Palladium Aminopyridine Complexes Catalyzed Selective Benzylic C-H Oxidations with Peracetic Acid

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Supporting Information

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Materials

For catalytic oxidation experiments, 35wt.% solution of peracetic acid in dilute acetic acid was used. $[Pd(CH_3CN)_4](OTf)_2$ was prepared from $Pd(OAc)_2$ as previously described.[1] Diethyl ether (Et_2O) was stored over NaOH and dried by heating under reflux over sodium in the presence of benzophenone as indicator and distilled. Dry acetonitrile (for syntheses) was obtained by distillation over P_2O_5 and stored over 4Å molecular sieves under argon. All other chemicals and solvents were purchased from Acros Organics, Aldrich, or Alfa Aesar and were used without additional purification.

Instrumentation

^1H and ^{13}C NMR spectra were measured on Bruker DPX-250 at 250.13 and 62.903 MHz, respectively, or on Bruker Avance 400 MHz spectrometer, at 400.13 and 100.613 MHz, respectively. For precise integration of ^{13}C NMR peaks during the NMR analyses of reaction mixtures, inverse-gated $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker DPX-250 at 62.903 MHz, with a 14 μs 90° pulse and with a 90 s delay between pulses; number of scans 1024-2048. Chemical shifts were internally referenced to tetramethylsilane. ^{19}F and ^{31}P NMR spectra were measured on Bruker DPX-250 at 235.330 and 101.255 MHz, respectively. Chemical shifts were externally referenced to 1,2-difluorobenzene (δ -139.0) and triphenylphosphine (-6.00), respectively.

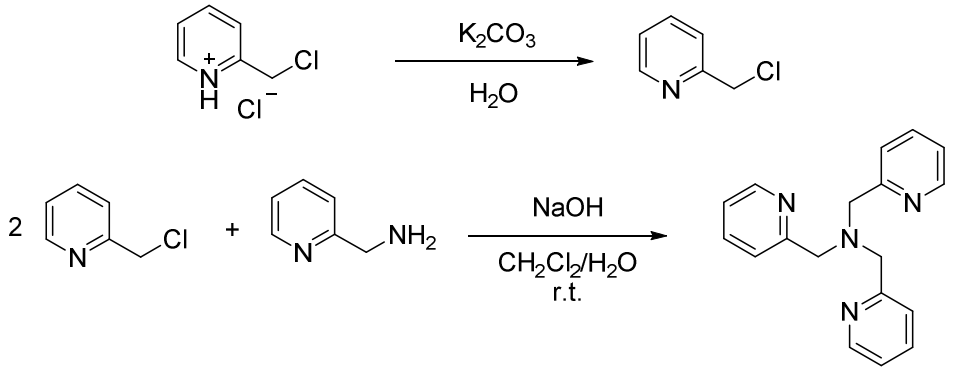
Shimadzu LC-20 with chiral stationary phase Chiralcel OD-H or Chiralcel OJ-H, 250×4.6 mm, was used for the analysis of reaction mixtures by HPLC method. For quantitative HPLC analysis, model mixtures containing arylalkanes and products of their oxidation were first analyzed by ^1H and/or quantitative ^{13}C NMR, and then sent to HPLC analysis in order to obtain the response coefficients of the UV/Vis detector (at λ 206 nm) for the components of the reaction mixtures.

Some of the reaction mixtures were analyzed by GC-MS using Agilent 7000B GC/MS with TripleQuad detector, EI – 70 eV, chromatograph Agilent 7890 equipped with a capillary column ZB-WAX [30 m × 0.25 mm × 0.25μm, He carrier gas].

CCDC 1994676 (**1**), 1994677 (**2**), 1992565 (**3**) and 1992566 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/data_request/cif and from the authors.

Synthetic procedures

tris(2-pyridylmethyl)amine (tpa)



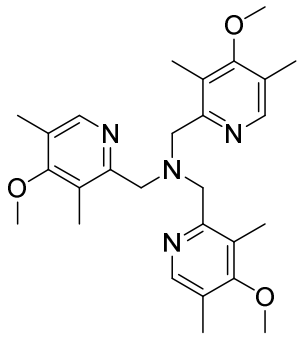
Potassium carbonate (1.45 g, 10.5 mmol) in water (1.4 ml) was added dropwise to the stirring solution of 2-chloromethylpyridine hydrochloride (1.17 g, 7 mmol) in water (0.8 ml). The resulting 2-chloromethylpyridine was then extracted with CH_2Cl_2 (10×7 ml). The organic phase was reduced under vacuum to ~10 ml, and CH_2Cl_2 was added to 20 ml. Then 2-(aminomethyl)pyridine (350 mg, 3.2 mmol) and solution of NaOH (252 mg, 6.3 mmol) in 10 ml H_2O were added, and resulting mixture was stirred for five days at room temperature. The organic phase was then separated and the aqueous phase was extracted with CH_2Cl_2 (2×20 ml). The organic extracts were combined and dried over sodium sulphate. The solvent was removed under reduced pressure, and the residue was dried under vacuum.

The obtained oil (tris(2-pyridylmethyl)amine) was mixed with 0.6 ml of water, cooled to 0°C and then concentrated $HClO_4$ (2.4 ml, 42 mmol) was accurately added in drops. After that the solution was stored at - 20°C for 24 hours. The precipitated ligand salt was filtered, washed with diethyl ether (4×10 ml) and dried in vacuum. The resulting product tpa·3HClO4 is a pale pink powder. The yield is 64 %.

^{1}H NMR of tpa·3$HClO_4$ (250.130 MHz, CD_3CN, 25°C), δ: 8.78 (d, $^3J_{HH}$ = 5.3 Hz, 3H, aromatic *H*), 8.56 (td, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 3H, aromatic *H*), 8.07 (d, $^3J_{HH}$ = 8.0 Hz, 3H, aromatic H), 8.04 – 7.96 (m, 3H, aromatic *H*), 4.28 (s, 6H, methylene *H*).

The free ligand was obtained just before the synthesis of Pd (II) complexes as follows. An aqueous solution of K_2CO_3 (6 equiv.) was added dropwise to the stirring solution of tpa·3$HClO_4$ (1 equiv.) in small amounts of water. The resulting ligand was extracted with CH_2Cl_2. The organic phase was dried over sodium sulfate. The solvent was carefully removed, and then the residue was dried under vacuum.

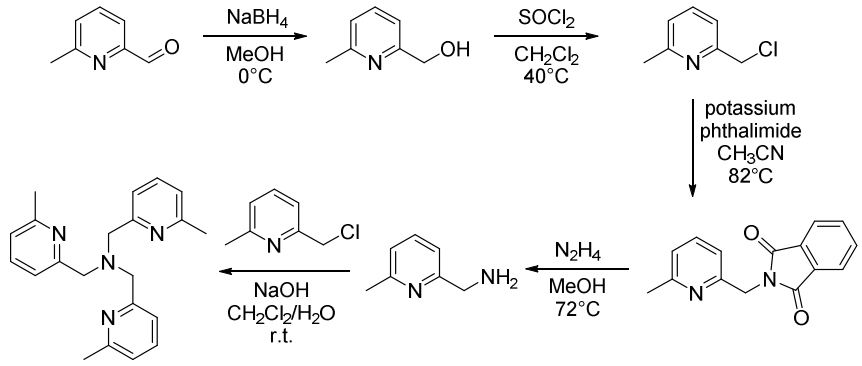
tris((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)amine



Ligand was synthesized in a similar way as tpa from 2-chloromethyl-4-methoxy-3,5-dimethylpyridine and (4-methoxy-3,5-dimethylpyridin-2-yl)methylamine.

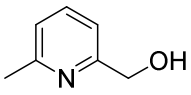
^{1}H NMR (250.13 MHz, CD_3CN, 25°C), δ: 8.19 (s, 3H, aromatic *H*), 3.75 (s, 6H, methylene *H*), 3.66 (s, 9H, OCH_3), 2.23 (s, 9H, methyl *H*), 1.62 (s, 9H, methyl *H*).

tris((6-methylpyridin-2-yl)methyl)amine (6Me-tpa)



Ligand **6Me-tpa** was obtained from 6-methylpyridine-2-carboxaldehyde in 5 steps.

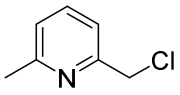
(6-methylpyridin-2-yl)methanol



$NaBH_4$ (497 mg, 12.9 mmol) was added to stirring solution of 6-methyl-2-pyridincarbaldehyde (1.2 g, 10 mmol) in methanol (10 ml) cooled in ice bath to 0°C. The resulting mixture was stirred for 20 minutes at 0°C, and then it was refluxed for 1 hour. After cooling to room temperature the reaction mixture was diluted with 30 ml of saturated NaCl solution and extracted with dichloromethane (6×10 ml). The collected organic phase was dried over sodium sulphate and evaporated under reduced pressure. Light yellow oil (1170 mg, 96% yield) was obtained.

^{1}H NMR (250.130 MHz, CDCl3, 25°C), δ: 7.56 (t, $^3J_{HH}$ = 7.7 Hz, *1H,* aromatic *H*), 7.11 – 6.97 (m, 2H, aromatic *H*), 4.71 (s, 2H, methylene *H*), 4.03 (br s, 1H, O*H*), 2.55 (s, 3H, methyl *H*).

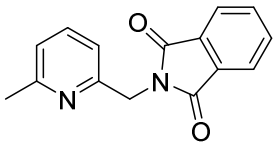
2-chloromethyl-6-methylpiridine



2-chloromethyl-6-methylpiridine was obtained as reported previously[2]. Product is clear oil (82% yield).

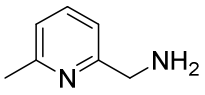
^{1}H NMR (250.130 MHz, CDCl3, 25°C), δ: 7.60 (t, $^3J_{HH}$ = 7.7 Hz, 1H, aromatic *H*), 7.29 (d, $^3J_{HH}$ = 7.7 Hz, 1H, aromatic *H*), 7.09 (d, $^3J_{HH}$ = 7.7 Hz, 1H, aromatic *H*), 4.63 (s, 2H, methylene *H*), 2.56 (s, 3H, methyl *H*).

2-phthalimidomethyl-6-methylpyridine



Potassium phthalimide (660 mg, 3.57 mmol) was added to solution of 2-chloromethyl-6-methylpyridine (500 mg, 3.53 mmol) in dry acetonitrile (15 ml), and the mixture was stirred at 82°C for 4 days. After evaporation of the solvent, water (10 ml) and dichloromethane (10 ml) were added to the solid residue, and mixture was extracted with 4×10 ml of dichloromethane. The organic phase was dried over sodium sulphate, and the solvent was removed under reduced pressure. Beige powder (665.3 mg) was obtained after drying in vacuum. After recrystallization from methanol white crystals (551 mg, 52 %) were obtained.

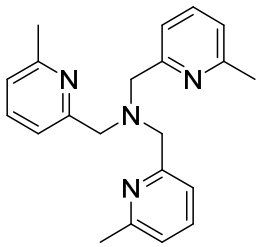
(6-methylpyridin-2-yl)methylamine



$N_2H_4 \cdot H_2O$ (329 mg, 5.24 mmol) in MeOH (4 ml) was added dropwise to solution of 2-phthalimidomethyl-6-methylpyridine (551 mg, 2.18 mmol) in MeOH (8 ml), cooled to 0°C. The resulting solution was refluxed for 3 hours and then cooled to room temperature. After evaporation of the methanol, the residue was dissolved in 8 ml of 1.5 M NaOH and extracted with dichloromethane (7×10 ml). The organic phase was dried over sodium sulphate, and the solvent was removed. Product was obtained as yellowish oil (259 mg, 96%).

^{1}H NMR (250.130 MHz, $CDCl_3$, 25°C), δ: 7.53 (t, $^3J_{HH}$ = 7.7 Hz, 1H, aromatic *H*), 7.08 (d, $^3J_{HH}$ = 7.7 Hz, 1H, aromatic *H*), 7.01 (d, $^3J_{HH}$ = 7.7 Hz, 1H, aromatic *H*), 3.93 (s, 2H, methylene *H*), 2.54 (s, 3H, methyl *H*).

