Supporting Information

Cationic Ruthenium Hydrido-Carbonyls Derived from Metallocene-Based Pincers: Unusual Rearrangements and H_2 Evolution with Formation of Cationic Ruthenium Metallocenylidenes

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The results of DFT calculations.

Table 1. Experimental and calculated parameters for the structures of complexes **3** and **4.**

Complex	**3**		**4**	
Parameter	X-ray	Calculation	X-ray	Calculation
r(C_1-H_1)	0.92	1.096	–	1.096
∠C_1H-ring	16.5°	16.8°	–	14.7°
r(Ru_1-C_1)	2.326	2.35	–	2.361
∠RuC_1-ring	79.1°	77.64°	–	77.91°
r(C_1-C_2)	1.448	1.465	–	1.466
r(C_1-C_5)	1.457	1.465	–	1.466
r(C_2-C_3)	1.424	1.435	–	1.437
r(C_4-C_5)	1.417	1.435	–	1.437
r(C_3-C_4)	1.431	1.435	–	1.438
r(Ru_1-H_1)	2.58	2.57	–	2.554
r(Fe-H_1)	2.50	2.68	–	
r(Ru_2-H_1)			–	2.813
∠Ru-CO	179.6°	179.5°	–	179.4°
r(Ru-C_1)	2.33	2.35	–	2.361
r(M-Cp)		2.04-2.05	–	2.21-2.22

Table 2. Calculated parameters for the structures of complexes **15**, **16** and **17.**

Complex	**15**	**16**	**17**
∠Cpring-Ru_1	28.97°	32.2°	9.3°
r(Ru_1-C_1)	2.051	2.048	2.06
∠RuCO cis	179.5°	178.9°	178.9°
∠RuCO trans	171.8°	172.8°	177.6°
r(C_1-C_2)	1.451	1.454	1.445
r(C_1-C_5)	1.451	1.454	1.446
r(C_2-C_3)	1.432	1.434	1.440
r(C_4-C_5)	1.432	1.434	1.438
r(C_3-C_4)	1.439	1.441	1.439

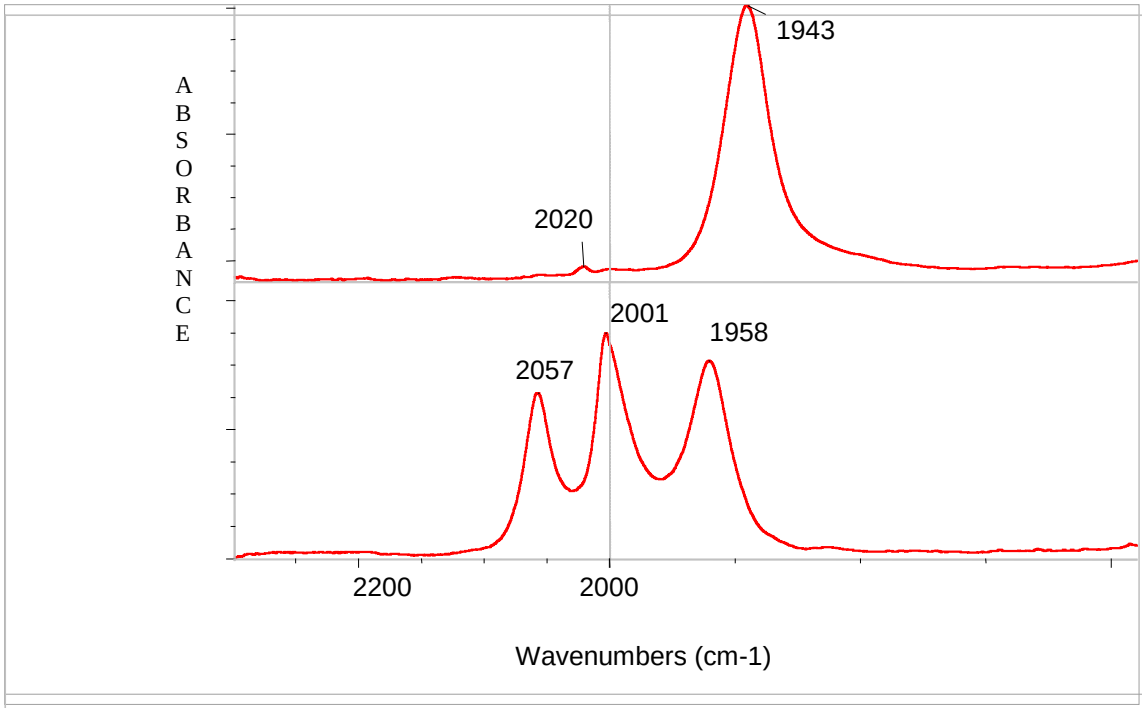


Figure 1. IR spectra of complexes **3** (upper) and **11** (lower) in CH_2Cl_2 solution.

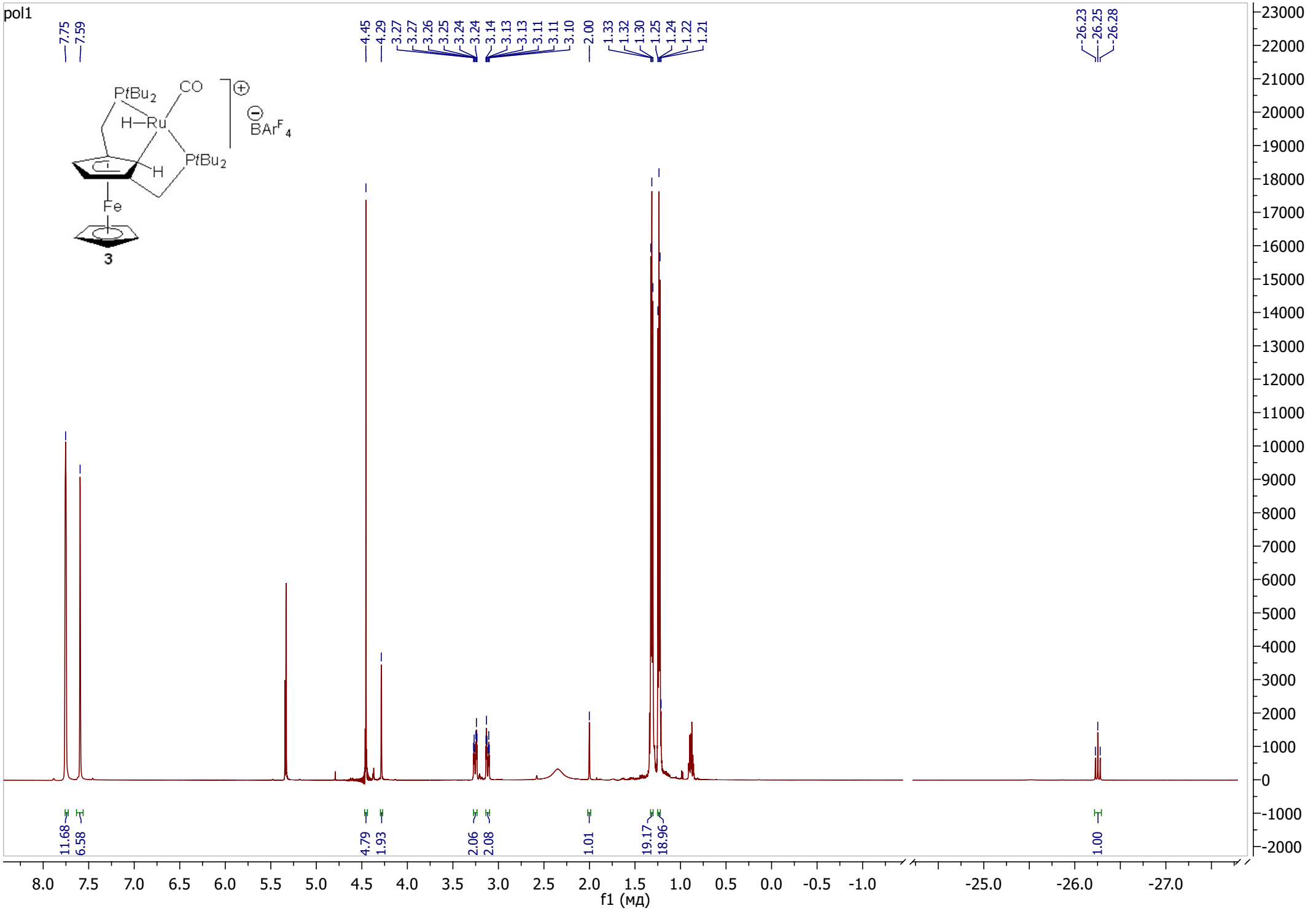
Table 3. Crystal data, data collection and structure refinement parameters for complexes **3, 11, 12,** and **16**.

