Electronic supplementary information

Guanidine centered reactivity of CNN Pd(II) pincer complexes including carboxylate assisted N–H activation and –CH_2– → –C(O)– oxygenation

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General considerations All chemicals were purchased from commercial vendors and used as received. $Pd(OC(O)^tBu)_2$ was prepared from $Pd(OAc)_2$ and pivalic acid as reported in the literature.[1] Guanidines **1** and **2** were prepared following the literature procedures.[2] The IR spectral data were obtained through ATR method from powdered samples on an IRAffinity−1 Shimadzu FTIR spectrometer in the frequency range 400–4000 cm^{-1}. Elemental analyses were performed on an Elementar Analysensysteme GmbH VarioEL V3.00. ^1H, $^{13}C\{^1H\}$, ^{19}F NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL ECX 400 NMR and Bruker AV-400 NMR spectrometers operating at 400, 100.5, 376.5 MHz and 161.8 MHz, respectively. All NMR measurements were made at room temperature unless mentioned otherwise. The δ (^1H) and δ ($^{13}C\{^1H\}$) are reported in ppm relative to tetramethylsilane or residual solvent signal. Melting points were recorded on a Buchi melting point apparatus (Model: M−560) and the reported values are uncorrected.

X-Ray crystallography Details of data collection, structure solution and refinement for structurally characterized compounds are presented in Tables S1–S3. X-ray crystallographic diffraction data were collected on Oxford Xcalibur S diffractometer (4-circle kappa goniometer, Sapphire−3 CCD detector, omega scans, graphite monochromator and a single wavelength Enhance X-ray source with MoKα radiation) or Rigaku XtaLAB Synergy (4-circle goniometer, Hybrid Pixel Array Detector, omega scans, graphite monochromator and PhotonJet (Mo) X-ray source type with micro-focus sealed X-ray tube).[3] Pre-experiment, data collection, data reduction and absorption corrections were performed with the CrysAlisPro software suite.[4] The structures were solved and refined using the SHELX-2017 program package[5] and SHELXL-2017/1 (within the Olex2 1.2 program package).[6] Non-hydrogen atoms were refined anisotropically. C−H/N−H hydrogen atoms were placed in geometrically calculated positions by using a riding model. The molecular structures were created using Olex2 1.2 program package[6] and Diamond software.[7]

DFT calculations The proposed pathway in Scheme 6 was evaluated computationally by using the B3LYP/6-31G*/ LANL2DZ level of theory[8–15] and simulating the complexes by substituting hydrogen in place of -CF_3 and CH_3NC in place of XylNC. Using the Gaussian 09 software,[16] DFT calculations were performed on **G**, **H**, **H•**, **H′, I**, **TS**, **J, K** and **K′** and all the molecules were successfully optimized without any imaginary frequency except **TS**. Solvent correction for toluene was performed using the polarizable continuum model on all the optimized systems.[17–19] The energies of DFT modelled species are listed in Table S4.

Experimental section Some complexes were not characterized by $^{13}C\{^1H\}$ NMR spectroscopy due to their poor solubility in $CDCl_3$ and DMSO-d_6.

Complexes 3·½ toluene, 4·¼ toluene and 5·½ toluene·½ pivalic acid A 25 mL Round Bottom (RB) was charged with the guanidine **1** (100 mg, 0.303 mmol) and $Pd(OC(O)R')_2$ (R' = CF_3 (101 mg, 0.304 mmol), Me (68.0 mg, 0.303 mmol) and ^{t}Bu (93.5 mg, 0.303 mmol)) separately and the resulting heterogeneous mixture dispersed in a freshly distilled toluene (10 mL). The contents in the RB flask were stirred and heated at 65 °C for 6 h. The complete consumption of the guanidine was verified by TLC in each case using MeOH/ethyl acetate (1/4, v/v) mixture as the eluent. The reaction mixture was filtered while hot through a Whatman filter paper and the filtrate stored at RT for one week to afford **3**·½ toluene as brown solid, **4**·¼ toluene as colourless crystals and **5**·½ toluene·½ pivalic acid as pale yellow crystals suitable for SCXRD.

Data for 3·½ toluene Yield = 78% (130 mg, 0.237 mmol). M.p. 226.4 °C (decomp.). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.48 (s, 1 H, N*H*), 8.12 (d, J_{HH} = 4.8 Hz, 1 H, Ar*H*), 7.42–7.36 (m, 2 H, Ar*H*), 7.14–7.09 (m, 2 H, Ar*H*), 7.05 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.89 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 6.83–6.80 (m, 3 H, Ar*H*), 6.23 (s, 1 H, N*H*), 5.82 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 5.76 (br, 2 H, CH_2), 1.96, 1.40 (each s, 2 × 3 H, CH_3). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –74.44. Anal. Calcd for

$C_{23}H_{21}F_3N_4O_2Pd$ (MW = 548.862 g/mol): C, 50.33; H, 3.86; N, 10.21; Found: C, 50.18; H, 3.70; N, 10.19. IR (KBr, cm^{-1}): υ(NH) 3420 (w), 3215 (br); υ_a(OCO) 1674 (s); ν(C=N) 1636 (s); ν_s(OCO) 1354 (m). ESI-MS (*m/z*): calcd for $[M - OC(O)CF_3 + MeCN]^+$ 476.1067, found 476.1072, calcd for $[M - OC(O)CF_3]^+$ 435.0801, found 435.0812.

Data for 4·¼ toluene Yield = 81% (121 mg, 0.244 mmol). M.p. 238.0 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 9.24 (s, 1 H, N*H*), 8.28 (d, J_{HH} = 4.8 Hz, 1 H, Ar*H*), 7.55 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.34 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.27–7.23 (m, 2 H, Ar*H*, toluene), 7.18–7.16 (m, 3 H, Ar*H*, toluene), 7.11 (t, J_{HH} = 6.6 Hz, 1 H, Ar*H*), 7.06 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.00 (t, J_{HH} = 7.4 Hz, 1 H, Ar*H*), 6.85–6.75 (m, 4 H, Ar*H*), 6.18 (s, 1 H, N*H*), 6.08 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 5.69 (br, 2 H, CH_2), 2.35 (s, 3 H, CH_3, toluene), 2.28, 1.95, 1.36 (each s, 3 × 3 H, CH_3). Anal. Calcd for $C_{23}H_{24}N_4O_2Pd$·¼ C_7H_8 (MW = 494.891 + 23.035 g/mol): C, 57.40; H, 5.06; N, 10.82; Found: C, 57.06; H, 5.01; N, 11.09. IR (KBr, cm^{-1}): υ(NH) 3421 (m); υ_a(OCO) 1641 (s); ν(C=N) 1589 (s); ν_s(OCO) 1381 (m). ESI-MS (*m/z*): calcd for $[M - OC(O)Me + MeCN]^+$ 476.1067, found 476.1074, calcd for $[M - OC(O)Me]^+$ 435.0801, found 435.0808.

Data for 5·½ toluene·½ pivalic acid Yield = 69% (112 mg, 0.209 mmol). M.p. 260.1 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 9.47 (s, 1 H, N*H*), 8.24 (d, J_{HH} = 5.2 Hz, 1 H, Ar*H*), 7.56 (br d, J_{HH} = 5.6 Hz, 1 H, Ar*H*), 7.28 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.10 (t, J_{HH} = 6.4 Hz, 1 H, Ar*H*), 7.07–7.00 (m, 3 H, Ar*H*), 6.96 (br t, J_{HH} = 6.8 Hz, 1 H, Ar*H*), 6.74–6.64 (m, 5 H, Ar*H* + CH_2), 6.01 (s, 1 H, N*H*), 1.92 (s, 3 H, CH_3), 1.33 (s, 9 H, C(CH_3)$_3$), 1.29 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): *δ* 185.9, 161.5, 146.8, 146.3, 137.1, 136.7, 134.7, 134.4, 133.9, 130.9, 126.8, 126.6, 126.5, 126.3, 125.3, 121.7, 120.3, 120.1, 120.0, 60.4, 40.0, 38.7, 28.8, 27.5, 17.8, 16.8. Anal. Calcd for $C_{26}H_{30}N_4O_2Pd$·½ C_7H_8 (MW = 536.972 + 46.070 g/mol): C, 60.77; H, 5.88; N, 9.61; Found: C, 61.12; H, 5.57; N, 9.73. IR (KBr, cm^{-1}): υ(NH) 3420 (w); υ_a(OCO) 1707 (s);

ν(C=N) 1640 (m); ν_s(OCO) 1354 (m). ESI-MS (*m/z*): calcd for [M – OC(O)^{t}Bu + MeCN]$^+$ 476.1067, found 476.1084; calcd for [M – OC(O)^{t}Bu]$^+$ 435.0801, found 435.0818.

Complexes 6–9 A 25 mL RB was charged with the guanidine, **2** (100 mg, 0.228 mmol) and Pd(OC(O)R')$_2$ (R' = CF_3 (75.8 mg, 0.228 mmol), Me (51.2 mg, 0.228 mmol) and ^{t}Bu (70.4 mg, 0.228 mmol)) separately and the resulting heterogeneous mixture dispersed in a freshly distilled toluene (10 mL). The contents in the RB flask were stirred and heated at 65 °C for 6 h. The complete consumption of the guanidine was verified by TLC in each case using ethyl acetate/*n*-hexane (1/1, v/v) mixture as the eluent. The reaction mixture was filtered while hot through a Whatman filter paper and the filtrate stored at RT for one week to afford **6**, an admixture of **7 + 9** and **8** as white, light brown and pale yellow solids, respectively. Complexes **6** and **7** were obtained as colorless crystals suitable for SCXRD in toluene at RT over the period of five days.

Data for 6 Yield = 66% (99.0 mg, 0.151 mmol). M.p. 255.0 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.75 (s, 1 H, N*H*), 8.12 (d, J_{HH} = 5.6 Hz, 1 H, Ar*H*), 7.71–7.68 (m, 2 H, Ar*H*), 7.48 (dt, J_{HH} = 7.6 Hz, J_{HH} = 1.6 Hz, 1 H, Ar*H*), 7.41 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.36 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.20–7.13 (m, 2 H, Ar*H*), 6.98–6.95 (m, 2 H, N*H* + Ar*H*), 6.64 (d, J_{HH} = 2.4 Hz, 1 H, Ar*H*), 5.97 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 5.69 (br, 2 H, CH_2). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –61.28, –61.38 and –74.50. Anal. Calcd for $C_{23}H_{15}N_4F_9O_2Pd$ (MW = 656.805 g/mol): C, 42.06; H, 2.30; N, 8.53. Found: C, 42.33; H, 2.01; N, 8.76. IR (KBr, cm^{-1}): υ(NH) 3433 (w), 3231 (br w); υ_a(OCO) 1672 (s); ν(C=N) 1647 (m); ν_s(OCO) 1308 (m). ESI-MS (*m/z*): calcd for [M – OC(O)CF_3 + MeCN]$^+$ 584.0501, found 584.0514.

Data for 7 + 9 Yield = 82% (113 mg, 0.187 mmol). M.p. 248.0 °C (decomp.). The ^{1}H NMR spectrum indicated the presence of two species in about 1.00:0.12 ratio as estimated from the integrals of aromatic and N*H* protons. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.74 (s, 1 H, N*H*, **7**),

9.35 (s, 1 H, N*H*, **9**), 8.23 (d, J_{HH} = 5.2 Hz, 1 H, Ar*H*, **7**), 8.12 (d, J_{HH} = 5.2 Hz, 1 H, Ar*H*, **9**), 7.90 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*, **7**), 7.72 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*, **9**), 7.68 (d, J_{HH} = 8.8 Hz, 1 H, Ar*H*, **9**), 7.64 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*, **7**), 7.50 (t, J_{HH} = 8.0 Hz, 1 H, Ar*H*, **9**), 7.41–7.30 (m, 5 H, Ar*H*, **7** (3 H) and **9** (2 H)), 7.21 (t, J_{HH} = 8.0 Hz, 1 H, Ar*H*, **9**), 7.13–7.05 (m, 4 H, Ar*H*, **7** (2 H) + **9** (2 H)), 6.96 (t, J_{HH} = 7.6 Hz, 1 H, **7**), 6.92 (t, J_{HH} = 8.0 Hz, 1 H, Ar*H*, **9**), 6.85 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*, **7**), 6.55 (s, 1 H, N*H*, **9**), 6.48 (s, 1 H, N*H*, **7**), 6.30 (d, J_{HH} = 5.2 Hz, 1 H, Ar*H*, **9**), 6.01 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*, **7**), 5.64 (br, 2 H, CH_2, **7**), 5.57 (br, 2 H, CH_2, **9**), 2.20 (s, 6 H, CH_3, **7** (3 H) and **9** (3 H)). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –61.37 (**7**), –61.40 (**9**), –61.47 (**9**), –61.54 (**7**). Anal. Calcd for $C_{23}H_{18}F_6N_4O_2Pd$ (MW = 602.833 g/mol): C, 45.83; H, 3.01; N, 9.29. Found: C, 45.88; H, 2.63; N, 9.64. IR (KBr, cm^{-1}): υ(NH) 3434 (w); υ_a(OCO) 1652 (s); ν(C=N) 1607 (m); ν_s(OCO) 1311 (m). ESI-MS (*m/z*): calcd for $C_{21}H_{15}F_6N_4Pd$ [M – OC(O)Me + MeCN]$^+$ 584.0501, found 584.0512; calcd for $C_{21}H_{15}F_6N_4Pd$ [M – OC(O)Me]$^+$ 543.0236, found 543.0244.

Data for 8 Yield = 88% (129 mg, 0.200 mmol). M.p. 240.0 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.03 (s, 1 H, N*H*), 8.19 (d, J_{HH} = 5.2 Hz, 1 H, Ar*H*), 8.02 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.63 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.38–7.32 (m, 2 H, Ar*H*), 7.27 (m, 2 H, Ar*H*), 7.16–7.11 (m, 2 H, Ar*H*), 6.93 (t, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 6.81 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.44 (s, 1 H, N*H*), 6.38 (br, 2 H, CH_2), 1.14 (s, 9 H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 186.3, 161.2, 147.1, 146.8, 140.1, 137.3, 135.0, 133.6, 133.0, 131.5, 129.5 (q, $^2J_{CF}$ = 29.8 Hz), 129.2, 128.3, 127.4 (q, $^3J_{CF}$ = 4.8 Hz), 124.1, 123.3 (each q, $^1J_{CF}$ = 273.6 Hz), 122.8 (q, $^3J_{CF}$ = 3.8 Hz), 122.1, 120.2, 119.6, 114.0 (q, $^2J_{CF}$ = 28.8 Hz), 60.2, 39.8, 28.5. ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –61.33, –61.52. Anal. Calcd for $C_{26}H_{24}N_4F_6O_2Pd$ (MW = 644.914 g/mol): C, 48.42; H, 3.75; N, 8.69. Found: C, 48.72; H, 3.60; N, 8.73. IR (KBr, cm^{-1}): υ(NH) 3438 (w); υ_a(OCO) 1653 (s); ν(C=N) 1605 (m); ν_s(OCO) 1311 (m). ESI-MS (*m/z*): calcd for $C_{21}H_{15}F_6N_4Pd$ [M – OC(O)^{t}Bu +

MeCN]$^{+}$ 584.0501, found 584.0523; calcd for $C_{21}H_{15}F_6N_4Pd$ [M – OC(O)^{t}Bu]$^{+}$ 543.0236, found 543.0254.

Procedure for pure 7

A 25 mL RB was charged with the guanidine, **2** (100 mg, 0.228 mmol) and $Pd(OAc)_2$ (51.2, 0.228 mmol) and the resulting heterogeneous mixture dispersed in a freshly distilled toluene (10 mL). The contents in the RB flask were stirred at RT for 6 h. The complete consumption of the guanidine was verified by TLC using ethyl acetate/*n*-hexane (1/1, v/v) mixture as the eluent. The reaction mixture was filtered through a Whatman filter paper and stored at RT for one week to afford **7** as white solid in 86% (118 mg, 0.195 mmol) yield.

Data for 7 Yield = 86% (118 mg, 0.196 mmol). M.p. 249.0 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.80 (s, 1 H, N*H*), 8.23 (d, J_{HH} = 5.6 Hz, 1 H, Ar*H*), 7.90 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.64 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.39–7.30 (m, 3 H, Ar*H*), 7.14–7.08 (m, 2 H, Ar*H*), 6.95 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.85 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 6.47 (s, 1 H, N*H*), 6.01 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 5.63 (br, 2 H, C*H*$_2$), 2.20 (s, 3 H, C*H*$_3$). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –61.28, –61.45. Anal. Calcd for $C_{23}H_{18}F_6N_4O_2Pd$ (MW = 602.833 g/mol): C, 45.83; H, 3.01; N, 9.29. Found: C, 45.88; H, 2.63; N, 9.64. IR (KBr, cm^{-1}): υ(NH) 3434 (w); υ_a(OCO) 1654 (s); ν(C=N) 1617 (m); ν_s(OCO) 1314 (m).

Complexes 10 and 11 A 25 mL RB was charged with **3** (104 mg, 0.190 mmol) or **6** (125 mg, 0.190 mmol) and PPh_3 (50.0 mg, 0.190 mmol) separately, dissolved the mixture in CH_2Cl_2 (10 mL) and set to stir for 24 h at RT. The reaction mixture was filtered through a Whatman filter paper, the filtrate layered with toluene and stored at RT for one week to afford **10** and **11** as colorless crystals.

Data of 10 Yield = 82% (126 mg, 0.155 mmol). M.p. 203.9 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.15 (s, 1 H, N*H*), 7.67–7.61 (m, 8 H, Ar*H*), 7.46 (dt, J_{HH} = 7.6 Hz, J_{HH} = 1.6 Hz, 3 H, Ar*H*), 7.39–7.35 (m, 7 H, Ar*H*), 7.32–7.30 (m, 1 H, Ar*H*), 7.23–7.19 (m, 3 H, Ar*H*), 6.95 (s, 1 H, N*H*), 6.72–6.69 (m, 1 H, Ar*H*), 6.58–6.54 (m, 2 H, Ar*H*), 6.03 (t, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 5.61 (d, J_{HH} = 2.0 Hz, 2 H, CH_2), 2.36, 1.75 (each s, 2 × 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 164.2, 161.6 (q, $^{2}J_{CF}$ = 32.7 Hz), 149.5, 149.0, 138.8, 138.6, 138.4, 136.5, 136.1, 135.4, 135.0, 134.9, 131.6, 131.4, 130.4, 129.9, 129.0, 128.9, 128.0, 127.6, 127.3, 127.0, 123.6, 122.5, 122.3, 121.8, 117.3 (q, $^{1}J_{CF}$ = 295.4 Hz), 58.5, 18.2, 17.9. ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –74.99. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 35.91. Anal. Calcd for $C_{41}H_{36}N_4F_3O_2PPd$ (MW = 811.154 g/mol): C, 60.71; H, 4.47; N, 6.91. Found: C, 60.72; H, 4.39; N, 6.88. IR (KBr, cm^{-1}): υ(NH) 3412 (w); υ_a(OCO) 1685 (s); ν(C=N) 1620 (m); ν_s(OCO) 1436 (m). Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 72.36 (10^{-3} M).

Data of 11 Yield = 85% (148 mg, 0.161 mmol). M.p. 184.7 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.81 (s, 1 H, N*H*), 7.82–7.79 (m, 2 H, Ar*H*), 7.74–7.62 (m, 9 H, Ar*H*), 7.57–7.53 (m, 1 H, Ar*H*), 7.50–7.47 (m, 3 H, Ar*H*), 7.39 (dt, J_{HH} = 7.4 Hz, J_{HH} = 2.0 Hz, 6 H, Ar*H*), 7.24 (d, J_{HH} = 5.6 Hz, 1 H, Ar*H*), 6.94–6.88 (m, 2 H, Ar*H* (1 H), N*H* (1 H)), 6.78 (d, J_{HH} = 2.4 Hz, 1 H, Ar*H*), 6.73 (t, J_{HH} = 6.6 Hz, 1 H, Ar*H*), 6.13 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 5.75 (br, 2 H, CH_2). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –60.73, –61.14, –75.04. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 36.34. Anal. Calcd for $C_{41}H_{30}N_4F_9O_2PPd$ (MW = 919.096 g/mol): C, 53.58; H, 3.29; N, 6.10; Found: C, 53.81; H, 3.05; N, 6.19. IR (KBr, cm^{-1}): υ(NH) 3437 (w); υ_a(OCO) 1683 (s); ν(C=N) 1598 (m); ν_s(OCO) 1420 (m). Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 75.84 (10^{-3} M).

Complex 12 In a 5 mm Wilmad NMR tube fitted with a w/J Young valve, complex **7** (22.9 mg, 0.038 mmol) and PPh_3 (10.0 mg, 0.038 mmol) were added and dissolved in $CDCl_3$ (0.6 mL). The

contents in the NMR tube was shaken well for about 5 min and ^{1}H, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectra were recorded. Complex **12** could not be isolated in solid form as it reverts back to the respective starting materials during crystallization. Hence, **12** was characterized only by ^{1}H, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectroscopies.

Data of 12 ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74–7.65 (m, 3 H, Ar*H*), 7.61–7.50 (m, 9 H, Ar*H* (8 H) + N*H* (1 H)), 7.44–7.41 (m, 3 H, Ar*H*), 7.37–7.34 (m, 8 H, Ar*H* (7 H)+ N*H* (1 H)), 7.25 (d, J_{HH} = 5.2 Hz, 1 H, Ar*H*), 6.91 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.88 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 6.70 (t, J_{HH} = 6.0 Hz, 1 H, Ar*H*), 6.08 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 5.76 (s, 2 H, CH_2), 1.89 (s, 3 H, CH_3). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –60.72, –61.40. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.8 MHz): δ 34.71.

Complex 13 A 25 mL RB was charged with 2,6-xylylisocyanide (20.0 mg, 0.152 mmol) and **3** (83.4 mg, 0.152 mmol) the resulting mixture dissolved in CH_2Cl_2 (10 mL) and set to stir at RT for 24 h. The reaction mixture was filtered through a Whatman filter paper, the filtrate layered with toluene and stored at RT for one week to afford **13** as light pink crystals, respectively.

Data of 13 Yield = 80% (82.7 mg, 0.122 mmol). M.p. 126.6 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.37 (s, 1 H, N*H*), 8.51 (d, J_{HH} = 5.6 Hz, 1 H, Ar*H*), 7.98–7.90 (m, 2 H, Ar*H*), 7.56 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.39–7.34 (m, 4 H, Ar*H*), 7.31–7.29 (m, 2 H, Ar*H*), 7.24 (br s, 1 H, Ar*H*), 7.17 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.90 (d, J_{HH} = 6.8 Hz, 1 H, Ar*H*), 6.78 (s, 1 H, N*H*), 6.66 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 5.82 (s, 2 H, CH_2), 2.56 (s, 2 × 3 H, CH_3), 2.36, 1.69 (each s, 2 × 3 H, CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 163.4, 161.6 (q, $^{2}J_{CF}$ = 33.4 Hz), 148.3, 147.4, 141.3, 139.2, 137.0, 135.9, 135.3, 135.0, 131.8, 130.7, 129.1, 128.8, 128.6, 128.4, 127.9, 125.6, 123.5, 123.4, 123.3, 121.8, 117.4 (q, $^{1}J_{CF}$ = 296.1 Hz), 60.5, 19.1, 18.0, 17.8. ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –75.08. Anal. Calcd for $C_{32}H_{30}N_5F_3O_2Pd$ (MW = 680.040 g/mol): C,

56.52; H, 4.45; N, 10.30. Found: C, 56.76; H, 4.51; N, 10.37. IR (KBr, cm^{-1}): υ(NH) 3411 (w); ν(C≡N) 2175 (s); υ_a(OCO) 1674 (s); ν(C=N) 1633 (m); ν_s(OCO) 1445 (m). Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 59.29 (10^{-3} M).

Complexes 14 A 25 mL RB was charged with 2,6-xylylisocyanide (20.0 mg, 0.152 mmol) and **6** (99.8 mg, 0.152 mmol), the resulting mixture dissolved in CH_2Cl_2 (10 mL) and set to stir at RT for 24 h. The reaction mixture was filtered through a Whatman filter paper, layered with toluene and stored at RT for one week to afford **14** as light pink crystals.

Data of 14 Yield = 81% (97.0 mg, 0.123 mmol). M.p. 179.8 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.83 (s, 1 H, N*H*), 8.51 (d, J_{HH} = 4.4 Hz, 1 H, Ar*H*), 7.95 (br, 2 H, Ar*H*), 7.89 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.81 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.71 (t, J_{HH} = 6.8 Hz, 1 H, Ar*H*), 7.64 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.58 (t, J_{HH} = 7.0 Hz, 1 H, Ar*H*), 7.39–7.33 (m, 3 H, Ar*H*), 7.27–7.25 (m, 2 H, Ar*H*), 6.92 (s, 1 H, N*H*), 6.82 (t, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 5.83 (br, 2 H, CH_2), 2.56 (s, 2 × 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 163.0, 161.6 (q, $^2J_{CF}$ = 32.7 Hz), 148.5, 147.7, 147.2, 139.5, 135.9, 134.1, 133.9, 133.7, 132.3, 131.0, 130.0 (q, $^2J_{CF}$ = 30.4 Hz), 129.4, 128.8, 128.6, 127.8 (q, $^3J_{CF}$ = 4.3 Hz), 125.6 (br), 124.3 (q, $^3J_{CF}$ = 5.1 Hz), 124.0 (q, $^1J_{CF}$ = 274.3 Hz), 123.8, 123.2 (q, $^1J_{CF}$ = 272.9 Hz), 123.1, 121.4, 118.7, 116.1 (q, $^2J_{CF}$ = 29.0 Hz), 60.7, 19.1. ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –61.16, –61.58, –75.18. Anal. Calcd for $C_{32}H_{24}N_5F_9O_2Pd$ (MW = 787.983 g/mol): C, 48.78; H, 3.07; N, 8.89. Found: C, 48.84; H, 3.05; N, 9.20. IR (KBr, cm^{-1}): υ(NH) 3447 (w), ν(C≡N) 2188 (m), υ_a(OCO) 1680 (s); ν(C=N) 1604 (m); ν_s(OCO) 1455 (m). Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 57.17 (10^{-3} M).

Complexes 15 A 25 mL RB was charged with 2,6-xylylisocyanide (20.0 mg, 0.152 mmol), **4** (78.7 mg, 0.152 mmol) or **5** (88.6 mg, 0.152 mmol) separately, the resulting mixture dissolved in CH_2Cl_2 (10 mL) and set to stir at RT for 24 h. The reaction mixture was filtered through a Whatman filter

paper, the filtrate layered with toluene and stored at RT for three weeks to afford **15** as dark red crystals suitable for SCXRD. Yields = 77% (68.8 mg, 0.118 mmol) from **4** and 81% (72.3 mg, 0.124 mmol) from **5**.

Alternate Method for 15

A 25 mL RB was charged with **4** (50.0 mg, 0.096 mmol) and ^{t}BuOK (43.0 mg, 0.384 mmol) in $CHCl_3$ (10 mL) and the resulting mixture stirred at RT for 5 min. To this solution 2,6-xylylisocyanide (15.1 mg 0.115 mmol) was added and stirred for 24 h. During the course of the reaction, color of the solution changed from yellow to dark red indicating the formation of oxygenated product, **15**. The reaction mixture was filtered through a Whatman filter paper and the filtrate evaporated under vacuum to afford **15** in 82% (46.1 mg, 0.079 mmol) yield.

Data of 15 M.p. 226.4 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.69 (s, 1 H, N*H*), 8.54 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 8.45 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 8.31 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 8.04 (dt, J_{HH} = 7.6 Hz; 1.2 Hz, 1 H, Ar*H*), 7.53 (t, J_{HH} = 6.0 Hz, 1 H, Ar*H*), 7.42 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 7.35 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.24–7.16 (m, 4 H, Ar*H*), 6.98 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 6.92 (t, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 6.53 (t, J_{HH} = 7.4 Hz, 1 H, Ar*H*), 2.57 (s, 2 × 3 H, CH_3), 2.43, 2.38 (each s, 2 × 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 172.6, 154.8, 148.3, 143.7, 141.4, 140.2, 140.1, 139.7, 135.9, 134.7, 133.2, 130.3, 129.8, 128.6, 128.5, 128.1, 127.8, 126.9, 125.8, 122.8, 121.5, 120.9, 21.9, 19.2, 18.9. Anal. Calcd for $C_{30}H_{27}N_5OPd\cdot¼\ H_2O$ (MW = 580.000 + 4.504 g/mol): C, 61.65; H, 4.74; N, 11.98. Found: C, 61.70; H, 4.72; N, 12.17. IR (KBr, cm^{-1}): υ(NH) 3425 (w); ν(C≡N) 2160 (s); υ(C=O) 1639 (s); ν(C=N) 1530 (s).

Complexes 16 A 25 mL RB was charged with 2,6-xylylisocyanide (20.0 mg, 0.152 mmol) and **7** (91.6 mg, 0.152 mmol), the resulting mixture dissolved in CH_2Cl_2 (10 mL) and set to stir at RT

for 24 h. The reaction mixture was filtered through a Whatman filter paper, layered with toluene and stored at RT for three weeks to afford **16** as red crystals suitable for SCXRD.

Data of 16 Yield = 78% (81.6 mg, 0.119 mmol). M.p. 242.3 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.10 (s, 1 H, N*H*), 8.41 (d, J_{HH} = 4.4 Hz, 1 H, Ar*H*), 8.29 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 8.18 (d, J_{HH} = 8.4 Hz, 1 H, Ar*H*), 7.90 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.71 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.56 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 7.49 (t, J_{HH} = 7.0 Hz, 2 H, Ar*H*), 7.39–7.35 (m, 2 H, Ar*H*), 7.24 (d, J_{HH} = 7.6 Hz, 2 H, Ar*H*), 7.10 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.62 (t, J_{HH} = 7.4 Hz, 1 H, Ar*H*), 2.57 (s, 2 × 3 H, C*H*$_3$). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –59.98, –61.34. Anal. Calcd for $C_{30}H_{21}N_5F_6OPd$ (MW = 687.942 g/mol): C, 52.38; H, 3.08; N, 10.18. Found: C, 52.55; H, 3.23; N, 10.47. IR (KBr, cm^{-1}): υ(NH) 3010 (br w), ν(C≡N) 2174 (m), υ(C=O) 1643 (m), ν(C=N) 1517 (s).

Complexes 17 A 25 mL RB was charged with 2,6-xylylisocyanide (20.0 mg, 0.152 mmol) and **8** (98.0 mg, 0.152 mmol), the resulting mixture dissolved in CH_2Cl_2 (10 mL) and set to stir at RT for 24 h. The reaction mixture was filtered through a Whatman filter paper, layered with toluene and stored at RT for three days to afford **17** as orange crystals suitable for SCXRD.

Data of 17: Yield = 76% (77.9 mg, 0.116 mmol). M.p. 198.5 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (d, J_{HH} = 5.6 Hz, 1 H, Ar*H*), 7.83 (t, J_{HH} = 8.4 Hz, 2 H, Ar*H*), 7.60 (d, J_{HH} = 7.6 Hz, 2 H, Ar*H*), 7.43 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.33 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.28–7.23 (m, 2 H, Ar*H*), 7.20 (d, J_{HH} = 7.6 Hz, 2 H, Ar*H*), 7.04 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 7.00 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.86 (br, 1 H, N*H*), 6.59 (t, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 5.55 (s, 2 H, C*H*$_2$), 2.53 (s, 6 H, 2 × C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 165.9, 149.6 (br), 148.6, 147.2, 146.5, 138.3, 138.0, 135.7, 132.6, 130.3, 129.1, 128.6, 128.3, 127.6, 126.9, 126.7 (q, $^{3}J_{CF}$ = 5.8 Hz), 126.3, 125.4, 124.9 (q, $^{2}J_{CF}$ = 28.3 Hz), 124.8, 124.7 (each q, $^{1}J_{CF}$ = 273.6 Hz), 123.7 (q, $^{3}J_{CF}$

= 5.8 Hz), 122.7, 121.9, 121.0, 118.4, 113.8 (q, $^{2}J_{CF}$ = 29.0 Hz), 62.1, 19.1. ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ –61.47, –61.84. Anal. Calcd for $C_{30}H_{23}N_5F_6Pd$ (MW = 673.959 g/mol): C, 53.46; H, 3.44; N, 10.39. Found: C, 53.19; H, 3.16; N, 10.63. IR (KBr, cm^{-1}): υ(NH) 3425 (w); ν(C≡N) 2175 (m); ν(C=N) 1523 (m).

General procedure for cycloisomerization of 4-pentynoic acid

In a 5 mm Wilmad NMR tube fitted with a w/J Young valve, 4-pentynoic acid (6 mg, 0.061 mmol) was dissolved in 0.6 mL $CDCl_3$. To this solution, 1 mol% catalyst solution of **3**–**8** prepared in $CDCl_3$ was added and the NMR tube was shaken briefly. The progress of the reaction involving 4-pentynoic acid (7.00 mg, 0.071 mmol) and **8** (0.46 mg, 1 mol%) in $CDCl_3$ was monitored by ^{1}H NMR spectroscopy at regular time interval. The signals of CH_2 protons of the product slowly emerged while corresponding signals of 4-pentynoic acid disappeared completely after 12 h.

Table S1 Crystallographic data for **3**·½ toluene, **5**·½ toluene·½ pivalic acid and **6**.

	3·½ toluene	**5**·½ toluene·½ pivalic acid	**6**
Formula	$C_{26.5}H_{25}F_3N_4O_2Pd$	$C_{32}H_{38.5}N_4O_3Pd$	$C_{23}H_{15}F_9N_4O_2Pd$
Fw	594.90	633.57	656.79
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$
a (Å)	11.2472(5)	11.8433(3)	13.8775(5)
b (Å)	11.6670(6)	18.0831(5)	22.4973(9)
c (Å)	20.8033(6)	29.6288(9)	16.1759(6)
α (deg)	99.053(3)	90	90
β (deg)	99.487(3)	90.847(2)	96.334(4)
γ (deg)	97.943(4)	90	90
Volume ($Å^3$)	2620.9(2)	6344.7(3)	5019.4(3)
Z	4	8	8
ρ_{calcd} (Mg/m^3)	1.508	1.327	1.738
μ(Mo Kα) (mm^{-1})	0.760	0.621	0.835
F(000)	1204.0	2628.0	2592.0
2θ range (deg)	7.088 to 52.742	6.828 to 49.998	6.806 to 52.744
No. of reflns collected	10696	81137	69215
No. of reflns used	10696	11155	12245
Parameters	657	673	758
R_1 [I>2σ(I)][a]	0.0782	0.0555	0.0501
wR_2 (all reflns)[b]	0.2199	0.1204	0.1126
GooF on F^2 [c]	1.053	1.0318	1.036
Largest diff. peak and hole, ($e·Å^{-3}$)	1.91/-1.07	0.50/–0.48	0.56/-0.64

[a] $R_1 = \Sigma|\,|F_o| - |F_c|\,|/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
[c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$

Table S2 Crystallographic data for **7**, **10** and **14**.

	7	**10**	**14**
Formula	$C_{46}H_{36}F_{12}N_8O_4Pd_2$	$C_{48}H_{44}F_3N_4O_2PPd$	$C_{32}H_{24}F_9N_5O_2Pd$
Fw	1205.63	903.24	787.96
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
a (Å)	14.2253(3)	10.8143(3)	8.2270(3)
b (Å)	19.3693(3)	14.5146(3)	26.1341(7)
c (Å)	17.4110(3)	14.5400(4)	15.2245(4)
α (deg)	90	94.143(2)	90
β (deg)	93.317(2)	109.681(2)	98.085(3)
γ (deg)	90	90.228(2)	90
Volume ($Å^3$)	4789.29(15)	2142.36(10)	3240.81(17)
Z	4	2	4
ρ_{calcd} (Mg/m^3)	1.672	1.400	1.615
μ(Mo Kα) (mm^{-1})	0.850	0.527	0.663
F(000)	2400.0	928.0	1576.0
2θ range (deg)	6.664 to 52.744	6.24 to 52.742	4.126 to 54.388
No. of reflns collected	67124	31624	8299
No. of reflns used	9772	8745	8299
Parameters	651	476	473
R_1 [I>2σ(I)][a]	0.0492	0.0502	0.1133
wR_2 (all reflns)[b]	0.1146	0.1481	0.3366
GooF on F^2 [c]	1.022	1.067	1.369
Largest diff. peak and hole, ($e \cdot Å^{-3}$)	0.59/-0.82	0.73/-0.61	1.53/-0.95

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
[c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$

Table S3 Crystallographic data for **15**, **16** and **17**·toluene.

	15	**16**	**17**·toluene
Formula	$C_{30}H_{27}N_5OPd$	$C_{30}H_{21}F_6N_5OPd$	$C_{33.5}H_{27}F_6N_5Pd$
Fw	579.96	687.92	720.027
Temperature (K)	293(2)	204.15	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a (Å)	7.3937(3)	8.4101(5)	8.7513(2)
b (Å)	13.2167(4)	11.9592(3)	12.4438(3)
c (Å)	13.2300(5)	14.4653(3)	14.6041(4)
α (deg)	89.666(3)	82.430(2)	92.799(2)
β (deg)	78.792(3)	74.423(4)	96.175(2)
γ (deg)	87.117(3)	72.257(4)	100.159(2)
Volume ($Å^3$)	1266.57(8)	1332.82(10)	1552.62(7)
Z	2	2	2
ρ_{calcd} (Mg/m^3)	1.521	1.714	1.540
μ(Mo Kα) (mm^{-1})	0.766	0.774	0.666
F(000)	592.0	688.0	724.6
2θ range (deg)	5.616 to 52.742	6.594 to 52.744	6.3 to 52.74
No. of reflns collected	10384	16195	31500
No. of reflns used	10384	5443	6336
Parameters	339	390	434
R_1 [I>2σ(I)][a]	0.0508	0.0417	0.0294
wR_2 (all reflns)[b]	0.1589	0.0995	0.0744
GooF on F^2 [c]	1.069	0.991	1.039
Largest diff. peak and hole, ($e·Å^{-3}$)	0.69/-0.76	0.96/-0.81	0.41/-0.53

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
[c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$

Table S4 List of electronic energies of **G, H, H•, H′, I, TS, K** and **K′** at the B3LYP/6-31G*/LANL2DZ level of theory and basis sets.

Systems	**E (Hartree)**	**ZPE (Hartree)**	**Thermal correction to energy (Hartree)**	**Thermal correction to Gibbs free energy (Hartree)**	**Solvation (Toluene) kcal/mol**	**Total energy including solvent, ZPE and thermal Corrections (Hartree)**
G	–1212.1564521	0.361729	0.386142	0.304495	–6.83	–1211.114967
H	–1211.585352	0.346434	0.371052	0.287614	–27.03	–1210.623335
H•	–1211.549814	0.349679	0.37389	0.291716	–5.50	–1210.54329
I	–1361.902723	0.355147	0.381579	0.295761	–33.09	–1360.922961
TS	–1361.871823	0.34949	0.375878	0.289782	–32.369	–1360.908247
K	–1286.192894	0.343056	0.368031	0.285312	–8.04	–1285.209303
K'	–1286.194096	0.342997	0.36803	0.283201	–7.75	–1285.212211
H'	–1211.585305	0.346289	0.370843	0.288111	–26.97	–1210.623049

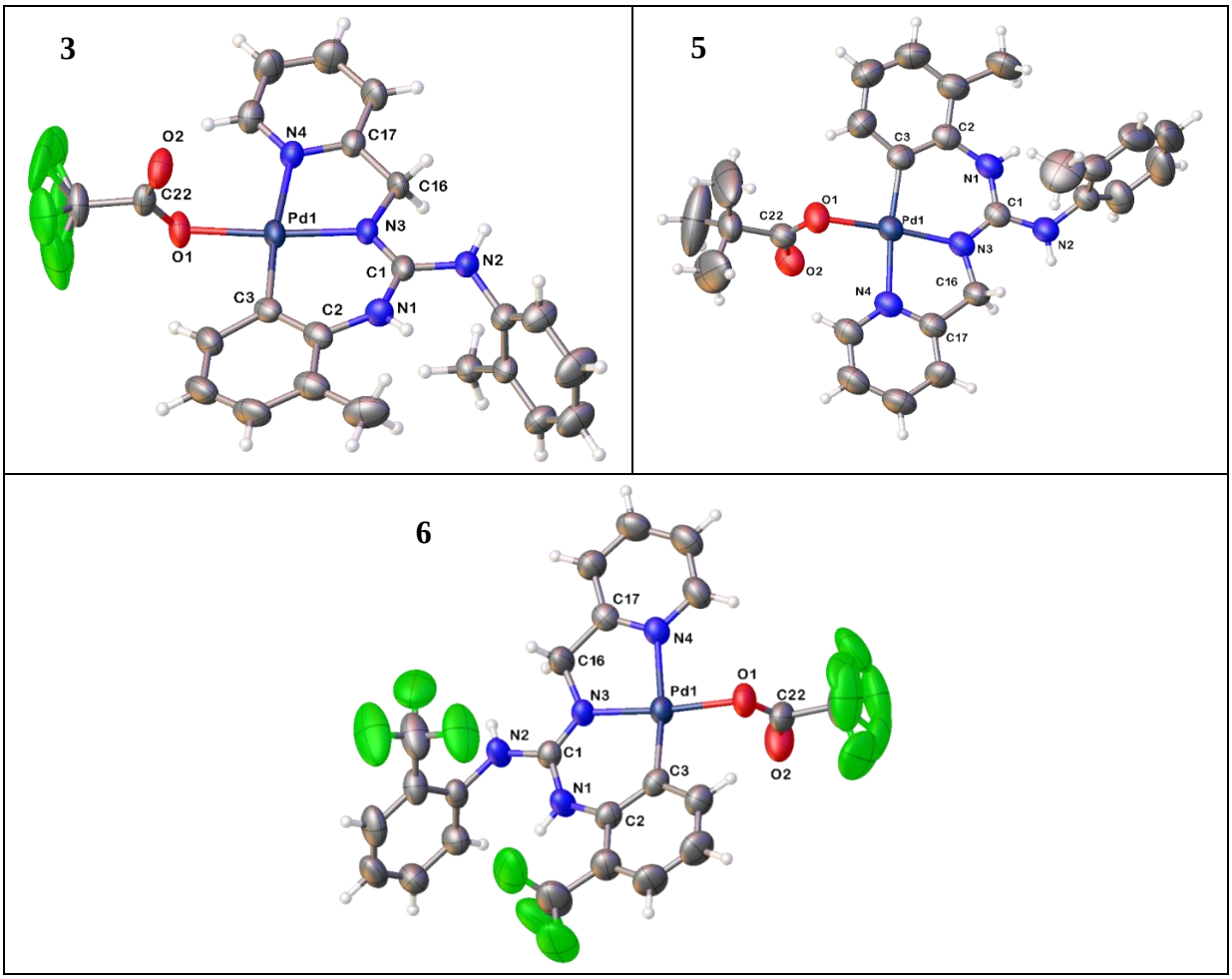
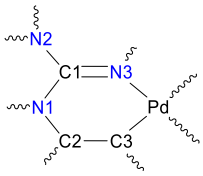


Fig. S1 Molecular structures of **3**·½ toluene, **5**·½ toluene·½ pivalic acid, **6** at the 50% probability level. Number of molecules in an asymmetric unit, Z' = 2. Only molecule 1 is shown for clarity. CF_3 unit of the carboxylate ligand revealed a rotational disorder.

Table S5 Selected bond parameters of **3**, **6**, **III** and **IV** around the CN_3 core of guanidines.



Bond	**3**·½ toluene	**6**	**IV**[a]	**V**[a]
C1–N1, Å	1.342(10)[b]	1.351(4)[b]	1.331(7)[b]	1.327(7)
	1.362(10)[c]	1.349(5)[c]	1.331(8)[c]	
C1–N2, Å	1.367(9)[b]	1.354(4)[b]	1.342(8)[b]	1.334(7)
	1.373(9)[c]	1.356(5)[c]	1.347(8)[c]	
C1–N3, Å	1.304(10)[b]	1.288(4)[b]	1.340(8)[b]	1.357(7)
	1.291(10)[c]	1.291(5)[c]	1.334(8)[c]	

[a] Ref. 20
[b] molecule 1
[c] molecule 2

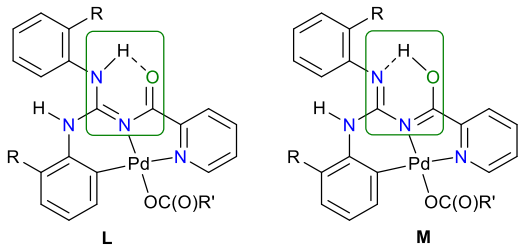


Fig. S2 Two types of resonance assisted hydrogen bond present in **IV** and **V**.[20]

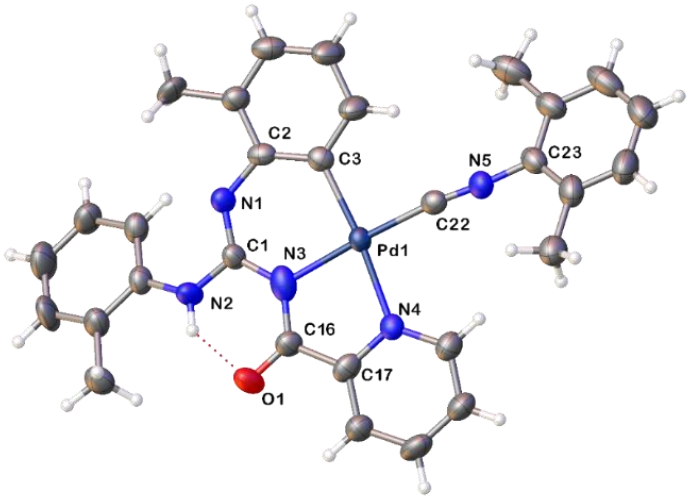


Fig. S3 Molecular structure of **15** at the 50% probability level. Hydrogen bond parameters (Å and deg): O1···H2 = 1.861; O1···N2 = 2.575; N2–H2···O1 = 139.334.

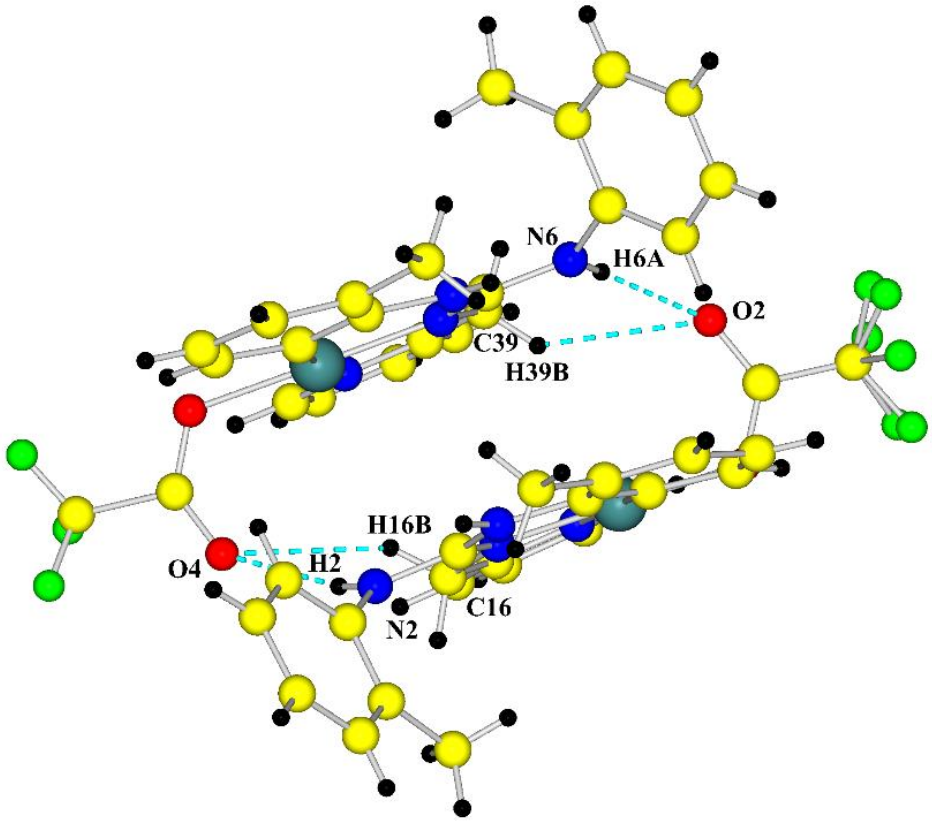


Fig. S4 Intermolecular hydrogen bond interactions in the crystal structure of **3**·½ toluene. Hydrogen bond parameters (Å and deg): O2···H6A = 2.066; O2···N6 = 2.870; N6–H6A···O2 = 155.45; O2···H39B = 2.671; O2···C39 = 3.450; C39–H39B···O2 = 137.68; O4···H2 = 2.061; O4···N2 = 2.859; N2–H2···O4 = 153.95; O4···H16B = 2.677; O4···C16 = 3.516; C16–H36B···O4 = 145.09.

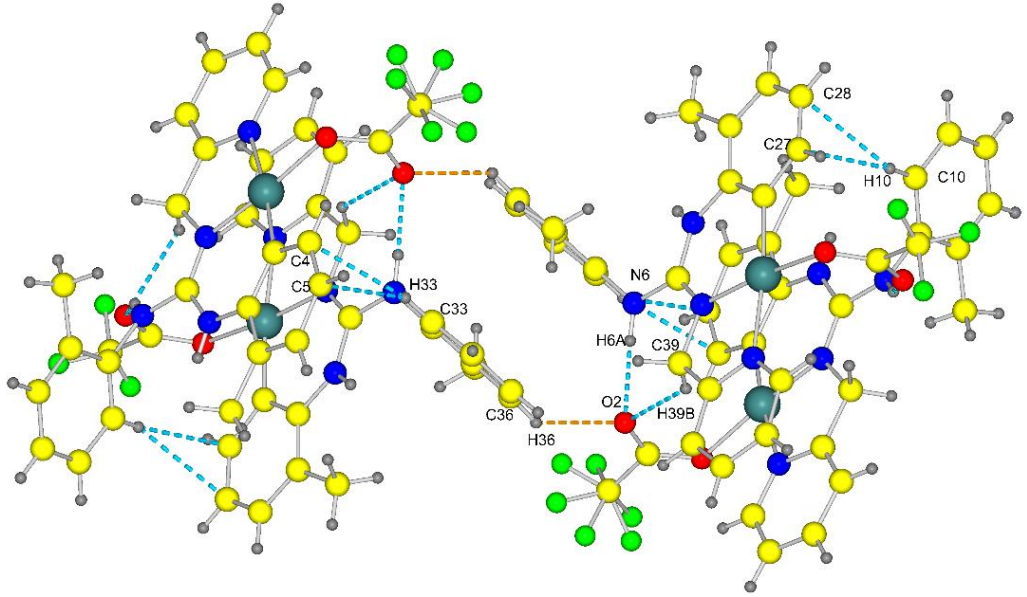


Fig. S5 Intermolecular hydrogen bond interactions in the crystal structure of **3**·½ toluene. Hydrogen bond parameters (Å and deg): O2···H6A = 2.060; O2···N6 = 2.864; N6–H6A···O2 = 155.18; O2···H39B = 2.672; O2···C39 = 3.448; C39–H39B···O2 = 137.35; O2···H36 = 2.787; O2···C36 = 3.540; C39–H39B···O2 = 142.35; C27···H10 = 2.745; C27···C10 = 3.662; C10–H10···C27 = 169.31; C28···H10 = 2.861; C28···C10 = 3.701; C10–H10···C28 = 150.91; H33···C4 = 2.726; H33···C5 = 2.766; C33–H33···C4 = 167.86; C33–H33···C5 = 148.02; O4···H16B = 3.575; O4···C16 = 3.518; C16–H36B···O4 = 144.82. In crystal structure of **3**·½ toluene, there are two molecules in an asymmetric unit arranged in a heat to tail fashion and linked with each other through N–H···O and C–H···O interactions, both interactions within the dimer and a C–H···O interaction with the adjacent dimer. Thus, the carbonyl O atom of trifluoroacetate acts as a trifurcated H bond acceptor. The head to tail dimer is also stabilized by a pair of C–H···π interactions.

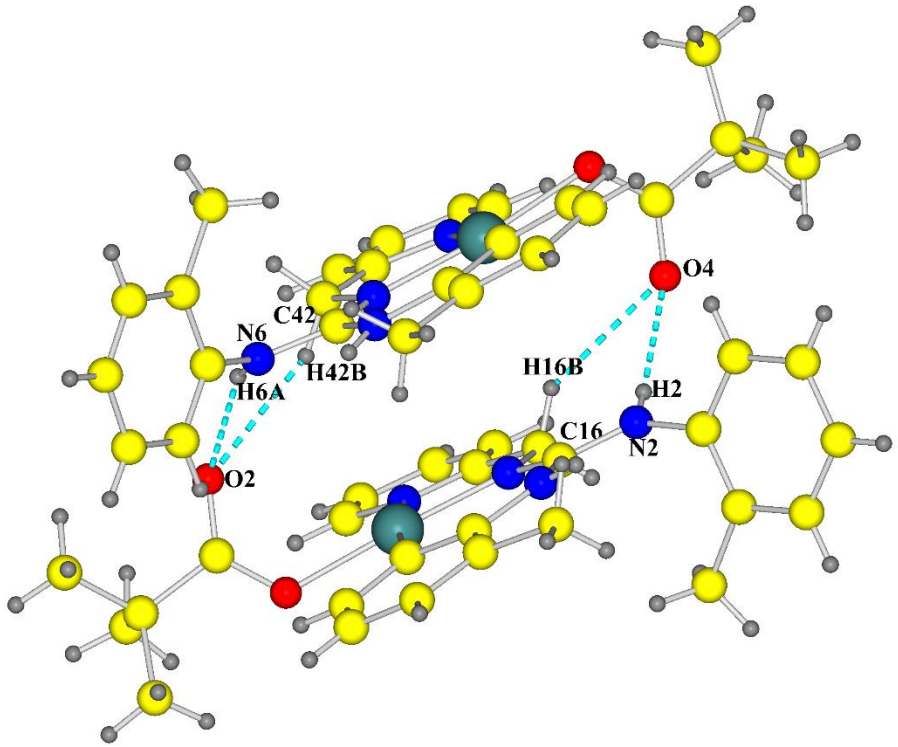


Fig. S6 Intermolecular hydrogen bond interactions in the crystal structure of **5**·½ toluene·½ pivalic acid. Hydrogen bond parameters (Å and deg): O2···H6A = 2.017; O2···N6 = 2.780; N6–H6A···O2 = 147.38; O2···H42B = 2.568; O2···C42 = 3.434; C42–H42B···O2 = 148.77; O4···H2 = 2.080; O4···N2 = 2.864; N2–H2···O4 = 151.17; O4···H16B = 2.591; O4···C16 = 3.427; C16–H36B···O4 = 144.34.

