Tetragonal Phosphorus(V) Cations: Tunable and Robust Catalytic Lewis Acids

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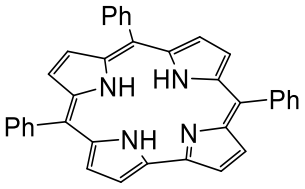
Contents

1. General procedures

Dichloromethane and toluene used for reaction chemistry were purified and collected under argon using a Glass Contour Solvent Purification System. Reagents were purchased from commercial vendors (Sigma-Aldrich, Alfa Aesar, Acros, TCI, or Oakwood Chemical). Tris(pentafluorophenyl)corrole,[1] bis(diethylamino)chlorophosphine,[2] trityl tetrakis(pentafluorophenylborate),[3] and diethyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate[4] were synthesized according to reported procedures. Tri-*n*-octylphosphine oxide and benzophenone were recrystallized before use. Pyrrole and benzaldehyde were distilled before use. Other reagents were used as received. Column chromatography was carried out on silica gel (SiliFlash® Irregular Silica Gel, P60 40-63μm) or aluminum oxide (activated, neutral, Brockmann I) as noted. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with either Bruker AVANCE-400, JEOL 500 MHz, or Bruker Avance-600 spectrometers and processed using MestReNova software. ^{1}H NMR chemical shifts are given in ppm with respect to solvent residual peak ($CDCl_3$, δ 7.26; CD_2Cl_2, δ 5.32; CD_3CN, δ 1.94). ^{13}C NMR shifts are given in ppm with respect to solvent residual peak ($CDCl_3$ δ 77.1, CD_2Cl_2 δ 53.8). ^{31}P shifts are given in ppm with respect to 85% H_3PO_4 (δ 0.0). Multiplicities are described as s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. Coupling constants are reported in Hertz (Hz). UV-visible spectra were obtained on an Agilent Cary 60 spectrometer. High-resolution ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the School of Chemical Sciences, University of Illinois at Urbana-Champaign. Nonlinear curve fitting for Michaelis-Menten and Hill analyses was performed using Mathematica 11.

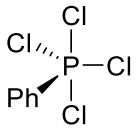
2. Synthesis of starting materials, 1•H–4•H, and 1^{+}–4^{+}



S1

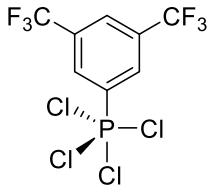
5,10,15-Triphenylcorrole was synthesized using a modification of the reported procedure.[5] Benzaldehyde and pyrrole were distilled before use and were stored in the dark at –30 °C under nitrogen. 400 mL of water and 400 mL of MeOH were charged to a 1-L RB flask. The flask was wrapped in aluminum foil to exclude light, and pyrrole (2.8 mL, 40 mmol) and benzaldehyde (2.0 mL, 20 mmol) were added. Concentrated aqueous HCl (17 mL) was added in one portion with vigorous stirring. The mixture was stirred at room temperature under nitrogen for 1 h. The mixture was then extracted with chloroform (2 x 100 mL). The combined organic layers were washed twice with water and dried over anhydrous magnesium sulfate. The mixture was diluted to a total volume of 600 mL with chloroform, and *p*-chloranil (4.9 g, 20 mmol) was added in one portion with vigorous stirring. The dark solution was heated to reflux under air for 1 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The resulting residue was dissolved in CH_2Cl_2, and dry silica was added. After removal of solvent, the adsorbed mixture was quickly charged to a silica column (note: the crude mixture adsorbed on silica is prone to rapid degradation). The mixture was eluted with CH_2Cl_2, and the dark green band (R_f = 0.6) containing crude product was collected. All fractions containing the product were combined and evaporated to dryness. The product was recrystallized by dissolving in a minimum volume of hot CH_2Cl_2 (ca. 50 mL) followed by addition of hexanes (200 mL) and cooling at –30 °C overnight. The black solids were collected by filtration and were washed with hexanes until the filtrate became almost

colorless, leaving the desired product as shiny, dark purple solids (1.2 g, 32% yield). Spectral data are consistent with reported values.[5]



S2

P,*P*-dichlorophenylphosphine (3.0 mL, 16 mmol) was charged to a 3-neck round bottom flask equipped with a Teflon-coated stir bar and was dissolved in anhydrous CH_2Cl_2 (10 mL). Chlorine gas (generated by mixing concentrated aqueous HCl and trichloroisocyanuric acid) was passed through a $CaSO_4$-packed drying column and was bubbled through the phosphine solution until the solution became bright yellow (ca. 20 min). Excess chlorine was removed by sparging the solution with nitrogen until the yellow color disappeared. Removal of volatiles in vacuo afforded the product as a white solid (3.9 g, 99%), contaminated by a small amount of phenylphosphonic dichloride. The product is stable indefinitely when stored in a nitrogen-filled glovebox at –30°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 6.8, 3.0 Hz, 1H), 8.01 (dd, *J* = 6.5, 2.7 Hz, 1H), 7.62 – 7.50 (m, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 152.1 (d, *J* = 154.5 Hz), 132.0 (d, *J* = 5.6 Hz), 128.6 (d, *J* = 24.9 Hz), 124.0 (d, *J* = 17.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -44.1 (tq, *J* = 27.1, 8.7 Hz).

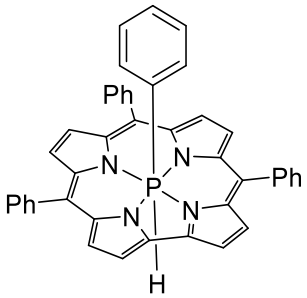


S3

To a –78 °C solution of 3,5-bis(trifluoromethyl)bromobenzene (3.6 mL, 21 mmol) in ether (11 mL) was added a solution of ^{n}BuLi (2.5 M in hexanes, 8.4 mL, 21 mmol) dropwise. The mixture was stirred at –78 °C for 1 h. The mixture was then cannula transferred to a solution of bis(diethylamino)chlorophosphine (4.9 mL, 23 mmol) in ether (47 mL) at –78 °C. The mixture was warmed to ambient temperature and stirred for 1 h. The reaction flask was then cooled to –78 °C, and a solution of HCl in ether (2.0 M, 47 mL, 94 mmol) was added slowly. The heterogeneous mixture was warmed to room temperature and stirred overnight (ca. 16 h). The mixture was then cannula filtered into a new flask. The remaining solids were washed with ether (2 x 20 mL), and the filtrates were also transferred to the new flask by cannula filtration. The volatiles were removed under high vacuum to afford an orange oil. The oil was vacuum distilled (35 °C, <1 torr) to afford a colorless liquid. The liquid was dissolved in anhydrous CH_2Cl_2 (10 mL) and chlorinated as in the procedure for **S2**. After removal of solvents, the product was obtained as a white solid in 58% overall yield (4.7 g, 12 mmol). The product was contaminated by ca. 3% of the phosphonic dichloride but was used without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 25.3 Hz, 2H), 8.07 (d, *J* = 3.1 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 153.3 (d, *J* = 172.9 Hz), 132.5 (qd, *J* = 34.5, 25.3 Hz), 125.5 (dq, *J* = 7.5, 3.7 Hz), 124.2 (dq, *J* = 20.5, 3.6 Hz), 122.5 (dd, *J* = 273.7, 4.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.9 (s). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -50.2 (t, *J* = 25.4 Hz).

$[Bu_4N][BH(OAc)_3]$
S4

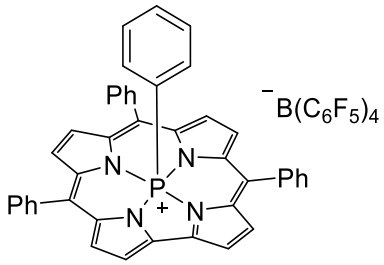
Tetrabutylammonium triacetoxyborohydride was prepared according to a procedure adapted from the literature.[6] A solution of tetrabutylammonium borohydride (3.0 g, 12 mmol) in toluene (25 mL) was cooled to 0 °C, and glacial acetic acid (2.3 mL, 41 mmol) was added dropwise. After the addition was complete, the mixture was stirred at room temperature for 3 h. Volatiles were removed by rotary evaporator, and further drying under high vacuum overnight afforded the product as an off-white semisolid (4.9 g, 97%). The product was contaminated with residual acetic acid but was used without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.30 – 3.16 (m, 8H), 2.02 (s, 8H), 1.64 (p, *J* = 7.7 Hz, 8H), 1.41 (h, *J* = 7.4 Hz, 8H), 0.98 (t, *J* = 7.3 Hz, 12H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.1, 58.7, 23.8, 23.4, 19.6, 13.6.



1•H

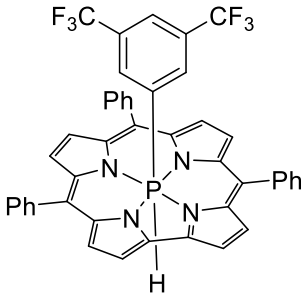
A solution of **S1** (1.1 g, 2.0 mmol) in toluene (25 mL) was charged to a 2-neck round bottom flask fitted with a stir bar and reflux condenser under nitrogen atmosphere. The solution was cooled to –78 °C and a solution of **S2** (500 mg, 2 mmol) in toluene (6 mL) was added via syringe with vigorous stirring. Triethylamine (900 µL, 6 mmol) was added, and the flask was warmed to room temperature. The reaction mixture was heated to reflux for 1 h before cooling back to room temperature. The mixture was washed with water and dried over magnesium sulfate before being concentrated to dryness by rotary evaporation. The mixture was separated by column chromatography on silica (1:5 EtOAc:hexanes as eluent), and the green band (R_f = 0.3) containing product was collected. This product contained a small amount of a partially chlorinated byproduct which was inseparable by chromatography or crystallization. To eliminate this impurity, the mixture of products was dissolved in ethyl acetate, and 10 mol % of 10 wt. % Pd/C (100 mg of wet material) was added. The mixture was stirred at room temperature under H_2 pressure (400 psi) overnight. The green residue was passed through a celite plug, and ethyl acetate was removed by rotary evaporator. The dark purple solids were dissolved in CH_2Cl_2 (5 mL), and TMS–OTf (100 µL, 0.6 mmol) was added, resulting in a dark red solution. The reaction was quenched with $[Bu_4N][BH_4]$ (300 mg, 1 mmol) to produce a brown-green solution. The desired product was purified on neutral alumina (5% EtOAc in hexanes) and was isolated as a blue solid (240 mg, 20% overall). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 4.3 Hz, 2H), 9.02 (d, *J* = 4.9 Hz, 2H), 8.94 (d, *J* = 4.3 Hz, 2H), 8.70 (d, *J* = 4.7 Hz, 2H), 8.45 – 8.13 (m, 5H), 7.73 (tt, *J* = 33.0, 7.2 Hz, 10H), 5.51 (td, *J* = 7.2, 3.7 Hz, 1H), 5.06 (q, *J* = 7.3 Hz, 2H), 0.87 (dd, *J* = 24.7, 8.3 Hz, 2H), -2.73 (d, *J* = 928.8 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 149.4 (d, *J* = 265.8 Hz), 141.0, 139.9 (d, *J* = 49.8 Hz), 137.2, 134.5, 131.1, 130.0 (d, *J* = 4.2 Hz), 127.8, 127.7, 127.4, 126.6, 125.1, 124.5 (d, *J* = 24.4 Hz), 124.1, 123.3 (d, *J* = 19.4 Hz), 114.0, 113.5, 106.3. **^{31}P NMR** (203 MHz, $CDCl_3$) δ -

231.3 (dt, *J* = 928.0, 25.1 Hz). **HRMS (ESI)** calculated for $C_{43}H_{28}N_4P$ $[M–H]^+$: 631.2052, found: 631.2047.



1$^+$

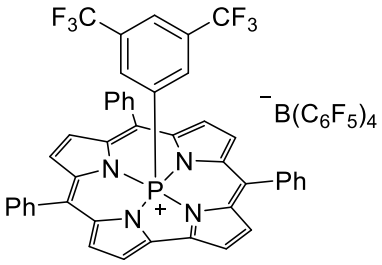
Inside a nitrogen-filled glovebox, a solution of **1•H** (200 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) was charged to a 20-mL glass vial containing a Teflon-coated stir bar. Trityl tetrakis(pentafluorophenyl)borate (280 mg, 0.30 mmol) was added with stirring. The color of the reaction mixture immediately changed from dark green to deep red. The mixture was stirred at room temperature for 5 min. With vigorous stirring, the desired product was precipitated from solution by dropwise addition of pentane (12 mL), and the supernatant containing triphenylmethane coproduct was decanted off. The precipitation was repeated for quantitative removal of triphenylmethane. The precipitated oily, maroon solid was then dried in vacuo to afford the product as a dark purple powder (290 mg, 74%). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 9.85 (dd, *J* = 4.6, 2.5 Hz, 2H), 9.53 (q, *J* = 4.2 Hz, 4H), 9.27 (dd, *J* = 5.2, 3.3 Hz, 2H), 8.23 – 8.06 (m, 6H), 7.94 – 7.83 (m, 9H), 6.17 (td, *J* = 7.6, 2.7 Hz, 1H), 5.64 (q, *J* = 7.4 Hz, 2H), 1.56 (dd, *J* = 20.3, 8.0 Hz, 2H). **^{19}F NMR** (376 MHz, CD_2Cl_2) δ -132.94 – -133.31 (m), -163.75 (t, *J* = 20.4 Hz), -167.56 (t, *J* = 19.6 Hz). **^{31}P NMR** (162 MHz, CD_2Cl_2) δ -97.1 (t, *J* = 20.6 Hz). HRMS (ESI) calculated for $C_{43}H_{28}N_4P$ $[M]^+$: 631.2052, found: 631.2050. ^{13}C NMR was not obtained due to poor solubility.



2•H

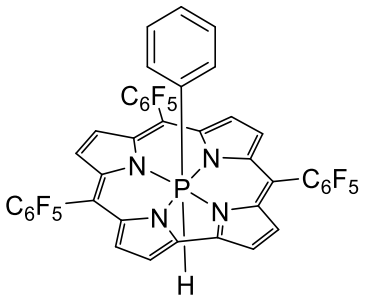
A solution of **S1** (530 mg, 1.0 mmol) in toluene (20 mL) was charged to a 2-neck round bottom flask fitted with a stir bar and reflux condenser under nitrogen atmosphere. The solution was cooled to –78°C and a solution of **S3** (390 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) was added via syringe with vigorous stirring. Triethylamine (450 µL, 3.0 mmol) was added, and the flask was warmed to room temperature. The reaction mixture was heated to reflux for 1 h before cooling back to room temperature. A solution of **S4** (2.2 g, 5.0 mmol) in CH_2Cl_2 (8 mL) was added via syringe, and the

mixture was stirred at room temperature overnight. The flask was opened to air, and the dark residue was concentrated by rotary evaporator. The mixture was separated by column chromatography on neutral alumina (7% EtOAc in hexanes as eluent), and the brown-green band containing product was collected. After removal of solvents the product was obtained as a dark blue solid (180 mg, 24%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.22 (d, *J* = 4.2 Hz, 2H), 9.08 (d, *J* = 4.8 Hz, 2H), 8.99 (d, *J* = 4.2 Hz, 2H), 8.75 (d, *J* = 4.8 Hz, 2H), 8.26 (s, 5H), 7.90 – 7.62 (m, 10H), 6.00 (s, 1H), 1.08 (dd, *J* = 23.6, 1.6 Hz, 2H), -2.66 (d, *J* = 923.6 Hz, 1H). **^{13}C{^{1}H,^{19}F} NMR** (126 MHz, $CDCl_3$) δ 151.2, 149.1, 146.5, 146.3, 146.3 (d, *J* = 48.4 Hz), 142.4, 142.1, 138.6, 138.0 (d, *J* = 12.7 Hz), 137.8 (d, *J* = 4.4 Hz), 137.1, 130.8, 127.9 (d, *J* = 24.6 Hz), 126.0 (d, *J* = 40.4 Hz), 124.3, 122.8 (d, *J* = 22.0 Hz), 121.5, 119.0 (d, *J* = 4.4 Hz), 117.1, 114.0, 112.9, 96.7, 90.4. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -64.0. **^{31}P NMR** (243 MHz, $CDCl_3$) δ -235.1 (dt, *J* = 923.2, 23.9 Hz). **HRMS (ESI)** calculated for $C_{45}H_{26}F_6N_4P$ $[M–H]^+$: 767.1799, found: 767.1802.



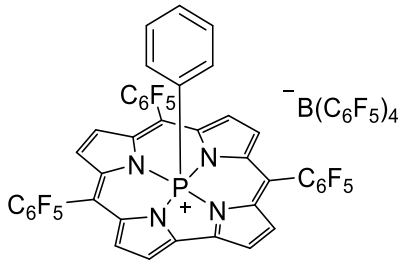
2^{+}

Inside a nitrogen-filled glovebox, a solution of **2•H** (130 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was charged to a 20-mL glass vial containing a Teflon-coated stir bar. Trityl tetrakis(pentafluorophenyl)borate (190 mg, 0.20 mmol) was added with stirring. The color of the reaction mixture immediately changed from dark green to deep red. The mixture was stirred at room temperature for 5 min. With vigorous stirring, the desired product was precipitated from solution by dropwise addition of pentane (12 mL), and the supernatant containing triphenylmethane coproduct was decanted off. The precipitation was repeated for quantitative removal of triphenylmethane. The precipitated oily, maroon solid was then dried in vacuo to afford the product as a dark purple powder (250 mg, 86%). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 9.93 (dd, *J* = 4.8, 2.7 Hz, 2H), 9.61 (q, *J* = 5.0 Hz, 4H), 9.34 (dd, *J* = 5.3, 3.4 Hz, 2H), 8.19 (br s, 4H), 8.10 – 8.01 (m, 2H), 7.97 – 7.81 (m, 9H), 6.68 (s, 1H), 1.82 (d, *J* = 20.0 Hz, 2H). **^{19}F NMR** (376 MHz, CD_2Cl_2) δ -64.9, -133.01 – -133.28 (m), -163.8 (t, *J* = 20.3 Hz), -167.6 (t, *J* = 19.9 Hz). **^{31}P NMR** (162 MHz, CD_2Cl_2) δ -102.2 (t, *J* = 18.7 Hz). HRMS (ESI) calculated for $C_{45}H_{26}F_6N_4P$ $[M]^+$: 767.1799, found: 767.1796. ^{13}C NMR was not obtained due to poor solubility.



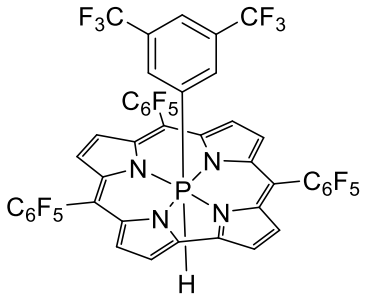
3•H

A solution of 5,10,15-tris(pentafluorophenyl)corrole (800 mg, 1 mmol) in toluene (25 mL) was charged to a 2-neck round bottom flask fitted with a stir bar and reflux condenser under nitrogen atmosphere. The solution was cooled to –78 °C and a solution of **S2** (250 mg, 1.0 mmol) in toluene (3 mL) was added via syringe with vigorous stirring. Triethylamine (450 µL, 3.0 mmol) was added, and the flask warmed to room temperature. The reaction mixture was heated to reflux for 1 h before cooling back to room temperature. A solution of **S4** (2.2 g, 5.0 mmol) in CH_2Cl_2 (8 mL) was added via syringe, and the mixture was stirred at room temperature overnight. The flask was opened to air, and the dark residue was concentrated by rotary evaporation. The mixture was purified by column chromatography on neutral alumina (1:2 CH_2Cl_2:hexanes as eluent), and the brown-yellow band containing product was collected. After removal of solvents the product was obtained as a dark blue solid (380 mg, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 4.3 Hz, 2H), 8.96 (d, *J* = 4.8 Hz, 2H), 8.91 (d, *J* = 4.4 Hz, 2H), 8.71 (d, *J* = 4.8 Hz, 2H), 5.50 (td, *J* = 7.1, 3.7 Hz, 1H), 5.01 (dt, *J* = 8.5, 6.8 Hz, 2H), 0.68 (dd, *J* = 25.4, 8.1 Hz, 2H), -3.03 (d, *J* = 962.0 Hz, 1H). **^{13}C{^{1}H,^{19}F} NMR** (126 MHz, $CDCl_3$) δ 148.81, 146.61 (d, *J* = 8.3 Hz), 146.47, 146.19, 142.20, 141.99, 138.79, 138.02, 137.78 (d, *J* = 10.0 Hz), 137.28, 130.94 (d, *J* = 18.6 Hz), 125.85, 125.29, 125.18 (d, *J* = 5.6 Hz), 124.79 (d, *J* = 24.6 Hz), 124.01, 122.70 (d, *J* = 20.0 Hz), 116.65, 114.74, 113.64, 96.35, 90.08. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -136.6 – -136.8 (m), -136.8 (dd, *J* = 24.9, 8.6 Hz), -137.0 (ddd, *J* = 24.0, 8.7, 3.3 Hz), -151.9 (t, *J* = 20.8 Hz), -152.6 (t, *J* = 20.9 Hz), -161.2 (ddd, *J* = 24.2, 20.9, 8.6 Hz), -161.3 (ddd, *J* = 24.5, 20.9, 8.5 Hz), -161.8 (dddd, *J* = 50.3, 24.7, 20.8, 8.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -230.8 (dt, *J* = 962.1, 25.6 Hz). **HRMS (ESI)** calculated for $C_{43}H_{13}N_4F_{15}P$ $[M–H]^+$: 901.0638, found: 901.0629.



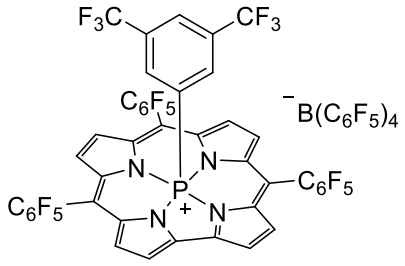
3$^+$

Inside a nitrogen-filled glovebox, a solution of **3•H** (370 mg, 0.42 mmol) in CH_2Cl_2 (2 mL) was charged to a 20-mL glass vial containing a Teflon-coated stir bar. Trityl tetrakis(pentafluorophenyl)borate (360 mg, 0.40 mmol) was added with stirring. The color of the reaction mixture immediately changed from dark green to deep red. The mixture was stirred at room temperature for 5 min. With vigorous stirring, the desired product was precipitated from solution by dropwise addition of pentane (12 mL), and the supernatant containing triphenylmethane coproduct was decanted off. The precipitation was repeated for quantitative removal of triphenylmethane. The precipitated oily, maroon solid was then dried in vacuo to afford the product as a red powder (570 mg, 90%). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 10.05 (dd, *J* = 4.9, 2.6 Hz, 2H), 9.57 (t, *J* = 4.5 Hz, 2H), 9.53 (t, *J* = 4.8 Hz, 2H), 9.35 (dd, *J* = 5.3, 3.3 Hz, 2H), 6.18 (td, *J* = 7.5, 2.9 Hz, 1H), 5.62 (q, *J* = 7.6 Hz, 2H), 1.43 (dd, *J* = 20.8, 8.0 Hz, 2H). **^{19}F NMR** (376 MHz, CD_2Cl_2) δ -133.04 – -133.41 (m), -137.46 (tdd, *J* = 26.1, 13.9, 6.5 Hz), -148.40 (tt, *J* = 20.8, 2.7 Hz), -148.59 (tt, *J* = 20.8, 2.7 Hz), -159.32 – -159.52 (m), -159.51 – -159.83 (m), -163.84 (t, *J* = 20.3 Hz), -167.68 (t, *J* = 19.7 Hz). **^{31}P NMR** (162 MHz, CD_2Cl_2) δ -95.2. **HRMS (ESI)** calculated for $C_{43}H_{13}F_{15}N_4P$ $[M]^+$: 901.0638, found: 901.0626. ^{13}C NMR was not obtained due to poor solubility.



4•H

A solution of 5,10,15-tris(pentafluorophenyl)corrole (800 mg, 1 mmol) in toluene (20 mL) was charged to a 2-neck round bottom flask fitted with a stir bar and reflux condenser under nitrogen atmosphere. The solution was cooled to –78 °C and a solution of **S3** (390 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) was added via syringe with vigorous stirring. Triethylamine (280 µL, 3.0 mmol) was added, and the flask warmed to room temperature. The reaction mixture was heated to reflux for 1 h before cooling back to room temperature. A solution of tetrabutylammonium triacetoxyborohydride (1.9 g, 4.3 mmol) in CH_2Cl_2 (8 mL) was added via syringe, and the mixture was stirred at room temperature overnight. The flask was opened to air, and the dark residue was concentrated by rotary evaporator. The mixture was separated by column chromatography on neutral alumina (1:2 CH_2Cl_2:hexanes as eluent), and the purple-yellow band containing product was collected. After removal of solvents the product was obtained as a dark blue solid (350 mg, 34%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 4.4 Hz, 2H), 9.06 (d, *J* = 4.9 Hz, 2H), 9.01 (d, *J* = 4.4 Hz, 2H), 8.80 (d, *J* = 4.9 Hz, 2H), 6.03 (s, 1H), 0.97 (d, *J* = 24.5 Hz, 2H), -2.97 (d, *J* = 951.8 Hz, 1H). **^{13}C{^{1}H,^{19}F} NMR** (126 MHz,$CDCl_3$) δ 151.33, 149.17, 146.63, 146.59, 146.44, 146.24, 142.45, 142.22, 138.69, 138.09 (d, *J* = 12.6 Hz), 137.87 (d, *J* = 4.4 Hz), 137.25, 130.91, 128.00 (d, *J* = 24.7 Hz), 126.11 (d, *J* = 40.4 Hz), 124.36, 122.90 (d, *J* = 22.0 Hz), 121.63, 119.09 (d, *J* = 4.4 Hz), 117.16, 114.12, 113.04, 96.75, 90.46. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.41 (t, *J* = 6.0 Hz), -136.79 – -136.92 (m), -136.98 (dd, *J* = 24.4, 8.7 Hz), -137.21 (ddd, *J* = 24.2, 8.8, 3.6 Hz), -151.33 (t, *J* = 21.0 Hz), -151.97 (t, *J* = 21.0 Hz), -160.69 (ddd, *J* = 23.9, 20.8, 8.4 Hz), -161.04 (ddd, *J* = 23.9, 20.8, 8.6 Hz), -161.17 (ddd, *J* = 24.5, 21.2, 8.8 Hz), -161.40 (ddd, *J* = 24.3, 20.8, 8.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -234.3 (dt, *J* = 952.3, 24.4 Hz). **HRMS (ESI)** calculated for $C_{45}H_{11}F_{21}N_4P$ $[M–H]^+$: 1037.0386, found: 1037.0415.



4$^+$

A solution of **4•H** (320 mg, 0.31 mmol) in CH_2Cl_2 (2 mL) was charged to a 20-mL glass vial containing a Teflon-coated stir bar. Trityl tetrakis(pentafluorophenyl)borate (270 mg, 0.30 mmol) was added with stirring. The color of the reaction mixture immediately changed from dark green to deep red. The mixture was stirred at room temperature for 5 min. With vigorous stirring, the desired product was precipitated from solution by dropwise addition of pentane (12 mL), and the supernatant containing triphenylmethane coproduct was decanted off. The precipitation was

repeated for quantitative removal of triphenylmethane. The precipitated oily, maroon solid was then dried in vacuo to afford the product as a red powder (370 mg, 68%). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 10.15 (dd, *J* = 5.0, 2.7 Hz, 2H), 9.68 (t, *J* = 4.6 Hz, 2H), 9.64 (t, *J* = 4.8 Hz, 2H), 9.46 (t, *J* = 4.4 Hz, 2H), 6.72 (s, 1H), 1.76 (d, *J* = 20.4 Hz, 2H). **^{19}F NMR** (376 MHz, CD_2Cl_2) δ -65.2, -133.0 – -133.4 (m), -137.3 (ddt, *J* = 22.8, 14.7, 7.1 Hz), -137.9 (ddq, *J* = 18.4, 9.5, 5.0 Hz), -138.1 (d, *J* = 22.9 Hz), -147.7 (t, *J* = 20.7 Hz), -147.9 (t, *J* = 20.7 Hz), -159.1 (ddtd, *J* = 44.5, 30.4, 21.8, 8.5 Hz), -163.9 (t, *J* = 20.3 Hz), -167.7 (t, *J* = 19.8 Hz). **^{31}P NMR** (162 MHz, CD_2Cl_2) δ -100.3. **HRMS (ESI)** calculated for $C_{45}H_{11}N_4F_{21}P$ [M^+]: 1037.0386, found: 1037.0377. ^{13}C NMR was not obtained due to poor solubility.

3. Gutmann-Beckett tests for 1^+–4^+

Inside a nitrogen-filled glovebox, 0.20 mmol of the phosphacorrole was charged to a glass vial, and a solution of tri-*n*-octylphosphine oxide (7.7 mg, 0.20 mmol) in CH_2Cl_2 (0.6 mL) was added. The mixture quickly changed color and became homogeneous. The solution was transferred to an NMR tube with threaded end and was stoppered with a cap with a PTFE septum. The mixture was then analyzed by ^{31}P NMR. The Δδ value was obtained by subtracting the chemical shift of the bound (*n*-octyl)$_3$P=O signal from that of free (*n*-octyl)$_3$P=O in CH_2Cl_2 (δ 46.7).

We observed that (*n*-octyl)$_3$P=O reacted slowly with the $B(C_6F_5)_4$ anion to generate a minor impurity with a new ^{31}P resonance at δ 72.2 ppm. We have assigned the structure of the byproduct as the cationic $[(n\text{-Oct})_3POC_6F_4H]^+$ (detected by HRMS (ESI), calculated for $C_{30}H_{52}F_4OP$ [M^+]: 535.3692, found 535.3725), which is presumably formed from an S_NAr-like reaction on a C_6F_5 group of the $B(C_6F_5)_4$ anion. This assignment is further supported by the concomitant appearance of the fluoride adducts of **1^+**–**4^+** (^{31}P NMR δ ca. –200 ppm, $^1J_{P\text{-}F}$ ca. 770 Hz), indicating formation of a P–F bond. The ^{19}F NMR spectrum showed a resonance with the same coupling constant at δ ca. –15 ppm. Furthermore, the sharp singlet resonance and the chemical shift of the byproduct (δ 72.2 ppm) are consistent with a phosphonium species. Although the identity of this impurity could not be confirmed definitively, its low abundance in the reaction mixture is expected to have a negligible effect on the Gutmann-Beckett measurement.

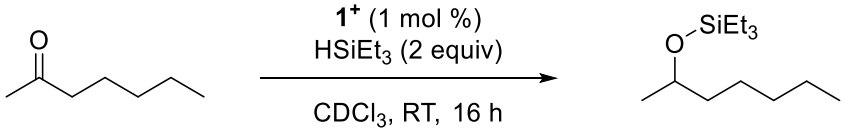
4. UV-vis spectrophotometric titrations

A stock solution (3.33 x 10^{-5} M) of each compound **1^+**–**4^+** in CH_2Cl_2 was prepared in a nitrogen-filled glovebox. 3.00 mL of this solution was transferred to a 1.00-cm long quartz cuvette with threaded end for a plastic cap lined with a silicone septum. The cuvette was removed from the glovebox for data acquisition and brought back inside for addition of each equivalent of (*n*-octyl)$_3$P=O. The solution was equilibrated (determined by constant absorbance between several consecutive scans) before acquiring each spectrum. Scans were acquired over the range of 700–300 nm. The Q band region of the spectrum (700–500 nm) proved most useful for spectroscopic analysis. λ_{max} was taken as 629 nm for **1^+**, 624 nm for **2^+**, 607 nm for **3^+**, and 603 nm for **4^+**. The molar absorptivity of the (*n*-octyl)$_3$P=O adduct was approximated by asymptotic convergence of absorbance at λ_{max} to a single value ($\log_{10}$ ε = 4.62 for **1^+**, 4.65 for **2^+**, 4.47 for **3^+**, and 4.48 for **4^+**). These molar absorptivities were used to compute fractional occupancy for fitting to the Hill equation. All titrations were performed with two replicates.

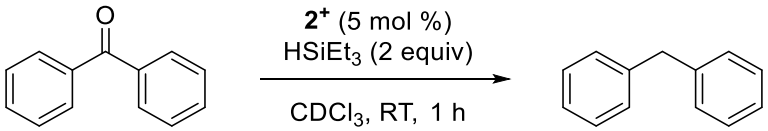
5. Water stability test for 3^+

A solution of **3^+** (16 mg, 0.010 mmol) in CD_3CN (0.6 mL) was charged to an NMR tube with threaded end and capped with a plastic cap with PTFE rubber septum. Water (2 µL, 0.1 mmol) was injected via syringe. The red solution immediately changed color to purple-green. The sample was then analyzed by NMR. A very small amount (< 1% as determined by ^{19}F NMR) of the counterion was observed to react with water as evidenced by formation of a P–F bond ($^1J_{P\text{-}F}$ = 725.6 Hz), but otherwise the only ^{31}P resonance corresponded to **3^+•OH_2**. **^1H NMR** (400 MHz, CD_3CN) δ 9.59 (d, *J* = 4.6 Hz, 2H), 9.28 (d, *J* = 5.0 Hz, 2H), 9.22 (t, *J* = 3.3 Hz, 2H), 9.04 (d, *J* = 5.0 Hz, 2H), 5.65 – 5.54 (m, 1H), 5.09 (q, *J* = 7.5 Hz, 2H), 0.70 (dd, *J* = 21.3, 8.1 Hz, 2H). **^{31}P NMR** (162 MHz, CD_3CN) δ -175.3 (br).

6. Experimental procedures for catalytic transformations

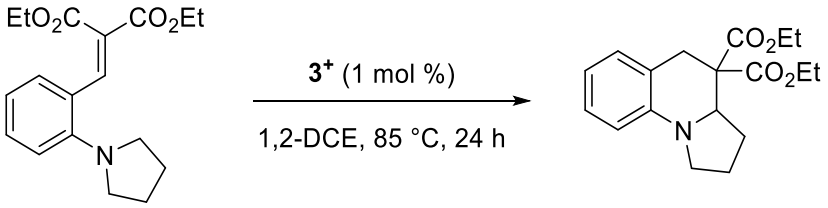


Catalytic hydrosilylation of 2-heptanone. Inside of a nitrogen-filled glovebox, **1^+** (7 mg, 0.005 mmol) was charged to a glass vial and dissolved in $CDCl_3$ (0.7 mL), followed by addition of 2-heptanone (57 mg, 0.50 mmol) and triethylsilane (160 uL, 1.0 mmol). CH_2Br_2 (26 uL, 0.38 mmol) was added as an internal standard. The mixture was transferred to an NMR tube with threaded end and stoppered with a cap with a PTFE septum. The mixture was aged at room temperature overnight (16 h). The reaction mixture was analyzed by NMR (^1H chemical shifts are referenced to CH_2Br_2, taken as δ 5.00), and the yield was determined by integration of the ^1H diagnostic peak (δ 3.86, h, *J* = 6.1 Hz) vs the internal standard (90% yield). The 2-heptanone was fully consumed, as evidenced by a lack of characteristic resonances (^1H: δ 2.12, s; $^{13}C\{^1H\}$: δ 208.9). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 68.5, 39.8, 32.0, 25.5, 23.8, 22.7, 14.0, 8.1, 6.9. Further characterization by ^1H NMR was precluded by overlapping signals from $HSiEt_3$. **HRMS (EI)** calculated for $C_{13}H_{29}OSi$ $[M–H]^+$: 229.1988, found: 229.1992.

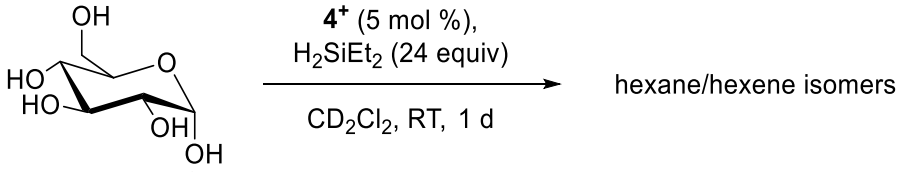


Catalytic deoxygenation of benzophenone. Inside of a nitrogen-filled glovebox, **1^+** (15 mg, 0.010 mmol) was charged to a glass vial and dissolved in $CDCl_3$ (0.7 mL), followed by addition of benzophenone (46 mg, 0.25 mmol) and triethylsilane (81 uL, 0.50 mmol). CH_2Br_2 (18 uL, 0.25 mmol) was added as an internal standard. The mixture was transferred to an NMR tube with threaded end and was stoppered with a cap with a PTFE septum. The mixture was aged at room temperature for 1 h. The reaction mixture was analyzed by NMR (^1H chemical shifts are referenced to CH_2Br_2, taken as δ 5.00), and the yield was determined by integration of the diagnostic ^1H peak (δ 4.11, s) vs the internal standard (97% yield). The benzophenone was fully

consumed, as evidenced by a lack of the characteristic resonance $^{13}C\{^1H\}$: δ 196.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.5 Hz, 5H), 7.36 – 7.22 (m, 5H), 4.11 (s, 2H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ 141.1, 129.0, 128.5, 126.1, 42.0.



Catalytic 1,5-hydride shift of diethyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate. Inside of a nitrogen-filled glovebox, **3$^+$** (16 mg, 0.010 mmol) was charged to a 10-mL glass culture tube with threaded end outfitted with a phenolic screw-cap open top cap and PTFE-lined silicone septum equipped with a Teflon-coated stir bar. The catalyst was dissolved in anhydrous 1,2-dichloroethane (3 mL), and the alkylidene starting material (317 mg, 1.00 mmol) was added. The tube was heated at 85 °C for 24 h. After cooling to room temperature, all volatiles were removed by rotary evaporation. The mixture was then purified on silica (gradient of 5% EtOAc to 10% EtOAc in hexanes) to afford the product as an oil (240 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 1H), 4.36 – 4.16 (m, 2H), 4.13 – 3.95 (m, 2H), 3.78 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.44 – 3.15 (m, 4H), 2.57 – 2.36 (m, 1H), 2.22 – 2.03 (m, 2H), 2.02 – 1.86 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ 171.1, 168.6, 143.8, 128.5, 127.5, 118.7, 115.8, 110.8, 62.2, 61.5, 60.8, 53.0, 47.4, 37.0, 27.8, 23.6, 14.1, 13.9. These values are consistent with the literature report.[4]



*Catalytic deoxygenation of $^{13}C_6$-*D*-glucose.* Inside of a nitrogen-filled glovebox, **4$^+$** (8.7 mg, 0.0050 mmol) was charged to a 1-dram glass vial with a Teflon-coated stir bar. The catalyst was suspended in CD_2Cl_2 (200 µL) and diethylsilane (310 µL, 2.4 mmol). To this mixture was added $^{13}C_6$-*D*-glucose (99 atom %, 18.0 mg, 0.100 mmol). The heterogenous mixture was sealed with a screw-cap open top cap and PTFE-lined silicone septum and was stirred for 24 h. At the end of the reaction, the system had become pressurized (presumably due to formation of hydrogen gas), and the mixture was homogeneous and green in color. The mixture was transferred to an NMR tube with a threaded end, and $Cr(acac)_3$ (25 mg, 0.072 mmol) was added to the reaction mixture as a paramagnetic relaxation reagent. Natural-abundance cyclooctane (108 uL, 0.800 mmol) was added as an internal standard. T1 values for each ^{13}C nucleus in the solution were obtained using standard inversion-recovery pulse sequences, and the longest T1 measured was 1.7 s. A delay time of 10.0 s was used in the quantitative measurement to ensure that all spins were fully relaxed. Peaks were assigned by comparing to the literature report.[7]

