

Supporting Information for:

Experimental and Computational Study of Steric and Electronic Effects on the Coordination of Bulky, Water-Soluble Alkylphosphines to Palladium under Reducing Conditions: Correlation to Catalytic Activity

*Rebecca B. DeVasher, Jason M. Spruell, David A. Dixon, Grant A. Broker, Robin D. Rogers,
and Kevin H. Shaughnessy**

Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Box
870336, Tuscaloosa, AL 35487-0336

Table of Contents

Experimental Details.....	S.2
References	S.9
X-Ray Crystallographic Data	S.10
Computational Materials.....	S.20
NMR Spectra.....	S.38

Experimental Details

General. Ligand syntheses were carried out under nitrogen using a dry box and Schlenk techniques unless noted. Coupling reactions were assembled in a drybox in screw-cap vials with a silicone/Teflon® septum or a round bottom sealed with a rubber septum. Pd(OAc)₂, TPPTS (**1**), di-*t*-butylphosphine, and dicyclohexylphosphine were purchased from Strem and stored in a drybox under nitrogen. All boronic acids and aryl halides were purchased from Aldrich and were used without further purification. Di-*t*-phosphine-borane adduct,¹ *N*-methyl-4-piperidinyl tosylate² and Cy-Pip-phos² were prepared by literature methods. THF and diethyl ether were freshly distilled from sodium-benzophenone ketyl under nitrogen prior to use. Anhydrous grade morpholine (Aldrich) was used as received and dispensed in a drybox. Water (deionized), acetonitrile, and methanol were degassed by sparging with nitrogen and/or exposure to vacuum.

A suitable crystal for X-ray characterization was mounted on a glass fiber and transferred to the goniometer. The crystal was cooled to -100 °C in a stream of nitrogen gas and the data was collected on a Bruker SMART diffractometer with a CCD are detector, using graphite monochromated Mo-K α radiation. SHELXTL software, version 6.14, was used for solution and refinement.³ Absorption corrections were made with SADABS.⁴ The structure was refined by full-matrix least-squares on F^2 .

(2-Di-*t*-butylphosphinoethyl)trimethylammonium chloride-borane adduct. Prepared by a modification of the synthesis reported by Grubbs.² Di(*t*-butyl)phosphine-borane (1.588 g, 9.984 mmol) adduct was dissolved in 50 mL of THF under nitrogen and cooled to -78 °C. Butyl lithium (4.20 mL, 10.5 mmol) was added drop-wise to the phosphine solution. After the addition was complete, the reaction was stirred at -78 °C for 15 minutes and then allowed to warm to room temperature and stirred for 2 hours. A second flask was charged with (2-

chloroethyl)trimethylammonium chloride that had been finely ground in the drybox. The phosphine solution was cooled back to $-78\text{ }^{\circ}\text{C}$ and added *via* cannula to the solid salt, which was also cooled to $-78\text{ }^{\circ}\text{C}$. After the addition was complete, the reaction was allowed to warm to room temperature and then was refluxed for 24 hours to give a heavy white suspension. The THF was removed under reduced pressure in air and the solid residue was extracted with chloroform ($3 \times 100\text{ mL}$). The chloroform was removed under reduced pressure to give a colorless oil that was triturated with ether to give a slightly hygroscopic, colorless solid. The solid was dried *in vacuo* and stored in a dry box. Recovered (2.2126 g, 79 %) of the borane adduct of *t*-Bu-Amphos. ^1H NMR (D_2O , 360 MHz): δ 3.70 (dt, $J=4.47$, $J=13.56\text{ Hz}$, 2H), 3.25 (s, 9H), 2.30-2.22 (m, 2H), 1.35 (d, $^3J_{\text{H-P}}=13.56\text{ Hz}$, 18H), 0.39 (brq (1:1:1:1), $^1J_{\text{H-B}}=83.2\text{ Hz}$, 3H). ^{31}P NMR (D_2O , 202.5 MHz): δ 43.0 (brs).

(2-Di-*t*-butylphospinoethyl)trimethylammonium chloride (*t*-Bu-Amphos). The phosphine-borane adduct (2.093 g, 7.432 mmol) was taken up in 50 mL of degassed, dry morpholine under nitrogen and heated to $110\text{ }^{\circ}\text{C}$. Upon heating, gas evolution was observed. After 3 hours, the reaction was allowed to cool to room temperature. The morpholine was removed *in vacuo*. The residue was dissolved in a minimum of degassed methanol and precipitated with ether (50 mL) to give a colorless crystalline solid, which was contaminated with morpholine-borane adduct. The crude material was placed in a sublimation apparatus and heated under vacuum (0.05 torr) at $110\text{ }^{\circ}\text{C}$ for 2 hours. The non-volatile solid (1.5892 g, 80 %) recovered was pure by NMR spectroscopy. ^1H NMR (CD_3OD , 360 MHz): δ 3.49 (dt, $J=4.32$, 14.56 Hz , 2H), 3.18 (s, 9H), 1.85 (dt, $J=4.32$, 9.63 Hz , 2H), 1.19 (d, $^3J_{\text{H-P}}=11.71\text{ Hz}$, 18H). ^{13}C NMR (CD_3OD , 90.6 MHz): δ 69.1 (dt, $^1J_{\text{C-N}}=2.65\text{ Hz}$, $^2J_{\text{C-P}}=49.09\text{ Hz}$), 53.1 (t, $^1J_{\text{C-N}}=3.98\text{ Hz}$), 32.8 (d, $J_{\text{C-P}}=19.90\text{ Hz}$), 30.0 (d, $J_{\text{C-P}}=13.26\text{ Hz}$), 16.2 (d, $J_{\text{C-P}}=25.21\text{ Hz}$). ^{31}P NMR (D_2O , 202.5

MHz): δ 22.3 (s). Calculated for $C_{13}H_{31}ClNP$: C, 58.30; H, 11.67; N, 5.23. Found: C, 57.55; H, 11.33; N, 5.35. Carbon analysis was consistently low.

4-(Di-*t*-butylphosphino)-*N*-methylpiperidine-borane adduct. Prepared by a modification of the procedure reported by Grubbs.² Di(*t*-butyl)phosphine-borane adduct (7.2062 g, 45.011 mmol) in THF (200 mL) was deprotonated with butyl lithium (19.0 mL, 47.5 mmol) as described for *t*-Bu-Amphos. This solution was cooled back to -78 °C and a solution of freshly prepared *N*-methyl-4-piperidinyl tosylate (11.54 g, 42.84 mmol) in 50 mL THF was added drop-wise via cannula. The resulting orange solution was allowed to warm to room temperature and then was refluxed overnight. The mixture was poured into 500 mL of saturated sodium bicarbonate and extracted with ether (3×150 mL). The crude material was flash chromatographed on a silica gel column eluting with methanol to give 1.8105 g (16 %) of (*N*-methylpiperidin-4-yl)di-*t*-butylphosphine-borane adduct. 1H NMR ($CDCl_3$, 360 MHz): δ 3.05-3.00 (brm, 2H), 2.30-2.25 (brm, 2H), 2.30 (s, 3H), 2.05-1.90 (m, 4H), 1.85-1.70 (m, 1H), 1.34 (d, $^3J_{H-P}=12.33$ Hz, 18H), 0.50 (brq (1:1;1:1), $^1J_{H-B}=85$ Hz, 3H).

4-(Di-*t*-butylphosphino)-*N,N*-dimethylpiperidinium iodide-borane adduct ([*t*-Bu-Pip-phos• BH_3] I). 4-(Di-*t*-butylphosphino)-*N*-methylpiperidine-borane adduct (1.81 g, 7.04 mmol) was dissolved in 100 mL THF and methyl iodide (1.10 mL, 17.7 mmol) was added. The reaction was refluxed overnight during which time a white precipitate formed. The precipitate was filtered off and washed with ether. The crude product was recrystallized from boiling methanol to give large, colorless, blocks (1.39 g, 50 %). 1H NMR (CD_3OD , 360 MHz): δ 3.58-3.50 (m, 4H), 3.33 (s, 3H), 3.13 (s, 3H), 2.51-2.42 (m, 2H), 2.35-2.20 (m, 3H), 1.39 (d, $^3J_{H-P}=20.35$ Hz, 18 H), 0.40 (brq (1:1:1:1), $^1J_{H-B} = 77.2$ Hz, 3H). ^{13}C NMR (CD_3OD , 90.6 MHz): δ 64.4 (d, $J_{C-P}=9.25$ Hz), 57.15 (d, $J_{C-P}=3.98$ Hz), 57.10 (d, $J_{C-P}=3.98$ Hz), 35.2 (d, $J_{C-P}=25.19$ Hz), 30.5 (d, $J_{C-P}=23.88$ Hz),

29.5, 25.5. ^{31}P NMR (CD_3OD , 202.5 MHz): δ 49.3 (s). Calculated for $\text{C}_{15}\text{H}_{36}\text{BINP}$: C, 45.14; H, 9.09; N, 3.51. Found: C, 44.93; H, 8.95; N, 3.46.

4-(Di-*t*-butylphosphino)-*N,N*-dimethylpiperidinium chloride-borane adduct (*t*-Bu-Pip-phos• BH_3)]Cl. The recrystallized iodide was dissolved in warm methanol (50 mL) and then 50 mL of water was added followed by 35 g of Amberlite® IR 400 (Cl) anion exchange resin. The mixture was stirred for 12 hours and then the resin was filtered off. Fresh resin was added to the filtrate. After an additional 12 hours, the resin was filtered off and fresh resin was added again along with 2 mL of 1M HCl. After an additional 12 hours, the resin was filtered off and the solvent was removed under reduced pressure to give a waxy solid. The solid was taken up in a small amount of methanol and precipitated by addition of ether. The solid was filtered off and washed with ether then dried *in vacuo*. Recovered 975.2 mg (91 %) of [*t*-Bu-Pip-phos• BH_3)]Cl as a fluffy, white solid. ^1H NMR (D_2O , 360 MHz): δ 3.62 (brd, $J=12.33$ Hz, 2H), 3.44 (brt, $J=11.72$, 13.56 Hz, 2H), 3.22 (s, 3H), 3.15 (s, 3H), 2.60-2.51 (m, 2H), 2.44-2.25 (m, 3H), 1.40 (d, $^3J_{\text{H-P}}=12.95$ Hz, 18 H) 0.40 (brq, $^1J_{\text{H-B}}=84.5$ Hz, 3H). ^{13}C NMR (D_2O , 90.6 MHz): δ 63.8 (d, $J_{\text{C-P}}=10.62$ Hz), 57.0, 47.8, 34.0 (d, $J_{\text{C-P}}=16.54$ Hz), 29.3 (d, $J_{\text{C-P}}=26.54$ Hz), 28.7, 24.3.

4-(Di-*t*-butylphosphino)-*N,N*-dimethylpiperidinium chloride (*t*-Bu-Pip-phos). [*t*-Bu-Pip-phos• BH_3)]Cl (953 mg, 3.10 mmol) was taken up in dry, degassed morpholine under nitrogen. The suspension was heated to 100 °C and stirred for 4 hours. The reaction was then allowed to cool to room temperature to give a suspension of a white crystalline material. THF (50 mL) was added to complete the precipitation of the product. The solvent was removed *via* cannula and the solid was washed with 20 mL of THF and dried *in vacuo*. The crude material was transferred to a sublimation apparatus in a drybox and heated under vacuum (0.05 torr) at 110 °C for 3 hours. A small amount of morpholine-borane adduct sublimed during this time. The pure product was

recovered as fine, colorless needles (532.3 mg, 58 %). ^1H NMR (D_2O , 360 MHz): δ 3.56 (brd, $J=11.1$ Hz, 2H), 3.42 (brt, $J=12.95$ Hz, 2H), 3.20 (s, 3H), 3.13 (s, 3H), 2.42-2.20 (m, 4H), 2.10-1.98 (m, 1H), 1.28 (d, $^3J_{\text{H-P}}=9.87$ Hz, 18H). ^{13}C NMR (D_2O , 90.6 MHz): δ 64.3 (d, $J_{\text{C-P}}=10.61$ Hz), 57.0, 47.6, 32.8 (d, $J_{\text{C-P}}=15.92$ Hz), 30.4 (d, $J_{\text{C-P}}=11.94$ Hz), 29.7 (d, $J_{\text{C-P}}=21.23$ Hz), 26.7 (d, $J_{\text{C-P}}=11.94$ Hz). ^{31}P NMR (D_2O , 202.5 MHz): δ 40.0 (s). Calculated for $\text{C}_{15}\text{H}_{33}\text{ClNP}$: C, 61.31; H, 11.32; N, 4.77. Found: C, 60.38; H, 11.12; N, 4.76. Carbon analysis was consistently low.

4-(Dicyclohexylphosphino)-*N,N*-dimethylpiperidinium chloride (Cy-Pip-phos). Cy-Pip-phos was prepared as described by Grubbs.² ^1H NMR (D_2O , 360 MHz): δ 3.55 (brd, 12.33 Hz, 2H), 3.38 (brt, $J=11.09$, 12.57 Hz, 2H), 3.19 (s, 3H), 3.11 (s, 3H), 2.15-1.70 (m, 17 H), 1.38-1.20 (m, 10H). ^{13}C NMR (D_2O , 90.6 MHz): δ 63.4 (d, $J_{\text{C-P}}=10.17\text{Hz}$), 56.9, 47.6, 31.4 (d, $J_{\text{C-P}}=8.48$ Hz), 31.1 (d, $J_{\text{C-P}}=3.39$ Hz), 30.0 (d, $J_{\text{C-P}}=5.93$ Hz), 27.6 (d, $J_{\text{C-P}}=10.18$ Hz), 26.6, 25.9 (d, $J_{\text{C-P}}=12.72$ Hz), 25.0 (d, $J_{\text{C-P}}=12.71$ Hz). ^{31}P NMR (D_2O , 202.5 MHz): δ 7.6 (s).

General procedure for measurement of χ electronic parameter. Solutions of $\text{LNi}(\text{CO})_3$ complexes were prepared according to the procedure reported by Grubbs.² Thus, the phosphine (0.18 mmol) was dissolved in 3 mL of CH_2Cl_2 in a drybox under nitrogen. $\text{Ni}(\text{CO})_4$ (20 μL , 0.18 mmol, CAUTION, highly toxic, volatile liquid) was added to the solution and the mixture was sealed and allowed to stir for 15 minutes. At this time, 100 μL of the reaction mixture was diluted to 1 mL with CH_2Cl_2 . The IR spectra were obtained in an air-free solution cell (NaCl windows). (*t*-Bu-Pip-phos) $\text{Ni}(\text{CO})_3$: 2060.3 cm^{-1} . (*t*-Bu-Amphos) $\text{Ni}(\text{CO})_3$: 2063.6 cm^{-1} . (Cy-Pip-phos) $\text{Ni}(\text{CO})_3$: 2061.9 cm^{-1} .

General procedure for generation of $\text{L}_2\text{Pd}(0)$ in the presence of phenylboronic acid. In a drybox, $\text{Pd}(\text{OAc})_2$ (0.035 mmol), ligand (0.5-3 equiv relative to Pd), Na_2CO_3 (0.67 mmol), and phenylboronic acid (0.29 mmol) were added to a screw-cap vial sealed with a septum. A

degassed solution of acetonitrile:water 1:1 (1 mL) was added *via* syringe under nitrogen purge. The reaction was allowed to stir at room temperature for 5 minutes. After 5 minutes formation of a biphasic solution was observed, and each layer was taken up by syringe and added to a septum sealed NMR tube under nitrogen and analyzed by ^{31}P NMR spectroscopy. Samples prepared from 2:1 ratios of *t*-Bu-Pip-phos or *t*-Bu-Amphos to $\text{Pd}(\text{OAc})_2$ were also characterized by ^1H , and ^{13}C NMR spectroscopy.

(*t*-Bu-Pip-phos) $_2$ Pd(0). An NMR sample was prepared as described above for a 2:1 ratio of *t*-Bu-Pip-phos: $\text{Pd}(\text{OAc})_2$. The aqueous-phase showed no resonances in the ^{31}P NMR spectrum and was not further analyzed. Acetonitrile layer: ^1H NMR ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 360 MHz): δ 3.28 (brd, $J=11.72$ Hz, 2H), 3.09 (brt, $J=12.96$ Hz, 2H), 2.95 (s, 3H), 2.84 (s, 3H), 2.50 (brd, $J=12.33$ Hz, 2.09 (brq, $J=13.55$ Hz, 2H), 1.82 (brm, 1H), 1.32 (virtual triplet (vt, $J_{\text{H-P}}=6.16$ Hz, 18H). ^{13}C NMR ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 90.6 MHz): δ 64.1 (vt, $J_{\text{C-P}}=5.31$ Hz), 56.9, 47.8, 36.2 (vt, $J_{\text{C-P}}=2.65$ Hz), 33.0, 31.7 (vt, $J_{\text{C-P}}=6.63, 5.31$ Hz), 28.3 (vt, $J_{\text{C-P}}=5.31$ Hz). ^{31}P NMR ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 202.5 MHz): δ 70.4 (s).

(*t*-Bu-Amphos) $_2$ Pd(0). An NMR sample was prepared as described above for a 2:1 ratio of *t*-Bu-Amphos: $\text{Pd}(\text{OAc})_2$. The aqueous-phase showed no resonances by ^{31}P NMR and was not further analyzed. Acetonitrile layer: ^1H NMR ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 360 MHz): δ 3.64 (brm, 2H), 2.98 (s, 9H), 1.75 (brm, 2H), 1.26 (vt, $J_{\text{H-P}}=6.38$ Hz, 18H). ^{13}C NMR ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 90.6 MHz): δ 69.9 (vt, $J=17.65, 18.03$ Hz), 53.5 (t (1:1:1), $J_{\text{C-N}}=4.16$ Hz), 35.5 (vt, $J=5.55$ Hz), 30.6 (vt, $J=5.55$ Hz), 16.7. ^{31}P NMR ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 202.5 MHz): δ 55.8 (s).

(Cy-Pip-phos) $_2$ Pd(0). An NMR sample was prepared as described above for a 1:1 ratio Cy-Pip-phos: $\text{Pd}(\text{OAc})_2$. Acetonitrile: ^{31}P NMR ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 202.5 MHz): δ 55.0 (s,

integral=0.07), 47.4 (s, integral=0.11), 42.6 (s, integral=0.17), 39.6 ppm (s, integral=1.0), 26.3 (s, integral=0.06), 21.2 (s, integral=0.02).

General procedure for preparation of $L_2Pd(0)$ in the presence of sodium formate. In the drybox, a vial was charged with $Pd(OAc)_2$ (0.035 mmol), ligand (0.5 – 3 equiv. to Pd), and sodium formate (0.7 mmol). A degassed solution of acetonitrile:water 1:1 (1 mL) was added by syringe to the sealed vial containing the solid reagents. The reaction was allowed to stir at room temperature for 5 minutes at which point the solution was transferred to a septum sealed NMR tube by syringe and analyzed by ^{31}P NMR. The sample produced from a 1:1 ratio of Cy-pip-phos: $Pd(OAc)_2$ was also analyzed by 1H and ^{13}C NMR.

(*t*-Bu-Pip-phos) $_2Pd(0)$. An NMR sample was prepared as described above with a 1:1 ratio of *t*-Bu-Pip-phos: $Pd(OAc)_2$. ^{31}P NMR (CH_3CN/H_2O , 202.5 MHz): δ 70 (s).

