Electronic supplementary material

Bis(alkyl) rare-earth complexes coordinated by bulky tridentate amidinate ligands bearing pendant $Ph_2P=O$ and $Ph_2P=NR$ groups. Synthesis, structures and catalytic activity in stereospecific isoprene polymerization

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Figure 25S. IR spectrum of {2-[Ph_2P=O]C_6H_4NC(*t*Bu)N(2,6-*i*$Pr_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**7**).

Figure 26S. ^{1}H NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

Figure 27S. ^{13}C NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

Figure 28S. ^{31}P NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

Figure 29S. IR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

Figure 30S. ^{1}H NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

Figure 31S. ^{13}C NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

Figure 32S. ^{31}P NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

Figure 33S. IR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

Figure 34S. ^{1}H NMR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

Figure 35S. ^{13}C NMR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

Figure 36S. ^{31}P NMR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

Figure 37S. IR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

Figure 38 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 5)

Figure 39 S. GPC of PIP sample (Table 1, Entry 5)

Figure 40 S. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 9)

Figure 41 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 9)

Figure 42 S. GPC of PIP sample (Table 1, Entry 9)

Figure 43 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 18)

Figure 44 S. GPC of PIP sample (Table 1, Entry 18)

Figure 45 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 2, Entry 1)

Figure 46 S. GPC of PIP sample (Table 2, Entry 1)

Figure 47 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 2, Entry 3)

Figure 48 S. GPC of PIP sample (Table 2, Entry 3)

Figure 49 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 3, Entry 3)

Figure 50 S. GPC of PIP sample (Table 3, Entry 3)

Figure 51 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 3, Entry 9)

Figure 52 S. GPC of PIP sample (Table 3, Entry 9)

Table 1S. Crystallographic data and structure refinement details for **1**, **3**, **6**-**8**.

Compound	**1**	**3**	**6**	**7**	**8**
Empirical formula	$C_{35}H_{41}N_2OP$	$C_{37}H_{38}N_3P$	$C_{50}H_{70}ErN_2OPSi_2$	$C_{50}H_{70}LuN_2OPSi_2$	$C_{52}H_{67}N_3PSi_2Y$
Formula weight	536.67	555.67	969.49	977.20	910.14
T [K]°	100(2)				
Wavelength [Å]	0.71073				
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P21/n	P-1	P-1	P2(1)/n
a [Å]	9.4677(12)	8.98190(10)	12.02608(14)	12.050(2)	11.5972(3)
b [Å]	12.1398(15)	29.7023(3)	12.31192(17)	12.305(3)	23.2241(5)
c [Å]	14.1647(18)	11.56075(13)	19.7345(3)	19.732(4)	18.9698(5)
α [°]	68.6616(18)	90	107.3635(12)	107.281(4)	90
β [°]	88.5542(19)	96.0995(10)	90.2711(10)	90.382(4)	23.2241(5)
γ [°]	82.884(2)	90	115.7358(12)	116.065(4)	90
Volume [$Å^3$]	1504.4(3)	3066.75(6)	2481.33(6)	2477.3(9)	5109.2(2)
Z	2	4	2	2	4
ρcalcd. [g cm^{-3}]	1.185	1.204	1.298	1.310	1.183
Absorption coefficient	0.121	0.120	1.807	2.109	1.255

[mm^{-1}]					
F(000)	576	1184	1006	1012	1928
Crystal size [mm]	0.440×0.230×0.070	0.400×0.400×0.100	0.300×0.200×0.200	0.360×0.180×0.150	0.400×0.200×0.200
θ range for data collection [°]	2.651 to 27.998	3.033 to 27.999	3.118 to 30.000	2.190 to 27.000	2.906 to 25.999
Index ranges	-12≤h≤12, -16≤k≤16, -18≤l≤18	-11≤h≤11, -39≤k≤39, -15≤l≤15	-16≤h≤16, -17≤k≤17, -27≤l≤27	-15≤h≤15, -15≤k≤15, -25≤l≤25	-14≤h≤14, -28≤k≤28, -23≤l≤23
Reflections collected	15667	55091	50037	25058	79454
Independent reflections	7218	7377	14452	10772	9966
R_{int}	0.0248	0.0333	0.0380	0.0408	0.0725
Completeness to θ [%]	99.1	99.5	99.7	99.3	0.0725
Data/restraints/parameters	7218/0/362	7377/0/379	14452/0/544	10772/0/532	9966/0/544
Goodness-of-fit on F^2	1.037	1.030	1.058	1.040	1.058
Final R indices [I>2σ(I)]	R1 = 0.0424, wR2 = 0.1062	R1 = 0.0368, wR2 = 0.0940	R1 = 0.0239, wR2 = 0.0560	R1 = 0.0395, wR2 = 0.0817	R1 = 0.0389, wR2 = 0.0961
R indices (all data)	R1 = 0.0555, wR2 = 0.1116	R1 = 0.0436, wR2 = 0.0975	R1 = 0.0282, wR2 = 0.0580	R1 = 0.0486, wR2 = 0.0842	R1 = 0.0546, wR2 = 0.1022

Largest diff. peak and hole [eÅ^{-3}]	0.533 and -0.235	0.360 and -0.286	0.970 and -1.041	3.441 and -1.514	0.739 and -0.380

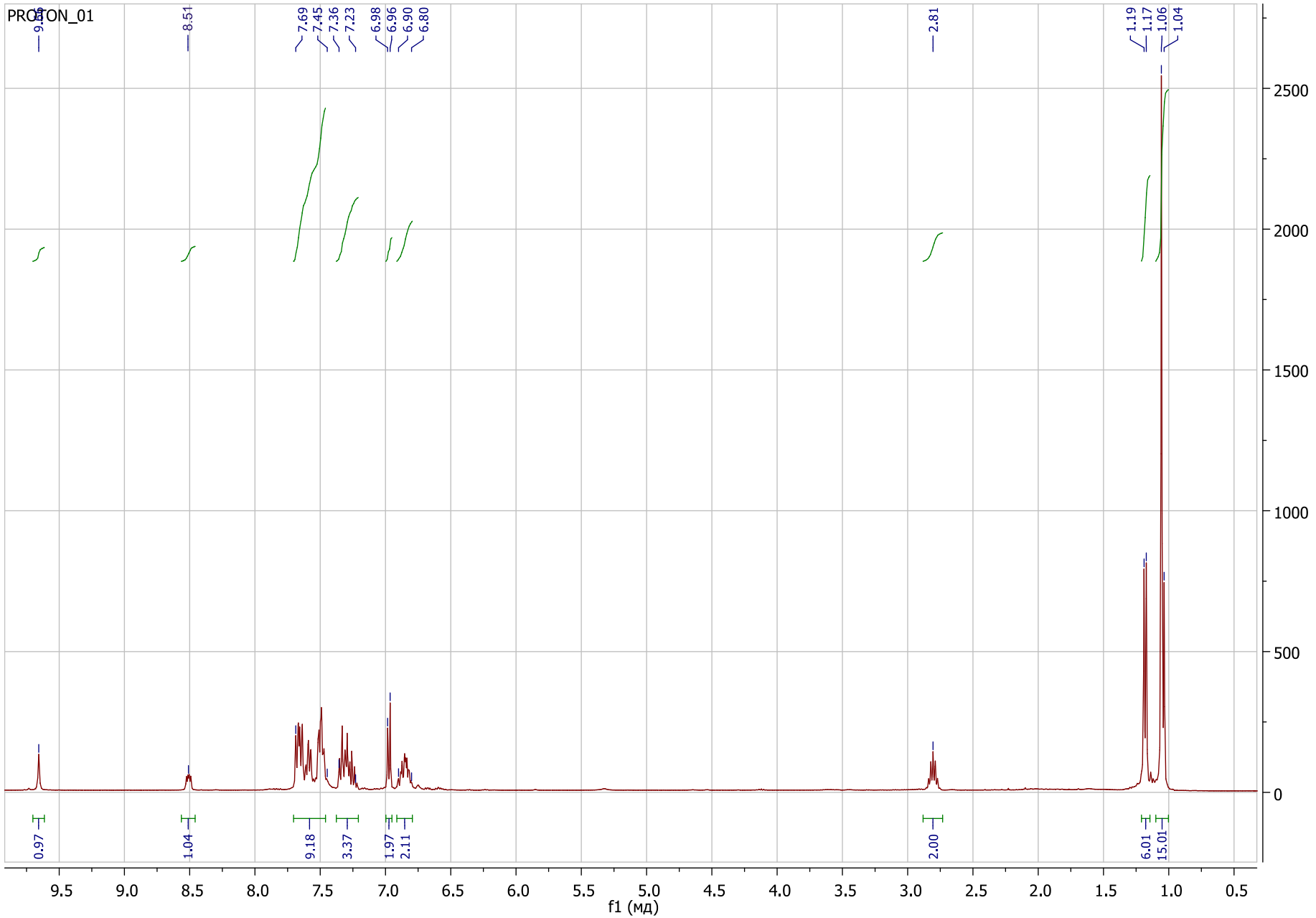


Figure 1S. ^{1}H NMR spectrum of 2-[Ph_2P=O]C_6H_4NHC(*t*Bu)=N(2,6-*i*$Pr_2C_6H_3$) (**1**).

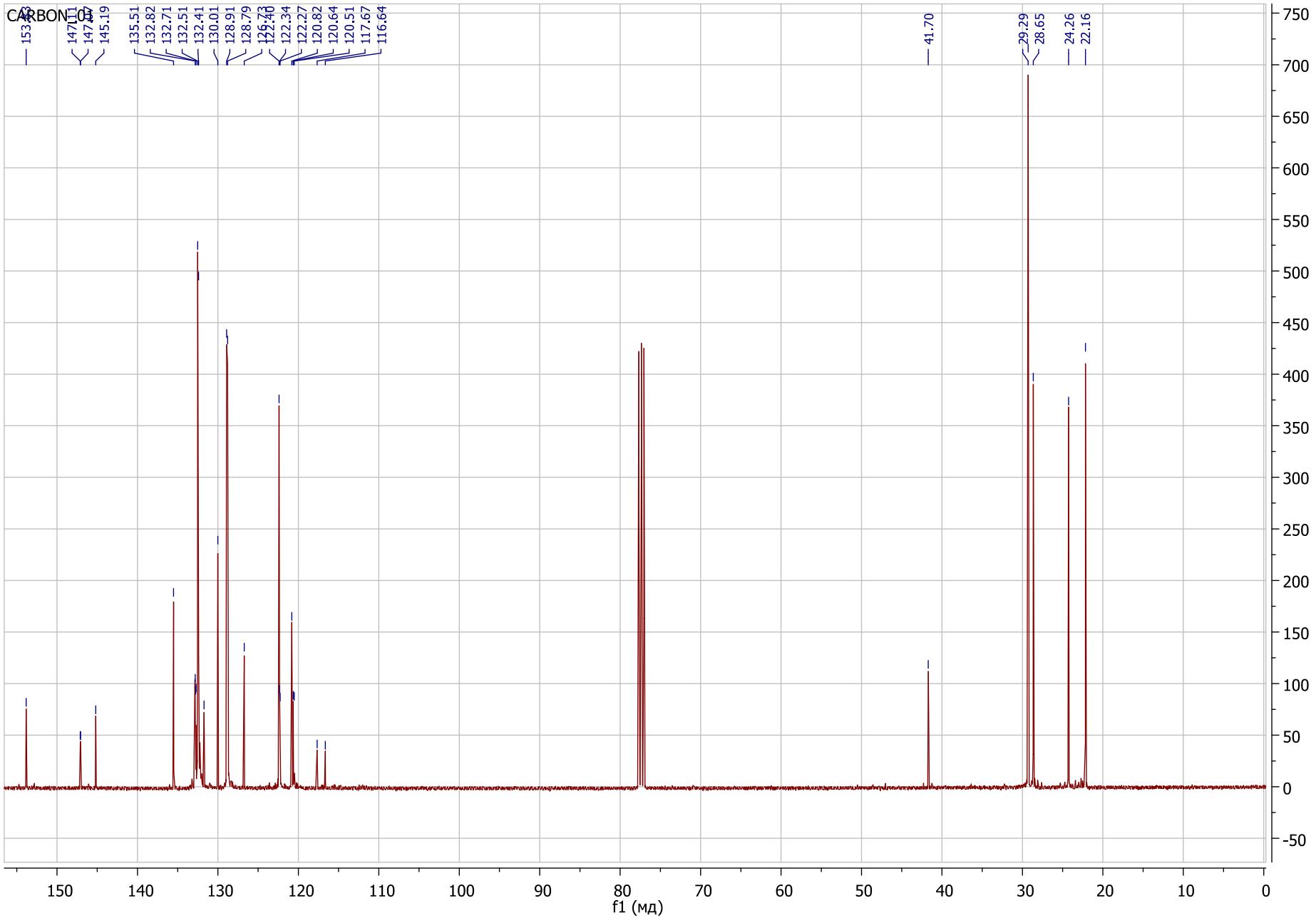


Figure 2S. ^{13}C NMR spectrum of 2-[Ph_2P=O]C_6H_4NHC(*t*Bu)=N(2,6-*i*$Pr_2C_6H_3$) (**1**).

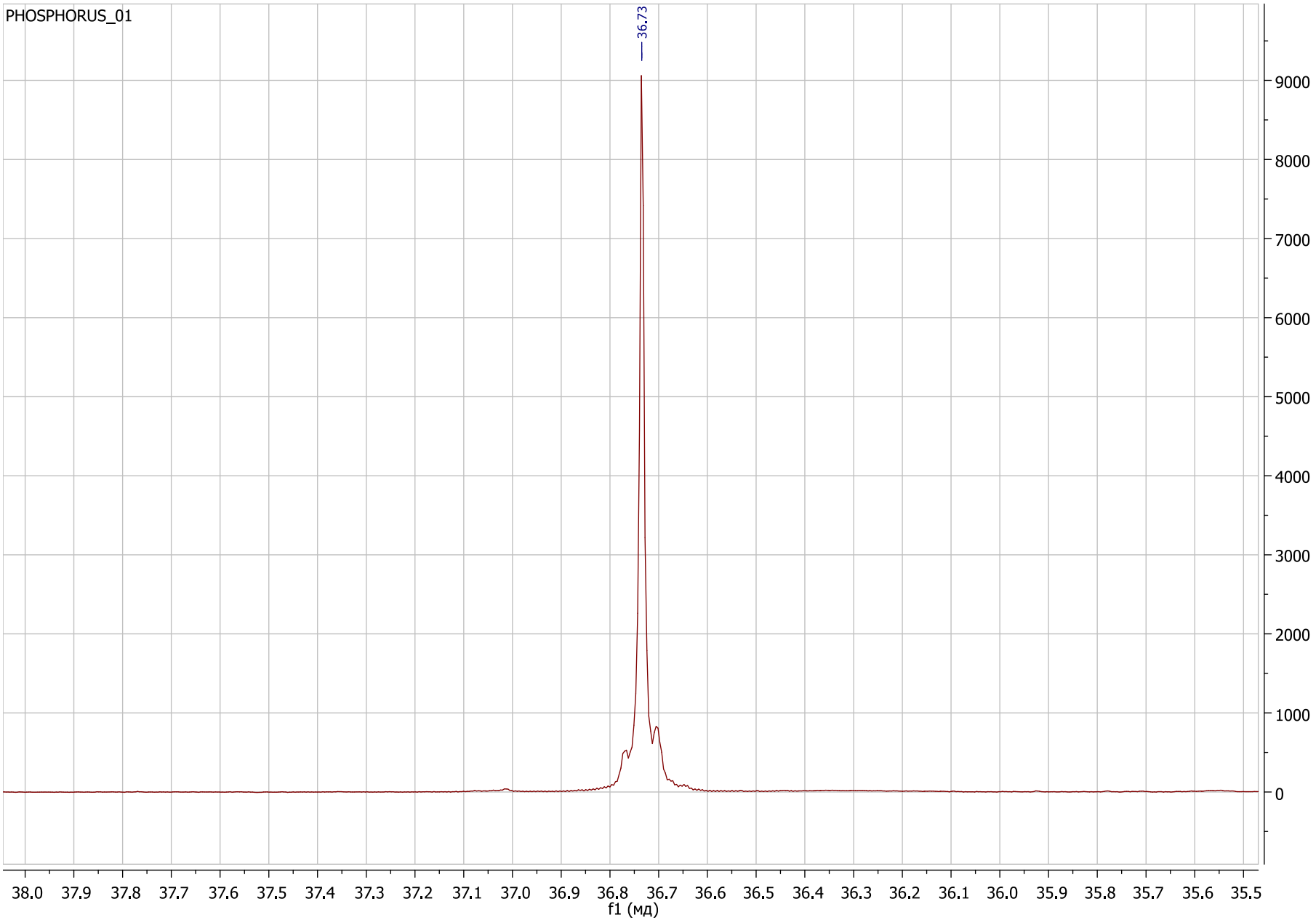


Figure 3S. ^{31}P NMR spectrum of 2-[Ph_2P=O]C_6H_4NHC(*t*Bu)=N(2,6-*i*$Pr_2C_6H_3$) (**1**).

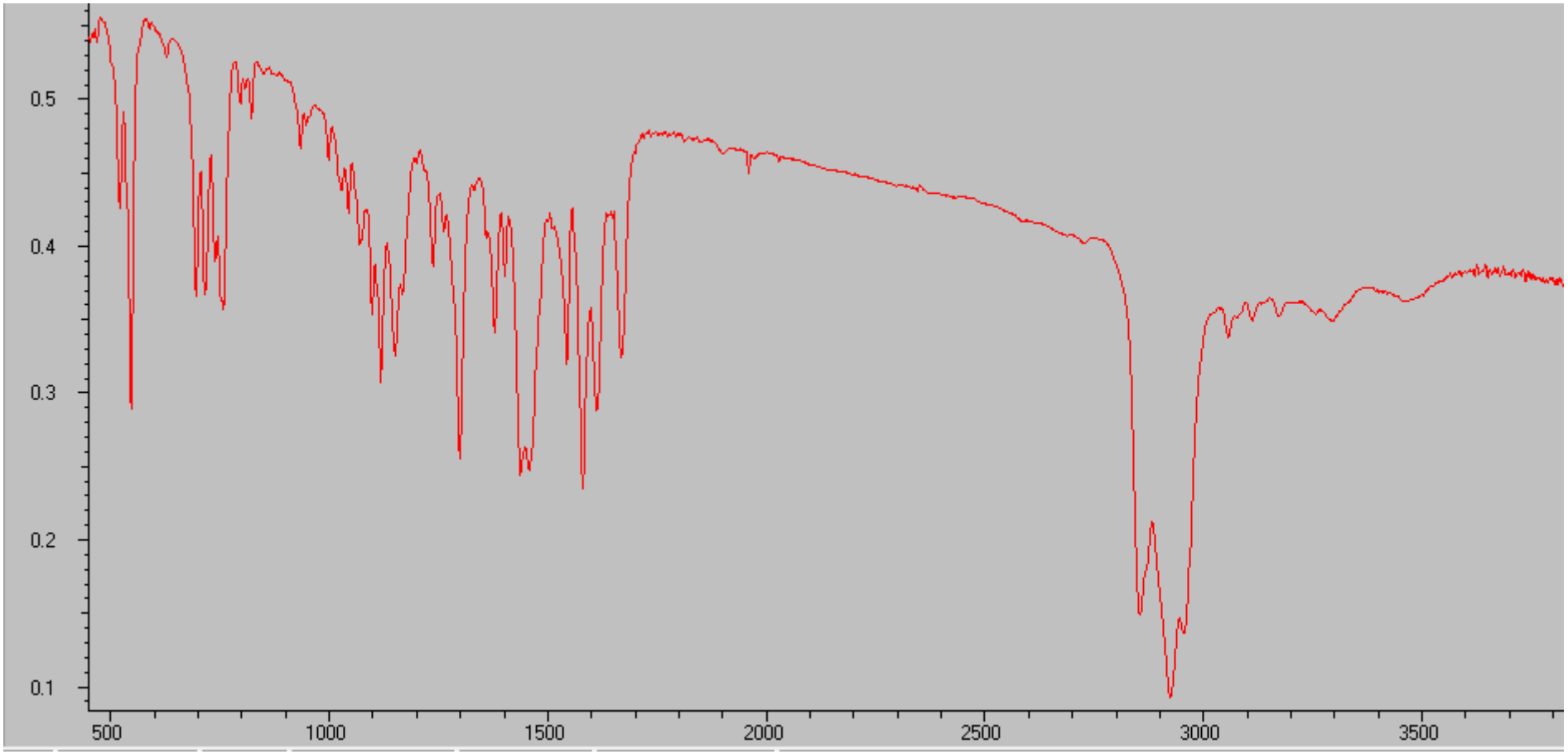


Figure 4S. IR spectrum of 2-[Ph_2P=O]C_6H_4NHC(*t*Bu)=N(2,6-*i*$Pr_2C_6H_3$) (**1**).

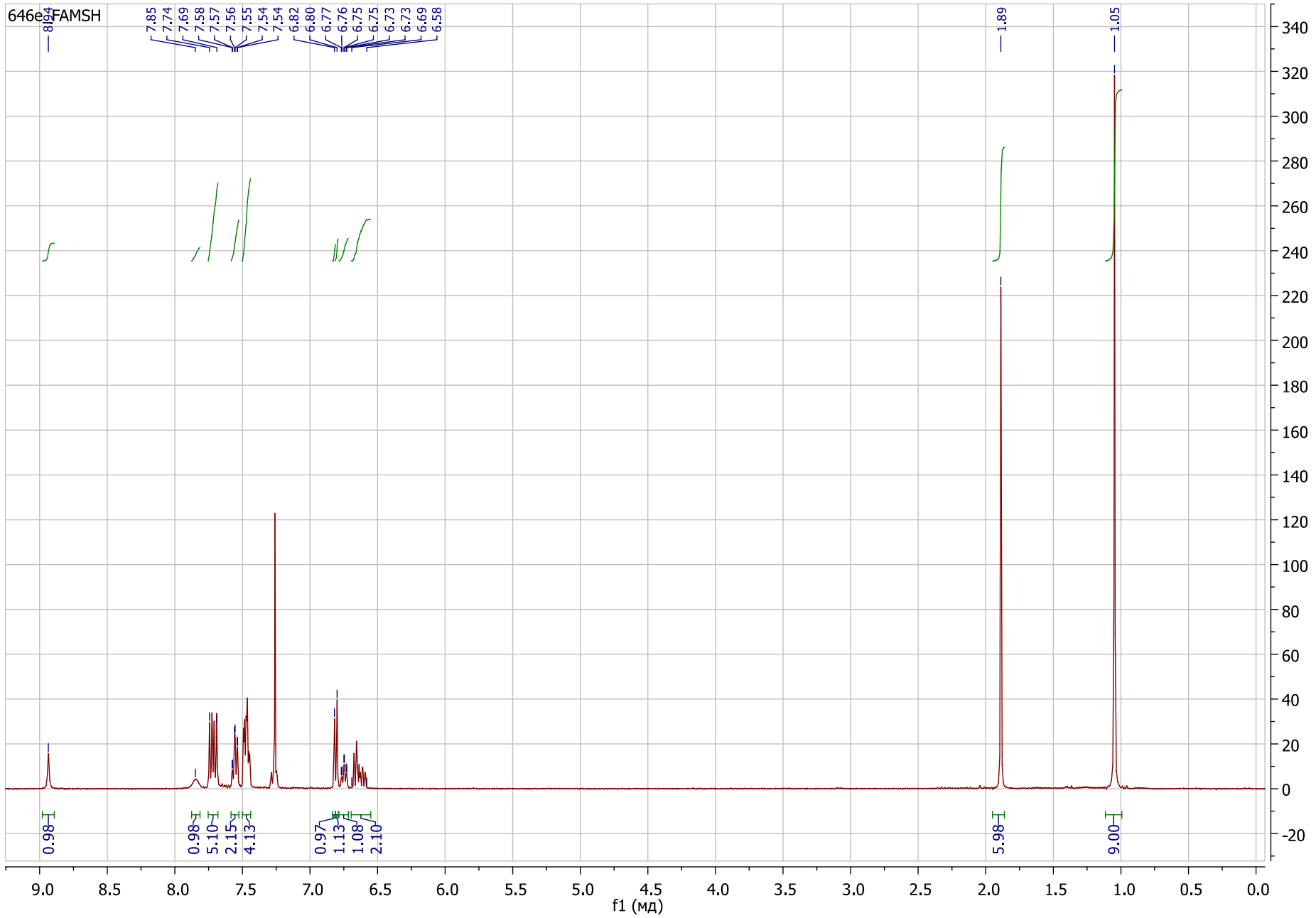


Figure 5S. ^{1}H NMR spectrum of 2-($Ph_2P{=}S$)$C_6H_4NHC(t\text{Bu})=N(2,6\text{-}Me_2C_6H_3)$ (**2**).

