

Supplementary Information

A theory-driven synthesis of symmetric and unsymmetric 1,2-bis(diphenylphosphino)ethane analogues via radical difunctionalization of ethylene

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Supplementary Analytical Data

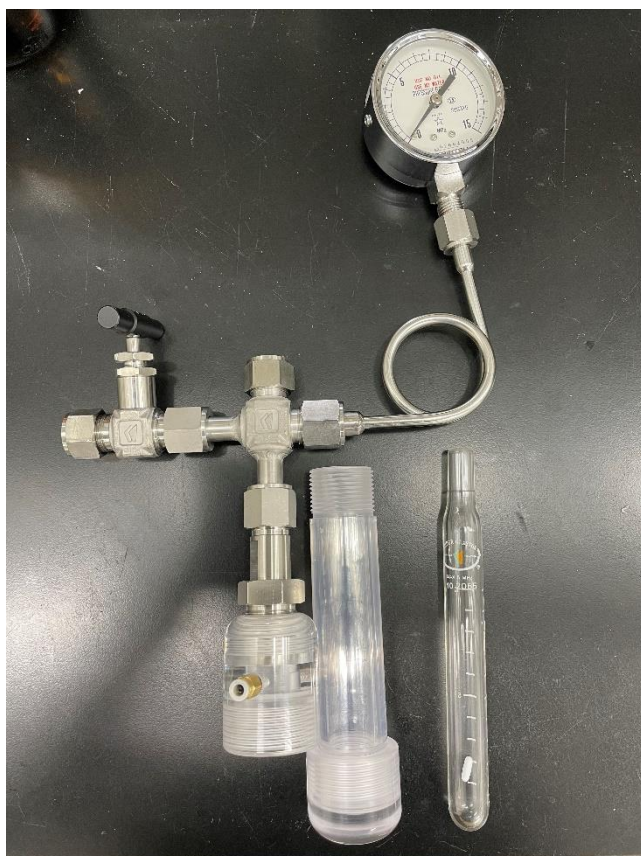
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Supplementary Methods

(A) General

All manipulations were carried out under an atmosphere of nitrogen unless otherwise noted. Infrared (IR) spectra were recorded on a JASCO FT/IR 4600 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ESZ-400S spectrometer, operating at 400 MHz (^1H), 100 MHz (^{13}C), 376 MHz (^{19}F), and 162 MHz (^{31}P). Chemical shifts in CDCl_3 were reported in the scale relative to CHCl_3 (7.26 ppm) or CH_2Cl_2 (5.32 ppm) for ^1H NMR and to CDCl_3 (77.16 ppm) or CD_2Cl_2 (53.84 ppm) for ^{13}C NMR as internal references. EI mass spectra were measured on a JEOL JMS-T100GCV and ESI mass spectra were measured on a Thermo Scientific Exactive. A cylinder of ethylene was purchased from Hokkaido Air Water, Inc. A 45W PR160L-440 nm (blue LED (440 nm), Kessil Lighting), A 160WE TUNA SUN (white LED, Kessil Lighting), TH2-140X105GY57 (yellow green LED (570 nm), CCS Inc.), and LED-PBULB/24WC (green LED (520 nm), yellow LED (600 nm), and red LED (630 nm), Life Partner Corp.) were used as the light source under photochemical conditions. HPG-10 (Taiatsu Techno Corporation) was used as an autoclave which consists of a polycarbonate cylinder. Emission spectra of monochromatic LEDs and white LED were measured by USB4000 (Ocean Photonics) and the strength of LEDs were measured by T-10MA (KONICA MINOLTA, Inc.). Optical resolution of **3jb** was performed by high performance liquid chromatography (HPLC) using JASCO Extrema HPLC systems with photo diode array detector MD-4010. Recycle preparative HPLC was performed using a JAI LaboACE LC-5060. All UV-Vis absorption spectra were measured on a V-770 (JASCO Corp.). Emission spectra and lifetime at 90 K were measured on a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system using a cryostat (SB1905HA, Thermal Block Company) and a temperature controller (Model 9700, Scientific Instruments). Emission lifetimes (τ_{obs}) were measured using a pulse diode light source SpectraLED with peak wavelength at 518 nm, 520 nm, 572 nm, and 620 nm recorded on a HORIBA Fluorolog-3 spectrofluorometer. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. Emission decay curves were analysed by multi-exponential curve fittings. All starting materials except phosphine oxides and hydrosilane ($\text{PhSiH}_2\text{-O-SiH}_2\text{Ph}$) are commercially available from TCI, Aldrich, Alfa Aesar and other suppliers, and used as received.

(B) Reaction Apparatus for High-Pressure Photochemical Reaction



(a)



(b)



(c)



(d)

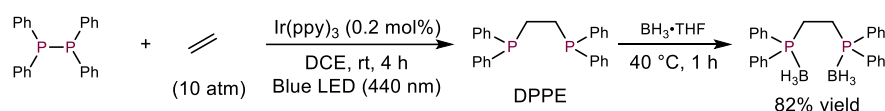
Supplementary Figure 1. (a) Autoclave with a polycarbonate cylinder and a pressure-resistant glass tube. (b) The apparatus setting (c) A reaction under blue LED (d) A reaction under white LED

(C) Synthesis of phosphine oxide 1

Phosphine oxide **1** was synthesized according to the literature¹.

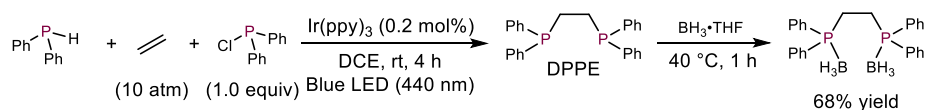
An oven dried two-neck flask with a reflux condenser was charged with magnesium turnings (72 mmol), I₂ (1 crystal) and THF (100 mL) under nitrogen atmosphere. Then aryl bromide (60 mmol) was added dropwise. If aryl bromide was solid, 50 mL solution of aryl bromide (60 mL) was added dropwise to 50 mL solution of magnesium turnings (72 mmol) and I₂ (1 crystal). After the bromide addition completed, the reaction mixture was stirred at reflux for 3 h. Next, the flask was placed in ice bath, diethyl phosphite (20 mmol) was added dropwise to the mixture via a syringe, and stirred for 4 h at room temperature. The reaction was quenched with 2 M aq. HCl (40 mL) at 0 °C, and was extracted with EtOAc three times and the combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. After the solvent removed under vacuum, the resulting crude product was purified by recrystallization from the mixture of EtOAc and hexane, or silica-gel column chromatography to yield phosphine oxide **1**.

(D) Procedure for the Synthesis of DPPE from Diphosphine



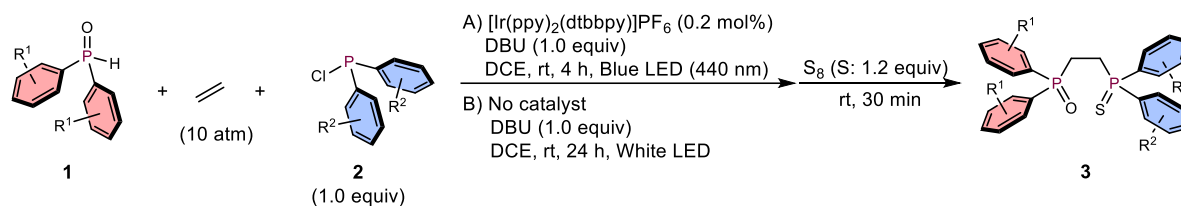
In an oven-dried 10 mL pressure-resistant glass tube were placed tetraphenyldiphosphine (185.2 mg, 0.5 mmol, 1.0 equiv) and $\text{Ir}(\text{ppy})_3$ (0.7 mg, 0.001 mmol, 0.2 mol%) in glove box. After the addition of DCE (1.5 mL) under nitrogen, the tube was placed into autoclave which consists of a polycarbonate cylinder, and ethylene gas was pressurised to 10 atm. After the resulting mixture was stirred at room temperature for 4 h under the irradiation of blue LED (45W PR160L-440 nm Kessil light $\times$ 2), the solvent was evaporated to give the crude mixture. THF (1.0 mL) and 1M BH_3 in THF (4 mL, 4 mmol, 8 equiv) were added, and then, the reaction mixture was stirred for 1 h at 40 °C. After the evaporation, the crude product was purified by silica-gel column chromatography (eluent: hexane/ethyl acetate, 9/1 to 1/1) to afford the product (174.2 mg, 0.41 mmol, 82%), of which spectra were consistent with a previous report².

(E) Procedure for the Synthesis of DPPE from Diphenylphosphine and Chlorodiphenylphosphine



In an oven-dried 10 mL pressure-resistant glass tube were placed diphenylphosphine (86.2 μL , 0.5 mmol, 1.0 equiv) and $\text{Ir}(\text{ppy})_3$ (0.7 mg, 0.001 mmol, 0.2 mol%) in glove box. After the addition of chlorodiphenylphosphine (91.9 μL , 0.5 mmol, 1.0 equiv) and DCE (1.5 mL) under nitrogen, the tube was placed into autoclave which consists of a polycarbonate cylinder, and ethylene gas was pressurised to 10 atm. After the resulting mixture was stirred at room temperature for 4 h under the irradiation of blue LED (45W PR160L-440 nm Kessil light $\times$ 2), the solvent was evaporated to give the crude mixture. THF (1.0 mL) and 1M BH_3 in THF (4 mL, 4 mmol, 8 equiv) were added, and then, the reaction mixture was stirred for 1 h at 40 °C. After the evaporation, the crude product was purified by silica-gel column chromatography (eluent: hexane/ethyl acetate, 9/1 to 1/1) to afford the product (145.6 mg, 0.34 mmol, 68%), of which spectra were consistent with a previous report².

(F) General Procedures for the Synthesis of DPPE Derivatives



General Procedure A (for blue LED)

In an oven-dried 10 mL pressure-resistant glass tube were placed phosphine oxide **1** (0.5 mmol, 1.0 equiv) and [Ir(ppy)₂(dtbbpy)]PF₆ (0.9 mg, 0.001 mmol, 0.2 mol%). After the addition of DCE (1.5 mL) under nitrogen, chlorophosphine **2** (0.5 mmol, 1.0 equiv) and DBU (74.8 μL, 0.5 mmol, 1.0 equiv) were added. Then, the tube was placed into autoclave which consists of a polycarbonate cylinder, and ethylene gas was pressurised to 10 atm. After the resulting mixture was stirred at room temperature for 4 h under the irradiation of blue LED (45W PR160L-440 nm Kessil light × 2), sulfur (19.2 mg, 0.6 mmol, 1.2 equiv of S) was added into the reaction mixture. After the mixture was stirred for 30 min, the solvent was evaporated to give the crude mixture. The crude product was purified by silica-gel column chromatography to afford the product **3**.

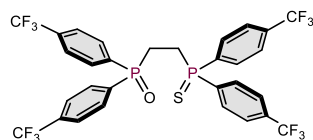
General Procedure B (for white LED)

In an oven-dried 10 mL pressure-resistant glass tube was placed phosphine oxide **1** (0.5 mmol, 1.0 equiv). After the addition of DCE (1.5 mL) under nitrogen, chlorophosphine **2** (0.5 mmol, 1.0 equiv) and DBU (74.8 μL, 0.5 mmol, 1.0 equiv) were added. Then, the tube was placed into autoclave which consists of a polycarbonate cylinder, and ethylene gas was pressurised to 10 atm. After the resulting mixture was stirred at room temperature for 24 h under the irradiation of white LED (A 160WE TUNA SUN × 2), sulfur (19.2 mg, 0.6 mmol, 1.2 equiv of S) was added into the reaction mixture. After the mixture was stirred for 30 min, the solvent was evaporated to give the crude mixture. The crude product was purified by silica-gel column chromatography to afford the product **3**.

(2-(Diphenylphosphorothioyl)ethyl)diphenylphosphine oxide (**3aa**)

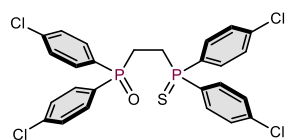
Diphenylphosphine oxide (**1a**; 101.1 mg, 0.5 mmol, 1.0 equiv) and chlorodiphenylphosphine (**2a**; 91.9 μL, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 9/1) afforded **3aa** (procedure A: 182.2 mg, 0.41 mmol, 82% yield, procedure B: 165.7 mg, 0.37 mmol, 74% yield). White solid; IR (ATR): 3051, 1592, 1437, 1255, 1184, 1173, 1120, 1101, 1026, 793, 730, 689, 610 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ: 7.81-7.75 (m, 4H), 7.73-7.68 (m, 4H), 7.52-7.40 (m, 12H), 2.74-2.66 (m, 2H), 2.57-2.49 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 132.0 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 99.1 Hz), 131.7 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 80.3 Hz), 130.9 (d, *J* = 10.2 Hz), 130.6 (d, *J* = 9.2 Hz), 128.7 (d, *J* = 11.6 Hz), 128.7 (d, *J* = 12.1 Hz), 24.6 (d, *J* = 55.9 Hz), 22.4 (d, *J* = 69.6 Hz) ppm; ³¹P NMR (162 MHz, CDCl₃) δ: 45.4 (d, *J* = 58.5 Hz), 33.6 (d, *J* = 58.5 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₂₆H₂₄OP₂SNa⁺ [*M*+Na]⁺: 469.0915, found: 469.0904.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(4-trifluoromethylphenyl)phosphine oxide (**3bb**)



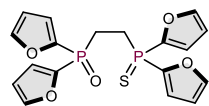
Bis(4-trifluoromethylphenyl)phosphine oxide (**1b**; 169.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μ L, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 9/1 to 1/1) afforded **3bb** (procedure A: 208.1 mg, 0.29 mmol, 58% yield, procedure B: 264.6 mg, 0.37 mmol, 74% yield). White solid; IR (ATR): 2922, 1400, 1323, 1164, 1123, 1104, 1061, 1015, 835, 729, 709, 640 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.97-7.86 (m, 8H), 7.77-7.71 (m, 8H), 2.80-2.71 (m, 2H), 2.64-2.55 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 135.9-133.7 (m, 4C), 131.6 (d, $J = 10.8$ Hz), 131.3 (d, $J = 9.8$ Hz), 126.2-125.9 (m, 2C), 123.3 (q, $J = 271.4$ Hz, two CF_3 groups were totally overlapped), 24.4 (d, $J = 55.9$ Hz), 22.2 (d, $J = 70.6$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.3, -63.3 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.4 (d, $J = 58.2$ Hz), 31.2 (d, $J = 58.2$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{20}\text{F}_{12}\text{OP}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 741.0411, found: 741.0390.

(2-(Bis(4-chlorophenyl)phosphorothioyl)ethyl)bis(4-chlorophenyl)phosphine oxide (**3cc**)



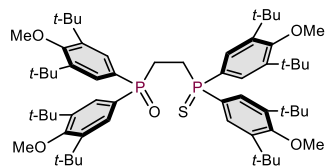
Bis(4-chlorophenyl)phosphine oxide (**1c**; 135.5 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-chlorophenyl)phosphine (**2c**; 144.8 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 1/1) afforded **3cc** (procedure A: 192.8 mg, 0.33 mmol, 66% yield, procedure B: 224.1 mg, 0.38 mmol, 77% yield). White solid; IR (ATR): 2920, 1580, 1480, 1389, 1196, 1175, 1085, 1012, 819, 747, 729, 642 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.73-7.60 (m, 8H), 7.46-7.41 (m, 8H), 2.67-2.58 (m, 2H), 2.50-2.41 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 139.2 (d, $J = 3.3$ Hz), 139.0 (d, $J = 3.4$ Hz), 132.5 (d, $J = 11.4$ Hz), 132.2 (d, $J = 10.1$ Hz), 130.4-129.3 (m, for 4C), 24.7 (d, $J = 56.4$ Hz), 22.5 (d, $J = 70.5$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.3 (d, $J = 58.5$ Hz), 32.4 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{26}\text{H}_{20}\text{Cl}_4\text{OP}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 604.9356, found: 604.9350.

(2-(Di(furan-2-yl)phosphorothioyl)ethyl)di(furan-2-yl)phosphine oxide (**3dd**)



Di(furan-2-yl)phosphine oxide (**1d**; 45.5 mg, 0.25 mmol, 1.0 equiv) and chlorodi(furan-2-yl)phosphine (**2d**; 39.0 μ L, 0.25 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 20/1 to 7/1) afforded **3dd** (procedure A: 30.8 mg, 0.076 mmol, 30% yield, procedure B: 16.9 mg, 0.042 mmol, 17% yield). White solid; IR (ATR): 3090, 1553, 1458, 1368, 1206, 1125, 1002, 909, 744, 707, 655, 634 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.69-7.66 (m, 4H), 7.18-7.16 (m, 2H), 7.14-7.13 (m, 2H), 6.52-6.48 (m, 4H), 2.76-2.67 (m, 2H), 2.57-2.47 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 148.9 (d, $J = 7.1$ Hz), 148.7 (d, $J = 8.0$ Hz), 146.2 (d, $J = 126.8$ Hz), 146.1 (d, $J = 133.6$ Hz), 123.2 (d, $J = 20.8$ Hz), 122.8 (d, $J = 19.4$ Hz), 111.4 (d, $J = 9.1$ Hz), 111.2 ($J = 8.7$ Hz), 24.5 (dd, $J = 62.6, 2.4$ Hz), 22.2 (dd, $J = 79.6, 1.8$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 17.1 (d, $J = 71.6$ Hz), 12.2 (d, $J = 71.6$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_5\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 429.0086, found: 429.0076.

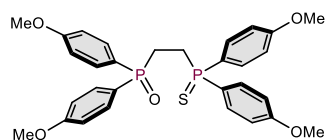
(2-(Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphorothioyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (**3ee**)



Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (**1e**; 121.7 mg, 0.25 mmol, 1.0 equiv) and chlorobis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine (**2e**; 126.3 mg, 0.25 mmol, 1.0 equiv) were employed as starting materials.

Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 4/1) afforded **3ee** (procedure A: 20.3 mg, 0.020 mmol, 8% yield, procedure B: 37.2 mg, 0.037 mmol, 15% yield). White solid; IR (ATR): 2963, 1409, 1394, 1227, 1213, 1169, 1146, 1117, 1008, 733 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (d, J = 13.5 Hz, 4H), 7.52 (d, J = 12.2 Hz, 4H), 3.68 (s, 12H), 2.63-2.53 (m, 4H), 1.38 (s, 36H), 1.37 (s, 36H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 162.9 (d, J = 3.3 Hz), 162.8 (d, J = 3.3 Hz), 144.5 (d, J = 11.9 Hz), 144.3 (d, J = 12.1 Hz), 130.0 (d, J = 11.9 Hz), 129.7 (d, J = 10.9 Hz), 125.8 (d, J = 102.8 Hz), 125.4 (d, J = 83.4 Hz), 64.6, 64.6, 36.2, 36.1, 32.0, 32.0, 26.6 (dd, J = 54.6, 2.5 Hz), 23.7 (dd, J = 69.7, 2.3 Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) 46.7 (d, J = 56.9 Hz), 36.7 (d, J = 56.9 Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{62}\text{H}_{96}\text{O}_5\text{P}_2\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: 1037.6346, found: 1037.6317.

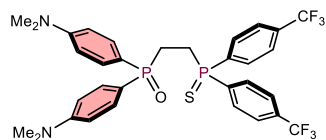
(2-(Bis(4-methoxyphenyl)phosphorothioyl)ethyl)bis(4-methoxyphenyl)phosphine oxide (**3ff**)



Bis(4-methoxyphenyl)phosphine oxide (**1f**; 131.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-methoxyphenyl)phosphine (**2f**; 140.3 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 9/1 to 4/1) afforded **3ff**

(procedure A: 102.8 mg, 0.18 mmol, 36% yield). White solid; IR (ATR): 2930, 1592, 1498, 1293, 1252, 1167, 1101, 1022, 799, 742, 665, 628 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.72-7.67 (m, 4H), 7.62-7.57 (m, 4H), 6.94-6.90 (m, 8H), 3.81-3.80 (m, 12H), 2.66-2.57 (m, 2H), 2.48-2.39 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 162.5 (d, J = 2.9 Hz), 162.3 (d, J = 2.9 Hz), 133.0 (d, J = 11.7 Hz), 132.7 (d, J = 10.8 Hz), 123.4 (d, J = 105.7 Hz), 123.1 (d, J = 86.7 Hz), 114.5-114.3 (m, 2C), 55.5, 55.4, 25.5 (d, J = 56.6 Hz), 23.1 (d, J = 70.9 Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.0 (d, J = 58.5 Hz), 34.2 (d, J = 58.5 Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{32}\text{O}_5\text{P}_2\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: 589.1338, found: 589.1320.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (**3gb**)

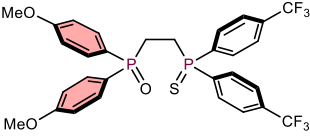


Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude

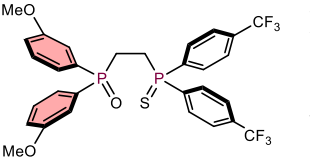
product by silica-gel column chromatography (eluent: DCM/acetone, 9/1 to 4/1) afforded **3gb** (procedure A: 209.8 mg, 0.32 mmol, 63% yield, procedure B: 254.2 mg, 0.41 mmol, 82% yield). White solid; IR (ATR): 2912, 1598, 1515, 1361, 1315, 1165, 1114, 1061, 1016, 815, 734, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.93 (dd, J = 12.4, 8.2 Hz, 4H), 7.69 (dd, J = 8.2, 1.9 Hz, 4H), 7.49 (dd, J = 10.8, 8.8 Hz, 4H), 6.72-6.69 (m, 4H), 2.99 (s, 12H), 2.82-2.73 (m, 2H), 2.42-2.33 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.5 (d, J = 2.4 Hz), 136.0 (d, J = 78.0 Hz), 133.8 (qd, J = 33.0, 3.0 Hz), 132.3 (d, J = 10.6 Hz), 131.7 (d, J = 10.6 Hz), 125.9-125.8 (m), 123.5 (q, J = 271.4 Hz), 116.9 (d, J = 111.6 Hz), 111.6 (d, J = 12.5 Hz), 40.1, 24.9 (d, J = 55.9 Hz), 24.9 (dd, J = 69.9, 3.3 Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm;

^{31}P NMR (162 MHz, CDCl_3) δ : 44.8 (d, $J = 57.5$ Hz), 34.4 (d, $J = 57.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{32}\text{F}_6\text{N}_2\text{OP}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 691.1507, found: 691.1480.

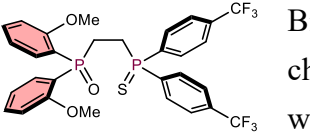
(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(4-methoxyphenyl)phosphine oxide (**3fb**)

 Bis(4-methoxyphenyl)phosphine oxide (**1f**; 131.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 9/1 to 7/3) afforded **3fb** (procedure A: 203.2 mg, 0.32 mmol, 63% yield, procedure B: 160.7 mg, 0.25 mmol, 50% yield). White solid; IR (ATR): 2942, 1597, 1504, 1397, 1315, 1256, 1167, 1118, 1061, 1015, 833, 741 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.93 (dd, $J = 12.6, 8.2$ Hz, 4H), 7.70 (dd, $J = 8.2, 2.3$ Hz, 4H), 7.60 (dd, $J = 11.2, 8.9$ Hz, 4H), 6.95 (dd, $J = 8.9, 2.3$ Hz, 4H), 3.81 (s, 6H), 2.79-2.70 (m, 2H), 2.47-2.38 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 162.7 (d, $J = 2.9$ Hz), 135.8 (d, $J = 78.5$ Hz), 134.0 (qd, $J = 32.8, 2.9$ Hz), 132.7 (d, $J = 10.7$ Hz), 131.7 (d, $J = 10.6$ Hz), 126.0-125.8 (m), 123.4 (q, $J = 271.5$ Hz), 123.0 (d, $J = 107.0$ Hz), 114.6 (d, $J = 12.9$ Hz), 55.5, 24.7 (dd, $J = 56.3, 2.8$ Hz), 22.9 (dd, $J = 70.1, 3.0$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.6 (d, $J = 58.2$ Hz), 33.6 (d, $J = 58.2$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{26}\text{F}_6\text{O}_3\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 665.0874, found: 665.0853.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(3-methoxyphenyl)phosphine oxide (**3hb**)

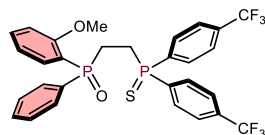
 Bis(3-methoxyphenyl)phosphine oxide (**1h**; 131.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 1/1) afforded **3hb** (procedure A: 204.4 mg, 0.32 mmol, 64% yield, procedure B: 196.6 mg, 0.31 mmol, 61% yield). White solid; IR (ATR): 2937, 1575, 1419, 1315, 1167, 1129, 1062, 1045, 1016, 836, 739, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.94 (dd, $J = 12.6, 8.0$ Hz, 4H), 7.68 (d, $J = 8.0$ Hz, 4H), 7.37-7.32 (m, 2H), 7.28-7.20 (m, 4H), 7.03-7.00 (m, 2H), 3.77 (s, 6H), 2.84-2.75 (m, 2H), 2.54-2.45 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 159.7 (d, $J = 14.6$ Hz), 135.5 (d, $J = 78.5$ Hz), 134.2-132.2 (m, 2C), 131.6 (d, $J = 10.7$ Hz), 130.2 (d, $J = 14.0$ Hz), 125.8-125.6 (m), 123.3 (q, $J = 271.6$ Hz), 122.6 (d, $J = 9.5$ Hz), 118.1, 115.7 (d, $J = 10.3$ Hz), 55.3, 24.4 (d, $J = 56.2$ Hz), 22.3 (d, $J = 69.5$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.6 (d, $J = 58.5$ Hz), 33.9 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{26}\text{F}_6\text{O}_3\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 665.0874, found: 665.0845.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(2-methoxyphenyl)phosphine oxide (**3ib**)

 Bis(2-methoxyphenyl)phosphine oxide (**1i**; 131.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 1/1) afforded **3ib** (procedure A: 198.2 mg, 0.31 mmol, 62% yield, procedure B: 235.8 mg, 0.37 mmol, 72% yield). White solid; IR (ATR): 2952, 1591, 1476, 1433, 1399, 1317, 1180, 1121, 1061, 1015, 738, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.94 (dd, $J = 12.3, 8.2$ Hz, 4H), 7.69 (dd, $J = 8.2, 2.3$ Hz, 4H), 7.60-7.54 (m, 2H), 7.51-7.46 (m, 2H), 7.03-6.98 (m,

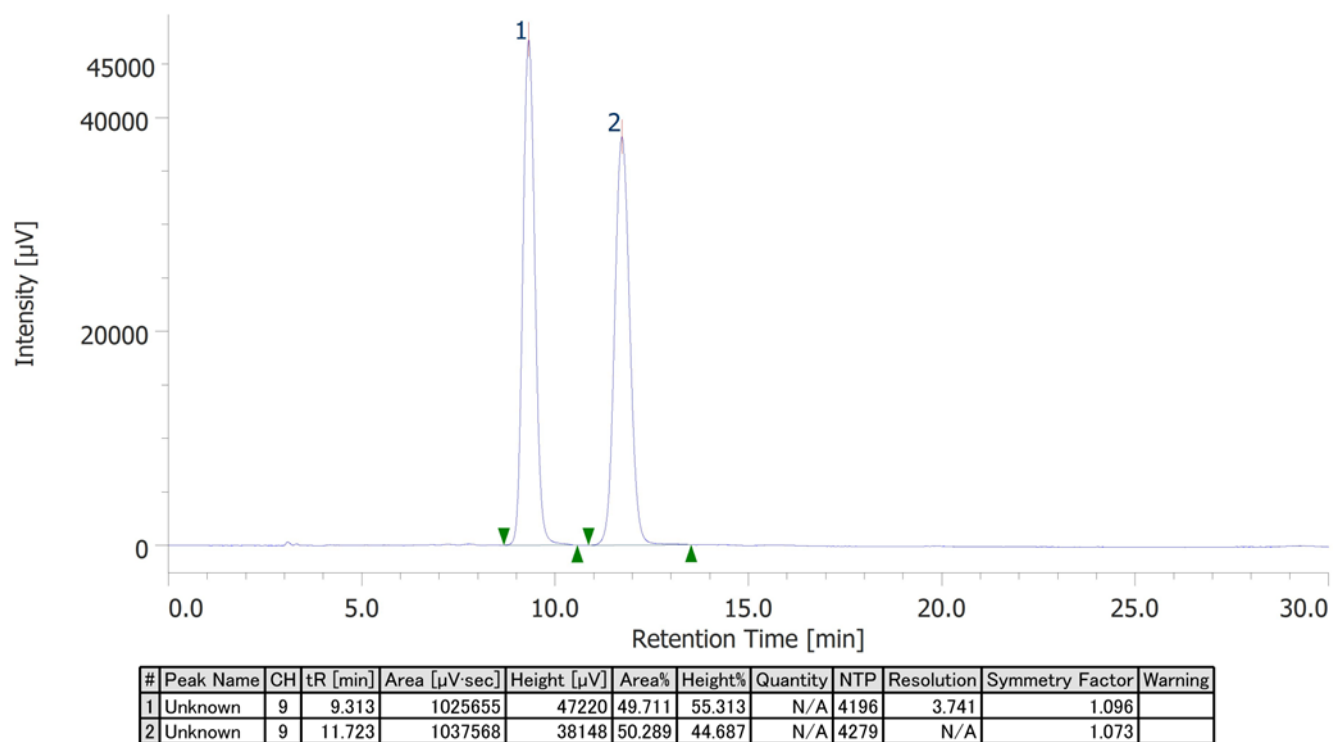
2H), 6.90-6.86 (m, 2H), 3.64 (s, 6H), 2.85-2.66 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 160.5 (d, $J = 3.6$ Hz), 136.1 (d, $J = 78.0$ Hz), 134.1-133.0 (m, 3C), 131.6 (d, $J = 10.6$ Hz), 125.7-125.4 (m), 123.3 (q, $J = 271.5$ Hz), 120.7 (d, $J = 11.6$ Hz), 119.2 (d, $J = 101.5$ Hz), 110.9 (d, $J = 6.7$ Hz), 55.3, 25.0 (d, $J = 56.4$ Hz), 22.0 (d, $J = 72.8$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 45.1 (d, $J = 67.2$ Hz), 34.1 (d, $J = 67.2$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{26}\text{F}_6\text{O}_3\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 665.0874, found: 665.0845.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)(2-methoxyphenyl)phenylphosphine oxide (**3jb**)

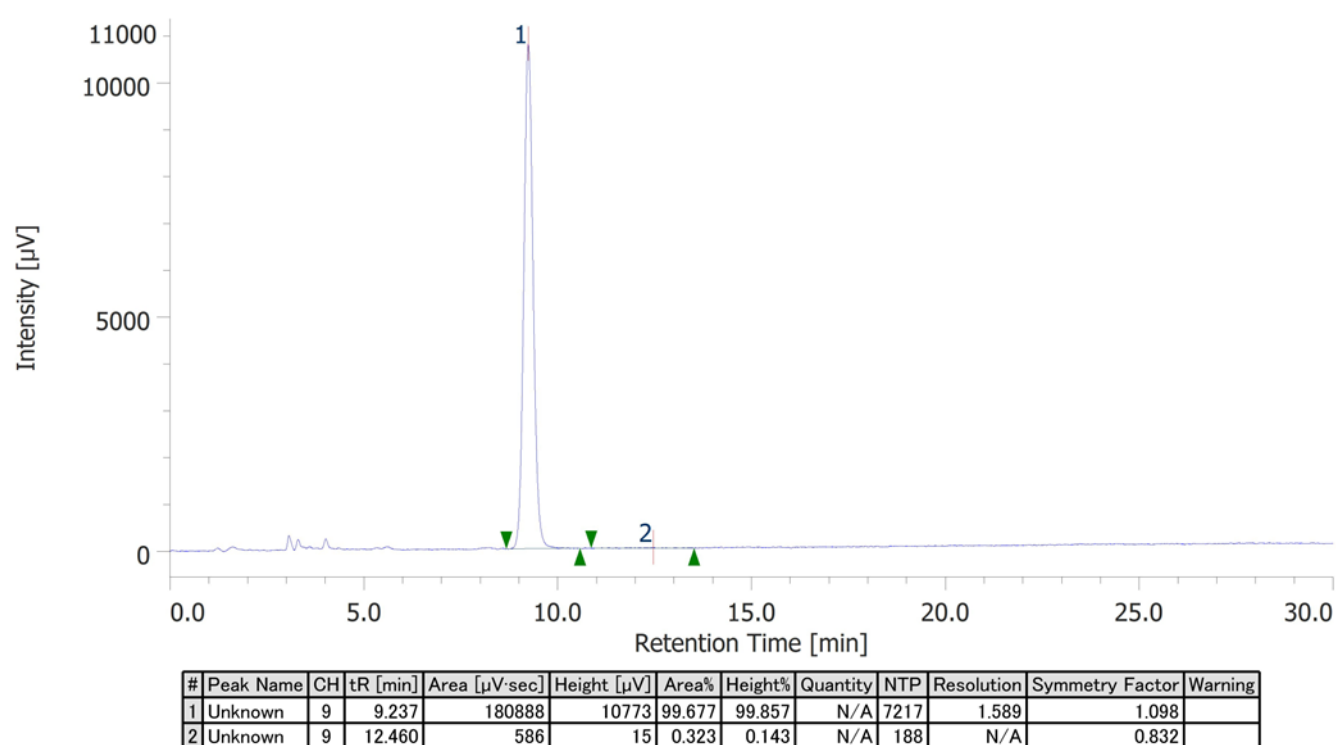


(2-Methoxyphenyl)phenylphosphine oxide (**1j**; 116.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel

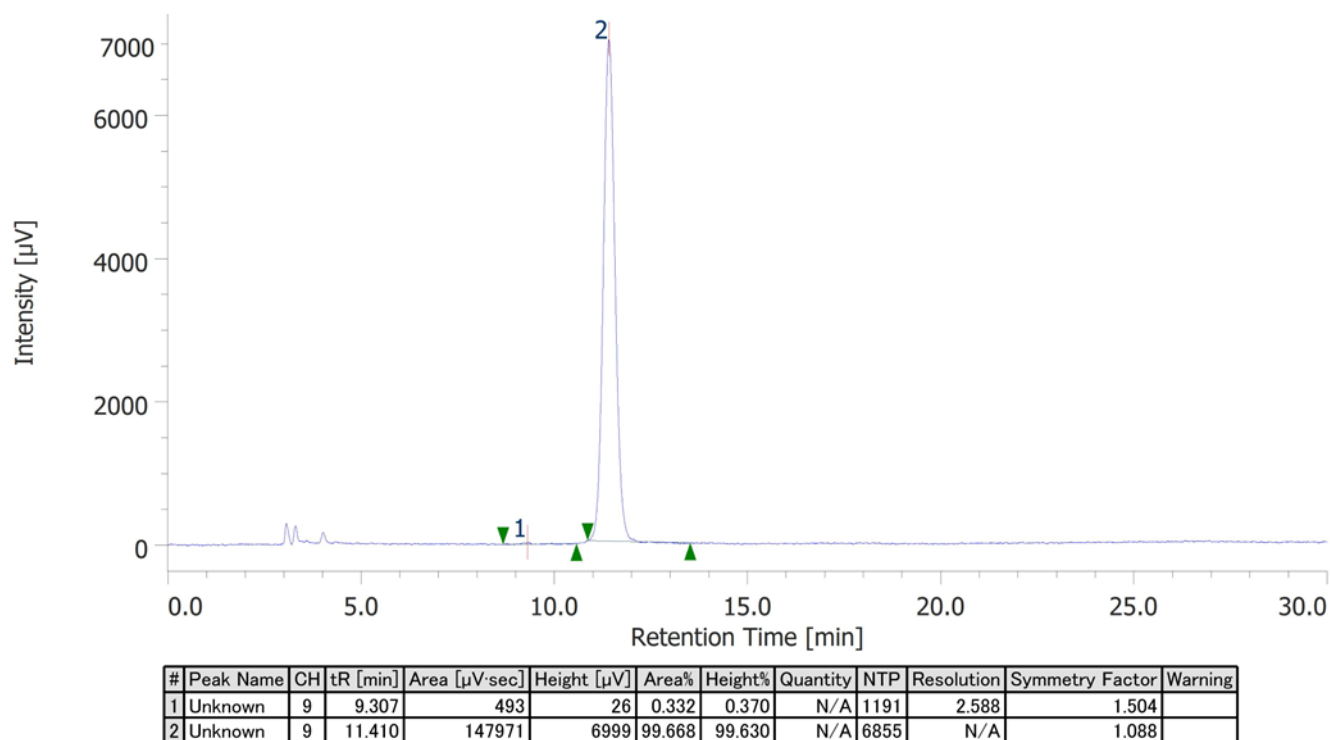
column chromatography (eluent: hexane/ethyl acetate, 1/1) afforded **3jb** (procedure A: 231.0 mg, 0.38 mmol, 75% yield, procedure B: 238.4 mg, 0.39 mmol, 78% yield). White solid; IR (ATR): 3064, 1590, 1477, 1397, 1320, 1166, 1124, 1060, 1014, 835, 799, 706 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.98-7.90 (m, 5H), 7.76-7.66 (m, 6H), 7.52-7.37 (m, 4H), 7.10-7.07 (m, 1H), 6.88-6.84 (m, 1H), 3.71 (s, 3H), 2.92-2.73 (m, 2H), 2.66-2.53 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 159.7 (d, $J = 4.6$ Hz), 136.2 (d, $J = 16.2$ Hz), 135.5 (d, $J = 15.9$ Hz), 134.5-133.1 (m, 3C), 132.0-131.6 (m, 3C), 130.6 (d, $J = 10.0$ Hz), 128.5 (d, $J = 12.0$ Hz), 125.8-125.6 (m), 122.4 (q, $J = 271.4$ Hz), 121.3 (d, $J = 10.9$ Hz), 118.7 (d, $J = 98.6$ Hz), 55.3, 24.7 (d, $J = 56.4$ Hz), 22.0 (d, $J = 70.8$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.8 (d, $J = 62.4$ Hz), 33.0 (d, $J = 62.4$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{24}\text{F}_6\text{O}_2\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 635.0769, found: 635.0742. Optical resolution was conducted by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4.6 $\times$ 250 mm, 254 nm PDA detector, 30 $^\circ\text{C}$, eluent: 20% 2-propanol in hexane, flow rate: 1 mL/min, retention time: 9.31 min and 11.7 min). Both enantiomers in the racemic mixture were separable by recycle preparative HPLC with a chiral column (Daicel Chiralpak IA: 20.0 $\times$ 250 mm, eluent: 20% 2-propanol in hexane, flow rate: 19 mL/min) to obtain enantioenriched **3jb**.



Supplementary Figure 2. HPLC data of *rac*-3jb

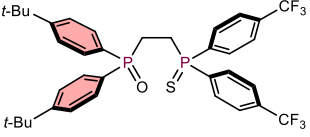


Supplementary Figure 3. HPLC data of 3jb after the separation by recycle preparative HPLC (1st peak)

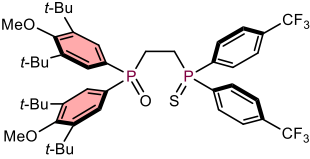


Supplementary Figure 4. HPLC data of **3jb** after the separation by recycle preparative HPLC (2nd peak)

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(4-*tert*-butylphenyl)phosphine oxide (**3kb**)

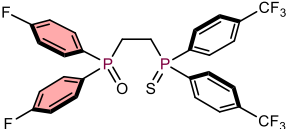
 Bis(4-*tert*-butylphenyl)phosphine oxide (**1k**; 157.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 µL, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 9/1 to 1/4) afforded **3kb** (procedure A: 184.9 mg, 0.27 mmol, 53% yield, procedure B: 128.6 mg, 0.19 mmol, 37% yield). White solid; IR (ATR): 2966, 1601, 1398, 1316, 1169, 1123, 1092, 1061, 1015, 831, 757, 704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ: 7.94 (dd, *J* = 12.5, 8.1 Hz, 4H), 7.70 (dd, *J* = 8.1, 2.2 Hz, 4H), 7.63 (dd, *J* = 11.3, 8.5 Hz, 4H), 7.47 (dd, *J* = 8.5 Hz, 2.7 Hz, 4H), 2.83-2.75 (m, 2H), 2.51-2.42 (m, 2H), 1.30 (s, 18H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 155.8 (d, *J* = 2.6 Hz), 135.8 (d, *J* = 78.4 Hz), 134.0 (qd, *J* = 33.0, 3.0 Hz), 131.7 (d, *J* = 10.7 Hz), 130.7 (d, *J* = 9.6 Hz), 128.6 (d, *J* = 102.6 Hz), 126.1-119.4 (m, 3C), 35.1, 31.2, 24.6 (dd, *J* = 56.1, 1.7 Hz), 22.7 (dd, *J* = 69.3, 2.1 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ: -63.1 ppm; ³¹P NMR (162 MHz, CDCl₃) δ: 44.6 (d, *J* = 58.6 Hz), 32.9 (d, *J* = 58.6 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₆H₃₈F₆OP₂SNa⁺ [*M*+Na]⁺: 717.1915, found: 717.1885.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (**3eb**)

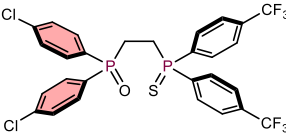
 Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (**1e**; 243.3 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 µL, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 2/1) afforded **3eb** (procedure A: 260.3 mg, 0.30 mmol, 60% yield, procedure B: 335.5 mg, 0.39 mmol, 77% yield). White solid; IR (ATR): 2960, 1396, 1322, 1169, 1131, 1062, 1014, 884, 840, 793, 739,

707 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (dd, $J = 12.5, 8.3$ Hz, 4H), 7.72 (dd, $J = 8.3, 1.7$ Hz, 4H), 7.49 (d, $J = 12.3$ Hz, 4H), 3.68 (s, 6H), 2.86-2.77 (m, 2H), 2.48-2.39 (m, 2H), 1.37 (s, 36H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 163.2 (d, $J = 3.3$ Hz), 144.8 (d, $J = 12.0$ Hz), 136.0 (d, $J = 78.2$ Hz), 134.0 (qd, $J = 32.6, 2.6$ Hz), 131.8 (d, $J = 10.7$ Hz), 129.6 (d, $J = 11.0$ Hz), 126.0-125.7 (m), 125.2 (d, $J = 103.5$ Hz), 123.5 (q, $J = 271.4$ Hz), 64.6, 36.1, 32.0, 25.2 (dd, $J = 55.5, 1.4$ Hz), 22.9 (dd, $J = 68.8, 2.2$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.8 (d, $J = 58.5$ Hz), 36.5 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{46}\text{H}_{58}\text{F}_6\text{O}_3\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 889.3378, found: 889.3339.

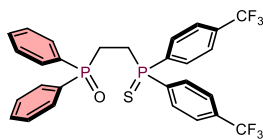
(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)bis(4-fluorophenyl)phosphine oxide (**3lb**)

 Bis(4-fluorophenyl)phosphine oxide (**11**; 119.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 9/1 to 0/100) afforded **3lb** (procedure A: 199.1 mg, 0.32 mmol, 64% yield, procedure B: 195.8 mg, 0.32 mmol, 63% yield). White solid; IR (ATR): 3042, 1592, 1499, 1397, 1321, 1237, 1162, 1119, 1060, 1014, 829, 705 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.93 (dd, $J = 12.6, 8.0$ Hz, 4H), 7.74-7.67 (m, 8H), 7.18-7.14 (m, 4H), 2.77-2.68 (m, 2H), 2.53-2.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 165.3 (dd, $J = 254.4, 3.3$ Hz), 135.5 (d, $J = 78.8$ Hz), 134.1 (qd, $J = 32.9, 3.0$ Hz), 133.3 (dd, $J = 10.9, 8.9$ Hz), 131.7 (d, $J = 10.7$ Hz), 127.4 (dd, $J = 103.1, 3.6$ Hz), 126.1-125.9 (m), 123.4 (q, $J = 271.6$ Hz), 116.6 (dd, $J = 21.6, 13.0$ Hz), 24.5 (dd, $J = 56.3, 2.1$ Hz), 22.7 (dd, $J = 70.7, 1.8$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1, -105.3--105.4 (m) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.5 (d, $J = 58.3$ Hz), 32.1 (d, $J = 58.3$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{28}\text{H}_{20}\text{F}_8\text{OP}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 641.0475, found: 641.0449.

Bis(4-chlorophenyl)(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)phosphine oxide (**3cb**)

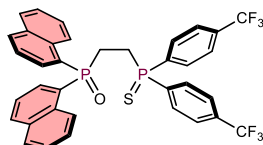
 Bis(4-chlorophenyl)phosphine oxide (**1c**; 135.5 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 2/1) afforded **3cb** (procedure A: 255.2 mg, 0.39 mmol, 78% yield, procedure B: 173.0 mg, 0.27 mmol, 53% yield). White solid; IR (ATR): 3043, 1582, 1397, 1320, 1169, 1126, 1088, 1061, 1013, 822, 754, 705 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.93 (dd, $J = 12.6, 8.1$ Hz, 4H), 7.72 (dd, $J = 8.1, 1.8$ Hz, 4H), 7.63 (dd, $J = 11.3, 8.5$ Hz, 4H), 7.45 (dd, $J = 8.5$ Hz, 2.4 Hz, 4H), 2.77-2.68 (m, 2H), 2.53-2.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 139.3 (d, $J = 2.9$ Hz), 135.4 (d, $J = 78.8$ Hz), 134.1 (q, $J = 32.8$ Hz), 132.2 (d, $J = 10.5$ Hz), 131.6 (d, $J = 10.6$ Hz), 129.6 (d, $J = 11.9$ Hz), 129.6 (d, $J = 101.1$ Hz), 126.1-125.9 (m), 123.3 (q, $J = 271.8$ Hz), 24.4 (d, $J = 55.9$ Hz), 22.4 (d, $J = 70.3$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.5 (d, $J = 58.0$ Hz), 32.2 (d, $J = 58.0$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{28}\text{H}_{20}\text{Cl}_2\text{F}_6\text{OP}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 672.9884, found: 672.9864.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)diphenylphosphine oxide (**3ab**)



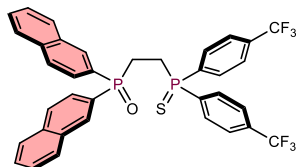
Diphenylphosphine oxide (**1a**; 101.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μ L, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 5/1 to 0/100) afforded **3ab** (procedure A: 243.0 mg, 0.42 mmol, 83% yield, procedure B: 203.4 mg, 0.35 mmol, 70% yield). White solid; IR (ATR): 2942, 1436, 1399, 1321, 1188, 1175, 1120, 1061, 1015, 741, 717, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.93 (dd, J = 12.6, 8.1 Hz, 4H), 7.74-7.69 (m, 8H), 7.56-7.45 (m, 6H), 2.81-2.73 (m, 2H), 2.56-2.47 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 135.6 (d, J = 78.6 Hz), 134.0 (qd, J = 33.0, 3.0 Hz), 132.4, 131.7 (d, J = 10.8 Hz), 131.6 (d, J = 100.0 Hz), 130.9 (d, J = 9.0 Hz), 129.1 (d, J = 11.4 Hz), 126.0-125.9 (m), 123.4 (q, J = 271.5 Hz), 24.5 (d, J = 56.4 Hz), 22.5 (d, J = 69.1 Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.6 (d, J = 58.5 Hz), 33.4 (d, J = 58.5 Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{28}\text{H}_{22}\text{F}_6\text{OP}_2\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: 605.0663, found: 605.0642.

(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)di(naphthalen-1-yl)phosphine oxide (**3mb**)



Di(naphthalen-1-yl)phosphine oxide (**1m**; 151.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μ L, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 9/1 to 1/2) afforded **3mb** (procedure A: 230.4 mg, 0.34 mmol, 68% yield, procedure B: 226.3 mg, 0.33 mmol, 66% yield). White solid; IR (ATR): 3044, 1506, 1397, 1320, 1166, 1125, 1061, 1015, 800, 772, 705, 624 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.48 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.2 Hz, 2H), 7.95-7.83 (m, 8H), 7.61-7.59 (m, 4H), 7.49-7.45 (m, 4H), 7.36-7.32 (m, 2H), 3.00-2.80 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 135.5 (d, J = 78.5 Hz), 134.1-131.2 (m, 6C), 129.2, 127.5-119.2 (m, 7C), 24.7 (d, J = 56.1 Hz), 23.0 (d, J = 70.9 Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.4 (d, J = 56.4 Hz), 37.7 (d, J = 56.4 Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{36}\text{H}_{26}\text{F}_6\text{OP}_2\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: 705.0976, found: 705.0955.

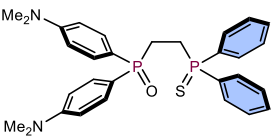
(2-(Bis(4-trifluoromethylphenyl)phosphorothioyl)ethyl)di(naphthalen-2-yl)phosphine oxide (**3nb**)



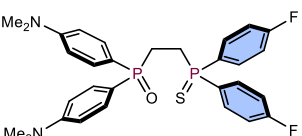
Bis(4-dimethylaminophenyl)phosphine oxide (**1n**; 151.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-trifluoromethylphenyl)phosphine (**2b**; 125.6 μ L, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 9/1 to 1/2) afforded **3nb** (procedure A: 273.7 mg, 0.40 mmol, 80% yield, procedure B: 276.1 mg, 0.40 mmol, 81% yield). White solid; IR (ATR): 2938, 1326, 1314, 1165, 1123, 1093, 1061, 817, 741, 707 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (d, J = 13.4 Hz, 2H), 7.96-7.84 (m, 10H), 7.71-7.66 (m, 6H), 7.61-7.53 (m, 4H), 2.91-2.81 (m, 2H), 2.78-2.68 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 135.6 (d, J = 78.6 Hz), 134.9 (d, J = 2.3 Hz), 134.0 (qd, J = 33.0, 3.0 Hz), 133.1 (d, J = 8.6 Hz), 132.6 (d, J = 12.9 Hz), 131.7 (d, J = 10.6 Hz), 129.1 (d, J = 11.6 Hz), 129.0, 128.6 (d, J = 100.2 Hz), 128.6 128.0, 127.3, 126.0-125.8 (m), 125.4 (d, J = 10.6 Hz), 123.4 (q, J = 271.5 Hz), 24.7 (d, J = 56.2 Hz), 22.4 (d, J = 69.6 Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.1 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.6 (d, J = 58.0 Hz), 33.6 (d, J =

58.0 Hz) ppm; HRMS (ESI) m/z calcd. for $C_{36}H_{26}F_6OP_2SNa^+$ $[M+Na]^+$: 705.0976, found: 705.0968.

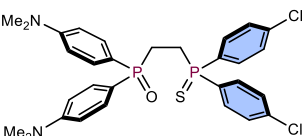
Bis(4-dimethylaminophenyl)(2-(diphenylphosphorothioyl)ethyl)phosphine oxide (3ga)

 Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorodiphenylphosphine (**2a**; 91.9 μ L, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: ethyl acetate/MeOH, 20/1) afforded **3ga** (procedure A: 126.2 mg, 0.24 mmol, 47% yield, procedure B: 216.2 mg, 0.41 mmol, 81% yield). White solid; IR (ATR): 2899, 1596, 1518, 1438, 1365, 1182, 1167, 1108, 810, 730, 693, 604 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ : 7.81-7.75 (m, 4H), 7.52-7.26 (m, 10H), 6.65 (dd, J = 9.0, 2.3 Hz, 4H), 2.96 (s, 12H), 2.74-2.65 (m, 2H), 2.44-2.35 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ : 152.3 (d, J = 2.3 Hz), 132.5-131.6 (m, 3C), 131.2 (d, J = 10.2 Hz), 128.8 (d, J = 12.0 Hz), 117.3 (d, J = 110.9 Hz), 111.5 (d, J = 12.3 Hz), 40.0, 25.2 (dd, J = 55.9, 2.2 Hz), 23.1 (dd, J = 70.6, 2.7 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ : 45.6 (d, J = 58.5 Hz), 34.8 (d, J = 58.5 Hz) ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{35}N_2OP_2S^+$ $[M+H]^+$: 533.1940, found: 533.1931.

(2-(Bis(4-fluorophenyl)phosphorothioyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (3gg)

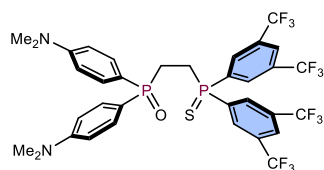
 Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-fluorophenyl)phosphine (**2g**; 128.3 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/MeOH, 99/1 to 92/8) afforded **3gg** (procedure A: 194.4 mg, 0.34 mmol, 68% yield, procedure B: 188.0 mg, 0.33 mmol, 66% yield). White solid; IR (ATR): 2896, 1592, 1515, 1495, 1361, 1227, 1158, 1113, 1102, 811, 734, 661 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ : 7.81-7.75 (m, 4H), 7.48 (dd, J = 11.0, 9.0 Hz, 4H), 7.13-7.08 (m, 4H), 6.67 (dd, J = 9.0, 2.4 Hz, 4H), 2.98 (s, 12H), 2.72-2.63 (m, 2H), 2.41-2.31 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ : 164.8 (dd, J = 254.0, 3.3 Hz), 152.2 (d, J = 2.4 Hz), 133.6 (dd, J = 11.9, 8.8 Hz), 132.1 (d, J = 10.7 Hz), 127.8 (dd, J = 83.4, 3.3 Hz), 117.0 (d, J = 111.3 Hz), 116.0 (dd, J = 21.6, 13.4 Hz), 111.4 (d, J = 12.5 Hz), 39.9, 25.4 (d, J = 56.3 Hz), 23.0 (dd, J = 70.0, 2.4 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ : -107.0-107.1 (m) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ : 44.3 (d, J = 58.6 Hz), 34.6 (d, J = 58.6 Hz) ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{33}F_2N_2OP_2S^+$ $[M+H]^+$: 569.1751, found: 569.1737.

(2-(Bis(4-chlorophenyl)phosphorothioyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (3gc)

 Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-chlorophenyl)phosphine (**2c**; 144.8 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: ethyl acetate/MeOH, 100/0 to 95/5) afforded **3gc** (procedure A: 163.6 mg, 0.27 mmol, 54% yield, procedure B: 212.8 mg, 0.37 mmol, 74% yield). White solid; IR (ATR): 2801, 1597, 1514, 1356, 1164, 1116, 1083, 1012, 815, 747, 737, 644 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ : 7.69 (dd, J = 12.4, 8.5 Hz, 4H), 7.46 (dd, J = 11.1, 8.9 Hz, 4H), 7.37 (dd, J = 8.5, 2.1 Hz, 4H), 6.64 (dd, J = 8.9, 2.2 Hz, 4H), 2.95 (s, 12H), 2.71-2.62 (m, 2H), 2.38-2.29 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ : 151.7 (d, J = 2.2 Hz), 137.8 (d, J = 3.4 Hz), 132.0 (d, J = 11.2 Hz), 131.5 (d, J = 10.6 Hz), 129.8 (d, J = 81.3 Hz), 128.5 (d, J = 12.8 Hz), 116.4 (d, J = 111.0 Hz), 110.9 (d, J = 12.4 Hz), 39.4, 24.6 (d, J = 56.1 Hz),

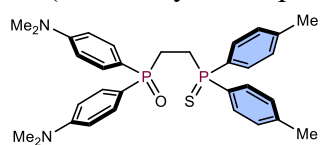
22.6 (d, $J = 70.1$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.6 (d, $J = 58.5$ Hz), 34.6 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{33}\text{Cl}_2\text{N}_2\text{OP}_2\text{S}^+ [\text{M}+\text{H}]^+$: 601.1160, found: 601.1148.

(2-(Bis(3,5-bis(trifluoromethyl)phenyl)phosphorothioyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (**3gh**)



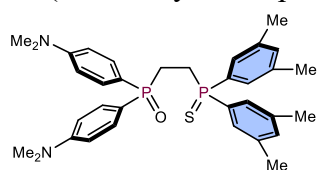
Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(3,5-bis(trifluoromethyl)phenyl)phosphine (**2h**; 246.3 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 1/1) afforded **3gh** (procedure A: 204.3 mg, 0.25 mmol, 51% yield, procedure B: 281.2 mg, 0.35 mmol, 70% yield). White solid; IR (ATR): 2907, 1598, 1518, 1358, 1277, 1179, 1114, 1096, 909, 701, 681, 644 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.28 (d, $J = 12.4$ Hz, 4H), 8.03 (s, 2H), 7.48 (dd, $J = 11.1$, 9.0 Hz, 4H), 6.68 (dd, $J = 9.0$, 2.3 Hz, 4H), 2.99 (s, 12 H), 2.90-2.81 (m, 2H), 2.40-2.31 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.5 (d, $J = 2.4$ Hz), 134.8 (d, $J = 77.9$ Hz), 133.3-132.1 (m, 2C), 131.2-131.1 (m), 126.2 (br), 122.6 (q, $J = 272.1$ Hz), 116.4 (d, $J = 112.3$ Hz), 111.6 (d, $J = 12.5$ Hz), 40.0, 25.0 (d, $J = 56.5$ Hz), 23.0 (d, $J = 68.1$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -62.7 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.8 (d, $J = 58.5$ Hz), 34.0 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{34}\text{H}_{30}\text{F}_{12}\text{N}_2\text{OP}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 827.1255, found: 827.1223.

Bis(4-dimethylaminophenyl) (2-(Bis(4-methylphenyl)phosphorothioyl)ethyl)phosphine oxide (**3gi**)



Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-methylphenyl)phosphine (**2i**; 107.3 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 95/5 to 3/2) afforded **3gi** (procedure A: 118.9 mg, 0.21 mmol, 42% yield, procedure B: 122.0 mg, 0.22 mmol, 44% yield). White solid; IR (ATR): 2909, 1596, 1517, 1363, 1164, 1116, 1101, 809, 768, 733, 654, 631 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.66 (dd, $J = 12.7$, 8.2 Hz, 4H), 7.49 (dd, $J = 11.0$, 8.8 Hz, 4H), 7.20 (dd, $J = 8.2$, 2.7 Hz, 4H), 6.66 (dd, $J = 8.8$, 2.2 Hz, 4H), 2.97 (s, 12H), 2.70-2.56 (m, 2H), 2.43-2.35 (m, 8H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.1 (d, $J = 2.3$ Hz), 141.9 (d, $J = 2.9$ Hz), 132.1 (d, $J = 10.6$ Hz), 131.1 (d, $J = 10.6$ Hz), 129.4-128.4 (m, 2C), 117.3 (d, $J = 110.7$ Hz), 111.4 (d, $J = 12.4$ Hz), 39.9, 25.2 (d, $J = 56.1$ Hz), 23.0 (d, $J = 70.7$ Hz), 21.4 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 45.1 (d, $J = 58.5$ Hz), 34.7 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{39}\text{N}_2\text{OP}_2\text{S}^+ [\text{M}+\text{H}]^+$: 561.2226, found: 561.2241.

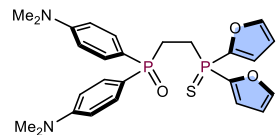
Bis(4-dimethylaminophenyl)(2-(Bis(3,5-dimethylphenyl)phosphorothioyl)ethyl)phosphine oxide (**3gj**)



Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(3,5-dimethylphenyl)phosphine (**2j**; 125.6 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: ethyl acetate/MeOH, 20/1) afforded **3gj** (procedure A: 99.6 mg, 0.17 mmol, 34% yield, procedure B: 224.9 mg, 0.38 mmol, 76% yield). White solid; IR (ATR): 2911, 1595, 1515, 1361, 1161, 1114, 812, 768, 734, 691, 642 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.49 (dd, $J = 11.0$, 8.6 Hz, 4H), 7.37 (d, $J = 13.1$ Hz, 4H), 7.06 (s, 2H), 6.65 (dd, $J = 8.6$,

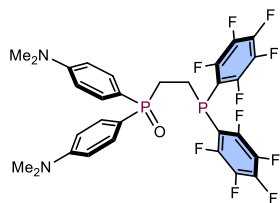
1.8 Hz, 4H), 2.95 (s, 12H), 2.73-2.64 (m, 2H), 2.44-2.33 (m, 2H), 2.29 (s, 12H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.2, 138.4 (d, $J = 12.7$ Hz), 133.4 (d, $J = 3.4$ Hz), 132.2 (d, $J = 10.6$ Hz), 131.9 (d, $J = 79.1$ Hz), 128.7 (d, $J = 10.1$ Hz), 117.5 (d, $J = 110.7$ Hz), 111.5 (d, $J = 12.4$ Hz), 40.0, 24.9 (d, $J = 55.6$ Hz), 22.9 (d, $J = 70.6$ Hz), 21.3 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 45.5 (d, $J = 58.5$ Hz), 34.9 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{34}\text{H}_{43}\text{N}_2\text{OP}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 589.2566, found: 589.2550.

(2-(Di(furan-2-yl)phosphorothioyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (**3gd**)



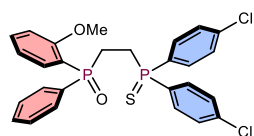
Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorodi(furan-2-yl)phosphine (**2d**; 77.8 μL , 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 9/1 to 1/1 and DCM/MeOH, 97/3) afforded **3gd** (procedure A: 92.0 mg, 0.18 mmol, 36% yield, procedure). White solid; IR (ATR): 2910, 1595, 1516, 1363, 1162, 1114, 1003, 813, 736, 654 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (ddd, $J = 2.4, 1.7, 0.8$ Hz, 2H), 7.49 (dd, $J = 11.0, 8.8$ Hz, 4H), 7.12 (ddd, $J = 3.4, 2.2, 0.8$ Hz, 2H), 6.67 (dd, $J = 8.8, 2.1$ Hz, 4H), 6.44 (ddd, $J = 3.4, 1.6, 1.6$ Hz, 2H), 2.96 (s, 12H), 2.71-2.62 (m, 2H), 2.42-2.30 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.3, 148.7 (d, $J = 7.1$ Hz), 146.4 (d, $J = 117.7$ Hz), 132.2 (d, $J = 10.6$ Hz), 122.8 (d, $J = 20.5$ Hz), 117.2 (d, $J = 111.0$ Hz), 111.5 (d, $J = 12.4$ Hz), 111.2 (d, $J = 9.0$ Hz), 40.0, 25.3 (d, $J = 62.0$ Hz), 22.5 (d, $J = 70.9$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 34.3 (d, $J = 63.6$ Hz), 18.1 (d, $J = 63.6$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_3\text{P}_2\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 535.1345, found: 535.1332.

(2-(Bis(pentafluorophenyl)phosphanyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (**3gk**)



Bis(4-dimethylaminophenyl)phosphine oxide (**1g**; 144.2 mg, 0.5 mmol, 1.0 equiv) and chlorobis(pentafluorophenyl)phosphine (**2k**; 200.3 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. The reactions were conducted without the treatment of sulfur. Purification of the crude product by silica-gel column chromatography (eluent: ethyl acetate/MeOH, 99/1) afforded **3gk** (procedure A: 112.4 mg, 0.17 mmol, 33% yield, procedure B: 15.5 mg, 0.023 mmol, 5% yield). White solid; IR (ATR): 2911, 1597, 1469, 1362, 1116, 1082, 974, 813, 734, 528 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.45 (dd, $J = 10.9, 8.9$ Hz, 4H), 6.67 (dd, $J = 8.9, 2.1$ Hz, 4H), 2.98 (s, 12H), 2.73-2.66 (m, 2H), 2.21-2.12 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.4 (d, $J = 1.9$ Hz), 149.0-146.3 (m), 143.9-141.0 (m), 139.0-136.1 (m), 132.2 (d, $J = 10.5$ Hz), 116.9 (d, $J = 111.1$ Hz), 111.4 (d, $J = 12.5$ Hz), 108.7-107.9 (m), 40.0, 27.4 (dd, $J = 69.7, 21.3$ Hz), 16.4-16.1 (m) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -129.3--129.5 (m), -149.3--149.5 (m), -159.7--159.8 (m) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 33.6 (d, $J = 58.6$ Hz), -41.9--42.9 (m) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{24}\text{F}_{10}\text{N}_2\text{OP}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 703.1096, found: 703.1067.

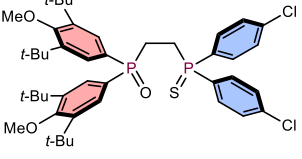
(2-(Bis(4-chlorophenyl)phosphorothioyl)ethyl)(2-methylphenyl)phenylphosphine oxide (**3jc**)



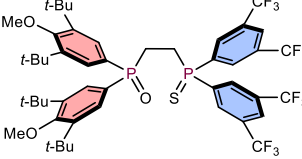
(2-Methoxyphenyl)phenylphosphine oxide (**1j**; 116.1 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-chlorophenyl)phosphine (**2c**; 144.8 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 4/1 to 1/3) afforded **3jc** (procedure A: 128.3 mg, 0.24 mmol, 47% yield, procedure B: 195.5 mg, 0.36 mmol, 71% yield). White solid; IR (ATR): 2935, 1577, 1476, 1271,

1177, 1113, 1085, 1011, 745, 692, 635, 620 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.97-7.92 (m, 1H), 7.76-7.67 (m, 6H), 7.53-7.45 (m, 2H), 7.43-7.37 (m, 6H), 7.12-7.07 (m, 1H), 6.87 (dd, $J = 8.3, 5.3$ Hz, 1H), 3.73 (s, 3H), 2.84-2.70 (m, 2H), 2.61-2.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 159.8 (d, $J = 4.7$ Hz), 138.7-138.6 (m), 134.6 (d, $J = 5.5$ Hz), 134.5 (d, $J = 1.5$ Hz), 133.3-132.3 (m, 2C), 131.9 (d, $J = 2.8$ Hz), 130.8-129.8 (m, 2C), 129.3-129.1 (m), 128.5 (d, $J = 12.1$ Hz), 121.3 (d, $J = 10.9$ Hz), 119.0 (d, $J = 98.2$ Hz), 110.9 (d, $J = 6.8$ Hz), 55.5, 25.1 (dd, $J = 57.0, 3.1$ Hz), 22.1 (dd, $J = 71.1, 1.8$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.6 (d, $J = 62.9$ Hz), 33.3 (d, $J = 62.9$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{27}\text{H}_{24}\text{Cl}_2\text{O}_2\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 567.0242, found: 567.0232.

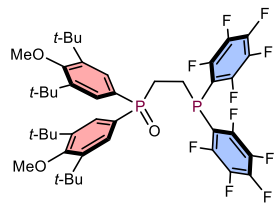
(2-(Bis(4-chlorophenyl)phosphorothioyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide
(**3ec**)

 Bis(3,5-di-*tert*-butyl-4-methoxyphenyl) oxide (**1e**; 243.3 mg, 0.5 mmol, 1.0 equiv) and chlorobis(4-chlorophenyl)phosphine (**2c**; 144.8 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 4/1 to 2/3) afforded **3ec** (procedure A: 240.8 mg, 0.30 mmol, 60% yield, procedure B: 178.6 mg, 0.22 mmol, 45% yield). White solid; IR (ATR): 2958, 1577, 1480, 1390, 1169, 1147, 1115, 1086, 1011, 884, 748, 639, 623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.73 (dd, $J = 12.4, 8.5$ Hz, 4H), 7.47 (d, $J = 12.3$ Hz, 4H), 7.38 (dd, $J = 8.5, 2.2$ Hz, 4H), 3.65 (s, 6H), 2.75-2.66 (m, 2H), 2.46-2.37 (m, 2H), 1.35 (s, 36H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 162.9 (d, $J = 3.3$ Hz), 144.5 (d, $J = 11.8$ Hz), 138.6 (d, $J = 3.4$ Hz), 132.5 (d, $J = 11.2$ Hz), 130.2 (d, $J = 81.8$ Hz), 129.4 (d, $J = 11.1$ Hz), 129.1 (d, $J = 12.8$ Hz), 125.2 (d, $J = 103.7$ Hz), 64.4, 36.0, 31.9, 25.3 (d, $J = 55.2$ Hz), 22.9 (d, $J = 69.0$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.6 (d, $J = 58.5$ Hz), 35.8 (d, $J = 58.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{44}\text{H}_{58}\text{Cl}_2\text{O}_3\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 821.2851, found: 821.2835.

(2-(Bis(3,5-bis(trifluoromethyl)phenyl)phosphorothioyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (**3eh**)

 Bis(3,5-di-*tert*-butyl-4-methoxyphenyl) oxide (**1e**; 243.3 mg, 0.5 mmol, 1.0 equiv) and chlorobis(3,5-bis(trifluoromethyl)phenyl)phosphine (**2h**; 246.3 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/acetone, 7/1) afforded **3eh** (procedure A: 301.7 mg, 0.30 mmol, 60% yield, procedure B: 282.1 mg, 0.28 mmol, 56% yield). White solid; IR (ATR): 2964, 1360, 1280, 1170, 1134, 1124, 1100, 1009, 902, 733, 682, 637 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 12.5$ Hz, 4H), 8.04 (s, 2H), 7.51 (d, $J = 12.4$ Hz, 4H), 3.68 (s, 6H), 2.92-2.84 (m, 2H), 2.51-2.41 (m, 2H), 1.37 (s, 36H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 163.3 (d, $J = 3.3$ Hz), 144.9 (d, $J = 12.0$ Hz), 134.7 (d, $J = 78.2$ Hz), 132.9 (qd, $J = 34.2, 12.2$ Hz), 131.2-131.1 (m), 129.6 (d, $J = 11.0$ Hz), 126.4-126.3 (m), 124.9 (d, $J = 104.5$ Hz), 122.6 (q, $J = 272.0$ Hz), 64.5, 36.1, 31.9, 25.4 (d, $J = 56.5$ Hz), 22.8 (d, $J = 67.5$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -62.7 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 44.8 (d, $J = 58.4$ Hz), 35.3 (d, $J = 58.4$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{48}\text{H}_{56}\text{F}_{12}\text{O}_3\text{P}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 1025.3126, found: 1025.3104

(2-(Bis(pentafluorophenyl)phosphanyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide
(**3ek**)



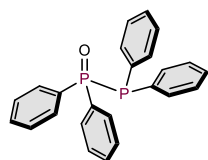
Bis(3,5-di-*tert*-butyl-4-methoxyphenyl) oxide (**1e**; 243.3 mg, 0.5 mmol, 1.0 equiv) and chlorobis(pentafluorophenyl)phosphine (**2k**; 200.3 mg, 0.5 mmol, 1.0 equiv) were employed as starting materials. The reactions were conducted without the treatment of sulfur. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 50/1) afforded **3ek** (procedure A: 130.6 mg, 0.15 mmol, 30% yield, procedure B: 55.8 mg, 0.064 mmol, 13% yield). White solid; IR (ATR): 2964, 1516, 1469, 1148, 1116, 1086, 1008, 974, 881, 476 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.51 (d, $J = 12.3$ Hz, 4H), 3.69 (s, 6H), 2.74-2.67 (m, 2H), 2.33-2.24 (m, 2H), 1.39 (s, 36H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 163.1 (d, $J = 3.3$ Hz), 149.1-146.3 (m), 144.7 (d, $J = 11.9$ Hz), 144.0-141.2 (m), 139.1-136.2 (m), 129.6 (d, $J = 10.9$ Hz), 125.3 (d, $J = 103.4$ Hz), 108.9-107.7 (m), 64.6, 36.1, 31.9, 27.7 (dd, $J = 67.9, 22.5$ Hz), 17.0-16.8 (m) ppm; ^{19}F NMR (376 MHz, CDCl_3) -129.7–-129.9 (m), -148.9–-149.0 (m), -159.4–-159.5 (m) ppm; ^{31}P NMR (162 MHz, CDCl_3) 34.5 (d, $J = 58.2$ Hz), -41.4–-42.4 (m) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{44}\text{H}_{50}\text{F}_{10}\text{O}_3\text{P}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 901.2968, found: 901.2937.

(G) Synthesis of **4aa** and **4gb**

Diphosphine oxide **4aa** was synthesized according to the literature³.

To a 50 mL round bottom flask, methoxydiphenylphosphine (3.76 mL, 20 mmol) and chlorodiphenylphosphine (3.59 mL, 20 mmol) dissolved in degassed benzene (10 mL) was added under nitrogen atmosphere, and the mixture was refluxed for 3 h. The solvent was removed by decantation and washed with benzene under nitrogen atmosphere by using cannula to afford the product as a white solid.

1,1,2,2-Tetraphenyldiphosphine 1-oxide (**4aa**)

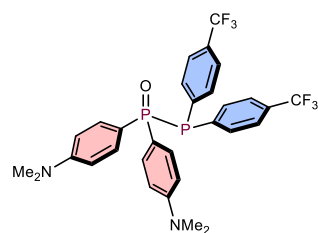


White solid; IR (ATR): 1434, 1175, 1092, 739, 690, 556, 513, 496, 463, 435 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.80-7.75 (m, 4H), 7.61-7.57 (m, 4H), 7.44-7.21 (m, 12H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 135.3 (dd, $J = 19.5, 7.1$ Hz), 133.8 (dd, $J = 85.4, 14.0$ Hz), 131.5-129.8 (m, 3C), 129.6, 128.5-128.2 (m, 2C) ppm; ^{31}P NMR (162 MHz, CDCl_3) 36.6 (d, $J = 227.6$ Hz), -22.0 (d, $J = 227.6$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{20}\text{OP}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 409.0882, found: 409.0884.

Diphosphine oxide **4gb** was synthesized by following procedure.

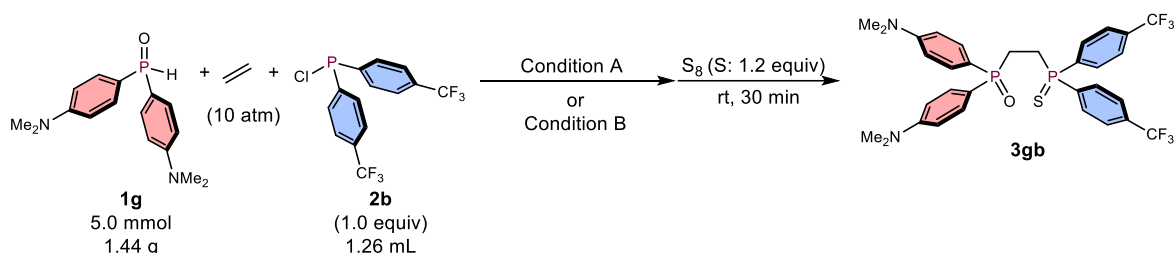
In an oven-dried test tube were placed phosphine oxide **1g** (1.44g, 5 mmol, 1.0 equiv). After the addition of DCM (15 mL) under nitrogen, chlorophosphine **2b** (1.26 mL, 5 mmol, 1.0 equiv) and DBU (0.75 mL, 5 mmol, 1.0 equiv) were added. After the resulting mixture was stirred at room temperature for 30 min, the solvent was evaporated, and crude product was purified by silica-gel column chromatography (eluent: DCM/Acetone, 9/1) under nitrogen to afford **4gb** in 70%, of which isolated yield was lower than NMR yield because only high-purity fractions of chromatography were collected.

1,1-Bis(4-dimethylaminophenyl)-2,2-bis(4-trifluoromethylphenyl)diphosphine 1-oxide (**4gb**)



White solid; IR (ATR): 1594, 1320, 1163, 1106, 1058, 1011, 811, 605, 549, 517 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.67-7.62 (m, 4H), 7.53-7.47 (m, 8H), 6.62 (dd, $J = 9.0, 2.6$ Hz, 4H), 2.98 (s, 12H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.3, 136.6-135.3 (m, 2C), 132.7 (dd, $J = 10.5, 5.8$ Hz), 131.2 (q, $J = 32.2$ Hz), 125.2-125.1 (m), 124.1 (q, $J = 270.9$ Hz), 118.1 (dd, $J = 100.0, 15.9$ Hz), 111.5 (d, $J = 12.6$ Hz), 40.1 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -62.8 ppm; ^{31}P NMR (162 MHz, CDCl_3) 37.9 (d, $J = 206.1$ Hz), -23.6 (d, $J = 206.1$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{28}\text{F}_6\text{N}_2\text{OP}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 631.1473, found: 631.1477.

(H) Gram Scale Synthesis of **3gb**



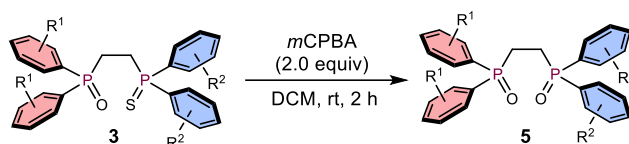
General Procedure A (for blue LED)

In an oven-dried 10 mL pressure-resistant glass tube were placed phosphine oxide **1g** (1.44 g, 5.0 mmol, 1.0 equiv) and $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (9.1 mg, 0.01 mmol, 0.2 mol%). After the addition of DCE (15 mL) under nitrogen, chlorophosphine **2b** (1.26 mL, 5.0 mmol, 1.0 equiv) and DBU (0.75 mL, 5.0 mmol, 1.0 equiv) were added. Then, the tube was placed into autoclave which consists of a polycarbonate cylinder, and ethylene gas was pressurised to 10 atm. After the resulting mixture was stirred at room temperature for 4h under the irradiation of blue LED (45W PR160L-440 nm Kessil light $\times$ 2), sulfur (192 mg, 6 mmol, 1.2 equiv of S) was added into the reaction mixture. After the mixture was stirred for 30 min, the solvent was evaporated to give the crude mixture. The crude product was purified by silica-gel column chromatography (DCM/acetone = 9/1 to 4/1) to afford the product **3gb** (2.19 g, 3.3 mmol, 65%).

General Procedure B (for white LED)

In an oven-dried 10 mL pressure-resistant glass tube was placed phosphine oxide **1g** (1.44 g, 5.0 mmol, 1.0 equiv). After the addition of DCE (15 mL) under nitrogen, chlorophosphine **2b** (1.26 mL, 5.0 mmol, 1.0 equiv) and DBU (0.75 mL, 5.0 mmol, 1.0 equiv) were added. Then, the tube was placed into autoclave which consists of a polycarbonate cylinder, and ethylene gas was pressurised to 10 atm. After the resulting mixture was stirred at room temperature for 24h under the irradiation of white LED (A 160WE TUNA SUN $\times$ 4), sulfur (192 mg, 6 mmol, 1.2 equiv of S) was added into the reaction mixture. After the mixture was stirred for 30 min, the solvent was evaporated to give the crude mixture. The crude product was purified by silica-gel column chromatography (DCM/acetone = 9/1 to 4/1) to afford the product **3gb** (2.20 g, 3.3 mmol, 66%).

(I) Transformation of Oxide Sulfide **3** to Dioxide **5**⁴



DPPE derivatives **3** (1.0 equiv) was placed in a round bottom flask and dissolved into DCM (0.05 M). After the solution was cooled to 0 °C, *m*CPBA (2.0 equiv) was slowly added, and then, the mixture was stirred for 2h. The reaction mixture was then quenched with 5% aq. NaHCO₃ and extracted with DCM. The organic layer was dried with Na₂SO₄, filtered, and concentrated under reduced pressure. The product was purified by silica-gel column chromatography to afford the product **5**.

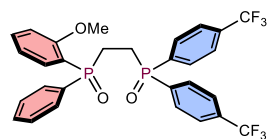
(2-(Bis(4-trifluoromethylphenyl)phosphinyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (**5gb**)

5gb (334.3 mg, 0.5 mmol, 1.0 equiv) was employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/MeOH, 9/1) afforded **5gb** (295.0 mg, 0.45 mmol, 90% yield). White solid; IR (ATR): 2910, 1599, 1517, 1317, 1165, 1117, 1061, 1017, 816, 781, 743, 709 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 7.84 (dd, *J* = 10.9, 8.2 Hz, 4H), 7.69 (dd, *J* = 8.2, 1.8 Hz, 4H), 7.46 (dd, *J* = 11.0, 9.0 Hz, 4H), 6.65 (dd, *J* = 9.0, 2.2 Hz, 4H), 2.96 (s, 12H), 2.62-2.53 (m, 2H), 2.39-2.31 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ : 152.4 (d, *J* = 2.4 Hz), 136.1 (d, *J* = 96.2 Hz), 134.1 (qd, *J* = 33.0, 2.9 Hz), 132.2 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 9.6 Hz), 125.9-125.8 (m), 128.0 (q, *J* = 271.5 Hz), 116.8 (d, *J* = 110.9 Hz), 111.5 (d, *J* = 12.3 Hz), 40.0, 22.0 (dd, *J* = 69.5, 3.9 Hz), 21.8 (dd, *J* = 70.8, 2.9 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ : -63.2 ppm; ³¹P NMR (162 MHz, CDCl₃) δ : 34.0 (d, *J* = 52.0 Hz), 32.0 (d, *J* = 52.0 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₂H₃₂F₆N₂O₂P₂Na⁺ [M+Na]⁺: 675.1735, found: 675.1727.

(2-(Bis(4-trifluoromethylphenyl)phosphinyl)ethyl)bis(4-methoxyphenyl)phosphine oxide (**5fb**)

5fb (125.5 mg, 0.2 mmol, 1.0 equiv) was employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 1/1) afforded **5fb** (114.4 mg, 0.18 mmol, 91% yield). White solid; IR (ATR): 2914, 1598, 1504, 1324, 1171, 1121, 1102, 1062, 1018, 830, 749, 710 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 7.86 (dd, *J* = 10.9, 8.2 Hz, 4H), 7.73 (dd, *J* = 8.2, 1.9 Hz, 4H), 7.60 (dd, *J* = 11.0, 8.8 Hz, 4H), 6.95 (dd, *J* = 8.8, 2.2 Hz, 4H), 3.83 (s, 6H), 2.62-2.52 (m, 2H), 2.49-2.39 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ : 162.7 (d, *J* = 2.8 Hz), 135.8 (d, *J* = 95.6 Hz), 134.3 (qd, *J* = 32.8, 2.4 Hz), 132.7 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 9.6 Hz), 126.1-125.9 (m), 123.4 (q, *J* = 271.5 Hz), 122.9 (d, *J* = 105.6 Hz), 114.6 (d, *J* = 12.6 Hz), 55.4, 22.1 (dd, *J* = 28.3, 2.9 Hz), 21.4 (dd, *J* = 29.2, 2.9 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ : -63.2 ppm; ³¹P NMR (162 MHz, CDCl₃) δ : 34.5 (d, *J* = 53.0 Hz), 32.2 (d, *J* = 53.0 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₀H₂₆F₆O₄P₂Na⁺ [M+Na]⁺: 649.1103, found: 649.1085.

(2-(Bis(4-trifluoromethylphenyl)phosphinyl)ethyl)bis(2-methoxyphenyl)phosphine oxide (**5jb**)

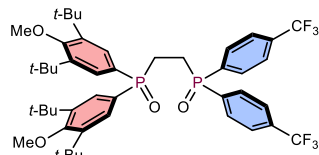


5jb (122.5 mg, 0.20 mmol, 1.0 equiv) was employed as starting materials.

Purification of the crude product by silica-gel column chromatography (eluent: DCM/MeOH, 100/0 to 15/1) afforded **5jb** (116.3 mg, 0.195 mmol, 97% yield).

White solid; IR (ATR): 2940, 1590, 1478, 1435, 1399, 1319, 1167, 1124, 1060, 1015, 800, 745 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.58-7.55 (m, 4H), 7.46-7.28 (m, 10H), 6.92-6.81 (m, 3H), 3.67 (s, 3H), 2.28-1.95 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 159.8 (d, $J = 4.2$ Hz), 136.5-131.9 (m, 6C), 131.4 (d, $J = 9.2$ Hz), 130.7 (d, $J = 9.4$ Hz), 128.5 (d, $J = 11.5$ Hz), 126.0-125.8 (m), 123.5 (q, $J = 271.5$ Hz), 121.4 (d, $J = 10.4$ Hz), 119.0 (dd, $J = 92.1, 6.9$ Hz), 111.0 (d, $J = 6.5$ Hz), 55.4, 21.6 (d, $J = 67.2$ Hz), 21.0 (d, $J = 66.4$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.2 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 32.5 (d, $J = 54.9$ Hz), 31.7 (d, $J = 54.9$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{24}\text{F}_6\text{O}_3\text{P}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 619.0997, found: 619.0982.

(2-(Bis(4-trifluoromethylphenyl)phosphinyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (**5eb**)

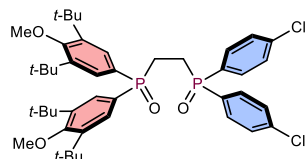


5eb (216.7 mg, 0.25 mmol, 1.0 equiv) was employed as starting materials.

Analytically pure product **5eb** was obtained without silica-gel column chromatography (212.3 mg, 0.25 mmol, quantitative yield). White solid; IR

(ATR): 2960, 1700, 1397, 1321, 1170, 1131, 1062, 1009, 885, 838, 794, 746 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.93 (dd, $J = 11.2, 8.0$ Hz, 4H), 7.74 (dd, $J = 8.0, 2.0$ Hz, 4H), 7.50 (d, $J = 12.3$ Hz, 4H), 3.68 (s, 6H), 2.75-2.67 (m, 2H), 2.47-2.39 (m, 2H), 1.36 (s, 36H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 163.2 (d, $J = 3.3$ Hz), 144.8 (d, $J = 12.0$ Hz), 136.0 (d, $J = 96.5$ Hz), 134.3 (qd, $J = 33.1, 2.6$ Hz), 131.5 (d, $J = 9.7$ Hz), 129.5 (d, $J = 11.0$ Hz), 126.1-125.9 (m), 125.1 (d, $J = 103.1$ Hz), 123.5 (q, $J = 271.7$ Hz), 64.6, 36.1, 31.9, 22.4-21.6 (m, 2C) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.2 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 35.3 (d, $J = 52.5$ Hz), 31.9 (d, $J = 52.5$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{46}\text{H}_{58}\text{F}_6\text{O}_4\text{P}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 873.3607, found: 873.3592.

(2-(Bis(4-chlorophenyl)phosphinyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (**5ec**)

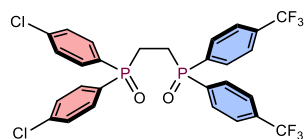


5ec (240.0 mg, 0.3 mmol, 1.0 equiv) was employed as starting materials.

Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 98/2 to 7/3) afforded **5ec** (249.4 mg, 0.32 mmol, quantitative yield). White solid; IR (ATR): 2961, 1582, 1408, 1391, 1198, 1172, 1148, 1116,

1090, 1011, 749, 728 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.64 (dd, $J = 11.0, 8.4$ Hz, 4H), 7.48-7.26 (m, 8H), 3.67 (s, 6H), 2.63-2.51 (m, 2H), 2.42-2.33 (m, 2H), 1.36 (s, 36H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 162.9 (d, $J = 3.3$ Hz), 144.5 (d, $J = 11.8$ Hz), 138.8 (d, $J = 3.3$ Hz), 132.1 (d, $J = 10.2$ Hz), 130.3 (d, $J = 100.1$ Hz), 129.4-129.2 (m, 2C), 125.3 (d, $J = 102.9$ Hz), 64.4, 35.9, 31.8, 22.4-21.7 (m, 2C) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 34.8 (d, $J = 52.0$ Hz), 32.5 (d, $J = 52.0$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{44}\text{H}_{58}\text{Cl}_2\text{O}_4\text{P}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 805.3080, found: 805.3082.

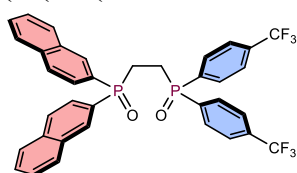
Bis(4-chlorophenyl)(2-(Bis(4-trifluoromethylphenyl)phosphinyl)ethyl)phosphine oxide (**5cb**)



3cb (130.3 mg, 0.2 mmol, 1.0 equiv) was employed as starting materials.

Purification of the crude product by silica-gel column chromatography (eluent: DCM/MeOH, 100/0 to 5/1) afforded **5cb** (127.1 mg, 0.20 mmol, quantitative yield). White solid; IR (ATR): 2914, 1583, 1483, 1400, 1327, 1183, 1164, 1123, 1063, 1015, 754, 711 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.87-7.82 (m, 4H), 7.74-7.72 (m, 4H), 7.61 (dd, J = 10.9, 8.4 Hz, 4H), 7.44 (dd, J = 8.4, 2.1 Hz, 4H), 2.58-2.42 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 139.4 (d, J = 2.9 Hz), 136.0-134.0 (m, 2C), 132.2 (d, J = 9.9 Hz), 131.3 (d, J = 9.2 Hz), 130.2-129.2 (m, 2C), 126.2-126.0 (m), 123.4 (q, J = 271.4 Hz), 21.8 (d, J = 2.9 Hz), 21.2 (d, J = 2.9 Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.2 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 31.8 (d, J = 52.0 Hz), 30.9 (d, J = 52.0 Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{28}\text{H}_{20}\text{Cl}_2\text{F}_6\text{O}_2\text{P}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 657.0112, found: 657.0093.

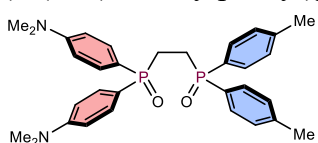
(2-(Bis(4-trifluoromethylphenyl)phosphinyl)ethyl)di(naphthalen-2-yl)phosphine oxide (**5nb**)



3na (136.5 mg, 0.2 mmol, 1.0 equiv) was employed as starting materials.

Purification of the crude product by silica-gel column chromatography (eluent: DCM/MeOH, 100/0 to 5/1) afforded **5nb** (127.7 mg, 0.19 mmol, 96% yield). White solid; IR (ATR): 3053, 1401, 1321, 1193, 1164, 1132, 1103, 1062, 1017, 833, 745, 654 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.41 (dd, J = 13.3, 1.5 Hz, 2H), 7.91-7.83 (m, 10H), 7.70-7.64 (m, 6H), 7.61-7.52 (m, 4H), 2.77-2.60 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 135.7 (d, J = 96.8 Hz), 134.9-133.8 (m, 2C), 133.0 (d, J = 8.7 Hz), 132.6 (d, J = 12.8 Hz), 131.4 (d, J = 9.7 Hz), 129.2-128.1 (m, 3C), 127.5, 127.4, 126.1-125.9 (m, 2C), 125.3 (d, J = 10.6 Hz), 123.4 (d, J = 271.5 Hz), 21.9-21.1 (m, 2C) ppm; ^{19}F NMR (376 MHz, CDCl_3) δ : -63.2 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 33.3 (d, J = 52.2 Hz), 31.5 (d, J = 52.2 Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{36}\text{H}_{26}\text{F}_6\text{O}_2\text{P}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 689.1204, found: 689.1190.

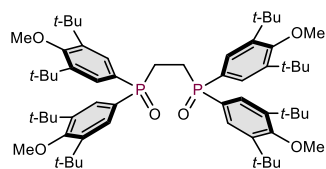
(2-(Bis(4-methylphenyl)phosphinyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (**5gi**)



3gi (140.2 mg, 0.25 mmol, 1.0 equiv) was employed as starting materials.

Purification of the crude product by silica-gel column chromatography (eluent: DCM/MeOH, 99/1 to 9/1) afforded **5gi** (129.6 mg, 0.24 mmol, 95% yield). White solid; IR (ATR): 2910, 1598, 1517, 1362, 1183, 1166, 1116, 809, 739, 653 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.58-7.54 (m, 4H), 7.50-7.45 (m, 4H), 7.21 (d, J = 7.7 Hz, 4H), 6.65 (d, J = 8.4 Hz, 4H), 2.96 (s, 12H), 2.47-2.35 (m, 10H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 152.2 (d, J = 1.3 Hz), 142.2 (d, J = 2.3 Hz), 132.1 (d, J = 9.2 Hz), 130.8 (d, J = 8.2 Hz), 130.0-128.3 (m, 2C), 118.3-116.6 (m), 111.4 (d, J = 10.7 Hz), 40.0, 22.5-21.8 (m, 2C), 21.5 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 34.4 (d, J = 52.0 Hz), 34.0 (d, J = 52.0 Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{38}\text{N}_2\text{O}_2\text{P}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 567.2301, found: 567.2296.

1,2-Ethanediyldis(bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine) dioxide (**5ee**)



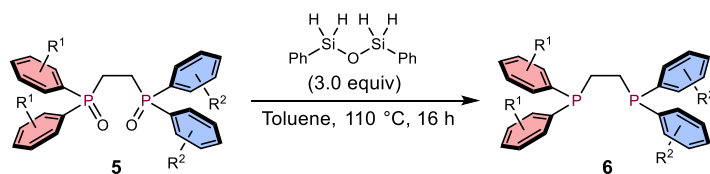
3ee (32.0 mg, 0.032 mmol, 1.0 equiv) was employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 2/1 to 1/1) afforded **5ee** (25.4 mg, 0.025 mmol, 81% yield). White solid; IR (ATR): 2960, 1445, 1406, 1225, 1213, 1149, 1117, 1003, 880, 741 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.54-7.51 (m, 8H), 3.67 (s, 12H), 2.49 (d, $J = 2.1$ Hz, 4H), 1.37 (s, 72H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 162.9, 144.5-144.4 (m), 129.7-129.6 (m), 126.6-125.2 (m), 64.6, 36.1, 32.0, 23.4-22.2 (m) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : 35.6 ppm; HRMS (ESI) m/z calcd. for $\text{C}_{62}\text{H}_{96}\text{O}_6\text{P}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 1021.6574, found: 1021.6551.

(J) Synthesis of $\text{PhSiH}_2\text{-O-SiH}_2\text{Ph}$

$\text{PhSiH}_2\text{-O-SiH}_2\text{Ph}$ was synthesized according to the literature⁵.

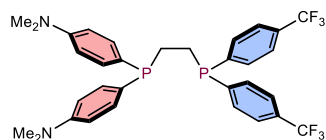
To a 200 mL round bottom flask was added CuCl_2 (5.4 g, 40 mmol), CuI (381 mg, 2 mmol), and Et_2O (27 mL). The reaction mixture was stirred at room temperature for 30 min (750 rpm). Phenylsilane (5.54 mL, 45 mmol, 1.0 equiv) was added dropwise, and after 20 h, the reaction was filtered directly onto ice and washed with Et_2O . The ether and ice were swirled every 5 min for 15 min, until the ice was melted. The organic layers were separated and washed with cold deionized water and then dried with MgSO_4 . The solvent was evaporated to afford $\text{PhSiH}_2\text{-O-SiH}_2\text{Ph}$ as pale yellow oil in 76% yield (1.76g, 7.62 mmol).

(K) Reduction of Dioxide **5**⁶



In a Teflon-cock sealed tube were placed 1,3-diphenyl-disiloxane (DPDS, 3.0 equiv) and **5** (1.0 equiv). The sealed tube was evacuated and backfilled with N_2 (3 times) followed by the addition of toluene. The mixture was stirred at 110 $^\circ\text{C}$ for 16 h, and then, after cooling to room temperature, the volatiles were removed under reduced pressure. Hexane was added to the crude mixture and the insoluble solid product **6** was collected by filtration with washing with hexane. If the product has high solubility for hexane, the filtrate was condensed to dryness and the mixture was purified by silica-gel column chromatography to afford the product **6**.

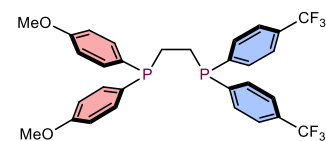
(2-(Bis(4-trifluoromethylphenyl)phosphanyl)ethyl)bis(4-dimethylaminophenyl)phosphine (**6gb**)



5gb (326.2 mg, 0.5 mmol, 1.0 equiv) was employed as starting materials and 1 mL of toluene was used as a solvent. After the addition of hexane, solid **6gb** was collected (262.8 mg, 0.42 mmol, 85% yield). White solid; IR (ATR): 2887, 1595, 1506, 1318, 1160, 1120, 1100, 1058, 1013, 826, 805, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.54-7.52 (m, 4H), 7.41-7.38 (m, 4H), 7.20 (dd, $J = 8.8$, 7.1 Hz, 4H), 6.66- 6.64 (m, 4H), 2.95 (s, 12H), 2.18-2.10 (m, 2H), 2.00-1.93 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 150.8, 142.9 (d, $J = 17.3$ Hz), 133.8 (d, $J = 19.7$ Hz), 133.2 (d, $J = 18.4$ Hz), 130.9 (q, $J = 32.5$ Hz), 128.2-120.0 (m, 3C), 112.4 (d, $J = 7.5$ Hz), 40.3, 24.6 (dd, $J = 13.9$, 13.9 Hz), 23.8 (dd, $J = 18.0$, 14.2 Hz) ppm; ^{19}F NMR

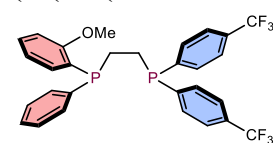
(376 MHz, CDCl₃) δ : -62.7 ppm; ³¹P NMR (162 MHz, CDCl₃) δ : -11.8 (d, J = 34.7 Hz), -16.7 (d, J = 34.7 Hz) ppm; HRMS (ESI) m/z calcd. for C₃₂H₃₃F₆N₂P₂⁺ [M+H]⁺: 621.2018, found: 621.2006.

(2-(Bis(4-trifluoromethylphenyl)phosphanyl)ethyl)bis(4-methoxyphenyl)phosphine (**6fb**)



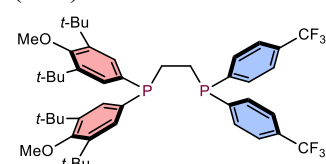
5fb (62.6 mg, 0.1 mmol, 1.0 equiv) was employed as starting materials and 0.2 mL of toluene was used as a solvent. Solidified product **6fb** was obtained and additional purification of the filtrate by silica-gel column chromatography (eluent: hexane/ethyl acetate, 100/0 to 10/1) afforded **6fb** (Total 46.8 mg, 0.079 mmol, 79% yield). White solid; IR (ATR): 2936, 1594, 1497, 1325, 1244, 1165, 1122, 1104, 1059, 1014, 830, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 7.57-7.28 (m, 4H), 7.43-7.39 (m, 4H), 7.28-7.24 (m, 4H), 6.87-6.84 (m, 4H), 3.80 (s, 6H), 2.15-2.06 (m, 2H), 2.04-1.97 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ : 160.4, 142.6 (d, J = 17.0 Hz), 134.2 (d, J = 19.8 Hz), 133.1 (d, J = 18.4 Hz), 131.1 (q, J = 32.4 Hz), 128.8 (d, J = 10.8 Hz), 128.1-120.0 (m, 2C), 114.3 (d, J = 7.6 Hz), 55.3, 24.4 (dd, J = 14.4, 14.4 Hz), 23.7 (dd, J = 17.3, 14.6 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ : -62.7 ppm; ³¹P NMR (162 MHz, CDCl₃) δ : -12.0 (d, J = 35.8 Hz), -15.8 (d, J = 35.8 Hz) ppm; HRMS (ESI) m/z calcd. for C₃₀H₂₇F₆O₂P₂⁺ [M+H]⁺: 595.1385, found: 595.1373.

(2-(Bis(4-trifluoromethylphenyl)phosphanyl)ethyl)bis(2-methoxyphenyl)phosphine (**6jb**)



5jb (59.6 mg, 0.1 mmol, 1.0 equiv) was employed as starting materials and 1 mL of toluene was used as a solvent. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 15/1) afforded **6jb** (50.0 mg, 0.089 mmol, 89% yield). Colorless liquid; IR (ATR): 2933, 1606, 1431, 1395, 1320, 1239, 1163, 1120, 1058, 1014, 828, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 7.58-7.55 (m, 4H), 7.46-7.26 (m, 10H), 6.92-6.81 (m, 3H), 3.70 (s, 3H), 2.67-1.95 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ : 161.1 (d, J = 12.9 Hz), 142.7 (dd, J = 41.6, 17.1 Hz), 136.5 (d, J = 12.6 Hz), 133.6-132.9 (m, 2C), 132.2 (d, J = 4.4 Hz), 131.3-130.8 (m), 130.4, 129.2, 128.6 (d, J = 7.2 Hz), 128.1-120.0 (m, 2C), 126.1 (d, J = 15.8 Hz), 121.0, 110.4, 55.5, 24.0 (dd, J = 18.8, 14.8 Hz), 21.8 (dd, J = 14.8, 14.8 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ : -62.7 ppm; ³¹P NMR (162 MHz, CDCl₃) δ : -11.8 (d, J = 34.7 Hz), -21.1 (d, J = 34.7 Hz) ppm; HRMS (ESI) m/z calcd. for C₂₉H₂₅F₆OP₂⁺ [M+H]⁺: 565.1279, found: 565.1269.

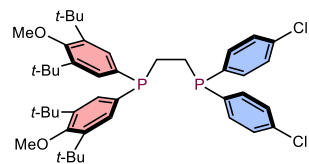
(2-(Bis(4-trifluoromethylphenyl)phosphanyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine (**6eb**)



5eb (212.7 mg, 0.25 mmol, 1.0 equiv) was employed as starting materials and 0.5 mL of toluene was used as a solvent. Purification of the crude product by silica-gel column chromatography (eluent: hexane/diethyl ether, 20/1) afforded **6eb** (176.1 mg, 0.22 mmol, 86% yield). White solid; IR (ATR): 2957, 1606, 1409, 1393, 1321, 1224, 1166, 1126, 1059, 1013, 828, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 7.57-7.55 (m, 4H), 7.46-7.42 (m, 4H), 7.18 (d, J = 7.3 Hz, 4H), 3.67 (s, 6H), 2.23-2.17 (m, 2H), 2.03-1.97 (m, 2H), 1.35 (s, 36H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ : 160.4, 143.9 (d, J = 6.2 Hz), 142.8 (d, J = 15.9 Hz), 133.4-133.0 (m, 2C), 131.6-120.0 (m, 4C), 64.4, 36.0, 32.1, 24.8 (dd, J = 13.1, 13.1 Hz), 24.3 (dd, J = 15.0, 12.4 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ : -62.7 ppm; ³¹P NMR (162 MHz, CDCl₃) δ : -11.1 (d, J =

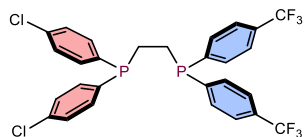
34.7 Hz), -11.5 (d, $J = 34.7$ Hz) ppm; HRMS (ESI) m/z calcd. for $C_{46}H_{59}F_6O_2P_2^+$ $[M+H]^+$: 819.3889, found: 819.3874.

(2-(Bis(4-chlorophenyl)phosphanyl)ethyl)bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine (**6ec**)



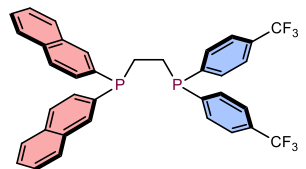
5ec (78.2 mg, 0.1 mmol, 1.0 equiv) was employed as starting materials and 0.2 mL of toluene was used as a solvent. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 100/0 to 9/1) afforded **6ec** (66.7 mg, 0.089 mmol, 89% yield). White solid; IR (ATR): 2956, 1480, 1404, 1390, 1223, 1086, 1011, 812, 739, 479 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ : 7.28-7.22 (m, 8H), 7.17 (d, $J = 7.7$ Hz, 4H), 3.66 (s, 6H), 2.13-2.07 (m, 2H), 2.00-1.94 (m, 2H), 1.34 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ : 160.3, 143.7 (d, $J = 6.8$ Hz), 136.6 (d, $J = 15.2$ Hz), 135.2, 134.1 (d, $J = 18.9$ Hz), 131.2-130.9 (m, 2C), 128.9 (d, $J = 6.8$ Hz), 64.4, 36.0, 32.1, 24.9-24.6 (m, 2C) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ : -11.3 (d, $J = 34.8$ Hz), -13.2 (d, $J = 34.8$ Hz) ppm; HRMS (ESI) m/z calcd. for $C_{44}H_{59}Cl_2O_2P_2^+$ $[M+H]^+$: 715.3362, found: 715.3361.

