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Supporting Information

Copper-promoted an efficient dehydrogenative cross-coupling reaction of dialkyl phosphites with sulfoximines

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1) GENERAL INFORMATION:

Sulfoximines have been prepared using literature procedures.[1] The data for the sulfoximines were reported previously by our group[2] and other groups. All solvents and chemicals were purchased from commercial sources and used without further purifications. Molecular sieves were purchased from Aldrich chemicals. The reactions were carried out in round bottom flask equipped with an air condenser at refluxed condition. Thin layer chromatography was performed using pre-coated plates purchased from E. Merck (*TLC silica gel 60 F254*). TLC plates were visualized by exposure to ultraviolet light (UV) with 254 nm of wavelength and then further analyzed by using iodine chamber. The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate/hexane as an eluent. Purity of the products was analyzed by proton NMR spectra. FT-IR of all the samples are recorded on ALPHA BRUKER Eco-ATR fitted out on ZnSe ATR crystal in the range of 500–3000 cm^{-1}. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on *Bruker Avance 500 MHz NMR spectrometer* using $CDCl_3$. HRMS-Mass spectra were recorded on UHD Q-Tof (ESI-Tof) using *water's Quattro Micro V 4.1* mass analyzer. For the unknown compounds, IR and NMR data are mentioned. In proton NMR, $CDCl_3$ peak is graduated to 7.26 ppm and it is 77.16 ppm for ^{13}C NMR spectra.

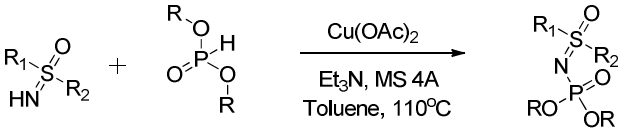
2) EXPERIMENTAL SECTION

2.1 Experimental Procedure for the Optimization Table

A mixture of *S,S*-methylphenylsulfoximine (155 mg, 1 mmol) and metal salt (appropriate amount) was stirred in a different solvent (5 mL) at room temperature for 5 minutes under open air condition. Round-bottom flask containing reaction mixture was transferred to pre-heated oil bath and stirred for 5 minutes at appropriate temperature to which diethyl phosphite (276 mg, in

3 mL of appropriate solvent) was added in the presence of or absence of molecular sieves (300 mg) and base (1 equiv.). The progress of the reaction was monitored by thin layer chromatography using ethyl acetate (EA)/hexane as an eluent. After completion of the reaction (or appropriate time), the reaction mixture was diluted with dichloromethane and washed with water and brine solution. The reaction mixture was dried over anhydrous sodium sulfate and evaporated. The crude product was purified on silica-gel (100-200 mesh) column chromatography using ethyl acetate/hexane as an eluent to obtain **3aa**. R_f (100% EA) 0.22.

2.2 Experimental Procedure for the Synthesis of Sulfoximine Derived Phosphoramidates with dialkyl phosphites

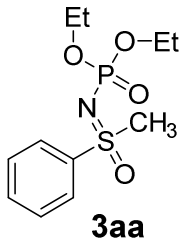


Sulfoximine (0.5 mmol, 1 equiv.), copper(II) acetate (0.5 equiv.), triethylamine (1 equiv.) and toluene (3 mL) were added in round-bottom flask containing pre-activated molecular sieve (150 mg) and stirred at room temperature for 5 minutes under open air condition. Round-bottom flask containing reaction mixture was transferred to pre-heated oil bath. In another round-bottom flask, dialkyl phosphite (1.0 mmol, 2 equiv.) was diluted with 2 mL toluene. The diluted dialkyl phosphite was added into the reaction mixture in 3 to 4 part for 10 minutes of time interval and kept for vigorous stirring at 110 °C. The RB flask was equipped with an air condenser. It is worth noting that while adding diluted dialkyl phosphite the color of reaction mixture changes from dark blue to pale blue and this color persists after consumption of the starting material. The progress of the reaction was monitored by thin layer chromatography using ethyl acetate/hexane as an eluent. After completion of the reaction, reaction mixture was diluted with dichloromethane and washed with water and brine solution. The reaction mixture was treated with anhydrous sodium sulfate and dried in rota evaporator. The crude product was further

purified on silica-gel (100–200 mesh) column chromatography using ethyl acetate/hexane as an eluent.

3) ANALYTICAL DATA FOR *N*-(DIALKYLPHOSPHITE)SULFOXIMINES

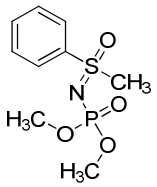
3.1 Diethyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3aa)[3]:



3aa

The reaction was carried out using 155 mg of sulfoximine according to general procedure. The title compound was obtained as transparent oil, 258 mg, 89% yield. The residue was isolated by silica-gel Column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% EA) 0.22. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3394, 2988, 1259, 1169, 1024, 746. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.63 (dt, *J* = 15.4, 7.4 Hz, 3H), 4.14–4.04 (m, 4H), 3.35 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.6 (d, *J* = 9.0 Hz), 133.9, 129.5, 127.4, 62.8 (dd, $J_{C\text{-}P}$ = 6.0, 3.7 Hz), 46.9 (d, *J* = 3.3 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.5, 4.3 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.94. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{19}NO_4PS$ $[M + H]^+$ 292.0772; found 292.0759.

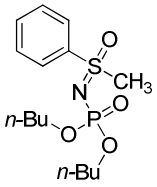
3.2 Dimethyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3ab)[3a]:



3ab

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 112 mg, 85% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3428, 2949, 2918, 1252, 1166, 1031, 831. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 3.74 (m, 6H), 3.36 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.4 (d, *J* = 9.2 Hz), 134.0, 129.6, 127.3, 53.6 (dd, $J_{C\text{-}P}$ = 6.2, 2.6 Hz), 46.9 (d, *J* = 3.0 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ 0.75. **HRMS** (ESI-TOF) calcd. for $C_9H_{15}NO_4PS$ $[M + H]^+$ 264.0459; found 264.0447.

3.3 Dibutyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3ac):

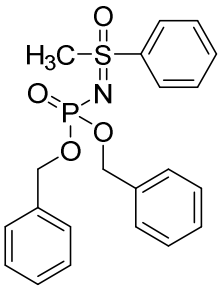


3ac

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 150 mg, 87% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3387, 2978, 1254, 1148, 1016, 816, 764. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 (dd, *J* = 7.7, 6.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 4.00 (dq, *J* = 23.8, 6.7 Hz, 4H), 3.33 (s, 3H), 1.65–1.56 (m, 4H), 1.36 (ddd, *J* = 25.8, 15.0, 7.5 Hz, 4H), 0.88 (dt, *J* = 13.4, 7.4 Hz, 6H); **^{13}C NMR (125 MHz,**

$CDCl_3$) δ 140.6 (d, *J* = 8.7 Hz), 133.8, 129.5, 127.4, 66.5 (dd, J_{C-P} = 6.4, 1.0 Hz), 45.9 (d, *J* = 3.5 Hz), 32.4 (dd, J_{C-P} = 7.5, 3.4 Hz), 18.8 (d, *J* = 5.6 Hz), 13.7 (d, *J* = 2.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.77 (p, *J* = 6.7 Hz). **HRMS** (ESI-TOF) calcd. for $C_{15}H_{27}NO_4PS$ $[M + H]^+$ 348.1398; found 348.1379.

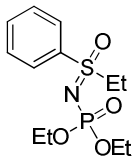
3.4 Dibenzyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3ad):



3ad

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 174 mg, 84% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3458, 2921, 1488, 1214, 1187, 1151, 919. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.33–7.29 (m, 10H), 5.03–4.97 (m, 4H), 3.26 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.3 (d, *J* = 8.9), 136.7 (dd, J_{C-P} = 7.7, 3.2 Hz),133.9, 129.5, 128.4, 128.1 (d, *J* = 3.0 Hz), 127.8 (d, *J* = 16.3 Hz), 127.3, 68.3 (d, J_{C-P} = 5.8 Hz), 46.9 (d, *J* = 3.5 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.83. **HRMS** (ESI-TOF) calcd. for $C_{21}H_{23}NO_4PS$ $[M+H]^+$: 416.1085, found 416.1071.

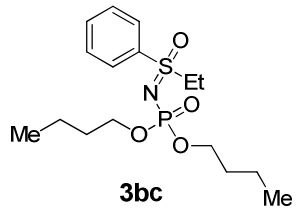
3.5 Diethyl (*S*-ethylsulfonimidoyl)benzene phosphoroamidate (3ba):



3ba

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 123 mg, 81% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3388, 2968, 1261, 1144, 1012, 879, 738. **^{1}H NMR (500 MHz, $CDCl_3$)** 7.93 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 4.08–3.97 (m, 4H), 3.42 (dt, *J* = 14.8, 7.3 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (td, *J* = 7.1, 2.8 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 137.80 (d, *J* = 7.5 Hz), 133.8, 129.3, 128.2, 62.63 (dd, J_{C-P} = 6.0, 3.5 Hz), 52.90 (d, *J* = 4.5 Hz), 16.14 (t, J_{C-P} = 7.1 Hz), 7.9; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.77 (p, *J* =7.2 Hz). **HRMS** (ESI-TOF) calcd. for $C_{12}H_{21}NO_4PS$ $[M + H]^+$ 306.0929; found 306.0910.

3.6 Dibutyl (*S*-ethylsulfonimidoyl)benzene phosphoroamidate (3bc):

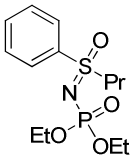


3bc

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 158 mg, 88% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3325, 2974, 1246, 1154, 1032, 877, 741. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96–7.94 (m, 2H), 7.65–7.62 (m, 1H), 7.57–7.54 (m, 2H), 3.99 (qd, *J* = 6.7, 1.1 Hz, 2H), 3.93 (q, *J* =

6.7 Hz, 2H), 3.44–3.38 (m, 2H), 1.64–1.58 (m, 2H), 1.55–1.49 (m, 2H), 1.38–1.34 (m, 2H), 1.29 (dd, *J* = 7.4, 5.8 Hz, 2H), 1.21 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.0 (d, *J* = 7.2 Hz), 133.7, 129.3, 128.3, 66.4 (dd, J_{C-P} = 6.4, 4.7 Hz), 52.9 (d, *J* = 4.7 Hz), 32.3 (dd, J_{C-P} = 7.5, 6.2 Hz), 18.8 (d, *J* = 8.5 Hz), 13.7 (d, *J* = 4.3 Hz), 7.9; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.62 (p, *J* =6.9 Hz). **HRMS** (ESI-TOF) calcd. for $C_{16}H_{29}NO_4PS$ $[M + H]^+$ 362.1555; found 362.1544.

3.7 Diethyl (*S*-propylsulfonimidoyl)benzene phosphoroamidate (3ca):

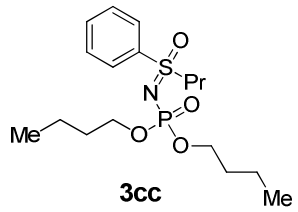


3ca

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 126 mg, 79% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.20. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3328, 3031, 2957, 1261, 1154, 1033, 814, 759. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 4.12–4.0 (m, 4H), 3.44–3.35 (m, 2H), 1.70–1.66 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.23 (d, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.6 (d, *J* = 7.4 Hz), 133.8, 129.4, 128.2, 62.8–62.5 (m), 60.07 (d, *J* = 4.4 Hz), 17.0, 16.4–16.1 (m), 12.5; **^{31}P NMR** (200 MHz, $CDCl_3$) δ -1.82. **HRMS** (ESI-TOF) calcd.

for $C_{13}H_{23}NO_4PS$ $[M + H]^+$ 320.1085; found 320.1071.

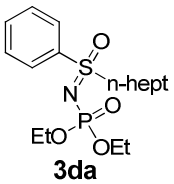
3.8 Dibutyl (*S*-propylsulfonimidoyl)benzene phosphoroamidate (3cc):



3cc

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 160 mg, 85% yield. The product was isolated by silica-gel column chromatography using 80% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~96%. **IR (Neat, cm^{-1})** 3326, 3033, 2969, 1271, 1143, 1026, 817, 776. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (dd, *J* = 7.4, 0.9 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.0 Hz, 2H), 3.97 (ddd, *J* = 18.6, 12.5, 5.2 Hz, 4H), 3.40–3.32 (m, 2H), 1.65–1.61 (m, 4H), 1.53–1.51 (m, 2H), 1.38 (dd, *J* = 13.6, 7.3 Hz, 2H), 1.29 (dd, *J* = 15.2, 7.8 Hz, 2H), 0.91 (dt, *J* = 15.1, 7.4 Hz, 6H), 0.85 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.7 (d, *J* = 7.1 Hz), 133.7, 129.4, 128.2, 66.4 (t, $J_{C\text{-}P}$ = 6.0 Hz), 60.0 (d, *J* = 4.6 Hz), 32.3 (t, $J_{C\text{-}P}$ = 7.4 Hz), 18.8 (t, *J* = 8.2 Hz), 16.9, 13.7 (t, *J* = 5.8 Hz), 12.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.67. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1691.

3.9 Diethyl (*S*-n-heptylsulfonimidoyl)benzene phosphoroamidate (3da):

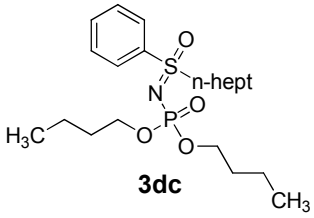


3da

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 148 mg, 79% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl

acetate) = 0.22. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3331, 2969, 2809, 1269, 1136, 1032, 821, 734. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 4.09–3.97 (m, 4H), 3.37 (dtd, *J* = 13.9, 8.9, 5.9 Hz, 2H), 1.61–1.57 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 4H), 1.24–1.14 (m, 10H), 0.79 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.5 (d, *J* = 7.2 Hz), 133.7, 129.3, 128.1, 62.6 (t, $J_{C\text{-}P}$ = 5.5 Hz), 58.3 (d, *J* = 4.5 Hz), 31.4, 28.6, 27.9, 23.0, 22.4, 16.1 (dd, $J_{C\text{-}P}$ = 9.0, 7.7 Hz), 14.0; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.87. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1688.

3.10 Dibutyl (*S*-n-heptylsulfonimidoyl)benzene phosphoroamidate (3dc):

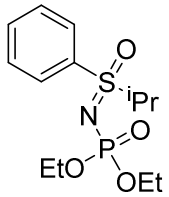


3dc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 174 mg, 81% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~96%. **IR (Neat, cm^{-1})** 3341, 2966, 2838, 1256, 1149, 1031, 820, 744. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 4.00 (q, *J* = 6.7 Hz, 2H), 3.93 (q, *J* = 6.7 Hz, 2H), 3.41–3.38 (m, 1H), 3.34–3.32 (m, 1H), 1.61 (dd, *J* = 14.6, 6.9 Hz, 3H), 1.55–1.49 (m, 2H), 1.37 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.28 (dd, *J* = 15.2, 7.6 Hz, 4H), 1.24–1.11 (m, 7H),

0.89 (t, J = 7.4 Hz, 3H), 0.83 (dt, J = 14.2, 7.3 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.7 (d, J = 6.9 Hz), 133.7, 129.3, 128.2, 66.4 (t, $J_{C\text{-}P}$ = 6.4 Hz), 58.4 (d, J = 4.6 Hz), 32.3 (t, $J_{C\text{-}P}$ = 7.8 Hz), 31.4, 28.7, 28.0, 23.0, 22.5, 18.8 (d, J = 10.5 Hz), 14.0, 13.7 (d, J = 4.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.63. **HRMS** (ESI-TOF) calcd. for $C_{21}H_{39}NO_4PS$ $[M + H]^+$ 432.2337; found 432.2312.

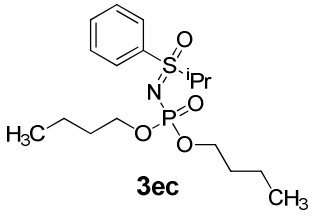
3.11 Diethyl (*S-iso*-propylsulfonimidoyl)benzene phosphoroamidate (3ea):



3ea

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 124 mg, 78% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~99%. **IR (Neat, cm^{-1})** 3338, 2971, 1259, 1157, 1047, 810, 747. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, J = 8.3 Hz, 2H), 7.66–7.61 (m, 1H), 7.55 (t, J = 7.5 Hz, 2H), 4.06–3.94 (m, 4H), 3.51 (dt, J = 13.6, 6.8 Hz, 1H), 1.26 (ddd, J = 16.9, 15.3, 6.4 Hz, 10H), 1.13 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.2 (d, J = 4.3 Hz), 133.7, 129.3, 129.1, 62.5 (dd, $J_{C\text{-}P}$ = 10.3, 6.2 Hz), 58.2 (d, J = 6.2 Hz), 16.1 (dd, $J_{C\text{-}P}$ = 15.6, 8.2 Hz), 15.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.61 (p, J =7.5 Hz). **HRMS** (ESI-TOF) calcd. for $C_{13}H_{22}NO_4PS$ $[M + H]^+$ 320.1085; found 320.1089.

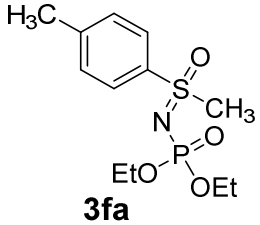
3.12 Dibutyl (*S-iso*-propylsulfonimidoyl)benzene phosphoroamidate (3ec):



3ec

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 142 mg, 76% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.25. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3386, 2967, 1504, 1258, 1145, 1011, 874, 732. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93–7.91 (m, 2H), 7.63 (dd, *J* = 10.9, 3.9 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 3.97 (qd, *J* = 6.6, 2.2 Hz, 2H), 3.88 (q, *J* = 6.7 Hz, 2H), 3.49 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.59–1.58 (m, 2H), 1.44 (dd, *J* = 8.4, 6.7 Hz, 2H), 1.35 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.29–1.19 (m, 5H), 0.87 (dd, *J* = 7.7, 7.1 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.4(d, *J* = 4.0 Hz), 133.6, 129.3, 129.0, 66.2(dd, $J_{C\text{-}P}$ = 16.4, 6.5 Hz), 58.2(d, *J* = 6.5 Hz), 32.3(dd, $J_{C\text{-}P}$ = 12.2, 7.6 Hz), 18.7(d, *J* = 16.1 Hz), 16.0, 15.6, 13.7(d, *J* = 7.6 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.39 (p, *J* =6.6 Hz). **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1698.

3.13 Diethyl (*S*-methylsulfonimidoyl)-4-methylbenzene phosphoroamidate (3fa):

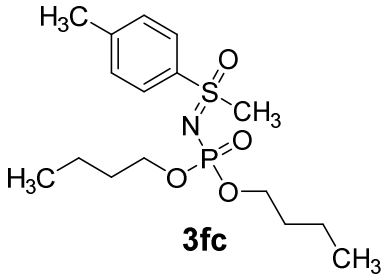


3fa

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 130 mg, 85% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl

acetate) = 0.22. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3023, 2948, 1508, 1277, 1184, 1091, 1038, 1027, 819, 742. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.07–3.99 (m, 4H), 3.27 (s, 3H), 2.39 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 144.8, 137.4 (d, *J* = 8.8 Hz), 130.0, 127.2, 62.6 (d, $J_{C\text{-}P}$ = 5.5 Hz), 46.9 (d, *J* = 3.1 Hz), 21.5, 16.1 (dd, $J_{C\text{-}P}$ = 7.4, 2.4 Hz); **^{31}P NMR (200 MHz, CDCl$_3$)** δ -1.88. **HRMS** (ESI-TOF) calcd. for $C_{12}H_{21}NO_4PS$ $[M + H]^+$ 306.0929; found 306.0909.

3.14 Dibutyl (*S*-methylsulfonimidoyl)-4-methylbenzene phosphoroamidate (3fc):

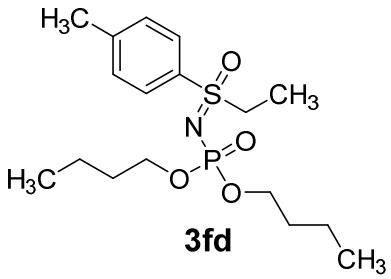


3fc

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 158 mg, 88% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~96%. **IR (Neat, cm^{-1})** 3034, 2946, 1512, 1269, 1176, 1098, 1041, 1021, 814, 748. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 3.99 (dq, *J* = 22.9, 6.7 Hz, 4H), 3.30 (s, 3H), 2.43 (s, 3H), 1.64 (dd, *J* = 14.3, 7.4 Hz, 2H), 1.57 (dd, *J* = 14.8, 6.8 Hz, 2H), 1.40–1.32 (m, 4H), 0.88 (dt, *J* = 12.7, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 144.8, 137.6 (d, *J* = 8.8 Hz), 130.0, 127.4, 66.5 (d, $J_{C\text{-}P}$ = 6.4 Hz), 47.0 (d, *J* =

3.5 Hz), 32.4 (dd, J_{C-P} = 7.6, 3.0 Hz), 21.6, 18.8 (d, J = 5.3 Hz), 13.7 (d, J = 2.5 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.73 (p, J =6.1 Hz). **HRMS** (ESI-TOF) calcd. for $C_{16}H_{29}NO_4PS$ $[M + H]^+$ 362.1555; found 362.1528.

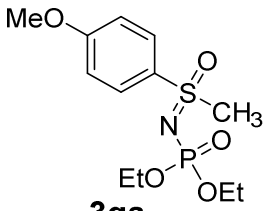
3.15 Dibutyl (*S*-ethylsulfonimidoyl)-4-methylbenzene phosphoroamidate (3fd):



3fd

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 172 mg, 92% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80 % ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3034, 2946, 1512, 1269, 1176, 1098, 1041, 1021, 814, 748. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 4.02–3.92 (m, 4H), 3.40 (td, J = 13.4, 7.0 Hz, 2H), 2.43 (s, 3H), 1.63–1.60 (m, 2H), 1.53–1.52 (m, 2H), 1.37 (dd, J = 15.0, 7.5 Hz, 2H), 1.29 (dd, J = 15.1, 7.5 Hz, 2H), 1.20 (t, J = 7.4 Hz, 3H), 0.86 (dt, J = 20.2, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.8, 134.9(d, J = 7.3 Hz), 129.9, 128.3, 66.3 (dd, J_{C-P} = 6.4, 3.5 Hz), 53.0 (d, J = 4.8 Hz), 32.4 (dd, J_{C-P} = 7.6, 5.0 Hz), 21.6, 18.8 (d, J = 7.9 Hz), 13.7 (d, J = 3.9 Hz), 7.9; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.53. HRMS (ESI-TOF) calcd. for $C_{17}H_{30}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1728.

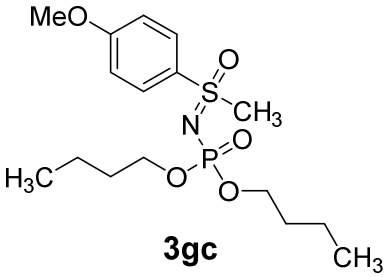
3.16 Diethyl (*S*-methylsulfonimidoyl)-4-methoxybenzene phosphoroamidate (3ga):



3ga

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 142 mg, 89% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3347, 2969, 2844, 1274, 1154, 1031, 747. **^{1}H NMR (500 MHz, $CDCl_3$)** 7.89 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 4.07–3.00 (m, 4H), 3.83 (s, 3H), 3.28 (s, 3H), 1.25 (dt, *J* = 19.0, 7.1 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.8, 131.7, 129.5, 114.5, 62.6 (dd, $J_{C\text{-}P}$ = 6.0, 1.5 Hz), 55.7, 47.2 (d, *J* = 3.5 Hz), 16.1 (d, $J_{C\text{-}P}$ = 0.9 Hz); **^{31}P NMR (203 MHz, $CDCl_3$)** δ -1.91 (p, *J* =7.1 Hz). **HRMS** (ESI-TOF) calcd. for $C_{12}H_{20}NO_5PS$ $[M + H]^+$ 322.0878; found 322.0864.

3.17 Dibutyl (*S*-methylsulfonimidoyl)-4-methoxybenzene phosphoroamidate (3gc):

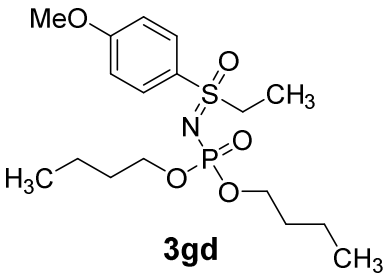


3gc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 172 mg, 91% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3023, 2920, 1516, 1291, 1171, 1056, 1034, 1021, 991, 764. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.03–3.97 (m, 4H), 3.87 (s, 3H), 3.31 (s, 3H), 1.66–1.58 (m, 4H), 1.37 (ddd, *J* = 24.0, 15.1, 7.5 Hz, 4H), 0.90

(dt, J = 12.0, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.9, 132.0 (d, J = 9.1 Hz), 129.6, 114.6, 66.5 (d, J_{C-P} = 6.4 Hz), 55.8, 47.3 (d, J = 3.6 Hz), 32.4 (dd, J_{C-P} = 7.6, 2.1 Hz),18.9 (d, J = 5.2 Hz), 13.8 (d, J = 1.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.71. **HRMS** (ESI-TOF) calcd. for $C_{16}H_{28}NO_5PS$ [M + H]$^+$ 378.1504 found 378.1512.

3.18 Dibutyl (*S*-ethylsulfonimidoyl)-4-methoxybenzene phosphoroamidate (3gd):

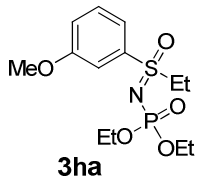


3gd

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 160 mg, 82% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~99%. **IR (Neat, cm^{-1})** 3023, 2920, 1516, 1291, 1171, 1056, 1034, 1021, 991, 764. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 3.99 (q, J = 6.6 Hz, 2H), 3.94 (q, J = 6.7 Hz, 2H), 3.86 (s, 3H), 3.39 (ddd, J = 14.4, 7.2, 2.6 Hz, 2H), 1.62 (dt, J = 14.5, 6.6 Hz, 2H), 1.54–1.53 (m, 2H), 1.38–1.36 (m, 2H), 1.31–1.29 (m, 2H), 1.21 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.8, 130.5, 129.2 (d, J = 7.4 Hz), 114.5, 66.3 (dd, J_{C-P} = 6.3, 3.8 Hz), 55.8, 53.3 (d, J = 4.6 Hz), 32.4 (dd, J_{C-P} = 7.5, 3.6 Hz), 18.8 (d, J = 7.3 Hz), 13.7 (d, J = 3.4 Hz), 8.0; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.72 (p, J =7.5 Hz). **HRMS** (ESI-TOF) calcd.

for $C_{17}H_{31}NO_5PS$ $[M + H]^+$ 392.1661; found 392.1636.

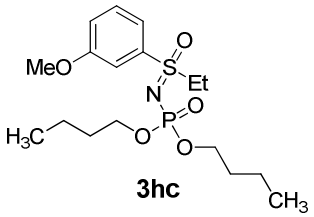
3.19 Diethyl (*S*-ethylsulfonimidoyl)-3-methoxybenzene phosphoroamidate (3ha):



3ha

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 139 mg, 83% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (60% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~99%. **IR (Neat, cm^{-1})** 3128, 3014, 2933, 1487, 1404, 1287, 1168, 1044, 1012, 894, 773. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54–7.52 (m, 1H), 7.47–7.44 (m, 2H), 7.16–7.14 (m, 1H), 4.11–4.01 (m, 4H), 3.85 (s, 3H), 3.48–3.39 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.23 (td, *J* = 7.2, 2.5 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 160.1, 139.1 (d, *J* = 7.2 Hz), 130.4, 120.4, 120.2, 112.8, 62.7 (dd, $J_{C\text{-}P}$ = 6.1, 3.1 Hz), 55.8, 52.9 (d, *J* = 4.5 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.3, 5.8 Hz), 7.9; ^{31}P NMR (200 MHz, $CDCl_3$) δ -1.81. **HRMS** (ESI-TOF) calcd. for $C_{13}H_{23}NO_5PS$ $[M + H]^+$ 336.1035; found 336.1015.

3.20 Dibutyl (*S*-ethylsulfonimidoyl)-3-methoxybenzene phosphoroamidate (3hc):

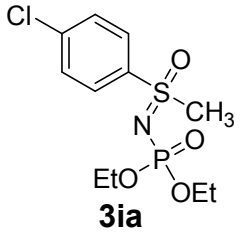


3hc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 164 mg, 84% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (60% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3130, 3011, 2930, 1481, 1407, 1292, 1153, 1046, 1016, 893,

787. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.48–7.44 (m, 2H), 7.16 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 4.01 (q, *J* = 6.8 Hz, 2H), 3.95 (q, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 3.46–3.41 (m, 2H), 1.63 (dt, *J* = 14.8, 6.7 Hz, 2H), 1.56–1.53 (m, 2H), 1.40–1.36 (m, 2H), 1.32–1.28 (m, 2H), 1.24 (s, 3H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 160.1, 139.2 (d, *J* = 7.0 Hz), 130.4, 120.4, 120.2, 112.8, 66.4 (dd, $J_{C\text{-}P}$ = 6.4, 3.9 Hz), 55.8, 53.0 (d, *J* = 4.8 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.6, 5.3 Hz), 18.8 (d, *J* = 7.6 Hz), 13.7 (d, *J* = 5.0 Hz), 7.9; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.68. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_5PS$ $[M + H]^+$ 392.1661; found 392.1636.

3.21 Diethyl (*S*-methylsulfonimidoyl)-4-chlorobenzene phosphoroamidate (3ia):

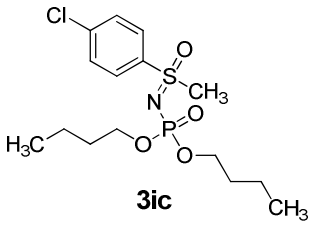


3ia

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 128 mg, 79% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3026, 2920, 1586, 1477, 1289, 1204, 1092, 1030, 849, 770; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 6.8 Hz, 2H), 7.55 (d, *J* = 6.8 Hz, 2H), 4.12–4.02 (m, 4H), 3.33 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.7, 139.0 (d, *J* = 8.8 Hz), 129.8, 128.9, 62.8 (dd, $J_{C\text{-}P}$ = 6.1,

3.5 Hz), 46.9 (d, J = 3.7 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.5, 3.0 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.21. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{18}ClNO_4PS$ $[M + H]^+$ 326.0377; found 326.0359.

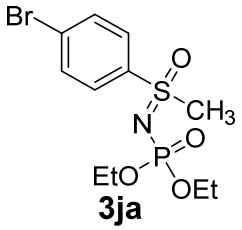
3.22 Dibutyl (*S*-methylsulfonimidoyl)-4-chlorobenzene phosphoroamidate (3ic):



3ic

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 152 mg, 80% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.26. Purity as per ^{1}H NMR: ~96%. **IR (Neat, cm^{-1})** 3029, 2927, 1584, 1471, 1275, 1218, 1079, 1033, 856, 786. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96–7.95 (m, 2H), 7.55–7.54 (m, 2H), 4.00 (dq, J = 22.1, 6.7 Hz, 4H), 3.32 (s, 3H), 1.66–1.57 (m, 4H), 1.41–1.31 (m, 4H), 0.89 (dt, J = 12.1, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.7, 139.1 (d, J = 8.5 Hz), 129.8, 129.0, 66.6 (dd, $J_{C\text{-}P}$ = 6.4, 2.6 Hz), 46.9 (d, J = 3.9 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.5, 2.7 Hz), 18.8 (d, J = 5.0 Hz), 13.7 (d, J = 2.7 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.05. HRMS (ESI-TOF) calcd. for $C_{15}H_{26}ClNO_4PS$ $[M + H]^+$ 382.1009; found 382.0987.

3.23 Diethyl (*S*-methylsulfonimidoyl)-4-bromobenzene phosphoroamidate (3ja):

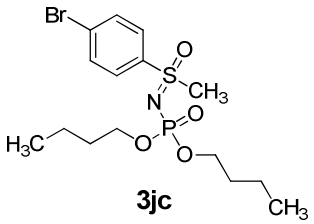


3ja

The reaction was carried out using general procedure. The title compound was obtained as brown liquid, 138 mg, 75% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl

acetate) = 0.20. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3109, 2891, 1584, 1491, 1288, 1212, 1093, 1034, 881, 793. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 4.15–4.02 (m, 4H), 3.34 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 139.5 (d, *J* = 8.6 Hz), 132.8, 129.3, 129.0, 62.9 (dd, $J_{C\text{-}P}$ = 6.0, 3.5 Hz), 46.9 (d, *J* = 3.7 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.5, 3.3 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.22. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{18}BrNO_4PS$ $[M + H]^+$ 369.9878; found 369.9856.

3.24 Dibutyl (*S*-methylsulfonimidoyl)-4-bromobenzene phosphoroamidate (3jc):

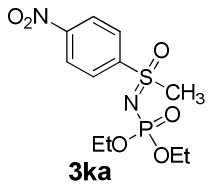


3jc

The reaction was carried out using general procedure. The title compound was obtained as brown liquid, 212 mg, 78% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3126, 2897, 1582, 1486, 1281, 1215, 1084, 1043, 824, 760. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85–7.83 (m, 2H), 7.68–7.67 (m, 2H), 3.95 (dq, *J* = 20.3, 6.7 Hz, 4H), 3.29 (s, 3H), 1.61–1.53 (m, 4H), 1.34–1.28 (m, 4H), 0.85 (dt, *J* = 11.1, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 139.5 (d, *J* = 8.4 Hz), 132.7, 128.9, 66.5 (dd, $J_{C\text{-}P}$ = 6.4, 2.0 Hz), 46.8 (d, *J* = 3.9 Hz), 32.2 (dd, $J_{C\text{-}P}$ = 7.5, 2.4 Hz), 18.7 (d, *J* = 4.5 Hz), 13.6 (d, *J* = 1.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.10 (p, *J* =6.7 Hz). **HRMS** (ESI-

TOF) calcd. for $C_{15}H_{26}BrNO_4PS$ $[M + H]^+$ 426.0504; found 426.0496.

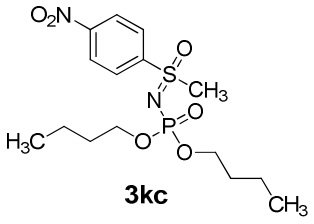
3.25 Diethyl (*S*-methylsulfonimidoyl)-4-nitrobenzene phosphoroamidate (3ka):



3ka

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 119 mg, 71% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~97%. **IR (Neat, cm^{-1})** 3306, 3128, 2892, 1561, 1492, 1279, 1204, 1087, 1017, 851, 778. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.42 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.8 Hz, 2H), 4.14–4.04 (m, 4H), 3.39 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 5.9 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 151.0, 146.2 (d, *J* = 8.0 Hz), 129.1, 124.7, 63.1 (t, $J_{C\text{-}P}$ = 6.0 Hz), 46.6 (d, *J* = 4.1 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.4, 2.8 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.67 (p, *J* =7.6 Hz). **HRMS** (ESI-TOF) calcd. for $C_{11}H_{18}N_2O_6PS$ $[M + H]^+$ 337.0623; found 337.0599.

3.26 Dibutyl (*S*-methylsulfonimidoyl)-4-nitrobenzene phosphoroamidate (3kc):

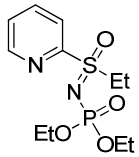


3kc

The reaction was carried out using general procedure. The title compound was obtained as yellow oil, 148 mg, 76% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~96%. **IR (Neat, cm^{-1})**

3301, 3122, 2898, 1566, 1493, 1274, 1203, 1088, 1015, 859, 771. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.42–8.40 (m, 2H), 8.24–8.22 (m, 2H), 4.00 (dq, *J* = 20.3, 6.7 Hz, 4H), 3.38 (s, 3H), 1.66–1.57 (m, 4H), 1.36 (ddd, *J* = 25.2, 15.0, 7.5 Hz, 4H), 0.92–0.86 (m, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 150.9, 146.2 (d, *J* = 7.8 Hz), 129.0, 124.7, 66.7 (dd, J_{C-P} = 6.1, 5.4 Hz), 46.6 (d, *J* = 4.2 Hz), 32.3 (dd, J_{C-P} = 7.5, 2.5 Hz), 18.8 (d, *J* = 4.6 Hz), 13.7 (d, *J* = 2.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.50. **HRMS** (ESI-TOF) calcd. for $C_{15}H_{26}N_2O_6PS$ $[M + H]^+$ 393.1249; found 393.1240.

3.27 Diethyl (*S*-methylsulfonimidoyl)pyridine phosphoroamidate (3la):

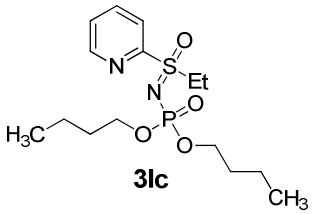


3la

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 130 mg, 85% yield. The product was isolated by silica-gel column chromatography using 70% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate, 3 times) = 0.22. Purity as per ^{1}H NMR: ~96%. **IR (Neat, cm^{-1})** 3342, 3213, 3046, 2891, 2775, 2347, 2038, 1584, 1476, 1344, 1264, 1187, 1081, 963, 816, 748. **^{1}H NMR (500 MHz, CDCl3)** δ 8.73 (d, *J* = 4.3 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.97 (t, *J* = 7.7 Hz, 1H), 7.56–7.54 (m, 1H), 4.04 (dd, *J* = 14.1, 7.0 Hz, 4H), 3.72 (qd, *J* = 14.3, 7.1 Hz, 2H), 1.29–1.24 (m, 9H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 156.4 (d, *J* = 7.1 Hz), 150.1, 138.3, 127.4, 123.2, 62.7 (t, J_{C-P} = 5.8 Hz), 48.5 (d, *J* =

5.8 Hz), 16.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 7.3; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.81. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{20}N_2O_4PS$ $[M + H]^+$ 307.0881; found 307.0862.

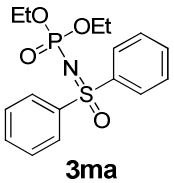
3.28 Dibutyl (*S*-methylsulfonimidoyl) pyridine phosphoroamidate (3lc):



3lc

The reaction was carried out using general procedure. The title compound was obtained as yellow oil, 163 mg, 90% yield. The product was isolated by silica-gel column chromatography using 80% ethyl acetate:hexane as an eluent. R_f (100% ethyl aceatae) = 0.24. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3331, 3204, 3048, 2897, 2783, 2351, 2041, 1586, 1484, 1376, 1261, 1189, 1084, 968, 819, 746. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 4.3 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 7.95 (t, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 7.4, 4.8 Hz, 1H), 4.98–3.93 (m, 4H), 3.69 (dt, *J* = 14.9, 7.3 Hz, 2H), 1.58 (dd, *J* = 14.5, 7.1 Hz, 4H), 1.34 (dt, *J* = 12.1, 7.3 Hz, 4H), 1.24 (t, *J* = 7.4 Hz, 3H), 0.87 (td, *J* = 7.4, 3.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 156.5 (d, *J* = 7.1 Hz), 150.0, 138.2, 127.3, 123.1, 66.3 (dd, $J_{C\text{-}P}$ = 6.2, 4.2 Hz), 48.4 (d, *J* = 5.7 Hz), 32.3 (d, $J_{C\text{-}P}$ = 7.5 Hz), 18.8, 13.7, 7.2; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.67 (p, *J* =6.9 Hz). **HRMS** (ESI-TOF) calcd. for $C_{15}H_{28}N_2O_4PS$ $[M + H]^+$ 363.1507; found 363.1487.

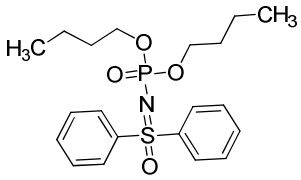
3.29 Diethyl (*S*-diphenylsulfonimidoyl) phosphoroamidate (3ma):



3ma

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 148 mg, 84% yield. The product was isolated by silica-gel column chromatography using 70% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~99%. **IR (Neat, cm^{-1})** 3308, 3184, 3038, 2906, 2871, 2388, 2343, 1476, 1277, 1211, 1114, 1084, 839, 724. **^{1}H NMR (500 MHz, CDCl3)** δ 8.02–8.00 (m, 4H), 7.57–7.53 (m, 2H), 7.51–7.48 (m, 4H), 4.07–3.98 (m, 4H), 1.19 (td, *J* = 7.1, 0.7 Hz, 6H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 141.8 (d, *J* = 6.6 Hz), 133.3, 129.3, 127.7, 62.7 (d, J_{C-P} = 6.2 Hz), 16.1 (d, J_{C-P} = 7.5 Hz); **^{31}P NMR (200 MHz, CDCl$_3$)** δ -2.35. **HRMS** (ESI-TOF) calcd. for $C_{16}H_{21}NO_4PS$ [M + H]$^+$ 354.0929; found 354.0911.

3.30 Dibutyl (*S*-diphenylsulfonimidoyl) phosphoroamidate (3mc):

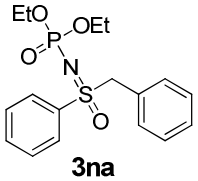


3mc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 174 mg, 85% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. Purity as per ^{1}H NMR: ~99%. **IR (Neat, cm^{-1})** 3316, 3178, 3010, 2903, 2876, 2384, 2347, 1478, 1278, 1206, 1108, 1081, 811, 728. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 8.0 Hz, 4H), 7.54 (t, *J* = 6.8 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 4H), 3.99–3.92 (m, 4H), 1.54–1.48 (m, 4H), 1.27 (dd, *J* = 15.0, 7.5

Hz, 4H), 0.84 (t, J = 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 141.9 (d, J = 6.7 Hz), 133.2, 129.3, 127.7, 66.4 (d, J_{C-P} = 6.5 Hz), 32.3 (d, J_{C-P} = 7.5 Hz), 18.8, 13.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.19. **HRMS** (ESI-TOF) calcd. for $C_{20}H_{29}NO_4PS$ $[M + H]^+$ 410.1555; found 410.1541.

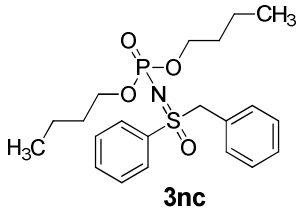
3.31 Diethyl (*S*-benzylsulfonimidoyl)benzene phosphoroamidate (3na):



3na

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 167 mg, 91% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. Purity as per ^{1}H NMR: ~95%. **IR (Neat, cm^{-1})** 3326, 3126, 2890, 2812, 2378, 2306, 1478, 1284, 1206, 1138, 1117, 1089, 876, 738. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (dd, J = 8.5, 1.2 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.42–7.39 (m, 2H), 7.25 (d, J = 8.5 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H), 6.99 (d, J = 7.1 Hz, 2H), 4.71 (d, J = 13.8 Hz, 1H), 4.65 (d, J = 13.8 Hz, 1H), 4.13–4.01 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H), 1.23 (d, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.9 (d, J = 8.9 Hz), 133.8, 131.3, 128.9 (d, J = 10.1 Hz), 128.7 (s), 128.4 (s), 127.9 (s), 64.7 (d, J = 3.2 Hz), 62.8 (dd, J_{C-P} = 6.1, 3.0 Hz), 16.1 (dd, J_{C-P} = 7.5, 3.4 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.62. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{23}NO_4PS$ $[M + H]^+$ 368.1085; found 368.1069.

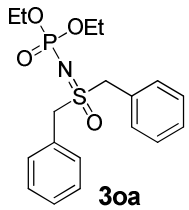
3.32 Dibutyl (*S*-benzylsulfonimidoyl)benzene phosphoroamidate (3nc):



3nc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 171 mg, 81% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. Purity as per ^{1}H NMR: ~95%. **IR (Neat, cm^{-1})** 3329, 3129, 2896, 2804, 2372, 2307, 1473, 1286, 1216, 1134, 1105, 1074, 886, 743. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.61 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.57–7.54 (m, 1H), 7.39 (dd, *J* = 11.7, 4.0 Hz, 2H), 7.24 (dd, *J* = 10.7, 4.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 4.70–4.54 (m, 2H), 4.02–3.93 (m, 4H), 1.62–1.53 (m, 4H), 1.33 (ddd, *J* = 29.5, 15.0, 7.5 Hz, 4H), 0.86 (dt, *J* = 15.0, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 136.9 (d, *J* = 8.5 Hz), 133.7, 131.2, 128.88 (d, *J* = 9.0 Hz), 128.69 (s), 128.38 (s), 127.93 (s), 66.5 (dd, $J_{C\text{-}P}$ = 6.3, 4.7 Hz), 64.7 (d, *J* = 3.4 Hz), 32.2 (dd, $J_{C\text{-}P}$ = 7.6, 3.5 Hz), 18.7 (d, *J* = 6.4 Hz), 13.6 (d, *J* = 4.2 Hz); **^{31}P NMR (200 MHz, CDCl$_3$)** δ -1.51. **HRMS** (ESI-TOF) calcd. for $C_{21}H_{31}NO_4PS$ $[M + H]^+$ 424.1711; found 424.1694.

3.33 Diethyl (*S*-dibenzylsulfonimidoyl) phosphoroamidate (3oa):

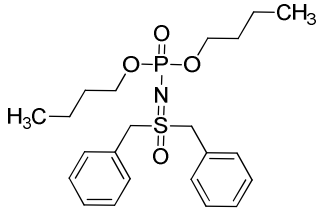


3oa

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 171 mg, 90% yield. The product was isolated by silica-gel column chromatography

using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3308, 3281, 3108, 3042, 3021, 2976, 2944, 1518, 1413, 1232, 1129, 1091, 891, 767, 689, 568. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43–7.40 (m, 4H), 7.38 (td, *J* = 4.4, 1.5 Hz, 6H), 4.47 (d, *J* = 13.7 Hz, 2H), 4.38 (dd, *J* = 13.7, 1.5 Hz, 2H), 3.95–3.89 (m, 4H), 1.21 (td, *J* = 7.1, 0.7 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.5, 129.3, 128.9, 127.1, 62.6 (d, J_{C-P} = 6.2 Hz), 59.5 (d, *J* = 3.8 Hz), 16.1 (d, J_{C-P} = 7.5 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.55. **HRMS** (ESI-TOF) calcd. for $C_{18}H_{25}NO_4PS$ $[M + H]^+$ 382.1242; found 382.1231.

3.34 Dibutyl (*S*-dibenzylsulfonimidoyl) phosphoroamidate (3oc):

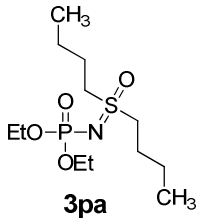


3oc

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 190 mg, 87% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (70% ethyl acetate) = 0.27. Purity as per ^{1}H NMR: ~99%. **IR (Neat, cm^{-1})** 3311, 3265, 3119, 3064, 3012, 2998, 2902, 1511, 1434, 1244, 1118, 1064, 916, 761, 690, 571. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (dd, *J* = 7.0, 2.6 Hz, 4H), 7.39–7.37 (m, 6H), 4.47 (d, *J* = 13.7 Hz, 2H), 4.38 (dd, *J* = 13.7, 1.4 Hz, 2H), 3.85 (qd, *J* = 6.7, 1.4 Hz, 4H), 1.58–1.53 (m, 4H), 1.35–1.30 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.5, 129.3,

128.8, 127.2, 66.4 (d, J_{C-P} = 6.5 Hz), 59.5 (d, J = 3.8 Hz), 32.3 (d, J_{C-P} = 7.6 Hz), 18.8, 13.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.27. **HRMS** (ESI-TOF) calcd. for $C_{22}H_{33}NO_4PS$ $[M + H]^+$ 438.1868; found 438.1859.

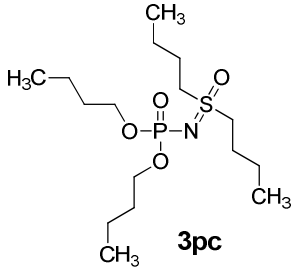
3.35 Diethyl (*S*-dibutylsulfonimidoyl) phosphoroamidate (3pa):



3pa

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 122 mg, 78% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~98%. **IR (Neat, cm^{-1})** 3313, 3261, 3011, 2842, 1714, 1482, 1384, 1231, 1130, 1039, 825, 733. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.02 (p, J = 7.1 Hz, 4H), 3.25–3.17 (m, 4H), 1.82–1.76 (m, 4H), 1.43 (dt, J = 14.7, 7.4 Hz, 4H), 1.27 (t, J = 7.1 Hz, 6H), 0.92 (t, J = 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** 62.5 (d, J_{C-P} = 6.0 Hz), 53.8 (d, J = 4.5 Hz), 24.3, 21.6, 16.2 (d, J_{C-P} = 7.5 Hz), 13.6; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.90. **HRMS** (ESI-TOF) calcd. for $C_{12}H_{29}NO_4PS$ $[M + H]^+$ 314.1555; found 314.1537.