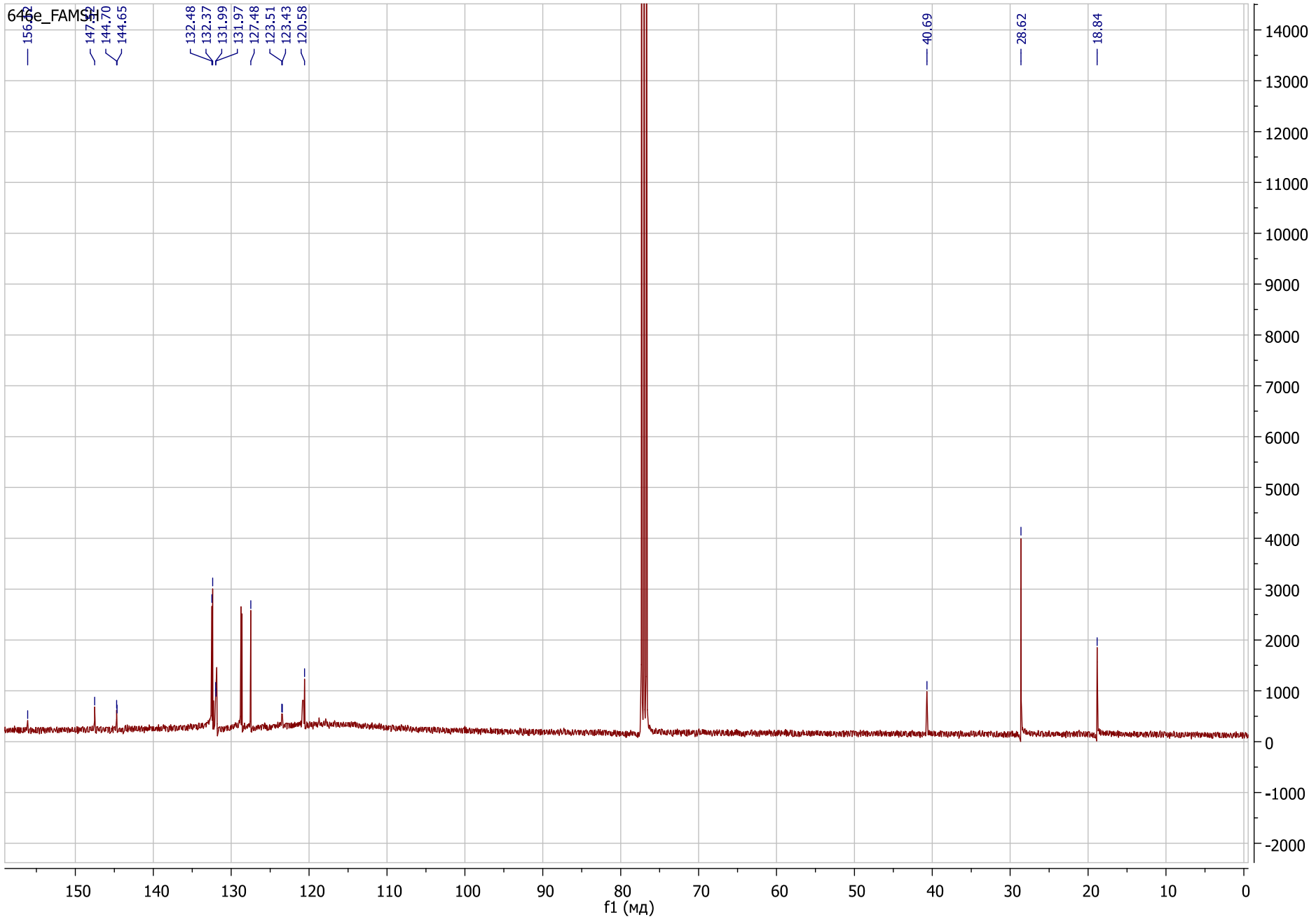


Figure 6S. ^{13}C NMR spectrum of 2-(Ph_2P=S)C_6H_4NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$) (**2**).

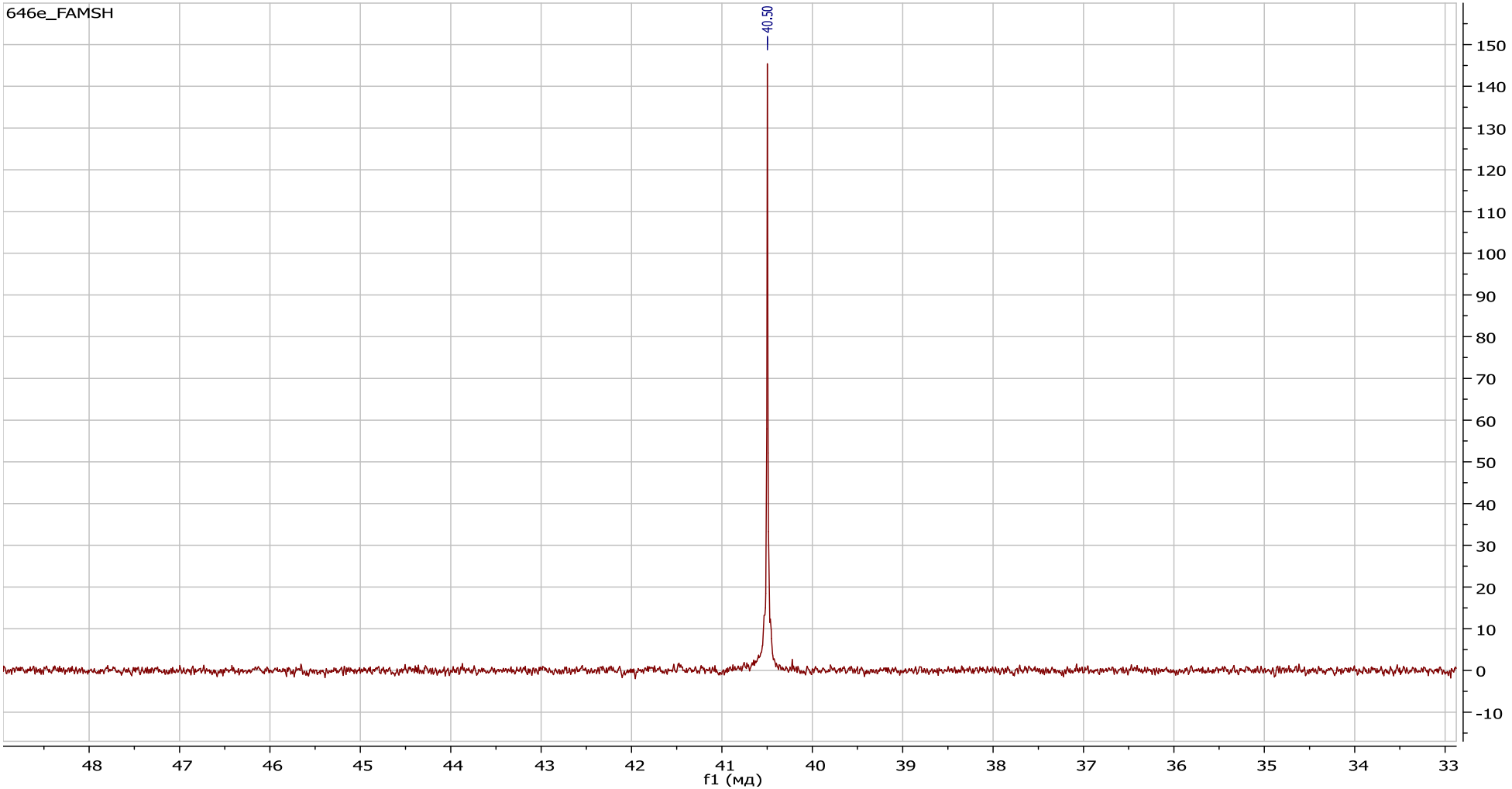


Figure 7S. ^{31}P NMR spectrum of 2-(Ph_2P=S)C_6H_4NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$) (**2**).

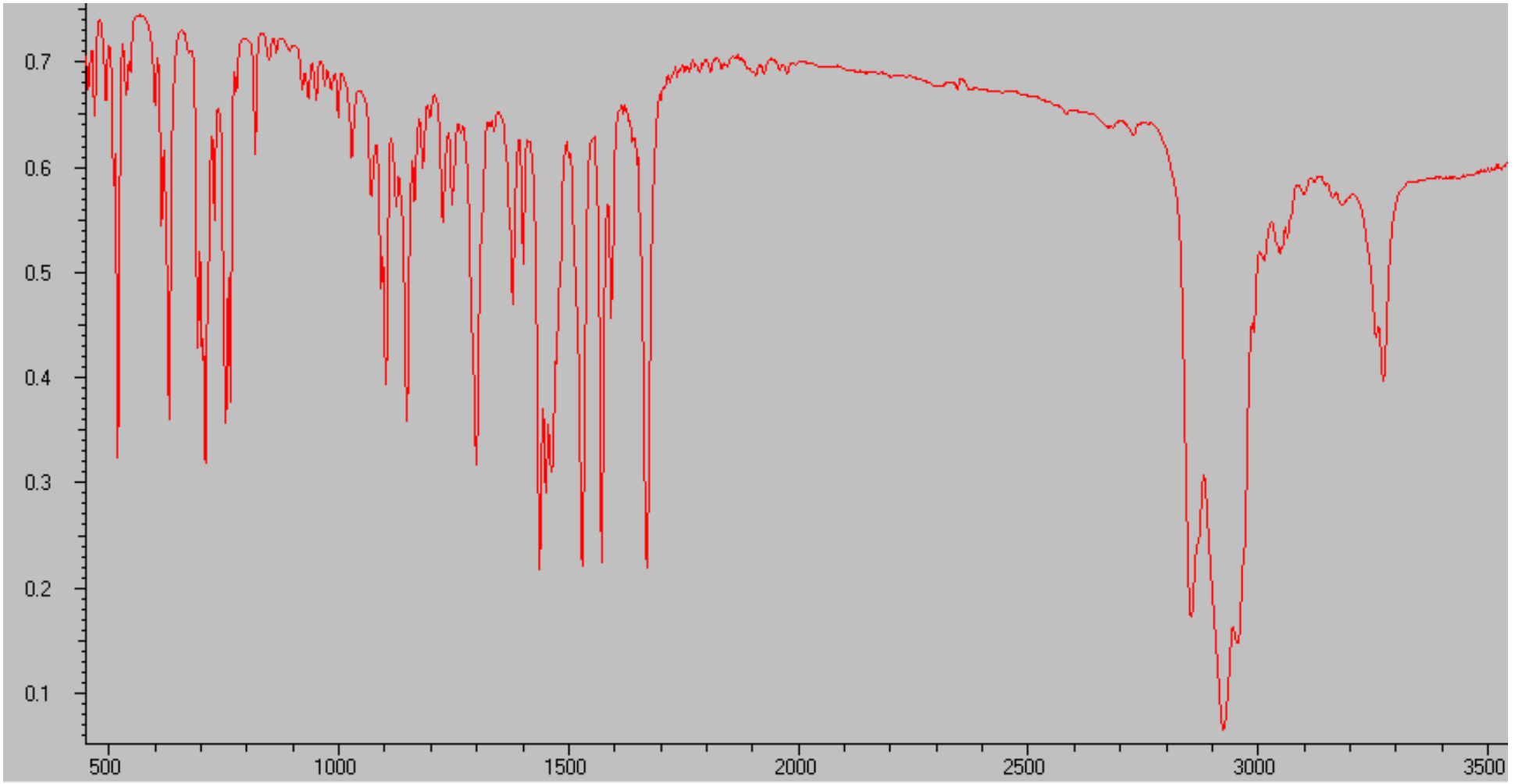


Figure 8S. IR spectrum of 2-(Ph_2P=S)C_6H_4NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$) (**2**).

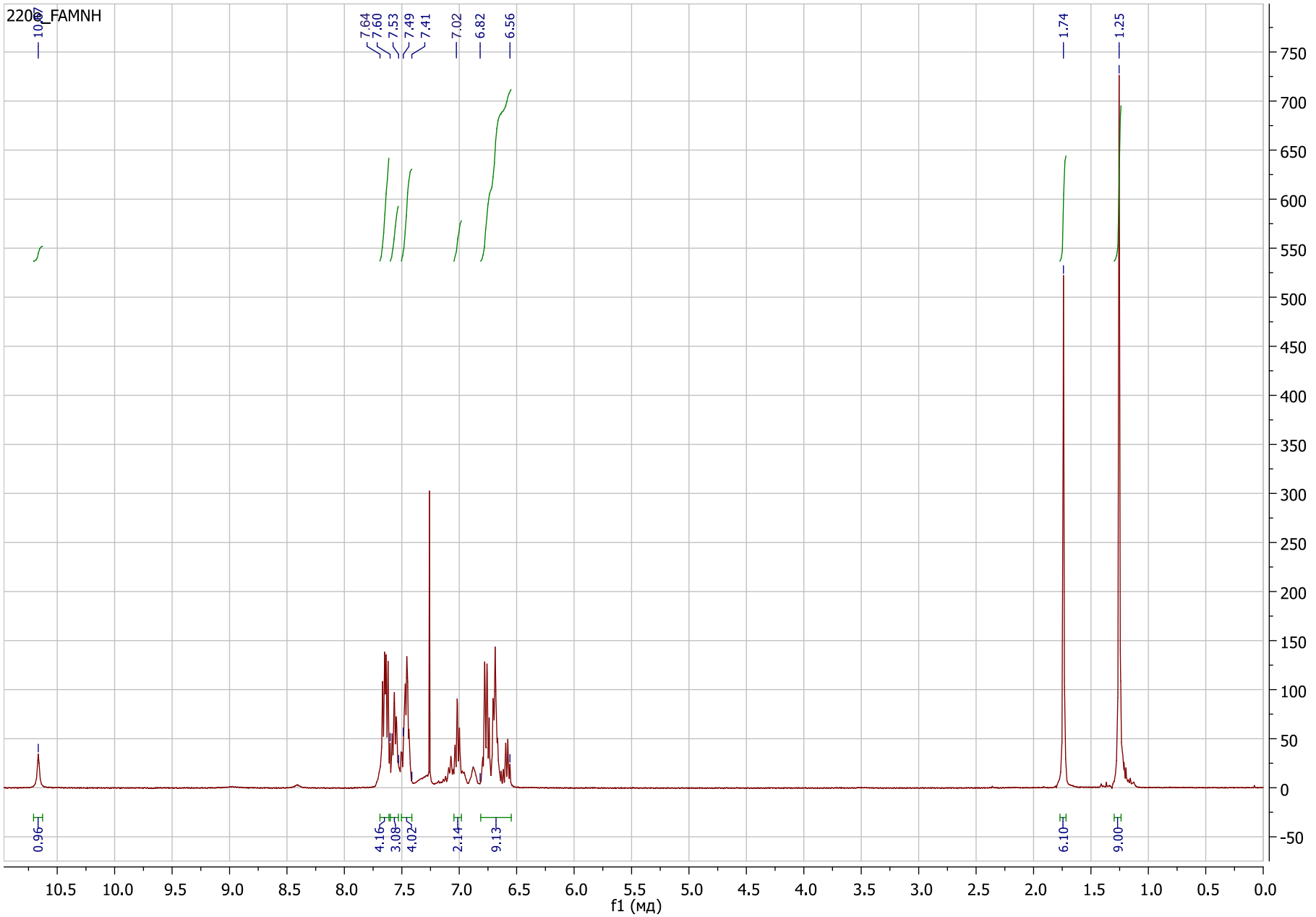


Figure 9S. ^{1}H NMR spectrum of 2-[Ph_2P=N(Ph)]C_6H_4NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$) (**3**).

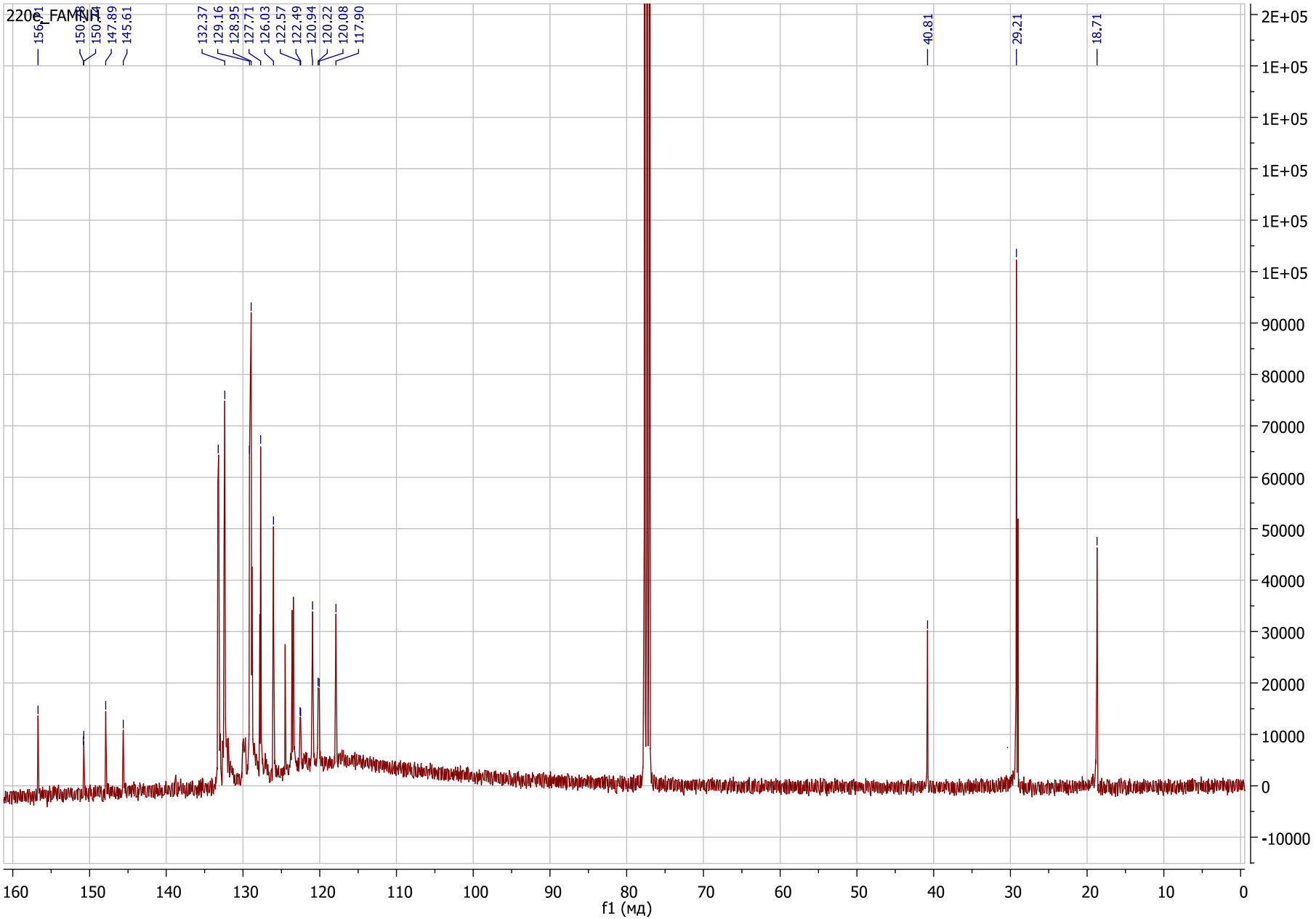


Figure 10S. ^{13}C NMR spectrum of 2-[Ph_2P=N(Ph)]C_6H_4NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$) (**3**).

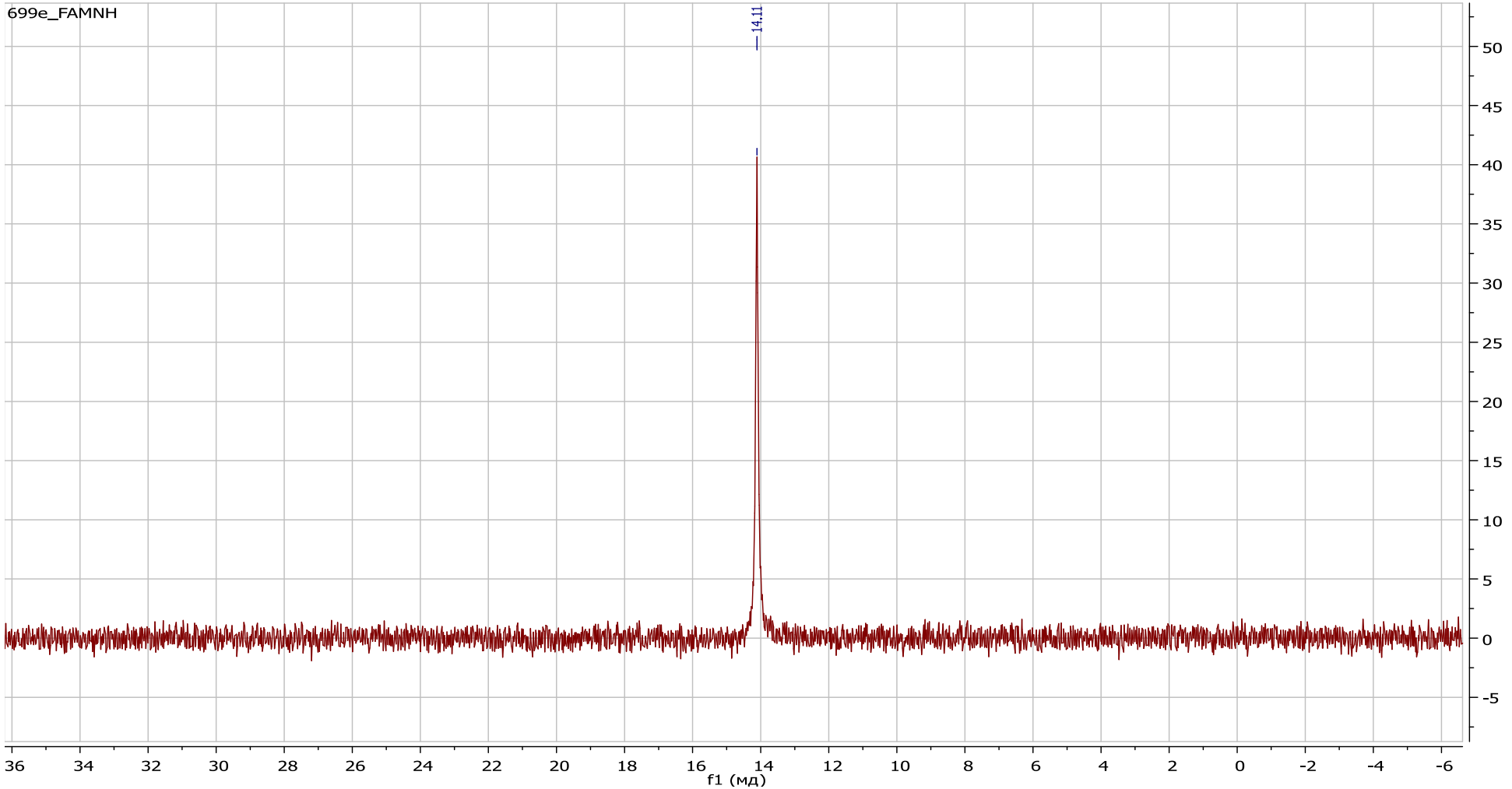


Figure 11S. ^{31}P NMR spectrum of 2-[Ph_2P=N(Ph)]C_6H_4NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$) (**3**).

