

Supplementary Materials

Synthesis of *N,O*-Chelating Hydrazidopalladium Complexes from 1,2-Bis(trifluoroacetyl)hydrazine

Yoshihito Kayaki,* Tomohiro Hayakawa, and Takao Ikariya

Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-E4-1 O-okayama, Meguro-ku Tokyo 152-8552, Japan

*E-mail: ykayaki@o.cc.titech.ac.jp

Contents

	Page
X-ray Crystallographic Data for 2 and 3	S2
Copies of NMR Spectra of 2–4	S3

X-ray Crystallographic Data for 2 and 3

Table S1. Crystallographic data for 2 and 3

	2	3
Empirical Formula	C ₃₁ H ₂₆ F ₆ N ₂ O ₂ P ₂ Pd	C ₁₀ H ₁₆ F ₆ N ₄ O ₂ Pd
Formula Weight	740.90	444.65
Crystal Color, Habit	yellow, prism	orange, prism
Crystal System	orthorhombic	monoclinic
Space Group	<i>Pbca</i> (#61)	<i>P2₁/n</i> (#14)
Lattice Parameters	<i>a</i> = 14.952(6) Å <i>b</i> = 18.858(8) Å <i>c</i> = 20.029(9) Å	<i>a</i> = 13.0204(19) Å <i>b</i> = 8.1491 (10) Å <i>c</i> = 15.1590(19) Å <i>β</i> = 91.198(8) °
<i>Z</i> value	8	4
<i>D</i> _{calc}	1.584 g/cm ³	1.836 g/cm ³
<i>F</i> ₀₀₀	2976.00	880.00
μ(MoKα)	7.687 cm ⁻¹	12.289 cm ⁻¹
Exposure Rate	8.0 sec./°	4.0 sec./°
No. of Reflections Measured	46879	12071
No. of Unique Reflections	7096	3647
No. Variables	397	208
<i>R</i> 1 (<i>I</i> > 2.00σ(<i>I</i>))	0.0742	0.0417
w <i>R</i> 2 (All Reflections)	0.1593	0.1130
GOF on <i>F</i> ²	1.368	1.146

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR2 = \left[\frac{\sum (w(F_o^2 - F_c^2))^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

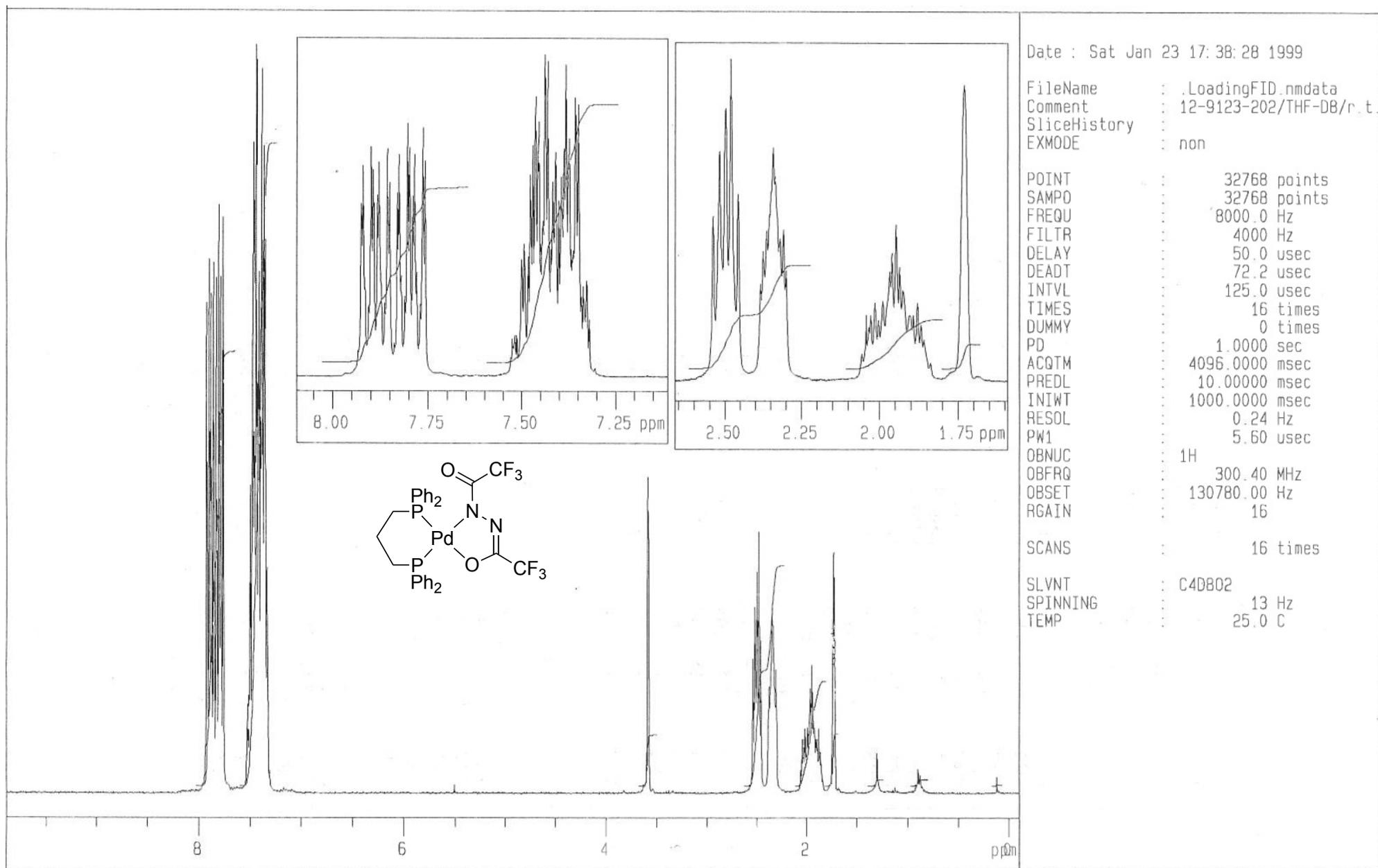


Figure S1. ¹H NMR Spectrum of **2** (THF-*d*₈, rt)

