Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Synthesis of chiral supramolecular bisphosphinite palladacycles through hydrogen transfer-promoted self-assembly process

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1) General information

All reactions were carried out under an atmosphere of argon, with dry oxygen-free organic solvent and using standard Schlenk techniques. All solvents and liquid reagents were transferred using plastic single-use graduated syringes and stainless steel needles. Toluene (HPLC grade, non-stabilized, BioLab) was dried using Solvent Purifier System (SPS Mbraun 800) (two columns of alumina) and kept under positive pressure of argon (99.9999% purity grade).

Progress of the reactions was monitored by analytical TLC using ready-made plates precoated with silica gel on aluminium with F254 indicator (Merck 60 F_{254}). Visualization of spots was done using UV-light, phosphomolybdic acid, *p*-anisaldehyde or potassium permanganate followed by heating. Purification of crude mixtures was accomplished by column chromatography on silica gel 60 - 200 µm deactivated with 15 – 20 wt % water using a mixture of petroleum ether/dichloromethane as eluent (from 80/20 to 40/60, v/v).

^{1}H, ^{13}C and ^{31}P NMR spectra were measured on Brucker Avance DPX-300 (300 MHz ^{1}H, 75 MHz ^{13}C) or Brucker Avance DPX-400 (400 MHz ^{1}H, 101 MHz ^{13}C) spectrometer in $CDCl_3$ (except for ^{1}H spectra related to deuterium labelling experiments which were measure in C_6D_6) and referenced to TMS. Chemical shifts values (δ) are reported in ppm (calibration of spectra to the residual peak of $CDCl_3$: δ = 7.26 ppm (s) for ^{1}H NMR; δ = 77.16 ± 0.06 ppm for ^{13}C NMR). All the proton spectra are reported as follows: δ value (multiplicity, J coupling constant in Hz, number of nuclei). Multiplicity contractions used: (bs) – broad singlet, (d) – doublet, (dd) – doublet of doublets, (dq) – doublet of quartets, (ddd) – doublet of doublets of doublets, (ddt) – doublet of doublet of triplets, (dt) – doublet of triplets, (m) – multiplet, (t) – triplet, (tt) – triplet of triplets, (q) – quartet, (s) – singlet, (sept) – septuplet. On ^{13}C NMR spectra of the products **4**, the CH signals of the phenyl and methyl groups exhibit a particular shape due to virtual coupling. All these signals appear as virtual triplets with a central peak weaker than the side peaks and are described as “vt”.

IR spectra were recorded using an Alpha FT-IR spectrometer from Bruker equipped with ALPHA‘s Platinum ATR single reflection diamond ATR module (Spectral range: 7500 cm^{-1} - 375 cm^{-1}; spectral resolution: < 3 cm^{-1}). Wavenumbers are listed in cm^{-1} and intensities are listed as follows: (s) – strong, (m) – medium, (w) – weak.

Melting points were measured in a capillary tube using a Buchi Melting Point B-545 apparatus. The values are reported in Celsius degrees. Used contractions for the report of melting points: (dec) – decomposition, (sub) – sublimation.

HRMS were recorded on SYNAPT G2 HDMS (Waters) or on QStar Elite (Applied Biosystems SGIEX) equipped with an Atmospheric Pressure Ionization (API) source. Mass spectra were obtained using a Time Of Flight (TOF) analyzer. Measurements were performed on the ^{108}Pd ion except for **4g**.

X-ray diffraction analyses were performed from suitable crystals selected and mounted on a Rigaku Oxford Diffraction SuperNova diffractometer at 293K at the CuKα radiation (λ=1.54184 Å). Data collection reduction and multiscan ABSPACK correction were performed with CrysAlisPro (Rigaku Oxford Diffraction). Using Olex2,[1] the structures were solved with SheIXT[2] structure solution program using Intrinsic Phasing and refined with the SheIXL[3] refinement package using Least Squares minimization.

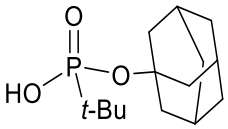
[1] O. V. Dolomov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.
[2] G. M. Sheldrick, Acta Cryst. 2015, A71, 3.
[3] G. M. Sheldrick, Acta Cryst. 2015, C71, 3.

2) Starting materials

Carboxylic acids **3** are commercially available and were used as received except for 3-(phenylthio)propionic acid which was prepared from benzenethiol and acrylic acid following a well-described procedure.[4] Tris(dibenzylideneacetone)dipalladium(0) (97% purity) was purchased from Aldrich and used as received. Enantiopure *t*-Butyl(phenyl)phosphine oxide **2H** was prepared following a procedure reported by our team.[5] Lastly, (*E*)-1,3-diphenylbut-2-en-1-ol (**5**) was synthesised according to a reported two-step protocol[6] and is fully charaterised in the literature. ^{1}H NMR and ^{13}C NMR are consistent with the literature data.

Synthesis of Adamantan-1-yl hydrogen *tert*-butylphosphonate:

A flamed-dried 250 mL-three neck flask was equipped with a Teflon-coated magnetic stir bar, a greased gas inlet adaptor with a glass plug, a dropping funnel and a rubber septum and then connected to the Schlenk line. The air was pumped out of the flask and the resulting vacuum was replaced with argon. This "vac-refill" operation was performed three times. The flask was then successively charged with dry dichloromethane (10 mL) and *t*-butyldichlorophosphine (3.0 g, 18 mmol) and the reaction mixture was stirred for 20 min at 0 °C (ice bath) while the dropping funnel was charged with a 60 mL-dry dichloromethane solution of 1-adamantanol (2.94 g, 8.0 mmol) and pyridine (1.45 mL, 18 mmol). The DCM solution of pyridine/1-adamantanol was added dropwise to the reaction mixture for 1 h at 0 °C and the resulting mixture was stirred at room temperature for 36 hours after which the reaction was quenched by adding water (10 mL) dropwise at 0 °C. The layers were separated and the aqueous phase was extracted with cyclohexane (3 x 50 mL). The combined organic fractions were concentrated and 80 mL of cyclohexane were added. The resulting solution was washed with an aqueous saturated solution of $NaHCO_3$. The layers were then separated and the aqueous phase was extracted with cyclohexane (3 x 10 mL). The combined organic fractions were dried over $MgSO_4$, filtered and concentrated under reduced pressure so as to obtain a white solid. The crude mixture was finally purified by silica gel column chromatography using a petroleum ether / EtOAc mixture as eluent (from 100/0 to 0/100, v/v). Adamantyl H-t-butylphosphinate was obtained as a white solid in a 14% yield (649.7 mg) while Adamantan-1-yl hydrogen *tert*-butylphosphonate was obtained as a white solid in a 34% yield (1.688 g).



Adamantan-1-yl hydrogen *tert*-butylphosphonate. White solid; 34%; **mp** 86 – 87 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.64 (bs, 6H), 2.19 (t, J = 8.5 Hz, 9H), 2.12 – 2.21 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 24.4 (d, $J_{P\text{-}C}$ = 1.4 Hz), 31.3, 35.7, 37.5, 39.1, 43.7 (d, $J_{P\text{-}C}$ = 4.3 Hz), 86.5 (d, $J_{P\text{-}C}$ = 12.8 Hz). **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 49.0 (s, 1P). **IR** (ATR) 538 (s), 567 (m), 637 (s), 646 (s), 771 (w), 817 (m), 851 (w), 934 (m), 960 (s), 982 (s), 1045 (m), 1103 (w), 1213 (w), 1250 (s), 1276 (w), 1356 (w), 1457 (w), 1477 (w), 2852 (m), 2911 (s), 2868 (w), 2969 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{26}O_3P^+$ $[M + H]^+$ 273.1614, found 273.1617.

[4] S. Gao, C. Tseng, C. H. Tsai and C.-F. Yao, *Tetrahedron*, 2008, **64**, 1955.
[5] D. Gatineau, D. H. Nguyen, D. Hérault, N. Vanthuyne, J. Leclaire, L. Giordano and G. Buono, *J. Org. Chem.*, 2015, **80**, 4132.
[6] A. A. Ott, C. S. Goshey and J. J. Topsczewski, *J. Am. Chem. Soc.,* 2017, **139**, 7737–7740.

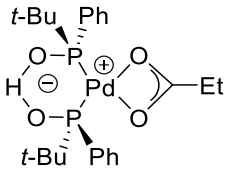
3) General procedure for the synthesis of the complexes 4a-h and 4j-n

A 50 mL-two-neck flask, equipped with a Teflon-coated magnetic stir bar, a greased gas inlet adaptor with a glass plug and a rubber septum, was successively charged with tris(dibenzylideneacetone)-dipalladium(0) (91.6 mg, 0.1 mmol), *t*-Butyl(phenyl)phosphine oxide **2H** (72.9 mg, 0.4 mmol) and acid **3**. The flask was connected to the Schlenk line and the air was pumped out of the flask. The resulting vacuum was thereafter replaced with argon. This "vac-refill" operation was performed three times. Dry toluene (5 mL) was added into the flask and the resulting mixture was stirred at 60 °C for 16 h. After cooling down the reaction mixture to rt, palladium on activated charcoal (15 mg, Pd/C 10%) was added to the reaction mixture and a gas bag of H_2 was fitted on the two-neck flask. After a 20 min-stirring period, the reaction mixture was filtered over celite® using Et_2O as eluent and concentrated under reduced pressure. The complexes **4** were obtained after purification by water deactivated-silica gel column chromatography (SiO_2/H_2O 20 wt %, petroleum ether/CH_2Cl_2, 20/80 – 60/40).

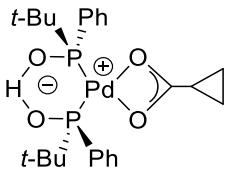
4) Procedure for deuterium labelling experiments and the synthesis of 4i

The procedures for deuterium labelling experiments and the synthesis of **4i** were similar to the general procedure but the reduction step (Pd/C, H_2) was not performed.

5) Characterization data of the products 4.

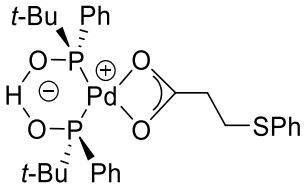


κ²-proprionato{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}-palladium(II) (4a). Yellow resin; 74%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.84 (d, J_{HP} = 16.9 Hz, 18H), 0.99 (t, J = 7.6 Hz, 3H), 2.16 (q, J = 7.6 Hz, 2H), 6.95 – 7.14 (m, 2H), 7.17 – 7.34 (m, 4H), 7.69 – 7.81 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 9.4, 25.7 (vt), 31.1, 39.1 (d, J_{cp} = 44.0 Hz), 125.8, 128.1 (vt), 128.4, 131.0, 131.7 (vt), 134.3 (d, J_{cp} = 55.5 Hz), 194.0. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.5 (s, 2P). **IR** (ATR) 514 (m), 605 (s), 695 (s), 743 (s), 806 (m), 894 (m), 936 (w), 1011 (s), 1033 (s), 1100 (s), 1184 (m), 1239 (w), 1295 (m), 1367 (m), 1392 (m), 1436 (s), 1468 (s), 1501 (m), 1574 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{34}O_4P_2PdCl^-$ $[M + Cl]^-$ 579.0661, found 579.0669.

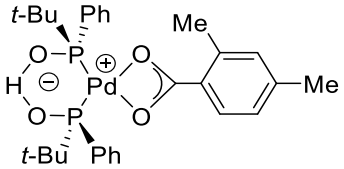


κ²-cyclopropylcarboxylate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}palladium(II) (4b). Yellow solid; 75%. **mp** 52 – 53 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.80 – 0.95 (m, 4H), 1.03 (d, J_{HP} = 16.9 Hz, 18H), 1.52 (tt, J = 8.3 Hz, 1H), 7.37 – 7.54 (m, 6H), 7.93 (ddd, J = 10.8, 7.8, 1.8 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 8.3, 15.7, 25.7, 39.0 (d, J_{cp} = 44.0 Hz), 128.0 (vt), 130.9,

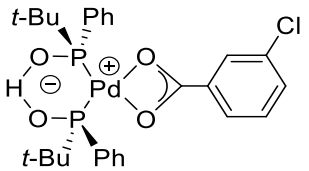
131.7 (vt), 134.3 (d, J_{cp} = 55.4 Hz), 193.6. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.6 (s, 2P). **IR** (ATR) 511 (s), 606 (s), 668 (s), 696 (s), 744 (s), 806 (m), 858 (w), 901 (w), 945 (m), 1011 (s), 1027 (s), 1101 (m), 1185 (m), 1301 (m), 1366 (w), 1391 (w), 1435, (s), 1461 (s), 1497 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{34}O_4P_2PdCl^-$ $[M + Cl]^-$ 591.0661, found 591.0665.



κ^2-3-(phenylthio)propanoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}palladium(II) (4c). Yellow resin; 79%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.84 (d, J_{HP} = 16.9 Hz, 18H), 2.47 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H), 6.96 – 7.13 (m, 4H), 7.20 – 7.31 (m, 7H), 7.69 – 7.79 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 25.8 (vt), 29.3, 37.8, 39.2 (d, J_{cp} = 43.8 Hz), 126.4, 128.1 (vt), 129.0, 130.1, 131.0, 131.8 (vt), 134.2 (d, J_{cp} = 55.6 Hz), 135.9, 190.3. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.6 (s, 2P). **IR** (ATR) 508 (w), 606 (s), 693 (s), 738 (s), 806 (m), 853 (w), 937 (w), 1011 (s), 1025 (s), 1035 (s), 1100 (s), 1184 (m), 1279 (m), 1306 (m), 1366 (m), 1392 (m), 1436 (s), 1473 (m), 1510 (m), 1555 (w), 1574 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{38}O_4P_2SPdCl^-$ $[M + Cl]^-$ 687.0694, found 687.0719.

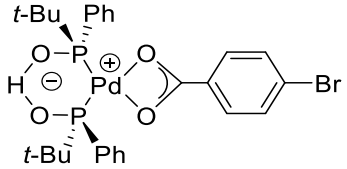


κ^2-2.4-dimethylbenzoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}palladium(II) (4d). Yellow solid; 78%. **mp** 128 – 130 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.89 (d, J_{HP} = 16.8 Hz, 18H), 2.16 (s, 3H), 2.46 (s, 3H), 6.87 (m, 2H), 7.15 – 7.35 (m, 6H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.79 – 7.90 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.4, 20.8, 24.7 (vt), 38.0 (d, J_{cp} = 44.0 Hz), 125.2, 127.0 (vt), 127.4, 128.9, 129.6, 129.9, 130.8 (vt), 131.3, 133.4 (d, J_{cp} = 55.3 Hz), 138.9, 141.0. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.7 (s, 2P). **IR** (ATR) 510 (w), 577 (m), 605 (s), 621 (m), 696 (s), 725 (m), 745 (s), 785 (s), 805 (m), 845 (s), 934 (w), 1011 (s), 1034 (s), 1069 (m), 1100 (s), 1150 (m), 1184 (m), 1236 (m), 1260 (m), 1287 (m), 1367 (m), 1381 (m), 1391 (m), 1415 (s), 1452 (m), 1472 (m), 1573 (w), 1614 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{29}H_{38}O_4P_2PdCl^-$ $[M + Cl]^-$ 655.0975, found 655.0981.

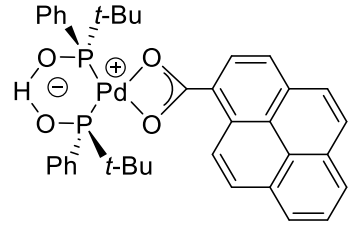


κ^2-3-chlorobenzoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]} palladium(II) (4e). Yellow solid; 54%. **mp** 146 – 148 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.11 (d, J_{HP} = 17.0 Hz, 18H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.44 – 7.54 (m, 7H), 7.97 – 8.10 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 20.8 (vt), 38.24 (d, J_{cp} = 43.8 Hz), 126.3, 127.1 (vt), 128.2, 128.3, 130.0, 130.8 (vt), 131.3, 132.9, 133.1, 133.2 (d, J_{cp} = 55.5 Hz), 134.5, 181.8. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.8 (s, 2P). **IR** (ATR) 510 (w), 605 (s), 661 (m), 674 (m), 695 (s), 743 (s), 804 (m), 858 (w), 884 (w), 937 (w), 1011 (s), 1038 (s), 1071 (m), 1103 (s), 1186 (m), 1262 (m), 1289 (m), 1366 (m), 1402 (s), 1426 (s), 1474 (m),

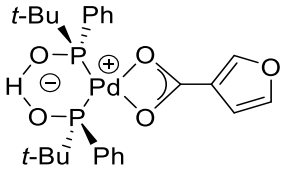
1505 (m), 1574 (w), 1599 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{27}H_{33}O_4P_2PdCl_2^-$ [M + Cl]$^-$ 661.0267, found 661.0267.



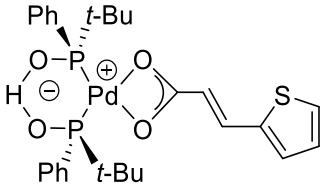
κ²-4-bromobenzoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]} palladium(II) (4f). Yellow solid; 53%. **mp** 135 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.10 (d, J_{HP} = 17.0 Hz, 18H), 7.41 – 7.51 (m, 6H), 7.59 (d, J = 8.4 Hz, 2H), 7.92 – 8.09 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 25.8 (vt), 39.2 (d, J_{cp} = 43.9 Hz), 127.3, 128.1 (vt), 130.8, 131.0, 131.3, 131.8 (vt), 132.6, 134.3 (d, J_{cp} = 55.4 Hz), 183.3. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ95.8 (s, 2P). **IR** (ATR) 607 (s), 696 (s), 714 (s), 743 (s), 766 (s), 807 (m), 855 (s), 935 (w), 1011 (s), 1039 (s), 1068 (m), 1100 (m), 1137 (w), 1169 (m), 1128 (m), 1180 (w), 1238 (w), 1280 (w), 1368 (w), 1414 (s), 1435 (w), 1458 (w), 1494 (m), 1588 (m). **HRMS** (ESI-TOF) *m/z* calcd for $C_{27}H_{32}O_4P_2BrPd^-$ [M - H]$^-$ 668.9998, found 669.0007.



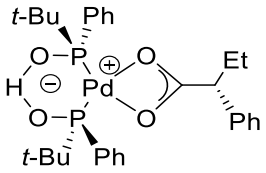
κ²-1-pyrenecarboxylate{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (4g). Yellow solid; 69%. **mp** 96 – 98 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.19 (d, J_{HP} = 16.8 Hz, 18H), 7.40 – 7.66 (m, 6H), 7.98 – 8.34 (m, 11H), 8.79 (d, J = 8.0 Hz, 1H), 9.51 (d, J = 9.5 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ25.9 (vt), 39.3 (d, J_{cp} = 44.0 Hz), 124.2, 124.4, 124.9, 125.7, 125.9, 126.1, 126.2, 127.3, 127.4, 128.2 (vt), 128.5, 128.9, 129.0, 129.3, 130.5, 130.9, 131.1, 131.9 (vt), 134.1, 134.5 (d, J_{cp} = 55.3 Hz), 143.3, 186.7. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ95.9 (s, 2P). **IR** (ATR) 512 (w), 576 (m), 608 (w), 637 (w), 696 (s), 708 (s), 754 (s), 804 (s), 819 (w), 852 (w), 891 (m), 1012 (s), 1036 (m), 1101 (w), 1163 (w), 1181 (w), 1236 (w), 1315 (w), 1358 (m), 1403 (s), 1436 (m), 1459 ((w), 1472 (w), 1507 (w), 1595 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{37}H_{37}O_4P_2Pd^-$ [M - H]$^-$ 713.1222, found 713.1230.



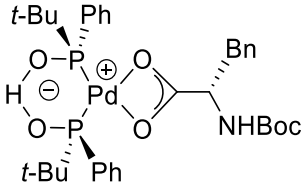
κ²-3-furoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]} palladium(II) (4h). Yellow solid; 81%. **mp** 181 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.08 (d, J_{HP} = 16.9 Hz, 18H), 6.77 (d, J = 1.8 Hz, 1H), 7.38 – 7.54 (m, 7H), 8.0 (ddt, J = 11.1, 6.6, 1.7 Hz, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ25.9 (vt), 39.2 (d, J_{cp} = 43.9 Hz), 109.9, 122.8, 128.1 (vt), 128.4, 129.0, 131.0, 131.8 (vt), 134.3 (d, J_{cp} = 55.4 Hz), 143.2, 147.2, 180.9. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ95.7 (s, 2P). **IR** (ATR) 604 (m), 696 (s), 743 (s), 776 (s), 810 (s), 818 (s), 871 (w), 931 (m), 966 (w), 1010 (s), 1037 (s), 1071 (w), 1103 (s), 1151 (m), 1185 (m), 1202 (m), 1226 (w), 1247 (w), 1290 (w), 1361 (m), 1394 (w), 1434 (s), 1474 (m), 1510 (m), 1578 (m), 1715 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{32}O_5P_2PdCl^-$ [M + Cl]$^-$ 617.0454, found 617.0455.



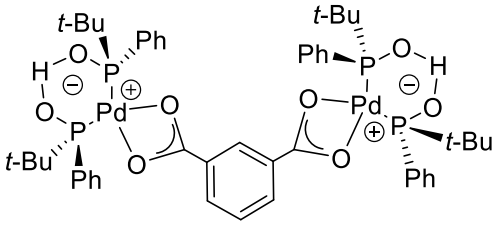
κ²-(*E*)-2-thiopheneacrylate{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (4i). Yellow solid; 74%. **mp** 148 - 150 °C (sub). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.08 (d, J_{HP} = 16.9 Hz, 18H), 6.28 (d, J = 15.7 Hz, 1H), 7.06 (dd, J = 5.1, 3.6 Hz, 1H), 7.26 – 7.28 (m, 2H), 7.36 (d, J = 5.1 Hz, 1H), 7.43 – 7.54 (m, 6H), 7.76 6.28 (d, J = 15.7 Hz, 1H), 7.94 – 8.06 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 25.8 (vt), 39.2 (d, J_{cp} = 44.0 Hz), 121.1, 128.1 (vt), 128.4, 129.0, 130.1, 131.0, 131.8 (vt), 134.4 (d, J_{cp} = 55.4 Hz), 135.8, 140.2, 184.7. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.7 (s, 2P). **IR** (ATR) 528 (w), 605 (s), 696 (s), 727 (s), 775 (w), 807 (w), 838 (w), 855 (w), 868 (w), 970 (m), 1013 (m), 1036 (m), 1102 (m), 1182 (m), 1213 (m), 1255 (m), 1279 (m), 1349 (m), 1402 (s), 1435 (m), 1459 (m), 1469 (m), 1517 (w), 1574 (w), 1625 (m). **HRMS** (ESI-TOF) *m/z* calcd for $C_{27}H_{34}O_4P_2SPdCl^-$ [M + Cl]$^-$ 659.0381, found 659.0391.



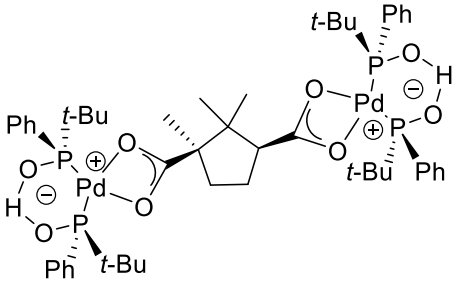
κ²-(*R*)-2-phenylbutanoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}palladium(II) (4j). Yellow resin; 66%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.80 – 0.86 (m, 3H), 0.83 (d, J_{HP} = 16.9 Hz, 18H), 1.65 (dt, J = 13.9, 7.2 Hz, 1H), 1.94 (dq, J = 15.1, 7.5 Hz, 1H), 3.22 (t, J = 7.7 Hz, 1H), 7.09 – 7.19 (m, 3H), 7.20 – 7.33 (m, 8H), 7.76 (ddd, J = 13.9, 7.2 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 12.4, 25.7 (vt), 27.6, 39.1 (d, J_{cp} = 43.9 Hz), 57.0, 126.7, 128 (vt), 128.2, 130.9, 131.8 (vt), 134.3 (d, J_{cp} = 55.5 Hz), 140.4, 193.0. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.7 (s, 2P). **IR** (ATR) 606 (m), 675 (s), 693 (s), 730 (s), 744 (m), 806 (s), 909 (w), 936 (w), 1010 (m), 1037 (s), 1102 (s), 1185 (m) 1236 (w), 1254 (w), 1295 (m), 1316 (w), 1366 (m), 1416 (m), 1437 (s), 1457 (s), 1508 (m), 1574 (m). **HRMS** (ESI-TOF) *m/z* calcd for $C_{30}H_{40}O_4P_2PdCl^-$ [M + Cl]$^-$ 669.1132, found 669.1137.



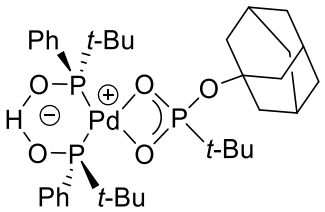
κ²-(*S*)-2-aminophenylpropanoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}palladium(II) (4k). Yellow solid; 77%. **mp** 168 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.07 (d, J_{HP} = 17.1 Hz, 18H), 1.58 (s, 9H), 3.24 – 3.31 (m, 2H), 4.55 – 4.67 (m, 1H), 5.14 (d, J = 7.0 Hz, 1H), 7.21 – 7.37 (m, 6H), 7.48 – 7.63 (m, 5H), 7.94 – 8.14 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 25.7 (vt), 38.2, 39.3 (d, J_{cp} = 43.9 Hz), 56.3, 79.5, 126.6, 128.2 (vt), 129.7, 129.9, 131.1, 131.2, 131.7, 131.8 (vt), 133.9 (d, J_{cp} = 55.5 Hz), 155.1, 188.5. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.7 (s, 2P). **IR** (ATR) 559 (w), 606 (s), 662 (s), 700 (s), 746 (s), 807 (w), 830 (w), 867 (w), 900 (w), 999 (m), 1041 (s), 1077 (m), 1102 (s), 1170 (w), 1215 (w), 1246 (w), 1308 (w), 1348 (w), 1367 (m), 1393 (m), 1435 (s), 1448 (s), 1474 (m), 1493 (m), 1522 (w), 1714 (s). **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{47}NO_6P_2PdCl^-$ [M + Cl]$^-$ 770.1607, found 770.1612.



κ²-isophtalate-di{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenyl-phosphinous]}-dipalladium(II) (4l). Yellow solid; 90%. **mp** 123 – 127 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.17 (d, J_{HP} = 16.8 Hz, 36H), 7.01 – 7.06 (m, 10H), 7.12 – 7.29 (m, 10H), 8.21 – 8.43 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 25.8 (vt), 39.3 (d, J_{cp} = 43.9 Hz), 127.8, 128.1 (vt), 130.0, 131.0, 131.8 (vt), 132.8, 133.8, 134.3 (d, J_{cp} = 55.4 Hz), 183.9. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 94.6 (s, 4P). **IR** (ATR) 514 (w), 540 (w), 575 (w), 607 (m), 659 (w), 697 (s), 735 (s), 772 (m), 805 (w), 822 (w), 844 (w), 919 (w), 1012 (m), 1036 (m), 1069 (w), 1100 (w), 1155 (w), 1189 (w), 1275 (w), 1313 (w), 1366 (w), 1397 (s), 1439 (m), 1484 (w), 1507 (w), 1519 (w), 1597 (w), 1609 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{48}H_{62}O_8P_4Pd_2Cl^-$ $[M + Cl]^-$ 1141.1158, found 1141.1151.

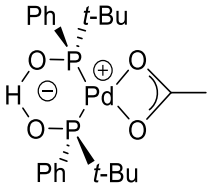


κ²-(+)-D-camphorate-di{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}-dipalladium(II) (4m). Yellow solid; 91%. **mp** 125 – 128 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.07 (d, J_{HP} = 16.0 Hz, 18H), 1.10 (d, J_{HP} = 16.0 Hz, 18H), 1.14 (s, 3H), 1.29 (s, 3H), 1.38 (s, 3H), 1.52 (dq, J = 9.6, 5.9, 4.8 Hz, 1H), 1.84 (ddt, J = 12.5, 6.0, 2.5 Hz, 1H), 2.18 – 2.38 (m, 1H), 2.59 – 2.88 (m, 1H), 7.37 – 7.54 (m, 12H), 7.91 – 8.08 (m, 8H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 11.42, 22.0, 23.0, 25.7 (vt), 29.6, 39.0 (d, J_{cp} = 44.1 Hz), 47.4, 56.2, 58.2, 128.0 (vt), 128.4, 130.9, 131.8 (vt), 134.5 (d, J_{cp} = 55.3 Hz), 193.9, 195.7. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.3 (s, 2P), 95.4 (s, 2P). **IR** (ATR) 507 (w), 607 (m), 695 (s), 743 (m), 796 (m), 807 (m), 836 (w), 926 (w), 1011 (m), 1036 (s), 1102 (m), 1123 (w), 1184 (w), 1242 (w), 1290 (w), 1319 (w), 1367 (m), 1392 (w), 1416 (s), 1436 (m), 1459 (m), 1495 (m). **HRMS** (ESI-TOF) *m/z* calcd for $C_{50}H_{72}O_8P_4Pd_2Cl^-$ $[M + Cl]^-$ 1175.1940, found 1175.1935.

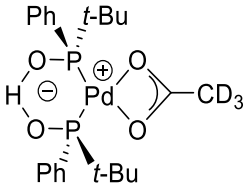


κ²-Adamantan-1-yl *tert*-butylphosphonate{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (4n). Yellow resin; 70%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.12 (d, J_{HP} = 16.4 Hz, 9H), 1.26 (d, J_{HP} = 20.5 Hz, 18H), 1.66 (bs, 6H), 2.21 (m, 9H), 7.06 – 7.22 (m, 2H), 7.35 – 7.54 (m, 6H), 7.86 – 7.99 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 24.4 (d, J_{P-C} = 1.4 Hz), 27.1 (vt), 31.3, 35.7, 37.5, 39.1, 40.42 (d, J = 40.9 Hz), 43.7 (d, J_{P-C} = 4.3 Hz), 86.5 (d, J_{P-C} = 12.9 Hz), 127.7 (vt), 128.3 (vt), 128.4 (d, J_{P-C} = 1.7 Hz), 128.5, 128.8, 128.9 (d, J_{P-C} = 3.4 Hz), 130.5, 132.0 (vt). **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 49.0 (s, 1P), 95.6 (s, 2P). **IR** (ATR) 540 (s), 568 (w), 602 (w), 638 (m), 647 (m), 695 (w), 742 (w), 771 (w), 935 (w), 961 (m), 983 (s), 993 (s), 1024 (m), 1046 (m), 1099 (w), 1184 (w), 1214 (w),

1251 (m), 1277 (w), 1303 (w), 1357 (w), 1394 (w), 1436 (w), 1457 (w), 1476 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{53}O_5P_3PdCl^-$ $[M + Cl]^-$ 777.1835, found 777.1830.



Acetato{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (4o).[7] Yellow solid; 73%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.97 (d, J_{HP} = 17.0 Hz, 18H), 2.05 (s, 3H), 6.99 – 7.50 (m, 6H), 7.62 – 7.68 (m, 1H), 7.86 (t, J = 9.1 Hz, 3H).



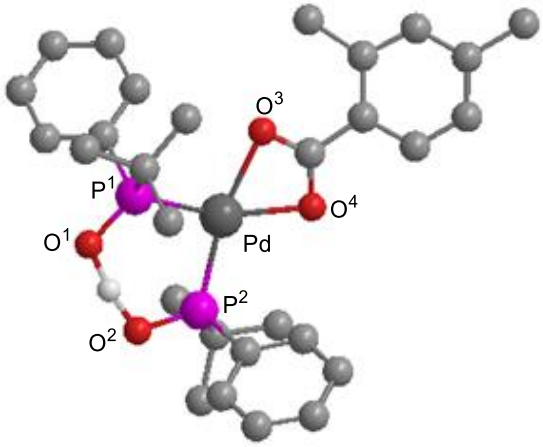
***d*$_3$-Acetato{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (*d*$_3$-4o)**. Yellow solid; 82%. **mp** 50 – 52 °C (dec). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.05 (d, J_{HP} = 16.9 Hz, 18H), 7.40 – 7.53 (m, 5H), 7.87 – 8.04 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 25.7 (vt), 26.4 – 26.6 (m, CD_3), 39.1 (d, $J_{P\text{-}C}$ = 43.9 Hz), 128.1 (vt), 131.0, 131.7 (vt), 134.2 (d, J_{HP} = 55.6 Hz), 190.8. **^{31}P {^{1}H} NMR** (121 MHz, $CDCl_3$) δ 95.5 (s, 2P). **IR** (ATR) 516 (w), 549 (w), 604 (m), 643 (m), 696 (s), 743 (m), 807 (w), 894 (w), 925 (w), 936 (w), 1011 (s), 1025 (s), 1101 (s), 1184 (w), 1257 (w), 1310 (w), 1366 (w), 1391 (w), 1433 (s), 1456 (s), 1473 (w), 1493 (w). **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{29}D_3O_4P_2PdCl^-$ $[M + Cl]^-$ 568.0693, found 568.0691.

[7] J. Bigeault, L. Giordano and G. Buono, *Angew. Chem. Int. Ed.,* 2005, **44**, 4753–4757.