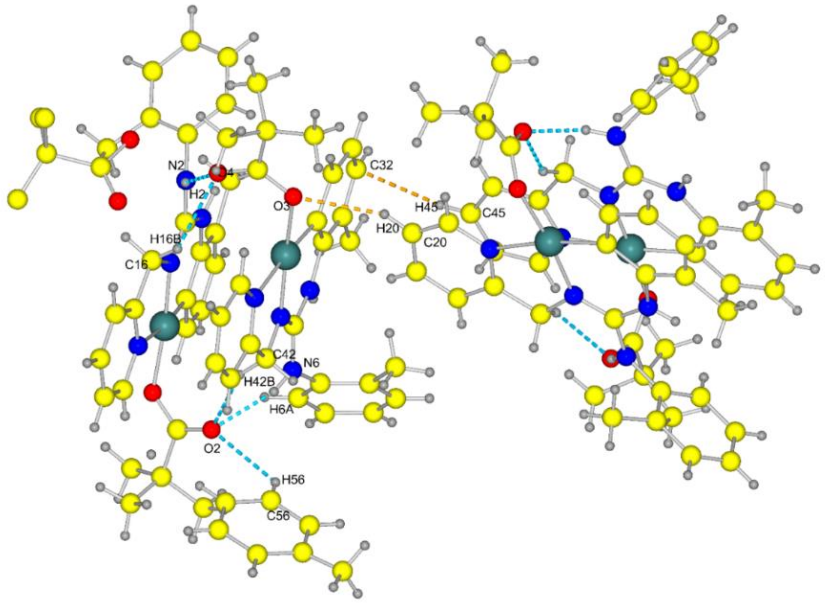


Fig. S7 Intermolecular hydrogen bond interactions in the crystal structure of **5**·½ toluene·½ pivalic acid. Hydrogen bond parameters (Å and deg): O2···H6A = 2.027; O2···N6 = 2.782; N6–H6A···O2 = 145.98; O2···H42B = 2.564; O2···C42 = 3.448; C42–H42B···O2 = 148.63; O2···H56 = 2.695; O2···C56 = 3.367; C56–H56···O2 = 129.81; O4···H2 = 2.084; O4···N2 = 2.867; N2–H2···O4 = 150.89; O2···H16B = 2.589; O2···C16 = 3.423; C16–H16B···O2 = 144.23; O3···H20 = 2.578; O3···C20 = 3.451; C20–H20···O3 = 156.34; C32···H45 = 3.104; C32···C45 = 3.688; C45–H45···C32 = 169.62. The head to tail dimer (dimer 1) is interlinked through a pair of N–H···O and C–H···O interactions wherein the carbonyl O atom of the pivalate is acceptor bifurcating. In another head to tail dimer (dimer 2) the molecule involved are linked with each other through N–H···O, C–H···O and C–H···O (toluene) interactions and the O atom of the pivalate is acceptor trifurcating. The dimer 1 and the dimer 2 are linked through one C–H···O and C–H···π interactions.

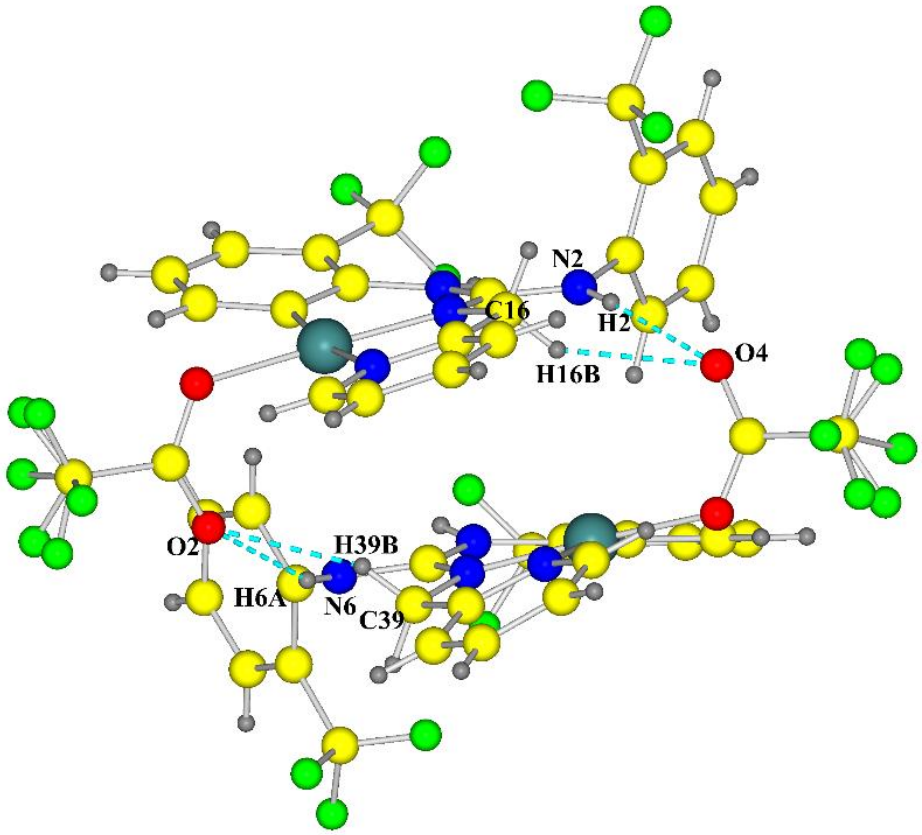


Fig. S8 Intermolecular hydrogen bond interactions in the crystal structure of **6**. Hydrogen bond parameters (Å and deg): O2···H6A = 2.084; O2···N6 = 2.860; N6–H6A···O2 = 149.87; O2···H39B = 2.437; O2···C39 = 3.316; C39–H39B···O2 = 150.60; O4···H2 = 2.099; O4···N2 = 2.902; N2–H2···O4 = 155.54; O4···H16B = 2.480; O4···C16 = 3.342; C16–H36B···O4 = 147.92.

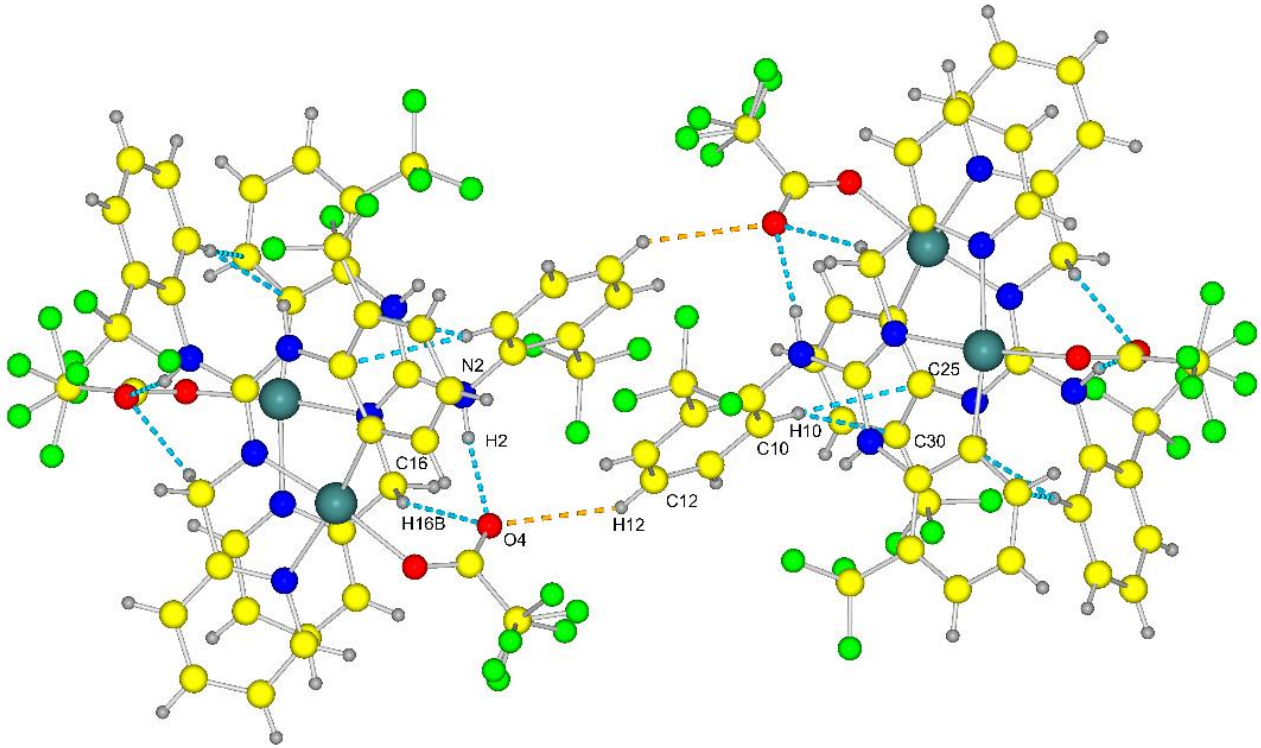


Fig. S9 Intermolecular hydrogen bond interactions in the crystal structure of **6**. Hydrogen bond parameters (Å and deg): O4···H2 = 2.099; O4···N2 = 2.904; N2–H2···O4 = 155.54; O4···H16B = 2.480; O4···C16 = 3.342; C16–H16B···O4 = 147.92; O4···H12 = 2.675; O4···C12 = 3.392; C12–H12···O4 = 134.49; C25···H10 = 2.733; C25···C10 = 3.654; C10–H10···C25 = 170.88; C30···H10 = 2.776; C30···C10 = 3.643; C10–H10···C30 = 155.51. The non-covalent interactions within and between the head to tail dimer in **6** are identical to those analogous interactions observed in the crystal structure of **3**·½ toluene.

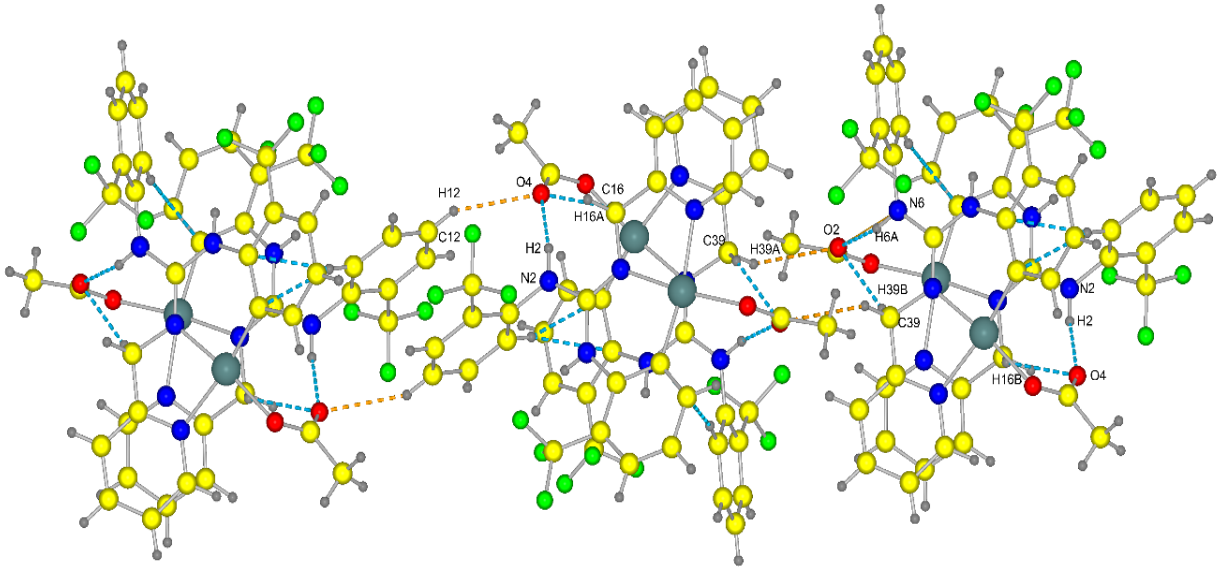


Fig S10 Intermolecular hydrogen bond interactions in the crystal structure of **7**. Hydrogen bond parameters (Å and deg): O4···H12 = 2.557; O4···C12 = 3.412; C12–H12···O4 = 152.92; O2···H39A = 2.700; O2···C39 = 3.575; C39–H39A···O2 = 150.23. The dimer 1 illustrated in Fig. S9 is linked to two adjacent dimers (dimers 2 and 3) in two different ways. The dimer 1 is linked to the dimer 2 by a pair of intermolecular C–H···O interactions while dimers 1 and 3 are linked through a pair of C–H···O interactions involving CH_2 protons and carbonyl O atom of the acetate ligand.

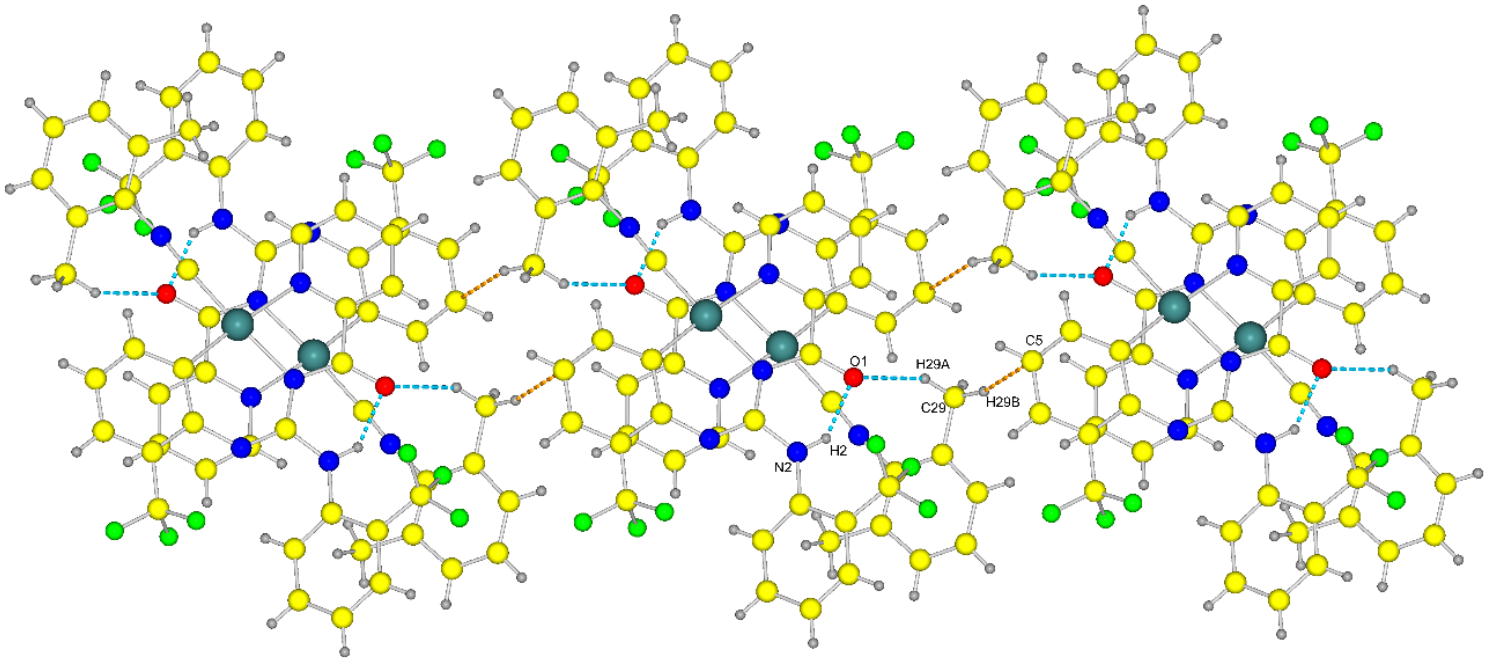
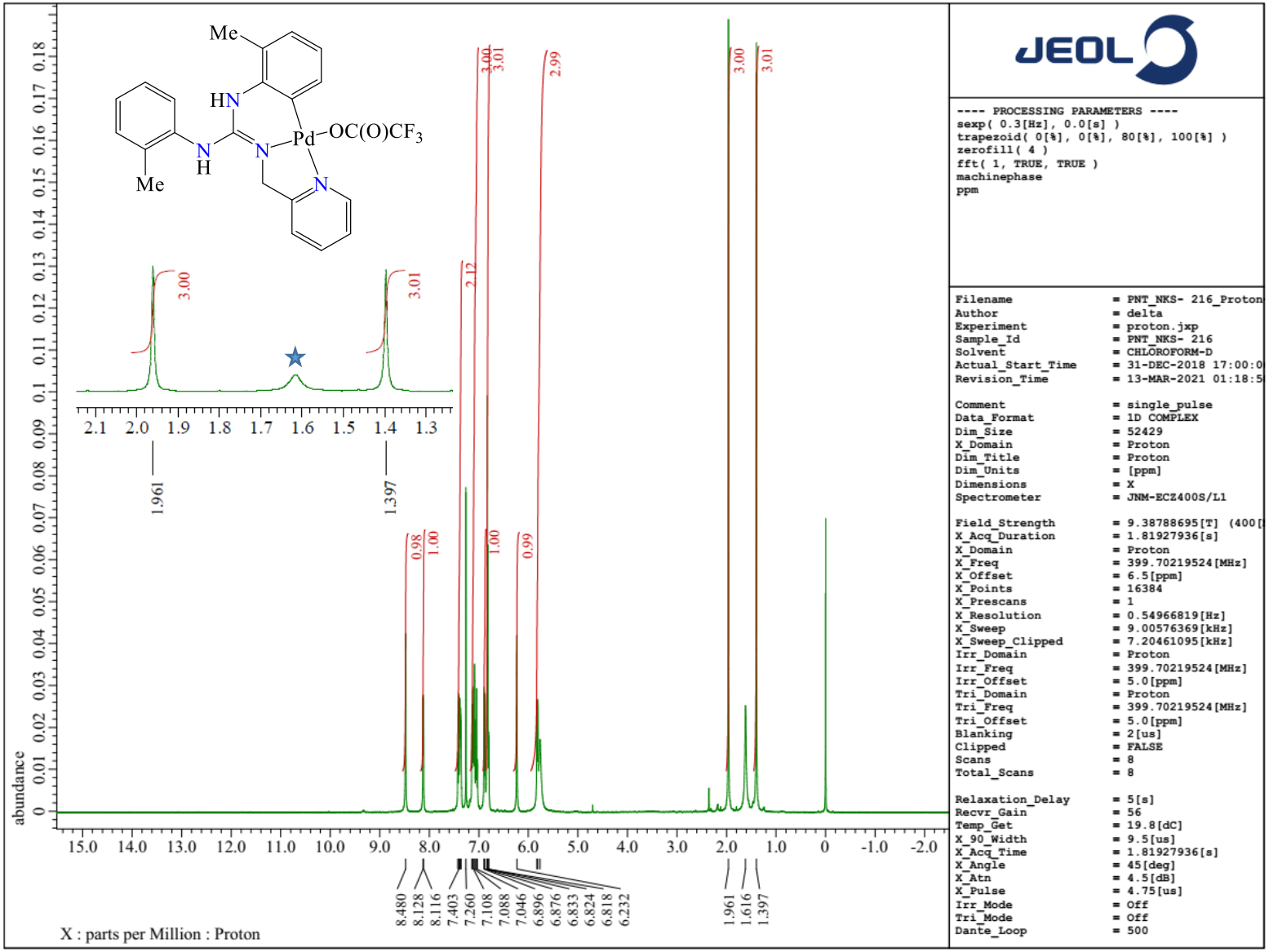
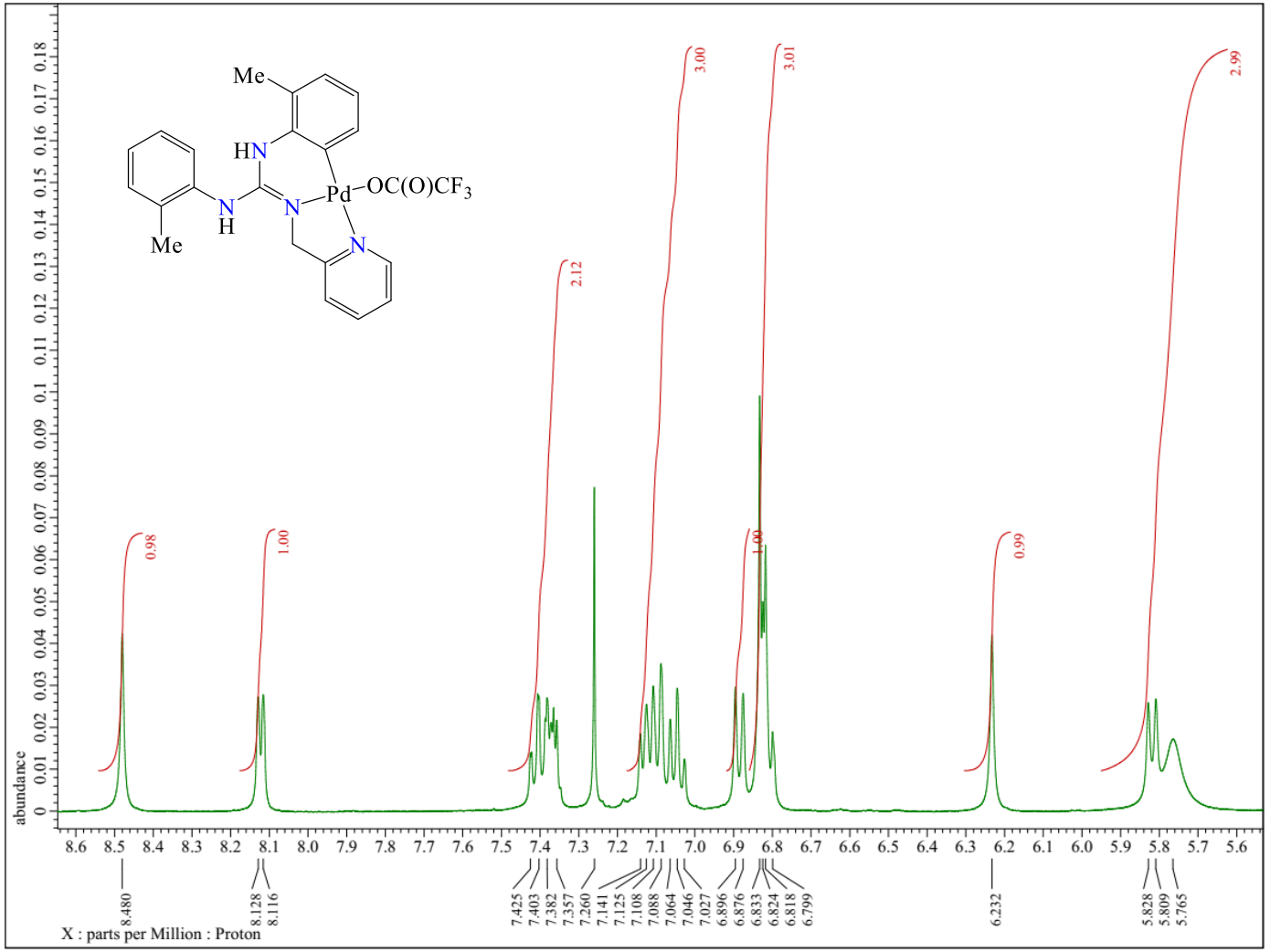


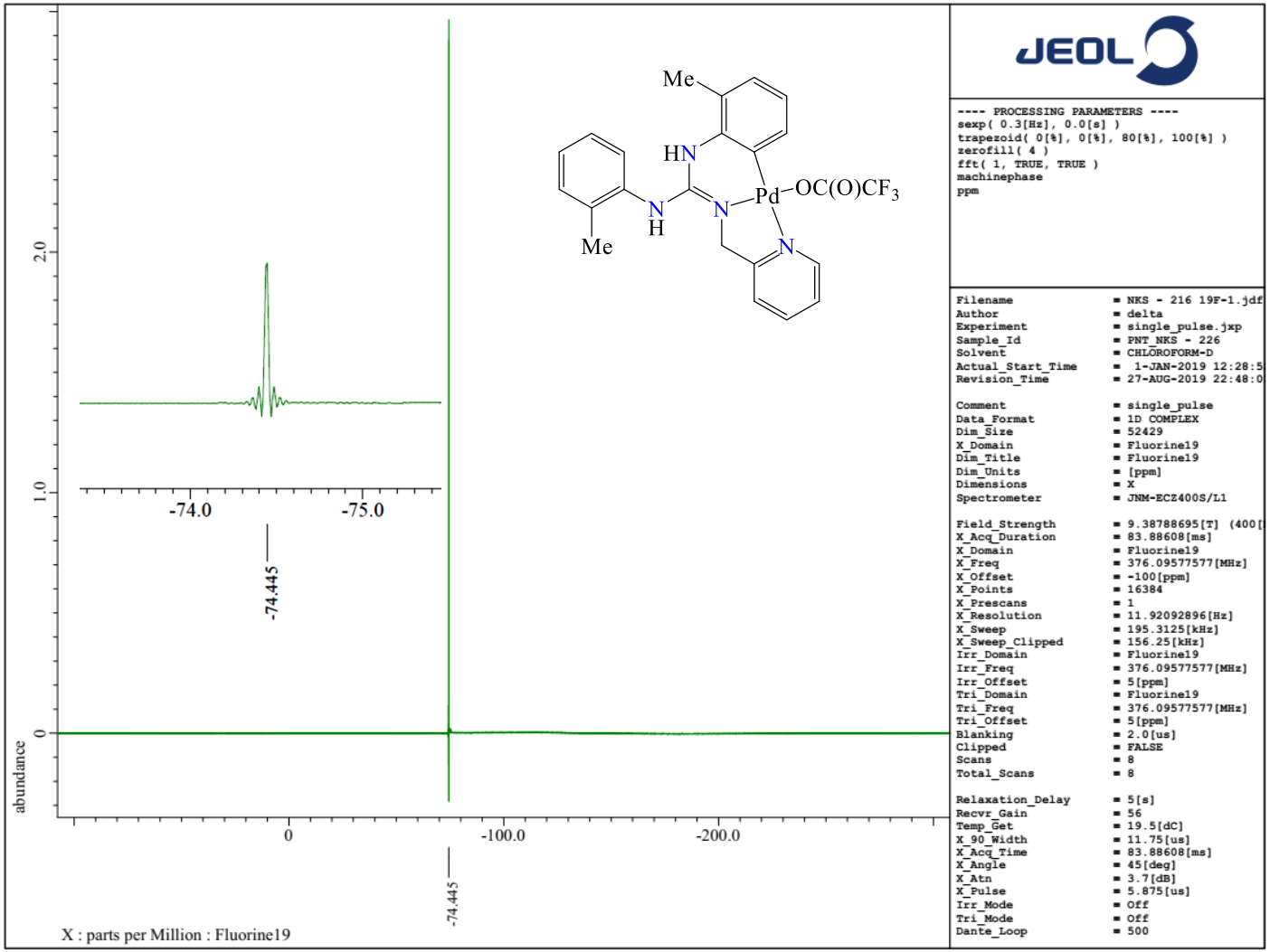
Fig. S11 Intermolecular hydrogen bond interactions in the crystal structure of **16**. Hydrogen bond parameters (Å and deg): O1···H2 = 1.785; O1···N2 = 2.515; N2–H2···O1 = 141.55; O1···H29A = 2.563; O1···C29 = 3.393; C29–H29A···O1 = 144.90; C5···H29B = 2.775; C5···C29B = 3.668; C29–H29B···C5 = 154.98. In crystal structure of **16**, the head to tail dimer is linked through a pair of intramolecular N–H···O and intermolecular C–H···O interactions. This dimer is linked to adjacent identical dimer through two pairs of C–H···π interaction.



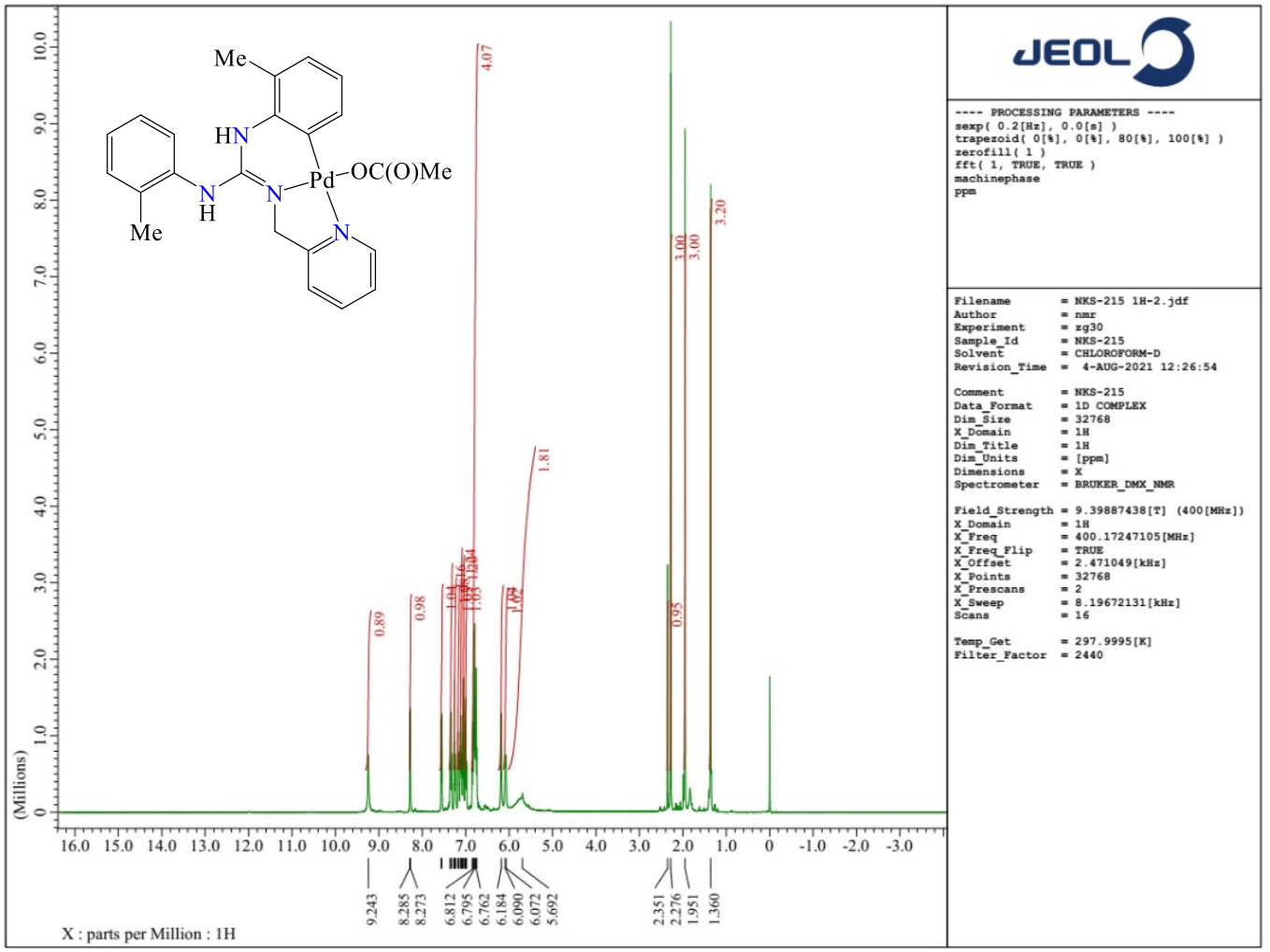
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3**·½ toluene. The ★ symbol indicates protons of residual water.



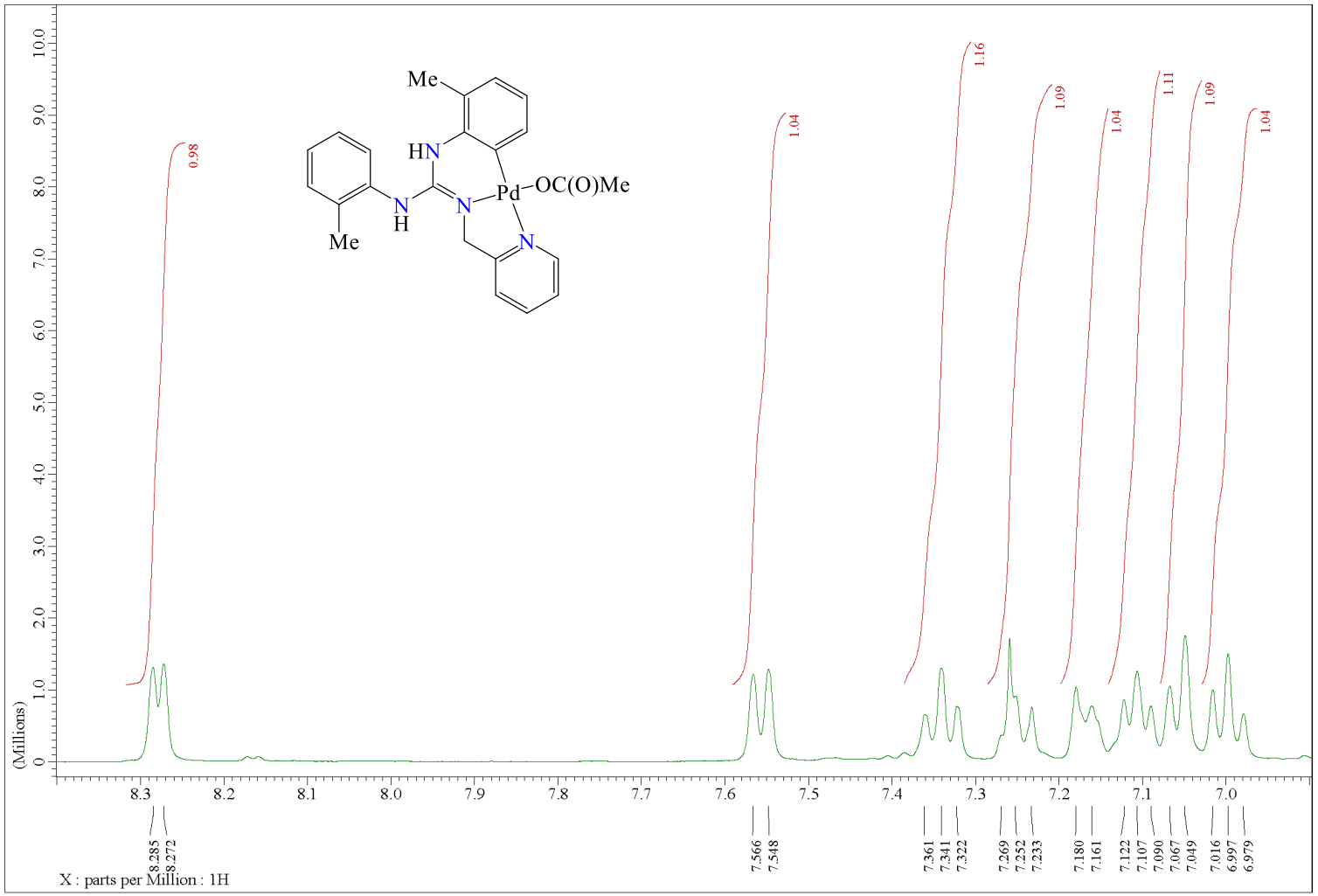
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3**·½ toluene in indicated region.



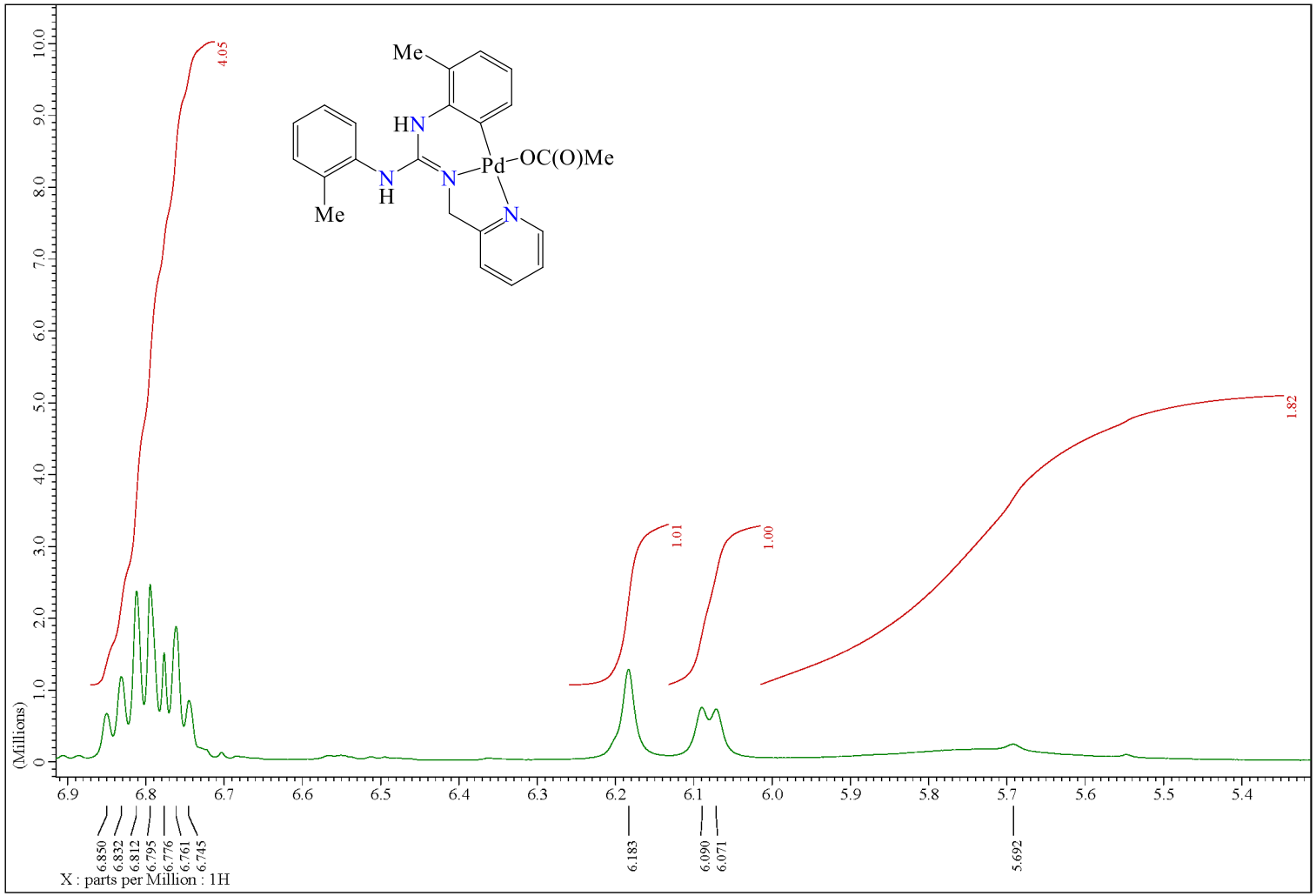
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376.5 MHz) spectrum of **3**·½ toluene.



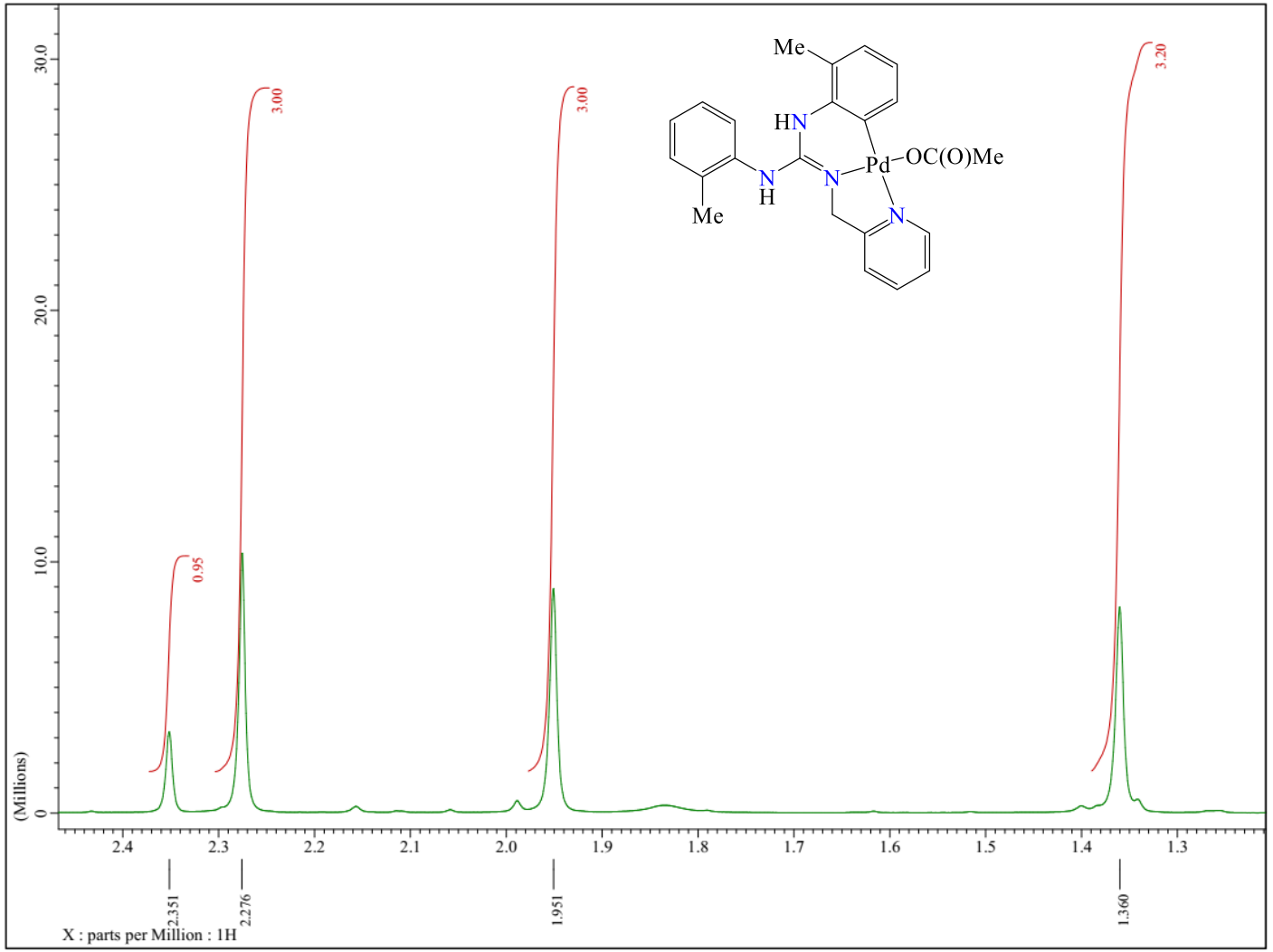
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4**·¼ toluene.



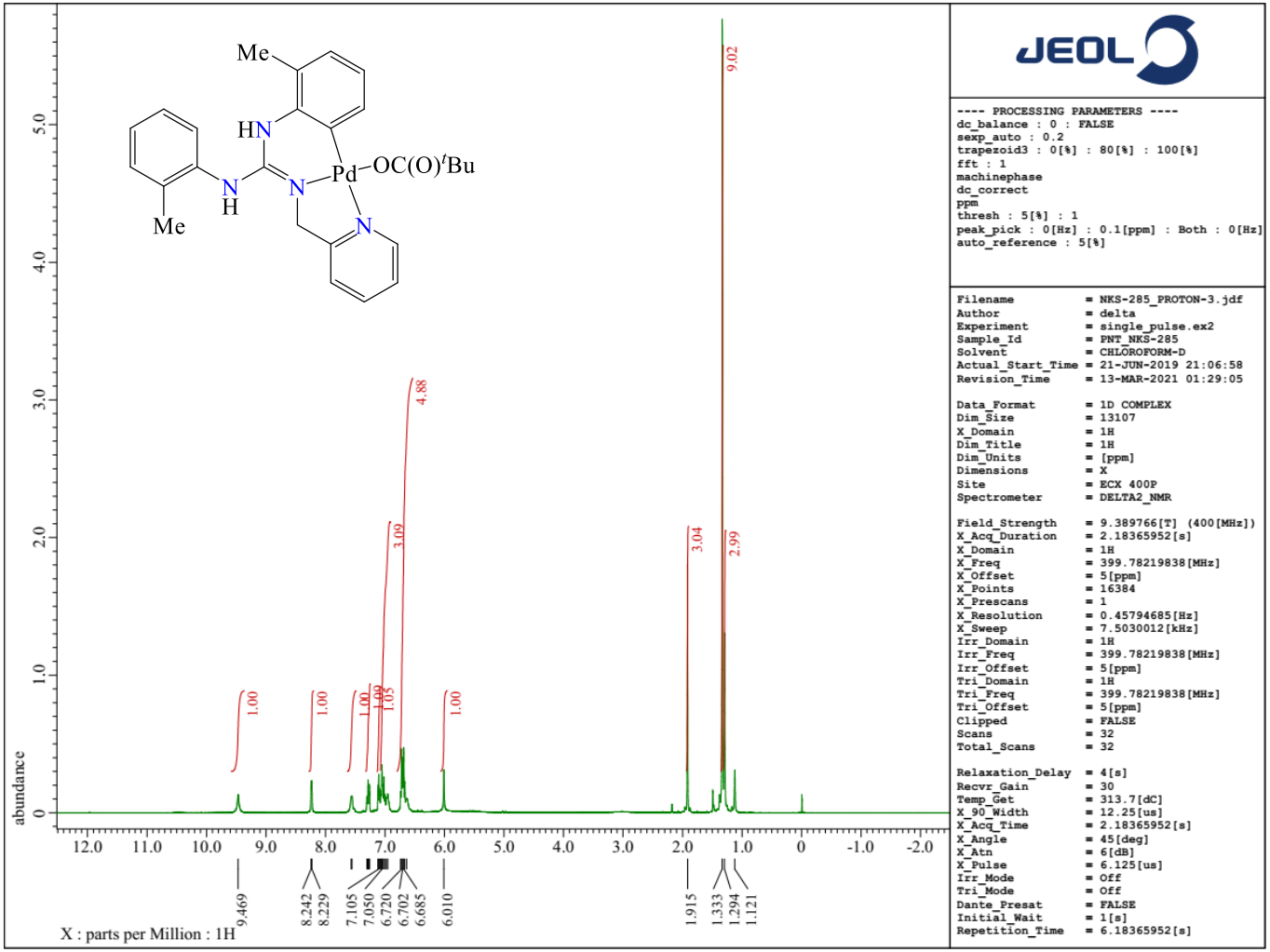
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4**·¼ toluene in indicated region.



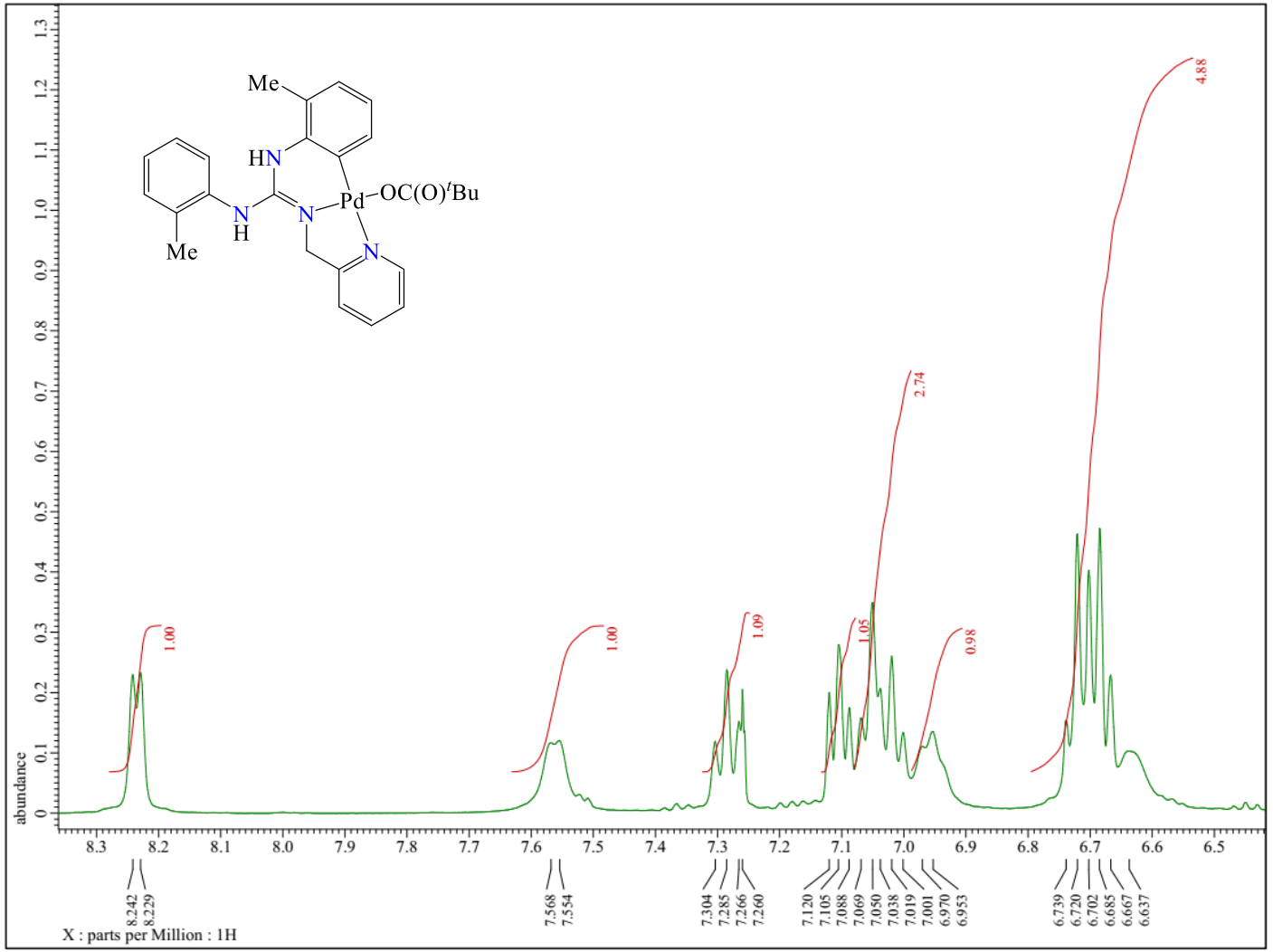
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4**·¼ toluene in indicated region.



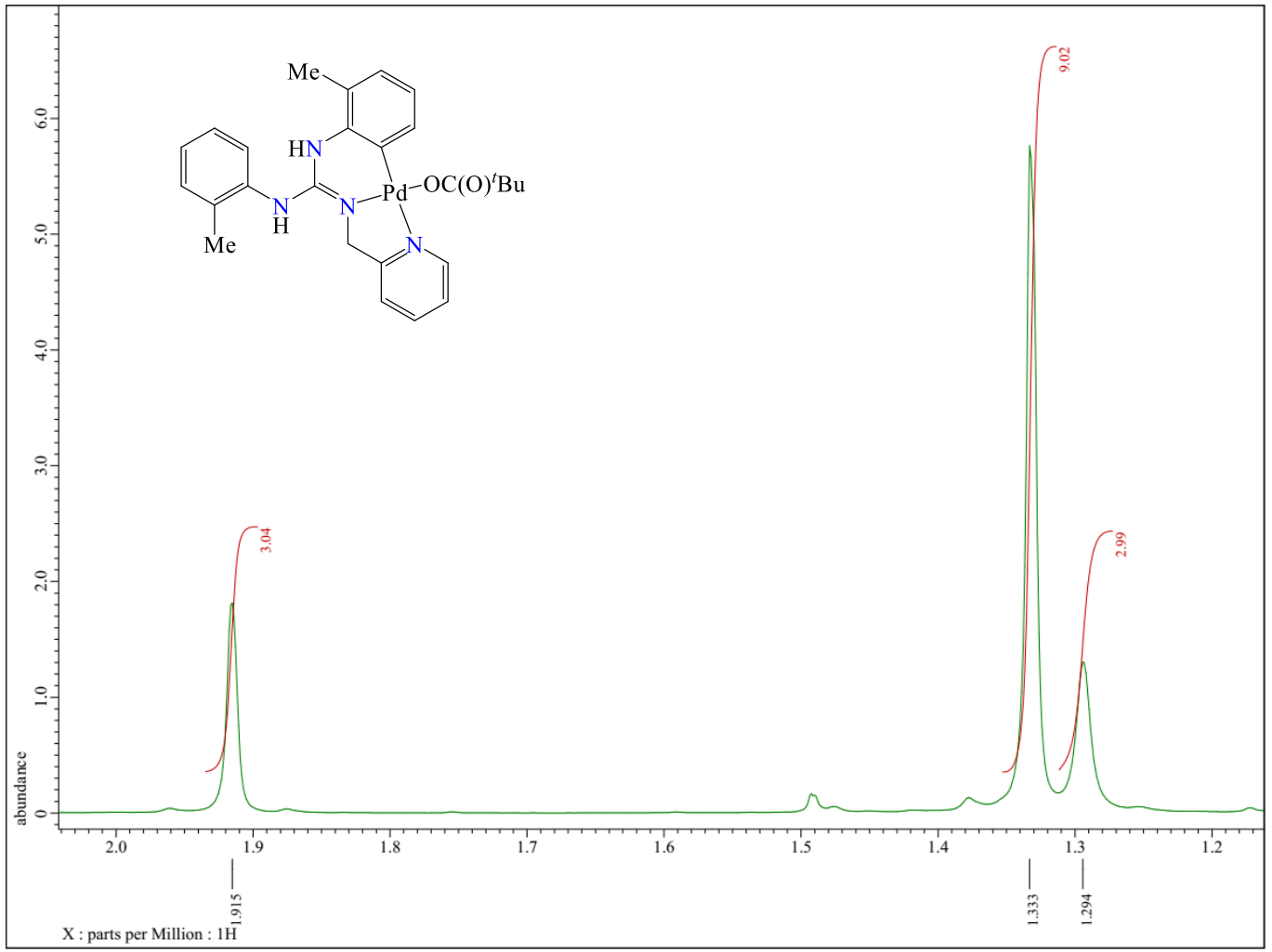
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4**·¼ toluene in indicated region.



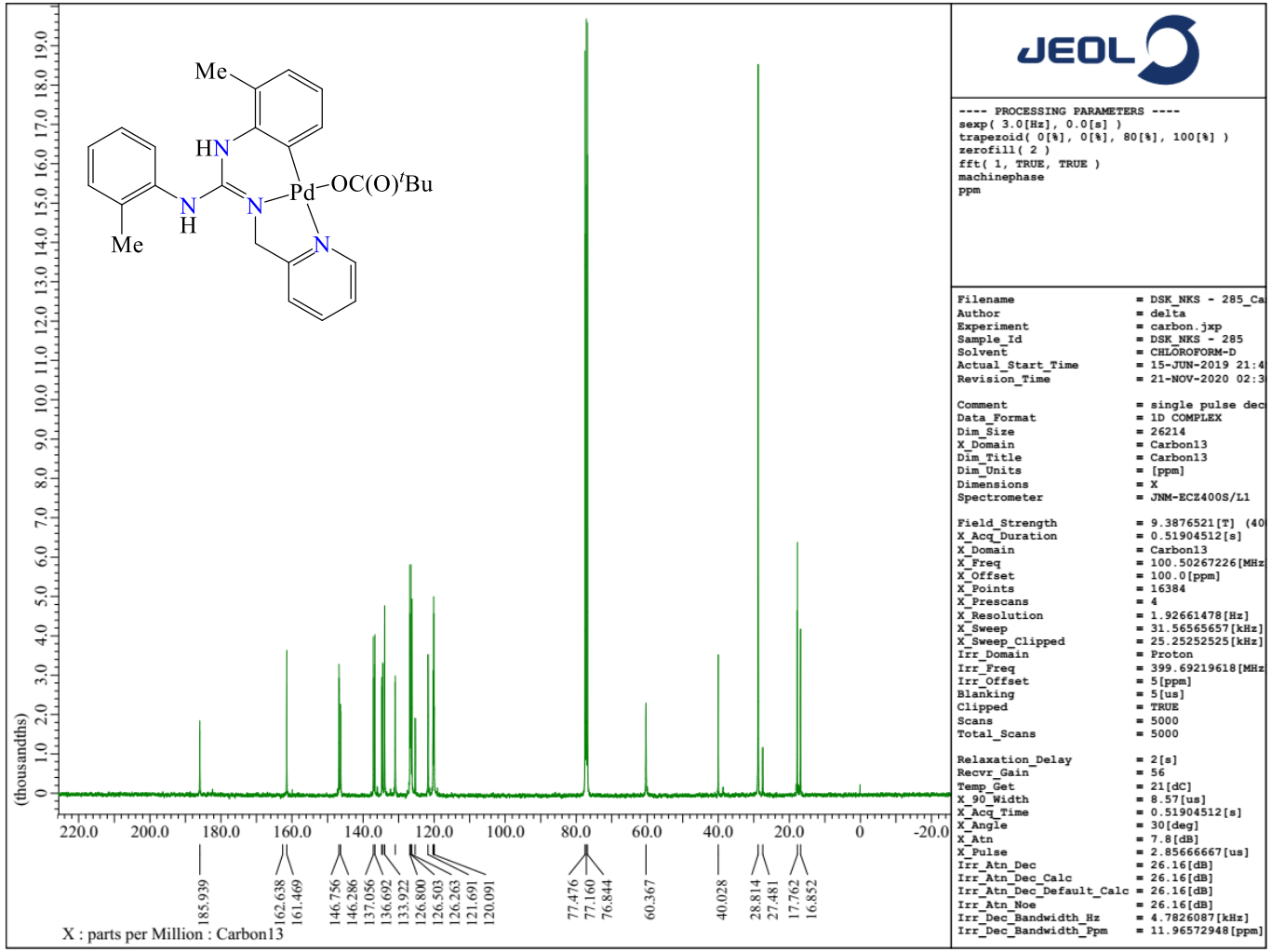
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **5**·½ toluene·½ pivalic acid in indicated region.



