Electronic supplementary material

Bis(alkyl) rare-earth complexes supported by new tridentate amidinate ligand with a pendant diphenylphosphine oxide group. Synthesis, structures and catalytic activity in isoprene polymerization

Aleksei O. Tolpygin,[a] Tatyana A. Glukhova,[a] Anton V. Cherkasov,[a] Georgy K. Fukin,[a] Diana V. Aleksanyan,[b] Dongmei Cui,[c] Alexander A. Trifonov[a,b,*]

[a]*Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, GSP-445, 630950, Nizhny Novgorod (Russia) Fax: 007831 4627497; Tel: 007831 4623532; E-mail: trif@iomc.ras.ru*

[b]*Institute of Organoelement compounds of Russian Academy of Sciences, Vavilova str. 28, 119334, Moscow (Russia)*

[c]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin street, Changchun 130022 (China)*

Table 1S. Crystallographic data and structure refinement details for **1, 2, 4** and **5.**

Table 2S. Catalytic tests in isoprene polymerization initiated by systems (**3**-**5**)/borate/$AlMe_3$ (borate: $[Et_3NH][BPh_4]$, $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$, [Ln]/[borate]/[$AlMe_3$]=1:1:10).

Figure 1S.^{1}H NMR spectrum of2-[$Ph_2P(O)$]$C_6H_4NHC(t$Bu)=N(2,6-$Me_2C_6H_3$) (**1**).

Figure 2S.^{13}C NMR spectrum of2-[$Ph_2P(O)$]$C_6H_4NHC(t$Bu)=N(2,6-$Me_2C_6H_3$) (**1**).

Figure 3S.^{31}P NMR spectrum of 2-[$Ph_2P(O)$]$C_6H_4NHC(t$Bu)=N(2,6-$Me_2C_6H_3$) (**1**).

Figure 4S.IR spectrum of2-[$Ph_2P(O)$]$C_6H_4NHC(t$Bu)=N(2,6-$Me_2C_6H_3$) (**1**).

Figure 5S.^{1}H NMR spectrum of{2-[$Ph_2P(O)$]$C_6H_4NC(t$Bu)N(2,6-$Me_2C_6H_3$)}YCl_2(DME) (**2**).

Figure 6S.^{13}C NMR spectrum of{2-[$Ph_2P(O)$]$C_6H_4NC(t$Bu)N(2,6-$Me_2C_6H_3$)}YCl_2(DME) (**2**).

Figure 7S.^{31}P NMR spectrumof{2-[$Ph_2P(O)$]$C_6H_4NC(t$Bu)N(2,6-$Me_2C_6H_3$)}YCl_2(DME) (**2**).

Figure 8S.IR spectrum of {2-[$Ph_2P(O)$]$C_6H_4NC(t$Bu)N(2,6-$Me_2C_6H_3$)}YCl_2(DME) (**2**).

Figure 9S. ^{1}H NMR spectrum of [2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Y(CH_2SiMe_3)$_2$THF] (**3**).

Figure 10S. ^{13}C NMR spectrum of [2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Y(CH_2SiMe_3)$_2$THF] **(3).**

Figure 11S. ^{31}P NMR spectrum of [2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Y(CH_2SiMe_3)$_2$THF] **(3).**

Figure 12S. ^{1}H NMR spectrum of [2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Lu(CH_2SiMe_3)$_2$] **(5).**

Figure 13S. ^{13}C NMR spectrum of [2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Lu(CH_2SiMe_3)$_2$] **(5).**

Figure 14S. ^{31}P NMR spectrum of [2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Lu(CH_2SiMe_3)$_2$] **(5).**

Table 1S. Crystallographic data and structure refinement details for **1, 2, 4** and **5**

Compound	**1**	**2**	**4**	**5**
Empirical formula	$C_{31}H_{33}N_2OP$	$C_{37}H_{47}Cl_2N_2O_4PY$	$C_{43}H_{62}ErN_2O_2PSi_2$	$C_{42.50}H_{58}LuN_2OPSi_2$
Formula weight	480.56	774.55	893.35	875.03
T [K]	100(2)	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal	Monoclinic	Triclinic
Space group	P2(1)/c	I-1	P2(1)/n	P-1
a [Å]	14.4270(2)	26.2291(7)	10.243(1)	11.6576(2)
b [Å]	18.0000(2)	26.2291(7)	19.035(2)	11.9319(2)
c [Å]	10.2803(2)	10.7386	21.678(3)	18.0960(3)
α [°]	90	90	90	74.619(1)
β [°]	102.366(1)	90	95.195(2)	72.630(1)
γ [°]	90	90	90	63.078(1)
Volume [$Å^3$]	2607.72(6)	7387.8(4)	4209.1(8)	2116.79(5)
Z	4	8	4	2
ρcalcd. [g cm^{-3}]	1.224	1.393	1.410	1.373
Absorption coefficient [mm^{-1}]	0.132	1.807	2.126	2.459
F(000)	1024	3224	1844	898
Crystal size [mm]	0.40×0.20×0.10	0.37×0.20×0.18	0.23×0.14×0.11	0.50×0.25×0.15
θ range for data collection [°]	3.04 to 28.00	2.05 to 26.00	2.169 to 26.00	2.83 to 27.00
Index ranges	-19≤h≤19, -23≤k≤23, -13≤l≤13	-32≤h≤32, -31≤k≤32, -13≤l≤13	-12≤h≤12, -23≤k≤23, -26≤l≤26	-14≤h≤14, 15≤k≤15, -23≤l≤23
Reflections collected	45921	31590	38140	34254
Independent reflections	6265	7213	8254	9179
Rint	0.0536	0.0490	0.0380	0.0406
Completeness to θ [%]	99.6	99.6	99.5	99.4
Data/restraints/parameters	6265/0/325	7213/21/432	8254/0/471	9179/0/490
Goodness-of-fit on F^2	1.036	1.001	1.066	1.037
Final R indices [I>2σ(I)]	R1 = 0.0383, wR2 = 0.0961	R1 = 0.0355, wR2 = 0.0788	R1 = 0.0309, wR2 = 0.0818	R1 = 0.0243, wR2 = 0.0504
R indices (all data)	R1 = 0.0509, wR2 = 0.1021	R1 = 0.0458, wR2 = 0.0818	R1 = 0.0367, wR2 = 0.0851	R1 = 0.0297, wR2 = 0.0516
Largest diff. peak and hole [$eÅ^{-3}$]	0.554/-0.260	1.157/-0.507	1.927/-0.702	1.136/-0.604

Table 2S. Catalytic tests in isoprene polymerization initiated by systems (**3-5**)/borate/$AlMe_3$ (borate: $[Et_3NH][BPh_4]$, $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$, [Ln]/[borate]/$[AlMe_3]$=1:1:10).

	comp.	borate	[IP]/[Ln]	t, h	Yield, %	Cis-1,4	Trans-1,4	3,4-	$M_n(\times10^{-3})^a$	$M_n(\times10^{-3})_{calc}{}^b$	M_w/M_n
1	3	Et_3NB	1000	24	0	-	-	-	-	65.0	-
2	3	$B(C_6F_5)_3$	1000	24	0	-	-	-	-	65.0	-
3	3	HNB	1000	24	0	-	-	-	-	65.0	-
4	3	TB	1000	24	0	-	-	-	-	65.0	-
5	4	Et_3NB	1000	24	0	-	-	-	-	65.0	-
6	4	$B(C_6F_5)_3$	1000	24	0	-	-	-	-	65.0	-
7	4	HNB	1000	24	0	-	-	-	-	65.0	-
8	4	TB	1000	24	0	-	-	-	-	65.0	-
9	5	Et_3NB	1000	24	0	-	-	-	-	65.0	-
10	5	$B(C_6F_5)_3$	1000	24	0	-	-	-	-	65.0	-
11	5	HNB	1000	24	0	-	-	-	-	65.0	-
12	5	TB	1000	24	0	-	-	-	-	65.0	-
13	3	-	1000	24	0	-	-	-	-	65.0	-
14	4	-	1000	24	0	-	-	-	-	65.0	-
15	5	-	1000	24	0	-	-	-	-	65.0	-

Conditions: complex (10 μmol in toluene, $[AlMe_3]$:[Ln]:[borate] = 10/1/1, T: 25 °C.); HNB = $[PhNHMe_2][B(C_6F_5)_4]$, TB = $[Ph_3C][B(C_6F_5)_4]$, Et_3NB = $[Et_3NH][BPh_4]$; a) Determined by GPC against polystyrene standard; *The catalytic tests were performed without the addition of borate; b)M_{calc}=([IP]/[Ln])× 68.12×(conversion).

