Simple NMR predictors of catalytic hydrogenation activity for Rh(cod)Cl(NHC) complexes featuring fluorinated NHC ligands.

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Supplementary Information

Catalytic testing method

The catalyst (0.01 mmol, 1 mol %) was dissolved in a solution of potassium hydroxide (5.61 mg, 0.1 mmol) and isopropanol (5 mL) in a two-necked flask. The solution was heated at 80°C for 30 min under reflux conditions. Subsequently, acetophenone (0.12 mL, 1.0 mmol) was added. After the desired reaction time, an aliquot of the reaction mixture was quenched with 1M HCl and extracted with diethyl ether. The organic phase was separated and collected. The reaction progress was monitored by ^{1}H NMR and the results for each experiment were averaged over three runs.

Plots of average conversion against NMR parameters.

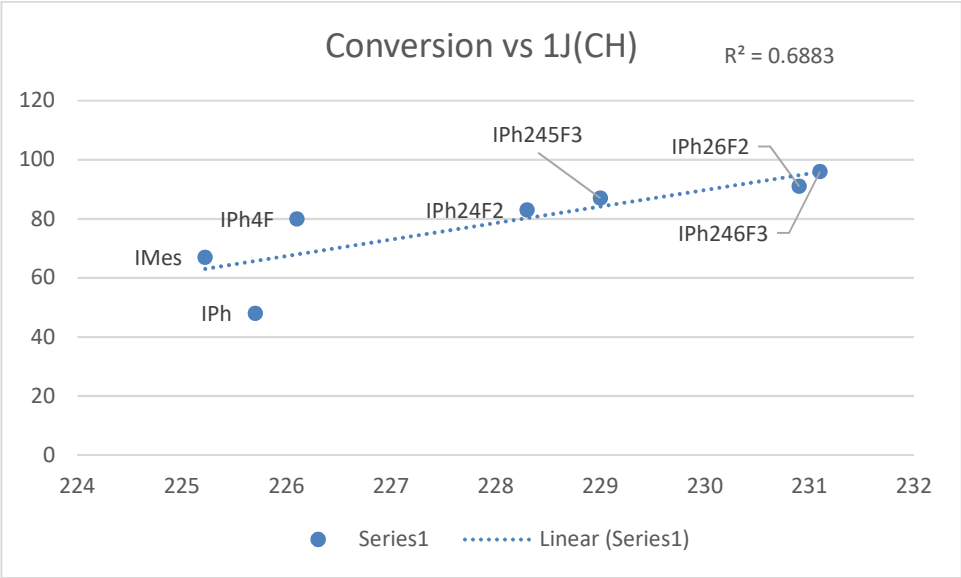


Figure S1 – plot of hydrogen transfer conversion against $^{1}J(CH)$ of NHC.HBF_4 salt.

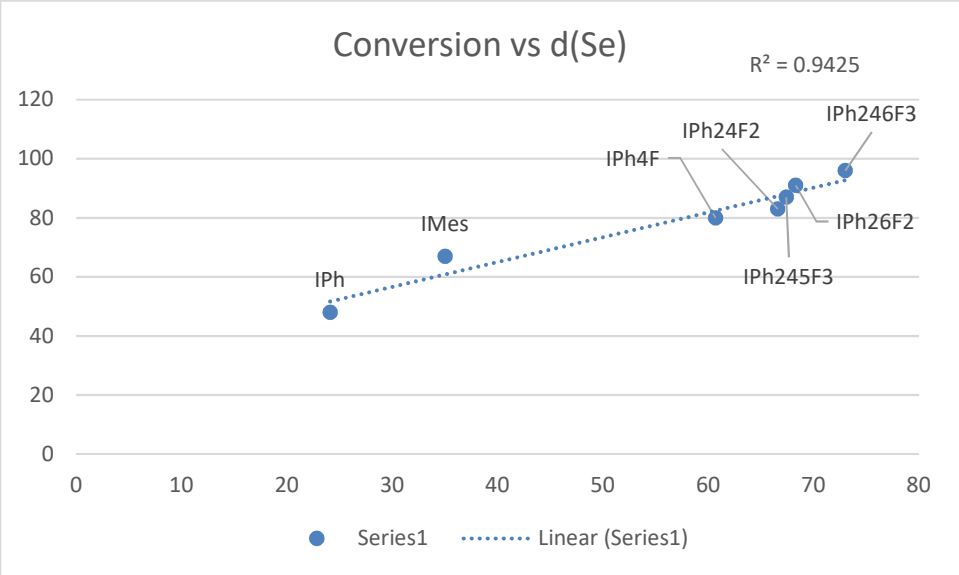


Figure S2 – plot of hydrogen transfer conversion against $\delta(^{77}Se)$of NHC selenide.

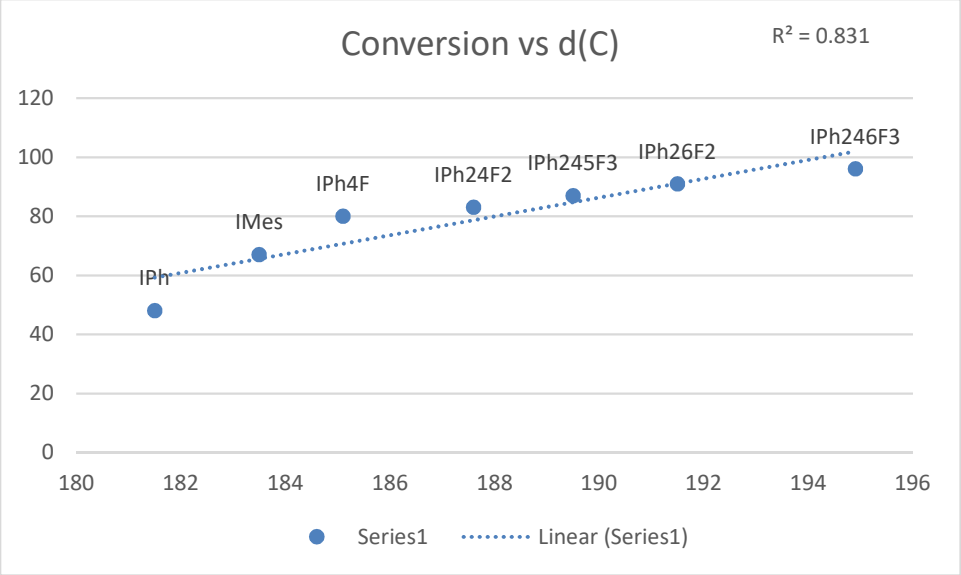


Figure S3 – plot of hydrogen transfer conversion against $\delta(^{13}C)$of Rh(cod)Cl(NHC) complex.

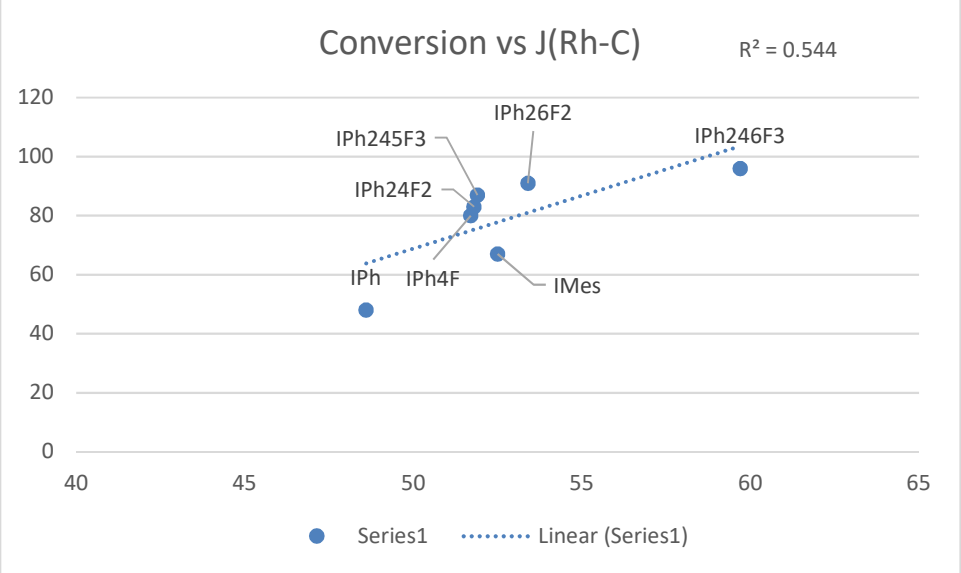


Figure S4 – plot of hydrogen transfer conversion against ^{1}J(Rh-C) of Rh(cod)Cl(NHC) complex.

Catalyst	Percentage Conversion after 10 min				Percentage Conversion after 20 min				Percentage Conversion after 30 min				Percentage Conversion after 40 min				Percentage Conversion after 50 min				Percentage Conversion after 60 min			
	1	2	3	A	1	2	3	A	1	2	3	A	1	2	3	A	1	2	3	A	1	2	3	A
0																					0	0	0	0
15	48	49	50	49	62	62	61	62	71	73	72	72	74	74	73	74	75	76	77	76	80	80	79	80
16	55	54	55	55	67	68	69	68	75	75	74	75	76	77	77	77	79	79	79	79	82	83	83	83
17	64	64	65	64	76	77	77	77	84	83	84	84	86	85	86	86	88	86	88	88	91	90	92	91
18	59	61	60	60	72	74	73	73	79	80	81	80	82	82	82	82	83	84	85	84	87	87	87	87
19	71	72	71	71	85	84	84	84	91	91	91	91	92	93	93	93	95	95	94	95	97	95	96	96
[Rh(cod)Cl(IPh)], **20**	20	20	19	20	31	32	33	32	40	40	39	40	42	43	41	42	43	44	44	44	49	48	47	48
[Rh(cod)Cl(IMes)], **21**	40	38	39	39	52	53	53	53	60	58	59	59	62	61	61	61	63	62	64	63	66	67	67	67

1,2 and 3 indicate three repetitive runs whilst A represents the average value over three runs.

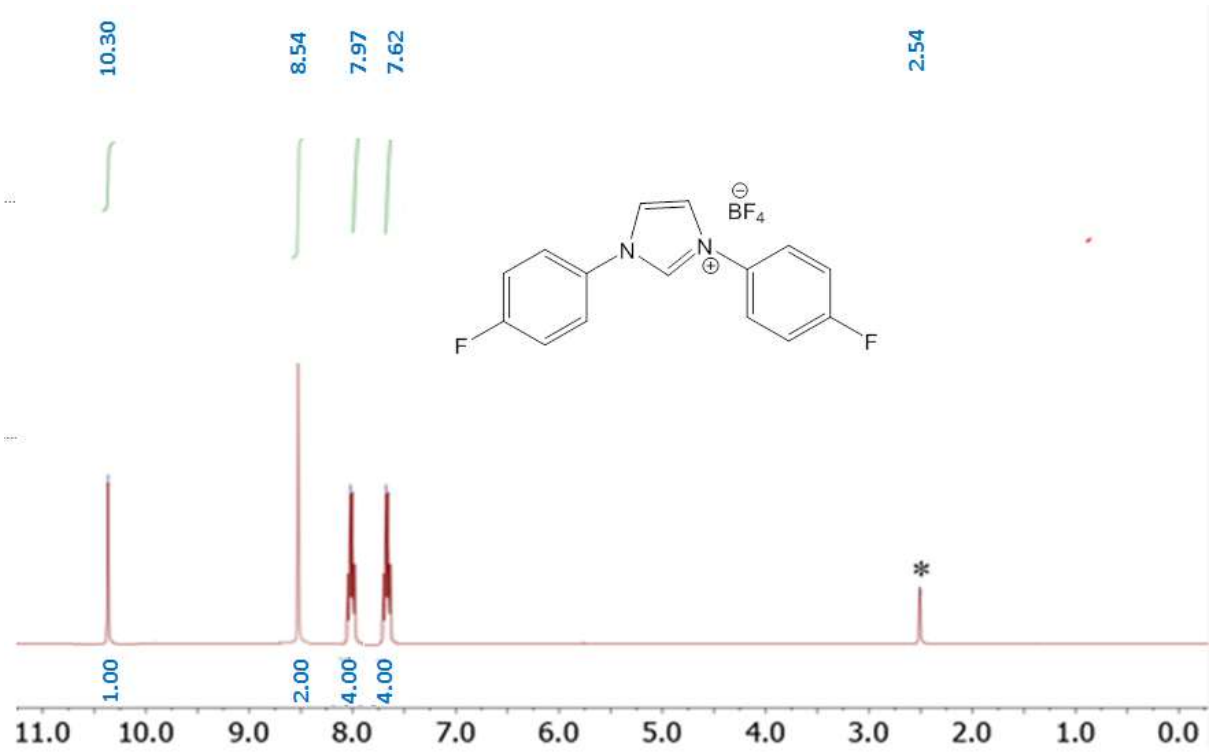
Entry 0 corresponds to the addition of no catalyst, for which the percentage conversion was measured only after 60 mins.

Table S1 – Conversions obtained in the transfer hydrogenation reaction of acetophenone with iPrOH and Rh(cod)Cl(NHC) catalysts **15**-**21**.

X-ray collection and analysis data

	15	**16**	**17**	**19**	**20**
Chemical formula	$4(C_{23}H_{22}ClF_2N_2Rh)$	$2(C_{23}H_{20}ClF_4N_2Rh)$	$8(C_{23}H_{20}ClF_4N_2Rh)$	$2(C_{23}H_{18}ClF_6N_2Rh)$	$C_{23}H_{24}ClN_2Rh$
M_r	2011.14	1077.54	4310.24	1149.52	466.80
Crystal system, space group	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$	Monoclinic, $I2/a$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	150	150	150	150	150
a, *b*, *c* (Å)	13.6184 (7), 17.4744 (8), 17.3930 (12)	9.8017 (8), 11.1592 (11), 11.2845 (13)	13.7678 (8), 10.2888 (6), 30.2124 (18)	7.6327 (5), 10.2120 (5), 13.8732 (8)	11.8815 (3), 8.3839 (3), 20.2800 (6)
α,β,γ (°)	90, 93.479 (5), 90	87.485 (9), 72.410 (9), 67.014 (9)	90, 97.959 (6), 90	94.178 (4), 100.162 (5), 98.840 (5)	90, 95.716 (3), 90
V (Å^3)	4131.4 (4)	1079.3 (2)	4238.5 (4)	1046.17 (11)	2010.11 (11)
Z	2	1	1	1	4
Radiation type	Mo *K*a	Mo *K*a	Mo *K*a	Mo *K*a	Mo *K*a
μ (mm^{-1})	0.99	0.96	0.98	1.01	0.99
Crystal size (mm)	0.2 x 0.5 x 0.3	0.3 x 0.4 x 0.2	0.15 x 0.25 x 0.35	0.1 x 0.3 x 0.2	0.3 x 0.3 x 0.2
T_{min}, T_{max}	0.607, 1.000	0.524, 1.000	0.314, 1.000	0.619, 1.000	0.674, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23100, 13506, 10534	7818, 4460, 3181	16366, 4923, 3010	8198, 4735, 3835	14846, 3952, 3390
R_{int}	0.063	0.072	0.115	0.050	0.053
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S*	0.072, 0.154, 1.04	0.063, 0.160, 1.07	0.061, 0.116, 1.01	0.051, 0.118, 1.03	0.035, 0.071, 1.06
No. of reflections	13506	4460	4923	4735	3952
No. of parameters	1033	290	286	298	244
No. of restraints	43	37			
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.31, -0.69	1.36, -1.05	1.87, -1.19	1.10, -1.26	0.47, -0.60