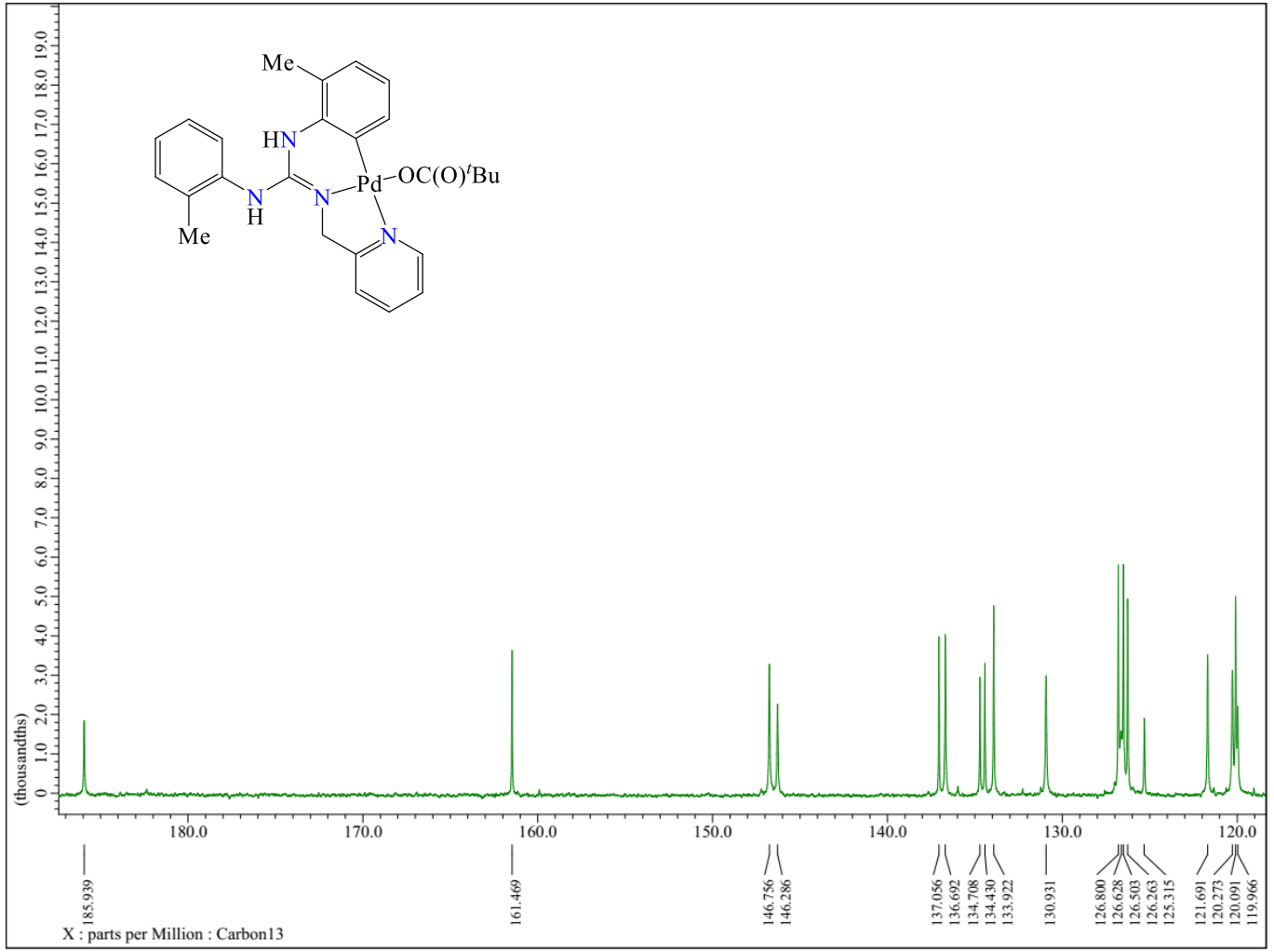
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **5**·½ toluene·½ pivalic acid in indicated region.



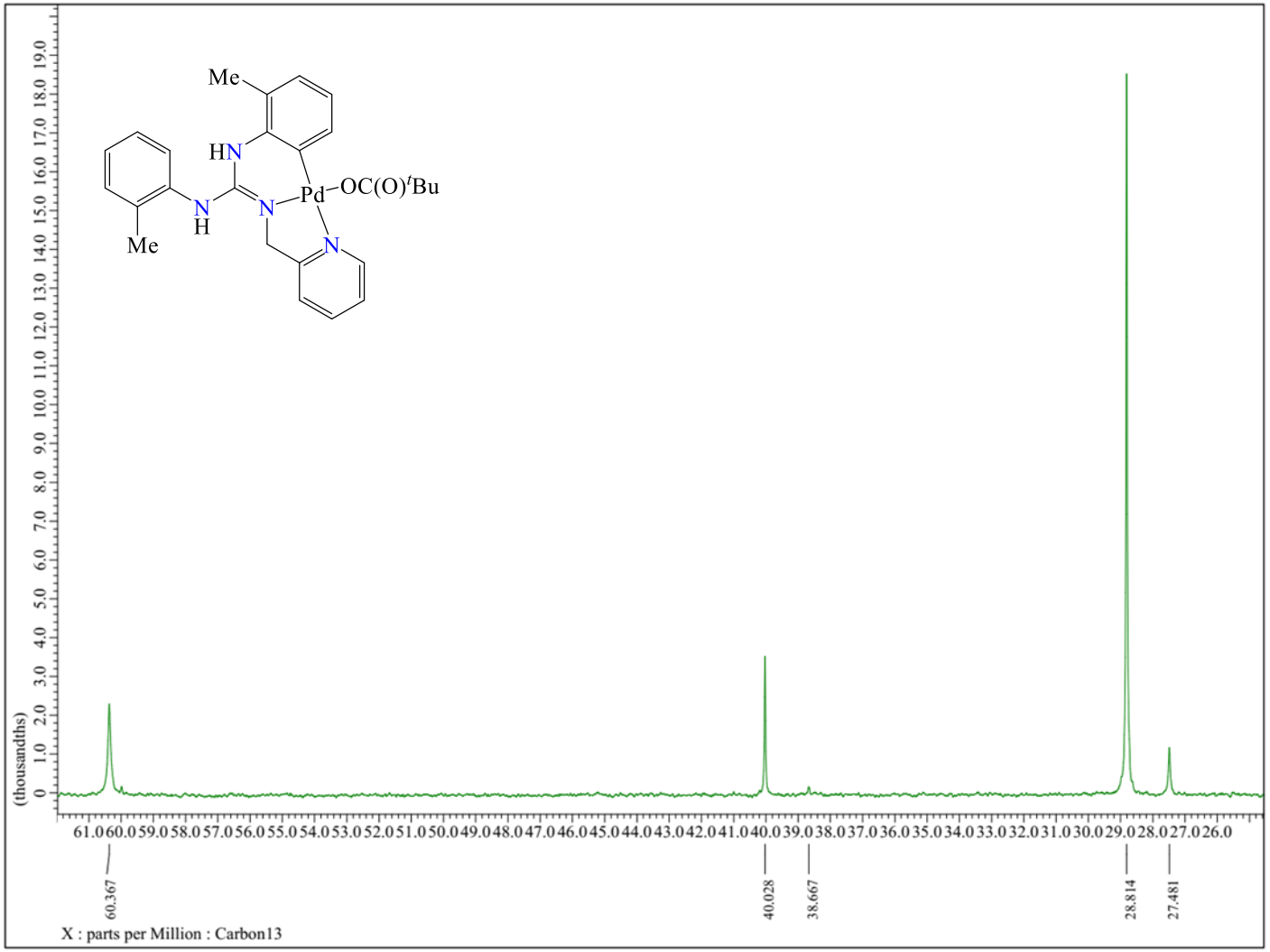
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **5**·½ toluene·½ pivalic acid in indicated region.



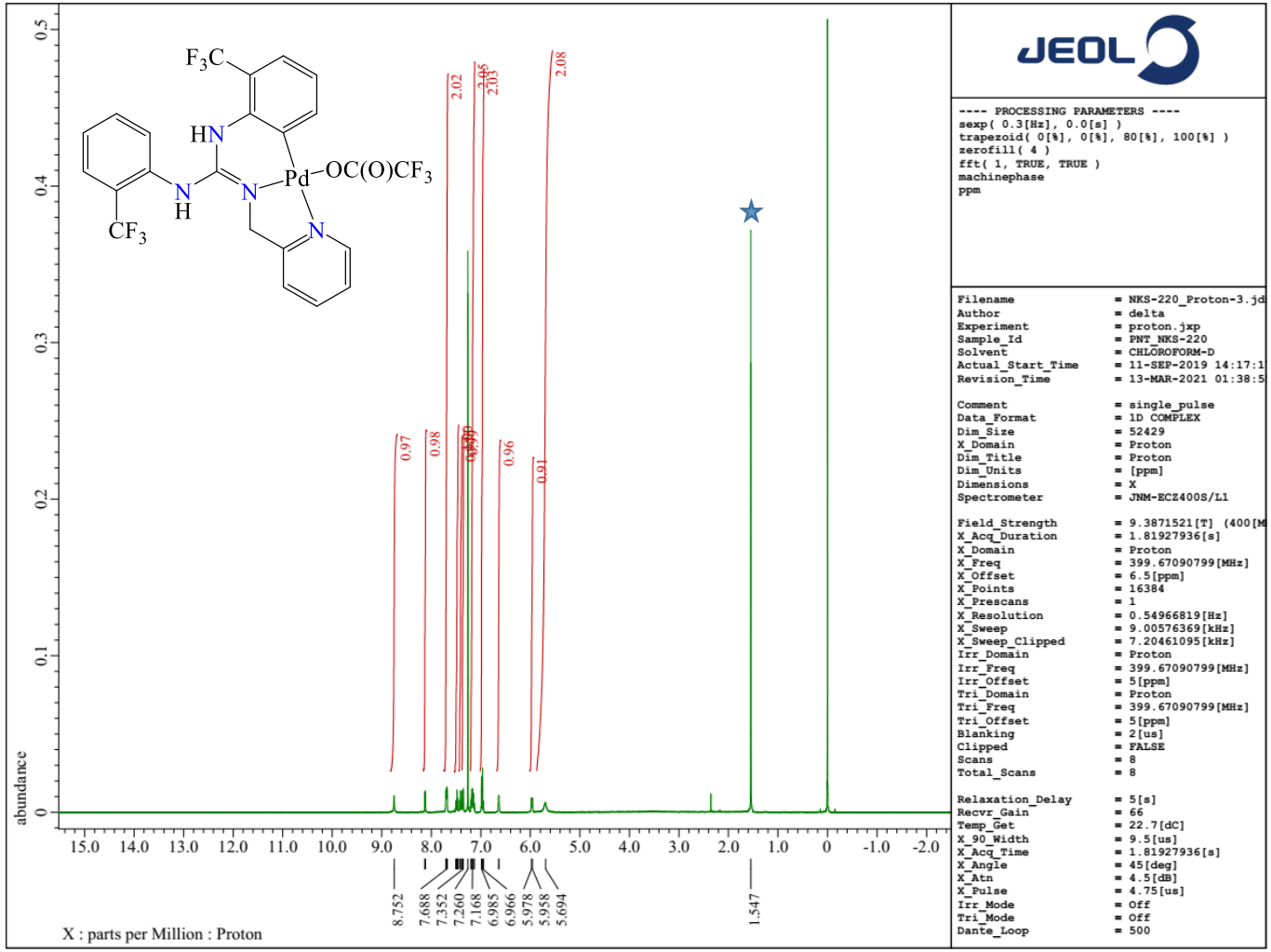
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **5**·½ toluene·½ pivalic acid in indicated region.



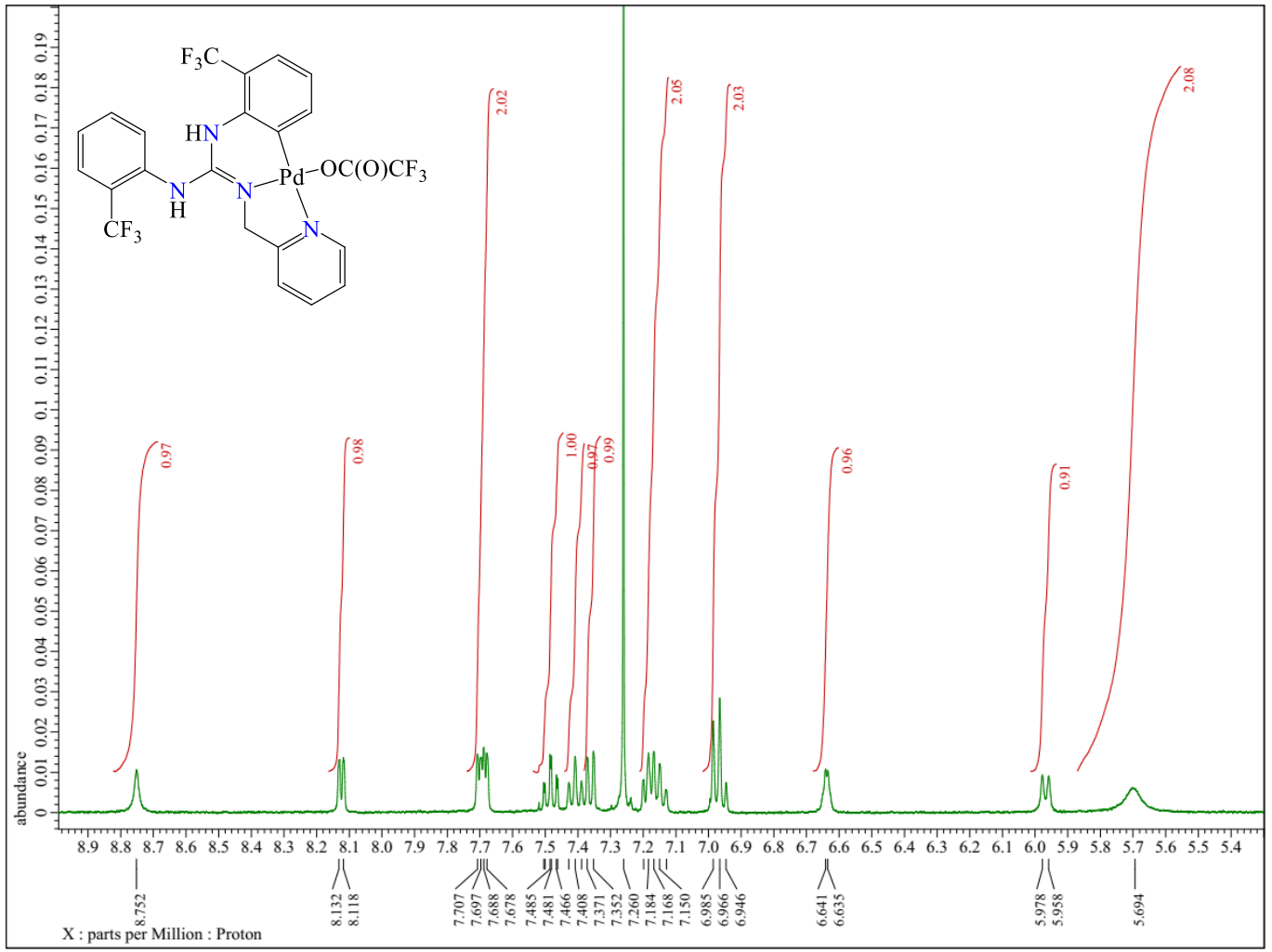
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **5**·½ toluene·½ pivalic acid in indicated region.



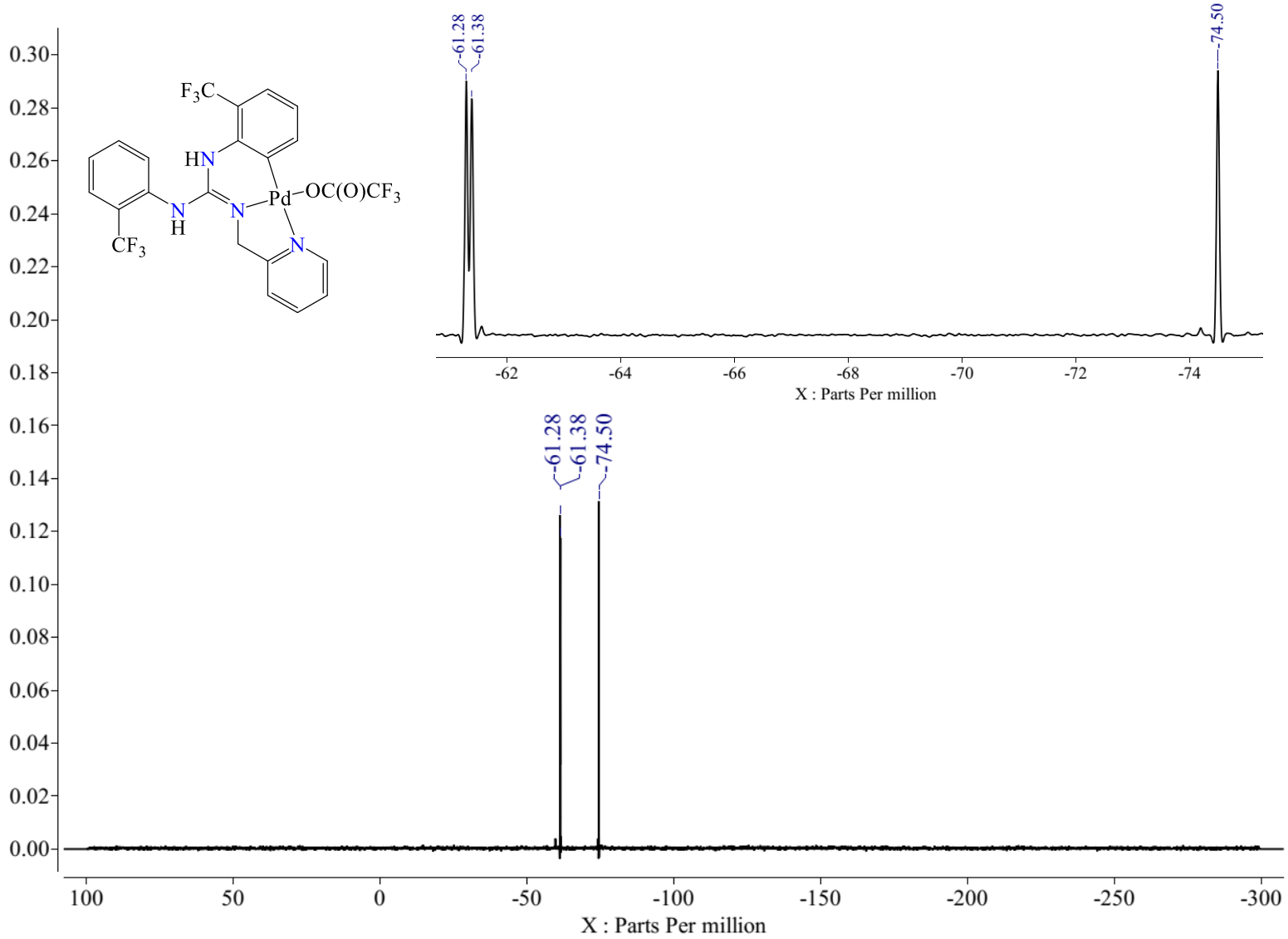
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **5**·½ toluene·½ pivalic acid in indicated region.



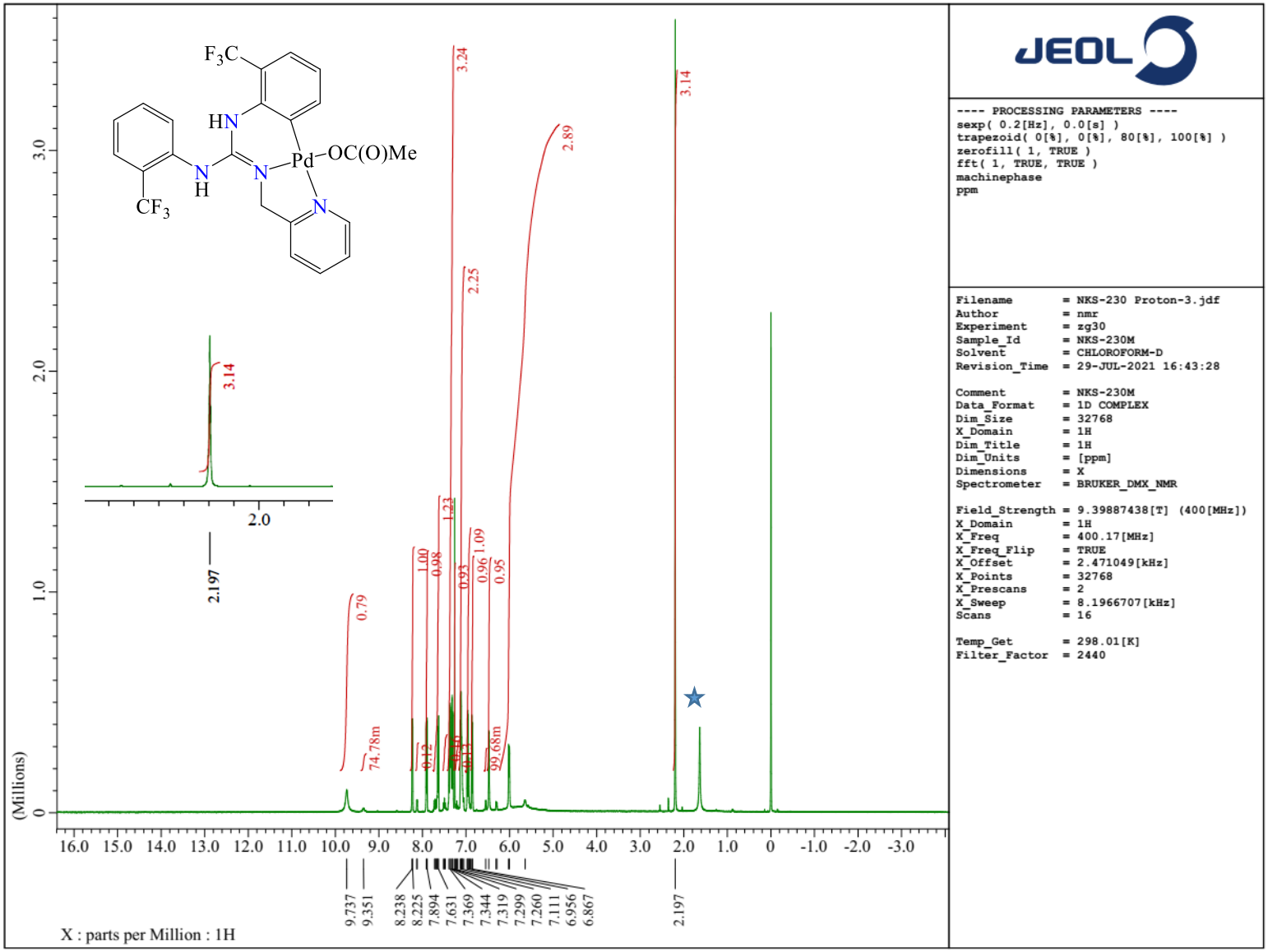
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **6**. ★ symbol indicate protons of residual water.



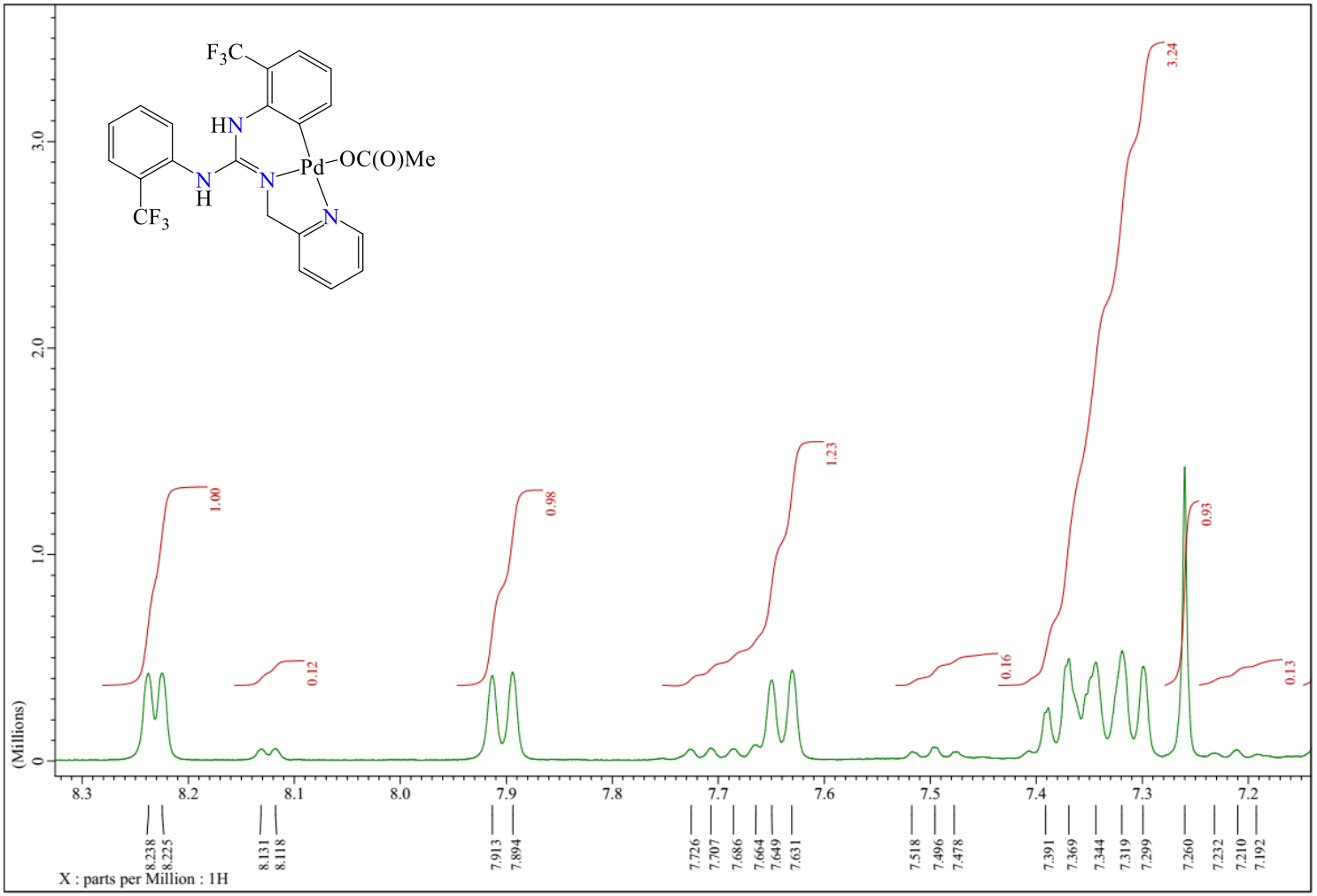
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **6** in indicated region.



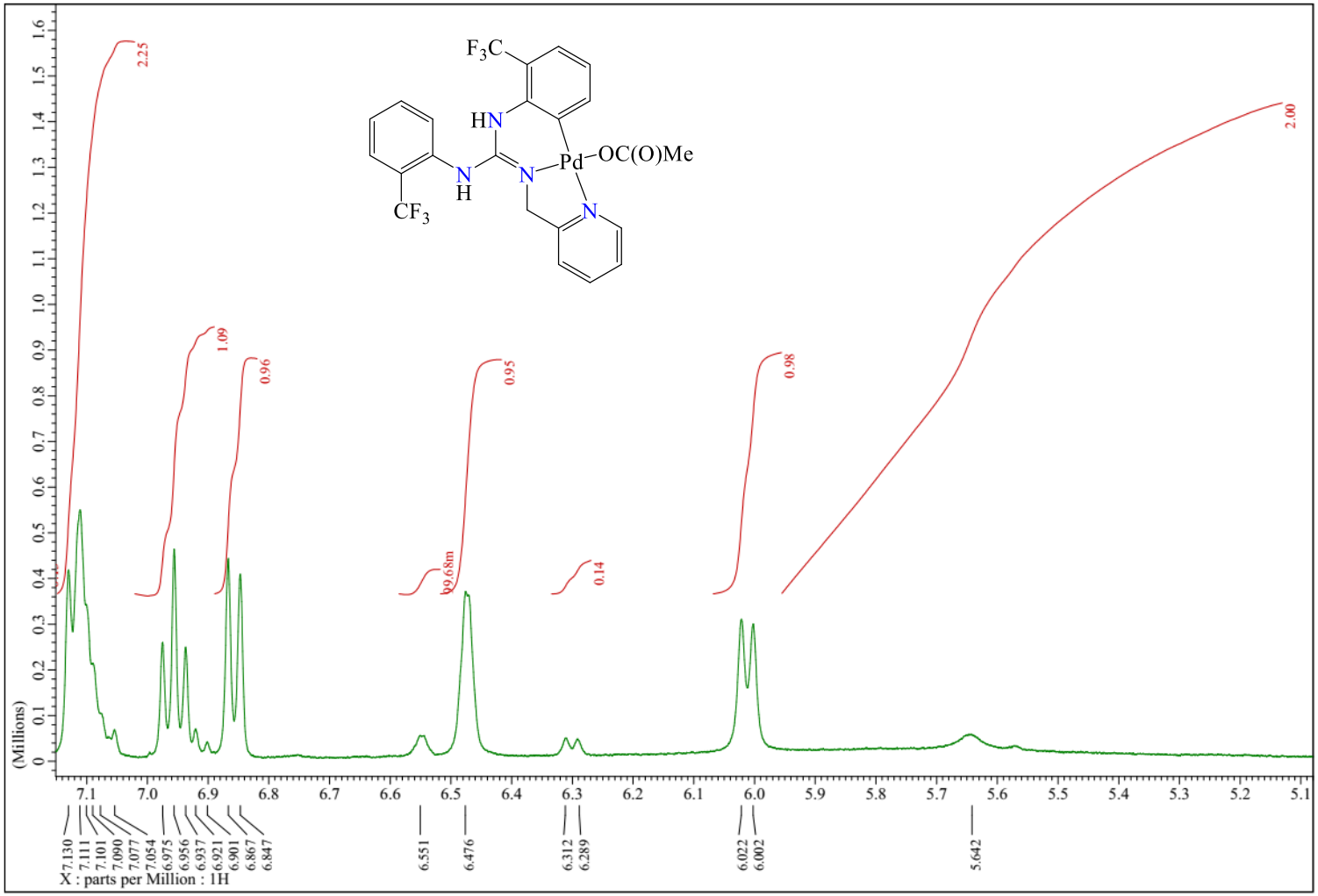
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376.5 MHz) spectrum of **6**.



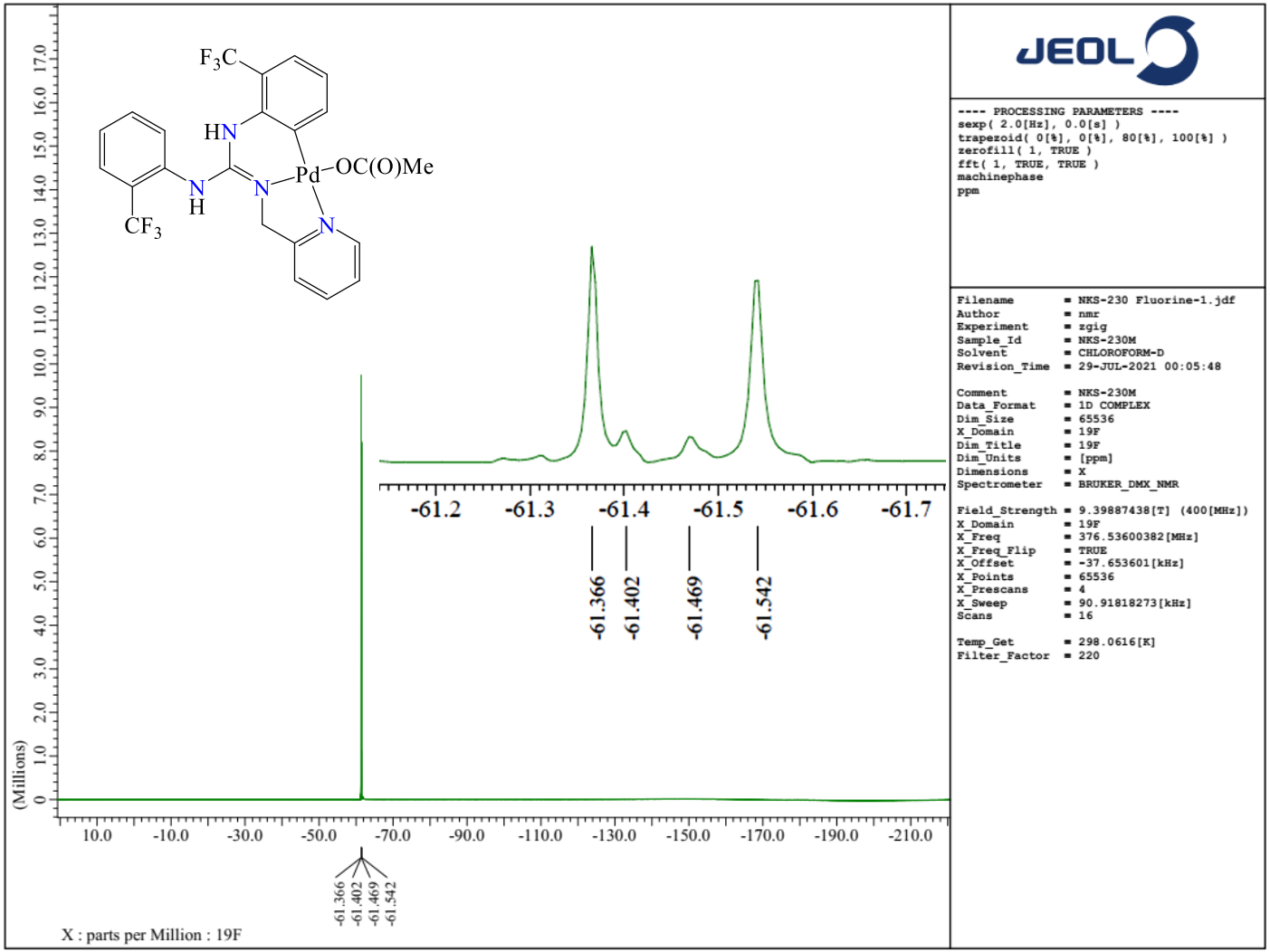
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7 + 9**. The★ symbol indicates protons of residual water.



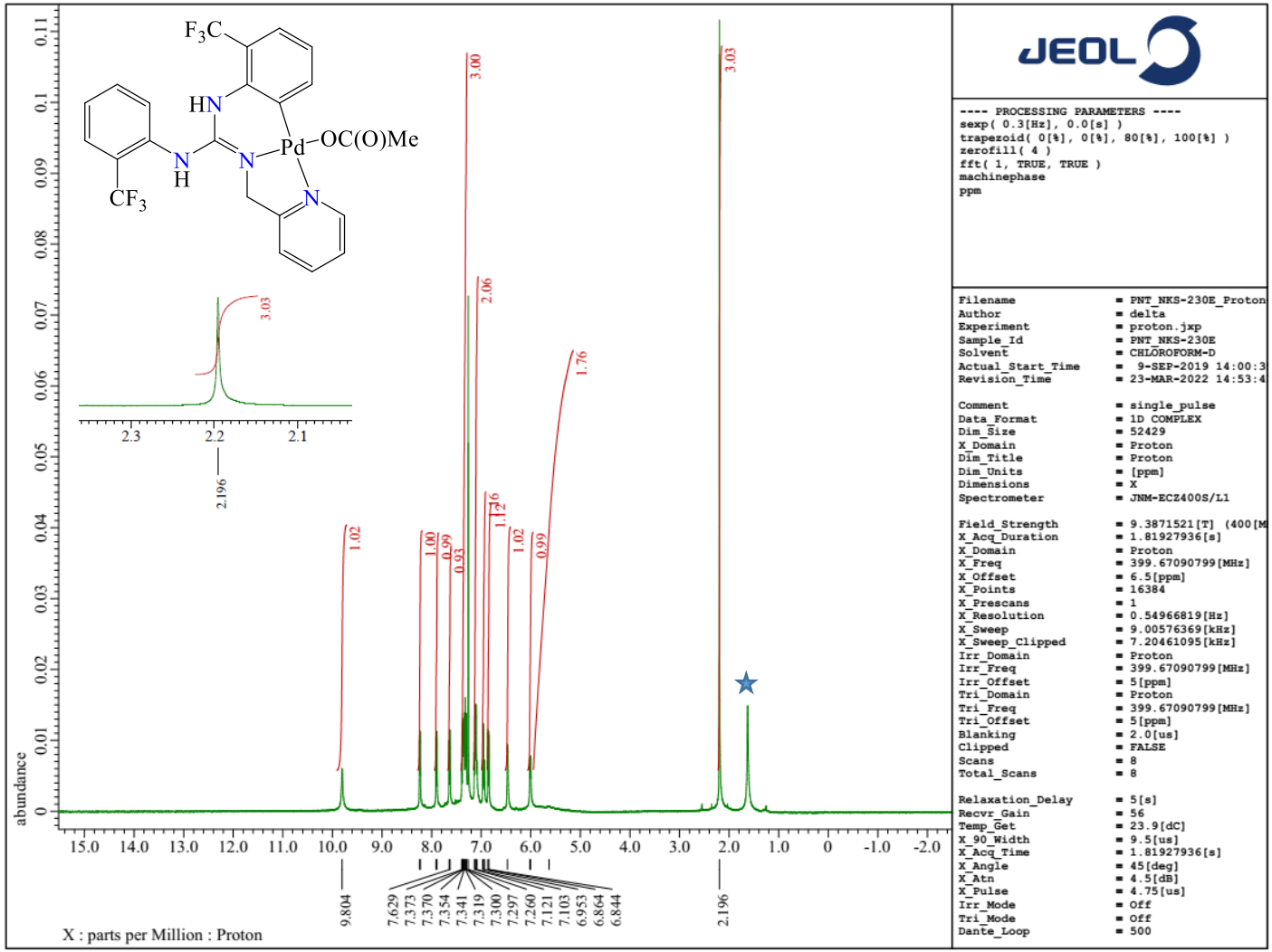
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7 + 9** in indicated region.



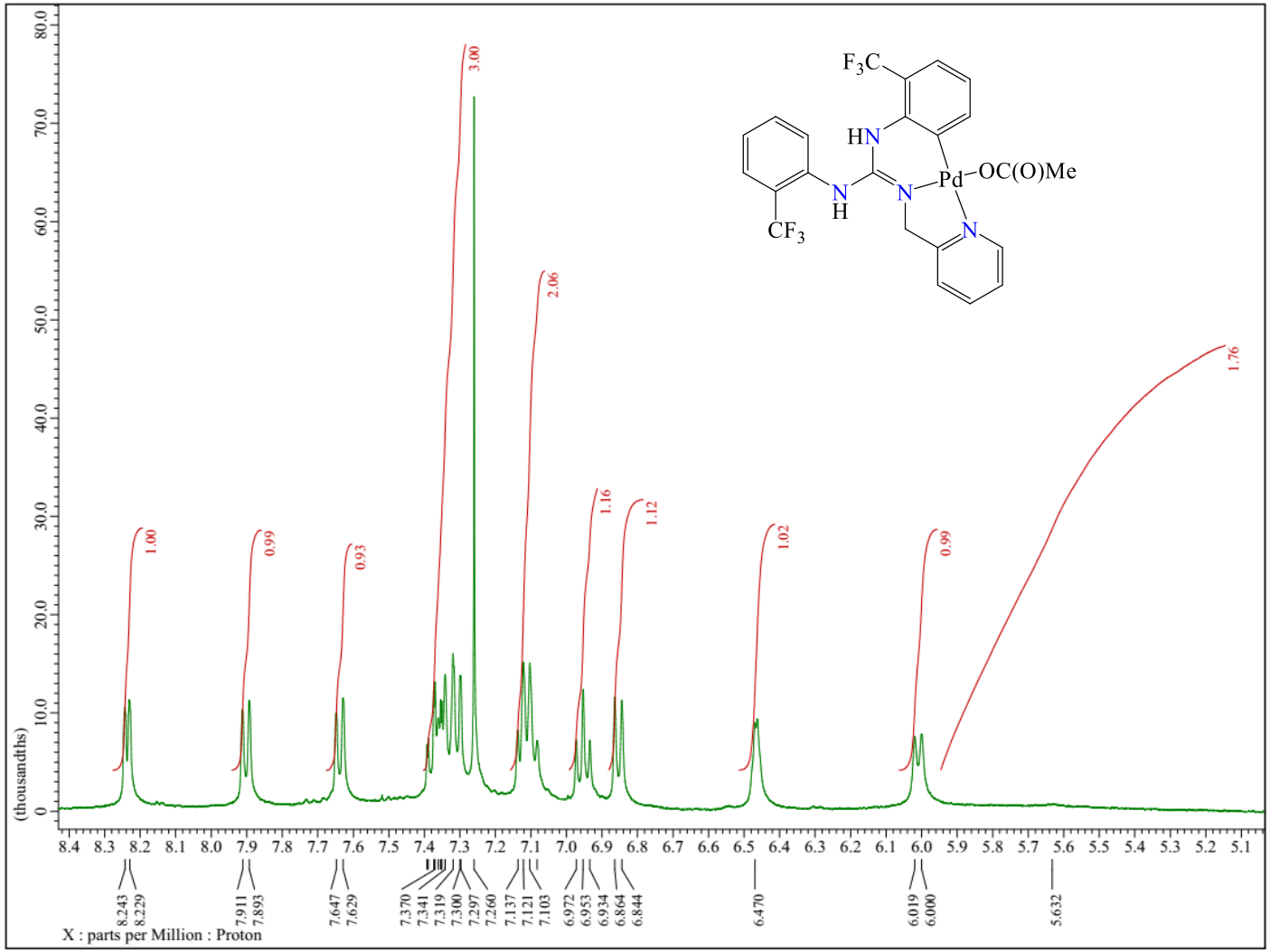
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7** + **9** in indicated region.



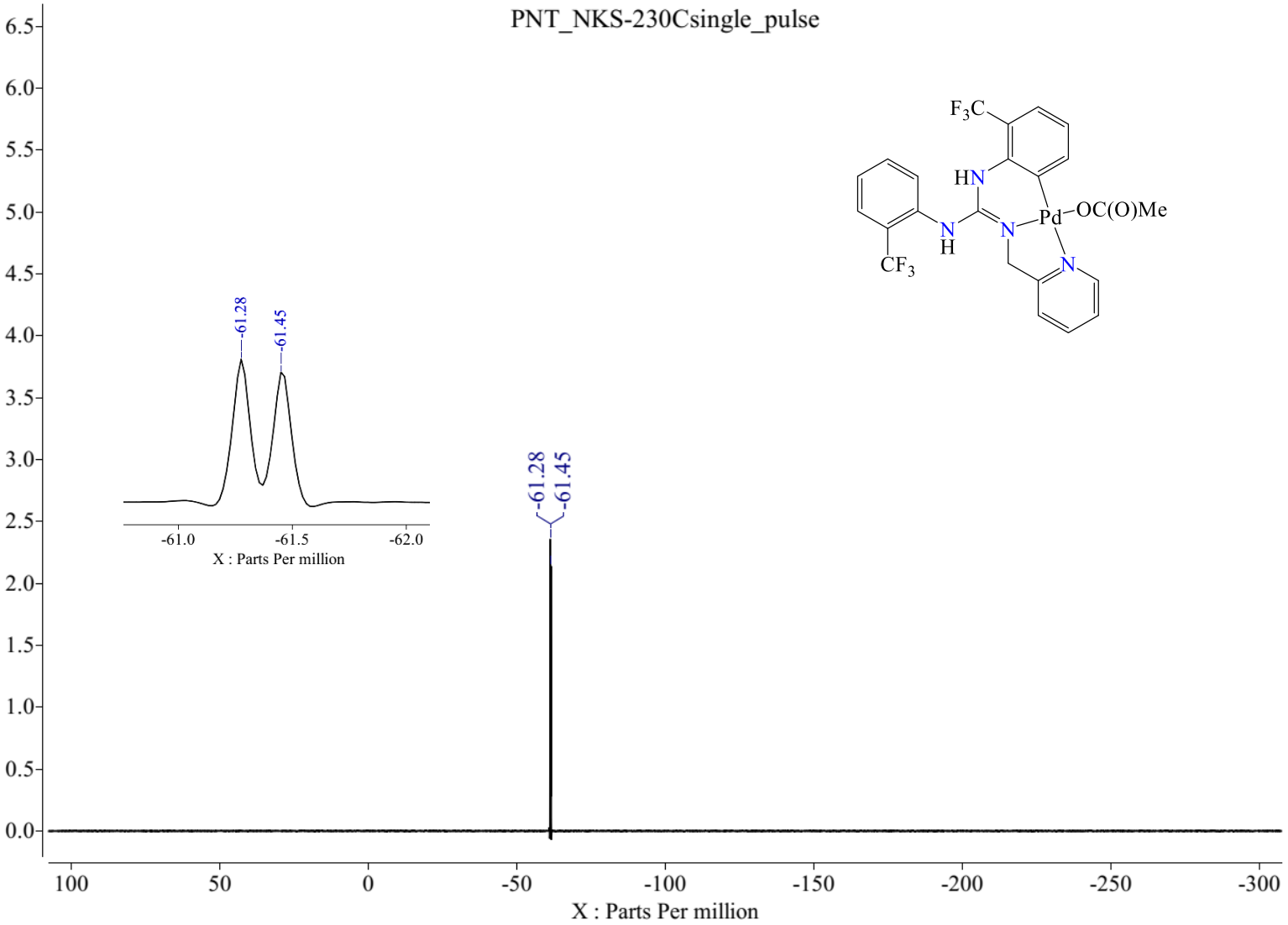
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376.5 MHz) spectrum of **7** + **9**.



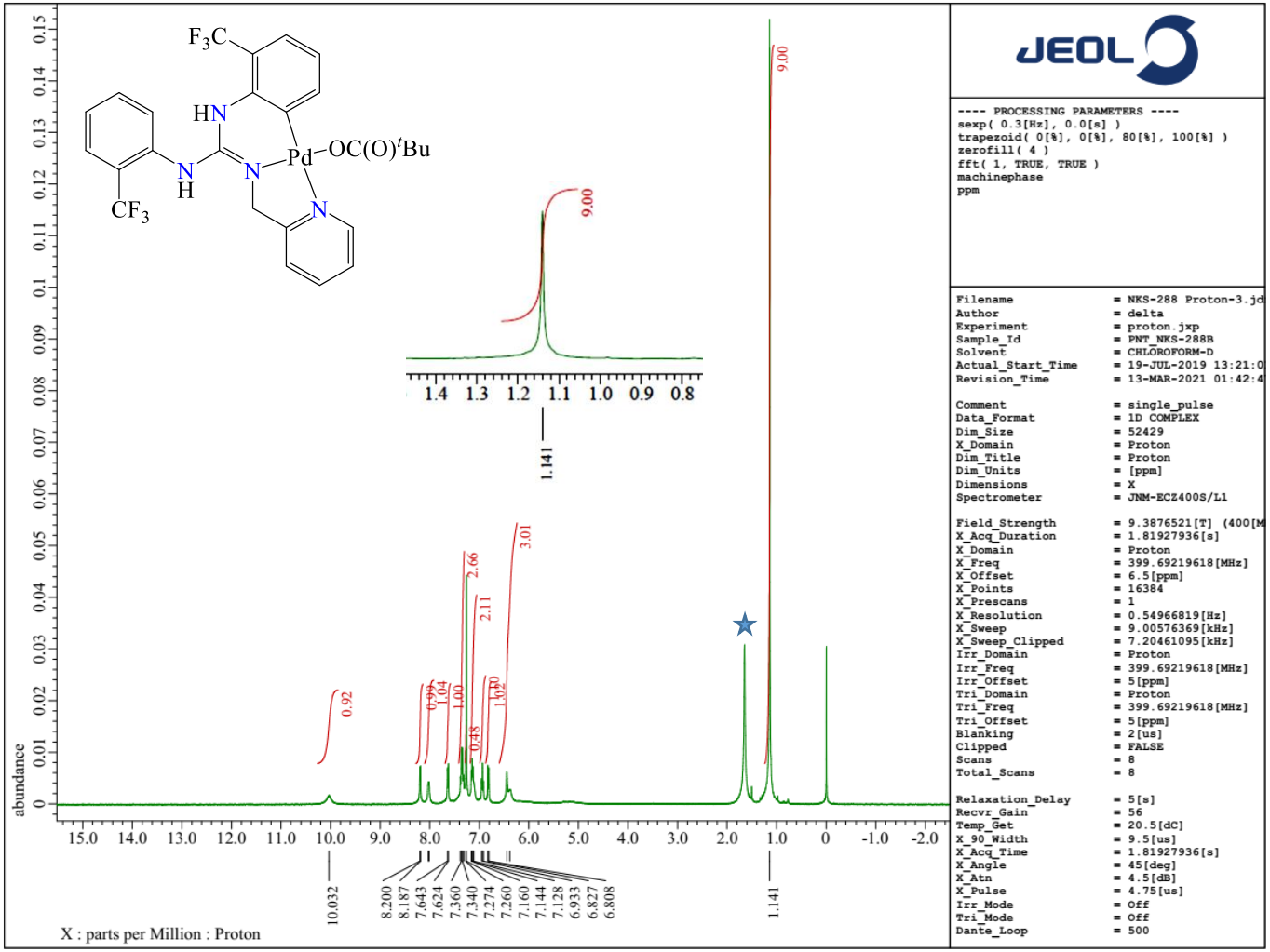
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7**. The ★ symbol indicates protons of residual water.



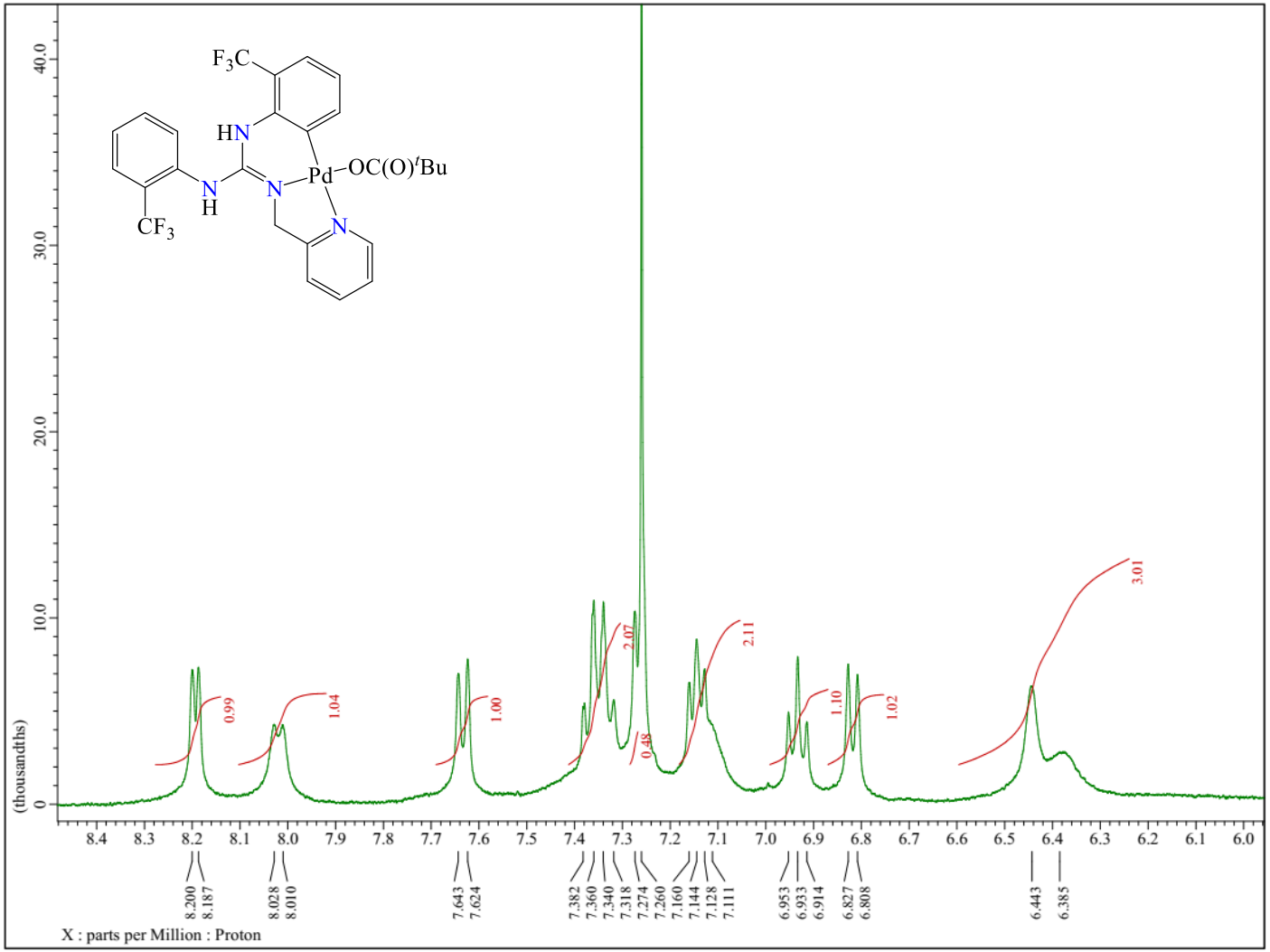
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7** in indicated region.