(Cy-Pip-phos) $_2Pd(0)$. A 1:1 mixture of Cy-Pip-phos: $Pd(OAc)_2$ was reduced by sodium formate as described above. ^{13}C NMR (CD_3CN/D_2O , 90.6 MHz): δ 63.4, 57.1, 47.8, 33.3 (vt, $J_{C,p}=10.61$ Hz), 30.5, 30.2, 27.9 (d, $J_{C,p}=14.6$ Hz), 26.7, 24.3, 23.6. A second minor set of resonances with similar pattern was also observed. Free acetate was also observed at 181.5 and 23.6 ppm. ^{31}P NMR (CD_3CN/D_2O , 202.5 MHz): δ 44 (s), 41 (s, minor).

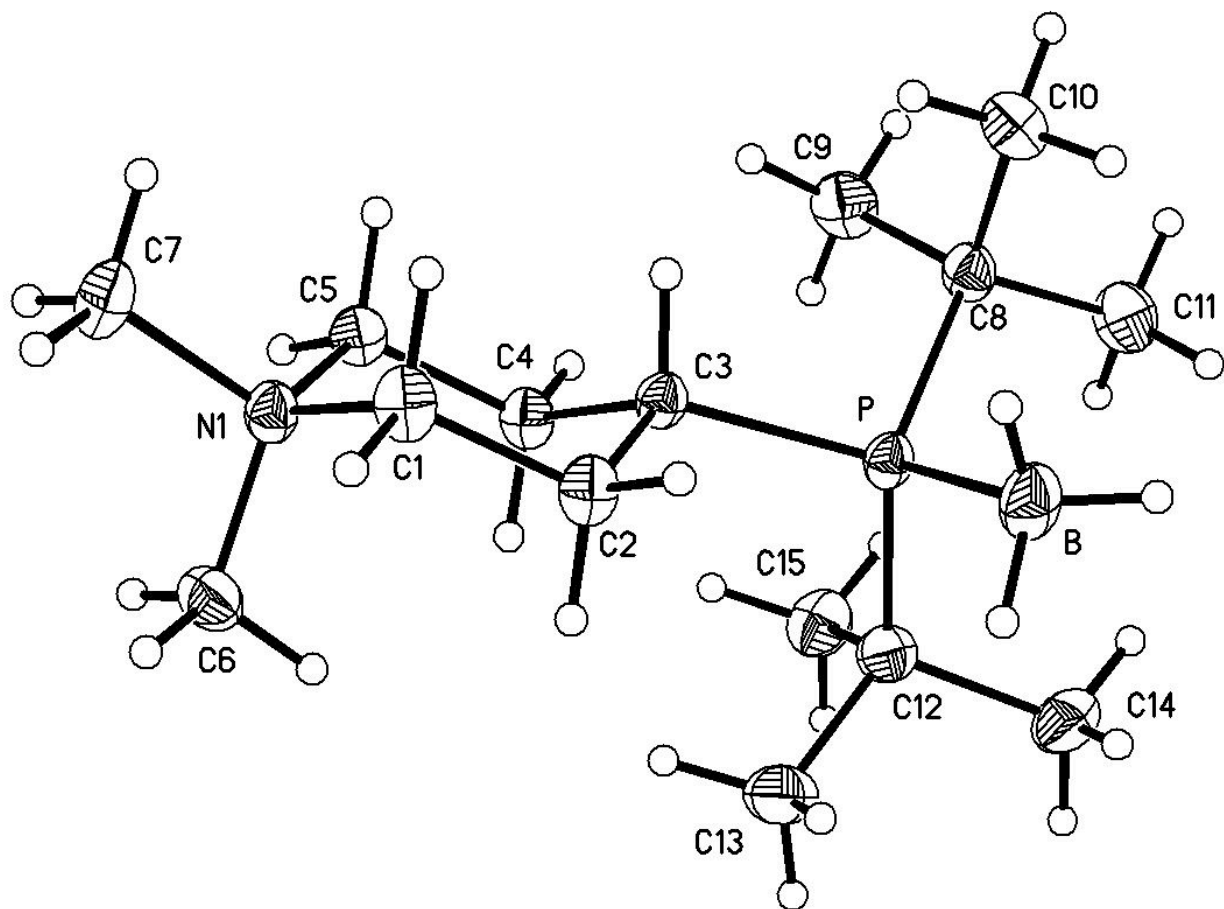
Complexation of *t*-Bu-Amphos with $Pd(OAc)_2$. In the drybox, $Pd(OAc)_2$ (9.0 mg, 0.04 mmol) and *t*-Bu-Amphos (20.7 mg, 0.08 mmol) were added to a screw-cap vial, which was sealed with a septum and dissolved in degassed D_2O . The reaction was allowed to stir at room temperature for 5 minutes, during which time a pale yellow precipitate formed. The D_2O solution showed resonances for *t*-Bu-Pip-phos and two new species at 37 and 38 ppm in the ^{31}P NMR spectrum. The solid precipitate was sparingly soluble in acetonitrile. A ^{31}P NMR spectrum of this mixture showed free *t*-Bu-Amphos and a pair of resonances at 38 and 40 ppm.

***trans*-(Cy-Pip-phos)₂PdCl₂.** In the drybox, Na₂PdCl₄ (3.0 mg, 0.020 mmol) and Cy-Pip-phos (13.8 mg, 0.040 mmol) were added to a screw-cap vial, which was sealed with a septum. A degassed solution of acetonitrile:water 1:1 (1 mL) was added by syringe under nitrogen. The reaction was allowed to stir at room temperature for 5 minutes, and then analyzed by ³¹P, ¹H, and ¹³C NMR spectroscopy. ¹H NMR (CD₃CN/D₂O, 360 MHz): δ 3.42 (d, *J*=12.76 Hz, 2H), 3.19 (brt, *J*=6.76, 6.11 Hz, 2H), 3.05 (s, 3H), 3.02 (s, 3H), 2.39-2.58 (m, 4H), 1.90-2.05 (m, overlapped with solvent peak), 1.58-1.76 (m, 10H), 1.18-1.29 (m, 6H) ¹³C NMR (CD₃CN/D₂O, 90.6 MHz): δ 62.6, 56.3, 47.1 32.5 (vt, *J*_{C-P}=9.71 Hz), 29.7, 29.4, 27.1 (d, *J*_{C-P}=9.71 Hz), 26.0, 22.9. ³¹P NMR (CD₃CN/D₂O, 202.5 MHz): δ 28.3 (s).

References

- (1) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244-5252.
- (2) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317-4325.
- (3) Sheldrick, G. M., *SHELXTL*, Version 6.14, Brüker Advanced X-Ray Solutions, Inc., 2000.
- (4) Sheldrick, G. M., *Program for Semiempirical Absorption Correlation of Area Detector Data*, University of Göttingen, Germany, 1996.

X-Ray Crystallographic Data



ORTEP diagram of [t-Bu-Pip-phos•BH₃]I drawn with thermal ellipsoids at the 50% level.

Table 1. Crystal data and structure refinement for [*t*-Bu-Pip-phos•BH₃]I

Empirical formula	C ₁₅ H ₃₆ BINP
Formula weight	399.13
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.7778(17) Å α = 90° b = 11.5772(17) Å β = 90.233(3)° c = 14.397(2) Å γ = 90°
Volume	1963.1(5) Å ³
Z	4
Density (calculated)	1.350 Mg/m ³
Absorption coefficient	1.704 mm ⁻¹
F(000)	824
Crystal size	0.24 x 0.28 x 0.48 mm ³
Theta range for data collection	2.26 to 23.30°
Index ranges	-11 ≤ h ≤ 13, -12 ≤ k ≤ 12, -16 ≤ l ≤ 13
Reflections collected	8409
Independent reflections	2824 [R(int) = 0.0253]
Completeness to theta =	23.30° 99.6 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2824 / 0 / 185
Goodness-of-fit on F ²	1.118
Final R indices	[I > 2σ(I)] R1 = 0.0204, wR2 = 0.0465
R indices (all data)	R1 = 0.0212, wR2 = 0.0470
Extinction coefficient	0.0051(2)
Largest diff. peak and hole	0.385 and -0.314 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [*t*-Bu-Pip-phos•BH₃]I. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
I(1)	1304(1)	2334(1)	8851(1)	29(1)
P(1)	3120(1)	-1775(1)	6698(1)	18(1)
N(1)	1400(1)	-5503(2)	6432(1)	20(1)
C(1)	1326(2)	-4788(2)	7307(1)	22(1)
C(2)	2248(2)	-3887(2)	7381(1)	22(1)
C(3)	2226(2)	-3081(2)	6535(1)	18(1)
C(4)	2370(2)	-3816(2)	5656(1)	20(1)
C(5)	1431(2)	-4709(2)	5598(1)	20(1)
C(6)	2411(2)	-6288(2)	6443(2)	27(1)
C(7)	355(2)	-6237(2)	6372(2)	27(1)
C(8)	2399(2)	-633(2)	5980(1)	21(1)
C(9)	2007(2)	-1050(2)	5016(2)	29(1)
C(10)	1345(2)	-240(2)	6521(2)	30(1)
C(11)	3177(2)	413(2)	5862(2)	32(1)
C(12)	4613(2)	-2074(2)	6317(2)	25(1)
C(13)	5014(2)	-3194(2)	6795(2)	33(1)
C(14)	5387(2)	-1097(2)	6677(2)	34(1)
C(15)	4768(2)	-2201(2)	5268(2)	30(1)
B(1)	3105(2)	-1353(2)	7998(2)	27(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for [*t*-Bu-Pip-phos•BH₃]*I*.

P(1)-C(3)	1.857(2)
P(1)-C(12)	1.876(2)
P(1)-C(8)	1.880(2)
P(1)-B(1)	1.934(2)
N(1)-C(7)	1.498(3)
N(1)-C(6)	1.498(3)
N(1)-C(1)	1.510(3)
N(1)-C(5)	1.513(3)
C(1)-C(2)	1.509(3)
C(2)-C(3)	1.535(3)
C(3)-C(4)	1.536(3)
C(4)-C(5)	1.516(3)
C(8)-C(11)	1.528(3)
C(8)-C(10)	1.538(3)
C(8)-C(9)	1.539(3)
C(12)-C(15)	1.529(3)
C(12)-C(14)	1.542(3)
C(12)-C(13)	1.542(3)
C(3)-P(1)-C(12)	110.17(10)
C(3)-P(1)-C(8)	104.38(9)
C(12)-P(1)-C(8)	112.96(10)
C(3)-P(1)-B(1)	108.72(10)
C(12)-P(1)-B(1)	110.01(11)
C(8)-P(1)-B(1)	110.40(11)
C(7)-N(1)-C(6)	108.03(17)
C(7)-N(1)-C(1)	108.02(16)
C(6)-N(1)-C(1)	111.83(16)
C(7)-N(1)-C(5)	108.79(15)
C(6)-N(1)-C(5)	110.79(16)
C(1)-N(1)-C(5)	109.29(16)

C(2)-C(1)-N(1)	113.23(17)
C(1)-C(2)-C(3)	110.72(17)
C(2)-C(3)-C(4)	108.41(17)
C(2)-C(3)-P(1)	112.75(14)
C(4)-C(3)-P(1)	119.40(14)
C(5)-C(4)-C(3)	109.89(17)
N(1)-C(5)-C(4)	113.01(16)
C(11)-C(8)-C(10)	107.90(19)
C(11)-C(8)-C(9)	109.06(18)
C(10)-C(8)-C(9)	108.02(18)
C(11)-C(8)-P(1)	110.45(15)
C(10)-C(8)-P(1)	107.07(14)
C(9)-C(8)-P(1)	114.13(15)
C(15)-C(12)-C(14)	109.30(19)
C(15)-C(12)-C(13)	108.8(2)
C(14)-C(12)-C(13)	106.66(19)
C(15)-C(12)-P(1)	115.01(16)
C(14)-C(12)-P(1)	108.67(16)
C(13)-C(12)-P(1)	108.06(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [*t*-Bu-Pip-phos•BH₃]**I**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
I(1)	30(1)	29(1)	28(1)	11(1)	-2(1)	-3(1)
P(1)	21(1)	17(1)	15(1)	0(1)	-2(1)	-3(1)
N(1)	24(1)	17(1)	19(1)	2(1)	-2(1)	-3(1)
C(1)	32(1)	22(1)	13(1)	1(1)	2(1)	-3(1)
C(2)	29(1)	21(1)	15(1)	1(1)	-1(1)	-4(1)
C(3)	20(1)	18(1)	16(1)	0(1)	-2(1)	-2(1)
C(4)	26(1)	19(1)	16(1)	2(1)	0(1)	-2(1)
C(5)	26(1)	21(1)	14(1)	1(1)	-3(1)	-1(1)
C(6)	31(1)	22(1)	29(1)	2(1)	-4(1)	4(1)
C(7)	30(1)	27(1)	26(1)	1(1)	-2(1)	-11(1)
C(8)	25(1)	18(1)	21(1)	2(1)	-2(1)	-2(1)
C(9)	38(1)	29(1)	22(1)	6(1)	-5(1)	2(1)
C(10)	32(1)	24(1)	32(1)	0(1)	1(1)	4(1)
C(11)	37(1)	22(1)	38(1)	9(1)	-1(1)	-3(1)
C(12)	23(1)	25(1)	26(1)	1(1)	-2(1)	0(1)
C(13)	25(1)	33(1)	40(1)	4(1)	-4(1)	3(1)
C(14)	25(1)	36(1)	40(1)	-1(1)	-6(1)	-5(1)
C(15)	26(1)	34(1)	30(1)	1(1)	6(1)	-5(1)
B(1)	36(2)	27(1)	19(1)	-3(1)	-6(1)	-3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [*t*-Bu-Pip-phos•BH₃]**I**.

	x	y	z	U(eq)
H(1B)	593	-4406	7324	26
H(1A)	1373	-5297	7841	26
H(2B)	2982	-4264	7422	26
H(2A)	2141	-3437	7943	26
H(3A)	1445	-2791	6503	21
H(4B)	2345	-3323	5111	24
H(4A)	3102	-4200	5671	24
H(5B)	707	-4315	5543	24
H(5A)	1535	-5169	5041	24
H(6C)	2429	-6729	5879	41
H(6B)	2361	-6802	6964	41
H(6A)	3092	-5835	6493	41
H(7A)	367	-6675	5805	41
H(7B)	-306	-5752	6379	41
H(7C)	334	-6756	6892	41
H(9C)	1711	-409	4669	44
H(9B)	1425	-1624	5087	44
H(9A)	2640	-1379	4691	44
H(10C)	932	318	6160	44
H(10B)	1577	102	7098	44
H(10A)	867	-894	6641	44
H(11C)	2764	1026	5563	48
H(11B)	3817	202	5488	48
H(11A)	3437	668	6460	48
H(13A)	5808	-3308	6677	49
H(13B)	4591	-3837	6555	49
H(13C)	4894	-3134	7453	49
H(14A)	6164	-1280	6542	50

H(14B)	5295	-1017	7336	50
H(14C)	5185	-385	6377	50
H(15A)	5551	-2354	5135	45
H(15B)	4539	-1500	4965	45
H(15C)	4310	-2830	5046	45
H(1B1)	3602	-1857	8339	47(8)
H(2B1)	2347	-1422	8234	41(7)
H(3B1)	3360	-569	8065	41(7)

Table 6. Torsion angles [°] for [*t*-Bu-Pip-phos•BH₃]I.

C(7)-N(1)-C(1)-C(2)	-171.88(17)
C(6)-N(1)-C(1)-C(2)	69.4(2)
C(5)-N(1)-C(1)-C(2)	-53.7(2)
N(1)-C(1)-C(2)-C(3)	57.1(2)
C(1)-C(2)-C(3)-C(4)	-57.9(2)
C(1)-C(2)-C(3)-P(1)	167.60(15)
C(12)-P(1)-C(3)-C(2)	88.31(16)
C(8)-P(1)-C(3)-C(2)	-150.15(15)
B(1)-P(1)-C(3)-C(2)	-32.32(18)
C(12)-P(1)-C(3)-C(4)	-40.71(19)
C(8)-P(1)-C(3)-C(4)	80.83(17)
B(1)-P(1)-C(3)-C(4)	-161.34(16)
C(2)-C(3)-C(4)-C(5)	58.4(2)
P(1)-C(3)-C(4)-C(5)	-170.69(14)
C(7)-N(1)-C(5)-C(4)	172.23(18)
C(6)-N(1)-C(5)-C(4)	-69.2(2)
C(1)-N(1)-C(5)-C(4)	54.5(2)
C(3)-C(4)-C(5)-N(1)	-58.4(2)
C(3)-P(1)-C(8)-C(11)	-166.96(15)
C(12)-P(1)-C(8)-C(11)	-47.28(18)
B(1)-P(1)-C(8)-C(11)	76.37(18)
C(3)-P(1)-C(8)-C(10)	75.81(16)
C(12)-P(1)-C(8)-C(10)	-164.51(14)
B(1)-P(1)-C(8)-C(10)	-40.86(18)
C(3)-P(1)-C(8)-C(9)	-43.66(18)
C(12)-P(1)-C(8)-C(9)	76.02(18)
B(1)-P(1)-C(8)-C(9)	-160.33(16)
C(3)-P(1)-C(12)-C(15)	70.81(19)
C(8)-P(1)-C(12)-C(15)	-45.5(2)
B(1)-P(1)-C(12)-C(15)	-169.34(17)
C(3)-P(1)-C(12)-C(14)	-166.32(15)

C(8)-P(1)-C(12)-C(14)	77.39(17)
B(1)-P(1)-C(12)-C(14)	-46.47(19)
C(3)-P(1)-C(12)-C(13)	-50.95(18)
C(8)-P(1)-C(12)-C(13)	-167.24(15)
B(1)-P(1)-C(12)-C(13)	68.90(18)

Symmetry transformations used to generate equivalent atoms:

Computational Materials

The local DFT optimized geometries (coordinates) of the free ligand (L), LPd(0) and L₂Pd(0) for ligand = Cy-Pip-phos, *t*-Bu-Pip-phos, *t*-Bu-Amphos, and *t*-Bu₃P in x,y,z format in Å.

