Facile Synthesis of Highly Congested 1,2-Diphosphinobenzenes from Bis(phosphine)boronium Salts

Supporting Information

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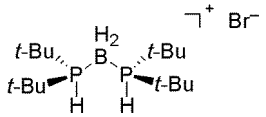
General. All manipulations were carried out under nitrogen atmosphere. NMR spectra were recorded on a JEOL JNM-ECX (400 MHz for ^{1}H, 162 MHz for ^{31}P, and 100 MHz for ^{13}C). Chemical shifts were reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. IR spectra were recorded on a JASCO FT/IR-6300. Optical rotations were recorded on a JASCO P-1030 polarimeter with a sodium lamp. MS (ESI) spectra were recorded on JEOL JMS-T100LC spectrometers. HPLC analyses were performed on a Hitachi L-2130 pump, and L-2450 Diode Array detector with a chiral column. X-ray crystal structure data were collected using a Bruker SMART APEX II diffractmeter with Mo-Kα radiation.

Materials. All reagents were obtained from commercial sources and used without further purification. All solvents were freshly distilled. Compound **2** and (*R*)-**5** were prepared according to the literature procedure.[1]

Bis(di-*tert*-butylphosphine)boronium bromide (3a·Br)



Di-*tert*-butylchlorophosphine (1.08 mL, 6.0 mmol) was slowly added to a stirred suspension of lithium aluminum hydride (229 mg, 6.0 mmol) in Et_2O (5.0 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction mixture was passed through a column of basic alumina gel with ca. 15 mL of Et_2O elution. The volatiles were removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (10 mL). To the solution was added monobromoborane–methylsulfide complex (2.7 mL of 1.0 M CH_2Cl_2 solution, 2.7 mmol) at room temperature, and the mixture was stirred at intact temperature. After 40 h, the volatiles were removed *in vacuo*, and the residue was purified by column chromatography on silica gel with $CHCl_3$/MeOH (20/1 to 10/1) to give **3a**·Br as a white solid (743 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, J = 410 Hz, 2H), 1.7-0.6 (m, 2H), 1.49 (d, J = 15 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.9 (m), 28.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.8 (d, J = 95 Hz); IR (KBr) 2990, 2966, 2433, 2404, 2302, 1474, 820 cm^{-1}; MS (ESI) *m/z* 305 (M–Br); Anal. Calcd. for: C, 49.89; H, 10.47. Found: C, 49.97; H, 10.51.

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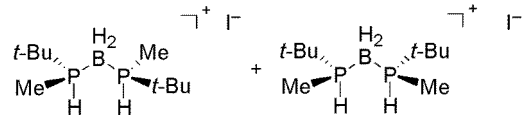
[1]Katagiri, K.; Danjo, H.; Yamaguchi, K.; Imamoto, T. *Tetrahedron* **2005**, *61*, 4701-4707

(*S,S*)-Bis(*tert*-butyl(methyl)phosphine)boronium Iodide (3b·I) and Its meso-Isomer

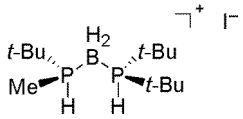


The mixture of K_2CO_3 (25.4 g, 183 mmol) and *tert*-butylmethylphosphonium iodide (8.5 g, 36.6 mmol) was stirred in CH_2Cl_2 (50 mL) at room temperature. After 1 h, the solution was passed through a column of basic alumina gel with CH_2Cl_2 elution to give CH_2Cl_2 solution of rac-*tert*-butyl(methyl)lphosphine. To the solution was added dropwise the mixture of iodine (2.32 g, 9.16 mmol) and (*S*)-*tert*-butyl(methyl)phosphine-borane (2.16 g, 18.3 mmol) in CH_2Cl_2, which was previously stirred at room temperature for 7 h. After 24 h, borane–THF complex (27.5 mL of 1.0 M THF solution, 27.5 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 30 min (to trap the remaining free phosphine). The reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined extract was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel (chloroform/methanol = 20/1 to 10/1) to give a diastereomeric mixture of **3b**·I as a white solid (4.44 g, 70%). Diastereomerically enriched (*S*,*S*)-**3b**·I could be obtained by recrystallization from THF (96% de).

***meso*-3b·I**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (dm, *J* = 416 Hz, 2H), 2.2-0.7 (m, 2H), 1.71 (dd, *J* = 6 Hz, *J* = 6 Hz 6H), 1.30 (d, *J* = 16 Hz, 18H); ^{31}P NMR (162 MHz, $CDCl_3$) δ –3.7 (m).

(*S,S*)- 3b·I: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (dm, *J* = 416 Hz, 2H), 2.2-0.7 (m, 2H), 1.74 (dd, *J* = 6 Hz, *J* = 6 Hz, 6H), 1.29 (d, *J* = 16 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.8 (d, *J* = 43 Hz), 26.1, 27.1 (d, *J* = 47 Hz), 28.4, 28.2, 27.6 (dd, *J* = 7 Hz, *J* = 40 Hz), 26.1, 2.7 (d, *J* = 41 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ –3.7 (m). IR (KBr) 2959, 2903, 2865, 2431, 2337, 1465, 893, 868, 808 cm^{-1}; $[\alpha]_D^{25}$ = 23.1 (*c* 1.0, $CHCl_3$); HRMS (ESI): *m/z* Calcd. for $C_{20}H_{56}B_2IP_4$ (2M–I): 569.2563. Found 569.25684.

(*S*)-(*tert*-Butyl(methyl)phosphine)(di-*tert*-butylphosphine)boronium Iodide ((*S*)-3c·I)



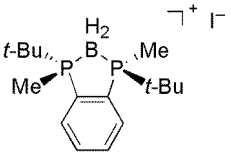
Chloro-di-*tert*-butylphosphine (627 μL, 3.30 mmol) was slowly added to a stirred suspension of lithium aluminum hydride (133 mg, 3.48 mmol) in Et_2O (4.0 mL) at 0 °C, and the mixture was stirred at room temperature. After 1 h, the solution was passed through a column of basic alumina gel with ca. 10 mL of Et_2O elution. The volatiles were removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5 mL). To the solution was added dropwise the mixture of iodine (323 mg, 1.27 mmol) and (*S*)-*tert*-butyl(methyl)phosphine–borane (300 mg, 2.54 mmol) in CH_2Cl_2, which was previously stirred at room temperature for 7 h. After stirring at room temperature for 24 h, borane–THF complex (1.0 mL of 1.2 M THF solution, 1.3 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 30 min (to trap the remaining free phosphine). The reaction mixture was diluted with water and extracted with CH_2Cl_2, and the combined extract was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel (chloroform/methanol = 20/1 to 10/1) to give **3c**·I as a white solid (793 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ; 6.77 (dm, *J* = 403 Hz, 1H), 5.84 (dm, *J* = 402 Hz, 1H), 2.2-0.7 (m, 2H), 1.77 (dd, *J* = 6 Hz, *J* = 6 Hz 3H), 1.48 (d, *J* = 16 Hz, 9H), 1.41 (d, *J* = 16 Hz, 9H), 1.30 (d, *J* = 16 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.6 (d, *J* = 31 Hz), 31.9 (dd, *J* = 6 Hz, *J* = 31 Hz), 28.4, 28.2, 27.6 (dd, *J* = 7 Hz, *J* = 40 Hz), 26.1, 2.7 (d, *J* = 41 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ17.5 (d, *J* = 91 Hz), –0.1 (d, *J* = 100 Hz); IR (KBr) 2990, 2963, 2943, 2891, 2866, 2454, 2416, 2296, 1470, 1372, 1192, 847 cm^{-1}; $[\alpha]_D^{23}$ = 13.5 (*c* 1.0, $CHCl_3$);

MS (ESI) m/z 263 (M–I); Anal. Calcd. for: C, 40.03; H, 8.79. Found: C, 39.88; H, 8.63.

Typical Procedure for the Preparation of [1,2-Bis(dialkylphosphino)benzene-κ^2P,P']boronium Salts

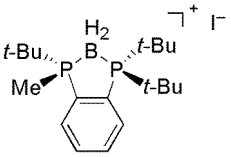
To a suspension of bis(dialkylphosphine)boronium salt (0.74 mmol) and *N,N,N',N'*-tetramethylethylenediamine (225 μL, 0.74 mmol) in THF (2 mL) was added *n*-BuLi (930 μL of 1.6 M *n*-hexane solution, 1.48 mmol) at –78 °C, and the mixture was warmed to room temperature. After 30 min, a solution of 1,2-difluorobenzenetricarbonylchromium (**2**) (0.74 mmol) in THF (2 mL) was added to the reaction mixture at –78°C. After stirring for an additional 24 h at –40 °C, the reaction mixture was diluted with water and extracted with $CHCl_3$. The combined extract was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel (chloroform/methanol = 20/1 to 10/1) to give a yellow solid. The solution of a yellow solid in chloroform was exposed to UV under air at room temperature for 1 h. The mixture was passed through a celite pad to give [1,2-bis(dialkylphosphino)benzene-κ^2P,P']boronium salt.

(*R*,*R*)-[1,2-Bis(*tert*-butyl(methyl)phosphino)benzene-κ^2P,P']boronium Iodide ((*R*,*R*)-4b·I)



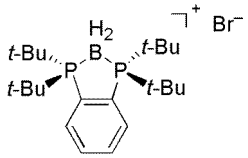
87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (m, 2H), 8.00 (m, 2H), 2.02 (d, *J* =11 Hz, 6H), 1.24 (d, *J* = 16.5 Hz, 18H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9 (s), 134.4 (s), 133 (t, *J* = 6.5 Hz), 30.6 (m), 25.0 (s), 7.43 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.3 (d, *J* = 91 Hz); IR (KBr) 2968, 2457, 2418,1471, 1122, 896, 769, 666 cm^{-1}; $[\alpha]_D^{26}$ = –45.5 (*c* 1.0, $CHCl_3$); HRMS (ESI): *m/z* Calcd. for $C_{32}H_{60}B_2IP_4$ (2M–I): 717.2876. Found 717.29327. The ee of the compound was determined to be >99% using HPLC analysis on a SUMICHIRAL OA-7000 column. pH 3.0 phosphate buffer/acetonitrile = 70:30, flow rate: 1 mL/min (retention times: 12.3 min (*meso*), 15.8 min (*R*,*R*), 29.2 min (*S*,*S*)).

(*R*)-[(1-*tert*-Butyl(methyl)phosphino-2-di-*tert*-butylphosphino)benzene-κ^2P,P']boronium Iodide ((*R*)-4c·I)



83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.33 (m, 1H), 8.05-8.09 (m, 1H), 7.95-8.02 (m, 2H), 2.3-0.8 (m, 2H), 1.89 (d, *J* = 11 Hz, 3H), 1.47 (d, *J* = 15 Hz, 9H), 1.33 (d, *J* = 15 Hz, 9H) 1.29 (d, *J* = 15 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2 (d, *J* = 20 Hz), 135.7 (d, *J* = 20 Hz), 134.7-134.6 (m), 134.3-134.2 (m), 133.9-133.7 (m), 133.6-133.4 (m), 121.0 (d, *J* = 319 Hz), 35.5 (dd, *J* =4 Hz, *J* = 28 Hz), 34.6 (d, *J* = 28 Hz), 31.9 (dd, *J* =4 Hz, *J* = 36 Hz), 28.8, 27.7, 25.4, 6.8 (dd, *J* = 4 Hz, *J* = 38 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.5 (d, *J* = 95 Hz), 37.0 (d, *J* = 91 Hz); IR (KBr) 3086, 2980, 2875, 2474, 2434, 1473, 1262, 1223, 1144, 1030, 896, 760, 637 cm^{-1}; $[\alpha]_D^{23}$ = –12.9 (*c* 1.0, $CHCl_3$); Anal. Calcd. for: C, 49.39; H, 7.46. Found: C, 49.45; H, 7.20.