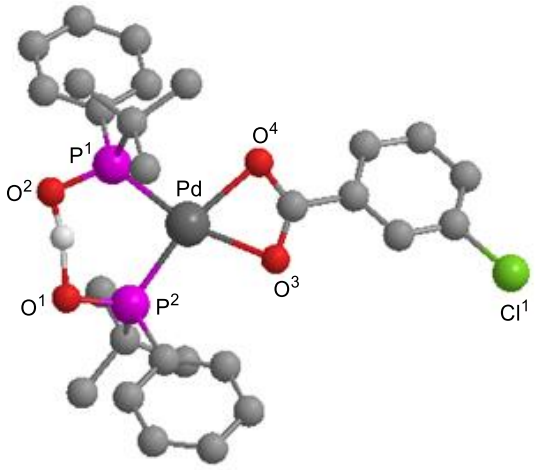
6) X-ray crystallography of the compounds 4

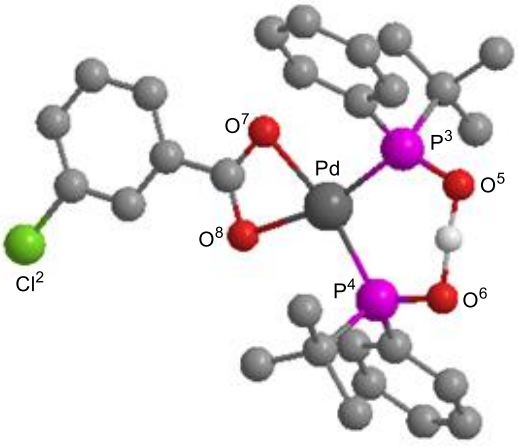
Complete crystallographic data of complexes **4d**-**f**, **4h**-**l** and **4k**-**l** are deposited at the Cambridge Crystallographic Data Centre, where it can be downloaded free of charge from www.ccdc.cam.ac.uk/data_request/cif.

κ^2-2.4-dimethylbenzoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}palladium(II) (4d). CCDC number: 1836992. Recrystallised from Et_2O/*n*-hexane by slow evaporation. Most hydrogens are omitted for clarity.

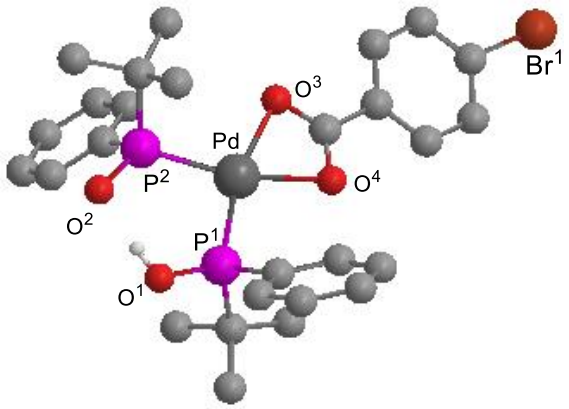


κ^2-3-chlorobenzoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]} palladium(II) (4e). CCDC number: 1836989. Recrystallised from Et_2O/*n*-hexane by slow evaporation. Most hydrogens are omitted for clarity.
Commentary: there are two independent molecules in the asymmetric unit. Both are shown in separate pictures.



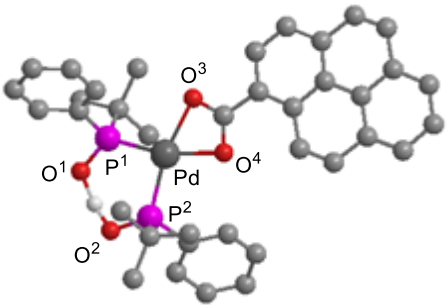


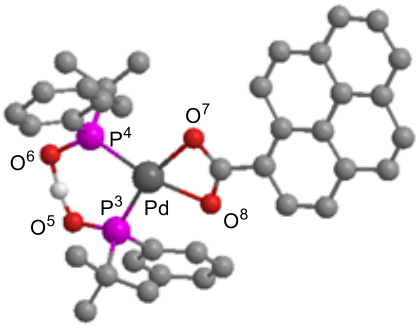
κ²-4-bromobenzoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]} palladium(II) (4f). CCDC number: 1836990. Recrystallised from Et_2O/CH_2Cl_2 by slow evaporation. Most hydrogens are omitted for clarity.

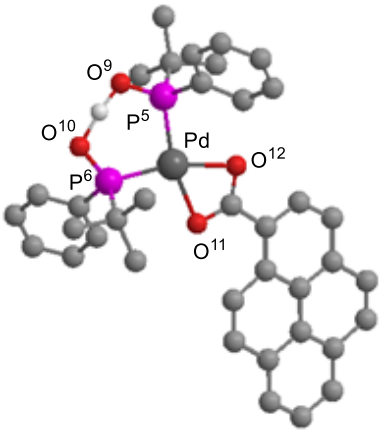


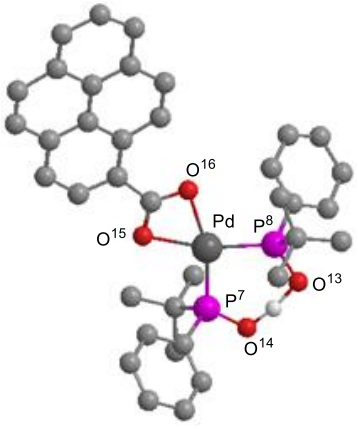
κ²-1-pyrenecarboxylate{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (4g). CCDC number: 1836988. Recrystallised from CH_2Cl_2/Et_2O by slow evaporation. Most hydrogens are omitted for clarity.

Commentary: there are four independent molecules in the asymmetric unit with identical absolute configurations. All of them are shown in separate pictures. Some solvent could not be identified because of a strong disorder and the Olex2 solvent mask procedure was applied before the final refinements. Some residual pics could not be attributed and are located close to the absorbing metal atoms. Despite the alert A, the collected data were sufficient to confirm with certainty the absolute configuration at the *P* atoms as well as the κ²-coordination fashion of the 1-pyrenecarboxylate ligand to the metal centre.



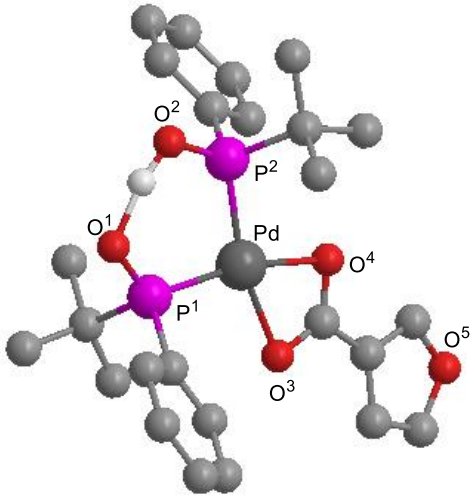


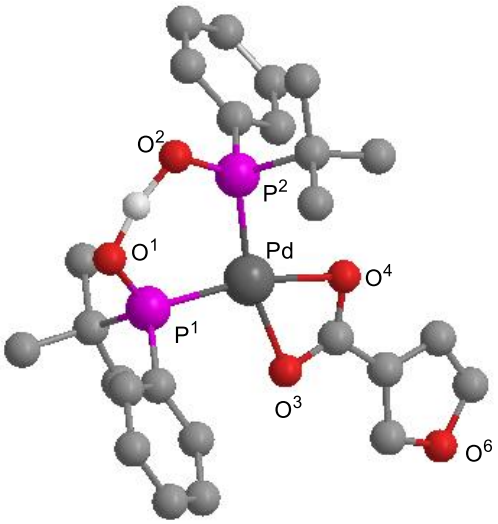




κ²-3-furoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]} palladium(II) (4h). CCDC number: 1836986. Recrystallised from Et_2O/*n*-hexane by slow evaporation. Most hydrogens are omitted for clarity.

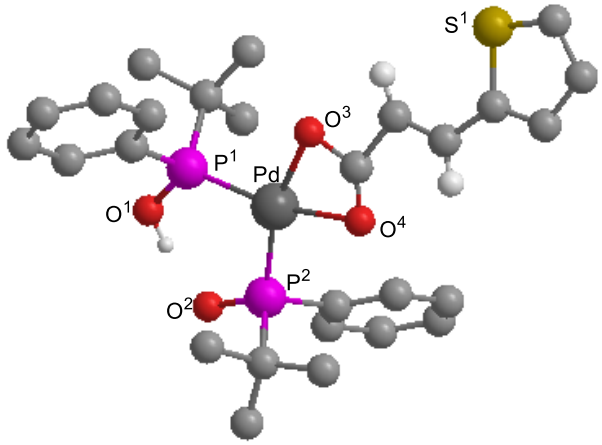
Commentary: the 3-furoate ligand alternatively occupies two positions with each position 180 degrees from the other. The sites at the β-position of the furan – carboxylate bond are therefore common to both an oxygen and a carbon atom. Each structure is shown in separate pictures.

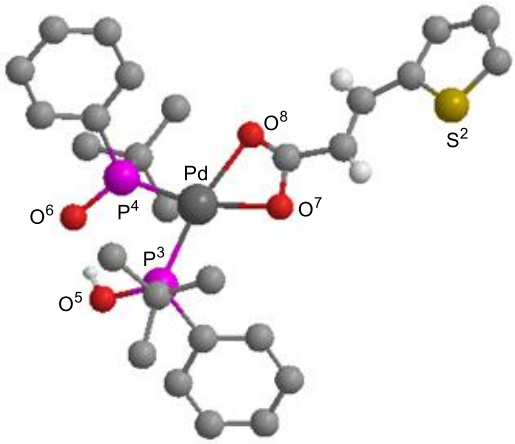




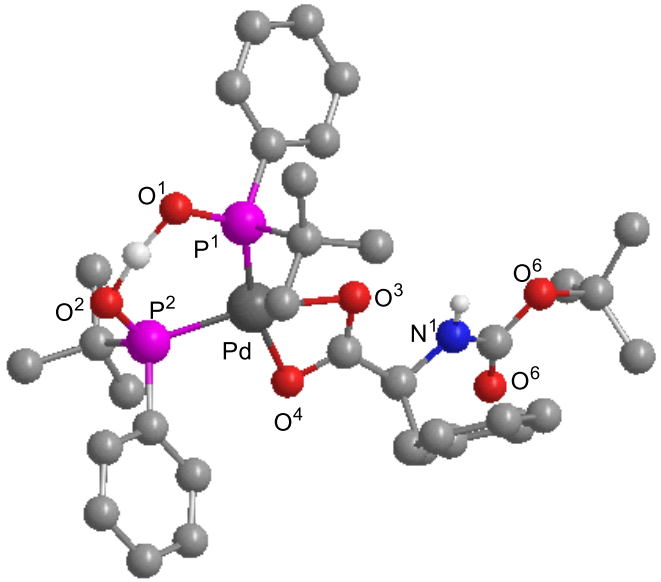
κ²-(*E*)-2-thiopheneacrylate{[(*S*)-(-)-*tert*-butylphenylphosphinito][(*S*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (4i). CCDC number: 1839614. Recrystallised from Et_2O/*n*-hexane by slow evaporation. Most hydrogens are omitted for clarity.

Commentary: the (*E*)-2-thiopheneacrylate ligand alternatively occupies two positions with each position 180 degrees from the other. Both structures are shown in separate pictures.

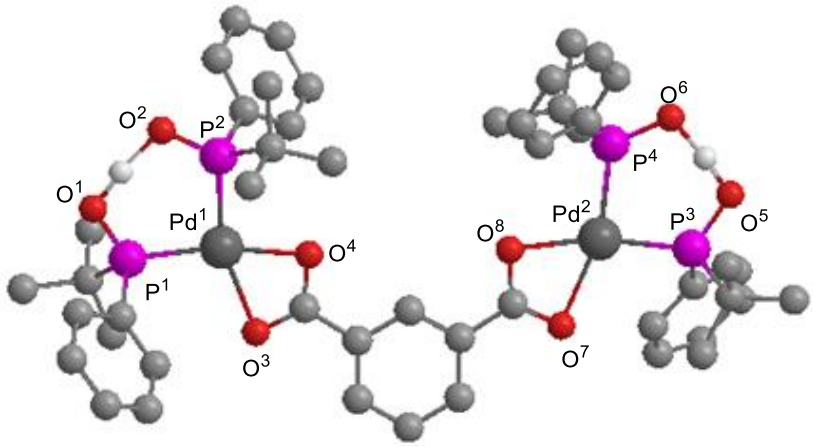




κ²-(*S*)-2-aminophenylpropanoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenyl-phosphinous]}palladium(II) (4k). CCDC number: 1836985. Recrystallised from Et_2O/*n*-hexane by slow evaporation. Most hydrogens are omitted for clarity.



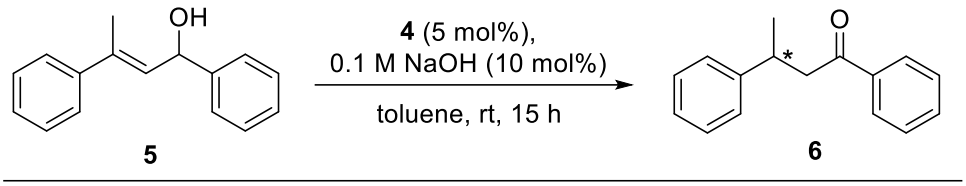
κ²-isophtalate-di{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenyl-phosphinous]}-dipalladium(II) (4l). CCDC number: 1836984. Recrystallised from CH_2Cl_2/Et_2O by slow evaporation. Most hydrogens are omitted for clarity.



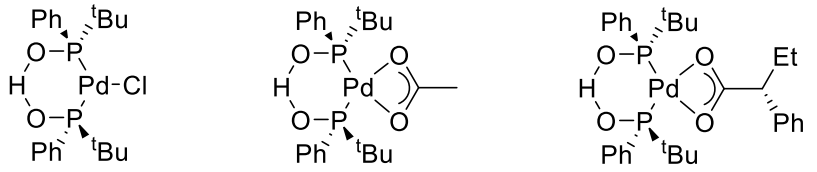
7) Impact of chiral supramolecular bisphosphinite palladacycles on asymmetric catalysis

The impact of our chiral supramolecular bisphosphinite palladacycles on asymmetric catalysis was checked in the asymmetric isomerisation reaction involving the allylic alcohol (*E*)-1,3-diphenylbut-2-en-1-ol (**5**) (table 1). When the reaction was conducted with dihydrogen di-μ-chlorotetrakis[(*R*)-tert-butyl(phenyl)phosphinito-κ-*P*]dipalladium(II) (**4p**) as a catalyst, toluene as solvent and NaOH (10 mol%) as additive at rt for 15 h, the expected saturated ketone compound **6** was obtained in 50% isolated yield and with 57% ee (entry 1). Using acetato{[(*R*)-(-)-*tert*-butylphenylphosphinito][(*R*)-(-)-*tert*-butylphenylphosphinous]}palladium(II) (**4o**) instead of **4p** allowed for improving the yield (78%) without however improving the enatiomeric excess (58% ee) (entry 2). Finally, the use κ^2-(*R*)-2-phenylbutanoate{[(*R*)-(+)-*tert*-butylphenylphosphinito][(*R*)-(+)-*tert*-butylphenylphosphinous]}-palladium(II) (**4j**) as a catalyst in which the carboxylate X-type ligand is chiral afforded **6** in a yield similar to that obtained with **4o** (76%) but with a better ee (64%) (entry 3). To the best of our knowledge, we now report a very rare example of transition metal-catalysed asymmetric reaction involving a supramolecular P-P bidentate chelate architecture in which chirality is no longer centered on a carbon backbone, but on phosphorus atoms. Moreover, this result suggests that a chiral carboxylate X-type ligand can exert an amplifying effect on the enantiomeric excess.

Table 1. Asymmetric isomerisation reaction of 5.



5 **6**



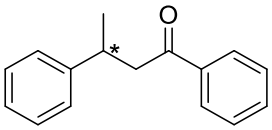
4p **4o** **4j**

Entry	Catalyst	Yield (%)[a]	ee (%)[b]
1	**4p**	50	57
2	**4o**	78	58
3	**4j**	76	64

[a] Isolated yield of the pure product **6** after purification by column chromatography. [b] Determined by chiral HPLC analysis

Experimental procedure for asymmetric isomerisation of 5.

A flame-dried 25 mL Schlenk tube was charged under argon atmosphere with palladium catalyst 4 (0.011 mmol , 5 mol %) and 2.5 ml of a dry toluene solution of (*E*)-1,3-diphenylbut-2-en-1-ol **5** (50 mg, 0.22 mmol). 0.2 mL (0.02 mmol, 10 mol %) of 0.1 M NaOH solution (0.2 mL, 0.02 mmol) was then added and the resulting reaction mixture was stirred overnight at rt. The reaction was then quenched by the successive addition AcOEt (2 mL) and water (2 mL). The aqueous layer was removed while the organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (SiO_2, petroleum ether/EtOAc, 96/4) to give the desired 1,3-diphenylbutan-1-one **6** as a white solid.



1,3-diphenylbutan-1-one (**6**).[8] White solid; 76%; ee = 64%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (d, *J* = 6.93 Hz, 3H), 3.20 (dd, *J* = 8.29, 16.45 Hz, 1H), 3.31 (dd, *J* = 5.71, 16.45 Hz, 1H), 3.53 (sept, *J* = 6.93 Hz, 1H), 7.16 – 7.19 (m, 1H), 7.28 – 7.34 (m, 4H), 7.44 – 7.47 (m, 2H), 7.54 – 7.58 (m, 1H), 7.93 – 7.95 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 21.9, 35.6, 47.1, 126.3, 126.9, 128.1, 128.5, 128.6, 133.0, 137.3, 146.6, 199.1. **HPLC separation:** Lux – Amylose – 2, Heptane / Isopropanol (90:10), 1 mL / min, detection 230 nm and 254 nm. Retention times: first eluted 6,138 min; second eluted 7.408 min.

[8] Y. Yu and L. S. Liebeskind, *J. Org. Chem.*, 2004, **69**, 3554–3557.

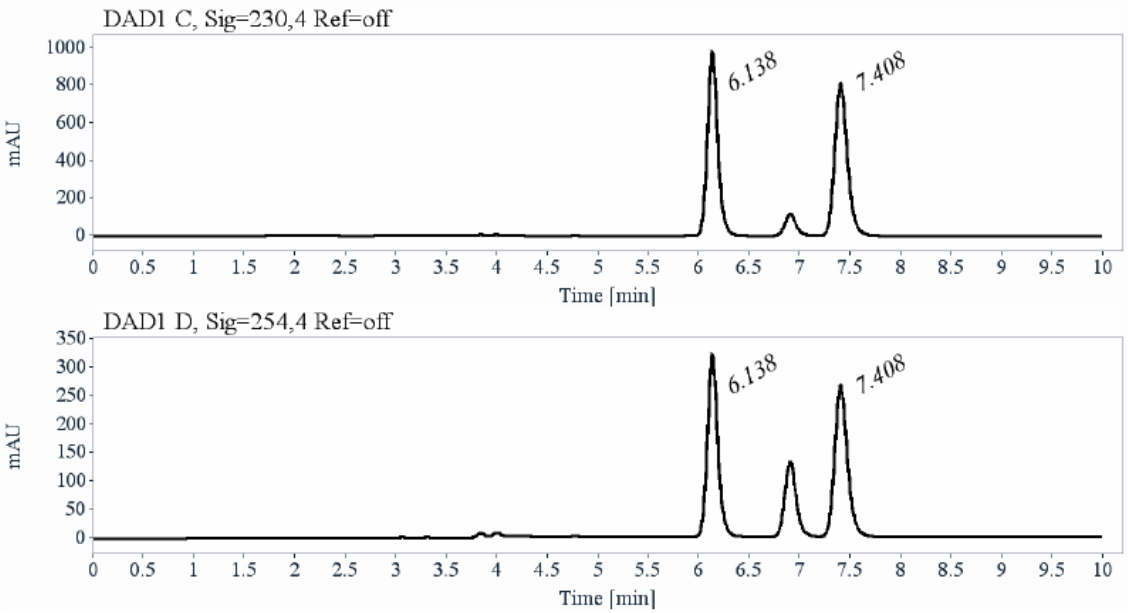
8) HPLC analysis of the product 6

*HPLC analysis of the racemic **6**:*

Column: Lux-Amylose-2

Temperature:

Mobile phase: Heptane/isopropanol (90/10), 1 mL/min



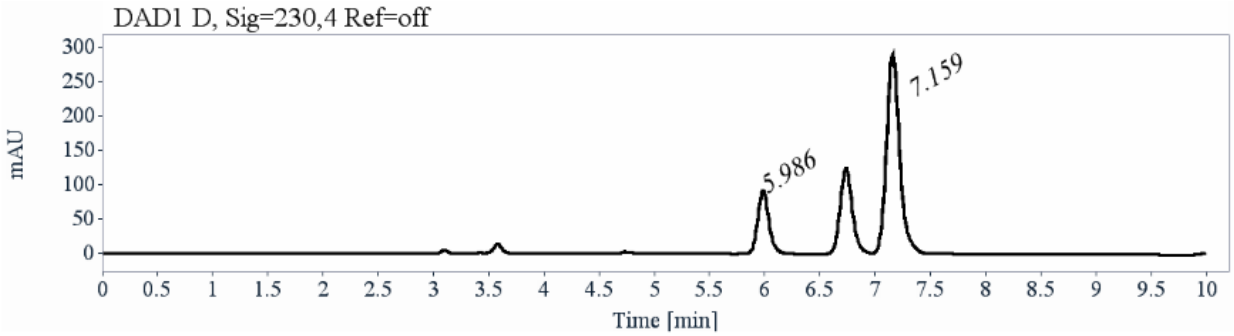
Signal: DAD1 C, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.14	7053	49.90	1.08		
7.41	7082	50.10	1.51	1.40	6.16
Sum	14135	100.00			

Signal: DAD1 D, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.14	2318	49.84	1.08		
7.41	2332	50.16	1.51	1.40	6.12
Sum	4650	100.00			

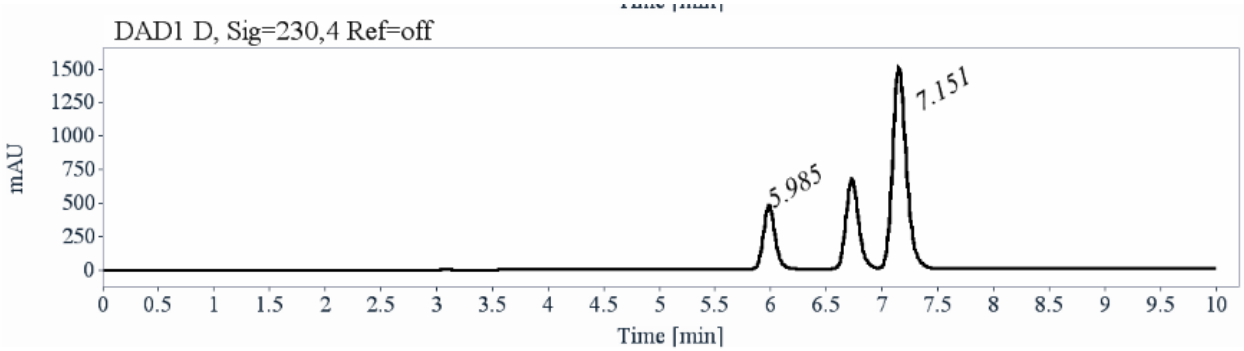
*HPLC analysis of **6** resulting from the reaction performed with **4p** (table 1, entry 1):*



Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.99	644	21.37	1.03		
7.16	2368	78.63	1.43	1.39	5.99
Sum	3012	100.00			

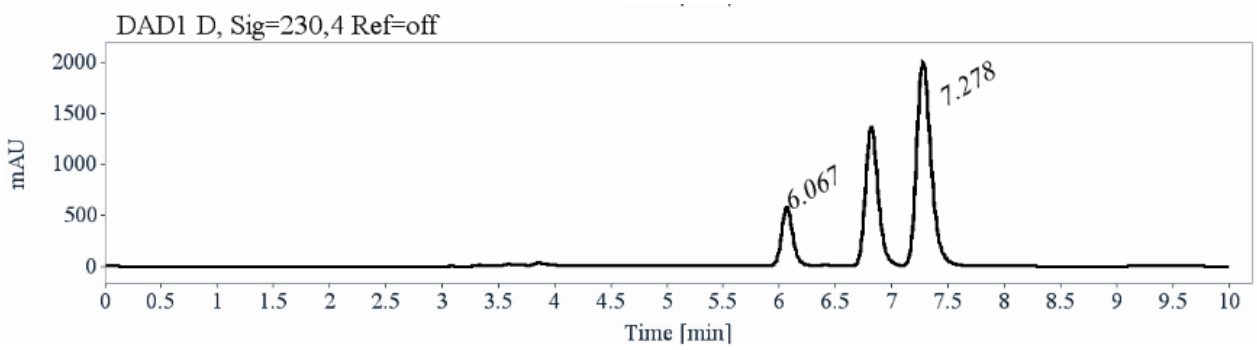
*HPLC analysis of **6** resulting from the reaction performed with **4o** (table 1, entry 2):*



Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.98	3417	21.16	1.03		
7.15	12728	78.84	1.42	1.38	5.72
Sum	16145	100.00			

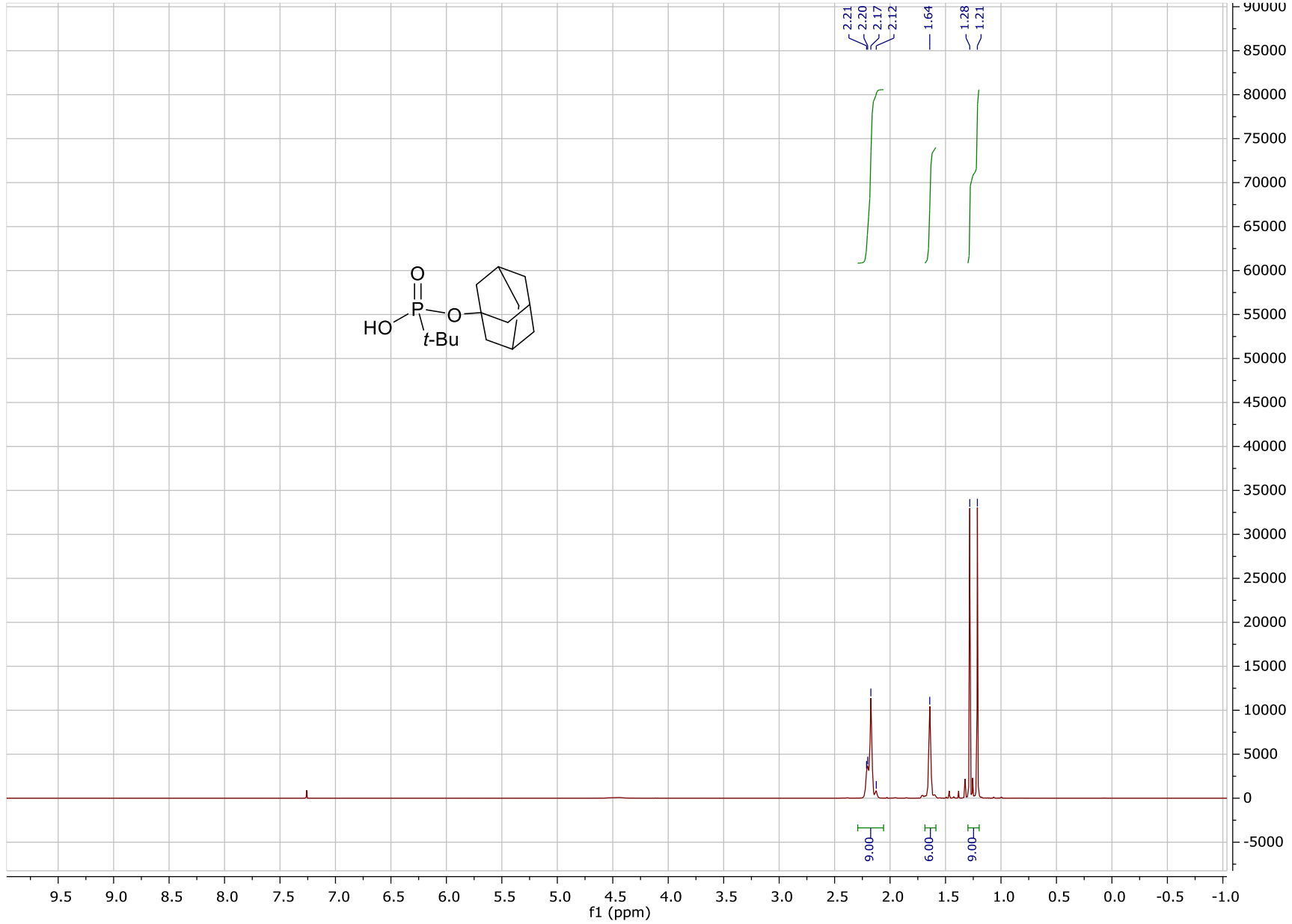
*HPLC analysis of **6** resulting from the reaction performed with **4j** (table 1, entry 3):*



Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.07	4029	18.36	1.06		
7.28	17917	81.64	1.47	1.39	5.91
Sum	21946	100.00			