Cy-Pip-phos

58

15 -0.86715353 -0.21876755 -0.23718132
6 1.06634212 1.30485141 1.30759263
6 0.88977516 0.16132168 0.31752941
6 1.82604945 0.32486963 -0.87301010
6 3.25296736 0.53264862 -0.42957082
6 2.51422429 1.52334619 1.68720615
1 2.64691925 2.41422129 2.33063412
1 2.91493940 0.64346224 2.22877169
1 3.94244456 0.69550294 -1.27961743
1 3.60962677 -0.34719047 0.14298774
1 1.17718565 -0.78662038 0.83069986
1 1.80110848 -0.59174132 -1.49387538
1 1.48872197 1.13914299 -1.54487443
1 0.61670053 2.24108720 0.92074090
1 0.52327251 1.08292377 2.24761629
7 3.41297603 1.71091461 0.49417904
6 3.08979559 2.97352743 -0.21502319
6 4.82225657 1.77696657 0.95021969
1 3.75342035 3.07117057 -1.09167922
1 3.24948692 3.82436371 0.46960863
1 2.03966141 2.96297073 -0.55097228
1 5.48244619 1.89718032 0.07288378
1 5.08141708 0.84527671 1.48171353
1 4.94956684 2.63887715 1.62853885
6 -3.06148291 1.16639566 -1.06567132
6 -1.69173074 1.44552302 -0.44033915
6 -0.90781492 2.37801170 -1.35951567
6 -1.67478740 3.65912962 -1.65608287
6 -3.02526689 3.35827827 -2.28044581
6 -3.83276749 2.43644977 -1.38472950
1 -4.79213905 2.17266440 -1.86922383
1 -4.09161615 2.96709895 -0.44335970
1 -3.57800603 4.29581118 -2.48176646
1 -2.86879563 2.86688805 -3.26507616
1 -1.07772279 4.31378746 -2.31999898
1 -1.82887137 4.21938753 -0.70831966
1 -1.83395672 1.94547009 0.54519635
1 0.07603853 2.64214945 -0.91496181
1 -0.69258887 1.84909475 -2.31513619

1 -2.89831614 0.59233749 -2.00345135
1 -3.66216636 0.51140666 -0.40723178
6 -1.38590670 -2.38815117 1.40183640
6 -1.46621728 -0.86302364 1.42169631
6 -2.85301232 -0.42063811 1.86486387
6 -3.16965723 -0.98351747 3.24292803
6 -3.08918905 -2.50018358 3.25060821
6 -1.73539388 -2.98448324 2.75754809
1 -1.71875525 -4.08977985 2.69720984
1 -0.95320404 -2.69889522 3.49421501
1 -3.28902078 -2.89277291 4.26607990
1 -3.88625956 -2.90904999 2.59377170
1 -4.17154312 -0.64637321 3.56921721
1 -2.44480085 -0.57178503 3.97898412
1 -0.75425583 -0.49293572 2.19784975
1 -2.93534684 0.68511999 1.87403822
1 -3.61289358 -0.79418987 1.14506447
1 -2.09172177 -2.76380277 0.62979537
1 -0.37837917 -2.72620368 1.07987928

(Cy-Pip-phos)Pd(0)

59

46 -1.94534016 0.62726635 2.42726922
6 0.96228445 -1.45142460 -0.66158479
6 0.02852473 -1.21789539 0.51804155
6 -1.21801305 -2.08579874 0.44271383
6 -0.87120736 -3.53494334 0.23123282
6 1.23768806 -2.92564273 -0.86522436
1 1.84407341 -3.11496544 -1.77167654
1 1.78079283 -3.34451866 0.00566080
1 -1.77020943 -4.16975498 0.11268393
1 -0.27753139 -3.92803073 1.08190143
1 0.57173657 -1.51938510 1.44245529
1 -1.77000189 -1.97227597 1.40208817
1 -1.92282927 -1.72470343 -0.33078748
1 0.57761371 -0.98941946 -1.59240806
1 1.94329524 -0.97023994 -0.47821119
7 -0.01924634 -3.74287128 -0.99733365
6 -0.76619899 -3.34913659 -2.21819592
6 0.33910197 -5.17729759 -1.10452592
1 -1.68733525 -3.95296025 -2.29055548
1 -0.13122439 -3.52470493 -3.10356736
1 -1.03892446 -2.28120470 -2.17094636
1 -0.58503526 -5.77659178 -1.18474317
1 0.90251058 -5.48546124 -0.20685600
1 0.95970994 -5.33536053 -2.00374365

6 -1.63136733 2.68739367 -0.30367315
6 -0.87714422 1.40699756 -0.67461437
6 -1.75708222 0.56879675 -1.59654045
6 -2.19082975 1.34792483 -2.82995534
6 -2.93691802 2.61268783 -2.44725990
6 -2.09402895 3.46945691 -1.52070749
1 -2.66705680 4.35454512 -1.18378210
1 -1.21284747 3.85992527 -2.07374477
1 -3.22402978 3.18139529 -3.35181355
1 -3.88197660 2.33696318 -1.93206799
1 -2.81719160 0.70495468 -3.47852778
1 -1.29142392 1.61869240 -3.42433381
1 0.06814865 1.66810632 -1.20571637
1 -1.23099709 -0.35393178 -1.92240489
1 -2.65767908 0.24657676 -1.02621746
1 -2.50475550 2.37982368 0.31729010
1 -1.01766050 3.32856083 0.35502446
6 1.64983106 0.65015346 2.72437692
6 1.24262822 1.22006595 1.36788332
6 1.24463463 2.74595904 1.38505423
6 2.55318570 3.31248999 1.91268444
6 2.86952305 2.76588535 3.29198837
6 2.94447541 1.25029433 3.24820209
1 3.15947175 0.83584648 4.25151491
1 3.79252195 0.94819683 2.59611034
1 3.81567311 3.19141388 3.67591071
1 2.07134461 3.07459307 4.00115490
1 2.49592662 4.41790342 1.92596352
1 3.37943029 3.04782867 1.21767402
1 1.96738517 0.88434333 0.58885521
1 1.05294621 3.14018965 0.36716855
1 0.40894580 3.09461594 2.03211045
1 0.81841469 0.85404438 3.43721676
1 1.74302065 -0.45524117 2.67714858
15 -0.42874789 0.54986006 0.91433769

(Cy-Pip-phos)₂Pd(0)

117

46 0.27229869 -0.02548452 0.30420104
6 3.29058719 -2.14806485 -2.80722308
6 2.35302234 -1.90218484 -1.63204002
6 1.10124326 -2.76758003 -1.70032120
6 1.44511330 -4.21867037 -1.91363883
6 3.54238272 -3.62379479 -3.03300142
1 4.12814045 -3.80377173 -3.95440531
1 4.09920740 -4.06180239 -2.18136048

1 0.54531497 -4.85437918 -2.01843786
1 2.04984093 -4.61154985 -1.07126307
1 2.89281201 -2.20421672 -0.70513499
1 0.55006522 -2.65822339 -0.74015355
1 0.39352575 -2.40963769 -2.47318625
1 2.92761326 -1.66742063 -3.73659348
1 4.27916718 -1.68993127 -2.60647082
7 2.27860093 -4.43151903 -3.15046811
6 1.51619136 -4.03806448 -4.36119175
6 2.63152671 -5.86793709 -3.25768328
1 0.58393645 -4.62756538 -4.40771961
1 2.12908196 -4.23616076 -5.25713205
1 1.26469779 -2.96530461 -4.31703997
1 1.70588195 -6.46554232 -3.32940674
1 3.20052910 -6.17367506 -2.36309648
1 3.24621916 -6.02869606 -4.16032410
6 0.65664947 1.97268128 -2.45586658
6 1.46580577 0.72626895 -2.83269787
6 0.63093859 -0.13386558 -3.77668071
6 0.18852638 0.64288688 -5.00684786
6 -0.63262767 1.85446680 -4.61247158
6 0.15452635 2.74205756 -3.66643858
1 -0.46928009 3.59226847 -3.32753921
1 1.01446199 3.18627477 -4.21095610
1 -0.94586891 2.41905904 -5.51050091
1 -1.56156456 1.50983465 -4.10830259
1 -0.38432041 -0.01690923 -5.68644428
1 1.08566105 0.97629559 -5.57184649
1 2.40368986 1.02772772 -3.35287786
1 1.19762874 -1.02996850 -4.10277939
1 -0.26767519 -0.49579558 -3.22602725
1 -0.19776779 1.62104309 -1.82626915
1 1.25404608 2.63441467 -1.80011165
6 3.90866852 -0.01164619 0.64338601
6 3.55705476 0.53044945 -0.74126375
6 3.56252909 2.05444121 -0.72314811
6 4.88730860 2.60135746 -0.21524864
6 5.21976423 2.05813122 1.16194892
6 5.22932386 0.54091835 1.15330005
1 5.43125296 0.14736867 2.16781116
1 6.05652332 0.18361989 0.50355512
1 6.19313908 2.45063710 1.51177502
1 4.45328665 2.40957761 1.88596797
1 4.85009623 3.70690107 -0.20047474
1 5.69721317 2.32370305 -0.92375529
1 4.31804848 0.19144940 -1.48235452

1 3.35062885 2.45950317 -1.73252380
1 2.73884654 2.39507055 -0.05430867
1 3.08146906 0.27166909 1.33580780
1 3.94212770 -1.12048578 0.64318496
15 1.90338266 -0.13468492 -1.24228966
6 -2.98444057 2.12780070 3.14738917
6 -1.73853970 1.86125875 2.31223869
6 -1.62990975 2.80243516 1.11904657
6 -1.79066396 4.24095345 1.53685963
6 -3.14678884 3.59737825 3.47299385
1 -4.10985327 3.80132747 3.97851634
1 -2.33040524 3.94465303 4.13636112
1 -1.76659501 4.93557692 0.67562360
1 -0.99168634 4.54044676 2.24478865
1 -0.85269004 2.06817317 2.95573664
1 -0.62822455 2.66553092 0.65512818
1 -2.34784436 2.53847551 0.31805420
1 -3.89983010 1.73057592 2.66705084
1 -2.90980363 1.59962738 4.11837959
7 -3.09006739 4.48390675 2.25881362
6 -4.23913288 4.21545887 1.35899770
6 -3.14746284 5.90089798 2.69243646
1 -4.15588856 4.86005116 0.46668819
1 -5.17899799 4.43586922 1.89358425
1 -4.23369503 3.15855217 1.04472232
1 -3.09056973 6.55547667 1.80509377
1 -2.29757595 6.11453104 3.36288977
1 -4.09588671 6.08360291 3.22683096
6 -2.62262177 -1.84509289 0.30424267
6 -3.00414634 -0.62540299 1.15054786
6 -3.80584788 0.34024540 0.28291750
6 -5.02994633 -0.32916108 -0.32276863
6 -4.63035107 -1.51818109 -1.17367387
6 -3.82106018 -2.50724435 -0.35521981
1 -3.47356319 -3.34229326 -0.99438053
1 -4.47303867 -2.96107054 0.42102134
1 -5.52537060 -2.00386596 -1.60478389
1 -4.01641989 -1.15737581 -2.02740288
1 -5.60754395 0.40415248 -0.91784000
1 -5.70149708 -0.67115730 0.49393186
1 -3.63240695 -0.94567257 2.01286030
1 -4.13241959 1.22377694 0.86876798
1 -3.14450479 0.71301013 -0.53296226
1 -1.89513874 -1.48558462 -0.46460661
1 -2.06541109 -2.57926917 0.91723275
6 0.26426855 -0.25792775 3.94058132

6 -1.11253452 -0.68802547 3.43749452
6 -1.18651807 -2.20804453 3.34911180
6 -0.83000797 -2.86243749 4.67470026
6 0.54166168 -2.42914796 5.15650320
6 0.62213695 -0.91771805 5.26177788
1 1.63622332 -0.60283309 5.57313824
1 -0.07527433 -0.56842571 6.05276680
1 0.77830166 -2.90055966 6.12909603
1 1.30905175 -2.78135324 4.43394041
1 -0.87800604 -3.96258926 4.56875849
1 -1.58977878 -2.58781123 5.43783617
1 -1.89755666 -0.34502760 4.15117407
1 -2.19568133 -2.53295255 3.02761817
1 -0.47029540 -2.54300618 2.56365609
1 1.00931680 -0.53663492 3.15884709
1 0.32728359 0.84494734 4.04319811
15 -1.41526794 0.10162985 1.79006112

t-Bu-Pip-phos

50

15 -1.50331628 -0.49365744 -0.07556121
6 -1.77147293 1.29208934 -2.12615252
6 -2.24296284 1.14111793 -0.68018019
6 -3.75078654 0.89593989 -0.75159431
6 -1.97860718 2.41896939 0.09811816
6 -1.92407227 -0.80584979 1.74347317
6 -1.40392363 0.19873638 2.75819898
6 -3.43506145 -0.93586344 1.88653135
6 -1.31347132 -2.17803669 2.03051782
1 -1.59067869 -2.49665833 3.05541253
1 -0.20537874 -2.17216349 1.98833013
1 -0.30328819 0.32384259 2.72502303
1 -1.64853573 -0.15443052 3.78154016
1 -1.86488986 1.19503212 2.63914537
1 -2.34242654 2.35815477 1.13969350
1 -2.51746774 3.26168299 -0.38278994
1 -0.90934223 2.69911289 0.12359530
1 -0.70688260 1.57544124 -2.21227908
1 -1.93847716 0.36417729 -2.70634675
1 -2.35008717 2.10194349 -2.61473274
1 -3.98995662 -0.09744326 -1.17944515
1 -4.21118307 1.66210794 -1.40790021
1 -4.24126816 0.97559267 0.23294748
1 -3.88098955 -1.55322051 1.08309472
1 -3.67079568 -1.42183137 2.85492373
1 -3.93869019 0.04665193 1.88990211

1 -1.68631959 -2.94437456 1.32355726
6 1.10286510 0.92070752 -0.35696656
6 0.38225758 -0.33861029 0.09303576
6 0.97561920 -1.55106068 -0.61589360
6 2.47529912 -1.62862360 -0.46050835
6 2.60557604 0.80201918 -0.22931698
1 3.11856341 1.69575500 -0.63318795
1 2.90613055 0.68165851 0.83091509
1 2.91440225 -2.48594069 -1.00594187
1 2.75059557 -1.72091413 0.60958439
1 0.59011859 -0.45088357 1.18021202
1 0.54931712 -2.48095846 -0.19135027
1 0.67179328 -1.56700563 -1.68248224
1 0.83243930 1.20101547 -1.39275146
1 0.80444533 1.78412008 0.26668537
7 3.16796994 -0.38886198 -0.95722663
6 2.97700930 -0.24288146 -2.42275071
6 4.61997890 -0.49040055 -0.67535305
1 3.33603215 -1.15695608 -2.92645121
1 3.54987836 0.63149846 -2.77752209
1 1.90913463 -0.10047676 -2.64945436
1 5.04081726 -1.34956217 -1.22608542
1 4.77551174 -0.63230842 0.40761504
1 5.12270355 0.43695480 -1.00051272

(*t*-Bu-Pip-phos)Pd(0)

51

46 -0.61617953 -2.75112009 1.05546784
6 1.88222528 -0.87990457 2.38229728
6 2.17466354 -0.88648784 0.88324881
6 3.09560156 -2.07904649 0.63161159
6 2.86872768 0.41739857 0.45696205
6 0.90562892 -1.69787371 -1.80654132
6 1.93545628 -0.77491981 -2.44164658
6 1.34969127 -3.15463424 -1.89541948
6 -0.40024281 -1.59025931 -2.58509517
1 -0.22440247 -1.95235884 -3.61791348
1 -0.76638061 -0.54873228 -2.67456889
1 1.63030672 0.29035190 -2.40298796
1 2.04200673 -1.03485954 -3.51440644
1 2.93588424 -0.86388808 -1.98118126
1 2.49366999 0.84524977 -0.49091044
1 3.95250726 0.24320164 0.31045610
1 2.78539443 1.19195616 1.24238634
1 1.25478947 -0.02753514 2.70088792
1 1.35450613 -1.81129265 2.67596316

1 2.83964109 -0.81488258 2.93851113
1 2.58206296 -3.03864646 0.84111208
1 3.96580410 -2.00295949 1.31411636
1 3.49117208 -2.10151172 -0.39943126
1 0.60364157 -3.81746292 -1.41289735
1 1.43346000 -3.43949962 -2.96410680
1 2.32586479 -3.34567976 -1.42173505
1 -1.18855596 -2.22735524 -2.13568377
6 -0.19365793 1.34614420 0.93818402
6 -0.41428921 0.33925441 -0.18154480
6 -1.90076494 -0.00372974 -0.24476774
6 -2.78901863 1.20986736 -0.32966316
6 -1.09506297 2.54963470 0.79997241
1 -0.94941288 3.27554011 1.62327909
1 -0.90592289 3.07483959 -0.15770675
1 -3.85920763 0.92975032 -0.29369962
1 -2.61480045 1.77536595 -1.26717448
1 -0.09894202 0.80361515 -1.14418757
1 -2.12197757 -0.62324780 -1.13153517
1 -2.14533854 -0.67243046 0.61556762
1 -0.33591774 0.86182672 1.92577374
1 0.84547913 1.72467601 0.93258965
7 -2.55018997 2.18149114 0.79121304
6 -2.94167113 1.57470155 2.08901000
6 -3.36284447 3.39910674 0.57075870
1 -4.02857256 1.38323843 2.07736444
1 -2.69014168 2.27609777 2.90341854
1 -2.40527844 0.62367797 2.23942113
1 -4.42926311 3.11780596 0.51576138
1 -3.05912375 3.87919807 -0.37543288
1 -3.20531201 4.09950399 1.40989852
15 0.54430646 -1.27318704 0.00501241

(*t*-Bu-Pip-pho)₂Pd(0)

101

46 -0.19416609 -0.05605376 -0.17701188
6 2.35078549 1.95648432 1.36707914
6 2.69187546 1.93173063 -0.12199572
6 3.58927393 0.71316212 -0.33367798
6 3.44541240 3.20982218 -0.52465659
6 1.48847222 1.24706149 -2.86634254
6 2.54467630 2.16436100 -3.46139669
6 1.91669512 -0.21480903 -2.98076701
6 0.19265667 1.38605833 -3.65922618
1 0.38314793 1.09577239 -4.71221828
1 -0.19143444 2.42407441 -3.68523264

1 2.25597048 3.23350382 -3.41010356
1 2.67222738 1.92387283 -4.53604031
1 3.53504133 2.05160522 -2.98269939
1 3.07919836 3.68055129 -1.45513189
1 4.51752090 2.99272370 -0.69385058
1 3.41048050 3.96621203 0.28127334
1 1.68306684 2.78953600 1.64766157
1 1.85582983 1.01226270 1.67287469
1 3.28497529 2.08176565 1.95112193
1 3.02494717 -0.23079860 -0.17668092
1 4.41676950 0.75164473 0.40371794
1 4.04993725 0.69264466 -1.33800113
1 1.17162383 -0.86817890 -2.47549438
1 1.97156549 -0.49498370 -4.05268860
1 2.90726757 -0.40870041 -2.53524089
1 -0.59172618 0.71138883 -3.25949454
6 0.42231947 4.25028133 -0.06719892
6 0.17325071 3.24573421 -1.18228233
6 -1.32620633 2.95771074 -1.22739863
6 -2.16030097 4.20975447 -1.35410559
6 -0.40528196 5.49997425 -0.25027776
1 -0.22926053 6.23047447 0.56203556
1 -0.16781554 5.99453545 -1.21367276
1 -3.24321699 3.98563027 -1.30852783
1 -1.95652449 4.72374821 -2.31526399
1 0.49161398 3.71602821 -2.14104152
1 -1.58178329 2.31717038 -2.09183145
1 -1.60130477 2.33790302 -0.34303299
1 0.21671921 3.79945755 0.92424470
1 1.47958159 4.57098007 -0.04364710
7 -1.88076317 5.22164297 -0.27764520
6 -2.34083414 4.71755123 1.04117000
6 -2.60501385 6.47954416 -0.58491576
1 -3.43645024 4.58791208 1.01470125
1 -2.07351208 5.45096827 1.82174623
1 -1.86398780 3.74903321 1.26240063
1 -3.68901205 6.27545881 -0.63603586
1 -2.25681019 6.87392950 -1.55497384
1 -2.40483975 7.22058153 0.20951998
15 1.08034074 1.60030317 -1.04991388
6 -1.25738597 -0.46074665 2.98369813
6 -2.22629476 -1.38808465 2.25388479
6 -3.45165396 -0.55555940 1.88295865
6 -2.66005969 -2.52838206 3.17356539
6 -2.62612700 -2.60046411 -0.57505631
6 -3.47948766 -3.68982458 0.05494122

