## Electronic Supplementary Information

# Facile Synthesis and Utilization of Bis(*o*-phosphinophenyl)zinc as Isolable PZnP-pincer Ligands Enabled by Boron-Zinc Double Transmetallation

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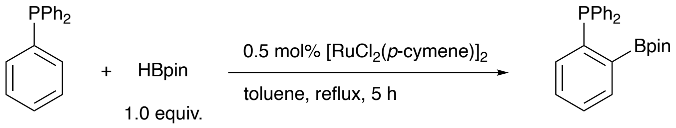
**General**: All operations were performed under an argon atmosphere. $^1H$, $^{11}B$, $^{13}C$ and $^{31}P$ spectra were recorded on a JEOL ECS-400 (400 MHz for $^1H$, 128 MHz for $^{11}B$, 100 MHz for $^{13}C$, and 160 MHz for $^{31}P$) or a JEOL ECX-400 (400 MHz for $^1H$ and 160 MHz for $^{31}P$) or a JEOL ECZ-500 (500 MHz for $^1H$, 125 MHz for $^{13}C$, and 200 MHz for $^{31}P$) or a JEOL ECX-500 (500 MHz for $^1H$, 160 MHz for $^{11}B$, 125 MHz for $^{13}C$, and 200 MHz for $^{31}P$) spectrometer in $CDCl_3$ or $C_6D_6$ or THF-$d_8$. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane ($\delta_H$ 0.00, $\delta_C$ 0.00), $BF_3 \bullet OEt_2$ ($\delta_B = 0.00$), 85% $H_3PO_4$ aq. ($\delta_P$ 0.00) and are referenced to residual solvents ($\delta_H$ 7.26 and $\delta_C$ 77.0 for chloroform, $\delta_H$ 7.16 and $\delta_C$ 128.1 for $C_6D_6$, and $\delta_H$ 3.58 and $\delta_C$ 67.2 for THF-$d_8$). IR spectra were recorded on an FT/IR-460 plus (JASCO Co., Ltd.) with ATR PRO450-S accessory (JASCO Co., Ltd.) or an Agilent Cary 630 FTIR (Agilent Technologies Co., Ltd.). High resolution mass spectra (HRMS) were recorded on a BRUKER micrOTOF II. Crystal data were collected by a Rigaku XtaLAB Synergy R DW HyPix system equipped with a Rigaku GNNP low-temperature device. Silica Gel 60 (Kanto Chemical Co., Inc.) was used for flash column chromatography. Merck Kieselgel 60 $F_{254}$ (0.25 mm thickness, coated on glass 20 x 20 $cm^2$) plate was used for analytical thin layer chromatography (TLC). $Et_2O$, THF, toluene, and hexane were purified by solvent purification system of Glass-Contour. Benzene-$d_6$ and THF-$d_8$ were purchased from Kanto Chemicals and dried and degassed by benzophenone ketyl. Chloroform-$d_1$ was purchased from Kanto Chemicals. Benzene was purchased from Kanto Chemicals and degassed by freeze-dry technique.

## Preparation of arylboronate 1a

*o*-(Diphenylphosphino)phenylboronate **1a** was synthesized in a 30 mmol scale by the Ru-catalyzed *ortho* C–H borylation reaction reported by our group.[S1]

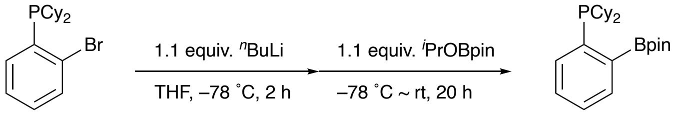


**1a** 77%

A solution of dichloro(*p*-cymene)ruthenium dimer (91.9 mg, 0.15 mmol) and triphenylphosphine (7.87 g, 30.0 mmol) in toluene (20.0 mL) was placed in a Schlenk flask under Ar. HBpin (4.40 mL, 30.6 mmol) was added to the solution at room temperature, then the mixture was stirred at 140 ºC in the closed system. After 6 h, saturated $NaHCO_3$ aq. was added to the solution at room temperature, and the mixture was extracted with AcOEt three times, and the combined organic layers were washed with brine and dried over $MgSO_4$. After filtration to remove the drying agent, the filtrate was evaporated to give a crude product. Reprecipitation from $Et_2O$ afforded *o*-(diphenylphosphino)phenylboronate **1a** as white solids (7.63 g, 19.7 mmol, 65.7%). The resulting filtrate was purified by silica gel column chromatography (Hexane:AcOEt = 19:1) to give **1a** (1.38 g, 3.55 mmol, 11.8%). $^{1}$H NMR ($CDCl_3$, 500 MHz) δ = 7.83-7.79 (m, 1H), 7.32-7.27 (m, 12H), 6.80-6.76 (m, 1H), 1.09 (s, 12H); $^{31}$P NMR ($CDCl_3$, 200 MHz) δ = –3.5. The spectral data were in good agreement with literature values.[S1]

## Preparation of arylboronate 1b

*o*-(Dicyclohexylphosphino)phenylboronate **1b** can be synthesized by the Rh-catalyzed *ortho* C–H borylation reaction of dicyclohexylphenylphosphine reported by Shi.[S2] However, we prepared it in a 15 mmol scale by a classical method, that is a reaction of *o*-(dicyclohexylphosphino)phenyllithium with a boron electrophile, due to the availability of reagents and reliability in a large scale.

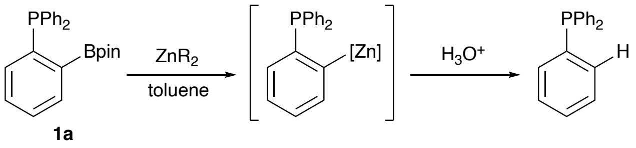


**1b** 85%

A solution of (*o*-dicyclohexylphosphino)bromobenzene (5.30 g, 15 mmol) in THF (60 mL) was placed in a 200 mL two necked flask under Ar. $^{n}$BuLi (1.59 M hexane solution, 10.4 mL, 16.5 mmol) was added to the solution at –78 ºC, and then the mixture was stirred at –78 ºC. After 2 h, $^{i}$PrOBpin was added to the solution at –78 ºC, and the reaction mixture was allowed to stand at room temperature gradually. After 20 h, the reaction was quenched with sat. $NH_4Cl$ aq. The resulting mixture was extracted with $Et_2O$ three times, and the combined organic layers were washed with water, brine, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography (Hexane:AcOEt = 9:1, $R_f$ = 0.39) to give **1b** as colorless oil (5.11 g, 12.7 mmol, 85%). $^{1}$H NMR ($CDCl_3$, 500 MHz) δ = 7.51-7.44 (m, 2H), 7.34-7.26 (m, 2H), 1.92-1.83 (m, 4H), 1.79-1.73

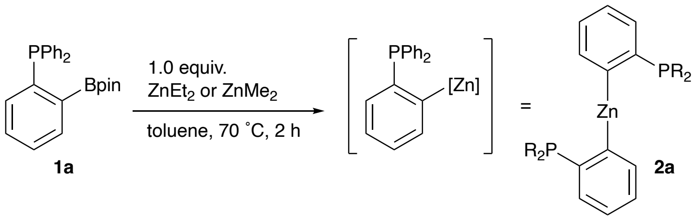
(m, 2H), 1.70-1.52 (m, 6H), 1.39 (s, 12H), 1.35-1.04 (m, 10H); $^{11}$B NMR ($CDCl_3$, 160 MHz) δ = 29.3 (br s); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ = 140.4 (d, *J* = 19.3 Hz), 132.5 (d, *J* = 14.4 Hz), 131.8 , 128.4, 127.6, 83.9, 34.1 (d, *J* = 13.3 Hz), 30.1 (d, *J* = 16.8 Hz), 29.5 (d, *J* = 9.6 Hz), 27.2 (d, *J* = 21.5 Hz), 27.1, 26.5, 25.0, 1C(*C*–B) is missing.; $^{31}$P NMR ($CDCl_3$, 200 MHz) δ = –0.6; IR (ATR) 2976.6, 2921.6, 2847.4, 1445.4, 1372.1, 1348.0, 1304.6, 1143.6, 1099.2, 1048.1 cm$^{-1}$. HRMS (ESI): Calcd for $C_{24}H_{39}BO_2P$ [M+H]$^+$:401.2781; Found: 401.2759.

## Investigation on reaction conditions for the boron-zinc transmetallation (Table 1)



A solution of **1a** (77.7 mg, 0.20 mmol) in toluene (2.0 mL) was placed in a two-necked flask equipped with a three-way stopcock and balloon under Ar. Diethylzinc (1.0 M in hexane) or dimethylzinc (0.72 M in hexane) was added to the solution at room temperature, and then the mixture was stirred under the conditions depicted in Table 1. The reaction was quenched with 1 M HCl aq., and the resulting mixture was extracted with $Et_2O$ three times, and the combined organic layers were washed with water, brine, and dried over $MgSO_4$. After filtration, the yields of triphenylphosphine and triphenylphosphine oxide were determined by GC analysis of the filtrate using $^n$dodecane as an internal standard. After evaporation of the solvent, the crude product was also analyzed by $^1$H NMR to determine the yield of **1a** using 1,1,2,2-tetrachloroethane as an internal standard. The combined yields of triphenylphosphine and triphenylphosphine oxide were depicted in the Table 1 as yields of protonation products.

## Monitoring of the reaction of 1a with alkylzinc reagents by $^{31}$P NMR



A solution of **1a** (19.4 mg, 50.0 μmol) and dialkylzinc (50 μmol) in toluene (0.5 mL) was placed in a sealed NMR tube under Ar and heated at various temperatures (40~70 ˚C). In both cases using $ZnEt_2$ or $ZnMe_2$ as alkylzinc reagents, the $^{31}$P NMR exhibited the generation of a singlet around δ = 4 as a major species, which is identical to that of the isolated bis(*o*-(diphenylphosphino)phenyl)zinc **2a** (Figure S1 and S2). **2a** existed as a major compound even at 40 ˚C after 1 h along with a small amount of boronate **1a**, demonstrating the facile boron-zinc transmetallation (Figure S1-d). These results support that the reaction affords diarylzinc **2a** selectively regardless of the type of alkylzinc reagents ($ZnEt_2$ or $ZnMe_2$). It should also be noted that the formation of monoarylzinc, ArZnEt, is not a major pathway despite the use of a stoichiometric amount of dialkylzinc to boronate, indicating that the formation of diarylzinc with the *ortho* $PPh_2$ substituent is thermodynamically favored.

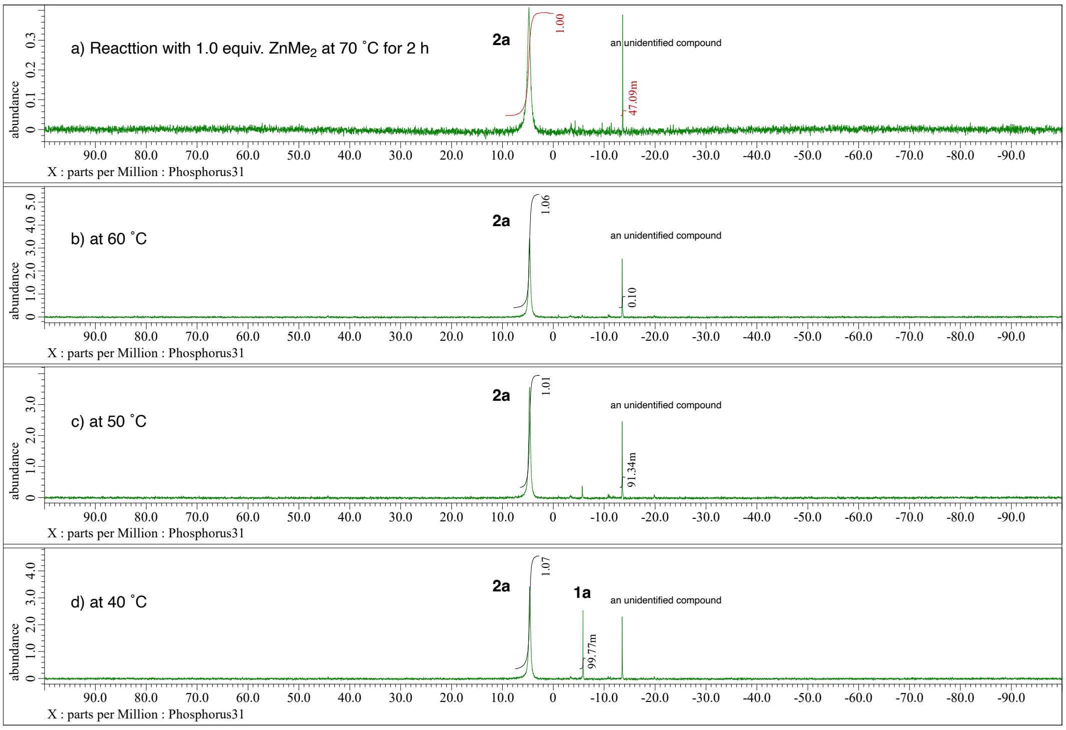


**Figure S1.** $^{31}P$ NMR of the reaction of **1a** with $ZnMe_2$ at 70 ˚C (a), 60 ˚C (b), 50 ˚C (c), 40 ˚C (d).

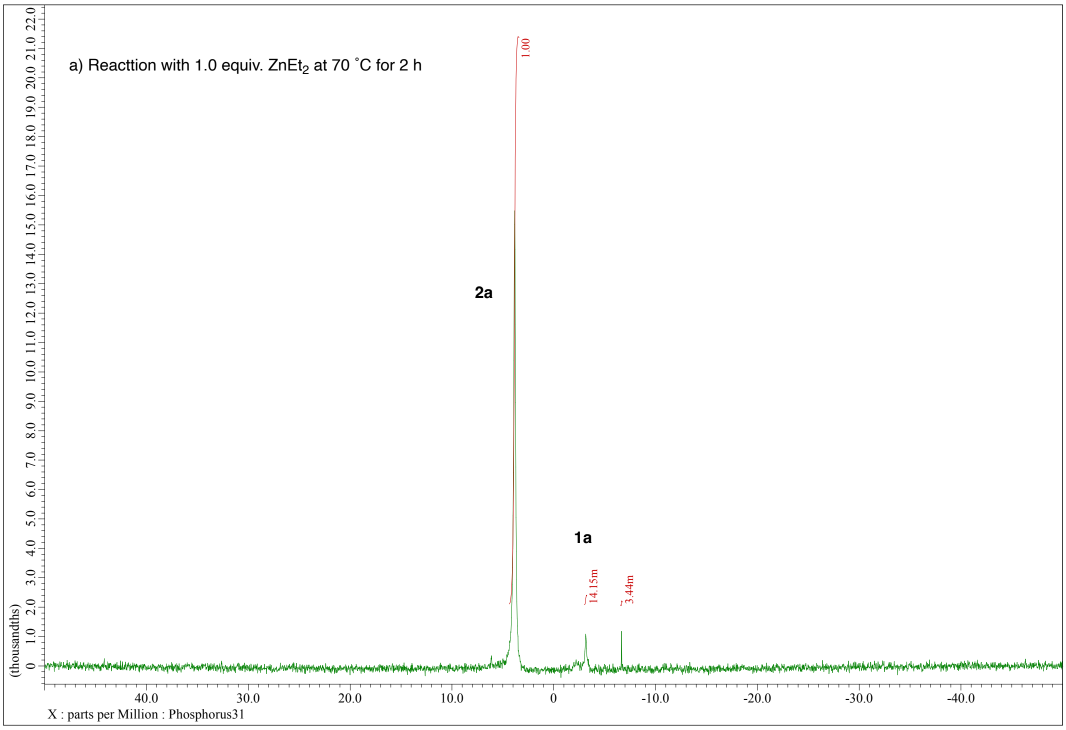
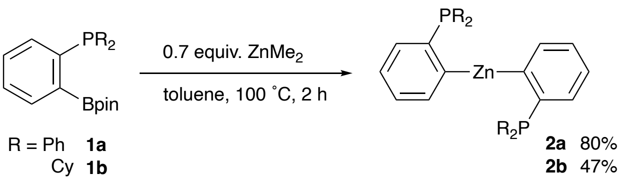


**Figure S2.** $^{31}P$ NMR of the reaction of **1a** with $ZnEt_2$ at 70 ˚C.

## **Synthesis of bis(*o*-phosphinophenyl)zinc 2 via boron-zinc double transmetallation** (Scheme 1)



### Bis(*o*-(diphenylphosphino)phenyl)zinc **2a**

A solution of **1a** (1.94 g, 5.0 mmol) in toluene (12 mL) was placed in a Schlenk tube equipped with a glass cock under Ar. Dimethylzinc (1.0 M in heptane, 3.5 mL, 3.5 mmol) was added to the solution at room temperature, and then the mixture was stirred at 100 ºC. After 2 h, the solvent was removed under reduced pressure, and the obtained crude material was purified by reprecipitation from THF/hexane to give **2a** as white solids (1.18 g, 2.01 mmol, 80%). $^{1}$H NMR ($C_6D_6$, 500 MHz) $\delta$ = 7.65 (d, $J$ = 6.5 Hz, 2H), 7.38-7.32 (m, 8H), 7.27 (dd, $J$ = 7.5, 5.0 Hz, 2H), 7.18 (td, $J$ = 7.5, 1.5 Hz, 2H), 7.06 (t, $J$ = 8.0 Hz, 2H), 6.97-6.92 (m, 12H); $^{13}$C NMR ($C_6D_6$, 125 MHz) $\delta$ = 168.5 (d, $J$ = 78.7 Hz), 144.2 (d. $J$ = 21.3 Hz), 138.9 (d, $J$ =30.0 Hz), 136.7, 134.1 (d, $J$ = 15.0 Hz), 132.1 (d, $J$ = 5.0 Hz), 129.0, 128.8 (d, $J$ = 7.5 Hz), 128.5, 127.5; $^{31}$P NMR ($C_6D_6$, 200 MHz) $\delta$ = 3.5; IR (ATR) 3045.2, 3030.3, 1477.9, 1431.3, 1420.1, 1086.5, 1025.0 cm$^{-1}$. The satisfactory data for elemental analysis and high resolution mass spectrometry were not obtained due to decomposition during the analyses.