NMR spectra related to starting materials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1.28
1.21
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HO
O
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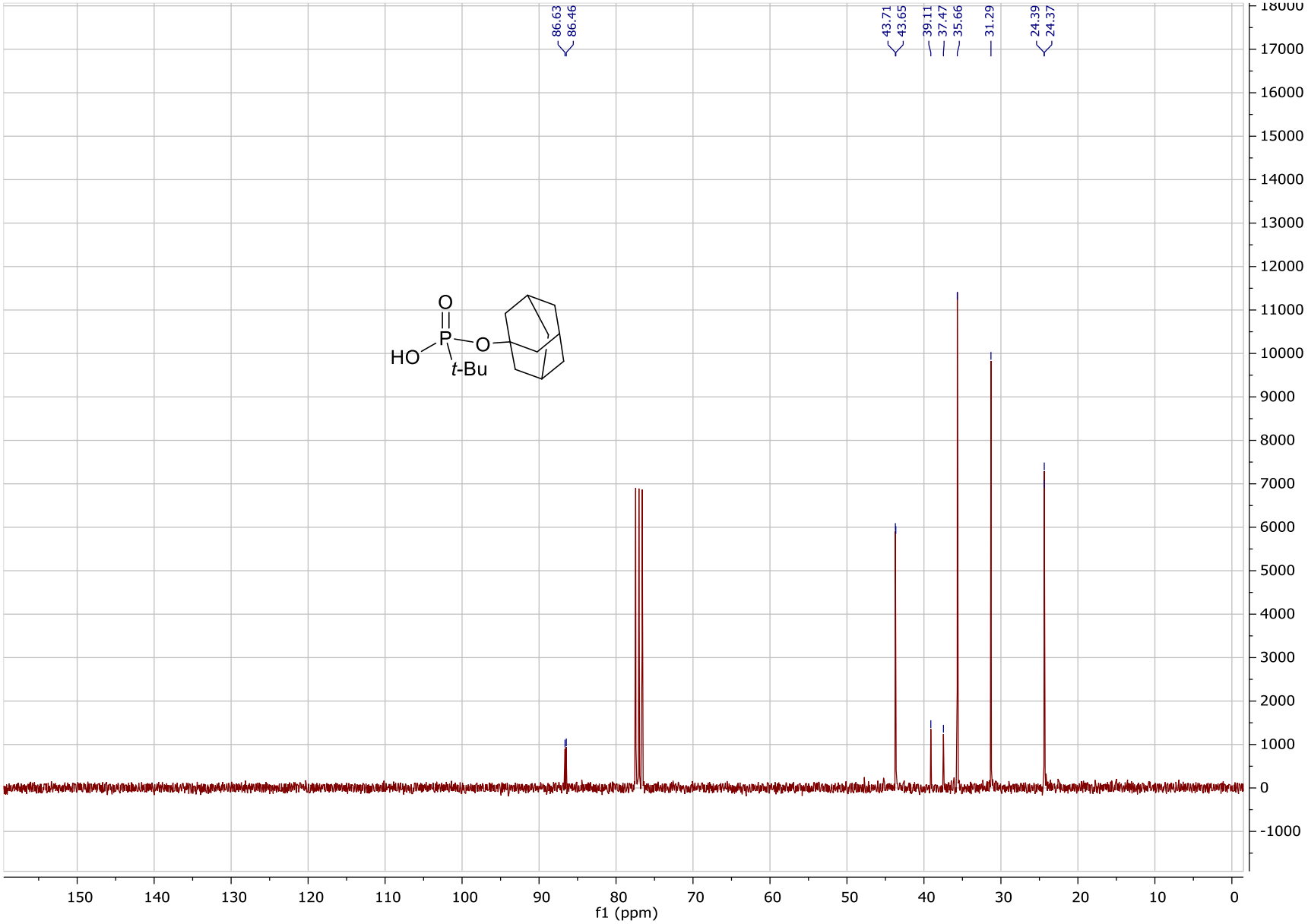
6.00
9.00
f1 (ppm)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86.46
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39.11
37.47
35.66
31.29
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24.37
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P
HO
O
t-Bu
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
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110
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50
40
30
20
10
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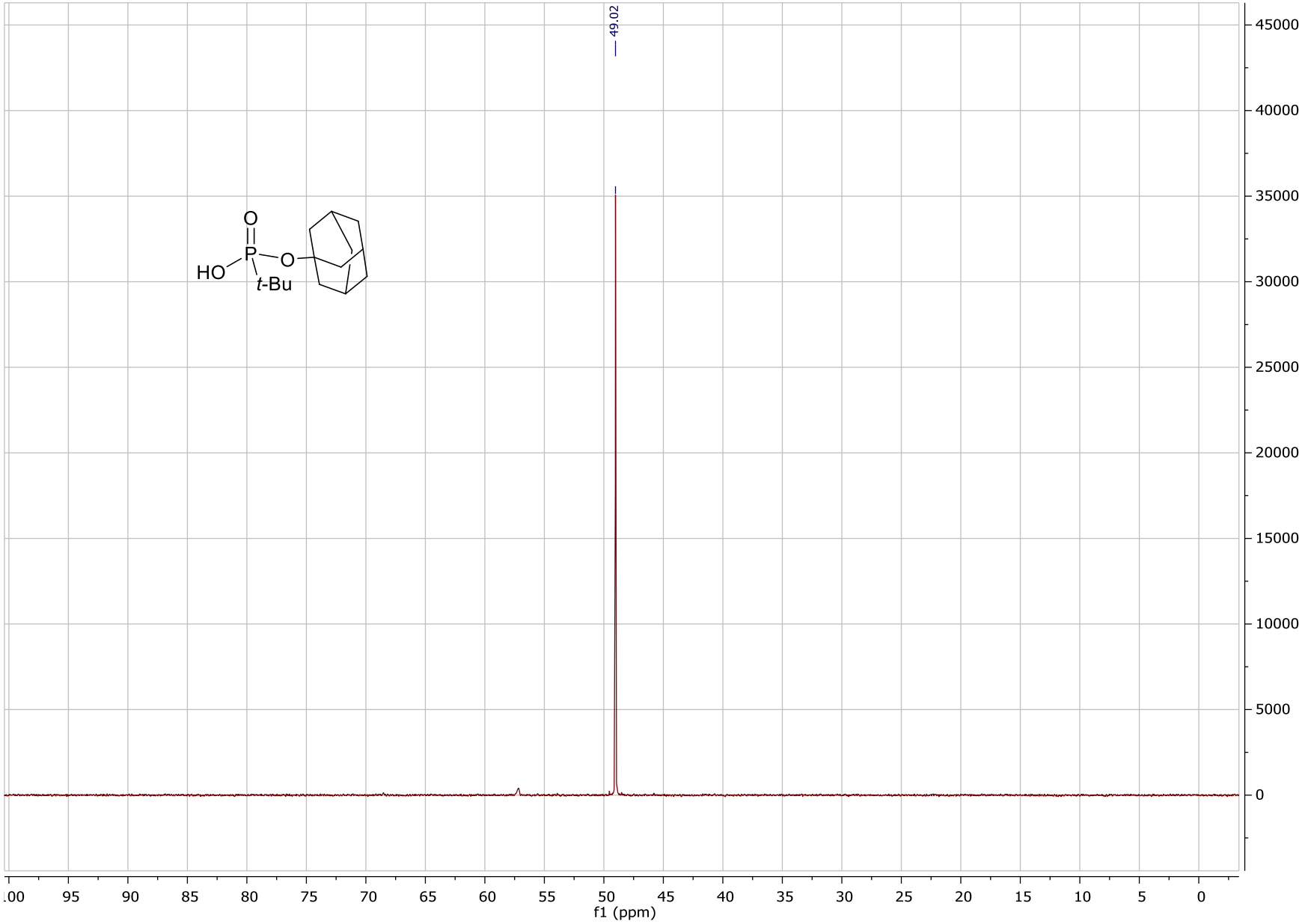
f1 (ppm)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85
80
75
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50
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35
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25
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15
10
5
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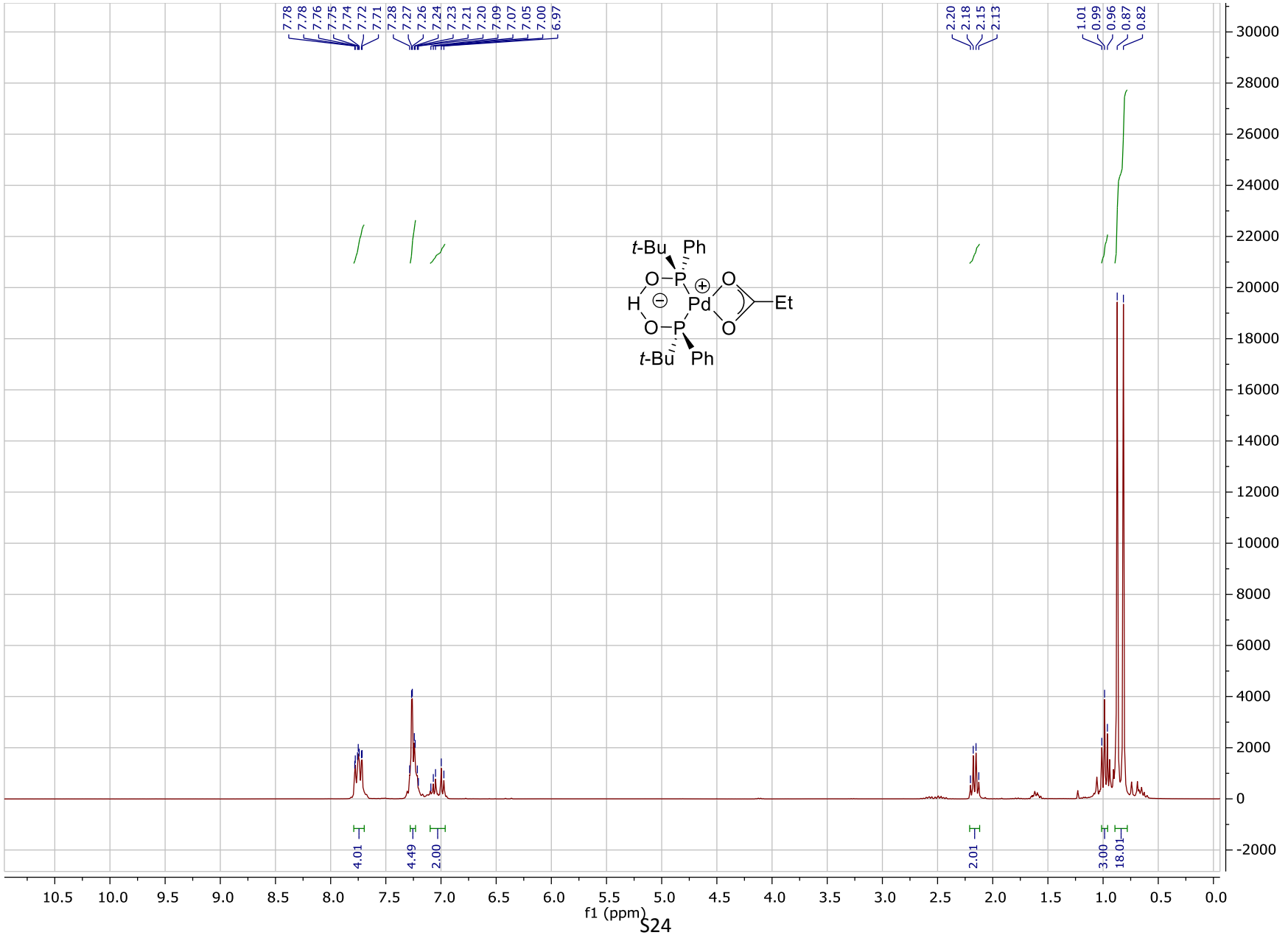
f1 (ppm)