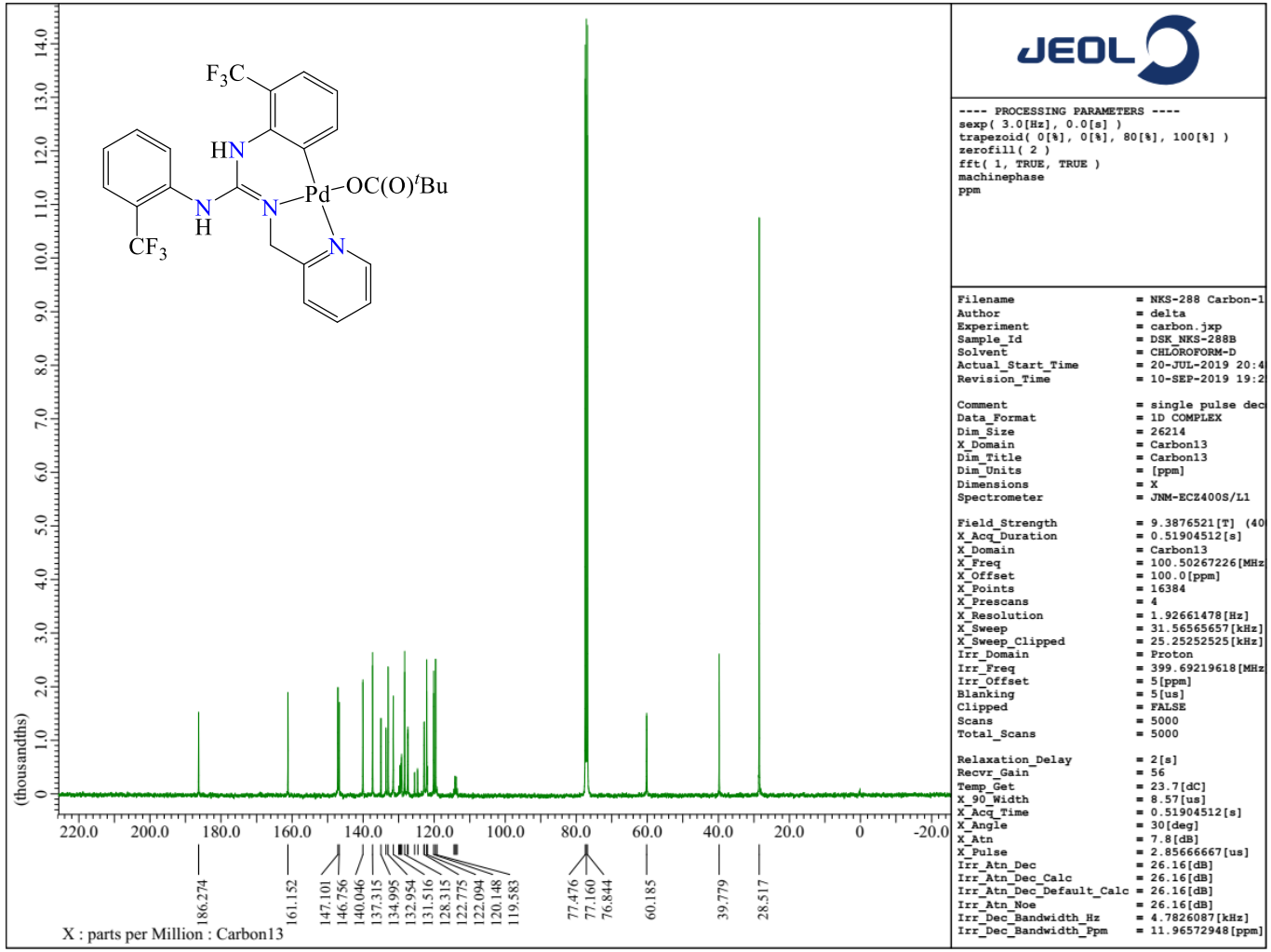
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376.5 MHz) spectrum of **7**.



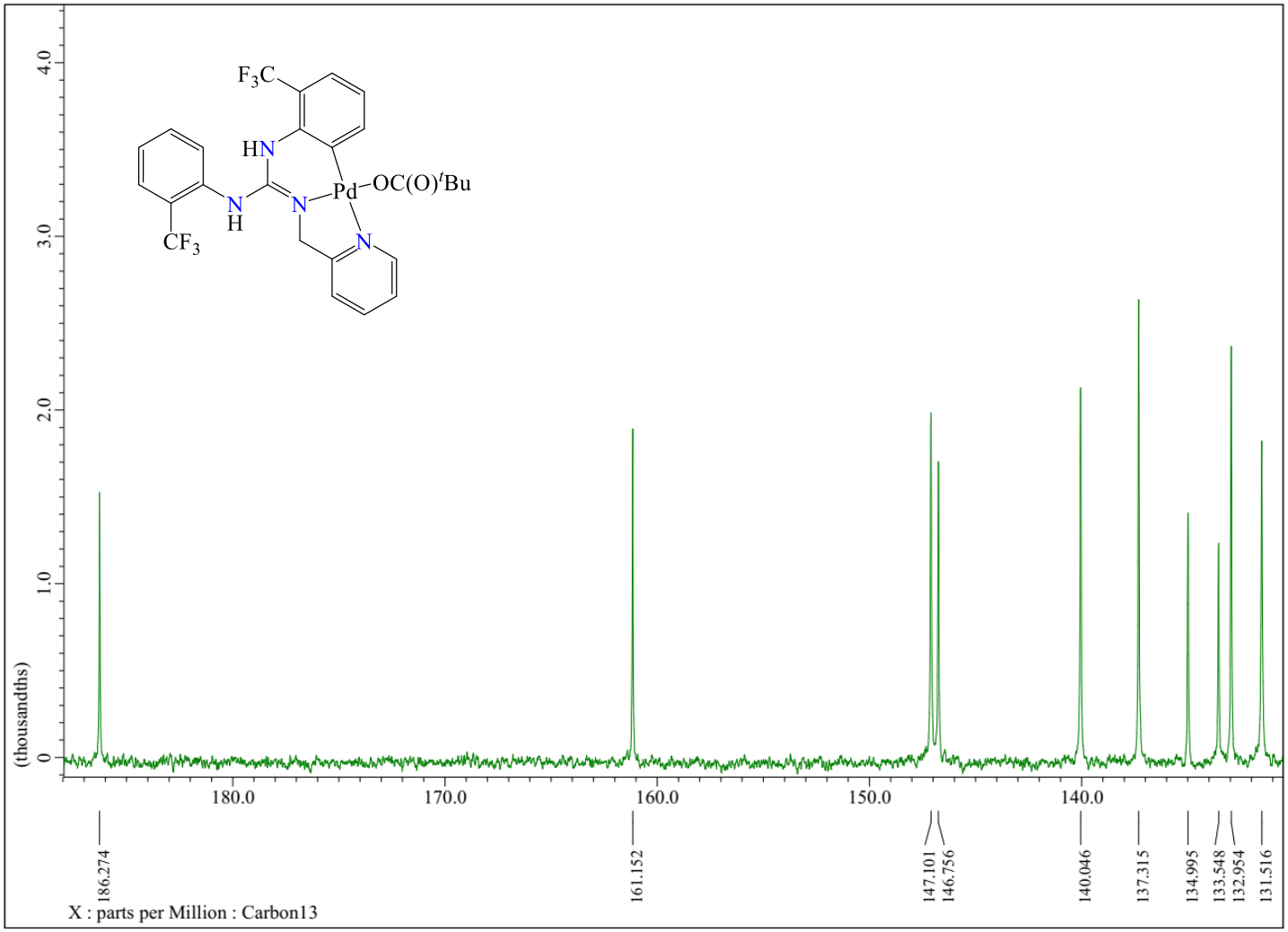
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **8**. The ★ symbol indicates protons of residual water.



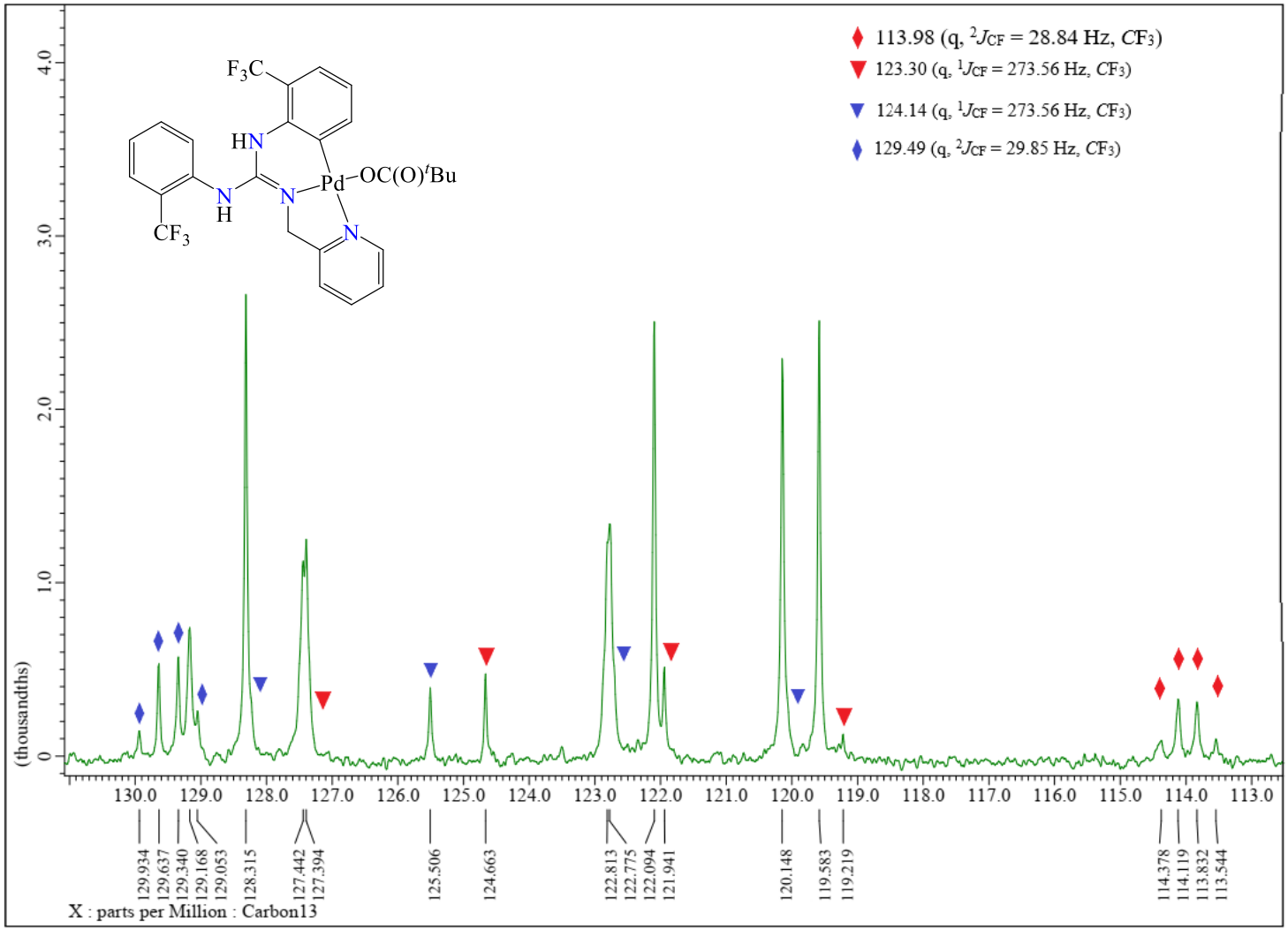
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **8** in indicated region.



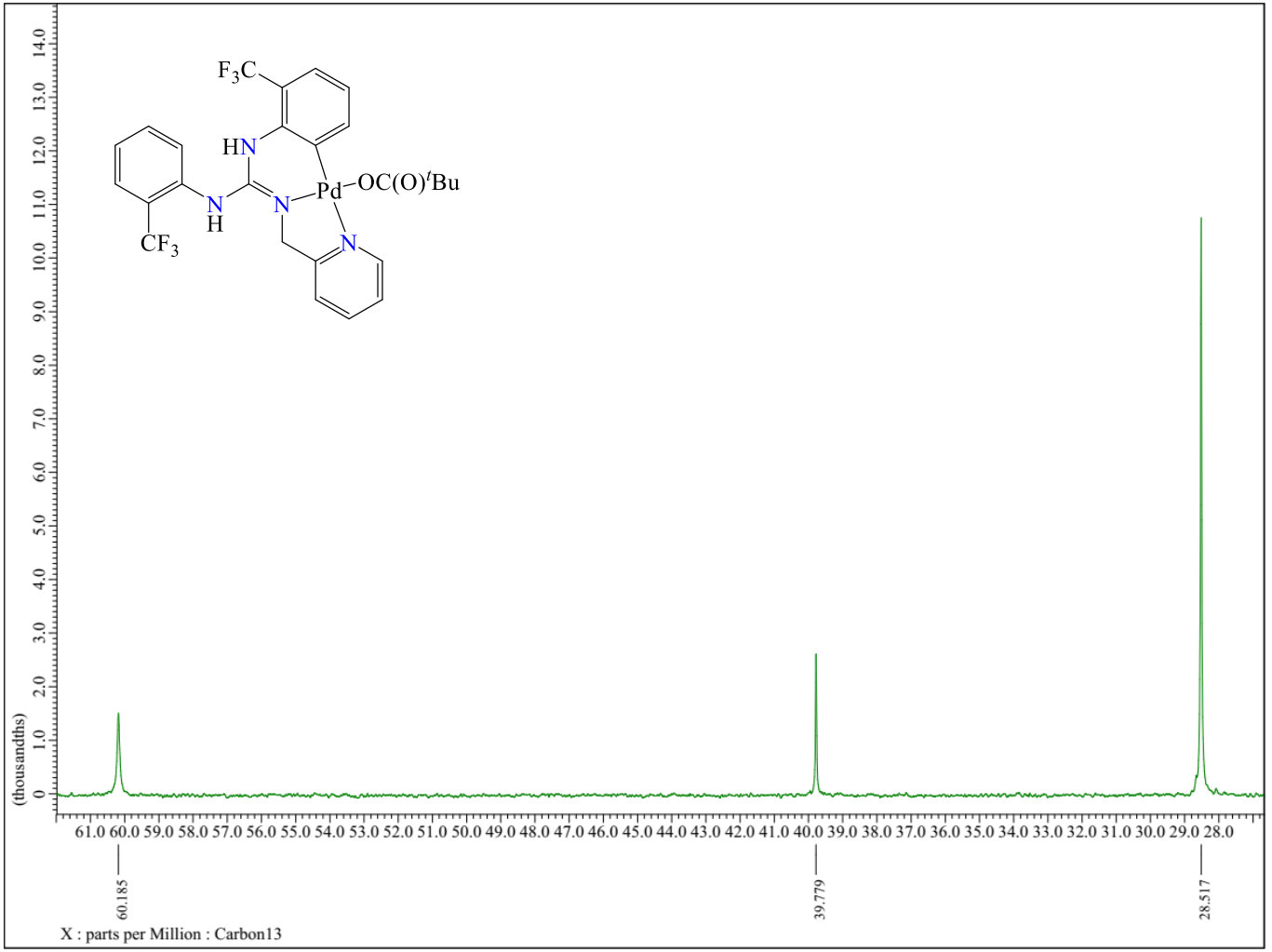
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **8**.



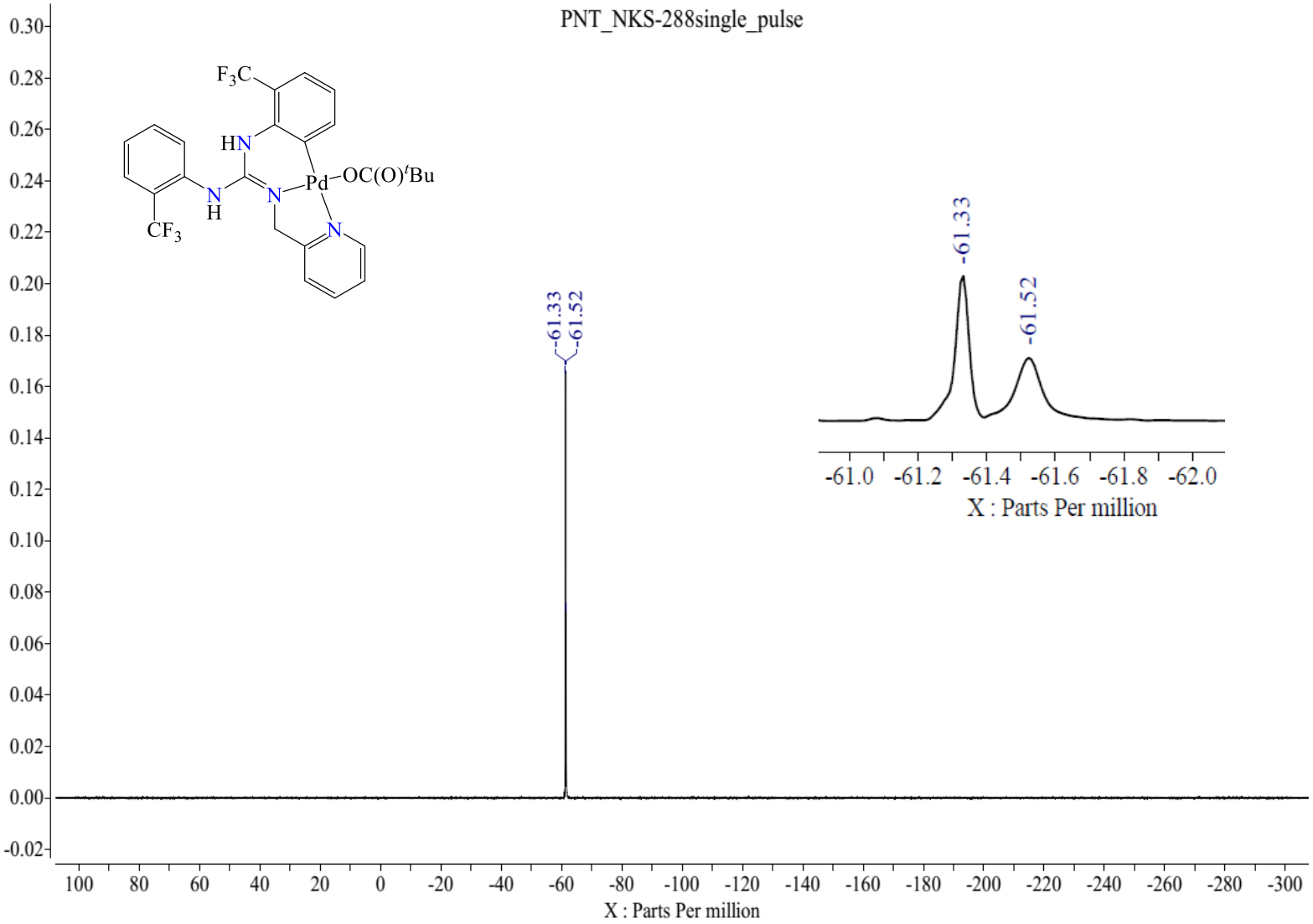
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **8** in indicated region.



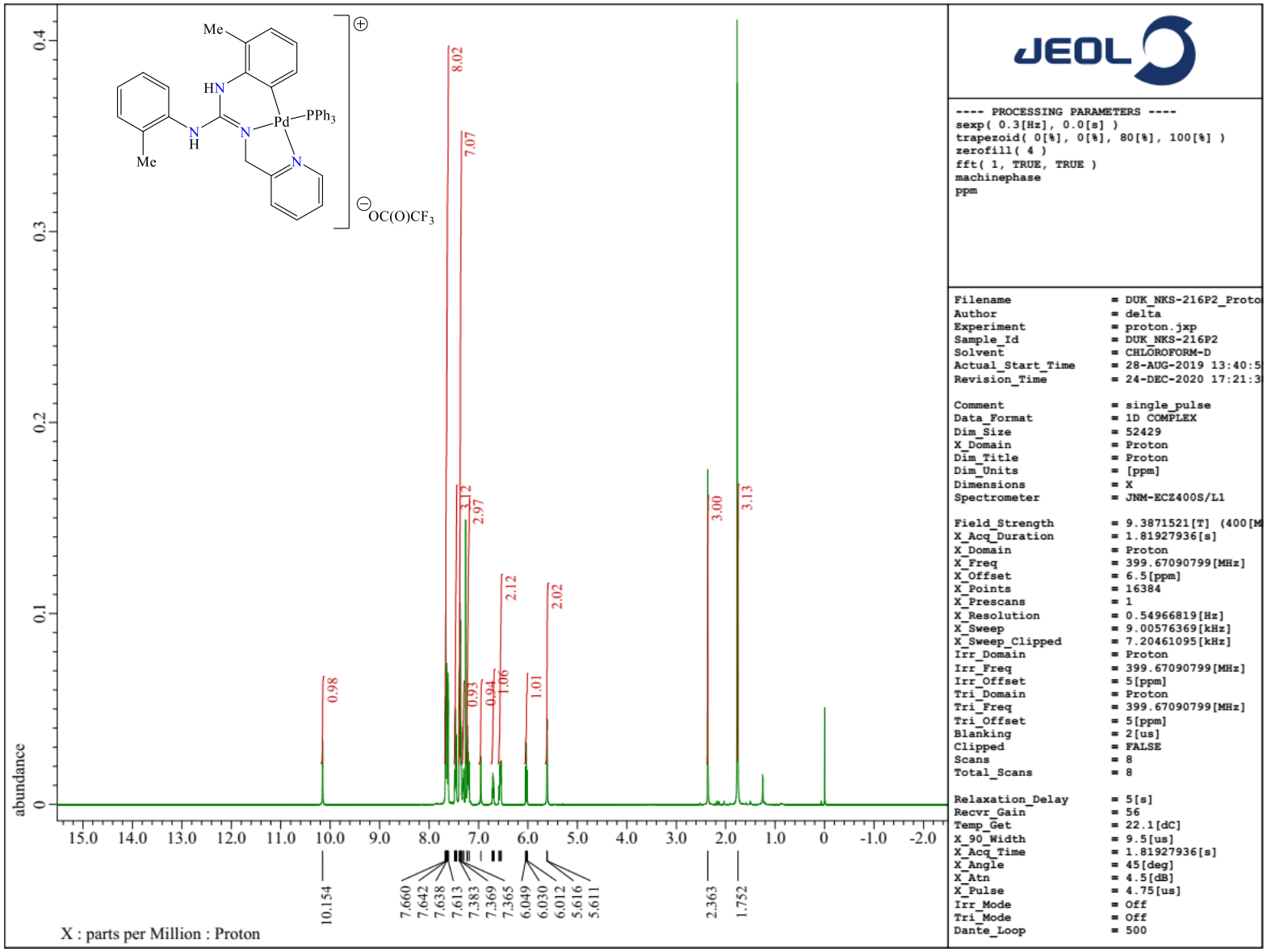
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **8** in indicated region.



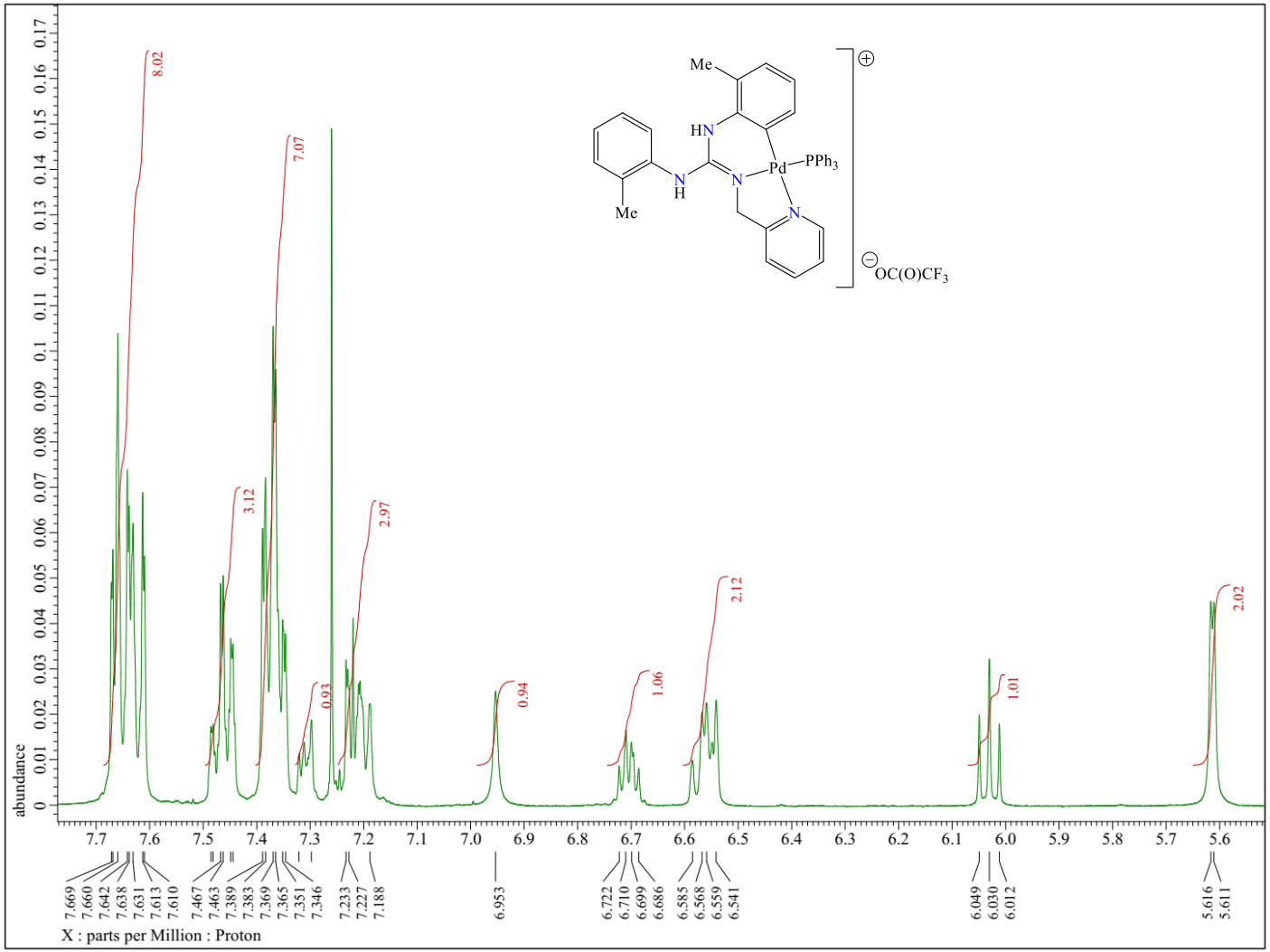
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **8** in indicated region.



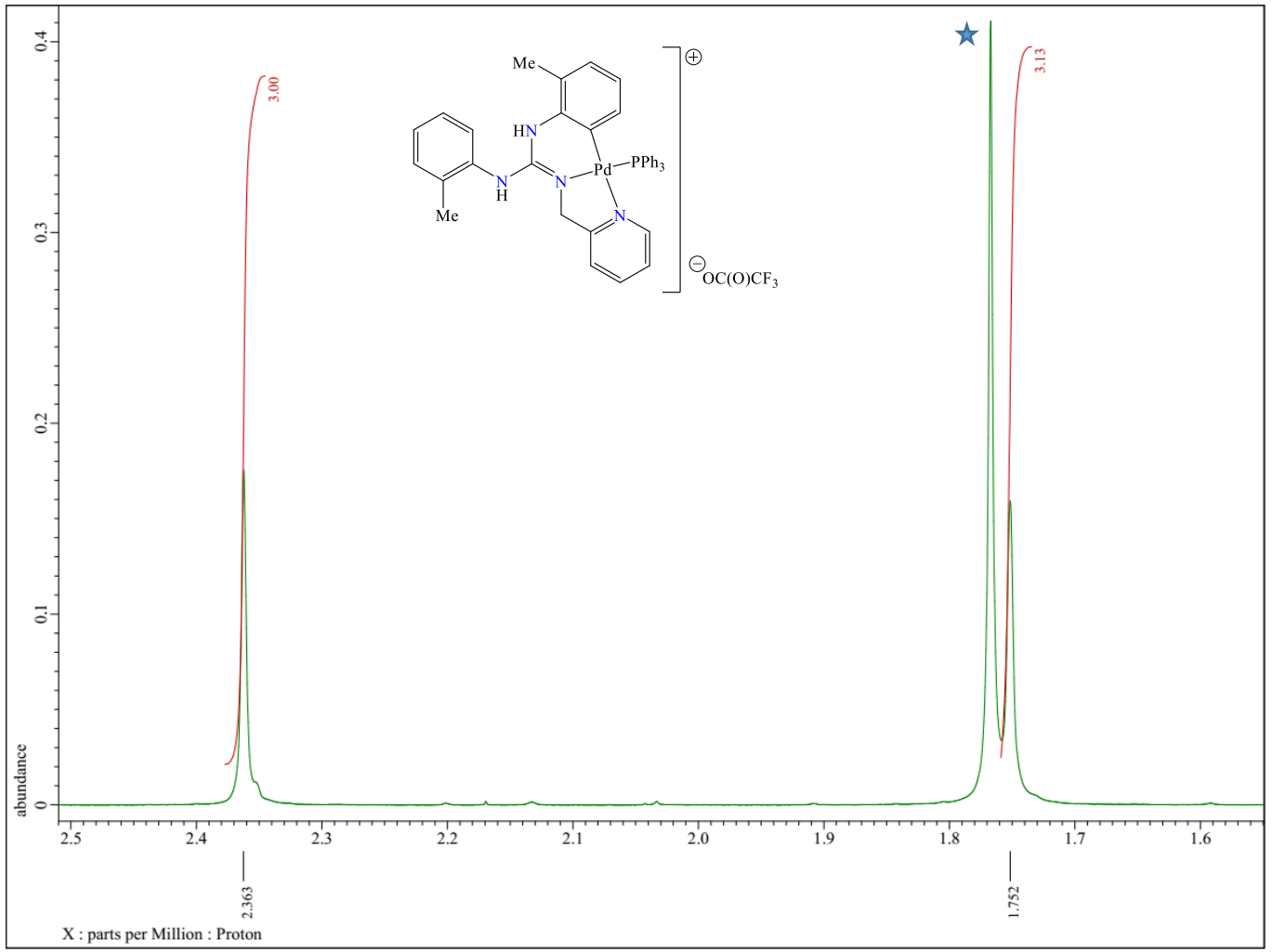
$^{13}F\{^{1}H\}$ NMR ($CDCl_3$, 376.5 MHz) spectrum of **8**.



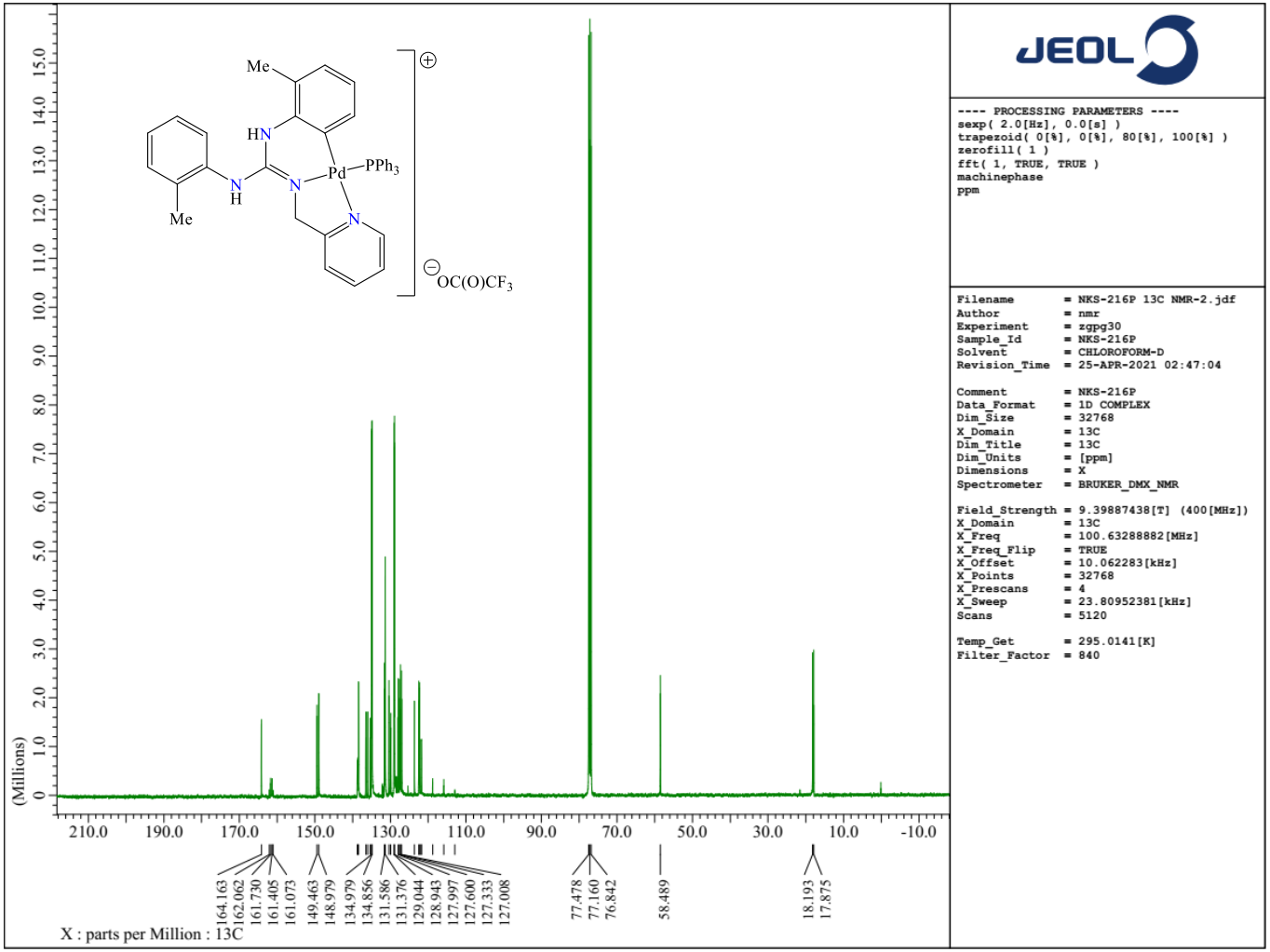
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **10**.



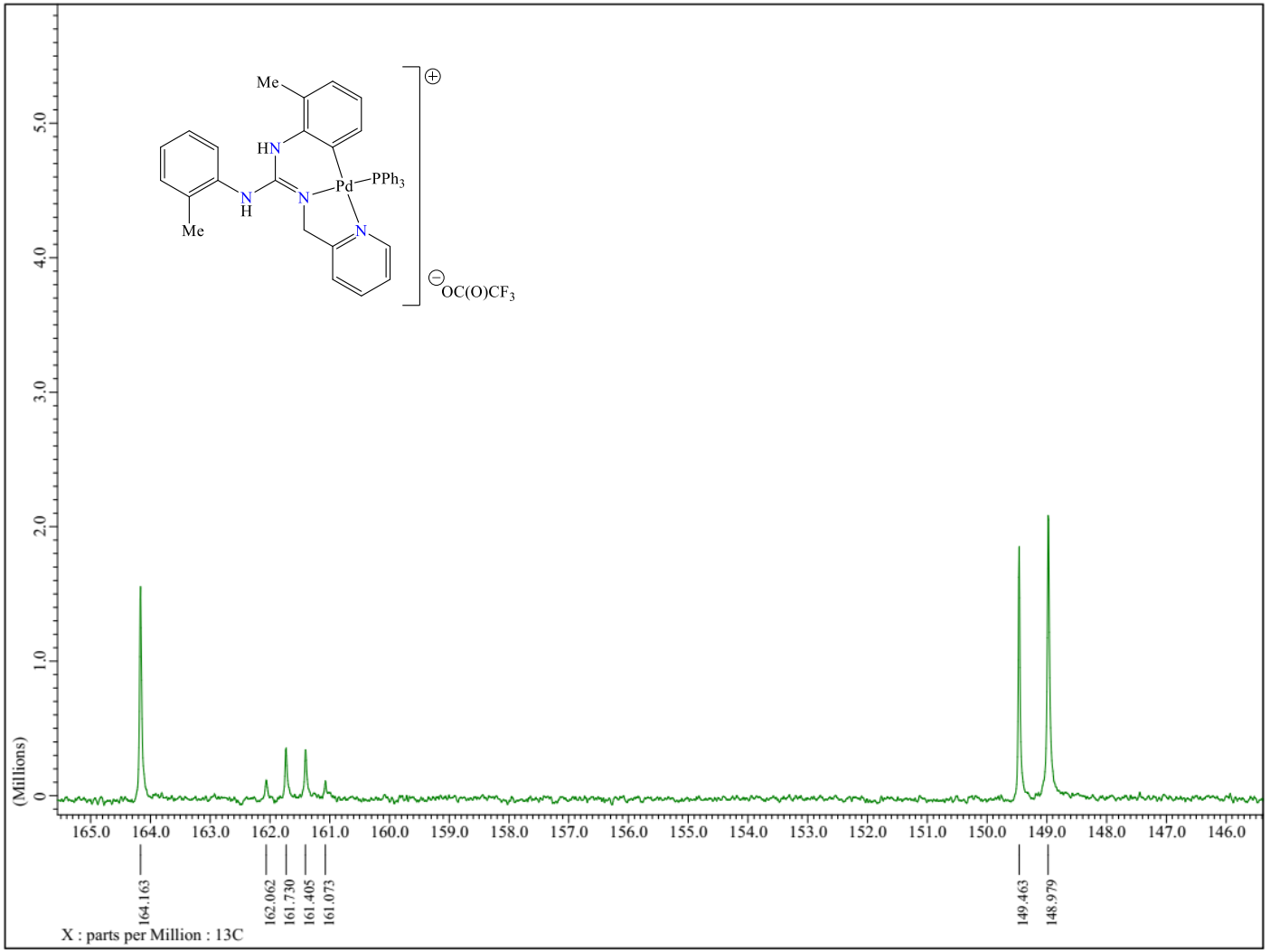
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **10** in indicated region.



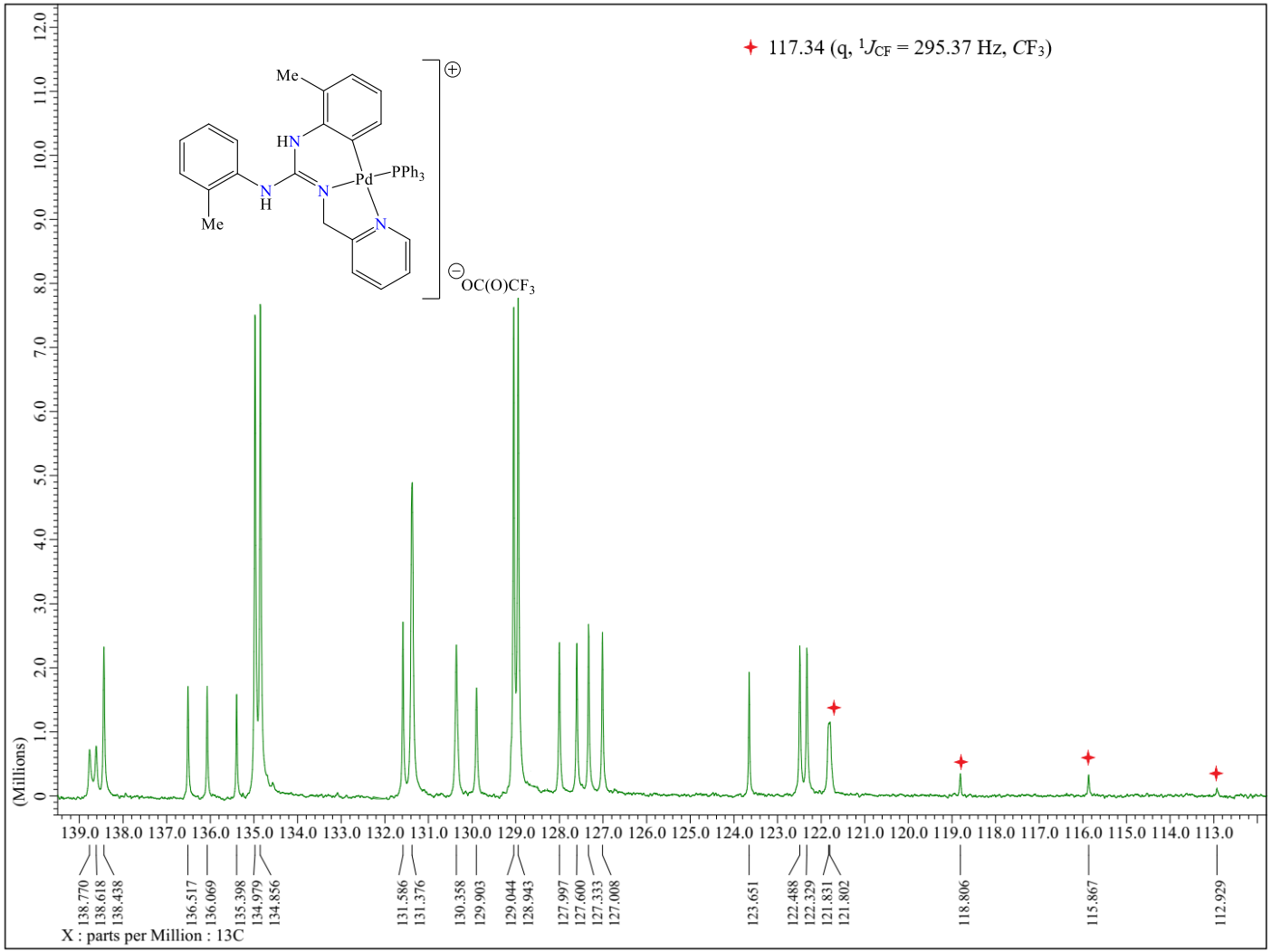
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **10** in indicated region. The ★ symbol indicates protons of residual water.



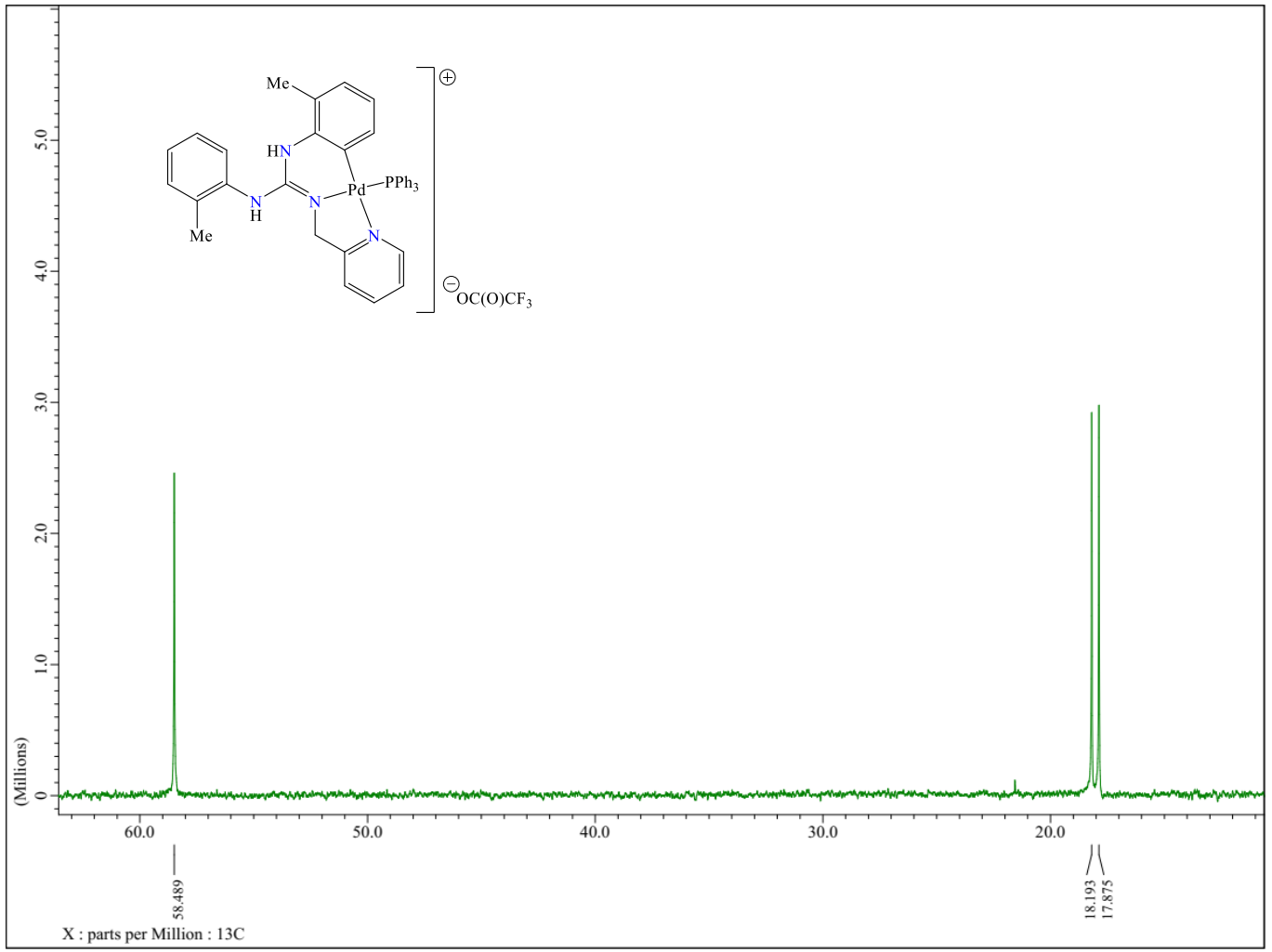
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **10**.



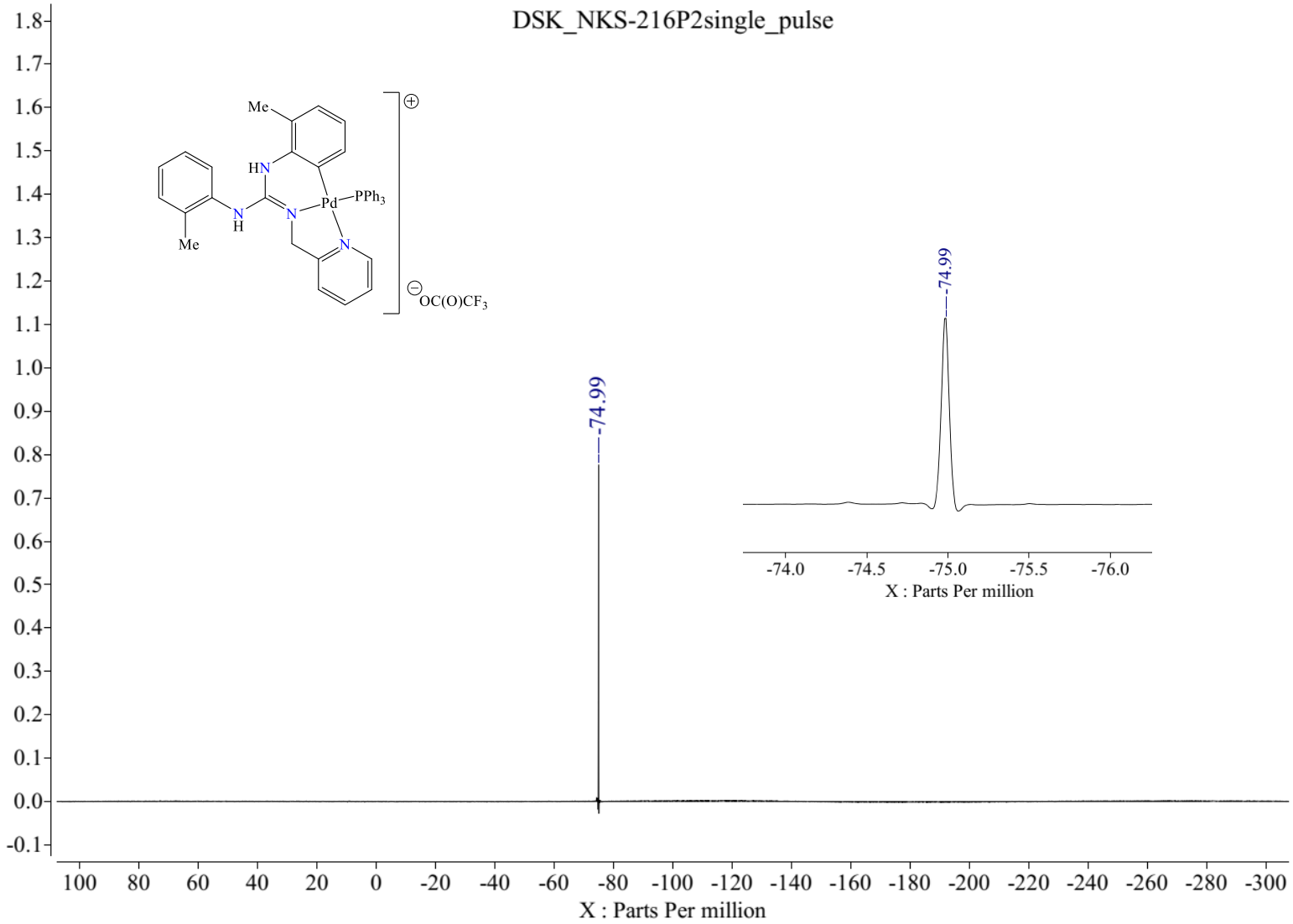
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **10** in indicated region.



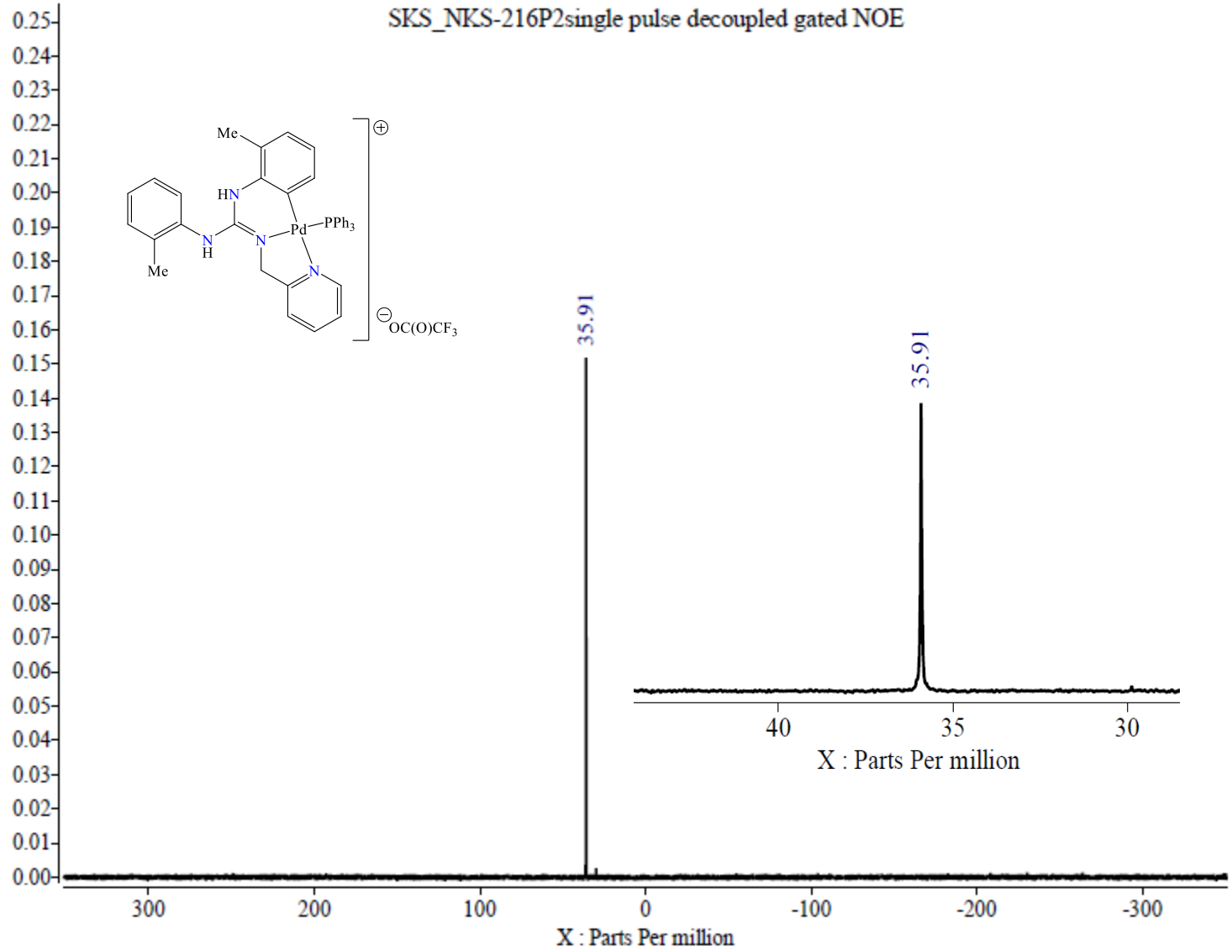
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **10** in indicated region.



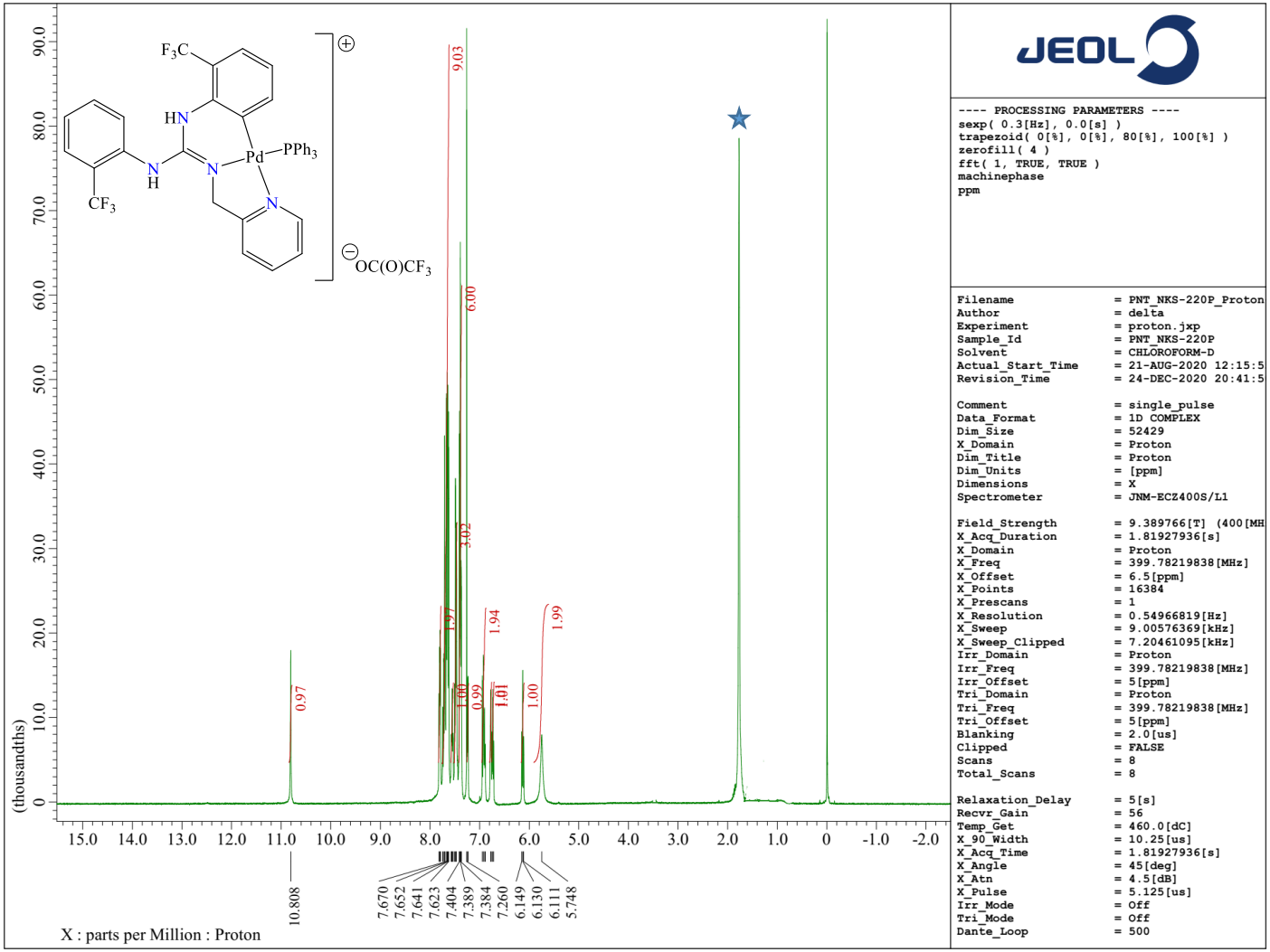
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **10** in indicated region.



