SUPPORTING INFORMATION

Stereospecific Synthesis of *trans*-1,4-Diphosphacyclohexanes

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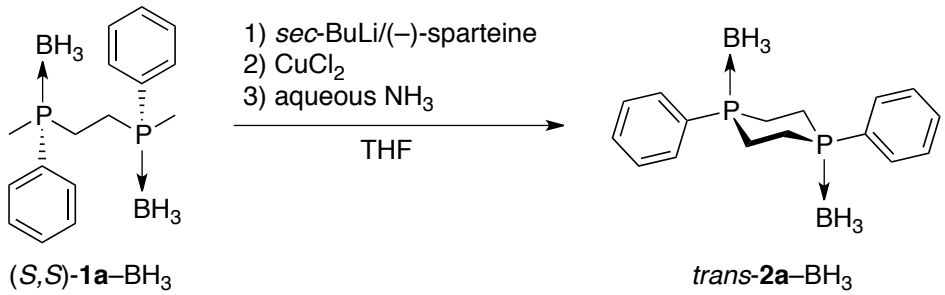
Contents **page**

General. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX400 or AL400 instrument. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. ^{31}P NMR spectra were recorded on a JEOL EX400 spectrometer at 161.9 MHz, and samples were analyzed in $CDCl_3$ using H_3PO_4 as an external standard. Mass analysis was performed at technical support office at Department of Synthetic Chemistry and Biological Chemistry, Kyoto University; high-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer for EI, JEOL JMS-HX110A for FAB, and Thermo Scientific EXACTIVE for ESI. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-300 SiO_2. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials. THF was purchased and purified by passage through purification column under Ar pressure.[1] Dehydrated grade solvents of toluene and $CHCl_3$ were purchased and used without further purification. *N*,*N*,*N*´,*N*´-Tetramethylethylenediamine (TMEDA) and (–)-sparteine were purchased and distilled from KOH under Ar atmosphere. *sec*-BuLi (1.0 M in cyclohexane and n-hexane solution), 1,4-diazabicyclo[2.2.2]octane (DABCO), $CuCl_2$, aqueous NH_3 (28%) were purchased and used without purification. All (*S*,*S*)-BisP* borane complexes — (*S*,*S*)-**1a**–BH_3,[2] (*S*,*S*)-**1b**–BH_3,[2] (*S*,*S*)-**1c**–BH_3,[3] (*S*,*S*)-**1d**–BH_3,[3] (*S*,*S*)-**1e**–BH_3,[3] and (*S*,*S*)-**1f**–BH_3[3] — were prepared by the literature's procedures. Reactions were performed under Ar atmosphere using standard Schlenk techniques.

Synthesis of *trans*-2a–BH_3

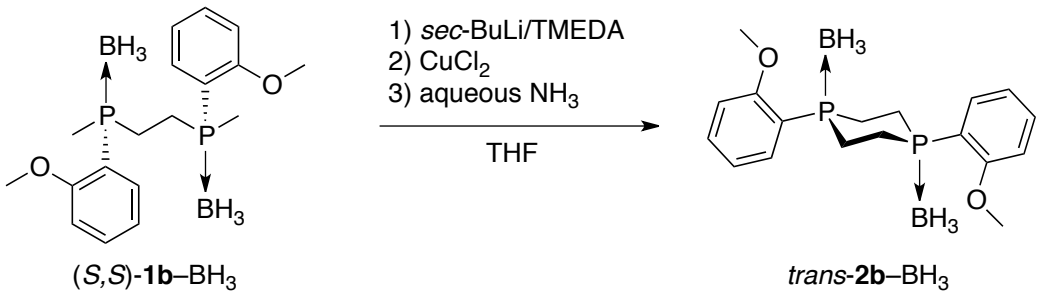


(*S,S*)-**1a**–BH_3 *trans*-**2a**–BH_3

A solution of (–)-sparteine (0.55 mL, 2.5 mmol) as a ligand in THF (10 mL) was cooled to –78 °C. To this solution, *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution, 2.5 mL, 2.5 mmol) was added by a syringe. After 15 minutes, a solution of (*S,S*)-**1a**–BH_3 (0.302 g, 1.0 mmol) in THF (10 mL) was added dropwise, and the mixture was stirred at –78 °C for 3 h. $CuCl_2$ (0.270 g, 2.0 mmol) was added in one portion with vigorous stirring, and the mixture was allowed to slowly warm to room temperature. After 15 h, aqueous NH_3 (10 mL) was added, and the organic species were extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with 5% aqueous NH_3, 2 N HCl, and brine, and then dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on SiO_2 with hexane-CH_2Cl_2 (v/v = 1:1) and recrystallization from hot toluene-hexane to give *trans*-**2a**–BH_3 (167 mg, 0.56 mmol, 56%) as a colorless solid.

56% isolated yield; R_f = 0.83 (CH_2Cl_2 100%, SiO_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87 (br q, J_{HB} = 108.4Hz, -B*H*$_3$, 6H), 2.19 (dd, J = 10.5 Hz, J_{HP} = 21.4 Hz, -PC*H*$_2$-, 4H), 2.81 (m, -PC*H*$_2$-, 4H), 7.56 (m, -*Ar*, 6H) 7.88 (m, -*Ar*, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.7 (d, J_{CP} = 33.7 Hz, -P*C*H$_2$-), 127.3-132.2 (m, -*Ph*) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +6.3 ppm. HRMS (EI) calcd. for $C_{16}H_{24}B_2P_2$ [M]$^+$: 300.1539, found 300.1532. Anal. calcd. for $C_{16}H_{24}B_2P_2$: C 64.07; H 8.07, found: C 63.85; H 7.97.

Synthesis of *trans*-2b–BH_3

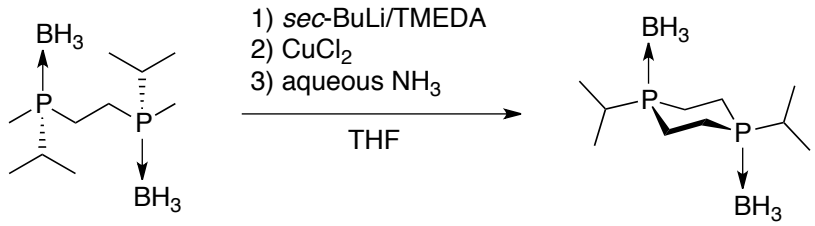


(*S,S*)-**1b**–BH_3 *trans*-**2b**–BH_3

A THF solution (20 mL) of (*S,S*)-**1b**–BH_3 (181 mg, 0.50 mmol) and TMEDA (0.18 mL, 1.1 mmol) was cooled to –78 °C. To this solution, *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution, 1.1 mL, 1.1 mmol) was added with a syringe. After stirring for 3 h, $CuCl_2$ (174 mg, 1.3 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight. Aqueous NH_3 (30 mL) was added, and the organic layer was extracted with chloroform (50 mL × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2 with AcOEt-hexane (v/v = 1/4) as an eluent. Recrystallization from hot toluene-hexane gave *trans*-**2b**–BH_3 (54 mg, 0.15 mmol,) as a colorless solid.

30% isolated yield; R_f = 0.5 (hexane/AcOEt: v/v = 4:1, SiO_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (br q, J_{HB} = 123.0 Hz, -B*H*$_3$, 6H), 2.04 (m, P-C*H*$_2$-, 4H), 3.43 (m, P-C*H*$_2$, 4H), 4.05 (s, -C*H*$_3$, 6H), 6.99 (d, J = 8.6 Hz, -*Ar*, 2H), 7.10 (t, J = 7.3 Hz, -*Ar*, 2H), 7.56 (t, J = 7.3 Hz, -*Ar*, 2H), 8.00 (q, J = 4.8 Hz, -*Ar*, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.0 (d, J_{CP} = 34.6 Hz, -P*C*H$_2$-), 55.6 (s, -O*C*H$_3$), 110.7, 120.9, 134.1, 136.4, 136.5 and 162.0 (-*Ar*) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +6.6 (J_{PB} = 60.5 Hz) ppm. HRMS (ESI) calcd. for $C_{18}H_{28}B_2O_2P_2$ [M+Na]$^+$: 383.1643, found 383.1638. Anal. calcd. for $C_{18}H_{28}B_2O_2P_2$: C 60.06; H 7.84; found: C 59.89; H 8.11.

Synthesis of *trans*-2c–BH_3

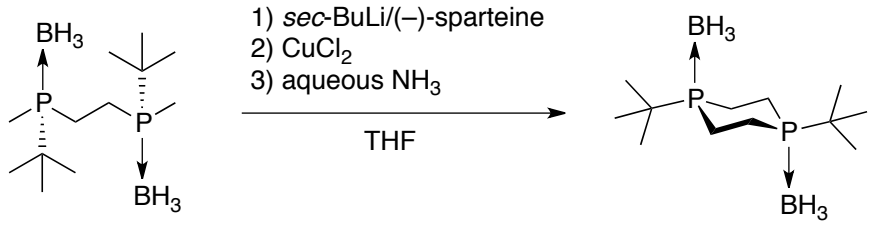


(*S,S*)-**1c**–BH_3 *trans*-**2c**–BH_3

A THF solution (20 mL) of (*S,S*)-**1c**–BH_3 (234 mg, 1.0 mmol) and TMEDA (0.33 mL, 2.2 mmol) was cooled to –78 °C. To this solution, *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution, 2.2 mL, 2.2 mmol) was added with a syringe. After stirring for 3 h, $CuCl_2$ (335 mg, 2.5 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight. Aqueous NH_3 (30 mL) was added, and the organic layer was extracted with AcOEt (50 mL × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to recrystallization from hot toluene and hexane to obtain *trans*-**2c**–BH_3 (101.5 mg, 0.44 mmol) as a colorless solid.

44% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.39 (br q, J_{HB} = 100.6 Hz, -BH_3, 6H), 1.19 (q, J = 8.3 Hz, -(CH_3)$_2$, 12H), 1.88-2.03 (m, -PCH_2- and -CH(CH$_3$)$_2$, 6H), 2.24 (m, -PCH_2-, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.8 (d, J_{CP} = 29.7 Hz, -PCH$_2$-), 16.1 (s, -CH(*C*H$_3$)$_2$), 24.2 (d, J_{CP} = 35.5 Hz, -P*C*H-) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +18.1 (J_{PB} = 65.9 Hz) ppm. HRMS (ESI) calcd. for $C_{10}H_{28}B_2P_2$ [M+H]$^+$: 233.1925, found 233.1926.

Synthesis of *trans*-2d–BH_3

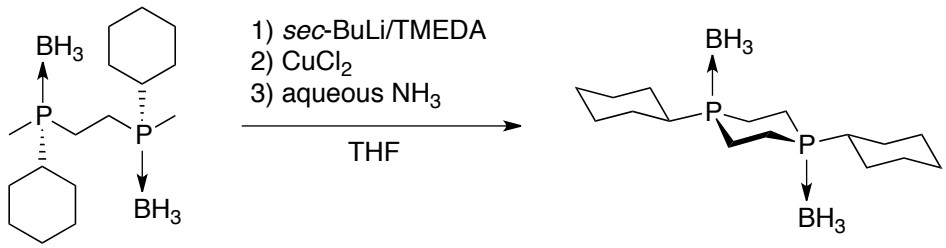


(*S,S*)-**1d**–BH_3 *trans*-**2d**–BH_3

A solution of (–)-sparteine (0.75 mL, 3.3 mmol) as a ligand in THF (10 mL) was cooled to –78 °C. To this solution, *sec*-BuLi (0.97 M in cyclohexane and *n*-hexane solution, 3.38 mL, 3.3 mmol) was added with a syringe. After 15 minutes, a solution of (*S,S*)-**1d**–BH_3 (0.35 g, 1.4 mmol) in THF (5.0 mL) was added dropwise, and the mixture was stirred at –78 °C over 3 h. $CuCl_2$ (1.10 g, 8.1 mmol) was added in one portion with vigorous stirring, and the mixture was allowed to slowly warm to room temperature. After 15 h, the reaction was quenched by the addition of aqueous NH_3 (8.0 mL), and extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with 5% aqueous NH_3, 2 N HCl, and brine, and then dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on SiO_2 with hexane-CH_2Cl_2 (v/v = 4:1 to 0:10) and recrystallization from hot toluene-hexane to give *trans*-**2d**–BH_3 (266 mg, 1.02 mmol, 73%) as a colorless solid

73% isolated yield; R_f = 0.78 (CH_2Cl_2 100%, SiO_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.40 (br q, J_{HB} = 98.8Hz, -B*H*$_3$, 6H), 1.19 (d, J_{HP} = 14.0 Hz, -Bu^t, 18H), 1.88 (dd, J = 9.7 Hz, J_{HP} =20.8Hz, -PC*H*$_2$-, 4H), 2.36 (t, J = 10.0Hz, -PC*H*$_2$-, 4H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 12.9 (d, J_{CP} = 29.2 Hz, -P*C*H$_2$-), 24.8 (s, -PC(*C*H$_3$)$_3$), 27.2 (d, -P*C*(CH$_3$)$_3$, J_{CP} = 32.9 Hz) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 242.9 MHz) δ +26.6 ppm. HRMS (FAB) calcd. for $C_{12}H_{31}B_2P_2$ [M-H]$^+$: 259.2087, found 259.2086. Anal. calcd. for $C_{12}H_{32}B_2P_2$: C 55.44; H 12.41, found: C 55.45; H 12.63.