NMR spectra related to the complexes 4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7.23
7.21
7.20
7.09
7.07
7.05
7.00
6.97
2.20
2.18
2.15
2.13
1.01
0.99
0.96
0.87
0.82
t-Bu
Ph
O
P
H
Pd
Et
t-Bu
Ph
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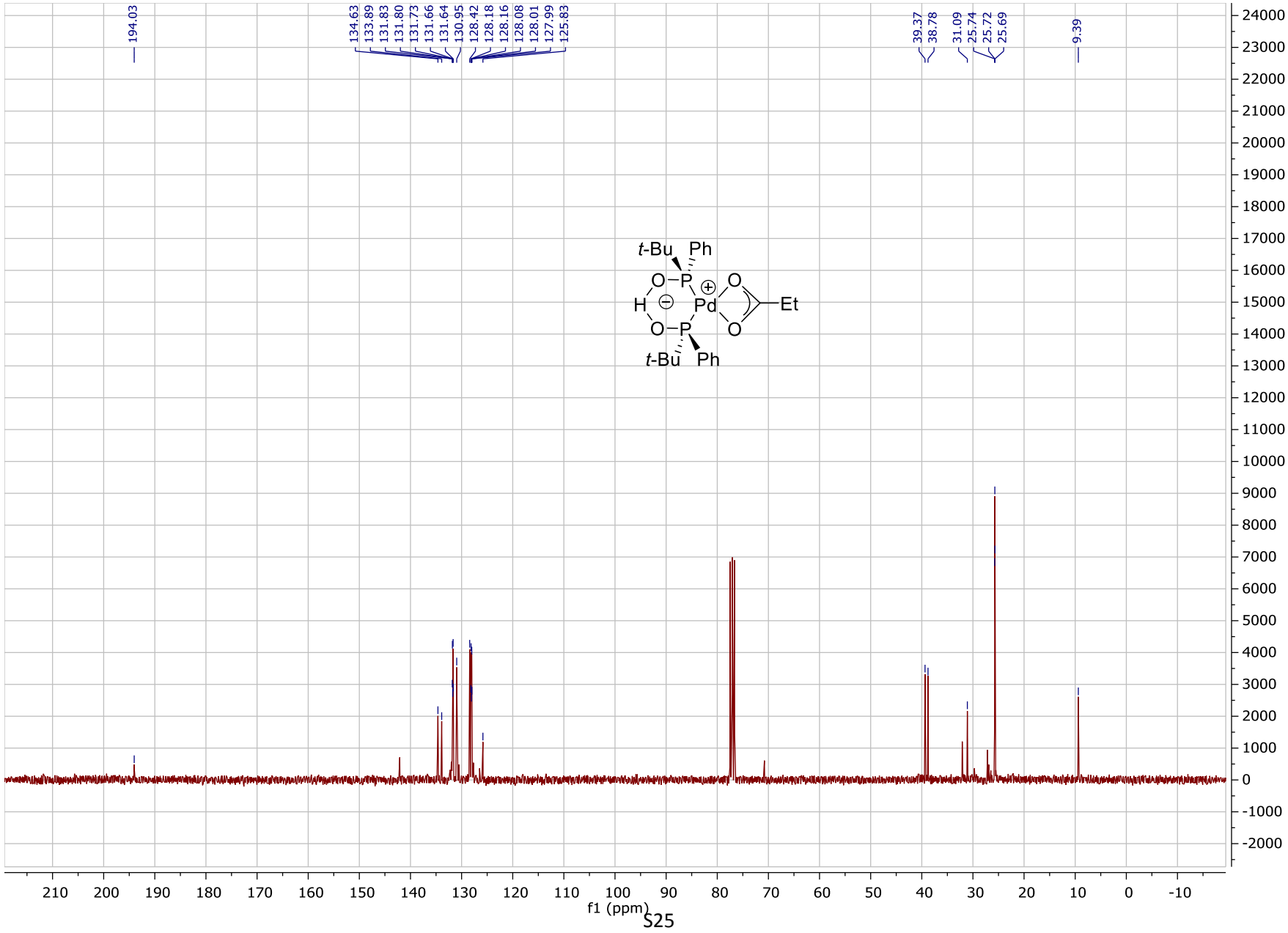
2.01
3.00
18.01
f1 (ppm)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131.73
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131.64
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39.37
38.78
31.09
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Ph
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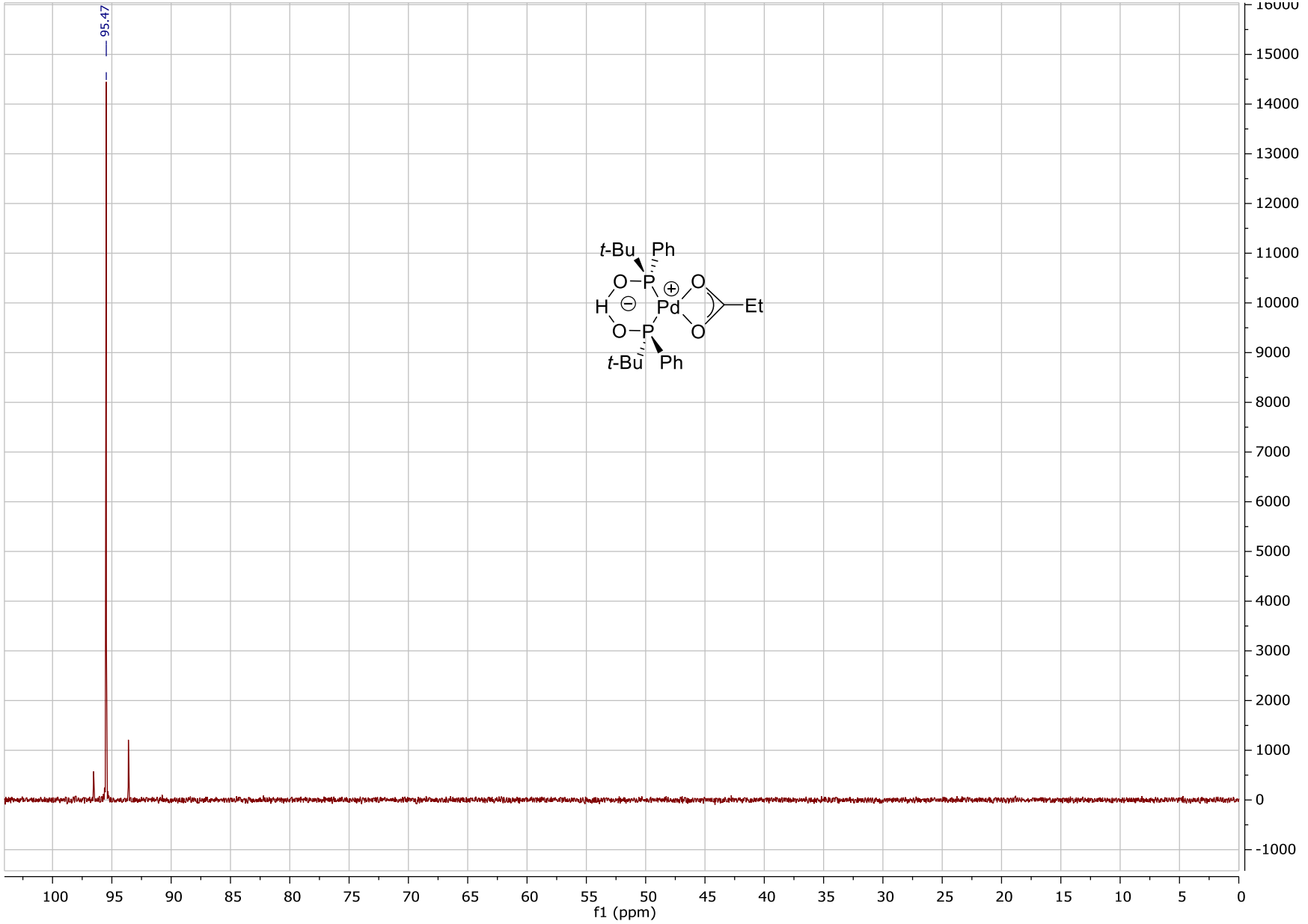
P
H
Pd
Et
t-Bu
Ph
f1 (ppm)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12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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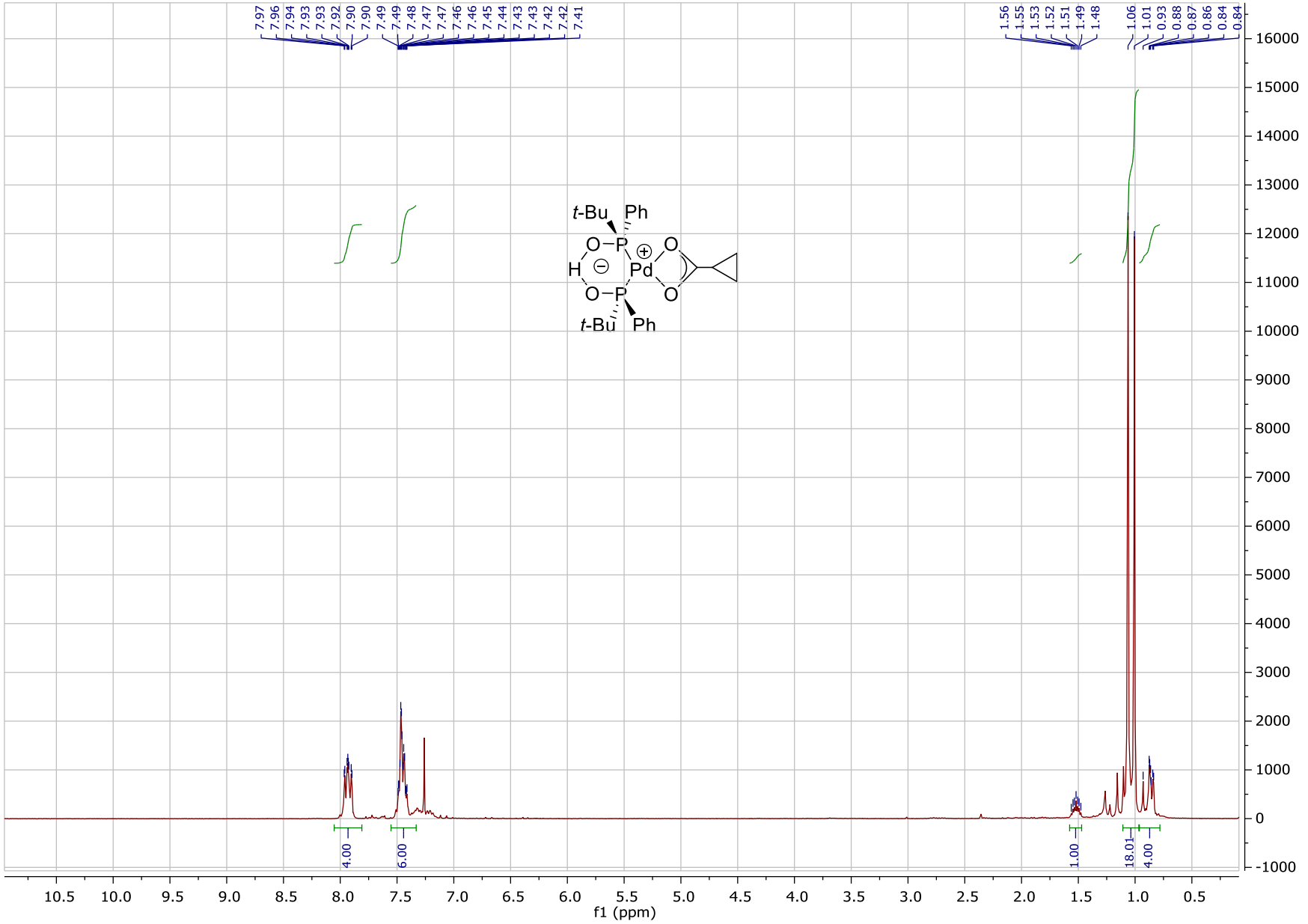
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7.92
7.90
7.90
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7.48
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7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.42
7.41
1.56
1.55
1.53
1.52
1.51
1.49
1.48
1.06
1.01
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Ph
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O
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Ph
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1.00
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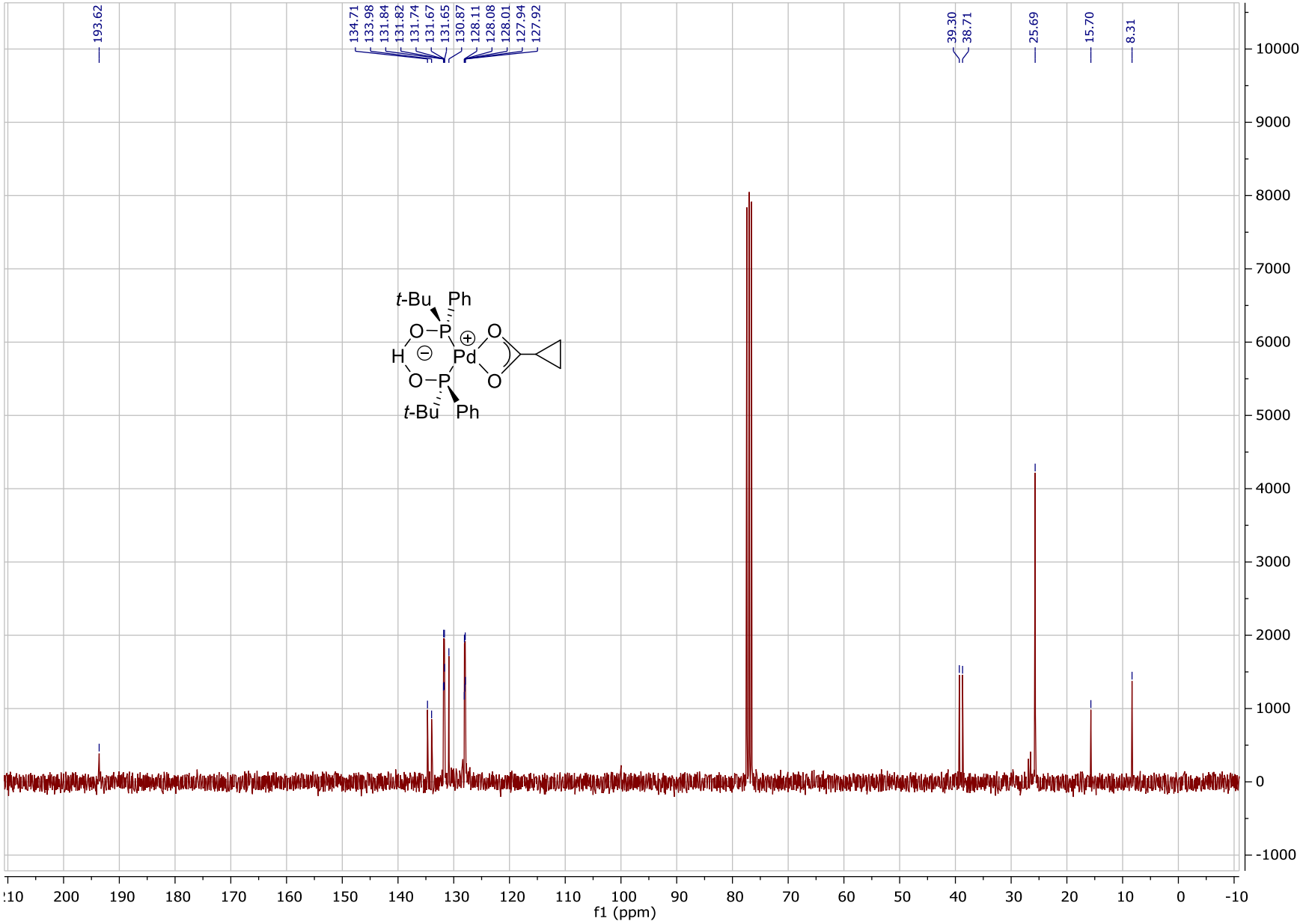
4.00
f1 (ppm)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P
H
Pd
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O
P
O
t-Bu
Ph
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5000
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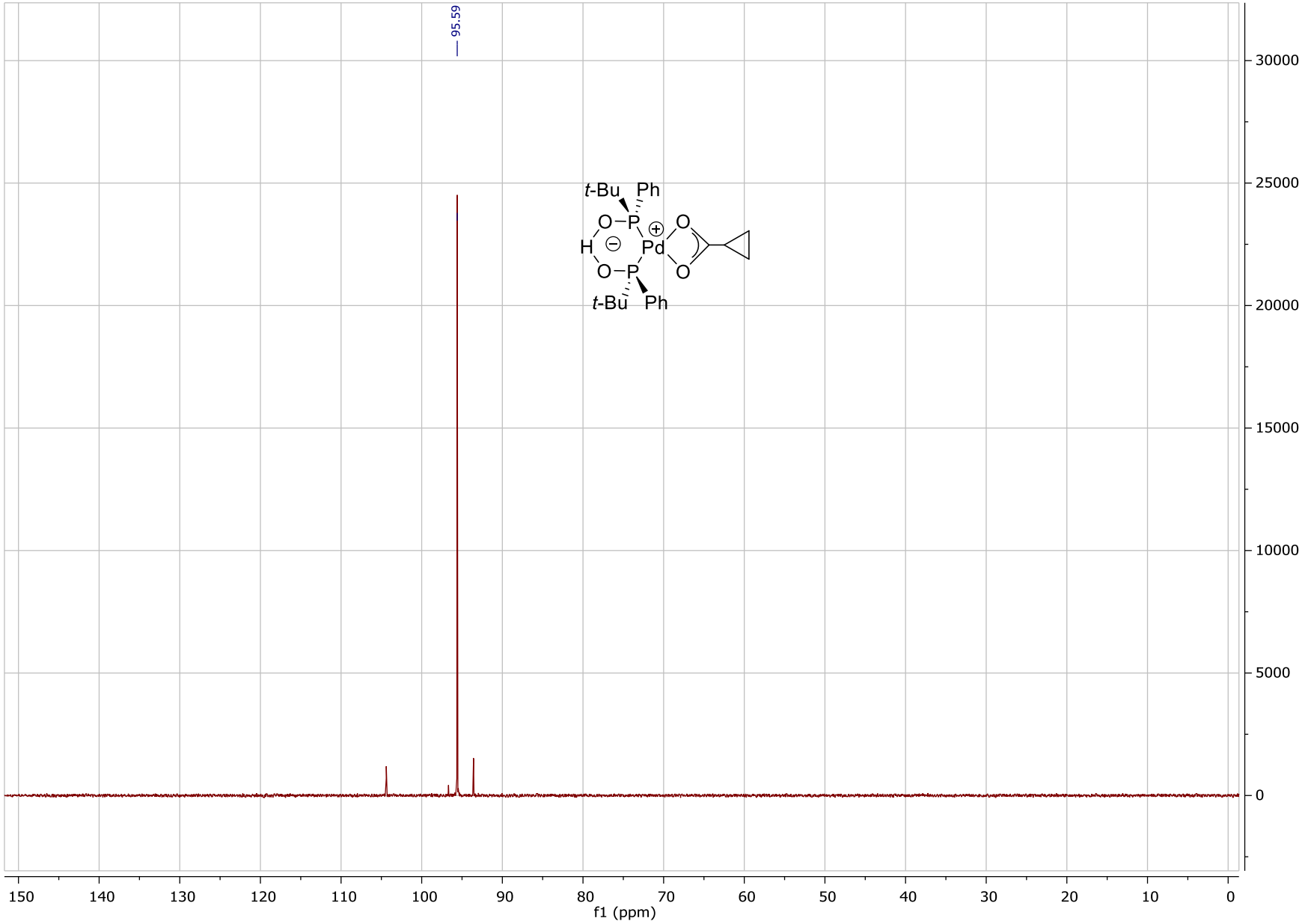
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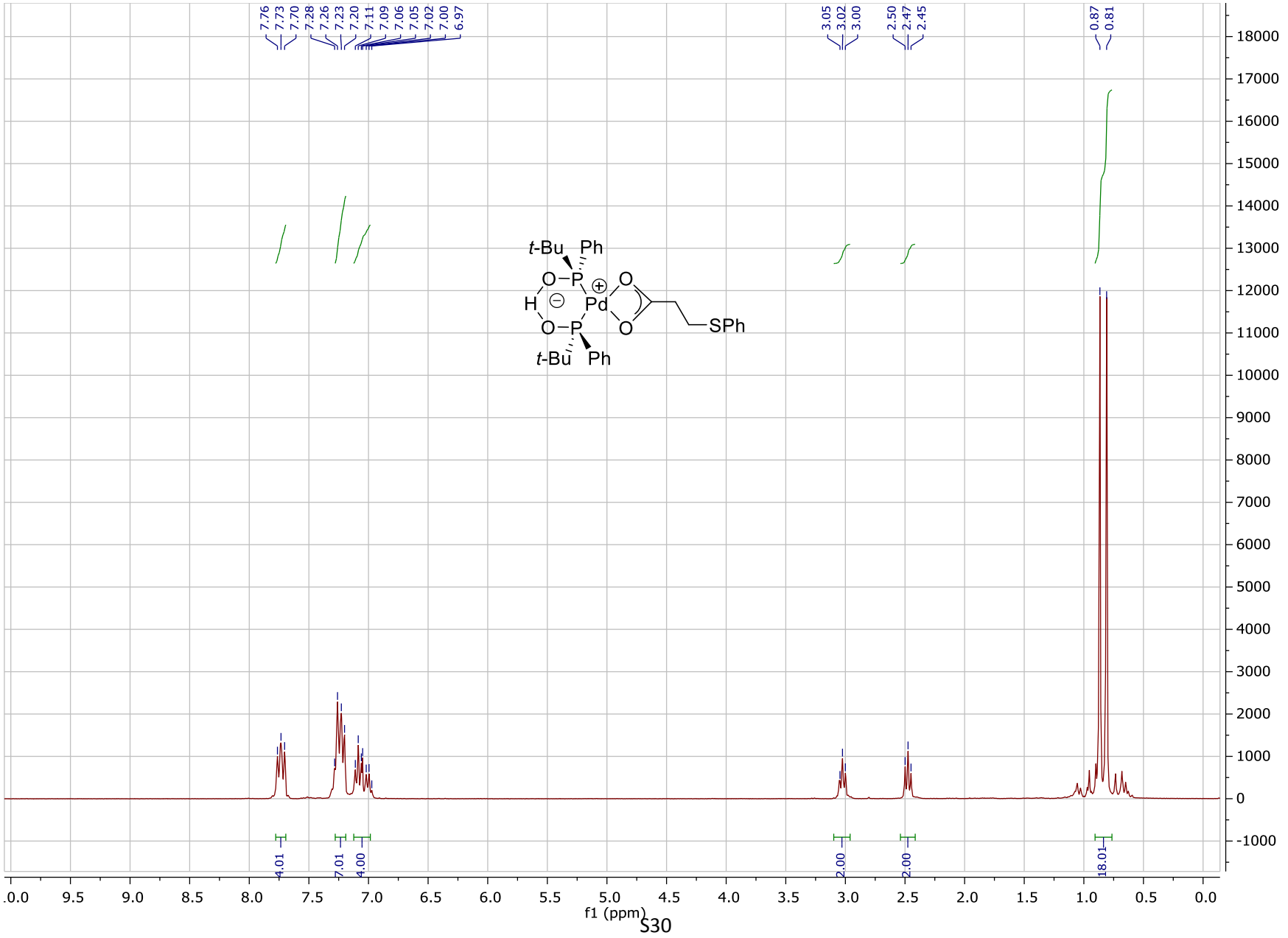
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6.97
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Pd
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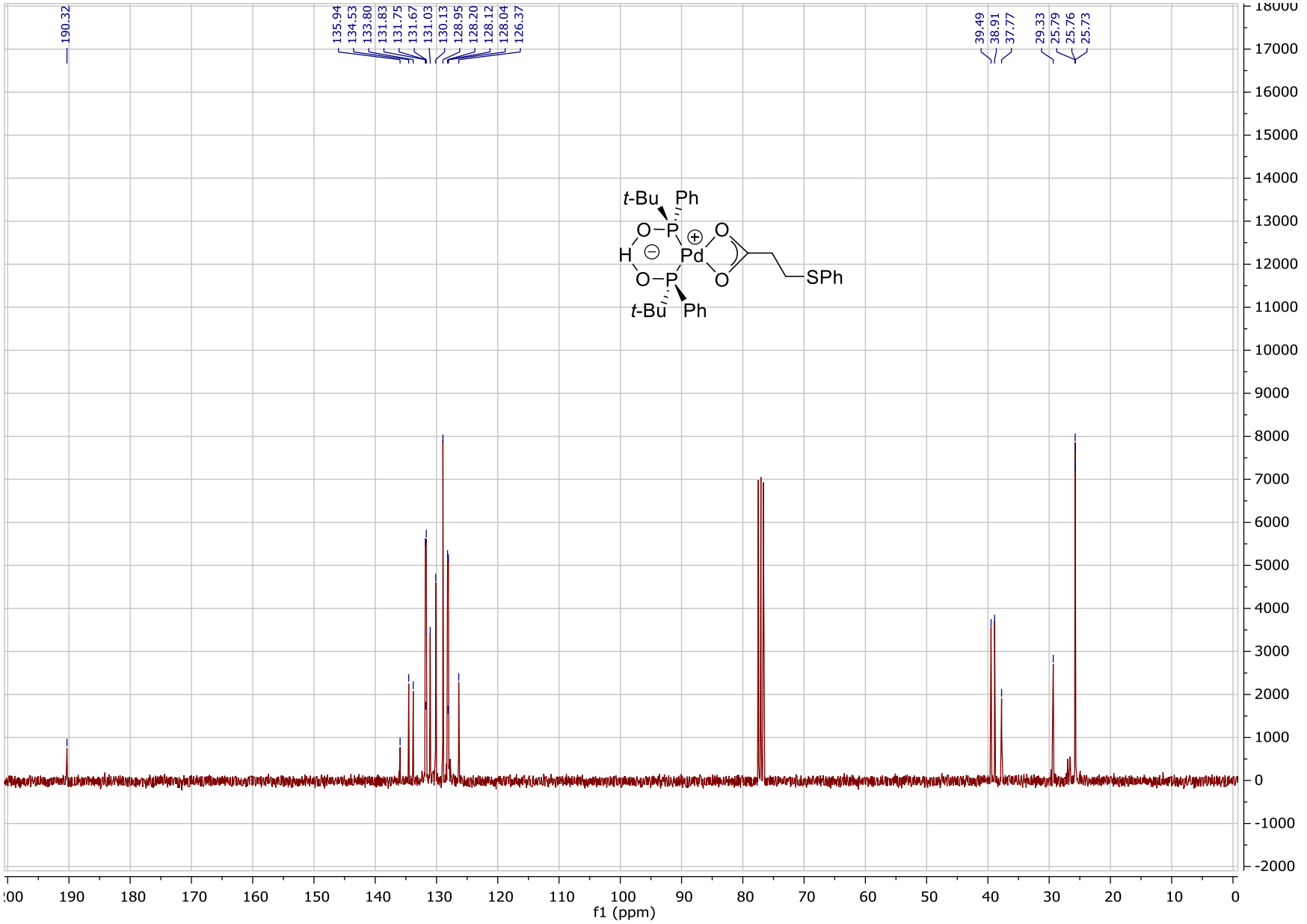
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130.13
128.95
128.20
128.12
128.04
126.37
39.49
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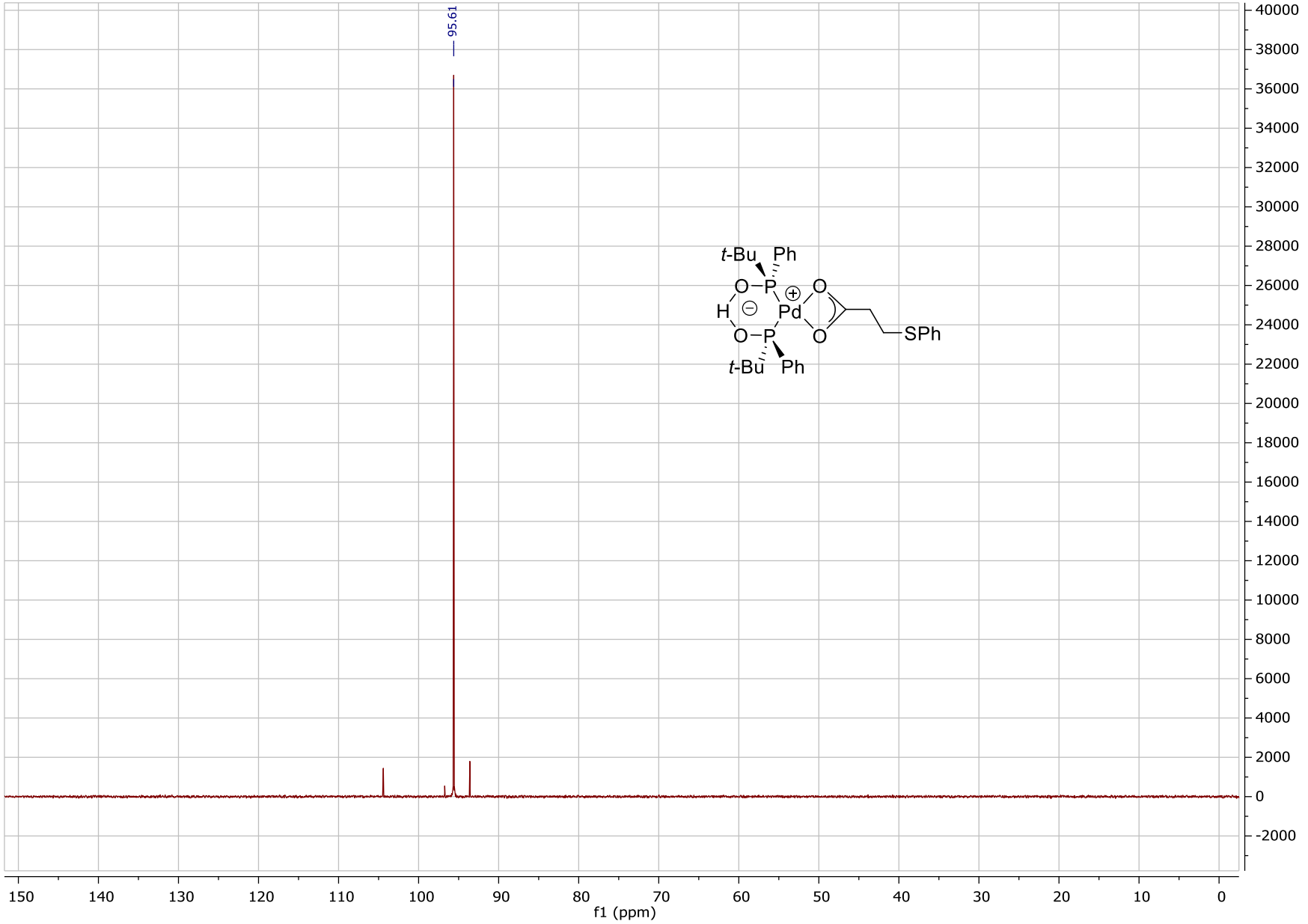
Pd
SPh
f1 (ppm)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O
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Ph
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34000
32000
30000
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26000
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22000
20000
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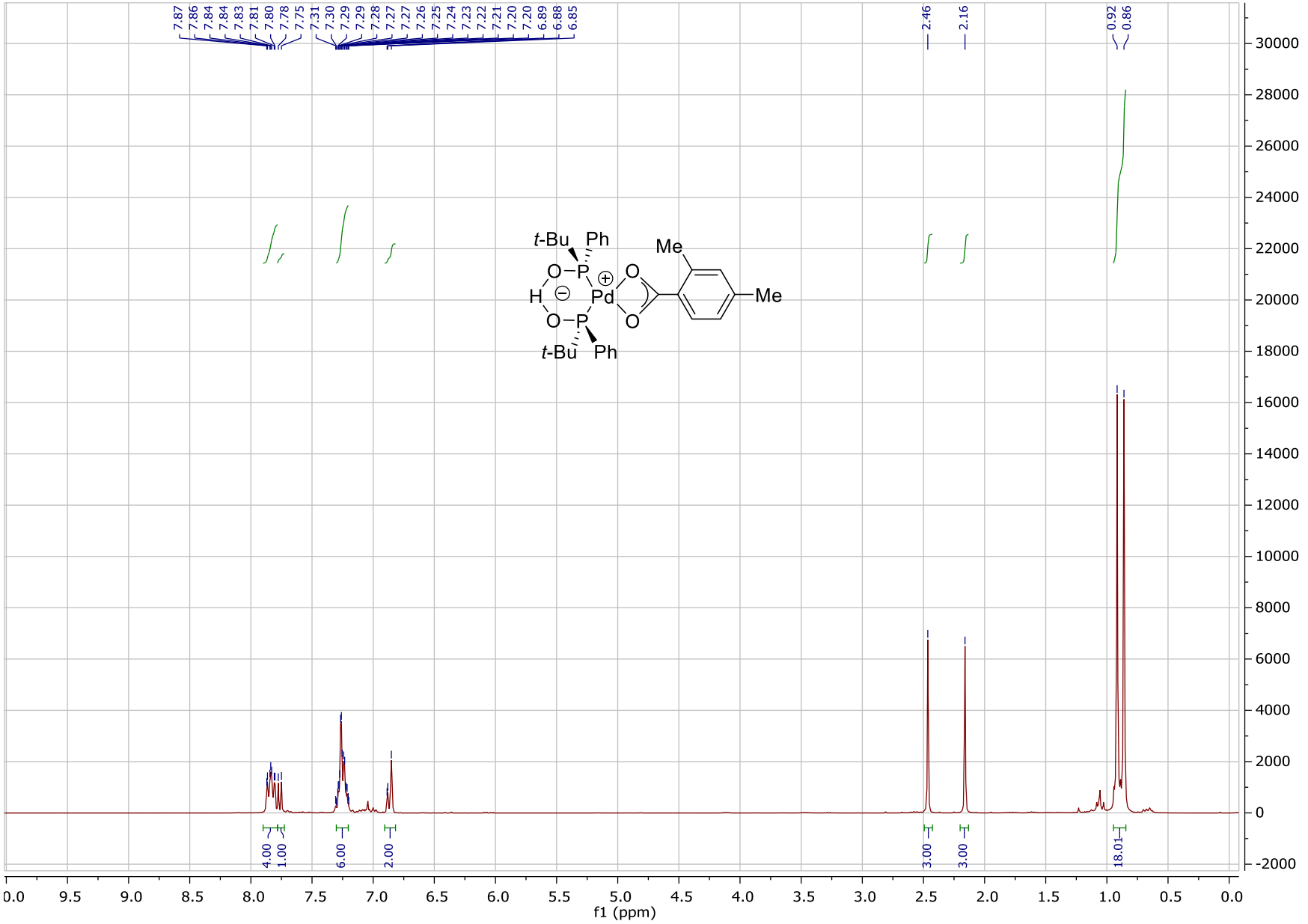
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7.24
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H
Pd
O
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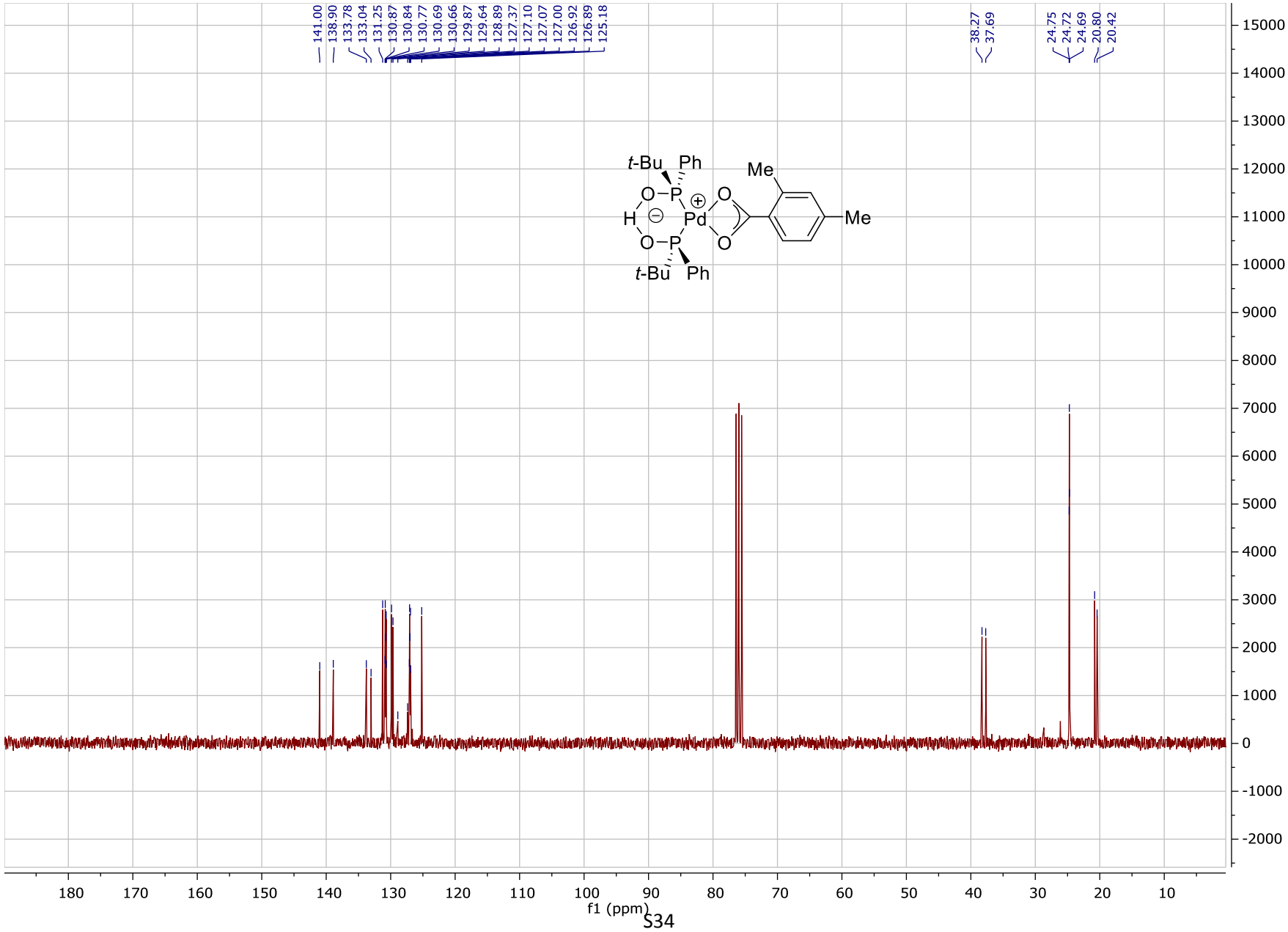
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127.10
127.07
127.00
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126.89
125.18
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24.69
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Pd
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t-Bu
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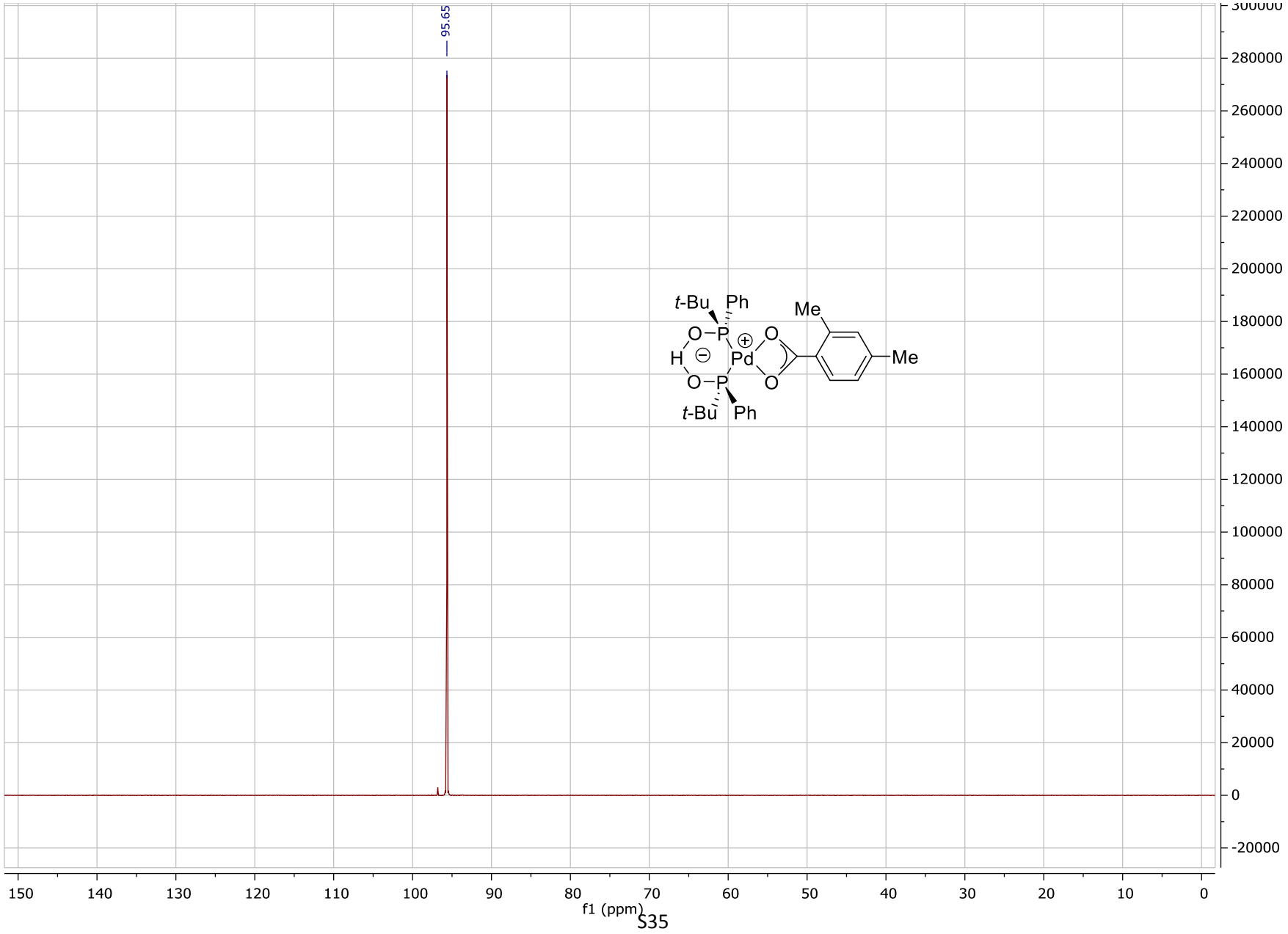
f1 (ppm)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240000
220000
200000
180000
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140000
120000
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60000
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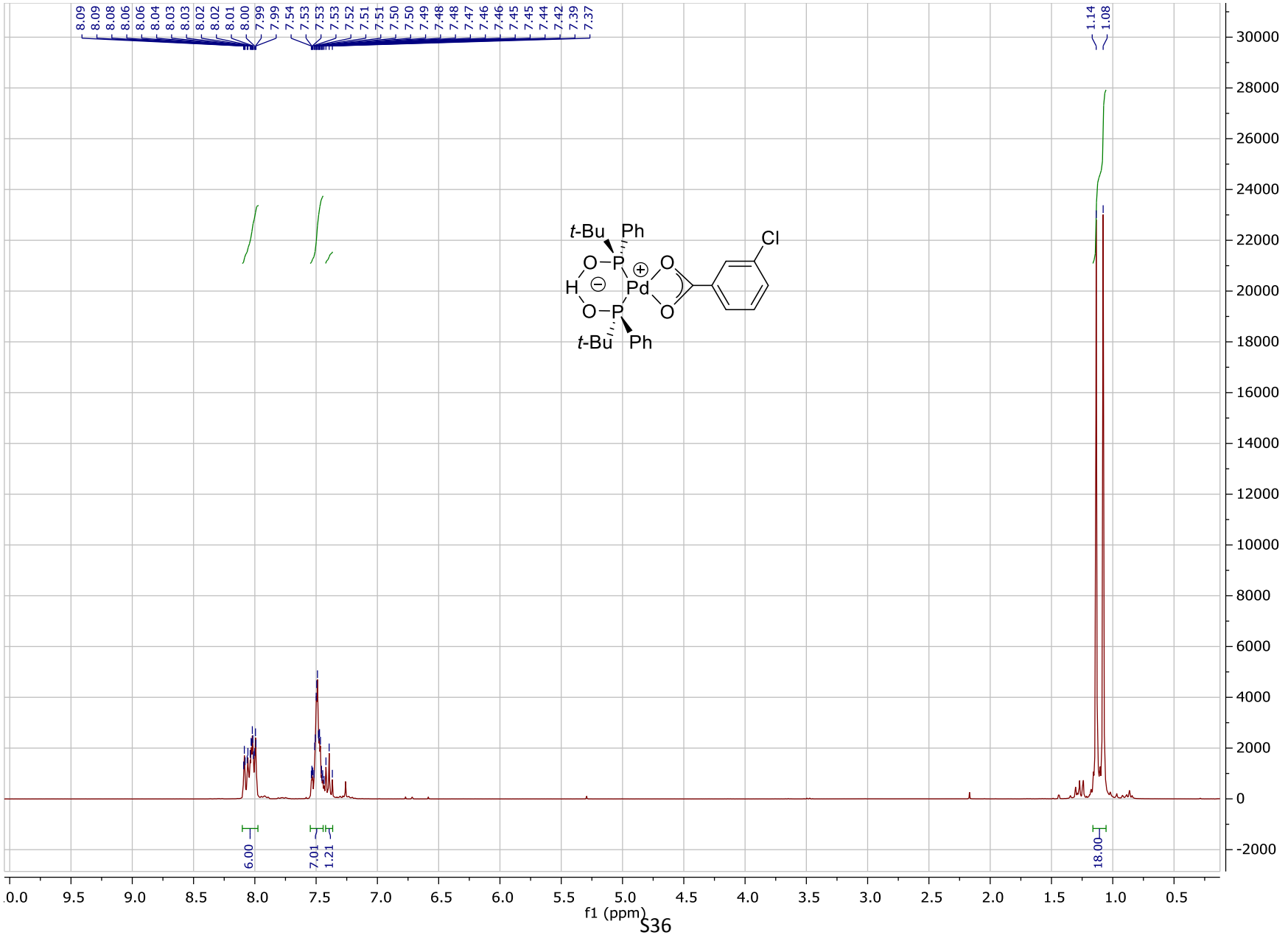
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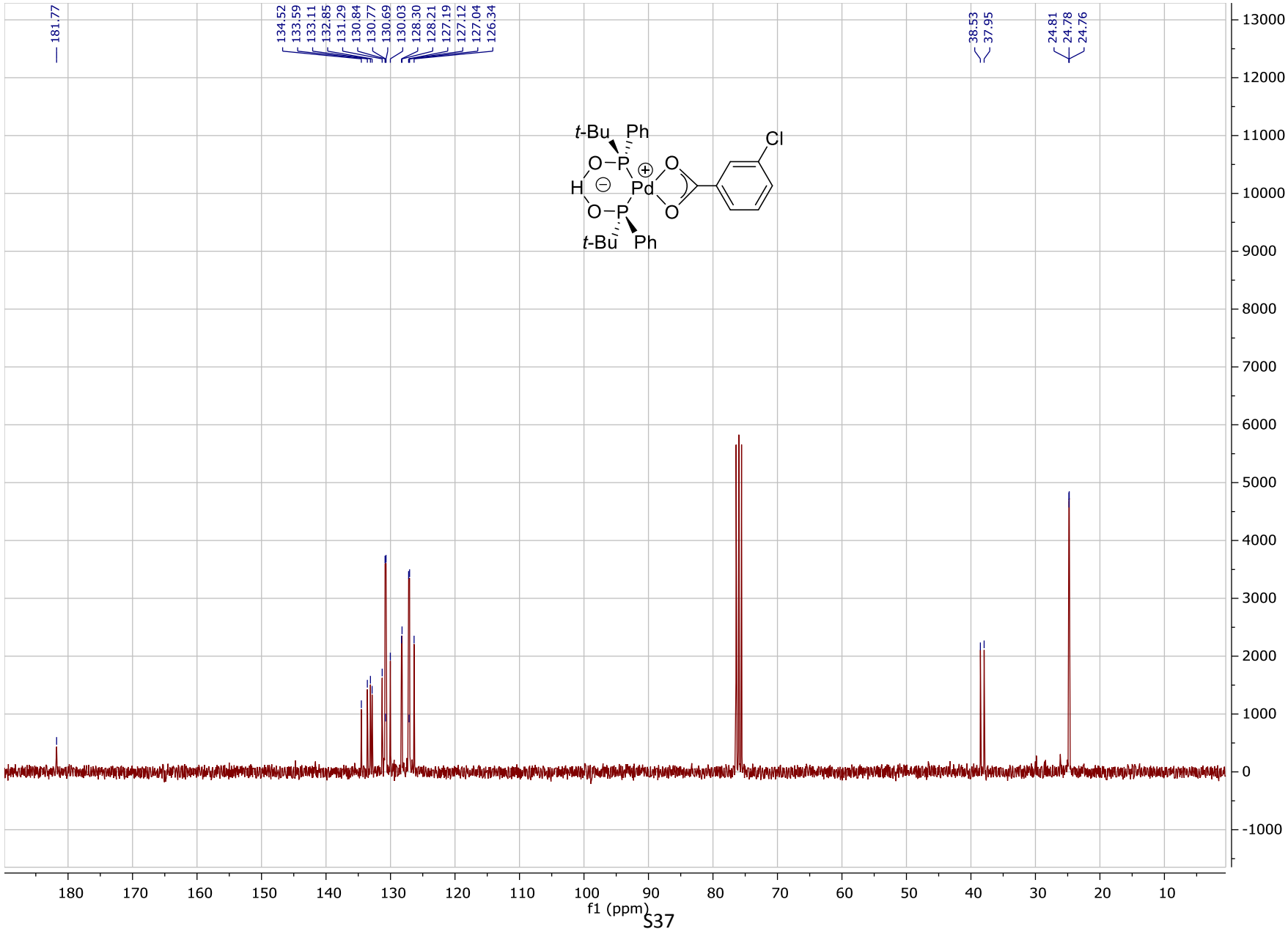
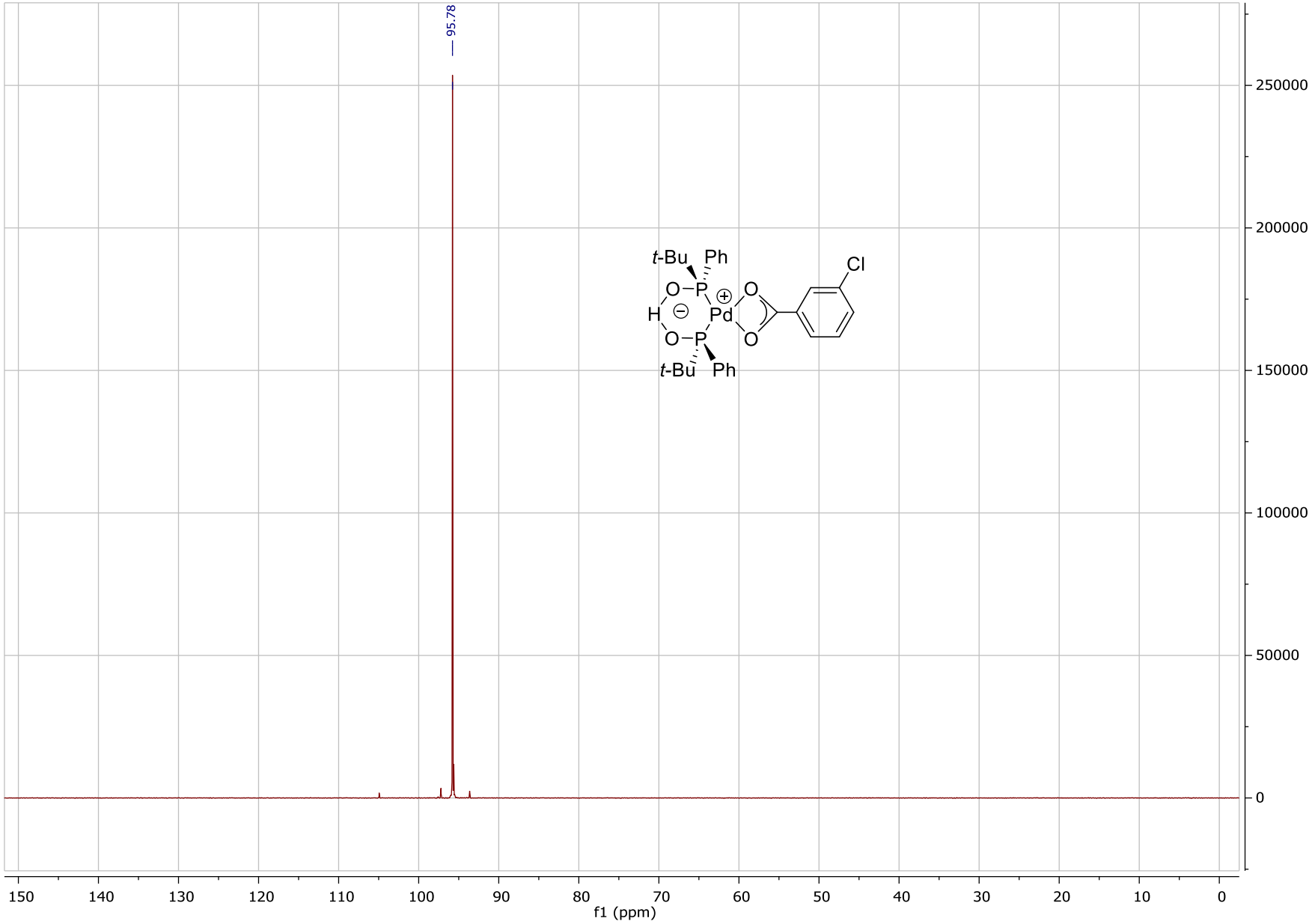
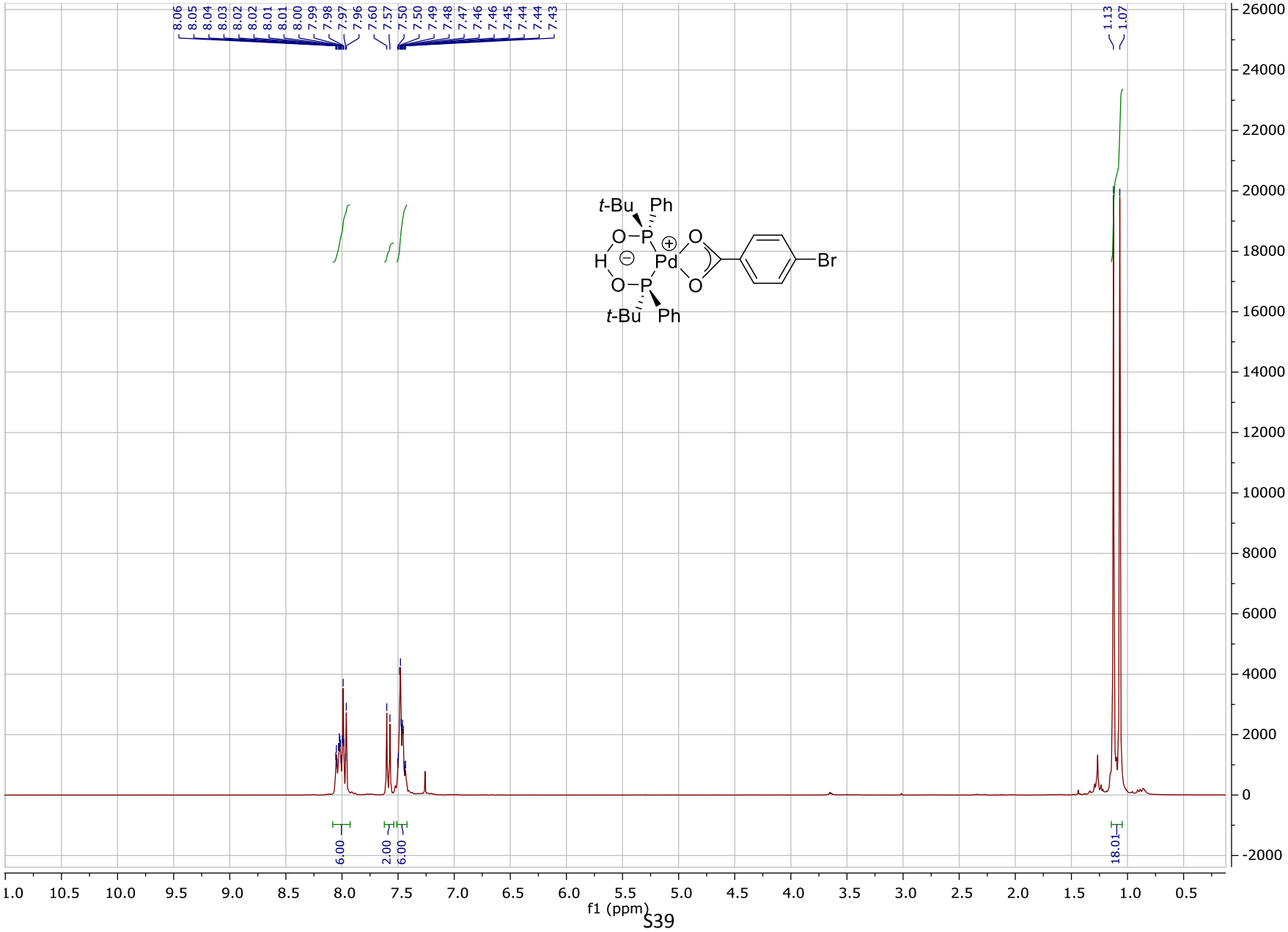
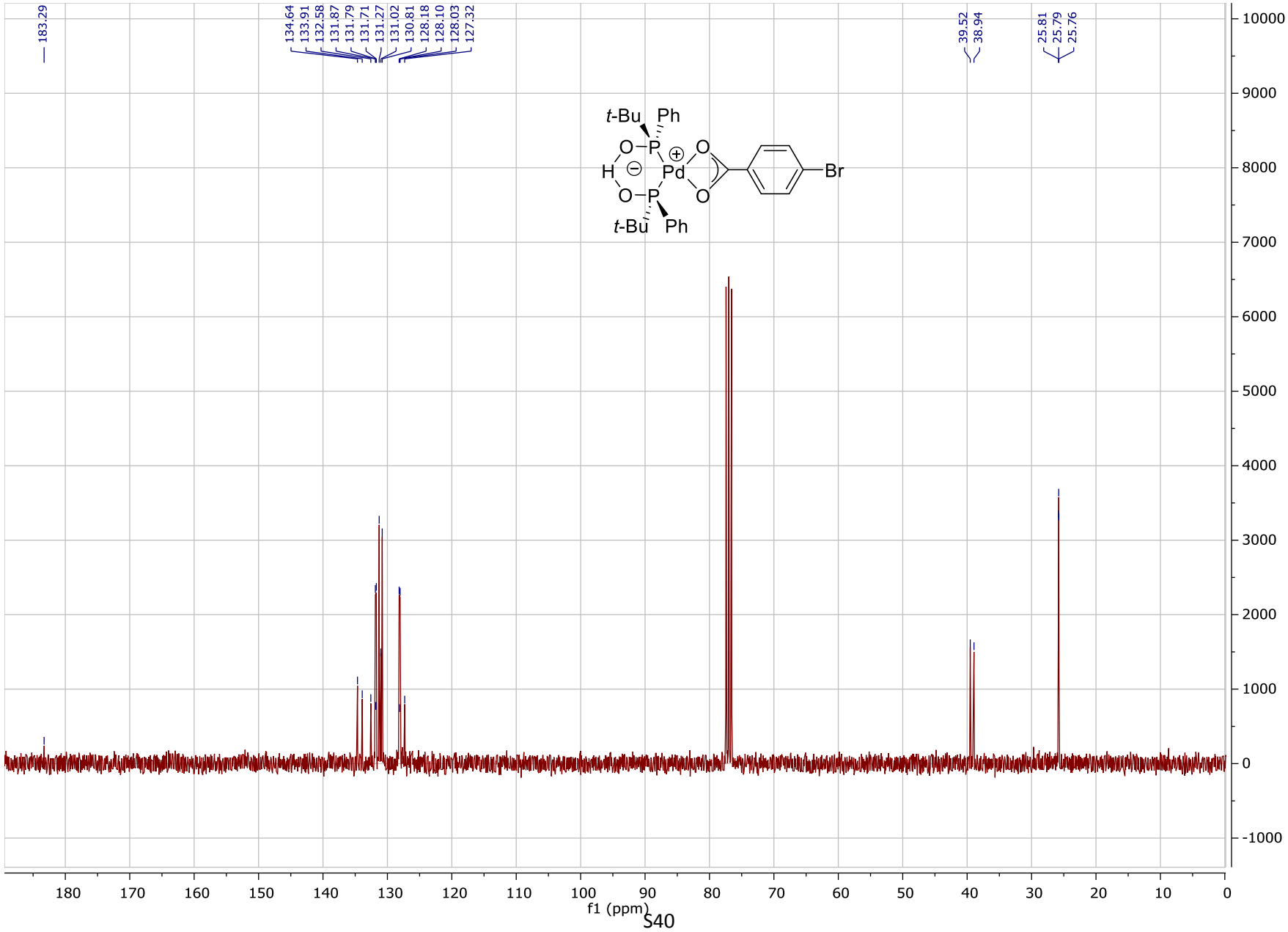
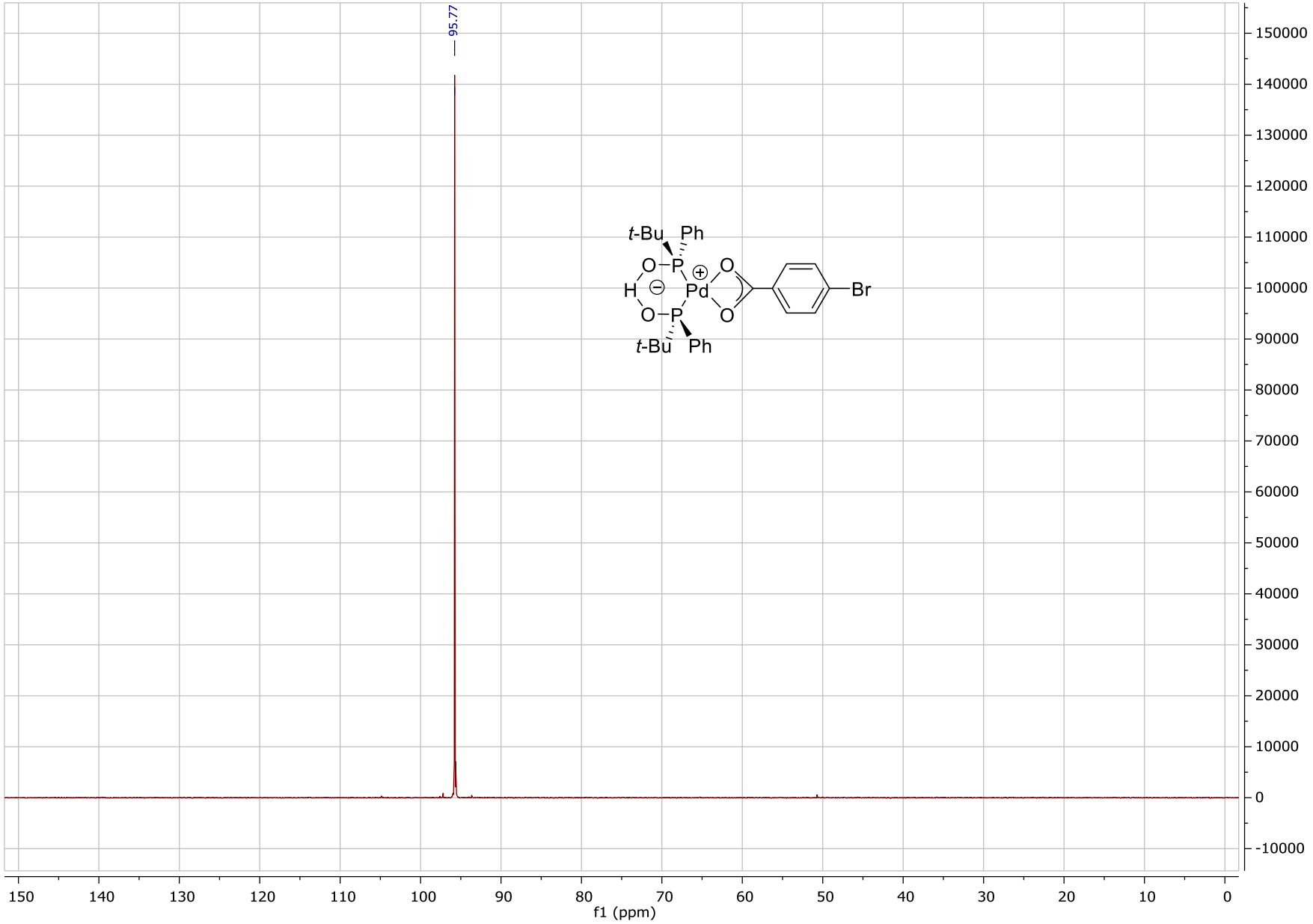
1.14 1.08
t-Bu Ph
O–P
H
Pd
O–P
t-Bu Ph
O
O
O
Cl
6.00
7.01
1.21
18.00
30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