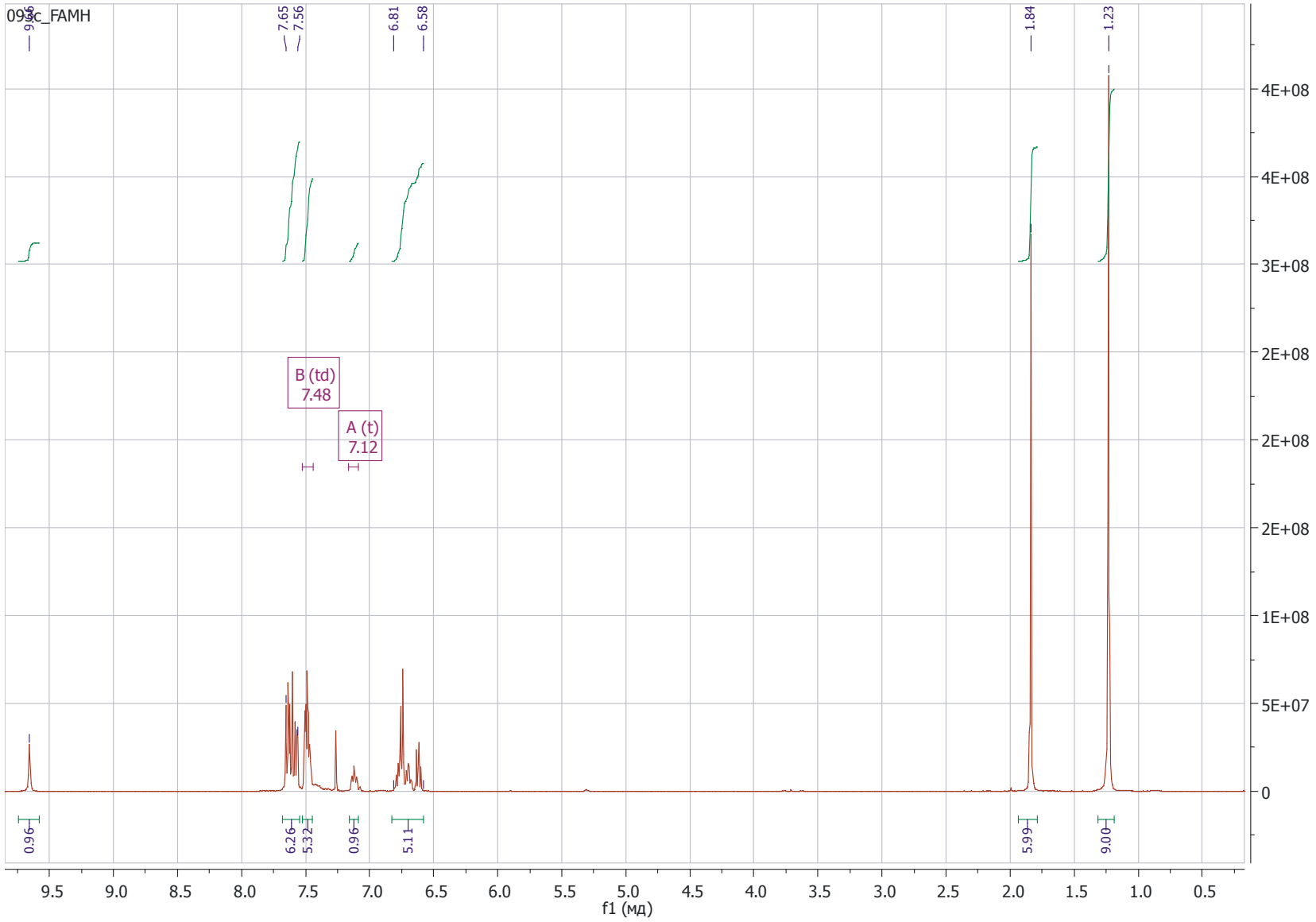

Figure 1S. ^{1}H NMR spectrum(400 MHz, $CDCl_3$, 298 K) of2-[$Ph_2P(O)$]$C_6H_4NHC(t$Bu)=N(2,6-$Me_2C_6H_3$) (**1**).

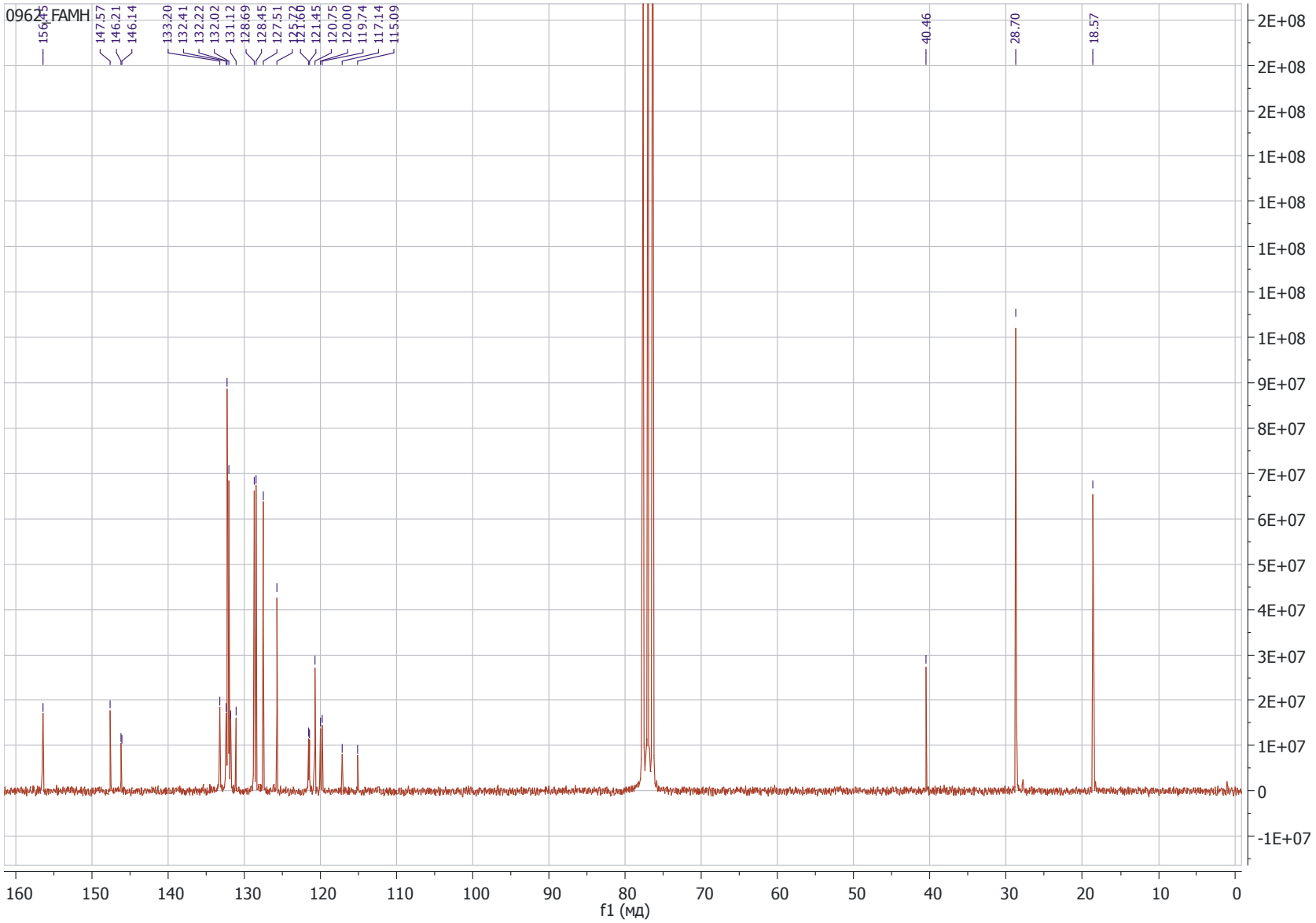

Figure 2S. ^{13}C NMR spectrum(50 MHz, $CDCl_3$, 298 K) of2-[$Ph_2P(O)$]$C_6H_4NHC(t$Bu)=N(2,6-$Me_2C_6H_3$) (**1**).