7. Multinuclear NMR spectra

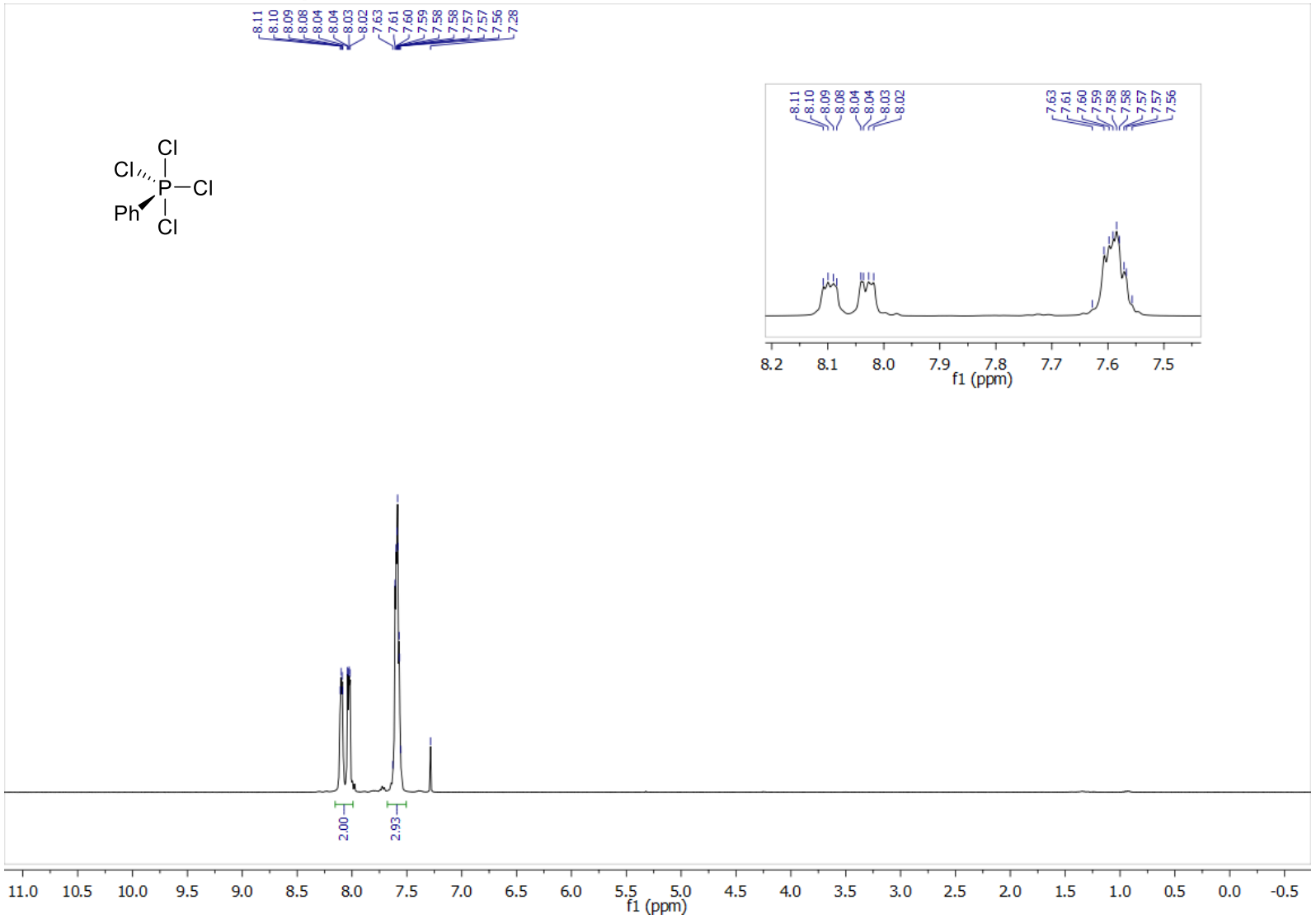


Figure S1. *^{1}H NMR spectrum of* ***S2****.*

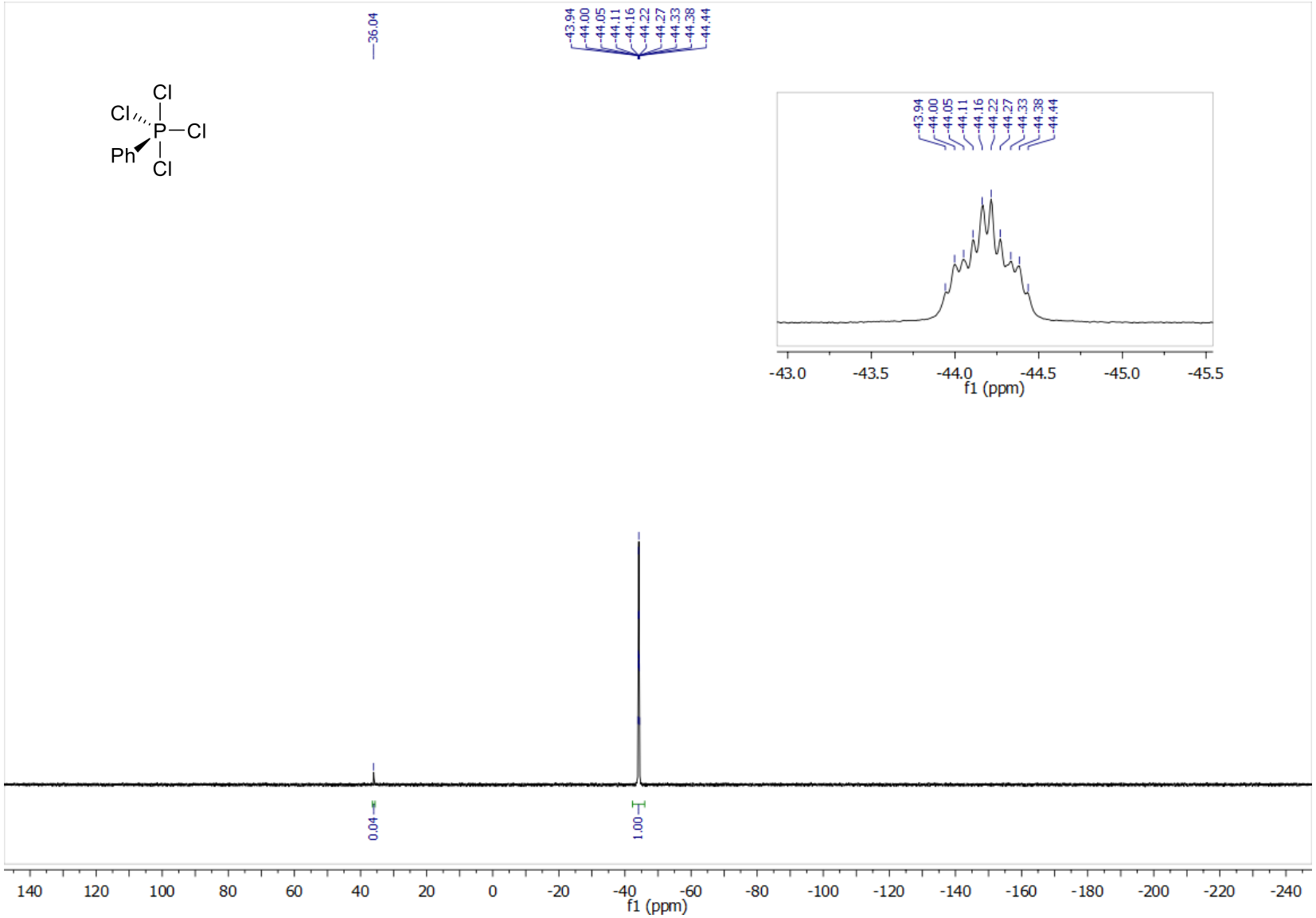


Figure S2. *^{31}P NMR spectrum of* ***S2****.*

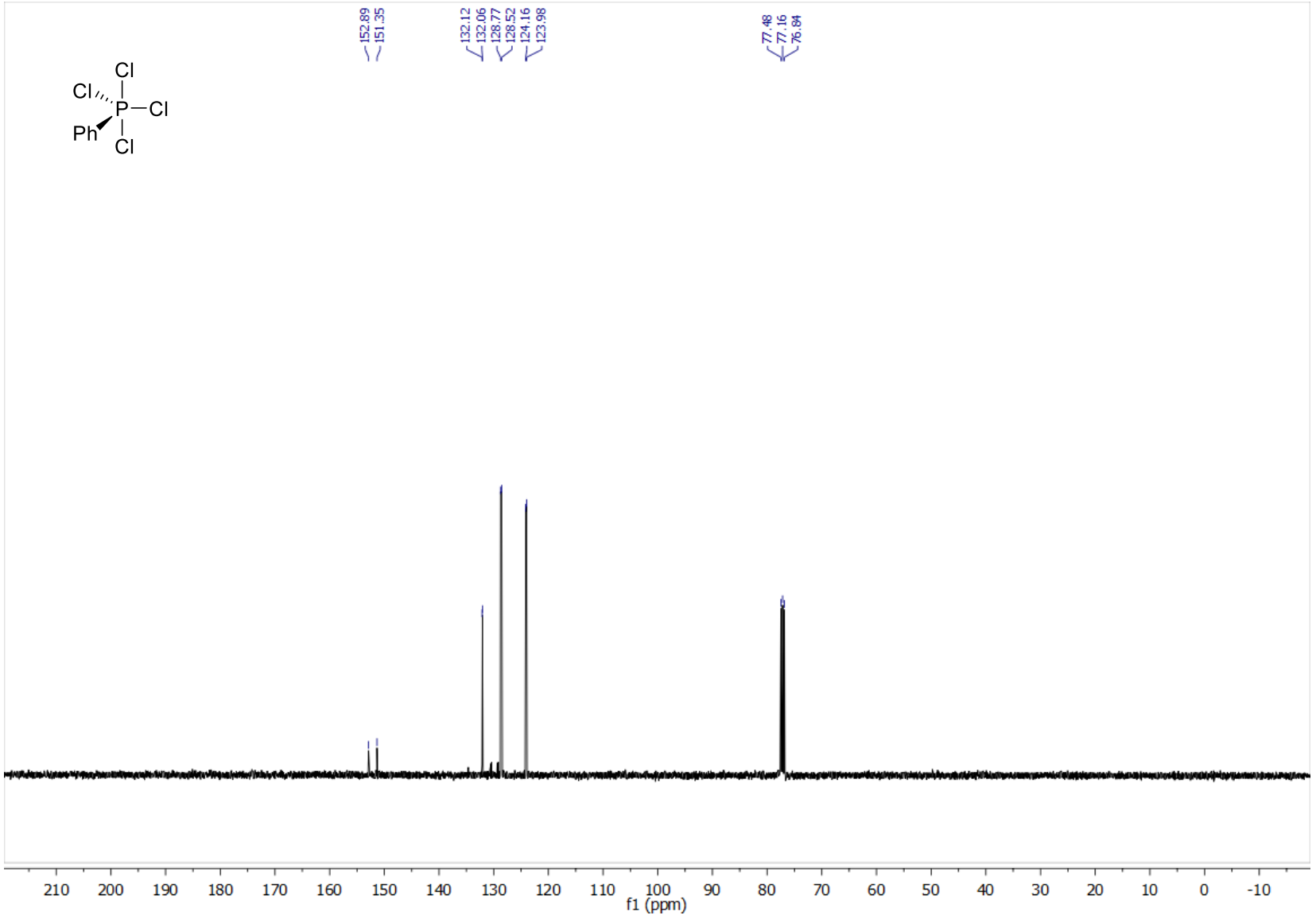


Figure S3. *^{13}C NMR spectrum of* ***S2****.*

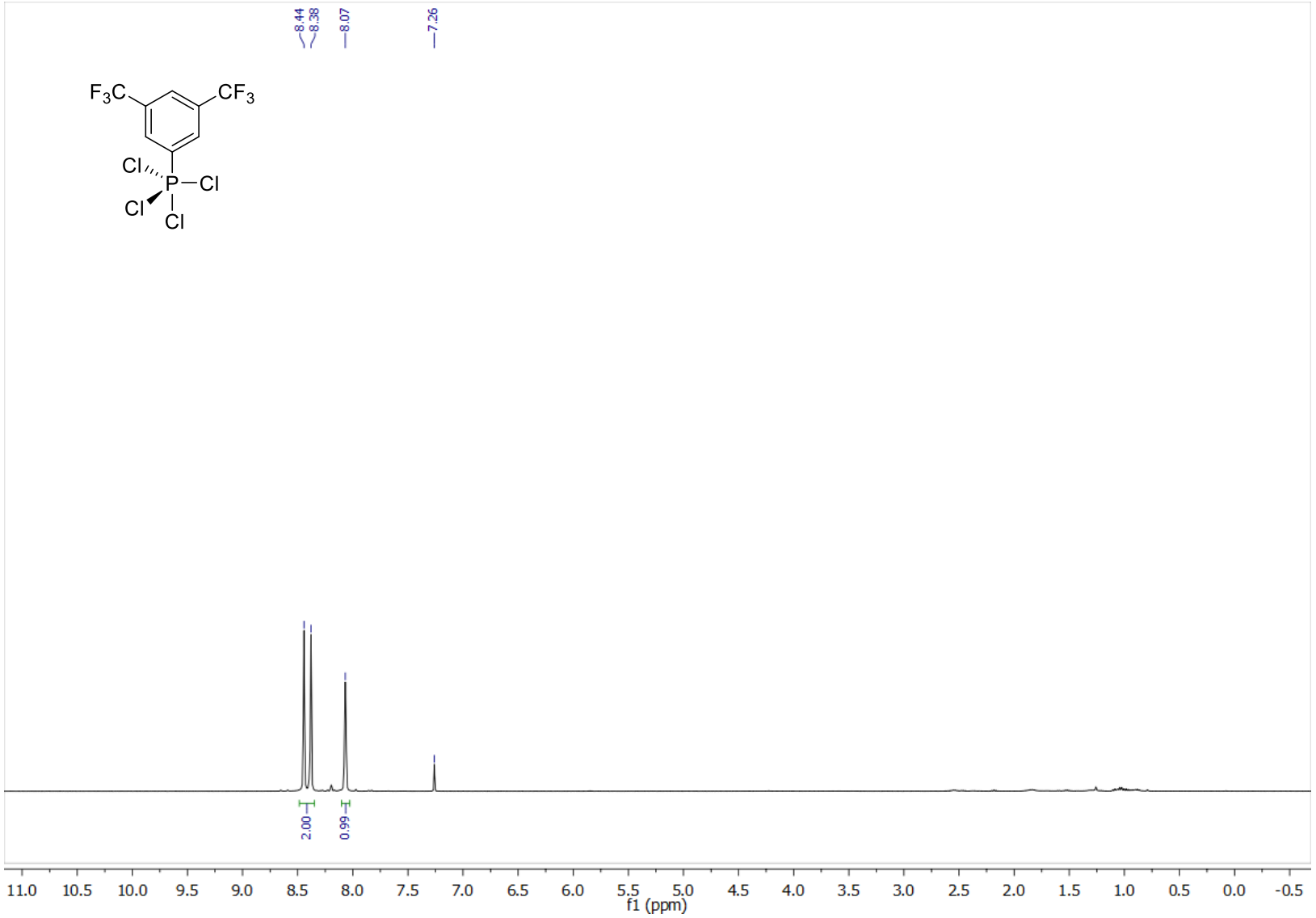


Figure S4. *^{1}H NMR spectrum of* ***S3****.*

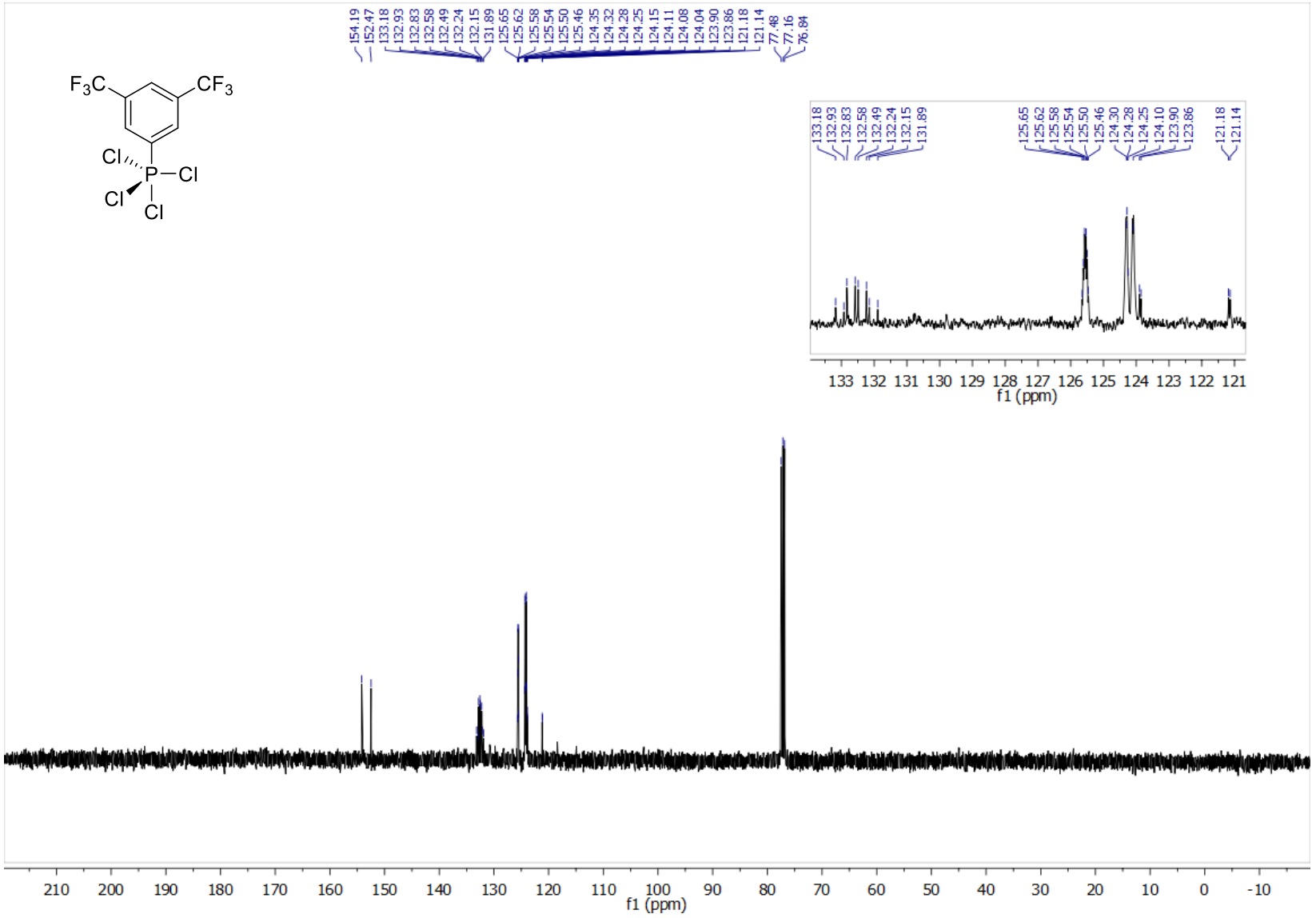


Figure S5. *$^{13}C\{^{1}H\}$ NMR spectrum of* ***S3****.*

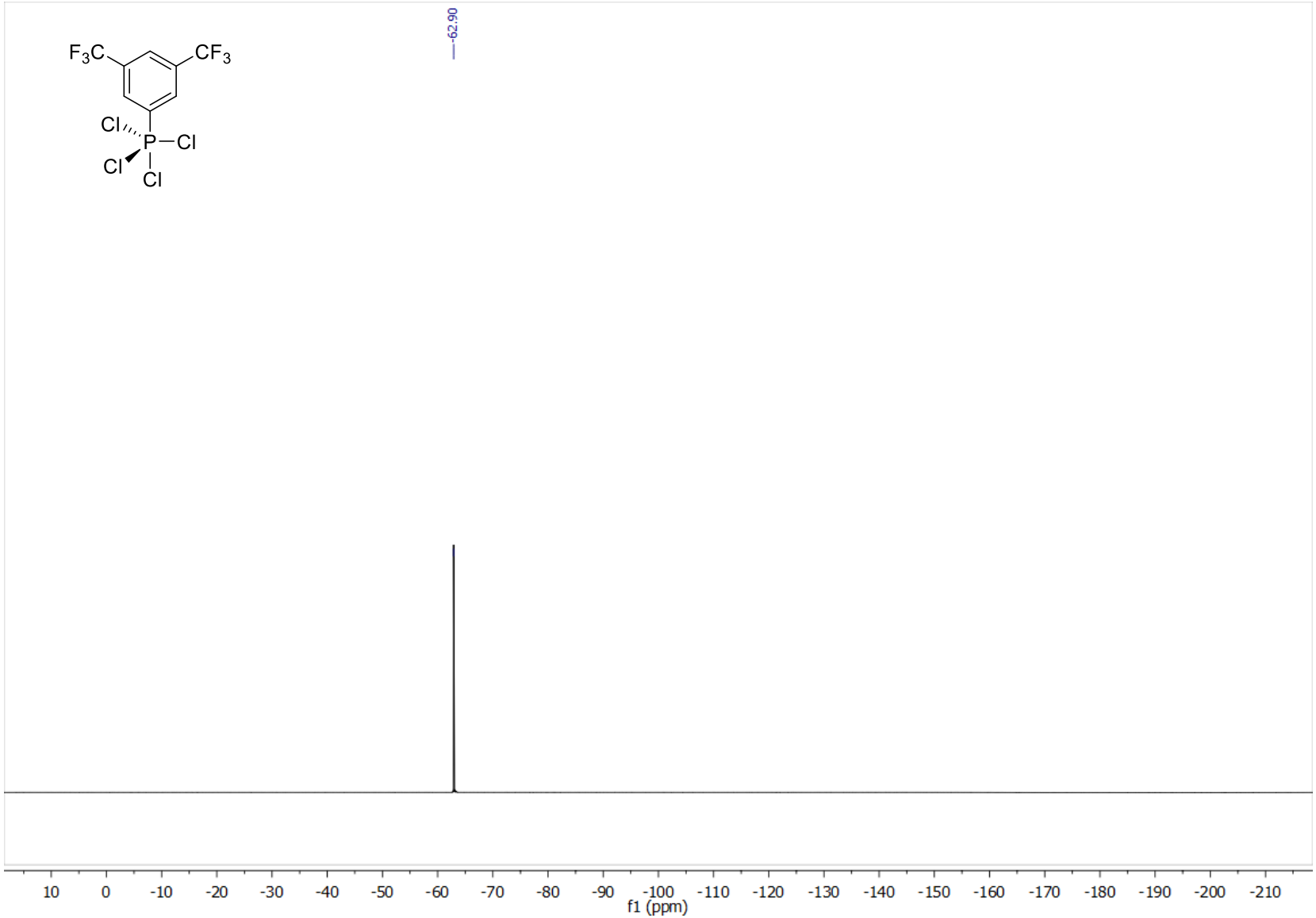


Figure S6. *^{19}F NMR spectrum of* ***S3****.*

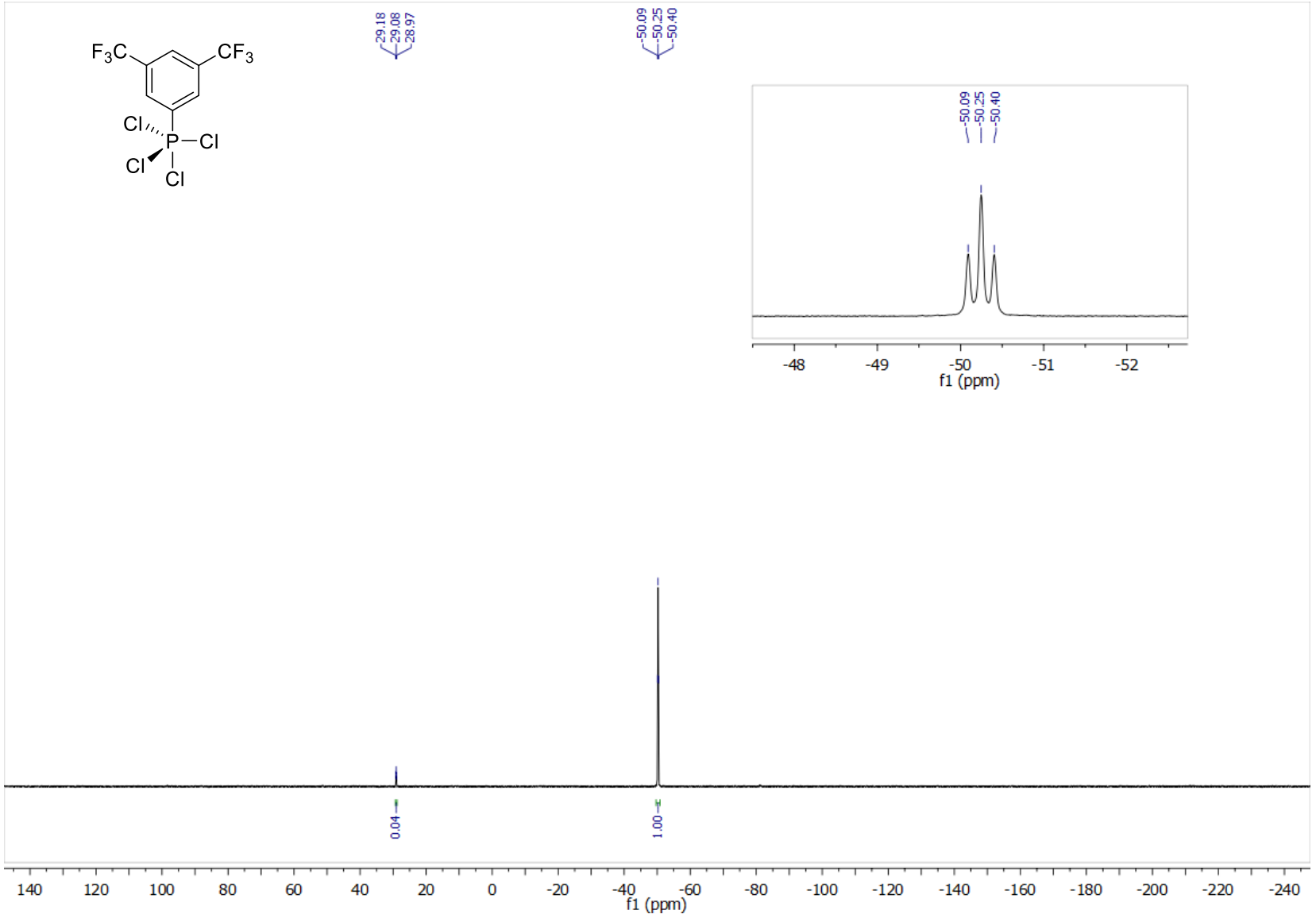


Figure S7. *^{31}P NMR spectrum of* ***S3****.*

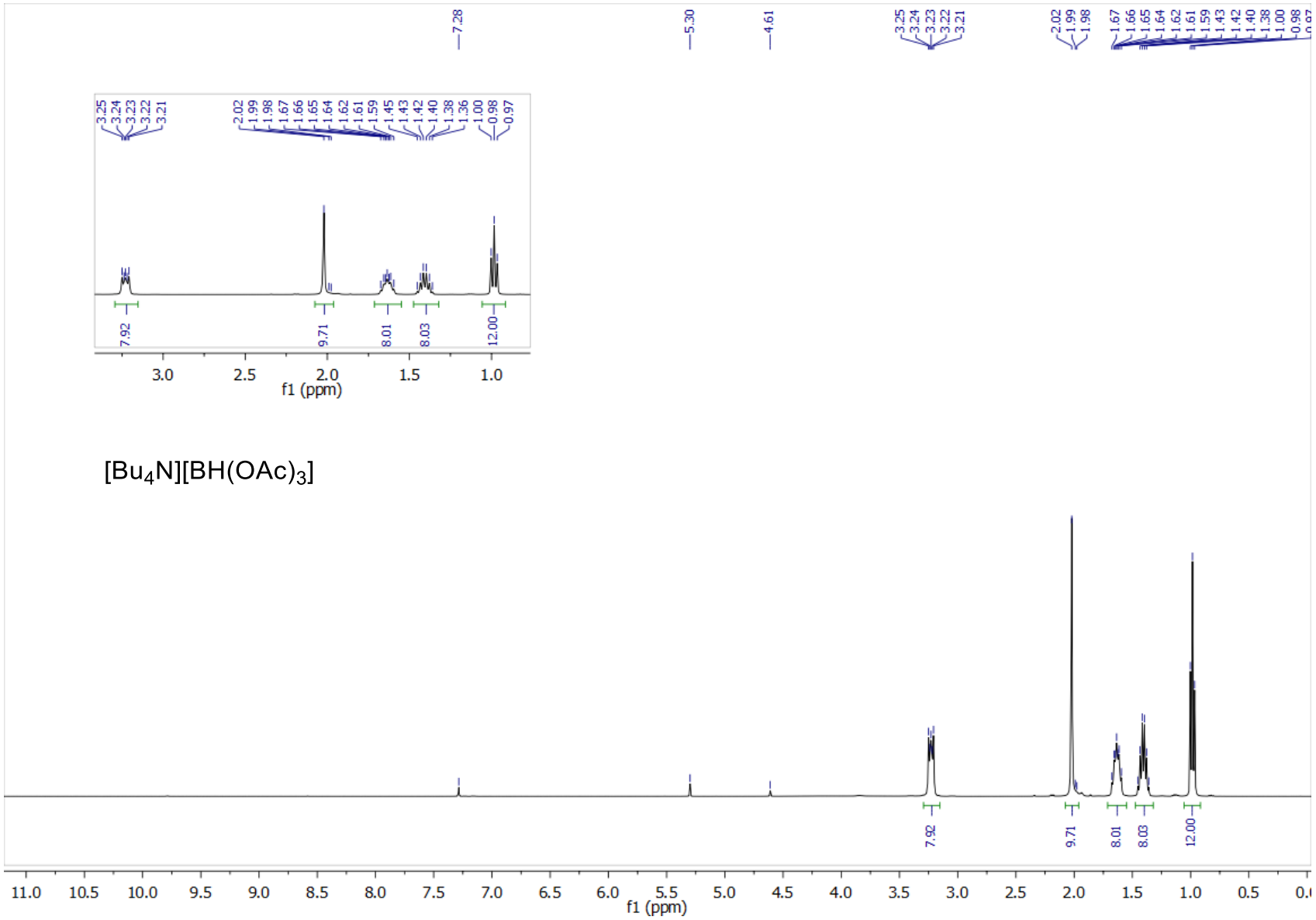


Figure S8. *^{1}H NMR spectrum of* ***S4****.*

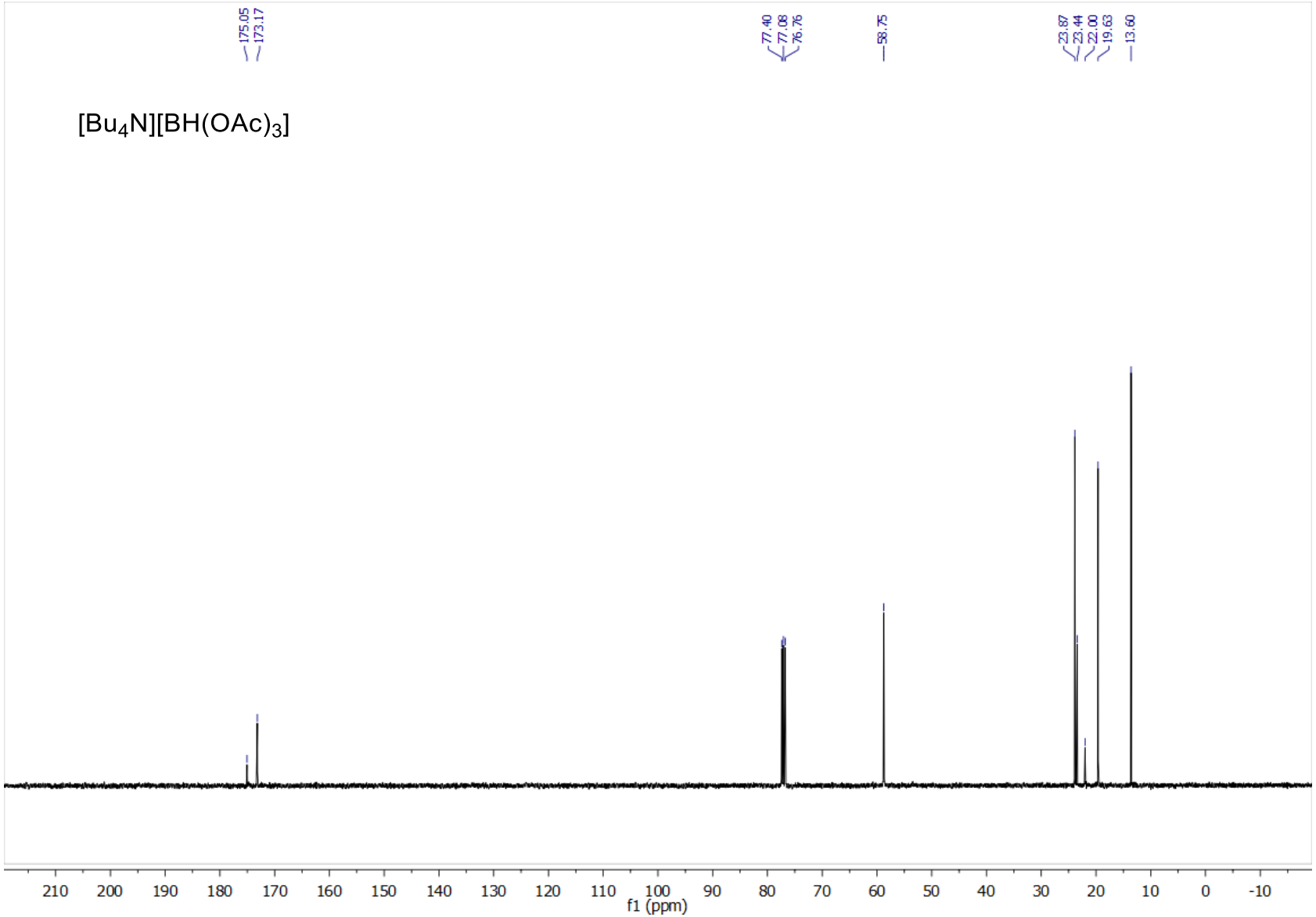


Figure S9. *$^{13}C\{^{1}H\}$ NMR spectrum of* ***S4****. Residual HOAc is a minor contaminant.*

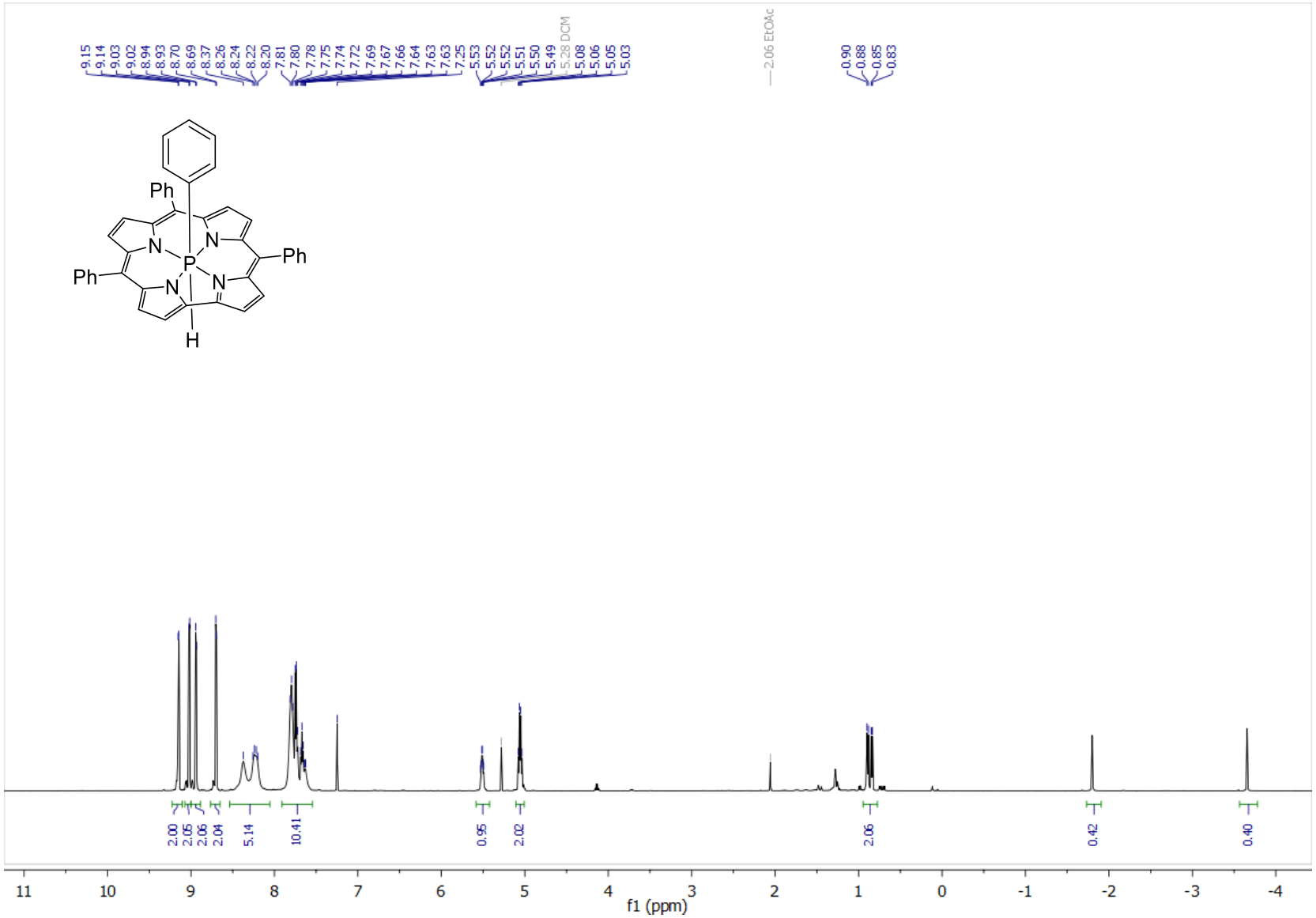


Figure S10. *^{1}H NMR spectrum of* ***1•H****.*

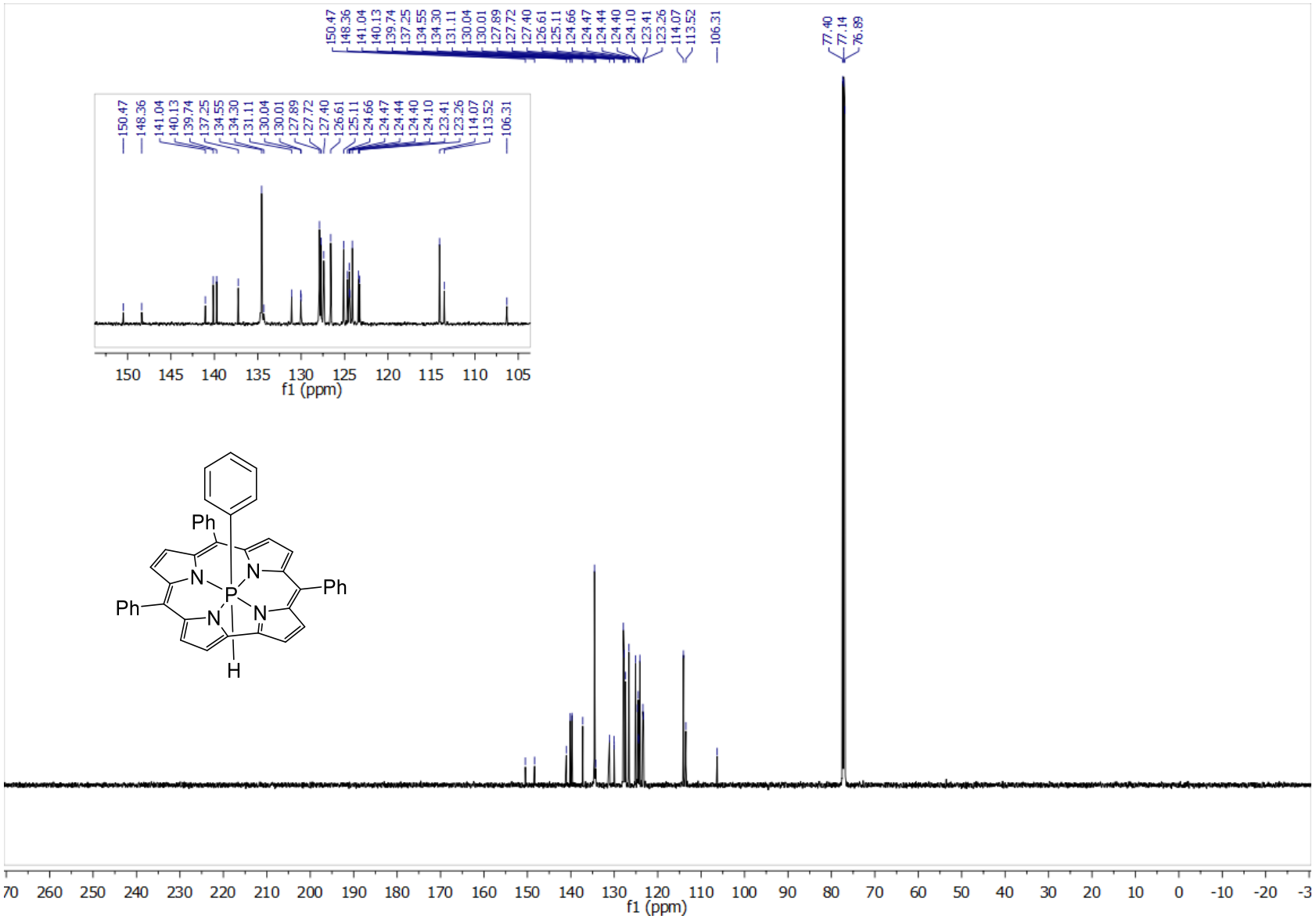


Figure S11. *$^{13}C\{^{1}H\}$ NMR spectrum of* ***1•H****.*

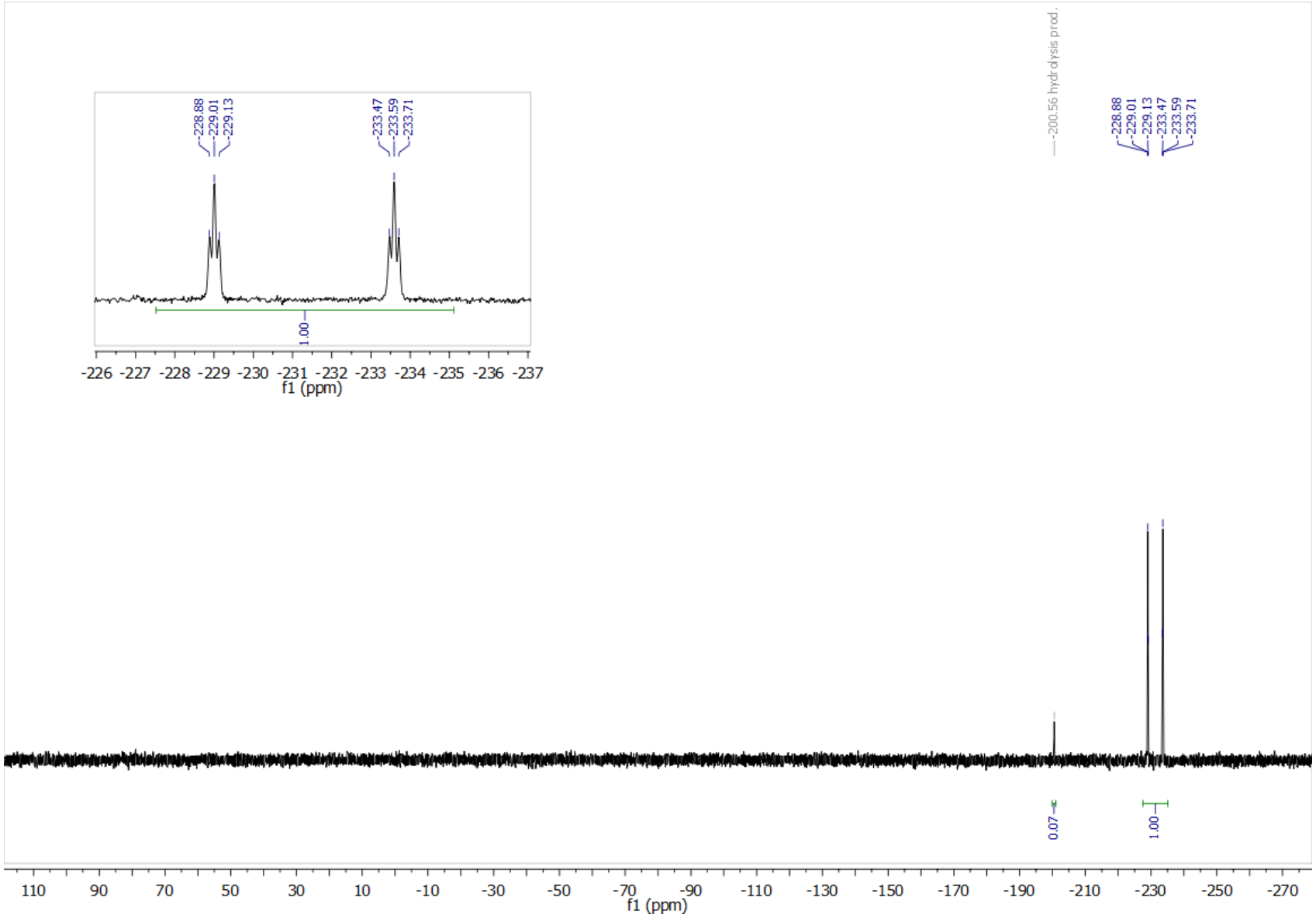


Figure S12. *^{31}P NMR spectrum of **1•H**. The compound containing a P–OH bond is evident at δ –200.6 ppm.*

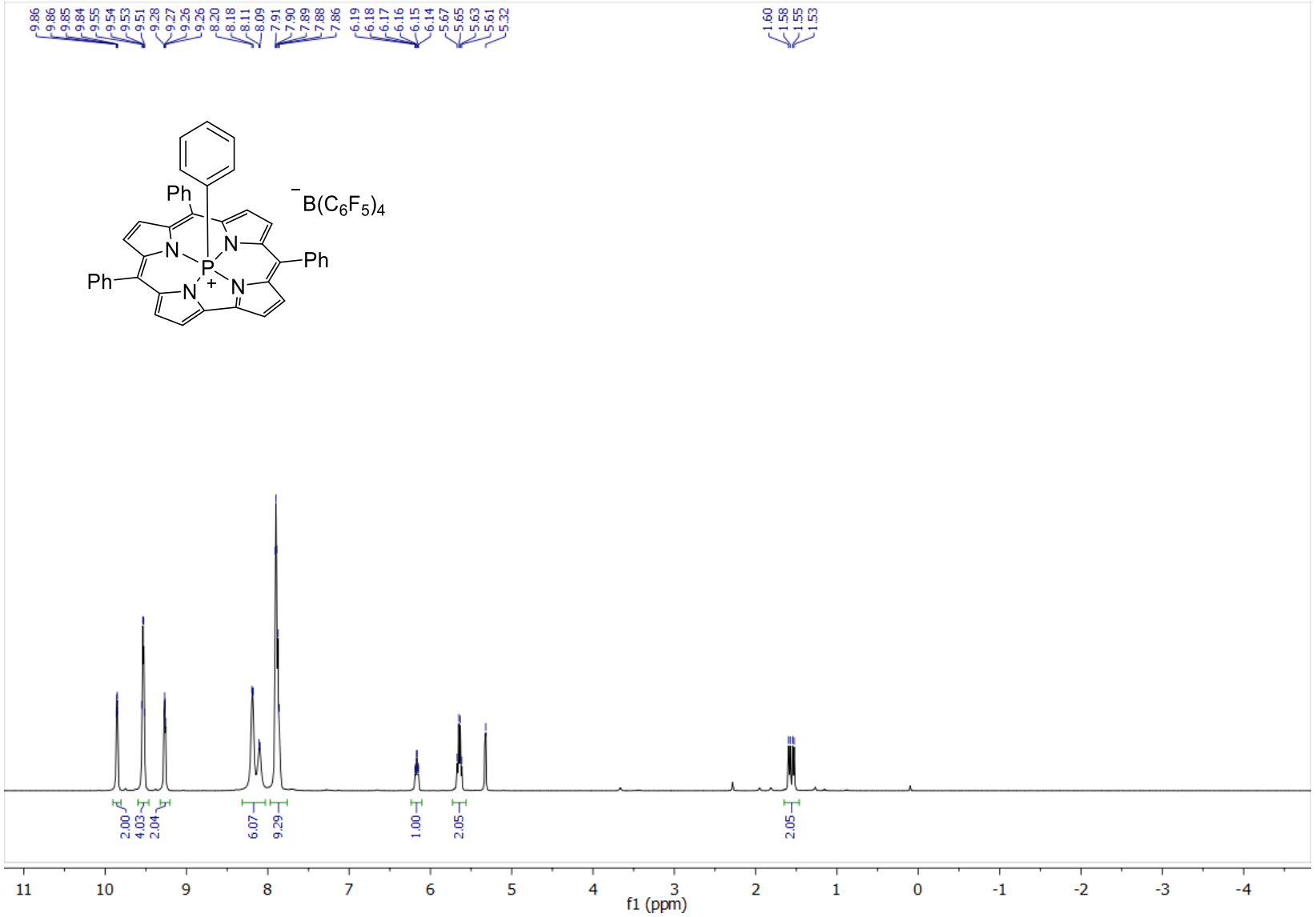


Figure S13. *^{1}H NMR spectrum of **1**$^{+}$.*

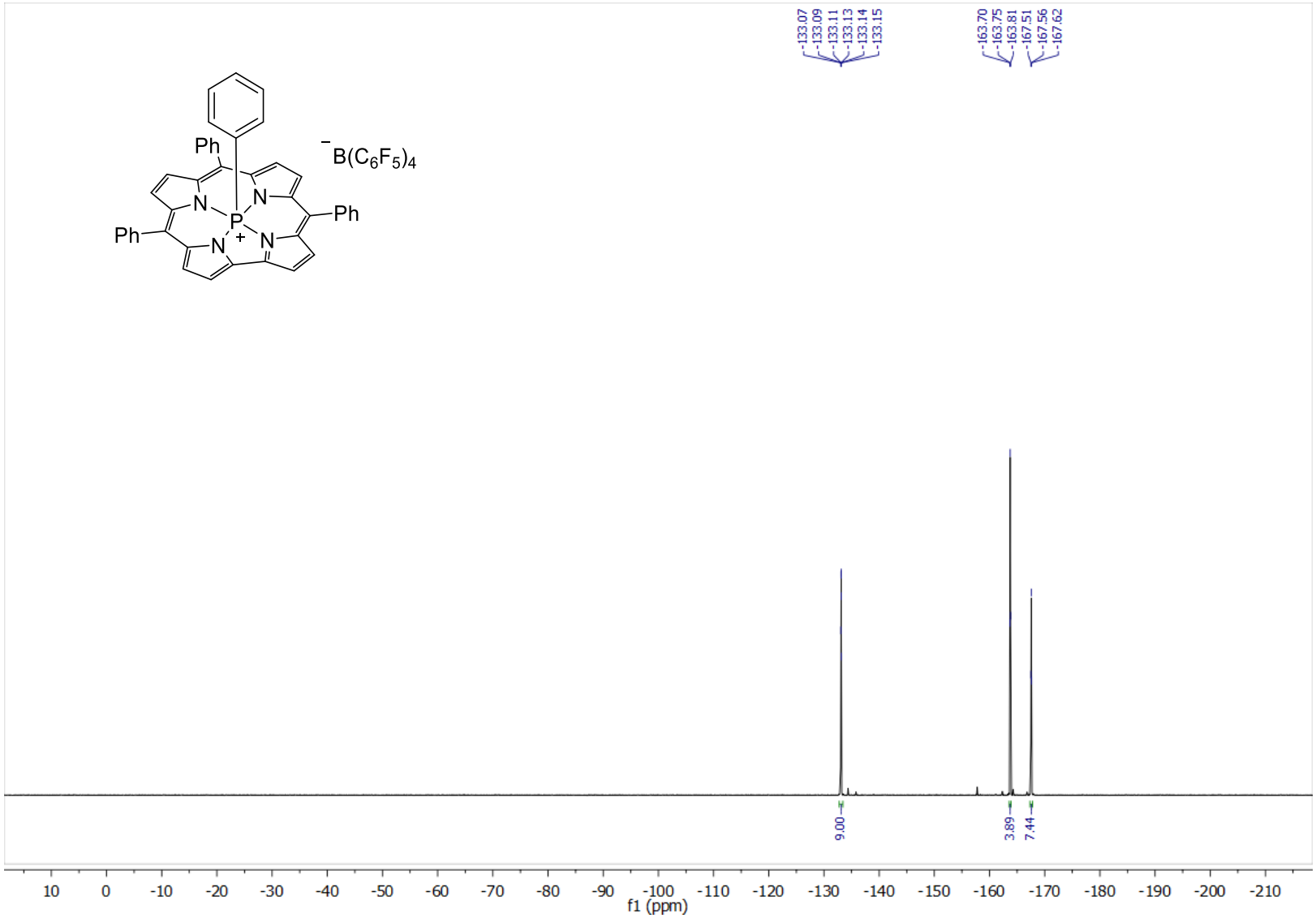


Figure S14. *^{19}F NMR spectrum of **1**$^{+}$.*

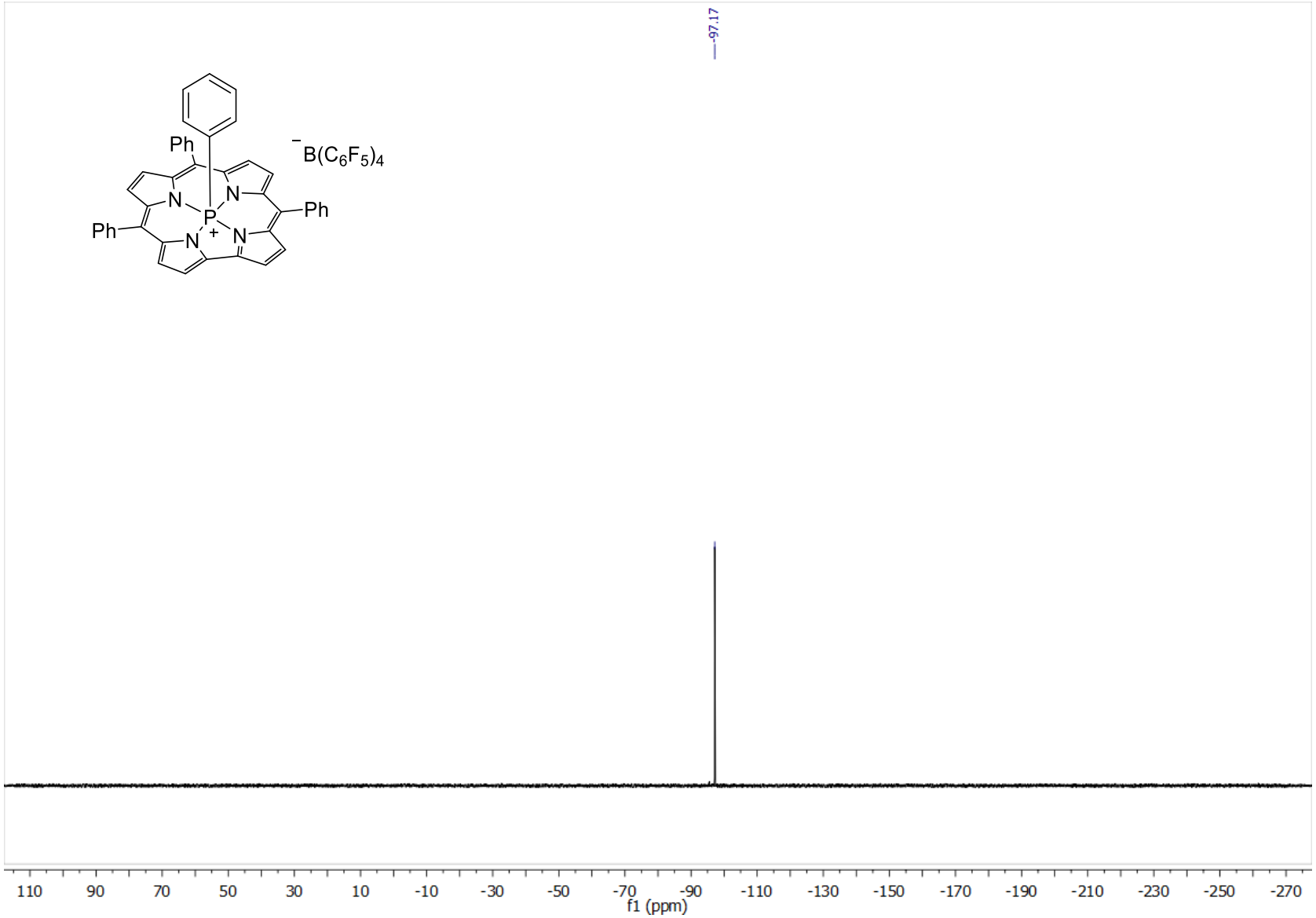


Figure S15. *$^{31}P\{^{1}H\}$ NMR spectrum of* ***1*****$^{+}$***.