[1,2-Bis(di-*tert*-butylphosphino)benzene-κ^2P,P']boronium Bromide (4a·Br))



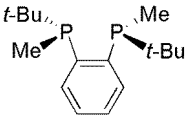
To a suspension of **3a** (154 mg, 0.4 mmol) and hexamethylphosphoramide (330 μL, 2.0 mmol) in THF (1 mL) was added *n*-BuLi (930 μL of 1.6 M hexane solution, 1.48 mmol) at –78 °C and the mixture was warmed to room temperature. After 1 h, to this mixture was added chromium complex **2** (50 mg, 0.2 mmol) in THF (2 mL) at –78 °C and the mixture was warmed to 70 °C. After 24 h, H_2O (5 mL) and $CHCl_3$ (7 mL) were added, and the layers were allowed to separate. After the organic layer was collected, the aqueous layer was extracted with $CHCl_3$ (7 mL) twice, and the combined organic extract was dried over Na_2SO_4. After the solution was filtered, the volatiles were removed *in vacuo*, and the residue

was purified by column chromatography on silica gel eluting with $CHCl_3$/MeOH (20/1 to 10/1 to 3/1) to give **4a**·Br as a white solid (57.4 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.21 (m, 2H), 8.18-8.15 (m, 2H), 2.3-0.8 (m, 2H), 1.46 (d, *J* = 15 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4-134.7 (m), 135.1-135.0 (m), 134.5, 36.8 (t, *J* = 30 Hz), 29.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.8 (d, *J* = 95 Hz); IR (KBr) 2989, 2968, 2872, 2483, 2445, 1371, 1181, 1108, 789, 674; HRMS (ESI): *m/z* Calcd. for $C_{22}H_{42}BP_2$ (M–Br): 379.2855. Found 379.2891; Anal. Calcd. for: C, 57.54; H, 9.22. Found: C, 57.18; H, 9.09.

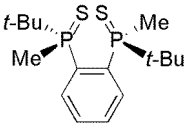
Typical Procedure for the Preparation of 1,2-Diphosphines

A mixture of boronium salt (0.1 mmol) and tetrabutylammonium fluoride trihydrate (63.1 mg, 0.2 mmol) in chrolobenzene (3 mL) was stirred at 70 °C. After 48 h, the reaction mixture was cooled to room temperature, and the volatiles were removed *in vacuo*. Et_2O was added to the residue and the mixture was passed through a column of basic alumina gel with ca. 10 mL of Et_2O elution. The volatiles were removed *in vacuo* to give a 1,2-diphosphines.

(*R*,*R*)-1,2-Bis(*tert*-butyl(methyl)phosphino)benzene ((*R*,*R*)-1b)

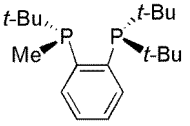


78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (sep, *J* = 2.7, 2H), 7.32 (m, 2H), 1.22 (t, *J* = 3.2 Hz, 6H), 0.95 (t, *J* = 6.4 Hz, 18H); ^{31}P NMR (162 MHz, $CDCl_3$) δ –25.1 (s).

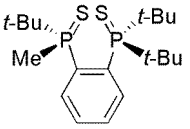


The enantiomeric excess of this diphosphine was determined after converted into diphosphine disulfide derivative by treatment with excess sulfur in refluxing hexane for 20 h. The product was isolated by preparative TLC (hexane/AcOEt = 5/1) and the ee of the compound was determined to be >99% using HPLC analysis on a Daicel CHIRALPAK AS-H column. EtOH/hexane = 1:99, flow rate: 1 mL/min (retention times: 20.5 min (*meso*), 23.3 min (*R*,*R*), 35.9 min (*S*,*S*)).

(*R*)-(1-*tert*-Butyl(methyl)phosphino-2-di-*tert*-butylphosphino)benzene ((*R*)-1c)

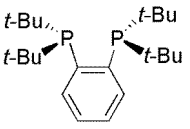


69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 1H), 7.58-7.55 (m, 1H), 7.29 (quin, *J* = 7.32, 2H), 1.29 (d, *J* = 11.8 Hz, 9H), 1.19 (d, *J* = 6.44, 3H), 1.10 (d, *J* = 11, 9H), 1.03 (d, *J* = 11.4, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.98 (d, *J* = 173), –24.80 (d, *J* = 173)



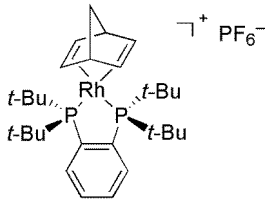
The enantiomeric excess of this diphosphine was determined after converted into diphosphine disulfide derivative by treatment with excess sulfur in refluxing hexane for 20 h. The product was isolated by preparative TLC (hexane/AcOEt = 5/1) and the ee of the compound was determined to be >99% using HPLC analysis on a Daicel CHIRALPAK AD-H column. iPrOH/hexane = 1:99, flow rate: 0.5 mL/min (retention times: 27.2 min (*R*), 30.4 min (*S*)).

1,2-Bis(di-*tert*-butylphosphino)benzene (1a)



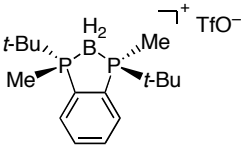
A mixture of boronium salt (45.9 mg, 0.1 mmol) and tetrabutylammonium fluoride trihydrate (94.7 mg, 0.3 mmol) in chrolobenzene (3 mL) was stirred at 70 °C. After 48 h, the reaction mixture was cooled to room temperature, and the volatiles were removed *in vacuo*. Et_2O was added to the residue and the mixture was passed through a column of basic alumina gel with ca. 10 mL of Et_2O elution. The volatiles were removed *in vacuo* to give a **1a** (57.4 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.29 (m, 2H), 1.21 (t, *J* = 5.96, 36H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21 (s).

[1a·Rh(nbd)]PF_6



A solution of $[RhCl(nbd)_2]PF_6$ (56.2 mg, 0.13 mmol) and 1,2-bis(di-*tert*-butylphosphino)benzene (**1a**) (51.2 mg, 0.14 mmol) in THF (5 mL) was stirred at room temperature for 10 h. The reaction mixture was passed through a Celite pad, and the volatiles were removed in vacuo. The residual solid was washed with hexane to give a red powder. Recrystallization from THF afforded red crystal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 2H), 7.65 (m, 2H), 5.64 (d, J = 2.3 Hz, 2H), 4.18 (s), 1.38 (d, J = 13.7 Hz, 36H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 81.0 (d, J = 152 Hz), –143.6 (quin, J = 715 Hz).

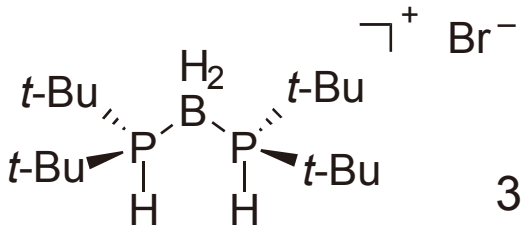
Preparation of (*R*,*R*)-4b·OTf According to the Stepwise Protocol.



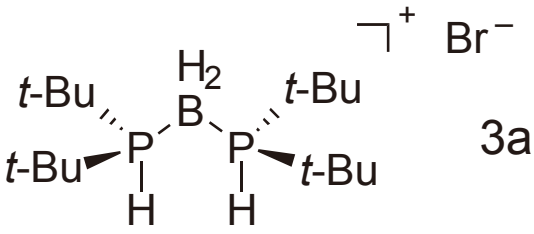
To a solution of (*S*)-*tert*-butyl(methyl)phosphine-borane (65 mg, 550 μmol) in benzene (1 mL) was slowly added trifluoromethanesulfonic acid (48 μL, 543 μmol) at room temperature. After 10 min, the volatiles were removed under reduced pressure. A solution of (*R*)-**5** (91.4 mg, 273 μmol) in CH_2Cl_2 (1 mL) was then added to the residue at room temperature under N_2, and the mixture was stirred at intact temperature. After 36 h, the volatiles were removed under reduced pressure, and the residue was subjected to column chromatography on silica gel eluting with $CHCl_3$/MeOH (1/0 to 10/1) to give int-**A** as a yellow solid (110 mg). To a solution of int-**A** in THF (2 mL) was added *s*-BuLi (181 μL of 1.01 M in cyclohexane/*n*-hexane solution, 183 μmol) at –78 °C, and the mixture was stirred at –40 °C. After 24 h, the reaction mixture was diluted with water and extracted with $CHCl_3$. The combined extract was dried over Na_2SO_4, and was exposed to UV under air at room temperature for 1 h. The mixture was passed through a Celite pad and concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel (chloroform/methanol = 1/0 to 10/1) to give (*R*,*R*)-**4b**·OTf as a white solid (70 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (m, 2H), 7.97 (m, 2H), 1.94 (d, J =11.0 Hz, 6H), 1.23 (d, J = 16.5 Hz, 18H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8 (s), 134.1 (t, J = 42Hz), 133 (t, J = 7.6 Hz), 121 (d, J = 318 Hz), 30.5 (m), 24.7 (s), 6.53 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.8 (d, J = 95 Hz); IR (KBr) 2971, 2468, 2424, 2342, 1471, 1280, 1260, 1152, 1030, 895, 770, 637 cm^{-1}; $[\alpha]_D^{22.5}$ = –28.8 (*c* 0.510, $CHCl_3$); HRMS (ESI): *m/z* Calcd. for $C_{33}H_{60}B_2F_3O_3P_4S$ $[2M\text{-}OTf]^+$ 739.33518. Found 739.33359. The enantiomeric excess was determined to be >99% (99% de) by chiral HPLC analysis after converted into **4b·I** by treatment with sat. aqueous NaI solution.

Typical Procedure for the Pd-catalyzed Hydroesterification of Unsaturated Compounds

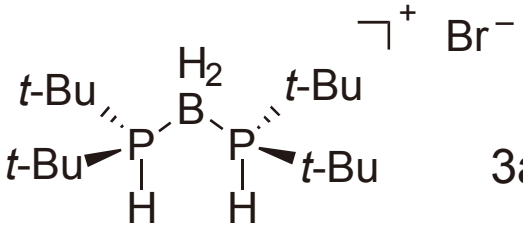
A 50 mL glass autoclave equipped with a pressure gauge and a stirring bar was charged with $Pd(OAc)_2$ (1.12 mg, 5.0 μmol) and **1a** (2.33 mg, 6.25 μmol). After the atmosphere was replaced with nitrogen, substrate (2.5 mmol), toluene (1 mL), and methanesulfonic acid (38.5 μmol, 2.5 μL) in ethanol (400 μL) was added to the reaction vessel. The autoclave was then immersed in a dryice/methanol bath and nitrogen atmosphere was replaced with carbon monoxide, pressurized to 6 atm, and then heated in a preheated oil bath at 80 °C. The mixture was left for 12 h under vigorous stirring, and after being allowed to ambient temperature, it was filtered through silica gel with ethyl acetate elution. After concentration under reduced pressure, the yield was determined by ^{1}H NMR.