Bis(4-chlorophenyl)(2-(Bis(4-trifluoromethylphenyl)phosphanyl)ethyl)phosphine (**6cb**)



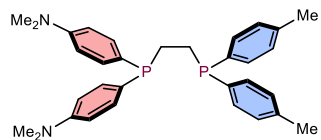
5cb (63.5 mg, 0.1 mmol, 1.0 equiv) was employed as starting materials and 0.2 mL of toluene was used as a solvent. After the addition of hexane, solid **6cb** was collected (46.9 mg, 0.078 mmol, 78% yield). White solid; IR (ATR): 3051, 1607, 1478, 1396, 1324, 1164, 1118, 1103, 1059, 1012, 816, 698 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ : 7.58-7.56 (m, 4H), 7.42-7.38 (m, 4H), 7.30-7.27 (m, 4H), 7.24-7.20 (m, 4H), 2.13-1.98 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ : 142.2 (d, $J = 17.1$ Hz), 135.9 (d, $J = 14.7$ Hz), 135.6, 134.1 (d, $J = 19.2$ Hz), 133.1 (d, $J = 18.6$ Hz), 131.3 (q, $J = 32.5$ Hz), 129.1 (d, $J = 6.8$ Hz), 125.6-125.5 (m), 124.0 (q, $J = 270.9$ Hz), 24.1-23.4 (m, 2C) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ : -62.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ : -12.4 (d, $J = 36.8$ Hz), -14.4 (d, $J = 36.8$ Hz) ppm; HRMS (ESI) m/z calcd. for $C_{28}H_{21}Cl_2F_6P_2^+$ $[M+H]^+$: 603.0394, found: 603.0386.

(2-(Bis(4-trifluoromethylphenyl)phosphanyl)ethyl)di(naphthalen-2-yl)phosphine (**6nb**)



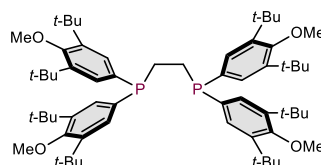
5nb (66.6 mg, 0.1 mmol, 1.0 equiv) was employed as starting materials and 1 mL of toluene was used as a solvent. After the addition of hexane, solid **6nb** was collected (35.8 mg, 0.056 mmol, 56% yield). White solid; IR (ATR): 3048, 1607, 1396, 1325, 1164, 1122, 1102, 1060, 1015, 815, 743, 698 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ : 7.96-7.93 (m, 2H), 7.84-7.75 (m, 6H), 7.54-7.49 (m, 8H), 7.40-7.32 (m, 6H), 2.33-2.17 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ : 142.4 (d, $J = 16.9$ Hz), 135.1 (d, $J = 13.2$ Hz), 133.6-133.0 (m, 4C), 131.1 (q, $J = 32.6$ Hz), 128.9 (d, $J = 14.0$ Hz), 128.3 (d, $J = 6.0$ Hz), 128.1, 127.9-120.0 (m, 5C), 24.0-23.6 (m, 2C) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ : -62.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ : -11.2 (d, $J = 34.7$ Hz), -12.0 (d, $J = 34.7$ Hz) ppm; HRMS (ESI) m/z calcd. for $C_{36}H_{27}F_6P_2^+$ $[M+H]^+$: 635.1487, found: 635.1476.

(2-(Bis(4-methylphenyl)phosphanyl)ethyl)bis(4-dimethylaminophenyl)phosphine (**6gi**)



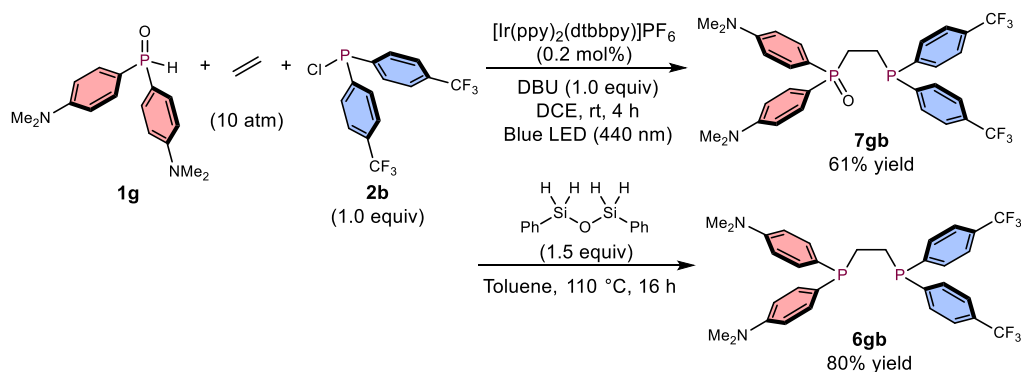
5gi (54.4 mg, 0.1 mmol, 1.0 equiv) was employed as starting materials and 1 mL of toluene was used as a solvent. Purification of the crude product by silica-gel column chromatography (eluent: DCM/acetone, 50/2) afforded **6ee** (44.3 mg, 0.0864 mmol, 86% yield). White solid; IR (ATR): 2916, 1594, 1507, 1351, 1197, 1095, 803, 684, 511, 498 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.26-7.22 (m, 8H), 7.10 (d, $J = 7.8$ Hz, 4H), 6.66 (d, $J = 7.9$ Hz, 4H), 2.94 (s, 12H), 2.33 (s, 6H), 2.10-1.96 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 150.7, 138.4, 135.2 (d, $J = 12.2$ Hz), 133.9 (d, $J = 19.4$ Hz), 132.8 (d, $J = 18.5$ Hz), 129.3 (d, $J = 6.8$ Hz), 124.1 (d, $J = 7.9$ Hz), 112.4 (d, $J = 7.5$ Hz), 40.4, 24.7-24.0 (m, 2C), 21.4 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : -13.7 (d, $J = 32.7$ Hz), -16.4 (d, $J = 32.7$ Hz) ppm; HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{39}\text{N}_2\text{P}_2^+$ $[\text{M}+\text{H}]^+$: 513.2583, found: 513.2579.

1,2-Bis(bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino)ethane (**6ee**)



5ee (44.8 mg, 0.0448 mmol, 1.0 equiv) was employed as starting materials and 0.1 mL of toluene was used as a solvent. Purification of the crude product by silica-gel column chromatography (eluent: DCM) afforded **6ee** (41.1 mg, 0.0425 mmol, 95% yield). White solid; IR (ATR): 2956, 1408, 1391, 1224, 1114, 1008, 835, 737, 696, 604 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.25 (d, $J = 3.9$ Hz, 8H), 3.67 (s, 12H), 2.12-2.10 (m, 4H), 1.36 (s, 72H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 160.2, 143.6-143.5 (m), 133.4-131.1 (m, 2C), 64.3, 36.0, 32.2, 25.5 (d, $J = 2.5$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : -11.6 ppm; HRMS (ESI) m/z calcd. for $\text{C}_{62}\text{H}_{97}\text{O}_4\text{P}_2^+$ $[\text{M}+\text{H}]^+$: 967.6857, found: 967.6847.

(L) Synthesis of Unsymmetric DPPE Oxide **7gb** and Its Reduction

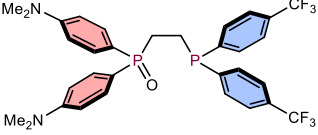


In an oven-dried 10 mL pressure-resistant glass tube were placed phosphine oxide **1g** (0.5 mmol, 1.0 equiv) and $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (0.9 mg, 0.001 mmol, 0.2 mol%). After the addition of DCE (1.5 mL) under nitrogen, chlorophosphine **2b** (0.5 mmol, 1.0 equiv) and DBU (74.8 μL , 0.5 mmol, 1.0 equiv) were added. Then, the tube was placed into autoclave which consists of a polycarbonate cylinder, and ethylene gas was pressurised to 10 atm. After the resulting mixture was stirred at room temperature for 4h under the irradiation of blue LED (45W PR160L-440 nm Kessil light $\times$ 2), the solvent was evaporated to give the crude mixture. The crude product was purified by silica-gel column chromatography to afford the product **7gb** (193.9 mg, 0.30 mmol, 61%).

In a Teflon-cock sealed tube were placed 1,3-diphenyl-disiloxane (DPDS, 34.6 mg, 0.15 mmol, 1.5 equiv) and **7gb** (63.7 mg, 0.1 mmol, 1.0 equiv). The sealed tube was evacuated and backfilled with N_2 (3 times)

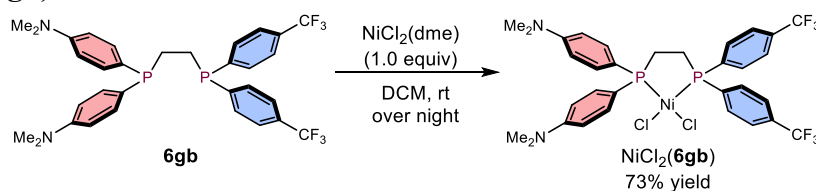
followed by the addition of toluene (0.2 mL). The mixture was stirred at 110 °C for 16 h, and then, after cooling to room temperature, the volatiles were removed under reduced pressure. Hexane was added to the crude mixture and the insoluble solid product **6gb** was collected by filtration with washing with hexane (49.4mg, 0.08 mmol, 80%).

(2-(Bis(4-trifluoromethylphenyl)phosphanyl)ethyl)bis(4-dimethylaminophenyl)phosphine oxide (**7gb**)

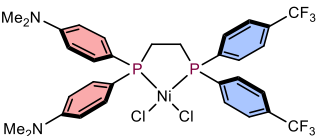
 White solid; IR (ATR): 2889, 1598, 1322, 1161, 1117, 1060, 1015, 814, 723, 502 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ: 7.54 (d, *J* = 7.9 Hz, 4H), 7.45-7.38 (m, 8H), 6.65 (dd, *J* = 8.9, 2.3 Hz, 4H), 2.98 (s, 12H), 2.35-2.29 (m, 2H), 2.17-2.08 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 152.4 (d, *J* = 2.4 Hz), 142.2 (d, *J* = 16.9 Hz), 133.2 (d, *J* = 18.8 Hz), 132.3 (d, *J* = 6.7 Hz), 131.1 (q, *J* = 32.6 Hz), 125.5-125.4 (m), 124.0 (d, *J* = 270.9 Hz), 117.4 (d, *J* = 110.1 Hz), 111.5 (d, *J* = 12.4 Hz), 40.2-40.0 (m), 26.3 (dd, *J* = 70.3, 15.4 Hz), 19.3 (d, *J* = 14.7 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ: -62.7 ppm; ³¹P NMR (162 MHz, CDCl₃) δ: 34.3 (d, *J* = 47.7 Hz), -11.3 (d, *J* = 47.7 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₂H₃₂F₆N₂OP₂Na⁺ [M+Na]⁺: 659.1786, found: 659.1764.

(M) Synthesis of Transition-Metal Complexes

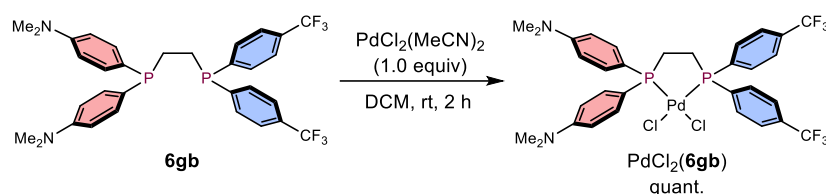
Synthesis of NiCl₂(**6gb**)



In an oven-dried test tube were placed **6gb** (62.1mg, 0.1 mmol, 1.0 equiv) and NiCl₂(dme) (22.0 mg, 0.1 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred over night at room temperature. The solvent was removed under reduced pressure and small amount of hexane was added. The resulting slurry was filtrated to obtain the product NiCl₂(**6gb**) (54.7 mg, 0.073 mmol, 73%).

 Red solid; IR (ATR): 1594, 1320, 1168, 1124, 1103, 1060, 1014, 810, 706, 543 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ: 8.14-8.09 (m, 4H), 7.79-7.70 (m, 8H), 6.72-6.70 (m, 4H), 3.02 (s, 12H), 2.14-2.05 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 152.4, 134.8 (d, *J* = 9.7 Hz), 134.3-131.4 (m, 3C), 125.9-125.8 (m), 123.6 (q, *J* = 271.5 Hz), 112.5-111.5 (m, 2C), 40.1, 28.3 (dd, *J* = 32.4, 18.4 Hz), 26.4 (dd, *J* = 29.4, 15.4 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ: -63.1 ppm; ³¹P NMR (162 MHz, CDCl₃) δ: 56.6 (d, *J* = 69.4 Hz), 55.9 (d, *J* = 69.4 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₂H₃₂ClF₆N₂NiP₂⁺ [M-Cl]⁺: 713.0981, found: 713.0997.

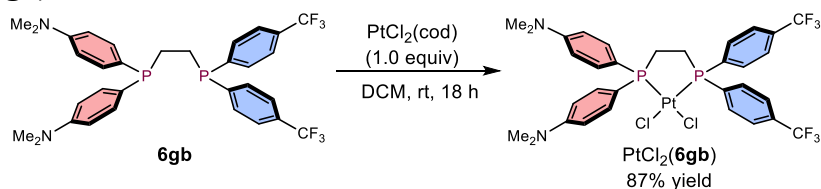
Synthesis of PdCl₂(**6gb**)



In an oven-dried test tube were placed **6gb** (31.1mg, 0.05 mmol, 1.0 equiv) and PdCl₂(MeCN)₂ (13 mg, 0.05 mmol, 1.0 equiv) in DCM (1 mL). The resulting mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and small amount of hexane was added. The resulting slurry was filtrated to obtain the product PdCl₂(**6gb**) (39.8 mg, 0.05 mmol, quantitative yield).

Yellow solid; IR (ATR): 1592, 1320, 1127, 1104, 1061, 1014, 813, 708, 698, 545 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂) δ: 8.04 (dd, *J* = 11.8, 8.0 Hz, 4H), 7.76 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.61 (dd, *J* = 12.0, 8.8 Hz, 4H), 6.73 (dd, *J* = 8.8, 2.2 Hz, 4H), 3.02 (s, 12H), 2.51-2.47 (m, 2H), 2.42-2.34 (m, 2H) ppm; ¹³C NMR (100 MHz, CD₂Cl₂) δ: 152.9, 135.0 (d, *J* = 12.1 Hz), 134.7-132.9 (m, 3C), 126.2-126.1 (m), 123.9 (q, *J* = 271.4 Hz), 112.2-111.6 (m, 2C), 40.2, 30.0 (dd, *J* = 36.7, 16.8 Hz), 27.3 (dd, *J* = 33.4, 12.6 Hz) ppm; ¹⁹F NMR (376 MHz, CD₂Cl₂) δ: -65.4 ppm; ³¹P NMR (162 MHz, CD₂Cl₂) δ: 62.3 (d, *J* = 10.8 Hz), 61.1 (d, *J* = 10.8 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₂H₃₂ClF₆N₂P₂Pd⁺ [M-Cl]⁺: 757.0684, found: 757.0690.

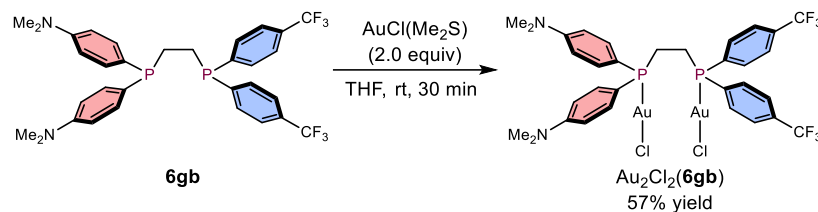
Synthesis of PtCl₂(**6gb**)



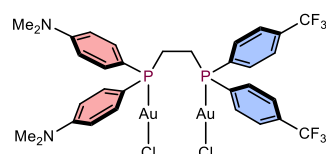
In an oven-dried test tube were placed **6gb** (62.1mg, 0.1 mmol, 1.0 equiv) and PtCl₂(cod) (37.4 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL). The resulting mixture was stirred for 18 h at room temperature. The solvent was removed under reduced pressure and diethyl ether was added. The resulting slurry was filtrated and washed with ethanol to obtain the product PtCl₂(**6gb**) (77.4 mg, 0.087 mmol, 87%).

White solid; IR (ATR): 2906, 1594, 1319, 1130, 1106, 1061, 1014, 811, 699, 500 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ: 8.03 (dd, *J* = 11.9, 8.0 Hz, 4H), 7.66-7.58 (m, 8H), 6.70 (br, 4H), 2.97 (s, 12H), 2.46-2.22 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 152.1-151.8 (m), 134.7 (d, *J* = 12.1 Hz), 134.2-133.1 (m, 3C), 132.0 (d, *J* = 60.2 Hz), 127.9-127.4 (m), 123.5 (q, *J* = 271.7 Hz), 112.5-112.1 (m), 40.4, 29.7-29.2 (m), 27.8-27.3 (m) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ: -63.1 ppm; ³¹P NMR (162 MHz, CDCl₃) δ: 40.9 (s, *J*_{Pt-P} = 3773 Hz), 38.8 (s, *J*_{Pt-P} = 3489 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₂H₃₂ClF₆N₂Pt⁺ [M-Cl]⁺: 851.1276, found: 851.1268.

Synthesis of Au₂Cl₂(**6gb**)

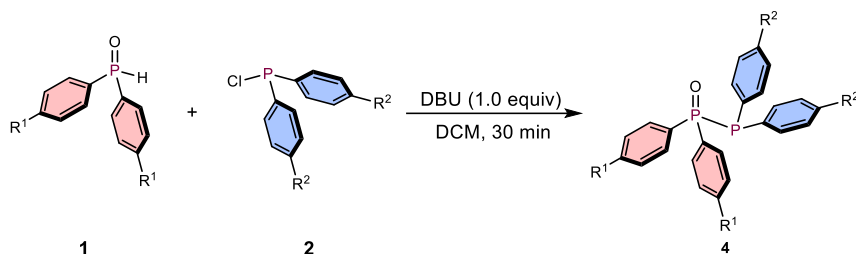


In an oven-dried test tube were placed **6gb** (62.1 mg, 0.1 mmol, 1.0 equiv) and AuCl(Me₂S) (58.9 mg, 0.2 mmol, 2.0 equiv) in THF (3 mL). The resulting mixture was stirred for 30 min at room temperature. The solvent was removed under reduced pressure and purification of the crude product by silica-gel column chromatography (eluent: DCM) afforded Au₂Cl₂(**6gb**) (61.7 mg, 0.057 mmol, 57%).

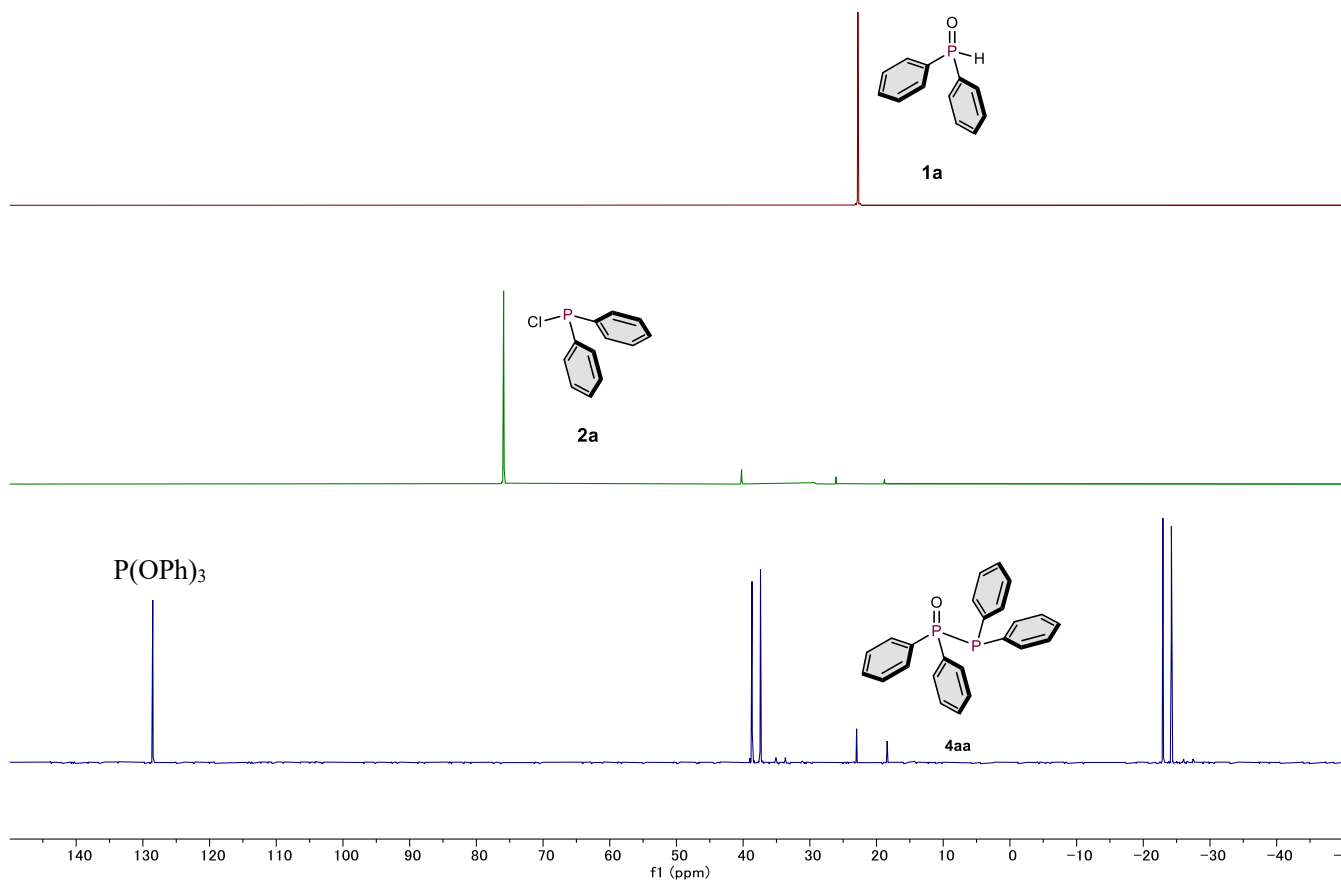


White solid; IR (ATR): 2895, 1593, 1513, 1322, 1104, 1061, 813, 712, 702, 535 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ: 7.80-7.72 (m, 8H), 7.44 (dd, *J* = 12.5, 8.9 Hz, 4H), 6.66 (dd, *J* = 9.0, 2.1 Hz, 4H), 3.00 (s, 12H), 2.76-2.67 (m, 2H), 2.54-2.45 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 152.6, 135.1-131.7 (m, 3C), 132.0 (d, *J* = 57.4 Hz), 126.7-126.5 (m), 123.2 (q, *J* = 271.6 Hz), 112.4-111.5 (m, 2C), 40.1, 25.3 (dd, *J* = 37.2, 4.3 Hz), 23.7 (dd, *J* = 35.7, 5.7 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ: -63.2 ppm; ³¹P NMR (162 MHz, CDCl₃) δ: 32.4 (d, *J* = 60.7 Hz), 28.4 (d, *J* = 60.7 Hz) ppm; HRMS (ESI) *m/z* calcd. for C₃₂H₃₂Au₂Cl₂F₆N₂P₂Na⁺ [M+Na]⁺: 1107.0554, found: 1107.0545.

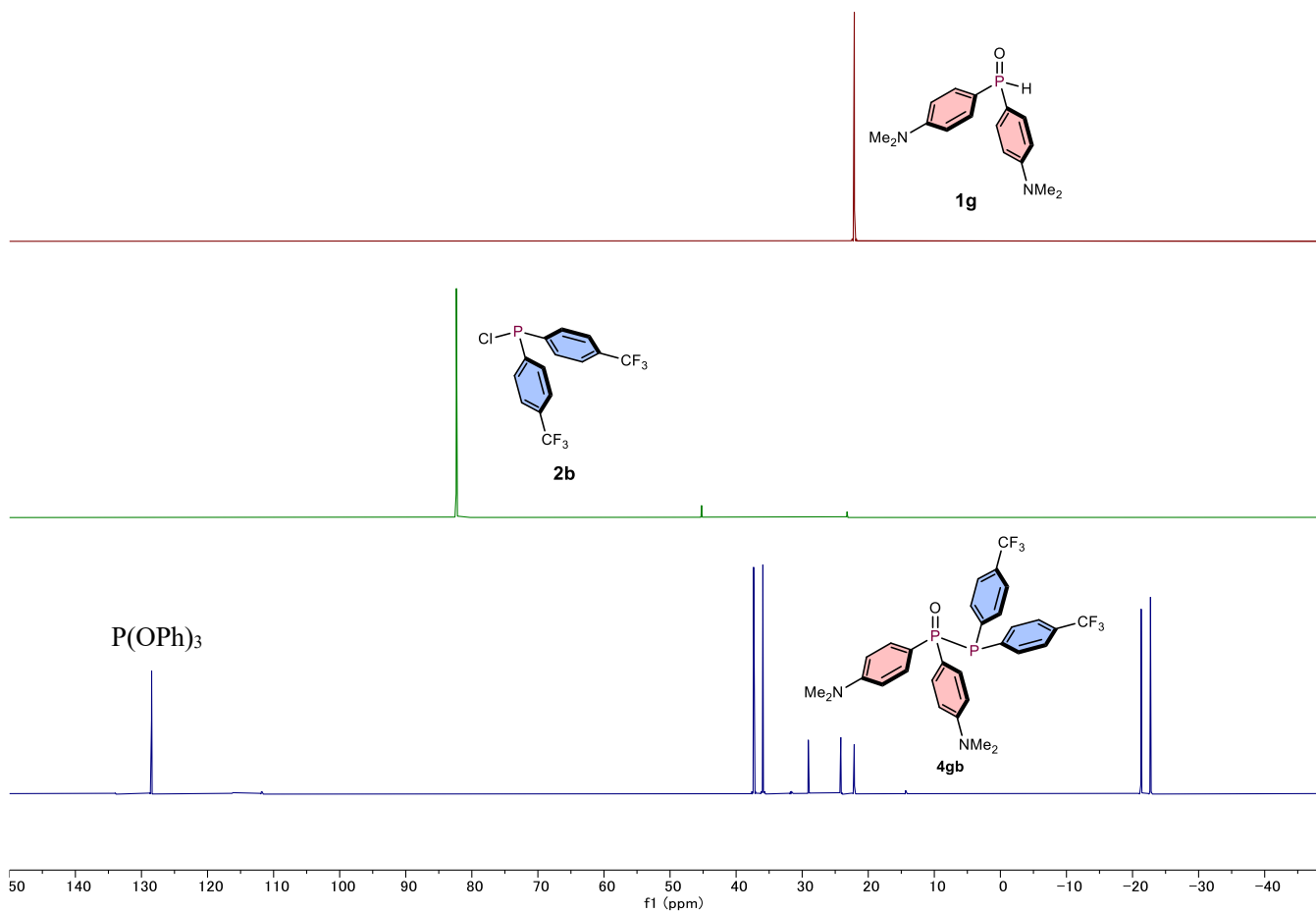
(N) NMR studies



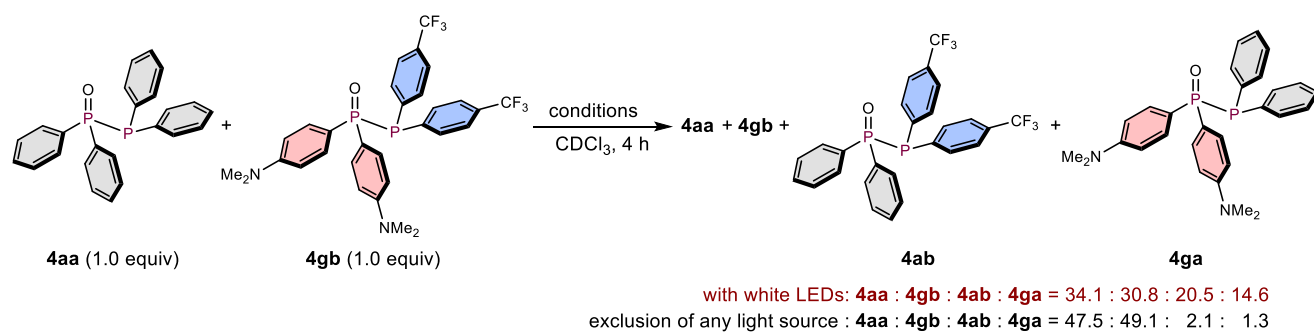
In an oven-dried test tube were placed phosphine oxide **1** (**1a**: 20.2 mg or **1g**: 28.8 mg, 0.1 mmol, 1.0 equiv). After the addition of DCM (0.3 mL) under nitrogen, chlorophosphine **2** (**2a**: 18.0 μL or **2b**: 25.1 μL, 0.1 mmol, 1.0 equiv) and DBU (14.9 μL, 0.1 mmol, 1.0 equiv) were added. After the resulting mixture was stirred at room temperature for 30 min, the solvent was evaporated, and CDCl₃ was then added to measure ³¹P NMR with P(OPh)₃ as an internal standard.



Supplementary Figure 5. ^{31}P NMR spectra (162 MHz, Red: **1a**, Green: **2a**, Blue: **4aa**) in CDCl_3



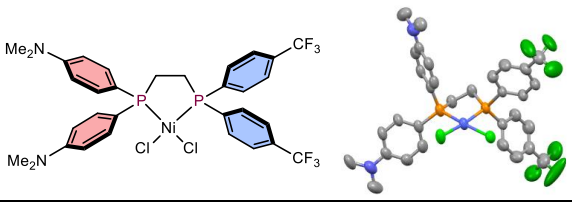
Supplementary Figure 6. ^{31}P NMR spectra (162 MHz, Red: **1g**, Green: **2b**, Blue: **4ga**) in CDCl_3



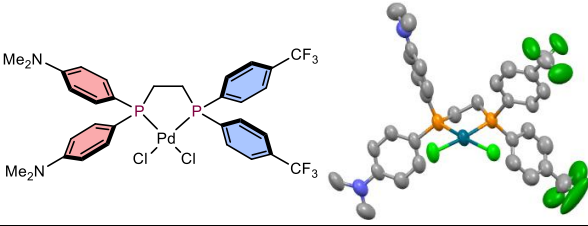
Supplementary Figure 7. Scrambling experiments.

(O) Crystal structures

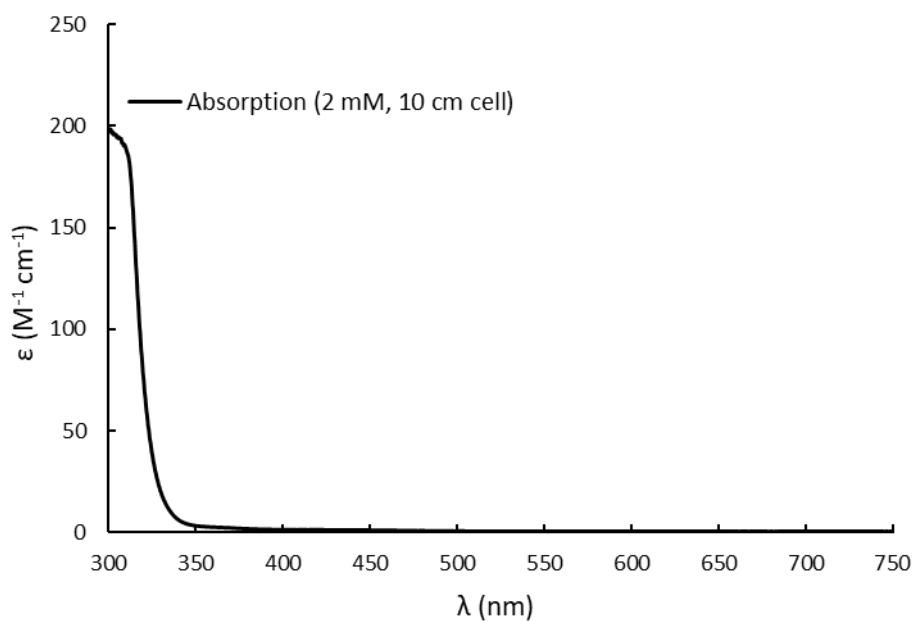
Supplementary Table 1. The detail of crystal structure of NiCl₂(**6gb**)

Compound	
CCDC Name	CCDC 2152051
Empirical Formula	C ₃₂ H ₃₂ Cl ₂ F ₆ N ₂ NiP ₂
Formula Weight	750.14
Crystal System	orthorhombic
Crystal Size / mm	0.2 × 0.15 × 0.04
<i>a</i> / Å	8.87800(10)
<i>b</i> / Å	25.6005(4)
<i>c</i> / Å	29.3762(3)
<i>α</i> / °	90
<i>β</i> / °	90
<i>γ</i> / °	90
<i>V</i> / Å ³	6676.66(15)
Space Group	P b c a
<i>Z</i> value	8
<i>D</i> _{calc} / g cm ⁻³	1.493
Temperature / K	123(2)
2 θ _{max} / °	74.5410
μ (CuK α) / mm ⁻¹	3.742
No. of Reflections Measured	6118
No. of Observations (All reflections)	96902
Residuals: <i>R</i> ₁ (<i>I</i> > 2.00 σ (<i>I</i>))	0.0834
Residuals: <i>wR</i> ₂ (All reflections)	0.2189
Goodness of Fit Indicator (<i>GOF</i>)	1.208
Maximum peak in Final Diff. Map / Å ³	1.220
Minimum peak in Final Diff. Map / Å ³	-0.535

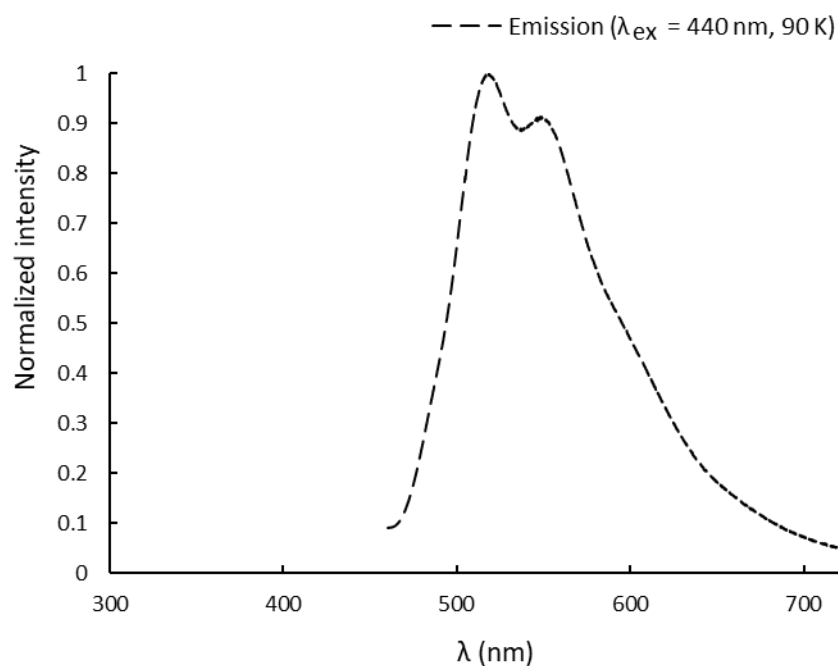
Supplementary Table 2. The detail of crystal structure of PdCl₂(**6gb**)

Compound	
CCDC Name	CCDC 2152052
Empirical Formula	C ₃₂ H ₃₂ Cl ₂ F ₆ N ₂ P ₂ Pd
Formula Weight	797.83
Crystal System	orthorhombic
Crystal Size / mm	0.2 × 0.15 × 0.04
<i>a</i> / Å	8.96760(10)
<i>b</i> / Å	25.3443(5)
<i>c</i> / Å	29.6064(3)
<i>α</i> / °	90
<i>β</i> / °	90
<i>γ</i> / °	90
<i>V</i> / Å ³	6728.87(17)
Space Group	P b c a
<i>Z</i> value	8
<i>D</i> _{calc} / g cm ⁻³	1.575
Temperature / K	123(2)
2 θ _{max} / °	68.500
μ (CuK α) / mm ⁻¹	7.332
No. of Reflections Measured	6041
No. of Observations (All reflections)	52916
Residuals: <i>R</i> ₁ (<i>I</i> > 2.00 σ (<i>I</i>))	0.0913
Residuals: <i>wR</i> ₂ (All reflections)	0.2636
Goodness of Fit Indicator (<i>GOF</i>)	1.030
Maximum peak in Final Diff. Map / Å ³	2.362
Minimum peak in Final Diff. Map / Å ³	-1.148

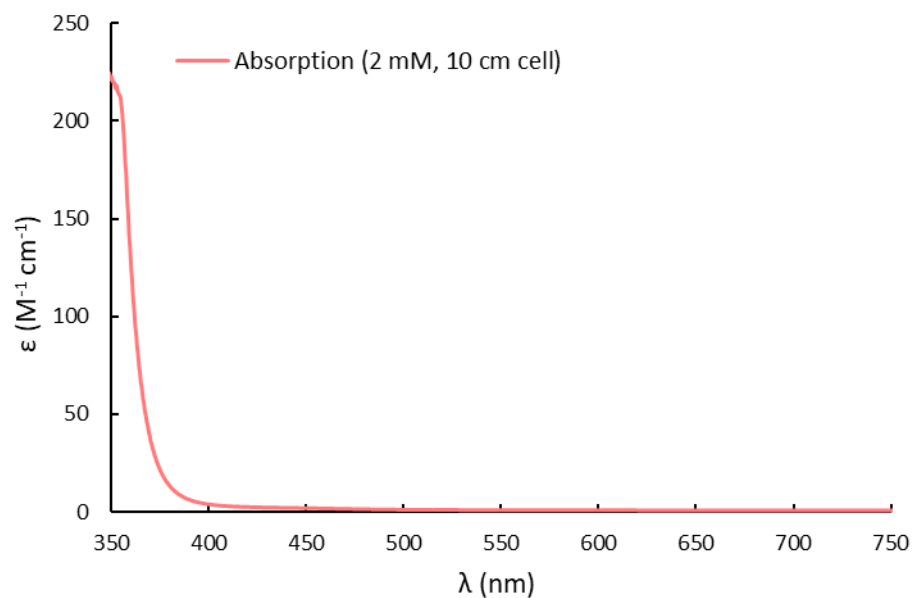
(P) Measurement of Photophysical Properties



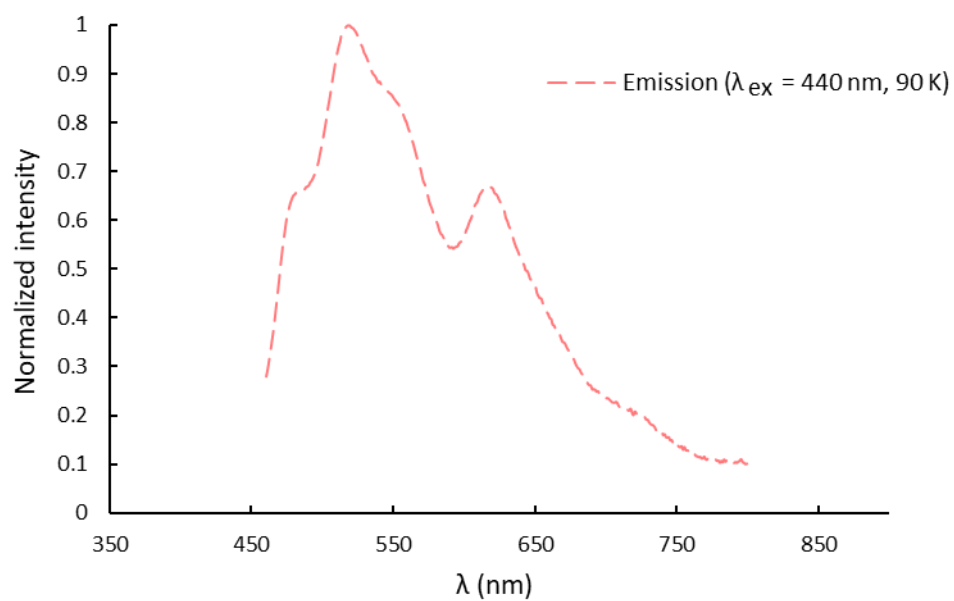
Supplementary Figure 8. Absorption spectrum of diphosphine **4aa** in DCM (2.0 mM) by 10 cm length quartz cell.



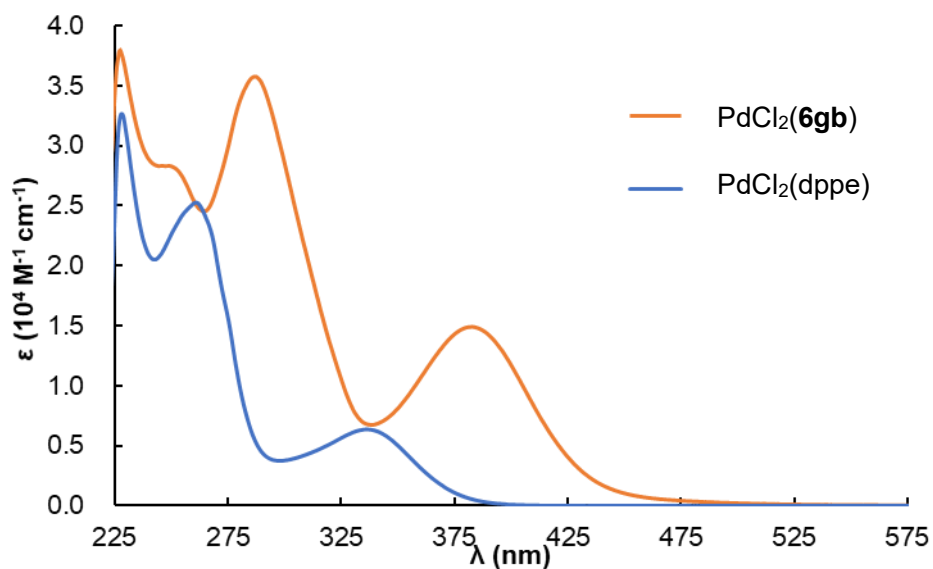
Supplementary Figure 9. Emission spectrum of diphosphine **4aa** in DCM (0.33 M) by 1 cm length quartz cell at 90 K



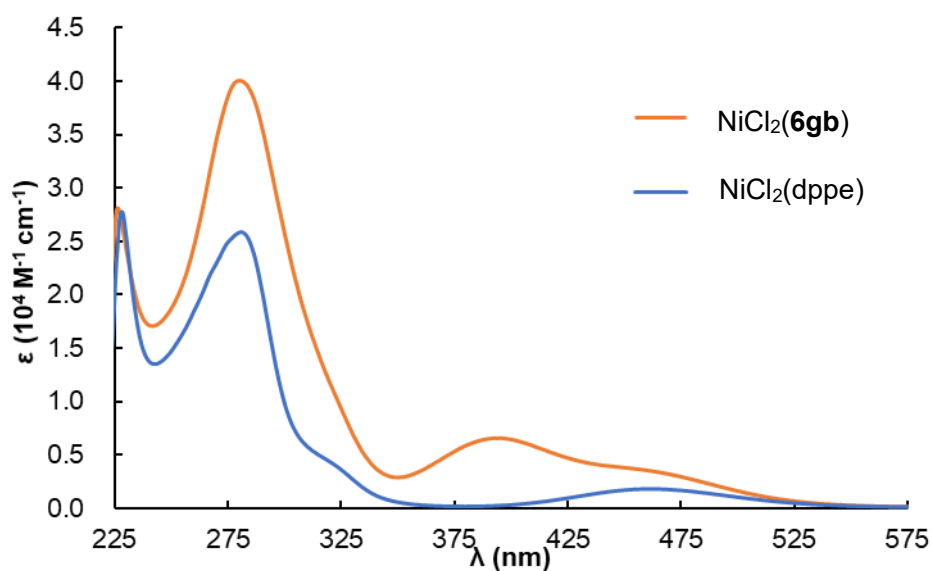
Supplementary Figure 10. Absorption spectrum of diphosphine **4gb** in DCM (2.0 mM) by 10 cm length quartz cell



Supplementary Figure 11. Emission spectrum of diphosphine **4gb** in DCM (0.33 M) by 1 cm length quartz cell at 90 K



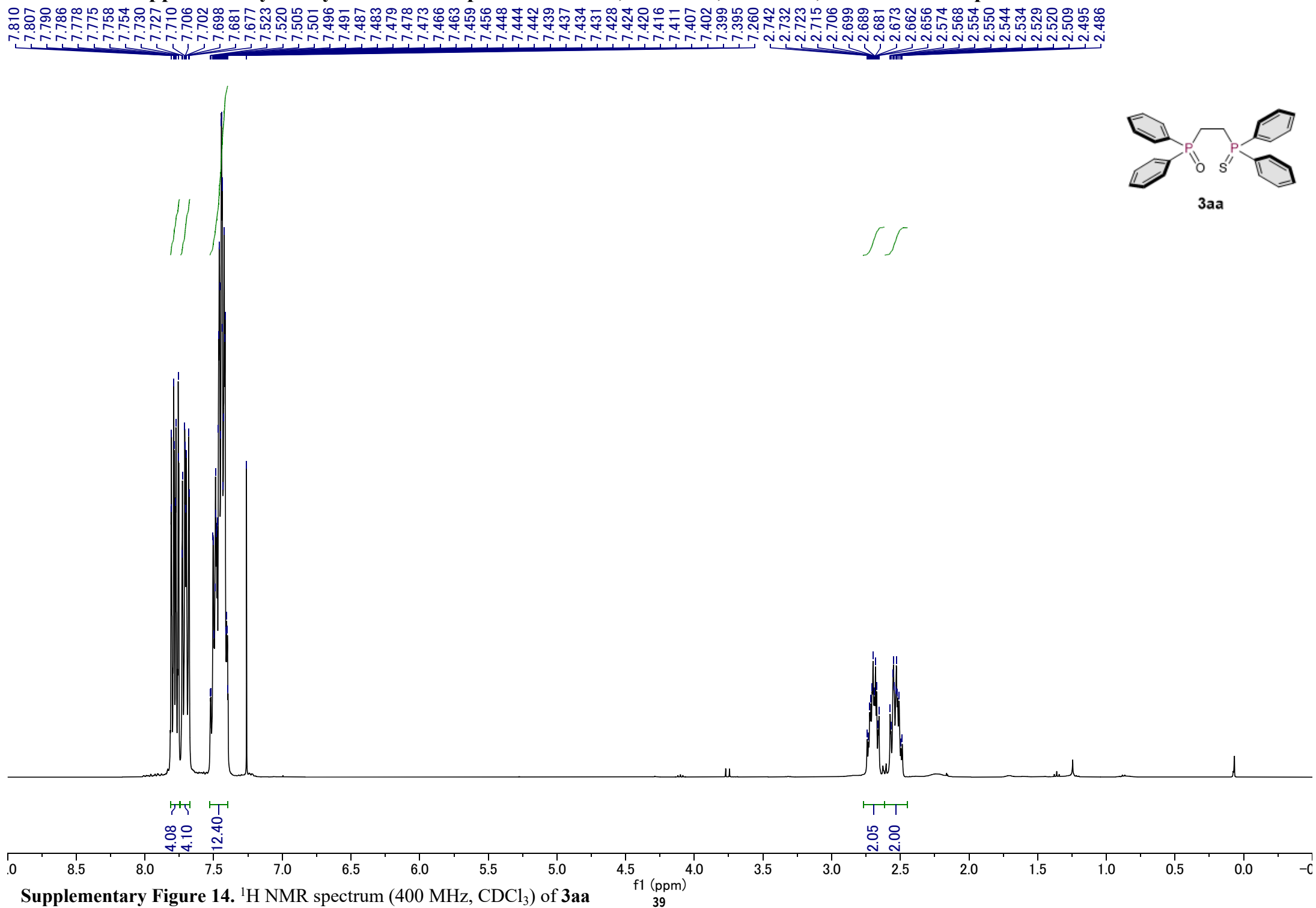
Supplementary Figure 12. Absorption spectra of Pd complexes in DCM by 1 cm length quartz cell. (PdCl₂(**6gb**): 5×10^{-5} M, PdCl₂(dppe): 6×10^{-5} M)



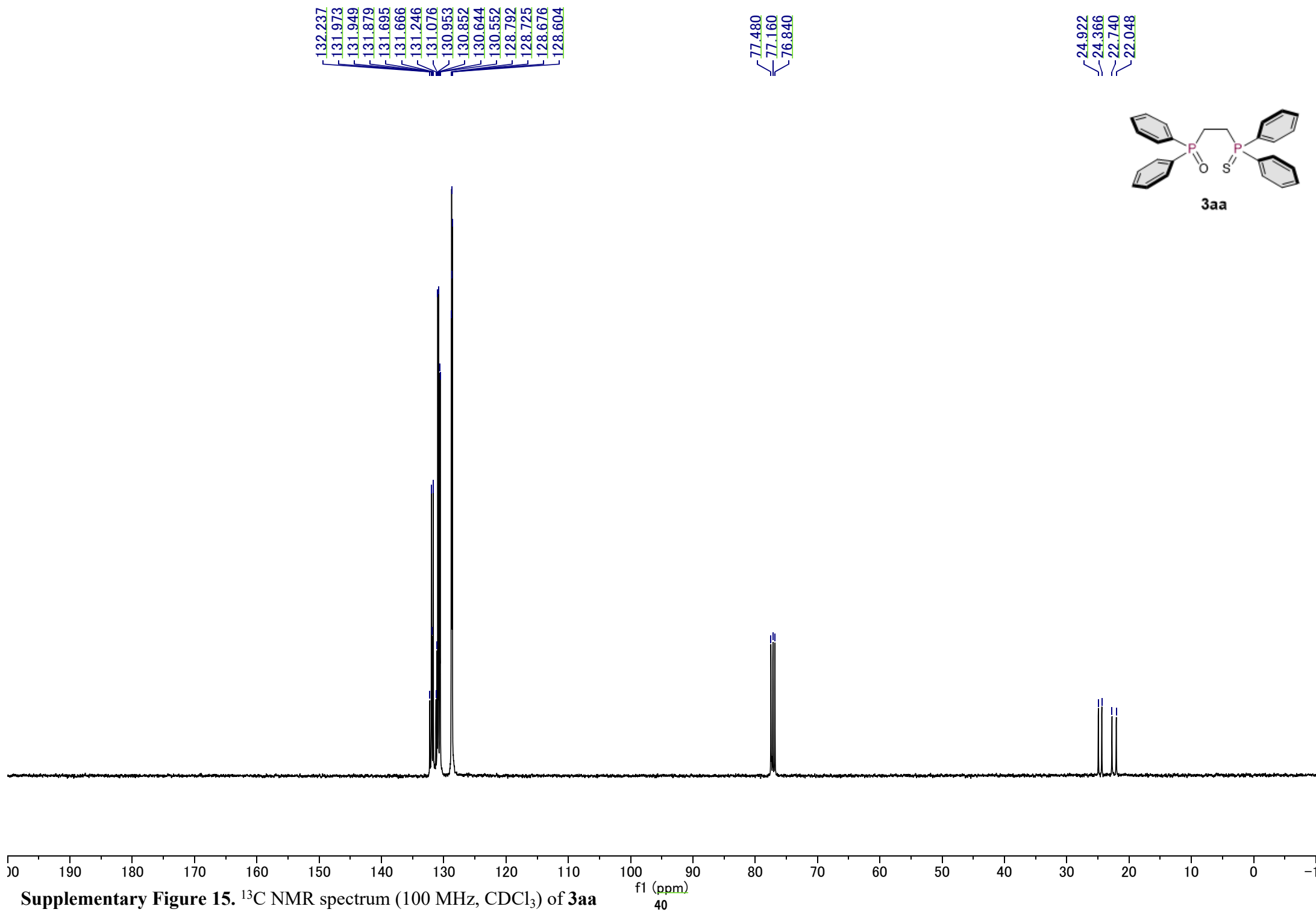
Supplementary Figure 13. Absorption spectra of Ni complexes in DCM by 1 cm length quartz cell. (NiCl₂(**6gb**): 3×10^{-5} M, NiCl₂(dppe): 8×10^{-5} M)

Supplementary References

1. Liu, W., Sahoo, B., Spannenberg, A., Junge, K. & Beller, M. Tailored cobalt-catalysts for reductive alkylation of anilines with carboxylic acids under mild conditions. *Angew. Chem. Int. Ed.* **57**, 11673–11677 (2018).
2. Imamoto, T., Kikuchi, S. I., Miura, T. & Wada, Y. Stereospecific reduction of phosphine oxides to phosphines by the use of a methylation reagent and lithium aluminum hydride. *Org. Lett.* **3**, 87–90 (2001).
3. Sato, Y., Kawaguchi, S.-i., Nomoto, A. & Ogawa, A. Highly selective phosphinylphosphination of alkenes with tetraphenyldiphosphine monoxide. *Angew. Chem. Int. Ed.* **55**, 9700–9703 (2016).
4. Yue, W.-J., Xiao, J.-Z., Zhang, S. & Yin, L. Rapid synthesis of chiral 1,2-bisphosphine derivatives through copper(I)-catalyzed asymmetric conjugate hydrophosphination. *Angew. Chem. Int. Ed.* **59**, 7057–7062 (2020).
5. Buonomo, J. A., Eiden, C. G. & Aldrich, C. C. Scalable synthesis of hydrido-disiloxanes from silanes: A one-pot preparation of 1,3-diphenyldisiloxane from phenylsilane. *Synthesis* **50**, 278–281 (2018).
6. Buonomo, J. A., Eiden, C. G. & Aldrich, C. C. Chemoselective reduction of phosphine oxides by 1,3-diphenyl-disiloxane. *Chem. Eur. J.* **23**, 14434–14438 (2017).

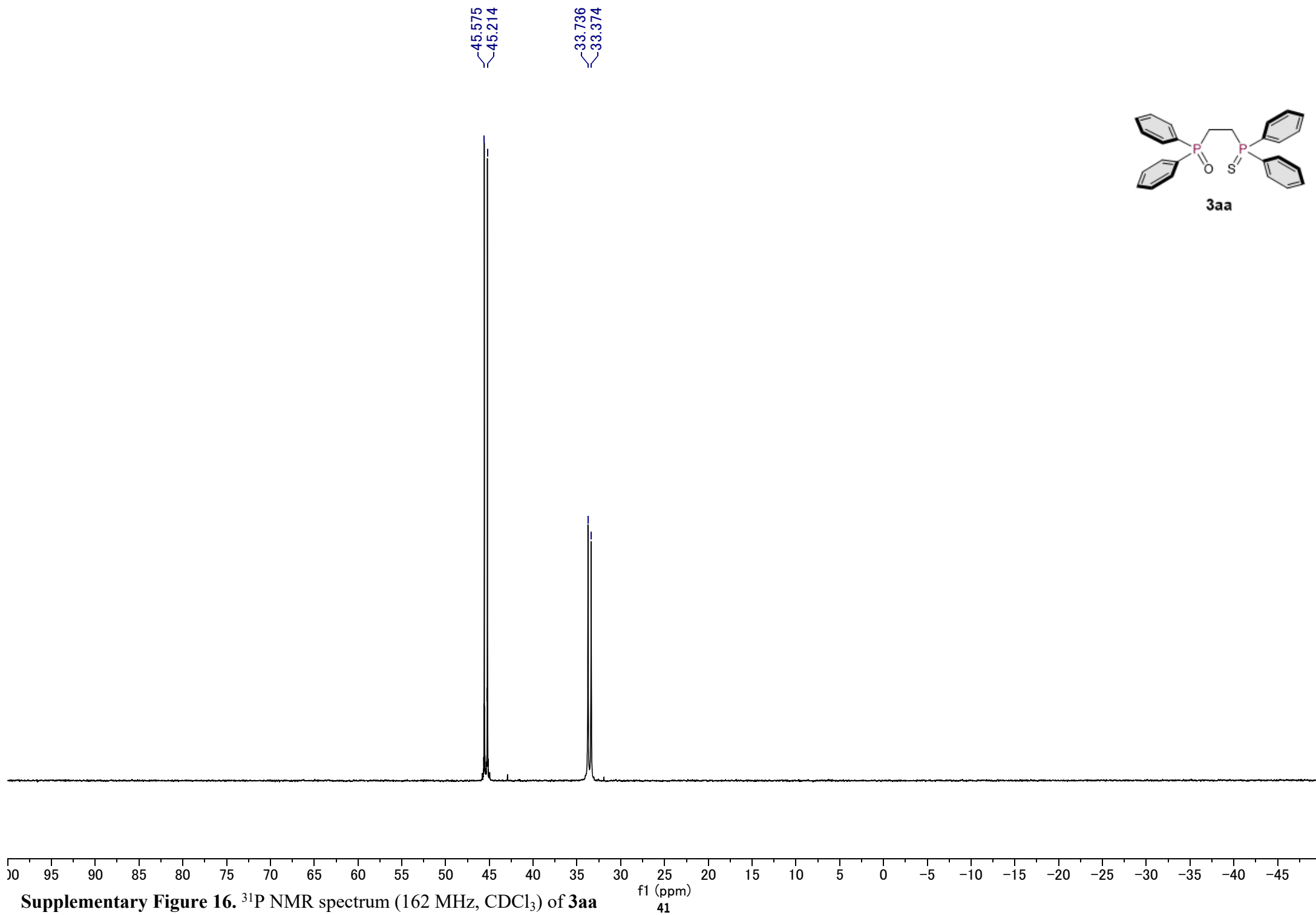


CDCl₃, 100 MHz



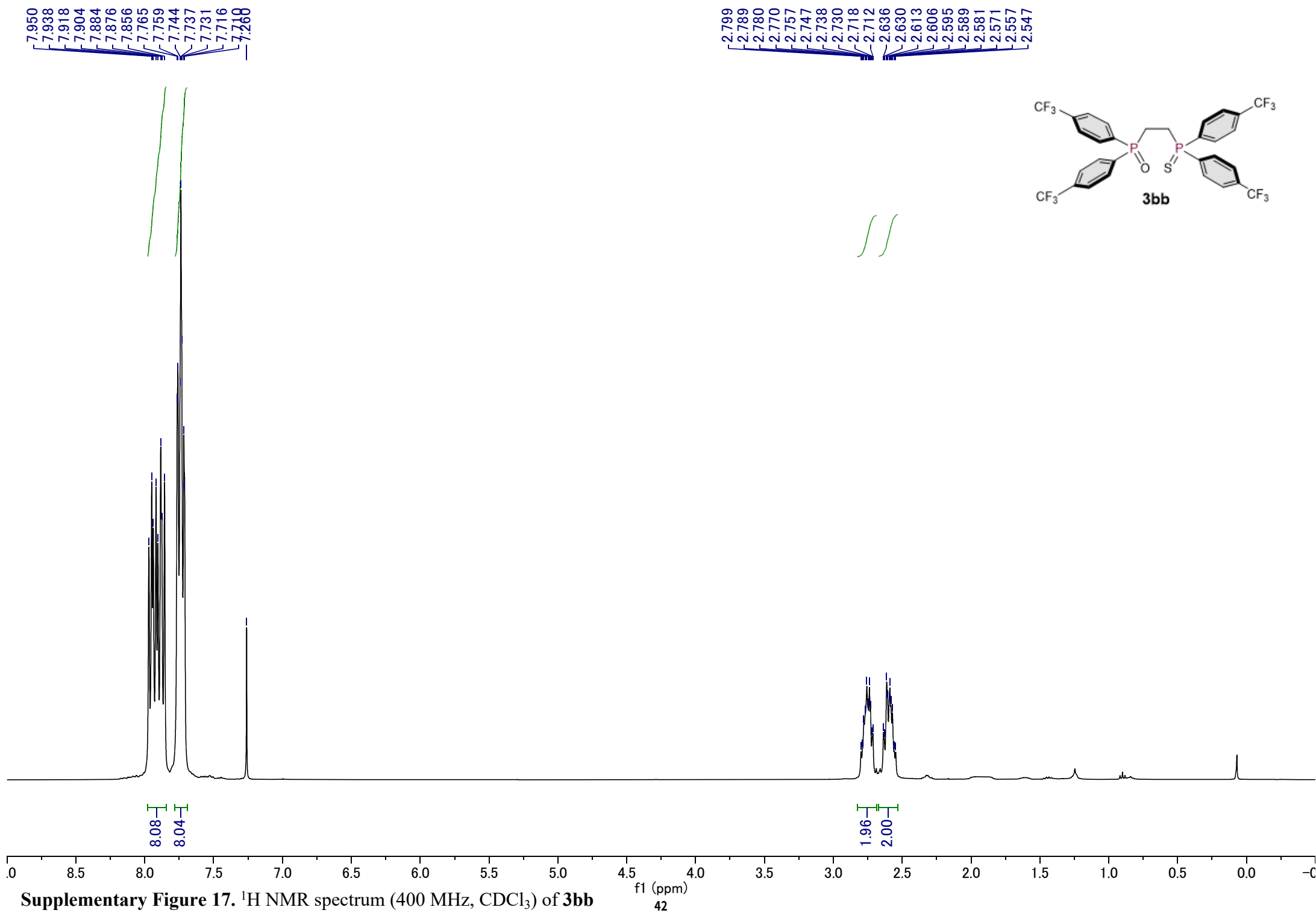
Supplementary Figure 15. ¹³C NMR spectrum (100 MHz, CDCl₃) of 3aa

CDCl₃, 162 MHz

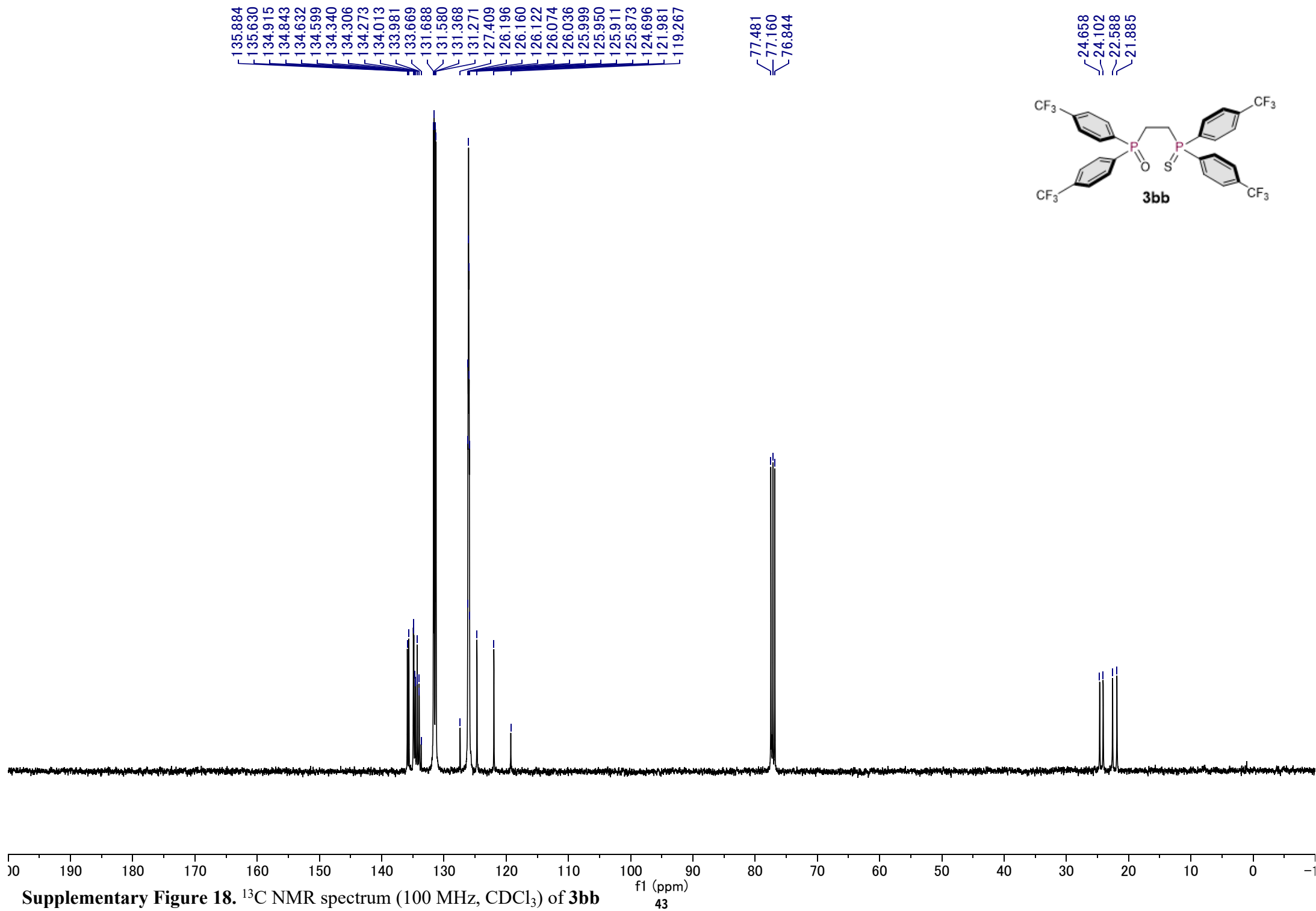


Supplementary Figure 16. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3aa**

CDCl₃, 400 MHz



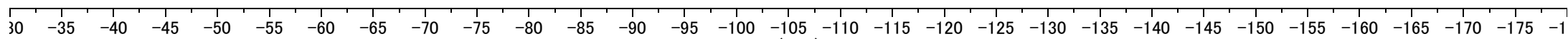
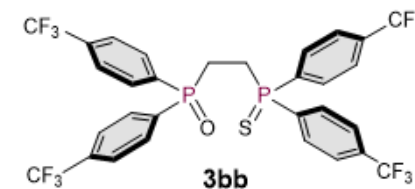
CDCl₃, 100 MHz



Supplementary Figure 18. ¹³C NMR spectrum (100 MHz, CDCl₃) of **3bb**

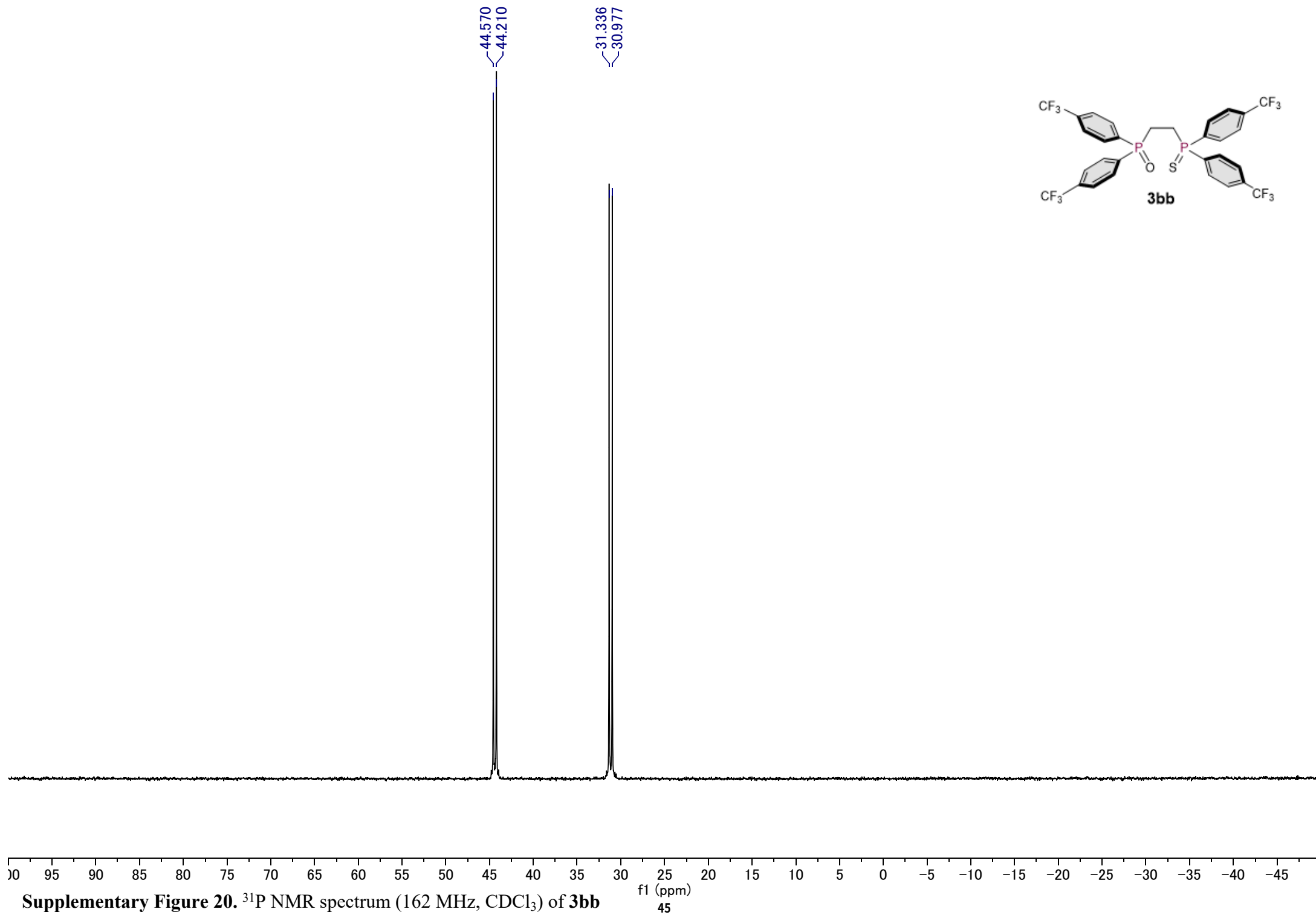
CDCl₃, 376 MHz

63.288
63.347



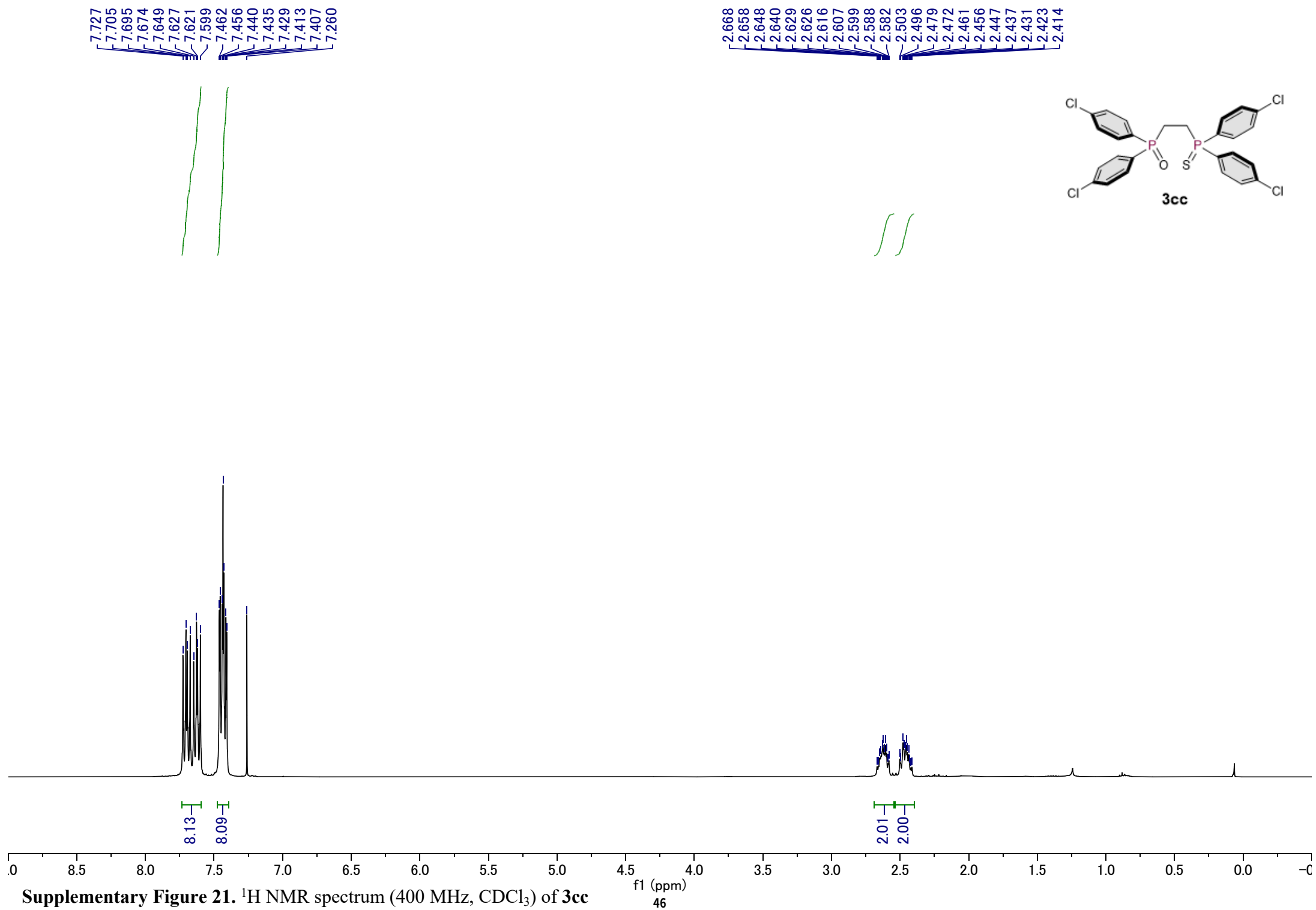
Supplementary Figure 19. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3bb**

CDCl₃, 162 MHz



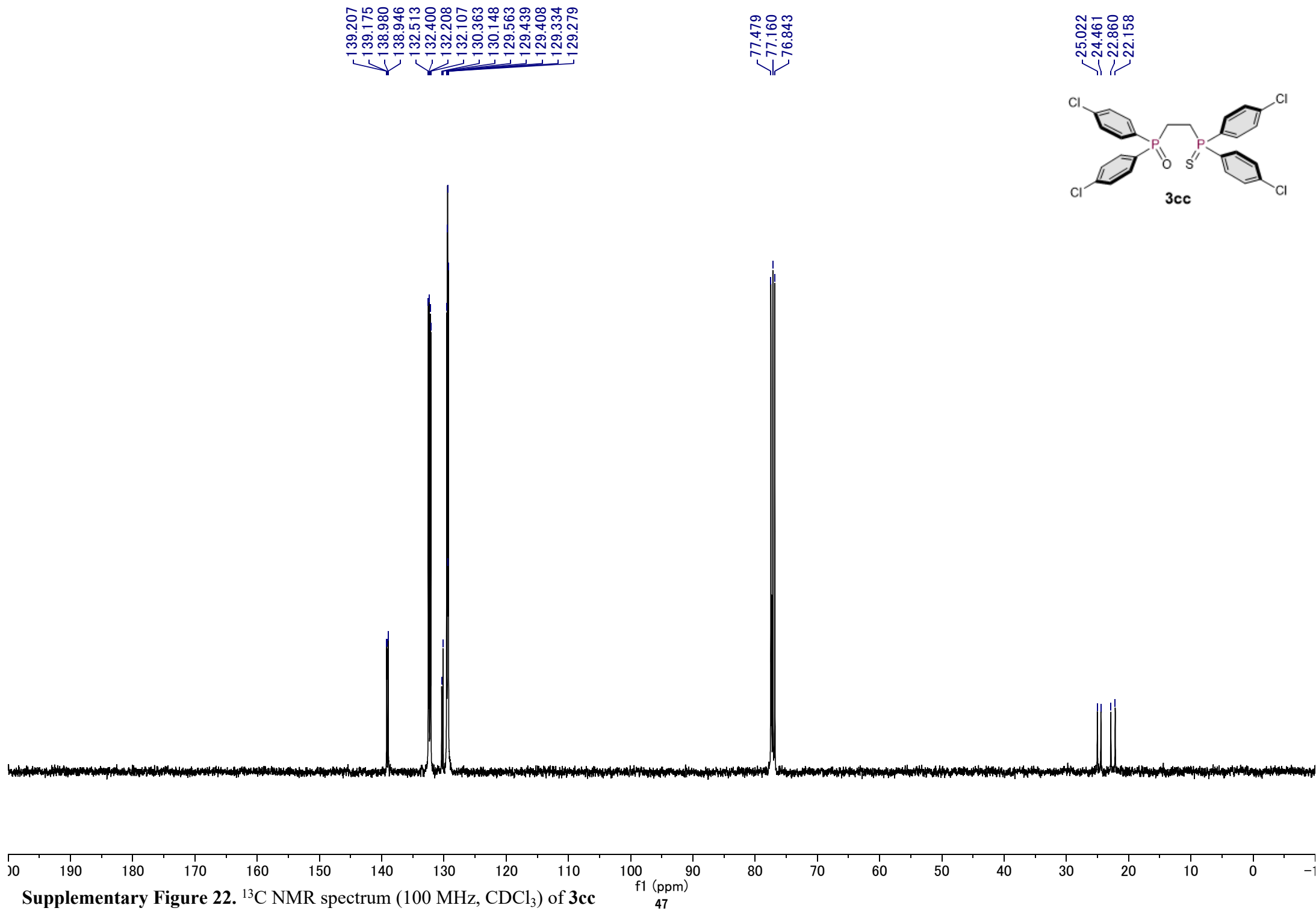
Supplementary Figure 20. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3bb**

CDCl₃, 400 MHz

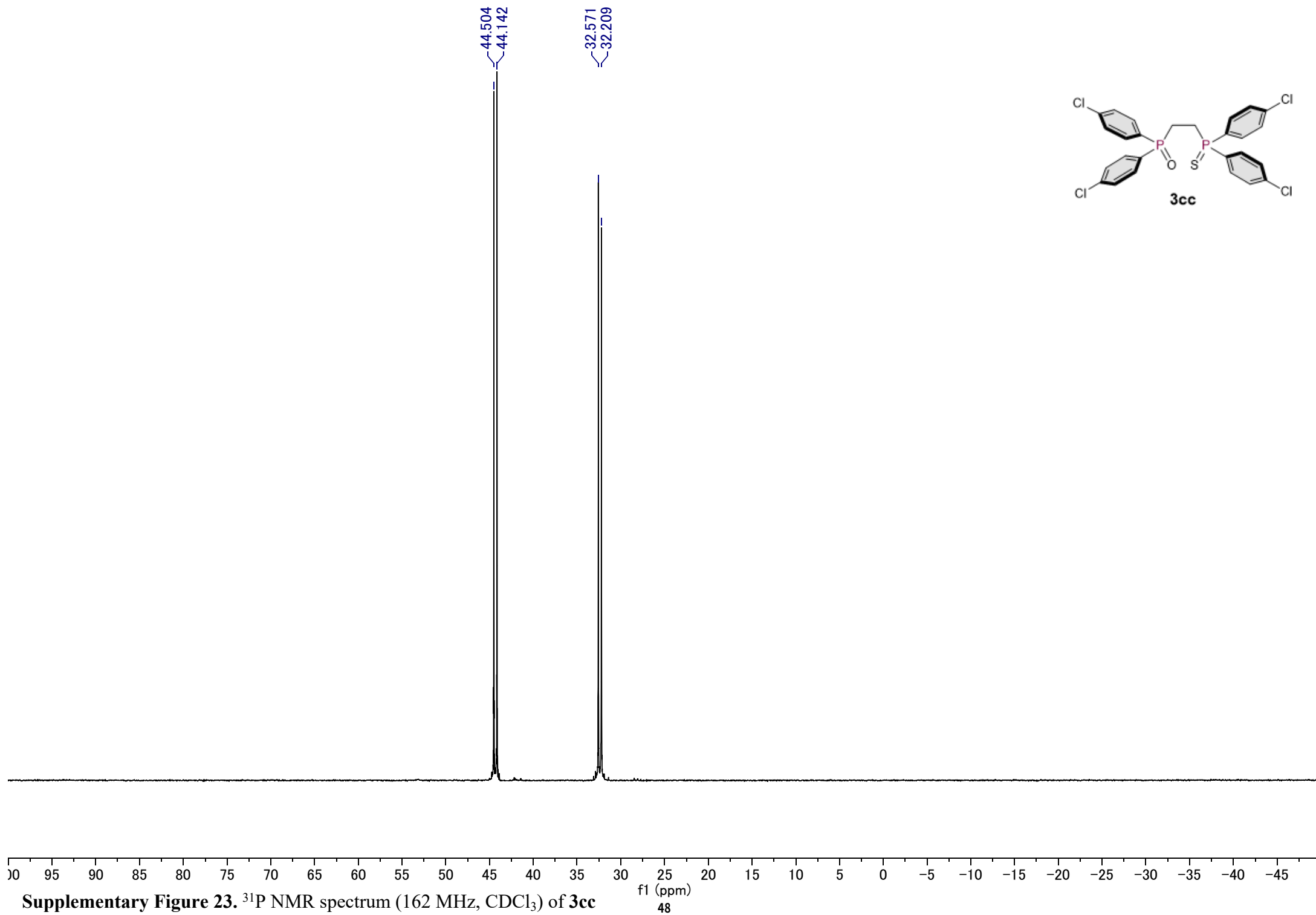


Supplementary Figure 21. ¹H NMR spectrum (400 MHz, CDCl₃) of 3cc

CDCl₃, 100 MHz

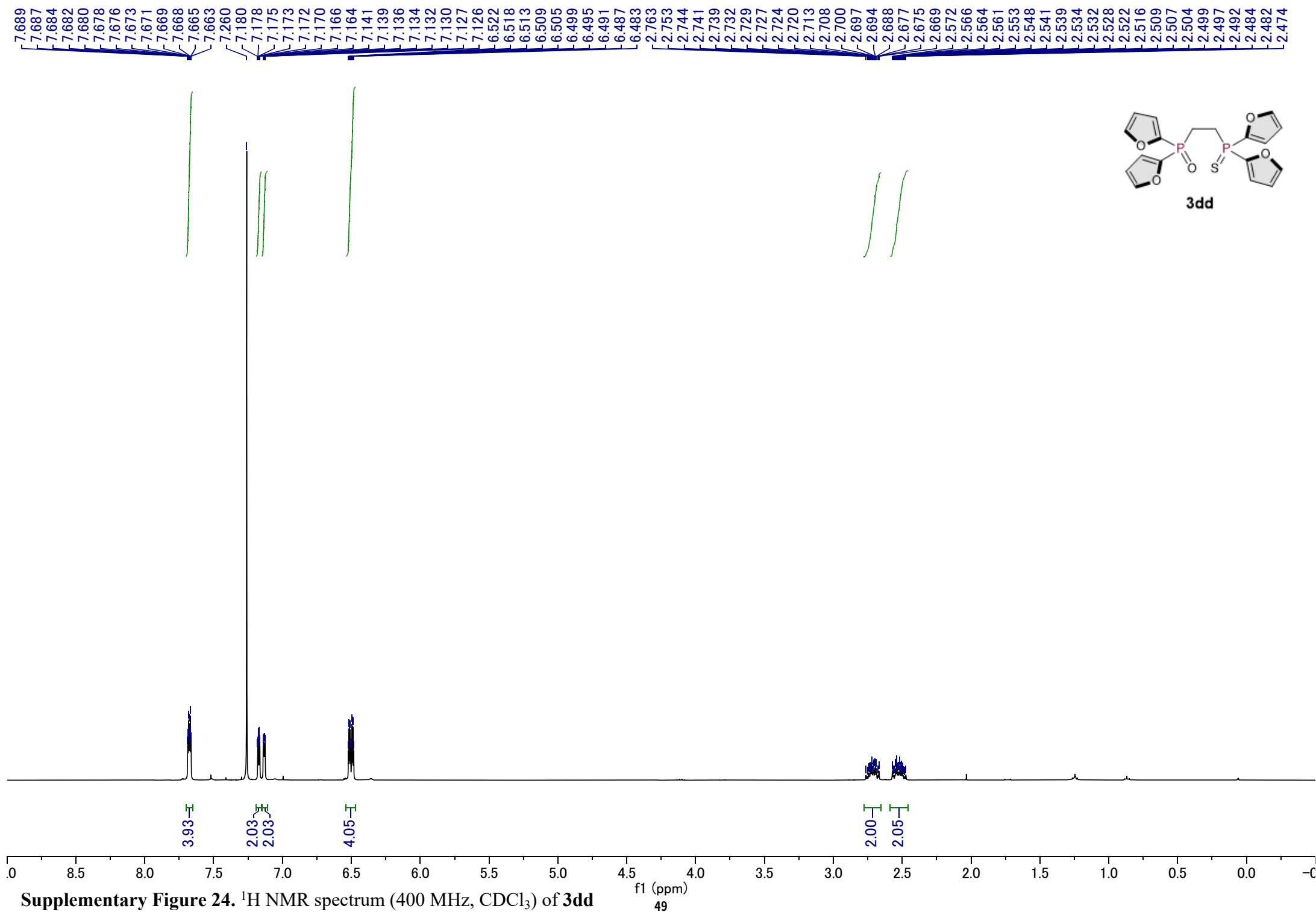


CDCl₃, 162 MHz

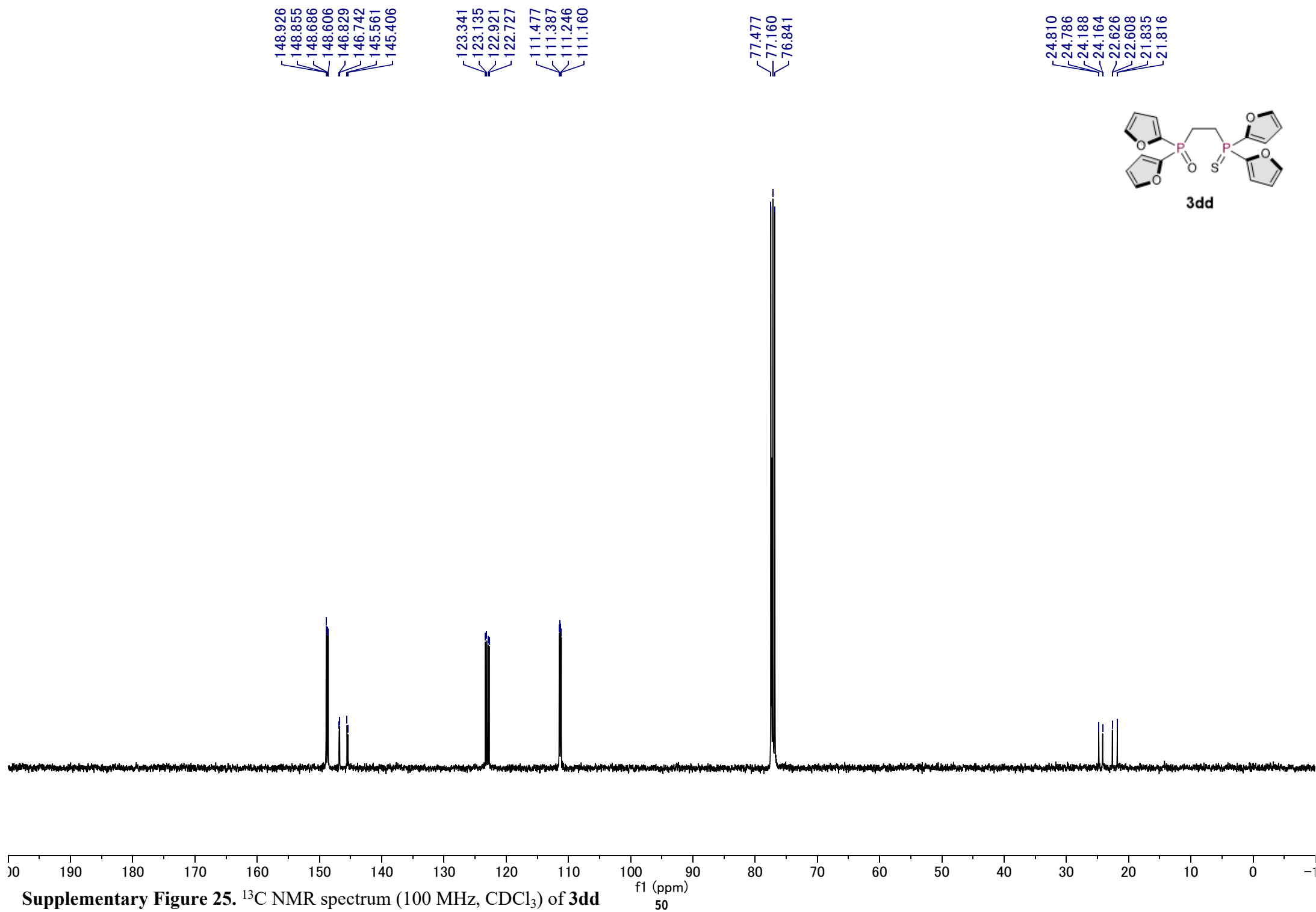


Supplementary Figure 23. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3cc**

CDCl₃, 400 MHz

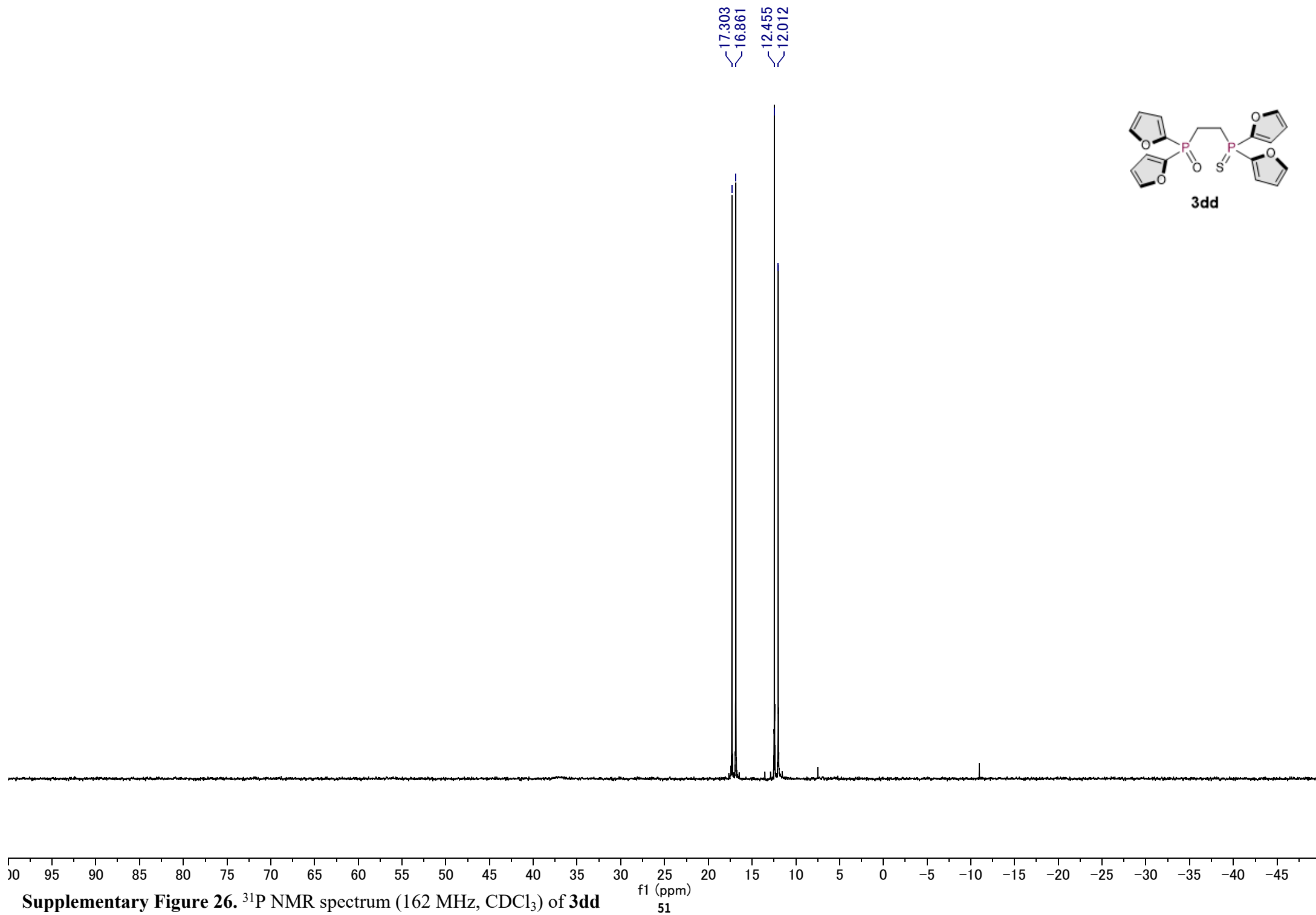


CDCl₃, 100 MHz



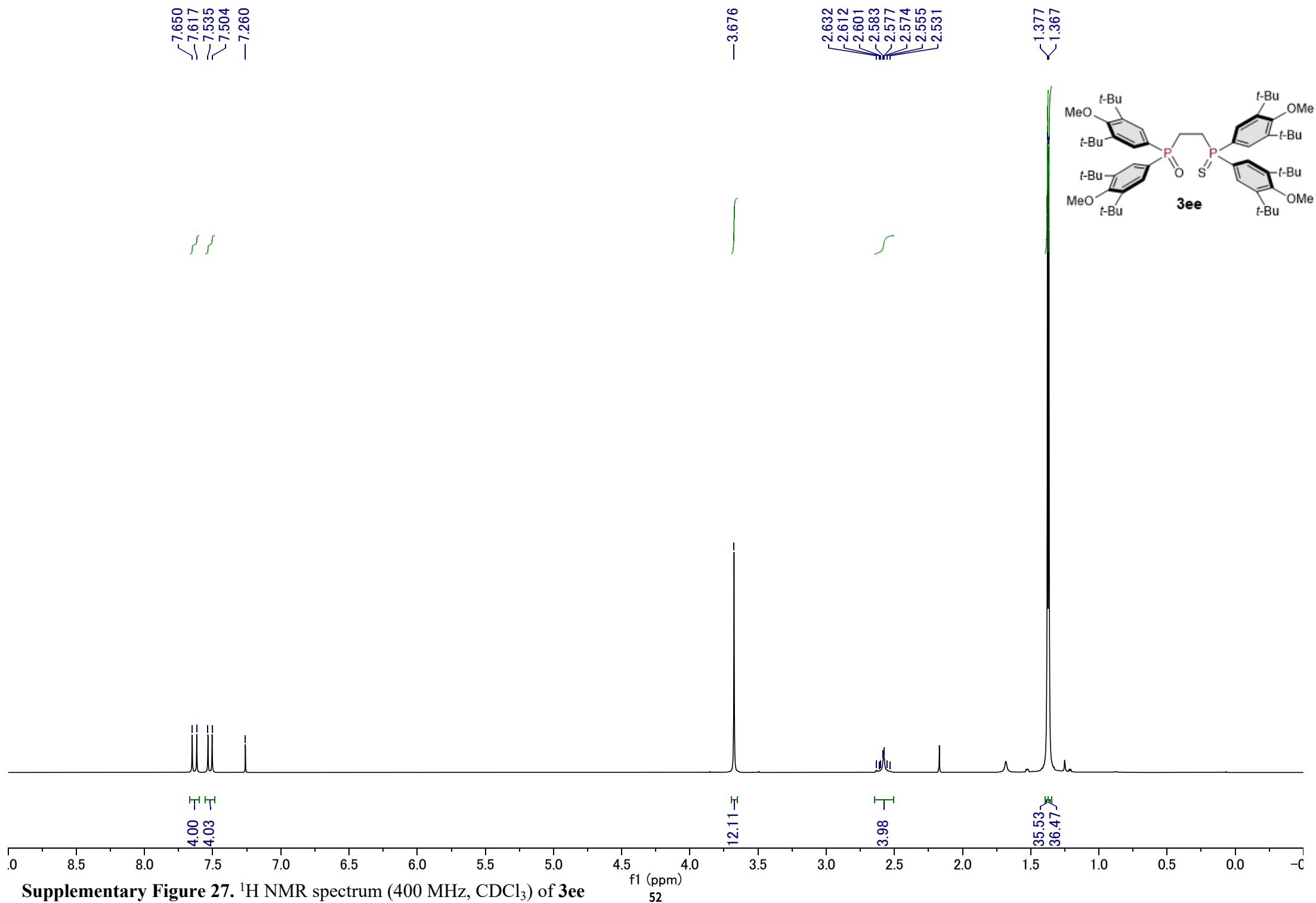
Supplementary Figure 25. ¹³C NMR spectrum (100 MHz, CDCl₃) of **3dd**

CDCl₃, 162 MHz

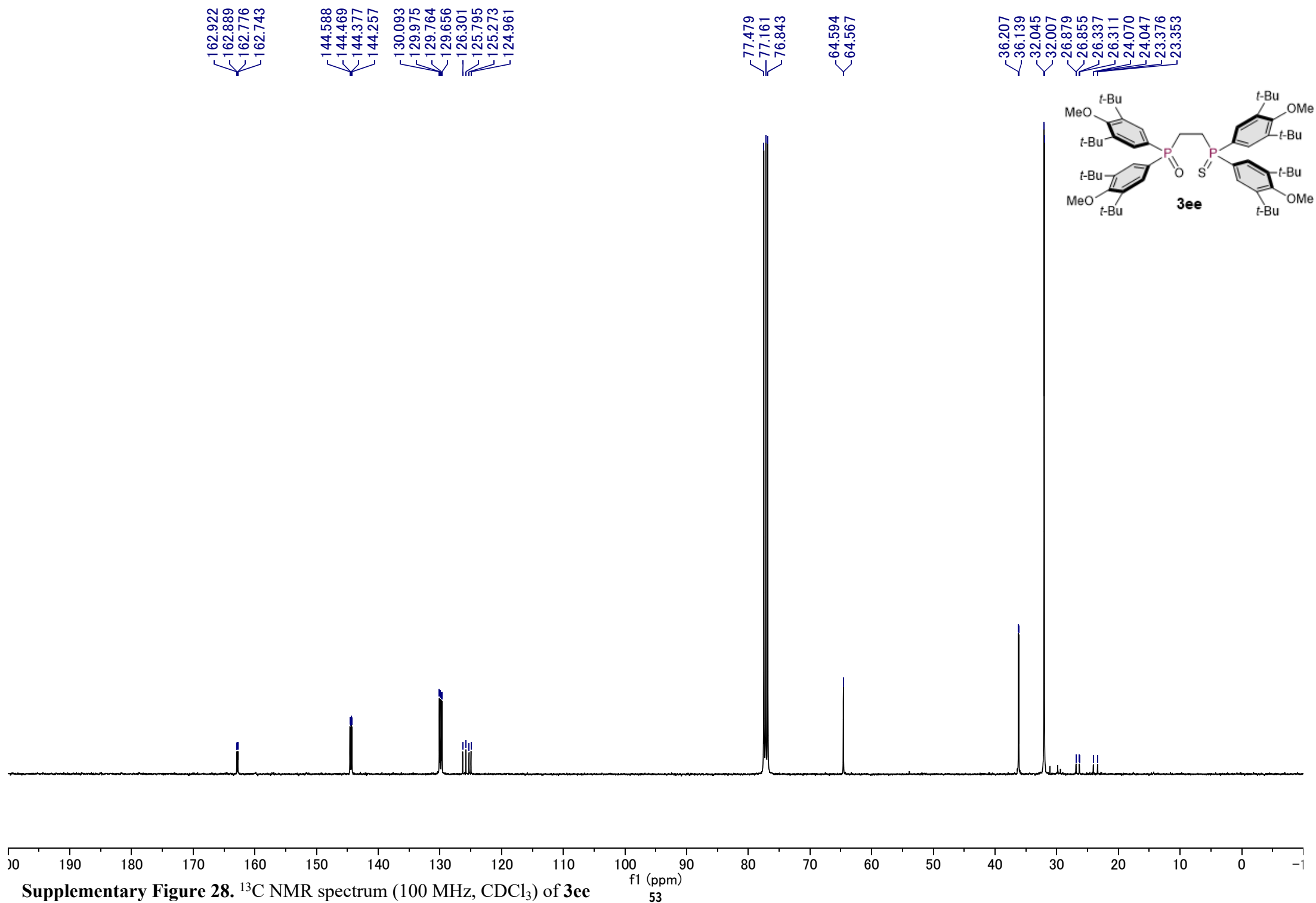


Supplementary Figure 26. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3dd**