Complex	**3**	**11**	**12**	**16**
Formula	$C_{61}H_{61}BF_{24}FeOP_2Ru$	$C_{65.5}H_{69}BClF_{24}FeO_2P_2Ru$	$C_{66.5}H_{71.4}BCl_{0.6}F_{24}O_2P_2Ru_2$	$C_{62}H_{59}BF_{24}O_2P_2Ru_2$
Molecular weight	1495.77	1609.33	1654.80	1566.98
Crystal color, habit	red prism	brown prism	orange prism	orange prism
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	10.7430(4)	13.3169(7)	13.2689(7)	46.020(2)
b, Å	15.6477(6)	13.7437(8)	13.6066(7)	19.9475(10)
c, Å	18.9522(7)	20.2072(11)	20.5591(11)	35.3888(18)
α, deg.	90	79.380(1)	79.460(1)	90
β, deg.	95.636(1)	75.653(1)	75.353(1)	129.579(1)
γ, deg.	90	81.396(1)	81.245(1)	90
V, Å^3	3170.5(2)	3500.6(3)	3508.6(3)	25039(2)
Z	2	2	2	16
d(calc.), g cm^{-3}	1.567	1.527	1.566	1.663
θ_{max}, deg.	30.0	29.0	28.0	28.0

μ, cm^{-1}	6.29	6.13	6.06	6.49
Transmission, T_{min}/T_{max}	0.739/0.874	0.782/0.919	0.784/0.942	0.764/0.870
No. unique refls (R_{int})	18182 (0.0313)	18512 (0.0291)	16838 (0.0390)	30077 (0.0545)
No. obs. refls ($I>2\sigma(I)$)	16478	14329	12694	21582
R_1 (on F for obs. refls)[a]	0.0354	0.0487	0.0444	0.0575
wR_2 (on F^2 for all refls)[b]	0.0795	0.1342	0.1104	0.1587
GOF	1.015	1.034	1.006	1.018

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$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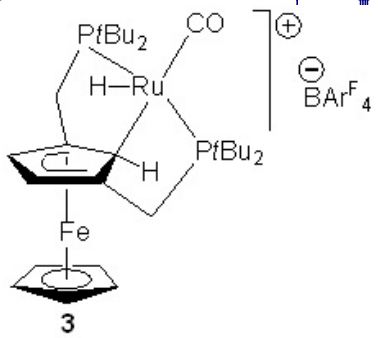
pol1
fraction 24