3.36 Dibutyl (*S*-dibutylsulfonimidoyl) phosphoroamidate (3pc):

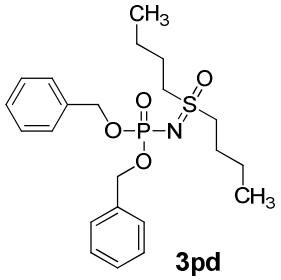


3pc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 150 mg, 81% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl

acetate) = 0.24. Purity as per ^{1}H NMR: ~99%. **IR (Neat, cm^{-1})** 3303, 3254, 3016, 2939, 1719, 1481, 1378, 1251, 1119, 1053, 1019, 828, 751. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 3.92 (dd, *J* = 9.0, 3.7 Hz, 4H), 3.22–3.13 (m, 4H), 1.76–1.71 (m, 4H), 1.58 (d, *J* = 6.3 Hz, 4H), 1.41–1.33 (m, 8H), 0.89 (dddd, *J* = 14.5, 8.0, 7.3, 3.9 Hz, 12H); **^{13}C NMR (125 MHz, CDCl$_3$)** 66.2 (d, $J_{C\text{-}P}$ = 5.8 Hz), 53.7, 32.3 (d, $J_{C\text{-}P}$ = 7.2 Hz), 24.3, 21.5, 18.8, 13.6 (d, *J* = 9.8 Hz); **^{31}P NMR (200 MHz, CDCl$_3$)** δ -1.88. **HRMS** (ESI-TOF) calcd. for $C_{16}H_{37}NO_4PS$ $[M + H]^+$ 370.2181; found 370.2165.

3.37 Dibenzyl (*S*-dibutylsulfonimidoyl) phosphoroamidate (3pd):



3pd

The reaction was carried out using general procedure. The title compound was obtained as white solid, 166 mg, 76% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. Purity as per ^{1}H NMR: ~99%. **IR (KBr, cm^{-1})** 3372, 3011, 2946, 2814, 1721, 1476, 1379, 1244, 1104, 1068, 1012, 819, 746. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.36–7.27 (m, 10H), 5.01 (p, *J* = 11.8 Hz, 4H), 3.24–3.09 (m, 4H), 1.76 (dd, *J* = 15.3, 7.6 Hz, 4H), 1.39 (dd, *J* = 14.5, 7.2 Hz, 4H), 0.90 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 136.8 (d, *J* = 7.7 Hz), 128.3, 128.0, 127.8, 68.1 (d, *J* = 5.8 Hz), 54.0–53.7 (m), 29.7, 24.3, 21.6, 13.6. **^{31}P NMR (200 MHz, CDCl$_3$)** δ 0.73.

HRMS (ESI-TOF) calcd. for $C_{22}H_{33}NO_4$ $[M + H]^+$ 438.1868; found 438.1854.

References

[1] (a) H. R. Bentley, J. K. Whitehead, *J. Chem. Soc.* **1952**, 1572. (b) M. Zenzola, R. Doran, L. Degennaro, R. Luisi, J. A. Bull, *Angew. Chem. Int. Ed.* **2016**, *55*, 7203. (c) H. Yu , Z. Li, C. Bolm, *Angew. Chem. Int. Ed.* **2018**, *57*, 324. (d) A. Tota, M. Zenzola, S.J. Chawner, S. St. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull and R. Luisi *Chem. Commun.,* **2017**, 53, 348. (e) J.-F. Lohier, T. Glachet, H. Marzag, A. -C. Gaumont and V. Reboul *Chem. Commun.,* **2017**, 53, 2064-2067

[2] S. Gupta, P. Chaudhary, N. Muniyappan, S. Sabiah, J. Kandasamy, *Org. Biomol. Chem.* **2017**, *15*, 8493-8498.

[3] (a) J. Dhineshkumar, K. R. Prabhu, *Org. Lett.* **2013**, *15*, 6062; (e) M. B. Reinhard, S. A. de Licastro, *Molecules* **2005**, *10*, 1369

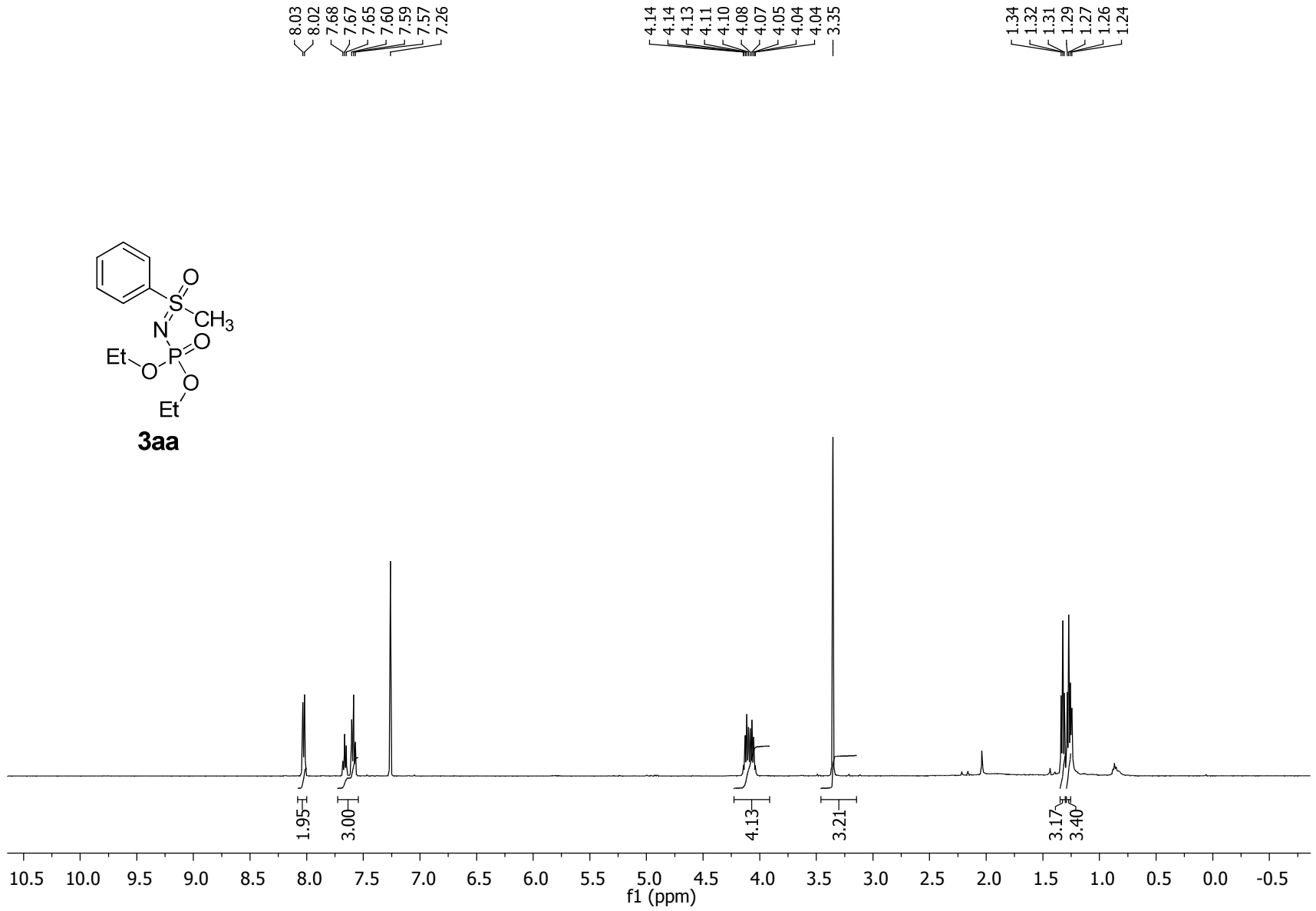


Figure S1. ^{1}H NMR for **3aa**

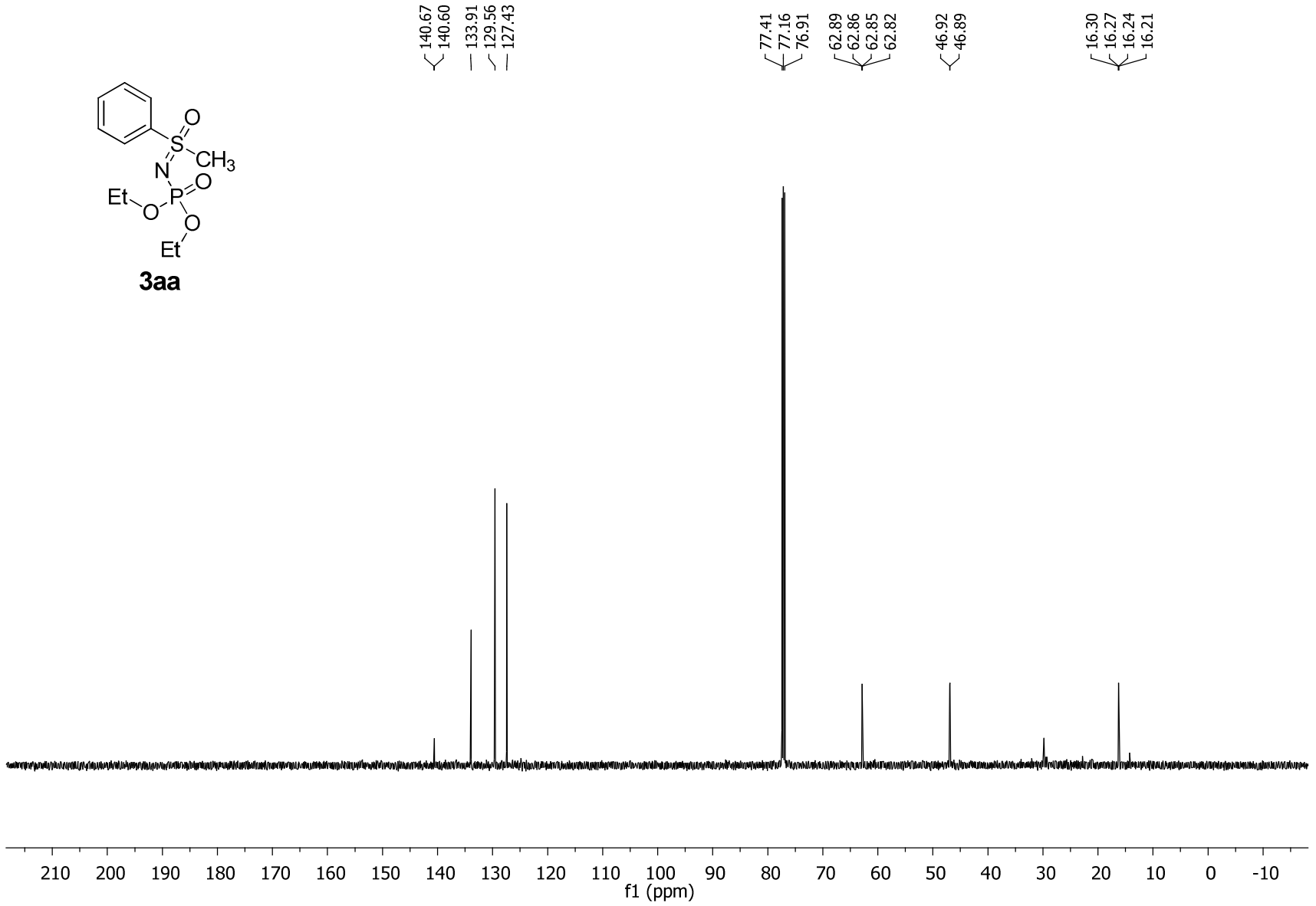


Figure S2. ^{13}C NMR for **3aa**

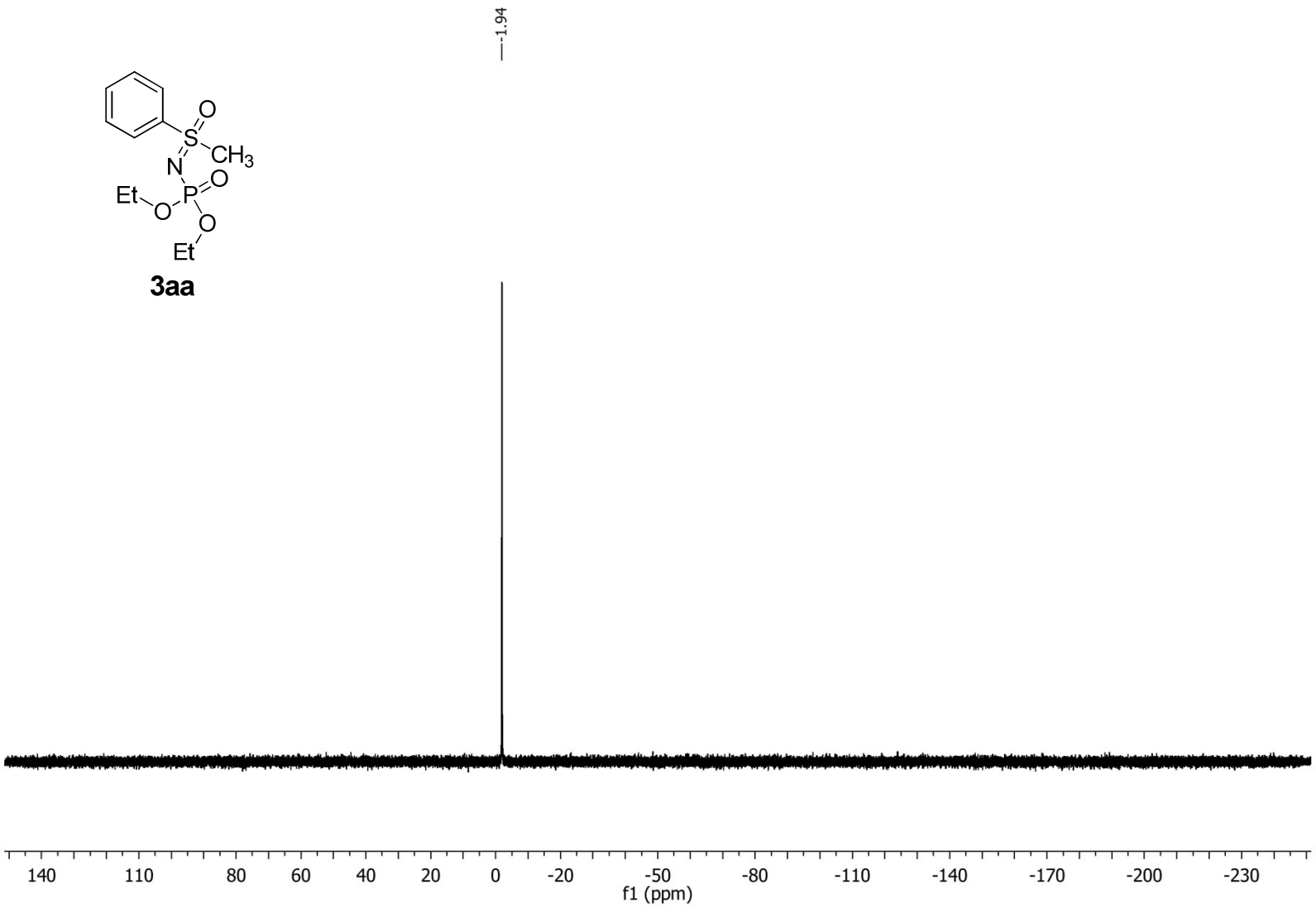
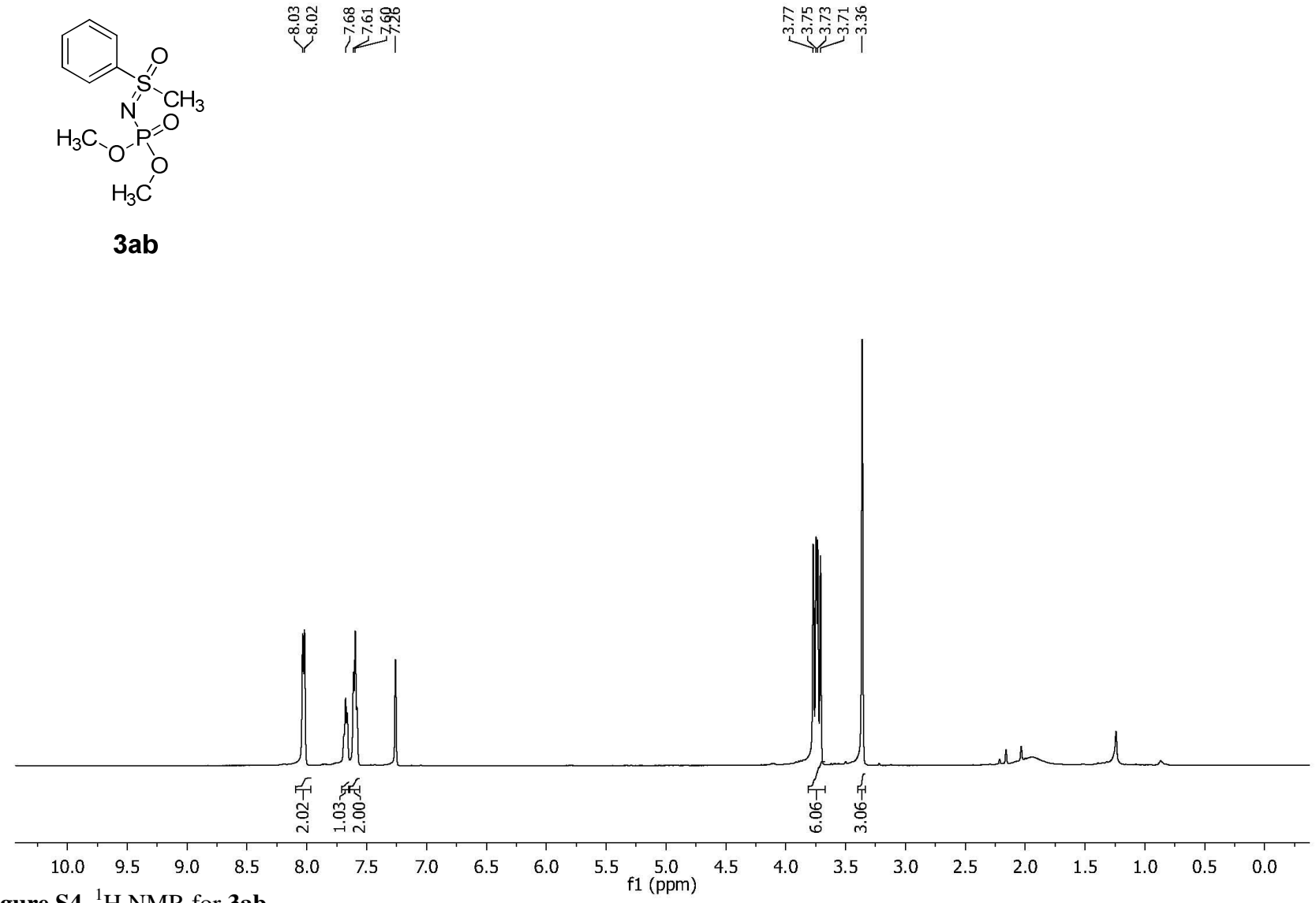