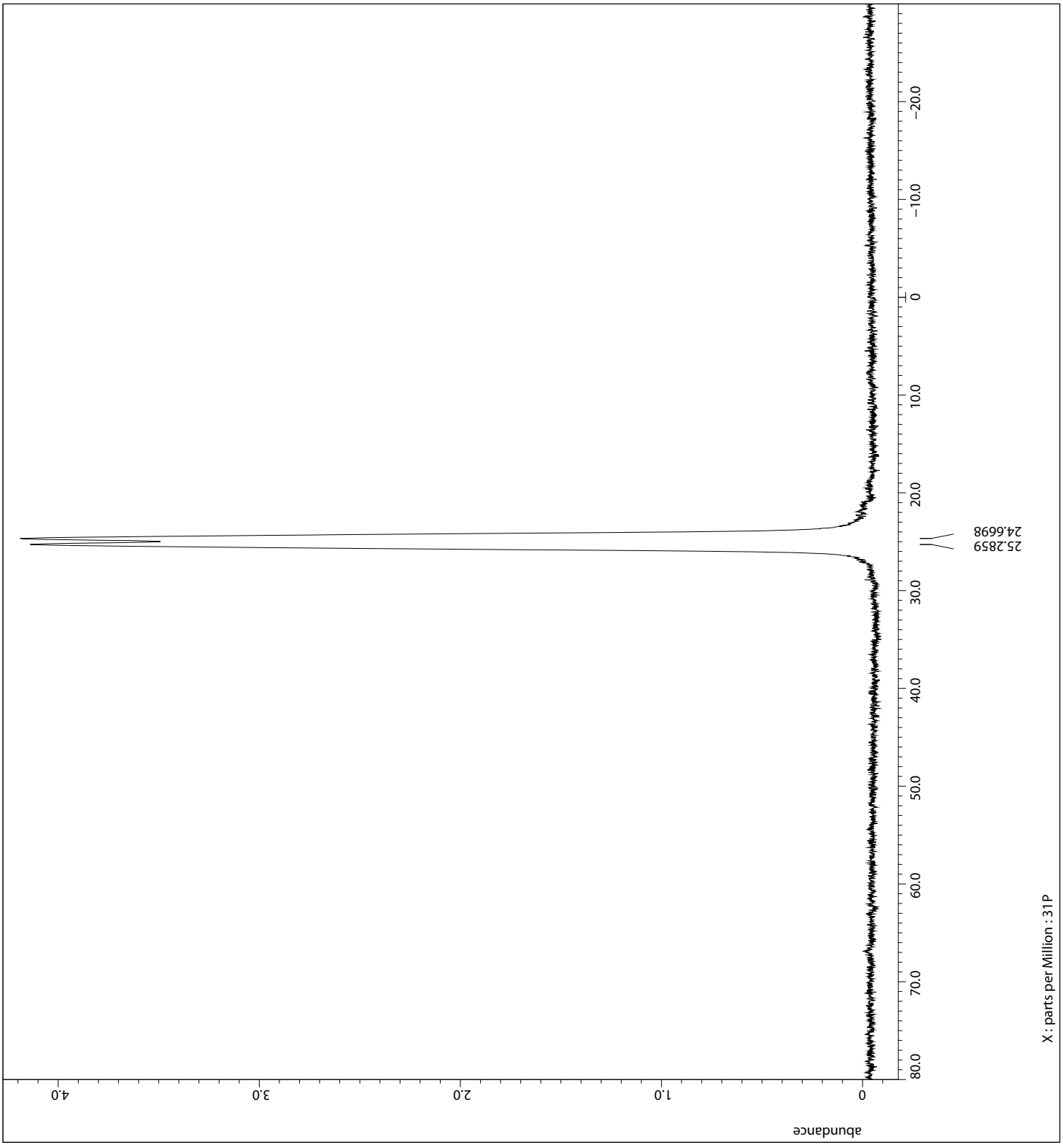
3a•Br, ^{1}H in $CDCl_3$ (400 MHz)

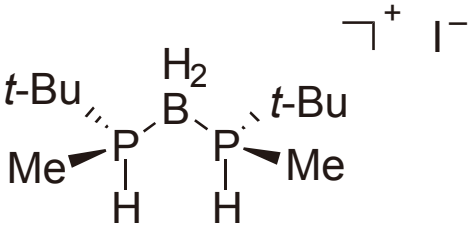


3a•Br, ^{13}C in $CDCl_3$ (100 MHz)

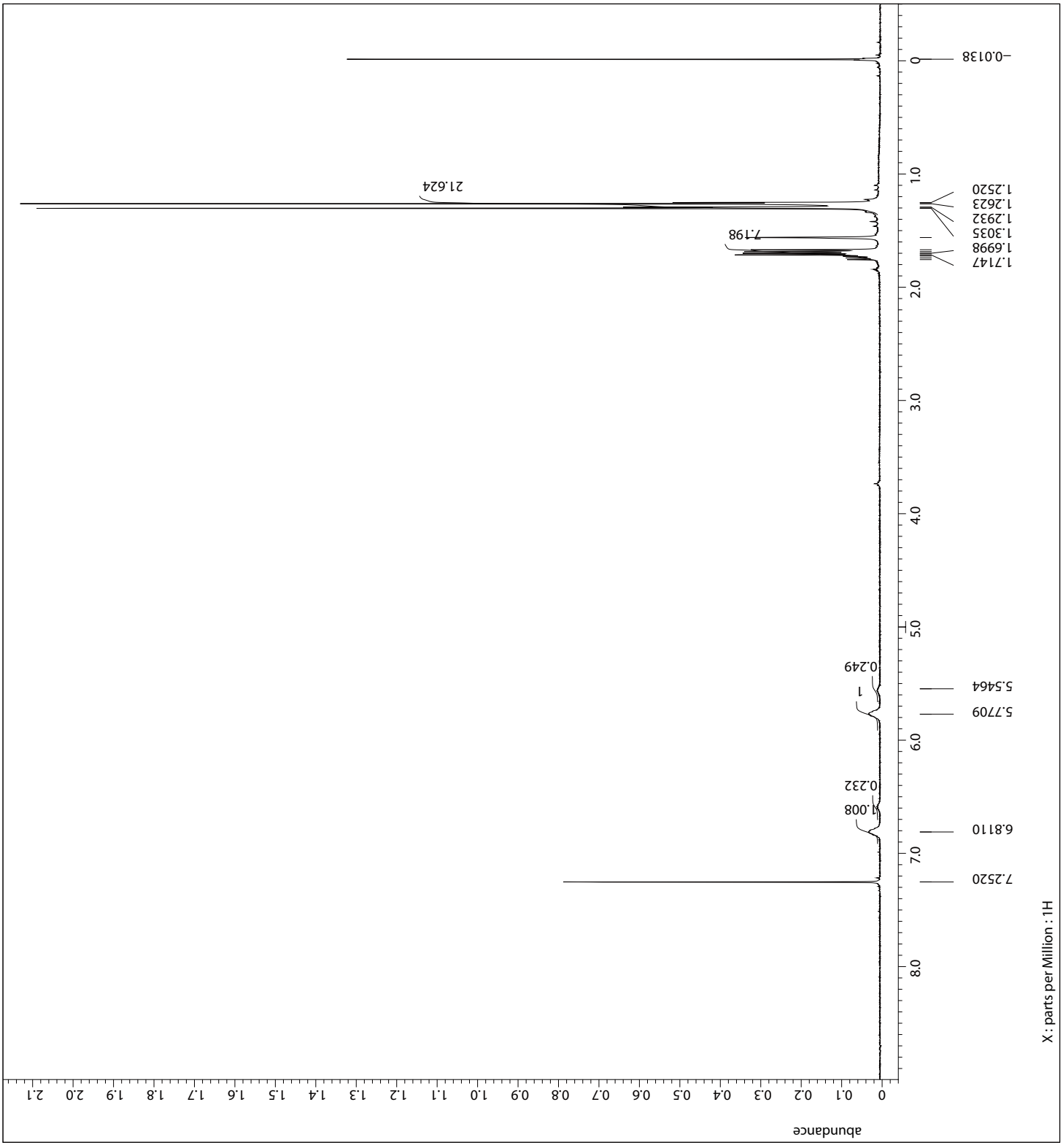


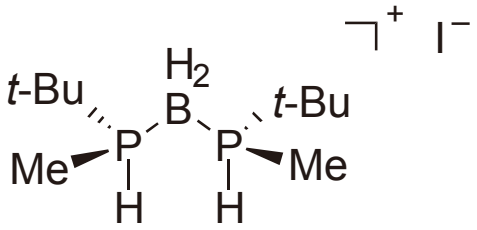
3a•Br, ^{31}P in $CDCl_3$ (162 MHz)



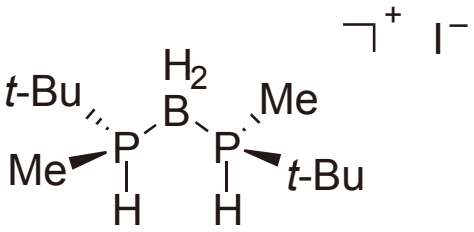


meso-3b•I, ^{1}H in $CDCl_3$ (400 MHz)

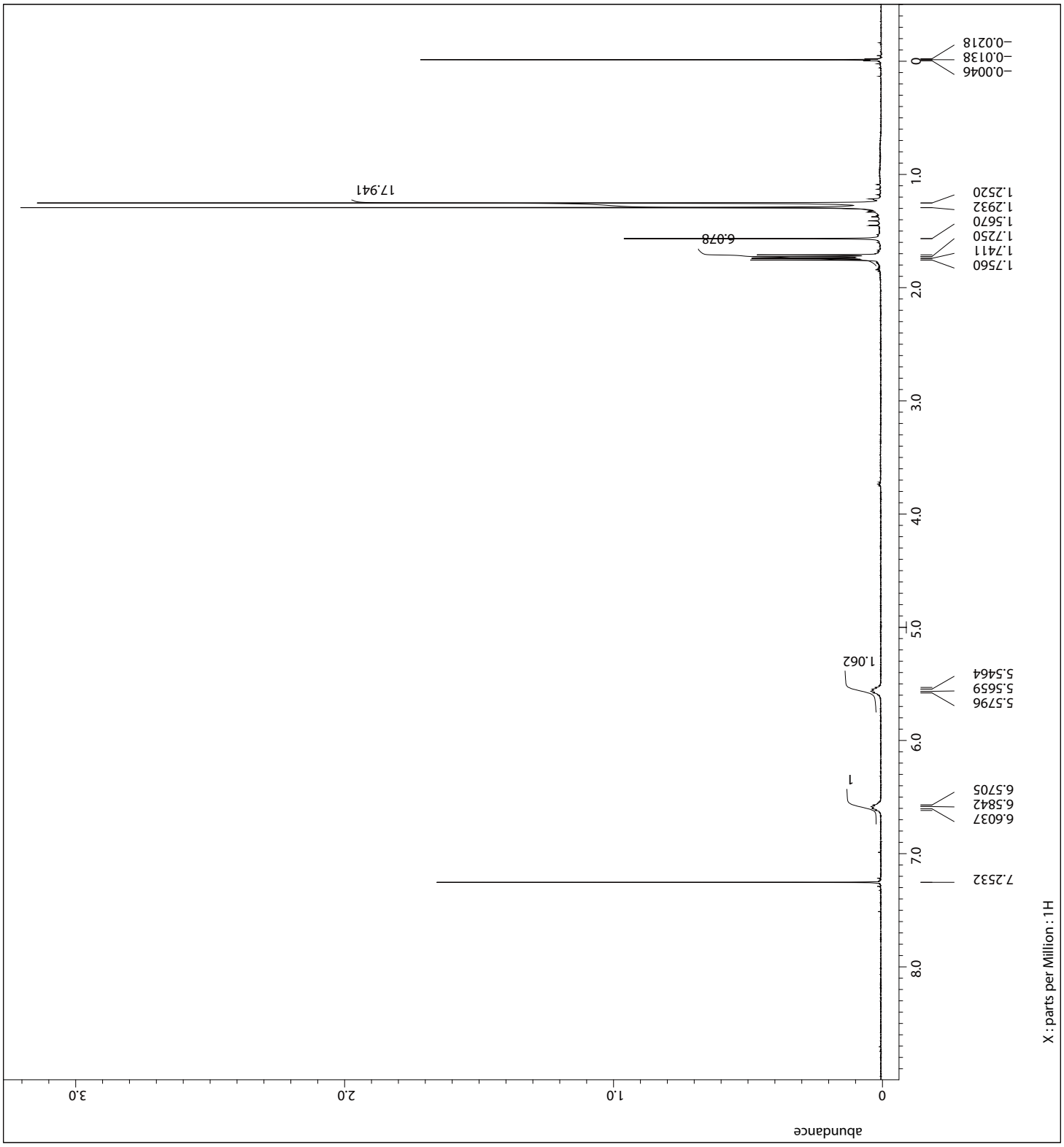


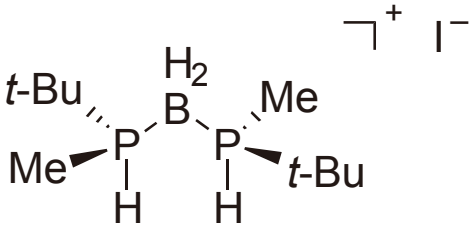


meso-3b•I, ^{31}P in $CDCl_3$ (162 MHz)

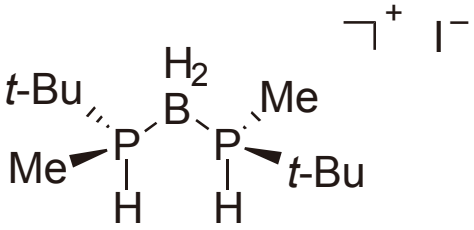


(*S*,*S*)-3b•I, ^{1}H in $CDCl_3$ (400 MHz)