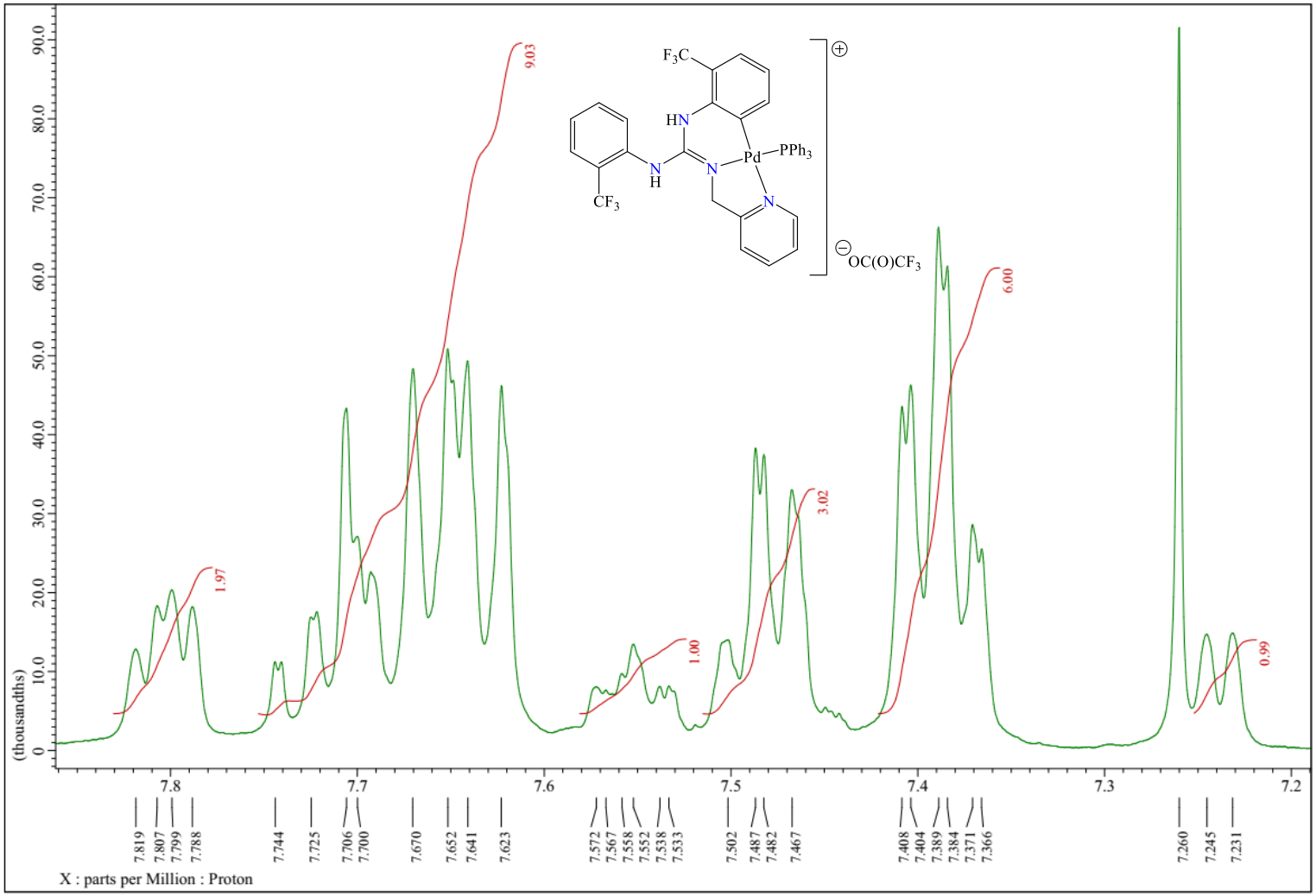
^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of **10**.



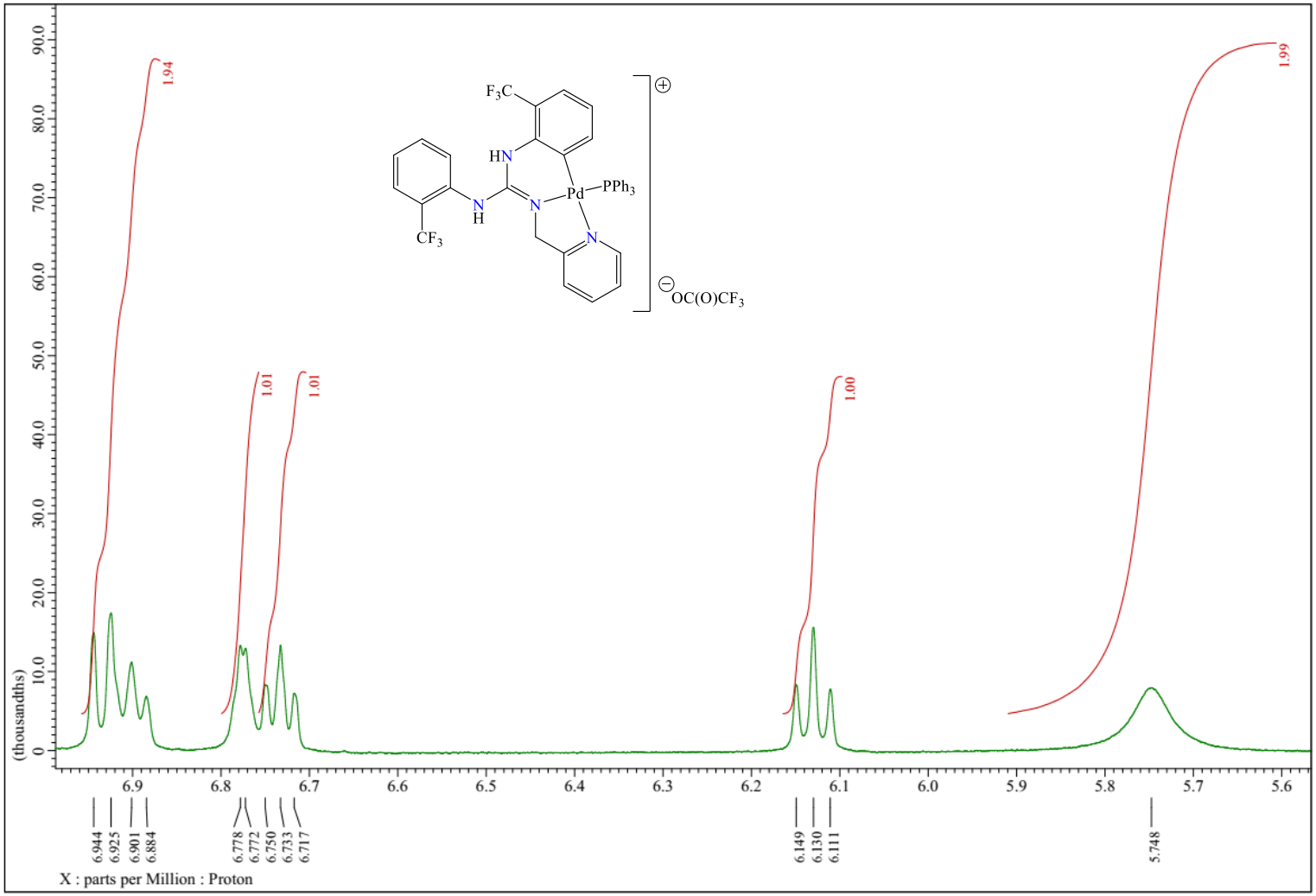
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.8 MHz) spectrum of **10**.



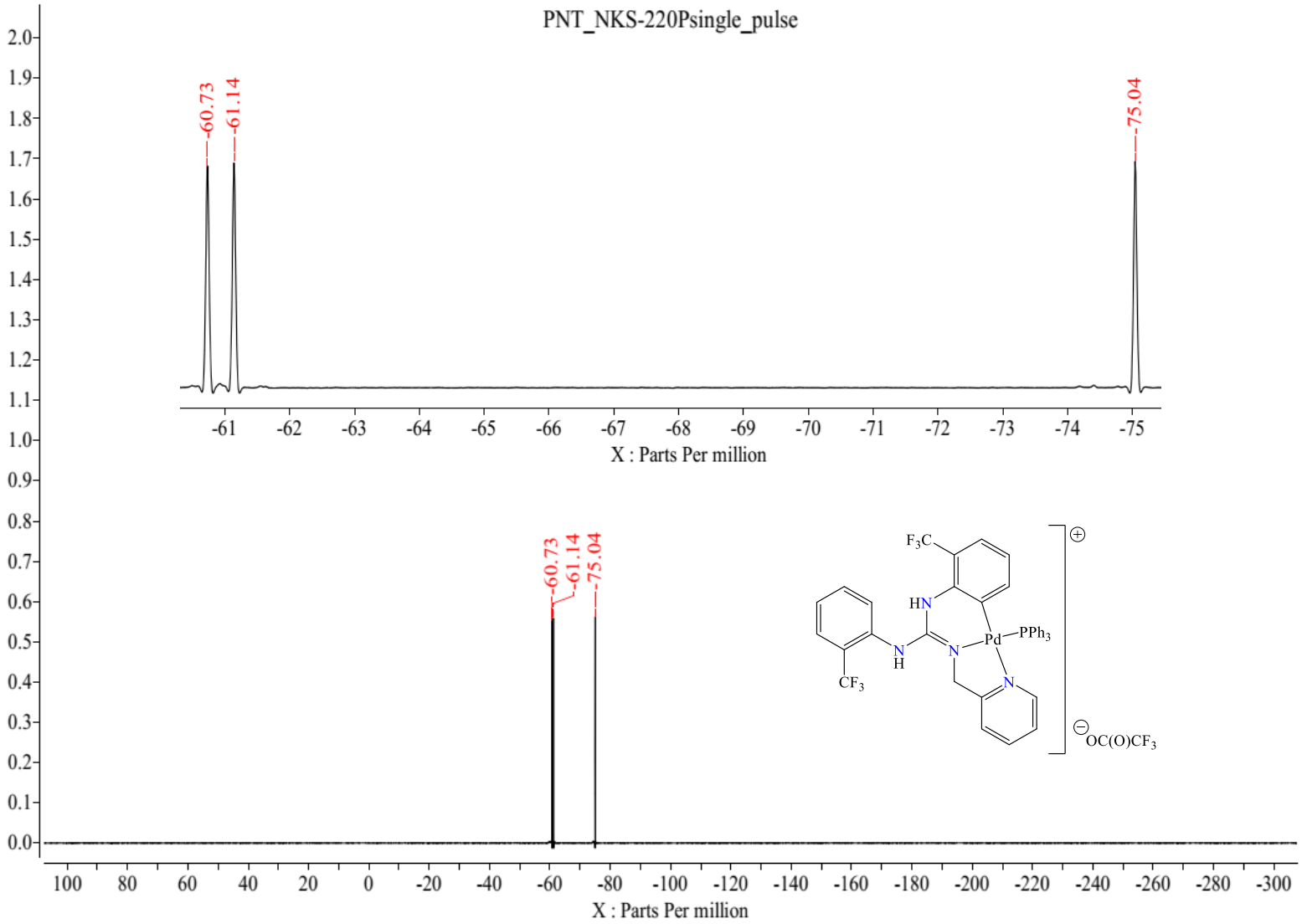
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **11**. The ★ symbol indicates protons of residual water.



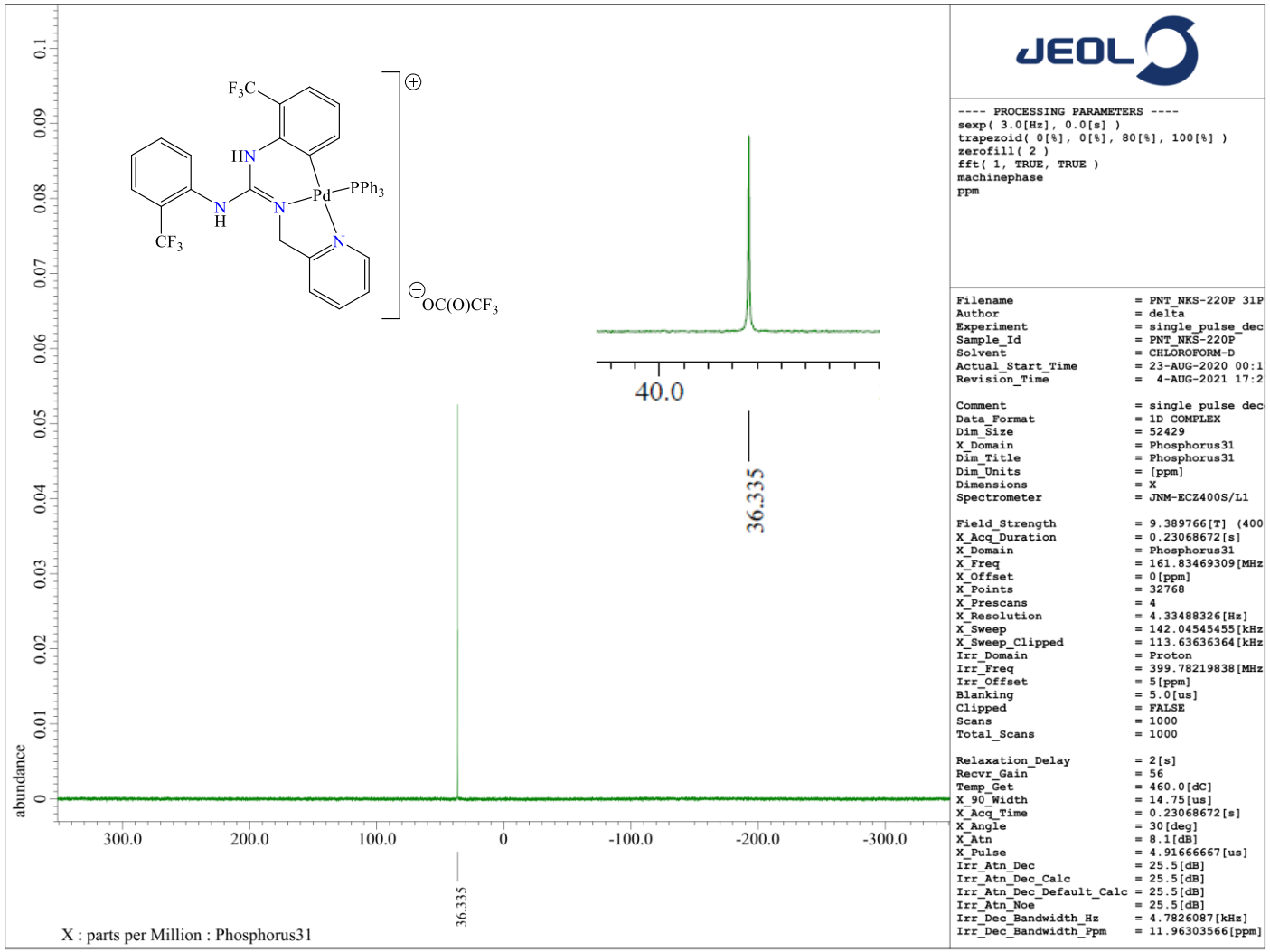
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **11** in indicated region.



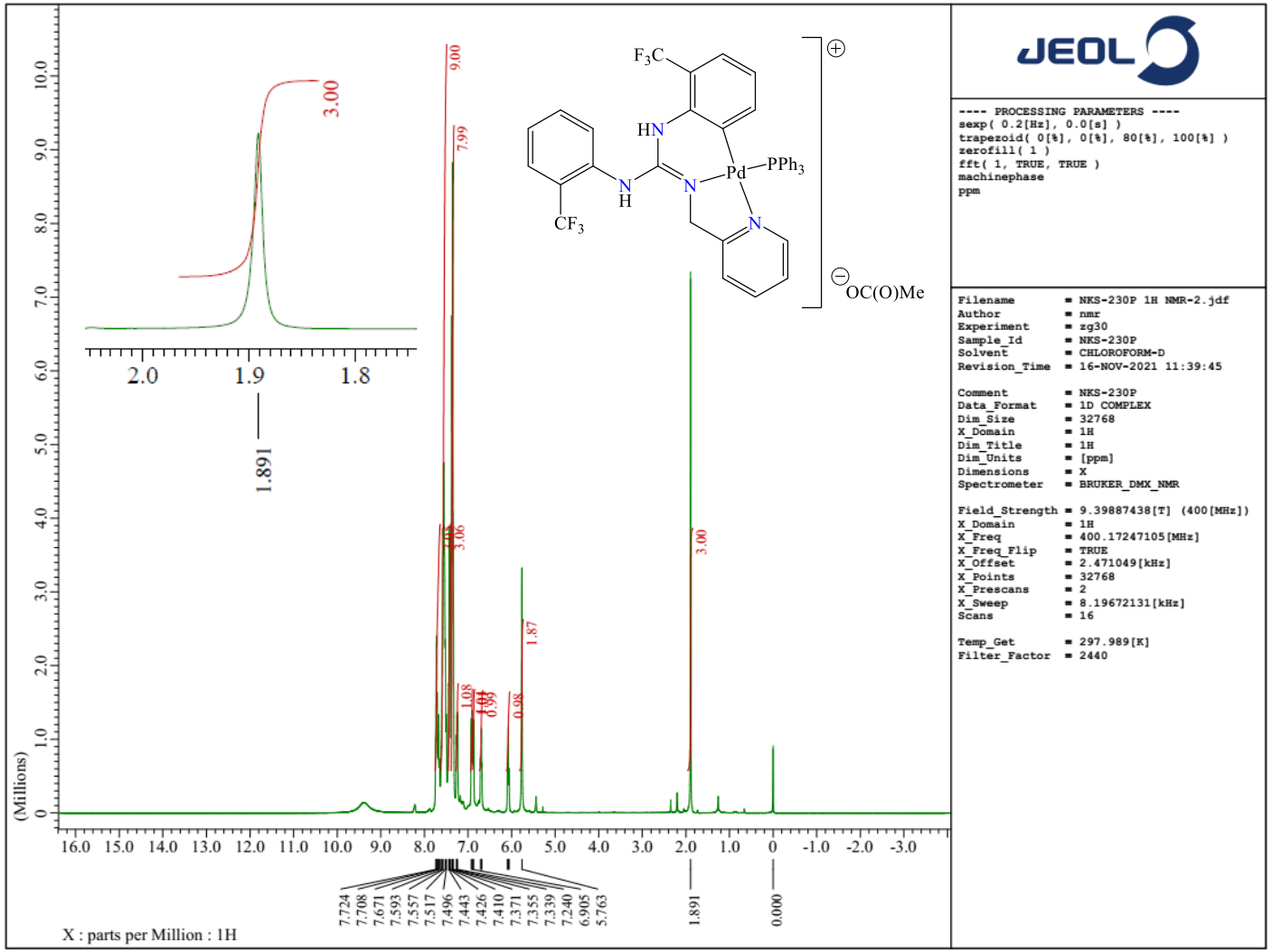
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **11** in indicated region.



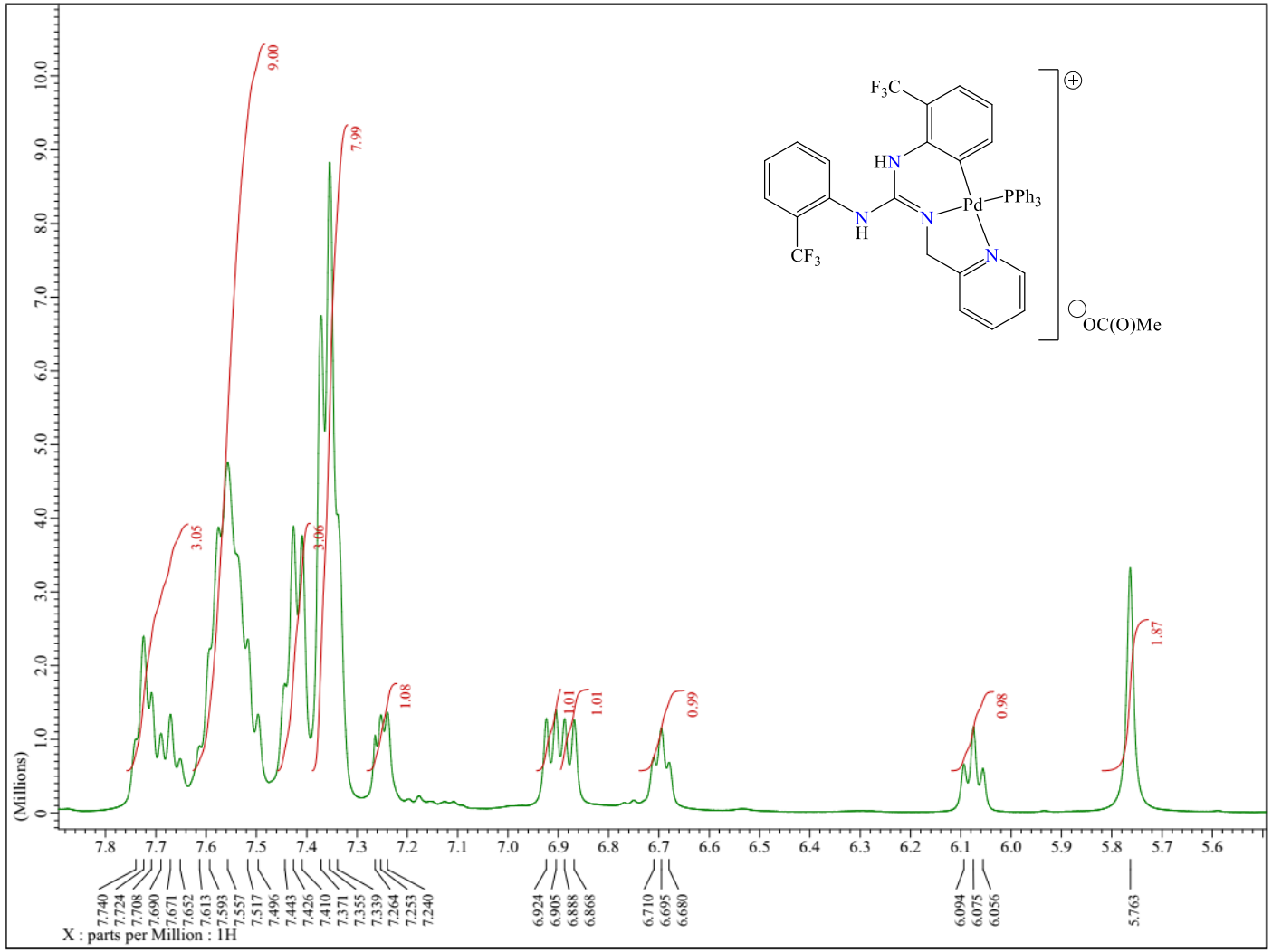
^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of **11**.



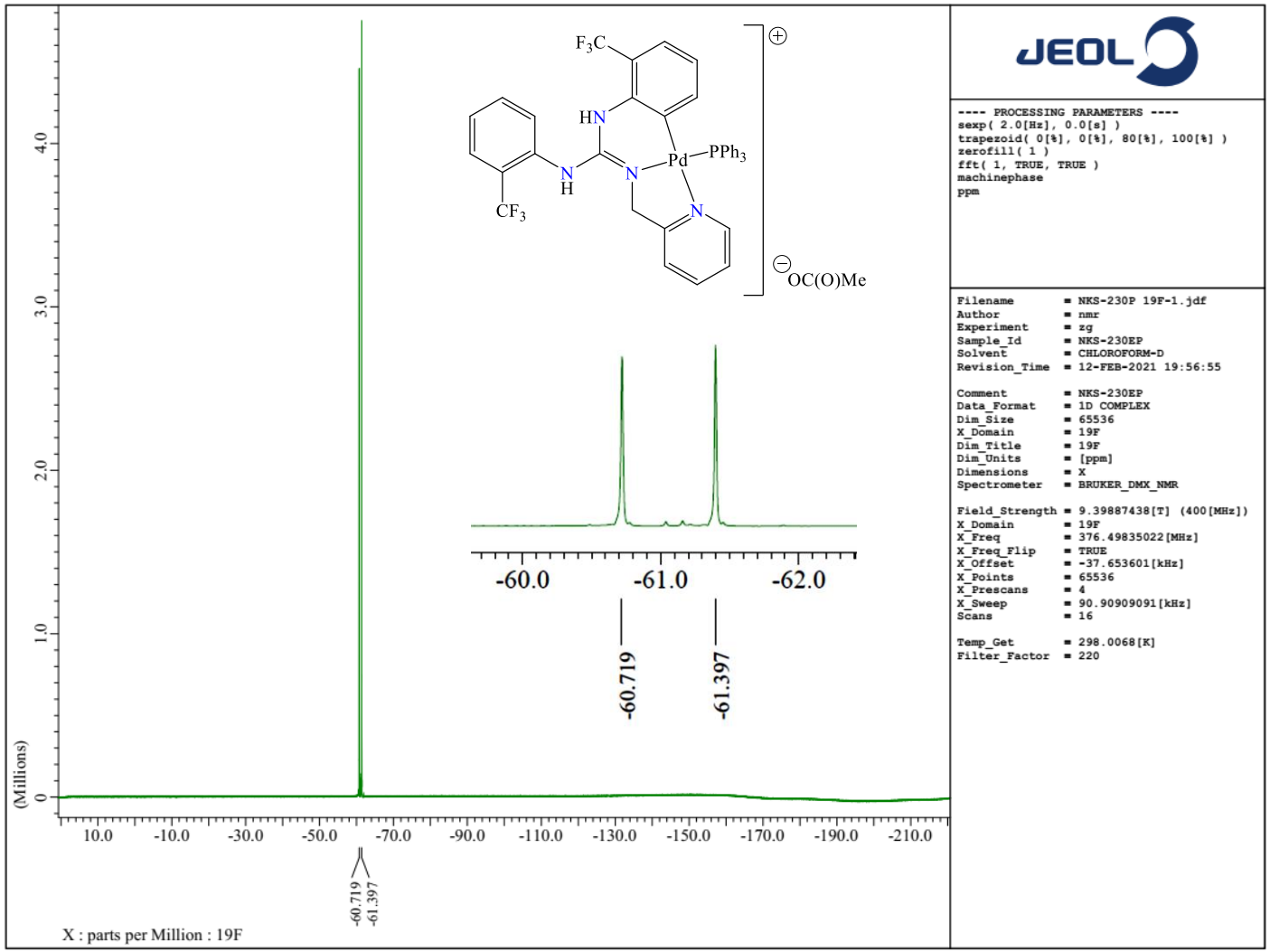
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.8 MHz) spectrum of **11**.



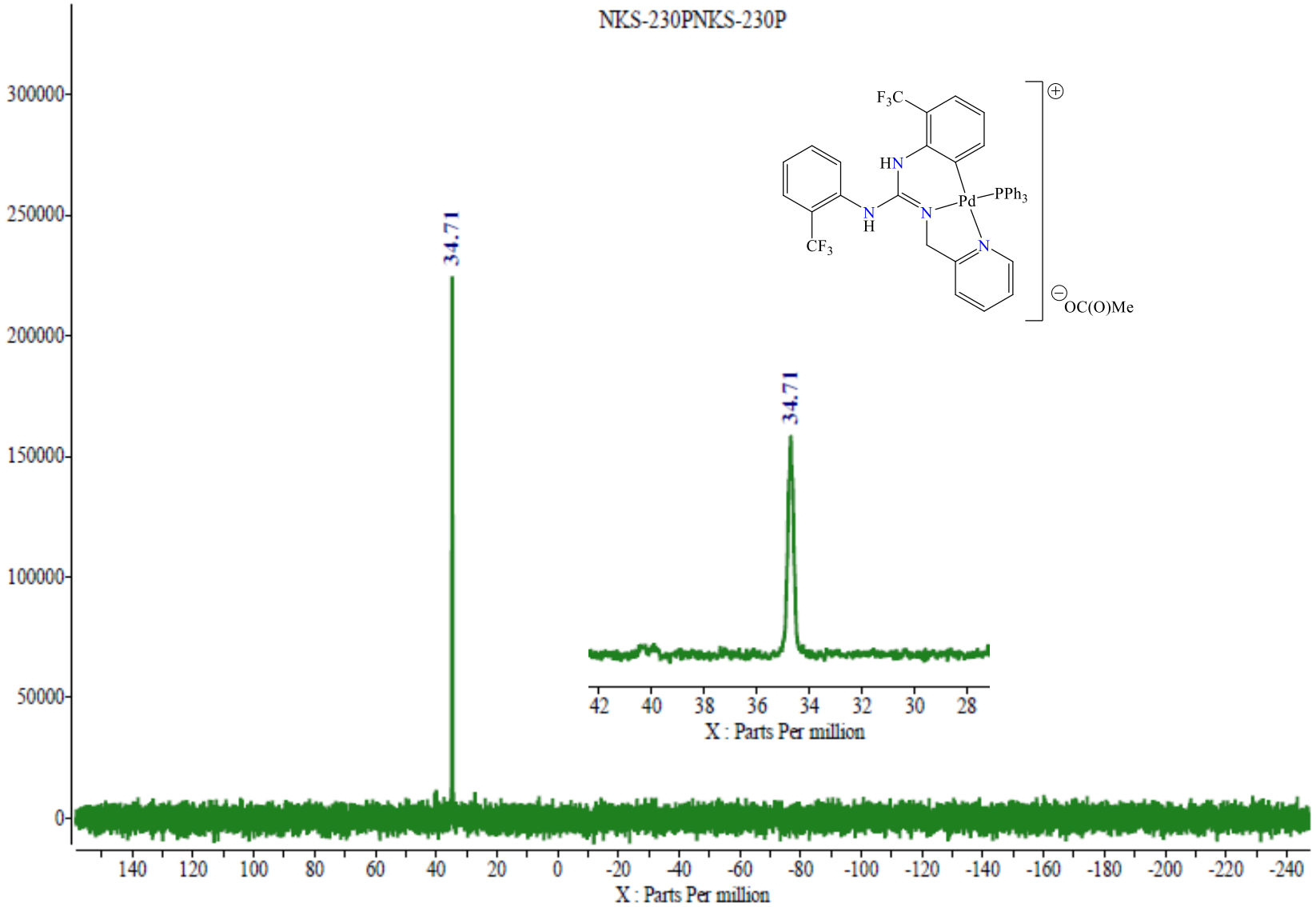
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **12** in indicated region.



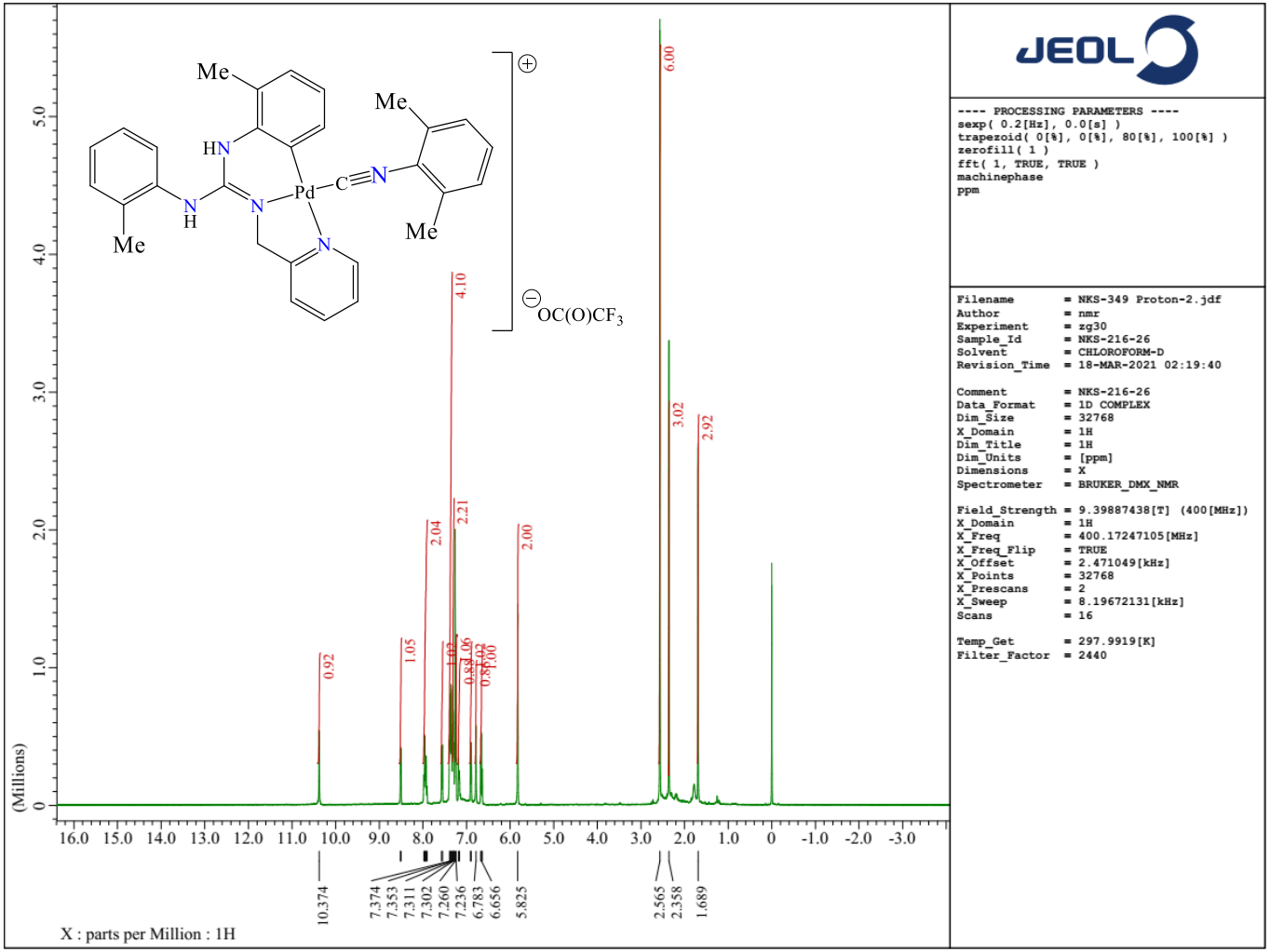
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **12** in indicated region.



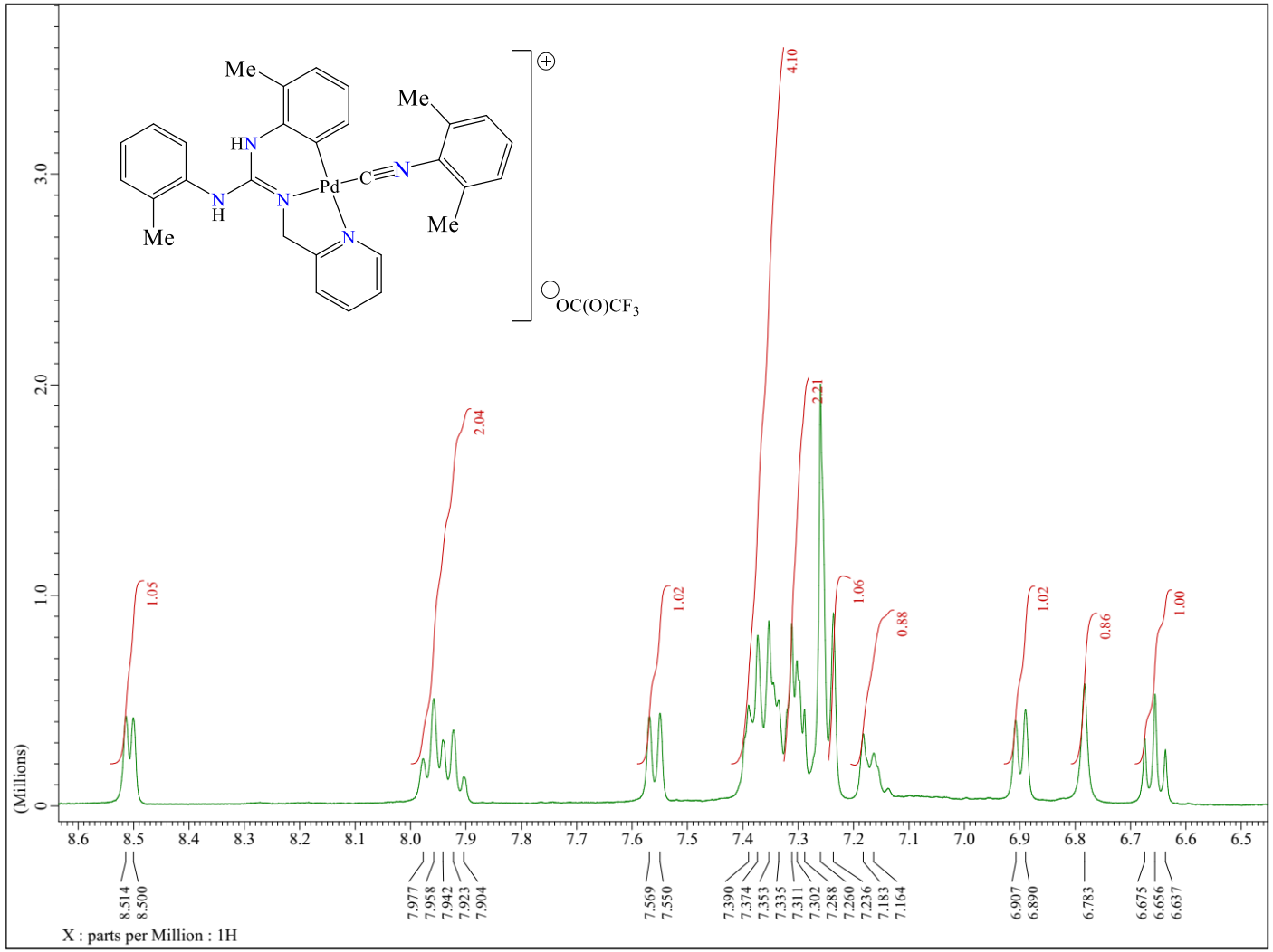
^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of **12** in indicated region.



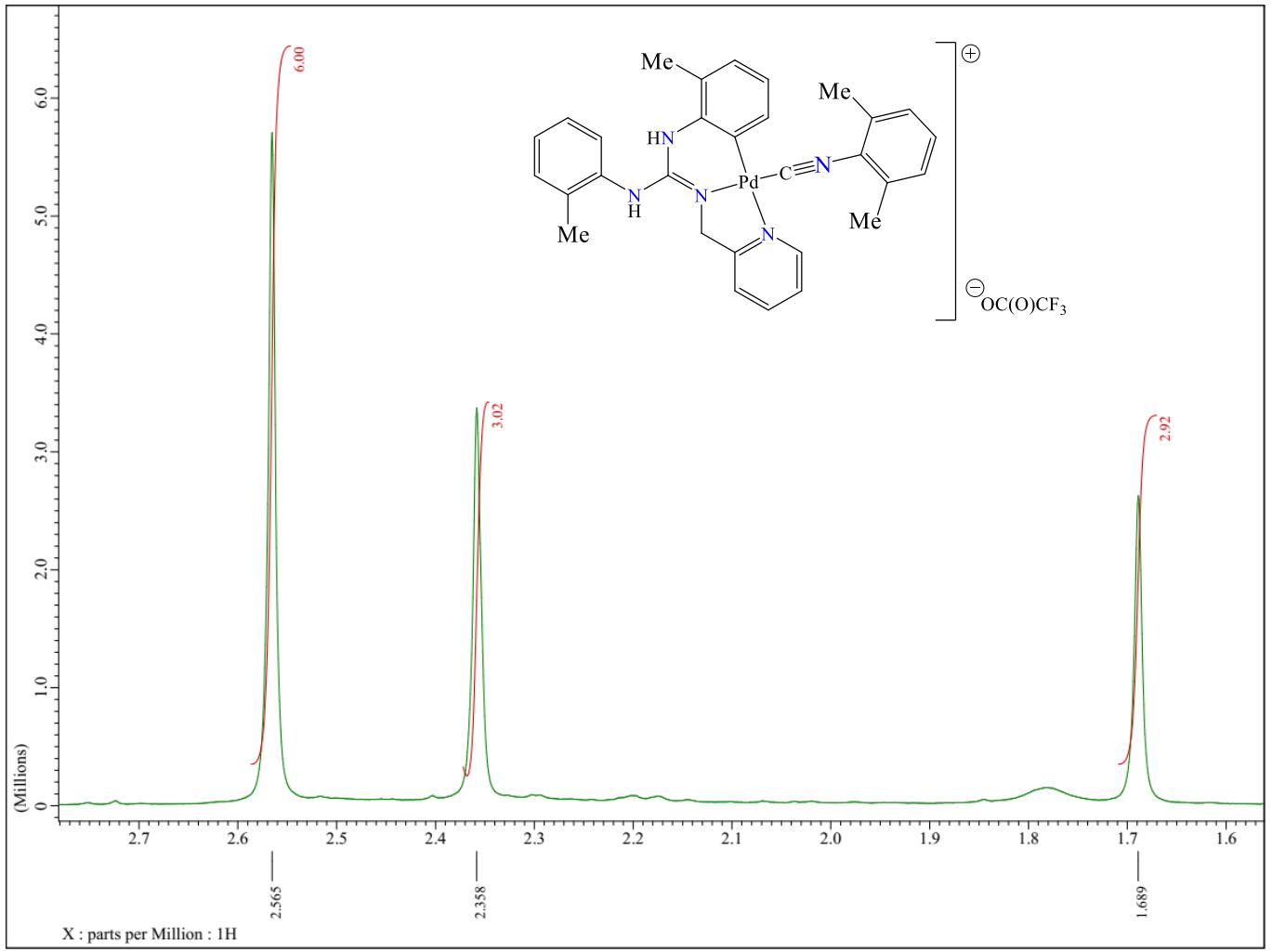
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.8 MHz) spectrum of **12**.



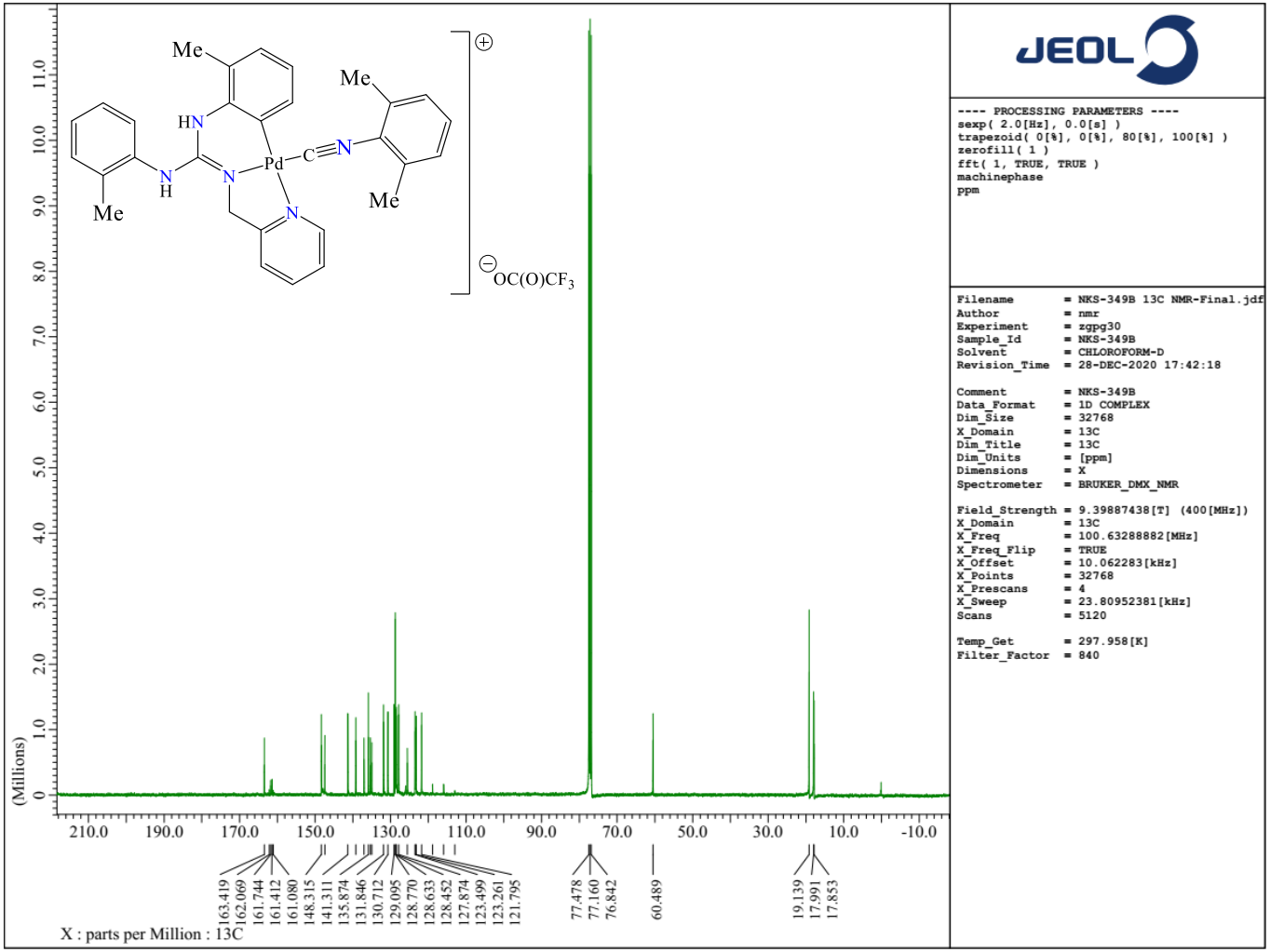
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **13**.



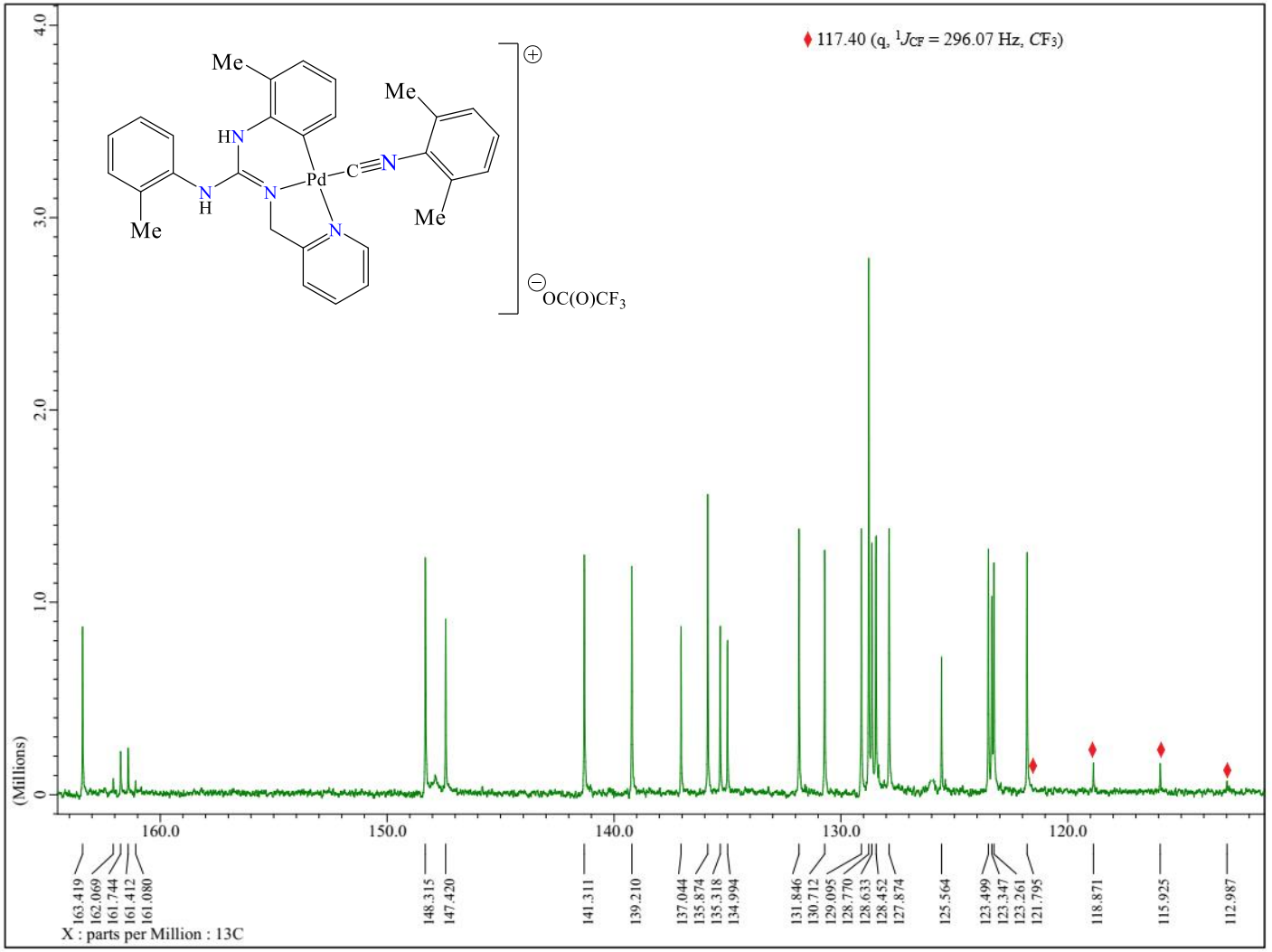
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **13** in indicated region.



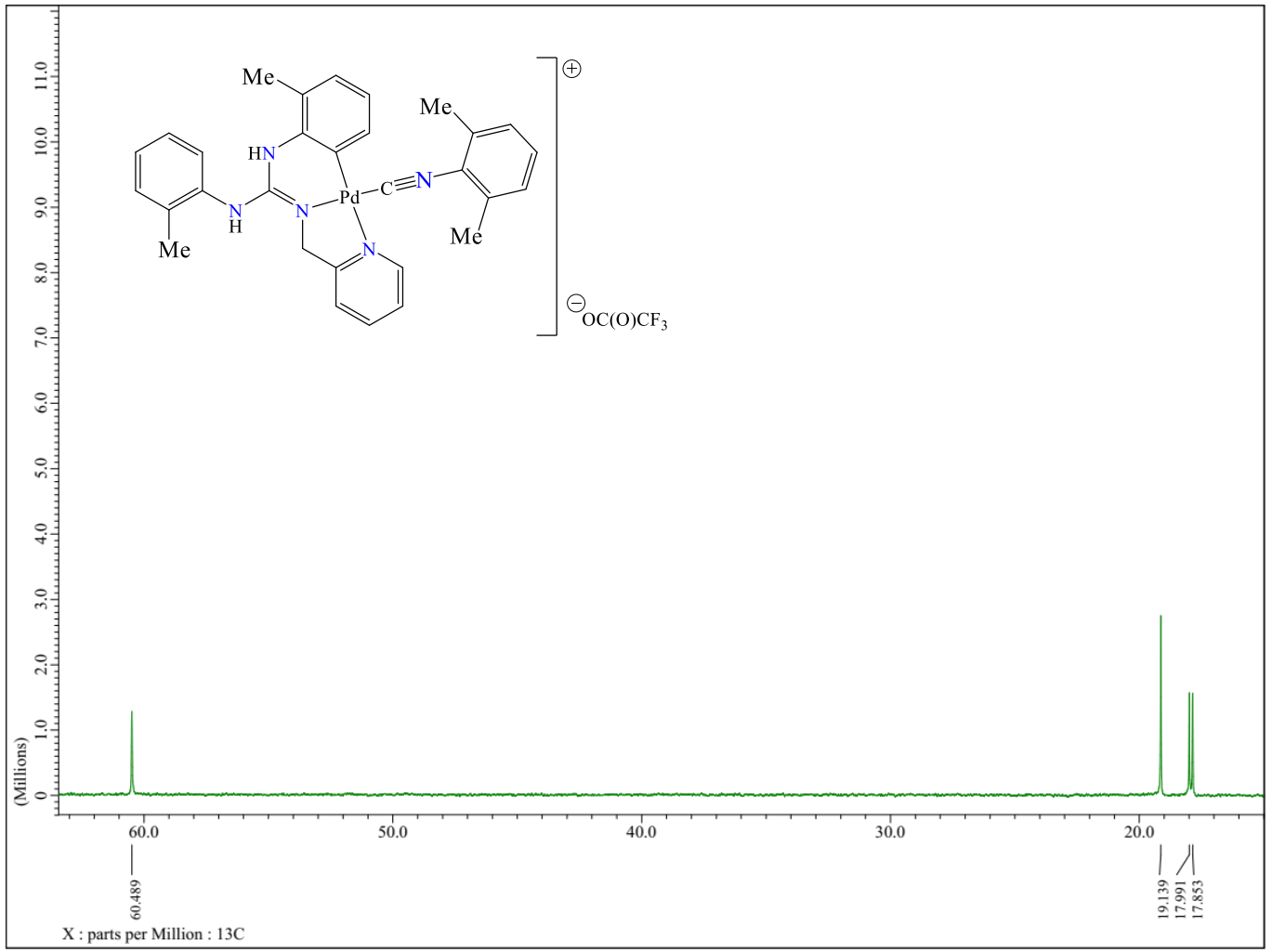
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **13** in indicated region.



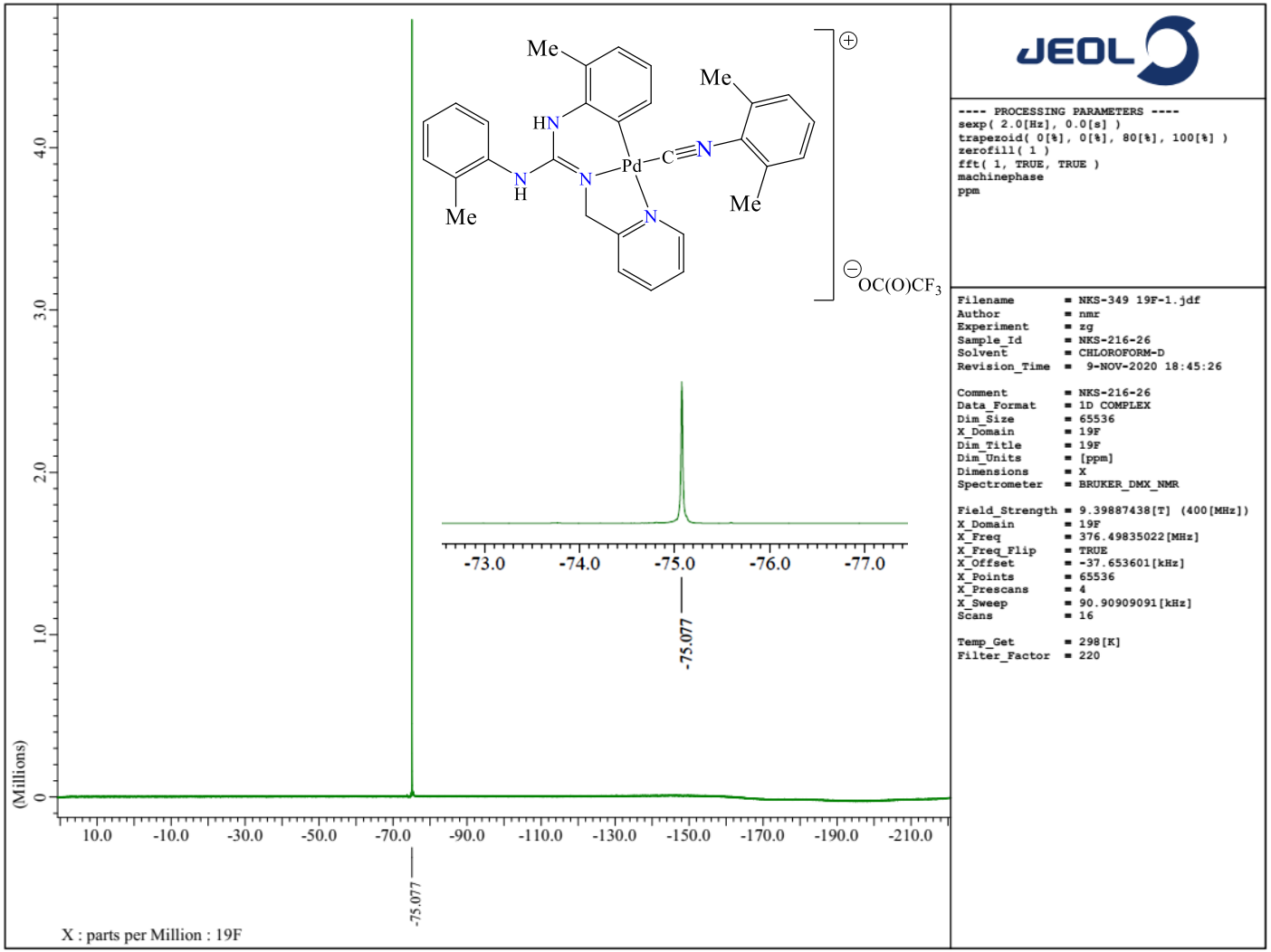
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **13**.