### Bis(*o*-(dicyclohexylphosphino)phenyl)zinc **2b**

**2b** was prepared in the same manner as described above using **1b** (3.83 g, 9.6 mmol) and dimethylzinc (1.0 M in heptane, 6.7 mL, 6.7 mmol). The obtained crude material was dissolved into hexane and recrystallized at –30 ºC to give **2b** as white solids (1.37 g, 2.24 mmol, 47%). $^{1}$H NMR ($C_6D_6$, 500 MHz) $\delta$ = 7.99 (d, $J$ = 7.0 Hz, 2H), 7.45 (t, $J$ = 7.0 Hz, 2H), 7.40 (td, $J$ = 7.5, 1.0 Hz, 2H), 7.26 (t, $J$ = 7.5 Hz, 2H), 2.03-1.93 (m, 8H), 1.82-1.51 (m, 16H), 1.38-1.02 (m, 20H); $^{13}$C NMR ($C_6D_6$, 125 MHz) $\delta$ = 170.5 (d, $J$ = 96.3 Hz), 144.3 (d, $J$ = 12.5 Hz), 137.9 (d, $J$ = 36.3 Hz), 130.8, 129.2, 127.2, 33.6 (d, $J$ = 8.8 Hz), 30.7 (d, $J$ = 13.6 Hz), 29.4, 27.5 (d, $J$ = 12.5 Hz), 27.4 (d, $J$ = 6.3 Hz), 26.8; $^{31}$P NMR ($C_6D_6$, 200 MHz) $\delta$ = 21.0; IR (ATR) 3021.0, 2918.5, 2845.8, 1444.3, 1341.8, 1254.2, 1176.0, 1090.2, 1043.7 cm$^{-1}$. The satisfactory data for elemental analysis and high resolution mass spectrometry were not obtained due to decomposition during the analyses.

## X-ray diffraction analysis of 2a and 2b

Crystal data were collected by a Rigaku XtaLAB Synergy R DW HyPix system equipped with a Rigaku GNNP low-temperature device using Cu Ka radiation ($\lambda = 1.54184$ Å). Recrystallization of **2a** and **2b** from $Et_2O$/hexane afforded single crystals suitable for X-ray diffraction analysis (Figure S3 and Table S1).

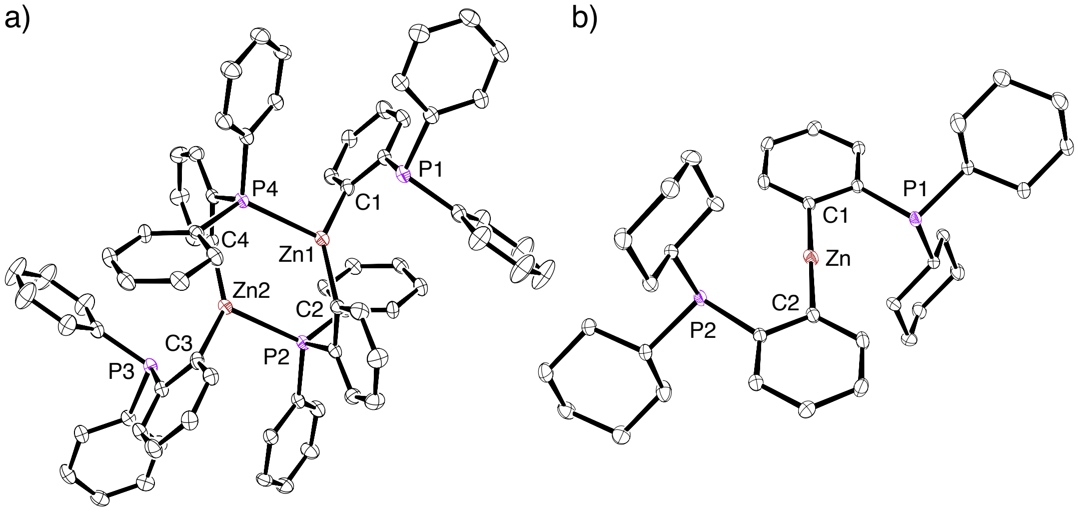


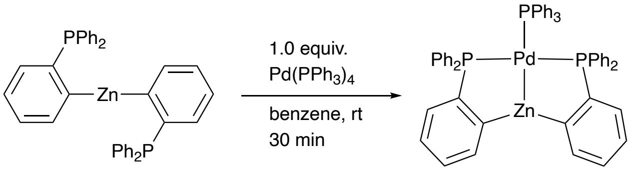
**Figure S3.** ORTEP drawings of **2a** (a) and **2b** (b) at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2a**: Zn1–C1 = 2.002(3), Zn1–C2 = 2.003(4), Zn1–P4 = 2.478(1), Zn1–P1 = 2.941(1), C1–Zn1–C2 = 142.2(1); for **2b**: Zn1–C1 = 1.9407(16), Zn1–C2 = 1.9407(16), C1–Zn1–C2 = 180.0.

**Table S1.** Crystallographic data of **2a** and **2b**

| | **2a** | **2b** |
|---|---|---|
| Formula | $C_{36}H_{28}P_2Zn$ | $C_{36}H_{52}P_2Zn$ |
| Formula weight | 587.89 | 612.08 |
| Temperature /K | 123(2) | 123(2) |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ (#14) | $P2_1/n$ (#14) |
| Crystal color | colorless | colorless |
| Crystal size | 0.05 x 0.02 x 0.02 | 0.10 x 0.10 x 0.03 |
| $a$ /Å | 14.8373(2) | 9.46080(10) |
| $b$ /Å | 9.6322(2) | 8.88880(10) |
| $c$ /Å | 20.4511(2) | 19.8948(2) |
| α /deg | 90 | 90 |
| β /deg | 92.515(2) | 103.4176(12) |
| γ /deg | 90 | 90 |
| $V$ /Å$^3$ | 2919.97(9) | 1627.39(3) |
| $Z$ | 4 | 2 |
| μ (Cu Kα) /cm$^{-1}$ | 1.54184 | 1.54184 |
| Reflections collected | 19673 | 11128 |
| Unique reflections | 5808 | 3282 |
| Refined parameters | 352 | 178 |
| GOF on $F^2$ | 1.066 | 1.064 |
| $R_1$ $[I > 2\sigma(I)]^a$ | 0.0542 | 0.0344 |
| w$R_2$ (all data)$^b$ | 0.1481 | 0.0971 |

$^a$ $R_1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$, $^b$ w$R_2 = [\Sigma(w(Fo^2 – Fc^2)^2/\Sigma w(Fo^2)^2)^{1/2}$

## Synthesis of the PZnP-Pd complex 3 (Scheme 2)



**2a** **3a** 95%

Bis(*o*-(diphenylphosphino)phenyl)zinc **2a** (176 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (347 mg, 0.30 mmol) were placed in a round bottom flask and dissolved in benzene at room temperature, and then the mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure, and the obtained crude material was purified by reprecipitation from THF/hexane to give the PZnP-Pd complex **3a** as yellow solids (272 mg, 0.284 mmol, 95%). $^1$H NMR (THF-$d_8$, 500 MHz) $\delta$ = 7.80 (d, $J$ = 6.0 Hz, 2H), 7.16-6.93 (m, 41H); $^{13}$C NMR (THF-$d_8$, 125 MHz) $\delta$ = 171.8 (vt, $J$ = 45.0 Hz), 149.2 (vt, $J$ = 22.5 Hz), 140.0 (vt, $J$ = 13.8 Hz), 138.5 (vt, $J$ = 18.8 Hz), 134.4 (d, $J$ = 16.3 Hz), 134.1 (vt, $J$ = 6.3 Hz), 131.2, 128.8, 128.5, 128.4 (d, $J$ = 6.3 Hz), 128.2 (vt, $J$ = 3.8 Hz), 128.0, 126.2, 1C is missing due to overlapping.; $^{31}$P NMR ($C_6D_6$, 200 MHz) $\delta$ = 44.1, 12-16 (br). ; IR (ATR) 3035.9, 1476.0, 1431.3, 1086.5, 1035.0 cm$^{-1}$. Anal. Calcd for $C_{54}H_{43}P_3PdZn$: C, 67.80; H, 4.53; Found: C, 67.07; H, 4.70. Although the %C is slightly outside the acceptable range, this is the best value obtained to date.

## X-ray diffraction analysis of 3a

Crystal data were collected by a Rigaku XtaLAB Synergy R DW HyPix system equipped with a Rigaku GNNP low-temperature device using Cu Ka radiation ($\lambda$ = 1.54184 Å). Recrystallization of **3a** from $Et_2O$/hexane afforded single crystals suitable for X-ray diffraction analysis (Figure S4 and Table S2).

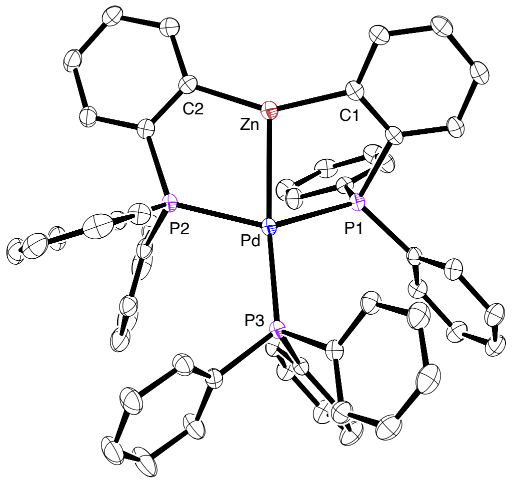


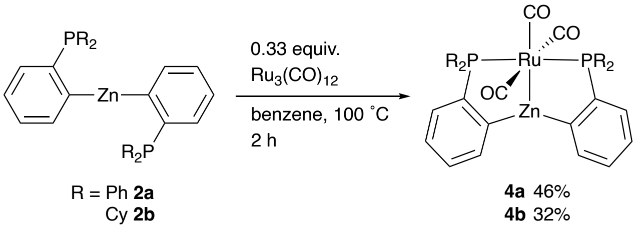
**Figure S4.** ORTEP drawing of **3a** at 30% probability level. Hydrogen atoms and a solvent molecule ($Et_2O$) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–Zn = 2.6399(5), Pd–P1 = 2.3270(7), Pd–P2 = 2.3095(7), Pd–P3 = 2.3917(7), Zn–C1 = 1.983(3), Zn–C2 = 1.973(3), C1–Zn–C2 = 149.3(1), P1–Pd–P2 = 140.41(3), P3–Pd–Zn = 166.21(2).

**Table S2.** Crystallographic data of **3a**

| | **3a** |
|---|---|
| Formula | $C_{56}H_{48}O_{0.5}P_3PdZn$ |
| Formula weight | 993.62 |
| Temperature /K | 123(2) |
| Crystal system | triclinic |
| Space group | *P*–1 (#2) |
| Crystal color | yellow |
| Crystal size | 0.10 x 0.02 x 0.01 |
| *a* /Å | 9.1351(2) |
| *b* /Å | 13.0286(3) |
| *c* /Å | 20.1713(6) |
| α /deg | 93.909(2) |
| β /deg | 97.565(2) |
| γ /deg | 96.028(2) |
| *V* /Å$^3$ | 2358.48(10) |
| *Z* | 2 |
| μ (Cu Kα) /cm$^{-1}$ | 1.54184 |
| Reflections collected | 26767 |
| Unique reflections | 9091 |
| Refined parameters | 557 |
| GOF on $F^2$ | 1.037 |
| $R_1$ [$I > 2\int(I)$]$^a$ | 0.0333 |
| w$R_2$ (all data)$^b$ | 0.0851 |

$^a$ $R_1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$, $^b$ $wR_2 = [\Sigma(w(Fo^2–Fc^2)^2/\Sigma w(Fo^2)^2)^{1/2}$

**Synthesis of PZnP-Ru complexes 4a and 4b** (Scheme 3)



PZnP-Ru complex **4a**

**2a** (176 mg, 0.30 mmol) and $Ru_3(CO)_{12}$ (63.9 mg, 0.10 mmol) were placed in a round bottom flask and dissolved in toluene at room temperature, and then the mixture was stirred at 100 ºC. After 2 h, the solvent was removed under reduced pressure, and the obtained crude material was purified by reprecipitation from THF/hexane to give the PZnP-Ru complex **4a** as pale yellow solids (108 mg, 0.140 mmol, 47%). $^1H$ NMR ($C_6D_6$, 500 MHz) $\delta$ = 8.32 (d, *J* = 7.0 Hz, 2H), 7.70-7.64 (m, 8H), 7.60-7.56 (m, 2H), 7.33 (td, *J* = 7.0, 1.0 Hz, 2H), 7.01 (td, *J* = 7.5, 2.0 Hz, 2H), 6.95-6.89 (m, 12H); $^{31}P$ NMR (THF-$d_8$, 200 MHz) $\delta$ = 62.6. These spectral data were in good agreement with literature values.[S3]

PZnP-Ru complex **4b**

**4b** was prepared in the same manner as above using **2b** (184 mg, 0.30 mmol) and $Ru_3(CO)_{12}$ (63.9 mg, 0.10 mmol). The obtained crude material was purified by reprecipitation from toluene/hexane to give **4b** as a pale yellow solid (77.5 mg, 0.0972 mmol, 32%). $^1H$ NMR ($C_6D_6$, 500 MHz) $\delta$ = 8.28 (d, *J* = 6.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 6.5 Hz, 2H), 7.19 (td, *J* = 7.5, 1.5 Hz, 2H), 2.32-2.34 (m, 4H), 2.03 (d, *J* = 13.5 Hz, 4H), 1.86 (d, *J* = 13.5 Hz, 4H), 1.70-1.41 (m, 20H), 1.29-1.00 (m, 12H); $^{13}C$ NMR (THF-$d_8$, 125 MHz) = 207.9 (t, *J* = 15.0 Hz), 205.6, 173.2 (t, *J* = 26.3 Hz), 144.7 (vt, *J* = 26.4 Hz), 139.10, 139.09 (d, *J* = 25.0 Hz), 130.8 (vt, *J* = 3.8 Hz), 128.4, 125.2, 41.6 (vt, *J* = 11.3 Hz), 30.7, 29.8, 28.1 (vt, *J* = 3.8 Hz), 27.7 (vt, *J* = 3.8 Hz), 27.0; $^{31}P$ NMR (THF-$d_8$, 200 MHz) $\delta$ = 69.7; IR (ATR) 2972.6, 2899.9, 2842.1, 2007.3, 1947.5, 1928.9, 1900.9, 1444.3, 1259.8, 1086.5, 1045.5, 1000.8 $cm^{-1}$. Anal. Calcd for $C_{39}H_{52}O_3P_2RuZn$: C, 58.76; H, 6.57; Found: C, 58.17; H, 6.57. Although the %C is slightly outside the acceptable range, this is the best value obtained to date.

## X-ray diffraction analysis of 4a and 4b

Crystal data were collected by a Rigaku XtaLAB Synergy R DW HyPix system equipped with a Rigaku GNNP low-temperature device using Cu Ka radiation (λ = 1.54184 Å). Recrystallization of **4a** from toluene/$Et_2O$ and **4b** from toluene/hexane afforded single crystals suitable for X-ray diffraction analysis (Figure S5 and Table S3).

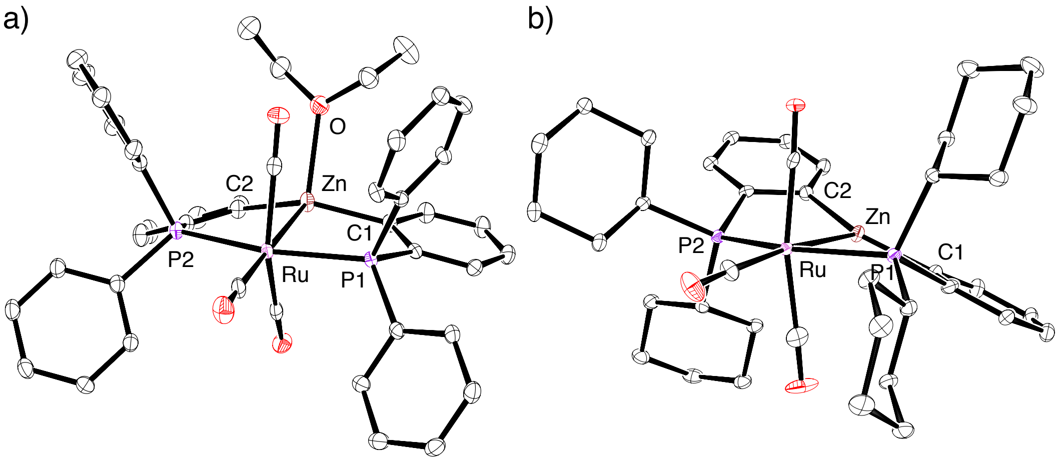


**Figure S5.** ORTEP drawing of **4a** (b) and **4b** (b) at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **4a**: Ru–Zn = 2.7343(5), Ru–P1 = 2.3490(9), Ru–P2 = 2.3604(9), Zn–C1 = 2.013(3), Zn–C2 = 2.012(3), Zn–O = 2.297(3), P1–Pd–P2 = 164.01(3), C1–Zn–C2 = 145.3(1); for **4b**: Ru–Zn = 2.6983(5), Ru–P1 = 2.3954(9), Ru–P2 = 2.385(1), Zn–C1 = 1.975(4), Zn–C2 = 1.978(4), P1–Pd–P2 = 153.13(3), C1–Zn–C2 = 152.7(1).