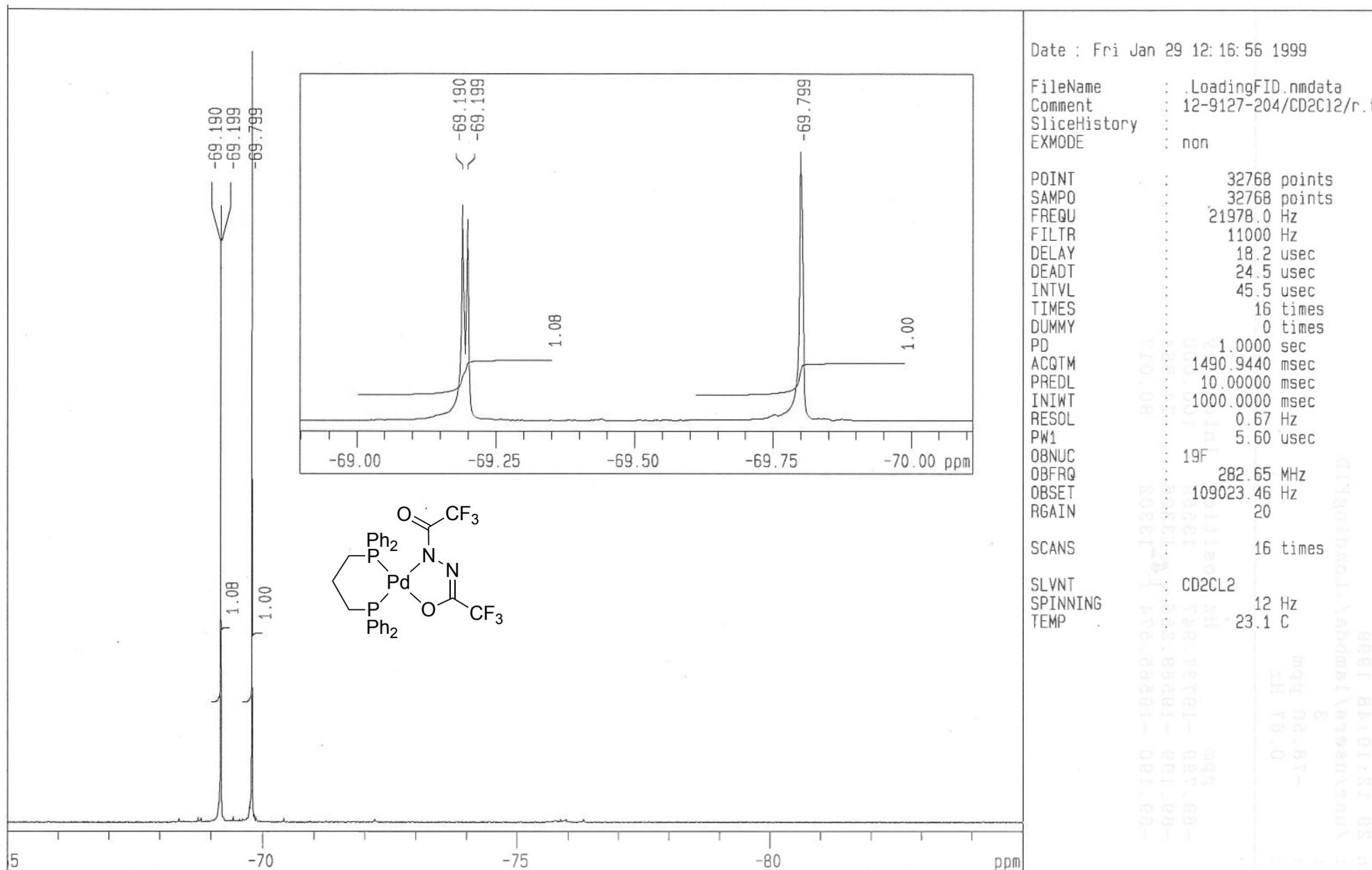


Figure S2. ^{19}F NMR Spectrum of **2** (CD_2Cl_2 , rt)

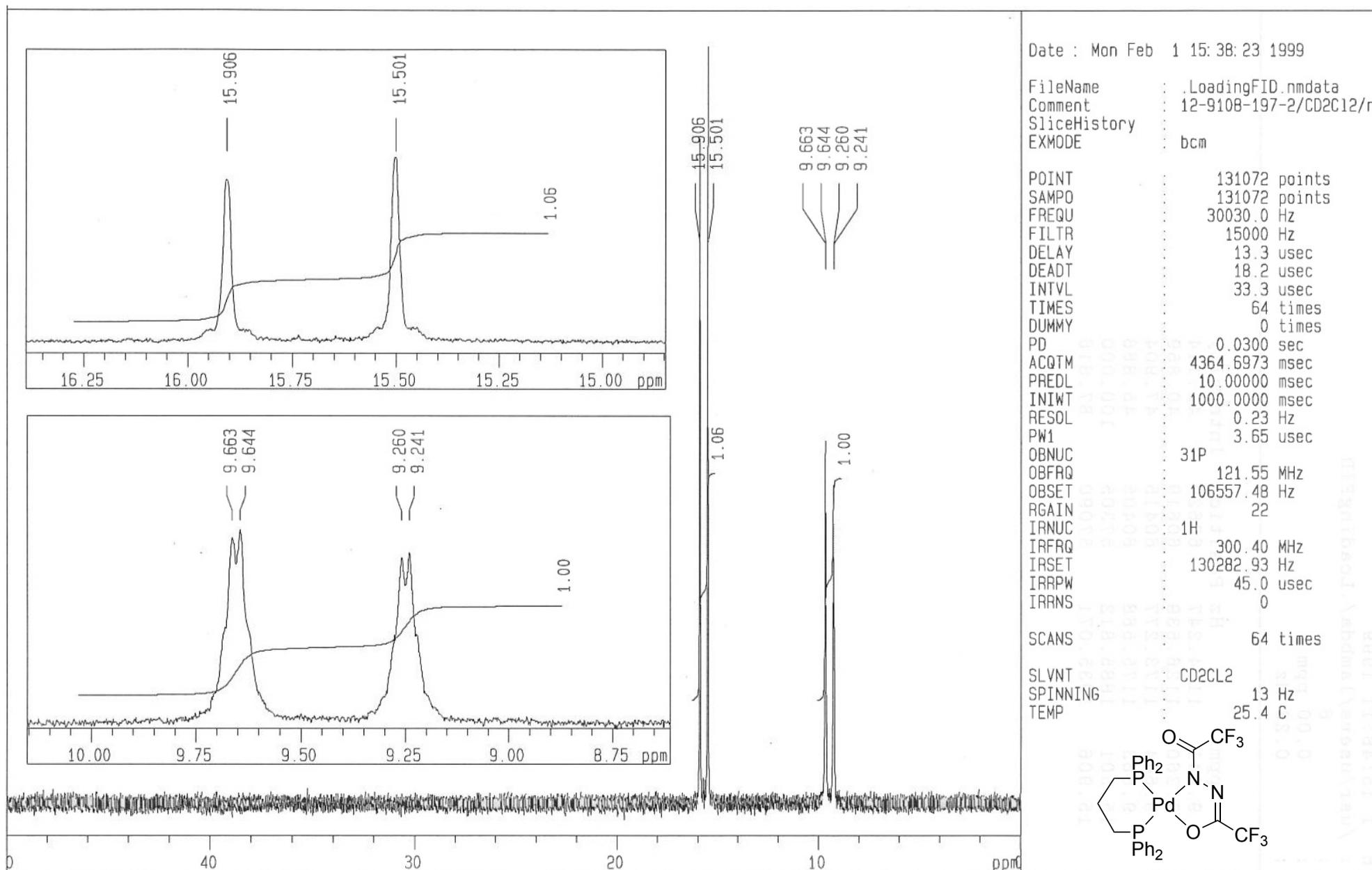


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of **2** (CD_2Cl_2 , rt)

