

Supporting Information

Base-promoted perfluoroalkylation of rhodium(III) porphyrin complexes

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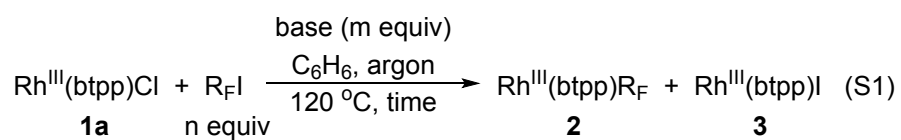
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Table of Contents

Supplementary Optimization Results	p. S2
Competition Experiment	p. S3
X-Ray Diffraction Data	p. S5
NMR Spectra	p. S7
MS Spectra	p. S17
GCMS Spectra	p. S26

Supplementary Optimization Results



entry	R _F I	base	n	m	time / h	yield / %	
						2	3
1	ⁿ C ₆ F ₁₃ I	K ₃ PO ₄	15	10	10.5	31 (2e)	21
2			15	15	10.5	43 (2e)	43
3			20	10	10.5	42 (2e)	49
4		KOH	15	10	8	27 (2e)	32
5			20	10	8	75 (2e)	0
6	^c C ₆ F ₁₁ I	KOH	15	10	8	40 (2b)	36

Competition Experiment

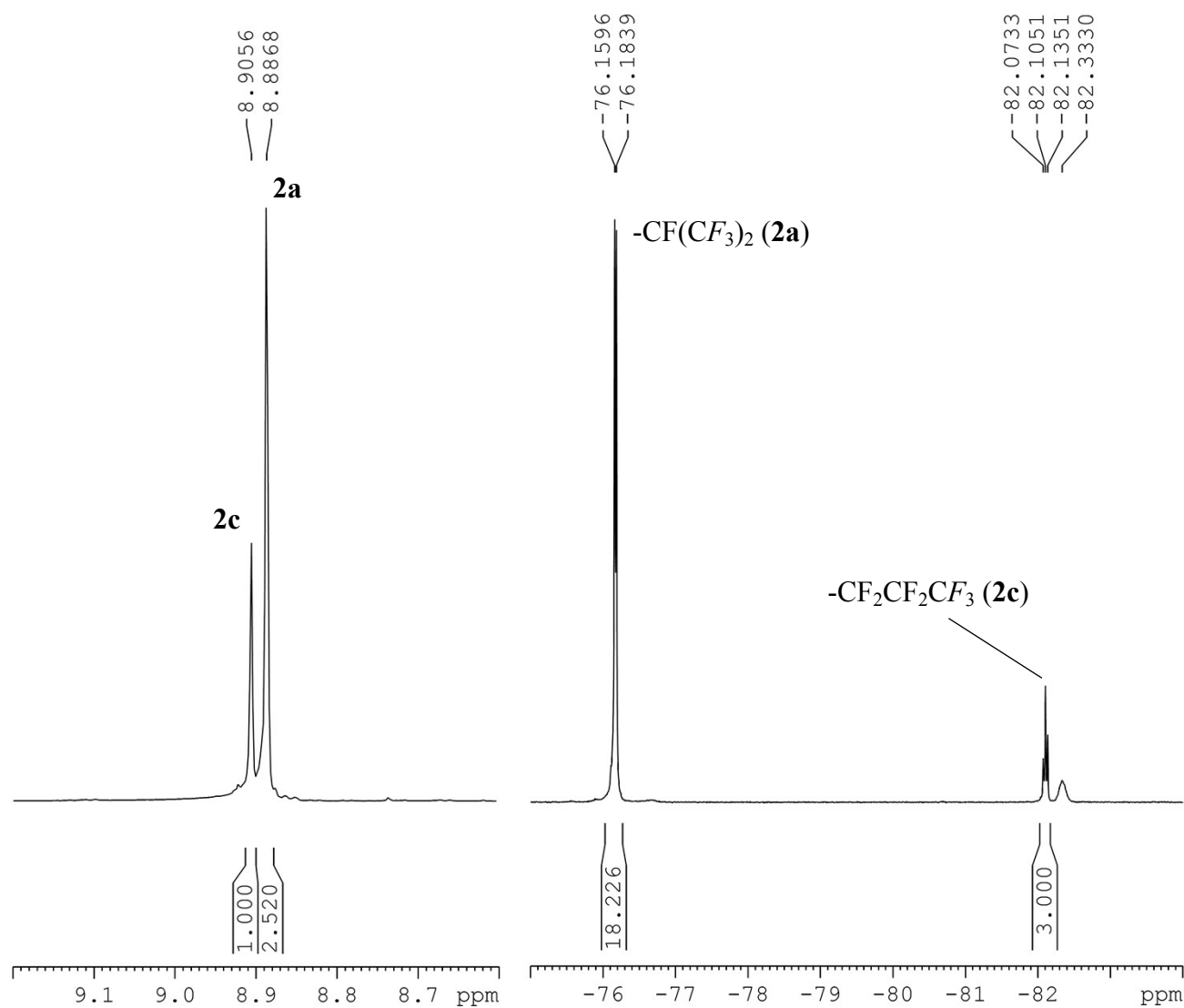
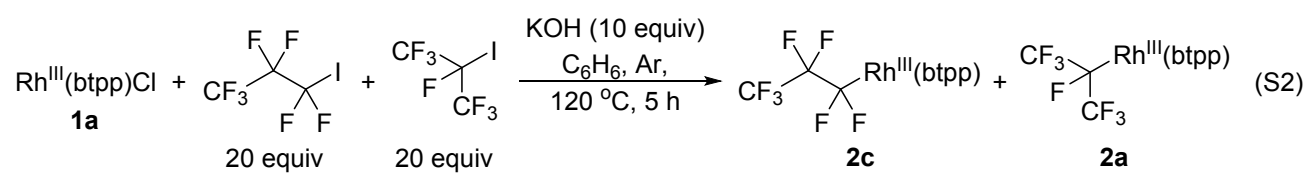


Figure S1. Expanded ^1H NMR (pyrrolic proton) and ^{19}F NMR spectra of isolated mixture of **2a** and **2c** (trial 1).

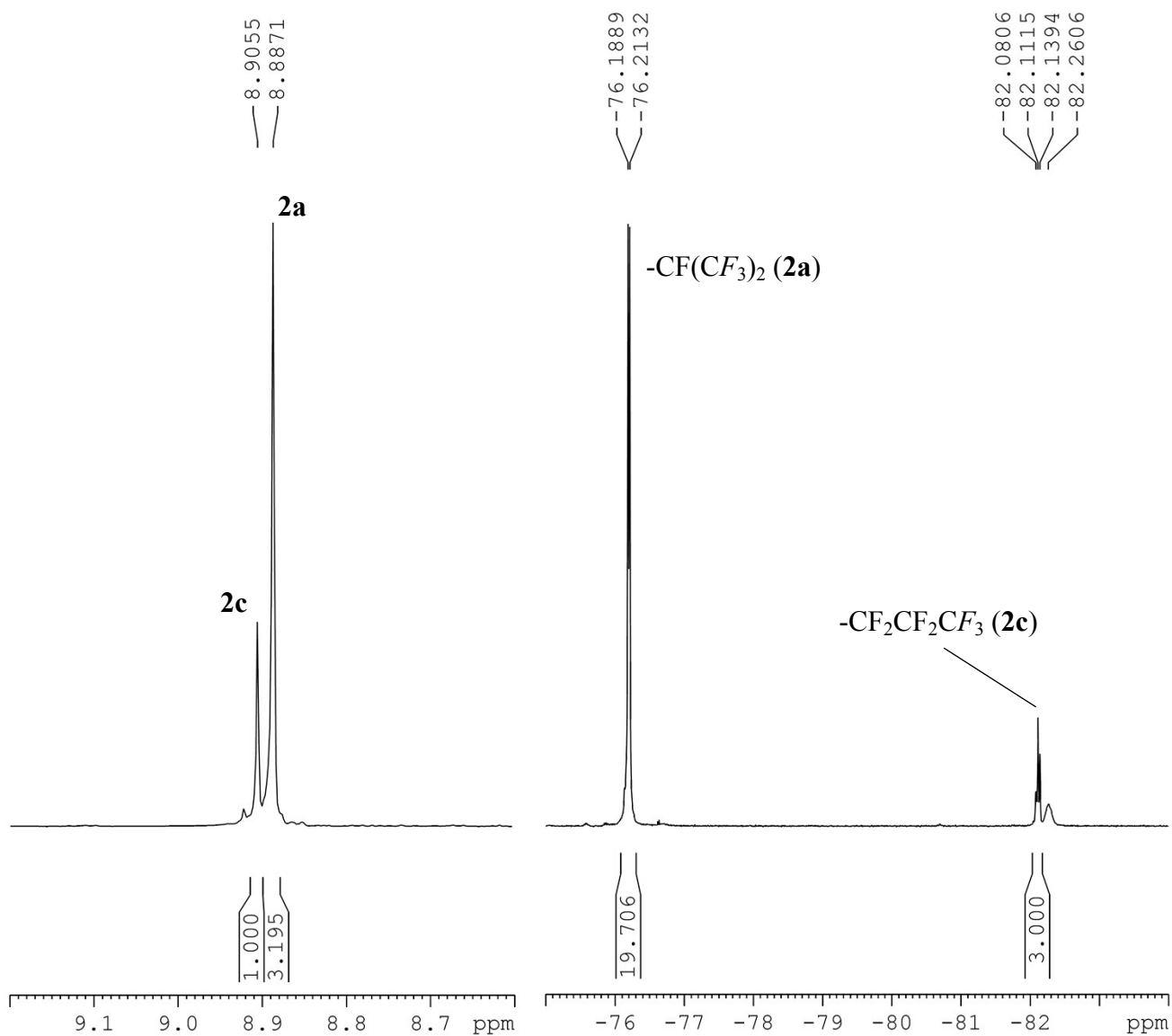


Figure S2. Expanded ^1H NMR (pyrrolic proton) and ^{19}F NMR spectra of isolated mixture of **2a** and **2c** (trial 2).

Averaged **2c** : **2a** ratio from ^1H NMR = $(2.525+3.195)/2 = 2.86 : 1$

Averaged **2c** : **2a** ratio from ^{19}F NMR = $[(18.226+19.706)/4]/3 = 3.16 : 1$

X-Ray Diffraction Data

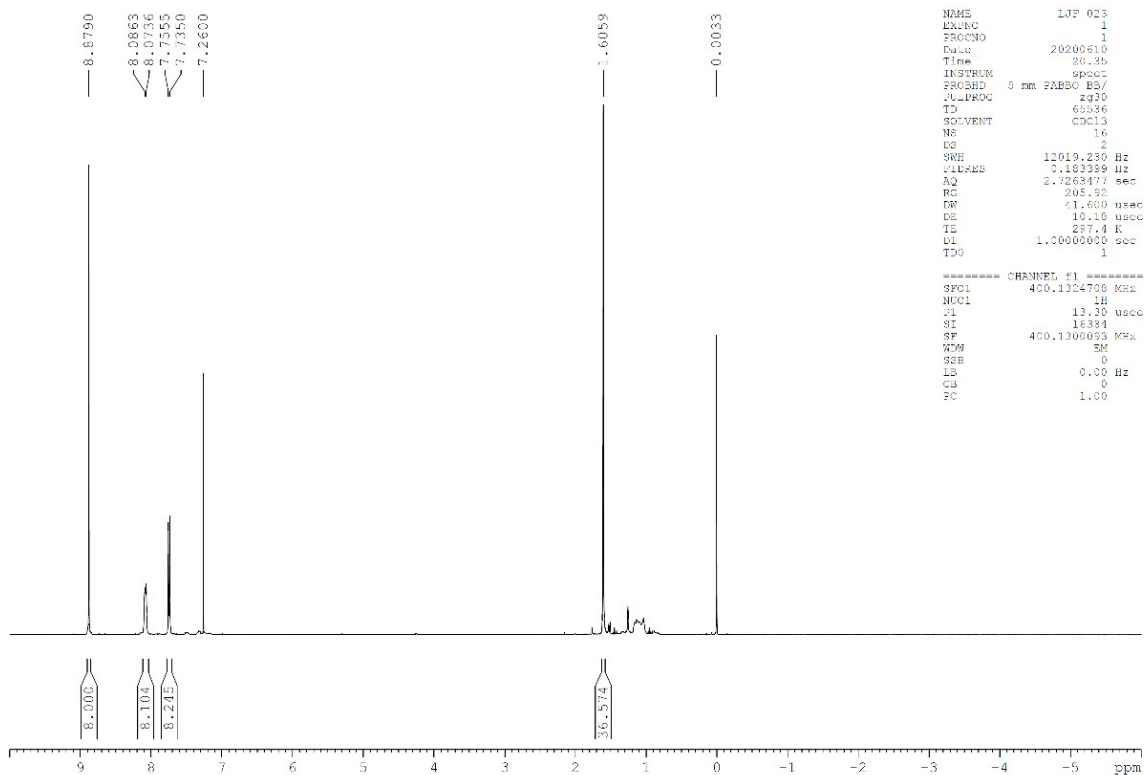
Compound	Rh ^{III} (btp ^p) ⁿ C ₃ F ₇ ·MeOH 2a	Rh ^{III} (btp ^p) ⁿ C ₃ F ₇ ·MeOH 2c
Empirical formula	C ₆₄ H ₆₄ F ₇ N ₄ ORh	C ₆₅ H _{65.3} Cl ₃ F ₇ N ₄ O _{1.15} Rh
Formula weight	1141.10	1263.17
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	C2/c	P21/c
Unit cell dimensions	a = 29.171(5) Å α = 90° b = 10.6913(18) Å β = 110.572(9)° c = 21.741(3) Å γ = 90°	a = 14.8018(8) Å α = 90° b = 29.3344(15) Å β = 107.663(2)° c = 14.4537(7) Å γ = 90°
Volume	6348.3(18) Å ³	5979.9(5) Å ³
Z	4	4
Density (calculated)	1.194 g/cm ³	1.403 g/cm ³
Absorption coefficient	0.330 mm ⁻¹	0.488 mm ⁻¹
F(000)	2368	2606
Crystal size	0.560 x 0.280 x 0.130 mm ³	0.560 x 0.350 x 0.120 mm ³
Theta range for data collection	2.390 to 28.107°	2.460 to 28.004°
Limiting indices	-38 ≤ h ≤ 38 -14 ≤ k ≤ 14 -28 ≤ l ≤ 26	-19 ≤ h ≤ 19 -38 ≤ k ≤ 38 -19 ≤ l ≤ 19
Reflections collected	50400	13323
Independent reflections	14779 [R(int) = 0.0763]	13323 [R(int) = 0]
Completeness to theta = 25.242°	99.7%	92.2%
Absorption correction	Semi-empirical from equivalents	Multi-scan
Max. and min. transmission	0.9281 and 0.6753	0.7456 and 0.6262
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	14779 / 33 / 709	13323 / 3 / 744
Goodness-of fit on F ²	1.053	0.962
Final R indices [I > 2σ(I)]	R1 = 0.0961, wR2 = 0.2483	R1 = 0.0674, wR2 = 0.1916
R indices (all data)	R1 = 0.1325, wR2 = 0.2857	R1 = 0.0890, wR2 = 0.2062

Absolute structure parameter	0.27(8)	--
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	1.187 and -1.440e.Å ⁻³	1.674 and -1.312e.Å ⁻³