**Table S3.** Crystallographic data of **4a** and **4b**

| | **4a** | **4b** |
|---|---|---|
| Formula | $C_{43}H_{38}O_4P_2RuZn$ | $C_{39}H_{52}O_3P_2RuZn$ |
| Formula weight | 847.11 | 797.18 |
| Temperature /K | 123(2) | 123(2) |
| Crystal system | triclinic | Orthorhombic |
| Space group | *P*–1 (#2) | *P*na21 (#33) |
| Crystal color | yellow | yellow |
| Crystal size | 0.07 x 0.03 x 0.02 | 0.06 x 0.05 x 0.04 |
| $a$ /Å | 9.8387(2) | 17.5815(2) |
| $b$ /Å | 13.5839(4) | 11.45430(10) |
| $c$ /Å | 15.1541(6) | 18.0955(2) |
| α /deg | 100.156(3) | 90 |
| β /deg | 91.955(3) | 90 |
| γ /deg | 108.525(2) | 90 |
| $V$ /$Å^3$ | 1881.45(10) | 3644.14(7) |
| $Z$ | 2 | 4 |
| μ (Cu Kα) /$cm^{-1}$ | 1.54184 | 1.54184 |
| Reflections collected | 20345 | 19129 |
| Unique reflections | 7214 | 4864 |
| Refined parameters | 462 | 416 |
| GOF on $F^2$ | 1.044 | 1.046 |
| $R_1$ [$I > 2 \int(I)$]$^a$ | 0.0343 | 0.0248 |
| w$R_2$ (all data)$^b$ | 0.0877 | 0.0588 |

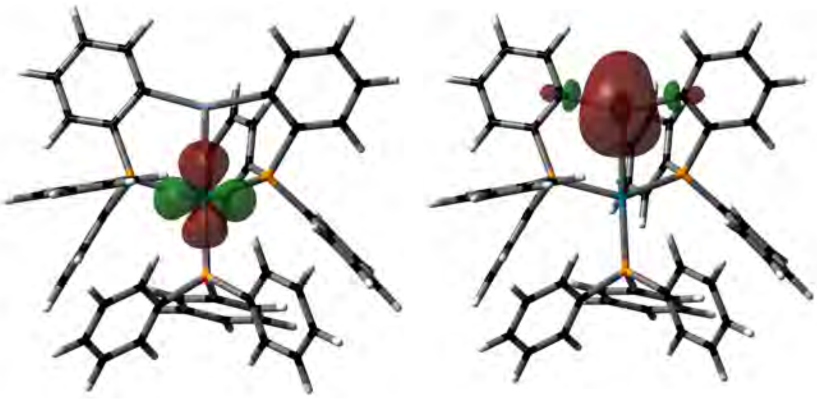
$^a$ $R_1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$, $^b$ $wR_2 = [\Sigma(w(Fo^2–Fc^2)^2/\Sigma w(Fo^2)^2)^{1/2}$

## Computational details

All calculations were performed with the Gaussian 16 program package (revision A.03).[S4] Equilibrium structures were optimized by density functional theory (DFT) using the B3PW91 hybrid functional with tight SCF convergence and ultrafine integration grids. Empirical dispersion correction was included. The LANL2DZ basis set, including a double-z valence basis set with the Hay and Wadt effective core potential (ECP), was used for palladium and zinc, and the 6-31G(d,p) basis set was used for carbon, hydrogen, and phosphorus. Each of the stationary points was adequately characterized by normal coordinate analysis (no imaginary frequency for an equilibrium structure). In all calculations, the temperature was set to 298.15 K. Natural bond orbital (NBO) analysis was performed at the same level of theory using the NBO 7 package.[S5]

### NBO analysis on the PZnP-Pd complex **3a**

NBO analysis was performed on the optimized structure of **3a**. The Pd–Zn bond mainly consists of a donor-acceptor interactions between an occupied $d_{x2-y2}$ orbital of Pd and an unoccupied s-type orbital of Zn as shown in Figure S6. This donor-acceptor interaction lead to stabilization in 7.5 kcal/mol. This result strongly supports that the Zn-metalloligand serves as a Z-type, σ-acceptor ligand for palladium.



LP5(Pd, $d_{x2-y2}$), occ = 1.85 LV1(Zn, s 98.5%), occ = 0.64

LP5(Pd) → LV1(Zn) = 7.5 kcal/mol

**Figure S6.** Donor and acceptor orbitals for the Pd–Zn bond and the stabilization energy calculated by NBO analysis. LP denotes a lone pair orbital, LV denotes a lone vacancy (unoccupied valence orbital), and occ denotes the electron occupancy.

**TableS4.** Cartesian coordinates of the optimized structure of **3a**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 46 | 0 | 0.020433 | -0.199148 | -0.512718 |
| 2 | 30 | 0 | -0.054902 | -2.957615 | -1.096426 |
| 3 | 15 | 0 | -2.188852 | -0.835564 | -0.142765 |
| 4 | 15 | 0 | 2.168522 | -1.067395 | -0.167881 |
| 5 | 15 | 0 | 0.137679 | 2.158935 | -0.209573 |
| 6 | 6 | 0 | -2.695088 | -2.586219 | 0.146485 |
| 7 | 6 | 0 | -1.862382 | -3.586790 | -0.382834 |
| 8 | 6 | 0 | -2.290413 | -4.917245 | -0.229856 |
| 9 | 1 | 0 | -1.675679 | -5.726841 | -0.620946 |
| 10 | 6 | 0 | -3.476345 | -5.237026 | 0.430186 |
| 11 | 1 | 0 | -3.777333 | -6.276372 | 0.542571 |
| 12 | 6 | 0 | -4.274349 | -4.221764 | 0.962637 |
| 13 | 1 | 0 | -5.193080 | -4.466381 | 1.489856 |
| 14 | 6 | 0 | -3.886990 | -2.893613 | 0.819486 |
| 15 | 1 | 0 | -4.501005 | -2.104411 | 1.247052 |
| 16 | 6 | 0 | 2.835822 | -2.420257 | -1.212597 |
| 17 | 6 | 0 | 1.874788 | -3.333165 | -1.695033 |
| 18 | 6 | 0 | 2.355240 | -4.414878 | -2.447696 |
| 19 | 1 | 0 | 1.655769 | -5.155648 | -2.833035 |
| 20 | 6 | 0 | 3.714170 | -4.565355 | -2.736593 |
| 21 | 1 | 0 | 4.053728 | -5.401992 | -3.343498 |
| 22 | 6 | 0 | 4.638896 | -3.642371 | -2.248793 |
| 23 | 1 | 0 | 5.697219 | -3.758389 | -2.468511 |
| 24 | 6 | 0 | 4.203212 | -2.569980 | -1.472072 |
| 25 | 1 | 0 | 4.922143 | -1.856825 | -1.076579 |
| 26 | 6 | 0 | -2.673796 | -0.022670 | 1.431664 |
| 27 | 6 | 0 | -2.171459 | -0.597804 | 2.611003 |
| 28 | 1 | 0 | -1.580129 | -1.507878 | 2.557237 |
| 29 | 6 | 0 | -2.415252 | -0.004856 | 3.845299 |
| 30 | 1 | 0 | -2.018505 | -0.463335 | 4.746888 |
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| 32 | 1 | 0 | -3.349027 | 1.638939 | 4.887619 |
| 33 | 6 | 0 | -3.641355 | 1.763170 | 2.755450 |
| 34 | 1 | 0 | -4.197415 | 2.695149 | 2.797585 |
| 35 | 6 | 0 | -3.397991 | 1.172574 | 1.514236 |
| 36 | 1 | 0 | -3.758602 | 1.660457 | 0.615148 |
| 37 | 6 | 0 | -3.412507 | -0.295447 | -1.401730 |
| 38 | 6 | 0 | -4.771959 | -0.090844 | -1.137899 |
| 39 | 1 | 0 | -5.157640 | -0.231420 | -0.132849 |
| 40 | 6 | 0 | -5.634540 | 0.310784 | -2.155228 |
| 41 | 1 | 0 | -6.685116 | 0.480414 | -1.935322 |
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| 75 | 6 | 0 | 1.872294 | 2.506767 | 4.063564 |
| 76 | 1 | 0 | 2.279258 | 2.517250 | 5.070884 |
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<u>**References**</u>

1. K. Fukuda, N. Iwasawa, J. Takaya, *Angew. Chem. Int. Ed.* **2019**, *58*, 2850–2853.
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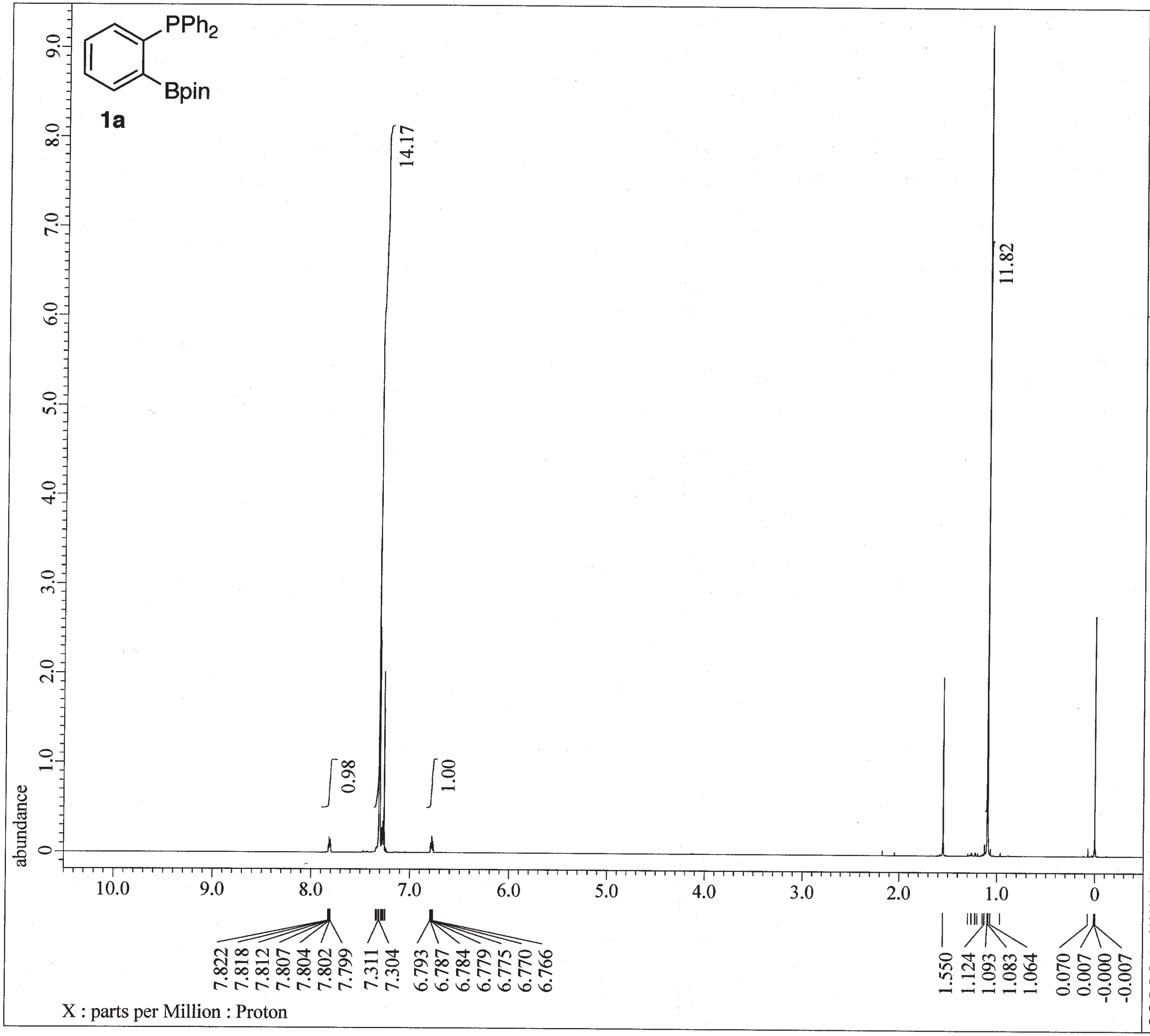

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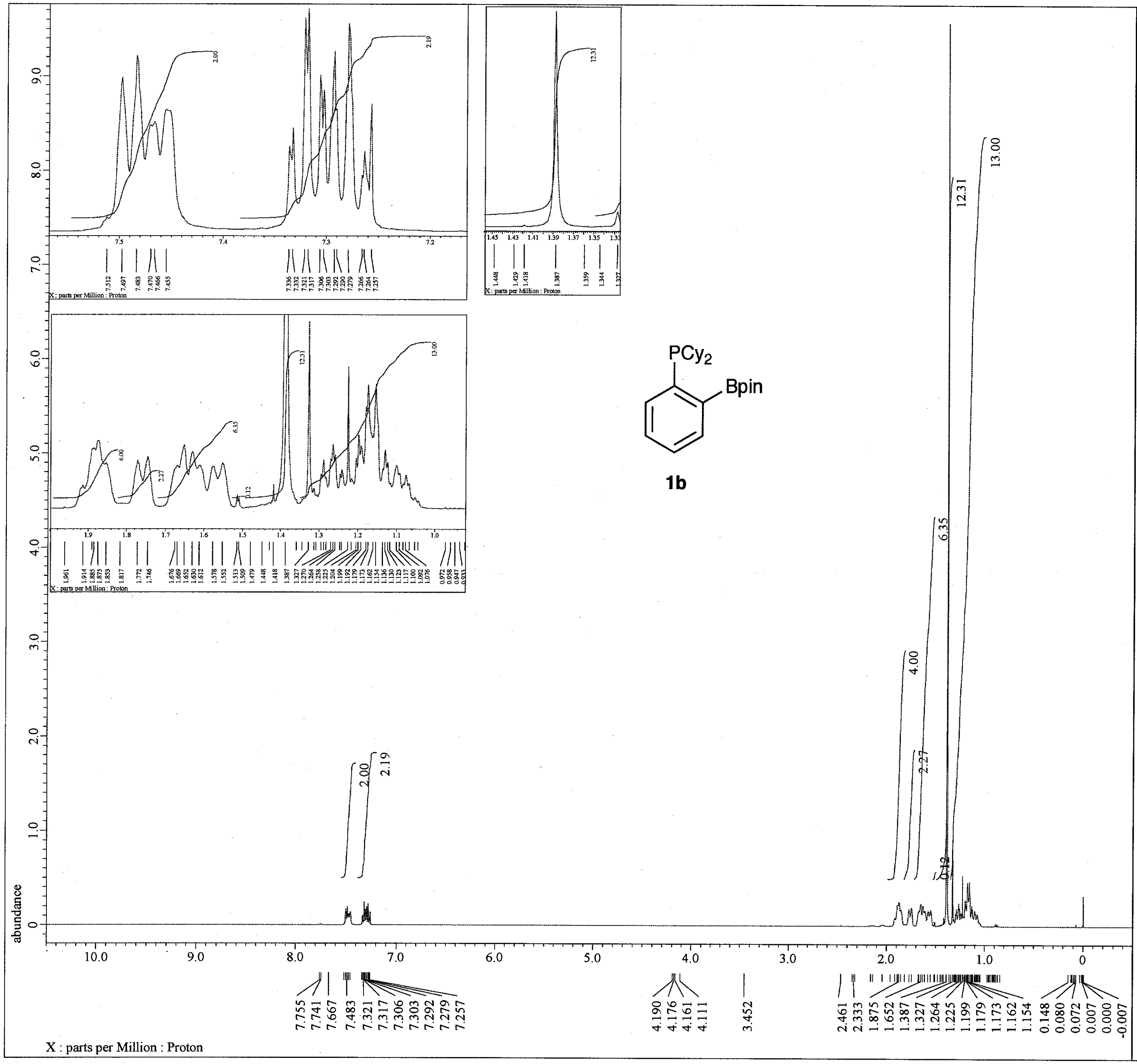

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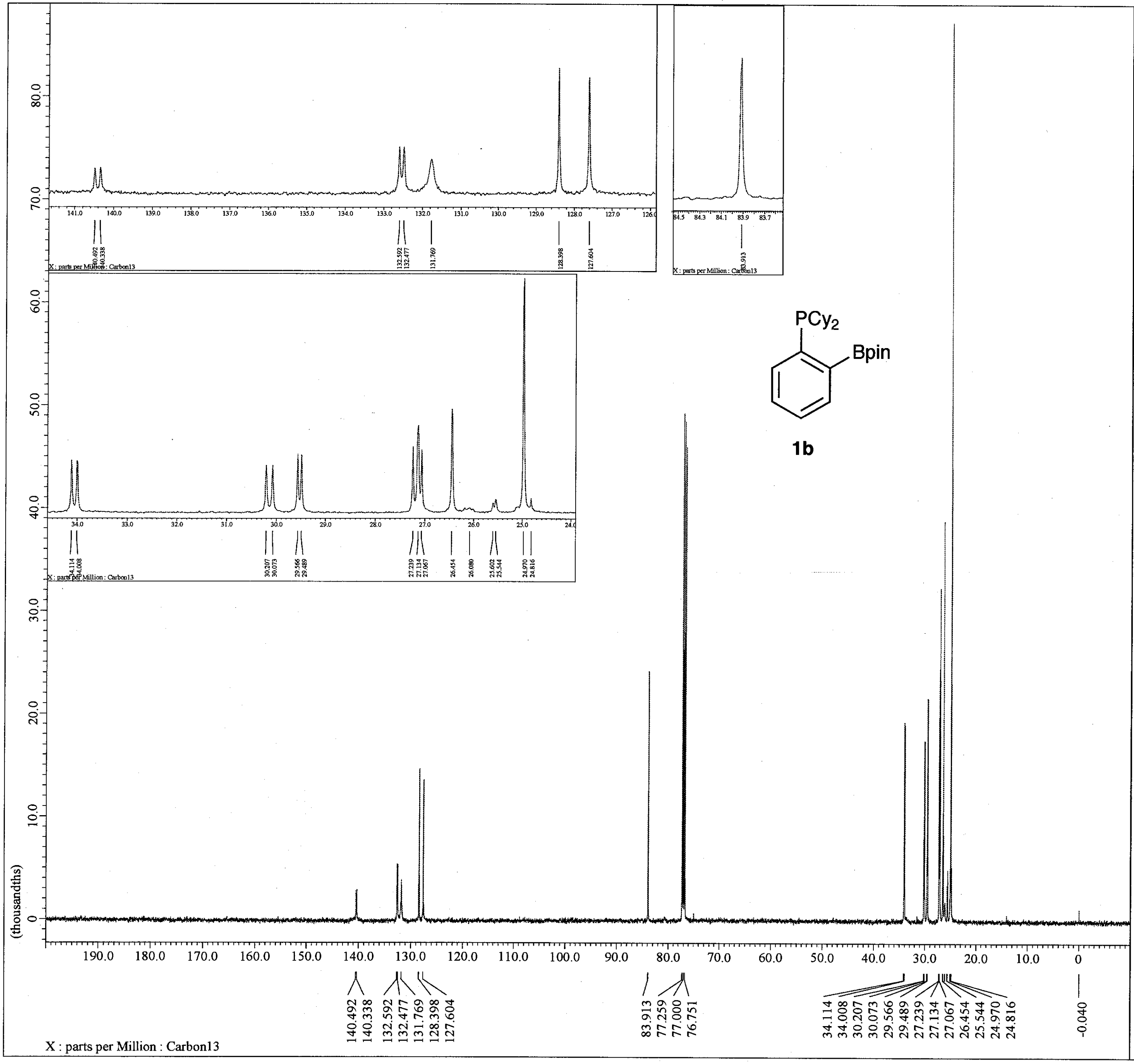