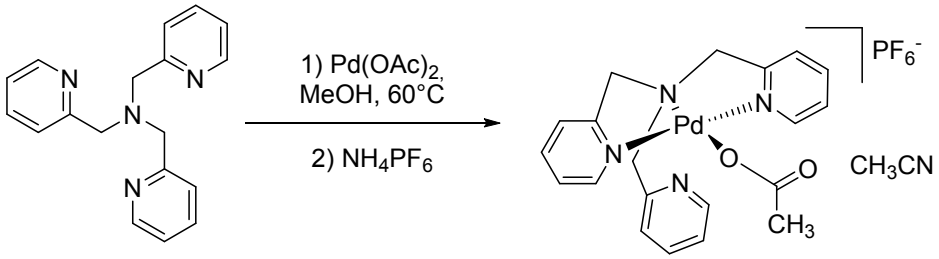
tris((6-methylpyridin-2-yl)methyl)amine (6Me-tpa)



2-chloromethyl-6-methylpyridine (628.4 mg, 4.438 mmol) and then 1 M aqueous NaOH (4.44 ml) were added dropwise to stirring solution of (6-methylpyridine-2-yl)methylamine (258 mg, 2.11 mmol) in dichloromethane (5 ml). The resulting mixture was vigorously stirred at room temperature for 5 days. Then the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (5×10 ml). The organic extracts were combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was dried in vacuum. After recrystallization from hexane white crystalline product was obtained (375 mg, 53% yield).

^{1}H NMR (250.130 MHz, CD_3CN, 25°C), $\underline{\delta}$: 7.58 (t, $^3J_{HH}$ = 7.7 Hz, 3H, aromatic *H*), 7.39 (d, $^3J_{HH}$ = 7.7 Hz, 3H, aromatic *H*), 7.04 (d, $^3J_{HH}$ = 7.7 Hz, 3H, aromatic *H*), 3.75 (s, 6H, methylene *H*), 2.44 (s, 9H, methyl *H*).

Complex 1



$Pd(OAc)_2$ (53.5 mg, 0.238 mmol) was added to the solution of tris-(2-pyridilmethyl)amine (69.1 mg, 0.238 mmol) in methanol (4 mL). The reaction mixture was stirred at 60 °C for 1 h. To the resulting solution, NH_4PF_6 (77.6 mg, 0.476 mmol) was added and the mixture was further stirred at room temperature overnight. Then reaction mixture was kept for 6 h at -20 °C. The precipitate was filtered off, washed with hexane (2×1 ml), redissolved in acetonitrile (3 mL) and separated from fine dark precipitate by centrifugation. The filtrate was concentrated to ~1.5 ml, layered with Et_2O (8 mL) and stored at + 4 °C for several days to afford 135 mg (75% yield) of yellow crystals. X-ray quality crystals were obtained after another recrystallization from CH_3CN/Et_2O.

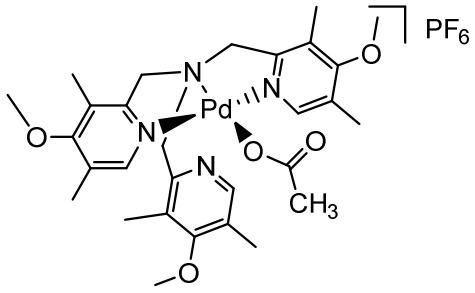
^{1}H NMR (250.130 MHz, CD_3CN, 25°C), δ: 8.13 (d, $^3J_{HH}$ = 4.6 Hz, 3H, aromatic *H*), 7.98 – 7.26 (m, 3H, aromatic *H*), 7.56 (d, $^3J_{HH}$ = 7.8 Hz, 3H, aromatic *H*), 7.41 – 7.26 (m, 3H, aromatic *H*), 4.69 (br s, 6H, methylene *H*), 3.22 (s, 3H).

^{13}C NMR (62.903 MHz, CD_3CN, 25°C), δ: 178.03 (1C, *C*(O)O), 151.31 (3C, aryl *C*), 150.35 (3C, aryl *C*H), 141.33 (3C, aryl *C*), 125.69 (3C, aryl *C*H), 125.36 (3C, aryl *C*H), 68.55 (3C, C*H*$_2$), 23.46 (1C, *C*H$_3$).

^{19}F NMR (235.330 MHz, CD_3CN, 25°C), δ: -72.87 (d, $^1J_{PF}$ = 706.8 Hz).

^{31}P NMR (101.255 MHz, CD_3CN, 25°C), δ: -144.66 (septet, $^1J_{PF}$ = 706.8 Hz).

Complex 2



Complex **2** was prepared in a similar way from $Pd(OAc)_2$ and tris-((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)amine.

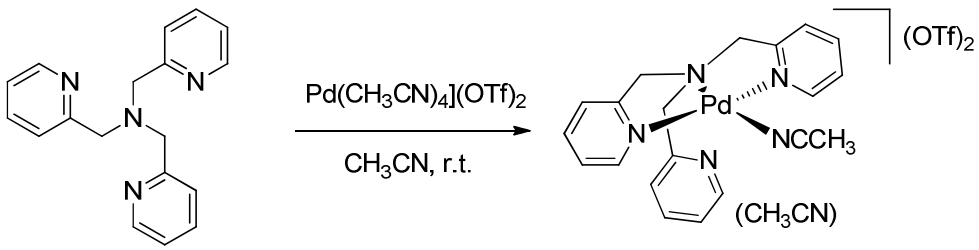
^{1}H NMR (250.130 MHz, CD_3CN, 25°C), δ: 7.77 (s, 3H, aromatic *H*), 4.65 (br s, 6H, methylene *H*), 3.80 (s, 9H, C*H*$_3$O), 3.05 (br. s, 3H, acetate), 2.38 (s, 9H, methyl *H*), 2.17 (s, 3H, methyl *H*).

^{13}C NMR (62.903 MHz, CD_3CN, 25°C), δ: 177.73 (1C, *C*(O)O), 149.69 (3C, aryl *C*H), 128.88 (3C, aryl *C*), 128.37 (3C, aryl *C*), 67.04 (3C, *C*H$_2$), 61.30 (3C, *C*H$_3$O), 23.73 (1C, *C*H$_3$C(O)O), 13.71 (3C, *C*H$_3$), 13.09 (3C, *C*H$_3$).

^{19}F NMR (235.330 MHz, CD_3CN, 25°C), δ: -72.97 (d, $^1J_{PF}$ = 706.8 Hz, P*F*$_6$).

^{31}P NMR (101.255 MHz, CD_3CN, 25°C), δ: -144.84 (septet, $^1J_{PF}$ = 706.8 Hz, *P*F$_6$).

Complex 3



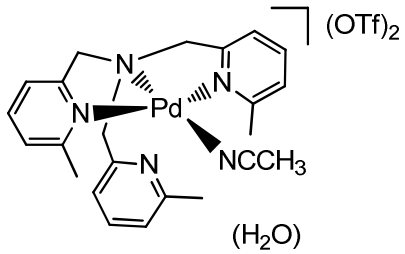
Tris-(2-pyridilmethyl)amine (68.6 mg, 0.237 mmol) in acetonitrile (2 ml) was added dropwise to the solution of $[Pd(CH_3CN)_4](OTf)_2$ (134.5 mg, 0.237 mmol) in dry acetonitrile (2 ml). The resulting yellow solution was stirred at room temperature for 4 days. Then the solution was reduced to ~1.5 ml and filtered. Diethyl ether (~7 ml) was layered upon the filtrate, and storing at 4° C over a week yielded yellowish crystalline precipitate (112 mg, 64% yield).

^{1}H NMR (250.130 MHz, CD_3CN, 25°C), δ: 8.31 (d, $^{3}J_{HH}$ = 4.4 Hz, 3H, aromatic *H*), 7.94 – 7.86 (m, 3H, aromatic *H*), 7.55 (d, $^{3}J_{HH}$ = 7.5 Hz, 3H, aromatic *H*), 7.42 – 7.29 (m, 3H, aromatic *H*), 4.75 (s, 6H, methylene *H*).

^{13}C NMR (62.903 MHz, CD_3CN, 25°C), δ: 151.53 (aryl *C*H), 141.56 (aryl *C*), 125.85 (aryl *C*H), 122.15 (q, *C*$F_3SO_3^-$, $^{1}J_{CF}$ = 320.6 Hz), 69.75 (*C*H_2).

^{19}F NMR (235.330 MHz, CD_3CN, 25°C), δ: -79.45 (s, C*F*$_3SO_3^-$ anion).

Complex 4



Complex **4** was synthesized in a similar way from $[Pd(CH_3CN)_4](OTf)_2$ (96.3 mg, 0.169 mmol) and tris-((6-methylpyridin-2-yl)methyl)amine (56.3 mg, 0.169 mmol) in 93% yield.

^{1}H NMR (250.130 MHz, CD_3CN, 25°C), δ, ppm: 7.74 (t, $^{3}J_{HH}$ = 7.8 Hz, 3H, aromatic *H*), 7.31 (d, $^{3}J_{HH}$ = 7.8 Hz, 3H, aromatic *H*), 7.22 (d, $^{3}J_{HH}$ = 7.8 Hz, 3H, aromatic *H*), 4.71 (s, 6H, methylene *H*), 2.66 (s, 9H, methyl *H*).

^{13}C NMR (62.903 MHz, CD_3CN, 25°C), δ, ppm: 161.85 (aromatic *C*), 160.05 (aryl *C*), 141.21 (aryl *C*H), 126.60 (aryl *C*H), 122.61 (aryl *C*H), 122.17 (q, *C*$F_3SO_3^-$, $^{1}J_{CF}$ = 320.6 Hz), 70.59 (*C*H_2) , 26.12 (*C*H_3).

^{19}F NMR (235.330 MHz, CD_3CN, 25°C), δ, ppm: -79.47 (s, C*F*$_3SO_3^-$ anion).

Kinetic isotope effect (KIE) measurement for benzene oxidation

Ethylbenzene (100 μmol) and ethylbenzene-d_{10} (300 μmol) were added to the solution of the appropriate Pd complex (ether **1** or **2**, 1.5 μmol) in CH_3CN (0.20 mL) and CD_3CN (0.3 mL). Then 54 μL 35wt.% solution of AcOOH (300 μmol) was added to reaction mixture. The resulting mixture was stirred for 0.5 h at 60 °C. After that, additional 54 μL AcOOH (300 μmol) was added, and the mixture was stirred for 24 h at 60 °C. The mixture of products was analyzed by quantitative ^{13}C NMR spectroscopy to obtain the relative amounts of deuterated and non-deuterated ethylbenzene, 1-phelylethanol, and acetophenone.

Kinetic isotope effect was calculated as KIE = k_H/k_D = ln[1-(PhEt conversion)]/ln[1−(PhEt-d_{10} conversion)].

Kinetic isotope effect (KIE) measurement for 1-phenylethanol oxidation

A mixture of 1-phenylethanol (33.8%) and 1-D-1-phenylethylanol (66.2 %) (total substrates 200 μmol) were added to the solution of the desired Pd catalyst (either **1** or **2**, 0.7 μmol) in CH_3CN (0.20 mL) and CD_3CN (0.3 mL). Then 25 μL 35wt.% solution of peracetic acid (140 μmol) was added to reaction mixture. The resulting mixture was stirred for 24 h at 60 °C. The mixture of products was analyzed by quantitative ^{13}C NMR spectroscopy and GC-MS to obtain the relative amounts of deuterated and non-deuterated 1-phelylethanol, 1-phelylethanol acetate and acetophenone.

Kinetic isotope effect (KIE) values were calculated as:

$$\frac{k_H}{k_D} = \frac{\ln\left(\frac{[\text{1-phenylethanol}]}{[\text{1-phenylethanol}]_0}\right)}{\ln\left(\frac{[\text{1-D-1-phenylethanol}]}{[\text{1-D-1-phenylethanol}]_0}\right)}$$

Competitive catalytic oxidations of substituted ethylbenzenes

Ethylbenzene (200 μmol), followed by the desired substituted ethylbenzene (200 μmol), was added to the solution of desired Pd catalyst (either **1** or **2**, 1.2 μmol,) in CH_3CN (200 μL). Then, peracetic acid (500 μmol) was added and the mixture was stirred for 24 h at 60 °C. The resulting mixture was directly analyzed by ^1H and quantitative ^{13}C NMR spectroscopy.

The ratio of the rate constants of oxidation of the corresponding substrate (X-C_6H_4Et) and ethylbenzene k_X/k_0 was calculated as $k_X/k_0 = \ln[1-(X\text{-}C_6H_4Et \text{ conversion})]/\ln[1-(\text{PhEt conversion})]$.