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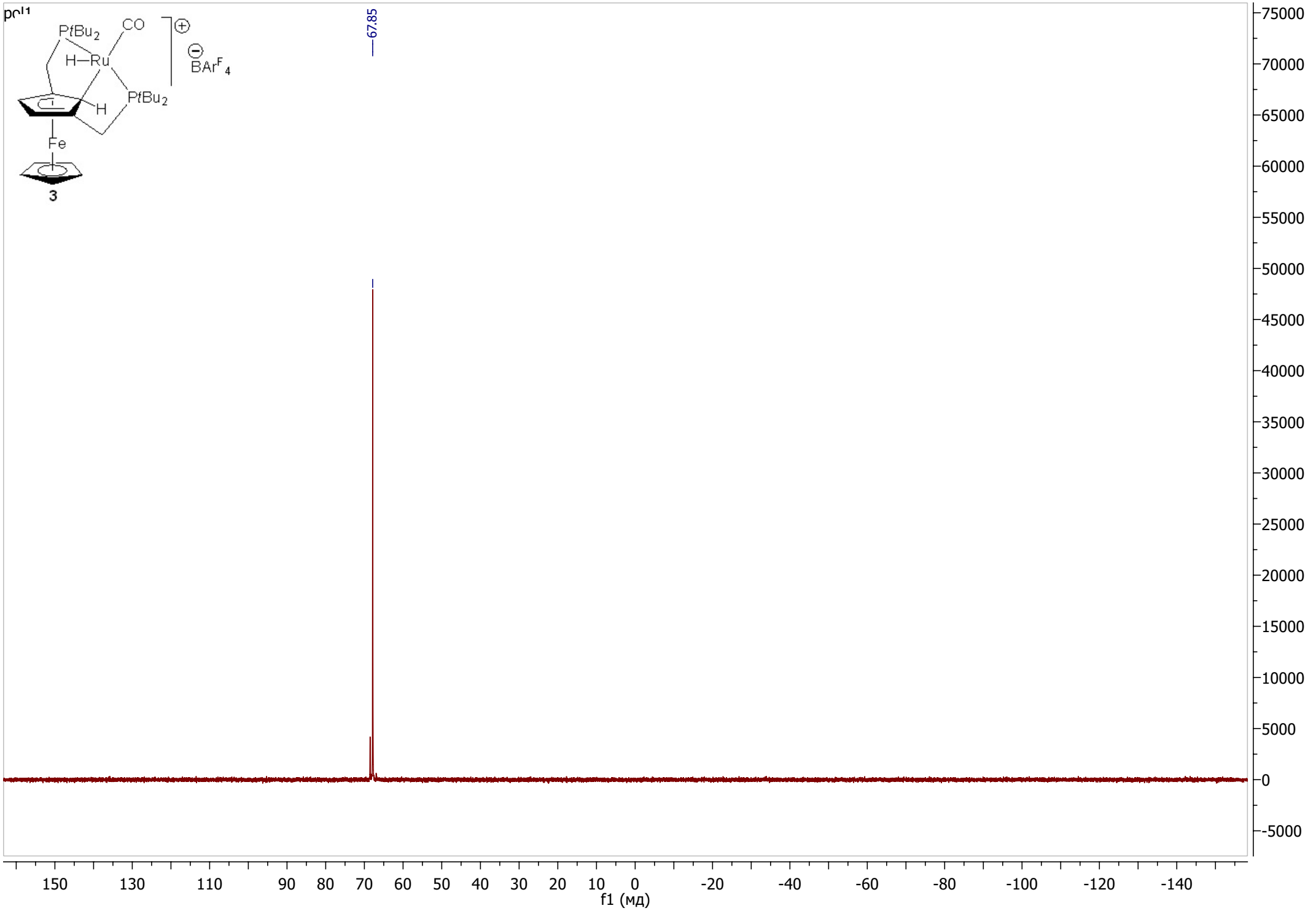
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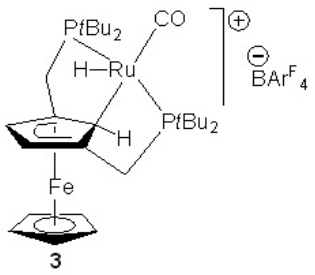
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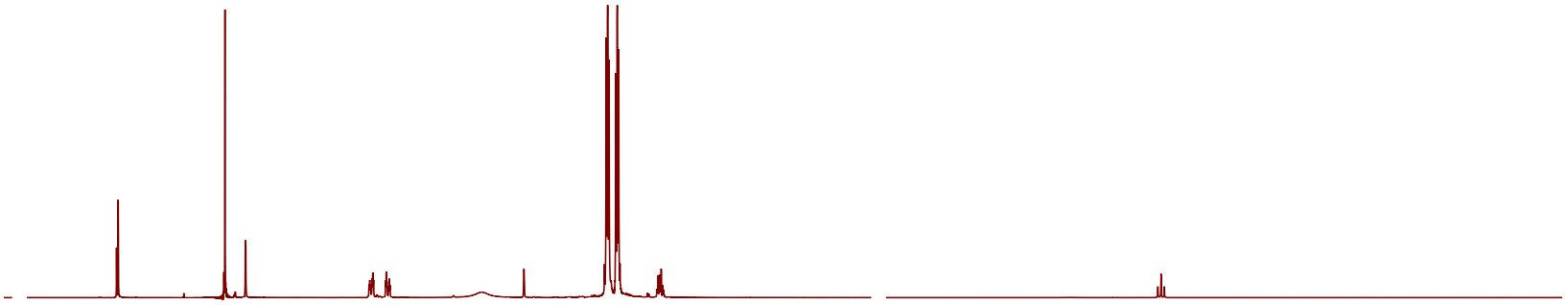
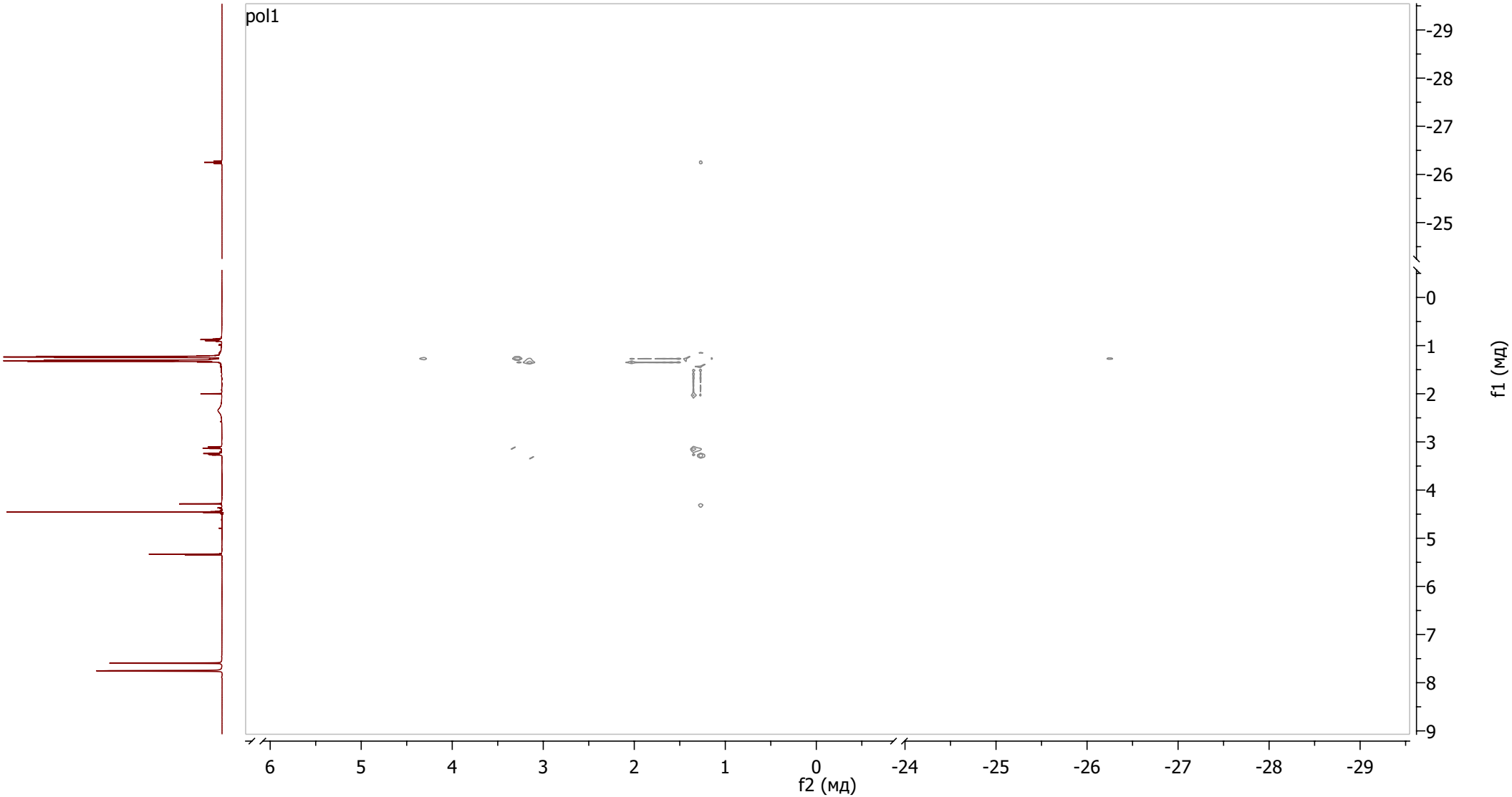
3