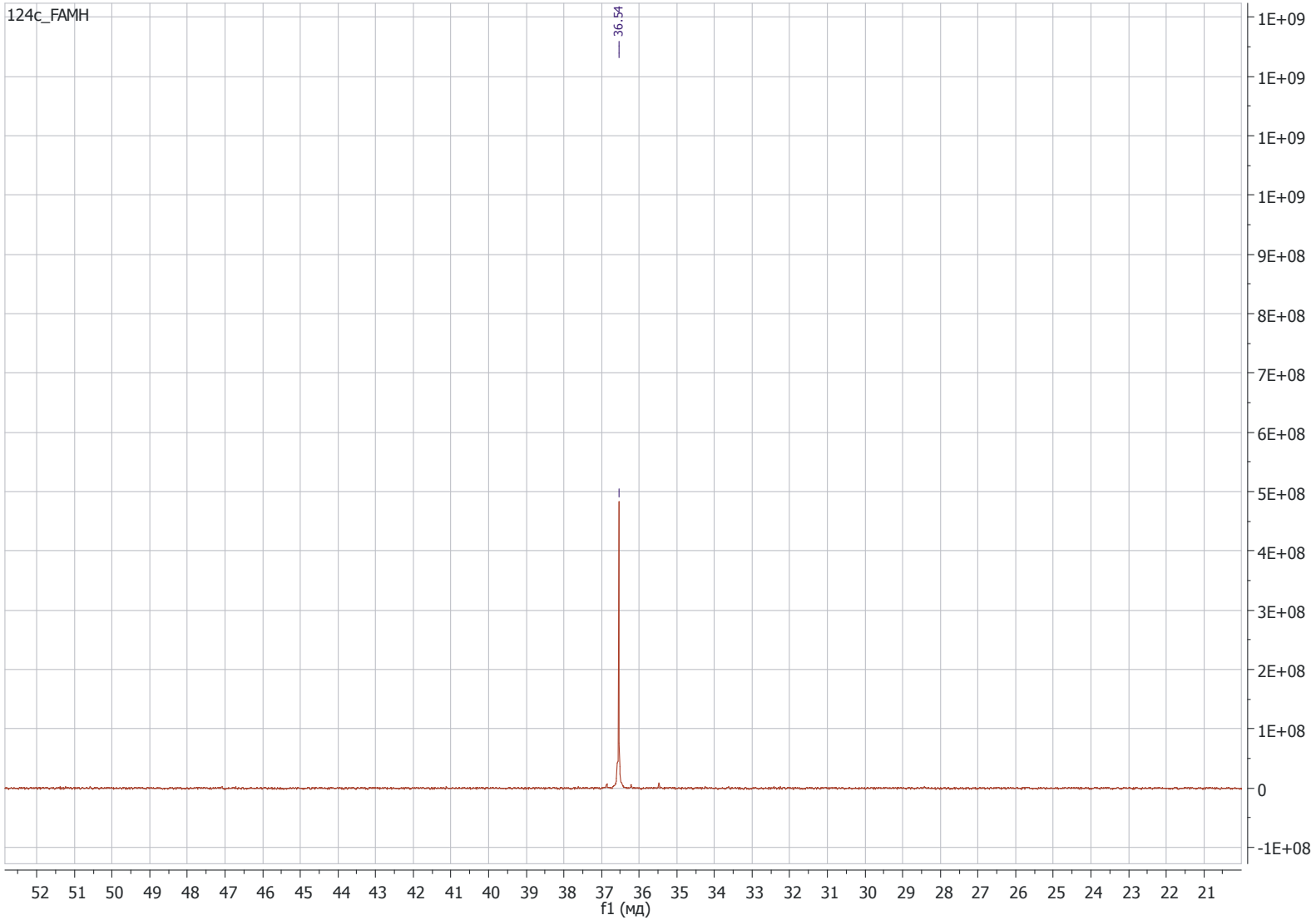

Figure 3S. ^{31}P NMR spectrum(81 MHz, $CDCl_3$, 298 K)of 2-[$Ph_2P(O)$]$C_6H_4NHC(t\text{Bu})$=N(2,6-$Me_2C_6H_3$) (**1**).

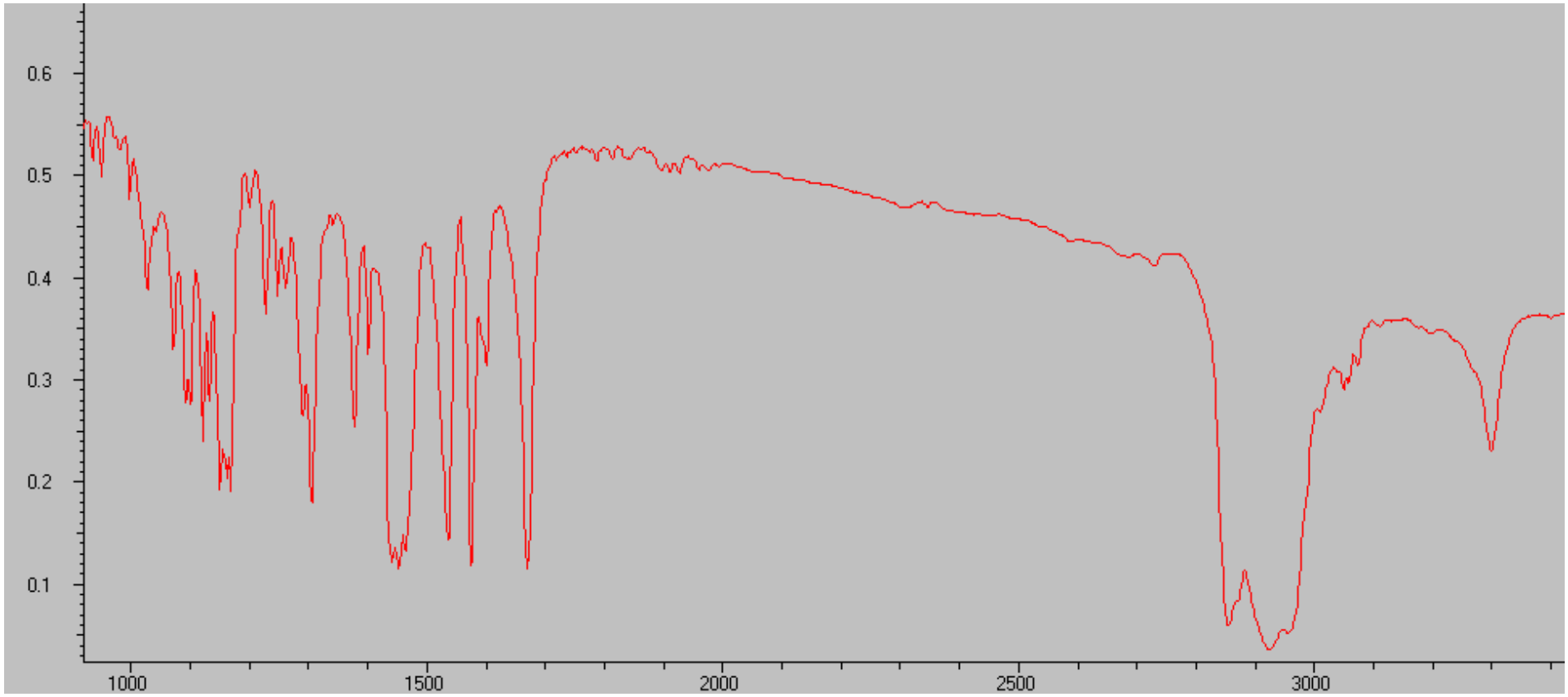

Figure 4S.IR spectrum of2-[$Ph_2P(O)$]$C_6H_4NHC(t$Bu)=N(2,6-$Me_2C_6H_3$) (**1**).