NMR spectra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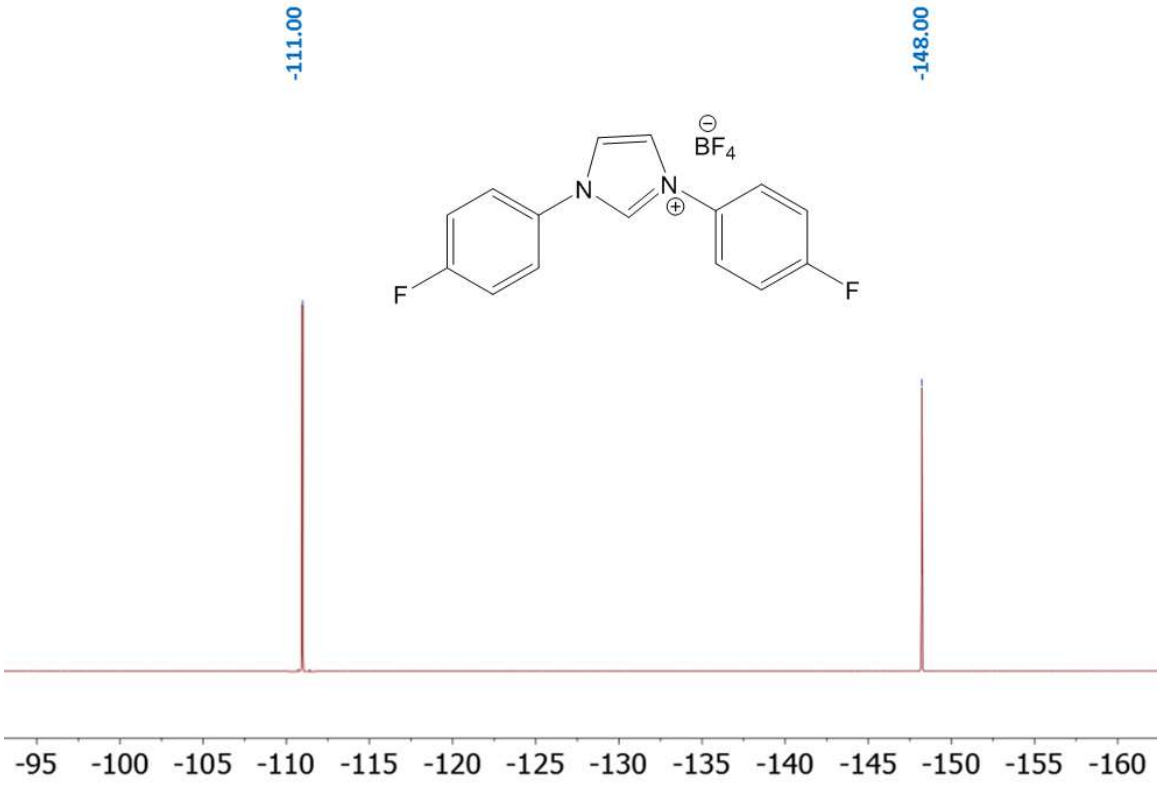
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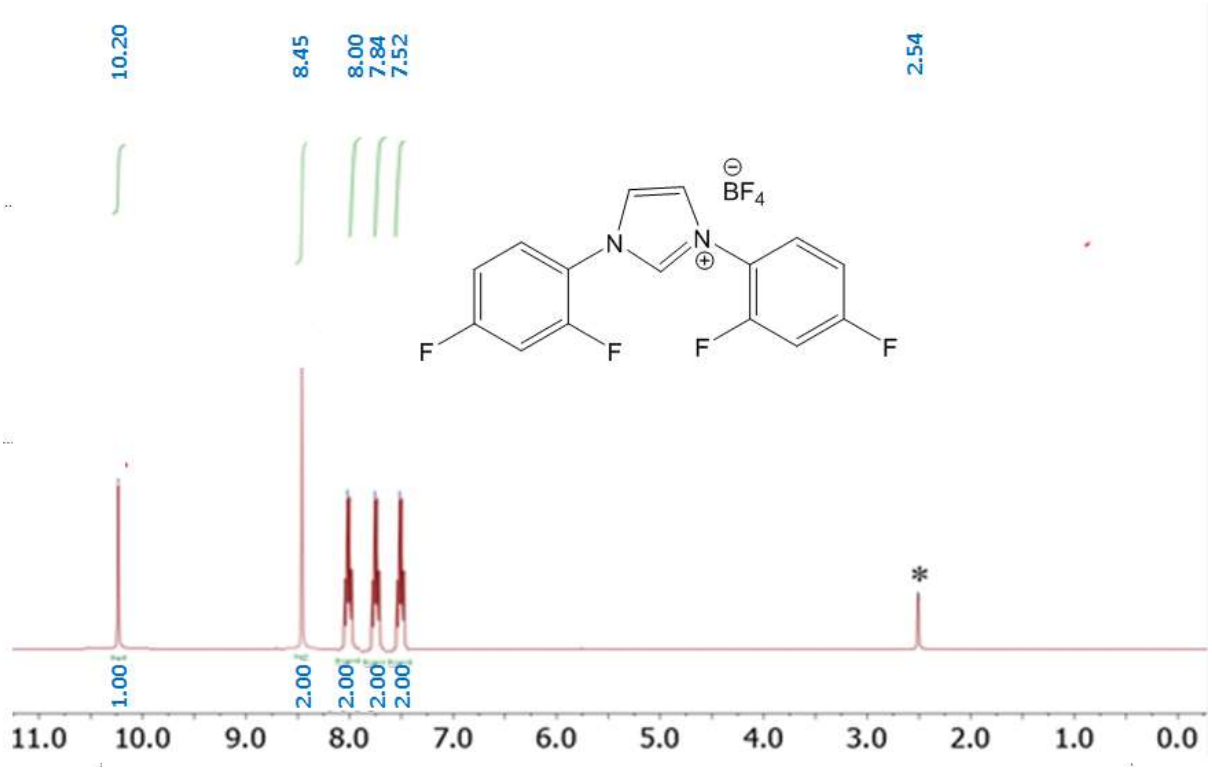
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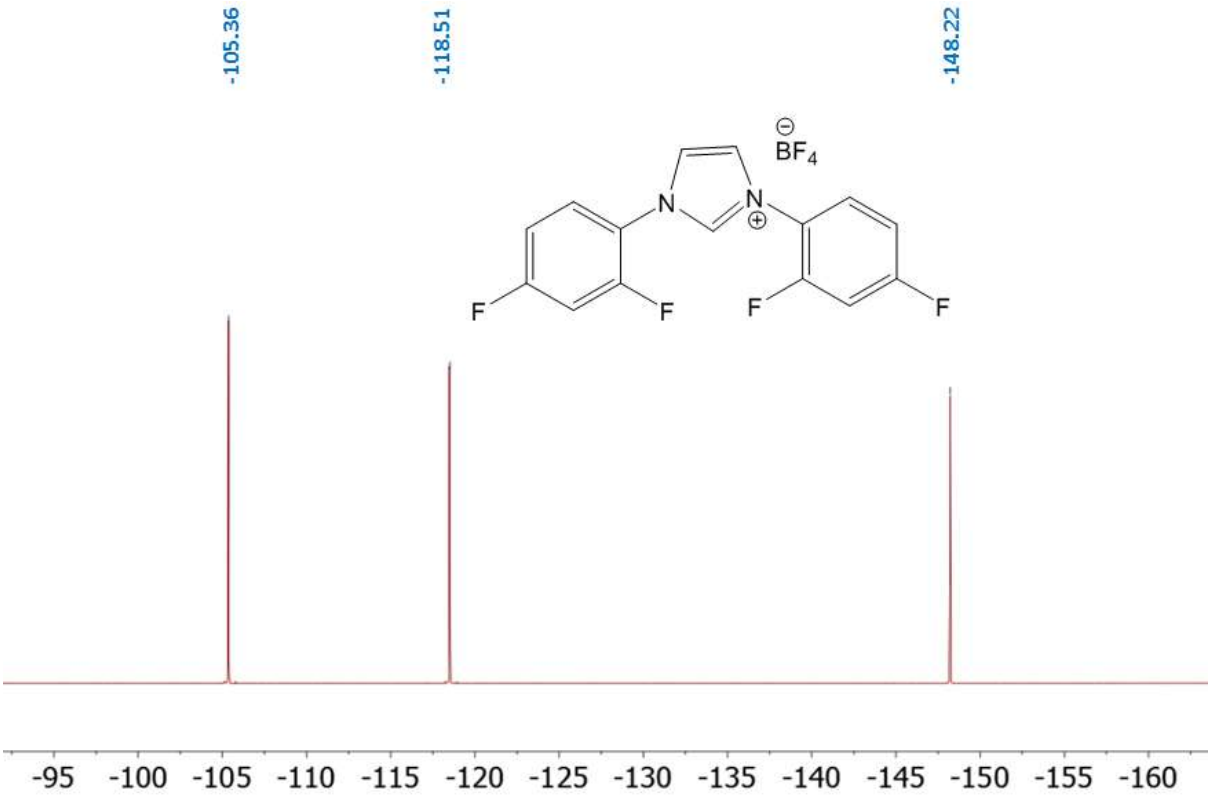
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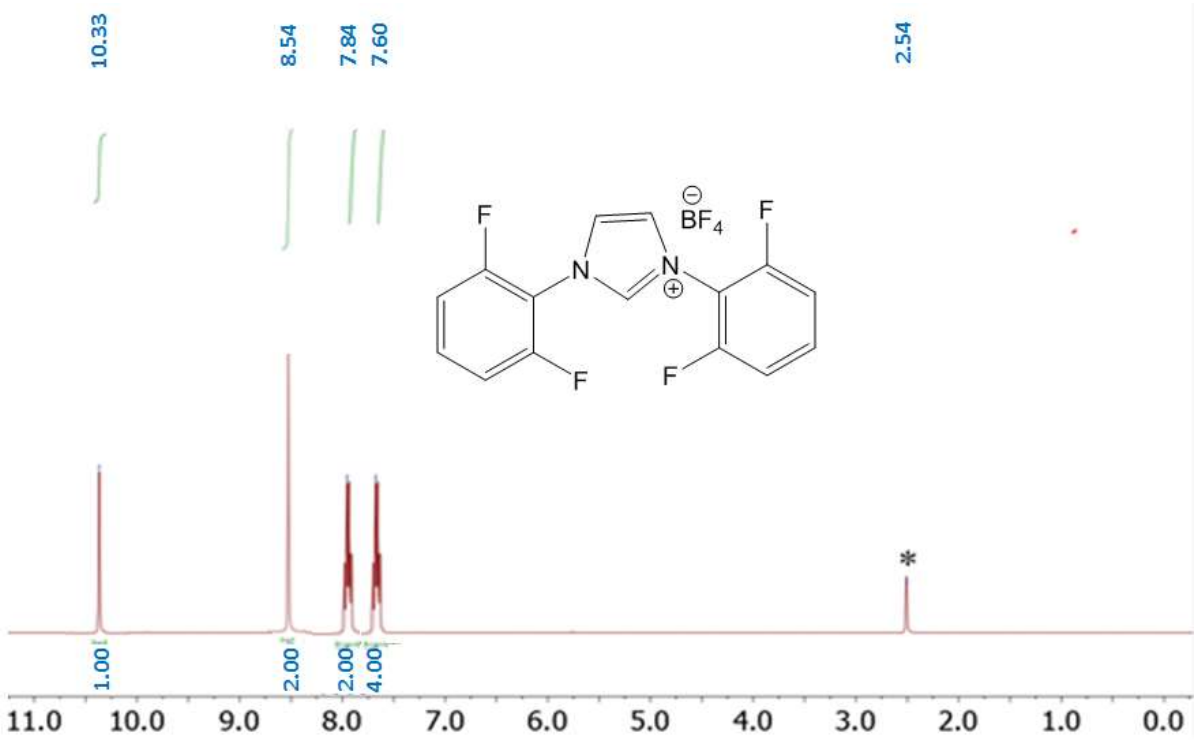
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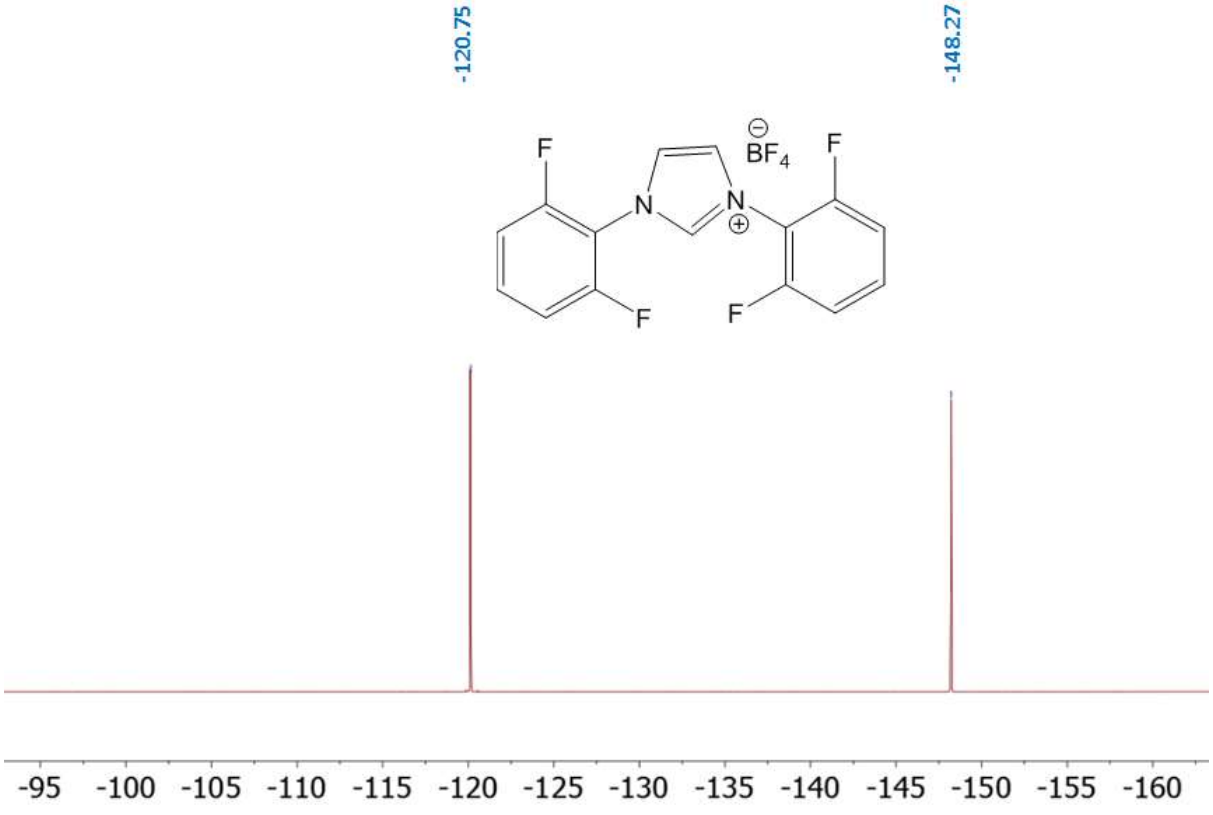