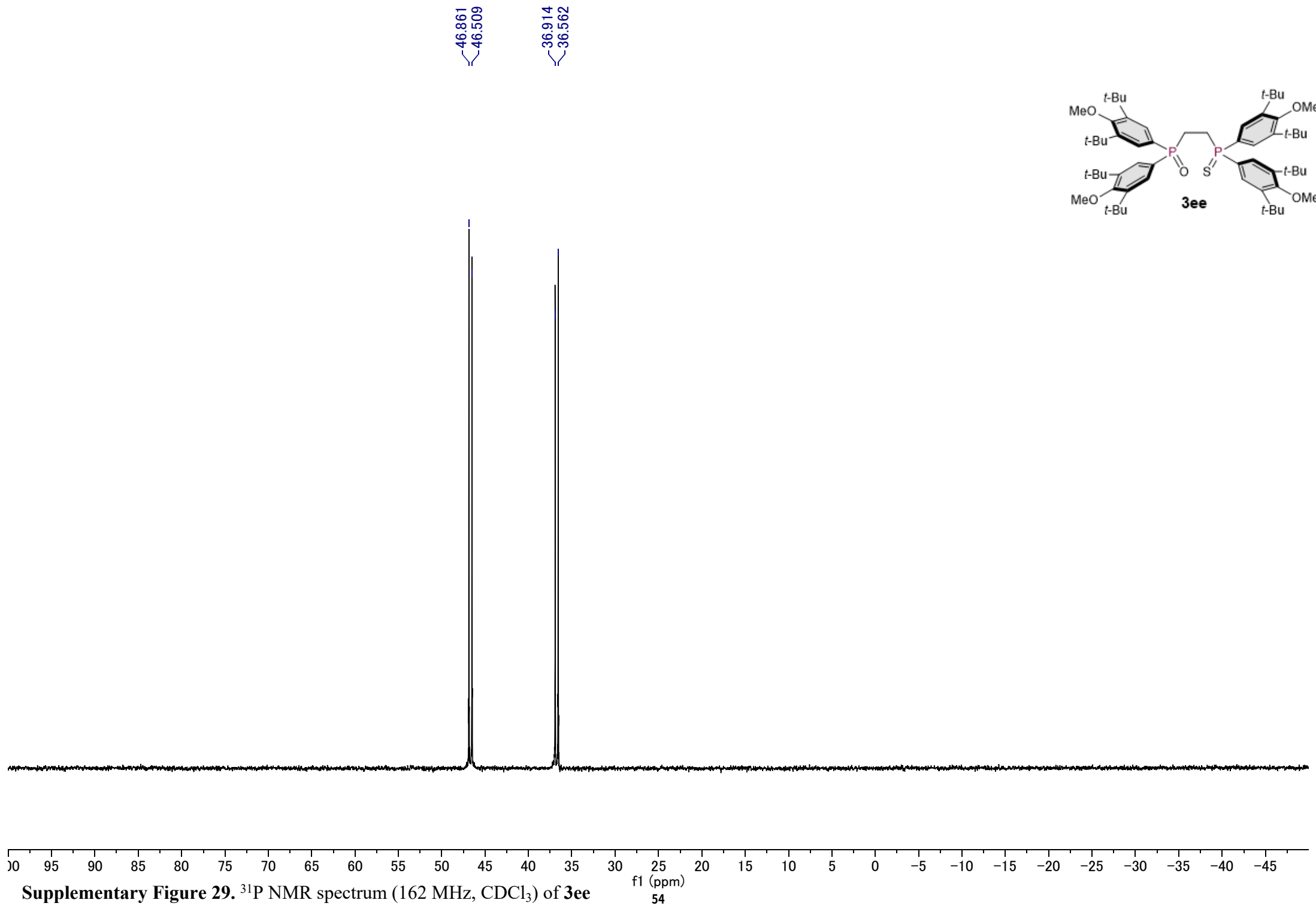
CDCl₃, 400 MHz



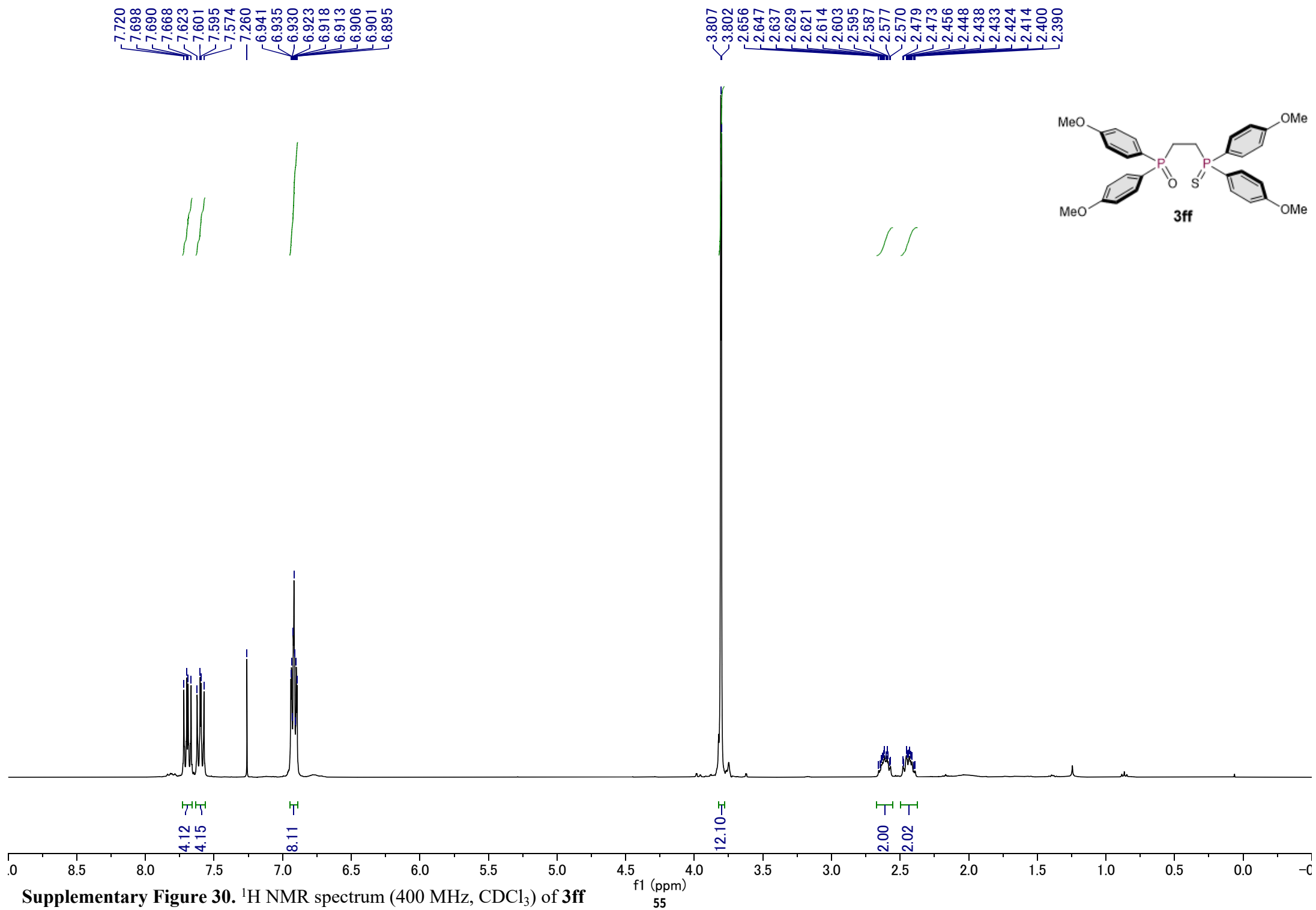
CDCl₃, 100 MHz



CDCl₃, 162 MHz



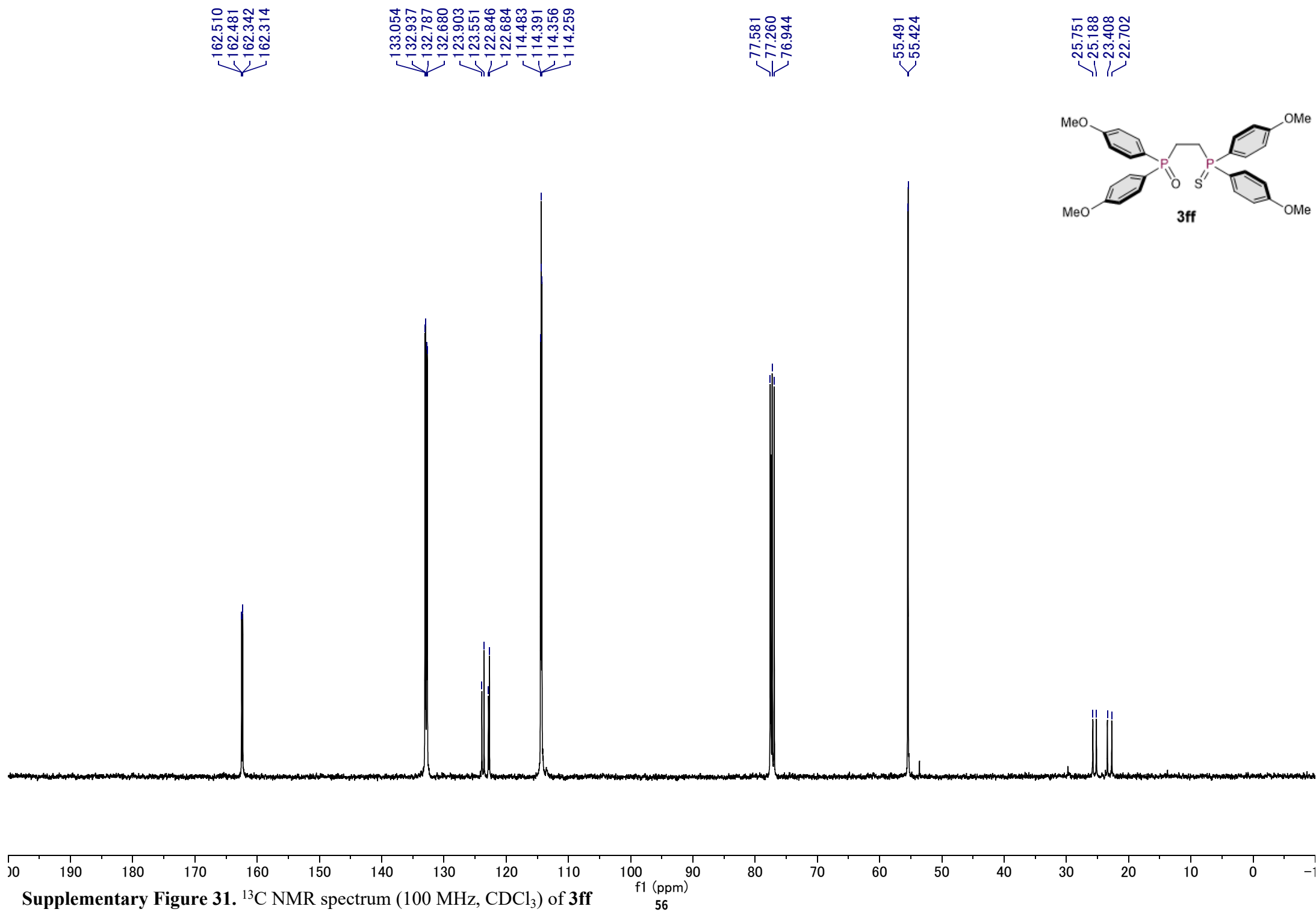
CDCl₃, 400 MHz



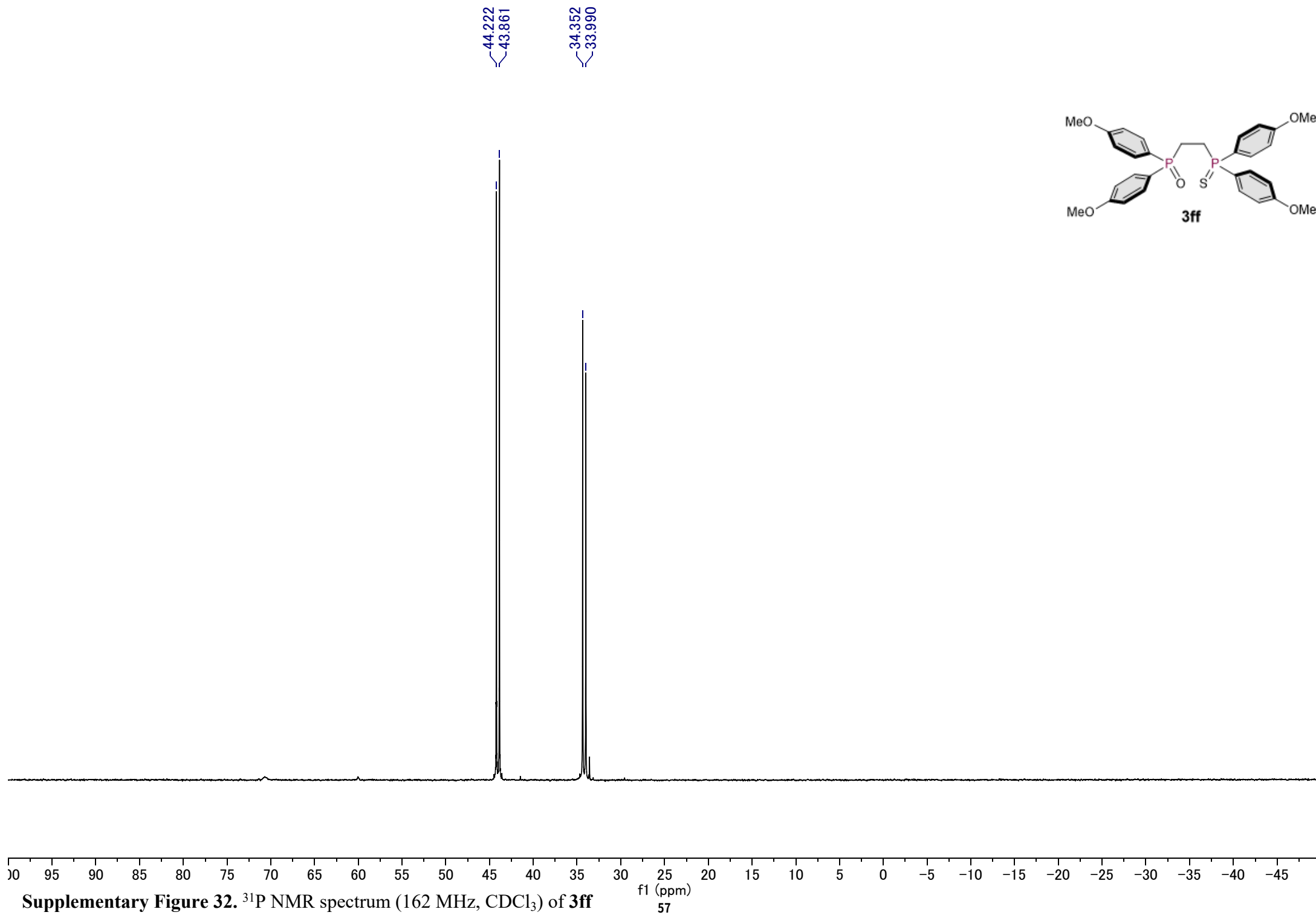
Supplementary Figure 30. ¹H NMR spectrum (400 MHz, CDCl₃) of **3ff**

f1 (ppm)
55

CDCl₃, 100 MHz



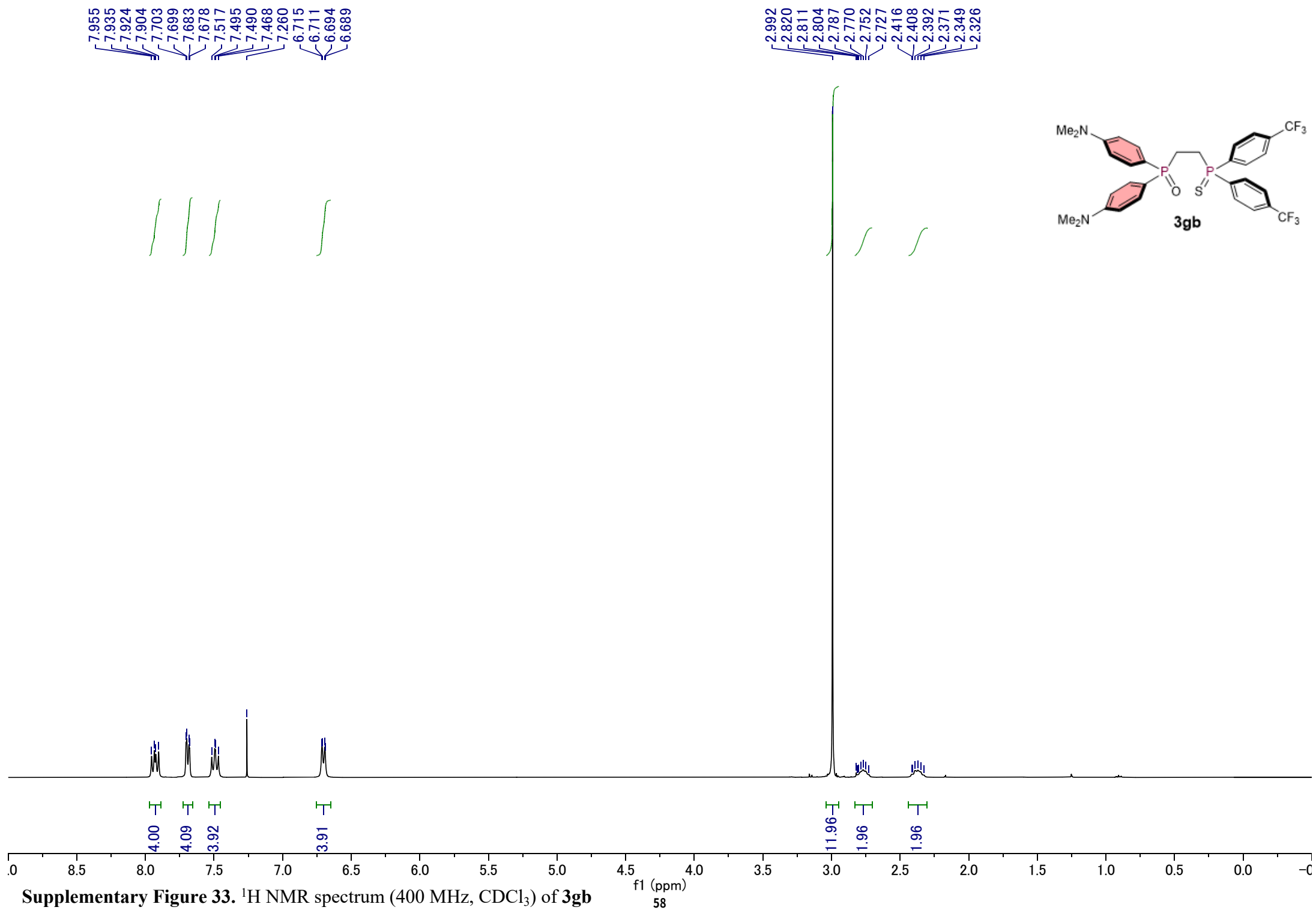
CDCl₃, 162 MHz



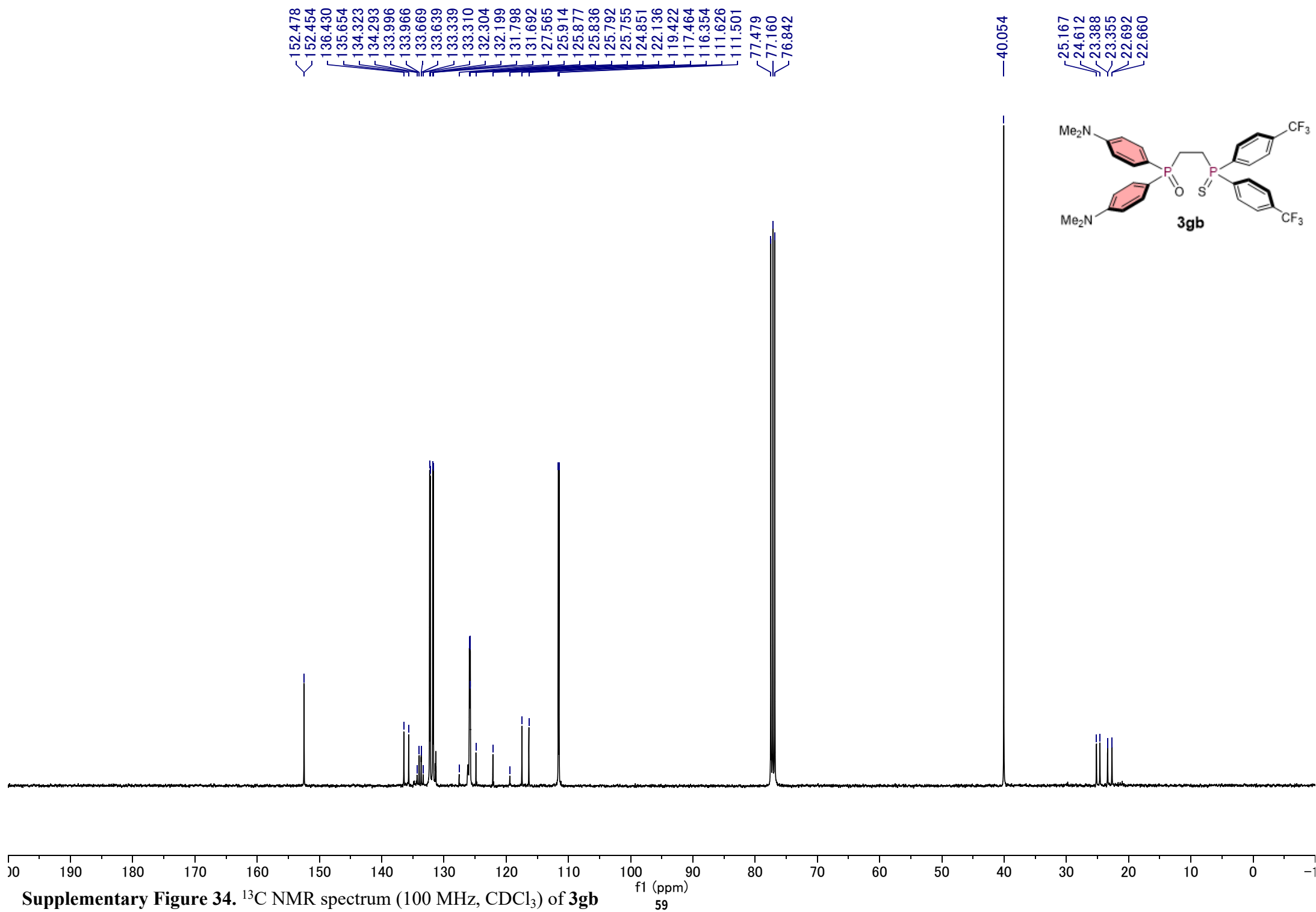
Supplementary Figure 32. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3ff**

f1 (ppm)
57

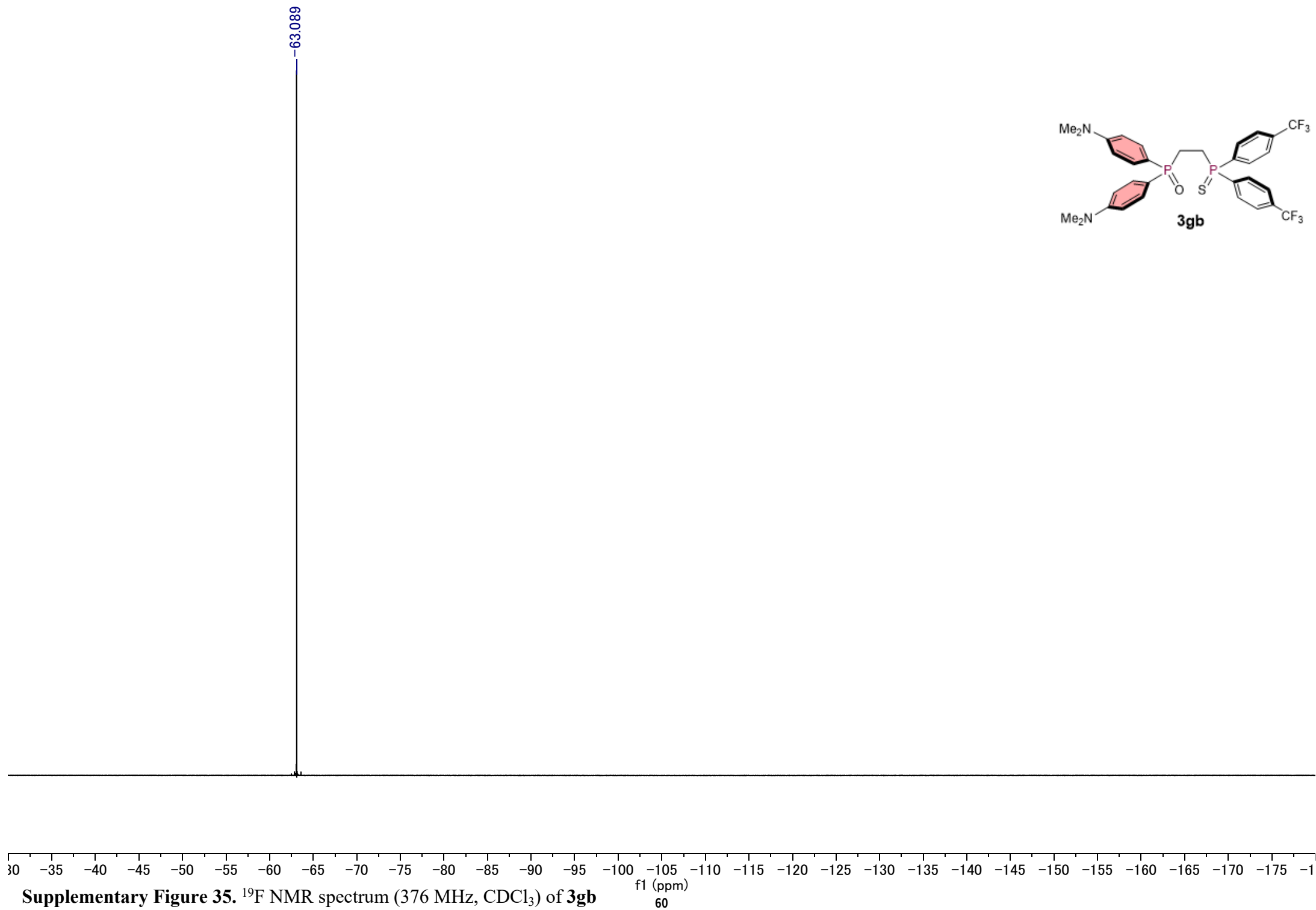
CDCl₃, 400 MHz



CDCl₃, 100 MHz



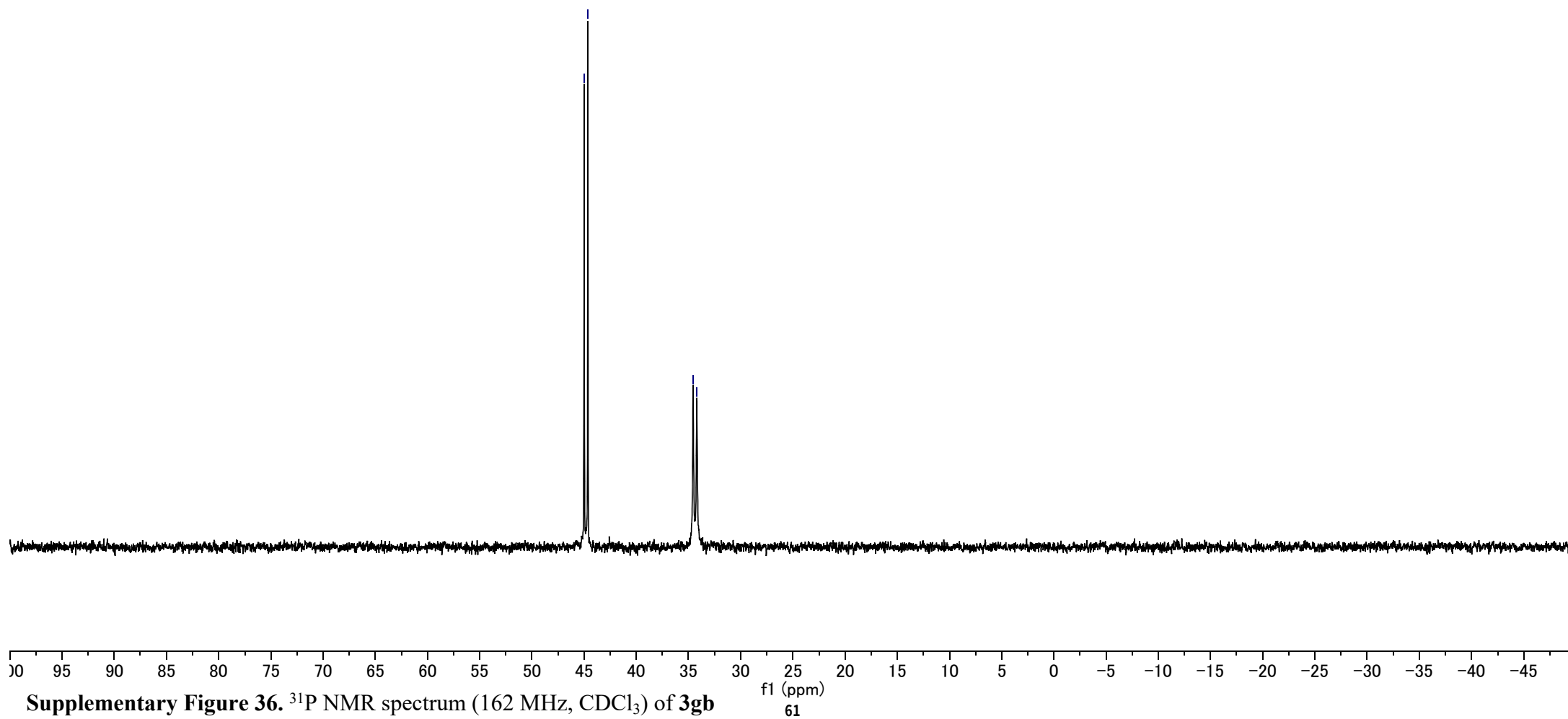
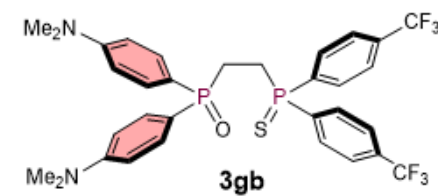
CDCl₃, 376 MHz



Supplementary Figure 35. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3gb**

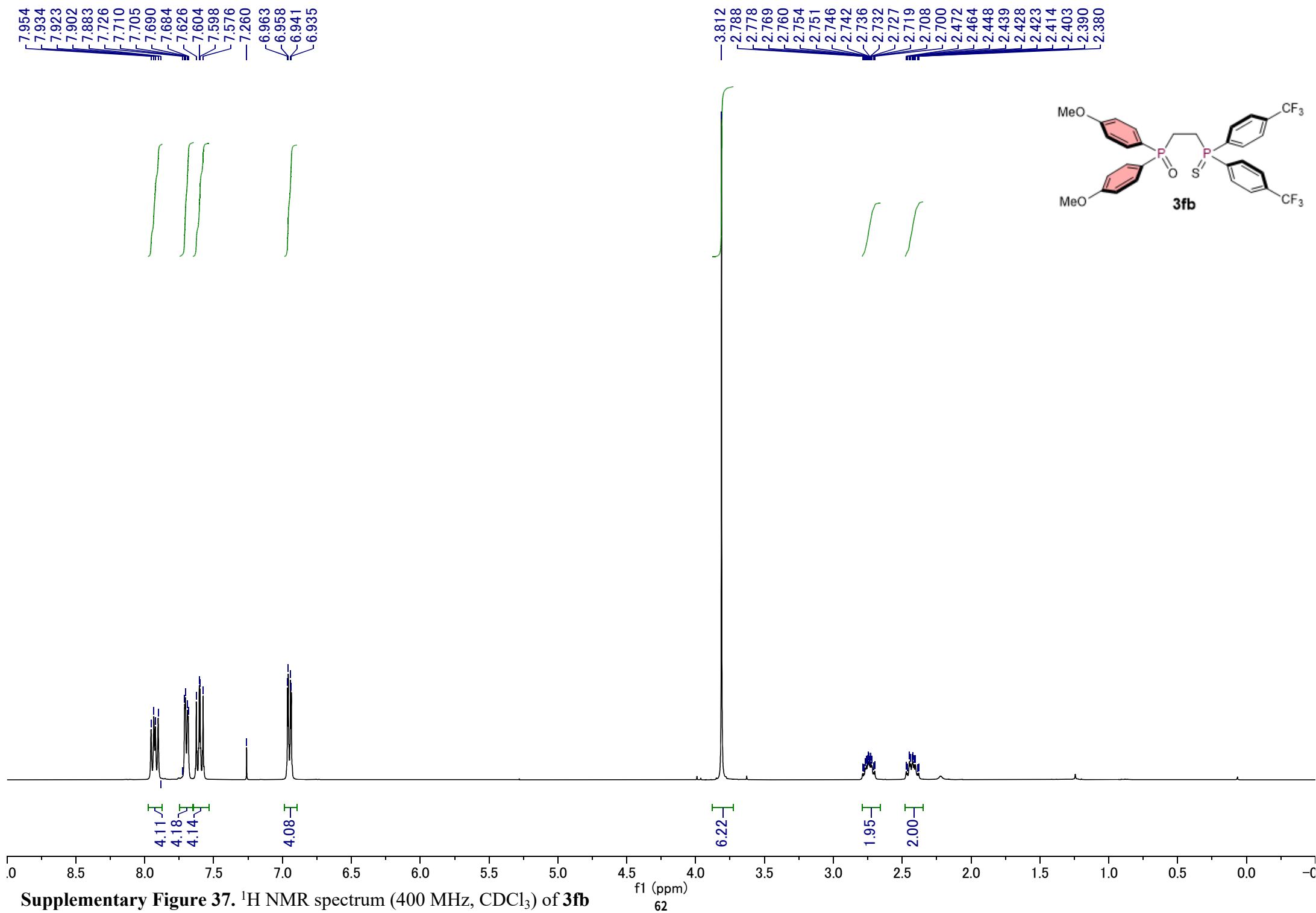
CDCl₃, 162 MHz

44.993
44.638
34.556
34.201



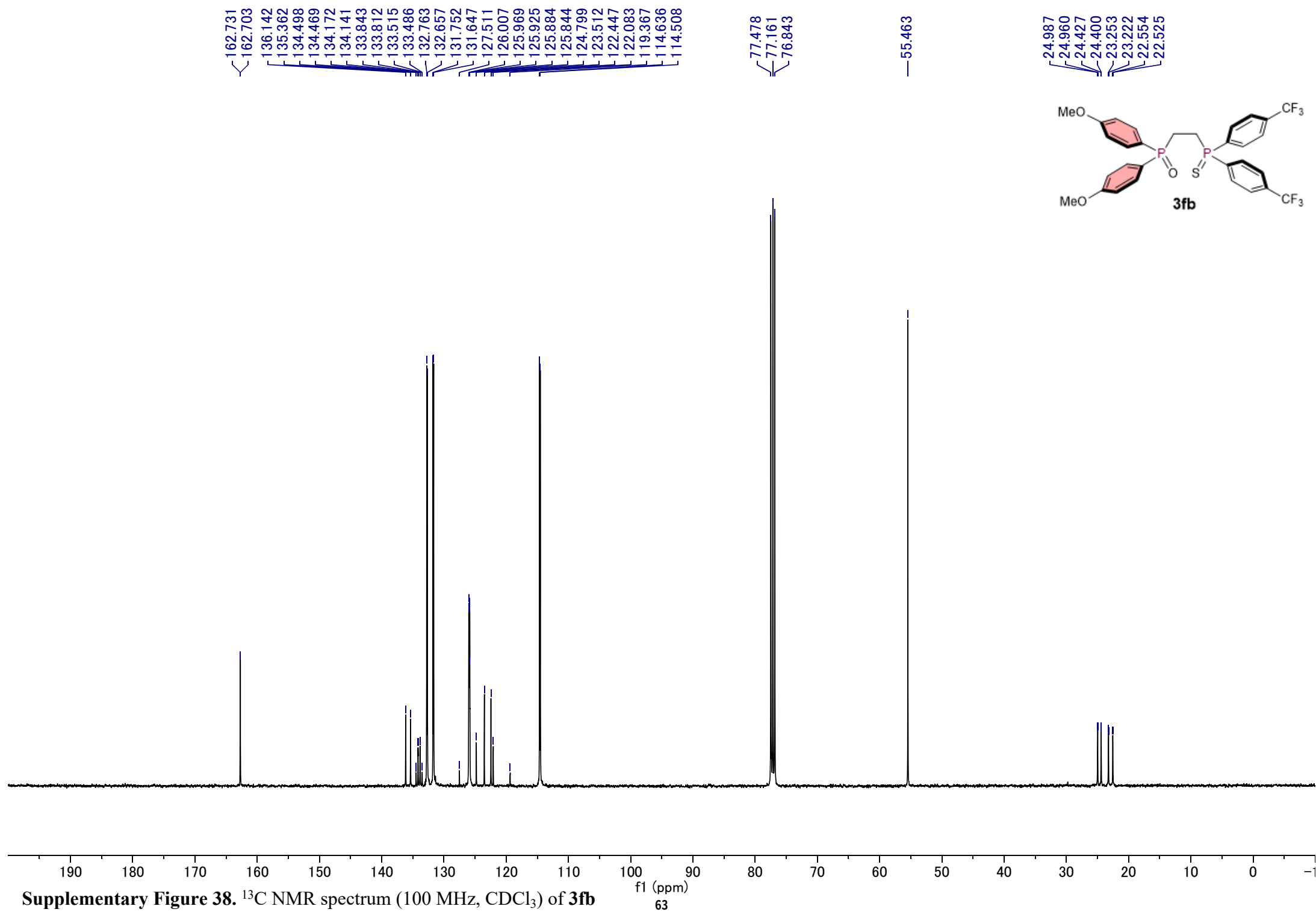
Supplementary Figure 36. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3gb**

CDCl₃, 400 MHz

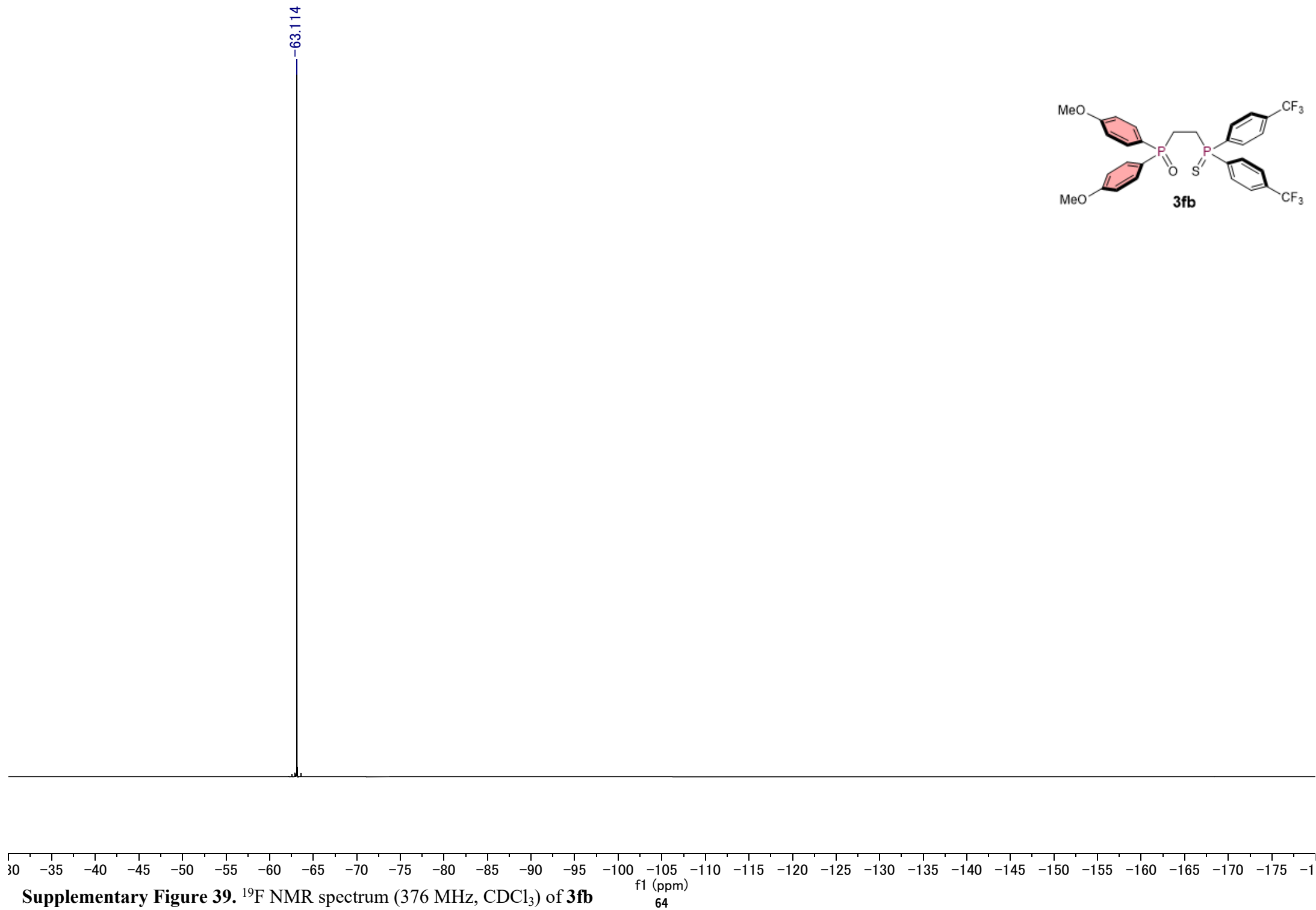


Supplementary Figure 37. ¹H NMR spectrum (400 MHz, CDCl₃) of **3fb**

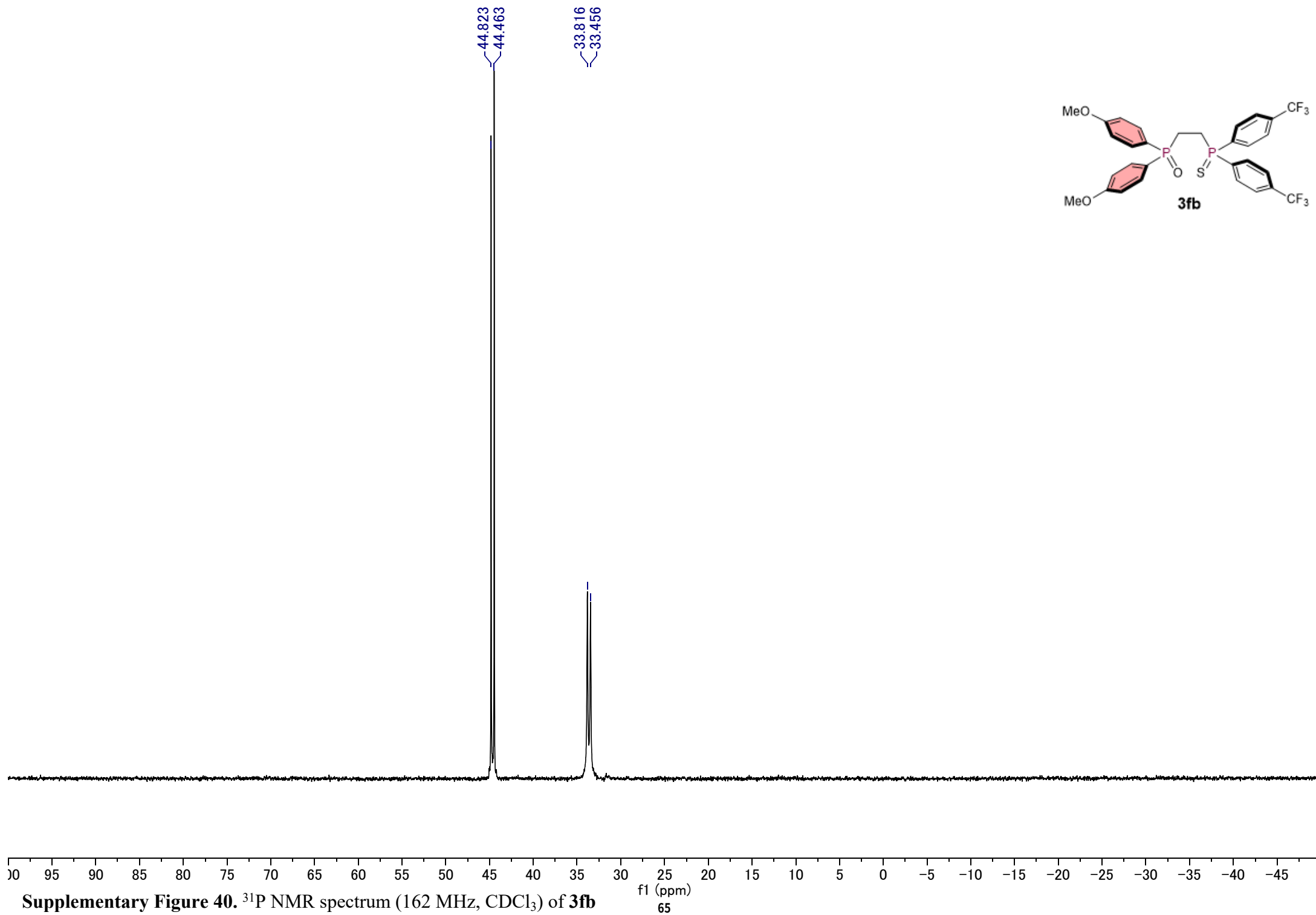
CDCl₃, 100 MHz



CDCl₃, 376 MHz

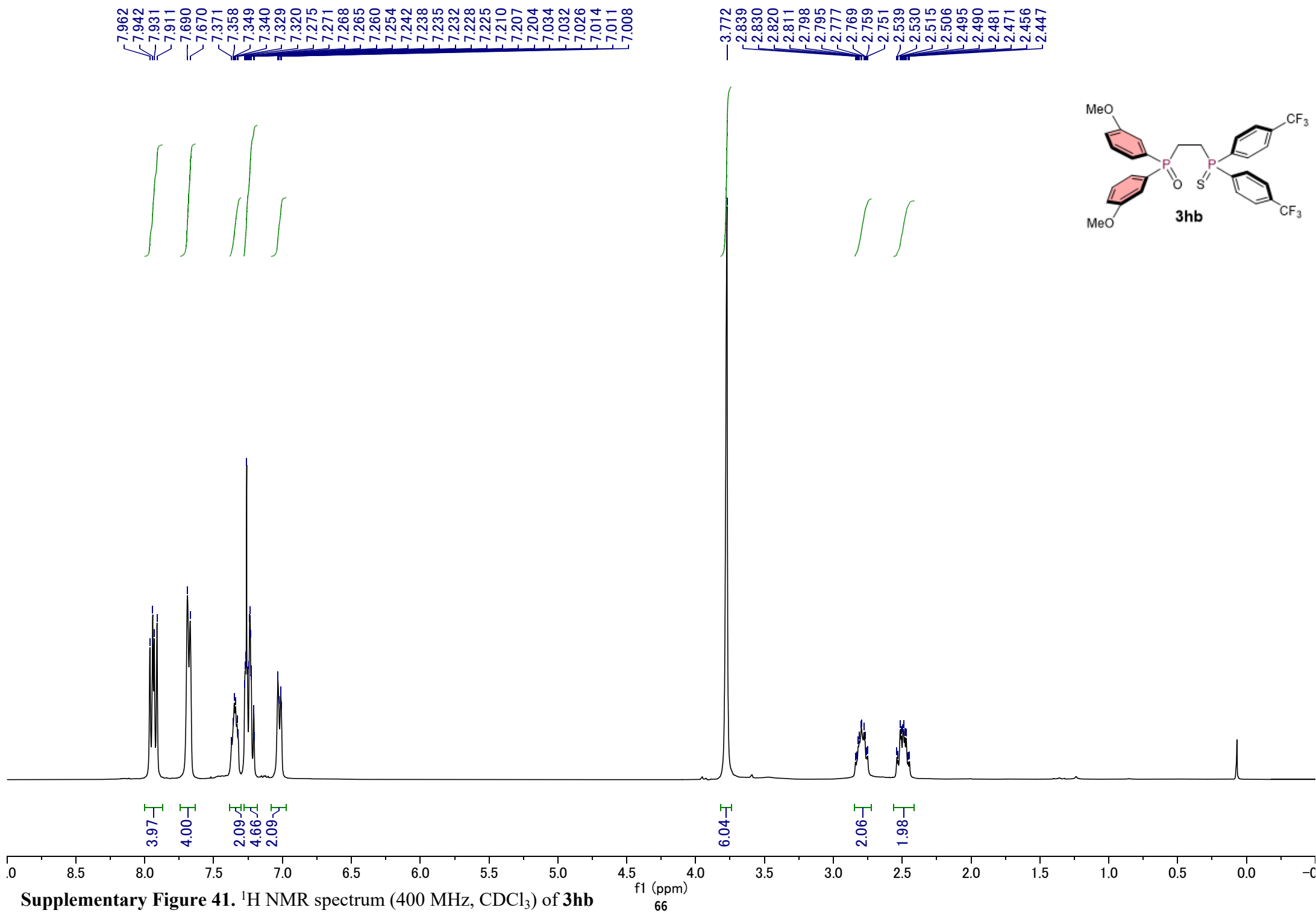


CDCl₃, 162 MHz



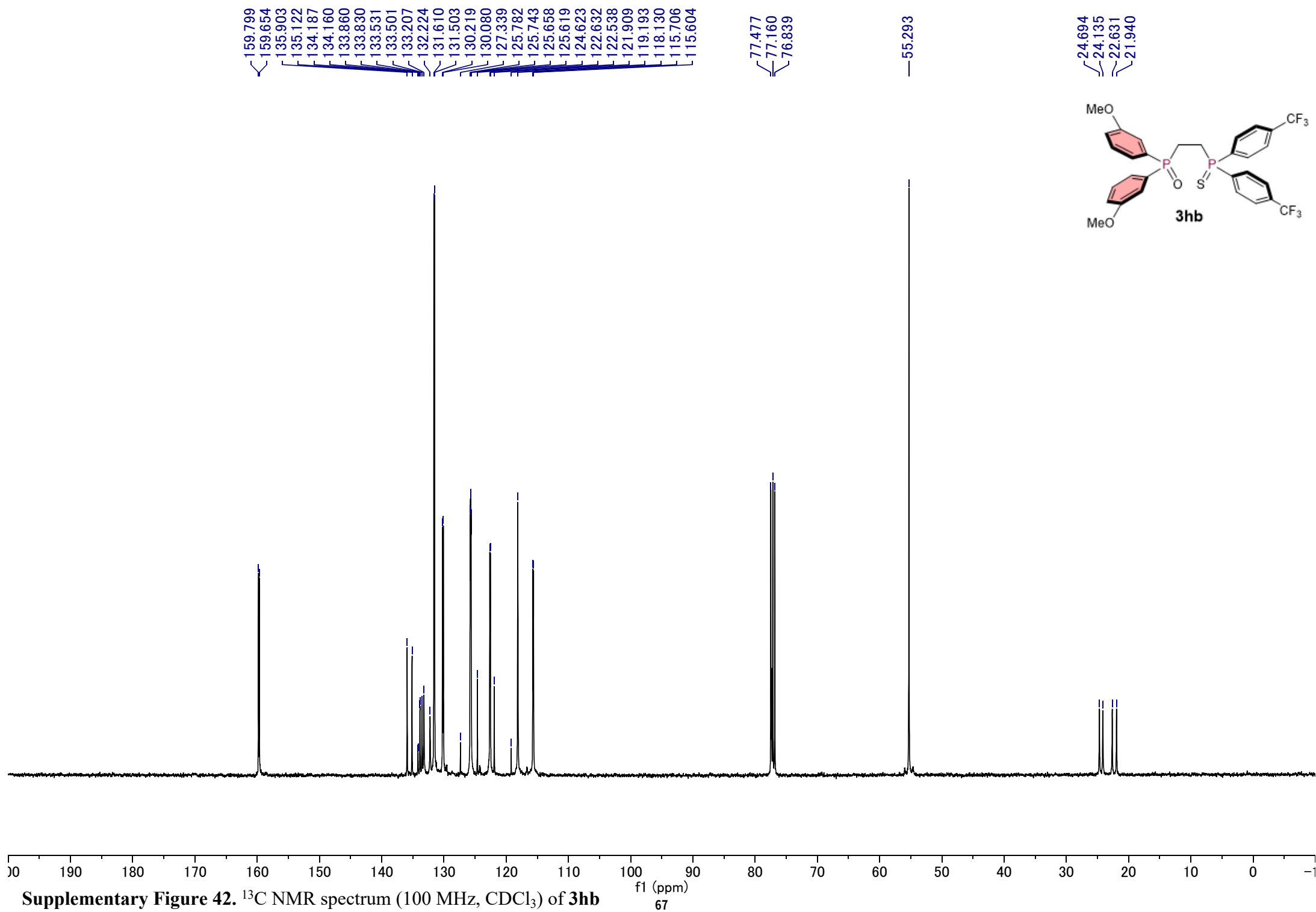
Supplementary Figure 40. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3fb**

CDCl₃, 400 MHz

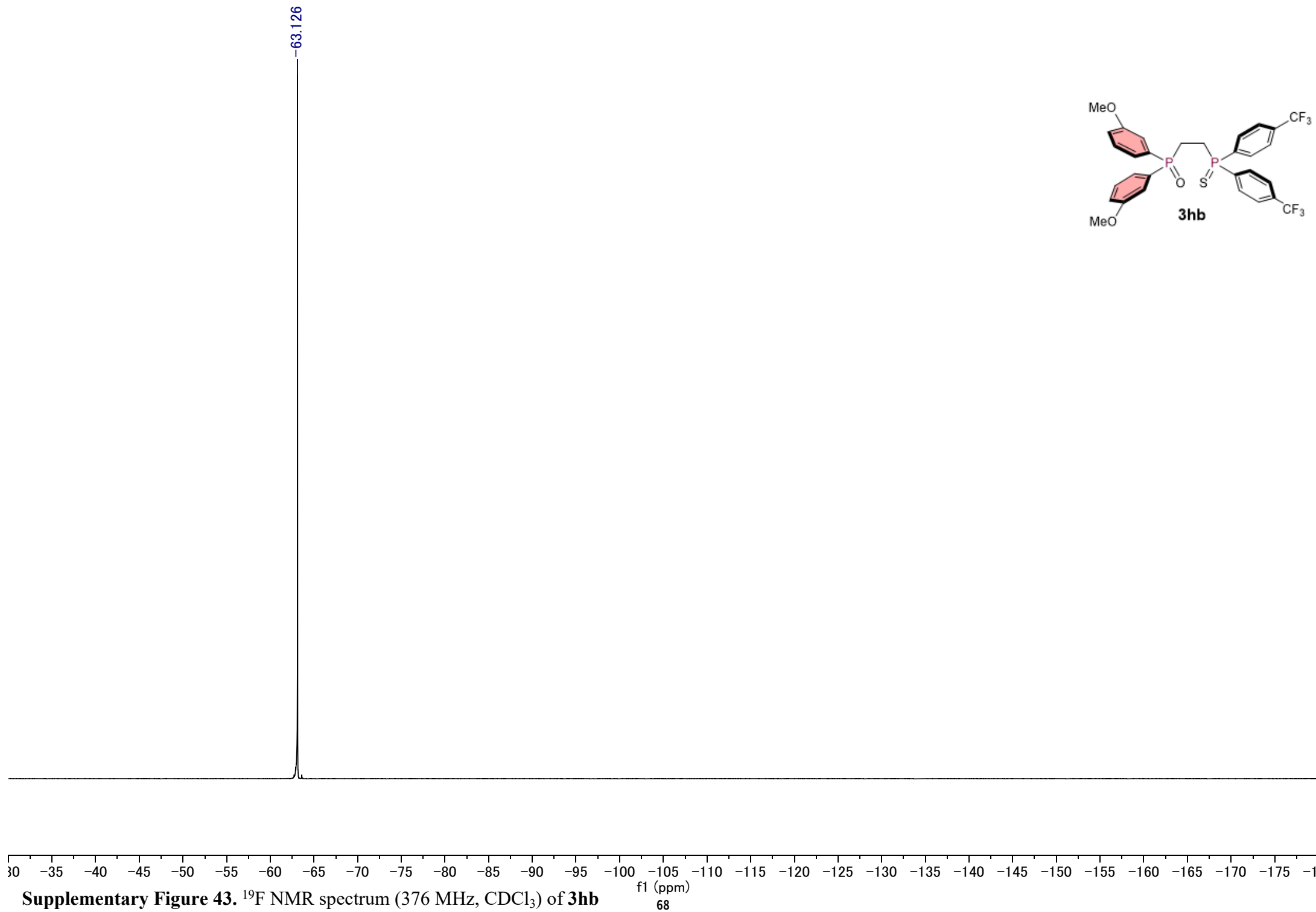


Supplementary Figure 41. ¹H NMR spectrum (400 MHz, CDCl₃) of **3hb**

CDCl₃, 100 MHz

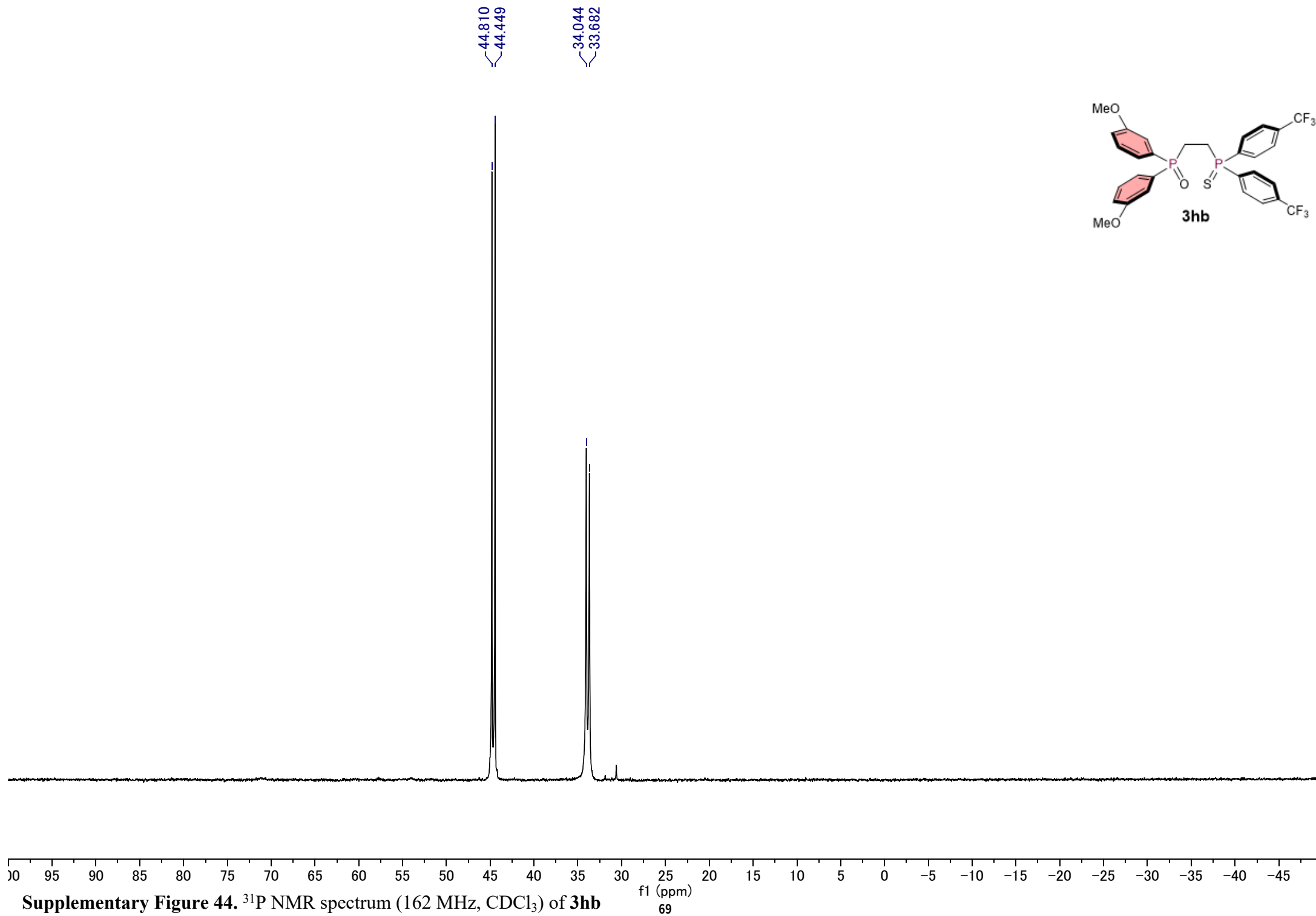


CDCl₃, 376 MHz



Supplementary Figure 43. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3hb**

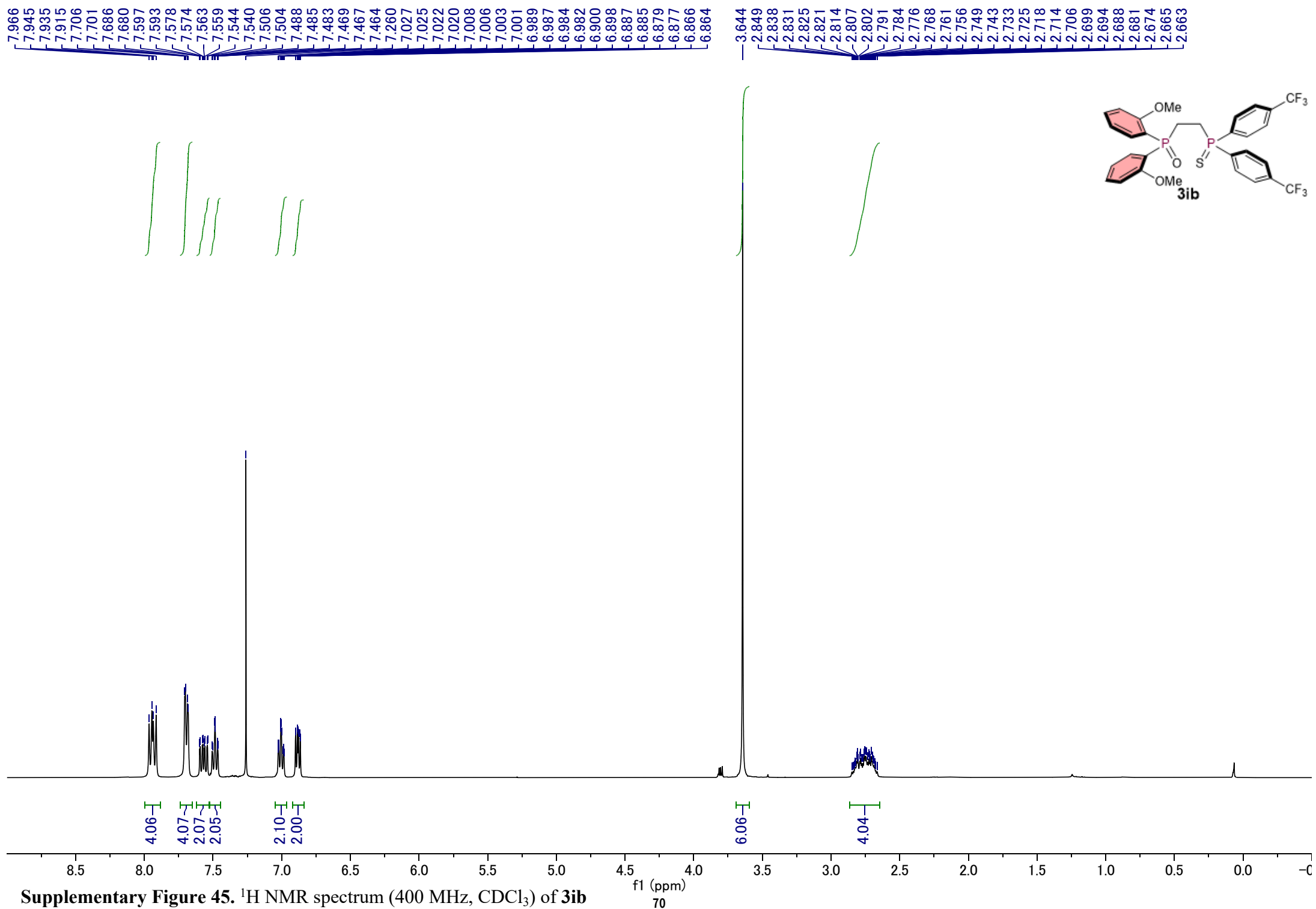
CDCl₃, 162 MHz



Supplementary Figure 44. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3hb**

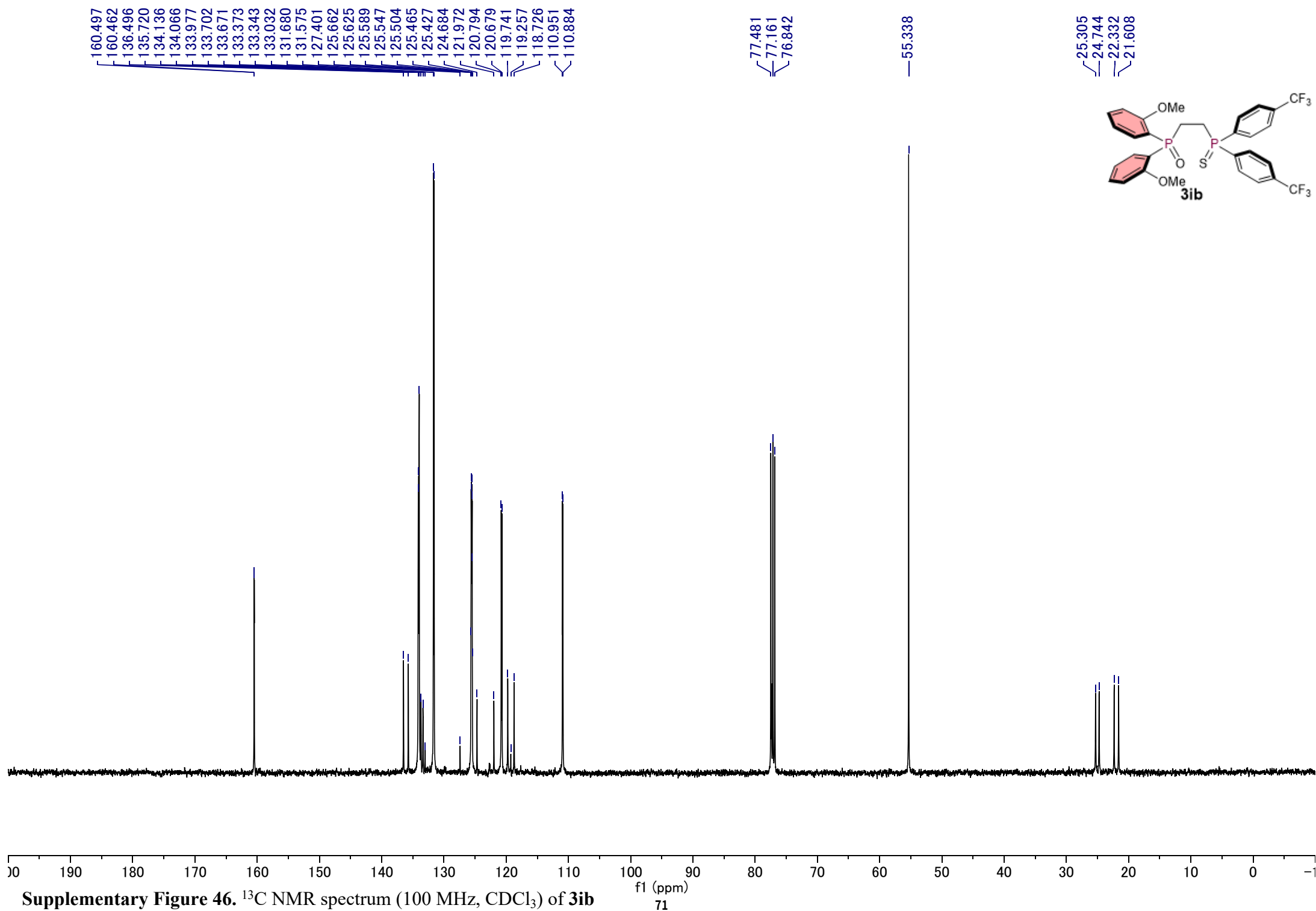
f1 (ppm)
69

CDCl₃, 400 MHz

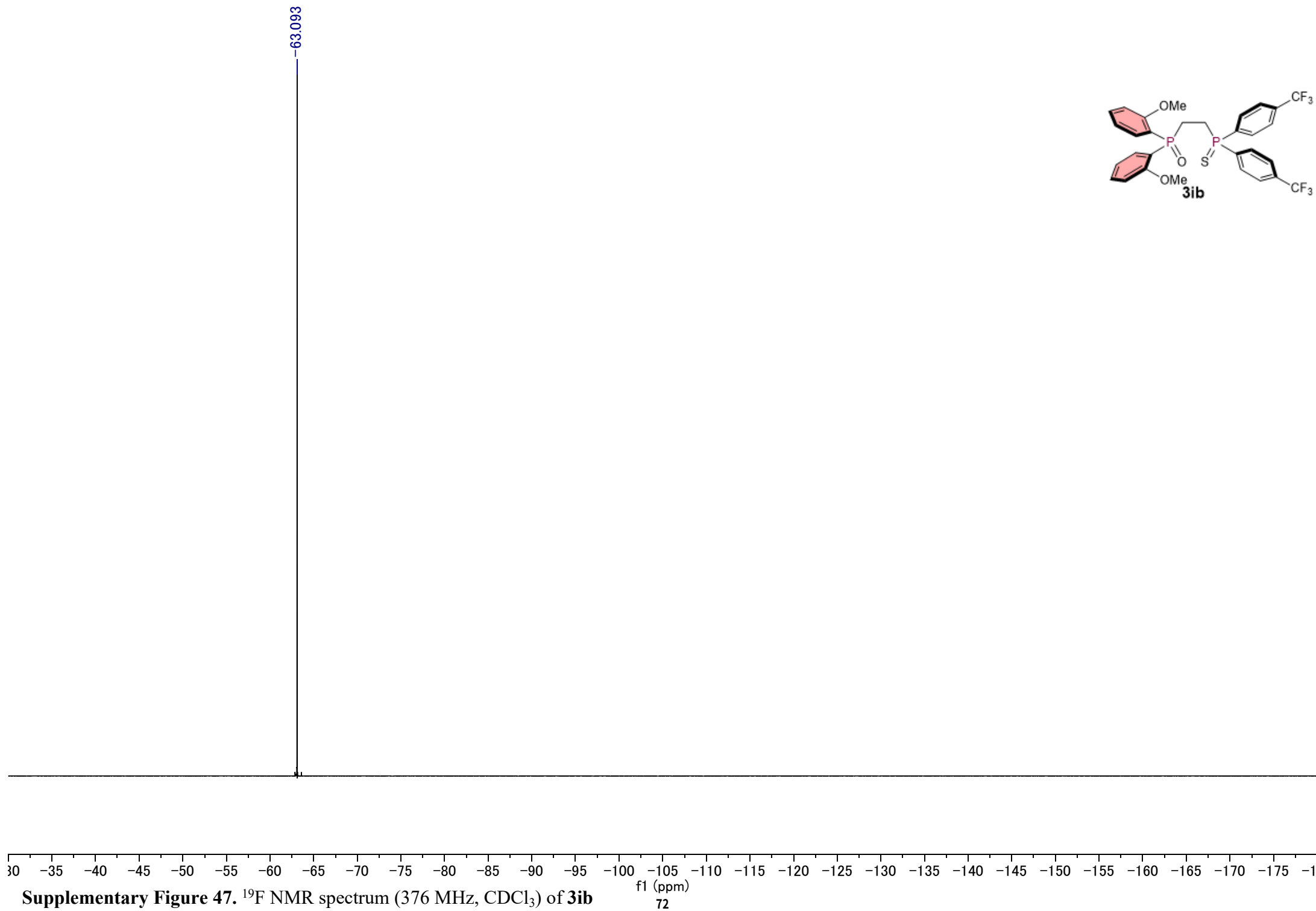


Supplementary Figure 45. ¹H NMR spectrum (400 MHz, CDCl₃) of **3ib**

CDCl₃, 100 MHz

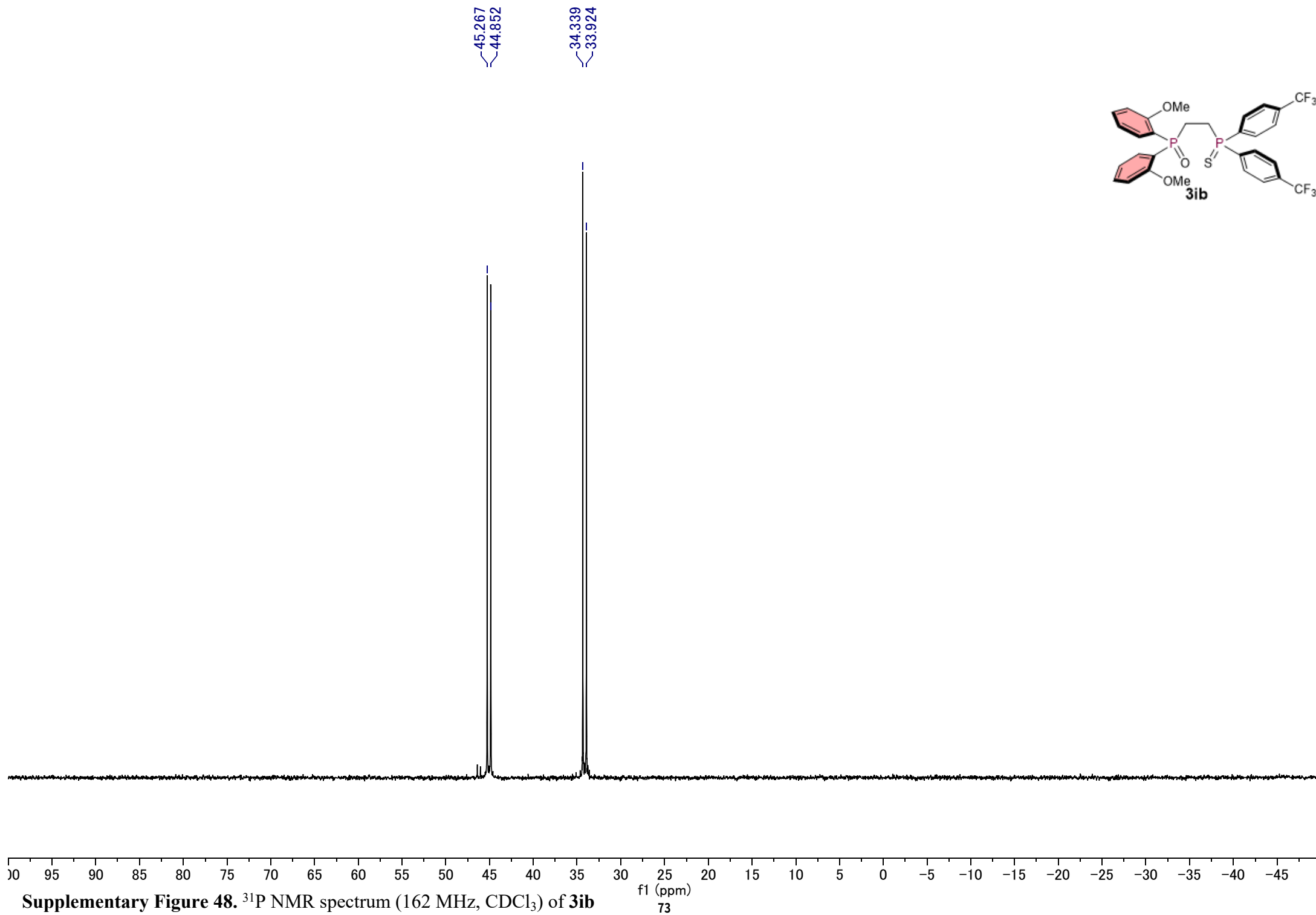


CDCl₃, 376 MHz



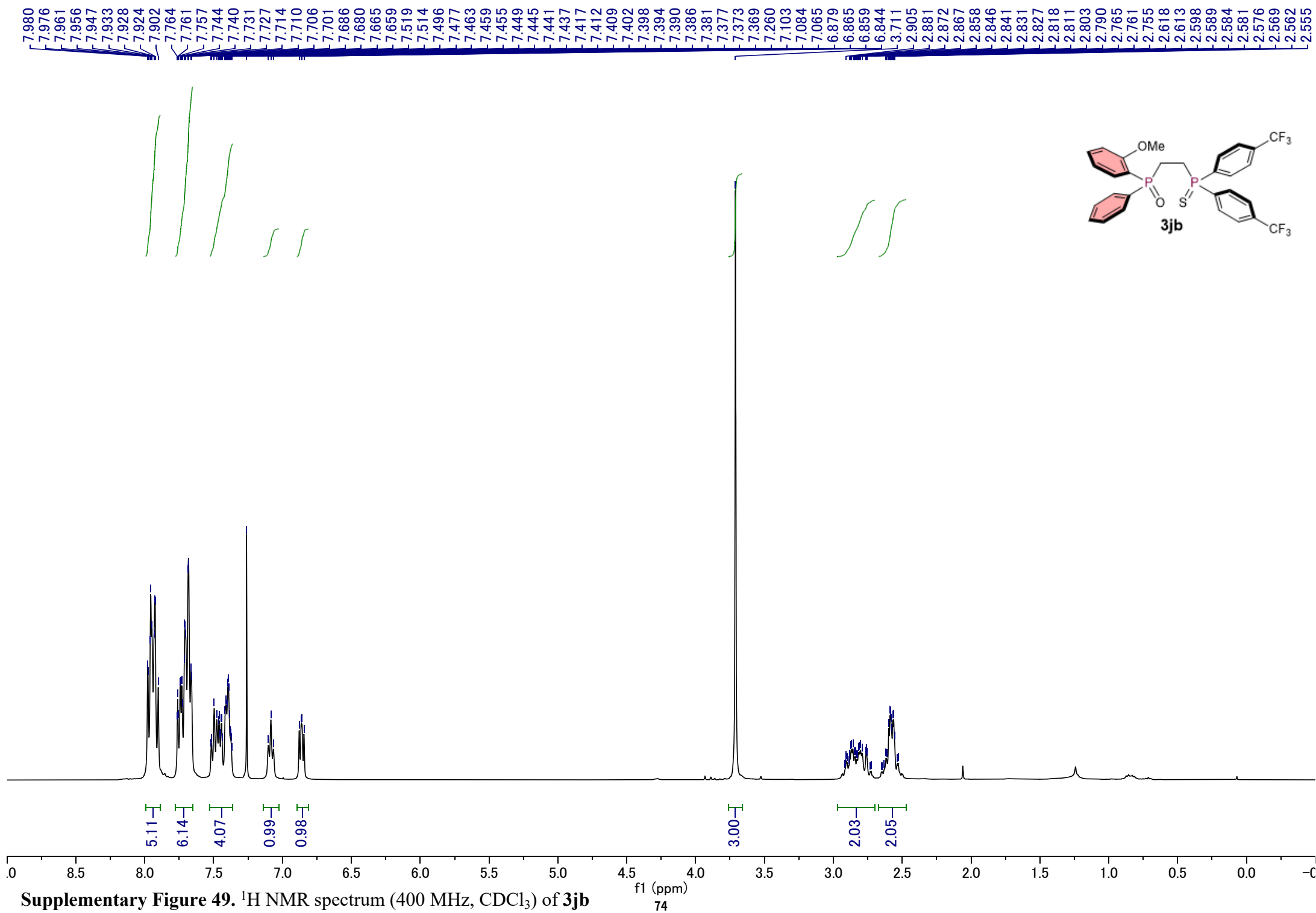
Supplementary Figure 47. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3ib**

CDCl₃, 162 MHz



Supplementary Figure 48. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3ib**

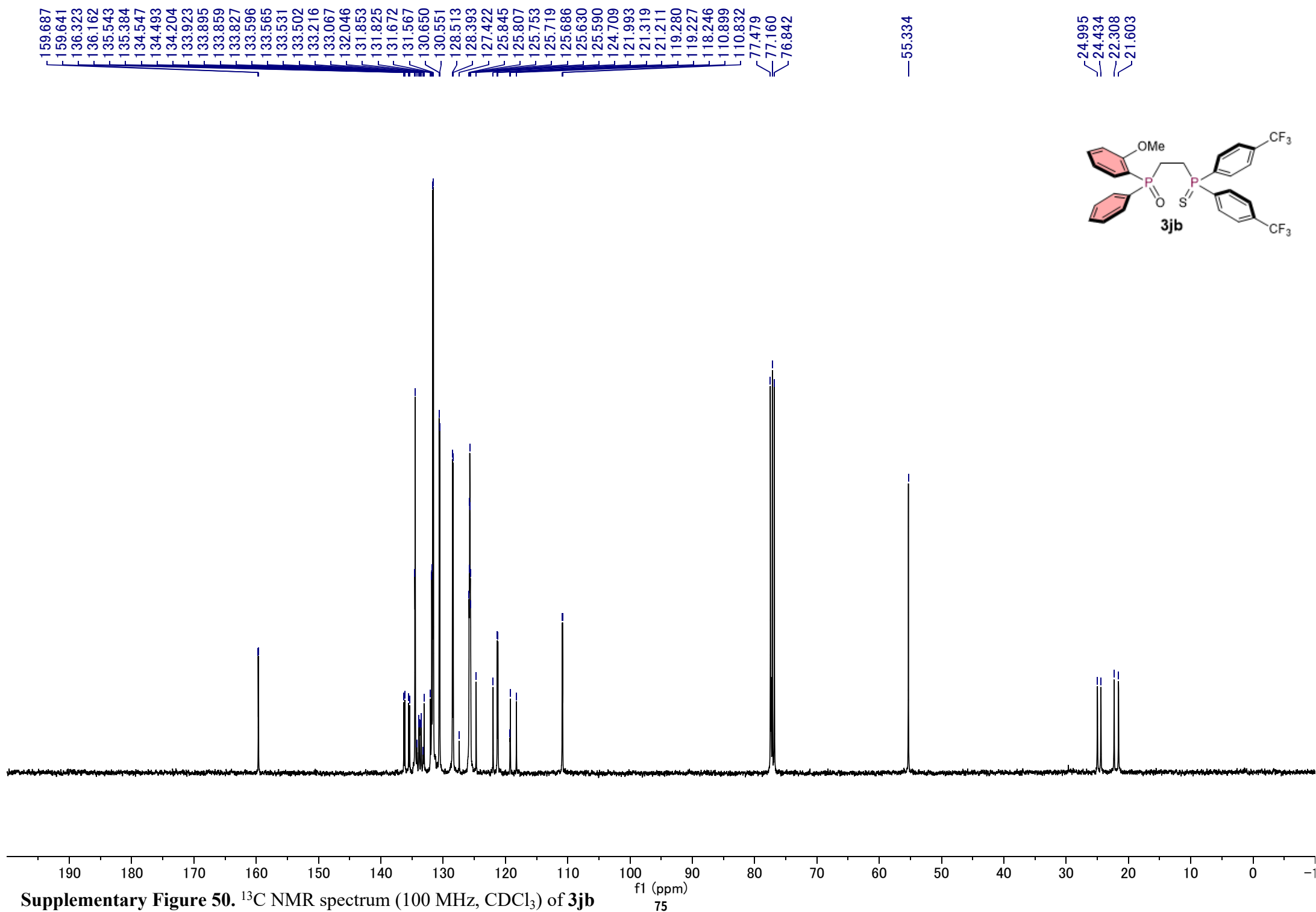
CDCl₃, 400 MHz



Supplementary Figure 49. ¹H NMR spectrum (400 MHz, CDCl₃) of 3jb

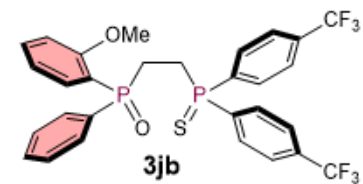
f1 (ppm)
74

CDCl₃, 100 MHz



CDCl₃, 376 MHz

-63.105



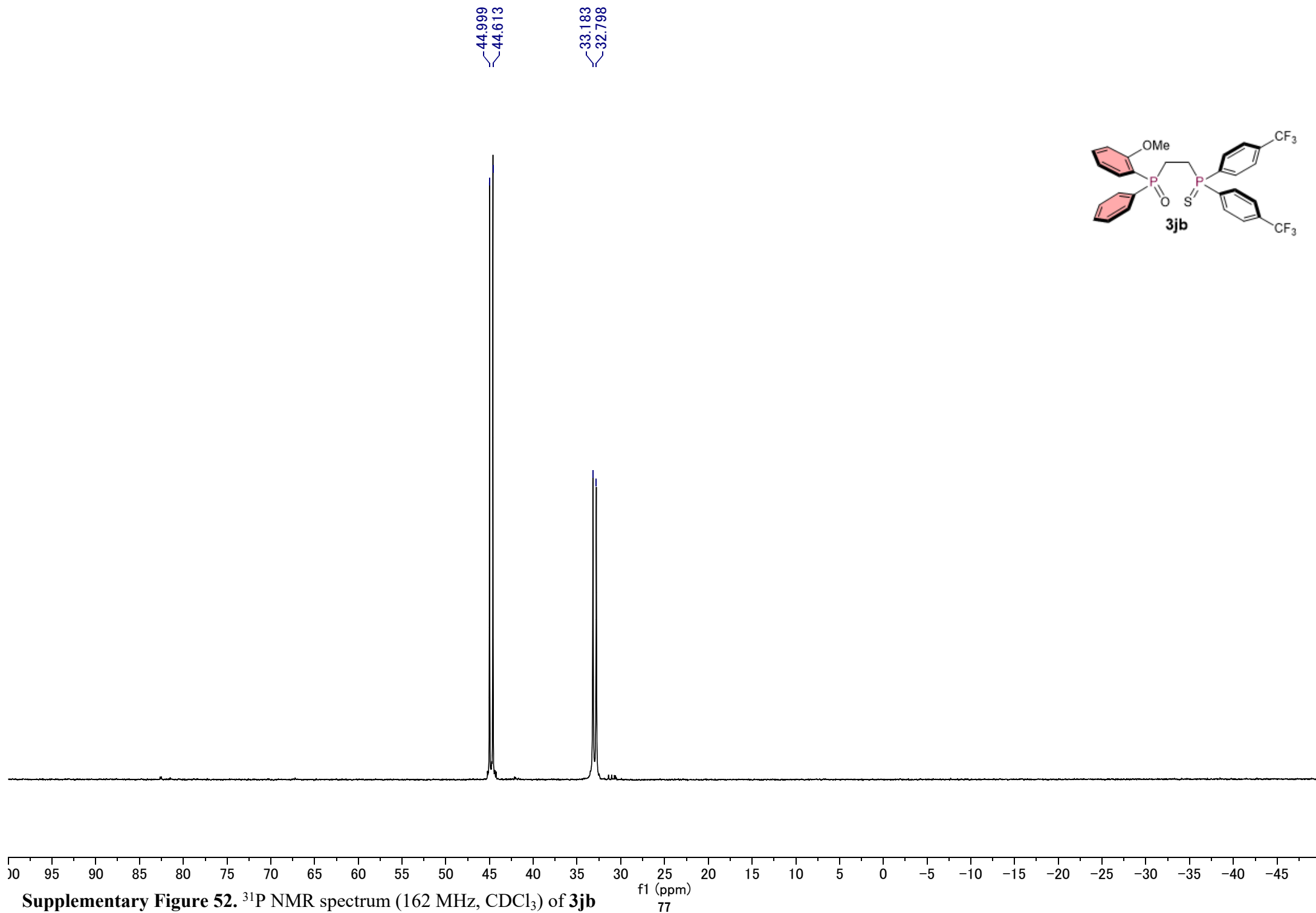
30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

f1 (ppm)

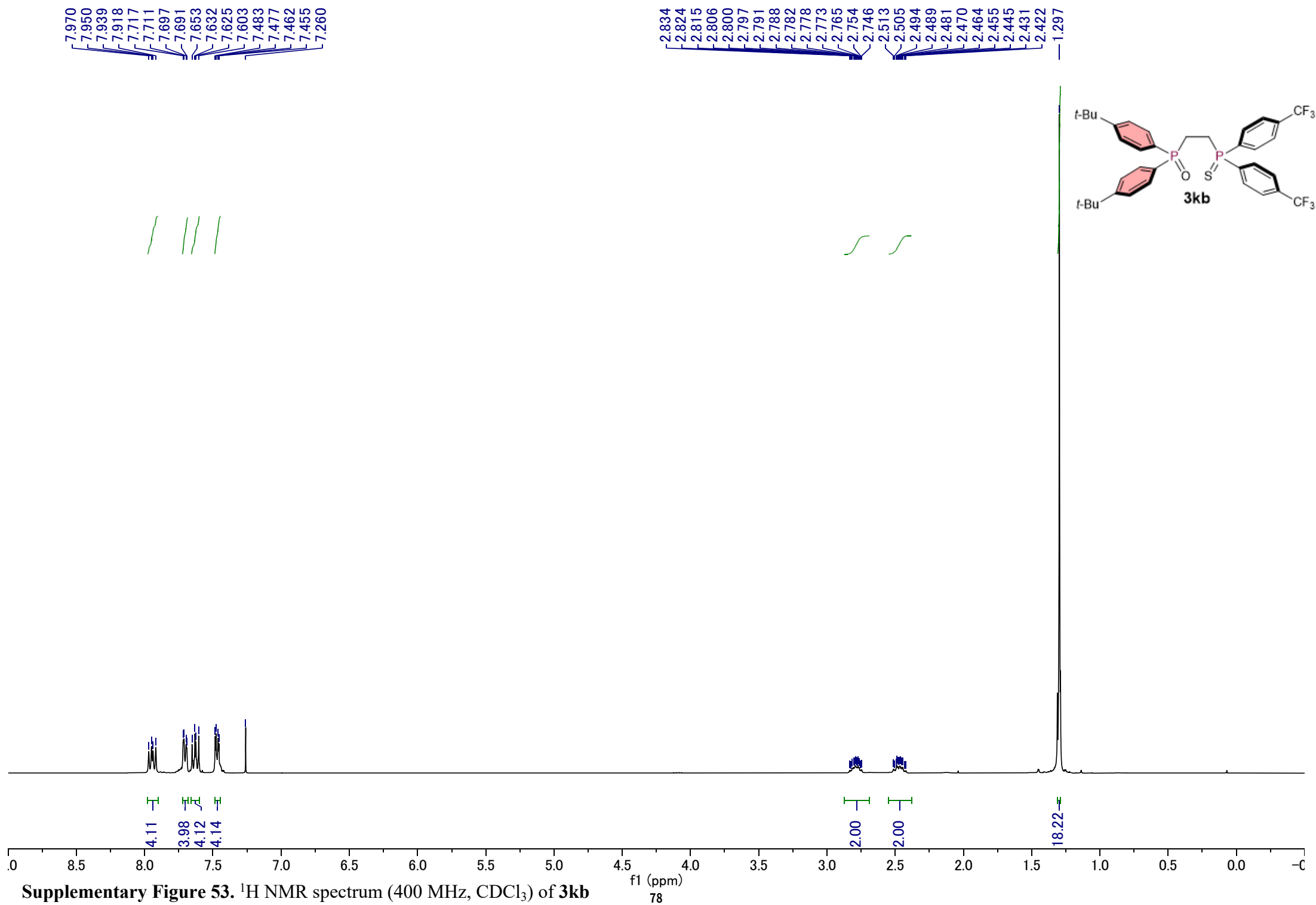
76

Supplementary Figure 51. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3jb**

CDCl₃, 162 MHz

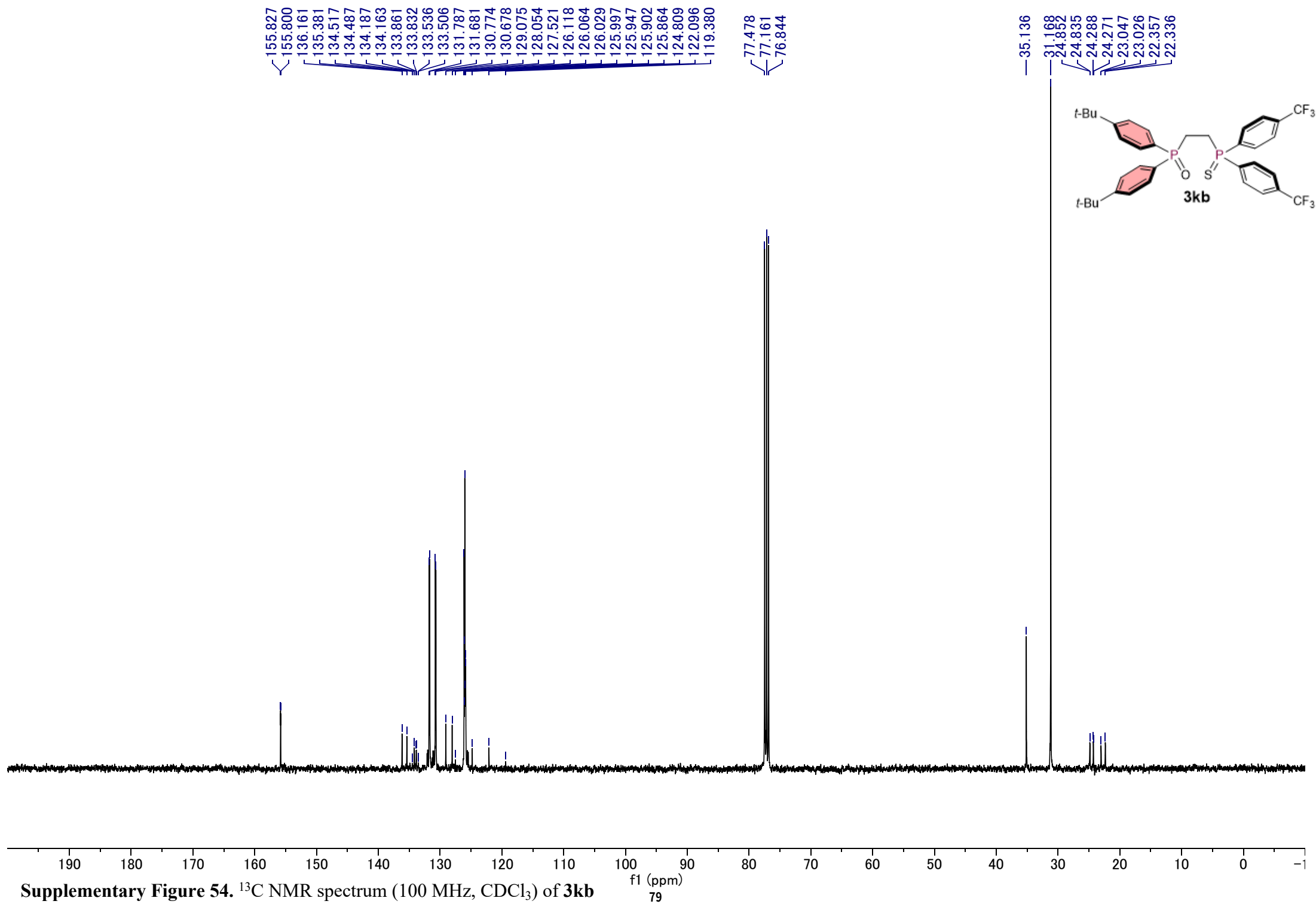


CDCl₃, 400 MHz

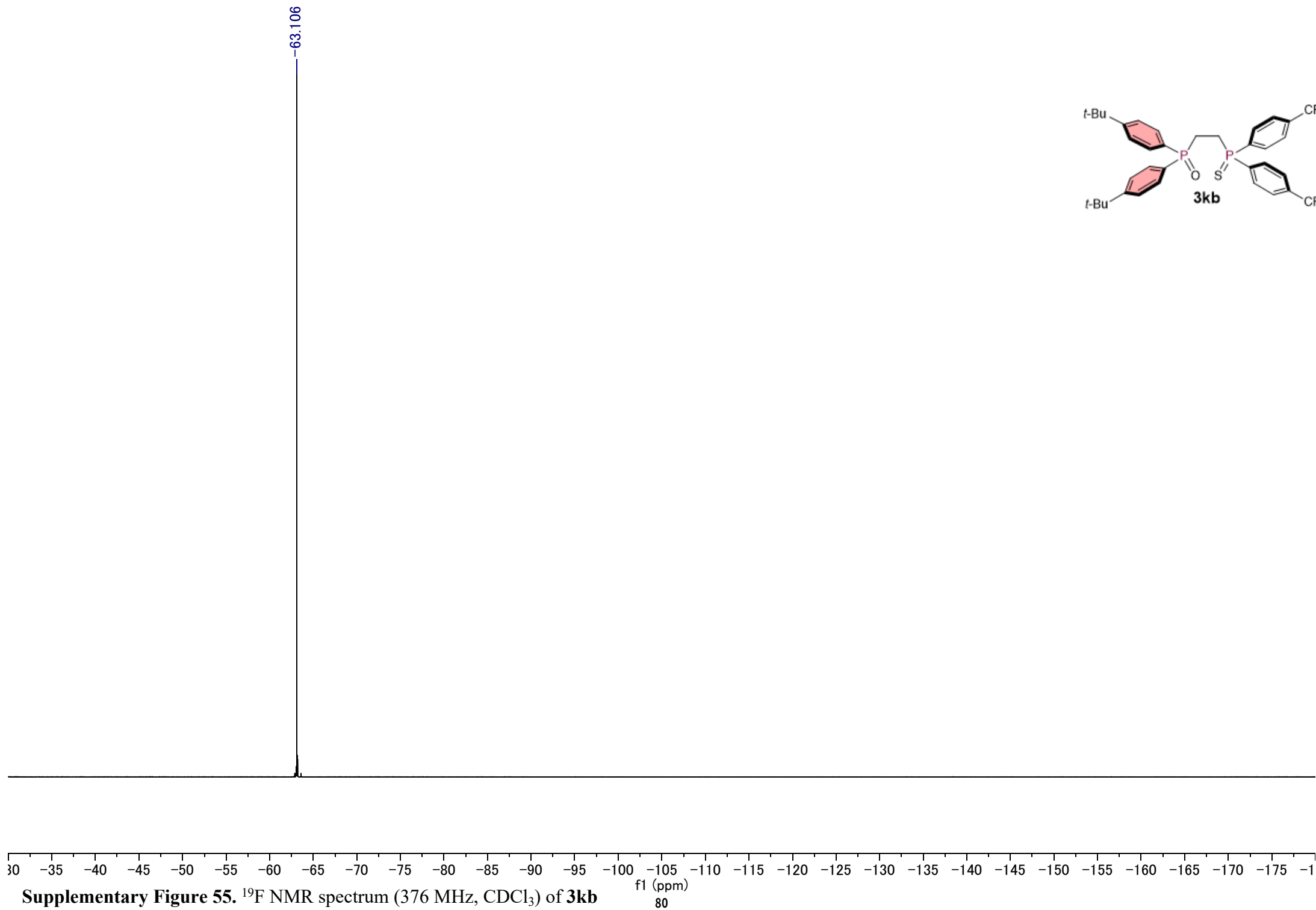


Supplementary Figure 53. ¹H NMR spectrum (400 MHz, CDCl₃) of **3kb**

CDCl₃, 100 MHz

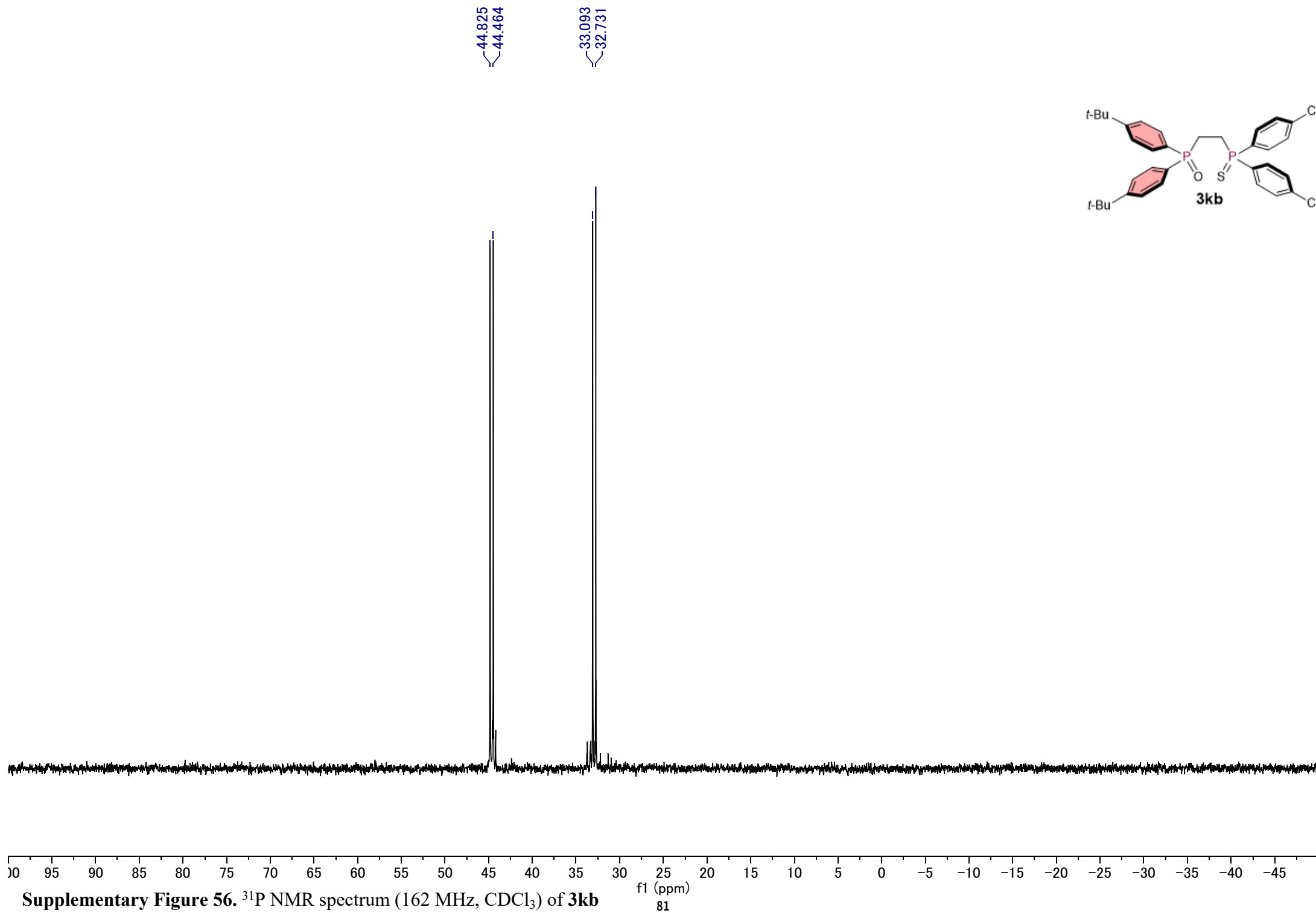


CDCl₃, 376 MHz

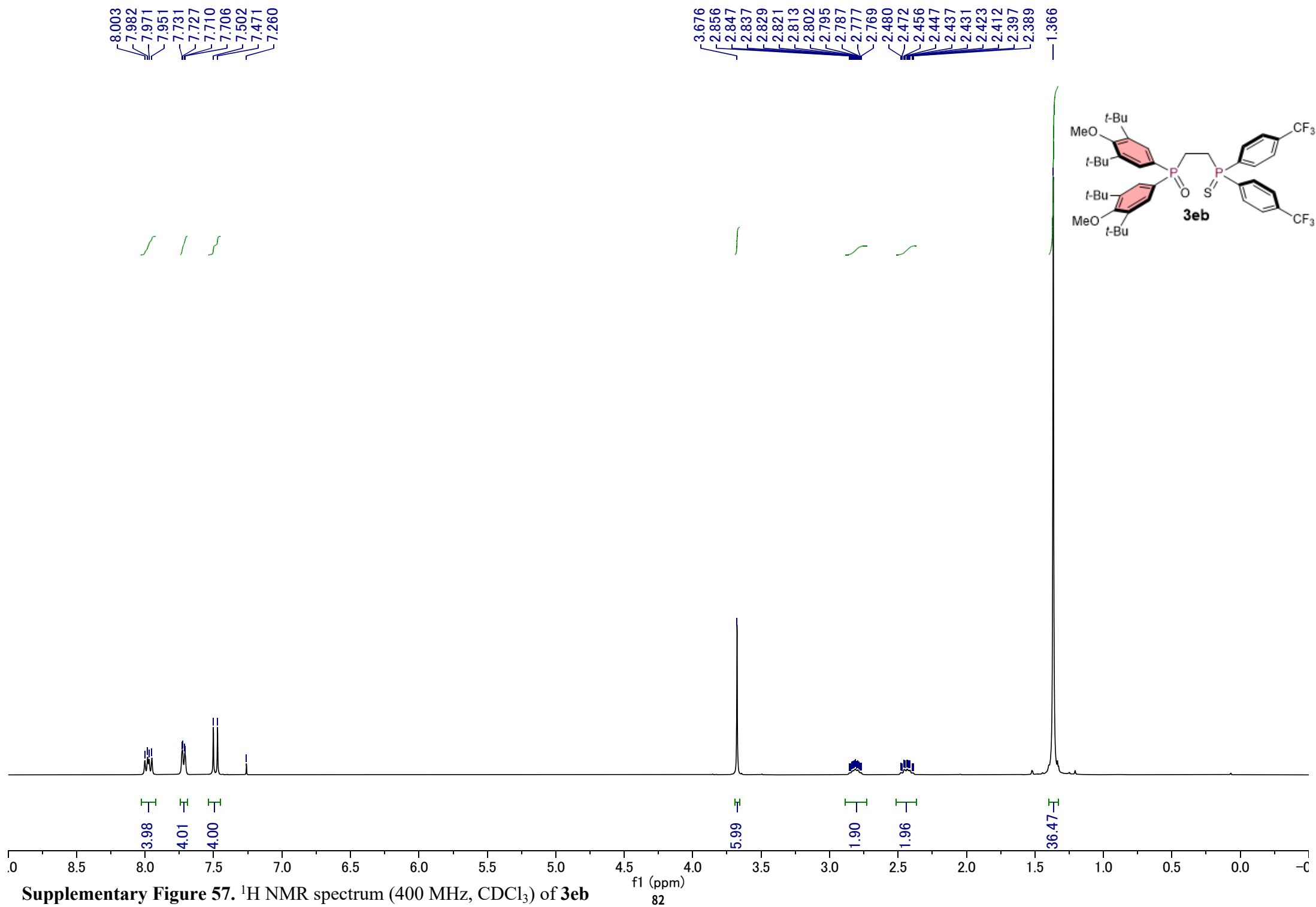


Supplementary Figure 55. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3kb**

