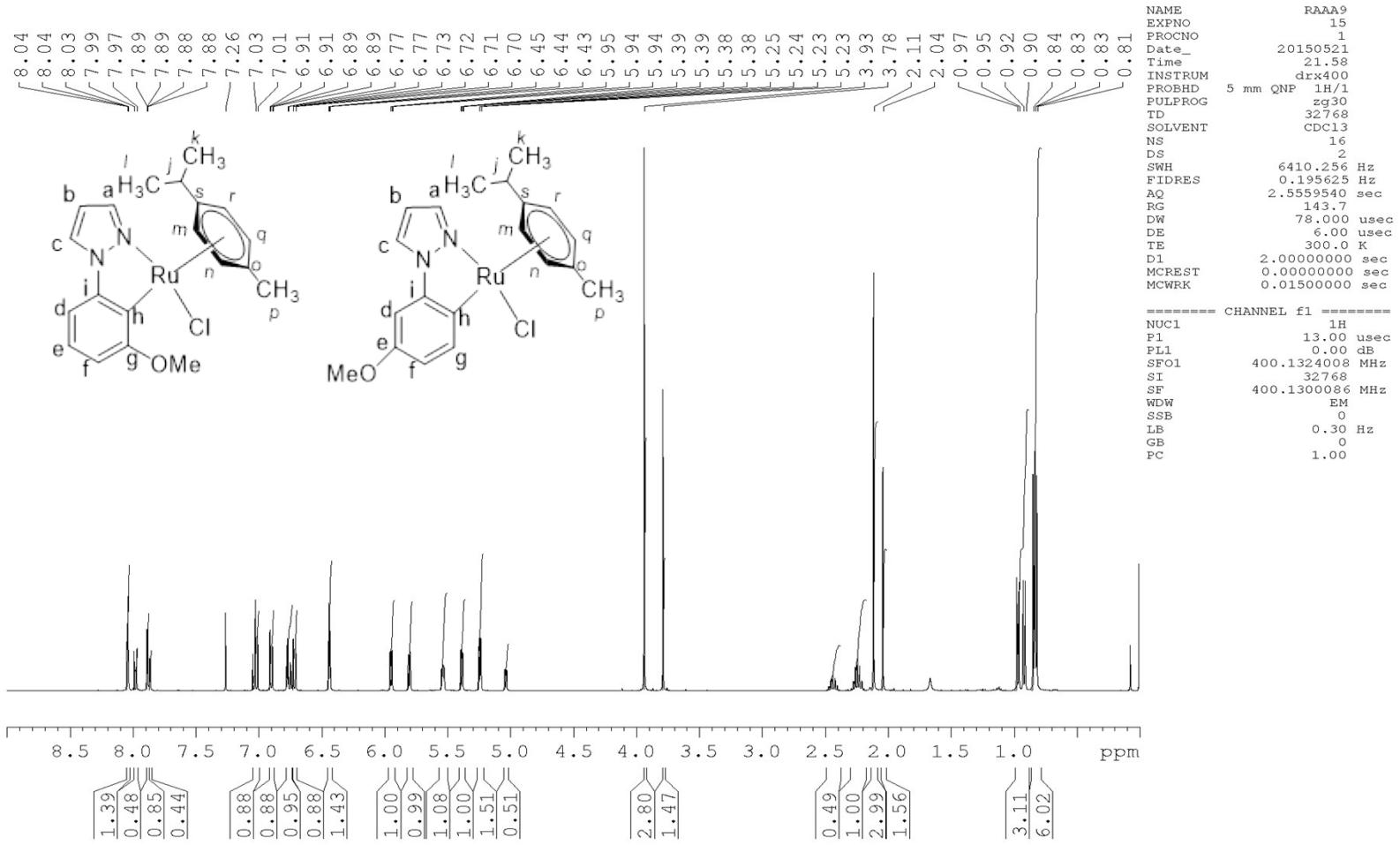
======== CHANNEL f1 ========

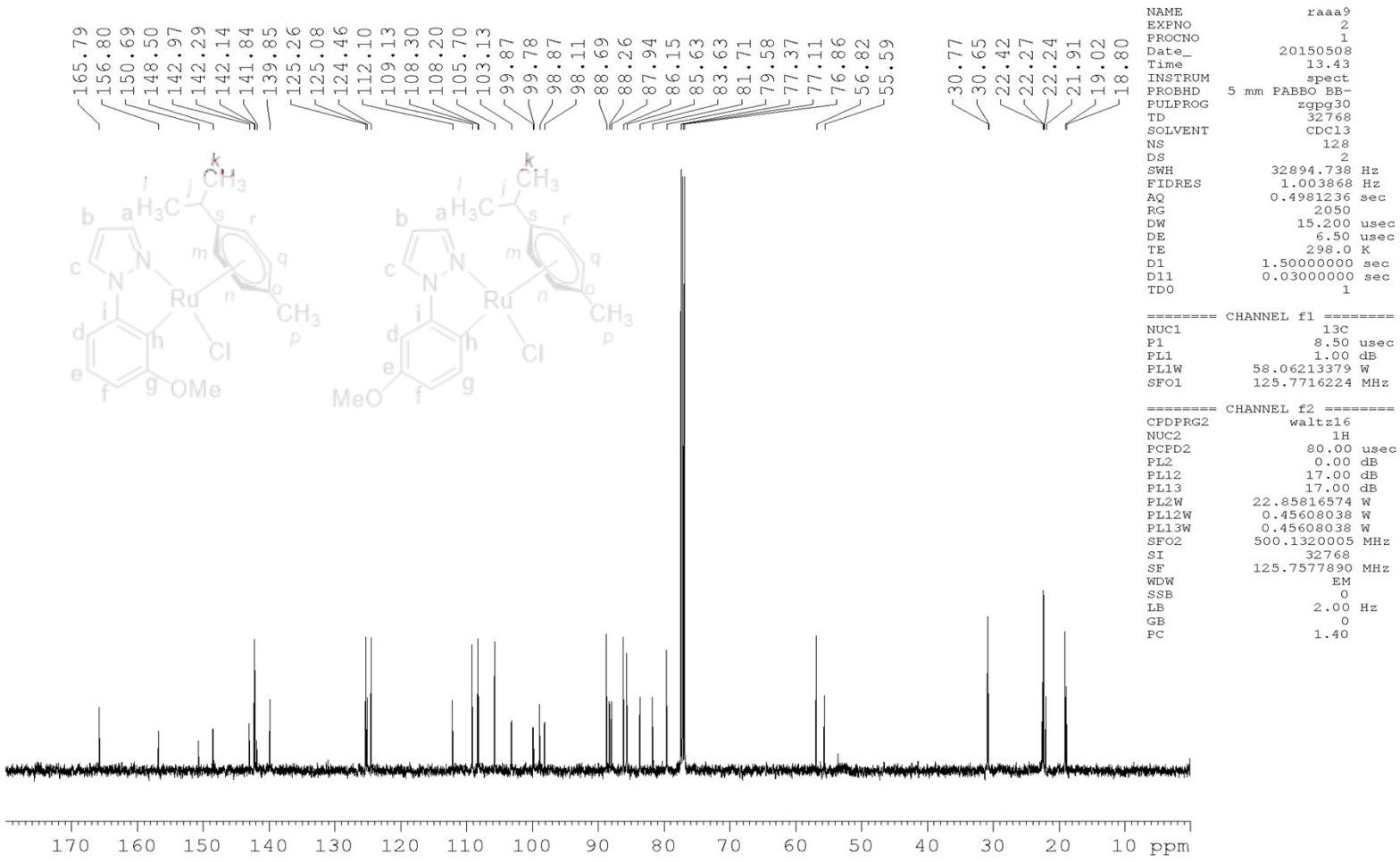
NUC1	1H
P1	13.00 usec
PL1	0.00 dB
SFO1	400.1324008 MHz