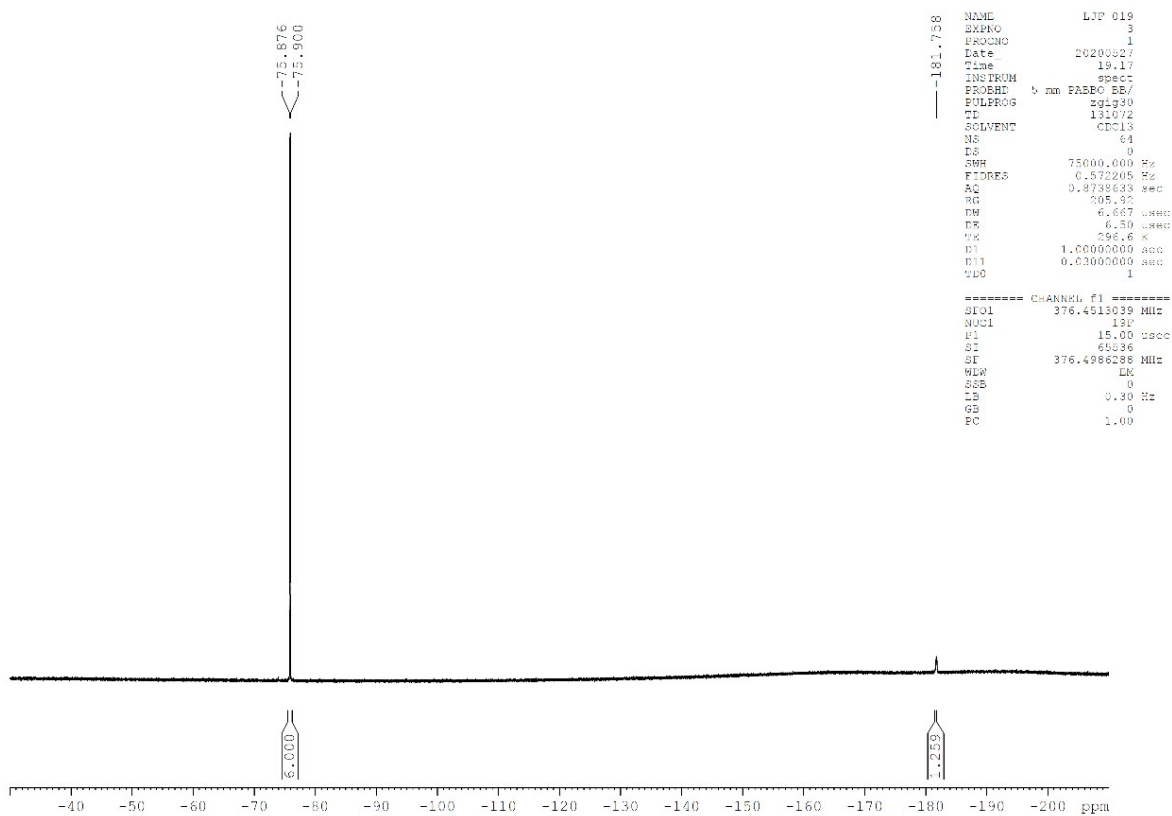
NMR Spectra

No.	Spectra	Page
1	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^i\text{C}_3\text{F}_7$ 2a	S8
2	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^i\text{C}_3\text{F}_7$ 2a	S8
3	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^c\text{C}_6\text{F}_{11}$ 2b	S9
4	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^c\text{C}_6\text{F}_{11}$ 2b	S9
5	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_3\text{F}_7$ 2c	S10
6	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_3\text{F}_7$ 2c	S10
7	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_4\text{F}_9$ 2d	S11
8	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_4\text{F}_9$ 2d	S11
9	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_6\text{F}_{13}$ 2e	S12
10	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_6\text{F}_{13}$ 2e	S12
11	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_{10}\text{F}_{21}$ 2f	S13
12	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})^n\text{C}_{10}\text{F}_{21}$ 2f	S13
13	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})\text{CF}_2\text{C}_6\text{F}_5$ 2g	S14
14	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{btp})\text{CF}_2\text{C}_6\text{F}_5$ 2g	S14
15	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{tp})^i\text{C}_3\text{F}_7$ 4a	S15
16	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{tp})^i\text{C}_3\text{F}_7$ 4a	S15
17	^1H NMR Spectrum of $\text{Rh}^{\text{III}}(\text{t}_4\text{-CF}_3\text{pp})^i\text{C}_3\text{F}_7$ 5a	S16
18	^{19}F NMR Spectrum of $\text{Rh}^{\text{III}}(\text{t}_4\text{-CF}_3\text{pp})^i\text{C}_3\text{F}_7$ 5a	S16

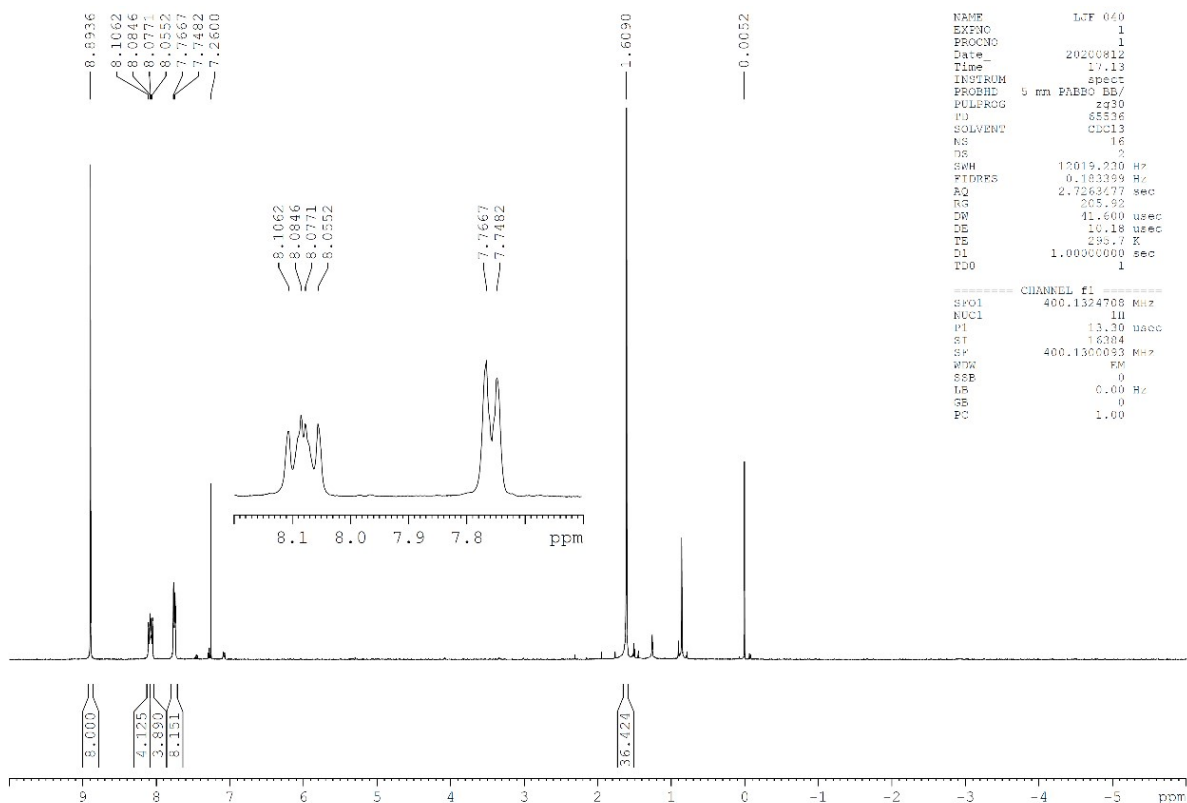
¹H NMR Spectrum of Rh^{III}(btp)ⁱC₃F₇ **2a**



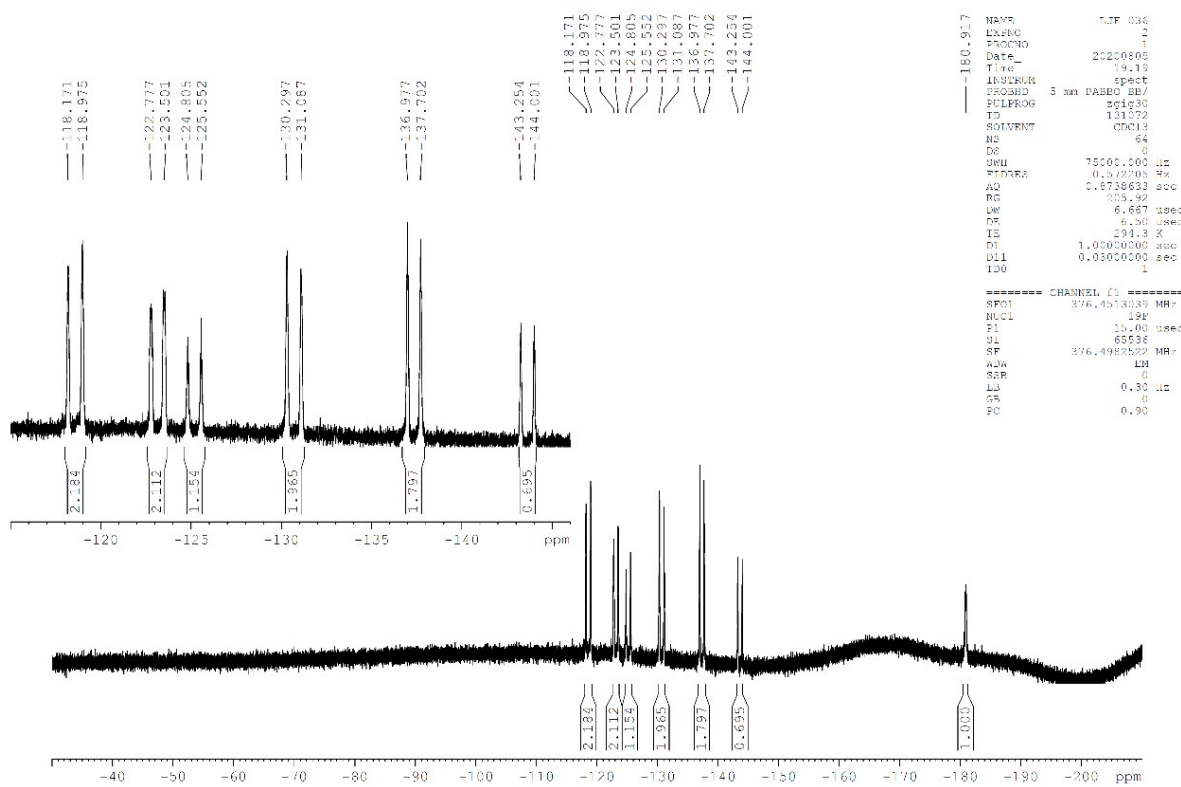
¹⁹F NMR Spectrum of Rh^{III}(btp)ⁱC₃F₇ **2a**



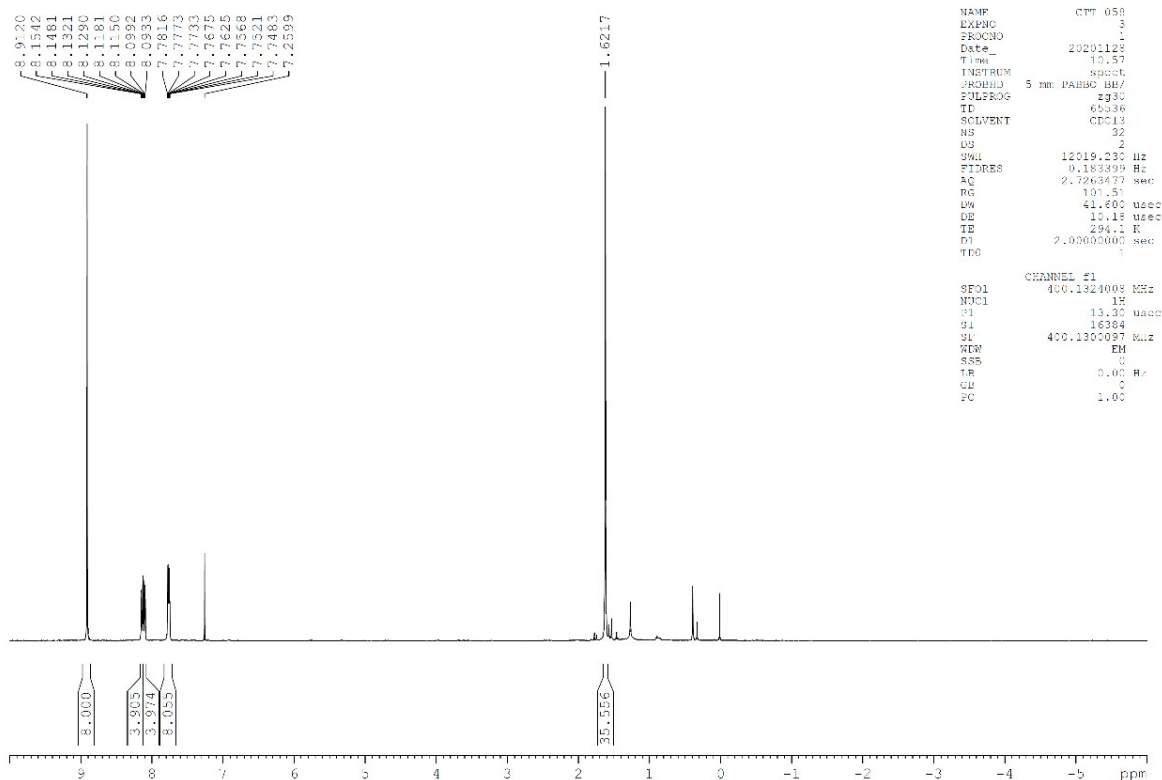
¹H NMR Spectrum of Rh^{III}(btp)^cC₆F₁₁ **2b**