CDCl₃, 162 MHz

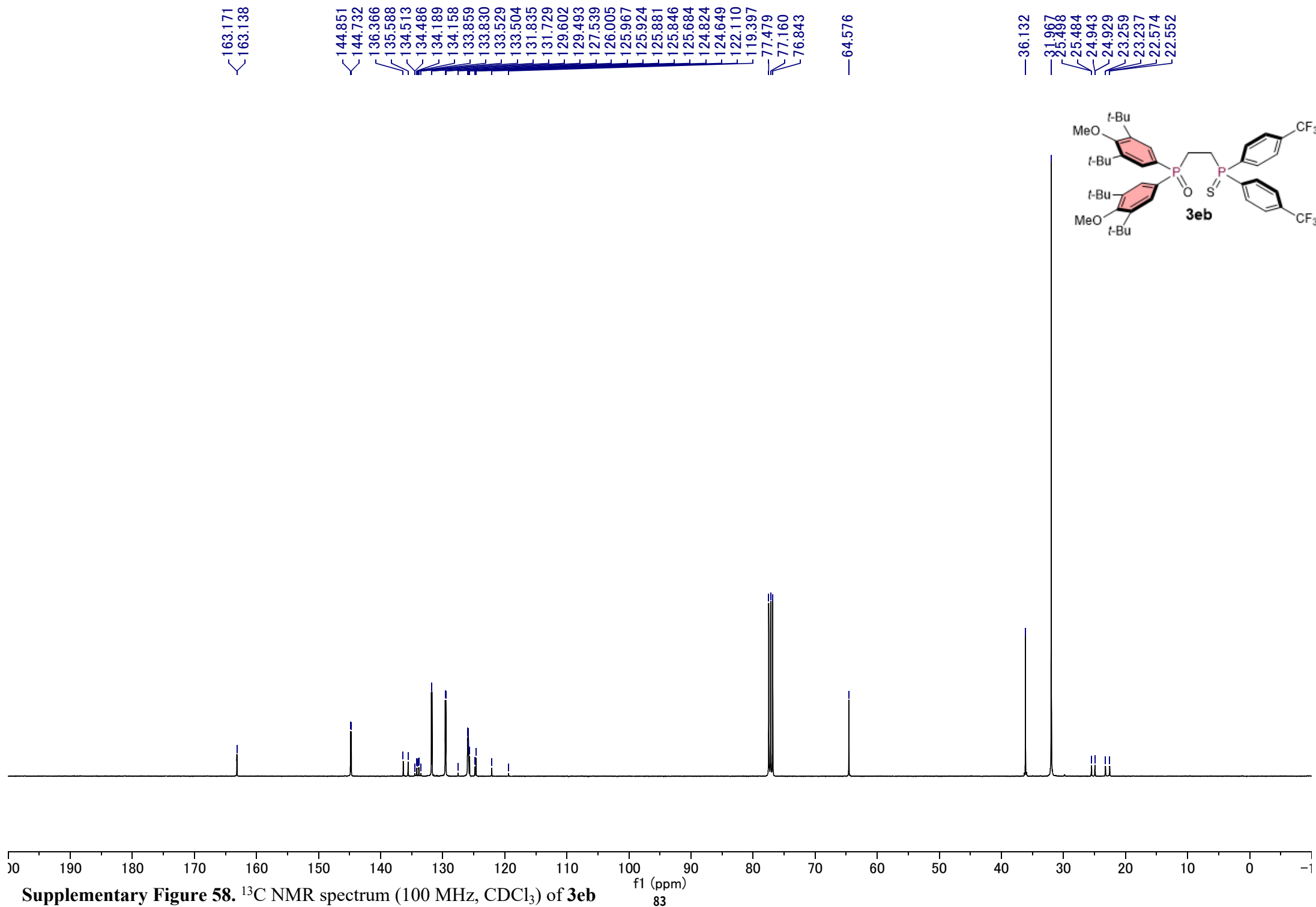


CDCl₃, 400 MHz

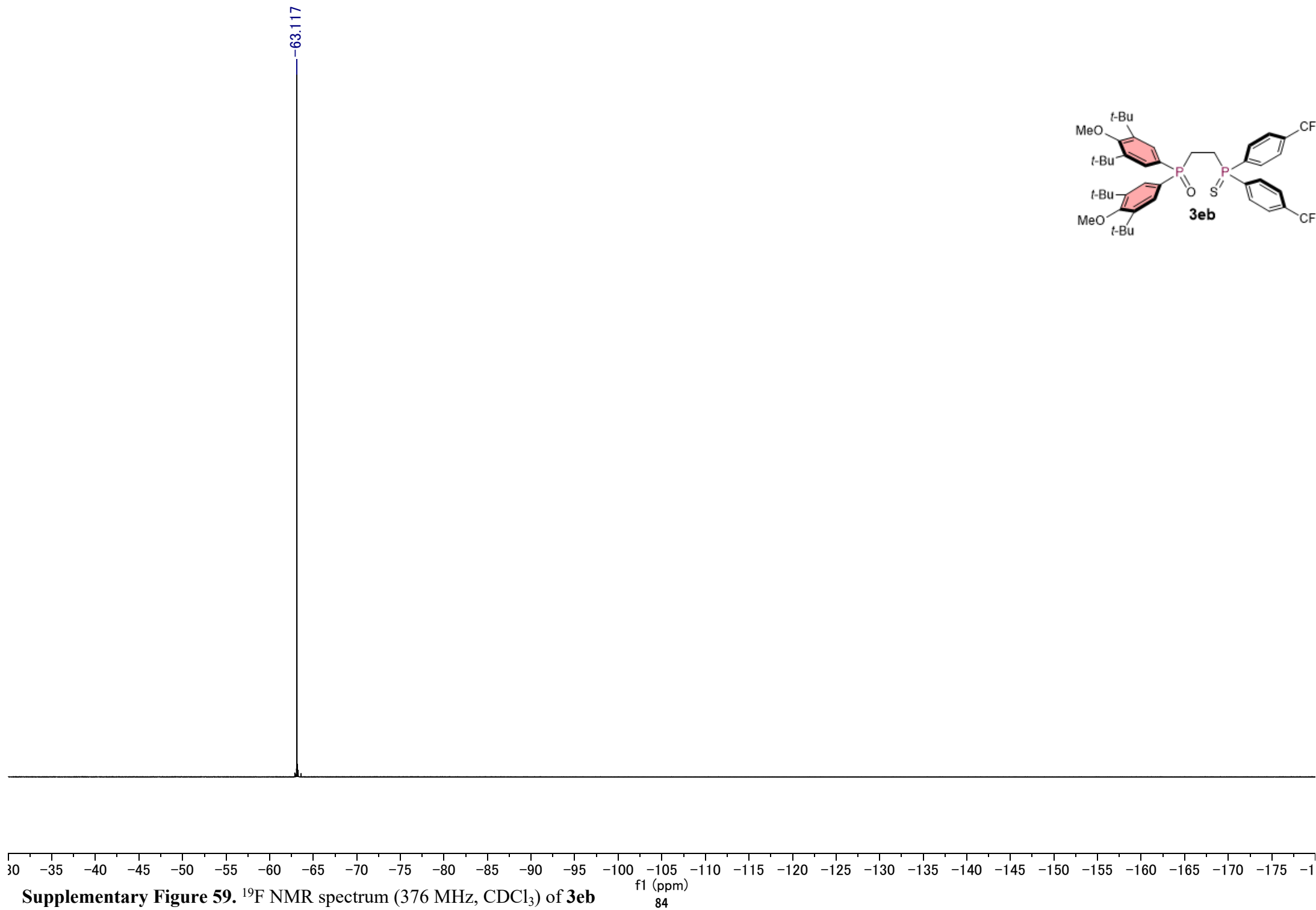


Supplementary Figure 57. ¹H NMR spectrum (400 MHz, CDCl₃) of **3eb**

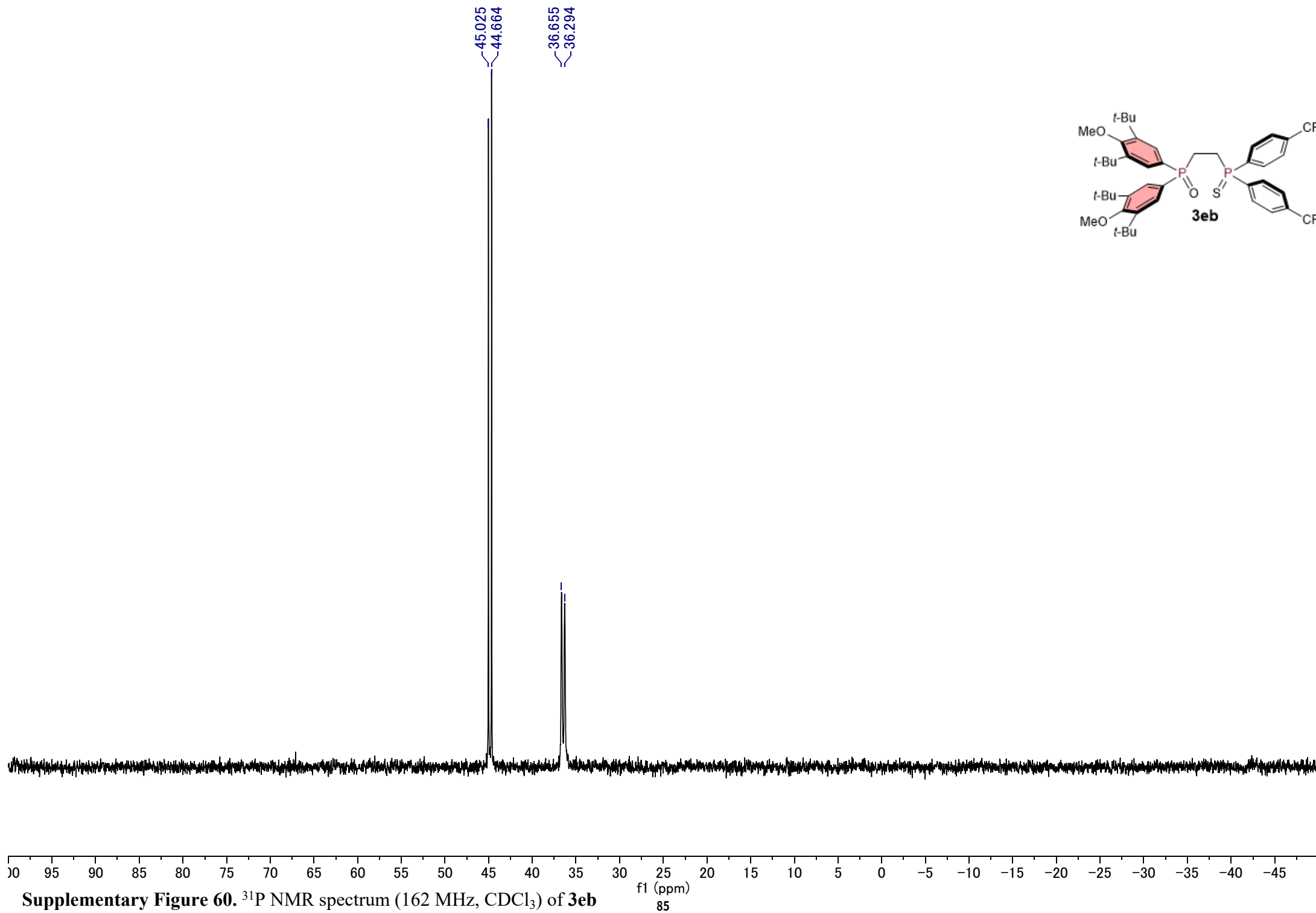
CDCl₃, 100 MHz



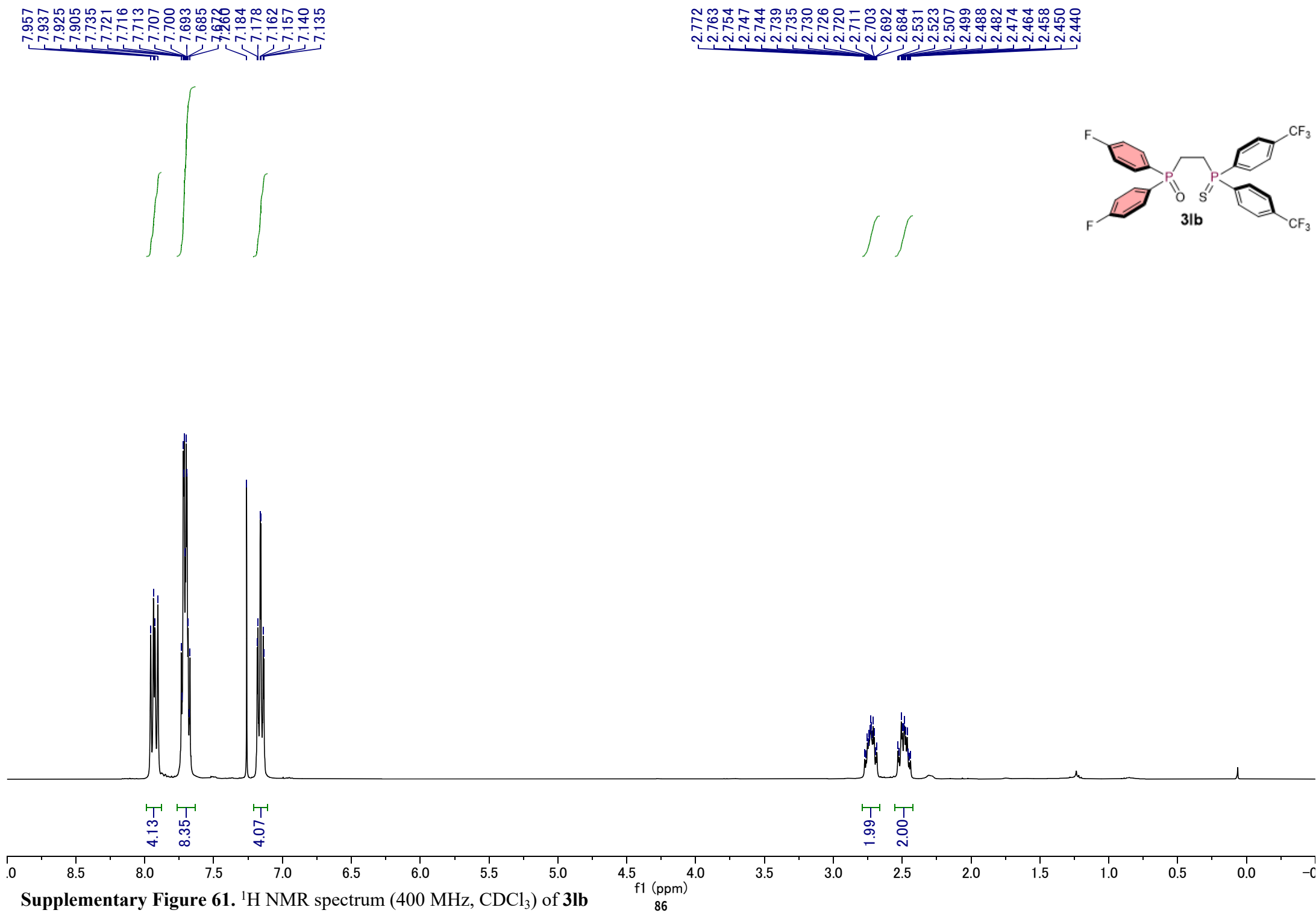
CDCl₃, 376 MHz



CDCl₃, 162 MHz



CDCl₃, 400 MHz

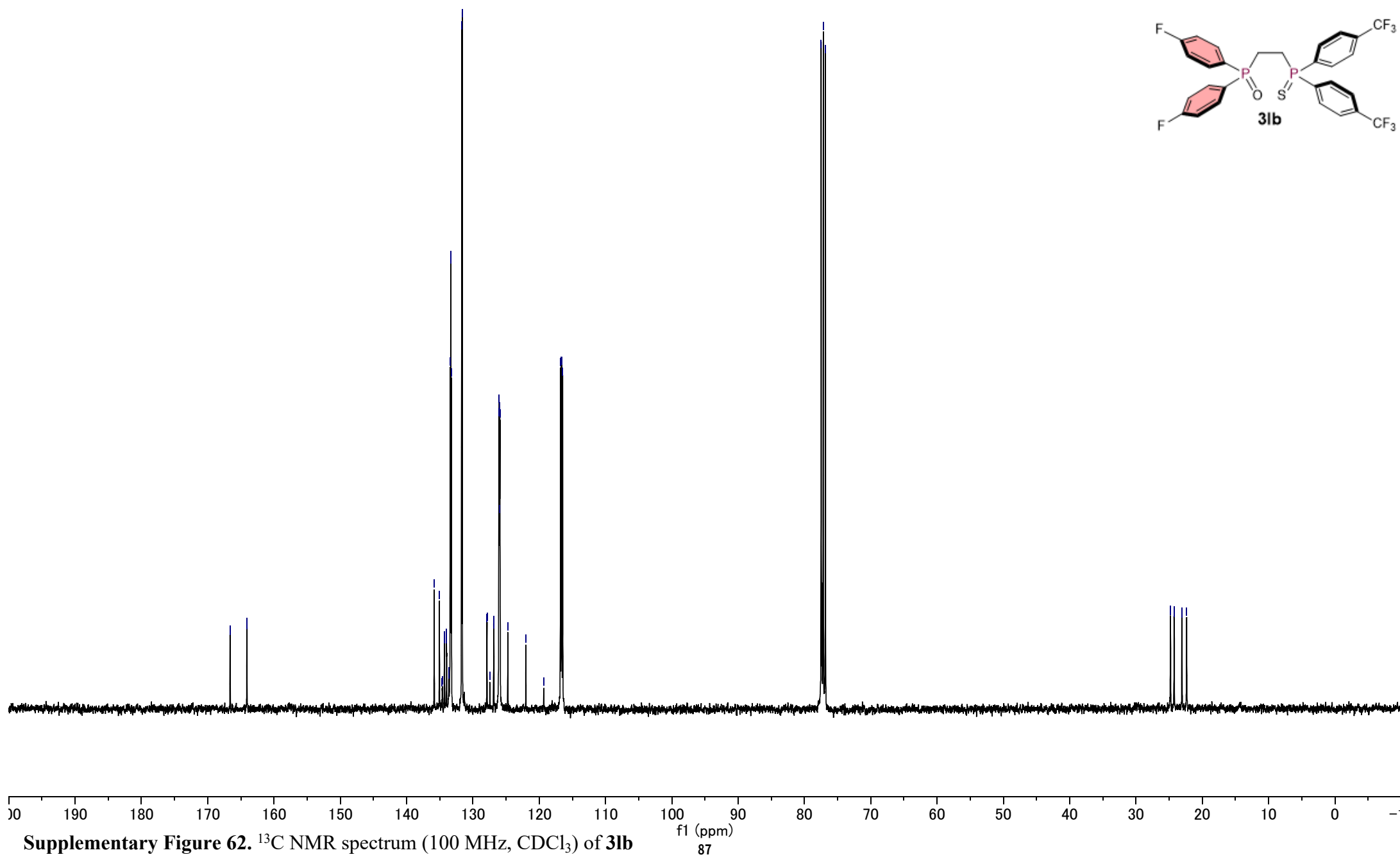
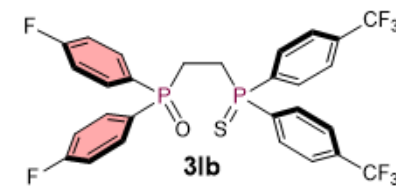


CDCl₃, 100 MHz

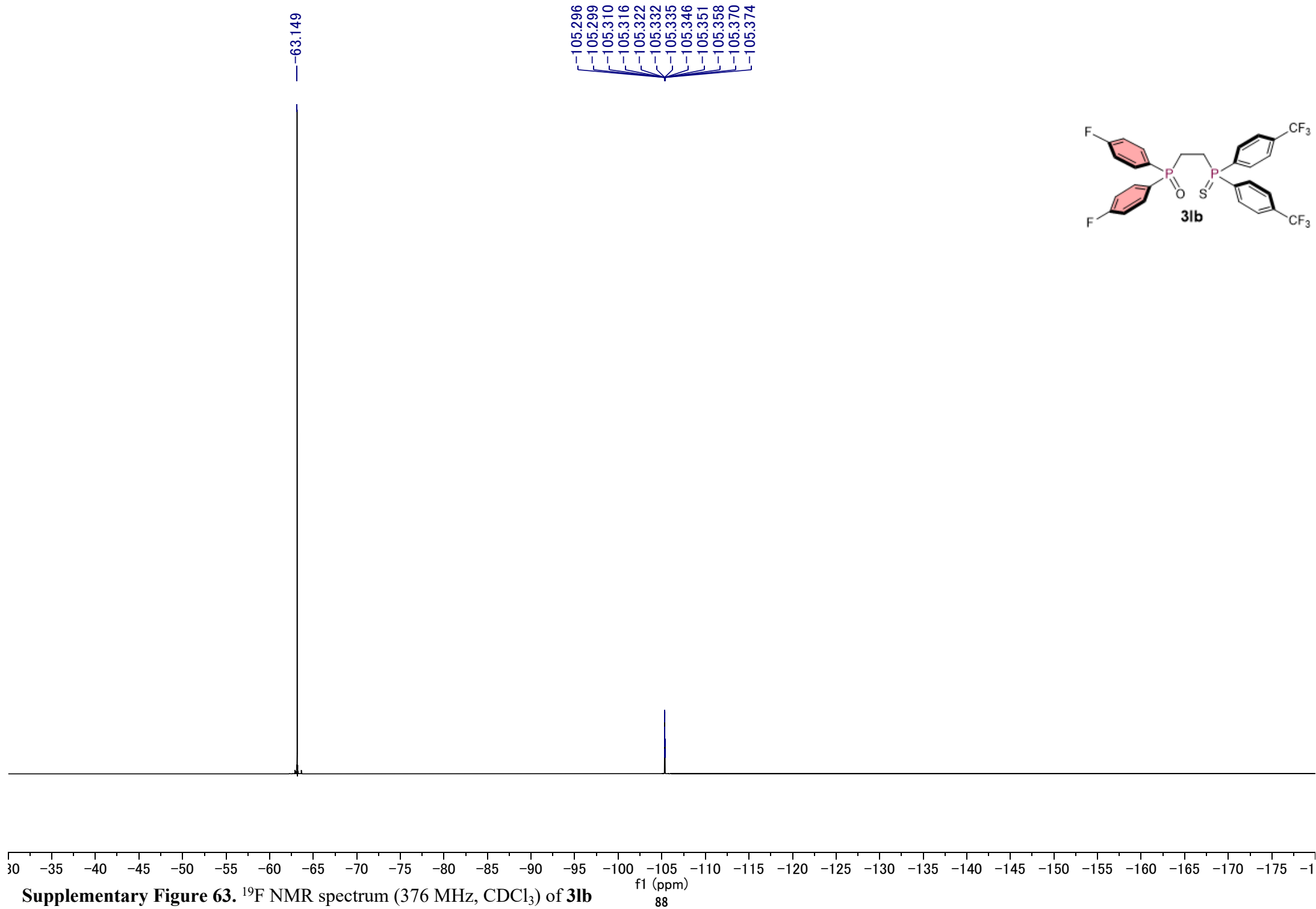
166.627
166.594
164.096
164.063

135.840
135.056
134.638
134.608
134.311
134.279
133.982
133.952
133.654
133.624
133.438
133.348
133.328
133.240
131.706
131.599
127.904
127.868
127.450
126.873
126.837
126.076
126.039
125.997
125.953
125.916
124.733
122.019
119.303
116.802
116.672
116.587
116.457
77.478
77.160
76.841

24.813
24.792
24.253
24.232
23.080
23.063
22.377
22.360

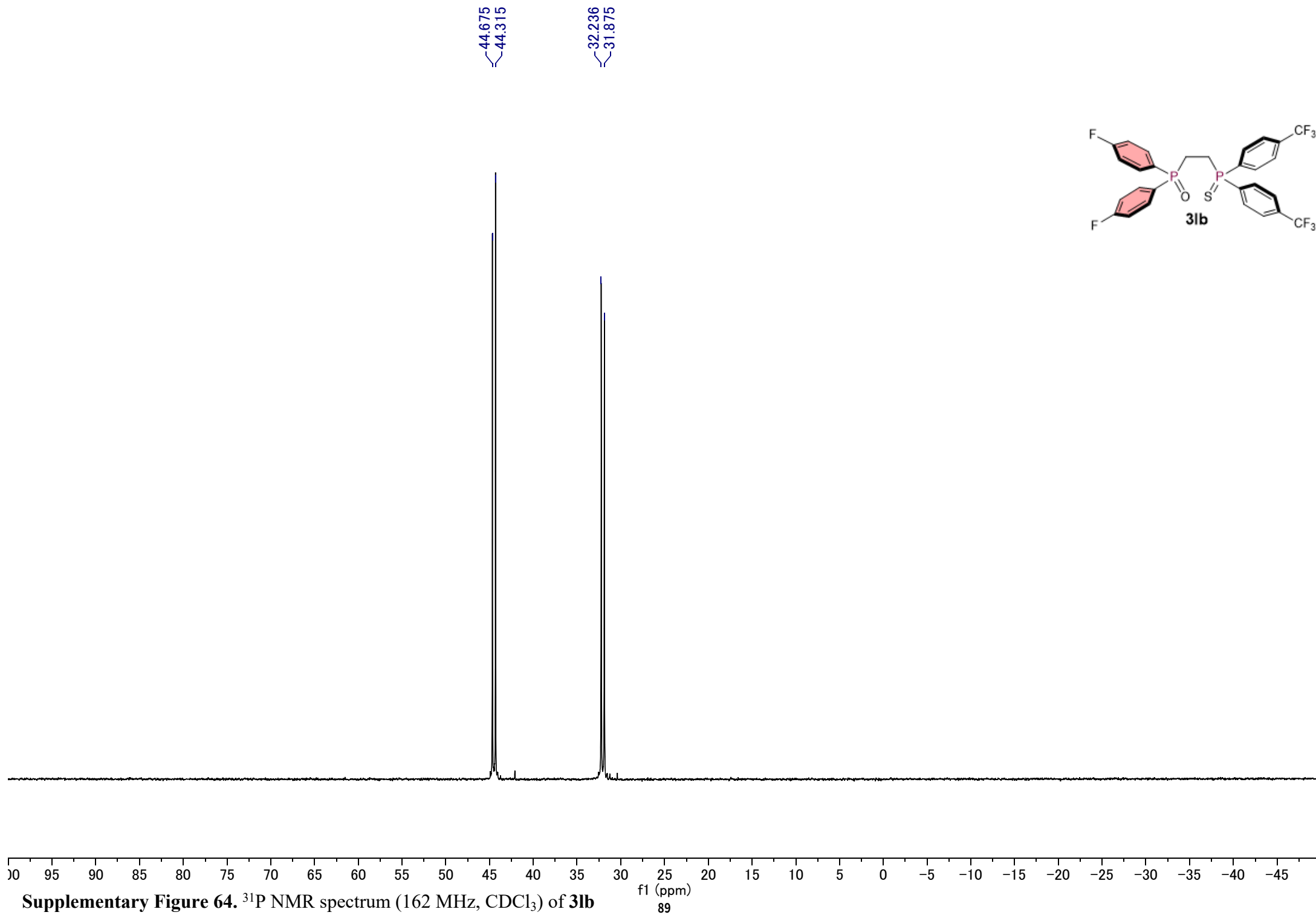


CDCl₃, 376 MHz



Supplementary Figure 63. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3lb**

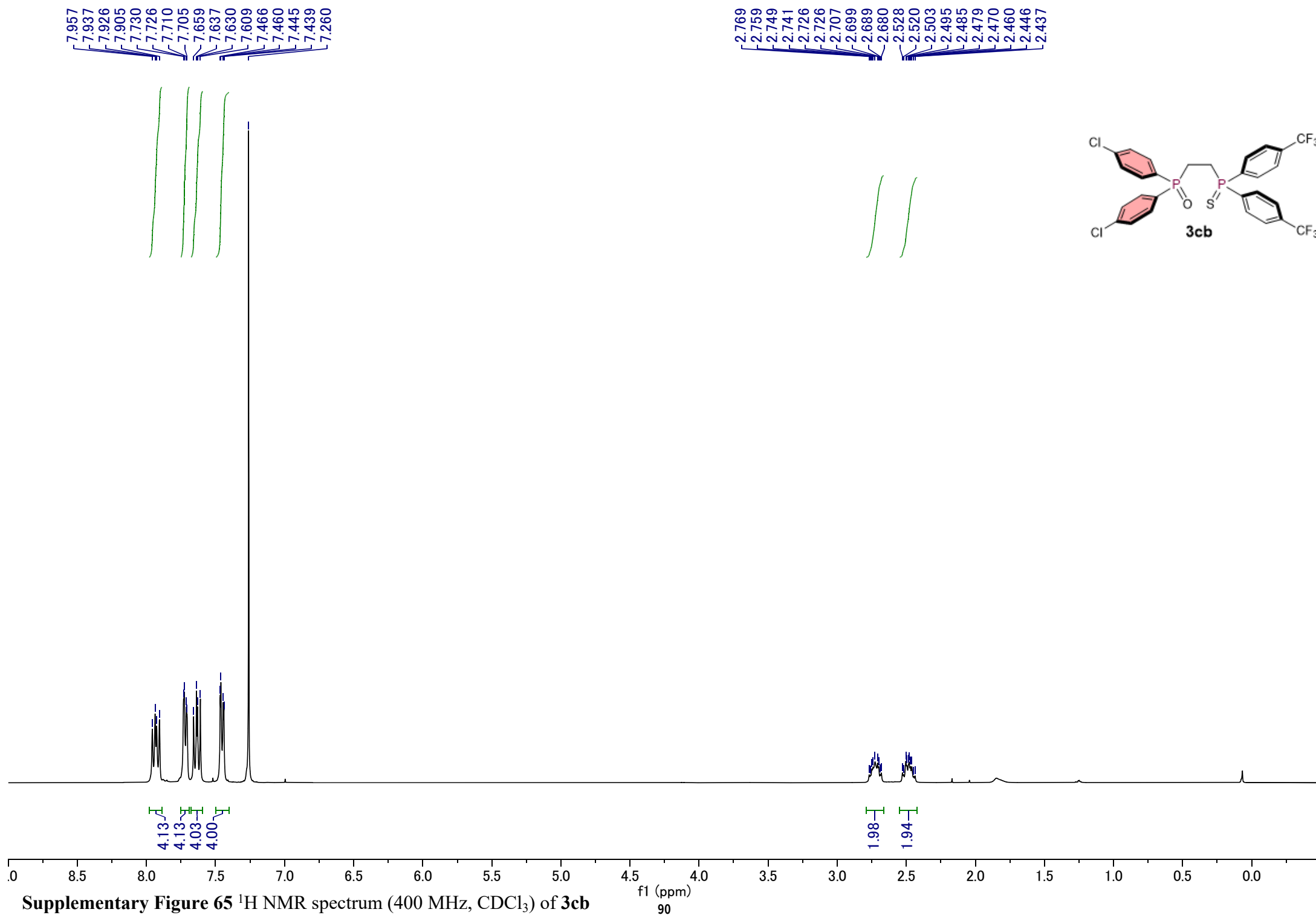
CDCl₃, 162 MHz



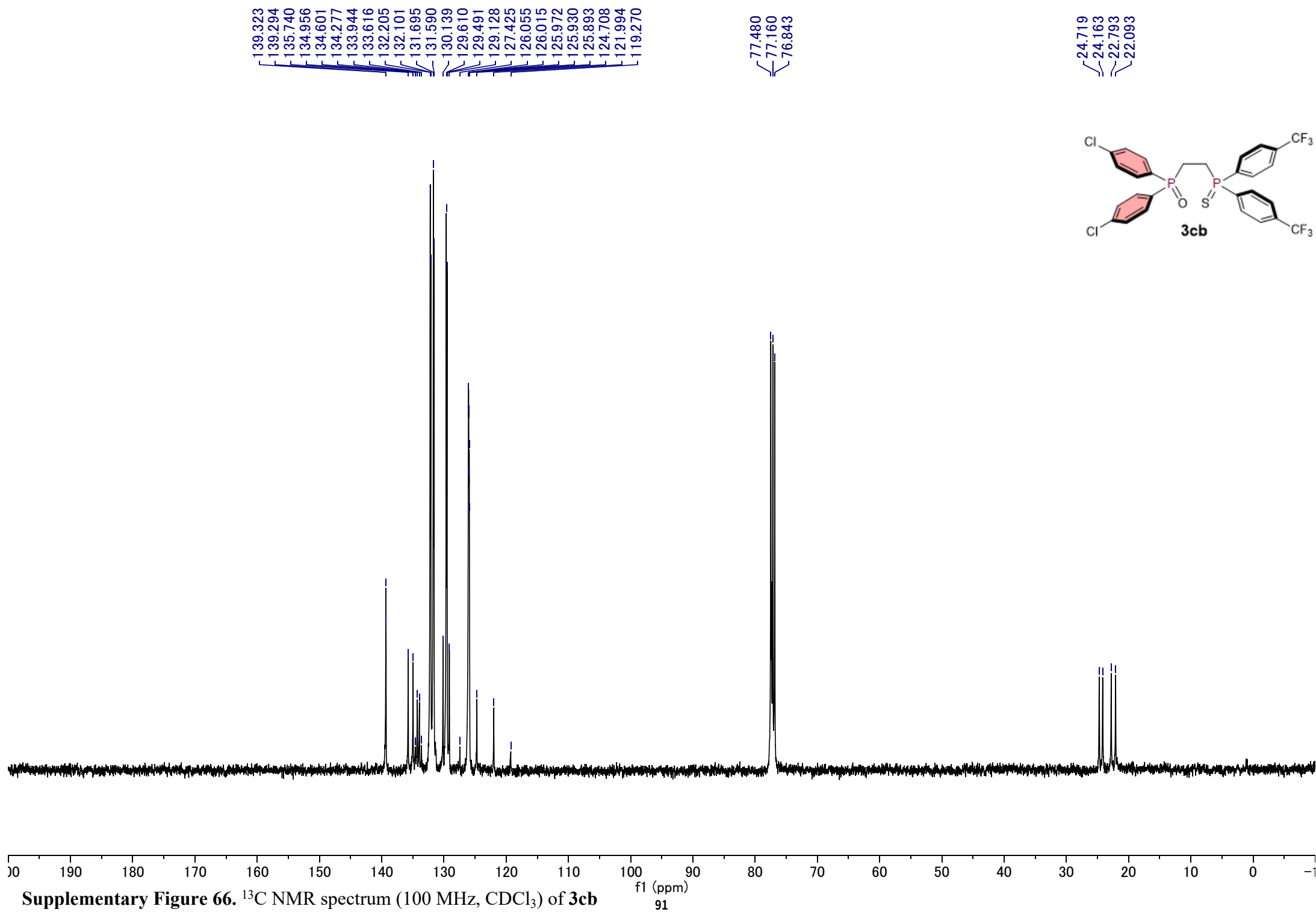
Supplementary Figure 64. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3lb**

f1 (ppm)
89

CDCl₃, 400 MHz



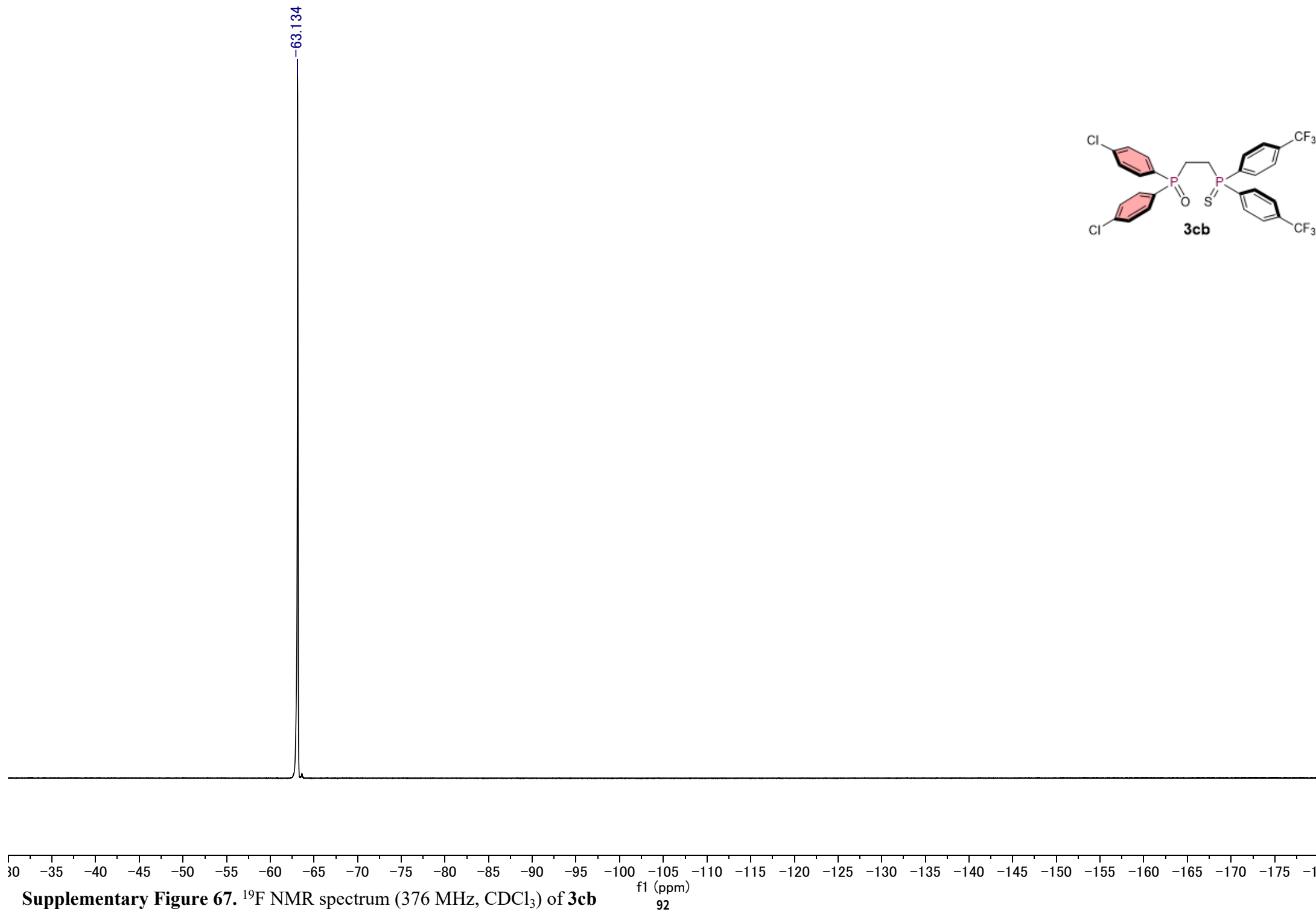
CDCl₃, 100 MHz



Supplementary Figure 66. ¹³C NMR spectrum (100 MHz, CDCl₃) of **3cb**

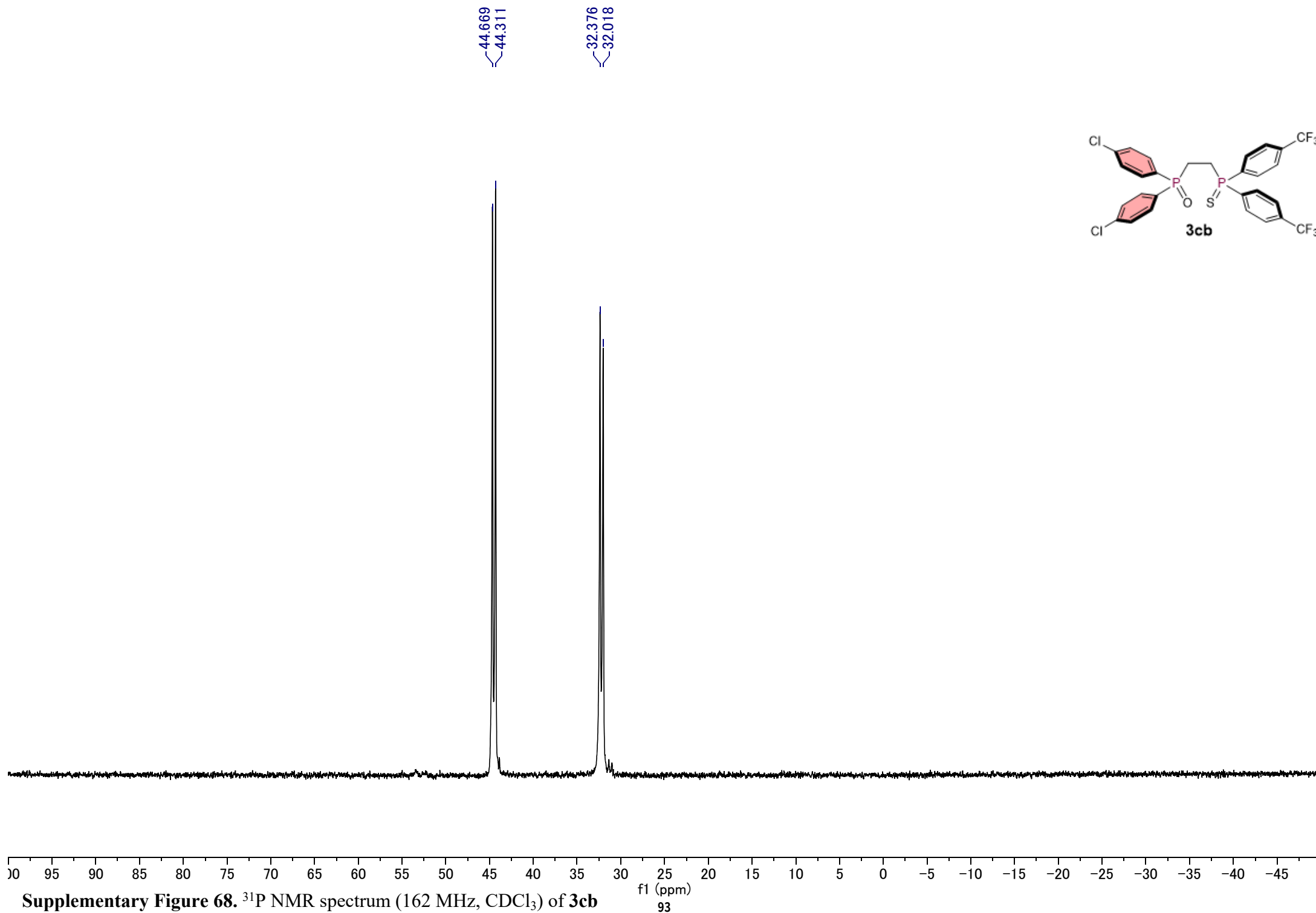
f1 (ppm)
91

CDCl₃, 376 MHz



Supplementary Figure 67. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3cb**

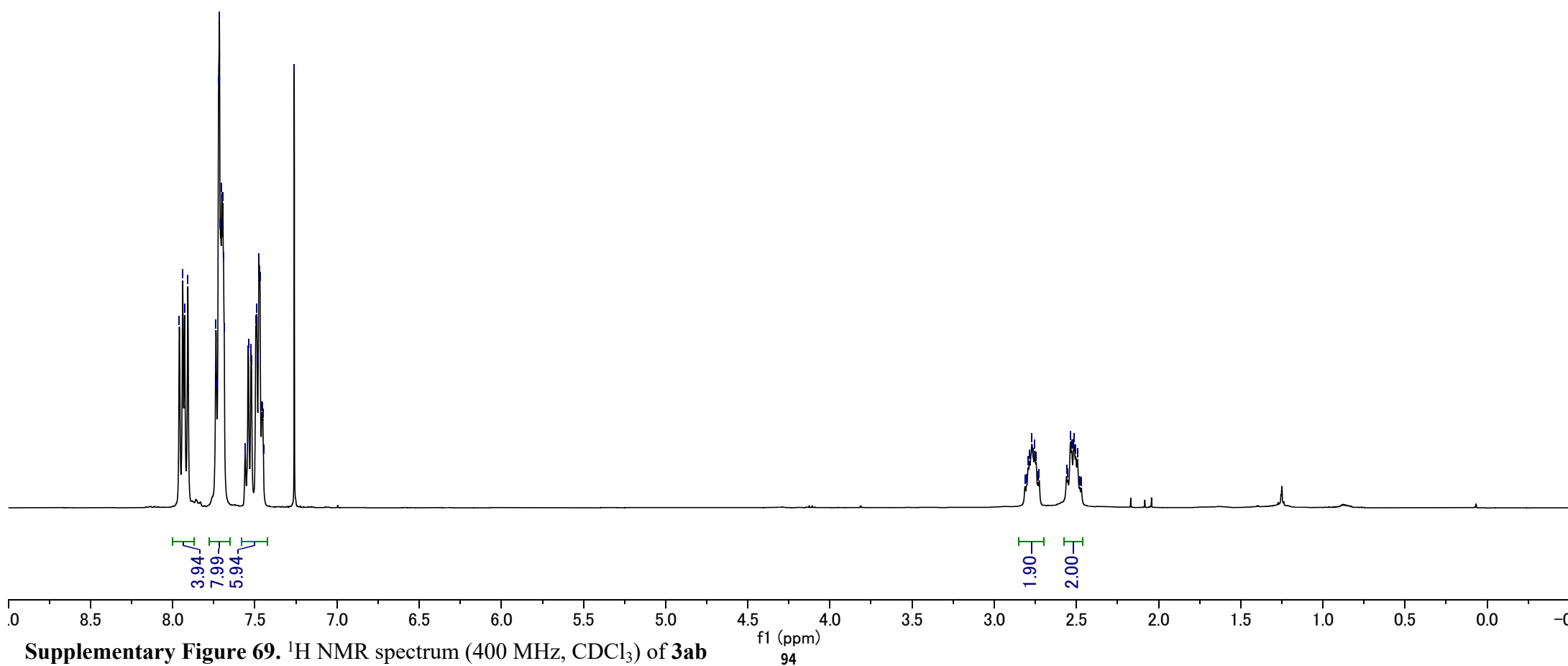
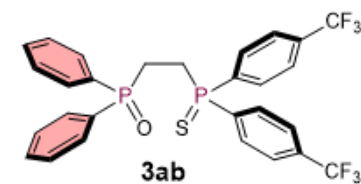
CDCl₃, 162 MHz



CDCl₃, 400 MHz

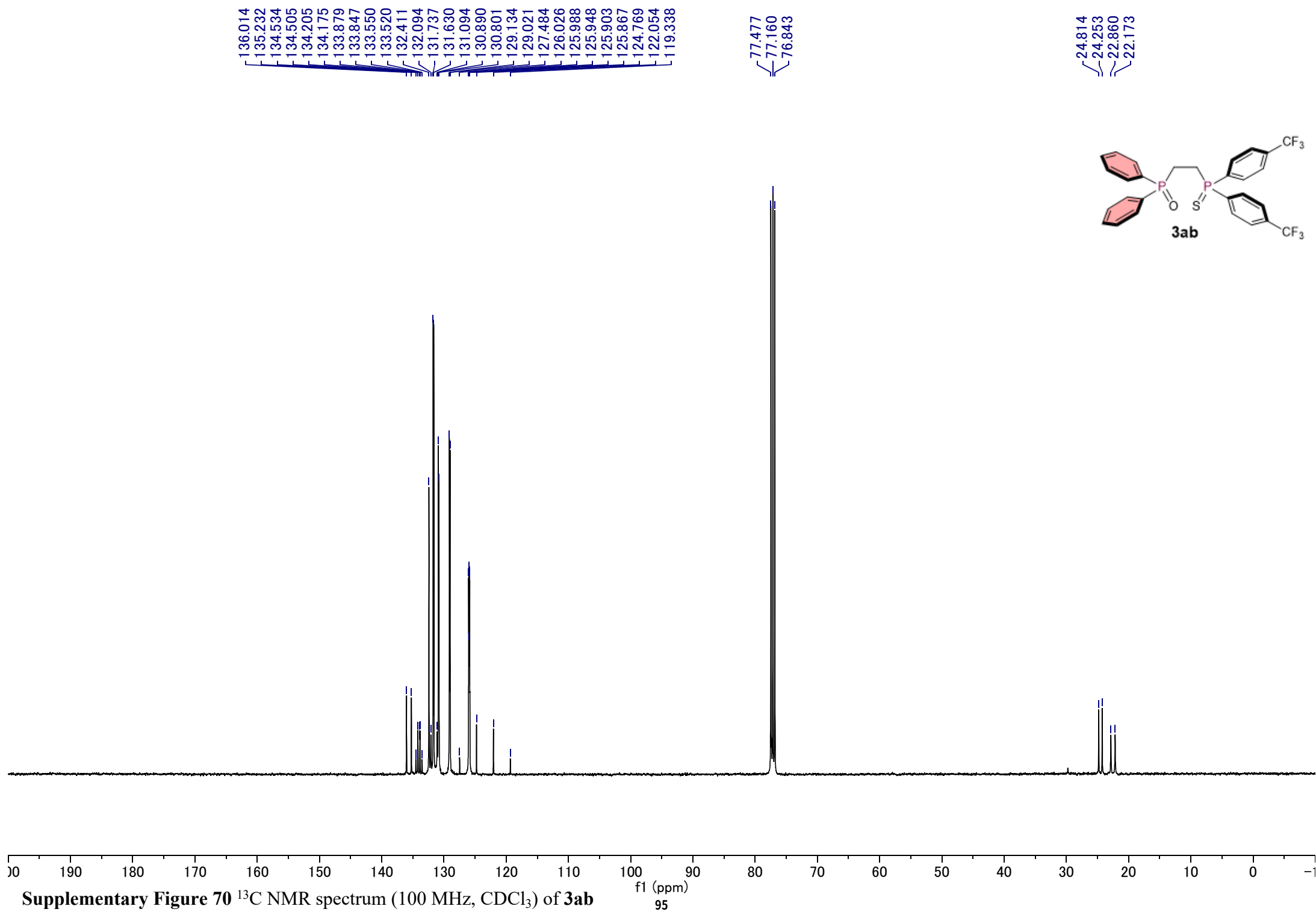
7.959
7.939
7.928
7.908
7.740
7.736
7.732
7.721
7.716
7.710
7.707
7.702
7.695
7.690
7.686
7.561
7.557
7.542
7.539
7.534
7.524
7.520
7.495
7.488
7.480
7.476
7.472
7.469
7.458
7.454
7.451
7.447
7.260

2.814
2.805
2.795
2.786
2.772
2.761
2.753
2.745
2.734
2.726
2.561
2.553
2.537
2.528
2.518
2.512
2.504
2.494
2.479
2.470



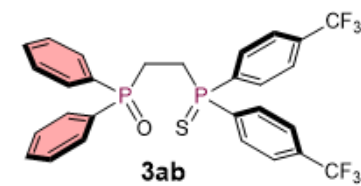
Supplementary Figure 69. ¹H NMR spectrum (400 MHz, CDCl₃) of **3ab**

CDCl₃, 100 MHz



CDCl₃, 376 MHz

-63.123

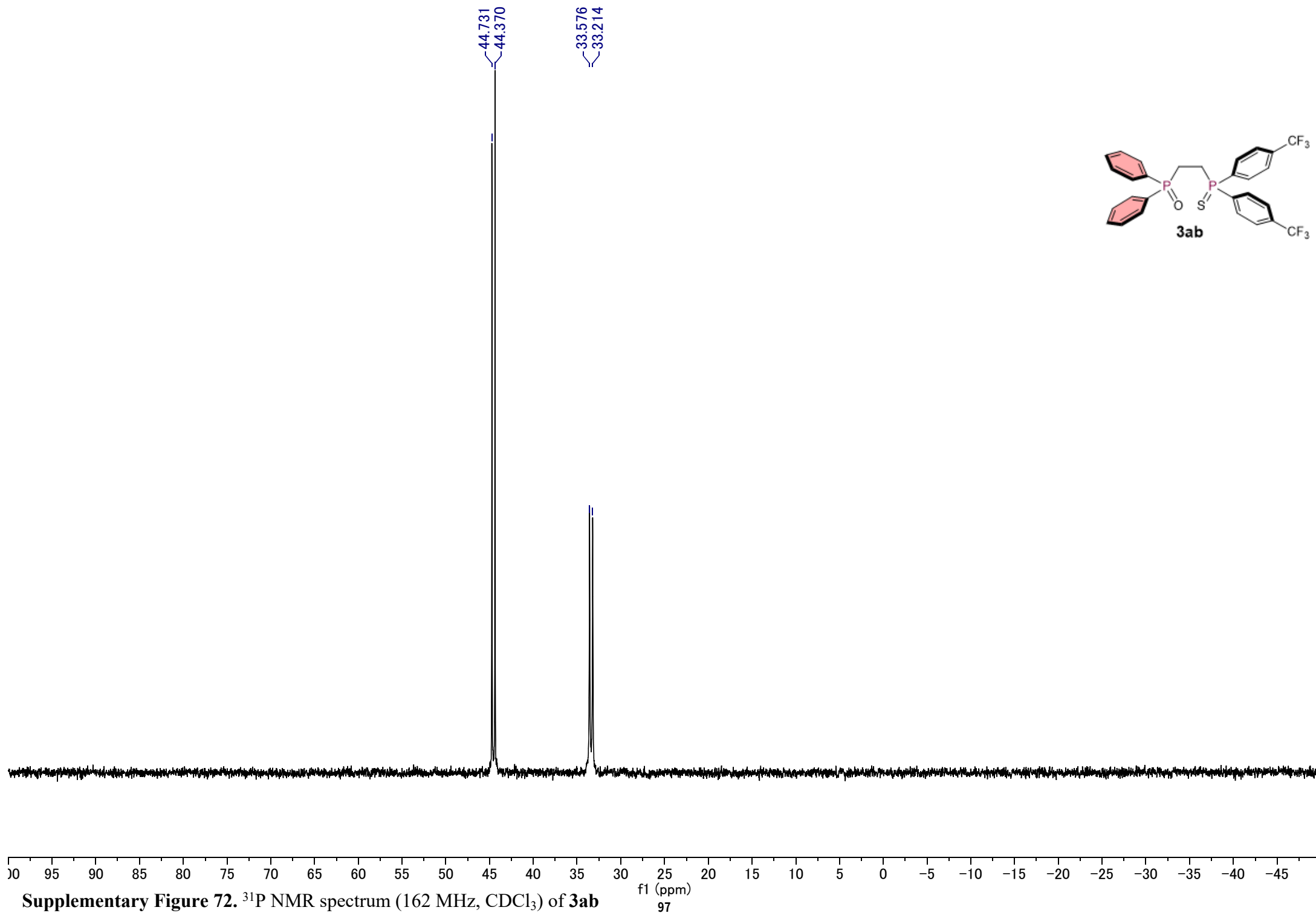


30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

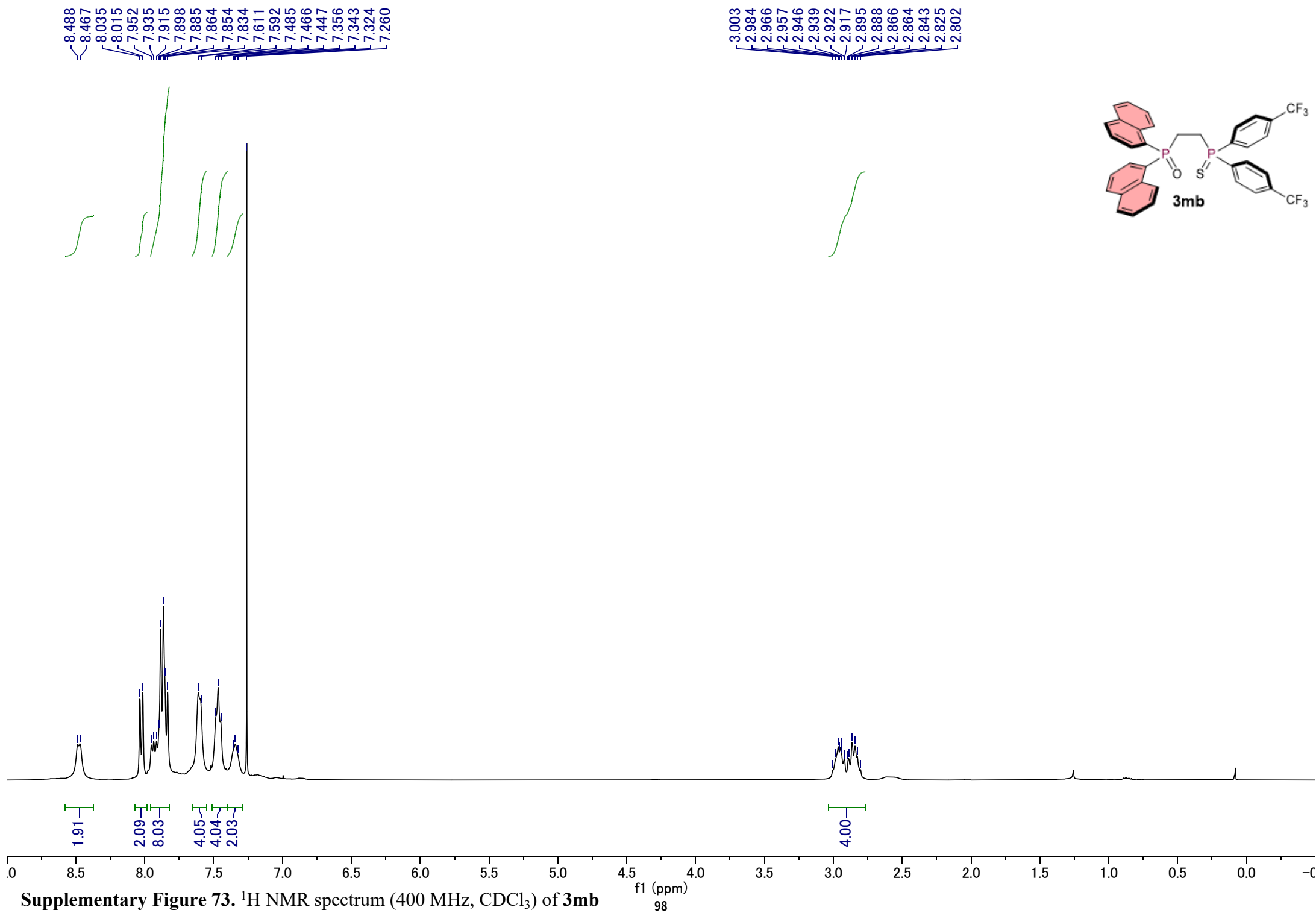
f1 (ppm)
96

Supplementary Figure 71. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3ab**

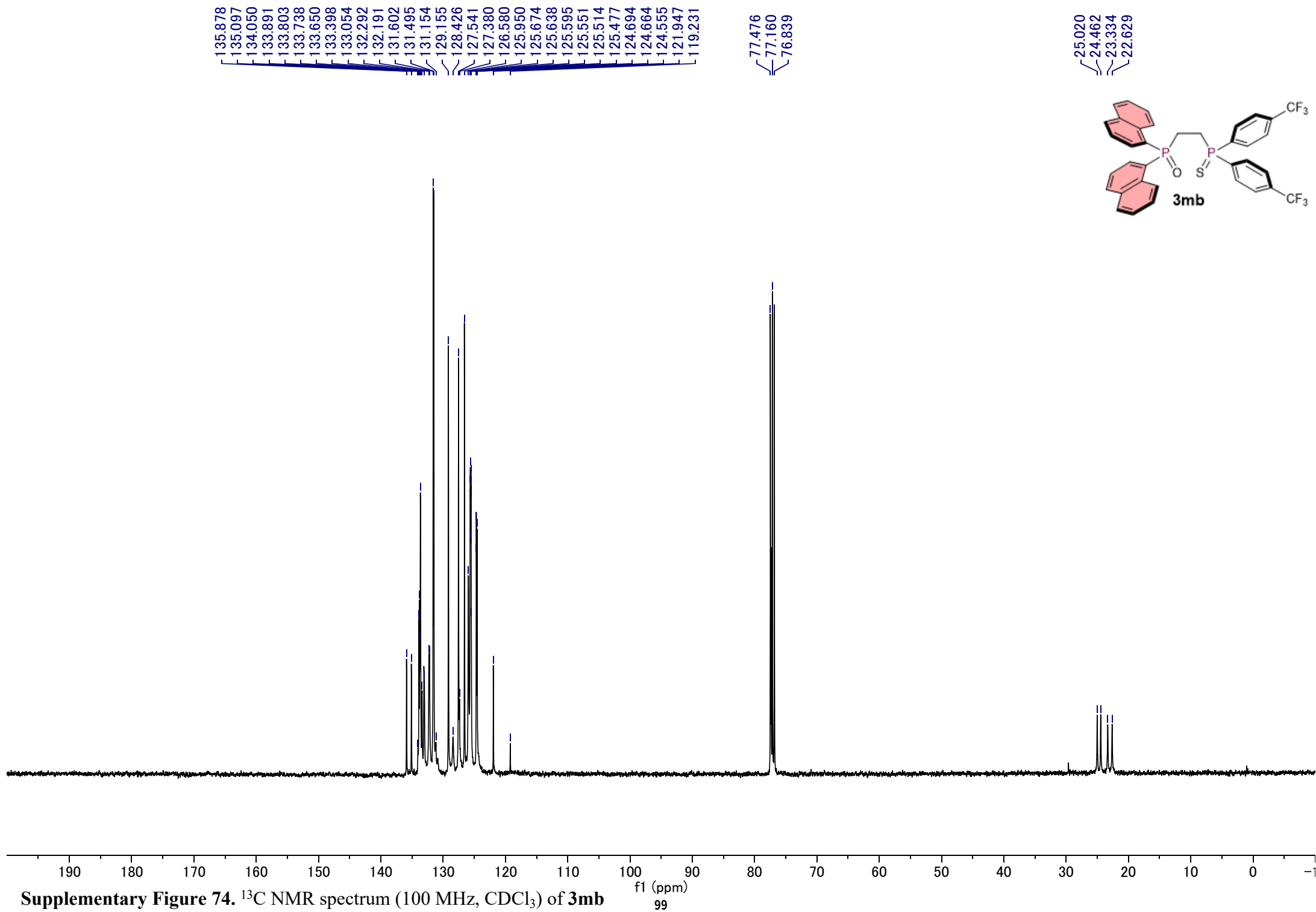
CDCl₃, 162 MHz



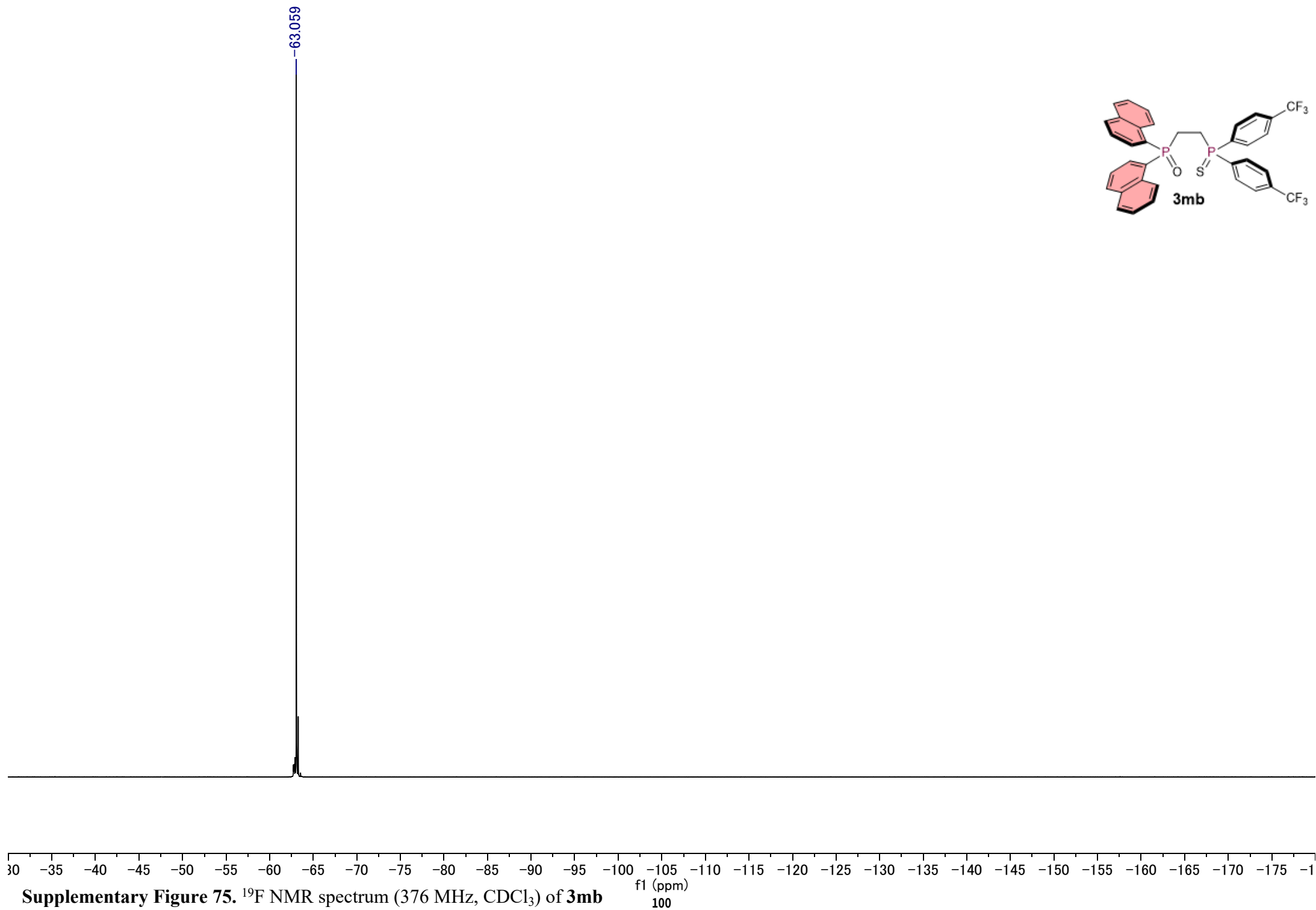
CDCl₃, 400 MHz



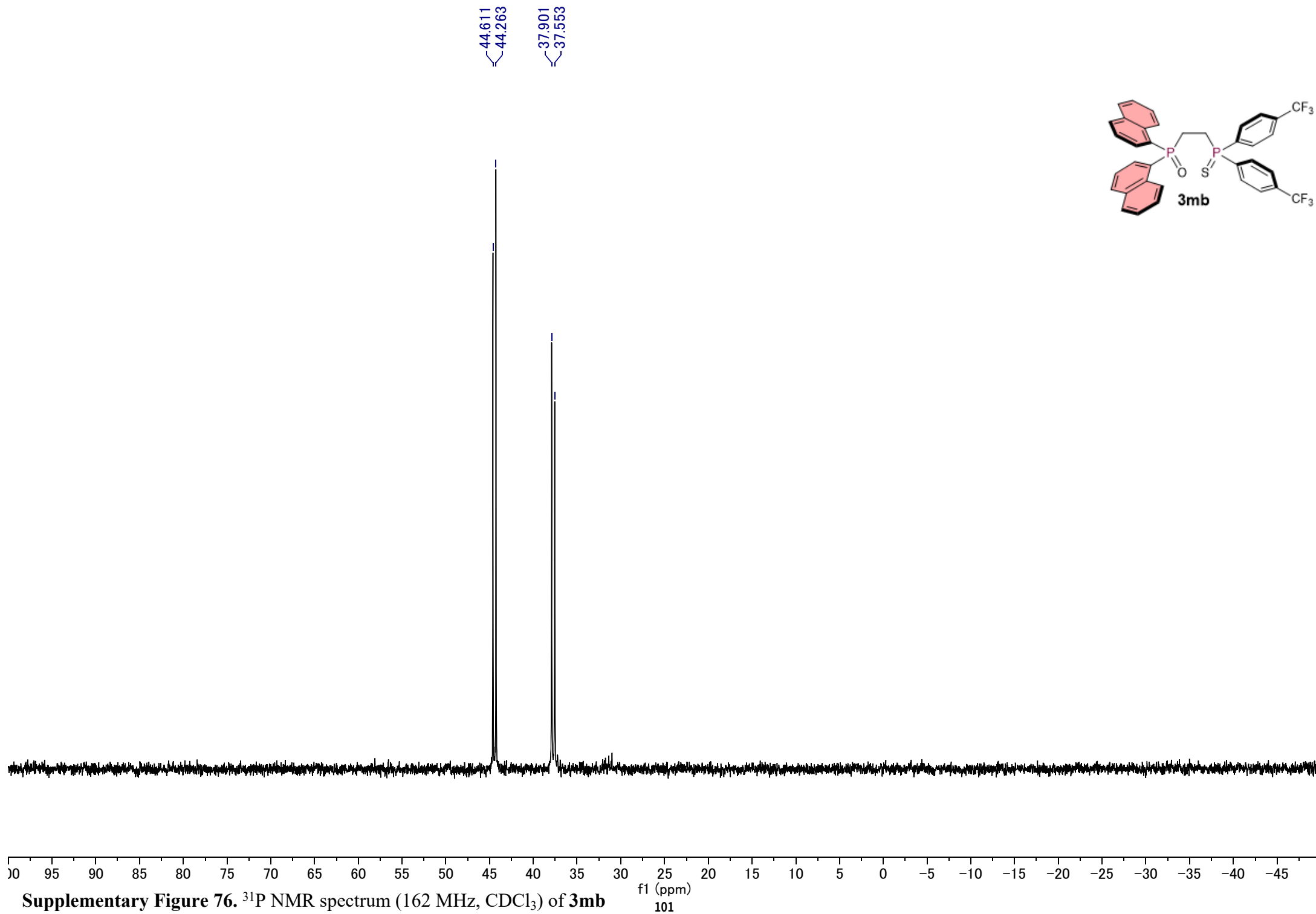
CDCl₃, 100 MHz



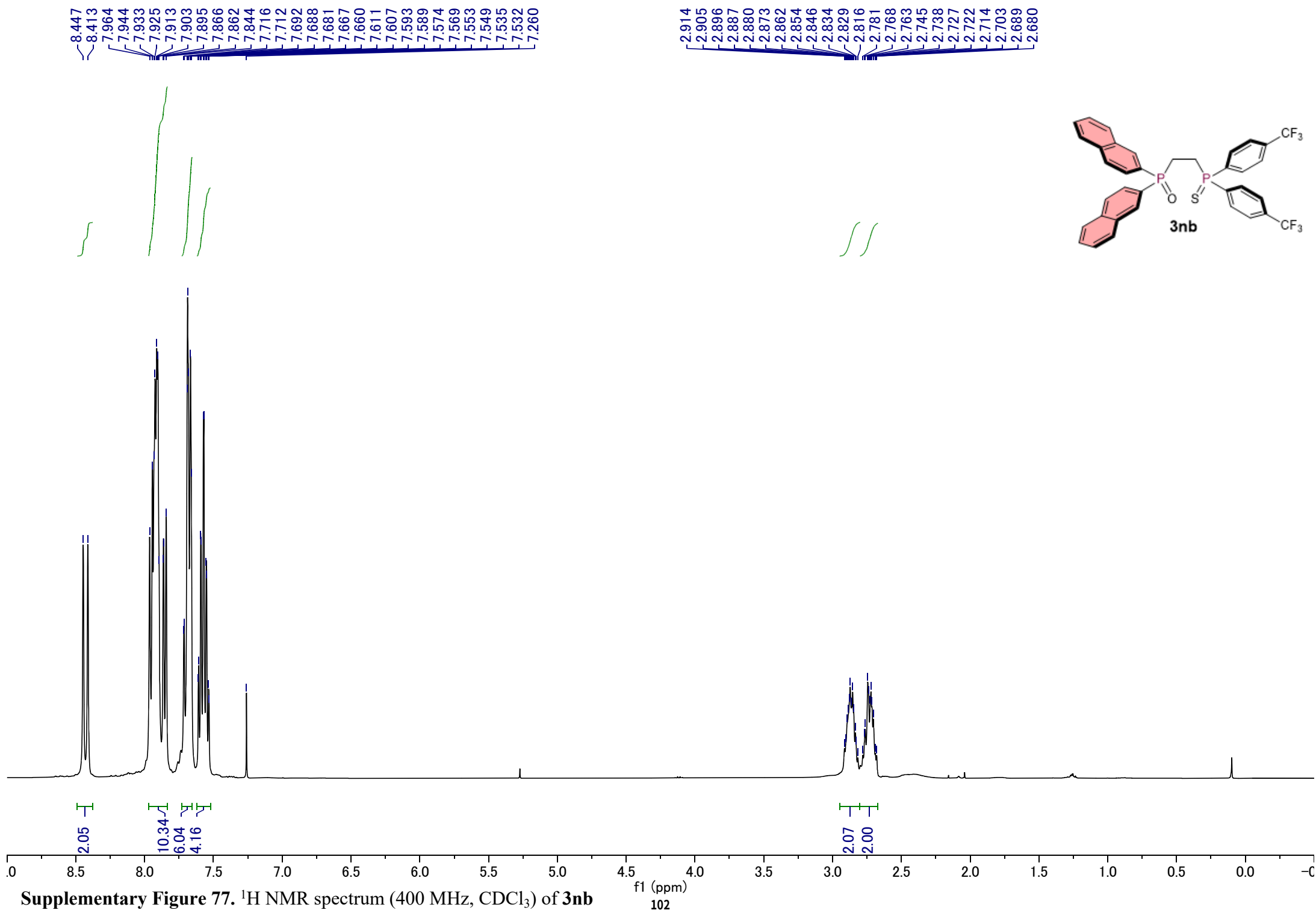
CDCl₃, 376 MHz



CDCl₃, 162 MHz



CDCl₃, 400 MHz



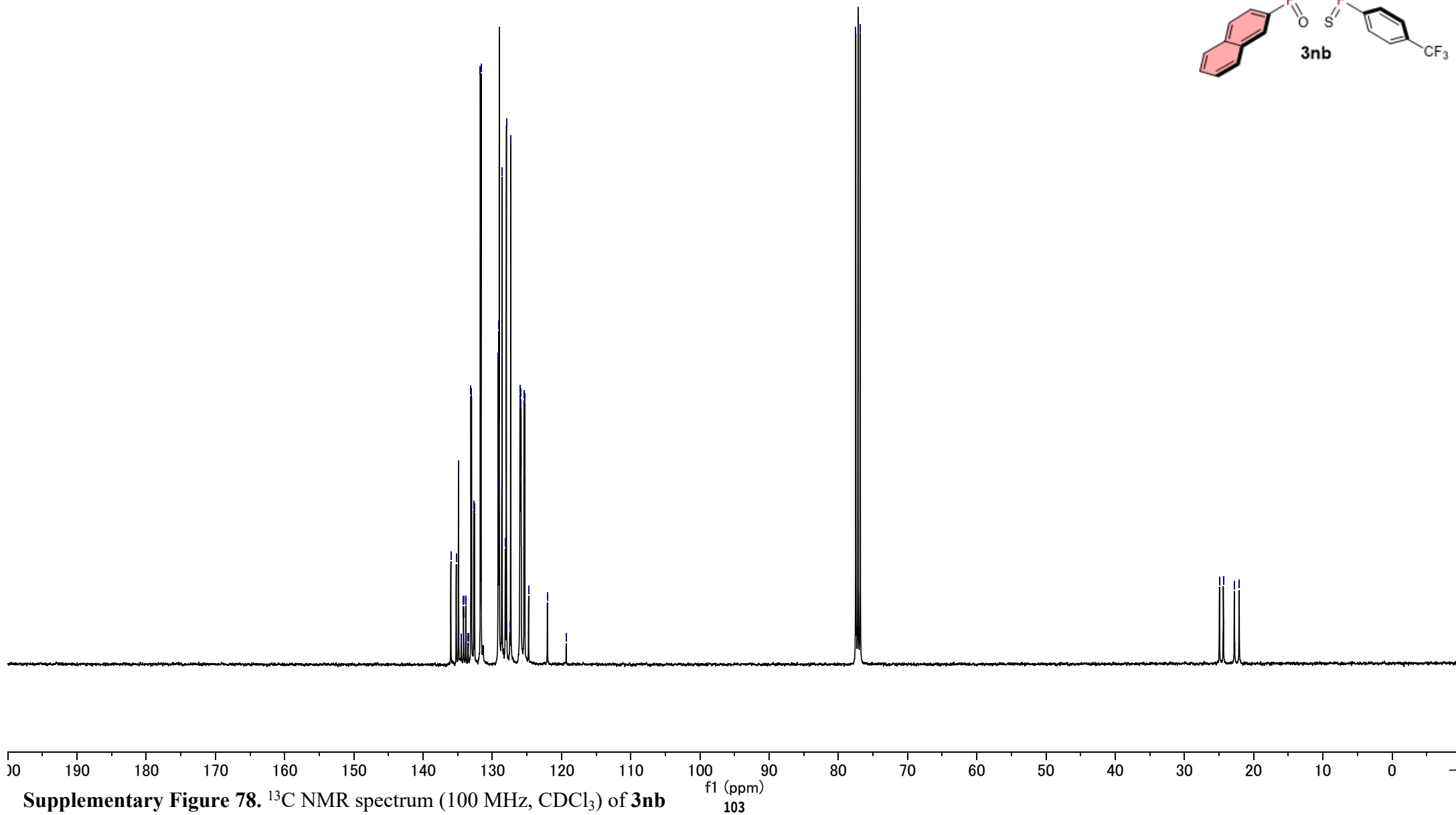
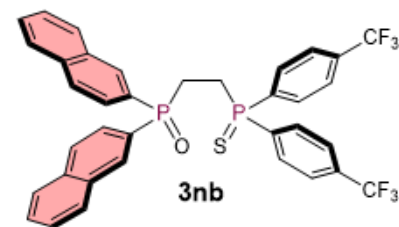
Supplementary Figure 77. ¹H NMR spectrum (400 MHz, CDCl₃) of 3nb

f1 (ppm)
102

CDCl₃, 100 MHz

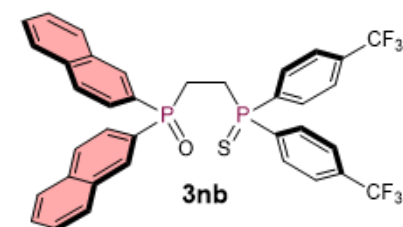
135.989
135.207
134.886
134.863
134.497
134.467
134.168
134.138
133.841
133.810
133.514
133.483
133.089
133.003
132.677
132.548
131.724
131.618
129.156
129.122
129.040
128.993
128.604
128.120
127.968
127.468
127.336
126.002
125.964
125.921
125.878
125.841
125.416
125.310
124.753
122.037
119.322
77.478
77.160
76.842

24.935
24.375
22.784
22.091



CDCl₃, 376 MHz

-63.065



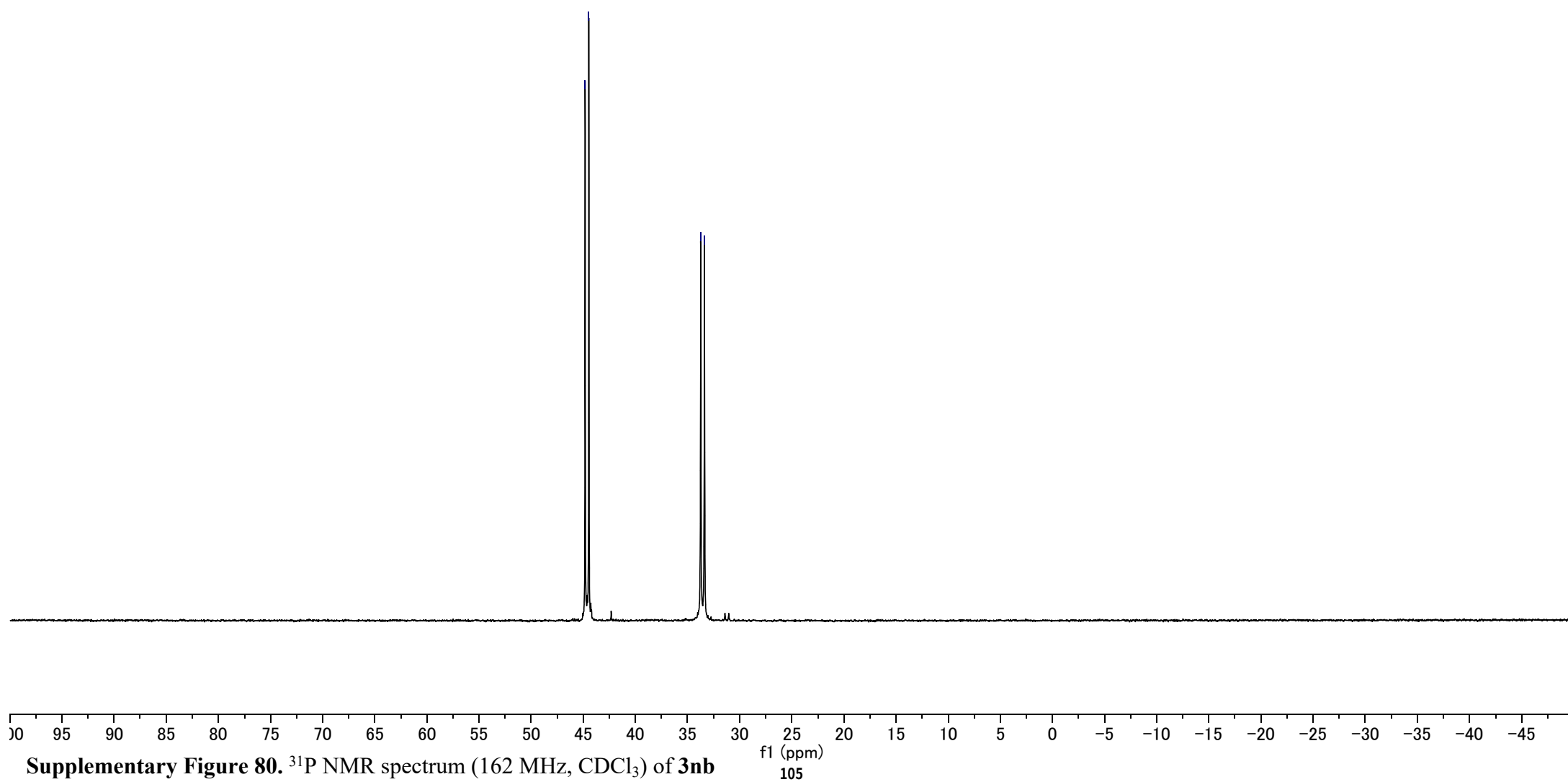
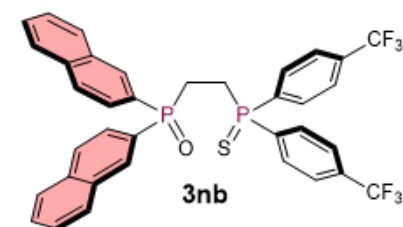
30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 79. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3nb**

f1 (ppm)
104

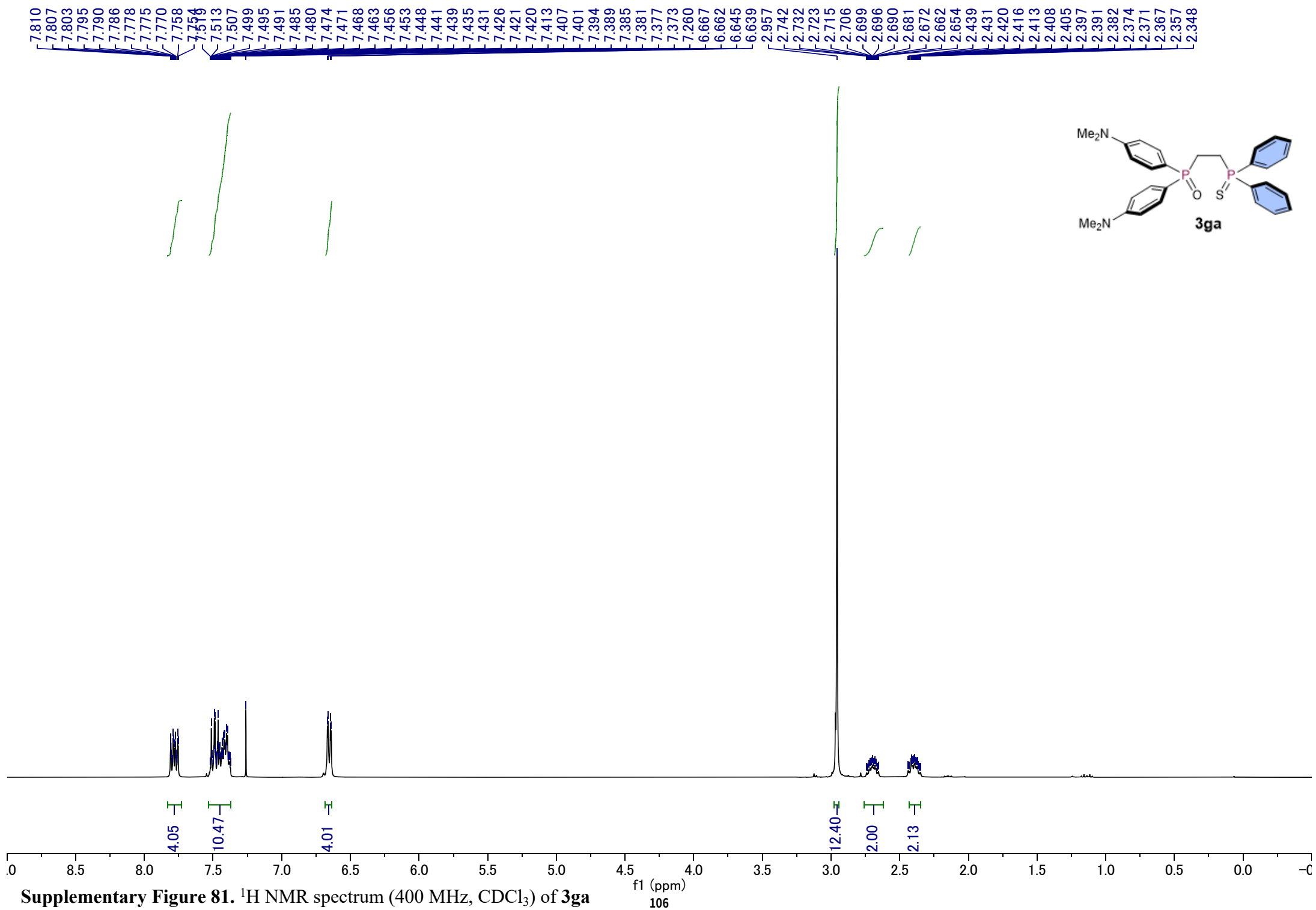
CDCl₃, 162 MHz

44.823
44.464
33.733
33.375



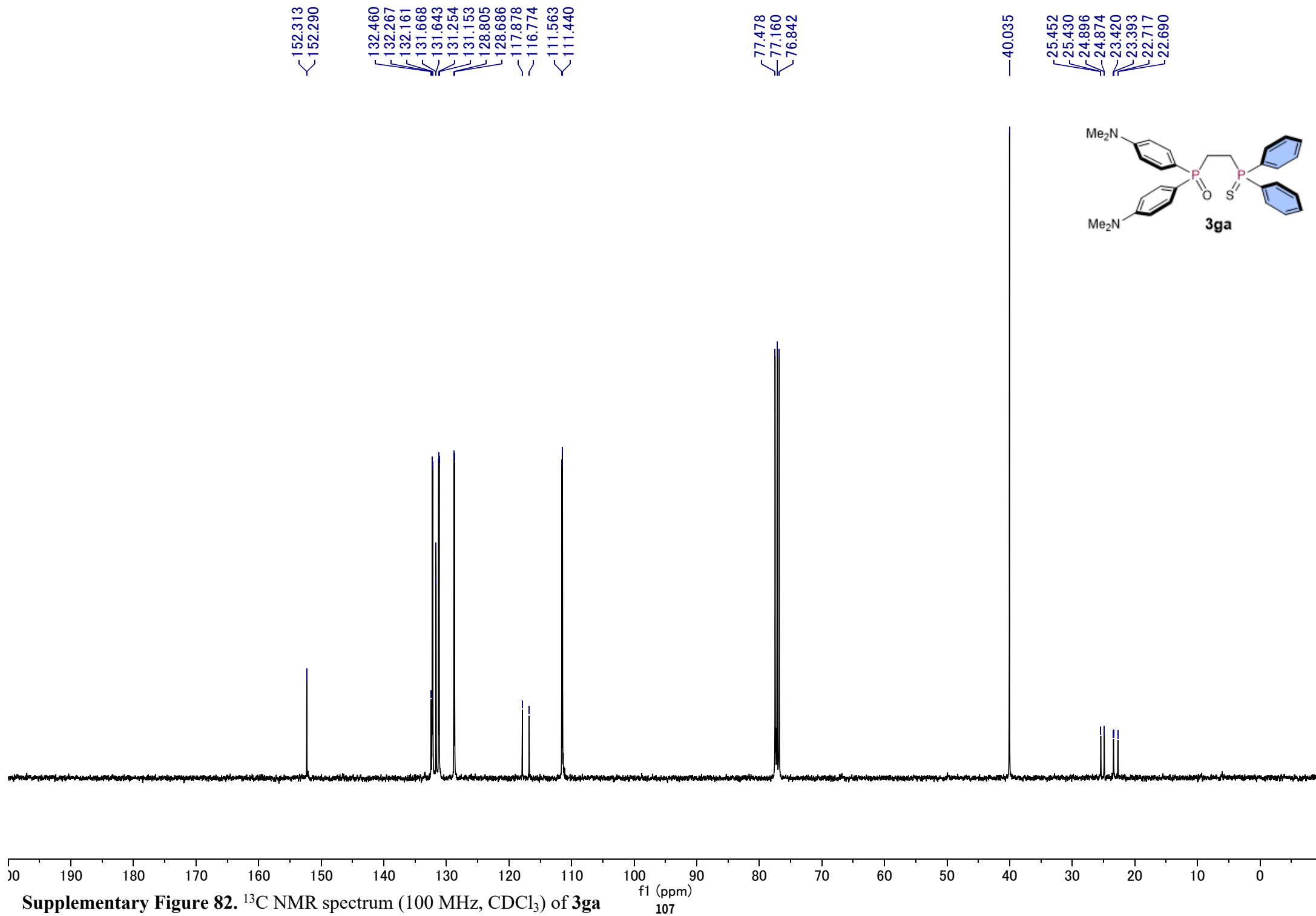
Supplementary Figure 80. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3nb**

CDCl₃, 400 MHz

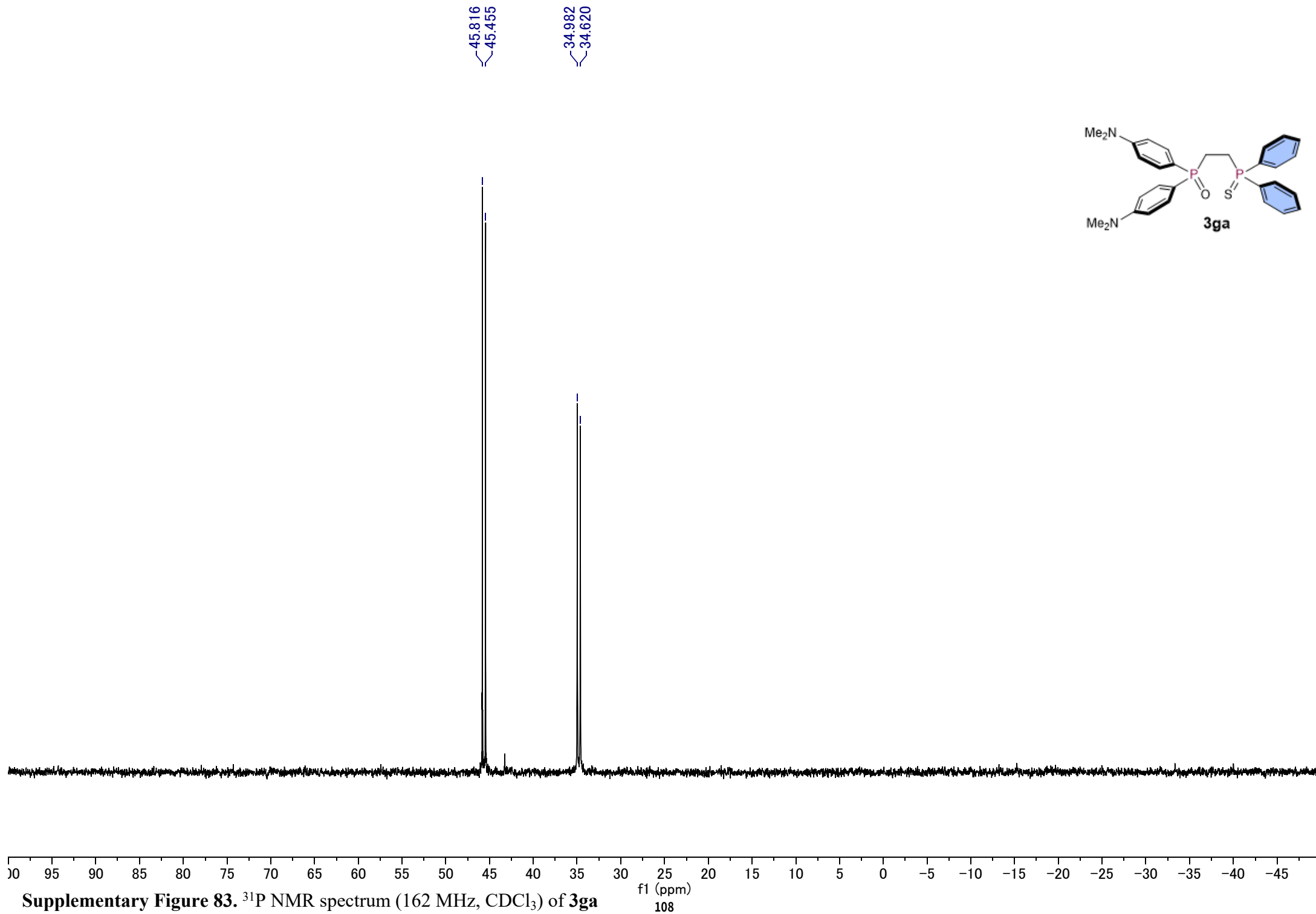


Supplementary Figure 81. ¹H NMR spectrum (400 MHz, CDCl₃) of **3ga**

CDCl₃, 100 MHz



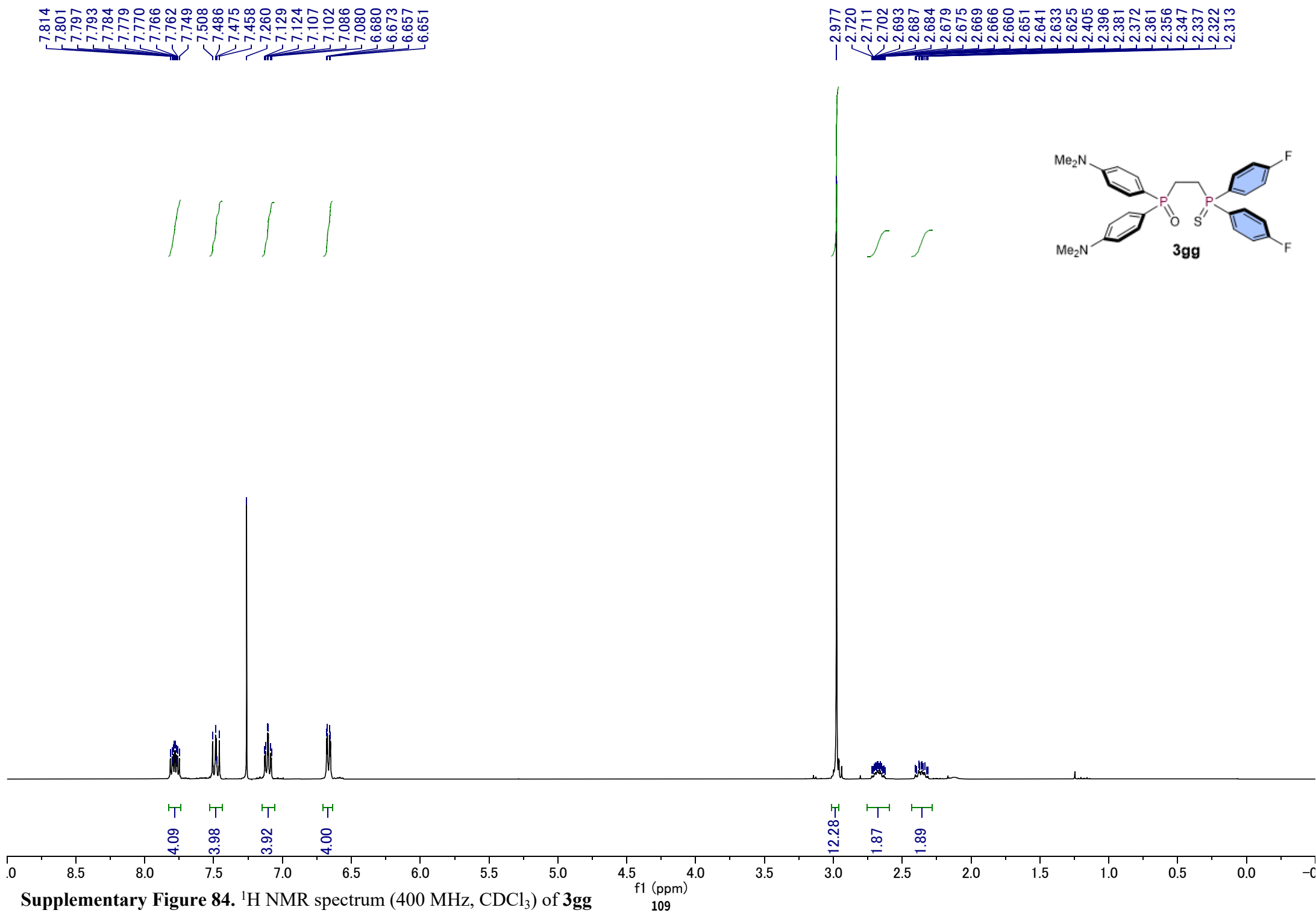
CDCl₃, 162 MHz



Supplementary Figure 83. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3ga**

f1 (ppm)
108

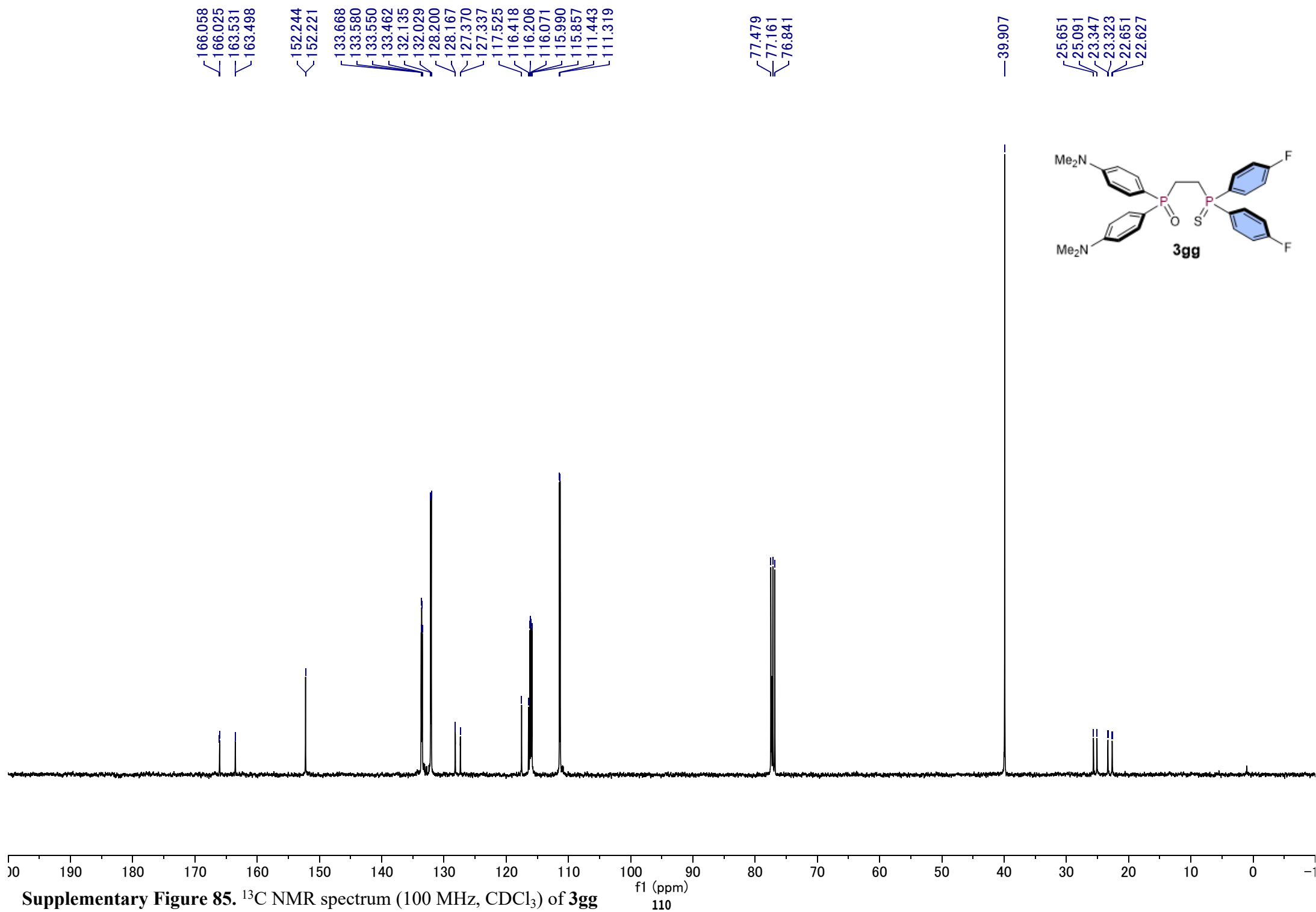
CDCl₃, 400 MHz



Supplementary Figure 84. ¹H NMR spectrum (400 MHz, CDCl₃) of **3gg**

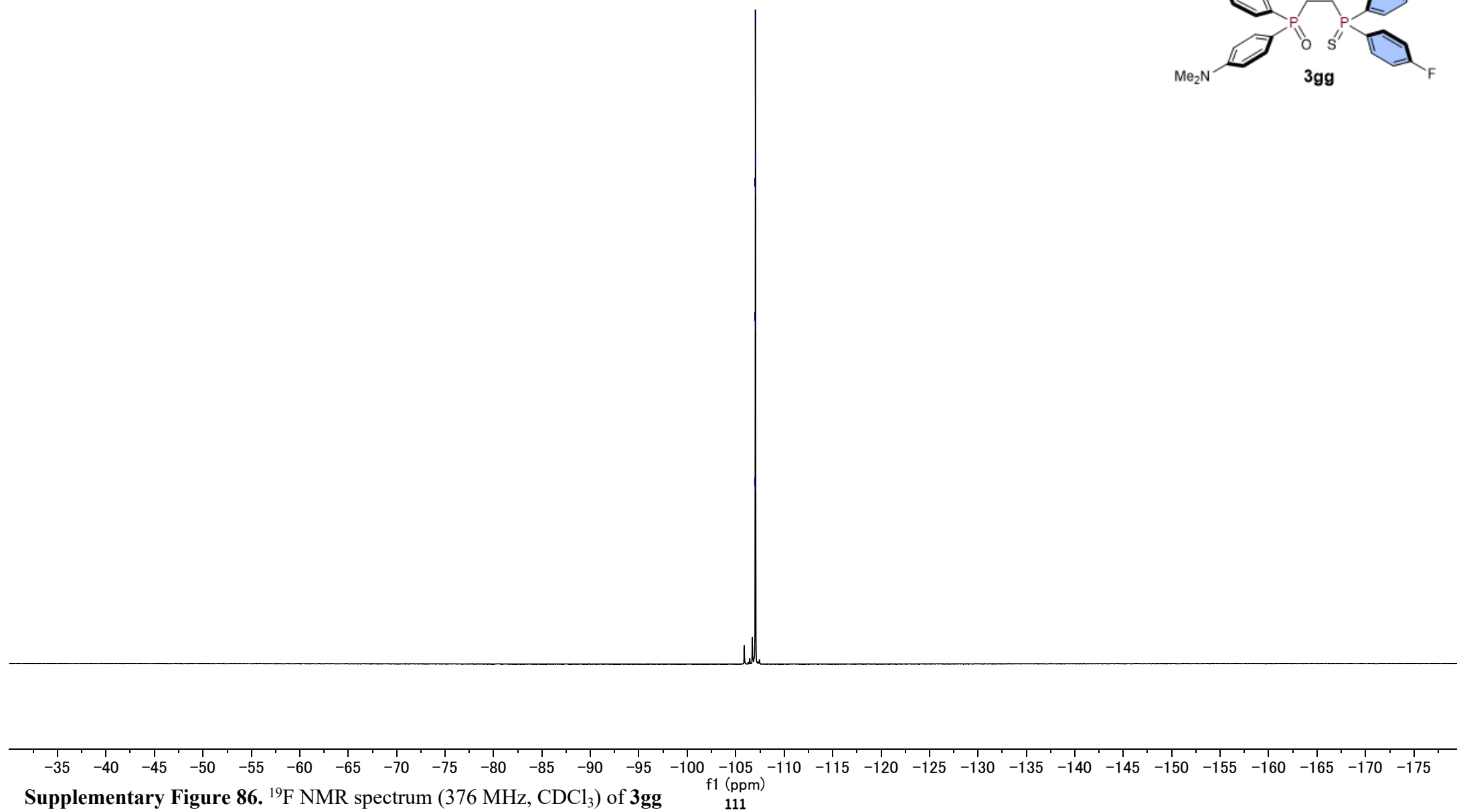
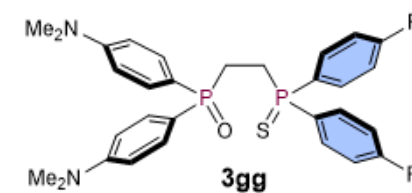
f1 (ppm)
109