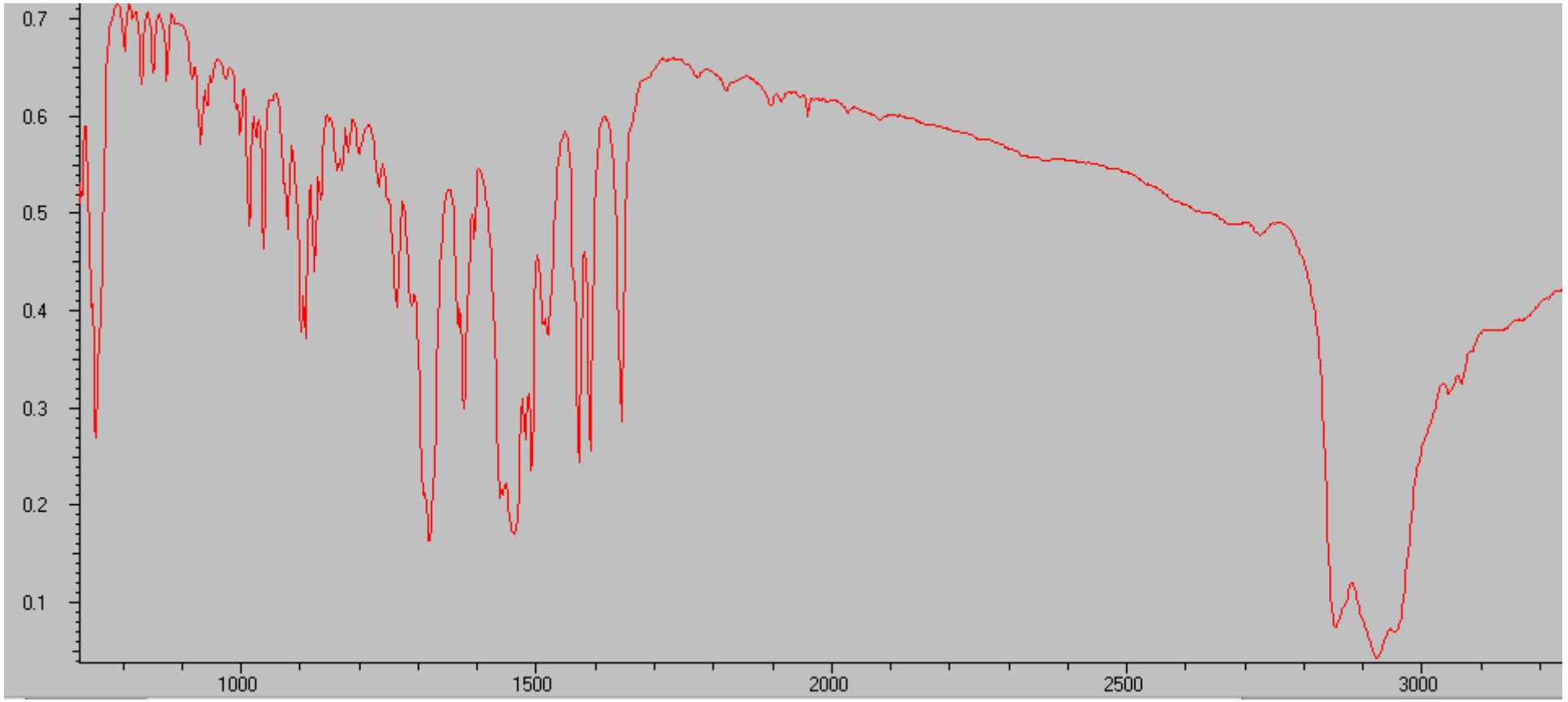
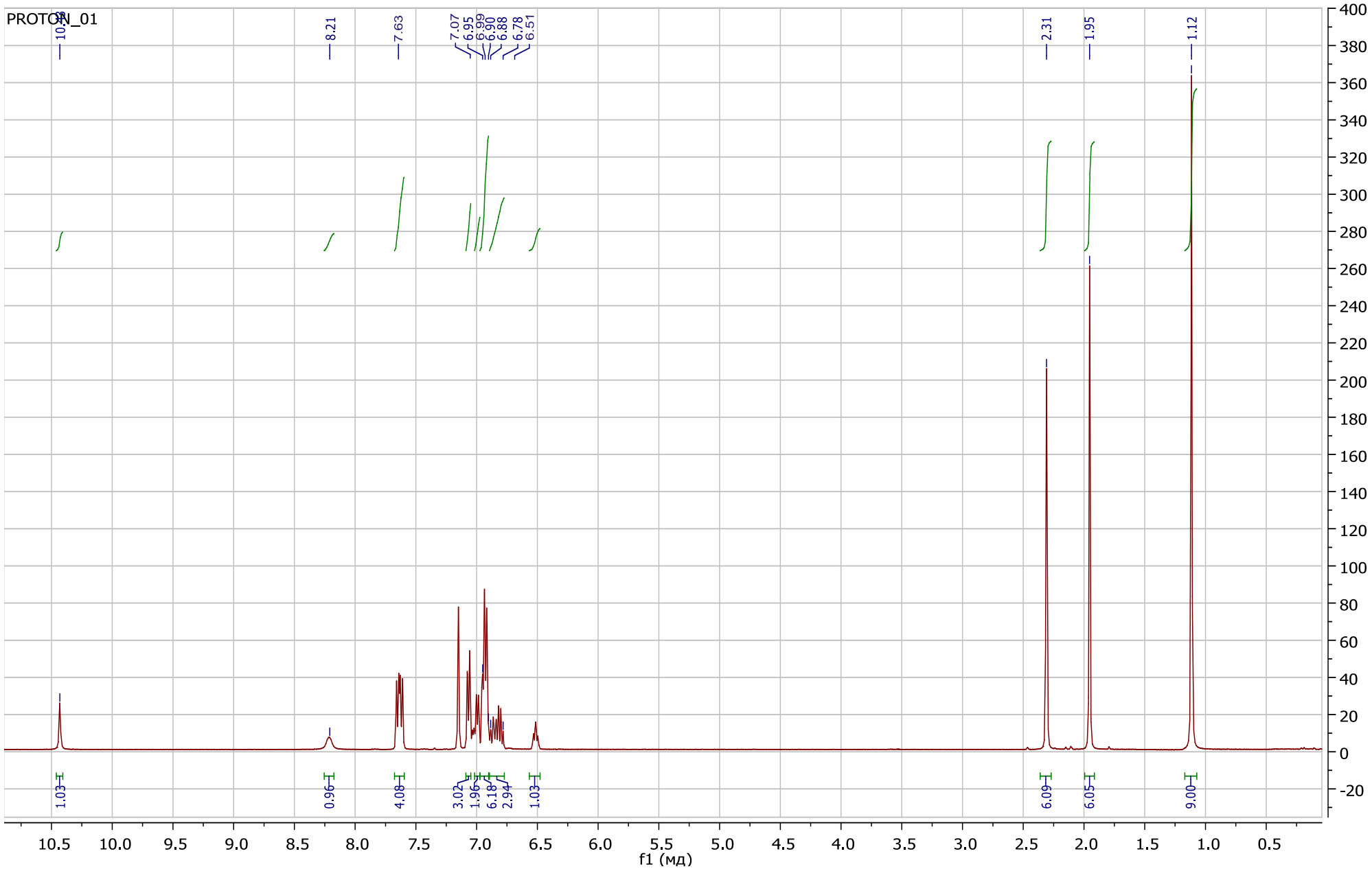


Figure 12S. IR spectrum of 2-[Ph_2P=N(Ph)]C_6H_4NHC(*t*Bu)=N(2,6-$Me_2C_6H_3$) (**3**).



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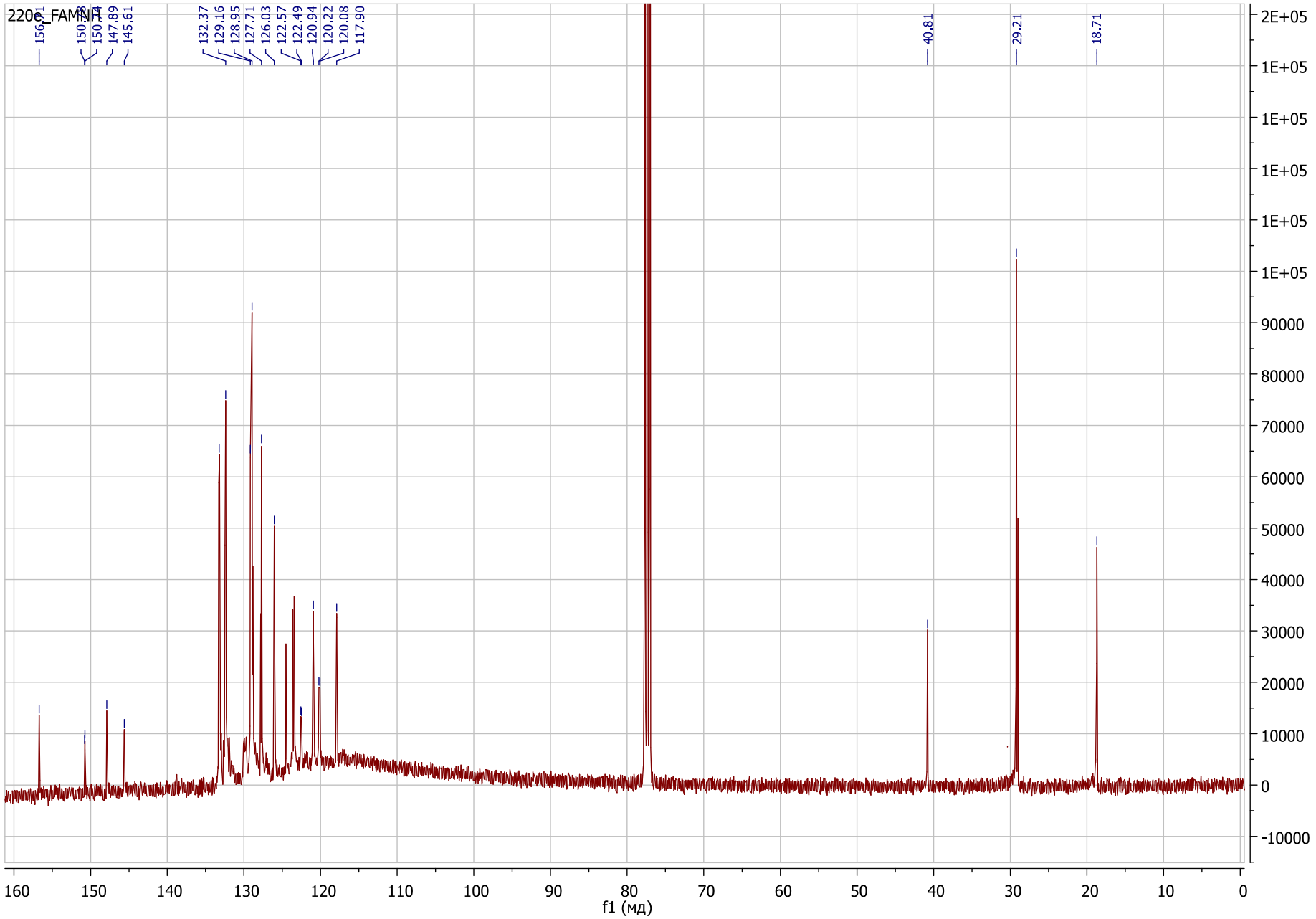

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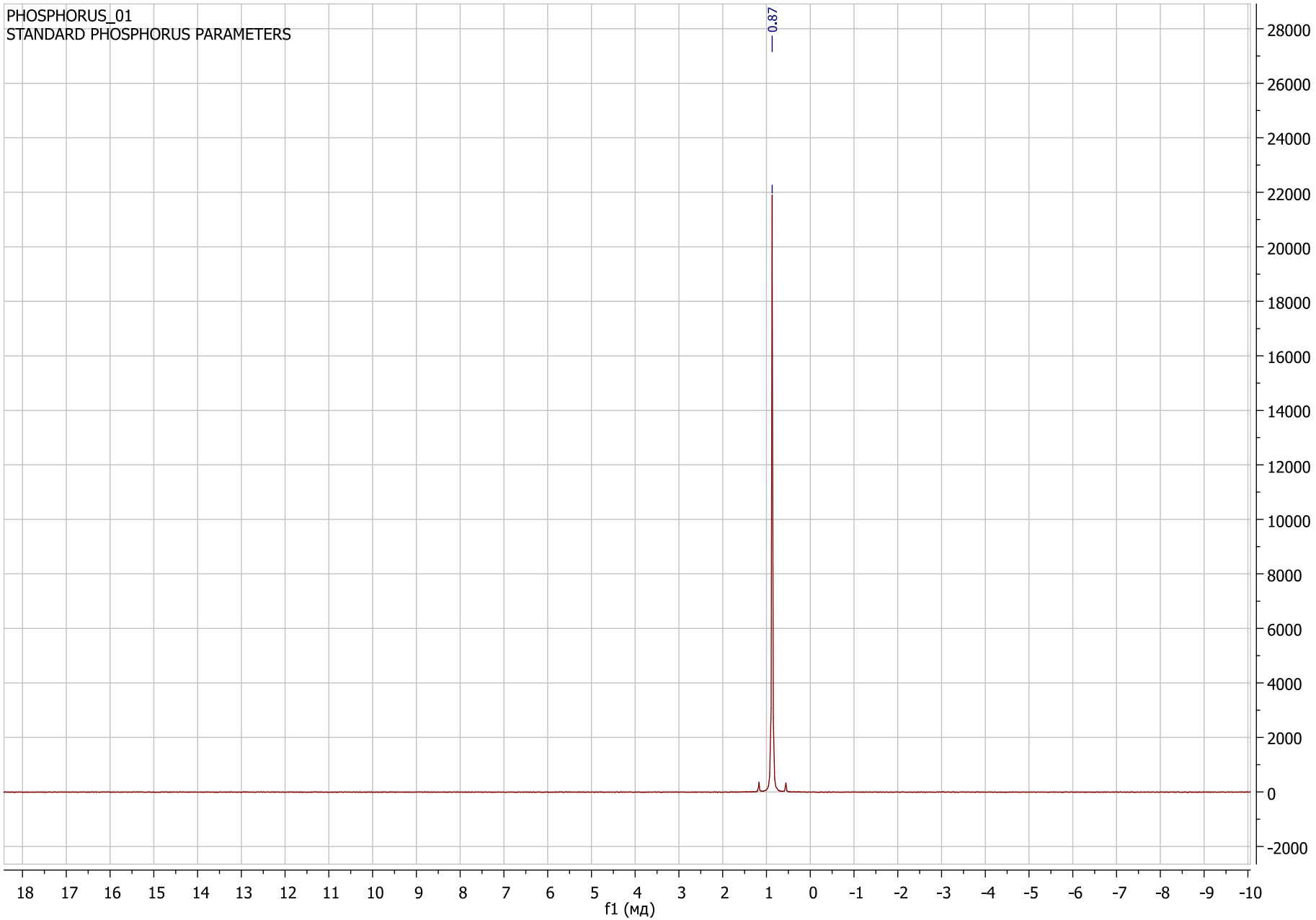

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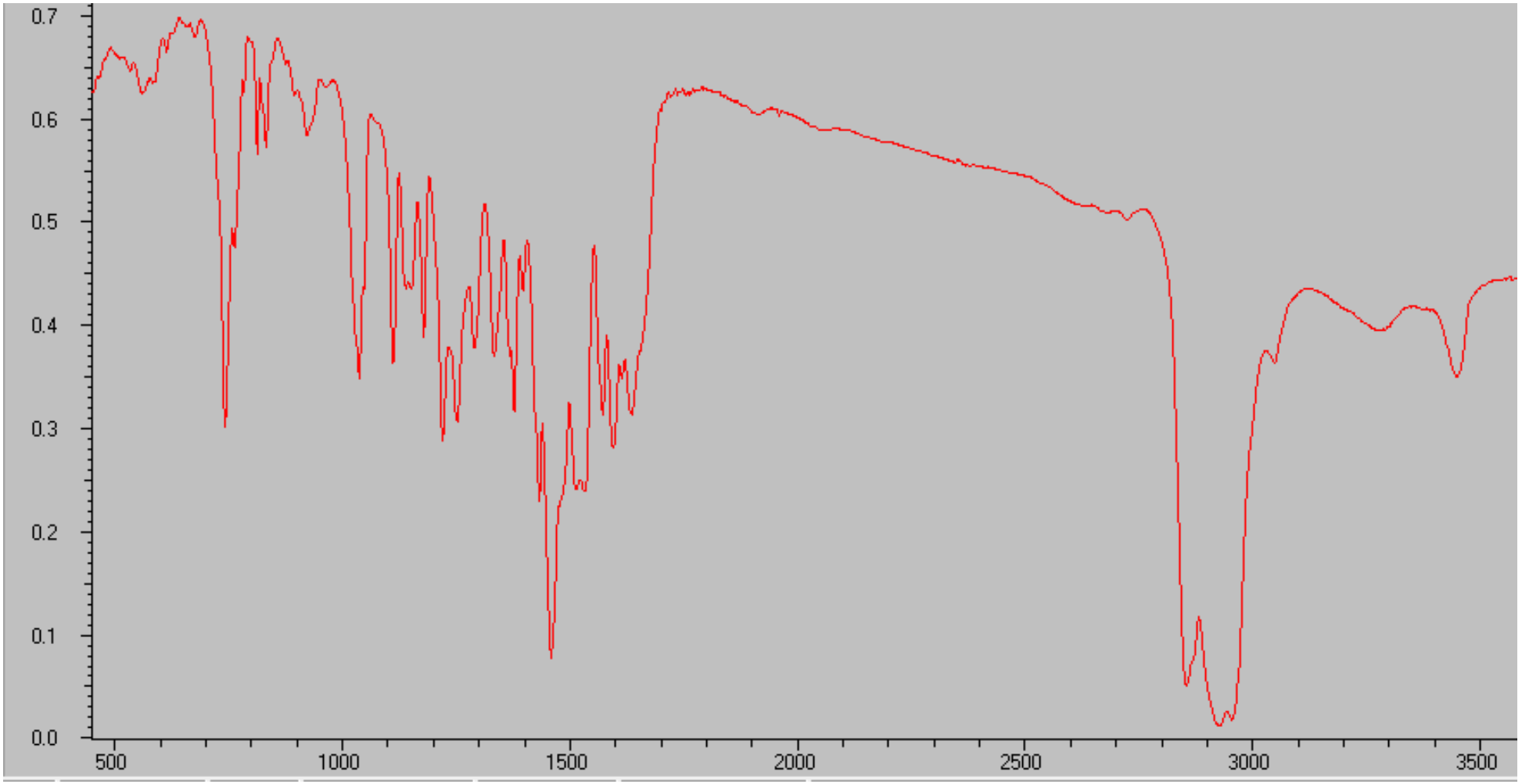

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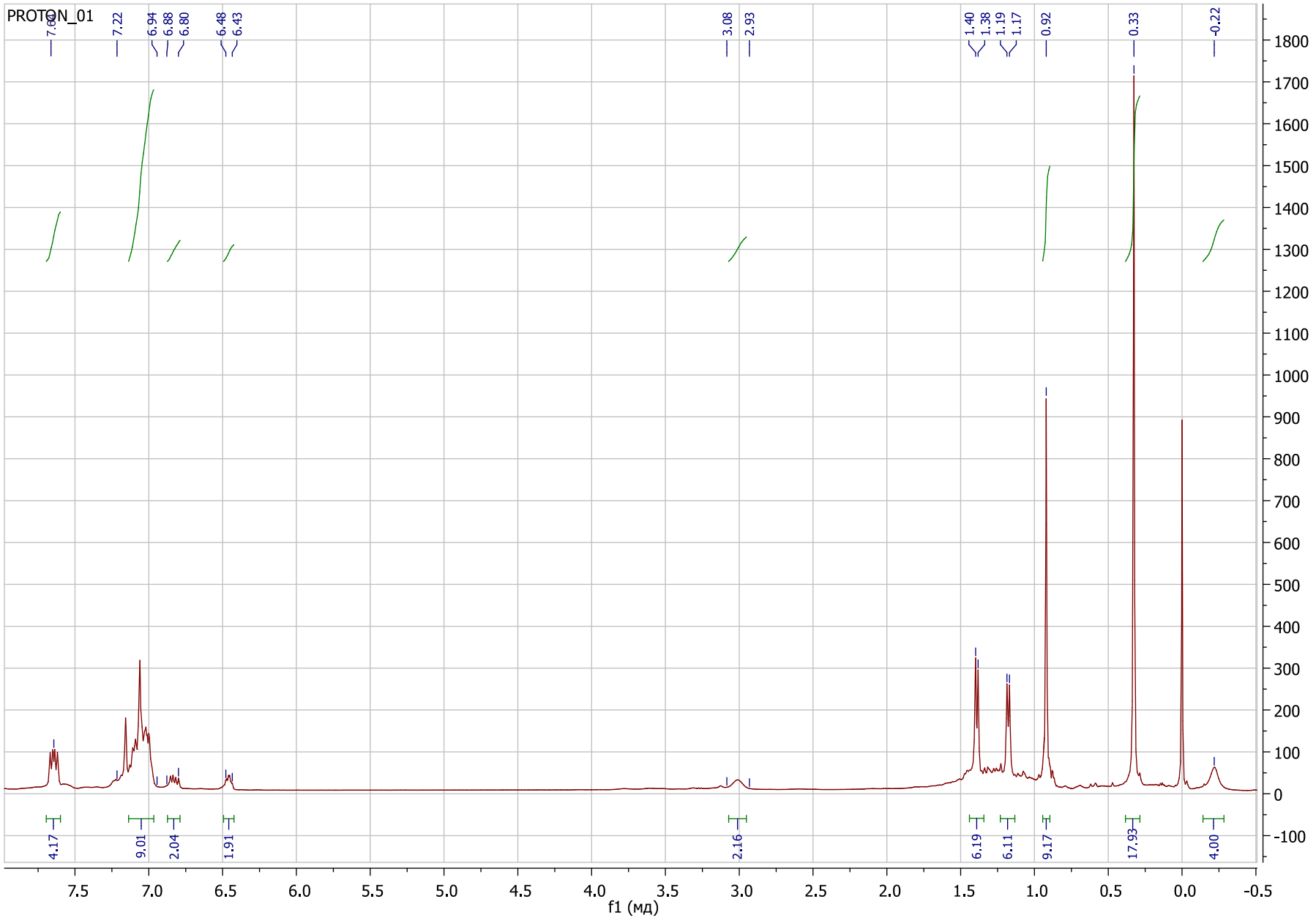