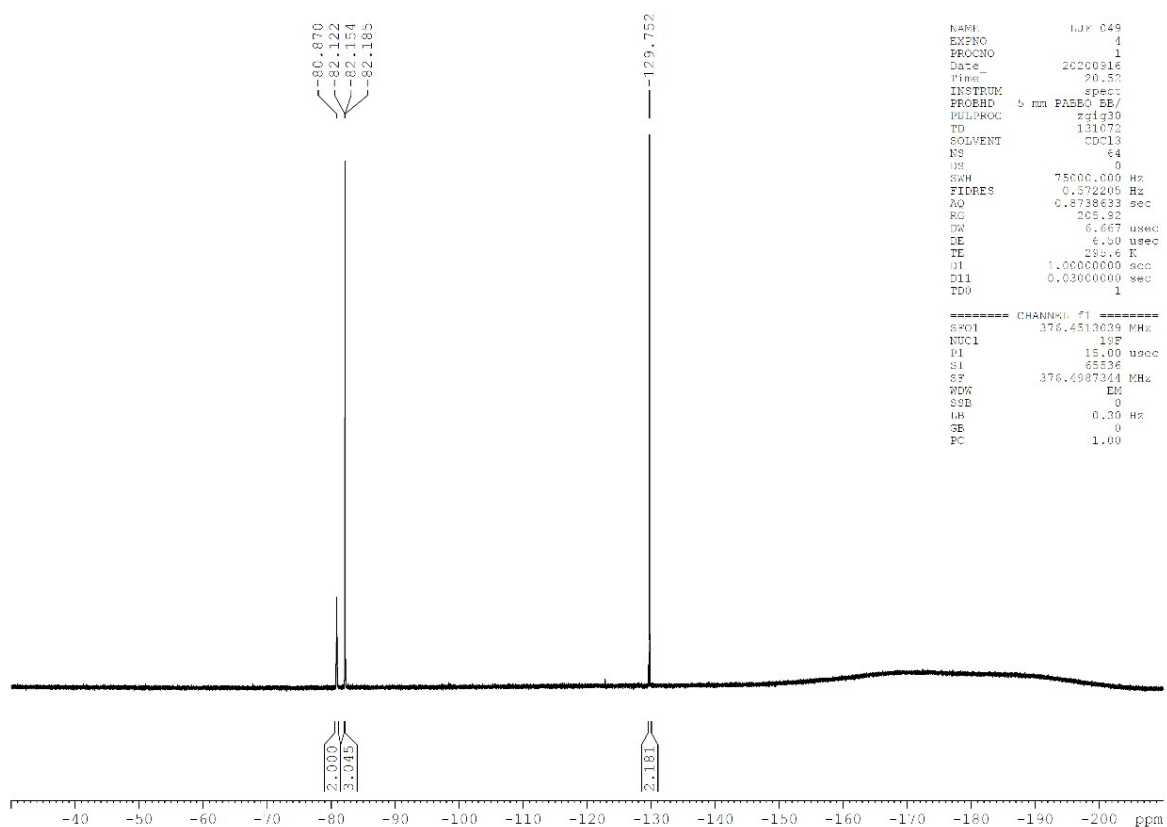
¹⁹F NMR Spectrum of Rh^{III}(btp)^cC₆F₁₁ **2b**



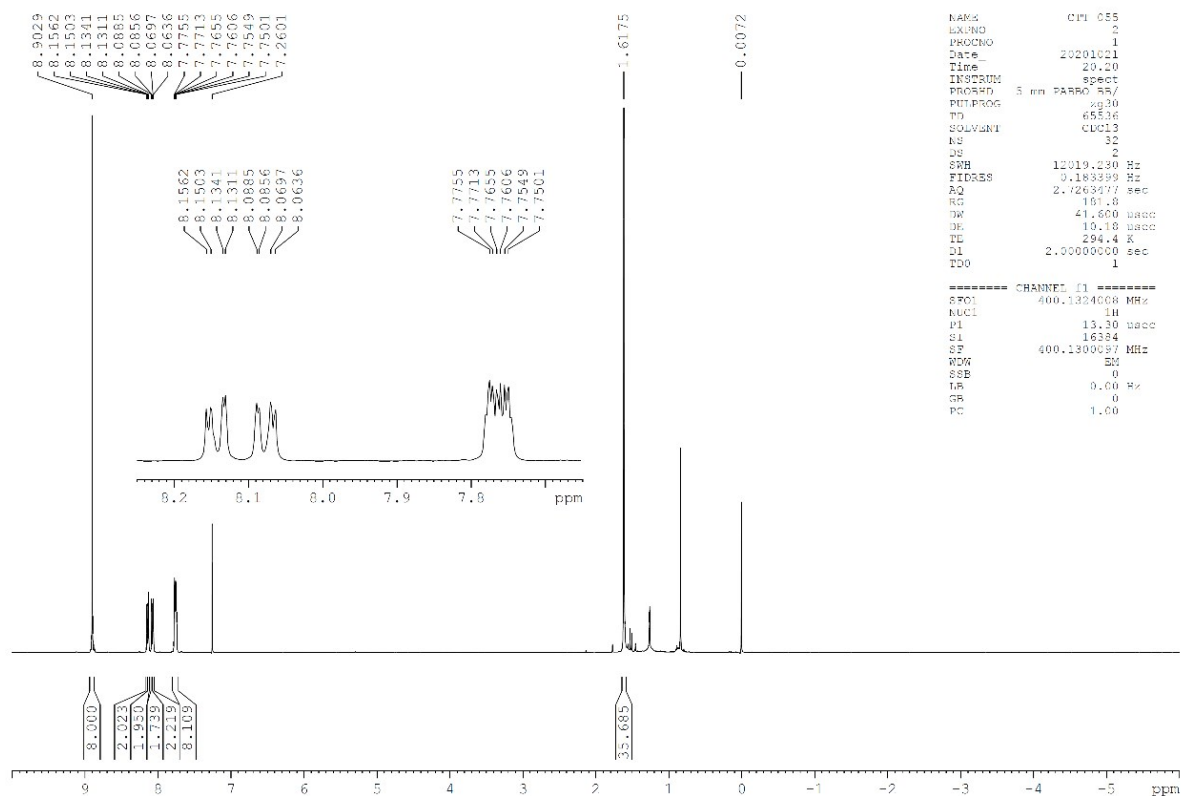
¹H NMR Spectrum of Rh^{III}(btp)ⁿC₃F₇ 2c



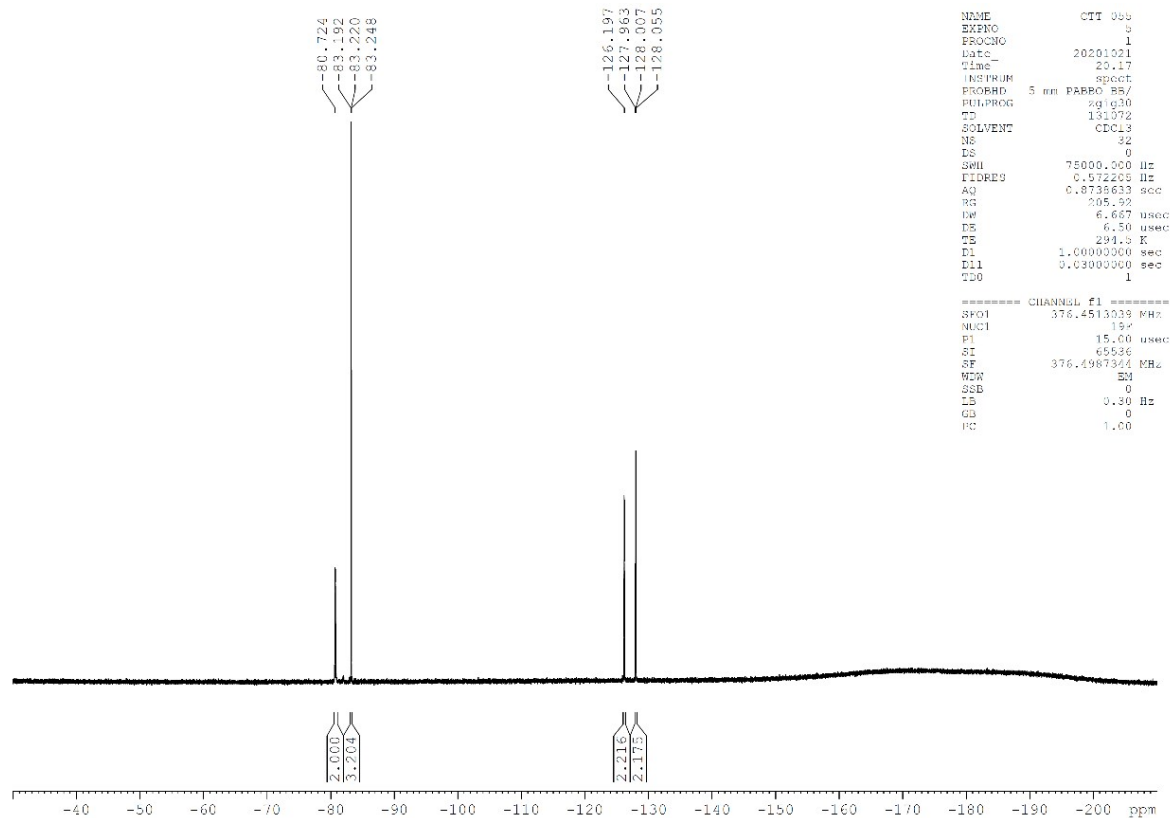
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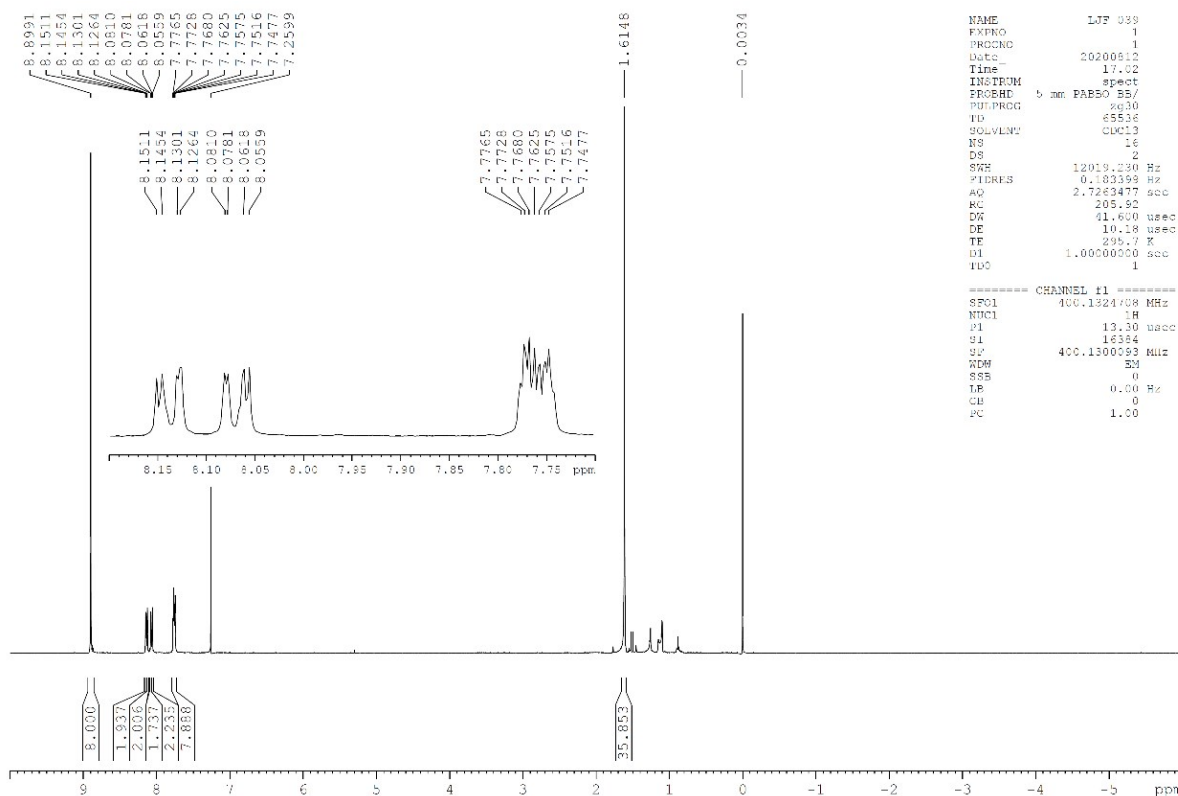
¹H NMR Spectrum of Rh^{III}(btp)ⁿC₄F₉ 2d



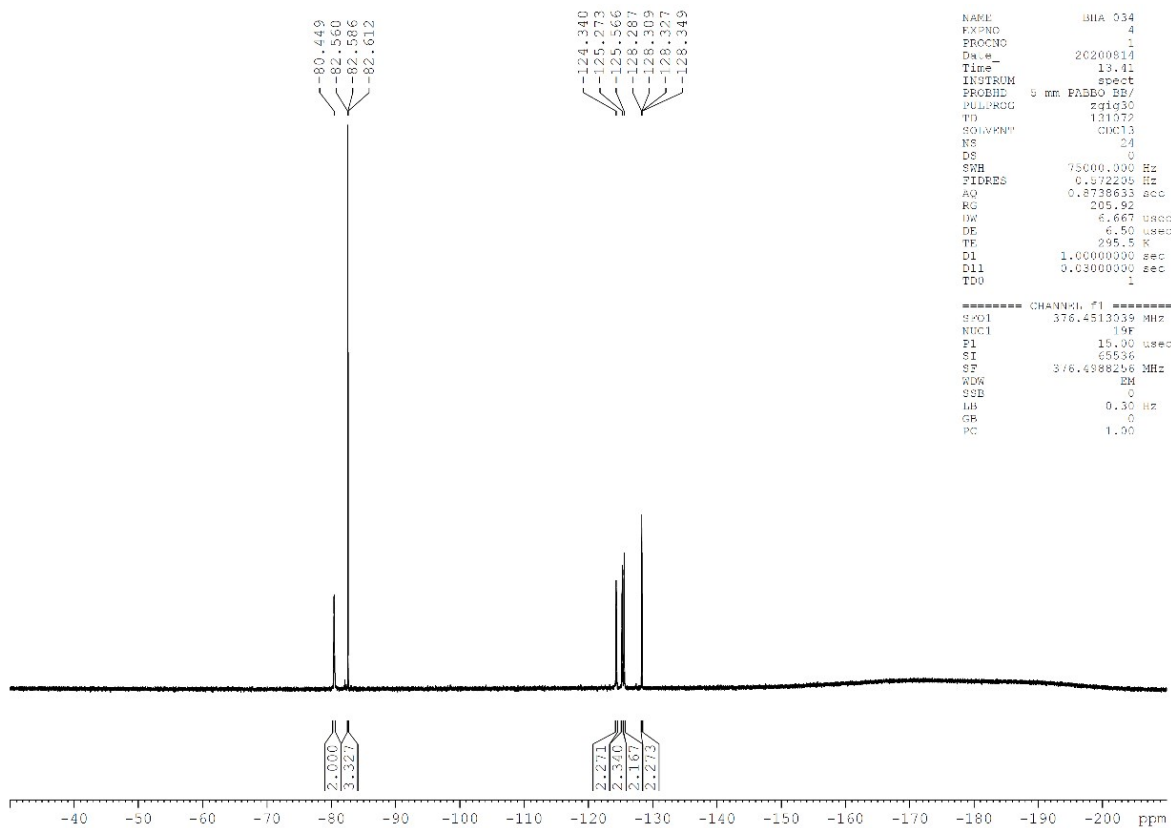
¹⁹F NMR Spectrum of Rh^{III}(btp)ⁿC₄F₉ 2d