Figure S3. ^{31}P NMR for **3aa**



3ab

Figure S4. ^{1}H NMR for **3ab**

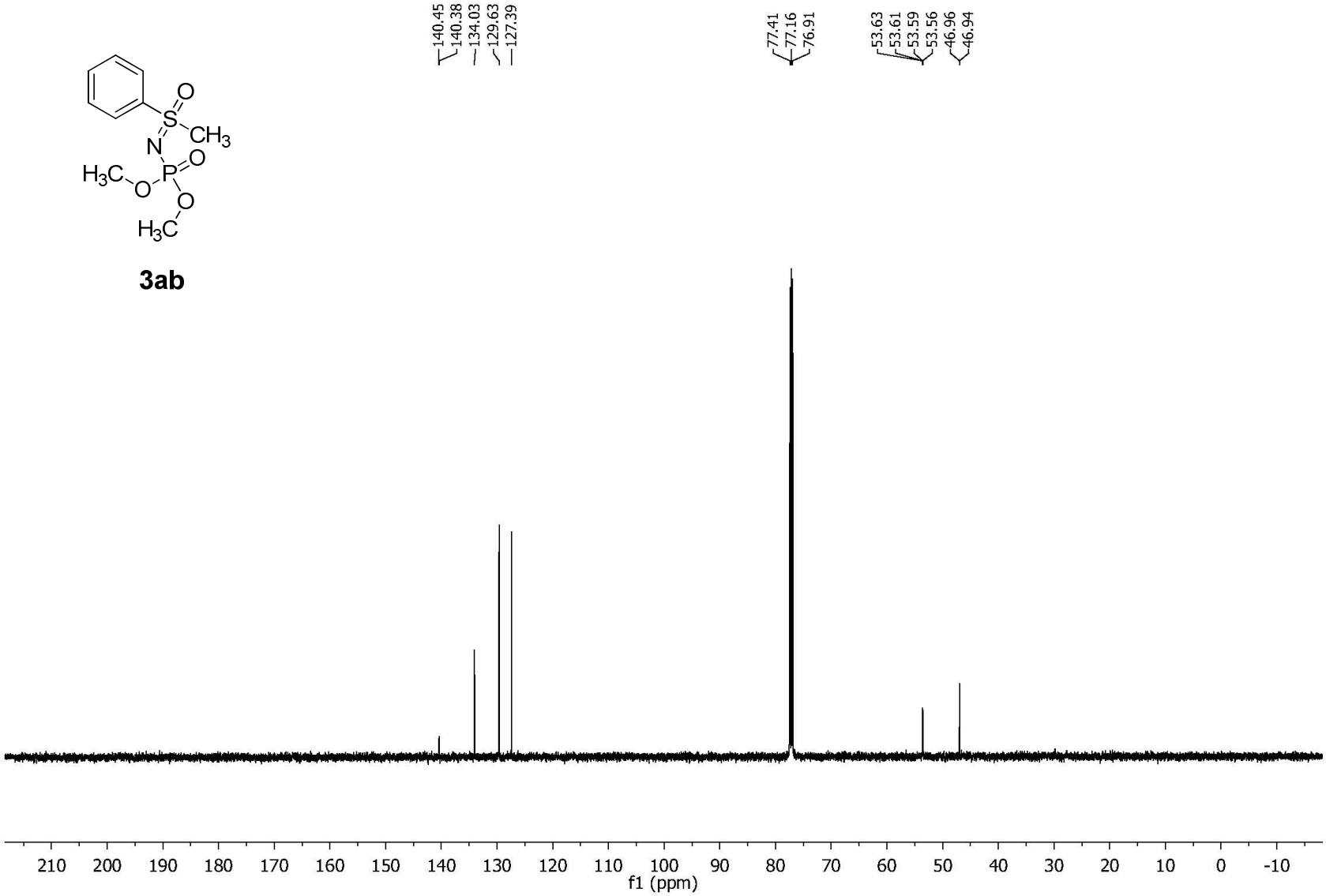


Figure S5. ^{13}C NMR for **3ab**

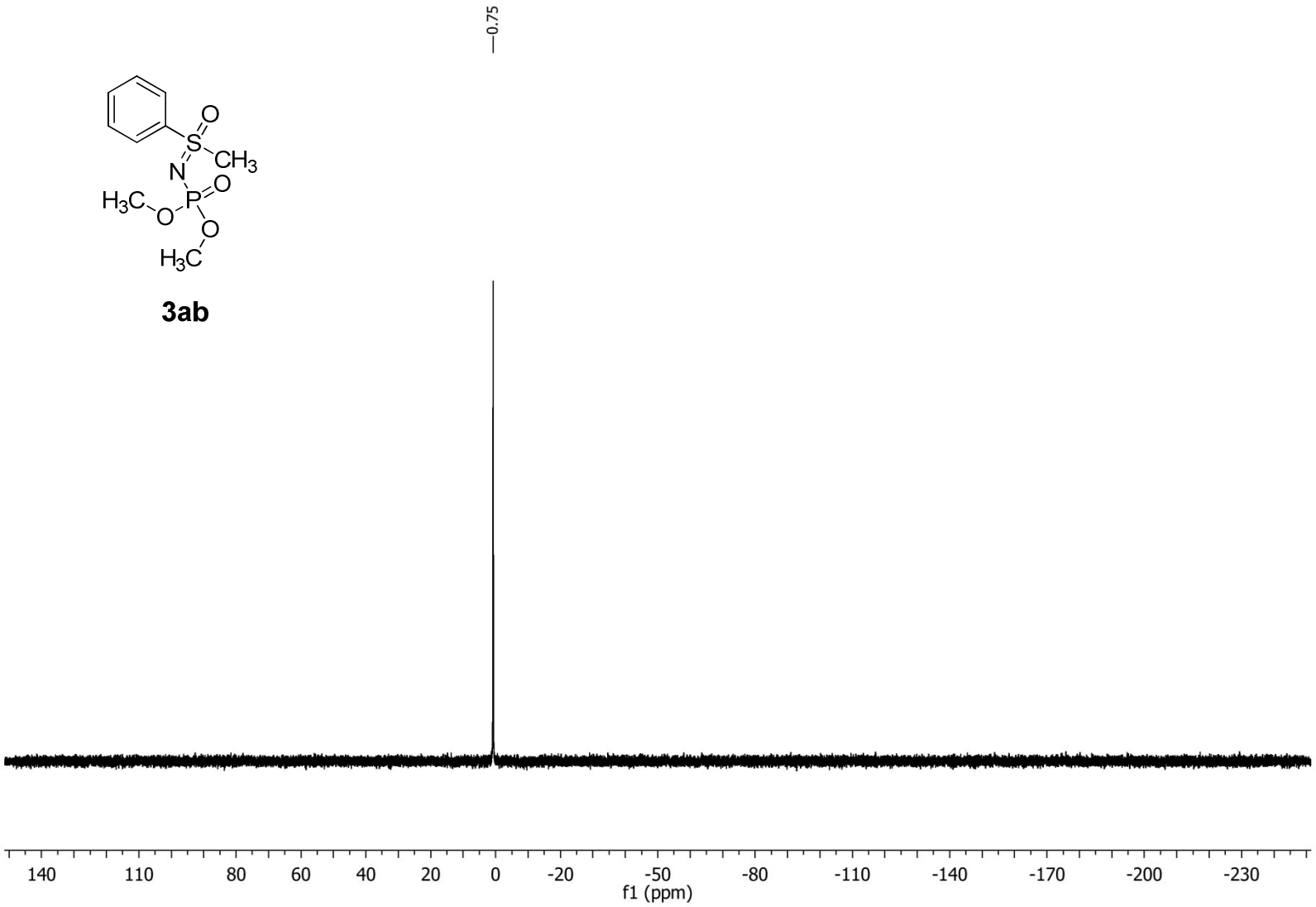


Figure S6. ^{31}P NMR for **3ab**

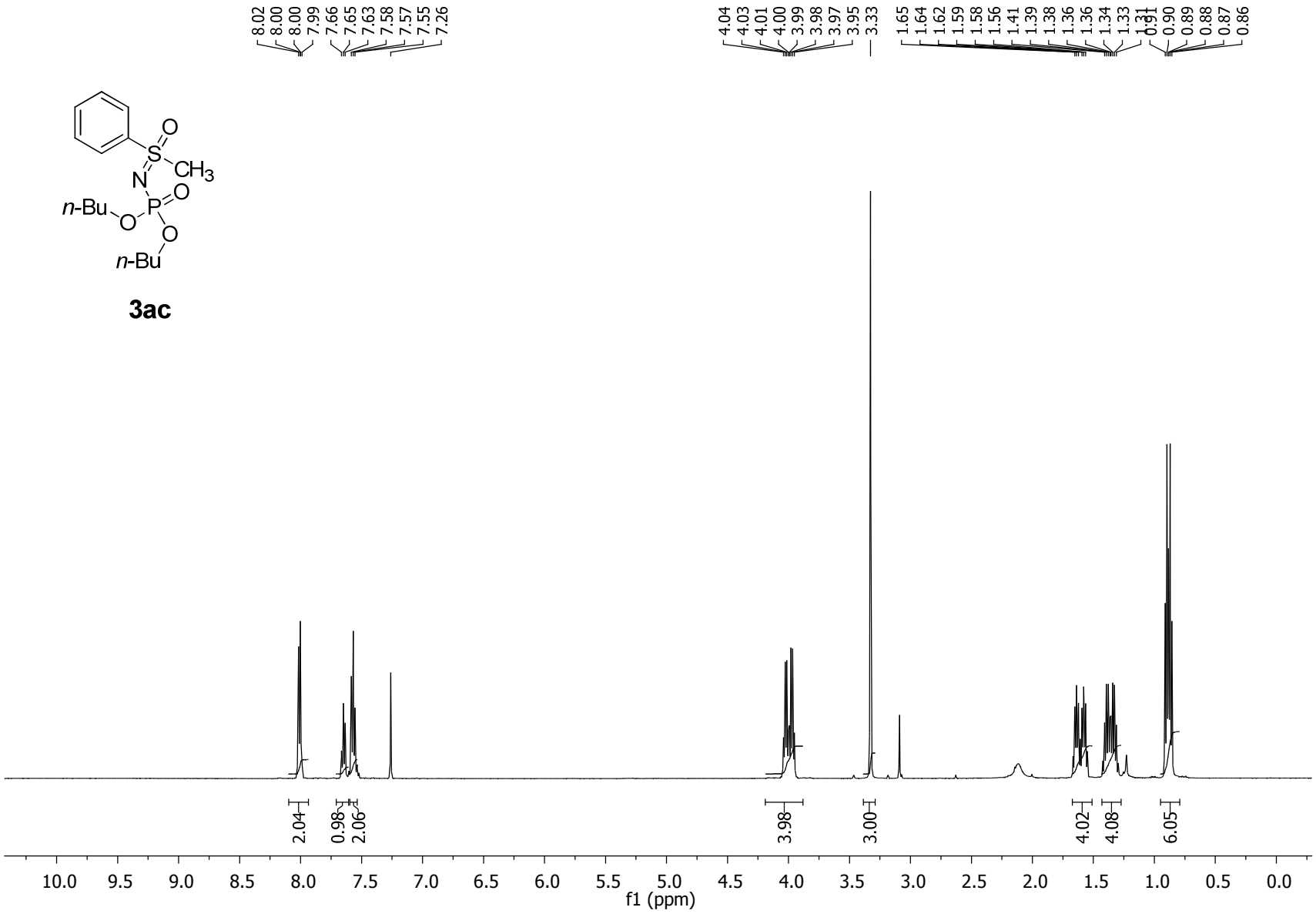


Figure S7. ^{1}H NMR for **3ac**

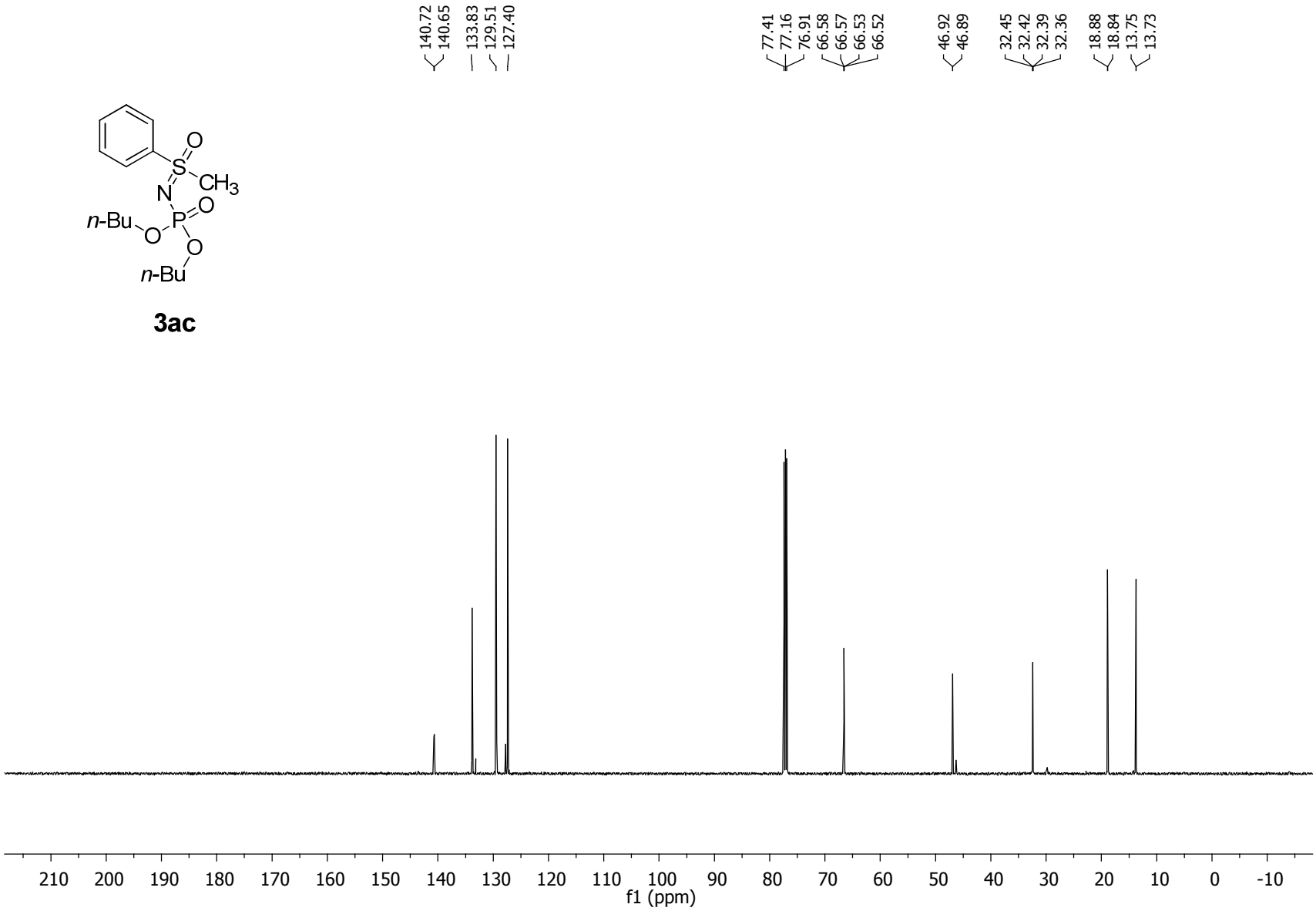


Figure S8. ^{13}C NMR for **3ac**

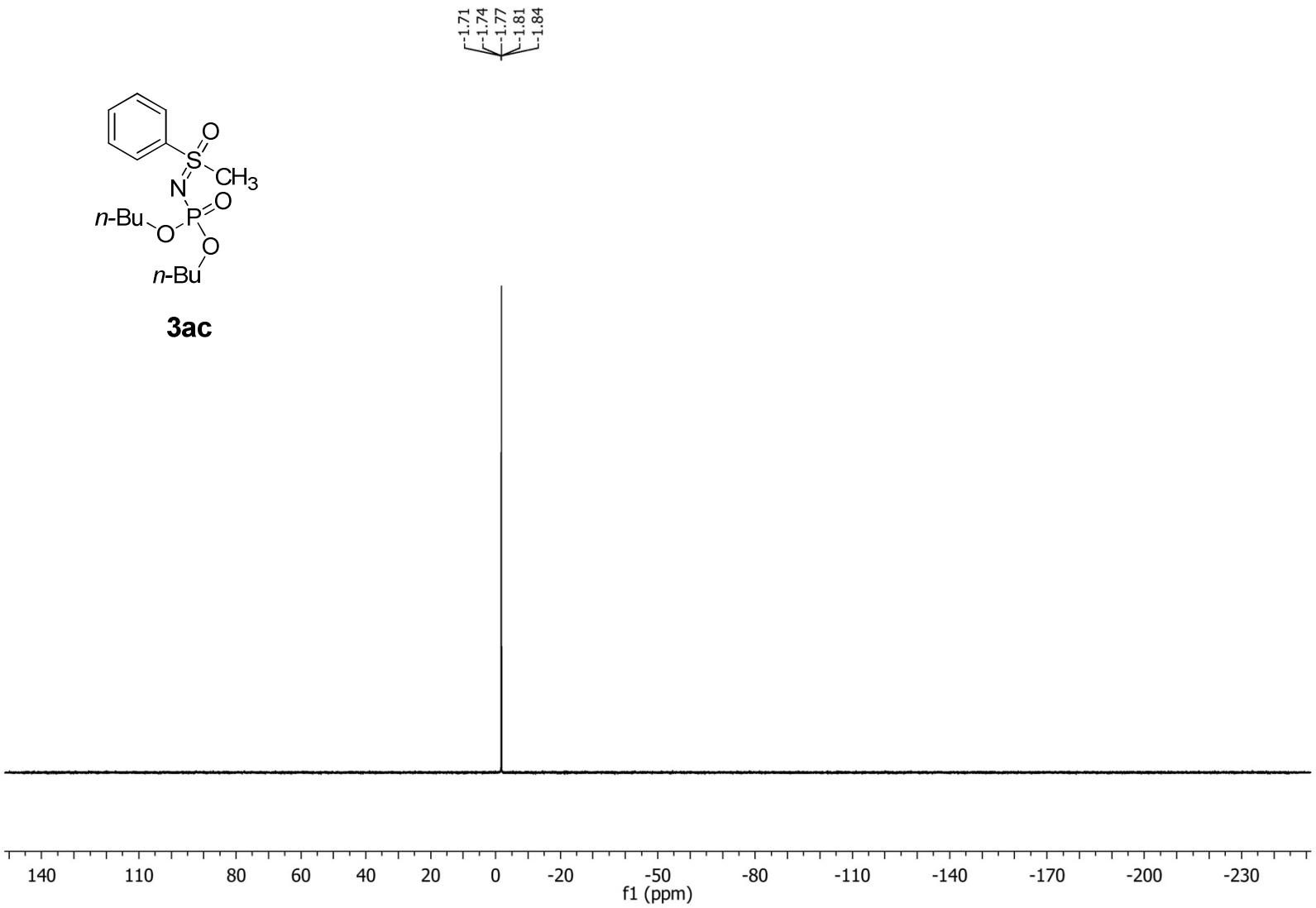


Figure S9. ^{31}P NMR for **3ac**

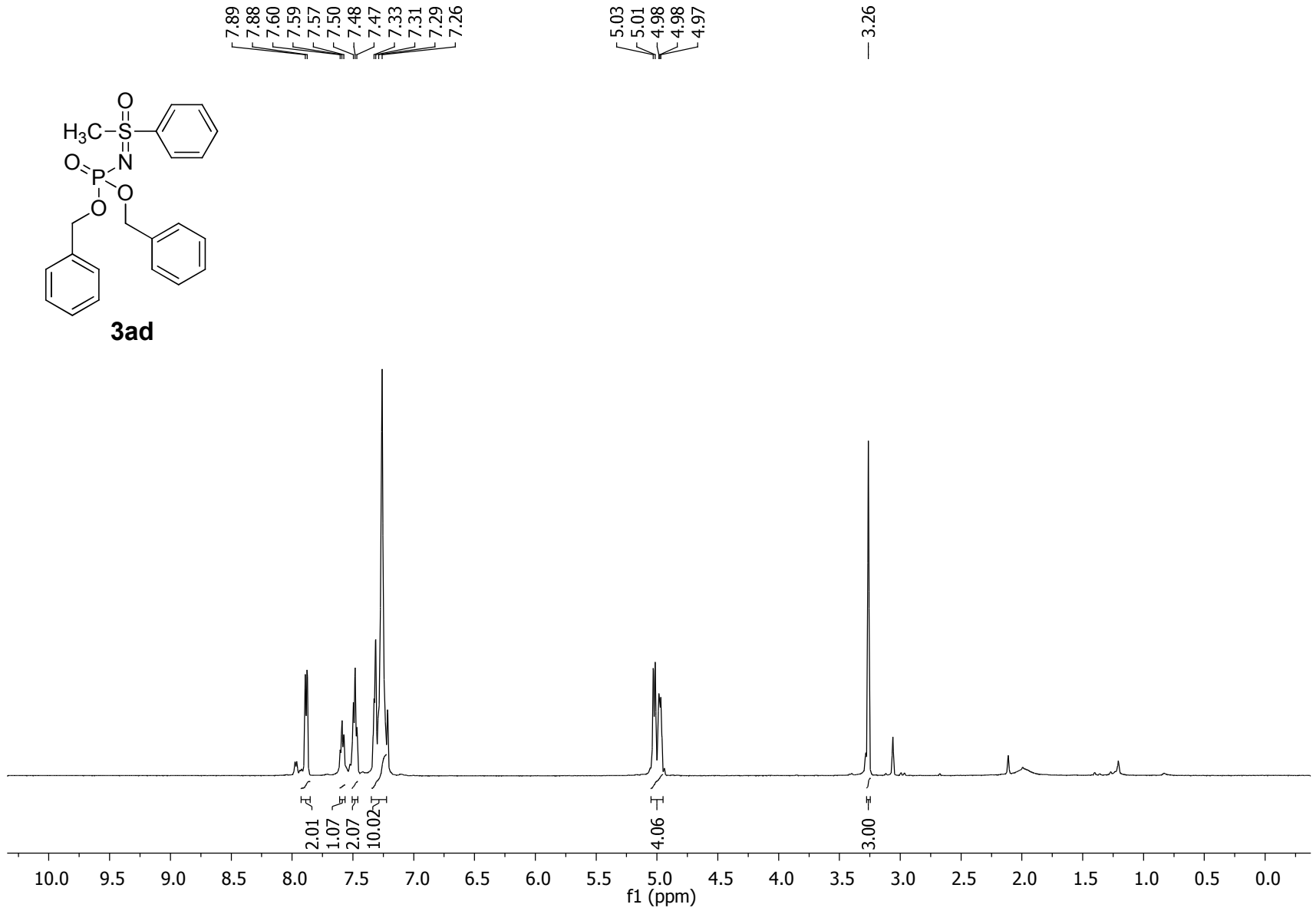


Figure S10. ^{1}H NMR for **3ad**

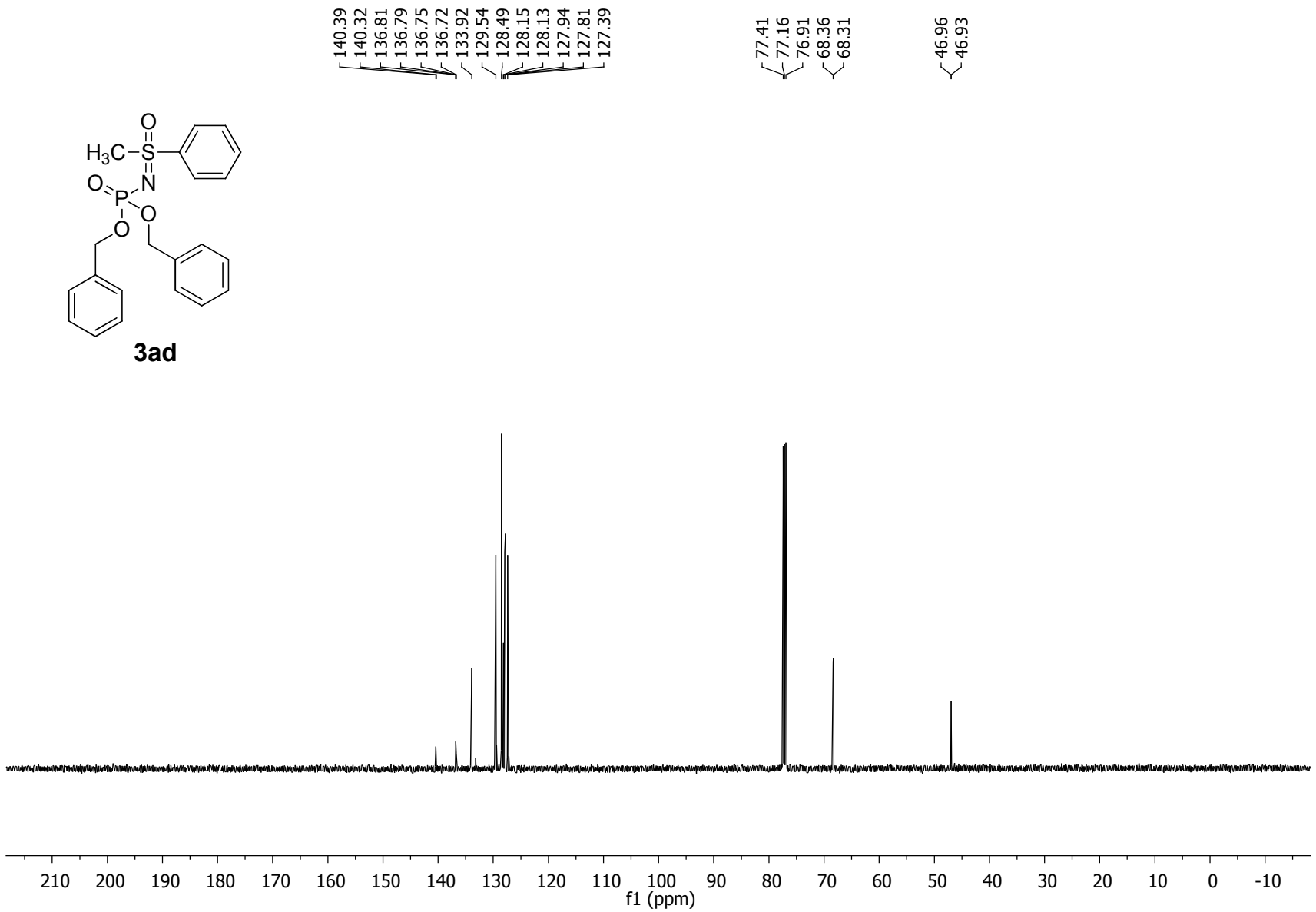


Figure S11. ^{13}C NMR for **3ad**

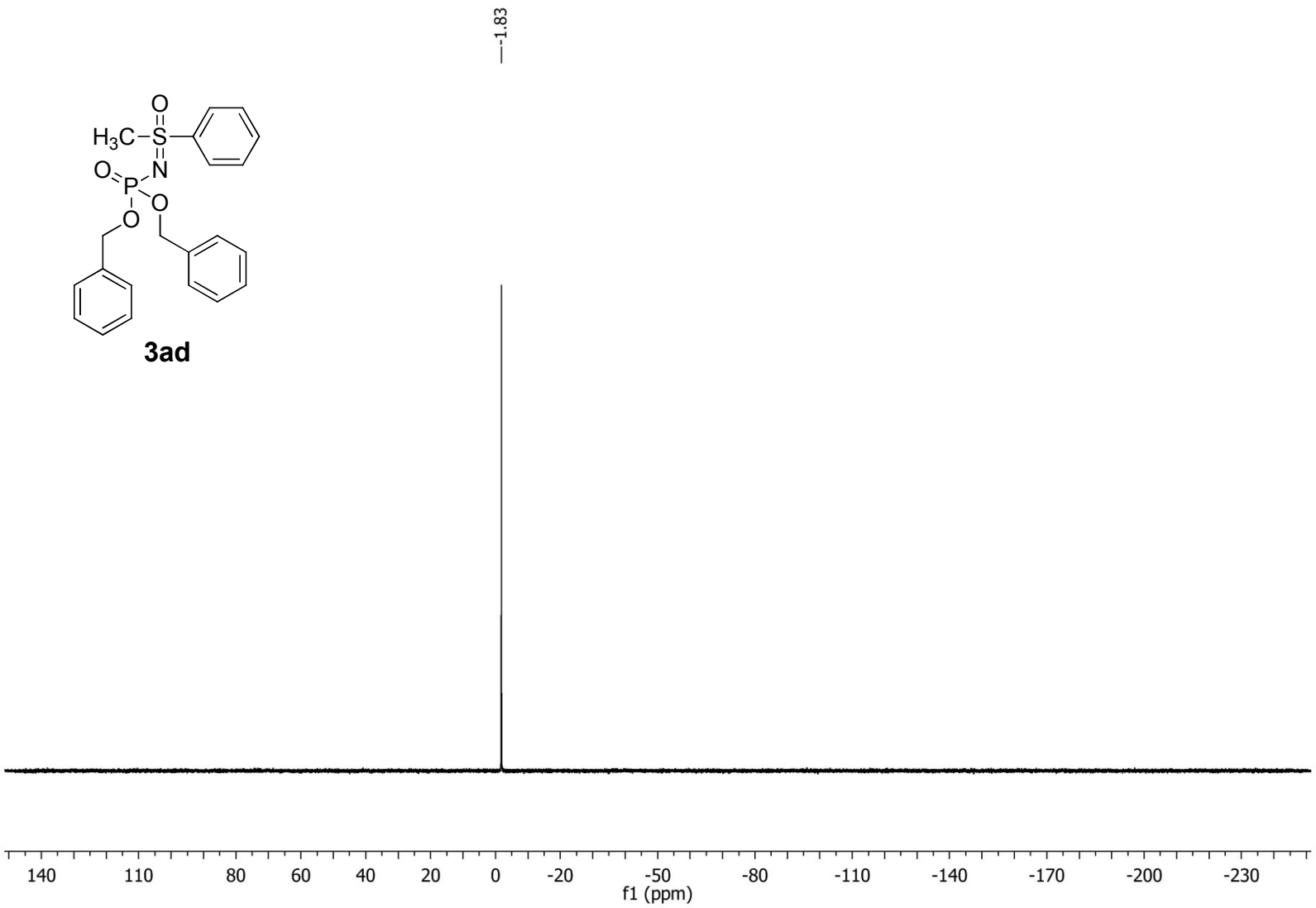


Figure S12. ^{31}P NMR for **3ad**

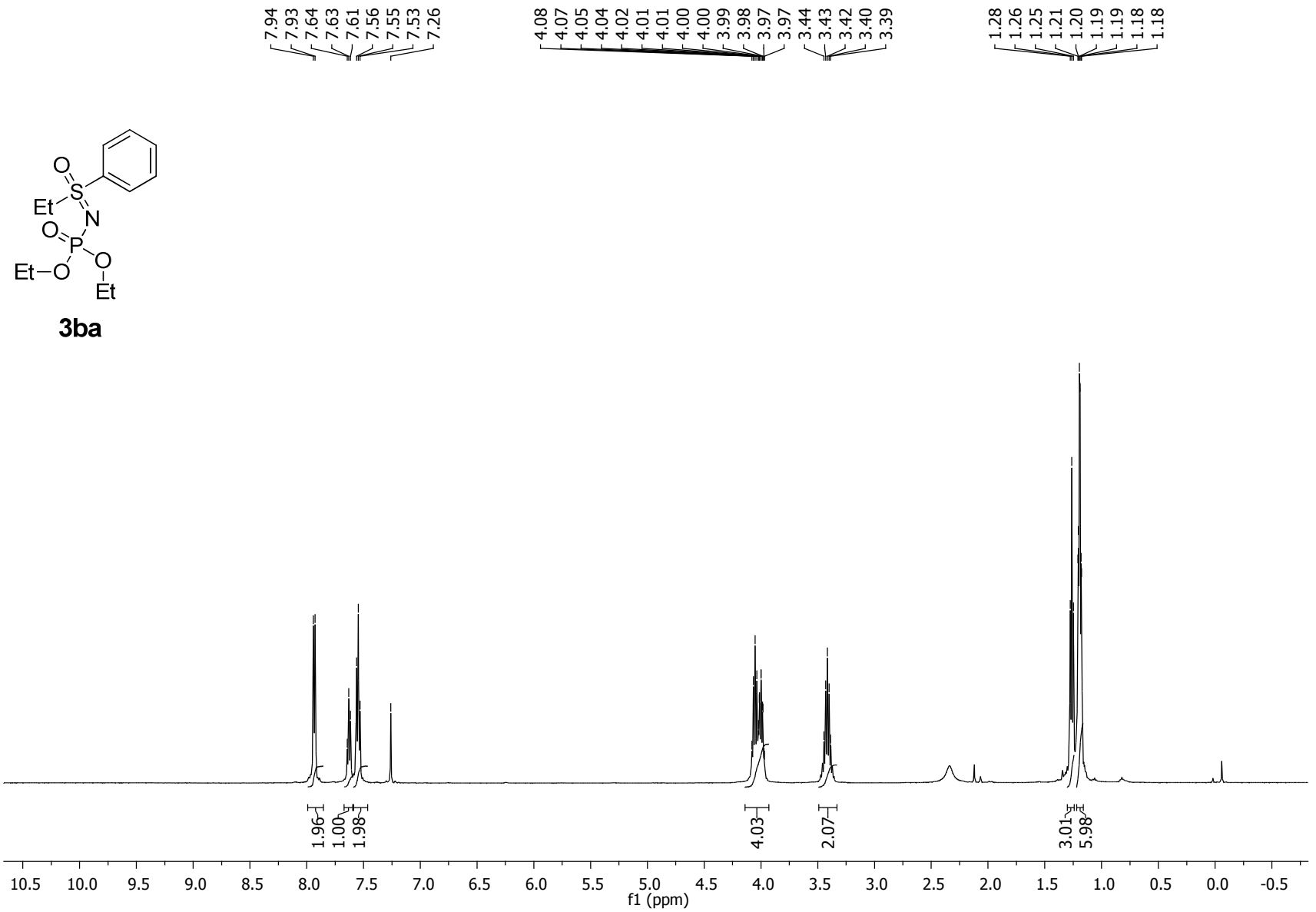


Figure S13. ^{1}H NMR for **3ba**

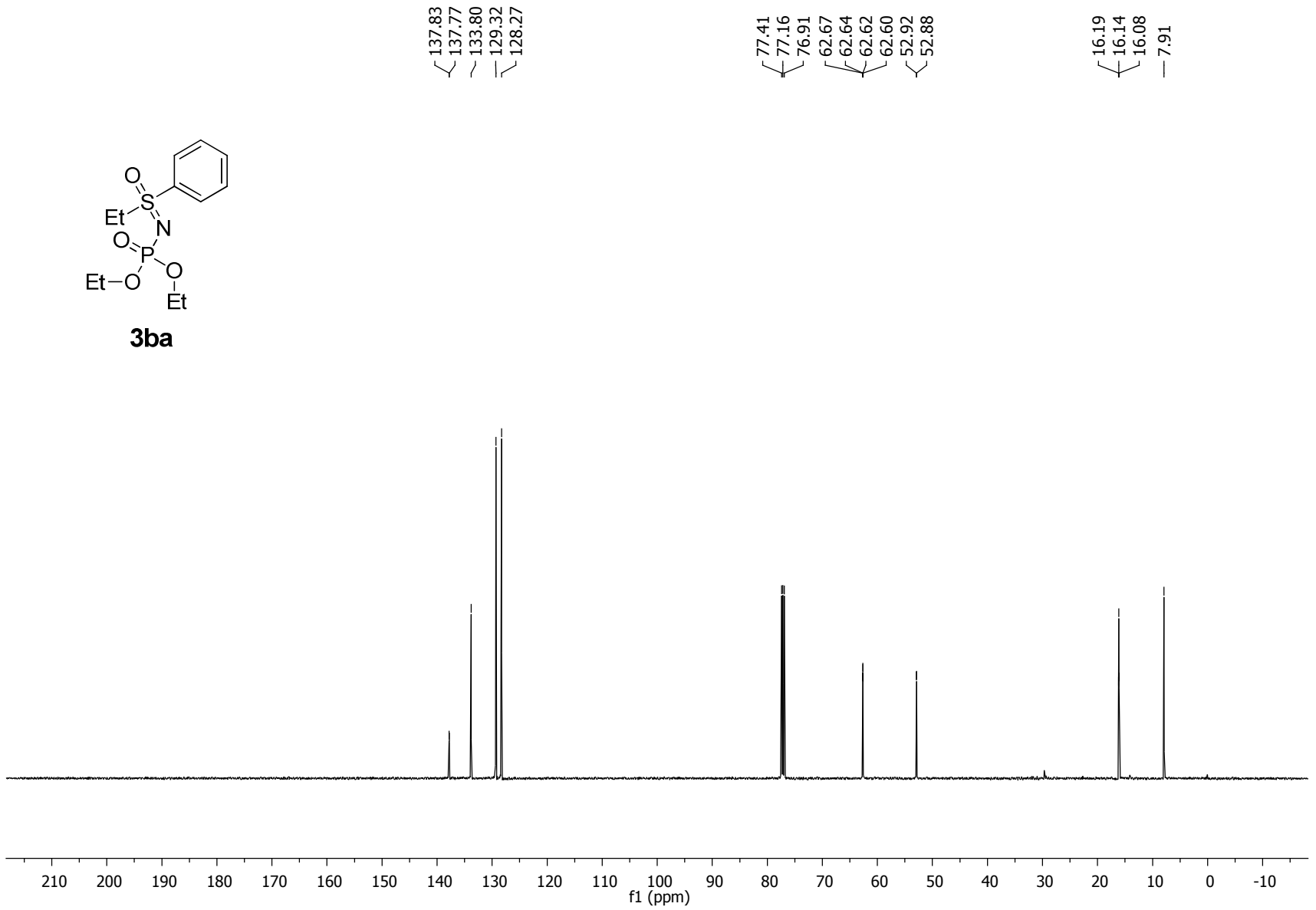


Figure S14. ^{13}C NMR for **3ba**

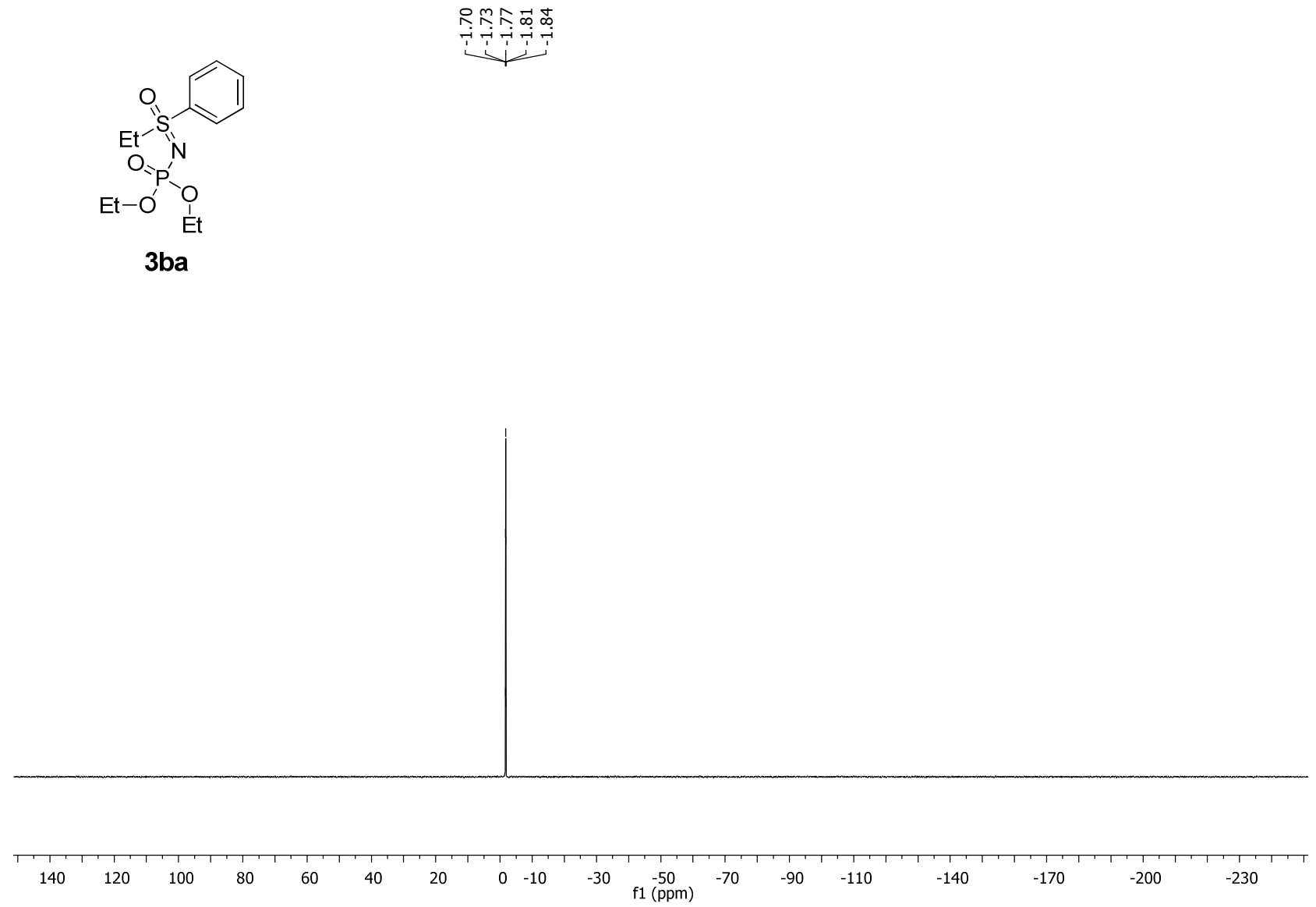


Figure S15. ^{31}P NMR for **3ba**

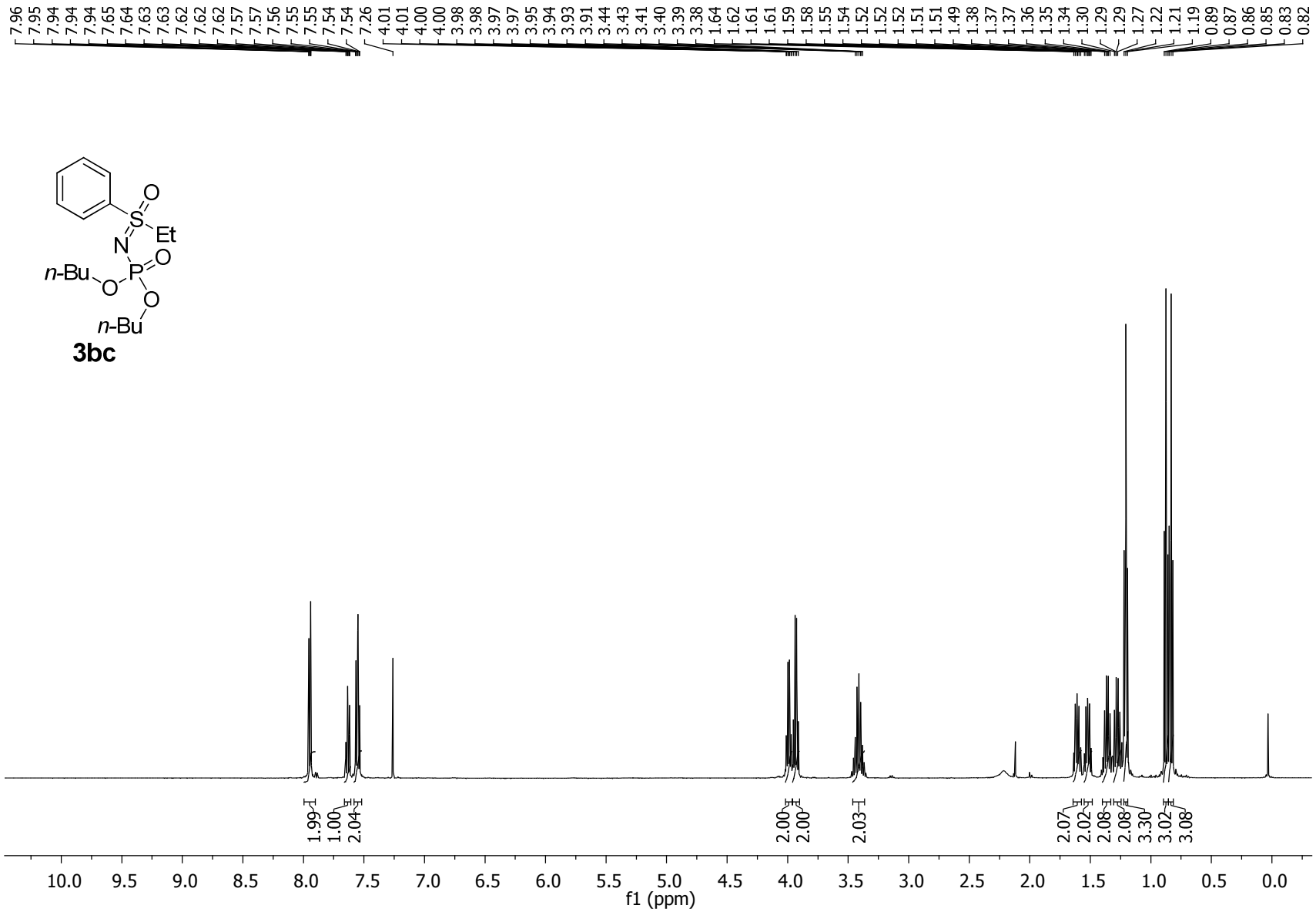


Figure S16. ^{1}H NMR for **3bc**

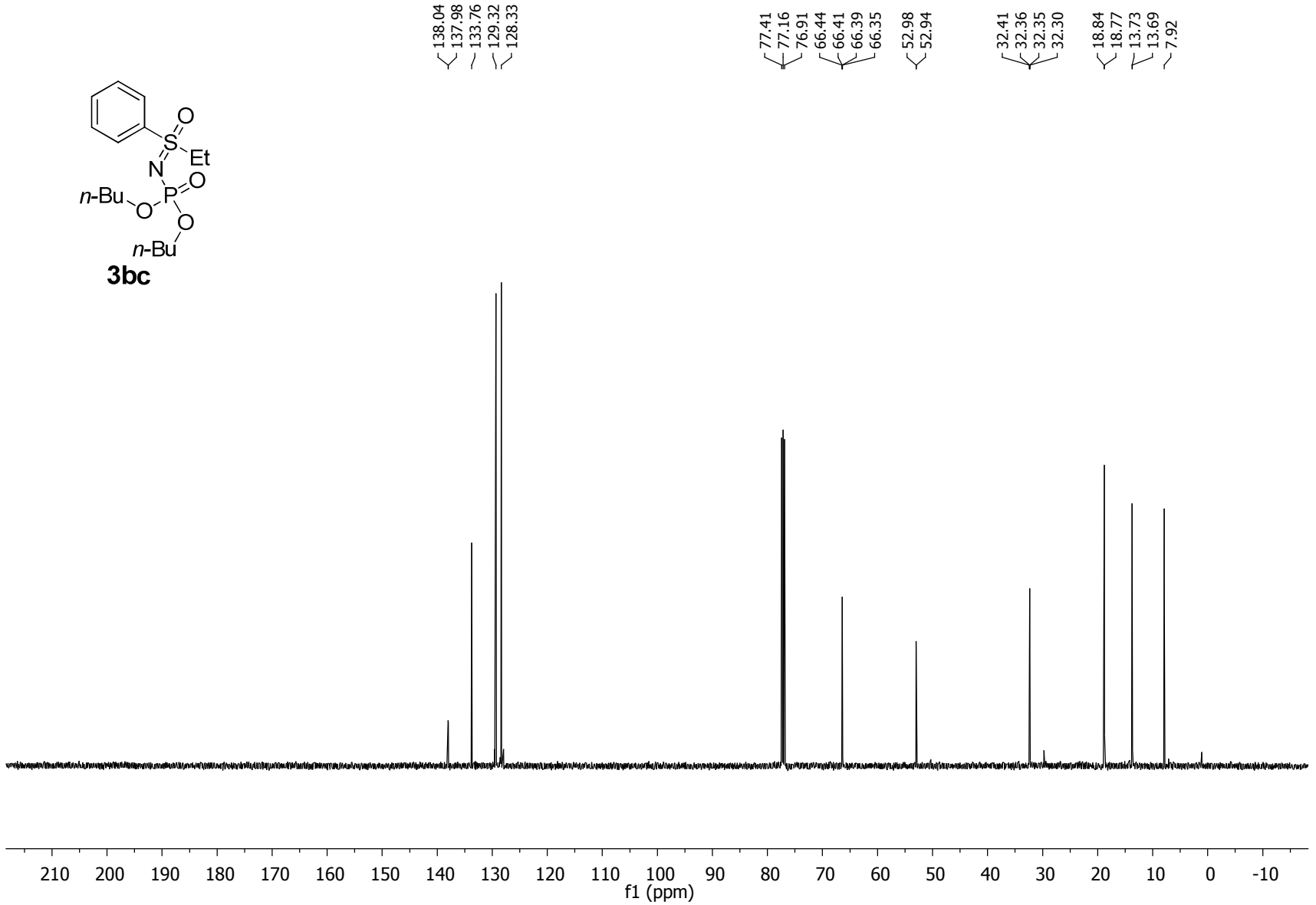


Figure S17. ^{13}C NMR for **3bc**

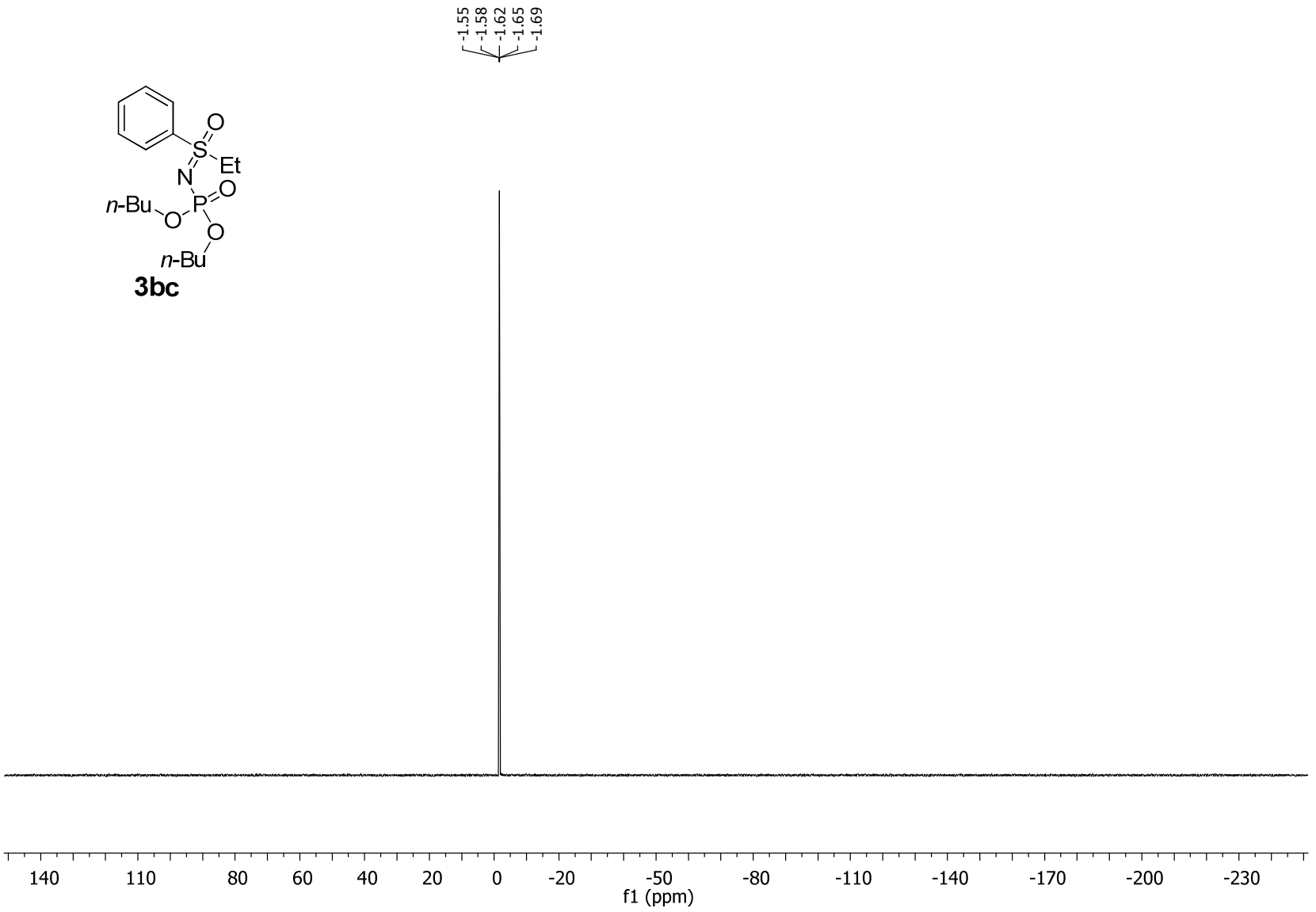