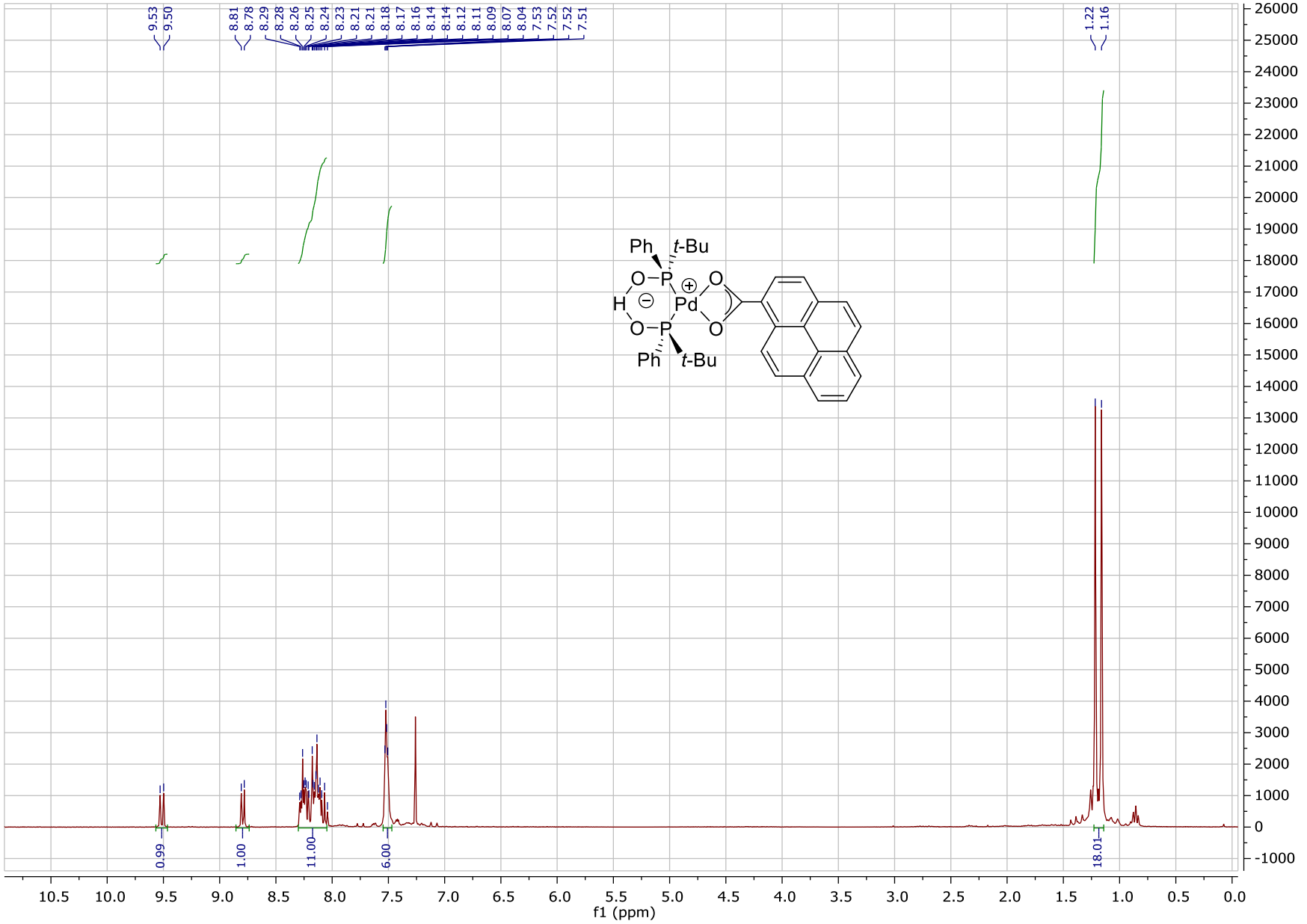

181.77
134.52
133.59
133.11
132.85
131.29
130.84
130.77
130.69
130.03
128.30
128.21
127.19
127.12
127.04
126.34
38.53
37.95
24.81
24.78
24.76
t-Bu
Ph
O
P
H
Pd
Cl
f1 (ppm)

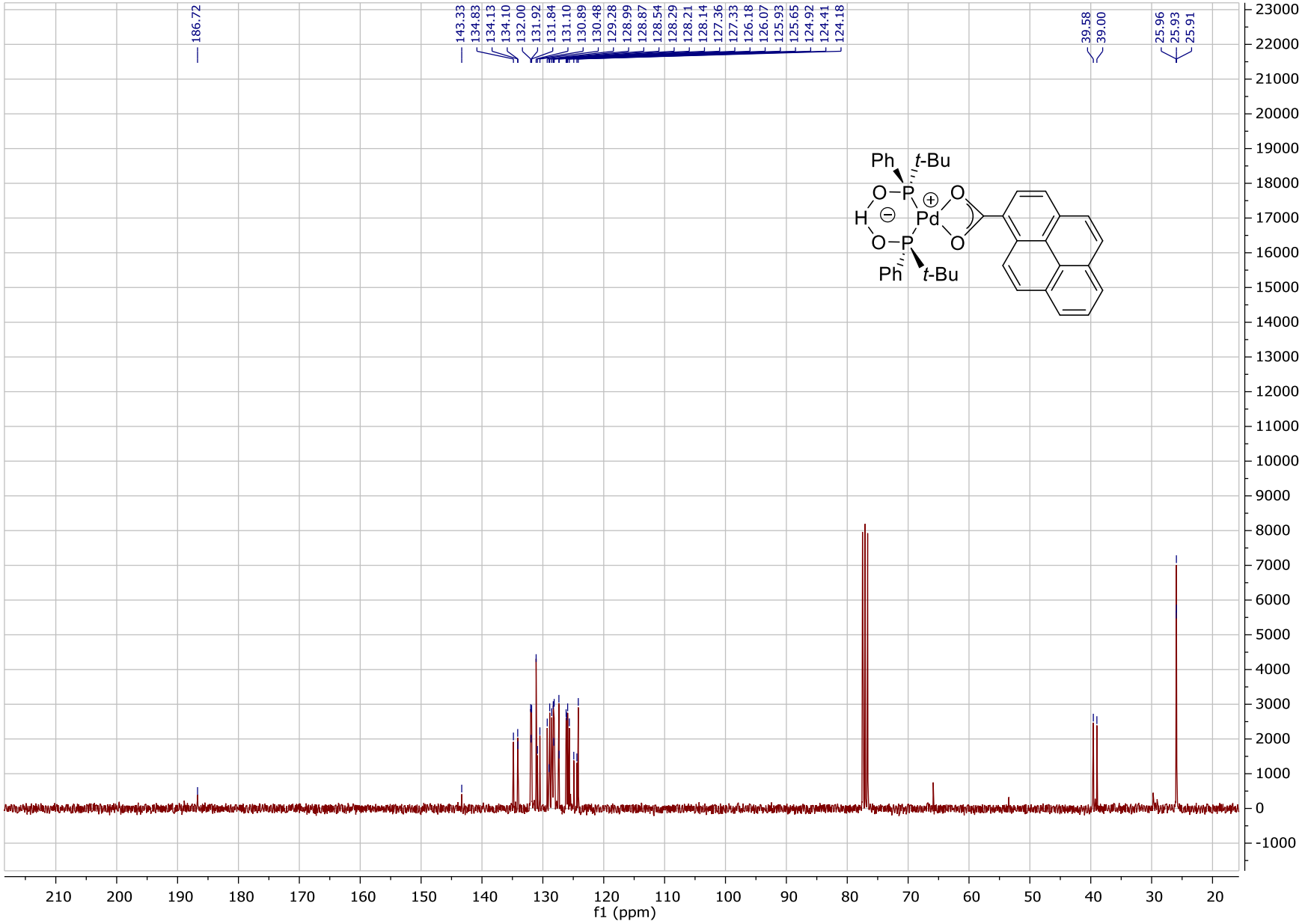

95.78
250000
200000
150000
100000
50000
0
t-Bu
Ph
O
P
H
Pd
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

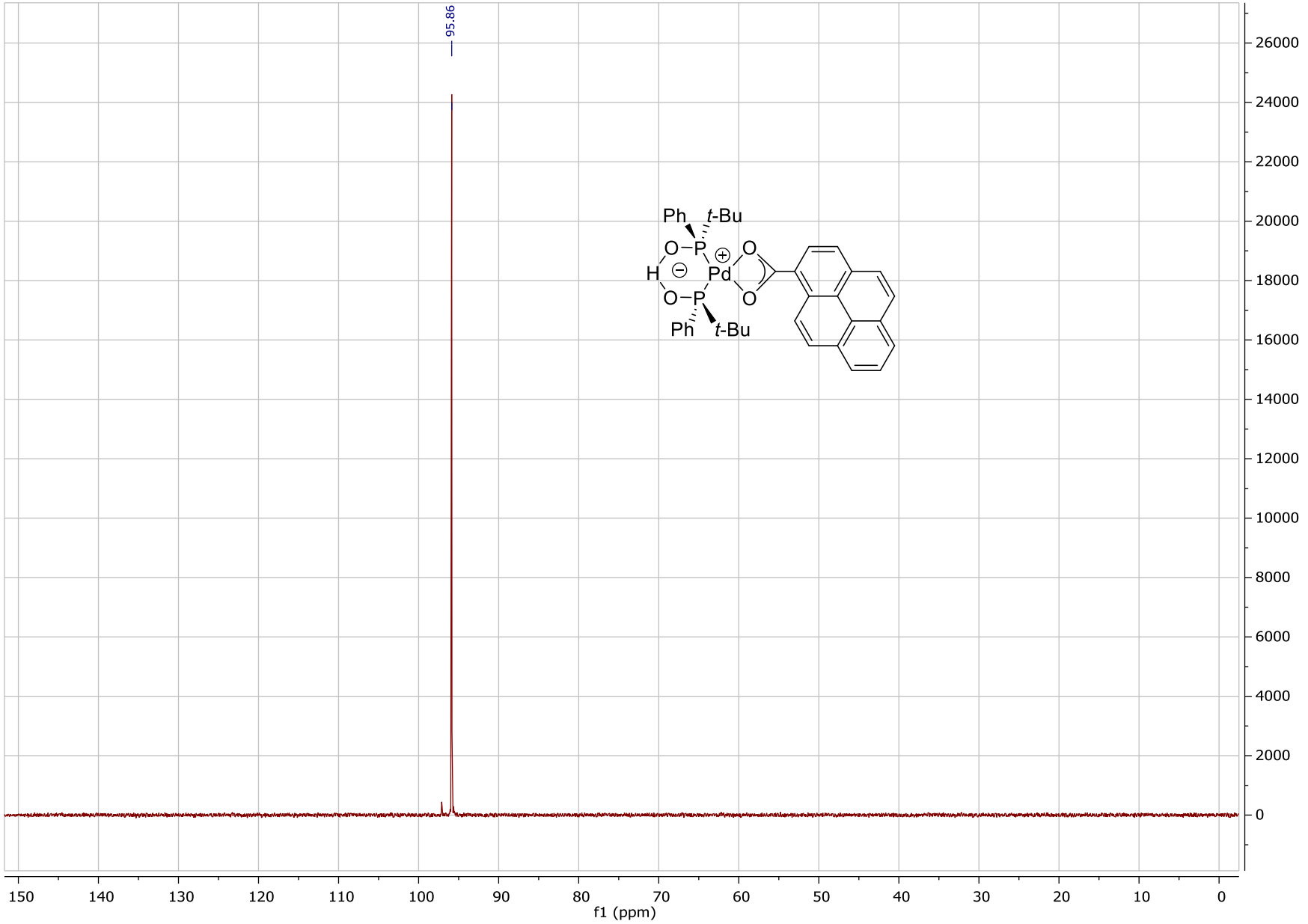

8.06
8.05
8.04
8.03
8.02
8.02
8.01
8.01
8.00
7.99
7.98
7.97
7.96
7.60
7.57
7.50
7.50
7.49
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
1.13
1.07
t-Bu
Ph
O
P
H
Pd
Br
6.00
2.00
6.00
18.01
f1 (ppm)

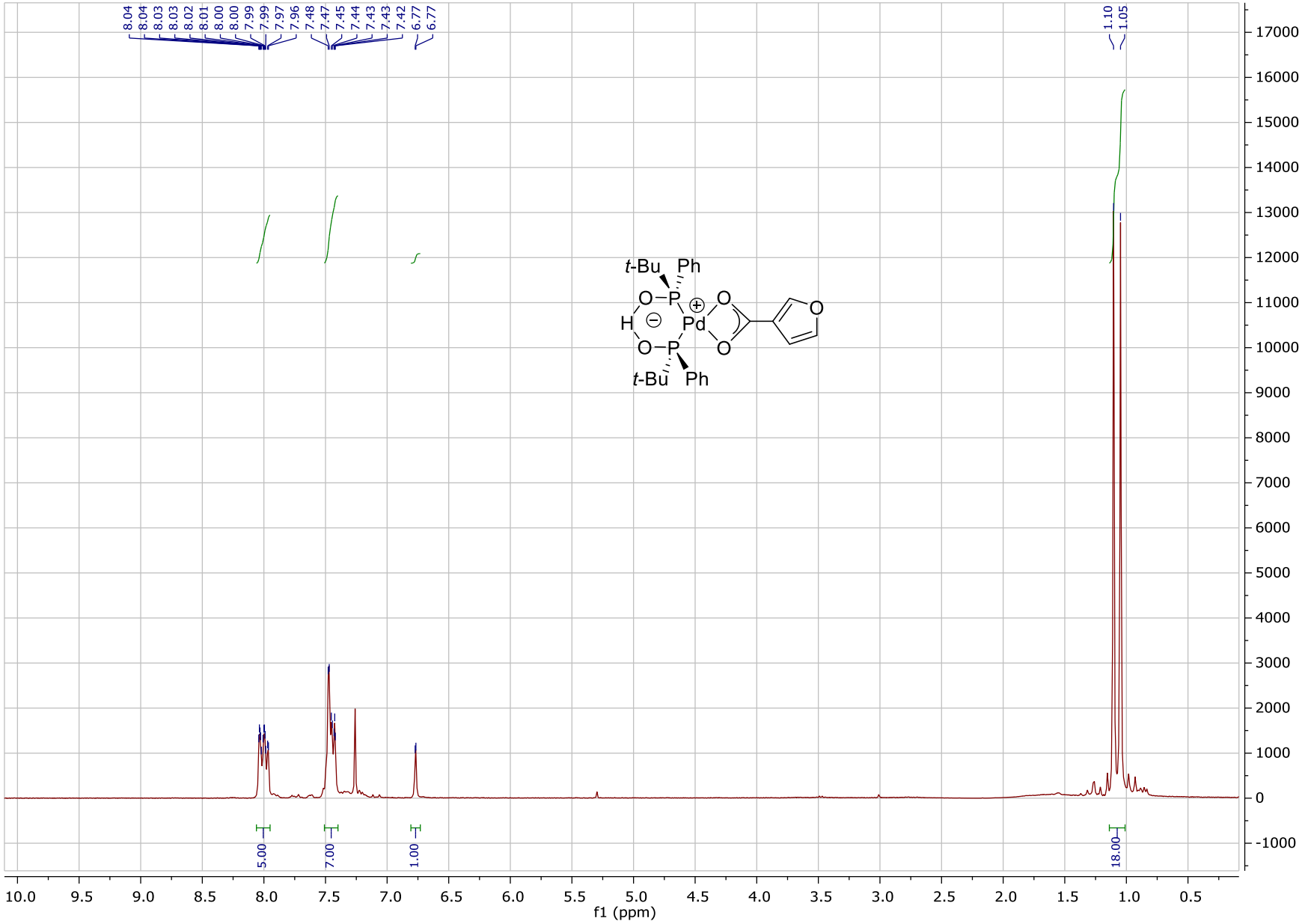

183.29
134.64
133.91
132.58
131.87
131.79
131.71
131.27
131.02
130.81
128.18
128.10
128.03
127.32
39.52
38.94
25.81
25.79
25.76
t-Bu
Ph
O
P
H
Pd
Br
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

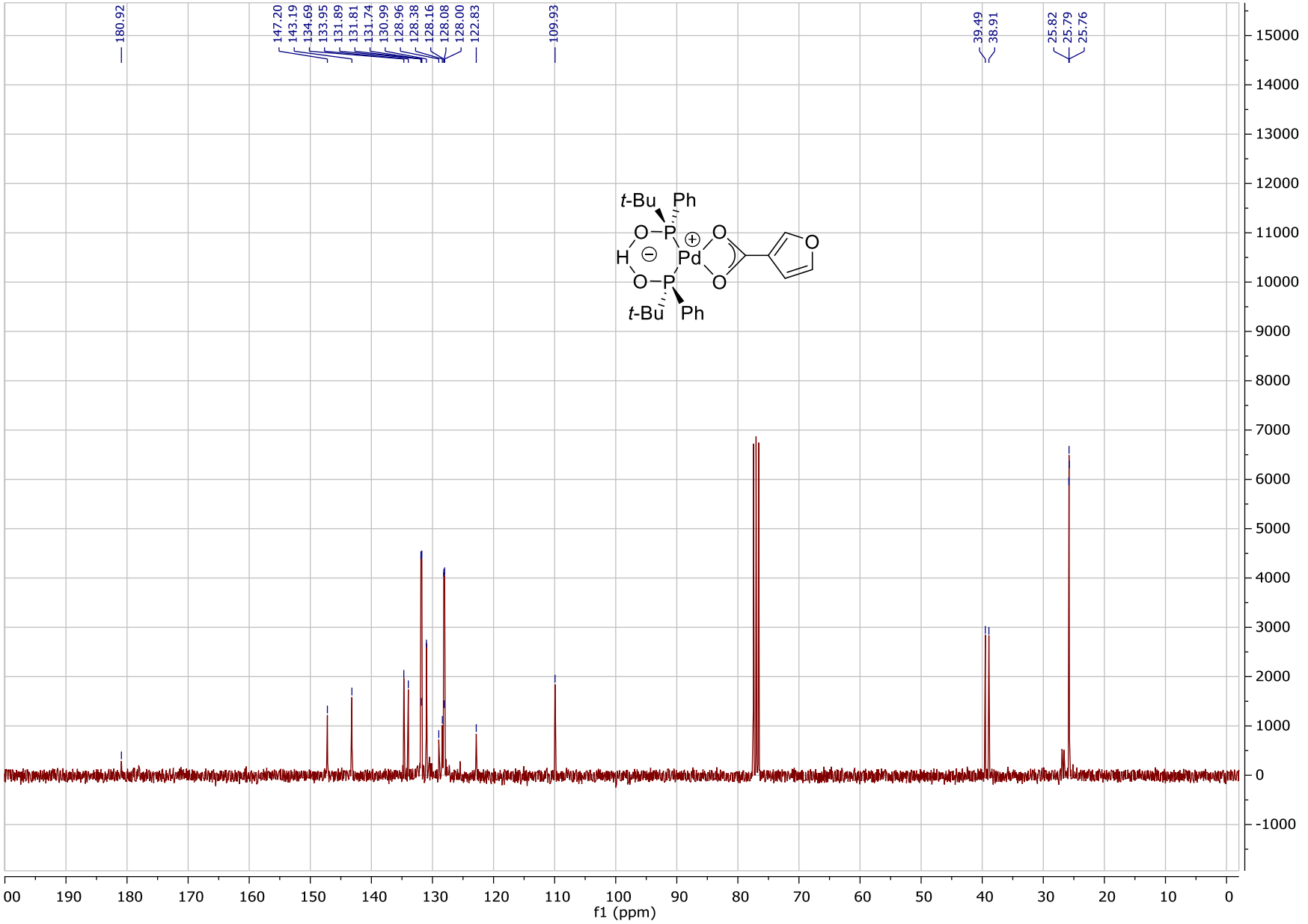

95.77
t-Bu
Ph
O
P
H
Pd
O
Br
t-Bu
Ph
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

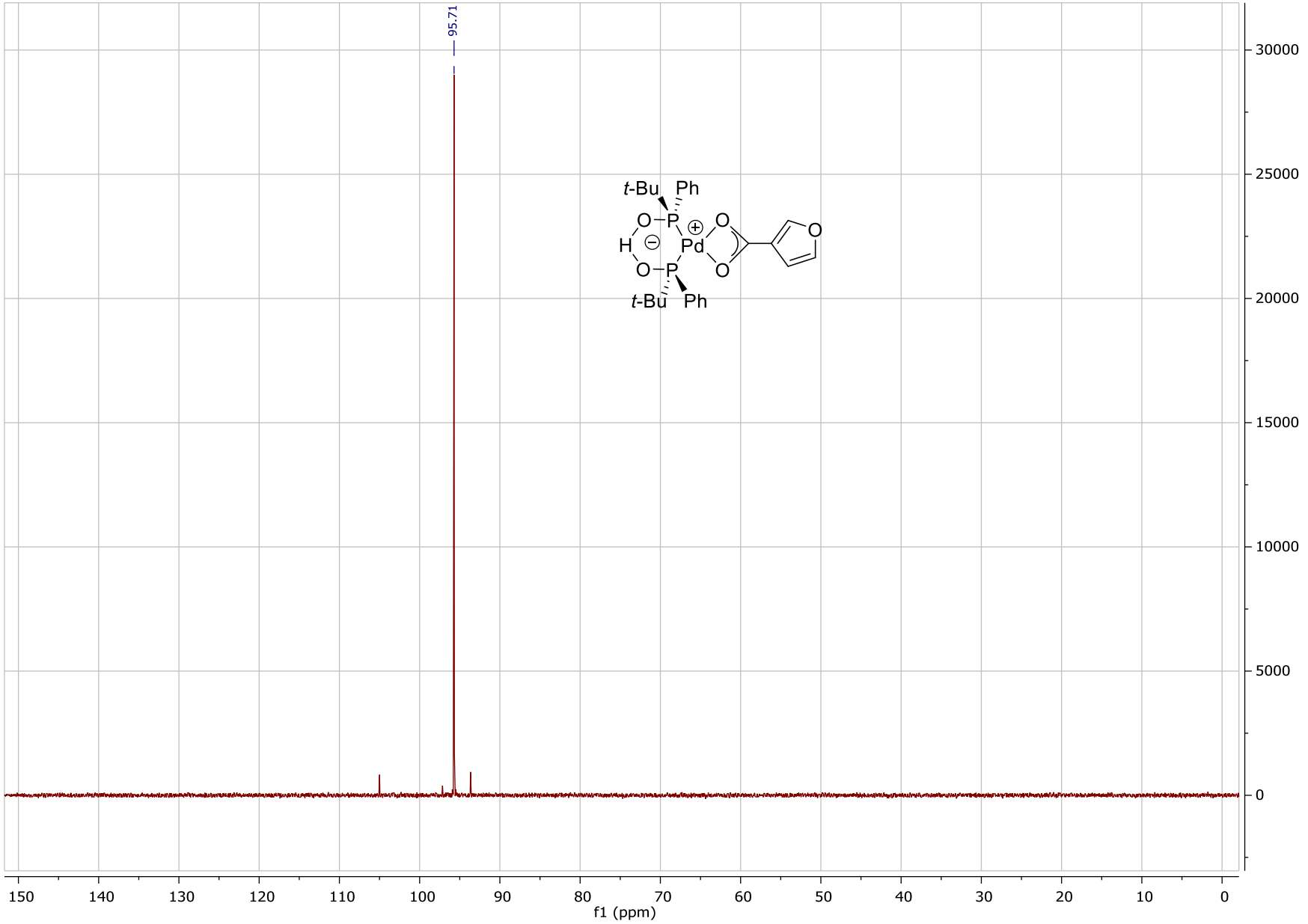

9.53
9.50
8.81
8.78
8.29
8.28
8.26
8.25
8.24
8.23
8.21
8.21
8.18
8.17
8.16
8.14
8.14
8.12
8.11
8.09
8.07
8.04
7.53
7.52
7.52
7.51
1.22
1.16
Ph
t-Bu
O
P
O
H
Pd
O
O
P
Ph
t-Bu
0.99
1.00
11.00
6.00
18.01
f1 (ppm)

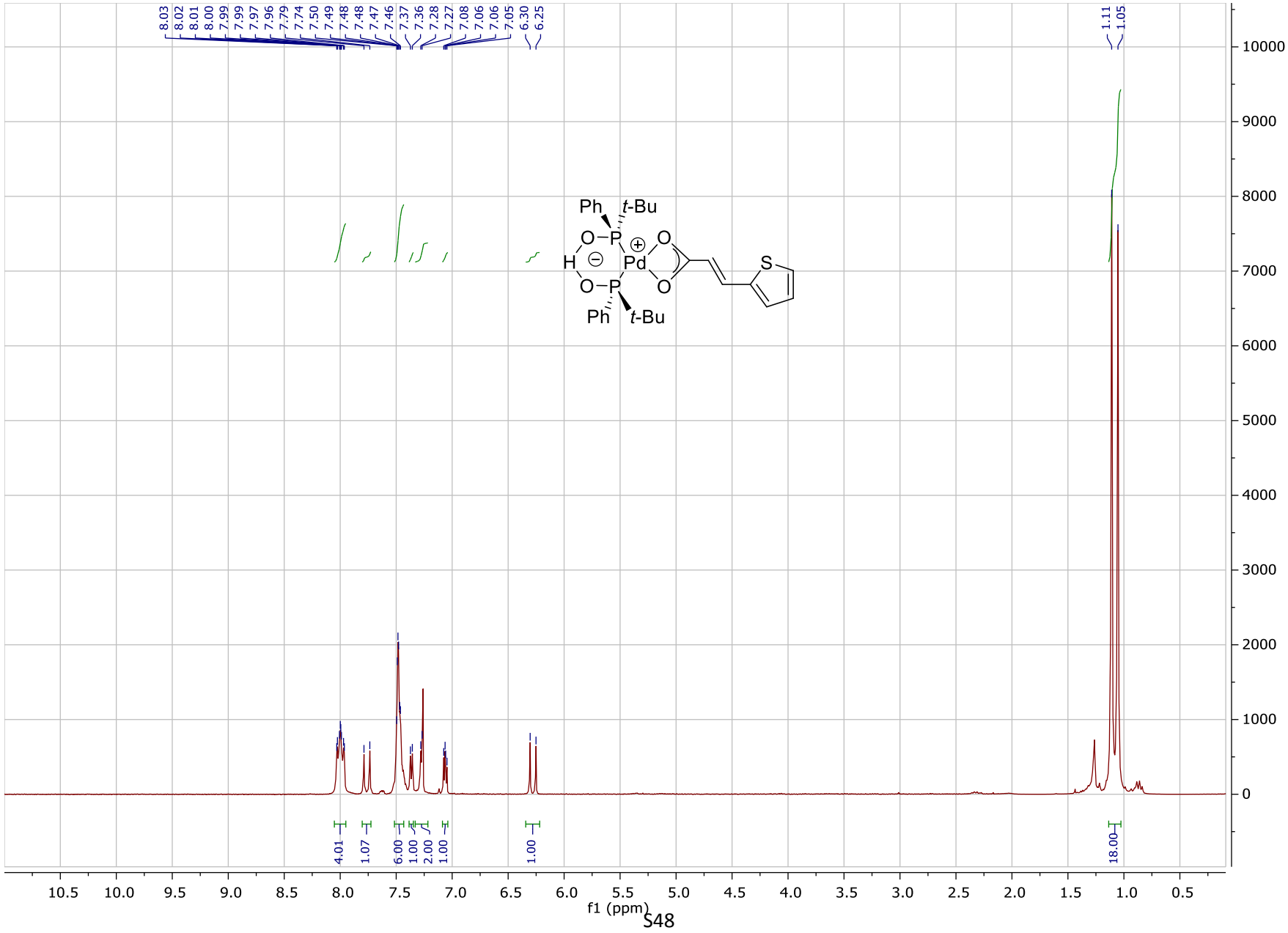

186.72
143.33
134.83
134.13
134.10
132.00
131.92
131.84
131.10
130.89
130.48
129.28
128.99
128.87
128.54
128.29
128.21
128.14
127.36
127.33
126.18
126.07
125.93
125.65
124.92
124.41
124.18
39.58
39.00
25.96
25.93
25.91
Ph
t-Bu
O
P
H
Pd
O
O
P
O
Ph
t-Bu
f1 (ppm)