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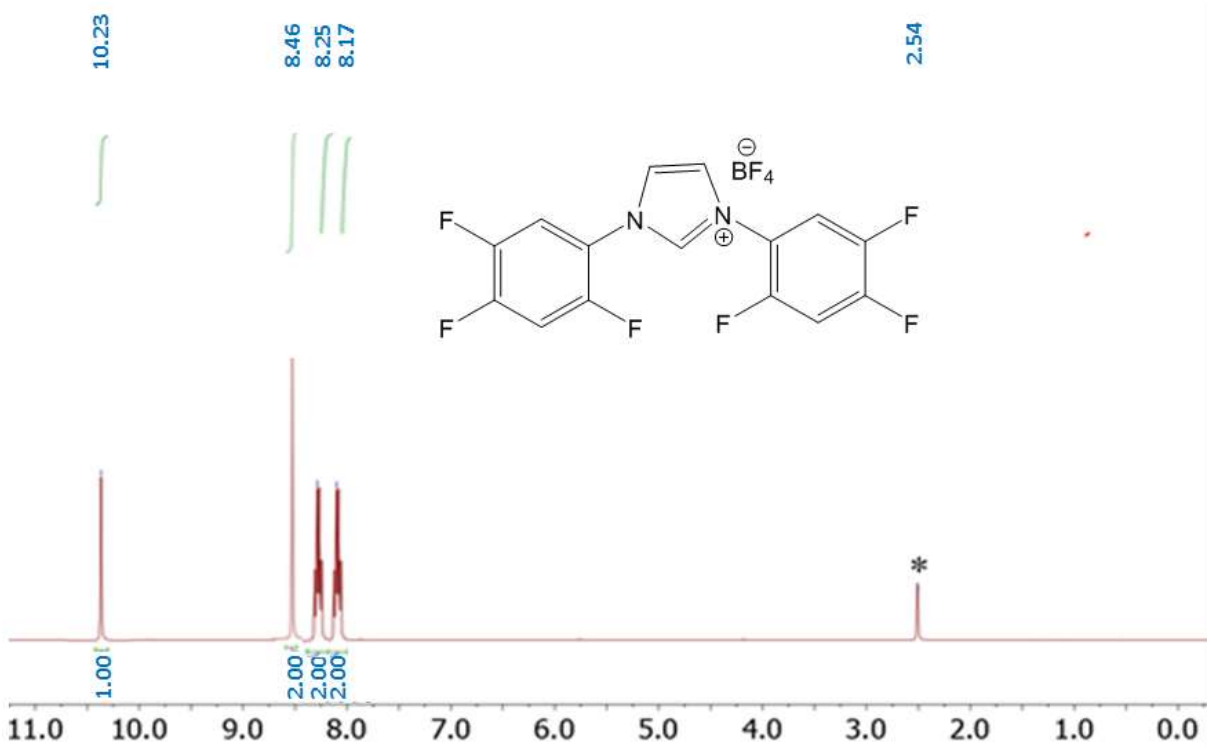
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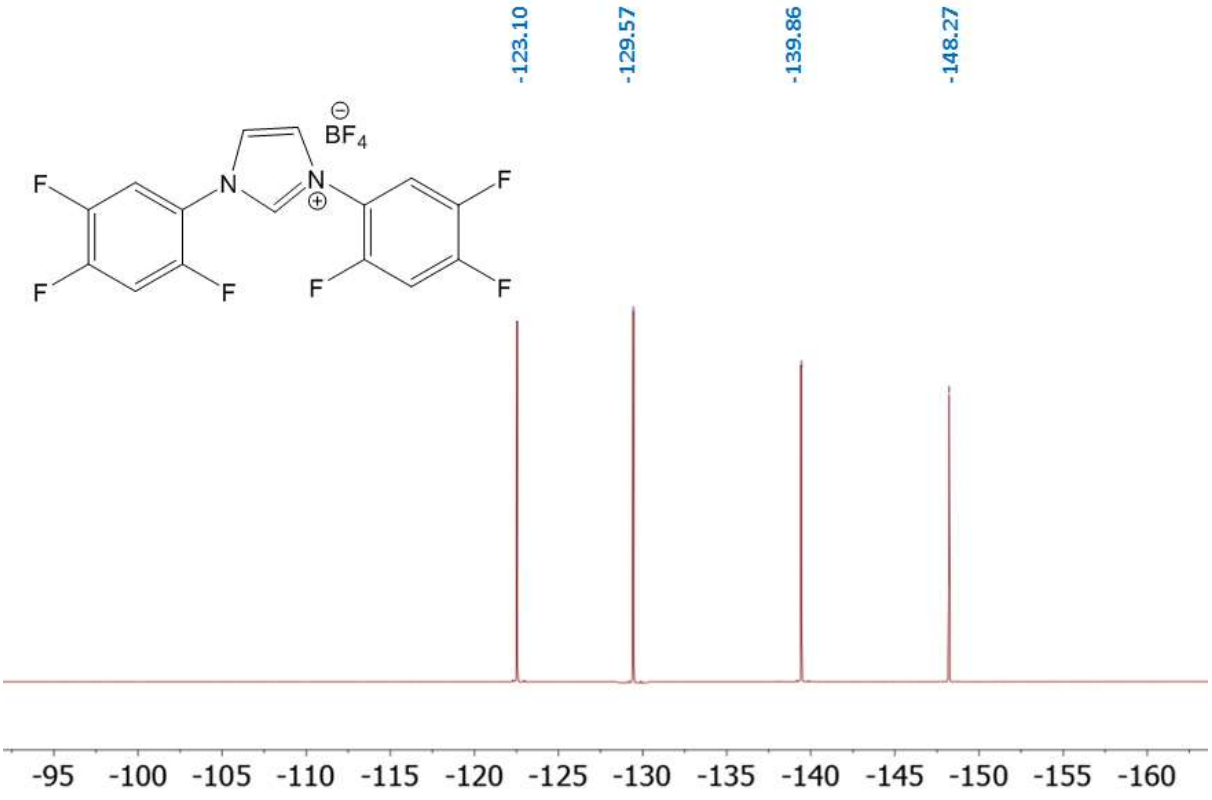
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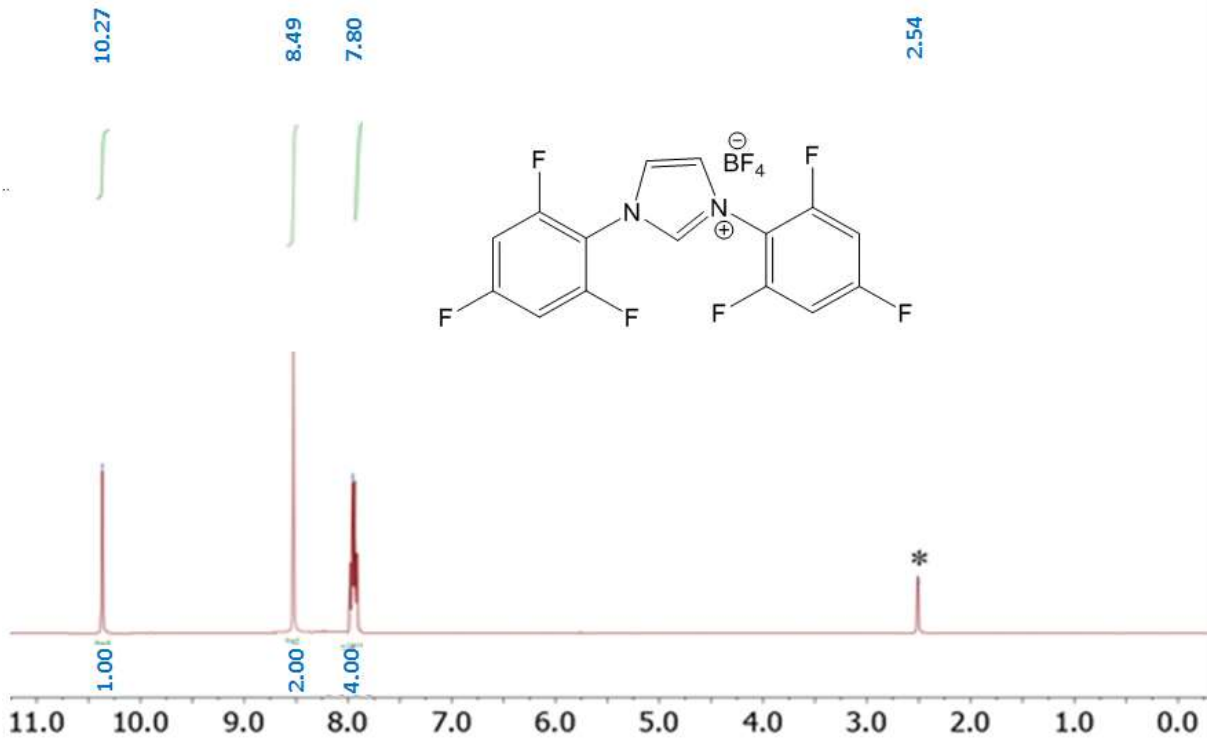
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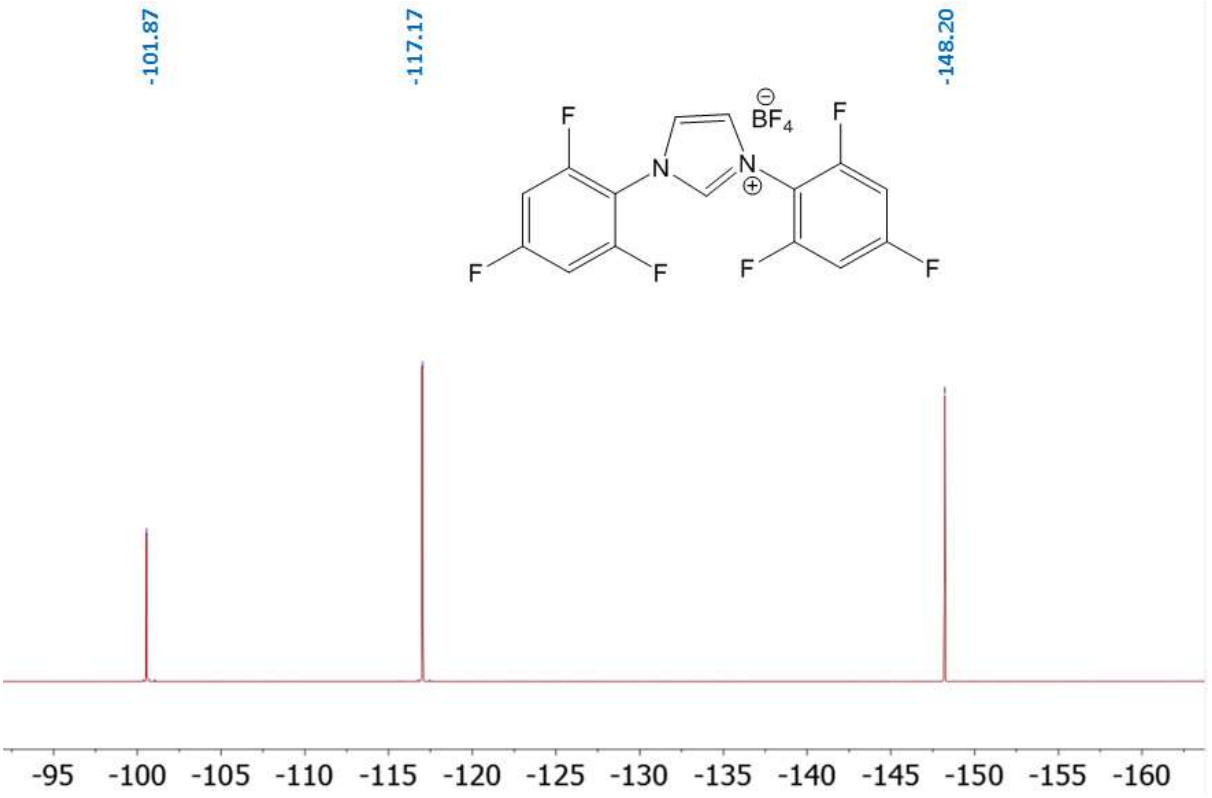
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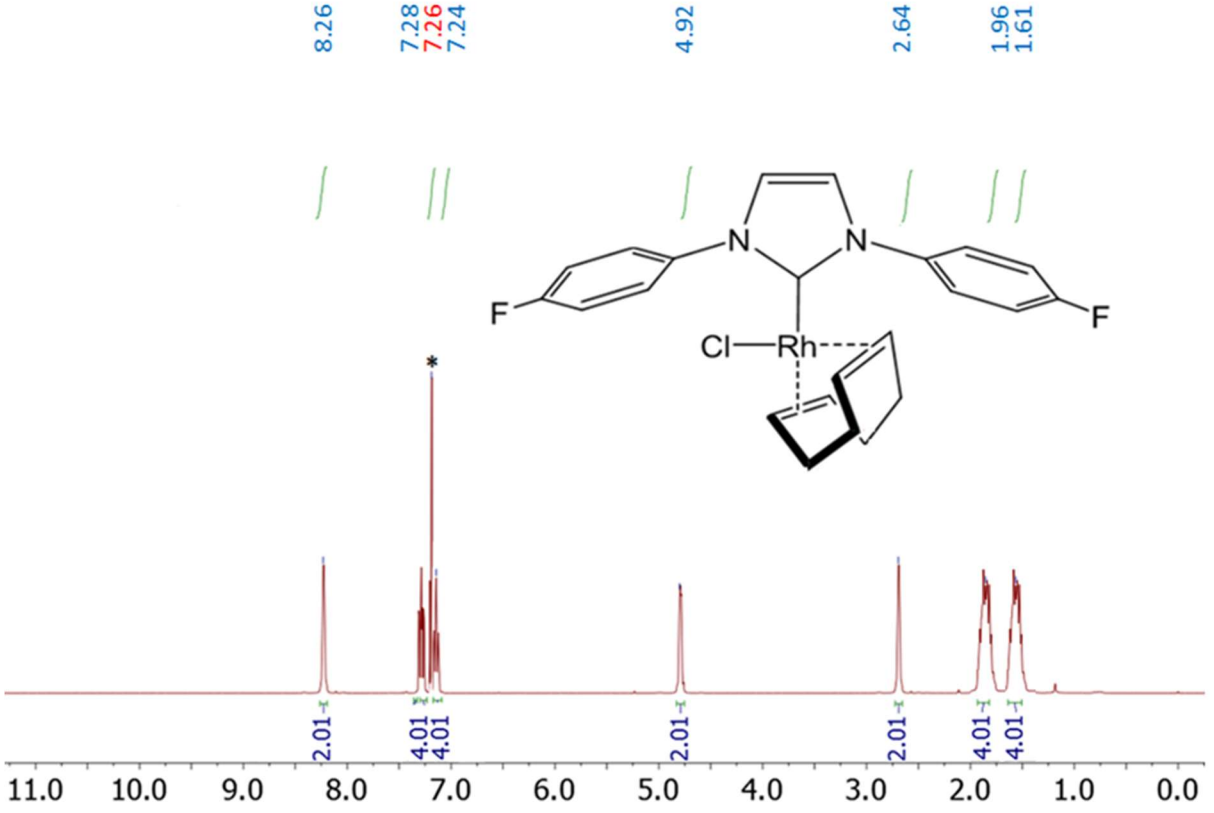