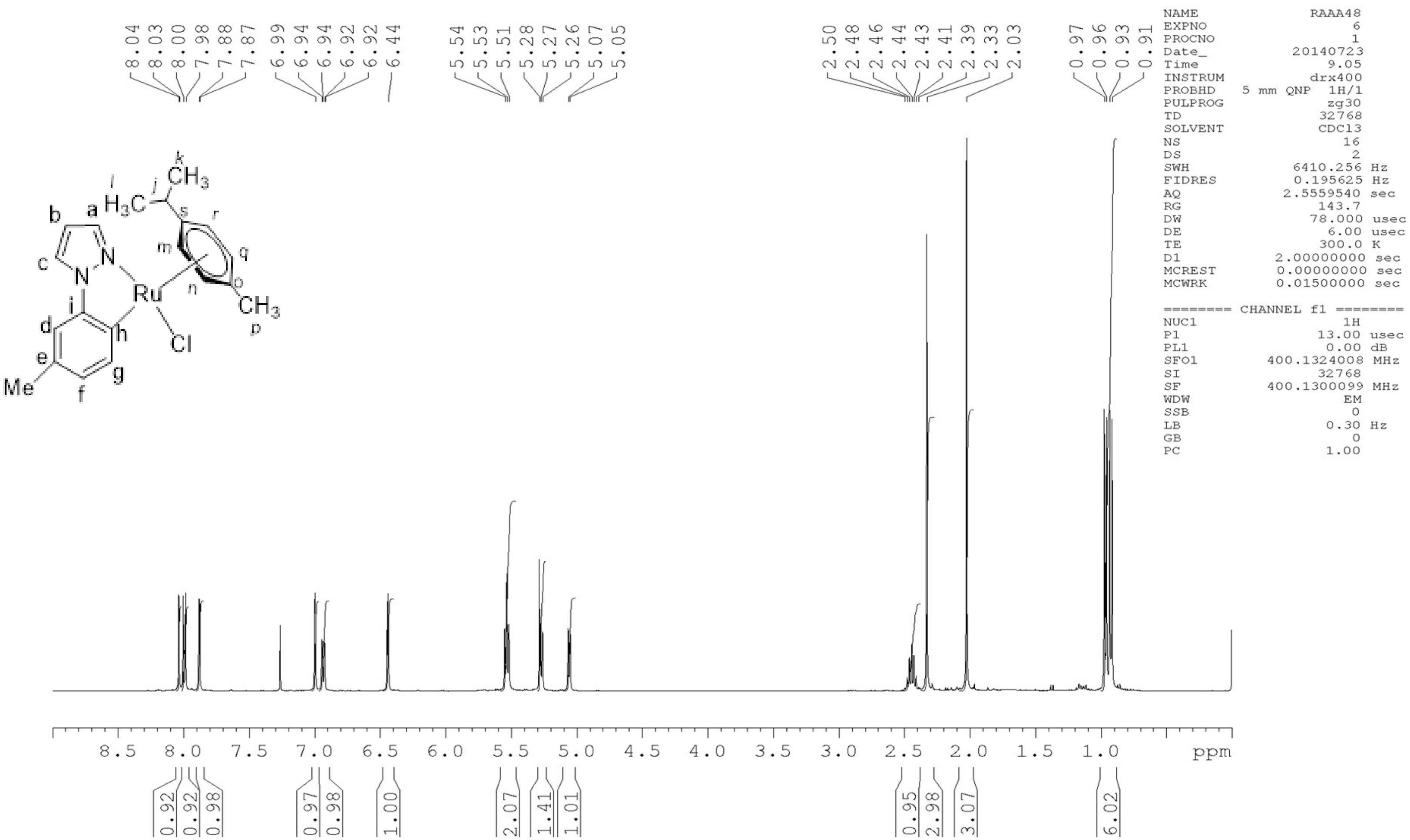
F2 - Processing parameters

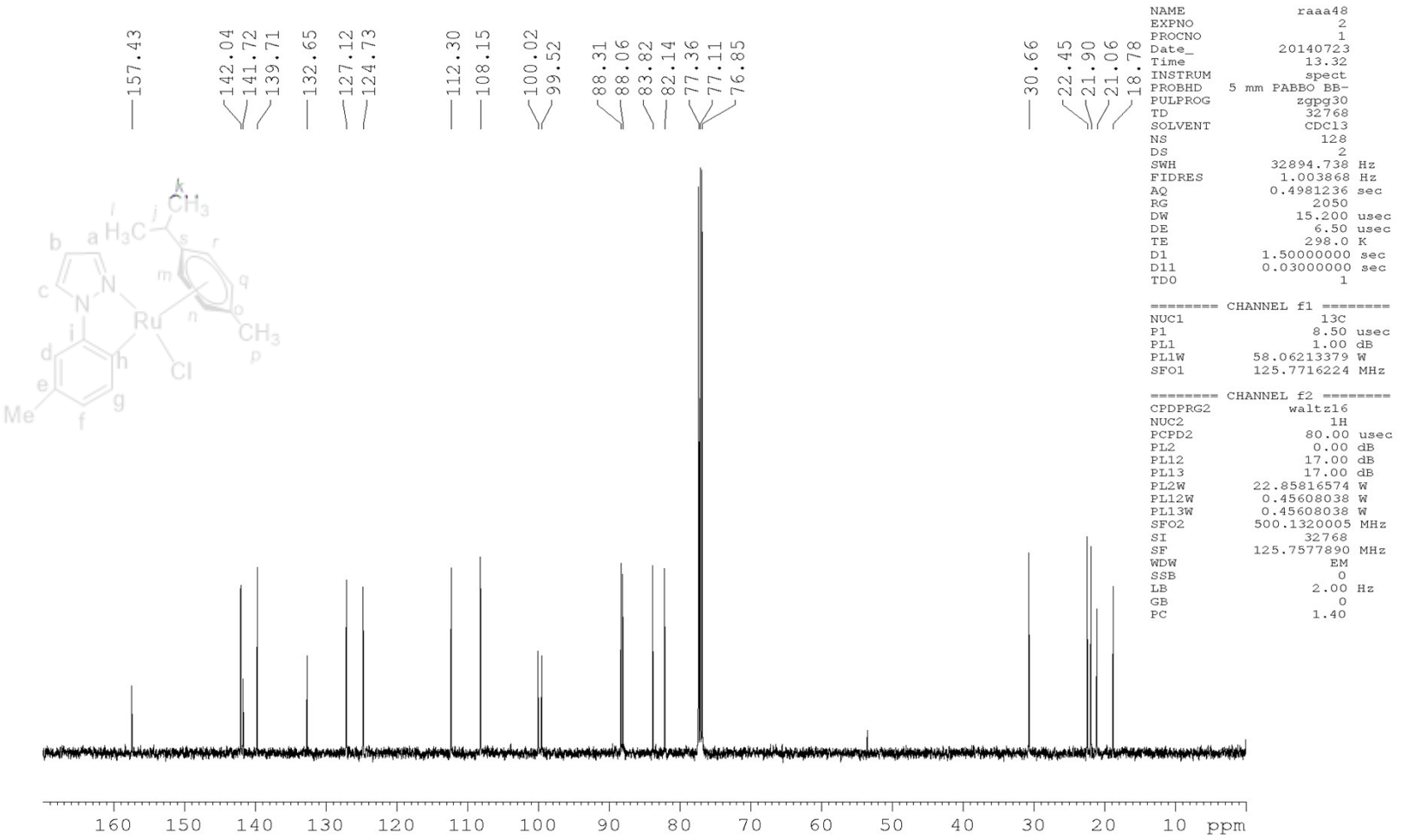
SI	32768
SF	400.1300091 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