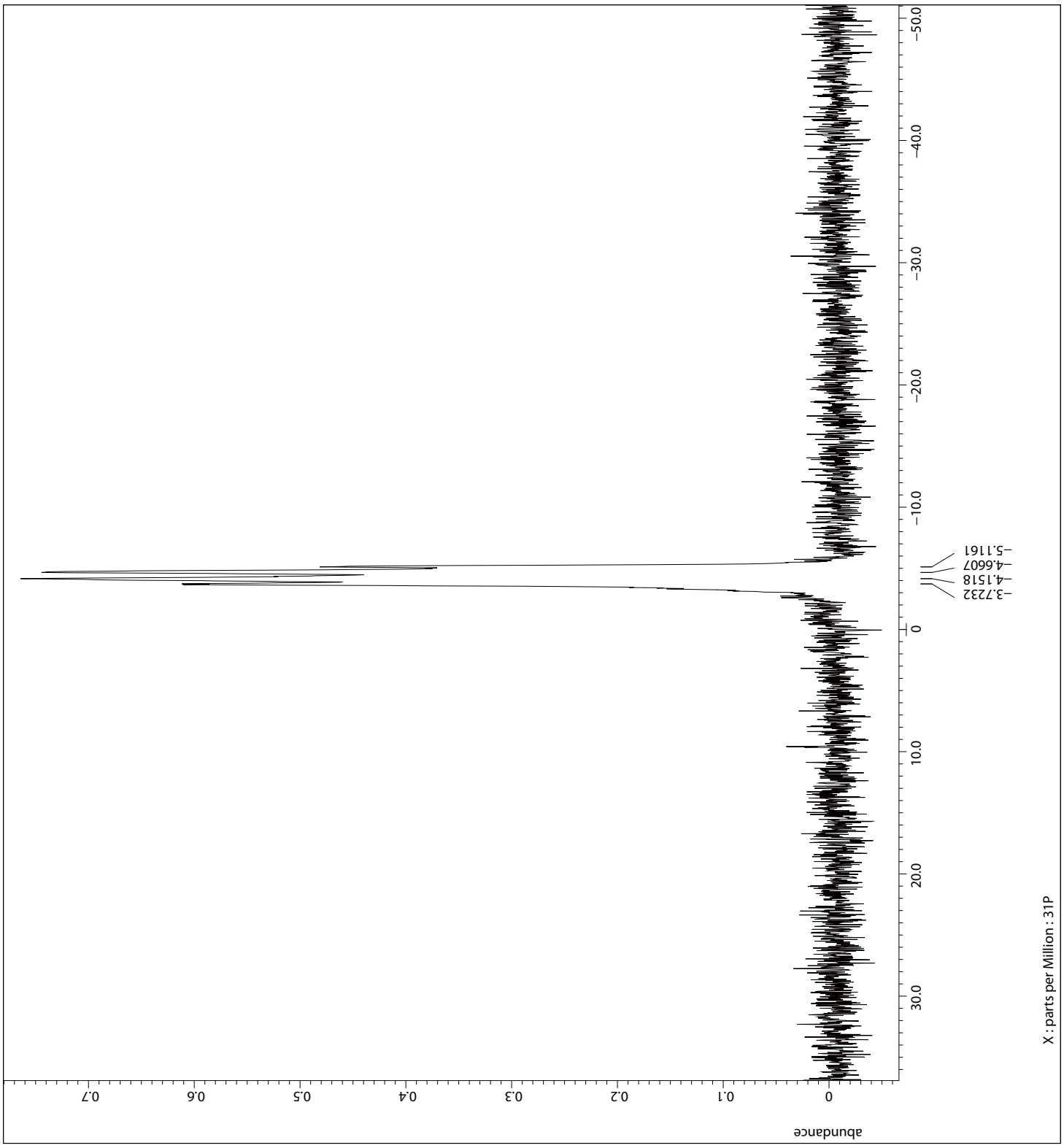


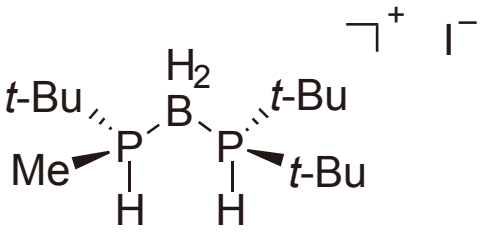


(*S*,*S*)-3b•I, ^{13}C in $CDCl_3$ (100 MHz)

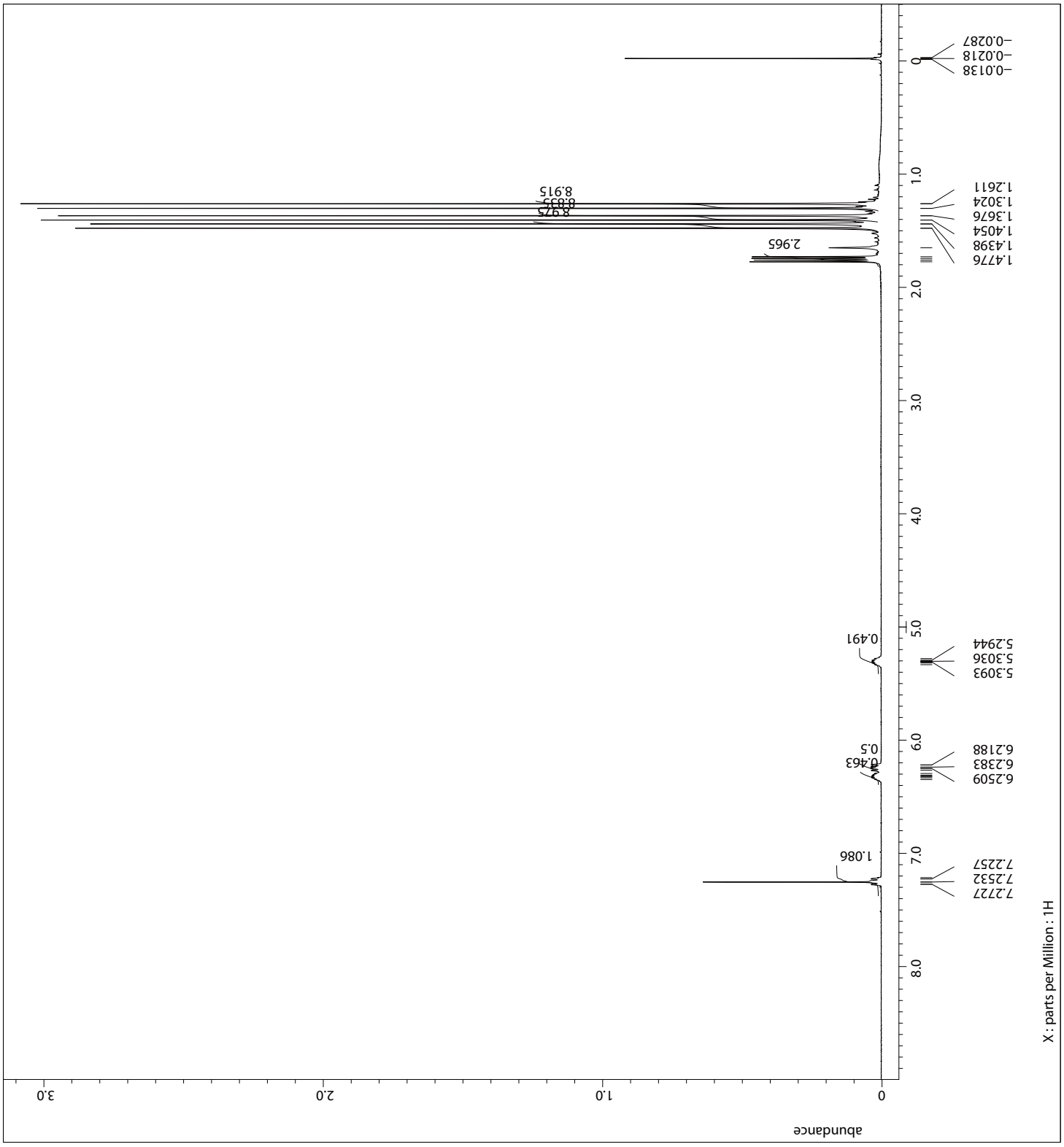


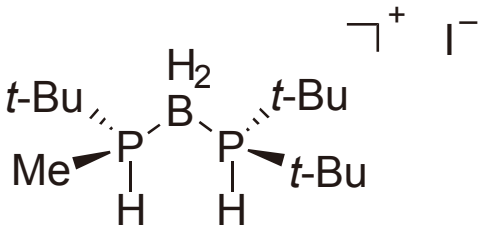
(*S*,*S*)-3b•I, ^{31}P in $CDCl_3$ (162 MHz)



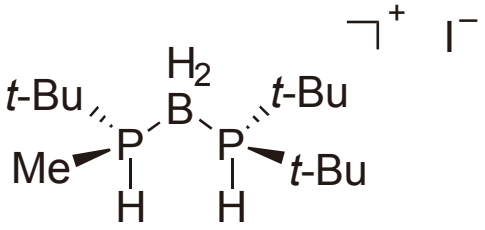


(*S*)-3c•I, ^{1}H in $CDCl_3$ (400 MHz)

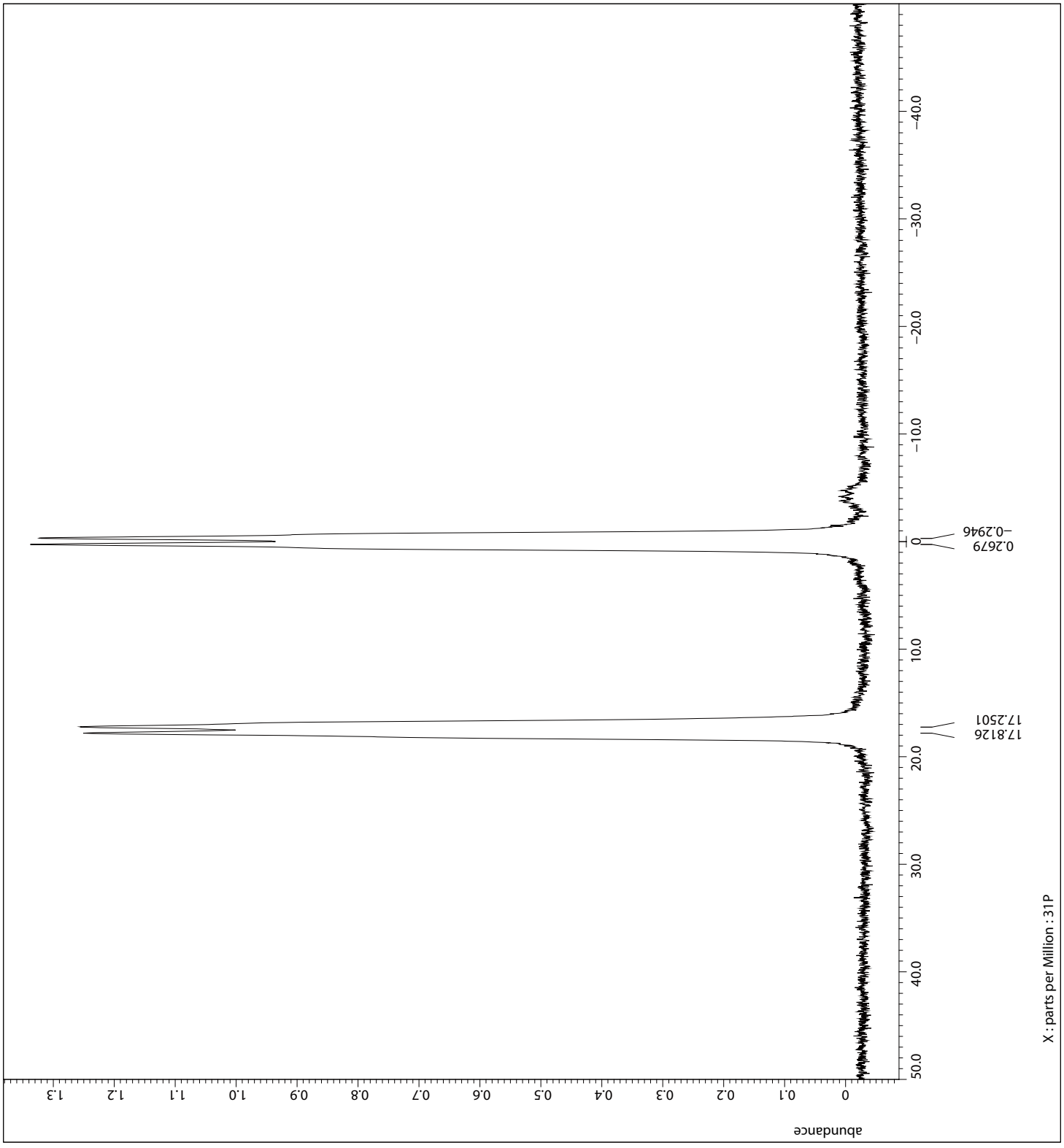


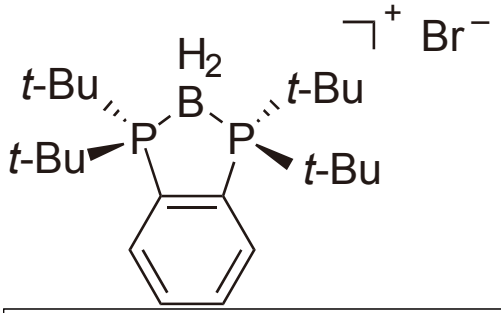


(*S*)-3c•I, ^{13}C in $CDCl_3$ (100 MHz)