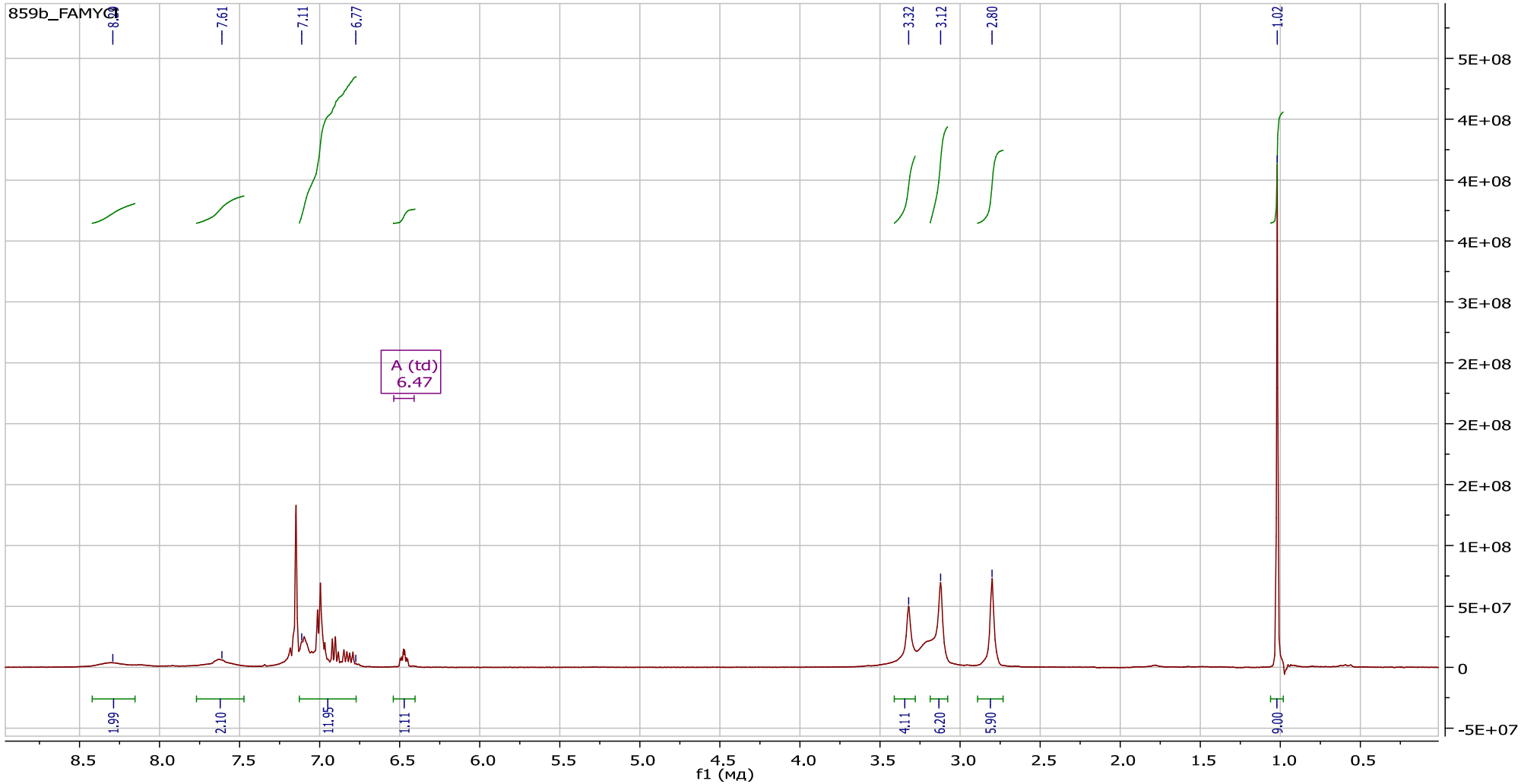

Figure 5S. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K)of{2-[$Ph_2P(O)$]$C_6H_4NC(t$Bu)N(2,6-$Me_2C_6H_3$)}YCl_2(DME) (**2**).

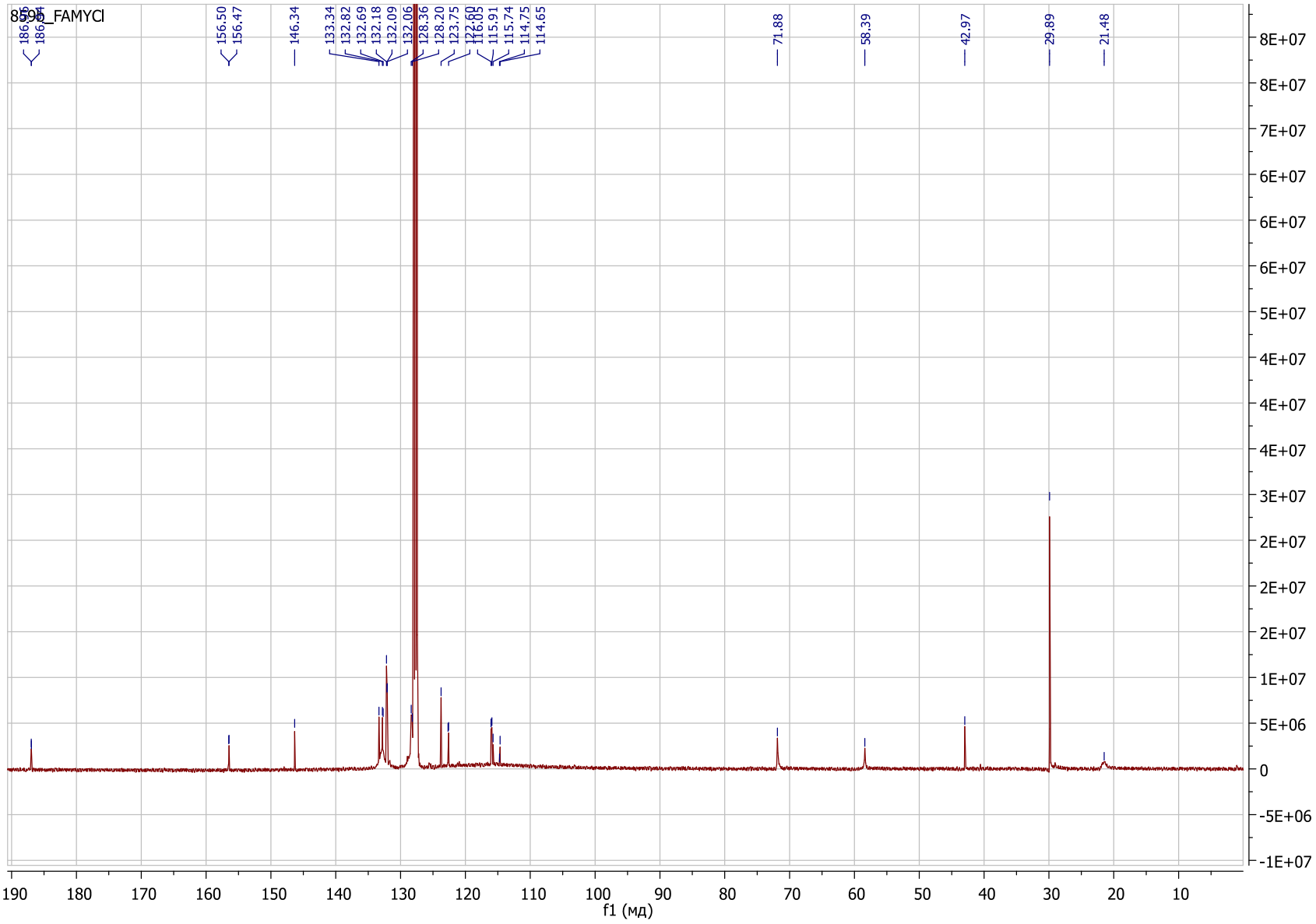

Figure 6S. ^{13}C NMR spectrum(100 MHz, C_6D_6, 298 K) of{2-[$Ph_2P(O)$]$C_6H_4NC(t$Bu)N(2,6-$Me_2C_6H_3$)}YCl_2(DME) (**2**).