CDCl₃, 100 MHz

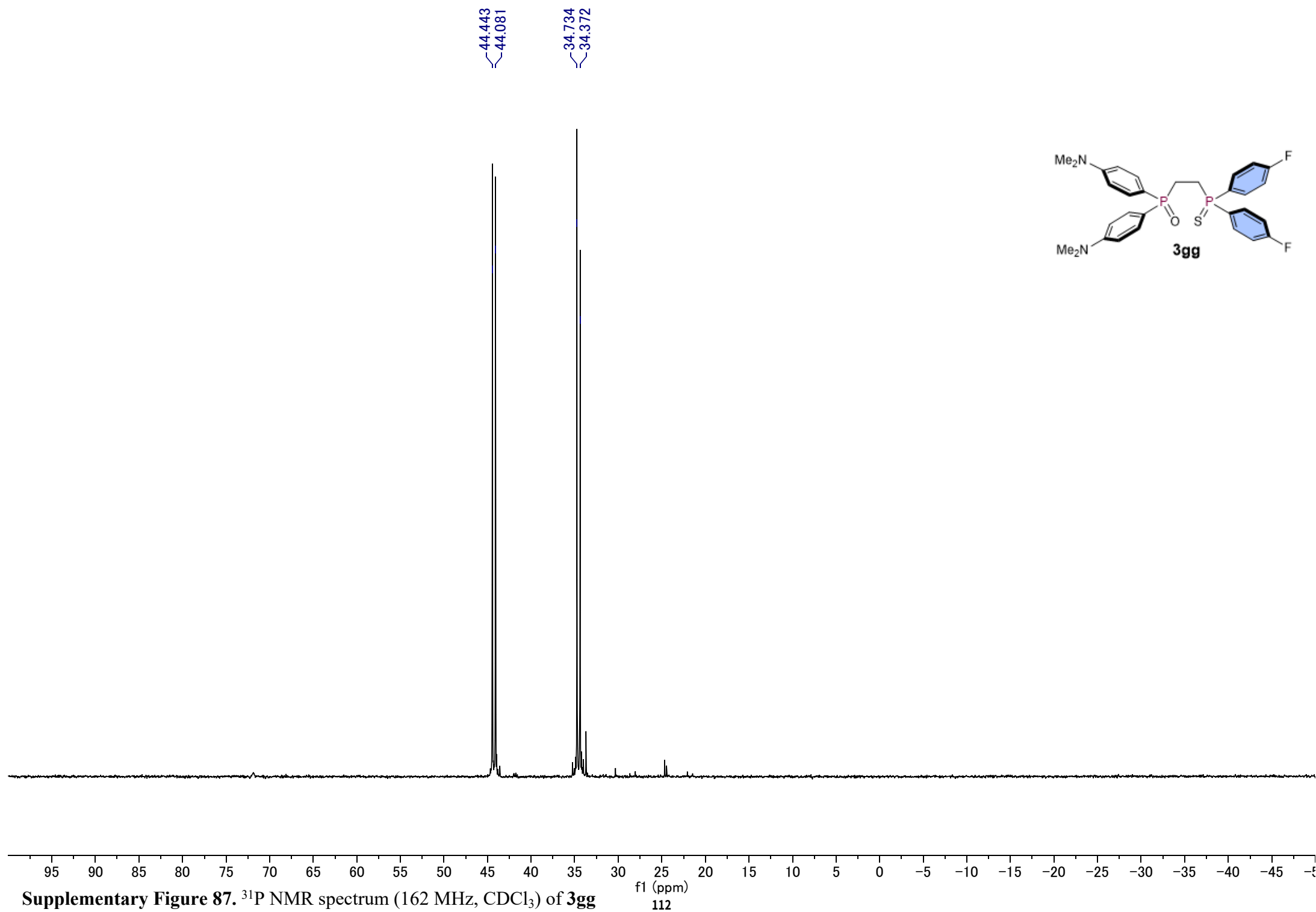


CDCl₃, 376 MHz

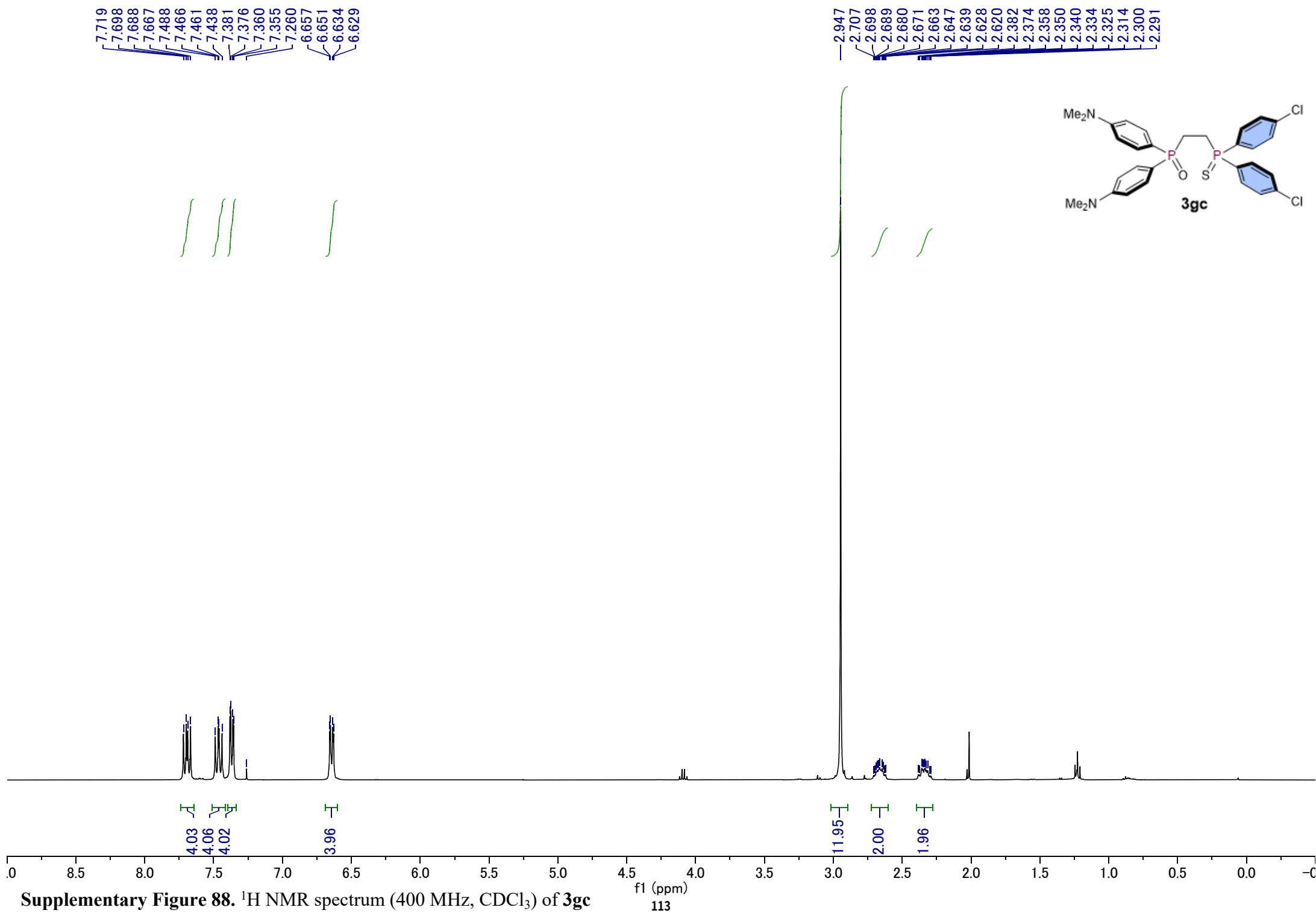
106.988
107.001
107.007
107.014
107.023
107.028
107.039
107.045
107.051
107.064



CDCl₃, 162 MHz

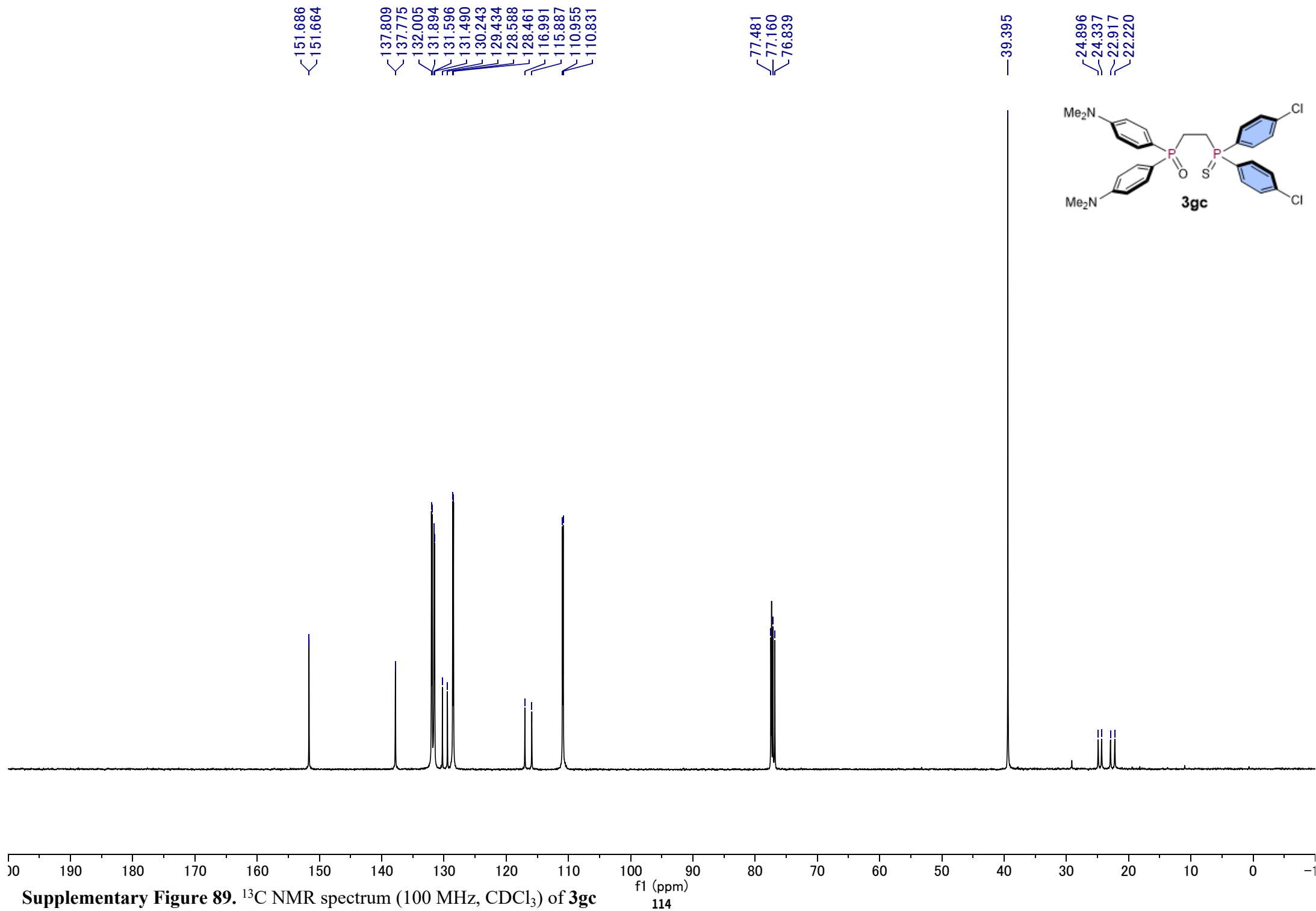


CDCl₃, 400 MHz

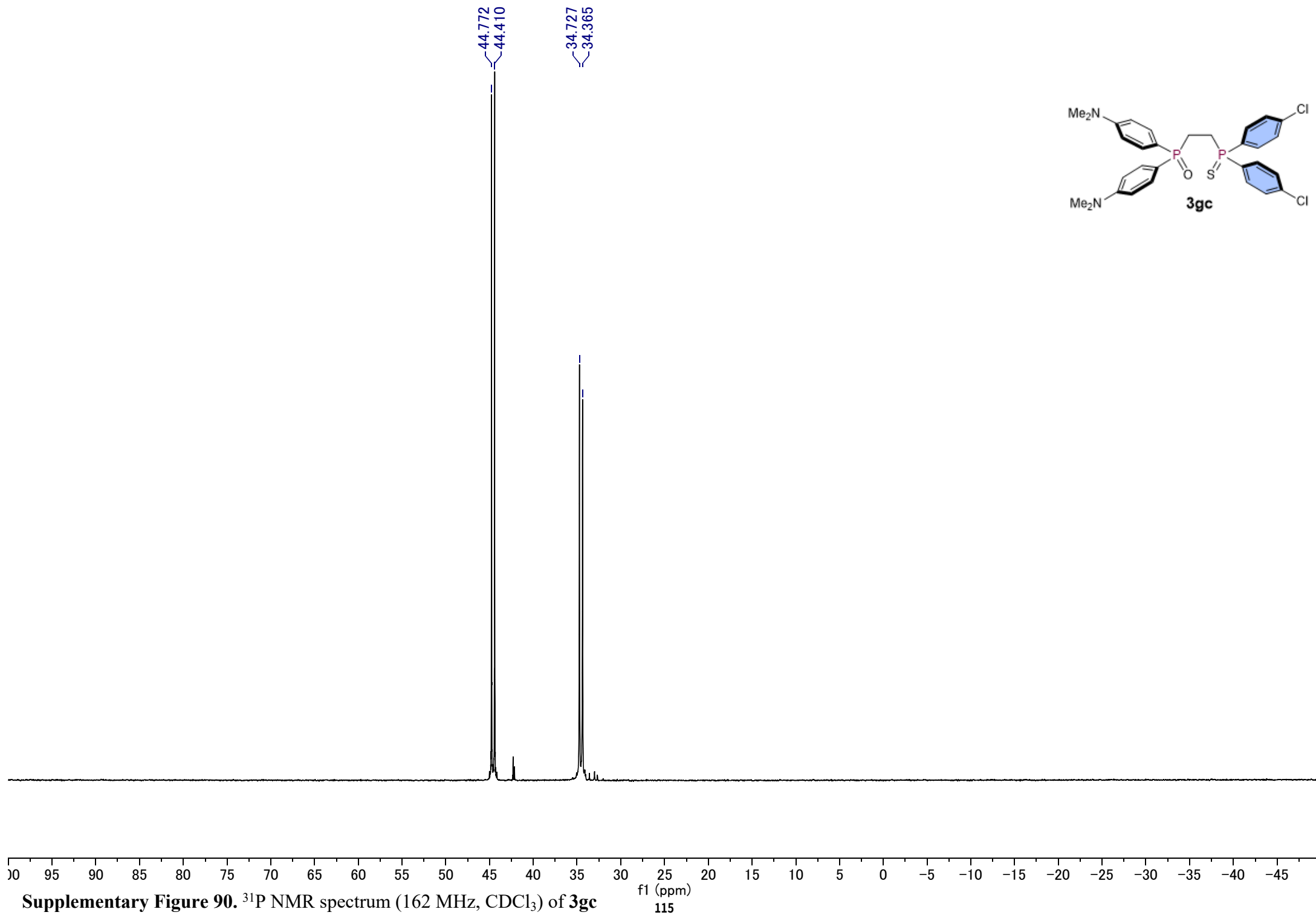


Supplementary Figure 88. ¹H NMR spectrum (400 MHz, CDCl₃) of **3gc**

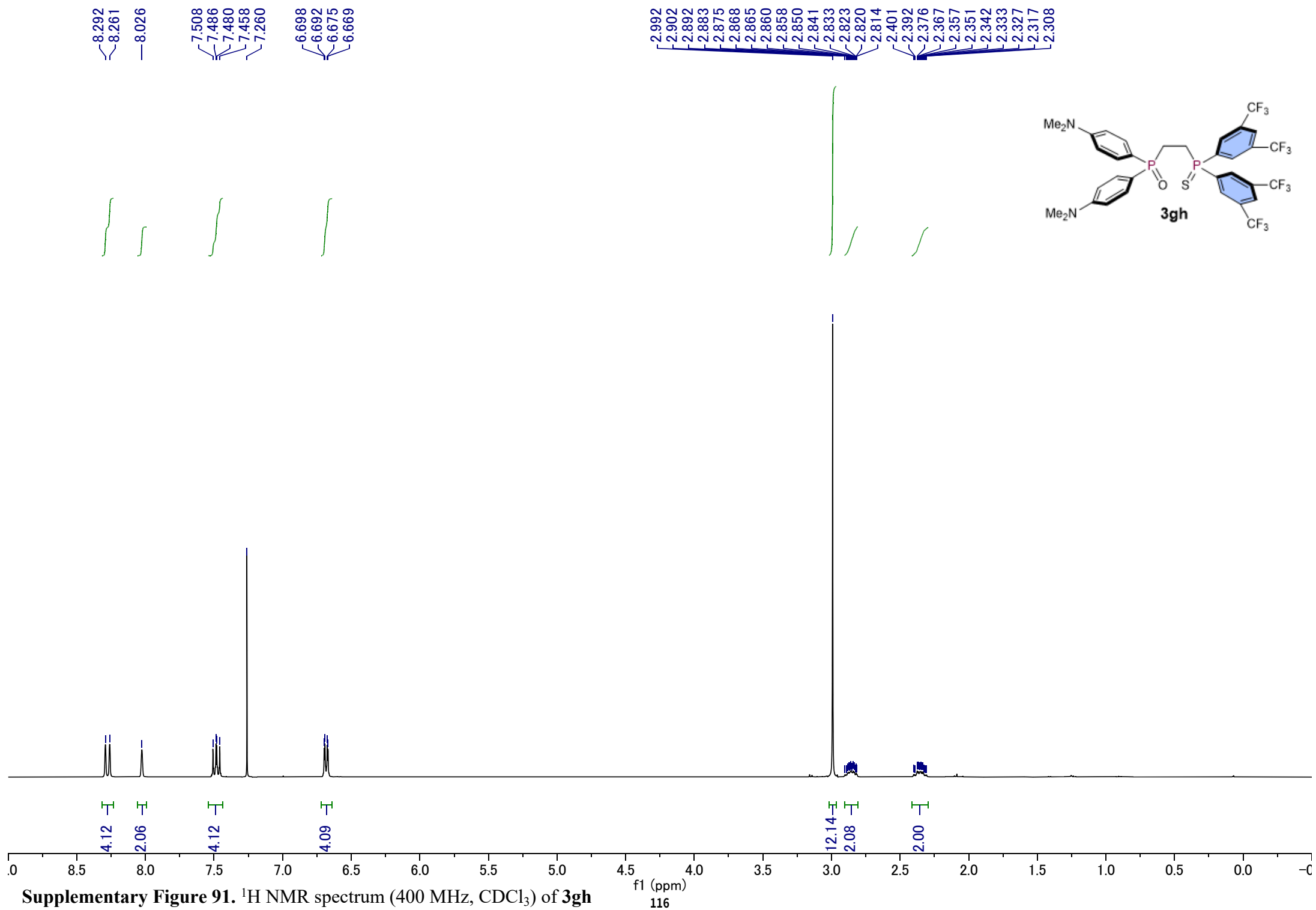
CDCl₃, 100 MHz



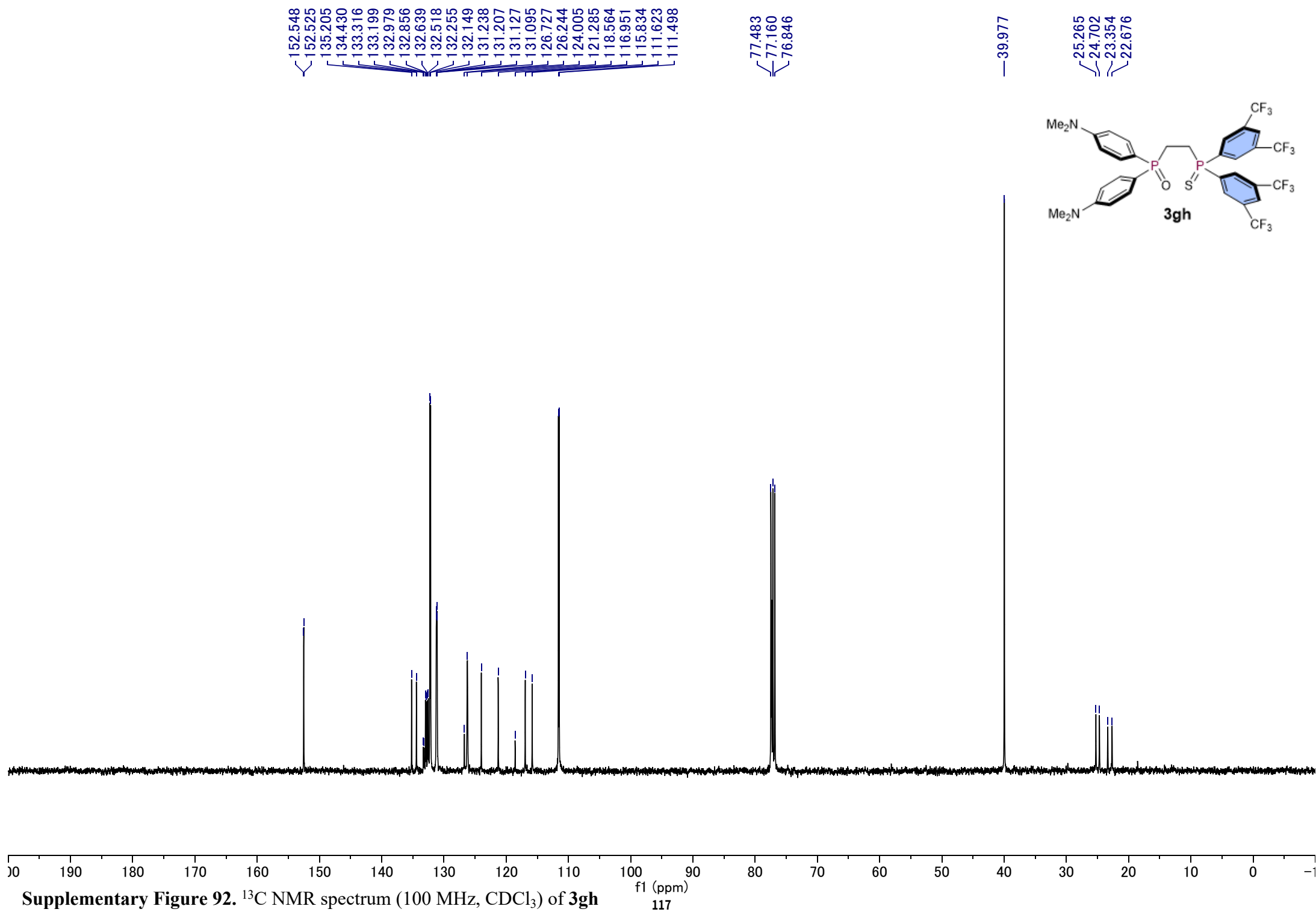
CDCl₃, 162 MHz



CDCl₃, 400 MHz

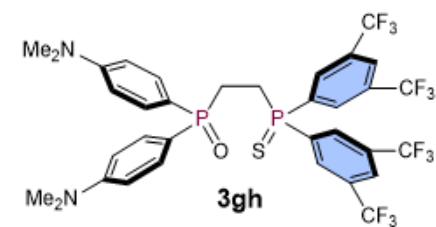


CDCl₃, 100 MHz



CDCl₃, 376 MHz

-62.691

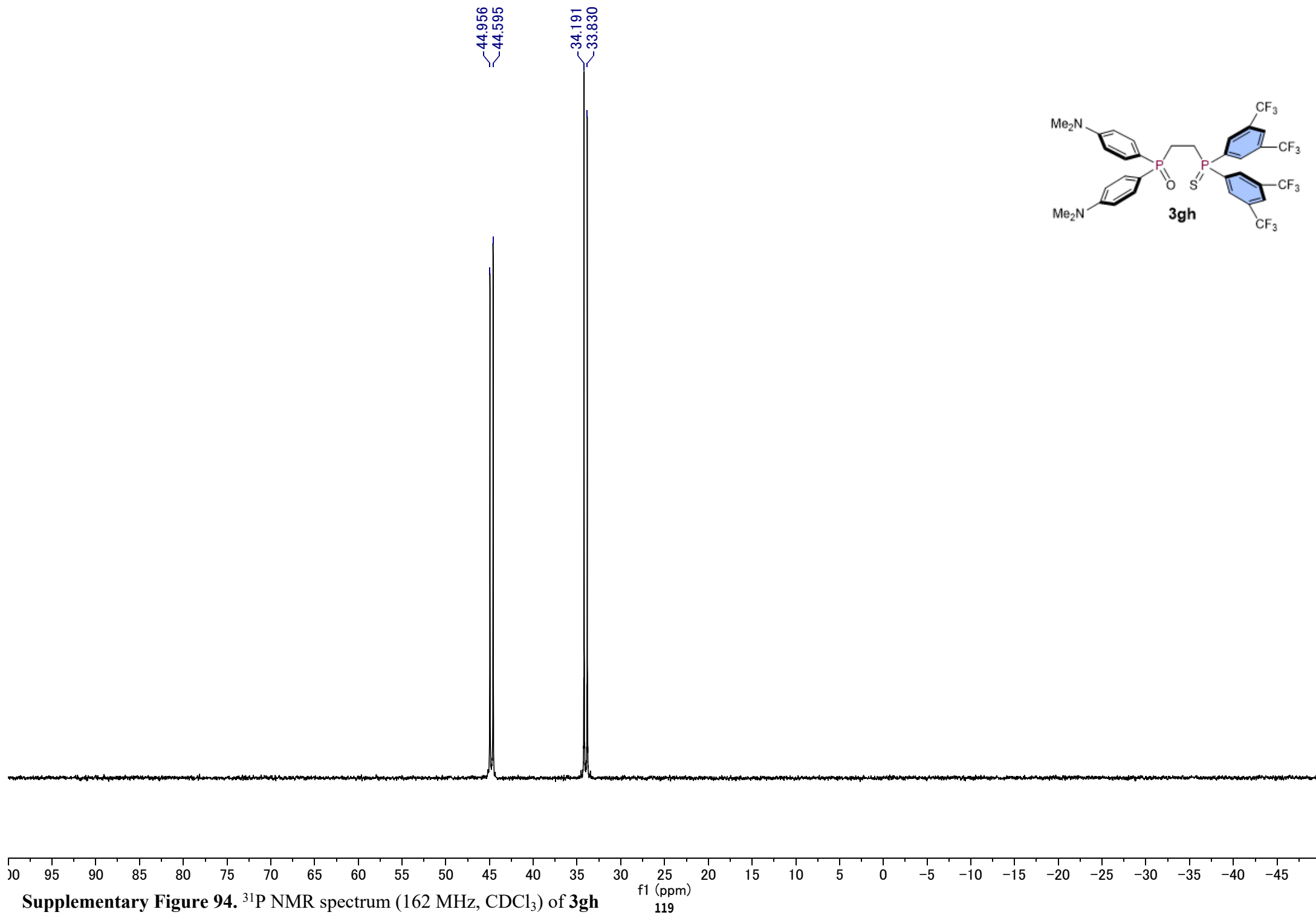


30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

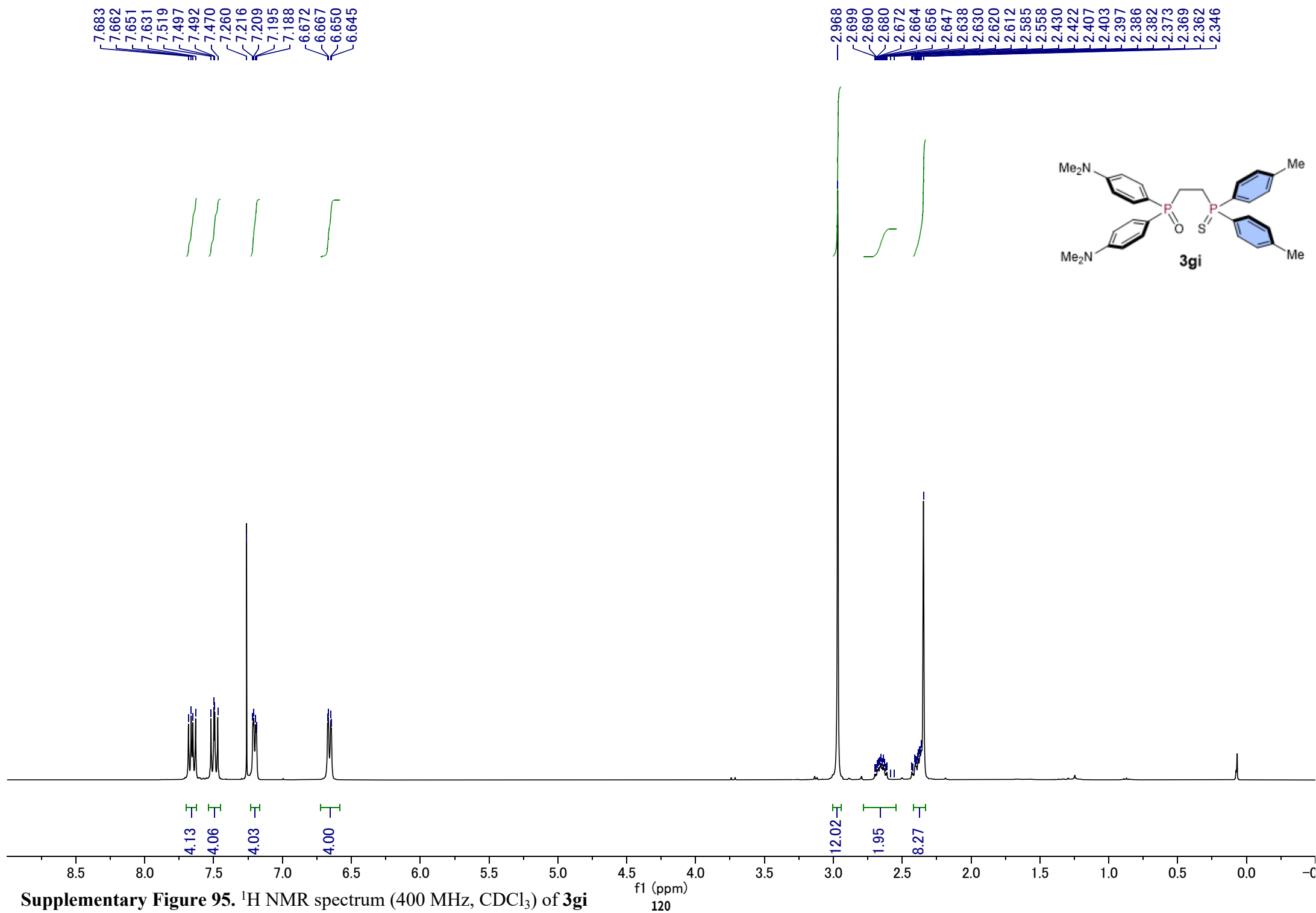
Supplementary Figure 93. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3gh**

f1 (ppm)
118

CDCl₃, 162 MHz

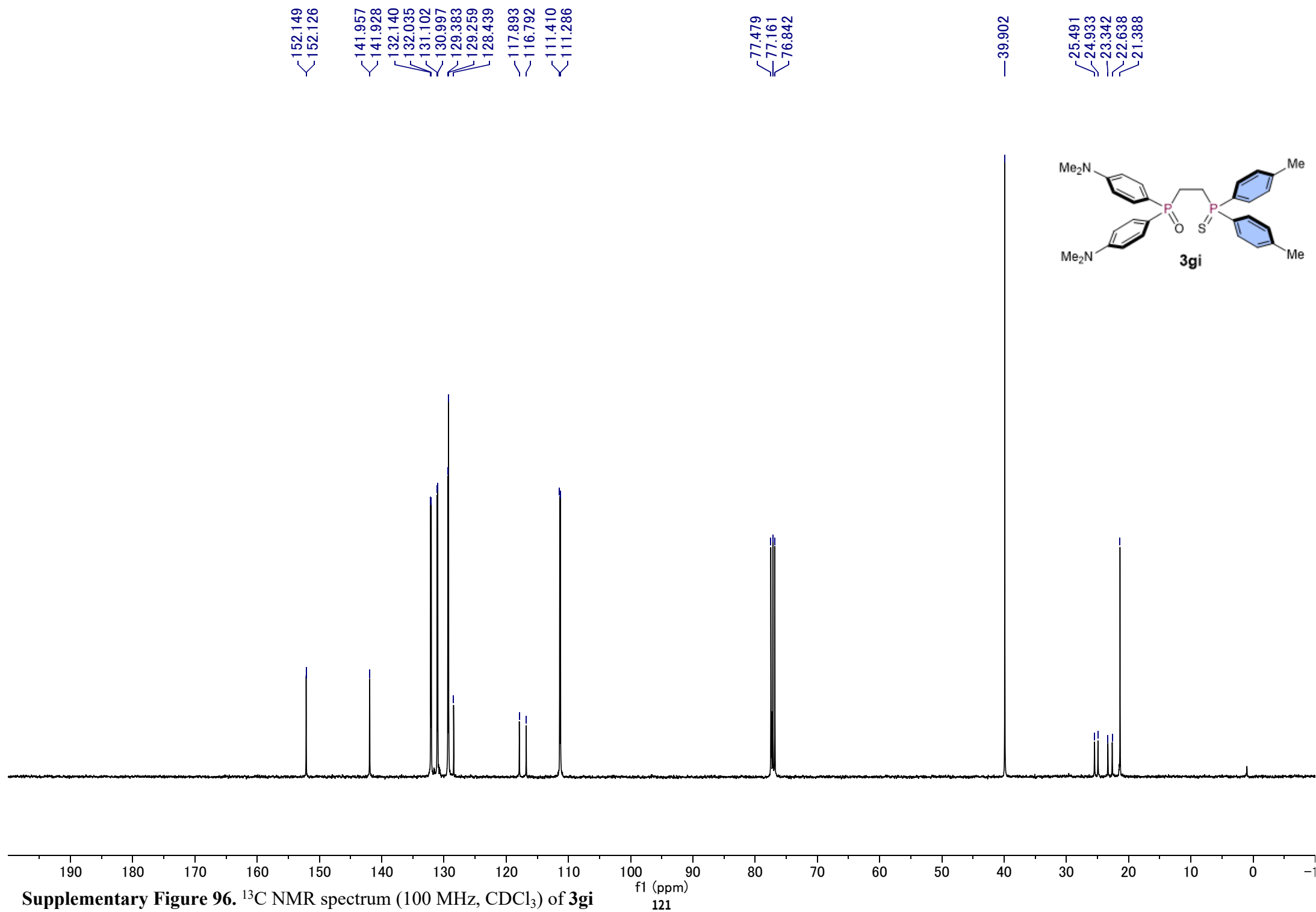


CDCl₃, 400 MHz

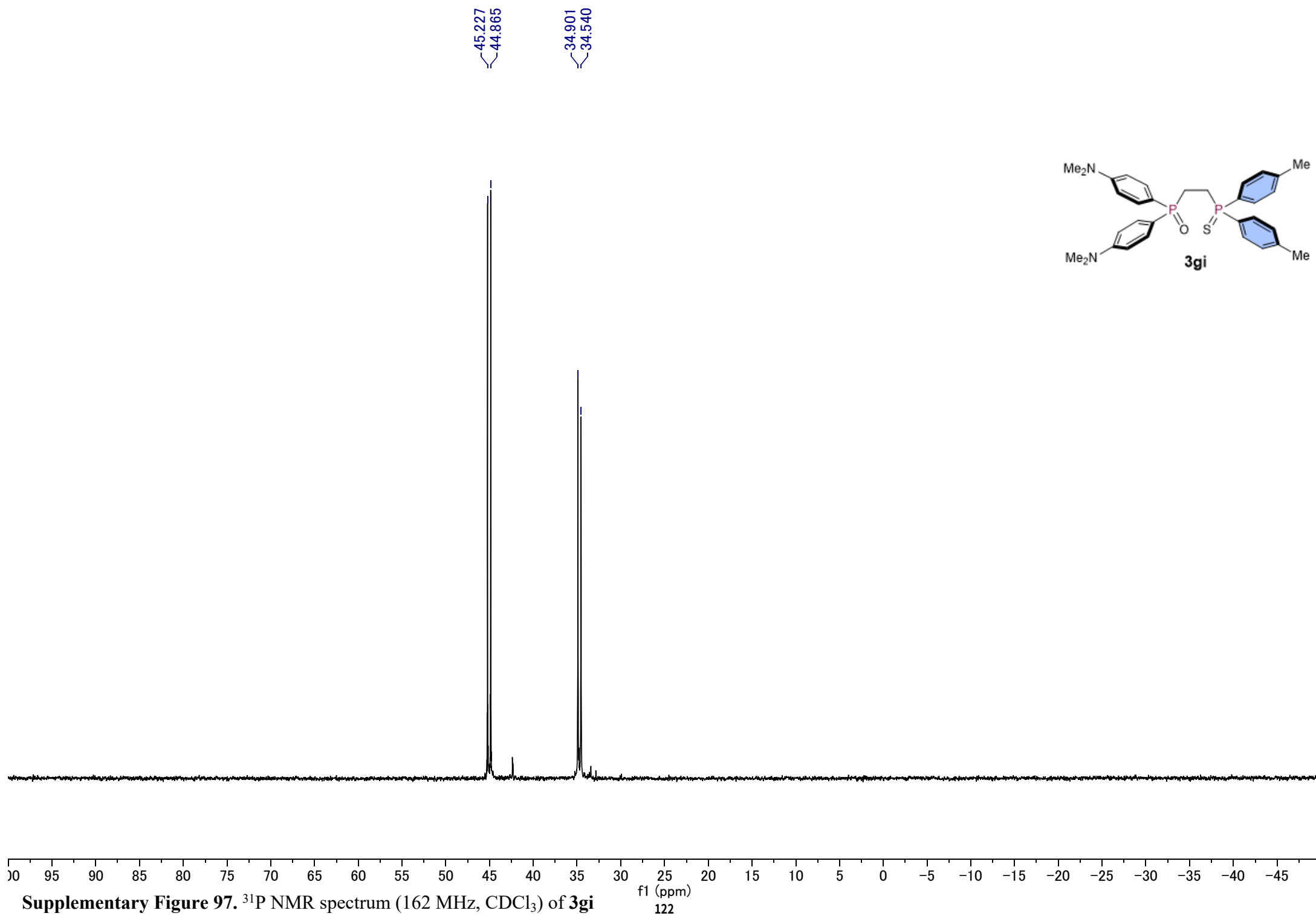


Supplementary Figure 95. ¹H NMR spectrum (400 MHz, CDCl₃) of **3gi**

CDCl₃, 100 MHz



CDCl₃, 162 MHz



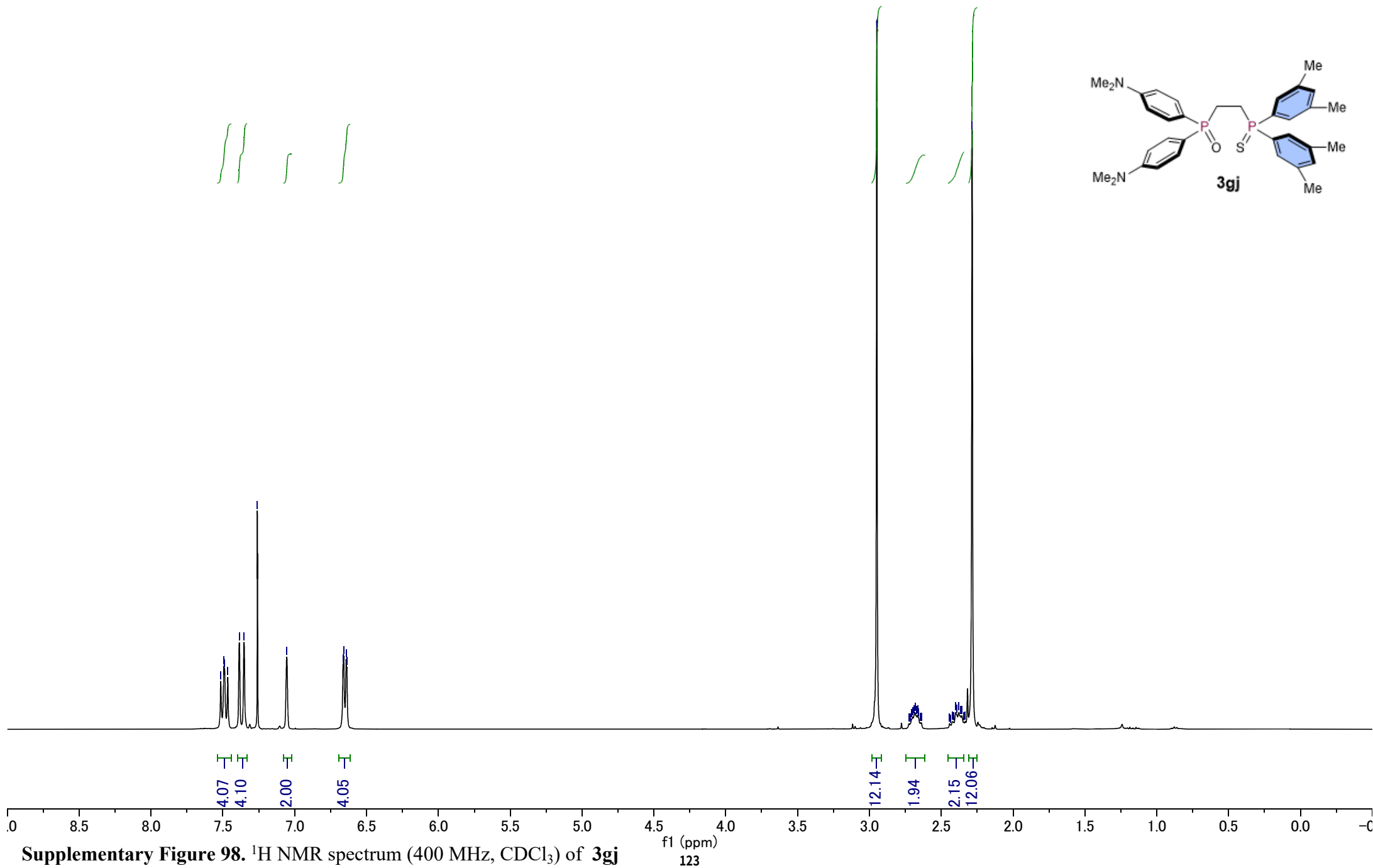
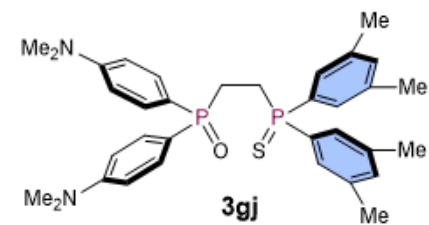
Supplementary Figure 97. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3gi**

f1 (ppm)
122

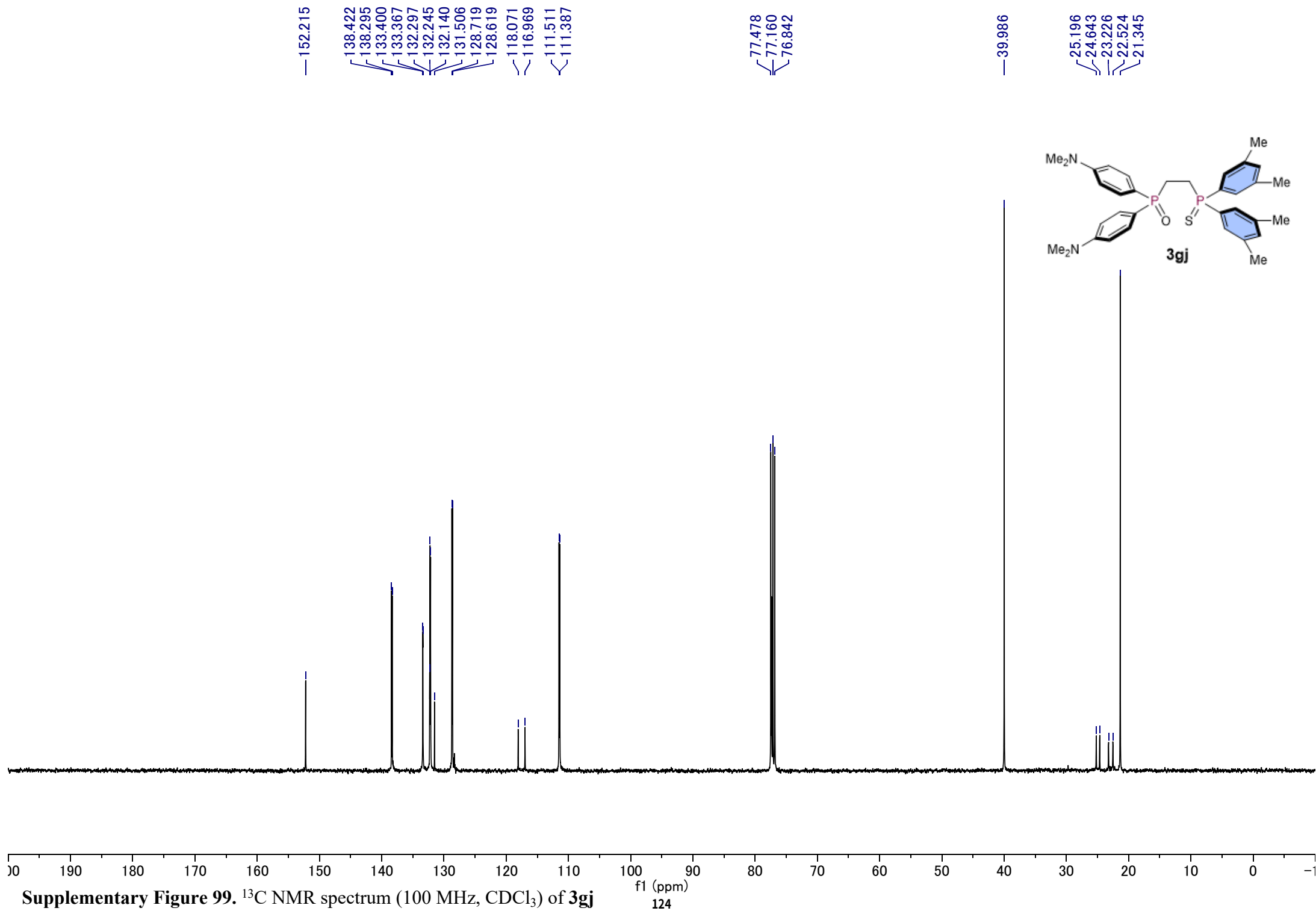
CDCl₃, 400 MHz

7.515
7.493
7.487
7.466
7.386
7.353
7.260
7.055
6.663
6.059
6.642
6.637

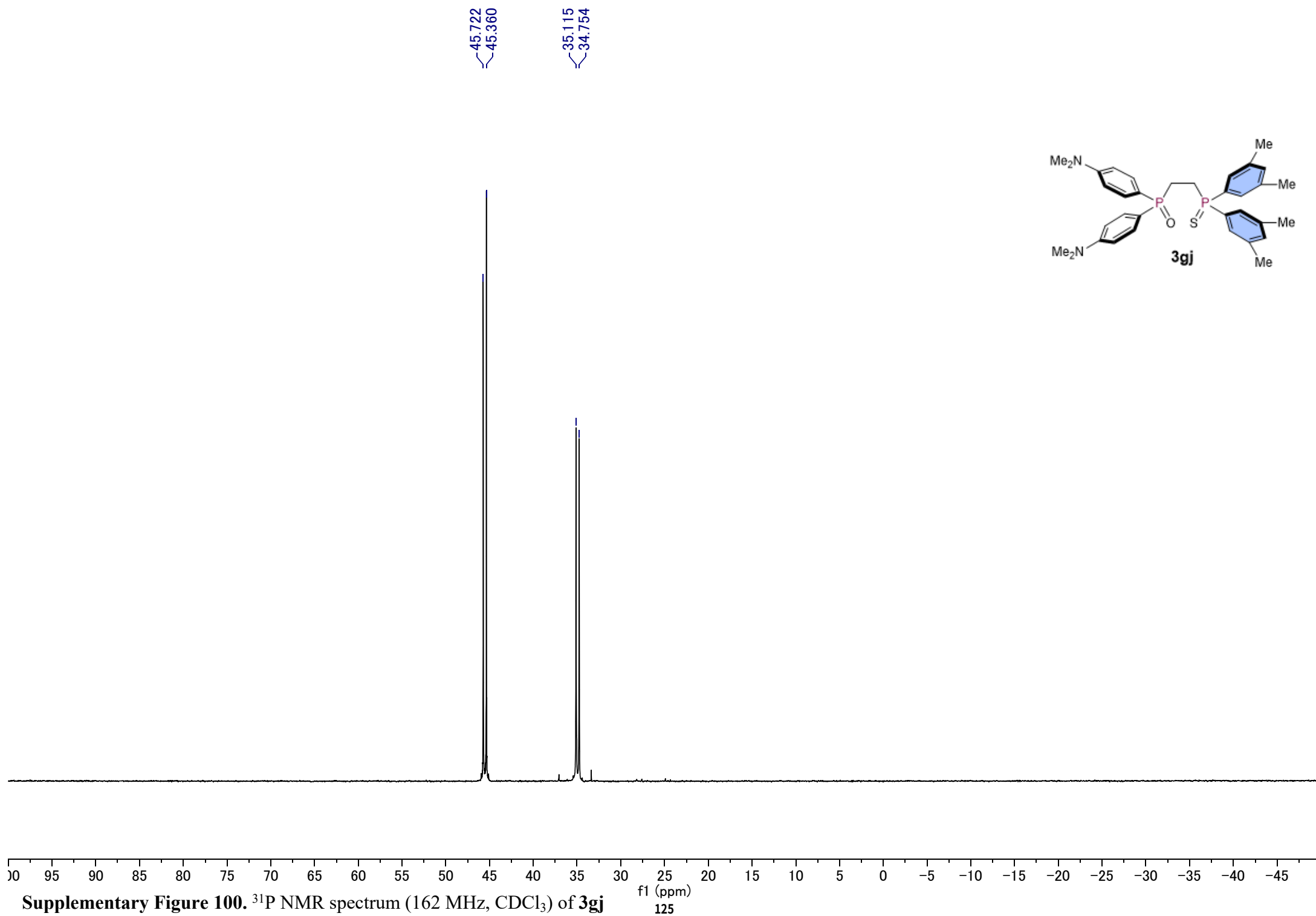
2.949
2.726
2.717
2.707
2.699
2.690
2.682
2.673
2.664
2.656
2.646
2.639
2.442
2.436
2.424
2.416
2.400
2.391
2.377
2.367
2.357
2.342
2.333
2.285



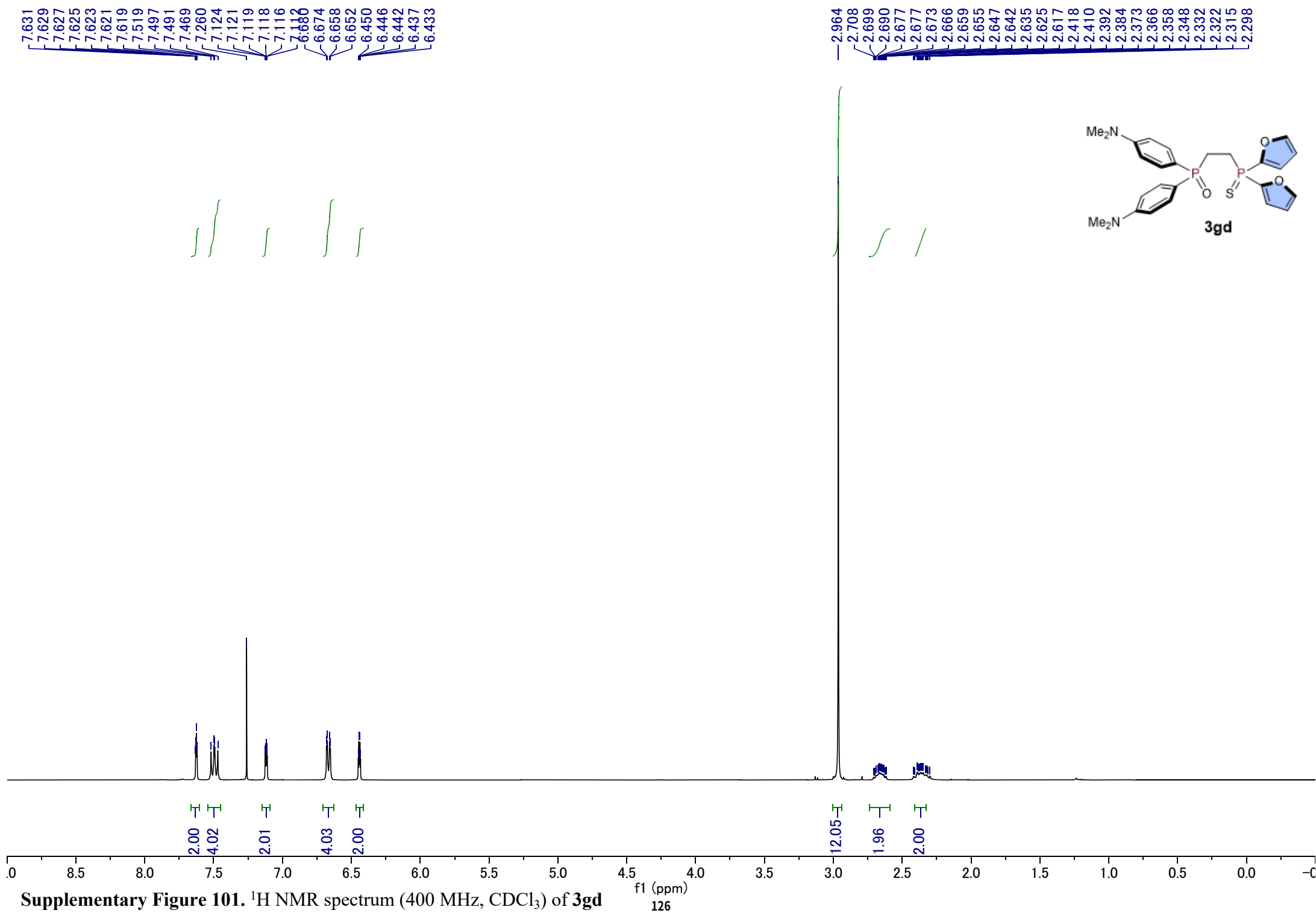
CDCl₃, 100 MHz



CDCl₃, 162 MHz



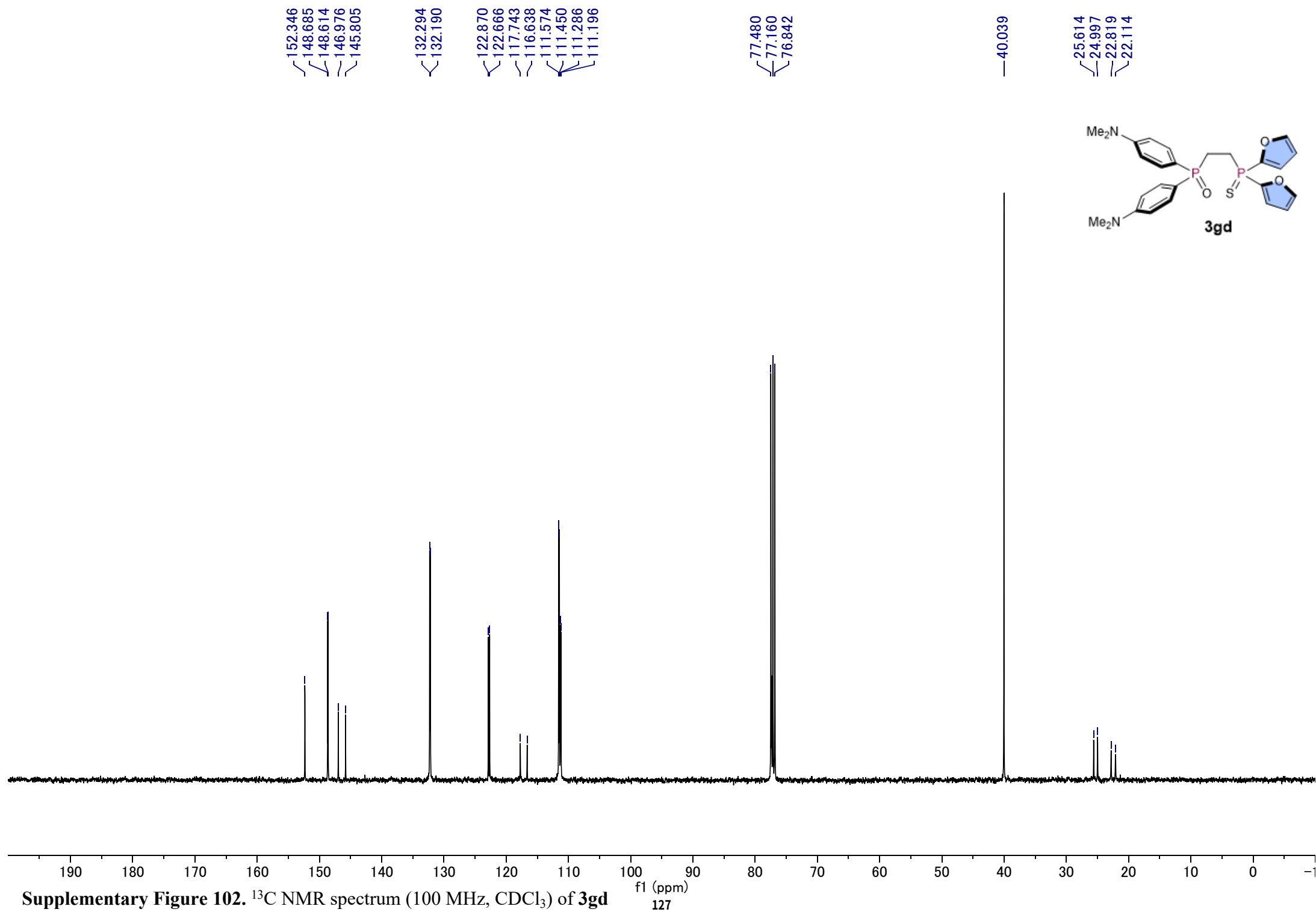
CDCl₃, 400 MHz



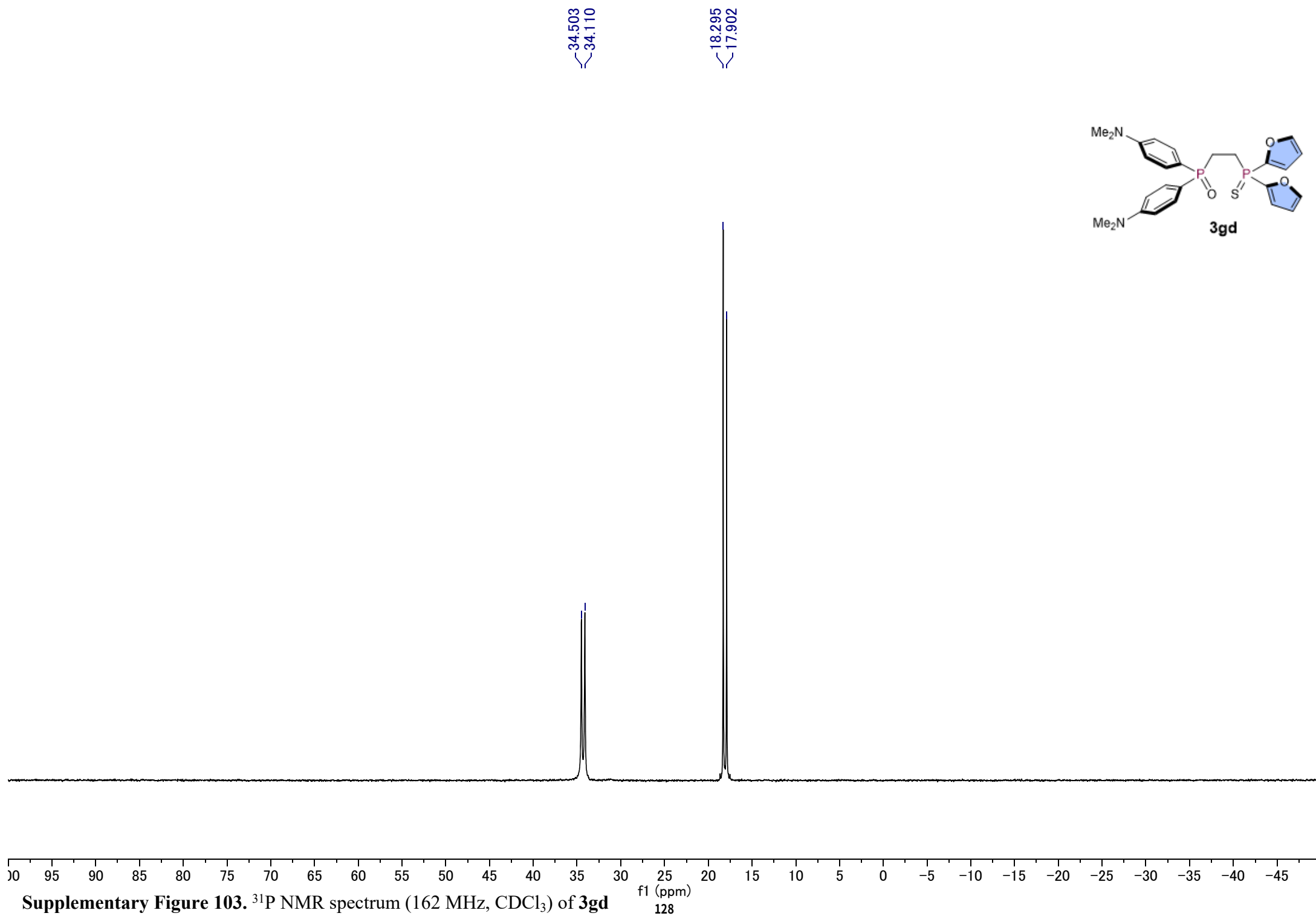
Supplementary Figure 101. ¹H NMR spectrum (400 MHz, CDCl₃) of **3gd**

f1 (ppm)
126

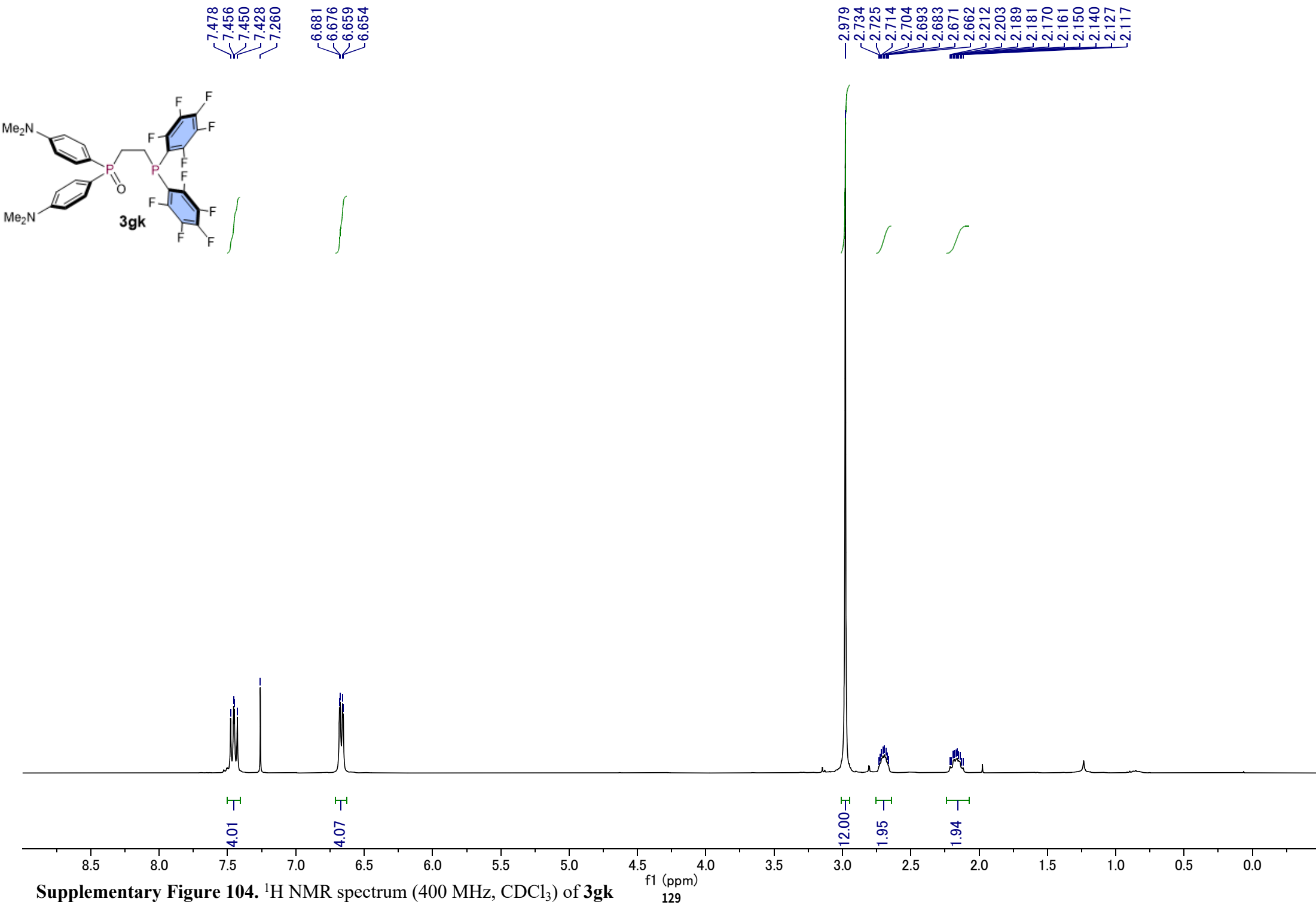
CDCl₃, 100 MHz



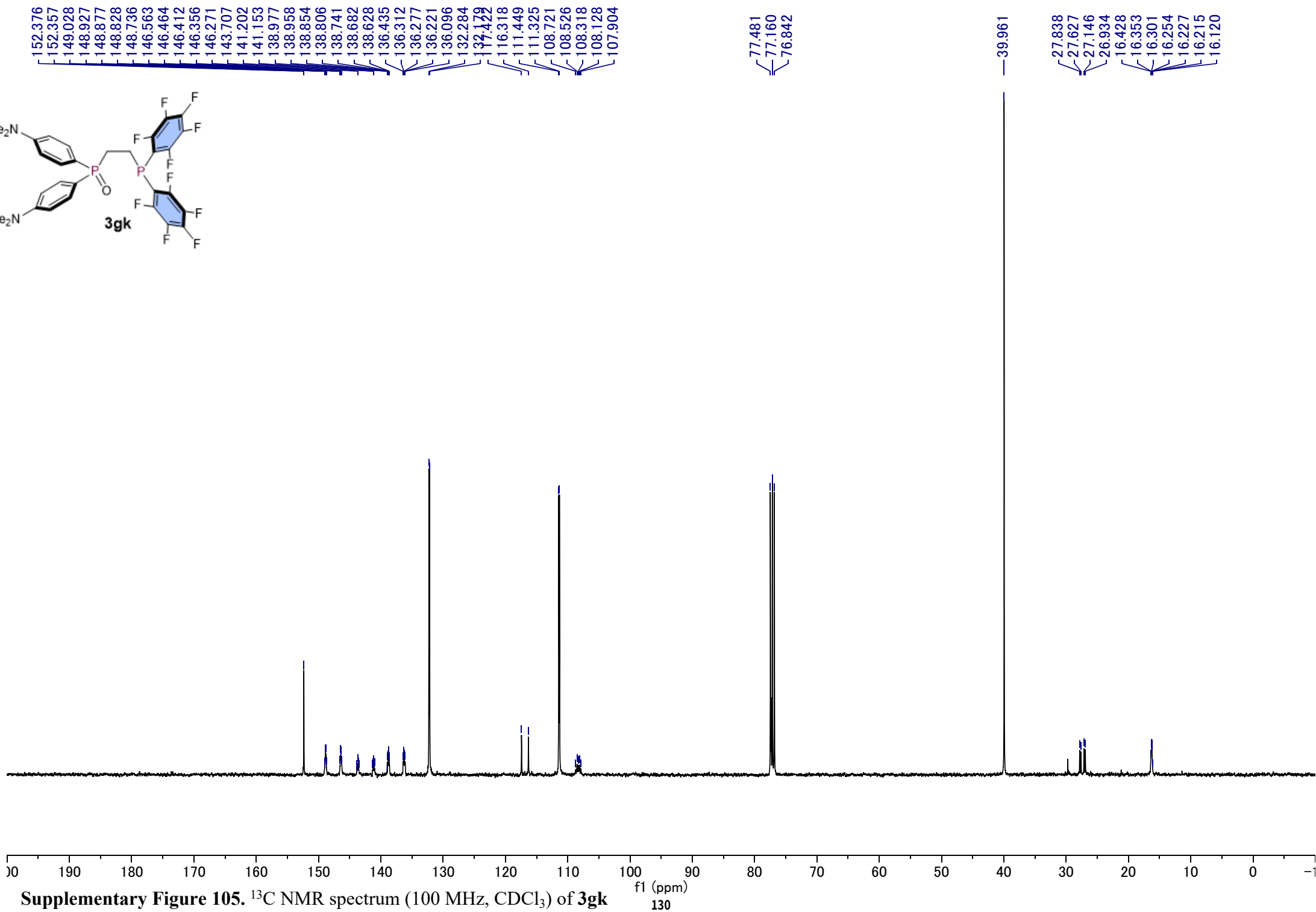
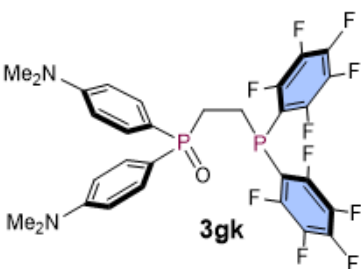
CDCl₃, 162 MHz



CDCl₃, 400 MHz

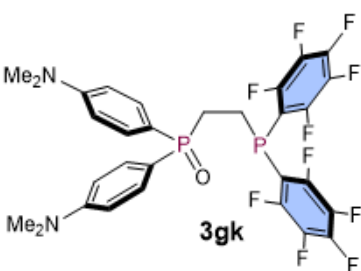


CDCl₃, 100 MHz

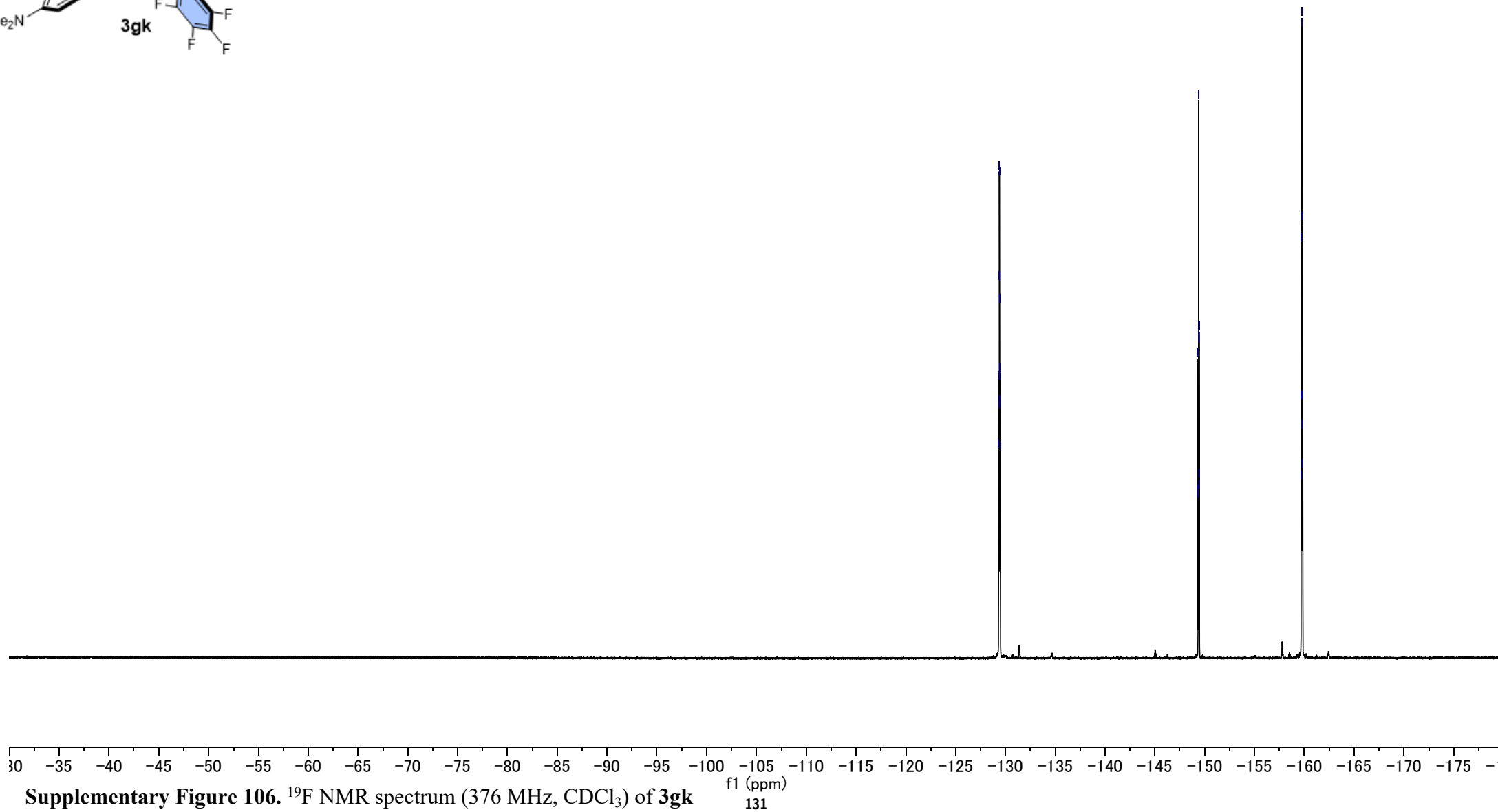


Supplementary Figure 105. ¹³C NMR spectrum (100 MHz, CDCl₃) of **3gk**

CDCl₃, 376 MHz



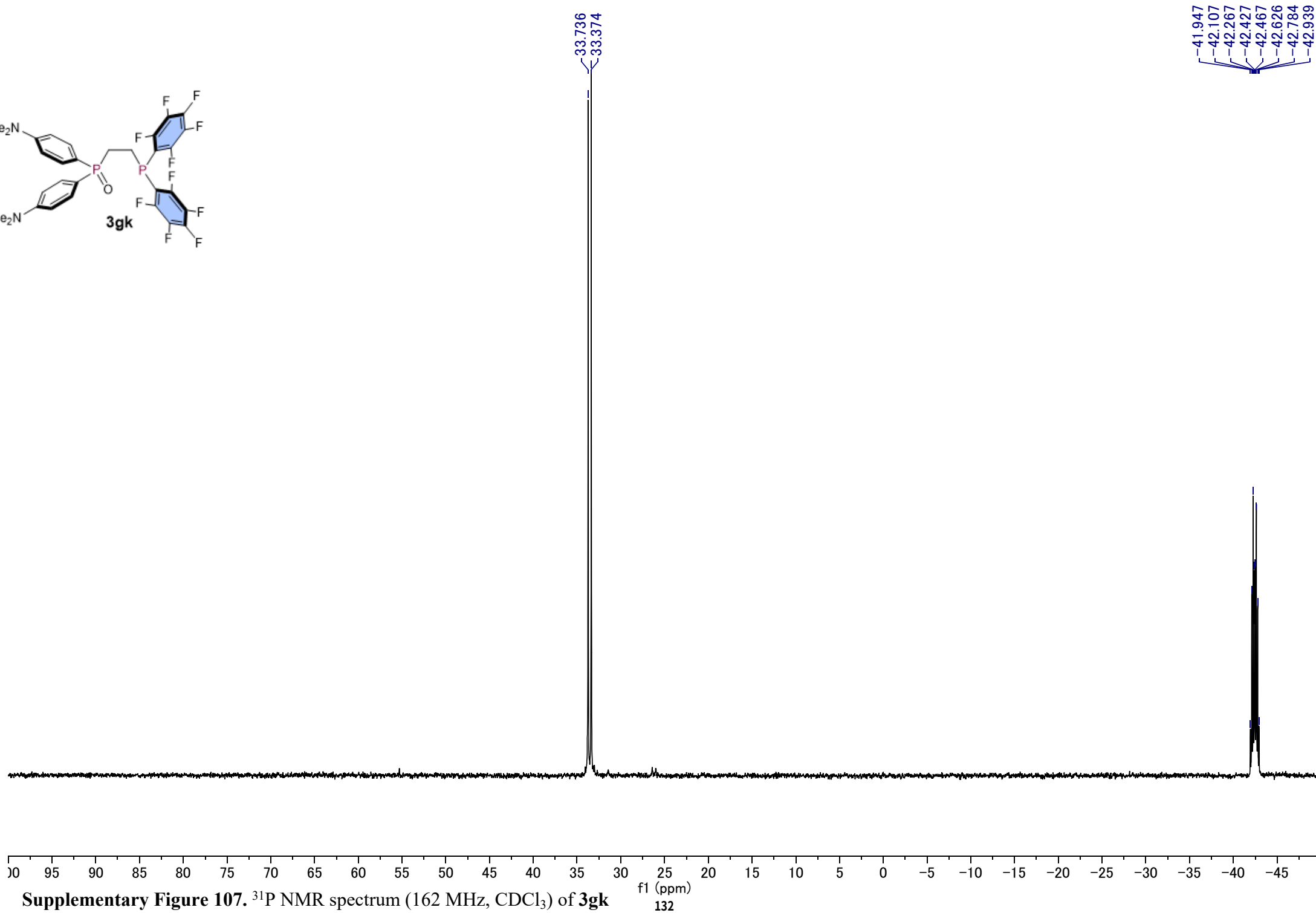
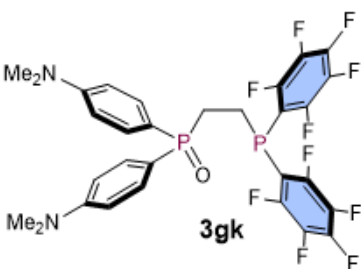
129.317
129.336
129.345
129.376
129.386
129.405
129.414
129.444
129.454
129.474
149.330
149.339
149.350
149.384
149.394
149.404
149.439
149.449
149.459
159.686
159.698
159.717
159.740
159.756
159.772
159.786
159.812
159.830
159.842



Supplementary Figure 106. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3gk**

f1 (ppm)
131

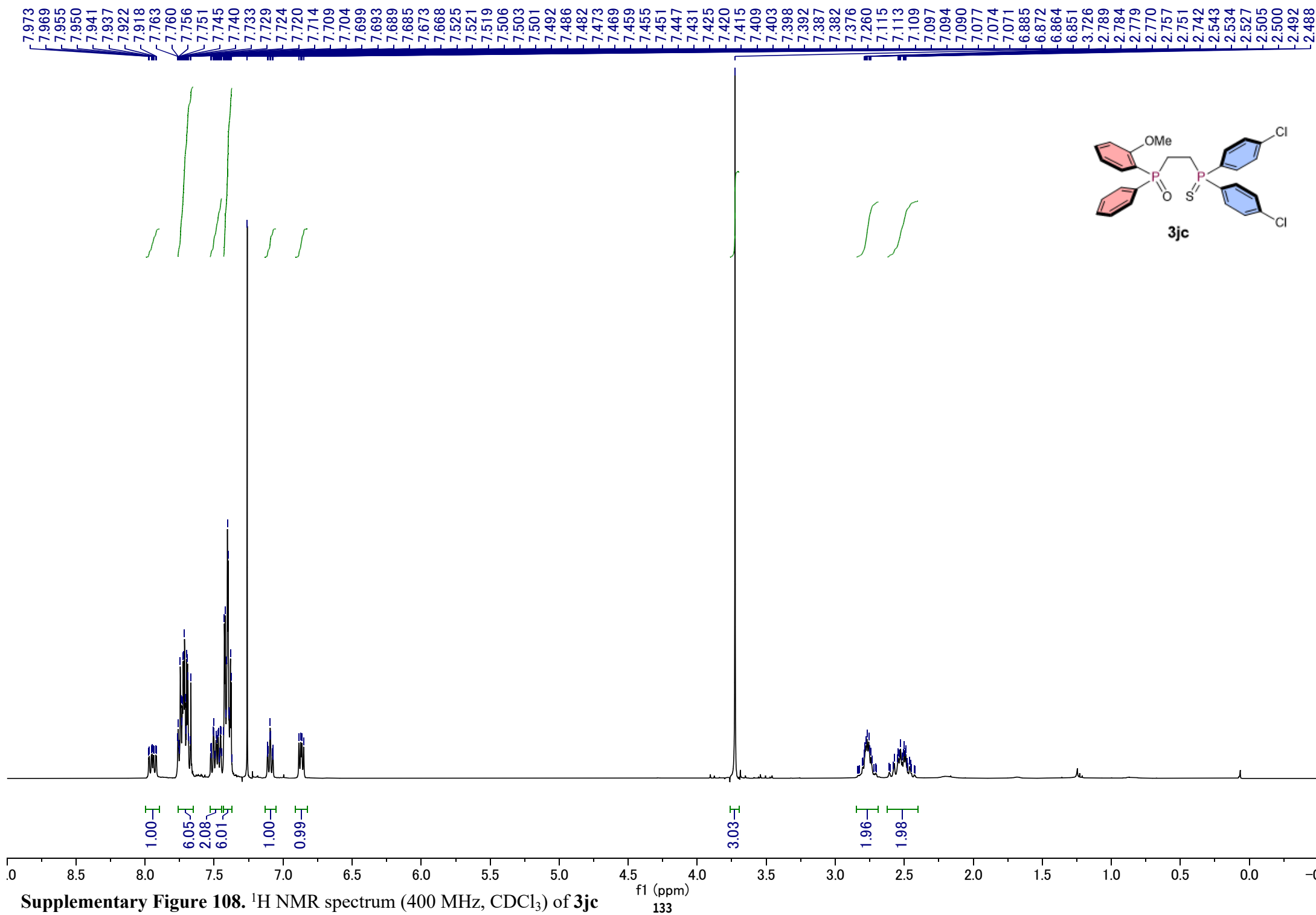
CDCl₃, 162 MHz



Supplementary Figure 107. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3gk**

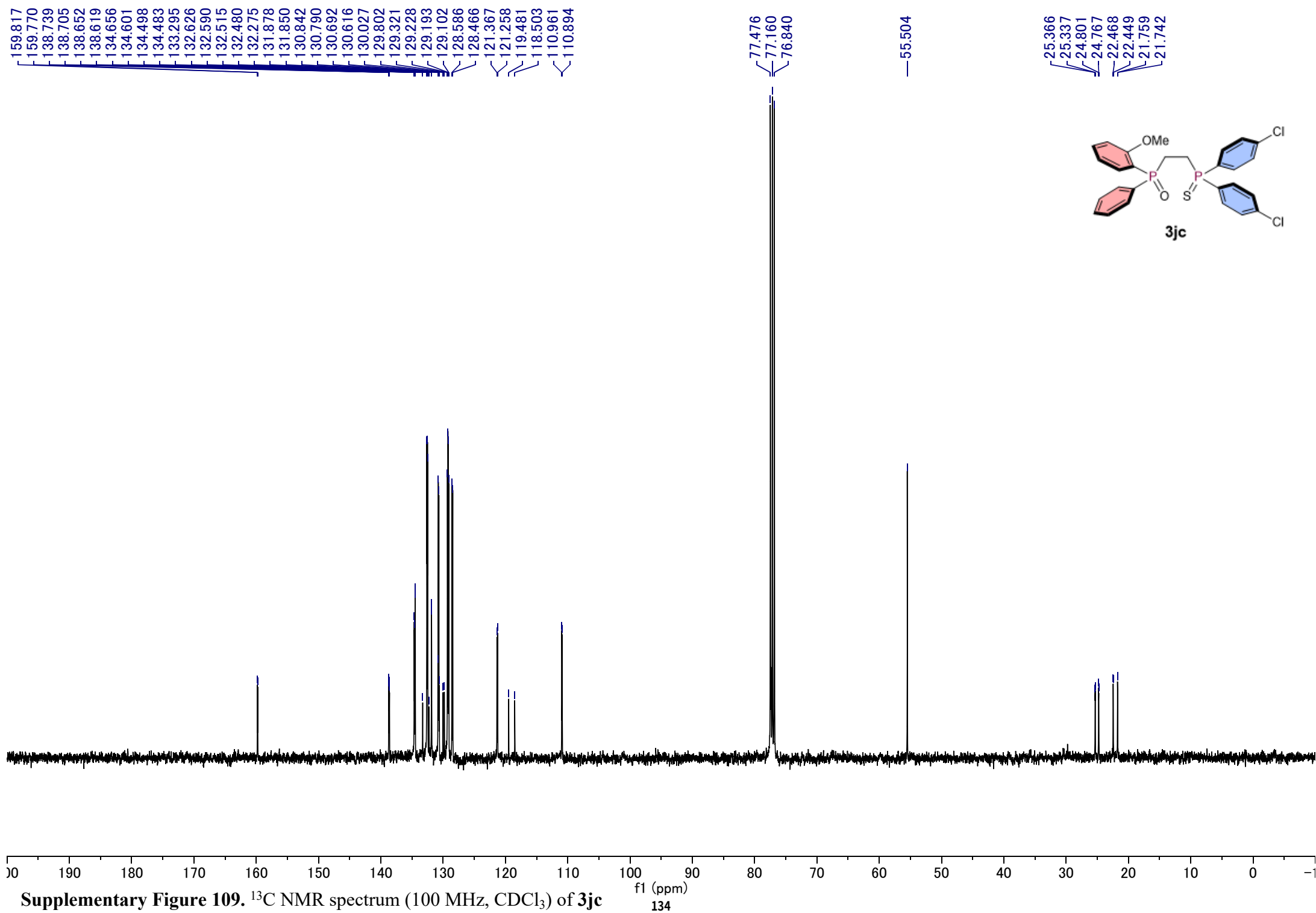
f1 (ppm)
132

CDCl₃, 400 MHz

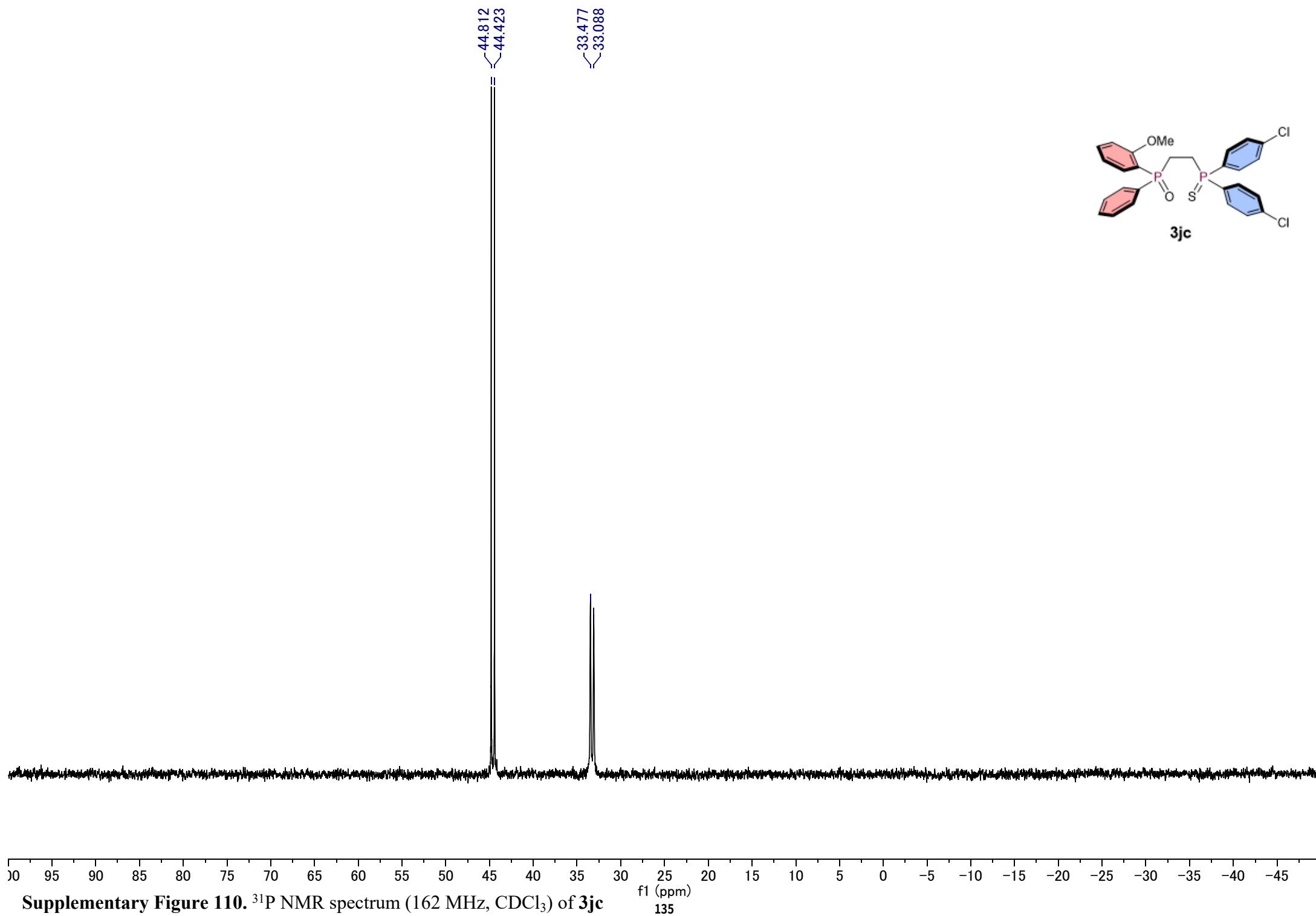


Supplementary Figure 108. ¹H NMR spectrum (400 MHz, CDCl₃) of 3jc

CDCl₃, 100 MHz



CDCl₃, 162 MHz

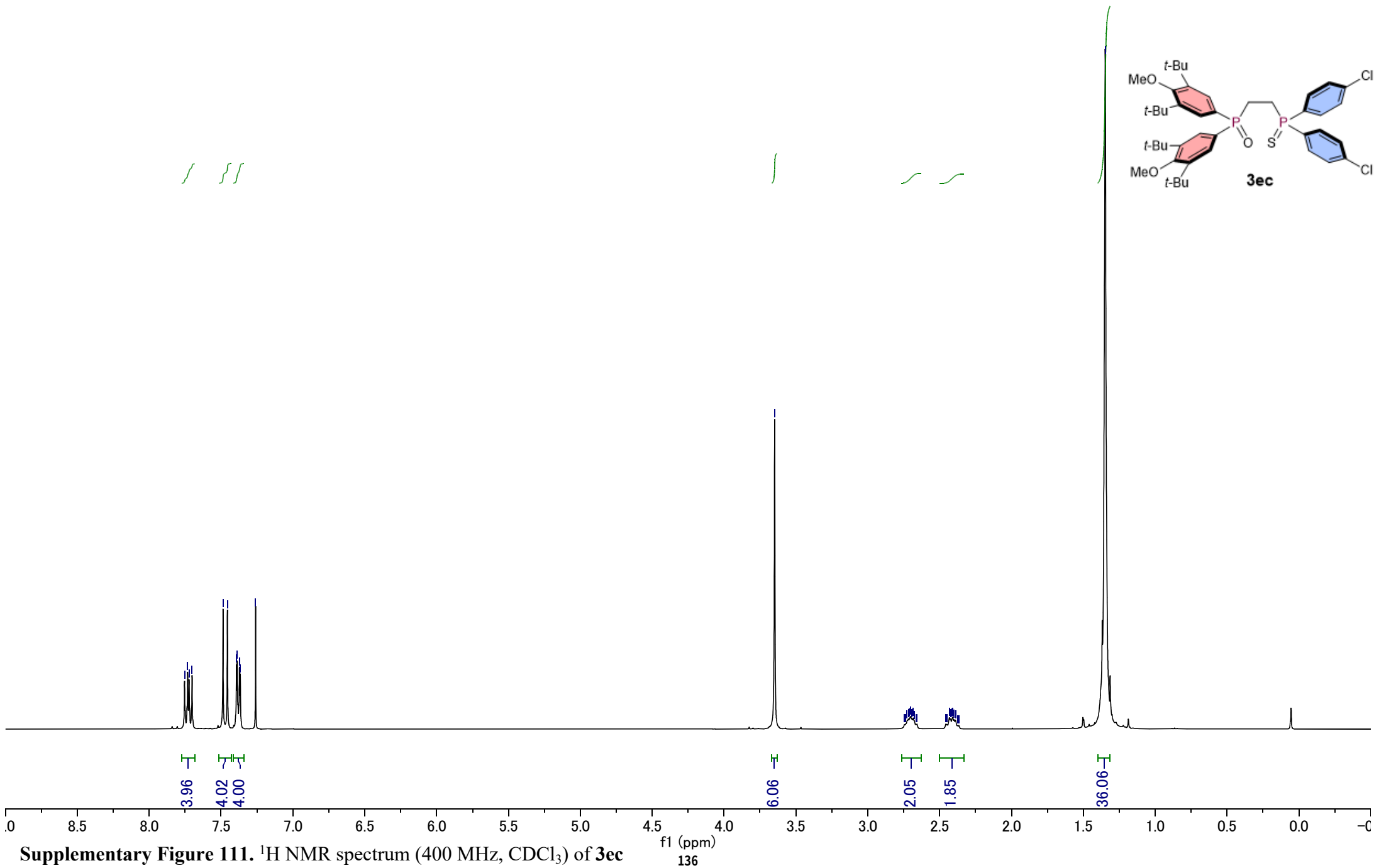
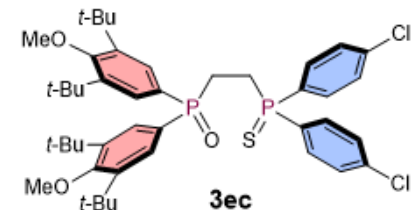


CDCl₃, 400 MHz

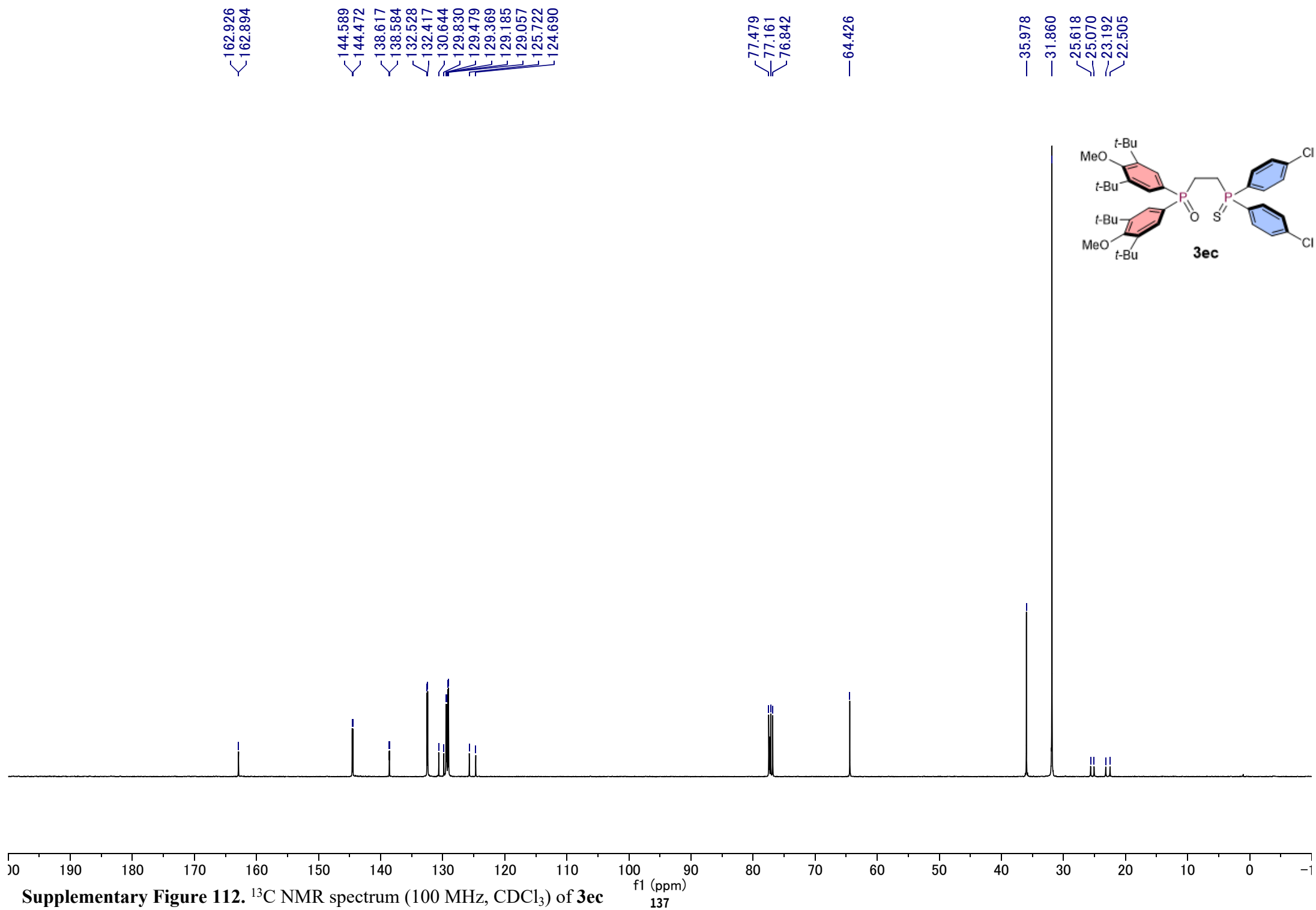
7.754
7.732
7.723
7.701
7.486
7.456
7.393
7.388
7.372
7.366
7.260