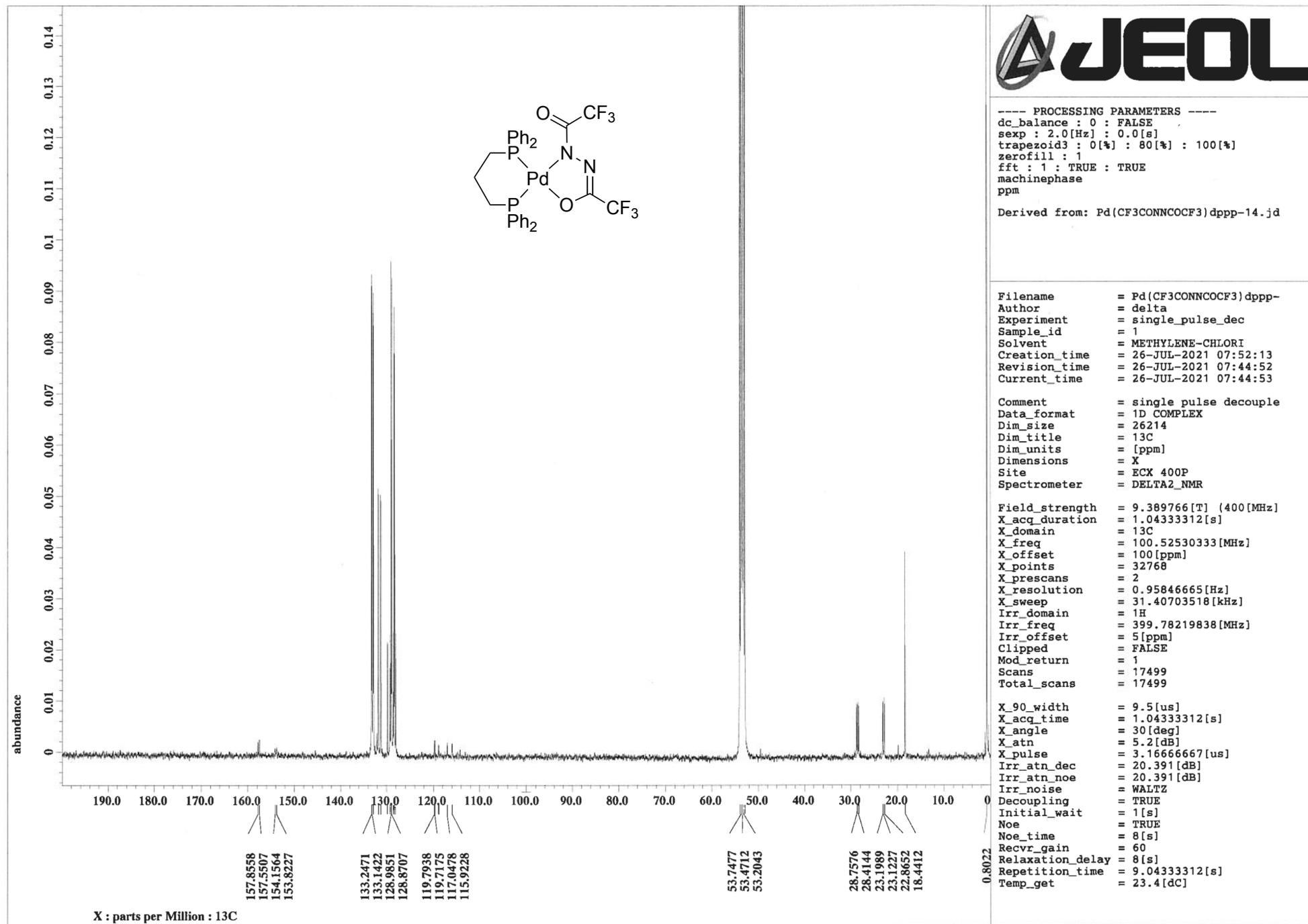


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2** (CD_2Cl_2 , rt)

---- PROCESSING PARAMETERS ----
 dc_balance : 0 : FALSE
 sexp : 0.2[Hz] : 0.0[s]
 trapezoid3 : 0[%] : 80[%] : 100[%]
 zerofill : 1
 fft : 1 : TRUE : TRUE
 machinephase
 ppm

Derived from: Pd(CF3CONNCOF3)(tmeda)-5.

Filename = Pd(CF3CONNCOF3)(tmeda)
 Author = delta
 Experiment = single_pulse.ex2
 Sample_id = 1
 Solvent = METHYLENE-CHLORI
 Creation_time = 14-MAY-2021 11:56:01
 Revision_time = 14-MAY-2021 11:44:29
 Current_time = 14-MAY-2021 11:44:52

Comment = single_pulse
 Data_format = 1D COMPLEX
 Dim_size = 26214
 Dim_title = 1H
 Dim_units = [ppm]
 Dimensions = X
 Site = ECX 400P
 Spectrometer = DELTA2_NMR

Field_strength = 9.389766[T] (400[MHz])
 X_acq_duration = 3.2768[s]
 X_domain = 1H
 X_freq = 399.78219838[MHz]
 X_offset = 5[ppm]
 X_points = 32768
 X_prescans = 0
 X_resolution = 0.30517578[Hz]
 X_sweep = 10[kHz]
 Irr_domain = 1H
 Irr_freq = 399.78219838[MHz]
 Irr_offset = 5[ppm]
 Tri_domain = 1H
 Tri_freq = 399.78219838[MHz]
 Tri_offset = 5[ppm]
 Clipped = FALSE
 Mod_return = 1
 Scans = 16
 Total_scans = 16

X_90_width = 14[us]
 X_acq_time = 3.2768[s]
 X_angle = 45[deg]
 X_atn = 2.1[dB]
 X_pulse = 7[us]
 Irr_mode = Off
 Tri_mode = Off
 Dante_presat = FALSE
 Initial_wait = 1[s]
 Recvr_gain = 44
 Relaxation_delay = 2[s]
 Repetition_time = 5.2768[s]
 Temp_get = 23.5[dC]