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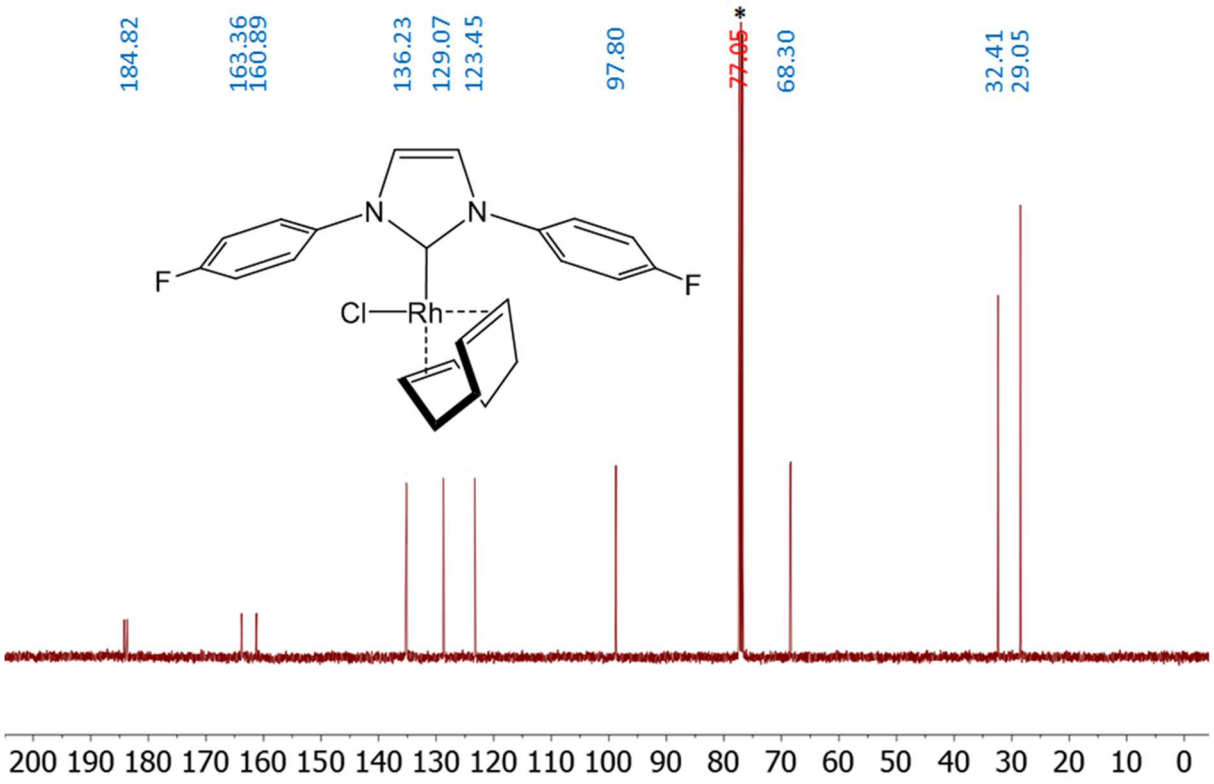
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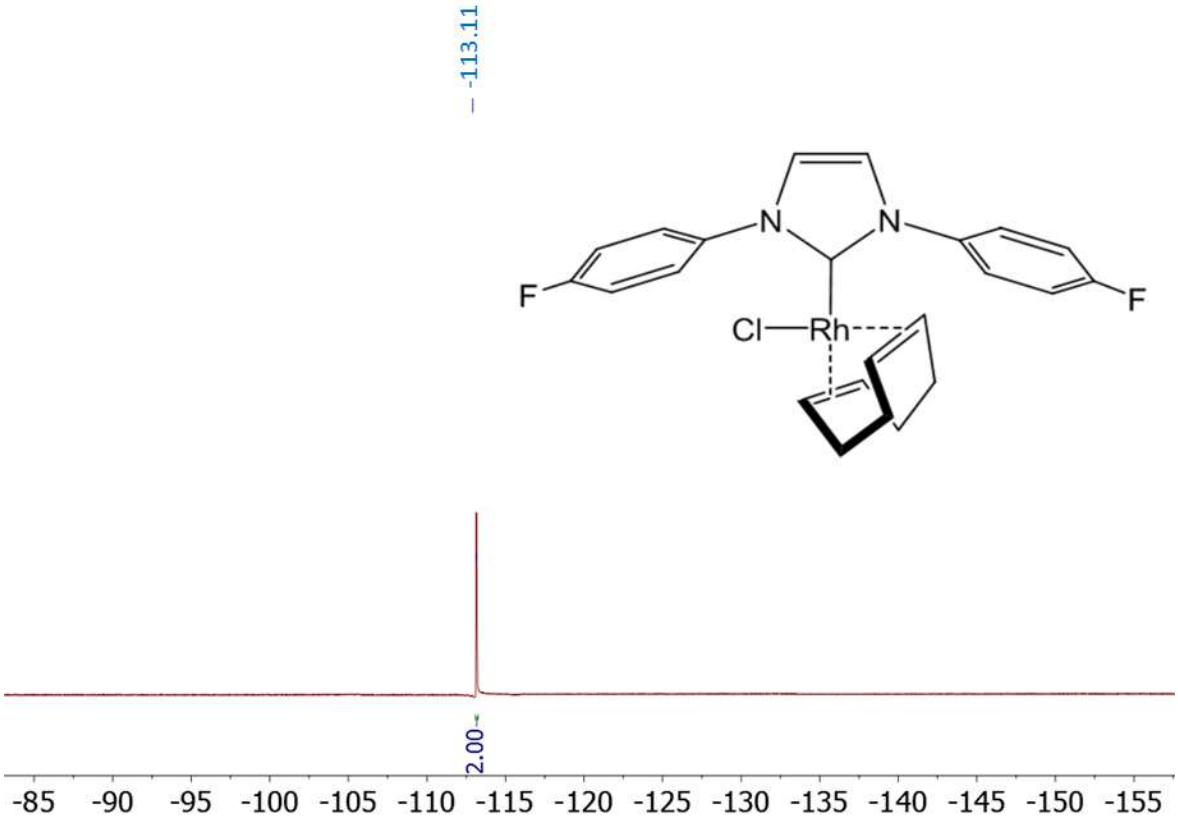
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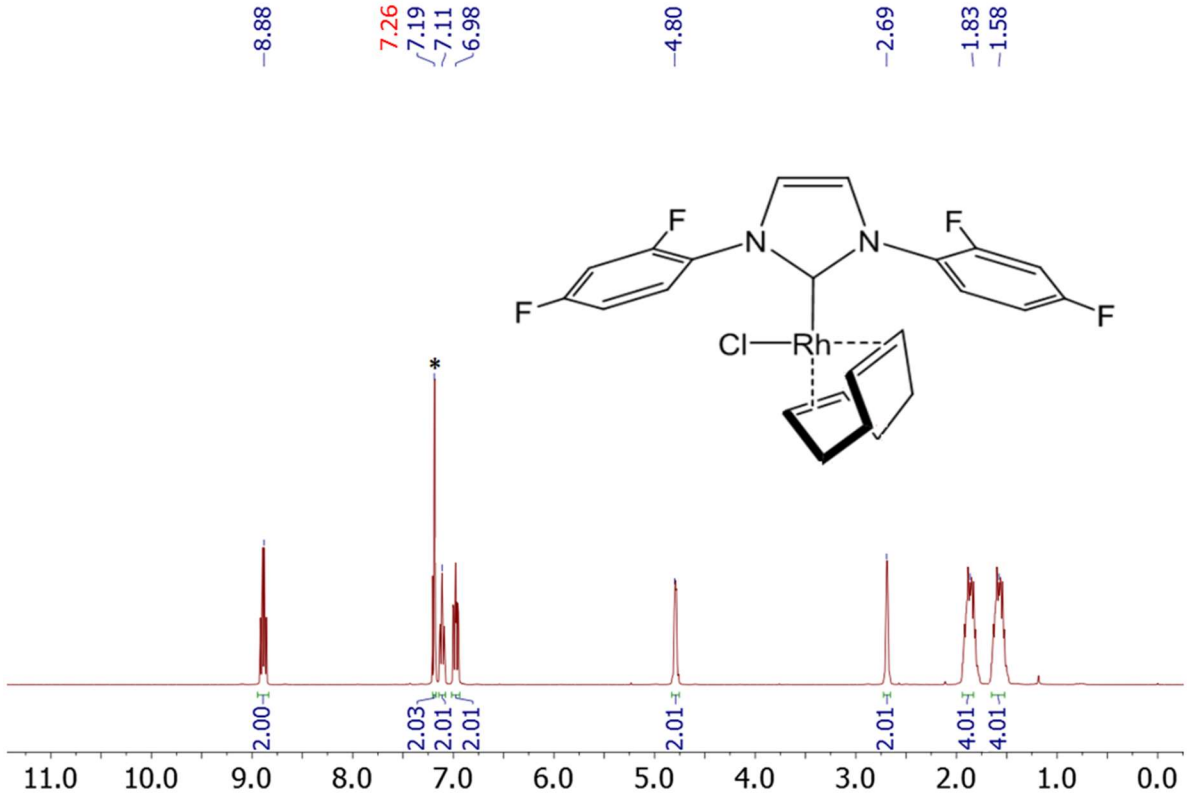
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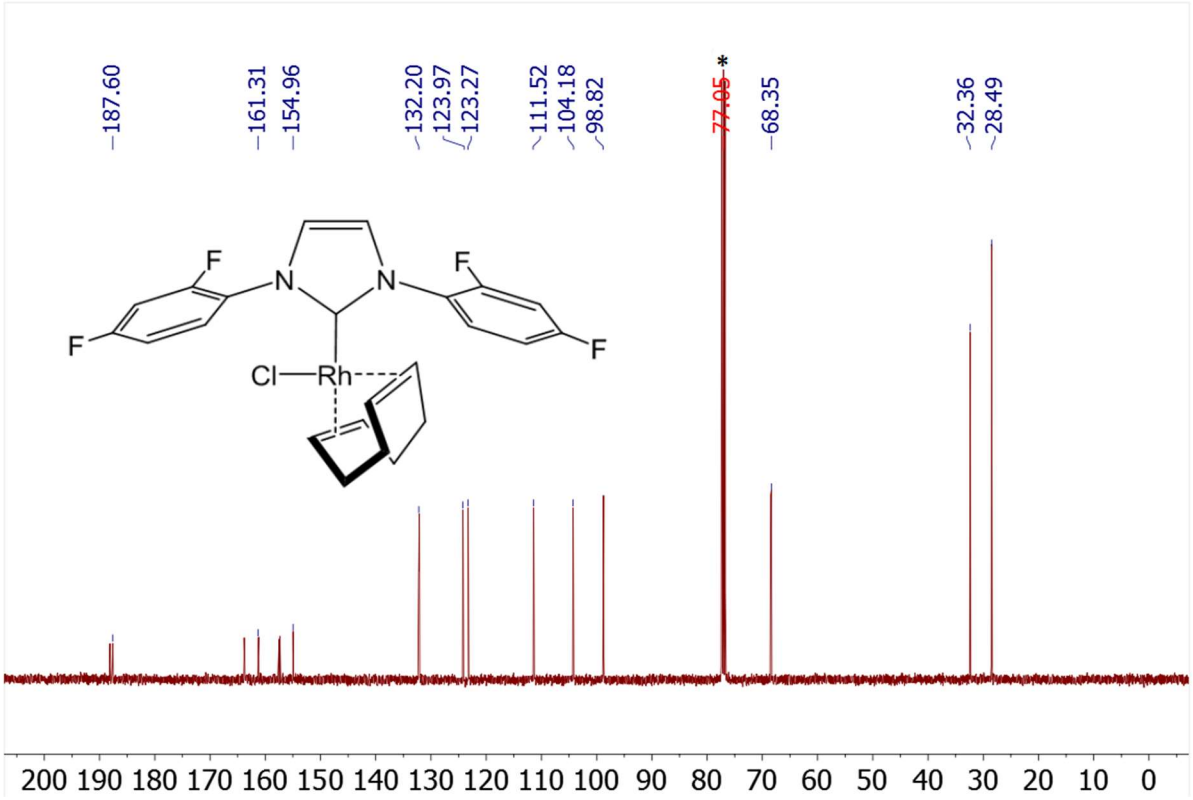
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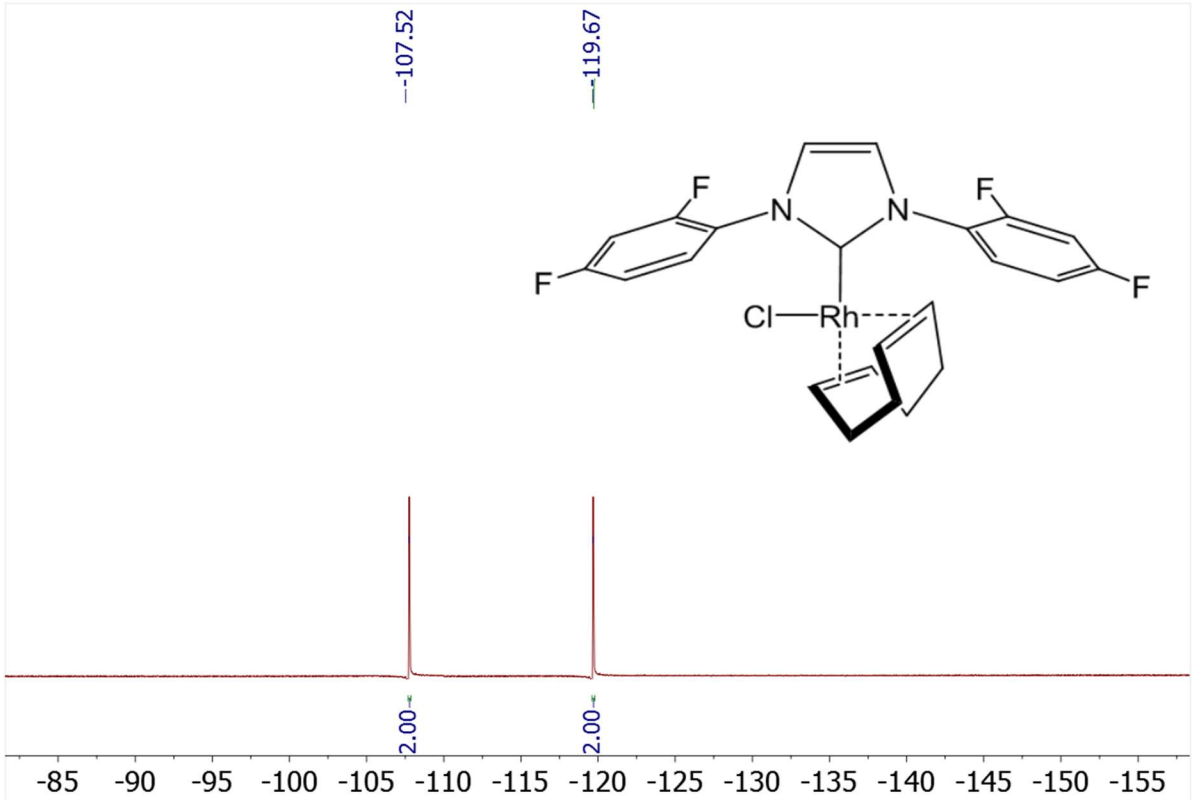