3.648

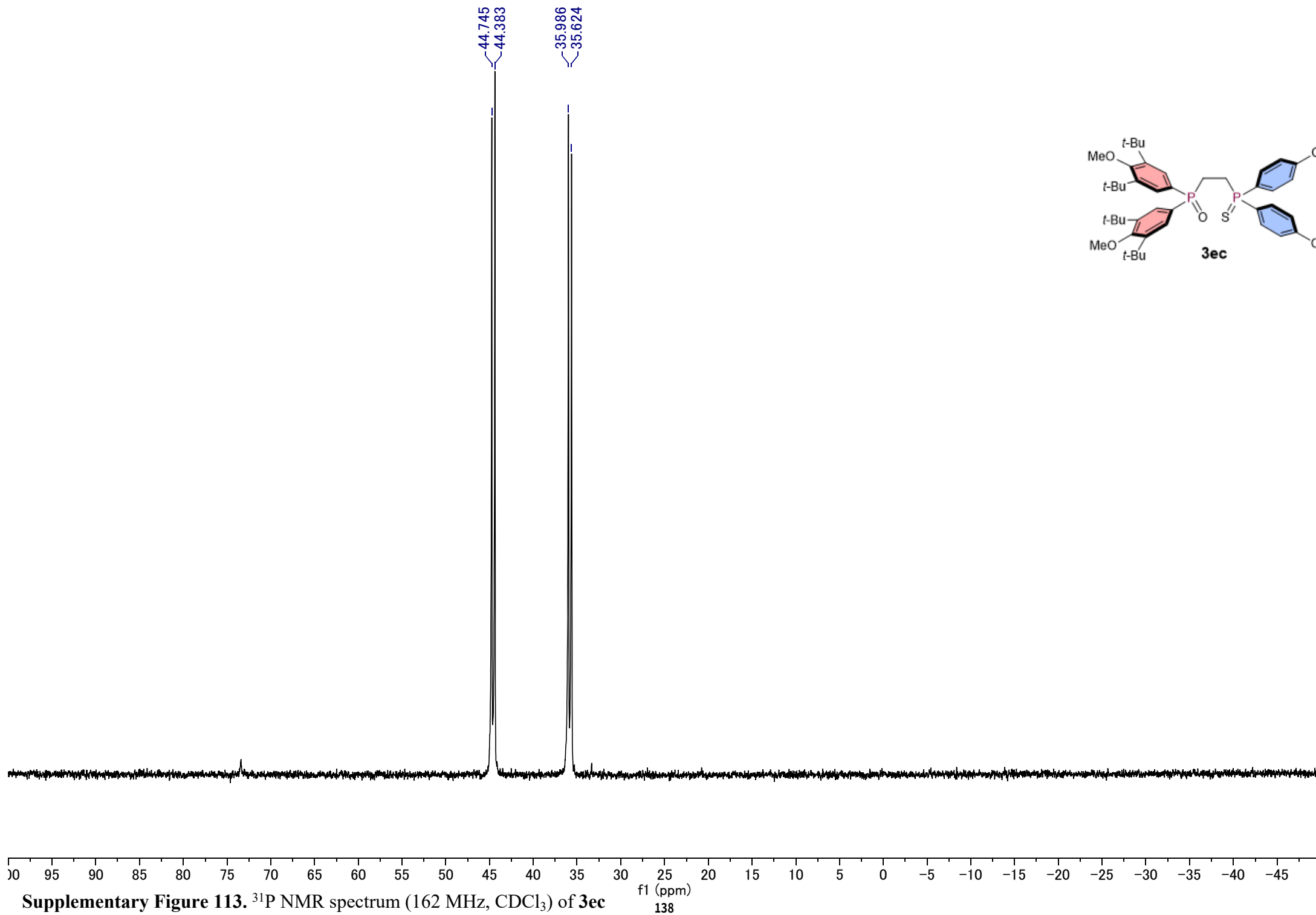
2.745
2.736
2.727
2.718
2.709
2.702
2.693
2.684
2.675
2.666
2.658
2.457
2.449
2.433
2.424
2.414
2.409
2.400
2.389
2.375
2.366
1.348



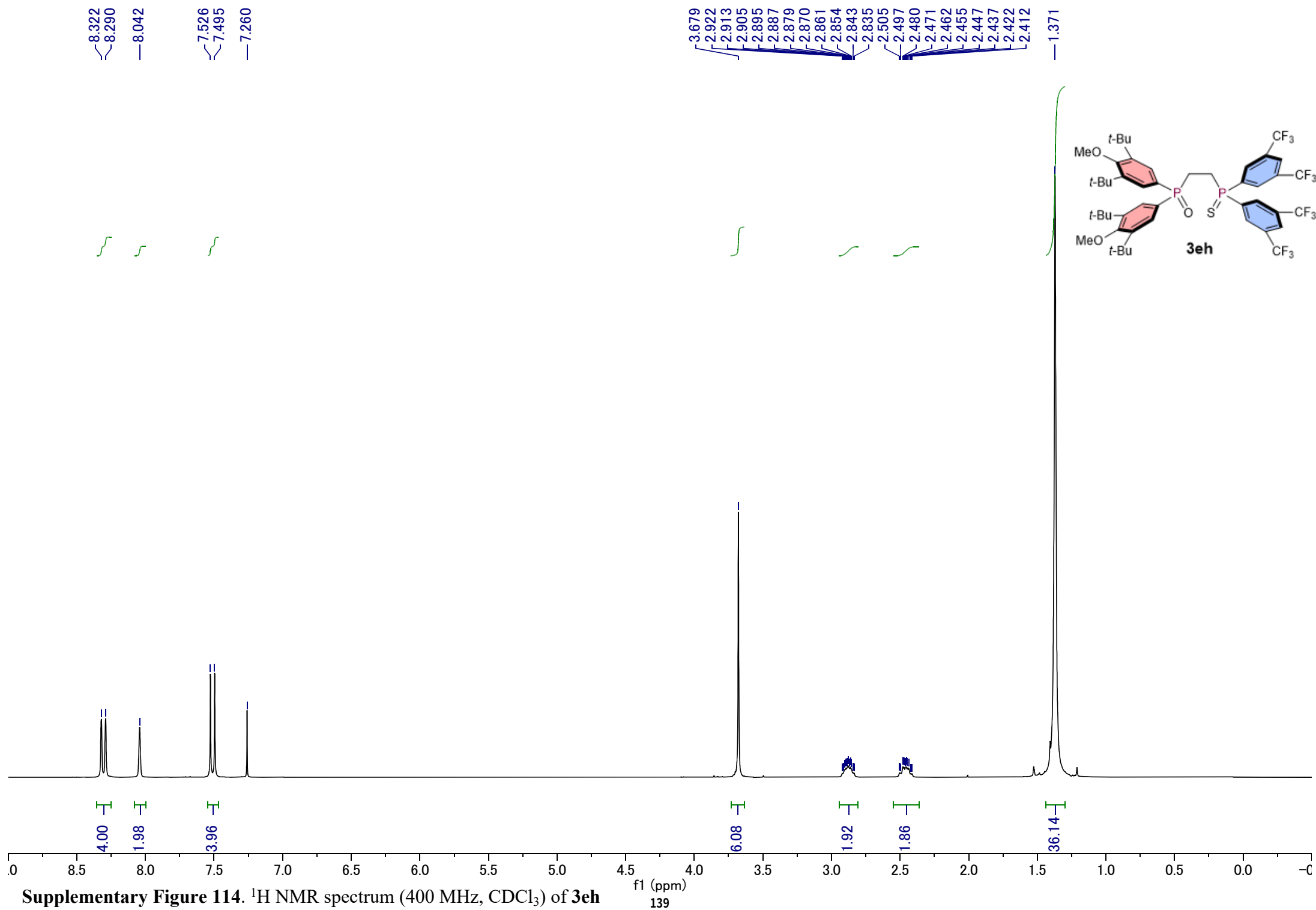
CDCl₃, 100 MHz



CDCl₃, 162 MHz



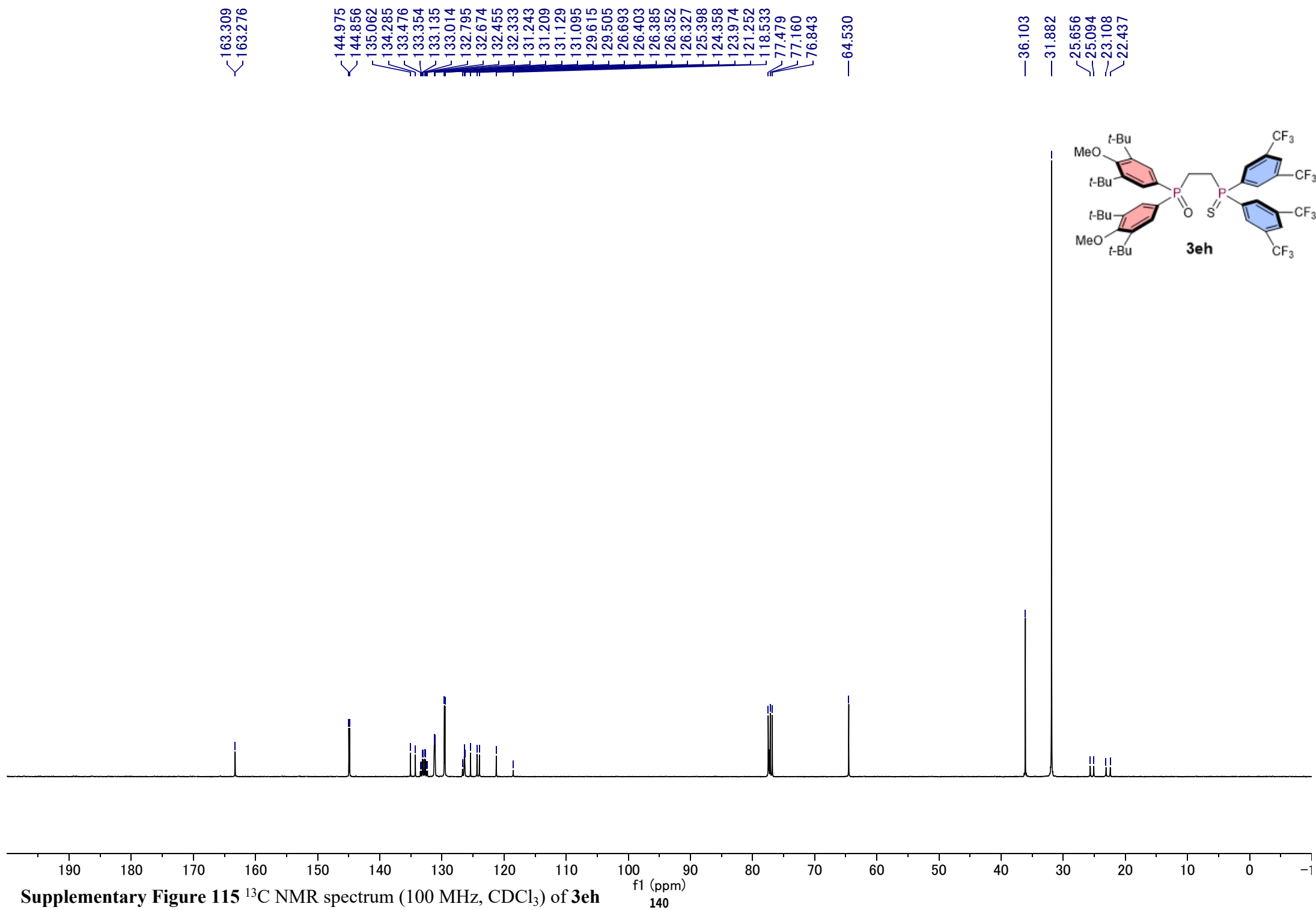
CDCl₃, 400 MHz



Supplementary Figure 114. ¹H NMR spectrum (400 MHz, CDCl₃) of **3eh**

f1 (ppm)
139

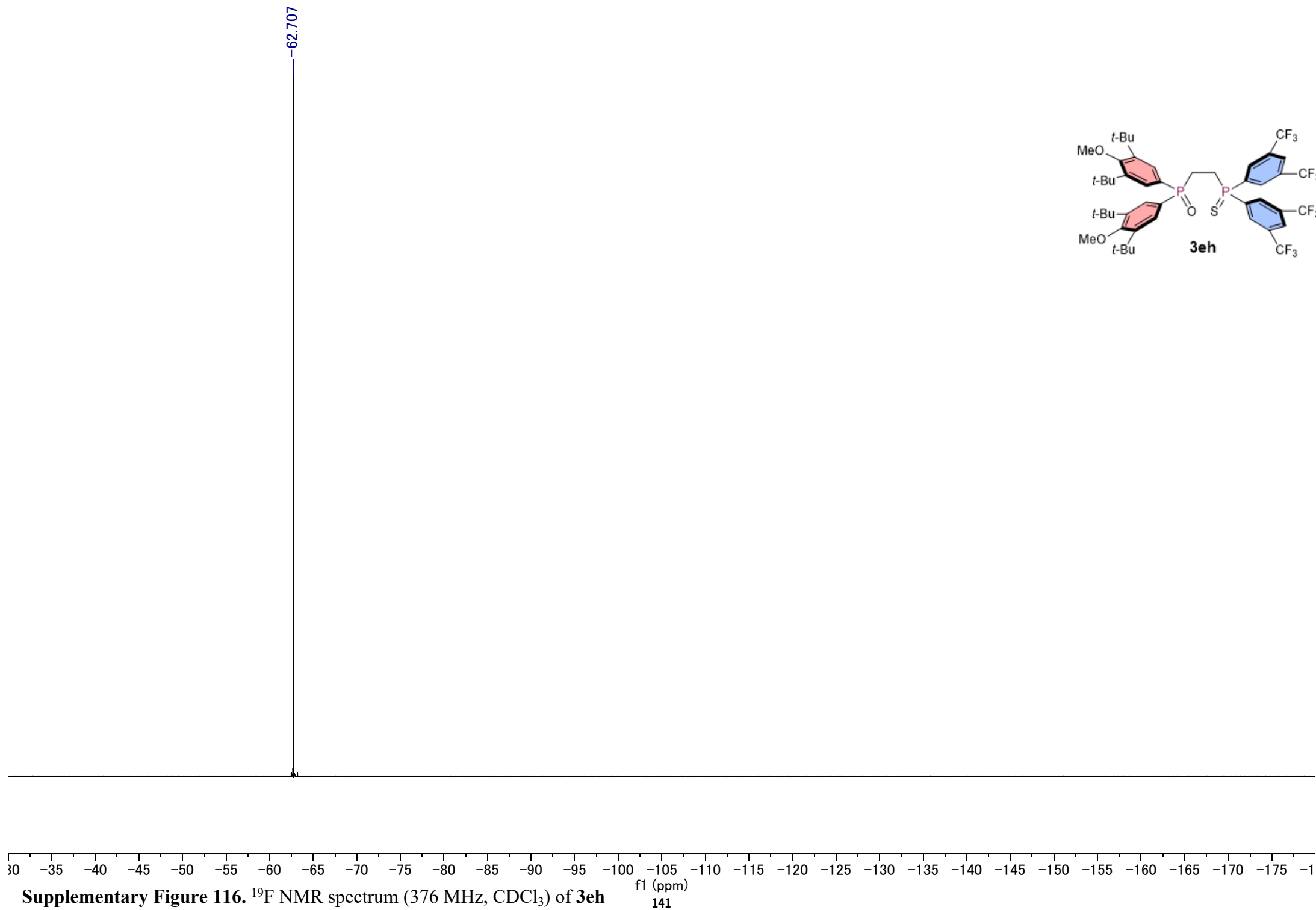
CDCl₃, 100 MHz



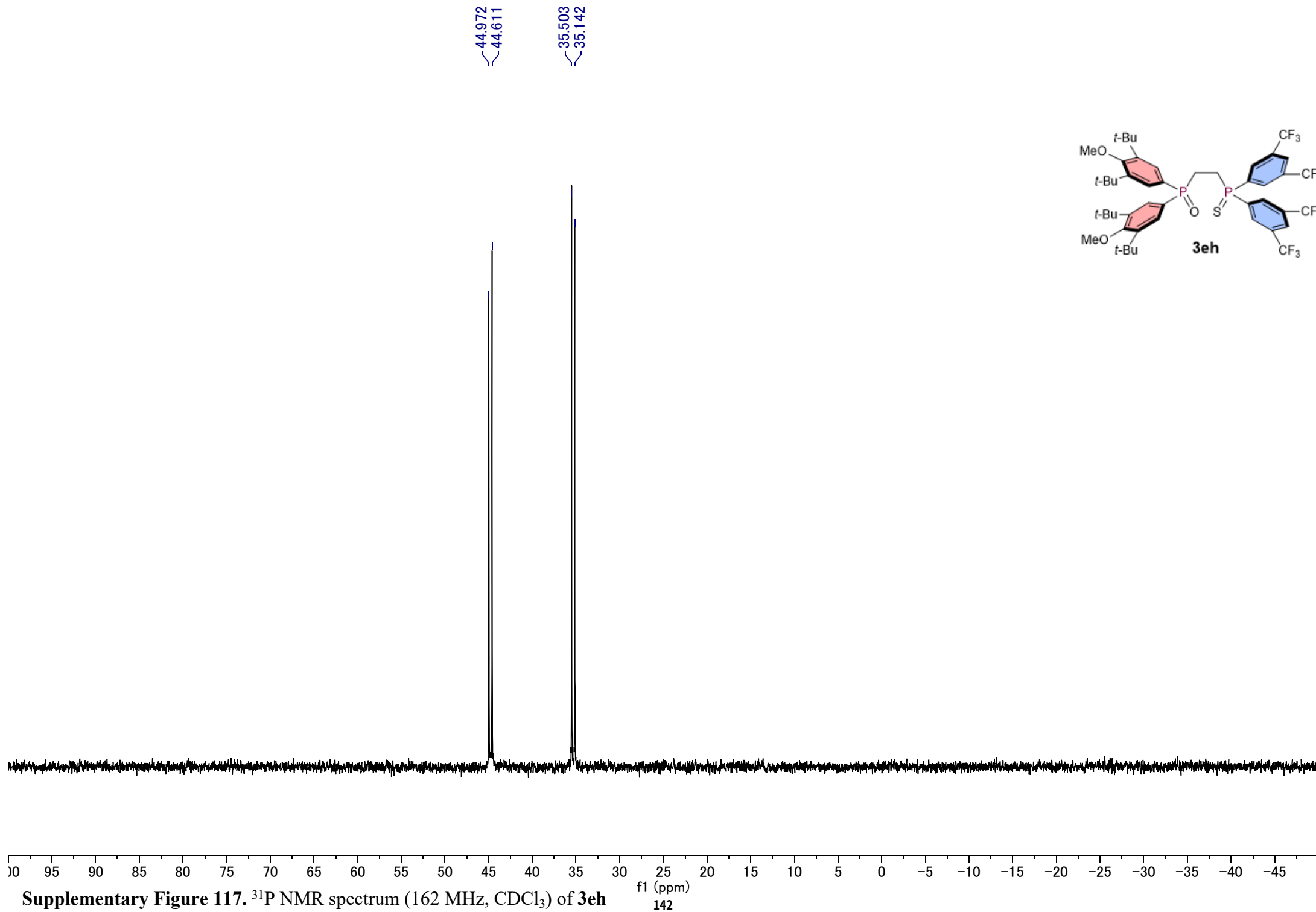
Supplementary Figure 115 ¹³C NMR spectrum (100 MHz, CDCl₃) of 3eh

f1 (ppm)
140

CDCl₃, 376 MHz



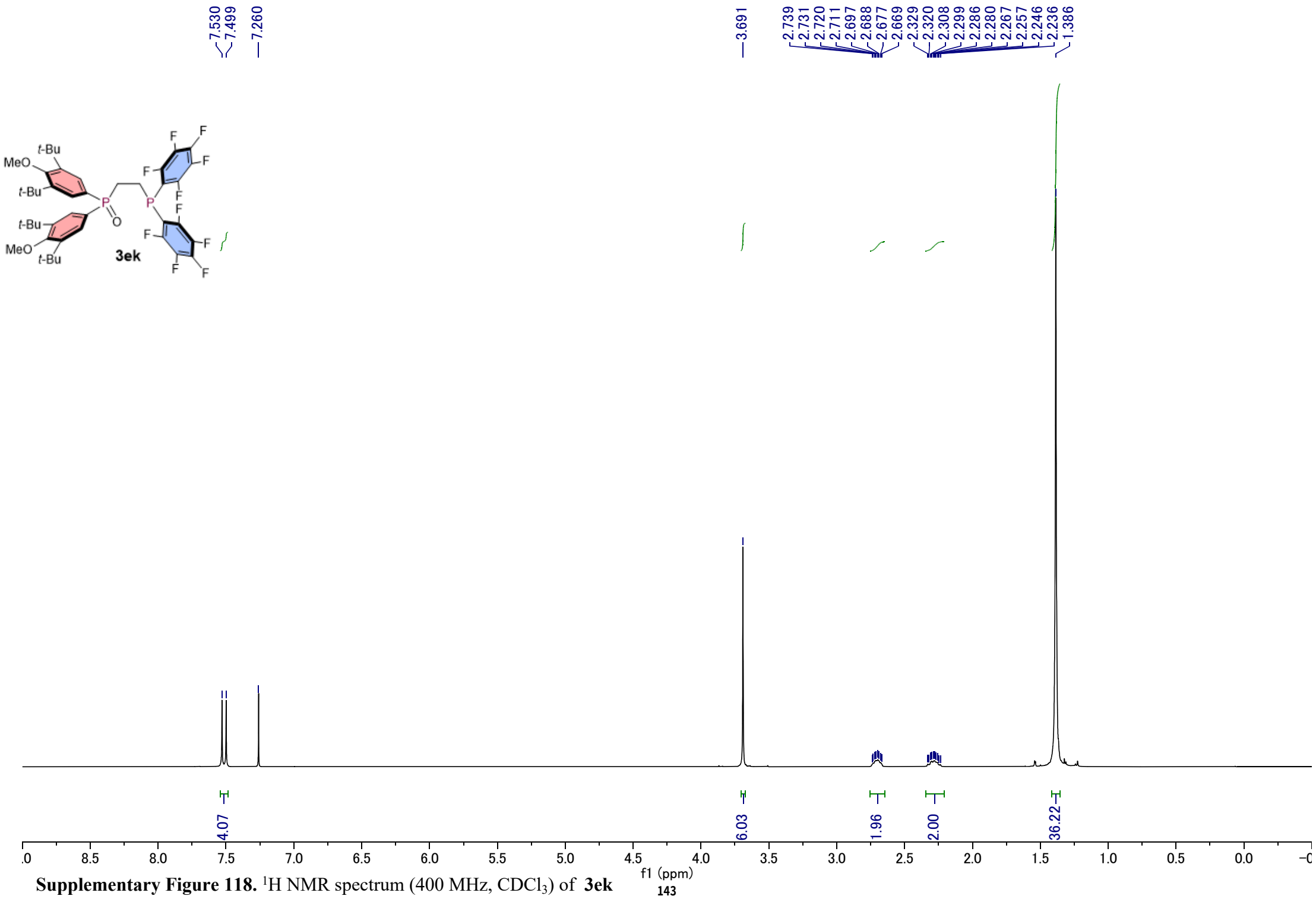
CDCl₃, 162 MHz



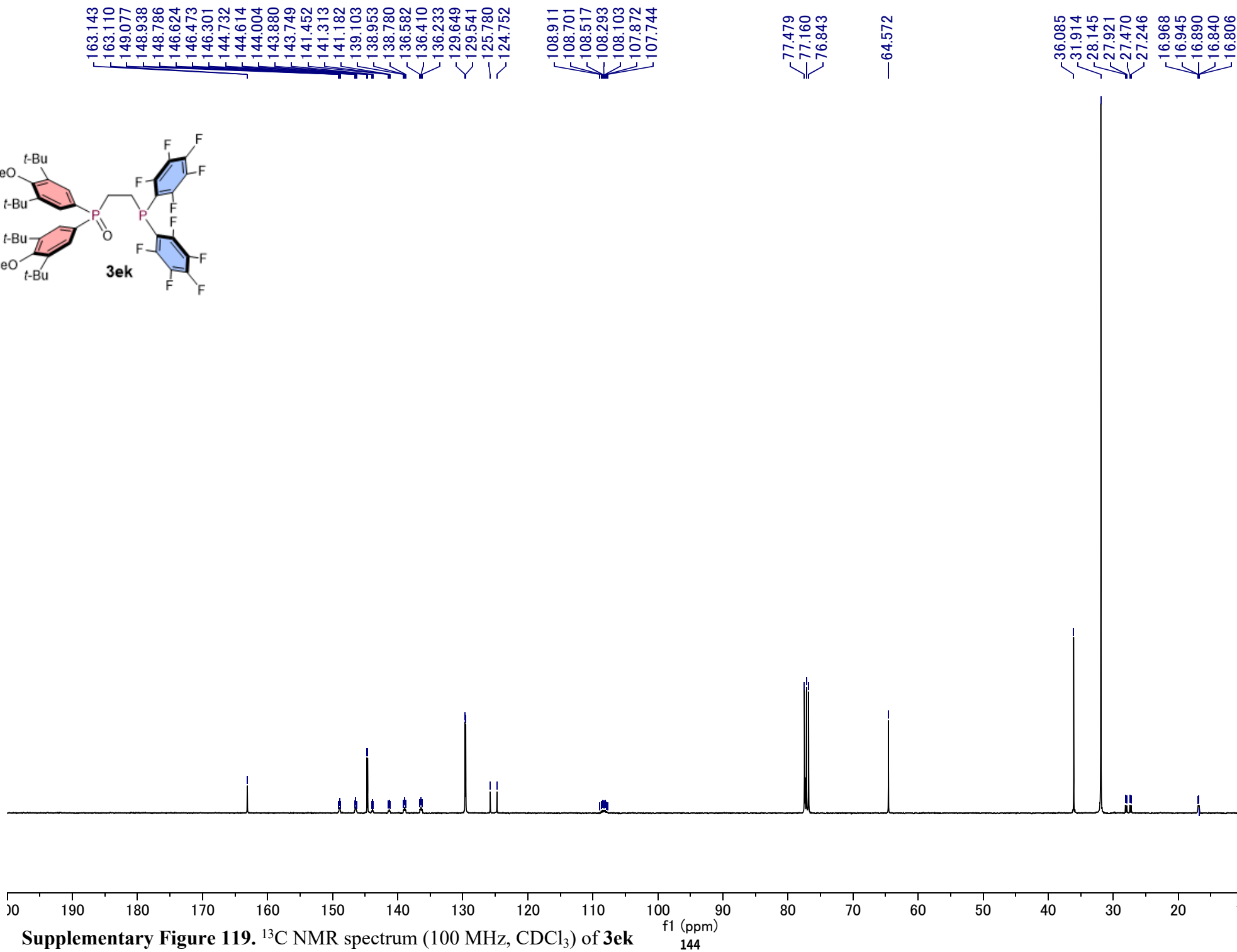
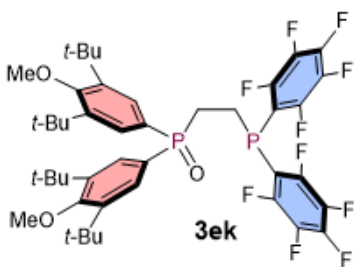
Supplementary Figure 117. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3eh**

f1 (ppm)
142

CDCl₃, 400 MHz

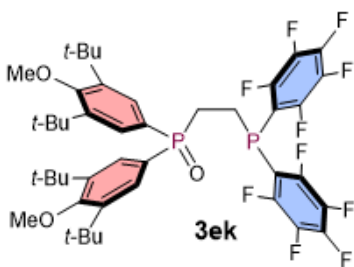


CDCl₃, 100 MHz



f1 (ppm)
144

CDCl₃, 376 MHz



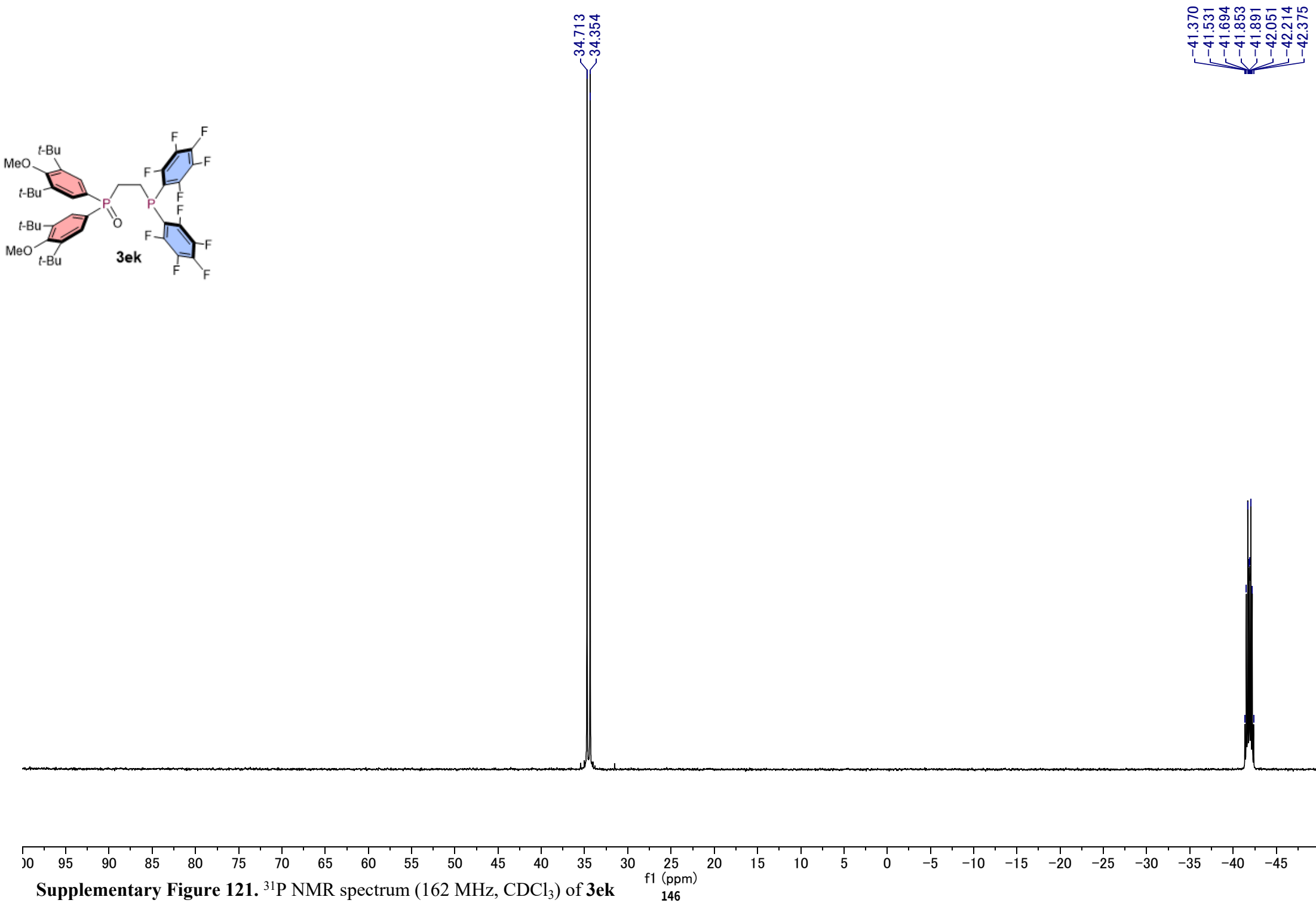
129.718
129.737
129.746
129.777
129.787
129.806
129.815
129.847
129.856
129.874
148.874
148.884
148.894
148.929
148.939
148.949
148.983
148.993
149.003
159.381
159.393
159.411
159.436
159.451
159.468
159.483
159.507
159.525
159.537

30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 120. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **3ek**

f1 (ppm)
145

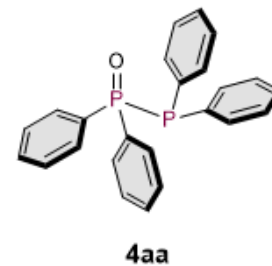
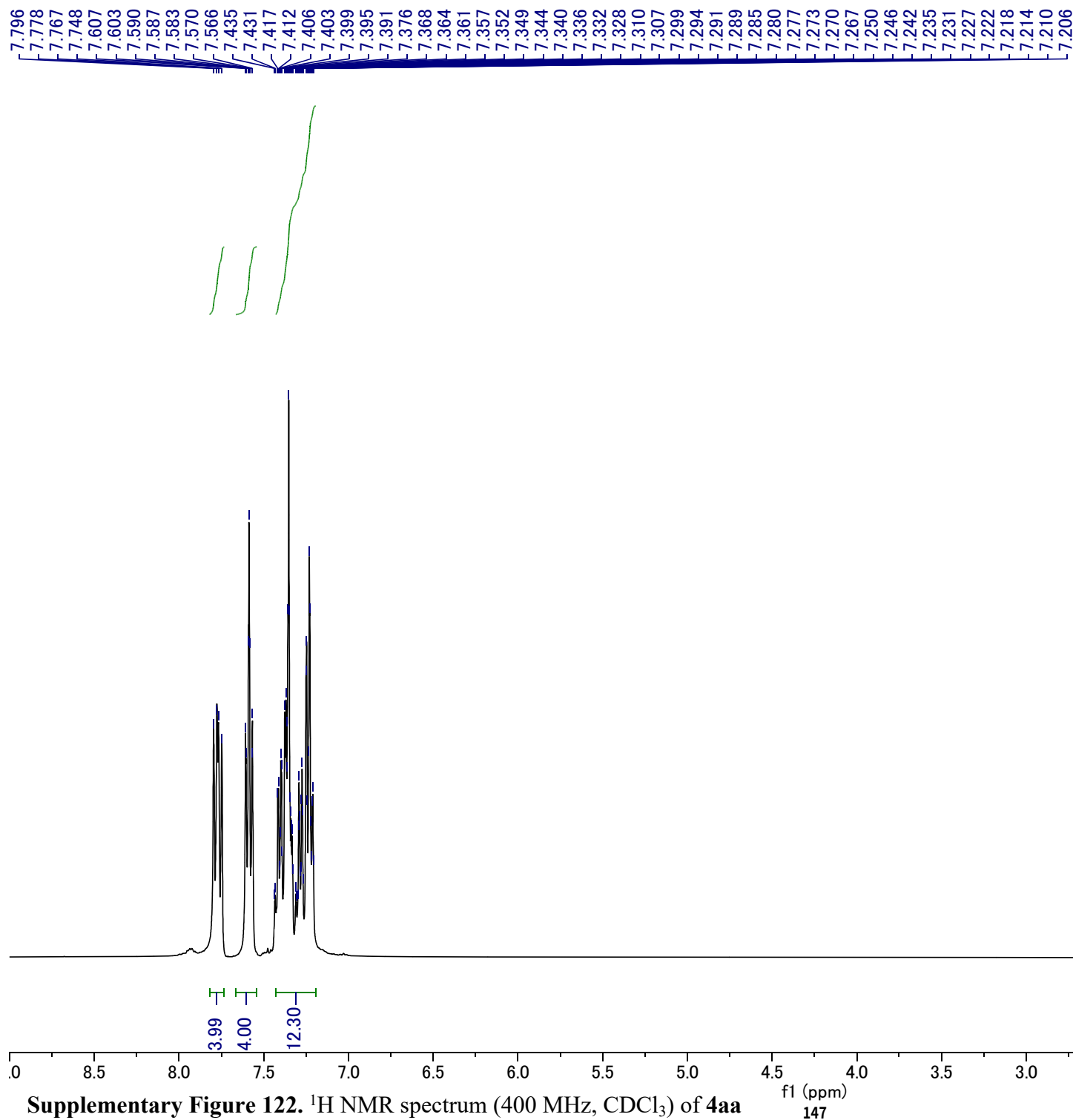
CDCl₃, 162 MHz



Supplementary Figure 121. ³¹P NMR spectrum (162 MHz, CDCl₃) of **3ek**

f1 (ppm)
146

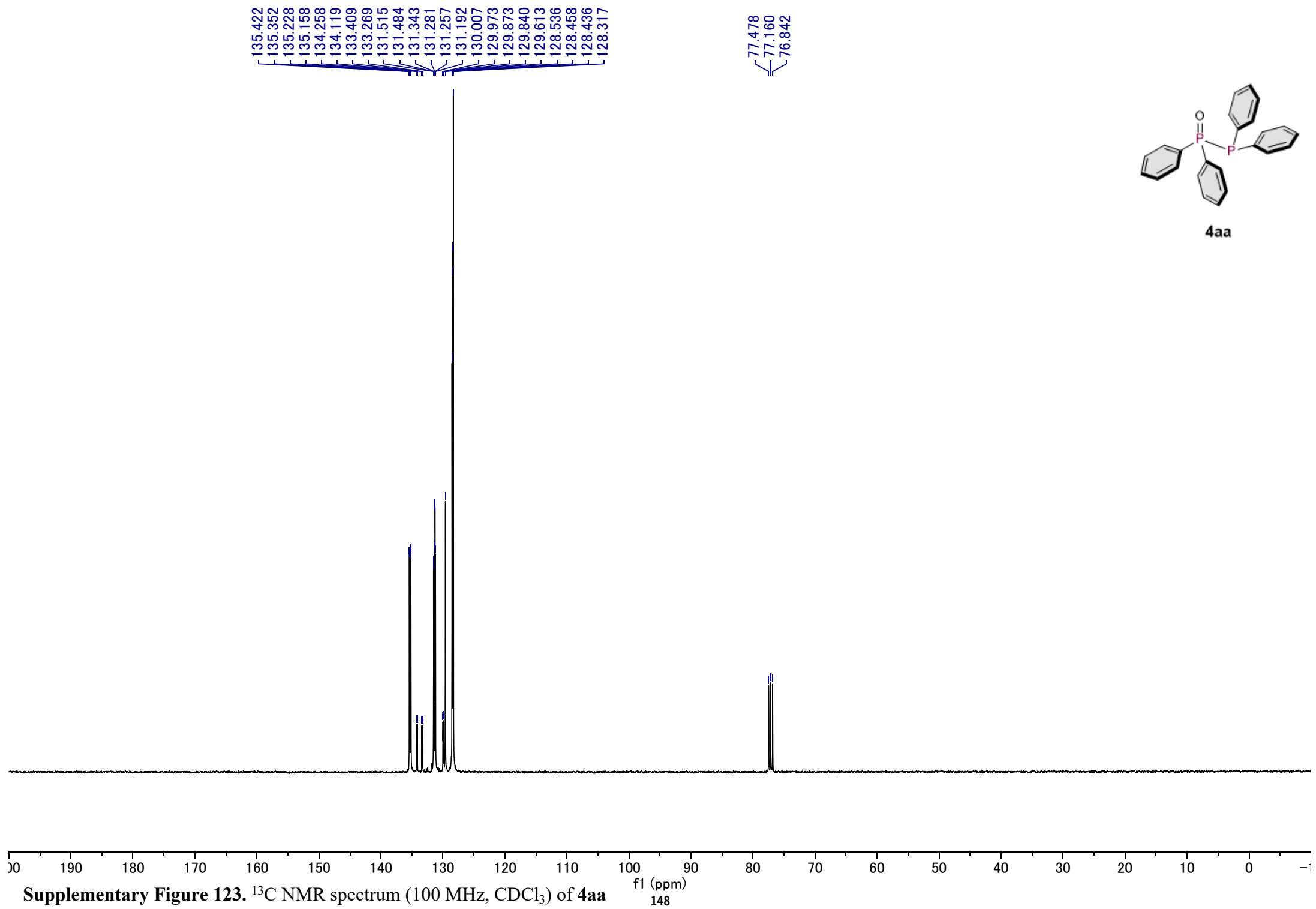
CDCl₃, 400 MHz



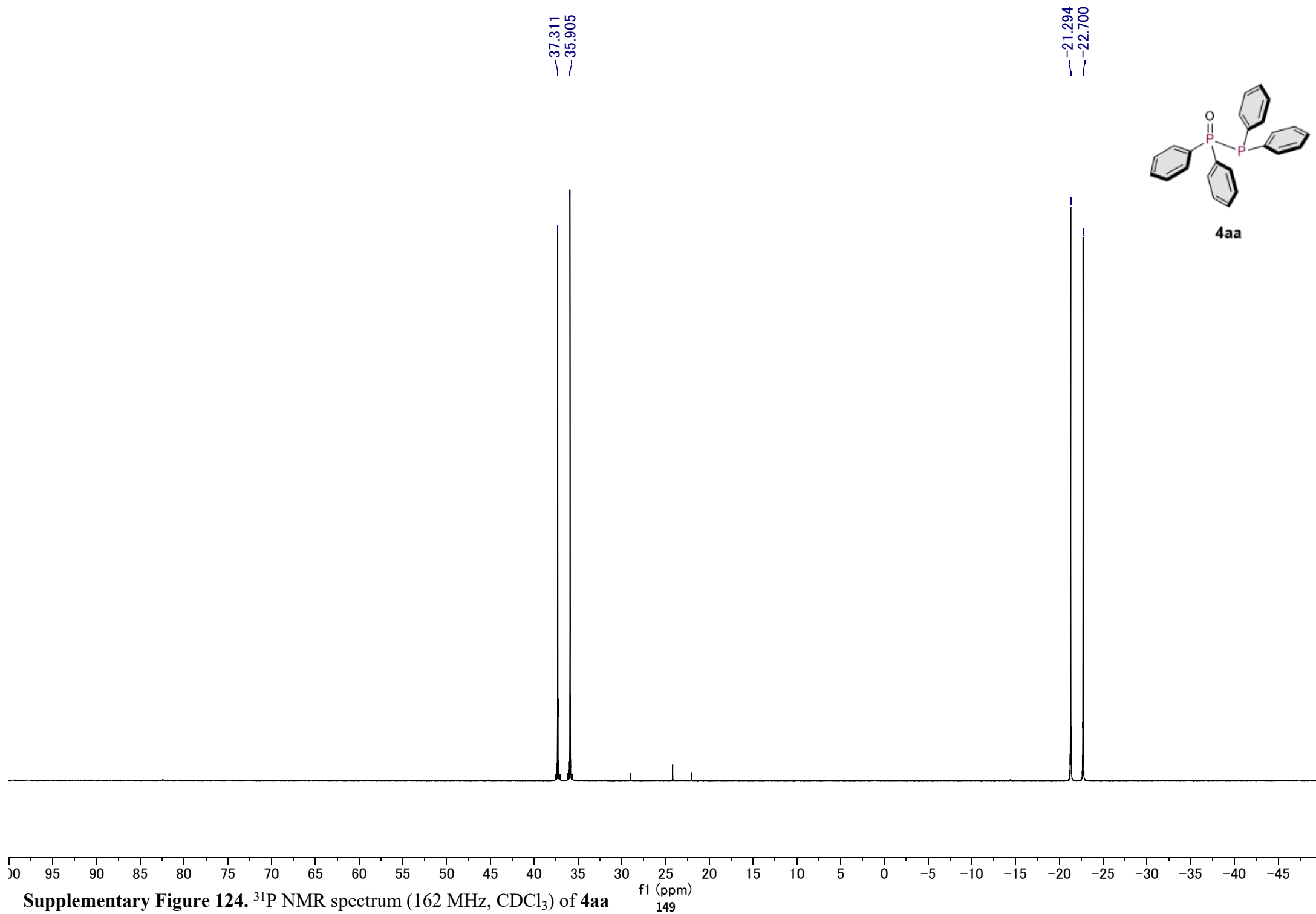
Supplementary Figure 122. ¹H NMR spectrum (400 MHz, CDCl₃) of **4aa**

f1 (ppm)
147

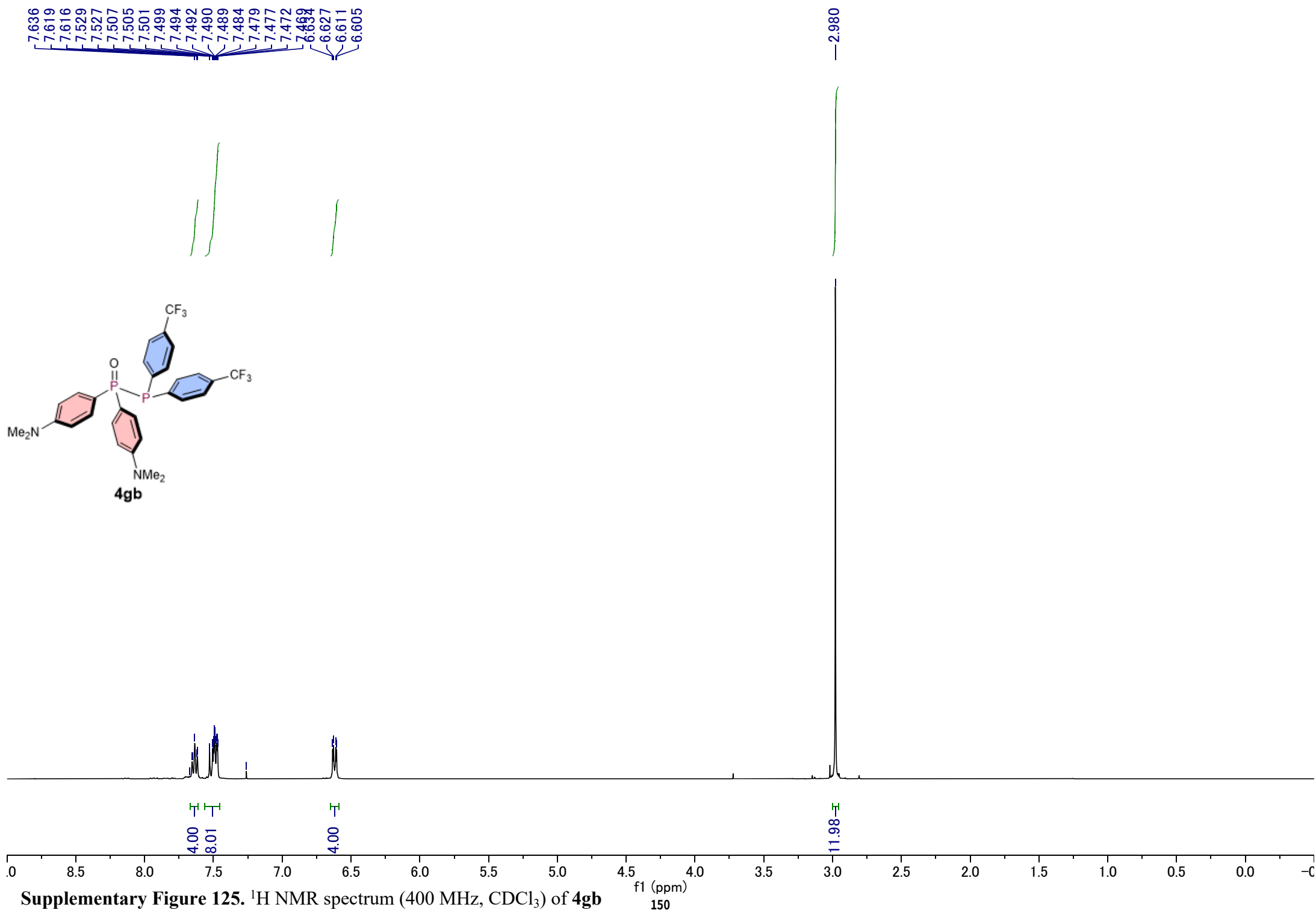
CDCl₃, 100 MHz



CDCl₃, 162 MHz

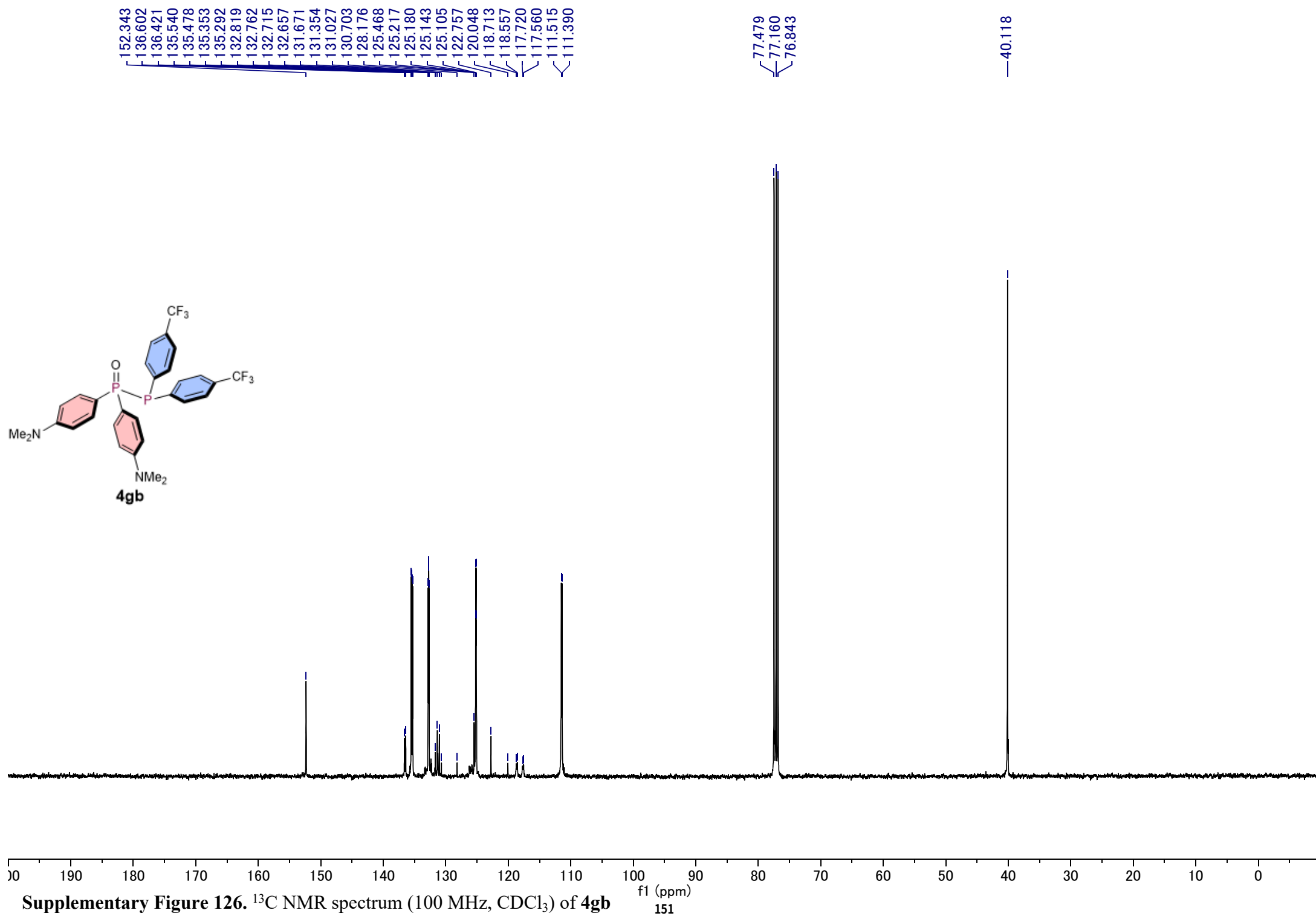


CDCl₃, 400 MHz



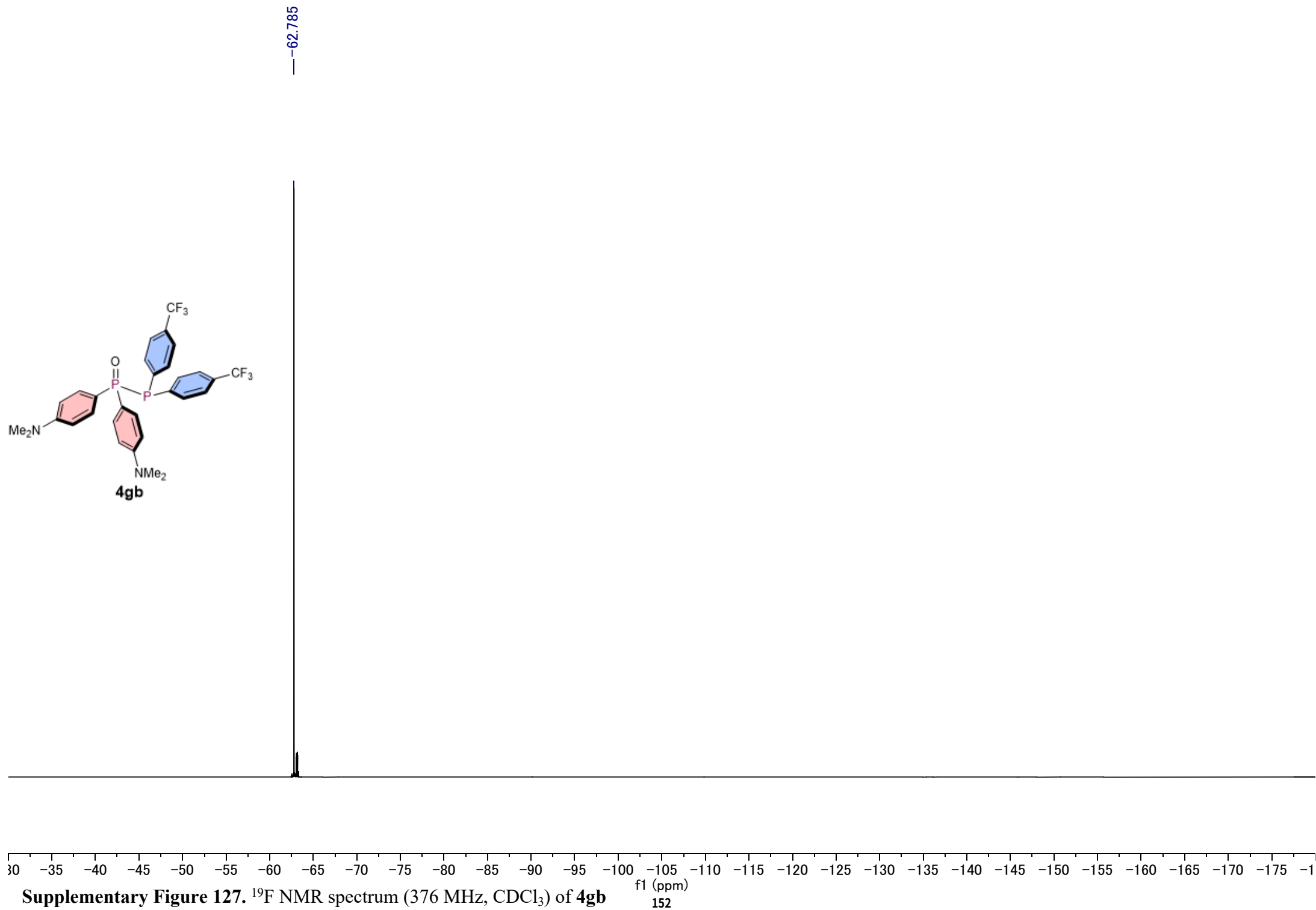
Supplementary Figure 125. ¹H NMR spectrum (400 MHz, CDCl₃) of **4gb**

CDCl₃, 100 MHz

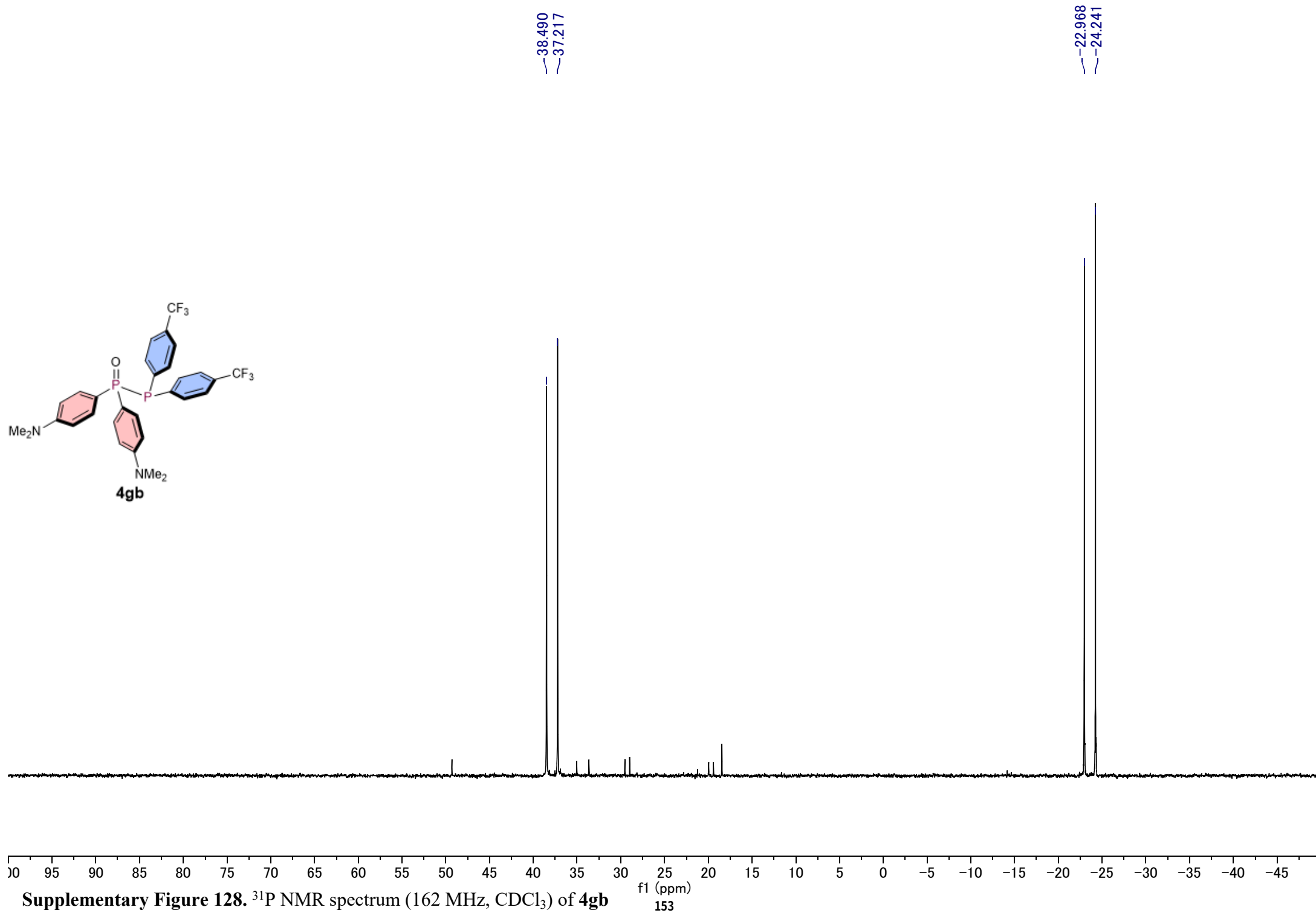


Supplementary Figure 126. ¹³C NMR spectrum (100 MHz, CDCl₃) of **4gb**

CDCl₃, 376 MHz

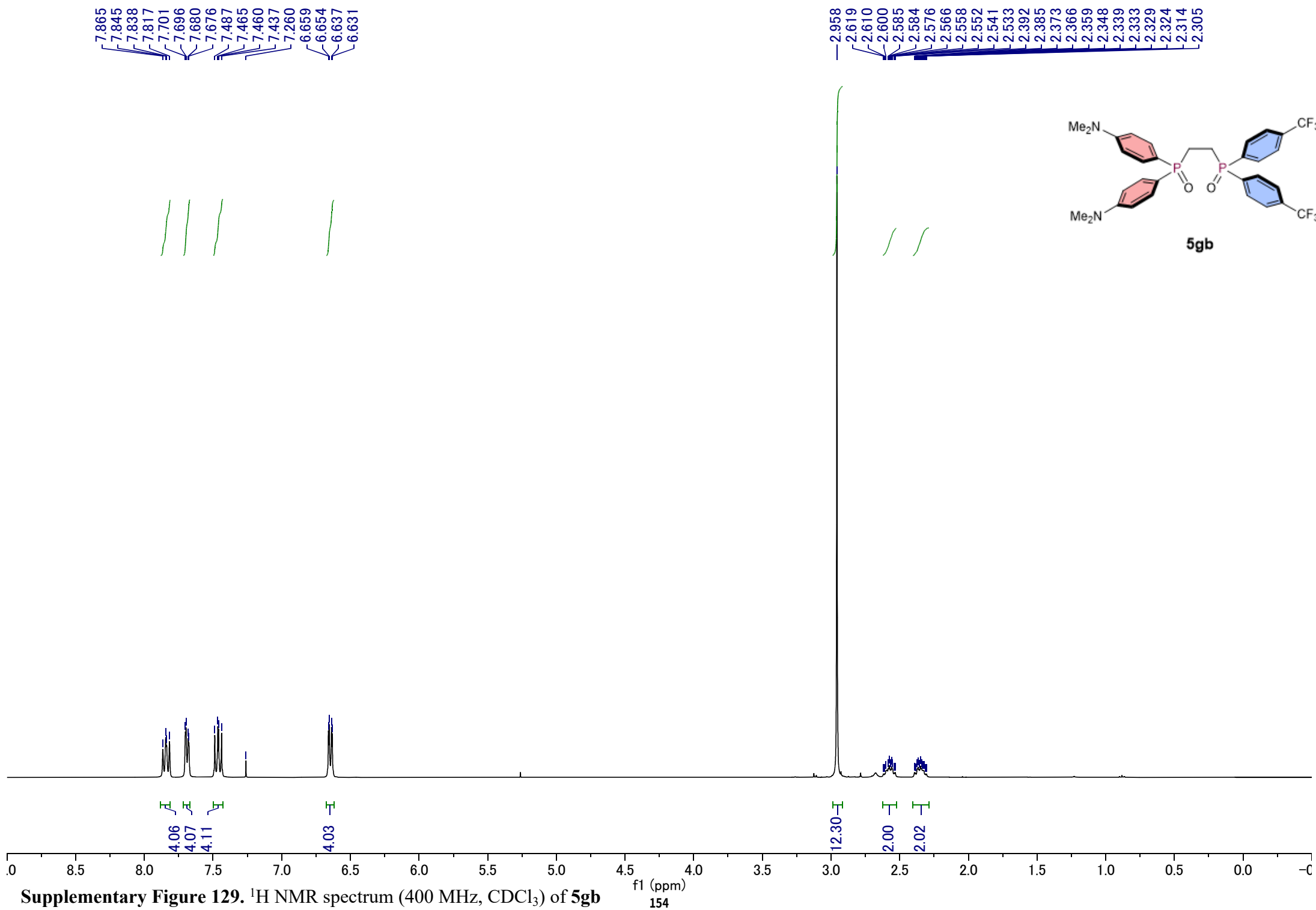


CDCl₃, 162 MHz



Supplementary Figure 128. ³¹P NMR spectrum (162 MHz, CDCl₃) of **4gb**

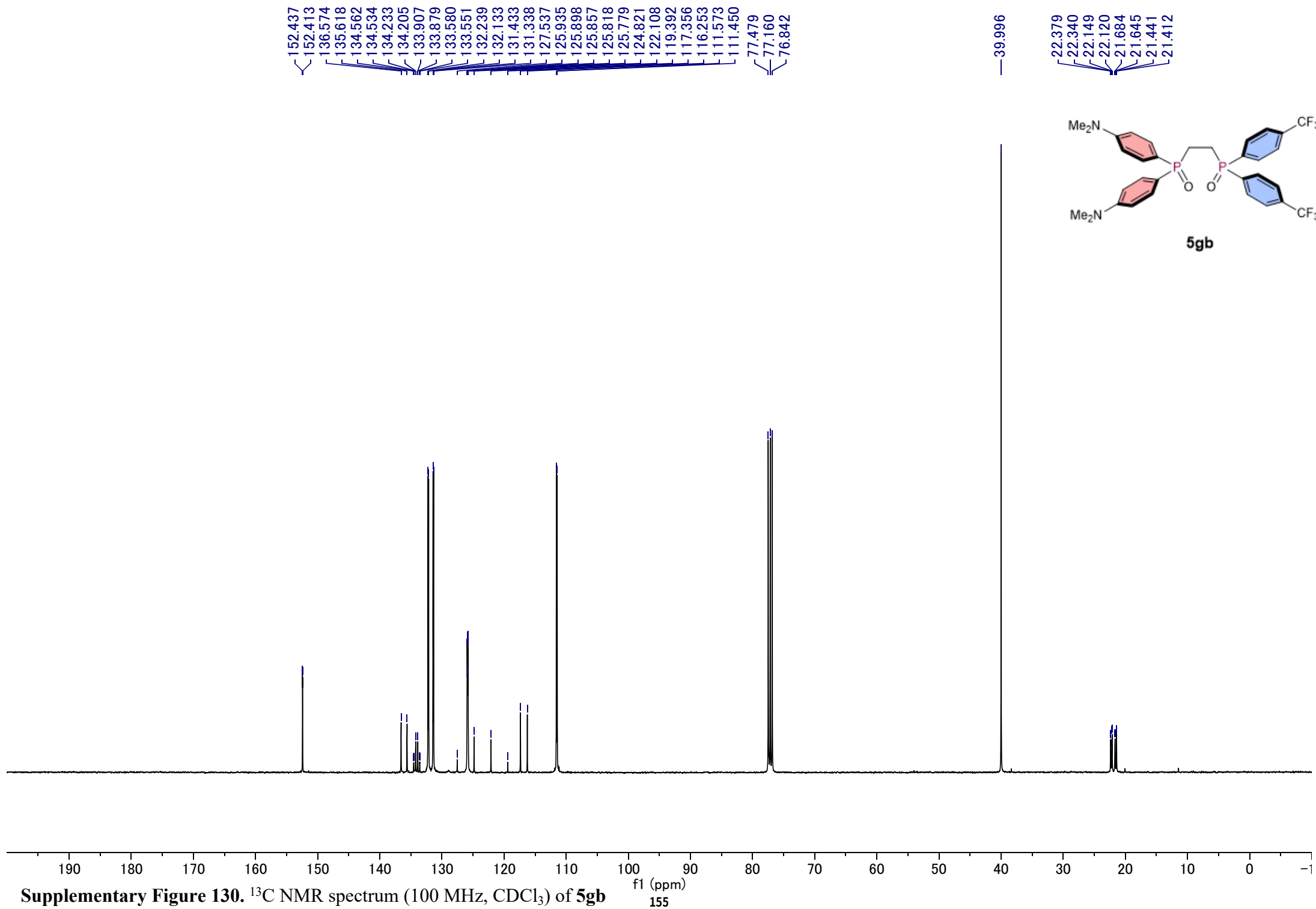
CDCl₃, 400 MHz



Supplementary Figure 129. ¹H NMR spectrum (400 MHz, CDCl₃) of **5gb**

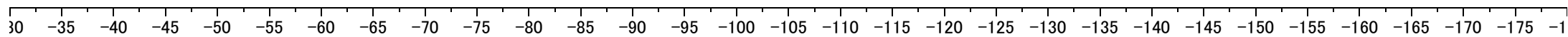
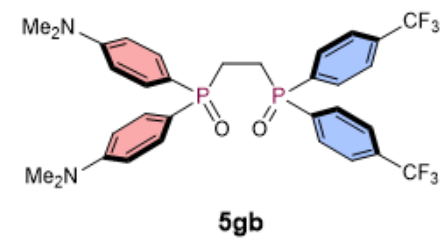
f1 (ppm)
154

CDCl₃, 100 MHz



CDCl₃, 376 MHz

---63.154

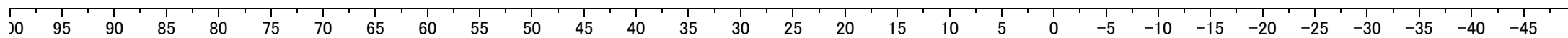
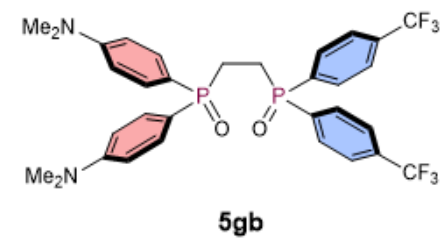


Supplementary Figure 131. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **5gb**

f1 (ppm)
156

CDCl₃, 162 MHz

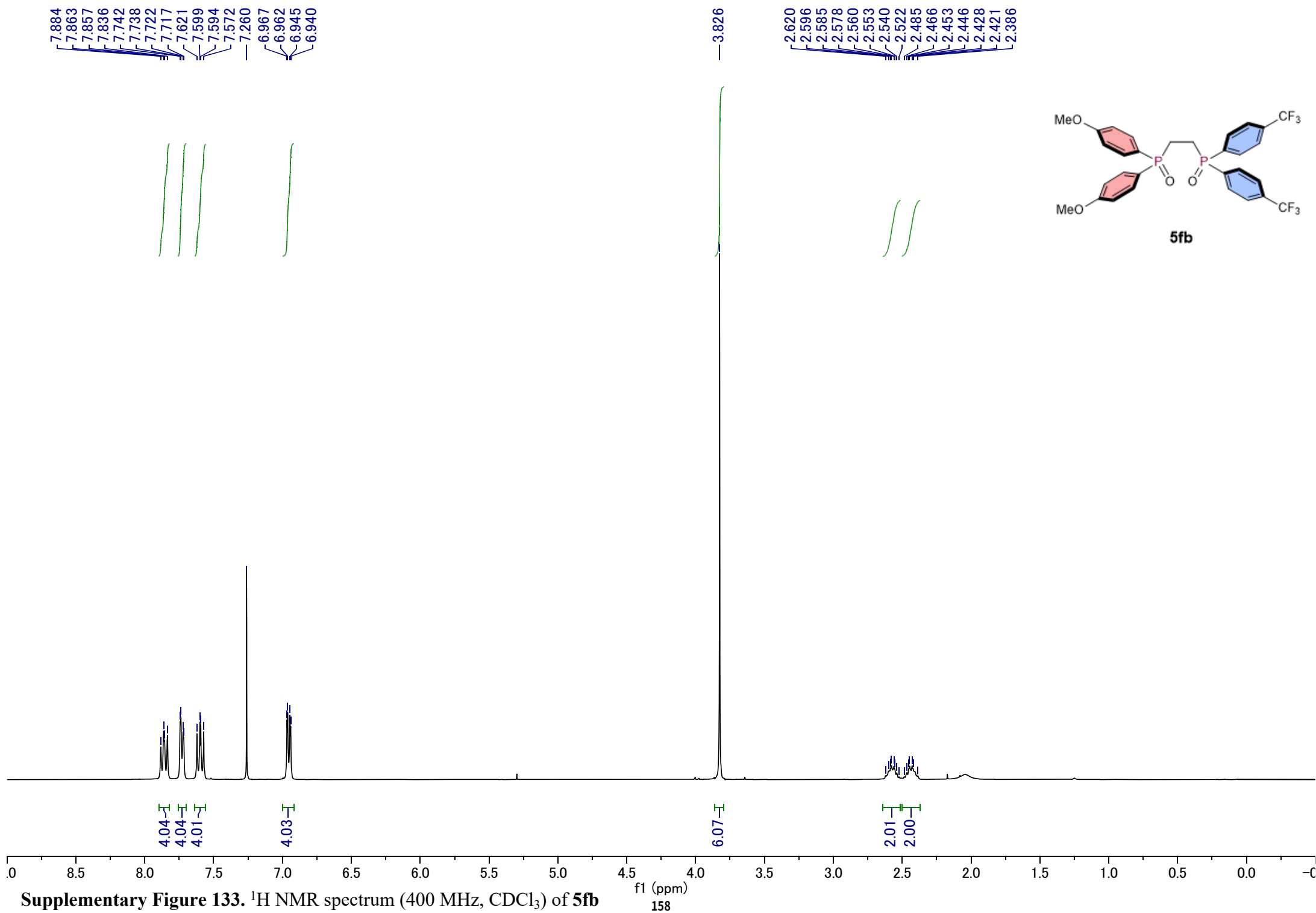
34.178
33.857
32.142
32.111
31.821



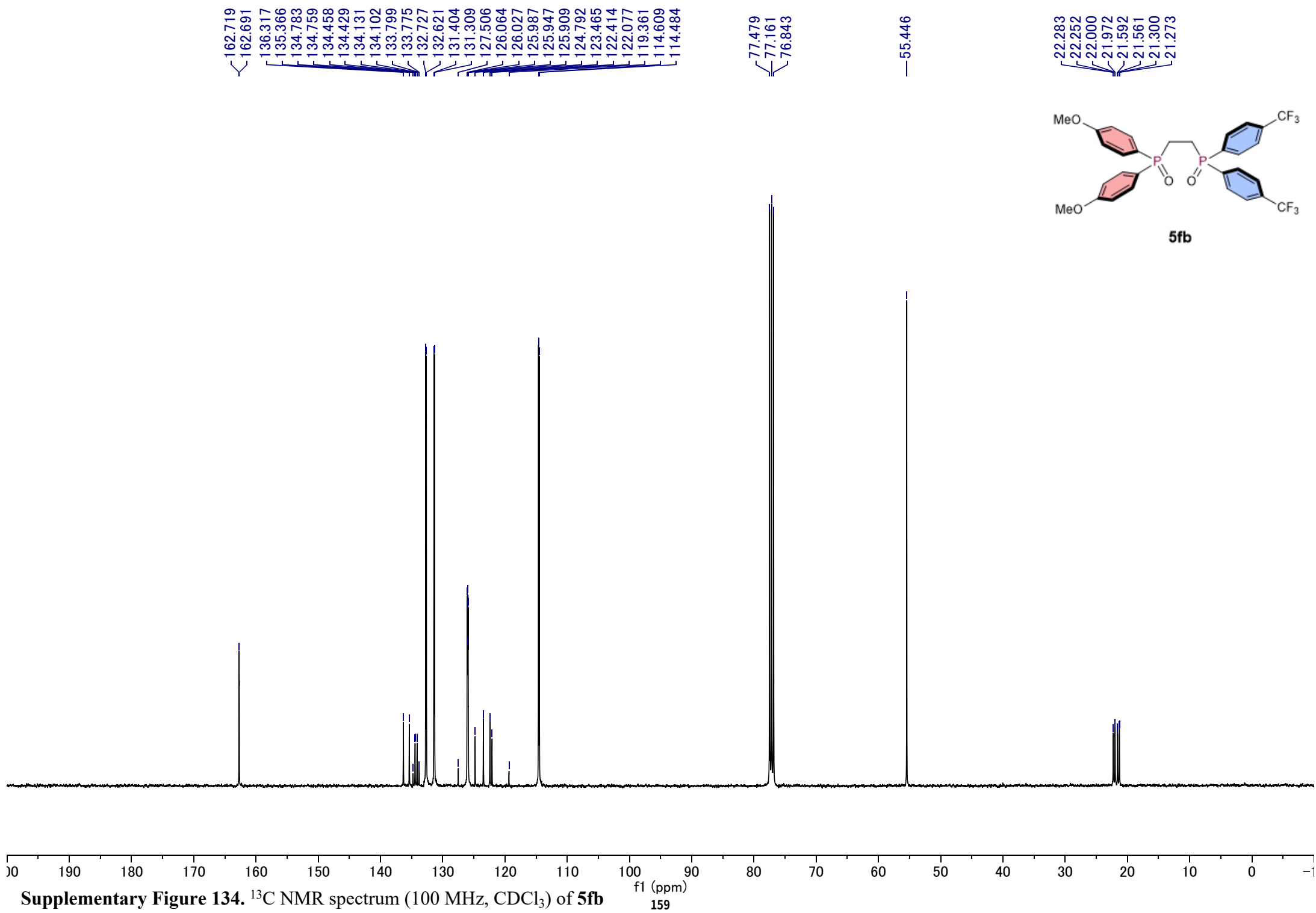
Supplementary Figure 132. ³¹P NMR spectrum (162 MHz, CDCl₃) of **5gb**

f1 (ppm)
157

CDCl₃, 400 MHz

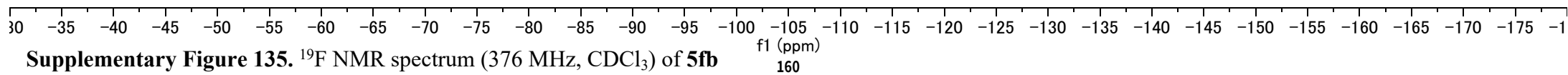
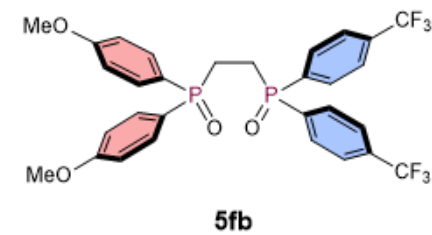


Supplementary Figure 133. ¹H NMR spectrum (400 MHz, CDCl₃) of **5fb**



CDCl₃, 376 MHz

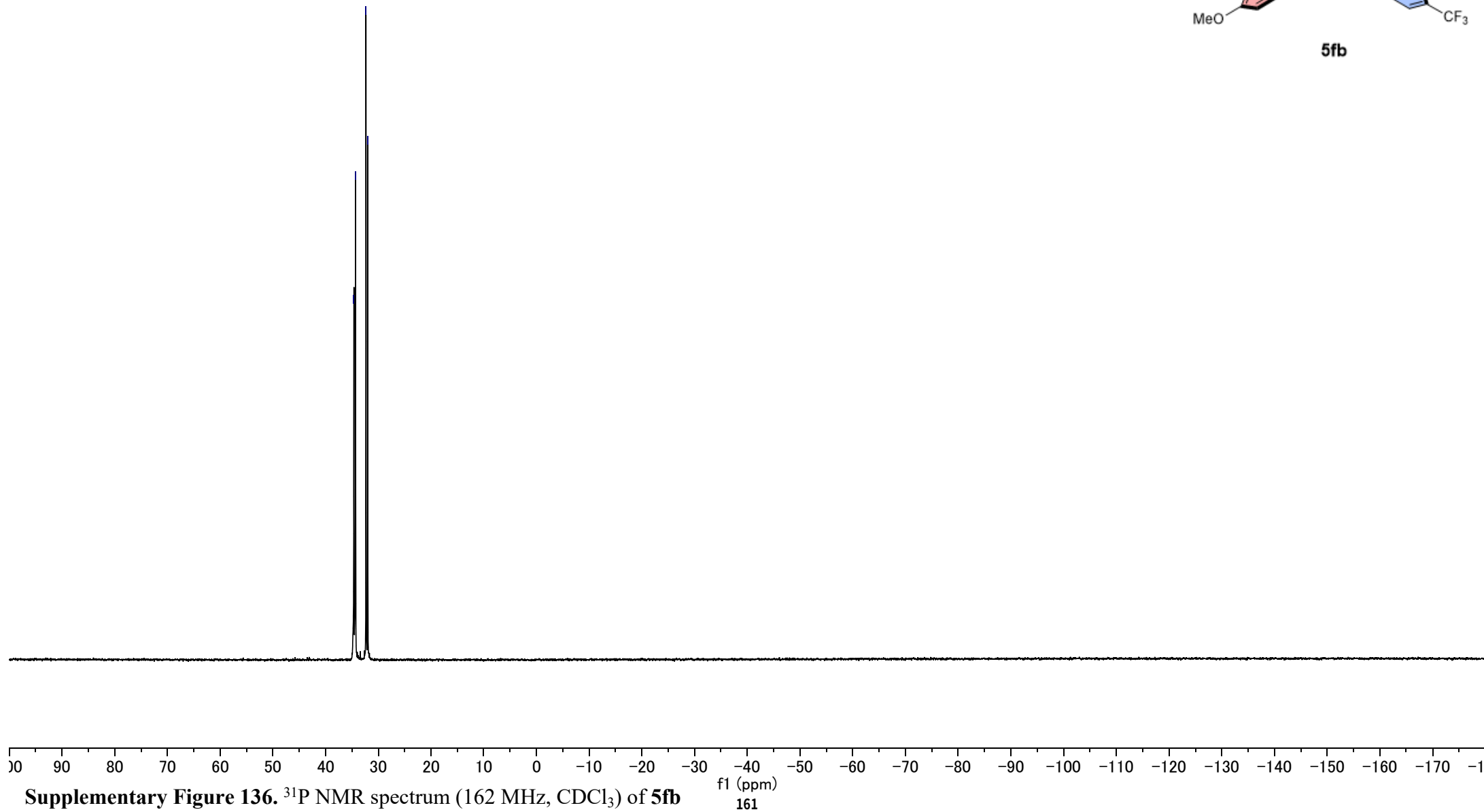
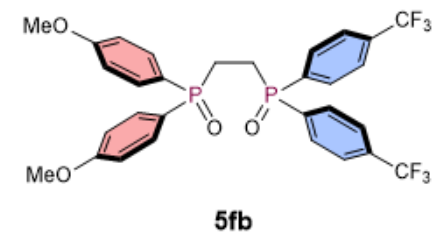
— -63.202



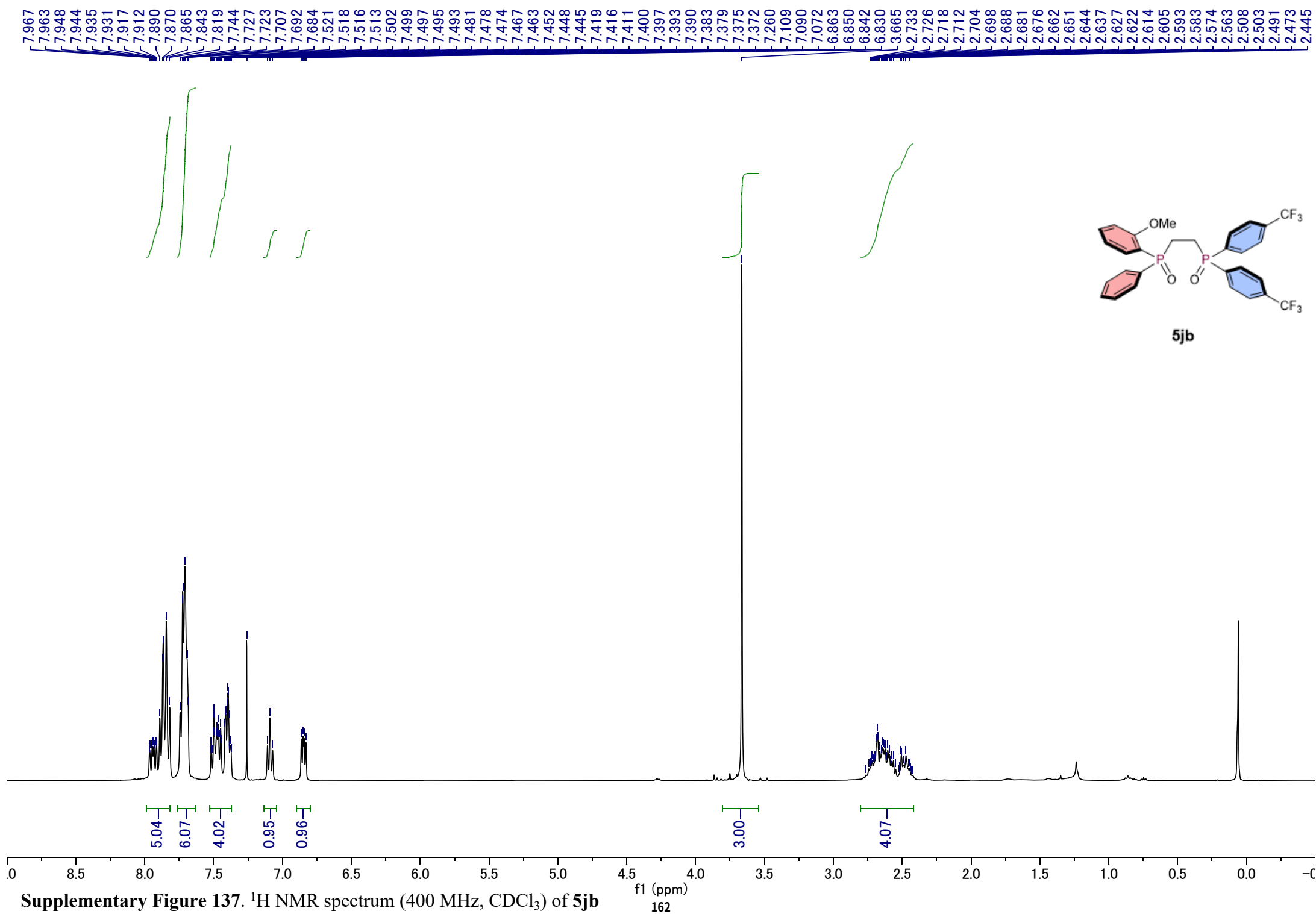
Supplementary Figure 135. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **5fb**

CDCl₃, 162 MHz

34.638
34.311
32.335
32.007

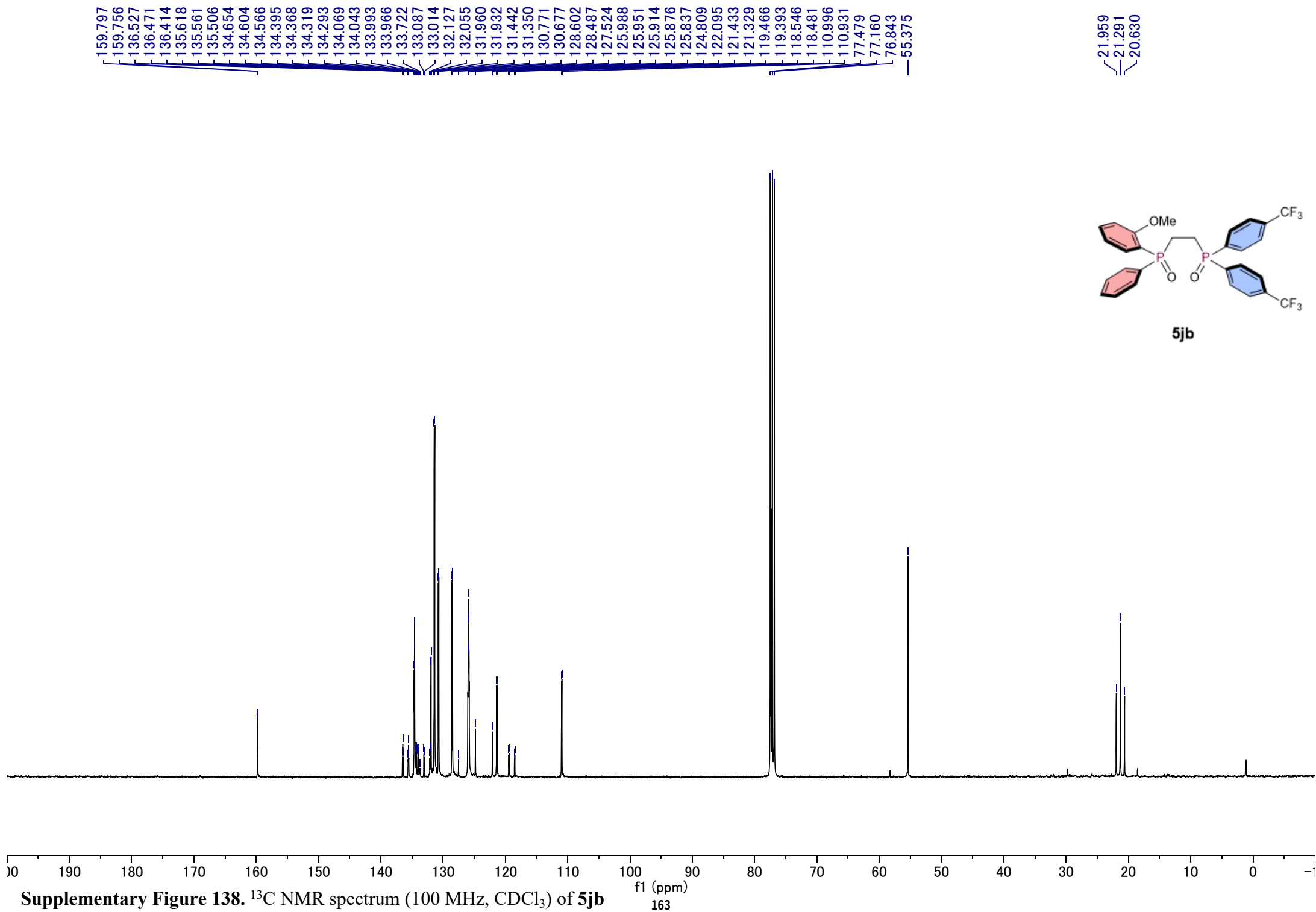


CDCl₃, 400 MHz



Supplementary Figure 137. ¹H NMR spectrum (400 MHz, CDCl₃) of 5jb

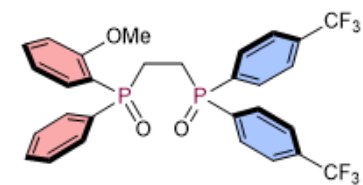
CDCl₃, 100 MHz



Supplementary Figure 138. ¹³C NMR spectrum (100 MHz, CDCl₃) of **5jb**

CDCl₃, 376 MHz

—63.198



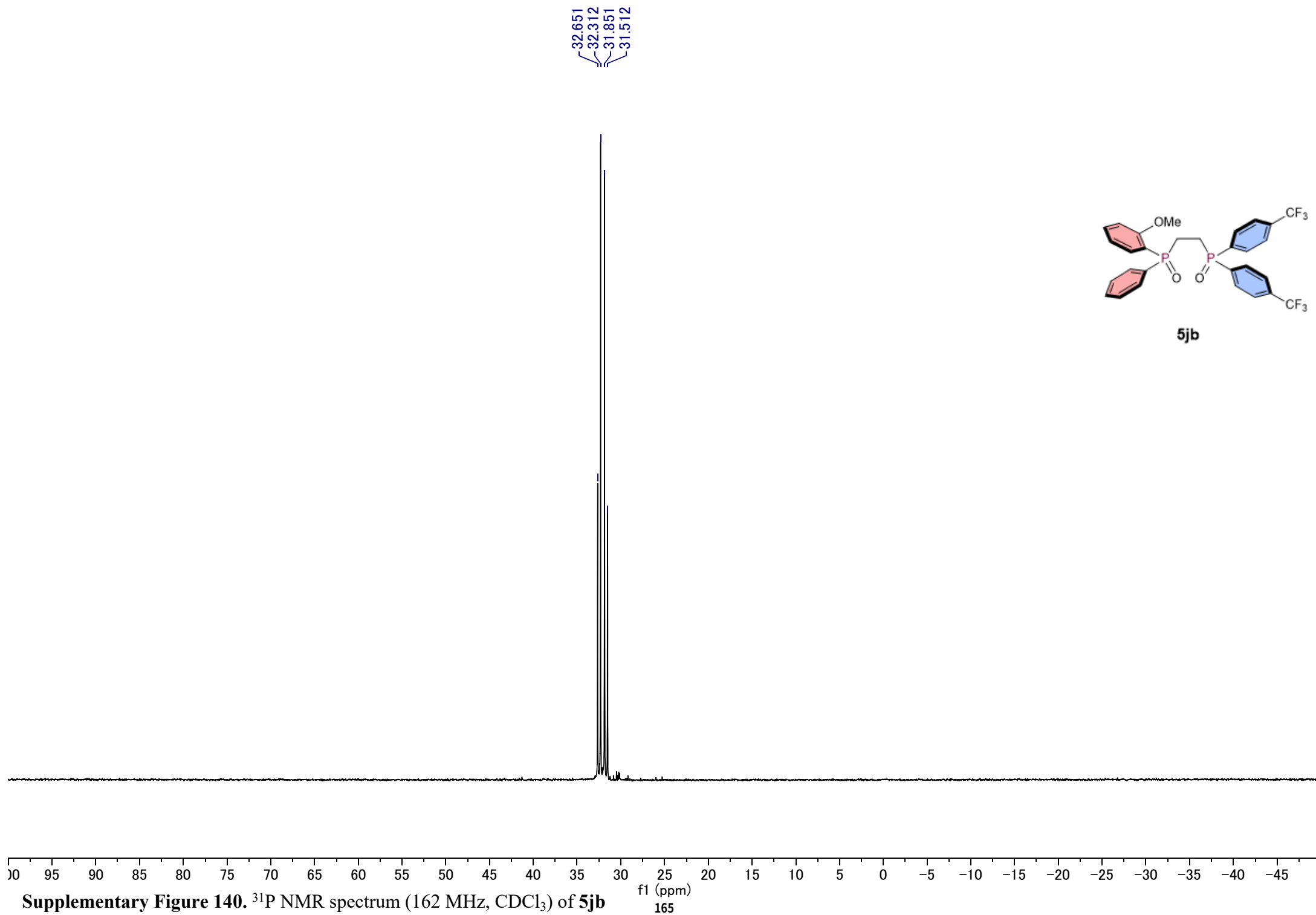
5jb

30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 139. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **5jb**

f1 (ppm)
164

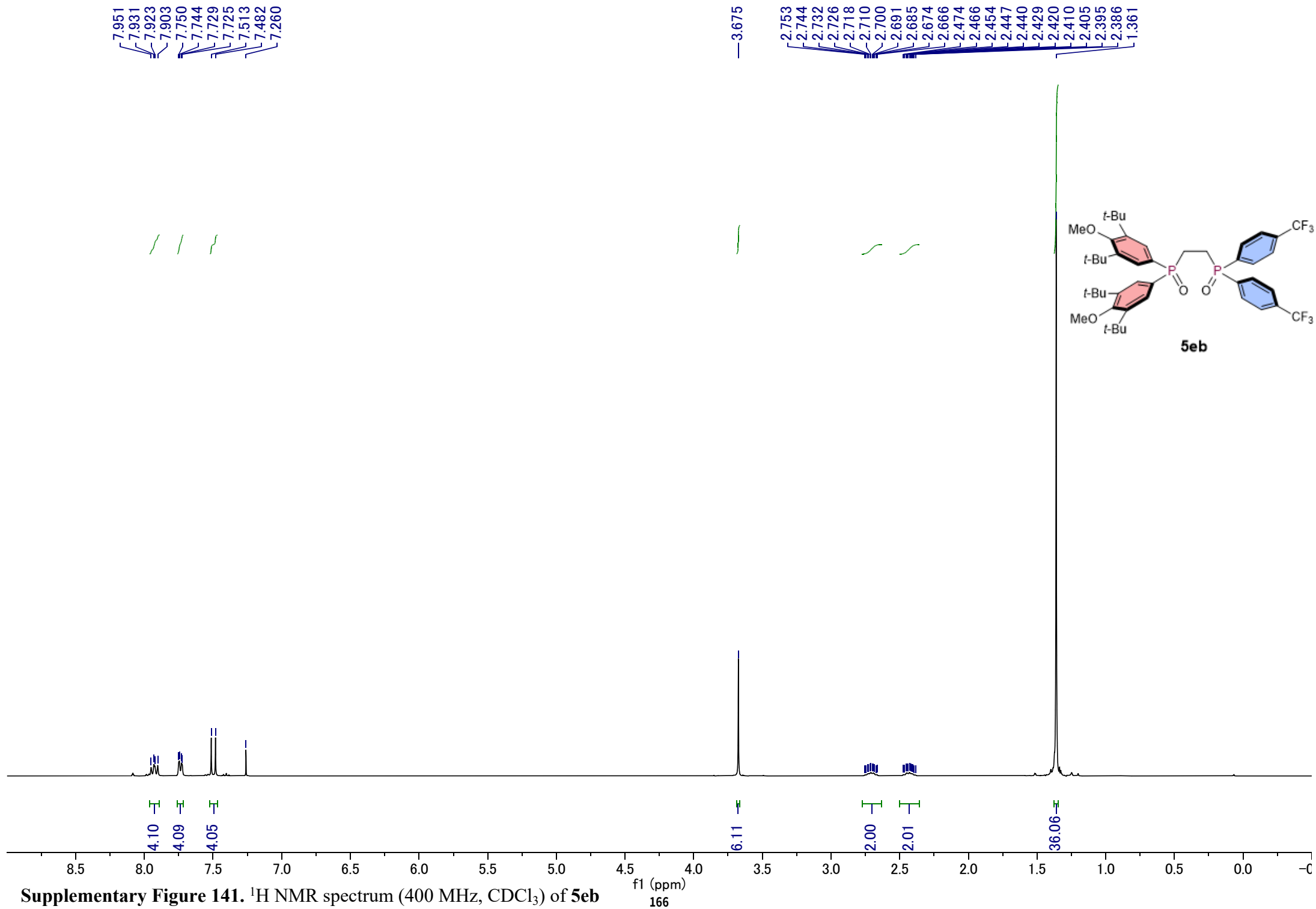
CDCl₃, 162 MHz



Supplementary Figure 140. ³¹P NMR spectrum (162 MHz, CDCl₃) of **5jb**

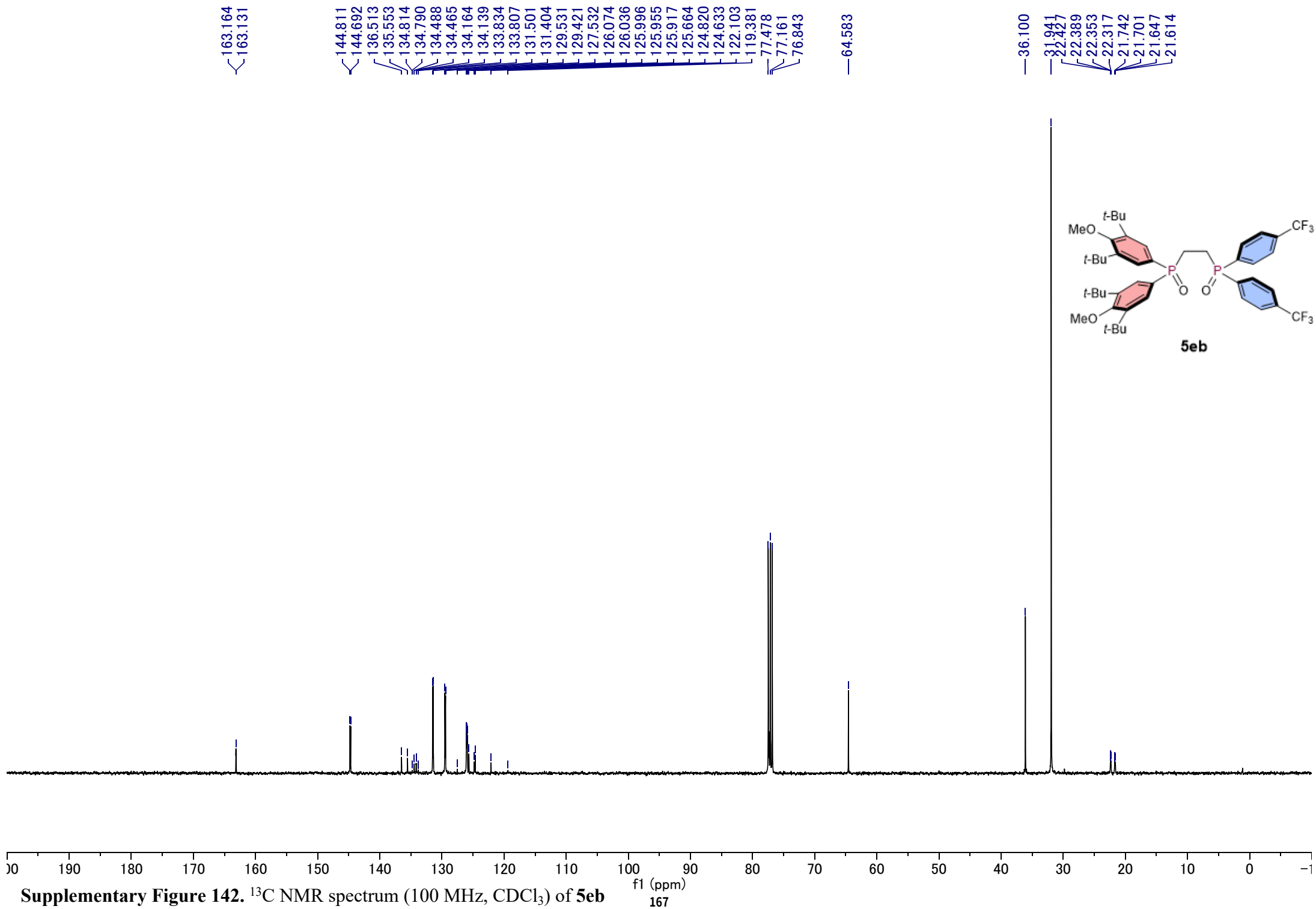
f1 (ppm)
165

CDCl₃, 400 MHz



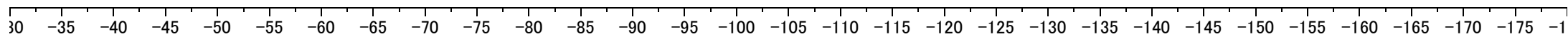
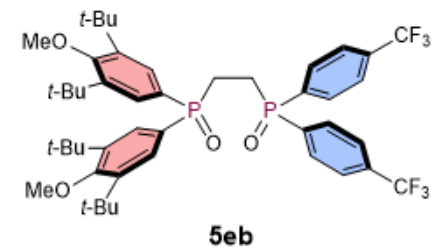
Supplementary Figure 141. ¹H NMR spectrum (400 MHz, CDCl₃) of **5eb**