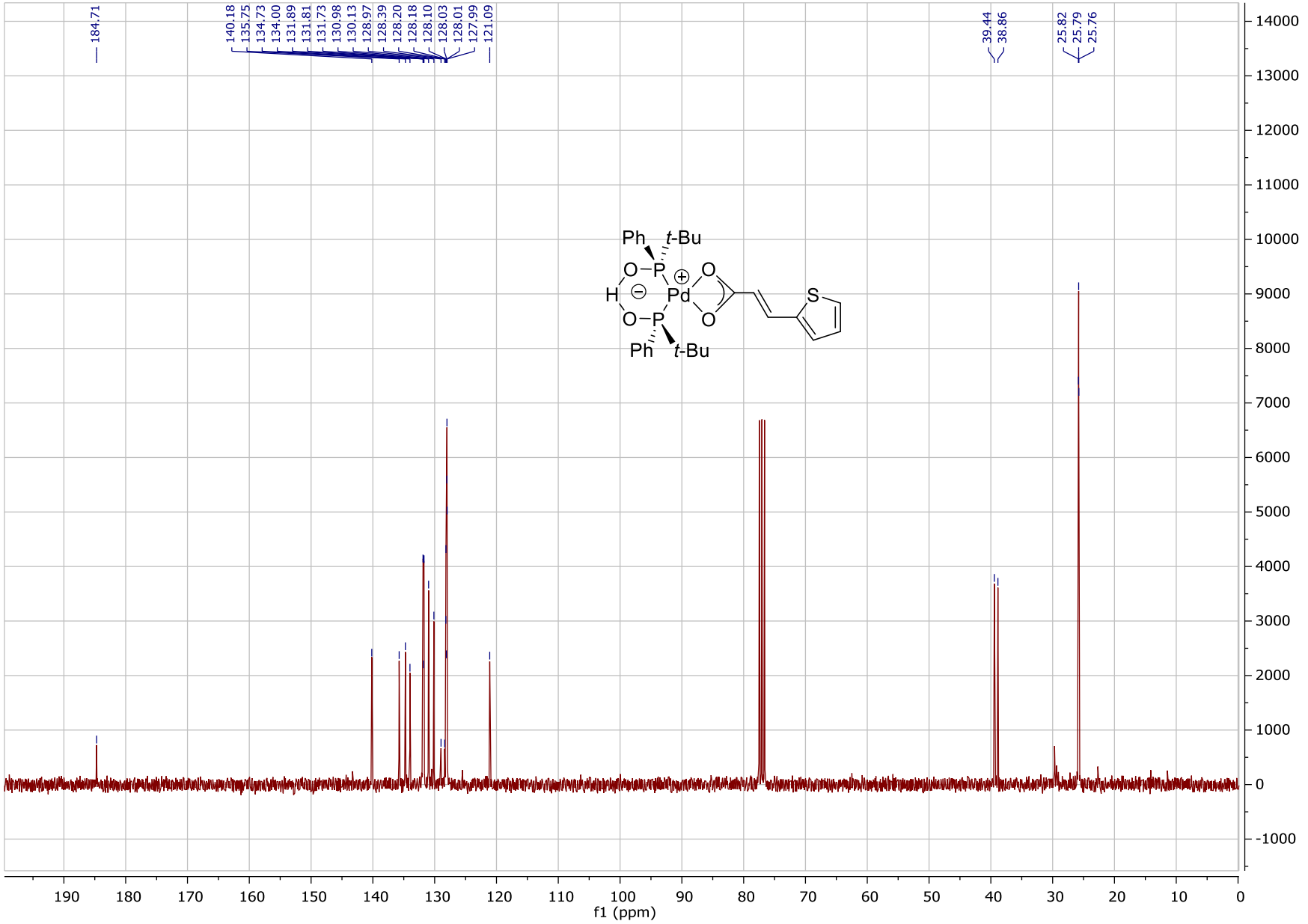

95.86
Ph
t-Bu
O
P
H
Pd
O
O
P
O
Ph
t-Bu
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

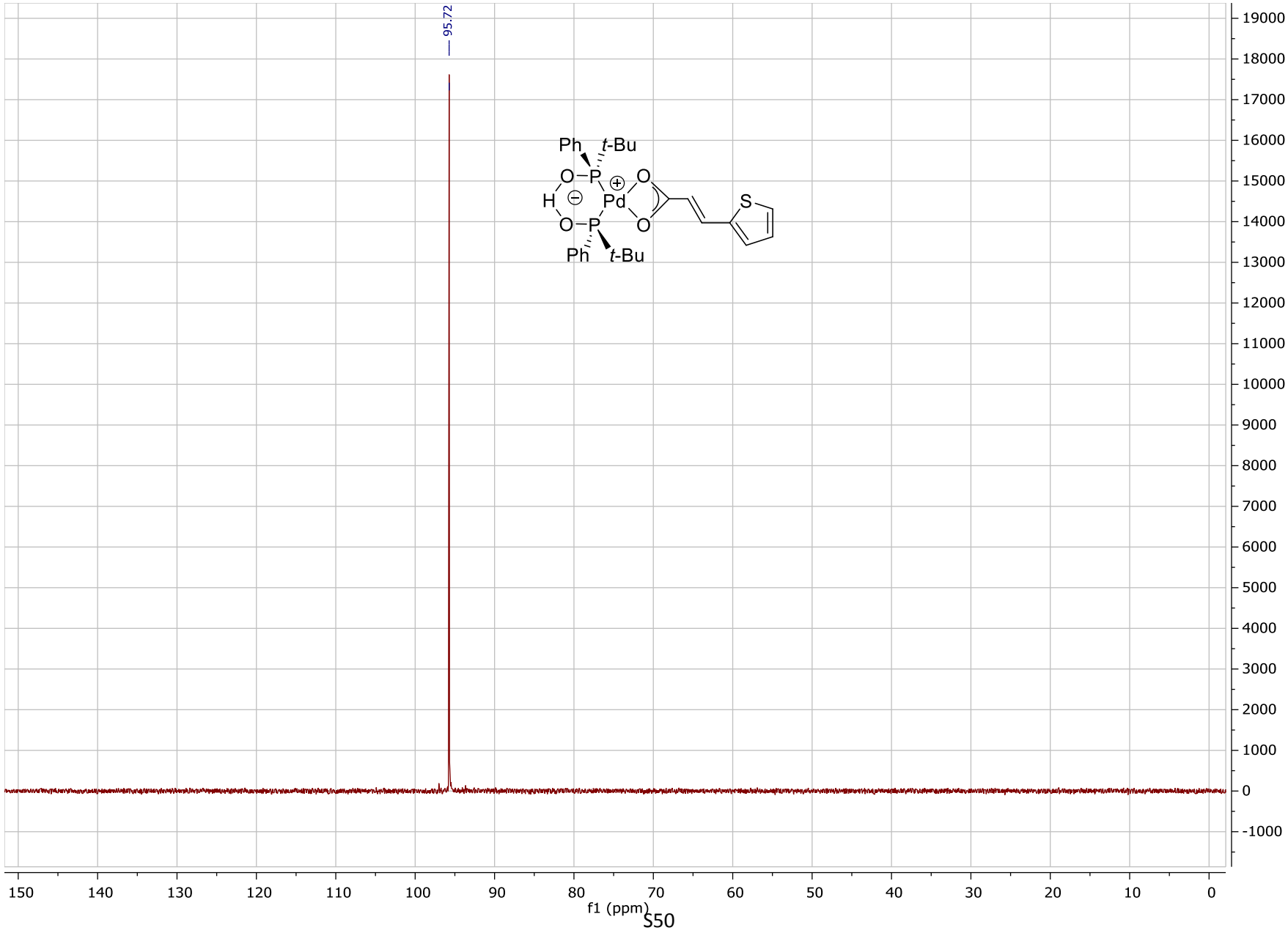

8.04
8.04
8.03
8.03
8.02
8.01
8.00
8.00
7.99
7.99
7.97
7.96
7.48
7.47
7.45
7.44
7.43
7.43
7.42
6.77
6.77
1.10
1.05
t-Bu
Ph
O
P
O
H
Pd
O
O
P
O
t-Bu
Ph
O
5.00
7.00
1.00
18.00
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

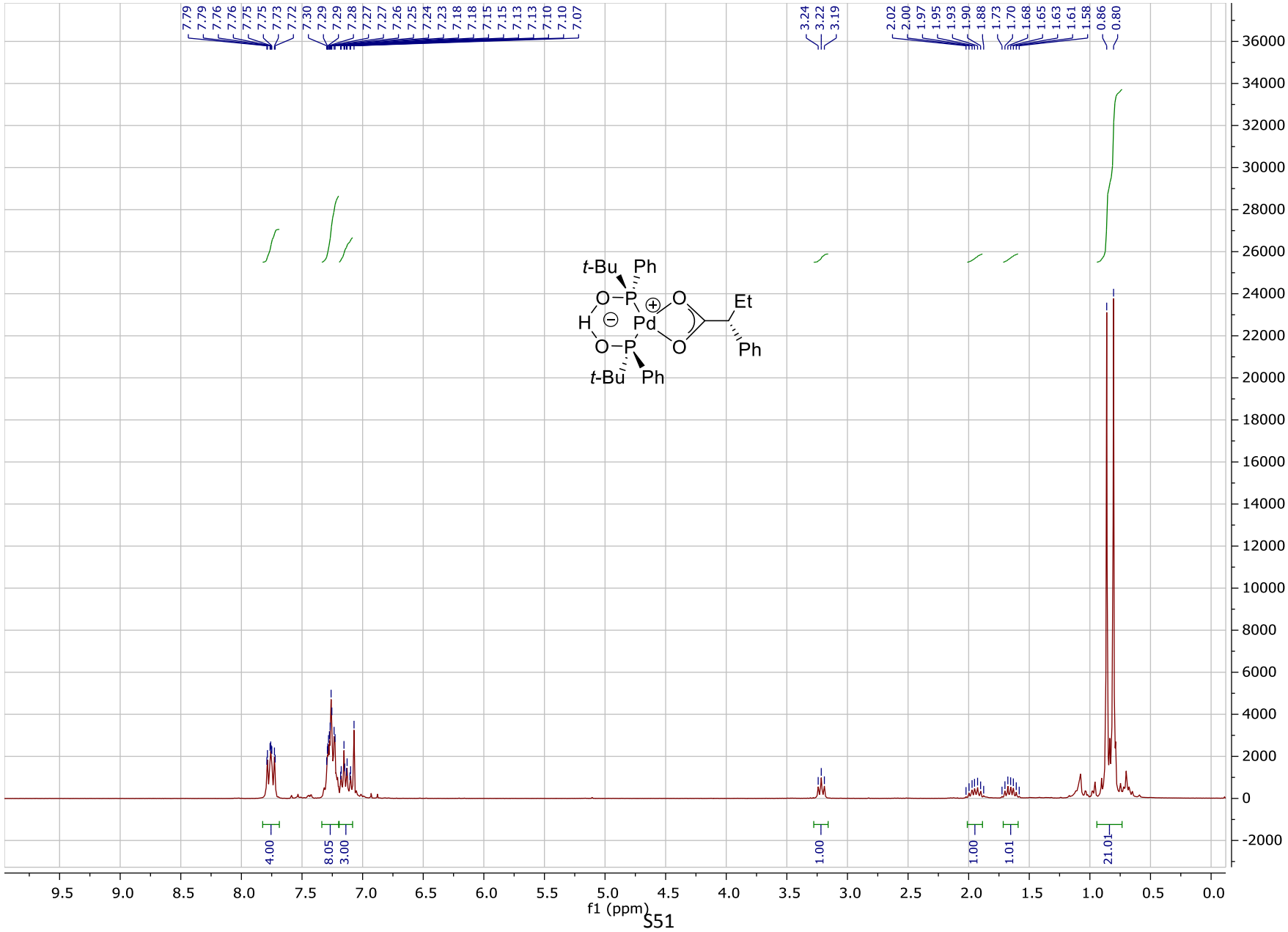

180.92
147.20
143.19
134.69
133.95
131.89
131.81
131.74
130.99
128.96
128.38
128.16
128.08
128.00
122.83
109.93
39.49
38.91
25.82
25.79
25.76
t-Bu
Ph
O
P
H
Pd
O
O
O
P
t-Bu
Ph
O
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

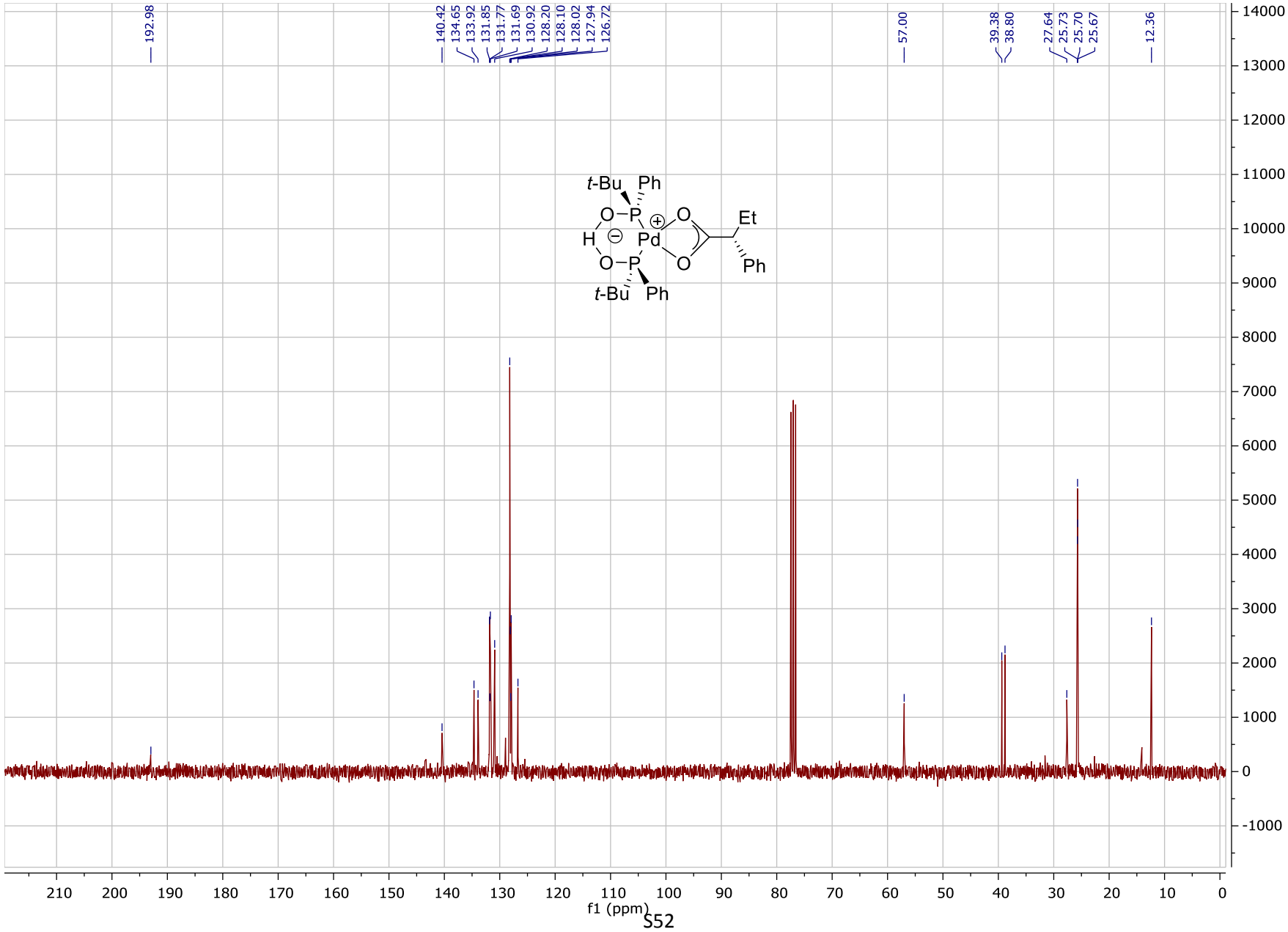

95.71
30000
25000
20000
15000
10000
5000
0
t-Bu
Ph
O
P
H
Pd
O
O
O
P
t-Bu
Ph
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

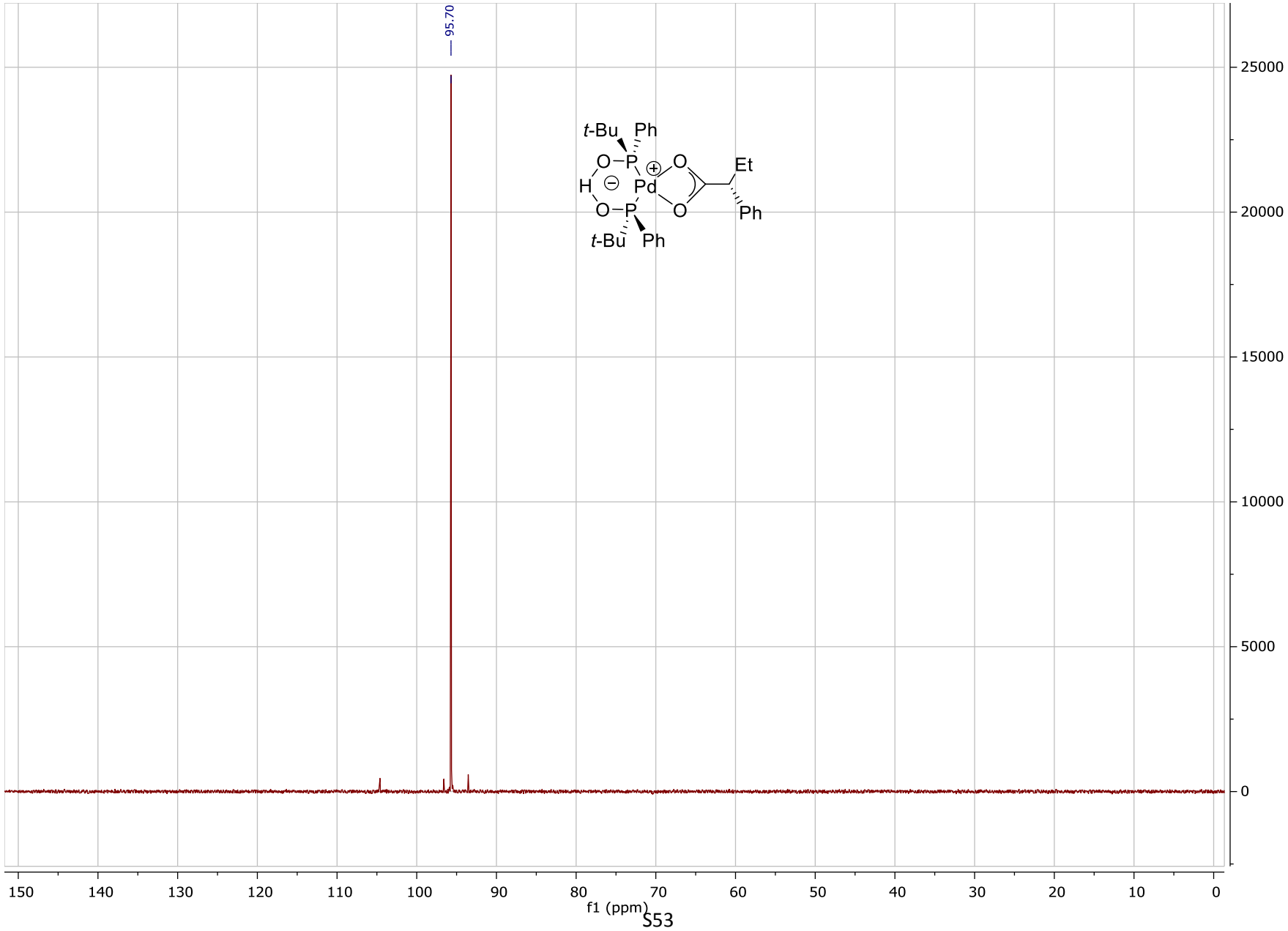

8.03
8.02
8.01
8.00
7.99
7.99
7.97
7.96
7.79
7.74
7.50
7.49
7.48
7.48
7.47
7.46
7.37
7.36
7.28
7.27
7.08
7.06
7.06
7.05
6.30
6.25
1.11
1.05
Ph
t-Bu
O
P
H
Pd
O
S
4.01
1.07
6.00
1.00
2.00
1.00
1.00
18.00
f1 (ppm)

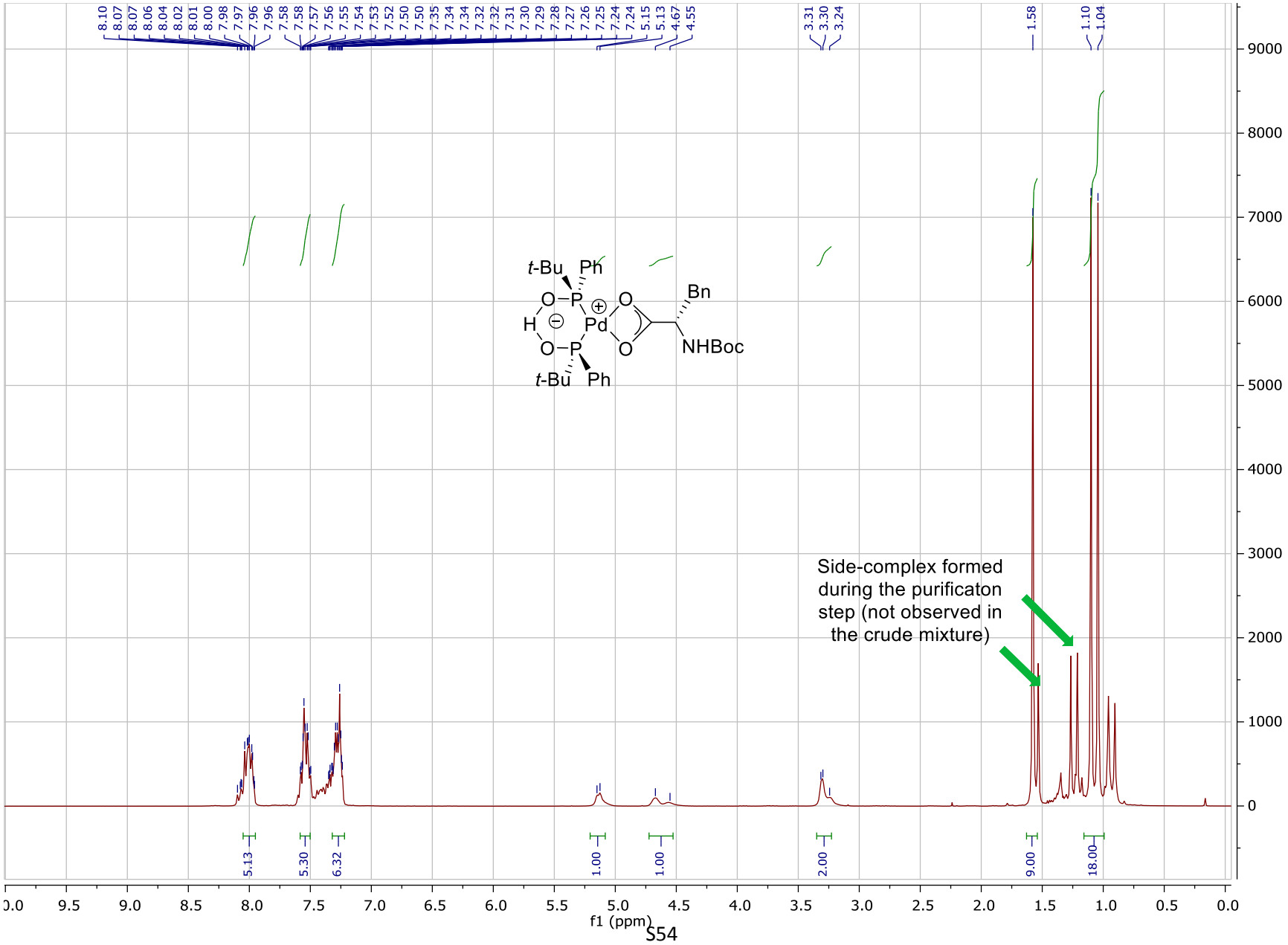

184.71
140.18
135.75
134.73
134.00
131.89
131.81
131.73
130.98
130.13
128.97
128.39
128.20
128.18
128.10
128.03
128.01
127.99
121.09
39.44
38.86
25.82
25.79
25.76
Ph
t-Bu
O
P
H
Pd
S
f1 (ppm)

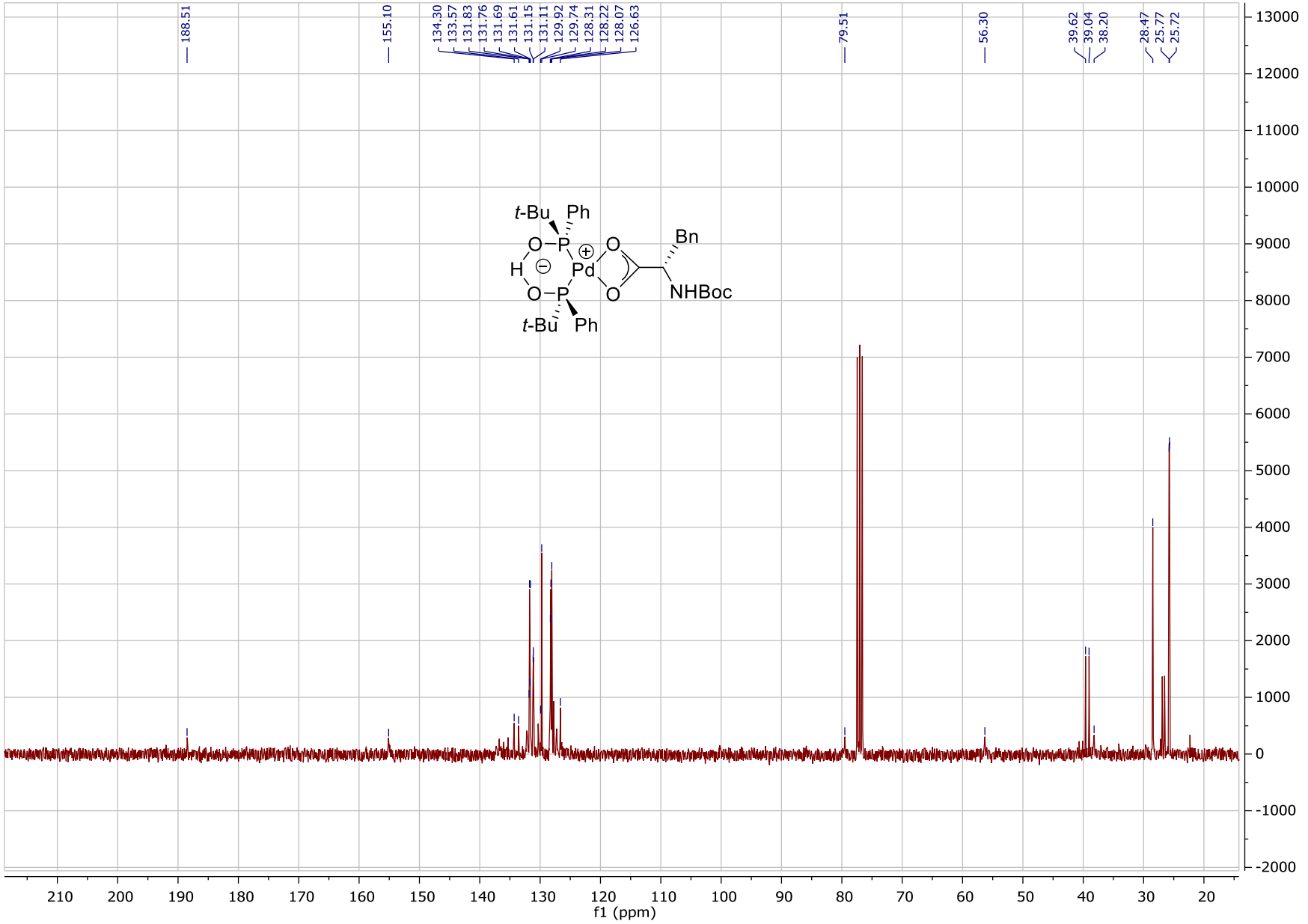

95.72
Ph
t-Bu
O
P
H
Pd
S
Ph
t-Bu
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

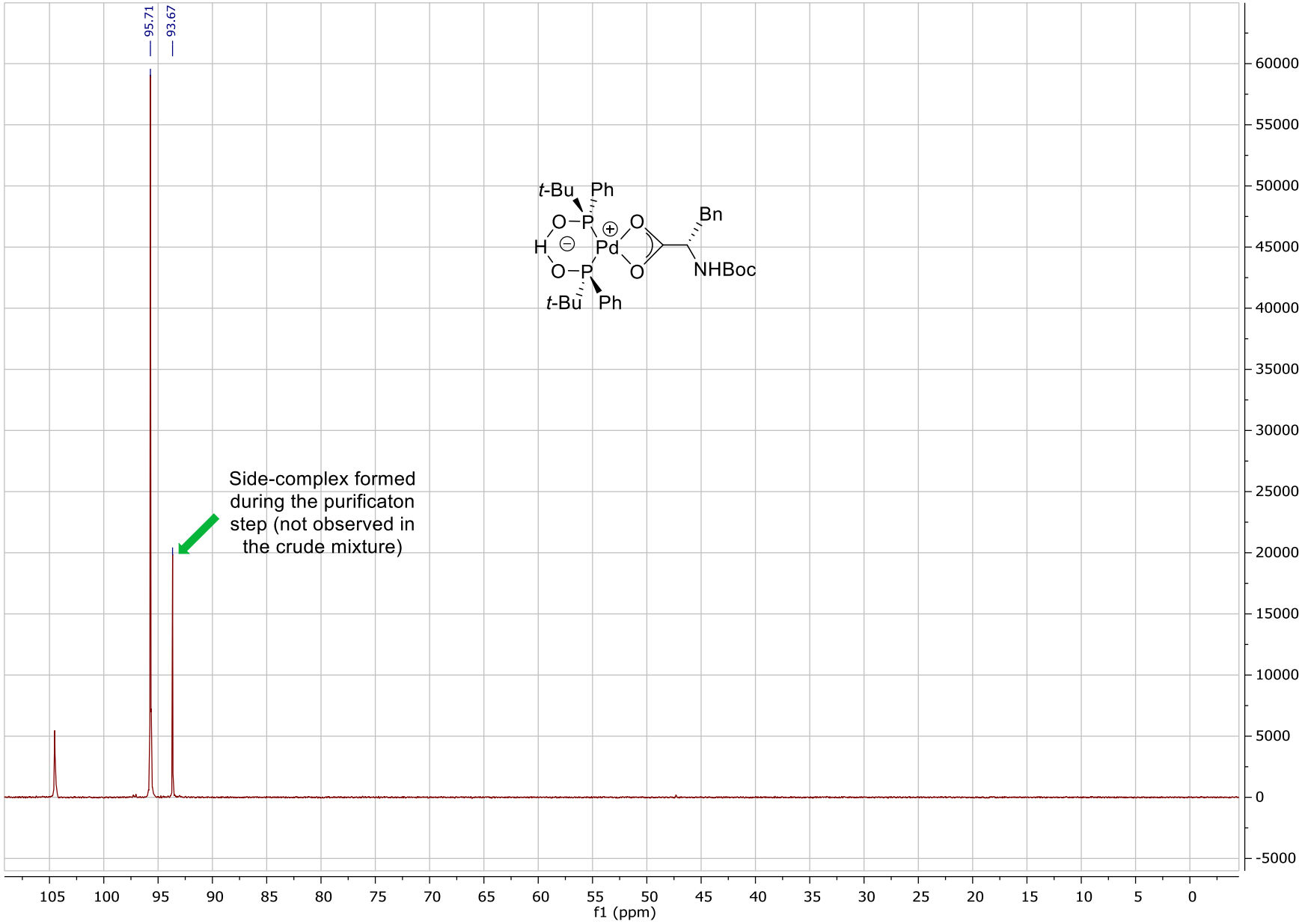

7.79 7.79 7.76 7.76 7.75 7.75 7.73 7.72 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.18 7.18 7.15 7.15 7.13 7.13 7.10 7.10 7.07
3.24 3.22 3.19
2.02 2.00 1.97 1.95 1.93 1.90 1.88 1.73 1.70 1.68 1.65 1.63 1.61 1.58
0.86 0.80
t-Bu Ph
O–P
H
Pd
O–P
t-Bu Ph
O
O
Et
O
Ph
4.00
8.05
3.00
1.00
1.00
1.01
21.01
f1 (ppm)