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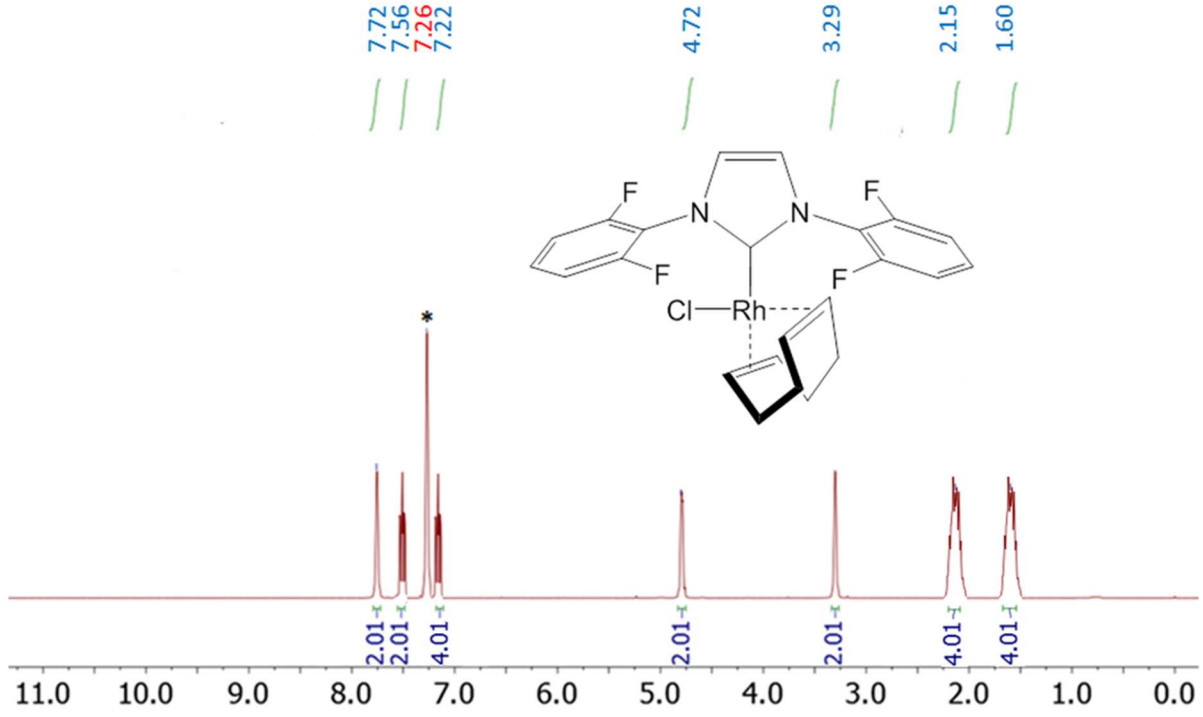
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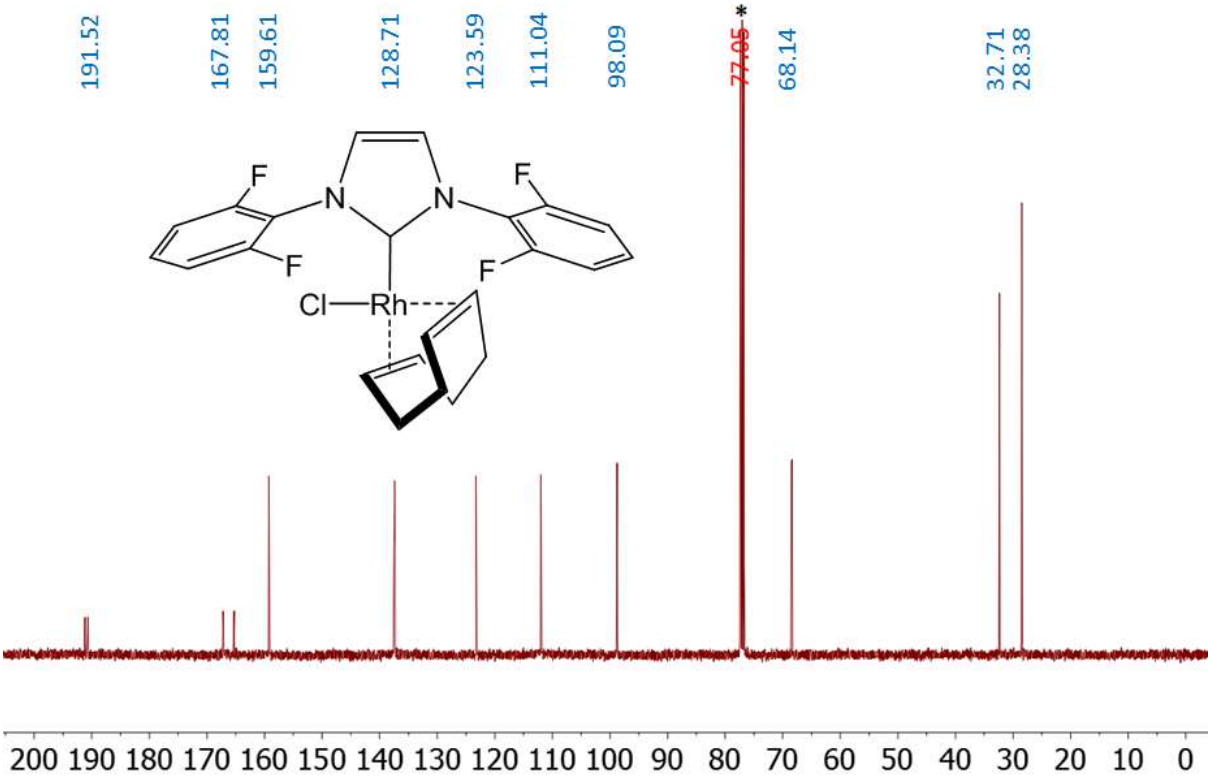
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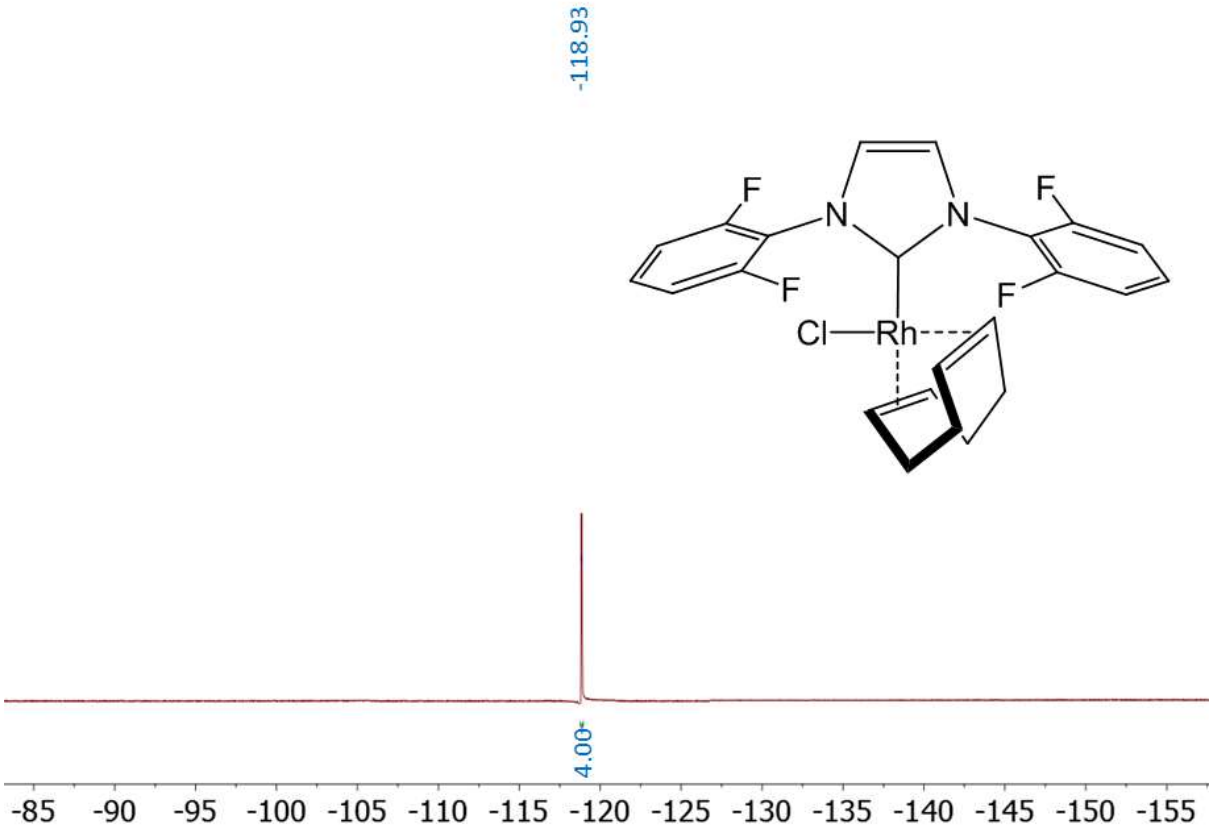
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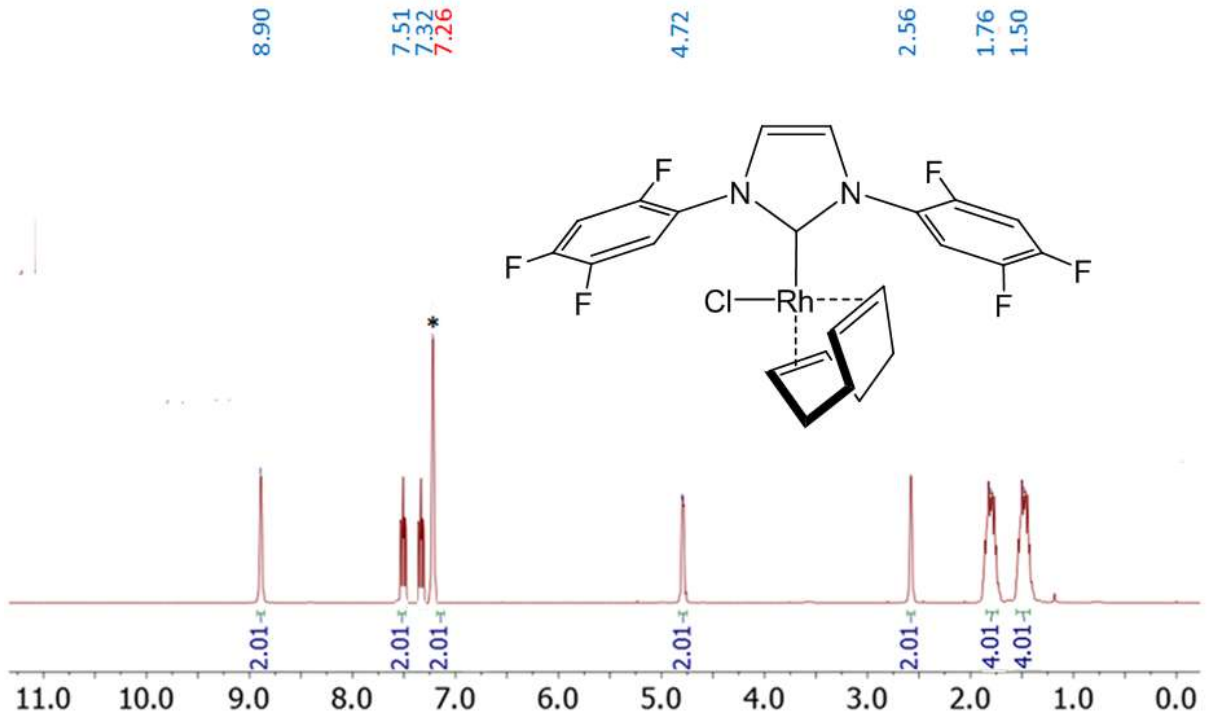
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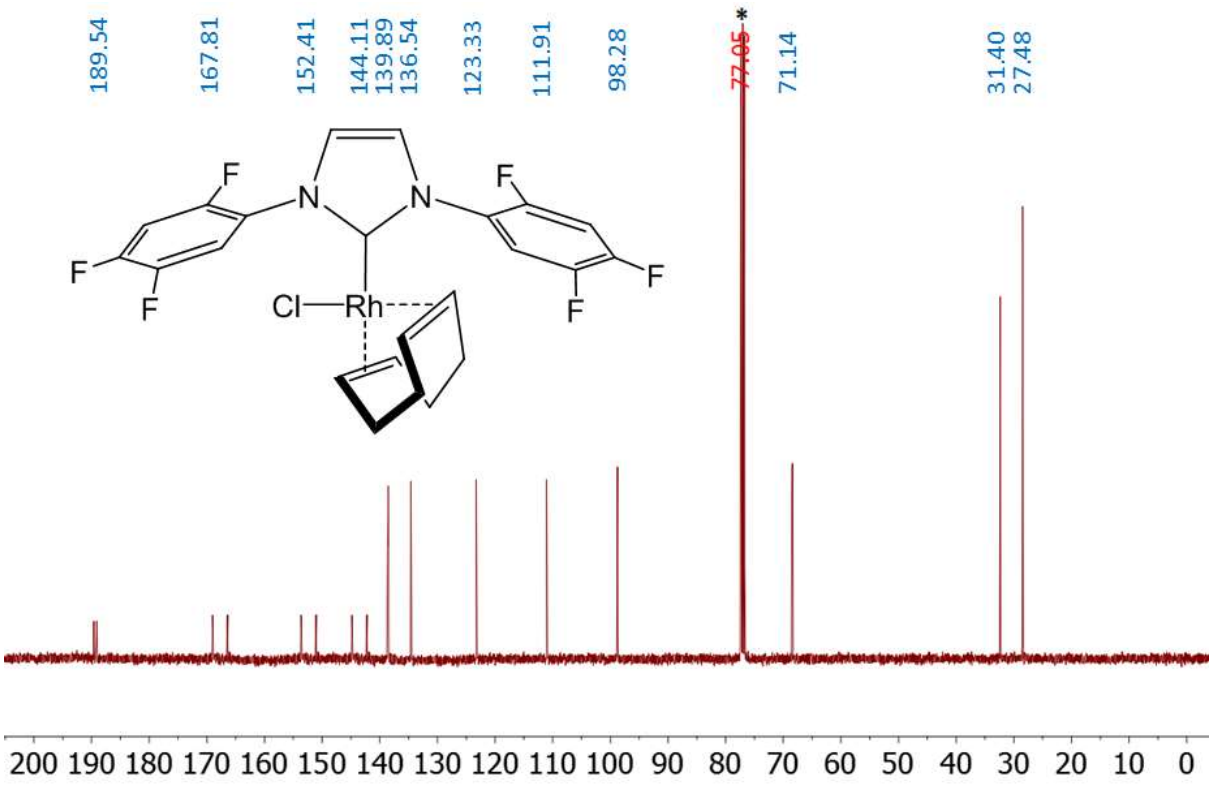