Synthesis of *trans*-2e–BH_3

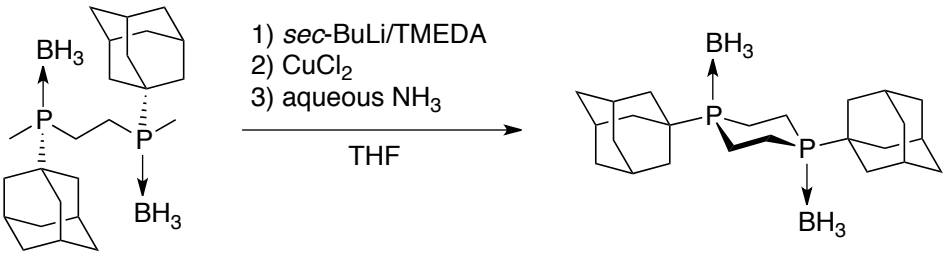


(*S,S*)-**1e**–BH_3 *trans*-**2e**–BH_3

A THF solution (150 mL) of (*S,S*)-**1e**–BH_3 (950 mg, 3.0 mmol) and TMEDA (1.1 mL, 7.3 mmol) was cooled to –78 °C. To this solution, *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution, 7.3 mL, 37.3 mmol) was added with a syringe. After stirring for 3 h, $CuCl_2$ (1.22 g, 9.1 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight. Aqueous NH_3 (30 mL) was added, and the organic layer was extracted with AcOEt (50 mL × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2 with AcOEt-hexane (v/v = 1/10) as an eluent. Recrystallization from hot toluene-hexane gave *trans*-**2e**–BH_3 (334 mg, 1.07 mmol, 36%) as a colorless solid.

36% isolated yield; R_f = 0.6 (hexane/AcOEt: v/v = 4:1, SiO_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.39 (br q, J_{HB} = 101.0 Hz, -BH_3, 6H), 1.29 (m, -C_6H_{11}, 12H), 1.61-2.02 (m, -PCH_2- and -C_6H_{11}, 14H), 2.24 (m, -PCH_2-, 4H), ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.7 (d, J_{CP} = 23.1 Hz, -PCH_2-), 25.7, 25.8, 26.3, 26.4, 33.9 and 34.2 (-C_6H_{12}) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +14.1 (J_{PB} = 60.5 Hz) ppm. HRMS (ESI) calcd. for $C_{16}H_{36}B_2P_2$ [M+Na]$^+$: 335.2371, found 335.2364. Anal. calcd. for $C_{16}H_{36}B_2P_2$: C 61.59; H 11.63; found: C 61.30; H 11.63.

Synthesis of *trans*-2f–BH_3

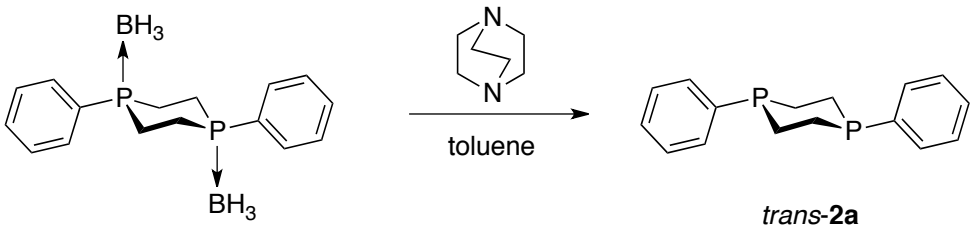


(*S,S*)-**1f**–BH_3 *trans*-**2f**–BH_3

A THF solution (20 mL) of (*S,S*)-**1f**–BH_3 (209 mg, 0.50 mmol) and TMEDA (0.18 mL, 1.1 mmol) was cooled to –78 °C. To this solution, *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution, 1.1 mL, 1.1 mmol) was added with a syringe. After stirring for 3 h, $CuCl_2$ (174 mg, 1.3 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight. Aqueous NH_3 (30 mL) was added, and the organic layer was extracted with chloroform (50 mL × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2 with $CHCl_3$-hexane (v/v = 1/1) as an eluent. Recrystallization from hot toluene-hexane gave *trans*-**2f**–BH_3 (80.6 mg, 0.193 mmol) as a colorless solid.

39% isolated yield; R_f = 0.3 ($CHCl_3$/hexane: v/v = 1:1, SiO_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.36 (br q, J_{HB} = 106.4 Hz, -BH_3, 6H), 1.69-1.84 (m, C-CH_2-C and P-CH_2, 28H), 2.04 (s, -CH-, 6H), 2.35 (m, -PCH_2-, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.3 (d, J_{CP} = 29.7 Hz, -PCH$_2$-), 27.6 (d, J_{CP} = 9.1 Hz, -P-C-), 30.2 (d, J_{CP} = 34.6 Hz, -PCH$_2$-), 35.7 and 36.5 (s, adamantyl) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +19.6 (J_{PB} = 76.8 Hz) ppm. Anal. calcd. for $C_{24}H_{44}B_2P_2$: C 69.26; H 10.66; found: C 68.99; H 10.74.

Removal of BH_3 from *trans*-2a–BH_3

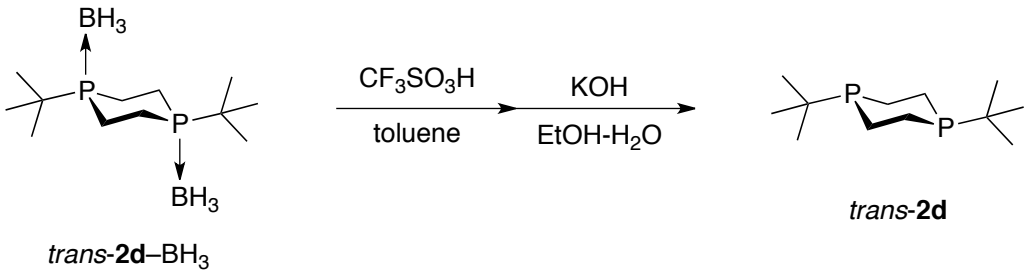


trans-**2a**–BH_3 *trans*-**2a**

A solution of *trans*-**2a**–BH_3 (90 mmol, 0.3 mmol) and DABCO (336 mg, 3.0 mmol) in toluene (6.0 ml) was stirred at 70 °C. After stirring for 15 h, toluene was removed in vacuo. The residue was solved in Et_2O, and purified with column chromatography on Al_2O_3 to give *trans*-**2a** (77 mg, 0.28 mmol, 94%) as a colorless solid. Another synthetic method and characterization of *trans*-**2a** were reported.[4]

^1H NMR ($CDCl_3$, 400 MHz) δ 2.13–2.26 (m, -PCH_2-, 8H), 7.25-7.42 (m, Ar-H, 10H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.3 (s, -PCH$_2$-), 128.2-130.9 (m, -PC_6H_5) ppm; $^{31}P\{^1H\}$NMR ($CDCl_3$, 161.9 MHz) δ -28.9 ppm. HRMS (FAB) calcd. for $C_{16}H_{18}P_2$ $[M]^+$: 232.0884, found 232.0891.

Removal of BH_3 from *trans*-2d–BH_3

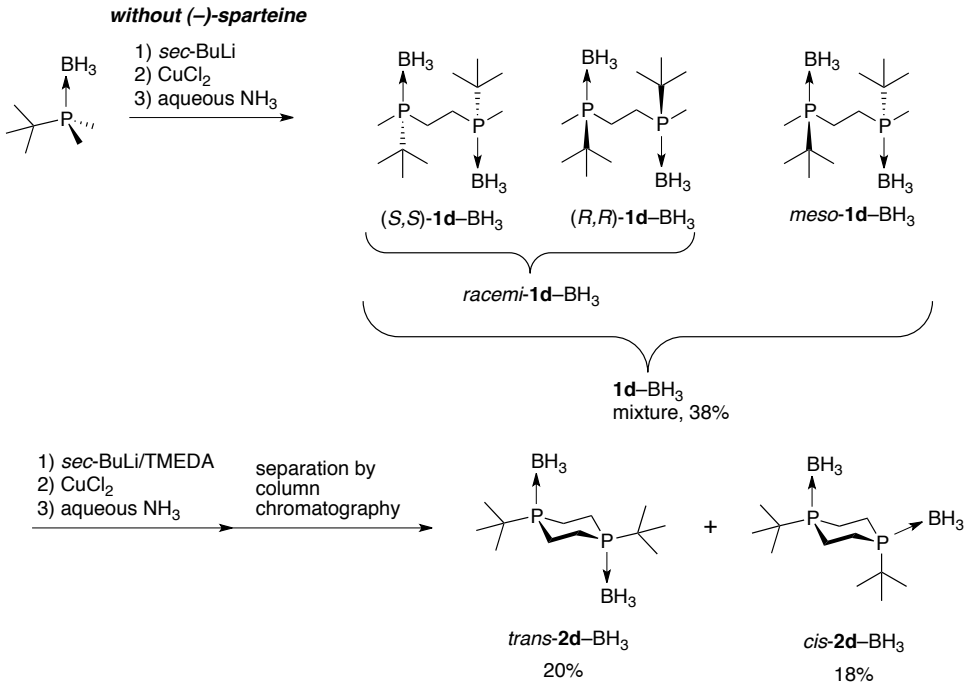


trans-**2d**–BH_3 *trans*-**2d**

A solution of *trans*-**2d**–BH_3 (260 mg, 1.0 mmol) in toluene (10 ml) was cooled to 0 °C. To this solution, CF_3SO_3H (1.0 ml, 11 mmol) was added by a syringe. Then, the solution was allowed to warm to room temperature. After stirring for 2 h, toluene was removed in vacuo. KOH (1.2 g, 22 mmol) in degassed EtOH and H_2O (v/v = 10:1) was added to the residue. After stirring for 3 h at 50 °C under Ar atmosphere, extraction with degassed dry diethyl ether was carried out. The organic layer was dryied over $MgSO_4$ and purified with column chromatography on Al_2O_3 to give *trans*-**2d** (211 mg, 0.91 mmol, 91%) as a colorless solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.959 (br s, -Bu^t, 18H), 1.76 (m, -PCH_2-, 8H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.6 (s, -P*C*H_2-), 24.0 (s, -PC(*C*H_3)$_3$), 27.0 (s, -P*C*(CH$_3$)$_3$) ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ -4.5 ppm. HRMS (FAB) calcd. for $C_{12}H_{26}P_2$ [M]$^+$: 232.1510, found 232.1511.

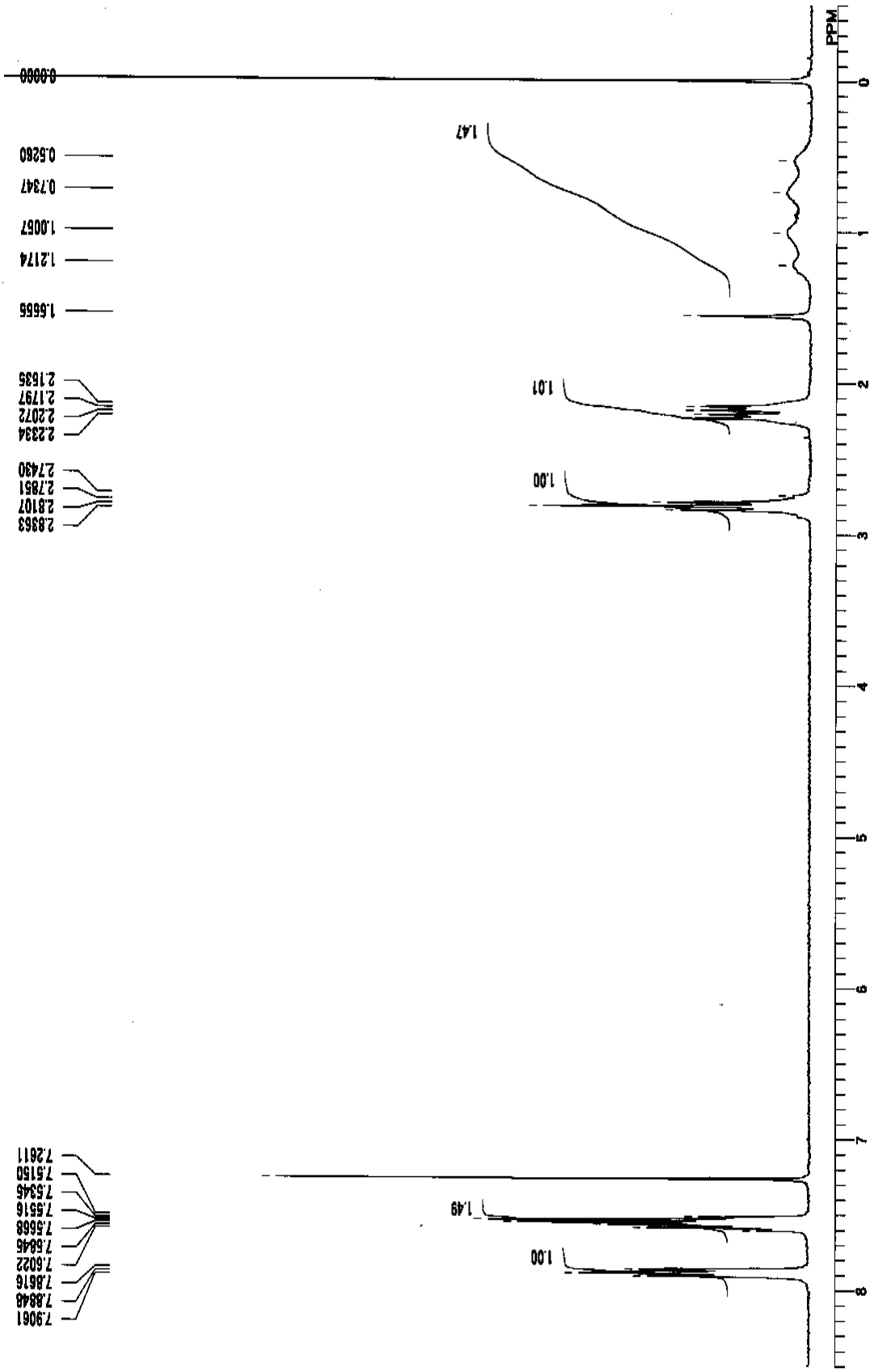
Scheme S1. Oxidative coupling reaction of the mixture of *racemi*- and *meso*-1b–BH_3.