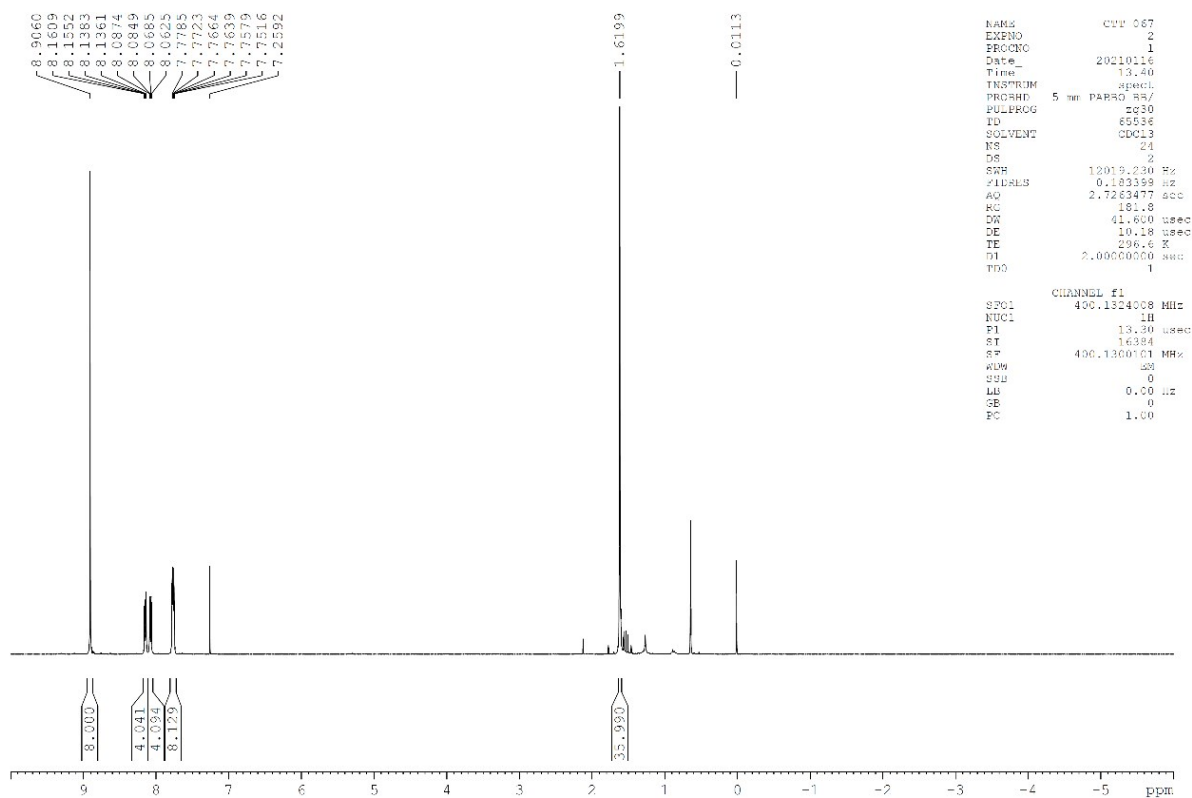
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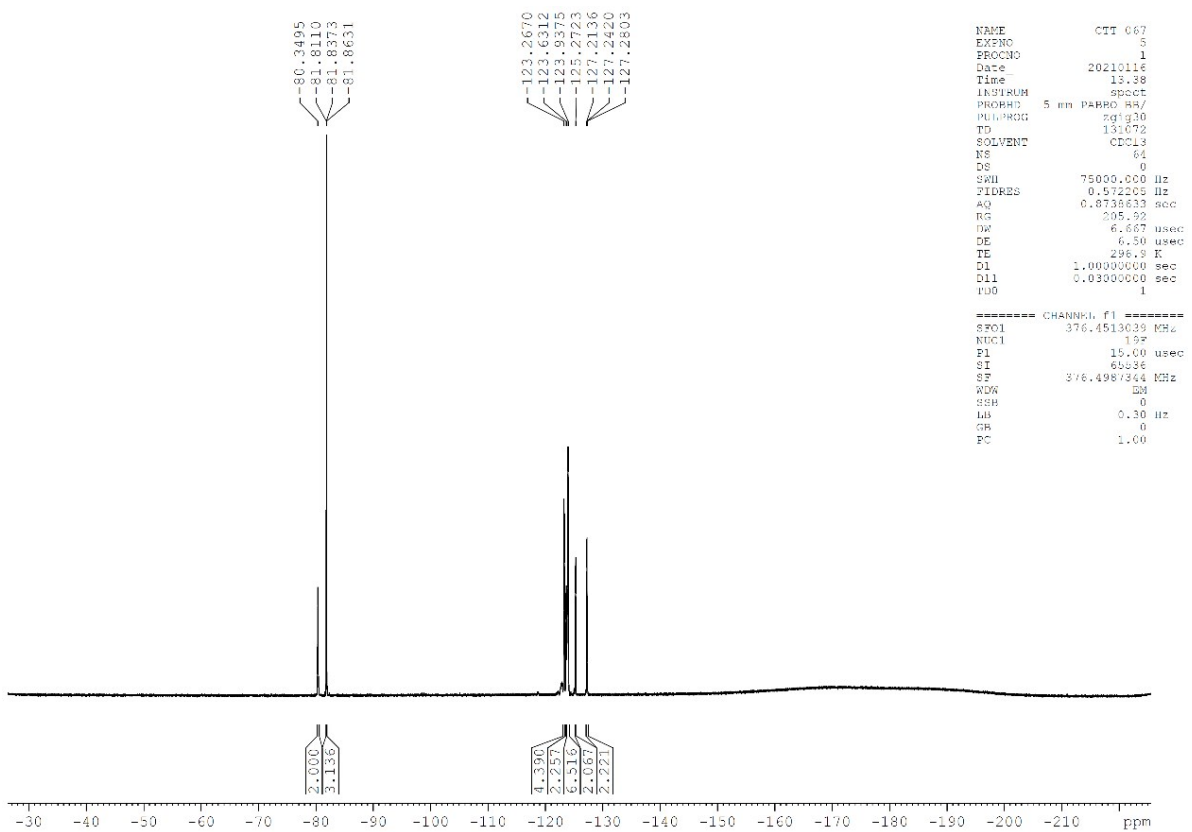
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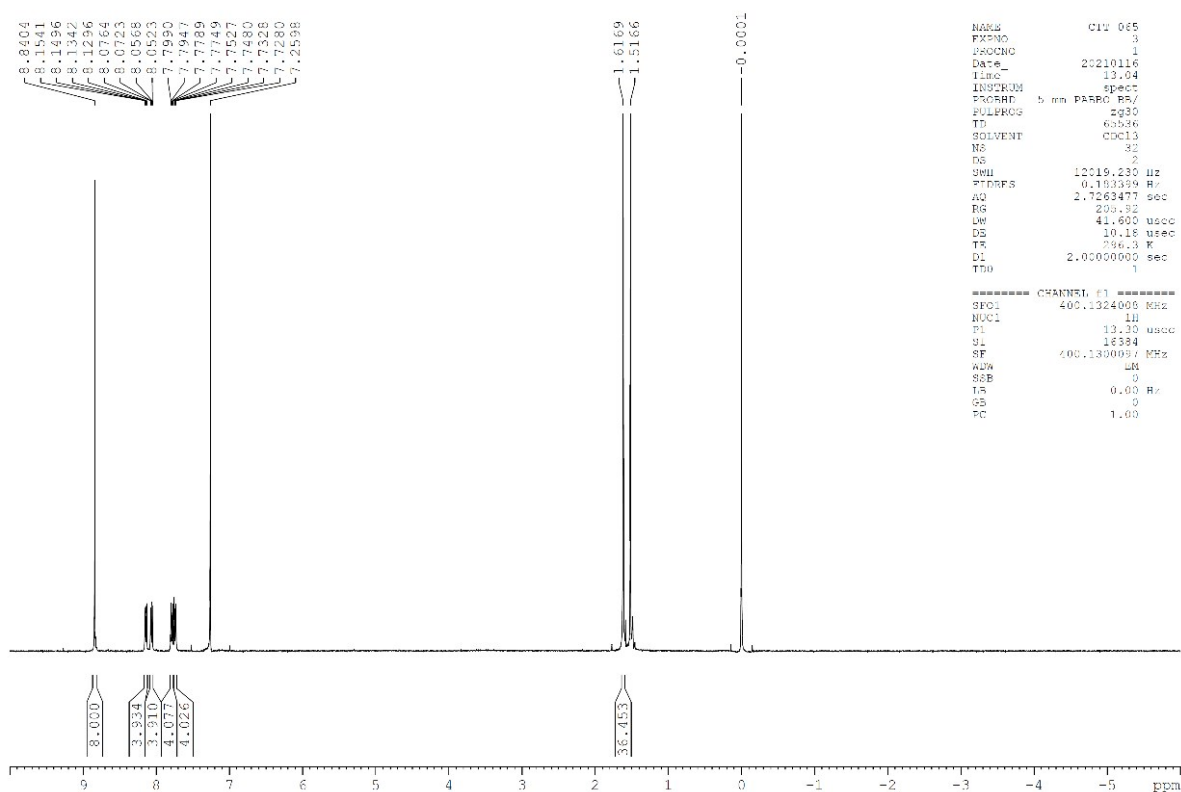
¹H NMR Spectrum of Rh^{III}(btp⁺)ⁿC₁₀F₂₁ **2f**



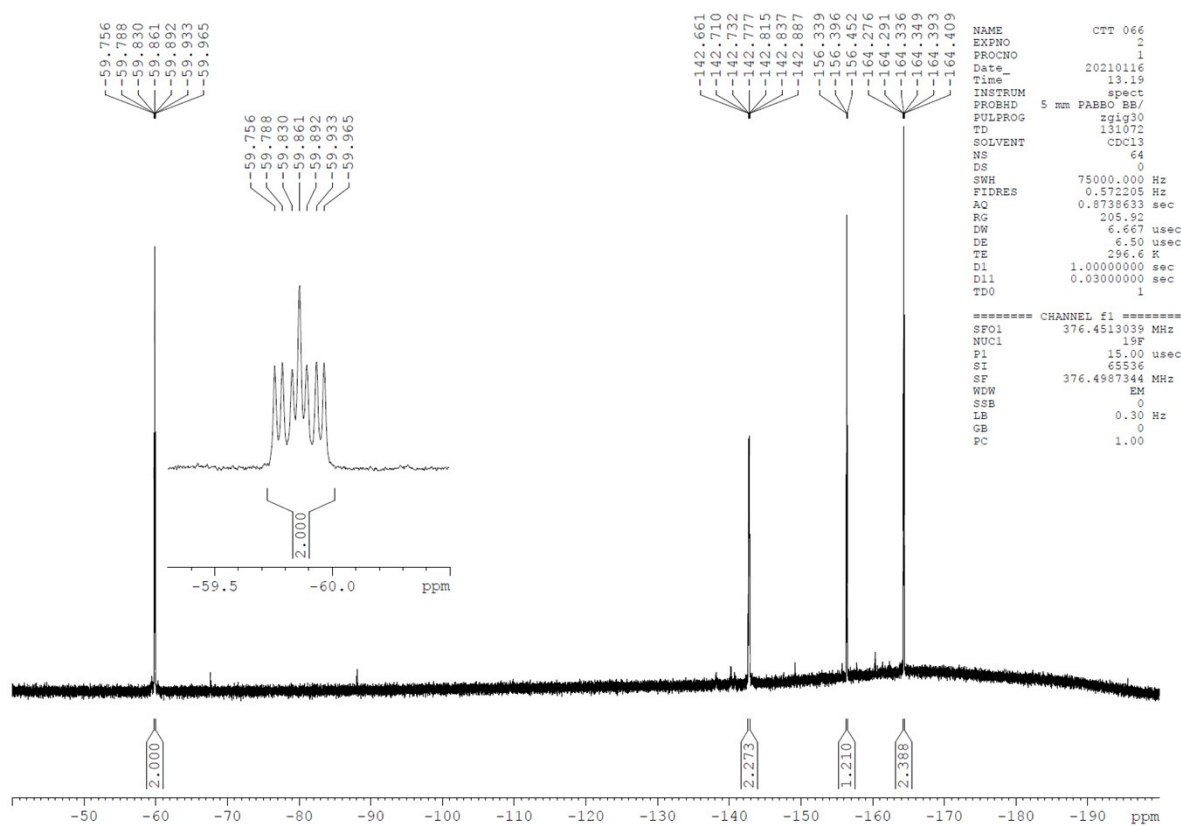
¹⁹F NMR Spectrum of Rh^{III}(btp⁺)ⁿC₁₀F₂₁ **2f**



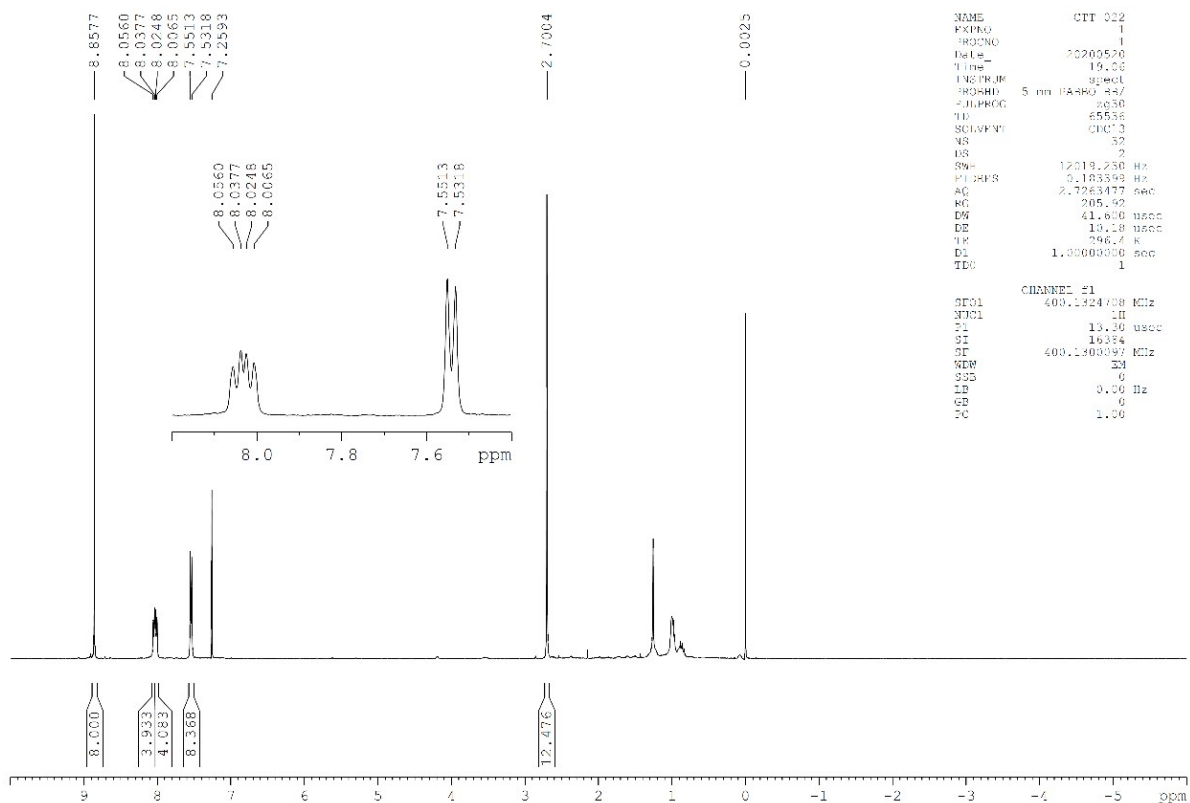
¹H NMR Spectrum of Rh^{III}(btp_p)CF₂C₆F₅ 2g