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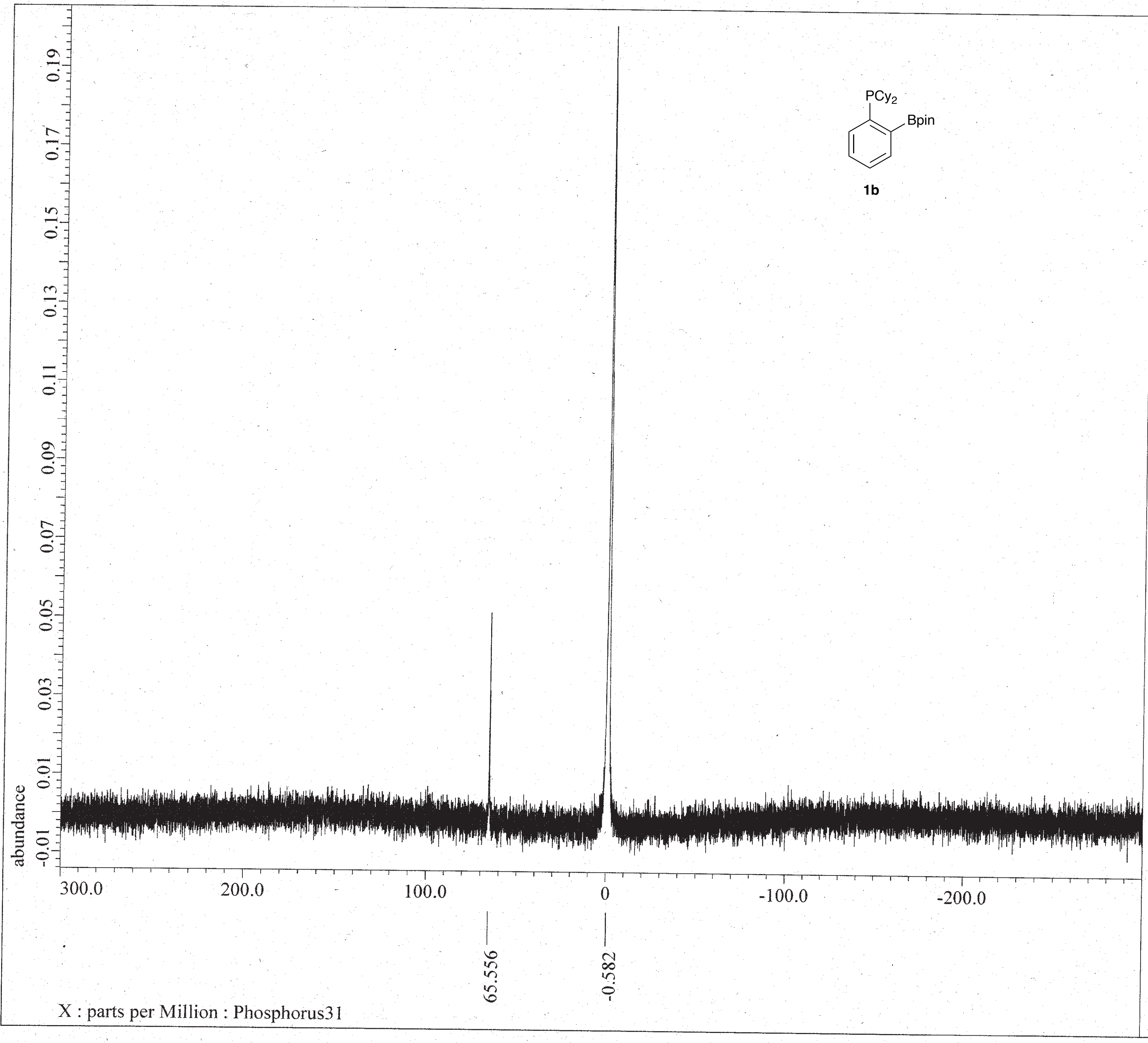
Irr_Dec_Freq               = 495.13191398[MHz]
Irr_Dec_Merit_Factor       = 2.2
Irr_Decoupling             = TRUE
Irr_Noe                    = TRUE
Irr_Noise                  = WALTZ
Irr_Offset_Default         = 5[ppm]
Irr_Pwidth                 = 92[us]
Irr_Pwidth_Default         = 92[us]
Irr_Pwidth_Default_Calc    = 92[us]
Irr_Pwidth_Templ           = 92[us]
Irr_Wurst                  = FALSE
Decimation_Rate            = 0
Initial_Wait               = 1[s]
Noe_Time                   = 2[s]
Noe_Time_Flag              = FALSE
Relaxation_Delay_Calc      = 0[s]
Relaxation_Delay_Temp      = 2[s]
Repetition_Time            = 2.8388608[s]
```



**1b**

```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
phase( -4.80782, 7.15754, 50.07439[%] )

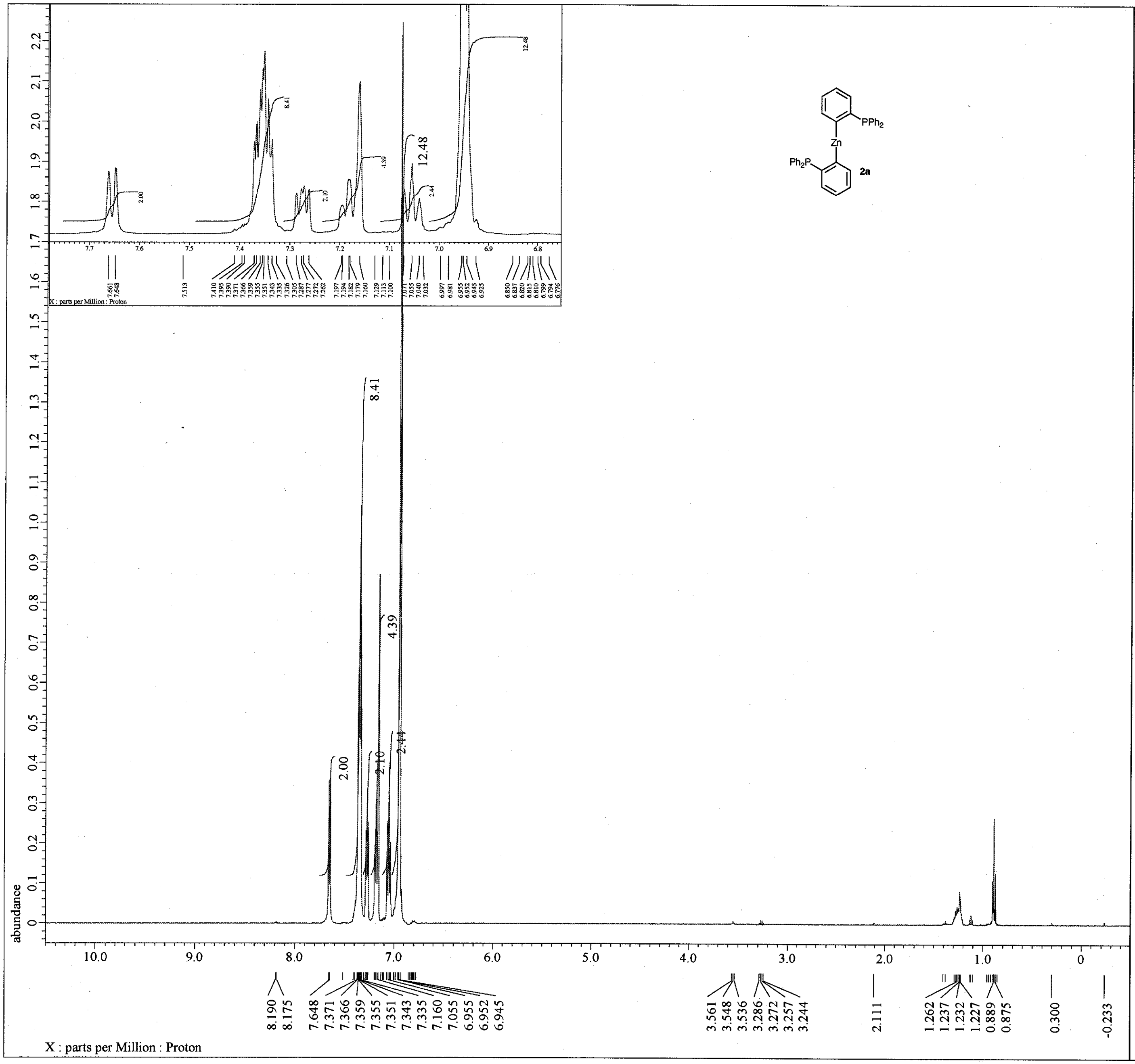
以下に由来：: KF PCy2Bpin 31P 1Hdec-1-1.jdf

Filename                    = KF_PCy2Bpin_31P_
Author                      = delta
Experiment                  = single_pulse_dec
Sample_Id                   = KF_PCy2Bpin
Solvent                     = CHLOROFORM-D
Creation_Time               = 17-JAN-2020 10:5
Revision_Time               = 17-JAN-2020 19:1
Current_Time                = 17-JAN-2020 19:1

Comment                     = single pulse dec
Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
Dim_Title                   = Phosphorus31
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ500R/S1

Field_Strength              = 11.62926421[T] (
X_Acq_Duration              = 0.18874368[s]
X_Domain                    = 31P
X_Freq                      = 200.43293989[MHz
X_Offset                    = 0[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 5.29819065[Hz]
X_Sweep                     = 173.61111111[kHz
X_Sweep_Clipped             = 138.88888889[kHz
Irr_Domain                  = Proton
Irr_Freq                    = 495.13191398[MHz
Irr_Offset                  = 5[ppm]
Clipped                     = FALSE
Decimation_Reg              = r: 36( 35),g: 26
Scans                       = 50
Total_Scans                 = 50

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 56
Temp_Get                    = 21.7[dC]
X_90_Width                  = 14.5[us]
X_Acq_Time                  = 0.18874368[s]
X_Angle                     = 30[deg]
X_Atn                       = 9.3[dB]
X_Pulse                     = 4.83333333[us]
Irr_Atn_Dec                 = 26.4[dB]
Irr_Atn_Dec_Calc            = 26.4[dB]
Irr_Atn_Dec_Default_Calc    = 26.4[dB]
Irr_Atn_Noe                 = 26.4[dB]
Irr_Dec_Bandwidth_Hz        = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 12.07407703[ppm]
Irr_Dec_Freq                = 495.13191398[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
```

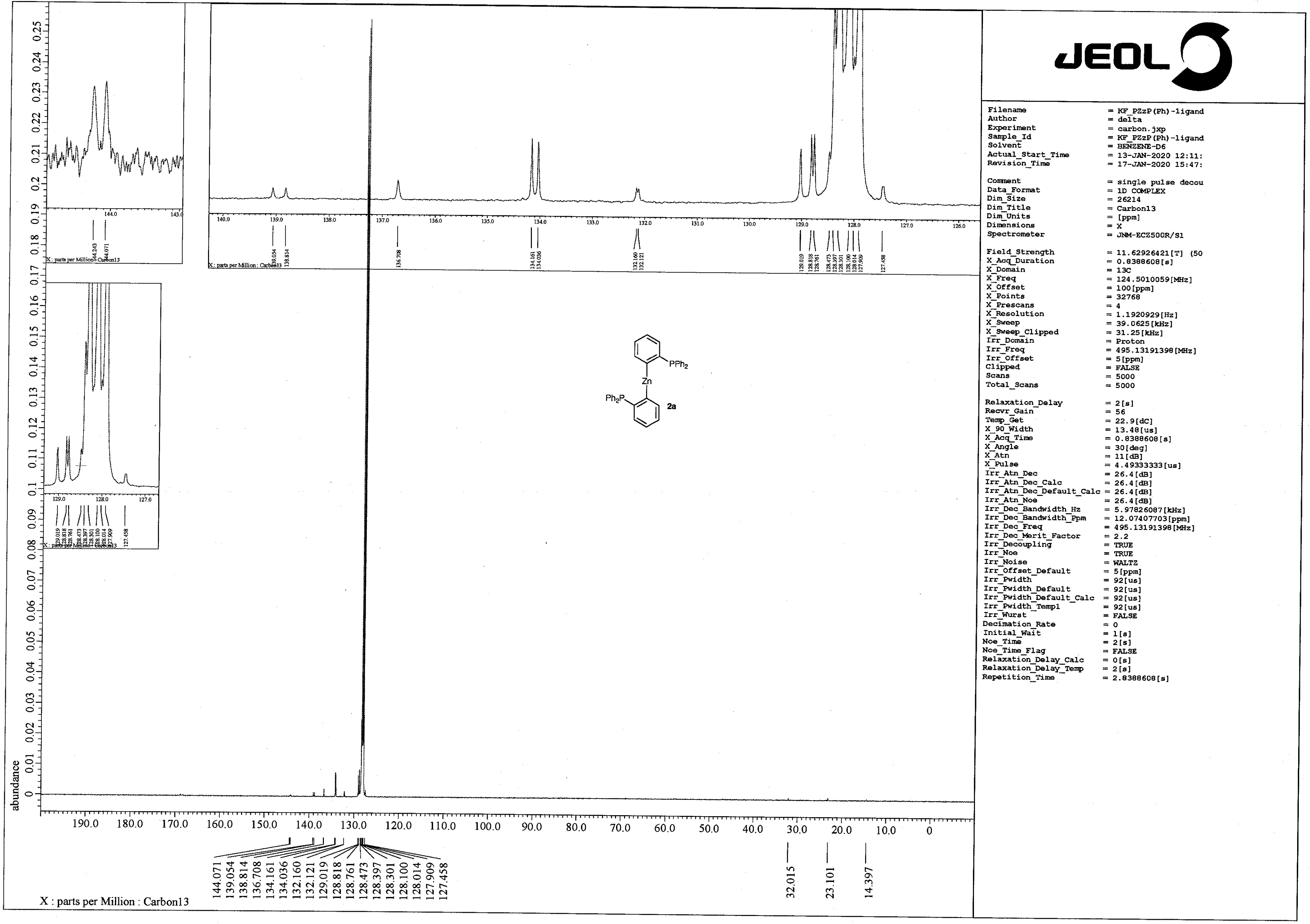


```
Filename              = KF_PZzP(Ph)-ligand_Pr
Author                = delta
Experiment            = proton.jxp
Sample_Id             = KF_PZzP(Ph)-ligand
Solvent               = BENZENE-D6
Actual_Start_Time     = 13-JAN-2020 12:02:50
Revision_Time         = 17-JAN-2020 15:45:29

Comment               = single_pulse
Data_Format           = 1D REAL
Dim_Size              = 13107
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ500R/S1

Field_Strength        = 11.62926421[T] (500[M
X_Acq_Duration        = 1.76422912[s]
X_Domain              = 1H
X_Freq                = 495.13191398[MHz]
X_Offset              = 5[ppm]
X_Points              = 16384
X_Prescans            = 1
X_Resolution          = 0.5668198[Hz]
X_Sweep               = 9.28677563[kHz]
X_Sweep_Clipped       = 7.42942051[kHz]
Irr_Domain            = Proton
Irr_Freq              = 495.13191398[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 495.13191398[MHz]
Tri_Offset            = 5[ppm]
Clipped               = FALSE
Scans                 = 8
Total_Scans           = 8