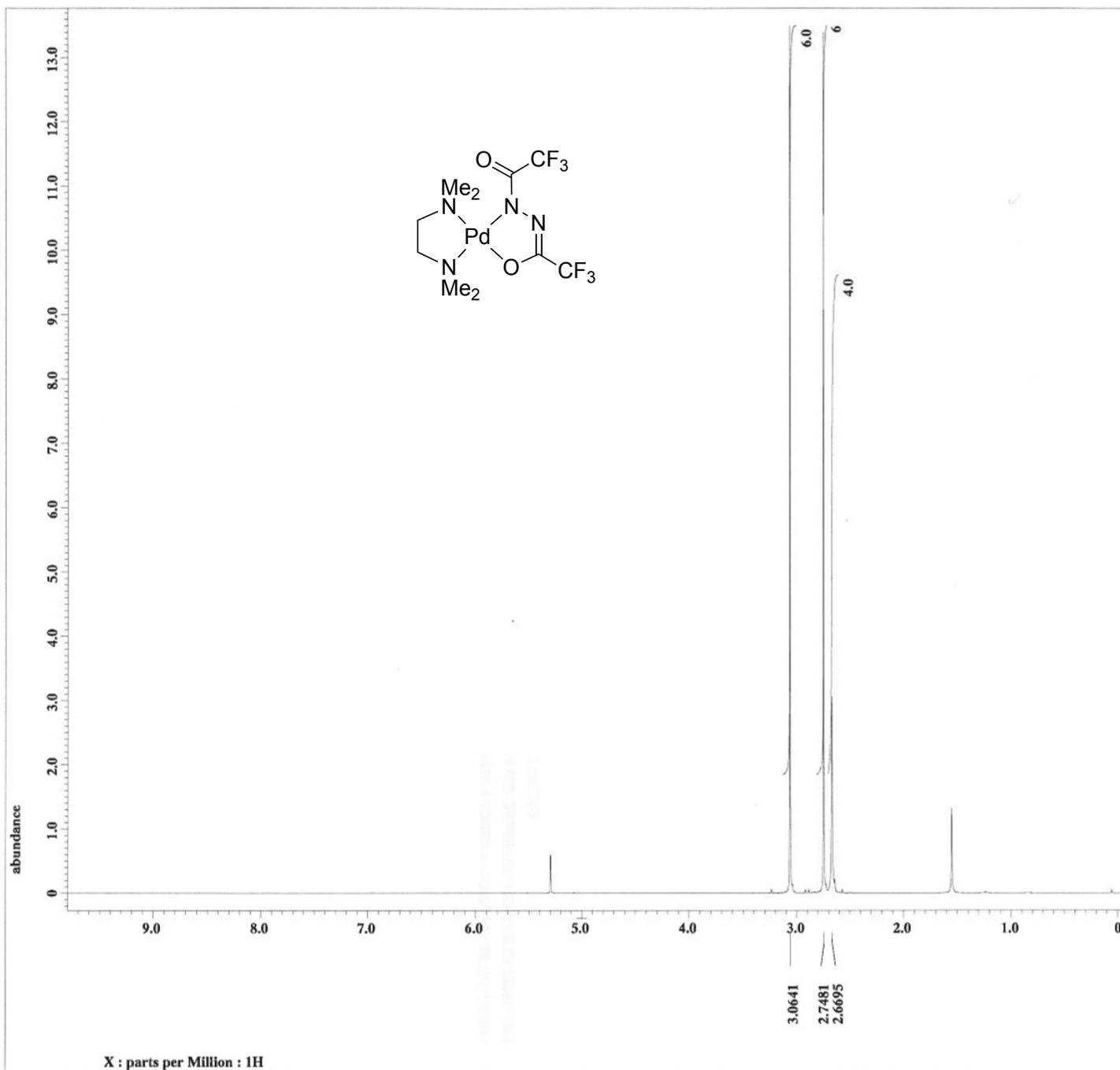


Figure S5. ¹H NMR Spectrum of **3** (CD₂Cl₂, rt)

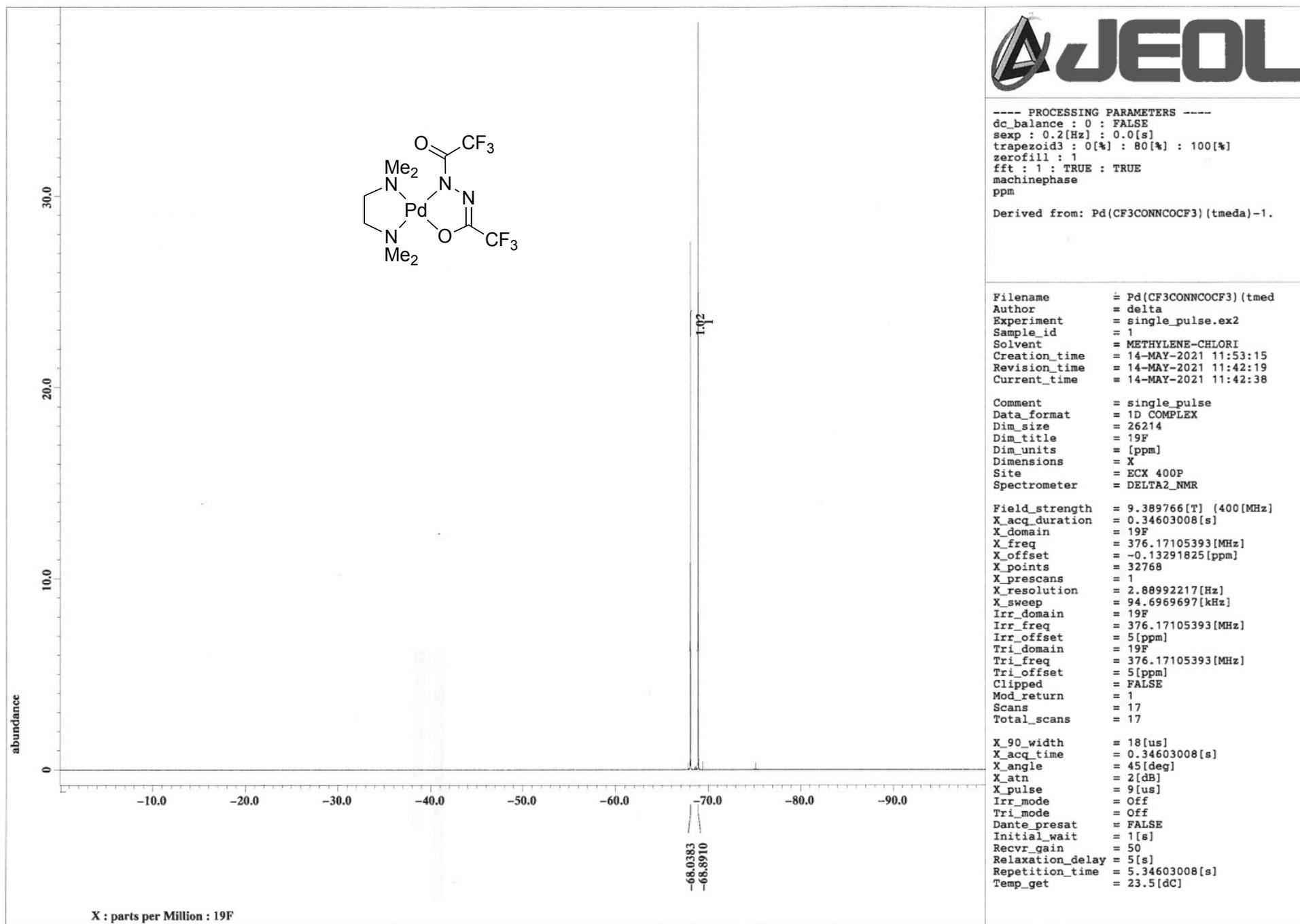


Figure S6. ^{19}F NMR Spectrum of **3** (CD_2Cl_2 , rt)