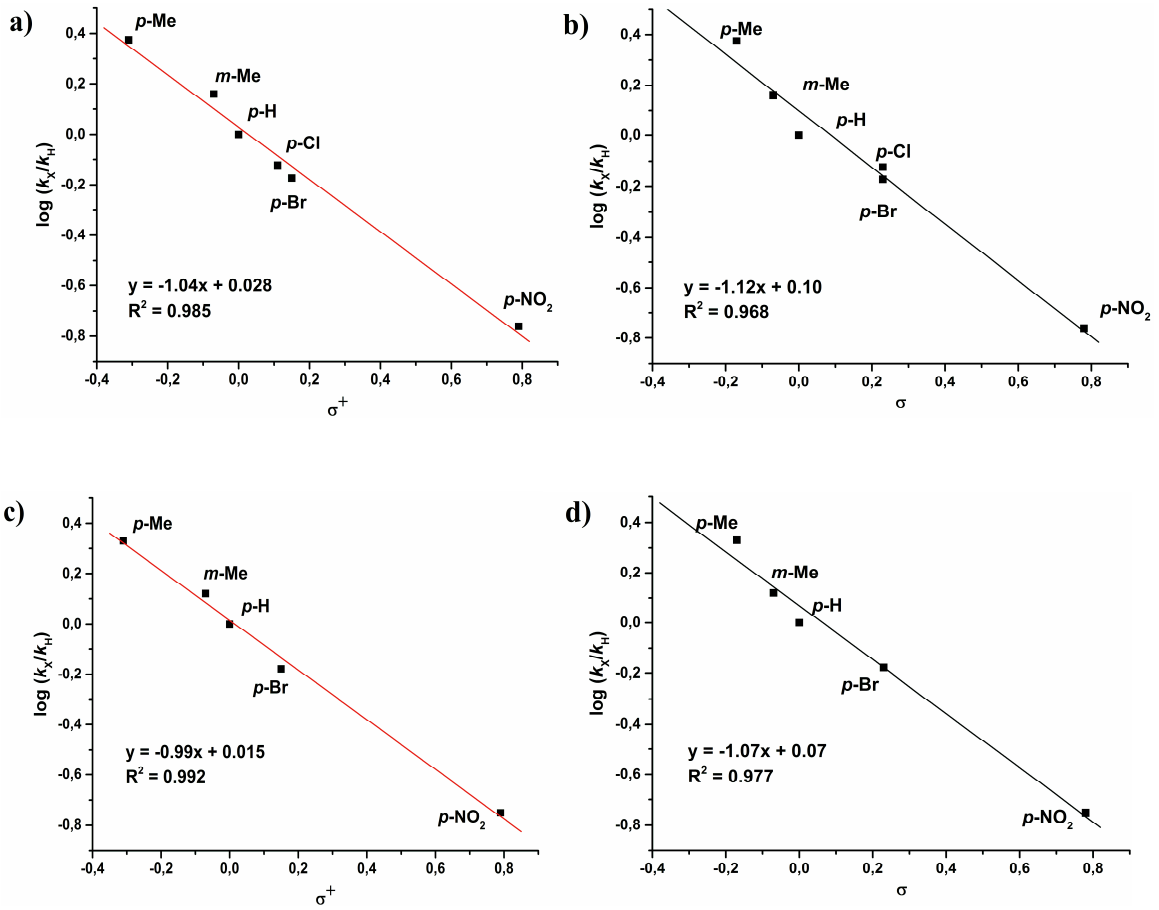
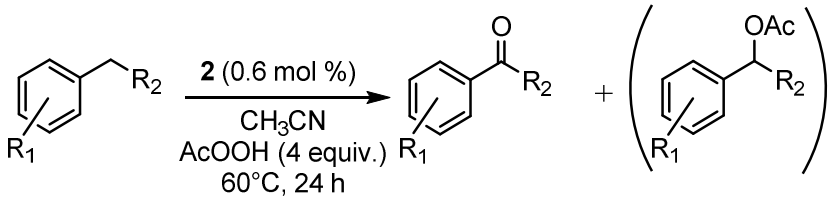
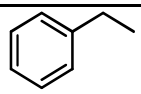
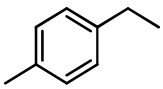
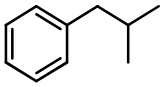
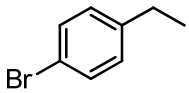
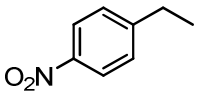
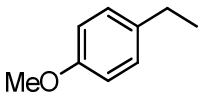
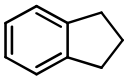
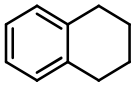
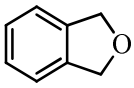


Figure S1. Hammett plots for catalytic oxidations of substituted ethylbenzenes for complex **1** (a and b) and for complex **2** (c and d).

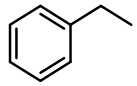
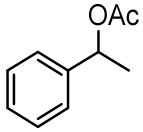
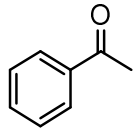
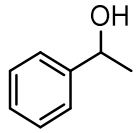
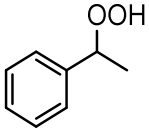
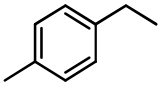
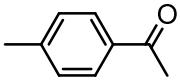
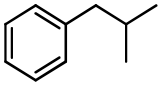
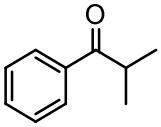
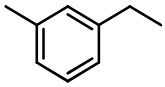
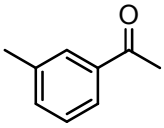
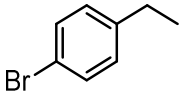
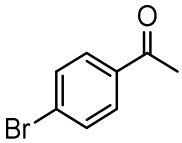
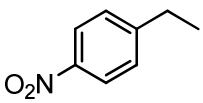
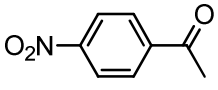
Table S1. Benzylic oxidation of substituted ethylbenzenes with AcOOH in the presence of complex **2**.[a]

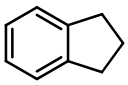
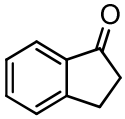
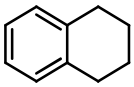
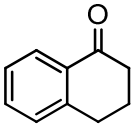
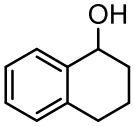


entry	substrate	conversion (%)	ketone yield (%)
1		61	60
2		53	48
3		34	27
4		35	31
5		37	32
6		<30% [b]	<8% [b]
7		20	17
8		5	4.5
9		99	98 [c]

[a] Reaction conditions: 60 °C; substrate (100 μmol), AcOOH (0.4 mmol), catalyst (0.6 μmol Pd), CH_3CN (200 μL); oxidant was added in one portion, and the mixture was stirred for 24 h. Conversion and yield were determined by HPLC and NMR. [b] Conversion and yield was estimated by GC-MS. Main byproducts were hydroquinone (<10%), p-methoxyphenol (<3%) and 4-ethylresorcinol (<2%). [c] Yield of the major product, phthalide.

Table S2. HPLC separation conditions and retention times.

Analyte	Column	Eluent: *i*-PrOH/ hexane	λ, nm	V, ml/min	t_R, min (config.)	t_R, min (config.)
	Chiralcel OD-H	3:97	206	1.0	3.5 (−)	–
	Chiralcel OD-H	3:97	206	1.0	4.8 (*R*)	5.0 (*S*)
	Chiralcel OD-H	3:97	206	1.0	8.90 (−)	–
	Chiralcel OD-H	3:97	206	1.0	11.4 (*R*)	13.8 (*S*)
	Chiralcel OD-H	3:97	206	1.0	18.8	25.0
	Chiralcel OD-H	3:97	206	0.7	4.7 (−)	–
	Chiralcel OD-H	3:97	206	0.7	9.3 (−)	–
	Chiralcel OD-H	3:97	206	0.7	15.9 (−)	–
	Chiralcel OD-H	3:97	206	0.7	6.8 (−)	–
	Chiralcel OD-H	3:97	206	0.7	4.8 (−)	–
	Chiralcel OD-H	3:97	206	0.7	8.4 (−)	–
	Chiralcel OD-H	3:97	206	0.7	6.1 (−)	–
	Chiralcel OD-H	3:97	206	0.7	12.0 (−)	–
	Chiralcel OD-H	3:97	206	0.7	7.1 (−)	–
	Chiralcel OD-H	3:97	206	0.7	27.7 (−)	–

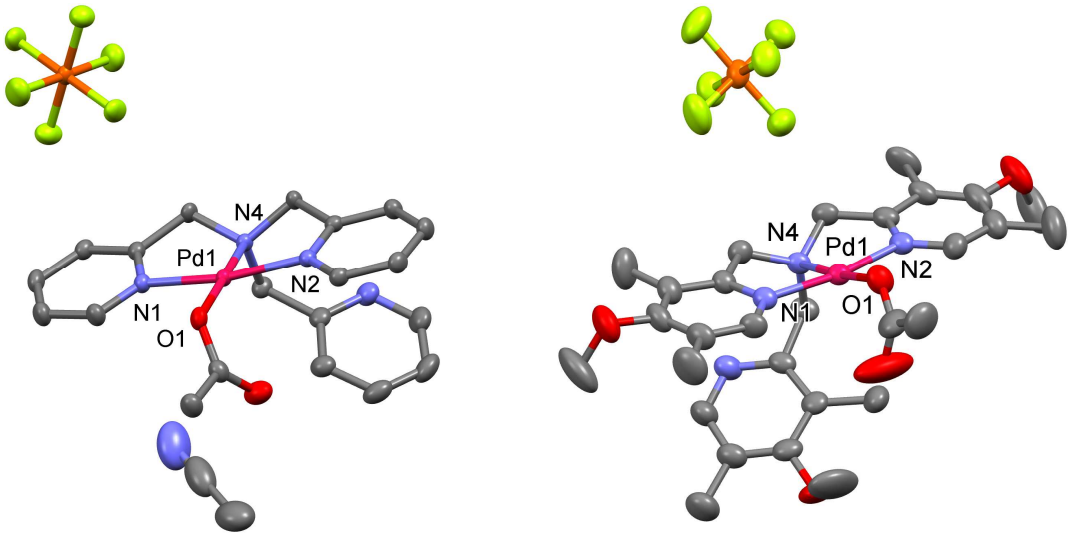
	Chiralcel OJ-H	3:97	206	1.0	4.1 (−)	−
	Chiralcel OJ-H	3:97	206	1.0	11.6 (−)	−
	Chiralcel OJ-H	3:97	206	1.0	4.2 (−)	−
	Chiralcel OJ-H	3:97	206	1.0	8.5 (−)	−
	Chiralcel OJ-H	3:97	206	1.0	15.0 *(R)*	18.9 *(S)*

X-ray measurements

Diffraction data for single crystal of compounds **1**, **3** and **4** were obtained at 130 K (**1**) and 140 K (**3**, **4**) on an automated Agilent Xcalibur diffractometer equipped with a CCD AtlasS2 detector (MoKα, graphite monochromator, ω-scans with a step of 0.5°). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package.[S3] The structures were solved by dual space algorithm (SHELXT [S4]) and refined by the full-matrix least squares technique (SHELXL [S5]) in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. Part of $CF_3SO_3^-$ anions and solvate acetonitrile molecule are disordered.

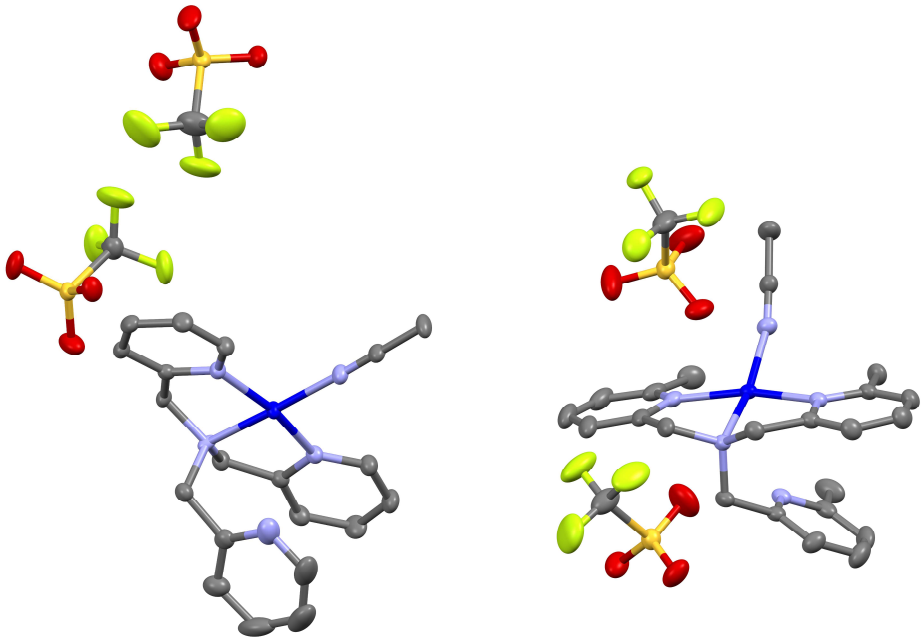
Single-crystal diffraction data for **2** were collected at 200(2) K on a Bruker Kappa Apex II CCD diffractometer using *φ, ω* scans of narrow (0.5°) frames with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Absorption corrections were applied empirically using *SADABS* programs.[S6] The structures were solved by direct methods with *SHELXS97* program[S7] and refined by full-matrix least-squares method against all F^2 in anisotropic (isotropic for H) approximation using the *SHELXL2014*/7 programs.[S5] The hydrogen atoms positions were calculated geometrically and refined in riding model. The asymmetric unit of **2** contains two independent molecules. Free solvent accessible volume in compound **2** derived from PLATON [S8] routine analysis was found to be 11.5% (838.7 $Å^3$). This volume is occupied by highly disordered solvent molecules that could not be modeled as a set of discrete atomic sites. We employed PLATON/SQUEEZE procedure to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. It is probably a mixture of solvents: CH_3CN, $(C_2H_5)_2O$ and H_2O.