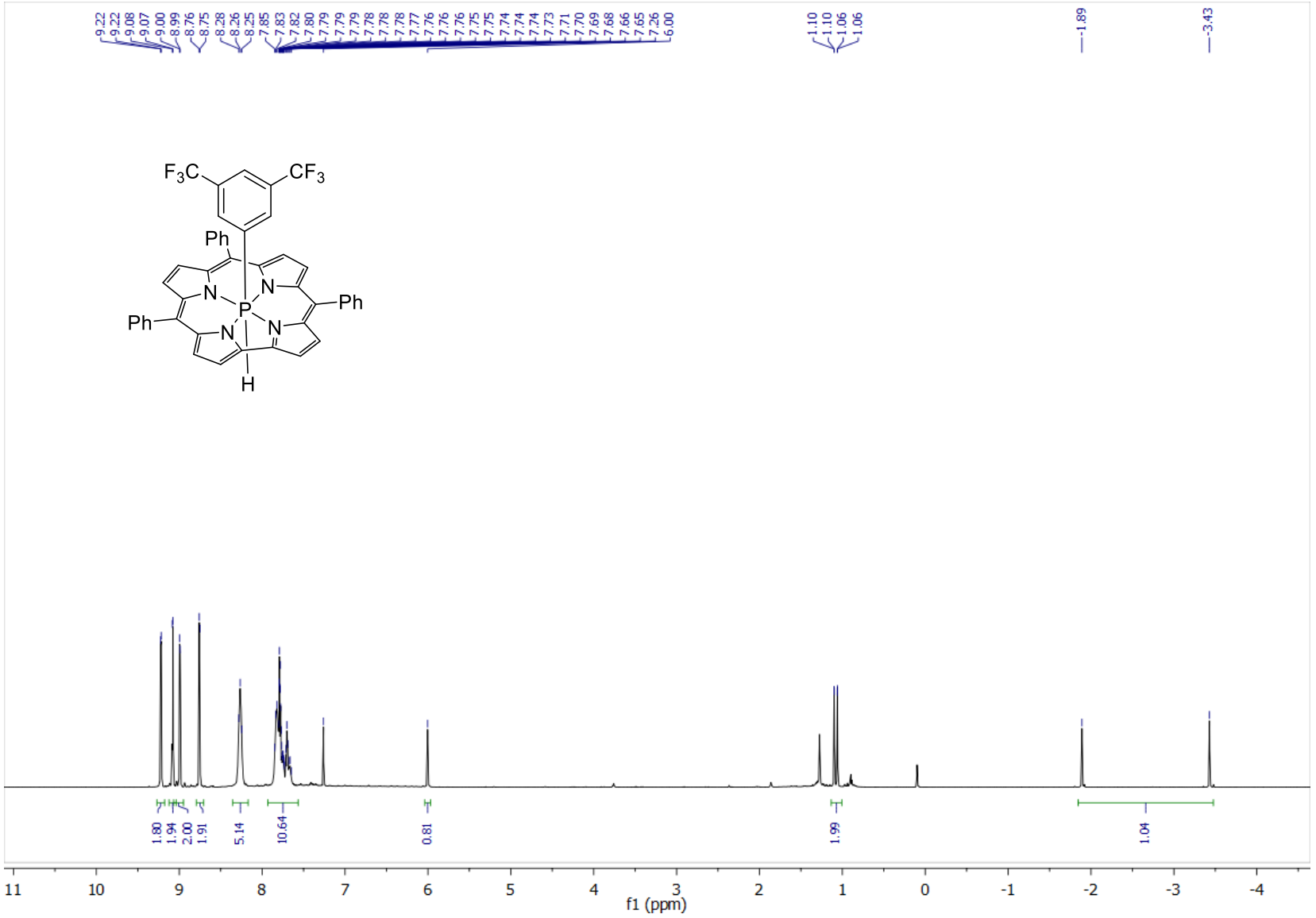


Figure S16. *^{1}H NMR spectrum of **2•H**.*

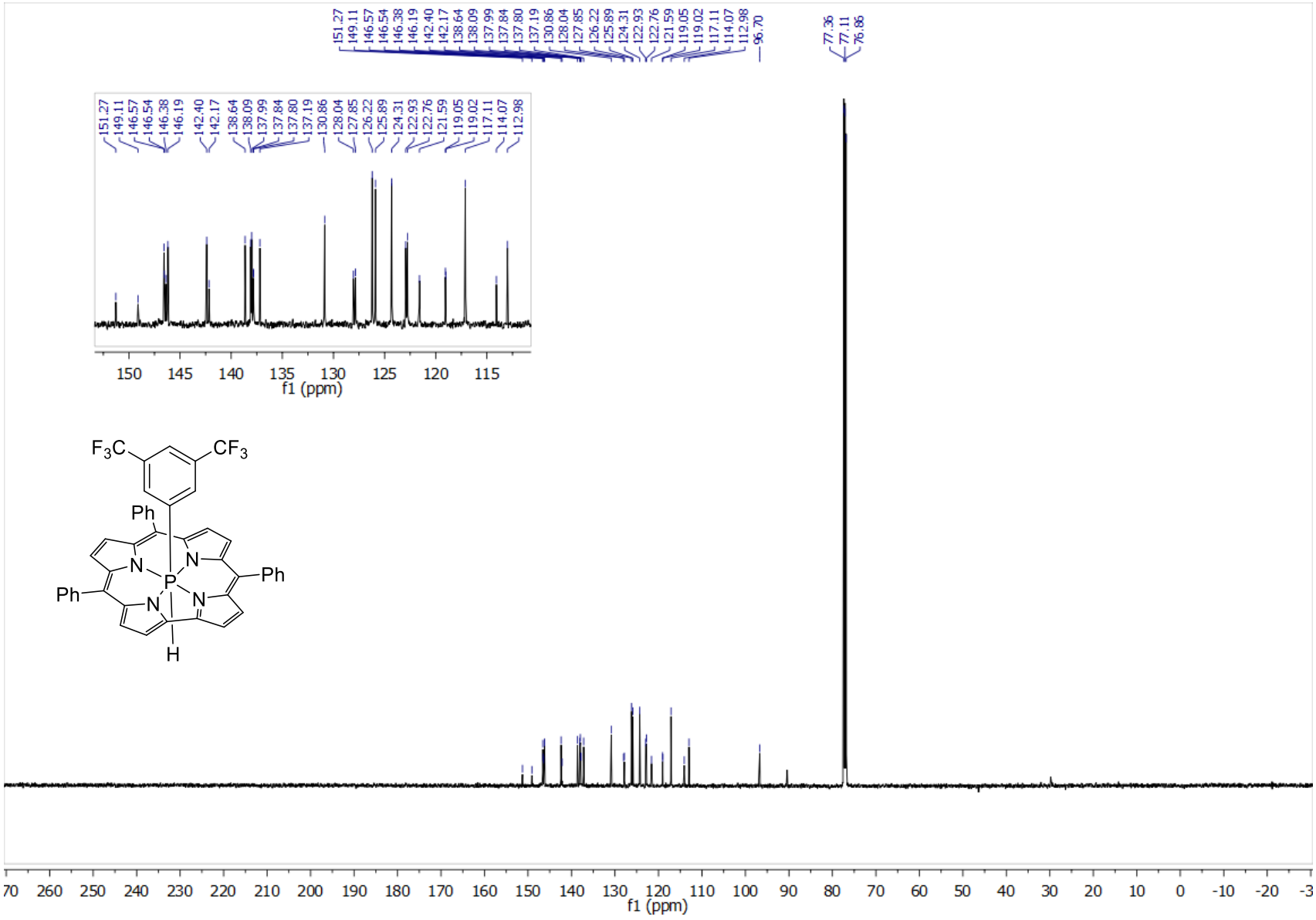


Figure S17. *$^{13}C\{^{1}H,^{19}F\}$ NMR spectrum of **2•H**.*

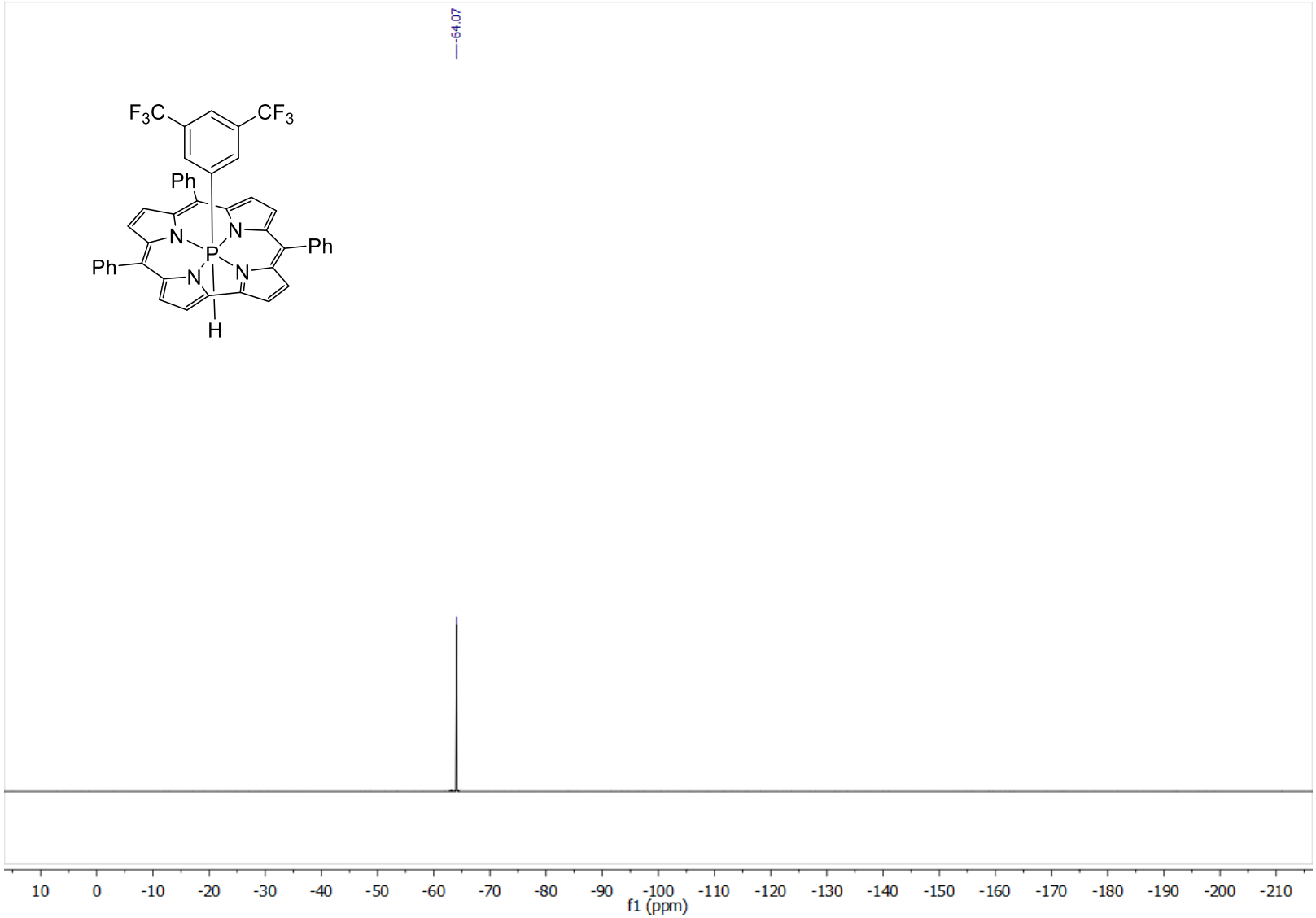


Figure S18. *^{19}F NMR spectrum of **2•H**.*

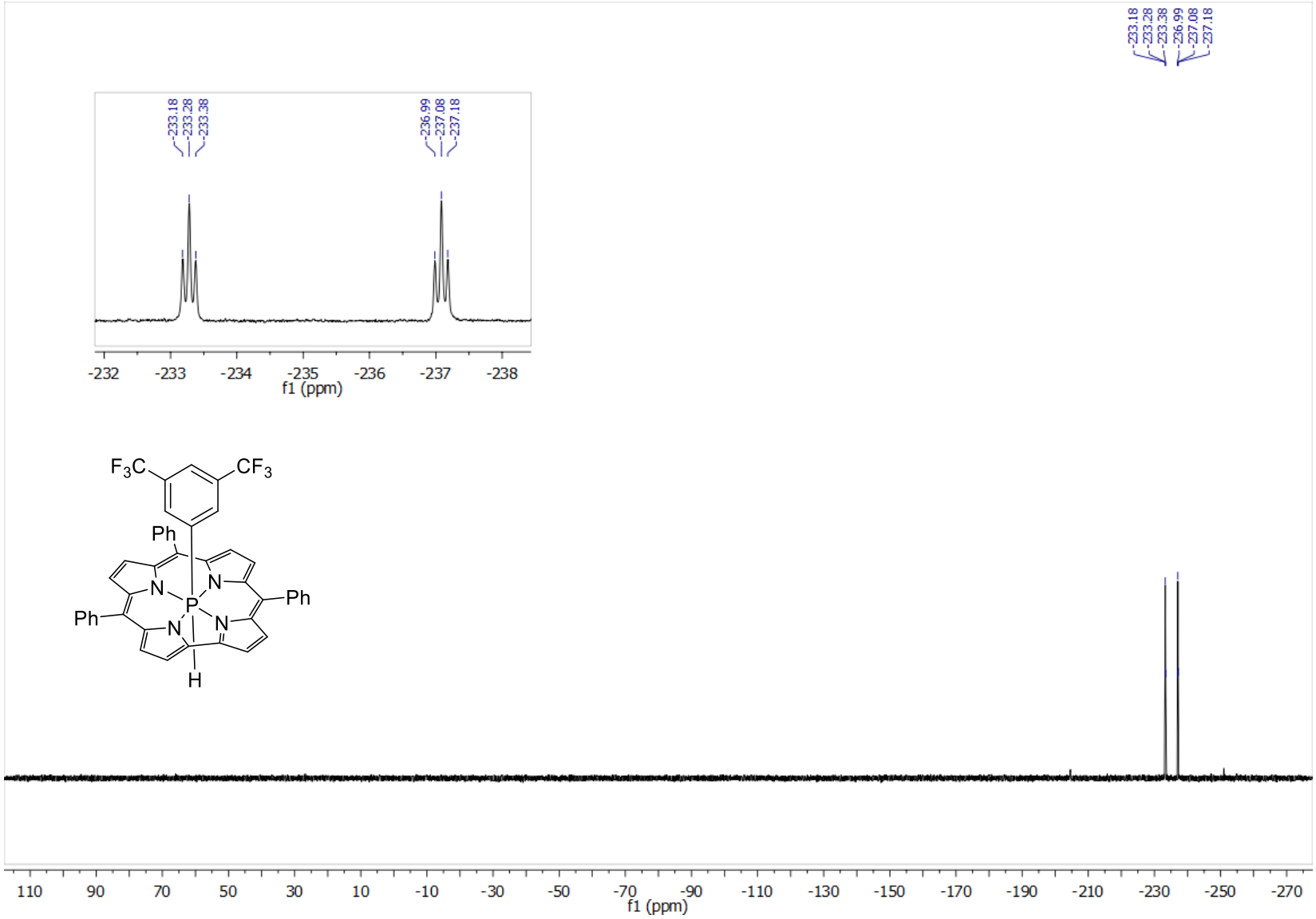


Figure S19. *^{31}P NMR spectrum of **2•H**.*

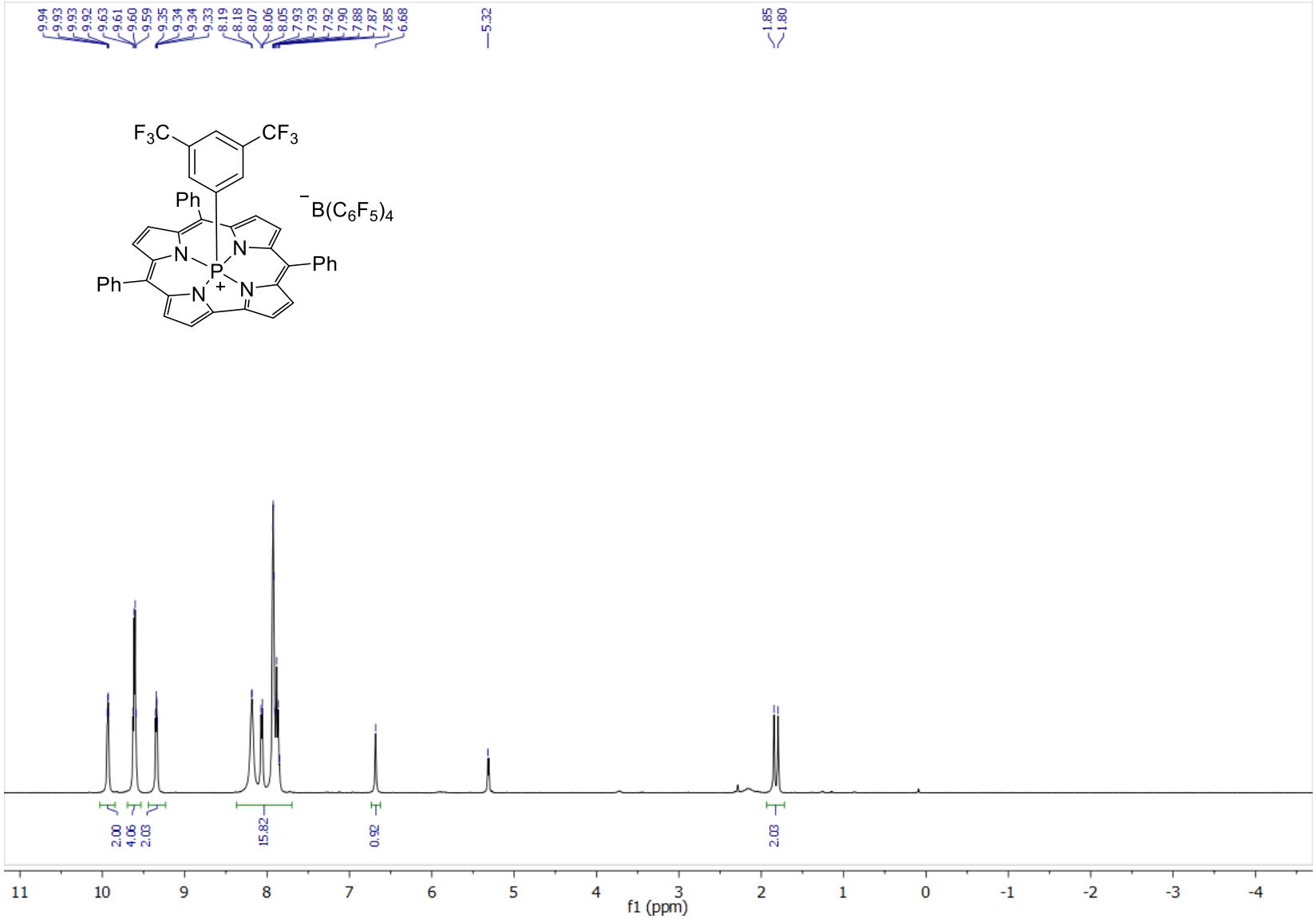


Figure S20. *^{1}H NMR spectrum of **2**$^{+}$.*

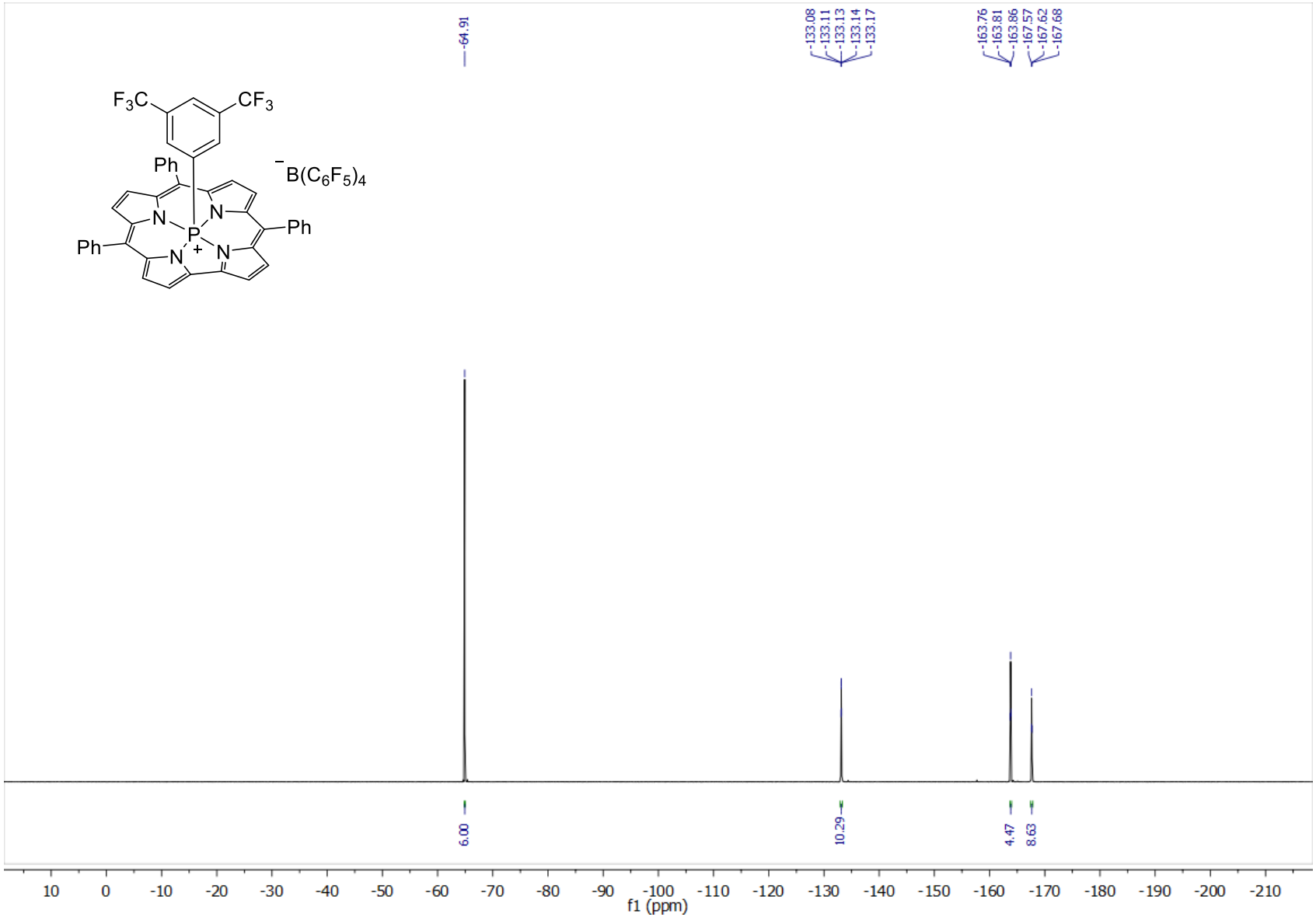


Figure S21. *^{19}F NMR spectrum of **2**$^{+}$.*

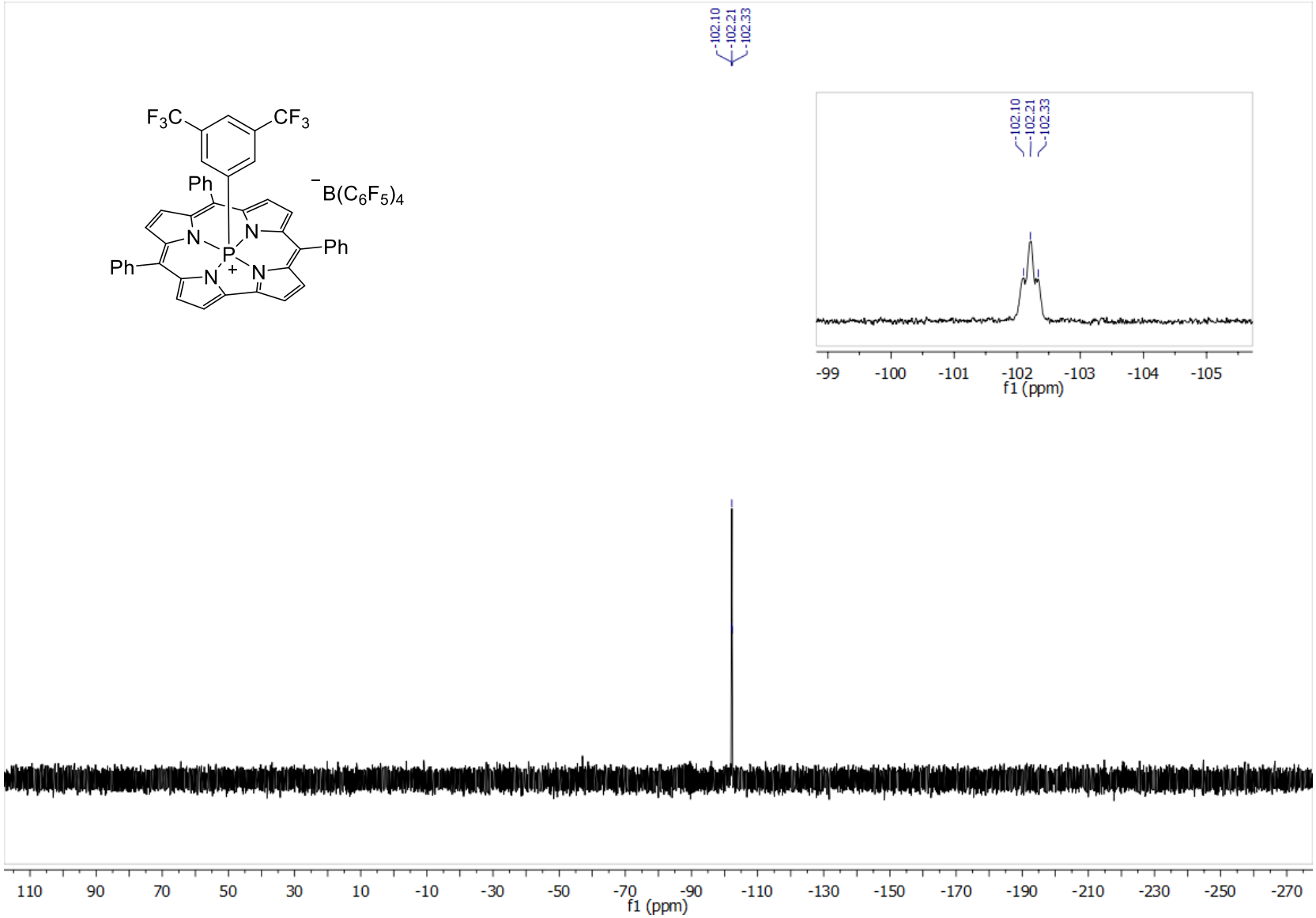


Figure S22. *^{31}P NMR spectrum of **2**$^{+}$.*

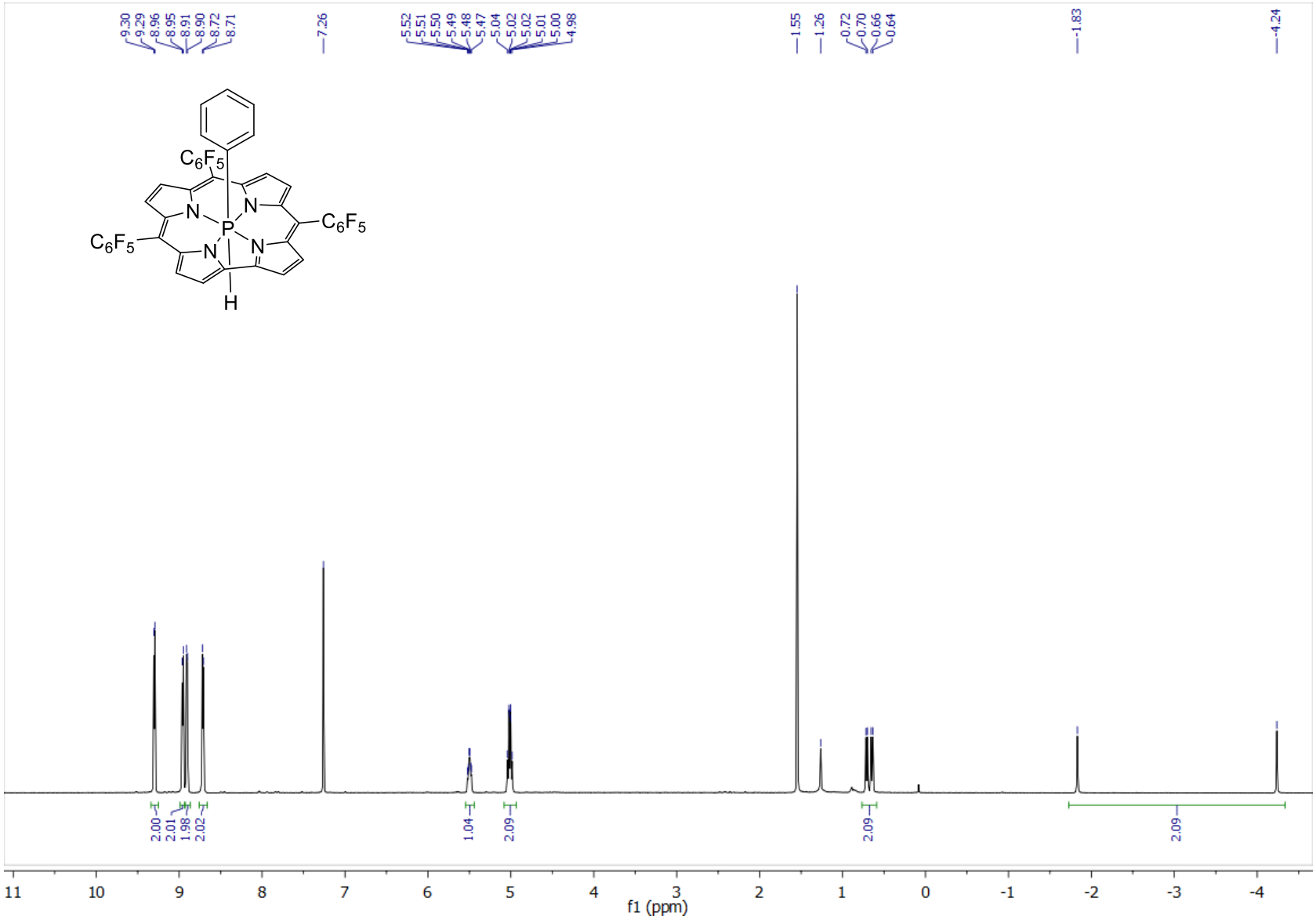


Figure S23. *^{1}H NMR spectrum of* ***3•H****.*

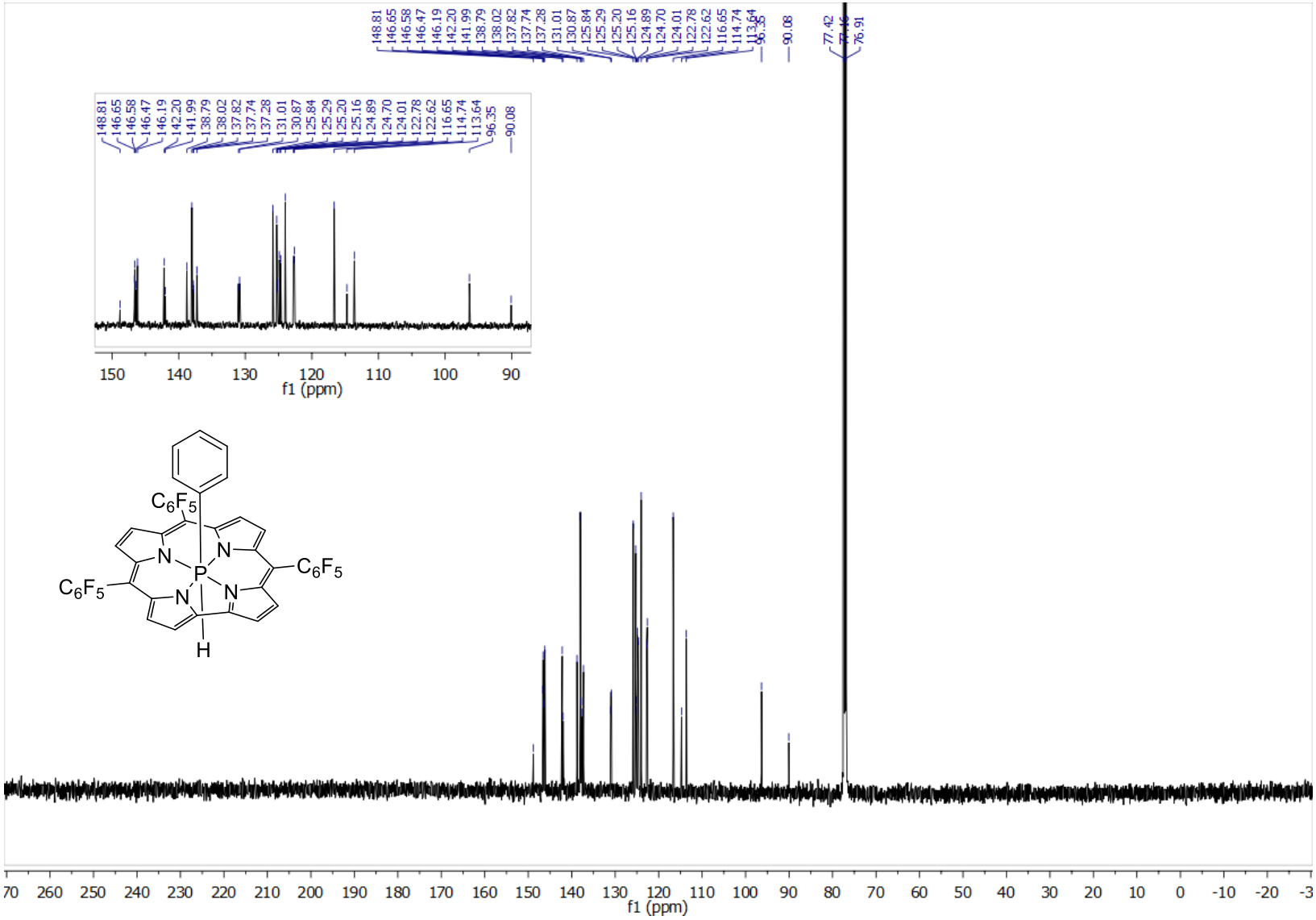


Figure S24. *$^{13}C\{^{1}H,^{19}F\}$ NMR spectrum of* ***3•H****.*

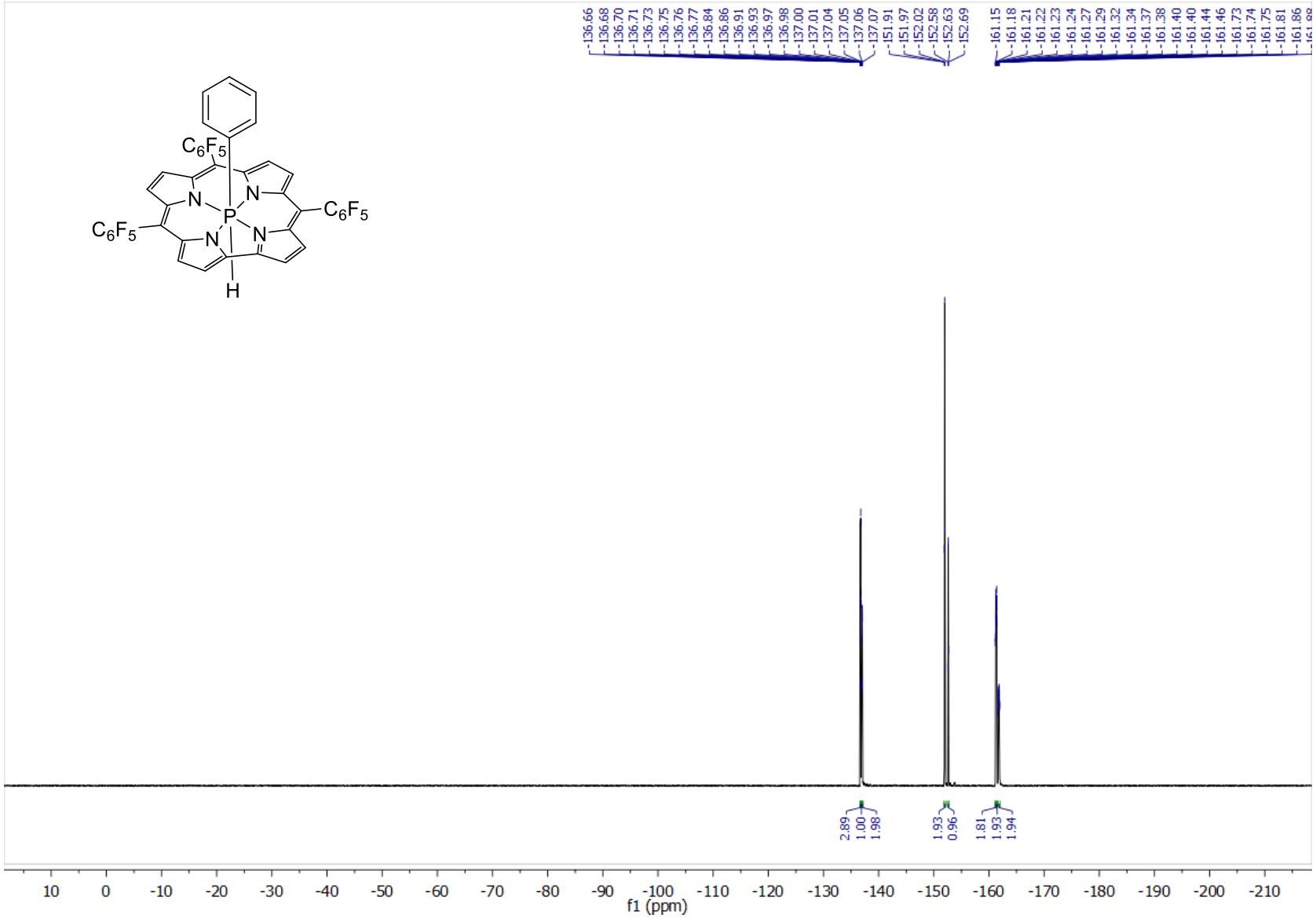


Figure S25. *^{19}F NMR spectrum of* ***3•H.***

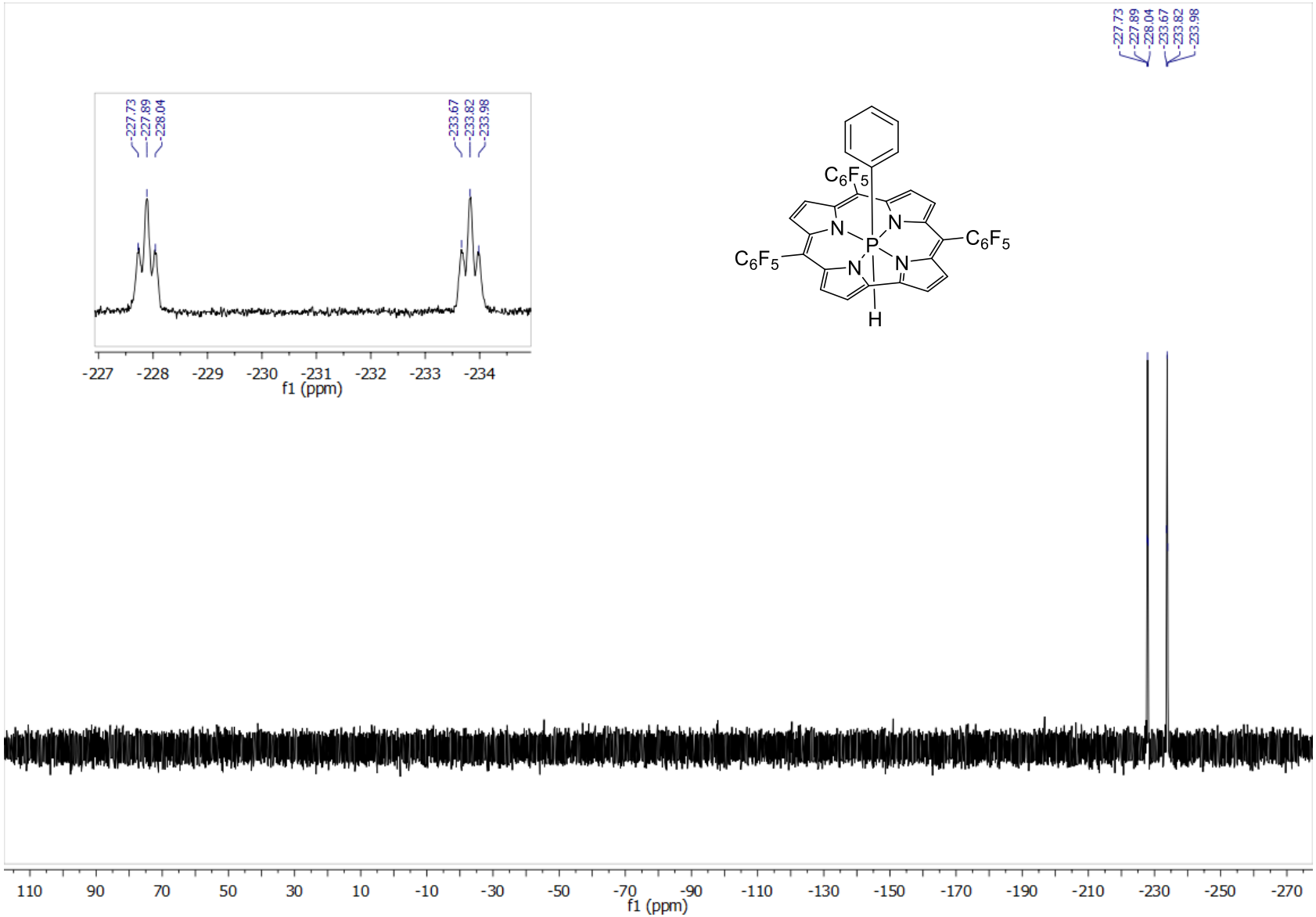


Figure S26. *^{31}P NMR spectrum of **3•H**.*

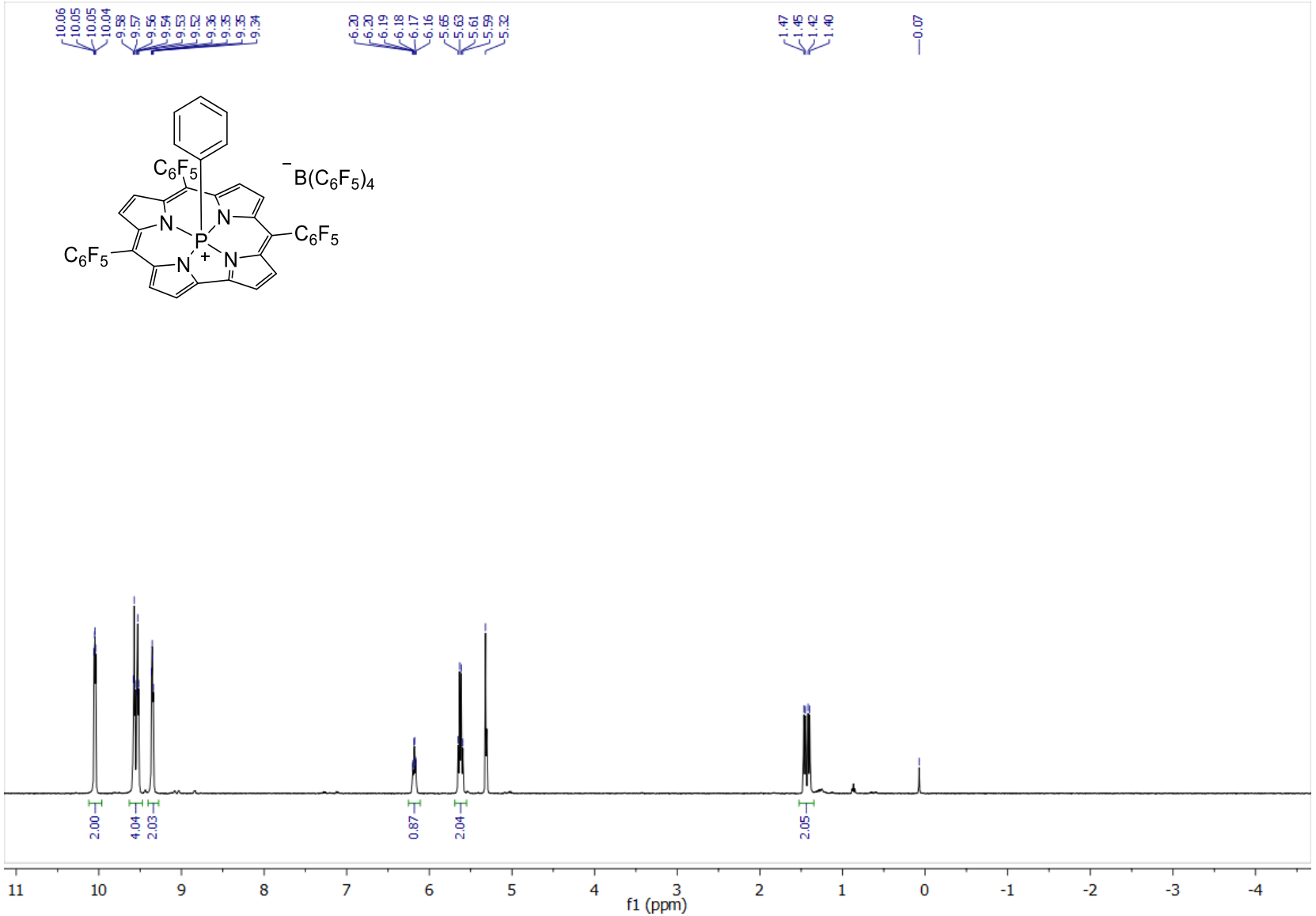


Figure S27. *^{1}H NMR spectrum of* ***3*****$^{+}$**.

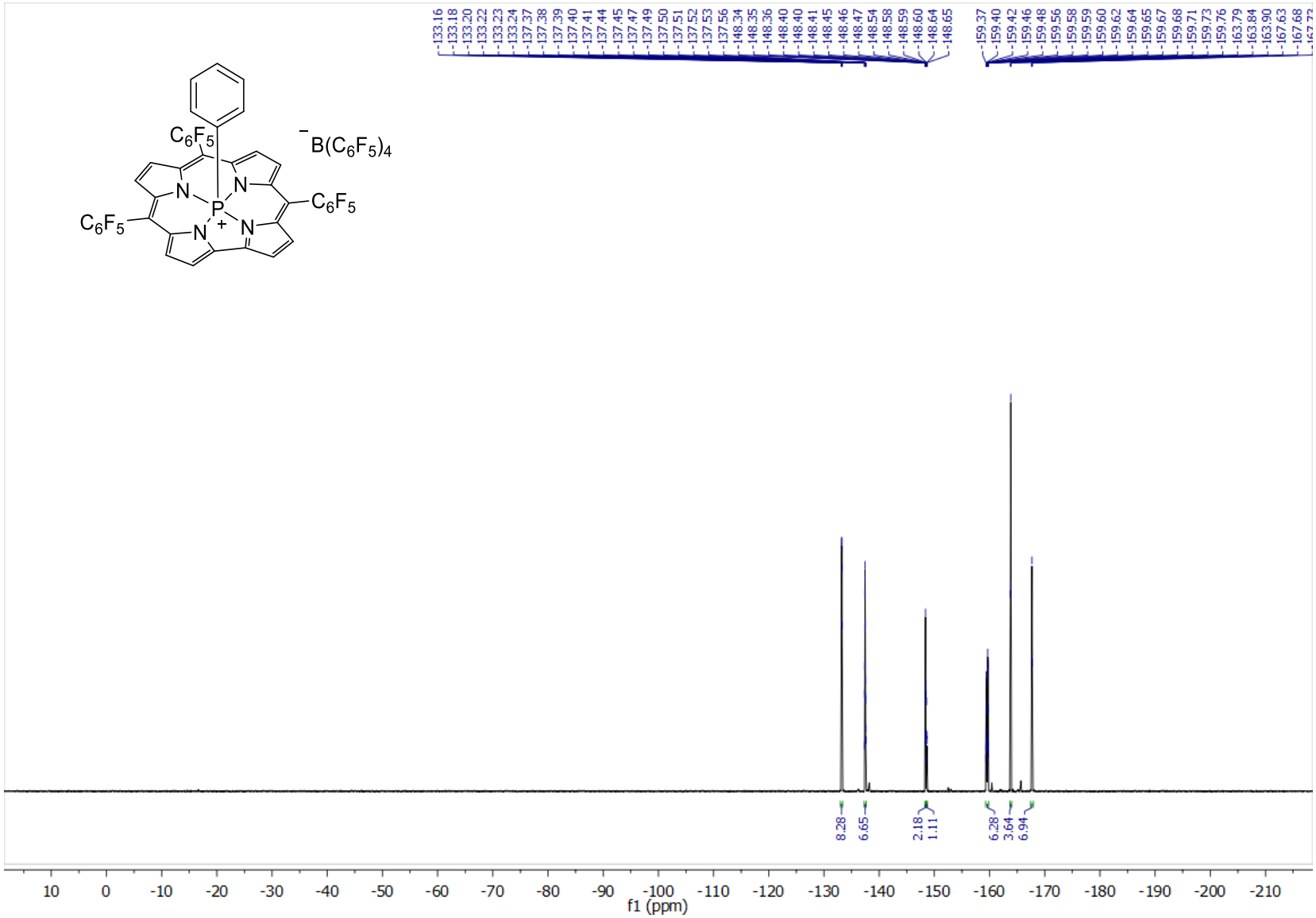


Figure S28. *^{19}F NMR spectrum of **3**$^{+}$.*

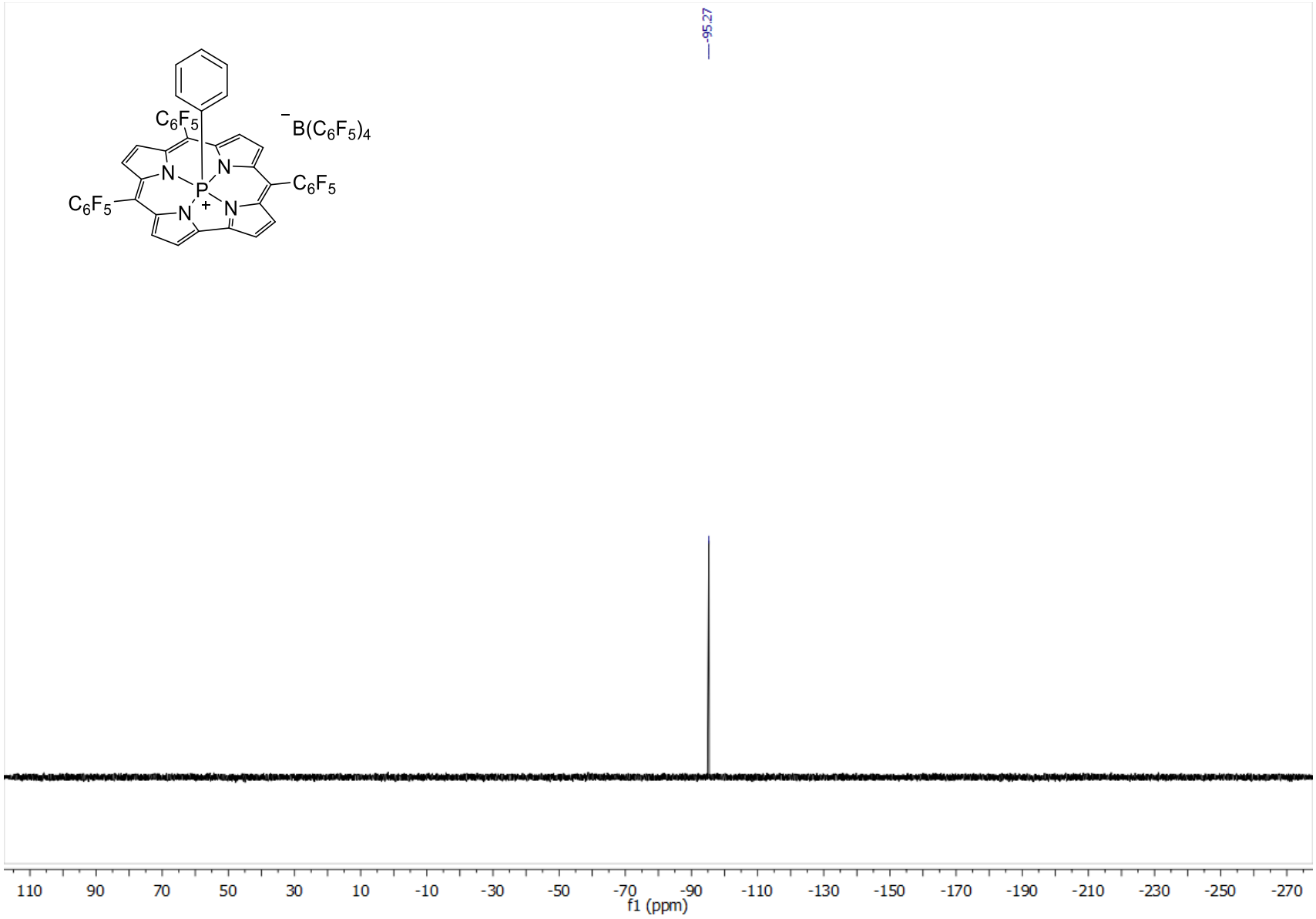


Figure S29. *$^{31}P\{^{1}H\}$ NMR spectrum of* ***3*****$^{+}$**.