Figure S18. ^{31}P NMR for **3bc**

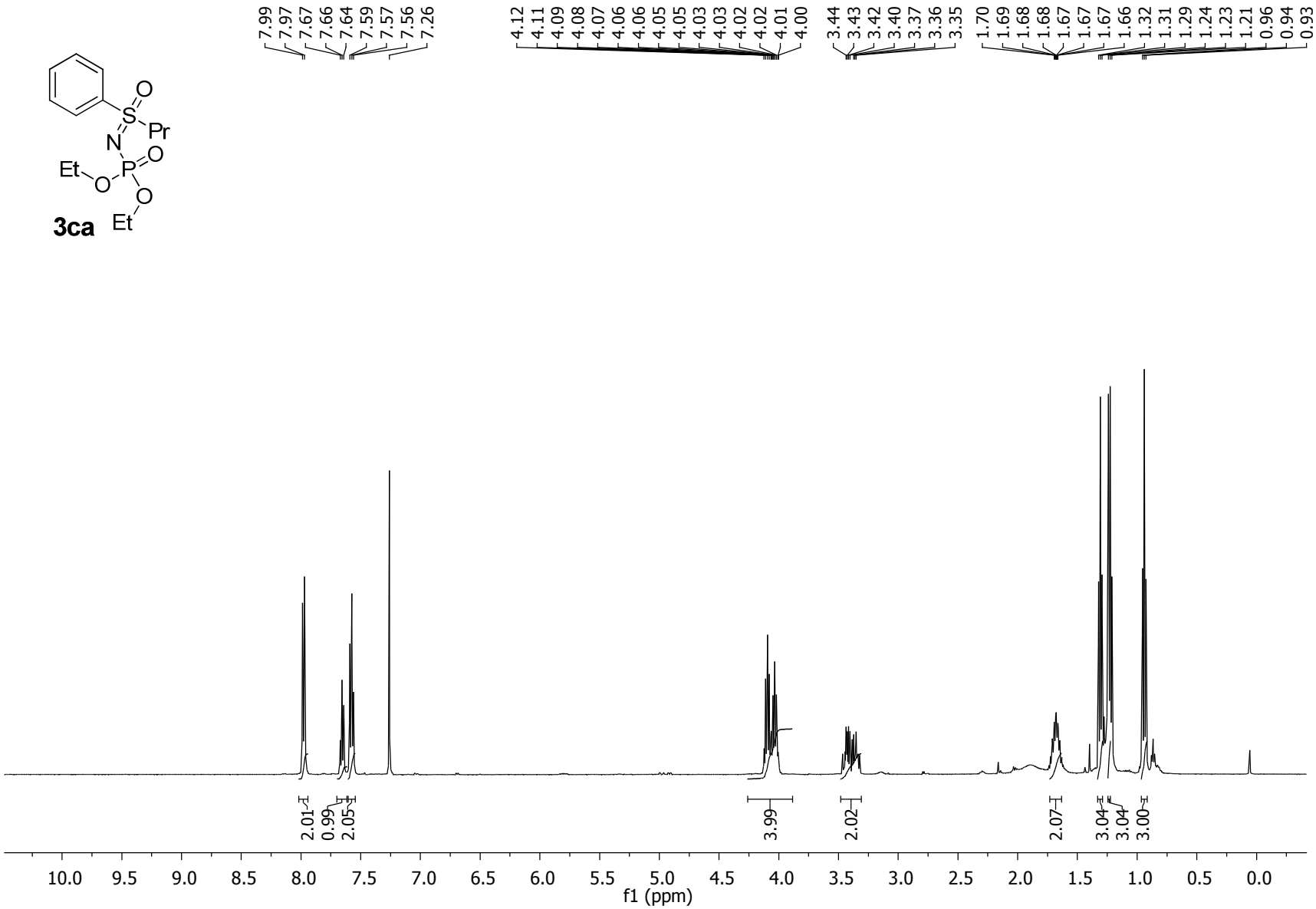


Figure S19. ^{1}H NMR for **3ca**

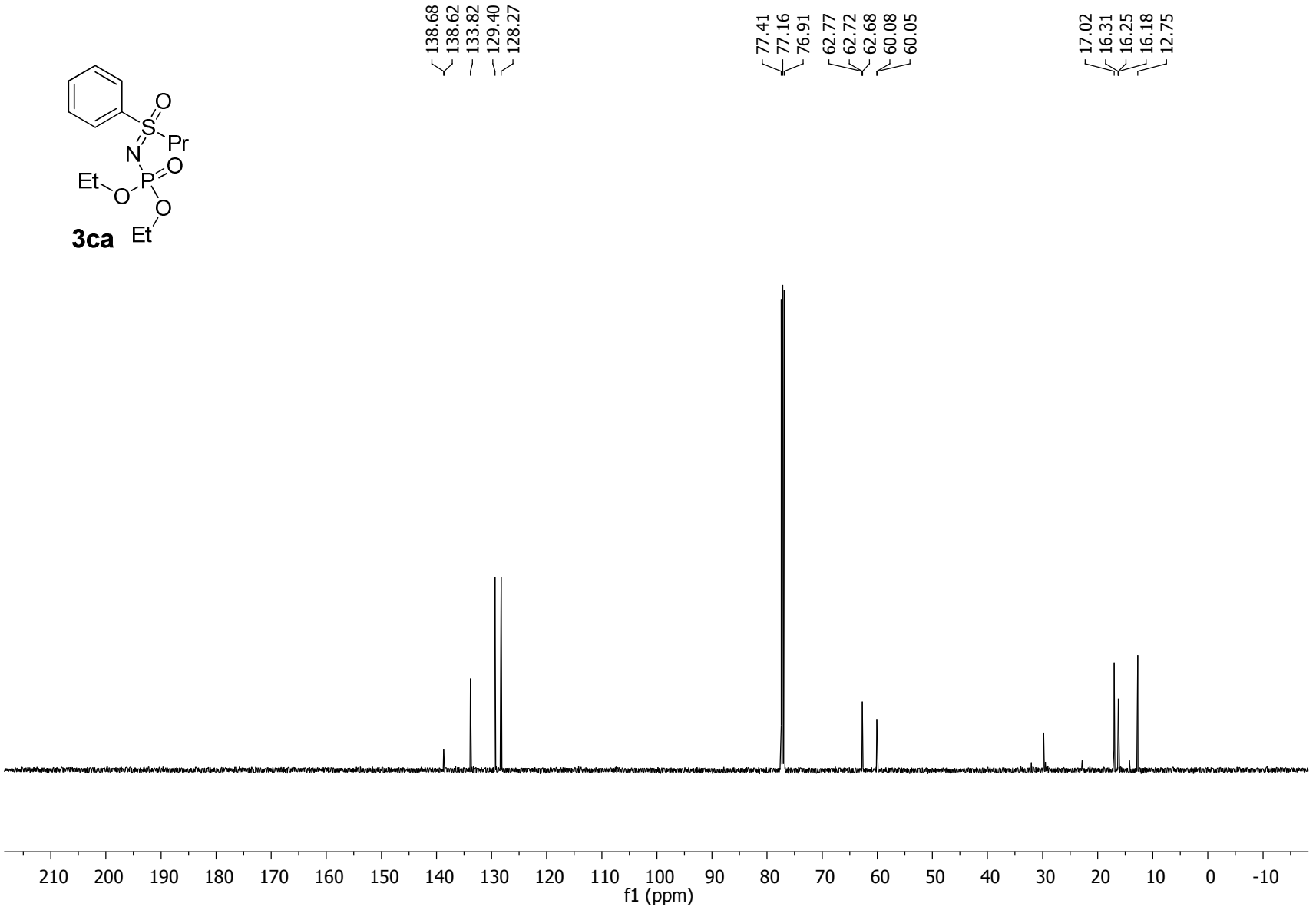


Figure S20. ^{13}C NMR for **3ca**

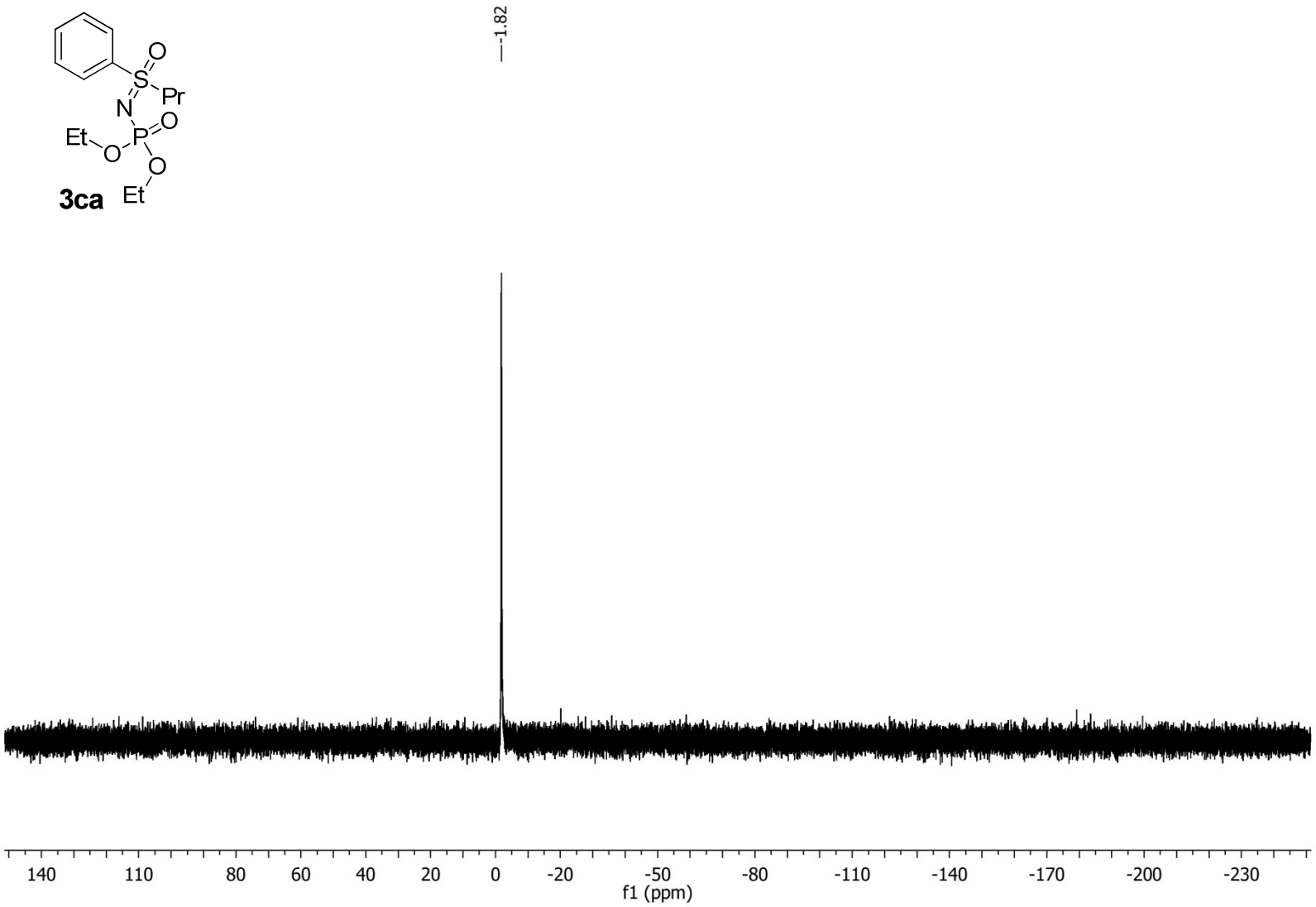


Figure S21. ^{31}P NMR for **3ca**

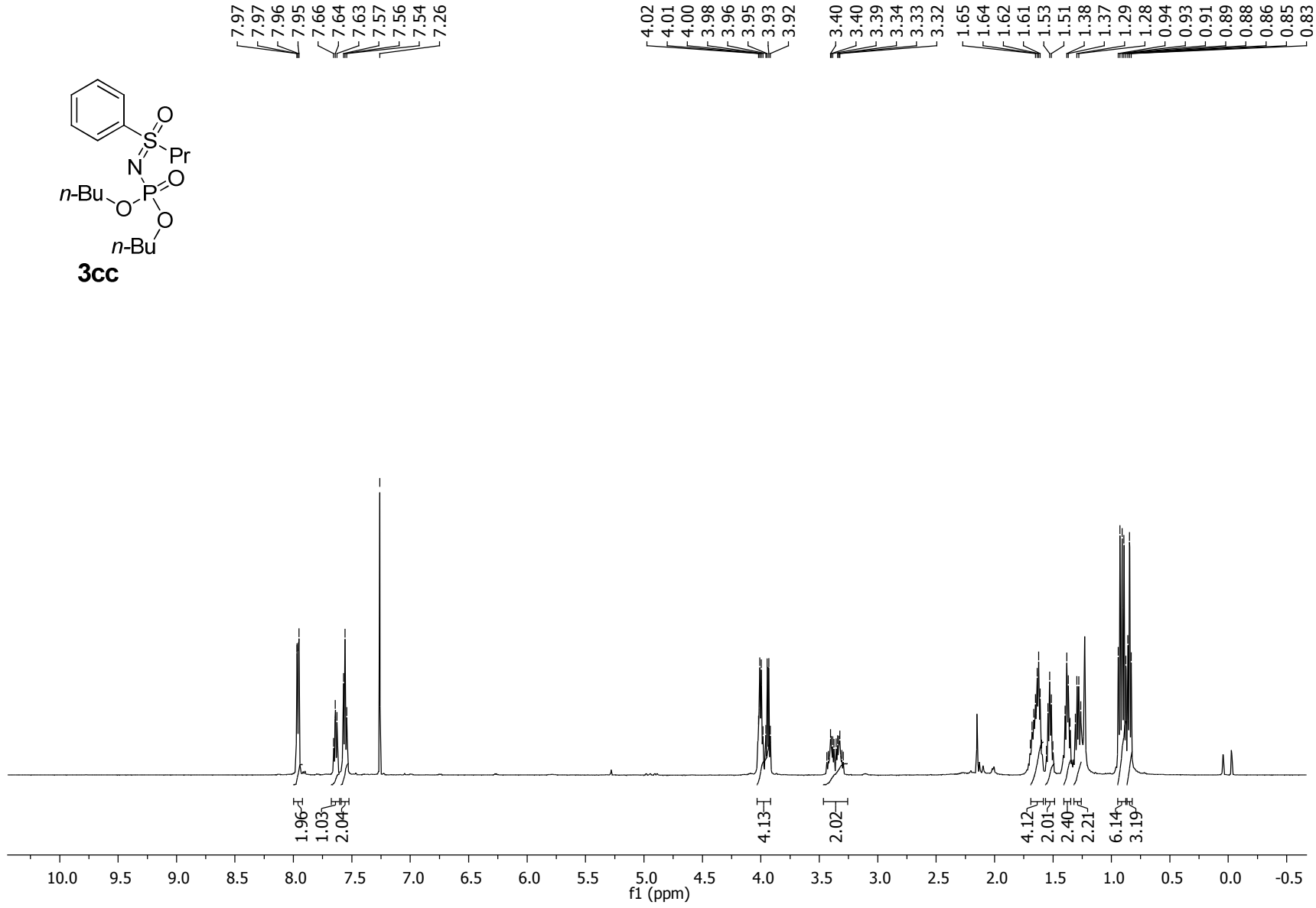


Figure S22. ^{1}H NMR for **3cc**

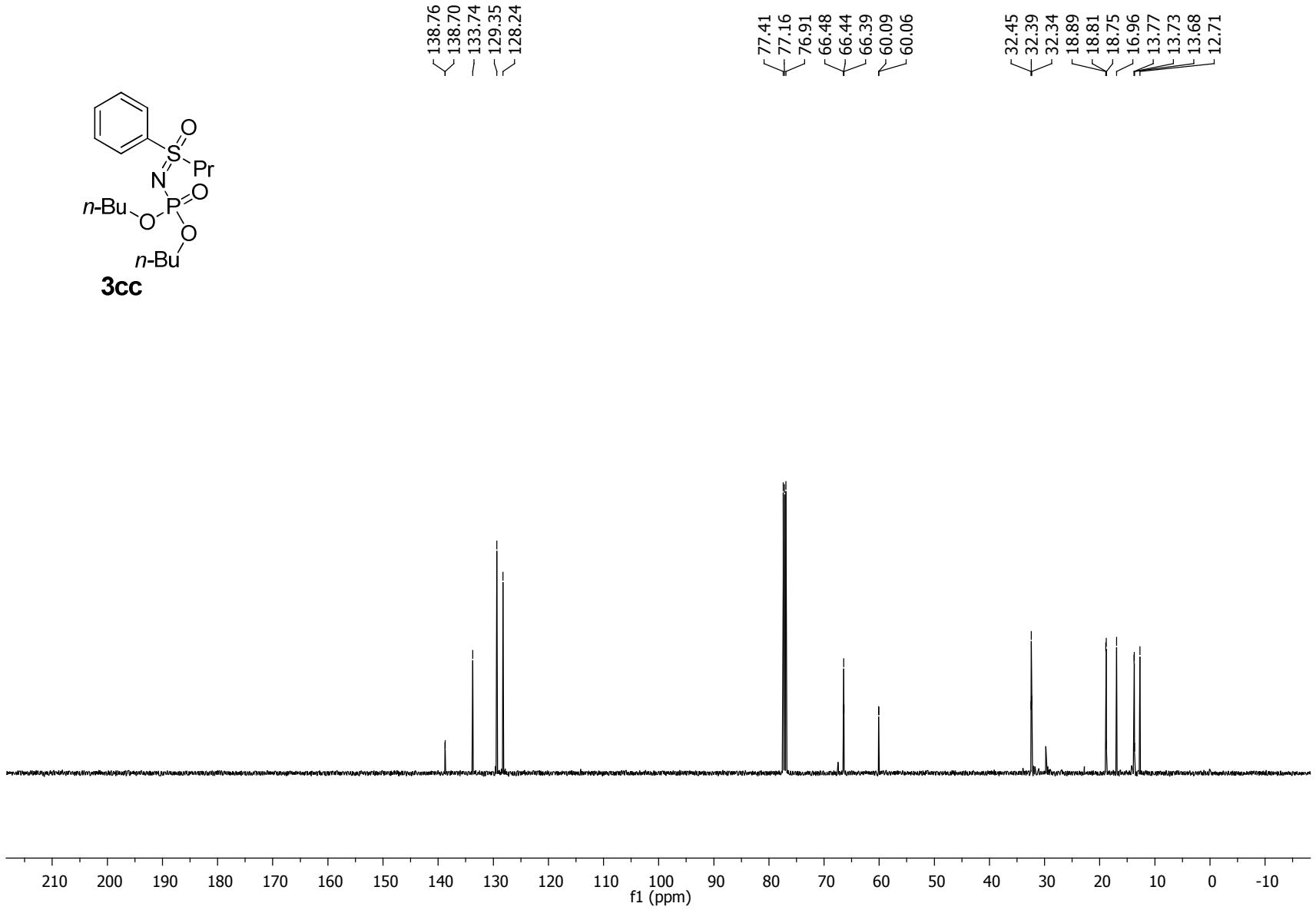


Figure S23. ^{13}C NMR for **3cc**

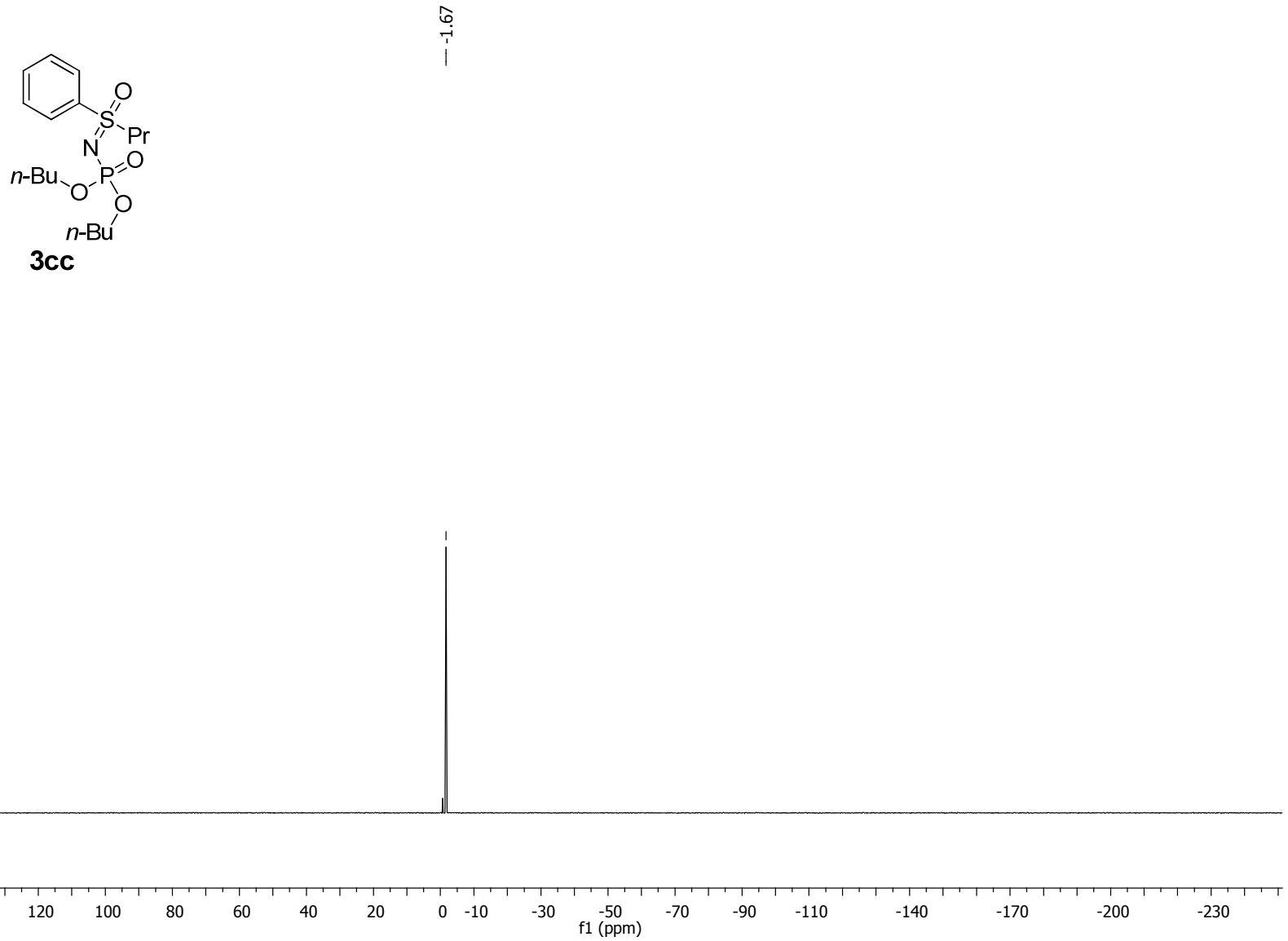


Figure S24. ^{31}P NMR for **3cc**

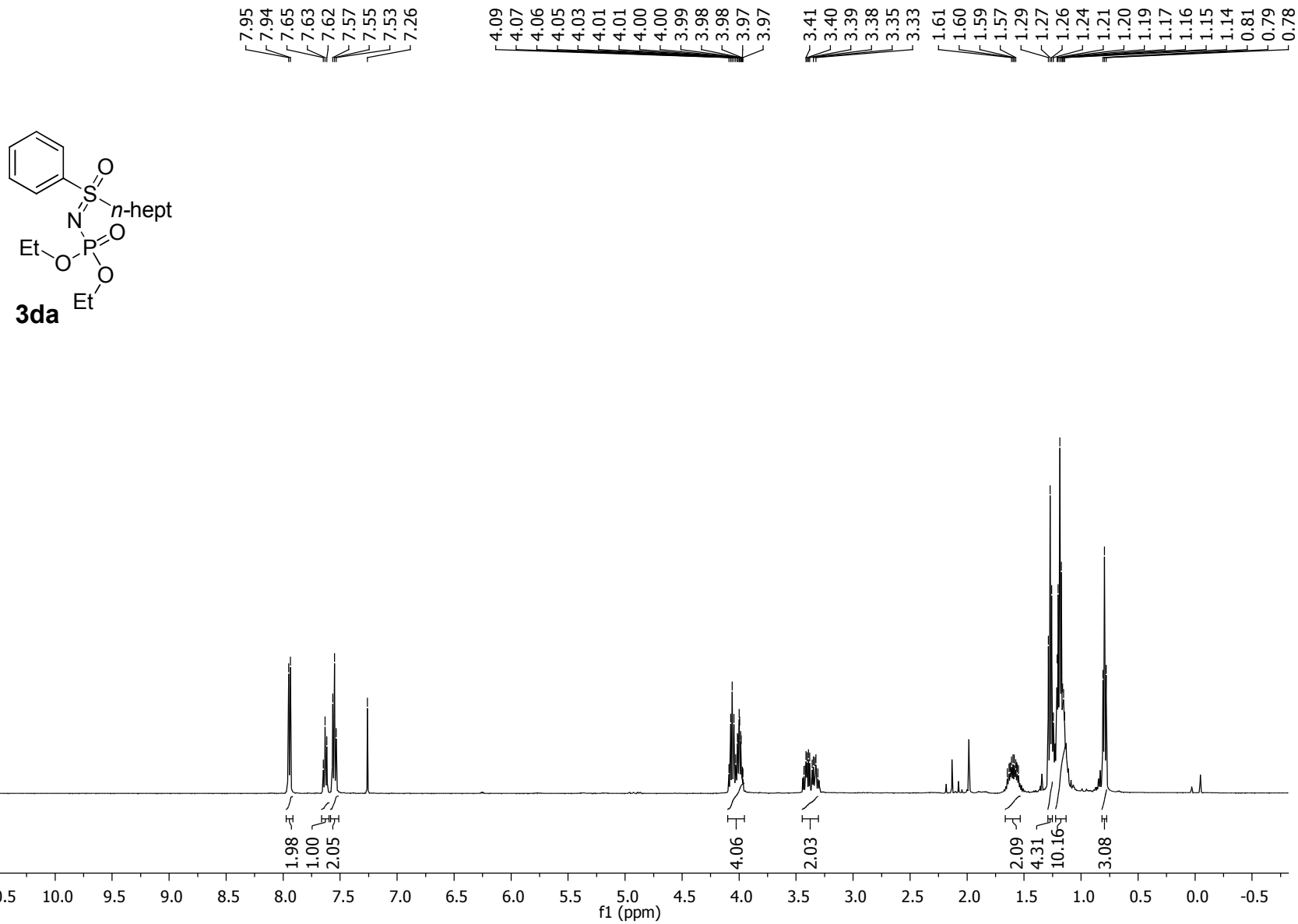


Figure S25. ^{1}H NMR for **3da**

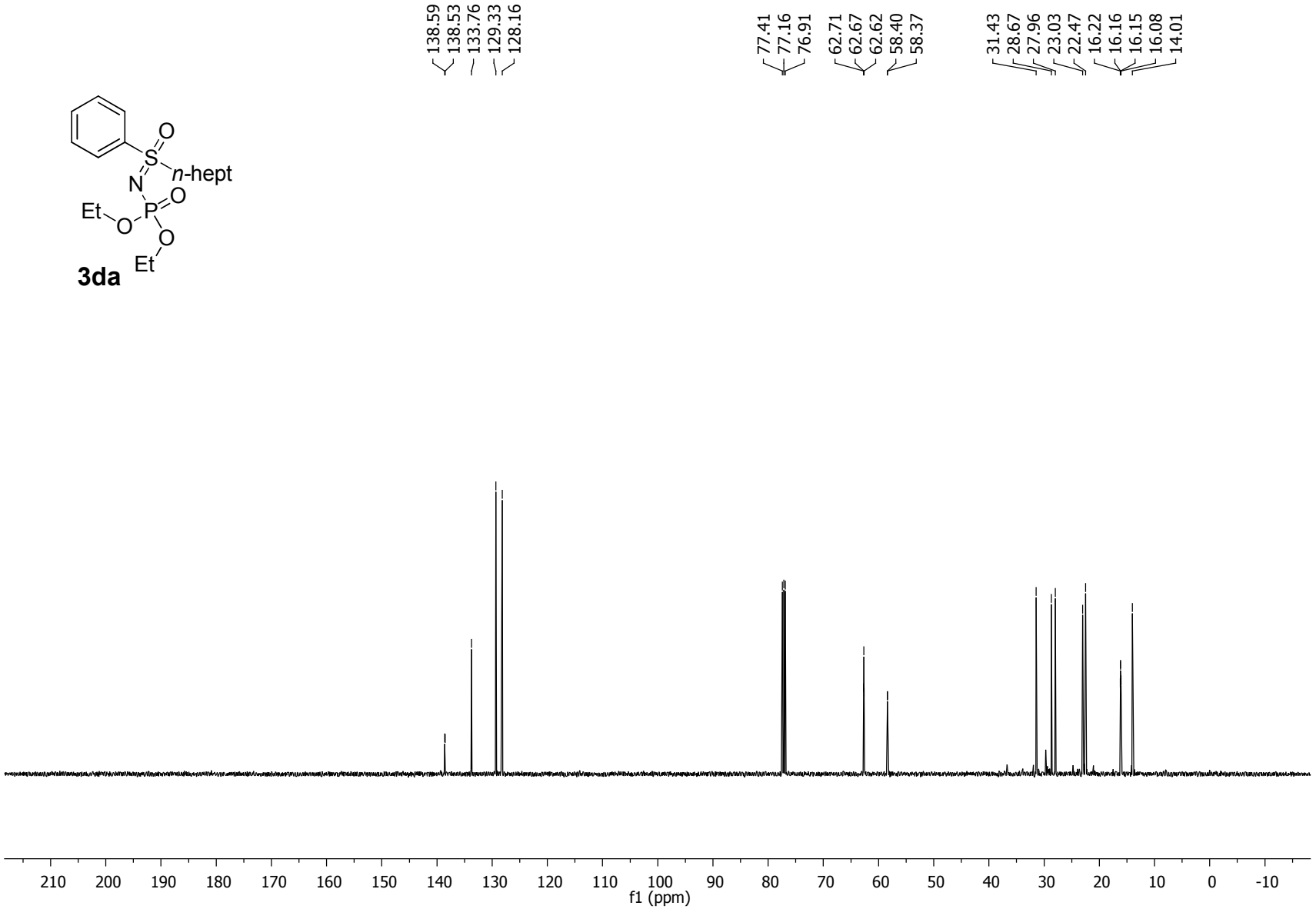


Figure S26. ^{13}C NMR for **3da**

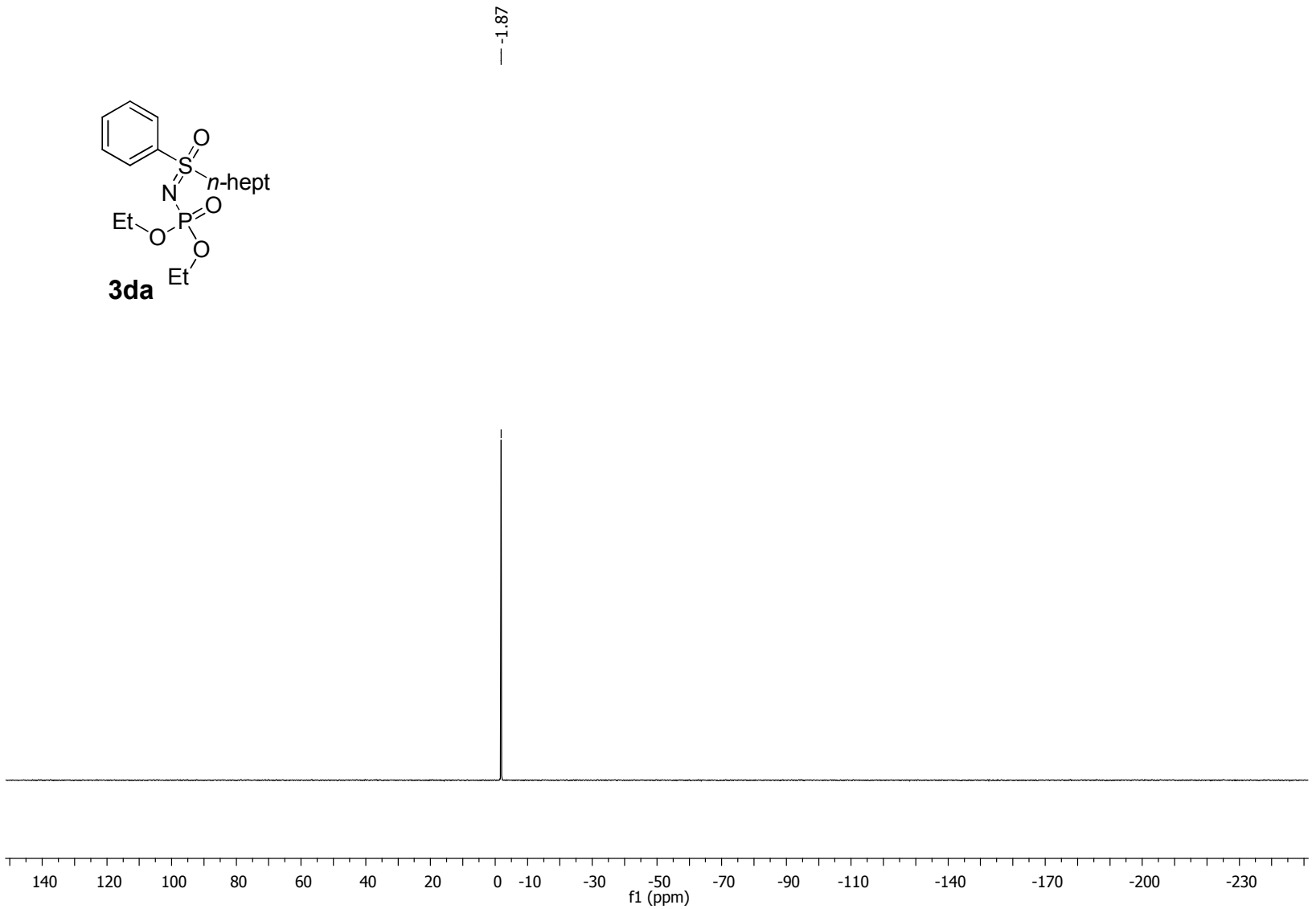


Figure S27. ^{31}P NMR for **3da**

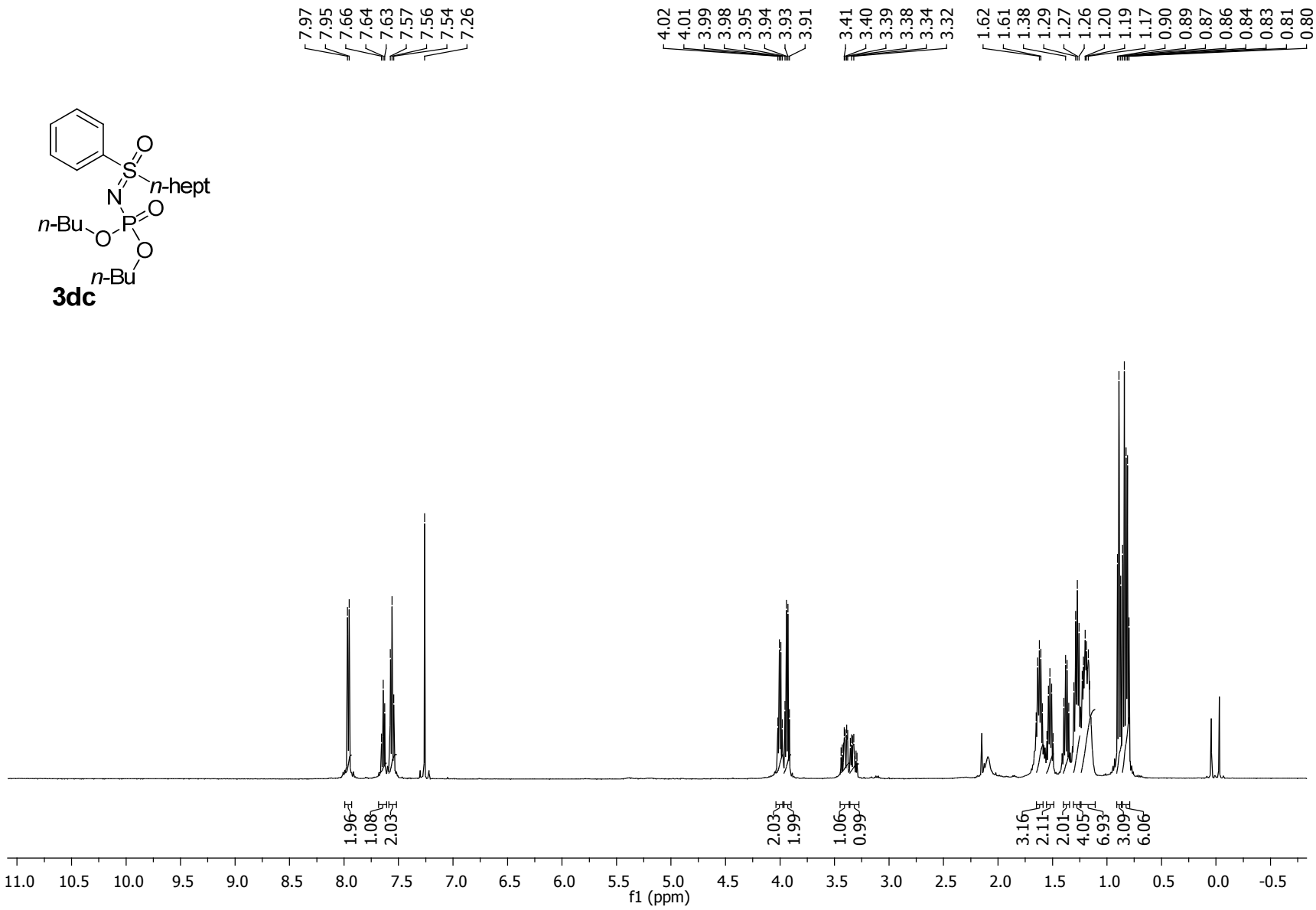


Figure S28. ^{1}H NMR for **3dc**

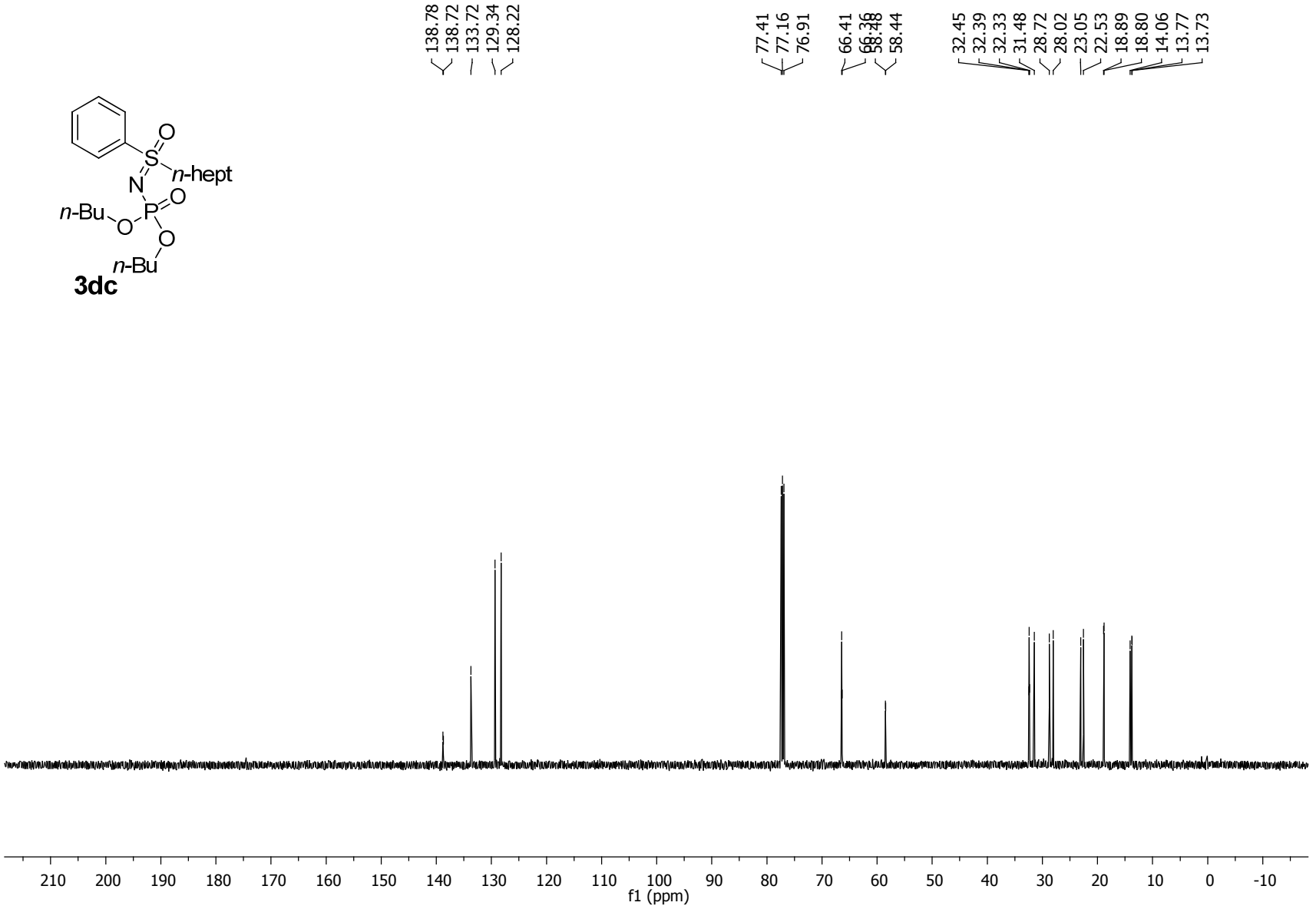


Figure S29. ^{13}C NMR for **3dc**

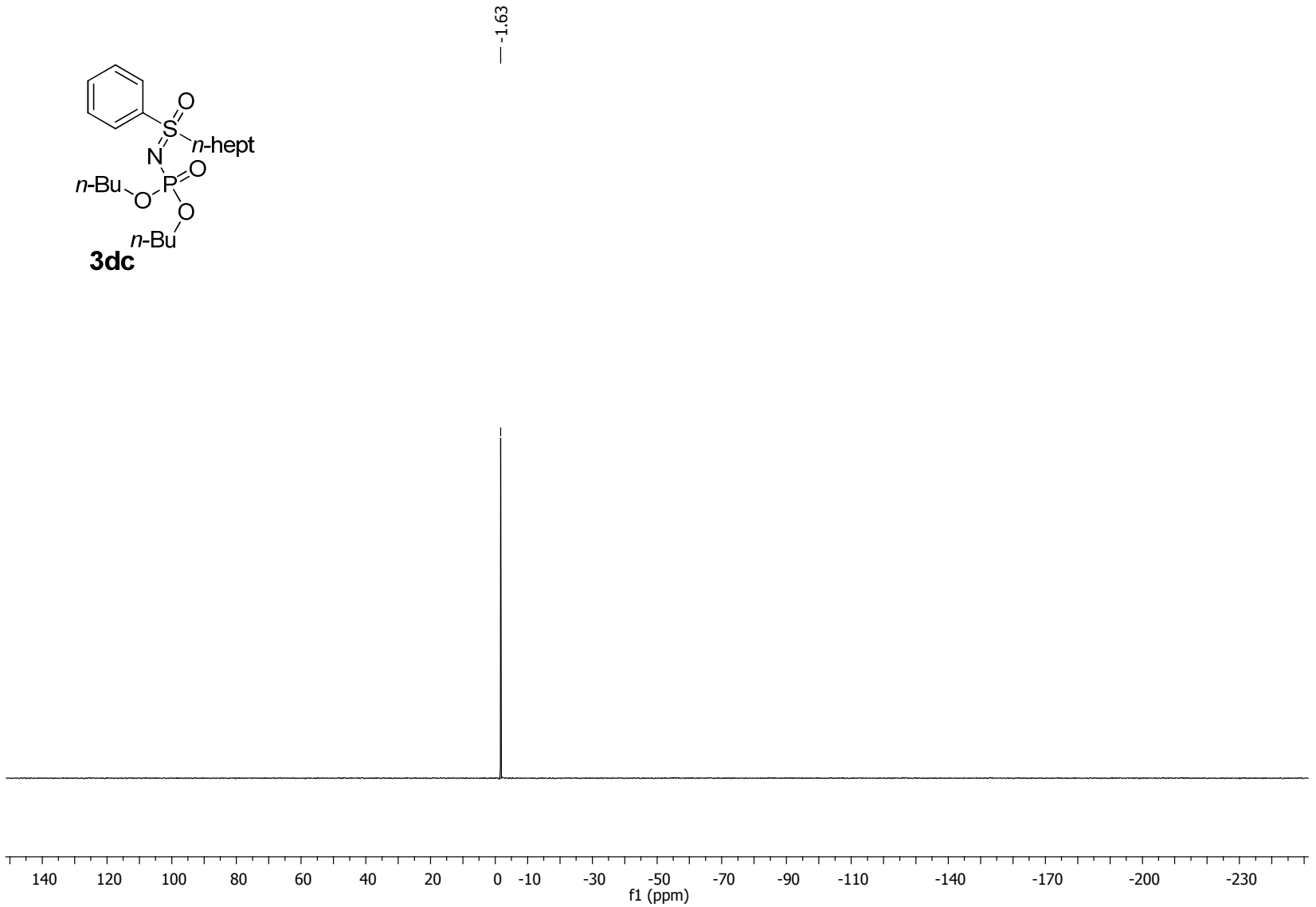


Figure S30. ^{31}P NMR for **3dc**

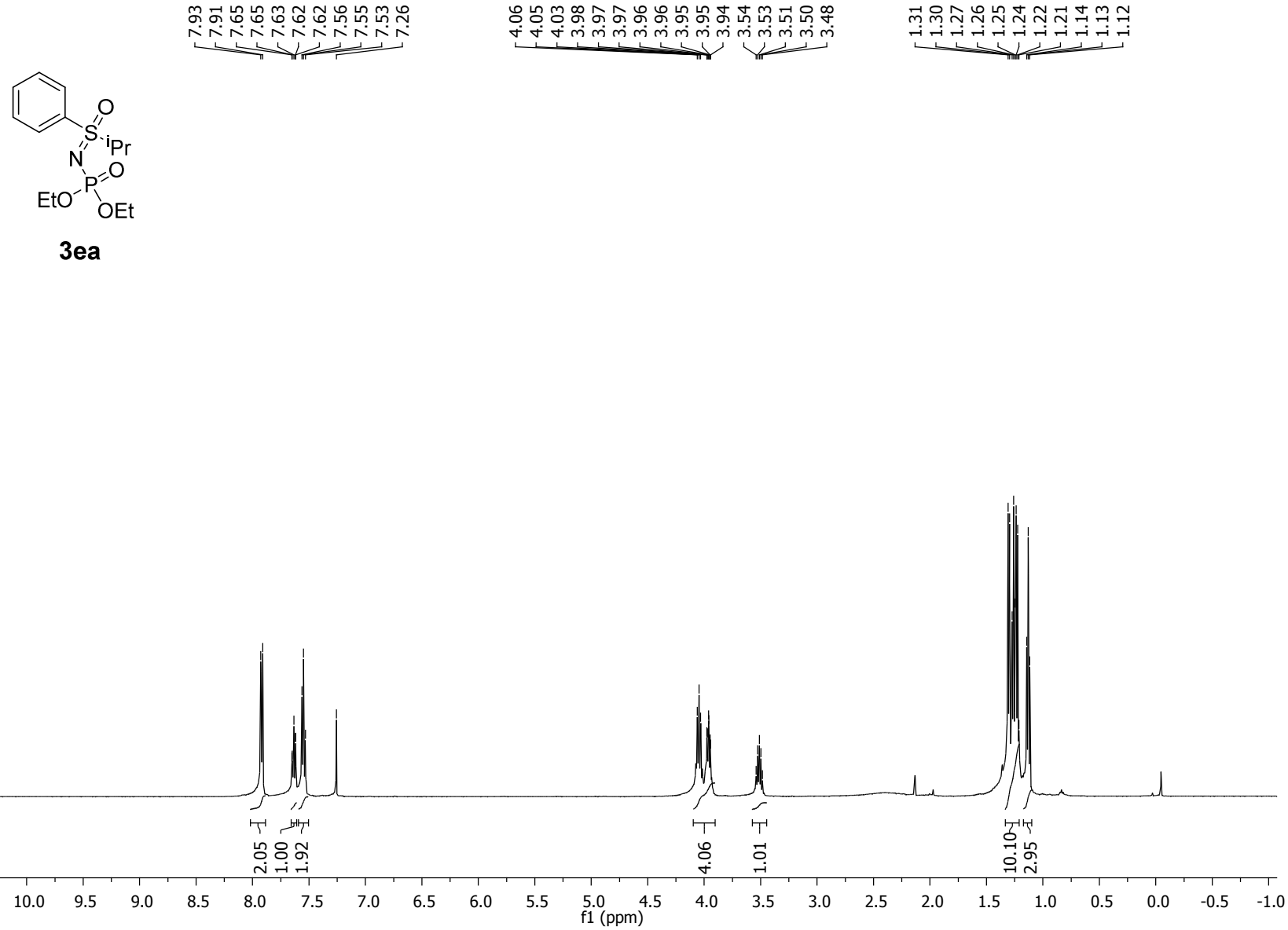


Figure S31. ^{1}H NMR for **3ea**

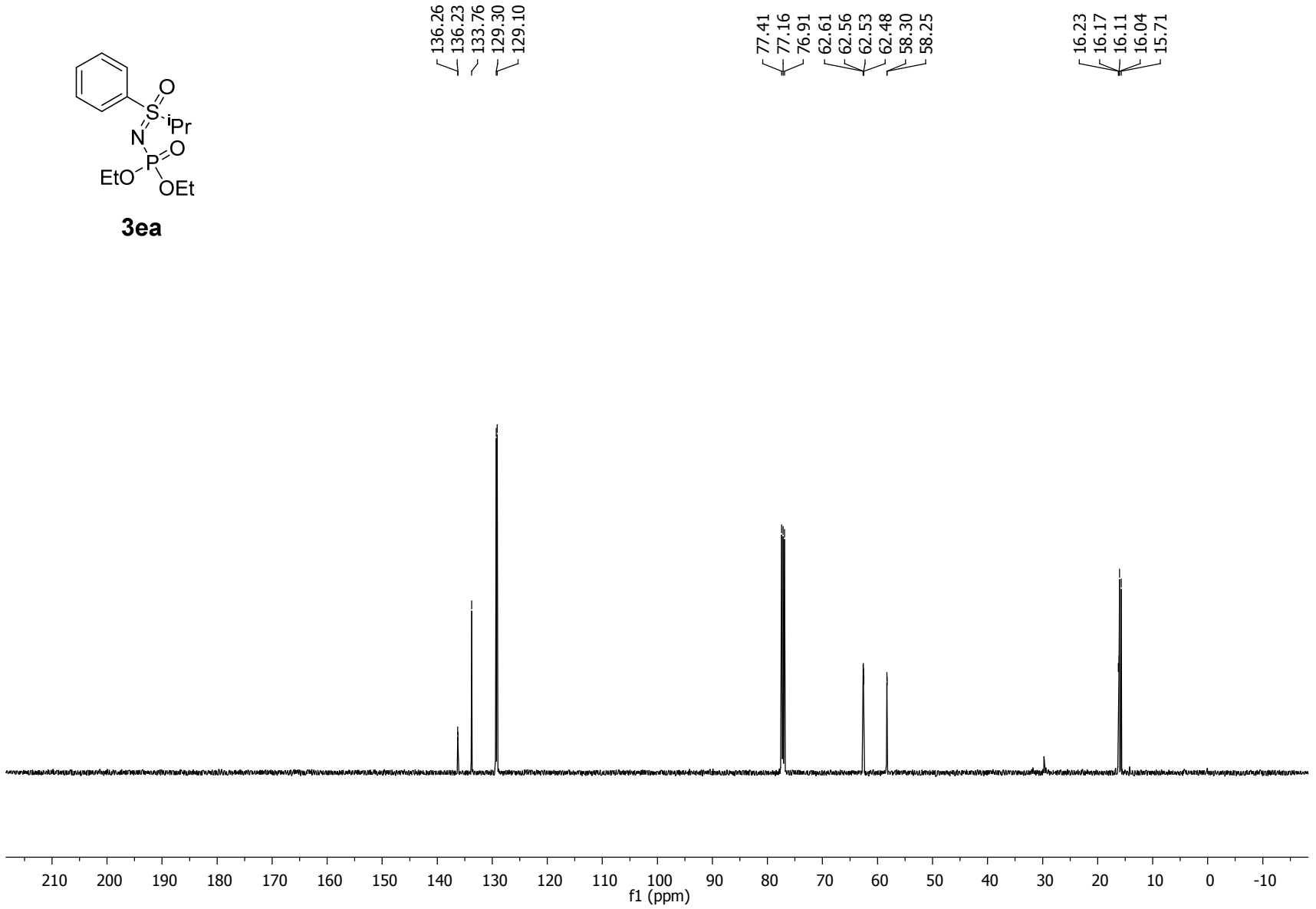