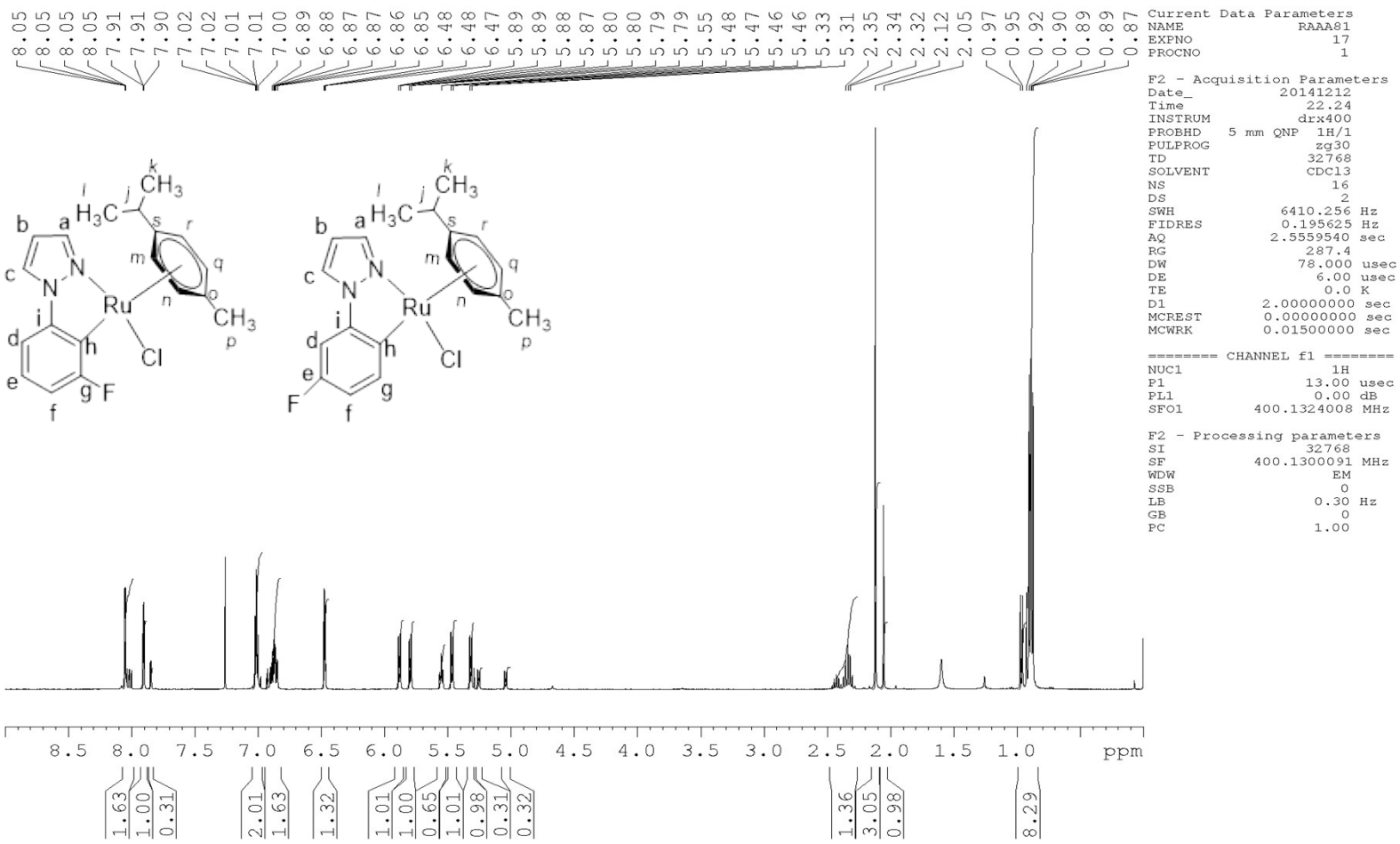

148.18
147.17
142.01
141.99
139.71
124.67
112.92
107.94
99.63
99.19
98.04
87.99
87.89
83.48
81.83
77.43
77.12
76.80
41.44
30.66
22.48
21.91
18.78
NAME RAAA224
EXPNO 10
PROCNO 1
Date_ 20160403
Time 17.48
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG apt
TD 32768
SOLVENT CDC13
NS 1000
DS 4
SWH 26178.010 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 2.00000000 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
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

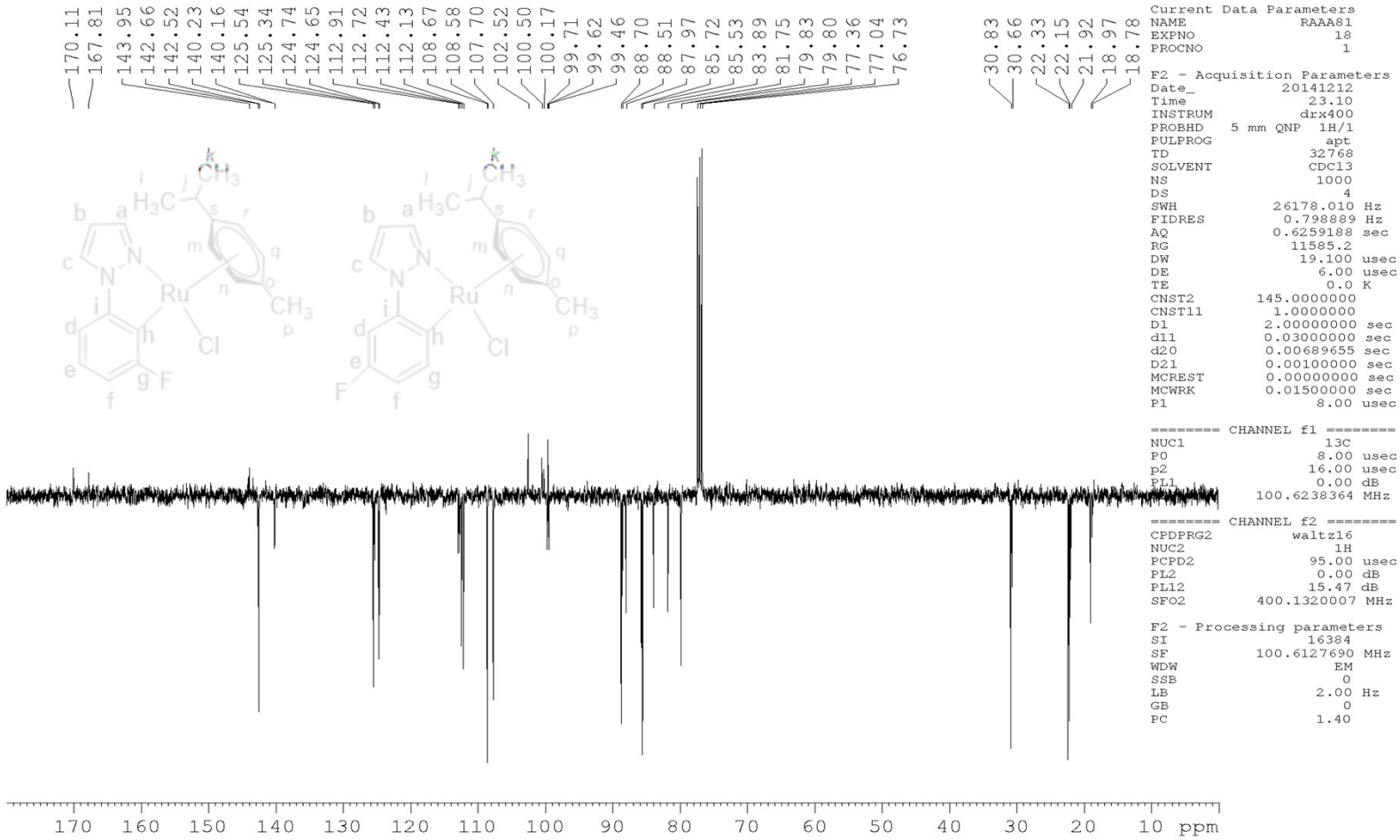

8.04 8.04 8.03 7.99 7.97 7.89 7.89 7.88 7.88 7.26 7.03 7.01 6.91 6.91 6.89 6.89 6.77 6.77 6.73 6.72 6.71 6.70 6.45 6.44 6.43 5.95 5.94 5.94 5.39 5.39 5.38 5.38 5.25 5.24 5.23 5.23 3.93 3.78 2.11 2.04 0.97 0.95 0.92 0.90 0.84 0.83 0.81
NAME RAAA9
EXPNO 15
PROCNO 1
Date_ 20150521
Time 21.58
INSTRUM drx400
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 400.1300086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.39 0.48 0.85 0.44 0.88 0.88 0.95 0.88 1.43 1.00 0.99 1.08 1.00 1.51 0.51 2.80 1.47 0.49 1.00 2.99 1.56 3.11 6.02


165.79
156.80
150.69
148.50
142.97
142.29
142.14
141.84
139.85
125.26
125.08
124.46
112.10
109.13
108.30
108.20
105.70
103.13
99.87
99.78
98.87
98.11
88.69
88.26
87.94
86.15
85.63
83.63
81.71
79.58
77.37
77.11
76.86
56.82
55.59
30.77
30.65
22.42
22.27
22.24
21.91
19.02
18.80
NAME raaa9
EXPNO 2
PROCNO 1
Date_ 20150508
Time 13.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
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
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