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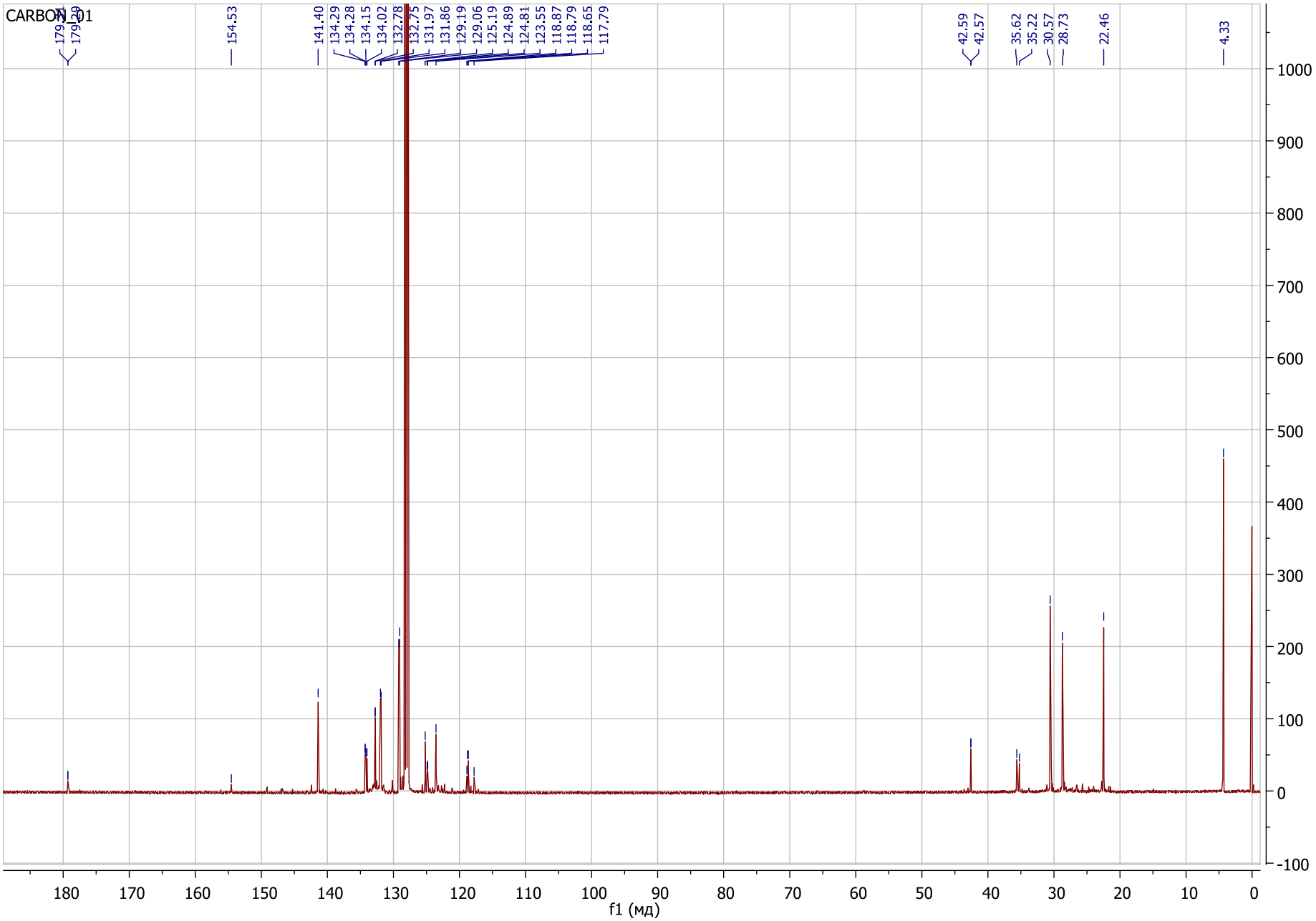

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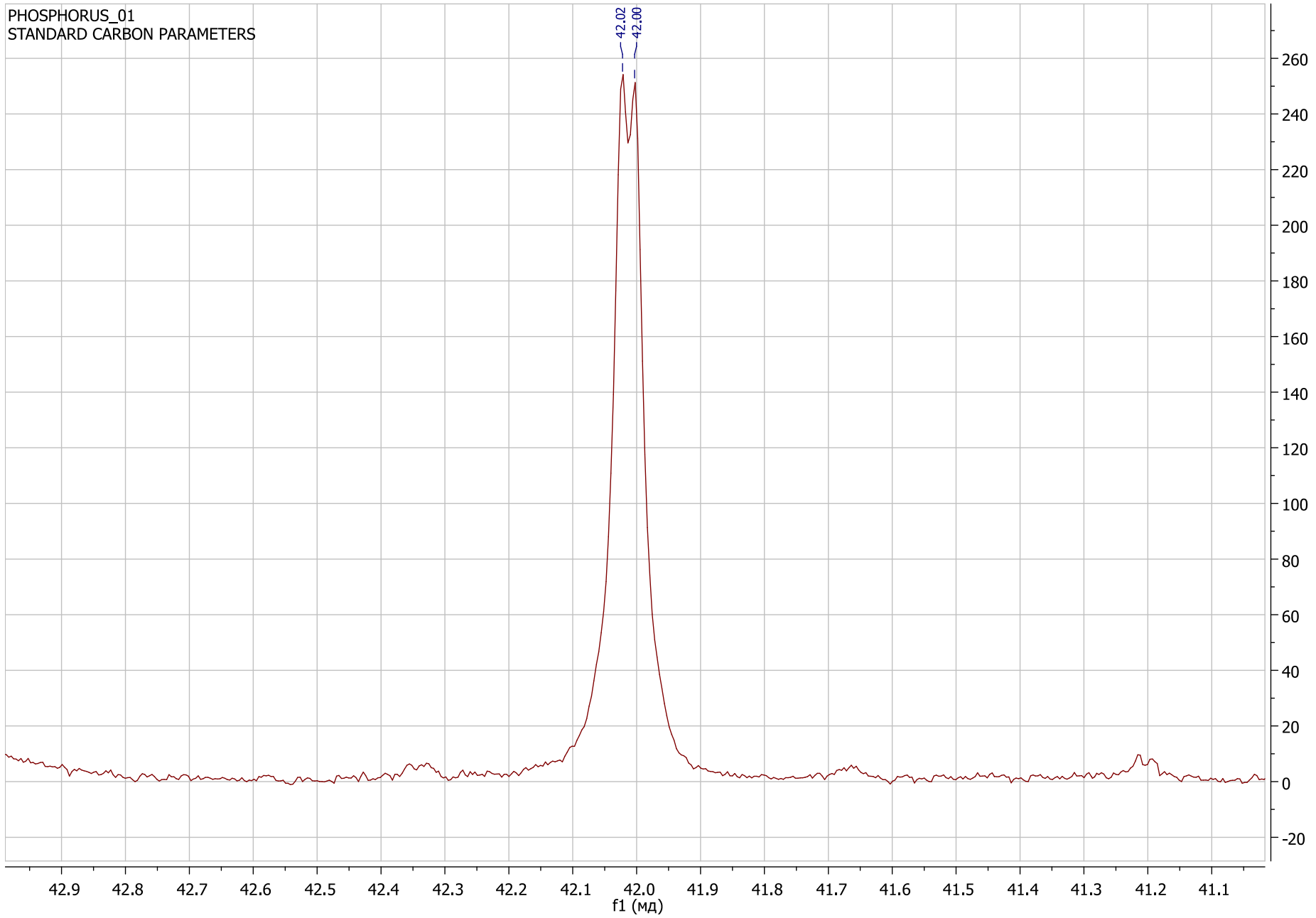

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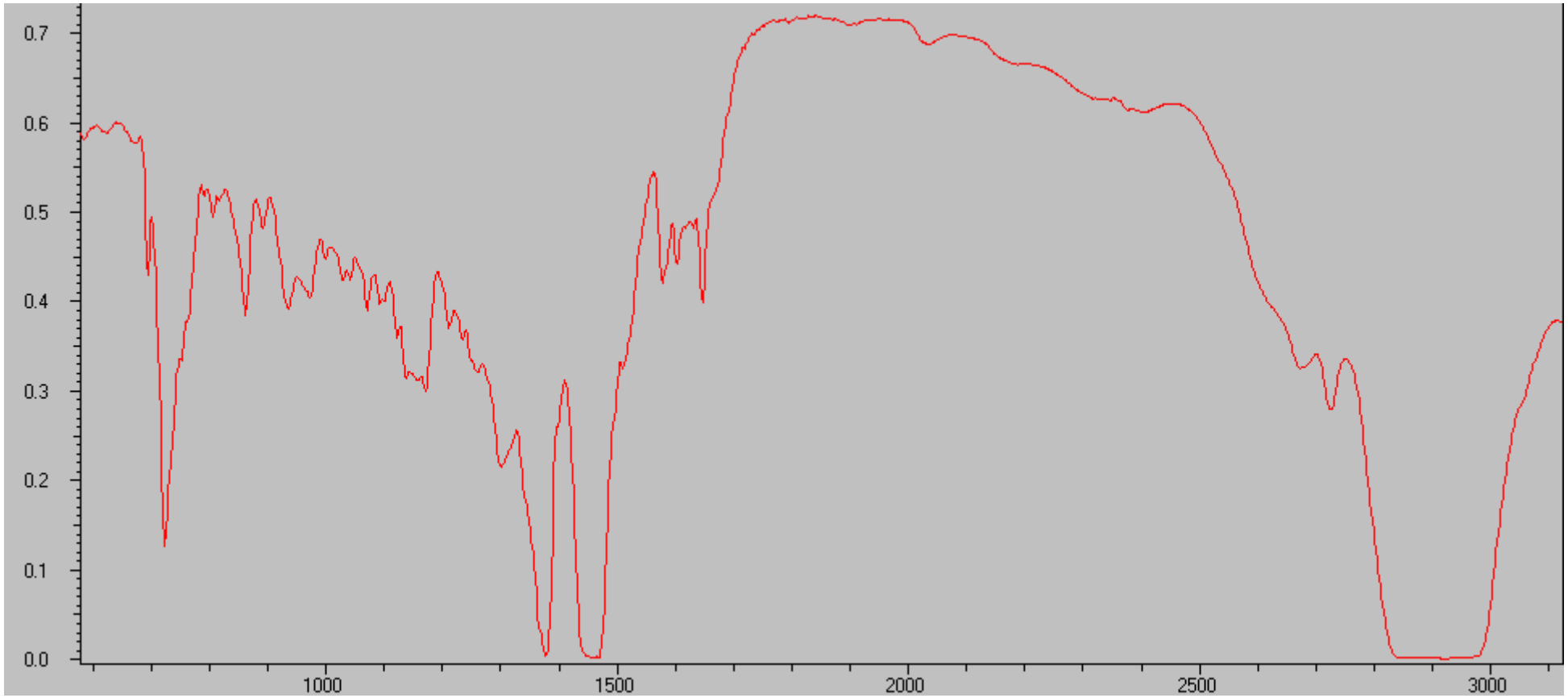

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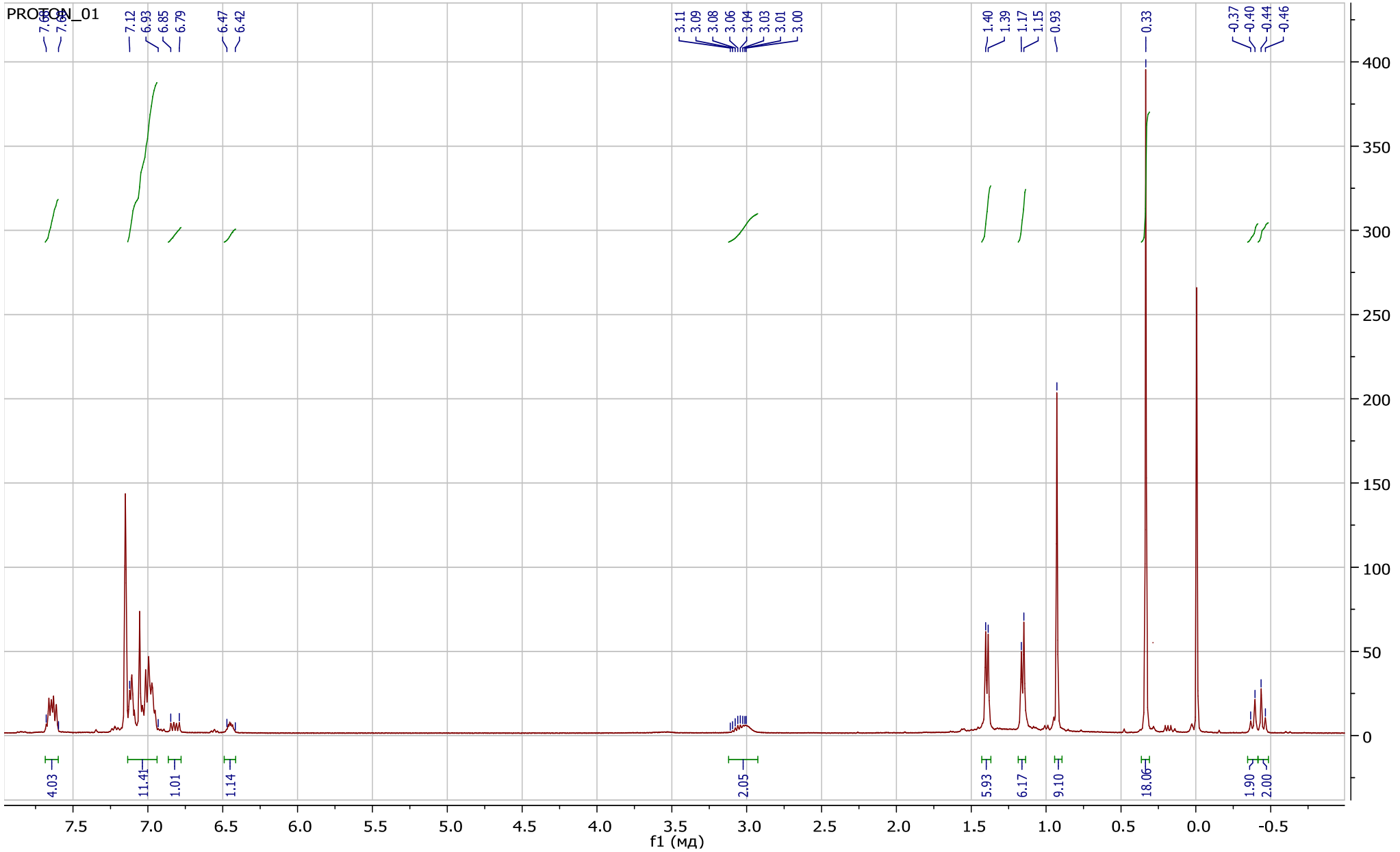

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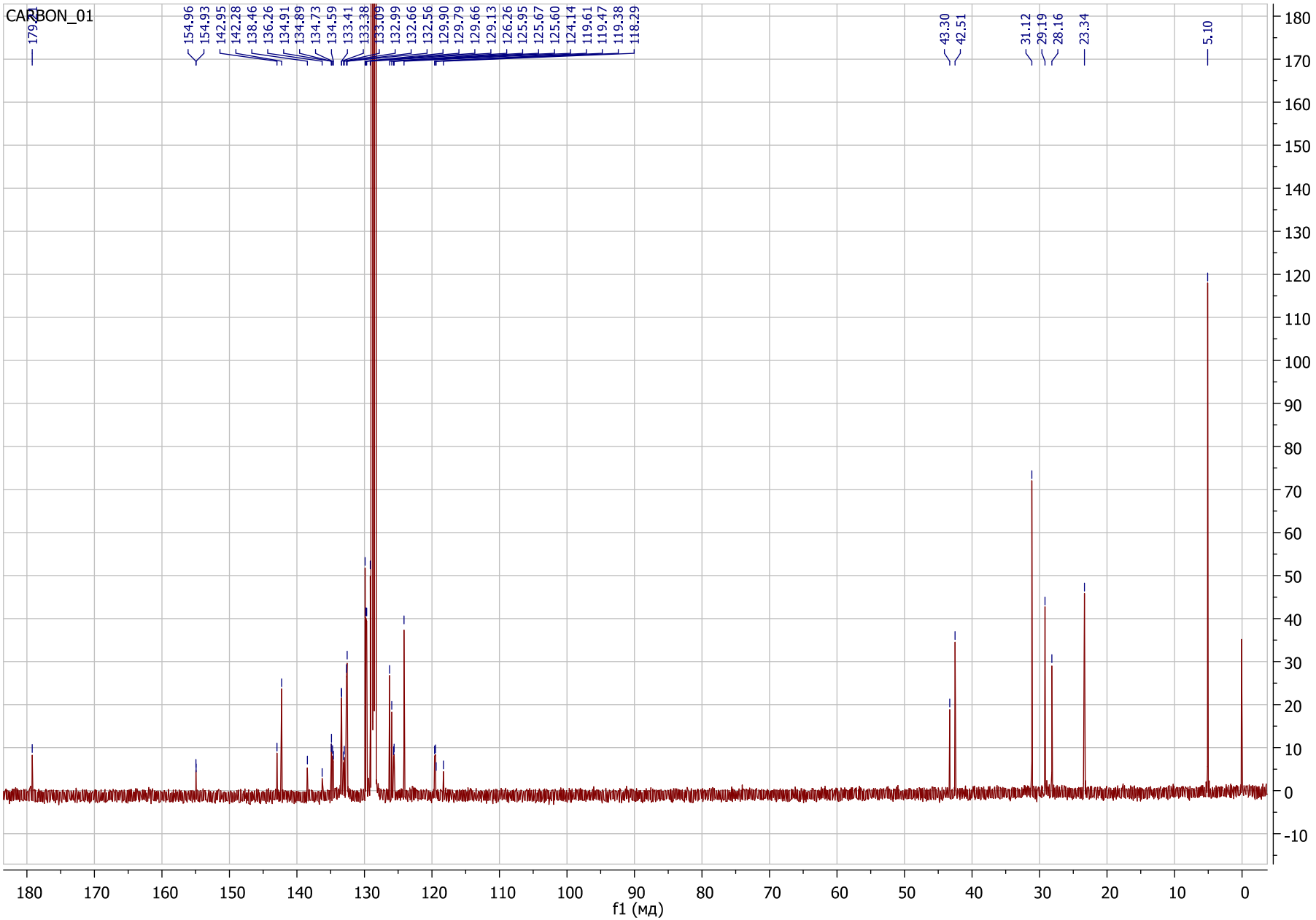


Figure 23S. ^{13}C NMR spectrum of {2-[Ph_2P=O]C_6H_4NC(*t*Bu)N(2,6-*i*$Pr_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**7**).

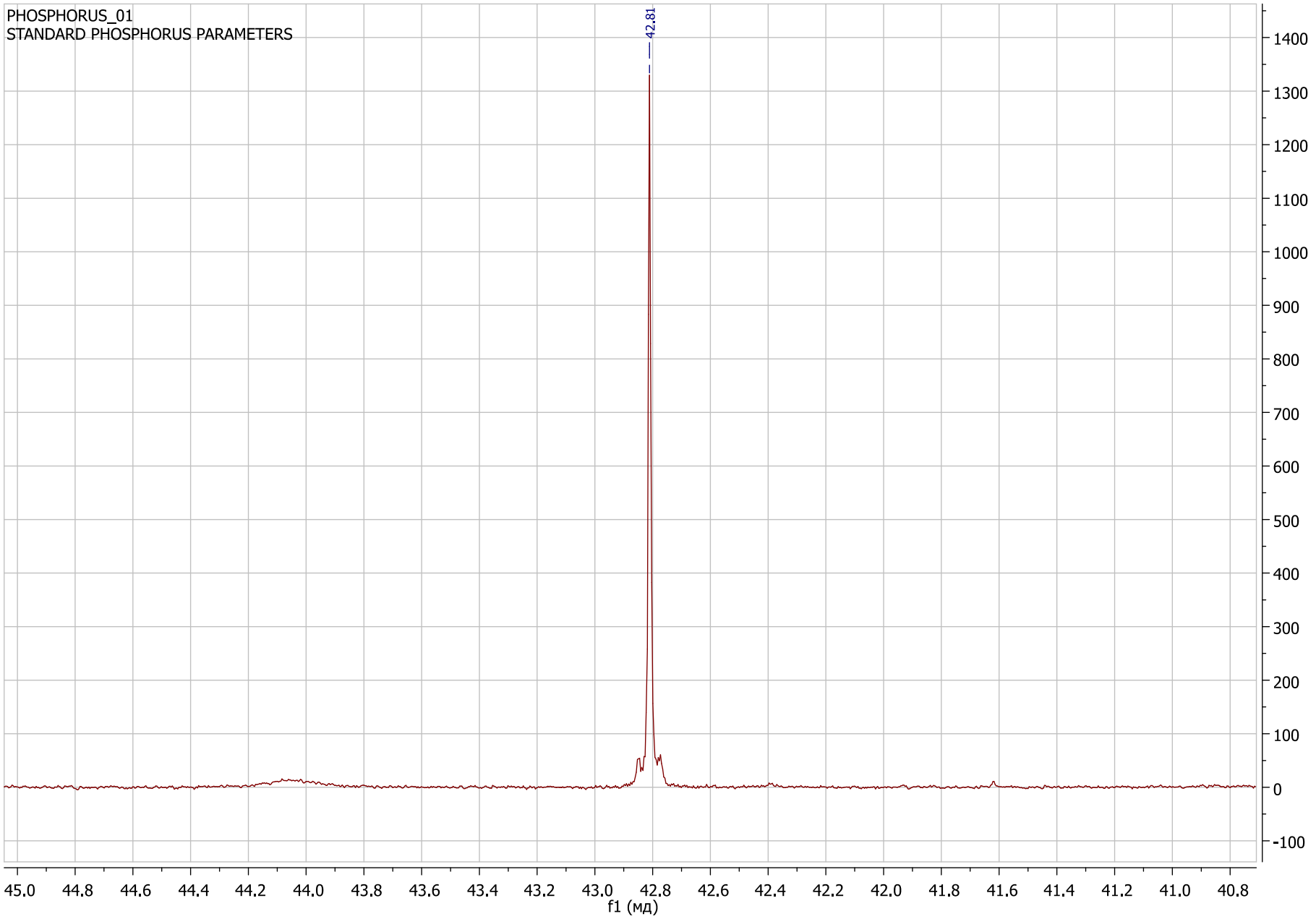


Figure 24S. ^{31}P NMR spectrum of {2-[Ph_2P=O]C_6H_4NC(*t*Bu)N(2,6-*i*$Pr_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**7**).