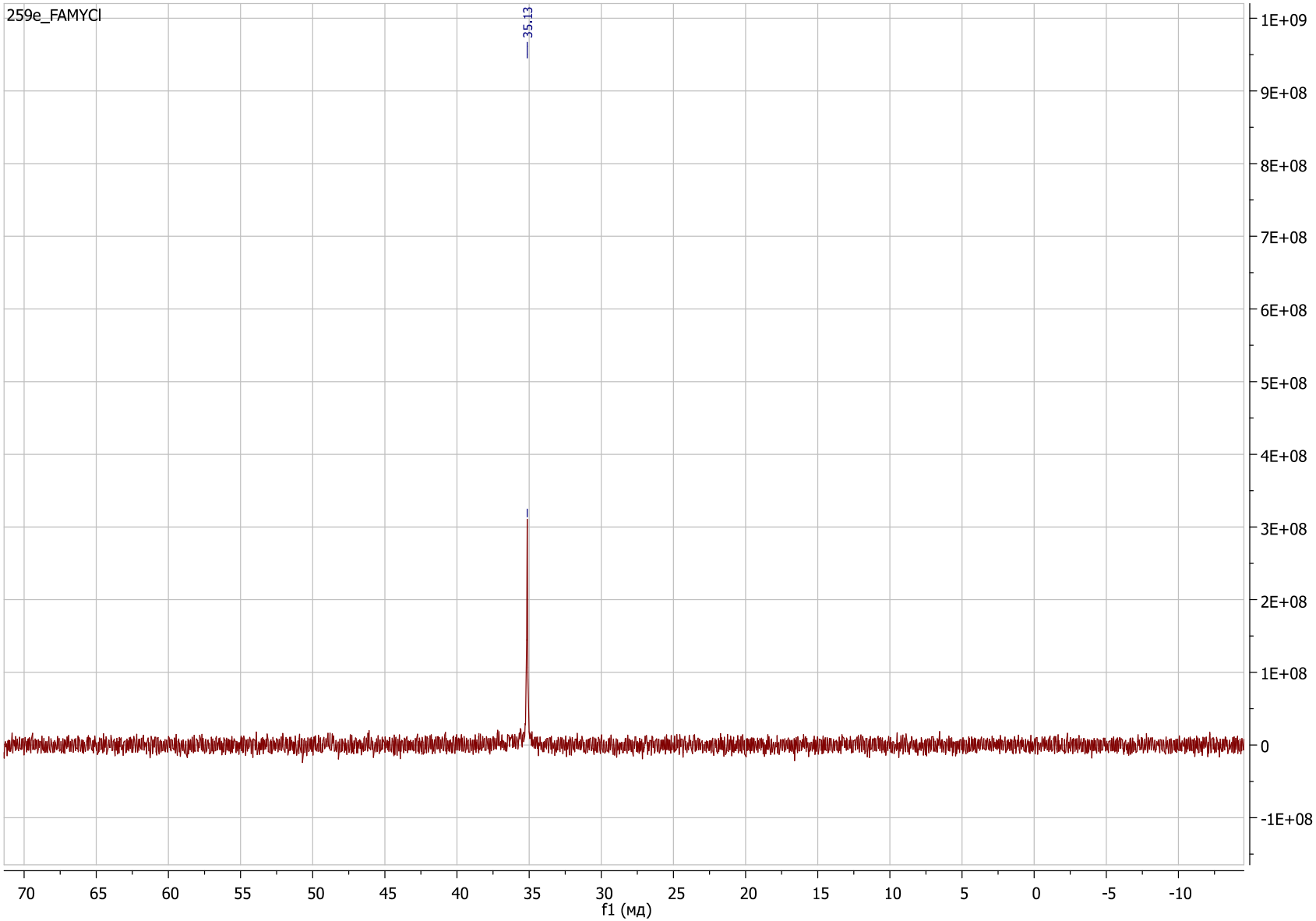

Figure 7S.^{31}P NMR spectrum(81 MHz, C_6D_6, 298 K)of{2-[$Ph_2P(O)$]$C_6H_4NC(t\text{Bu})N(2,6\text{-}Me_2C_6H_3)$}$YCl_2$(DME) (**2**).

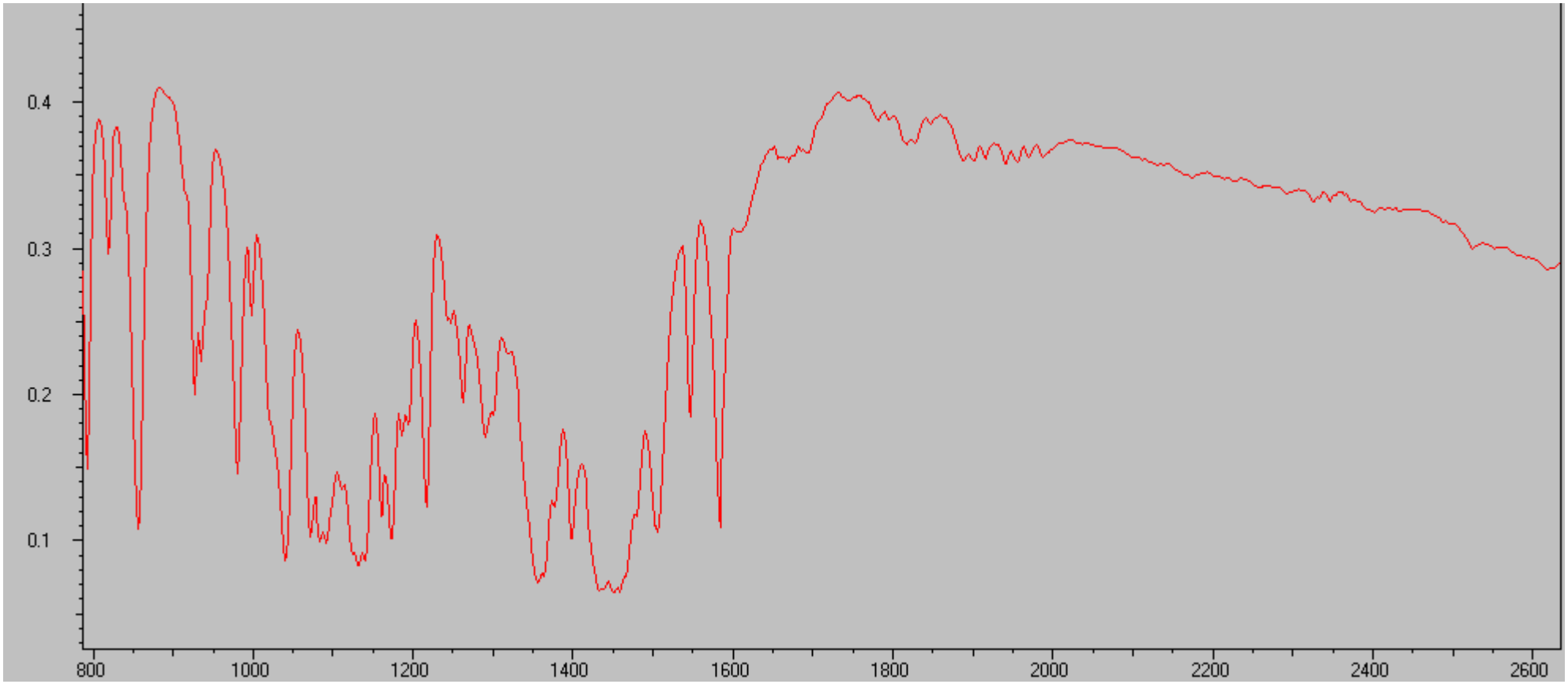

Figure 8S.IR spectrum of{2-[$Ph_2P(O)$]$C_6H_4NC(t$Bu)N(2,6-$Me_2C_6H_3$)}YCl_2(DME) (**2**).