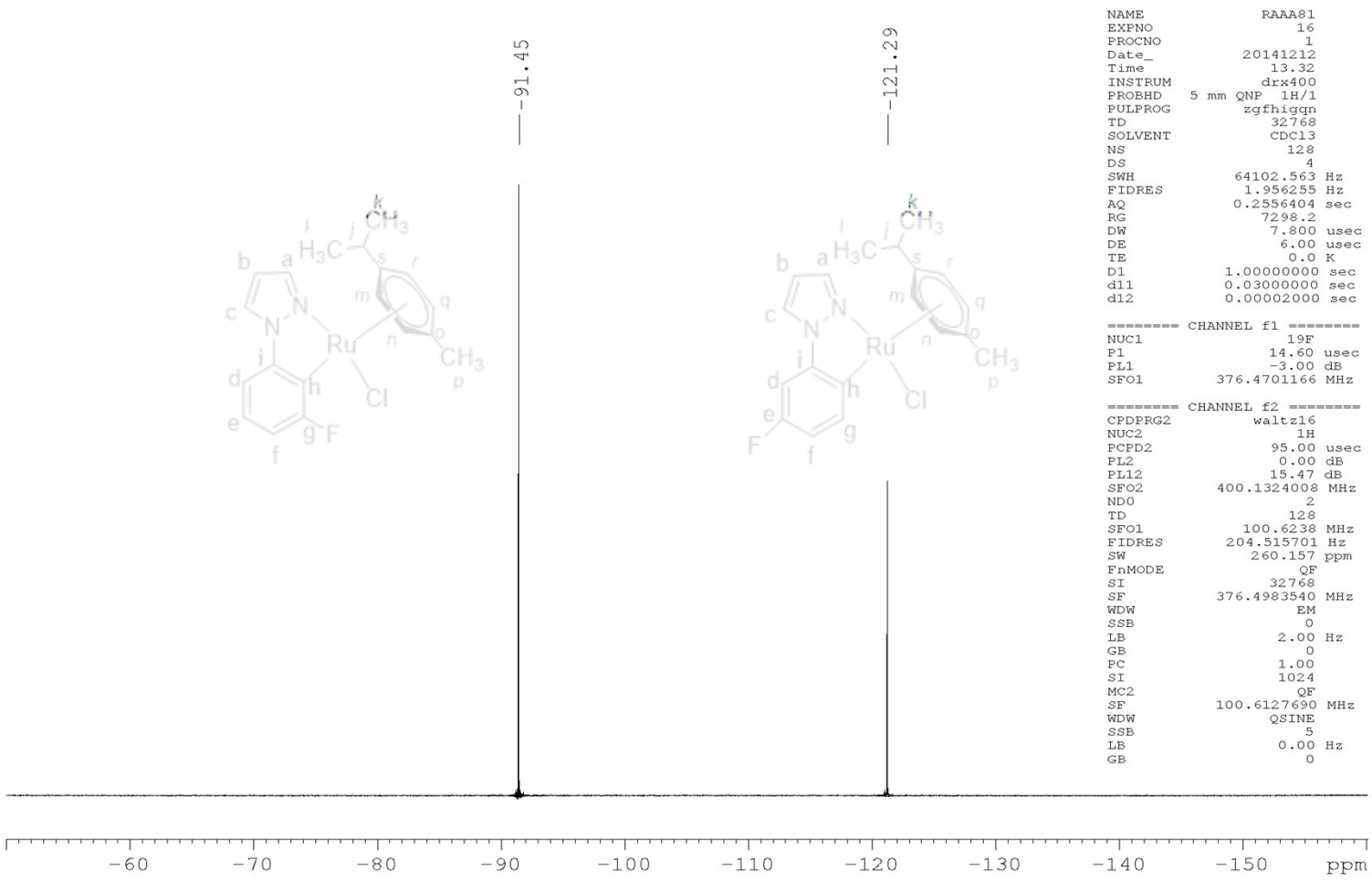

8.04 8.03 8.00 7.98 7.88 7.87 6.99 6.94 6.94 6.92 6.92 6.44 5.54 5.53 5.51 5.28 5.27 5.26 5.07 5.05
2.50 2.48 2.46 2.44 2.43 2.41 2.39 2.33 2.03 0.97 0.96 0.93 0.91
NAME RAAA48
EXPNO 6
PROCNO 1
Date_ 20140723
Time 9.05
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
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 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.92 0.92 0.98 0.97 0.98 1.00 2.07 1.41 1.01 0.95 2.98 3.07 6.02
Ru
Cl
Me
CH3
H3C


157.43
142.04
141.72
139.71
132.65
127.12
124.73
112.30
108.15
100.02
99.52
88.31
88.06
83.82
82.14
77.36
77.11
76.85
30.66
22.45
21.90
21.06
18.78
NAME raaa48
EXPNO 2
PROCNO 1
Date_ 20140723
Time 13.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
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
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

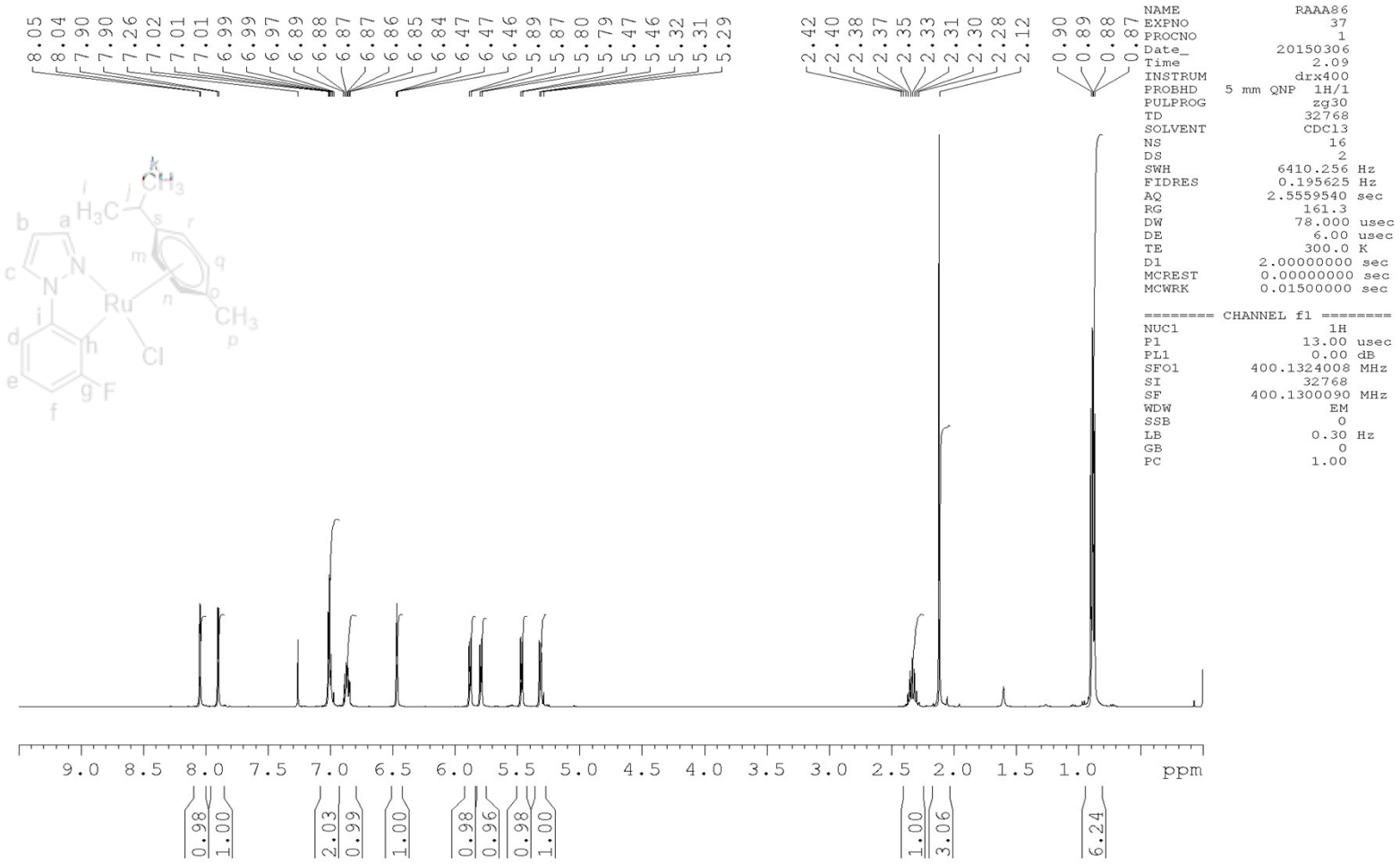

8.05 8.05 8.05 8.05 7.91 7.91 7.90 7.02 7.02 7.01 7.01 7.00 6.89 6.88 6.87 6.87 6.86 6.85 6.48 6.48 6.47 5.89 5.89 5.88 5.87 5.80 5.80 5.79 5.79 5.55 5.48 5.47 5.46 5.46 5.33 5.31 2.35 2.34 2.32 2.12 2.05 0.97 0.95 0.92 0.90 0.89 0.89 0.87
Current Data Parameters
NAME RAAA81
EXPNO 17
PROCNO 1
F2 - Acquisition Parameters
Date_ 20141212
Time 22.24
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 287.4
DW 78.000 usec
DE 6.00 usec
TE 0.0 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 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.63 1.00 0.31 2.01 1.63 1.32 1.01 1.00 0.65 1.01 0.98 0.31 0.32 1.36 3.05 0.98 8.29