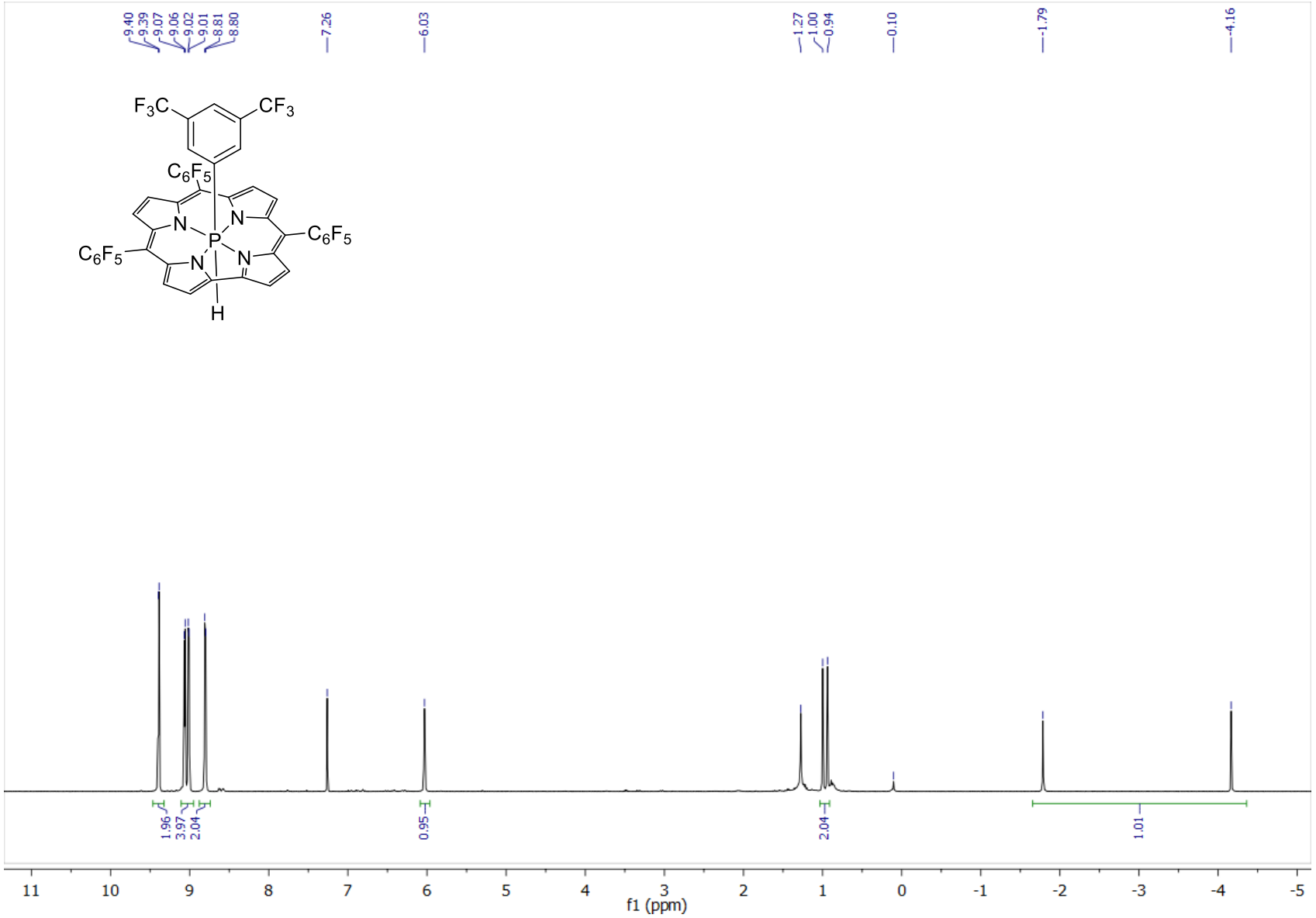


Figure S30. *^{1}H NMR spectrum of **4•H**.*

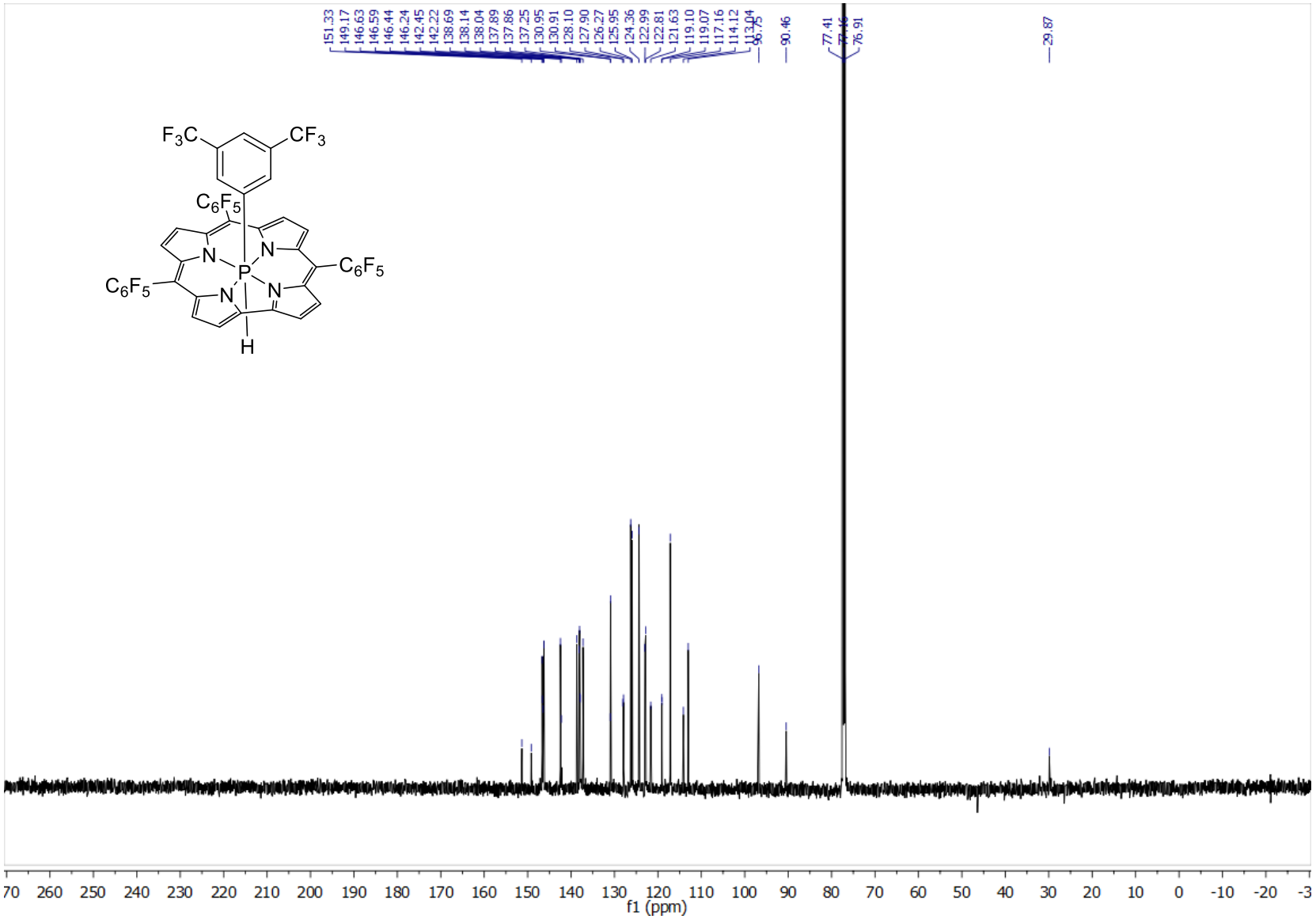


Figure S31. *$^{13}C\{^{1}H,^{19}F\}$ NMR spectrum of* ***4•H****.*

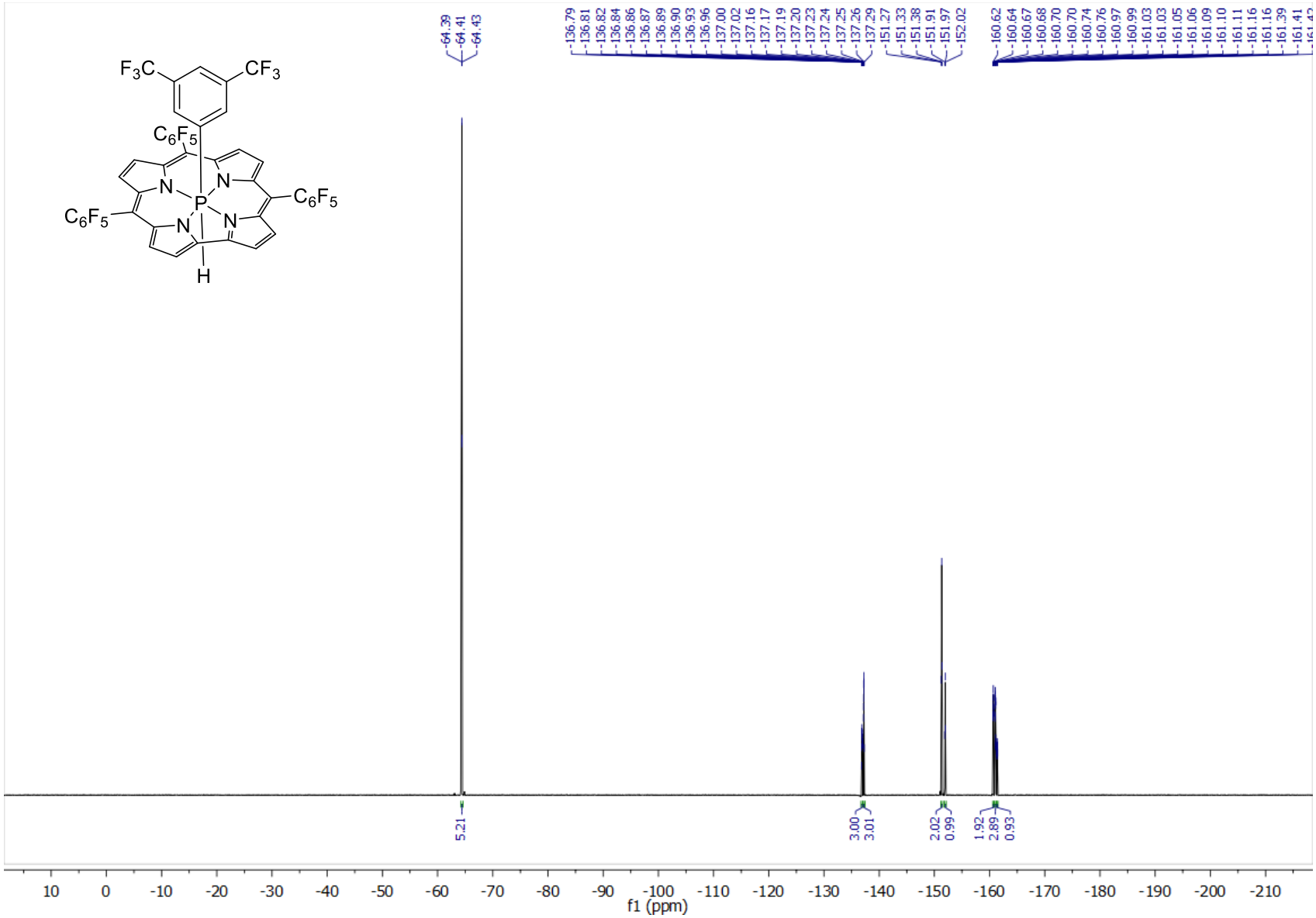


Figure S32. *^{19}F NMR spectrum of **4•H**.*

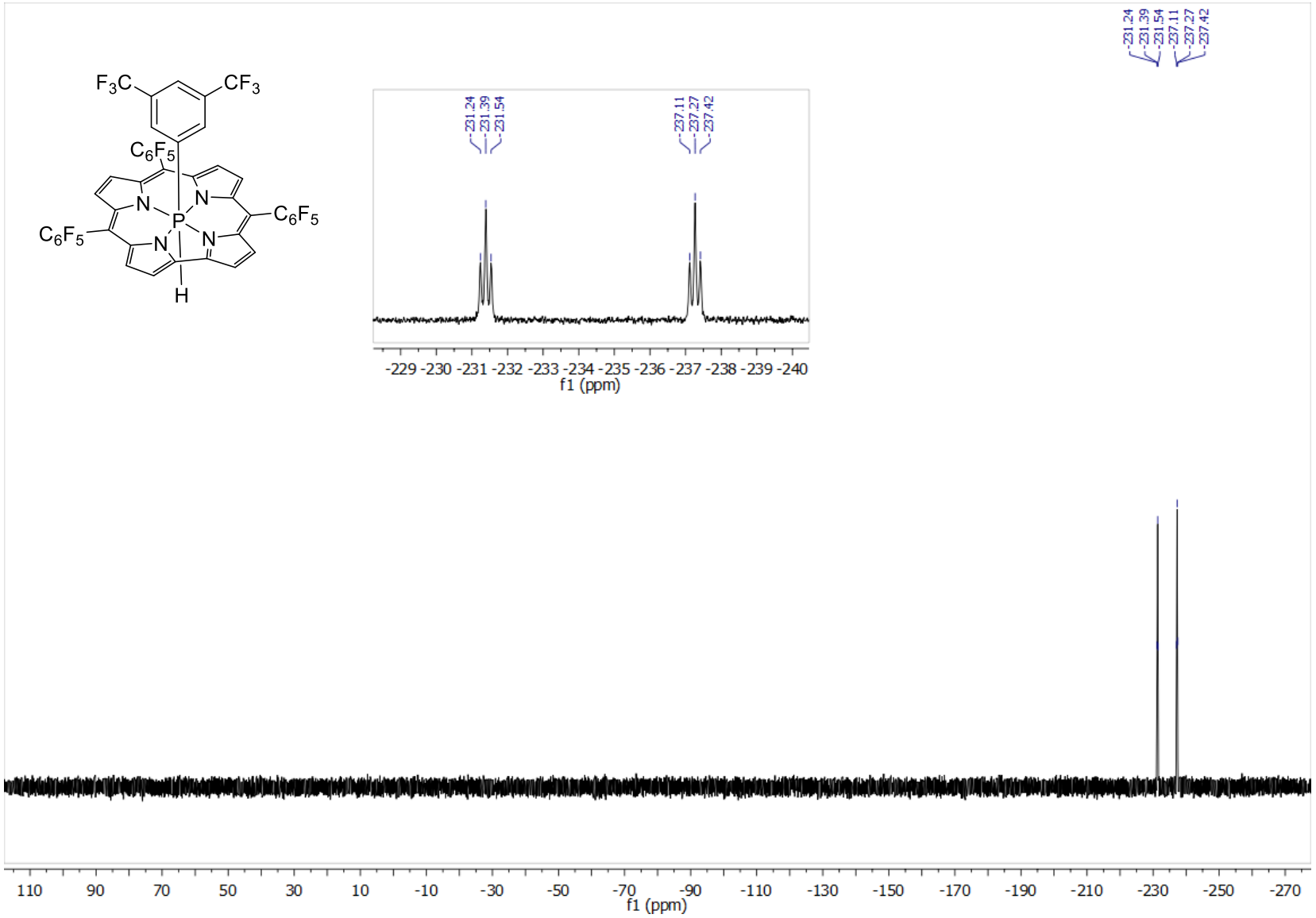


Figure S33. *^{31}P NMR spectrum of **4•H**.*

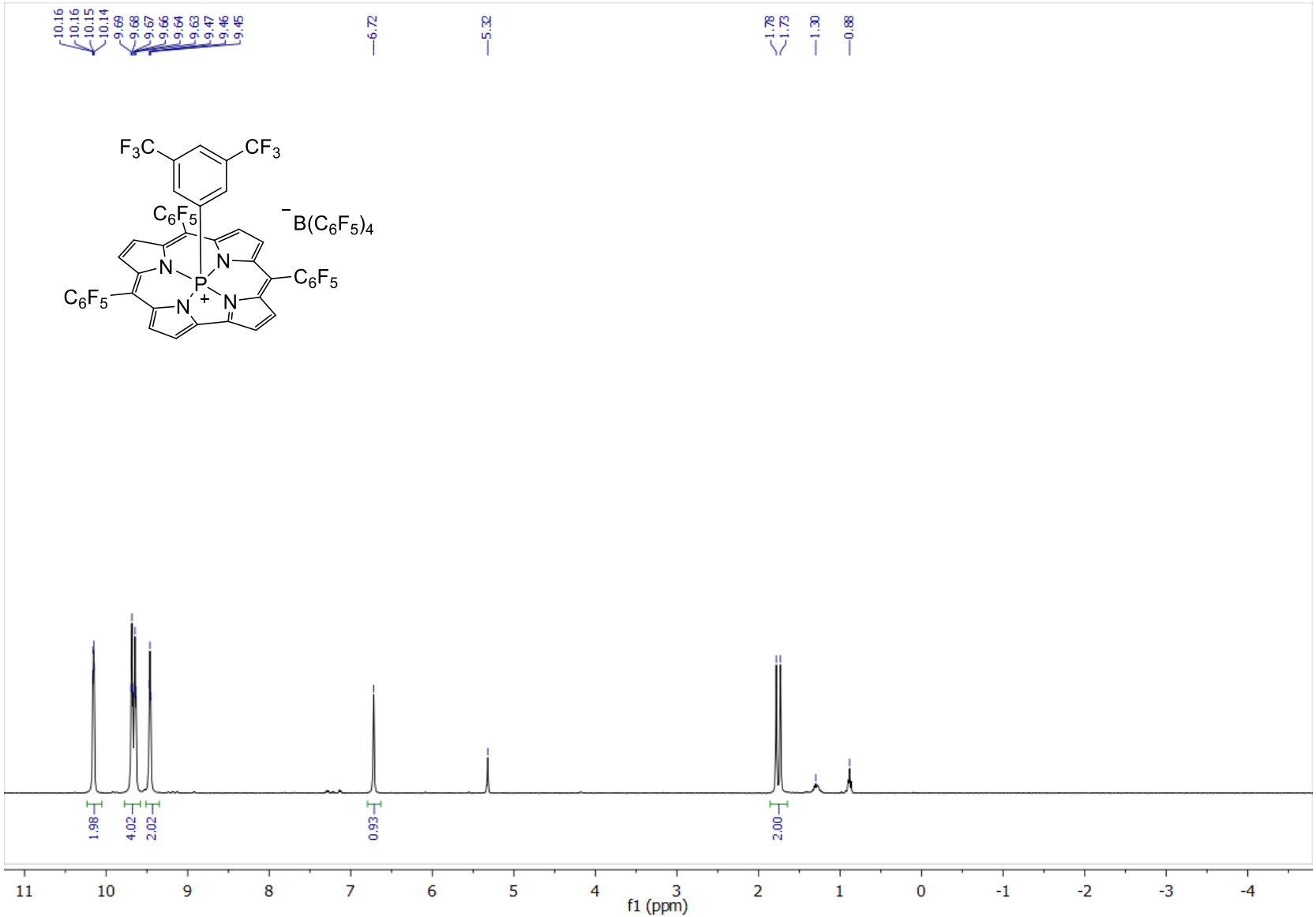


Figure S34. *^{1}H NMR spectrum of* ***4*****$^{+}$**.

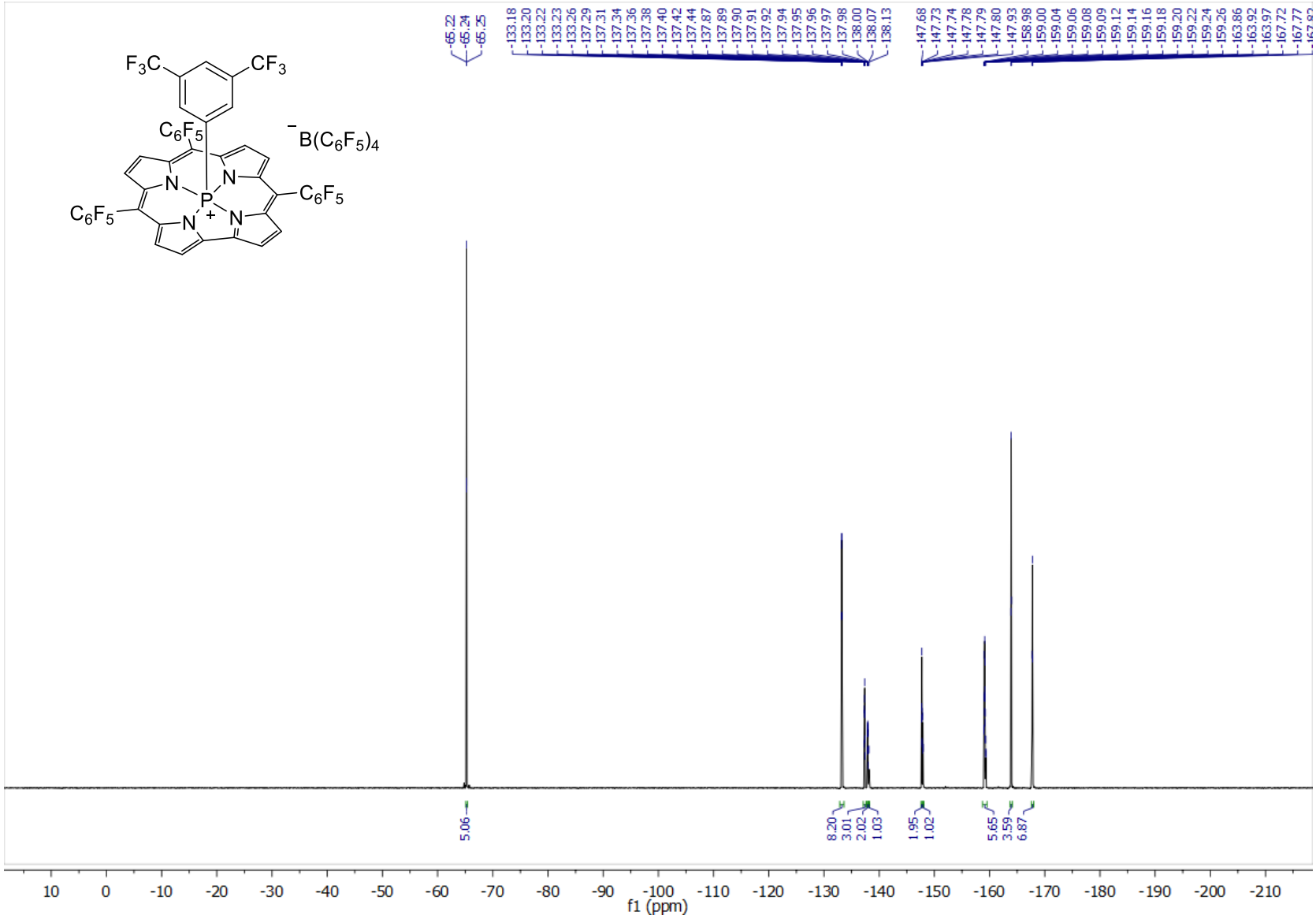


Figure S35. *^{19}F NMR spectrum of **4**$^{+}$.*

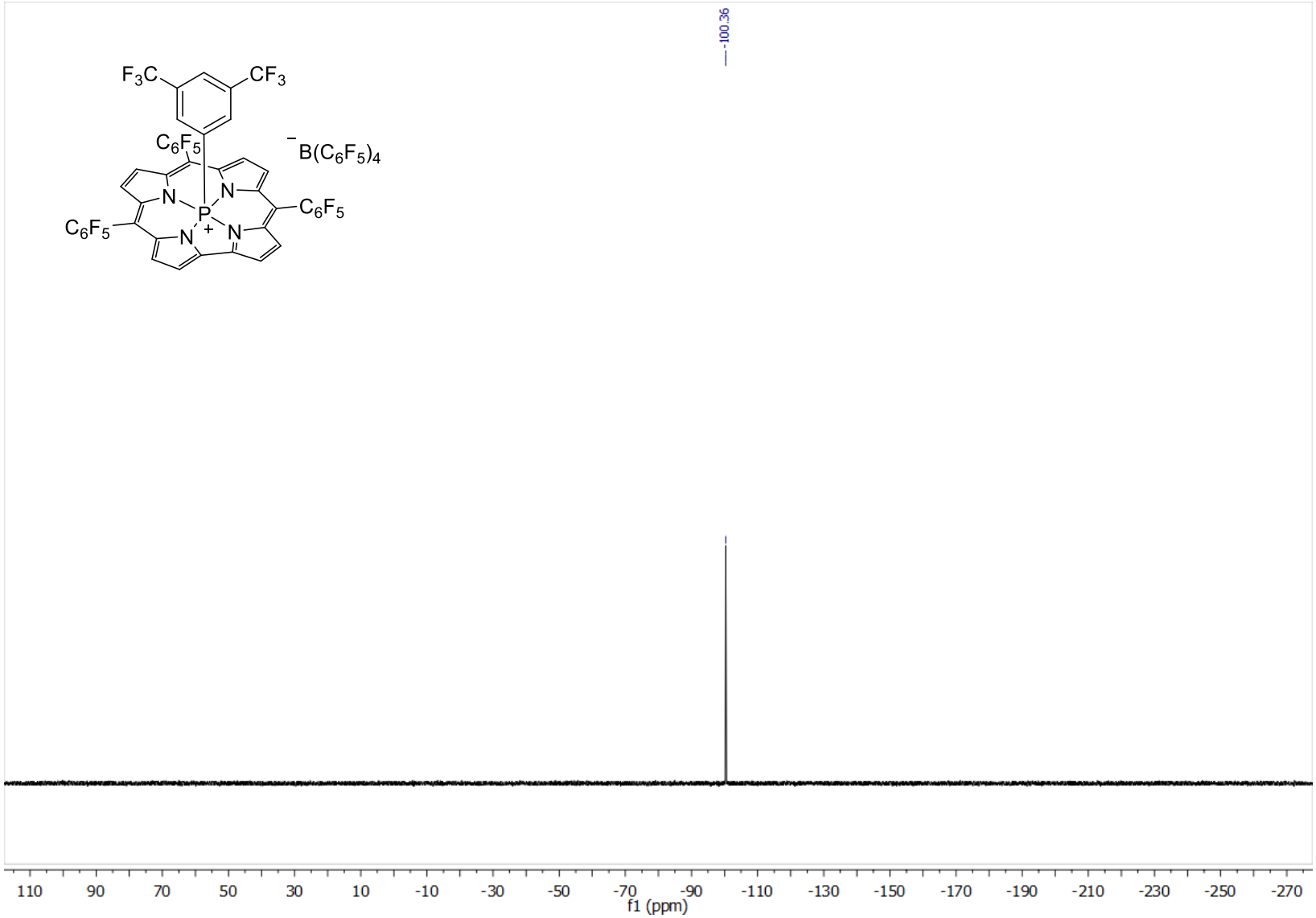


Figure S36. *^{31}P NMR spectrum of* ***4*****$^{+}$***.*

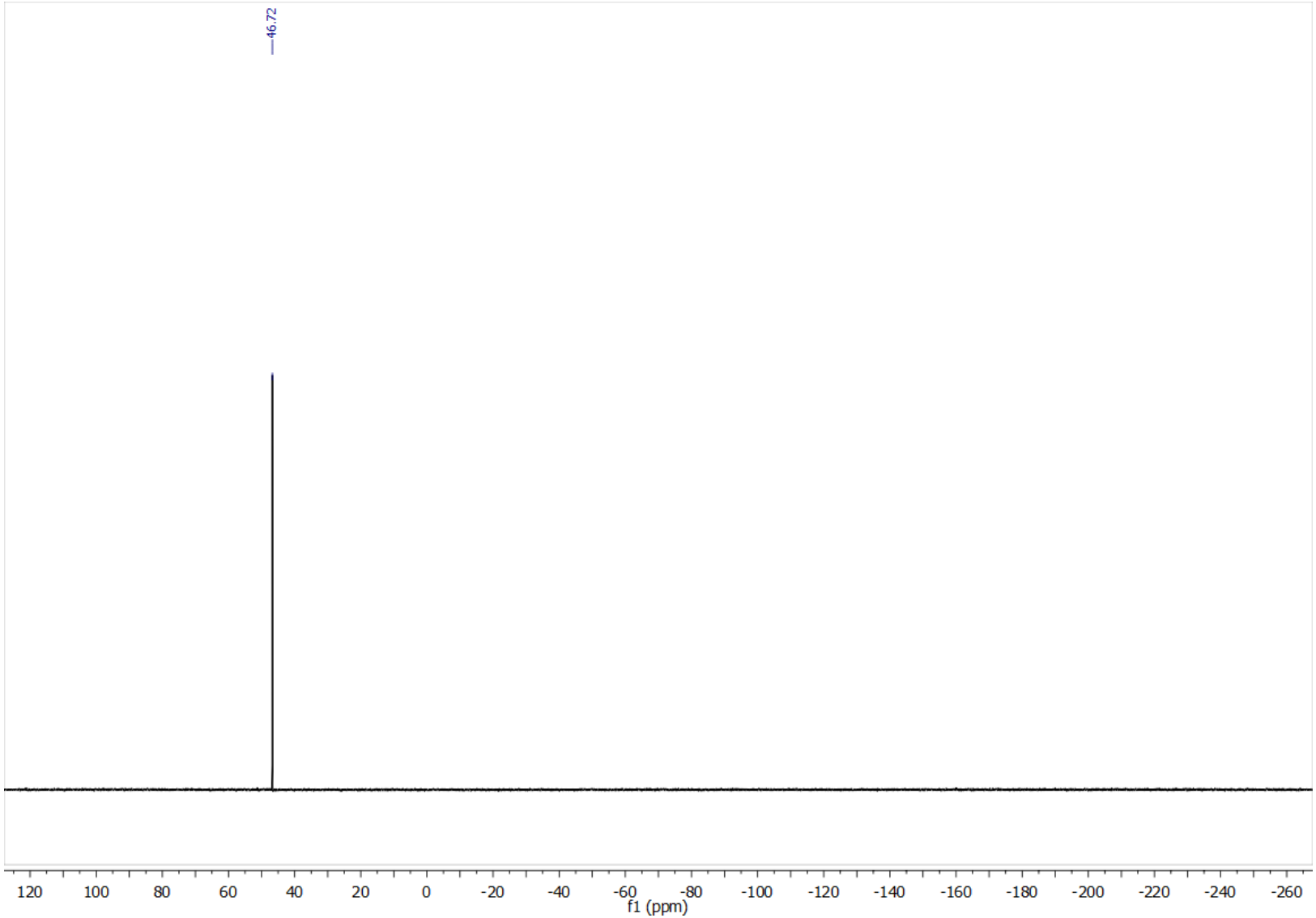


Figure S37. *$^{31}P\{^{1}H\}$ NMR spectrum of tri-*n*-octylphosphine oxide.*

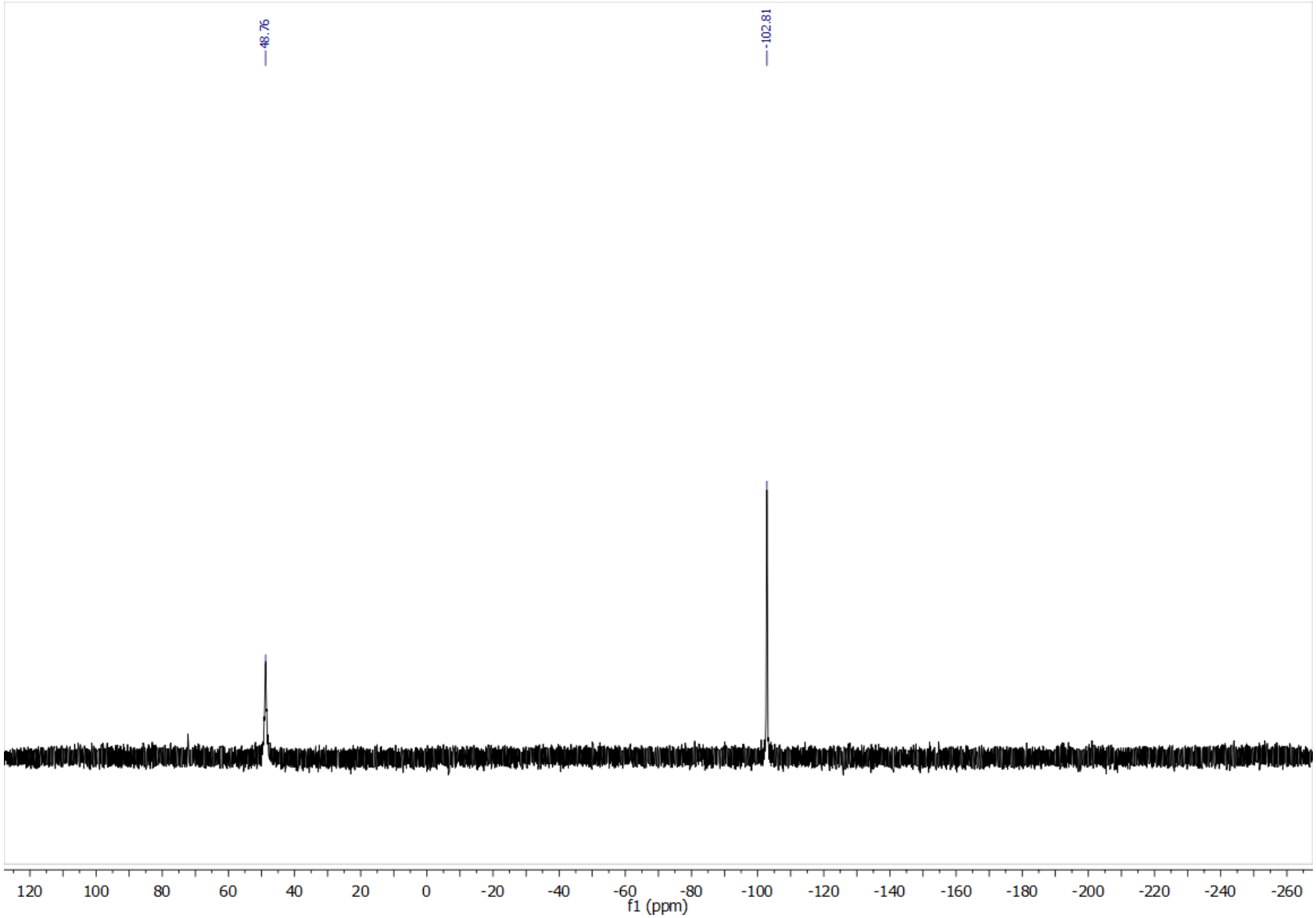


Figure S38. *^{31}P NMR spectrum of the Gutmann-Beckett test for* ***1*****$^{+}$***.*

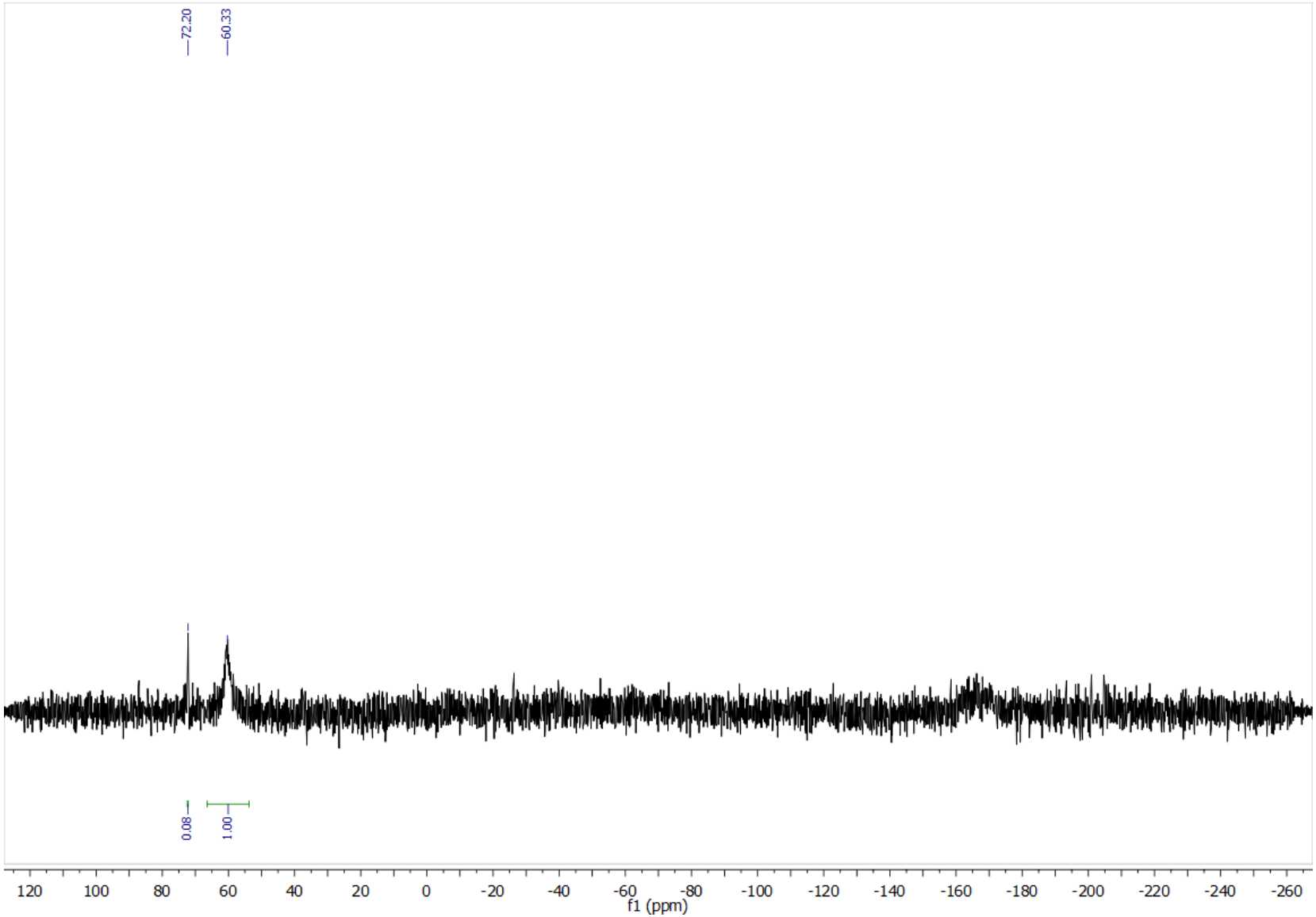


Figure S39. *^{31}P NMR spectrum of the Gutmann-Beckett test for **2**$^{+}$. The minor resonance at δ 72.2 ppm is attributed to a slow reaction of (n-octyl)$_3$PO with B(C$_6$F$_5$)$_4^-$.*

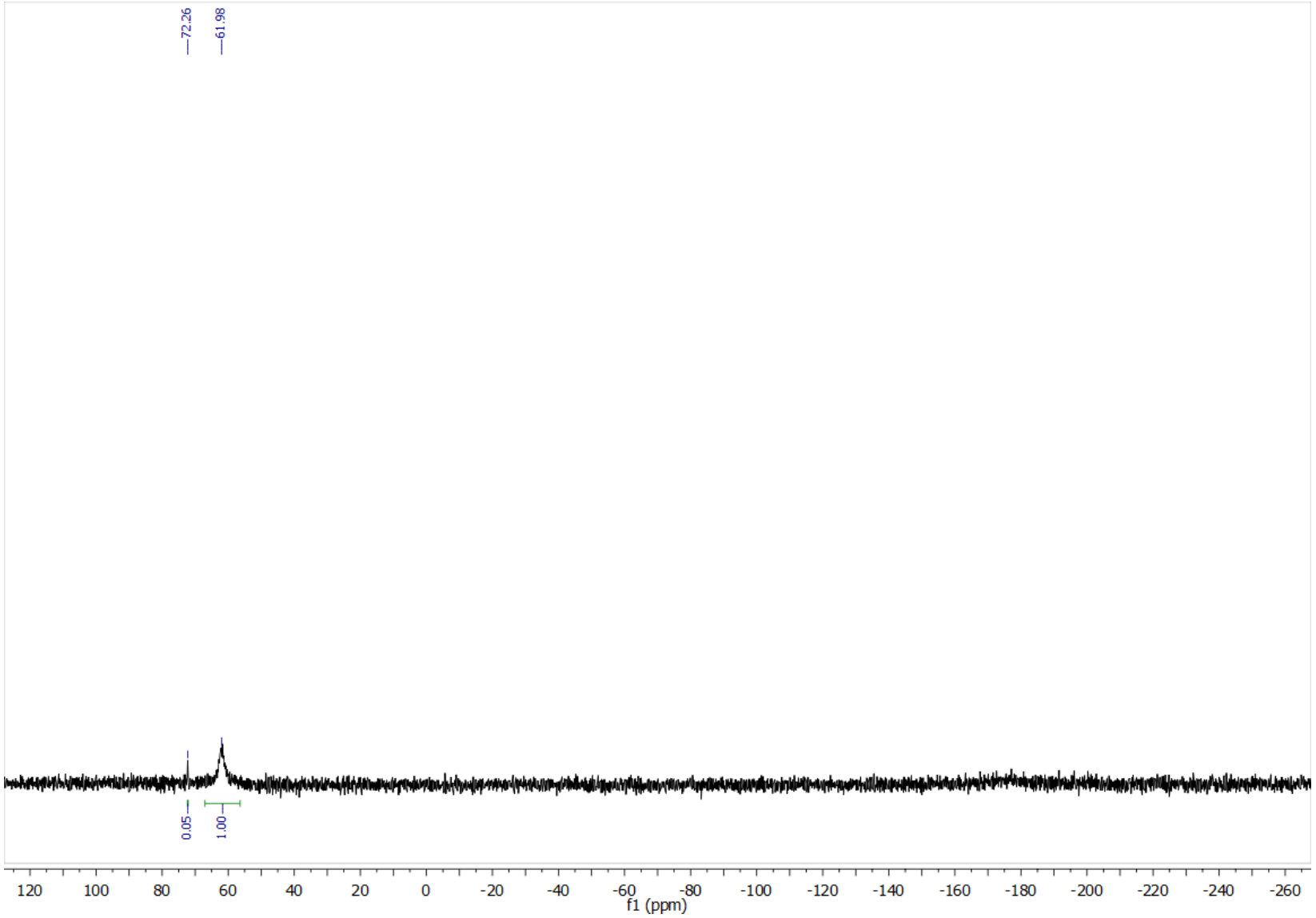


Figure S40. *^{31}P NMR spectrum of the Gutmann-Beckett test for **3**$^{+}$. The minor resonance at δ 72.2 ppm is attributed to a slow reaction of Oct_3PO with $B(C_6F_5)_4^-$.*

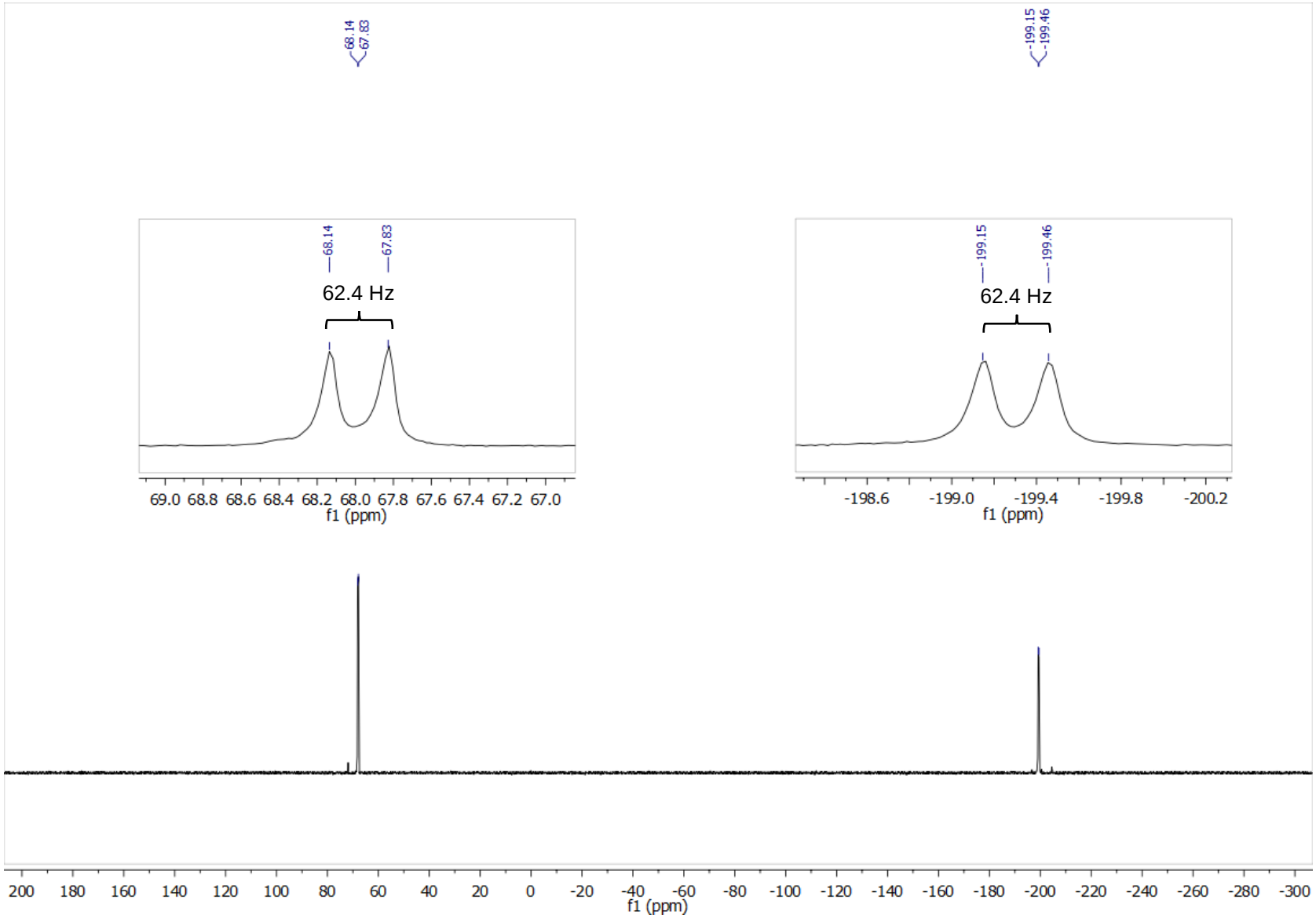


Figure S41. *^{31}P NMR spectrum of the Gutmann-Beckett test for **4**$^{+}$. $^{2}J_{P\text{-}P}$ coupling is observed between the two P centers.*