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8
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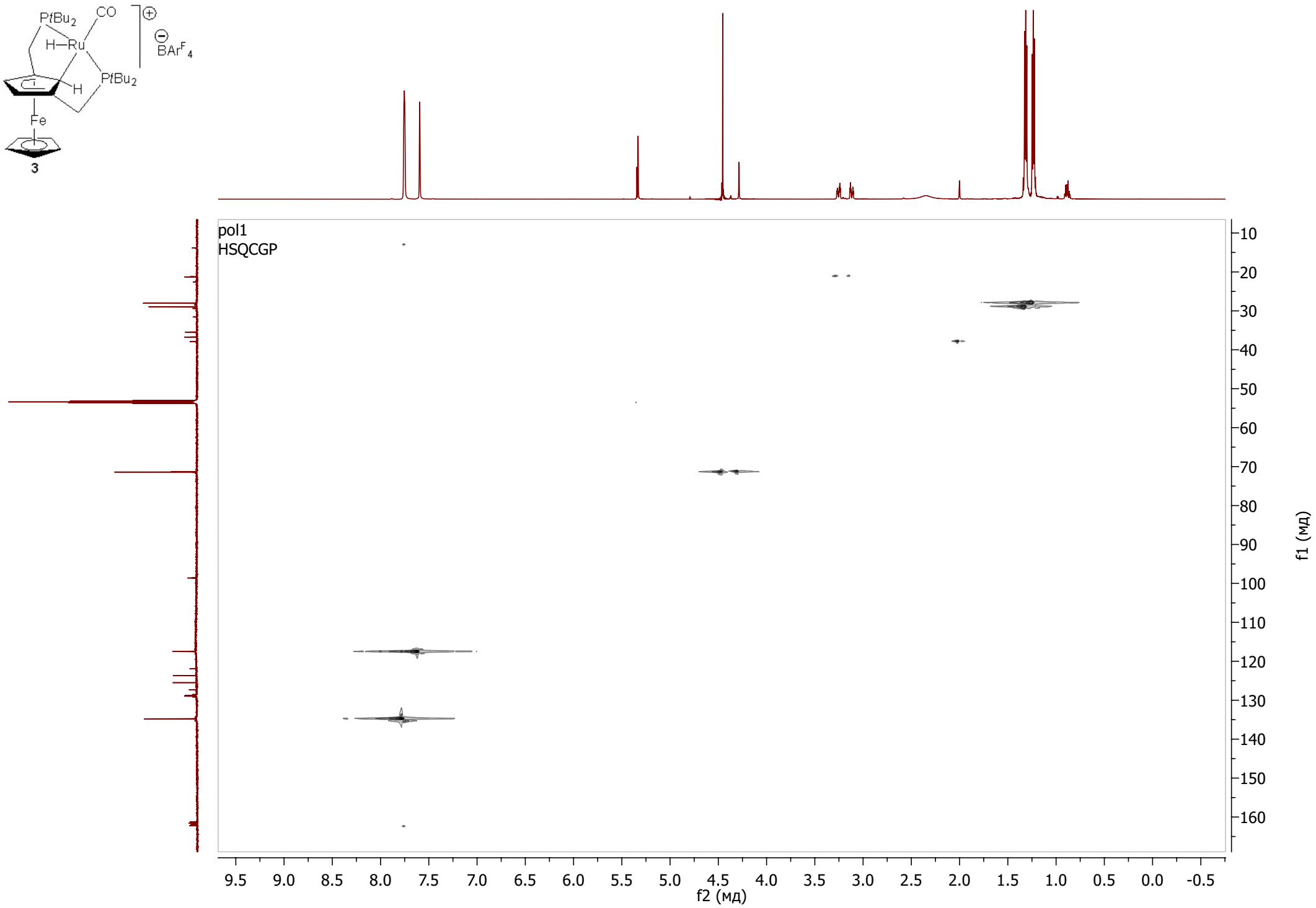
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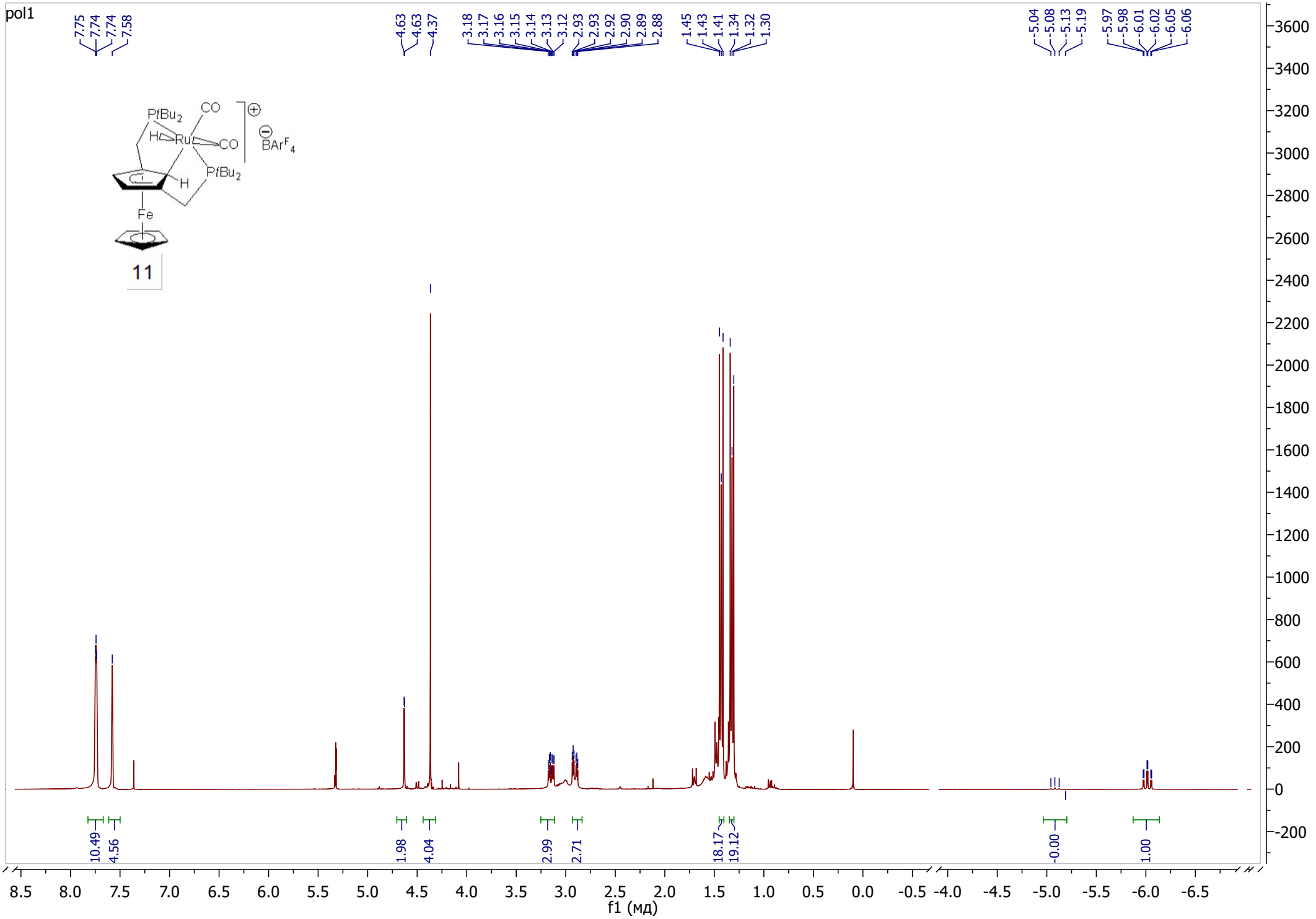
f1 (мд)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1.41
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1.32
1.30
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CO
H
Ru
CO
BArF4
PfBu2
H
Fe
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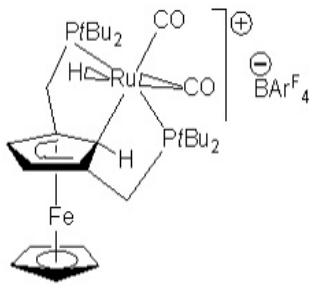