6 -3.51093078 -1.50893223 -1.17037749
6 -1.82469499 -3.18637156 -1.73492455
1 -2.53145647 -3.53004265 -2.51657701
1 -1.21915150 -4.06805086 -1.44784975
1 -2.87241840 -4.50558996 0.49657521
1 -4.11983871 -4.15356779 -0.72327393
1 -4.15200853 -3.29906750 0.84042072
1 -2.97788572 -3.43916202 2.63495874
1 -3.52407289 -2.19836807 3.78495622
1 -1.86773443 -2.80071330 3.89292765
1 -0.31208259 -0.96242422 3.26579070
1 -0.98764342 0.40139857 2.33556342
1 -1.73238337 -0.08768754 3.91486597
1 -3.22011781 0.18730237 1.09283388
1 -3.78747892 -0.00556654 2.78560424
1 -4.29890060 -1.18269897 1.54946864
1 -2.89299965 -0.68481791 -1.58146369
1 -4.10284138 -1.94356704 -2.00156379
1 -4.22559881 -1.08387506 -0.44763750
1 -1.16491342 -2.41955781 -2.19204760
6 0.32457048 -3.50957394 2.28585625
6 -0.22363396 -3.29857993 0.88314712
6 0.95881504 -3.14251399 -0.07064154
6 1.91413915 -4.30669022 0.00486193
6 1.27240252 -4.68611002 2.33478642
1 1.69148338 -4.83962488 3.34800220
1 0.74764466 -5.61564684 2.03646493
1 2.79595399 -4.16420841 -0.64898252
1 1.41014969 -5.24564409 -0.30197555
1 -0.80363399 -4.21020746 0.61197668
1 0.62116152 -3.07447195 -1.12181151
1 1.44788063 -2.15700984 0.11590876
1 0.81360495 -2.59053731 2.66917896
1 -0.48854819 -3.74359226 2.99599290
7 2.43567538 -4.55006886 1.39408362
6 3.31765199 -3.43447208 1.81904197
6 3.21827435 -5.81088209 1.40420401
1 4.18708706 -3.38612247 1.14067936
1 3.66000819 -3.61946702 2.85217810
1 2.76636839 -2.48083663 1.77555954
1 4.06791782 -5.72101974 0.70451784
1 2.56891274 -6.64571333 1.08846331
1 3.59551764 -6.00216532 2.42429900
15 -1.37623715 -1.82944036 0.62212563

t-Bu-Amphos

46

15 -0.42965454 -0.44067252 -0.49386775
6 1.44301724 -0.30112949 -0.35663837
6 2.03514576 -1.62497878 -0.75648779
6 -0.17977977 1.29095852 -2.57346559
6 -0.85654962 1.25265205 -1.20515180
6 -2.36441302 1.26145649 -1.43763006
6 -0.43607178 2.45990849 -0.38576090
6 -0.88654476 -0.57312953 1.33365166
6 -0.28737101 0.43970421 2.29533529
6 -2.40692806 -0.53431344 1.43522465
6 -0.40651268 -1.96807635 1.72761619
1 -0.75183380 -2.20232677 2.75478292
1 0.70134622 -2.03453922 1.74634624
1 1.59736335 -1.98389030 -1.70916164
1 1.82068086 -2.39518428 0.01073104
1 0.81966615 0.40146598 2.33581066
1 -0.64170671 0.21328139 3.32228470
1 -0.58499199 1.47700572 2.06600714
1 -1.06093943 2.58460712 0.51698029
1 -0.55613250 3.38350248 -0.98860490
1 0.62400043 2.41165066 -0.06572108
1 0.90987027 1.48290467 -2.51277232
1 -0.34719691 0.35576111 -3.14253092
1 -0.60822445 2.12216973 -3.16816425
1 -2.68088865 0.41728058 -2.07928205
1 -2.65388775 2.20226860 -1.94844842
1 -2.94002604 1.20761597 -0.49707270
1 -2.89681768 -1.15496647 0.65983325
1 -2.72308111 -0.92034906 2.42500901
1 -2.79744291 0.49660546 1.35290229
1 -0.79923493 -2.75103045 1.05080962
1 1.71994102 -0.01124652 0.67487234
1 1.75468683 0.51041770 -1.04205549
7 3.54122496 -1.63819945 -0.95682585
6 4.23243666 -1.04930031 0.21495129
6 3.89012885 -0.87365943 -2.17919612
6 3.97771287 -3.04729509 -1.12598407
1 3.38833642 -1.33351231 -3.04763651
1 4.98340702 -0.89192969 -2.32634664
1 3.55168200 0.17023599 -2.07198620
1 3.43076634 -3.49815965 -1.97201455
1 3.75583172 -3.60998583 -0.20296539
1 5.06330490 -3.07663488 -1.32568014
1 5.32352209 -1.15003729 0.08280879
1 3.91862607 -1.58109689 1.13033676

1 3.96518183 0.01714838 0.30076560

(*t*-Bu-Amphos)Pd(0)

47

46 -2.25855446 1.18595469 1.31952453
6 0.09897815 -0.70881164 -0.09765673
6 -0.26269719 -1.43901789 1.16618764
6 -2.30609465 0.64465040 -2.04230189
6 -0.97597659 1.35156560 -1.80865073
6 -1.17116070 2.84936762 -1.99544239
6 0.05941288 0.81956750 -2.79021955
6 0.91037220 2.02970552 0.58390939
6 2.02317929 2.18135405 -0.44022578
6 0.39751881 3.39819360 1.01240432
6 1.44116402 1.30565143 1.81436729
1 2.19981170 1.94203651 2.31201863
1 1.94296896 0.35128358 1.55287111
1 -1.34704781 -1.27325952 1.37225711
1 0.29218197 -1.04111660 2.03734207
1 2.40964866 1.21081579 -0.81145388
1 2.87461138 2.71042204 0.03455605
1 1.71439314 2.79115224 -1.31016195
1 1.06136441 1.26060963 -2.64924502
1 -0.26710948 1.06760740 -3.82032537
1 0.15492834 -0.28309226 -2.75293899
1 -2.24630713 -0.44490030 -1.84413886
1 -3.09383893 1.05545318 -1.38034952
1 -2.61496758 0.77220839 -3.09940004
1 -1.86686027 3.26306129 -1.23858738
1 -1.60878861 3.04179883 -2.99609423
1 -0.21710517 3.40768099 -1.94245565
1 -0.38738966 3.29552579 1.78828609
1 1.23642612 3.98978209 1.43141210
1 -0.03372723 3.96845698 0.17060807
1 0.62879711 1.11661398 2.54630303
1 1.18770063 -0.68824303 -0.30974799
1 -0.42052498 -1.14905679 -0.97090316
7 -0.00305056 -2.93074417 1.14965761
6 1.45274293 -3.19861436 1.05016232
6 -0.71851021 -3.56934905 0.01856403
6 -0.51984197 -3.48890543 2.42481804
1 -1.78469539 -3.28519797 0.06292483
1 -0.61703956 -4.66529417 0.09431196
1 -0.28826684 -3.22801471 -0.93699825
1 -1.60844827 -3.31728101 2.47692037
1 -0.02893688 -2.97688389 3.26959848

1 -0.30745661 -4.57095289 2.46902704
1 1.63056374 -4.28801250 1.04712296
1 1.96241820 -2.74192858 1.91663933
1 1.84423327 -2.75709271 0.11840969
15 -0.56902826 1.03523111 -0.00291364

(*t*-Bu-Amphos)₂Pd(0)

93

46 -0.08475558 -0.07625561 -0.06164121
6 2.32870746 -1.97925317 -1.64629877
6 1.99754107 -2.75404859 -0.39822820
6 -0.10175275 -0.60043019 -3.51885557
6 1.22779834 0.11255115 -3.29387546
6 1.01036394 1.61127365 -3.45031929
6 2.24684143 -0.37901148 -4.31131506
6 3.16350460 0.75271982 -0.93657398
6 4.29082584 0.86099964 -1.94918835
6 2.66097021 2.13849425 -0.54289949
6 3.67185473 0.06012058 0.32325816
1 4.44080687 0.69796228 0.80425698
1 4.16351652 -0.90835148 0.09941673
1 0.91185182 -2.64125609 -0.17583516
1 2.54848218 -2.35933709 0.47747394
1 4.64080524 -0.12574811 -2.31093836
1 5.16348267 1.35485530 -1.47617364
1 4.01491070 1.47275007 -2.82754517
1 3.23831487 0.09031003 -4.19398785
1 1.88578427 -0.13067766 -5.32945633
1 2.37735343 -1.47775447 -4.28973103
1 -0.02913087 -1.69726145 -3.37163520
1 -0.87834972 -0.22112098 -2.82428956
1 -0.43856651 -0.43610513 -4.56232405
1 0.34641075 2.00304198 -2.65257931
1 0.52381146 1.81202567 -4.42590809
1 1.96075118 2.17737651 -3.43790746
1 1.83361328 2.04487872 0.19363762
1 3.48807979 2.71770620 -0.08432667
1 2.29064512 2.70919752 -1.41410768
1 2.85291839 -0.09741616 1.05643094
1 3.41236401 -1.94621968 -1.87915051
1 1.80313134 -2.40261412 -2.52453756
7 2.29997563 -4.23810339 -0.44551185
6 3.76099157 -4.47461128 -0.57354754
6 1.59255755 -4.88568163 -1.57889712
6 1.81906545 -4.83273554 0.82943970
1 0.52009815 -4.62597847 -1.53674459

1 1.71405149 -5.98045349 -1.50560522
1 2.02033448 -4.53772497 -2.53353882
1 0.72524321 -4.70201159 0.89998460
1 2.30636907 -4.31961775 1.67595041
1 2.06869125 -5.90777683 0.85666776
1 3.95548964 -5.56126690 -0.59423196
1 4.28238344 -4.02342558 0.28881669
1 4.12632275 -4.02003431 -1.50963902
15 1.66652226 -0.23697492 -1.49820113
6 -2.50094223 1.91694057 1.29085720
6 -1.34409499 2.85513997 1.06558836
6 -3.34864926 -0.60769576 -0.85644835
6 -3.41480160 -0.75255328 0.66100293
6 -3.28735256 -2.23084474 1.00370061
6 -4.74153137 -0.20511644 1.16774917
6 -1.60041356 -0.19648439 3.12571168
6 -2.85989499 -0.17851354 3.97679496
6 -0.89823556 -1.54518604 3.23907423
6 -0.63247681 0.87304574 3.62106347
1 -0.28886166 0.60715783 4.64089537
1 -1.11090457 1.86958611 3.70407796
1 -0.77591556 2.53029704 0.16266537
1 -0.63578415 2.82850218 1.91475821
1 -3.42670298 0.76928681 3.88682747
1 -2.58448696 -0.28334329 5.04580545
1 -3.54415131 -1.01306498 3.73830390
1 -4.82974339 -0.22394700 2.26778841
1 -5.56545830 -0.82678491 0.76236606
1 -4.93583012 0.82774621 0.82077610
1 -3.37217665 0.44954994 -1.18916643
1 -2.41581798 -1.05879402 -1.25394177
1 -4.22072506 -1.11732364 -1.31479859
1 -2.28192592 -2.61836934 0.74318928
1 -4.03196335 -2.80423093 0.41540757
1 -3.48606539 -2.43981957 2.07160115
1 0.02655791 -1.55385911 2.62447119
1 -0.61891919 -1.72386515 4.29749966
1 -1.54137790 -2.38353848 2.91777253
1 0.26264793 0.94366664 2.96800137
1 -3.06280112 2.11931968 2.22584009
1 -3.21425414 1.96208680 0.44441250
7 -1.70998907 4.31423378 0.88788909
6 -2.36228728 4.84402752 2.11322951
6 -2.61506963 4.49442530 -0.27451780
6 -0.45275843 5.06730413 0.64120609
1 -2.14983153 4.04591513 -1.16994548

1 -2.78129649 5.57291222 -0.43960026
1 -3.58320570 4.00599766 -0.07532276
1 0.02396304 4.68164301 -0.27670750
1 0.23102580 4.92794561 1.49638343
1 -0.68061924 6.14117956 0.52201319
1 -2.58092093 5.91811943 1.97947407
1 -1.68411744 4.71037436 2.97473717
1 -3.30405378 4.29972124 2.29260993
15 -1.88876152 0.15022083 1.29912663

t-Bu₃P

40

15 0.05794504 0.01447655 -0.83584541
6 1.77265036 -0.04777405 0.00476696
6 1.84341395 0.29530784 1.48601794
6 2.36795616 -1.43737745 -0.20351972
6 2.67652130 0.90145588 -0.78307116
6 -0.83555192 1.56175745 -0.15108377
6 -1.34455657 1.50192094 1.28259075
6 0.09699312 2.76248837 -0.28596002
6 -2.00324106 1.84523952 -1.09657669
6 -0.91303098 -1.50753021 -0.21195194
6 -0.77174383 -1.87291300 1.25929224
6 -2.39328313 -1.30883420 -0.52394938
6 -0.47515145 -2.68917990 -1.07967997
1 2.63019991 0.68267399 -1.86713314
1 3.72586536 0.76265091 -0.44800878
1 2.41800284 1.96331656 -0.63978839
1 2.33137965 -1.74498630 -1.26689184
1 1.88181353 -2.21590424 0.41149175
1 3.43495035 -1.40548027 0.09912738
1 1.57807112 1.34939992 1.68722665
1 2.88622642 0.15423493 1.84352589
1 1.18900836 -0.34841621 2.10118747
1 -1.66168141 1.88584578 -2.14858961
1 -2.44445944 2.83134842 -0.84008664
1 -2.80715036 1.09433675 -1.02756000
1 0.54945403 2.82418013 -1.29466963
1 0.90414631 2.77059627 0.46853188
1 -0.49797970 3.68618965 -0.13064995
1 -2.14869213 0.75409442 1.41092229
1 -1.77591908 2.48854303 1.55884814
1 -0.54140556 1.27388775 2.00701356
1 -0.62671494 -2.46776056 -2.15350962
1 -1.09333265 -3.57369256 -0.81917453
1 0.58142817 -2.96873522 -0.93891555

1 -2.55428243 -0.98922908 -1.57176960
1 -2.88477921 -0.58456308 0.15087710
1 -2.91026640 -2.28204489 -0.39060208
1 0.25415242 -2.19294000 1.51910508
1 -1.44431579 -2.72691226 1.48942101
1 -1.05262899 -1.03967631 1.92904007

(*t*-Bu₃P)Pd(0)

41

15 0.05102446 0.01202439 -0.72804882
6 1.77902451 -0.04797561 0.07695116
6 1.83302441 0.29602439 1.55895118
6 2.36802450 -1.43897562 -0.13004883
6 2.68202439 0.90402437 -0.70604881
6 -0.84597555 1.56902439 -0.08104884
6 -1.34897551 1.49502439 1.35595111
6 0.09102446 2.76402433 -0.21404884
6 -2.01597557 1.84902437 -1.02204879
6 -0.92397556 -1.51797562 -0.14104884
6 -0.77497551 -1.87097566 1.33295111
6 -2.40197548 -1.30997555 -0.45204883
6 -0.48297554 -2.69997566 -1.00404878
1 2.62702456 0.68202437 -1.79204889
1 3.72902456 0.76602436 -0.36504884
1 2.41802445 1.96502442 -0.57004883
1 2.32002440 -1.73997562 -1.19604882
1 1.87902441 -2.21597569 0.48595117
1 3.43602457 -1.41097562 0.16795116
1 1.56602445 1.35002441 1.75895111
1 2.87502447 0.15302439 1.91695122
1 1.17902449 -0.35197561 2.17095117
1 -1.66497550 1.88402433 -2.07404872
1 -2.45697555 2.83302433 -0.75904884
1 -2.81497559 1.09302444 -0.96104886
1 0.53802445 2.81602437 -1.22604879
1 0.90102449 2.76502449 0.53795115
1 -0.49997553 3.68902428 -0.05604884
1 -2.15197548 0.74602438 1.48395113
1 -1.77797553 2.48102434 1.63195113
1 -0.54297552 1.26902444 2.07695107
1 -0.62997553 -2.46697562 -2.07904883
1 -1.10297558 -3.58297556 -0.74204882
1 0.57502445 -2.97397559 -0.86704882
1 -2.54997549 -0.98697560 -1.50204881
1 -2.88997564 -0.58397560 0.22295117
1 -2.92297563 -2.28097551 -0.31904884

1 0.25102445 -2.18997567 1.59095113
1 -1.44697556 -2.72497552 1.56295113
1 -1.05797550 -1.03497558 1.99995116
46 0.20702447 0.04902439 -2.94604893

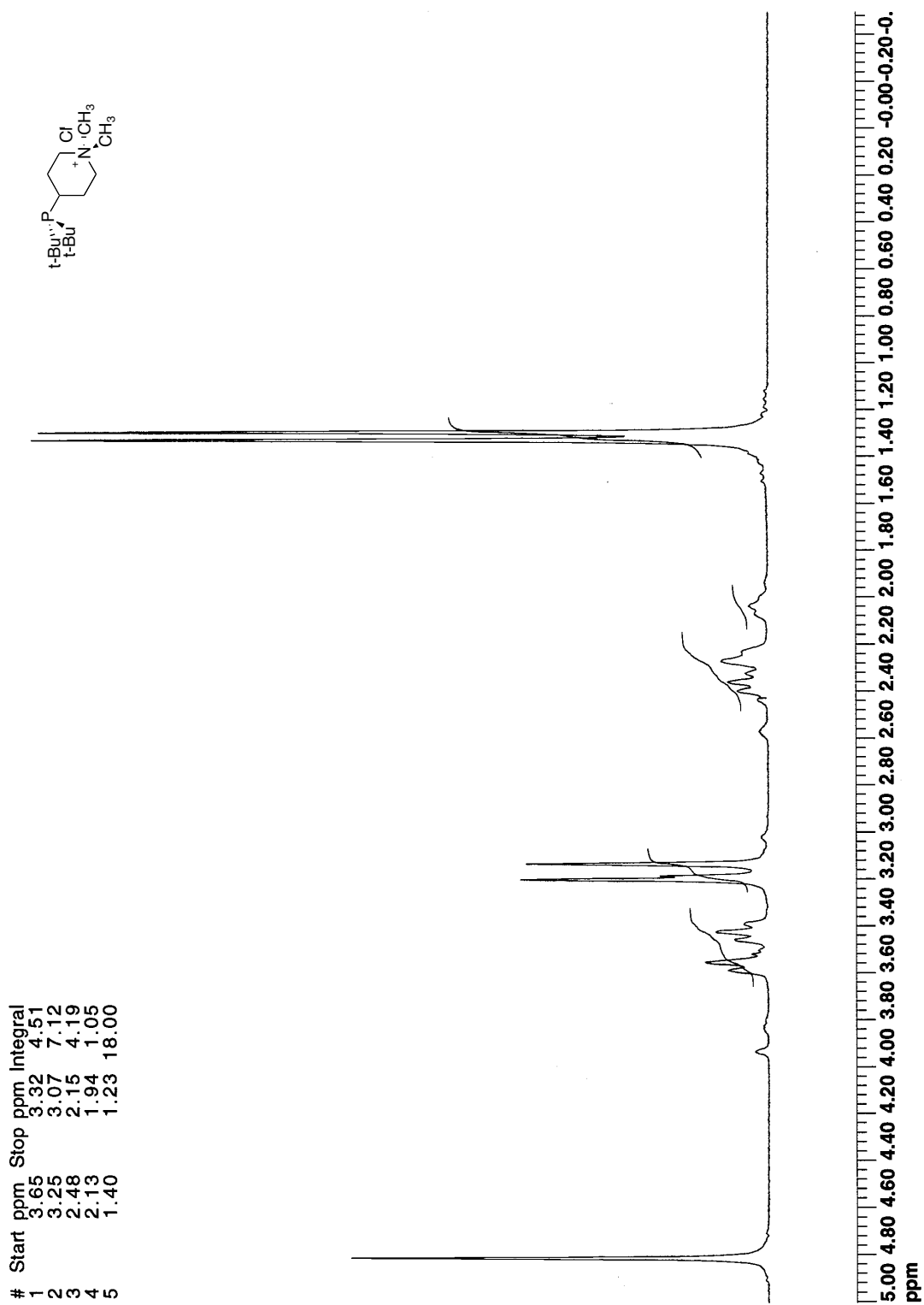
(*t*-Bu₃P)Pd(0)