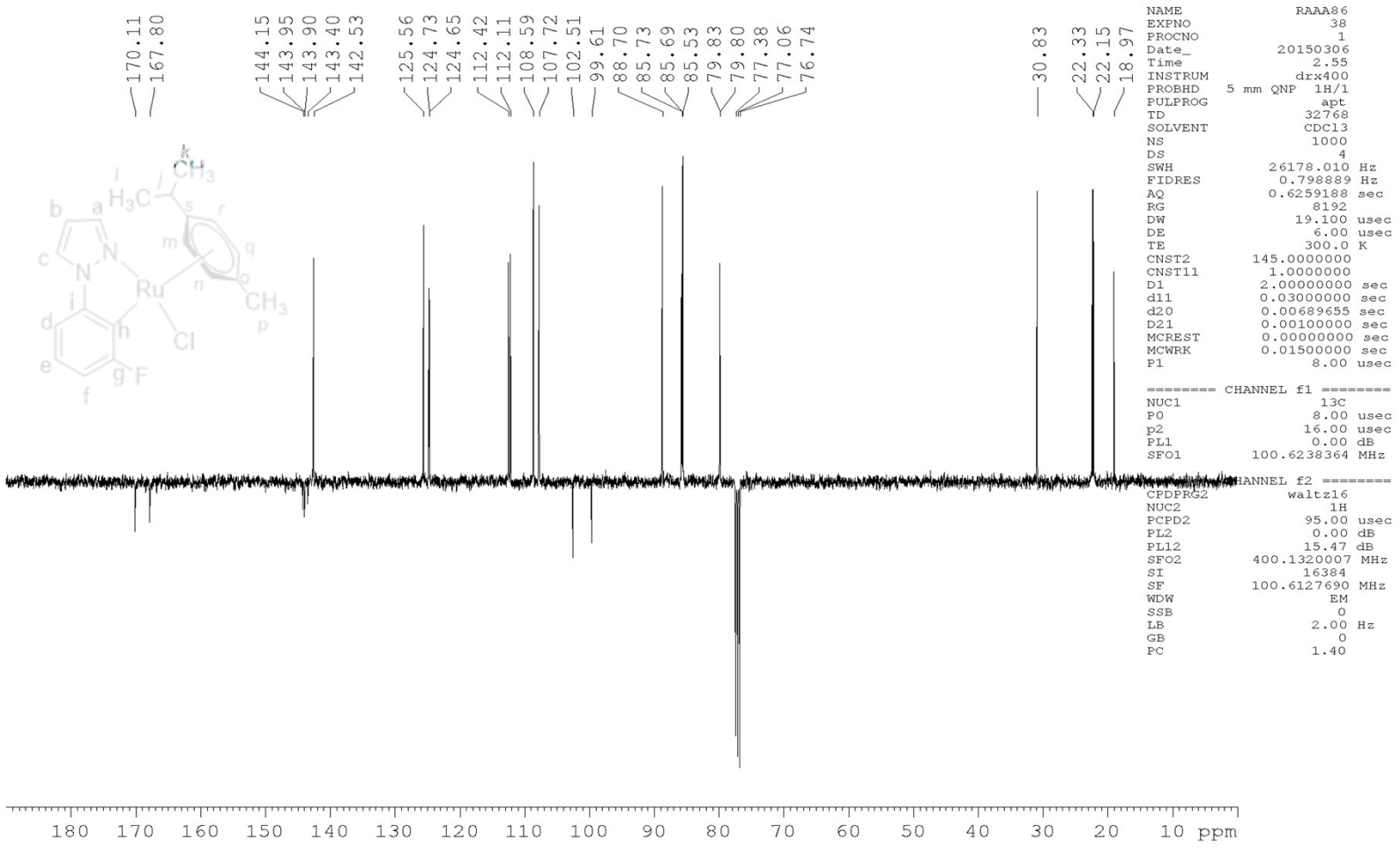


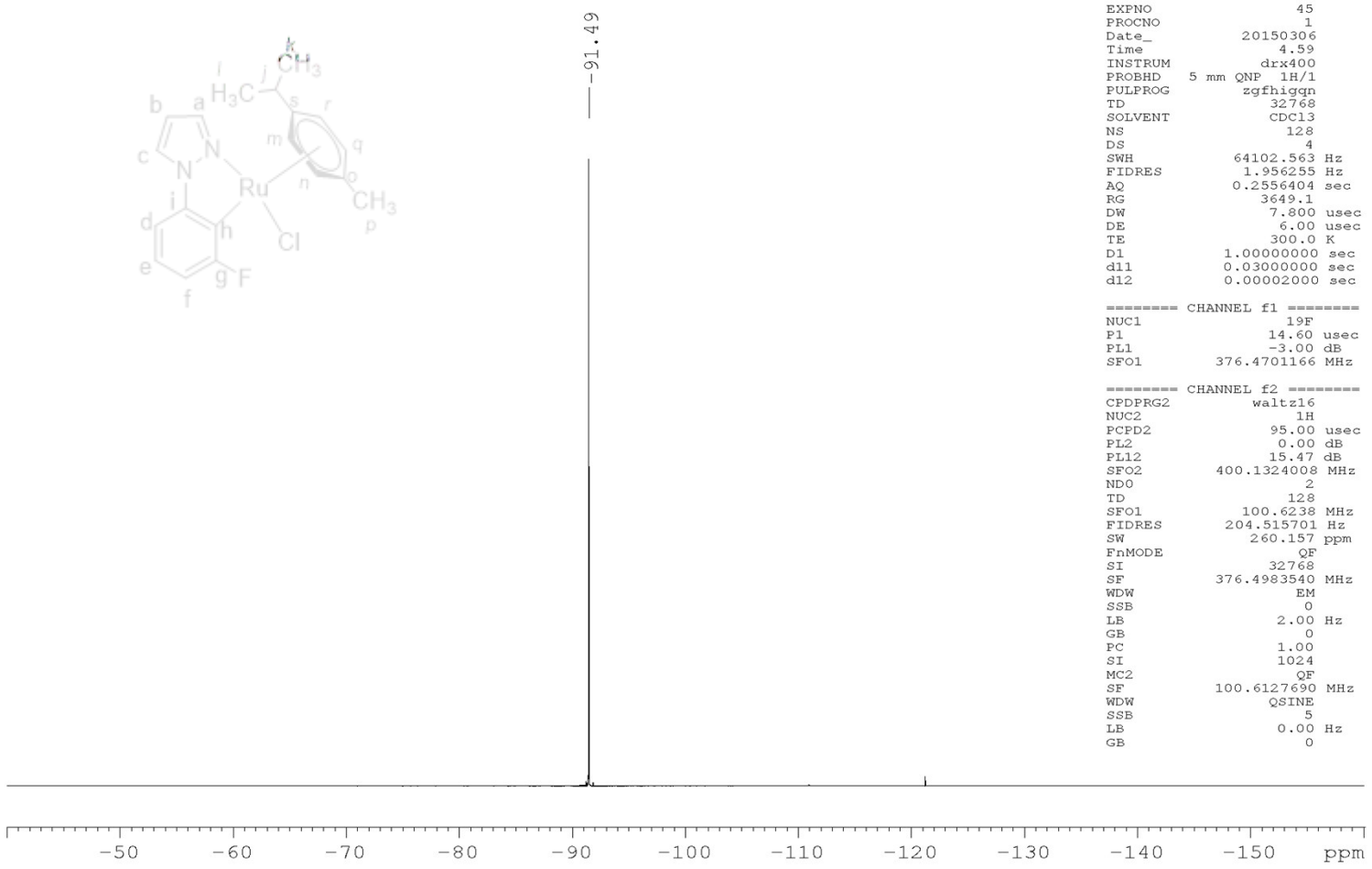

```
Current Data Parameters
NAME                  RAAA81
EXPNO                     18
PROCNO                     1

F2 - Acquisition Parameters
Date_               20141212
Time                   23.10
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                      0.0 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
                  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

F2 - Processing parameters
SI                       16384
SF                100.6127690 MHz
WDW                         EM
SSB                          0
LB                     2.00 Hz
GB                           0
PC                        1.40
```