Figure S32. ^{13}C NMR for **3ea**

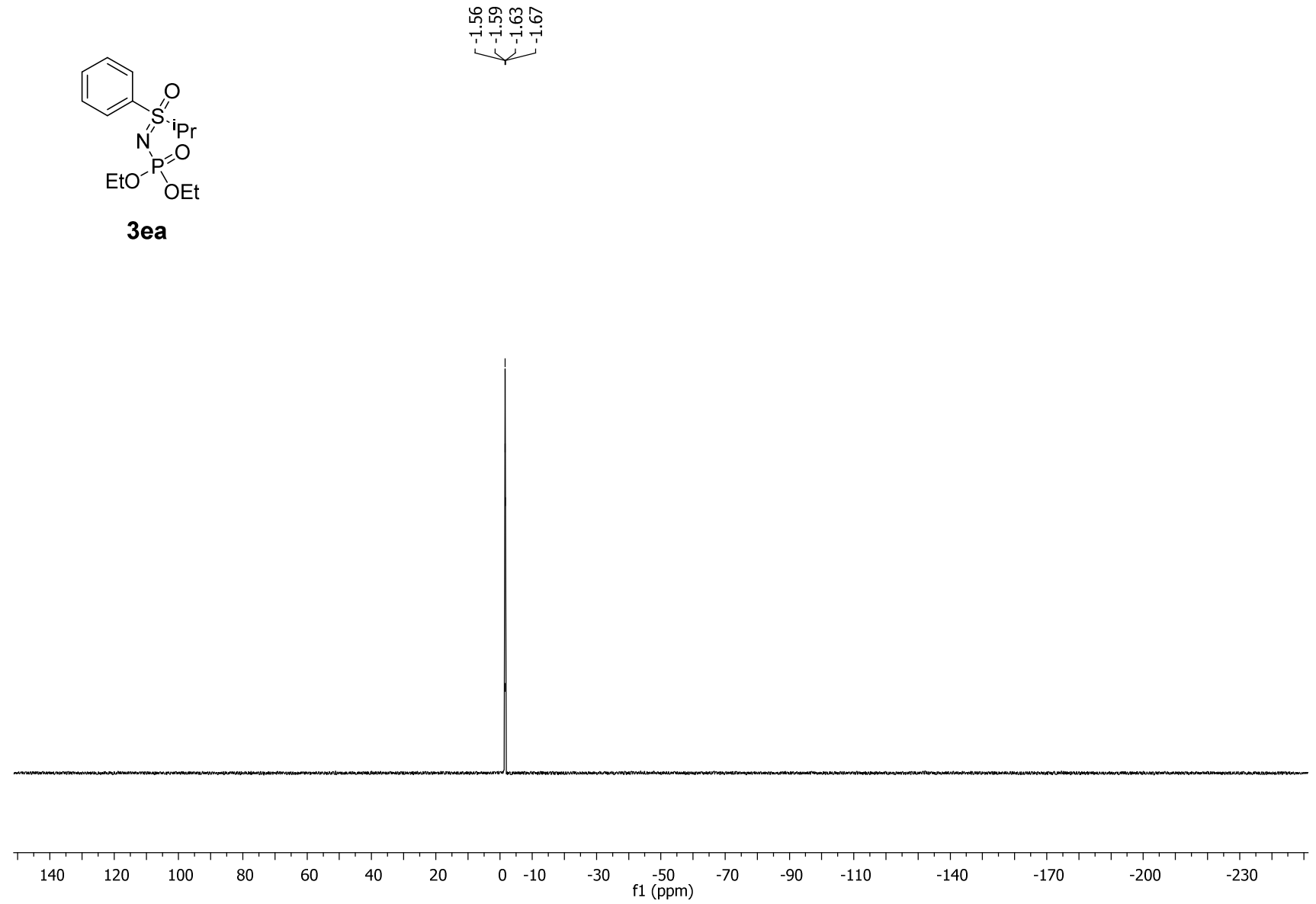


Figure S33. ^{31}P NMR for **3ea**

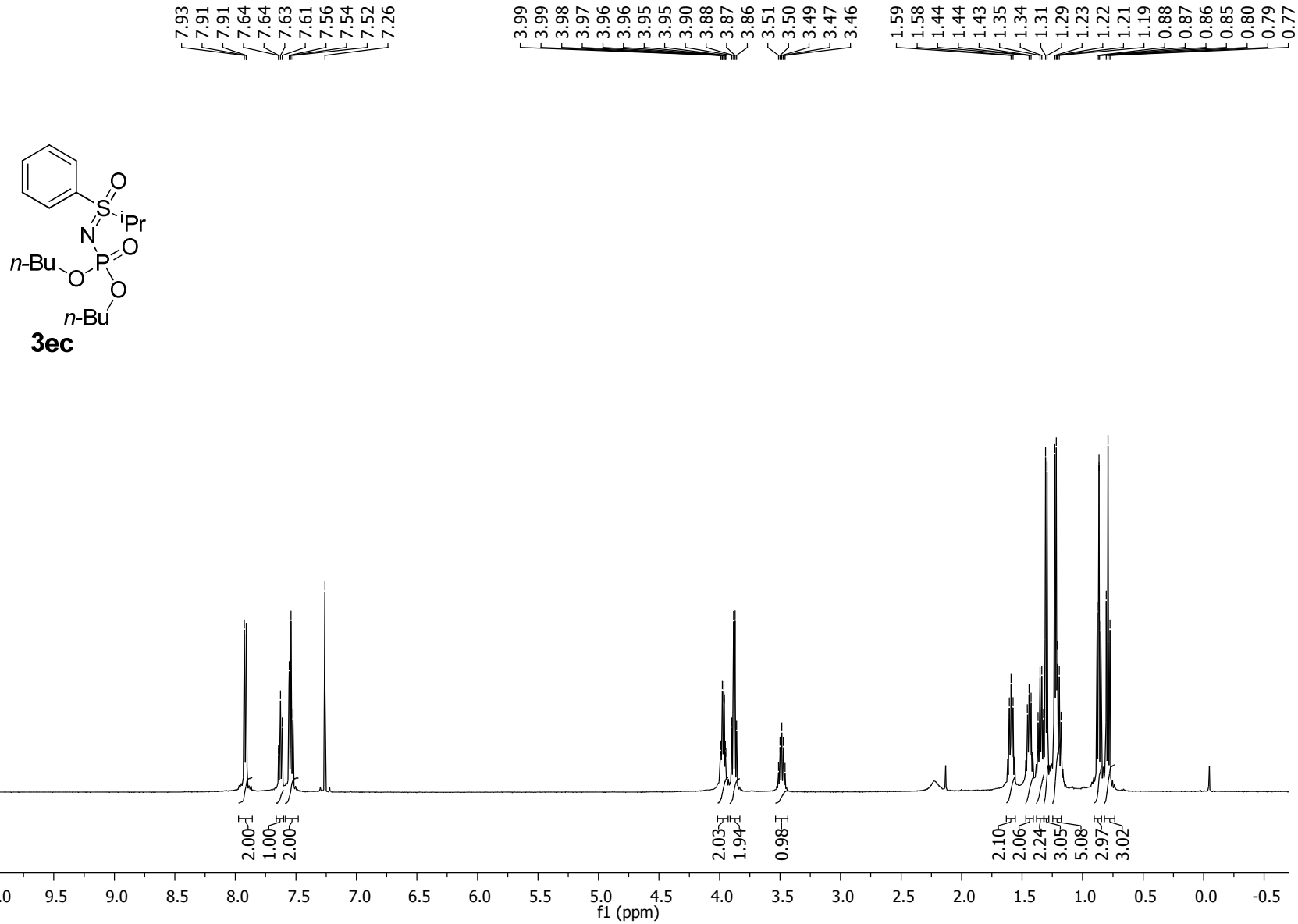


Figure S34. ^{1}H NMR for **3ec**

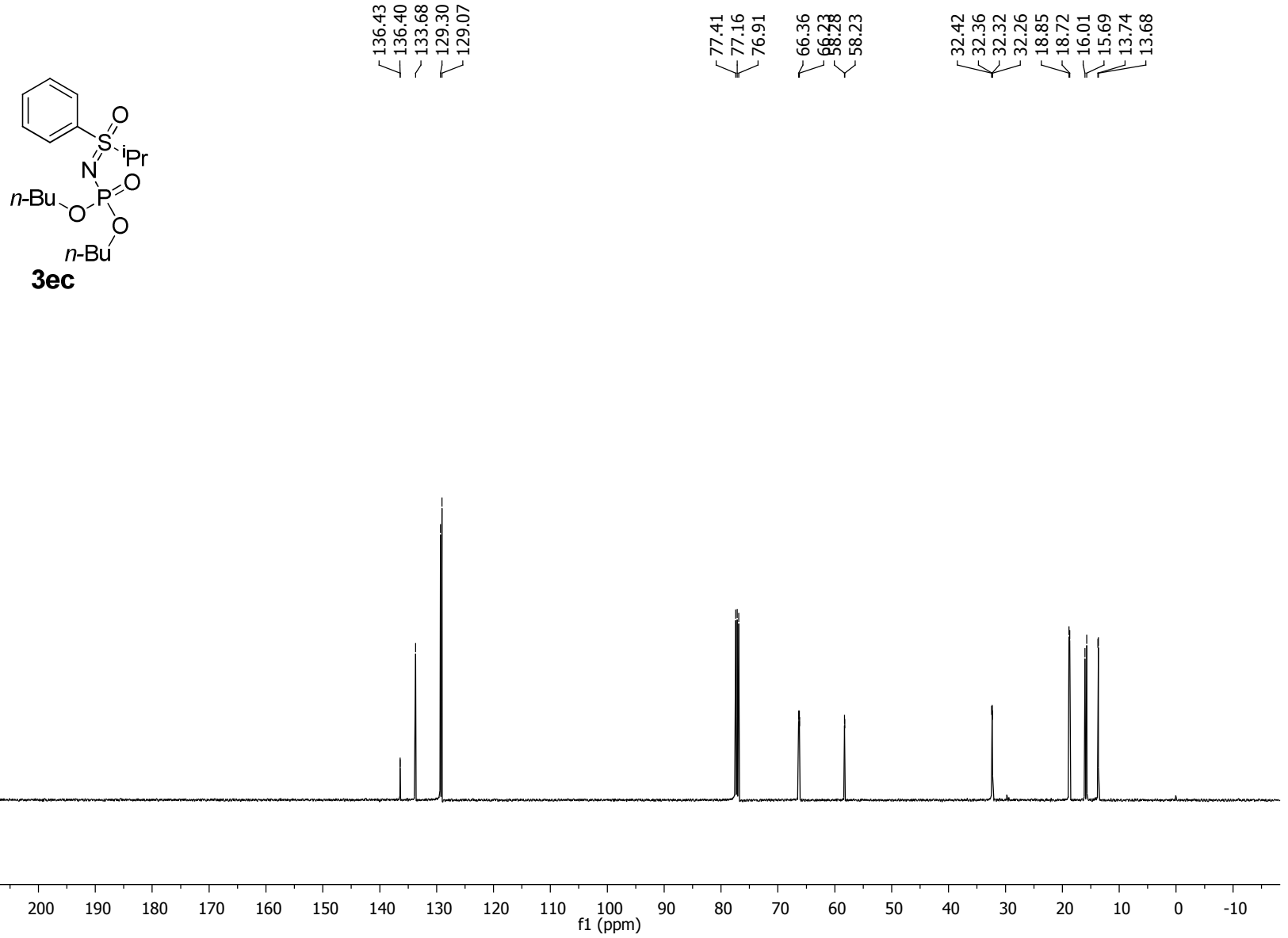


Figure S35. ^{13}C NMR for **3ec**

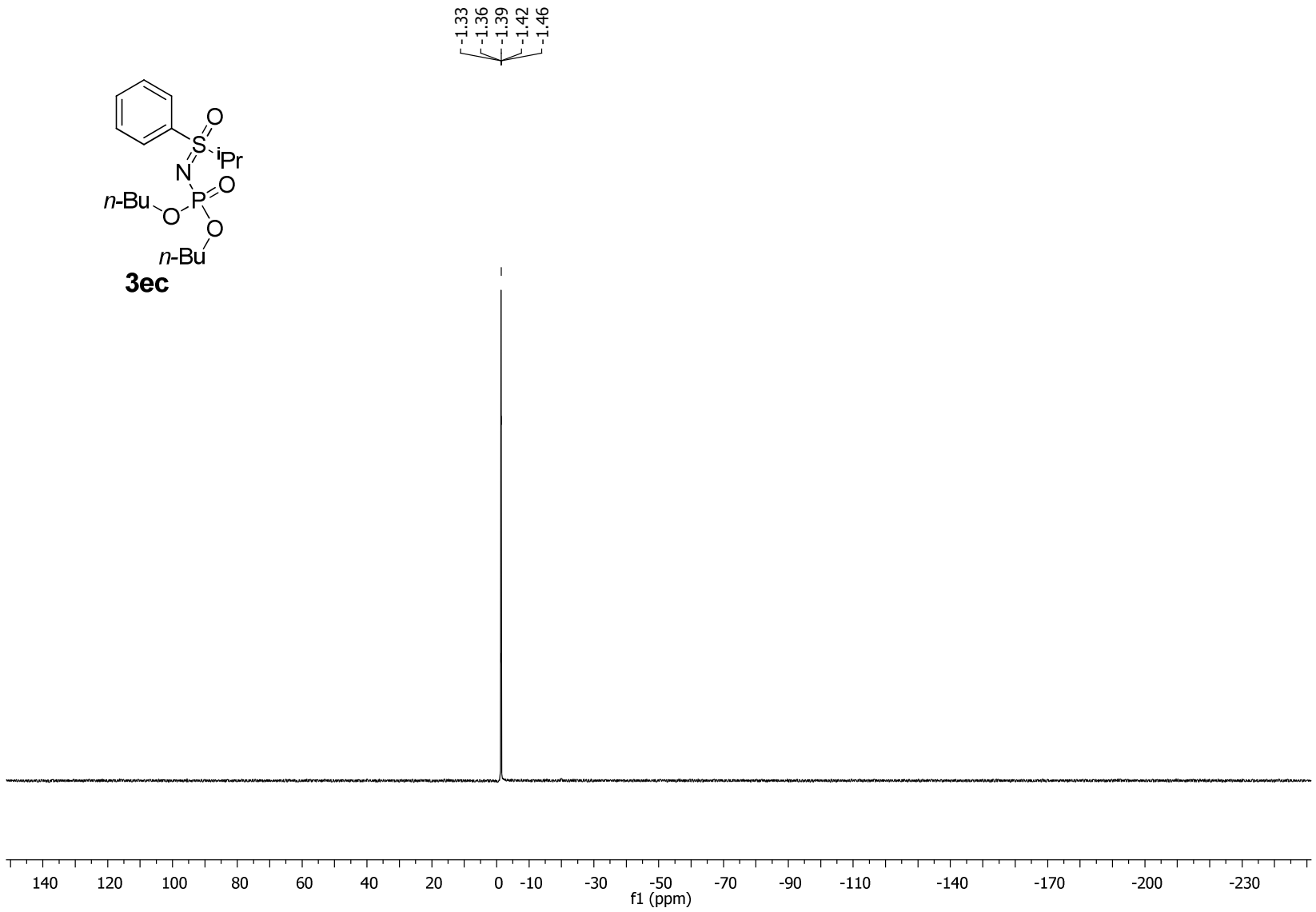


Figure S36. ^{31}P NMR for **3ec**

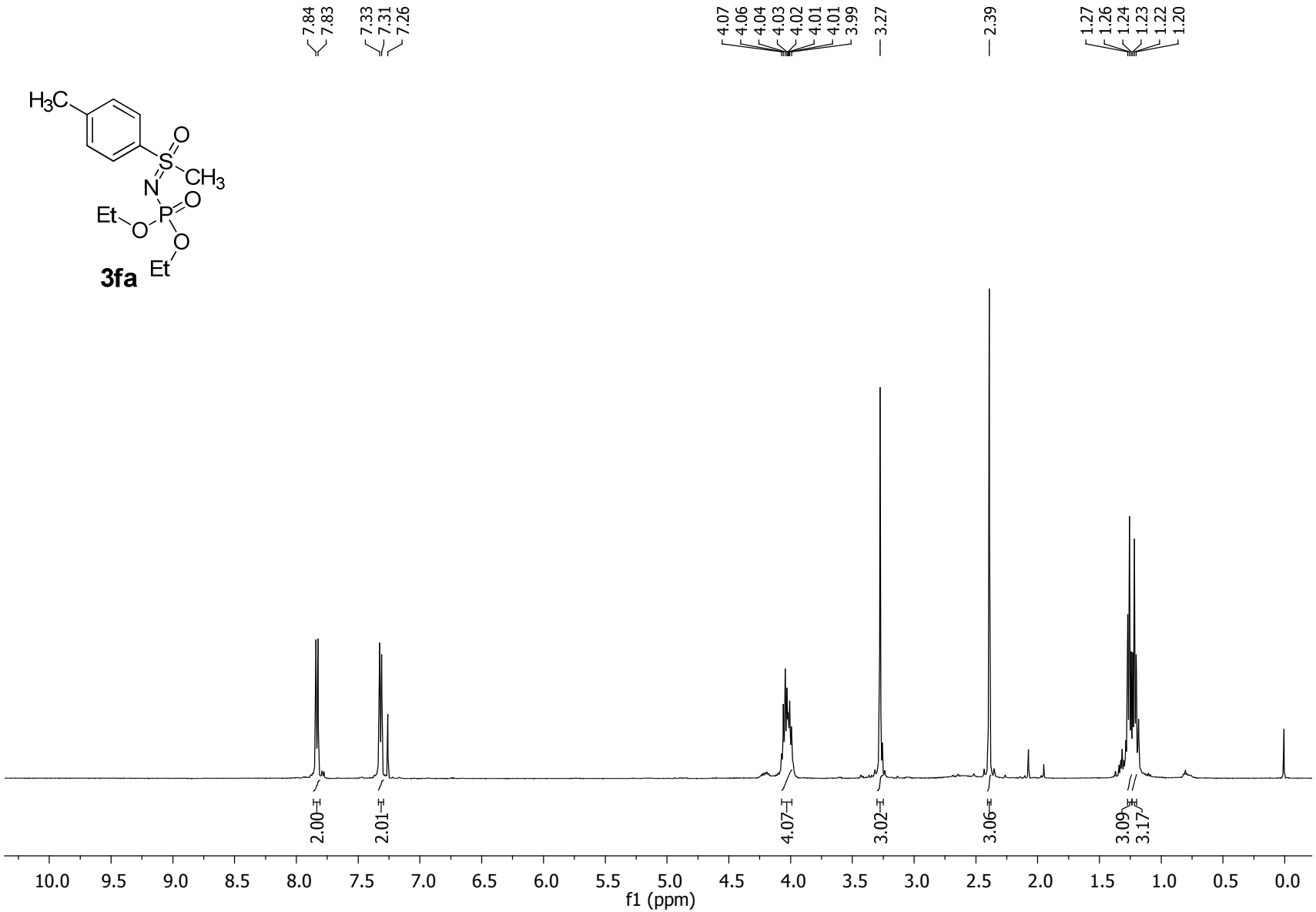


Figure S37. ^{1}H NMR for **3fa**

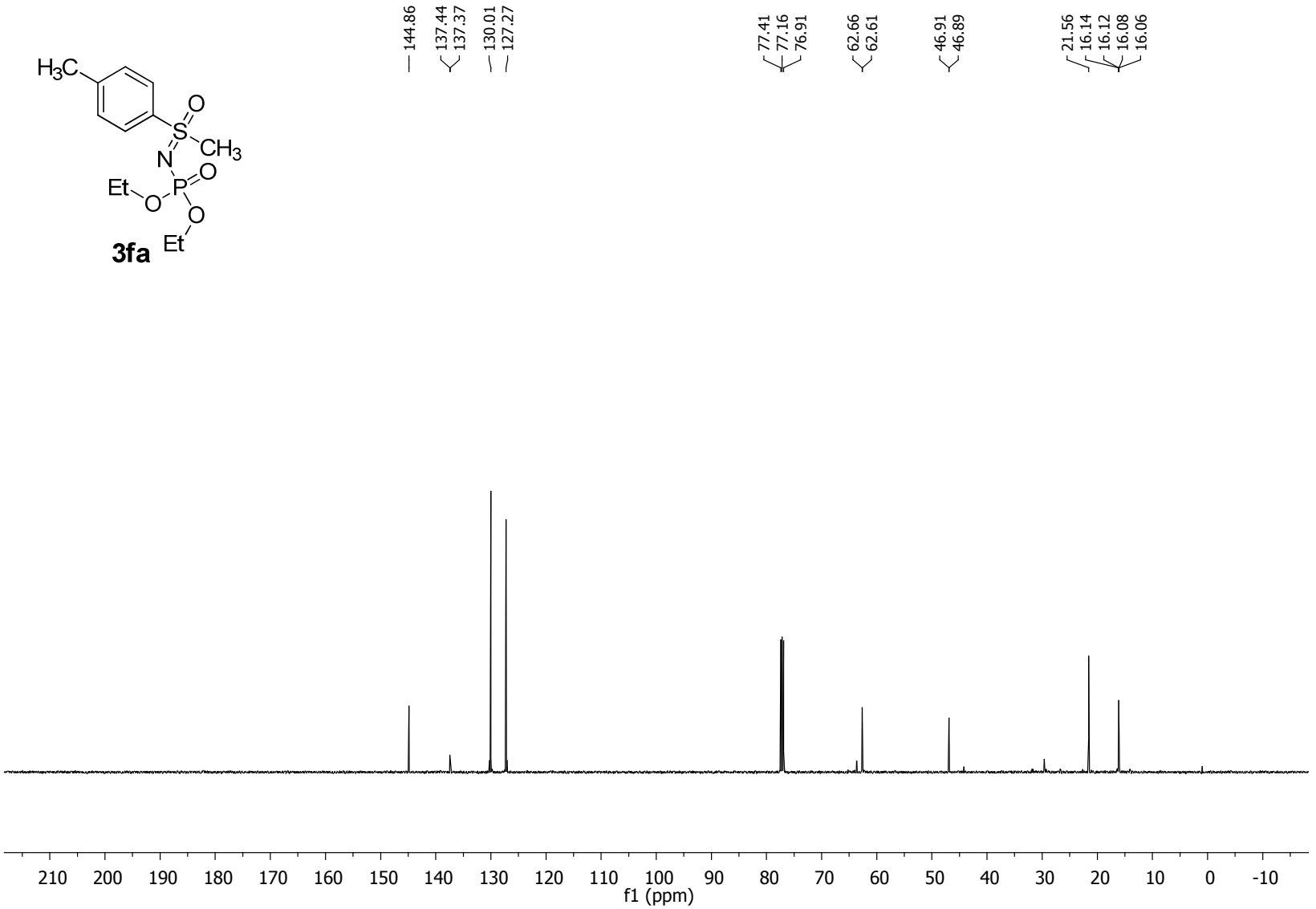


Figure S38. ^{13}C NMR for **3fa**

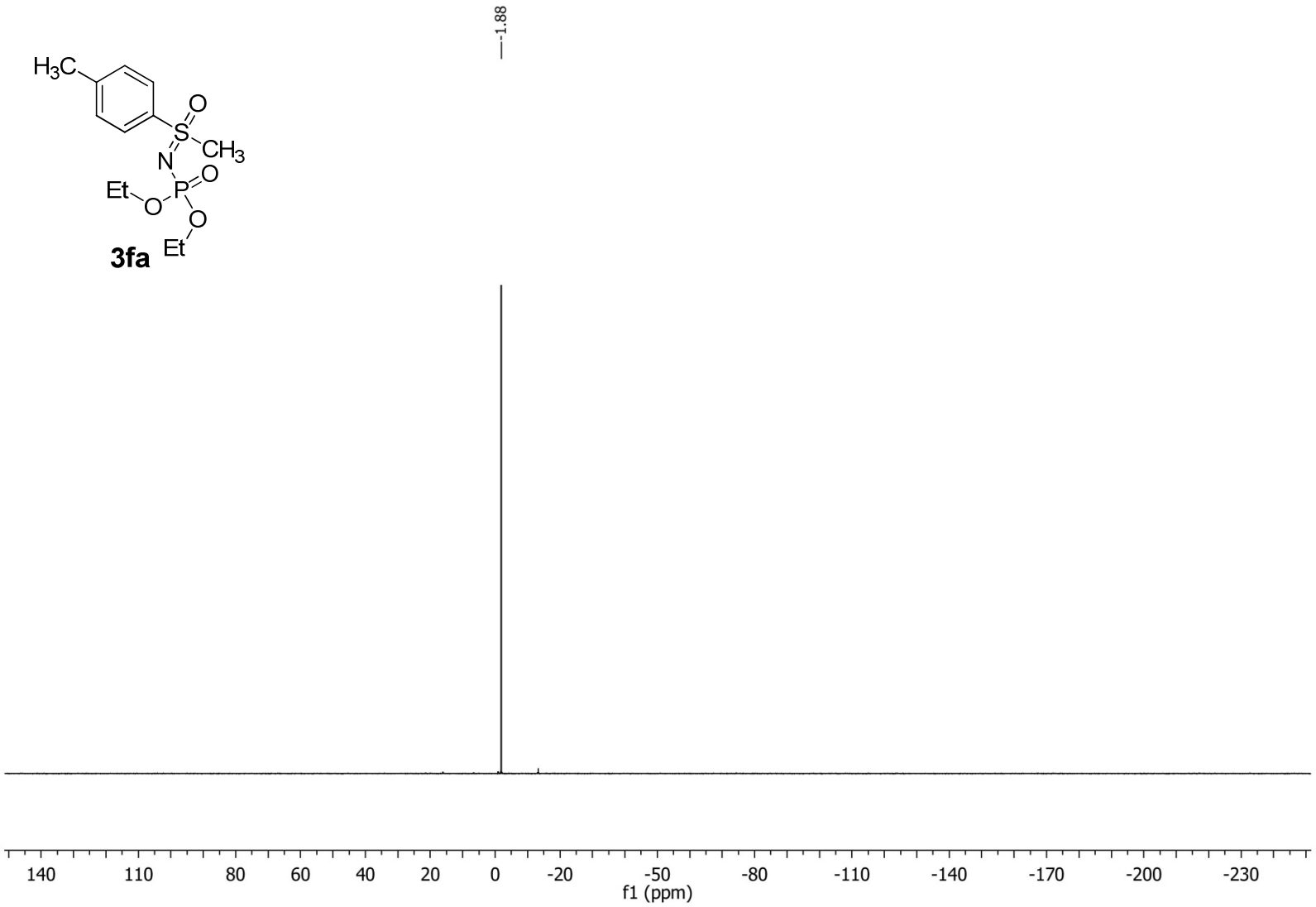


Figure S39. ^{31}P NMR for **3fa**

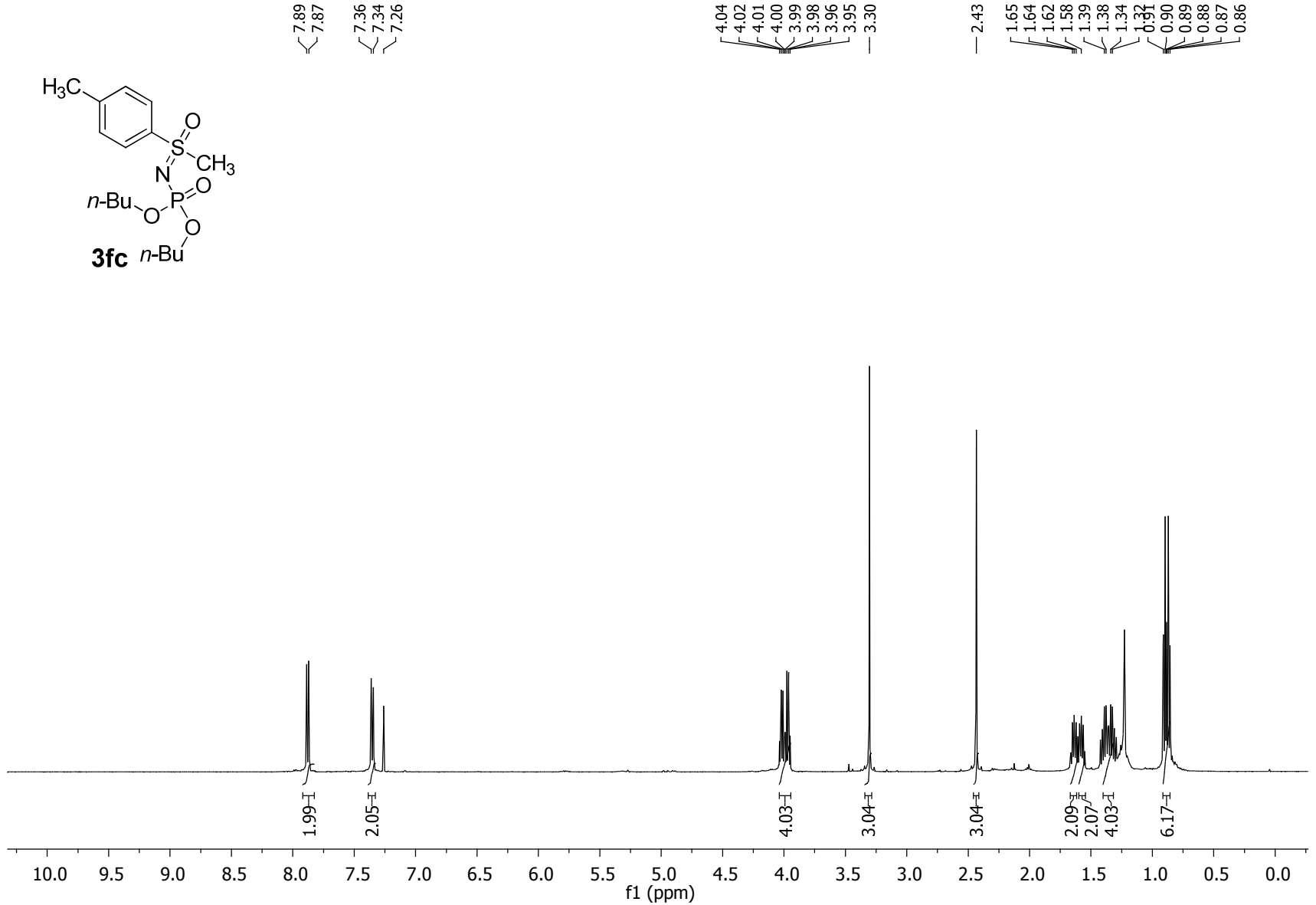


Figure S40. ^{1}H NMR for **3fc**

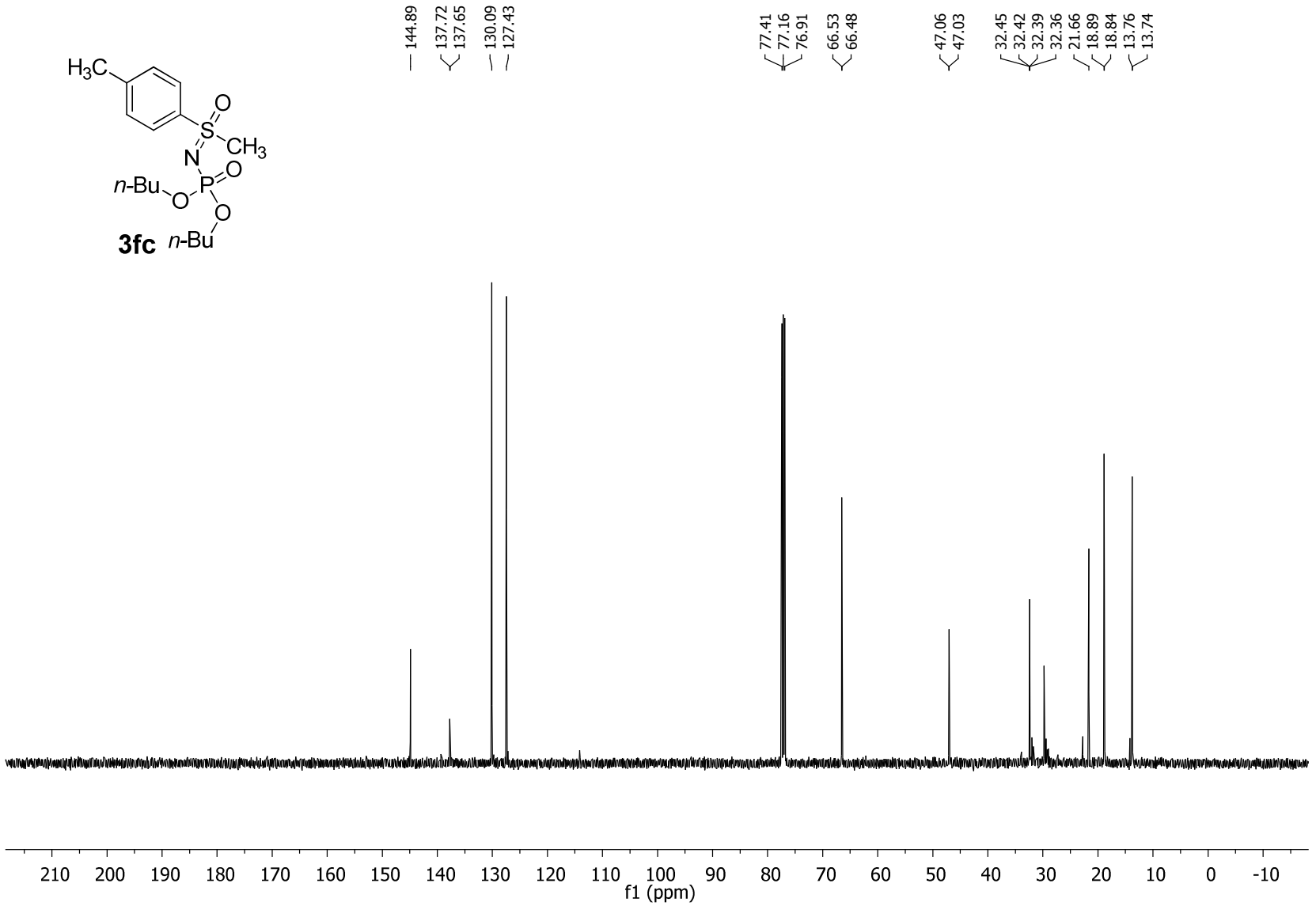


Figure S41. ^{13}C NMR for **3fc**

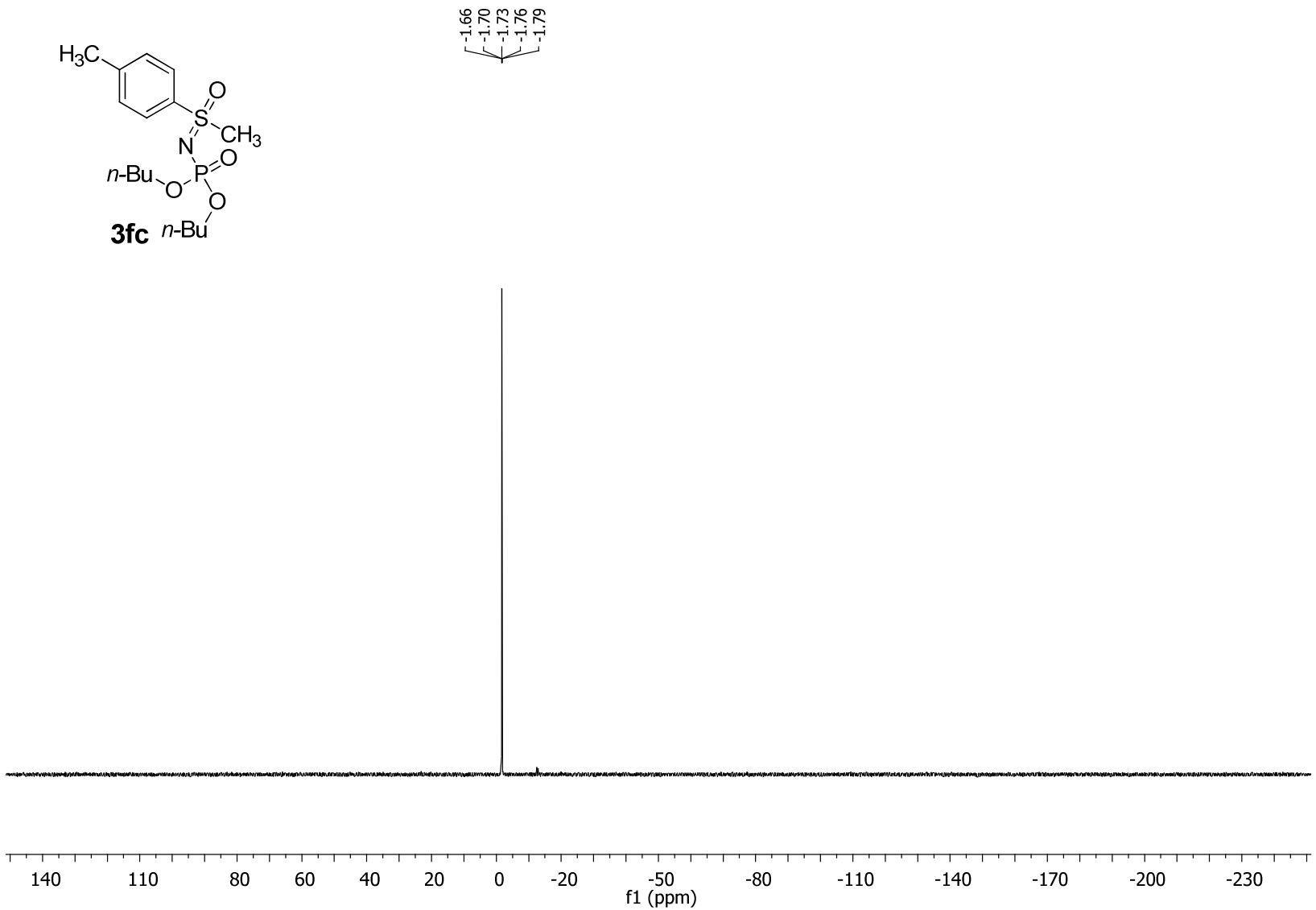


Figure S42. ^{31}P NMR for **3fc**

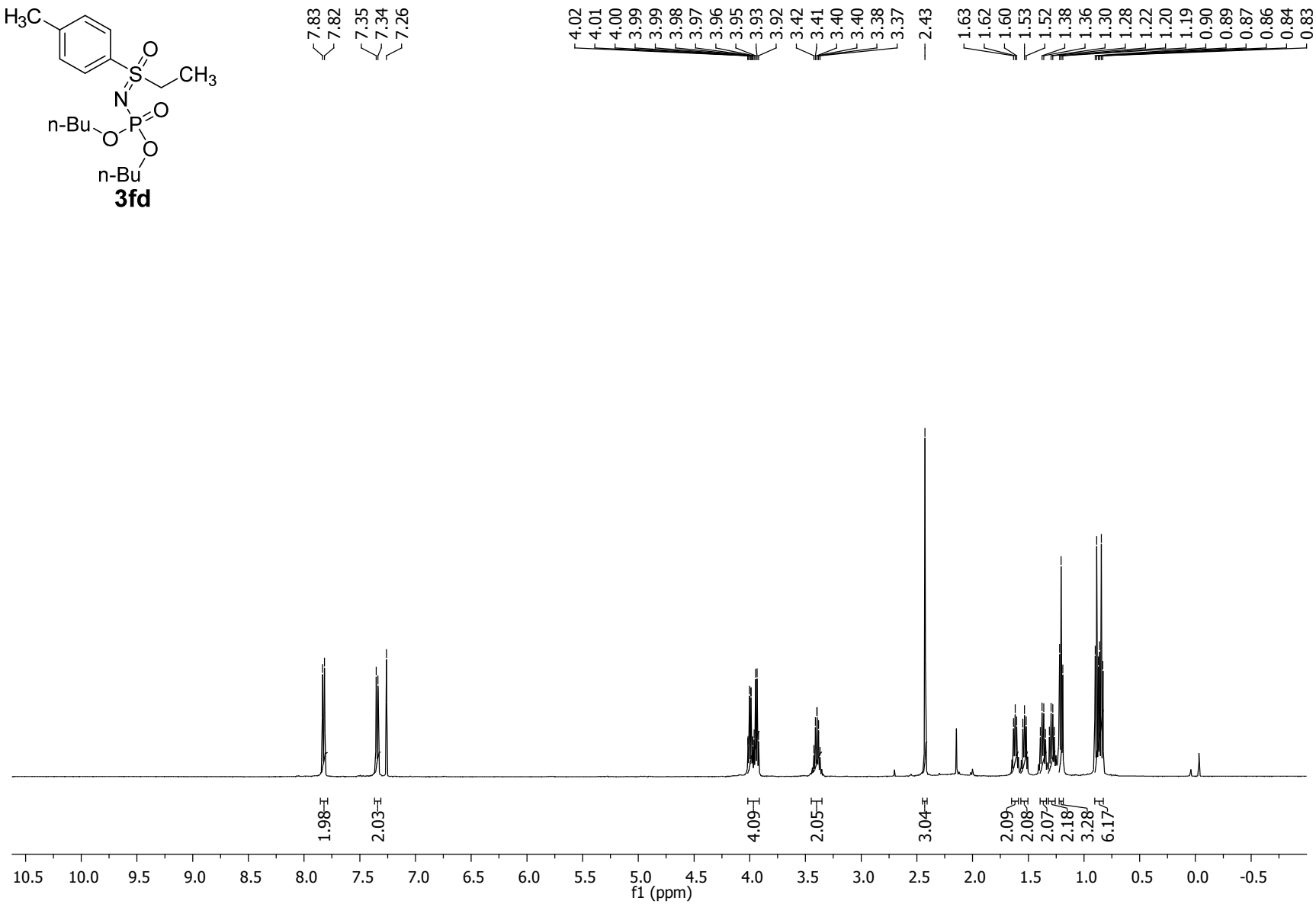


Figure S43. ^{1}H NMR for **3fd**

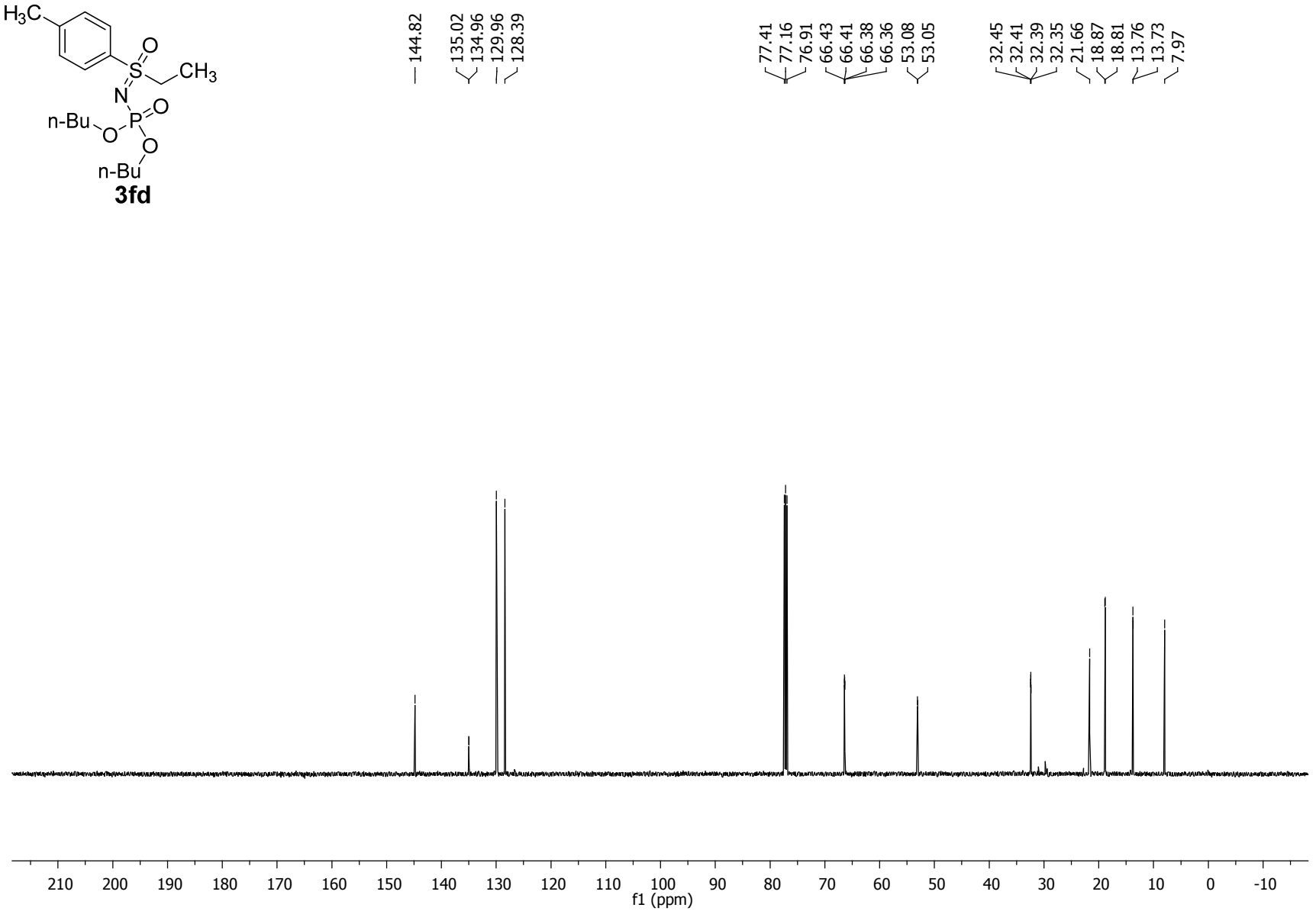


Figure S44. ^{13}C NMR for **3fd**

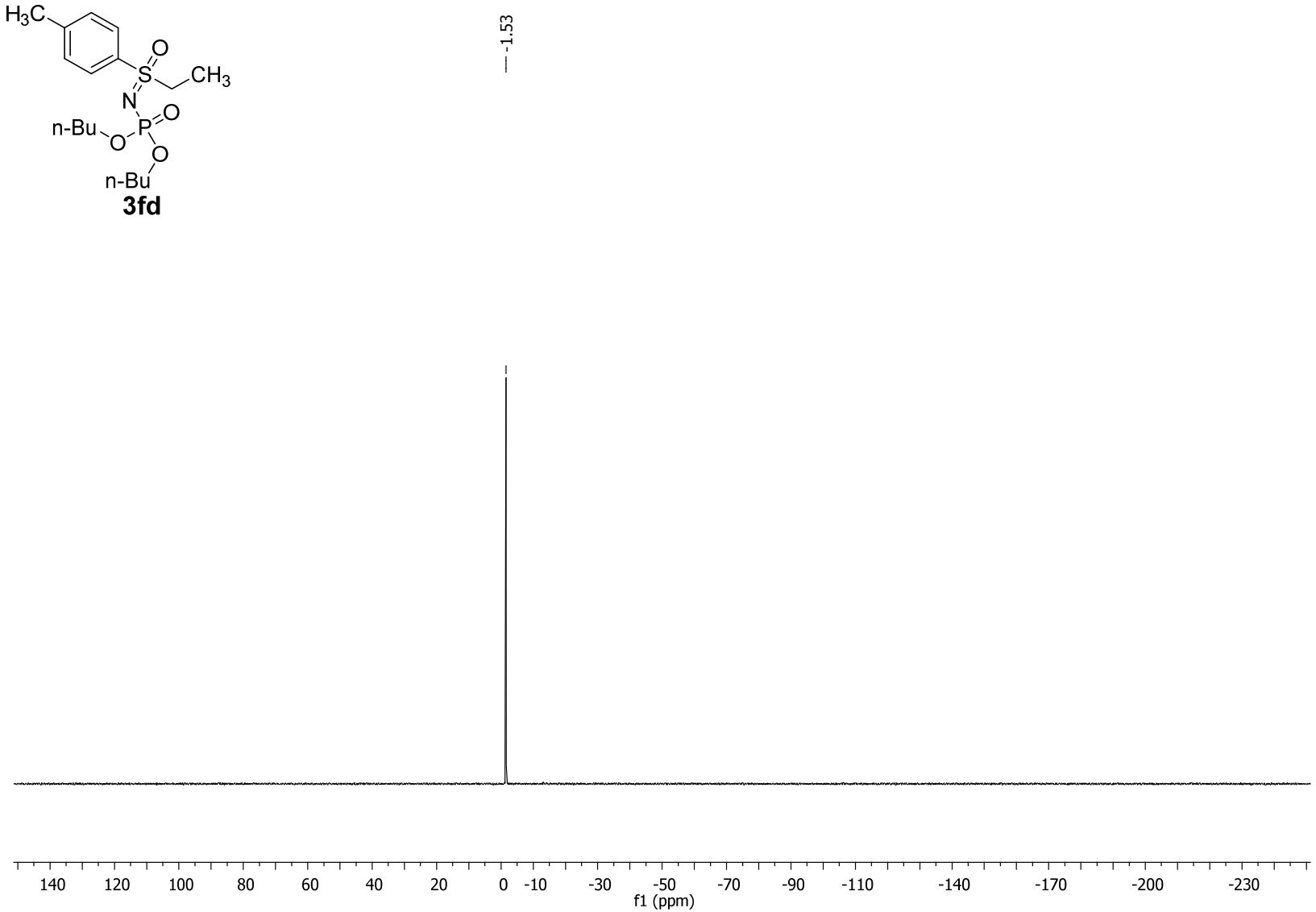


Figure S45. ^{31}P NMR for **3fd**

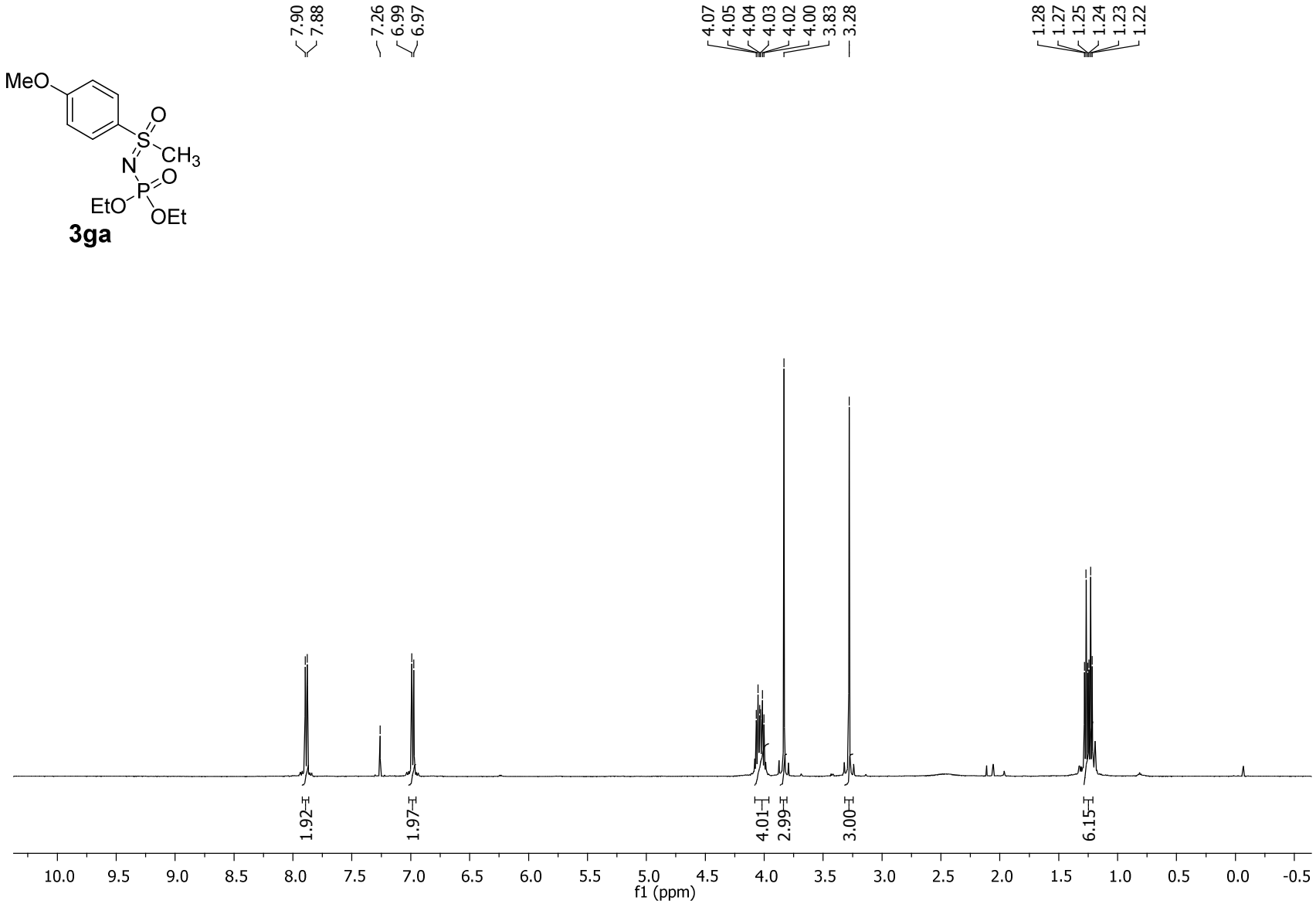


Figure S46. ^{1}H NMR for **3ga**