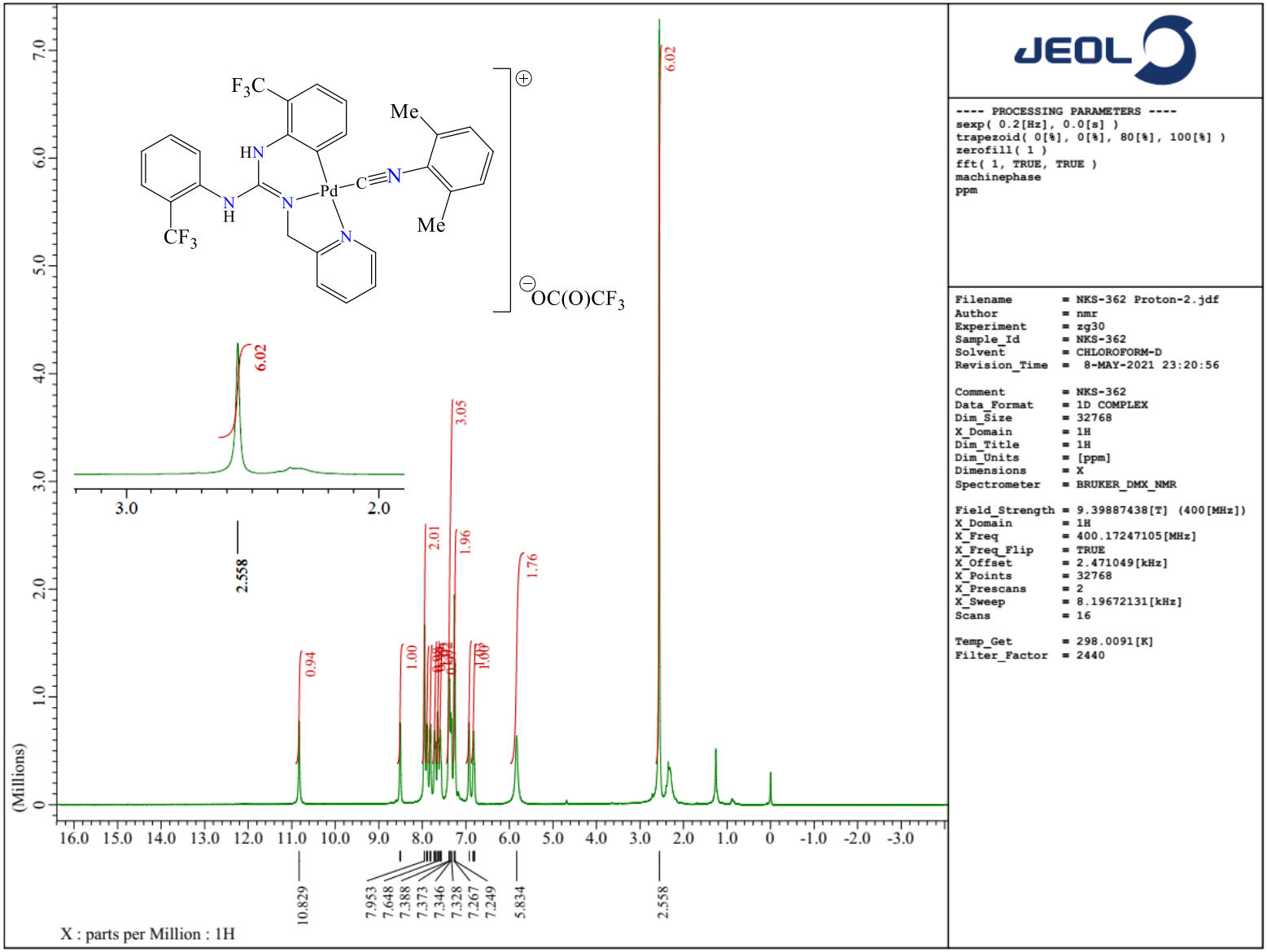
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **13** in indicated region.



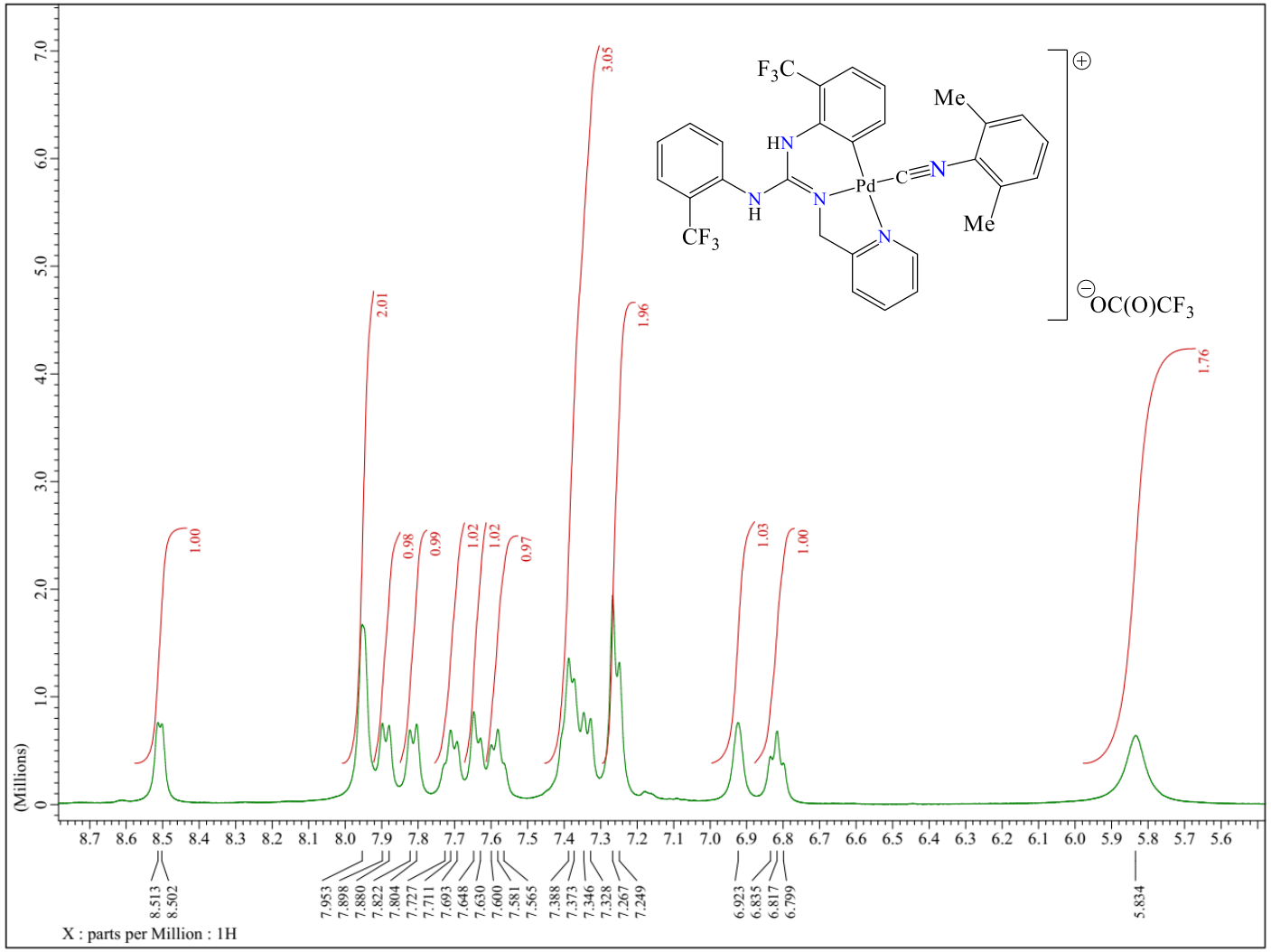
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **13** in indicated region.



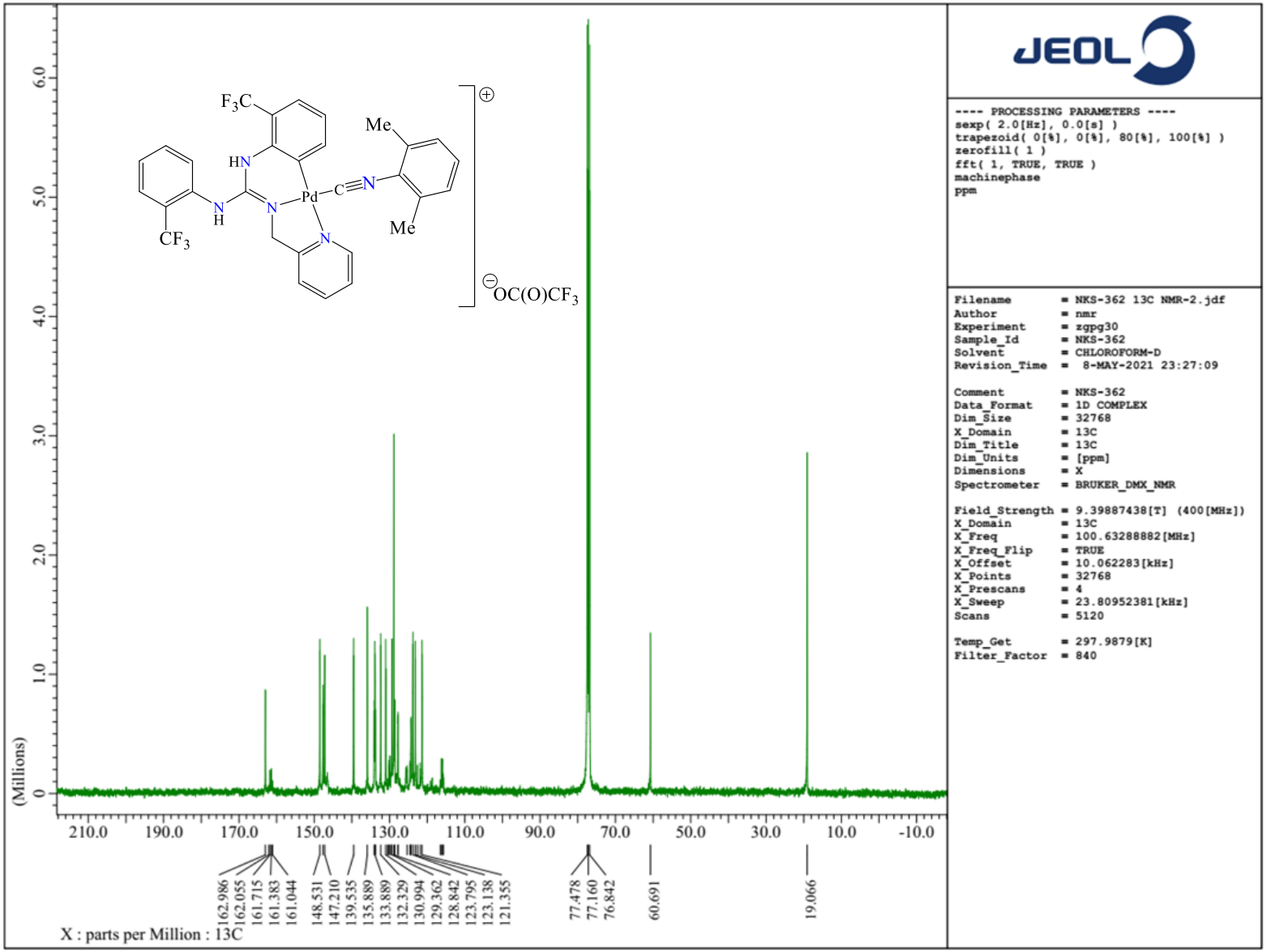
^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of **13** in indicated region.



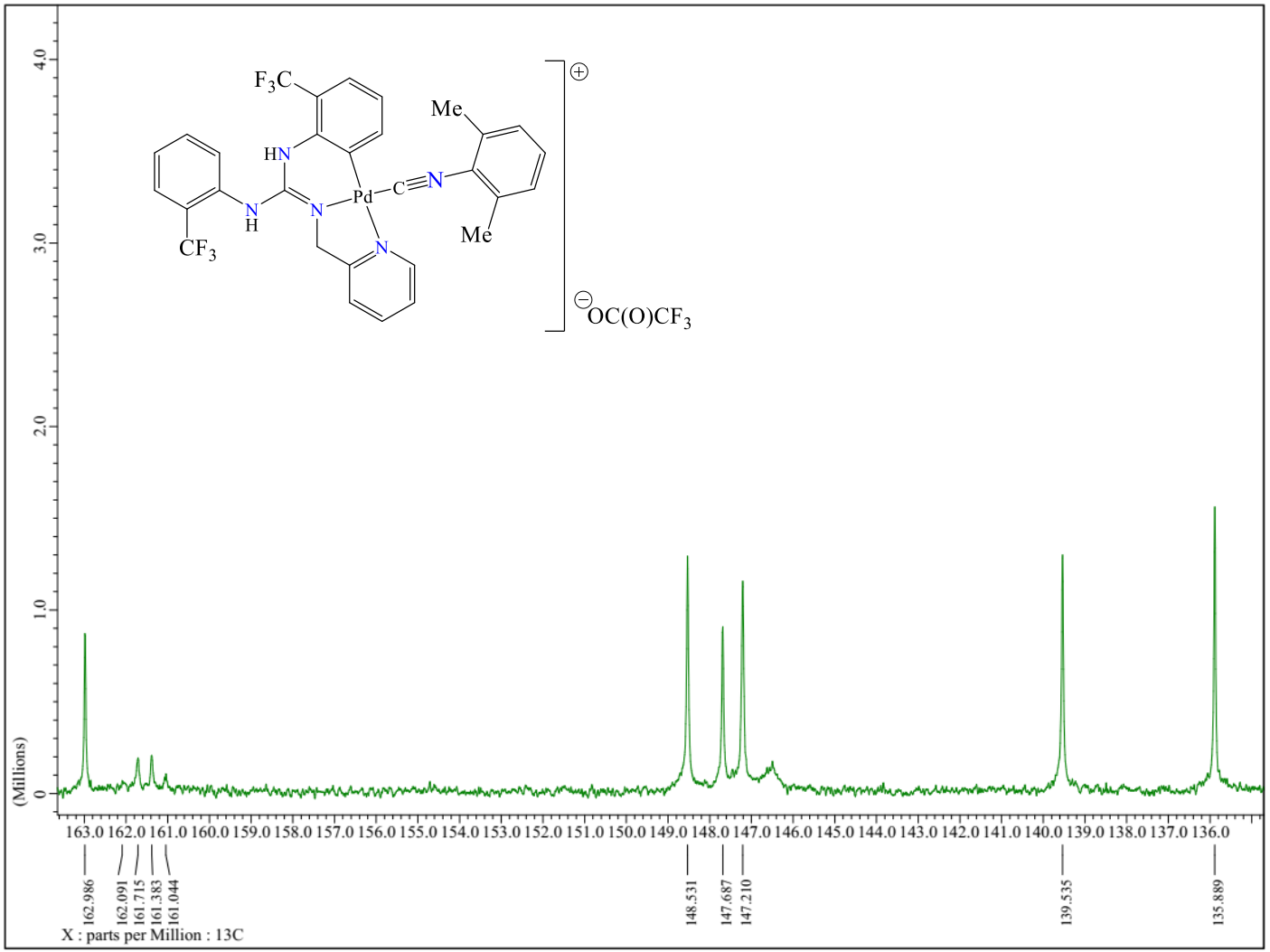
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **14**.



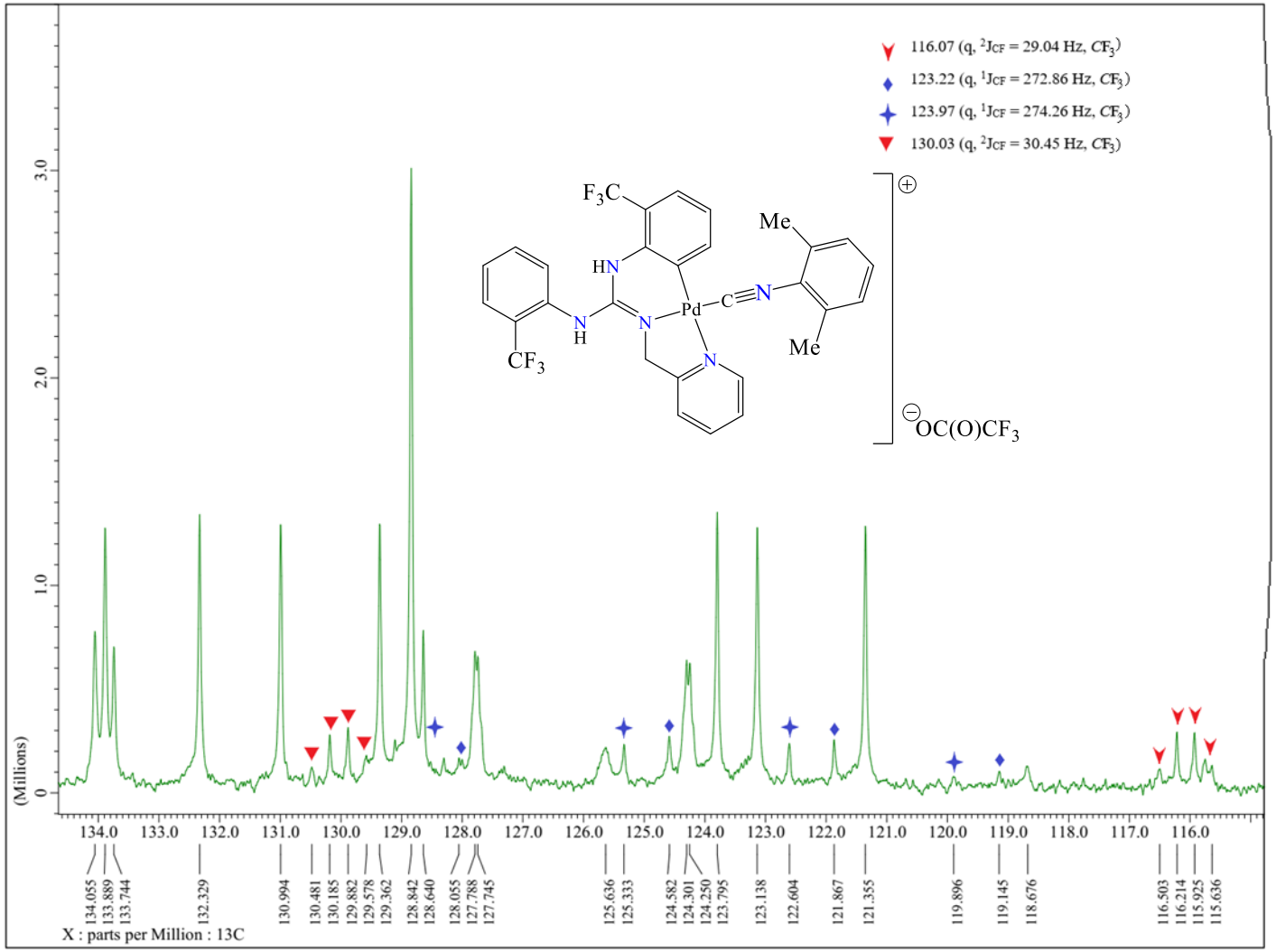
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **14** in indicated region.



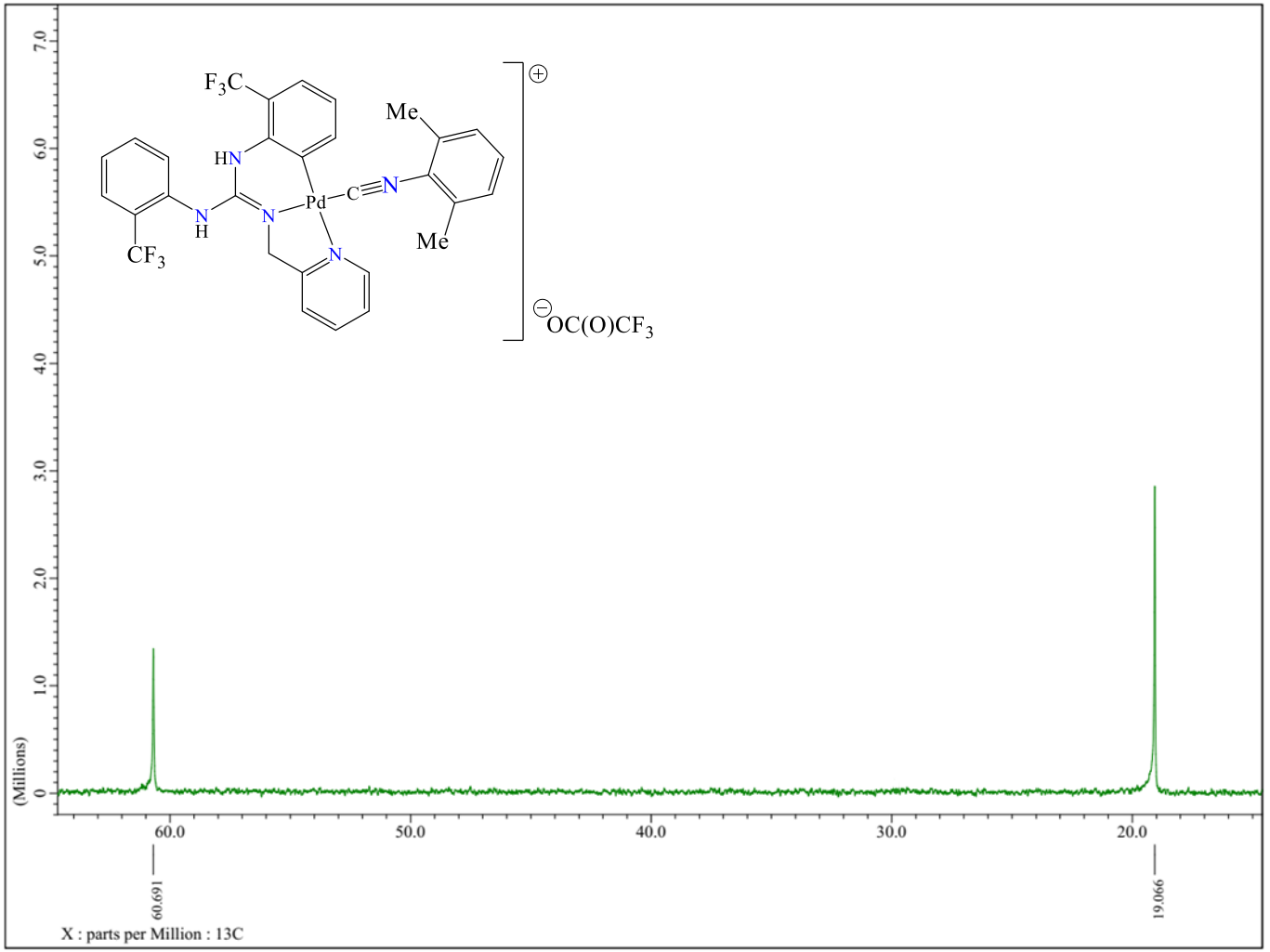
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **14.**



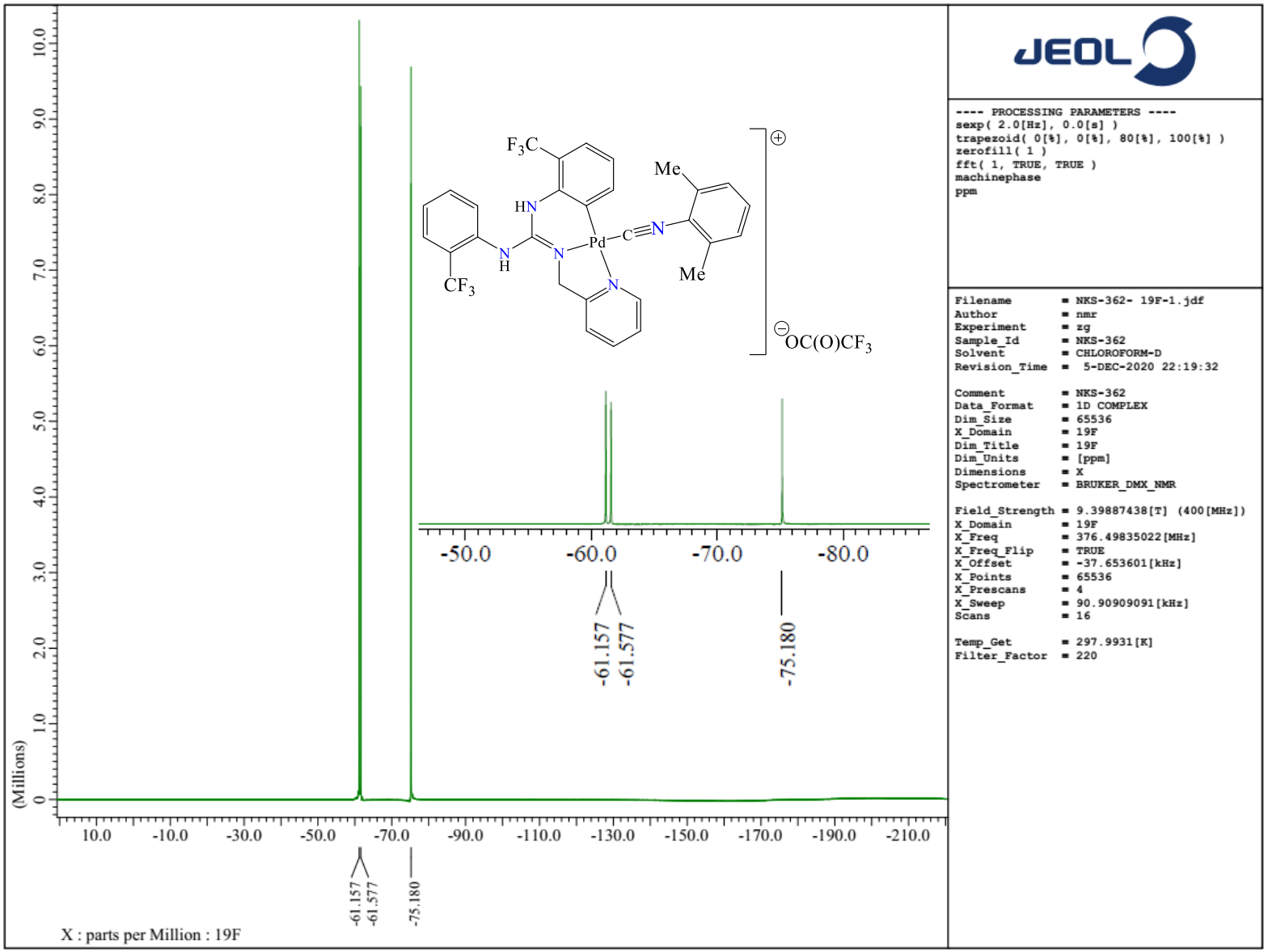
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **14** in indicated region.



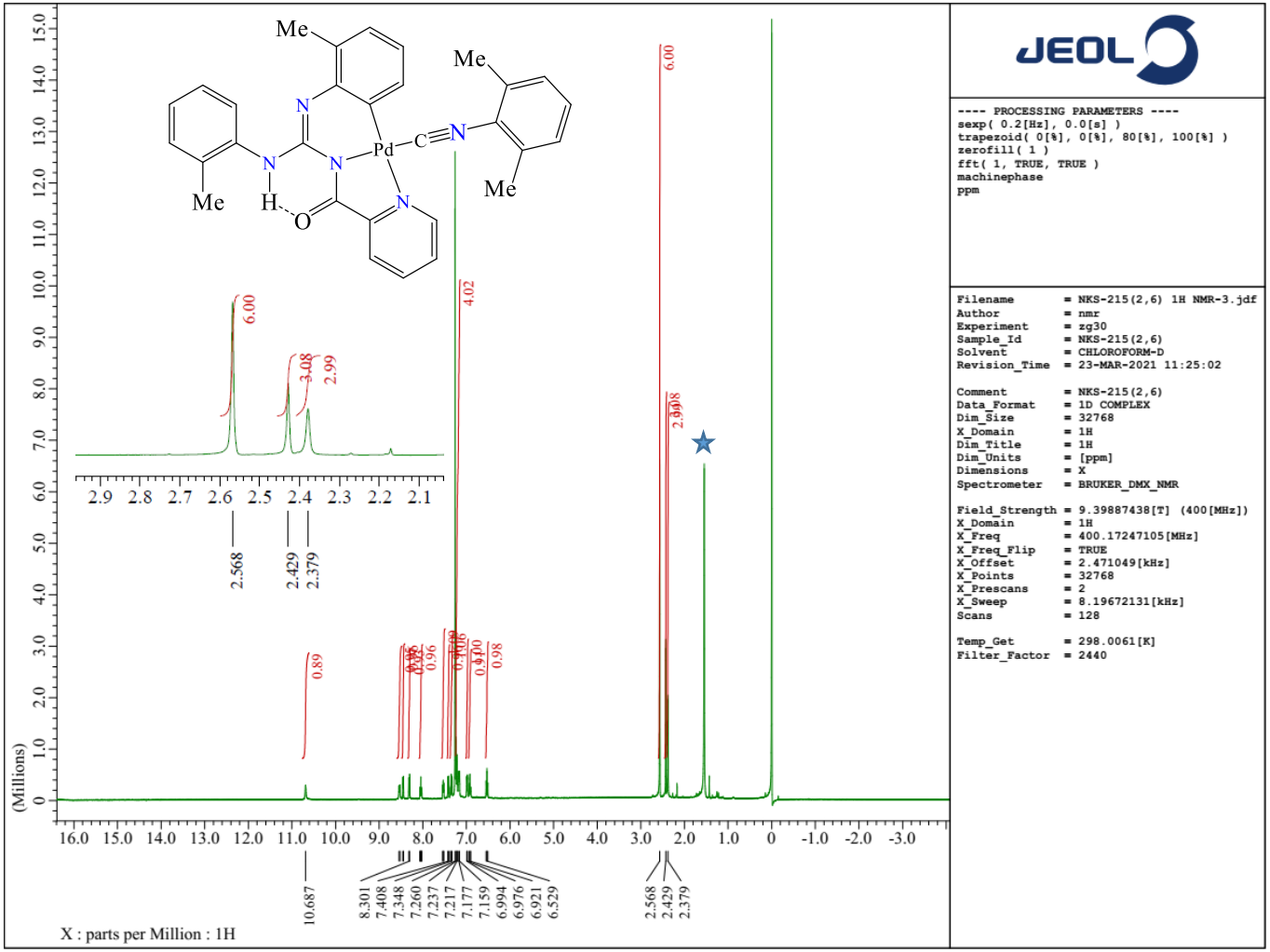
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **14** in indicated region.



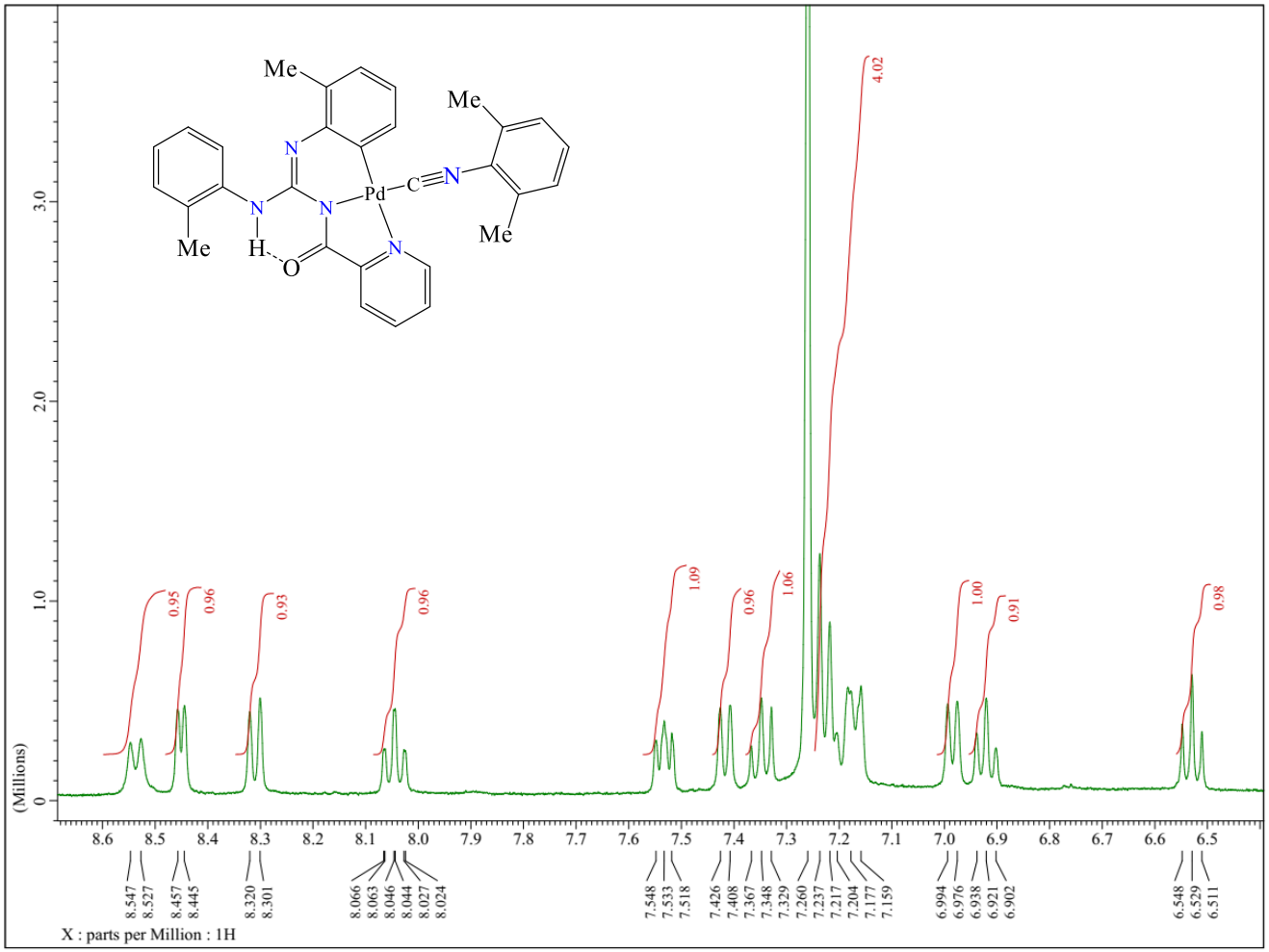
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **14** in indicated region.



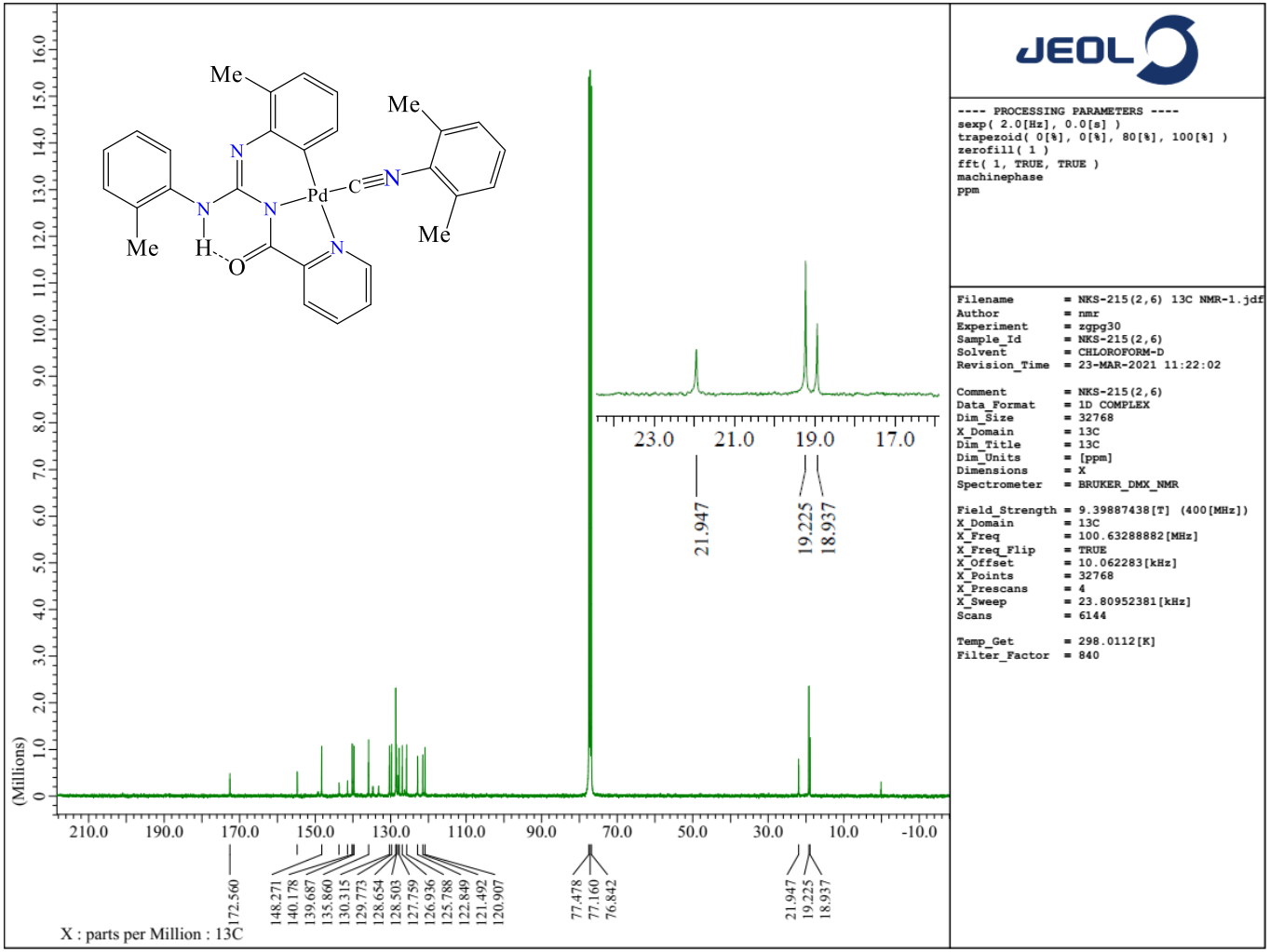
^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of **14**.



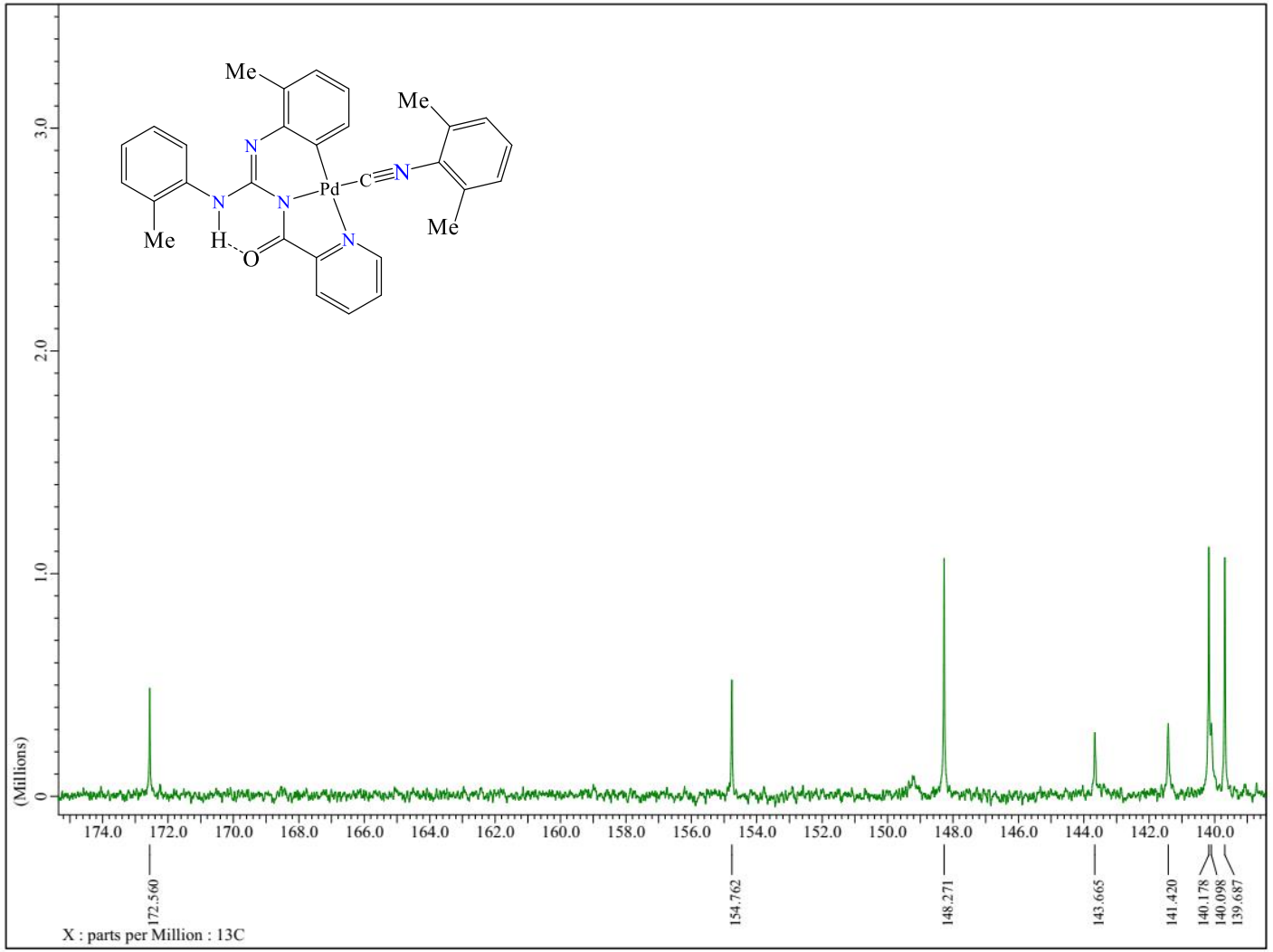
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **15**. The ★ symbol indicates protons of residual water.



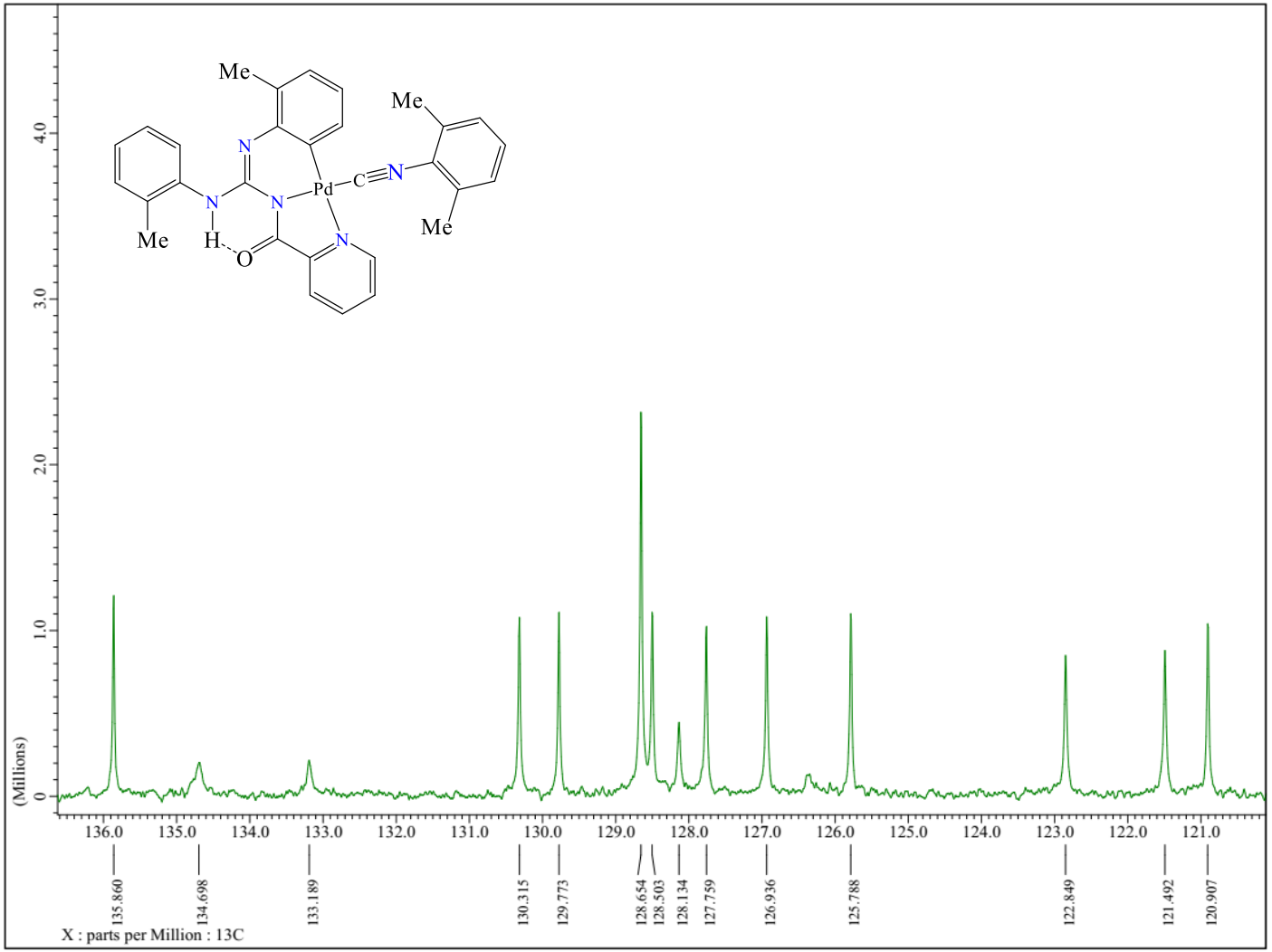
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **15** in indicated region.



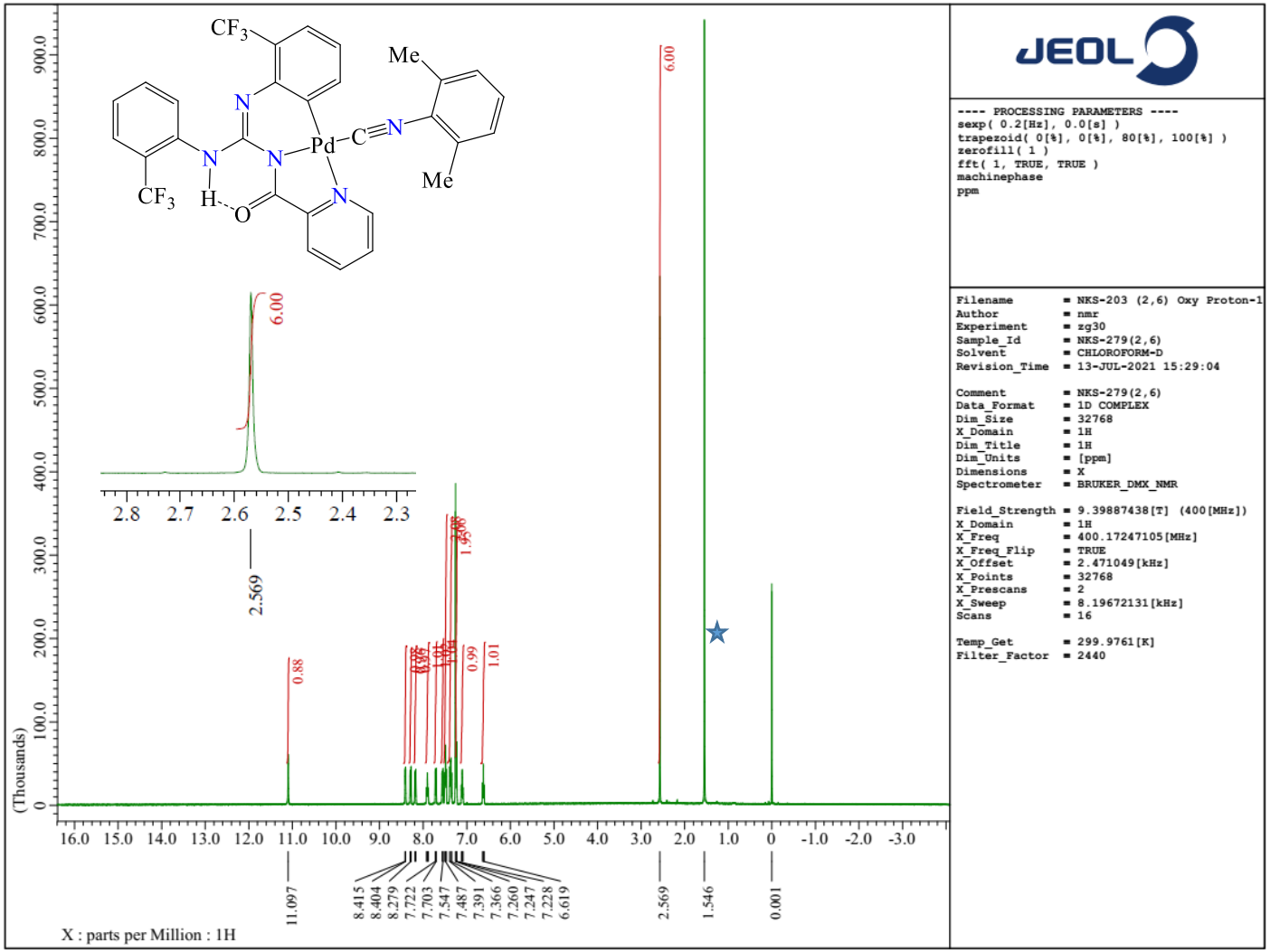
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **15**.



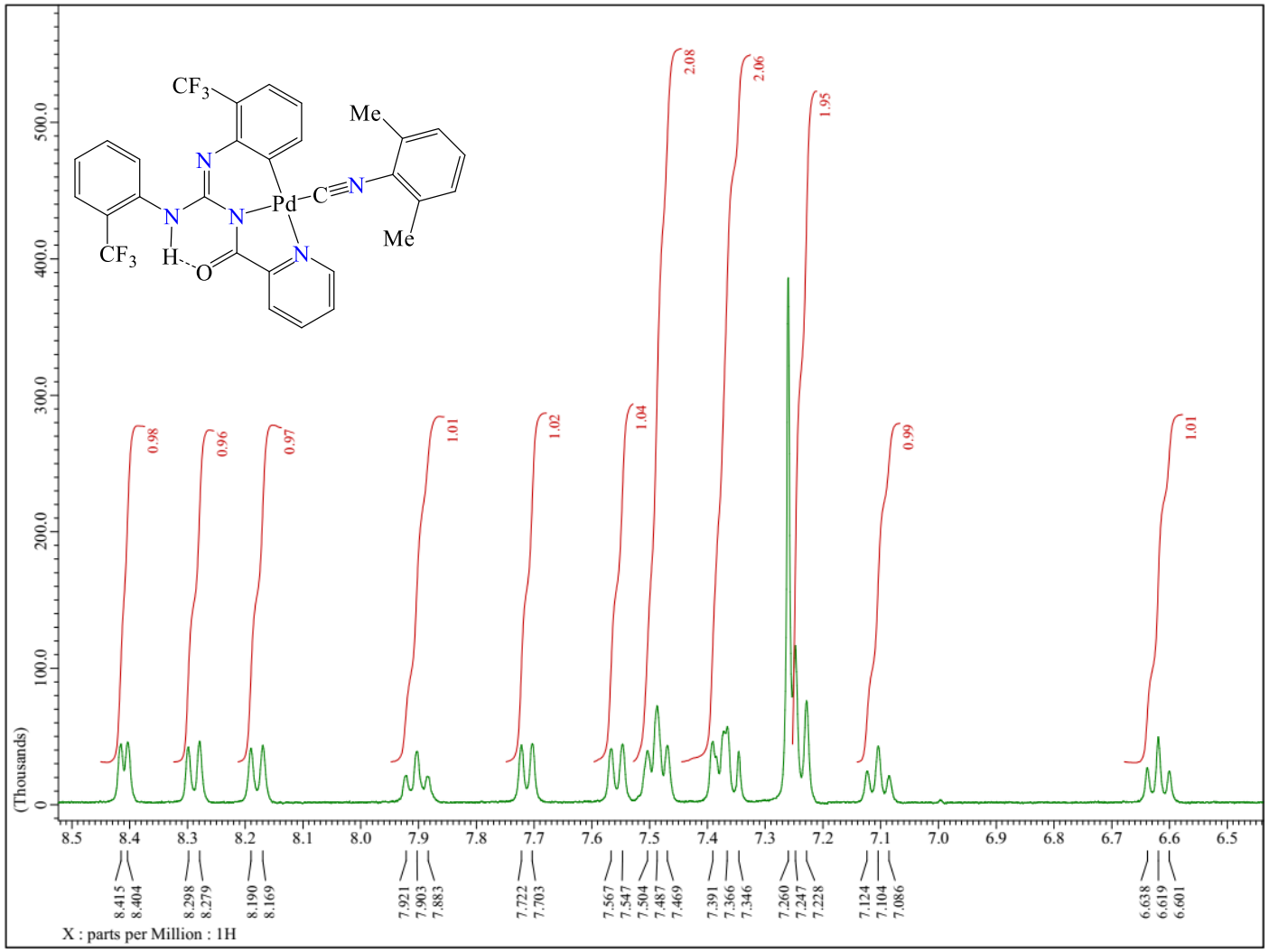
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **15** in indicated region.



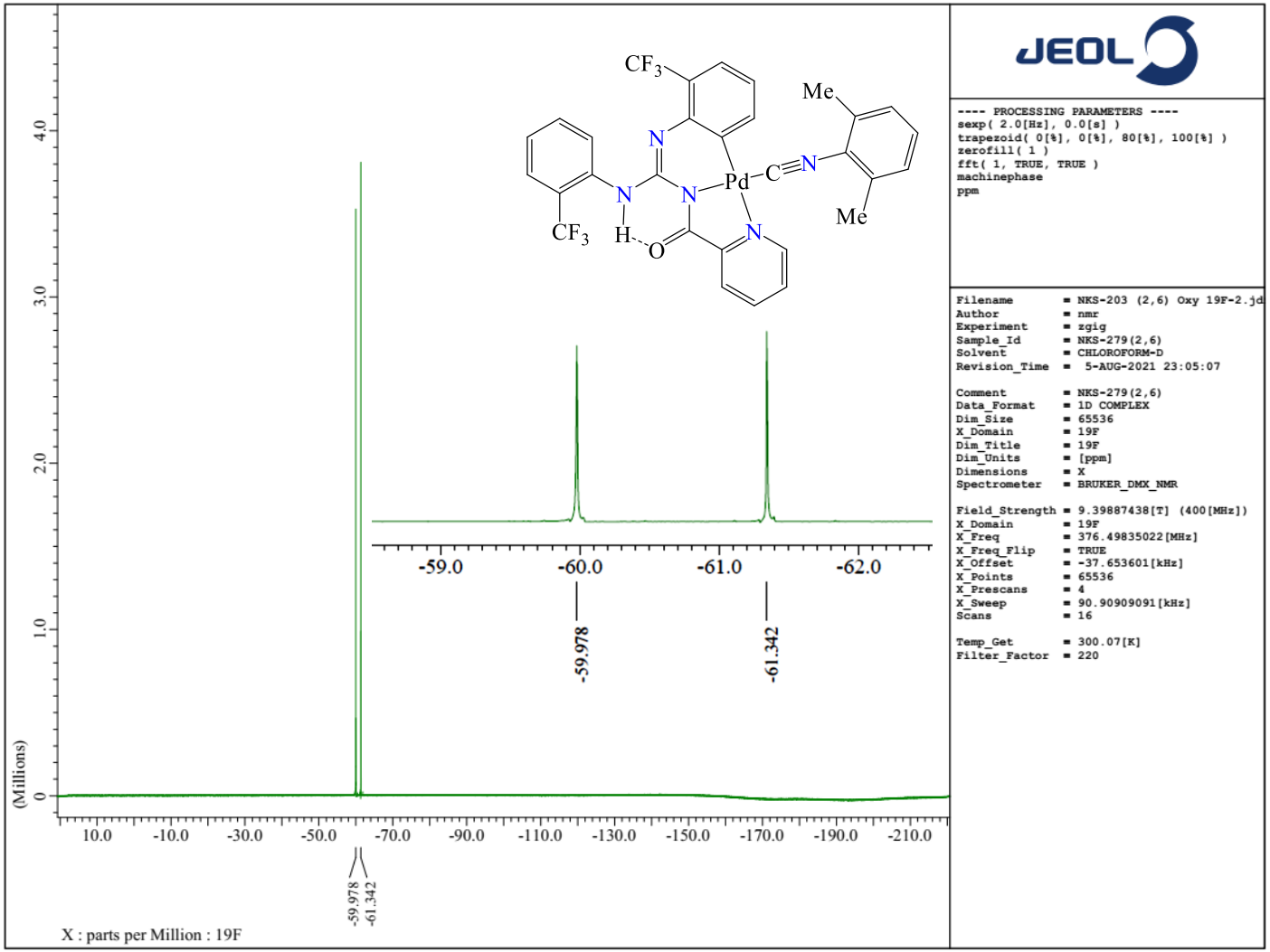
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **15** in indicated region.