The molecular structures of **1** and **2** are shown in Figure S2. The crystallographic data and details of the structure refinements are summarized in Table S3. Selected bond distances and angles are listed in Table S4. The molecular structures of the complexes **3** and **4** are shown in Figure S3. The crystallographic data and details of the structure refinements are summarized in Table S5. Selected bond distances and angles are listed in Tables S6 and S7.



1 **2**

Figure S2. X-ray structures of complexes **1** and **2**. Thermal ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity. In **2**, only one of the Pd complexes of the unit cell is shown.



3 **4**

Figure S3. Molecular structure of complexes **3** and **4**. Ellipsoids are of 50% probability level. Pd: blue, O: red, N: light blue, C: grey, P: orange, F: yellow. Hydrogen atoms and solvate CH_3CN and H_2O molecules are omitted for clarity. Only one of possible orientation of CF_3 groups is shown.

Table S3. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{20}H_{21}N_4O_2Pd \cdot PF_6 \cdot C_2H_3N$	$C_{29}H_{39}N_4O_5Pd \cdot F_6P$[+solvent]
Formula weight	641.83	775.01
Crystal system	Triclinic,	Monoclinic,
Space group [a]	$P\bar{1}$	$P2_1/c$
Temperature (K)	130	200
a, Å	10.3102(2)	20.6146(7)
b, Å	10.9549(1)	20.8157(8)
c, Å	13.0862(2)	17.7058(7)
A	112.271(1)	90
B	103.843(1)	107.008(1)
Γ	102.872(1)	90
V, Å^3	1244.63(3)	7265.4(5)
Z	2	8
D(calcd), g/cm^3	1.713	1.417
Absorption coefficient, mm^{-1}	0.89	0.63
F(000)	644	3168
Crystal size, mm	0.23 × 0.17 × 0.15	0.50 × 0.30 × 0.24
θ range for data collection, deg.	3.3 − 29.1	1.0 − 29.8
Index ranges	h = -12→14, k = -14→13, l = -17→17	h = -28→27, k = -29→29, l = -24→24
Reflections collected / independent	19823 / 5774	132444 / 20830
R_{int}	0.024	0.038
$T_{min} - T_{max}$	0.984 − 1.000	0.597 − 0.648
Reflections with $I > 2\sigma(I)$	5332	14183
Data / restraints / parameters	5774/ 0 / 336	20830/ 0 / 849
Goodness-of-fit on F^2	1.05	1.05
Final R_1 [$I > 2\sigma(I)$]	0.025	0.053
wR_2 (all data)	0.065	0.171
Largest diff. peak / hole, *e*/Å^3	0.97 / -0.60	1.03 / -0.90

[a] ADDSYM/PLATON does not suggest any higher symmetry space group. Perhaps, there is a pseudo symmetry.

Table S4. Selected bond lengths and angles for **1** and two independent molecules of **2**.

	1	**2**
Bond	*d*, Å	*d*, Å
Pd1—O1	2.037(1)	2.027(3) / 2.019(2)
Pd1—N1	2.013(2)	2.022(3) / 2.009(3)
Pd1—N2	2.014(2)	2.007(3) / 2.023 (3)
Pd1—N4	2.015(2)	2.003(3) / 1.995(3)
Angle	*θ*, º	*θ*, º
N1—Pd1—O1	93.41(6)	98.2(1) / 96.1(1)
N1—Pd1—N2	166.75(7)	166.4(1) / 166.7(1)
N1—Pd1—N4	83.58(7)	83.5(1) / 84.1(1)
N2—Pd1—O1	99.01(6)	94.5(1) / 96.3(1)
N2—Pd1—N4	84.21(7)	83.6(1) / 83.2(1)
N1—Pd1—N4	83.58(7)	175.6(1) / 175.3(1)

Table S5. Crystal data and structure refinement for **3** and **4**.

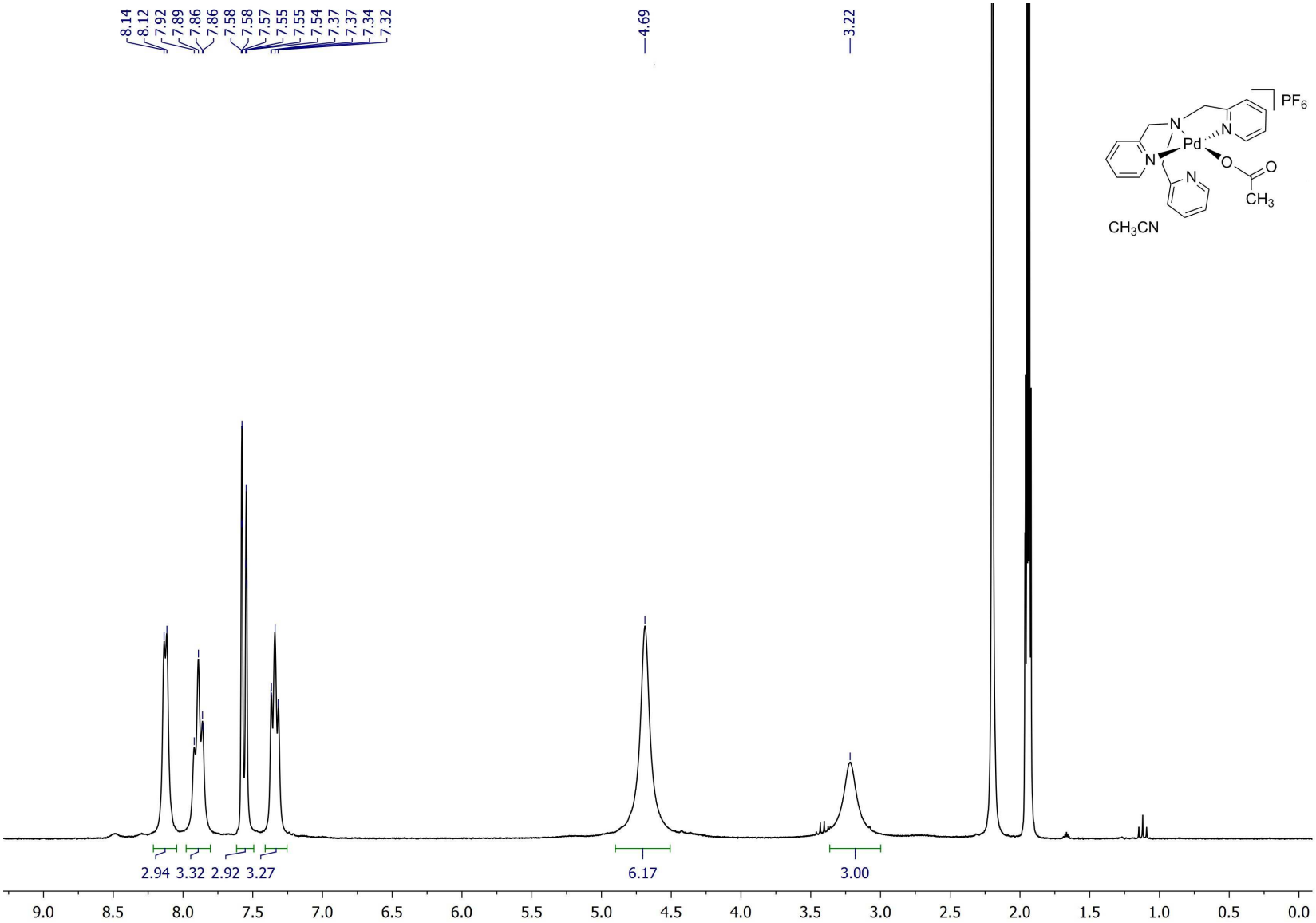
Identification code	**3**	**4**
Empirical formula	$C_{23}H_{22.5}F_6N_{5.5}O_6PdS_2$	$C_{25}H_{29}F_6N_5O_7PdS_2$
Formula weight	756.48	796.05
Crystal system	*Triclinic*	*Triclinic*
Space group	*P*−1	*P*−1
a, Å	10.7874(3)	11.01435(16)
b, Å	12.7380(5)	12.89589(19)
c, Å	13.2995(6)	12.98774(18)
α	106.700(4)	65.9788(14)
β	107.957(3)	71.1988(14)
γ	108.746(3)	84.5593(12)
V, Å^3	1487.07(11)	1593.69(4)
Z	2	2
D(calcd), g/cm^3	1.689	1.659
Absorption coefficient, mm^{-1}	0.849	0.799
F(000)	758	804
Crystal size, mm	0.35 × 0.21 × 0.05	0.32 × 0.23 × 0.22
θ range for data collection, deg.	1.87–29.0	1.94–29.03
Index ranges	$-13 \le h \le 11$, $-17 \le k \le 16$, $-17 \le l \le 18$	$-14 \le h \le 14$, $-17 \le k \le 16$, $-15 \le l \le 16$
Reflections collected / independent	12243 / 6509	25339 / 7331
R_{int}	0.0200	0.0213
Reflections with $I > 2\sigma(I)$	5841	
Goodness-of-fit on F^2	1.037	1.037
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0279$, $wR_2 = 0.0646$	$R_1 = 0.0304$, $wR_2 = 0.0748$
R indices (all data)	$R_1 = 0.0334$, $wR_2 = 0.0671$	$R_1 = 0.0337$, $wR_2 = 0.0765$
Largest diff. peak / hole, *e*/Å^3	0.935 / −0.657	0.829 / −0.754

Table S6. Selected bond lengths and angles for **3**.