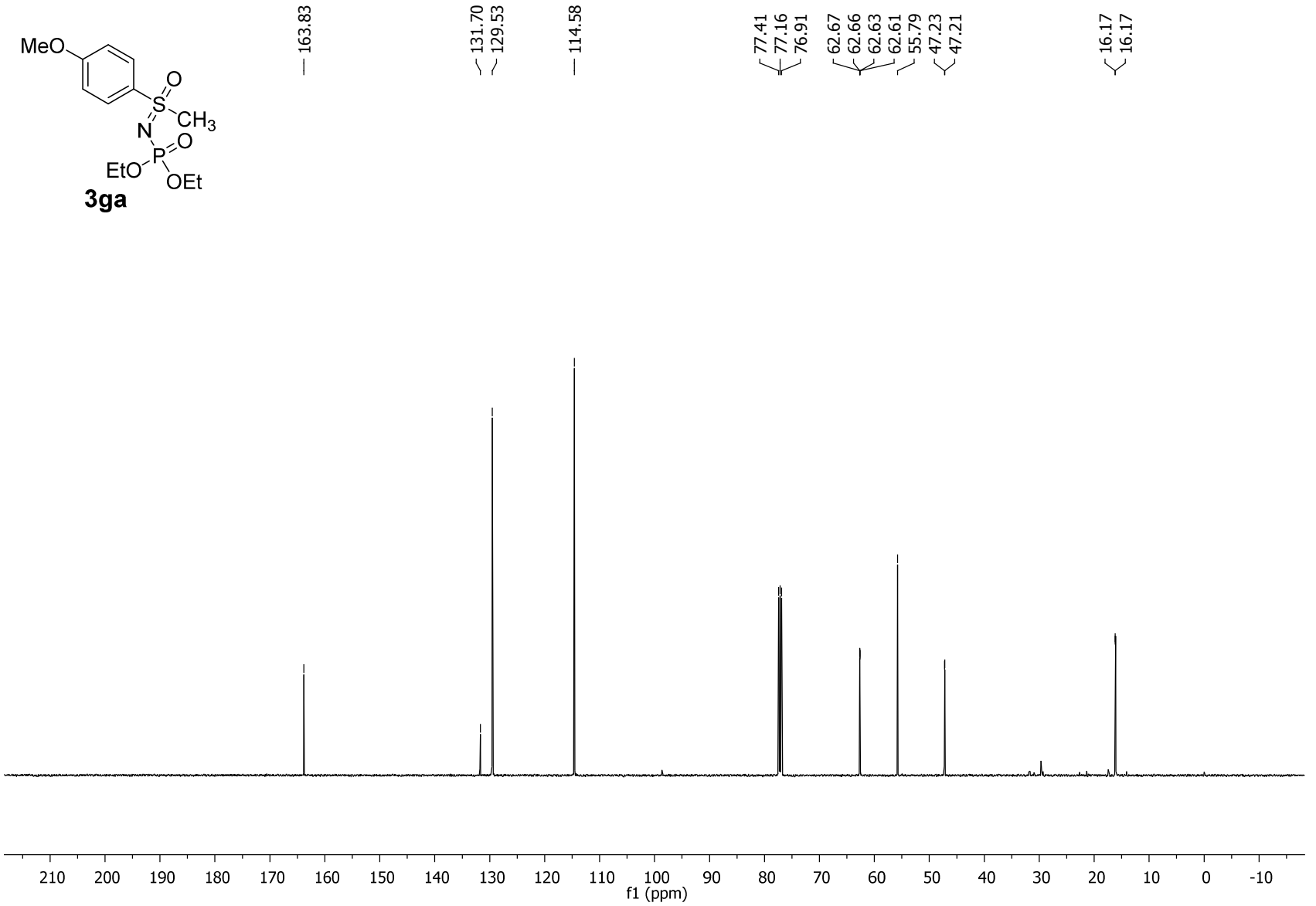


Figure S47. ^{13}C NMR for **3ga**

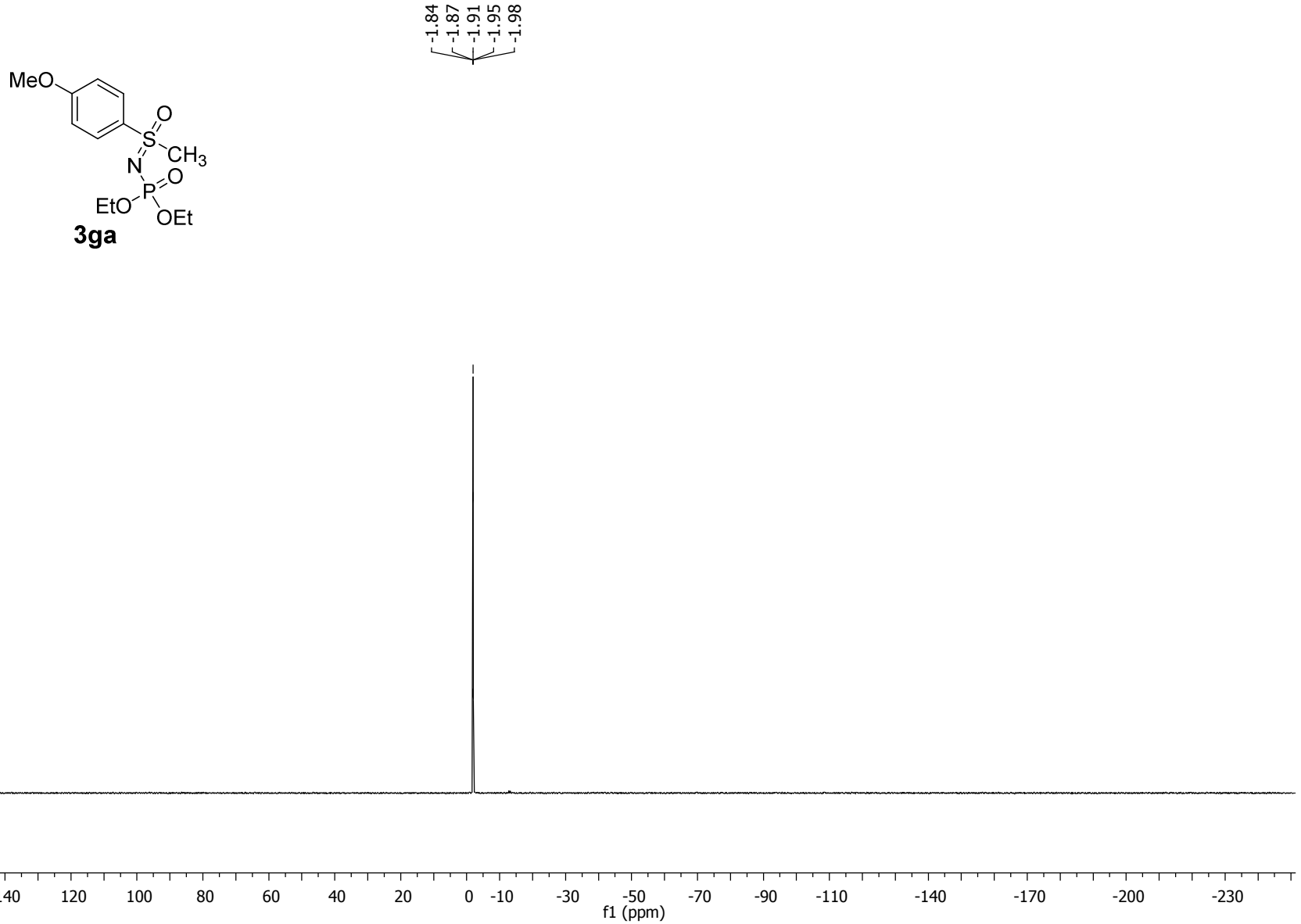


Figure S48. ^{31}P NMR for **3ga**

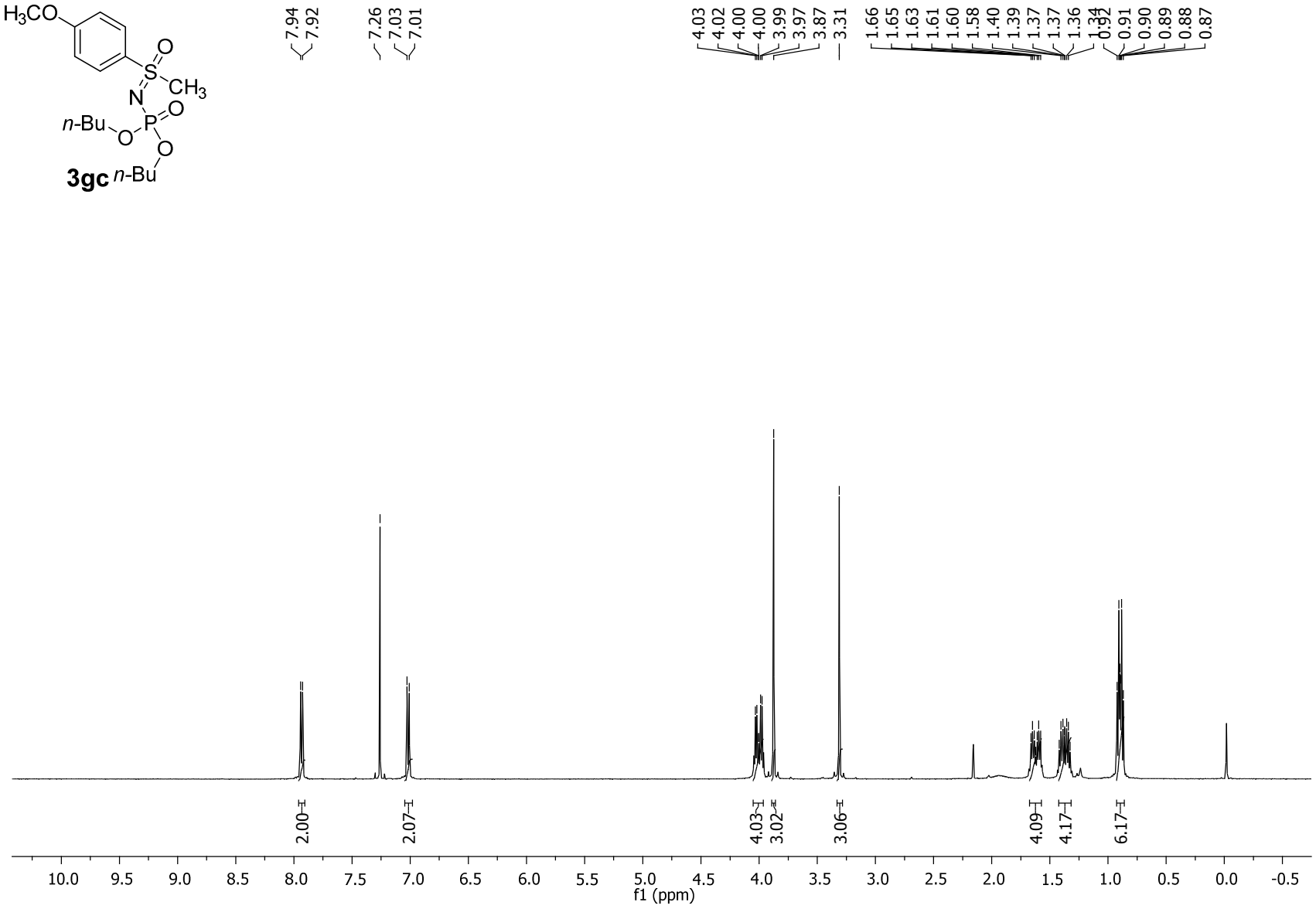


Figure S49. ^{1}H NMR for **3gc**

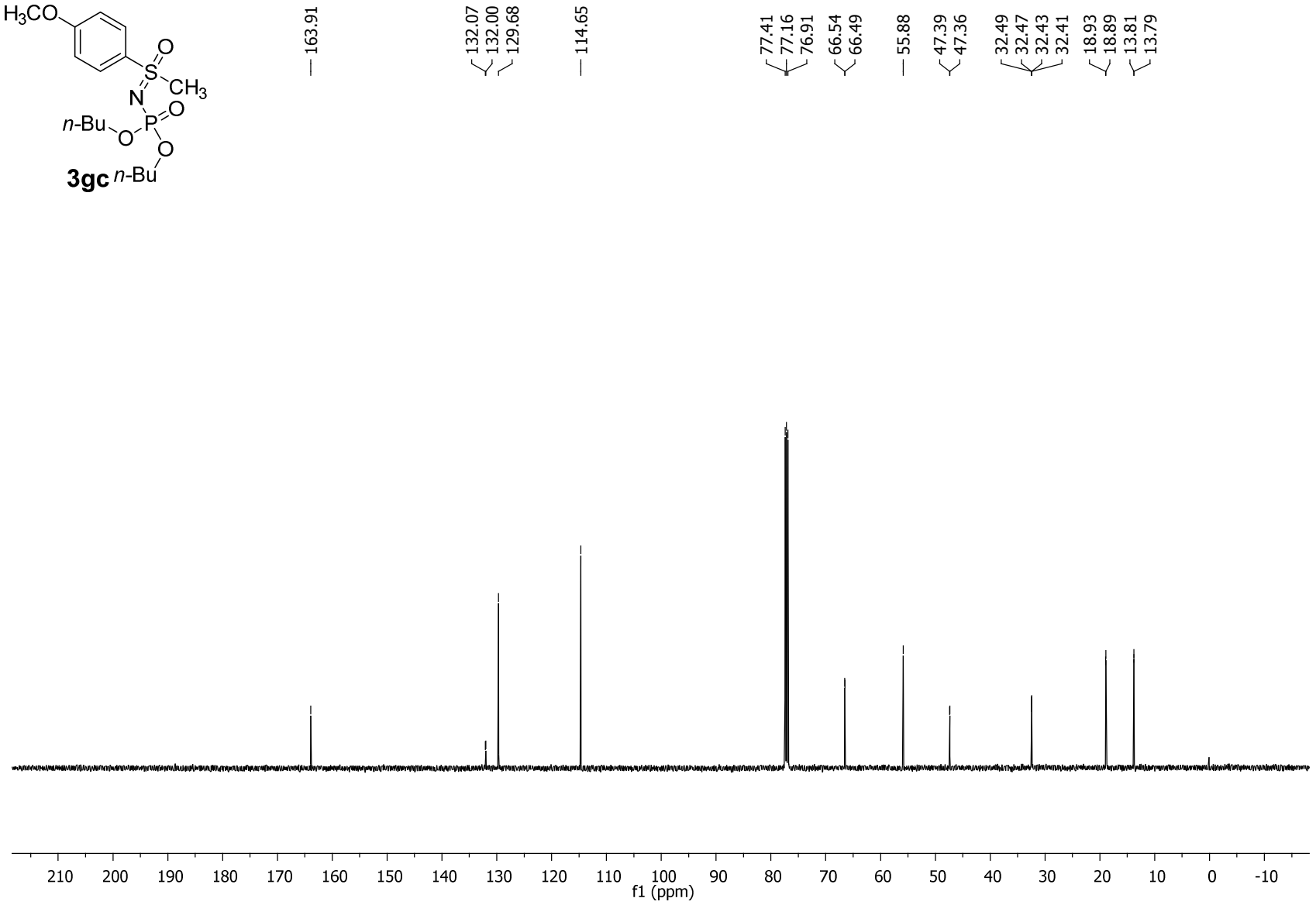


Figure S50. ^{13}C NMR for **3gc**

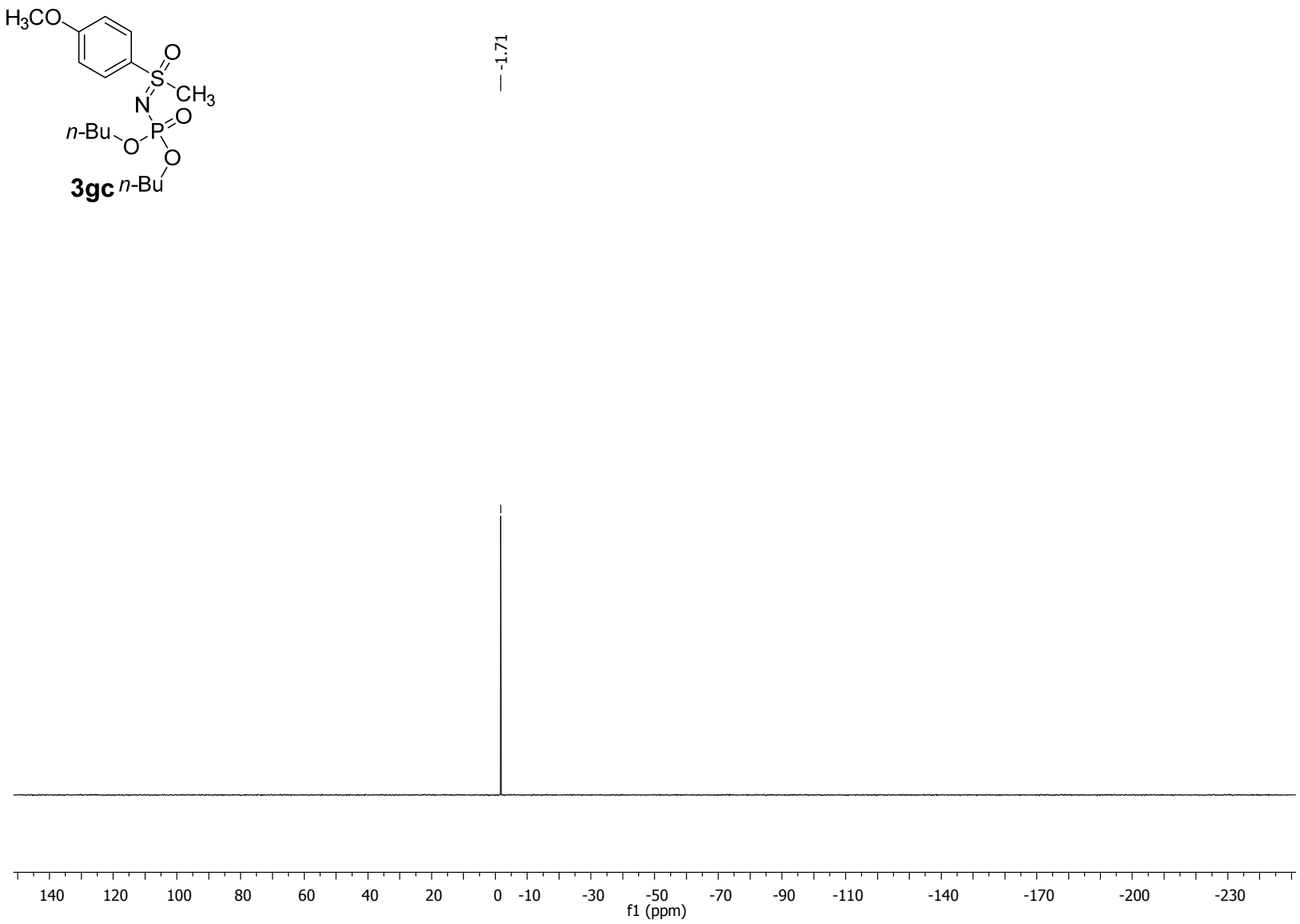


Figure S51. ^{31}P NMR for **3gc**

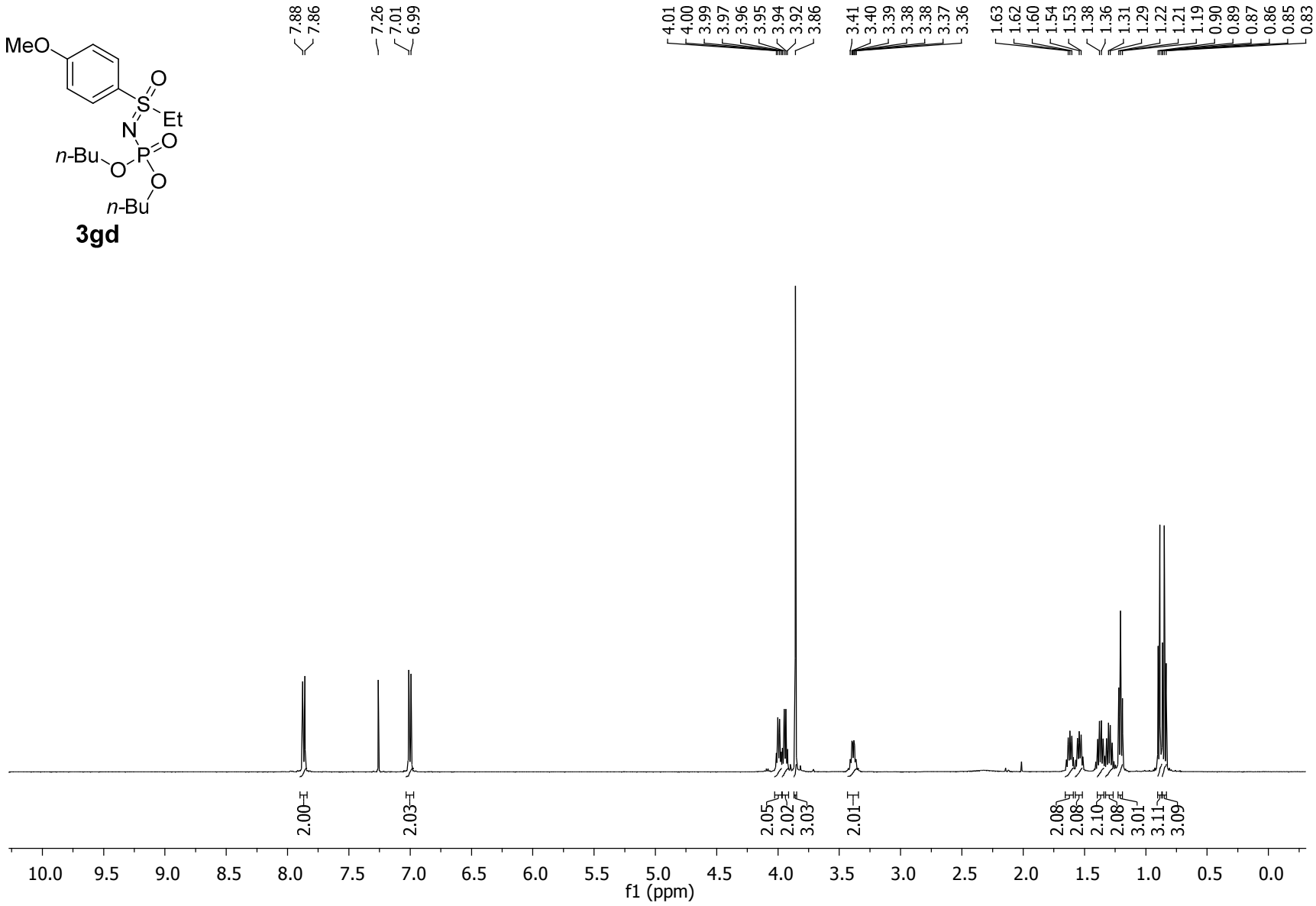


Figure S52. ^{1}H NMR for **3gd**

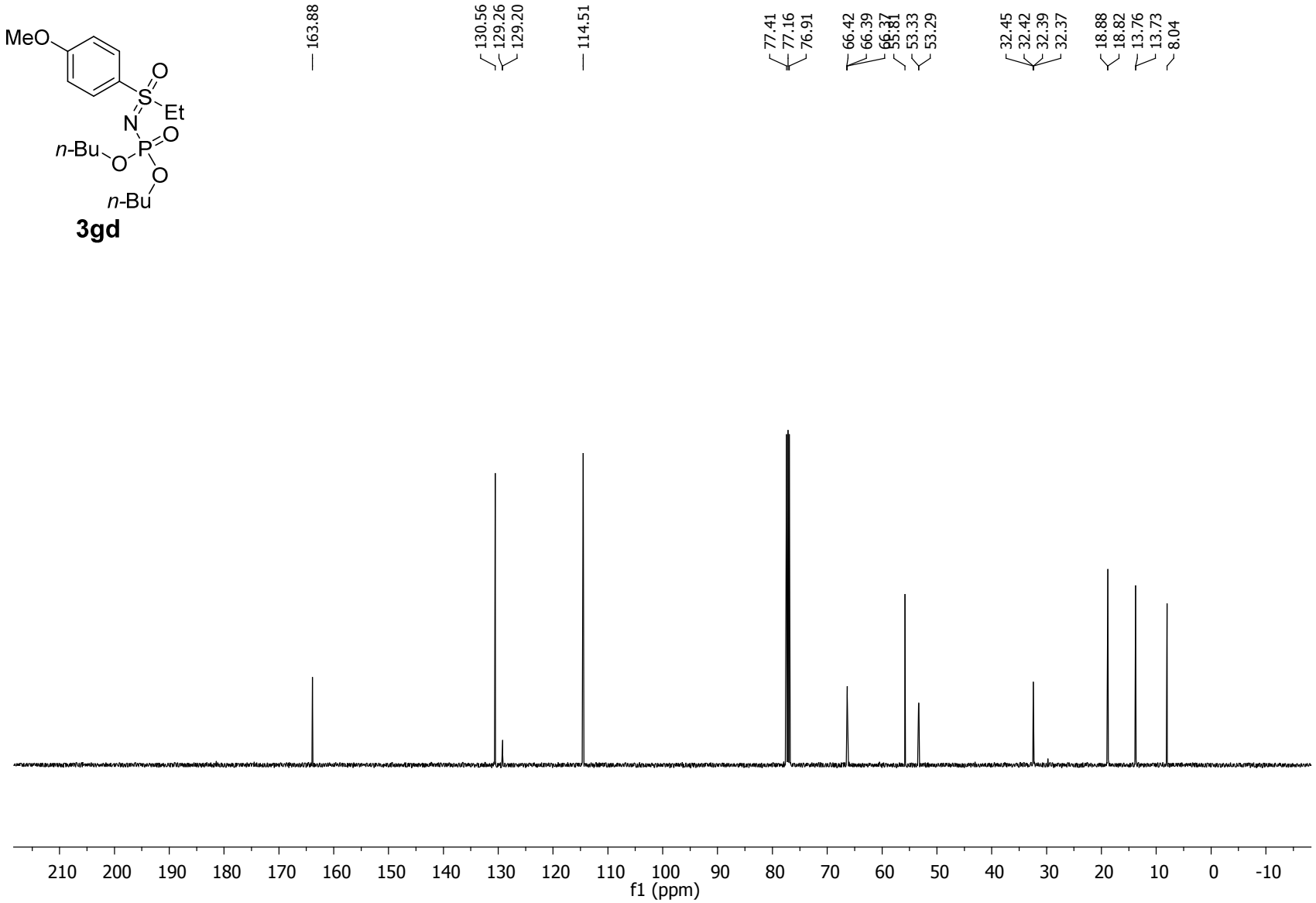


Figure S53. ^{13}C NMR for **3gd**

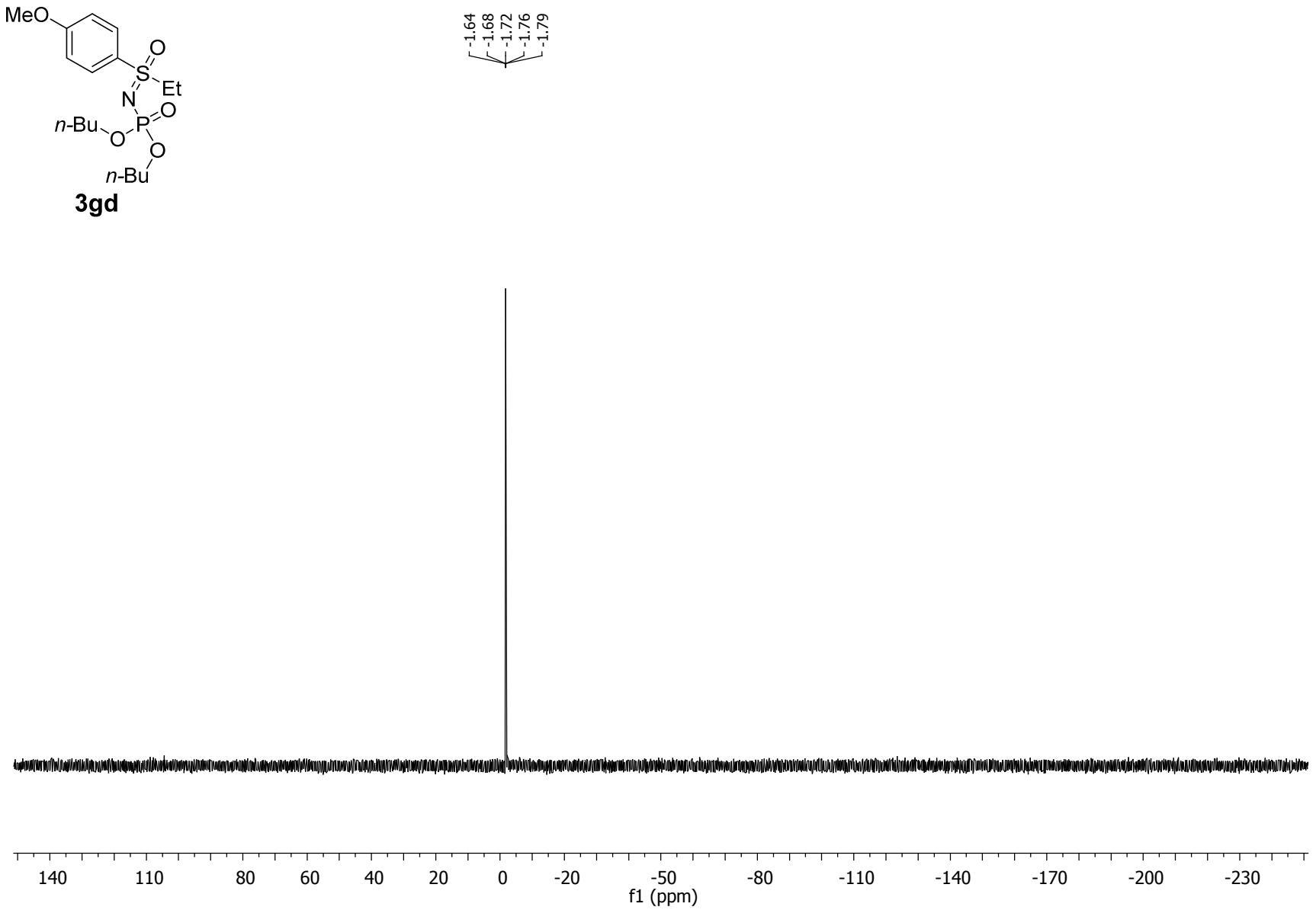


Figure S54. ^{31}P NMR for **3gd**

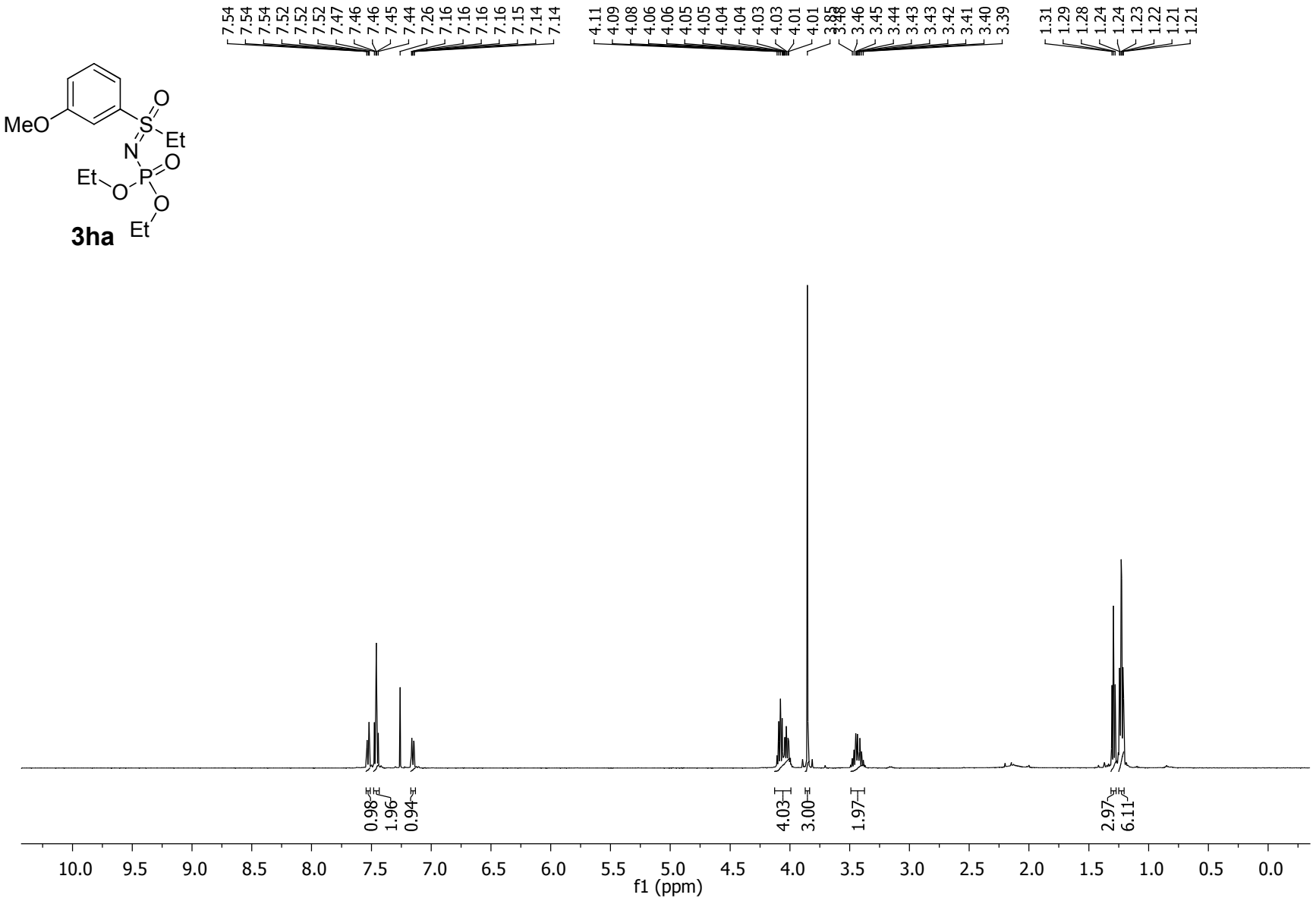


Figure S55. ^{1}H NMR for **3ha**

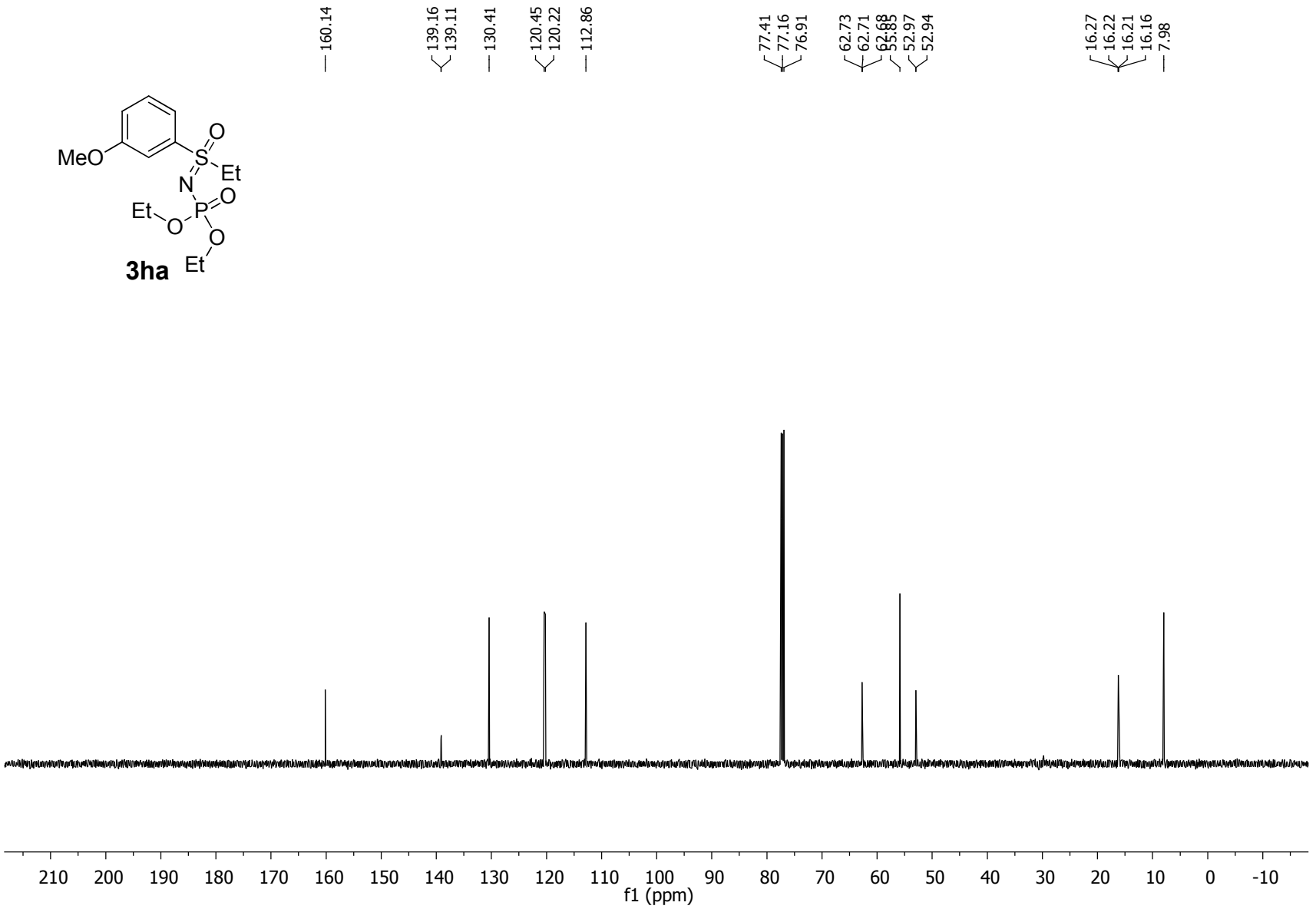


Figure S56. ^{13}C NMR for **3ha**

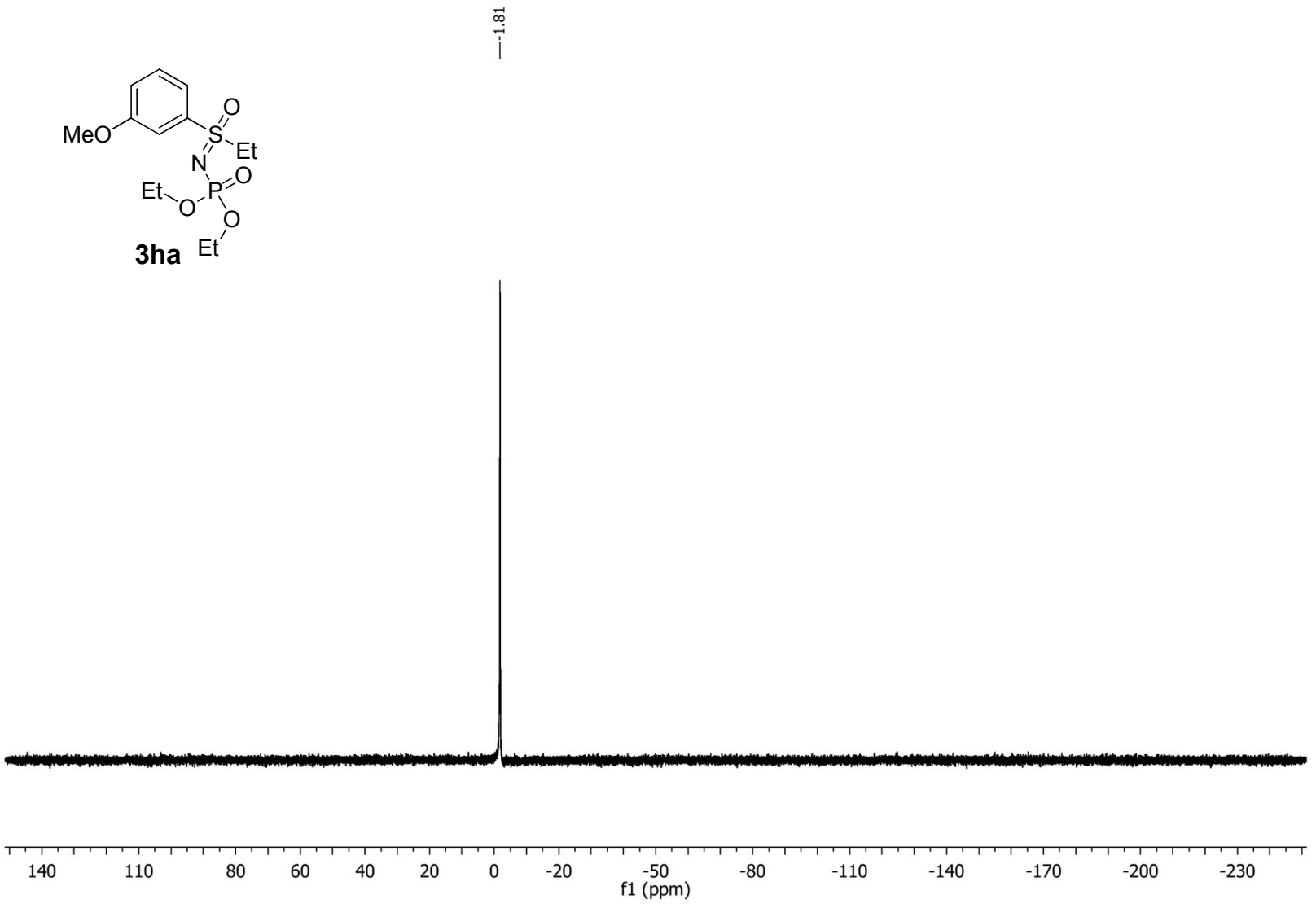


Figure S57. ^{31}P NMR for **3ha**

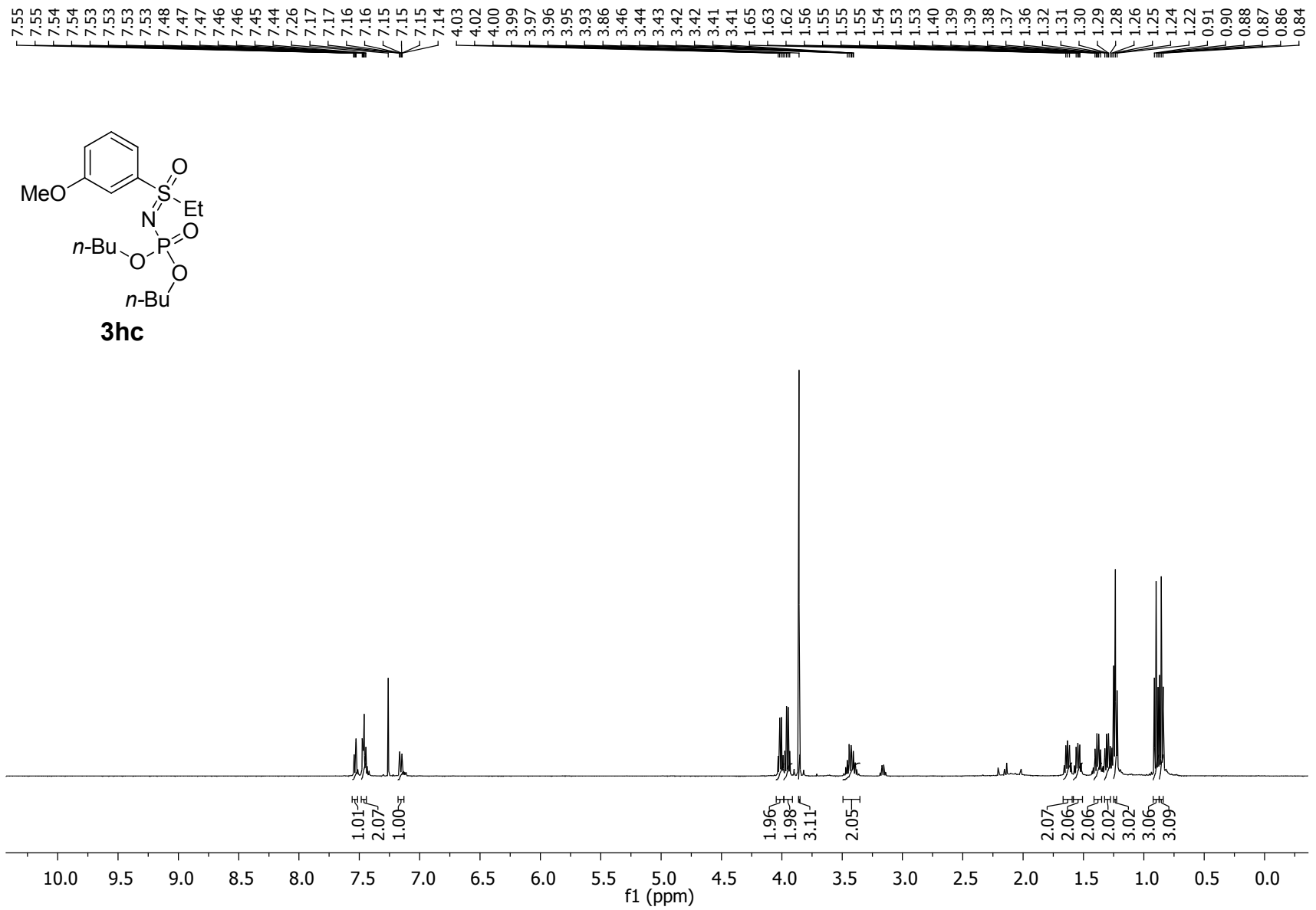


Figure S58. ^{1}H NMR for **3hc**

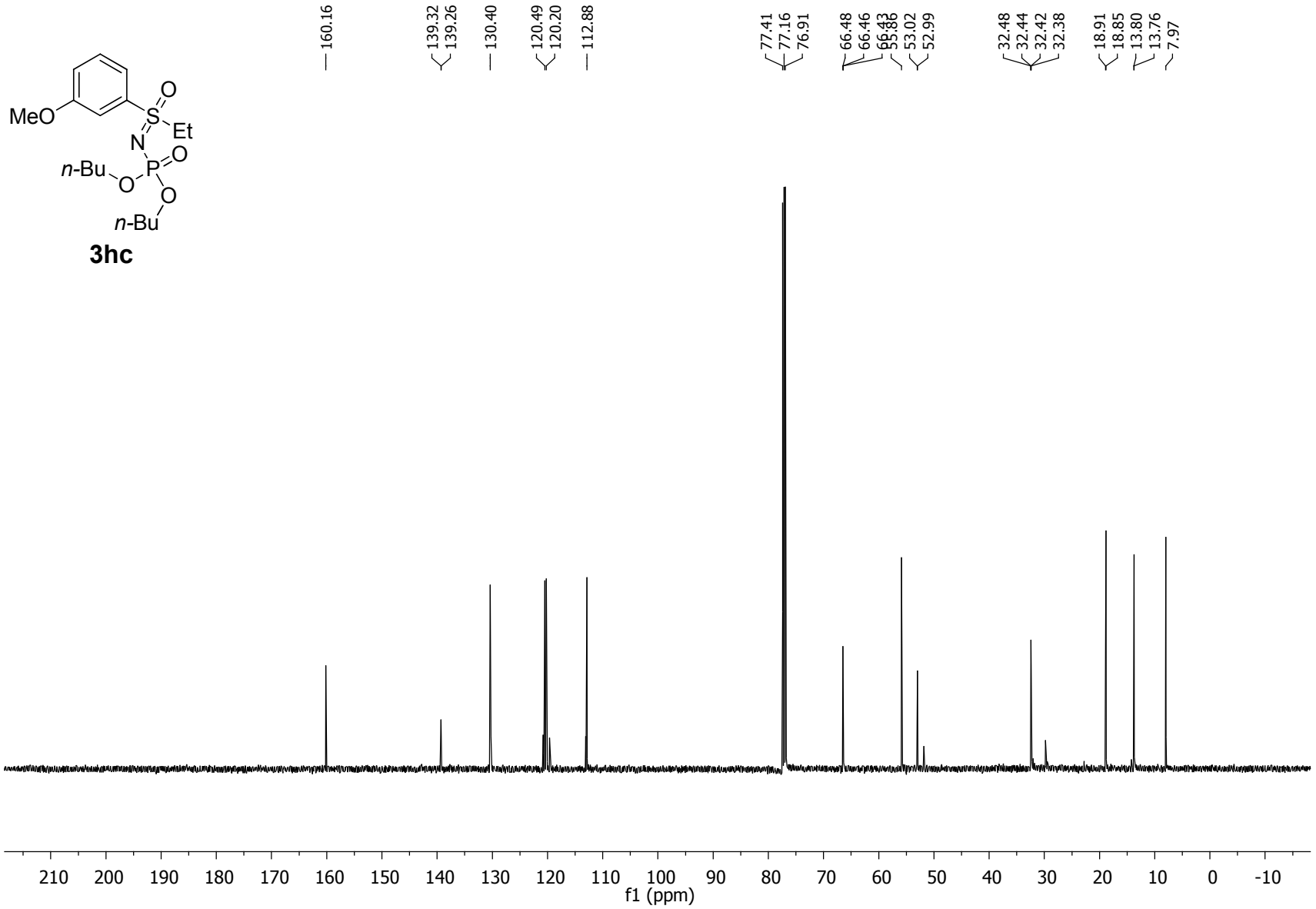


Figure S59. ^{13}C NMR for **3hc**

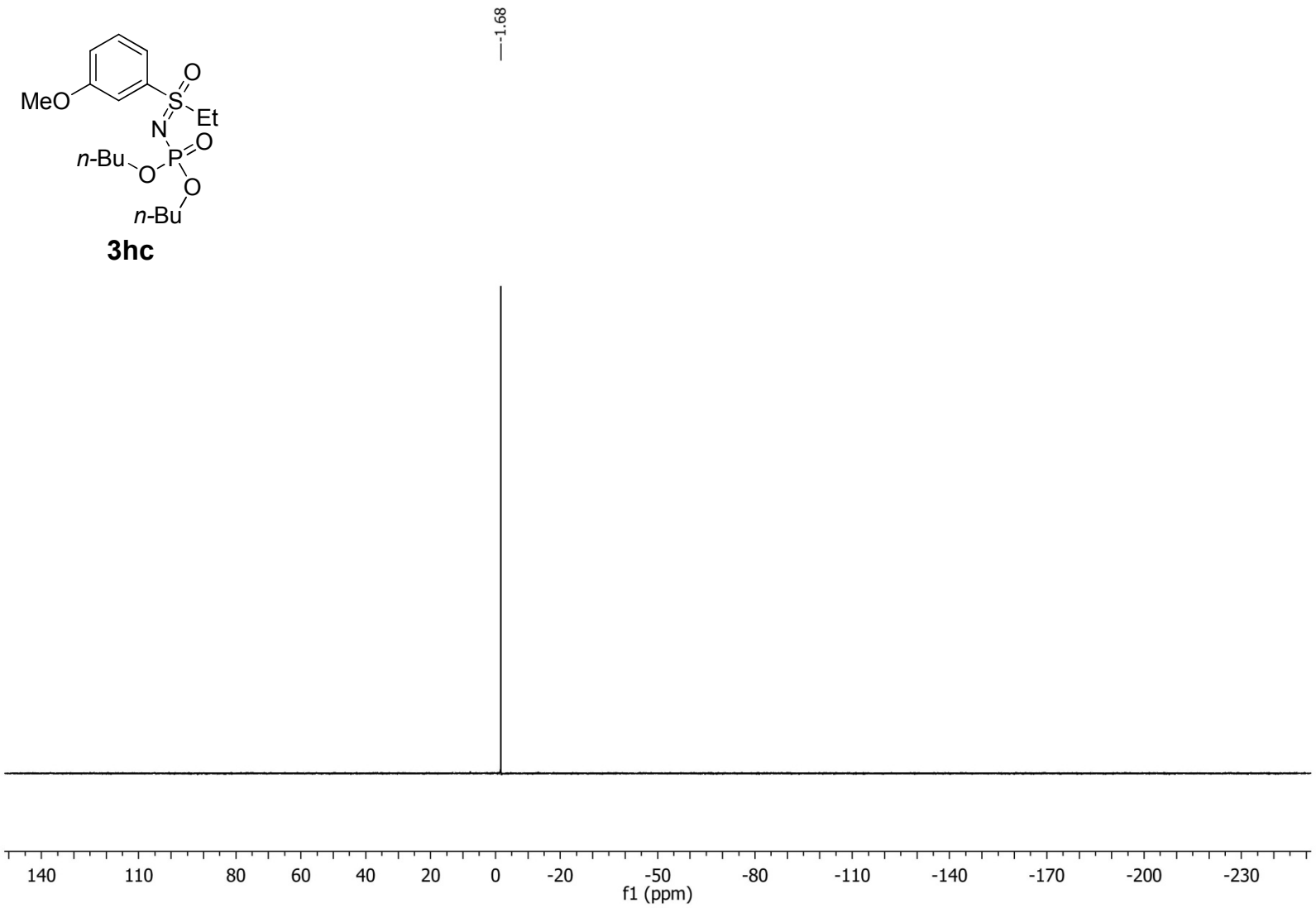


Figure S60. ^{31}P NMR for **3hc**

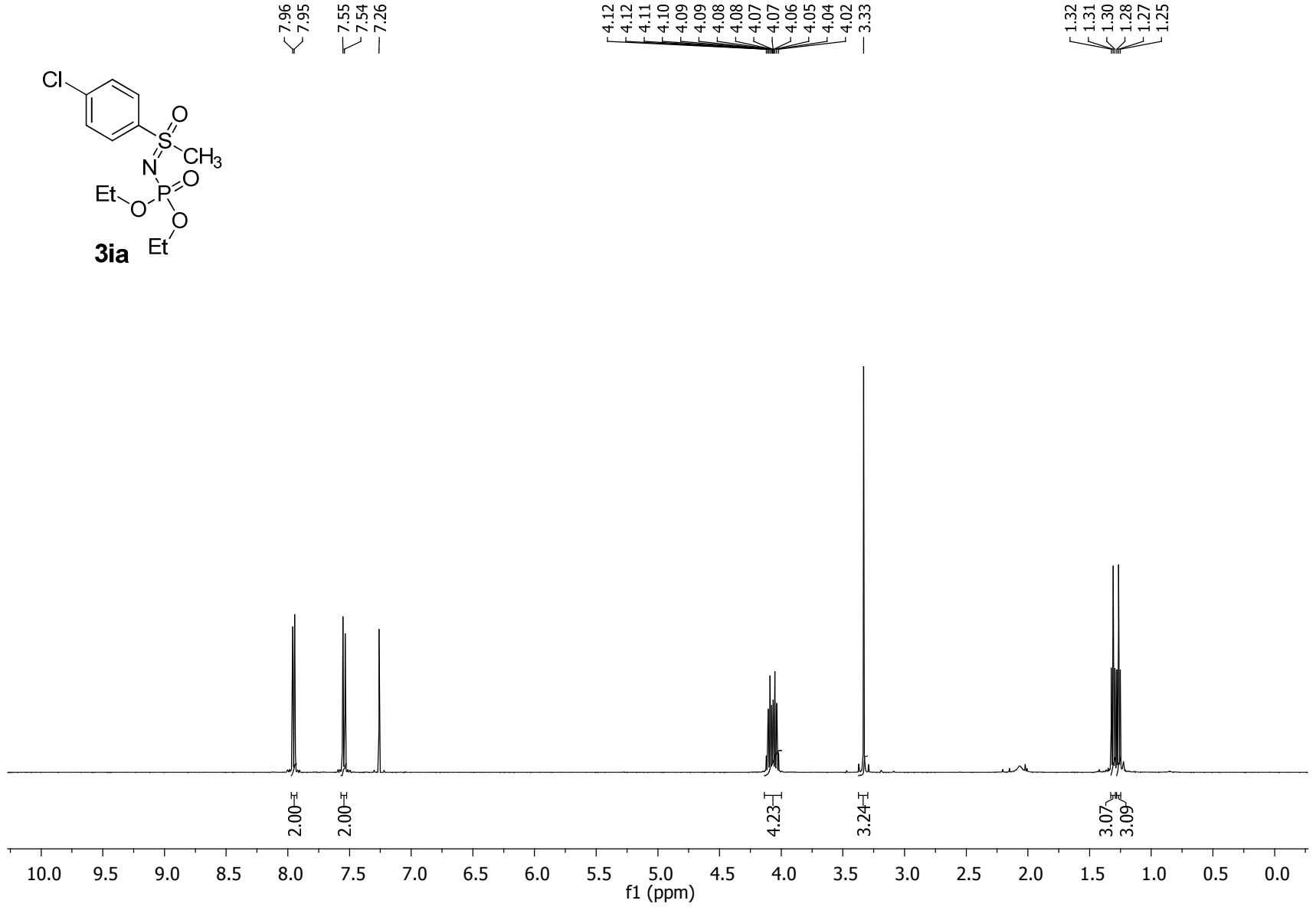