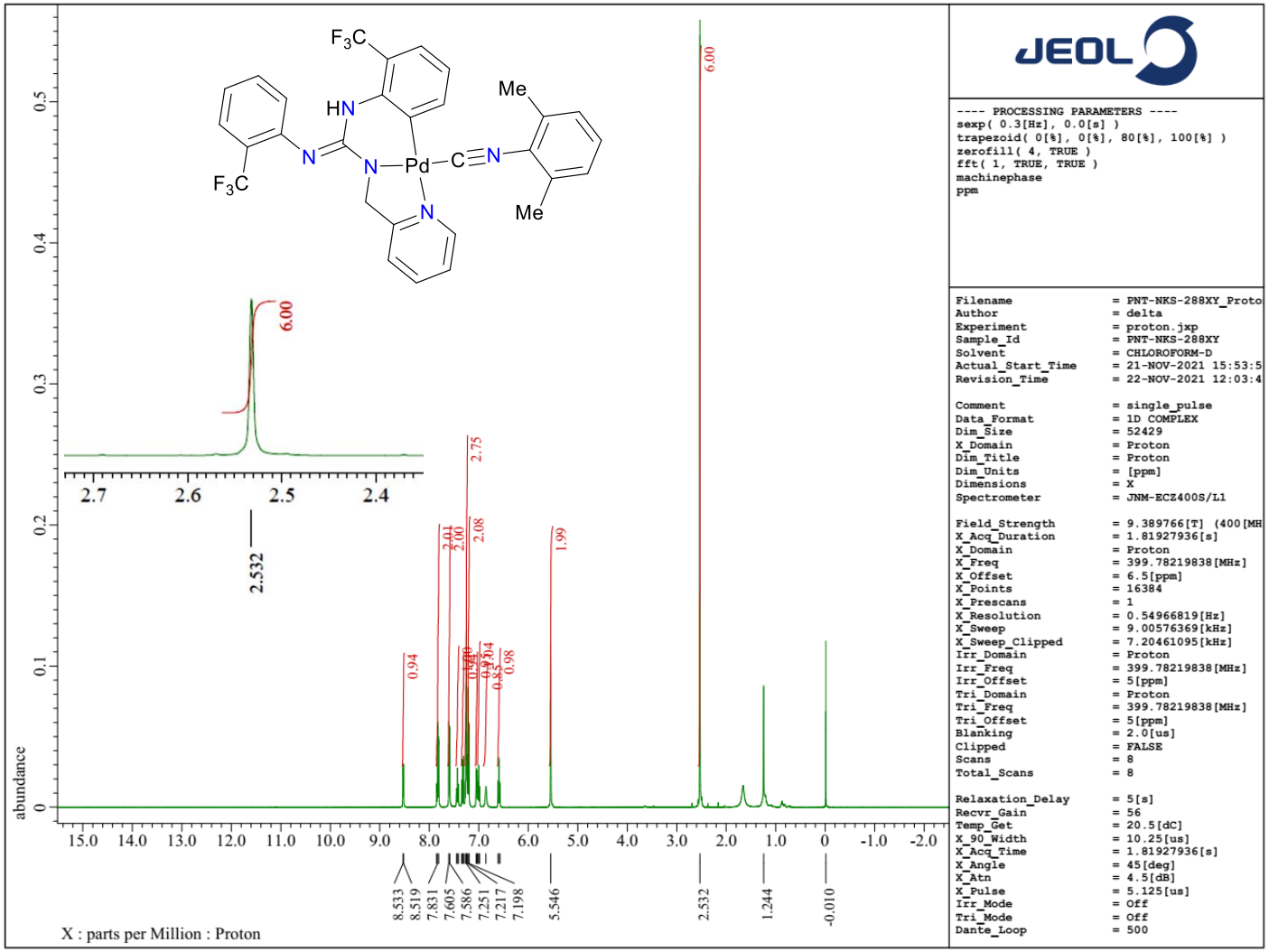
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **16**. The ★ symbol indicates protons of residual water.



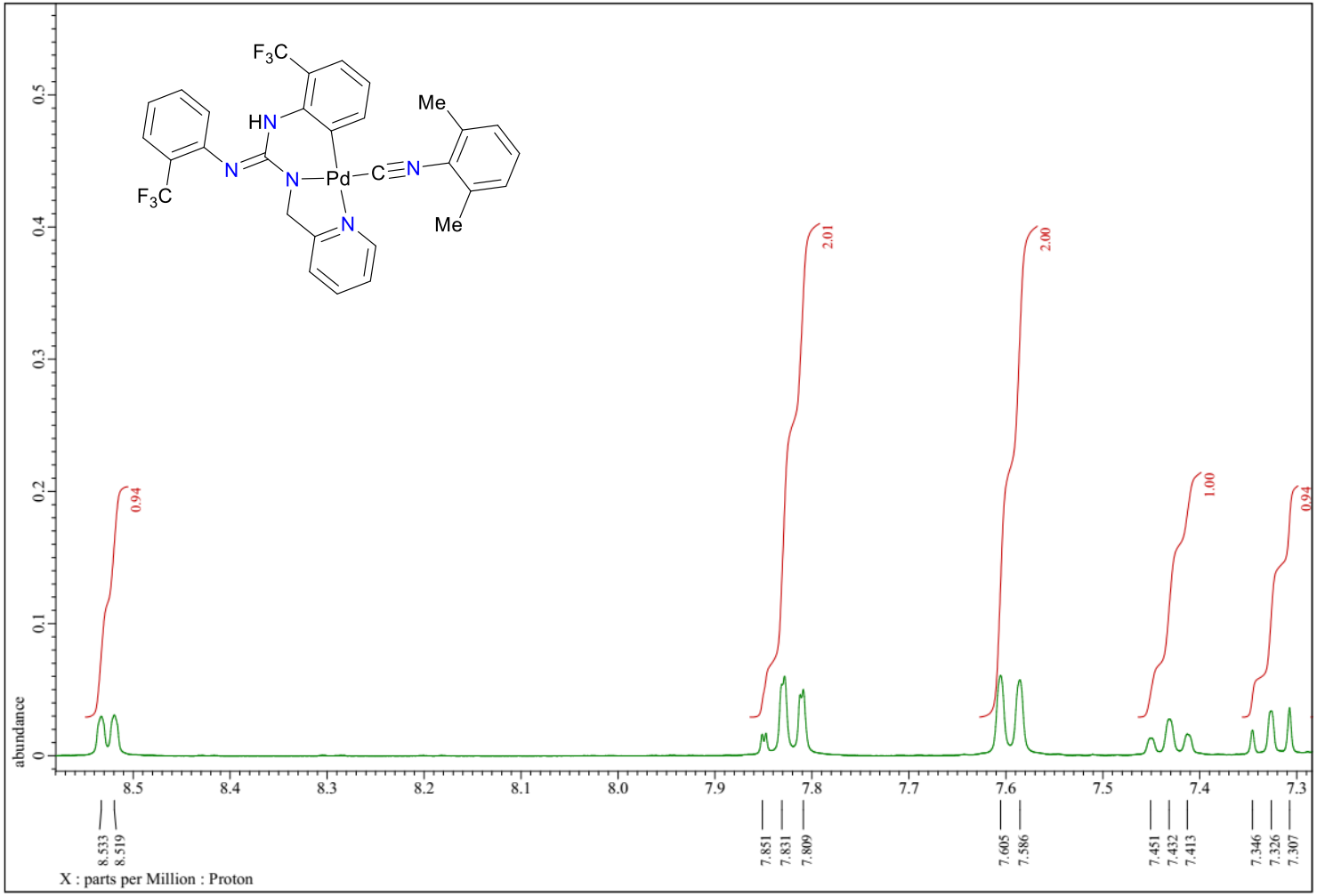
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **16** in indicated region.



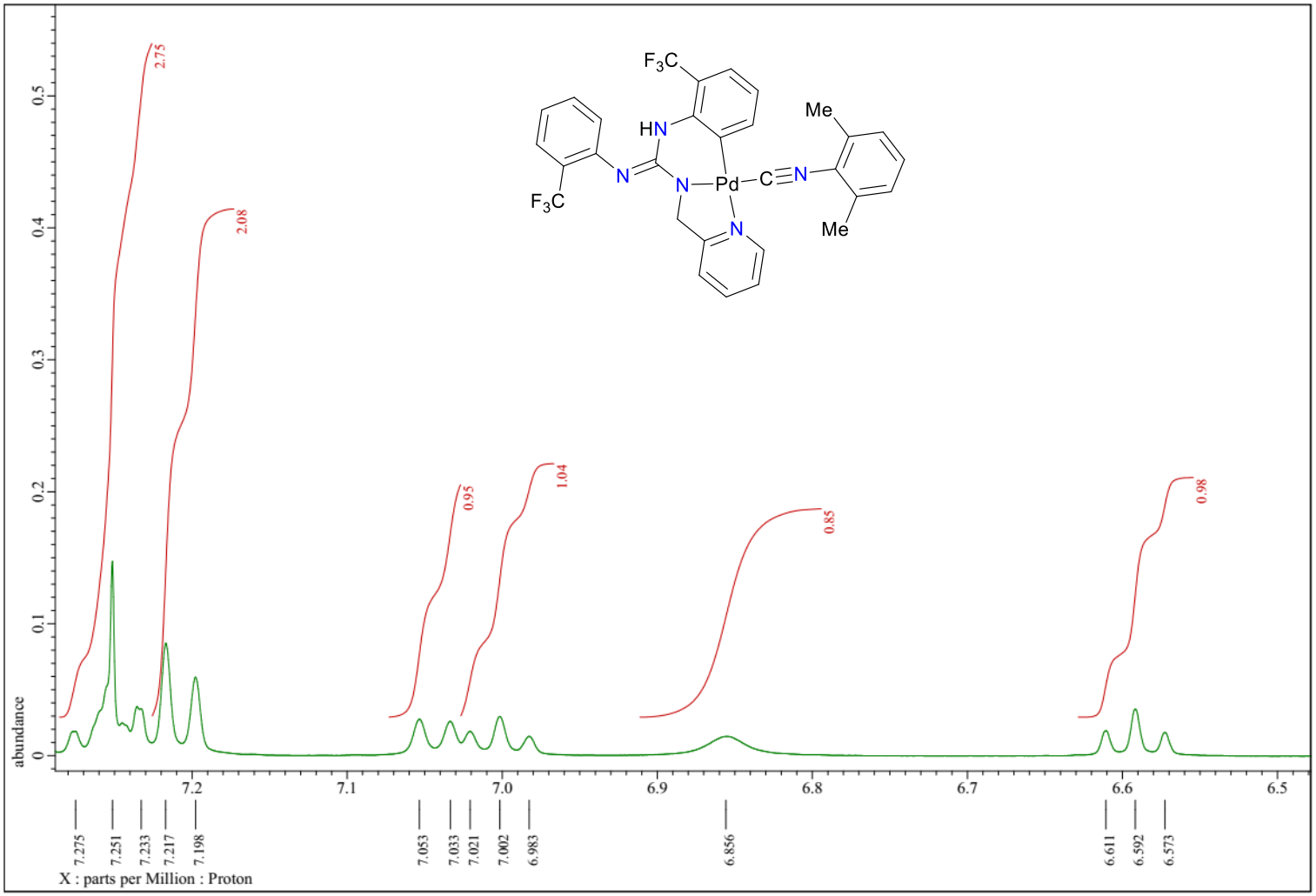
^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of **16**.



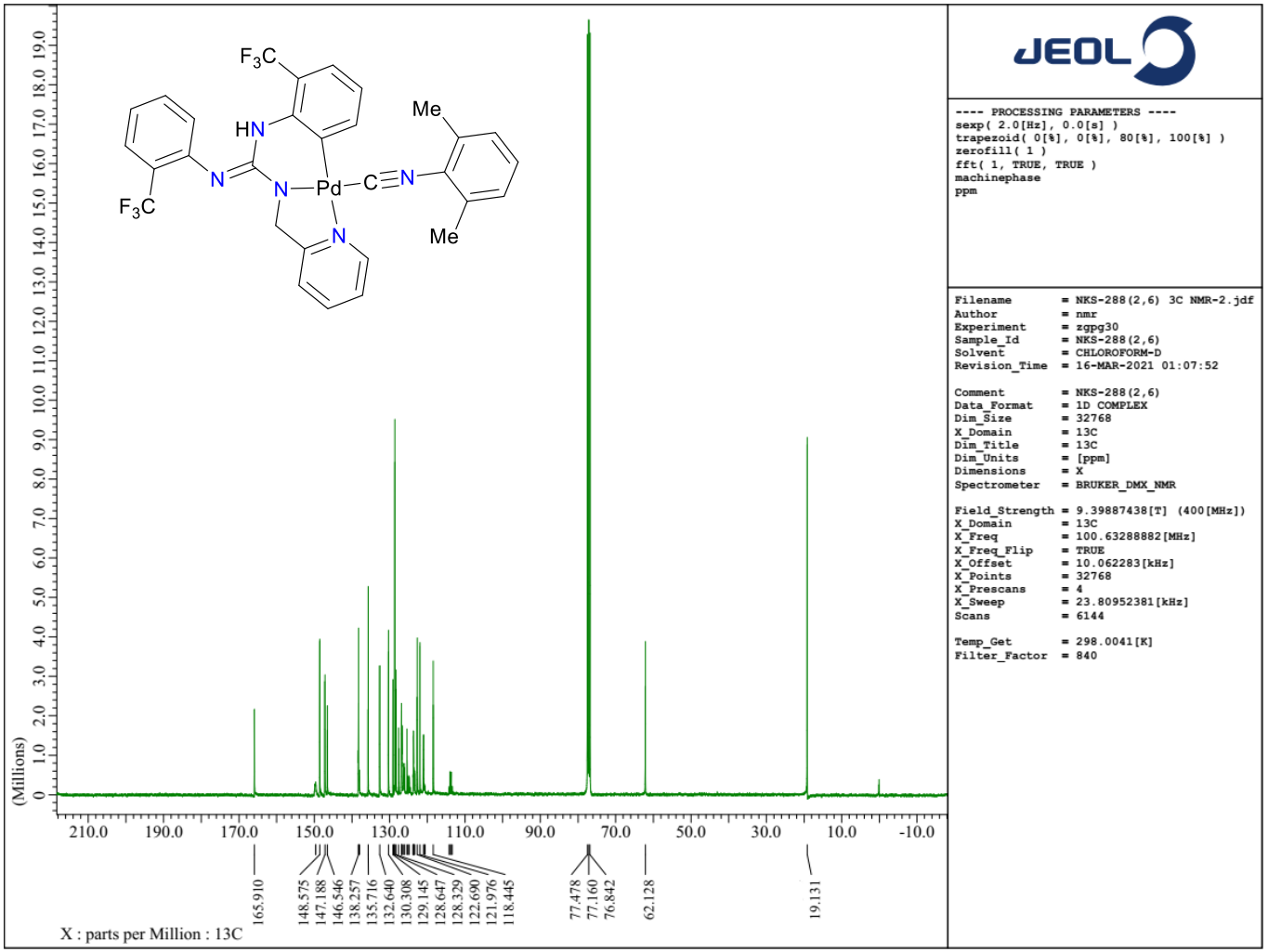
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **17**.



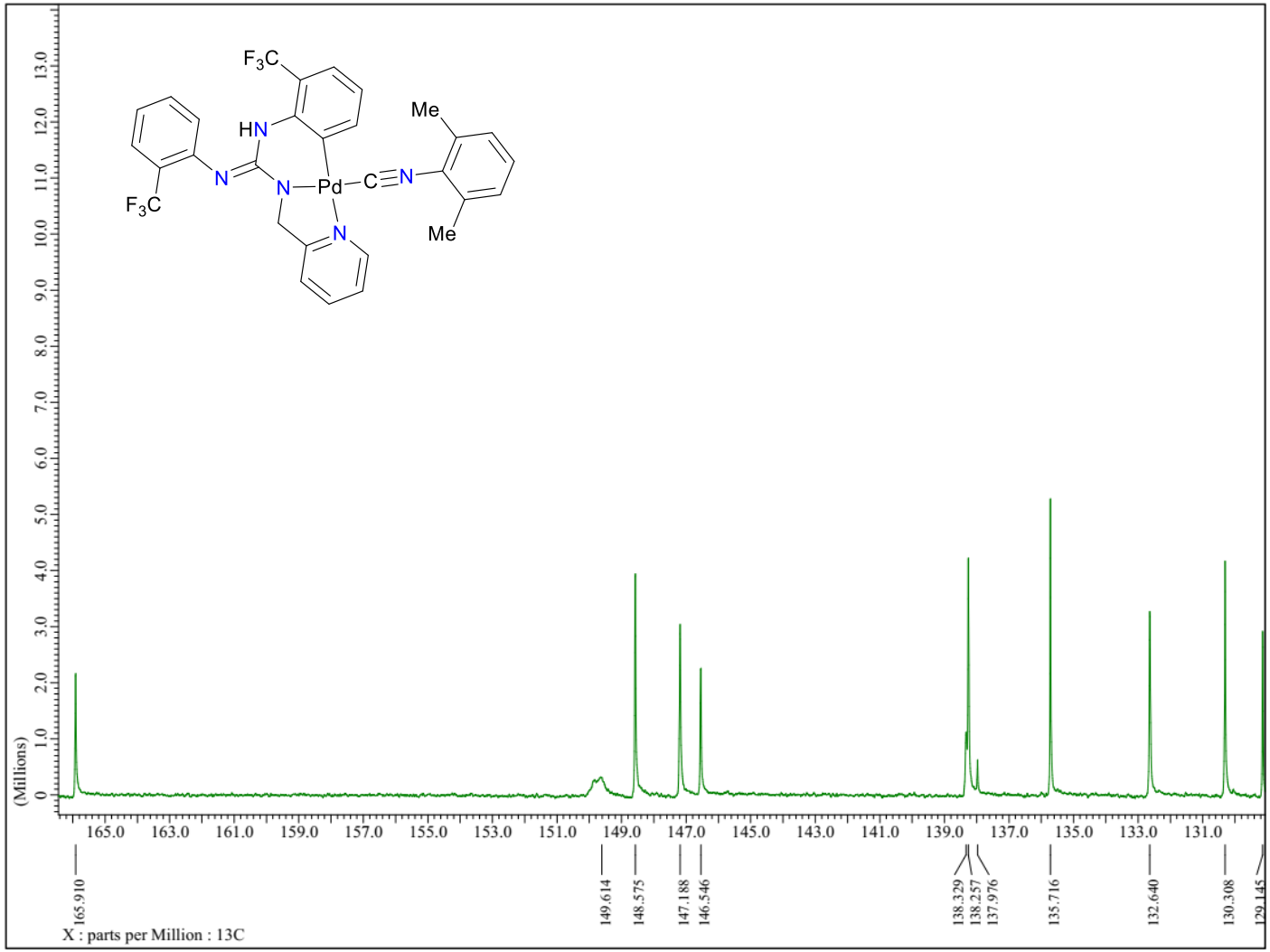
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **17** in indicated region.



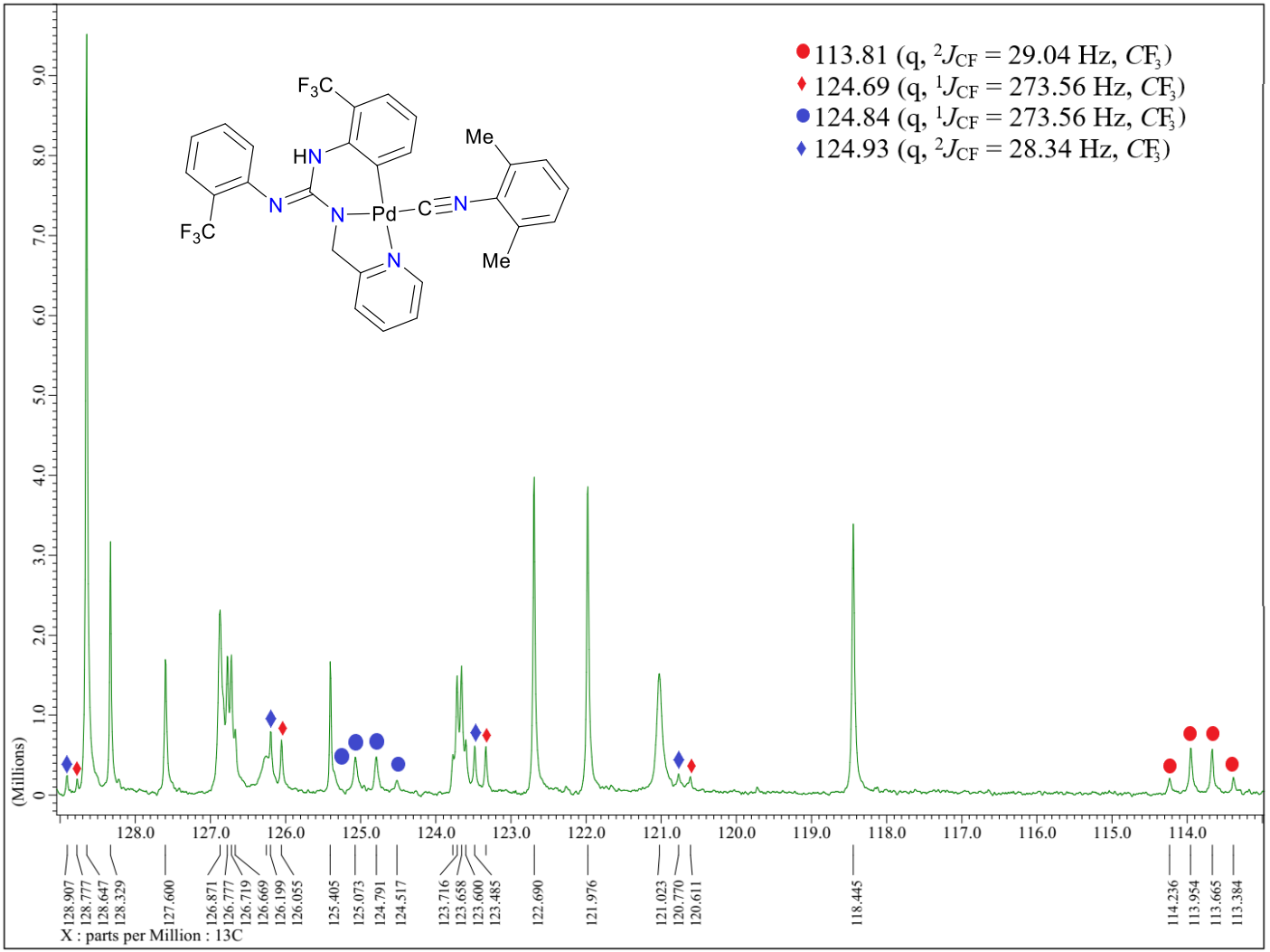
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **17** in indicated region.



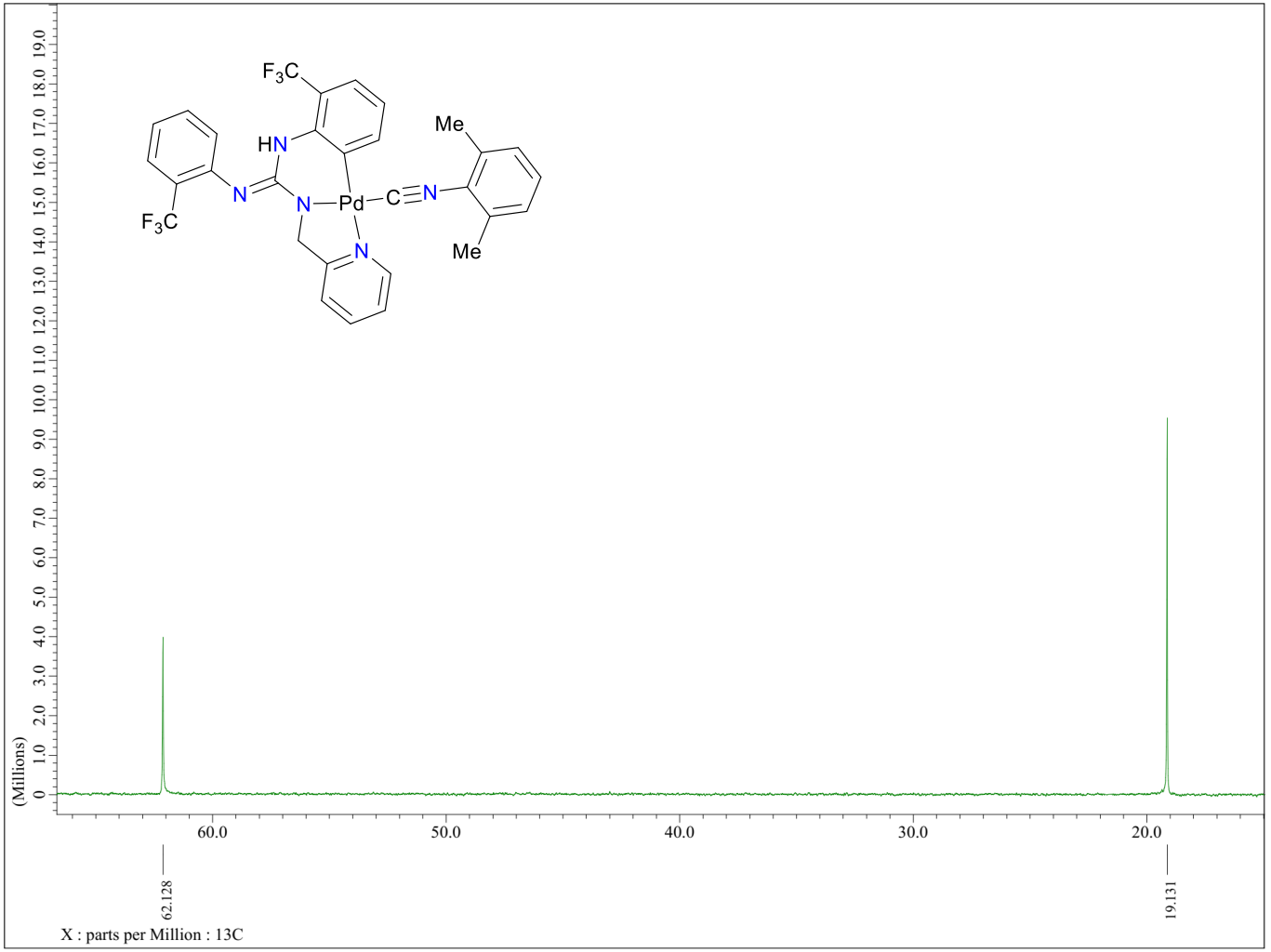
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **17**.



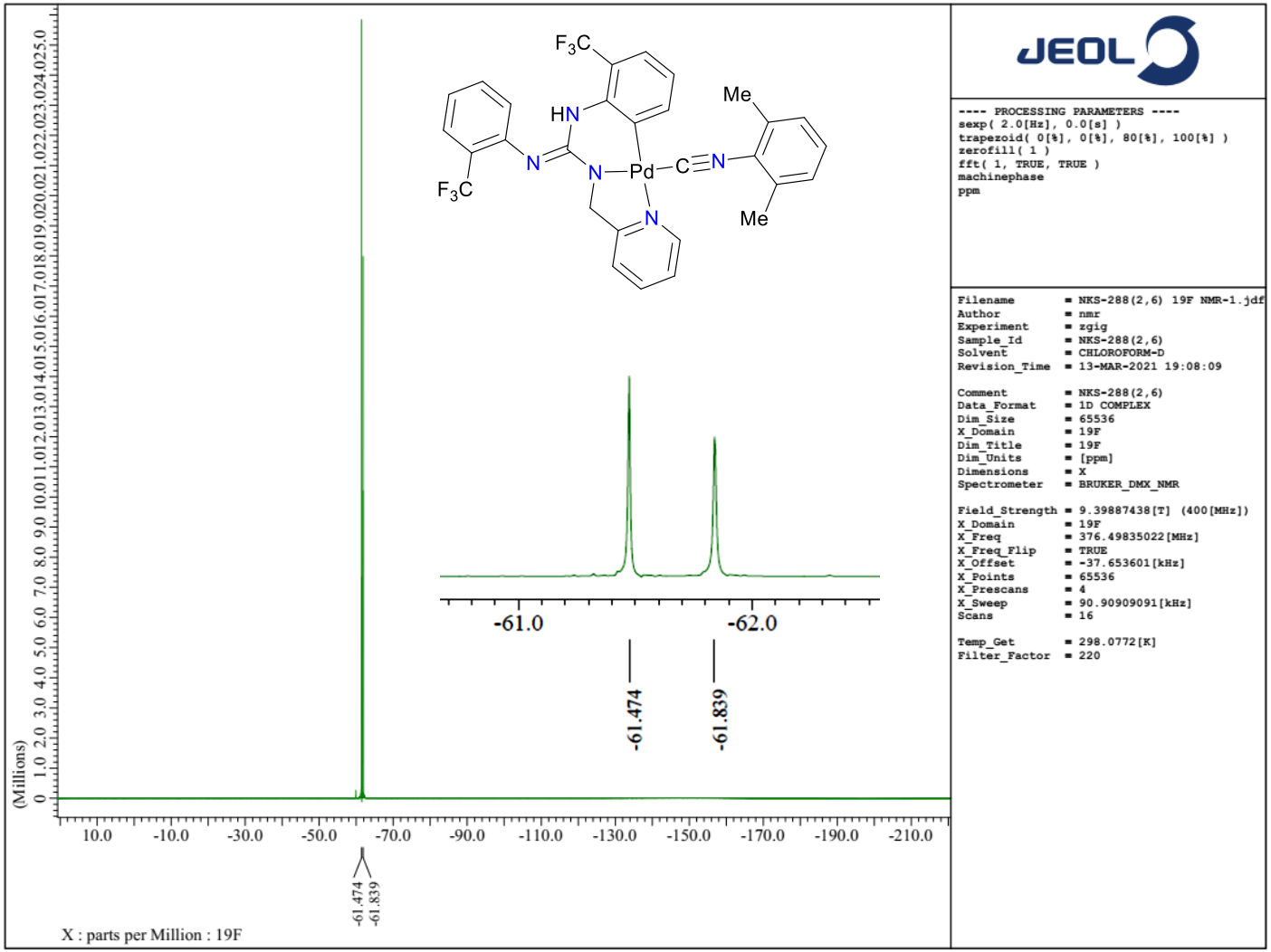
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **17** in indicated region.



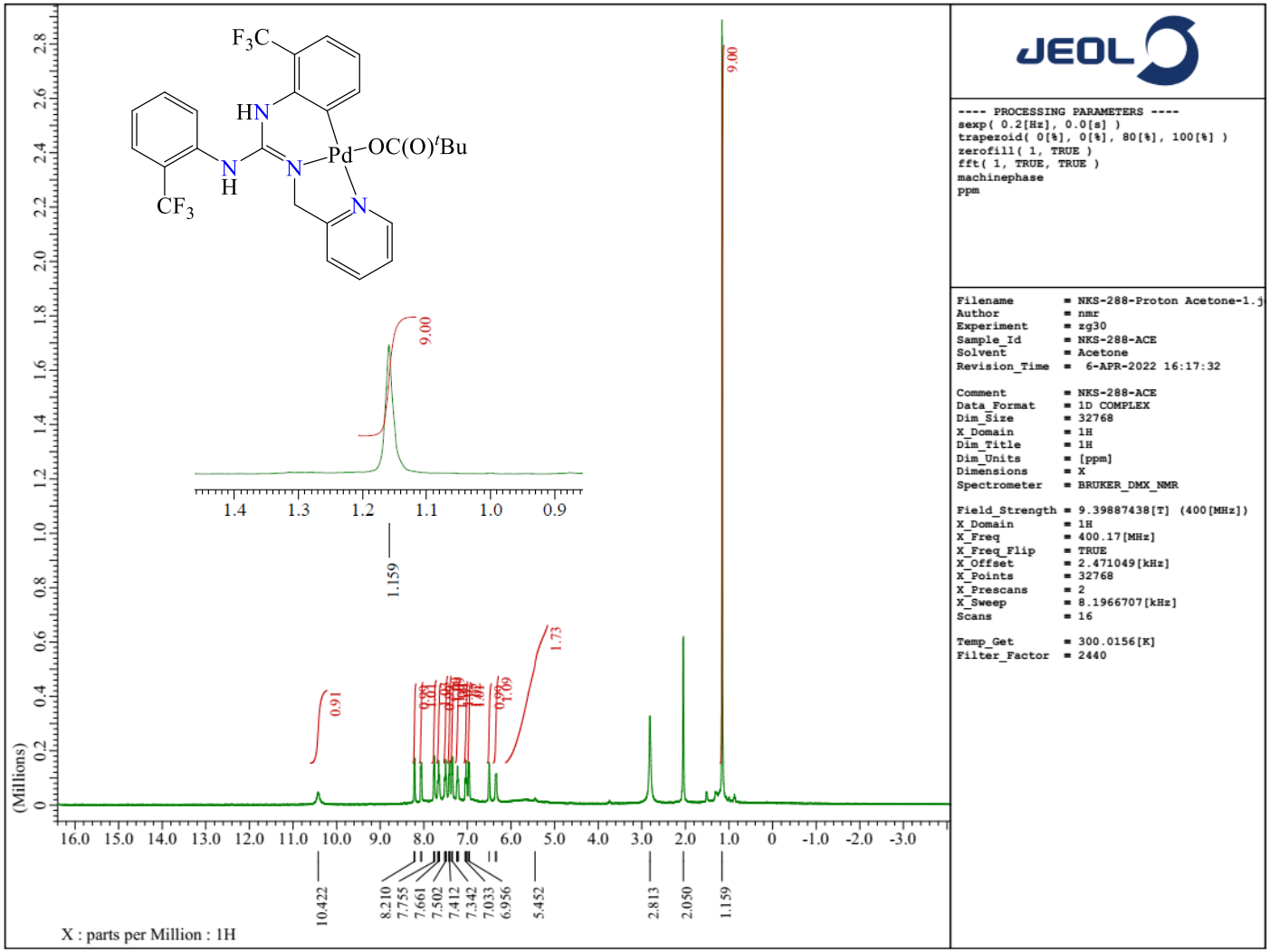
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **17** in indicated region.



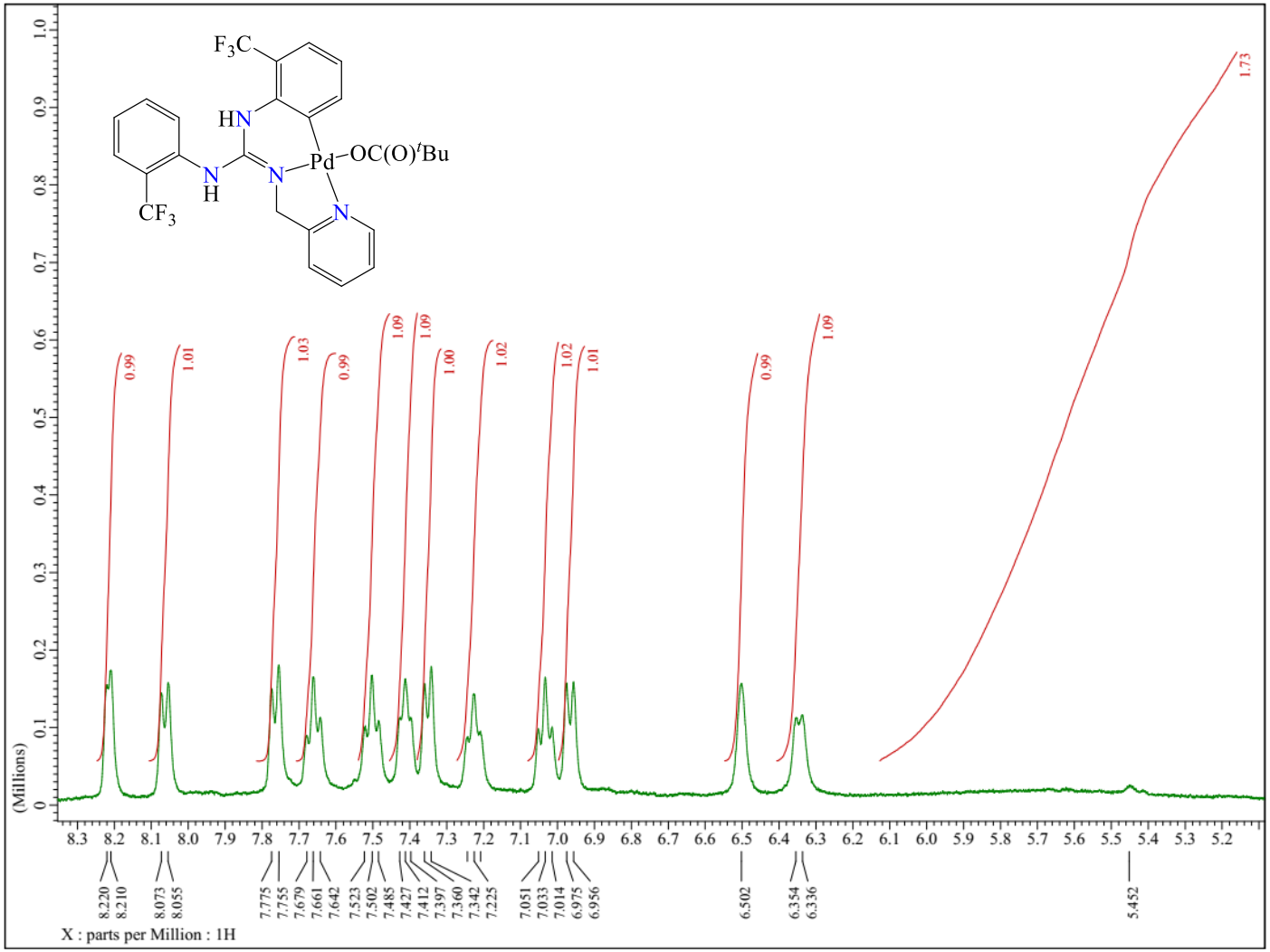
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz) spectrum of **17** in indicated region.



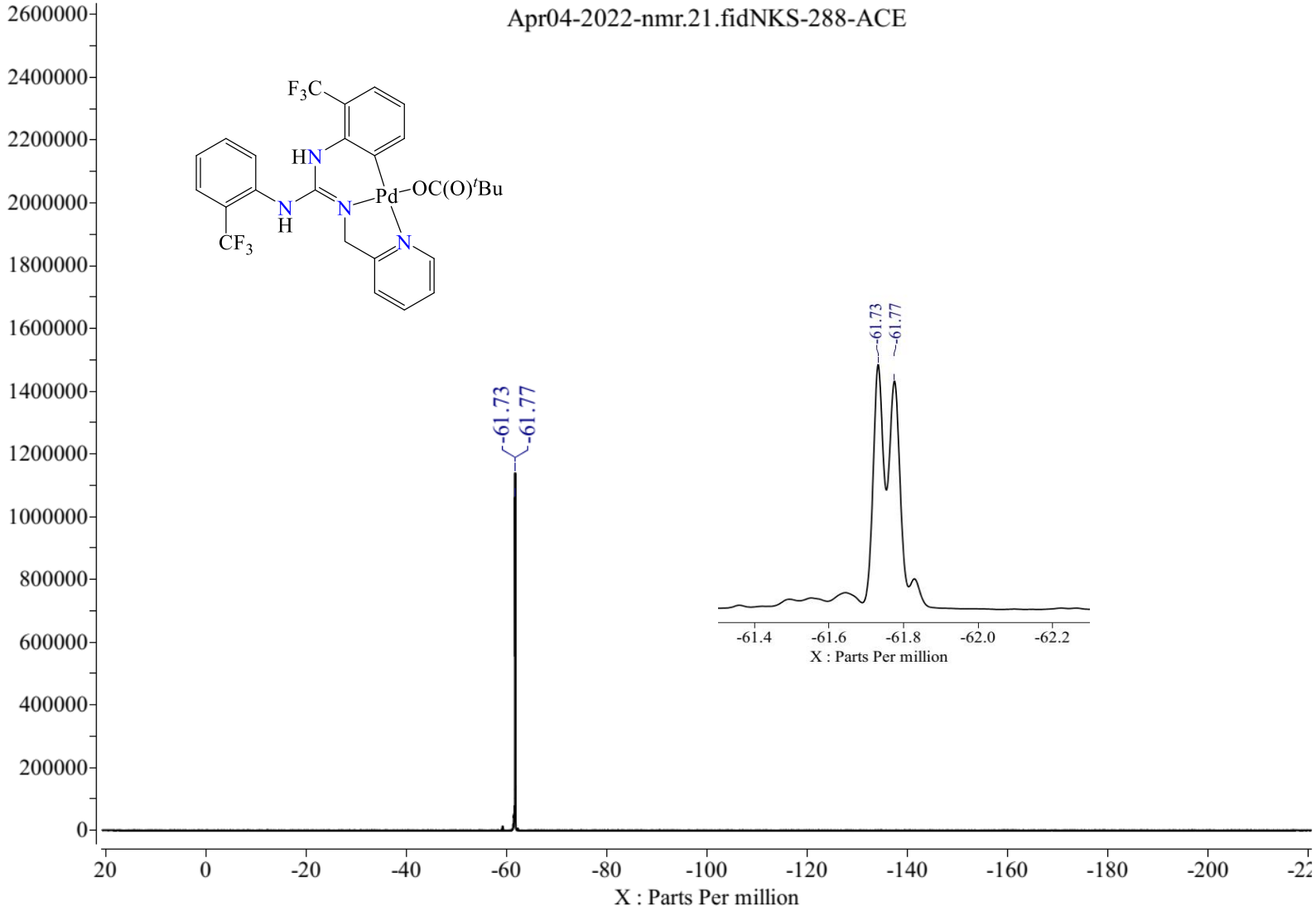
^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of **17**.



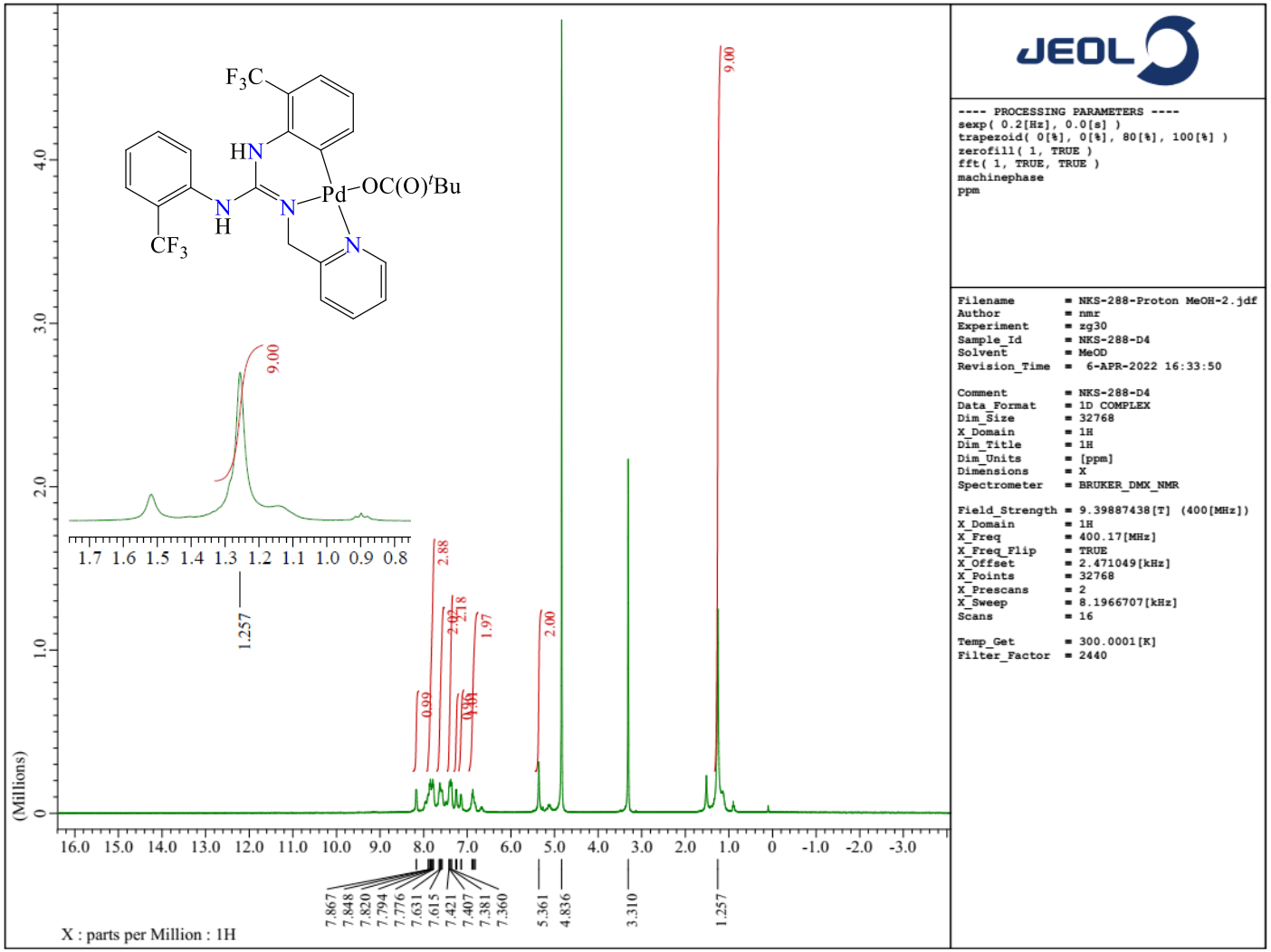
^{1}H NMR ((CD$_3$)$_2$CO, 400 MHz) spectrum of **8**.



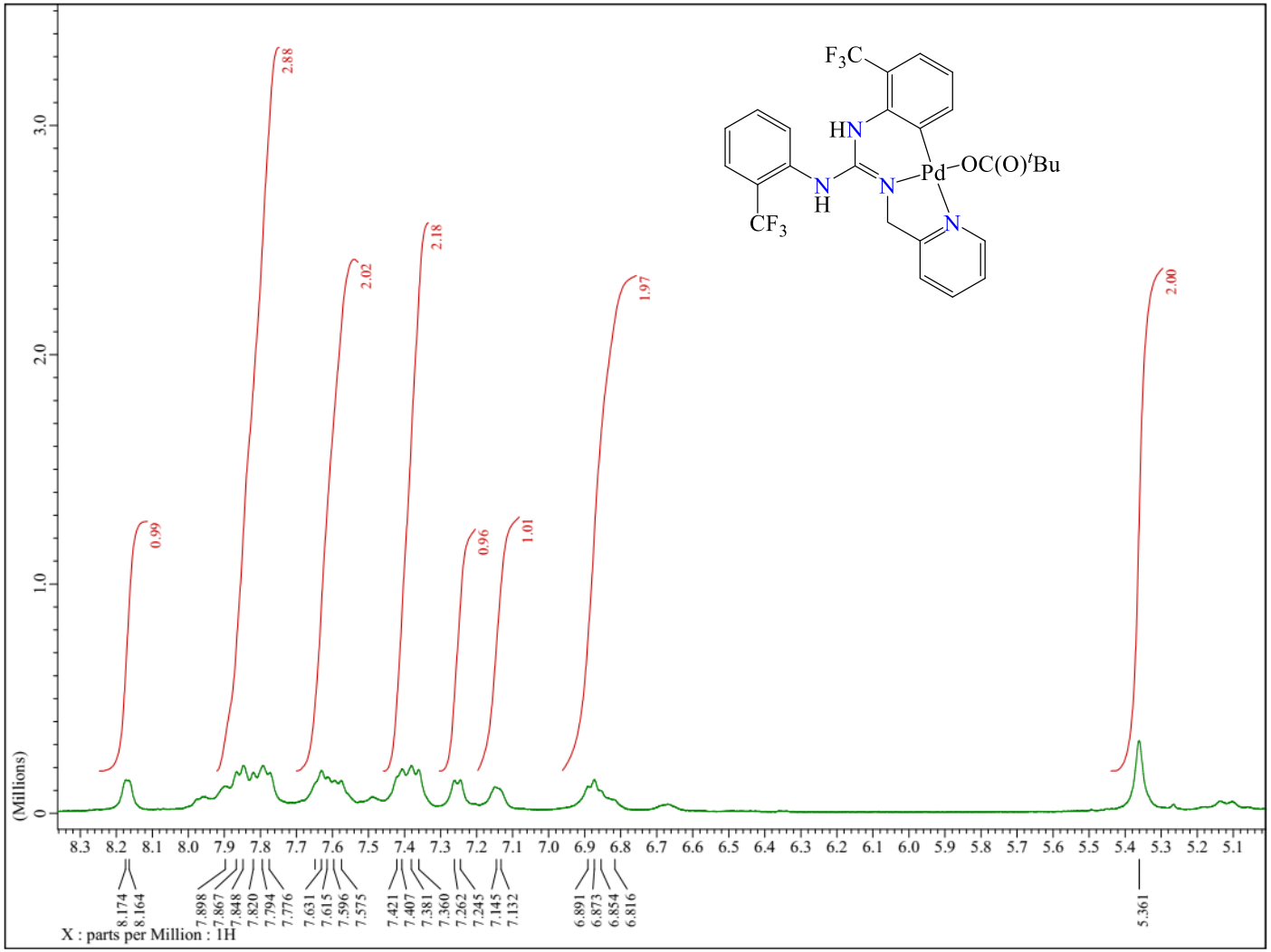
^{1}H NMR ((CD$_3$)$_2$CO, 400 MHz) spectrum of **8** in indicated region.



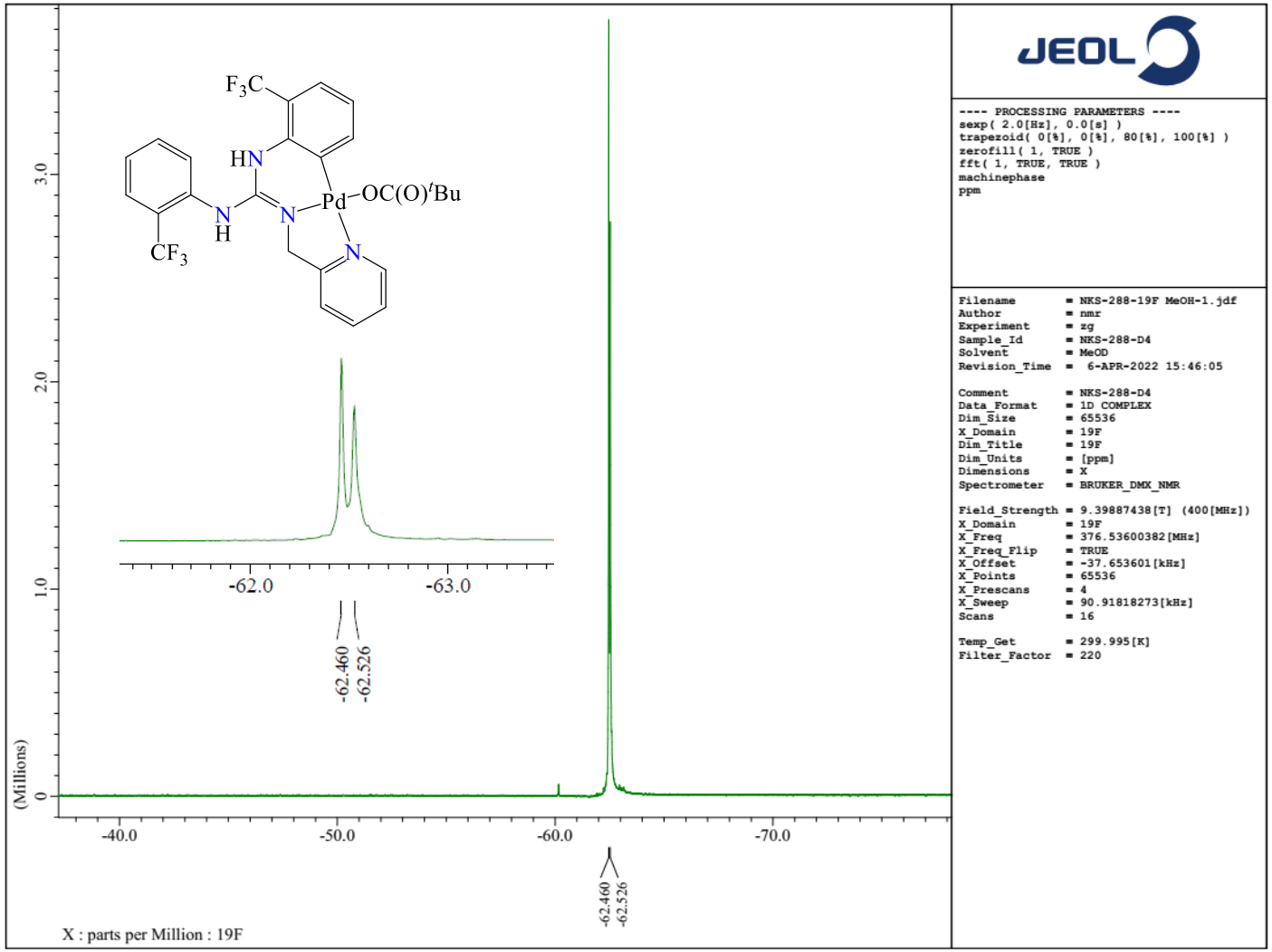
^{19}F NMR ((CD$_3$)$_2$CO, 376.5 MHz) spectrum of **8**.