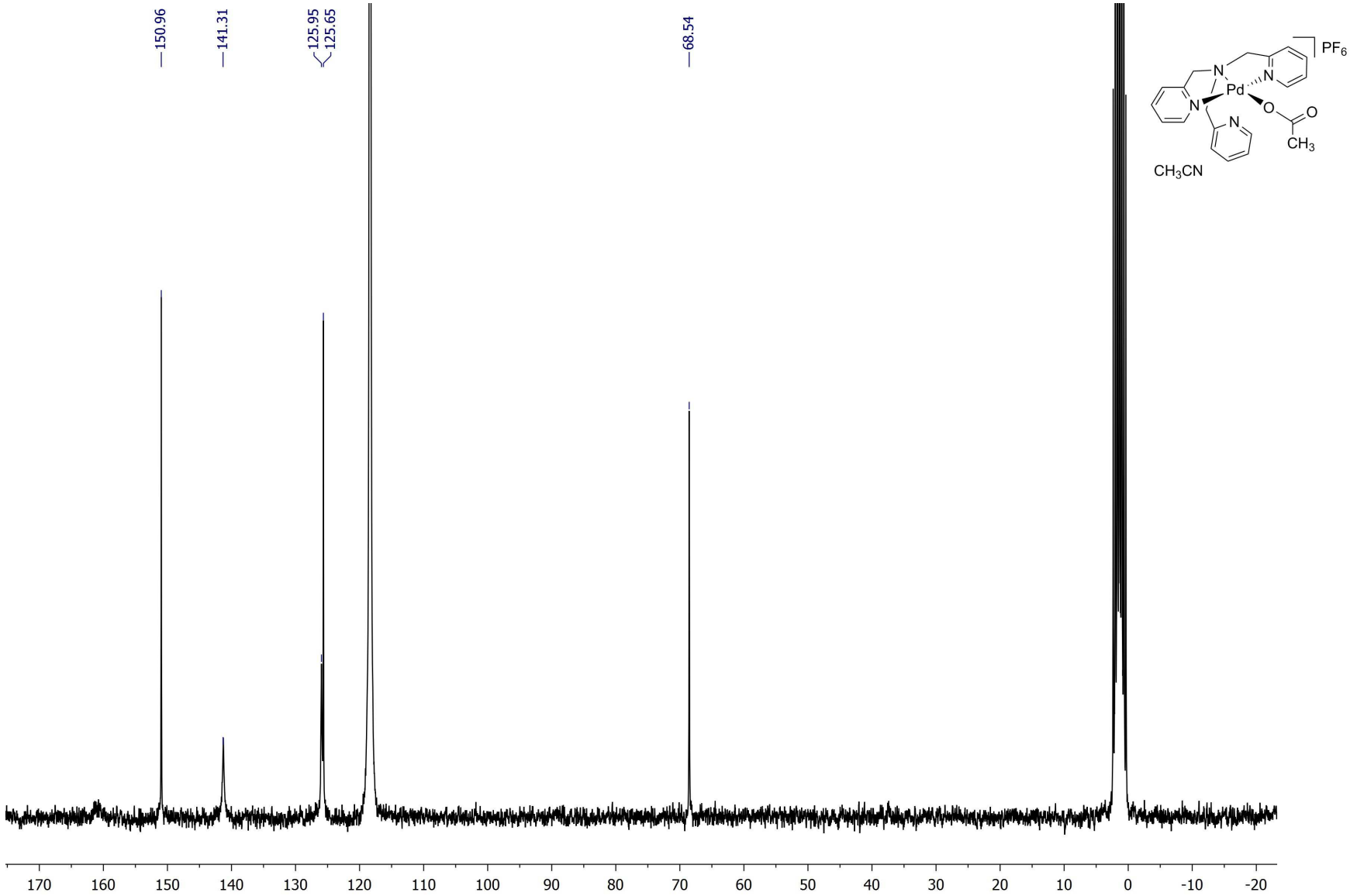
Bond	*d*, Å	Bond	*d*, Å
Pd(1)-N(1)	2.0158(18	Pd(1)-N(4)	1.9835(18)
Pd(1)-N(2)	2.0142(18)	Pd(1)-N(1A	2.0128(19)
Angle	ω, deg.	Angle	ω, deg.
N(2)-Pd(1)-N(1	167.04(7)	N(4)-Pd(1)-N(1A)	178.41(7)
N(4)-Pd(1)-N(1)	84.18(7)	N(1A)-Pd(1)-N(1)	96.95(7)
N(4)-Pd(1)-N(2)	83.11(7)	N(1A)-Pd(1)-N(2)	95.71(7)

Table S7. Selected bond lengths and angles for two independent molecules of **4**.

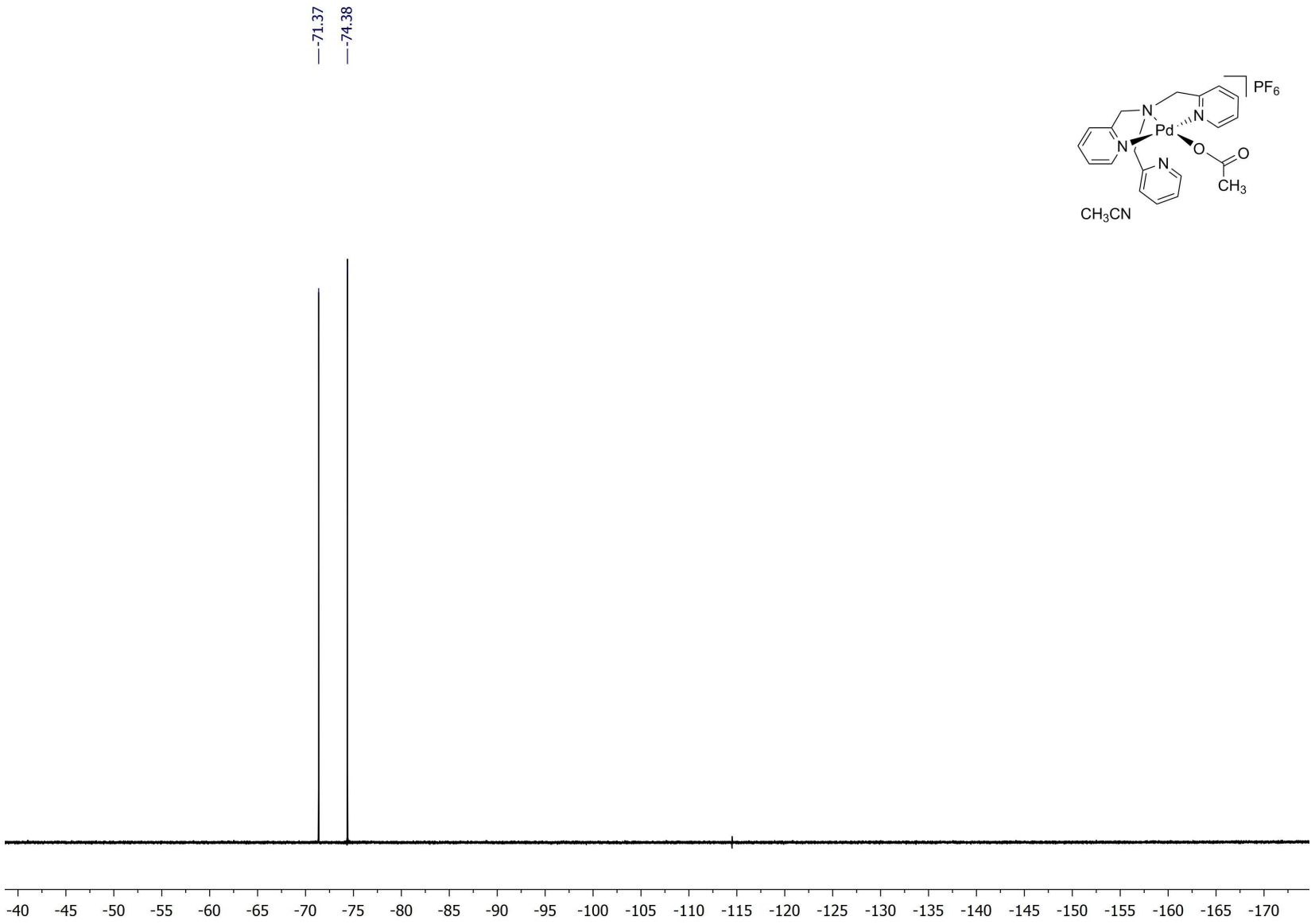
Bond	*d*, Å	Bond	*d*, Å
Pd(1)-N(1)	2.0464(19)	Pd(1)-N(4)	2.0078(17)
Pd(1)-N(2)	2.0445(18)	Pd(1)-N(1A)	2.0285(18)
Angle	ω, deg.	Angle	ω, deg.
N(2)-Pd(1)-N(1)	165.32(7)	N(4)-Pd(1)-N(1A)	165.66(7)
N(4)-Pd(1)-N(1)	82.17(7)	N(1A)-Pd(1)-N(1)	96.79(8)
N(4)-Pd(1)-N(2)	83.41(7)	N(1A)-Pd(1)-N(2)	97.86(7)



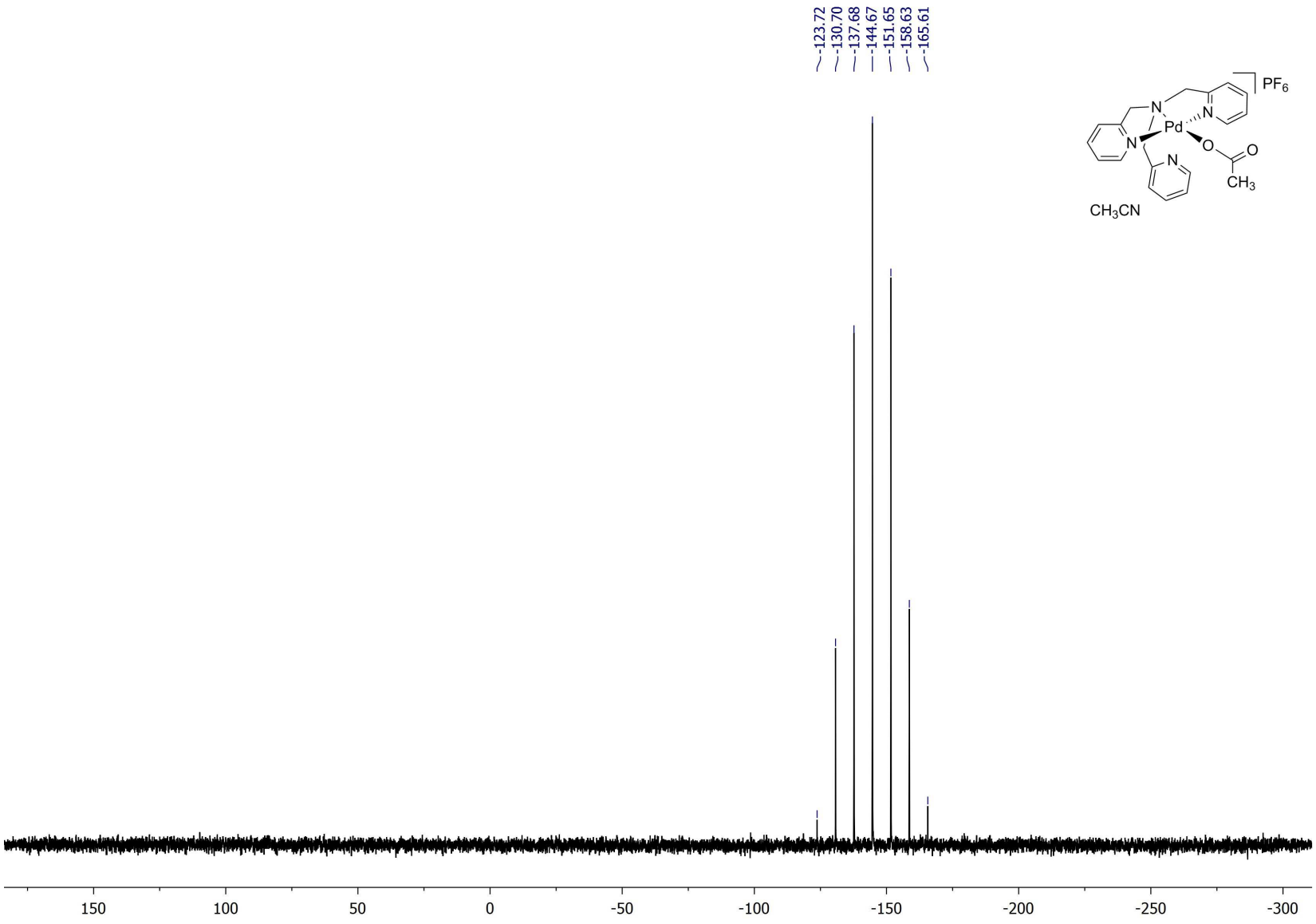
^{1}H NMR spectrum (250.130 MHz, CD_3CN, 25°C) of complex **1**