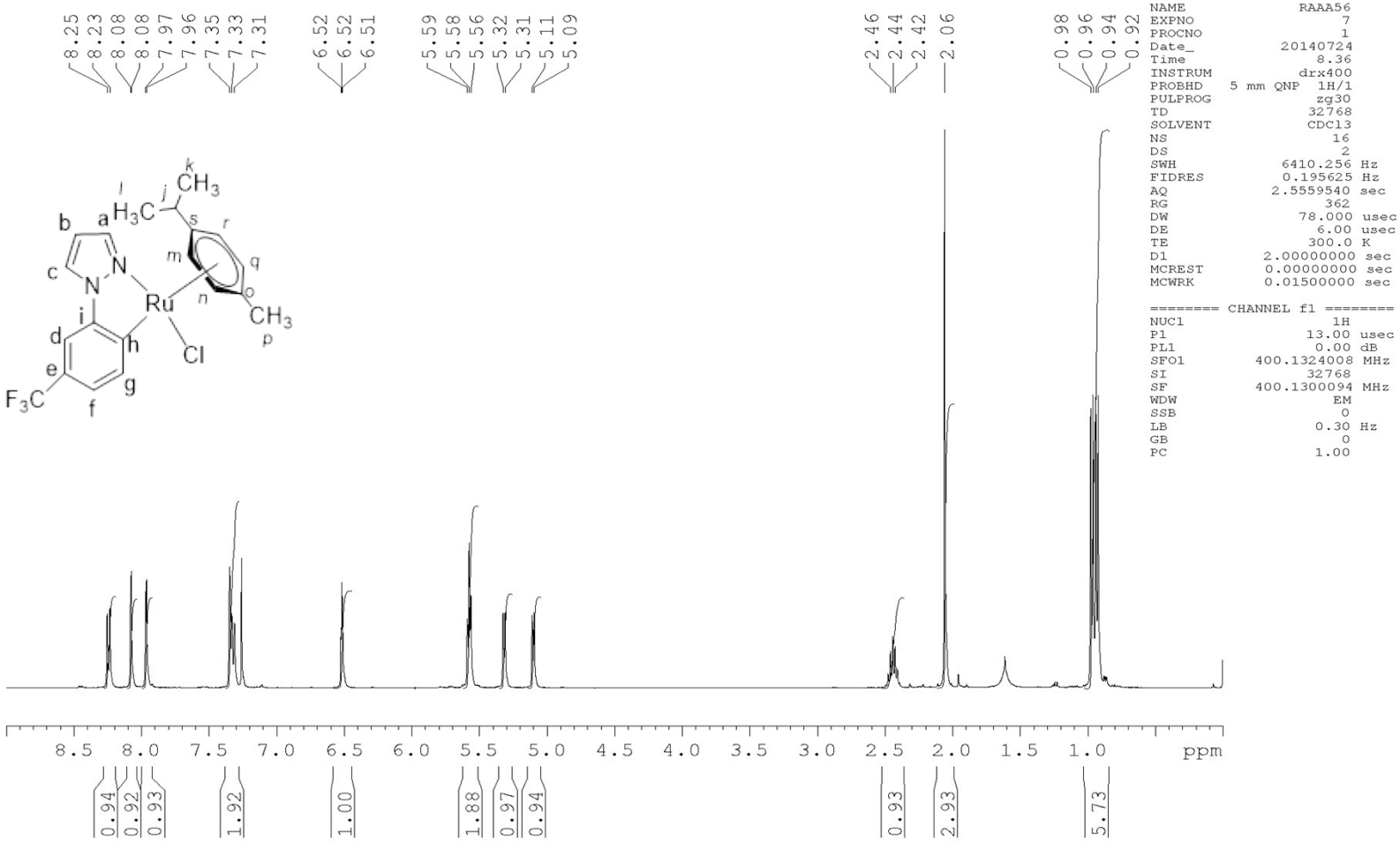
NAME	RAAA81
EXPNO	16
PROCNO	1
Date_	20141212
Time	13.32
INSTRUM	drx400
PROBHD	5 mm QNP 1H/1
PULPROG	zgfhigqn
TD	32768
SOLVENT	CDCl3
NS	128
DS	4
SWH	64102.563 Hz
FIDRES	1.956255 Hz
AQ	0.2556404 sec
RG	7298.2
DW	7.800 usec
DE	6.00 usec
TE	0.0 K
D1	1.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
======== 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