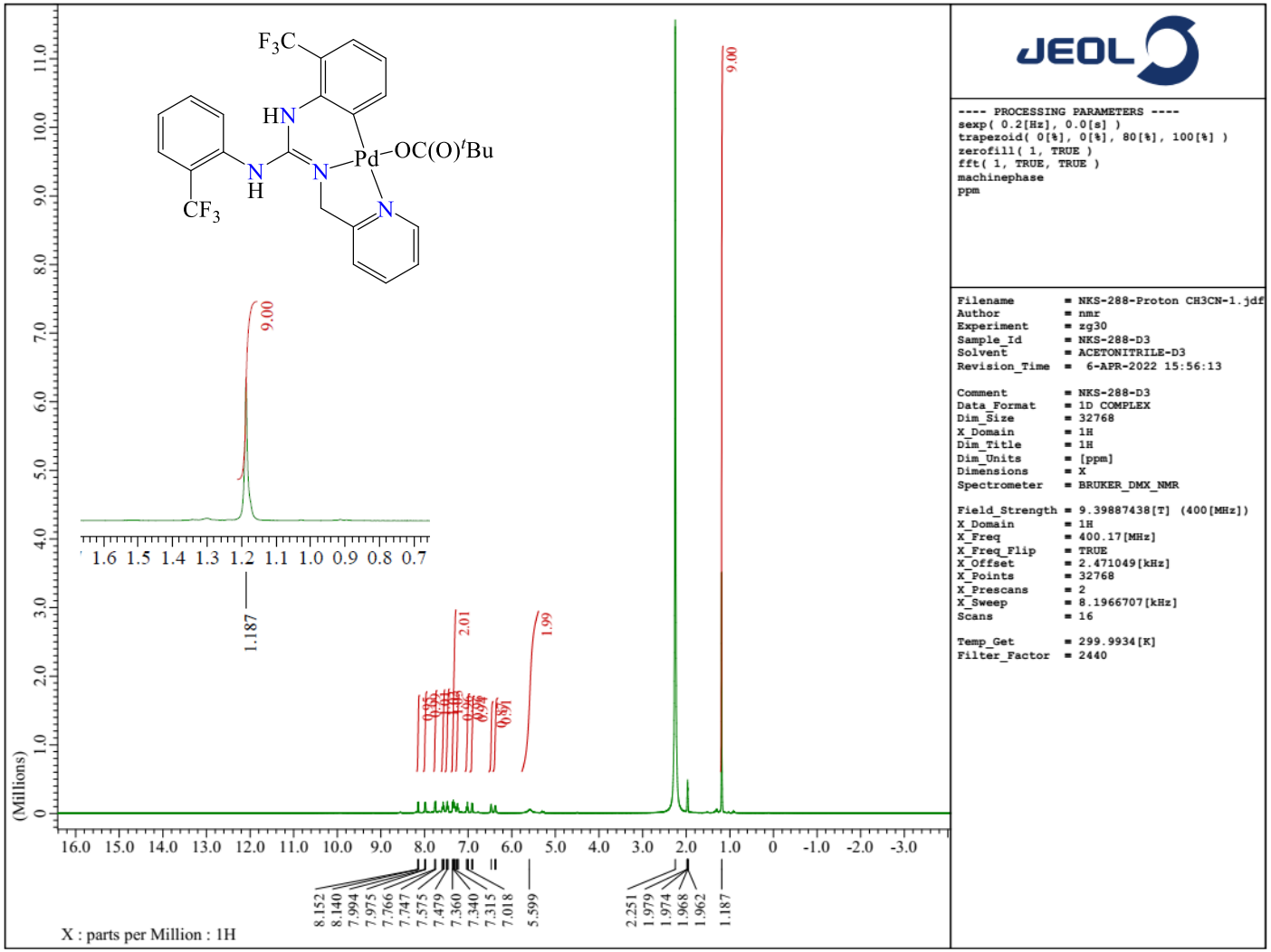
^{1}H NMR (CD_3OD, 400 MHz) spectrum of **8**.



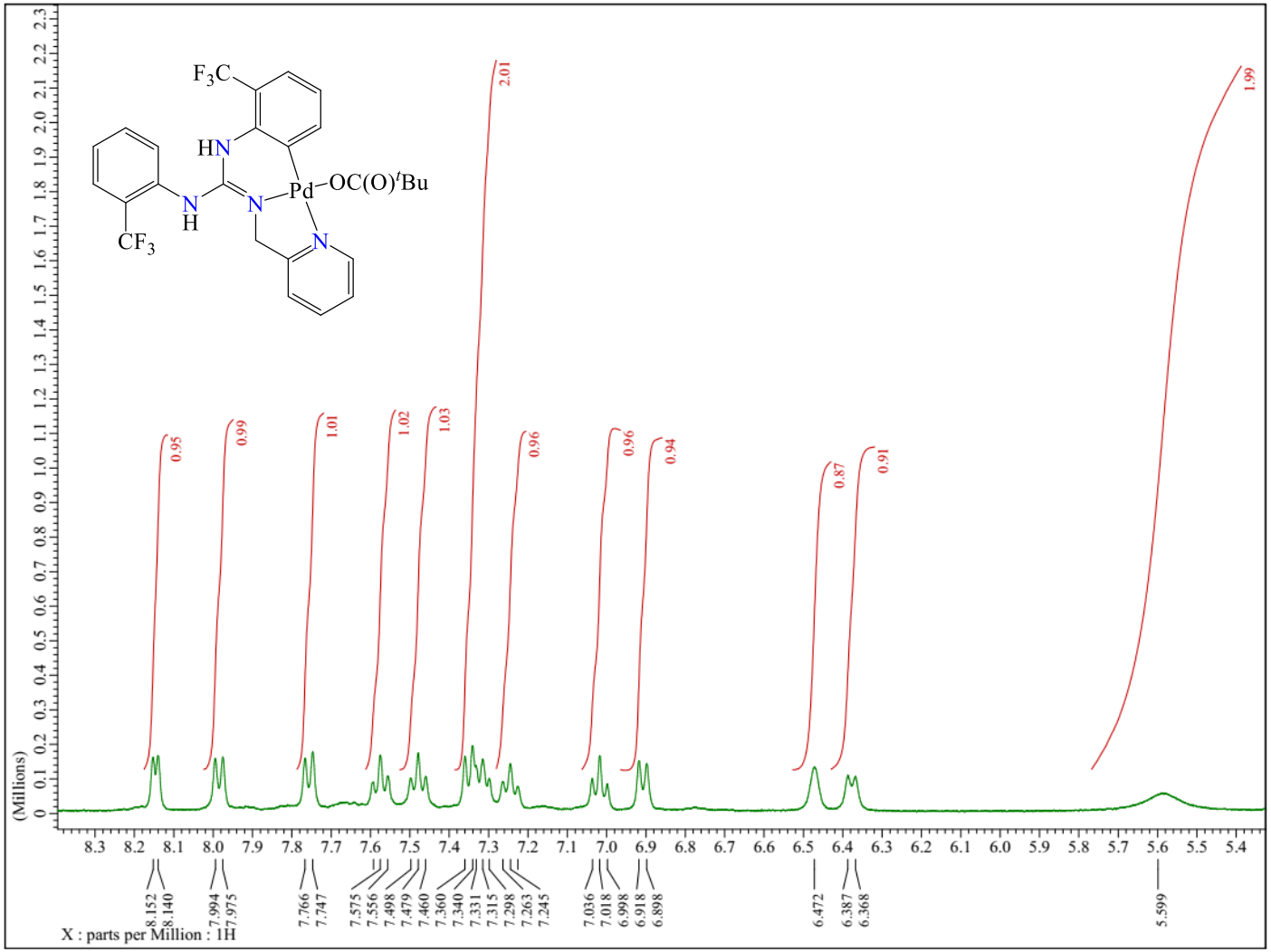
^{1}H NMR (CD_3OD, 400 MHz) spectrum of **8** in indicated region.



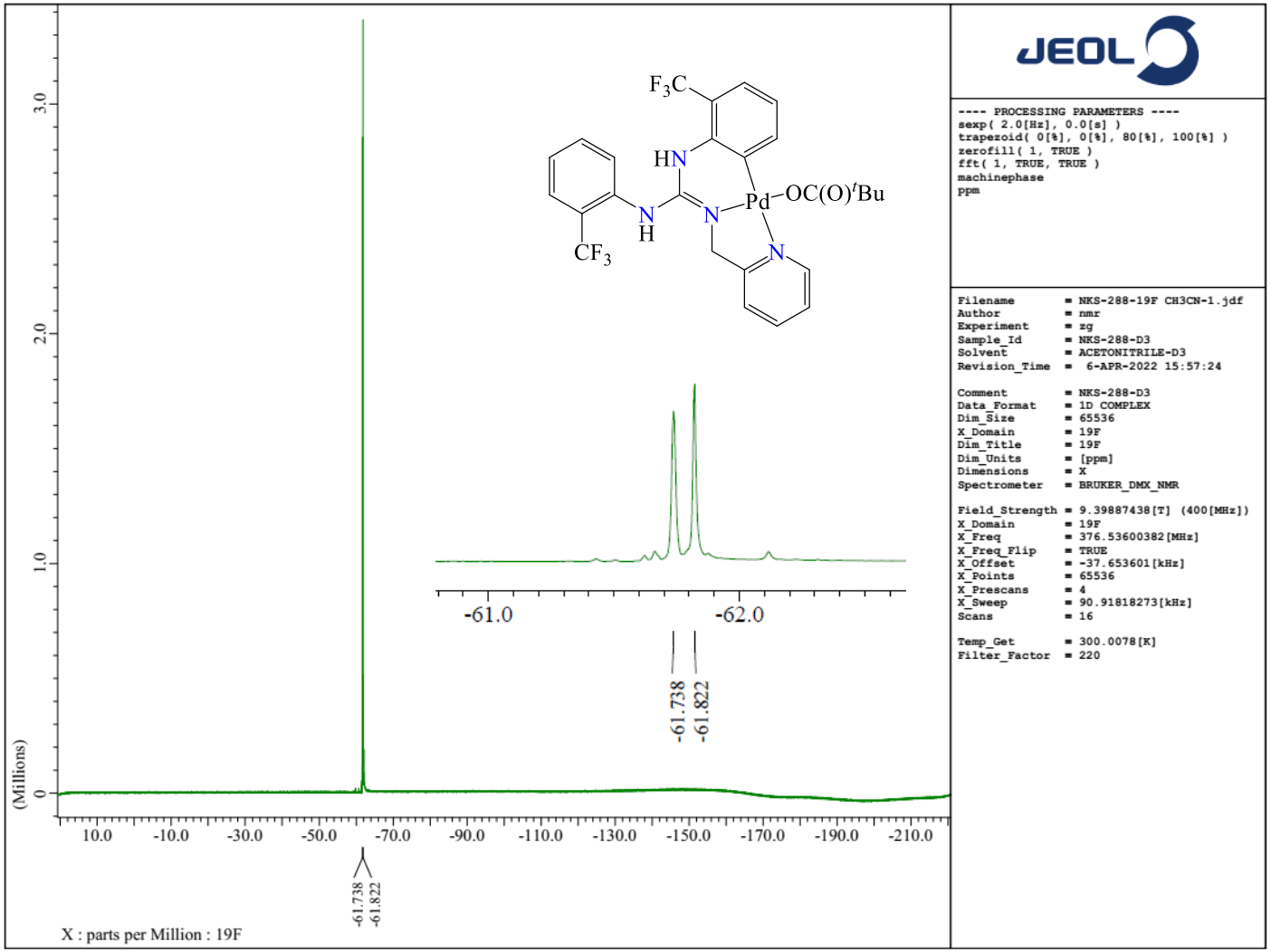
^{19}F NMR (CD_3OD, 376.5 MHz) spectrum of **8**.



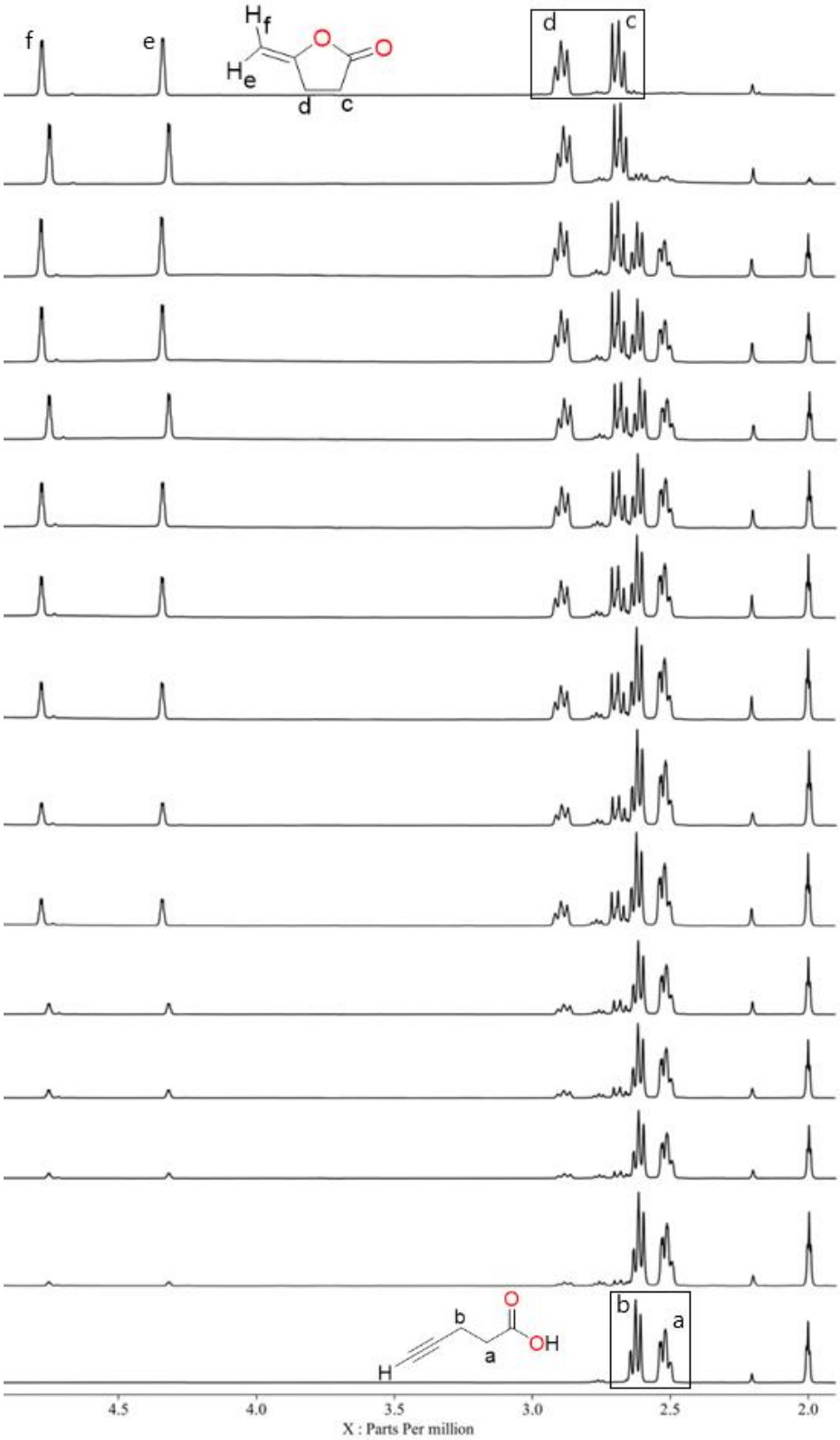
^{1}H NMR (CD_3CN, 400 MHz) spectrum of **8**.



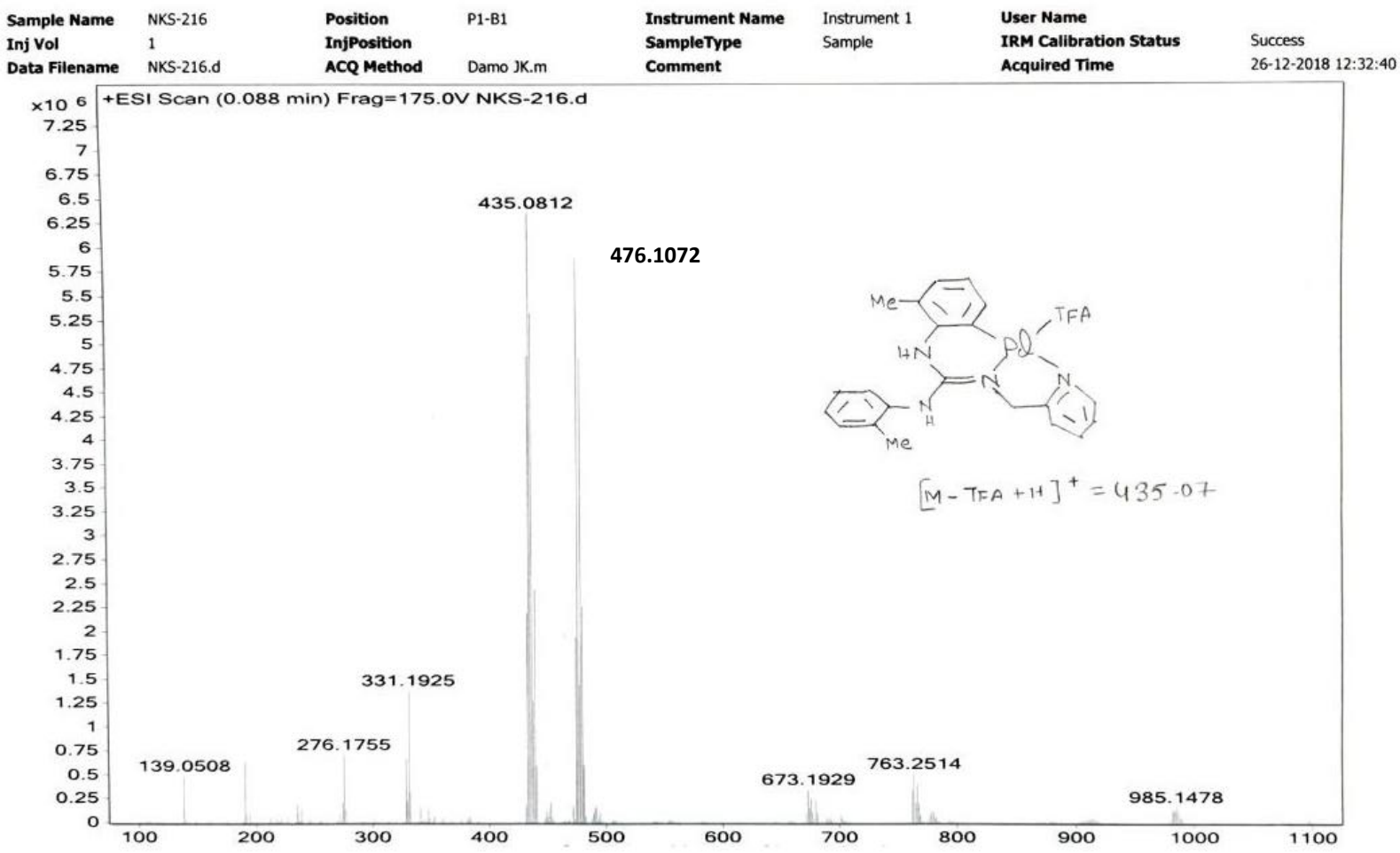
^{1}H NMR (CD_3CN, 400 MHz) spectrum of **8** in indicated region.



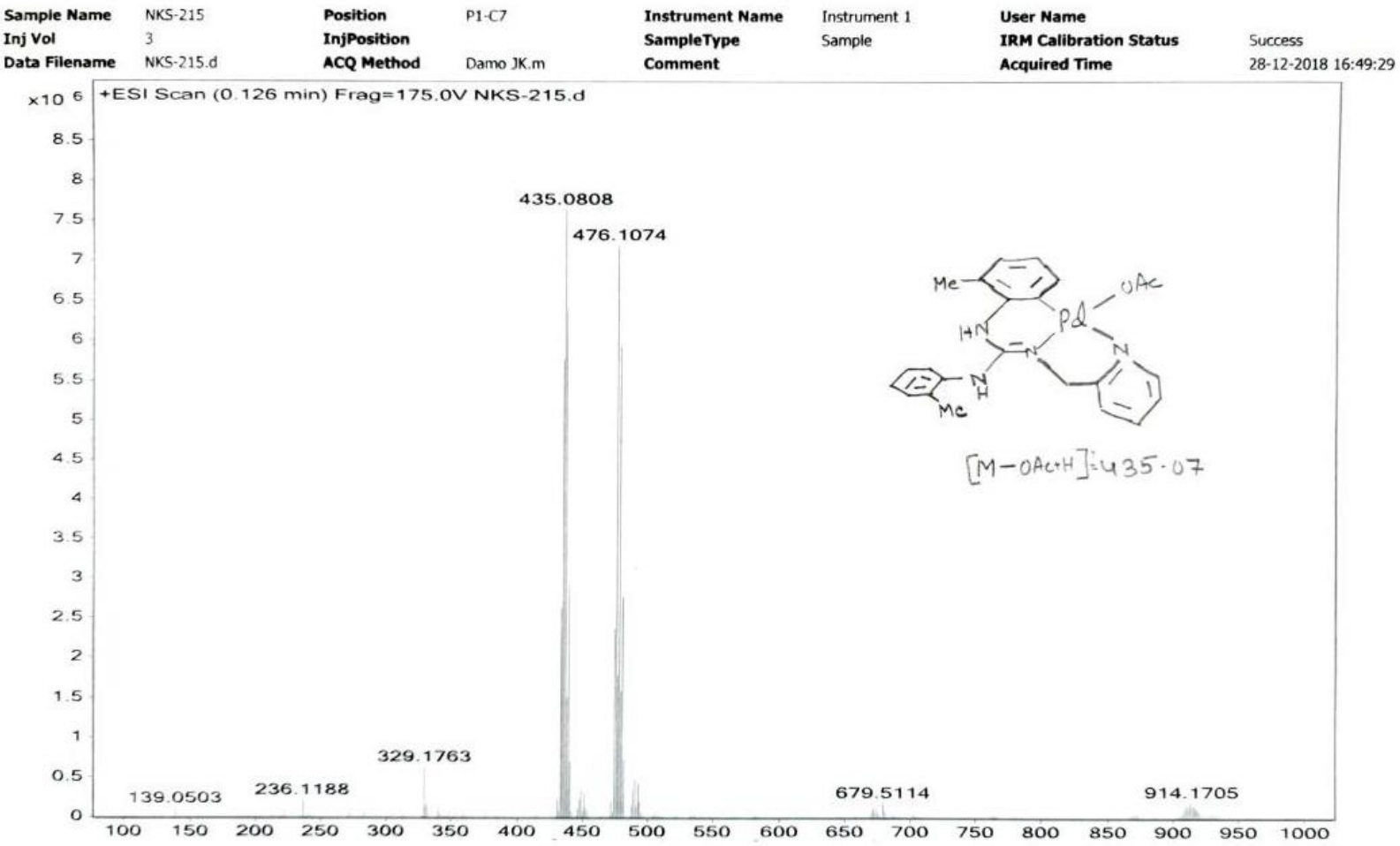
^{19}F NMR (CD_3CN, 376.5 MHz) spectrum of **8**.



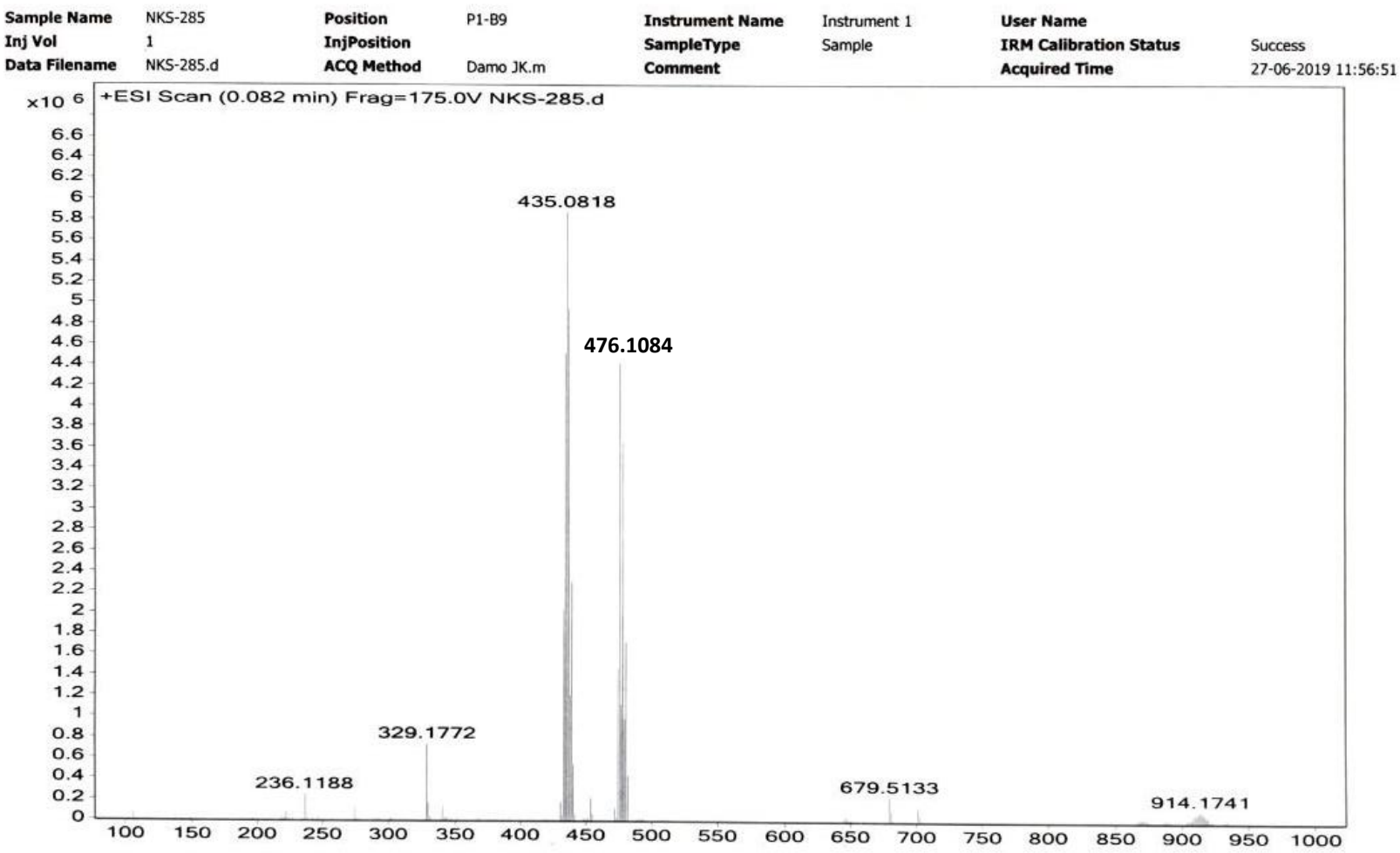
^{1}H NMR ($CDCl_3$, 400 MHz) optimization of time for cycloisomerization reaction of 4-pentynoic acid catalyzed by **8**.



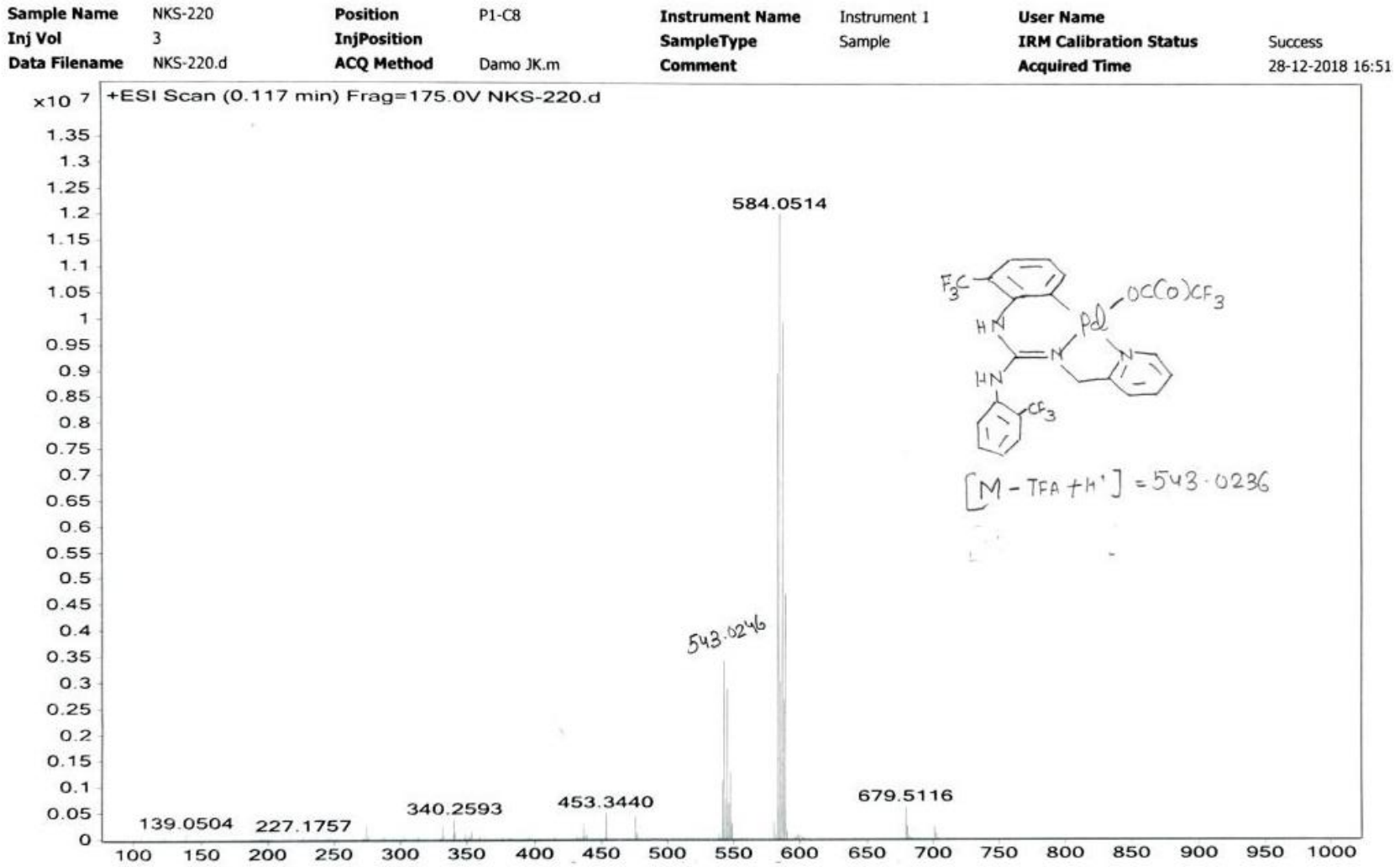
ESI-MS data of **3**.



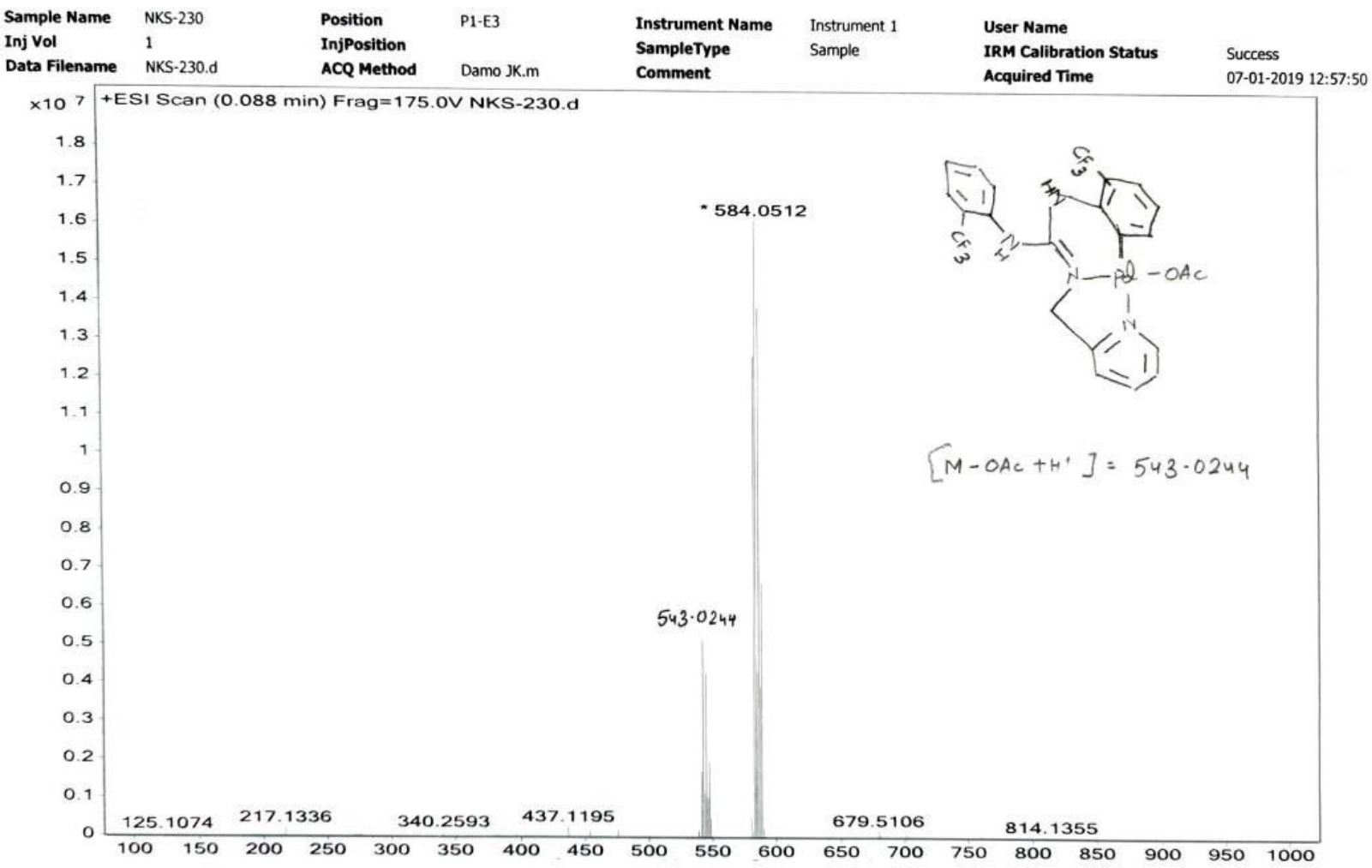
ESI-MS data of **4**.



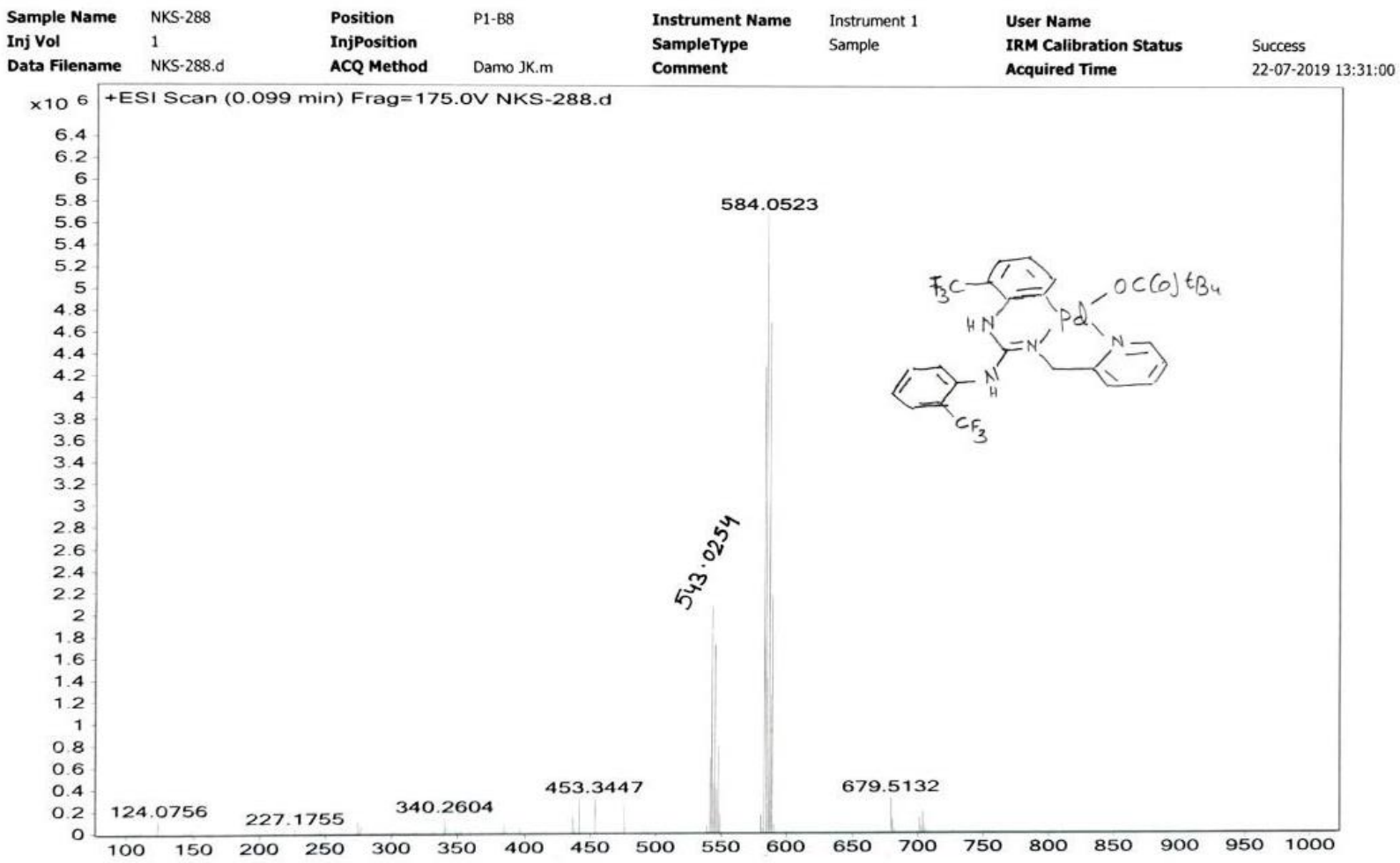
ESI-MS data of **5**.



ESI-MS data of **6**.



ESI-MS data of **7** + **9**.



ESI-MS data of **8**.

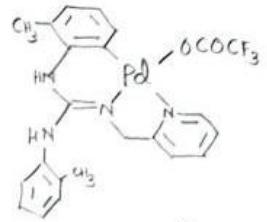
20-05-2019
varioELcube
serial number: 19171021

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	N Factor	C Factor	H Factor	S Factor	N Blank	C Bla	H Blank	S Blank	Moisture [%]	Prot. Factor	Prot. [%]	Memo	Date Time
13	5.0960	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	31 586	55 838	19 915	601 469	2.5738	8.9423	1.0760	1.0826	1.1455	1.0560	0	0	0	0	0.00	0.0000	0.000		20/05/2019 18:04
14	5.8560	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	36 241	64 087	22 858	694 479	2.5738	8.9423	1.0770	1.0820	1.1561	1.0555	0	0	0	0	0.00	0.0000	0.000		20/05/2019 18:17
22	5.2300	NKS-35	5mg90s	5.83	37.88	2.630	4.609	11 638	51 982	10 816	145 781	6.5024	14.4004	1.0754	1.0811	1.2018	1.0583	0	0	0	0	0.00	0.0000	0.000		20/05/2019 19:49
23	3.5880	NKS-36	5mg90s	12.29	66.27	4.024	0.142	16 844	62 261	11 403	2 764	5.3919	16.4679	1.0754	1.0811	1.2018	1.0583	0	0	0	0	0.00	0.0000	0.000		20/05/2019 20:00
24	7.3880	NKS-36A	5mg90s	12.17	66.31	3.979	0.143	34 278	127 158	23 625	5 736	5.4488	16.6662	1.0754	1.0811	1.2018	1.0583	0	0	0	0	0.00	0.0000	0.000		20/05/2019 20:12
25	3.9150	NKS-216	5mg90s	10.19	50.18	3.705	0.091	15 241	51 550	11 461	1 933	4.9233	13.5419	1.0754	1.0811	1.2018	1.0583	0	0	0	0	0.00	0.0000	0.000		20/05/2019 20:23
26	4.8560	NKS-216A	5mg90s	10.14	50.19	3.690	0.071	18 811	63 791	13 886	1 869	4.9476	13.6021	1.0754	1.0811	1.2018	1.0583	0	0	0	0	0.00	0.0000	0.000		20/05/2019 20:34
27	5.2990	VT-491	5mg90s	6.21	42.45	2.981	0.219	12 565	59 314	12 087	6 289	6.8389	14.2412	1.0754	1.0742	1.2018	1.0583	0	0	0	0	0.00	0.0000	0.000		20/05/2019 20:45
28	3.4840	NKS-179	5mg90s	16.35	73.20	5.631	0.171	21 744	66 715	15 329	3 229	4.4781	13.0005	1.0754	1.0811	1.2018	1.0583	0	0	0	0	0.00	0.0000	0.000		20/05/2019 20:56

NKS-216

$C_{23}H_{21}F_3N_4O_2Pd$



	calculated	found 1	found 2
C	50.33	50.18	50.19
H	3.86	3.705	3.690
N	10.21	10.19	10.14

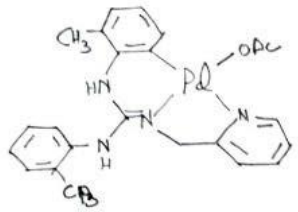
CHNS data of **3**.

Document: 30-04-2019 (VarioELcube) from:

28-06-2019
varioELcube
serial number: 19171021

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Date	Time
11	5.3800	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	33 363	58 417	18 516	628 889	2.5738	8.9423	29/04/2019	18:27
16	6.4080	NKS215	5mg90s	11.09	57.06	5.012	0.158	29 695	89 984	22 387	5 426	5.1435	11.3850	29/04/2019	19:25



	Calculated	Calculated. % td	observed
C	55.82	57.4	57.06
H	4.89	5.06	5.01
N	11.32	10.82	11.09

CHNS data of **4**.

Document: nks-17/9/19 (VarioELcube) from: []

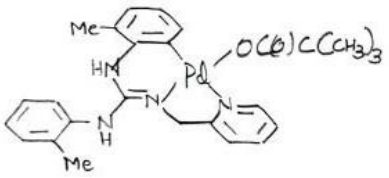
28-06-2019
varioELcube
serial number: 19171021

Text report

No.	Weight (mg)	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	N Factor	C Factor	H Factor	S Factor	N Blank	C Bla...	H Blank	S Blank	Moisture [%]	Prot. Factor	Prot. [%]	Memo	Date Time
13	5.7570	sulfanilamide	Smg90s	16.26	41.85	4.680	18.620	35 020	61 467	20 764	655 780	2.5738	8.9423	1.0959	1.1097	1.2443	1.0970	0	0	0	0	0.00	0.0000	0.000		17/09/2019 13:33
14	8.0650	sulfanilamide	Smg90s	16.26	41.85	4.680	18.620	48 891	85 914	28 478	928 882	2.5738	8.9423	1.0978	1.1089	1.2919	1.0982	0	0	0	0	0.00	0.0000	0.000		17/09/2019 13:47
43	4.6030	NKS 285A	Smg90s	9.77	61.23	5.557	0.043	16 835	71 681	19 449	1 025	6.2682	11.0180	1.0970	1.1108	1.2562	1.0933	0	0	0	0	0.00	0.0000	0.000		17/09/2019 19:08
44	4.7980	NKS 285B	Smg90s	9.73	61.12	5.574	0.031	17 481	74 535	20 395	772	6.2805	10.9636	1.0970	1.1108	1.2562	1.0933	0	0	0	0	0.00	0.0000	0.000		17/09/2019 19:19

NKS-285

$C_{26}H_{30}N_4O_2Pd$ ·



¹H ✓
M.P. 260°C
IR ✓
CHNS ✓
ScXRD ✓
HRMS ✓
Yield :

	Calculated	Calculated. ½ tol.	NKS-285A	NKS-285B
C	58.16	60.77	61.23	61.12
H	5.63	5.88	5.557	5.574
N	10.43	9.61	9.77	9.73

CHNS data of **5**.

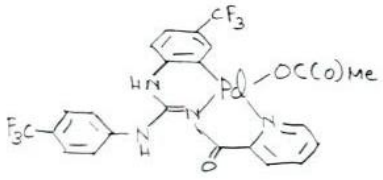
28-06-2019
varioELcube
serial number: 19171021

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	N Factor	C Factor	H Factor	S Factor	N Blank	C Bla..	H Blank	S Blank	Moisture [%]	Prot. Factor	Prot. [%]	Memo	Date	Time
37	4.5610	NKS 293B	5mg90s	9.46	44.04	2.485	0.060	16.149	51.302	8.490	1.432	4.6550	17.7231	1.0976	1.1108	1.2390	1.0906	0	0	0	0	0.00	0.0000	0.000		26/08/2019	19:10
38	4.5270	NKS 220A	5mg90s	8.76	42.33	2.007	0.090	14.843	49.411	6.707	2.139	4.8321	21.0923	1.0976	1.1008	1.2390	1.0906	0	0	0	0	0.00	0.0000	0.000		26/08/2019	19:21

Nks-293

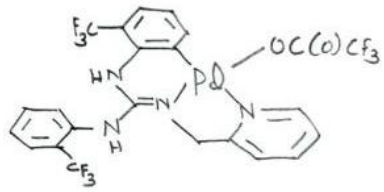
$C_{23}H_{16}F_6N_4O_3Pd$



	Calculated	observed
C	44.79	44.04
H	2.61	2.485
N	9.08	9.46

NKS-220

$C_{23}H_{15}F_9N_4O_2Pd$



	Calculated	observed
C	42.06	42.33
H	2.30	2.007
N	8.53	8.76

CHNS data of **6**.

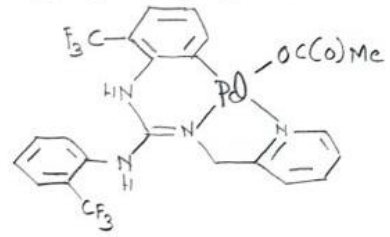
28-06-2019
varioELcube
serial number: 19171021

Text report

No	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	N Factor	C Factor	H Factor	S Factor	N Blank	C Bla	H Blank	S Blank	Moisture [%]	Prot Factor	Prot [%]	Memo	Date Time
7	9.9546	sulfanilamide	Smg90s	16.26	41.85	4.680	18.620	62.740	107.196	34.664	1.179.221	2.5738	8.9423	1.0540	1.0932	1.3206	1.0812	0	0	0	0	0.00	0.0000	0.000		23/10/2020 17:10
41	4.8830	NKS-230A	Smg90s	9.64	45.88	2.627	0.056	18.350	58.064	9.057	1.453	4.7576	17.4648	1.0540	1.0932	1.3206	1.0812	0	0	0	0	0.00	0.0000	0.000		23/10/2020 23:22
42	3.2670	NKS-230B	Smg90s	9.94	45.84	2.387	0.068	12.662	38.970	5.333	1.171	4.6097	19.2045	1.0540	1.0932	1.3206	1.0812	0	0	0	0	0.00	0.0000	0.000		23/10/2020 23:33
60	3.6460	CH3CN	Smg90s	11.90	45.79	2.294	0.050	17.829	45.758	6.076	1.023	3.8490	19.9621	1.0540	1.0932	1.3206	1.0812	0	0	0	0	0.00	0.0000	0.000		24/10/2020 02:50

NKS-230

$C_{23}H_{18}N_4O_2F_6Pd$



	Calculated	Observed	observed
C	45.83	45.88	45.84
H	3.01	2.63	2.39
N	9.29	9.64	9.94

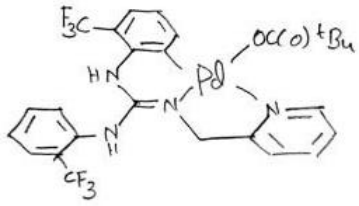
CHNS data of **7**.

28-06-2019
varioELcube
serial number: 19171021

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	N Factor	C Factor	H Factor	S Factor	N Blank	C Bla...	H Blank	S Blank	Moisture [%]	Prot. Factor	Prot. [%]	Memo	Date Time
13	4.0880	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	25 026	43 743	14 501	472 291	2.5738	8.9423	1.0902	1.1114	1.2334	1.0715	0	0	0	0	0.00	0.0000	0.000		26/08/2019 14:37
14	6.8540	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	41 496	72 970	24 500	788 107	2.5738	8.9423	1.1002	1.1102	1.2671	1.0931	0	0	0	0	0.00	0.0000	0.000		26/08/2019 14:51
22	6.5530	NKS-288A	5mg90s	8.67	48.90	3.873	0.127	21 287	81 223	19 543	4 397	5.6396	12.6254	1.0960	1.1125	1.2408	1.0865	0	0	0	0	0.00	0.0000	0.000		26/08/2019 16:20
23	5.5940	NKS-288B	5mg90s	8.73	48.72	3.603	0.168	18 306	69 248	15 249	4 951	5.5790	13.5211	1.0960	1.1125	1.2408	1.0865	0	0	0	0	0.00	0.0000	0.000		26/08/2019 16:32

$C_{26}H_{24}N_4F_6O_2Pd$



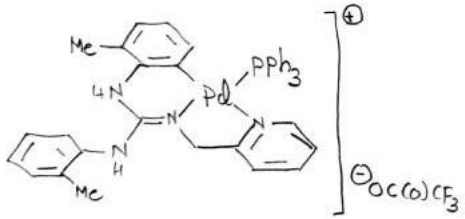
	Calculated	Nks-288A	Nks-288B
C	48.42	48.90	48.72
H	3.75	3.873	3.603
N	8.69	8.67	8.73

CHNS data of **8**.

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Info	Date Time
8	8.0050	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	53 279	87 133	28 870	915 112	2.5738	8.9423		08/04/2021 13:49
9	7.2900	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	48 041	79 464	26 465	838 469	2.5738	8.9423		08/04/2021 14:04
10	7.8600	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	51 313	85 593	28 666	918 979	2.5738	8.9423		08/04/2021 14:18
11	6.4260	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	42 149	70 281	23 103	752 814	2.5738	8.9423		08/04/2021 14:32
14	5.3520	NKS-216P	5mg90s	6.88	60.72	4.392	0.225	14 963	84 679	17 763	6 328	8.8252	13.8257	Su	08/04/2021 15:06

NKS-216P



$C_{41}H_{36}N_4F_3O_2PPd$

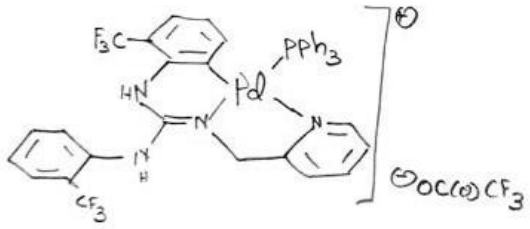
	calculated	observed
C	60.71	60.72
H	4.47	4.39
N	6.91	6.88

CHNS data of **10**.

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Info	Date Time
11	5.4490	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	37 088	58 602	19 456	569 388	2.5738	8.9423		21/08/2021 17:55
14	5.0130	NKS-220P	5mg90s	6.19	53.81	3.047	0.285	16 764	66 733	12 244	6 824	8.6983	17.6622	Su	21/08/2021 18:28

$C_{41}H_{30}N_4F_6O_2PPd$



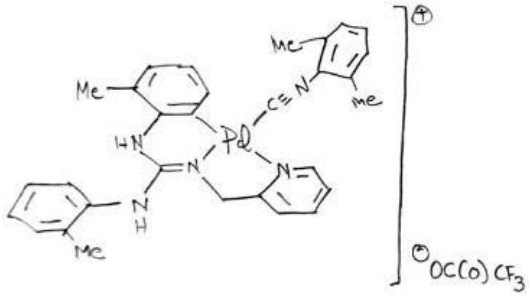
	Calculated	Observed
C	53.58	53.81
H	3.29	3.05
N	6.10	6.19

CHNS data of **11**.

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Info	Date Time
11	5.4490	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	37 088	58 602	19 456	569 388	2.5738	8.9423		21/08/2021 17:55
12	4.9640	NKS-216(2,6	5mg90s	10.37	56.76	4.510	0.443	23 226	74 142	18 563	10 485	5.4740	12.5848	Su	21/08/2021 18:06

$C_{32}H_{30}N_5F_3O_2Pd$



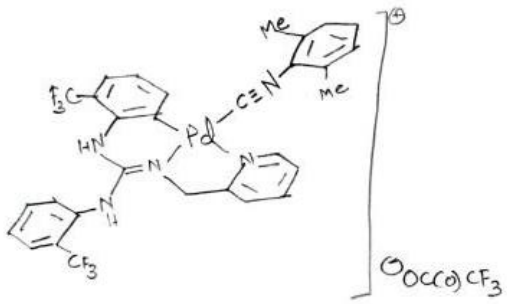
	calculated	observed
C	56.52	56.76
H	4.45	4.51
N	10.30	10.37

CHNS data of **13**.

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Info	Date Time
11	5.4490	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	37 088	58 602	19 456	569 388	2.5738	8.9423		21/08/2021 17:55
13	5.0890	nks-220(2,6)	5mg90s	9.20	48.84	3.052	0.285	21 137	66 121	12 472	6 924	5.3066	16.0039	Su	21/08/2021 18:17

$C_{32}H_{24}N_5F_6O_2Pd$



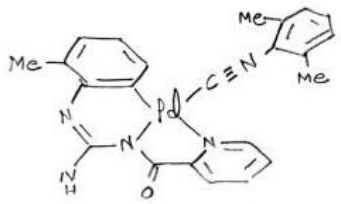
	Calculated	observed
C	48.78	48.84
H	3.07	3.05
N	8.89	9.20

CHNS data of **14**.

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Info	Date Time
10	7.8600	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	51 313	85 593	28 666	918 979	2.5738	8.9423		08/04/2021 14:18
11	6.4260	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	42 149	70 281	23 103	752 814	2.5738	8.9423		08/04/2021 14:32
12	5.3990	NKS-209(2,6)	5mg90s	12.17	61.70	4.725	0.432	26 665	86 769	19 389	12 261	5.0715	13.0599	Su	08/04/2021 14:44

$C_{30}H_{27}N_5O_1Pd$



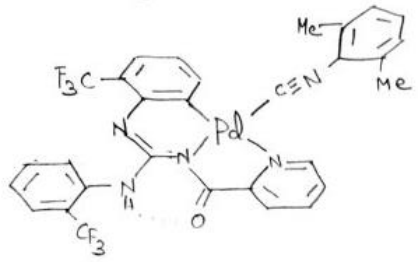
	Calculated	Observed	Calculated $2H_2O$
C	62.13	61.70	61.65
H	4.69	4.72	4.74
N	12.08	12.17	11.98

CHNS data of **15**.

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Info	Date Time
11	7.3980	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	47.619	80.378	27.352	850.139	2.5738	8.9423		28/06/2021 18:58
12	7.3600	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	47.370	79.780	27.092	849.730	2.5738	8.9423		28/06/2021 19:12
18	6.2610	NKS-279 (2.6)	5mg90s	10.47	52.55	3.232	0.081	25.958	85.284	15.226	2.631	5.0170	16.2589	Su	28/06/2021 20:18

$C_{30}H_{21}N_5F_6OPd$



	Calculated	Observed
C	52.38	52.55
H	3.08	3.23
N	10.18	10.47

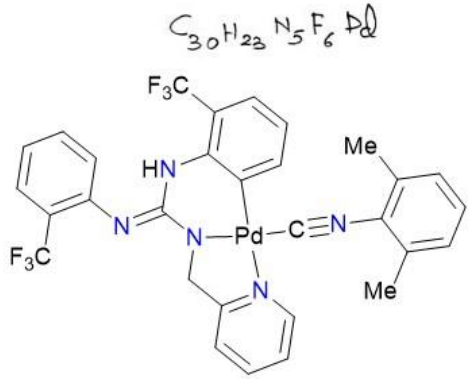
CHNS data of **16**.

Document: 21-08-2021 nks (VarioELcube) from:

28-06-2019
varioELcube
serial number: 19171021

Text report

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	C/N ratio	C/H ratio	Info	Date	Time
11	5.4490	sulfanilamide	5mg90s	16.26	41.85	4.680	18.620	37 088	58 602	19 456	569 388	2.5738	8.9423		21/08/2021	17:55
18	1.6160	NKS-288(2.6)	5mg90s	10.63	53.19	3.163	0.726	9 943	19 614	3 241	5 591	5.0029	16.8160	Su	21/08/2021	19:15



	Calculated	observed
C	53.46	53.19
H	3.44	3.16
N	10.39	10.63

CHNS data of **17**.

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