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16000
14000
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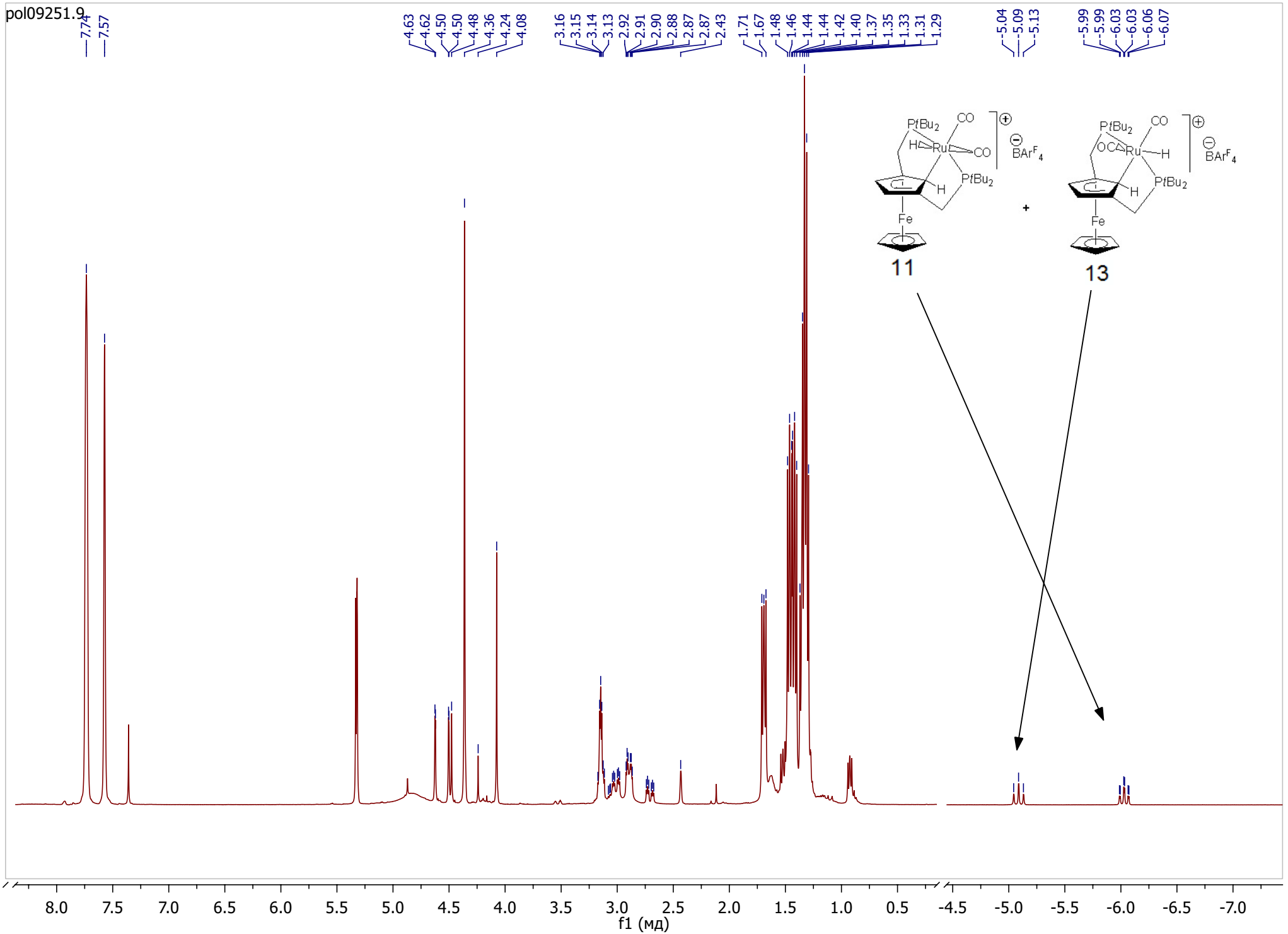
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BArF4
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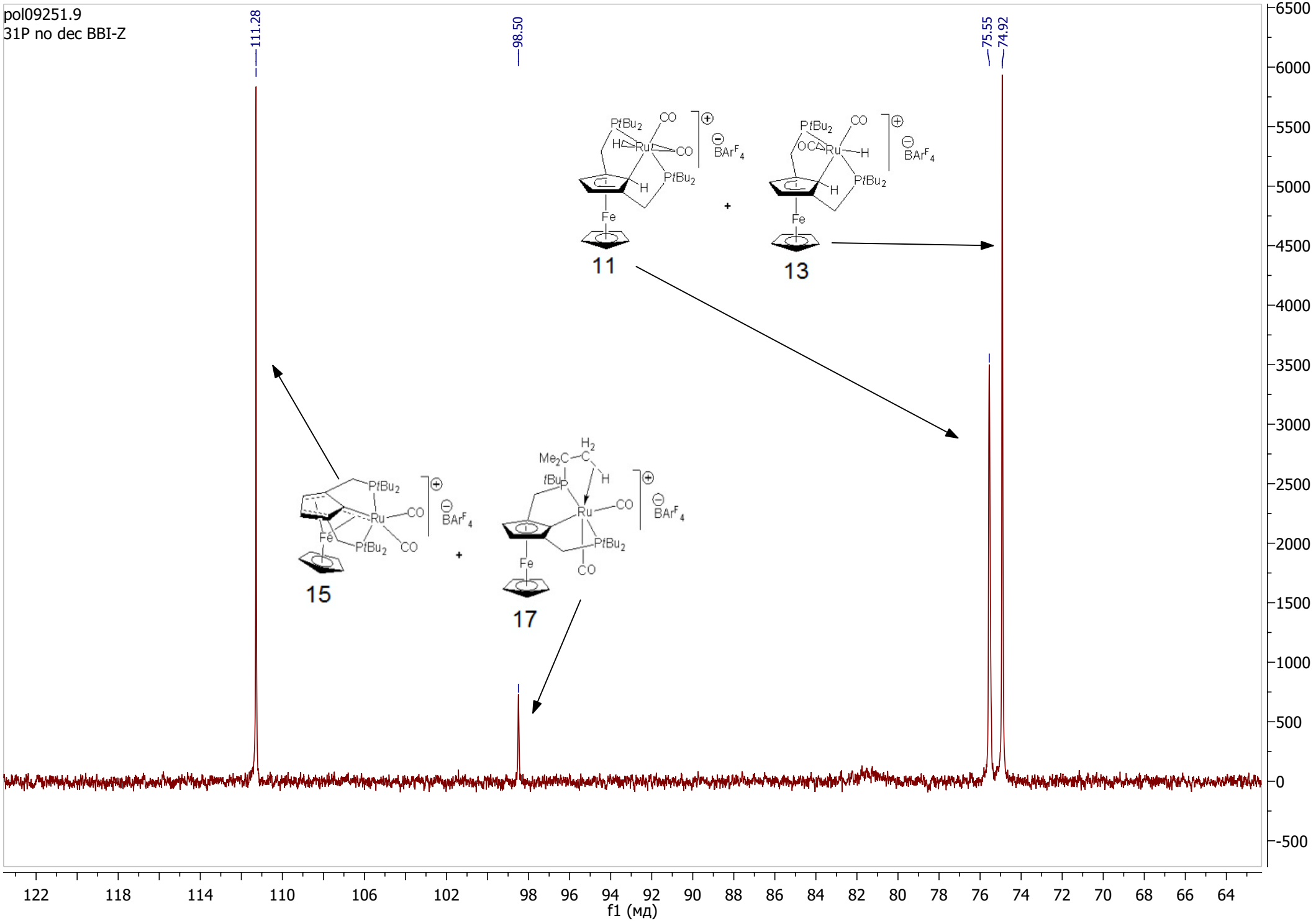
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15
17
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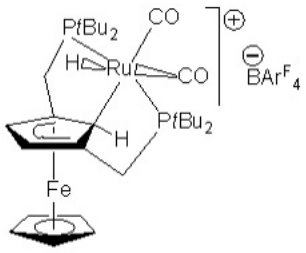