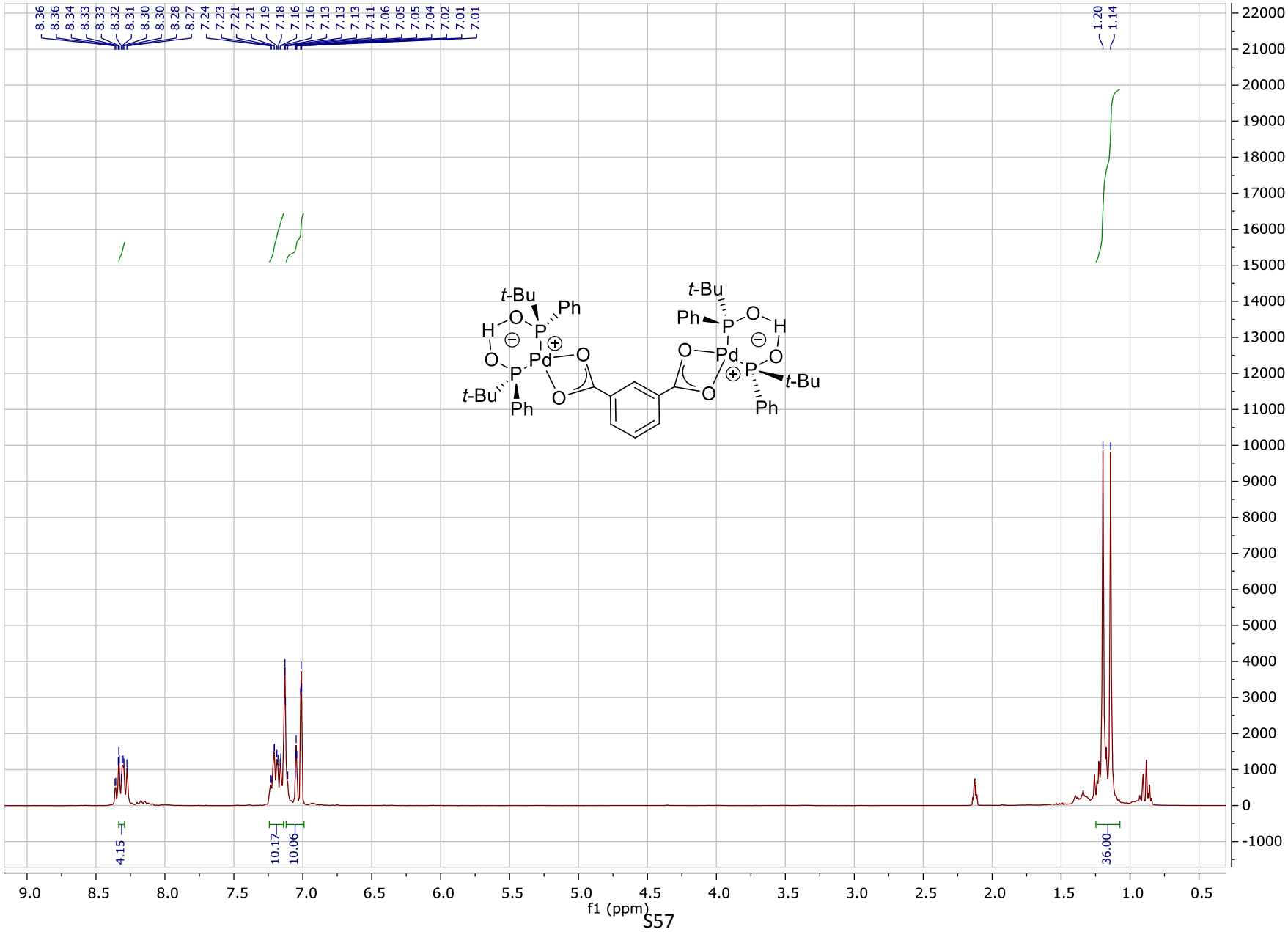

192.98
140.42
134.65
133.92
131.85
131.77
131.69
130.92
128.20
128.10
128.02
127.94
126.72
57.00
39.38
38.80
27.64
25.73
25.70
25.67
12.36
t-Bu
Ph
O
P
O
H
Pd
O
P
O
Et
Ph
t-Bu
Ph
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

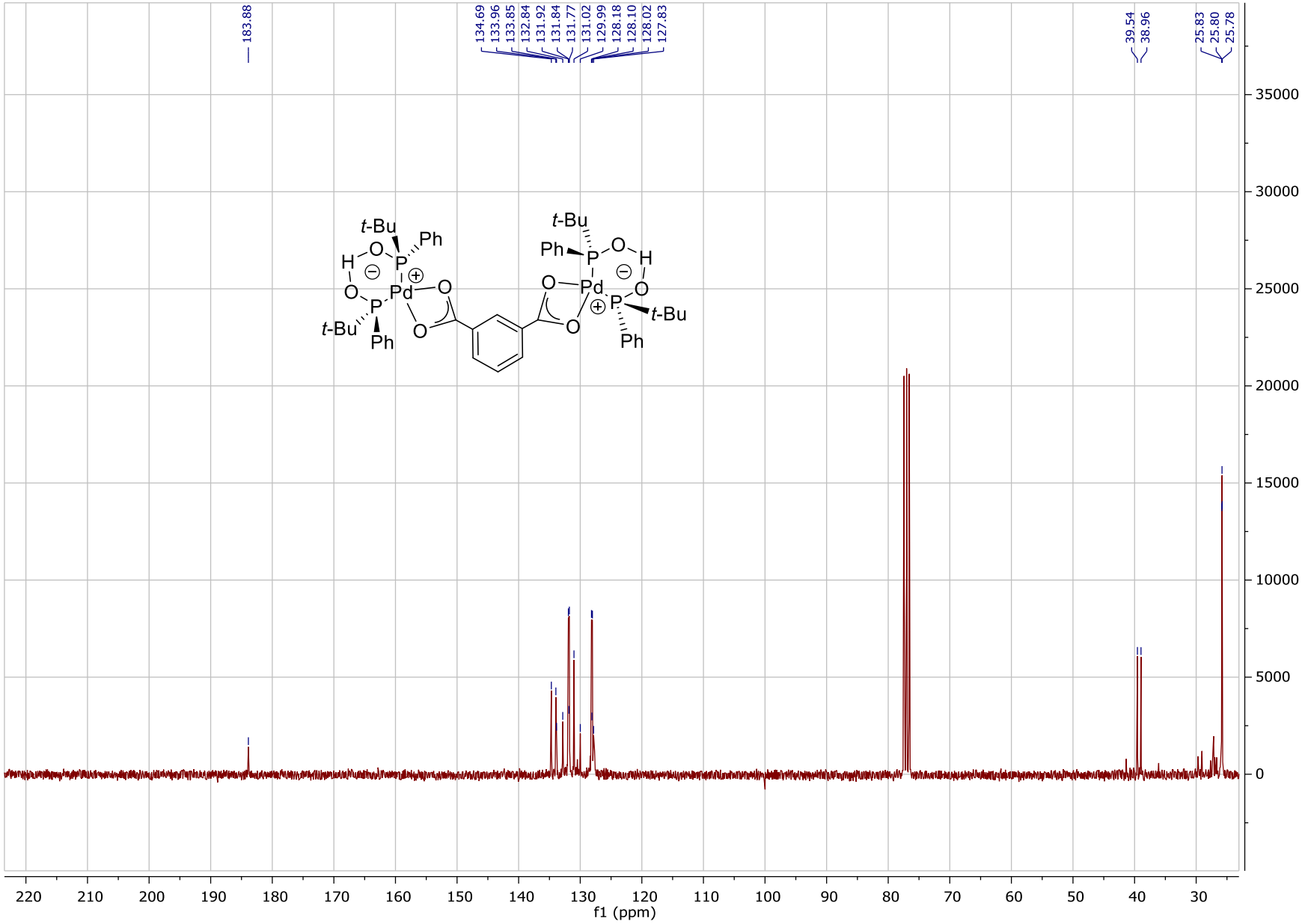

95.70
t-Bu
Ph
O
P
O
Et
H
Pd
O
P
O
Ph
t-Bu
Ph
25000
20000
15000
10000
5000
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

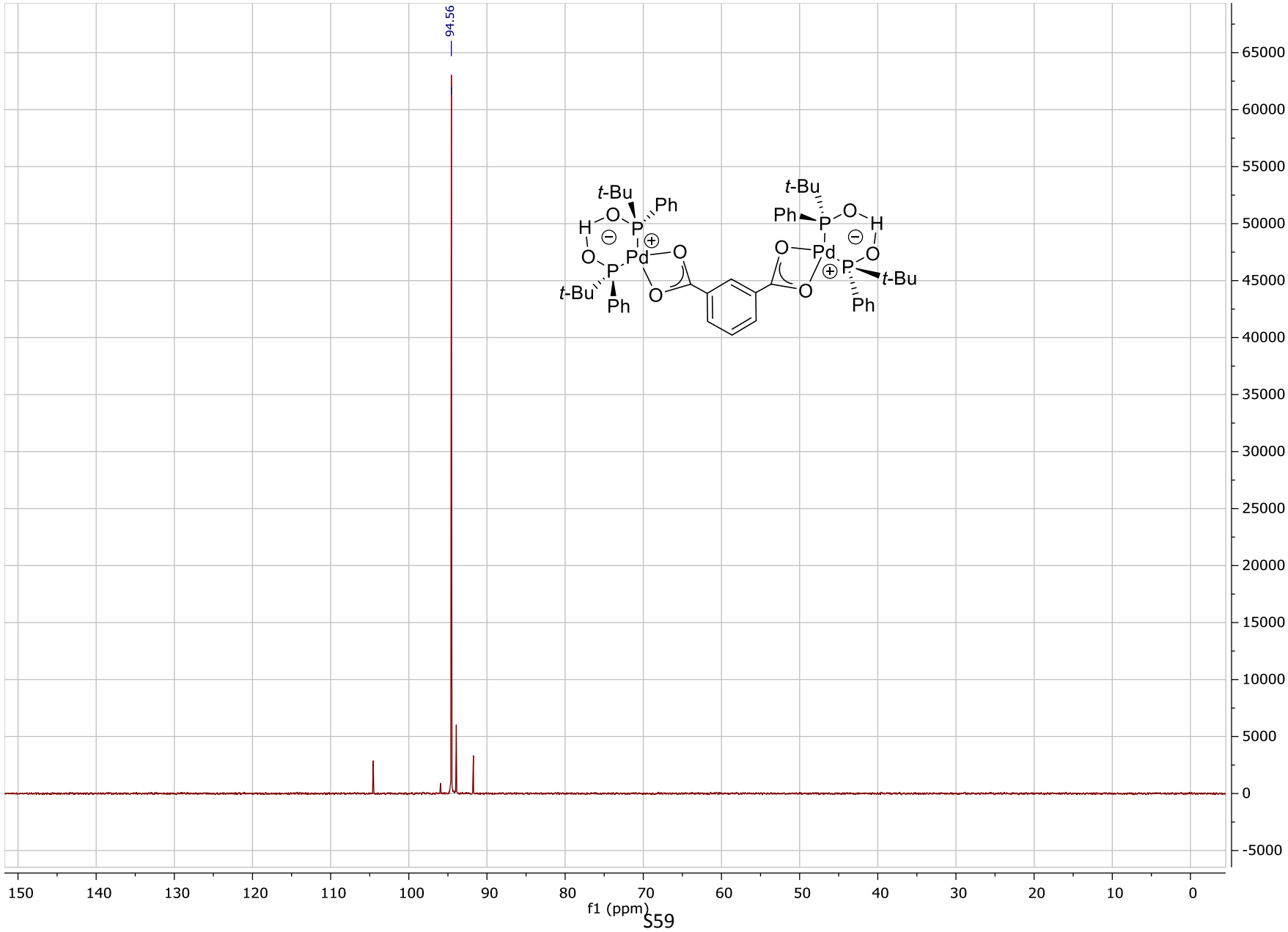

8.10 8.07 8.07 8.06 8.04 8.02 8.01 8.00 7.98 7.97 7.96 7.96 7.58 7.58 7.57 7.56 7.55 7.54 7.53 7.52 7.50 7.50 7.35 7.34 7.34 7.32 7.32 7.31 7.30 7.29 7.28 7.27 7.26 7.25 7.24 7.24 5.15 5.13 4.67 4.55
3.31 3.30 3.24
1.58
1.10 1.04
t-Bu Ph
O–P
H
Pd
O–P
t-Bu Ph
O
O
Bn
NHBoc
Side-complex formed during the purificaton step (not observed in the crude mixture)
5.13 5.30 6.32 1.00 1.00 2.00 9.00 18.00
9000 8000 7000 6000 5000 4000 3000 2000 1000 0
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

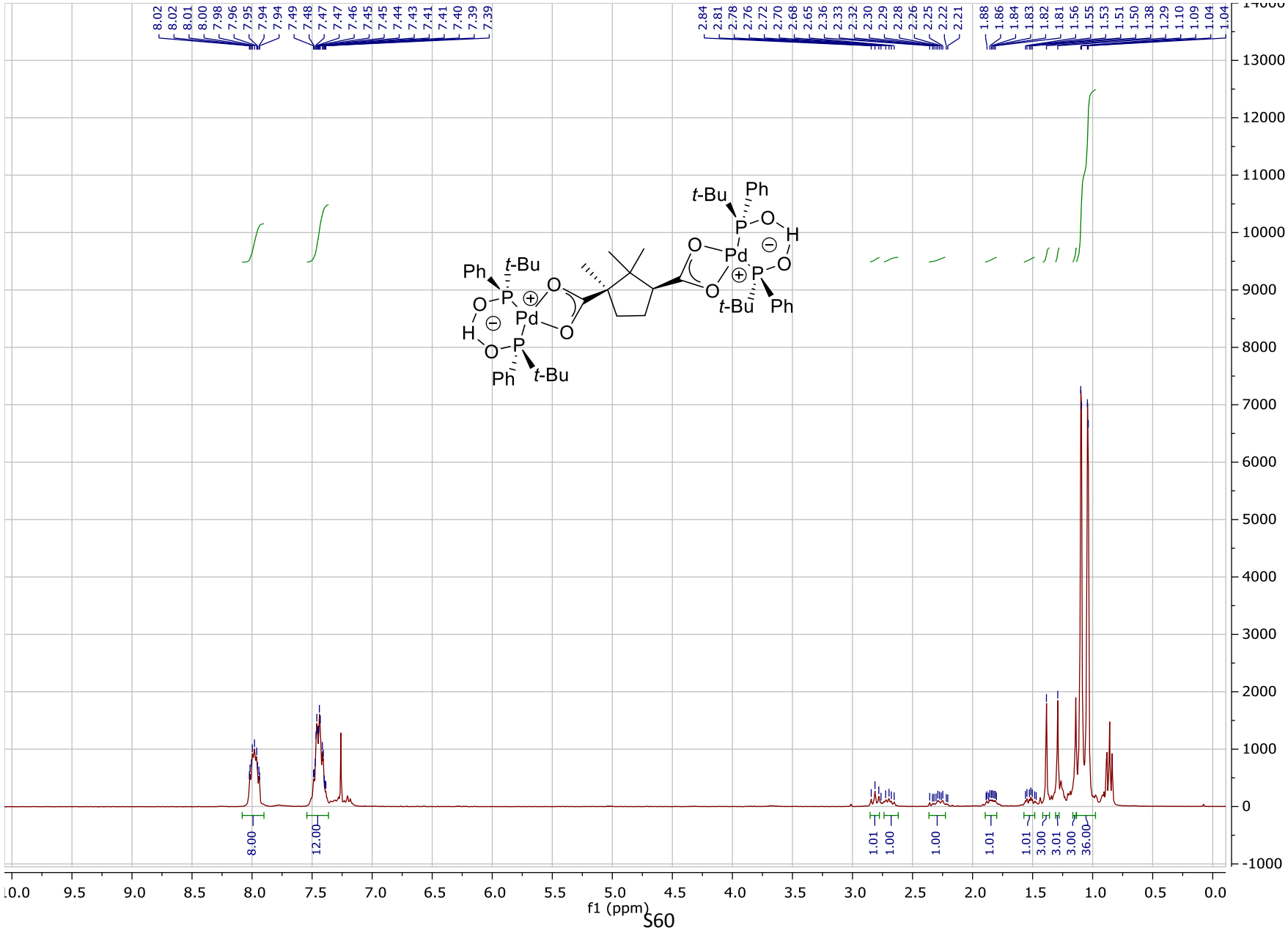

188.51
155.10
134.30
133.57
131.83
131.76
131.69
131.61
131.15
131.11
129.92
129.74
128.31
128.22
128.07
126.63
79.51
56.30
39.62
39.04
38.20
28.47
25.77
25.72
t-Bu
Ph
O
P
H
Pd
Bn
NHBoc
f1 (ppm)

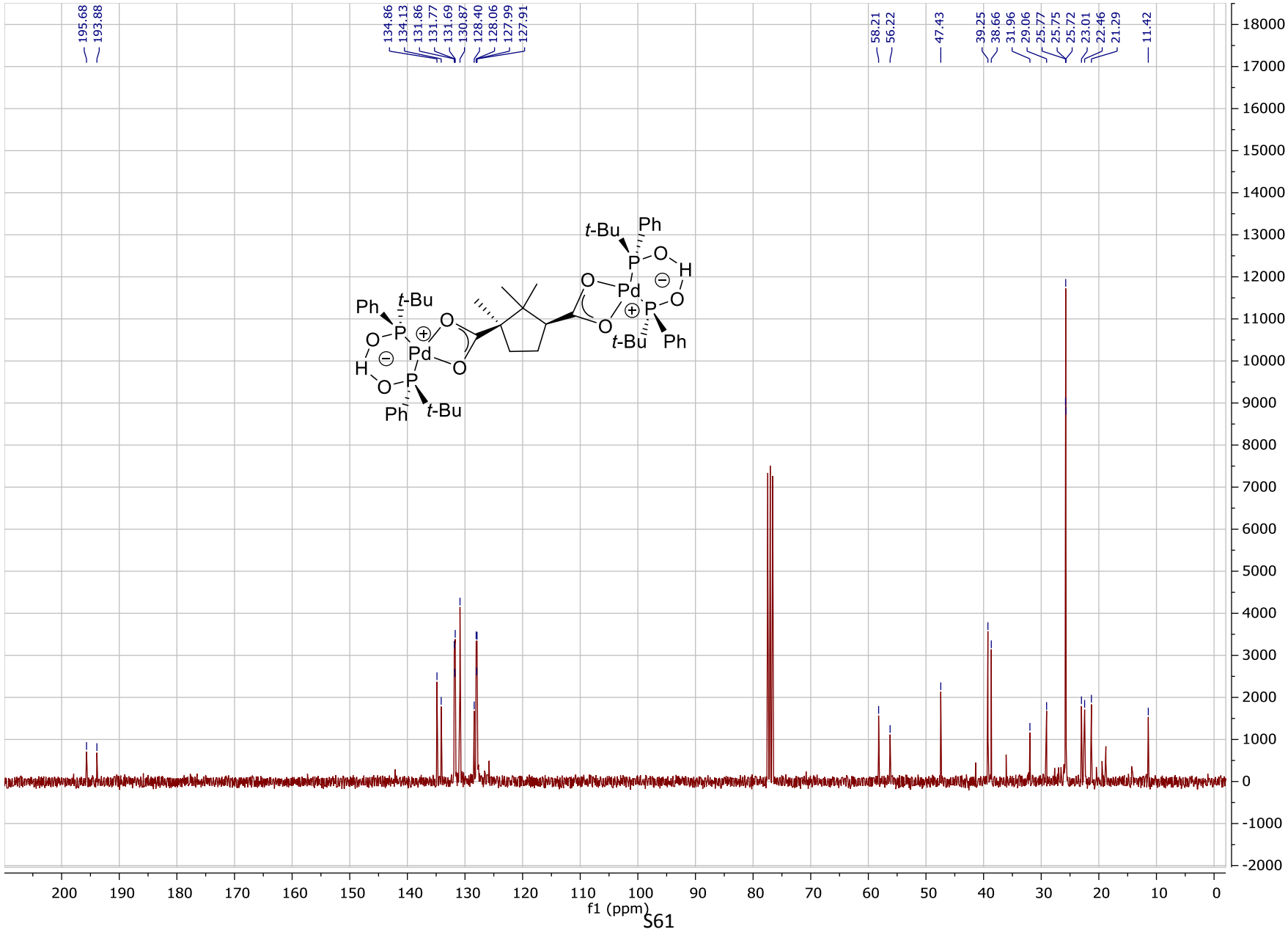

95.71
93.67
t-Bu
Ph
O
P
H
Pd
Bn
NHBoc
Side-complex formed during the purificaton step (not observed in the crude mixture)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

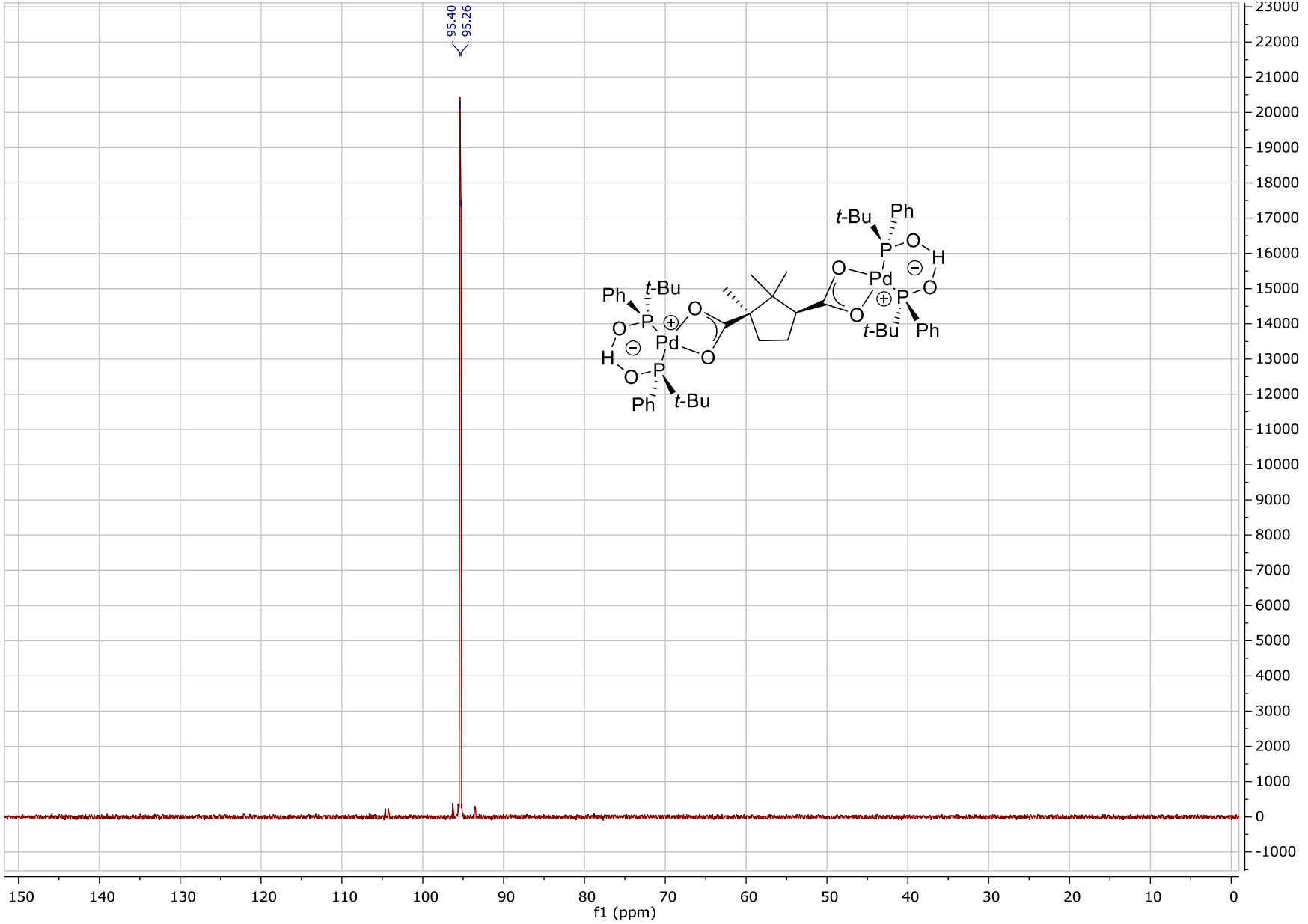

8.36
8.36
8.34
8.33
8.33
8.32
8.31
8.30
8.30
8.28
8.27
7.24
7.23
7.21
7.21
7.19
7.18
7.16
7.16
7.13
7.13
7.13
7.11
7.06
7.05
7.05
7.04
7.02
7.01
7.01
1.20
1.14
t-Bu
Ph
H
O
P
Pd
O
t-Bu
Ph
4.15
10.17
10.06
36.00
f1 (ppm)

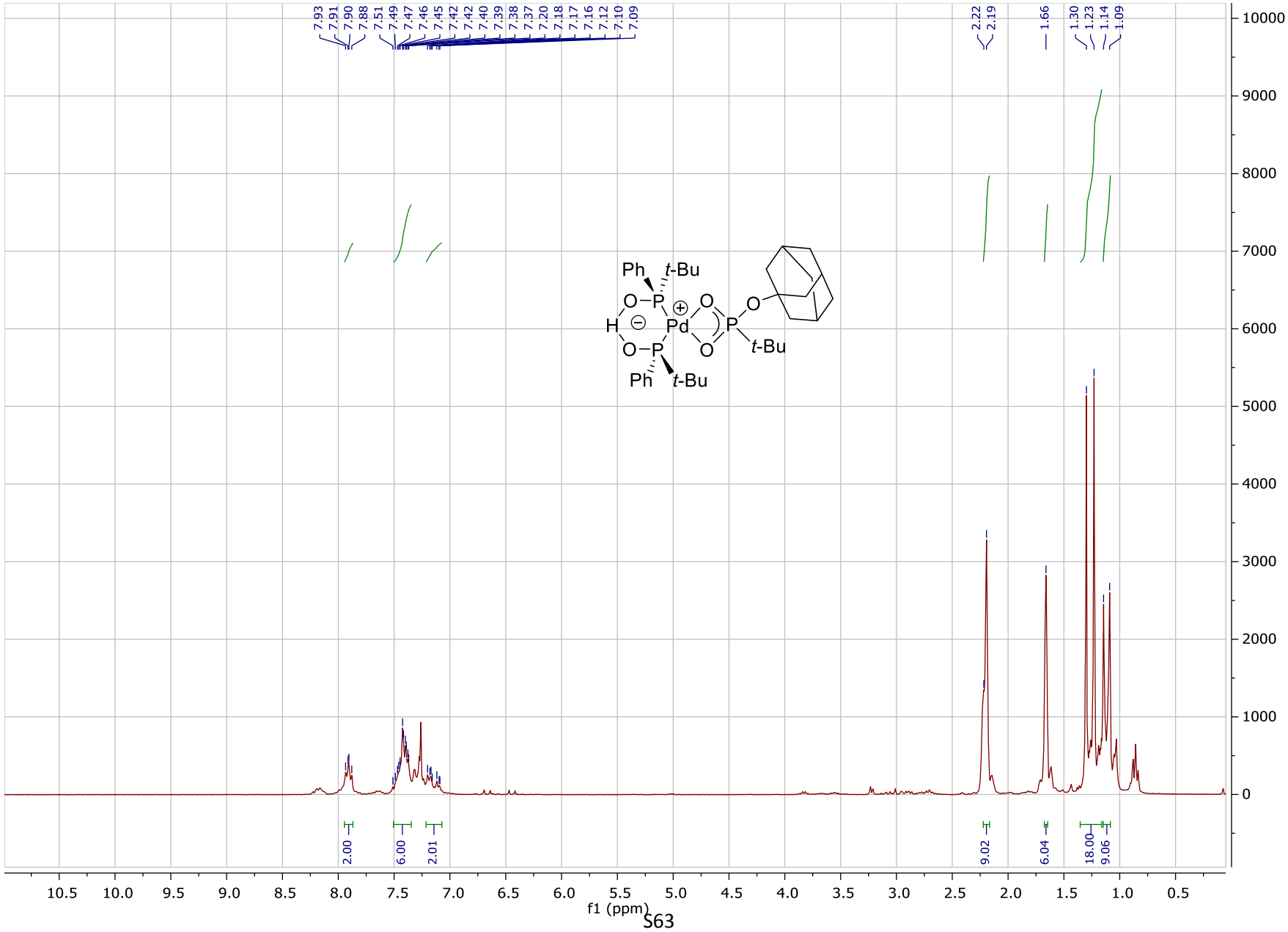

183.88
134.69
133.96
133.85
132.84
131.92
131.84
131.77
131.02
129.99
128.18
128.10
128.02
127.83
39.54
38.96
25.83
25.80
25.78
t-Bu
Ph
H
O
P
Pd
t-Bu
Ph
35000
30000
25000
20000
15000
10000
5000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

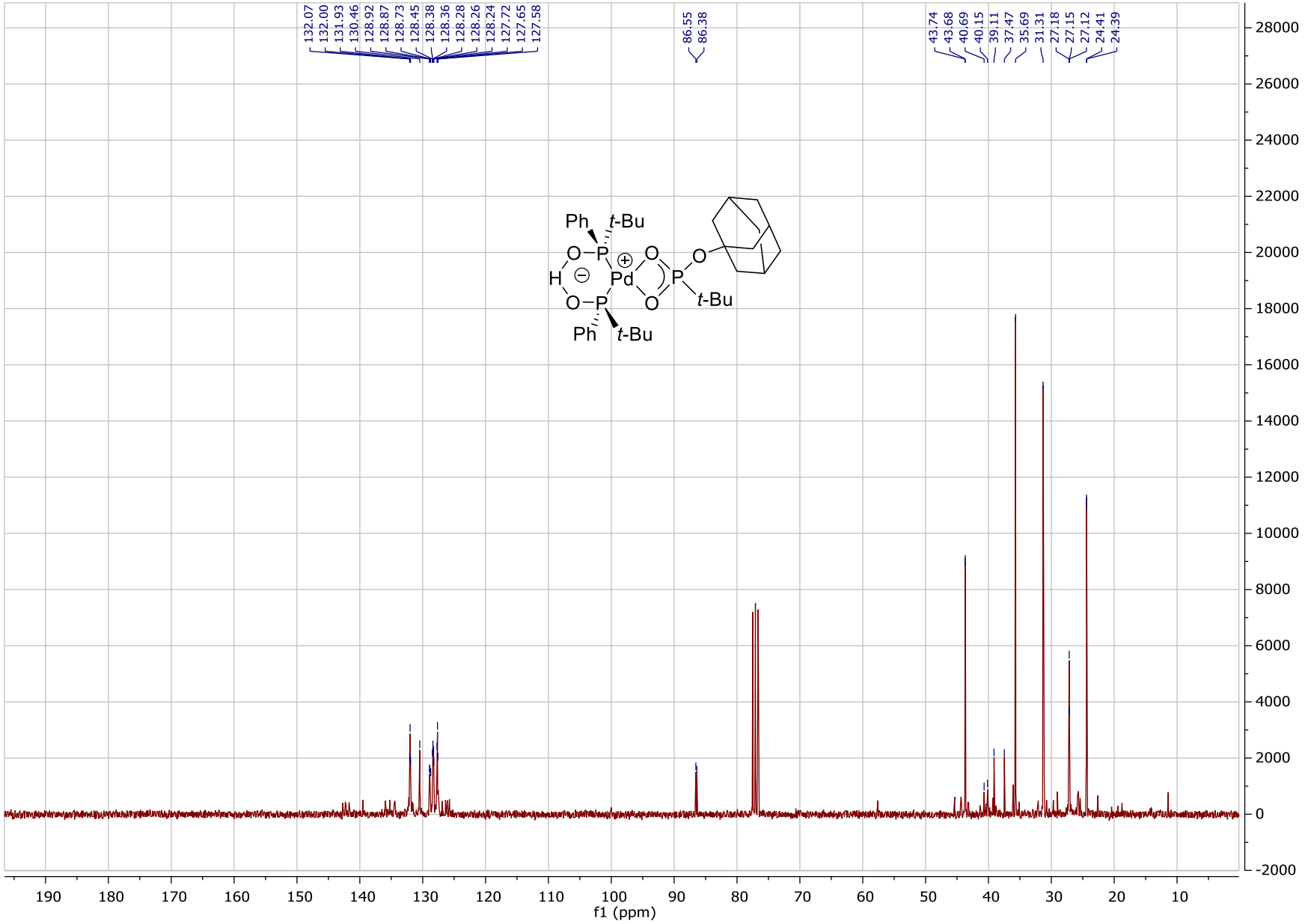

94.56
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
t-Bu
Ph
H
O
P
Pd
t-Bu
Ph