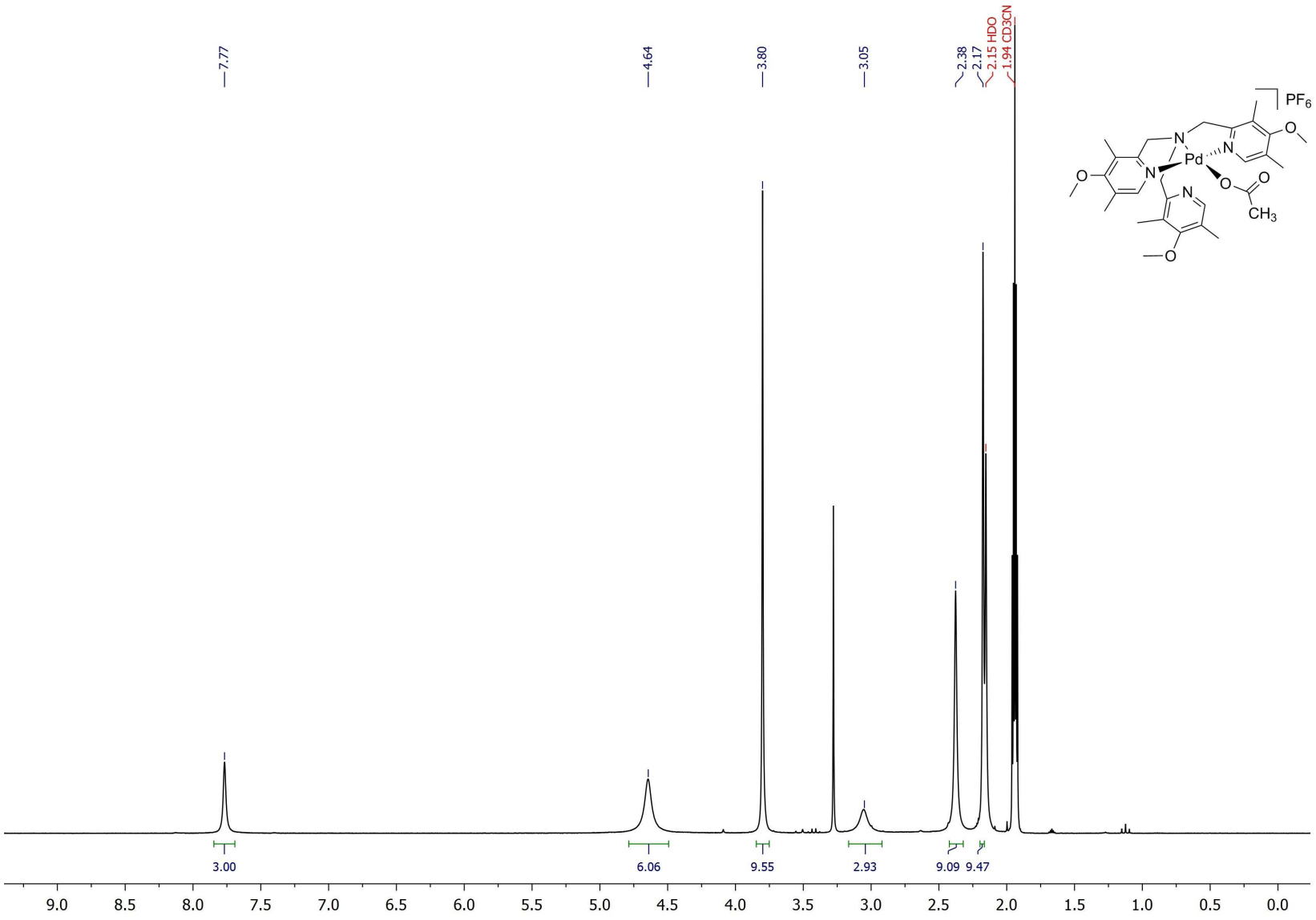
^{13}C NMR spectrum (62.903 MHz, CD_3CN, 25°C) of complex **1**



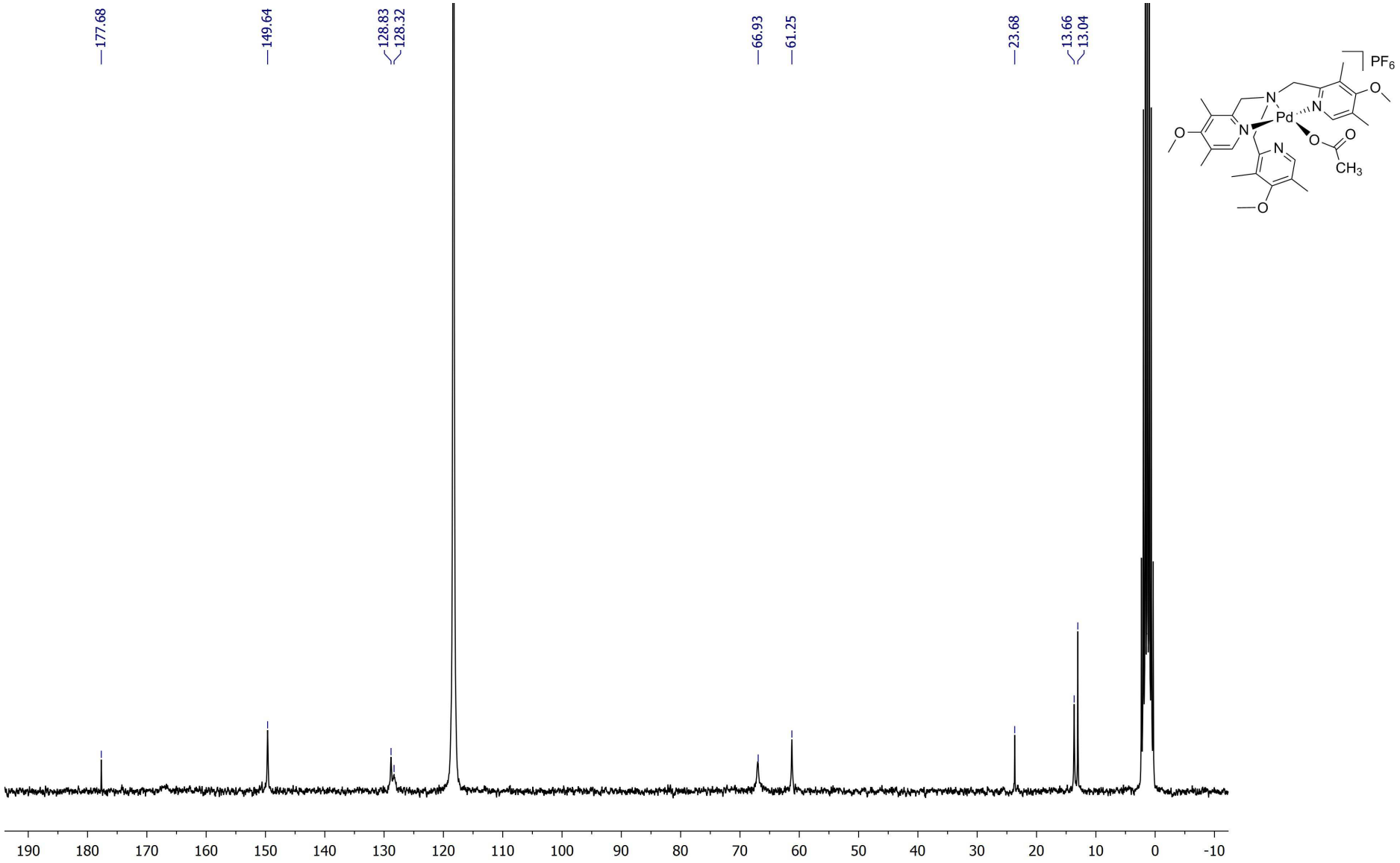
^{19}F NMR spectrum (235.330 MHz, CD_3CN, 25°C) of complex **1**



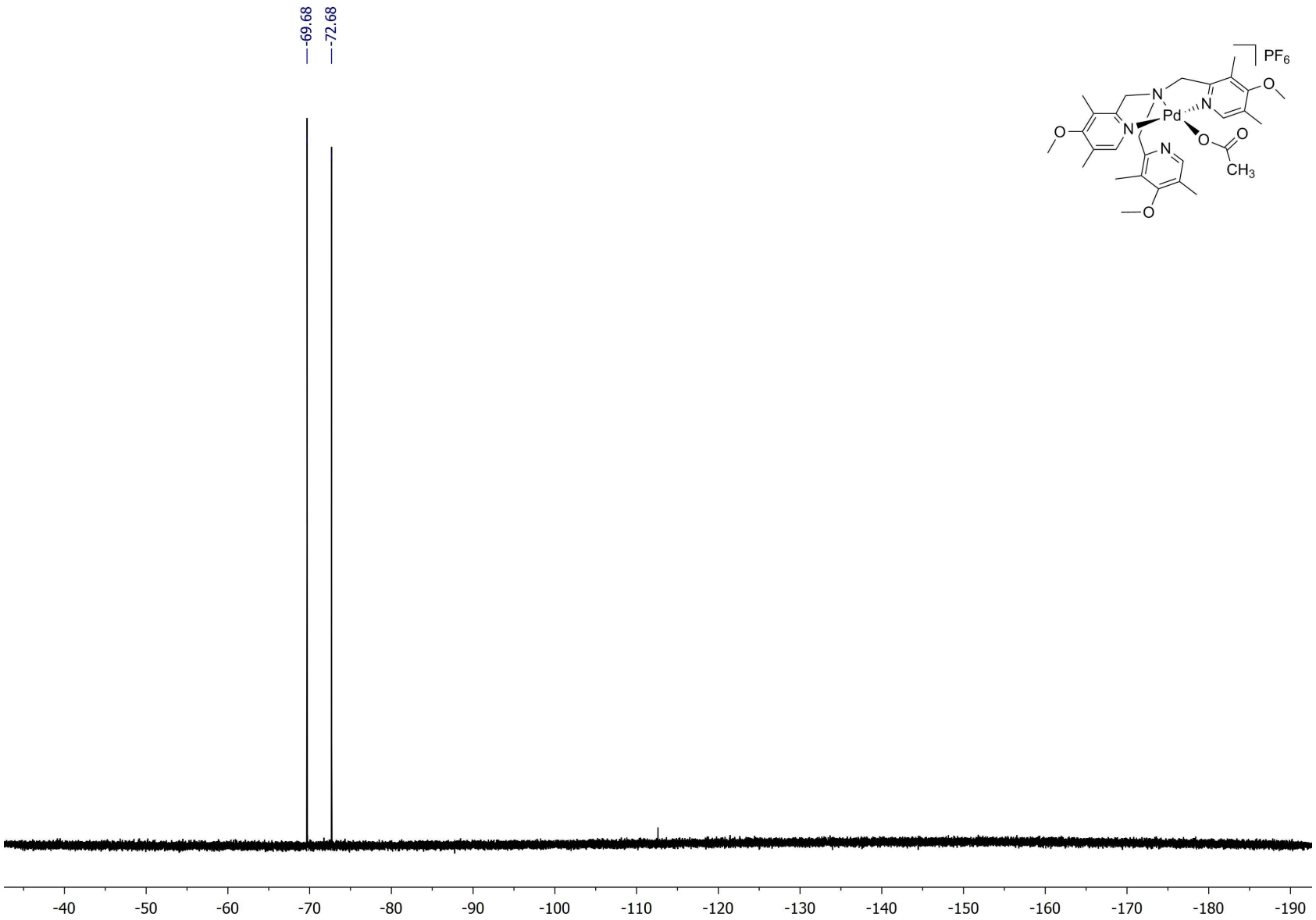
^{31}P NMR spectrum (101.255 MHz, CD_3CN, 25°C) of complex **1**



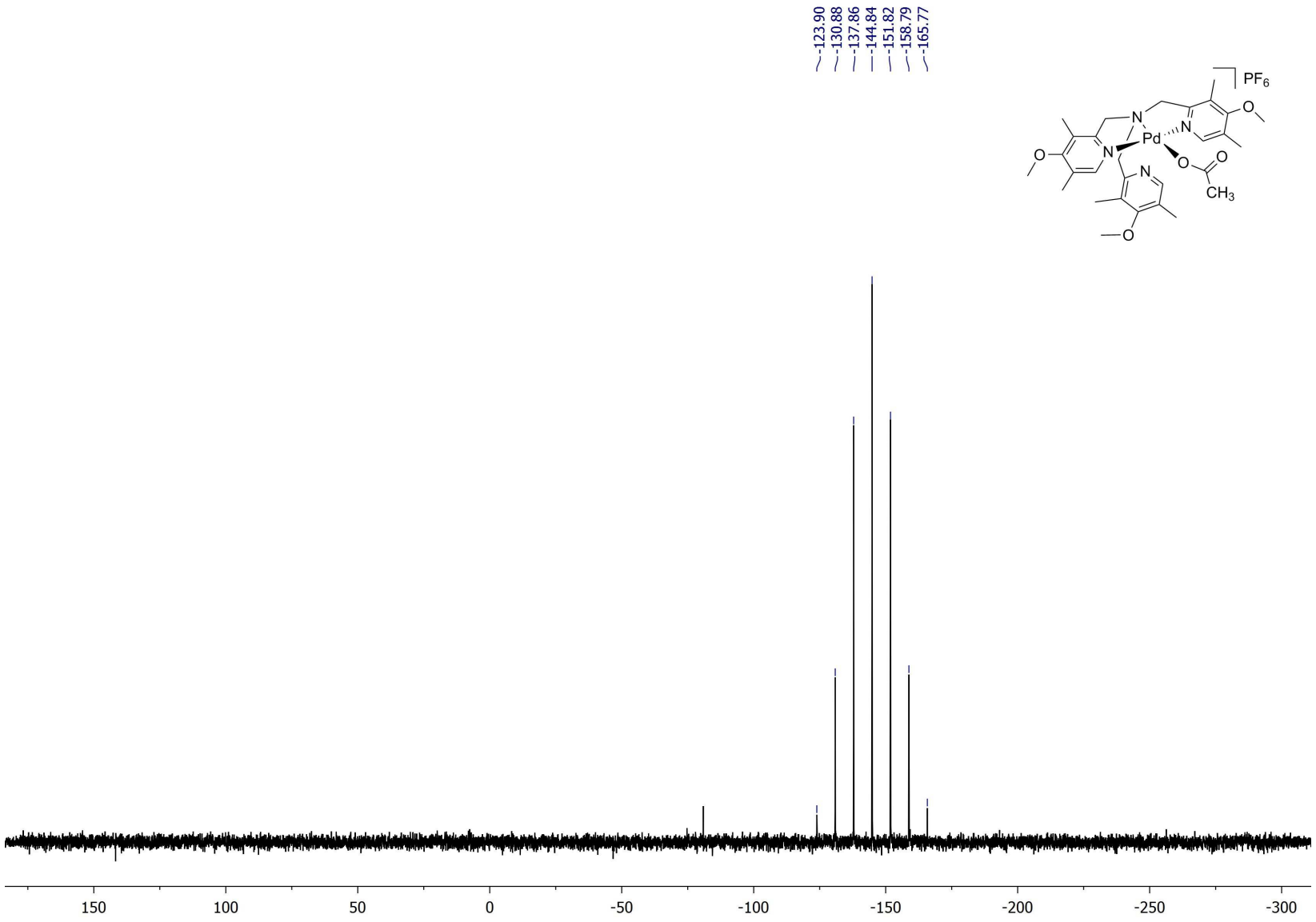
^{1}H NMR spectrum (250.130 MHz, CD_3CN, 25°C) of complex **2.** Peak at 3.28 was assigned to traces of methanol