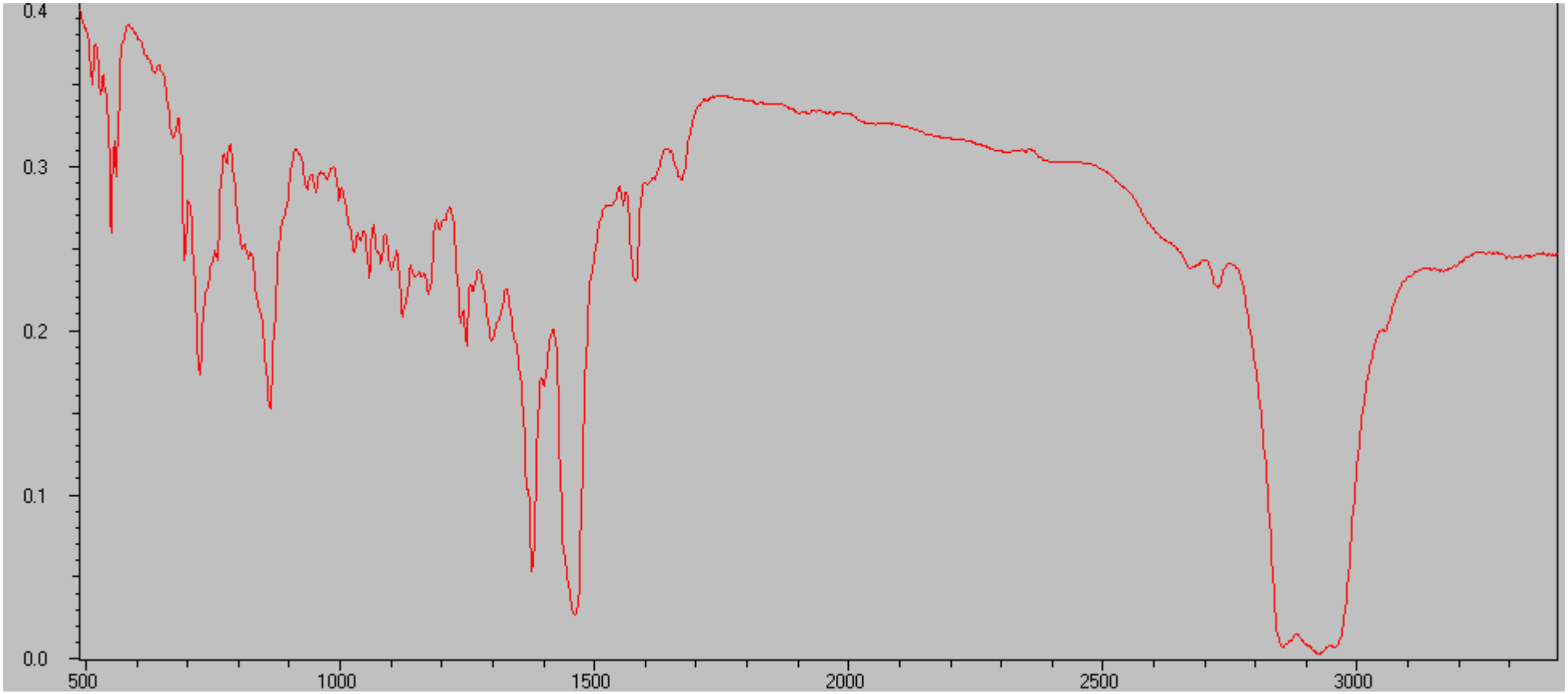


Figure 25S. IR spectrum of {2-[Ph_2P=O]C_6H_4NC(*t*Bu)N(2,6-*i*$Pr_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**7**).

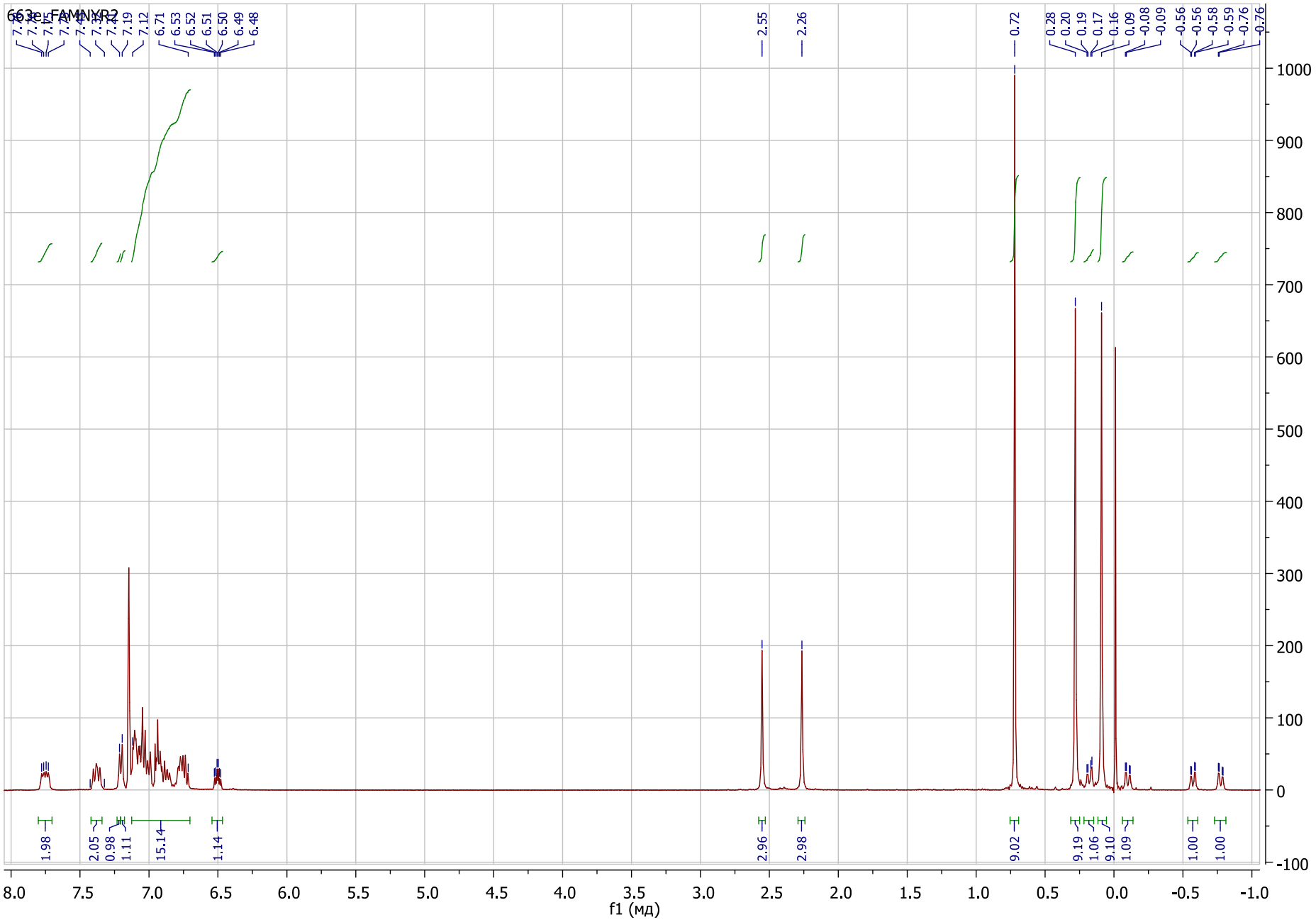


Figure 26S. ^{1}H NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

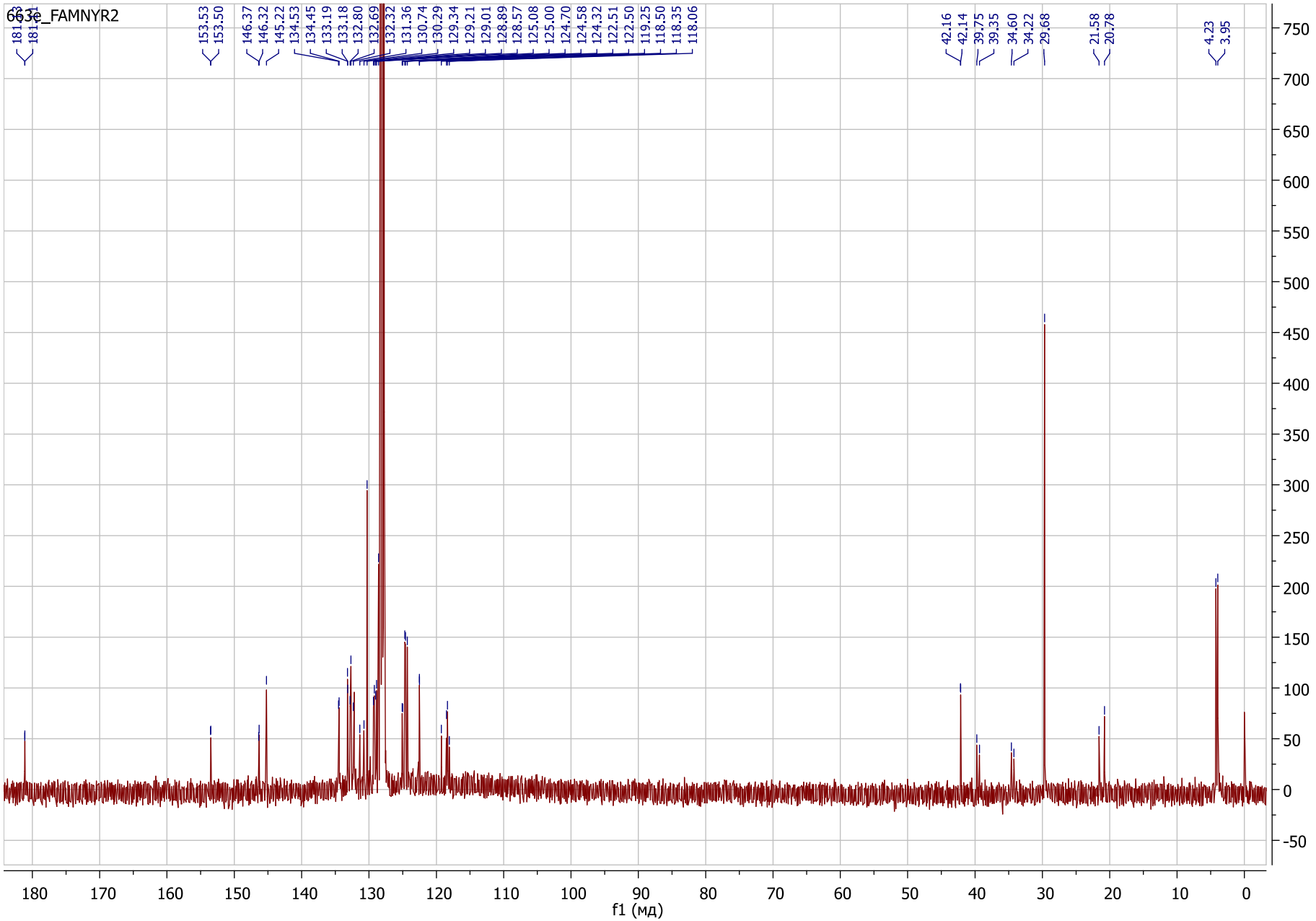


Figure 27S. ^{13}C NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

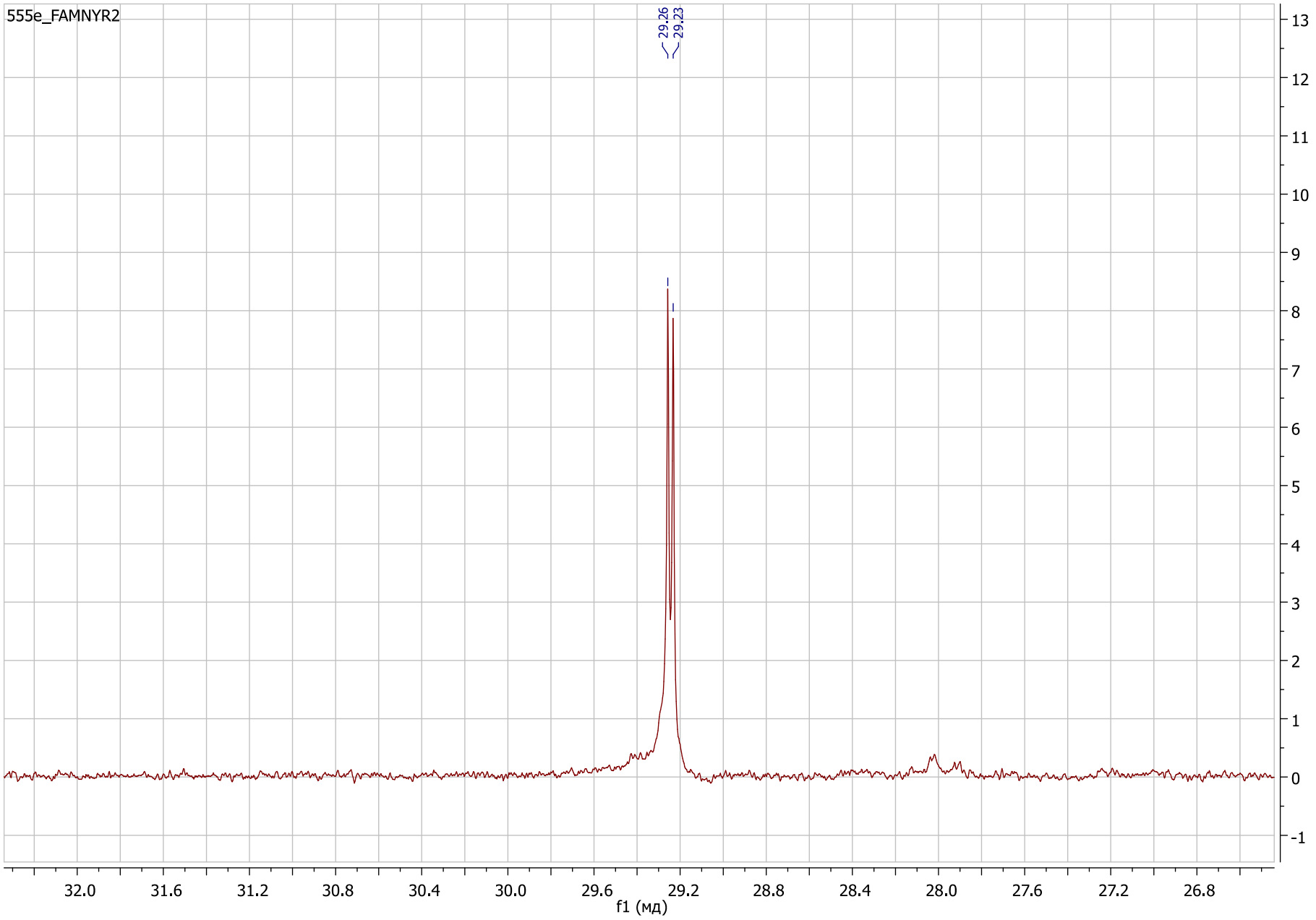


Figure 28S. ^{31}P NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

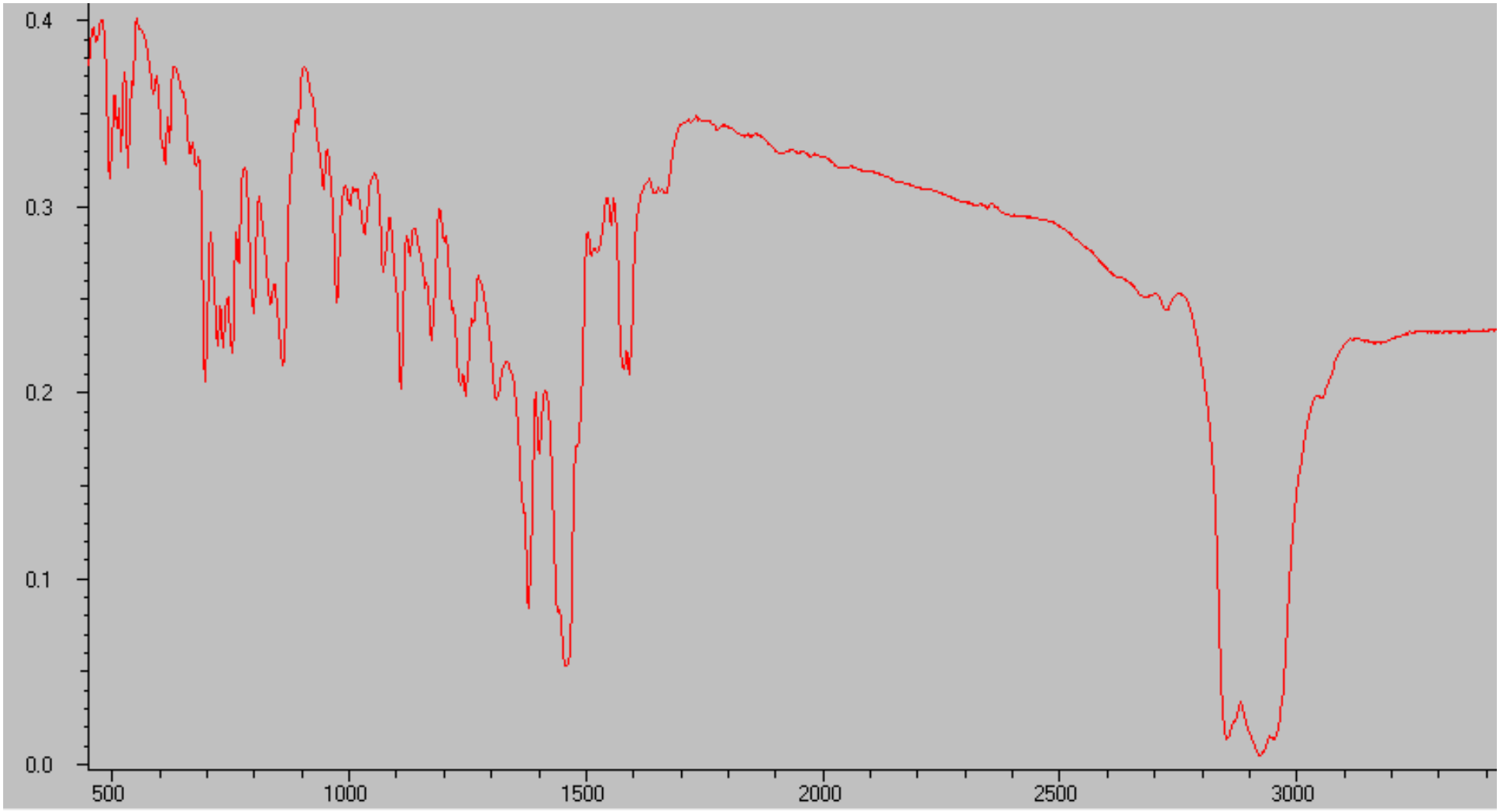


Figure 29S. IR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Y(CH_2SiMe_3)$_2$ (**8**).