Relaxation_Delay      = 3[s]
Recvr_Gain            = 56
Temp_Get              = 22.9[dC]
X_90_Width            = 7.12[us]
X_Acq_Time            = 1.76422912[s]
X_Angle               = 45[deg]
X_Atn                 = 3.3[dB]
X_Pulse               = 3.56[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Loop            = 299
Dante_Presat          = FALSE
Decimation_Rate       = 0
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
Presat_Time           = 3[s]
Presat_Time_Flag      = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 3[s]
Repetition_Time       = 4.76422912[s]
```

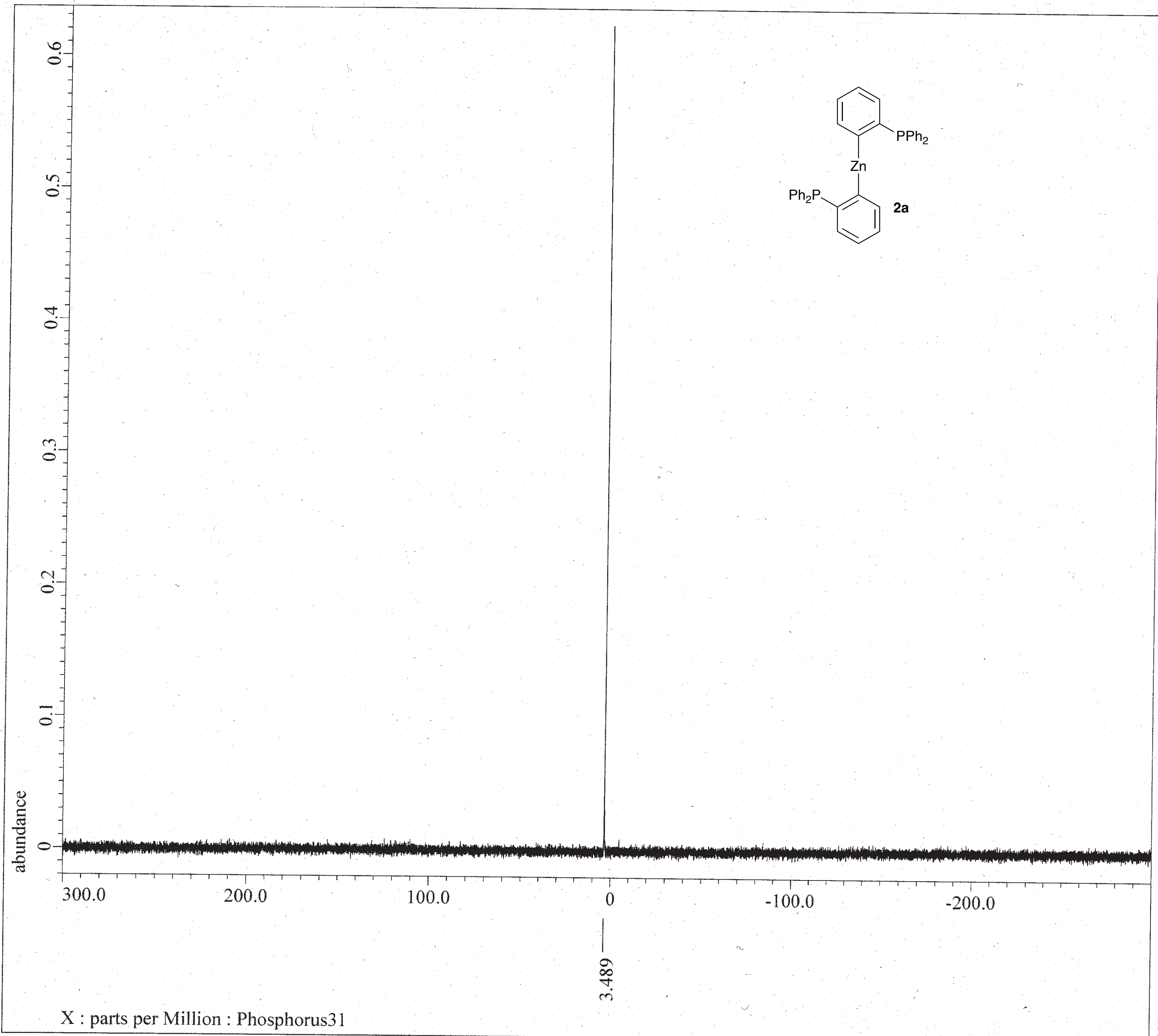


```
Filename                  = KF_PZzP(Ph)-ligand
Author                    = delta
Experiment                = carbon.jxp
Sample_Id                 = KF_PZzP(Ph)-ligand
Solvent                   = BENZENE-D6
Actual_Start_Time         = 13-JAN-2020 12:11:
Revision_Time             = 17-JAN-2020 15:47:

Comment                   = single pulse decou
Data_Format               = 1D COMPLEX
Dim_Size                  = 26214
Dim_Title                 = Carbon13
Dim_Units                 = [ppm]
Dimensions                = X
Spectrometer              = JNM-ECZ500R/S1

Field_Strength            = 11.62926421[T] (50
X_Acq_Duration            = 0.8388608[s]
X_Domain                  = 13C
X_Freq                    = 124.5010059[MHz]
X_Offset                  = 100[ppm]
X_Points                  = 32768
X_Prescans                = 4
X_Resolution              = 1.1920929[Hz]
X_Sweep                   = 39.0625[kHz]
X_Sweep_Clipped           = 31.25[kHz]
Irr_Domain                = Proton
Irr_Freq                  = 495.13191398[MHz]
Irr_Offset                = 5[ppm]
Clipped                   = FALSE
Scans                     = 5000
Total_Scans               = 5000

Relaxation_Delay          = 2[s]
Recvr_Gain                = 56
Temp_Get                  = 22.9[dC]
X_90_Width                = 13.48[us]
X_Acq_Time                = 0.8388608[s]
X_Angle                   = 30[deg]
X_Atn                     = 11[dB]
X_Pulse                   = 4.49333333[us]
Irr_Atn_Dec               = 26.4[dB]
Irr_Atn_Dec_Calc          = 26.4[dB]
Irr_Atn_Dec_Default_Calc = 26.4[dB]
Irr_Atn_Noe               = 26.4[dB]
Irr_Dec_Bandwidth_Hz      = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm     = 12.07407703[ppm]
Irr_Dec_Freq              = 495.13191398[MHz]
Irr_Dec_Merit_Factor      = 2.2
Irr_Decoupling            = TRUE
Irr_Noe                   = TRUE
Irr_Noise                 = WALTZ
Irr_Offset_Default        = 5[ppm]
Irr_Pwidth                = 92[us]
Irr_Pwidth_Default        = 92[us]
Irr_Pwidth_Default_Calc   = 92[us]
Irr_Pwidth_Templ          = 92[us]
Irr_Wurst                 = FALSE
Decimation_Rate           = 0
Initial_Wait              = 1[s]
Noe_Time                  = 2[s]
Noe_Time_Flag             = FALSE
Relaxation_Delay_Calc     = 0[s]
Relaxation_Delay_Temp     = 2[s]
Repetition_Time           = 2.8388608[s]
```



```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

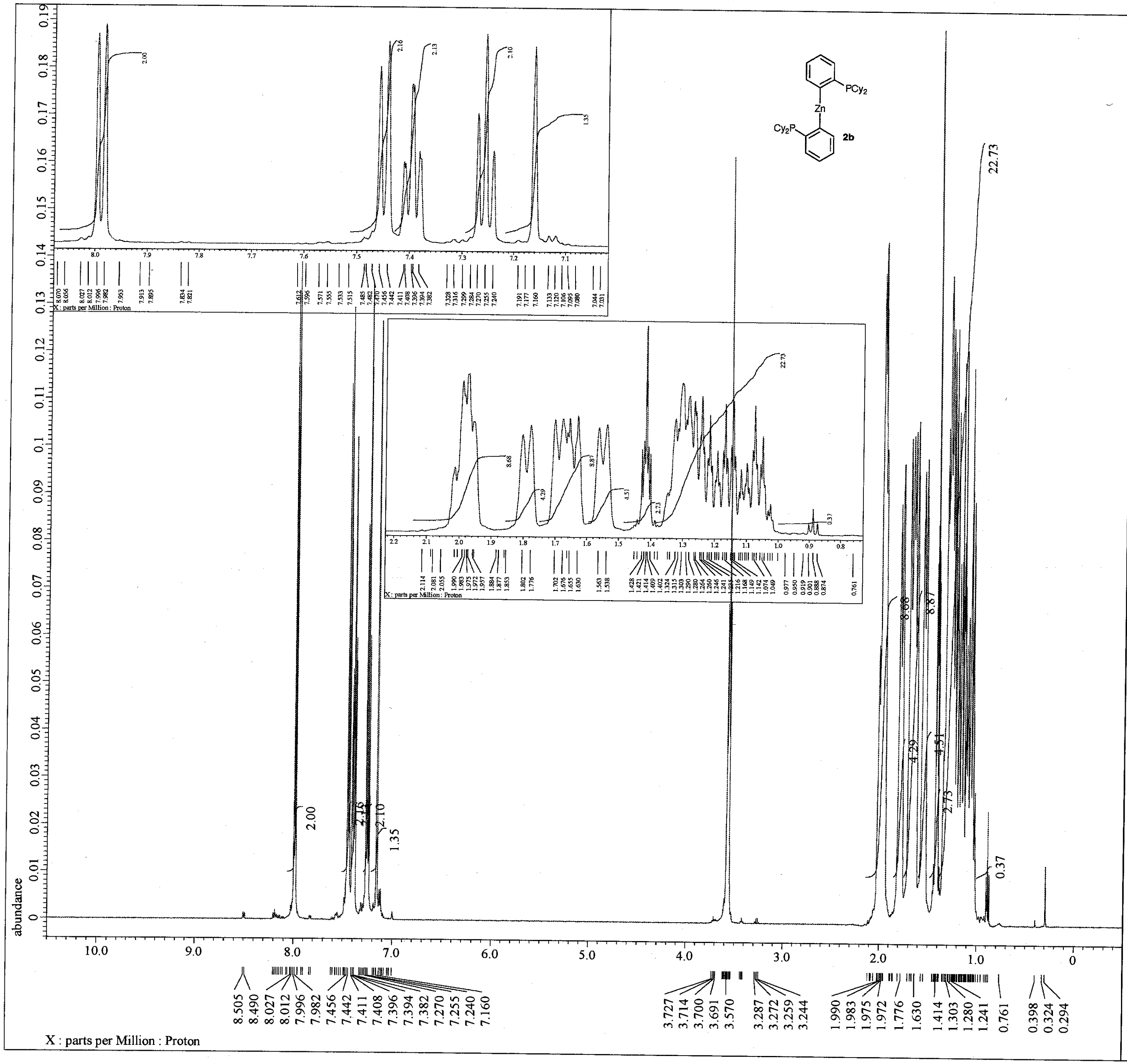
以下に由来：: KF PZzP(Ph)-ligand 31P 1Hdec-1-

Filename                  = KF_PZzP(Ph)-liga
Author                    = delta
Experiment                = single_pulse_dec
Sample_Id                 = KF_PZzP(Ph)-liga
Solvent                   = BENZENE-D6
Creation_Time             = 13-JAN-2020 12:0
Revision_Time             = 17-JAN-2020 19:0
Current_Time              = 17-JAN-2020 19:0

Comment                   = single pulse dec
Data_Format               = 1D COMPLEX
Dim_Size                  = 26214
Dim_Title                 = Phosphorus31
Dim_Units                 = [ppm]
Dimensions                = X
Spectrometer              = JNM-ECZ500R/S1

Field_Strength            = 11.62926421[T] (
X_Acq_Duration            = 0.18874368[s]
X_Domain                  = 31P
X_Freq                    = 200.43293989[MHz
X_Offset                  = 0[ppm]
X_Points                  = 32768
X_Prescans                = 4
X_Resolution              = 5.29819065[Hz]
X_Sweep                   = 173.61111111[kHz
X_Sweep_Clipped           = 138.88888889[kHz
Irr_Domain                = Proton
Irr_Freq                  = 495.13191398[MHz
Irr_Offset                = 5[ppm]
Clipped                   = TRUE
Decimation_Reg            = r: 36( 35),g: 26
Scans                     = 64
Total_Scans               = 64

Relaxation_Delay          = 2[s]
Recvr_Gain                = 56
Temp_Get                  = 22.8[dC]
X_90_Width                = 14.5[us]
X_Acq_Time                = 0.18874368[s]
X_Angle                   = 30[deg]
X_Atn                     = 9.3[dB]
X_Pulse                   = 4.83333333[us]
Irr_Atn_Dec               = 26.4[dB]
Irr_Atn_Dec_Calc          = 26.4[dB]
Irr_Atn_Dec_Default_Calc  = 26.4[dB]
Irr_Atn_Noe               = 26.4[dB]
Irr_Dec_Bandwidth_Hz      = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm     = 12.07407703[ppm]
Irr_Dec_Freq              = 495.13191398[MHz]
Irr_Dec_Merit_Factor      = 2.2
Irr_Decoupling            = TRUE
Irr_Noe                   = TRUE
```



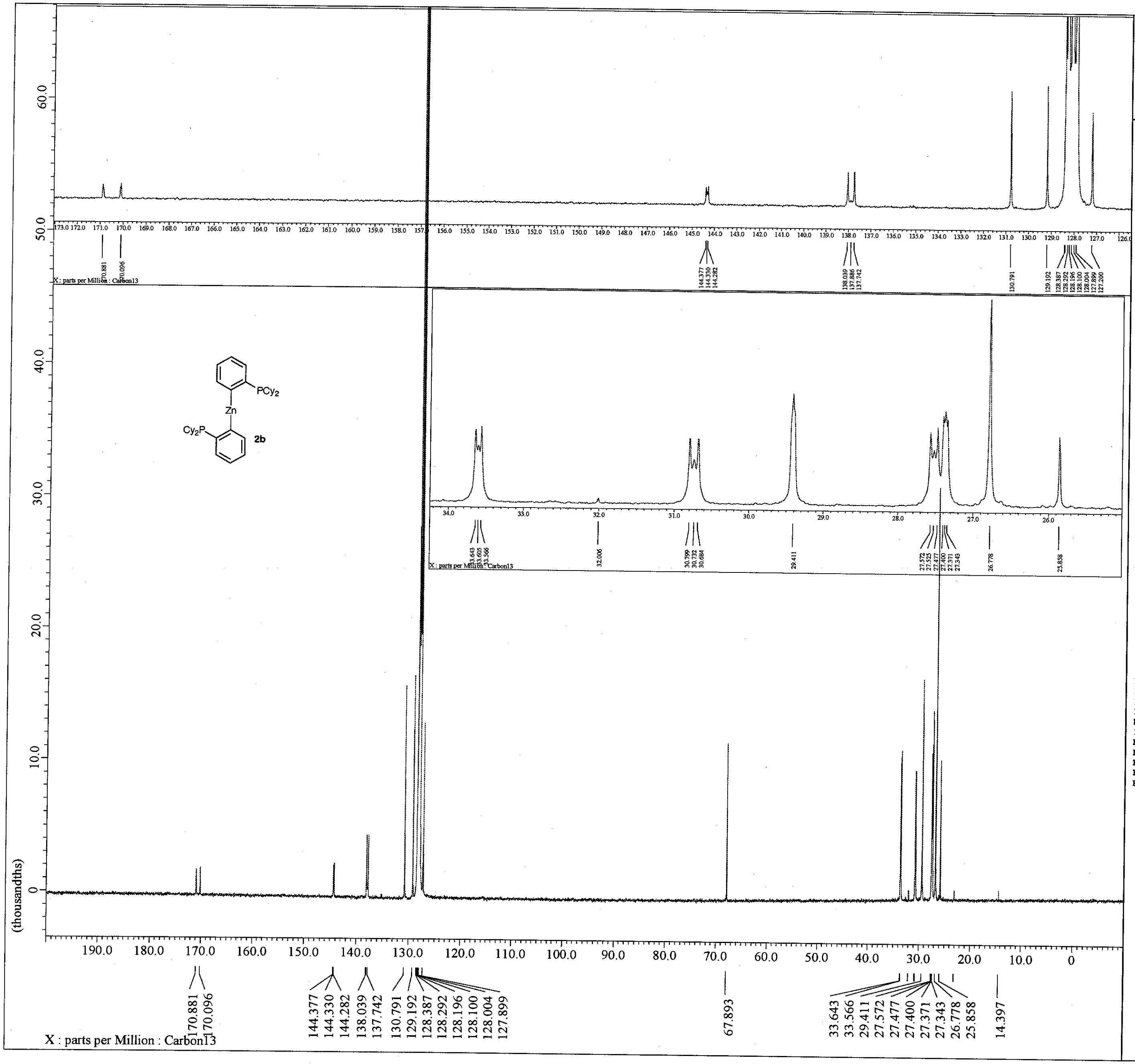
JEOL

```
Filename              = KF_PZnP(Cy)-ligand_Pr
Author                = delta
Experiment            = proton.jxp
Sample_Id             = KF_PZnP(Cy)-ligand
Solvent               = BENZENE-D6
Actual_Start_Time     = 13-JAN-2020 07:52:31
Revision_Time         = 17-JAN-2020 15:51:53

Comment               = single_pulse
Data_Format           = 1D REAL
Dim_Size              = 13107
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ500R/S1

Field_Strength        = 11.62926421[T] (500[M
X_Acq_Duration        = 1.76422912[s]
X_Domain              = 1H
X_Freq                = 495.13191398[MHz]
X_Offset              = 5[ppm]
X_Points              = 16384
X_Prescans            = 1
X_Resolution          = 0.5668198[Hz]
X_Sweep               = 9.28677563[kHz]
X_Sweep_Clipped       = 7.42942051[kHz]
Irr_Domain            = Proton
Irr_Freq              = 495.13191398[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 495.13191398[MHz]
Tri_Offset            = 5[ppm]
Clipped               = FALSE
Scans                 = 8
Total_Scans           = 8