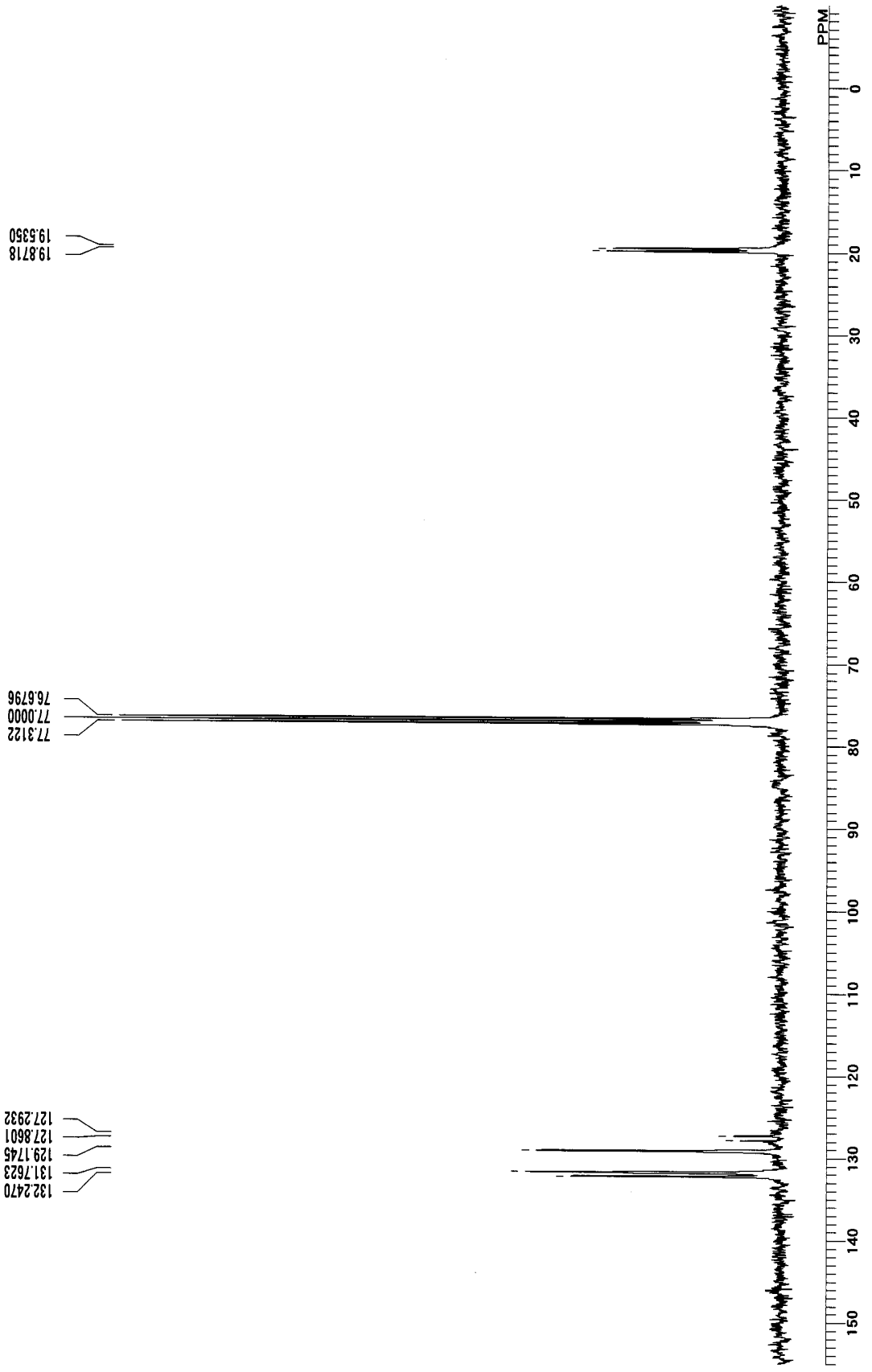
A THF solution (10 mL) of TMEDA (0.36 mL, 2.2 mmol) was cooled to –78 °C. To this solution, *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution, 2.2 mL, 2.2 mmol) was added by a syringe. After 15 minutes, a solution of the mixture of *racemi*- and *meso*-**1d**–BH_3 (0.26 g, 1.0 mmol) in THF (5.0 mL) was added dropwise, and the mixture was stirred at –78 °C over 3 h. $CuCl_2$ (0.27 g, 2.0 mmol) was added in one portion, and the mixture was allowed to slowly warm to room temperature. After 12 h, aqueous NH_3 was added, and extracted with CH_2Cl_2. The combined extracts were washed with 5% aqueous NH_3, 2 N HCl, and brine, and then dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on SiO_2 with hexane and CH_2Cl_2 (v/v = 3:2) to obtain and *trans*-**2d**–BH_3 (51 mg, 0.20 mmol, 20%) and *cis*-**2d**–BH_3 (46 mg, 0.18 mmol, 18%) as colorless solids.

cis-**2d**–BH_3; R_f = 0.67 (CH_2Cl_2 100%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.44 (br q, J_{HB} = 99.8Hz, -BH_3, 6H), 1.22 (d, J_{HP} = 13.2 Hz, -^{t}Bu, 18H), 2.04 (m, -PCH_2-, 8H) ppm; ^{13}C NMR (CD_2Cl_2, 150 MHz) δ 12.88 (d, J_{CP} = 31.1 Hz, -PCH_2-), 12.91 (d, J_{CP} = 30.3 Hz, -PCH_2-), 25.29 (s, -PC(CH_3)$_3$), 25.31 (s, -PC(CH_3)$_3$), 28.9 (d, -PC(CH_3)$_3$, J_{CP} = 30.5 Hz) ppm; ^{31}P{1H}NMR (CD_2Cl_2, 242.9 MHz) δ +24.2, +24.7 ppm. HRMS (FAB) calcd. for $C_{12}H_{31}B_2P_2$ [M-H]+: 259.2087, found 259.2085. Anal. calcd. for $C_{12}H_{31}B_2P_2$: C 55.44; H 12.41, found: C 55.73; H 12.60.

^{1}H NMR spectrum of *trans*-2a–BH_3



^{13}C NMR spectrum of *trans*-2a–BH_3



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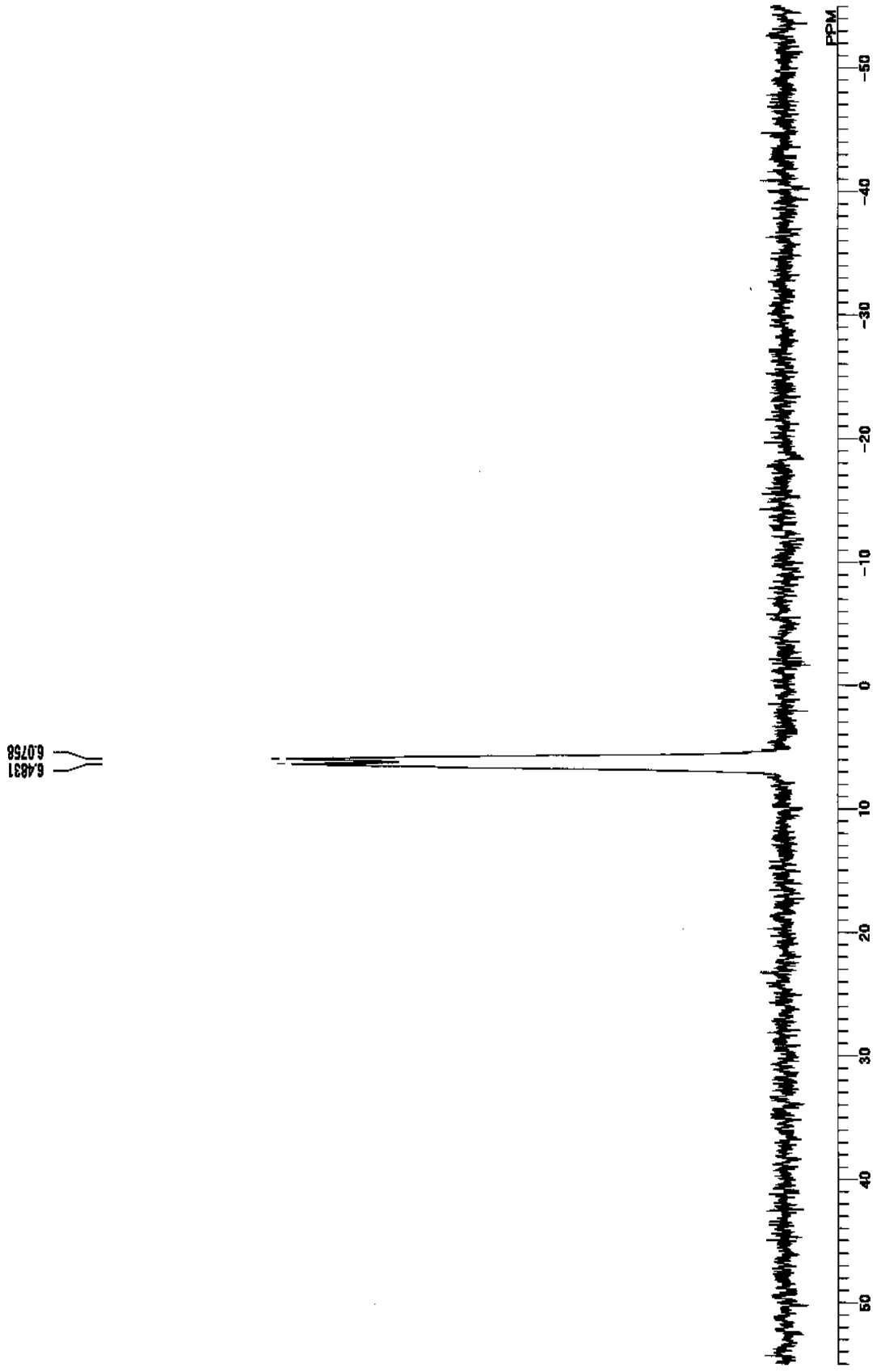
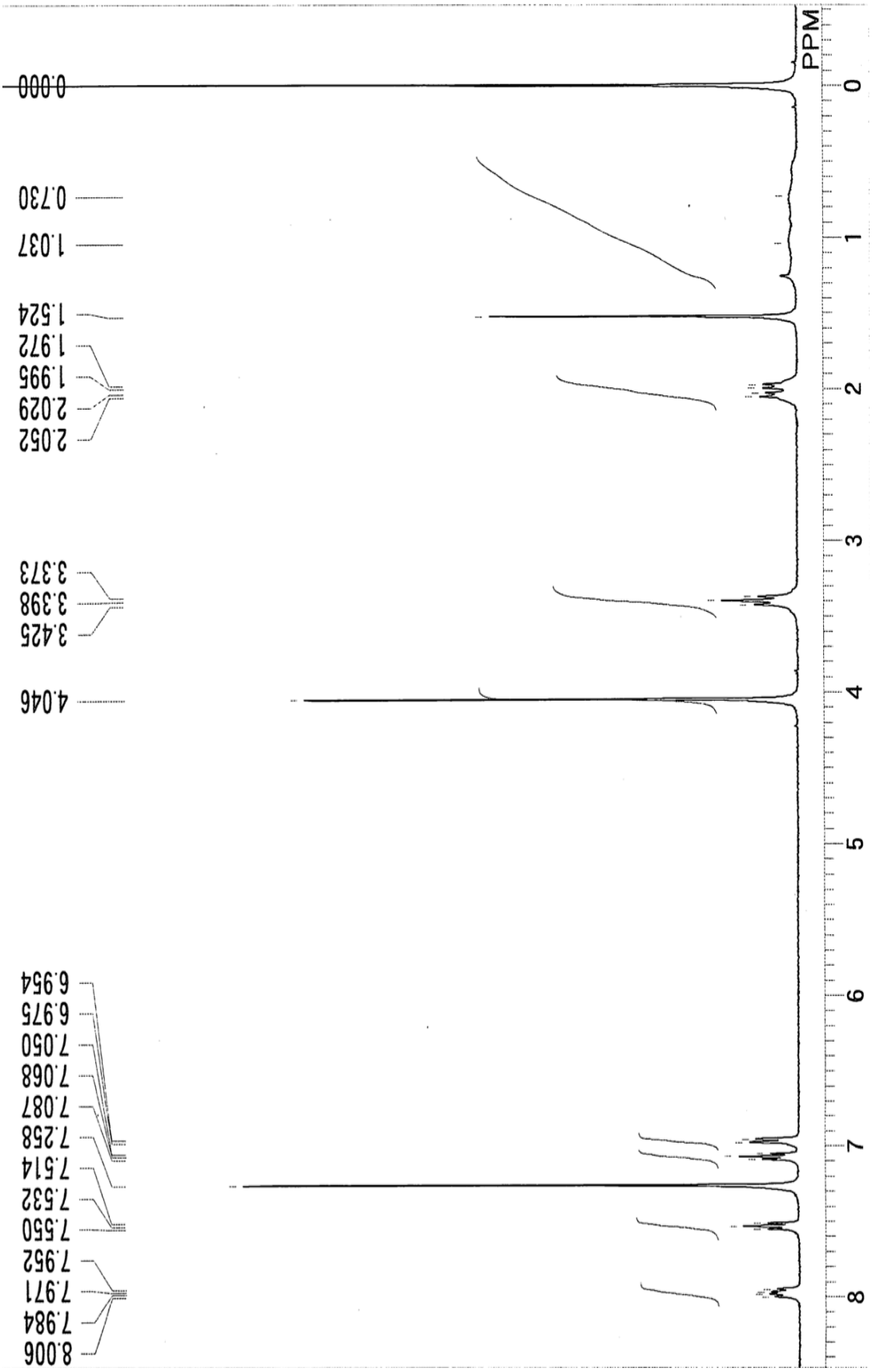
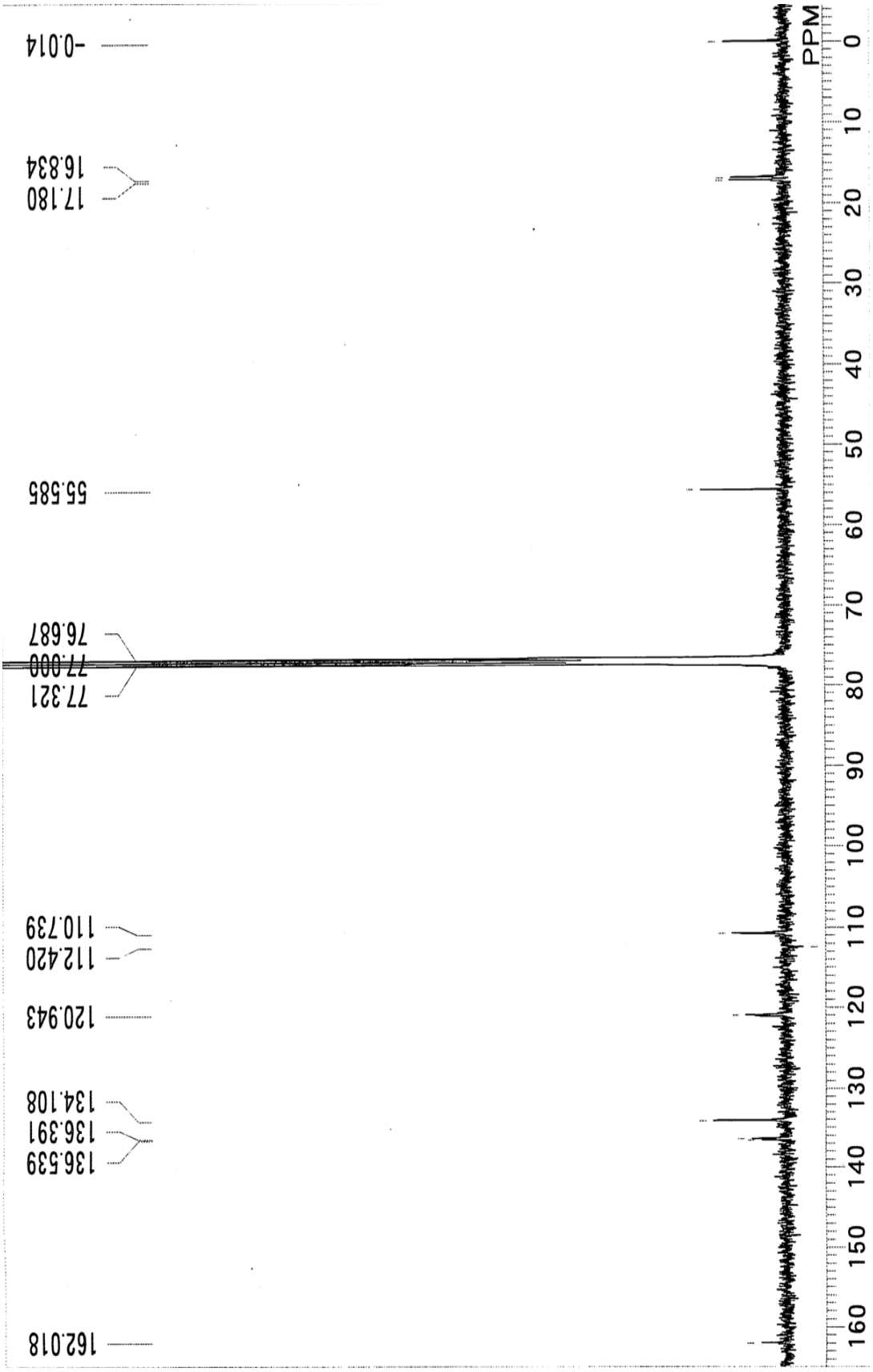