Figure S61. ^{1}H NMR for **3ia**

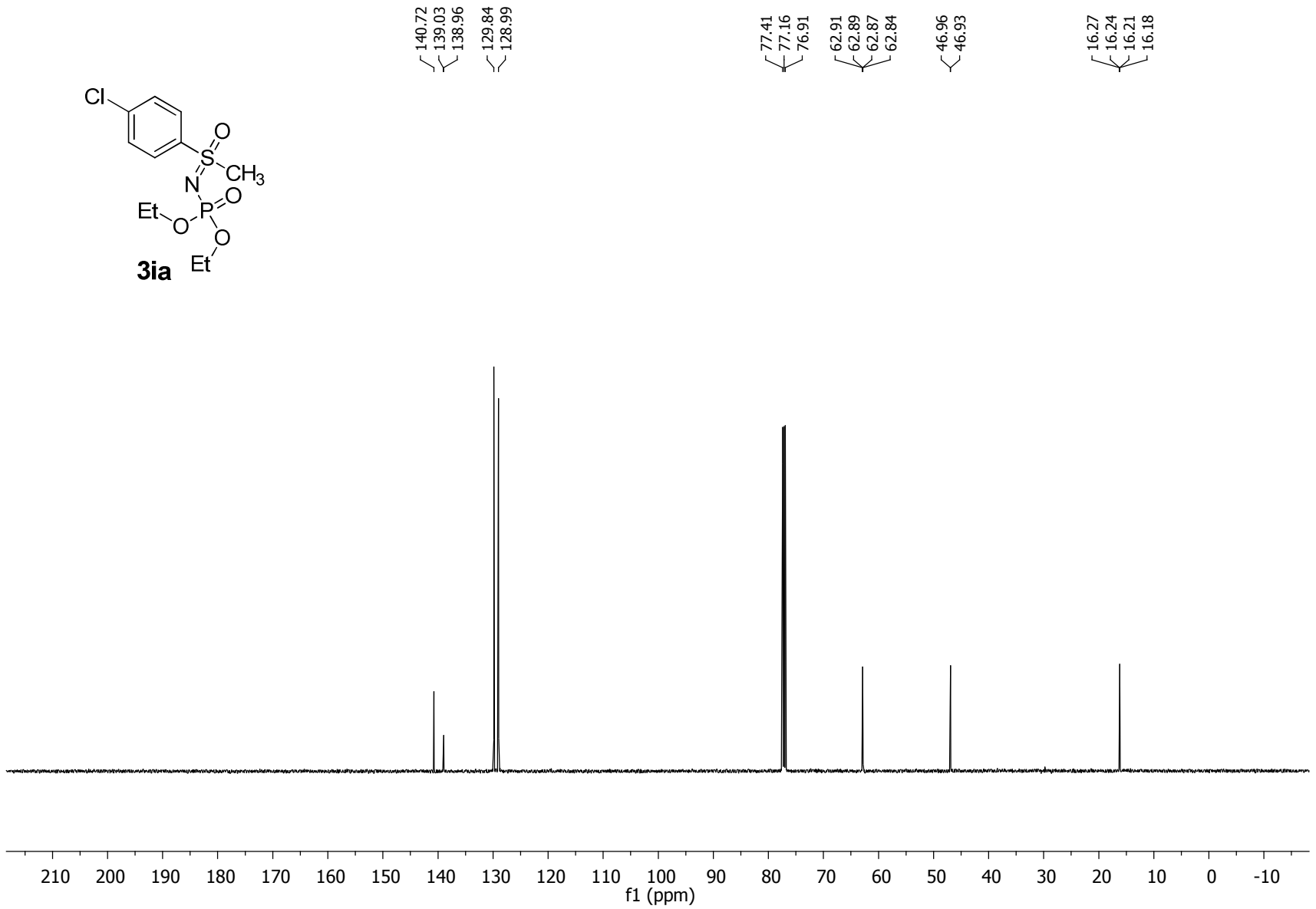


Figure S62. ^{13}C NMR for **3ia**

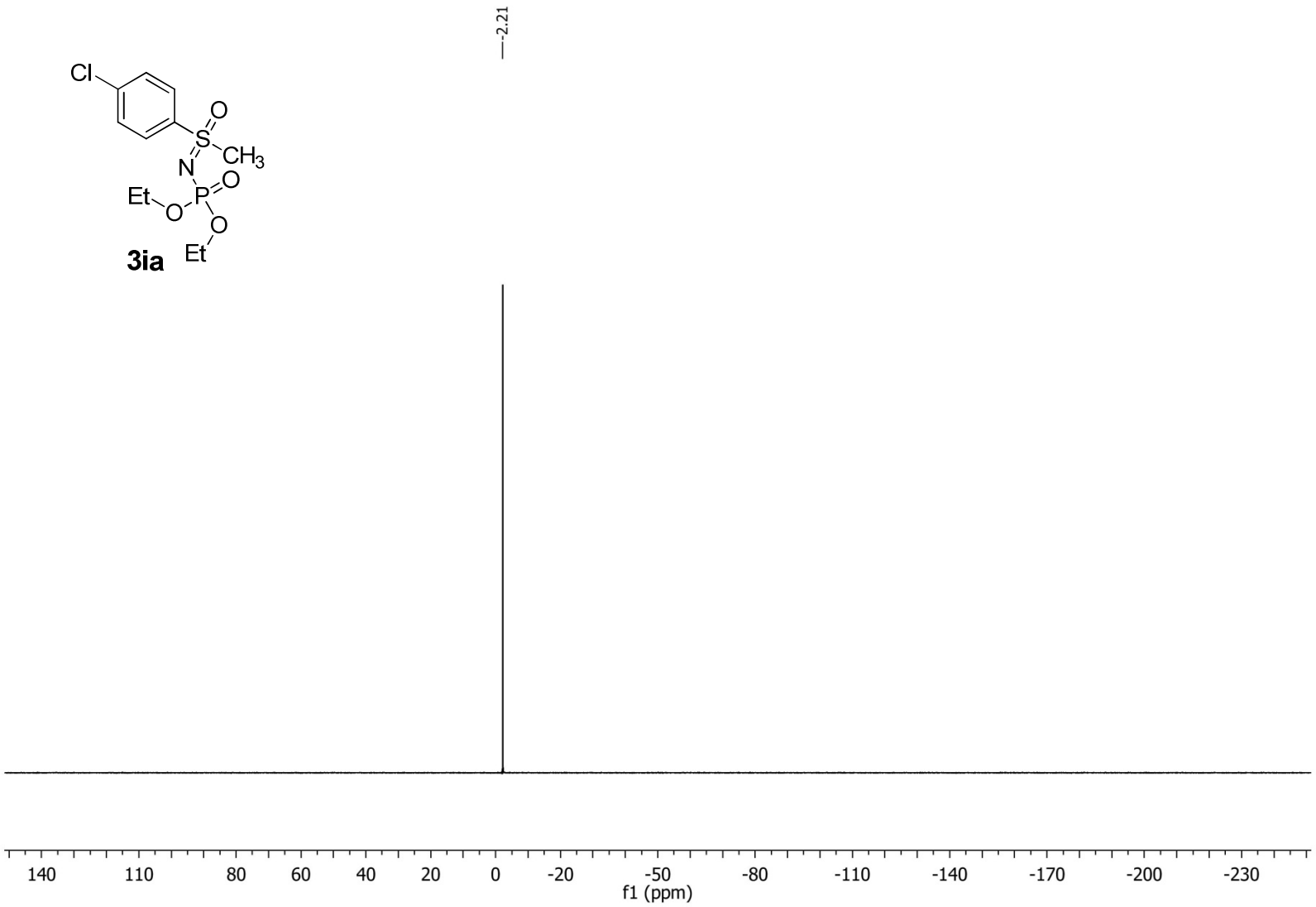


Figure S63. ^{31}P NMR for **3ia**

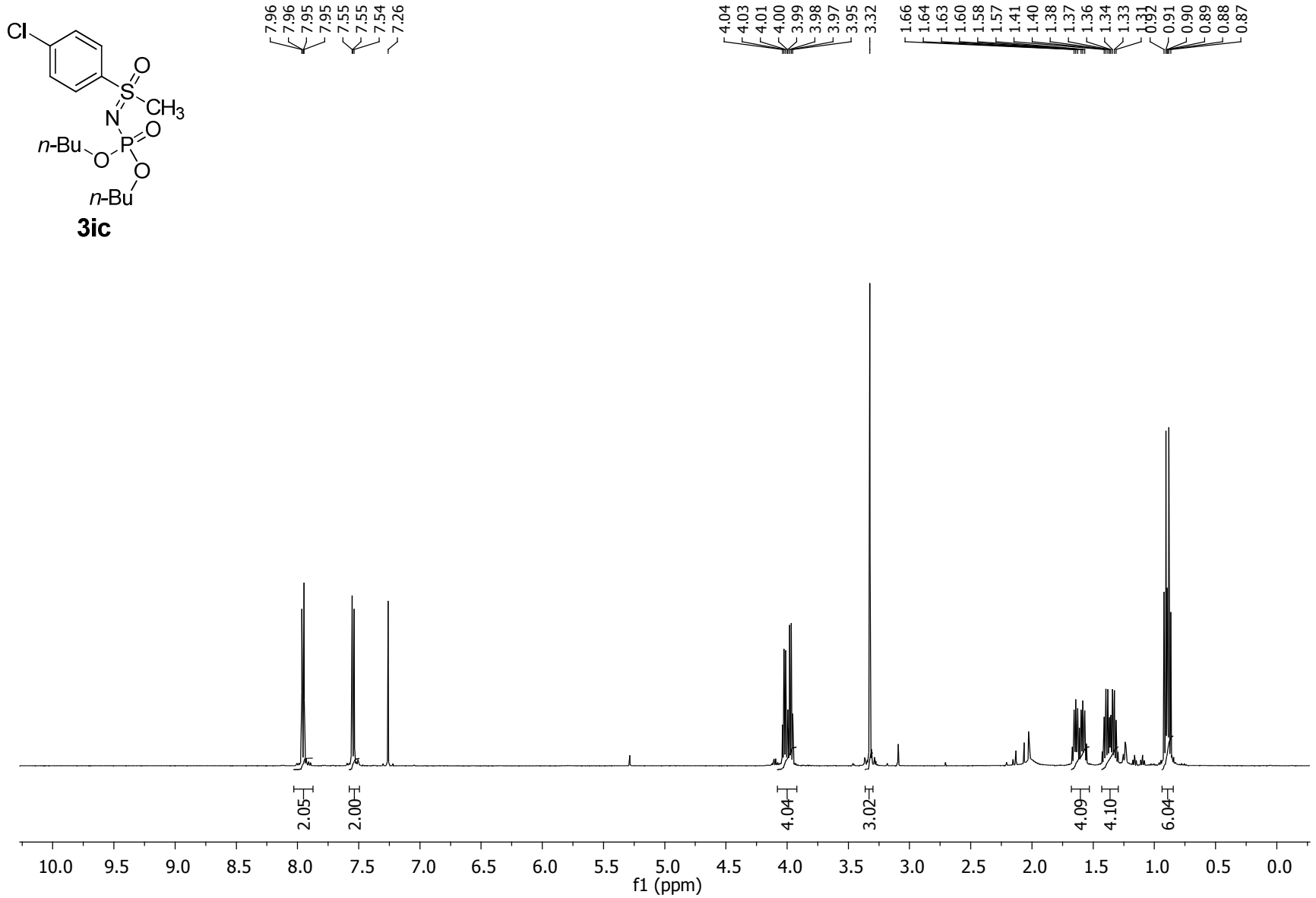


Figure S64. ^{1}H NMR for **3ic**

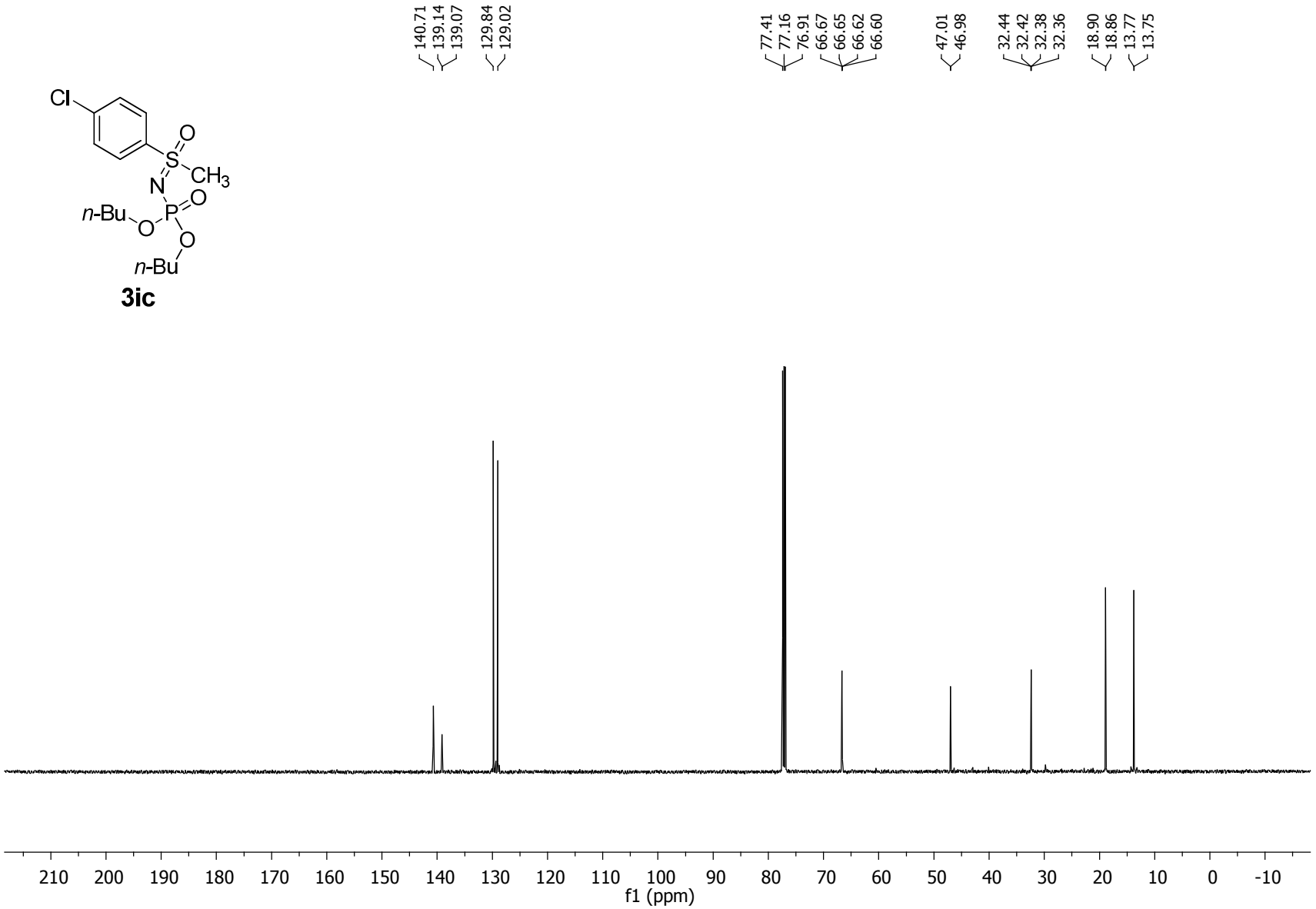


Figure S65. ^{13}C NMR for **3ic**

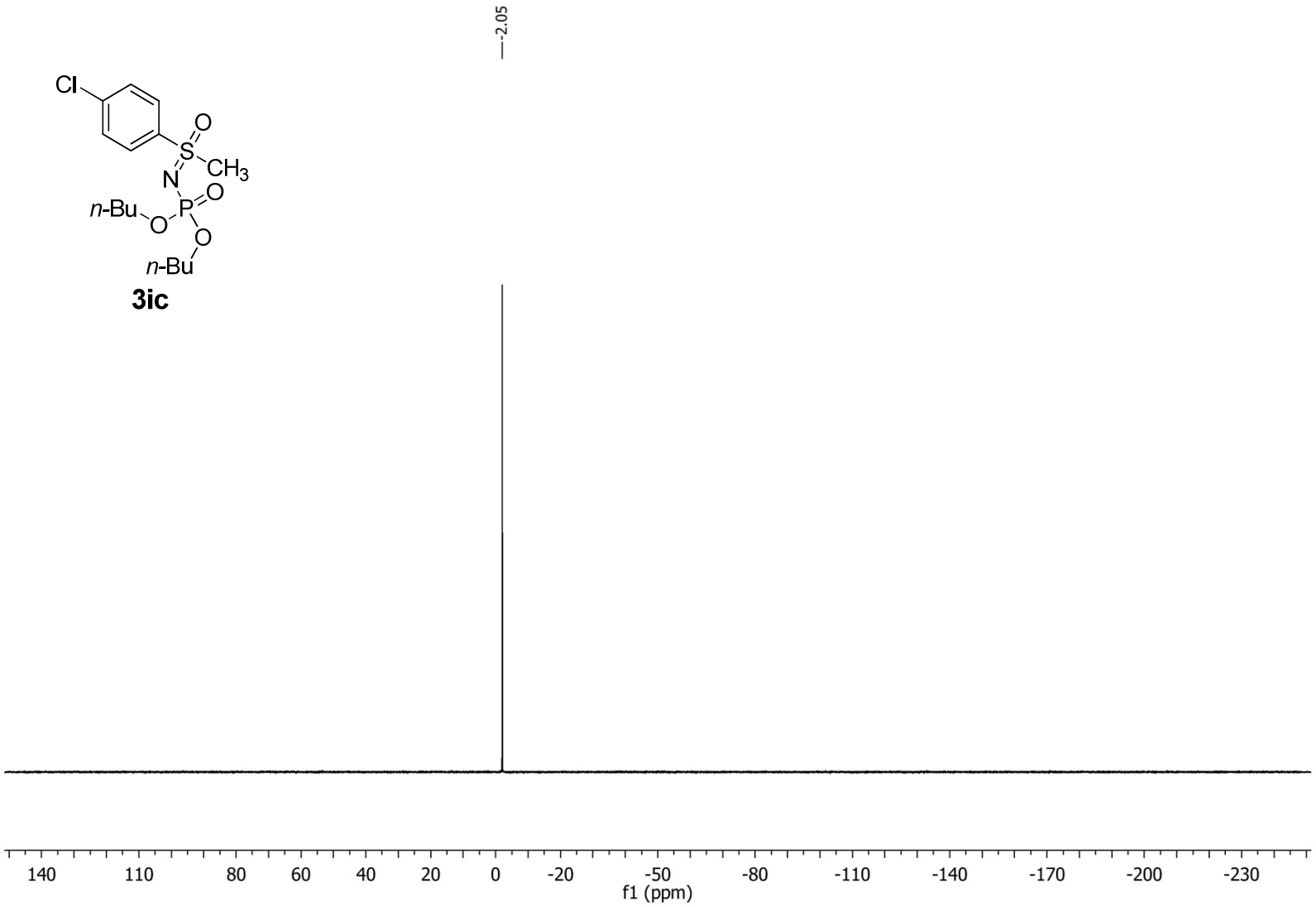


Figure S66. ^{31}P NMR for **3ic**

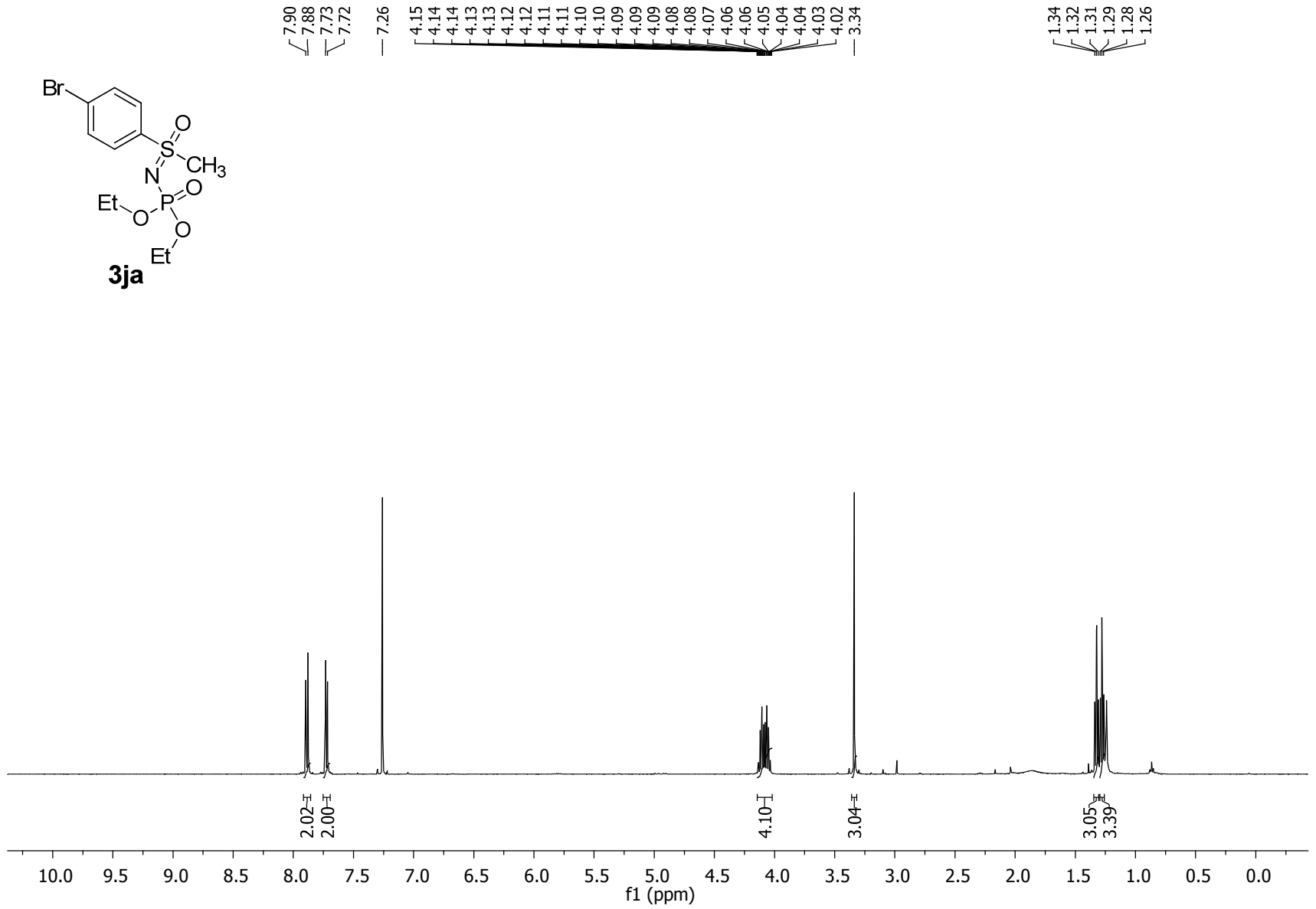


Figure S67. ^{1}H NMR for **3ja**

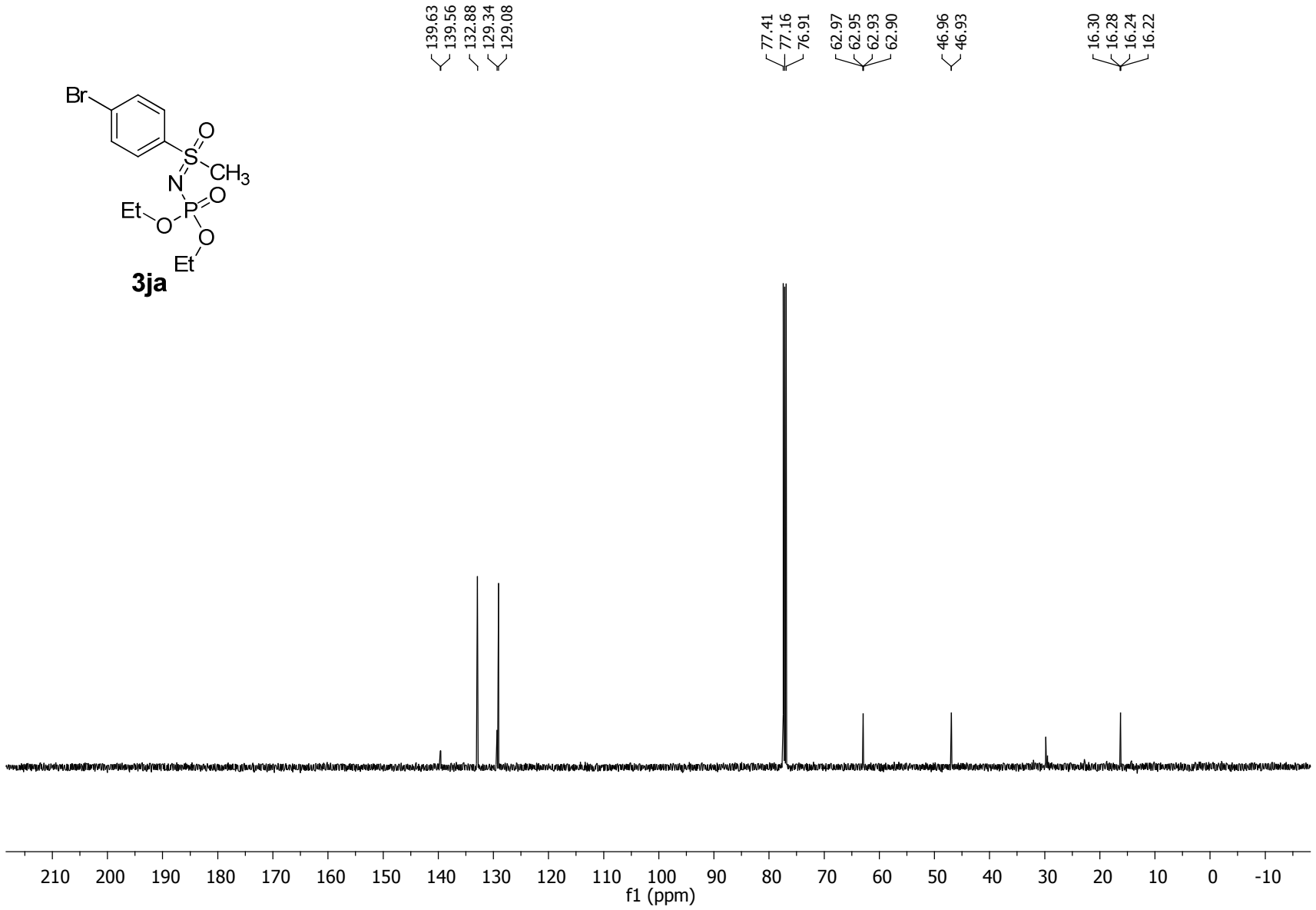


Figure S68. ^{13}C NMR for **3ja**

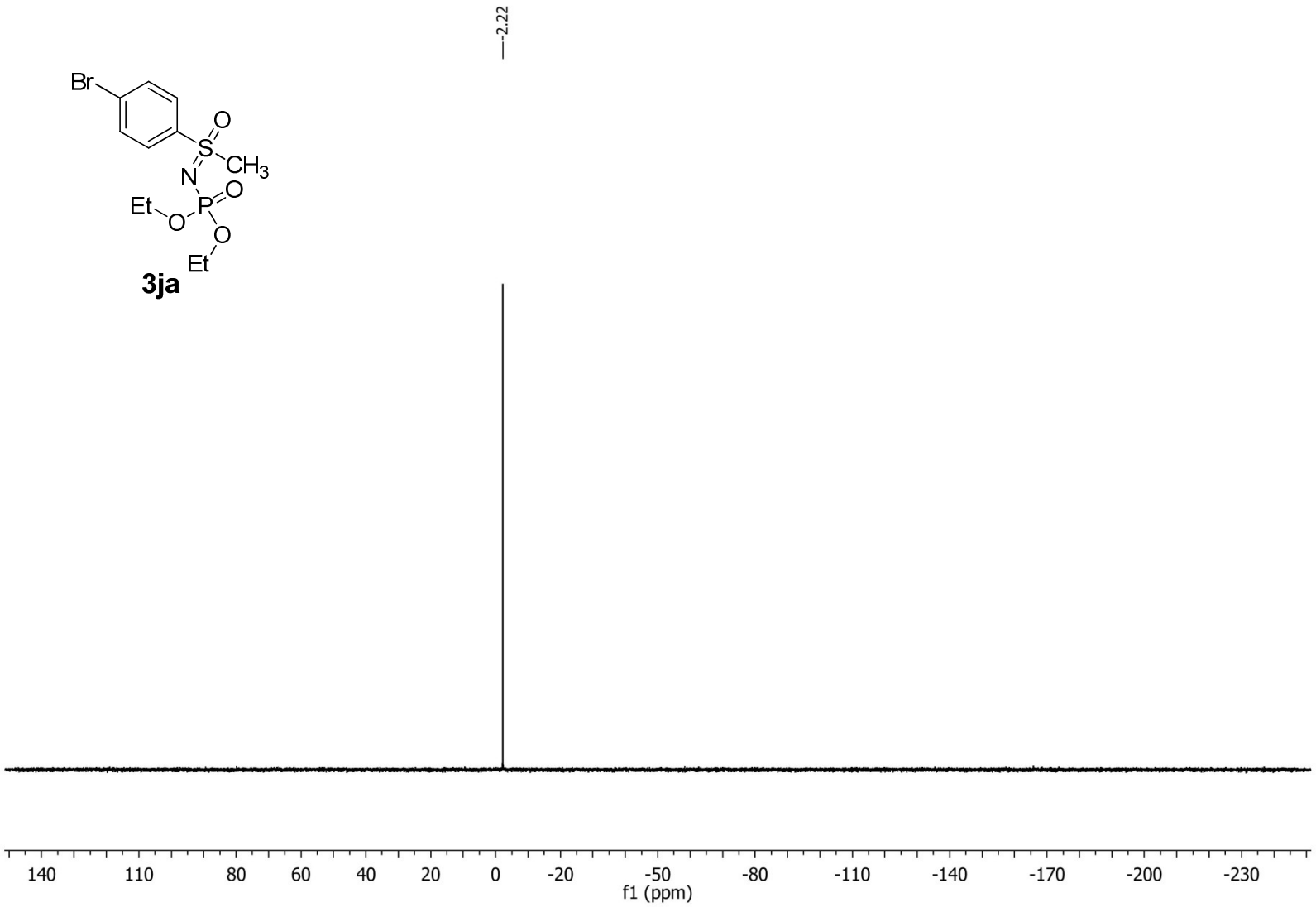


Figure S69. ^{31}P NMR for **3ja**

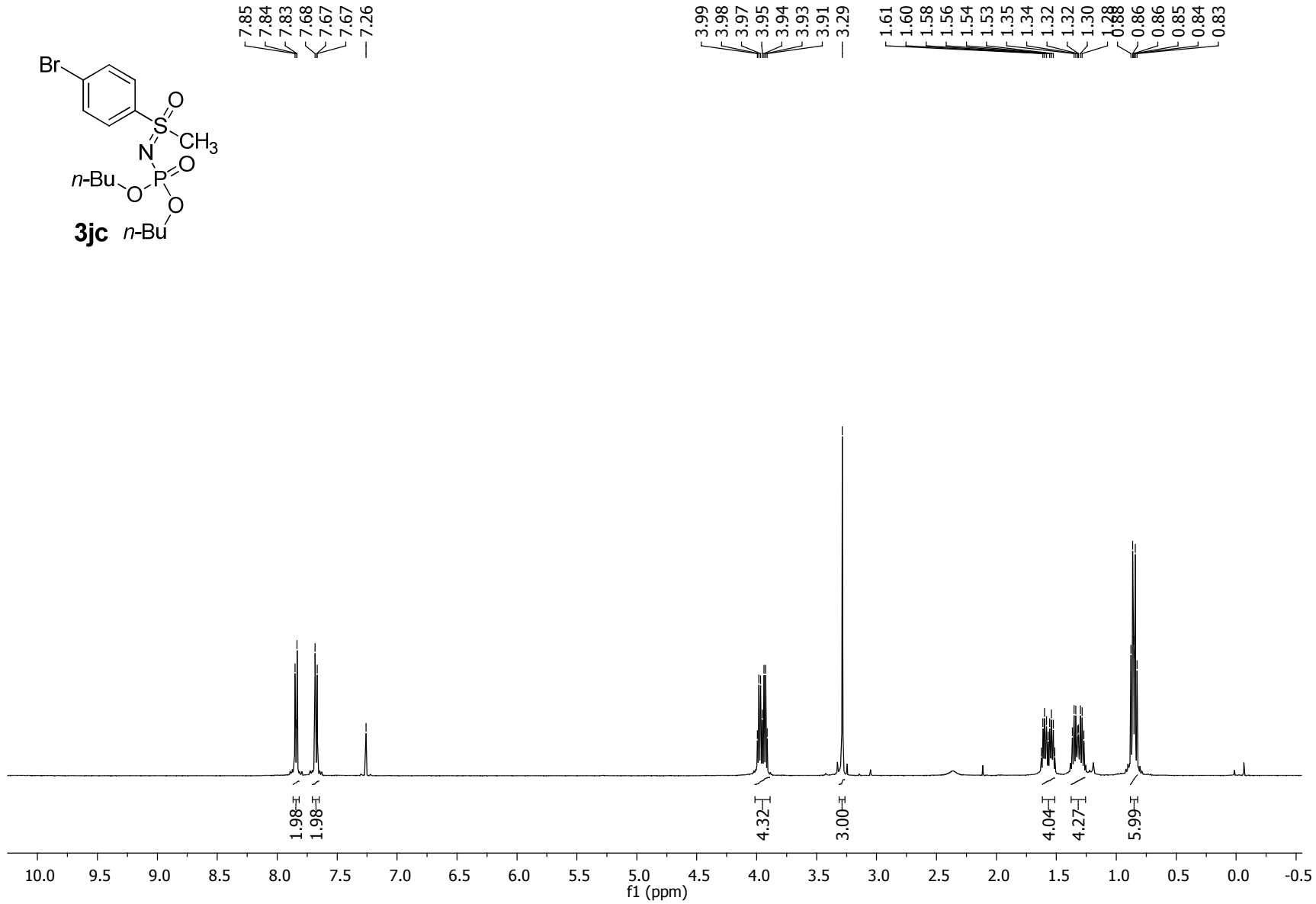


Figure S70. ^{1}H NMR for **3jc**

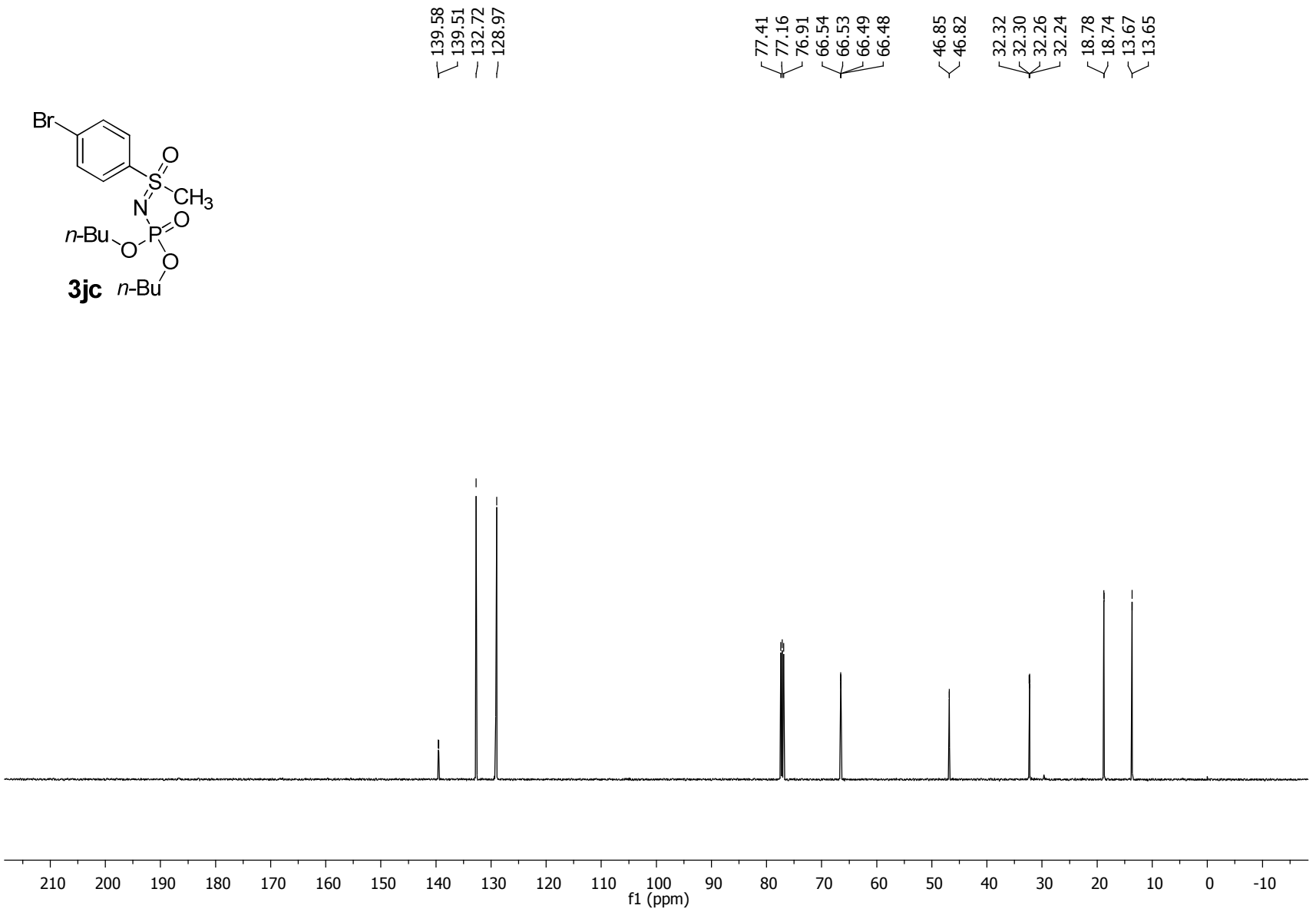


Figure S71. ^{13}C NMR for **3jc**

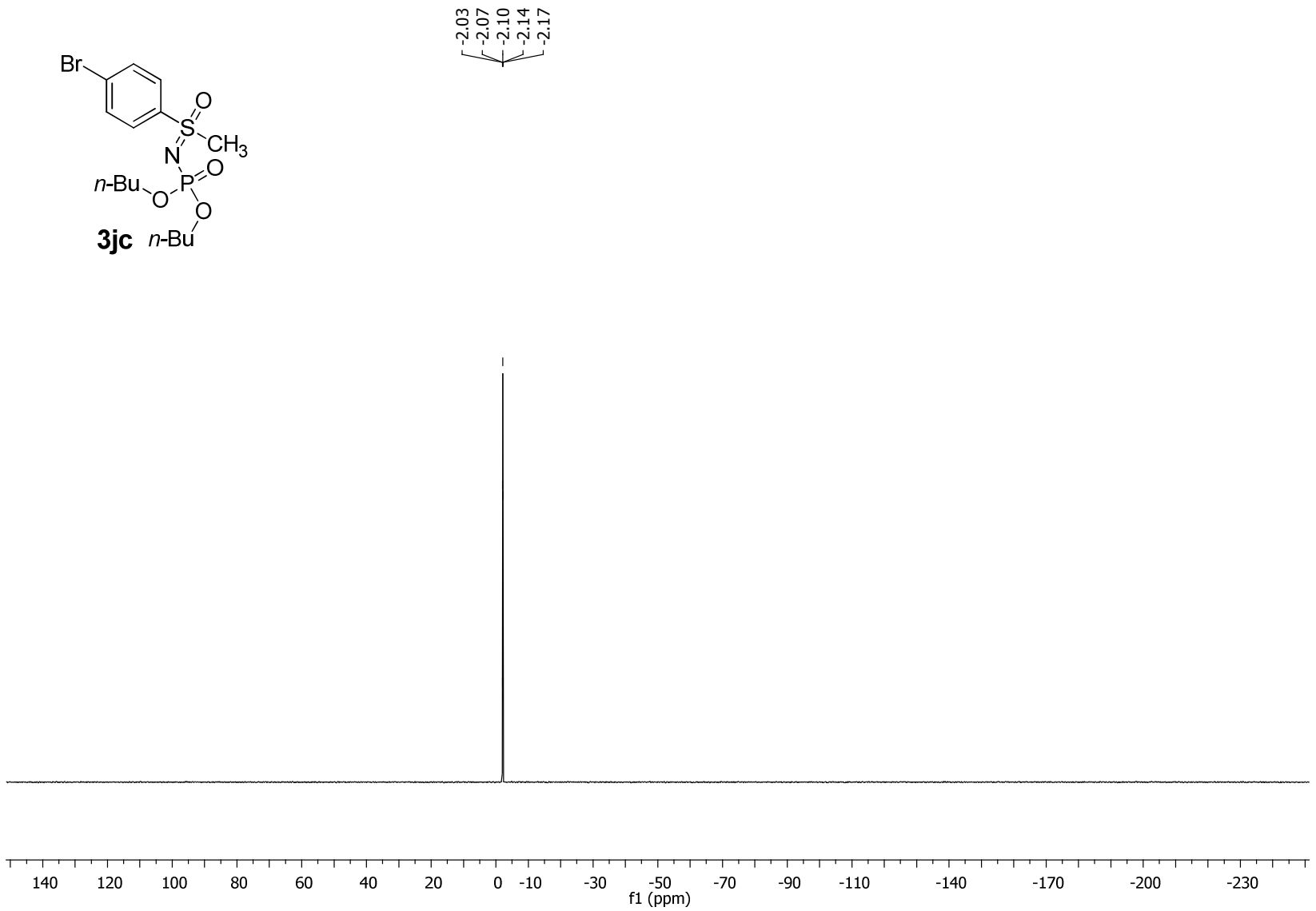


Figure S72. ^{31}P NMR for **3jc**

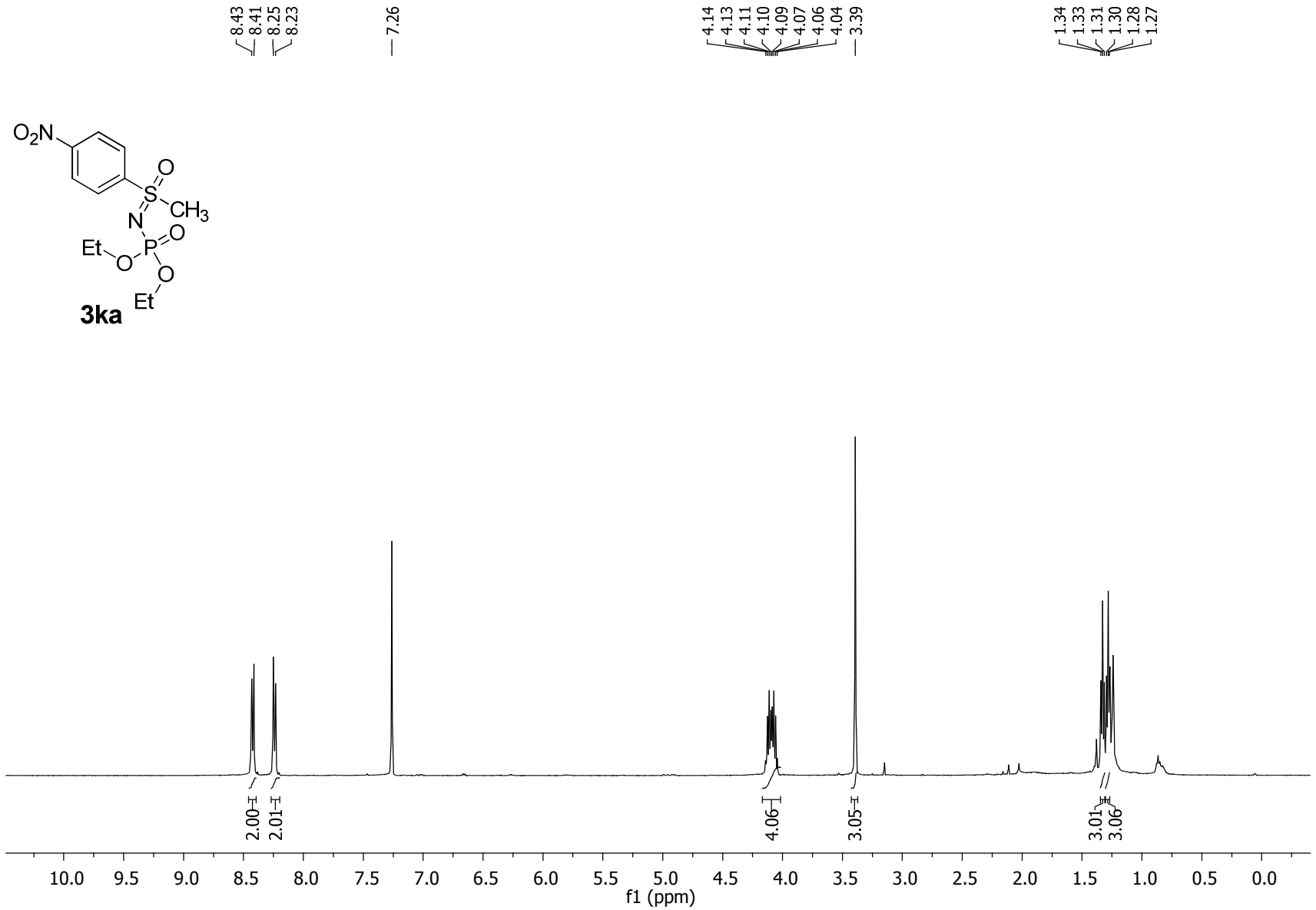


Figure S73. ^{1}H NMR for **3ka**

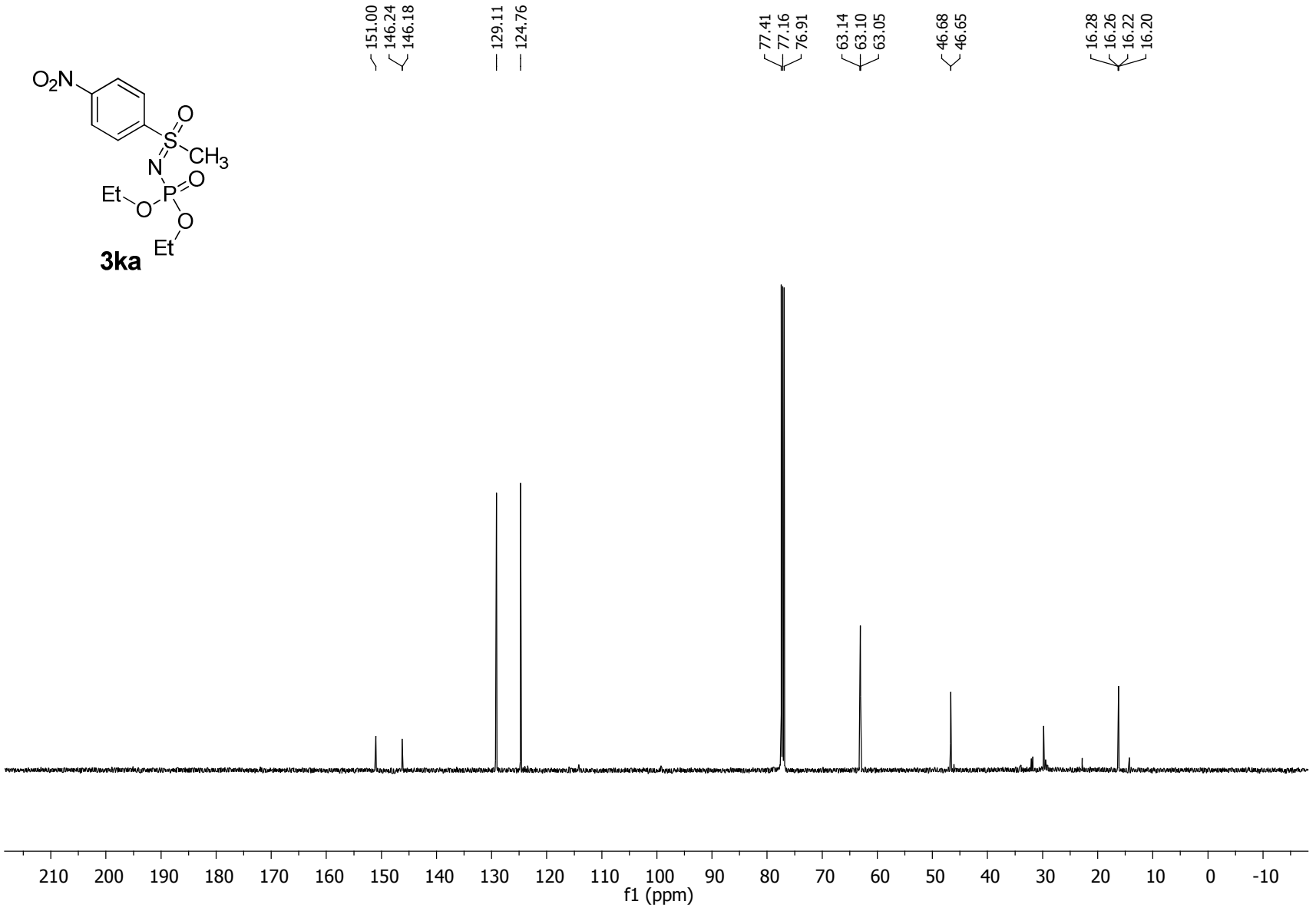


Figure S74. ^{13}C NMR for **3ka**

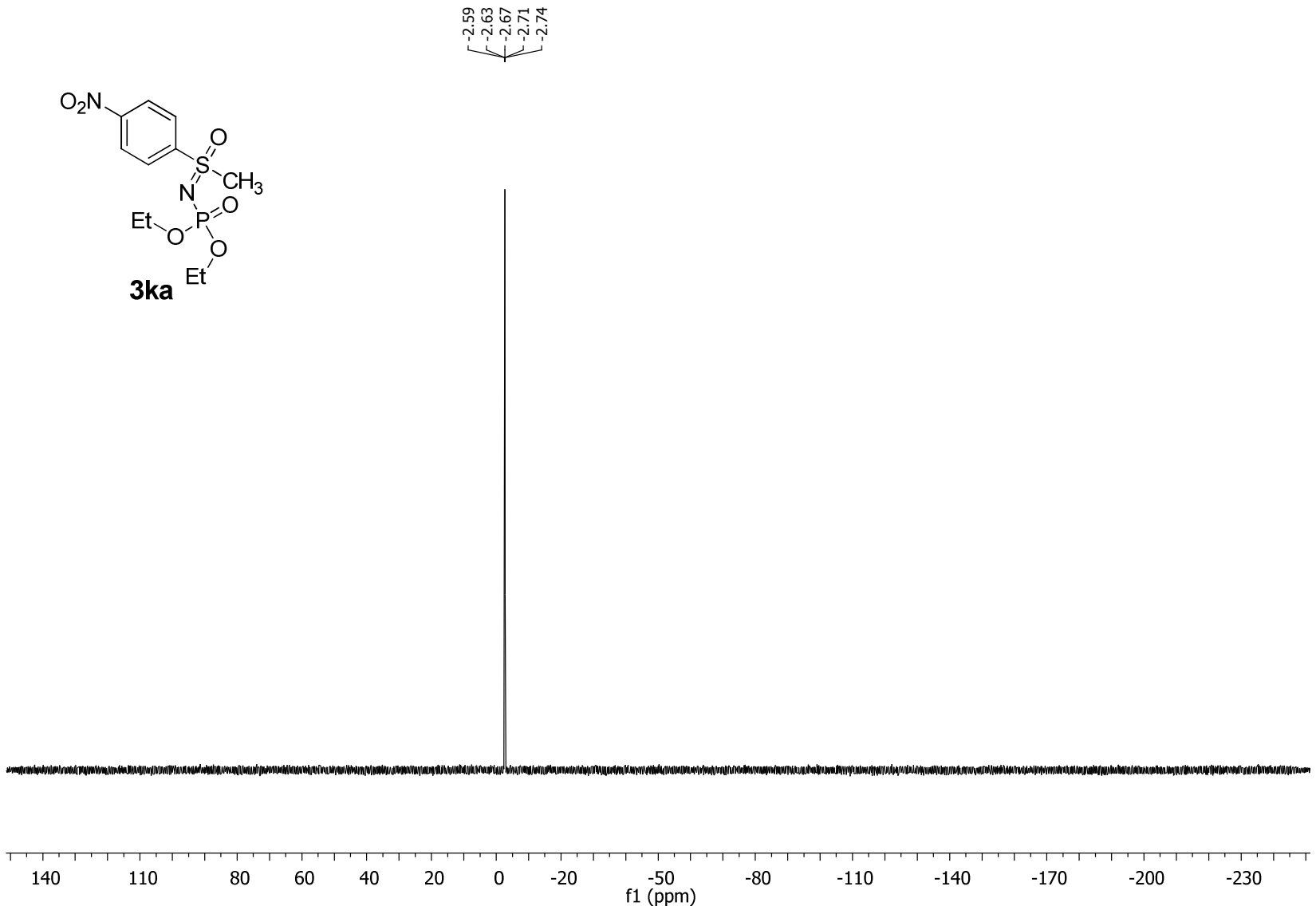