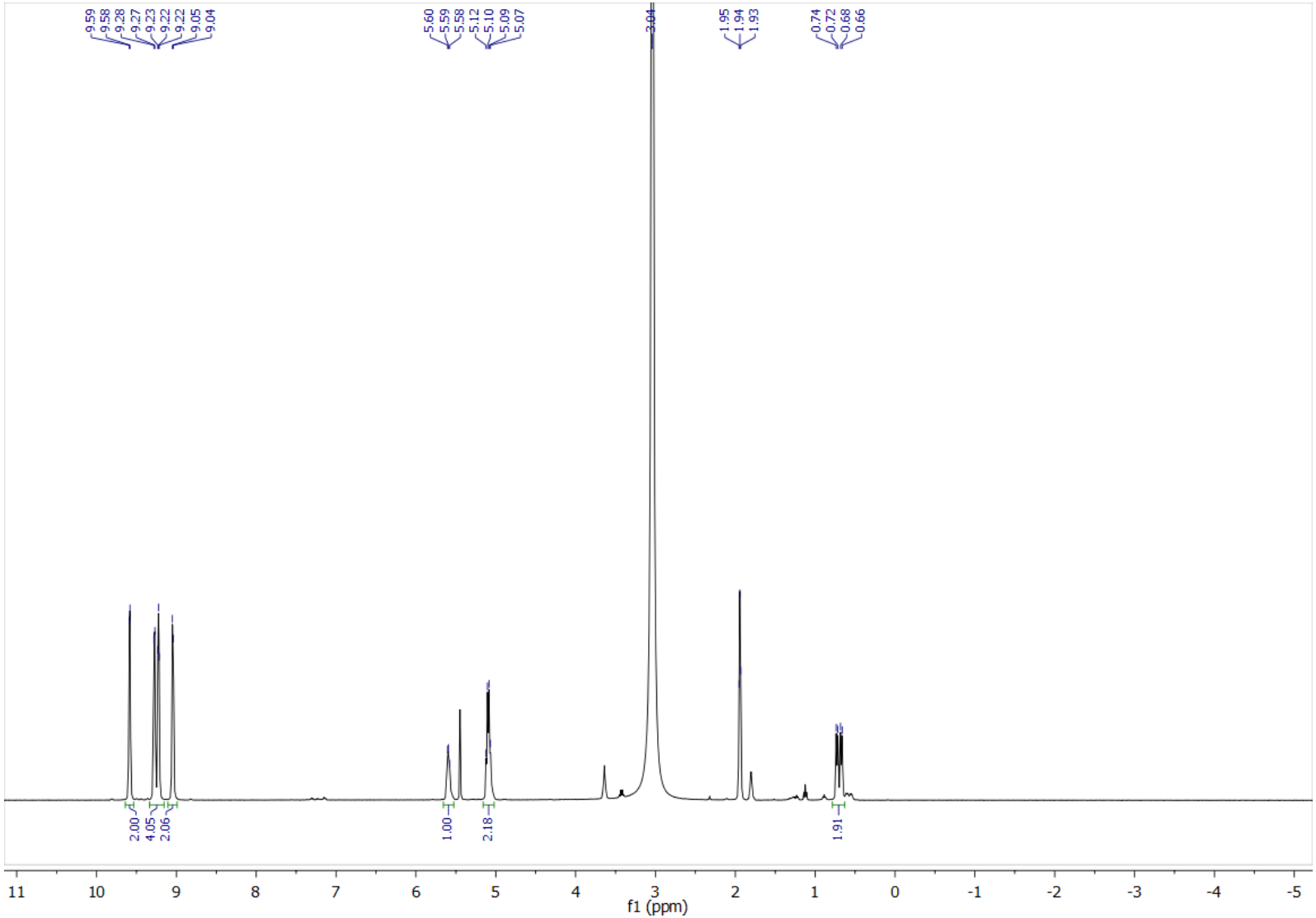


Figure S42. *^{1}H NMR spectrum of **3**$^{+}$ in CD_3CN with 10 equiv H_2O.*

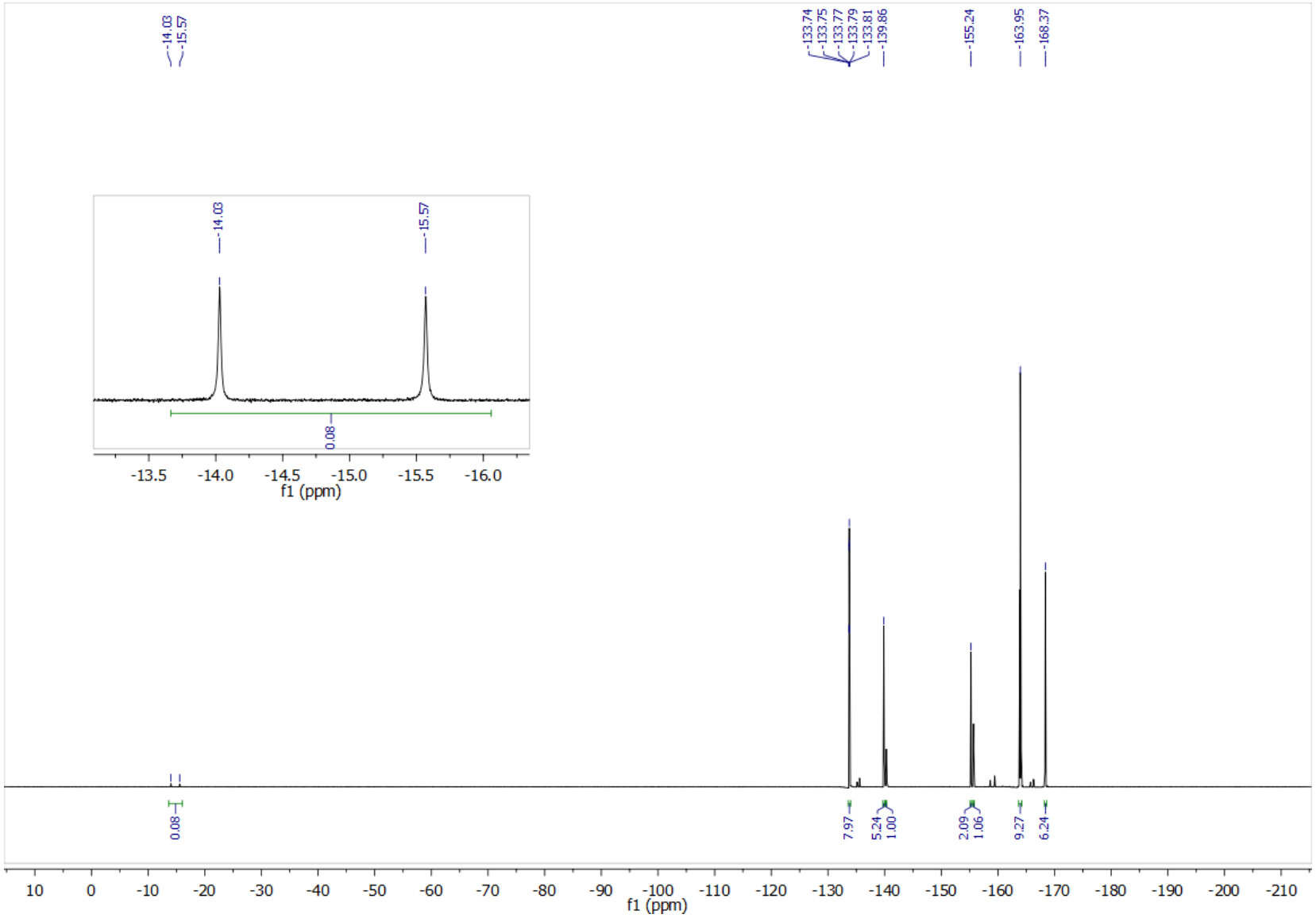


Figure S43. *^{19}F NMR spectrum of **3**$^{+}$ in CD_3CN with 10 equiv H_2O.*

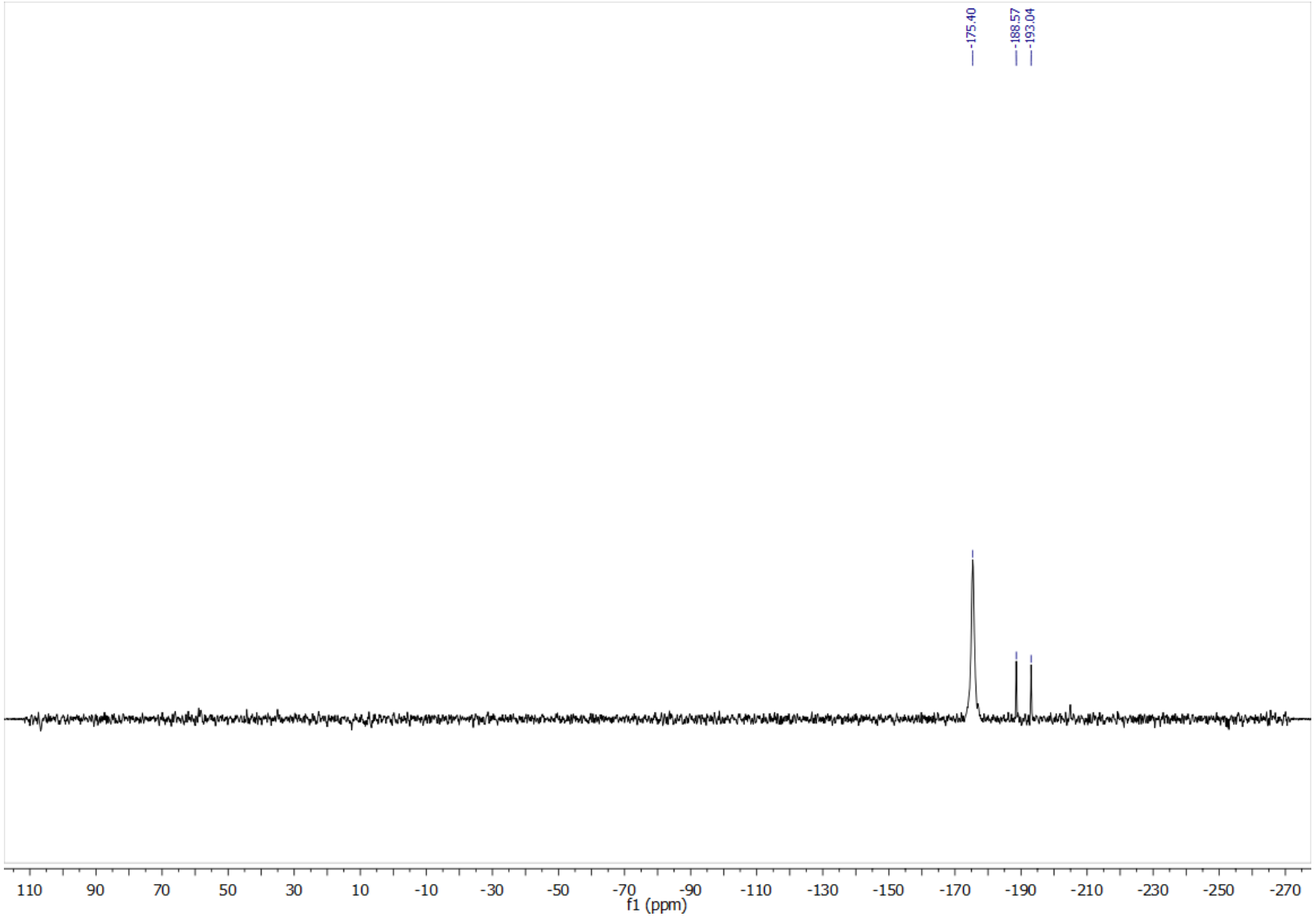


Figure S44. *$^{31}P\{^{1}H\}$ NMR spectrum of **3**$^{+}$ in CD_3CN with 10 equiv H_2O.*

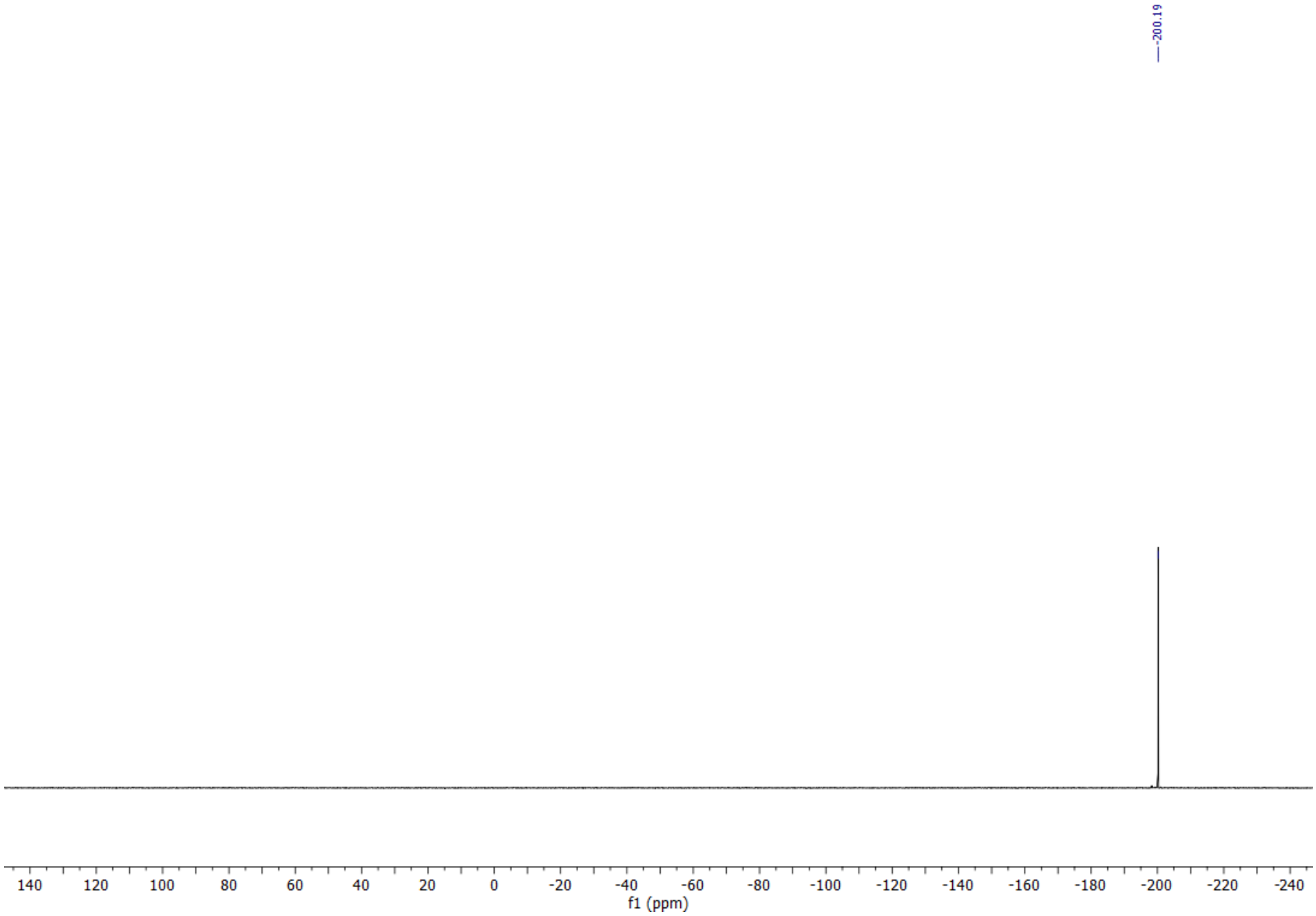


Figure S45. *$^{31}P\{^{1}H\}$ NMR spectrum of **3**$^{+}$ with water and magnesium sulfate.*

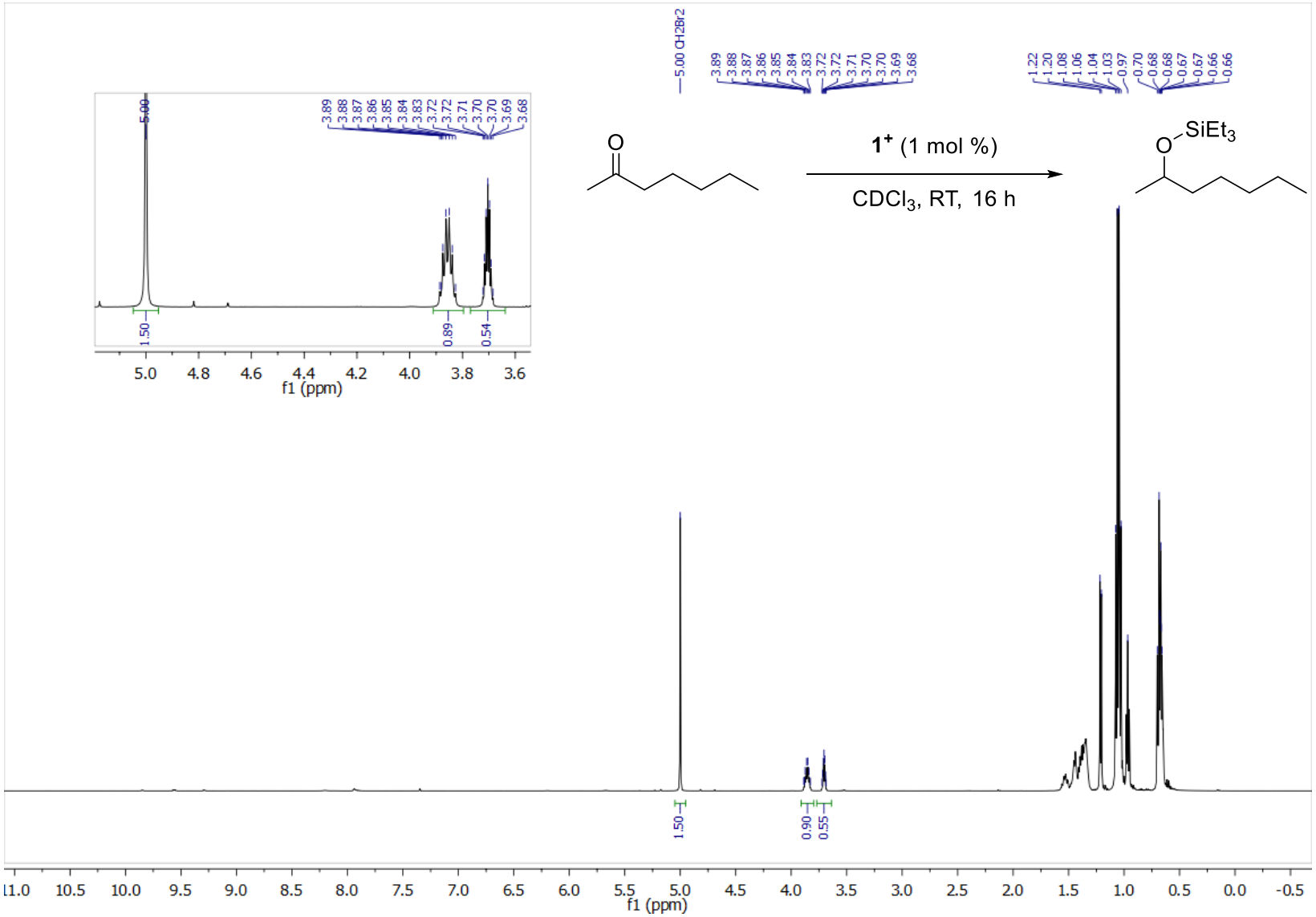


Figure S46. *^{1}H NMR spectrum of the 2-heptanone hydrosilylation reaction mixture. Excess $HSiEt_3$ is visible at δ 3.70.*

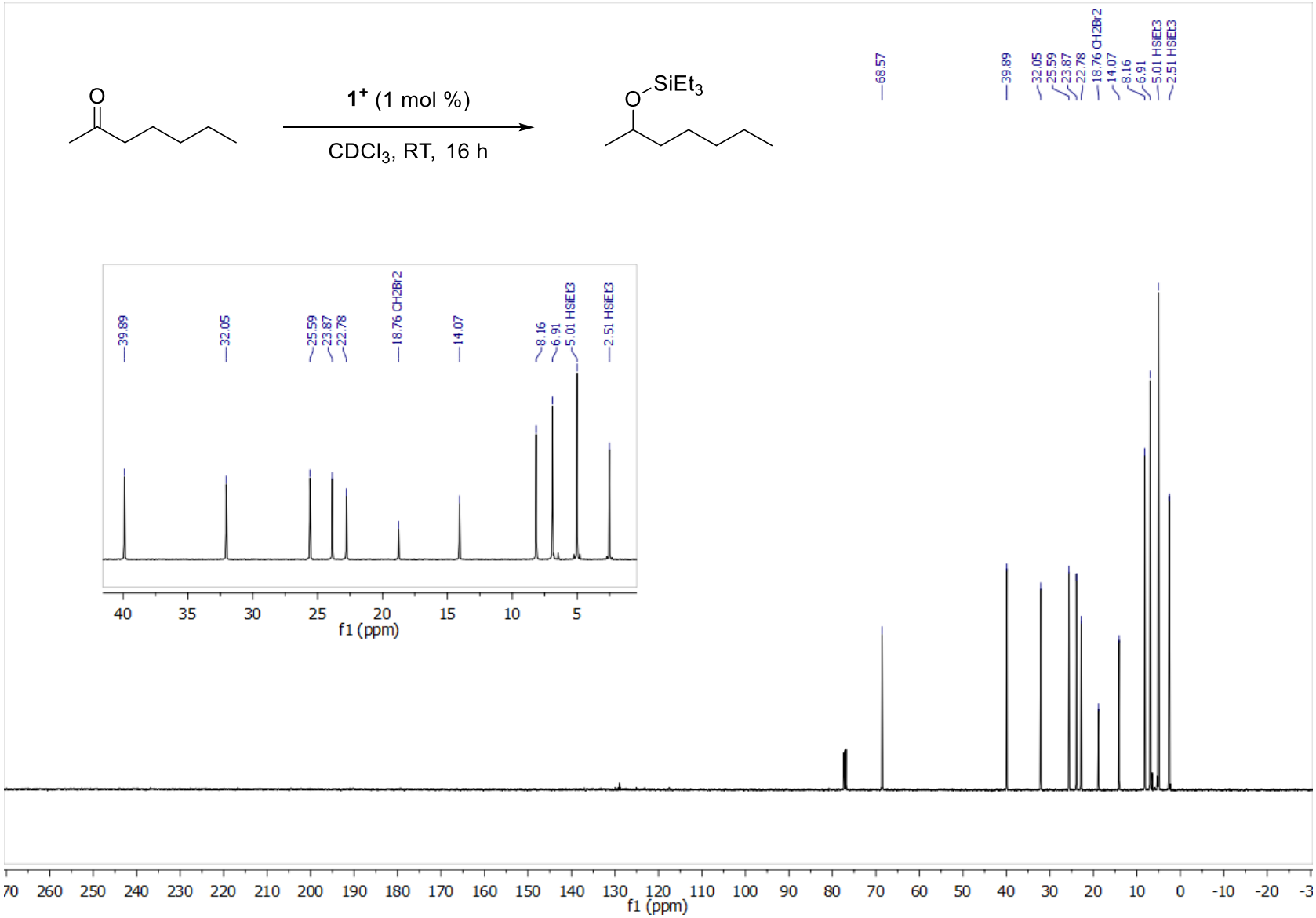


Figure S47. *$^{13}C\{^{1}H\}$ NMR spectrum of the 2-heptanone hydrosilylation reaction mixture.*

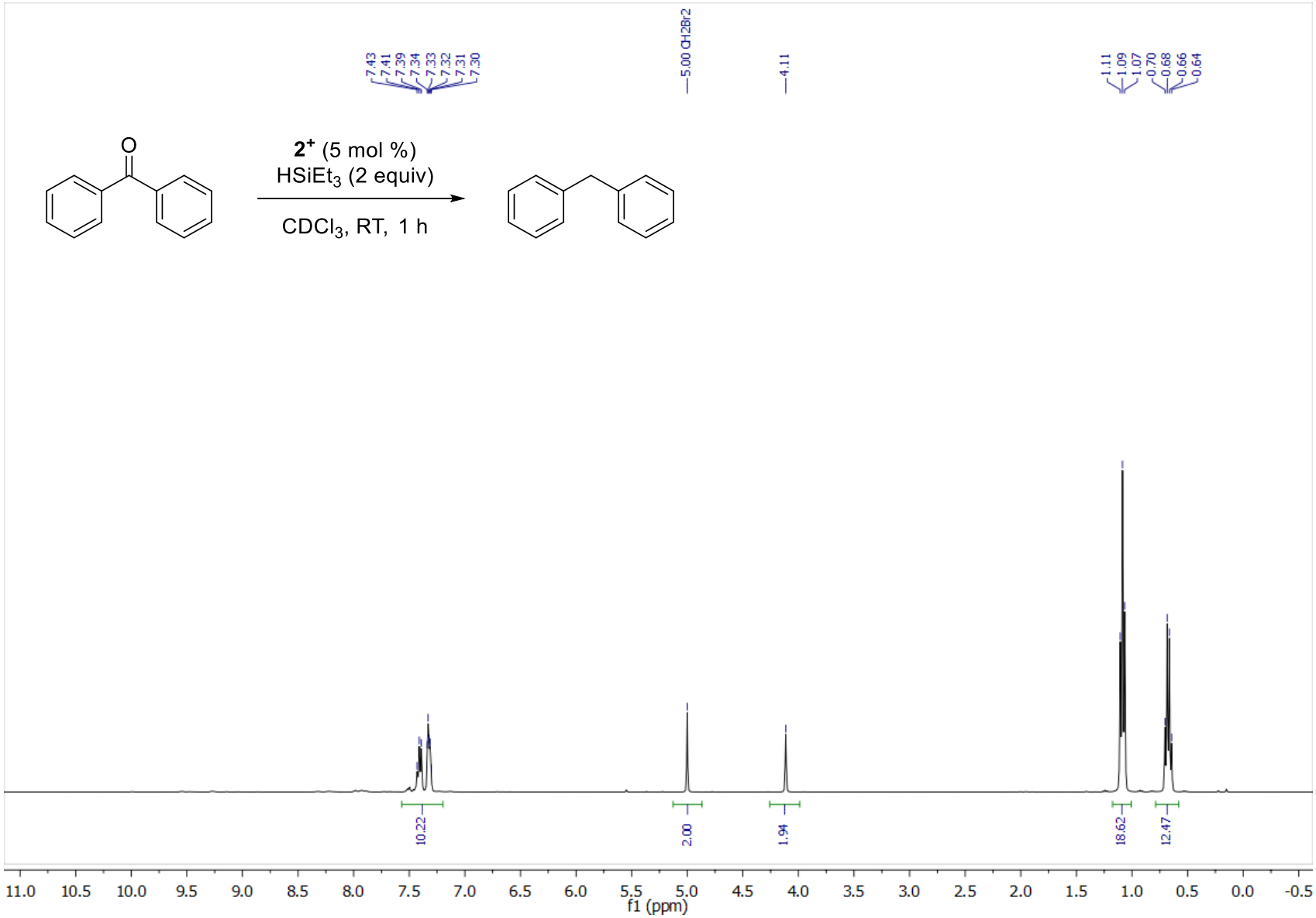


Figure S48. *^{1}H NMR spectrum of the benzophenone deoxygenation reaction mixture.*

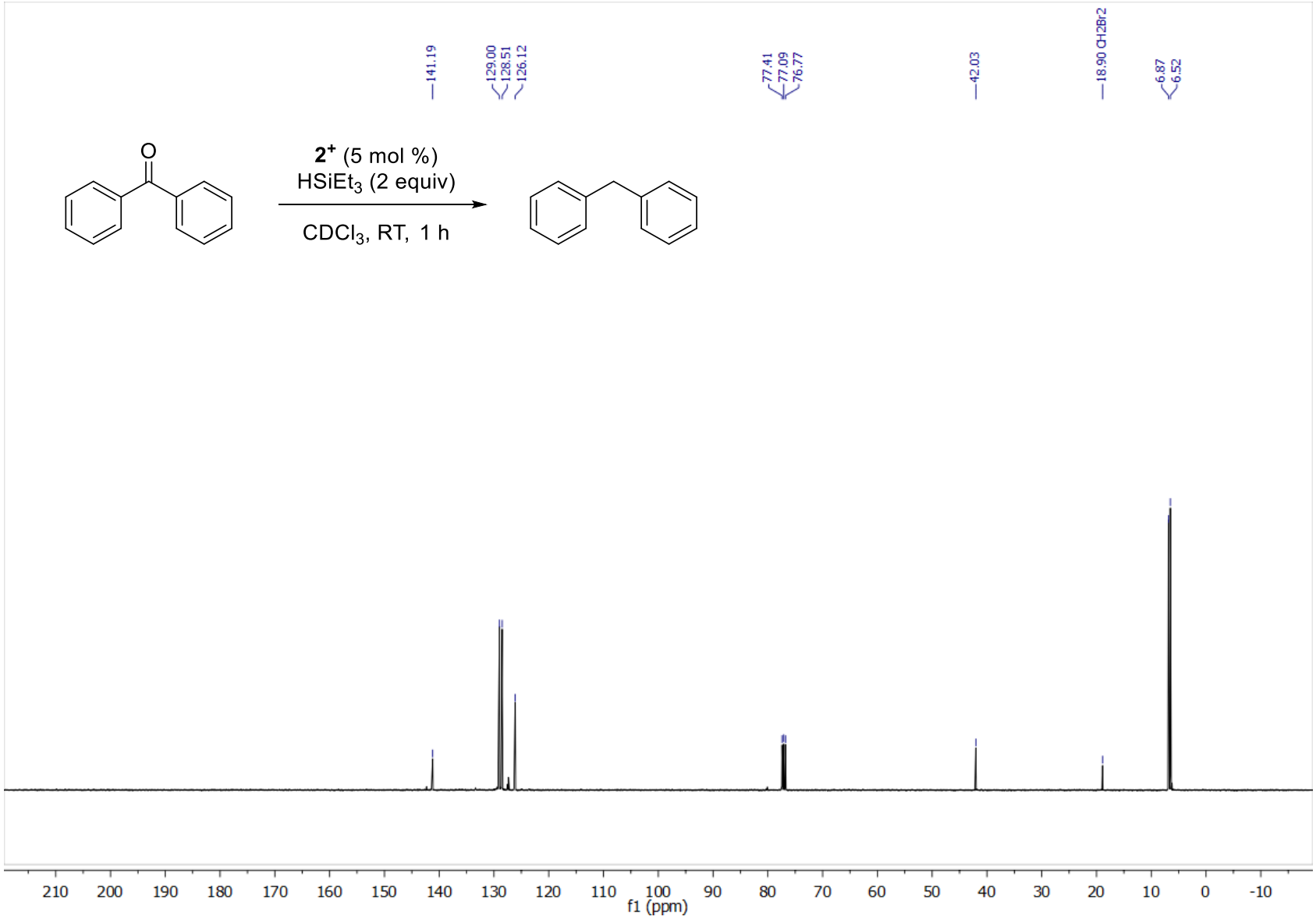


Figure S49. *$^{13}C\{^{1}H\}$ NMR spectrum of the benzophenone deoxygenation reaction mixture.*

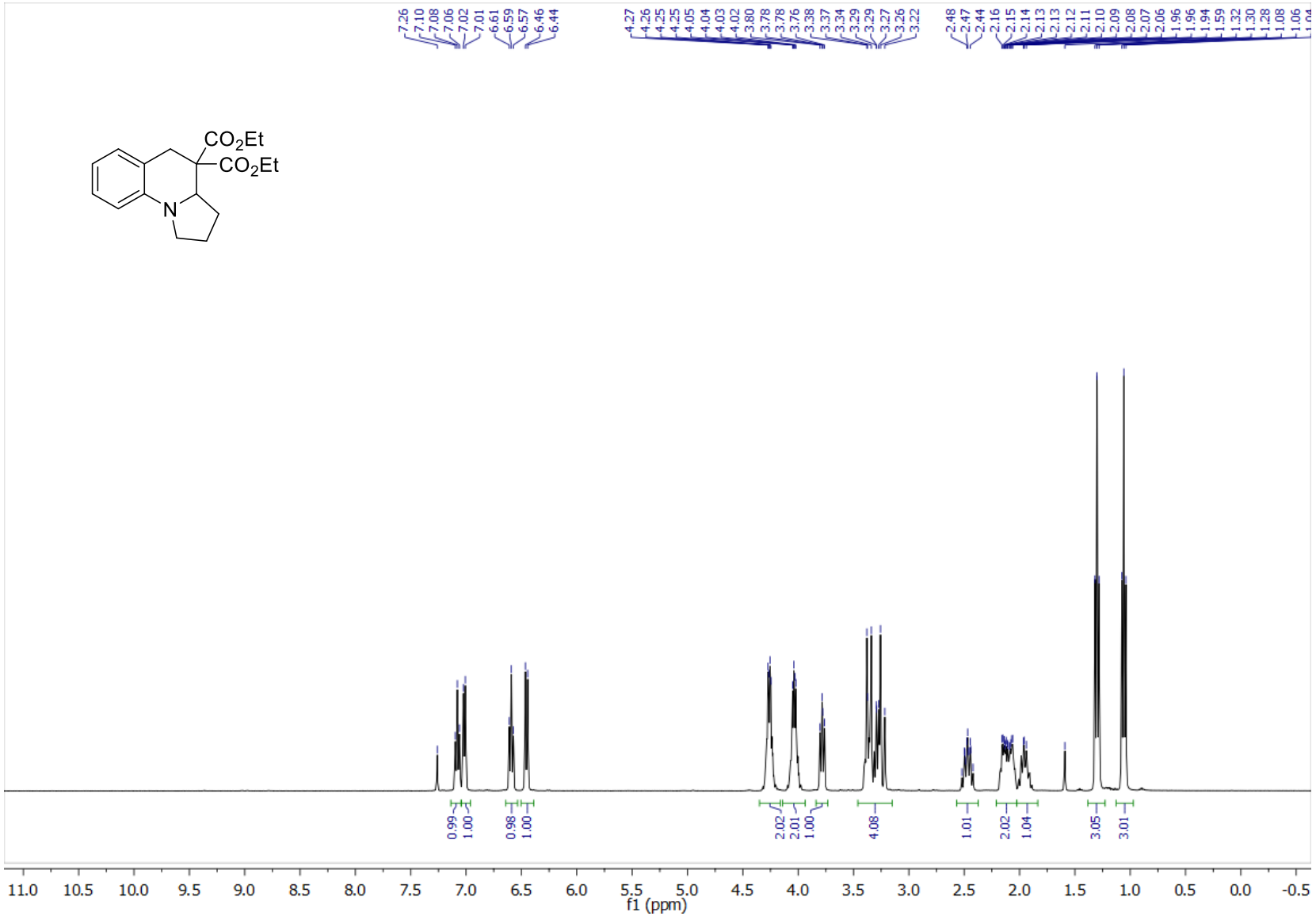


Figure S50. *^{1}H NMR spectrum of diethyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate.*

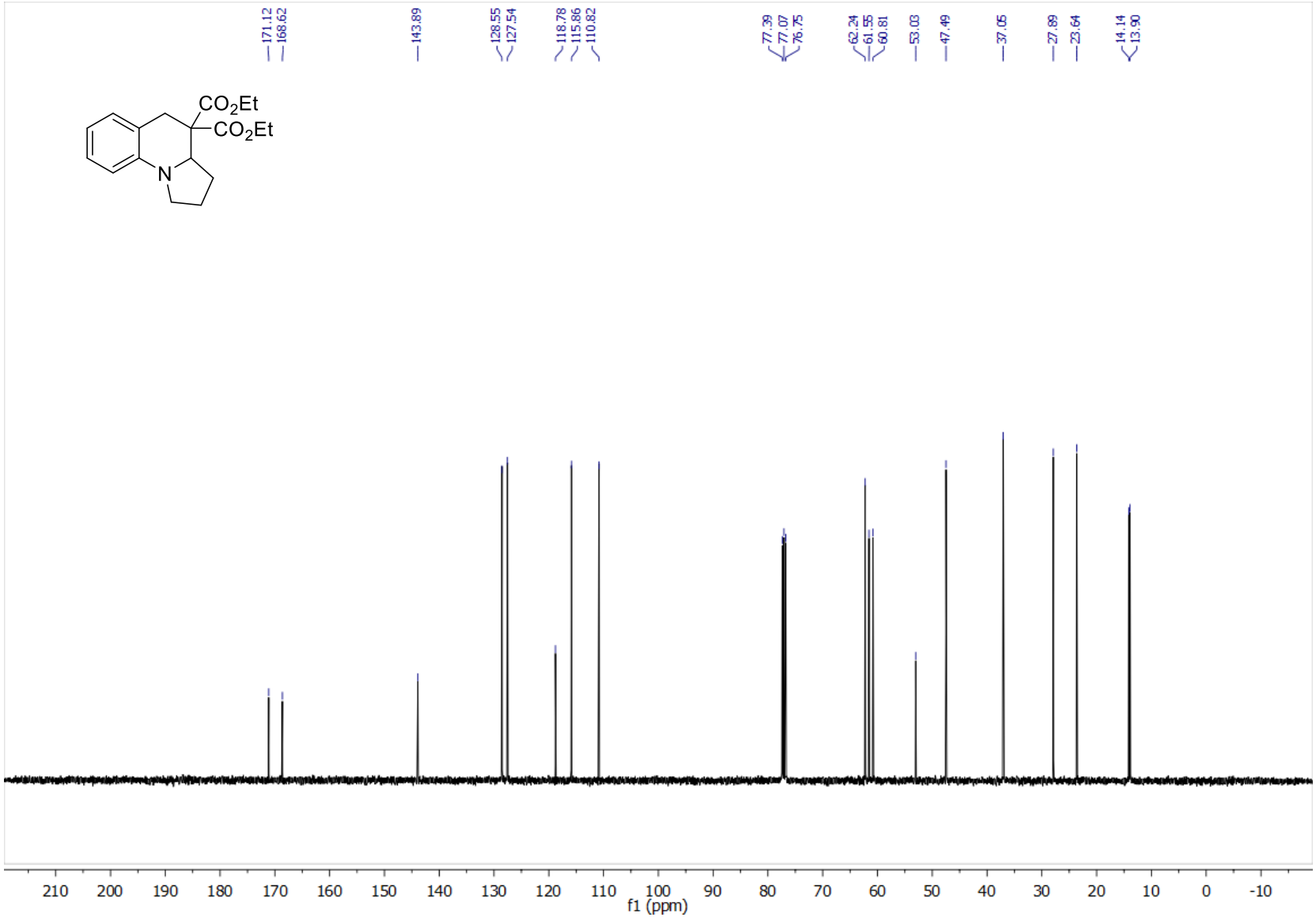


Figure S51. *$^{13}C\{^{1}H\}$ NMR spectrum of diethyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate.*

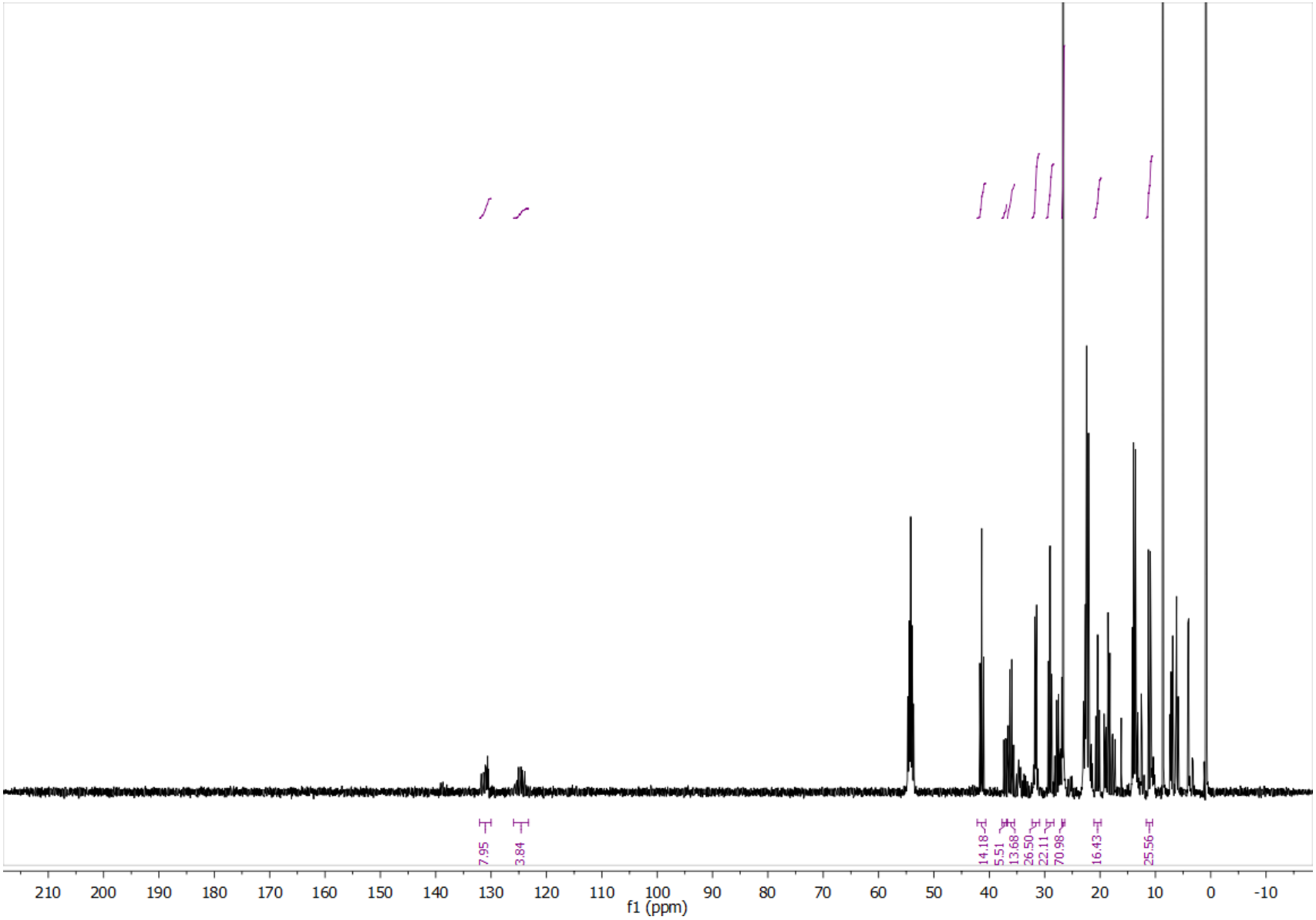


Figure S52. *Full $^{13}C\{^{1}H\}$ NMR spectrum of the $^{13}C_6$-D-glucose deoxygenation reaction mixture. Note that C–C coupling is observed.*

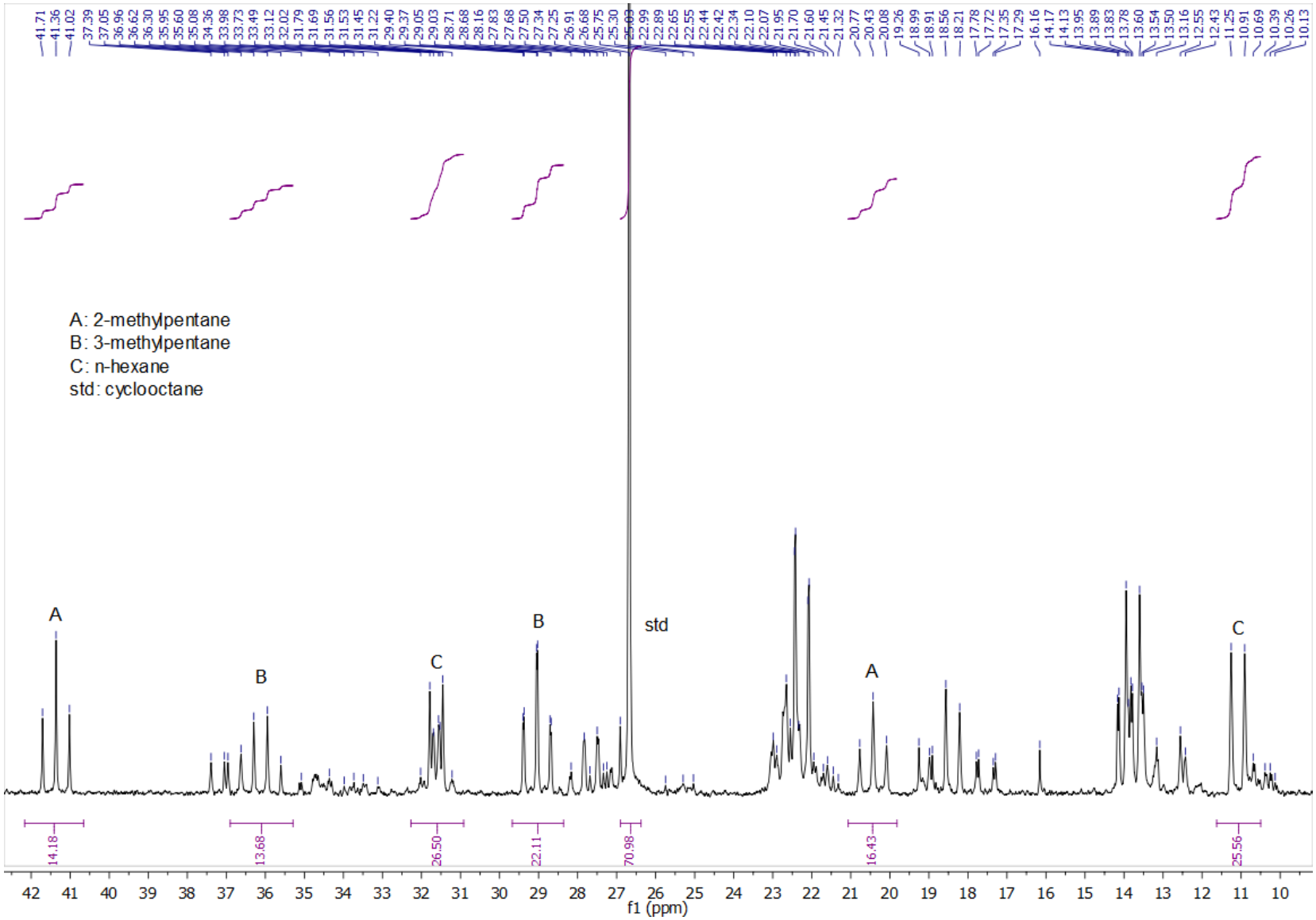


Figure S53. *Aliphatic region of the above $^{13}C\{^{1}H\}$ NMR spectrum of the $^{13}C_6$-D-glucose deoxygenation reaction. Note that C–C coupling is observed.*

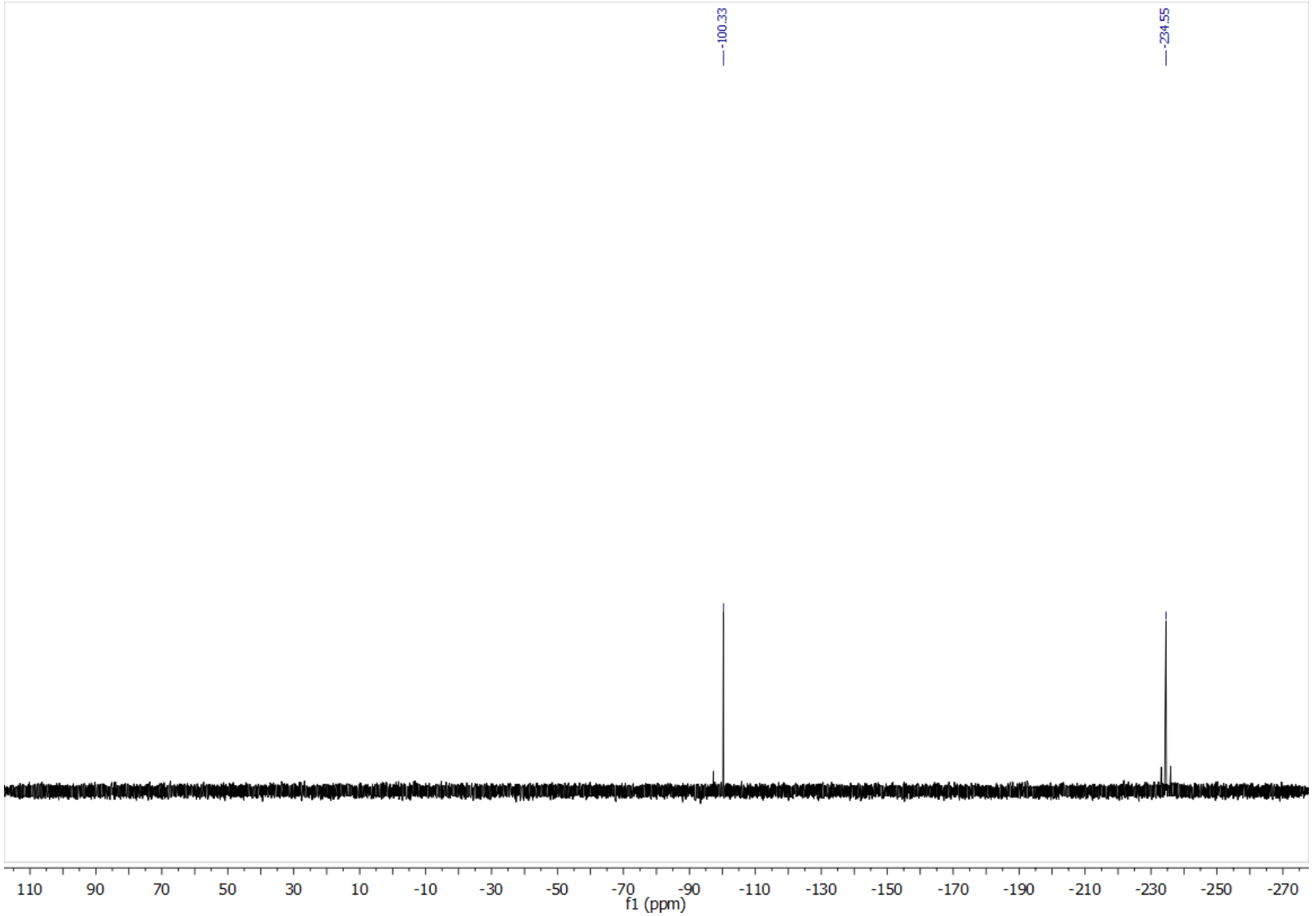


Figure S54. *$^{31}P\{^{1}H\}$ NMR spectrum of the glucose deoxygenation reaction after 1 d.*