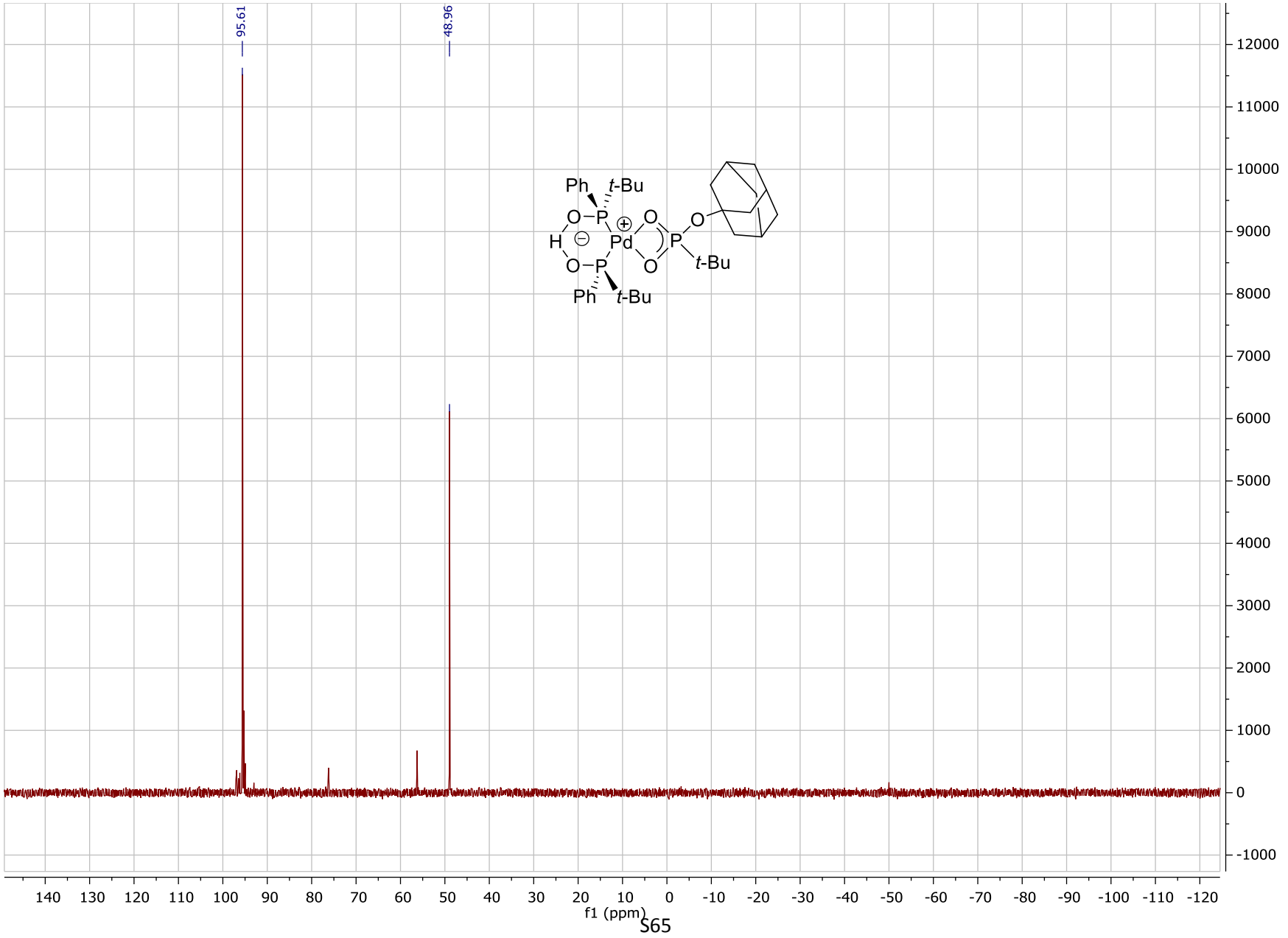

8.02 8.02 8.01 8.00 7.98 7.96 7.95 7.94 7.94 7.49 7.48 7.47 7.47 7.46 7.45 7.45 7.44 7.43 7.41 7.41 7.40 7.39 7.39
2.84 2.81 2.78 2.76 2.72 2.70 2.68 2.65 2.36 2.33 2.32 2.30 2.29 2.28 2.26 2.25 2.22 2.21
1.88 1.86 1.84 1.83 1.82 1.81 1.56 1.55 1.53 1.51 1.50 1.38 1.29 1.10 1.09 1.04 1.04
Ph t-Bu O P Pd O H O Ph t-Bu
t-Bu Ph O P Pd O H O P Ph t-Bu
8.00 12.00 1.01 1.00 1.00 1.01 1.01 3.00 3.01 3.00 36.00
f1 (ppm)

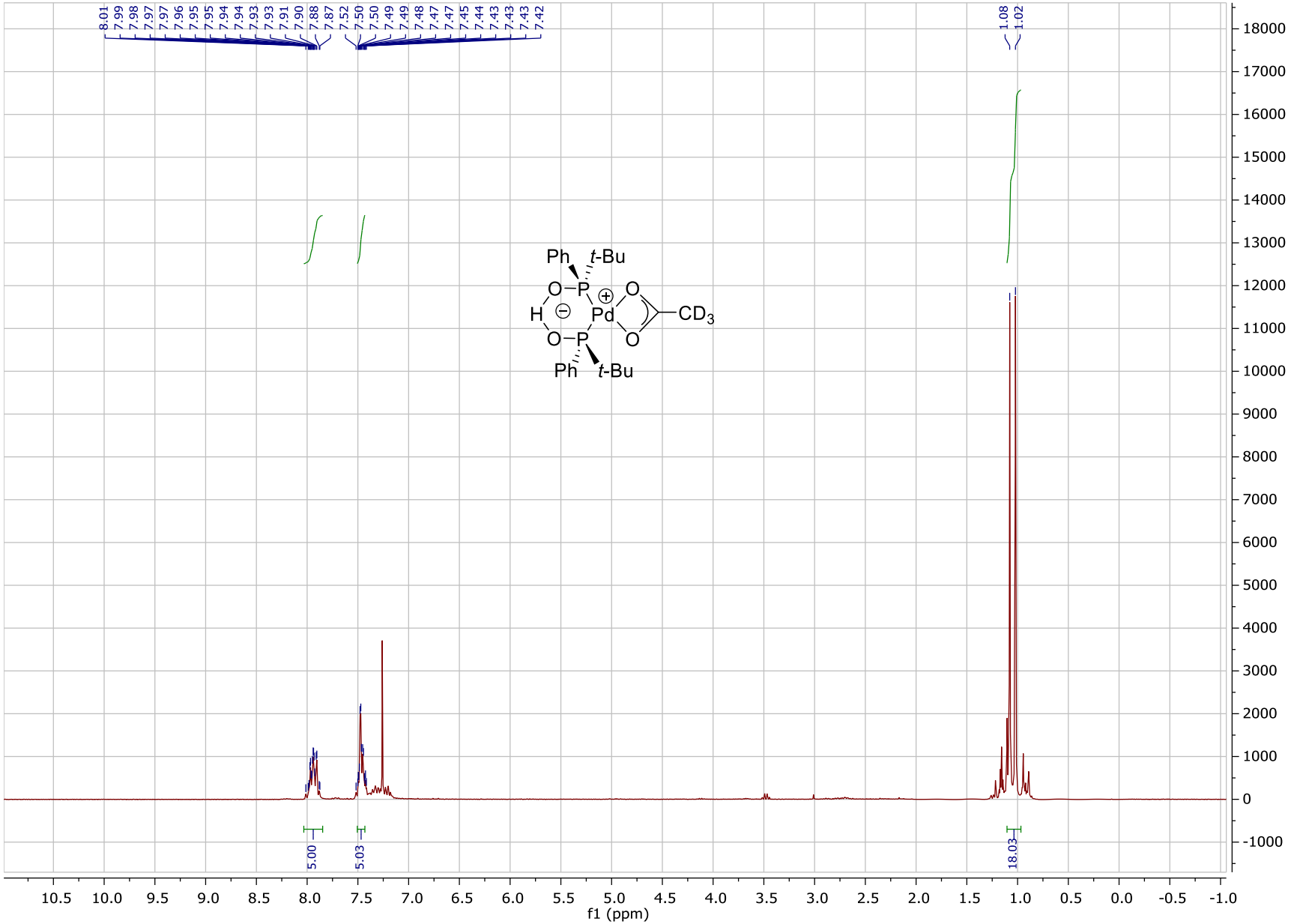

195.68
193.88
134.86
134.13
131.86
131.77
131.69
130.87
128.40
128.06
127.99
127.91
58.21
56.22
47.43
39.25
38.66
31.96
29.06
25.77
25.75
25.72
23.01
22.46
21.29
11.42
f1 (ppm)

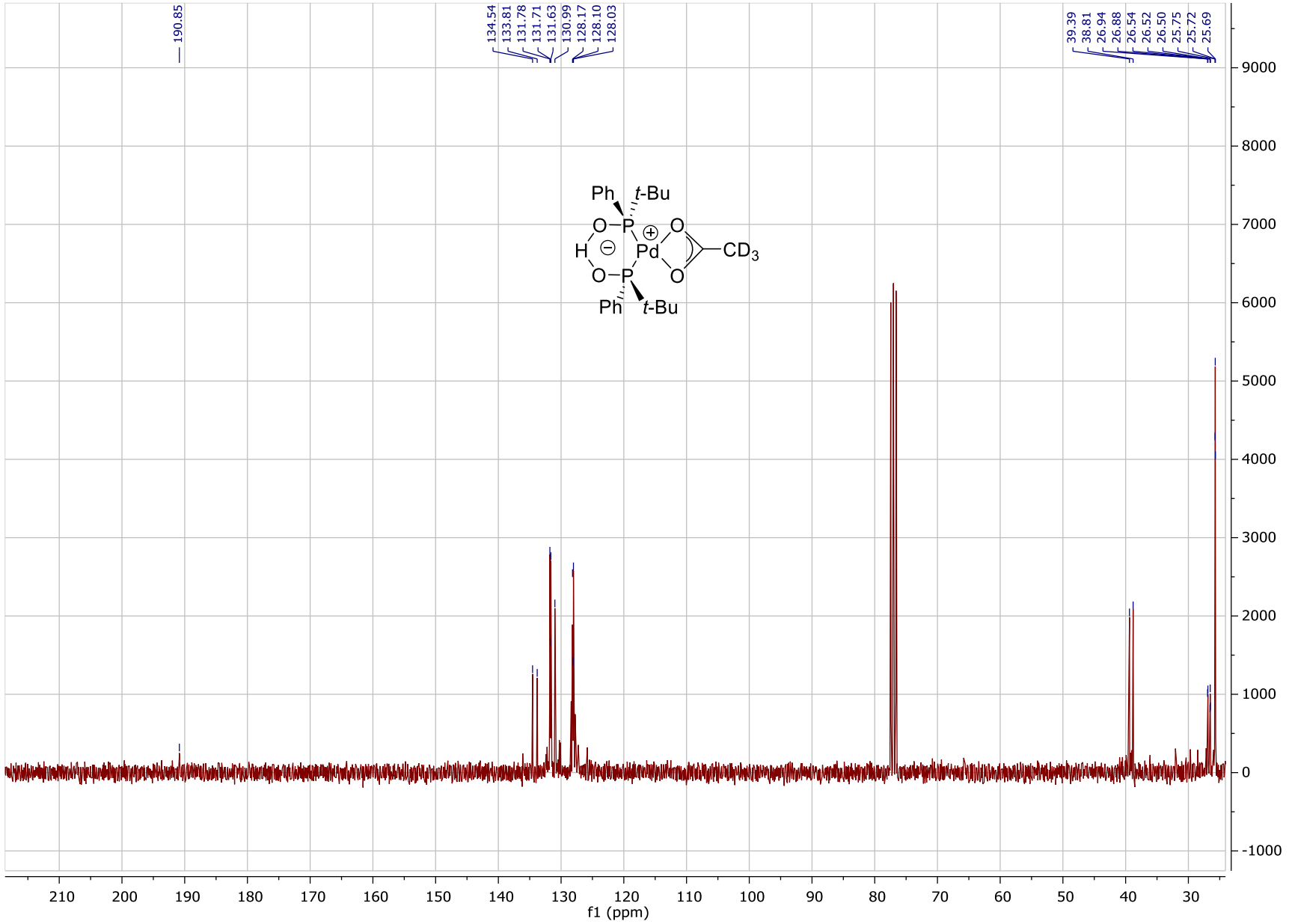

95.40
95.26
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
t-Bu
Ph
P
O
H
Pd
t-Bu
Ph
Ph
t-Bu
P
O
H
O
Pd
P
O
O
t-Bu
Ph
O
P
O
H
Pd
O
P
Ph
t-Bu

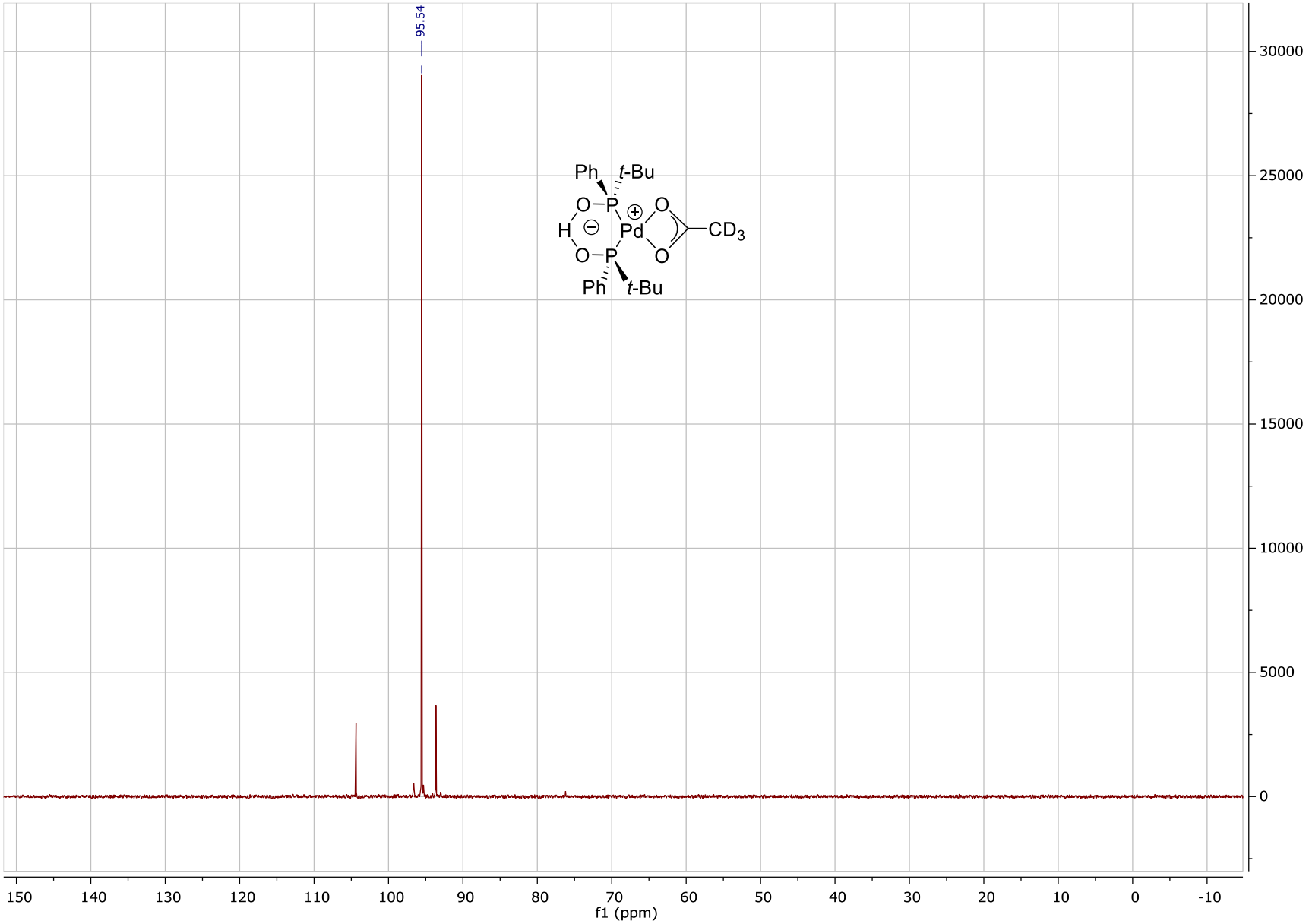

7.93
7.91
7.90
7.88
7.51
7.49
7.47
7.46
7.45
7.42
7.42
7.40
7.39
7.38
7.37
7.20
7.18
7.17
7.16
7.12
7.10
7.09
2.22
2.19
1.66
1.30
1.23
1.14
1.09
Ph
t-Bu
O
P
H
Pd
O
P
O
t-Bu
Ph
t-Bu
2.00
6.00
2.01
9.02
6.04
18.00
9.06
f1 (ppm)


132.07
132.00
131.93
130.46
128.92
128.87
128.73
128.45
128.38
128.36
128.28
128.26
128.24
127.72
127.65
127.58
86.55
86.38
43.74
43.68
40.69
40.15
39.11
37.47
35.69
31.31
27.18
27.15
27.12
24.41
24.39
Ph
t-Bu
O
P
H
Pd
t-Bu
Ph
t-Bu
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

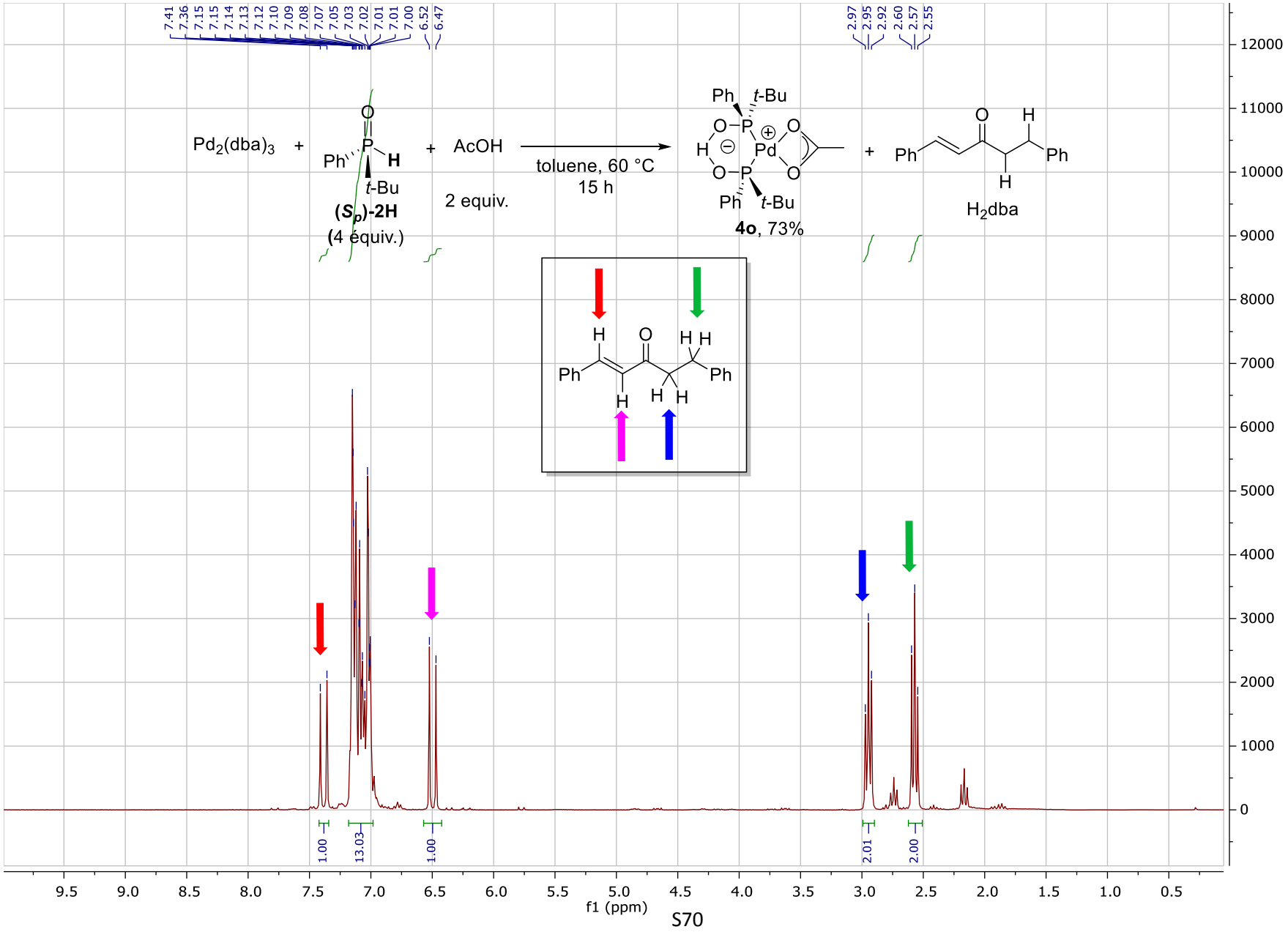

95.61
48.96
Ph
t-Bu
O
P
H
Pd
O
P
t-Bu
Ph
t-Bu
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

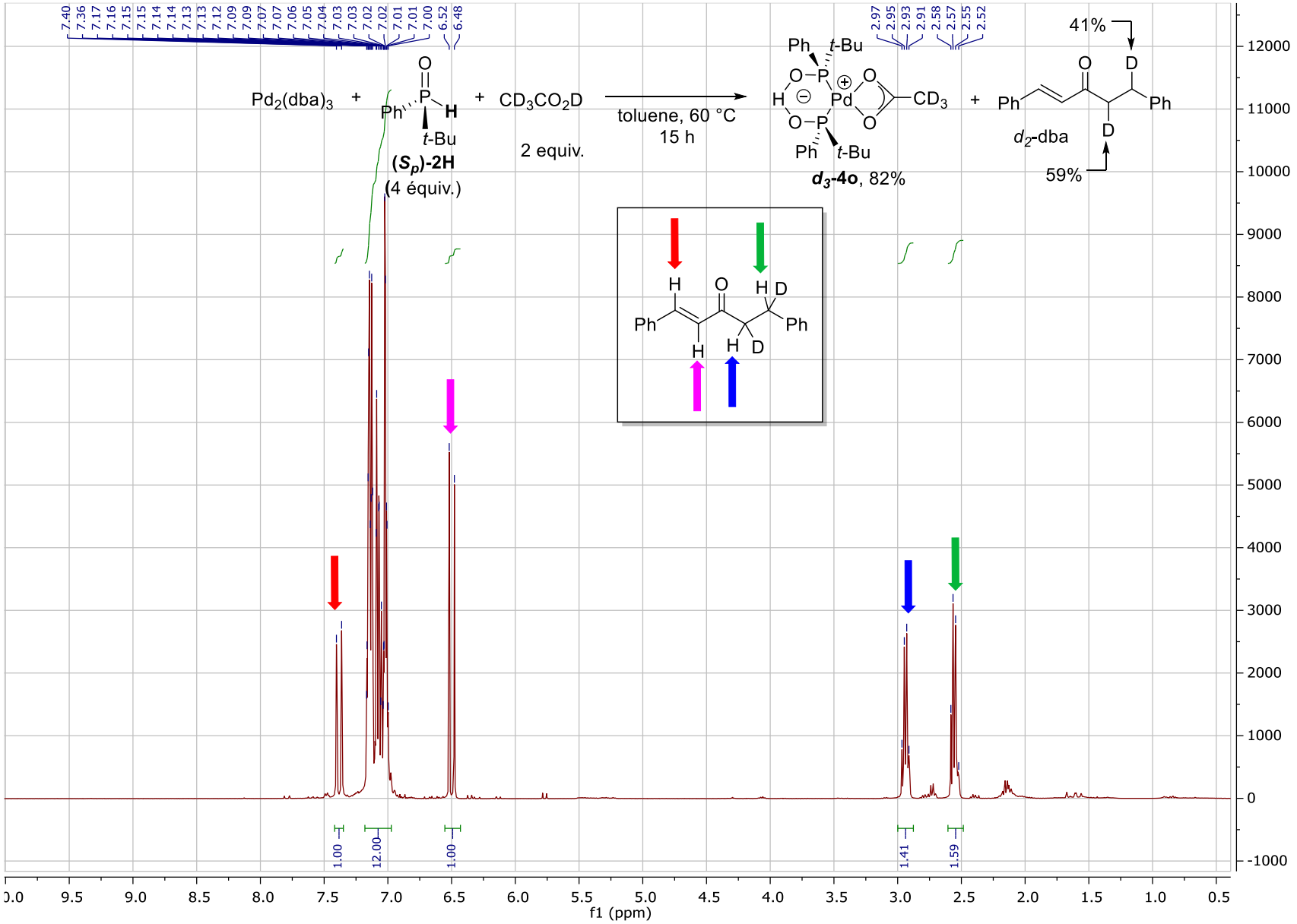

8.01
7.99
7.98
7.97
7.97
7.96
7.95
7.95
7.94
7.94
7.93
7.93
7.91
7.90
7.88
7.87
7.52
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.45
7.44
7.43
7.43
7.43
7.42
1.08
1.02
Ph
t-Bu
O
P
O
H
Pd
CD3
O
P
O
Ph
t-Bu
5.00
5.03
18.03
f1 (ppm)


190.85
134.54
133.81
131.78
131.71
131.63
130.99
128.17
128.10
128.03
39.39
38.81
26.94
26.88
26.54
26.52
26.50
25.75
25.72
25.69
Ph
t-Bu
O
P
H
Pd
CD3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

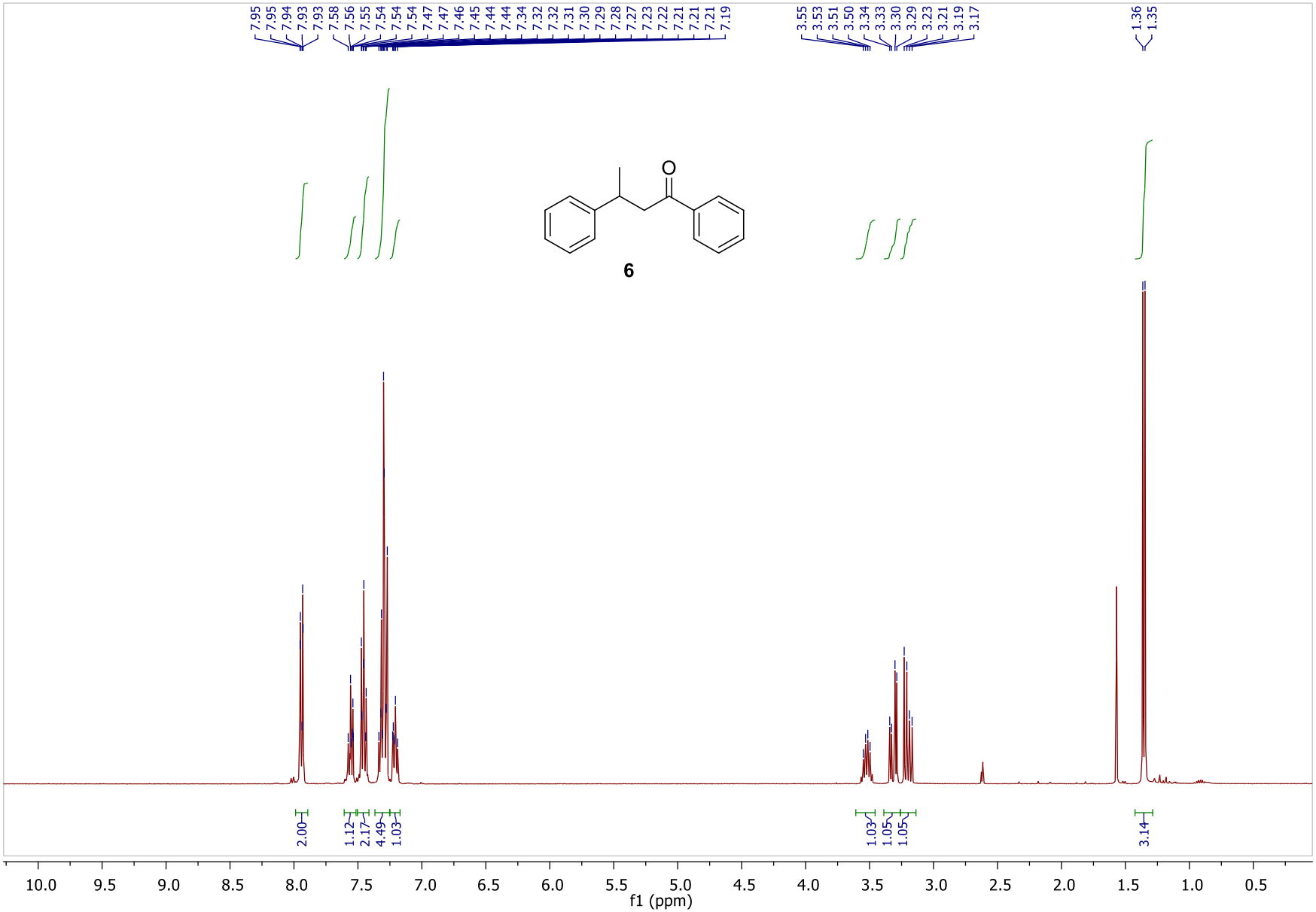

95.54
Ph
t-Bu
O
P
H
Pd
CD3
Ph
t-Bu
30000
25000
20000
15000
10000
5000
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

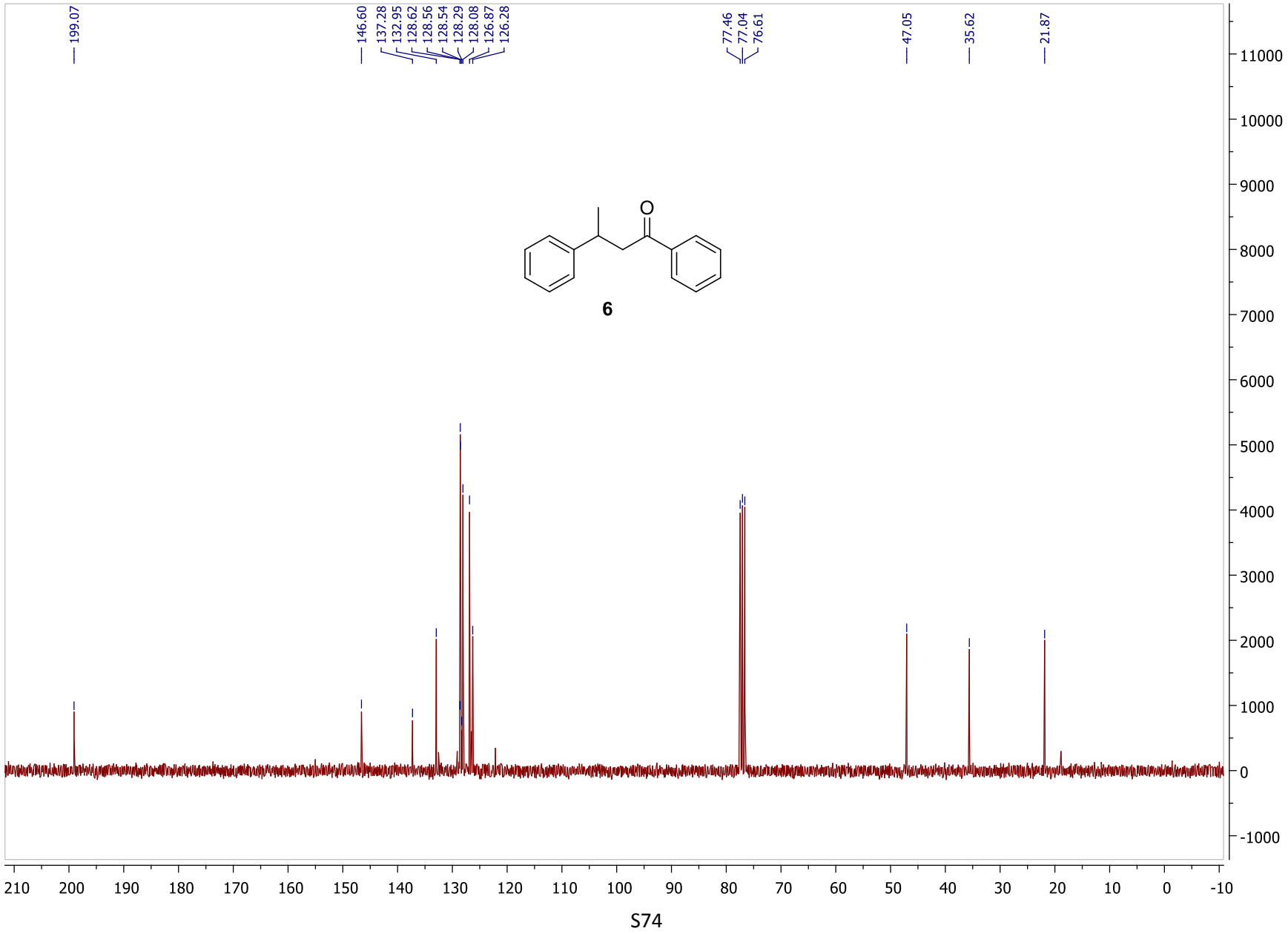
NMR spectra related to deuterium labelling experiments


7.41 7.36 7.15 7.15 7.14 7.13 7.12 7.10 7.09 7.08 7.07 7.05 7.03 7.02 7.01 7.01 7.00 6.52 6.47
2.97 2.95 2.92 2.60 2.57 2.55
Pd2(dba)3 + Ph P H t-Bu (Sp)-2H (4 équiv.) + AcOH 2 equiv.
toluene, 60 °C
15 h
Ph t-Bu O P O H Pd O P O Ph t-Bu
4o, 73%
+ Ph O H Ph H
H2dba
H O H H Ph H H H Ph
12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0
1.00 13.03 1.00 2.01 2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Pd2(dba)3
+
Ph
H
t-Bu
(Sp)-2H
(4 équiv.)
+ CD3CO2D
2 equiv.
toluene, 60 °C
15 h
Ph
t-Bu
O
P
H
Pd
CD3
d3-4o, 82%
+
41%
59%
d2-dba
D
Ph
f1 (ppm)

NMR spectra related to the compound 6


7.95
7.95
7.94
7.93
7.93
7.58
7.56
7.55
7.54
7.54
7.54
7.47
7.47
7.46
7.45
7.44
7.44
7.34
7.32
7.32
7.31
7.30
7.29
7.28
7.27
7.23
7.22
7.21
7.21
7.21
7.19
3.55
3.53
3.51
3.50
3.34
3.33
3.30
3.29
3.23
3.21
3.19
3.17
1.36
1.35
O
6
2.00
1.12
2.17
4.49
1.03
1.03
1.05
1.05
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


199.07
146.60
137.28
132.95
128.62
128.56
128.54
128.29
128.08
126.87
126.28
77.46
77.04
76.61
47.05
35.62
21.87
O
6
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10