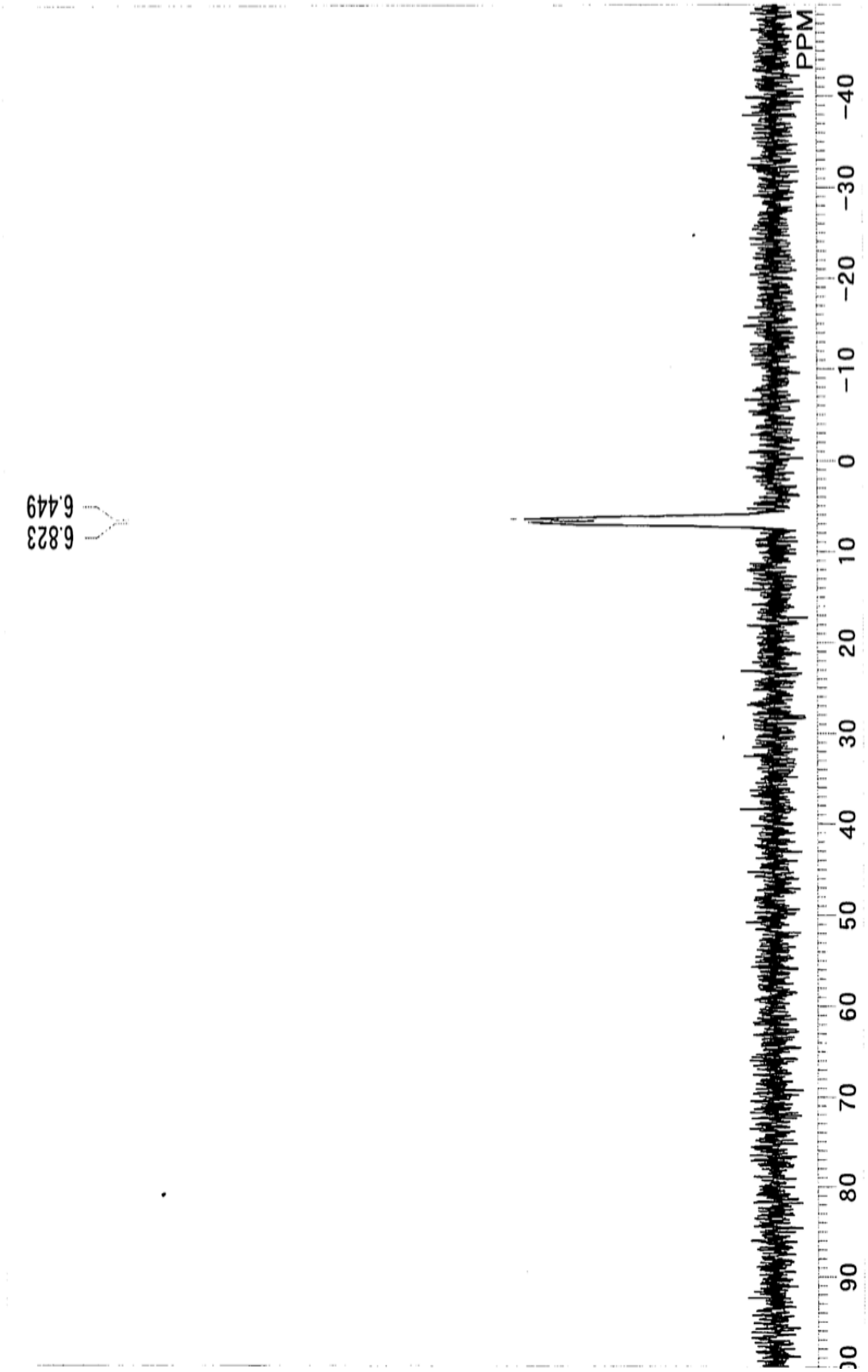
^{1}H NMR spectrum of *trans*-2b–BH_3



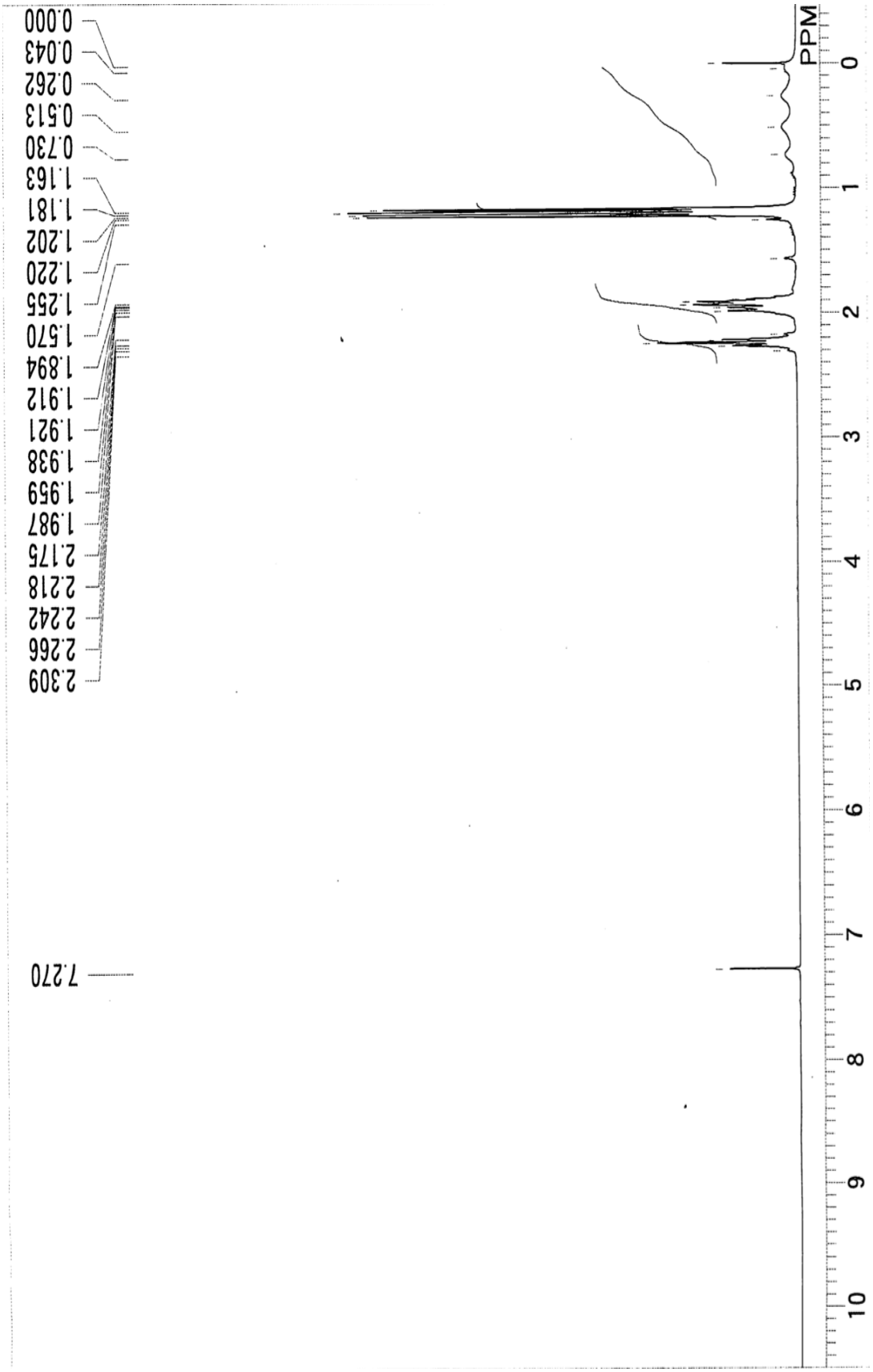
^{13}C NMR spectrum of *trans*-2b–BH_3



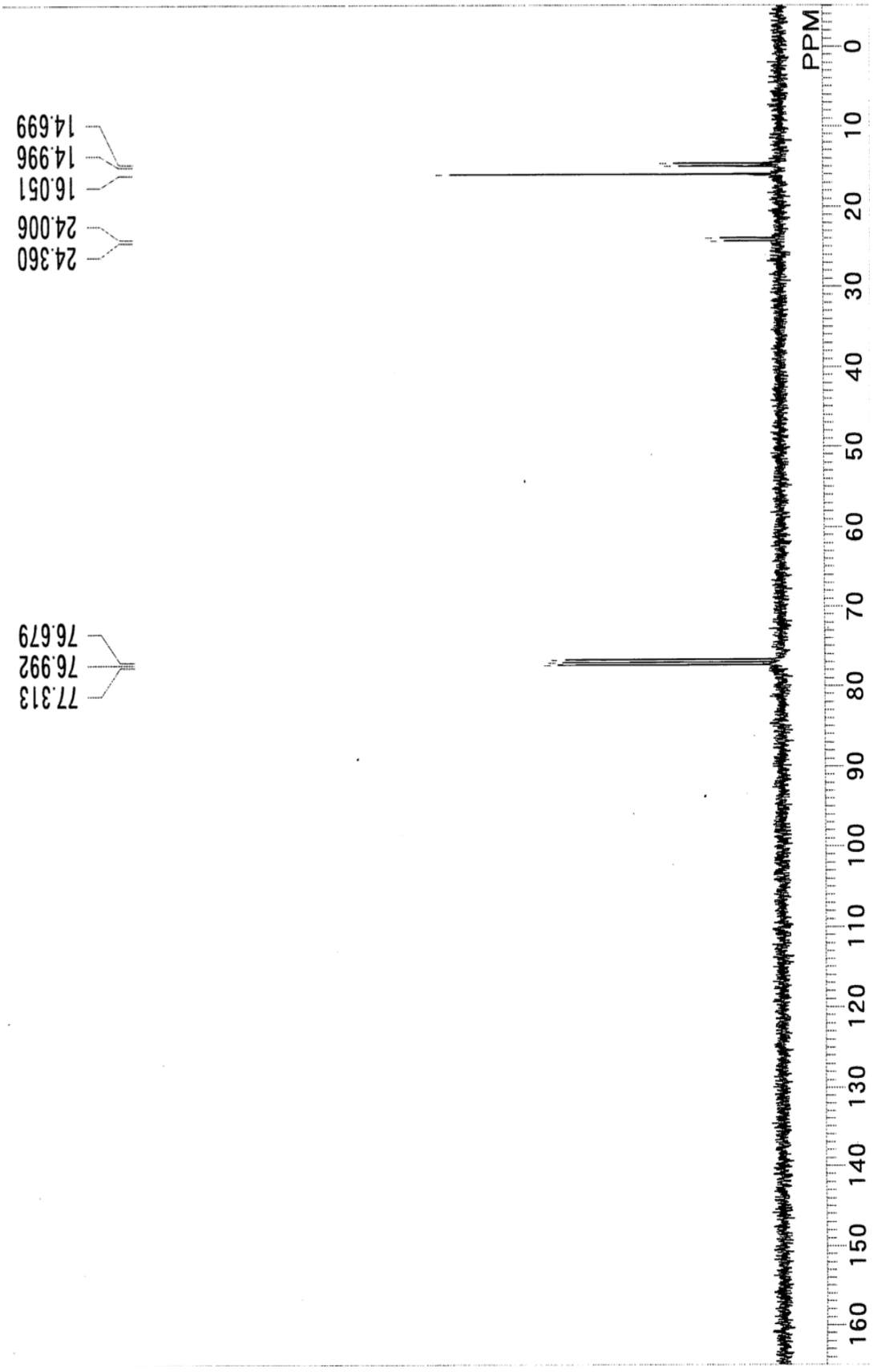
^{31}P NMR spectrum of *trans*-2b–BH_3



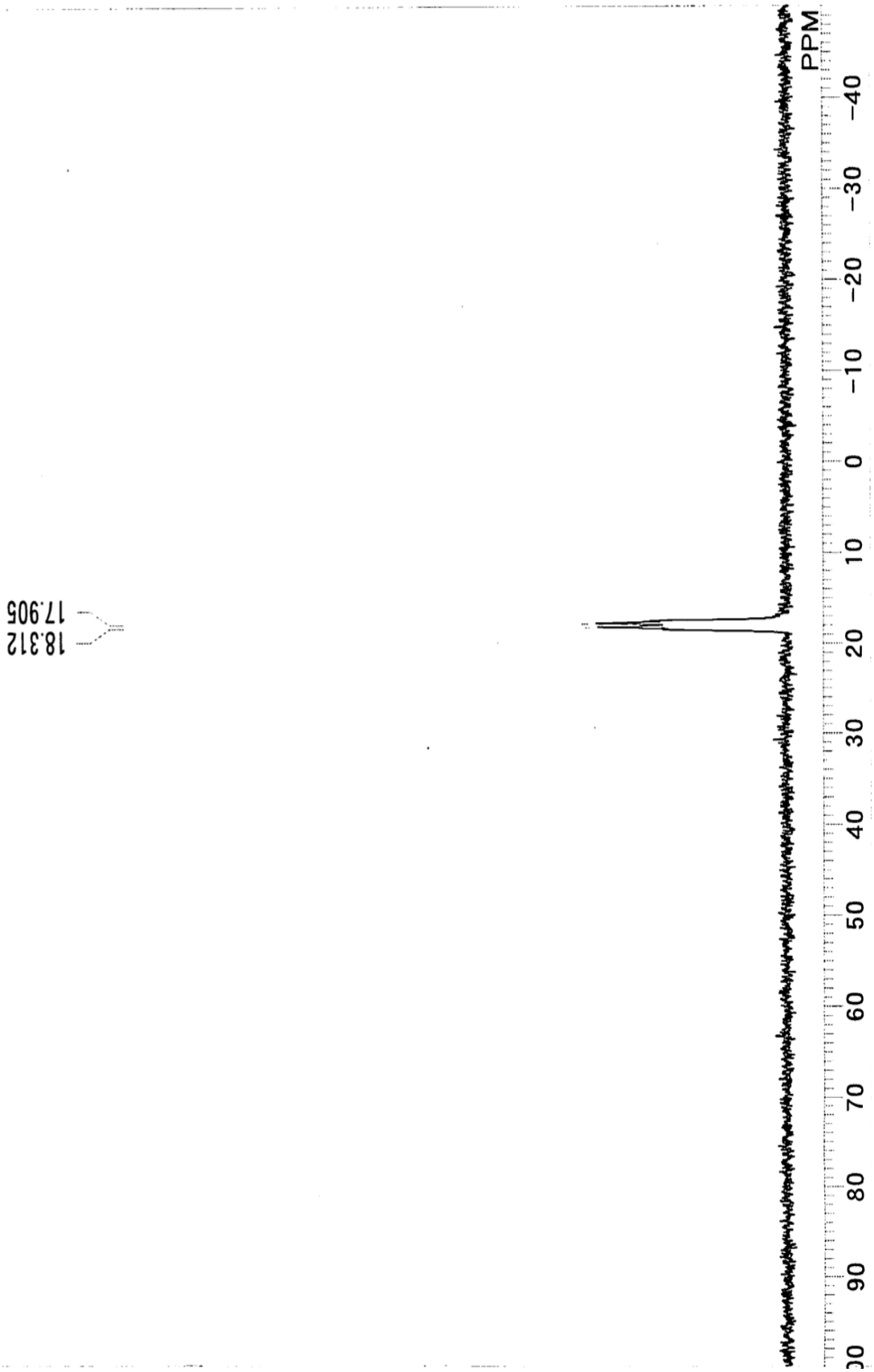
^{1}H NMR spectrum of *trans*-2c–BH_3



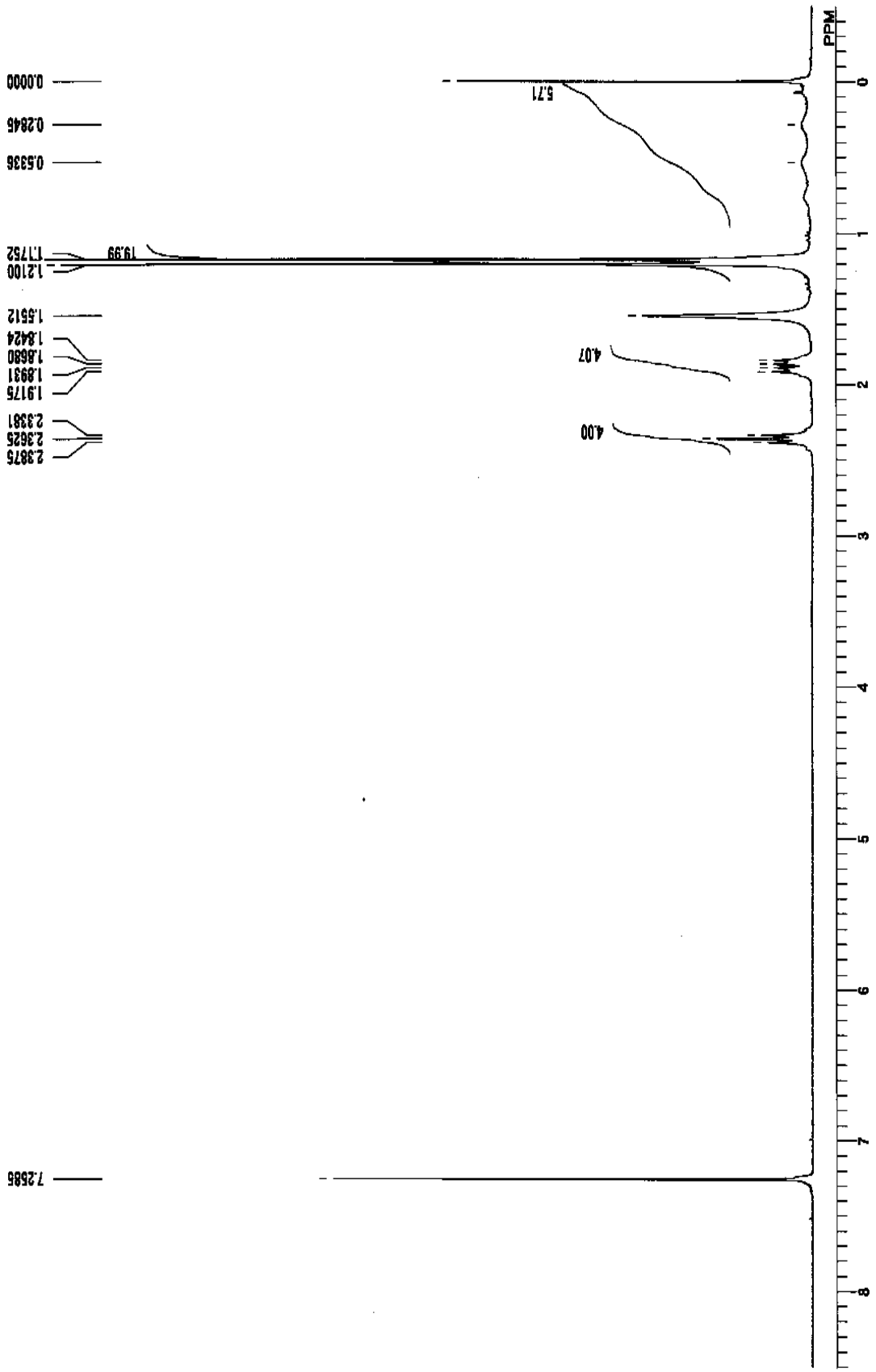
^{13}C NMR spectrum of *trans*-2c–BH_3



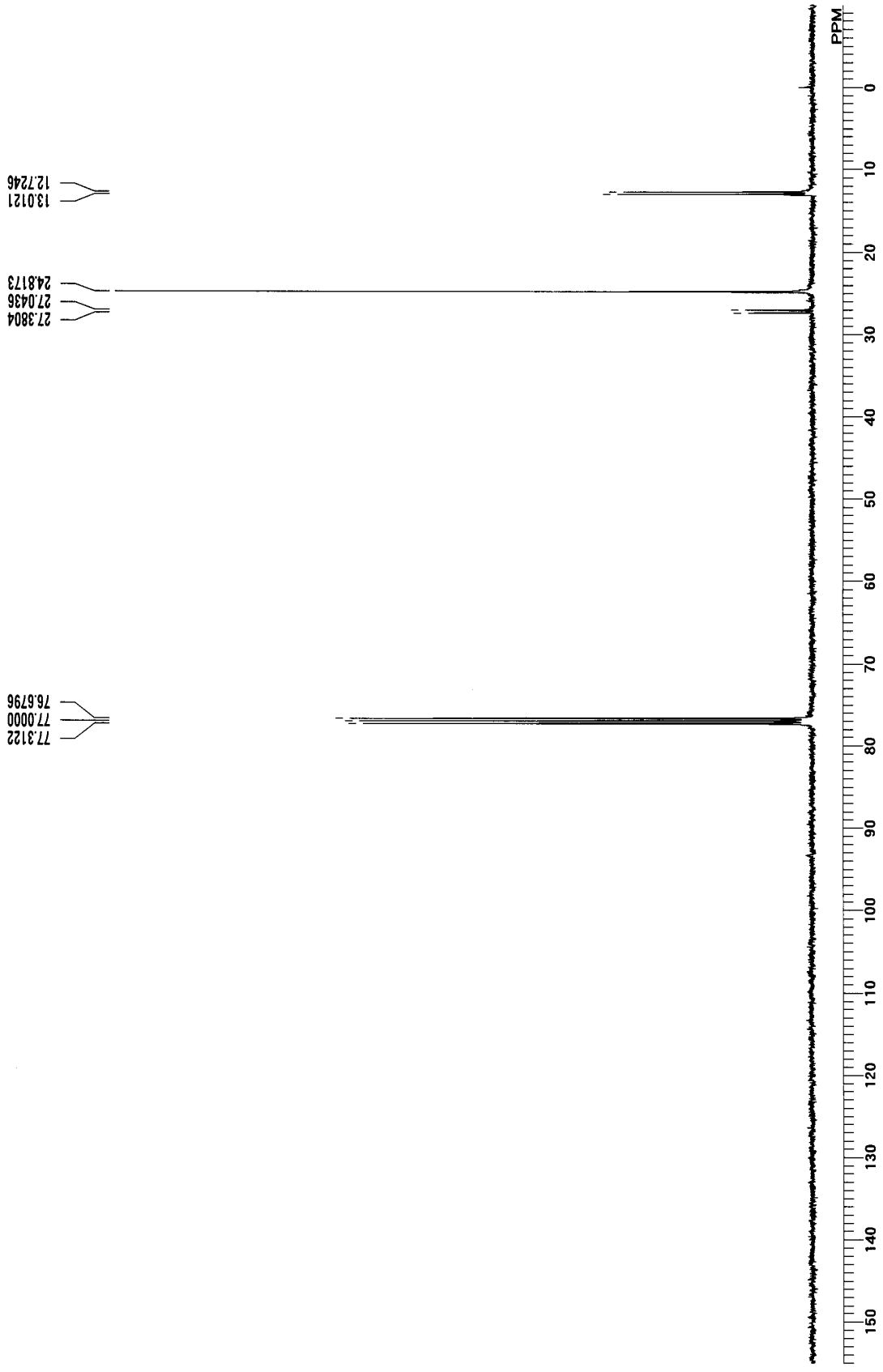
^{31}P NMR spectrum of *trans*-2c–BH_3



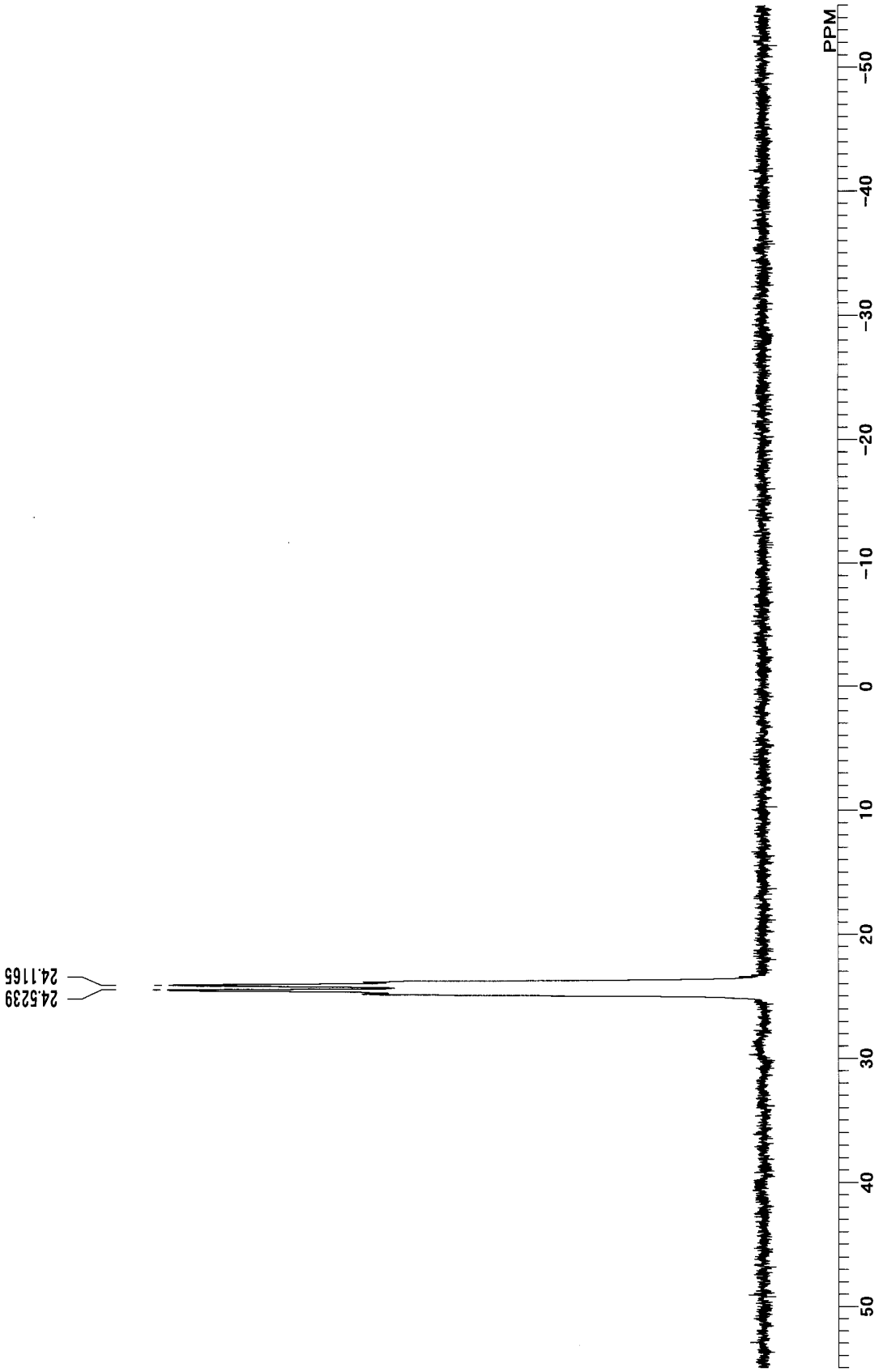
^{1}H NMR spectrum of *trans*-2d–BH_3



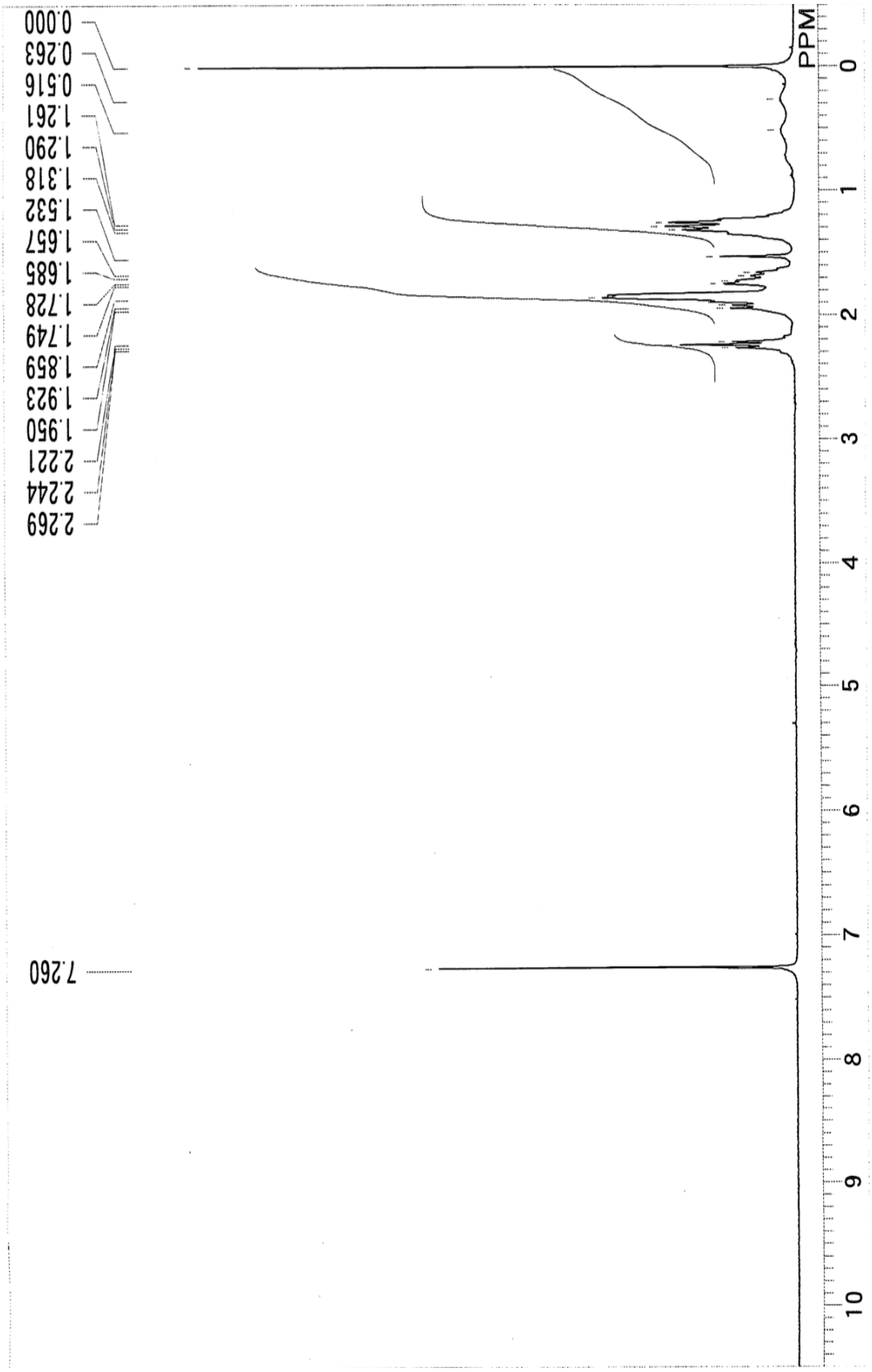
^{13}C NMR spectrum of *trans*-2d–BH_3



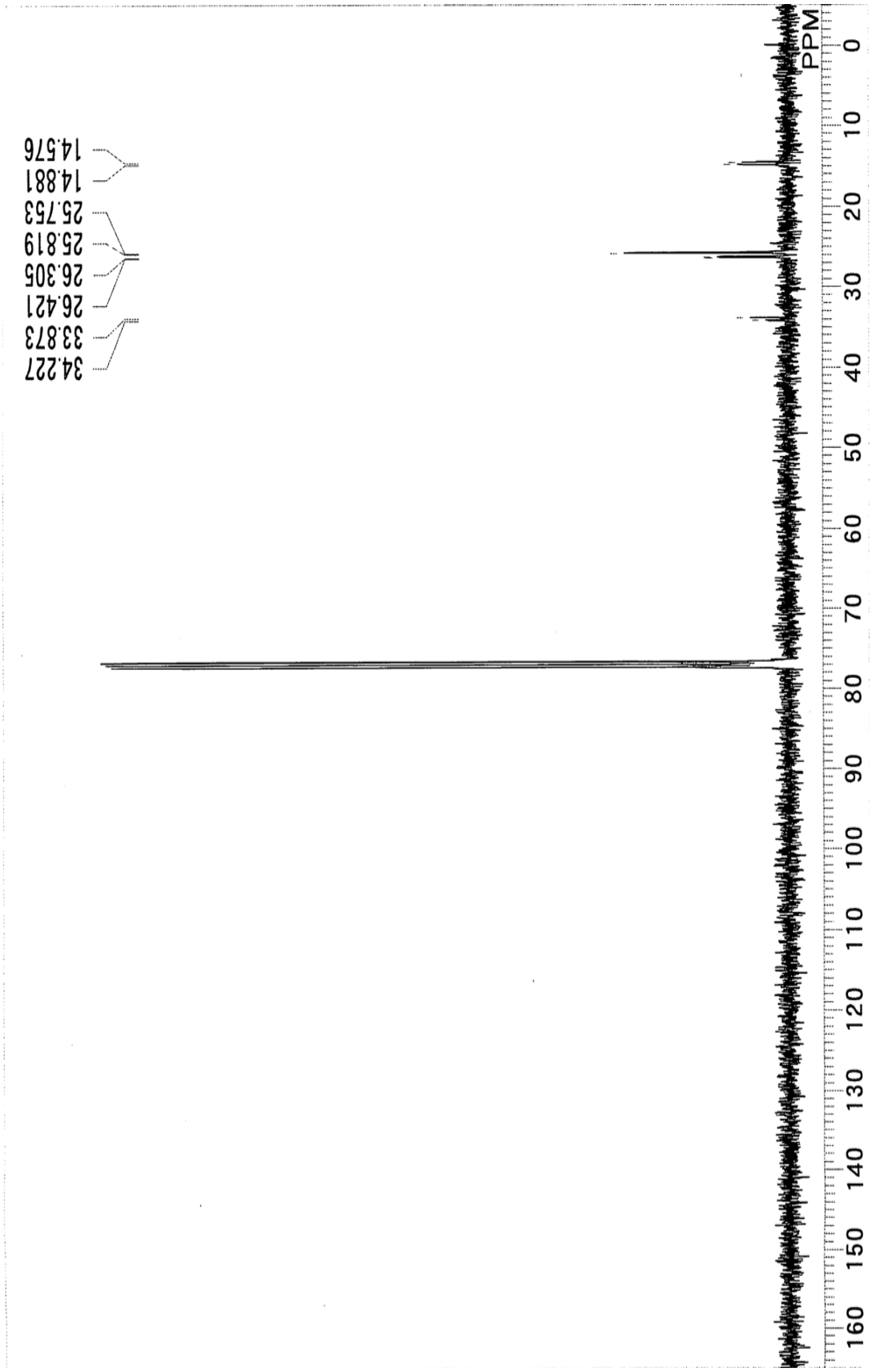