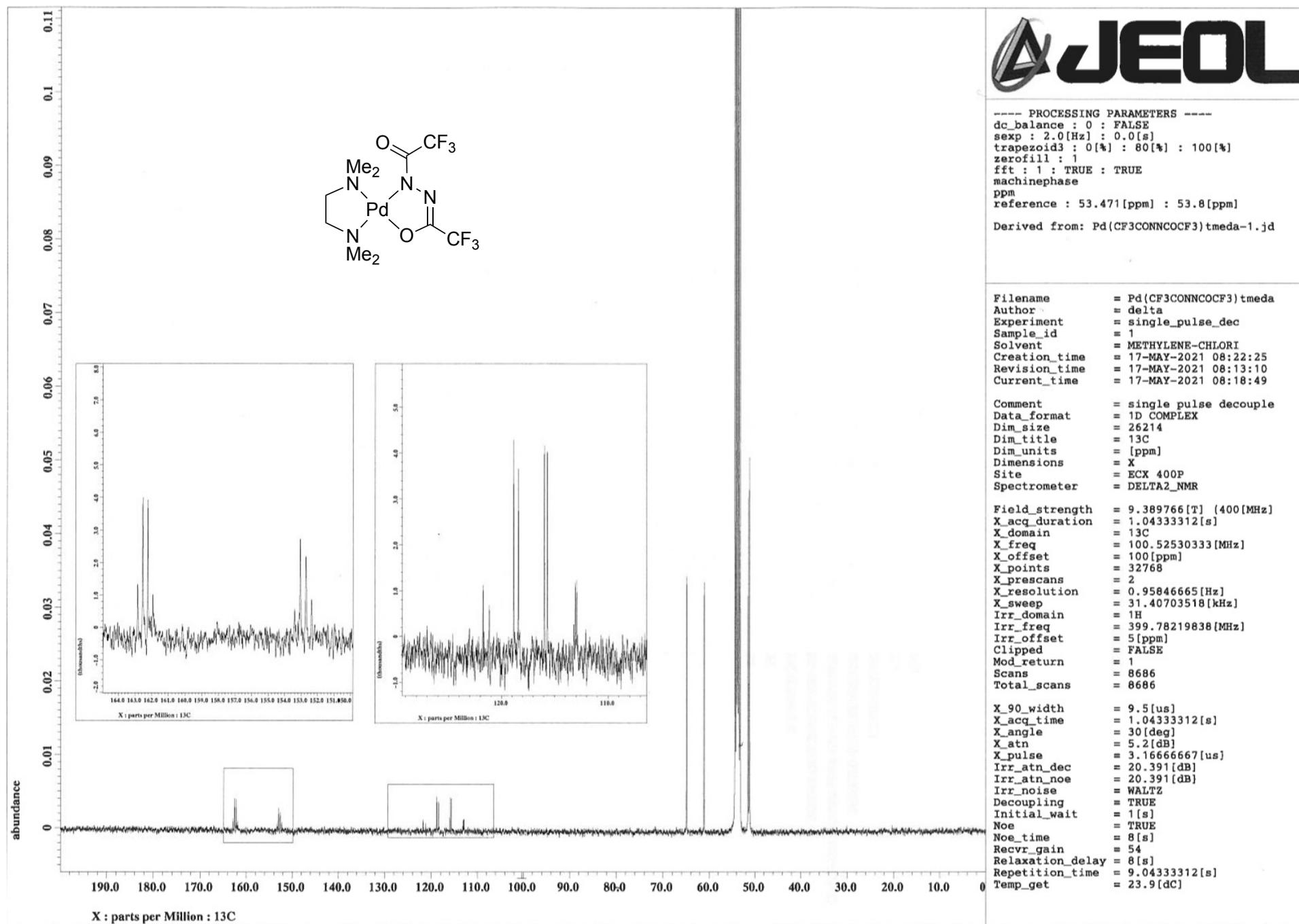


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **3** (CD_2Cl_2 , rt)