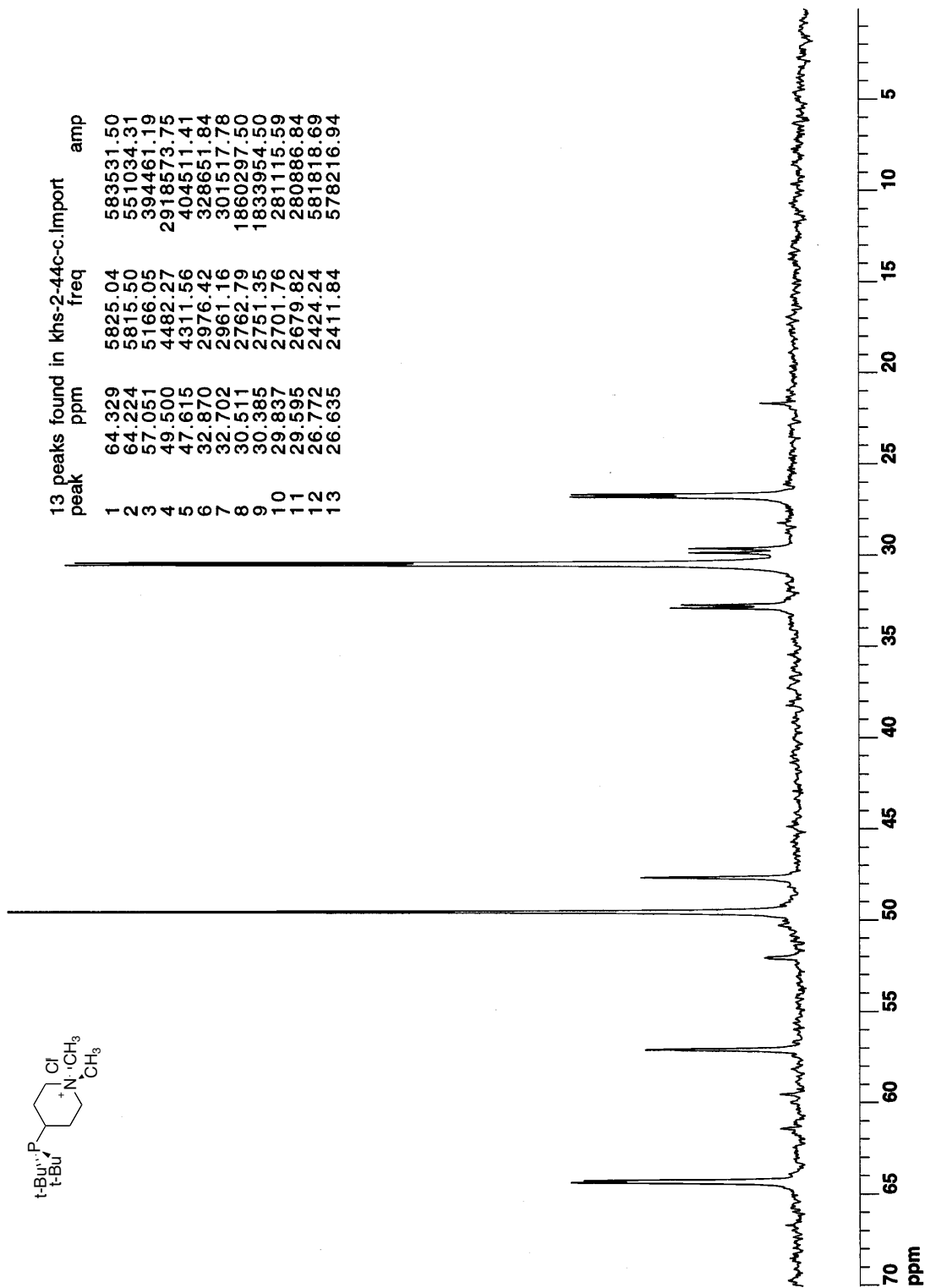
81

46 0.00502472 0.00401244 -0.00402465
15 0.00202472 2.27901249 -0.00402465
6 -0.46197529 2.96601252 1.71397534
6 -0.15697528 4.43801264 1.95497539
6 -1.95197530 2.72901253 1.93797531
6 0.25502472 2.11101250 2.75797525
6 1.71702473 2.97901253 -0.46002466
6 1.76002472 4.45101266 -0.85102466
6 2.65902464 2.75801234 0.71797534
6 2.27102463 2.12701254 -1.60202465
6 -1.25397522 2.97501235 -1.26002464
6 -1.61897523 4.44501261 -1.10102460
6 -0.70297528 2.75601248 -2.66502461
6 -2.51697524 2.11901240 -1.17302463
1 0.04902472 1.03501241 2.57597532
1 -0.12397527 2.38701253 3.76397529
1 1.34902470 2.24501233 2.75597539
1 -2.22997529 1.68201248 1.70497539
1 -2.59097536 3.41301255 1.34897533
1 -2.17597539 2.91301255 3.00897541
1 0.92702471 4.64901261 1.96097531
1 -0.54897530 4.72701268 2.95297542
1 -0.63297529 5.09801249 1.20697537
1 2.22902482 1.05001239 -1.33202467
1 3.32902472 2.41201238 -1.77702460
1 1.72202473 2.25301246 -2.54802475
1 2.61302464 1.71201245 1.07897534
1 2.45902484 3.44201235 1.56397536
1 3.69602482 2.95601253 0.37597534
1 1.22002475 4.65401225 -1.79202471
1 2.81802480 4.74701266 -1.01402471
1 1.34802477 5.11001258 -0.06602465
1 -2.25997527 1.04401247 -1.27402470
1 -3.19697530 2.40601234 -2.00202474
1 -3.06497533 2.24201254 -0.22502465
1 -0.36597527 1.70901243 -2.80302462
1 0.12802473 3.44001250 -2.91602454
1 -1.51897533 2.95201234 -3.39202461
1 -2.16497524 4.64401250 -0.16102465

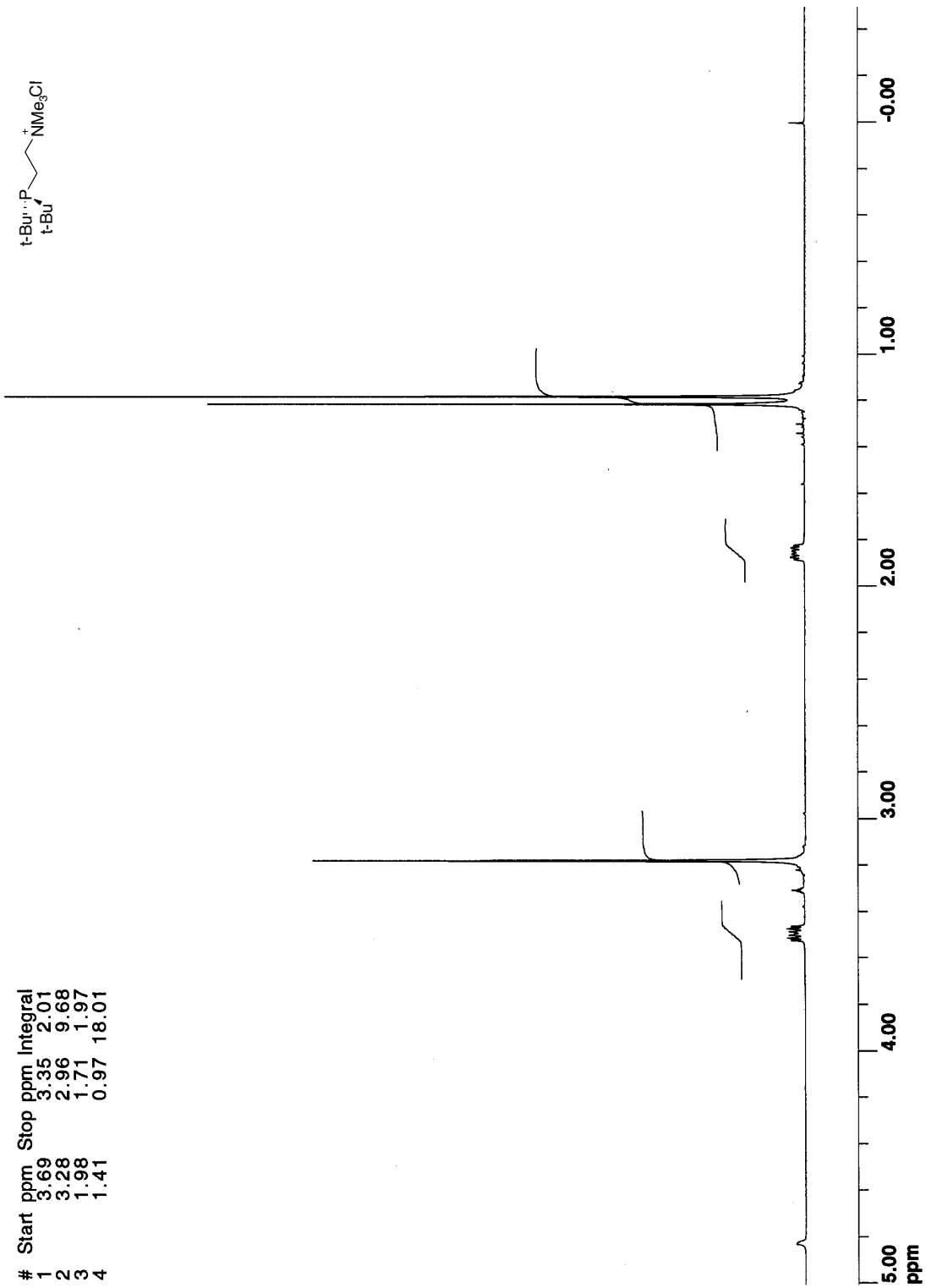
1 -2.29097516 4.74001221 -1.93502459
1 -0.73597528 5.10801224 -1.13602469
15 0.00202472 -2.27498765 0.00197535
6 -0.03697528 -2.97198744 1.77797535
6 -0.40297527 -4.44398733 1.91597536
6 1.33002477 -2.74698754 2.41497531
6 -1.01597531 -2.11998744 2.58497539
6 -1.51897533 -2.97098751 -0.91902468
6 -1.45397527 -4.44198747 -1.30902467
6 -2.75197537 -2.75098749 -0.04902465
6 -1.73197527 -2.11498757 -2.16502461
6 1.55702477 -2.97298761 -0.85202465
6 1.86202471 -4.44298740 -0.60002468
6 1.42102473 -2.75398751 -2.35502467
6 2.74502461 -2.11698766 -0.41302464
1 -0.76297529 -1.04398759 2.48097530
1 -0.93697525 -2.40598746 3.65497532
1 -2.06497533 -2.24698754 2.27397528
1 1.66802471 -1.69998761 2.28297534
1 2.10602467 -3.42998762 2.02297535
1 1.24202471 -2.94098754 3.50397530
1 -1.44697530 -4.64998765 1.61797538
1 -0.30597527 -4.73898740 2.98197546
1 0.26002472 -5.10298772 1.32697537
1 -1.77397532 -1.04098757 -1.88602469
1 -2.69497521 -2.40298767 -2.63502464
1 -0.93497528 -2.23198767 -2.91802463
1 -2.80497534 -1.70698758 0.31697535
1 -2.79797537 -3.44098754 0.81397536
1 -3.65197523 -2.94198747 -0.66802463
1 -0.67497529 -4.64698739 -2.06602464
1 -2.42597539 -4.73798747 -1.75702462
1 -1.27397532 -5.10198779 -0.44102467
1 2.52602475 -1.04198761 -0.58602468
1 3.63202469 -2.40498753 -1.01502464
1 3.00002472 -2.23698755 0.65197536
1 1.13202469 -1.70898755 -2.58502469
1 0.69502472 -3.44198747 -2.82502470
1 2.40702479 -2.94698758 -2.82602463
1 2.13302462 -4.64498754 0.45197534
1 2.73402469 -4.73898740 -1.22202465
1 1.02102475 -5.10498758 -0.87302468

NMR Spectra

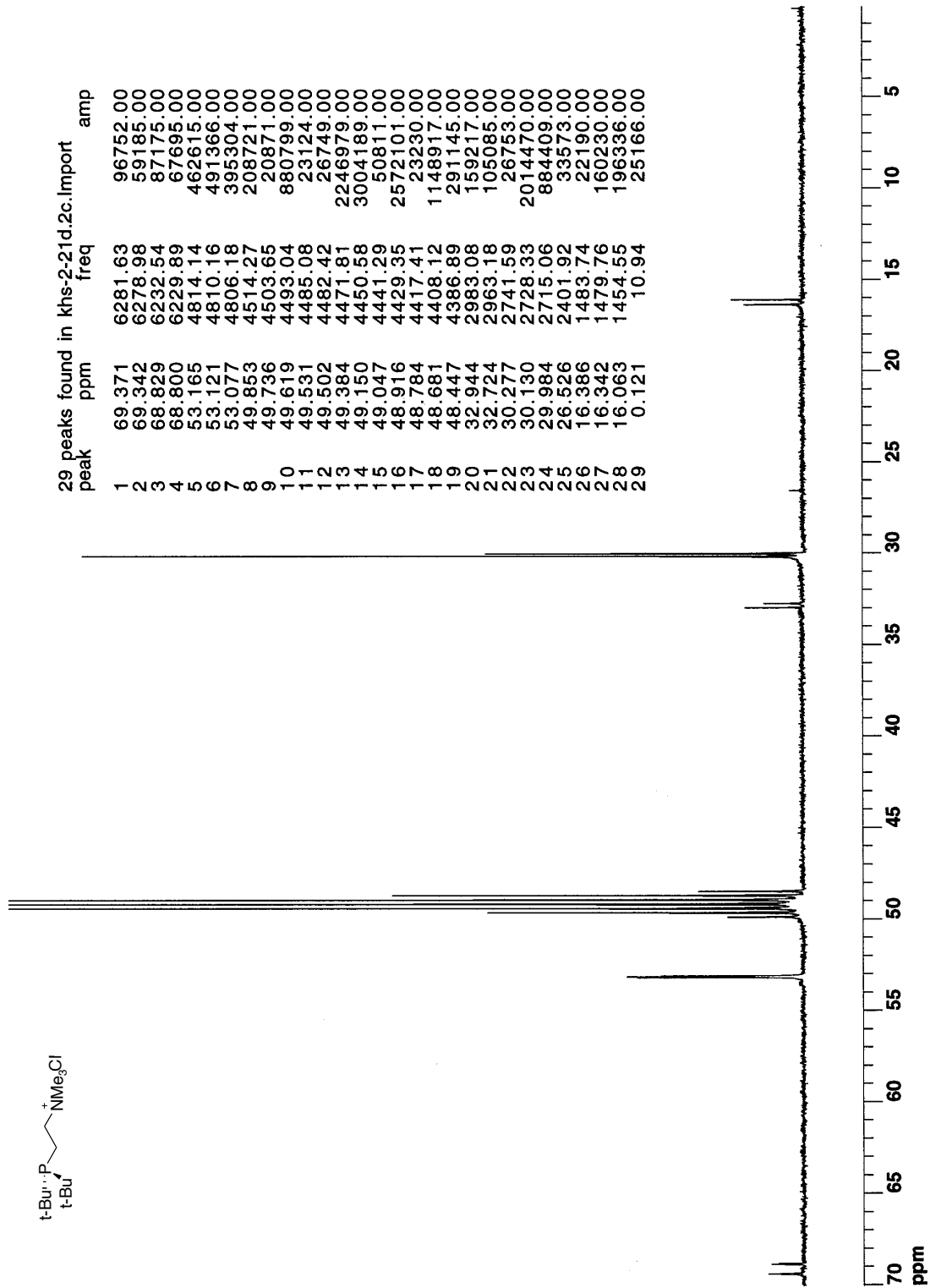




^{13}C NMR spectrum of *t*-Bu-Pip-phos (D_2O , 90.6 MHz). Peak at 49.5 is CH_3OH added as an internal standard.



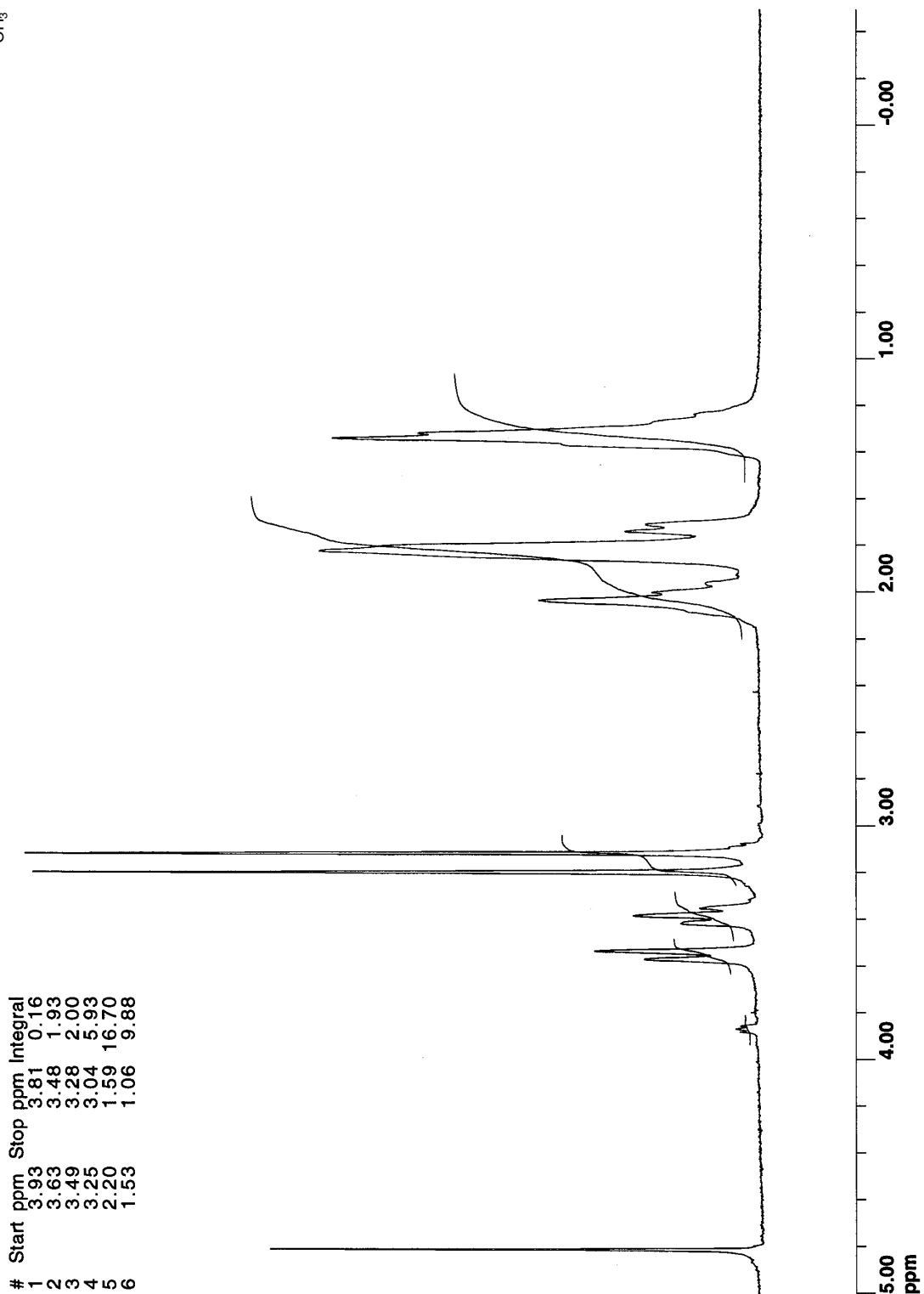
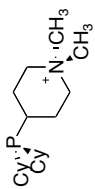
^1H NMR spectrum of *t*-Bu-Amphos (CD_3OD , 360 MHz).