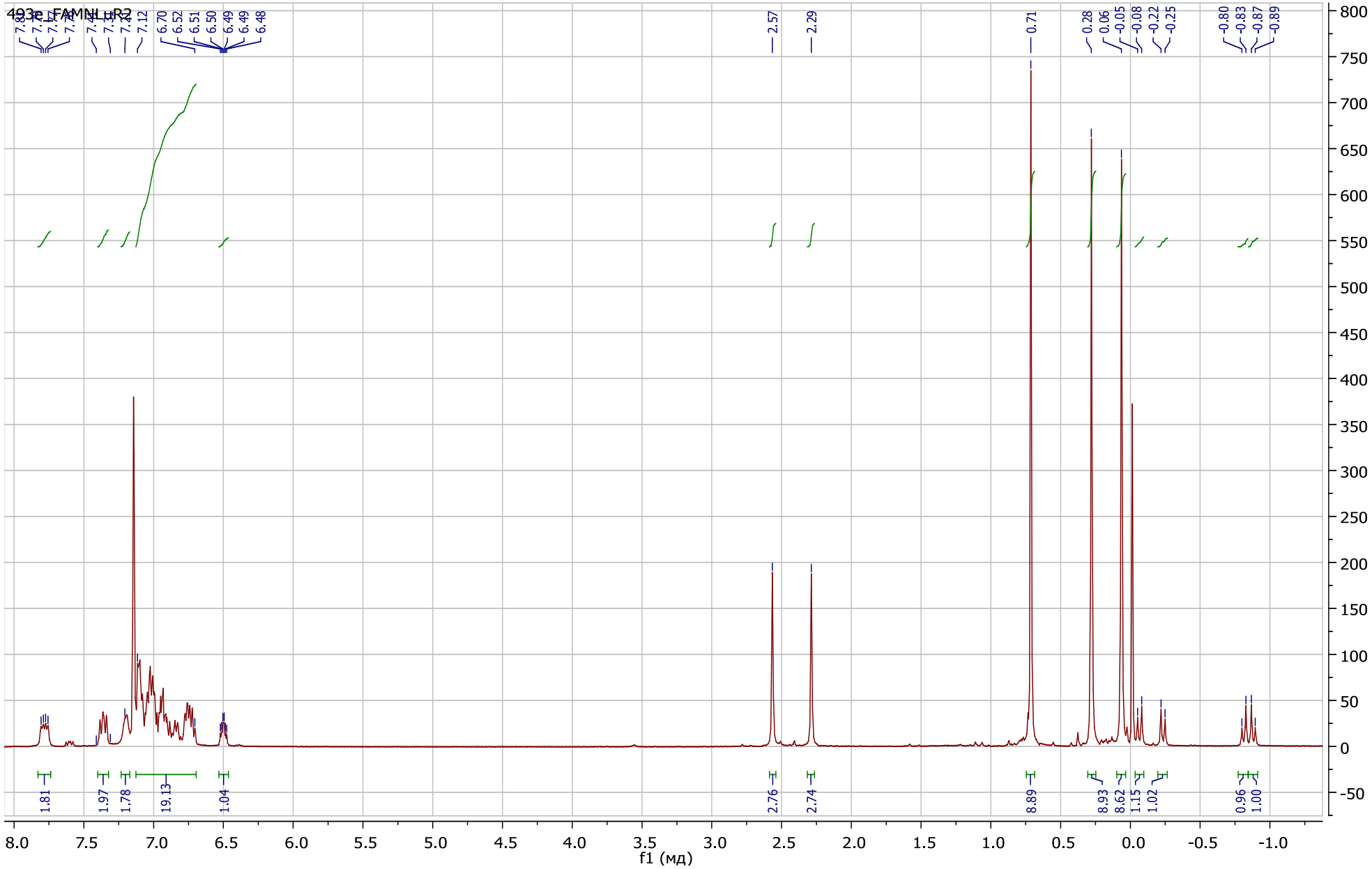


Figure 30S. ^{1}H NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

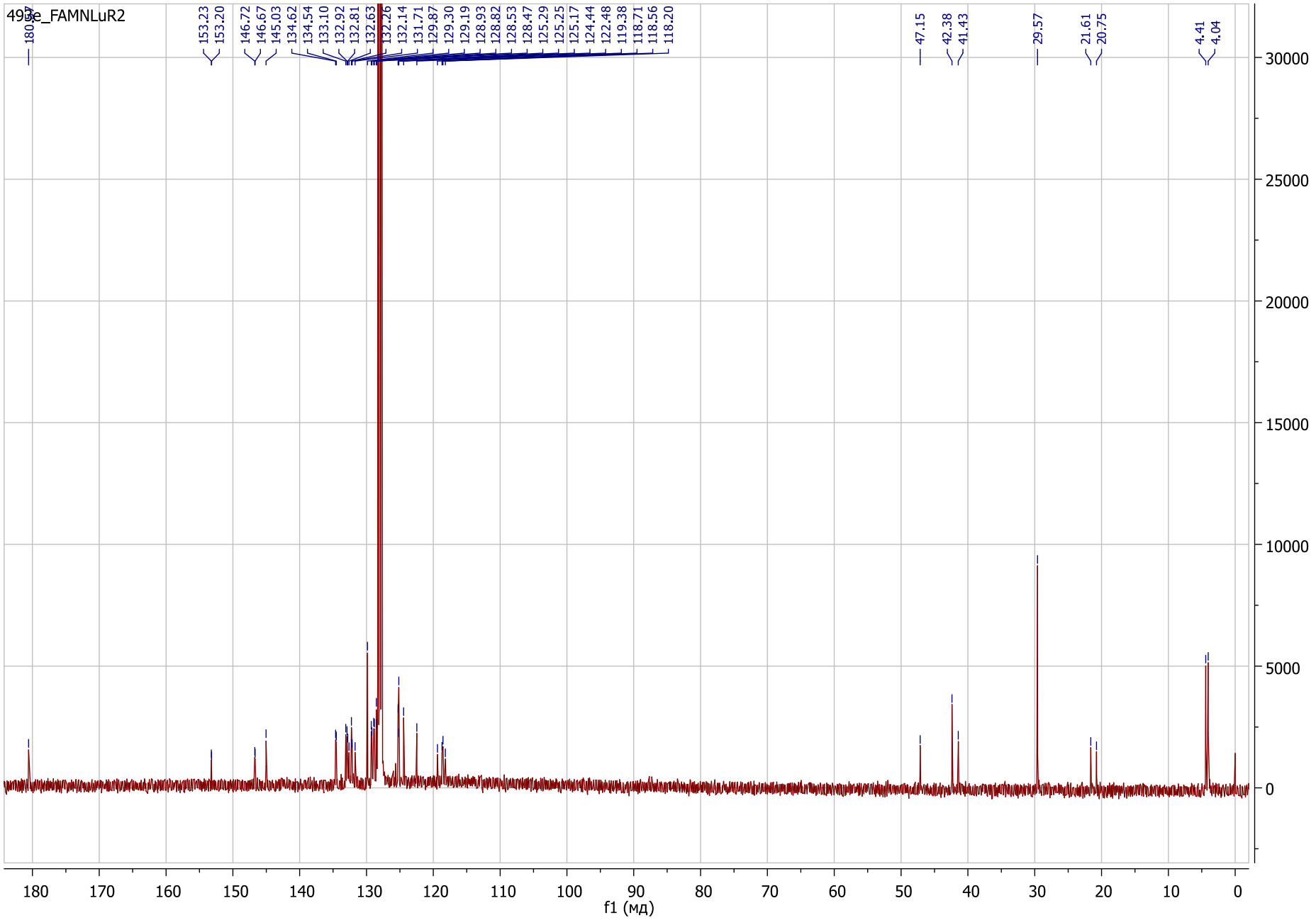


Figure 31S. ^{13}C NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

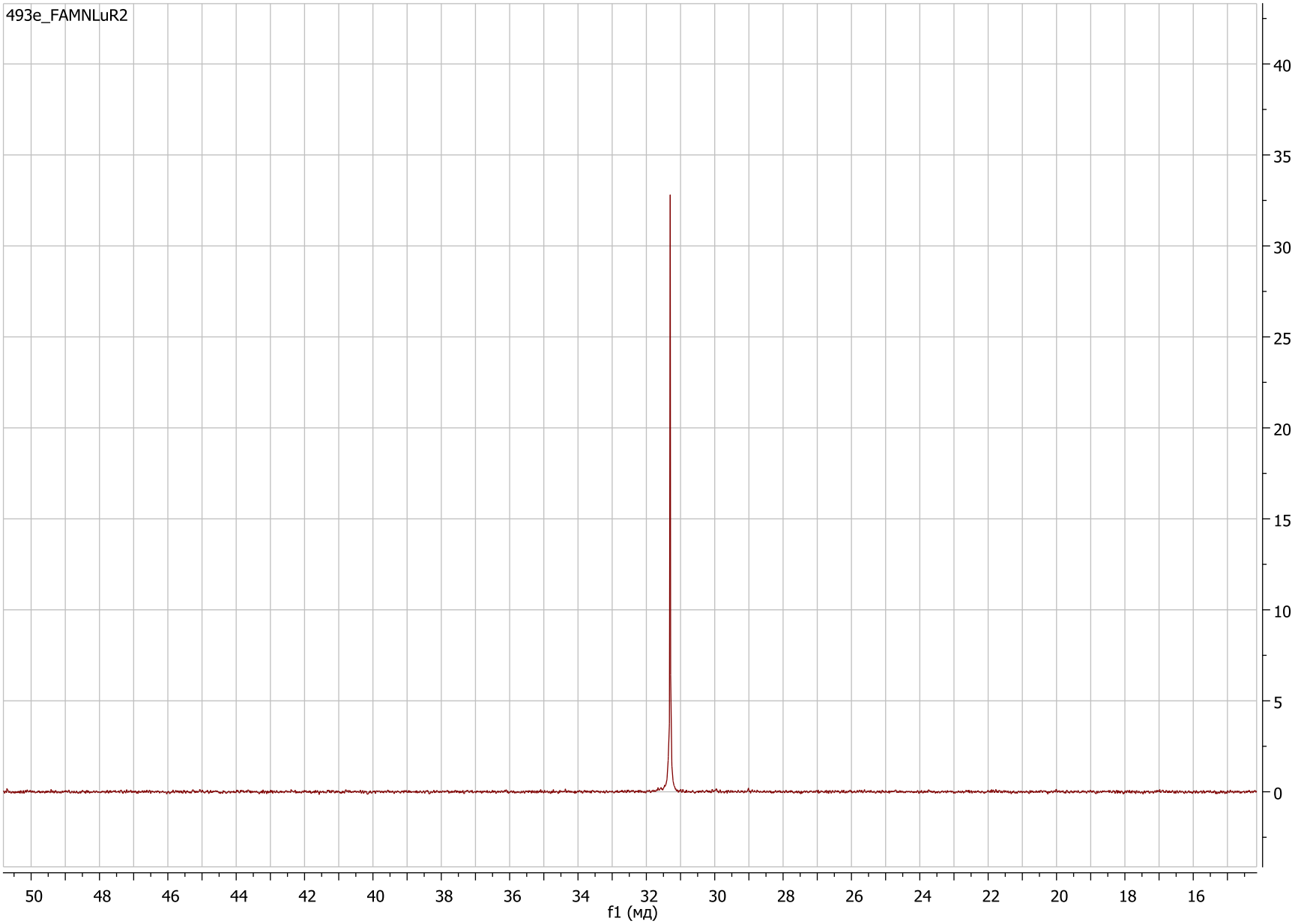


Figure 32S. ^{31}P NMR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

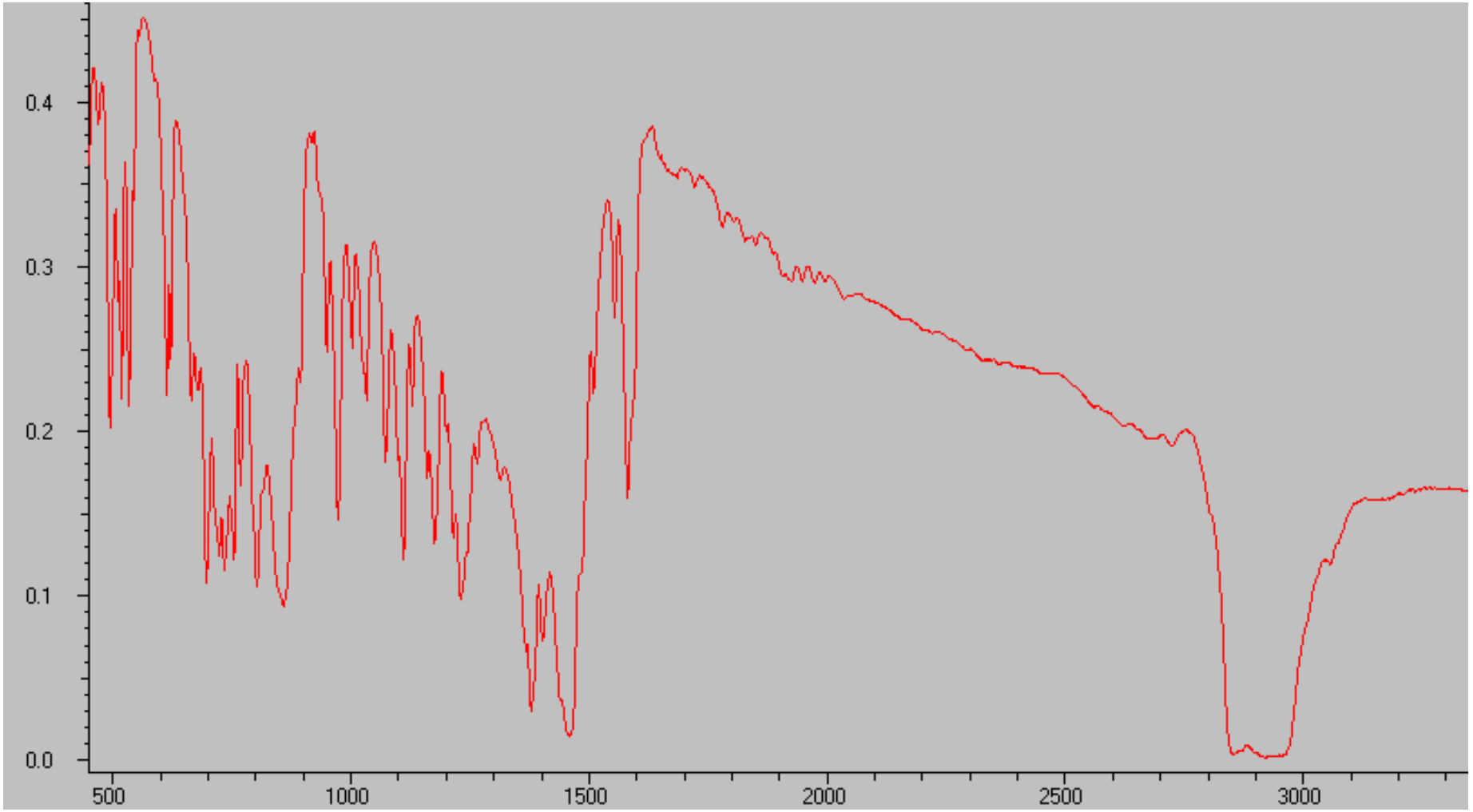


Figure 33S. IR spectrum of {2-[Ph_2P=N(Ph)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**9**).

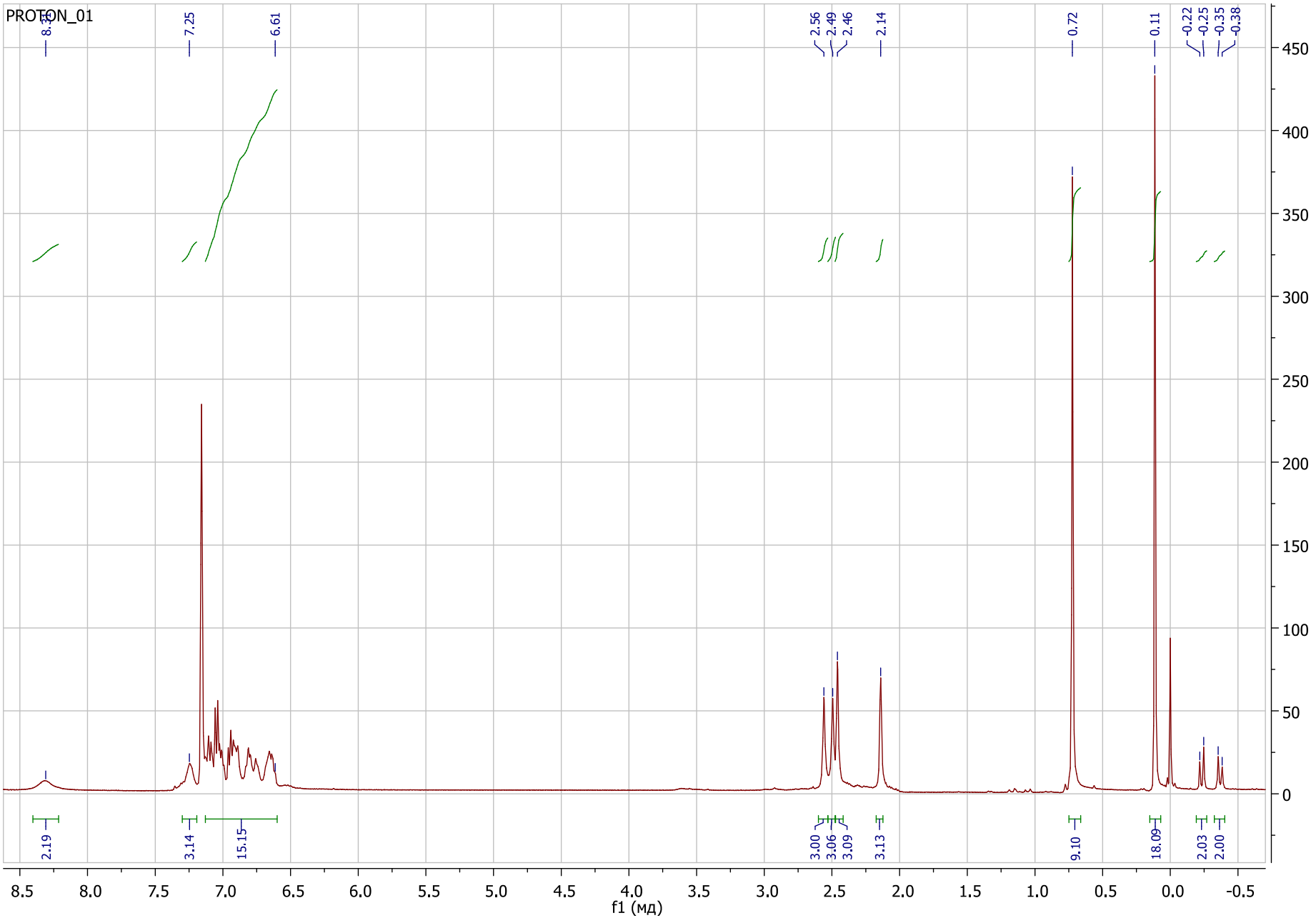


Figure 34S. ^{1}H NMR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

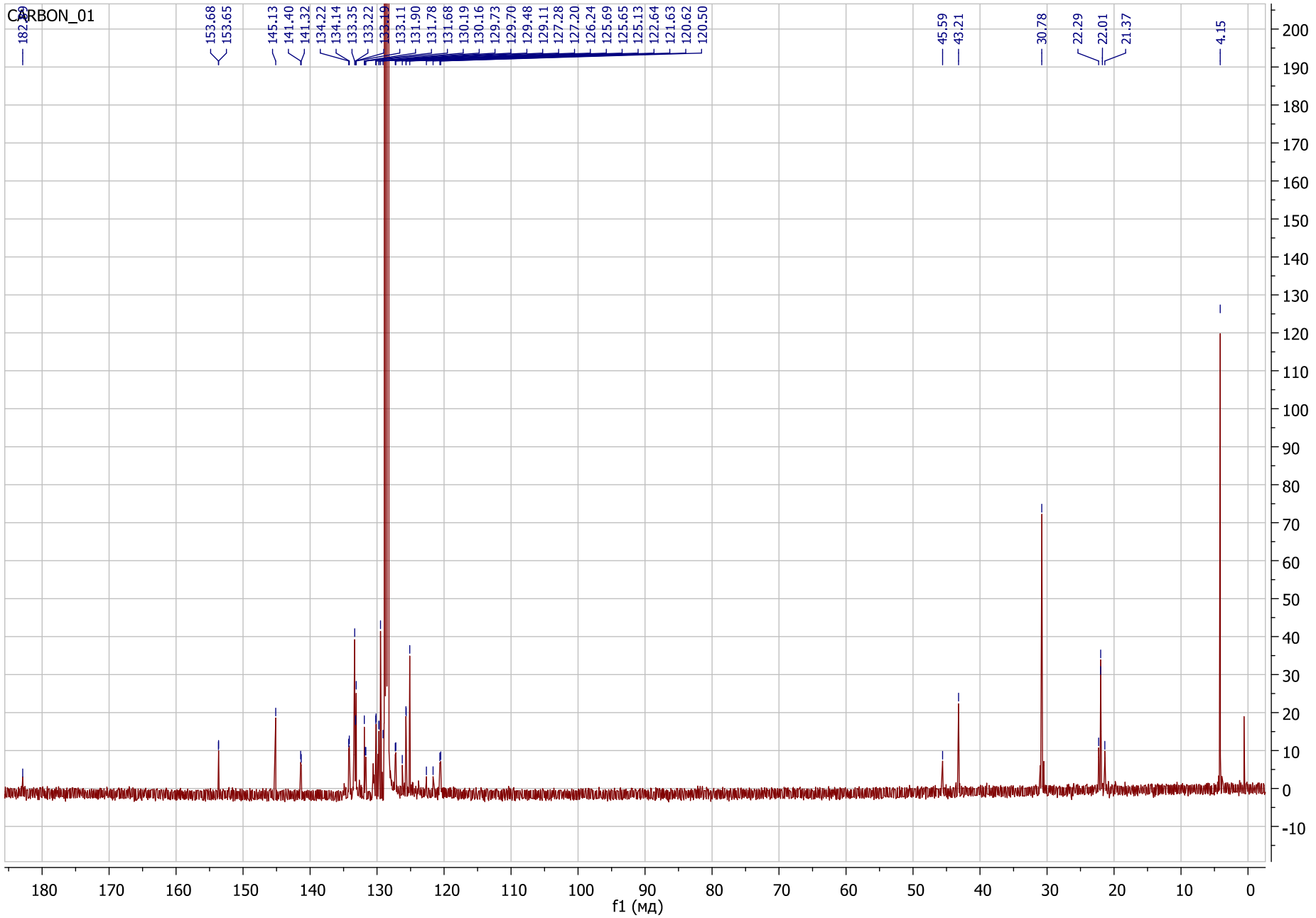


Figure 35S. ^{13}C NMR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

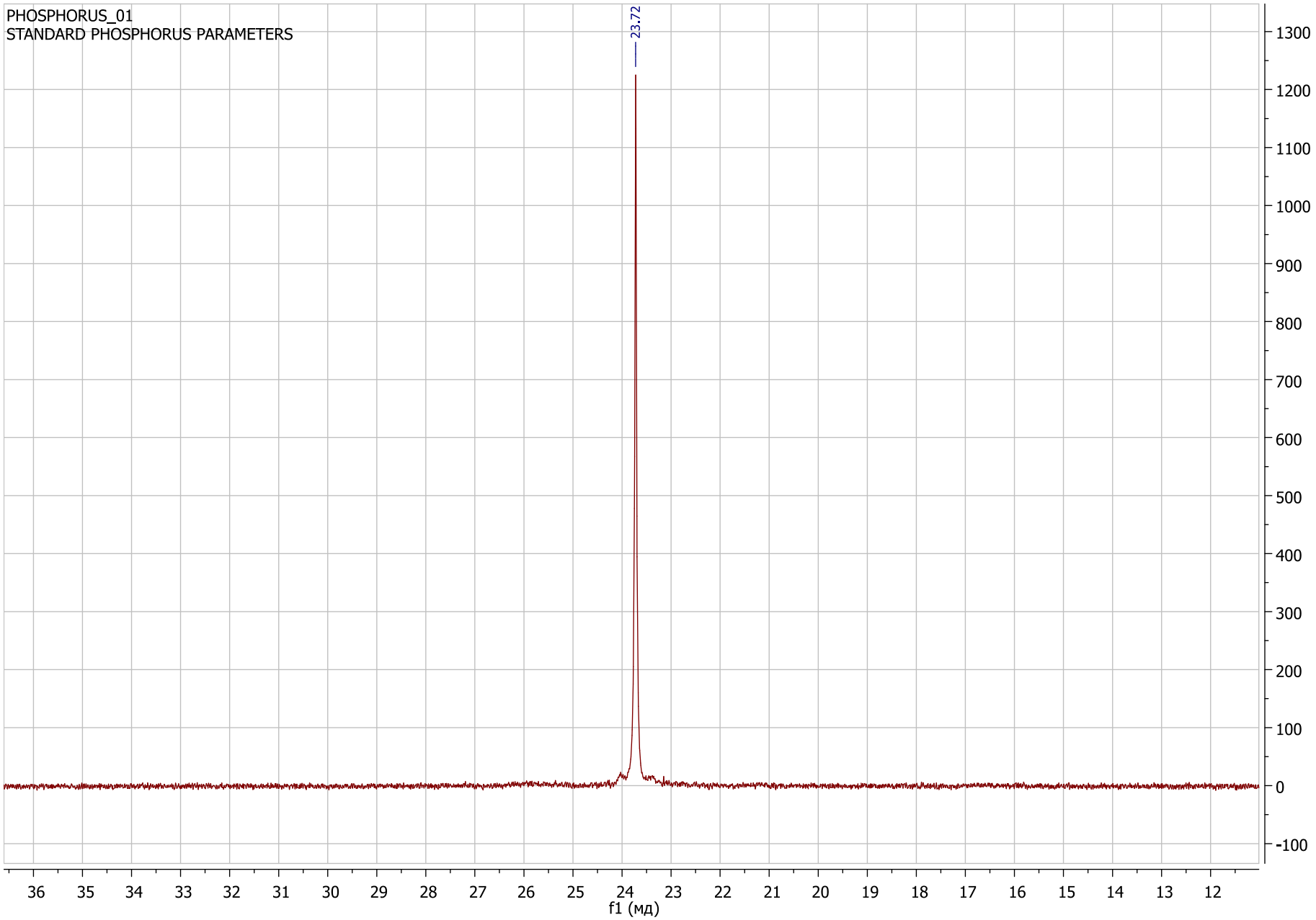


Figure 36S. ^{31}P NMR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

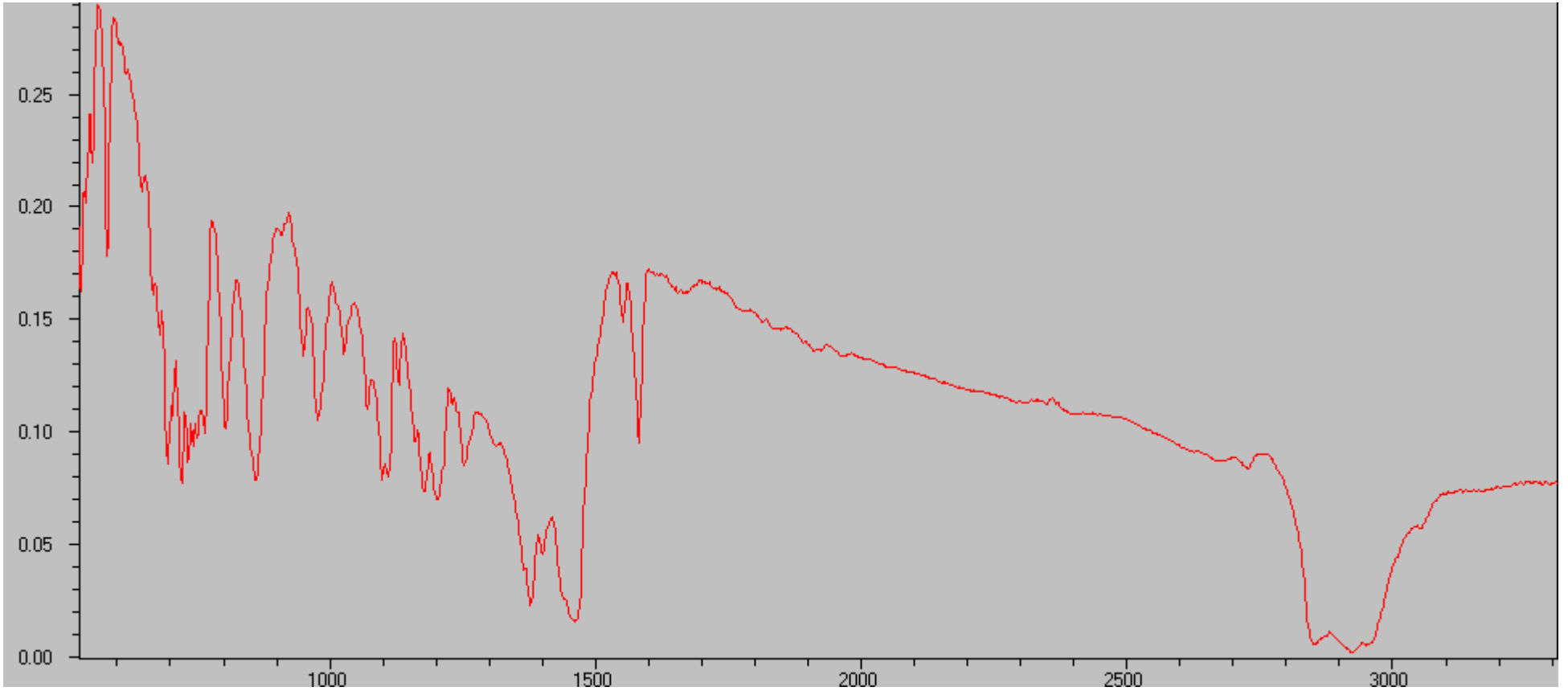


Figure 37S. IR spectrum of {2-[Ph_2P=N(2,6-$Me_2C_6H_3$)]C_6H_4NC(*t*Bu)N(2,6-$Me_2C_6H_3$)}Lu(CH_2SiMe_3)$_2$ (**10**).