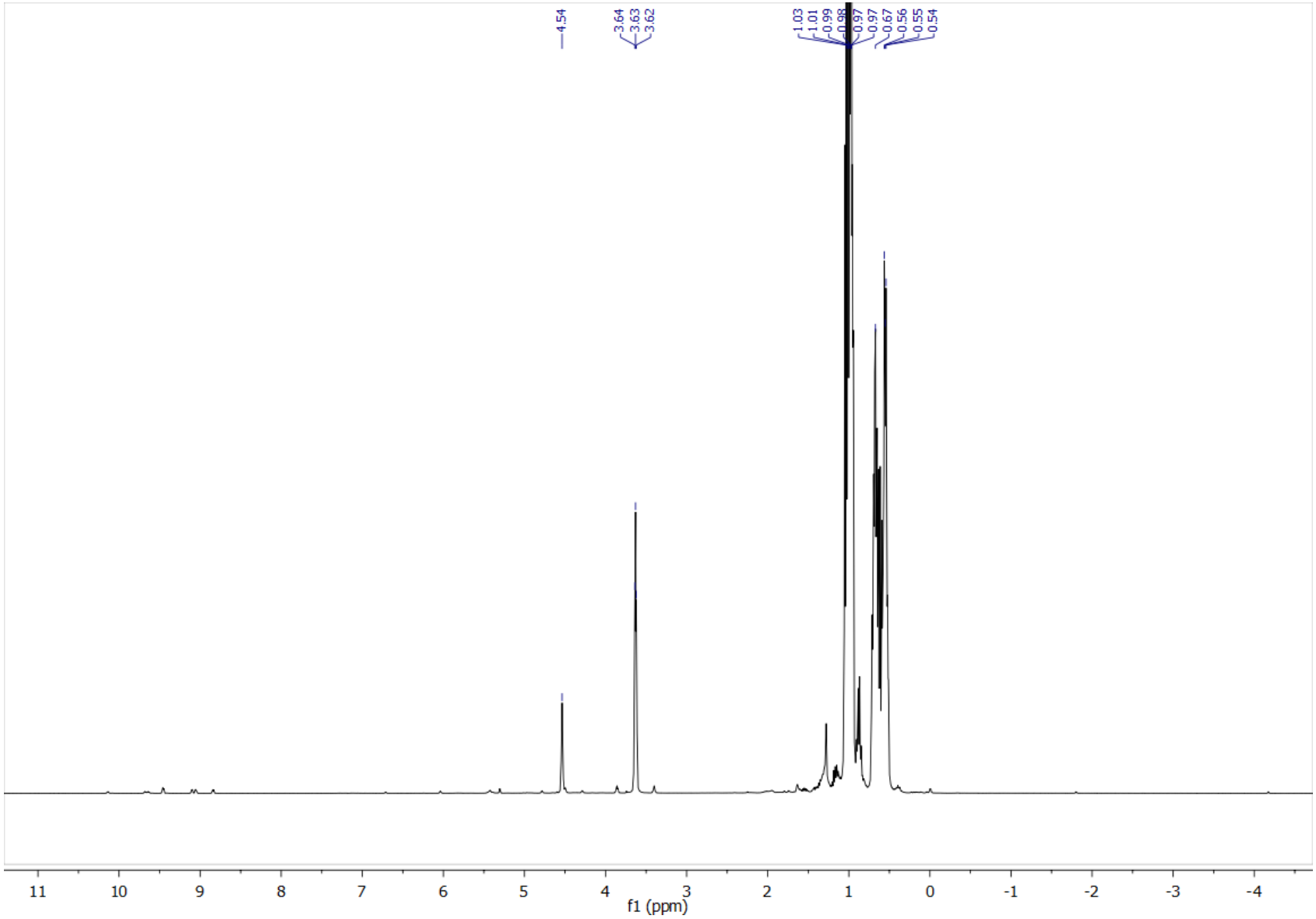


Figure S55. *^{1}H NMR spectrum of the glucose deoxygenation reaction after 1 d.*

8. UV-VIS spectra

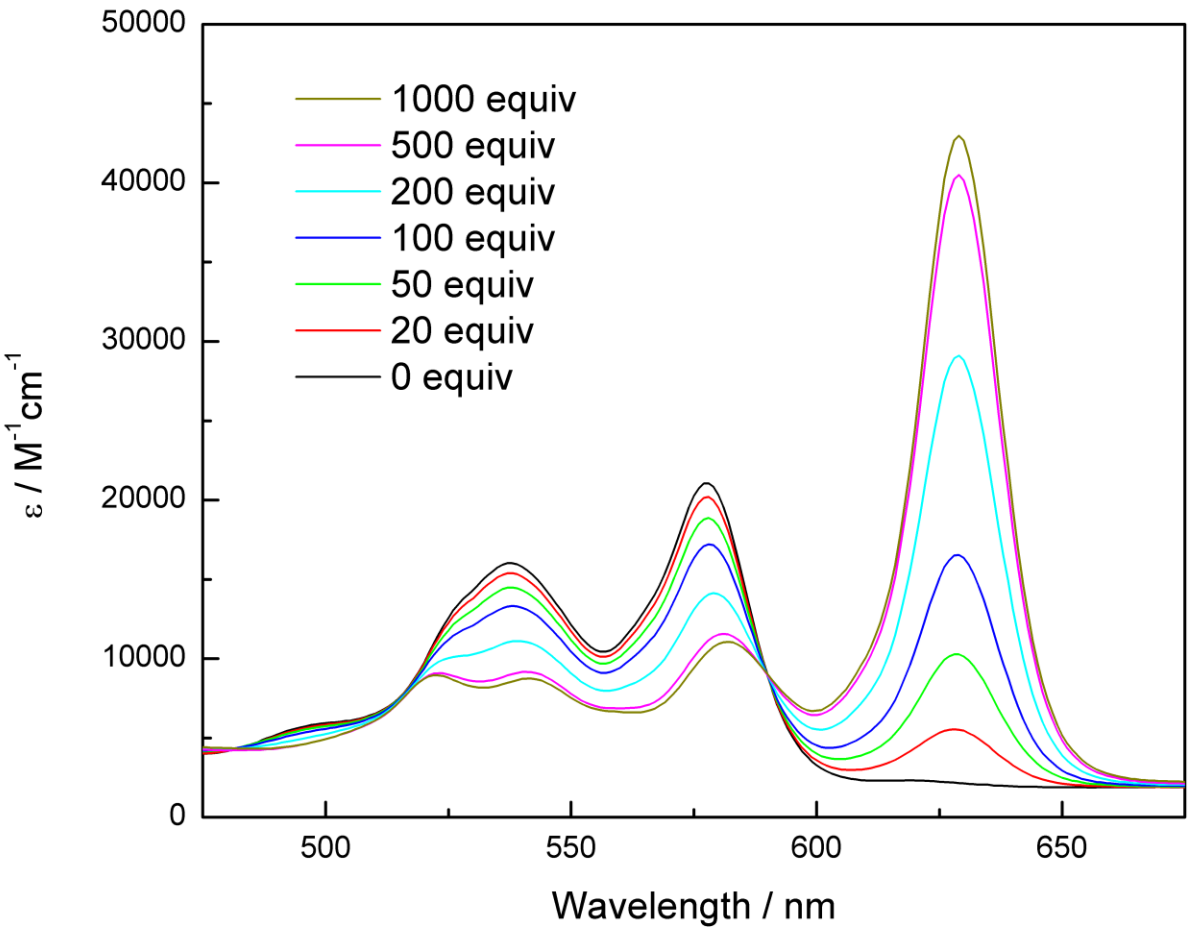


Figure S56. *Q-band region of* ***1***$^{+}$ *with varying equivalences of* (n-*octyl*)$_3$*P=O.*

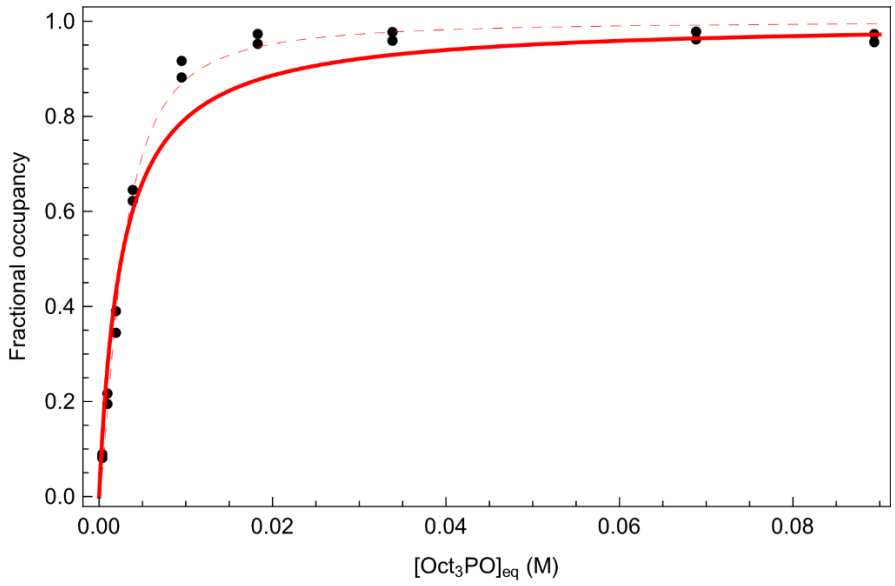


Figure S57. *Binding curves (solid: Michaelis-Menten; dashed: Hill) for titration of* ***1***$^{+}$ *with (*n-*octyl)*$_3$*P=O.*

Michaelis-Menten equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}}{K_d + [Oct_3PO]_{eq}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.00256969	0.00025298	10.1577	1.23044e-8

R^2 = 0.993

Hill equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}{}^{n}}{K_d{}^{n} + [Oct_3PO]_{eq}{}^{n}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.00265617	0.0000877992	30.2528	1.50296e-15
n	1.48117	0.0670867	22.0784	2.07298e-13

R^2 = 0.998

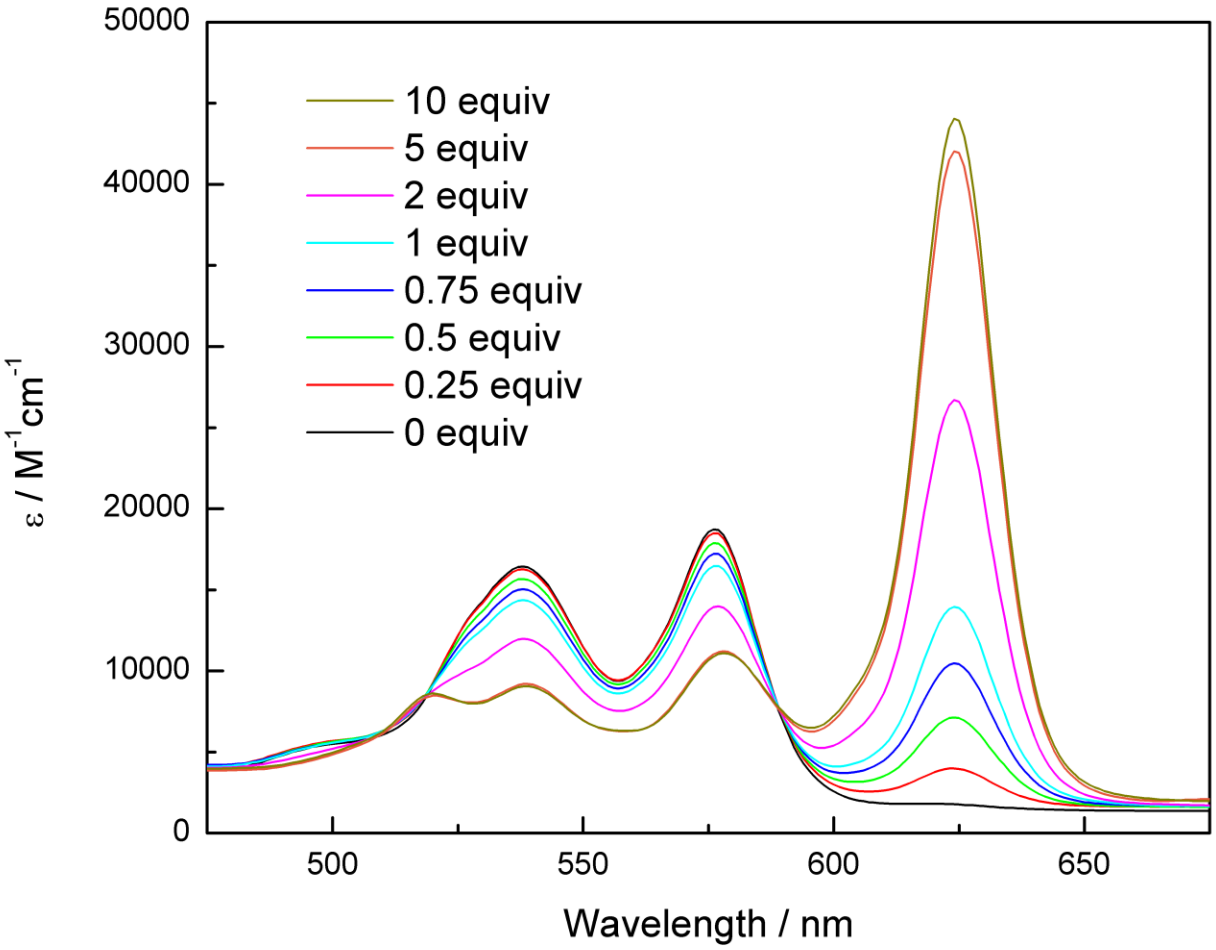


Figure S58. Q-band region of **2**$^{+}$ with varying equivalences of (*n*-octyl)$_3$P=O.

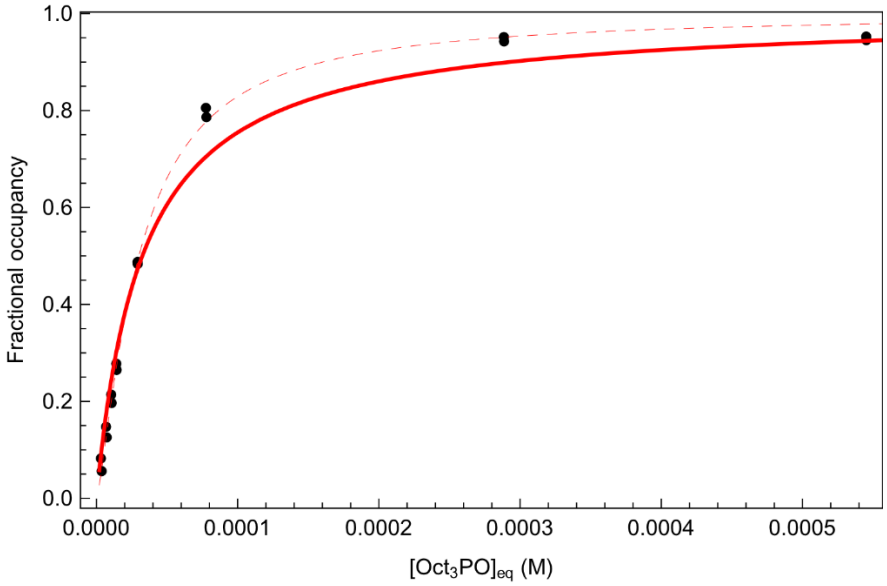


Figure S59. *Binding curves (solid: Michaelis-Menten; dashed: Hill) for titration of* ***2***$^{+}$ *with (*n-*octyl)*$_3$*P=O.*

Michaelis-Menten equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}}{K_d + [Oct_3PO]_{eq}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.0000324852	2.34497e-6	13.8531	5.93441e-10

R^2 = 0.993

Hill equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}{}^{n}}{K_d{}^{n} + [Oct_3PO]_{eq}{}^{n}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.000030052	7.43199e-5	40.4360	6.68284e-16
n	1.31334	0.0376445	34.8878	5.17596e-15

R^2 = 0.999

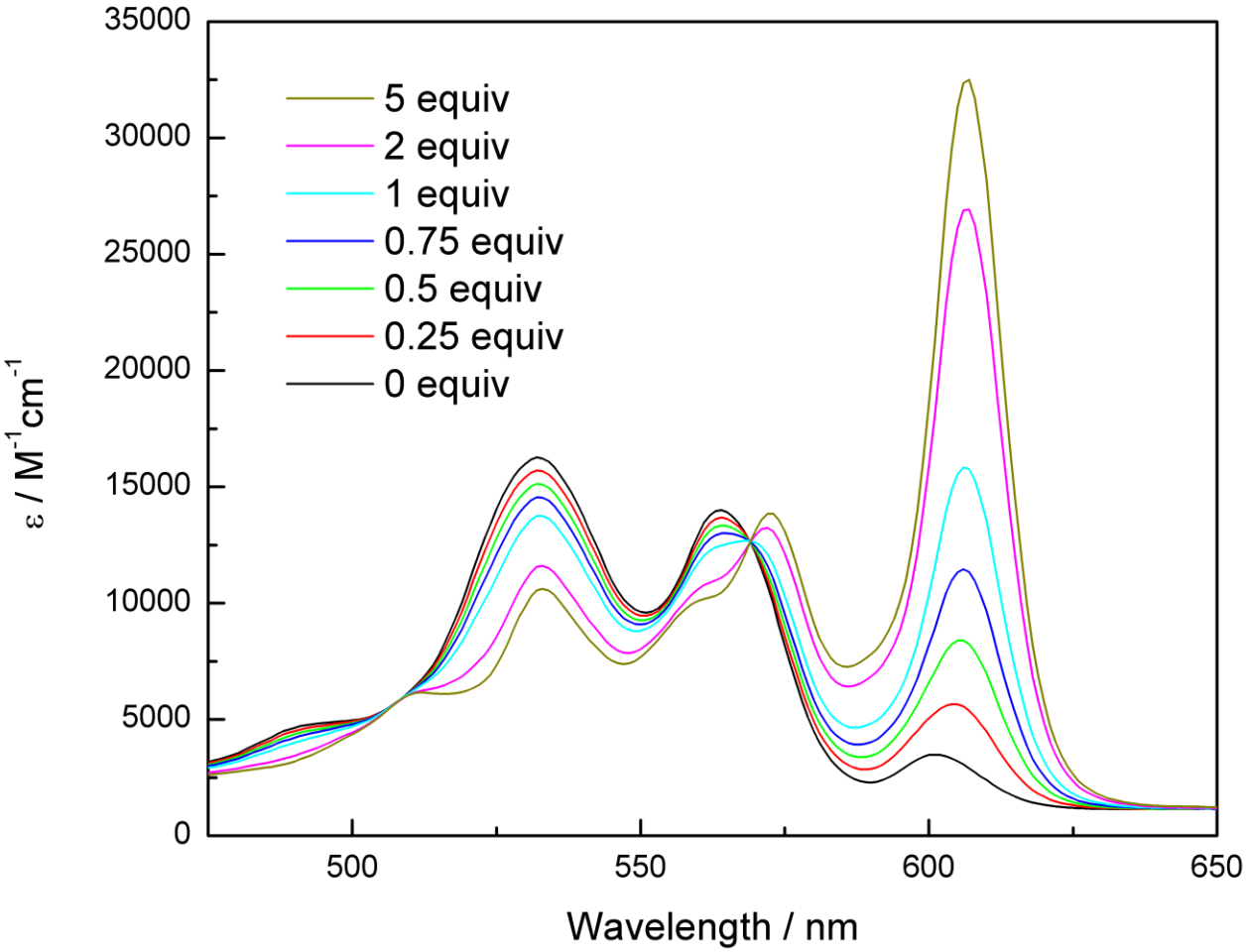


Figure S60. Q-band region of **3**$^{+}$ with varying equivalences of (*n*-octyl)$_3$P=O.

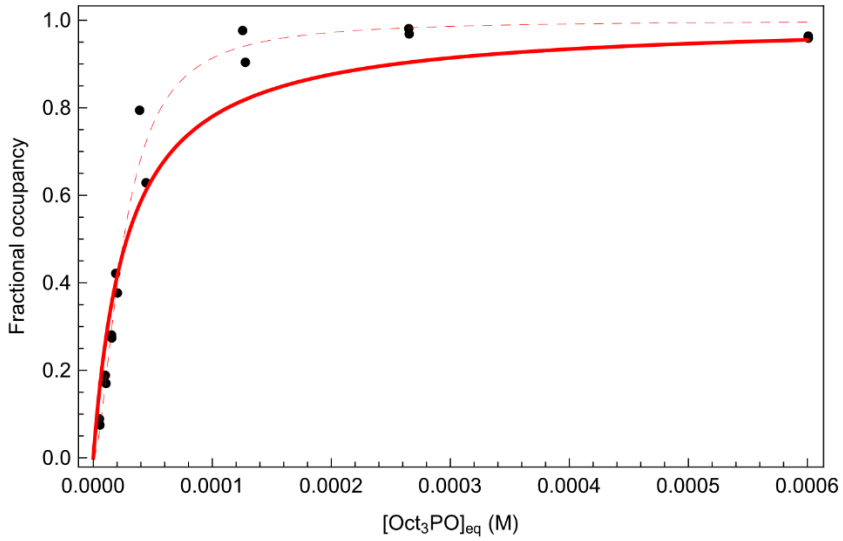


Figure S61. *Binding curves (solid: Michaelis-Menten; dashed: Hill) for titration of* ***3***$^{+}$ *with (*n-*octyl)*$_3$*P=O.*

Michaelis-Menten equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}}{K_d + [Oct_3PO]_{eq}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.0000282225	3.73091e-6	7.56451	1.70374e-6

R^2 = 0.980

Hill equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}{}^{n}}{K_d{}^{n} + [Oct_3PO]_{eq}{}^{n}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.0000255336	1.29969	19.6458	1.36988e-11
n	1.7256	0.148709	11.6039	1.43732e-8

R^2 = 0.995

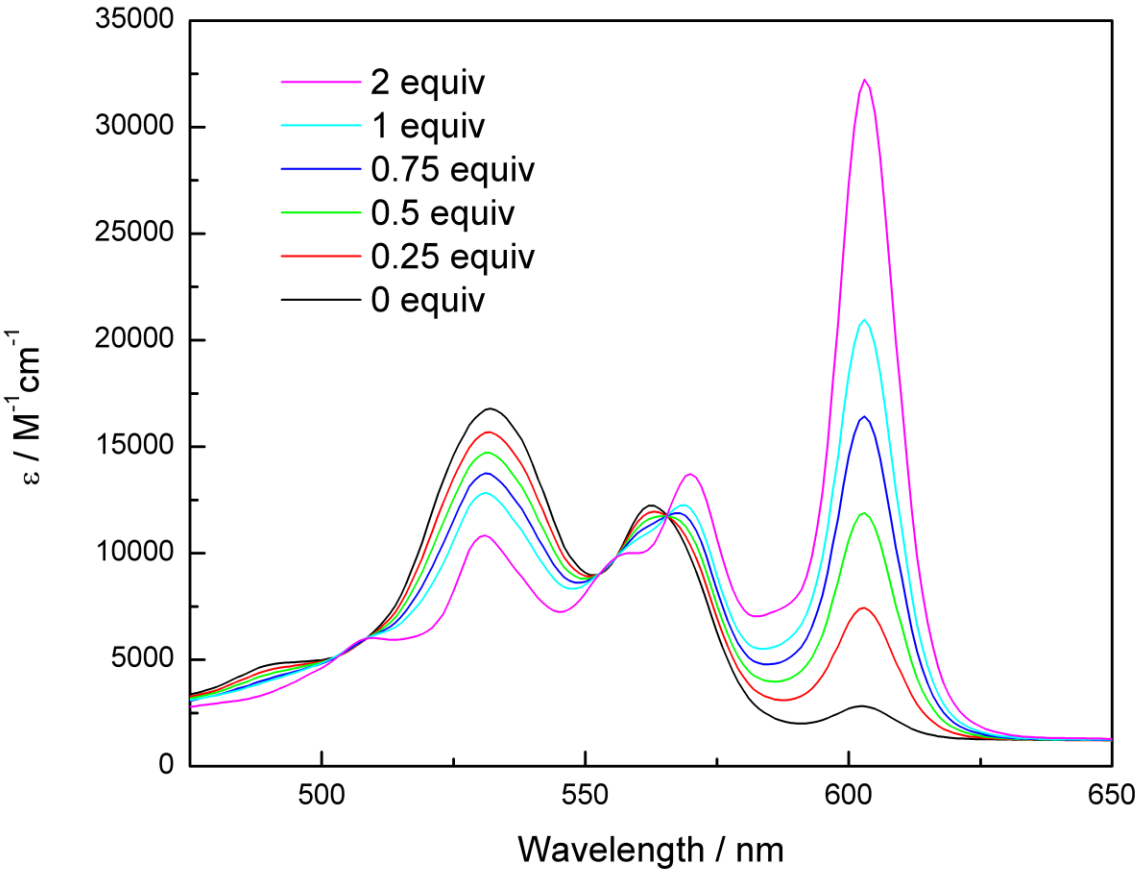


Figure S62. *Q-band region of* ***4***$^{+}$ *with varying equivalences of (*n*-octyl)*$_3$*P=O.*

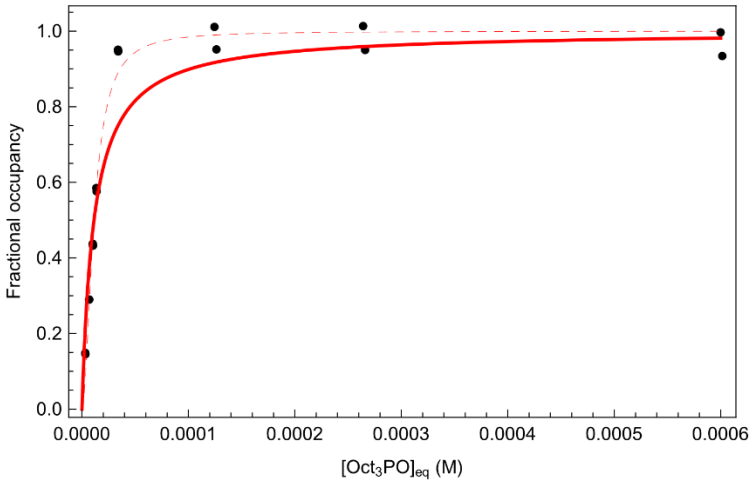


Figure S63. *Binding curves (solid: Michaelis-Menten; dashed: Hill) for titration of* ***4***$^{+}$ *with (*n-*octyl)*$_3$*P=O.*

Michaelis-Menten equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}}{K_d + [Oct_3PO]_{eq}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.0000112832	1.48123e-6	7.61742	1.56615e-6

R^2 = 0.984

Hill equation fit parameters:

$$Fractional\ occupancy = \frac{[Oct_3PO]_{eq}{}^{n}}{K_d{}^{n} + [Oct_3PO]_{eq}{}^{n}}$$

Parameter	Estimate	Standard error	t-statistic	p-value
K_d	0.0000112983	4.06365e-7	27.8034	1.18985e-13
n	1.8992	0.154184	12.3177	6.68298e-9

R^2 = 0.997

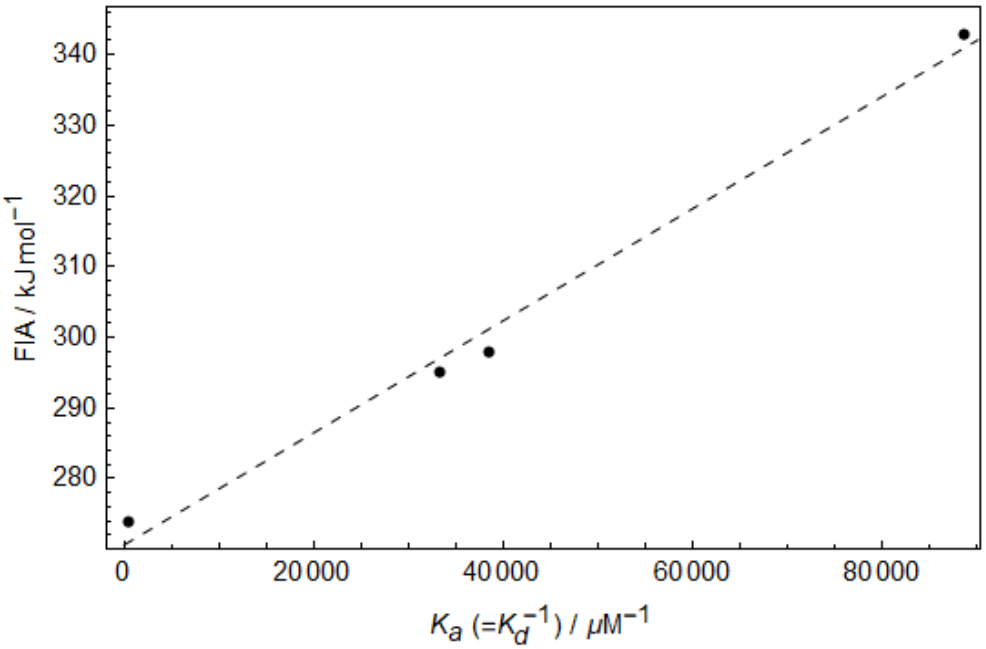


***Figure S64**. Correlation between association constant K_a (inverse of K_d) and FIA for **1**$^+$–**4**$^+$. R^2 = 0.989.*

9. Mass spectra

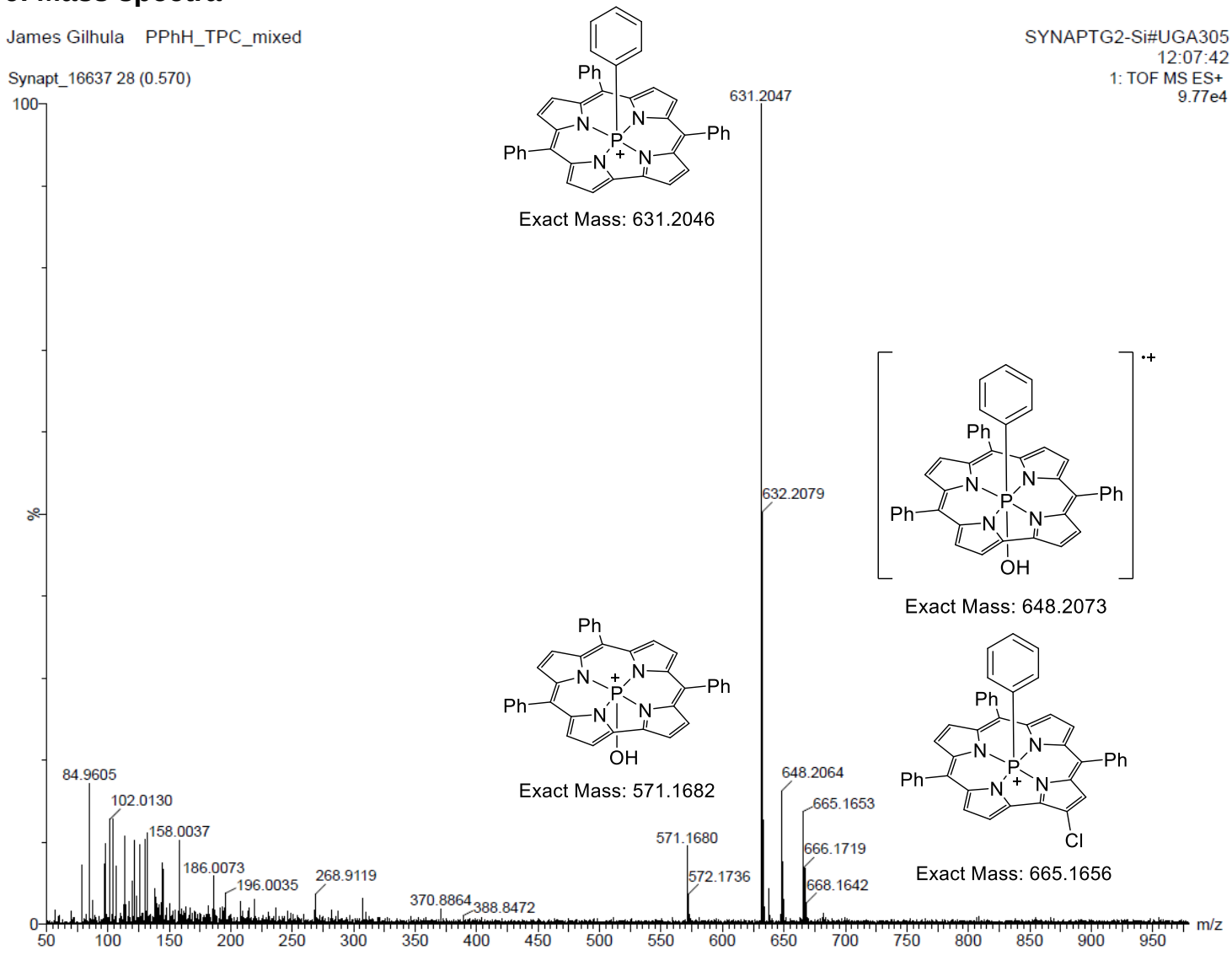


Figure S65. *HRMS (ESI) of* ***1•OH*** *before hydrodechlorination with* H_2 *and Pd/C.*

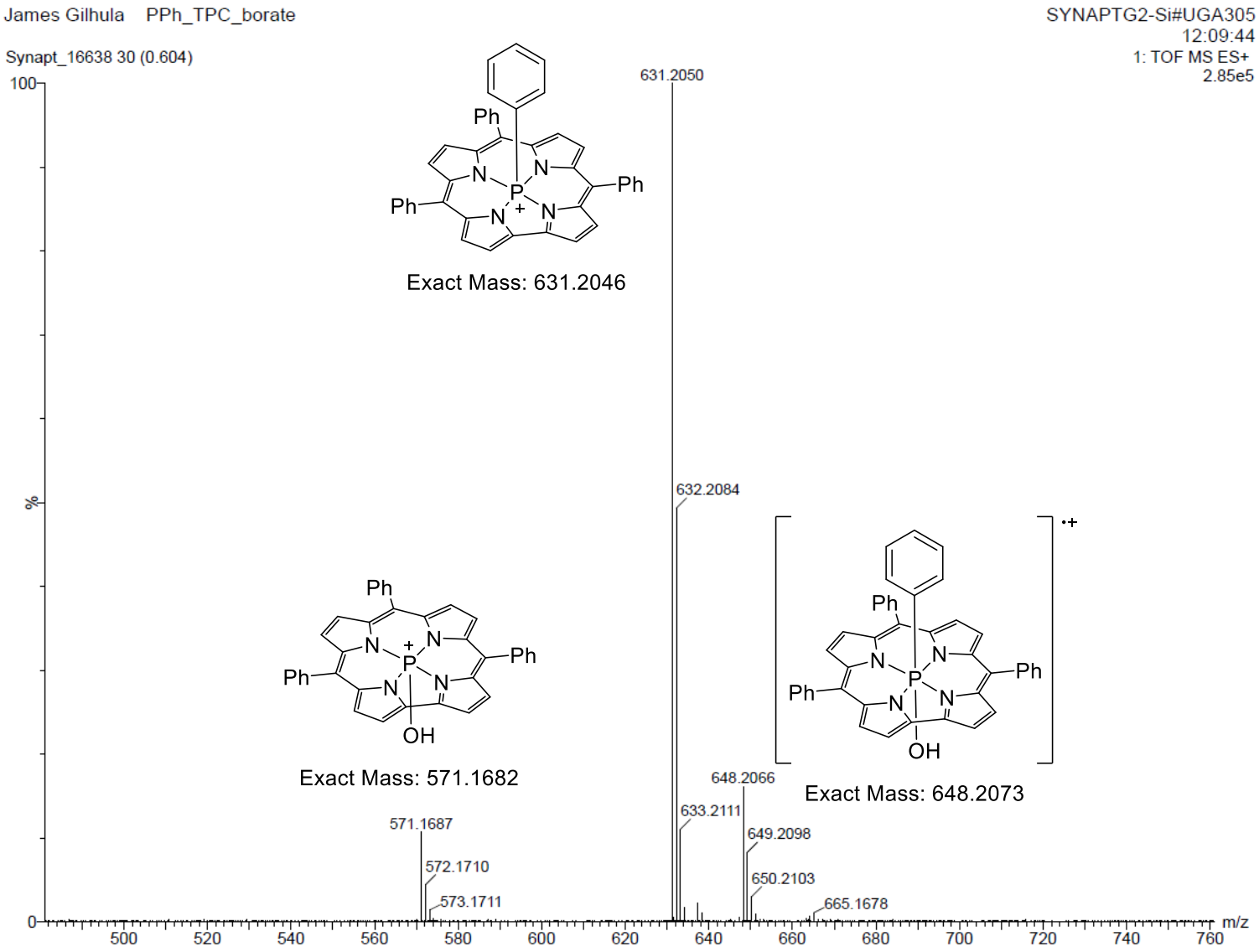


Figure S66. *HRMS (ESI) of* ***1*****⁺**.

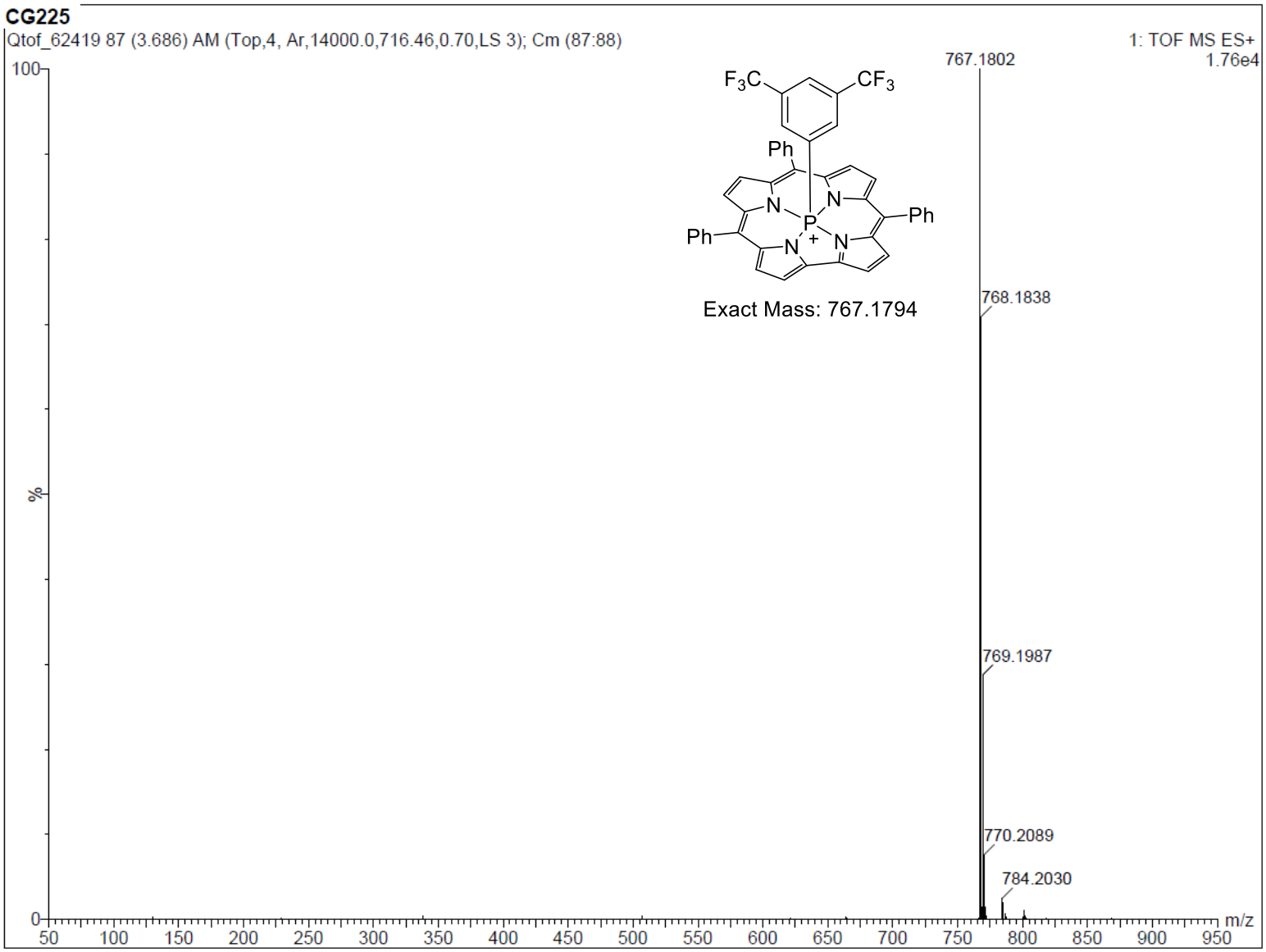


Figure S67. *HRMS (ESI) of* ***2•H****.*

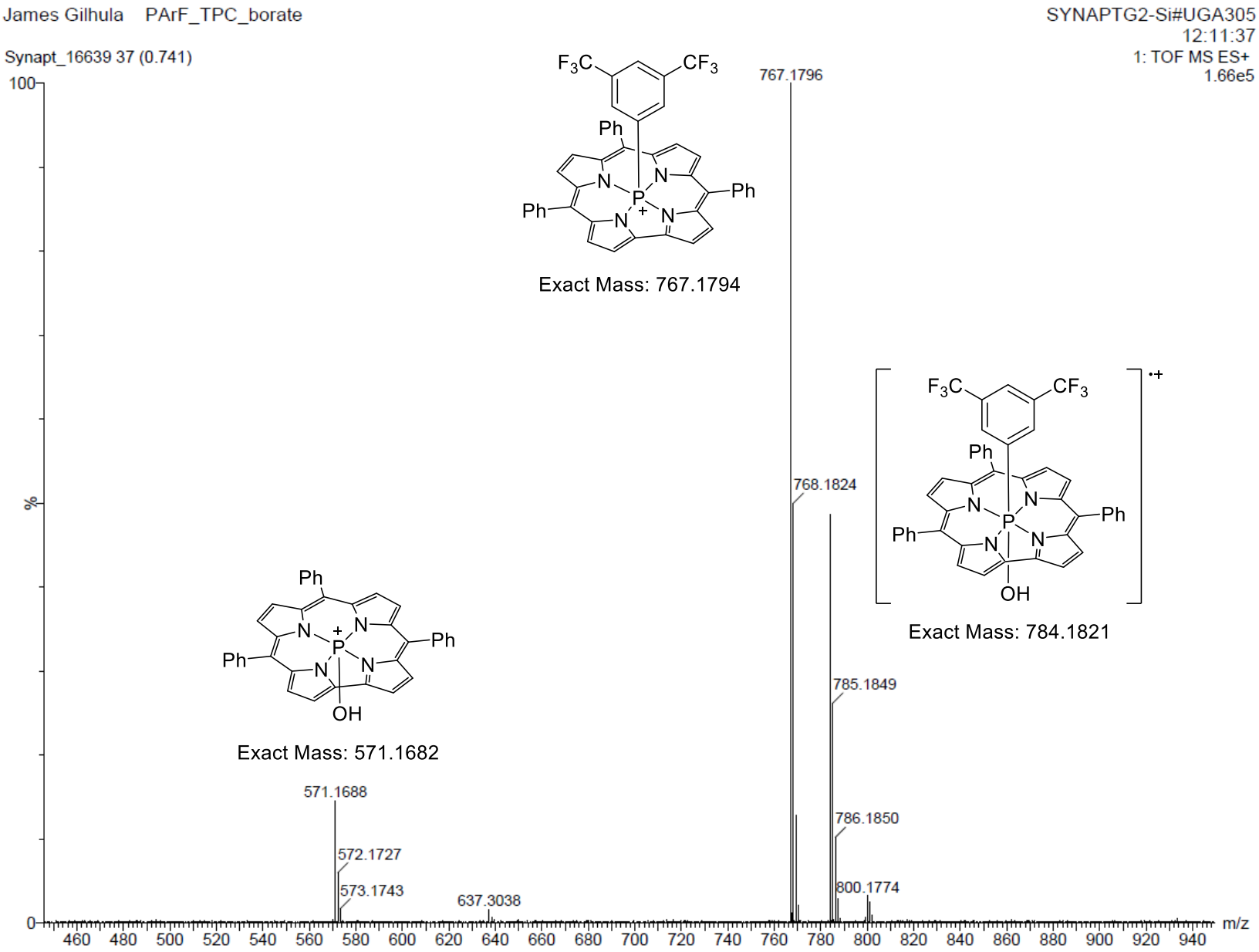


Figure S68. *HRMS (ESI) of* ***2***$^{+}$*.*

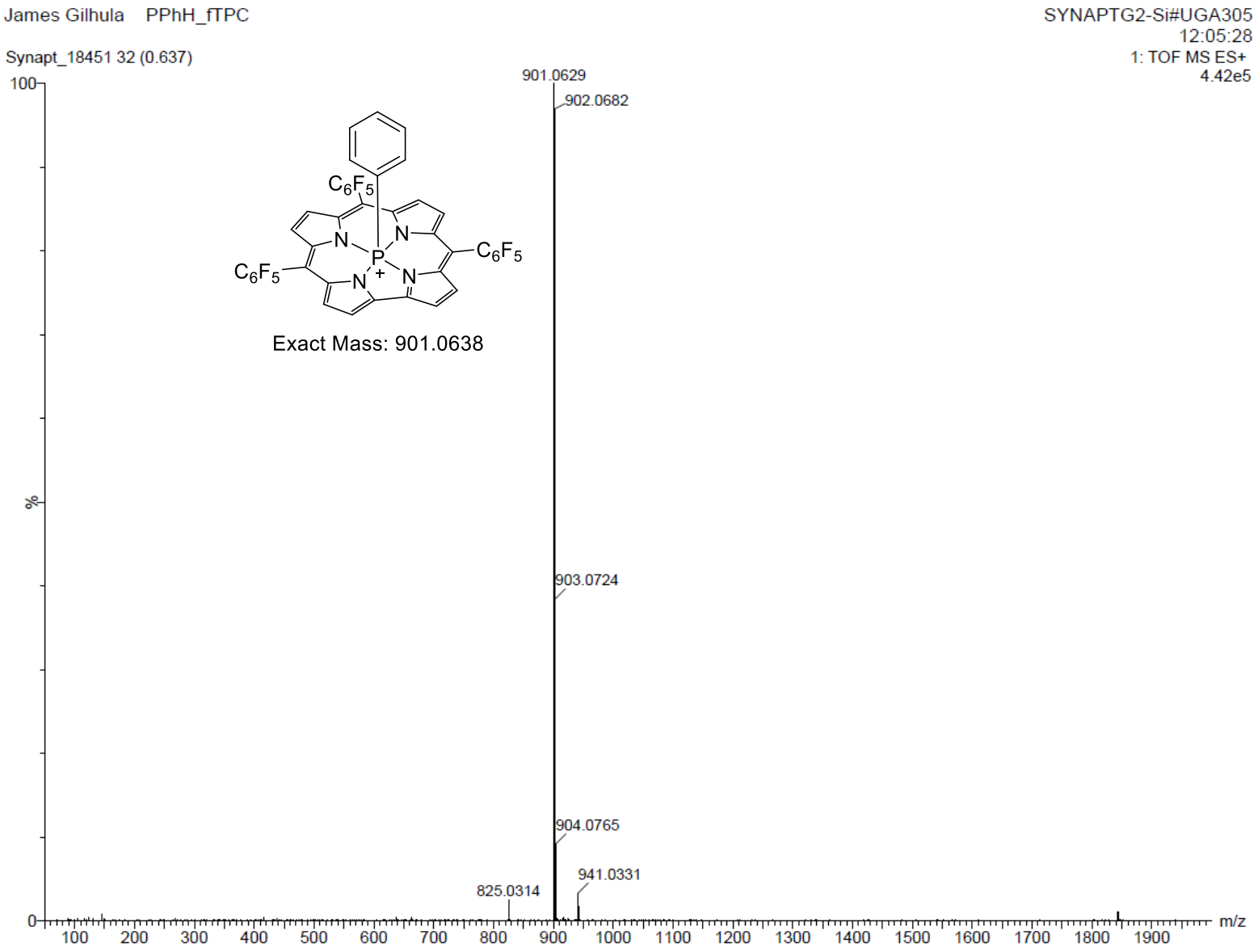


Figure S69. *HRMS (ESI) of* ***3•H****.*

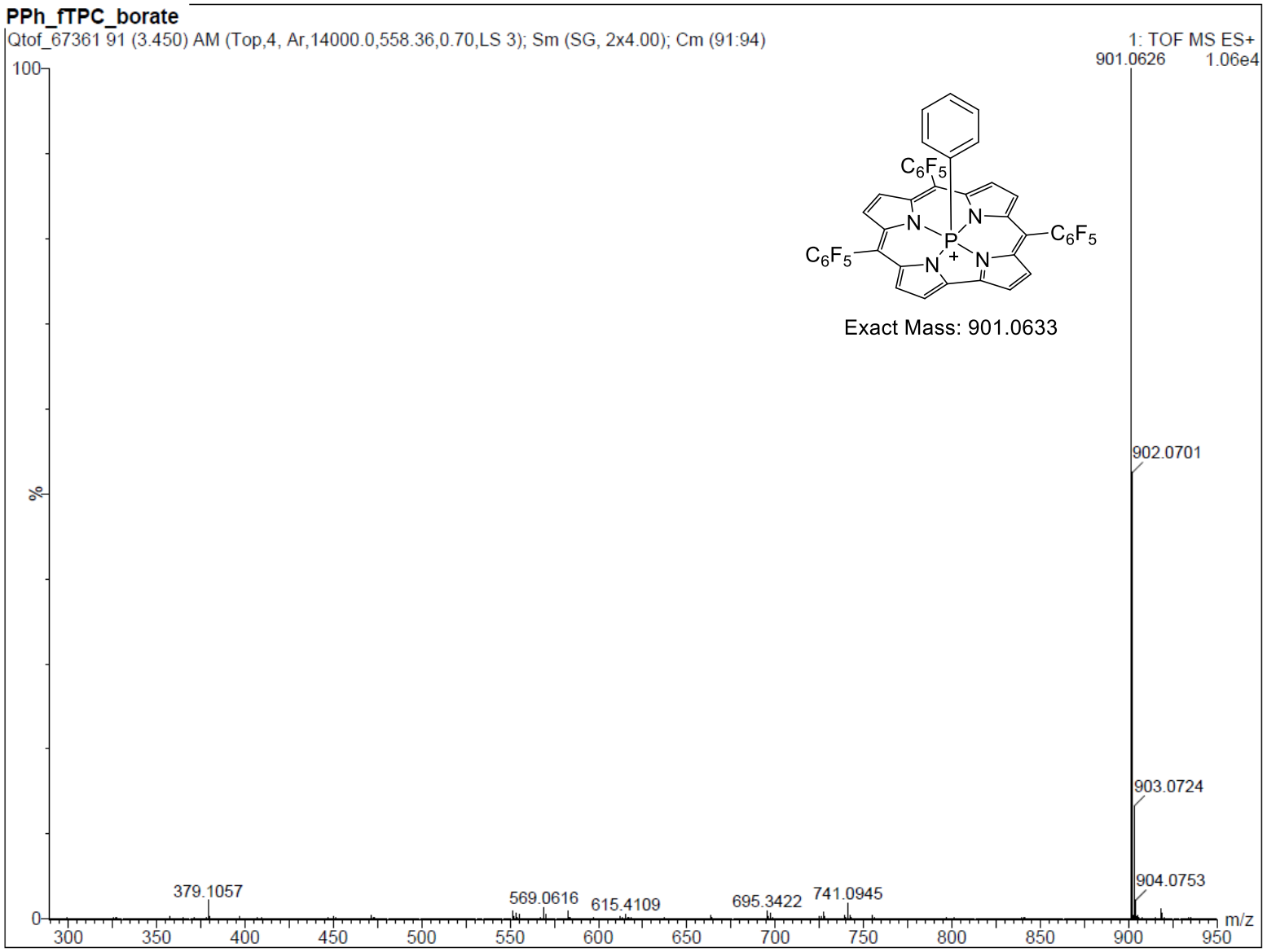


Figure S70. *HRMS (ESI) of* ***3***$^{+}$.