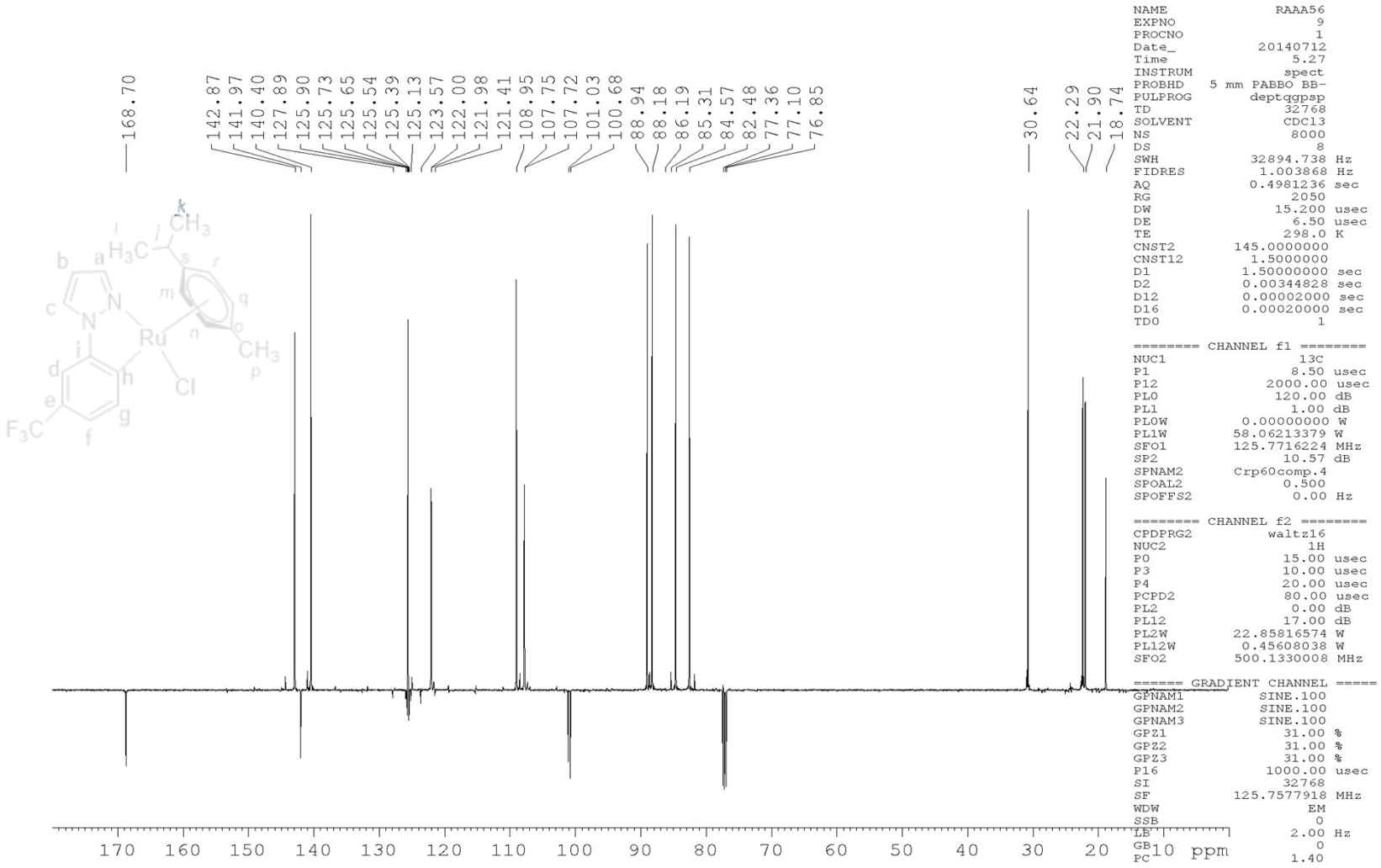

8.05 8.04 7.90 7.90 7.26 7.02 7.01 7.01 6.99 6.99 6.97 6.89 6.88 6.87 6.87 6.86 6.85 6.84 6.47 6.47 6.46 5.89 5.87 5.80 5.79 5.47 5.46 5.32 5.31 5.29
2.42 2.40 2.38 2.37 2.35 2.33 2.31 2.30 2.28 2.12
0.90 0.89 0.88 0.87
NAME RAAA86
EXPNO 37
PROCNO 1
Date_ 20150306
Time 2.09
INSTRUM drx400
PROBHD 5 mm 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 161.3
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 400.1300090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.98 1.00 2.03 0.99 1.00 0.98 0.96 0.98 1.00 1.00 3.06 6.24


170.11
167.80
144.15
143.95
143.90
143.40
142.53
125.56
124.73
124.65
112.42
112.11
108.59
107.72
102.51
99.61
88.70
85.73
85.69
85.53
79.83
79.80
77.38
77.06
76.74
30.83
22.33
22.15
18.97
NAME RAAA86
EXPNO 38
PROCNO 1
Date_ 20150306
Time 2.55
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG apt
TD 32768
SOLVENT CDC13
NS 1000
DS 4
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 8192
DW 19.100 usec
DE 6.00 usec
TE 300.0 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
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
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

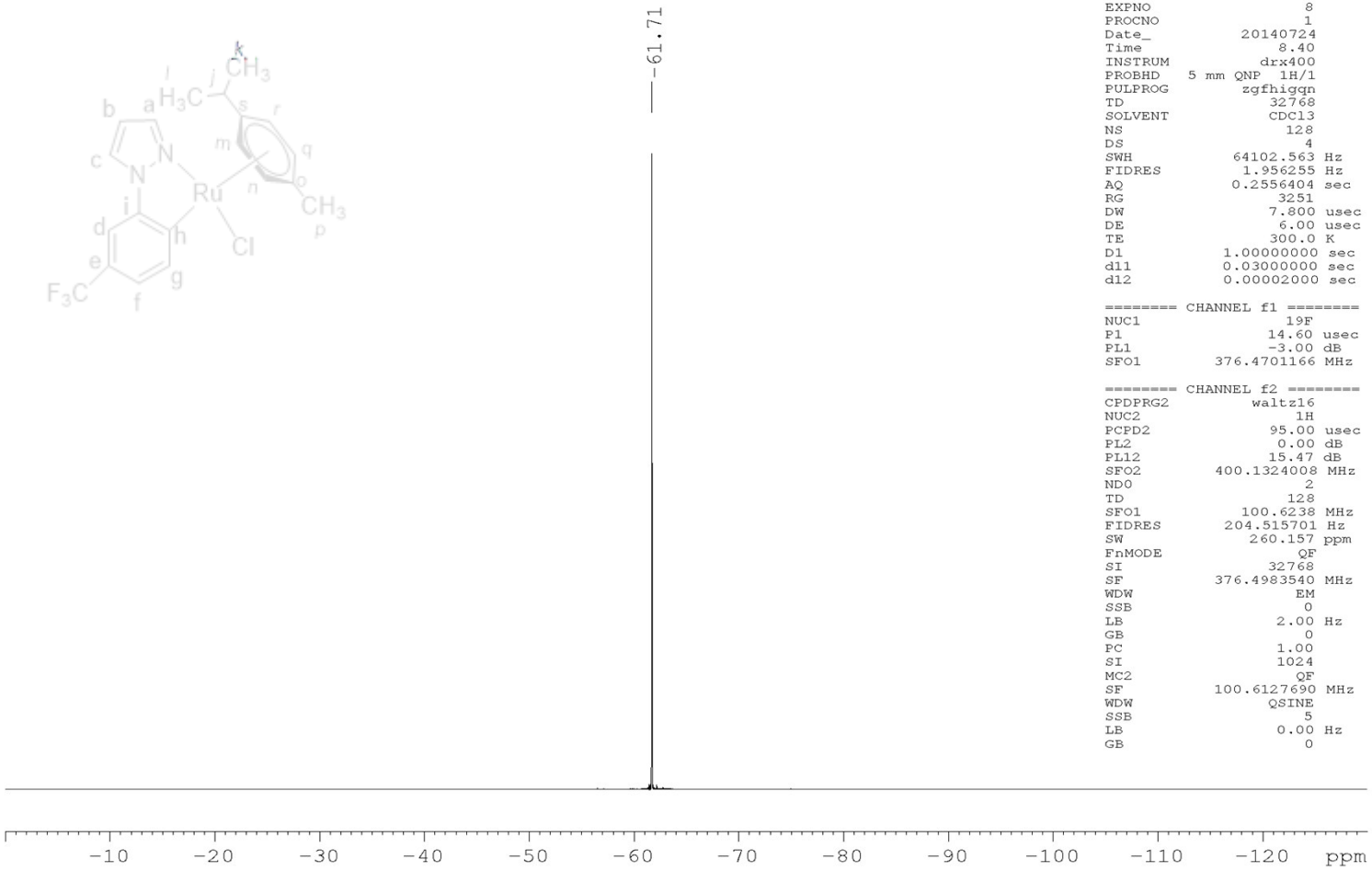


NAME	RAAA86
EXPNO	45
PROCNO	1
Date_	20150306
Time	4.59
INSTRUM	drx400
PROBHD	5 mm QNP 1H/1
PULPROG	zgfhigqn
TD	32768
SOLVENT	CDCl3
NS	128
DS	4
SWH	64102.563 Hz
FIDRES	1.956255 Hz
AQ	0.2556404 sec
RG	3649.1
DW	7.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
======== 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