CDCl₃, 100 MHz



CDCl₃, 376 MHz

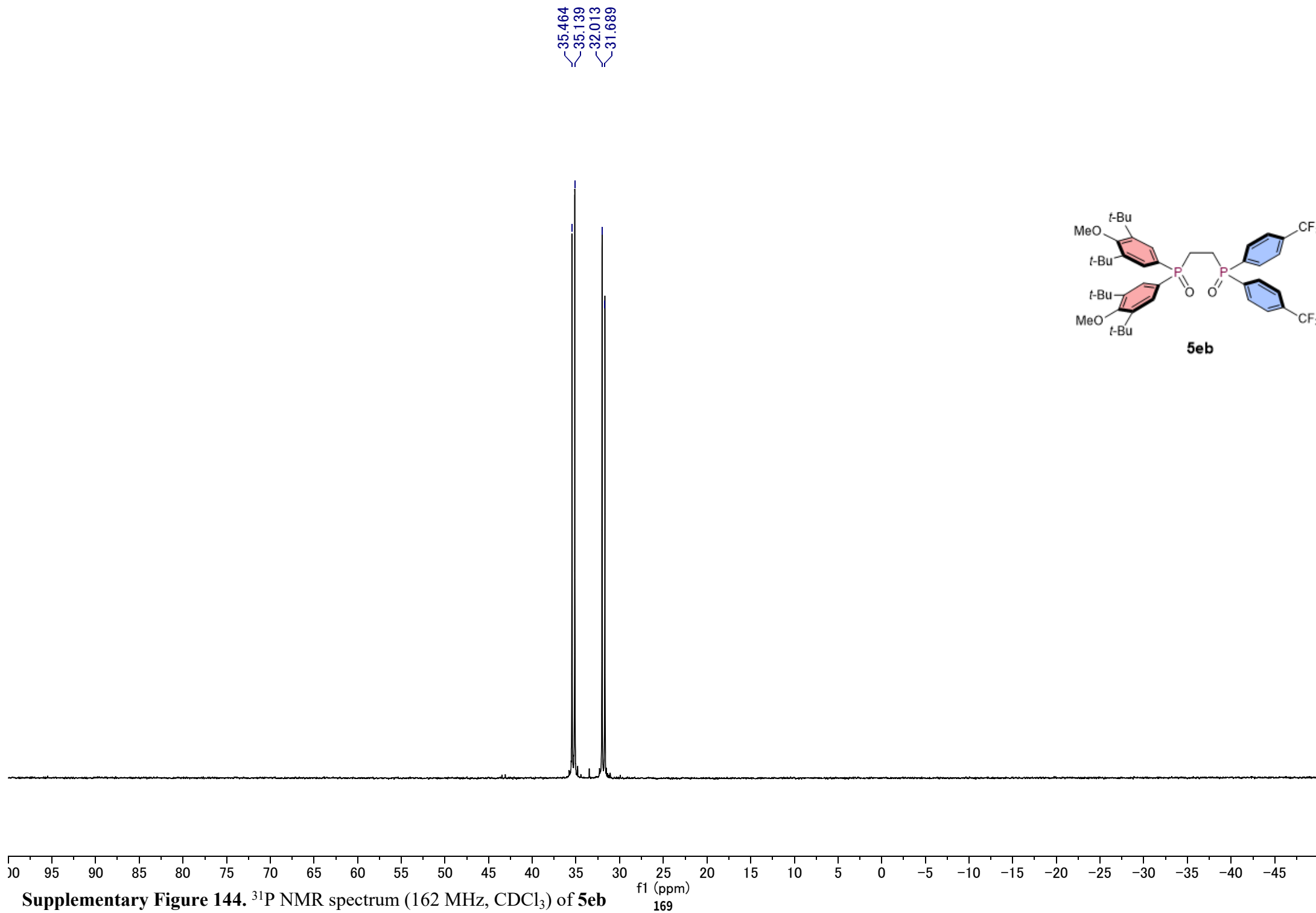
— -63.203



Supplementary Figure 143. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **5eb**

f1 (ppm)
168

CDCl₃, 162 MHz



Supplementary Figure 144. ³¹P NMR spectrum (162 MHz, CDCl₃) of **5eb**

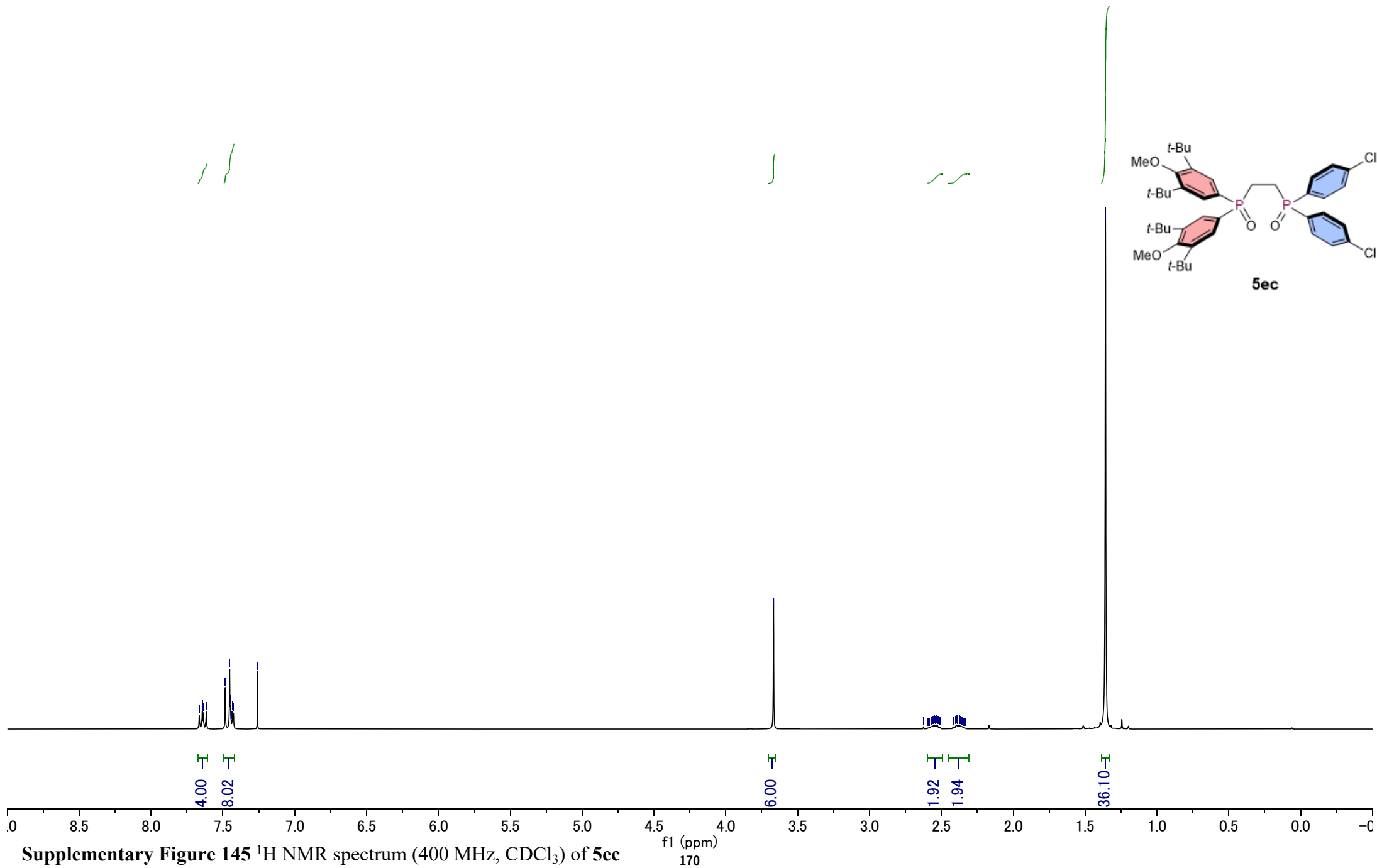
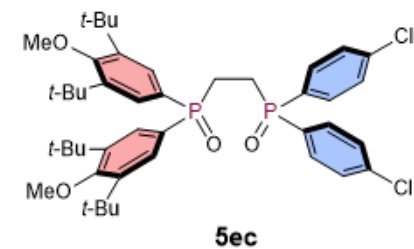
f1 (ppm)
169

CDCl₃, 400 MHz

7.665
7.644
7.637
7.616
7.484
7.453
7.447
7.442
7.432
7.426
7.260

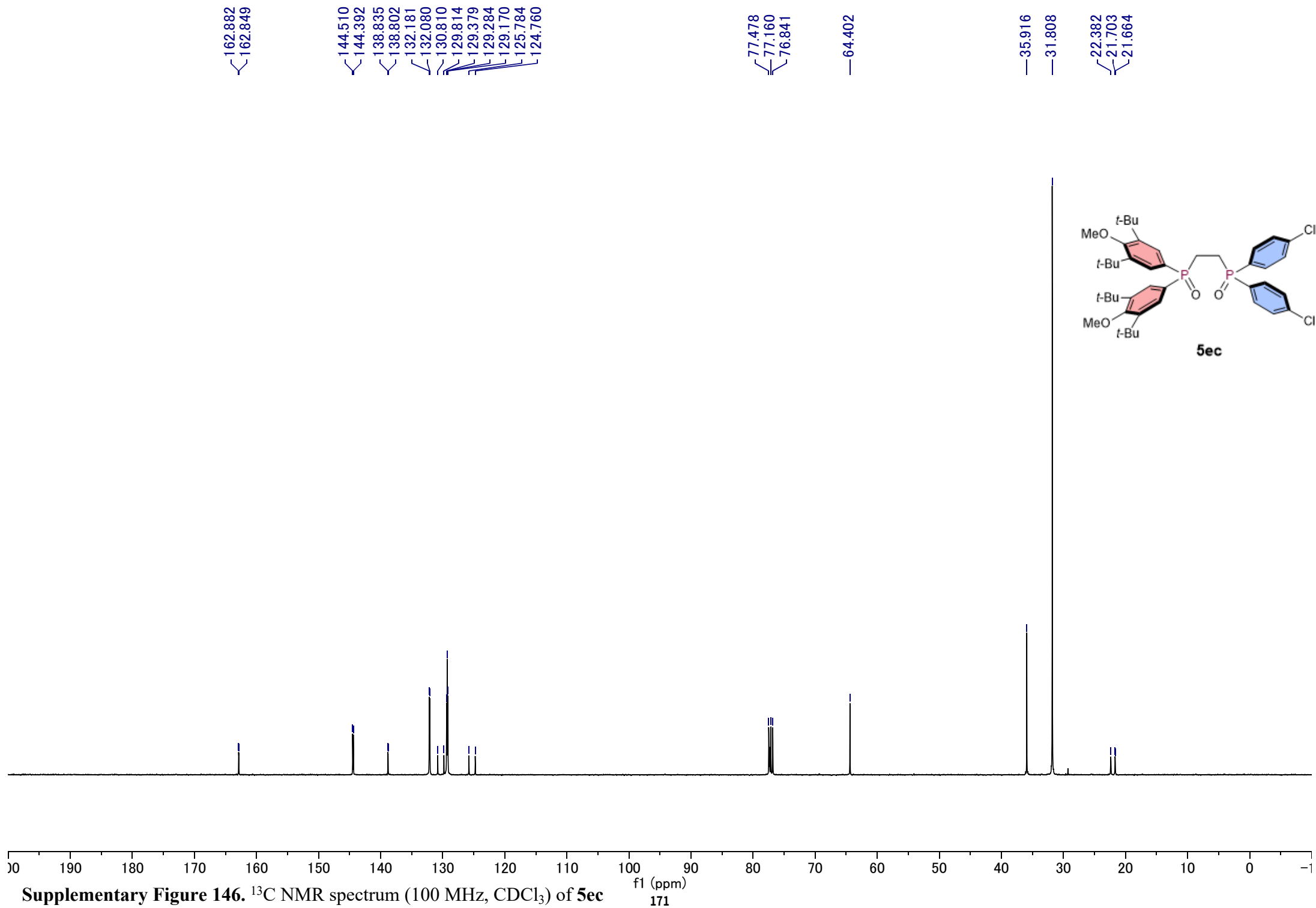
3.669

2.625
2.593
2.584
2.572
2.558
2.558
2.550
2.539
2.532
2.525
2.514
2.508
2.419
2.412
2.401
2.394
2.387
2.376
2.368
2.361
2.356
2.352
2.342
2.333
1.359

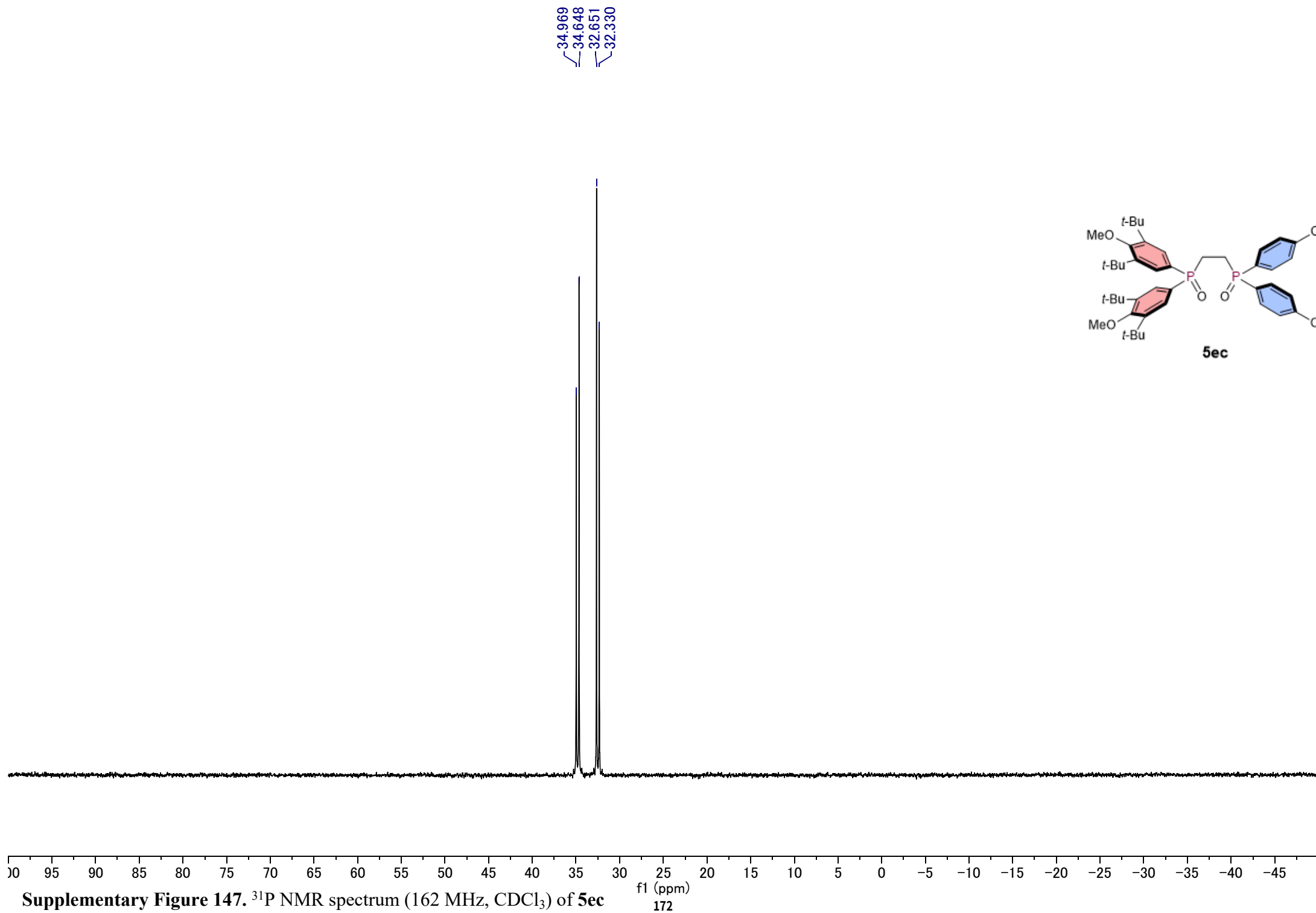


Supplementary Figure 145 ¹H NMR spectrum (400 MHz, CDCl₃) of **5ec**

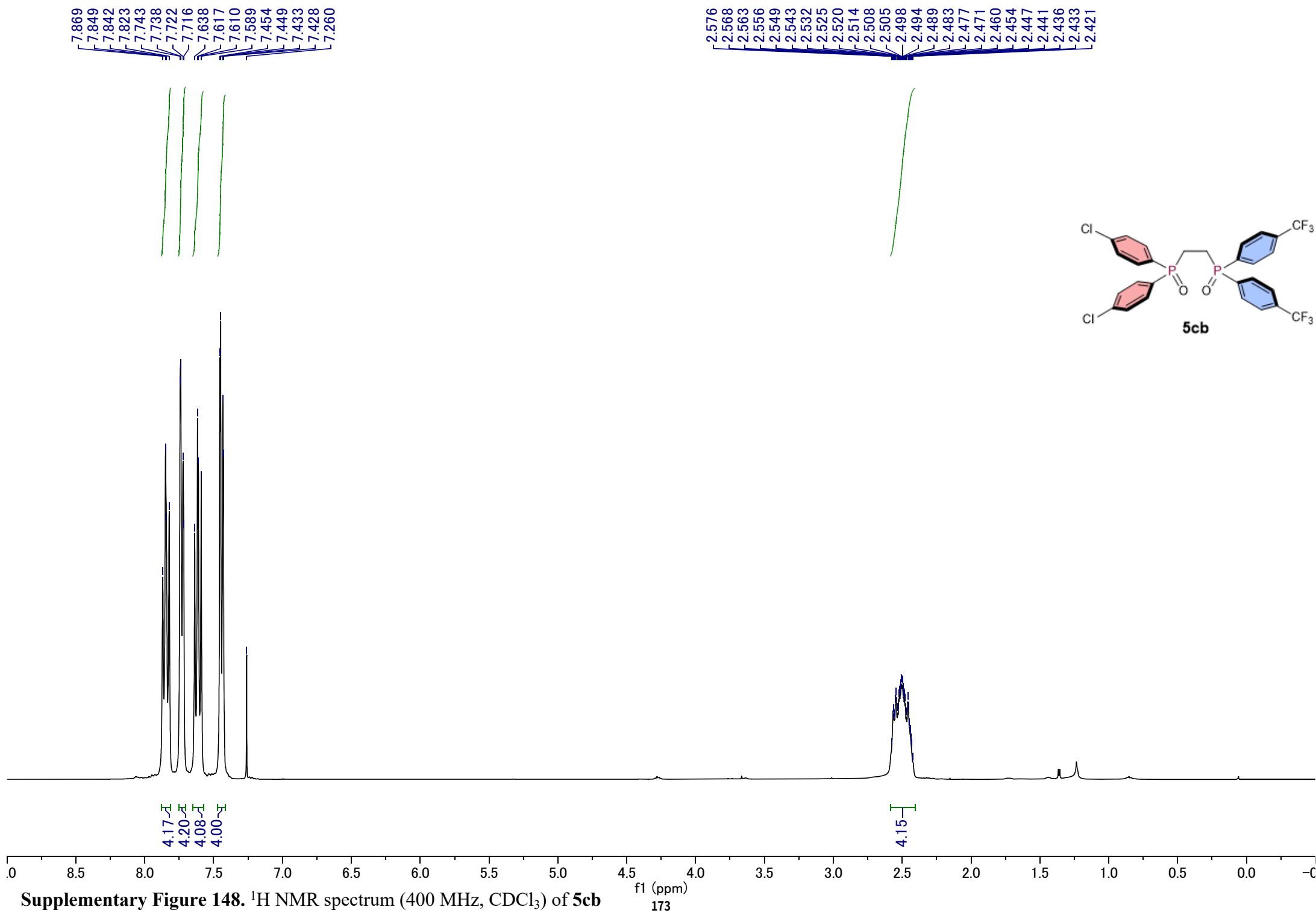
CDCl₃, 100 MHz



CDCl₃, 162 MHz



CDCl₃, 400 MHz

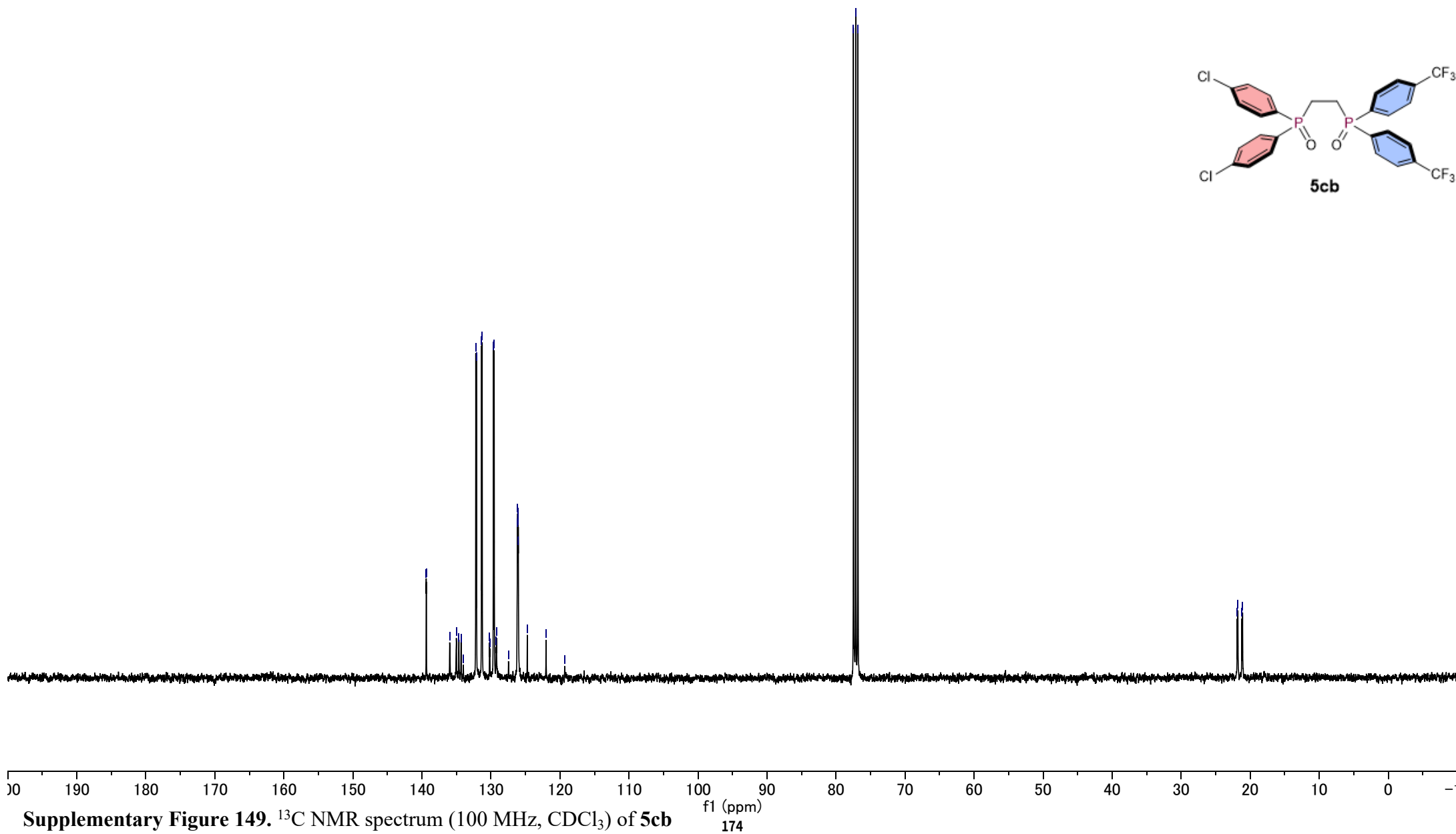
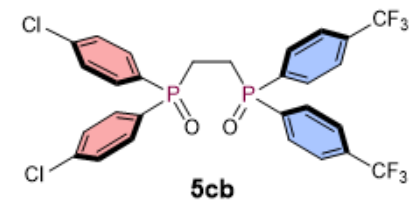


CDCl₃, 100 MHz

139.385
139.356
135.979
135.006
134.652
134.324
133.999
132.198
132.099
131.365
131.273
130.208
130.163
129.648
129.529
129.242
129.193
127.456
126.184
126.145
126.108
126.069
126.031
124.741
122.025
119.313

77.478
77.160
76.842

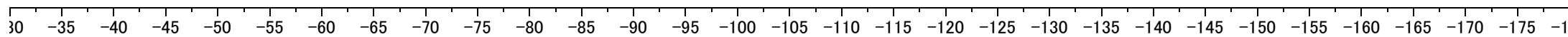
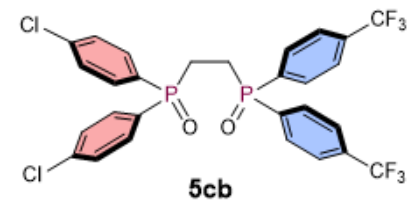
21.883
21.784
21.212
21.108



Supplementary Figure 149. ¹³C NMR spectrum (100 MHz, CDCl₃) of **5cb**

CDCl₃, 376 MHz

— -63.231

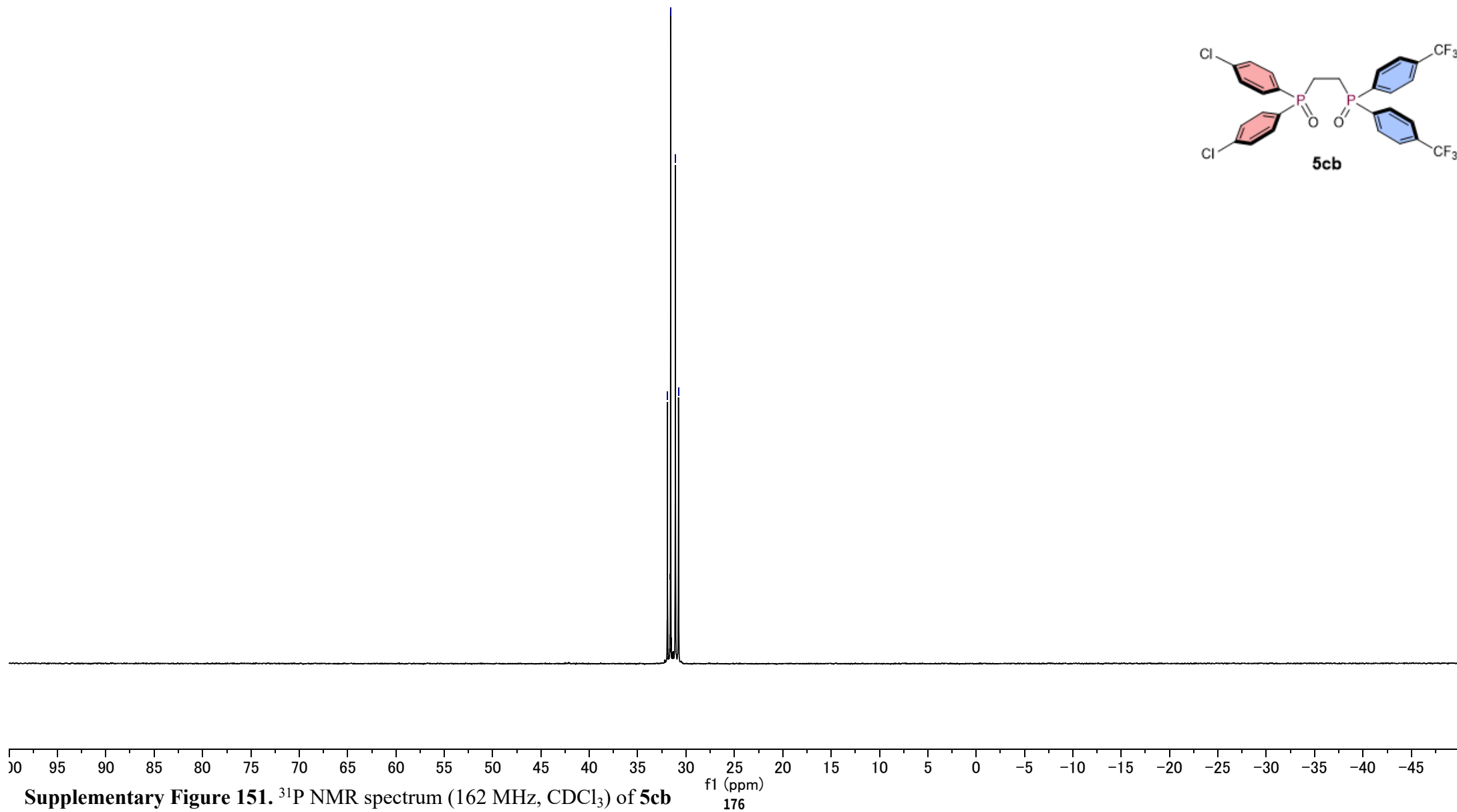
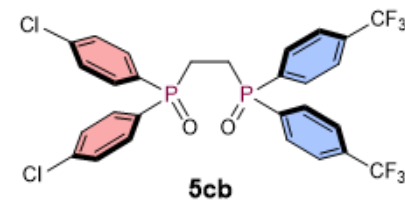


Supplementary Figure 150. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **5cb**

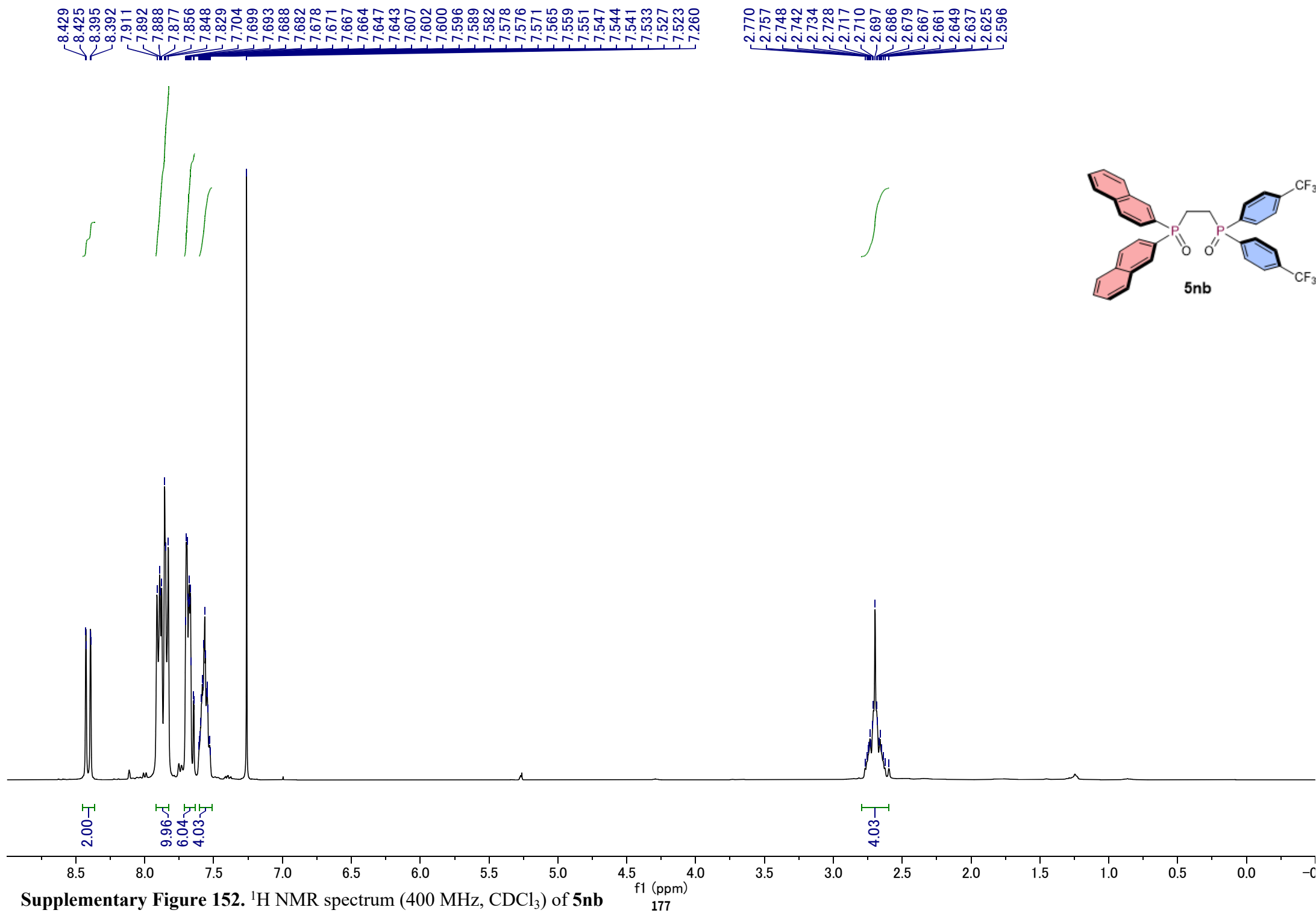
f1 (ppm)
175

CDCl₃, 162 MHz

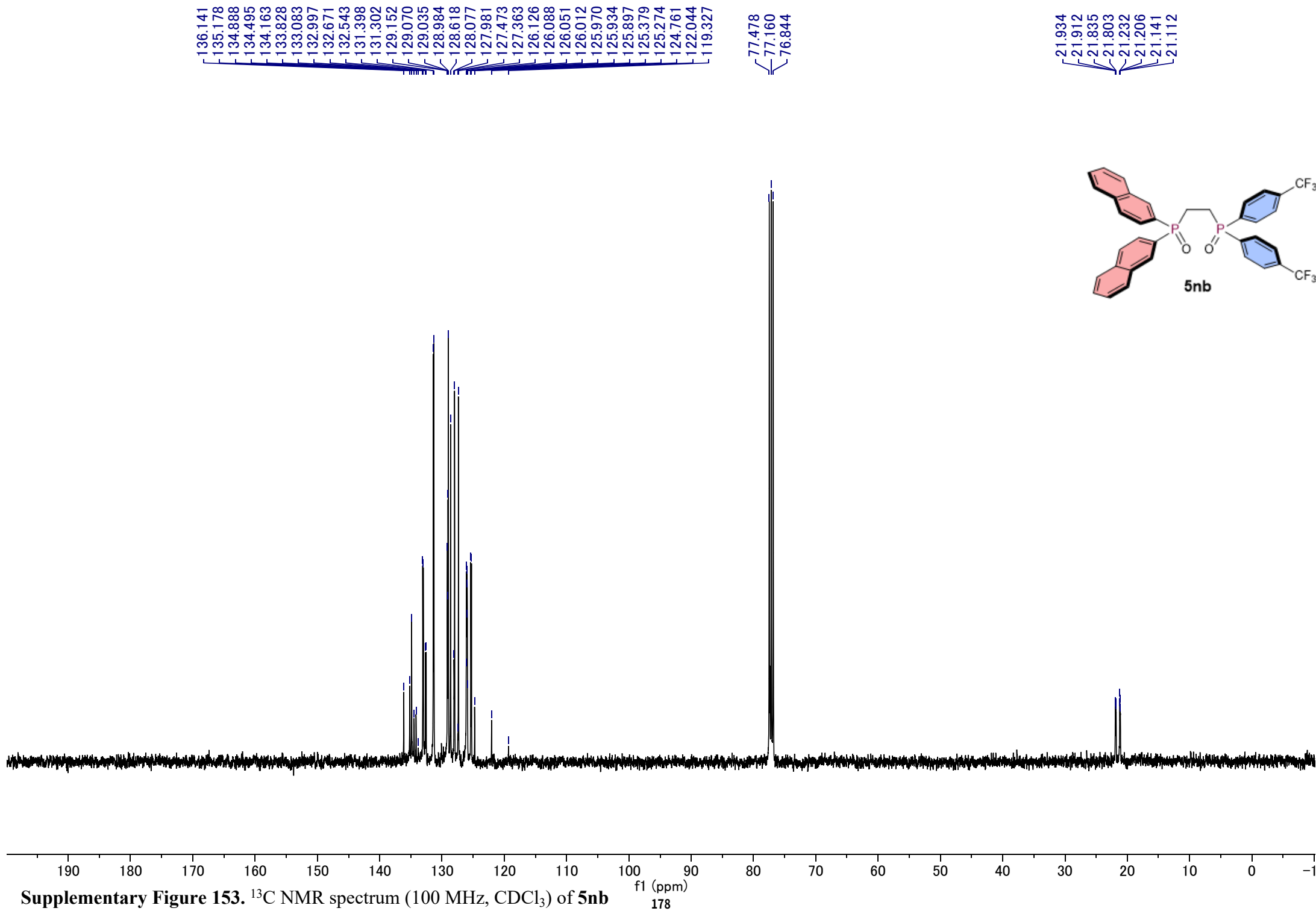
31.915
31.594
31.098
30.776



CDCl₃, 400 MHz

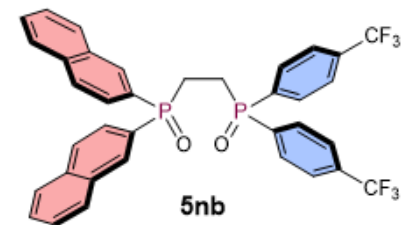


CDCl₃, 100 MHz



CDCl₃, 376 MHz

63.190

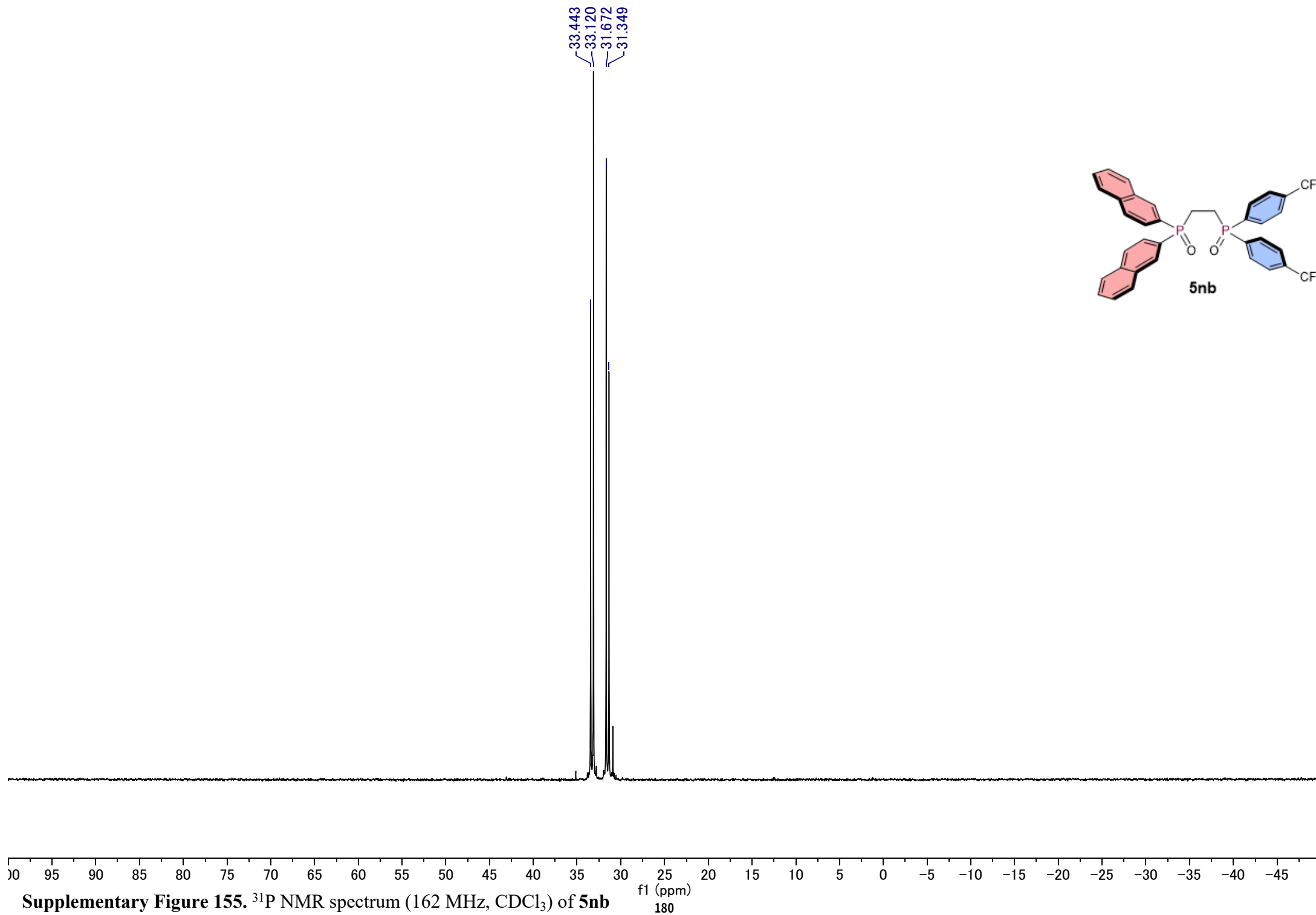


30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 154. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **5nb**

f1 (ppm)
179

CDCl₃, 162 MHz

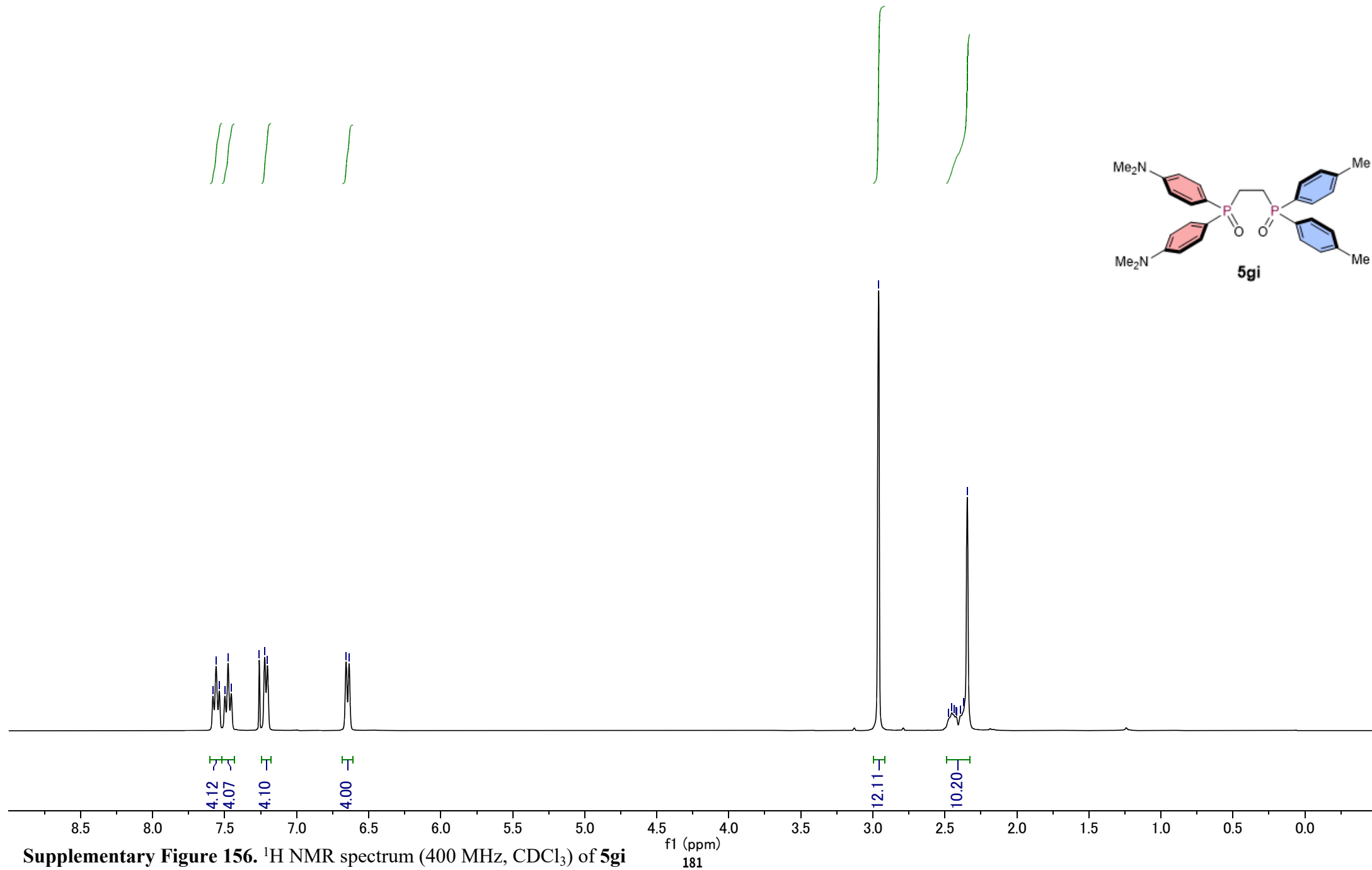
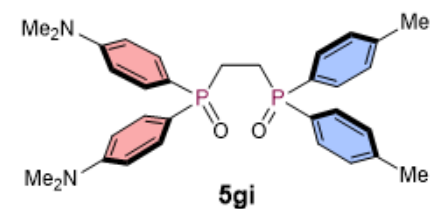


Supplementary Figure 155. ³¹P NMR spectrum (162 MHz, CDCl₃) of **5nb**

CDCl₃, 400 MHz

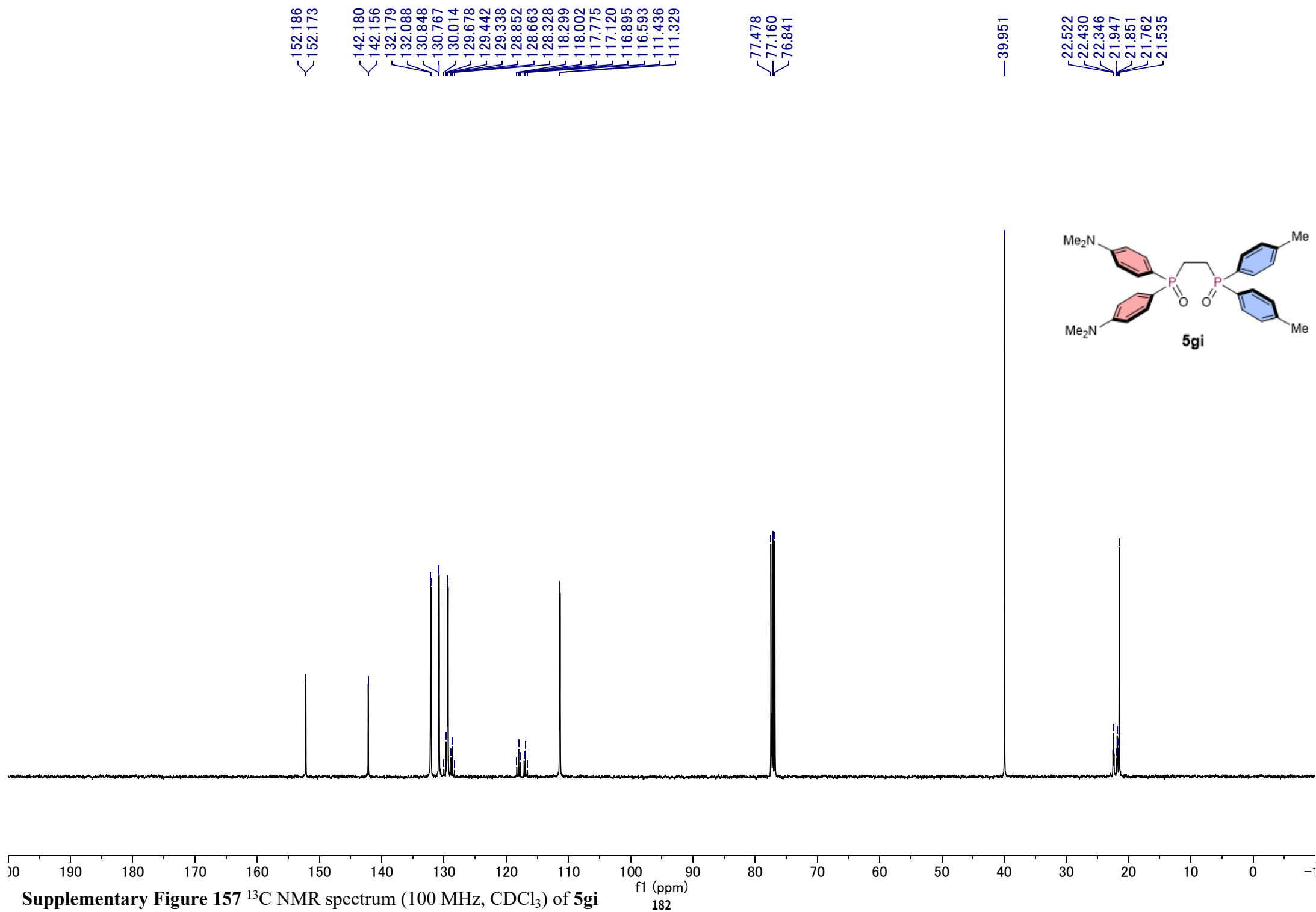
7.582
7.560
7.538
7.499
7.477
7.454
7.260
7.223
7.203
6.657
6.636

2.960
2.474
2.454
2.438
2.421
2.418
2.392
2.368
2.345



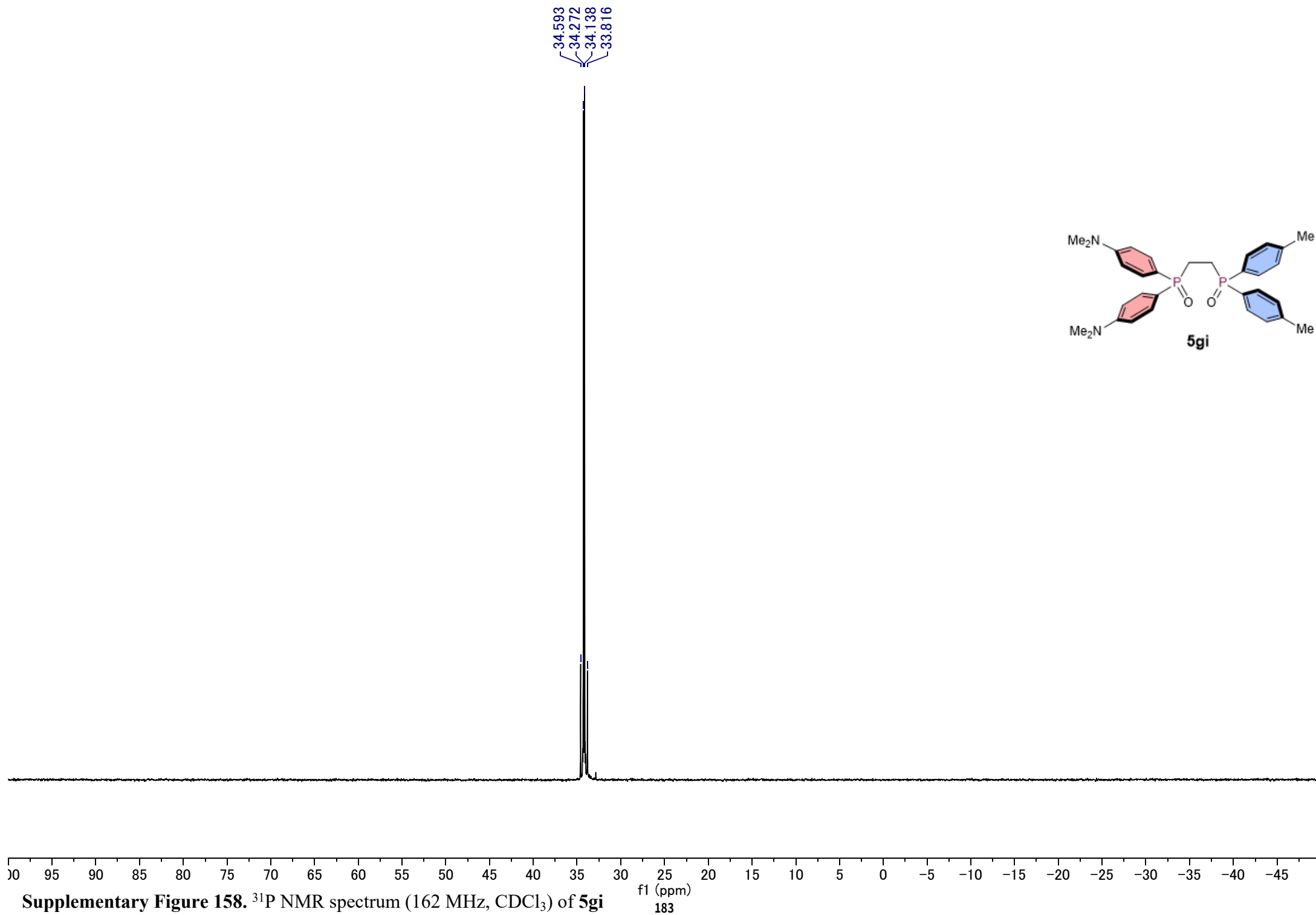
Supplementary Figure 156. ¹H NMR spectrum (400 MHz, CDCl₃) of **5gi**

CDCl₃, 100 MHz



Supplementary Figure 157 ¹³C NMR spectrum (100 MHz, CDCl₃) of **5gi**

CDCl₃, 162 MHz



Supplementary Figure 158. ³¹P NMR spectrum (162 MHz, CDCl₃) of **5gi**

f1 (ppm)
183

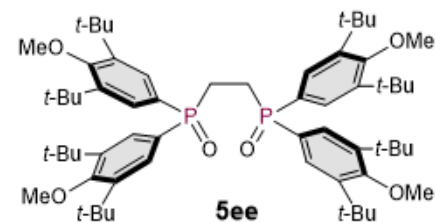
CDCl₃, 400 MHz

7.542
7.527
7.512
7.260

3.671

2.489
2.484

1.369



8.07

12.09

4.00

72.21

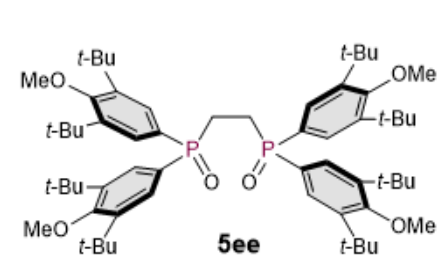
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

Supplementary Figure 159. ¹H NMR spectrum (400 MHz, CDCl₃) of **5ee**

f1 (ppm)
184

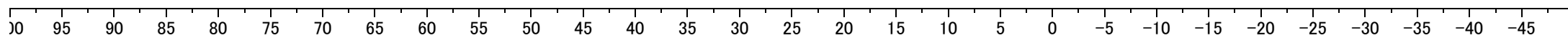
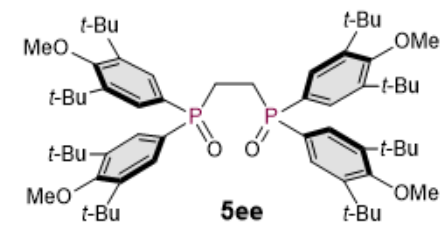
Supplementary Figure 160. ^{13}C NMR spectrum (100 MHz, CDCl_3) of **5ee**

Chemical structure of **5ee** is shown in the top right corner. It is a bisphosphonate derivative with two phosphonate groups linked by a central carbon atom. Each phosphonate group is substituted with a 3,5-dimethoxyphenyl group and a 3,5-dimethylphenyl group.



CDCl₃, 162 MHz

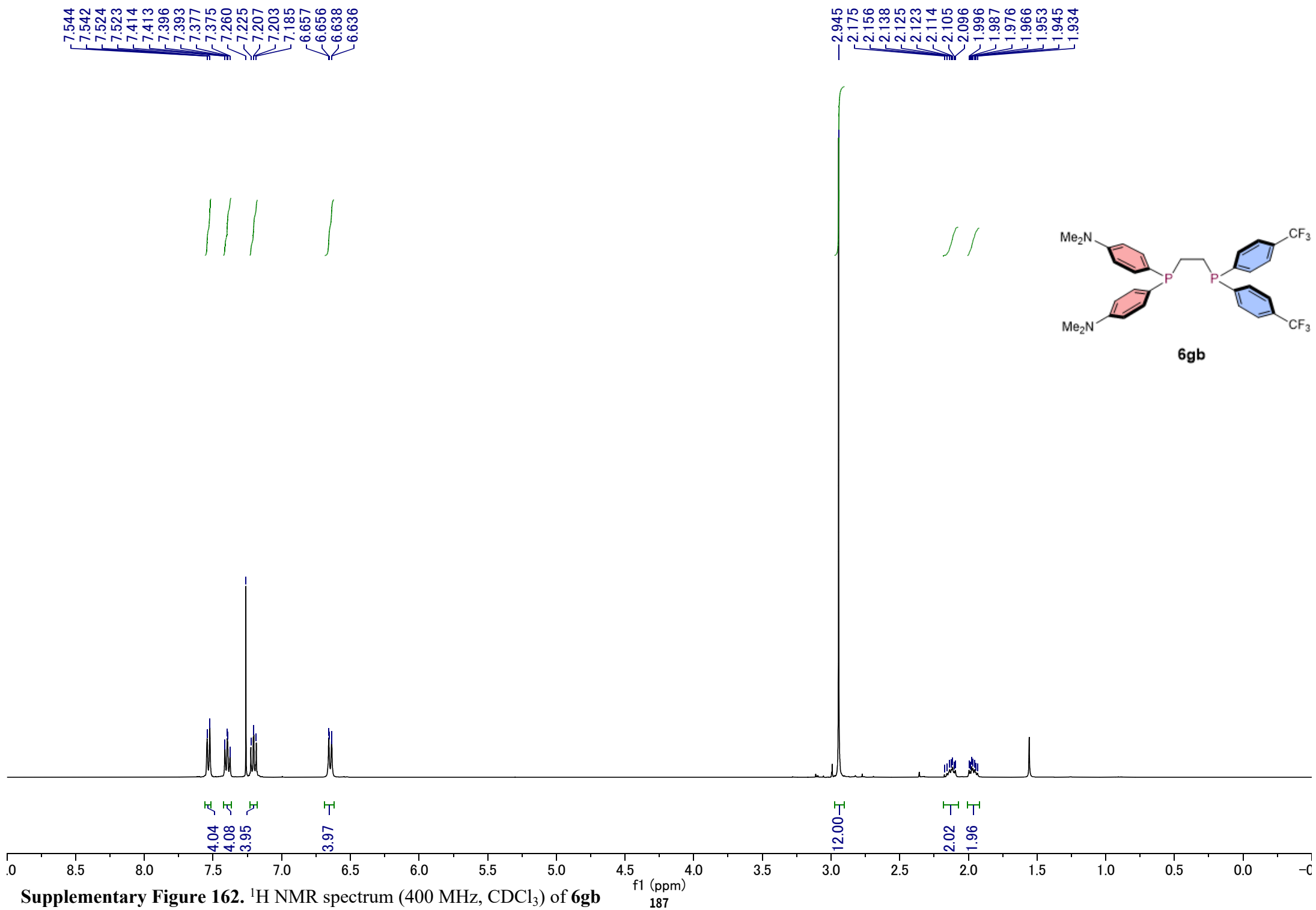
—35.557



Supplementary Figure 161. ³¹P NMR spectrum (162 MHz, CDCl₃) of **5ee**

f1 (ppm)
186

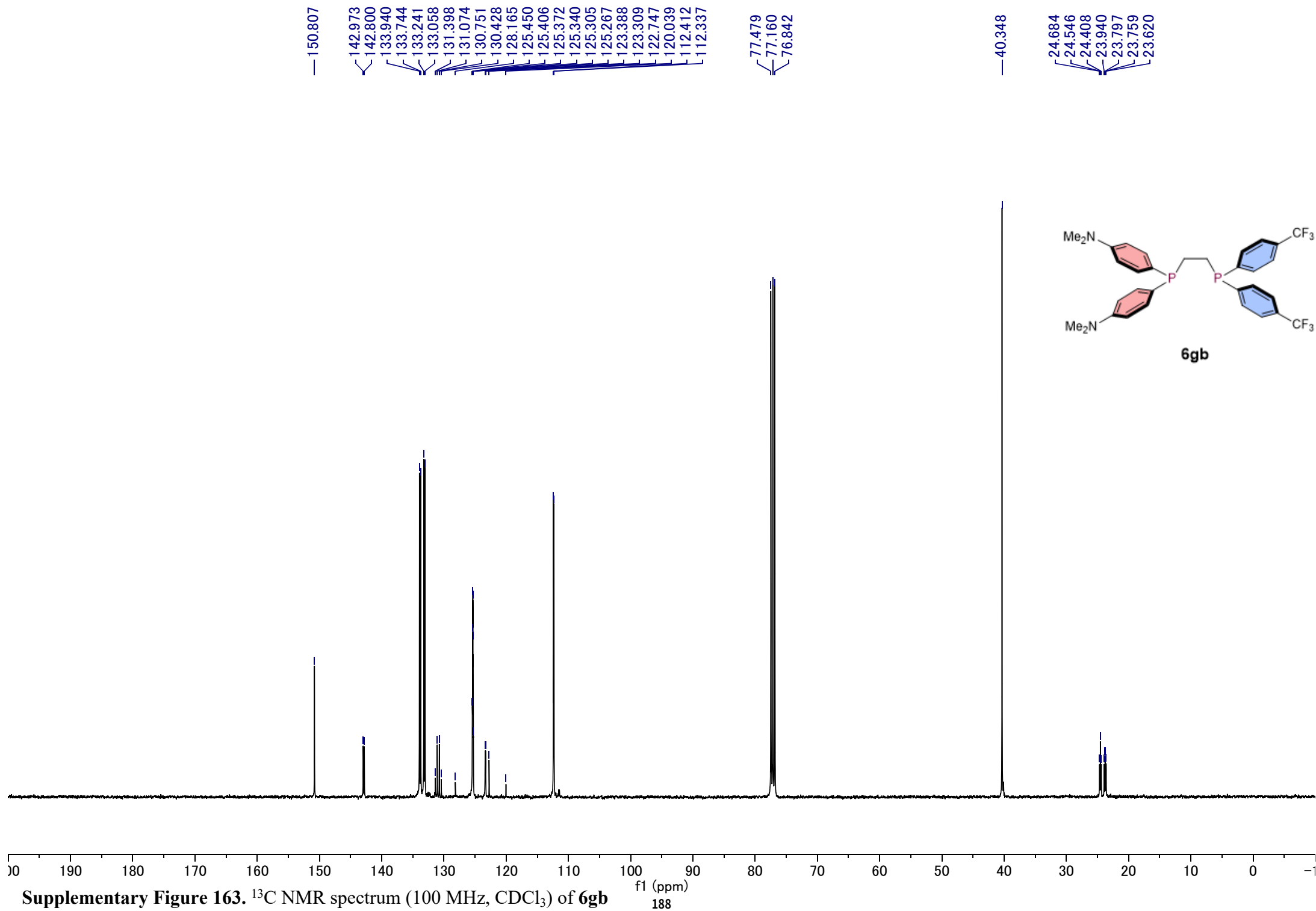
CDCl₃, 400 MHz



Supplementary Figure 162. ¹H NMR spectrum (400 MHz, CDCl₃) of **6gb**

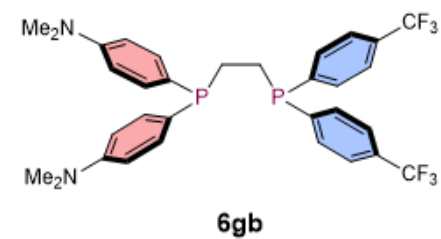
f1 (ppm)
187

CDCl₃, 100 MHz



CDCl₃, 376 MHz

-62.692



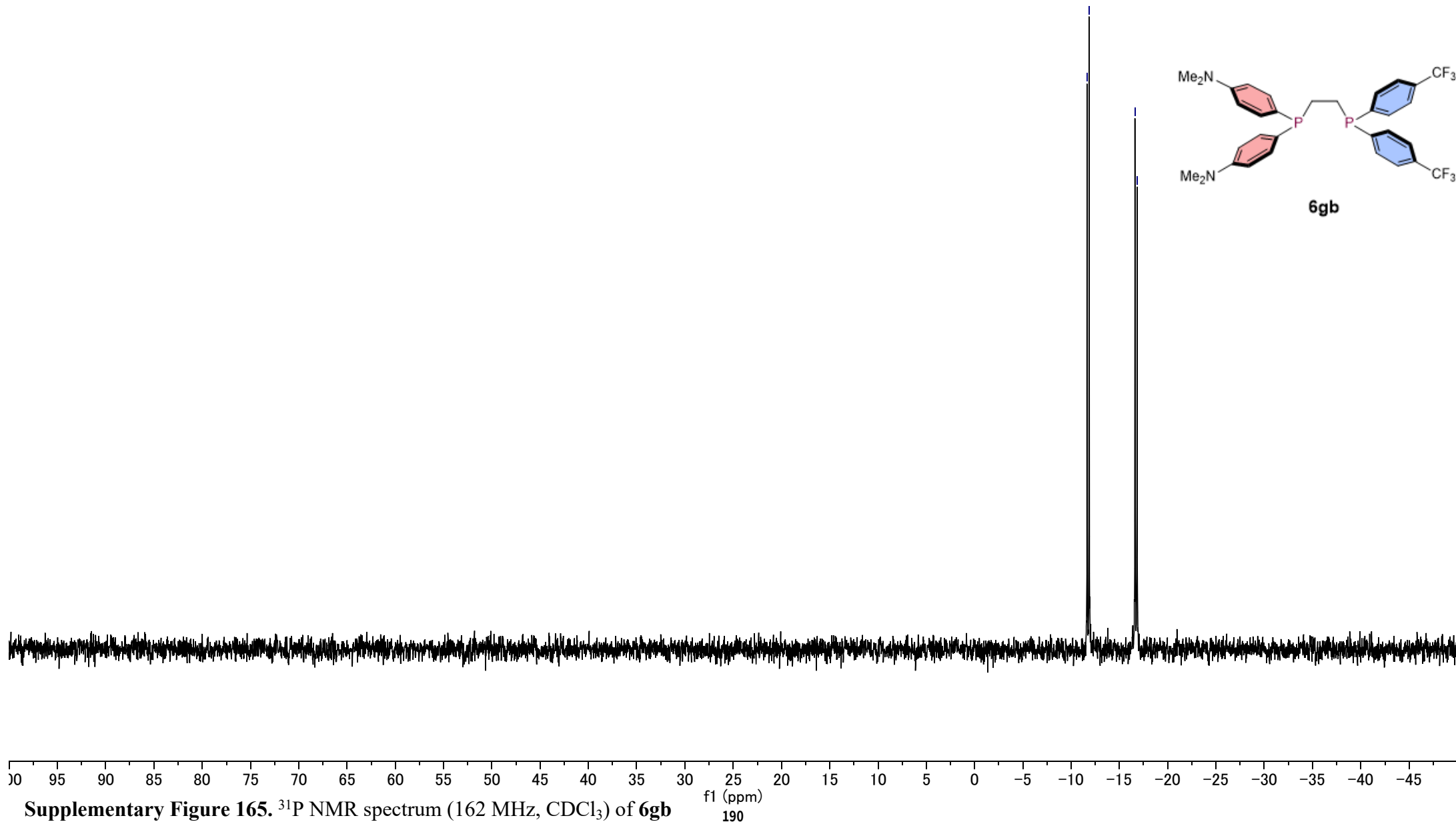
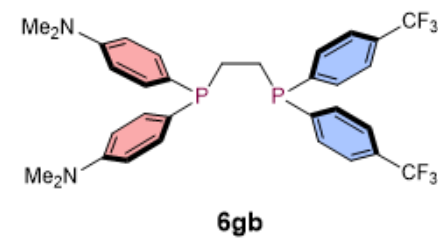
30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 164. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **6gb**

f1 (ppm)
189

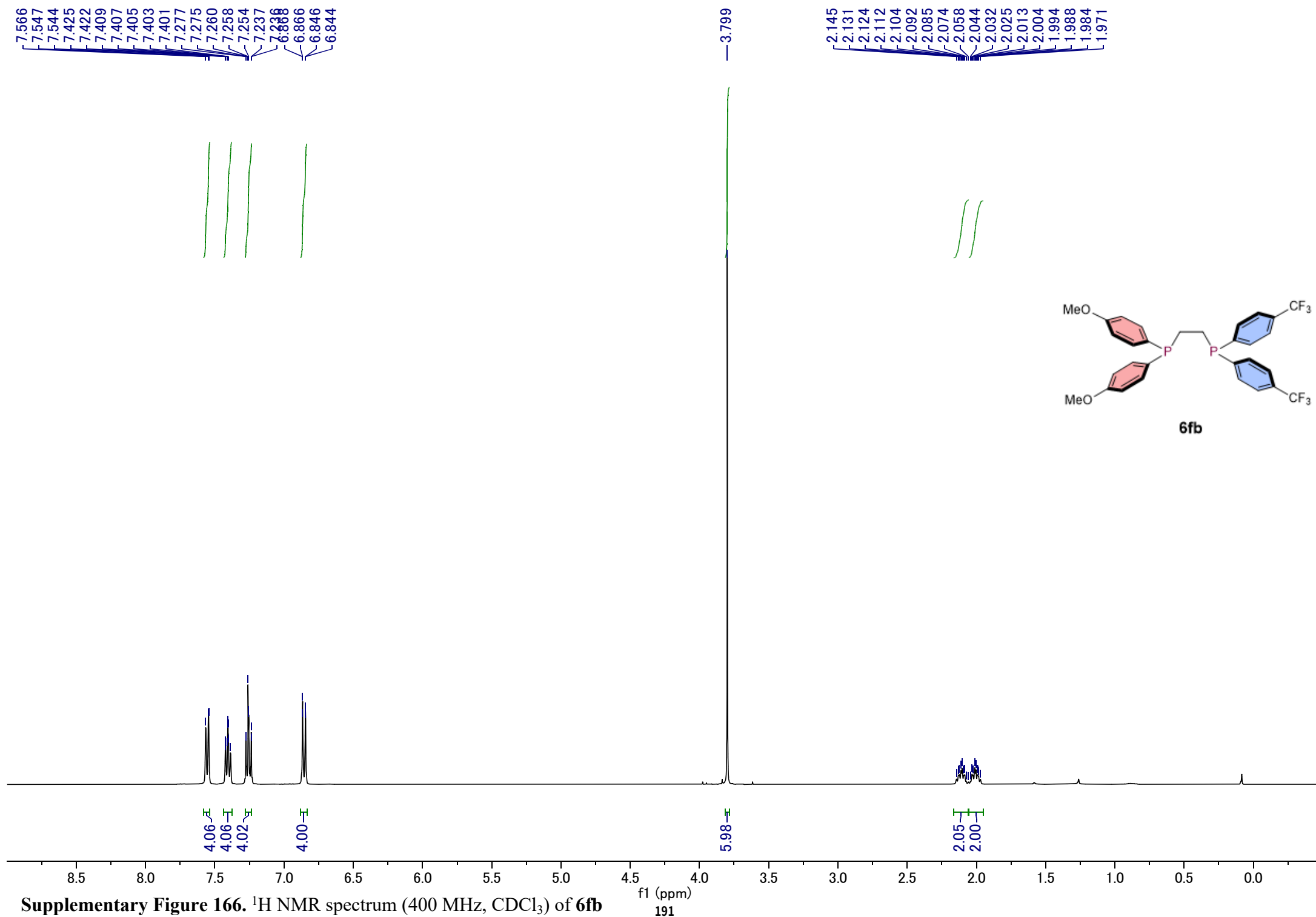
CDCl₃, 162 MHz

-11.652
-11.866
-16.620
-16.835



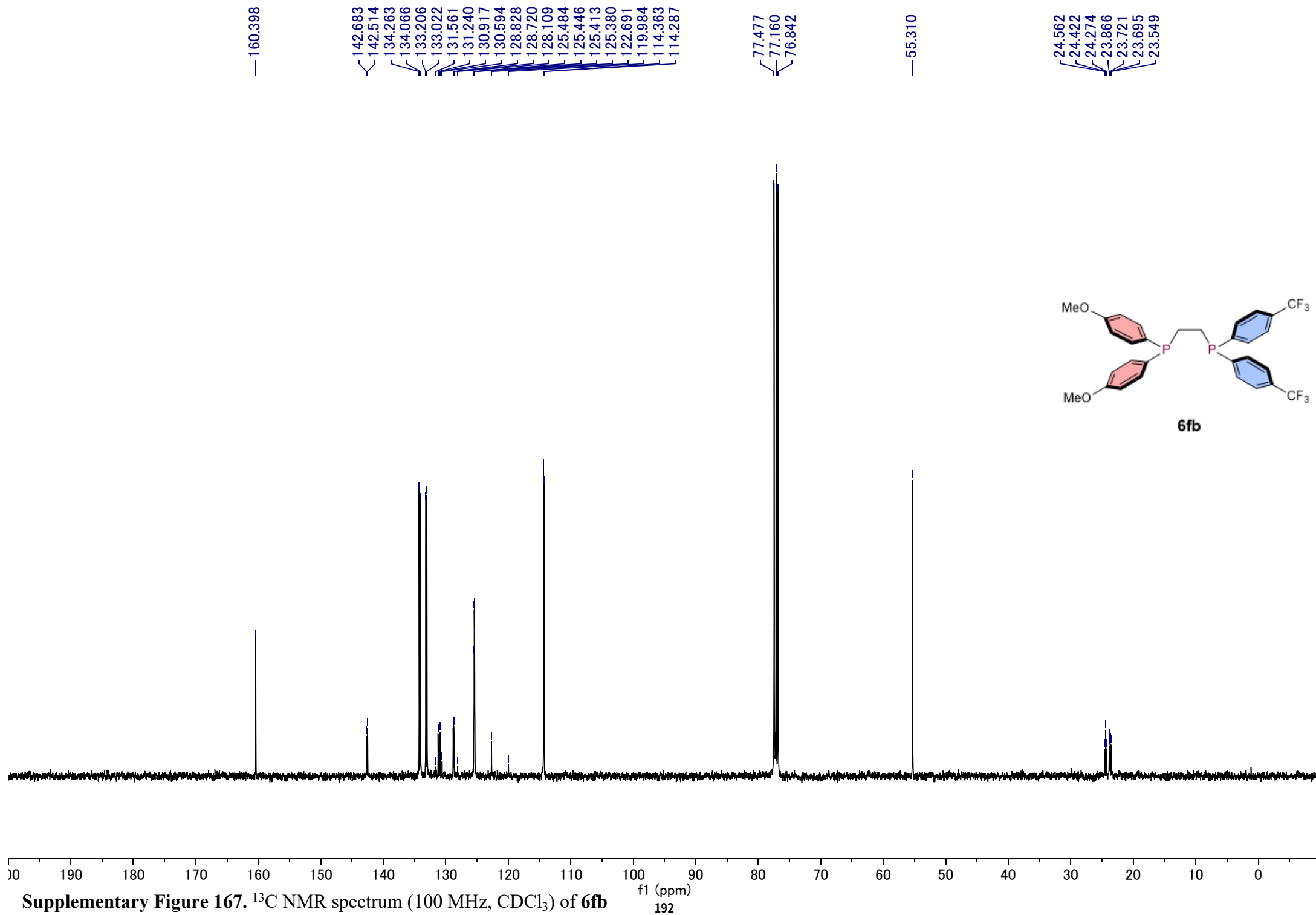
Supplementary Figure 165. ³¹P NMR spectrum (162 MHz, CDCl₃) of **6gb**

CDCl₃, 400 MHz



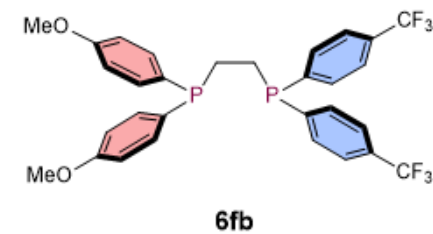
Supplementary Figure 166. ¹H NMR spectrum (400 MHz, CDCl₃) of **6fb**

CDCl₃, 100 MHz



CDCl₃, 376 MHz

-62.714



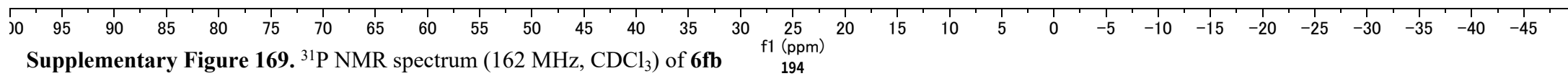
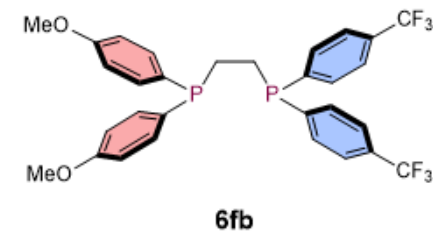
30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 168. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **6fb**

f1 (ppm)
193

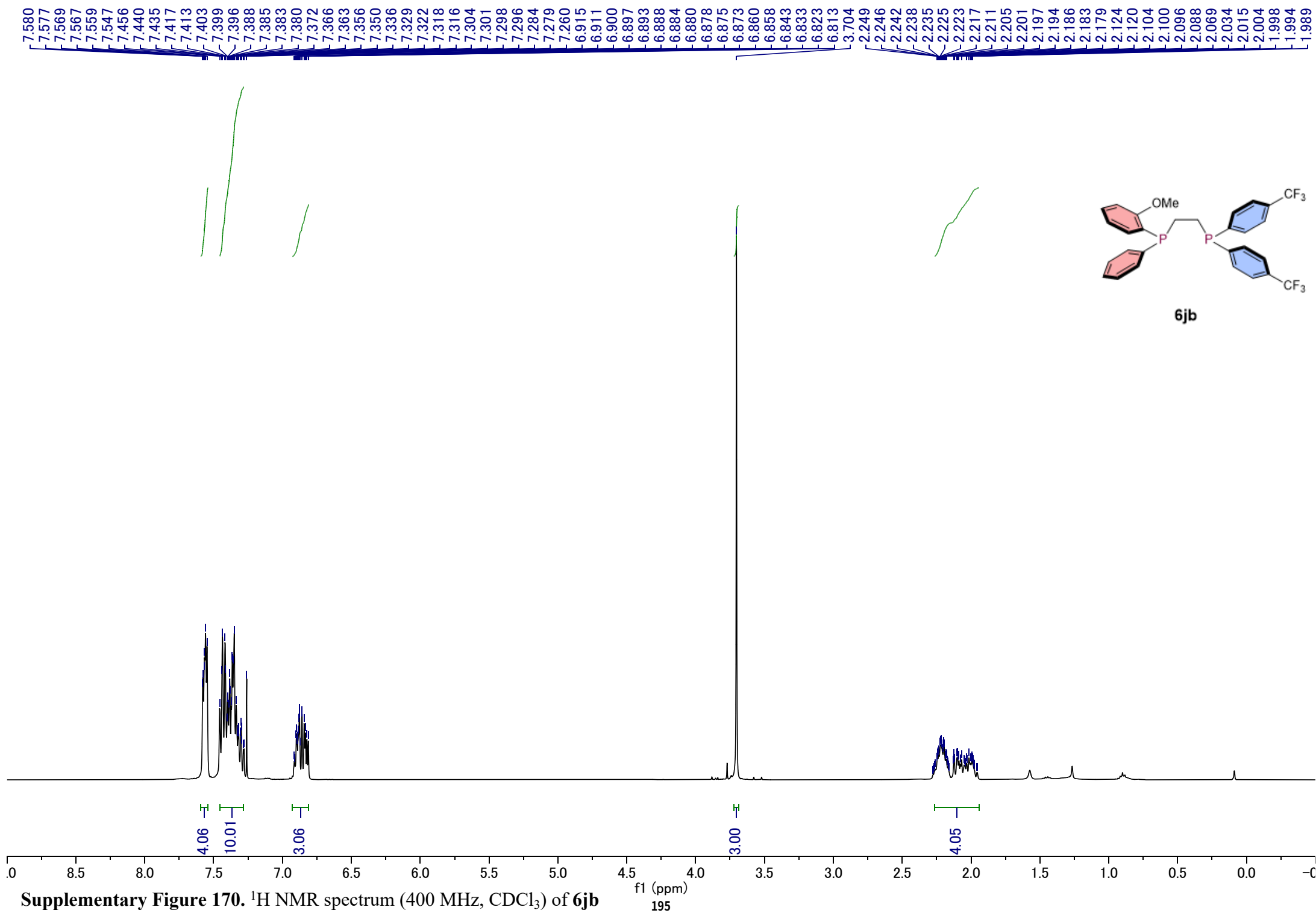
CDCl₃, 162 MHz

11.912
12.134
15.723
15.944



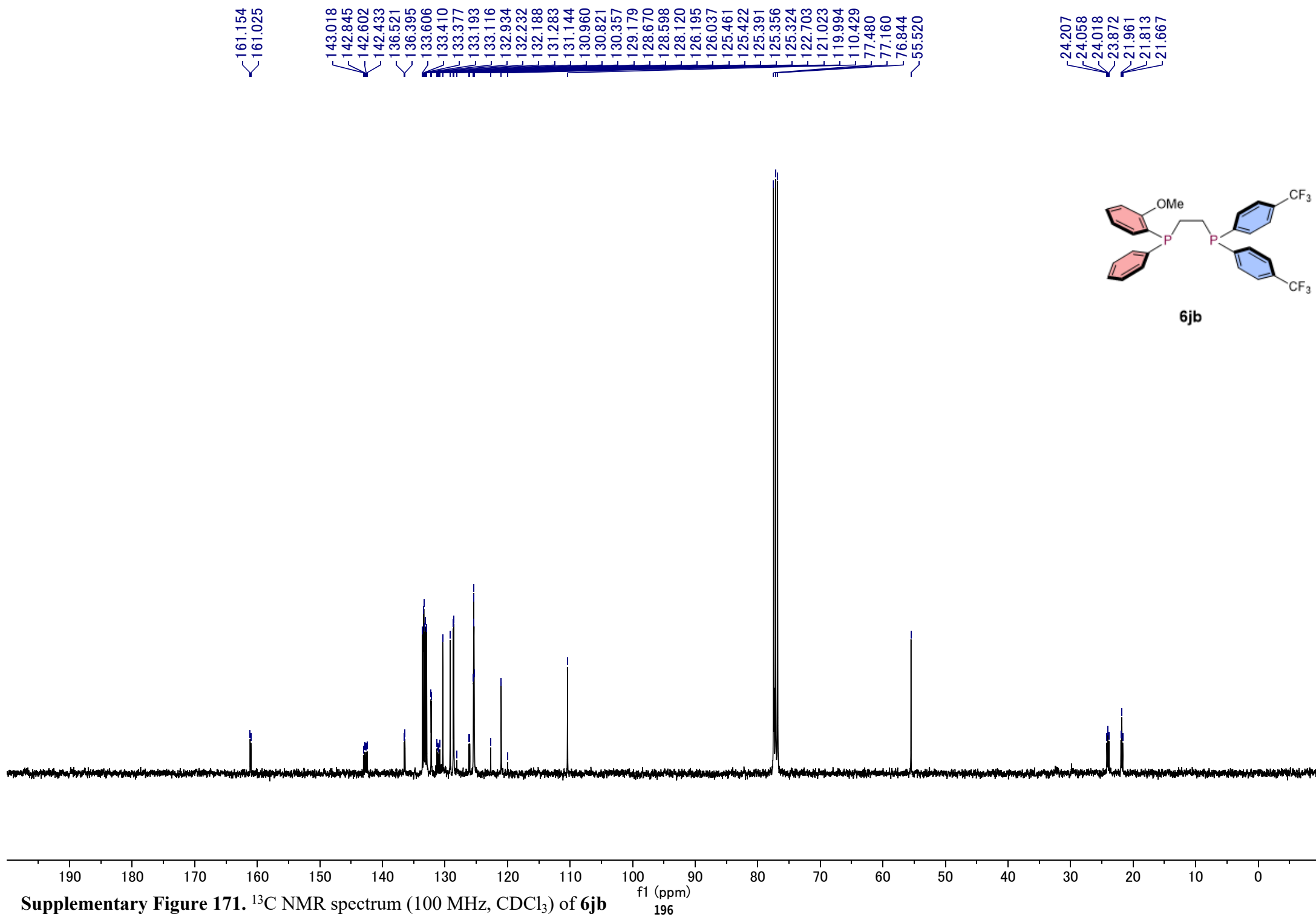
Supplementary Figure 169. ³¹P NMR spectrum (162 MHz, CDCl₃) of **6fb**

CDCl₃, 400 MHz



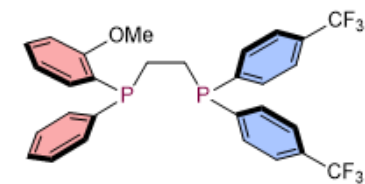
Supplementary Figure 170. ¹H NMR spectrum (400 MHz, CDCl₃) of **6jb**

CDCl₃, 100 MHz



CDCl₃, 376 MHz

--62.705



6jb

30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

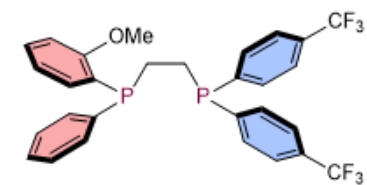
Supplementary Figure 172. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **6jb**

f1 (ppm)
197

CDCl₃, 162 MHz

-11.705
-11.919

-20.946
-21.160



6jb

100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45

Supplementary Figure 173. ³¹P NMR spectrum (162 MHz, CDCl₃) of **6jb**

f1 (ppm)
198

CDCl₃, 400 MHz

7.573
7.570
7.554
7.551
7.458
7.443
7.441
7.438
7.423
7.260
7.188
7.170

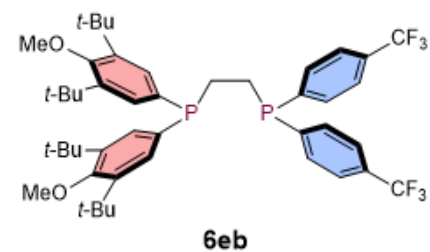
3.669
2.232
2.222
2.218
2.213
2.201
2.197
2.190
2.183
2.181
2.176
2.173
2.170
2.027
2.017
2.008
1.998
1.985
1.978
1.966
1.346

//

|

//

//



4.09
4.09
4.07

6.09

2.00
2.01

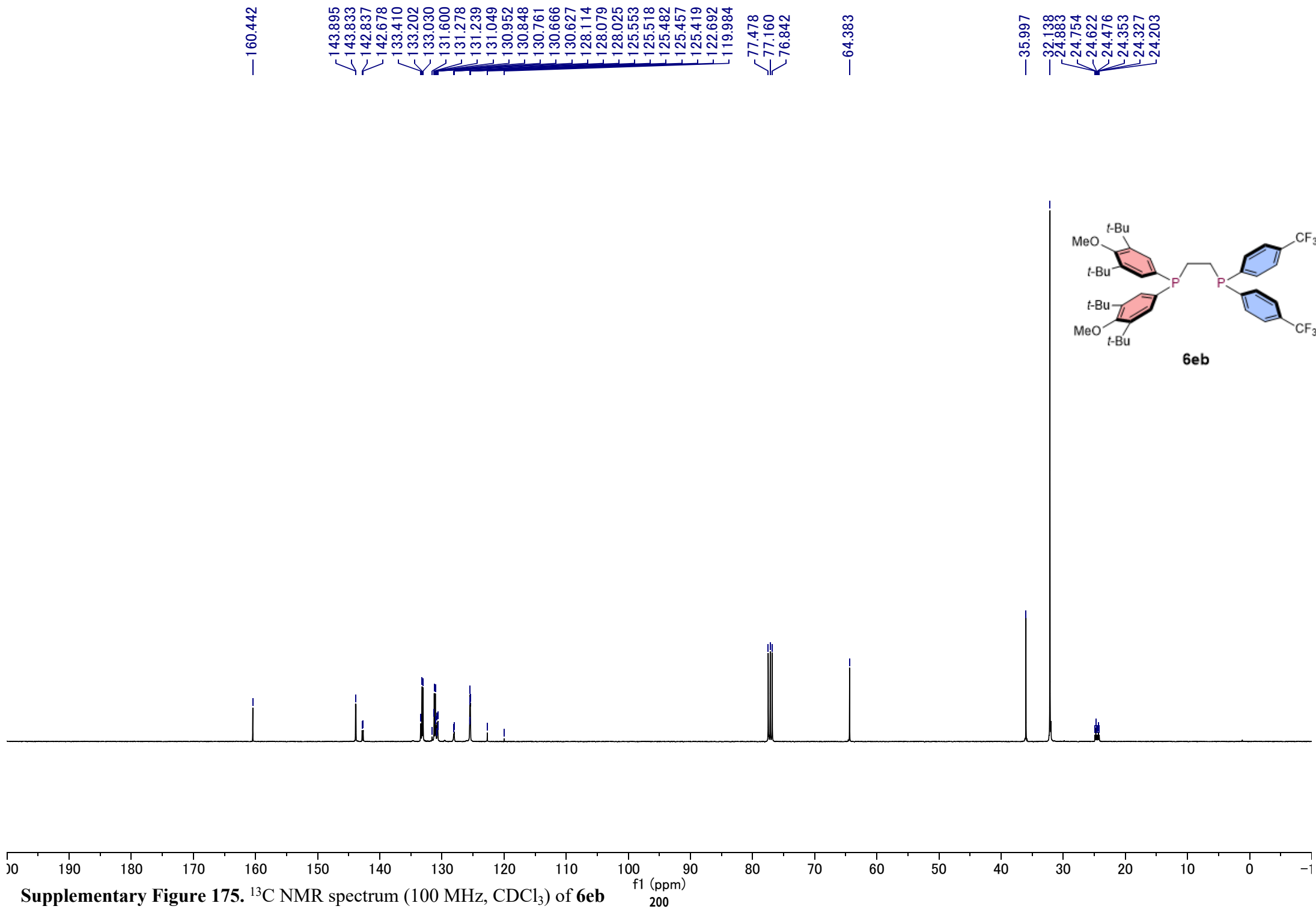
36.33

0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

Supplementary Figure 174. ¹H NMR spectrum (400 MHz, CDCl₃) of **6eb**

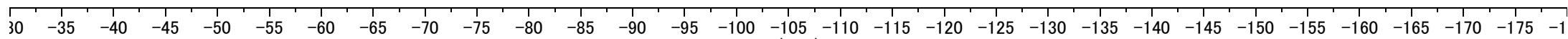
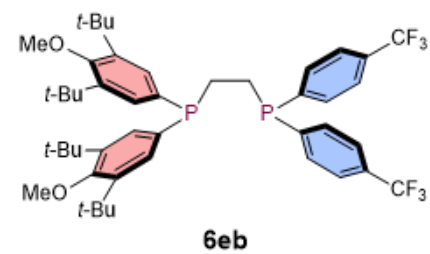
f1 (ppm)
199

CDCl₃, 100 MHz



CDCl₃, 376 MHz

--62.748

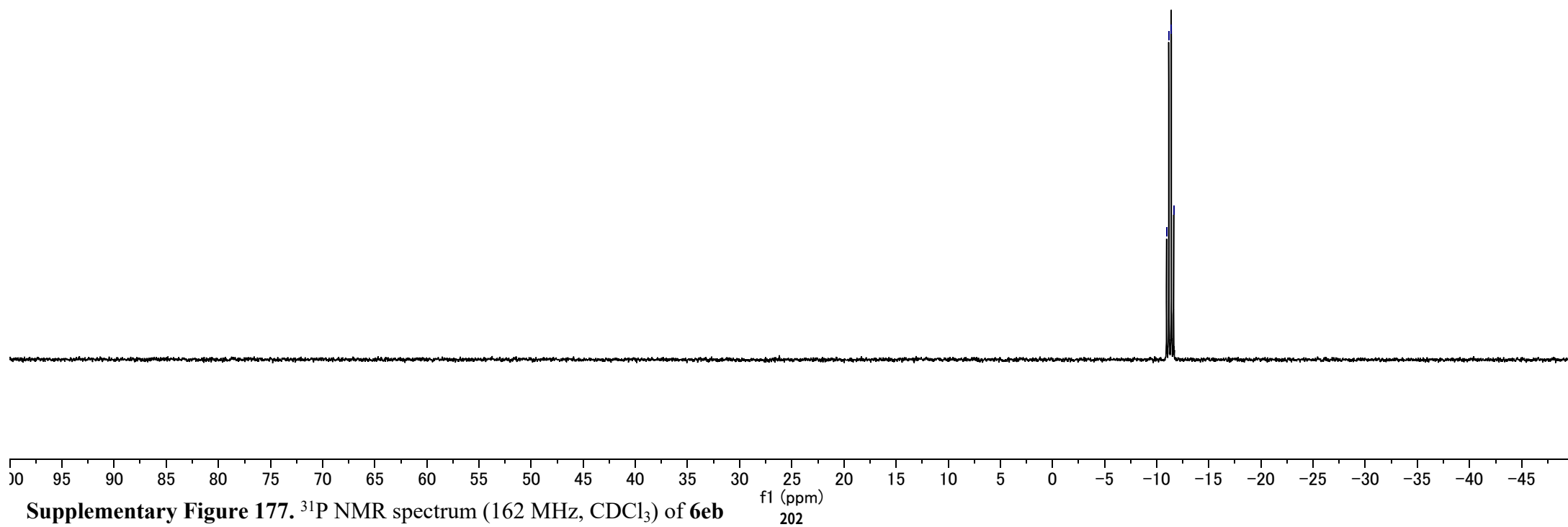
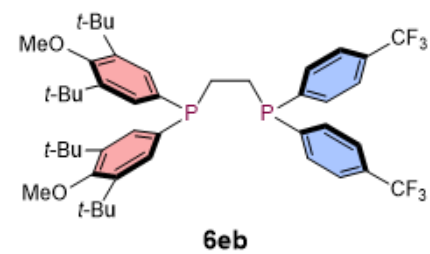


Supplementary Figure 176. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **6eb**

f1 (ppm)
201

CDCl₃, 162 MHz

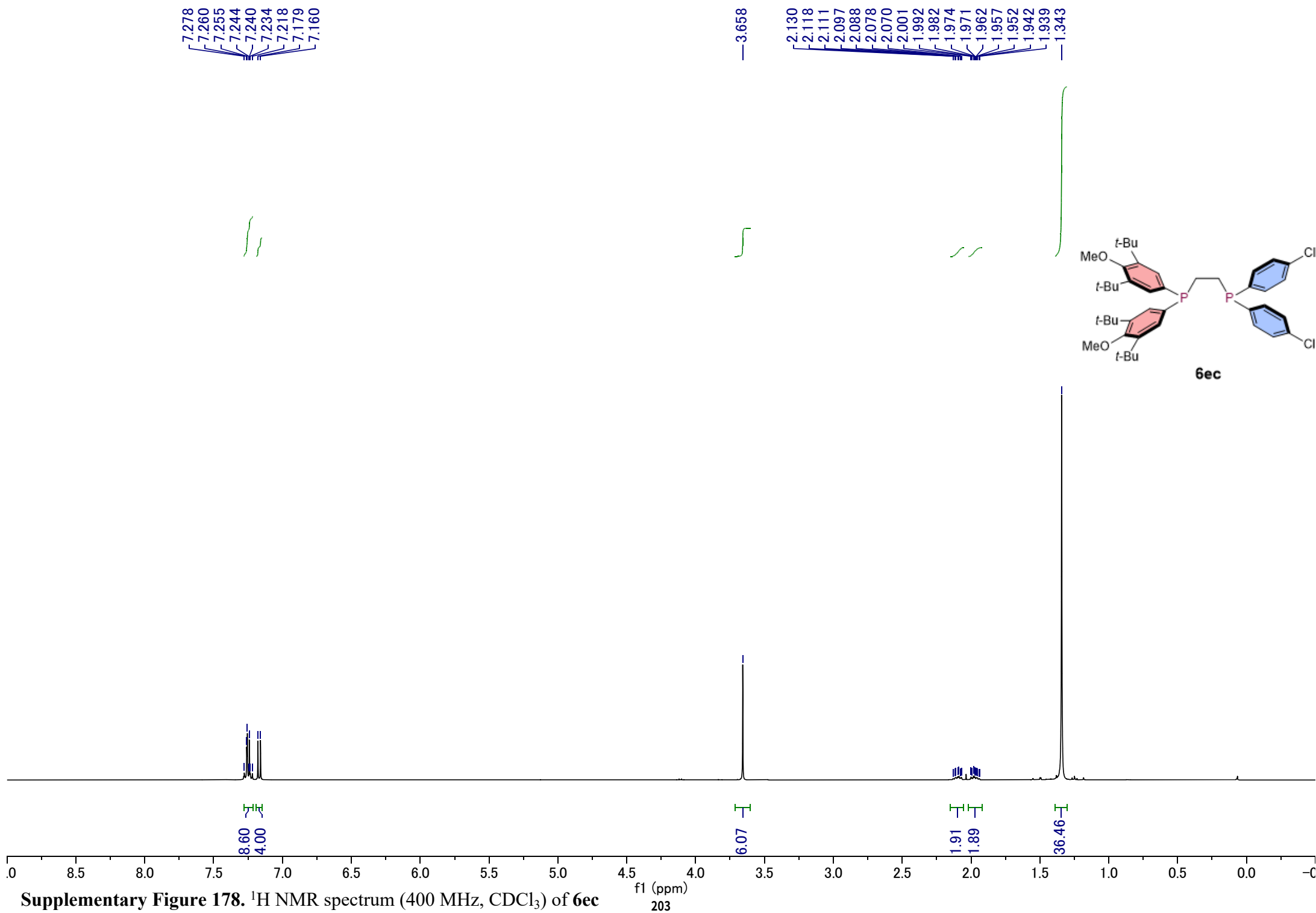
10.942
11.156
11.410
11.624



Supplementary Figure 177. ³¹P NMR spectrum (162 MHz, CDCl₃) of **6eb**

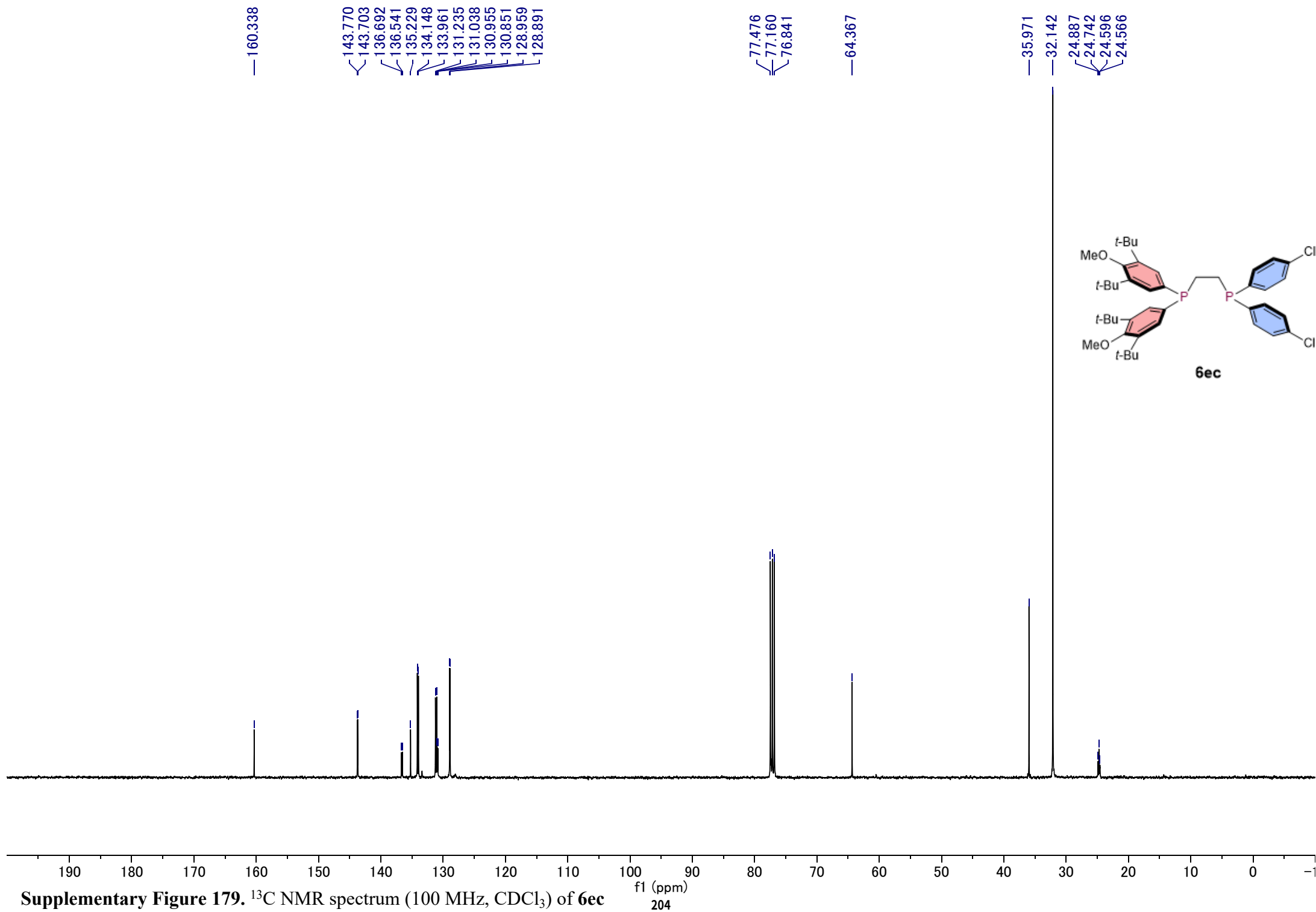
f1 (ppm)
202

CDCl₃, 400 MHz



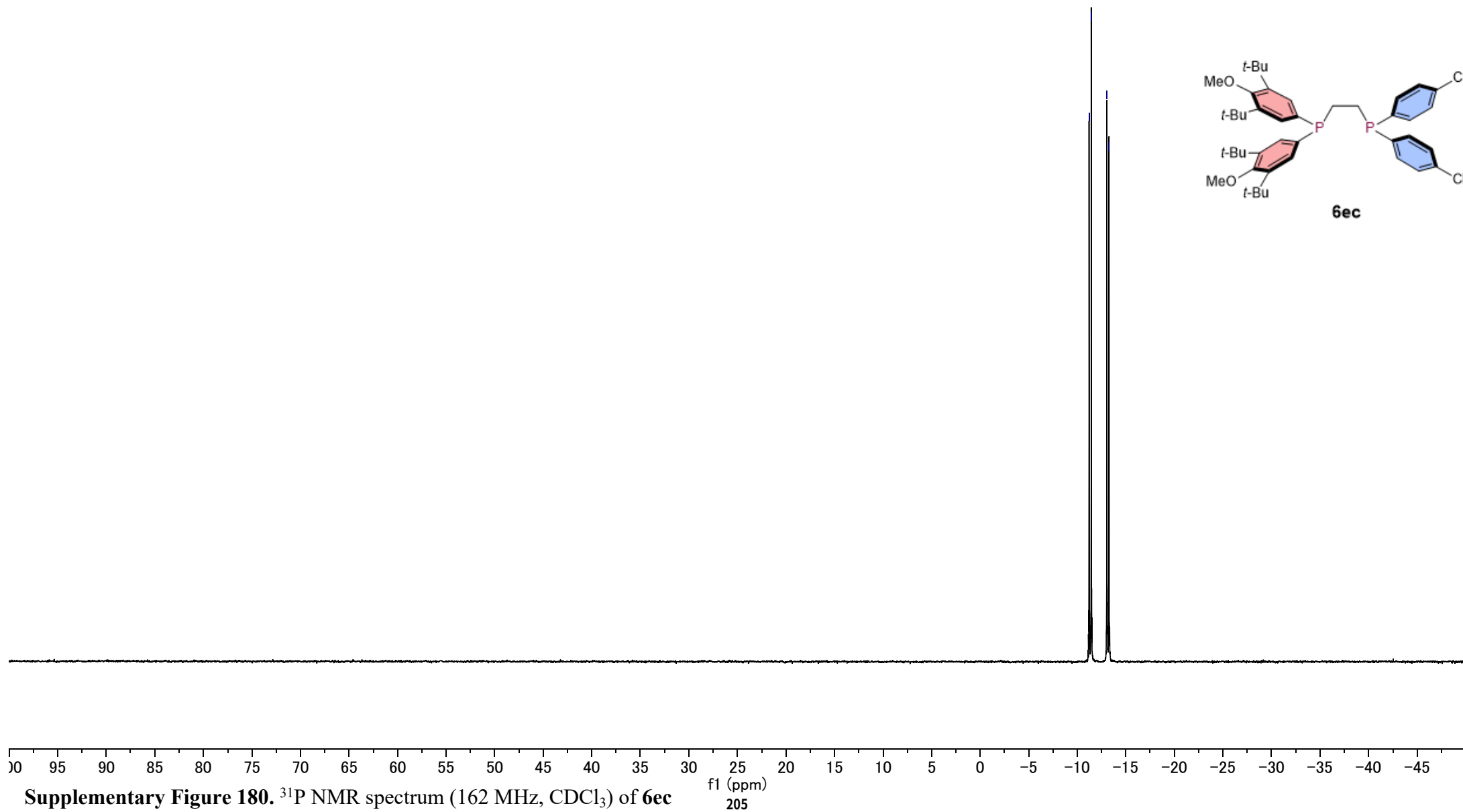
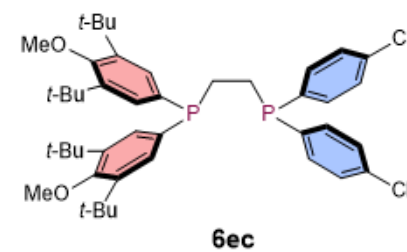
Supplementary Figure 178. ¹H NMR spectrum (400 MHz, CDCl₃) of 6ec