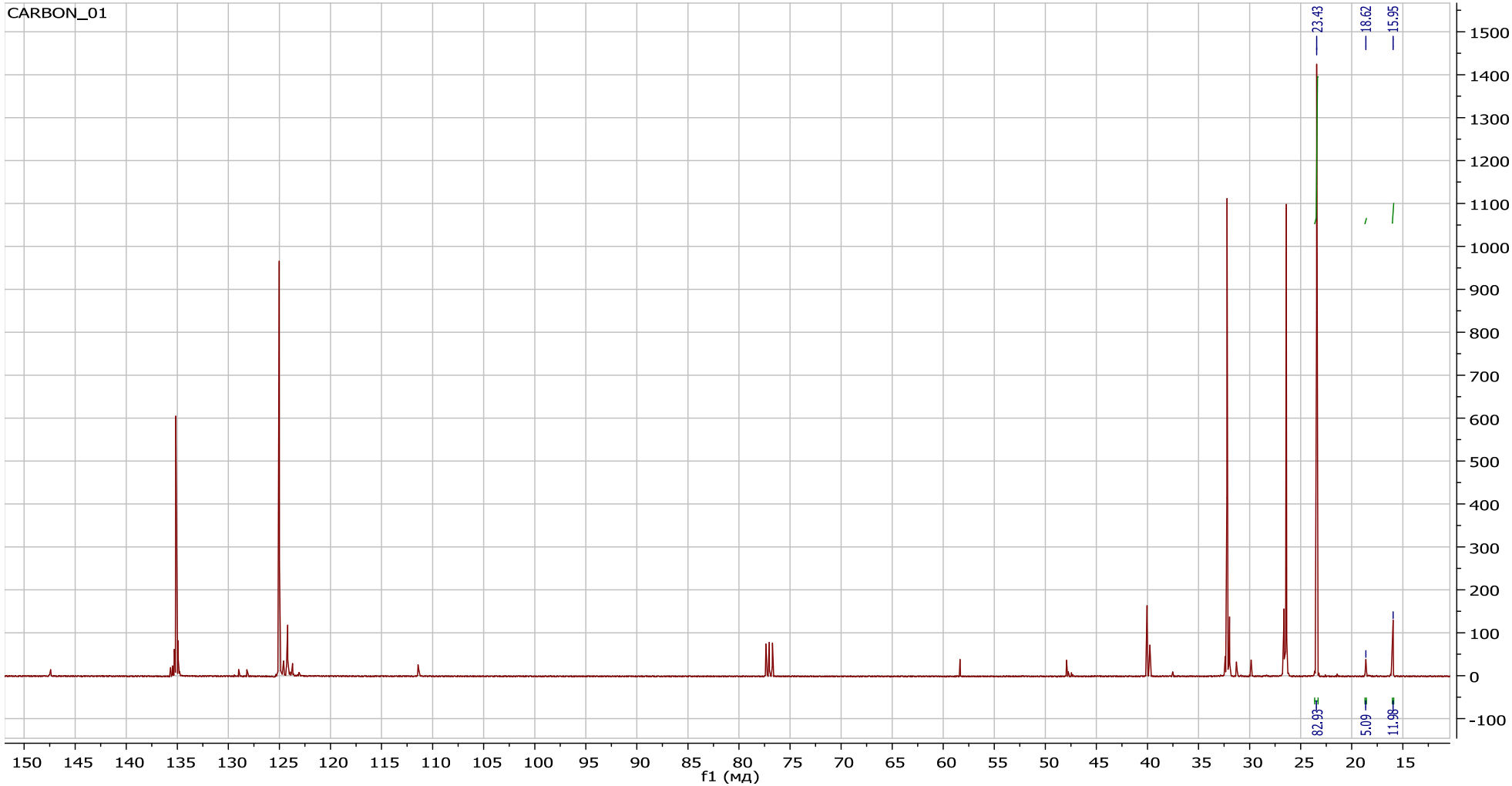


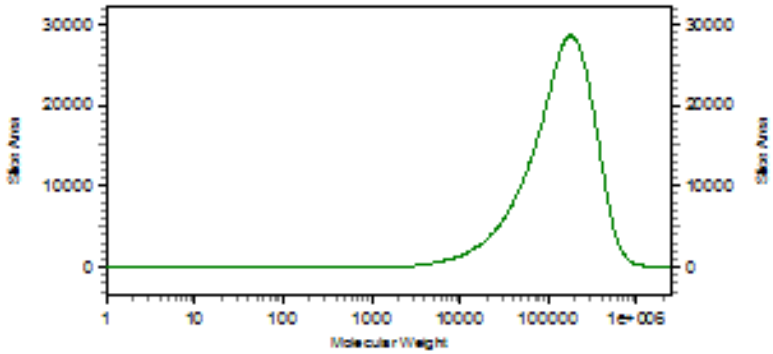
Figure 38 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 5)

SEC Summary information

15.03.05_6_Y 001

S 2300/S 2400

Processing Start Time (min) =	6,412
Processing Stop Time (min) =	10,844
Number of Slices =	266
Weight Average Molecular Weight =	164977
Number Average Molecular Weight =	76611
Z Average Molecular Weight =	264561
Z+1 Average Molecular Weight =	398447
Polydispersity index =	2,153
Peak Molecular Weight =	174421
Z Average / Weight Average =	1,604
Z+1 Average / Weight Average =	2,415



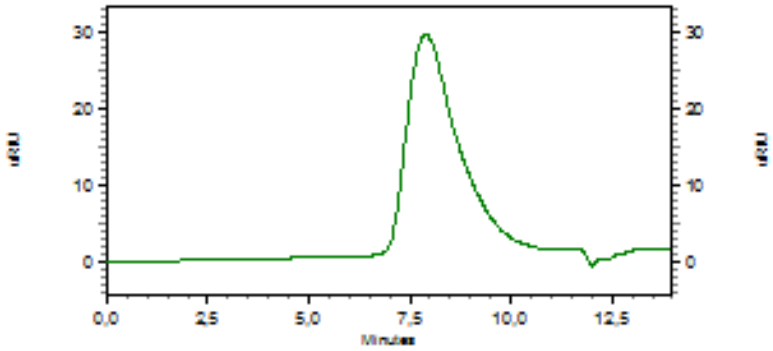


Figure 39 S. GPC of PIP sample (Table 1, Entry 5)

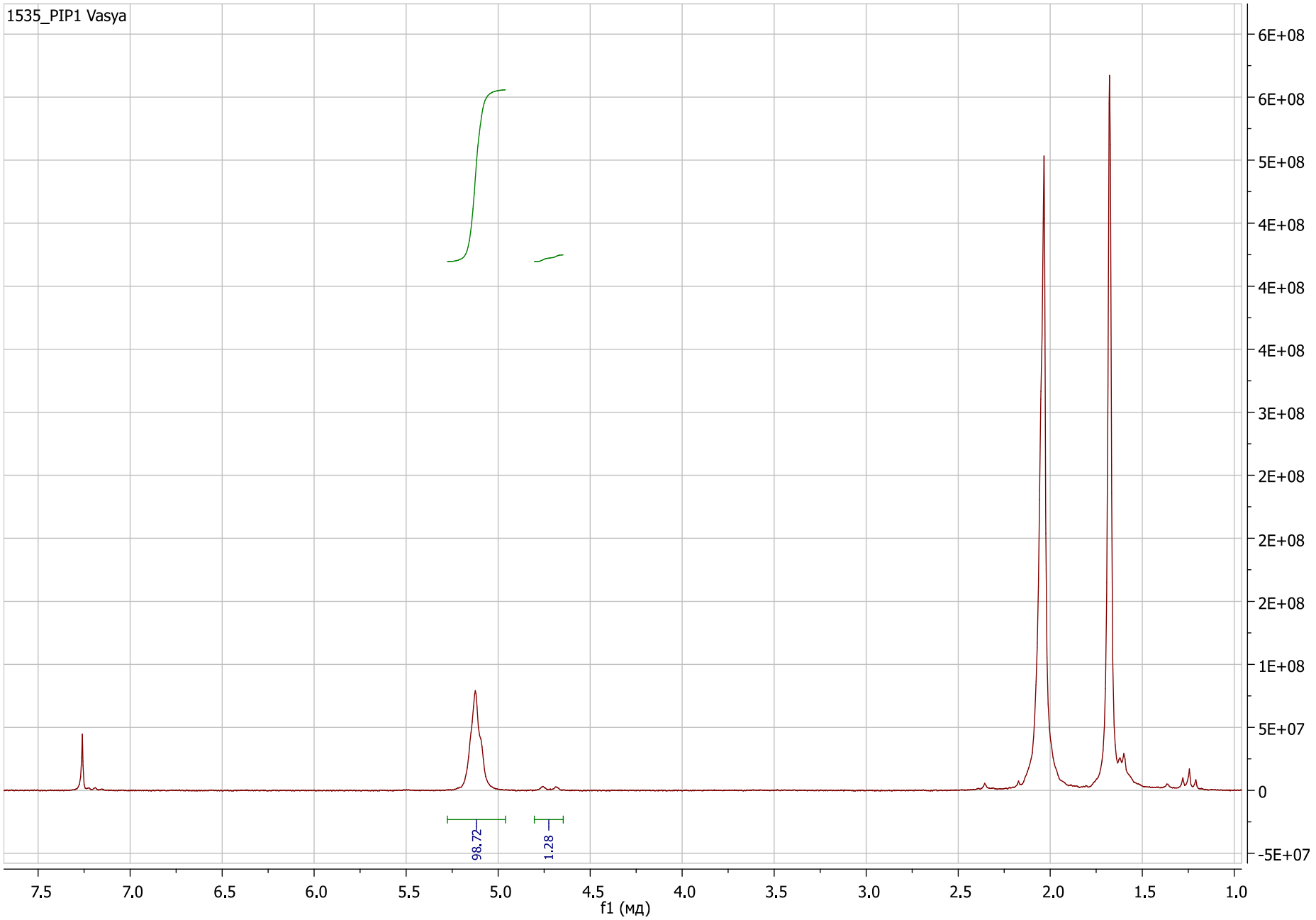


Figure 40 S. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 9)

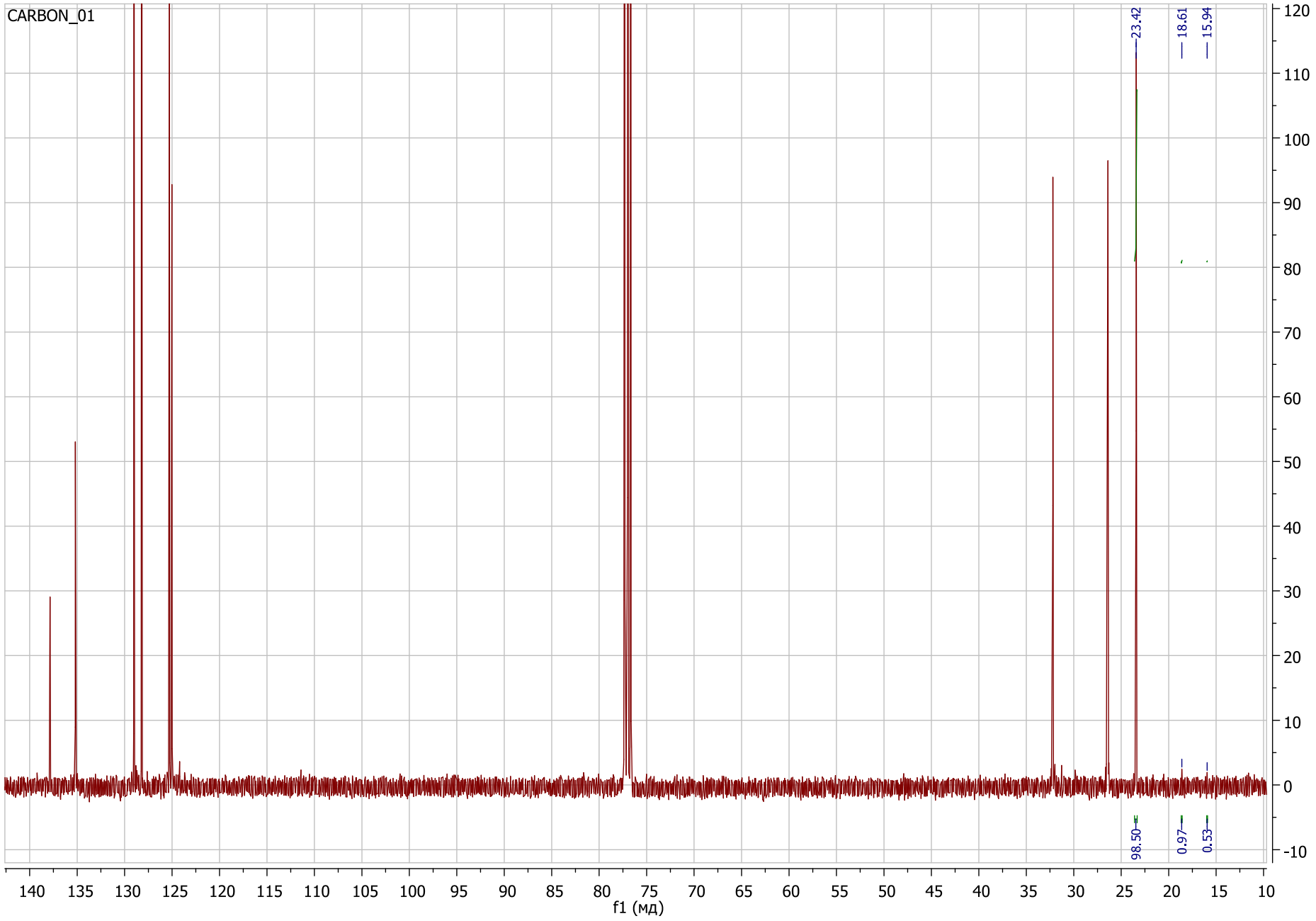


Figure 41 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 9)

SEC Summary information

15.03.06_5_Er 001

S 2300/S 2400

Processing Start Time(min) =	5,695
Processing Stop Time(min) =	10,844
Number of Slices =	309
Weight Average Molecular Weight =	718511
Number Average Molecular Weight =	206739
Z Average Molecular Weight =	1910615
Z+1 Average Molecular Weight =	5022317
Polydispersity index =	3,475
Peak Molecular Weight =	616302
Z Average / Weight Average =	2,659
Z+1 Average / Weight Average =	6,990

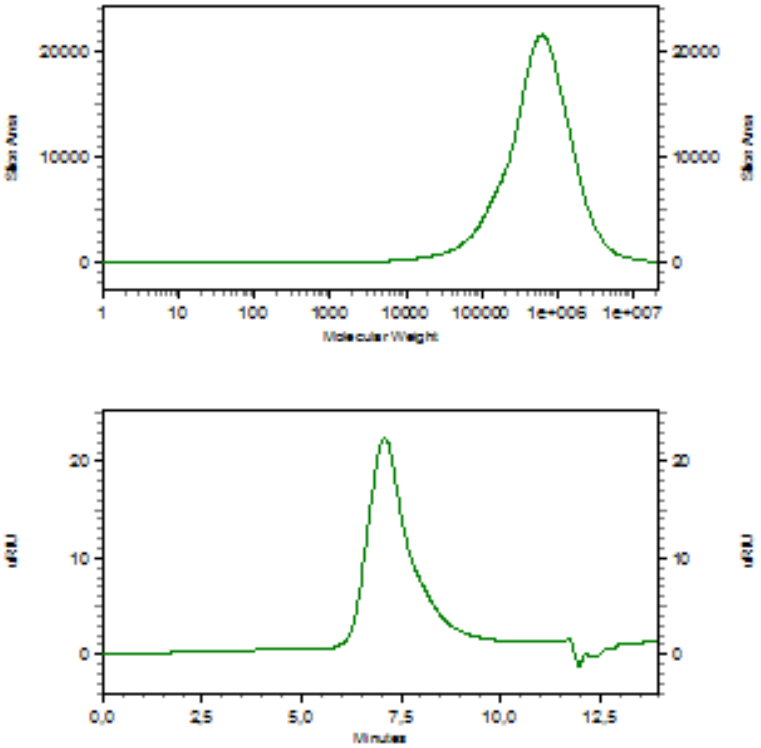


Figure 42 S. GPC of PIP sample (Table 1, Entry 9)

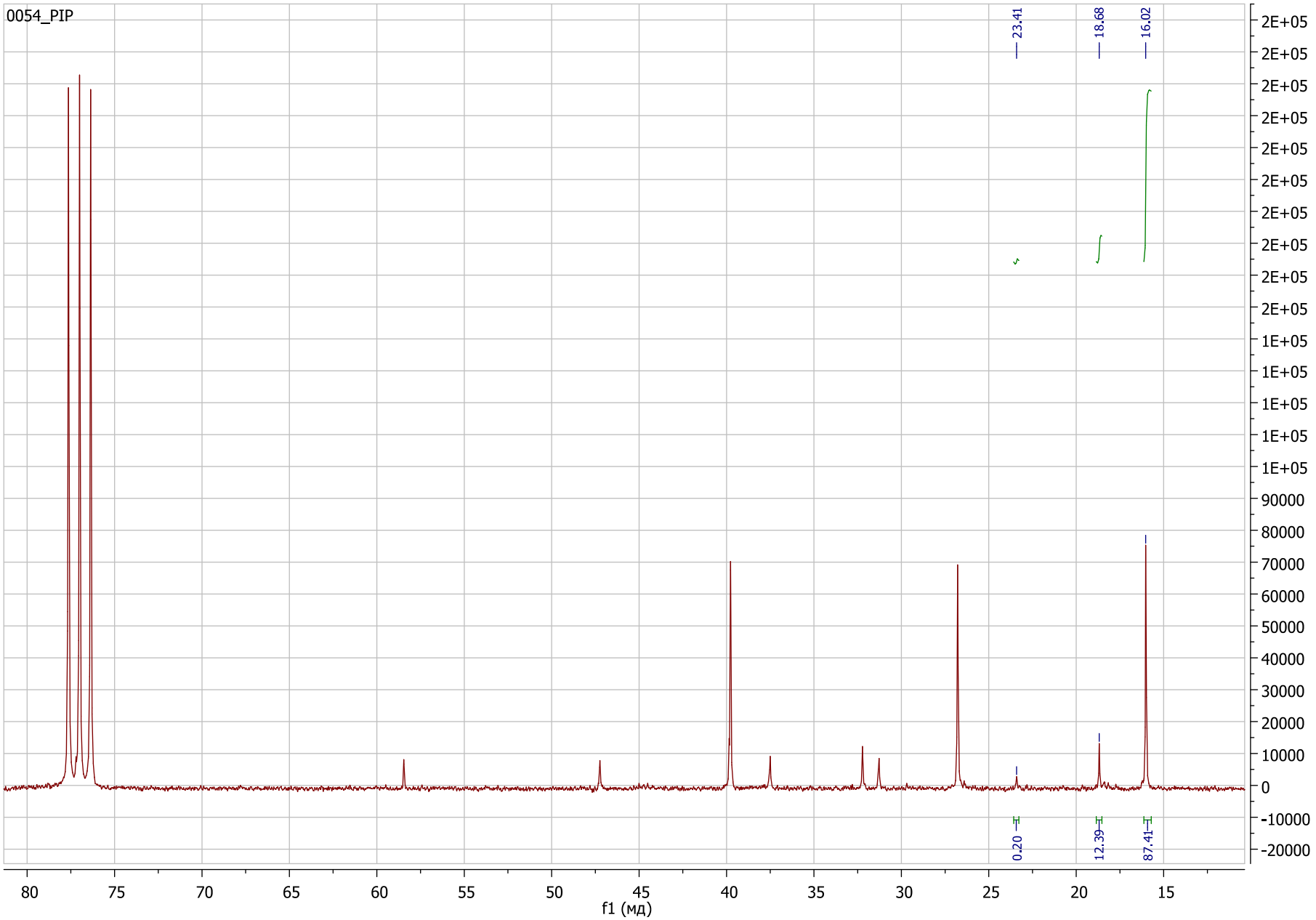


Figure 43 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 1, Entry 18)

SEC Summary information N120(6)6

S 2300/S 2400

Processing Start Time(min) =	6,729
Processing Stop Time(min) =	10,758
Number of Slices =	242
Weight Average Molecular Weight =	118439
Number Average Molecular Weight =	48634
Z Average Molecular Weight =	232923
Z+1 Average Molecular Weight =	389899
Polydispersity index =	2,435
Peak Molecular Weight =	95056
Z Average / Weight Average =	1,967
Z+1 Average / Weight Average =	3,292

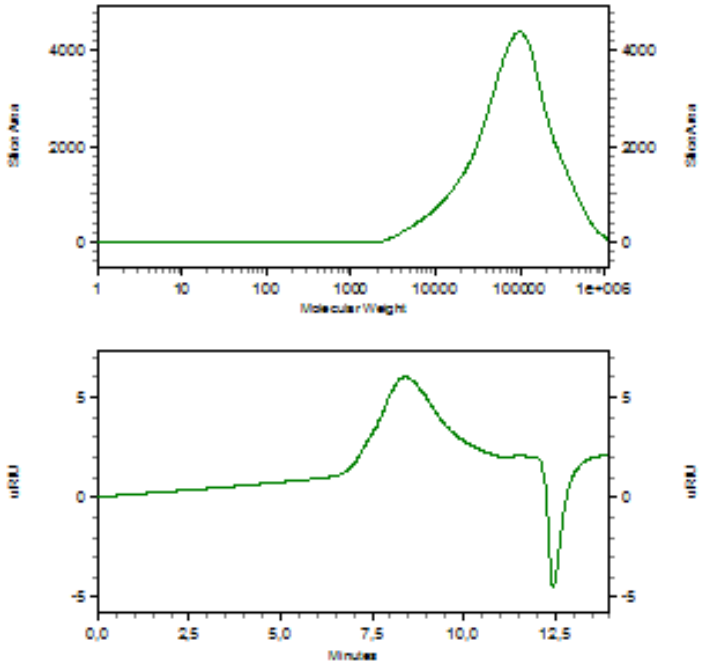


Figure 44 S. GPC of PIP sample (Table 1, Entry 18)