^{31}P NMR spectrum of *trans*-2d–BH_3



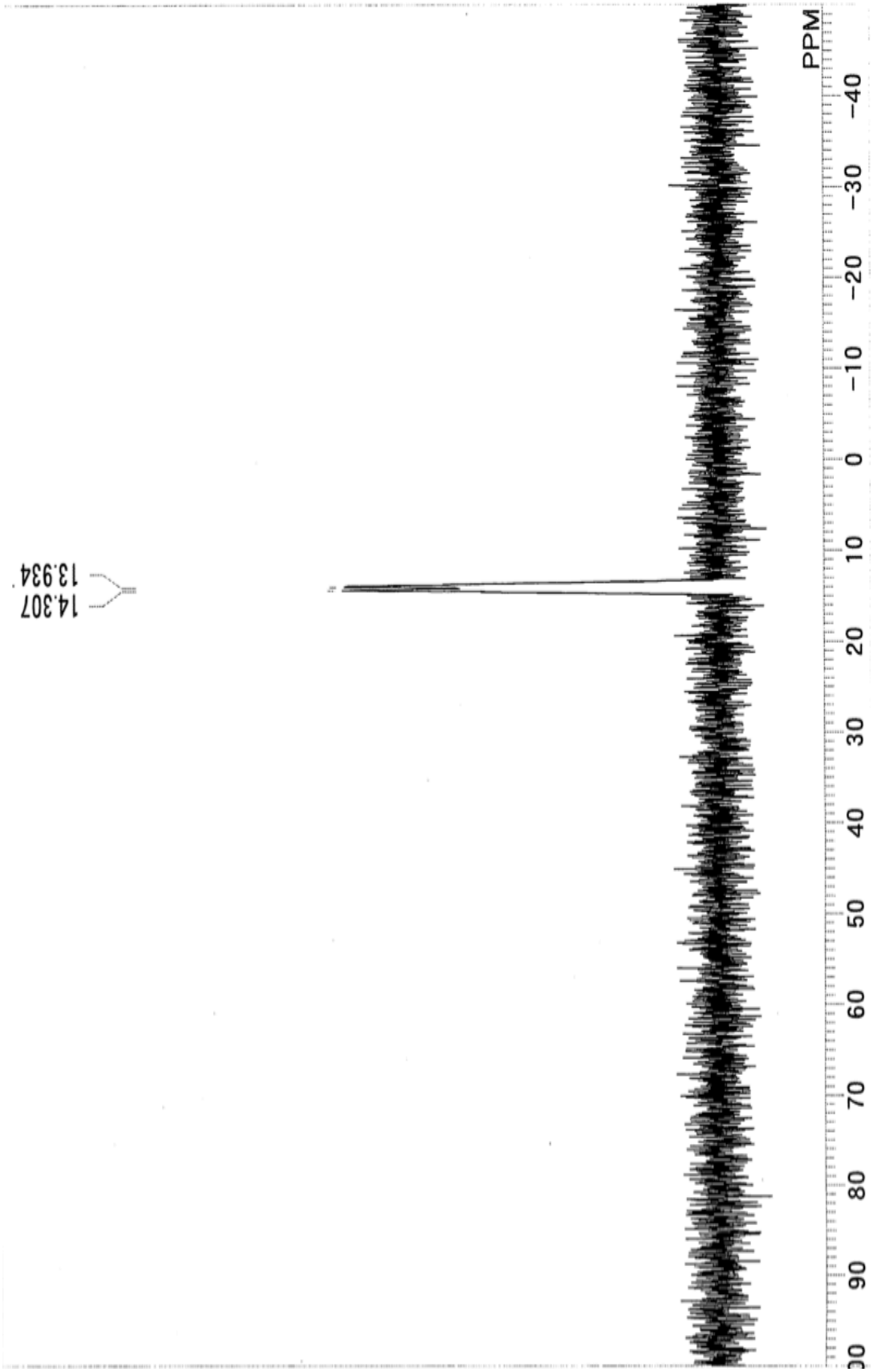
^{1}H NMR spectrum of *trans*-2e–BH_3



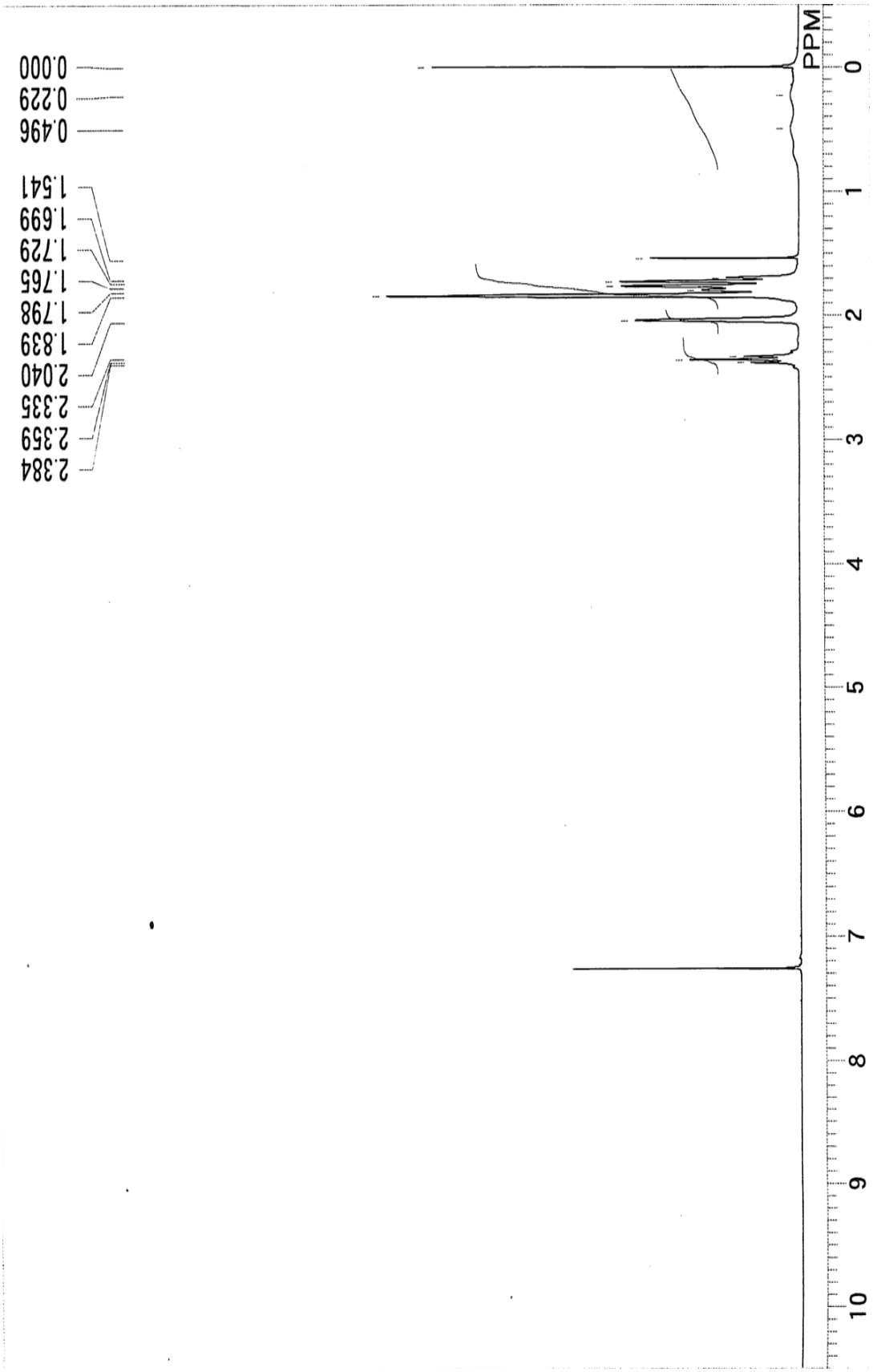
^{13}C NMR spectrum of *trans*-2e–BH_3



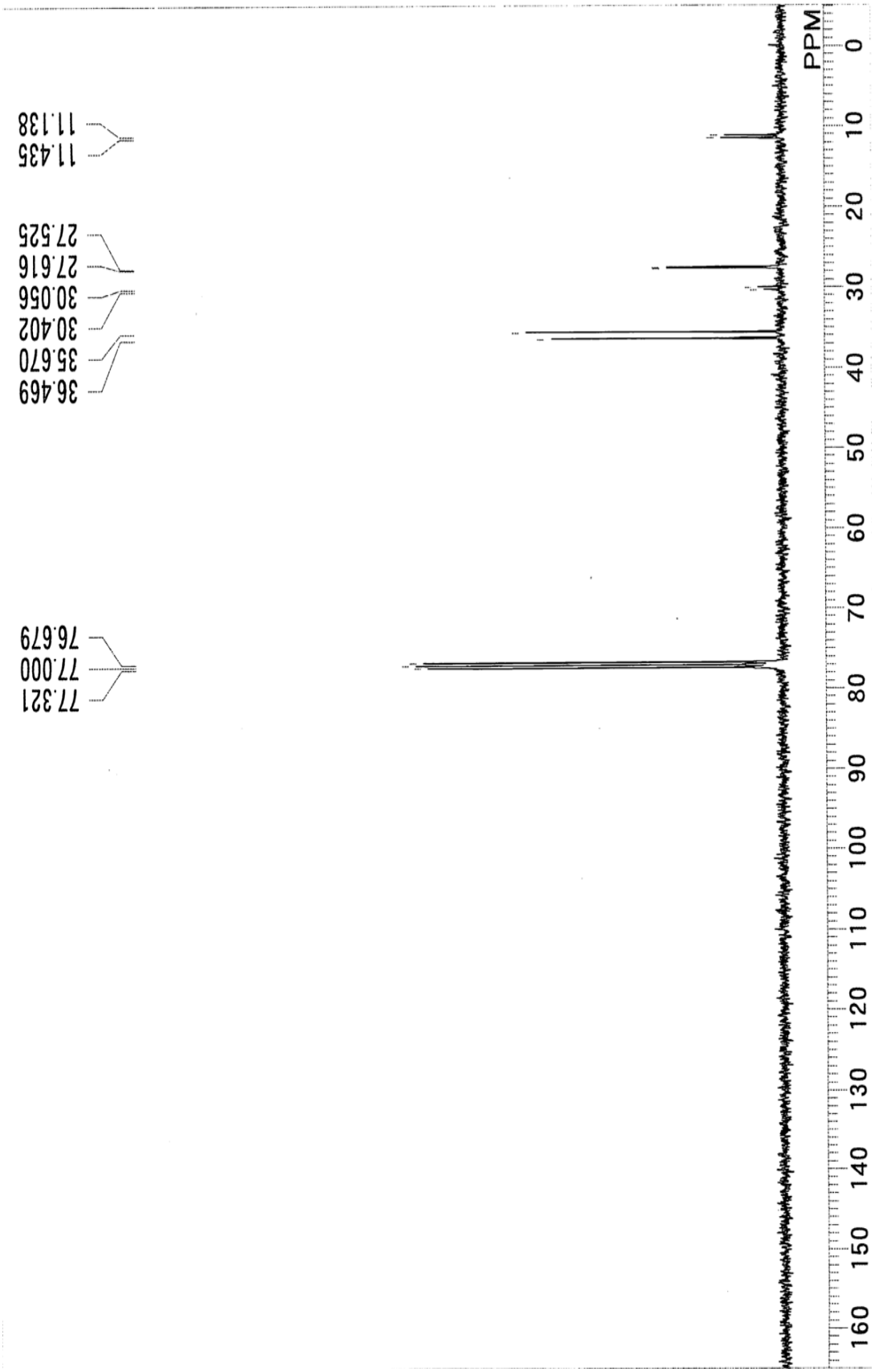
^{31}P NMR spectrum of *trans*-2e–BH_3



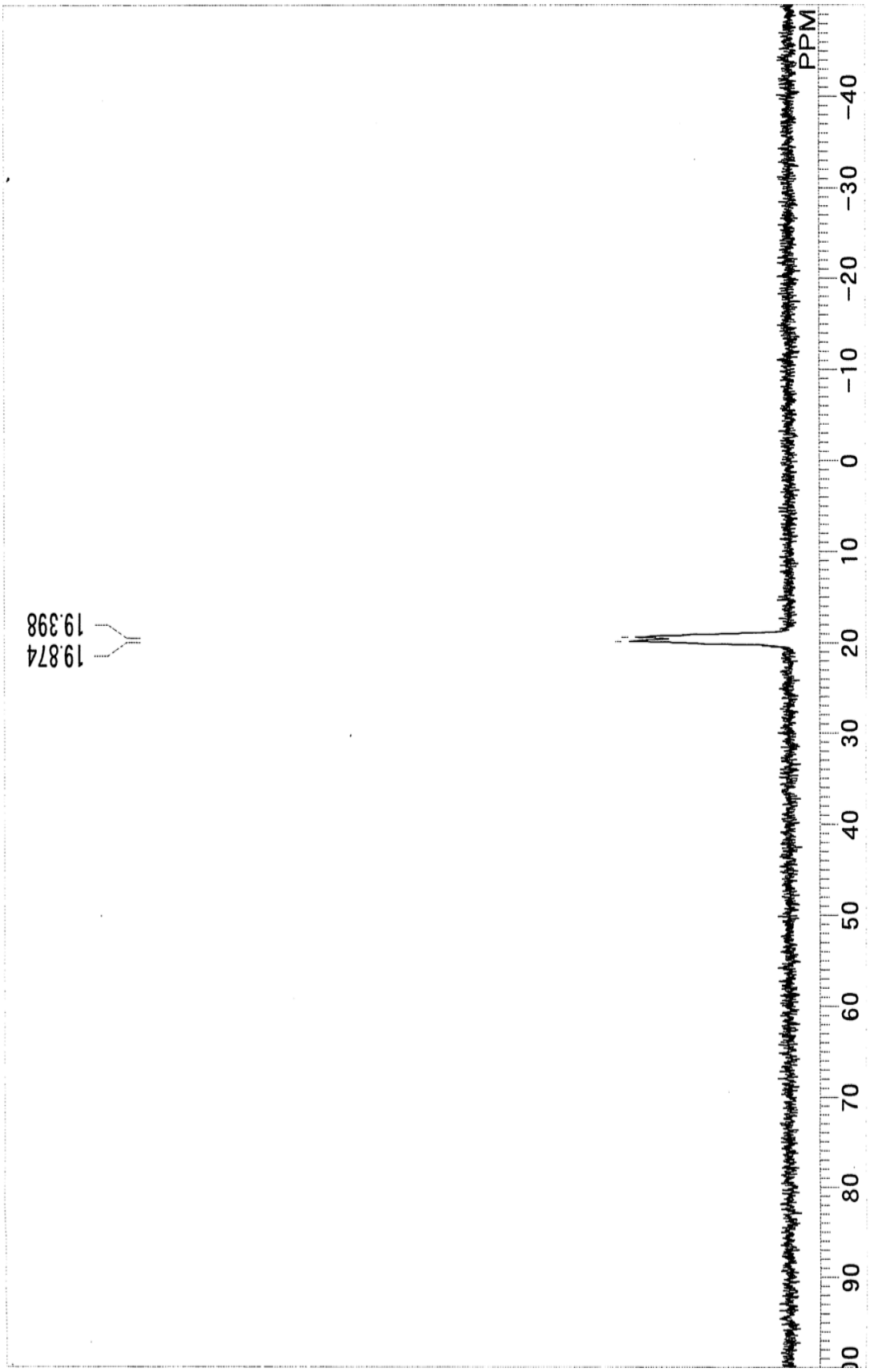
^{1}H NMR spectrum of *trans*-2f–BH_3



^{13}C NMR spectrum of *trans*-2f–BH_3



^{31}P NMR spectrum of *trans*-2f–BH_3



X-ray crystal structure analysis

Intensity data were collected on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The structures were solved by direct method (SIR97)[5] and refined by full-matrix least-squares procedures based on F^2 (SHELX-97).[6]