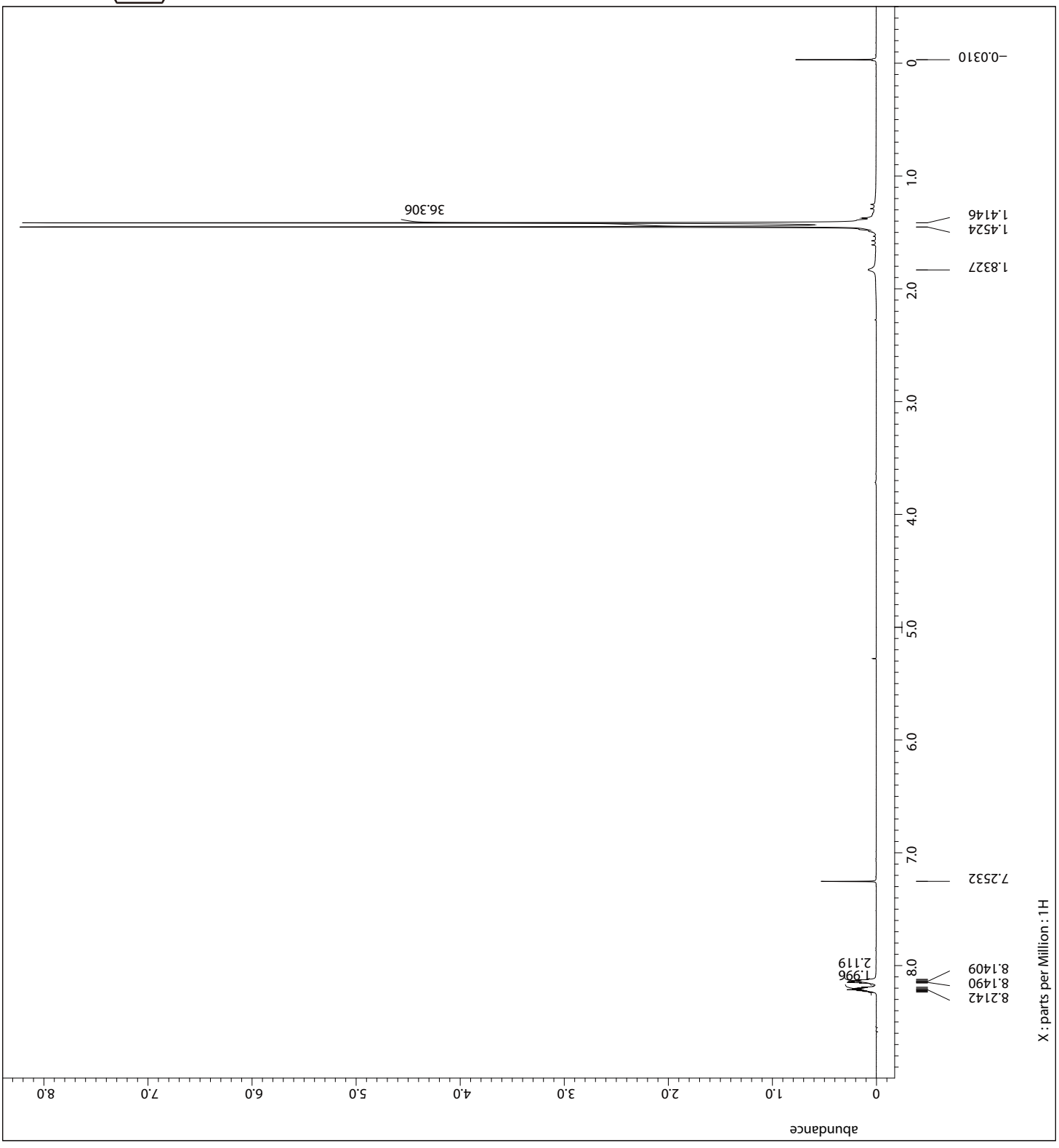


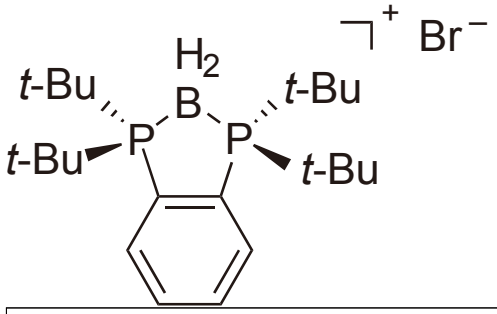
(*S*)-3c•I, ^{31}P in $CDCl_3$ (162 MHz)



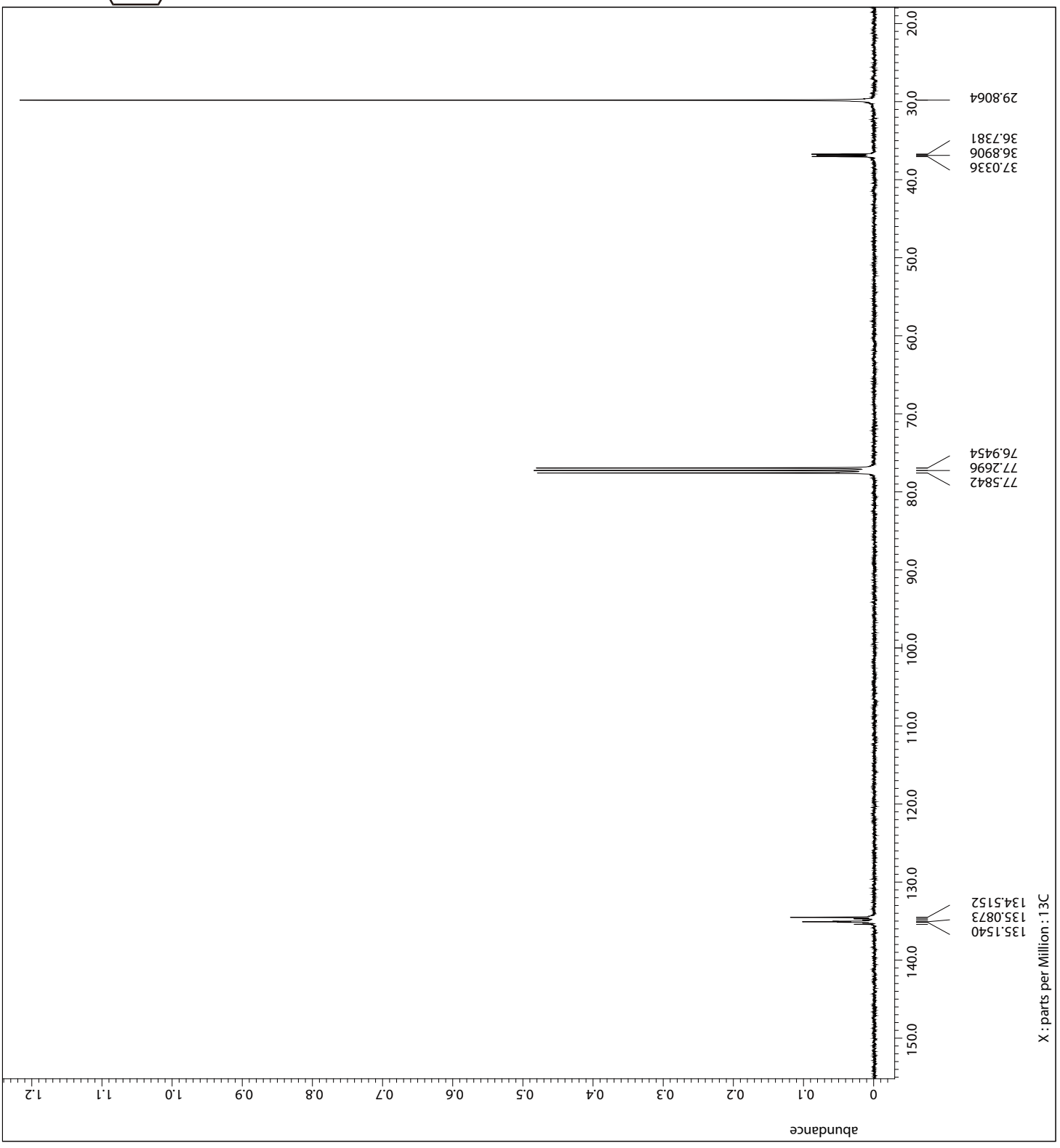


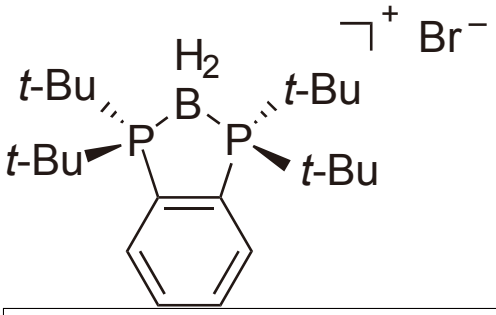
4a•Br, ^{1}H in $CDCl_3$ (400 MHz)