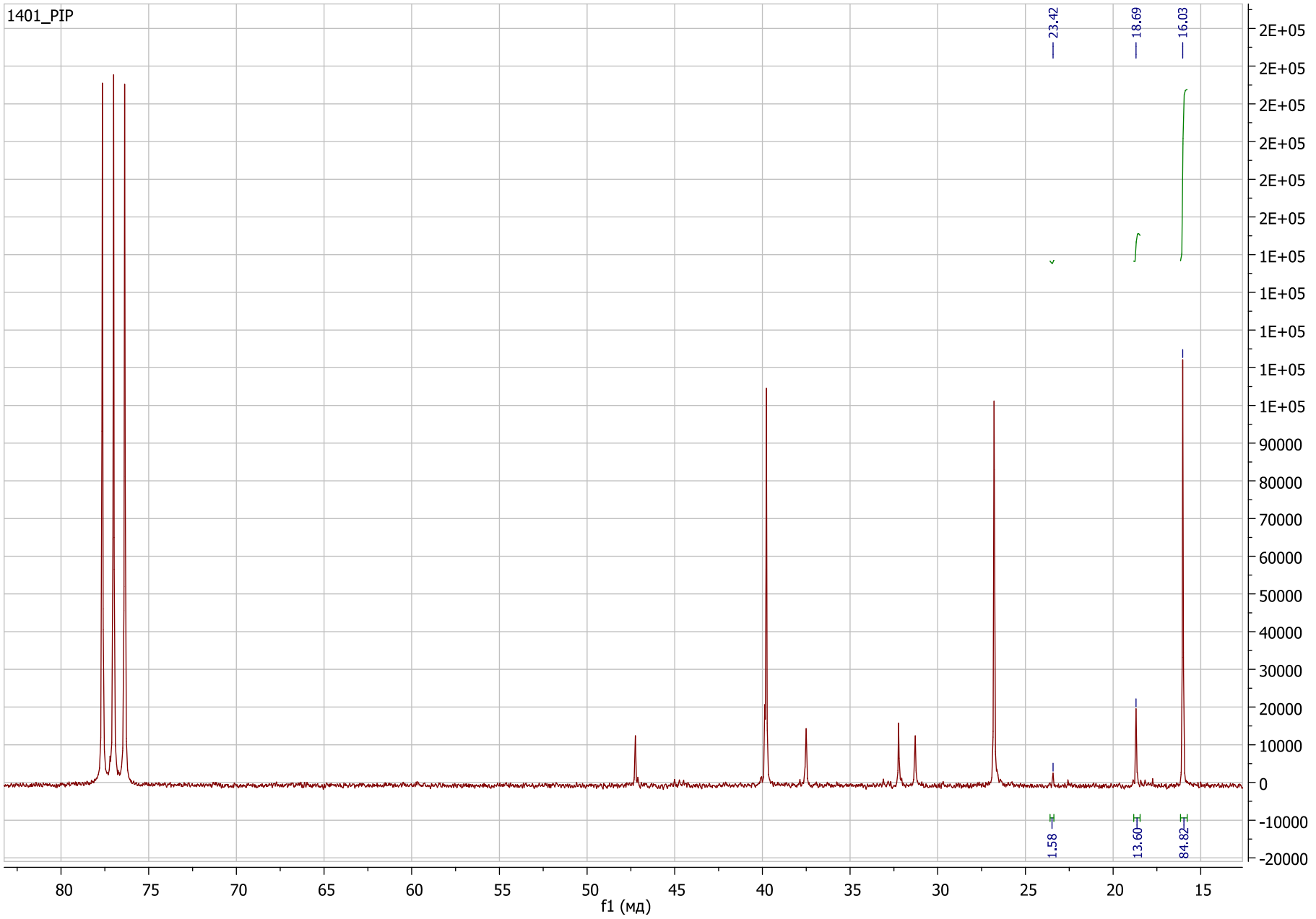
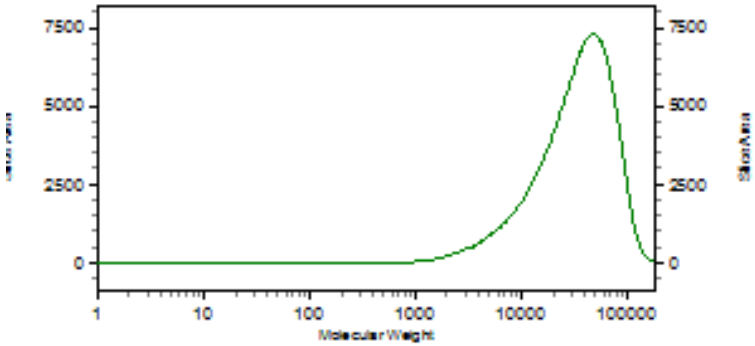


Figure 45 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 2, Entry 1)

SEC Summary information 16.01.19_PIP_423

S 2300/S 2400

Processing Start Time(min) =	7,816
Processing Stop Time(min) =	11,189
Number of Slices =	202
Weight Average Molecular Weight =	44756
Number Average Molecular Weight =	25029
Z Average Molecular Weight =	60354
Z+1 Average Molecular Weight =	73134
Polydispersity index =	1,788
Peak Molecular Weight =	46799
Z Average / Weight Average =	1,348
Z+1 Average / Weight Average =	1,634



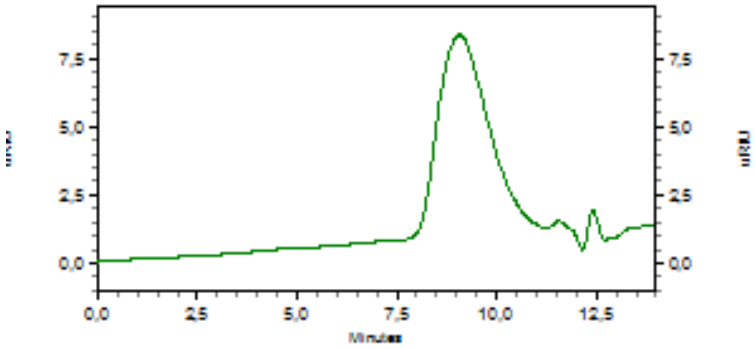


Figure 46 S. GPC of PIP sample (Table 2, Entry 1)

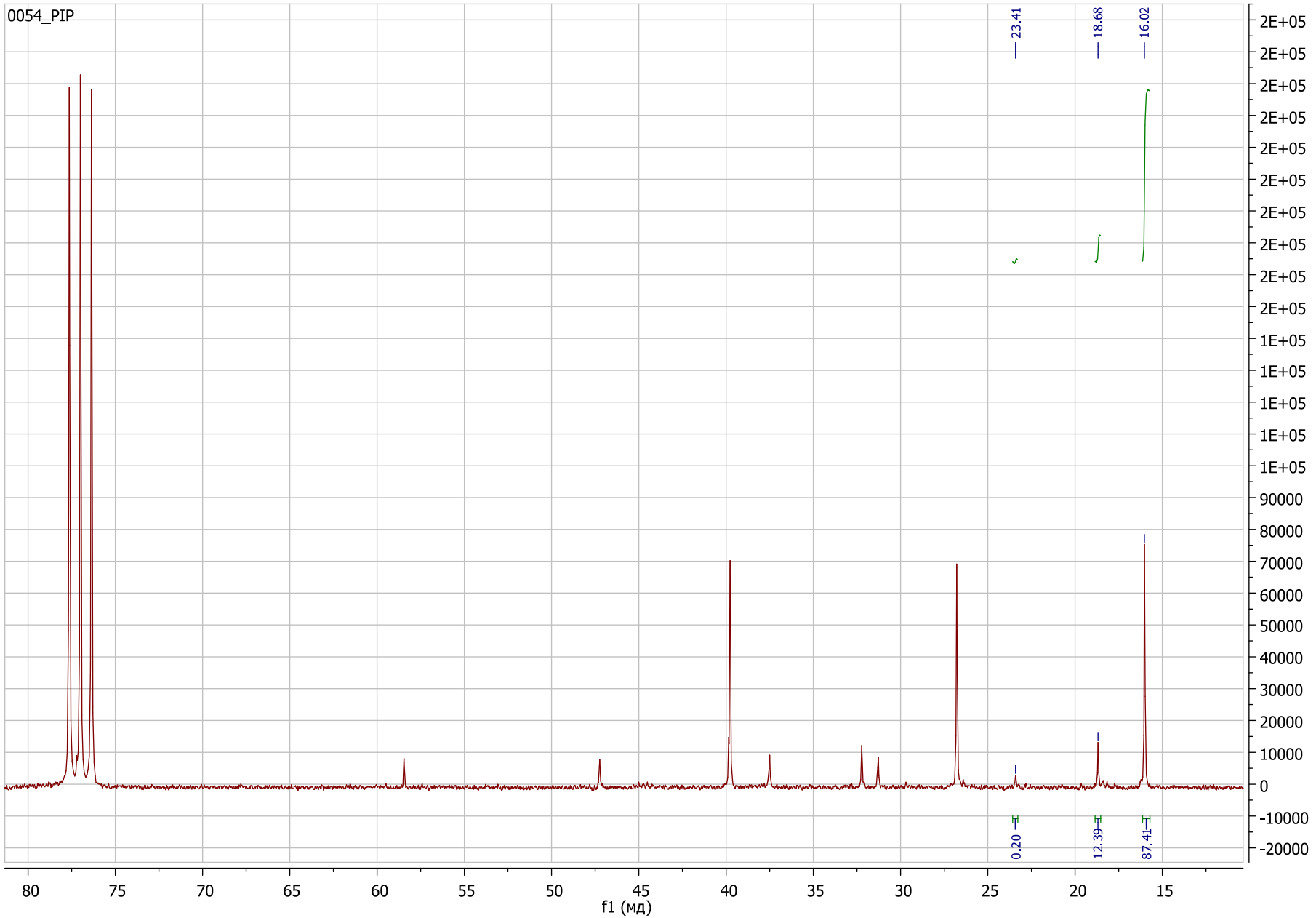


Figure 47 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 2, Entry 3)

SEC Summary information

14.03.19_PIP_439 001

S 2300/S 2400

Processing Start Time(min) =	7,153
Processing Stop Time(min) =	10,868
Number of Slices =	223
Weight Average Molecular Weight =	60599
Number Average Molecular Weight =	40616
Z Average Molecular Weight =	93213
Z+1 Average Molecular Weight =	122579
Polydispersity index =	1,492
Peak Molecular Weight =	61023
Z Average / Weight Average =	1,538
Z+1 Average / Weight Average =	2,022

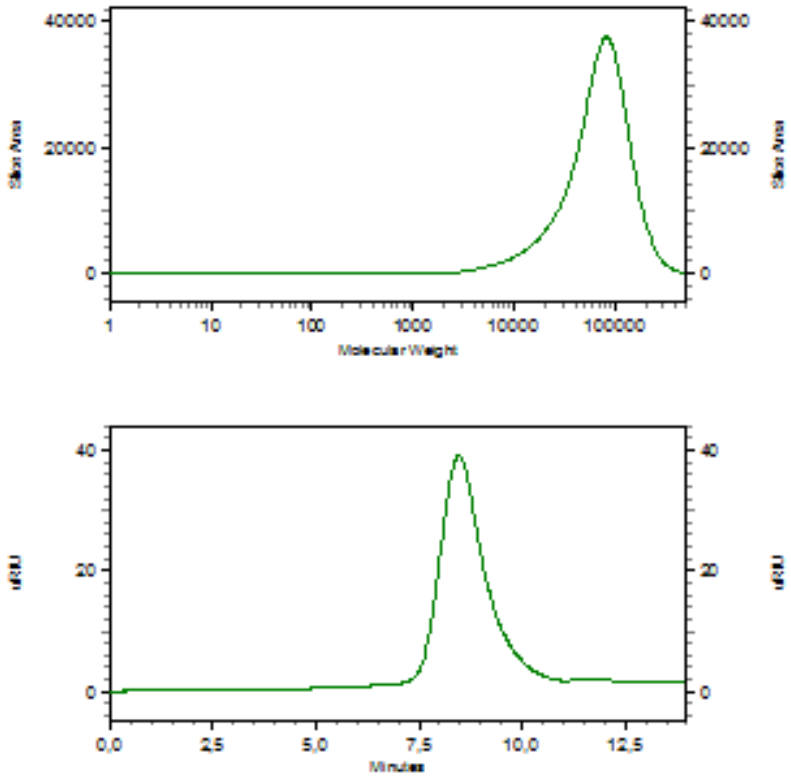


Figure 48 S. GPC of PIP sample (Table 2, Entry 3)

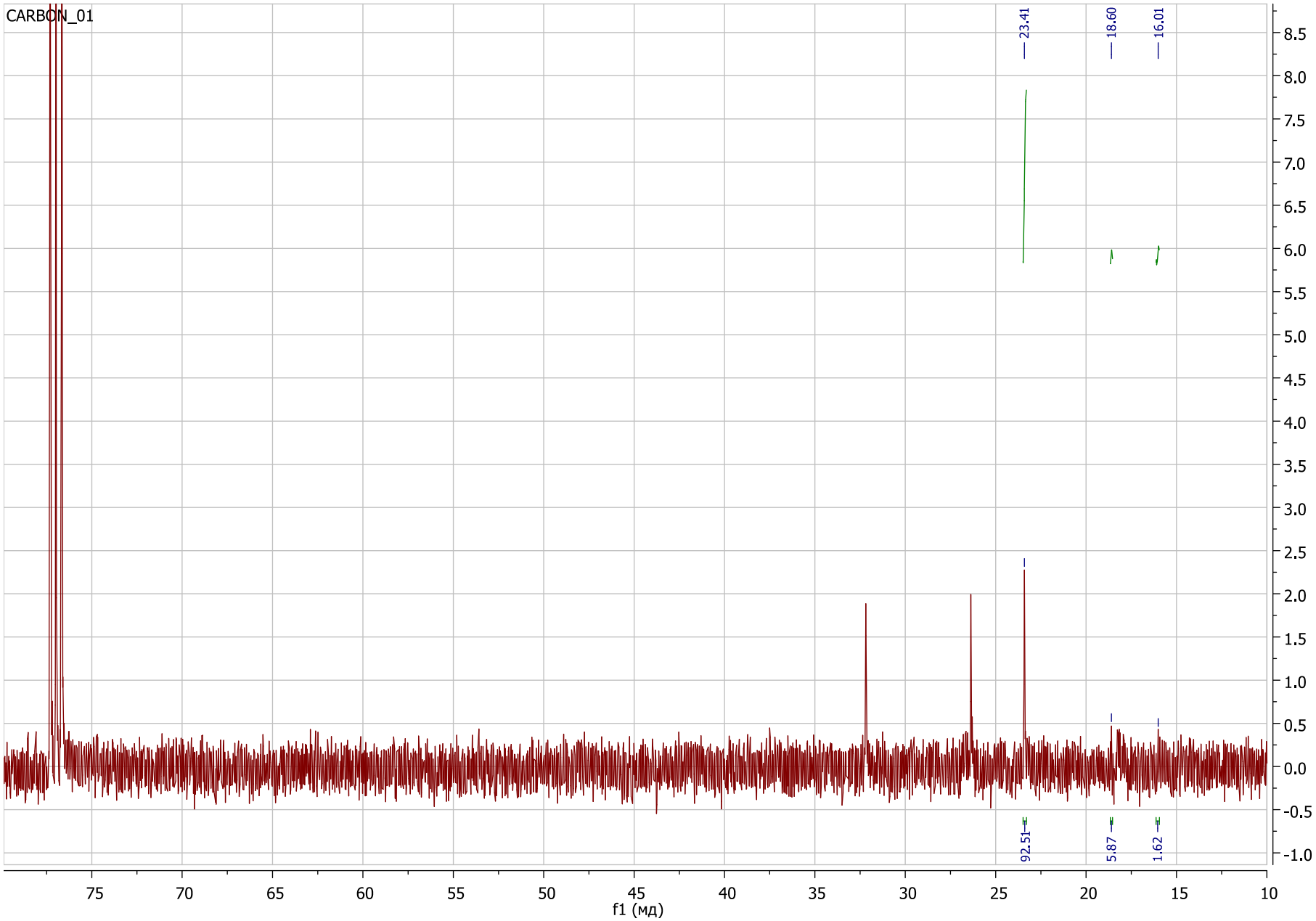


Figure 49 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 3, Entry 3)

SEC Summary information

S 2300/S 2400

Processing Start Time(min) =	5,738
Processing Stop Time(min) =	9,706
Number of Slices =	239
Weight Average Molecular Weight =	669135
Number Average Molecular Weight =	231135
Z Average Molecular Weight =	3806087
Z+1 Average Molecular Weight =	10466501
Polydispersity index =	2,895
Peak Molecular Weight =	711774
Z Average / Weight Average =	3,715
Z+1 Average / Weight Average =	10,216

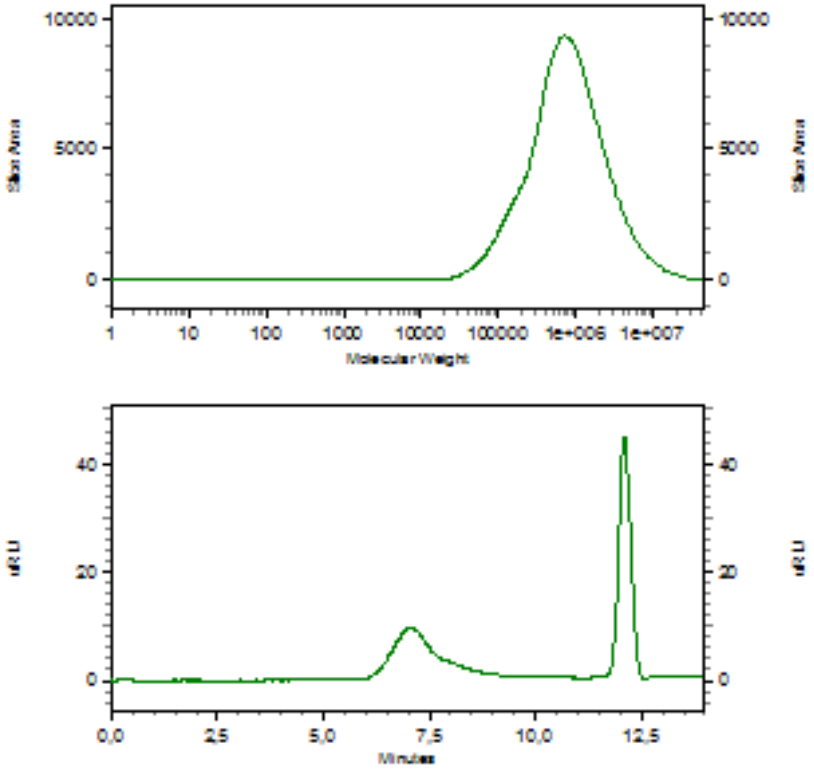


Figure 50 S. GPC of PIP sample (Table 3, Entry 3)

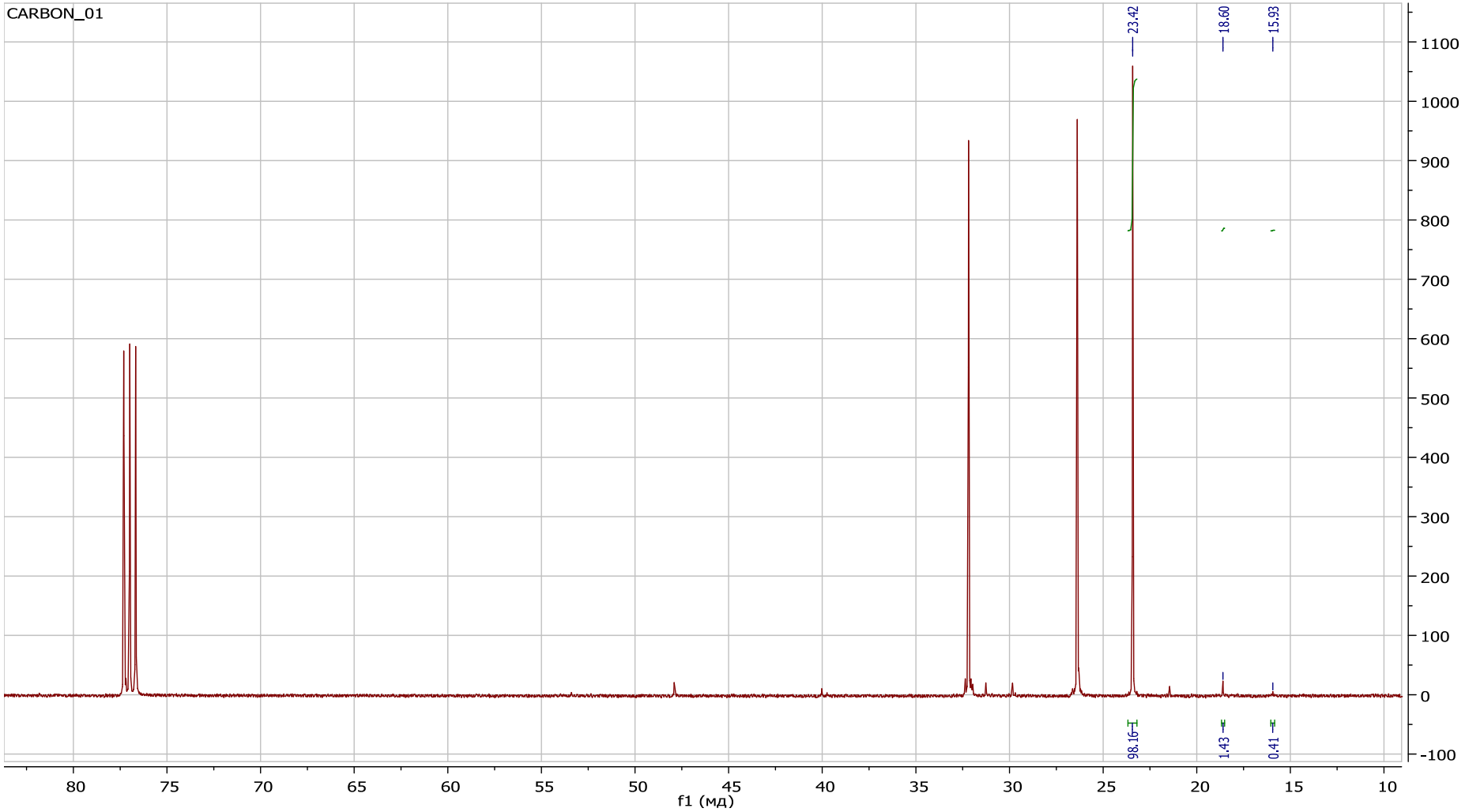


Figure 51 S. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of PIP sample (Table 3, Entry 9)

SEC Summary information 15.10.30_3

S 2300/S 2400

Processing Start Time(min) =	6,063
Processing Stop Time(min) =	9,135
Number of Slices =	184
Weight Average Molecular Weight =	677397
Number Average Molecular Weight =	318698
Z Average Molecular Weight =	1303980
Z+1 Average Molecular Weight =	2151965
Polydispersity index =	2,126
Peak Molecular Weight =	622617
Z Average / Weight Average =	1,925
Z+1 Average / Weight Average =	3,177

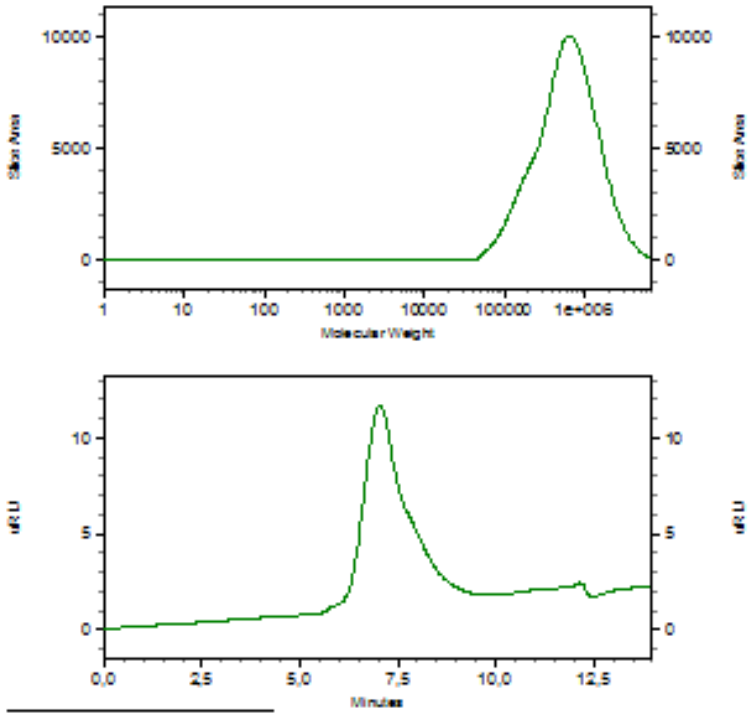


Figure 52 S. GPC of PIP sample (Table 3, Entry 9)