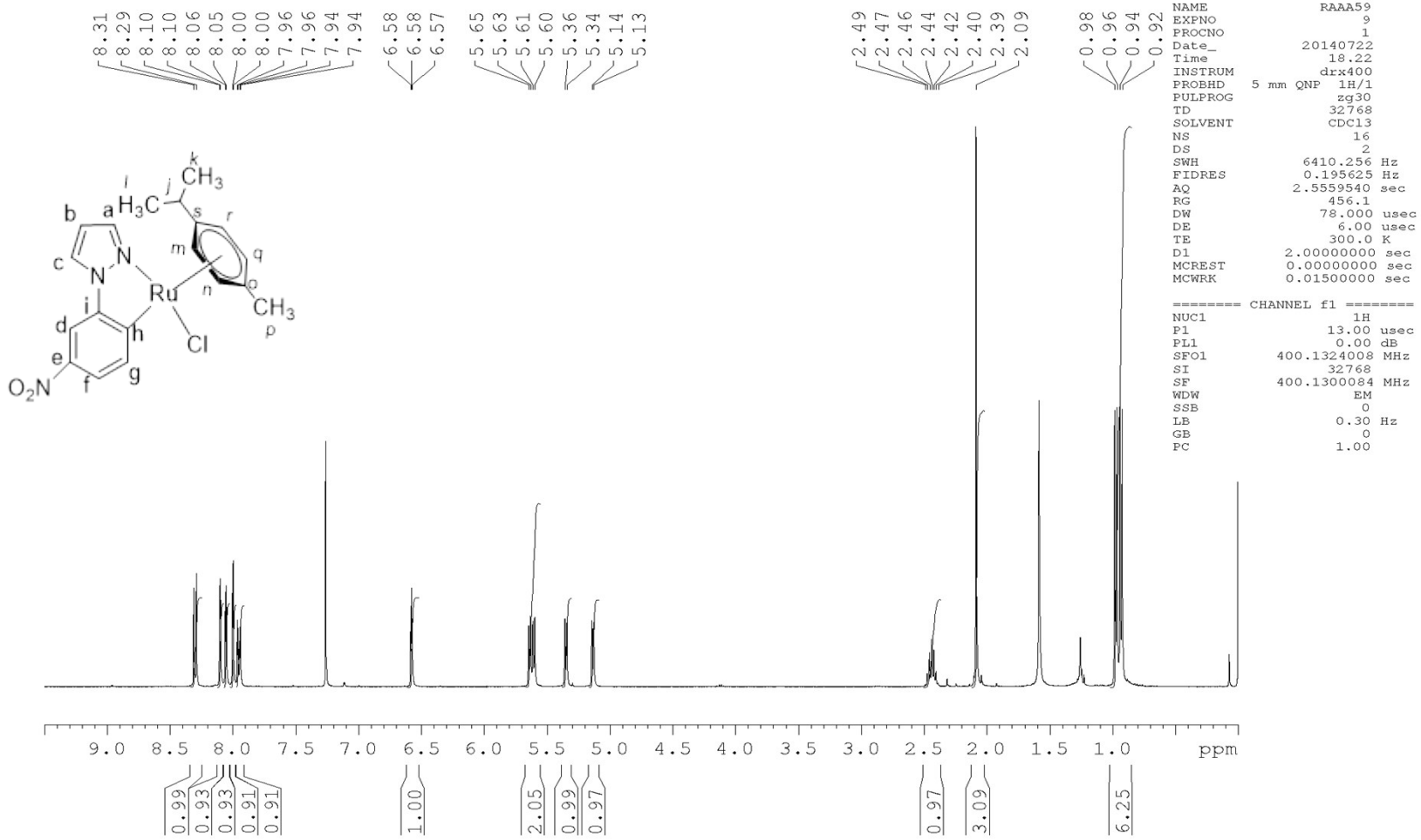

8.25
8.23
8.08
8.08
7.97
7.96
7.35
7.33
7.31
6.52
6.52
6.51
5.59
5.58
5.56
5.32
5.31
5.11
5.09
2.46
2.44
2.42
2.06
0.98
0.96
0.94
0.92
NAME RAAA56
EXPNO 7
PROCNO 1
Date_ 20140724
Time 8.36
INSTRUM drx400
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 362
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 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ru
Cl
CH3
F3C
ppm
0.94
0.92
0.93
1.92
1.00
1.88
0.97
0.94
0.93
2.93
5.73

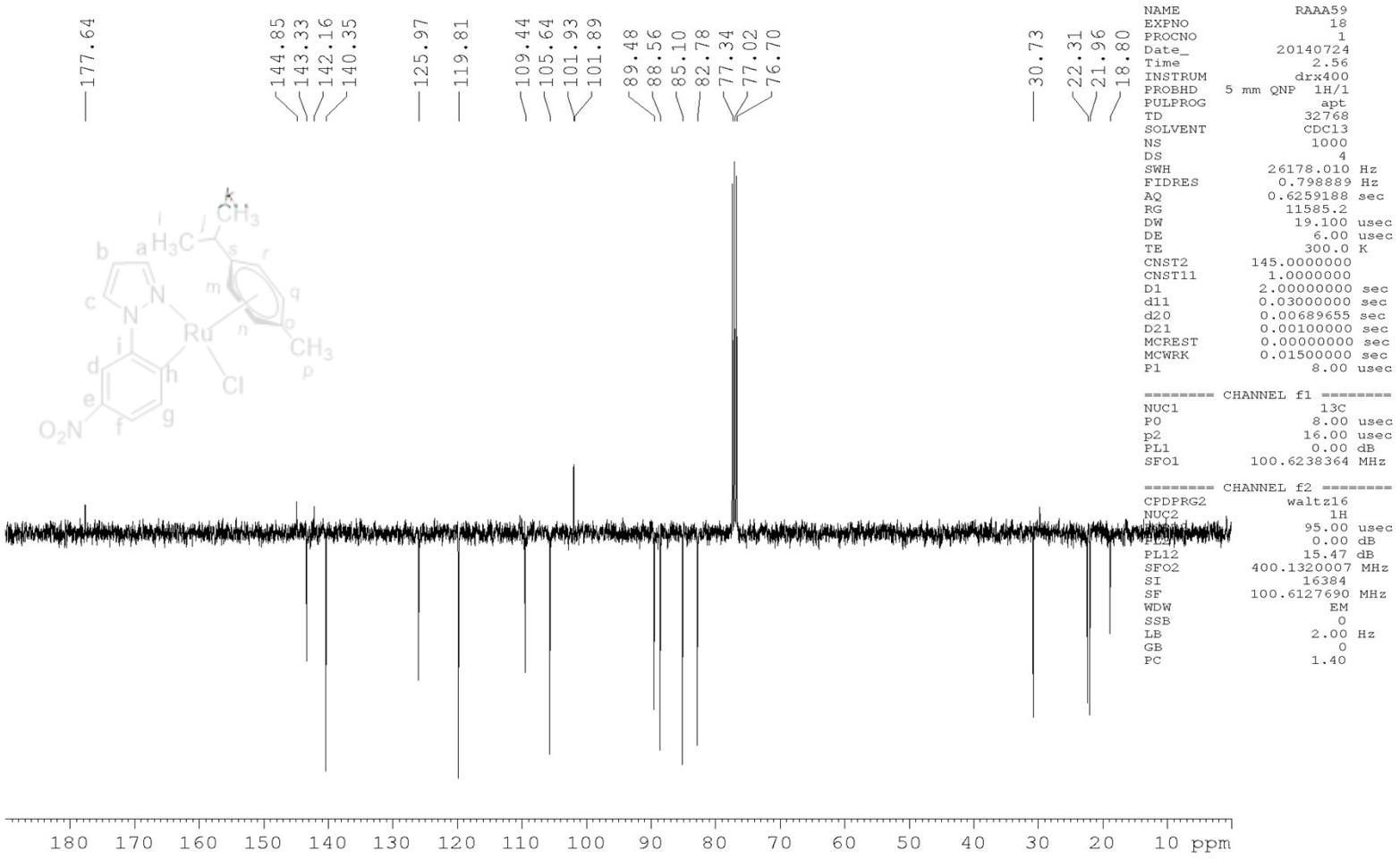


NAME	RAAA56
EXPNO	9
PROCNO	1
Date_	20140712
Time	5.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	deptqgpsp
TD	32768
SOLVENT	CDC13
NS	8000
DS	8
SWH	32894.738 Hz
FIDRES	1.003868 Hz
AQ	0.4981236 sec
RG	2050
DW	15.200 usec
DE	6.50 usec
TE	298.0 K
CNST2	145.0000000
CNST12	1.5000000
D1	1.50000000 sec
D2	0.00344828 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
SPOAL2	0.500
SPOFFS2	0.00 Hz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
P0	15.00 usec
P3	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	125.7577918 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40



NAME	RAAA56
EXPNO	8
PROCNO	1
Date_	20140724
Time	8.40
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	3251
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


8.31 8.29 8.10 8.10 8.06 8.05 8.00 8.00 7.96 7.96 7.94 7.94
6.58 6.58 6.57
5.65 5.63 5.61 5.60 5.36 5.34 5.14 5.13
2.49 2.47 2.46 2.44 2.42 2.40 2.39 2.09
0.98 0.96 0.94 0.92
NAME RAAA59
EXPNO 9
PROCNO 1
Date_ 20140722
Time 18.22
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 456.1
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 400.1300084 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ru
Cl
CH3
O2N
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.99 0.93 0.93 0.91 0.91
1.00
2.05 0.99 0.97
0.97 3.09
6.25


177.64
144.85
143.33
142.16
140.35
125.97
119.81
109.44
105.64
101.93
101.89
89.48
88.56
85.10
82.78
77.34
77.02
76.70
30.73
22.31
21.96
18.80
NAME RAAA59
EXPNO 18
PROCNO 1
Date_ 20140724
Time 2.56
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 2.00000000 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
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
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1. Y. Boutadla, D. L. Davies, R. C. Jones and K. Singh, *Chem. Eur. J.*, 2011, **17**, 3438-3448.