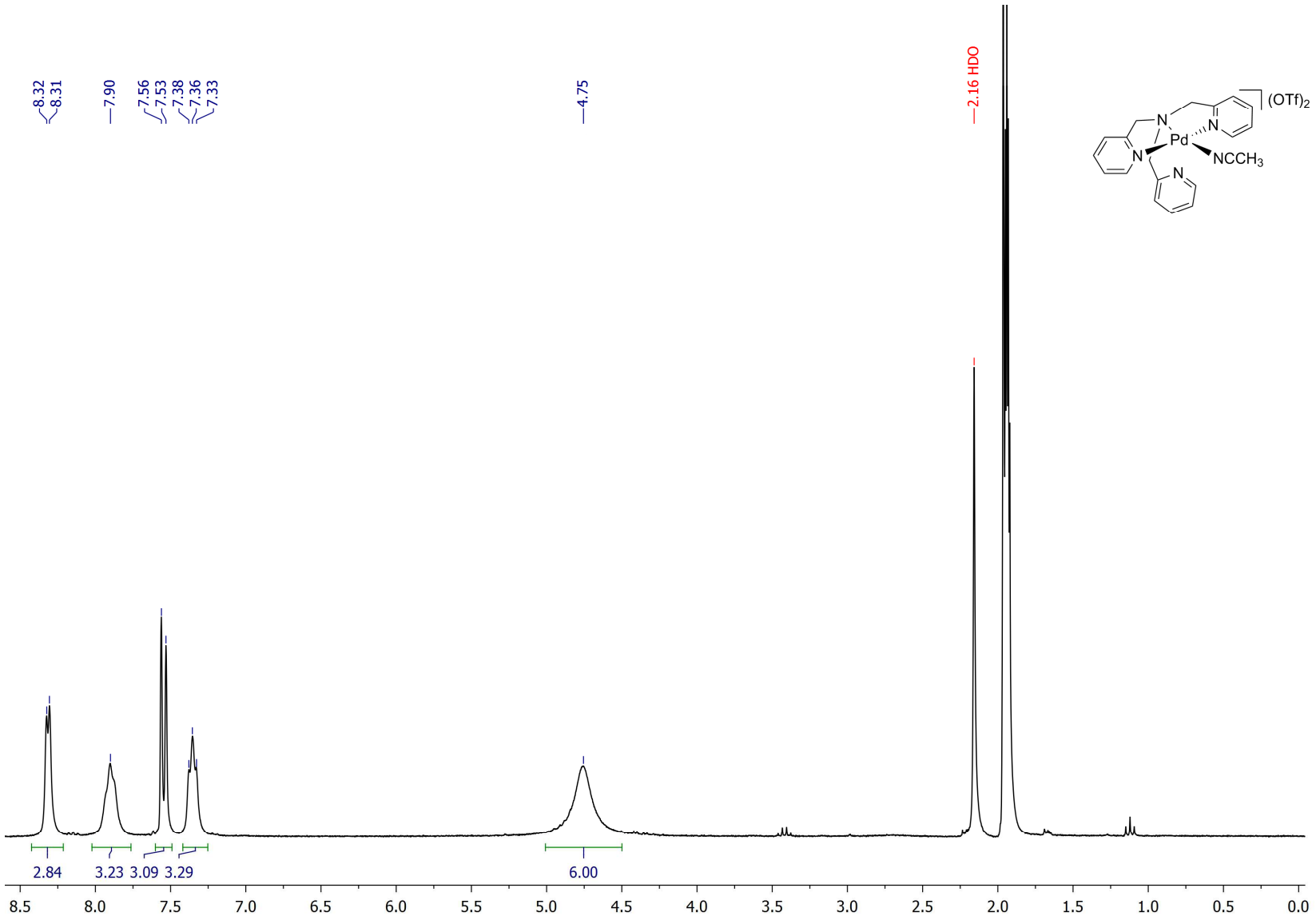
^{13}C NMR spectrum (62.903 MHz, CD_3CN, 25°C) of complex **2**



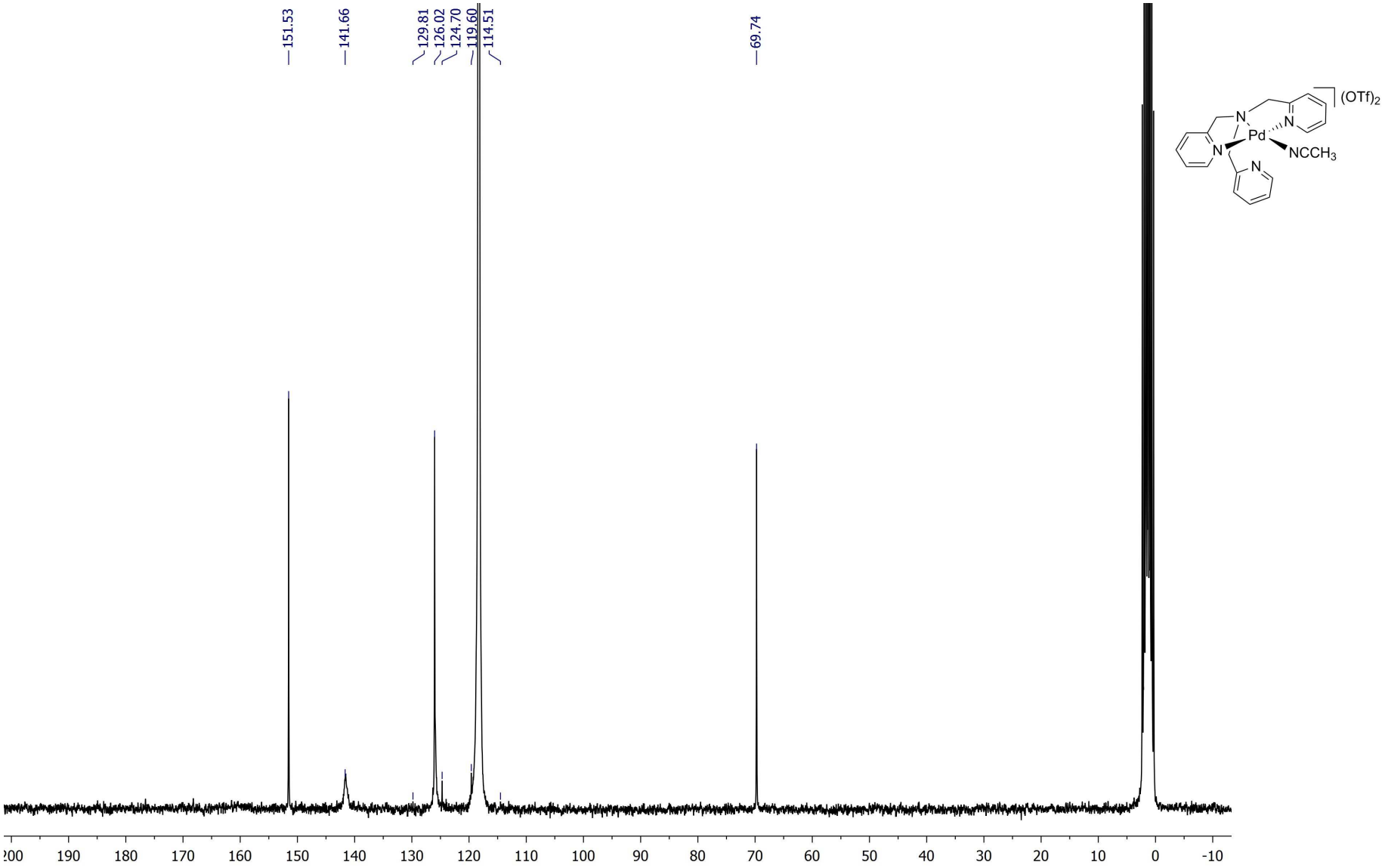
^{19}F NMR spectrum (235.330 MHz, CD_3CN, 25°C) of complex **2**



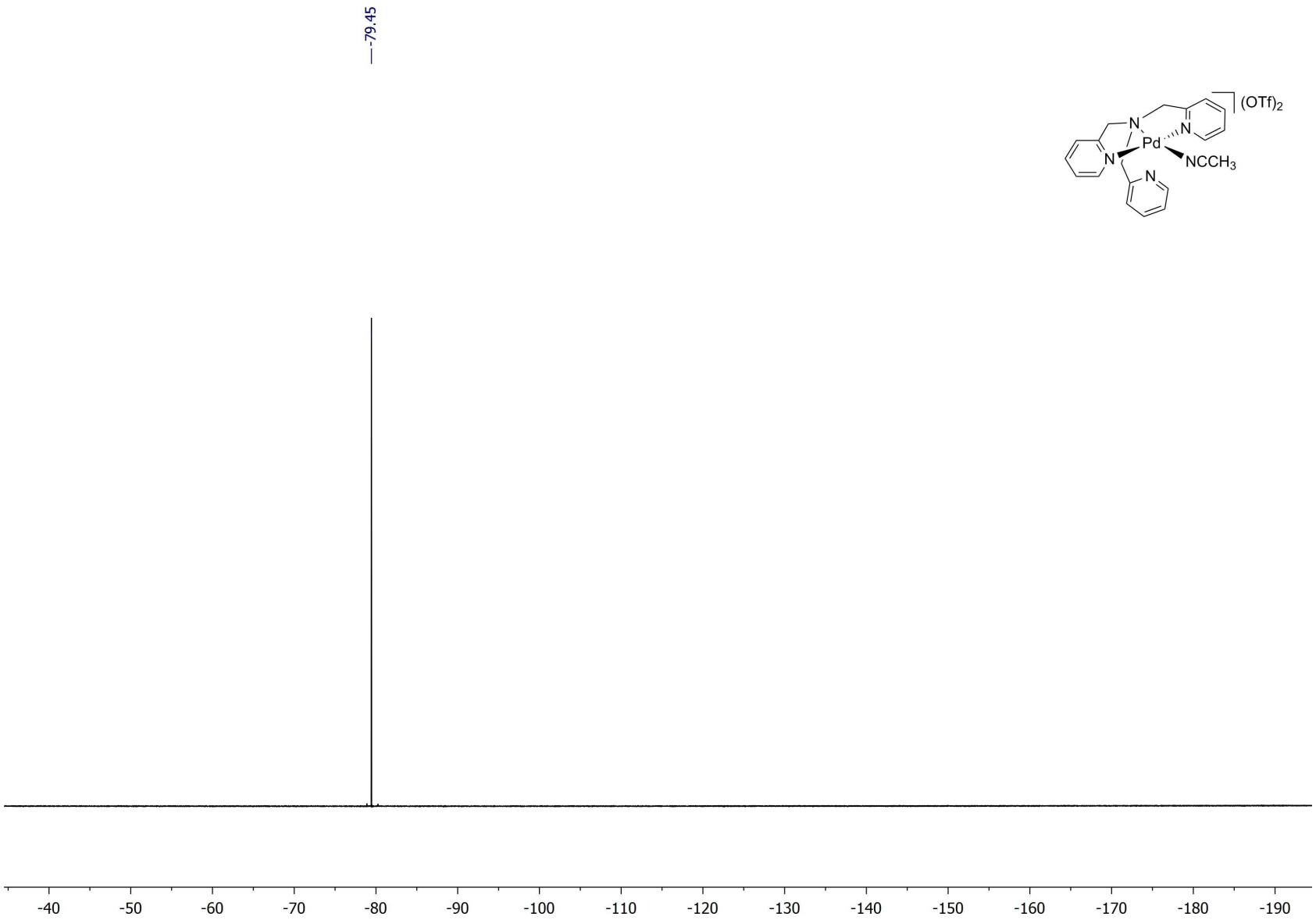
^{31}P NMR spectrum (101.255 MHz, CD_3CN, 25°C) of complex **2**