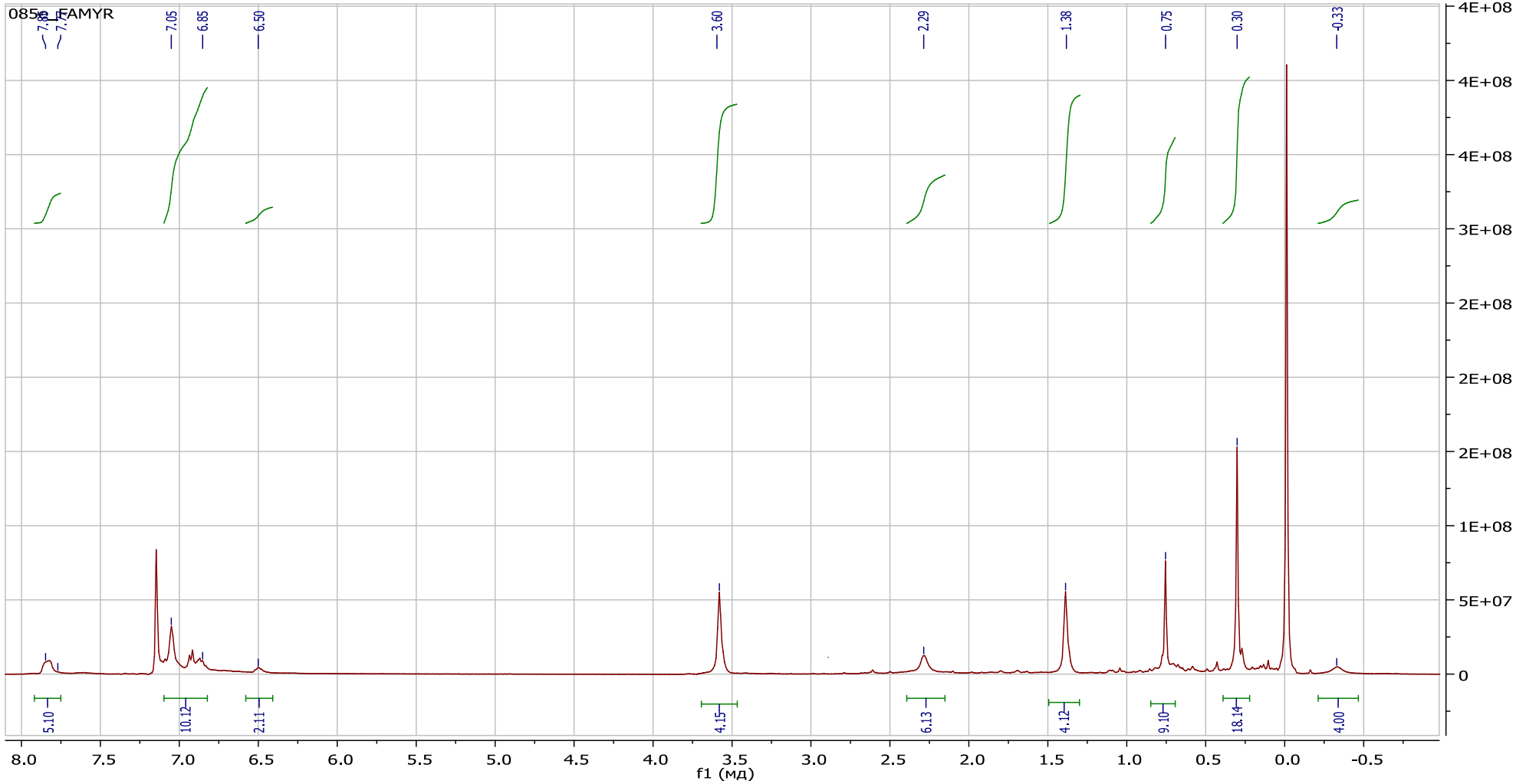

Figure 9S. ^{1}H NMR spectrum(400 MHz, C_6D_6, 298 K)of[2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Y(CH_2SiMe_3)$_2$THF] (**3**).

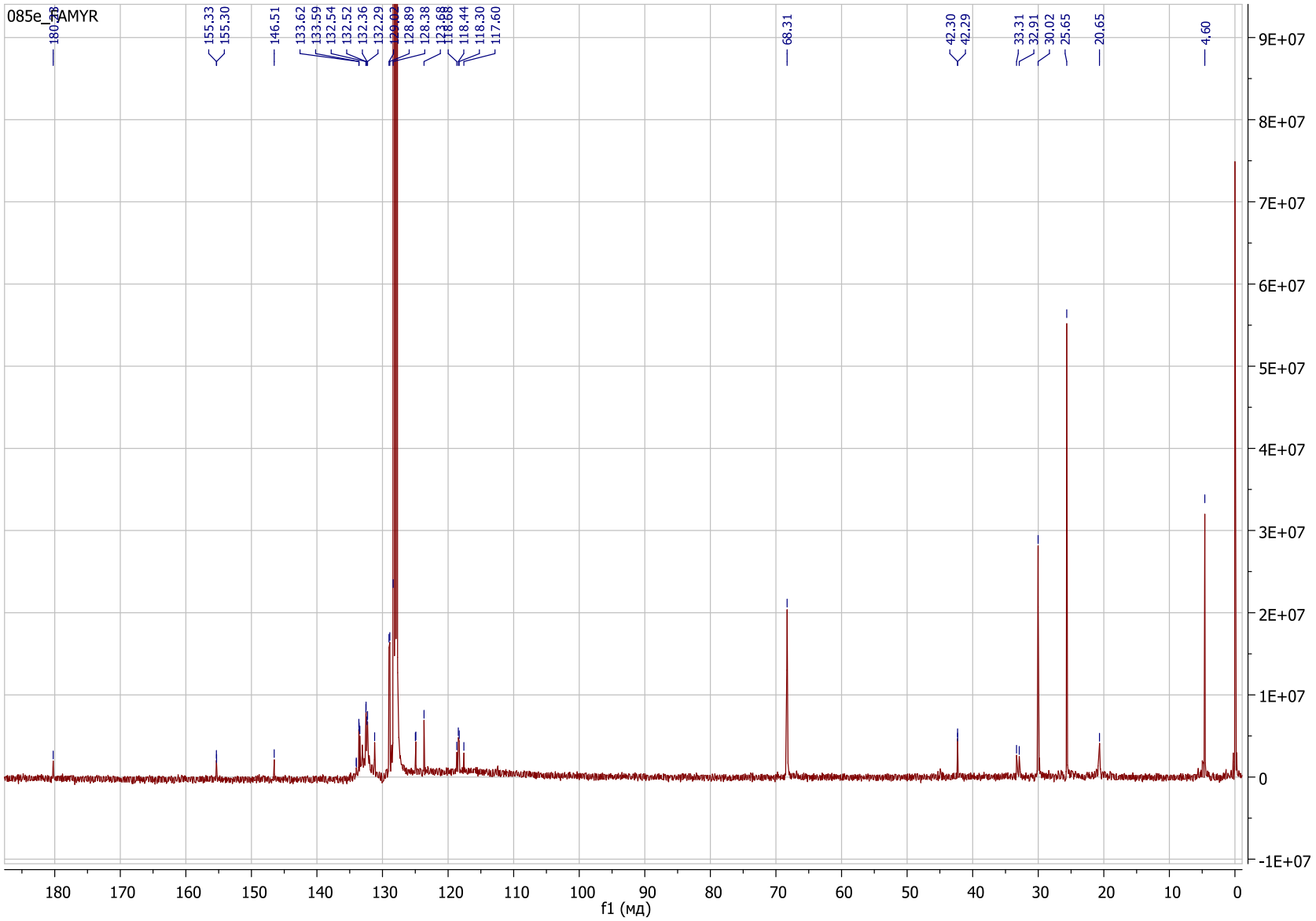

Figure 10S. ^{13}C NMR spectrum(100 MHz, C_6D_6, 298 K) of[2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Y(CH_2SiMe_3)$_2$THF] **(3).**