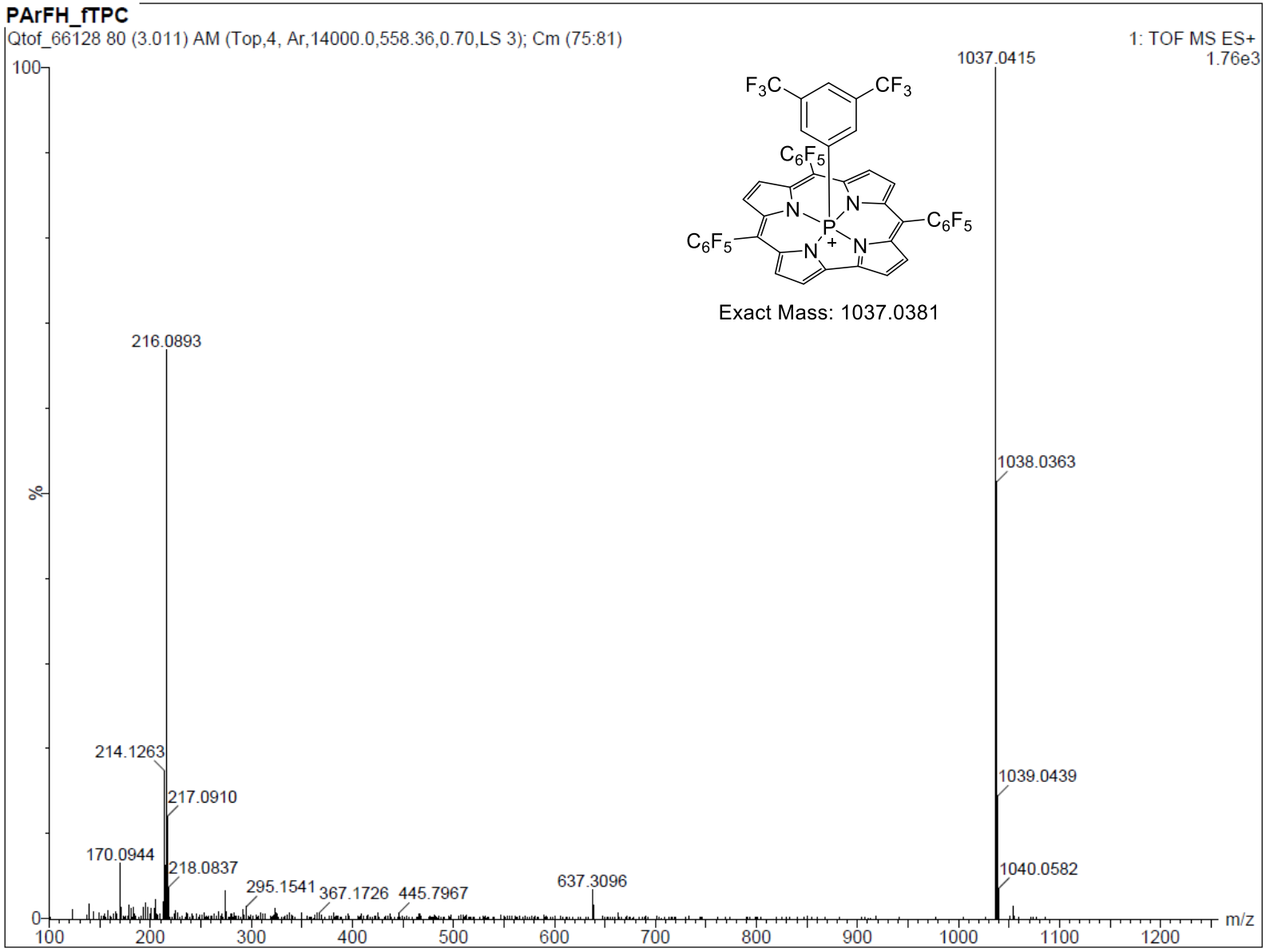


Figure S71. *HRMS (ESI) of* ***4•H****.*

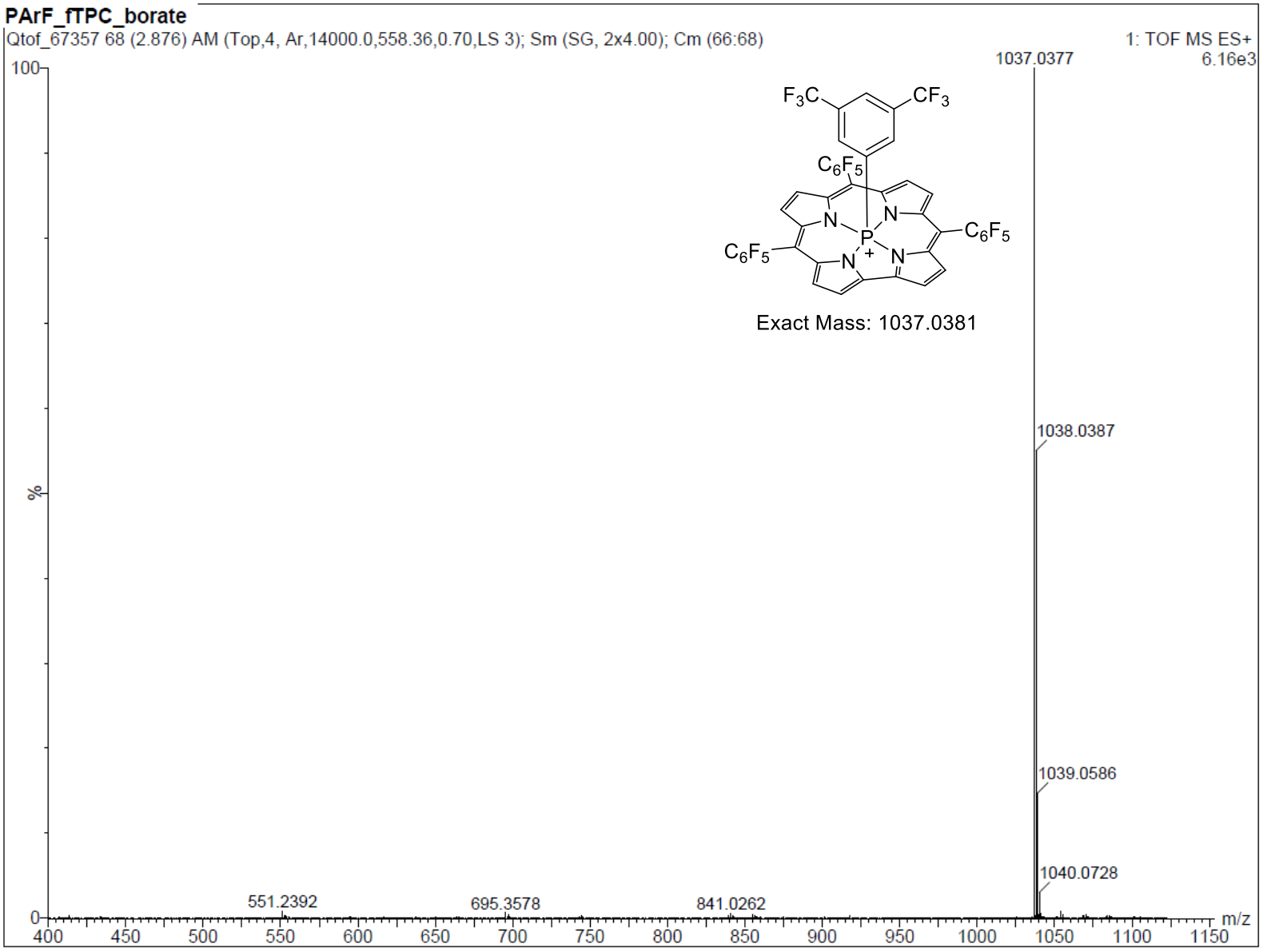


Figure S72. *HRMS (ESI) of* ***4*****⁺***.*

10. X-Ray structures

Single crystals suitable for X-ray diffraction were grown from solutions of chloroform and pentane or dichloromethane and pentane. X-ray diffraction data was collected on a Bruker APEX-II CCD area detector system using CuKα radiation or at the ANL/APS synchrotron source. Raw data integration and reduction were performed with the SAINT and SADABS programs. Structures were solved using direct methods using SHELXT and refined using least-squares methods on F^2 using SHELX-2018 with the WinGX software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed in their ideal geometries. XP was used for graphical representations.

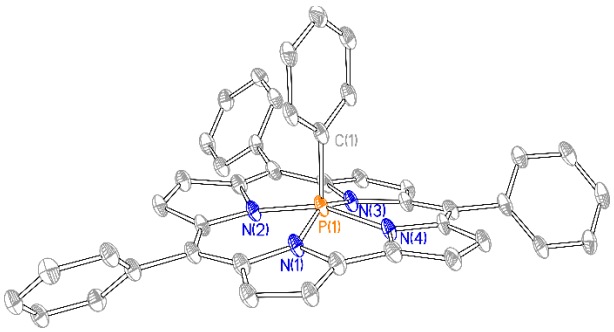


Table S1. Crystal data and structure refinement for **1**$^+$.

Identification code	pcorrole_a	
Empirical formula	C22.50 H14.50 Cl1.50 F1.50 N2 O1.50 P0.50 S0.50	
Formula weight	450.05	
Temperature	20(2) K	
Wavelength	0.41328 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.5292(8) Å	a= 78.0350(10)°.
	b = 12.5645(9) Å	b= 85.101(2)°.
	c = 14.1583(10) Å	g = 85.3720(10)°.
Volume	1994.9(2) Å^3	
Z	4	
Density (calculated)	1.498 Mg/m^3	
Absorption coefficient	0.204 mm^{-1}	
F(000)	920	
Crystal size	0.01 x 0.01 x 0.01 mm^3	
Theta range for data collection	0.86 to 14.23°.	
Index ranges	-13<=h<=13, -14<=k<=14, -16<=l<=16	
Reflections collected	39814	

Independent reflections	6857 [R(int) = 0.0791]
Completeness to theta = 14.23°	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9980 and 0.9980
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6857 / 0 / 657
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0571, wR2 = 0.1492
R indices (all data)	R1 = 0.0694, wR2 = 0.1603
Largest diff. peak and hole	0.935 and -0.525 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1^+**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(44)	6517(3)	8117(3)	7894(3)	30(1)
O(1)	4632(2)	8238(2)	7028(2)	39(1)
O(2)	4503(2)	8765(2)	8602(2)	36(1)
O(3)	4823(2)	6863(2)	8499(2)	34(1)
F(1)	6779(2)	9151(2)	7537(2)	47(1)
F(2)	7002(2)	7800(2)	8736(2)	46(1)
F(3)	7044(2)	7505(2)	7290(2)	37(1)
S(1)	4937(1)	7985(1)	8018(1)	24(1)
C(45)	2452(3)	10054(3)	9491(2)	26(1)
Cl(1)	3506(1)	11007(1)	9488(1)	34(1)
Cl(2)	1623(1)	9834(1)	10622(1)	36(1)
Cl(3)	1513(1)	10532(1)	8549(1)	31(1)
C(1)	9876(2)	6941(2)	2576(2)	20(1)
C(2)	10677(3)	7760(3)	2488(2)	22(1)
C(3)	10749(3)	8011(3)	3362(2)	23(1)
C(4)	10032(2)	7323(3)	4052(2)	21(1)
C(5)	9968(2)	7228(3)	5043(2)	21(1)
C(6)	9350(2)	6408(3)	5632(2)	21(1)
C(7)	9357(3)	6105(3)	6652(2)	22(1)
C(8)	8555(3)	5348(3)	6971(2)	22(1)
C(9)	8014(3)	5144(3)	6172(2)	21(1)
C(10)	7060(3)	4515(3)	6235(2)	22(1)
C(11)	6645(3)	4382(3)	5382(2)	21(1)
C(12)	5764(3)	3731(3)	5193(2)	22(1)
C(13)	5784(3)	3792(3)	4213(2)	23(1)
C(14)	6659(3)	4498(3)	3784(2)	21(1)
C(15)	7200(3)	4882(3)	2874(2)	22(1)
C(16)	7207(3)	4697(3)	1938(2)	22(1)
C(17)	8102(3)	5273(3)	1398(2)	24(1)
C(18)	8633(3)	5834(3)	2004(2)	21(1)
C(19)	9530(3)	6537(3)	1808(2)	21(1)

C(20)	10593(3)	7969(2)	5499(2)	21(1)
C(21)	11809(3)	8027(3)	5355(2)	24(1)
C(22)	12378(3)	8724(3)	5777(2)	27(1)
C(23)	11751(3)	9369(3)	6355(2)	27(1)
C(24)	10543(3)	9312(3)	6511(2)	25(1)
C(25)	9965(3)	8623(3)	6084(2)	23(1)
C(26)	6513(2)	3991(3)	7203(2)	22(1)
C(27)	6058(3)	4636(3)	7868(2)	24(1)
C(28)	5569(3)	4140(3)	8772(2)	28(1)
C(29)	5525(3)	3013(3)	9025(2)	28(1)
C(30)	5955(3)	2372(3)	8361(2)	26(1)
C(31)	6435(3)	2864(3)	7450(2)	24(1)
C(32)	10095(3)	6859(2)	806(2)	21(1)
C(33)	9410(3)	7250(3)	19(2)	24(1)
C(34)	9932(3)	7556(3)	-916(2)	26(1)
C(35)	11139(3)	7482(3)	-1080(2)	26(1)
C(36)	11831(3)	7090(3)	-302(2)	23(1)
C(37)	11315(3)	6777(3)	628(2)	22(1)
C(38)	7105(2)	7167(2)	4022(2)	21(1)
C(39)	6690(3)	7719(3)	3138(2)	23(1)
C(40)	5929(3)	8648(3)	3097(2)	24(1)
C(41)	5569(3)	9023(3)	3951(2)	25(1)
C(42)	5972(3)	8474(3)	4829(2)	25(1)
C(43)	6741(3)	7555(3)	4873(2)	22(1)
N(1)	9451(2)	6653(2)	3574(2)	20(1)
N(2)	8567(2)	5769(2)	5292(2)	21(1)
N(3)	7179(2)	4876(2)	4487(2)	21(1)
N(4)	8064(2)	5581(2)	2938(2)	20(1)
P(1)	8130(1)	5981(1)	4075(1)	19(1)

Table S3. Bond lengths [Å] and angles [°] for **1**$^{+}$.

C(44)-F(2)	1.331(4)
C(44)-F(1)	1.342(4)
C(44)-F(3)	1.343(4)
C(44)-S(1)	1.833(3)
O(1)-S(1)	1.439(3)
O(2)-S(1)	1.442(3)
O(3)-S(1)	1.444(3)
C(45)-Cl(3)	1.767(3)
C(45)-Cl(1)	1.772(3)
C(45)-Cl(2)	1.775(3)
C(45)-H(45)	1.00(3)
C(1)-C(19)	1.391(4)
C(1)-C(2)	1.417(4)
C(1)-N(1)	1.437(4)
C(2)-C(3)	1.350(5)
C(2)-H(2)	0.89(4)
C(3)-C(4)	1.418(4)
C(3)-H(3)	0.91(4)
C(4)-C(5)	1.381(4)
C(4)-N(1)	1.421(4)
C(5)-C(6)	1.387(4)
C(5)-C(20)	1.497(4)
C(6)-C(7)	1.415(4)
C(6)-N(2)	1.429(4)
C(7)-C(8)	1.362(4)
C(7)-H(7)	0.92(4)
C(8)-C(9)	1.414(4)
C(8)-H(8)	0.93(4)
C(9)-C(10)	1.392(4)
C(9)-N(2)	1.454(4)
C(10)-C(11)	1.383(4)
C(10)-C(26)	1.501(4)
C(11)-N(3)	1.404(4)
C(11)-C(12)	1.429(4)

C(12)-C(13)	1.372(5)
C(12)-H(12)	1.00(4)
C(13)-C(14)	1.411(4)
C(13)-H(13)	0.81(5)
C(14)-N(3)	1.385(4)
C(14)-C(15)	1.392(4)
C(15)-C(16)	1.391(5)
C(15)-N(4)	1.401(4)
C(16)-C(17)	1.389(4)
C(16)-H(16)	0.88(4)
C(17)-C(18)	1.421(4)
C(17)-H(17)	1.00(4)
C(18)-C(19)	1.387(4)
C(18)-N(4)	1.411(4)
C(19)-C(32)	1.499(4)
C(20)-C(25)	1.403(5)
C(20)-C(21)	1.405(4)
C(21)-C(22)	1.389(5)
C(21)-H(21)	0.99(4)
C(22)-C(23)	1.389(5)
C(22)-H(22)	0.92(4)
C(23)-C(24)	1.397(5)
C(23)-H(23)	0.94(4)
C(24)-C(25)	1.393(5)
C(24)-H(24)	0.91(3)
C(25)-H(25)	0.87(4)
C(26)-C(31)	1.395(5)
C(26)-C(27)	1.409(5)
C(27)-C(28)	1.396(5)
C(27)-H(27)	0.94(4)
C(28)-C(29)	1.391(5)
C(28)-H(28)	0.90(4)
C(29)-C(30)	1.396(5)
C(29)-H(29)	0.93(5)
C(30)-C(31)	1.398(5)
C(30)-H(30)	0.88(3)

C(31)-H(31)	0.87(3)
C(32)-C(33)	1.403(5)
C(32)-C(37)	1.407(4)
C(33)-C(34)	1.397(5)
C(33)-H(33)	0.95(4)
C(34)-C(35)	1.390(5)
C(34)-H(34)	0.79(4)
C(35)-C(36)	1.398(5)
C(35)-H(35)	0.94(4)
C(36)-C(37)	1.390(4)
C(36)-H(36)	0.92(4)
C(37)-H(37)	0.87(4)
C(38)-C(39)	1.401(4)
C(38)-C(43)	1.409(4)
C(38)-P(1)	1.819(3)
C(39)-C(40)	1.396(5)
C(39)-H(39)	0.92(4)
C(40)-C(41)	1.406(5)
C(40)-H(40)	0.95(4)
C(41)-C(42)	1.389(5)
C(41)-H(41)	0.91(4)
C(42)-C(43)	1.393(5)
C(42)-H(42)	0.94(4)
C(43)-H(43)	0.91(3)
N(1)-P(1)	1.819(2)
N(2)-P(1)	1.797(3)
N(3)-P(1)	1.809(3)
N(4)-P(1)	1.792(3)
F(2)-C(44)-F(1)	107.4(3)
F(2)-C(44)-F(3)	107.1(3)
F(1)-C(44)-F(3)	107.3(3)
F(2)-C(44)-S(1)	112.3(2)
F(1)-C(44)-S(1)	111.5(2)
F(3)-C(44)-S(1)	111.0(2)
O(1)-S(1)-O(2)	115.96(16)
O(1)-S(1)-O(3)	114.77(16)

O(2)-S(1)-O(3)	113.99(15)
O(1)-S(1)-C(44)	102.55(16)
O(2)-S(1)-C(44)	103.72(15)
O(3)-S(1)-C(44)	103.51(15)
Cl(3)-C(45)-Cl(1)	110.67(18)
Cl(3)-C(45)-Cl(2)	109.57(17)
Cl(1)-C(45)-Cl(2)	109.63(18)
Cl(3)-C(45)-H(45)	109.5(17)
Cl(1)-C(45)-H(45)	105.5(18)
Cl(2)-C(45)-H(45)	111.9(17)
C(19)-C(1)-C(2)	124.9(3)
C(19)-C(1)-N(1)	126.7(3)
C(2)-C(1)-N(1)	108.4(3)
C(3)-C(2)-C(1)	109.2(3)
C(3)-C(2)-H(2)	128(2)
C(1)-C(2)-H(2)	122(2)
C(2)-C(3)-C(4)	108.3(3)
C(2)-C(3)-H(3)	126(2)
C(4)-C(3)-H(3)	125(2)
C(5)-C(4)-C(3)	126.6(3)
C(5)-C(4)-N(1)	123.8(3)
C(3)-C(4)-N(1)	109.3(3)
C(4)-C(5)-C(6)	119.7(3)
C(4)-C(5)-C(20)	121.0(3)
C(6)-C(5)-C(20)	119.2(3)
C(5)-C(6)-C(7)	125.9(3)
C(5)-C(6)-N(2)	124.3(3)
C(7)-C(6)-N(2)	109.8(3)
C(8)-C(7)-C(6)	108.2(3)
C(8)-C(7)-H(7)	128(2)
C(6)-C(7)-H(7)	124(2)
C(7)-C(8)-C(9)	109.4(3)
C(7)-C(8)-H(8)	123(2)
C(9)-C(8)-H(8)	128(2)
C(10)-C(9)-C(8)	125.1(3)
C(10)-C(9)-N(2)	126.4(3)

C(8)-C(9)-N(2)	108.3(2)
C(11)-C(10)-C(9)	117.9(3)
C(11)-C(10)-C(26)	121.4(3)
C(9)-C(10)-C(26)	120.6(3)
C(10)-C(11)-N(3)	120.2(3)
C(10)-C(11)-C(12)	131.9(3)
N(3)-C(11)-C(12)	107.7(3)
C(13)-C(12)-C(11)	108.7(3)
C(13)-C(12)-H(12)	128(2)
C(11)-C(12)-H(12)	124(2)
C(12)-C(13)-C(14)	106.7(3)
C(12)-C(13)-H(13)	124(3)
C(14)-C(13)-H(13)	128(3)
N(3)-C(14)-C(15)	110.5(3)
N(3)-C(14)-C(13)	110.4(3)
C(15)-C(14)-C(13)	139.0(3)
C(16)-C(15)-C(14)	138.4(3)
C(16)-C(15)-N(4)	110.9(3)
C(14)-C(15)-N(4)	110.4(3)
C(17)-C(16)-C(15)	106.7(3)
C(17)-C(16)-H(16)	128(3)
C(15)-C(16)-H(16)	125(3)
C(16)-C(17)-C(18)	108.7(3)
C(16)-C(17)-H(17)	128(2)
C(18)-C(17)-H(17)	123(2)
C(19)-C(18)-N(4)	121.0(3)
C(19)-C(18)-C(17)	131.2(3)
N(4)-C(18)-C(17)	107.8(3)
C(18)-C(19)-C(1)	117.4(3)
C(18)-C(19)-C(32)	121.4(3)
C(1)-C(19)-C(32)	121.3(3)
C(25)-C(20)-C(21)	118.7(3)
C(25)-C(20)-C(5)	120.0(3)
C(21)-C(20)-C(5)	121.3(3)
C(22)-C(21)-C(20)	120.7(3)
C(22)-C(21)-H(21)	123(2)

C(20)-C(21)-H(21)	116(2)
C(23)-C(22)-C(21)	120.3(3)
C(23)-C(22)-H(22)	120(2)
C(21)-C(22)-H(22)	119(2)
C(22)-C(23)-C(24)	119.6(3)
C(22)-C(23)-H(23)	121(2)
C(24)-C(23)-H(23)	119(2)
C(25)-C(24)-C(23)	120.4(3)
C(25)-C(24)-H(24)	121(2)
C(23)-C(24)-H(24)	119(2)
C(24)-C(25)-C(20)	120.3(3)
C(24)-C(25)-H(25)	120(2)
C(20)-C(25)-H(25)	120(2)
C(31)-C(26)-C(27)	119.1(3)
C(31)-C(26)-C(10)	120.6(3)
C(27)-C(26)-C(10)	120.2(3)
C(28)-C(27)-C(26)	119.8(3)
C(28)-C(27)-H(27)	120(2)
C(26)-C(27)-H(27)	120(2)
C(29)-C(28)-C(27)	120.7(3)
C(29)-C(28)-H(28)	119(2)
C(27)-C(28)-H(28)	120(2)
C(28)-C(29)-C(30)	119.7(3)
C(28)-C(29)-H(29)	119(3)
C(30)-C(29)-H(29)	121(3)
C(29)-C(30)-C(31)	119.9(3)
C(29)-C(30)-H(30)	120(2)
C(31)-C(30)-H(30)	120(2)
C(26)-C(31)-C(30)	120.7(3)
C(26)-C(31)-H(31)	124(2)
C(30)-C(31)-H(31)	115(2)
C(33)-C(32)-C(37)	118.3(3)
C(33)-C(32)-C(19)	120.3(3)
C(37)-C(32)-C(19)	121.4(3)
C(34)-C(33)-C(32)	120.5(3)
C(34)-C(33)-H(33)	123(2)

C(32)-C(33)-H(33)	116(2)
C(35)-C(34)-C(33)	120.5(3)
C(35)-C(34)-H(34)	118(3)
C(33)-C(34)-H(34)	121(3)
C(34)-C(35)-C(36)	119.5(3)
C(34)-C(35)-H(35)	118(2)
C(36)-C(35)-H(35)	122(2)
C(37)-C(36)-C(35)	120.2(3)
C(37)-C(36)-H(36)	123(2)
C(35)-C(36)-H(36)	117(2)
C(36)-C(37)-C(32)	120.9(3)
C(36)-C(37)-H(37)	125(3)
C(32)-C(37)-H(37)	114(3)
C(39)-C(38)-C(43)	119.4(3)
C(39)-C(38)-P(1)	120.7(2)
C(43)-C(38)-P(1)	119.9(2)
C(40)-C(39)-C(38)	120.5(3)
C(40)-C(39)-H(39)	120(2)
C(38)-C(39)-H(39)	119(2)
C(39)-C(40)-C(41)	119.6(3)
C(39)-C(40)-H(40)	121(2)
C(41)-C(40)-H(40)	119(2)
C(42)-C(41)-C(40)	120.1(3)
C(42)-C(41)-H(41)	121(2)
C(40)-C(41)-H(41)	118(2)
C(41)-C(42)-C(43)	120.5(3)
C(41)-C(42)-H(42)	122(2)
C(43)-C(42)-H(42)	118(2)
C(42)-C(43)-C(38)	119.9(3)
C(42)-C(43)-H(43)	118(2)
C(38)-C(43)-H(43)	122(2)
C(4)-N(1)-C(1)	104.7(2)
C(4)-N(1)-P(1)	123.9(2)
C(1)-N(1)-P(1)	128.2(2)
C(6)-N(2)-C(9)	104.0(2)
C(6)-N(2)-P(1)	125.7(2)

C(9)-N(2)-P(1)	128.5(2)
C(14)-N(3)-C(11)	106.5(2)
C(14)-N(3)-P(1)	117.0(2)
C(11)-N(3)-P(1)	135.5(2)
C(15)-N(4)-C(18)	105.9(2)
C(15)-N(4)-P(1)	117.3(2)
C(18)-N(4)-P(1)	136.7(2)
N(4)-P(1)-N(2)	152.91(13)
N(4)-P(1)-N(3)	82.11(12)
N(2)-P(1)-N(3)	87.78(12)
N(4)-P(1)-C(38)	104.67(13)
N(2)-P(1)-C(38)	101.95(13)
N(3)-P(1)-C(38)	101.67(12)
N(4)-P(1)-N(1)	87.86(11)
N(2)-P(1)-N(1)	92.52(11)
N(3)-P(1)-N(1)	158.07(12)
C(38)-P(1)-N(1)	99.71(13)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1^+.** The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(44)	17(2)	40(2)	35(2)	-12(2)	1(1)	-7(1)
O(1)	25(1)	62(2)	29(1)	-5(1)	-1(1)	-8(1)
O(2)	18(1)	50(2)	40(2)	-16(1)	6(1)	-6(1)
O(3)	21(1)	42(1)	39(1)	-7(1)	5(1)	-8(1)
F(1)	28(1)	50(1)	66(2)	-18(1)	13(1)	-17(1)
F(2)	22(1)	83(2)	38(1)	-20(1)	-7(1)	-1(1)
F(3)	18(1)	56(1)	42(1)	-23(1)	7(1)	-6(1)
S(1)	14(1)	35(1)	24(1)	-6(1)	0(1)	-6(1)
C(45)	16(2)	35(2)	28(2)	-6(1)	6(1)	-7(1)
Cl(1)	18(1)	54(1)	35(1)	-16(1)	4(1)	-13(1)
Cl(2)	32(1)	40(1)	32(1)	-1(1)	13(1)	-4(1)
Cl(3)	19(1)	42(1)	33(1)	-9(1)	-1(1)	-7(1)
C(1)	10(1)	31(2)	19(2)	-4(1)	3(1)	-3(1)
C(2)	13(1)	34(2)	20(2)	-4(1)	4(1)	-5(1)
C(3)	11(1)	32(2)	25(2)	-5(1)	2(1)	-7(1)
C(4)	11(1)	30(2)	23(2)	-6(1)	0(1)	-4(1)
C(5)	10(1)	30(2)	22(2)	-6(1)	1(1)	-3(1)
C(6)	10(1)	33(2)	22(2)	-9(1)	1(1)	-5(1)
C(7)	12(1)	33(2)	22(2)	-9(1)	0(1)	-4(1)
C(8)	15(2)	29(2)	20(2)	-3(1)	3(1)	-3(1)
C(9)	12(1)	30(2)	20(2)	-4(1)	4(1)	-4(1)
C(10)	12(1)	31(2)	23(2)	-7(1)	2(1)	-2(1)
C(11)	12(1)	29(2)	21(2)	-3(1)	6(1)	-6(1)
C(12)	9(1)	31(2)	26(2)	-5(1)	3(1)	-6(1)
C(13)	10(1)	32(2)	29(2)	-9(1)	3(1)	-7(1)
C(14)	13(1)	31(2)	22(2)	-7(1)	0(1)	-3(1)
C(15)	10(1)	30(2)	26(2)	-6(1)	0(1)	-7(1)
C(16)	13(1)	32(2)	23(2)	-6(1)	2(1)	-7(1)
C(17)	13(2)	36(2)	22(2)	-8(1)	3(1)	-6(1)
C(18)	13(1)	31(2)	20(2)	-6(1)	1(1)	-4(1)
C(19)	11(1)	31(2)	21(2)	-6(1)	3(1)	-4(1)

C(20)	15(1)	30(2)	18(2)	-3(1)	1(1)	-7(1)
C(21)	14(2)	36(2)	23(2)	-7(1)	2(1)	-5(1)
C(22)	15(2)	42(2)	25(2)	-6(1)	0(1)	-8(1)
C(23)	22(2)	34(2)	26(2)	-7(1)	-1(1)	-13(1)
C(24)	21(2)	31(2)	25(2)	-9(1)	2(1)	-4(1)
C(25)	13(2)	36(2)	21(2)	-6(1)	2(1)	-6(1)
C(26)	7(1)	37(2)	21(2)	-5(1)	-1(1)	-5(1)
C(27)	12(1)	36(2)	25(2)	-5(1)	-1(1)	-5(1)
C(28)	13(2)	49(2)	25(2)	-11(2)	2(1)	-6(1)
C(29)	14(2)	48(2)	22(2)	-2(2)	0(1)	-11(1)
C(30)	11(2)	38(2)	28(2)	-1(1)	-3(1)	-9(1)
C(31)	9(1)	39(2)	24(2)	-8(1)	1(1)	-6(1)
C(32)	13(1)	30(2)	20(2)	-6(1)	3(1)	-6(1)
C(33)	15(2)	35(2)	25(2)	-8(1)	4(1)	-6(1)
C(34)	21(2)	36(2)	20(2)	-4(1)	-4(1)	-3(1)
C(35)	21(2)	34(2)	22(2)	-7(1)	6(1)	-7(1)
C(36)	13(2)	34(2)	24(2)	-8(1)	4(1)	-7(1)
C(37)	16(2)	29(2)	23(2)	-6(1)	-1(1)	-7(1)
C(38)	8(1)	31(2)	24(2)	-6(1)	2(1)	-7(1)
C(39)	13(1)	34(2)	22(2)	-6(1)	6(1)	-8(1)
C(40)	14(2)	35(2)	23(2)	-2(1)	1(1)	-7(1)
C(41)	12(1)	31(2)	32(2)	-7(1)	3(1)	-6(1)
C(42)	16(2)	34(2)	26(2)	-11(1)	6(1)	-9(1)
C(43)	12(1)	35(2)	21(2)	-5(1)	1(1)	-8(1)
N(1)	11(1)	30(1)	20(1)	-6(1)	4(1)	-6(1)
N(2)	10(1)	31(1)	22(1)	-6(1)	3(1)	-8(1)
N(3)	12(1)	32(1)	19(1)	-7(1)	4(1)	-7(1)
N(4)	10(1)	32(1)	19(1)	-6(1)	3(1)	-7(1)
P(1)	9(1)	30(1)	19(1)	-5(1)	3(1)	-6(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1^+.**

	x	y	z	U(eq)
H(45)	2910(30)	9370(20)	9380(20)	9(7)
H(43)	6920(30)	7170(30)	5470(30)	15(8)
H(25)	9210(40)	8640(30)	6140(30)	23(9)
H(12)	5270(30)	3280(30)	5710(30)	23(9)
H(39)	6970(30)	7500(30)	2580(30)	29(9)
H(7)	9850(40)	6380(30)	7010(30)	30(10)
H(8)	8420(30)	5020(30)	7620(30)	24(9)
H(42)	5700(30)	8680(30)	5420(30)	26(9)
H(2)	11010(30)	8070(30)	1920(30)	28(9)
H(13)	5430(40)	3410(40)	3960(30)	47(13)
H(36)	12620(40)	7050(30)	-440(30)	27(9)
H(40)	5670(30)	9050(30)	2500(30)	20(8)
H(33)	8590(40)	7300(30)	160(30)	29(9)
H(37)	11700(30)	6510(30)	1140(30)	29(10)
H(16)	6740(40)	4270(30)	1750(30)	31(10)
H(30)	6010(30)	1660(30)	8540(20)	8(7)
H(35)	11460(30)	7710(30)	-1720(30)	30(10)
H(24)	10150(30)	9730(30)	6900(20)	11(7)
H(17)	8370(40)	5310(30)	700(30)	38(10)
H(22)	13180(40)	8700(30)	5720(30)	32(10)
H(29)	5300(40)	2690(30)	9660(30)	41(11)
H(34)	9560(40)	7820(30)	-1360(30)	29(10)
H(23)	12130(30)	9820(30)	6670(30)	22(8)
H(27)	6100(30)	5390(30)	7710(30)	23(9)
H(3)	11170(30)	8540(30)	3490(20)	20(8)
H(31)	6720(30)	2410(20)	7080(20)	9(7)
H(28)	5260(30)	4550(30)	9190(30)	29(10)
H(41)	5110(30)	9660(30)	3900(20)	22(9)
H(21)	12220(30)	7530(30)	4960(30)	20(8)

Table S6. Torsion angles [°] for $\mathbf{1}^{+}$.

F(2)-C(44)-S(1)-O(1)	-173.3(2)
F(1)-C(44)-S(1)-O(1)	66.1(3)
F(3)-C(44)-S(1)-O(1)	-53.4(3)
F(2)-C(44)-S(1)-O(2)	65.7(3)
F(1)-C(44)-S(1)-O(2)	-54.9(3)
F(3)-C(44)-S(1)-O(2)	-174.4(2)
F(2)-C(44)-S(1)-O(3)	-53.6(3)
F(1)-C(44)-S(1)-O(3)	-174.2(2)
F(3)-C(44)-S(1)-O(3)	66.3(3)
C(19)-C(1)-C(2)-C(3)	175.6(3)
N(1)-C(1)-C(2)-C(3)	-1.4(4)
C(1)-C(2)-C(3)-C(4)	2.5(4)
C(2)-C(3)-C(4)-C(5)	171.8(3)
C(2)-C(3)-C(4)-N(1)	-2.7(4)
C(3)-C(4)-C(5)-C(6)	-170.8(3)
N(1)-C(4)-C(5)-C(6)	3.0(5)
C(3)-C(4)-C(5)-C(20)	6.8(5)
N(1)-C(4)-C(5)-C(20)	-179.4(3)
C(4)-C(5)-C(6)-C(7)	169.6(3)
C(20)-C(5)-C(6)-C(7)	-8.1(5)
C(4)-C(5)-C(6)-N(2)	-13.1(5)
C(20)-C(5)-C(6)-N(2)	169.2(3)
C(5)-C(6)-C(7)-C(8)	173.9(3)
N(2)-C(6)-C(7)-C(8)	-3.7(4)
C(6)-C(7)-C(8)-C(9)	0.0(4)
C(7)-C(8)-C(9)-C(10)	-172.1(3)
C(7)-C(8)-C(9)-N(2)	3.6(3)
C(8)-C(9)-C(10)-C(11)	-179.0(3)
N(2)-C(9)-C(10)-C(11)	6.0(5)
C(8)-C(9)-C(10)-C(26)	0.4(5)
N(2)-C(9)-C(10)-C(26)	-174.6(3)
C(9)-C(10)-C(11)-N(3)	-0.2(4)
C(26)-C(10)-C(11)-N(3)	-179.6(3)
C(9)-C(10)-C(11)-C(12)	174.2(3)

C(26)-C(10)-C(11)-C(12)	-5.2(5)
C(10)-C(11)-C(12)-C(13)	-172.8(3)
N(3)-C(11)-C(12)-C(13)	2.1(4)
C(11)-C(12)-C(13)-C(14)	-1.2(4)
C(12)-C(13)-C(14)-N(3)	-0.2(4)
C(12)-C(13)-C(14)-C(15)	175.4(4)
N(3)-C(14)-C(15)-C(16)	169.1(4)
C(13)-C(14)-C(15)-C(16)	-6.4(7)
N(3)-C(14)-C(15)-N(4)	-3.1(4)
C(13)-C(14)-C(15)-N(4)	-178.6(4)
C(14)-C(15)-C(16)-C(17)	-171.3(4)
N(4)-C(15)-C(16)-C(17)	0.9(4)
C(15)-C(16)-C(17)-C(18)	-1.1(4)
C(16)-C(17)-C(18)-C(19)	-177.9(3)
C(16)-C(17)-C(18)-N(4)	1.0(4)
N(4)-C(18)-C(19)-C(1)	2.7(4)
C(17)-C(18)-C(19)-C(1)	-178.5(3)
N(4)-C(18)-C(19)-C(32)	-176.6(3)
C(17)-C(18)-C(19)-C(32)	2.2(5)
C(2)-C(1)-C(19)-C(18)	-172.2(3)
N(1)-C(1)-C(19)-C(18)	4.3(5)
C(2)-C(1)-C(19)-C(32)	7.1(5)
N(1)-C(1)-C(19)-C(32)	-176.4(3)
C(4)-C(5)-C(20)-C(25)	121.3(3)
C(6)-C(5)-C(20)-C(25)	-61.0(4)
C(4)-C(5)-C(20)-C(21)	-58.8(4)
C(6)-C(5)-C(20)-C(21)	118.8(3)
C(25)-C(20)-C(21)-C(22)	-0.6(5)
C(5)-C(20)-C(21)-C(22)	179.6(3)
C(20)-C(21)-C(22)-C(23)	0.5(5)
C(21)-C(22)-C(23)-C(24)	0.1(5)
C(22)-C(23)-C(24)-C(25)	-0.6(5)
C(23)-C(24)-C(25)-C(20)	0.6(5)
C(21)-C(20)-C(25)-C(24)	0.0(5)
C(5)-C(20)-C(25)-C(24)	179.9(3)
C(11)-C(10)-C(26)-C(31)	57.5(4)

C(9)-C(10)-C(26)-C(31)	-121.9(3)
C(11)-C(10)-C(26)-C(27)	-121.7(3)
C(9)-C(10)-C(26)-C(27)	58.9(4)
C(31)-C(26)-C(27)-C(28)	1.9(4)
C(10)-C(26)-C(27)-C(28)	-178.9(3)
C(26)-C(27)-C(28)-C(29)	0.0(5)
C(27)-C(28)-C(29)-C(30)	-1.3(5)
C(28)-C(29)-C(30)-C(31)	0.6(5)
C(27)-C(26)-C(31)-C(30)	-2.6(4)
C(10)-C(26)-C(31)-C(30)	178.2(3)
C(29)-C(30)-C(31)-C(26)	1.4(4)
C(18)-C(19)-C(32)-C(33)	50.5(4)
C(1)-C(19)-C(32)-C(33)	-128.8(3)
C(18)-C(19)-C(32)-C(37)	-129.3(3)
C(1)-C(19)-C(32)-C(37)	51.4(4)
C(37)-C(32)-C(33)-C(34)	-0.5(5)
C(19)-C(32)-C(33)-C(34)	179.7(3)
C(32)-C(33)-C(34)-C(35)	-0.2(5)
C(33)-C(34)-C(35)-C(36)	0.5(5)
C(34)-C(35)-C(36)-C(37)	0.0(5)
C(35)-C(36)-C(37)-C(32)	-0.7(5)
C(33)-C(32)-C(37)-C(36)	1.0(5)
C(19)-C(32)-C(37)-C(36)	-179.2(3)
C(43)-C(38)-C(39)-C(40)	0.4(4)
P(1)-C(38)-C(39)-C(40)	-178.1(2)
C(38)-C(39)-C(40)-C(41)	-0.6(4)
C(39)-C(40)-C(41)-C(42)	0.2(4)
C(40)-C(41)-C(42)-C(43)	0.5(5)
C(41)-C(42)-C(43)-C(38)	-0.7(4)
C(39)-C(38)-C(43)-C(42)	0.3(4)
P(1)-C(38)-C(43)-C(42)	178.8(2)
C(5)-C(4)-N(1)-C(1)	-172.9(3)
C(3)-C(4)-N(1)-C(1)	1.7(3)
C(5)-C(4)-N(1)-P(1)	25.8(4)
C(3)-C(4)-N(1)-P(1)	-159.5(2)
C(19)-C(1)-N(1)-C(4)	-177.2(3)

C(2)-C(1)-N(1)-C(4)	-0.2(3)
C(19)-C(1)-N(1)-P(1)	-17.1(5)
C(2)-C(1)-N(1)-P(1)	159.9(2)
C(5)-C(6)-N(2)-C(9)	-172.0(3)
C(7)-C(6)-N(2)-C(9)	5.7(3)
C(5)-C(6)-N(2)-P(1)	-6.1(4)
C(7)-C(6)-N(2)-P(1)	171.6(2)
C(10)-C(9)-N(2)-C(6)	170.1(3)
C(8)-C(9)-N(2)-C(6)	-5.6(3)
C(10)-C(9)-N(2)-P(1)	4.7(5)
C(8)-C(9)-N(2)-P(1)	-170.9(2)
C(15)-C(14)-N(3)-C(11)	-175.4(3)
C(13)-C(14)-N(3)-C(11)	1.4(3)
C(15)-C(14)-N(3)-P(1)	14.3(3)
C(13)-C(14)-N(3)-P(1)	-168.9(2)
C(10)-C(11)-N(3)-C(14)	173.5(3)
C(12)-C(11)-N(3)-C(14)	-2.1(3)
C(10)-C(11)-N(3)-P(1)	-18.9(5)
C(12)-C(11)-N(3)-P(1)	165.5(2)
C(16)-C(15)-N(4)-C(18)	-0.3(3)
C(14)-C(15)-N(4)-C(18)	174.2(3)
C(16)-C(15)-N(4)-P(1)	176.3(2)
C(14)-C(15)-N(4)-P(1)	-9.2(3)
C(19)-C(18)-N(4)-C(15)	178.6(3)
C(17)-C(18)-N(4)-C(15)	-0.4(3)
C(19)-C(18)-N(4)-P(1)	3.0(5)
C(17)-C(18)-N(4)-P(1)	-176.0(2)
C(15)-N(4)-P(1)-N(2)	82.7(3)
C(18)-N(4)-P(1)-N(2)	-102.0(4)
C(15)-N(4)-P(1)-N(3)	13.6(2)
C(18)-N(4)-P(1)-N(3)	-171.1(3)
C(15)-N(4)-P(1)-C(38)	-86.4(2)
C(18)-N(4)-P(1)-C(38)	88.8(3)
C(15)-N(4)-P(1)-N(1)	174.1(2)
C(18)-N(4)-P(1)-N(1)	-10.6(3)
C(6)-N(2)-P(1)-N(4)	115.3(3)

C(9)-N(2)-P(1)-N(4)	-82.3(4)
C(6)-N(2)-P(1)-N(3)	-176.9(3)
C(9)-N(2)-P(1)-N(3)	-14.5(3)
C(6)-N(2)-P(1)-C(38)	-75.4(3)
C(9)-N(2)-P(1)-C(38)	87.0(3)
C(6)-N(2)-P(1)-N(1)	25.1(3)
C(9)-N(2)-P(1)-N(1)	-172.5(3)
C(14)-N(3)-P(1)-N(4)	-15.6(2)
C(11)-N(3)-P(1)-N(4)	177.7(3)
C(14)-N(3)-P(1)-N(2)	-170.4(2)
C(11)-N(3)-P(1)-N(2)	22.9(3)
C(14)-N(3)-P(1)-C(38)	87.8(2)
C(11)-N(3)-P(1)-C(38)	-78.9(3)
C(14)-N(3)-P(1)-N(1)	-79.2(4)
C(11)-N(3)-P(1)-N(1)	114.1(4)
C(39)-C(38)-P(1)-N(4)	-15.4(3)
C(43)-C(38)-P(1)-N(4)	166.1(2)
C(39)-C(38)-P(1)-N(2)	169.7(2)
C(43)-C(38)-P(1)-N(2)	-8.9(3)
C(39)-C(38)-P(1)-N(3)	-100.2(2)
C(43)-C(38)-P(1)-N(3)	81.3(2)
C(39)-C(38)-P(1)-N(1)	75.0(3)
C(43)-C(38)-P(1)-N(1)	-103.6(2)
C(4)-N(1)-P(1)-N(4)	172.9(2)
C(1)-N(1)-P(1)-N(4)	16.3(3)
C(4)-N(1)-P(1)-N(2)	-34.2(3)
C(1)-N(1)-P(1)-N(2)	169.1(3)
C(4)-N(1)-P(1)-N(3)	-124.5(3)
C(1)-N(1)-P(1)-N(3)	78.8(4)
C(4)-N(1)-P(1)-C(38)	68.4(3)
C(1)-N(1)-P(1)-C(38)	-88.3(3)

Symmetry transformations used to generate equivalent atoms:

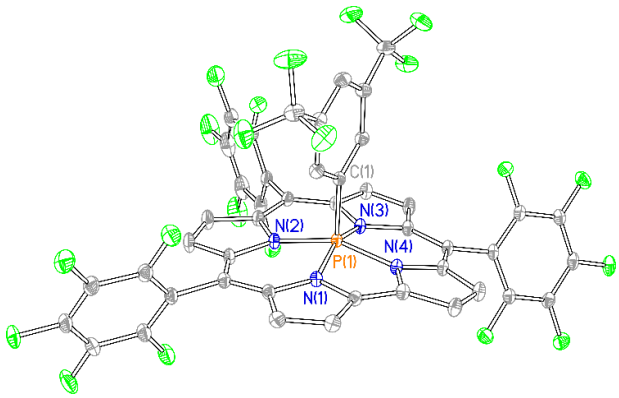


Table S7. Crystal data and structure refinement for $\mathbf{4}^{+}$.