Relaxation_Delay      = 3[s]
Recvr_Gain            = 36
Temp_Get              = 22.8[dC]
X_90_Width            = 7.12[us]
X_Acq_Time            = 1.76422912[s]
X_Angle               = 45[deg]
X_Atn                 = 3.3[dB]
X_Pulse               = 3.56[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Loop            = 299
Dante_Presat          = FALSE
Decimation_Rate       = 0
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
Presat_Time           = 3[s]
Presat_Time_Flag      = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 3[s]
Repetition_Time       = 4.76422912[s]
```



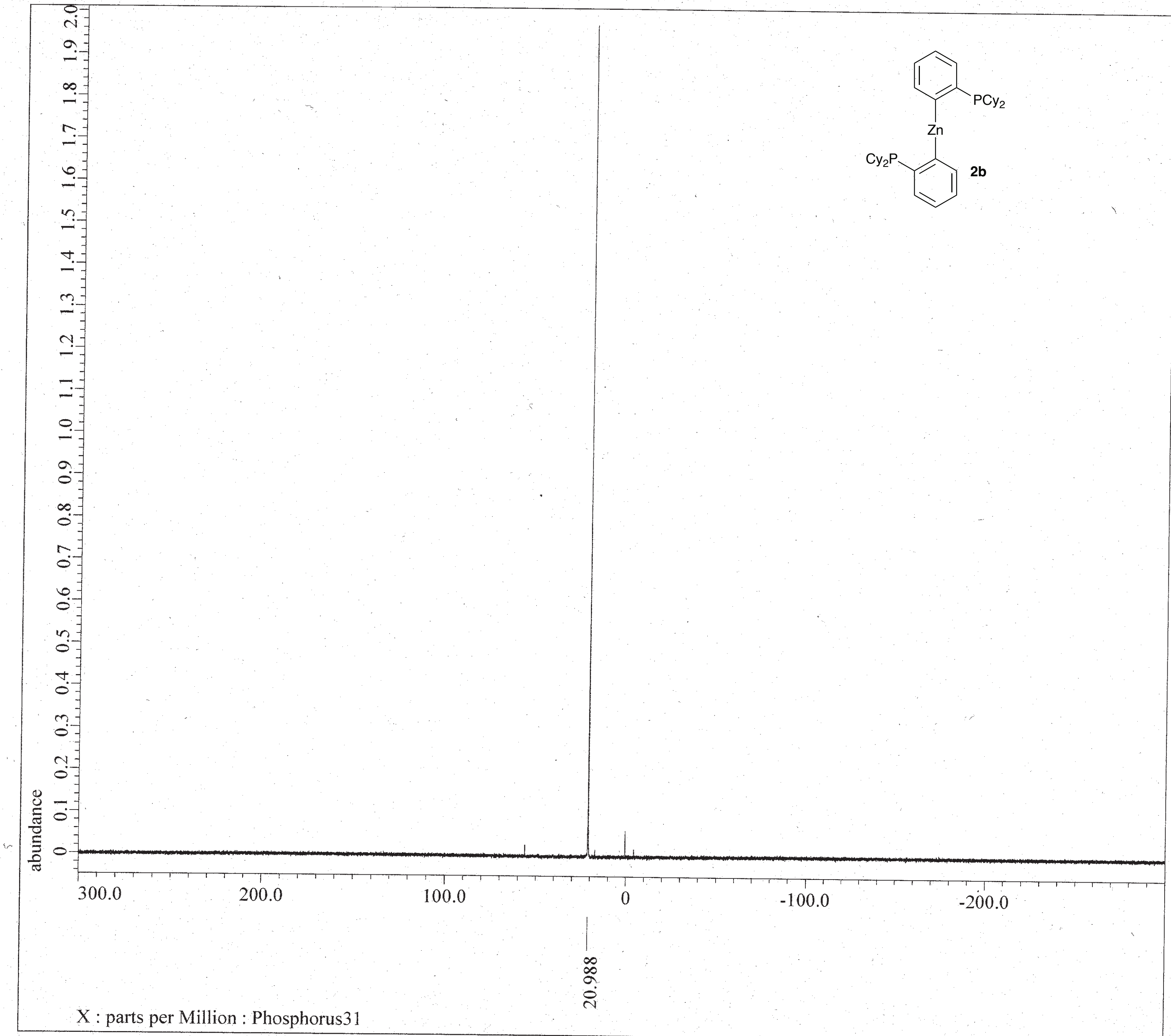
JEOL

```
Filename                  = KF_PZnP(Cy)-ligand
Author                    = delta
Experiment                = carbon.jxp
Sample_Id                 = KF_PZnP(Cy)-ligand
Solvent                   = BENZENE-D6
Actual_Start_Time         = 13-JAN-2020 08:01:
Revision_Time             = 17-JAN-2020 15:53:

Comment                   = single pulse decou
Data_Format               = 1D COMPLEX
Dim_Size                  = 26214
Dim_Title                 = Carbon13
Dim_Units                 = [ppm]
Dimensions                = X
Spectrometer              = JNM-ECZ500R/S1

Field_Strength            = 11.62926421[T] (50
X_Acq_Duration            = 0.8388608[s]
X_Domain                  = 13C
X_Freq                    = 124.5010059[MHz]
X_Offset                  = 100[ppm]
X_Points                  = 32768
X_Prescans                = 4
X_Resolution              = 1.1920929[Hz]
X_Sweep                   = 39.0625[kHz]
X_Sweep_Clipped           = 31.25[kHz]
Irr_Domain                = Proton
Irr_Freq                  = 495.13191398[MHz]
Irr_Offset                = 5[ppm]
Clipped                   = FALSE
Scans                     = 5000
Total_Scans               = 5000

Relaxation_Delay          = 2[s]
Recvr_Gain                = 56
Temp_Get                  = 22.9[dC]
X_90_Width                = 13.48[us]
X_Acq_Time                = 0.8388608[s]
X_Angle                   = 30[deg]
X_Atn                     = 11[dB]
X_Pulse                   = 4.49333333[us]
Irr_Atn_Dec               = 26.4[dB]
Irr_Atn_Dec_Calc          = 26.4[dB]
Irr_Atn_Dec_Default_Calc  = 26.4[dB]
Irr_Atn_Noe               = 26.4[dB]
Irr_Dec_Bandwidth_Hz      = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm     = 12.07407703[ppm]
Irr_Dec_Freq              = 495.13191398[MHz]
Irr_Dec_Merit_Factor      = 2.2
Irr_Decoupling            = TRUE
Irr_Noe                   = TRUE
Irr_Noise                 = WALTZ
Irr_Offset_Default        = 5[ppm]
Irr_Pwidth                = 92[us]
Irr_Pwidth_Default        = 92[us]
Irr_Pwidth_Default_Calc   = 92[us]
Irr_Pwidth_Templ          = 92[us]
Irr_Wurst                 = FALSE
Decimation_Rate           = 0
Initial_Wait              = 1[s]
Noe_Time                  = 2[s]
Noe_Time_Flag             = FALSE
Relaxation_Delay_Calc     = 0[s]
Relaxation_Delay_Temp     = 2[s]
Repetition_Time           = 2.8388608[s]
```



X : parts per Million : Phosphorus31

```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

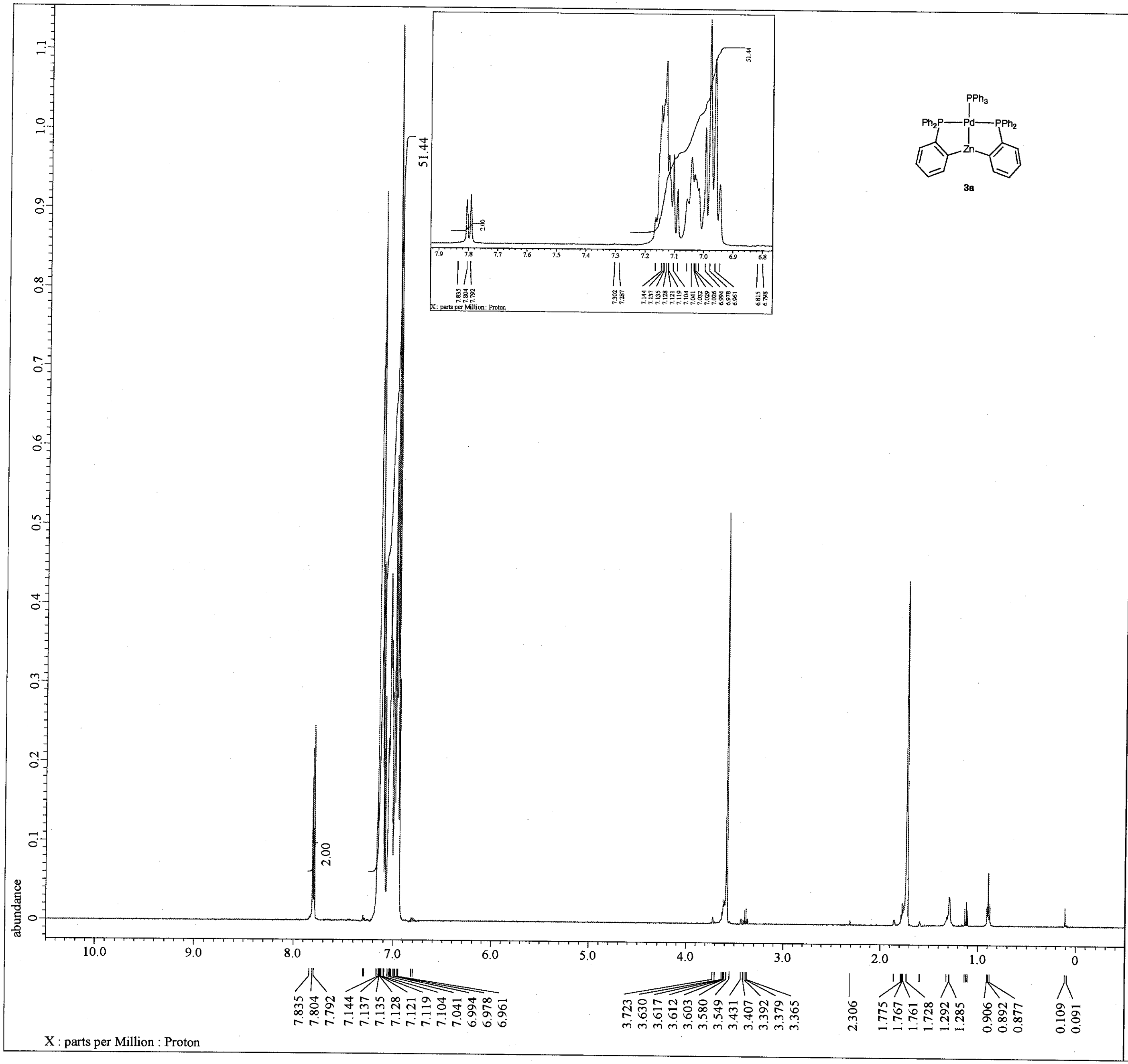
以下に由来：: KF PZnP(Cy)-ligand 31P 1Hdec-1-

Filename                    = KF_PZnP(Cy)-liga
Author                      = delta
Experiment                  = single_pulse_dec
Sample_Id                   = KF_PZnP(Cy)-liga
Solvent                     = BENZENE-D6
Creation_Time               = 13-JAN-2020 07:5
Revision_Time               = 17-JAN-2020 18:5
Current_Time                = 17-JAN-2020 18:5

Comment                     = single pulse dec
Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
Dim_Title                   = Phosphorus31
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ500R/S1

Field_Strength              = 11.62926421[T] (
X_Acq_Duration              = 0.18874368[s]
X_Domain                    = 31P
X_Freq                      = 200.43293989[MHz
X_Offset                    = 0[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 5.29819065[Hz]
X_Sweep                     = 173.61111111[kHz
X_Sweep_Clipped             = 138.88888889[kHz
Irr_Domain                  = Proton
Irr_Freq                    = 495.13191398[MHz
Irr_Offset                  = 5[ppm]
Clipped                     = FALSE
Decimation_Reg              = r: 36( 35),g: 26
Scans                       = 64
Total_Scans                 = 64

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 56
Temp_Get                    = 23[dC]
X_90_Width                  = 14.5[us]
X_Acq_Time                  = 0.18874368[s]
X_Angle                     = 30[deg]
X_Atn                       = 9.3[dB]
X_Pulse                     = 4.83333333[us]
Irr_Atn_Dec                 = 26.4[dB]
Irr_Atn_Dec_Calc            = 26.4[dB]
Irr_Atn_Dec_Default_Calc    = 26.4[dB]
Irr_Atn_Noe                 = 26.4[dB]
Irr_Dec_Bandwidth_Hz        = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 12.07407703[ppm]
Irr_Dec_Freq                = 495.13191398[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
```



X : parts per Million : Proton

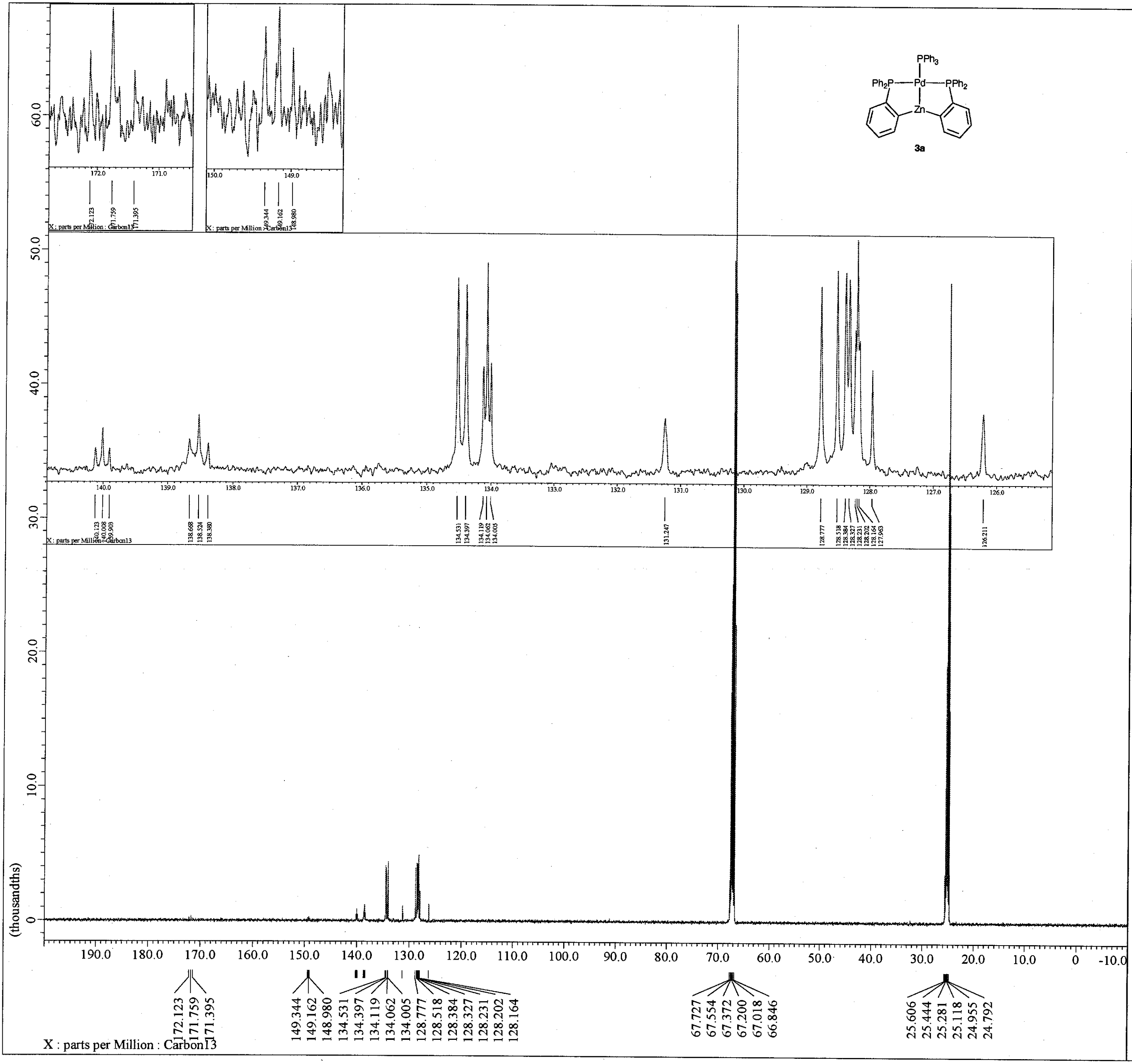
**3a**

```
Filename               = KF_PZnP(Ph)-Pd_Proton
Author                 = delta
Experiment             = proton.jxp
Sample_Id              = KF_PZnP(Ph)-Pd
Solvent                = TETRAHYDROFURAN-D8
Actual_Start_Time      = 13-JAN-2020 03:43:56
Revision_Time          = 16-JAN-2020 16:05:07

Comment                = single_pulse
Data_Format            = 1D REAL
Dim_Size               = 13107
Dim_Title              = Proton
Dim_Units              = [ppm]
Dimensions             = X
Spectrometer           = JNM-ECZ500R/S1

Field_Strength         = 11.62926421[T] (500[M
X_Acq_Duration         = 1.76422912[s]
X_Domain               = 1H
X_Freq                 = 495.13191398[MHz]
X_Offset               = 5[ppm]
X_Points               = 16384
X_Prescans             = 1
X_Resolution           = 0.5668198[Hz]
X_Sweep                = 9.28677563[kHz]
X_Sweep_Clipped        = 7.42942051[kHz]
Irr_Domain             = Proton
Irr_Freq               = 495.13191398[MHz]
Irr_Offset             = 5[ppm]
Tri_Domain             = Proton
Tri_Freq               = 495.13191398[MHz]
Tri_Offset             = 5[ppm]
Clipped                = FALSE
Scans                  = 8
Total_Scans            = 8