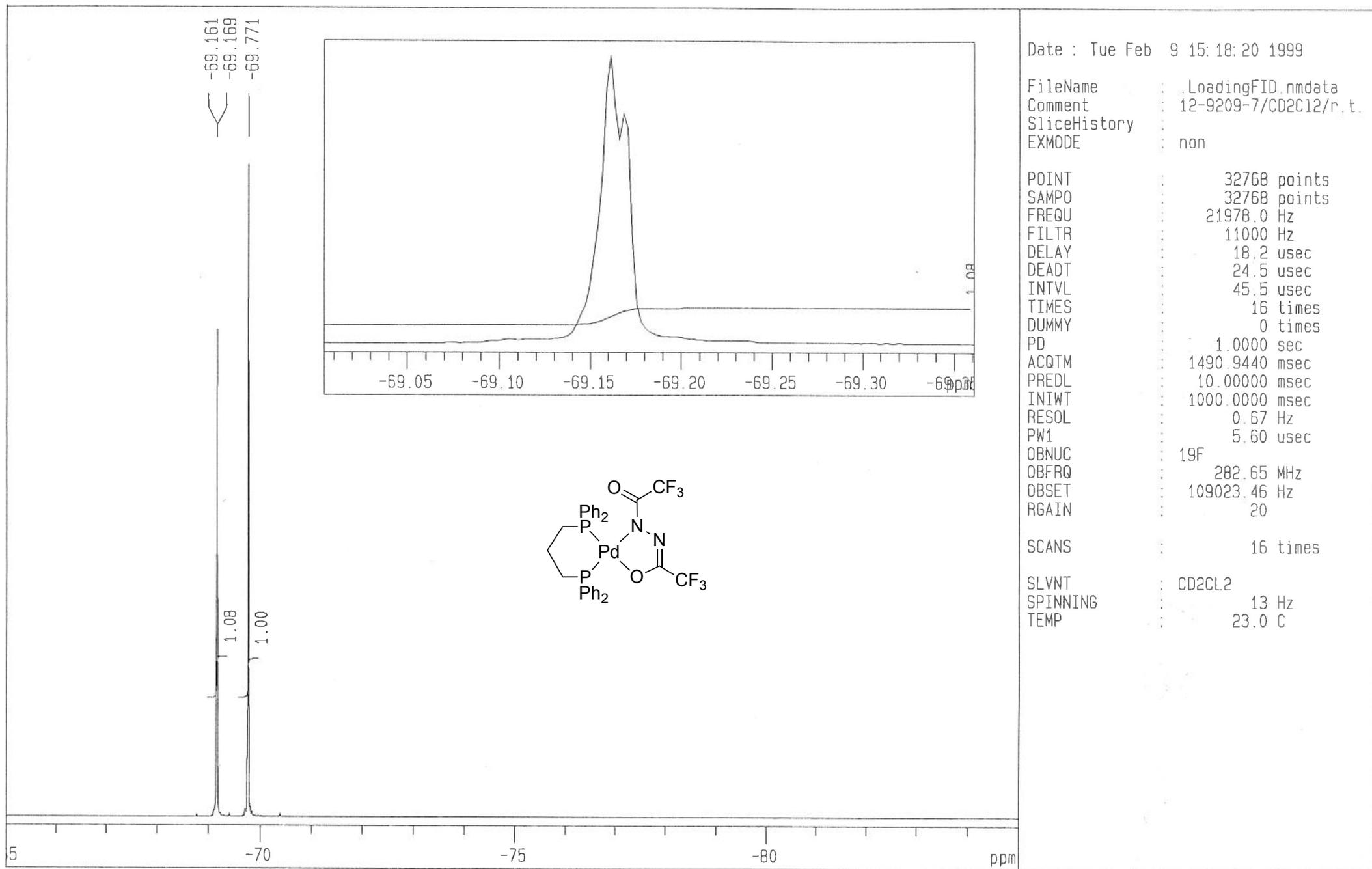


Figure S9. ^{19}F NMR Spectrum of **2** Prepared from $\text{Pd}(\text{OAc})_2$ (CD_2Cl_2 , rt)

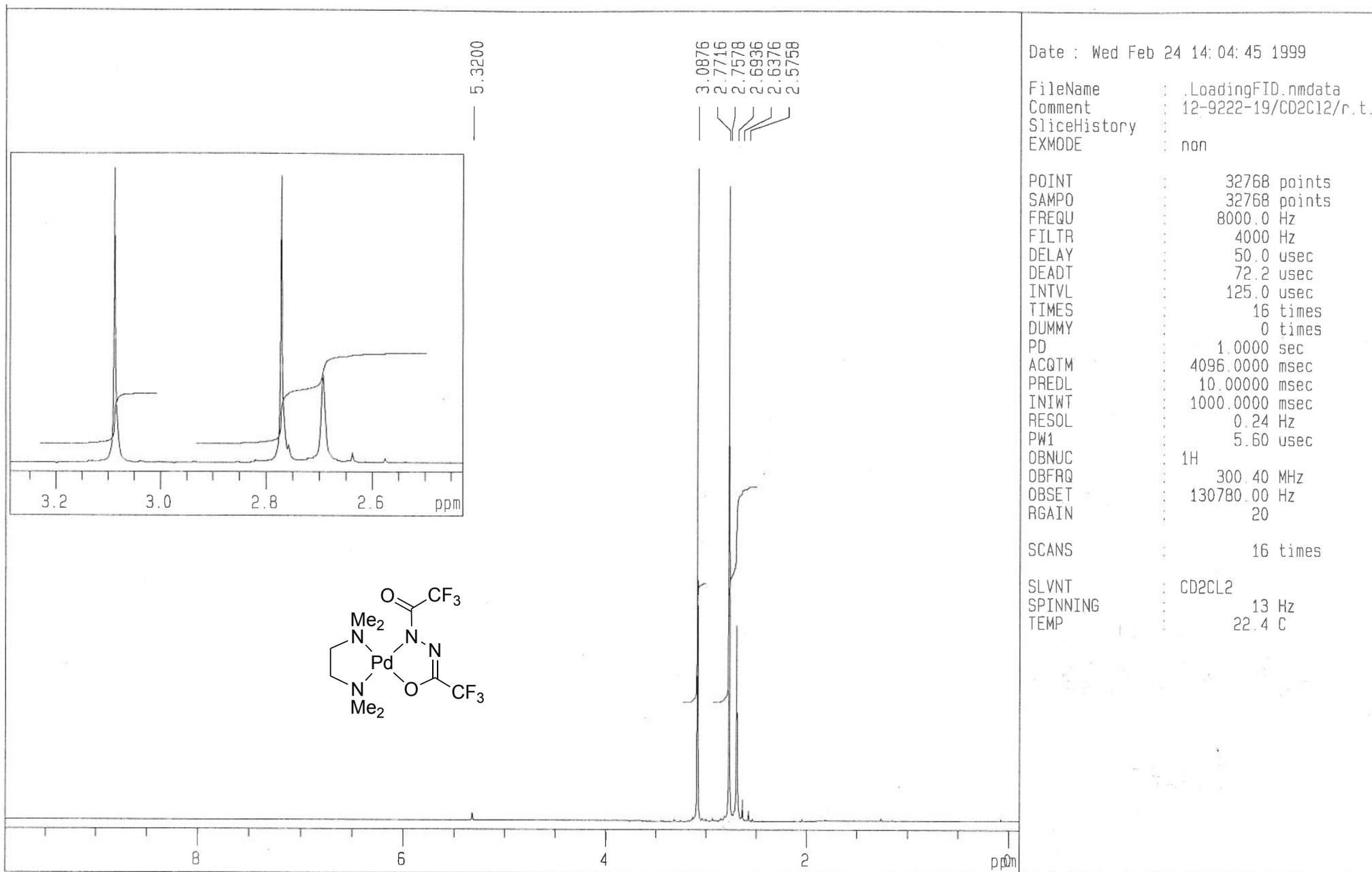


Figure S11. ¹H NMR Spectrum of **3** Prepared from Pd(OAc)₂ (CD₂Cl₂, rt)