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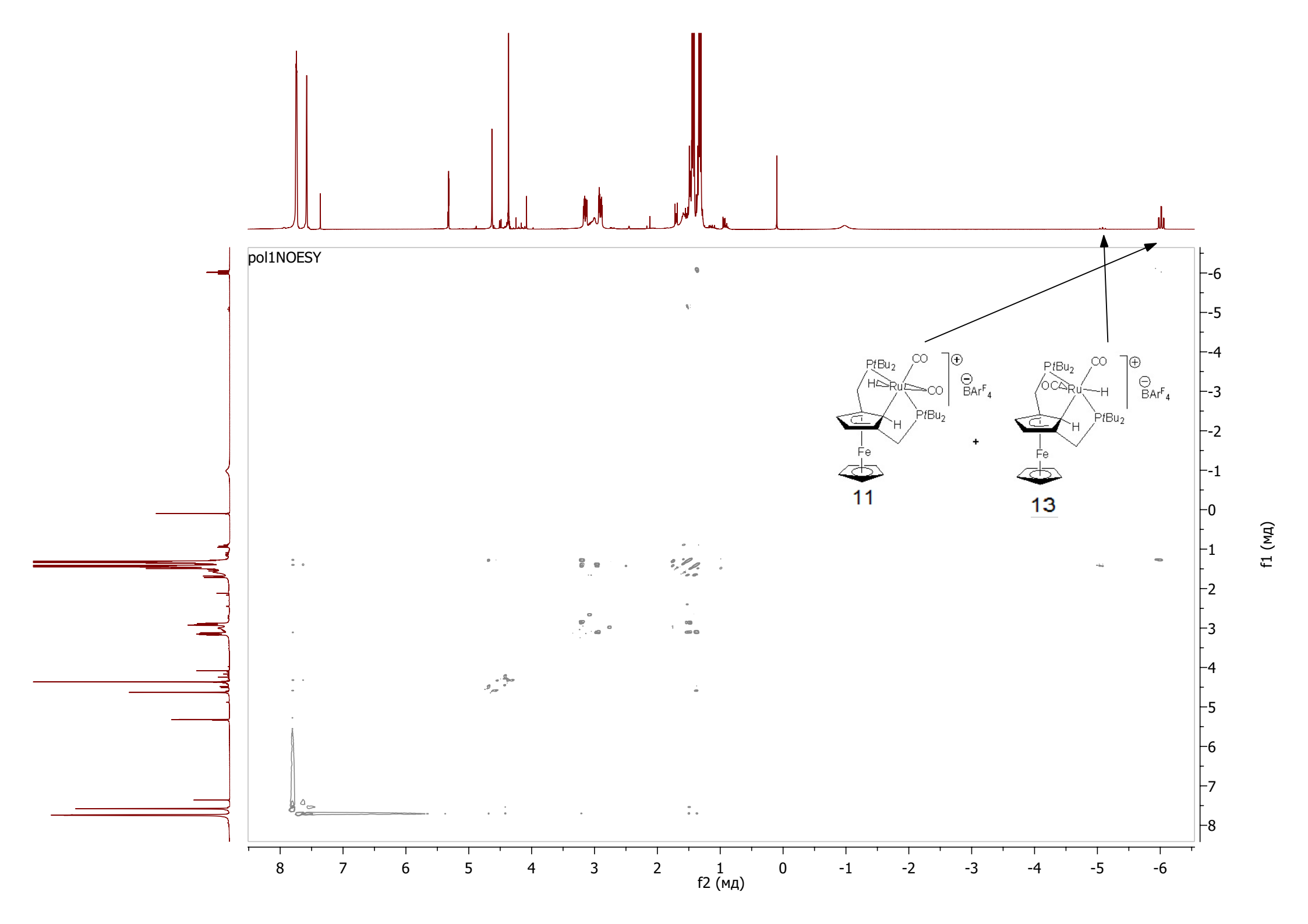
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Fe
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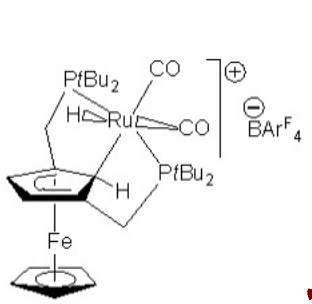
f1 (мд)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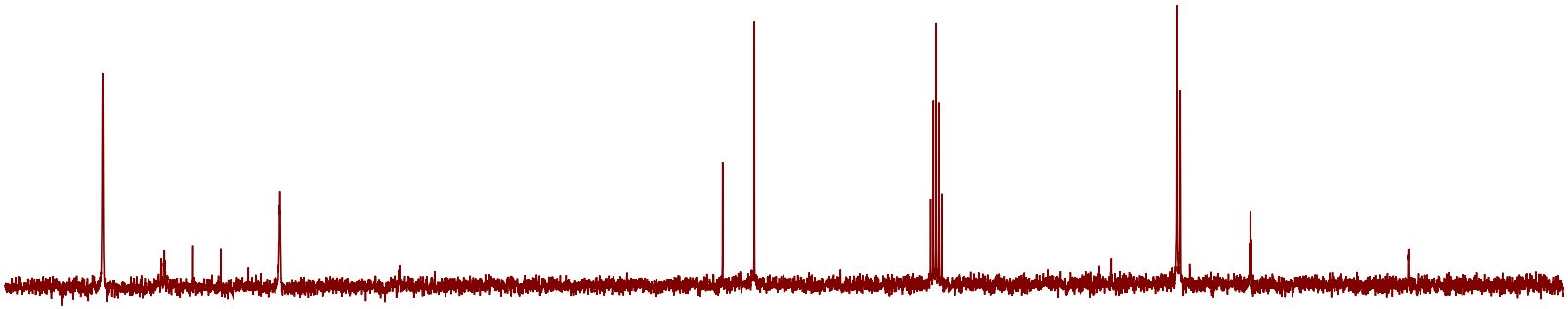

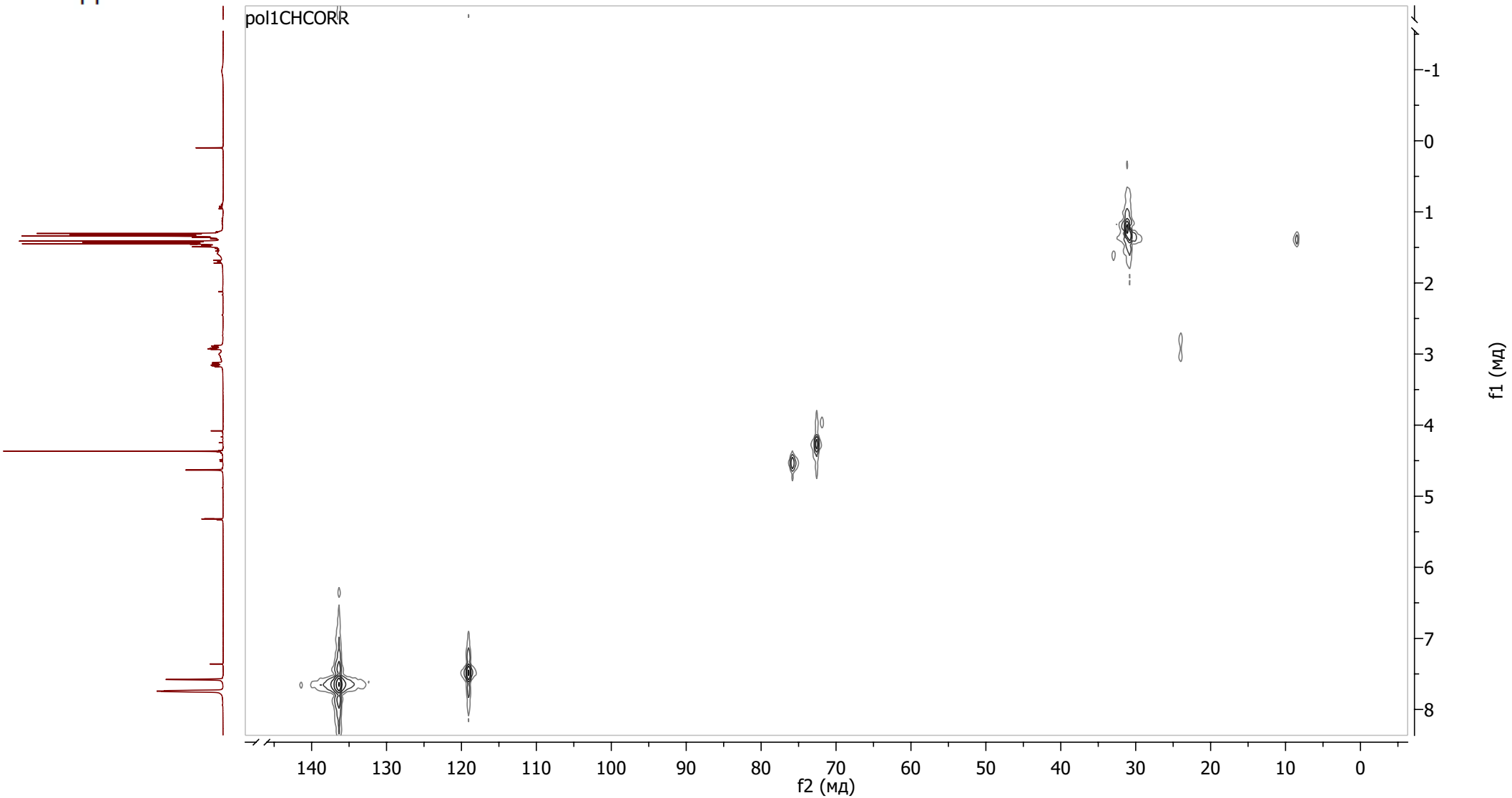
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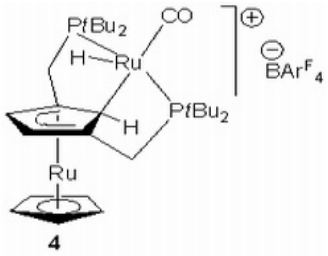
f2 (мд)