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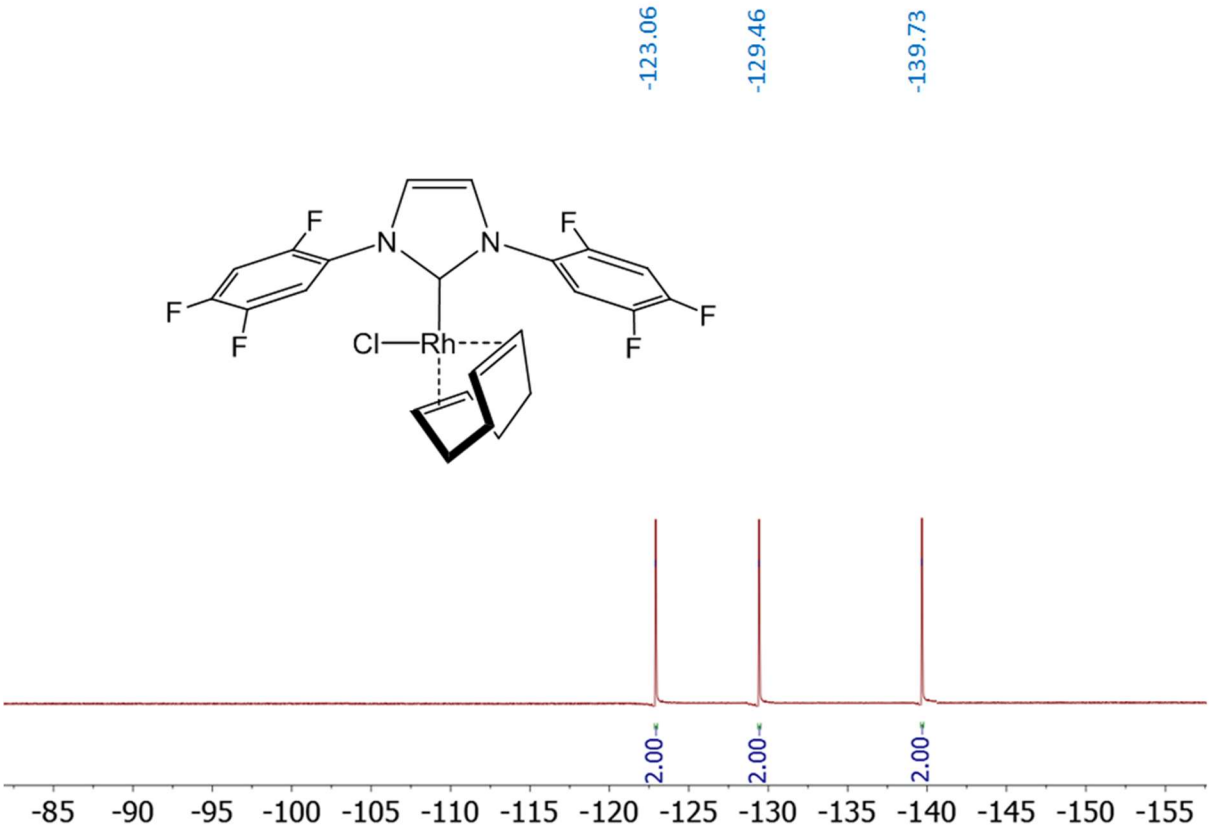
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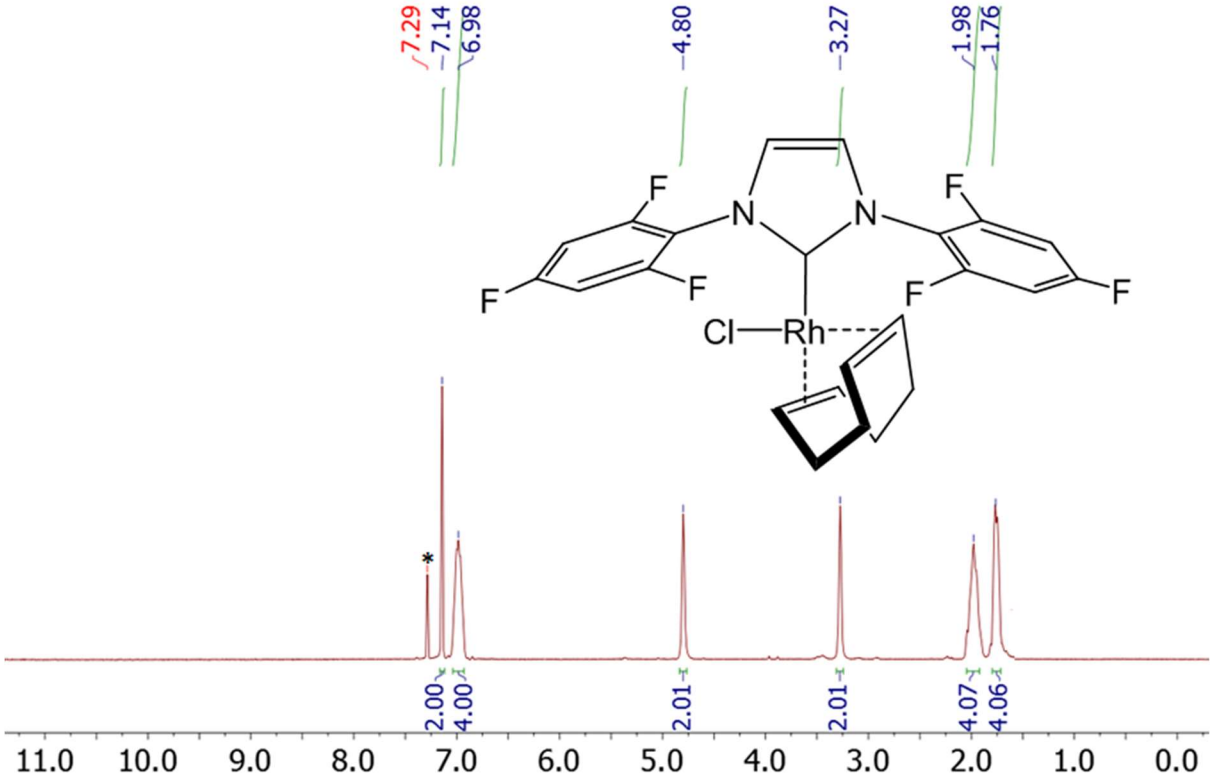
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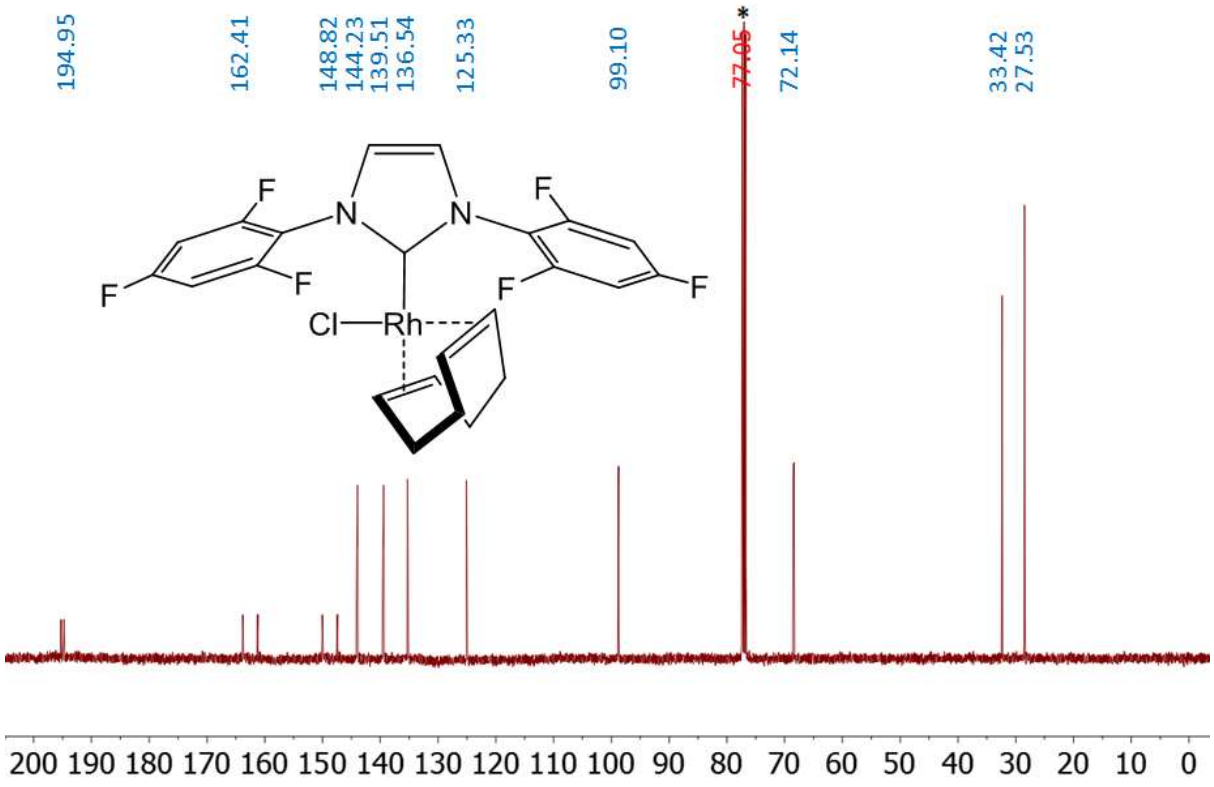
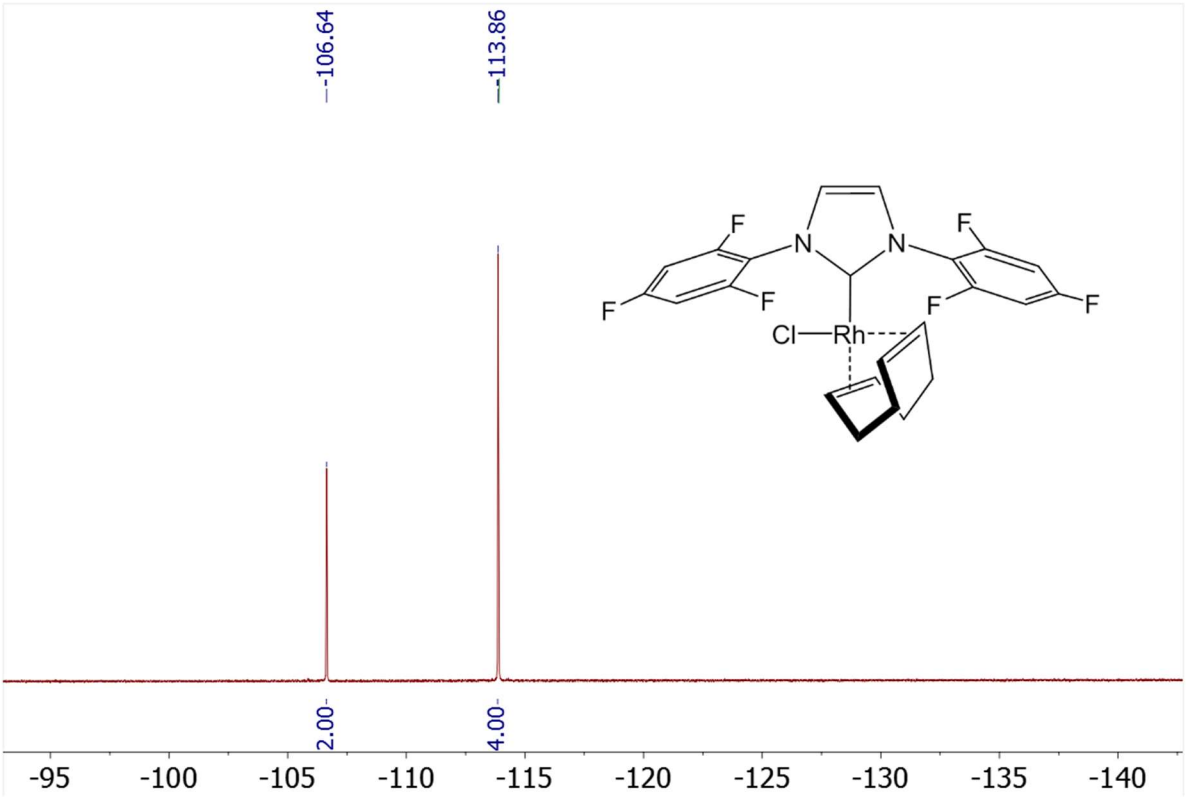
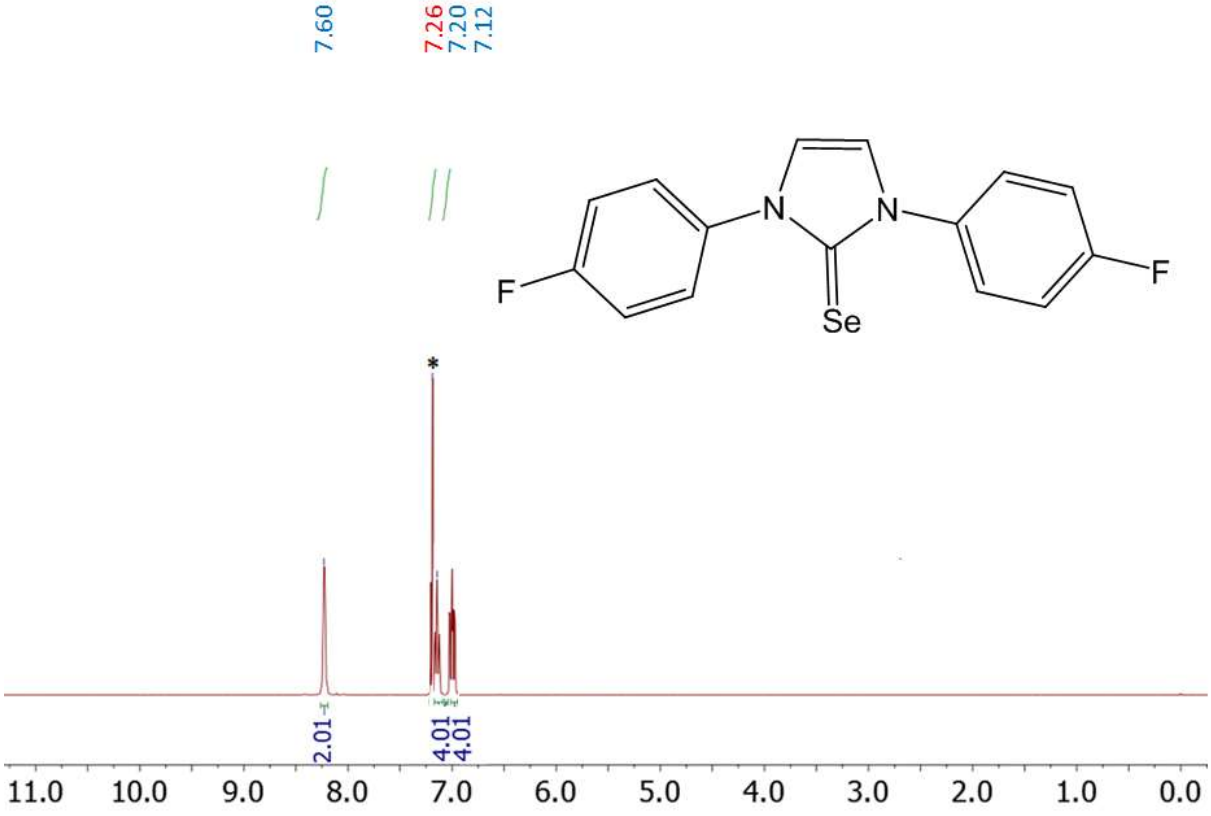
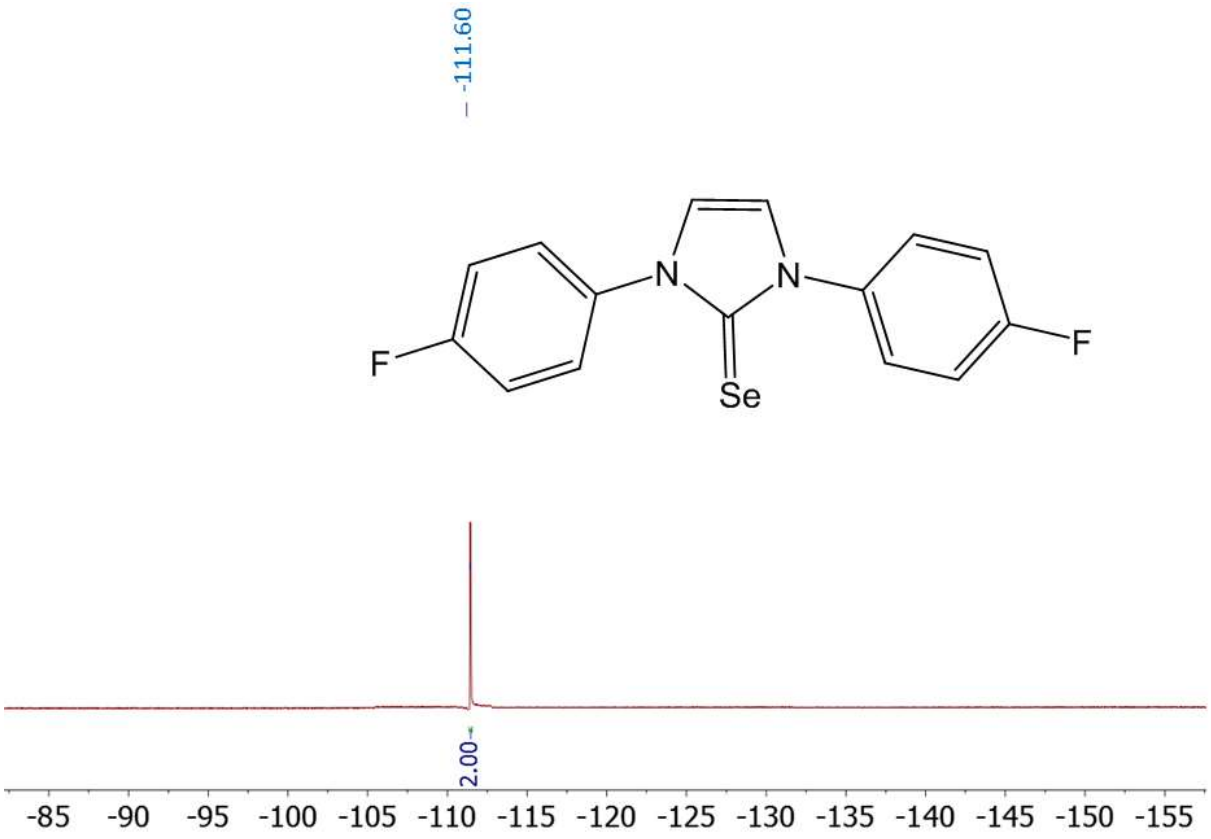
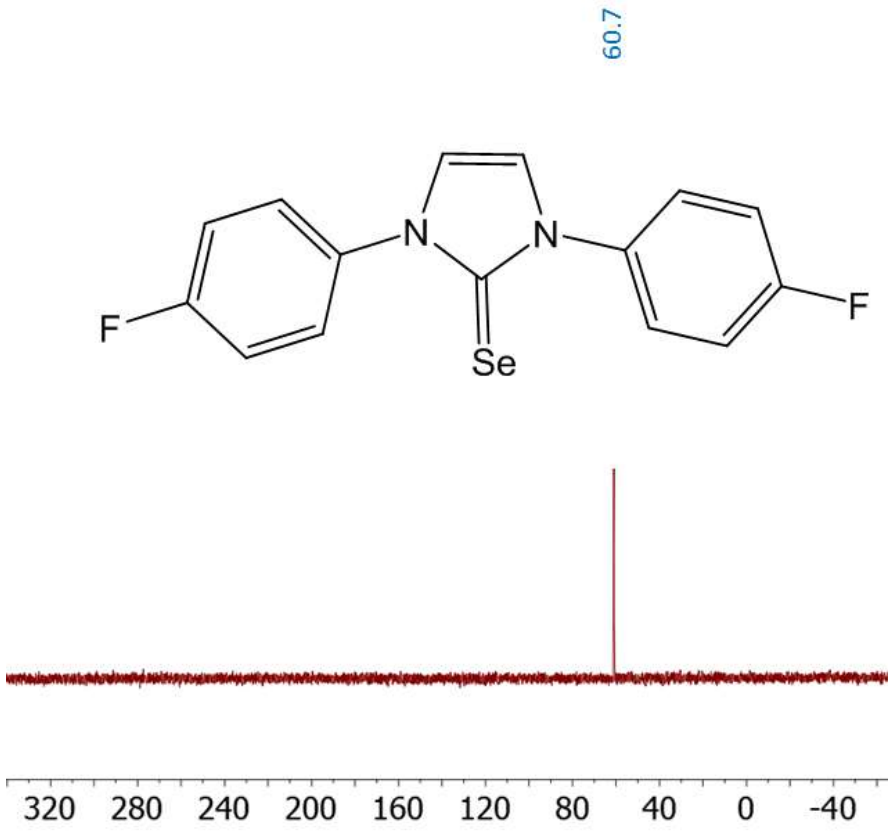
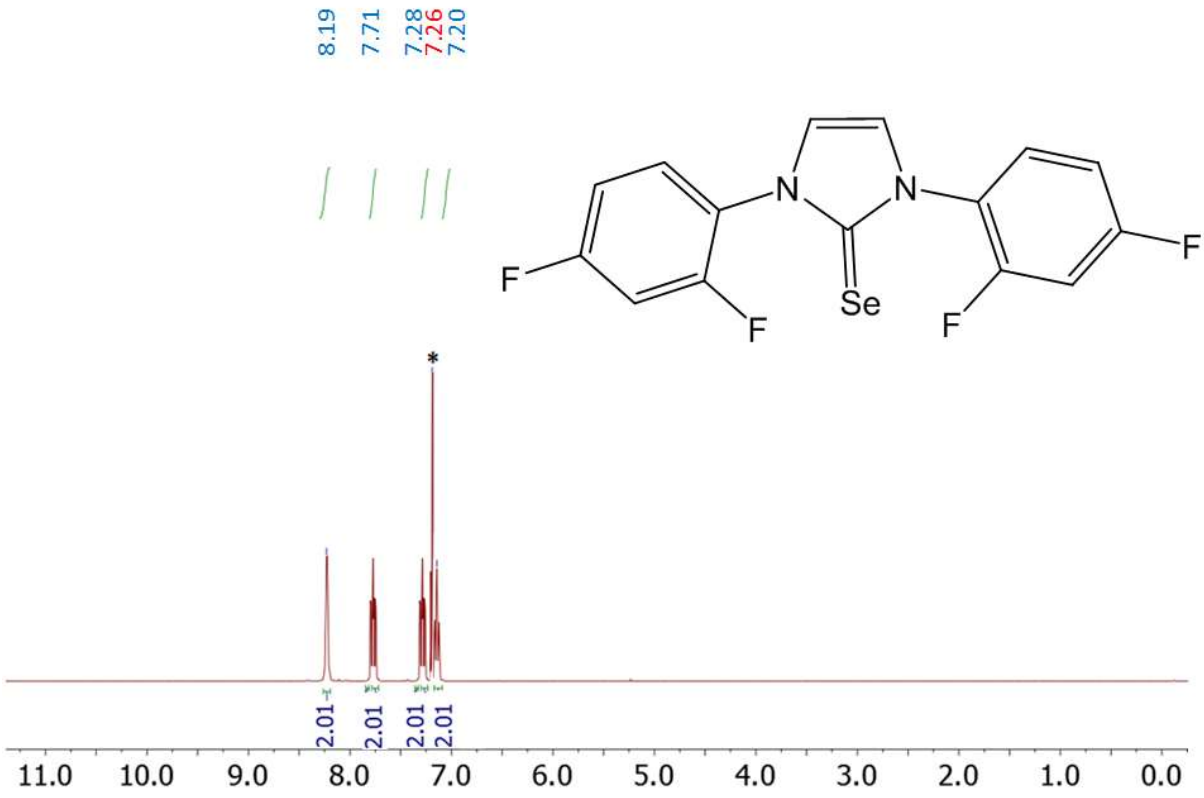