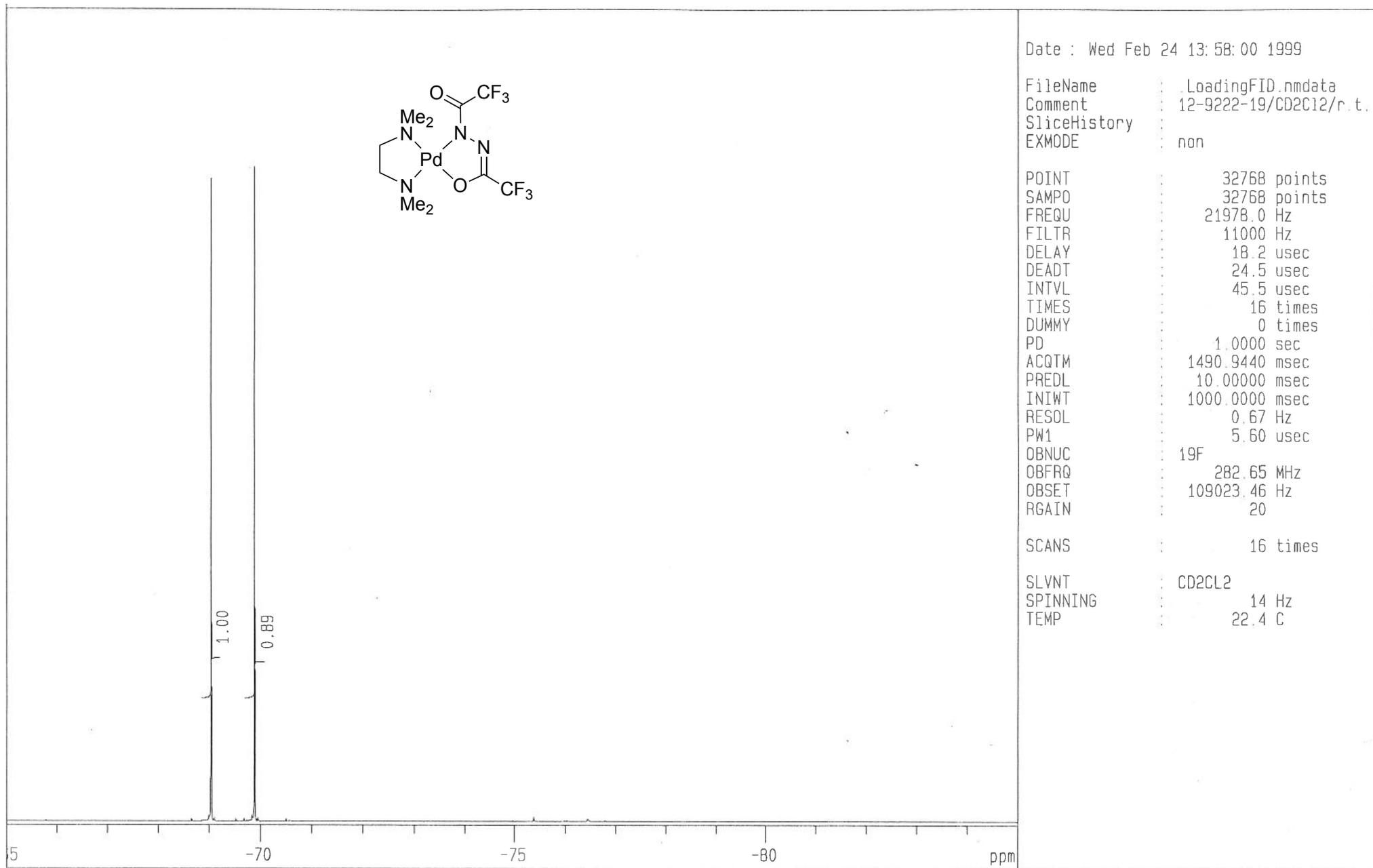


Figure S12. ¹⁹F NMR Spectrum of **3** Prepared from Pd(OAc)₂ (CD₂Cl₂, rt)

Solvent: CD₂Cl₂

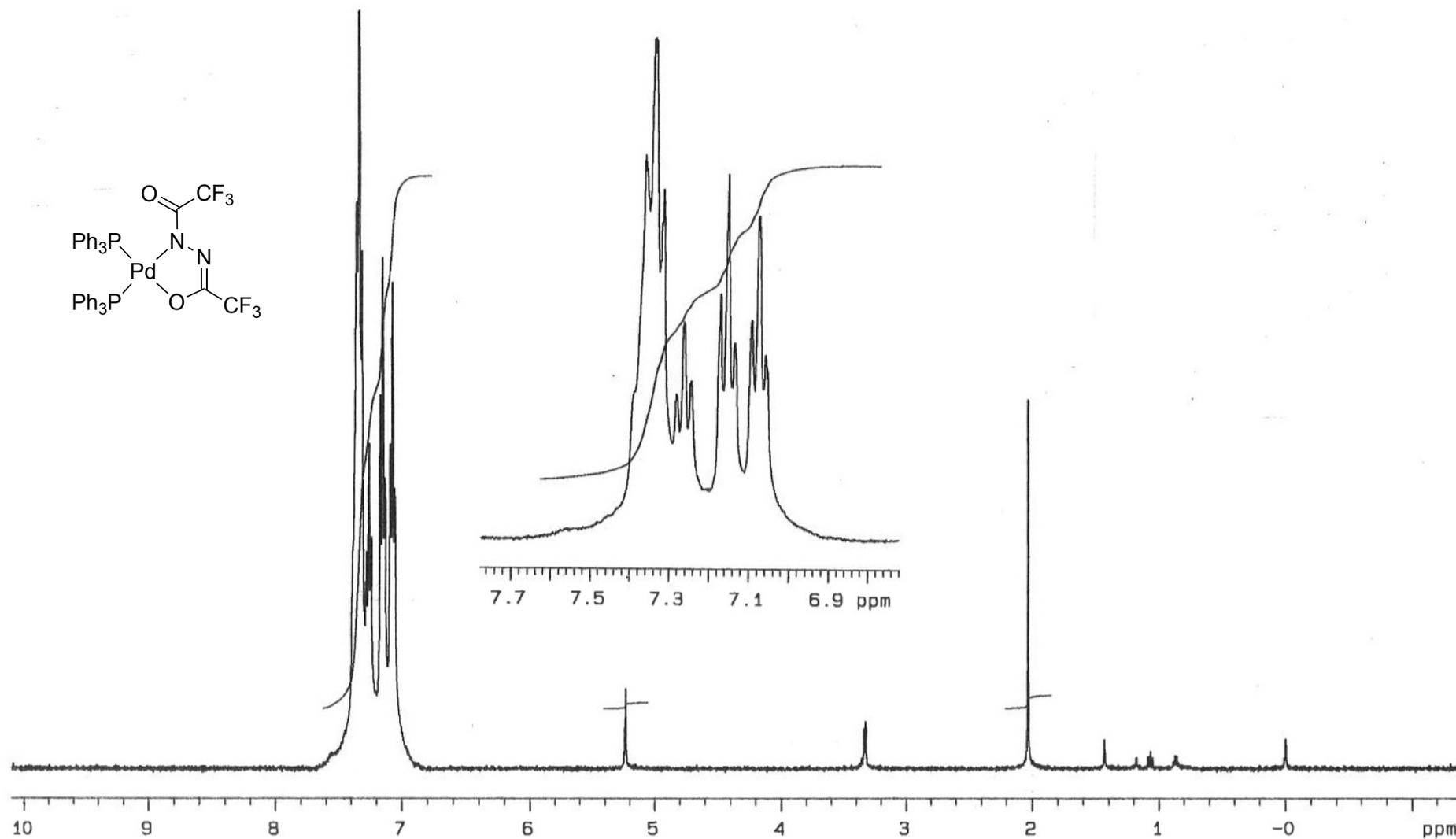


Figure S13. ¹H NMR Spectrum of **4** (CD₂Cl₂, rt)