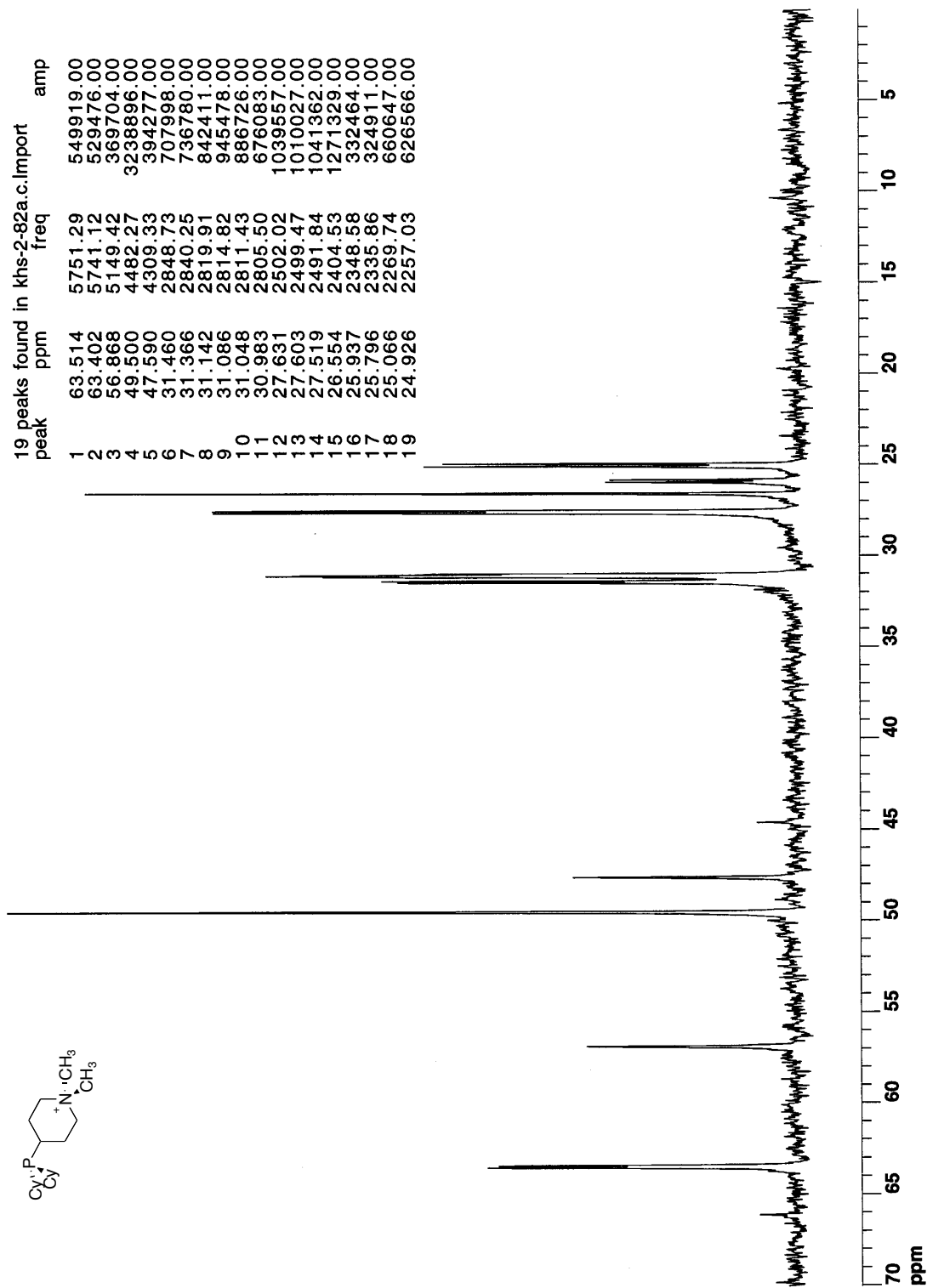
29 peaks found in khs-2-21d.2c.Import

peak	ppm	freq	amp
1	69.371	6281.63	96752.00
2	69.342	6278.98	59185.00
3	68.829	6232.54	87175.00
4	68.800	6229.89	67695.00
5	53.165	4814.14	462615.00
6	53.121	4810.16	491366.00
7	53.077	4806.18	395304.00
8	49.853	4514.27	208721.00
9	49.736	4503.65	20871.00
10	49.619	4493.04	880799.00
11	49.531	4485.08	23124.00
12	49.502	4482.42	26749.00
13	49.384	4471.81	2246979.00
14	49.150	4450.58	3004189.00
15	49.047	4441.29	50811.00
16	48.916	4429.35	2572101.00
17	48.784	4417.41	23230.00
18	48.681	4408.12	1148917.00
19	48.447	4386.89	291145.00
20	32.944	2983.08	159217.00
21	32.724	2963.18	105085.00
22	30.277	2741.59	26753.00
23	30.130	2728.33	2014470.00
24	29.984	2715.06	884409.00
25	26.526	2401.92	33573.00
26	16.386	1483.74	22190.00
27	16.342	1479.76	160230.00
28	16.063	1454.55	196336.00
29	0.121	10.94	25166.00

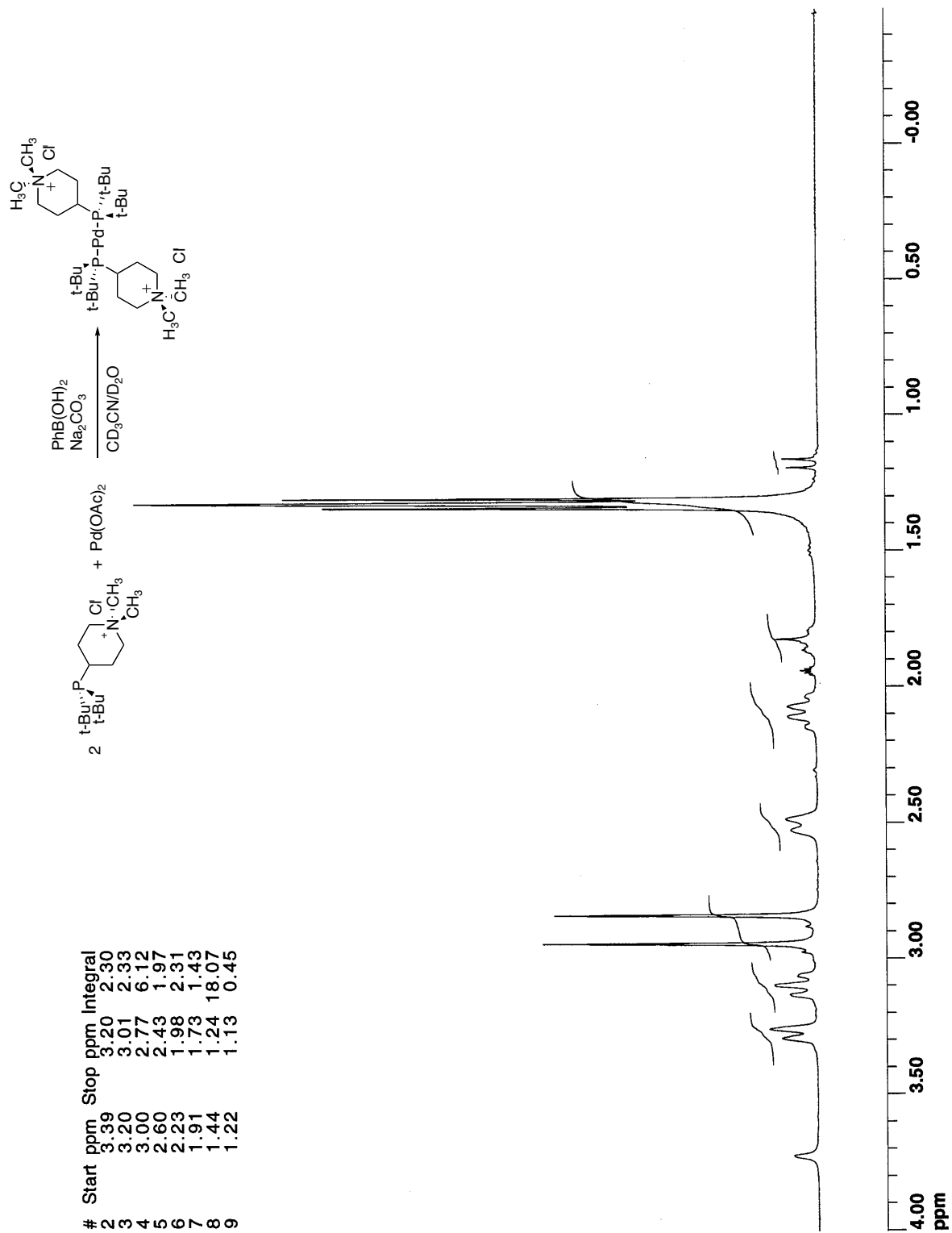
^{13}C NMR spectrum of *t*-Bu-Amphos (CD_3OD , 90.6 MHz).



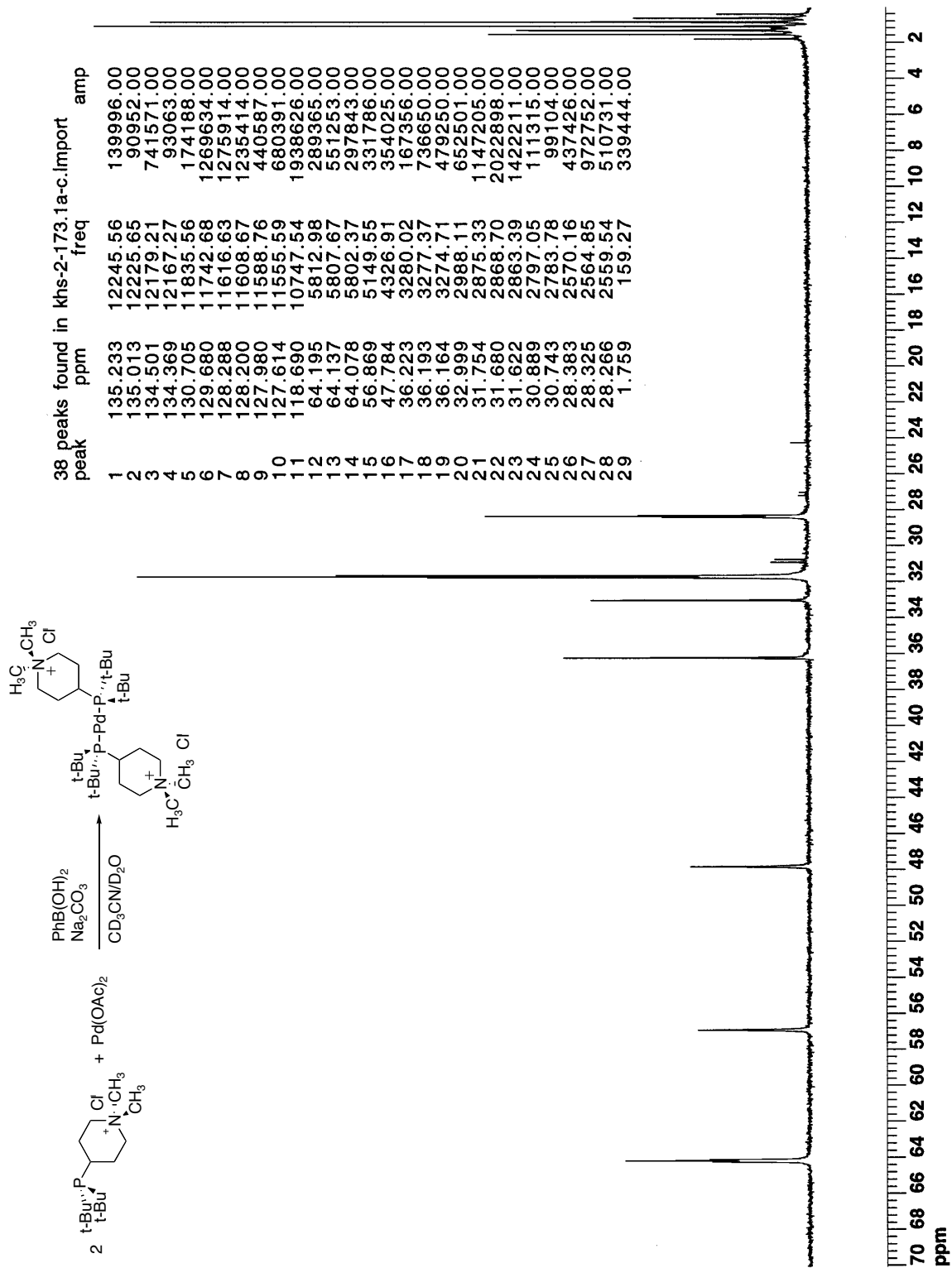
^1H NMR spectrum of Cy-Pip-phos (D_2O , 360 MHz).



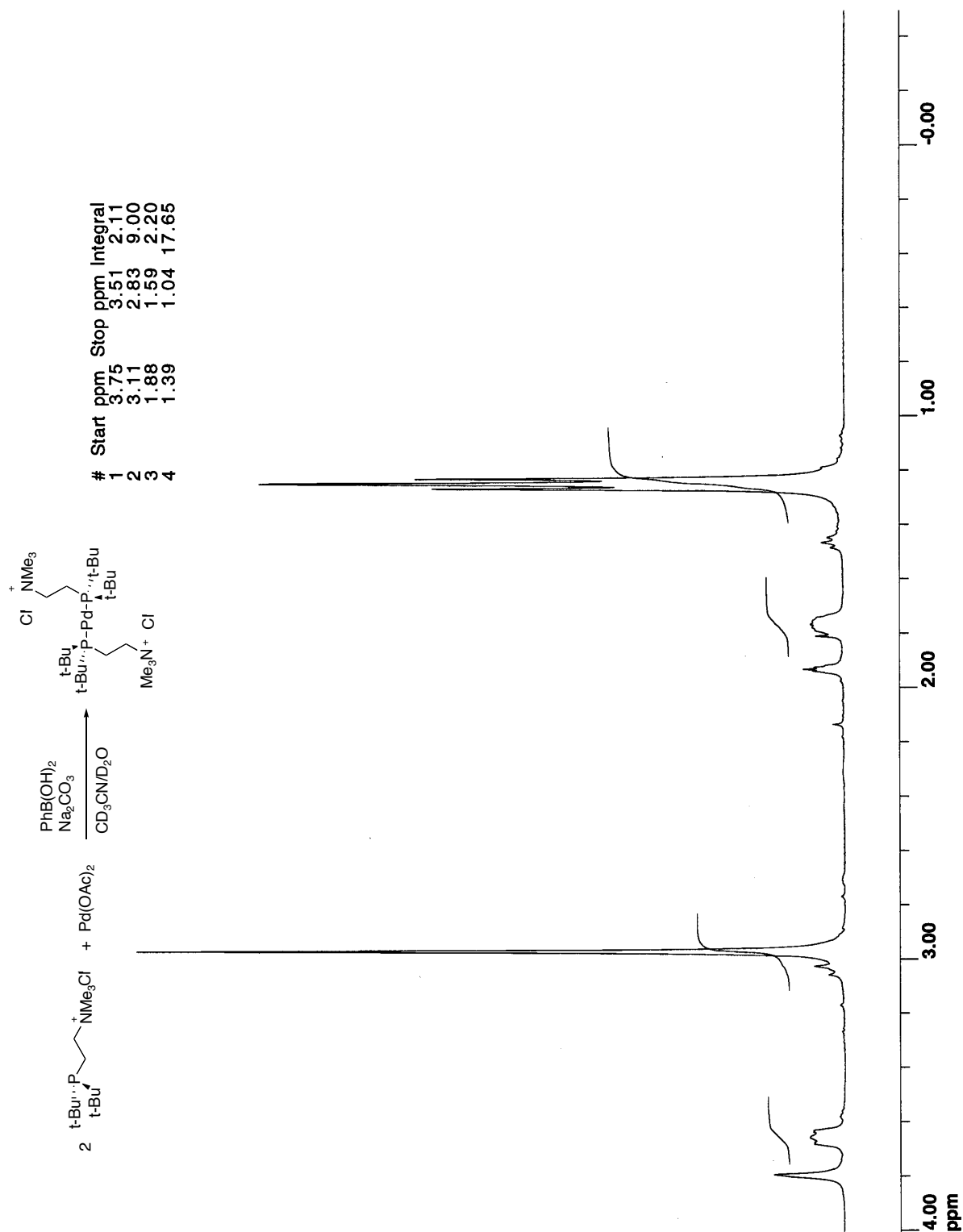
¹³C NMR spectrum of Cy-Pip-phos (D₂O, 90.6 MHz). Peak at 49.5 ppm is CH₃OH added as an internal standard.



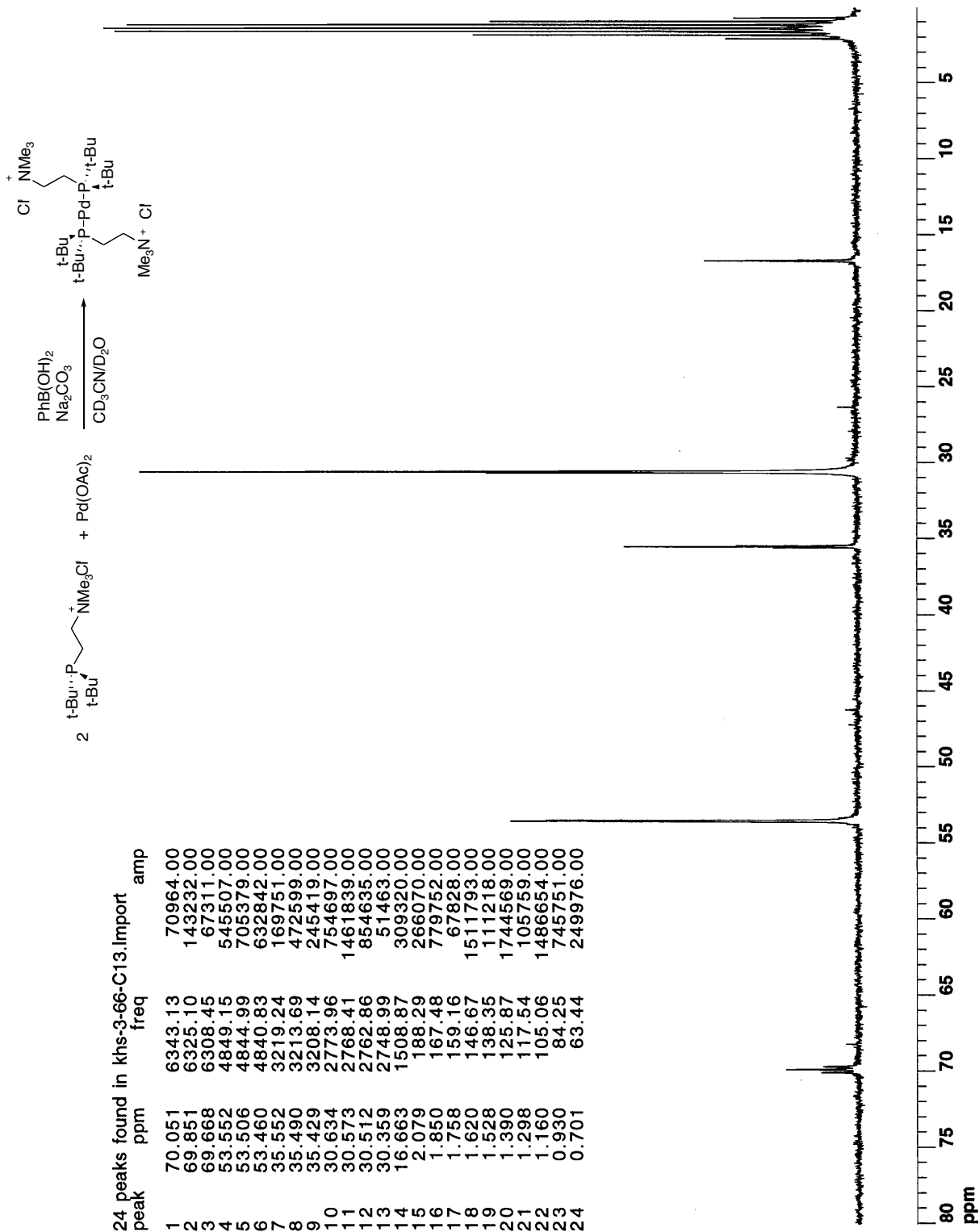
^1H NMR spectrum of $(t\text{-Bu-Pip-phos})_2\text{Pd}(0)$ generated *in situ* from $t\text{-Bu-Pip-phos}$ and $\text{Pd}(\text{OAc})_2$ (L: Pd=2:1) in the presence of $\text{PhB}(\text{OH})_2$ and Na_2CO_3 ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 360 MHz).