194.95
162.41
148.82
144.23
139.51
136.54
125.33
99.10
77.05
*
72.14
33.42
27.53
F
N
N
F
F
F
F
F
Cl—Rh
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

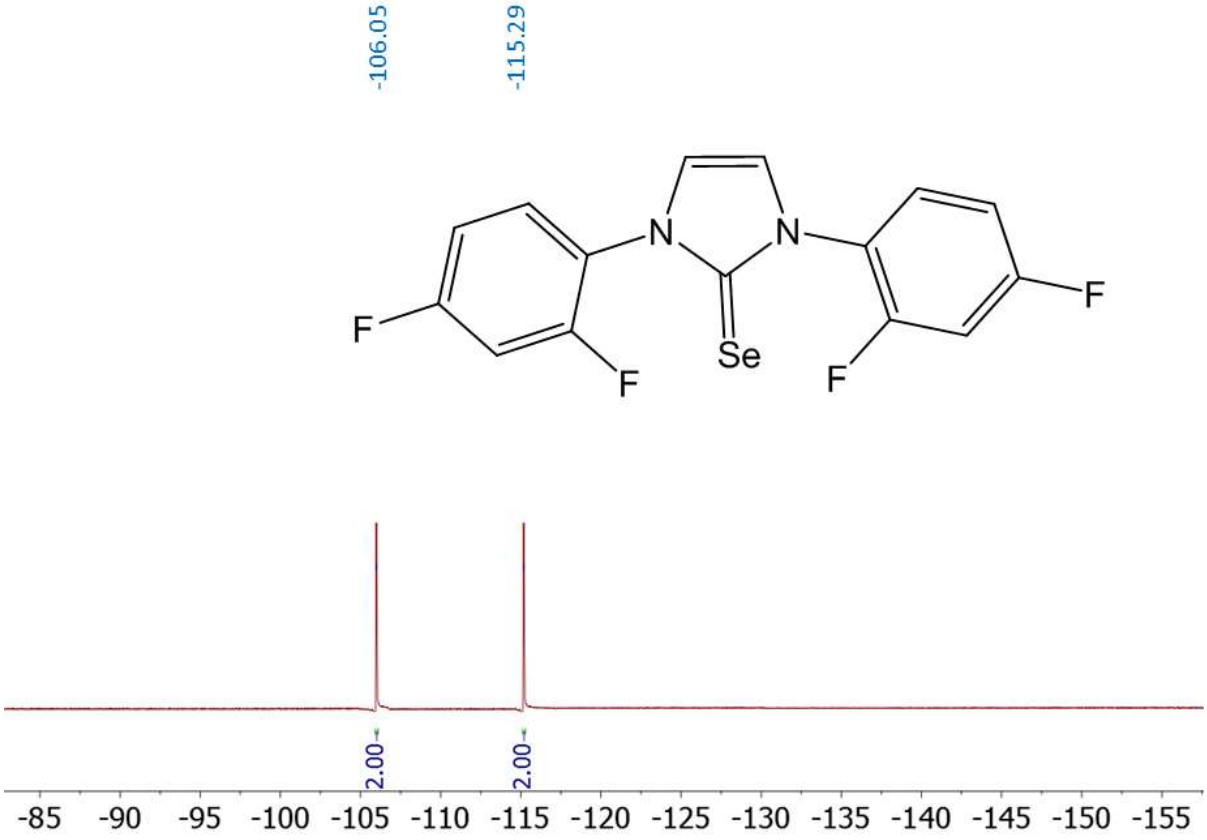

-106.64
-113.86
F
N
N
F
F
F
F
F
Cl—Rh
2.00
4.00
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140

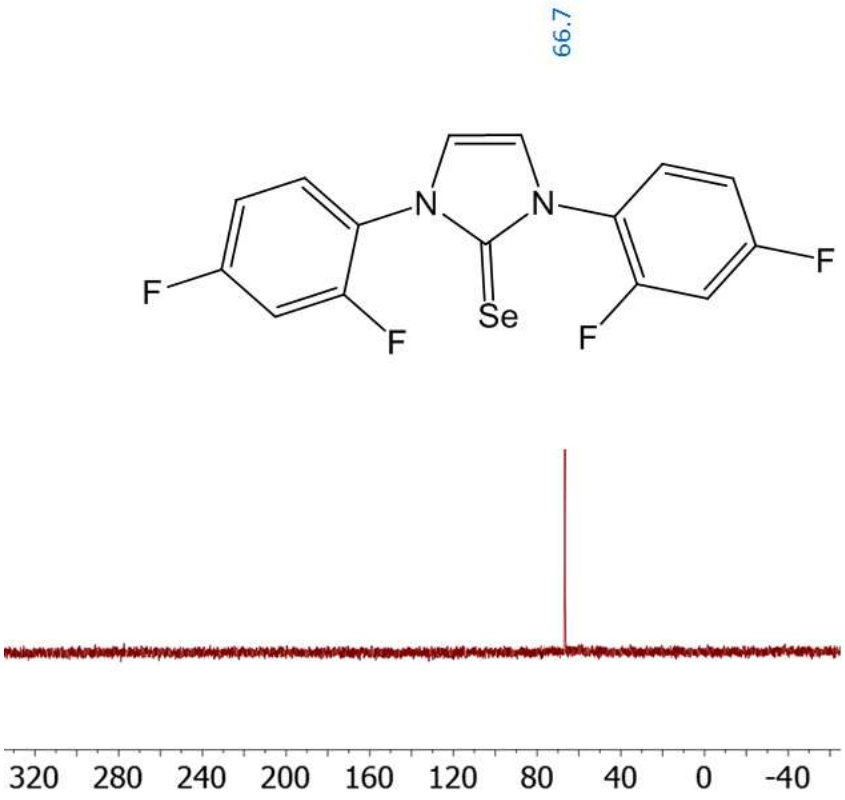

7.60
7.26
7.20
7.12
N
N
F
F
Se
*
2.01
4.01
4.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

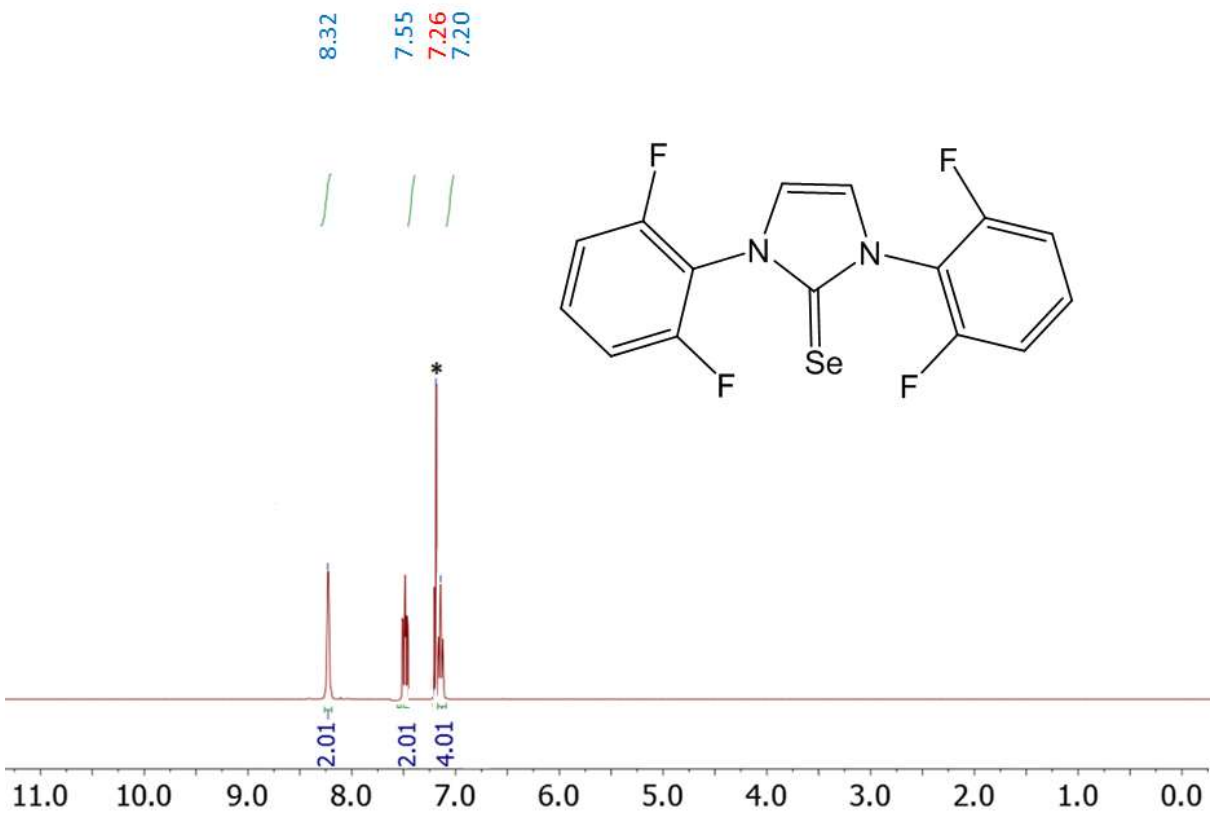

-111.60
N
N
F
F
Se
2.00
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155

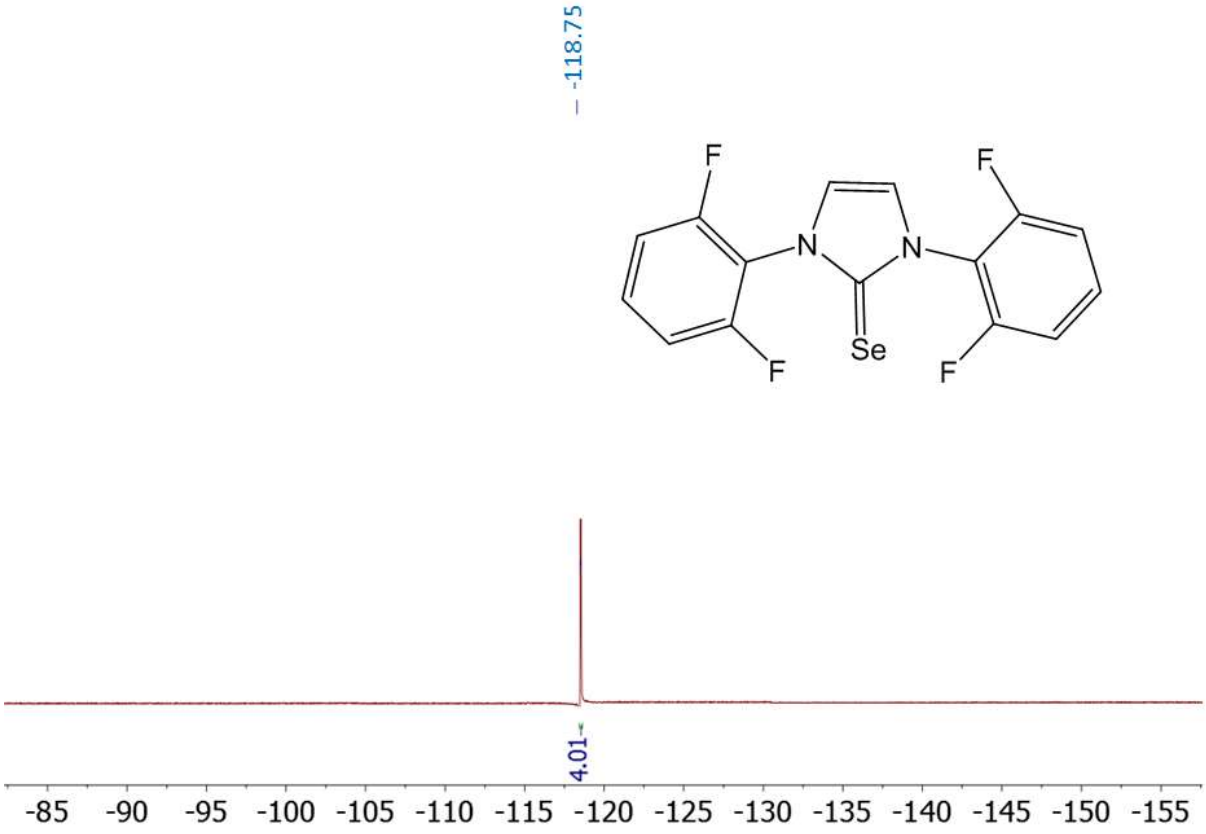

60.7
N
N
F
F
Se
320 280 240 200 160 120 80 40 0 -40

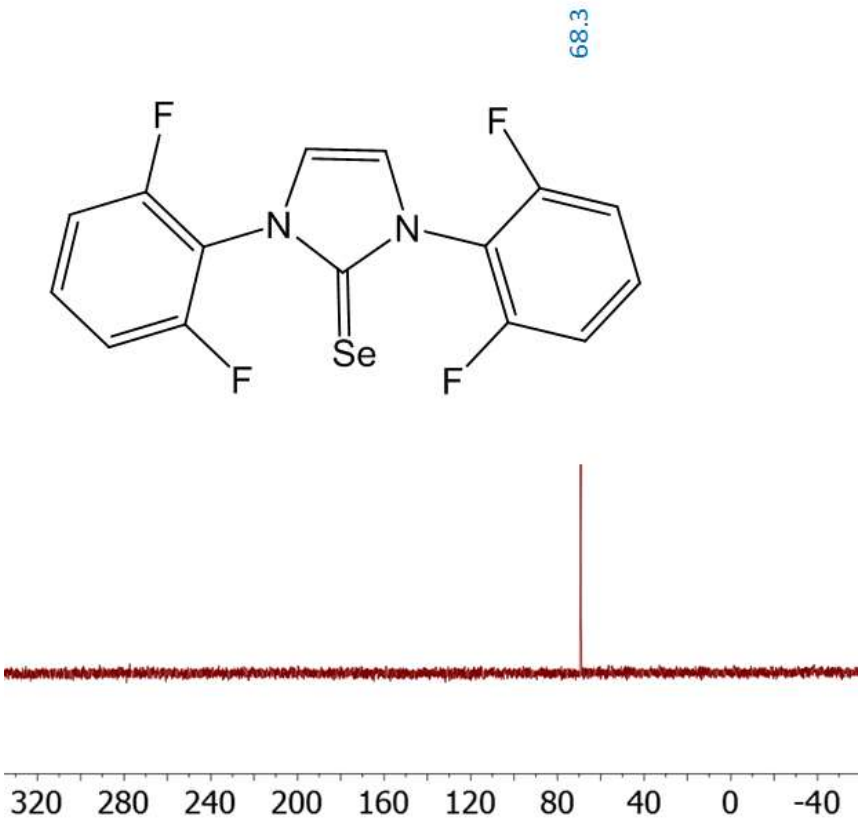

8.19
7.71
7.28
7.26
7.20
N
N
F
F
F
F
Se
*
2.01
2.01
2.01
2.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

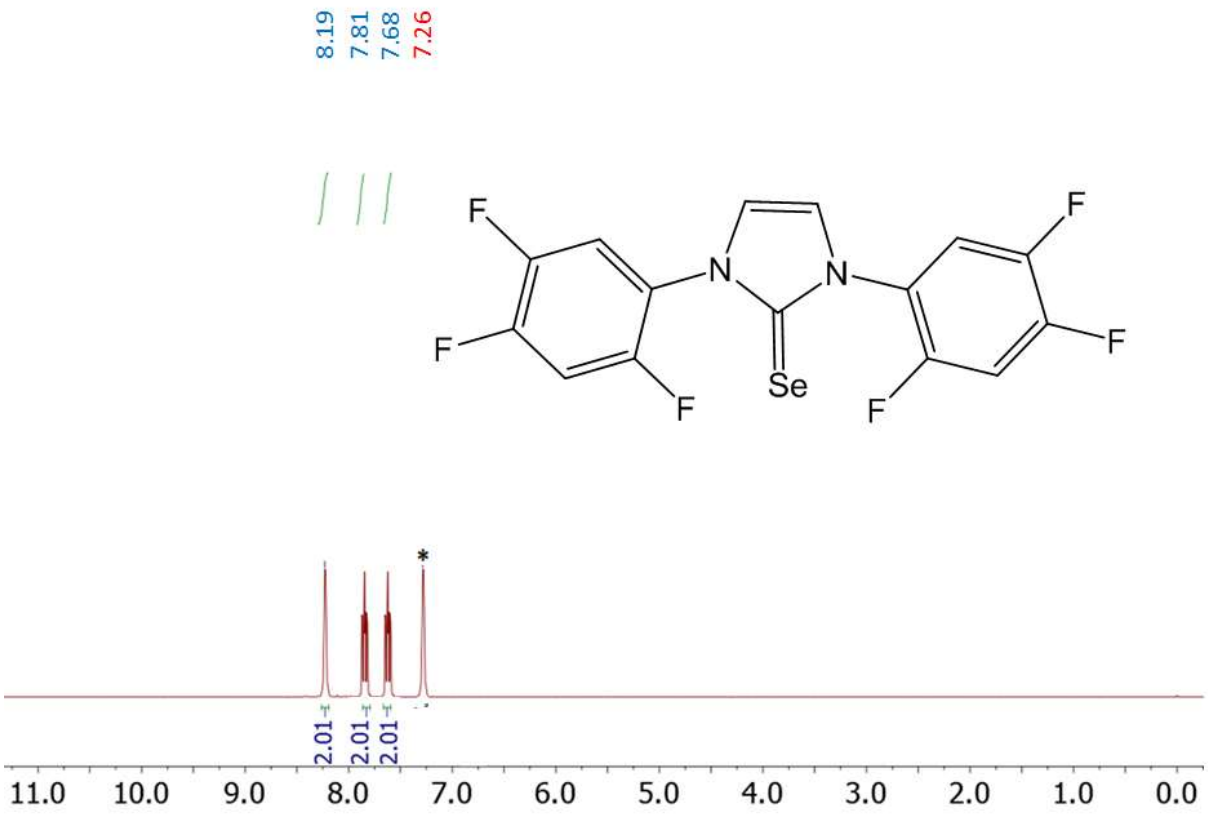

-106.05
-115.29
N
N
F
F
F
F
Se
2.00
2.00
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155