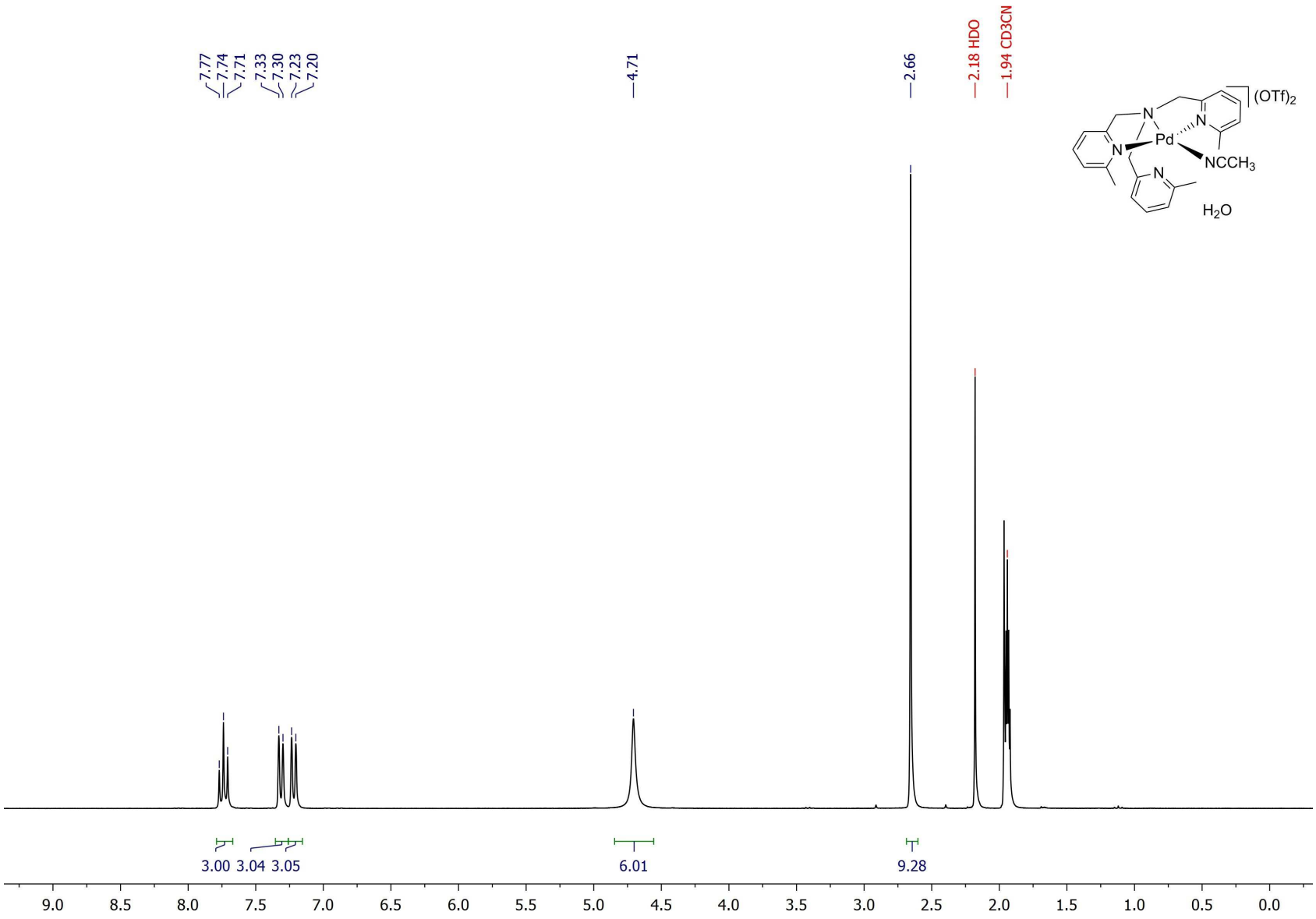
^{1}H NMR spectrum (250.130 MHz, CD_3CN, 25°C) of complex **3**



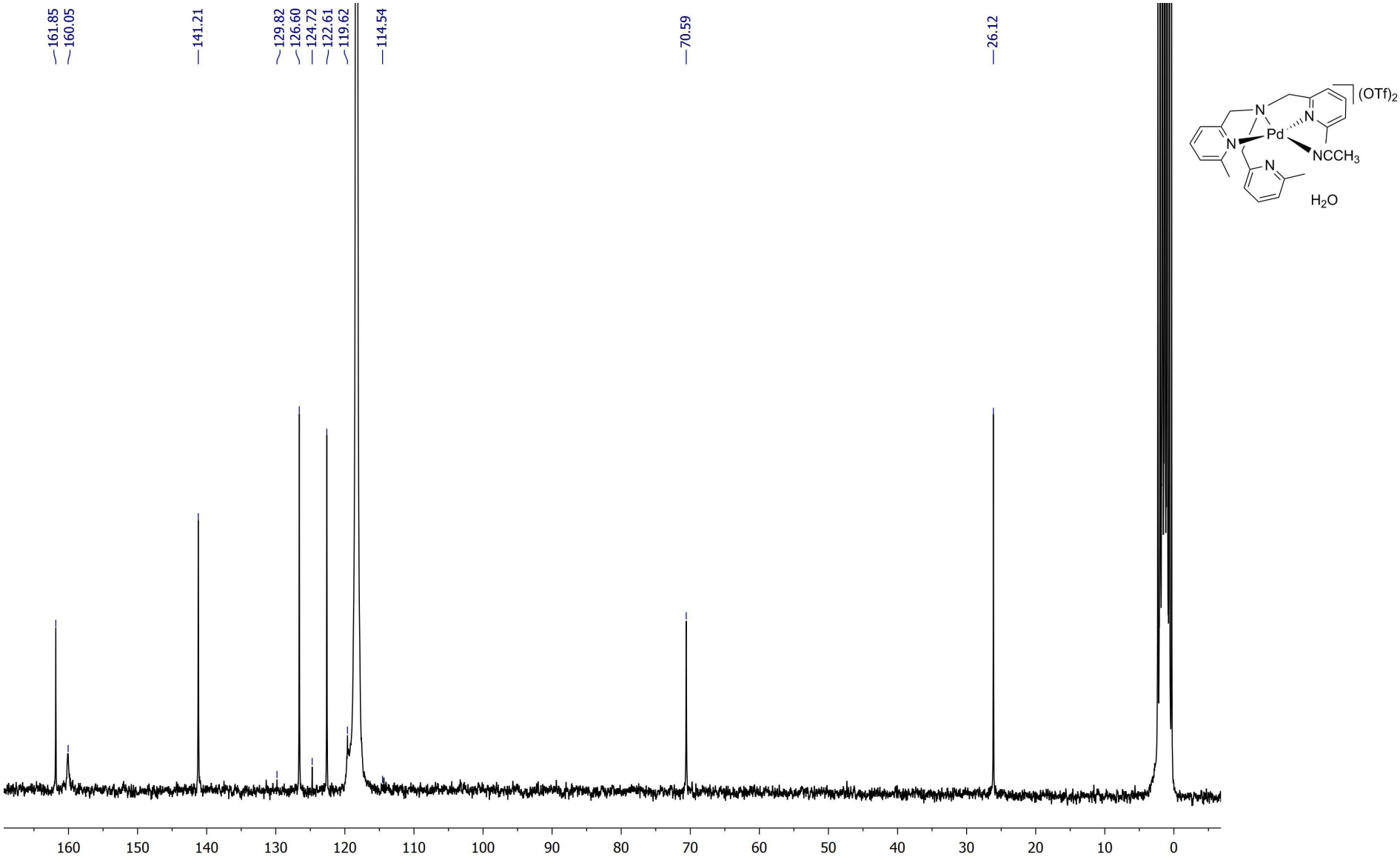
^{13}C NMR spectrum (62.903 MHz, CD_3CN, 25°C) of complex **3**



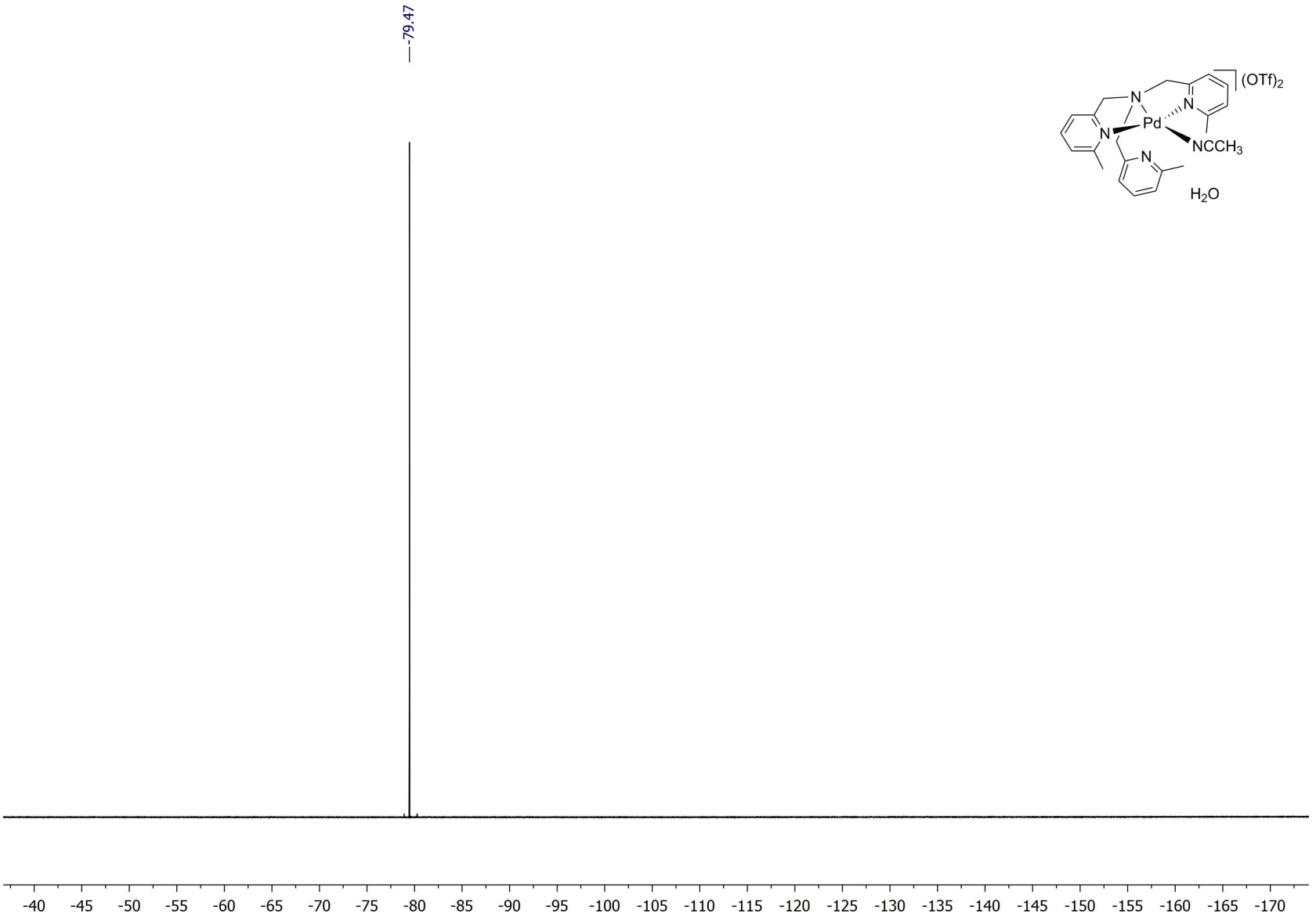
^{19}F NMR spectrum (235.330 MHz, CD_3CN, 25°C) of complex **3**



^{1}H NMR spectrum (250.130 MHz, CD_3CN, 25°C) of complex **4**



^{13}C NMR spectrum (62.903 MHz, CD_3CN, 25°C) of complex **4**



^{19}F NMR spectrum (235.330 MHz, CD_3CN, 25°C) of complex **4**

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