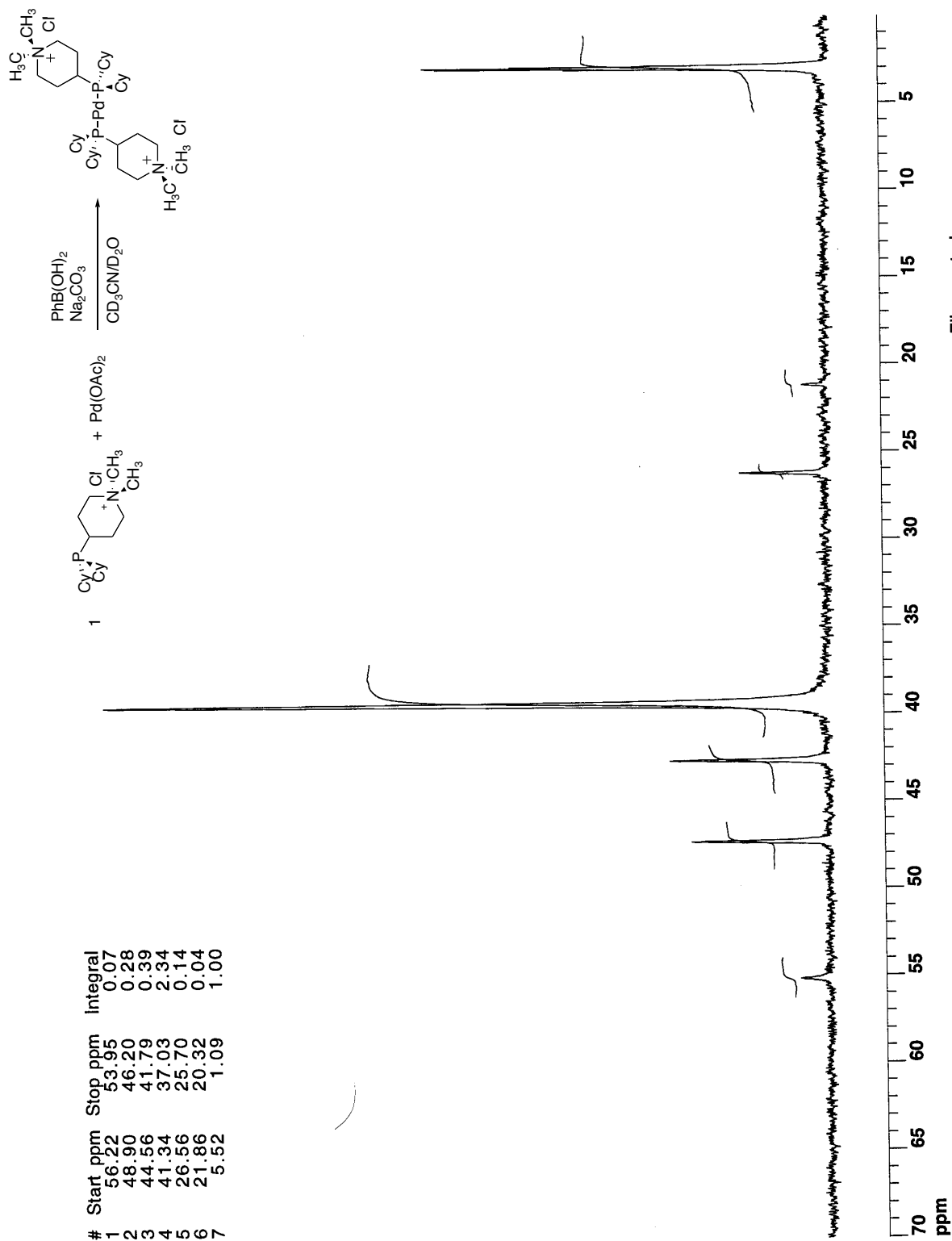
^{13}C NMR spectrum of $(t\text{-Bu-Pip-phos})_2\text{Pd(0)}$ generated *in situ* from $t\text{-Bu-Pip-phos}$ and Pd(OAc)_2 (L: Pd=2:1) in the presence of PhB(OH)_2 and Na_2CO_3 ($\text{CD}_3\text{CN/D}_2\text{O}$, 360 MHz).



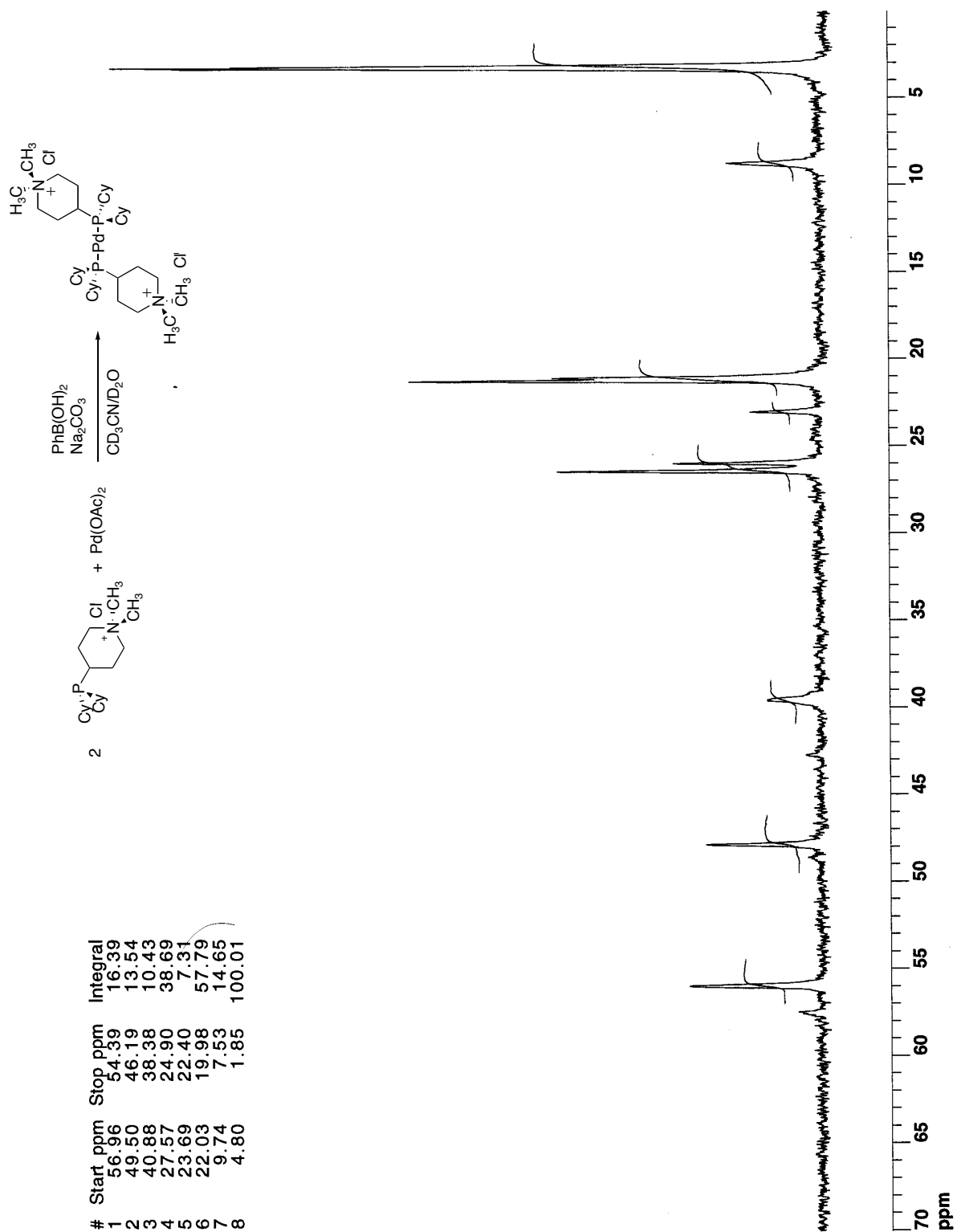
^1H NMR spectrum of $(t\text{-Bu-Amphos})_2\text{Pd}(0)$ generated *in situ* from $t\text{-Bu-Amphos}$ and $\text{Pd}(\text{OAc})_2$ (L:Pd=2:1) in the presence of $\text{PhB}(\text{OH})_2$ and Na_2CO_3 ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 360 MHz).



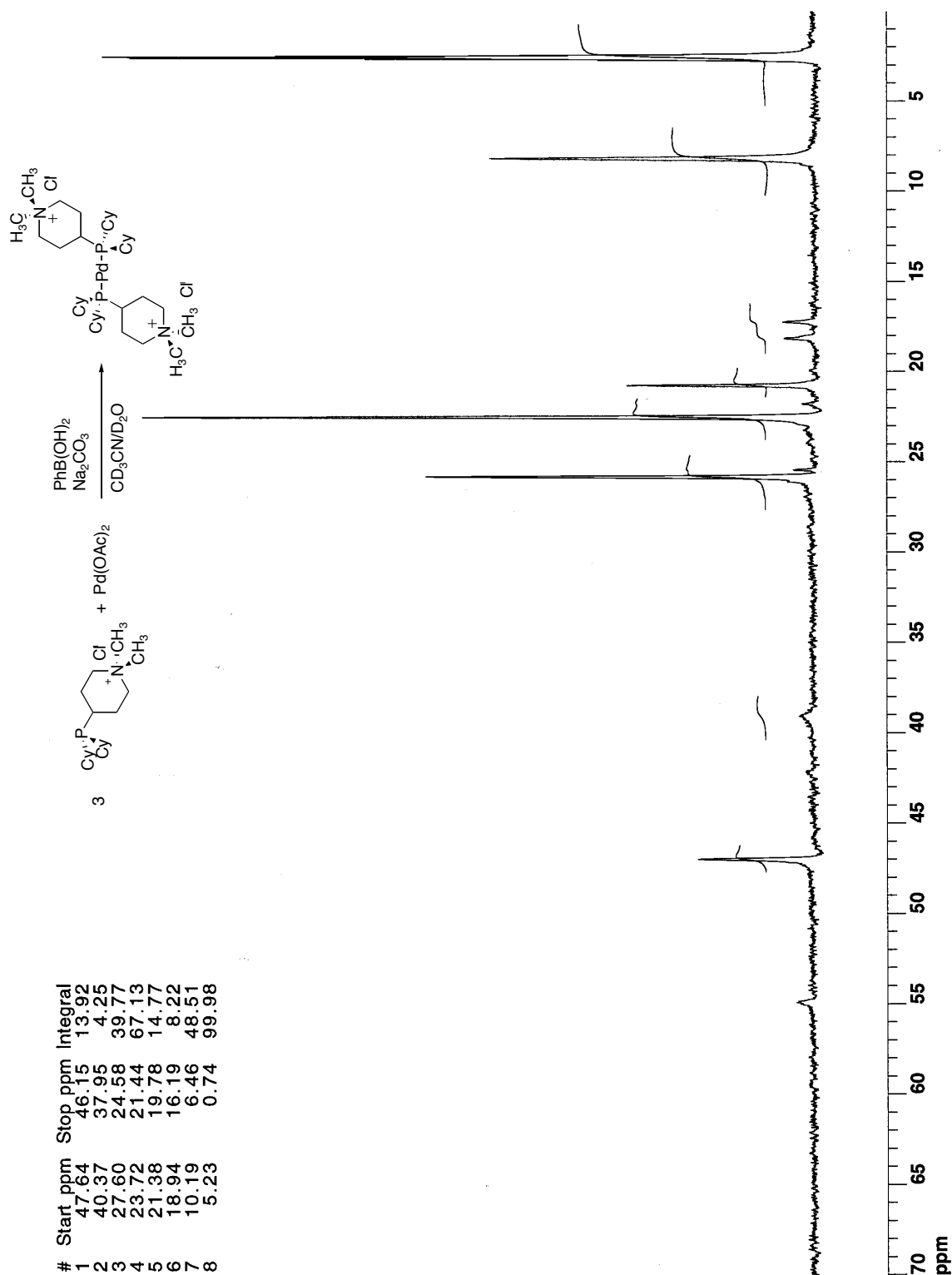
^{13}C NMR spectrum of $(t\text{-Bu-Amphos})_2\text{Pd}(0)$ generated *in situ* from $t\text{-Bu-Amphos}$ and Pd(OAc)_2 (L: Pd=2:1) in the presence of PhB(OH)_2 and Na_2CO_3 ($\text{CD}_3\text{CN/D}_2\text{O}$, 360 MHz).



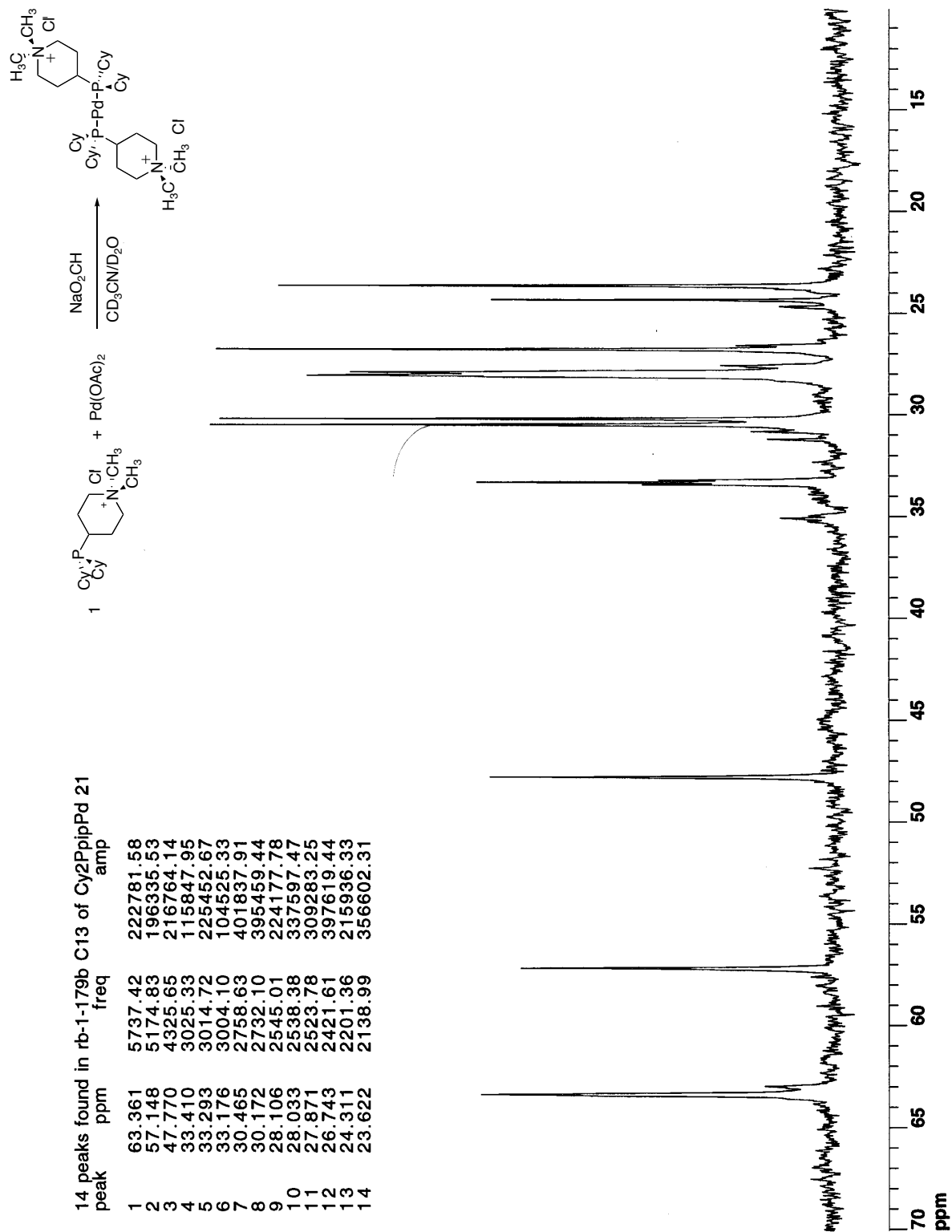
^{13}P NMR spectrum of a 1:1 ratio of Cy-Pip-phos: Pd(OAc)_2 in the presence of PhB(OH)_2 and Na_2CO_3 ($\text{CD}_3\text{CN/D}_2\text{O}$, 202.5 MHz). Peak at 3 ppm is trimethylphosphate used as an internal standard.