Relaxation_Delay       = 3[s]
Recvr_Gain             = 56
Temp_Get               = 22.2[dC]
X_90_Width             = 7.12[us]
X_Acq_Time             = 1.76422912[s]
X_Angle                = 45[deg]
X_Atn                  = 3.3[dB]
X_Pulse                = 3.56[us]
Irr_Mode               = Off
Tri_Mode               = Off
Dante_Loop             = 299
Dante_Presat           = FALSE
Decimation_Rate        = 0
Initial_Wait           = 1[s]
Phase                  = {0, 90, 270, 180, 180
Presat_Time            = 3[s]
Presat_Time_Flag       = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 3[s]
Repetition_Time        = 4.76422912[s]
```

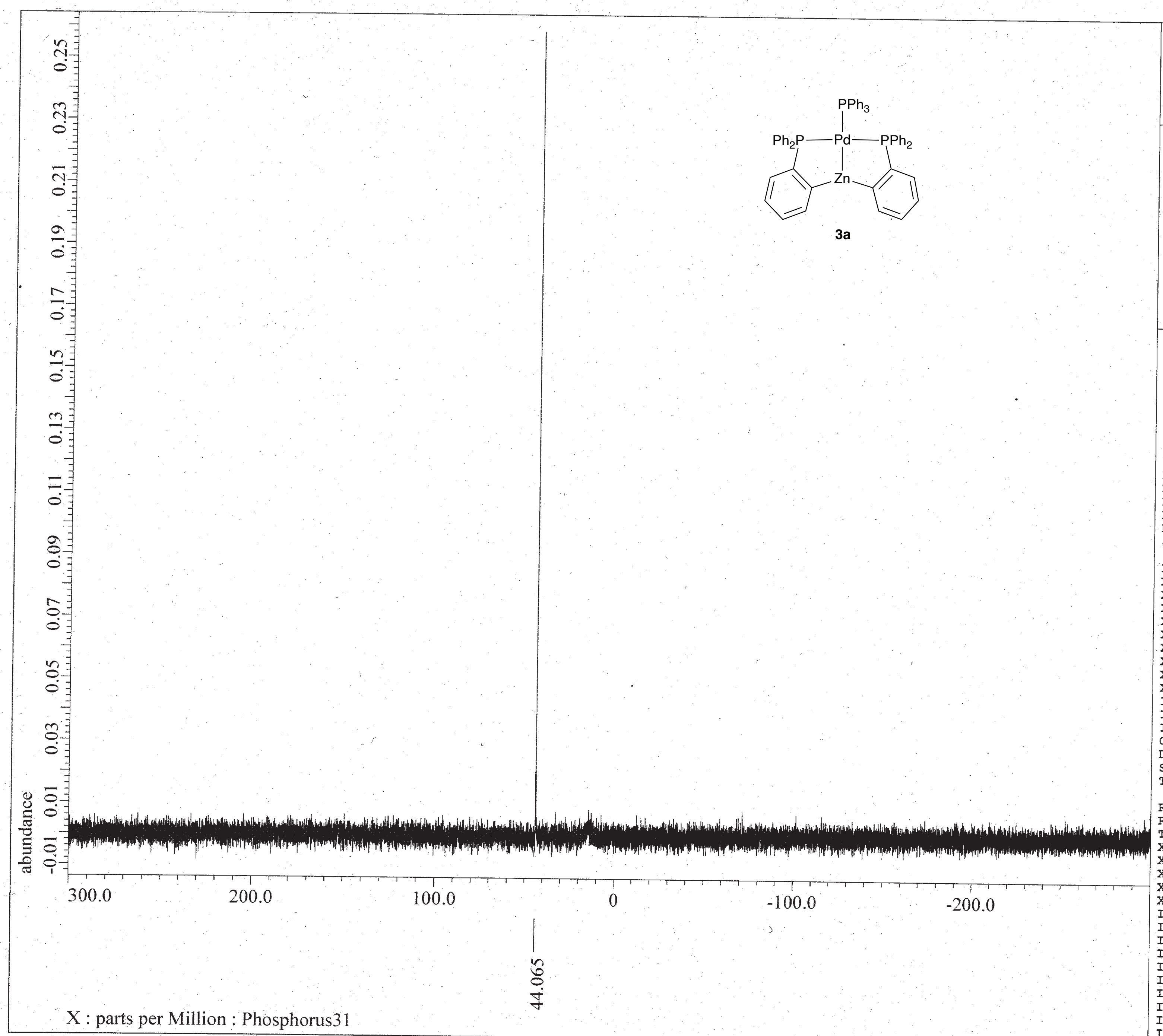


```
Filename                    = KF_PZnP(Ph)-Pd_Car
Author                      = delta
Experiment                  = carbon.jxp
Sample_Id                   = KF_PZnP(Ph)-Pd
Solvent                     = TETRAHYDROFURAN-D8
Actual_Start_Time           = 13-JAN-2020 03:51:
Revision_Time               = 16-JAN-2020 16:08:

Comment                     = single pulse decou
Data_Format                 = 1D REAL
Dim_Size                    = 26214
Dim_Title                   = Carbon13
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ500R/S1

Field_Strength              = 11.62926421[T] (50
X_Acq_Duration              = 0.8388608[s]
X_Domain                    = 13C
X_Freq                      = 124.5010059[MHz]
X_Offset                    = 100[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 1.1920929[Hz]
X_Sweep                     = 39.0625[kHz]
X_Sweep_Clipped             = 31.25[kHz]
Irr_Domain                  = Proton
Irr_Freq                    = 495.13191398[MHz]
Irr_Offset                  = 5[ppm]
Clipped                     = FALSE
Scans                       = 5000
Total_Scans                 = 5000

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 56
Temp_Get                    = 22.7[dC]
X_90_Width                  = 13.48[us]
X_Acq_Time                  = 0.8388608[s]
X_Angle                     = 30[deg]
X_Atn                       = 11[dB]
X_Pulse                     = 4.49333333[us]
Irr_Atn_Dec                 = 26.4[dB]
Irr_Atn_Dec_Calc            = 26.4[dB]
Irr_Atn_Dec_Default_Calc = 26.4[dB]
Irr_Atn_Noe                 = 26.4[dB]
Irr_Dec_Bandwidth_Hz        = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 12.07407703[ppm]
Irr_Dec_Freq                = 495.13191398[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
Irr_Noise                   = WALTZ
Irr_Offset_Default          = 5[ppm]
Irr_Pwidth                  = 92[us]
Irr_Pwidth_Default          = 92[us]
Irr_Pwidth_Default_Calc     = 92[us]
Irr_Pwidth_Templ            = 92[us]
Irr_Wurst                   = FALSE
Decimation_Rate             = 0
Initial_Wait                = 1[s]
Noe_Time                    = 2[s]
Noe_Time_Flag               = FALSE
Relaxation_Delay_Calc       = 0[s]
Relaxation_Delay_Temp       = 2[s]
Repetition_Time             = 2.8388608[s]
```



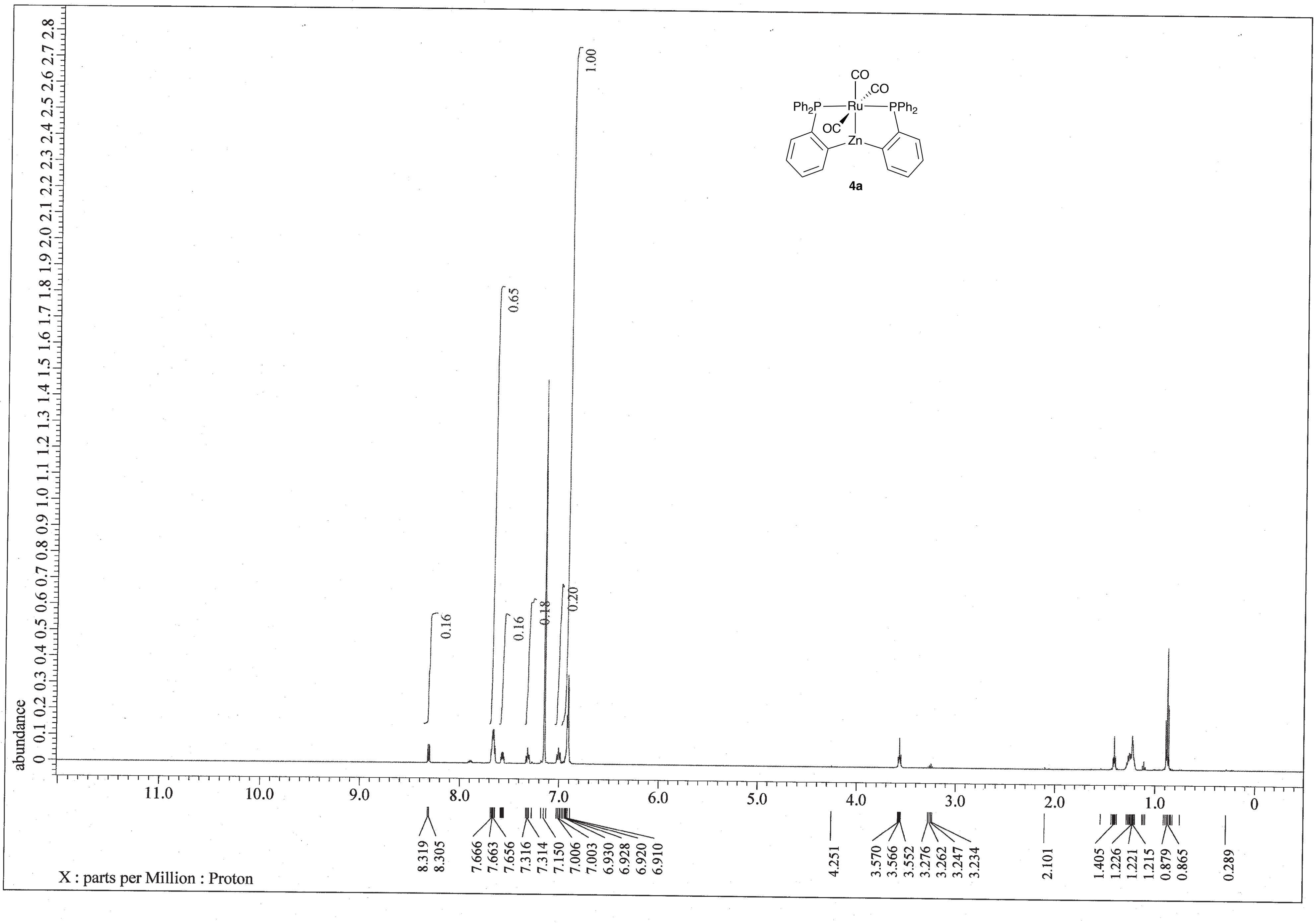
```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
phase( -28.28429, 252.10343, 43.64628[%] )
以下に由来：: KF PZnP(Ph)-Pd 31P 1Hdec-1-1.jc

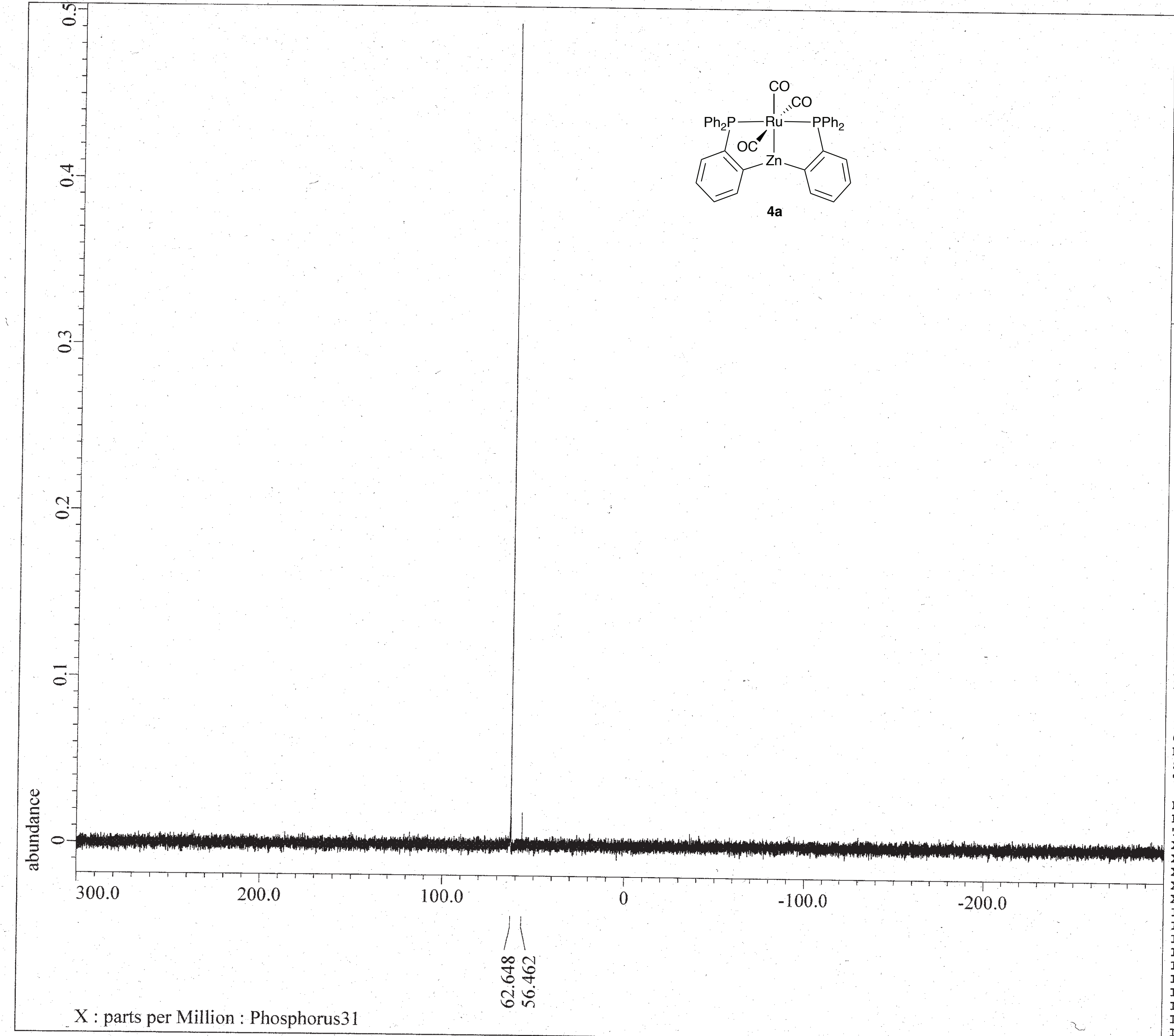
Filename                    = KF_PZnP(Ph)-Pd_3
Author                      = delta
Experiment                  = single_pulse_dec
Sample_Id                   = KF_PZnP(Ph)-Pd
Solvent                     = TETRAHYDROFURAN-
Creation_Time               = 13-JAN-2020 03:4
Revision_Time               = 17-JAN-2020 19:0
Current_Time                = 17-JAN-2020 19:0

Comment                     = single pulse dec
Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
Dim_Title                   = Phosphorus31
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ500R/S1

Field_Strength              = 11.62926421[T] (
X_Acq_Duration              = 0.18874368[s]
X_Domain                    = 31P
X_Freq                      = 200.43293989[MHz
X_Offset                    = 0[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 5.29819065[Hz]
X_Sweep                     = 173.61111111[kHz
X_Sweep_Clipped             = 138.88888889[kHz
Irr_Domain                  = Proton
Irr_Freq                    = 495.13191398[MHz
Irr_Offset                  = 5[ppm]
Clipped                     = FALSE
Decimation_Reg              = r: 36( 35),g: 26
Scans                       = 64
Total_Scans                 = 64

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 56
Temp_Get                    = 22.1[dC]
X_90_Width                  = 14.5[us]
X_Acq_Time                  = 0.18874368[s]
X_Angle                     = 30[deg]
X_Atn                       = 9.3[dB]
X_Pulse                     = 4.83333333[us]
Irr_Atn_Dec                 = 26.4[dB]
Irr_Atn_Dec_Calc            = 26.4[dB]
Irr_Atn_Dec_Default_Calc    = 26.4[dB]
Irr_Atn_Noe                 = 26.4[dB]
Irr_Dec_Bandwidth_Hz        = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 12.07407703[ppm]
Irr_Dec_Freq                = 495.13191398[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
```


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
X : parts per Million : Proton
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.16
0.65
0.16
0.18
0.20
1.00
8.319
8.305
7.666
7.663
7.656
7.316
7.314
7.150
7.006
7.003
6.930
6.928
6.920
6.910
4.251
3.570
3.566
3.552
3.276
3.262
3.247
3.234
2.101
1.405
1.226
1.221
1.215
0.879
0.865
0.289
CO
CO
Ph$_2$P
Ru
PPh$_2$
OC
Zn
4a



**4a**

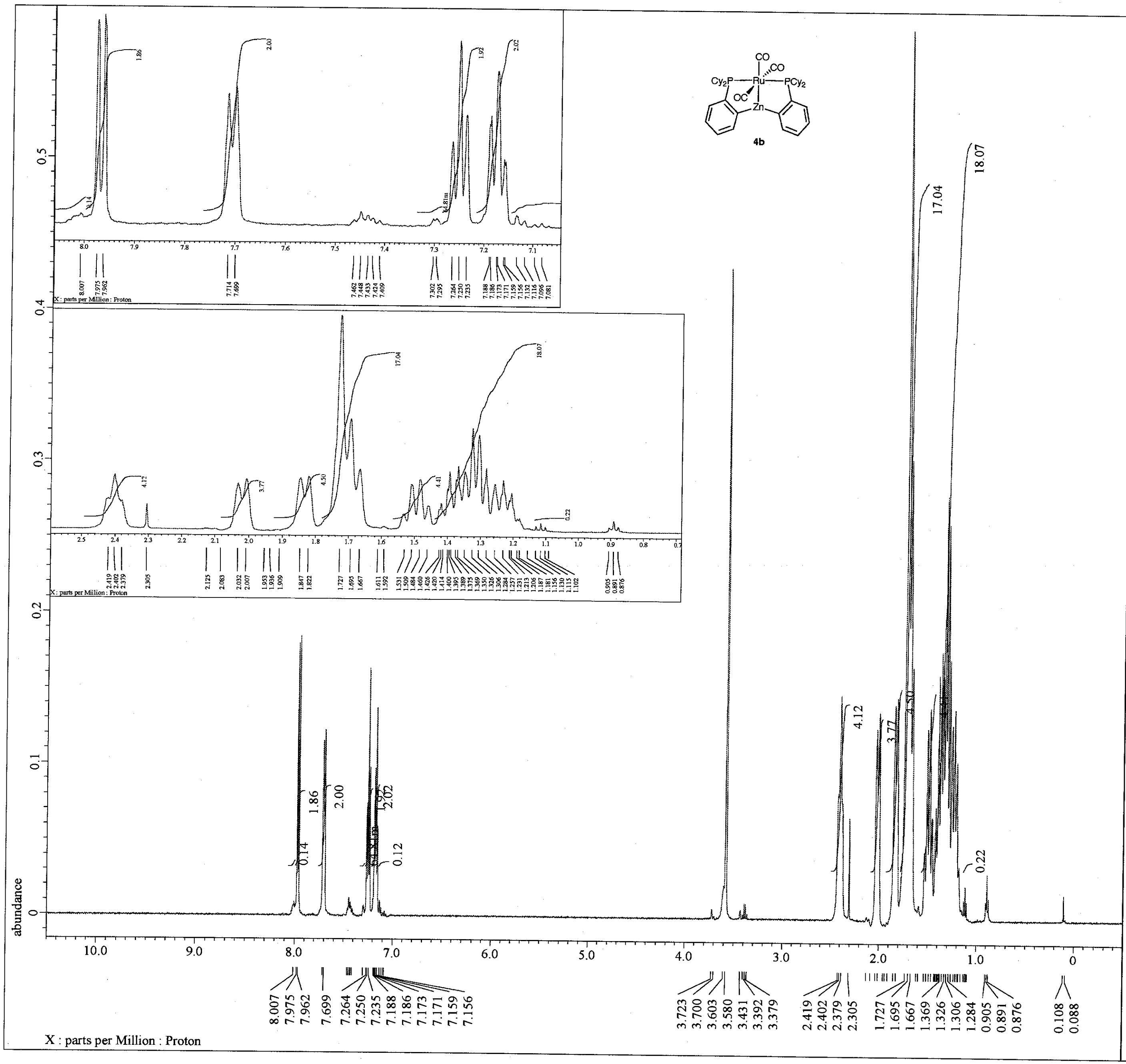
```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
phase( -77.89112, 0, 40.96822[%] )
以下に由来：: KF PZnP(Ph)-Pd 31P 1Hdec-1-1.jd
```