***trans*-2a–BH_3** (CCDC # 888064)

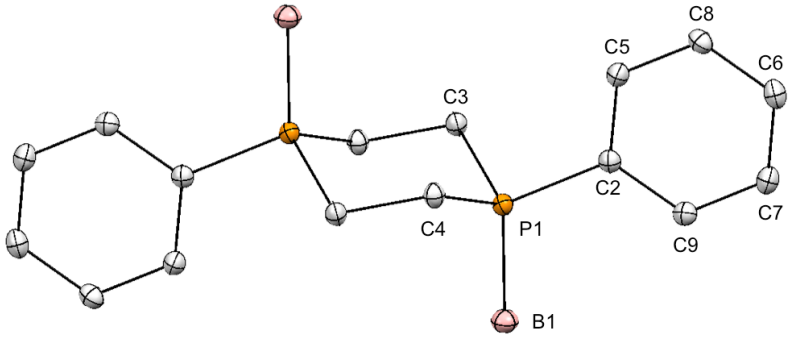


Table S1. Crystallographic data and selected bond lengths (Å) and angles (deg).

Formula	$C_{16}H_{24}B_2P_2$	P1–B1	1.9022(19)
Formula weight	299.91	P1–C2	1.8098(19)
Data collection temperature (K)	99(2)	P1–C3	1.8145(18)
Wavelength (Å)	0.71075	P1–C4	1.816(2)
Crystal system	triclinic	B1–P1–C2	115.20(9)
Space group	*P -1*	B1–P1–C3	112.34(9)
a (Å)	6.761(3)	B1–P1–C4	113.15(9)
b (Å)	7.616(4)	C2–P1–C3	106.02(8)
c (Å)	9.075(6)	C2–P1–C4	104.95(8)
α (deg)	99.12(3)	C3–P1–C4	104.24(8)
β (deg)	109.96(3)		
γ (deg)	100.07(2)		
Volume (Å^3)	420.3(4)		
Z	1		
Calculated density (g cm^{-3})	1.185		