RuPCPRu(CO)H2 CDCl3



4

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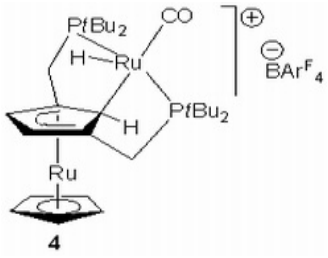

4

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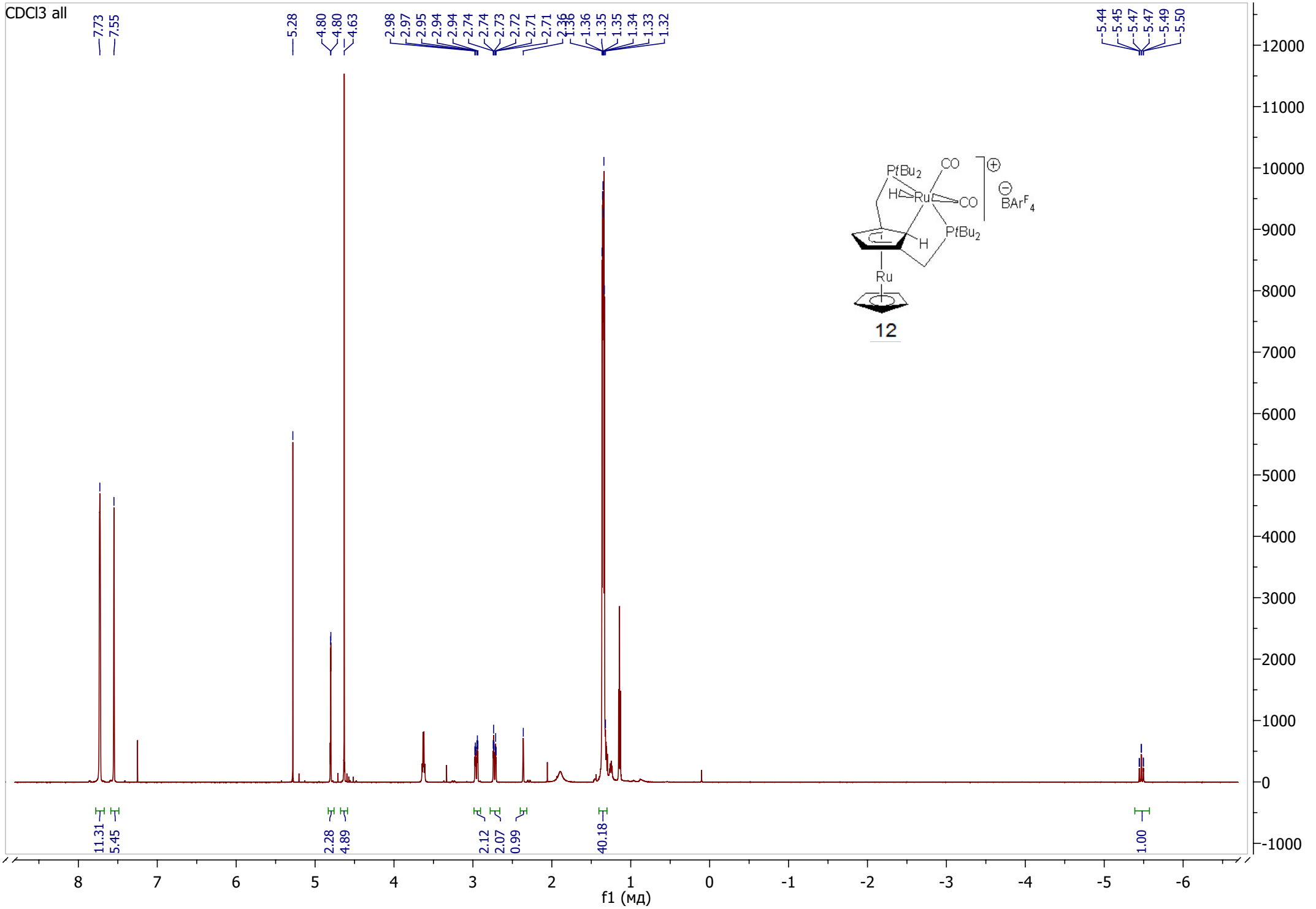
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CDCl3 all

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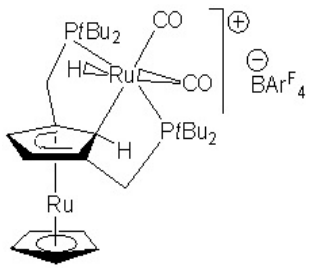

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f1 (мд)

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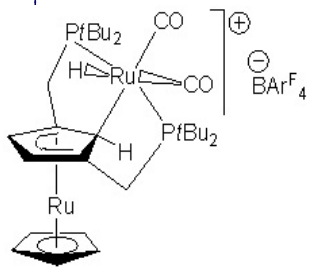
fraction 24