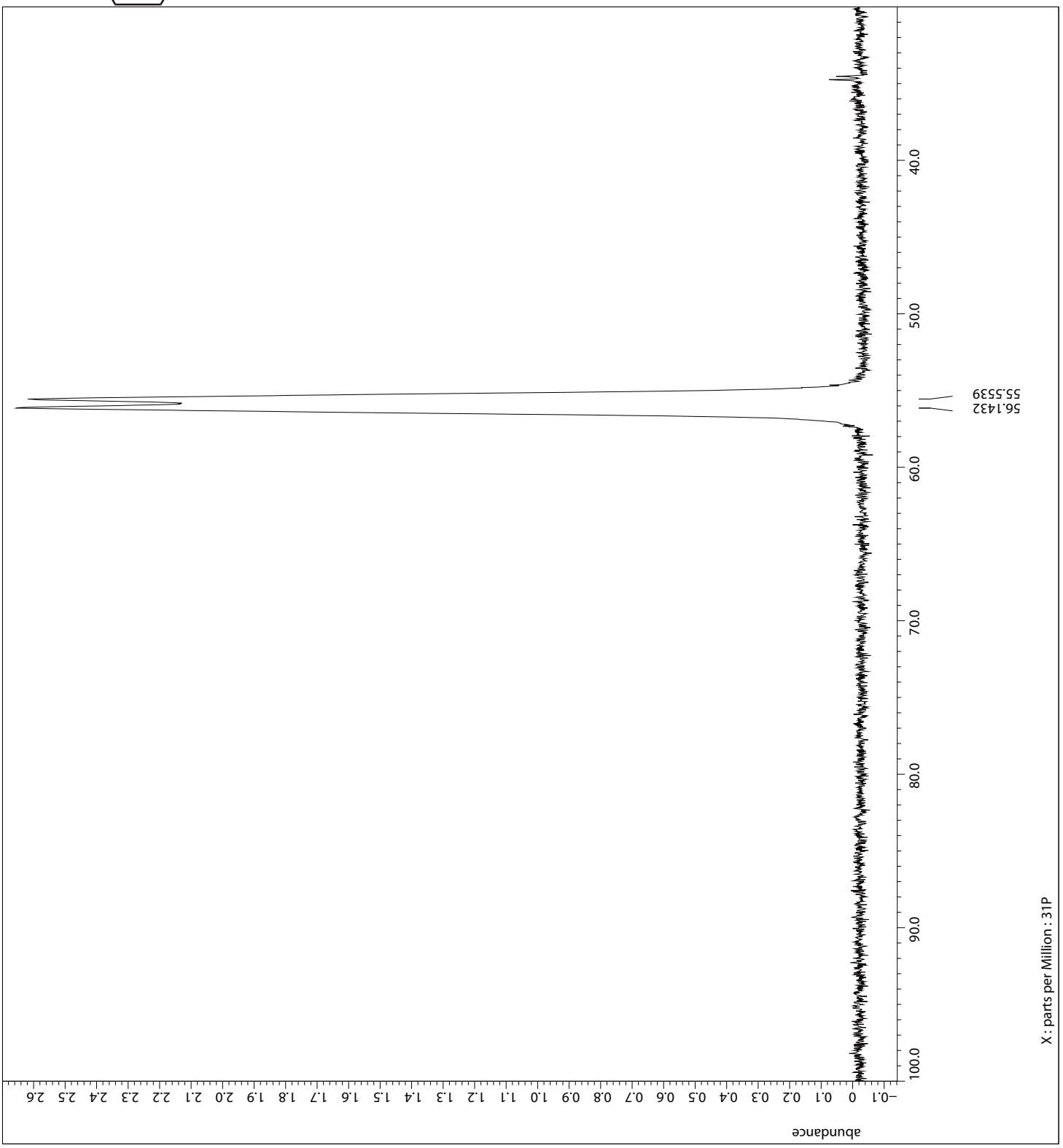


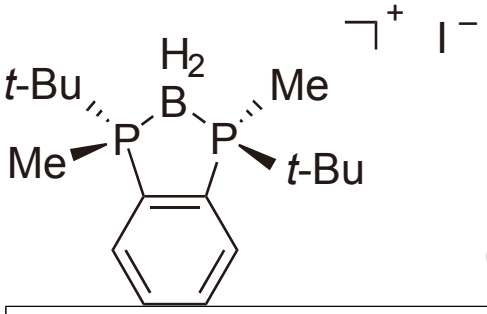
4a•Br, ^{13}C in $CDCl_3$ (100 MHz)



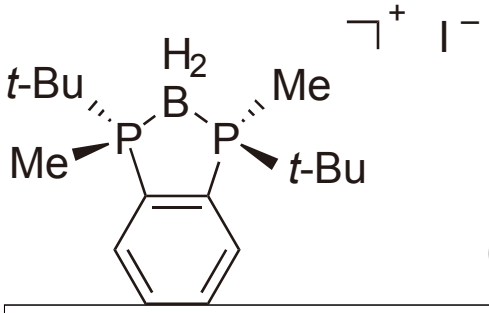


4a•Br, ^{31}P in $CDCl_3$ (162 MHz)

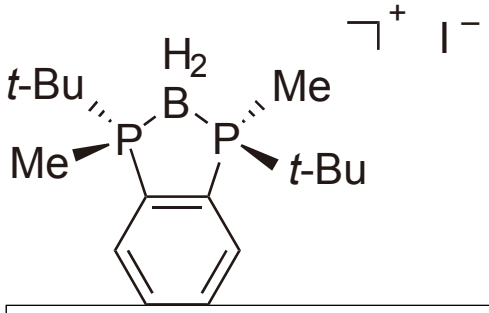




(*R*,*R*)-4b•I, ^{1}H in $CDCl_3$ (400 MHz)



(*R*,*R*)-4b•I, ^{13}C in $CDCl_3$ (100 MHz)



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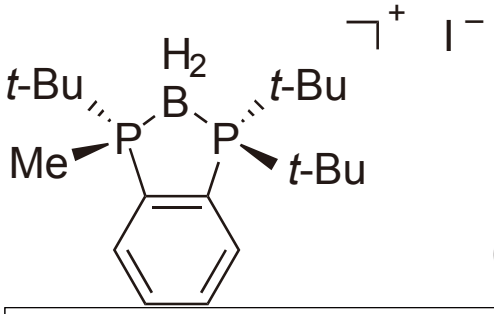

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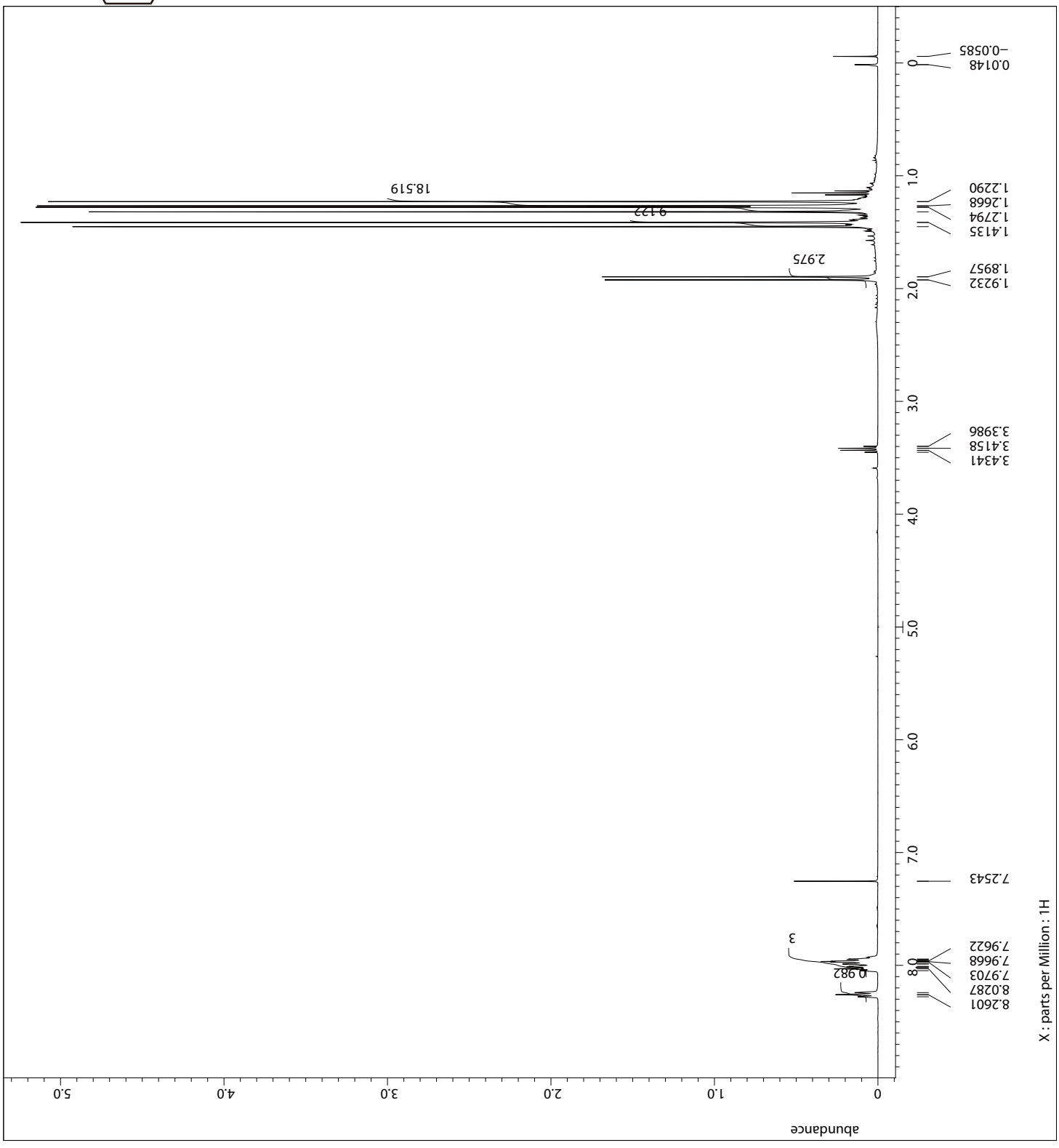