Absorption coefficient	0.246		
F(000)	160		
Crystal size (mm)	0.30 × 0.30 × 0.10		
Crystal color	colorless		
θ range for data collection	3.26–27.48		
Limiting indices	$-8 \le h \le 8$ $-9 \le k \le 9$ $-11 \le l \le 11$		
Reflections collected	3882/1897 *R*(int) = 0.0491		
Completeness to theta	= 27.48 0.986		
Max. and min. transmission	0.9759 and 0.9300		
Goodness-of-fit on F^2	1.092		
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0441 wR_2 = 0.1373		
R indices (all data)	R_1 = 0.0487 wR_2 = 0.1409		

***trans*-2b–BH$_3$** (CCDC # 888063)

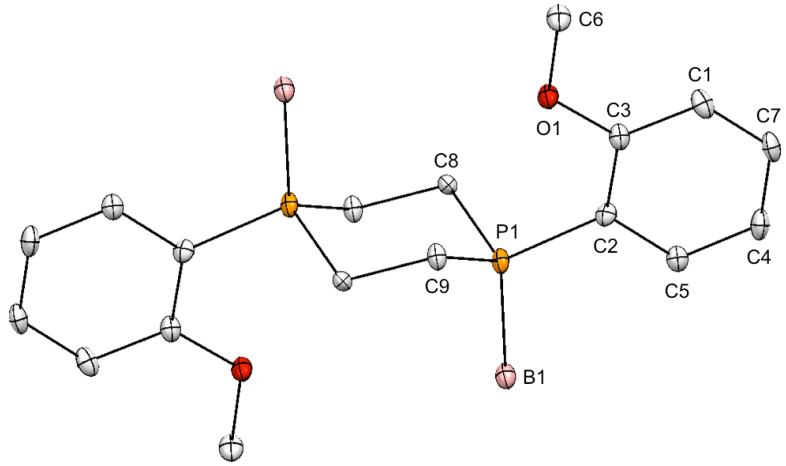


Table S2. Crystallographic data and selected bond lengths (Å) and angles (deg).