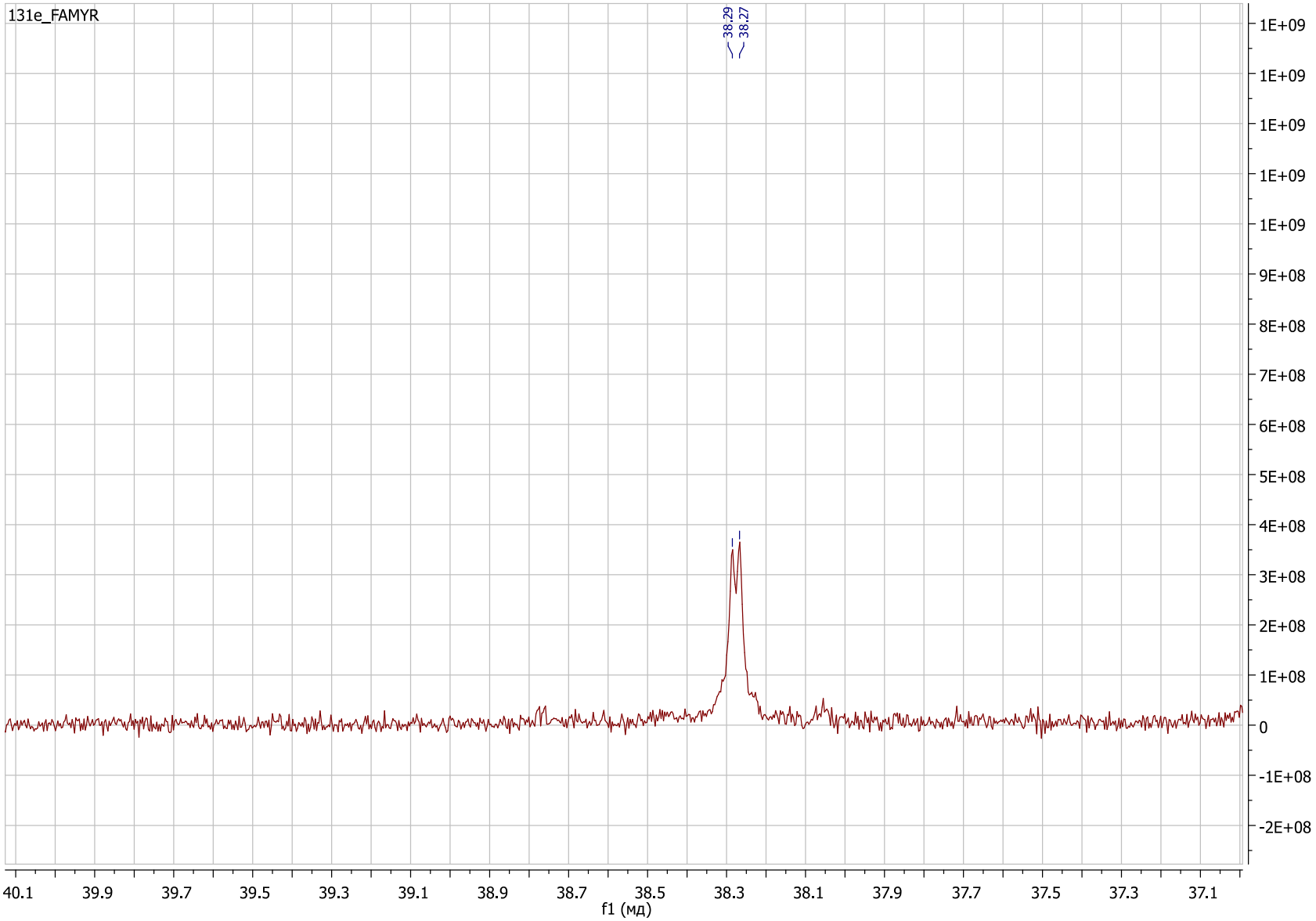

Figure 11S. ^{31}P NMR spectrum(81 MHz, C_6D_6, 298 K) of [2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Y(CH_2SiMe_3)$_2$THF] **(3).**

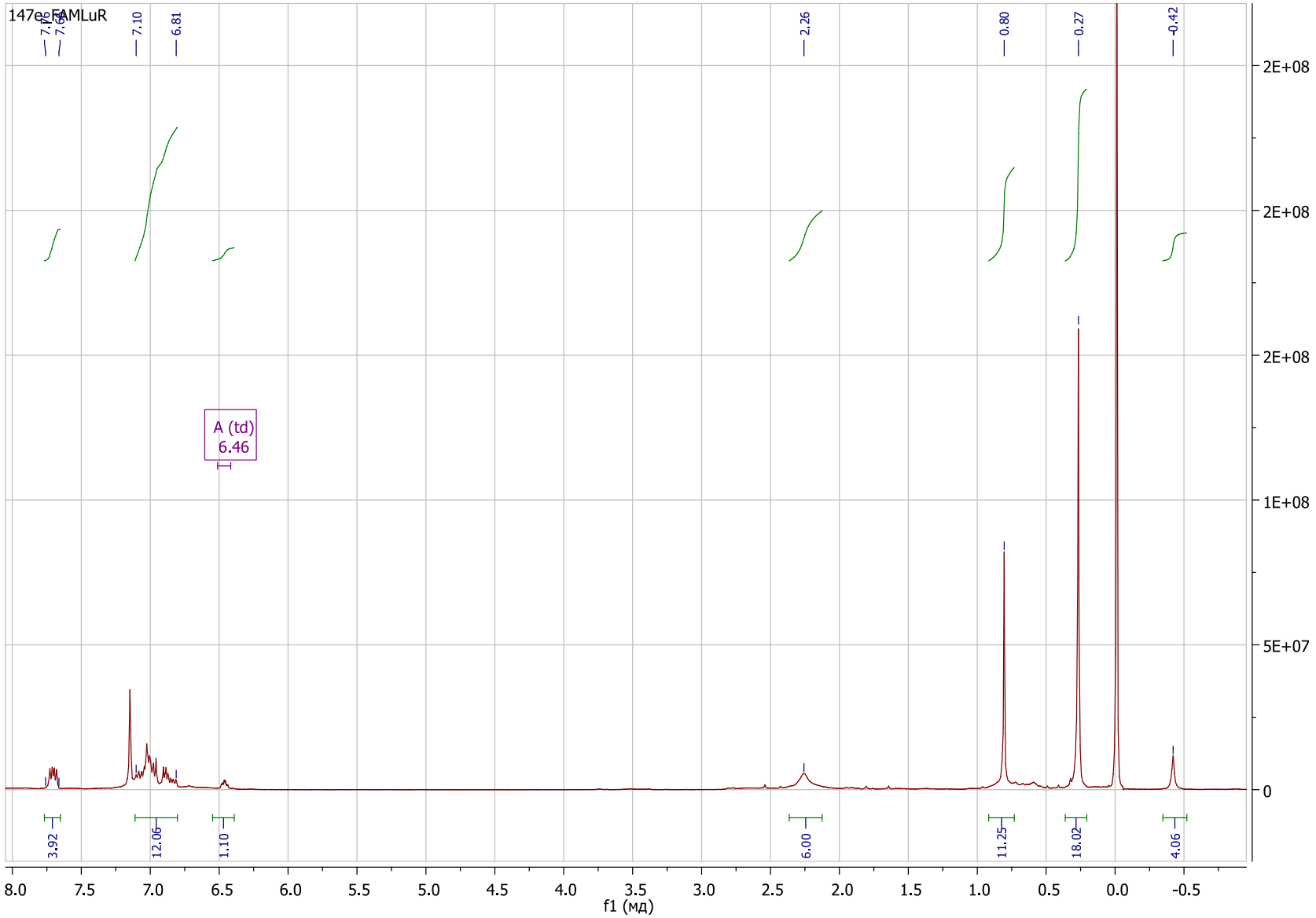

Figure 12S. ^{1}H NMR spectrum of(400 MHz, C_6D_6, 298 K)[2-(P(O)Ph_2)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Lu(CH_2SiMe_3)$_2$] **(5).**