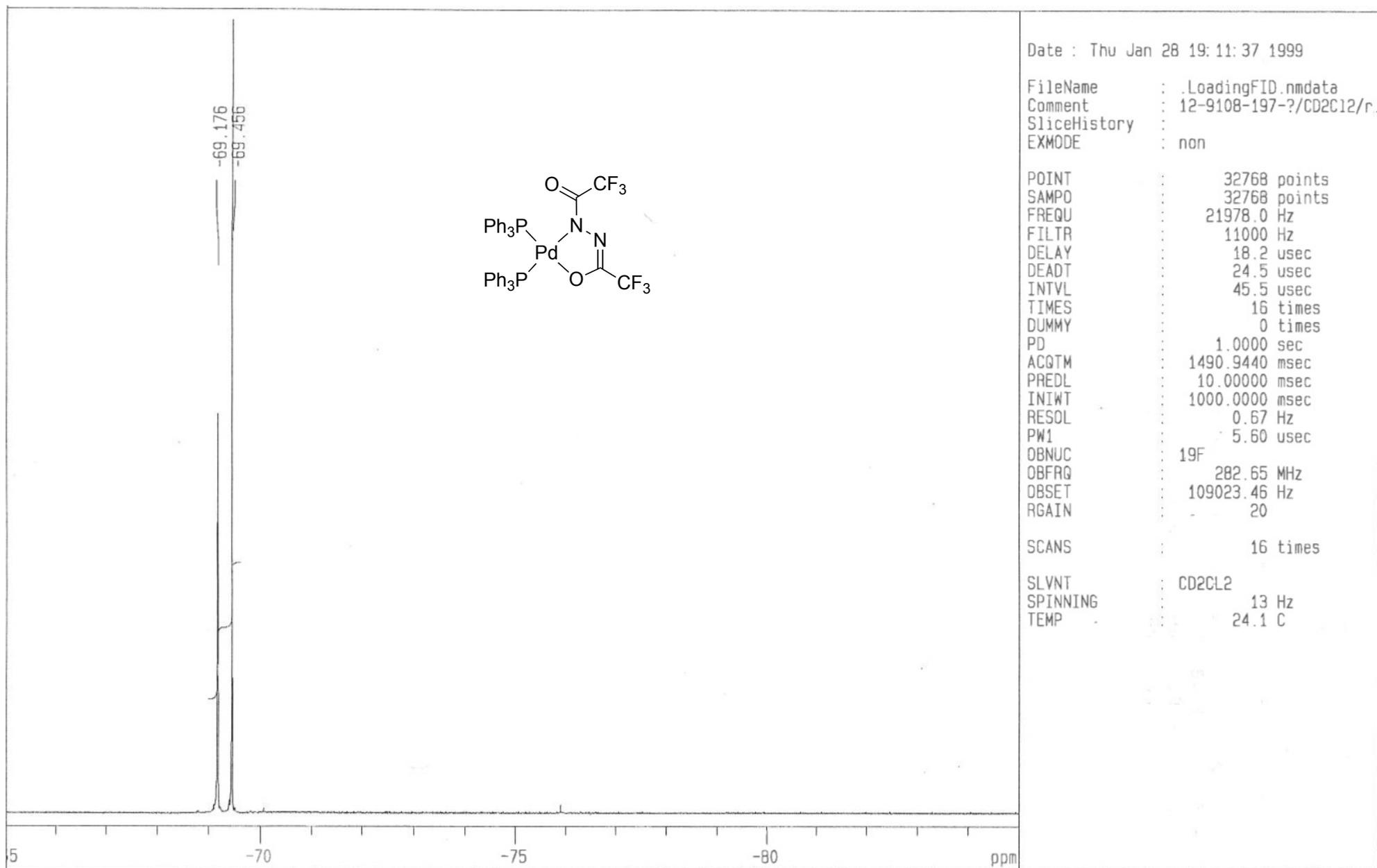


Figure S14. ¹⁹F NMR Spectrum of 4 (CD₂Cl₂, rt)

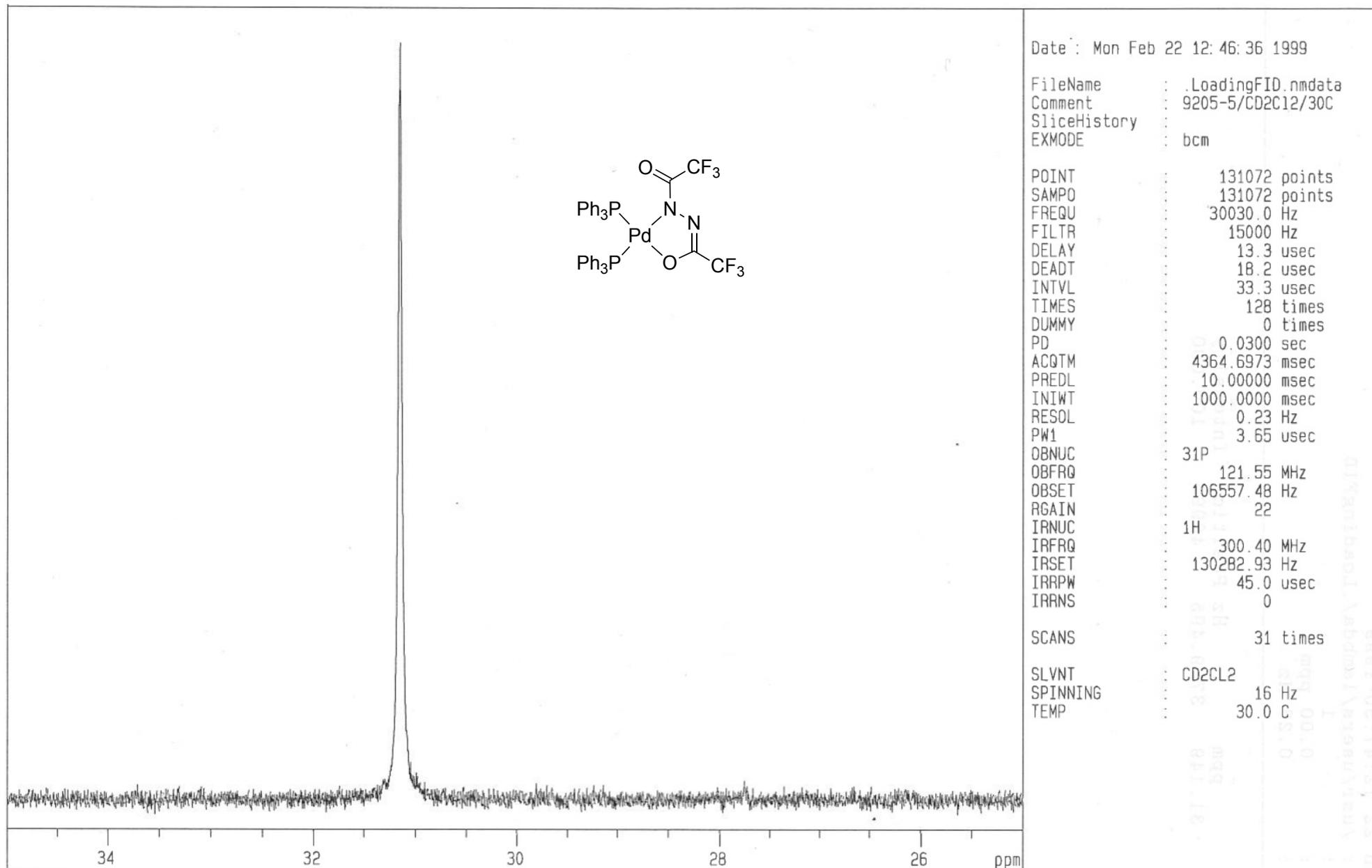


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of **4** (CD_2Cl_2 , rt)