Formula	$C_{18}H_{28}B_2P_2$	P1–B1	1.911(5)
Formula weight	359.96	P1–C2	1.819(4)
Data collection temperature (K)	99(2)	P1–C8	1.829(4)
Wavelength (Å)	0.71075	P1–C9	1.820(4)
Crystal system	triclinic	O1–C3	1.361(5)
Space group	*P -1*	O1–C6	1.436(5)
a (Å)	7.5390(8)	B1–P1–C2	113.16(18)
b (Å)	7.7193(9)	B1–P1–C8	114.35(18)
c (Å)	9.4210(10)	B1–P1–C9	110.5(2)
α (deg)	68.586(3)	C2–P1–C8	104.52(17)
β (deg)	66.988(3)	C2–P1–C9	109.75(16)
γ (deg)	78.362(3)	C8–P1–C9	104.05(18)
Volume (Å^3)	468.68(9)	C3–O1–C6	118.5(3)
Z	1		
Calculated density (g cm^{-3})	1.275		
Absorption coefficient	0.240		
F(000)	192		
Crystal size (mm)	0.40 × 0.40 × 0.30		
Crystal color	colorless		
θ range for data collection	3.12–27.46		
Limiting indices	$-9 \le h \le 9$ $-10 \le k \le 10$ $-12 \le l \le 12$		
Reflections collected	4471/2126 *R*(int) = 0.0469		
Completeness to theta	= 27.46 0.990		
Max. and min. transmission	0.9316 and 0.9103		
Goodness-of-fit on F^2	1.121		
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0662 wR_2 = 0.1872		
R indices (all data)	R_1 = 0.0896 wR_2 = 0.2599		

***trans*-2c–BH_3** (CCDC # 888062)

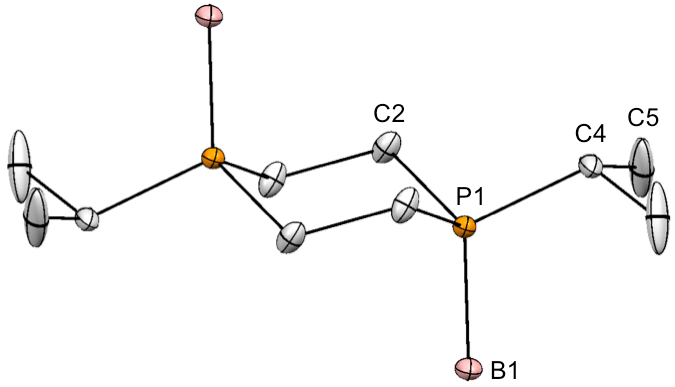


Table S3. Crystallographic data and selected bond lengths (Å) and angles (deg).

Formula	$C_{10}H_{28}B_2P_2$	P1–B1	1.920(3)
Formula weight	231.88	P1–C2	1.821(2)
Data collection temperature (K)	113(2)	P1–C4	1.825(3)
Wavelength (Å)	0.71075	B1–P1–C2	113.61(9)
Crystal system	monoclinic	B1–P1–C4	113.88(14)
Space group	*C 2/m*	C2–P1–C4	106.14(9)
a (Å)	6.4533(11)		
b (Å)	10.4179(18)		
c (Å)	10.7786(19)		
α (deg)	90.00		
β (deg)	100.945(5)		
γ (deg)	90.00		
Volume (Å^3)	711.5(2)		
Z	2		
Calculated density (g cm^{-3})	1.082		
Absorption coefficient	0.271		
F(000)	256		
Crystal size (mm)	0.30 × 0.30 × 0.10		
Crystal color	colorless		
θ range for data collection	3.76–25.00		
Limiting indices	$-7 \le h \le 7$ $-12 \le k \le 12$ $-12 \le l \le 12$		
Reflections collected	2710/667 *R*(int) = 0.0304		
Completeness to theta	= 25.00 0.997		
Max. and min. transmission	0.9734 and 0.9230		
Goodness-of-fit on F^2	1.074		
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0422 wR_2 = 0.1019		
R indices (all data)	R_1 = 0.0431 wR_2 = 0.1024		

***trans*-2d–BH$_3$** (CCDC # 888065)

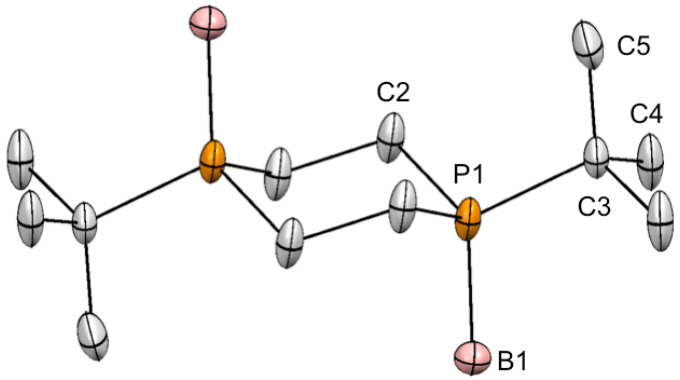


Table S4. Crystallographic data and selected bond lengths (Å) and angles (deg).

Formula	$C_{12}H_{32}B_2P_2$	P1–B1	1.875(10)
Formula weight	259.94	P1–C2	1.812(6)
Data collection temperature (K)	103(2)	P1–C3	1.833(8)
Wavelength (Å)	0.71075	B1–P1–C2	112.1(3)
Crystal system	orthorhombic	B1–P1–C3	114.3(5)
Space group	*C mca*	C2–P1–C3	107.2(3)
a (Å)	9.855(5)		
b (Å)	7.719(3)		
c (Å)	7.719(3)		
α (deg)	90.00		
β (deg)	90.00		
γ (deg)	90.00		
Volume (Å^3)	1595.4(12)		
Z	4		
Calculated density (g cm^{-3})	1.082		
Absorption coefficient	0.249		
F(000)	576		
Crystal size (mm)	0.10 × 0.10 × 0.10		
Crystal color	colorless		
θ range for data collection	3.49–24.99		
Limiting indices	$-11 \le h \le 11$ $-9 \le k \le 9$ $-23 \le l \le 24$		
Reflections collected	5886/747 *R*(int) = 0.1977		
Completeness to theta	= 24.99 0.997		
Max. and min. transmission	0.9756 and 0.9756		
Goodness-of-fit on F^2	1.121		
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1159 wR_2 = 0.2503		
R indices (all data)	R_1 = 0.1459 wR_2 = 0.2702		

***trans*-2e–BH_3** (CCDC # 888061)

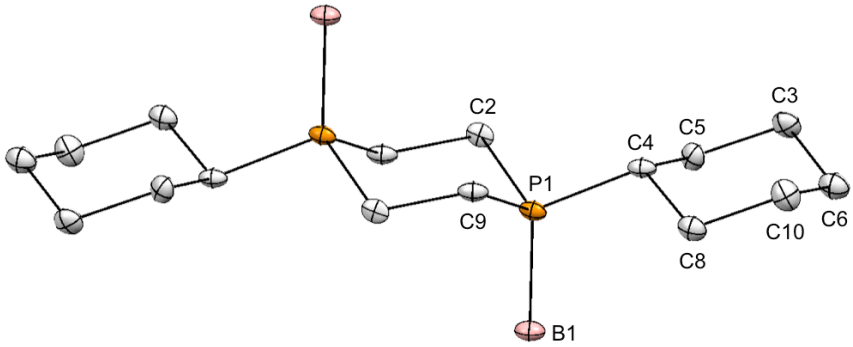


Table S5. Crystallographic data and selected bond lengths (Å) and angles (deg).

Formula	$C_{16}H_{36}B_2P_2$	P1–B1	1.921(4)
Formula weight	312.01	P1–C2	1.832(4)
Data collection temperature (K)	113(2)	P1–C4	1.824(4)
Wavelength (Å)	0.71075	P1–C9	1.818(4)
Crystal system	triclinic	B1–P1–C2	114.29(16)
Space group	*P -1*	B1–P1–C4	114.34(18)
a (Å)	6.2592(11)	B1–P1–C9	112.85(18)
b (Å)	6.4285(11)	C2–P1–C4	106.25(16)
c (Å)	13.9937(19)	C2–P1–C9	102.52(16)
α (deg)	86.181(5)	C4–P1–C9	105.51(16)
β (deg)	85.696(6)		
γ (deg)	56.746(5)		
Volume ($Å^3$)	469.32(13)		
Z	1		
Calculated density (g cm^{-3})	1.104		
Absorption coefficient	0.222		
F(000)	172		
Crystal size (mm)	0.30 × 0.30 × 0.20		
Crystal color	colorless		
θ range for data collection	3.66–27.48		
Limiting indices	$-8 \le h \le 8$ $-8 \le k \le 8$ $-18 \le l \le 18$		
Reflections collected	4562/2125 *R*(int) = 0.0469		
Completeness to theta	= 27.48 0.992		
Max. and min. transmission	0.9570 and 0.9365		
Goodness-of-fit on F^2	1.223		
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0690 wR_2 = 0.1903		
R indices (all data)	R_1 = 0.937 wR_2 = 0.2679		

***trans*-2f–BH$_3$** (CCDC # 888060)

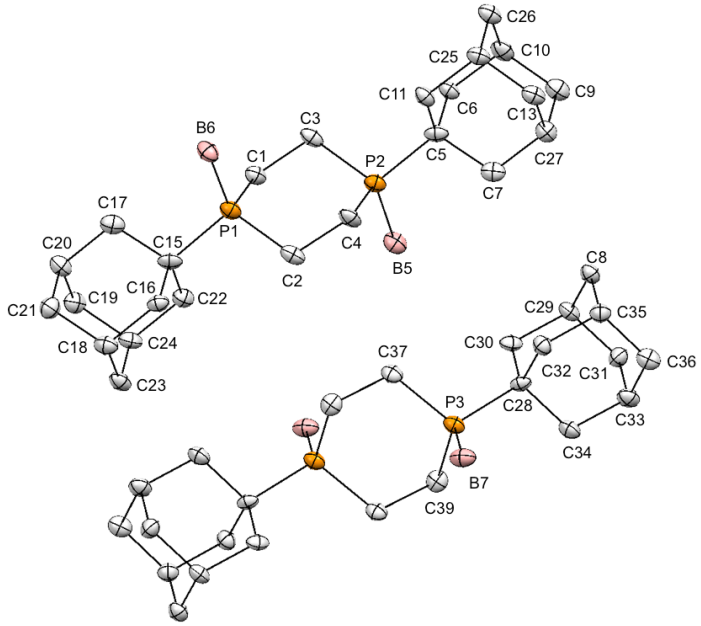


Table S6. Crystallographic data and selected bond lengths (Å) and angles (deg).

Formula	$C_{24}H_{44}B_2P_2$	P1–B6	1.906(7)
Formula weight	416.15	P1–C1	1.818(7)
Data collection temperature (K)	113(2)	P1–C2	1.803(7)
Wavelength (Å)	0.71075	P1–C15	1.840(7)
Crystal system	triclinic	P2–B5	1.930(7)
Space group	*P -1*	P2–C3	1.820(7)
a (Å)	6.5327(6)	P2–C4	1.830(6)
b (Å)	17.0615(15)	P2–C5	1.826(7)
c (Å)	17.6621(16)	B6–P1–C1	110.7(3)
α (deg)	62.126(2)	B6–P1–C2	113.5(3)
β (deg)	86.044(2)	B6–P1–C15	113.4(3)
γ (deg)	83.785(2)	C1–P1–C2	104.3(3)
Volume (Å^3)	1729.6(3)	C1–P1–C15	107.0(3)
Z	3	C2–P1–C15	107.3(3)
Calculated density (g cm^{-3})	1.199	B5–P2–C3	113.4(3)
Absorption coefficient	0.197	B5–P2–C4	110.9(3)
F(000)	684	B5–P2–C5	114.2(3)
Crystal size (mm)	0.80 × 0.20 × 0.20	C3–P2–C4	103.0(3)
Crystal color	colorless	C3–P2–C5	107.9(3)
θ range for data collection	3.14–24.50	C4–P2–C5	106.7(3)
Limiting indices	$-7 \le h \le 7$ $-19 \le k \le 19$ $-20 \le l \le 20$	P3–B7	1.908(8)
		P3–C28	1.843(6)
		P3–C37	1.810(6)
Reflections collected	12728/5671 *R*(int) = 0.0935	P3–C39	1.807(6)
		B7–P3–C28	112.4(3)
Completeness to theta	= 24.50 0.983	B7–P3–C37	113.0(3)
		B7–P3–C39	112.0(3)
Max. and min. transmission	0.9616 and 0.8582	C28–P3–C37	106.9(3)
Goodness-of-fit on F^2	1.031	C28–P3–C39	108.8(3)
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0954 wR_2 = 0.2362	C37–P3–C39	103.2(3)
R indices (all data)	R_1 = 0.1781 wR_2 = 0.3389		

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