```
                                  Ru
Filename                    = KF_PZnP(Ph)-~~Pd~~_3
Author                      = delta
Experiment                  = single_pulse_dec
Sample_Id                   = KF_PZnP(Ph)-Pd
Solvent                     = TETRAHYDROFURAN-
Creation_Time               = 17-JAN-2020 16:2
Revision_Time               = 17-JAN-2020 19:0
Current_Time                = 17-JAN-2020 19:0

Comment                     = single pulse dec
Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
Dim_Title                   = Phosphorus31
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ500R/S1

Field_Strength              = 11.62926421[T] (
X_Acq_Duration              = 0.18874368[s]
X_Domain                    = 31P
X_Freq                      = 200.43293989[MHz
X_Offset                    = 0[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 5.29819065[Hz]
X_Sweep                     = 173.61111111[kHz
X_Sweep_Clipped             = 138.88888889[kHz
Irr_Domain                  = Proton
Irr_Freq                    = 495.13191398[MHz
Irr_Offset                  = 5[ppm]
Clipped                     = FALSE
Decimation_Reg              = r: 36( 35),g: 26
Scans                       = 64
Total_Scans                 = 64

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 56
Temp_Get                    = 21.6[dC]
X_90_Width                  = 14.5[us]
X_Acq_Time                  = 0.18874368[s]
X_Angle                     = 30[deg]
X_Atn                       = 9.3[dB]
X_Pulse                     = 4.83333333[us]
Irr_Atn_Dec                 = 26.4[dB]
Irr_Atn_Dec_Calc            = 26.4[dB]
Irr_Atn_Dec_Default_Calc    = 26.4[dB]
Irr_Atn_Noe                 = 26.4[dB]
Irr_Dec_Bandwidth_Hz        = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 12.07407703[ppm]
Irr_Dec_Freq                = 495.13191398[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
```

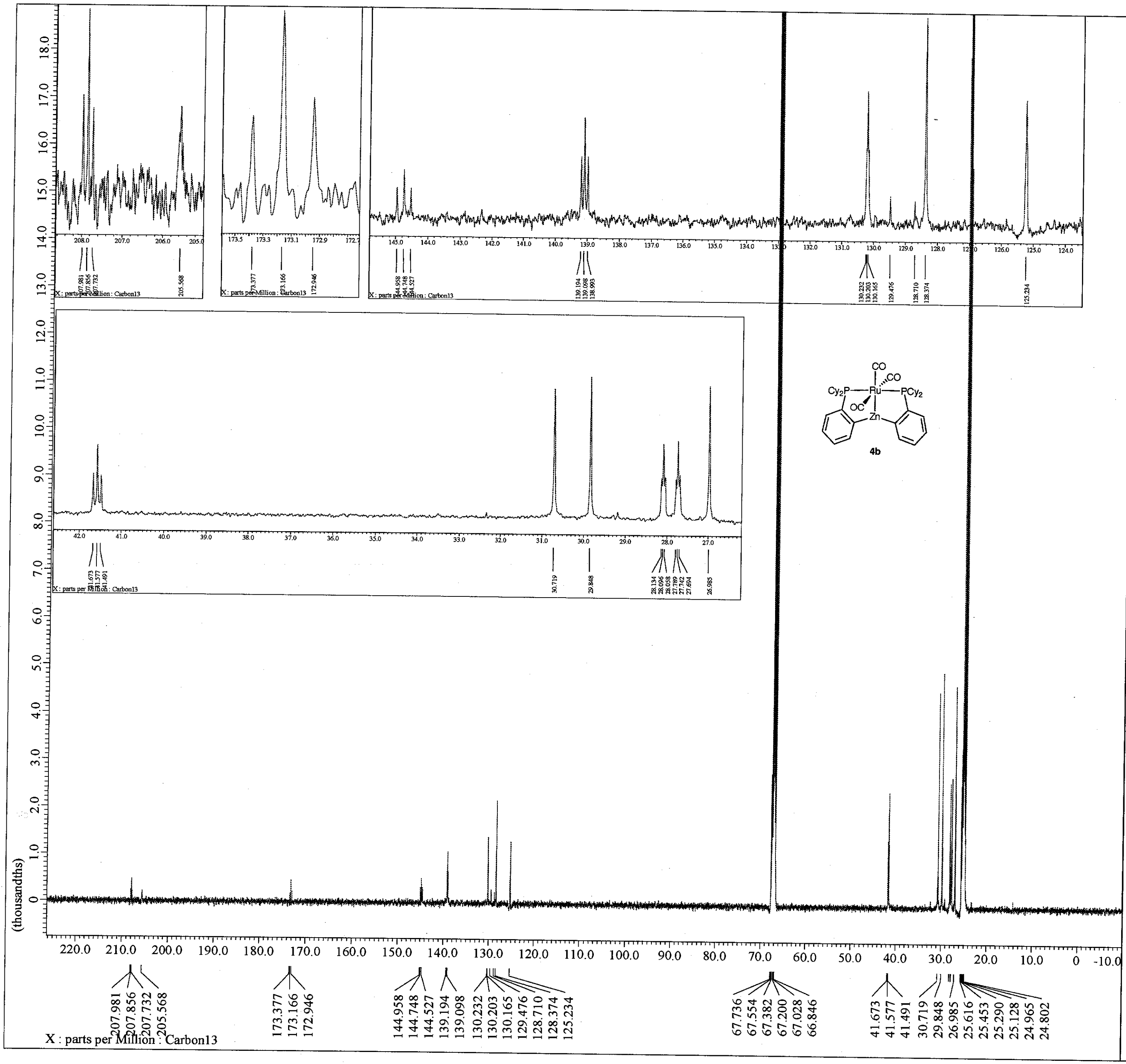


```
Filename                 = KF_PZnP(Cy)-Ru_Proton
Author                   = delta
Experiment               = proton.jxp
Sample_Id                = KF_PZnP(Cy)-Ru
Solvent                  = TETRAHYDROFURAN-D8
Actual_Start_Time        = 13-JAN-2020 16:12:30
Revision_Time            = 16-JAN-2020 16:01:59

Comment                  = single_pulse
Data_Format              = 1D REAL
Dim_Size                 = 13107
Dim_Title                = Proton
Dim_Units                = [ppm]
Dimensions               = X
Spectrometer             = JNM-ECZ500R/S1

Field_Strength           = 11.62926421[T] (500[M
X_Acq_Duration           = 1.76422912[s]
X_Domain                 = 1H
X_Freq                   = 495.13191398[MHz]
X_Offset                 = 5[ppm]
X_Points                 = 16384
X_Prescans               = 1
X_Resolution             = 0.5668198[Hz]
X_Sweep                  = 9.28677563[kHz]
X_Sweep_Clipped          = 7.42942051[kHz]
Irr_Domain               = Proton
Irr_Freq                 = 495.13191398[MHz]
Irr_Offset               = 5[ppm]
Tri_Domain               = Proton
Tri_Freq                 = 495.13191398[MHz]
Tri_Offset               = 5[ppm]
Clipped                  = FALSE
Scans                    = 8
Total_Scans              = 8

Relaxation_Delay         = 3[s]
Recvr_Gain               = 56
Temp_Get                 = 22.8[dC]
X_90_Width               = 7.12[us]
X_Acq_Time               = 1.76422912[s]
X_Angle                  = 45[deg]
X_Atn                    = 3.3[dB]
X_Pulse                  = 3.56[us]
Irr_Mode                 = Off
Tri_Mode                 = Off
Dante_Loop               = 299
Dante_Presat             = FALSE
Decimation_Rate          = 0
Initial_Wait             = 1[s]
Phase                    = {0, 90, 270, 180, 180
Presat_Time              = 3[s]
Presat_Time_Flag         = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 3[s]
Repetition_Time          = 4.76422912[s]
```

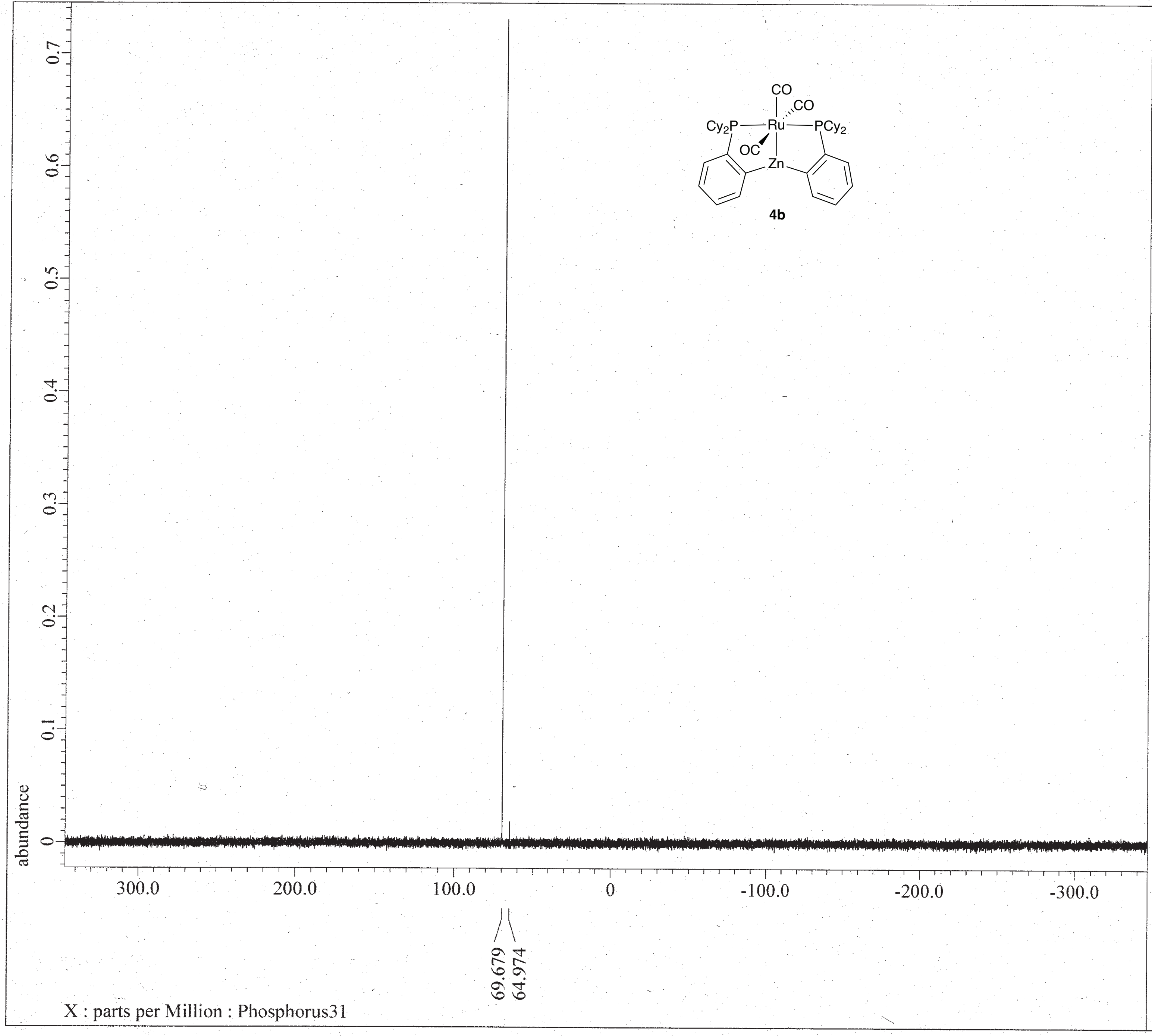


```
Filename              = KF_PZnP(Cy)-Ru_Car
Author                = delta
Experiment            = carbon.jxp
Sample_Id             = KF_PZnP(Cy)-Ru
Solvent               = TETRAHYDROFURAN-D8
Actual_Start_Time     = 13-JAN-2020 16:21:
Revision_Time         = 16-JAN-2020 15:57:

Comment               = single pulse decou
Data_Format           = 1D REAL
Dim_Size              = 26214
Dim_Title             = Carbon13
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ500R/S1

Field_Strength        = 11.62926421[T] (50
X_Acq_Duration        = 0.8388608[s]
X_Domain              = 13C
X_Freq                = 124.5010059[MHz]
X_Offset              = 100[ppm]
X_Points              = 32768
X_Prescans            = 4
X_Resolution          = 1.1920929[Hz]
X_Sweep               = 39.0625[kHz]
X_Sweep_Clipped       = 31.25[kHz]
Irr_Domain            = Proton
Irr_Freq              = 495.13191398[MHz]
Irr_Offset            = 5[ppm]
Clipped               = FALSE
Scans                 = 10000
Total_Scans           = 10000

Relaxation_Delay      = 2[s]
Recvr_Gain            = 56
Temp_Get              = 22.6[dC]
X_90_Width            = 13.48[us]
X_Acq_Time            = 0.8388608[s]
X_Angle               = 30[deg]
X_Atn                 = 11[dB]
X_Pulse               = 4.49333333[us]
Irr_Atn_Dec           = 26.4[dB]
Irr_Atn_Dec_Calc      = 26.4[dB]
Irr_Atn_Dec_Default_Calc = 26.4[dB]
Irr_Atn_Noe           = 26.4[dB]
Irr_Dec_Bandwidth_Hz  = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm = 12.07407703[ppm]
Irr_Dec_Freq          = 495.13191398[MHz]
Irr_Dec_Merit_Factor  = 2.2
Irr_Decoupling        = TRUE
Irr_Noe               = TRUE
Irr_Noise             = WALTZ
Irr_Offset_Default    = 5[ppm]
Irr_Pwidth            = 92[us]
Irr_Pwidth_Default    = 92[us]
Irr_Pwidth_Default_Calc = 92[us]
Irr_Pwidth_Templ      = 92[us]
Irr_Wurst             = FALSE
Decimation_Rate       = 0
Initial_Wait          = 1[s]
Noe_Time              = 2[s]
Noe_Time_Flag         = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 2[s]
Repetition_Time       = 2.8388608[s]
```



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```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
phase( 34.41509, 0, 39.94964[%] )
以下に由来：: KF PZnP(Cy)-Ru 31P 1Hdec-1-1.jd

Filename                  = KF_PZnP(Cy)-Ru_3
Author                    = delta
Experiment                = single_pulse_dec
Sample_Id                 = KF_PZnP(Cy)-Ru
Solvent                   = TETRAHYDROFURAN-
Creation_Time             = 13-JAN-2020 16:1
Revision_Time             = 17-JAN-2020 19:0
Current_Time              = 17-JAN-2020 19:0

Comment                   = single pulse dec
Data_Format               = 1D COMPLEX
Dim_Size                  = 26214
Dim_Title                 = Phosphorus31
Dim_Units                 = [ppm]
Dimensions                = X
Spectrometer              = JNM-ECZ500R/S1

Field_Strength            = 11.62926421[T] (
X_Acq_Duration            = 0.18874368[s]
X_Domain                  = 31P
X_Freq                    = 200.43293989[MHz
X_Offset                  = 0[ppm]
X_Points                  = 32768
X_Prescans                = 4
X_Resolution              = 5.29819065[Hz]
X_Sweep                   = 173.61111111[kHz
X_Sweep_Clipped           = 138.88888889[kHz
Irr_Domain                = Proton
Irr_Freq                  = 495.13191398[MHz
Irr_Offset                = 5[ppm]
Clipped                   = FALSE
Decimation_Reg            = r: 36( 35),g: 26
Scans                     = 64
Total_Scans               = 64

Relaxation_Delay          = 2[s]
Recvr_Gain                = 56
Temp_Get                  = 22.2[dC]
X_90_Width                = 14.5[us]
X_Acq_Time                = 0.18874368[s]
X_Angle                   = 30[deg]
X_Atn                     = 9.3[dB]
X_Pulse                   = 4.83333333[us]
Irr_Atn_Dec               = 26.4[dB]
Irr_Atn_Dec_Calc          = 26.4[dB]
Irr_Atn_Dec_Default_Calc  = 26.4[dB]
Irr_Atn_Noe               = 26.4[dB]
Irr_Dec_Bandwidth_Hz      = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm     = 12.07407703[ppm]
Irr_Dec_Freq              = 495.13191398[MHz]
Irr_Dec_Merit_Factor      = 2.2
Irr_Decoupling            = TRUE
Irr_Noe                   = TRUE
```