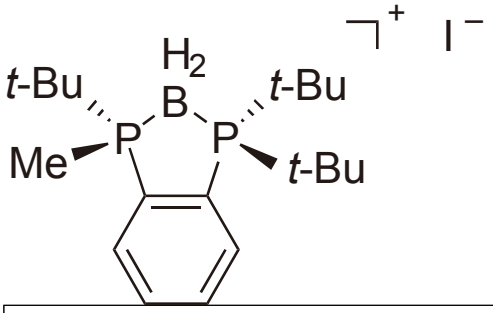

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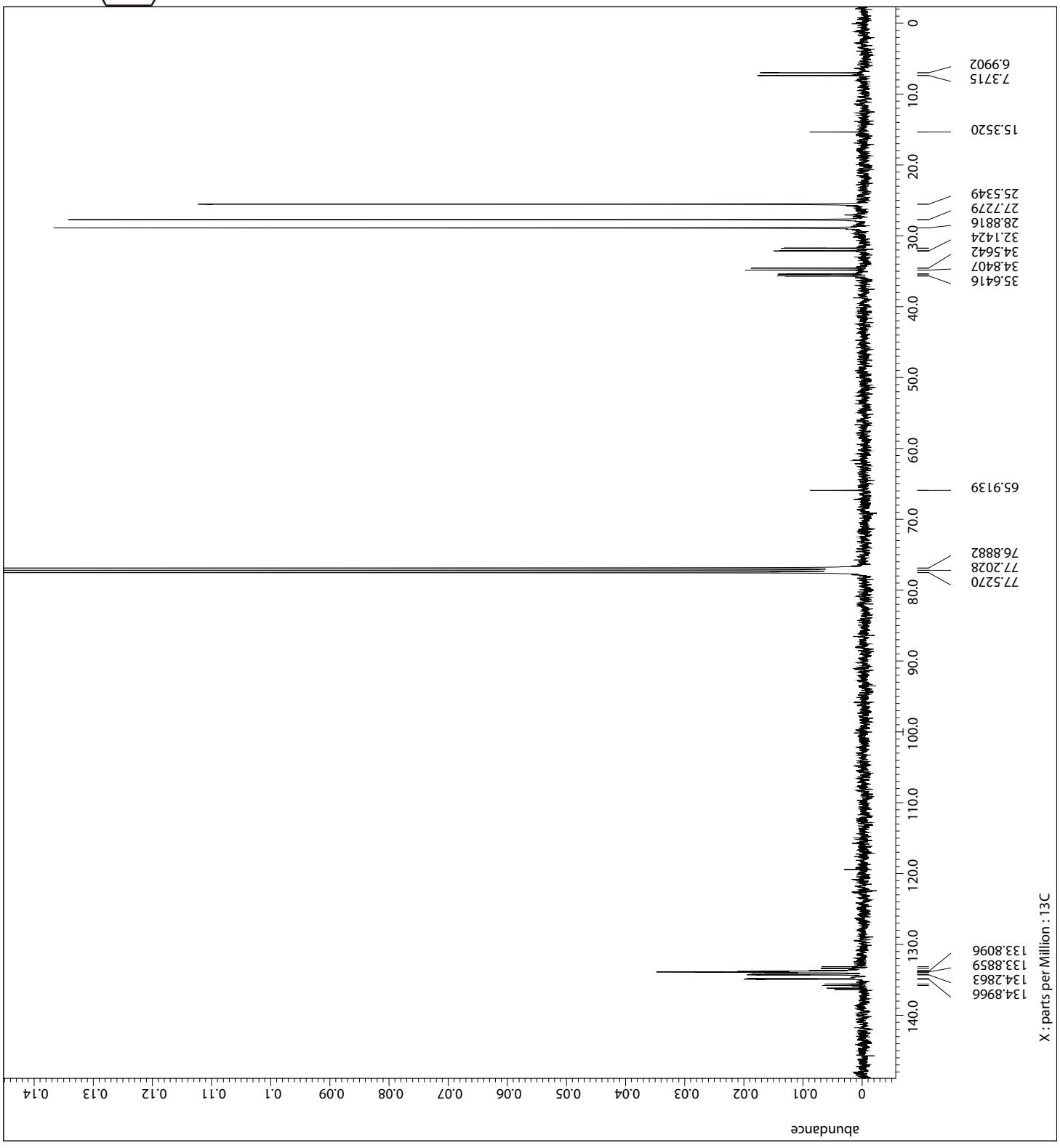
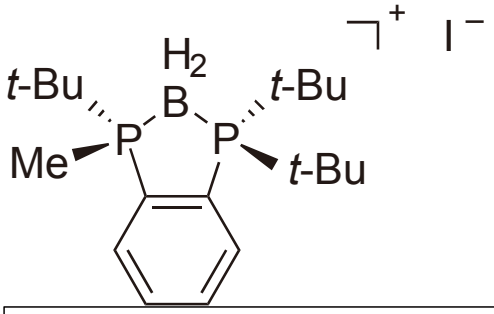
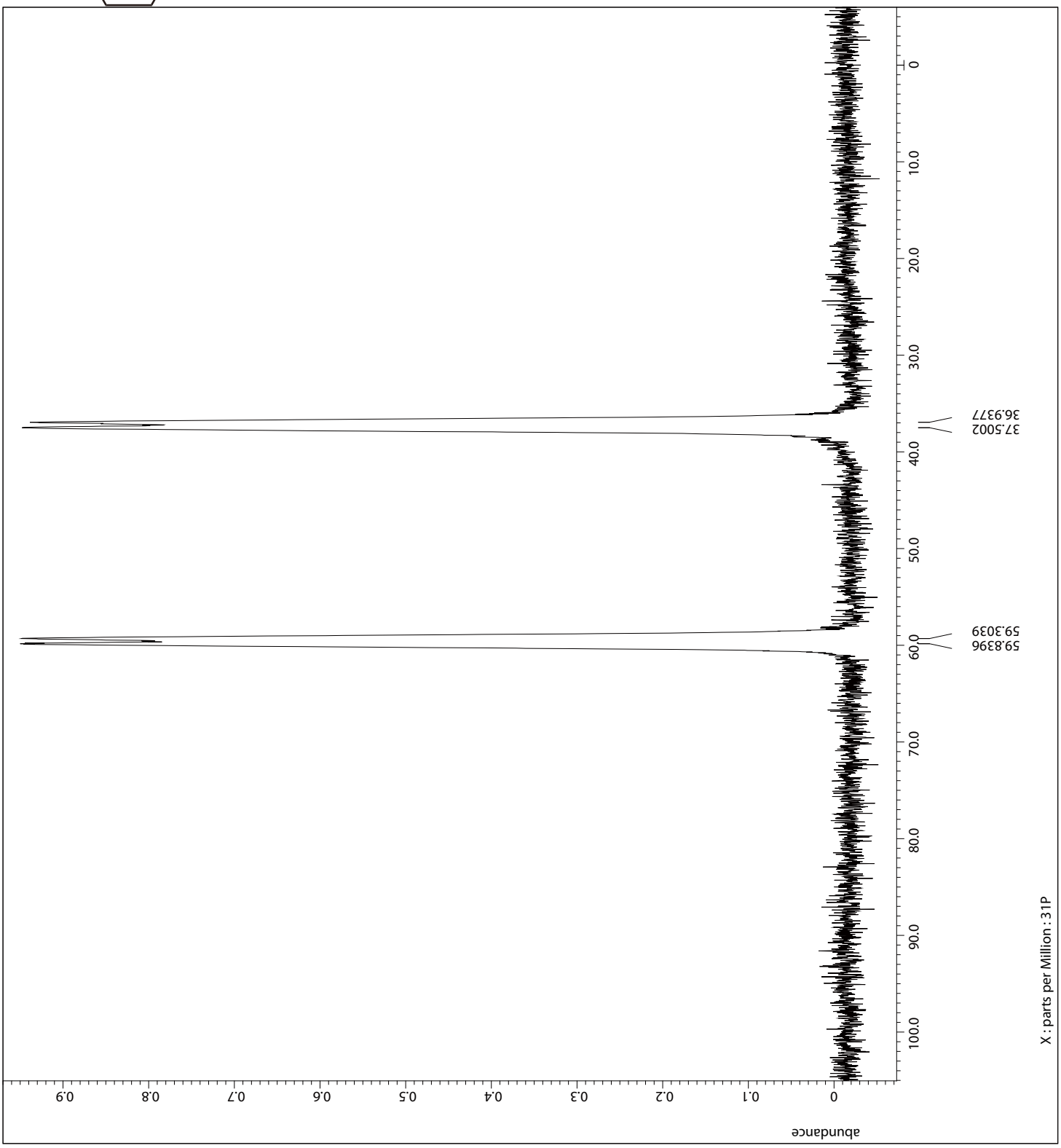
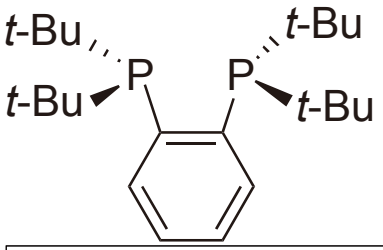


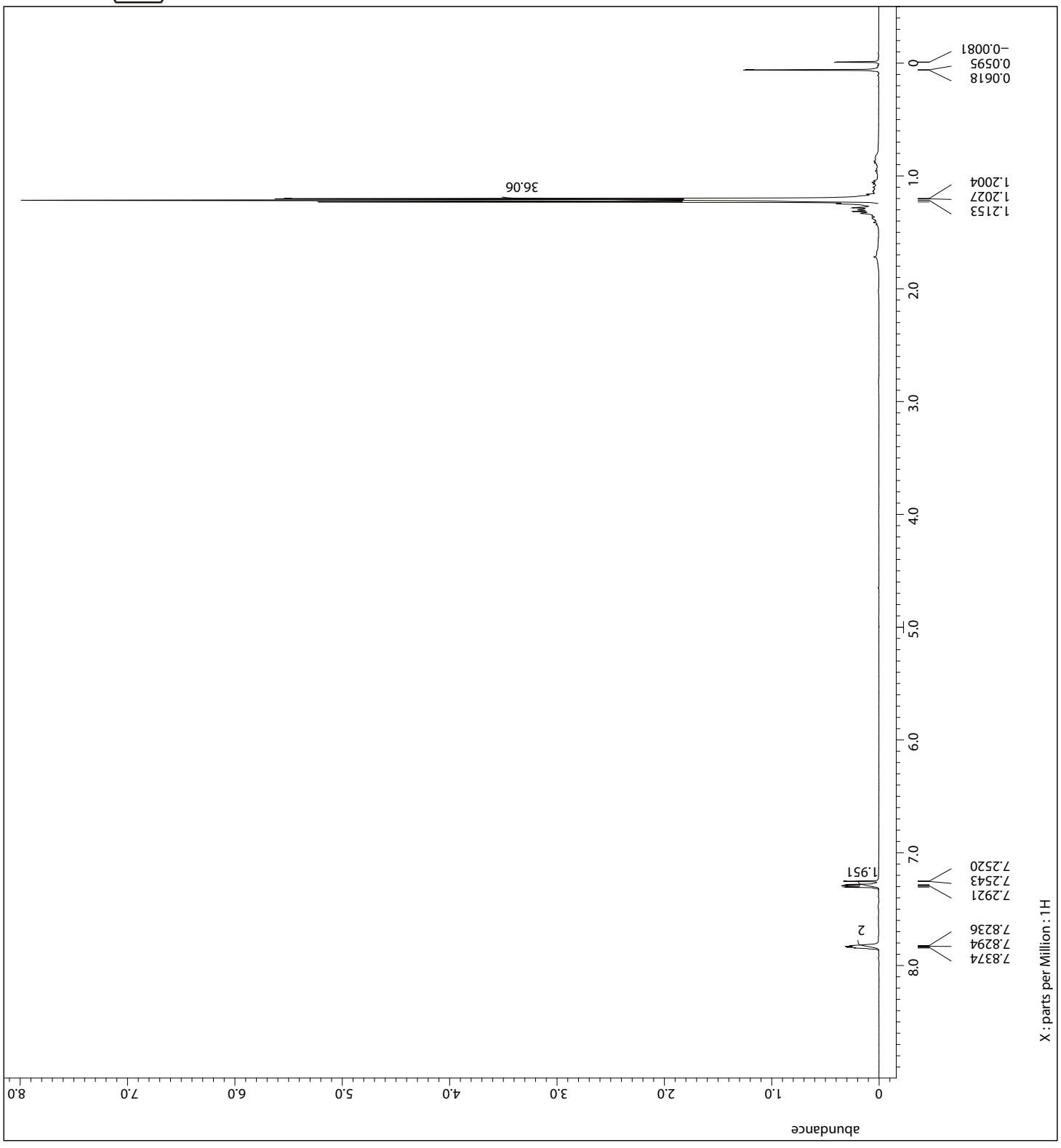


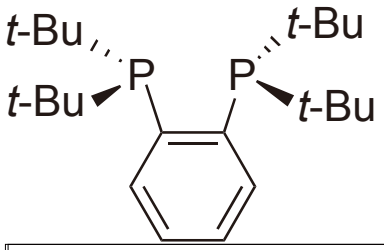
(*R*)-4c•I, ^{31}P in $CDCl_3$ (162 MHz)



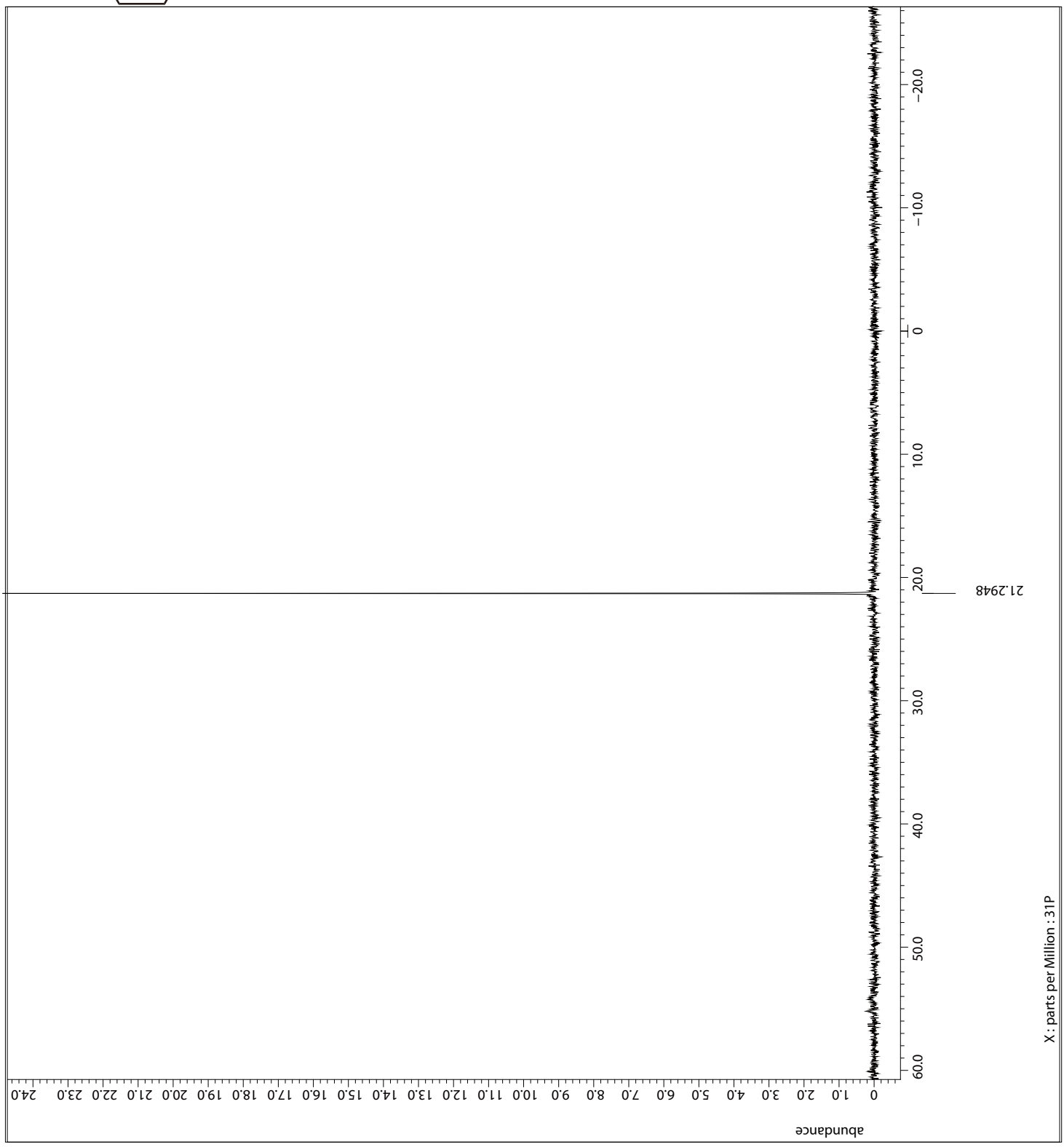


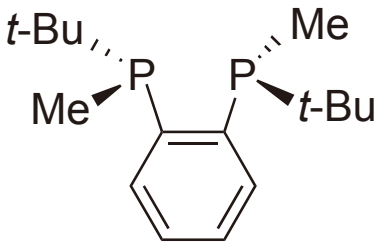
1a, ^{1}H in $CDCl_3$ (400 MHz)