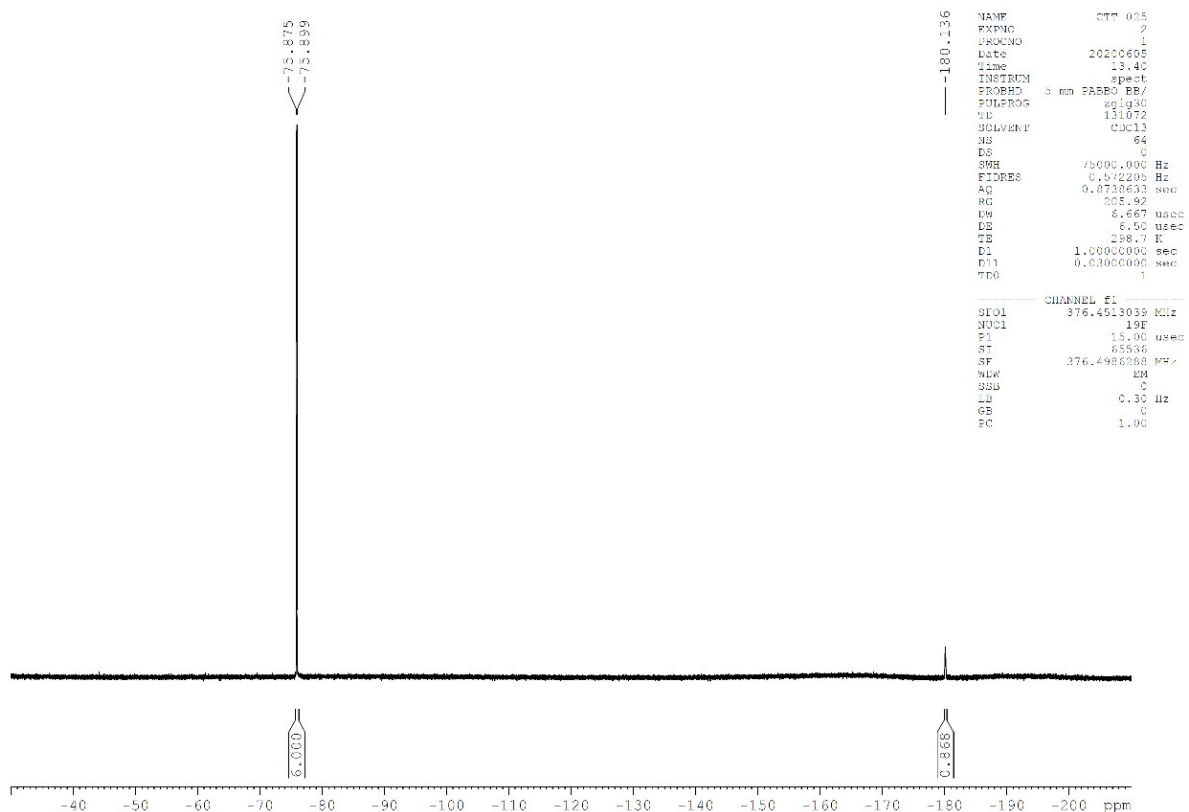
¹⁹F NMR Spectrum of Rh^{III}(btp_p)CF₂C₆F₅ 2g



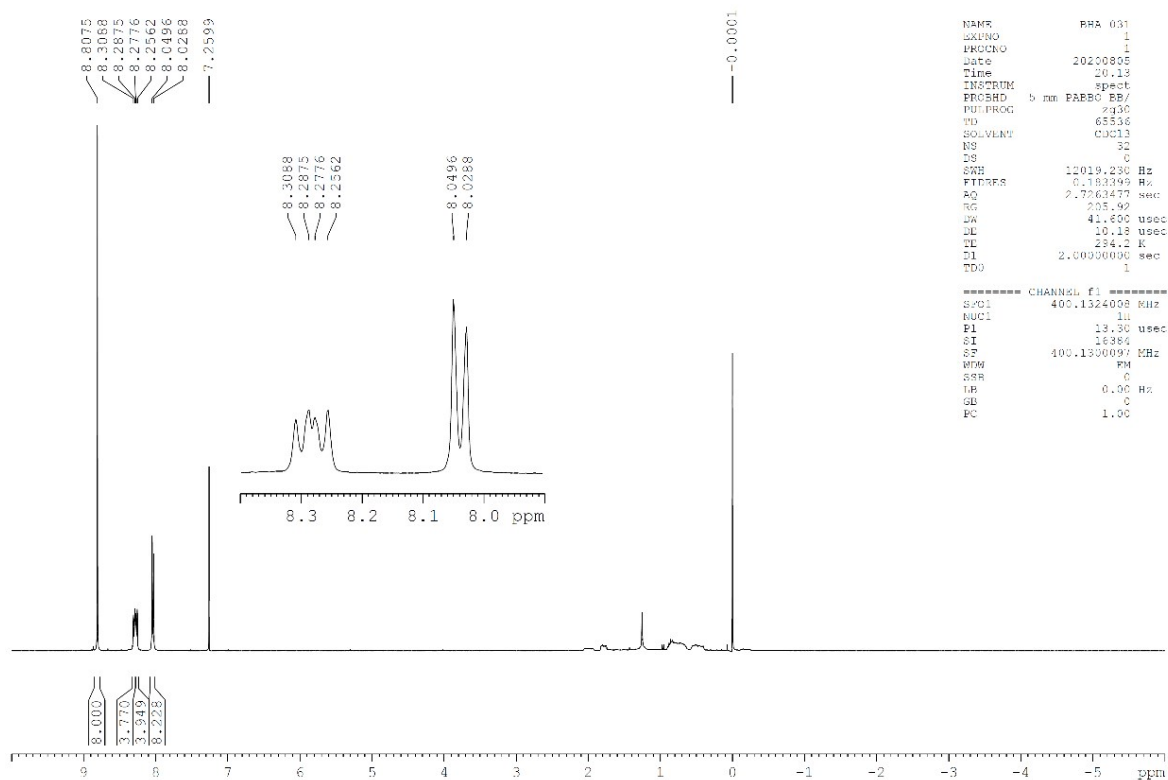
¹H NMR Spectrum of Rh^{III}(ttp)^dC₃F₇ **4a**



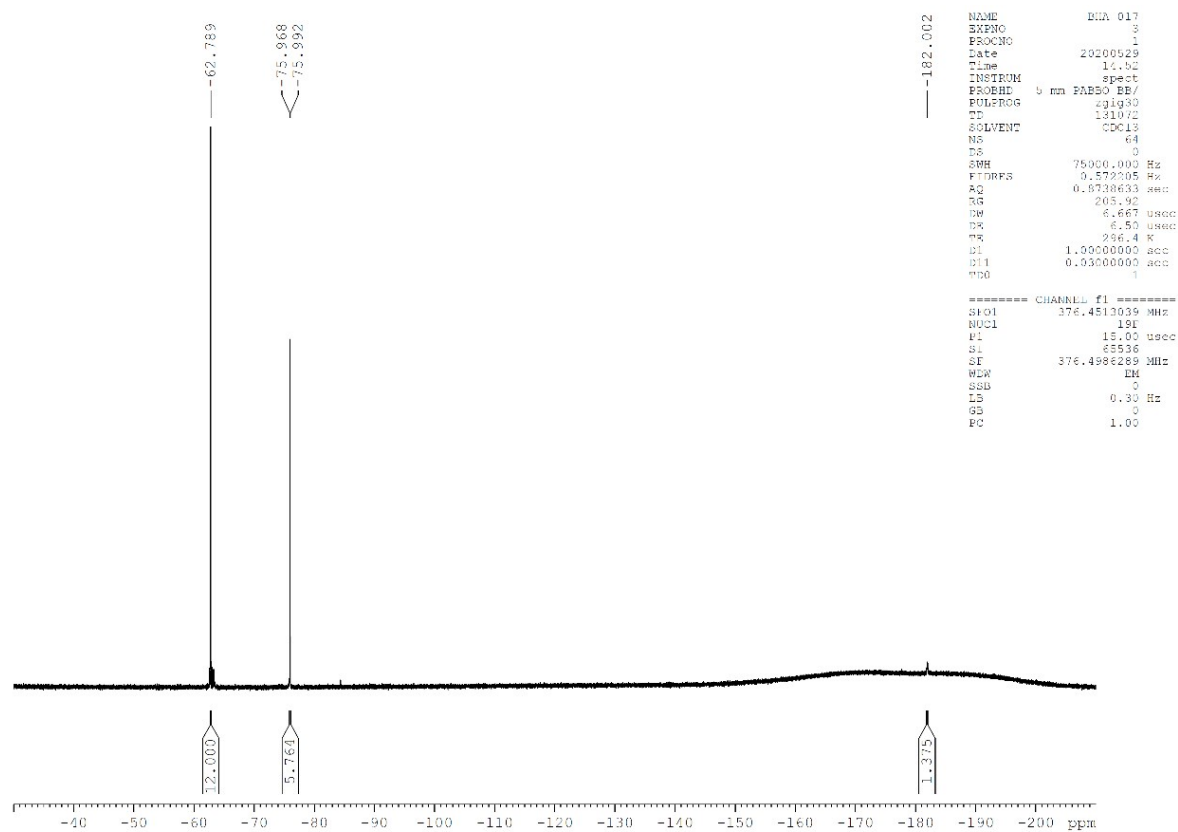
¹⁹F NMR Spectrum of Rh^{III}(ttp)^dC₃F₇ **4a**



¹H NMR Spectrum of Rh^{III}(t₄-CF₃pp)ⁱC₃F₇ **5a**



¹⁹F NMR Spectrum of Rh^{III}(t₄-CF₃pp)ⁱC₃F₇ **5a**



HRMS Spectra

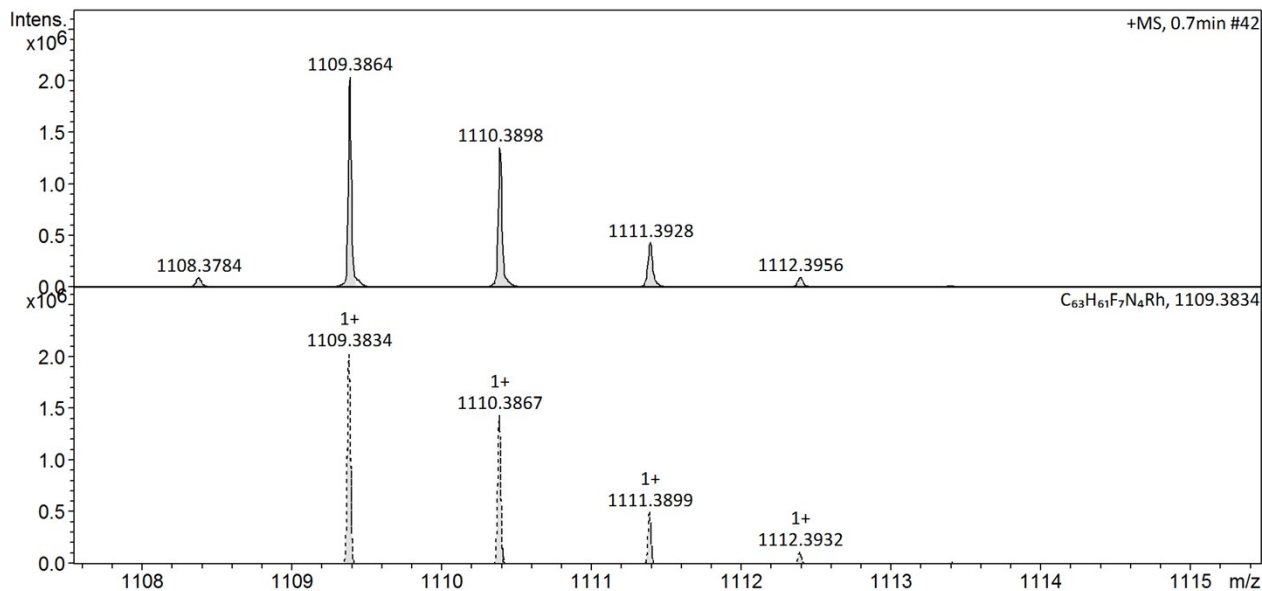
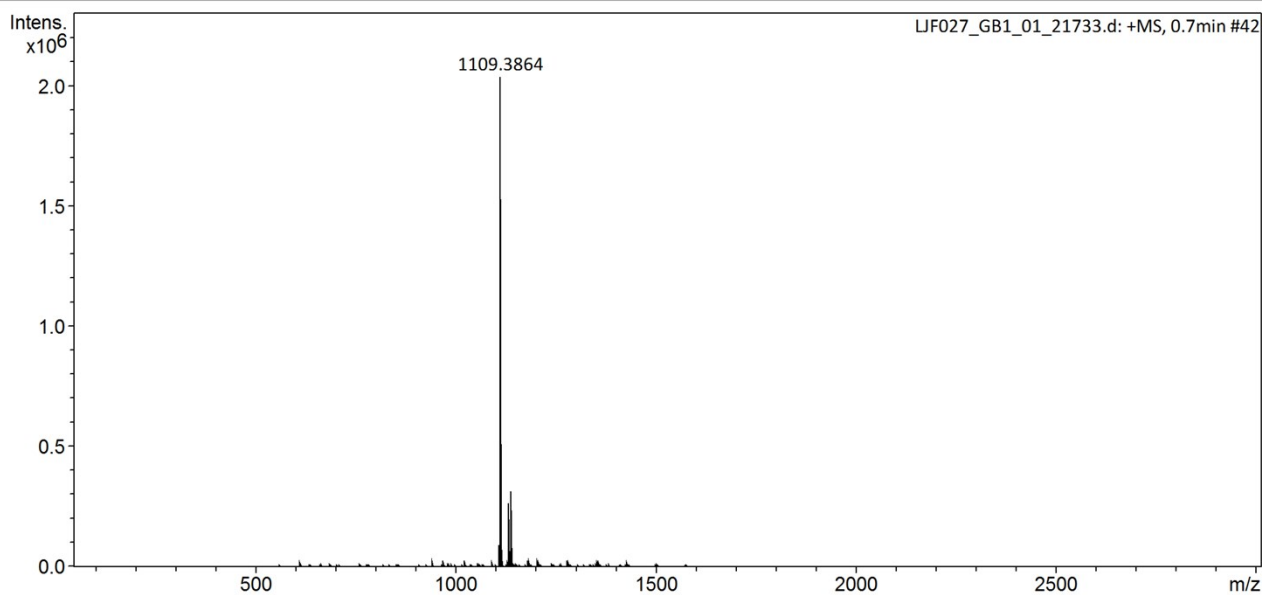
HRMS Spectrum of Rh^{III}(btp)₃C₃F₇ **2a**

Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1109.3864	1	C ₆₃ H ₆₁ F ₇ N ₄ Rh	1109.3834	2.7	22.9	1	100.00	32.5	even	ok	M+H