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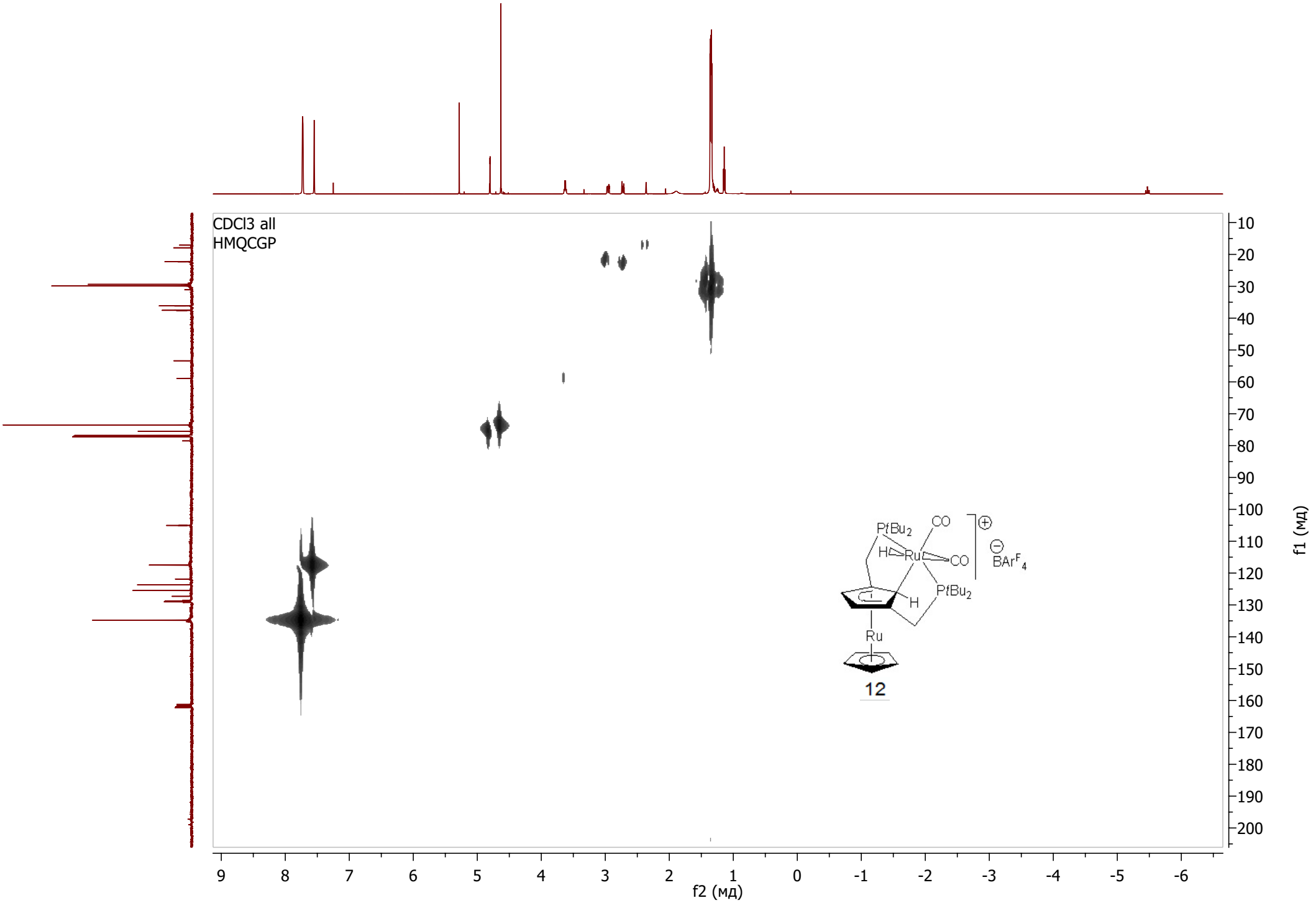
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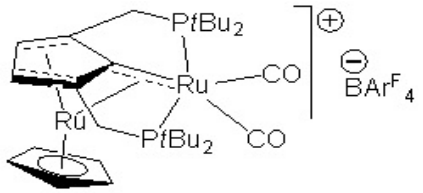
f1 (мд)

CDCl3 RuPCPRu(CO)2
F19CPD



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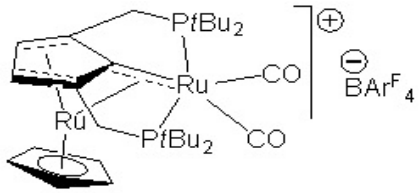

16

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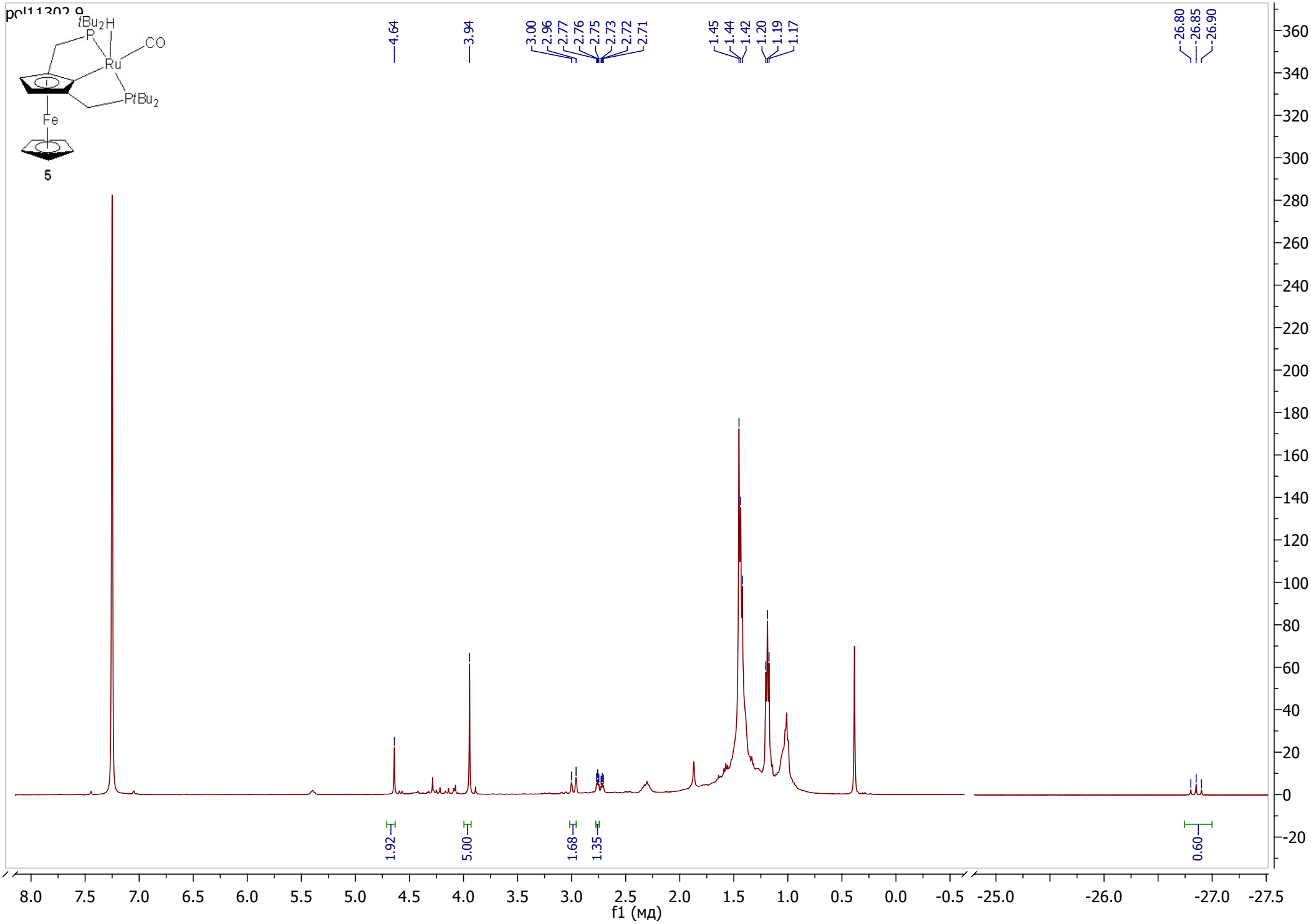
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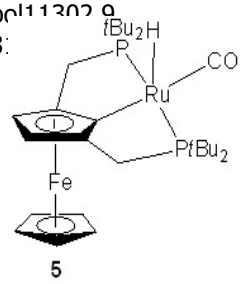
2.77
2.76
2.75
2.73
2.72
2.71
1.45
1.44
1.42
1.20
1.19
1.17
-26.80
-26.85
-26.90
1.92
5.00
1.68
1.35
0.60
f1 (мд)

pol11302-9

3:



5

117.81

15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 -56 -58 -60 -62 -64 -66 -68

f1 (мд)