CDCl₃, 100 MHz

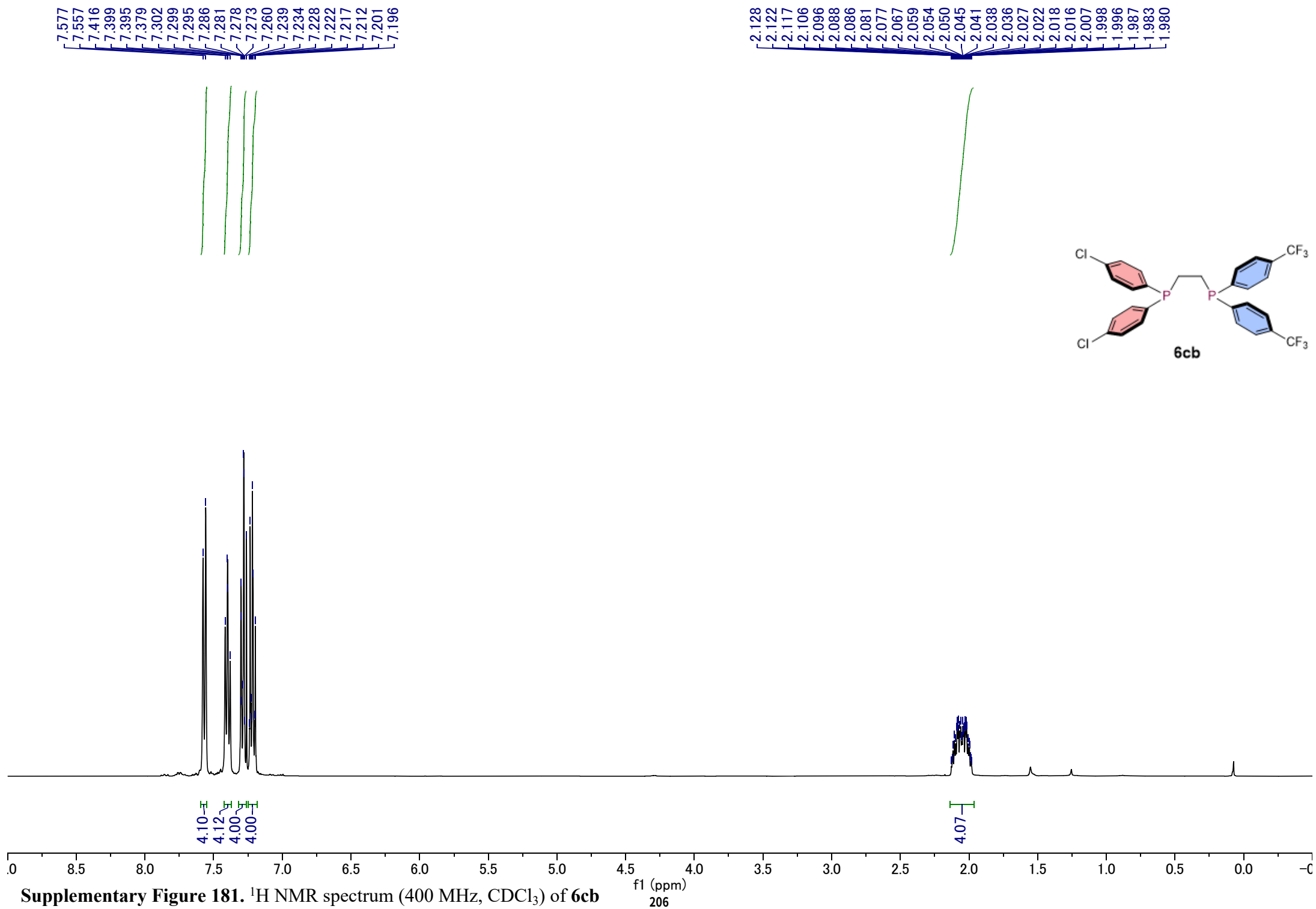


CDCl₃, 162 MHz

-11.223
-11.438
-13.056
-13.271



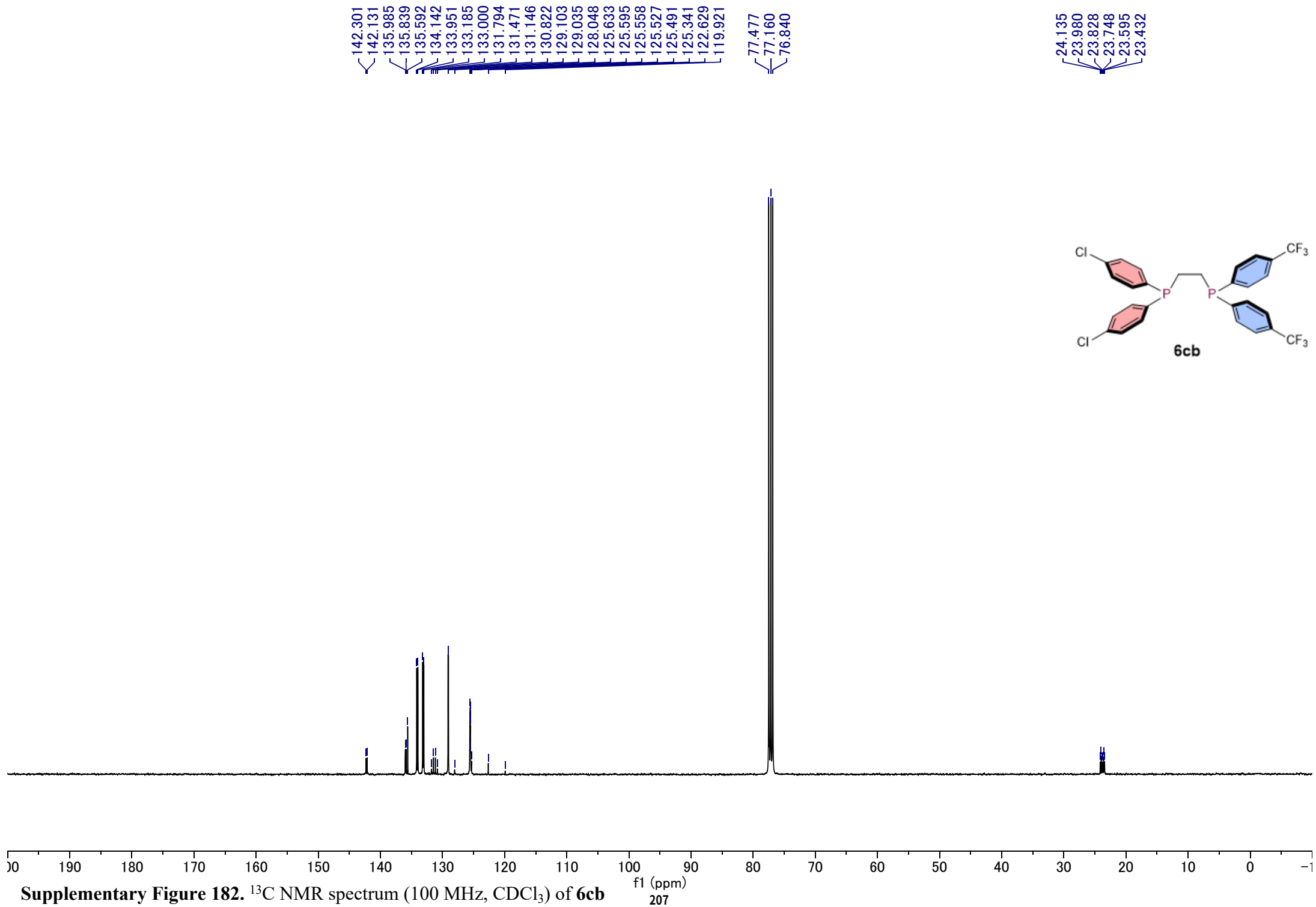
CDCl₃, 400 MHz



Supplementary Figure 181. ¹H NMR spectrum (400 MHz, CDCl₃) of 6cb

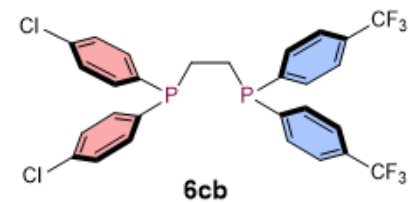
f1 (ppm)
206

CDCl₃, 100 MHz



CDCl₃, 376 MHz

-62.749

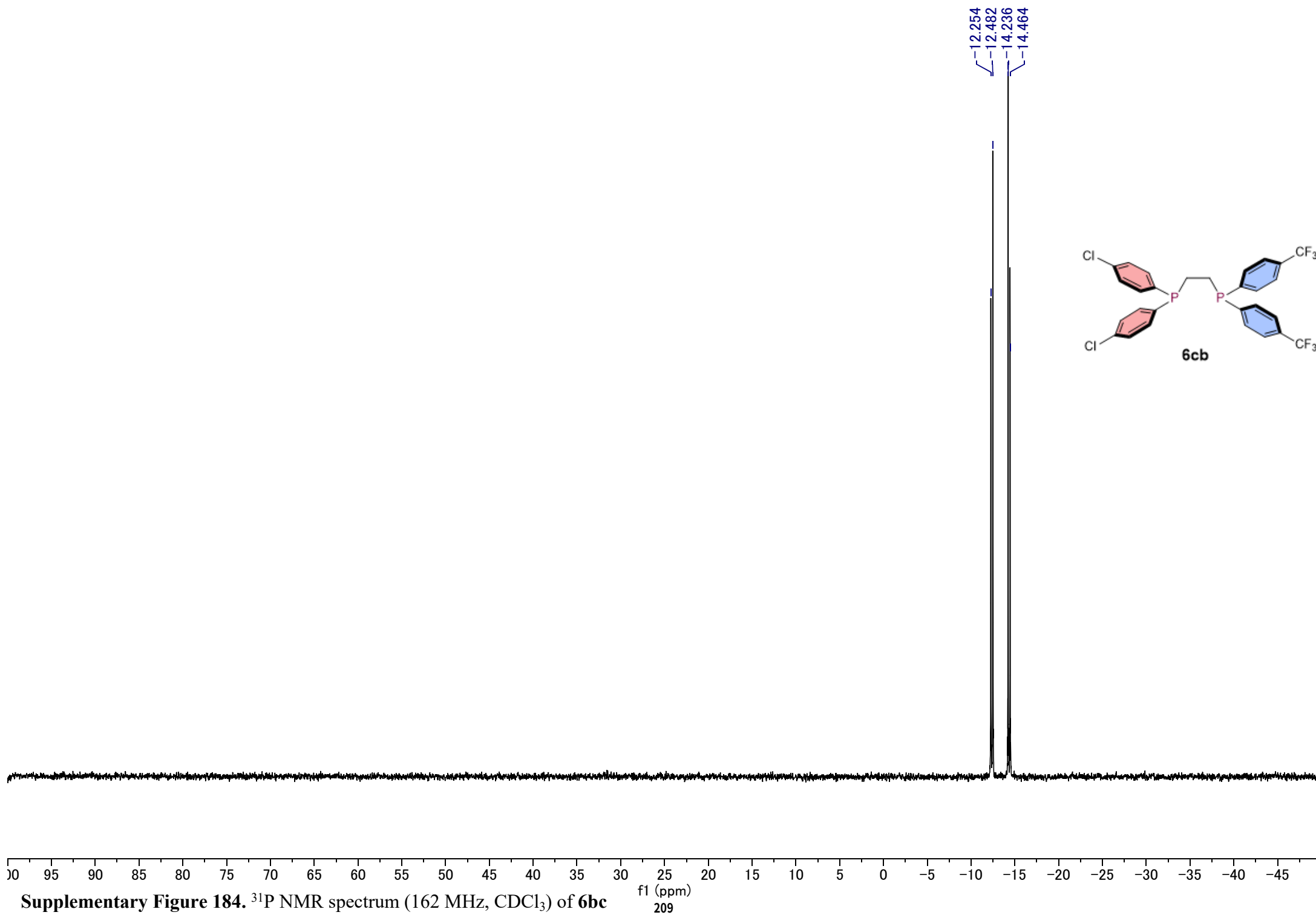


30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

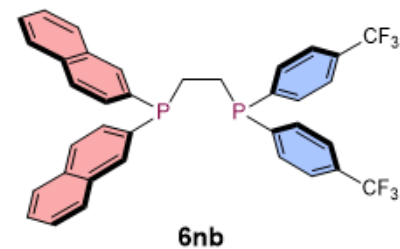
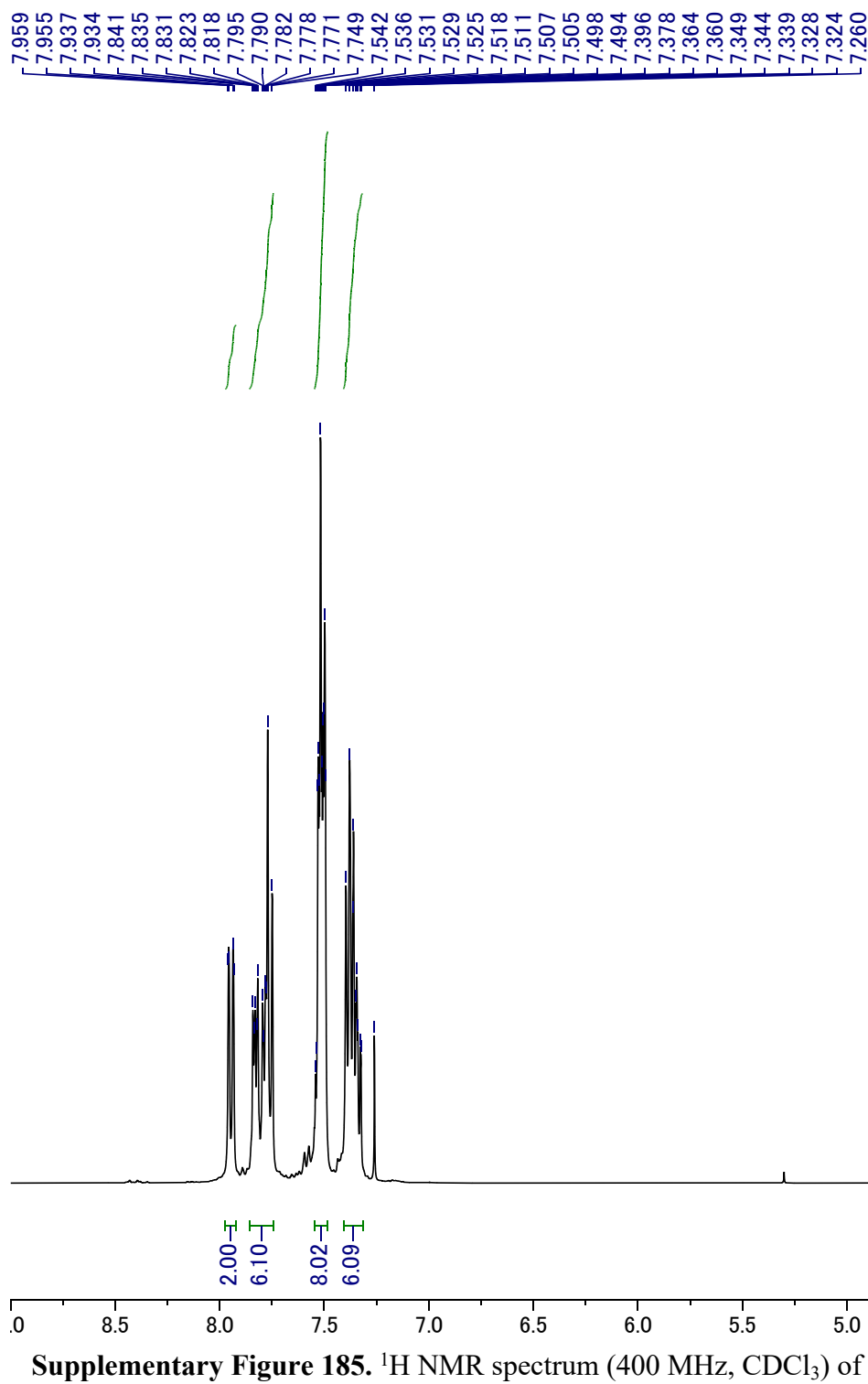
Supplementary Figure 183. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **6cb**

f1 (ppm)
208

CDCl₃, 162 MHz



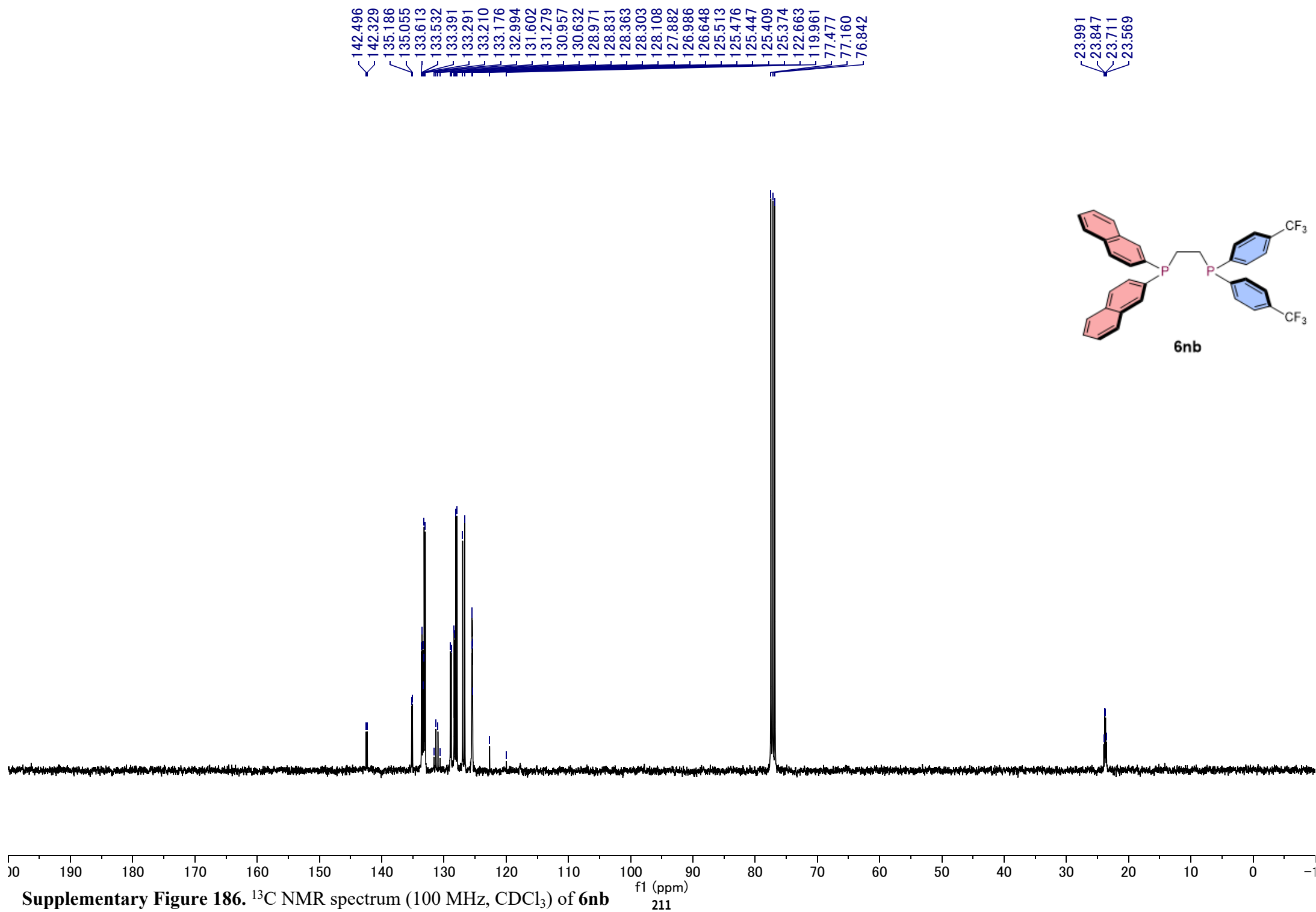
CDCl₃, 400 MHz



Supplementary Figure 185. ¹H NMR spectrum (400 MHz, CDCl₃) of **6nb**

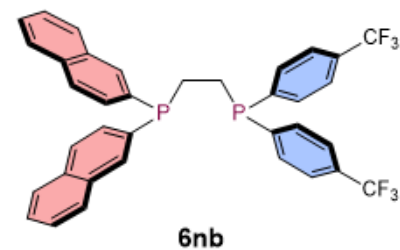
f1 (ppm)
210

CDCl₃, 100 MHz



CDCl₃, 376 MHz

-62.731

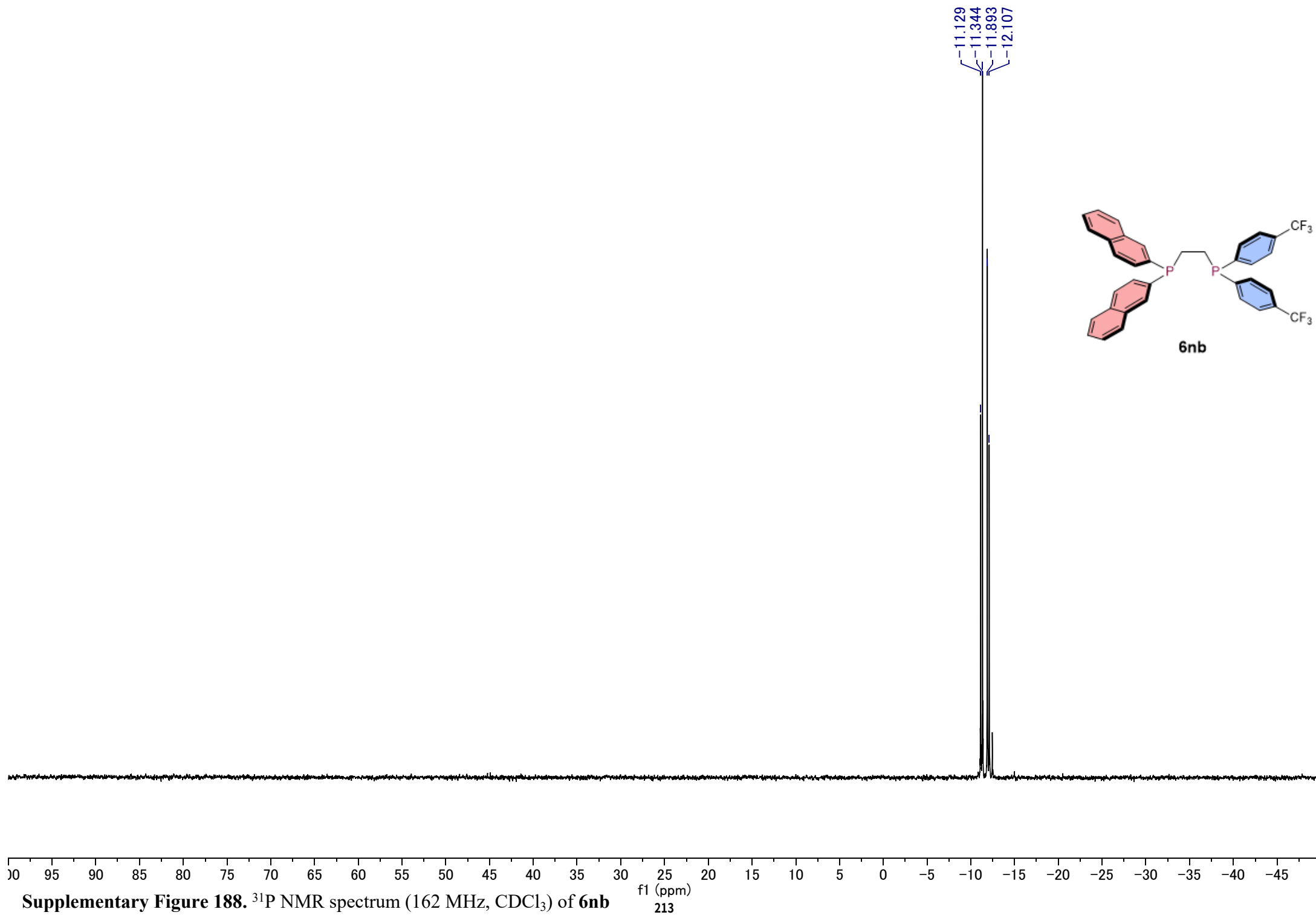


30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 187. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **6nb**

f1 (ppm)
212

CDCl₃, 162 MHz



Supplementary Figure 188. ³¹P NMR spectrum (162 MHz, CDCl₃) of **6nb**

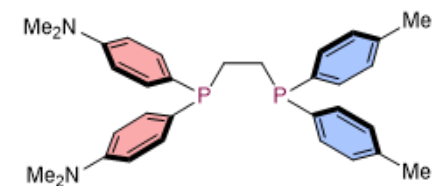
f1 (ppm)
213

CDCl₃, 400 MHz

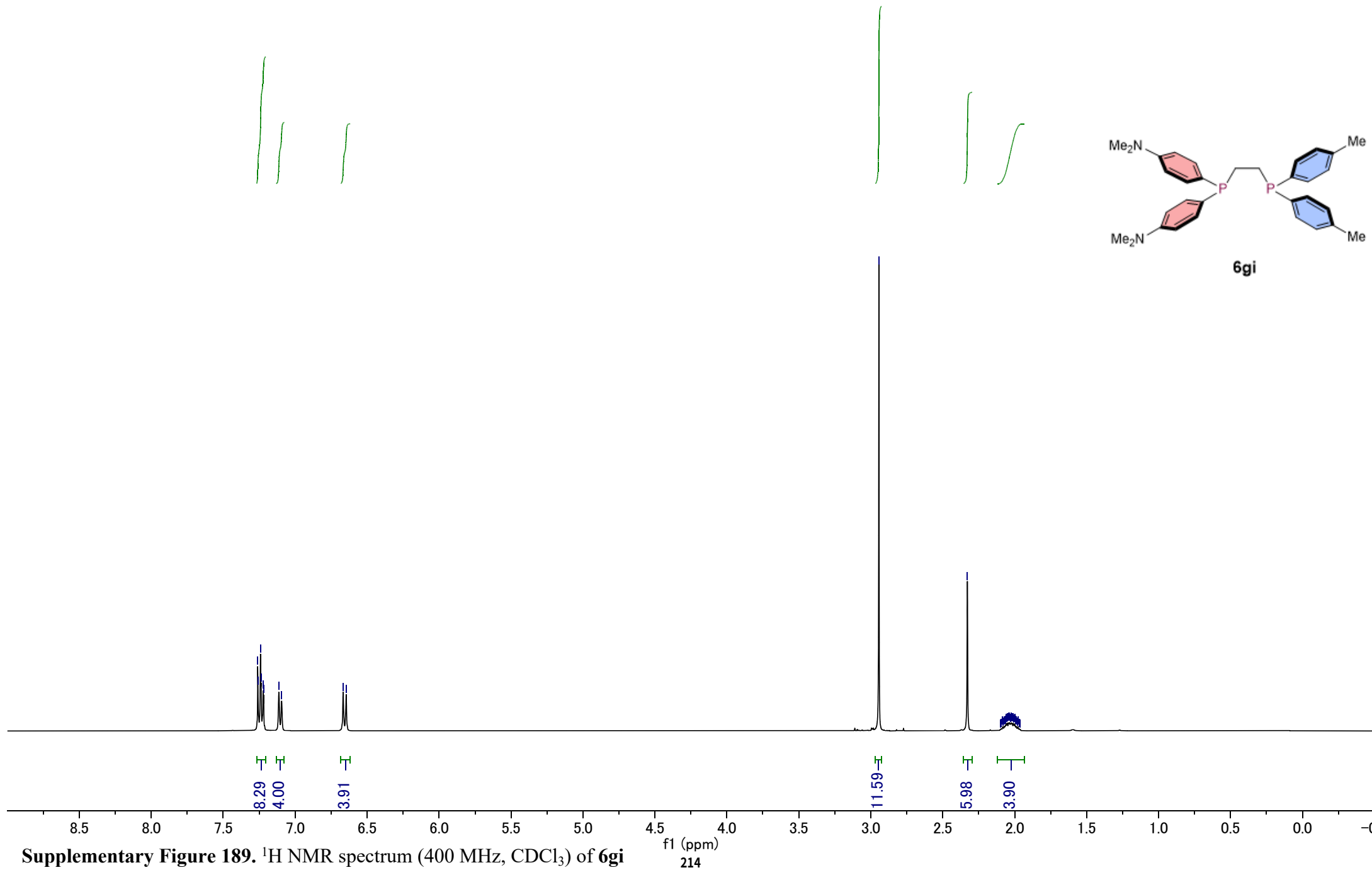
7.260
7.258
7.241
7.236
7.223
7.219
7.113
7.094
6.666
6.646

2.944

2.329
2.099
2.097
2.092
2.083
2.080
2.071
2.065
2.061
2.055
2.052
2.044
2.037
2.031
2.025
2.018
2.010
2.006
2.000
1.996
1.990
1.981
1.978
1.969
1.964

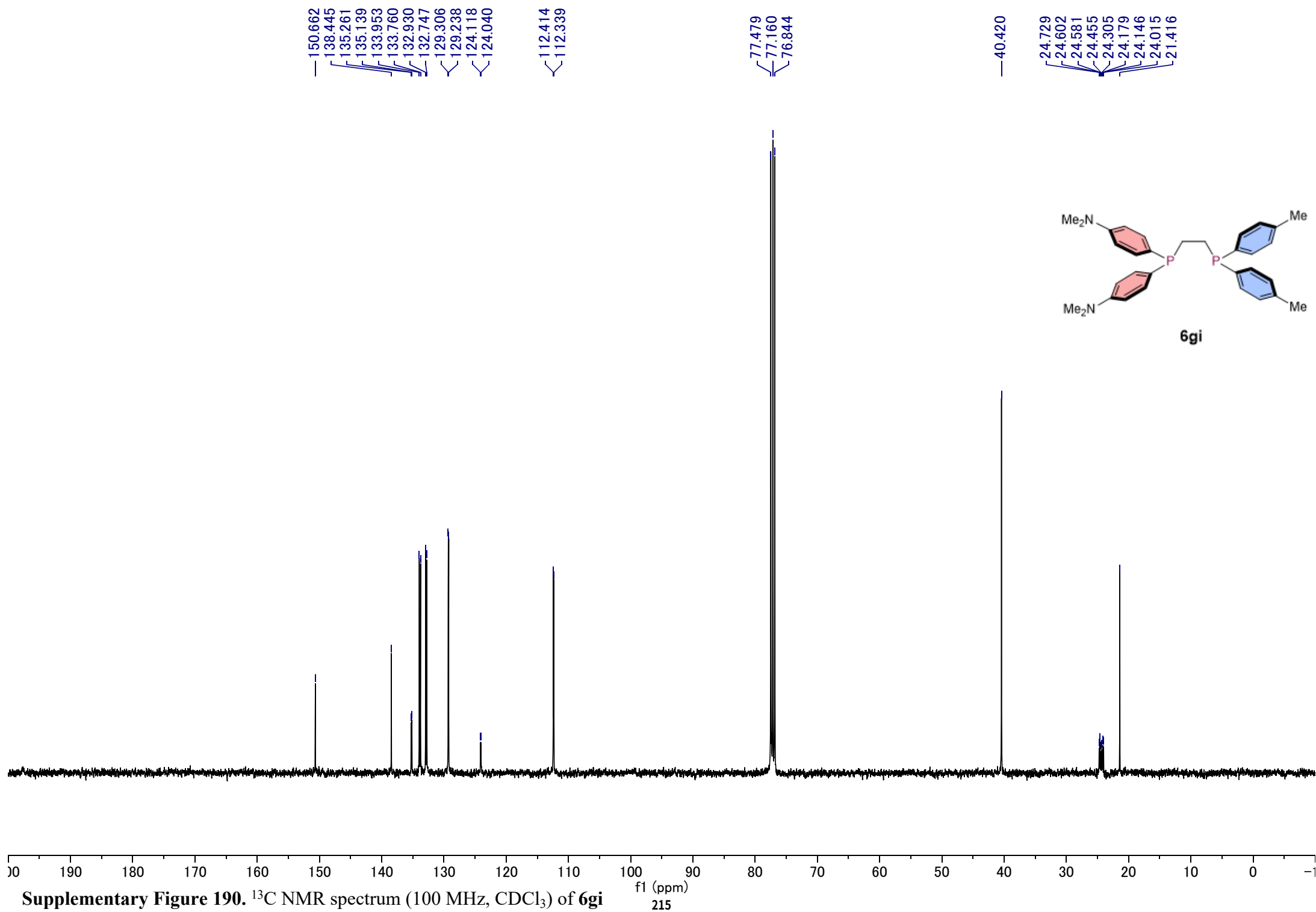


6gi



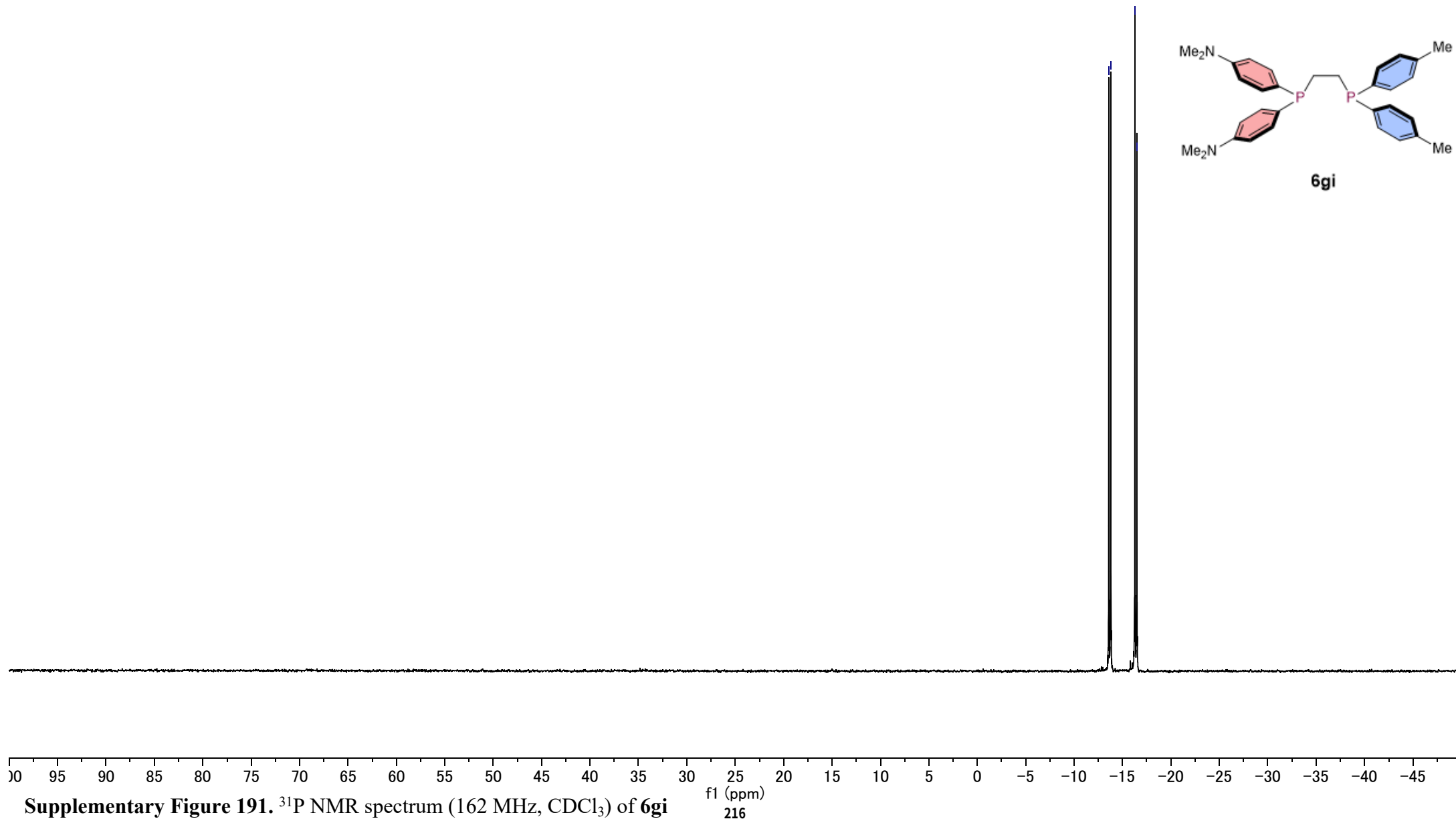
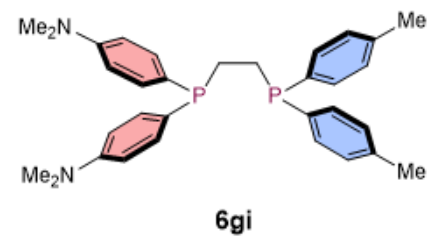
Supplementary Figure 189. ¹H NMR spectrum (400 MHz, CDCl₃) of **6gi**

CDCl₃, 100 MHz

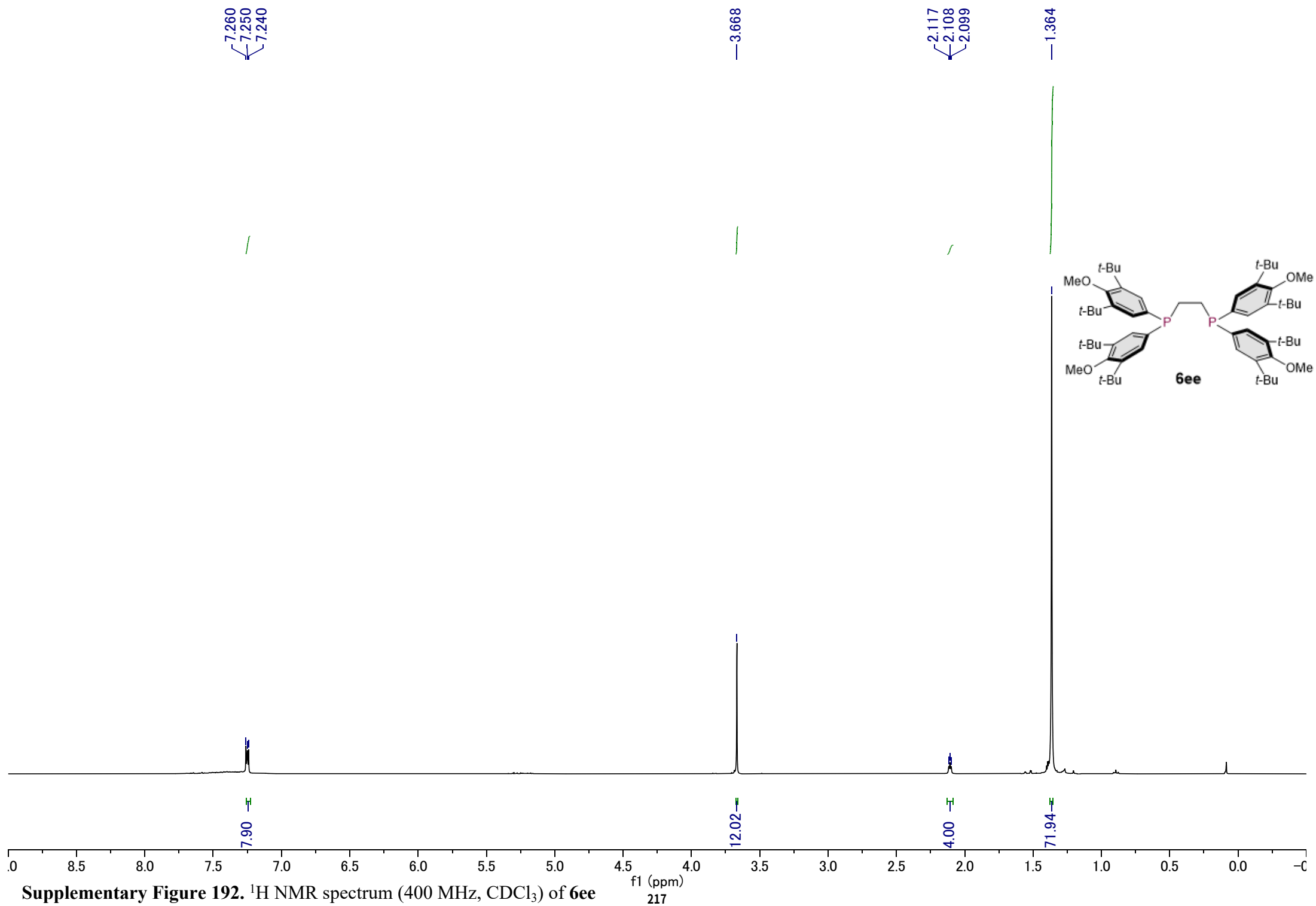


CDCl₃, 162 MHz

13.580
13.782
16.272
16.475

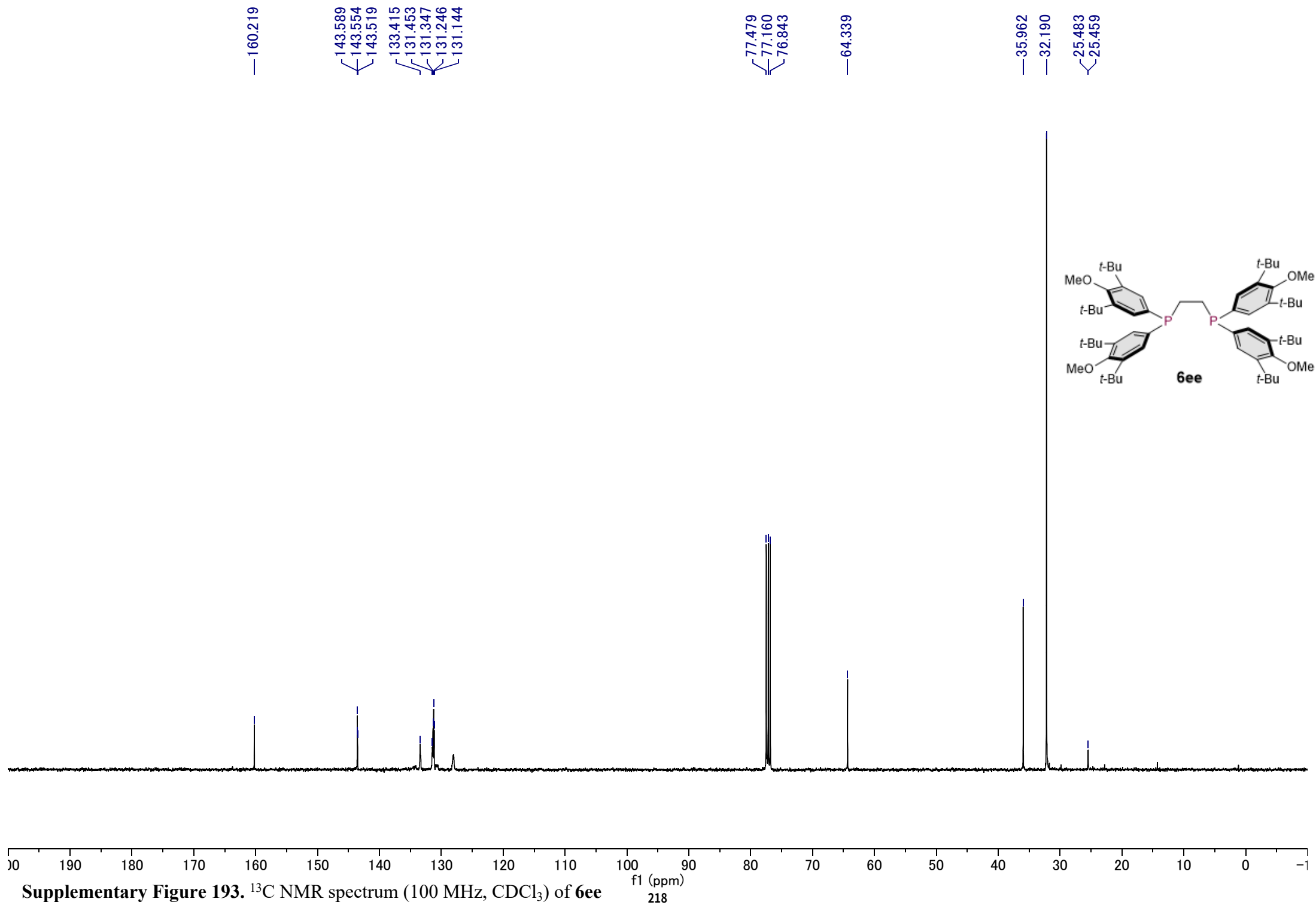


CDCl₃, 400 MHz



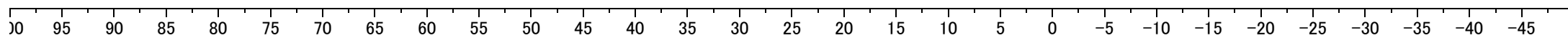
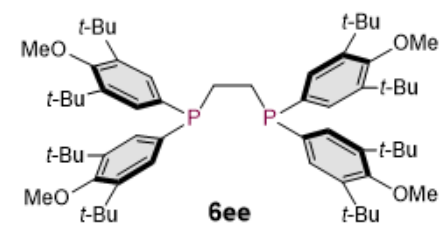
Supplementary Figure 192. ¹H NMR spectrum (400 MHz, CDCl₃) of **6ee**

CDCl₃, 100 MHz



CDCl₃, 162 MHz

---11.605



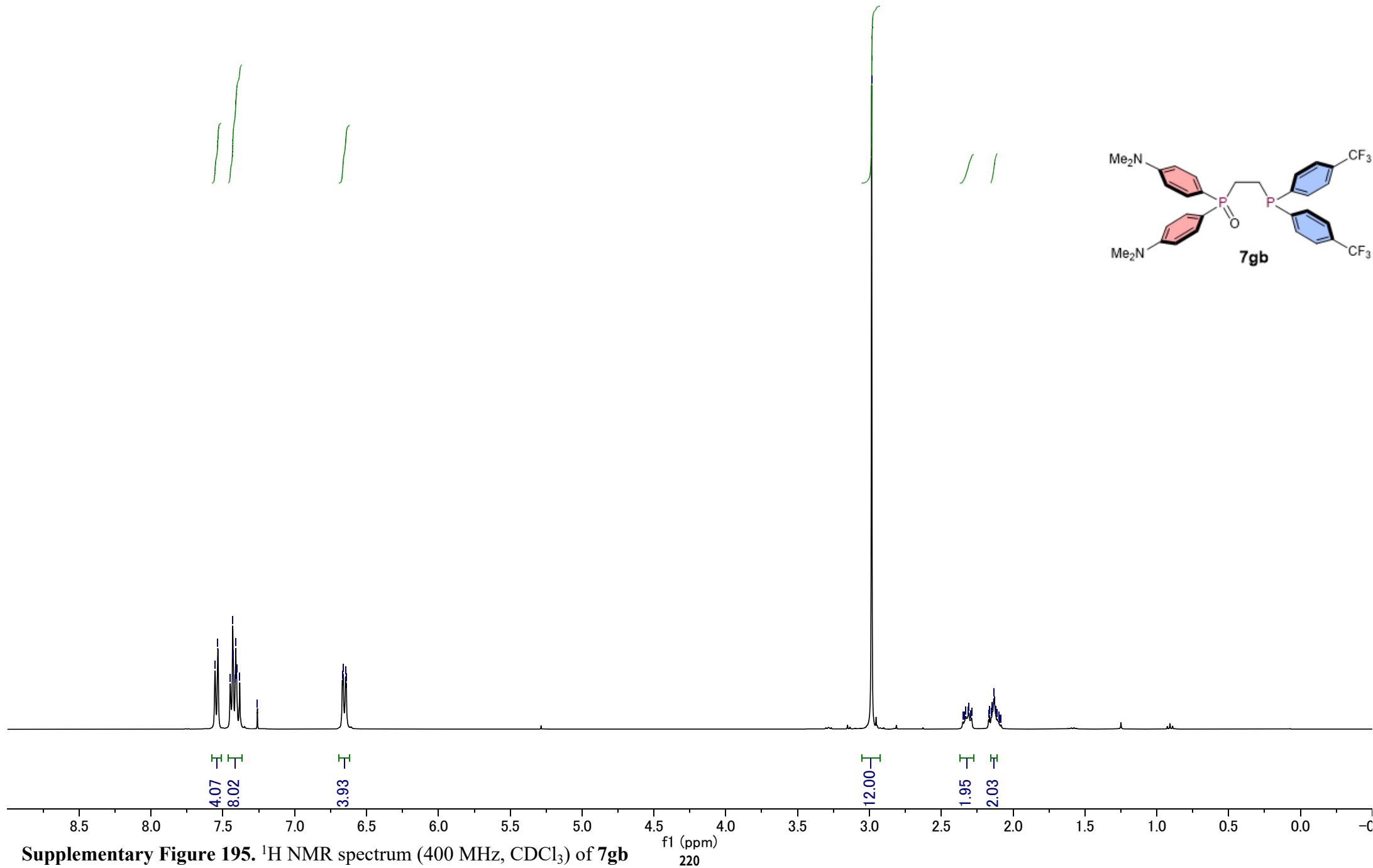
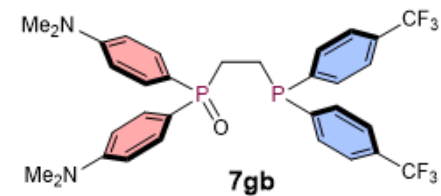
Supplementary Figure 194. ³¹P NMR spectrum (162 MHz, CDCl₃) of **6ee**

f1 (ppm)
219

CDCl₃, 400 MHz

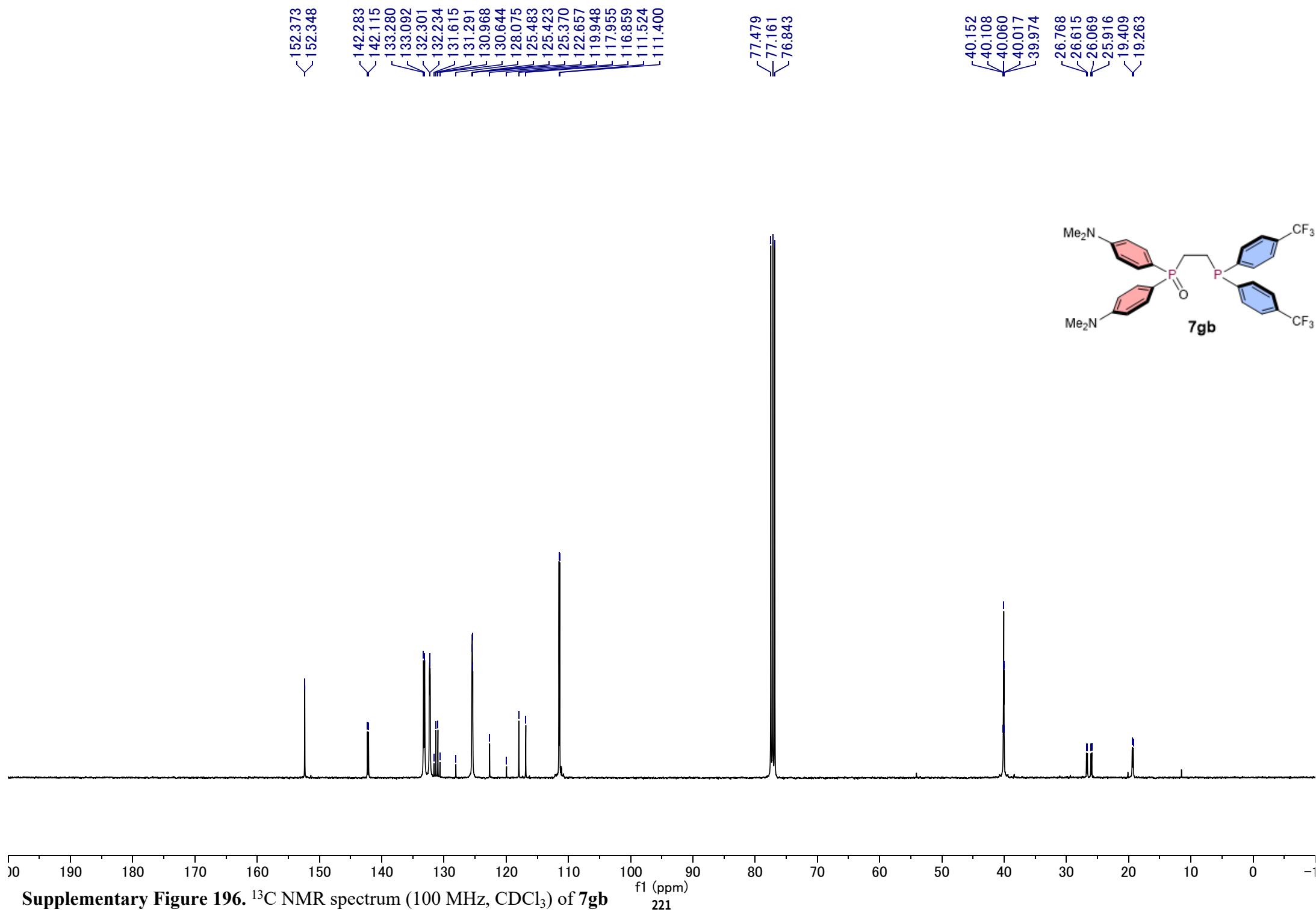
7.554
7.535
7.448
7.431
7.427
7.414
7.410
7.404
7.382
7.260
6.669
6.663
6.646
6.641

2.985
2.350
2.340
2.330
2.316
2.307
2.297
2.289
2.171
2.164
2.153
2.145
2.134
2.127
2.120
2.110
2.101
2.094
2.084



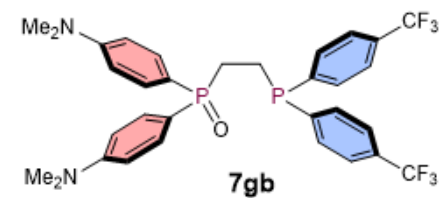
Supplementary Figure 195. ¹H NMR spectrum (400 MHz, CDCl₃) of **7gb**

CDCl₃, 100 MHz



CDCl₃, 376 MHz

-62.723

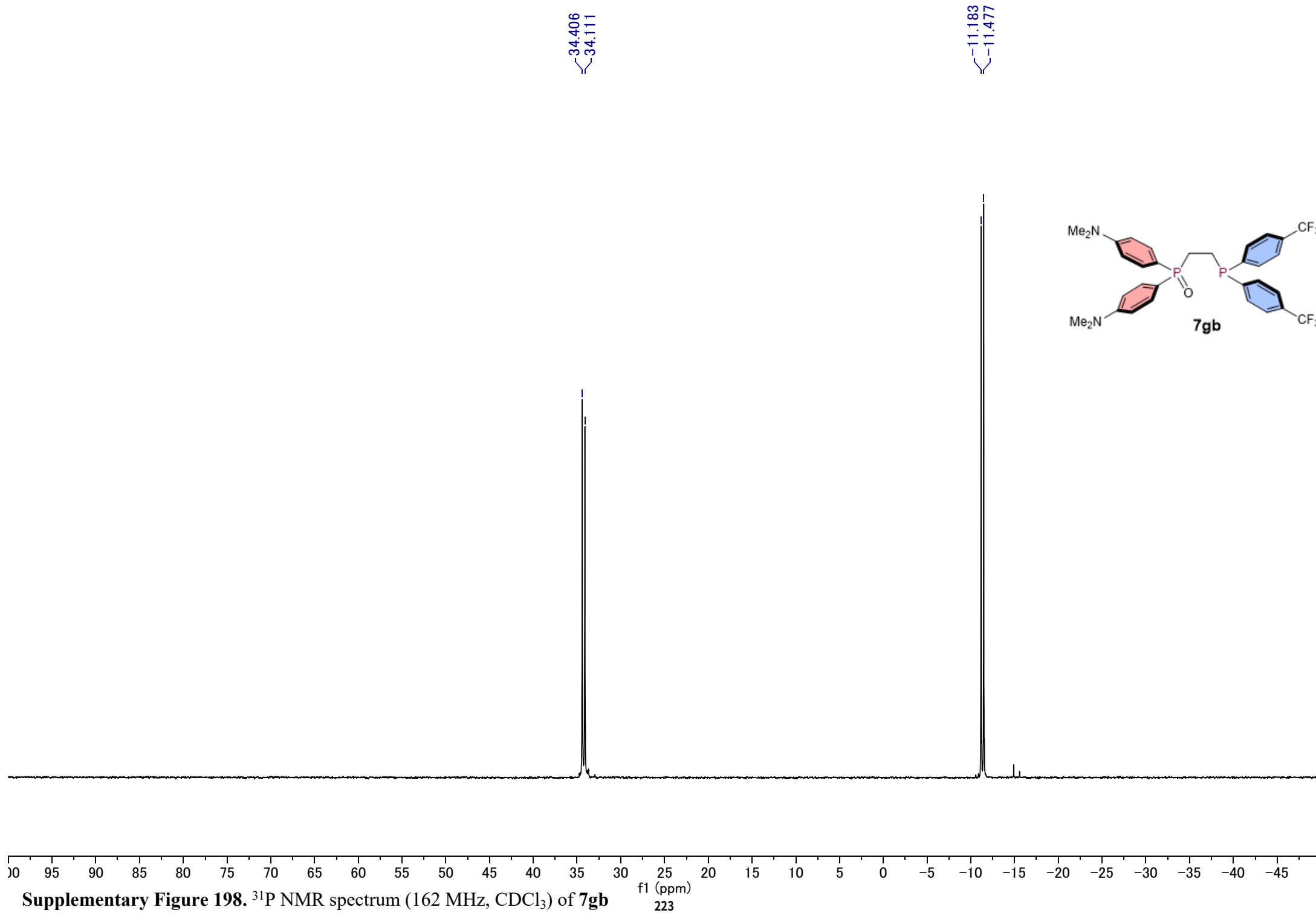


30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 197. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of **7gb**

f1 (ppm)
222

CDCl₃, 162 MHz

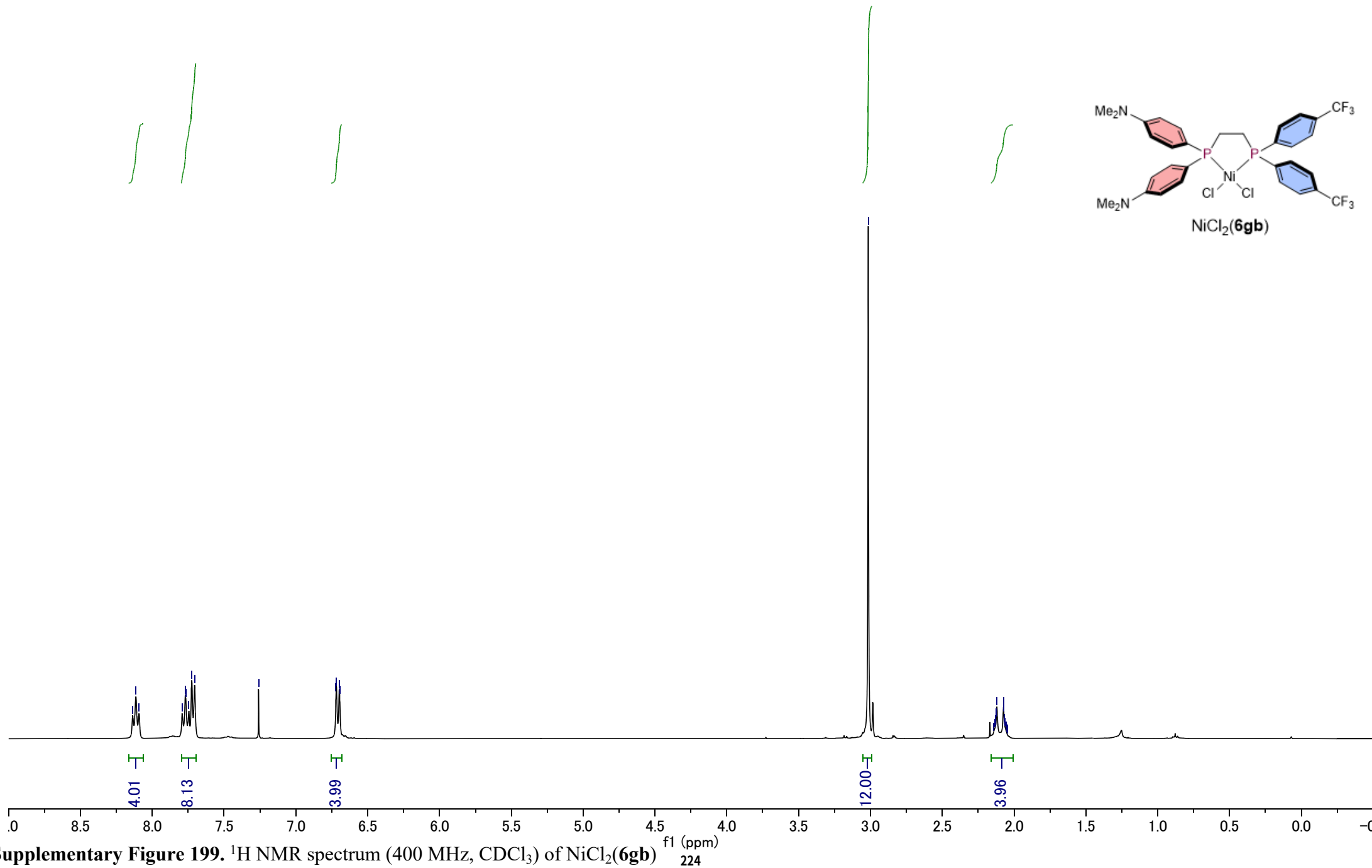
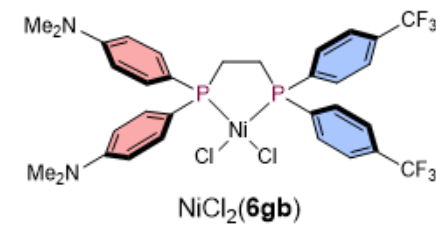


Supplementary Figure 198. ³¹P NMR spectrum (162 MHz, CDCl₃) of **7gb**

CDCl₃, 400 MHz

8.136
8.114
8.092
7.792
7.771
7.766
7.746
7.725
7.705
7.260
6.721
6.717
6.699
6.695

3.016
2.144
2.136
2.131
2.128
2.125
2.120
2.074
2.071
2.067
2.062
2.054
2.049
2.045



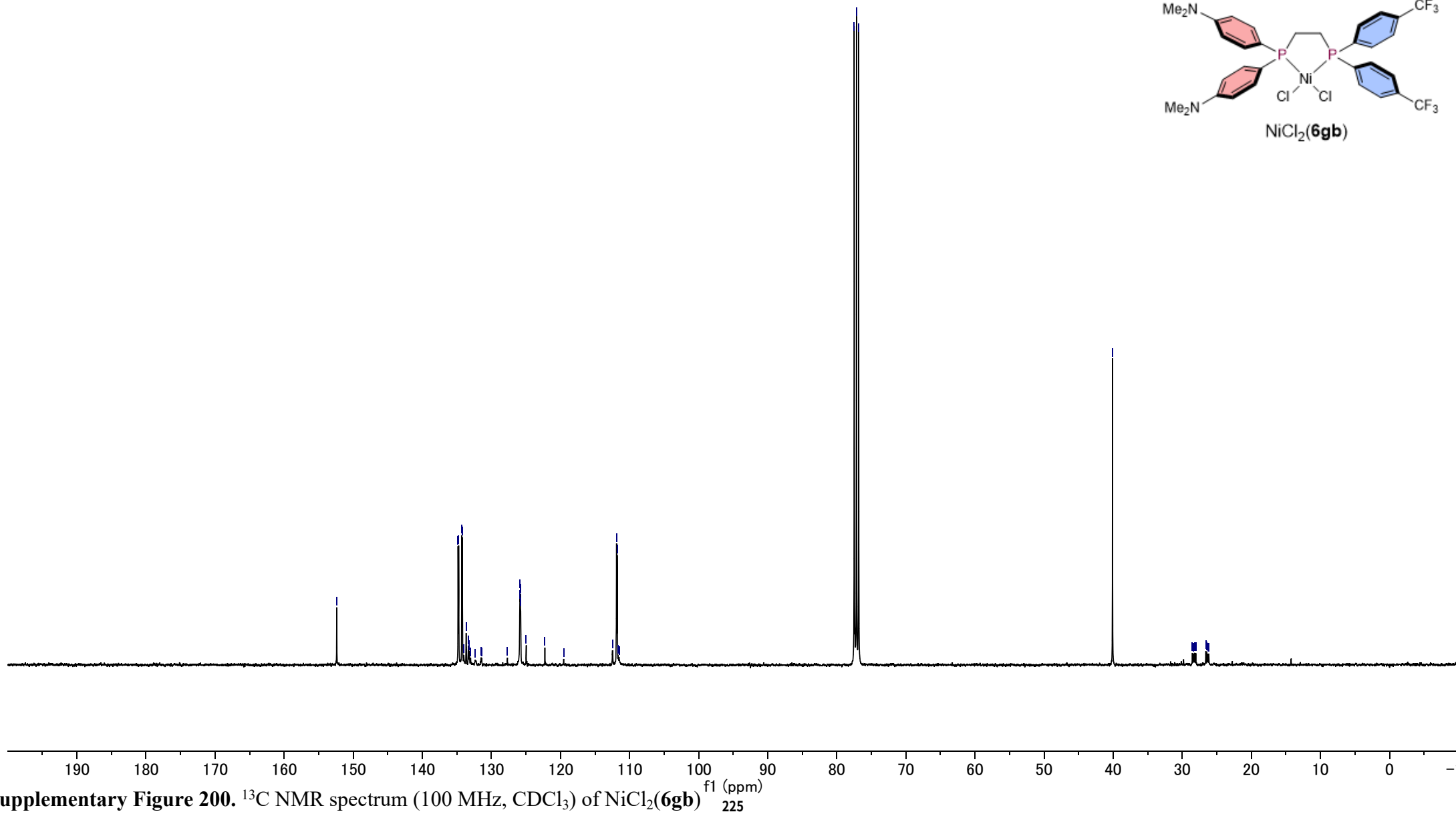
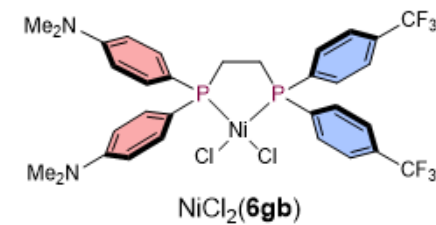
Supplementary Figure 199. ¹H NMR spectrum (400 MHz, CDCl₃) of NiCl₂(**6gb**)

CDCl₃, 100 MHz

152.383
134.821
134.724
134.288
134.197
133.987
133.655
133.336
133.203
133.182
133.004
132.332
131.500
131.415
127.686
125.893
125.855
125.798
125.757
124.970
122.256
119.540
112.491
112.433
111.888
111.784
111.649
111.524

77.478
77.161
76.843

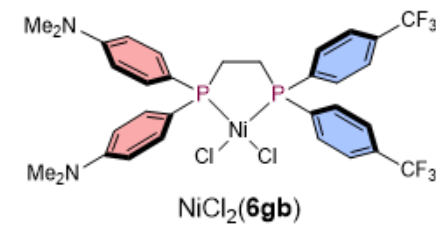
40.099
28.544
28.362
28.223
28.038
26.598
26.445
26.306
26.152



Supplementary Figure 200. ¹³C NMR spectrum (100 MHz, CDCl₃) of NiCl₂(**6gb**)

CDCl₃, 376 MHz

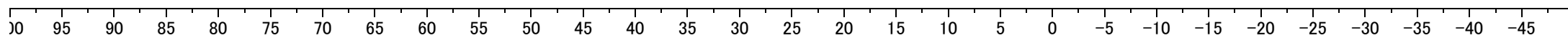
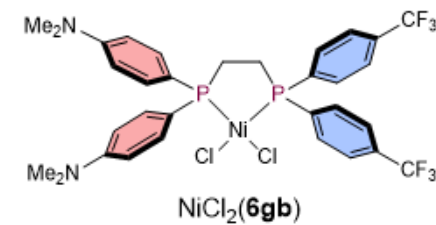
---63.065



30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

CDCl₃, 162 MHz

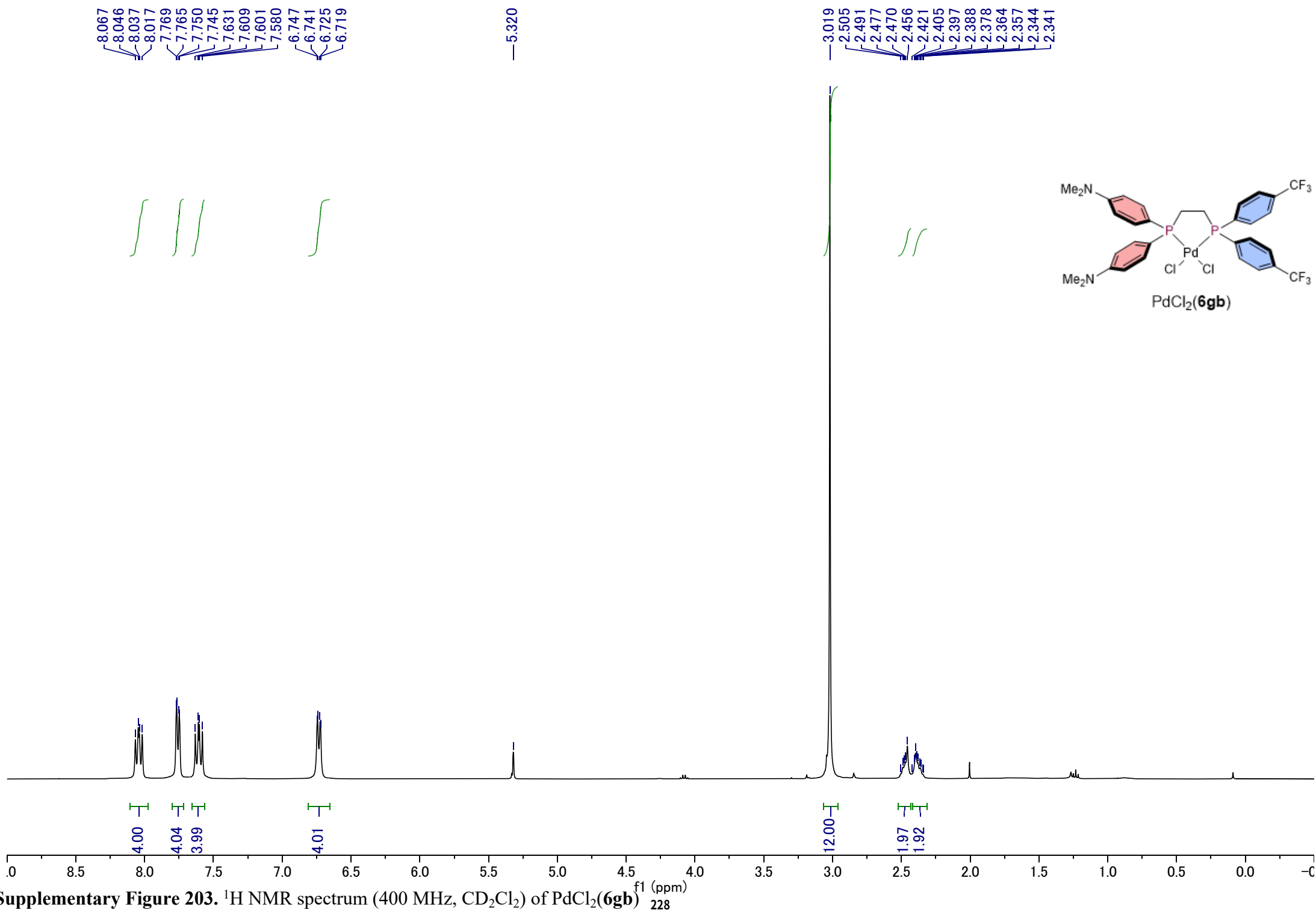
56.81
56.38
56.11
55.69



Supplementary Figure 202. ³¹P NMR spectrum (162 MHz, CDCl₃) of NiCl₂(**6gb**)

227

CD₂Cl₂, 400 MHz



Supplementary Figure 203. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of PdCl₂(**6gb**)

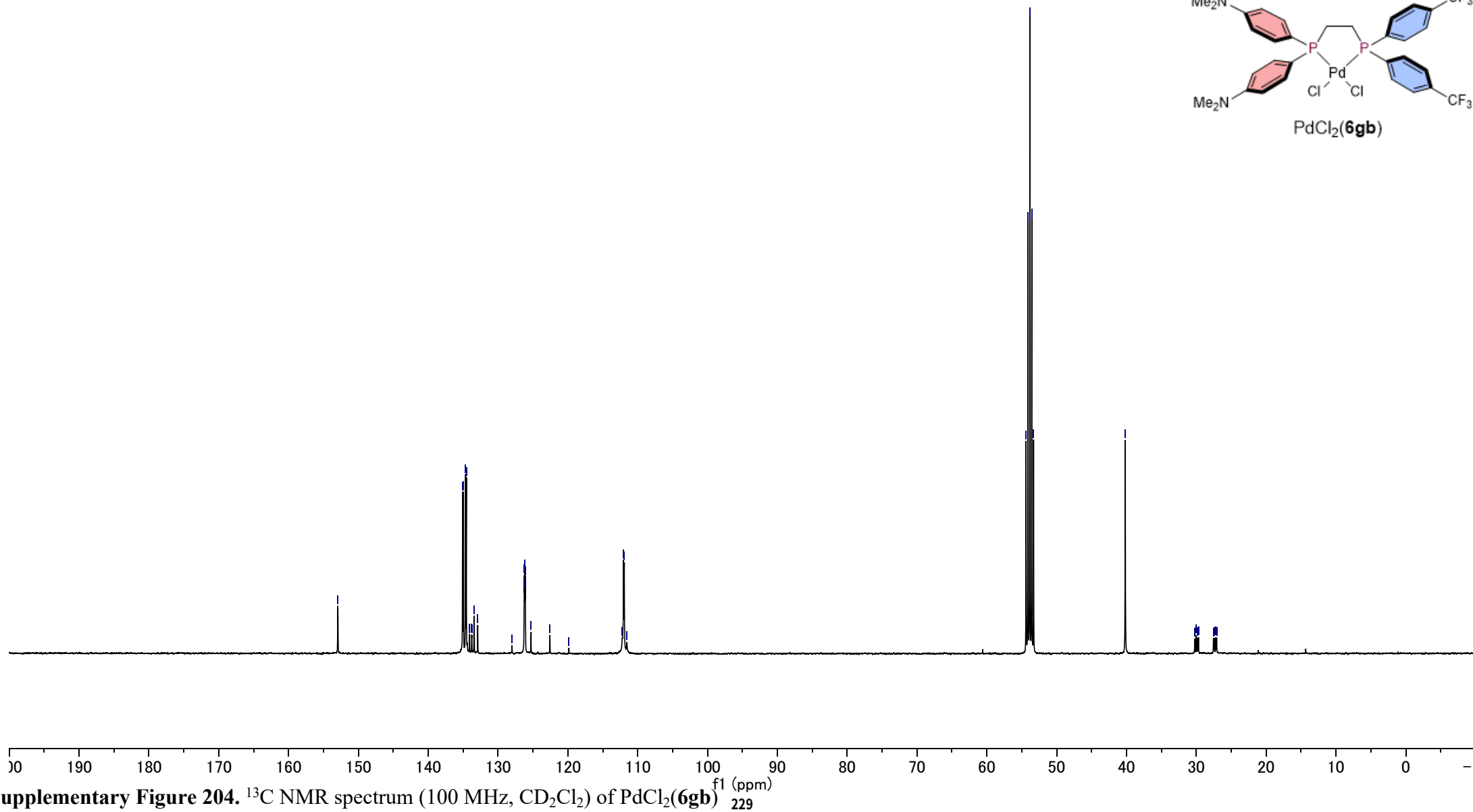
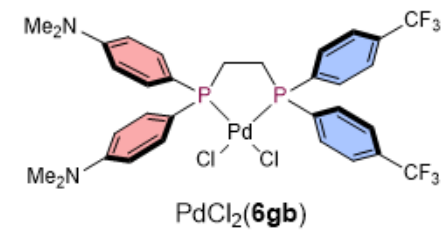
f1 (ppm)
228

CD₂Cl₂, 100 MHz

152.932
135.068
134.947
134.650
134.535
134.092
134.065
133.764
133.736
133.413
132.906
127.989
126.236
126.198
126.159
126.121
126.083
125.274
122.561
119.848
112.203
112.044
111.919
111.550

54.383
54.111
53.840
53.569
53.299

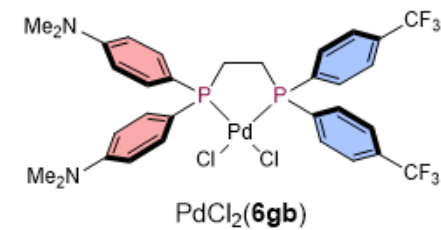
40.171
30.214
30.046
29.848
29.682
27.541
27.415
27.208
27.084



Supplementary Figure 204. ¹³C NMR spectrum (100 MHz, CD₂Cl₂) of PdCl₂(**6gb**)

CD₂Cl₂, 376 MHz

— -65.437

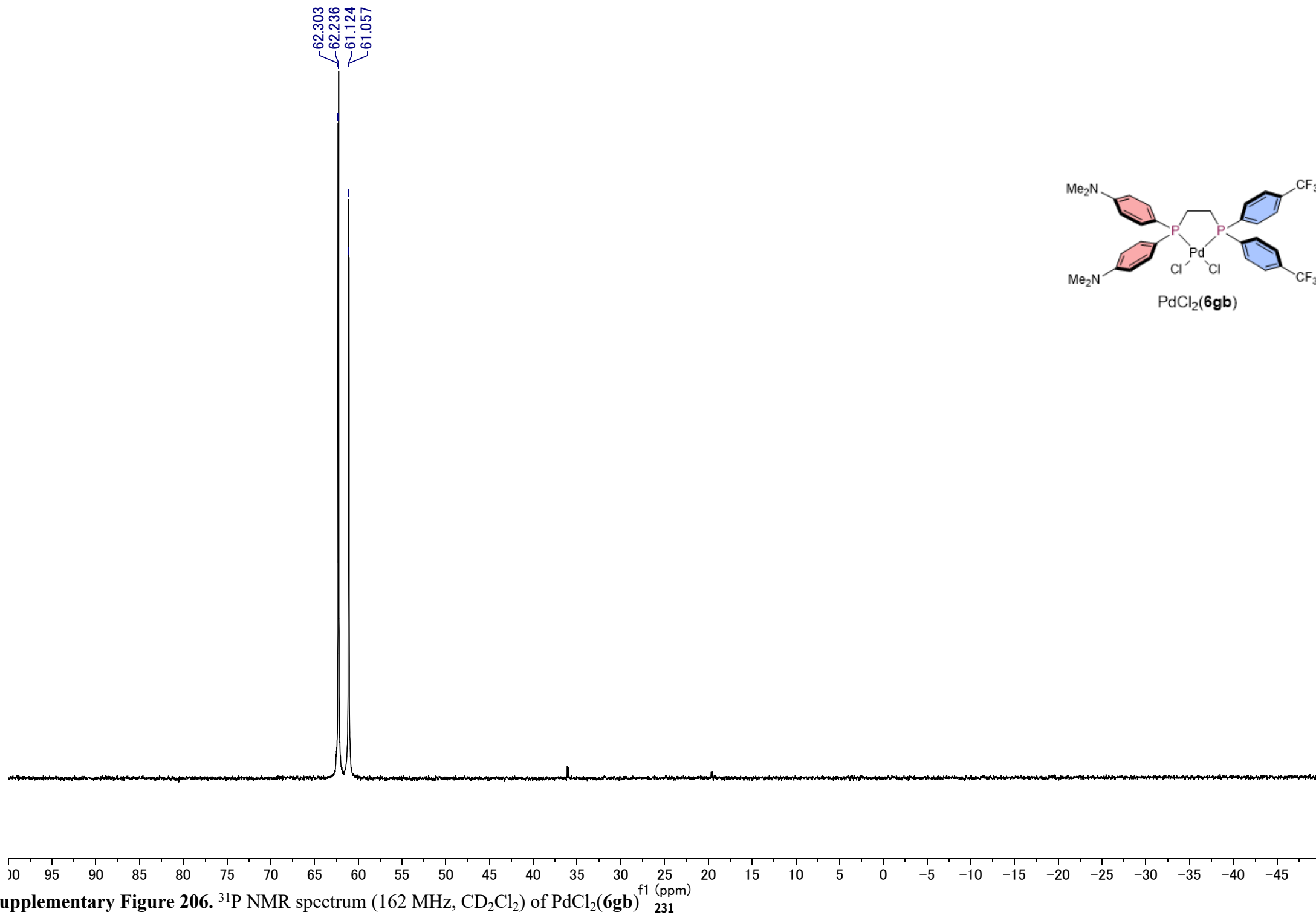


-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180

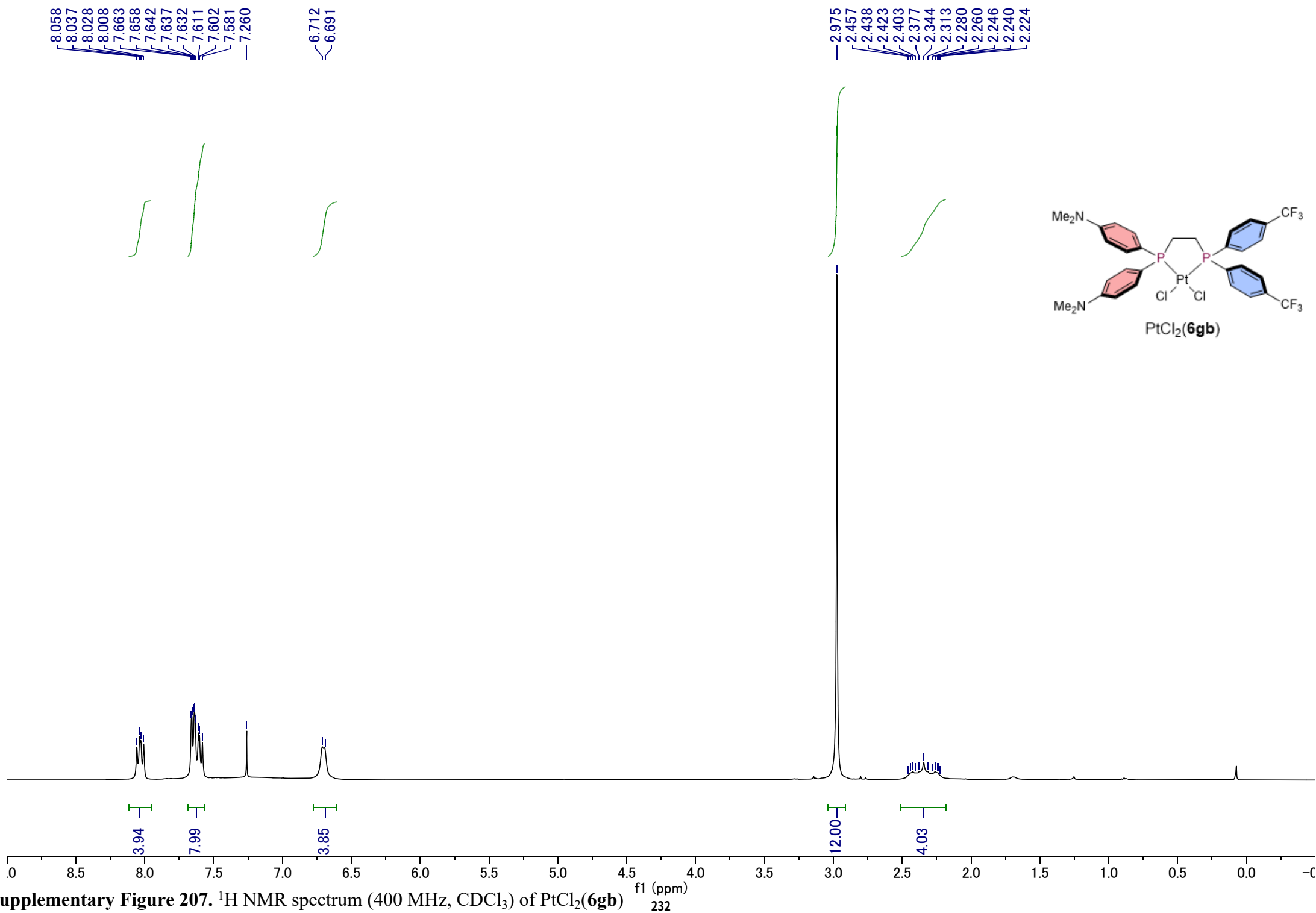
f1 (ppm)

Supplementary Figure 205. ¹⁹F NMR spectrum (376 MHz, CD₂Cl₂) of PdCl₂(**6gb**) 230

CD₂Cl₂, 162 MHz



CDCl₃, 400 MHz



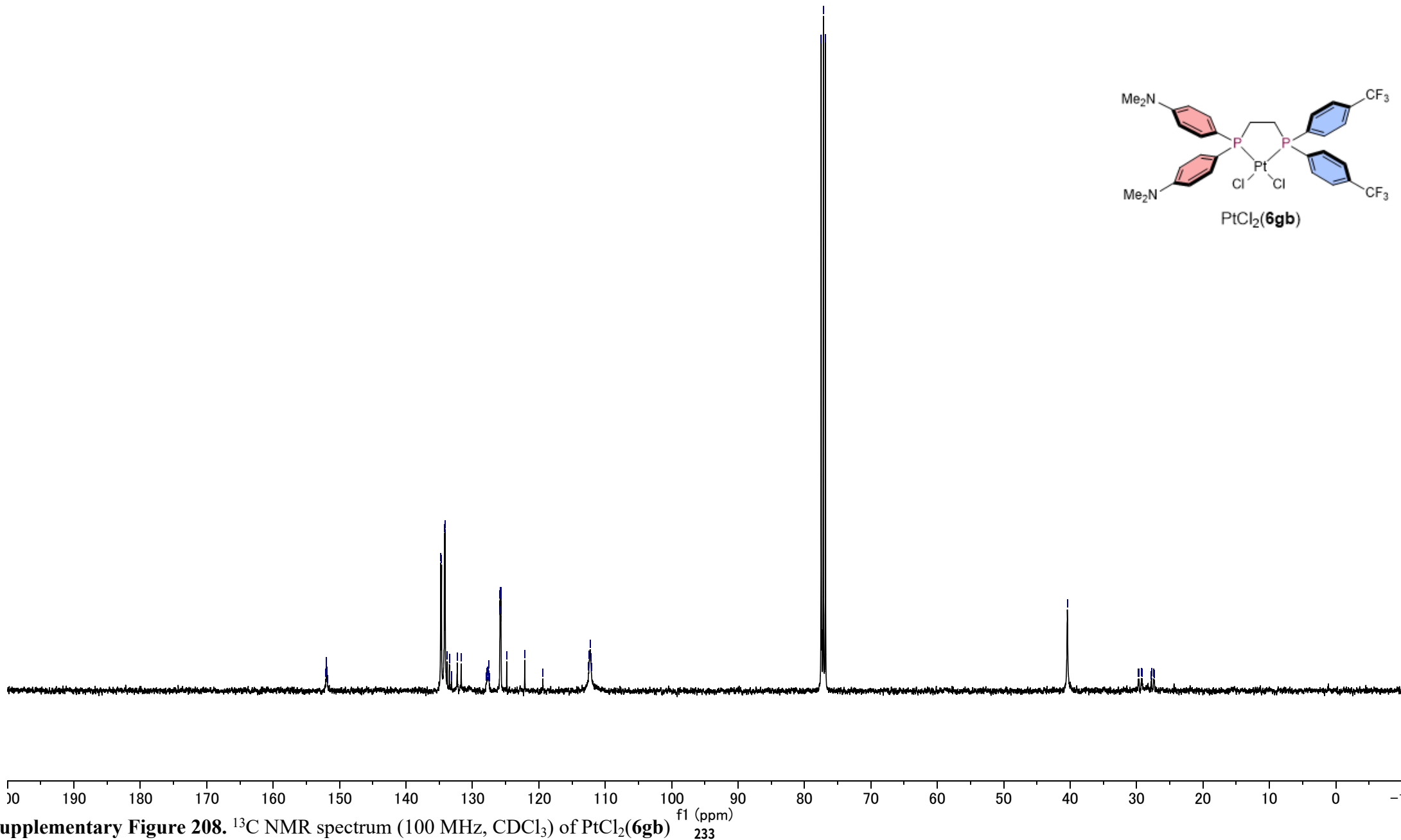
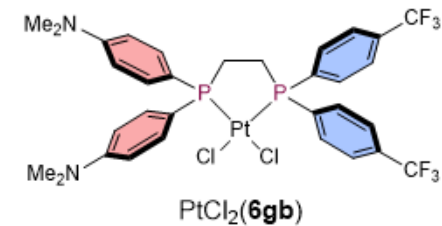
Supplementary Figure 207. ¹H NMR spectrum (400 MHz, CDCl₃) of PtCl₂(**6gb**)

CDCl₃, 100 MHz

152.070
152.004
151.954
151.883
151.820
134.770
134.649
134.208
134.096
133.808
133.784
133.483
133.458
133.155
133.127
132.287
131.685
127.921
127.825
127.772
127.712
127.650
127.540
127.481
127.434
125.849
125.811
125.772
125.733
125.695
124.823
122.107
119.394
112.522
112.402
112.281
112.162
112.070

77.478
77.160
76.842

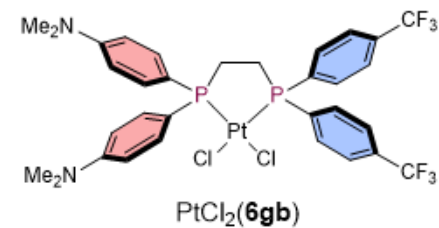
40.417
29.722
29.622
29.281
29.179
27.807
27.743
27.398
27.308



Supplementary Figure 208. ¹³C NMR spectrum (100 MHz, CDCl₃) of PtCl₂(**6gb**)

CDCl₃, 376 MHz

-63.051

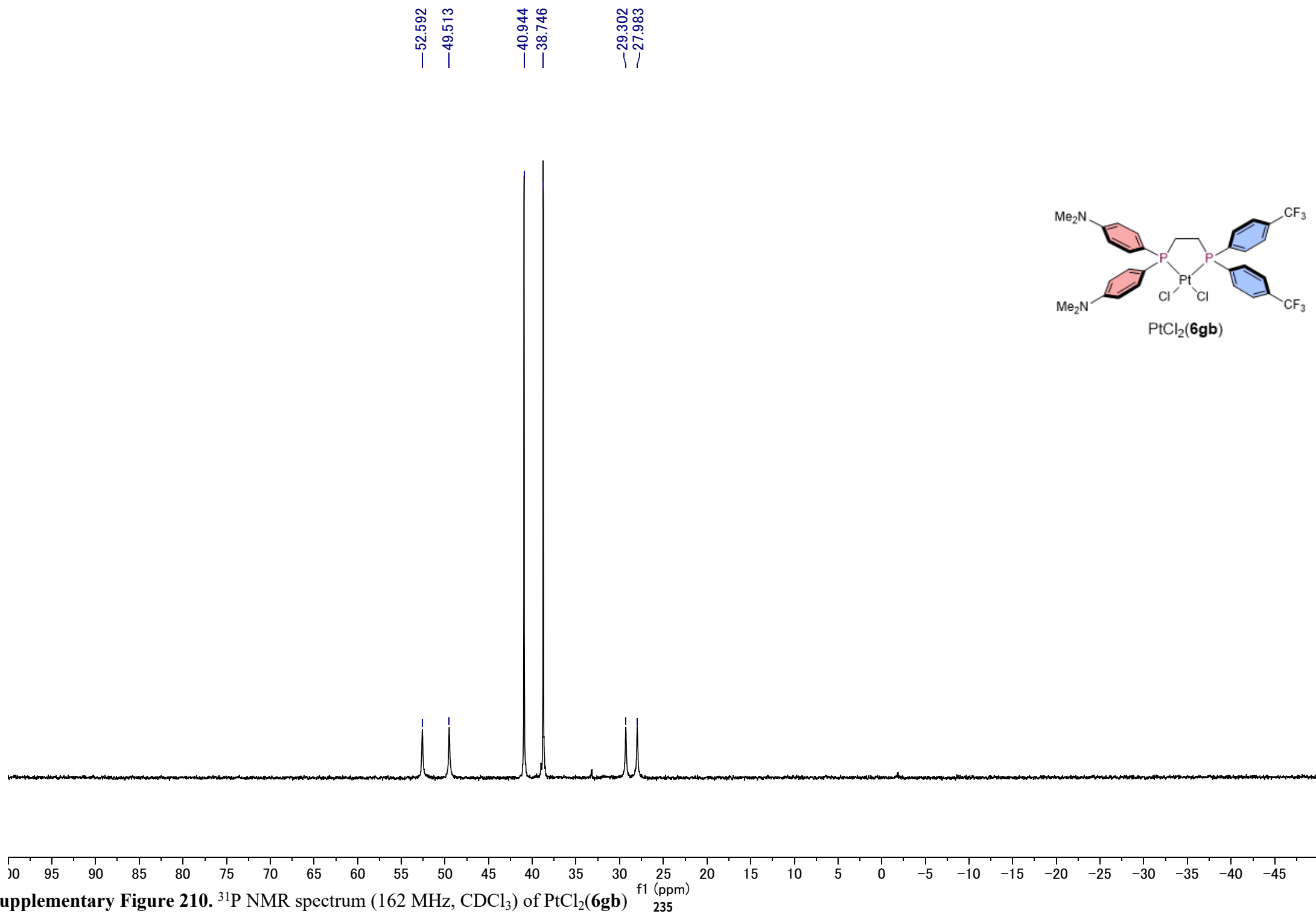


30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -1

Supplementary Figure 209. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of PtCl₂(**6gb**)

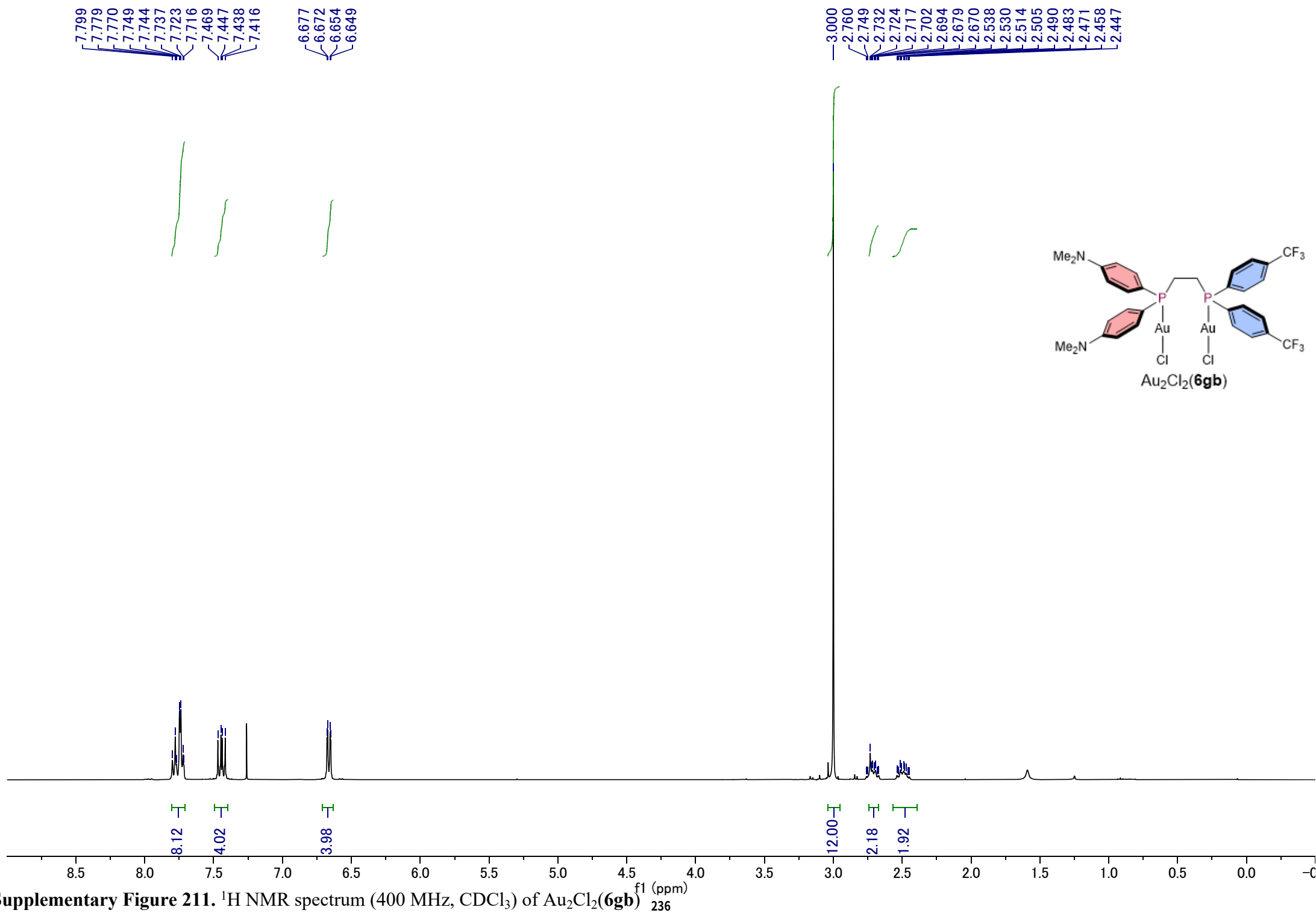
f1 (ppm)
234

CDCl₃, 162 MHz



Supplementary Figure 210. ³¹P NMR spectrum (162 MHz, CDCl₃) of PtCl₂(**6gb**)

CDCl₃, 400 MHz



Supplementary Figure 211. ¹H NMR spectrum (400 MHz, CDCl₃) of Au₂Cl₂(**6gb**)

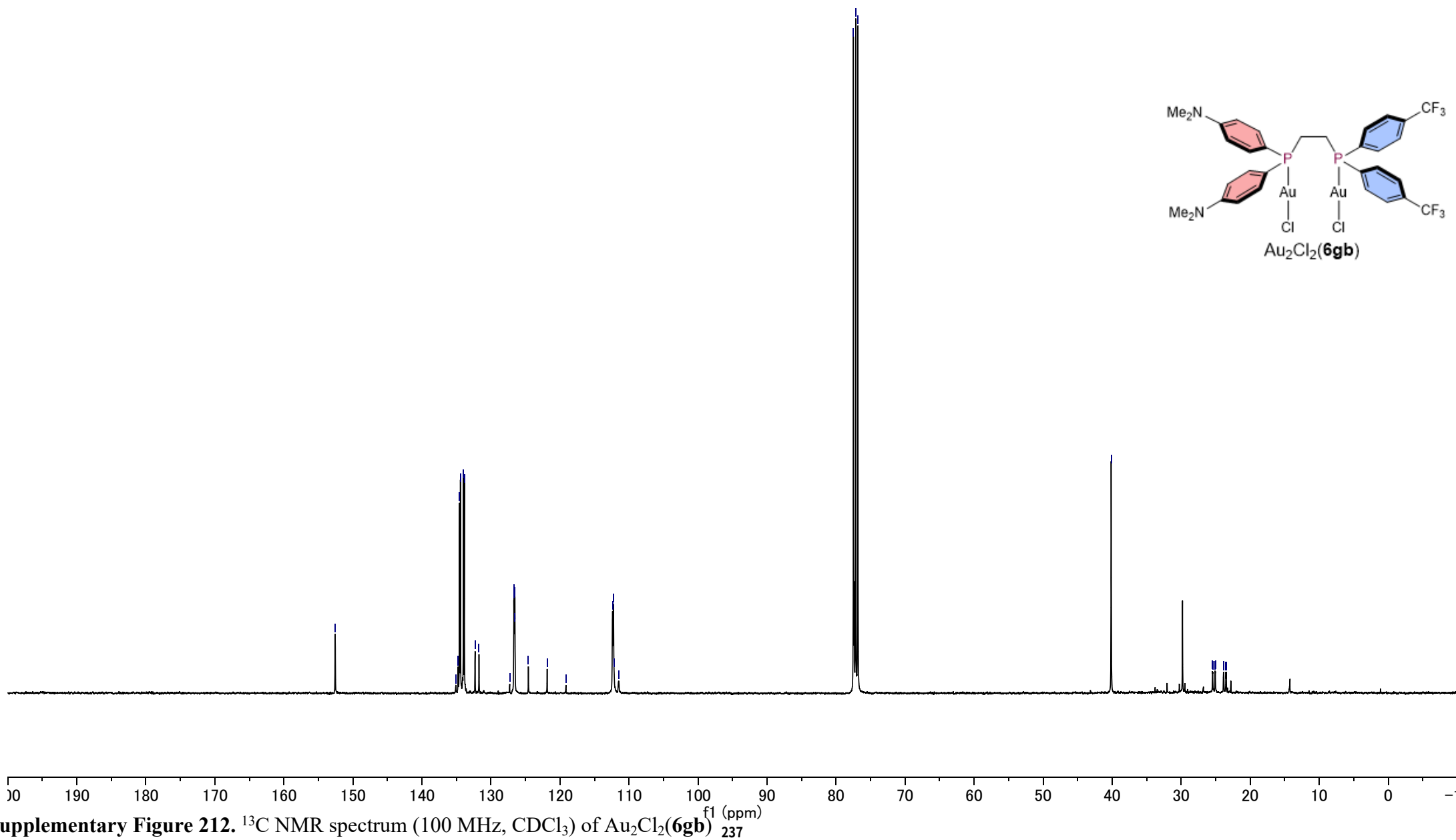
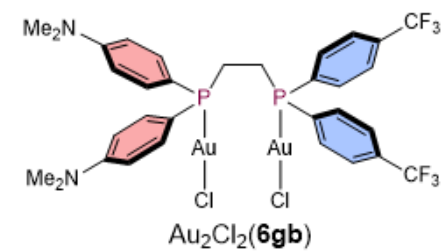
CDCl₃, 100 MHz

152.562
135.093
135.073
134.771
134.745
134.565
134.418
133.991
133.853
132.303
131.732
127.292
126.678
126.640
126.601
126.560
126.523
124.575
121.859
119.145
112.375
112.250
112.155
111.493

77.480
77.160
76.844

40.135

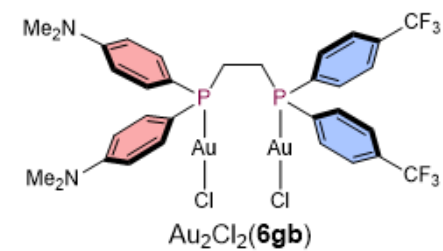
25.467
25.425
25.098
25.054
23.882
23.827
23.528
23.470



Supplementary Figure 212. ¹³C NMR spectrum (100 MHz, CDCl₃) of Au₂Cl₂(**6gb**)

CDCl₃, 376 MHz

-63.187



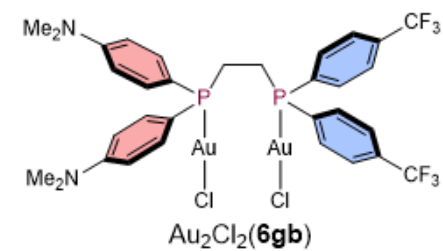
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180

f1 (ppm)

Supplementary Figure 213. ¹⁹F NMR spectrum (376 MHz, CDCl₃) of Au₂Cl₂(**6gb**) 238

CDCl₃, 162 MHz

32.624
32.249
28.540
28.165



Supplementary Figure 214. ³¹P NMR spectrum (162 MHz, CDCl₃) of Au₂Cl₂(**6gb**)

f1 (ppm)
239