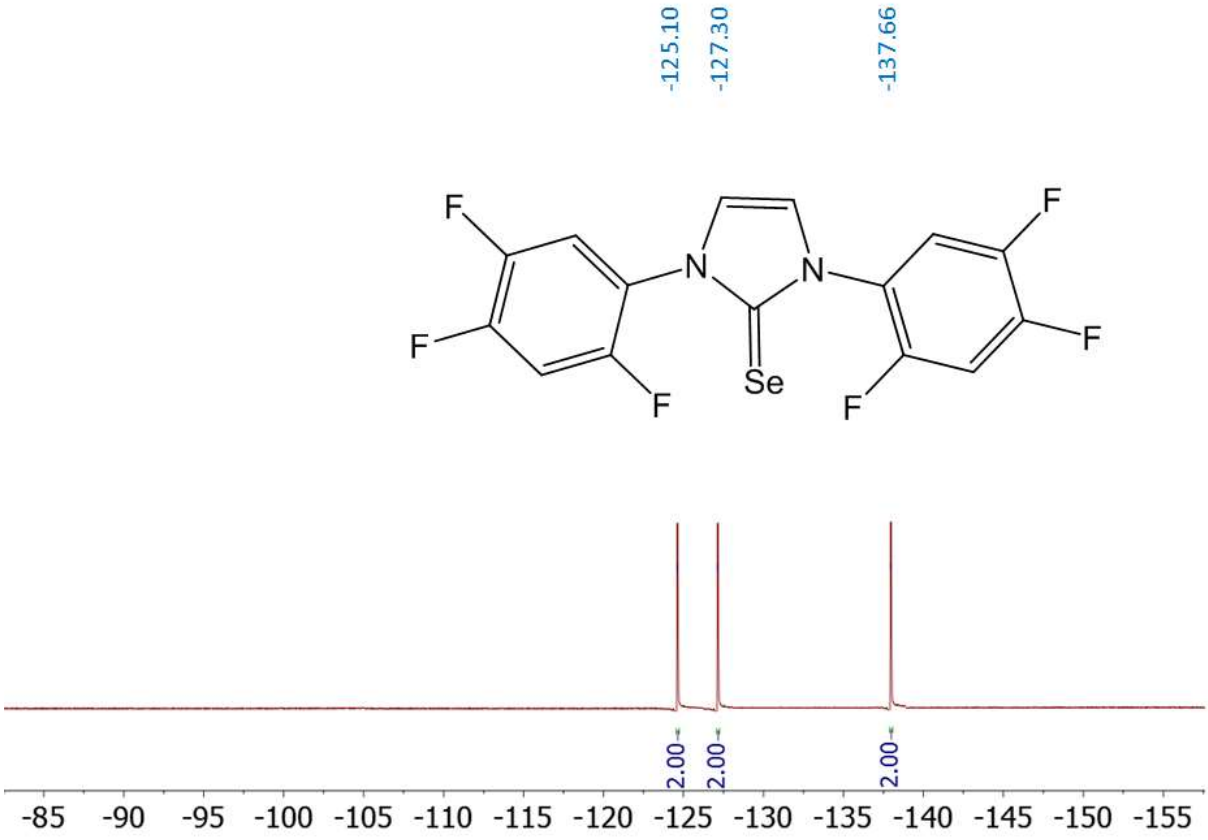

66.7
N
N
F
F
F
F
Se
320
280
240
200
160
120
80
40
0
-40

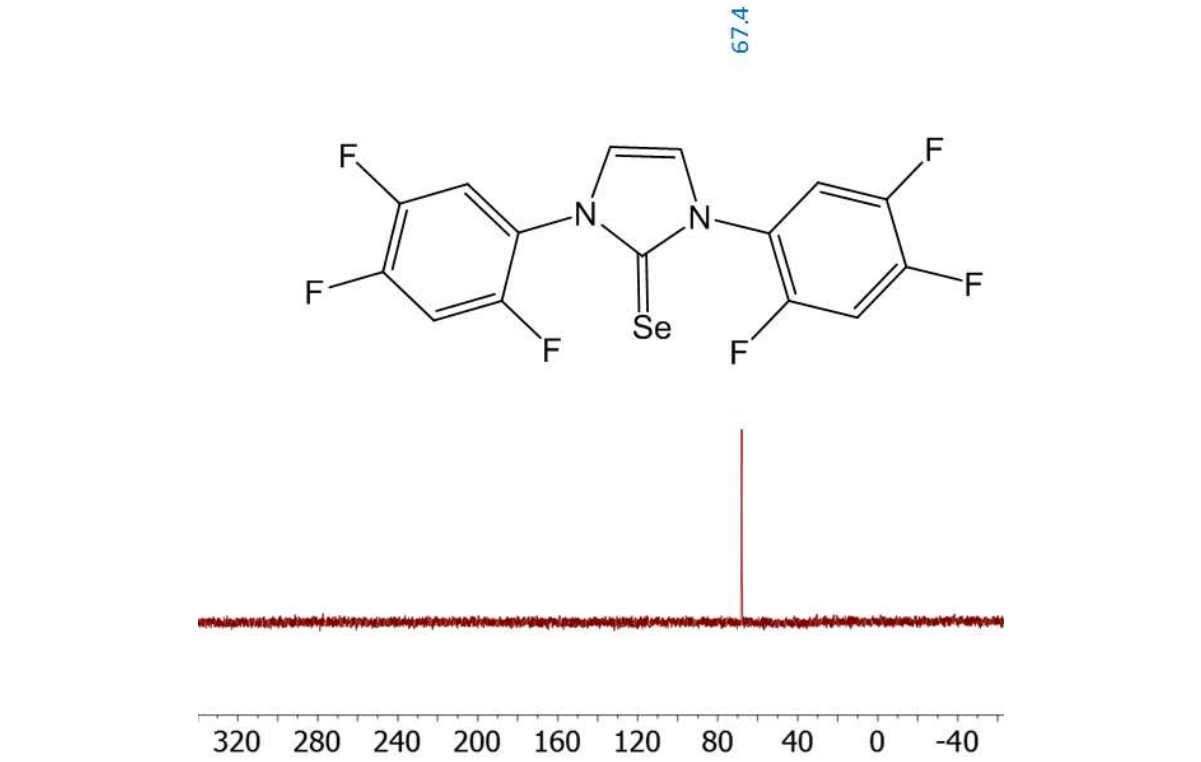

8.32
7.55
7.26
7.20
F
F
N
N
F
F
Se
*
2.01
2.01
4.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


-118.75
F
F
N
N
Se
F
F
4.01
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155


68.3
F
F
N
N
Se
F
F
320 280 240 200 160 120 80 40 0 -40


8.19
7.81
7.68
7.26
F
F
F
N
N
Se
F
F
F
*
2.01
2.01
2.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


-125.10
-127.30
-137.66
F
F
F
N
N
Se
F
F
F
2.00
2.00
2.00
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155


67.4
F
F
F
N
N
Se
F
F
F
320
280
240
200
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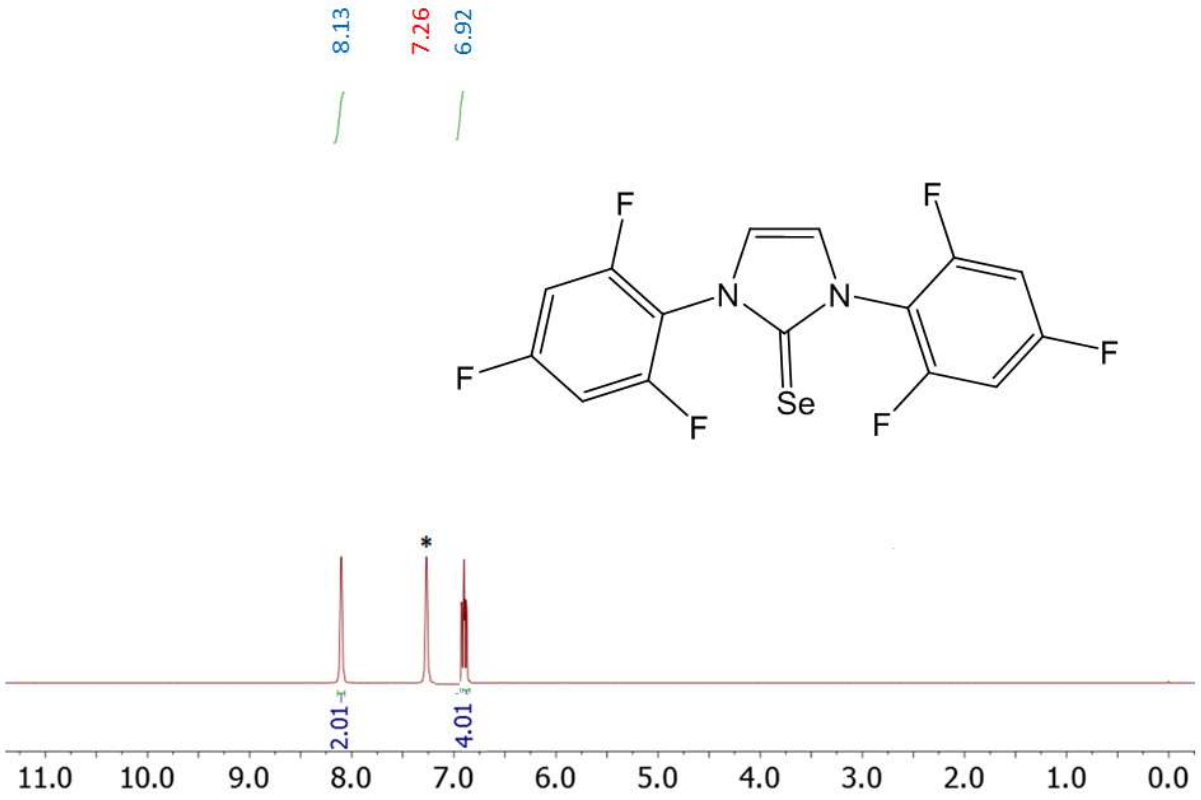
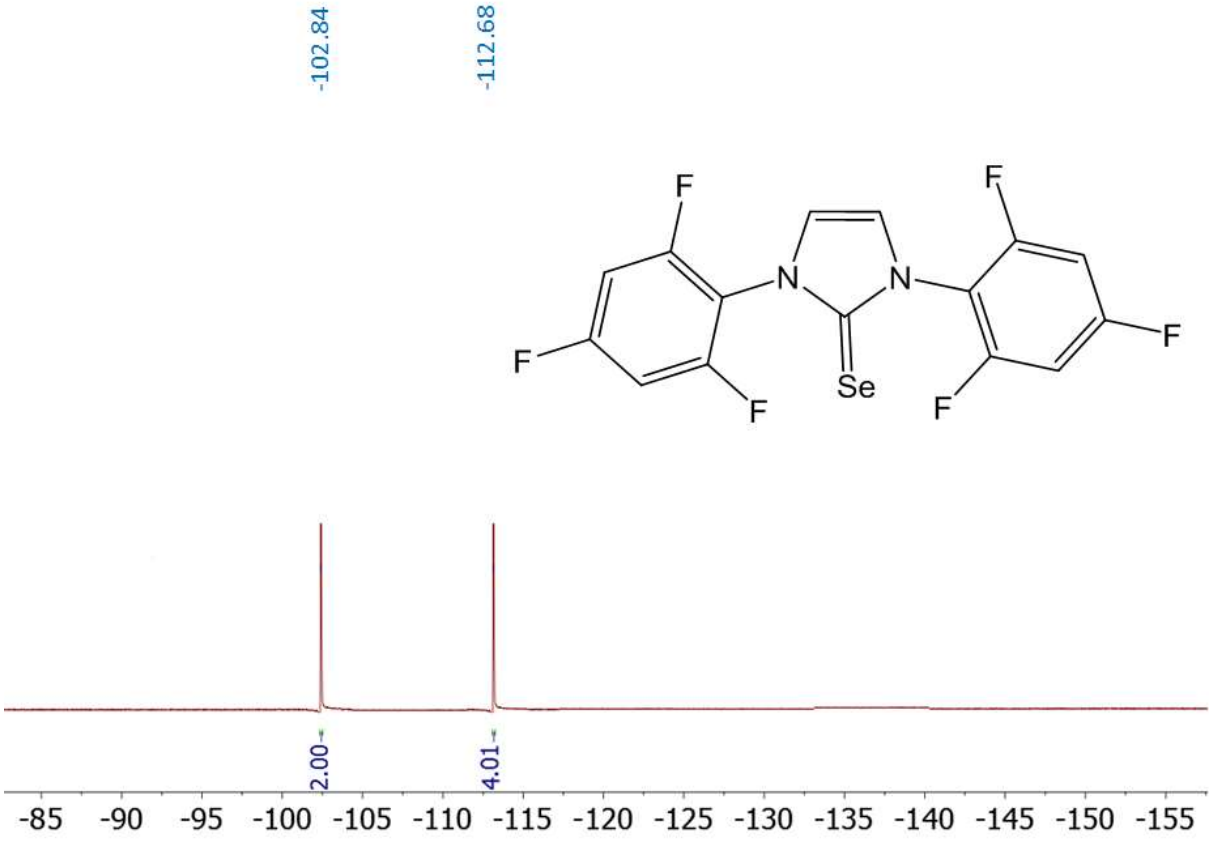
120
80
40
0
-40


8.13
7.26
6.92
F
F
F
N
N
Se
F
F
F
*
2.01
4.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


-102.84
-112.68
F
F
F
N
N
Se
F
F
F
2.00
4.01
-85
-90
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-100
-105
-110
-115
-120
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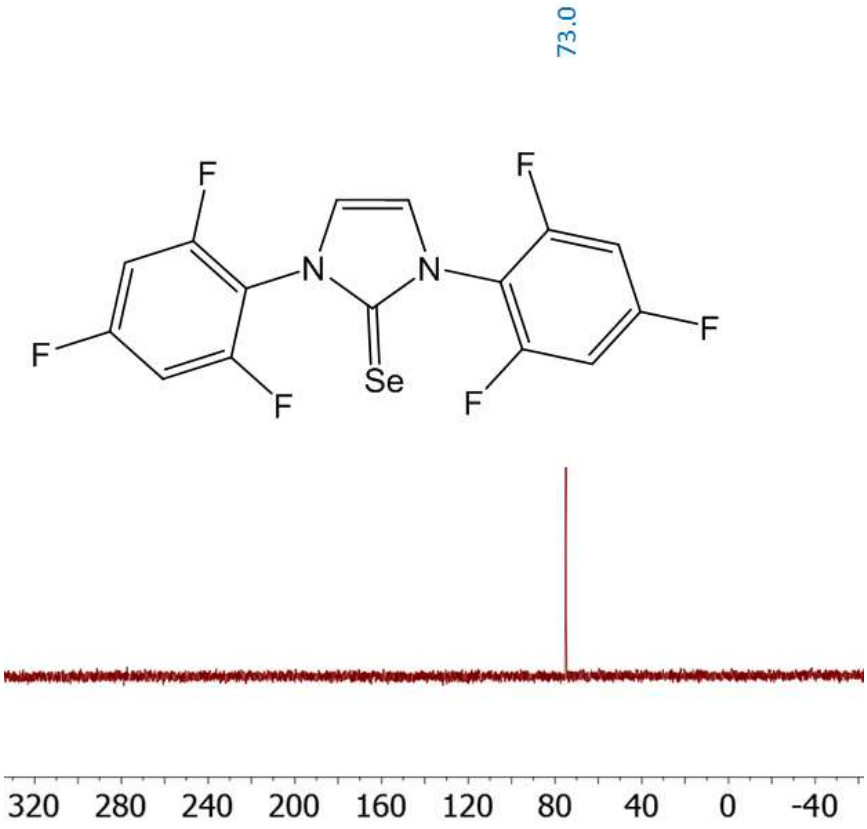
73.0
F
F
F
N
N
Se
F
F
F
320
280
240
200
160
120
80
40
0
-40