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



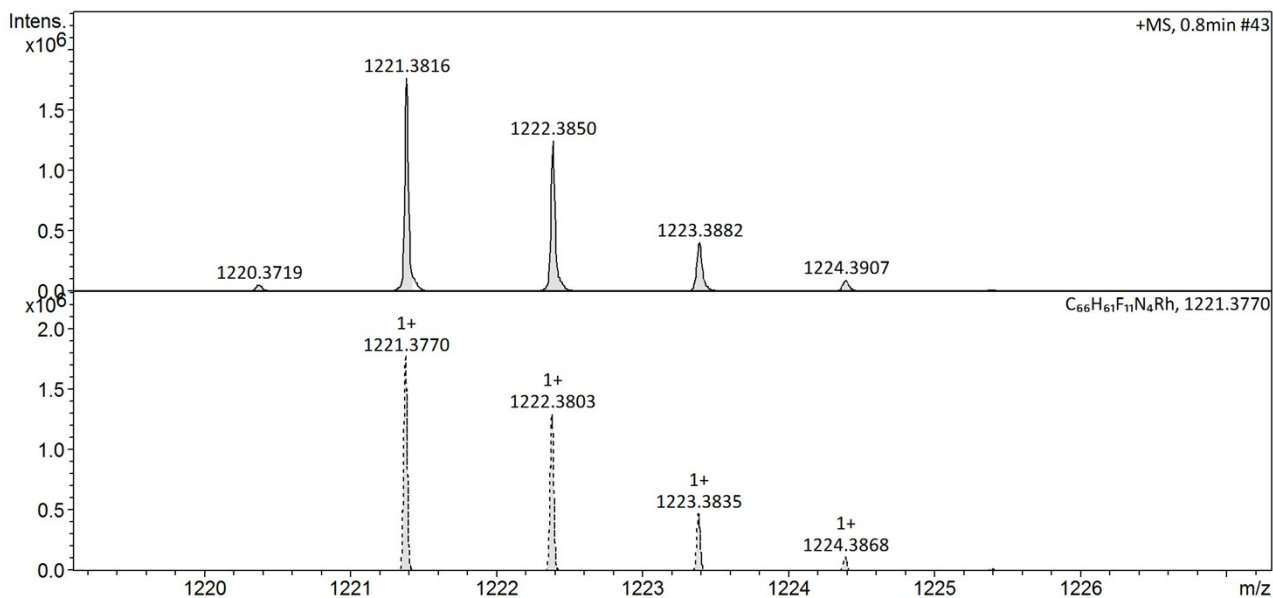
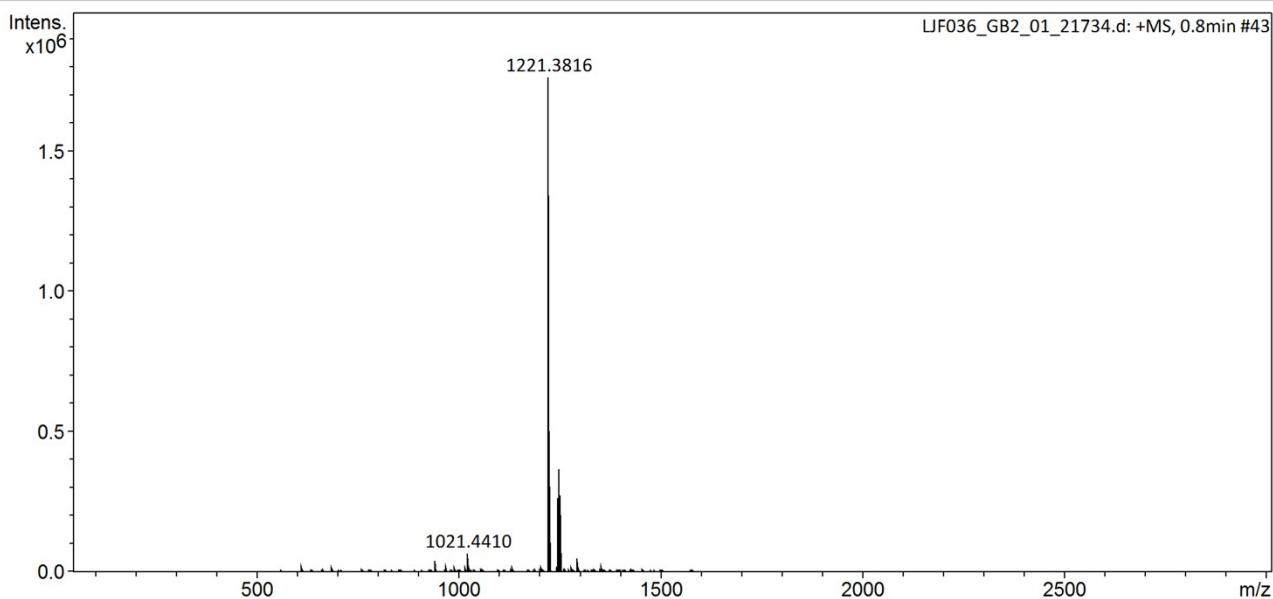
HRMS Spectrum of Rh^{III}(btp⁻)₃C₆F₁₁ **2b**

Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1221.3816	1	C ₆₆ H ₆₁ F ₁₁ N ₄ Rh	1221.3770	3.7	22.0	1	100.00	33.5	even	ok	M+H

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
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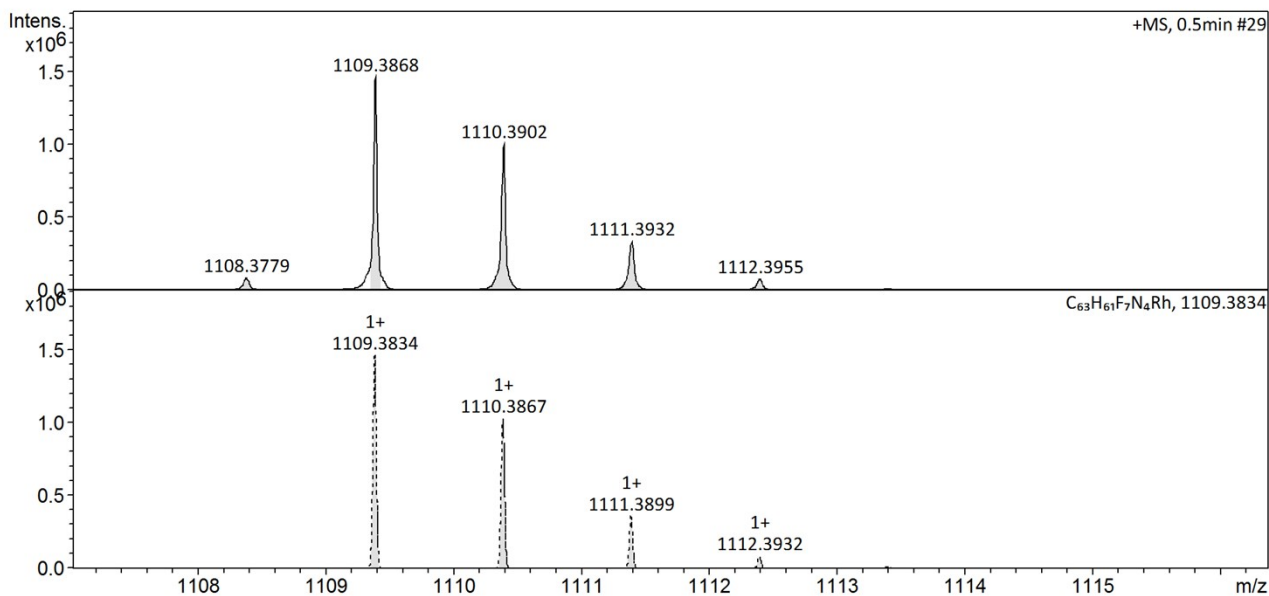
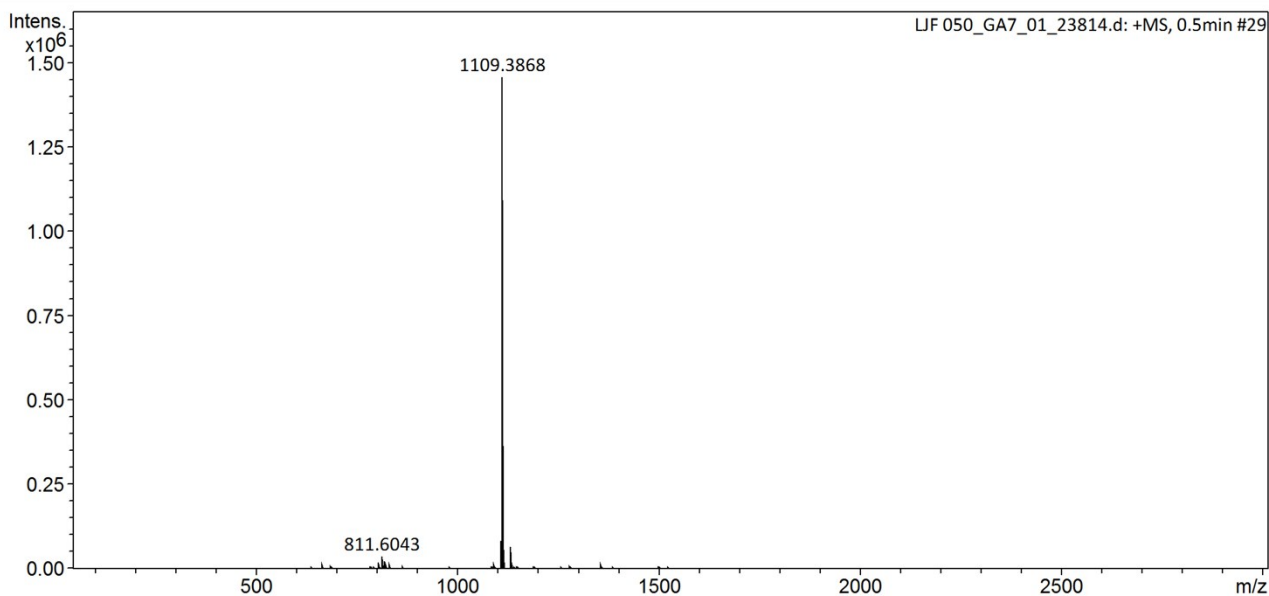
HRMS Spectrum of Rh^{III}(btp)₃C₃F₇ 2c

Display Report

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1109.3868	1	C ₆₃ H ₆₁ F ₇ N ₄ Rh	1109.3834	-3.1	9.0	1	100.00	32.5	even	ok	M+H

Acquisition Parameter

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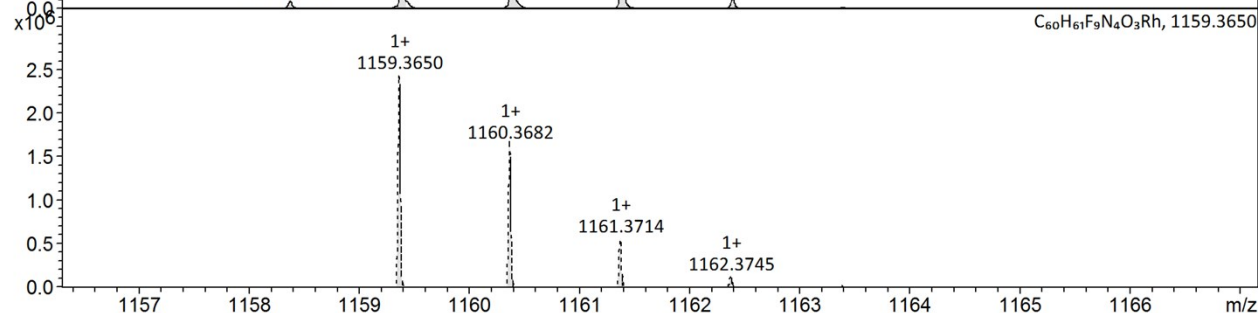
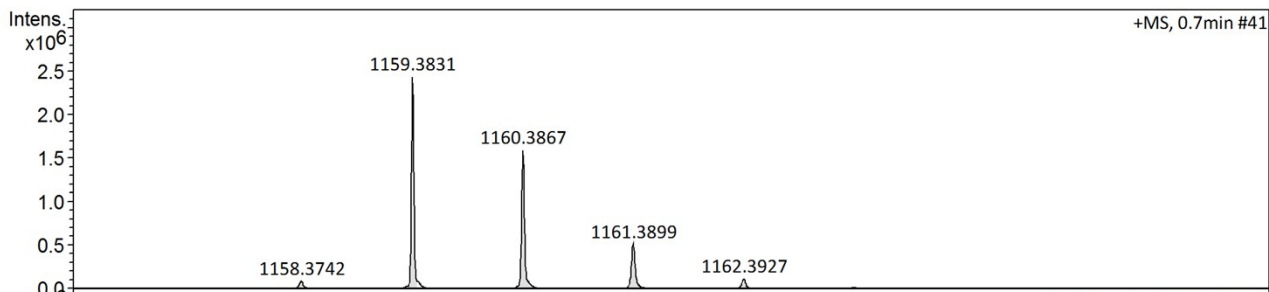
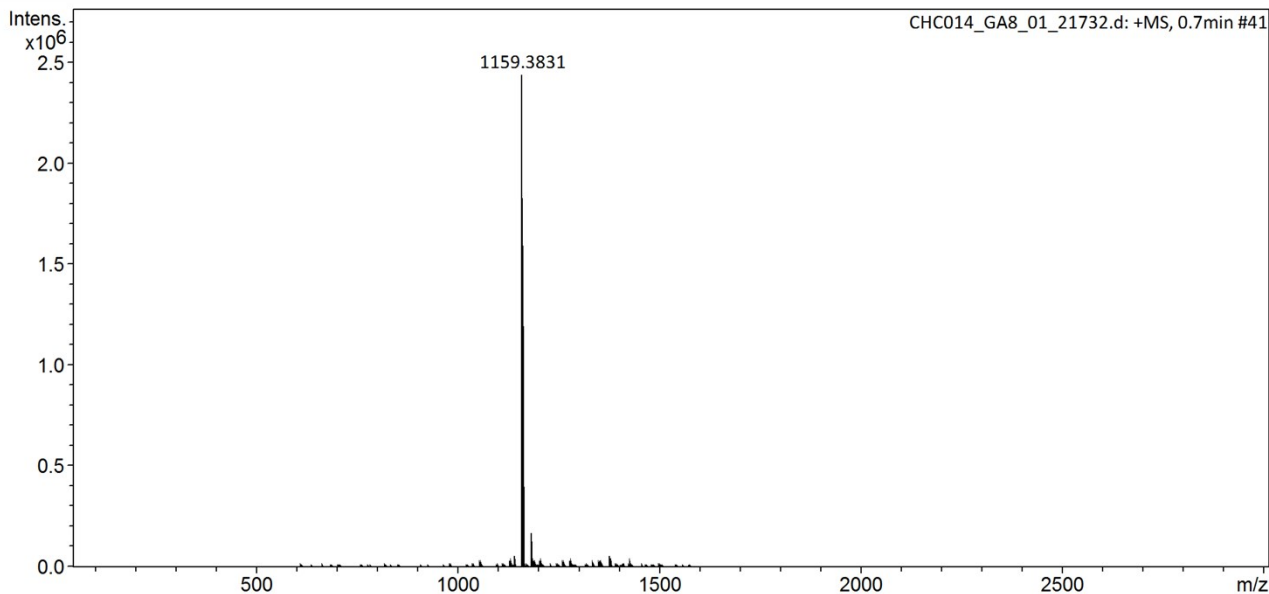
HRMS Spectrum of Rh^{III}(btp⁺)₃C₄F₉ 2d

Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1159.3831	1	C ₆₄ H ₆₁ F ₉ N ₄ Rh	1159.3802	-2.5	33.3	2	100.00	32.5	even	ok	M+H