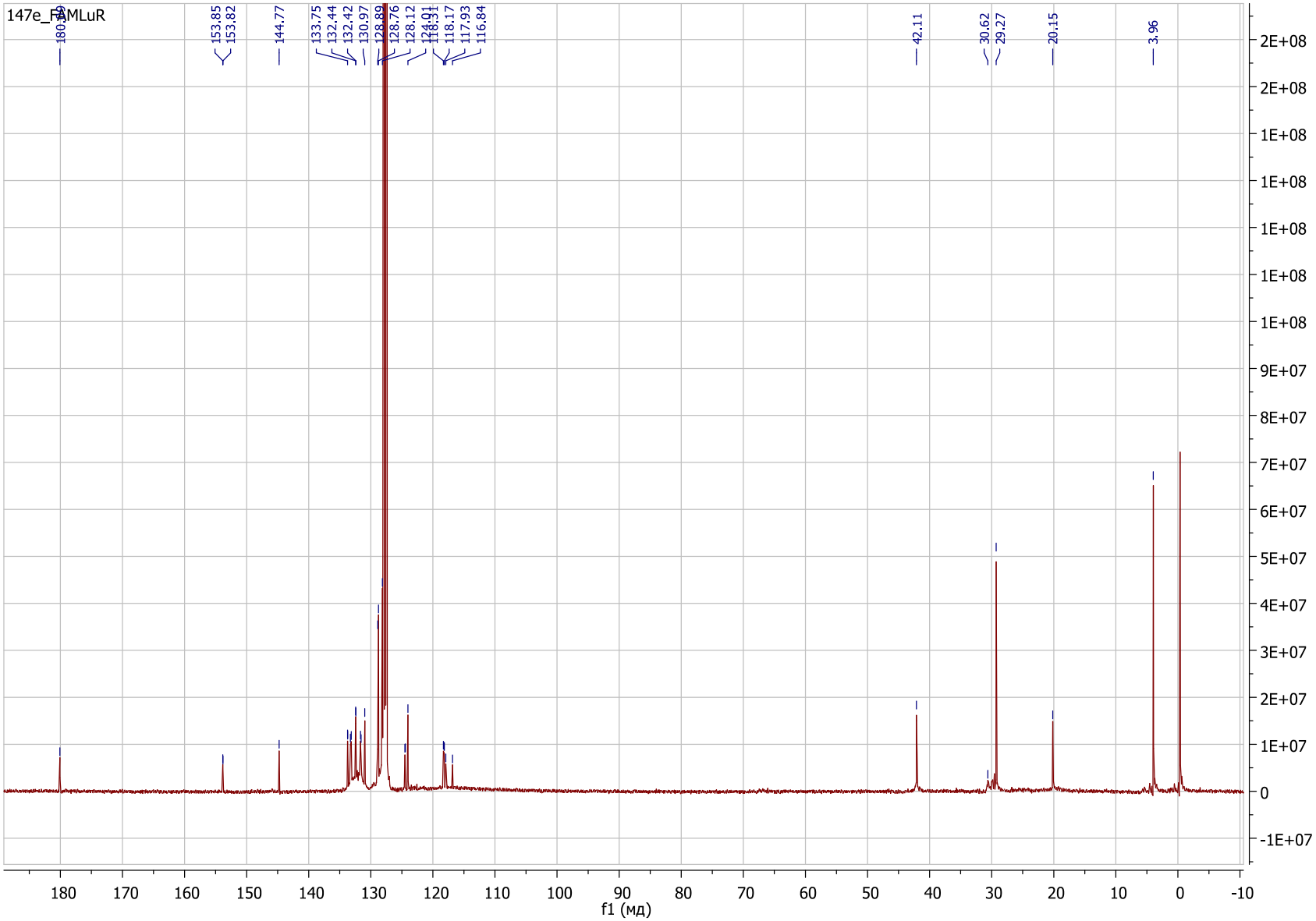

Figure 13S. ^{13}C NMR spectrum(100 MHz, C_6D_6, 298 K) of[2-($P(O)Ph_2$)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Lu(CH_2SiMe_3)$_2$] **(5).**

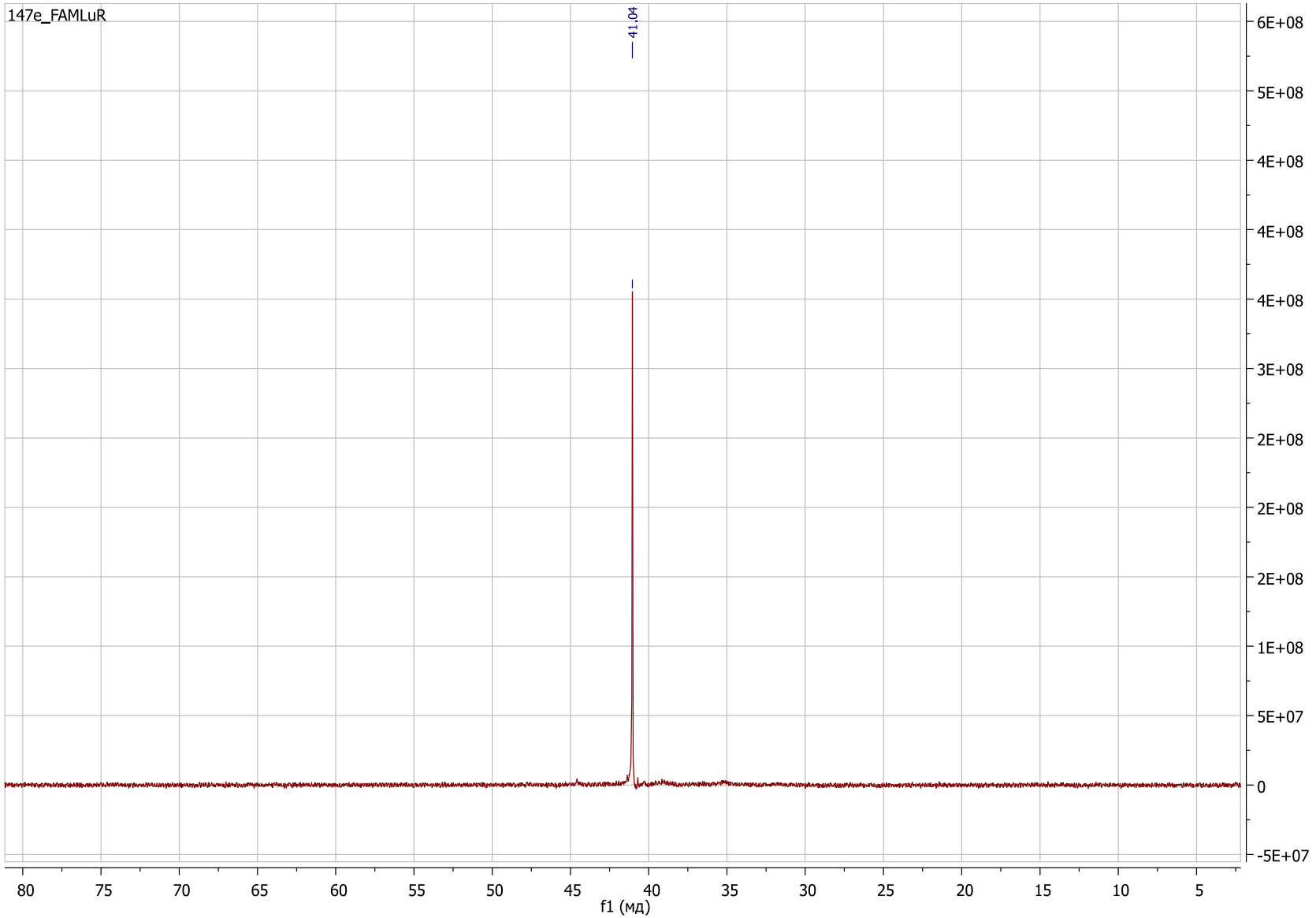

Figure 14S. ^{31}P NMR spectrum(81 MHz, C_6D_6, 298 K) of[2-($P(O)Ph_2$)PhNC(*t*Bu)(2,6-$Me_2C_6H_3$)Lu(CH_2SiMe_3)$_2$] **(5).**