Identification code	cg424	
Empirical formula	C69 H11 B F41 N4 P	
Formula weight	1716.60	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 23.0082(11) Å	a= 90°.
	b = 18.2410(9) Å	b= 127.241(2)°.
	c = 18.4271(9) Å	g = 90°.
Volume	6156.8(5) $Å^3$	
Z	4	
Density (calculated)	1.852 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	3368	
Crystal size	0.429 x 0.426 x 0.058 mm^3	
Theta range for data collection	1.576 to 36.420°.	
Index ranges	-38<=h<=38, -30<=k<=30, -30<=l<=30	
Reflections collected	290451	
Independent reflections	30013 [R(int) = 0.0635]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30013 / 2 / 1045	
Goodness-of-fit on F^2	1.026	

Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0901
R indices (all data)	R1 = 0.0499, wR2 = 0.0978
Absolute structure parameter	0.01(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.438 and -0.333 e.Å^{-3}

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4^+.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5360(1)	2632(1)	3152(1)	11(1)
F(21)	6294(1)	557(1)	5758(1)	22(1)
F(37)	3887(1)	1910(1)	7822(1)	22(1)
F(22)	5334(1)	1200(1)	9072(1)	23(1)
F(32)	3855(1)	2062(1)	5434(1)	22(1)
F(38)	2898(1)	852(1)	7277(1)	25(1)
F(17)	3771(1)	455(1)	3350(1)	21(1)
F(20)	6130(1)	-525(1)	6619(1)	24(1)
F(31)	5041(1)	3054(1)	6138(1)	24(1)
F(27)	5998(1)	998(1)	8106(1)	23(1)
F(2)	2246(1)	1588(1)	-86(1)	31(1)
F(19)	4818(1)	-1145(1)	5847(1)	24(1)
F(40)	3819(1)	-410(1)	5941(1)	31(1)
F(16)	5119(1)	4280(1)	5443(1)	28(1)
F(11)	5927(1)	4344(1)	1201(1)	26(1)
F(39)	2871(1)	-335(1)	6357(1)	30(1)
F(18)	3627(1)	-662(1)	4198(1)	25(1)
F(3)	2560(1)	1944(1)	1219(1)	29(1)
F(36)	4447(1)	3448(1)	7976(1)	32(1)
F(10)	6516(1)	5516(1)	972(1)	30(1)
F(28)	7055(1)	896(1)	7922(1)	31(1)
F(26)	5727(1)	3414(1)	8075(1)	28(1)
F(41)	4740(1)	668(1)	6368(1)	26(1)
F(7)	7311(1)	4879(1)	4338(1)	27(1)
F(9)	7494(1)	6382(1)	2434(1)	32(1)
F(5)	4570(1)	2279(1)	-343(1)	30(1)
F(1)	2088(1)	2713(1)	109(1)	30(1)
F(4)	3553(1)	2861(1)	-1177(1)	36(1)
F(25)	6828(1)	3741(1)	9799(1)	39(1)
F(30)	6066(1)	2912(1)	5911(1)	29(1)
F(29)	7117(1)	1851(1)	6833(1)	33(1)

F(8)	7908(1)	6039(1)	4105(1)	36(1)
F(23)	6434(1)	1534(1)	10770(1)	37(1)
F(6)	4545(1)	3432(1)	-167(1)	34(1)
F(12)	3183(1)	4360(1)	2310(1)	36(1)
F(24)	7207(1)	2794(1)	11177(1)	40(1)
F(33)	2709(1)	2923(1)	4329(1)	40(1)
F(35)	3317(1)	4302(1)	6865(2)	57(1)
N(2)	5431(1)	3607(1)	3328(1)	14(1)
N(1)	6065(1)	2694(1)	3018(1)	13(1)
F(13)	2522(1)	5400(1)	2641(2)	55(1)
F(15)	4405(1)	5233(1)	5774(2)	51(1)
F(34)	2423(1)	4073(1)	5028(2)	57(1)
N(4)	5666(1)	1703(1)	3427(1)	14(1)
N(3)	4951(1)	2505(1)	3721(1)	13(1)
F(14)	3102(1)	5794(1)	4359(2)	61(1)
C(17)	5016(1)	4043(1)	3495(1)	16(1)
C(19)	4548(1)	3032(1)	3813(1)	14(1)
C(27)	6105(1)	1459(1)	3196(1)	15(1)
C(45)	5632(1)	265(1)	5356(1)	16(1)
C(47)	5670(1)	1849(1)	9202(1)	19(1)
C(9)	6328(1)	2038(1)	2938(1)	14(1)
C(24)	5540(1)	1097(1)	3774(1)	14(1)
C(57)	5510(1)	2491(1)	6576(1)	18(1)
C(13)	6242(1)	3973(1)	2907(1)	16(1)
C(10)	6782(1)	2172(1)	2683(1)	17(1)
C(22)	4841(1)	1843(1)	4039(1)	15(1)
C(11)	6813(1)	2924(1)	2621(1)	16(1)
C(8)	2548(1)	2139(1)	519(1)	21(1)
C(23)	5127(1)	1163(1)	4084(1)	14(1)
C(14)	5798(1)	4126(1)	3155(1)	16(1)
C(44)	5559(1)	-295(1)	5804(1)	17(1)
C(7)	4173(1)	2810(1)	-339(1)	20(1)
C(67)	3350(1)	205(1)	6605(1)	21(1)
C(46)	5455(1)	2298(1)	8473(1)	17(1)
C(6)	3887(1)	2371(1)	1714(1)	15(1)
C(18)	4569(1)	3771(1)	3691(1)	15(1)

C(5)	3294(1)	2329(1)	798(1)	16(1)
C(66)	3372(1)	807(1)	7080(1)	19(1)
C(34)	4169(1)	4292(1)	3868(1)	18(1)
C(42)	4279(1)	-361(1)	4572(1)	17(1)
C(41)	4363(1)	208(1)	4146(1)	16(1)
C(1)	4572(1)	2568(1)	1962(1)	13(1)
C(26)	6243(1)	705(1)	3375(1)	18(1)
C(12)	6374(1)	3250(1)	2834(1)	14(1)
C(3)	4052(1)	2669(1)	367(1)	16(1)
C(2)	4650(1)	2723(1)	1282(1)	15(1)
C(43)	4884(1)	-608(1)	5412(1)	18(1)
C(4)	3371(1)	2473(1)	116(1)	18(1)
C(29)	7104(1)	5029(1)	3504(1)	20(1)
C(51)	5873(1)	2937(1)	8727(1)	21(1)
C(59)	3746(1)	2617(1)	5824(1)	20(1)
C(39)	4466(1)	4525(1)	4745(2)	22(1)
C(33)	6411(1)	4759(1)	1925(1)	18(1)
C(53)	5991(1)	1486(1)	7551(1)	18(1)
C(69)	4325(1)	739(1)	6658(1)	19(1)
C(20)	4187(1)	2700(1)	4131(1)	18(1)
C(32)	6706(1)	5364(1)	1793(1)	22(1)
C(40)	5037(1)	535(1)	4520(1)	14(1)
C(65)	3887(1)	1347(1)	7349(1)	17(1)
C(55)	6582(1)	1904(1)	6917(2)	23(1)
C(25)	5893(1)	481(1)	3734(1)	18(1)
C(31)	7202(1)	5799(1)	2534(2)	23(1)
C(52)	5444(1)	2016(1)	7113(1)	16(1)
C(68)	3832(1)	172(1)	6399(1)	22(1)
C(56)	6051(1)	2440(1)	6459(1)	22(1)
C(21)	4381(1)	1980(1)	4288(1)	18(1)
C(30)	7410(1)	5630(1)	3392(2)	23(1)
C(63)	4053(1)	3295(1)	7078(2)	25(1)
C(48)	6246(1)	2005(1)	10100(1)	24(1)
C(15)	5607(1)	4846(1)	3237(2)	22(1)
C(64)	4385(1)	1348(1)	7152(1)	16(1)
C(16)	5132(1)	4796(1)	3438(2)	22(1)

C(54)	6546(1)	1421(1)	7468(1)	22(1)
C(49)	6643(1)	2640(1)	10312(1)	27(1)
C(28)	6593(1)	4585(1)	2773(1)	16(1)
C(58)	4232(1)	2714(1)	6763(1)	18(1)
C(50)	6449(1)	3117(1)	9614(2)	26(1)
C(60)	3146(1)	3056(1)	5232(2)	28(1)
C(35)	3497(1)	4581(1)	3159(2)	26(1)
C(62)	3454(2)	3750(1)	6510(2)	35(1)
C(38)	4109(2)	5019(1)	4922(2)	34(1)
C(37)	3448(2)	5304(1)	4200(3)	40(1)
C(36)	3148(1)	5100(1)	3327(2)	37(1)
C(61)	3000(1)	3636(2)	5578(2)	36(1)
B(1)	4877(1)	2094(1)	7376(1)	16(1)

Table S9. Bond lengths [Å] and angles [°] for **4**$^{+}$.

P(1)-N(4)	1.7860(14)
P(1)-N(1)	1.7873(15)
P(1)-N(3)	1.7977(14)
P(1)-N(2)	1.7981(14)
P(1)-C(1)	1.8168(16)
F(21)-C(45)	1.336(2)
F(37)-C(65)	1.347(2)
F(22)-C(47)	1.353(2)
F(32)-C(59)	1.349(2)
F(38)-C(66)	1.343(2)
F(17)-C(41)	1.339(2)
F(20)-C(44)	1.330(2)
F(31)-C(57)	1.348(2)
F(27)-C(53)	1.349(2)
F(2)-C(8)	1.340(2)
F(19)-C(43)	1.331(2)
F(40)-C(68)	1.345(2)
F(16)-C(39)	1.332(3)
F(11)-C(33)	1.339(2)

F(39)-C(67)	1.335(2)
F(18)-C(42)	1.332(2)
F(3)-C(8)	1.324(2)
F(36)-C(63)	1.350(3)
F(10)-C(32)	1.326(2)
F(28)-C(54)	1.344(2)
F(26)-C(51)	1.350(2)
F(41)-C(69)	1.355(2)
F(7)-C(29)	1.333(2)
F(9)-C(31)	1.329(2)
F(5)-C(7)	1.334(2)
F(1)-C(8)	1.348(2)
F(4)-C(7)	1.327(2)
F(25)-C(50)	1.347(2)
F(30)-C(56)	1.344(2)
F(29)-C(55)	1.334(2)
F(8)-C(30)	1.331(2)
F(23)-C(48)	1.342(3)
F(6)-C(7)	1.340(2)
F(12)-C(35)	1.327(3)
F(24)-C(49)	1.341(2)
F(33)-C(60)	1.347(3)
F(35)-C(62)	1.339(3)
N(2)-C(17)	1.413(2)
N(2)-C(14)	1.426(2)
N(1)-C(9)	1.387(2)
N(1)-C(12)	1.392(2)
F(13)-C(36)	1.329(3)
F(15)-C(38)	1.337(3)
F(34)-C(61)	1.340(3)
N(4)-C(27)	1.385(2)
N(4)-C(24)	1.393(2)
N(3)-C(19)	1.415(2)
N(3)-C(22)	1.429(2)
F(14)-C(37)	1.342(3)
C(17)-C(18)	1.371(2)

C(17)-C(16)	1.416(2)
C(19)-C(18)	1.374(2)
C(19)-C(20)	1.409(2)
C(27)-C(9)	1.381(2)
C(27)-C(26)	1.405(2)
C(45)-C(44)	1.385(2)
C(45)-C(40)	1.392(2)
C(47)-C(46)	1.384(3)
C(47)-C(48)	1.387(3)
C(9)-C(10)	1.401(2)
C(24)-C(23)	1.378(2)
C(24)-C(25)	1.415(2)
C(57)-C(56)	1.388(3)
C(57)-C(52)	1.391(2)
C(13)-C(14)	1.377(2)
C(13)-C(12)	1.377(2)
C(13)-C(28)	1.484(2)
C(10)-C(11)	1.383(2)
C(10)-H(1)	0.9500
C(22)-C(23)	1.383(2)
C(22)-C(21)	1.409(2)
C(11)-C(12)	1.417(2)
C(11)-H(2)	0.9500
C(8)-C(5)	1.505(3)
C(23)-C(40)	1.485(2)
C(14)-C(15)	1.422(2)
C(44)-C(43)	1.380(3)
C(7)-C(3)	1.507(2)
C(67)-C(68)	1.373(3)
C(67)-C(66)	1.386(3)
C(46)-C(51)	1.399(3)
C(46)-B(1)	1.656(3)
C(6)-C(5)	1.389(2)
C(6)-C(1)	1.395(2)
C(6)-H(11)	0.9500
C(18)-C(34)	1.490(2)

C(5)-C(4)	1.395(3)
C(66)-C(65)	1.382(3)
C(34)-C(39)	1.386(3)
C(34)-C(35)	1.390(3)
C(42)-C(41)	1.385(2)
C(42)-C(43)	1.389(3)
C(41)-C(40)	1.393(2)
C(1)-C(2)	1.397(2)
C(26)-C(25)	1.377(3)
C(26)-H(8)	0.9500
C(3)-C(4)	1.386(3)
C(3)-C(2)	1.393(2)
C(2)-H(9)	0.9500
C(4)-H(10)	0.9500
C(29)-C(30)	1.385(3)
C(29)-C(28)	1.391(3)
C(51)-C(50)	1.383(3)
C(59)-C(60)	1.384(3)
C(59)-C(58)	1.392(3)
C(39)-C(38)	1.385(3)
C(33)-C(28)	1.388(3)
C(33)-C(32)	1.393(3)
C(53)-C(54)	1.379(3)
C(53)-C(52)	1.394(3)
C(69)-C(68)	1.389(3)
C(69)-C(64)	1.390(2)
C(20)-C(21)	1.360(2)
C(20)-H(5)	0.9500
C(32)-C(31)	1.381(3)
C(65)-C(64)	1.395(2)
C(55)-C(56)	1.383(3)
C(55)-C(54)	1.384(3)
C(25)-H(7)	0.9500
C(31)-C(30)	1.383(3)
C(52)-B(1)	1.650(3)
C(21)-H(6)	0.9500

C(63)-C(58)	1.385(3)
C(63)-C(62)	1.391(3)
C(48)-C(49)	1.376(3)
C(15)-C(16)	1.353(3)
C(15)-H(3)	0.9500
C(64)-B(1)	1.654(3)
C(16)-H(4)	0.9500
C(49)-C(50)	1.384(3)
C(58)-B(1)	1.652(3)
C(60)-C(61)	1.378(4)
C(35)-C(36)	1.391(3)
C(62)-C(61)	1.382(4)
C(38)-C(37)	1.379(4)
C(37)-C(36)	1.364(5)
N(4)-P(1)-N(1)	82.15(7)
N(4)-P(1)-N(3)	88.21(6)
N(1)-P(1)-N(3)	158.21(7)
N(4)-P(1)-N(2)	155.48(7)
N(1)-P(1)-N(2)	88.35(7)
N(3)-P(1)-N(2)	92.57(7)
N(4)-P(1)-C(1)	102.47(7)
N(1)-P(1)-C(1)	99.40(7)
N(3)-P(1)-C(1)	101.75(7)
N(2)-P(1)-C(1)	101.35(7)
C(17)-N(2)-C(14)	104.19(13)
C(17)-N(2)-P(1)	126.60(11)
C(14)-N(2)-P(1)	128.14(12)
C(9)-N(1)-C(12)	106.40(14)
C(9)-N(1)-P(1)	116.87(11)
C(12)-N(1)-P(1)	135.95(12)
C(27)-N(4)-C(24)	106.14(13)
C(27)-N(4)-P(1)	117.00(11)
C(24)-N(4)-P(1)	136.66(12)
C(19)-N(3)-C(22)	103.55(13)
C(19)-N(3)-P(1)	126.51(11)
C(22)-N(3)-P(1)	129.15(11)

C(18)-C(17)-N(2)	124.55(15)
C(18)-C(17)-C(16)	125.23(16)
N(2)-C(17)-C(16)	110.22(15)
C(18)-C(19)-C(20)	125.30(15)
C(18)-C(19)-N(3)	123.81(15)
C(20)-C(19)-N(3)	110.61(14)
C(9)-C(27)-N(4)	110.63(14)
C(9)-C(27)-C(26)	138.70(16)
N(4)-C(27)-C(26)	110.33(14)
F(21)-C(45)-C(44)	118.17(16)
F(21)-C(45)-C(40)	120.00(15)
C(44)-C(45)-C(40)	121.82(16)
F(22)-C(47)-C(46)	121.04(16)
F(22)-C(47)-C(48)	114.97(17)
C(46)-C(47)-C(48)	123.95(17)
C(27)-C(9)-N(1)	110.19(14)
C(27)-C(9)-C(10)	139.24(16)
N(1)-C(9)-C(10)	110.35(14)
C(23)-C(24)-N(4)	120.53(14)
C(23)-C(24)-C(25)	130.74(15)
N(4)-C(24)-C(25)	108.73(14)
F(31)-C(57)-C(56)	115.24(16)
F(31)-C(57)-C(52)	120.50(16)
C(56)-C(57)-C(52)	124.26(17)
C(14)-C(13)-C(12)	118.52(15)
C(14)-C(13)-C(28)	119.35(15)
C(12)-C(13)-C(28)	122.06(16)
C(11)-C(10)-C(9)	106.61(15)
C(11)-C(10)-H(1)	126.7
C(9)-C(10)-H(1)	126.7
C(23)-C(22)-C(21)	124.35(15)
C(23)-C(22)-N(3)	125.99(15)
C(21)-C(22)-N(3)	109.65(14)
C(10)-C(11)-C(12)	108.20(15)
C(10)-C(11)-H(2)	125.9
C(12)-C(11)-H(2)	125.9

F(3)-C(8)-F(2)	107.62(17)
F(3)-C(8)-F(1)	107.54(17)
F(2)-C(8)-F(1)	106.23(16)
F(3)-C(8)-C(5)	112.54(15)
F(2)-C(8)-C(5)	111.56(16)
F(1)-C(8)-C(5)	111.05(16)
C(24)-C(23)-C(22)	118.36(14)
C(24)-C(23)-C(40)	121.00(14)
C(22)-C(23)-C(40)	120.47(15)
C(13)-C(14)-C(15)	124.10(15)
C(13)-C(14)-N(2)	126.73(15)
C(15)-C(14)-N(2)	109.11(15)
F(20)-C(44)-C(43)	119.25(16)
F(20)-C(44)-C(45)	120.88(17)
C(43)-C(44)-C(45)	119.85(16)
F(4)-C(7)-F(5)	107.55(16)
F(4)-C(7)-F(6)	107.34(17)
F(5)-C(7)-F(6)	105.95(17)
F(4)-C(7)-C(3)	112.77(16)
F(5)-C(7)-C(3)	111.44(16)
F(6)-C(7)-C(3)	111.43(15)
F(39)-C(67)-C(68)	120.65(17)
F(39)-C(67)-C(66)	120.51(18)
C(68)-C(67)-C(66)	118.84(17)
C(47)-C(46)-C(51)	113.54(17)
C(47)-C(46)-B(1)	127.07(15)
C(51)-C(46)-B(1)	118.51(15)
C(5)-C(6)-C(1)	119.66(15)
C(5)-C(6)-H(11)	120.2
C(1)-C(6)-H(11)	120.2
C(17)-C(18)-C(19)	120.33(15)
C(17)-C(18)-C(34)	119.15(14)
C(19)-C(18)-C(34)	120.20(15)
C(6)-C(5)-C(4)	121.23(16)
C(6)-C(5)-C(8)	120.39(16)
C(4)-C(5)-C(8)	118.37(16)

F(38)-C(66)-C(65)	121.25(17)
F(38)-C(66)-C(67)	119.60(17)
C(65)-C(66)-C(67)	119.15(17)
C(39)-C(34)-C(35)	117.58(18)
C(39)-C(34)-C(18)	121.10(17)
C(35)-C(34)-C(18)	121.29(18)
F(18)-C(42)-C(41)	121.03(17)
F(18)-C(42)-C(43)	119.97(16)
C(41)-C(42)-C(43)	118.99(16)
F(17)-C(41)-C(42)	118.28(16)
F(17)-C(41)-C(40)	119.27(15)
C(42)-C(41)-C(40)	122.45(16)
C(6)-C(1)-C(2)	119.44(15)
C(6)-C(1)-P(1)	121.02(12)
C(2)-C(1)-P(1)	119.54(13)
C(25)-C(26)-C(27)	106.67(15)
C(25)-C(26)-H(8)	126.7
C(27)-C(26)-H(8)	126.7
C(13)-C(12)-N(1)	119.97(15)
C(13)-C(12)-C(11)	131.59(16)
N(1)-C(12)-C(11)	108.41(14)
C(4)-C(3)-C(2)	120.71(15)
C(4)-C(3)-C(7)	121.19(16)
C(2)-C(3)-C(7)	118.08(16)
C(3)-C(2)-C(1)	120.17(16)
C(3)-C(2)-H(9)	119.9
C(1)-C(2)-H(9)	119.9
F(19)-C(43)-C(44)	119.52(17)
F(19)-C(43)-C(42)	120.42(17)
C(44)-C(43)-C(42)	120.05(15)
C(3)-C(4)-C(5)	118.79(16)
C(3)-C(4)-H(10)	120.6
C(5)-C(4)-H(10)	120.6
F(7)-C(29)-C(30)	118.34(17)
F(7)-C(29)-C(28)	120.07(16)
C(30)-C(29)-C(28)	121.59(18)

F(26)-C(51)-C(50)	116.31(17)
F(26)-C(51)-C(46)	119.23(17)
C(50)-C(51)-C(46)	124.45(18)
F(32)-C(59)-C(60)	115.69(18)
F(32)-C(59)-C(58)	119.34(17)
C(60)-C(59)-C(58)	124.97(19)
F(16)-C(39)-C(38)	118.3(2)
F(16)-C(39)-C(34)	119.72(17)
C(38)-C(39)-C(34)	122.0(2)
F(11)-C(33)-C(28)	119.66(16)
F(11)-C(33)-C(32)	118.29(17)
C(28)-C(33)-C(32)	122.04(18)
F(27)-C(53)-C(54)	116.18(17)
F(27)-C(53)-C(52)	119.22(16)
C(54)-C(53)-C(52)	124.59(17)
F(41)-C(69)-C(68)	114.75(15)
F(41)-C(69)-C(64)	121.35(16)
C(68)-C(69)-C(64)	123.88(17)
C(21)-C(20)-C(19)	107.62(15)
C(21)-C(20)-H(5)	126.2
C(19)-C(20)-H(5)	126.2
F(10)-C(32)-C(31)	120.83(17)
F(10)-C(32)-C(33)	120.37(19)
C(31)-C(32)-C(33)	118.80(18)
C(45)-C(40)-C(41)	116.83(15)
C(45)-C(40)-C(23)	120.39(15)
C(41)-C(40)-C(23)	122.73(15)
F(37)-C(65)-C(66)	116.02(16)
F(37)-C(65)-C(64)	119.31(15)
C(66)-C(65)-C(64)	124.67(16)
F(29)-C(55)-C(56)	121.15(19)
F(29)-C(55)-C(54)	120.53(19)
C(56)-C(55)-C(54)	118.32(18)
C(26)-C(25)-C(24)	108.12(15)
C(26)-C(25)-H(7)	125.9
C(24)-C(25)-H(7)	125.9

F(9)-C(31)-C(32)	120.53(19)
F(9)-C(31)-C(30)	118.85(19)
C(32)-C(31)-C(30)	120.62(17)
C(57)-C(52)-C(53)	113.22(16)
C(57)-C(52)-B(1)	126.99(15)
C(53)-C(52)-B(1)	119.19(15)
F(40)-C(68)-C(67)	119.63(17)
F(40)-C(68)-C(69)	120.33(18)
C(67)-C(68)-C(69)	120.04(17)
F(30)-C(56)-C(55)	119.73(18)
F(30)-C(56)-C(57)	120.49(18)
C(55)-C(56)-C(57)	119.78(18)
C(20)-C(21)-C(22)	108.49(15)
C(20)-C(21)-H(6)	125.8
C(22)-C(21)-H(6)	125.8
F(8)-C(30)-C(31)	119.96(17)
F(8)-C(30)-C(29)	120.53(19)
C(31)-C(30)-C(29)	119.50(19)
F(36)-C(63)-C(58)	121.46(18)
F(36)-C(63)-C(62)	115.04(19)
C(58)-C(63)-C(62)	123.5(2)
F(23)-C(48)-C(49)	119.25(19)
F(23)-C(48)-C(47)	120.59(18)
C(49)-C(48)-C(47)	120.14(19)
C(16)-C(15)-C(14)	108.56(15)
C(16)-C(15)-H(3)	125.7
C(14)-C(15)-H(3)	125.7
C(69)-C(64)-C(65)	113.38(15)
C(69)-C(64)-B(1)	127.11(16)
C(65)-C(64)-B(1)	118.80(15)
C(15)-C(16)-C(17)	107.91(16)
C(15)-C(16)-H(4)	126.0
C(17)-C(16)-H(4)	126.0
F(28)-C(54)-C(53)	120.59(19)
F(28)-C(54)-C(55)	119.61(18)
C(53)-C(54)-C(55)	119.80(18)

F(24)-C(49)-C(48)	120.8(2)
F(24)-C(49)-C(50)	120.6(2)
C(48)-C(49)-C(50)	118.65(19)
C(33)-C(28)-C(29)	117.42(16)
C(33)-C(28)-C(13)	122.39(16)
C(29)-C(28)-C(13)	120.15(16)
C(63)-C(58)-C(59)	113.57(18)
C(63)-C(58)-B(1)	127.61(17)
C(59)-C(58)-B(1)	118.38(15)
F(25)-C(50)-C(51)	120.7(2)
F(25)-C(50)-C(49)	120.03(19)
C(51)-C(50)-C(49)	119.27(18)
F(33)-C(60)-C(61)	120.1(2)
F(33)-C(60)-C(59)	120.8(2)
C(61)-C(60)-C(59)	119.1(2)
F(12)-C(35)-C(34)	119.69(19)
F(12)-C(35)-C(36)	119.5(2)
C(34)-C(35)-C(36)	120.8(2)
F(35)-C(62)-C(61)	119.7(2)
F(35)-C(62)-C(63)	120.0(2)
C(61)-C(62)-C(63)	120.3(2)
F(15)-C(38)-C(37)	120.3(2)
F(15)-C(38)-C(39)	120.9(3)
C(37)-C(38)-C(39)	118.8(3)
F(14)-C(37)-C(36)	119.7(3)
F(14)-C(37)-C(38)	119.5(3)
C(36)-C(37)-C(38)	120.7(2)
F(13)-C(36)-C(37)	119.6(2)
F(13)-C(36)-C(35)	120.5(3)
C(37)-C(36)-C(35)	120.0(2)
F(34)-C(61)-C(60)	121.0(2)
F(34)-C(61)-C(62)	120.5(2)
C(60)-C(61)-C(62)	118.5(2)
C(52)-B(1)-C(58)	113.64(14)
C(52)-B(1)-C(64)	113.50(13)
C(58)-B(1)-C(64)	101.41(14)

C(52)-B(1)-C(46)	100.63(14)
C(58)-B(1)-C(46)	113.94(14)
C(64)-B(1)-C(46)	114.33(14)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4^+.** The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	14(1)	10(1)	11(1)	0(1)	8(1)	-1(1)
F(21)	21(1)	23(1)	19(1)	1(1)	10(1)	-4(1)
F(37)	30(1)	19(1)	24(1)	-6(1)	21(1)	-2(1)
F(22)	31(1)	18(1)	20(1)	0(1)	15(1)	-7(1)
F(32)	25(1)	26(1)	18(1)	-3(1)	14(1)	-1(1)
F(38)	26(1)	27(1)	30(1)	-1(1)	22(1)	-3(1)
F(17)	20(1)	20(1)	18(1)	3(1)	9(1)	0(1)
F(20)	28(1)	24(1)	16(1)	6(1)	11(1)	2(1)
F(31)	24(1)	22(1)	26(1)	9(1)	16(1)	3(1)
F(27)	32(1)	15(1)	26(1)	5(1)	19(1)	3(1)
F(2)	24(1)	36(1)	25(1)	-8(1)	11(1)	-11(1)
F(19)	38(1)	16(1)	27(1)	5(1)	23(1)	-2(1)
F(40)	38(1)	21(1)	41(1)	-18(1)	28(1)	-11(1)
F(16)	36(1)	22(1)	25(1)	0(1)	18(1)	1(1)
F(11)	30(1)	27(1)	20(1)	-1(1)	15(1)	-5(1)
F(39)	32(1)	24(1)	37(1)	-10(1)	23(1)	-14(1)
F(18)	25(1)	24(1)	28(1)	-1(1)	16(1)	-8(1)
F(3)	21(1)	46(1)	21(1)	5(1)	13(1)	-3(1)
F(36)	43(1)	23(1)	29(1)	-8(1)	21(1)	4(1)
F(10)	33(1)	37(1)	29(1)	12(1)	23(1)	1(1)
F(28)	29(1)	24(1)	40(1)	2(1)	21(1)	8(1)
F(26)	42(1)	14(1)	26(1)	-1(1)	19(1)	-8(1)
F(41)	33(1)	24(1)	35(1)	-14(1)	28(1)	-9(1)
F(7)	32(1)	27(1)	20(1)	-2(1)	14(1)	-11(1)

F(9)	31(1)	25(1)	45(1)	11(1)	25(1)	-6(1)
F(5)	41(1)	34(1)	29(1)	6(1)	28(1)	12(1)
F(1)	19(1)	39(1)	28(1)	7(1)	11(1)	8(1)
F(4)	26(1)	69(1)	14(1)	8(1)	12(1)	7(1)
F(25)	47(1)	29(1)	32(1)	-12(1)	20(1)	-22(1)
F(30)	31(1)	33(1)	32(1)	6(1)	23(1)	-4(1)
F(29)	30(1)	35(1)	47(1)	-4(1)	30(1)	-3(1)
F(8)	36(1)	30(1)	35(1)	-7(1)	18(1)	-20(1)
F(23)	43(1)	42(1)	17(1)	4(1)	14(1)	-10(1)
F(6)	53(1)	30(1)	32(1)	0(1)	33(1)	-8(1)
F(12)	26(1)	27(1)	34(1)	7(1)	7(1)	-1(1)
F(24)	39(1)	50(1)	19(1)	-12(1)	12(1)	-19(1)
F(33)	31(1)	51(1)	22(1)	7(1)	8(1)	9(1)
F(35)	61(1)	37(1)	60(1)	-7(1)	30(1)	25(1)
N(2)	18(1)	9(1)	18(1)	0(1)	12(1)	-1(1)
N(1)	16(1)	11(1)	15(1)	0(1)	11(1)	-1(1)
F(13)	23(1)	28(1)	99(2)	16(1)	28(1)	10(1)
F(15)	85(1)	36(1)	68(1)	-20(1)	66(1)	-10(1)
F(34)	47(1)	49(1)	52(1)	12(1)	18(1)	29(1)
N(4)	18(1)	10(1)	15(1)	1(1)	11(1)	1(1)
N(3)	18(1)	10(1)	14(1)	0(1)	12(1)	0(1)
F(14)	66(1)	26(1)	133(2)	-10(1)	83(2)	3(1)
C(17)	19(1)	12(1)	22(1)	1(1)	14(1)	0(1)
C(19)	17(1)	12(1)	15(1)	0(1)	11(1)	0(1)
C(27)	19(1)	13(1)	16(1)	-1(1)	12(1)	0(1)
C(45)	20(1)	14(1)	17(1)	0(1)	12(1)	-1(1)
C(47)	24(1)	16(1)	17(1)	-2(1)	13(1)	-4(1)
C(9)	16(1)	13(1)	13(1)	-1(1)	9(1)	1(1)
C(24)	20(1)	10(1)	15(1)	1(1)	12(1)	0(1)
C(57)	20(1)	18(1)	18(1)	1(1)	12(1)	-2(1)
C(13)	18(1)	13(1)	17(1)	2(1)	11(1)	-1(1)
C(10)	19(1)	18(1)	17(1)	0(1)	13(1)	1(1)
C(22)	21(1)	11(1)	15(1)	0(1)	13(1)	-1(1)
C(11)	18(1)	18(1)	16(1)	0(1)	12(1)	-1(1)
C(8)	16(1)	28(1)	15(1)	2(1)	8(1)	0(1)
C(23)	20(1)	11(1)	14(1)	0(1)	11(1)	-1(1)

C(14)	19(1)	11(1)	21(1)	1(1)	13(1)	-2(1)
C(44)	24(1)	15(1)	14(1)	2(1)	12(1)	1(1)
C(7)	22(1)	26(1)	14(1)	1(1)	12(1)	1(1)
C(67)	24(1)	18(1)	22(1)	-4(1)	14(1)	-7(1)
C(46)	23(1)	13(1)	17(1)	-2(1)	13(1)	-2(1)
C(6)	17(1)	15(1)	12(1)	1(1)	9(1)	1(1)
C(18)	17(1)	12(1)	18(1)	1(1)	12(1)	1(1)
C(5)	16(1)	19(1)	13(1)	0(1)	8(1)	0(1)
C(66)	22(1)	20(1)	19(1)	0(1)	14(1)	-2(1)
C(34)	19(1)	11(1)	28(1)	2(1)	16(1)	1(1)
C(42)	22(1)	14(1)	19(1)	-1(1)	14(1)	-3(1)
C(41)	21(1)	12(1)	17(1)	1(1)	12(1)	0(1)
C(1)	16(1)	12(1)	11(1)	0(1)	8(1)	0(1)
C(26)	25(1)	13(1)	21(1)	1(1)	16(1)	2(1)
C(12)	16(1)	14(1)	14(1)	1(1)	9(1)	-2(1)
C(3)	22(1)	17(1)	13(1)	1(1)	12(1)	2(1)
C(2)	17(1)	17(1)	13(1)	1(1)	10(1)	0(1)
C(43)	28(1)	12(1)	19(1)	1(1)	16(1)	-1(1)
C(4)	18(1)	20(1)	12(1)	0(1)	8(1)	1(1)
C(29)	22(1)	18(1)	22(1)	1(1)	14(1)	-4(1)
C(51)	30(1)	14(1)	20(1)	-3(1)	16(1)	-5(1)
C(59)	22(1)	20(1)	20(1)	2(1)	14(1)	0(1)
C(39)	30(1)	14(1)	33(1)	-1(1)	25(1)	0(1)
C(33)	21(1)	18(1)	21(1)	3(1)	14(1)	0(1)
C(53)	24(1)	14(1)	19(1)	-1(1)	13(1)	-1(1)
C(69)	25(1)	16(1)	22(1)	-6(1)	17(1)	-4(1)
C(20)	24(1)	14(1)	22(1)	1(1)	17(1)	1(1)
C(32)	23(1)	22(1)	26(1)	7(1)	18(1)	1(1)
C(40)	22(1)	10(1)	15(1)	0(1)	13(1)	-1(1)
C(65)	23(1)	15(1)	16(1)	-2(1)	13(1)	-2(1)
C(55)	22(1)	24(1)	27(1)	-6(1)	17(1)	-4(1)
C(25)	27(1)	12(1)	22(1)	1(1)	18(1)	1(1)
C(31)	22(1)	19(1)	34(1)	7(1)	19(1)	-2(1)
C(52)	20(1)	13(1)	16(1)	-1(1)	12(1)	-2(1)
C(68)	26(1)	17(1)	23(1)	-7(1)	16(1)	-5(1)
C(56)	23(1)	23(1)	22(1)	-1(1)	15(1)	-5(1)

C(21)	28(1)	14(1)	23(1)	1(1)	21(1)	0(1)
C(30)	22(1)	20(1)	27(1)	0(1)	14(1)	-6(1)
C(63)	31(1)	18(1)	27(1)	-2(1)	18(1)	3(1)
C(48)	29(1)	28(1)	16(1)	-2(1)	13(1)	-6(1)
C(15)	28(1)	10(1)	34(1)	1(1)	23(1)	-1(1)
C(64)	21(1)	14(1)	16(1)	-2(1)	12(1)	-2(1)
C(16)	28(1)	11(1)	37(1)	1(1)	24(1)	0(1)
C(54)	22(1)	18(1)	24(1)	-3(1)	14(1)	1(1)
C(49)	30(1)	31(1)	17(1)	-8(1)	12(1)	-9(1)
C(28)	18(1)	14(1)	21(1)	2(1)	14(1)	-1(1)
C(58)	22(1)	15(1)	19(1)	0(1)	14(1)	0(1)
C(50)	33(1)	22(1)	25(1)	-9(1)	17(1)	-11(1)
C(60)	26(1)	32(1)	22(1)	6(1)	12(1)	4(1)
C(35)	20(1)	16(1)	38(1)	5(1)	16(1)	2(1)
C(62)	40(1)	23(1)	41(1)	0(1)	24(1)	12(1)
C(38)	50(1)	19(1)	58(2)	-8(1)	47(1)	-4(1)
C(37)	42(1)	18(1)	87(2)	-5(1)	53(2)	0(1)
C(36)	21(1)	17(1)	71(2)	8(1)	27(1)	5(1)
C(61)	32(1)	32(1)	36(1)	8(1)	16(1)	14(1)
B(1)	22(1)	12(1)	16(1)	-2(1)	13(1)	-2(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4^+**.

	x	y	z	U(eq)
H(1)	7022	1815	2575	20
H(2)	7081	3179	2462	20
H(11)	3827	2266	2170	18
H(8)	6524	407	3269	22
H(9)	5112	2866	1446	18
H(10)	2963	2437	-509	21
H(5)	3866	2937	4219	21
H(7)	5890	-3	3921	22

H(6)	4231	1630	4526	22
H(3)	5784	5289	3163	26
H(4)	4915	5195	3525	27

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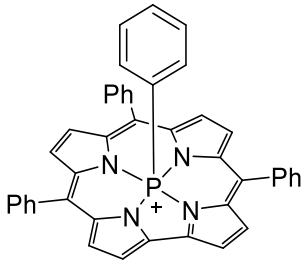
11. DFT calculations

The cationic portions of **1**$^+$–**3**$^+$ were optimized in the gas phase at the B3LYP/def2-TZVP level as implemented in the ORCA 4.0.0 package. The cationic fragment of **4**$^+$ was optimized using B3LYP/def2-SVP. The geometries of CF_2O and CF_3O were optimized in the gas phase at the B3LYP/def2-TZVP or def2-SVP level. All geometries were subjected to frequency calculations, and lack of any imaginary modes confirmed that the structures represented minima on their respective potential energy surfaces. The single point energies of **1**$^+$–**4**$^+$ were recomputed at the same level using the CPCM(CH_2Cl_2) solvent correction. These energies were used in calculating FIA and GEI. Fluoride ion affinities were computed according to Christe's method, taking 208.8 kJ/mol as the experimental FIA of CF_2O.[8]



1$^+$

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C	-1.38900	-0.84634	35.98511
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H	0.21257	-0.67804	37.47230
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C	1.85463	0.59430	35.56078
C	2.60506	0.44429	36.84383
C	3.22775	-0.76684	37.15756
H	3.17635	-1.59302	36.45853
C	3.91569	-0.91520	38.35750
H	4.39207	-1.85823	38.59295
C	3.99338	0.14457	39.25328
H	4.52711	0.02675	40.18734
C	3.38079	1.35474	38.94740
H	3.43673	2.18291	39.64274

C	2.68911	1.50317	37.75043
H	2.20184	2.44359	37.52345
C	2.39138	1.30975	34.51009
C	3.60161	2.03819	34.53977
H	4.29016	2.02560	35.36747
C	3.71445	2.72189	33.36799
H	4.51806	3.36687	33.05502
C	2.61572	2.39011	32.54416
C	2.51052	2.74784	31.20930
C	3.39234	3.78876	30.61848
C	3.20912	5.12332	30.99380
H	2.45188	5.37154	31.72753
C	3.97011	6.13075	30.41536
H	3.80454	7.15987	30.70854
C	4.93420	5.81547	29.46311
H	5.52817	6.59909	29.01137
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H	5.89172	4.23822	28.36306
C	4.36812	3.47880	29.66621
H	4.53738	2.44829	29.37823
C	1.58987	2.06230	30.43532
C	1.40337	1.99526	29.03617
H	1.97594	2.55724	28.31727
C	0.40599	1.07419	28.77533
H	0.02368	0.77112	27.81440
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C	-1.08261	-0.14561	30.54120
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H	-7.04940	-1.15752	34.00377
C	-6.06938	-2.80726	34.97173
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H	-2.84700	5.78978	33.65092
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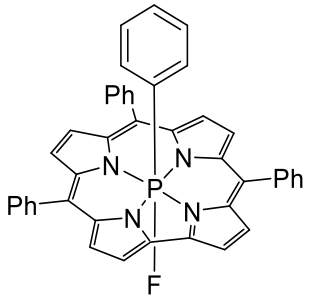
H	-3.47372	4.29630	31.77641
C	-1.93283	2.86667	32.19388

H	-2.22630	2.22458	31.37434
C	-0.85266	2.52868	33.01406
C	-0.50189	3.37964	34.06707
H	0.33148	3.14183	34.71378
P	0.10754	1.00909	32.72995



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H	0.14501	-0.65123	37.50719
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H	5.33291	-0.77682	38.13144
C	3.90851	0.34594	39.28342
H	4.44419	0.22458	40.21675
C	2.71906	1.06550	39.24640
H	2.32726	1.51675	40.14987
C	2.02800	1.21448	38.04915
H	1.10492	1.77941	38.02732
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H	4.47932	3.53949	33.10298
C	2.60351	2.49629	32.54568
C	2.50616	2.79853	31.18774
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H	-0.21321	1.11750	27.78042
C	-0.20315	0.83567	29.97819
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C	-5.97053	-3.05789	34.92061
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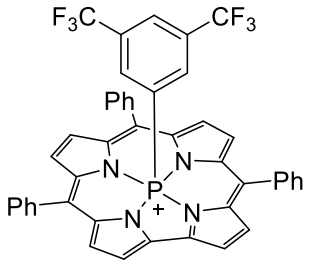

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H	4.26816	2.77838	32.21338
C	2.35303	1.69744	32.25173
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C	1.06061	0.73134	30.51991
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C	-2.63685	-0.65862	35.05059
C	-2.74574	4.36237	30.33538
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H	-6.15462	0.32078	37.91848
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C	3.54606	3.52236	28.02524
H	1.67452	3.44575	29.07242
C	4.83292	3.00647	27.92147
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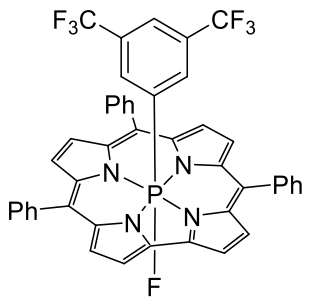

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H	4.43144	2.60026	32.91358
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H	-3.52659	-3.24907	34.95070
C	-1.30897	4.28719	34.49562
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C	-2.93719	4.93931	31.15797
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F	-1.37028	4.14895	36.85906
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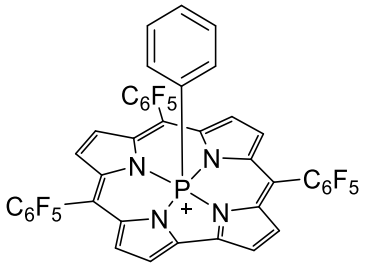

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F	2.68052	1.88623	39.97803
C	2.25221	0.98894	37.83925
F	1.56581	2.09526	37.52839
C	2.47948	0.71394	34.53153
C	3.79737	1.20399	34.64119
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C	4.12758	1.79124	33.46052
H	5.06334	2.25532	33.19890
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C	4.20905	2.86602	30.73057
C	4.37485	4.21961	31.02017
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C	5.45474	4.94721	30.54096
F	5.58217	6.23745	30.83255
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C	6.26988	2.96618	29.44247
F	7.18256	2.35908	28.69217
C	5.17805	2.26209	29.93095
F	5.07414	0.96341	29.63162
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C	1.81735	1.86115	29.04622
H	2.50752	2.34861	28.37767
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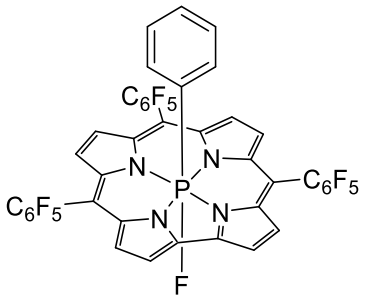

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C	2.43193	1.80251	37.69871

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C	3.75691	2.71270	33.21733
H	4.57916	3.31781	32.87413
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F	4.28613	7.11148	30.31165
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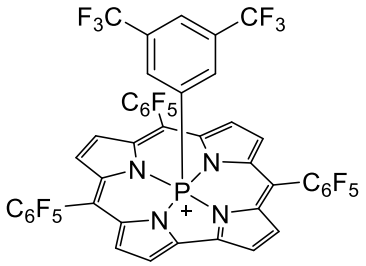

4^{+}

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F	5.43201	5.45387	-0.55102
F	4.51528	-2.46300	7.23383
F	5.44908	7.58476	8.33855
F	12.00450	7.62599	1.36749
F	3.97542	-1.08339	4.94849
F	5.21287	6.60118	1.28035
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F	11.99347	9.62972	5.65120
F	14.68938	11.38825	2.22365
F	9.34982	0.97192	1.40431
F	6.77135	7.10433	-0.13423
F	7.84865	1.23591	-0.14161
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F	9.81214	2.11280	-0.37822
F	4.99889	8.46126	3.71327
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N	10.70144	5.19525	4.65513
F	2.88889	10.08192	4.23099
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N	9.41167	3.36347	5.43339
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C	7.62860	7.58731	5.24394
C	6.29488	5.70713	5.93441
C	10.74911	3.01220	5.31864
C	6.85440	0.28340	7.54884
C	11.50485	4.08714	4.86403
C	8.71922	2.21373	5.80793
C	11.02918	7.50198	4.01726
C	12.84056	4.39113	4.53474
H	13.68690	3.71157	4.61181

C	6.71961	3.50008	6.04067
C	12.85104	5.71183	4.11286
H	13.71486	6.29613	3.80304
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C	9.71583	7.76199	4.40155
C	6.16349	-0.89482	7.84274
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H	7.13181	6.38569	2.87942
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C	7.05325	5.13671	1.13548
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H	11.86121	1.10933	5.63499
C	11.52488	6.21615	4.20011
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H	9.48380	2.73576	2.97824
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C	4.83561	8.19294	7.32437
C	12.42674	8.56091	2.21660
C	5.12161	5.05812	6.40032
H	4.20080	5.56793	6.66943
C	13.35142	9.50580	1.76516
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C	9.65538	1.15140	5.92001
H	9.40598	0.13406	6.21215
C	13.81256	10.49414	2.64224
C	5.37935	3.71722	6.45734
H	4.71031	2.92821	6.79083
C	13.34519	10.53341	3.96104
C	9.14295	9.05915	4.45685
H	9.65852	9.96452	4.14768
C	7.88842	8.95819	4.99020
H	7.19171	9.76428	5.20423
C	11.94221	8.57491	3.53352
C	4.60647	8.63816	4.97581
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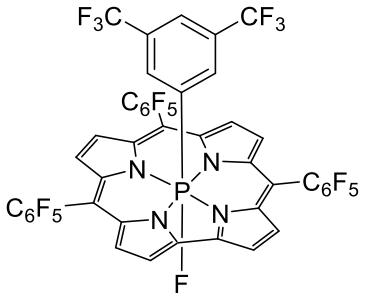

4•F

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C	2.50202	3.71346	30.85339
C	3.74850	4.13677	31.39664
H	4.57848	3.48129	31.60119
C	3.70408	5.48659	31.56140
H	4.48658	6.12487	31.93518
C	2.41598	5.93452	31.14900
C	1.92916	7.23783	31.22341
C	2.82673	8.30621	31.74795
C	3.83721	8.87395	30.97302
F	4.01040	8.47941	29.70808
C	4.68729	9.85295	31.47169
F	5.64731	10.37382	30.70634
C	4.53363	10.29407	32.77910
F	5.34178	11.23203	33.26689
C	3.53450	9.75379	33.57718
F	3.38751	10.17280	34.83428
C	2.70189	8.77348	33.05623
F	1.75840	8.26580	33.85533
C	0.61433	7.56240	30.89873
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H	0.51026	9.73997	31.33353
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H	-2.05240	9.49124	30.63904
C	-1.53235	7.36303	30.28454
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C	-3.91522	7.73111	29.63576
C	-4.89473	7.71797	30.62735
F	-4.73754	6.94963	31.70883
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F	-6.97128	8.44368	31.49519
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C	-1.97017	3.57004	28.63763
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H	-1.27571	0.63133	27.88803
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C	1.02659	2.16136	29.72291
C	2.20234	2.42459	30.42586
C	3.14971	1.31087	30.70583
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C	4.01152	-0.36624	32.24730
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C	4.88360	-0.82987	31.27146
F	5.70209	-1.84448	31.53713
C	4.89902	-0.23449	30.01724
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C	4.03853	0.82271	29.74976
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P	-0.05225	4.86804	30.09196
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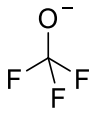
F	-2.77045	0.74585	32.83413
F	-4.32558	2.21736	32.50877
F	-3.69490	1.73703	34.52940
F	-0.76670	6.64658	35.45918
F	1.06153	5.48338	35.42751
F	-0.64494	4.79339	36.57629

CF_2O (def2-TZVP)

F	1.02054	0.05185	0.27277
C	-0.23765	-0.02128	0.60608
O	-0.65748	-0.06149	1.69029

F	-0.93419	-0.04412	-0.49582

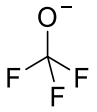


CF_3O (def2-TZVP)

F	0.93084	0.75207	0.49568
C	-0.17930	-0.10935	0.45464
O	-0.56719	-0.56402	1.51115
F	-1.08878	0.66831	-0.28203
F	0.23809	-1.03235	-0.52104

CF_2O (def2-SVP)

F	1.02233	0.05228	0.27347
C	-0.23548	-0.02226	0.60368
O	-0.65932	-0.06115	1.69050
F	-0.93632	-0.04392	-0.49433



CF_3O (def2-SVP)

F	0.93084	0.75207	0.49568
C	-0.17930	-0.10935	0.45464
O	-0.56719	-0.56402	1.51115
F	-1.08878	0.66831	-0.28203
F	0.23809	-1.03235	-0.52104

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