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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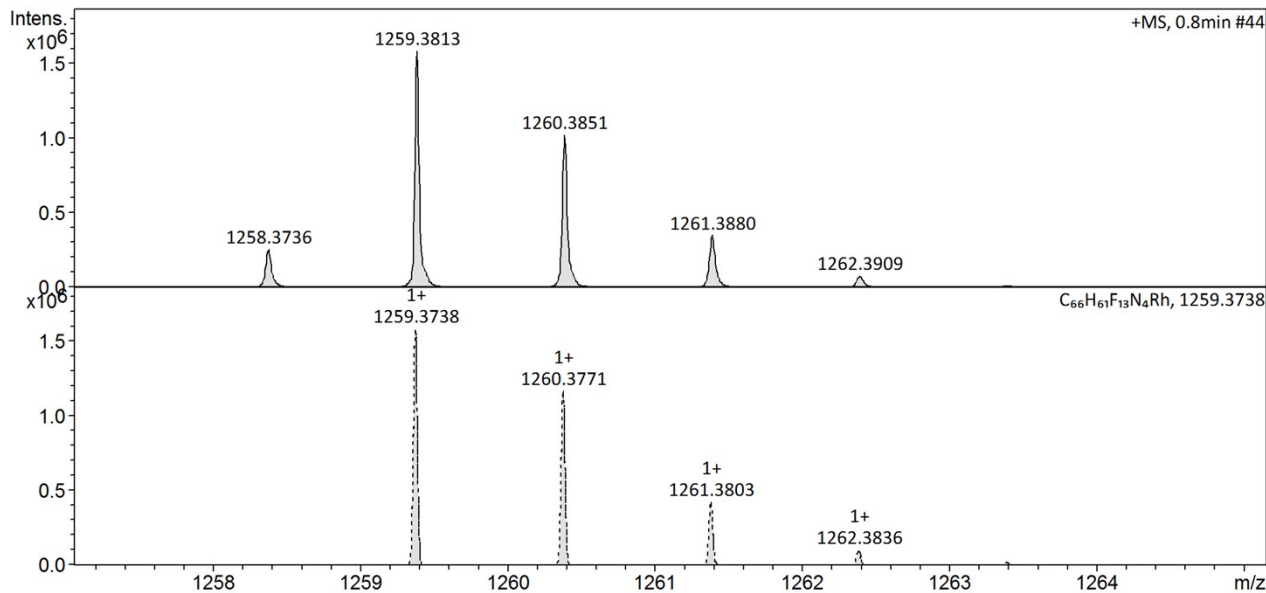
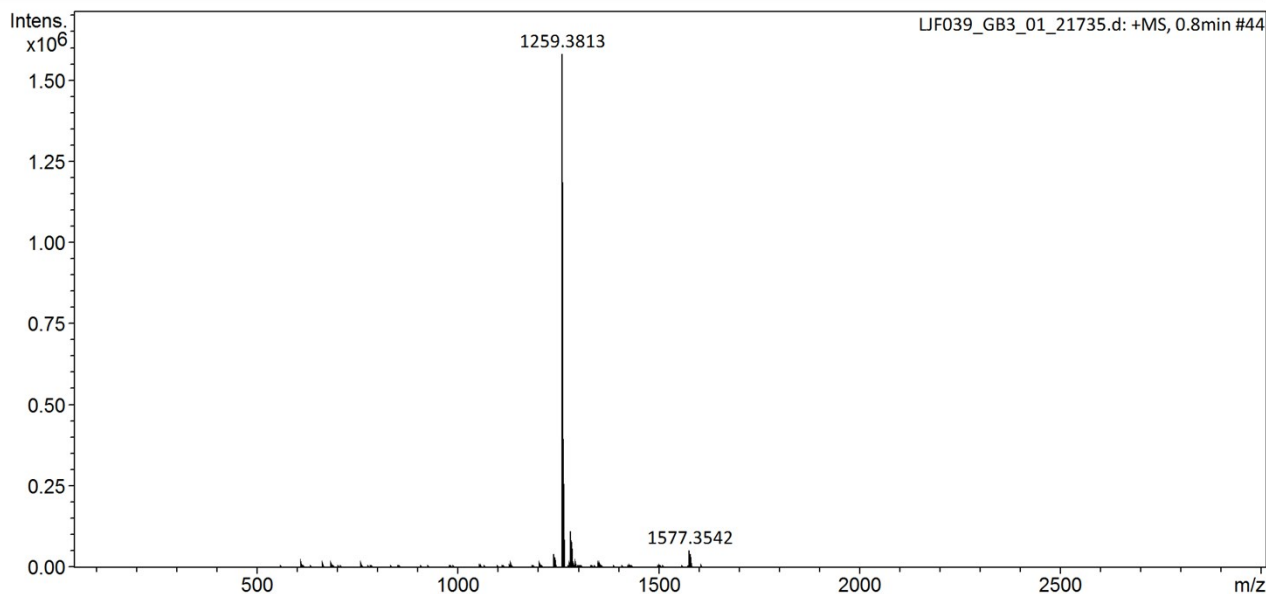
HRMS Spectrum of Rh^{III}(btp⁺)₃C₆F₁₃ 2e

Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1259.3813	1	C ₆₆ H ₆₁ F ₁₃ N ₄ Rh	1259.3738	6.0	47.2	1	100.00	32.5	even	ok	M+H

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
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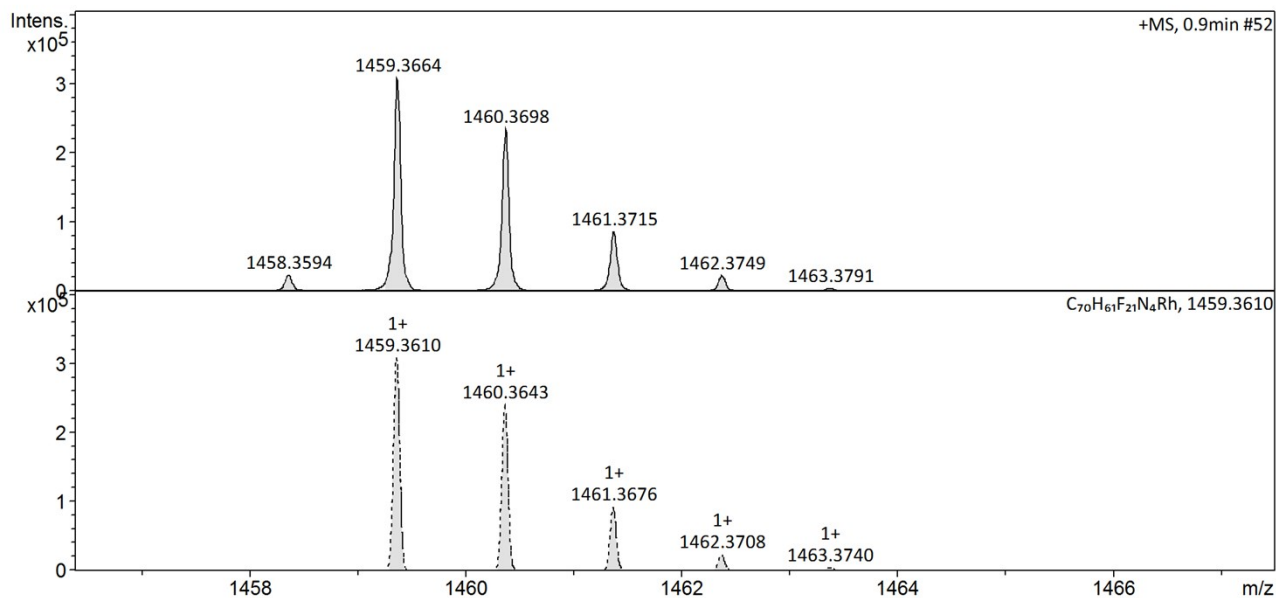
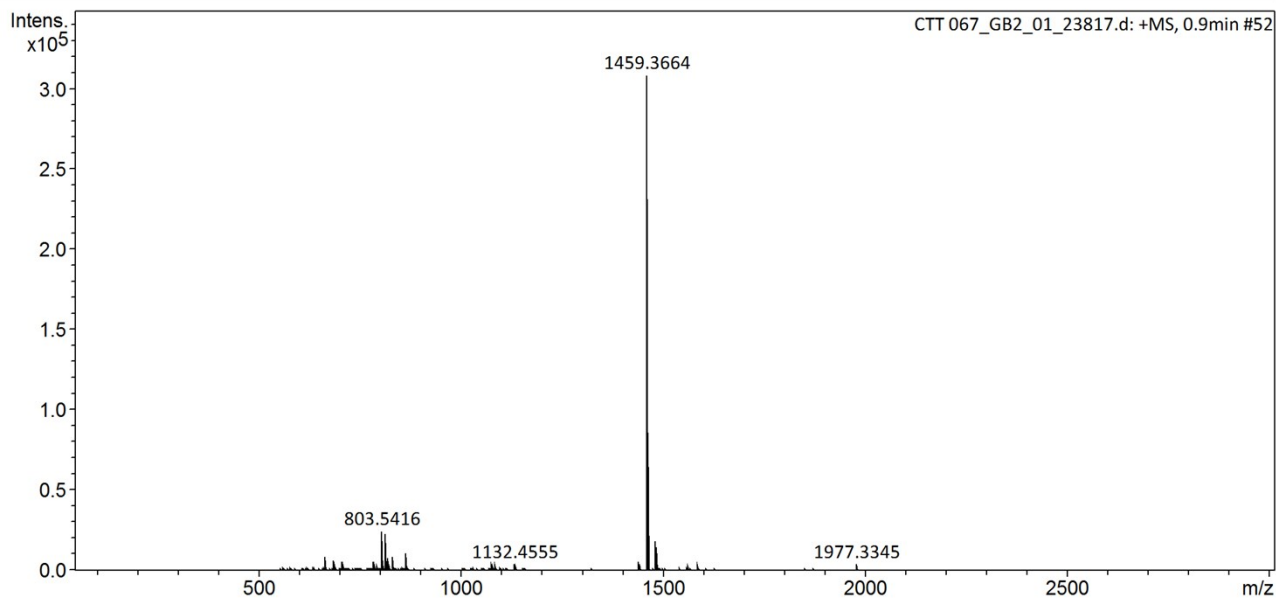
HRMS Spectrum of Rh^{III}(btp⁺)₃C₁₀F₂₁ 2f

Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1459.3664	1	C ₇₀ H ₆₁ F ₂₁ N ₄ Rh	1459.3610	-3.7	12.2	1	100.00	32.5	even	ok	M+H

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
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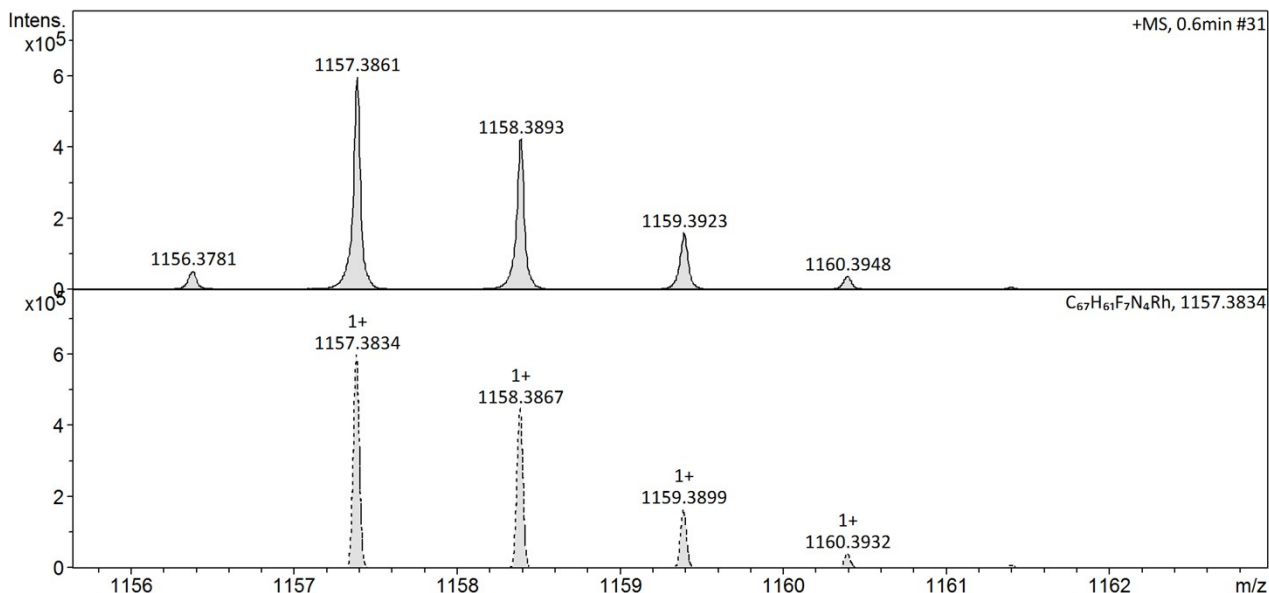
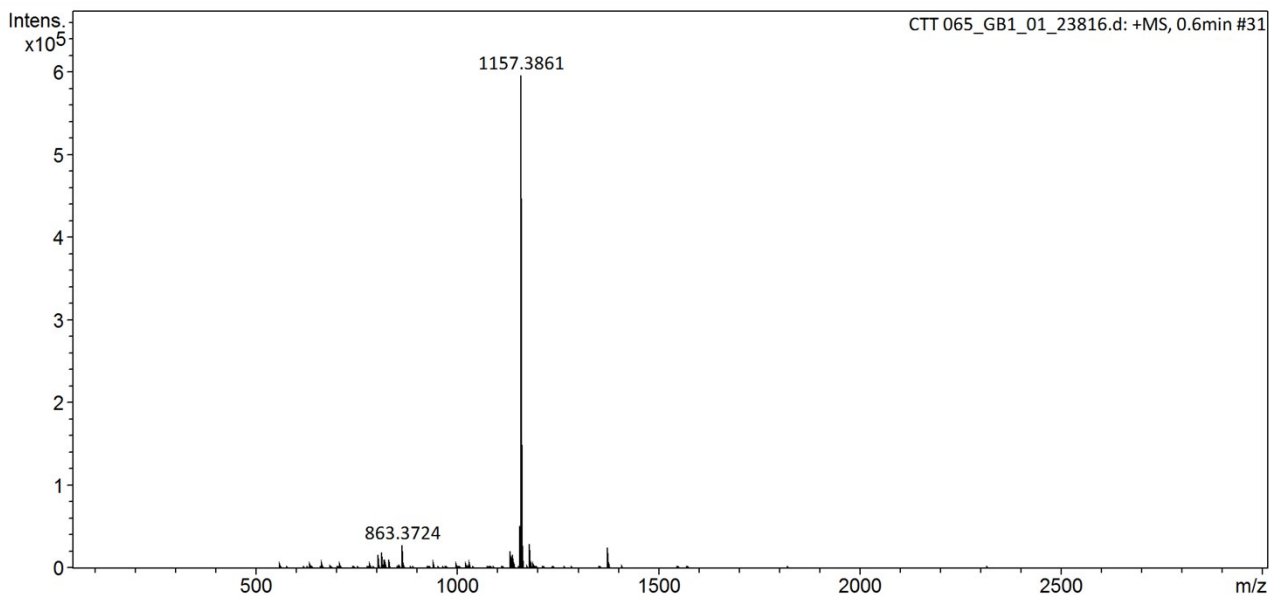
HRMS Spectrum of Rh^{III}(btp_p)CF₂C₆F₅ 2g

Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1157.3861	1	C ₆₇ H ₆₁ F ₇ N ₄ Rh	1157.3834	2.4	17.7	1	100.00	36.5	even	ok	M+H