1a, ^{31}P in $CDCl_3$ (162 MHz)





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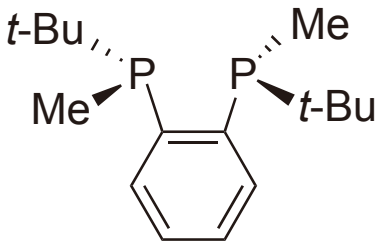
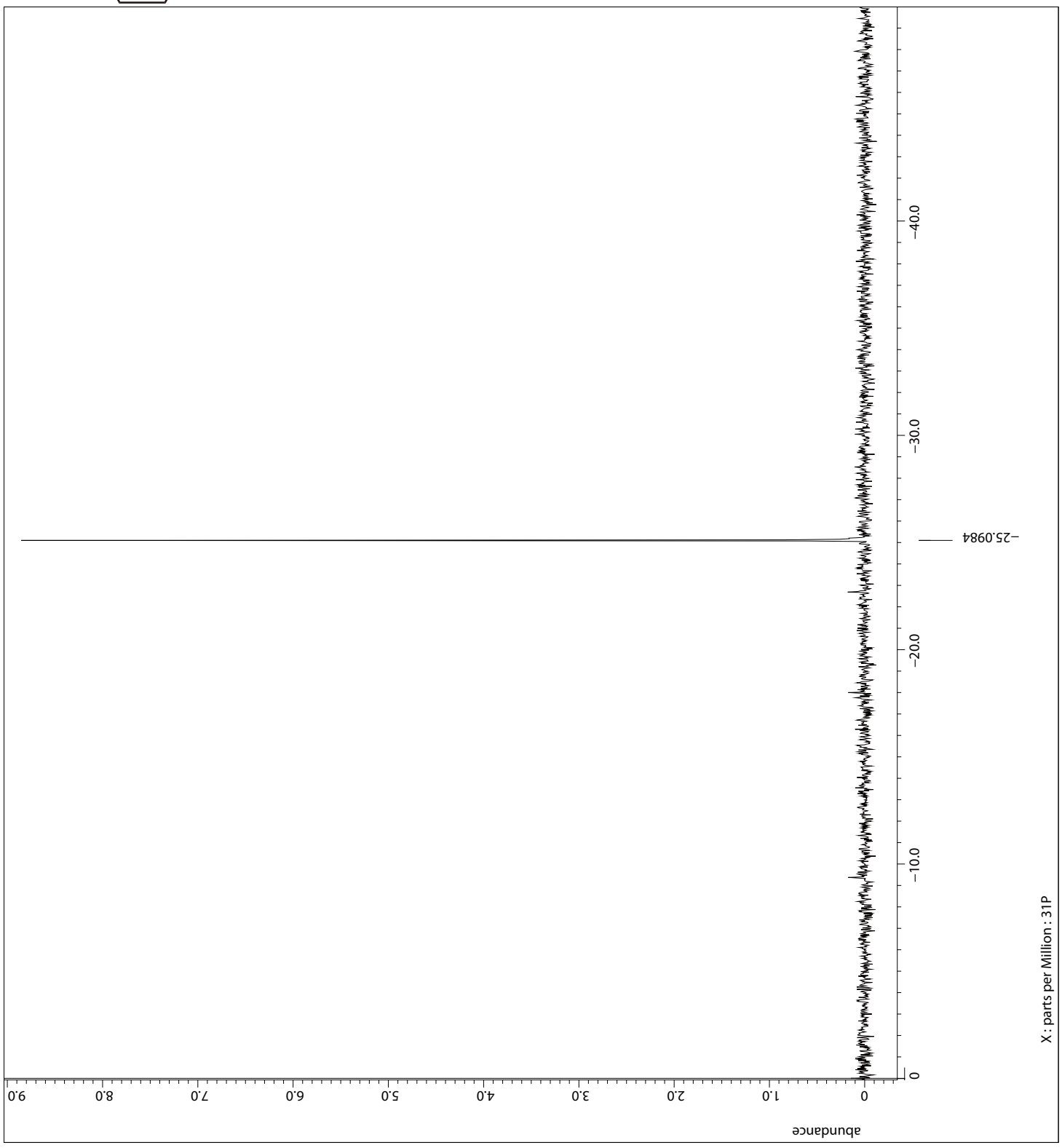
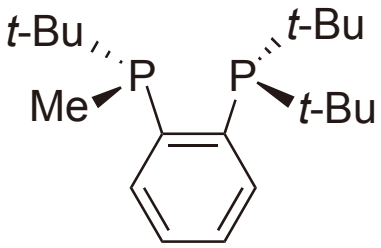
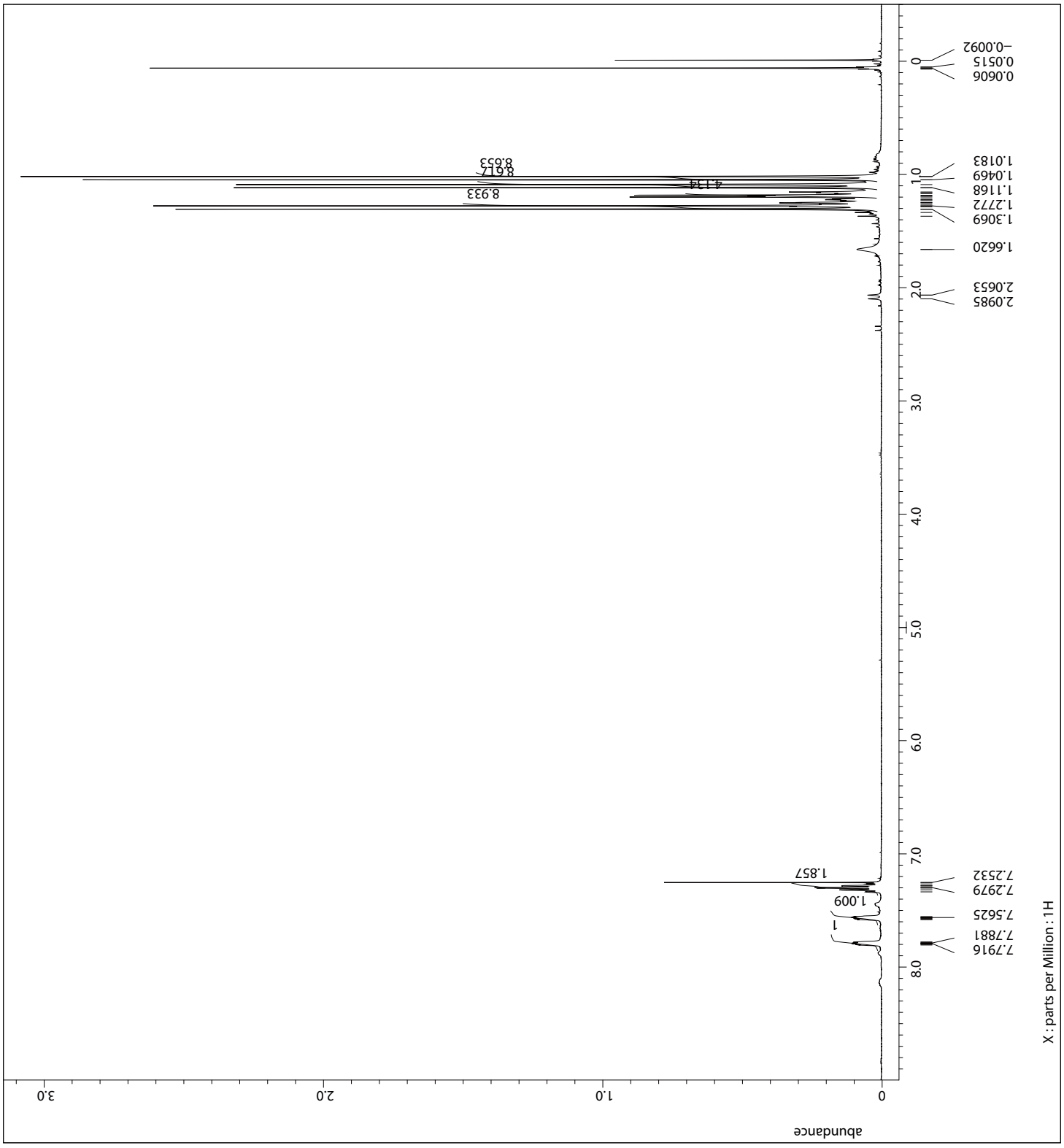


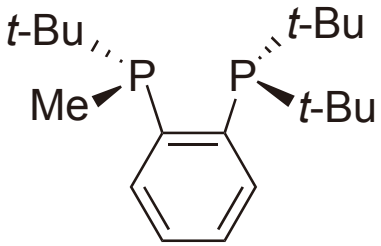
1b, ^{31}P in $CDCl_3$ (162 MHz)



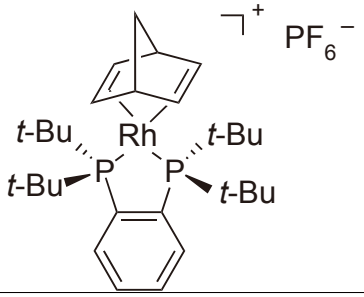


1c, ^{1}H in $CDCl_3$ (400 MHz)

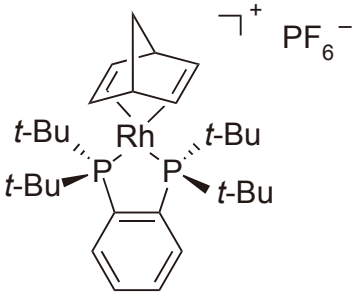




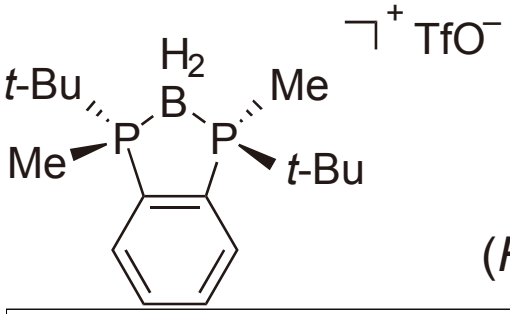
1c, ^{31}P in $CDCl_3$ (162 MHz)



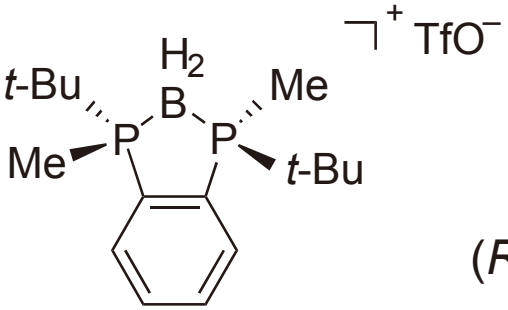
[1a•Rh(nbd)]PF_6, ^1H in $CDCl_3$ (400 MHz)



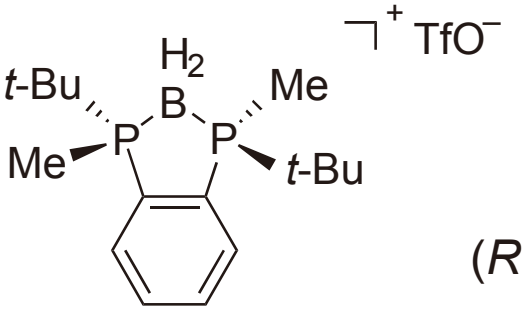
[1a•Rh(nbd)]PF_6, ^{31}P in $CDCl_3$ (162 MHz)



(*R*,*R*)-4b•OTf, ^{1}H in $CDCl_3$ (400 MHz)



(*R*,*R*)-4b•OTf, ^{13}C in $CDCl_3$ (100 MHz)



(*R*,*R*)-4b•OTf, ^{31}P in $CDCl_3$ (162 MHz)