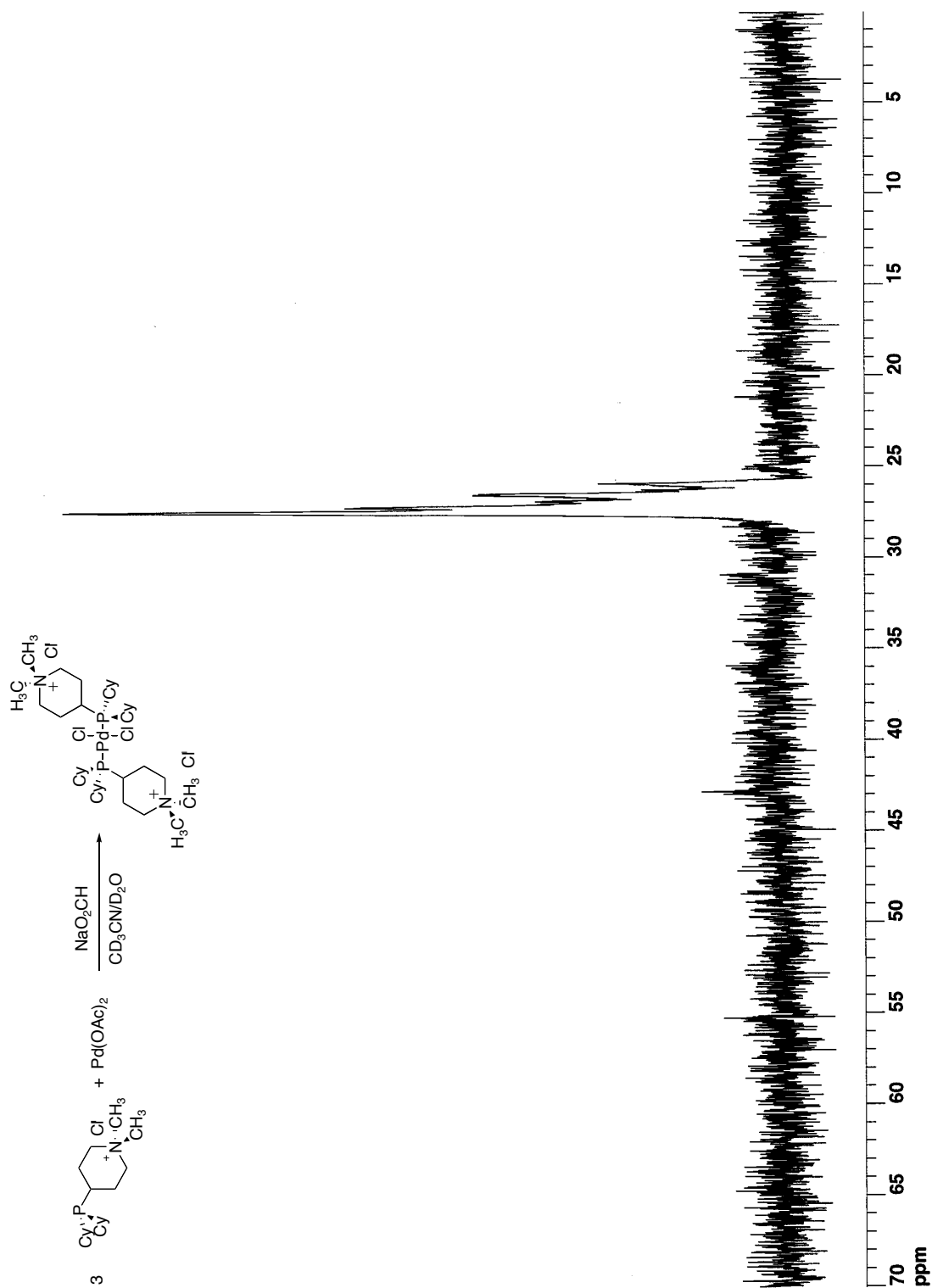
^{13}P NMR spectrum of a 2:1 ratio of Cy-Pip-phos: Pd(OAc)_2 in the presence of PhB(OH)_2 and Na_2CO_3 ($\text{CD}_3\text{CN/D}_2\text{O}$, 202.5 MHz). Peak at 3 ppm is trimethylphosphate used as an internal standard.



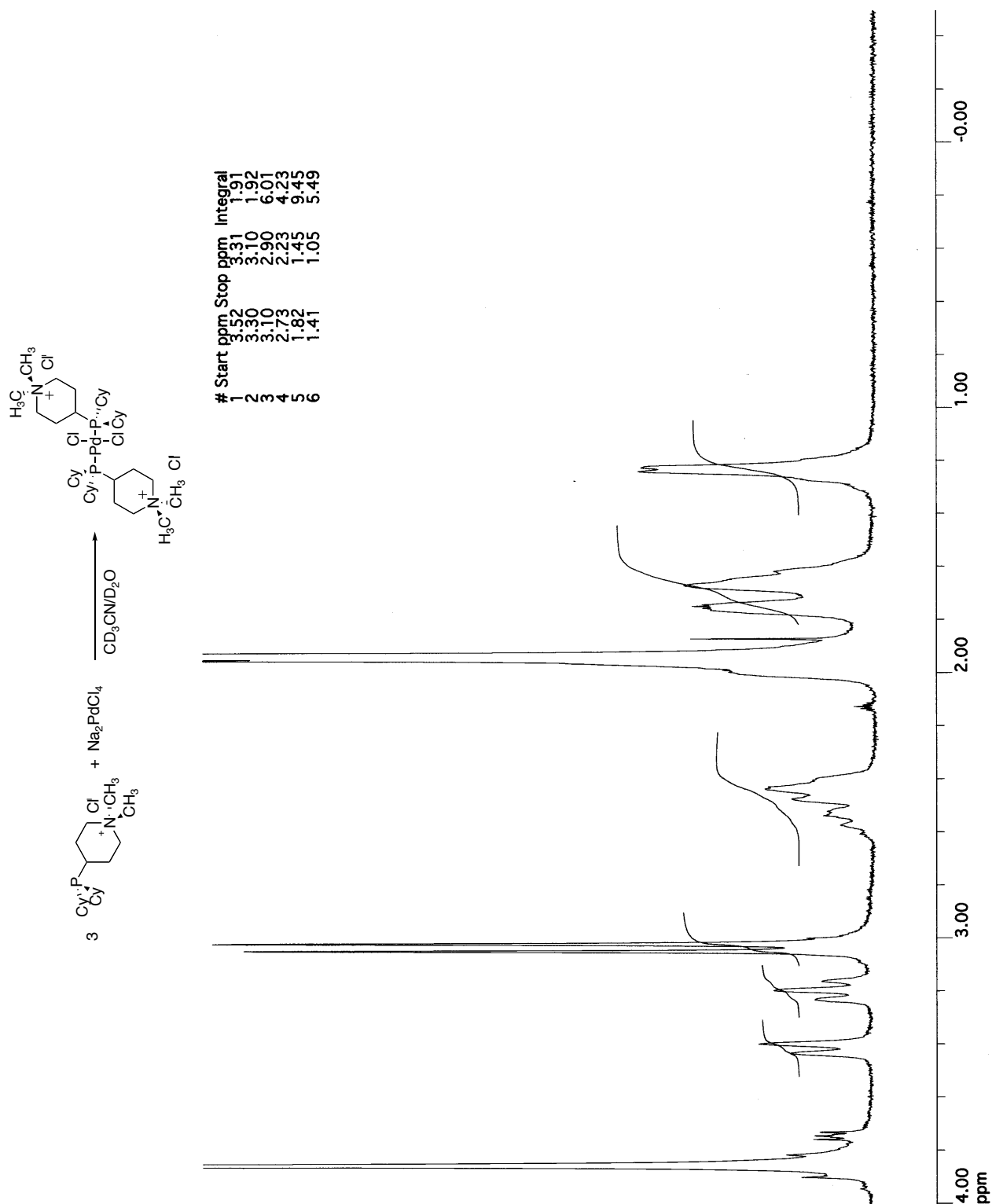
^{13}P NMR spectrum of a 3:1 ratio of Cy-Pip-phos: $\text{Pd}(\text{OAc})_2$ in the presence of $\text{PhB}(\text{OH})_2$ and Na_2CO_3 ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, 202.5 MHz). Peak at 3 ppm is trimethylphosphate used as an internal standard.



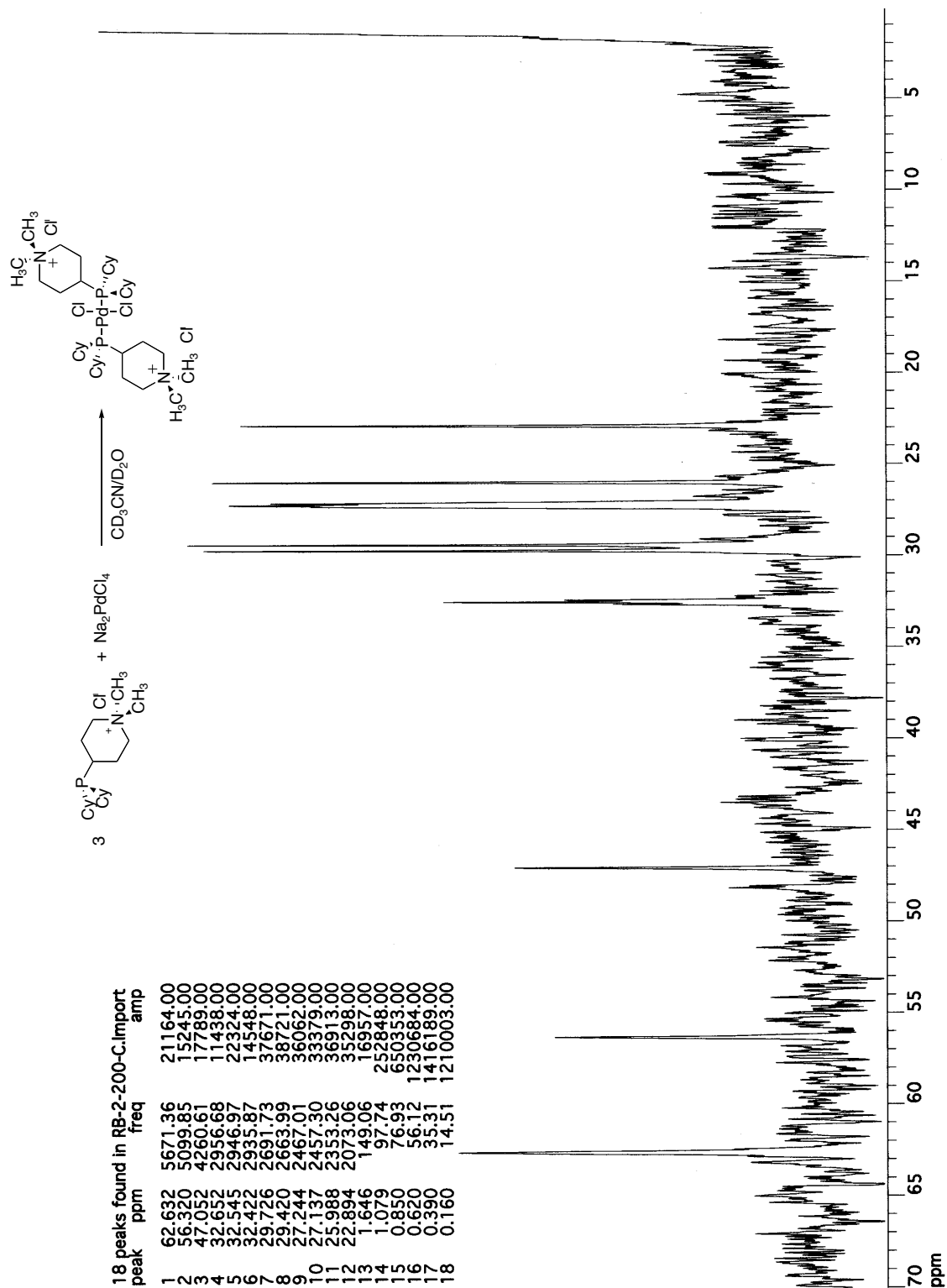
^{13}C NMR spectrum of $(\text{Cy-Pip-phos})_2\text{Pd}(0)$ generated from Cy-Pip-phos and $\text{Pd}(\text{OAc})_2$ (1:1) in the presence of sodium formate ($\text{CD}_3\text{CN/D}_2\text{O}$, 90.6 MHz).



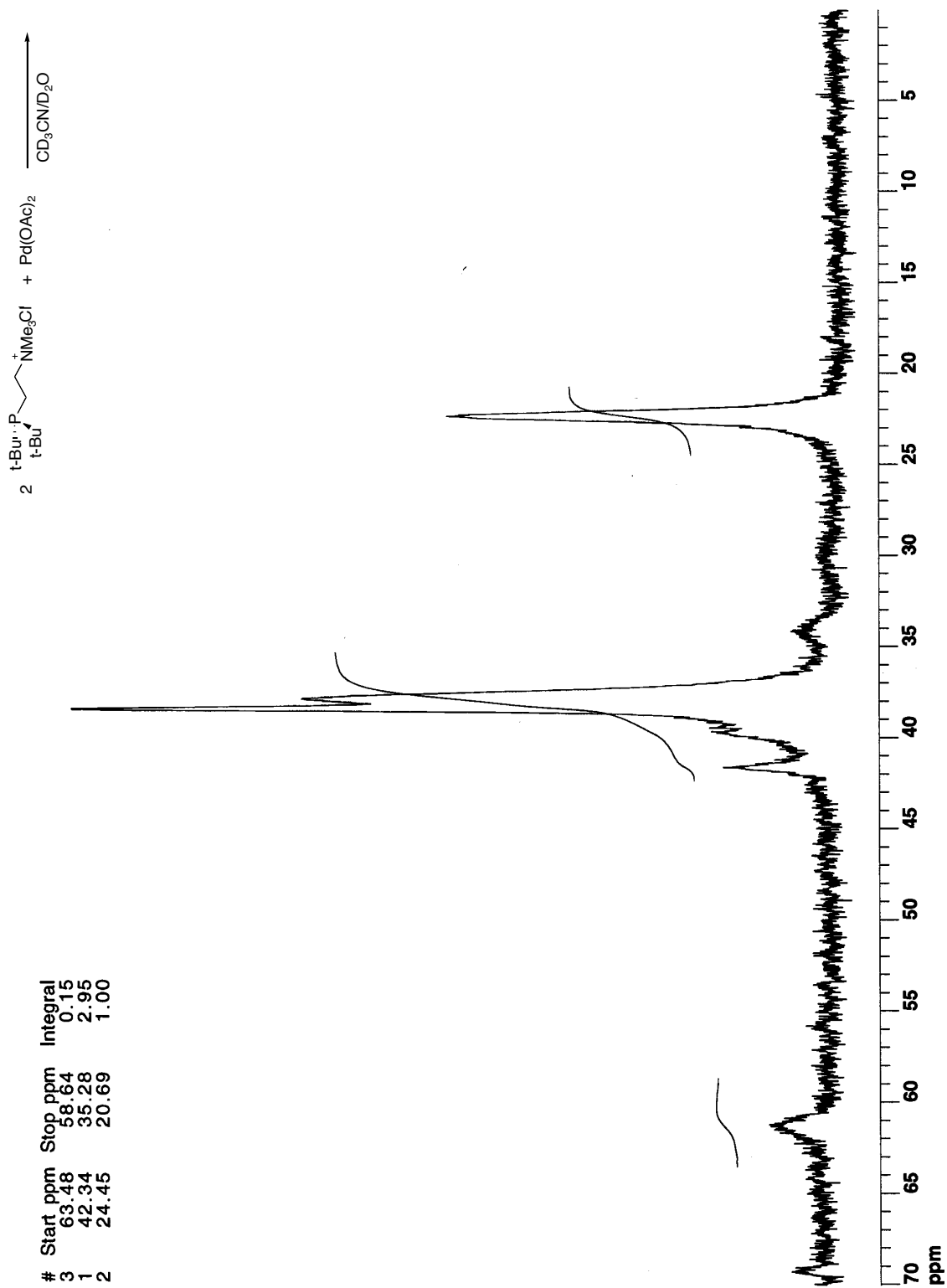
^{31}P NMR spectrum of a 3:1 mixture of Cy-Pip-phos: Pd(OAc)₂ in the presence of excess sodium formate after 24 h (CD₃CN/D₂O, 202.5 MHz).



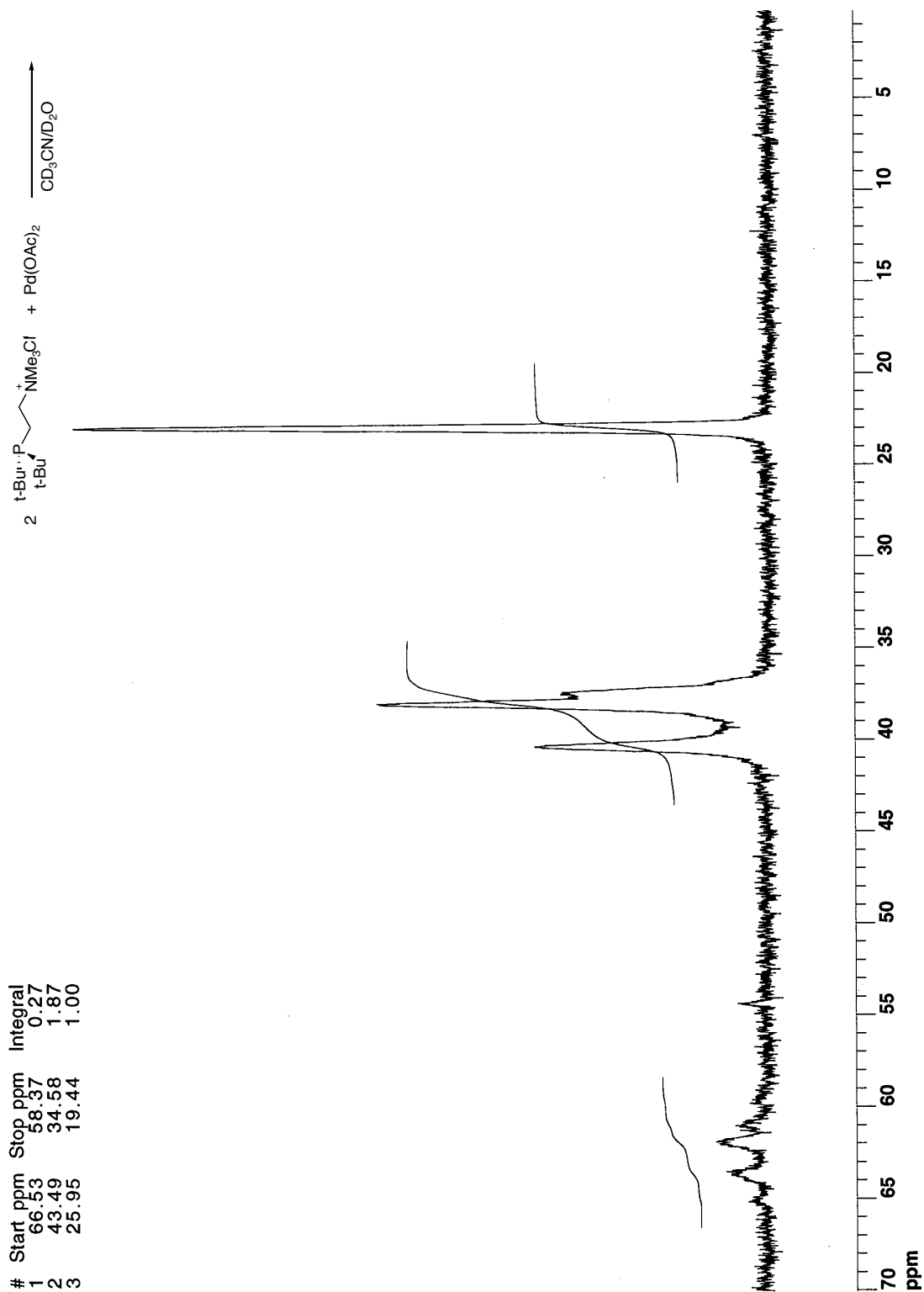
^{13}C NMR spectrum of *trans*-(Cy-Pip-phos) $_2$ PdCl $_2$ generated *in situ* from Cy-Pip-phos and Na $_2$ PdCl $_4$ (CD $_3$ CN/D $_2$ O, 90.6 MHz)



^{13}C NMR spectrum of *trans*-(Cy-Pip-phos) $_2$ PdCl $_2$ generated *in situ* from Cy-Pip-phos and Na $_2$ PdCl $_4$ (CD $_3$ CN/D $_2$ O, 90.6 MHz)



^{31}P NMR spectrum of the reaction of *t*-Bu-Amphos + Pd(OAc)₂ (L: Pd=2:1) (D₂O, 202.5 MHz).



^{31}P NMR spectrum of precipitate formed in reaction of *t*-Bu-Amphos + Pd(OAc)₂ (CH₃CN, 202.5 MHz).