Acquisition Parameter

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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
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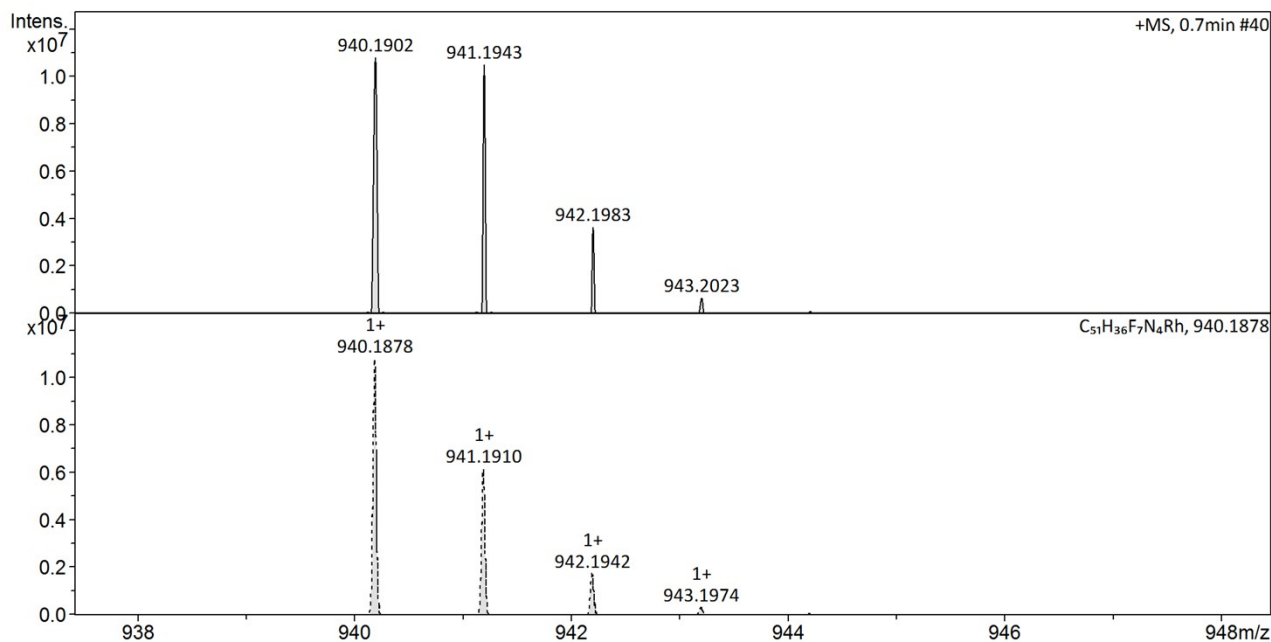
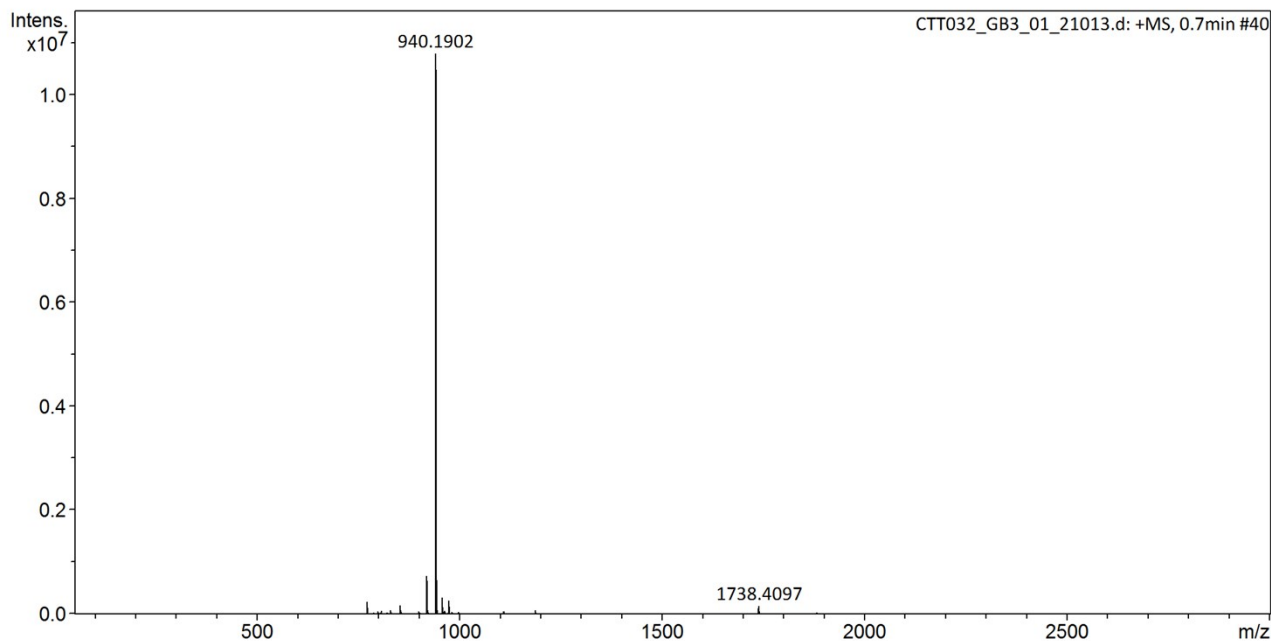
HRMS Spectrum of Rh^{III}(tp)⁺C₃F₇ 4a

Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
940.1902	1	C ₅₁ H ₃₆ F ₇ N ₄ Rh	940.1878	2.6	196.6	1	100.00	33.0	odd	ok	M
941.1943	1	C ₅₁ H ₃₇ F ₇ N ₄ Rh	941.1956	1.4	109.1	1	100.00	32.5	even	ok	M+H

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



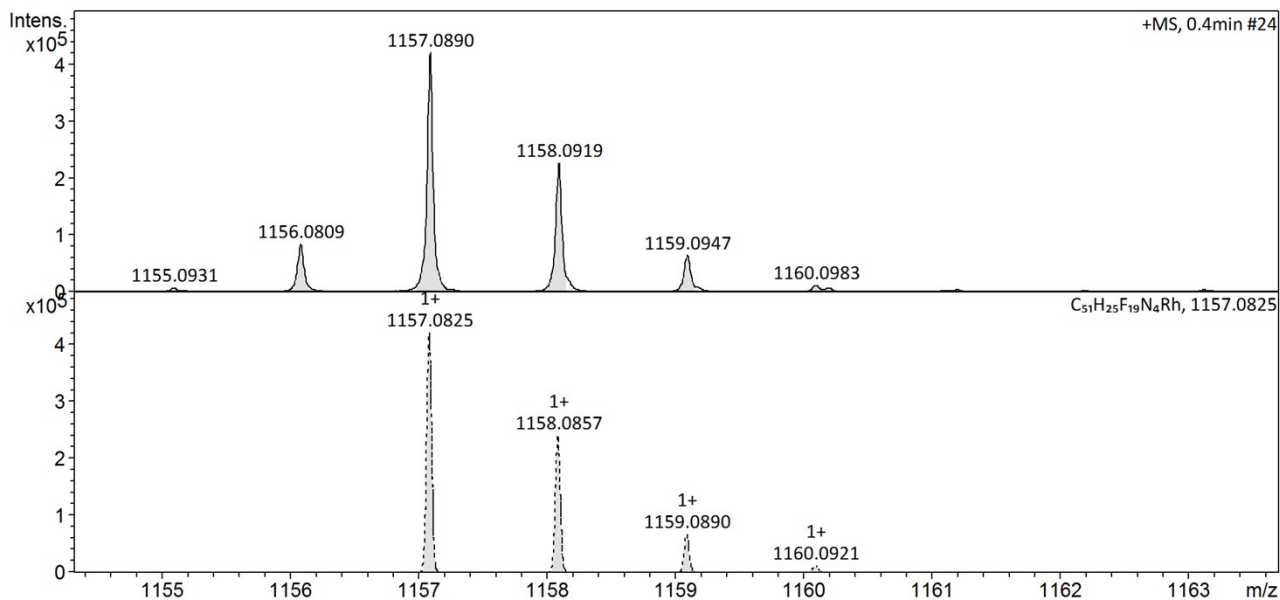
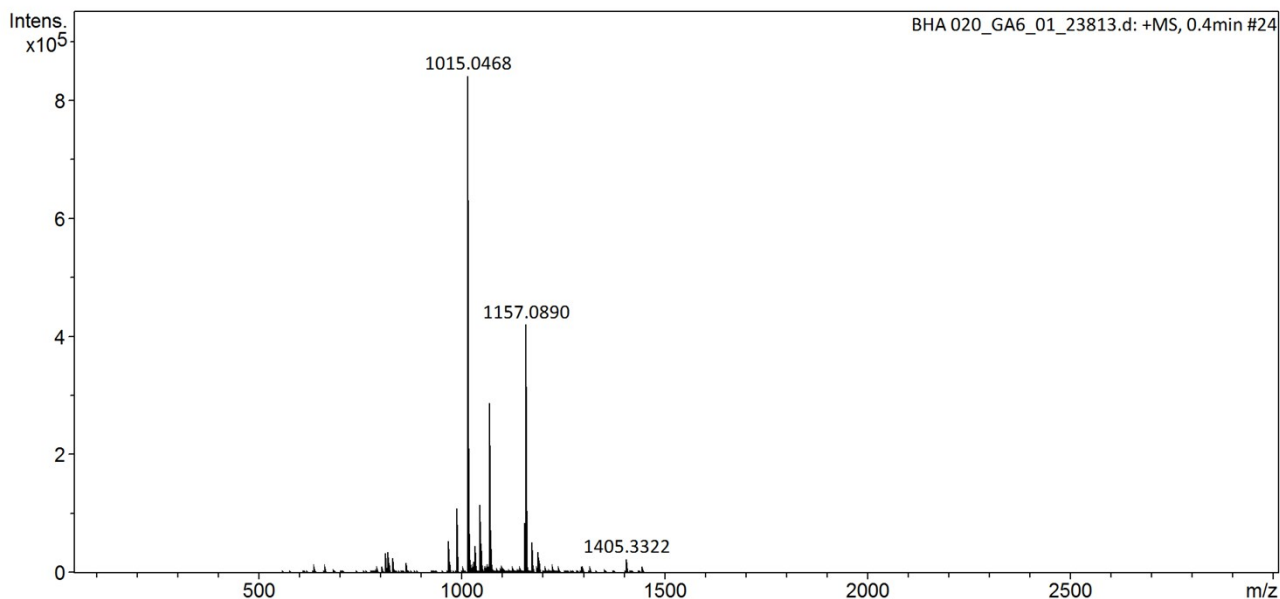
HRMS Spectrum of Rh^{III}(t₄-CF₃pp)ⁱC₃F₇ 5a

Display Report

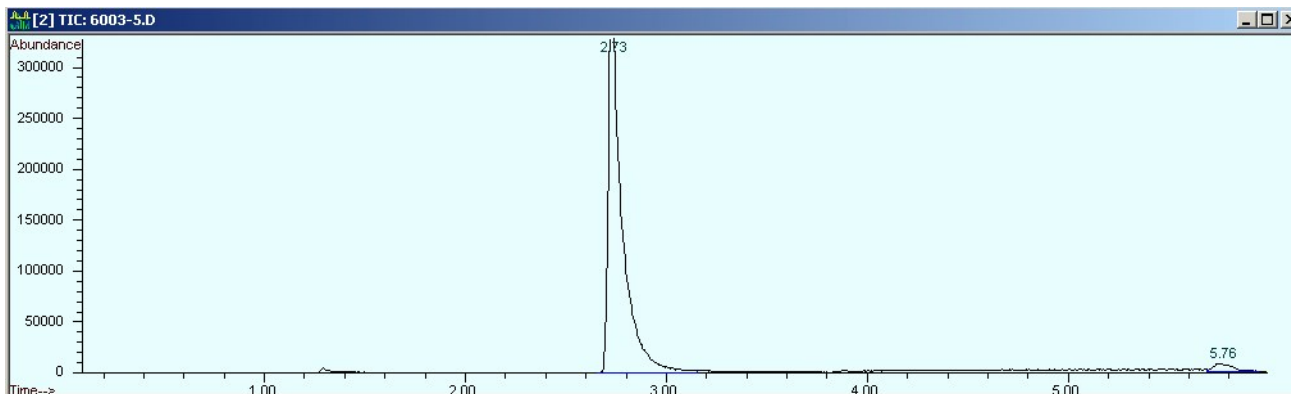
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1157.0890	1	C ₅₁ H ₂₅ F ₁₉ N ₄ Rh	1157.0825	-5.6	14.5	1	100.00	32.5	even	ok	M+H

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

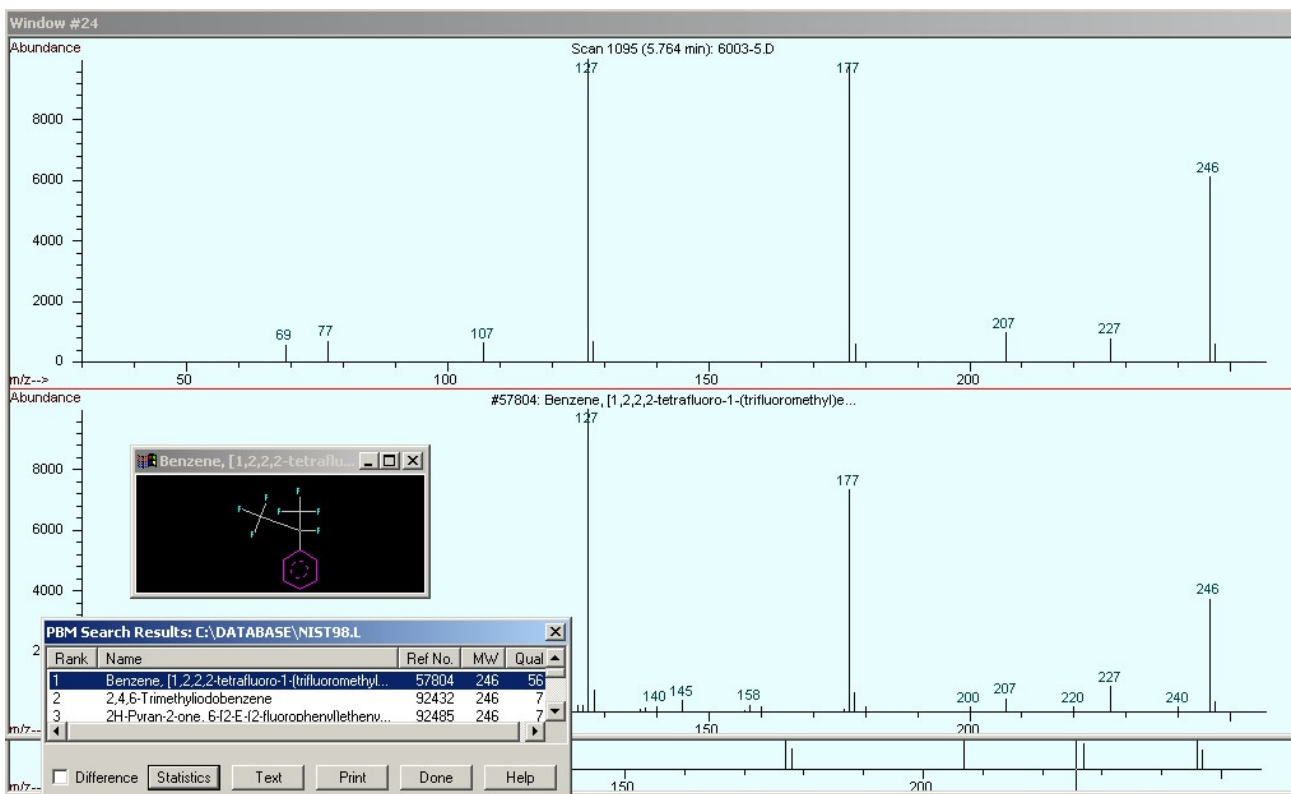


GCMS Spectra



Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	2.727	rVB	0.497	1742819	2.654	3.152
2	5.764	rVB	0.259	49774	5.691	5.950

Mass spectrum at $t_R = 5.764$ min



Mass spectrum at $t_R = 2.732$ min