Figure S75. ^{31}P NMR for **3ka**

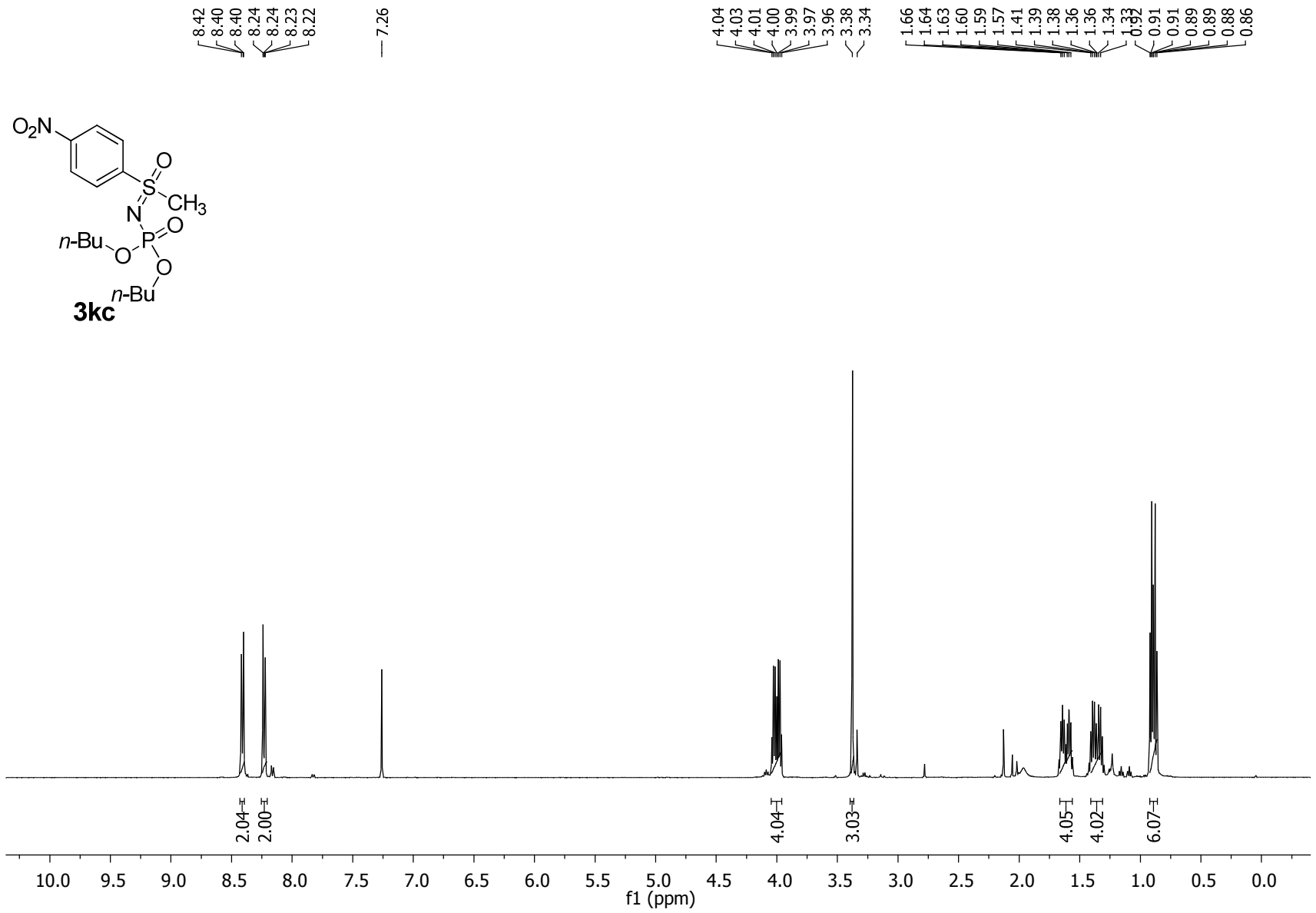


Figure S76. ^{1}H NMR for **3kc**

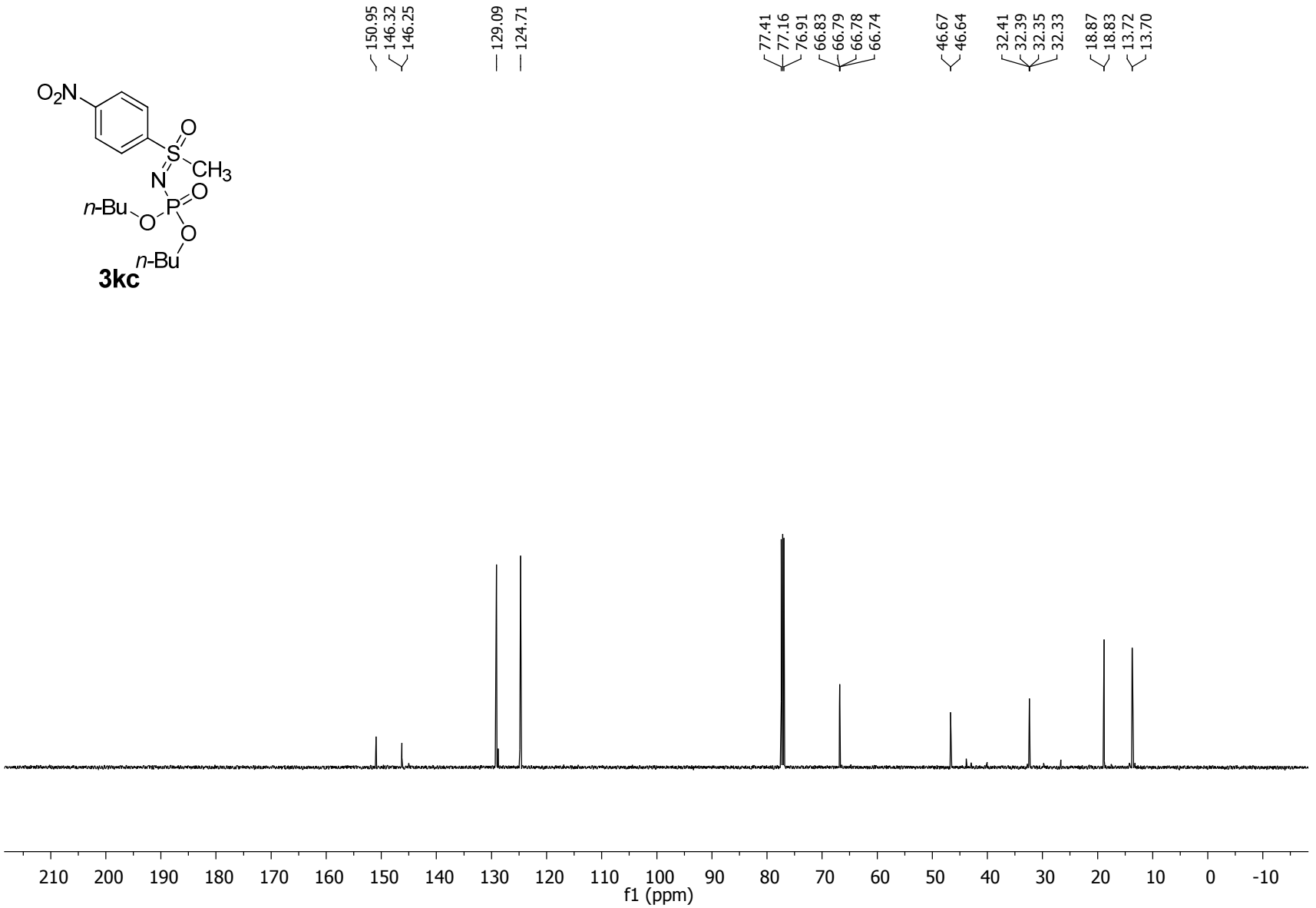


Figure S77. ^{13}C NMR for **3kc**

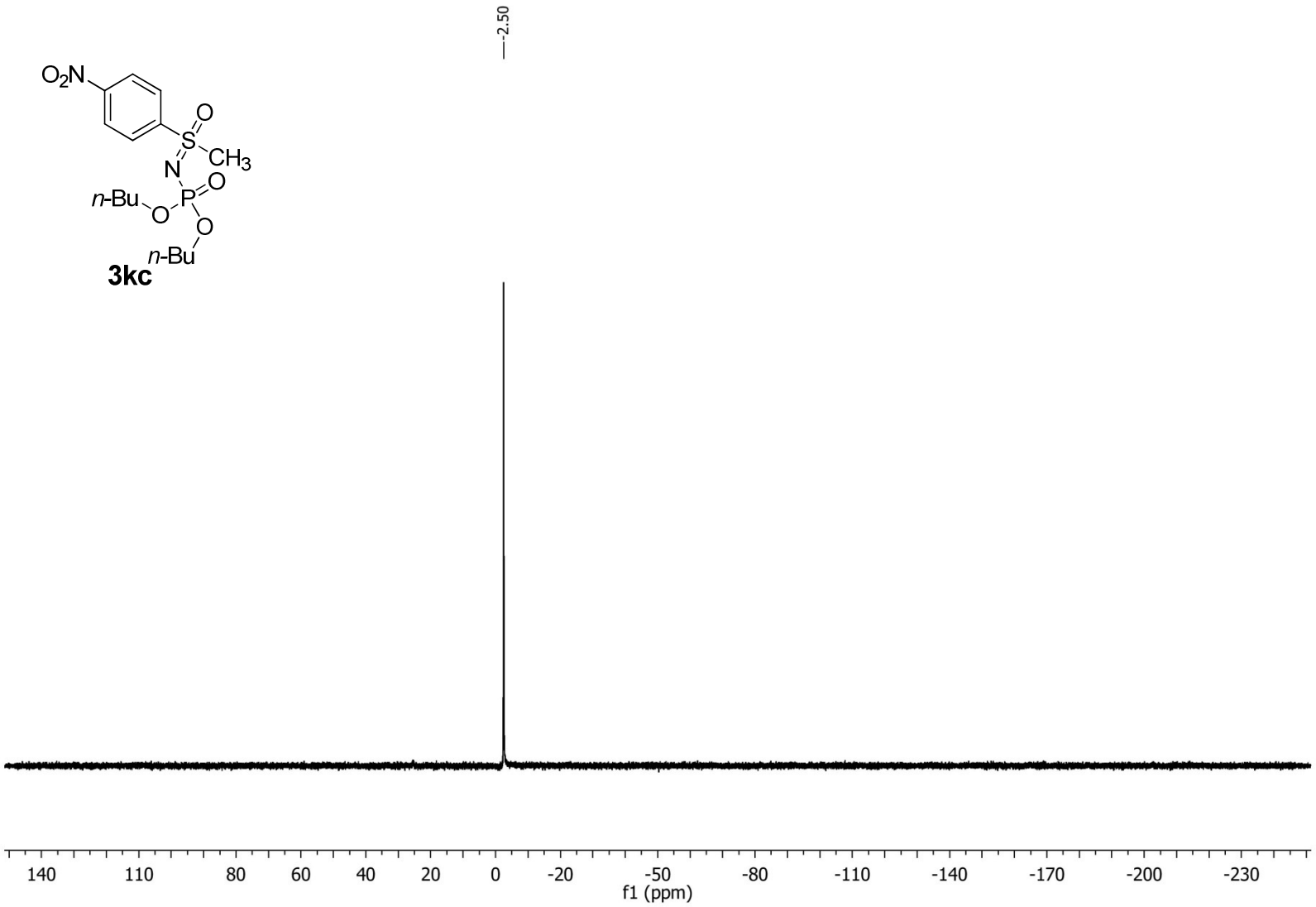


Figure S78. ^{31}P NMR for **3kc**

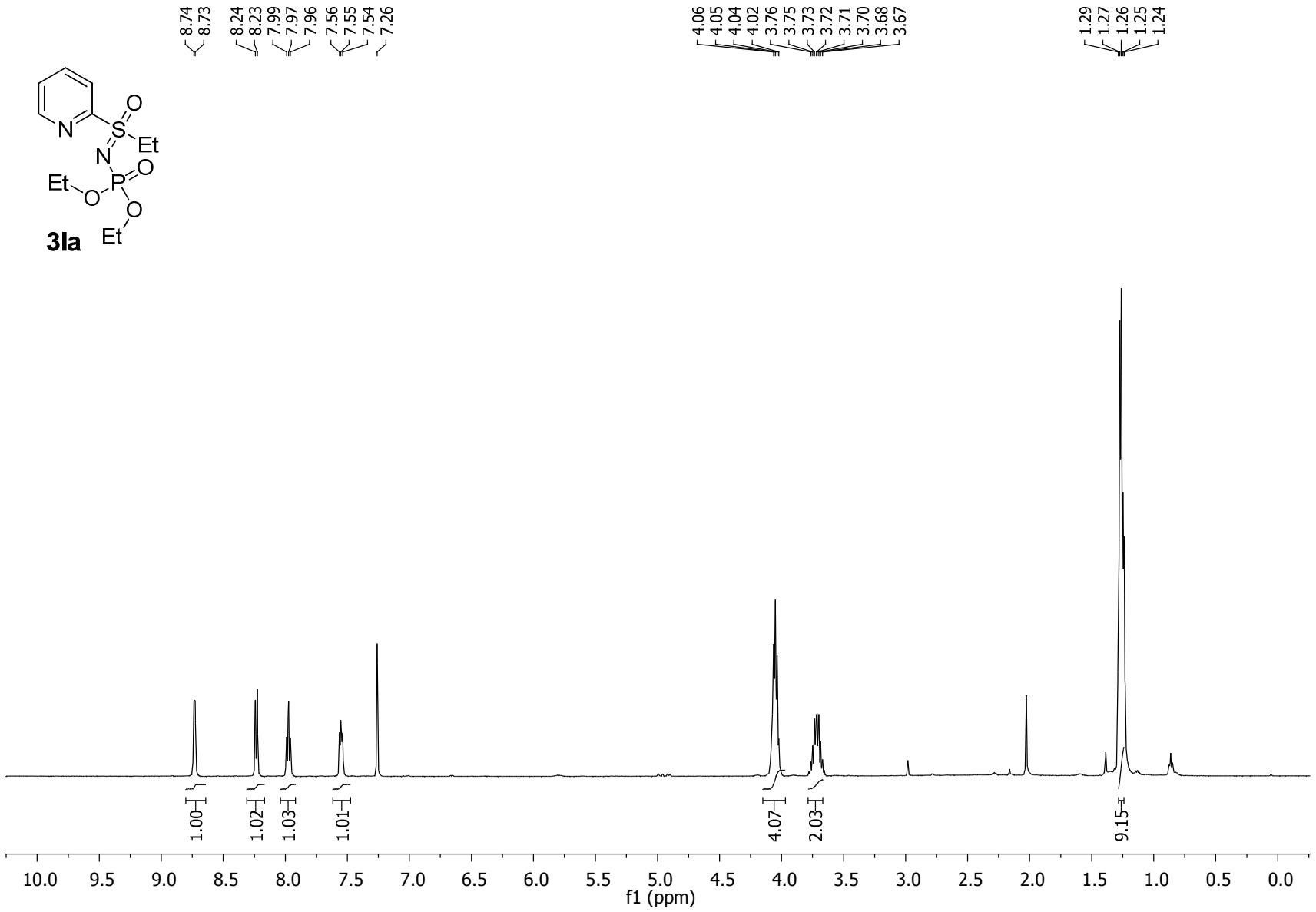


Figure S79. ^{1}H NMR for **3la**

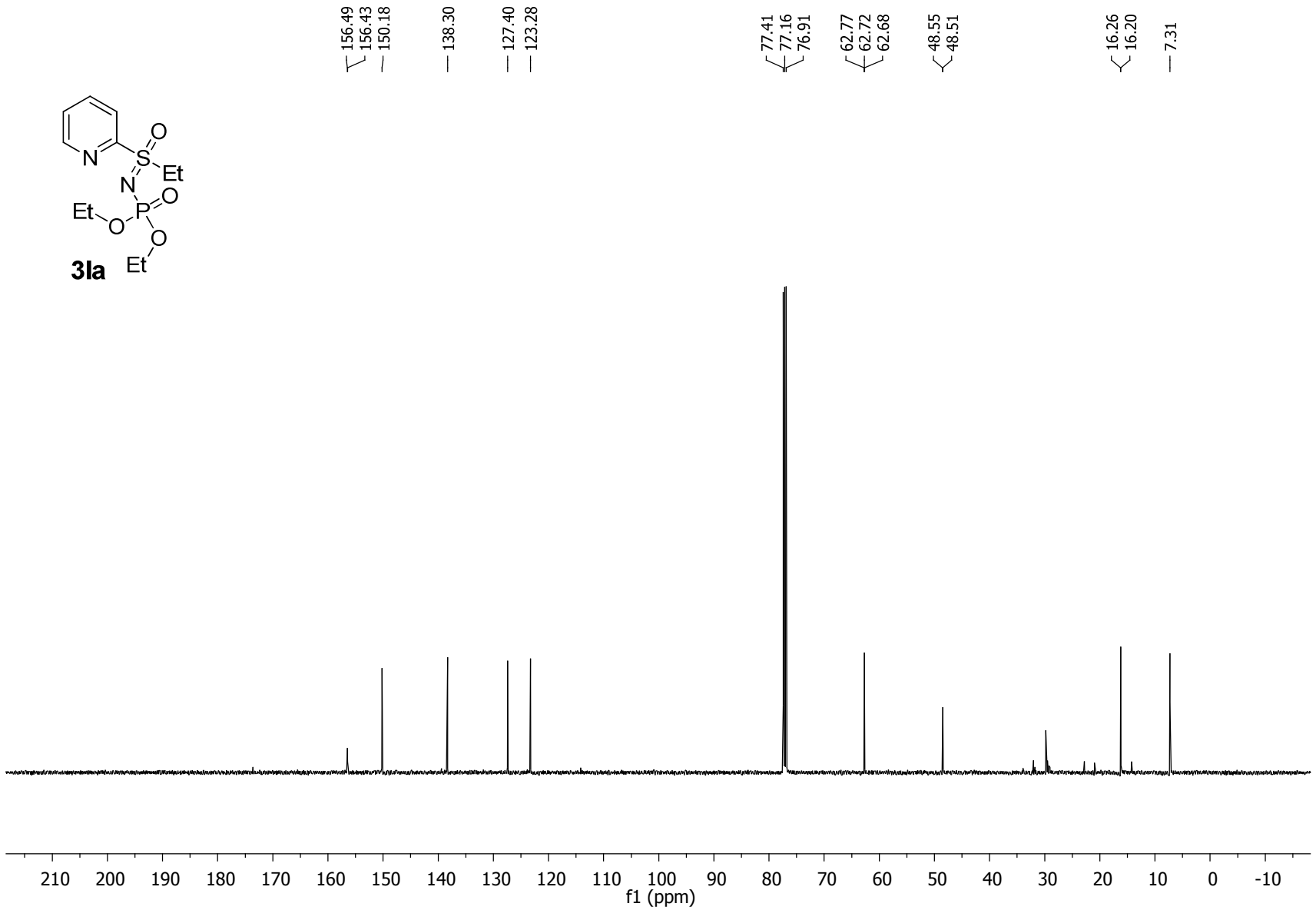


Figure S80. ^{13}C NMR for **3la**

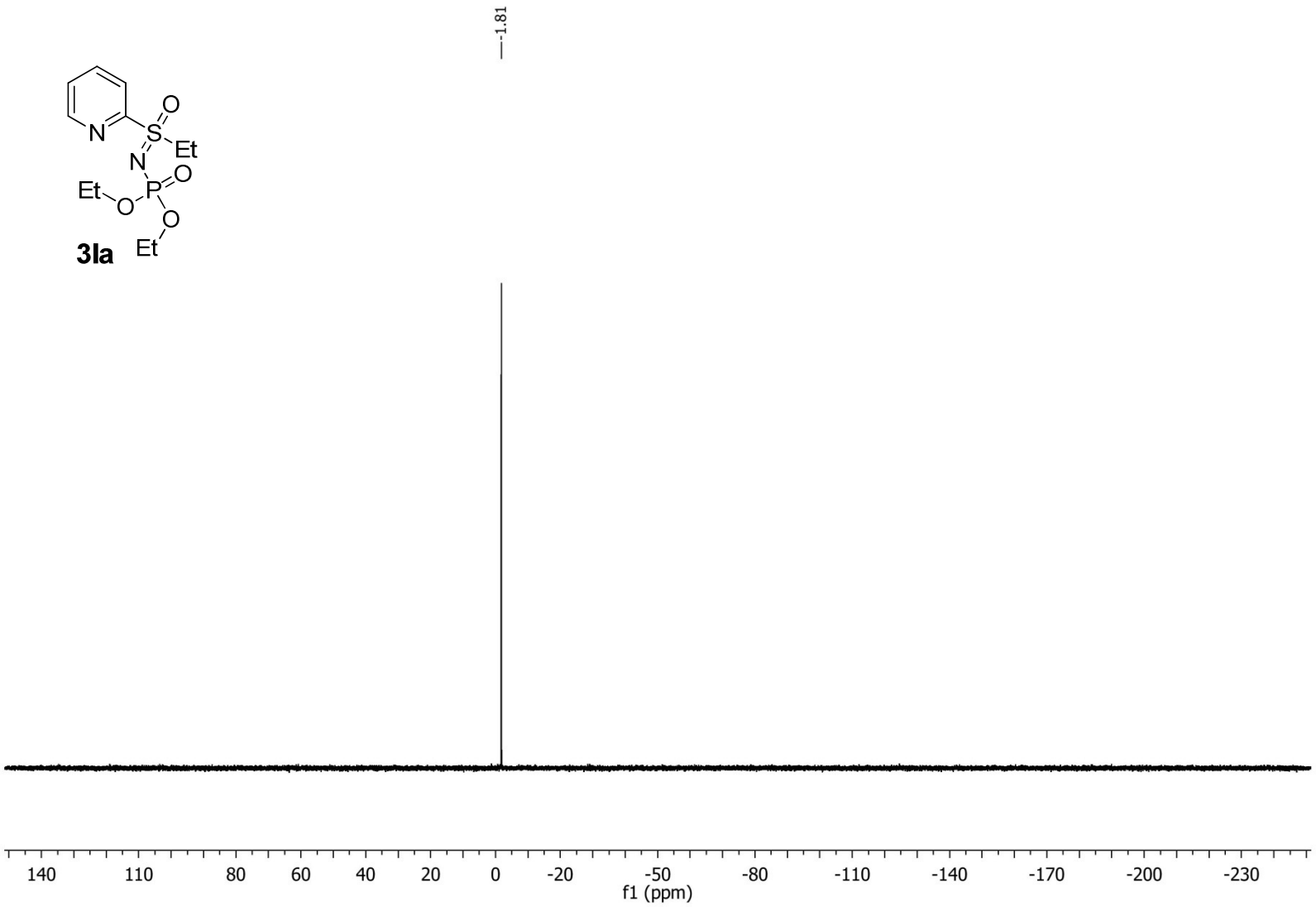


Figure S81. ^{31}P NMR for **3la**

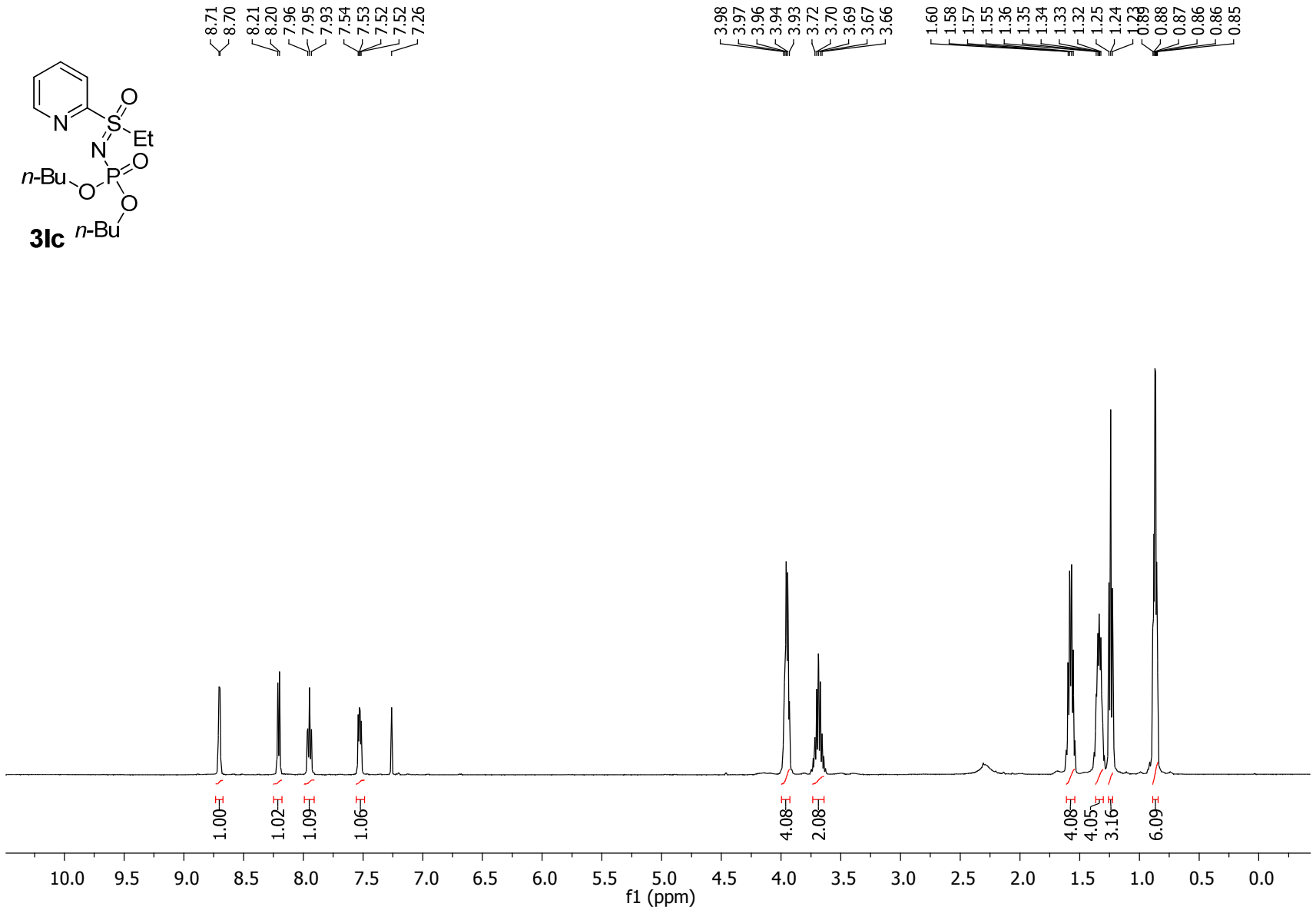


Figure S82. ^{1}H NMR for **3lc**

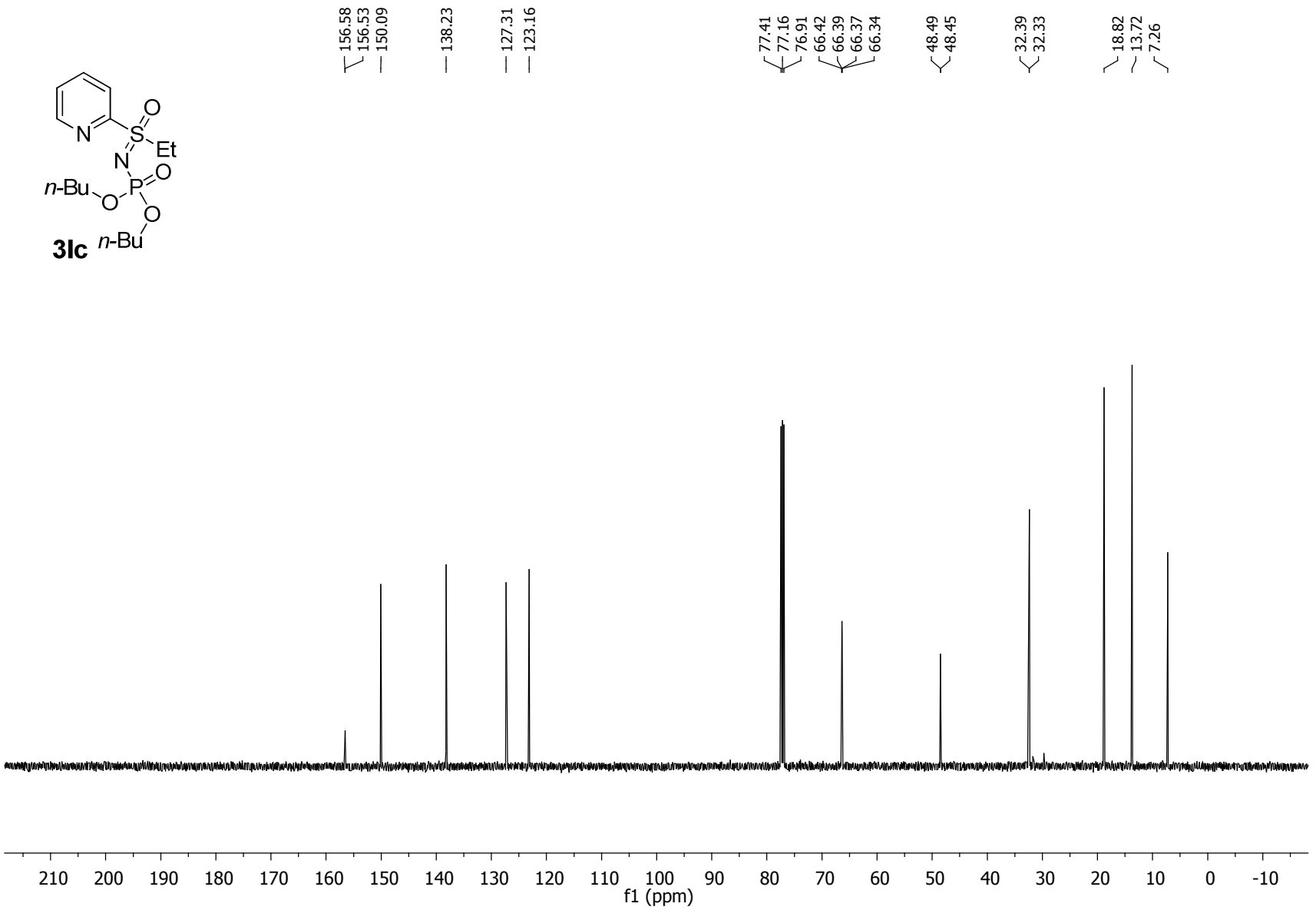


Figure S83. ^{13}C NMR for **3lc**

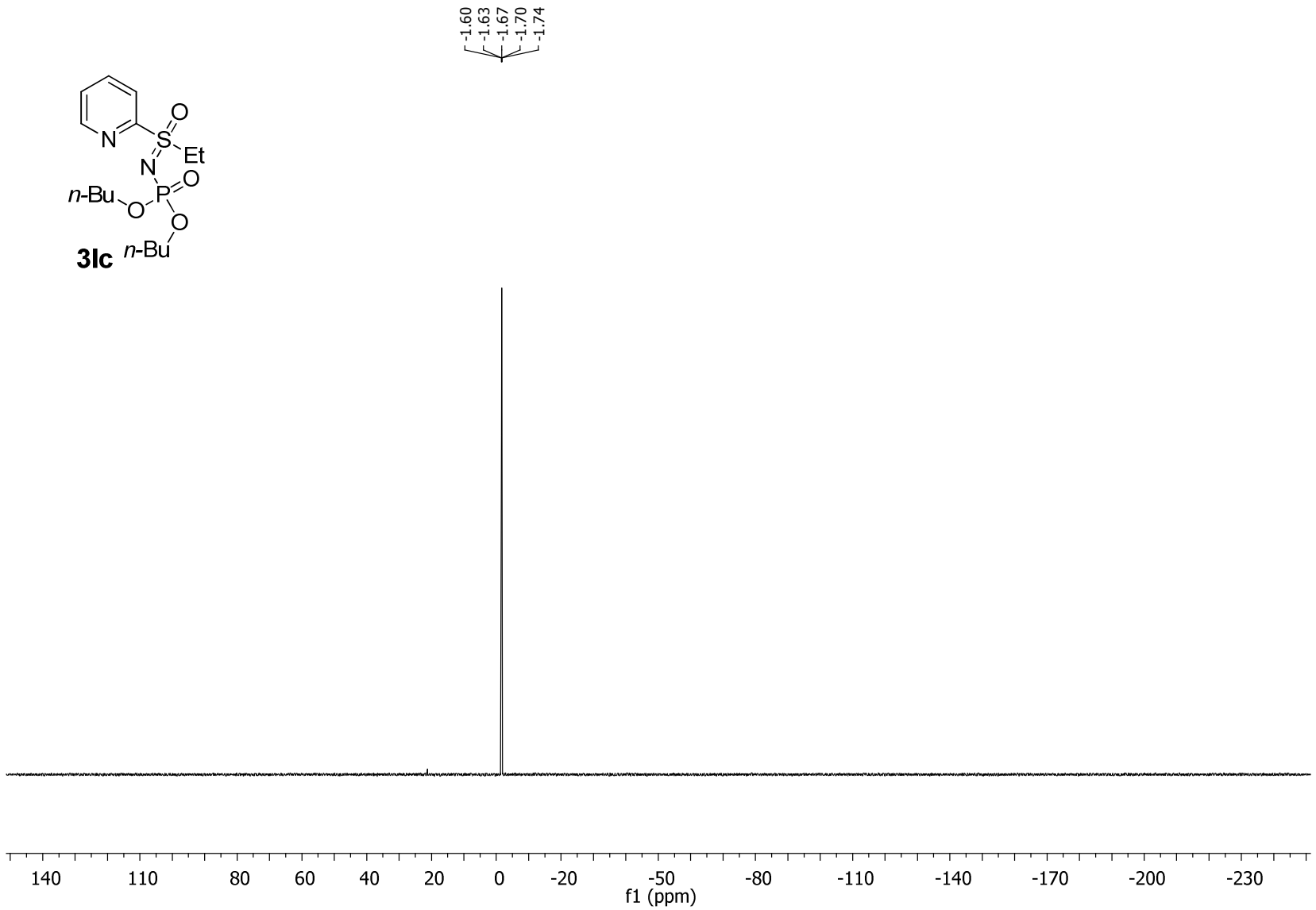


Figure S84. ^{31}P NMR for **3lc**

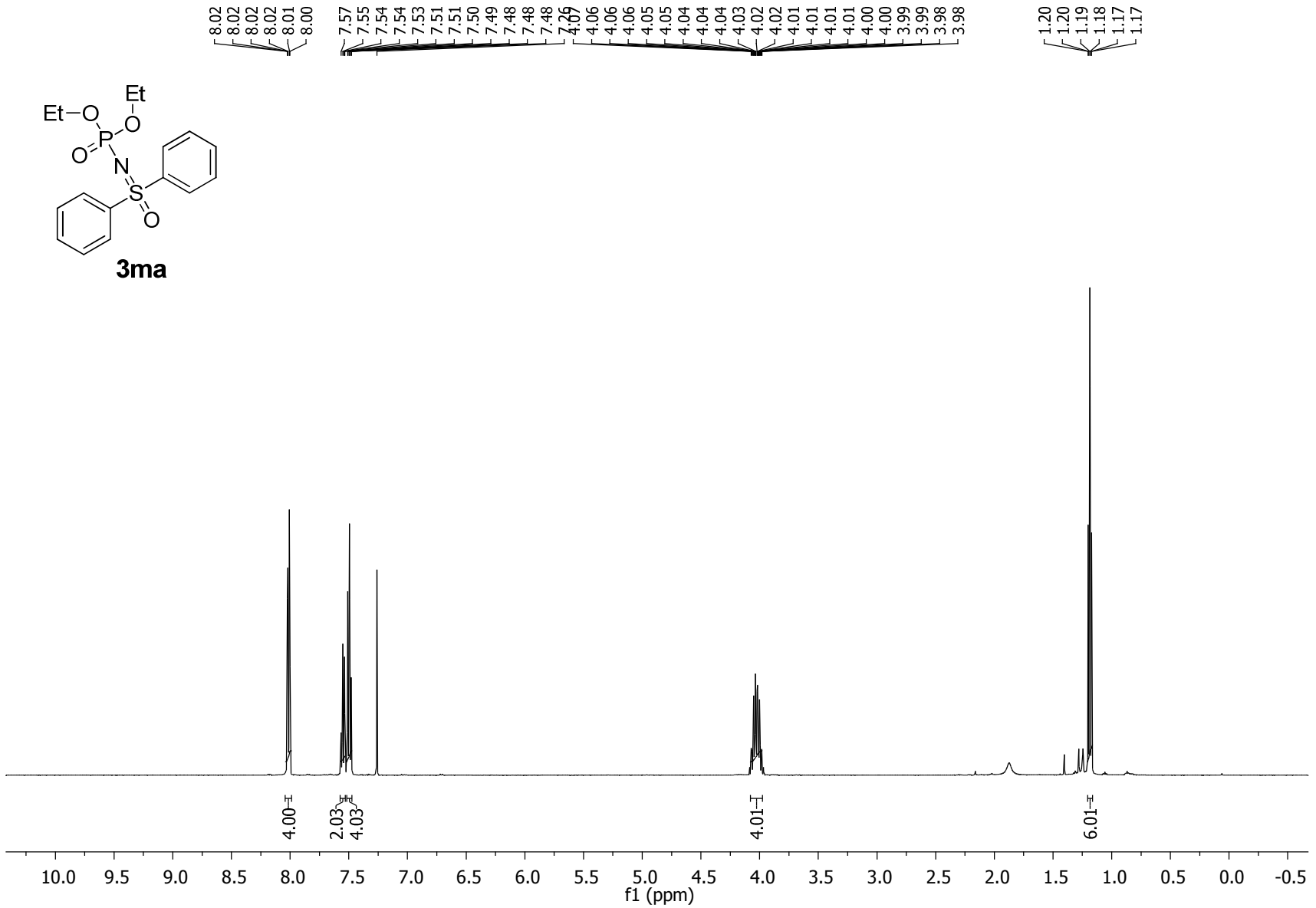


Figure S85. ^{1}H NMR for **3ma**

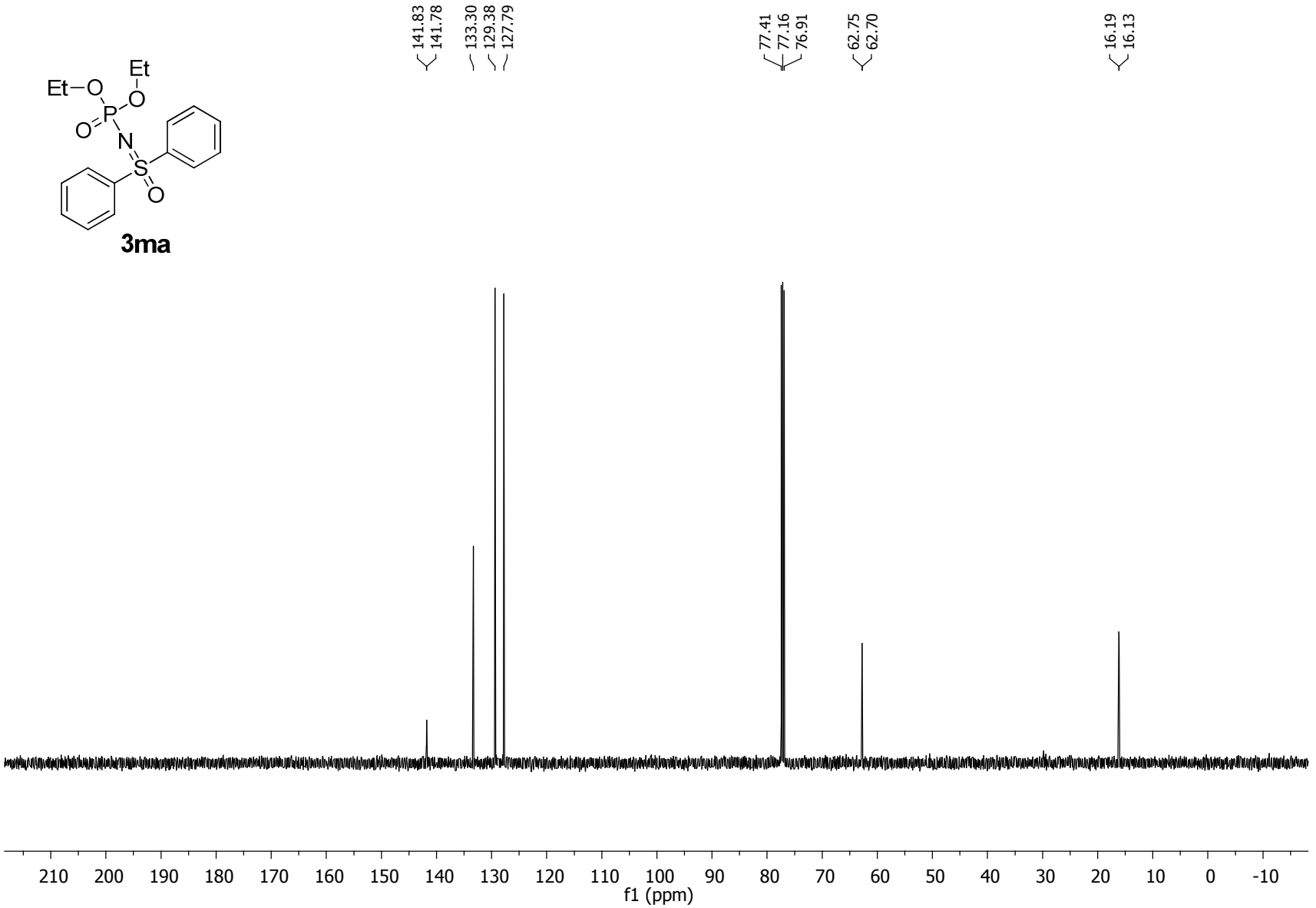


Figure S86. ^{13}C NMR for **3ma**

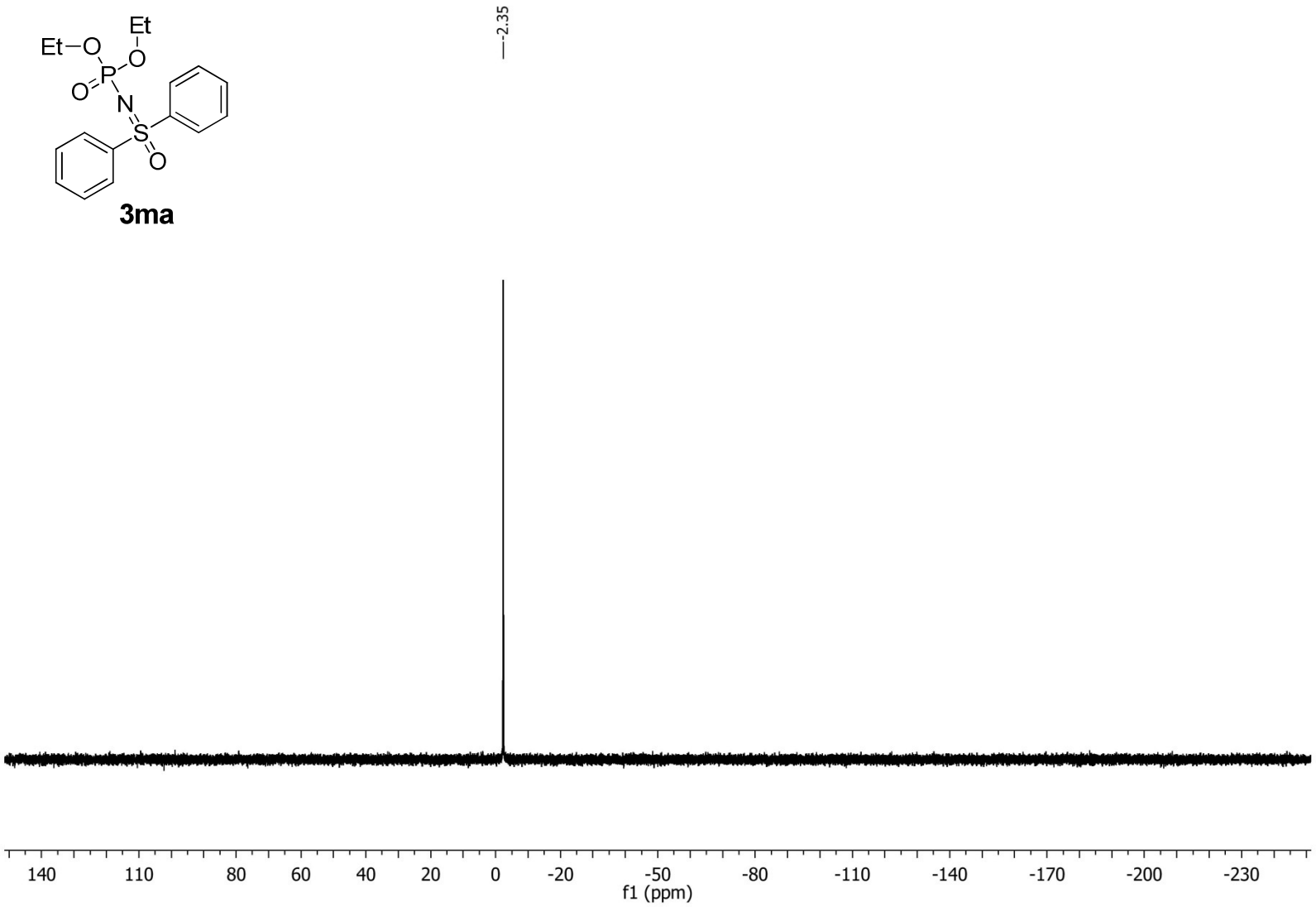


Figure S87. ^{31}P NMR for **3ma**

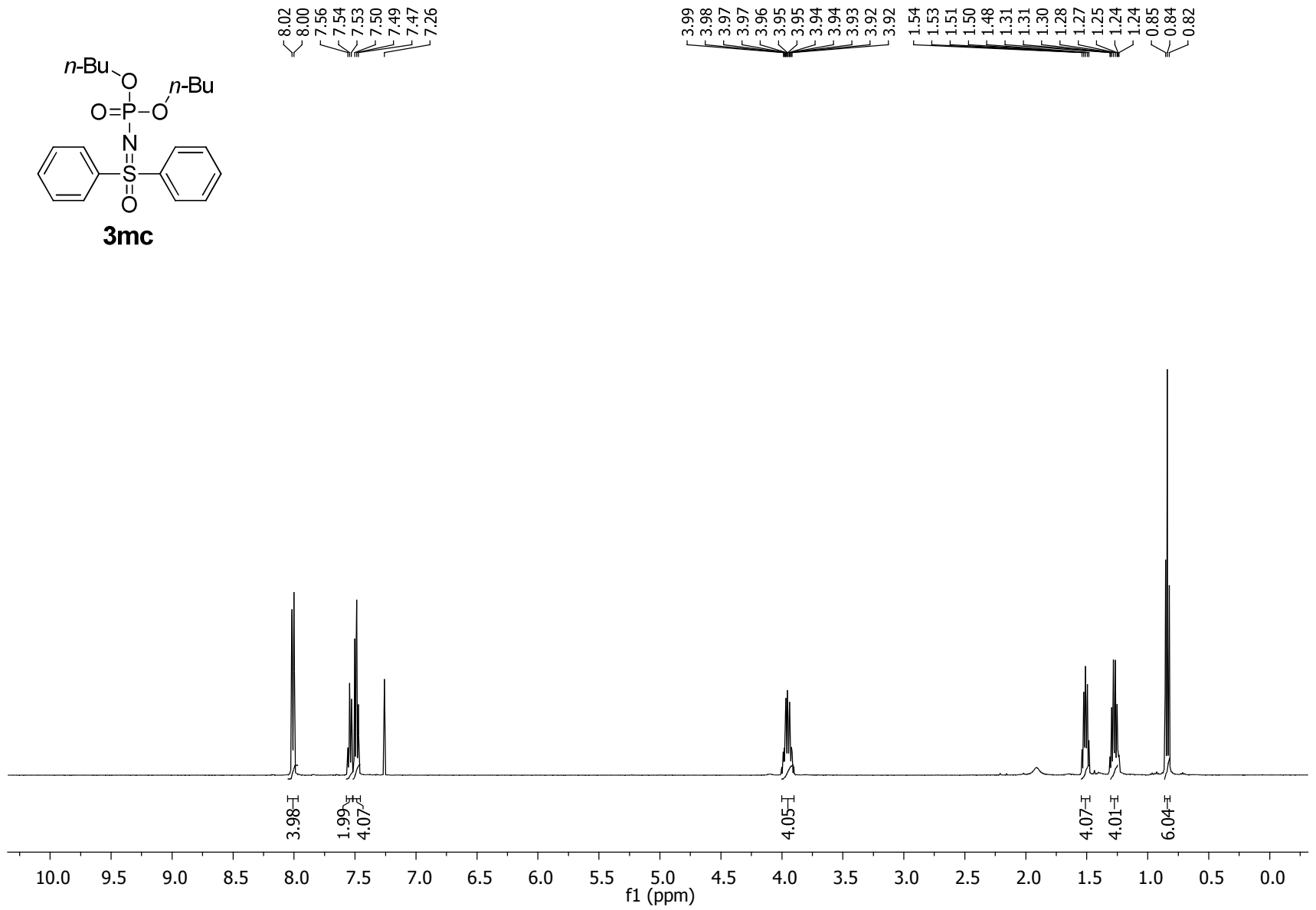


Figure S88. ^{1}H NMR for **3mc**

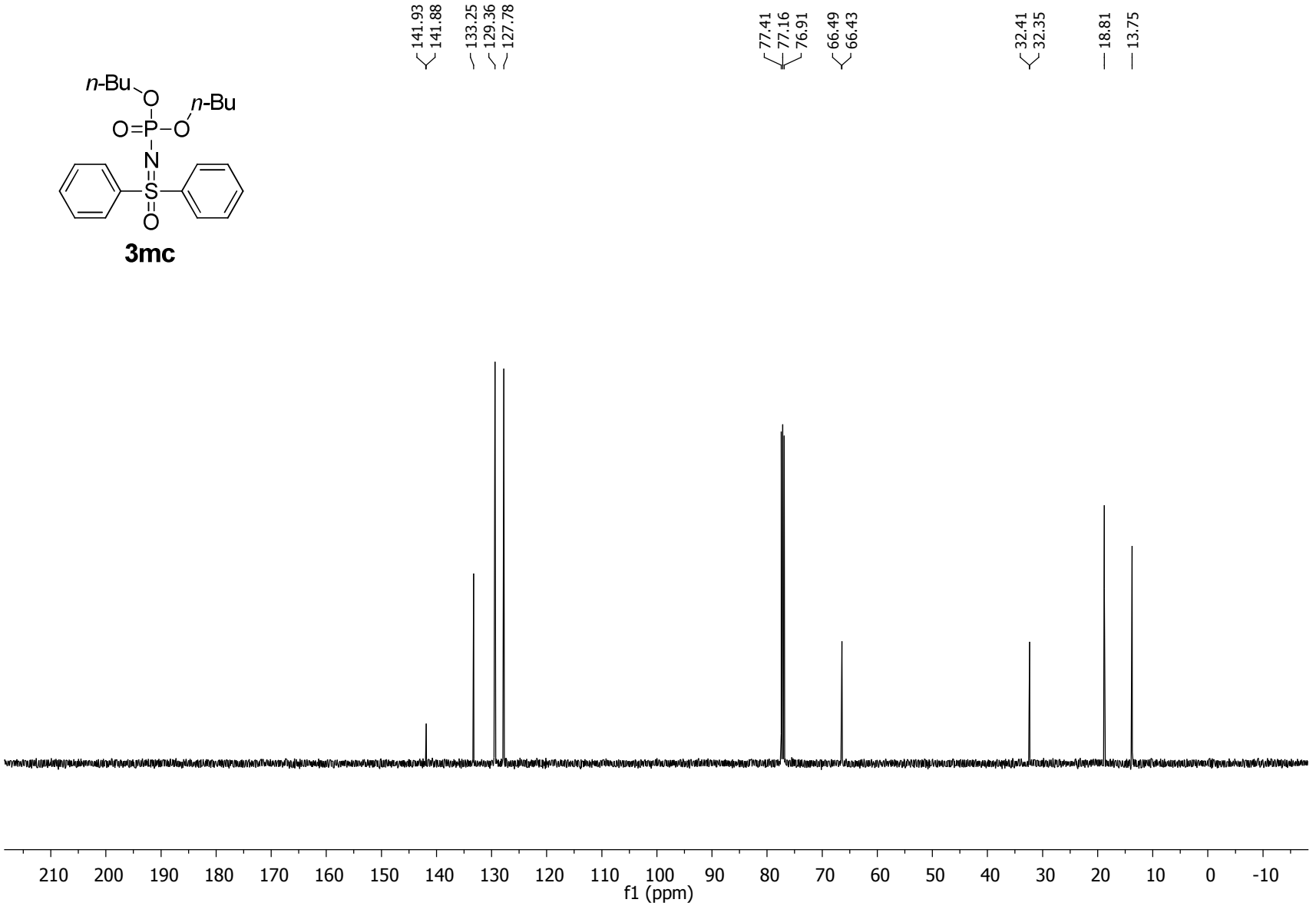


Figure S89. ^{13}C NMR for **3mc**

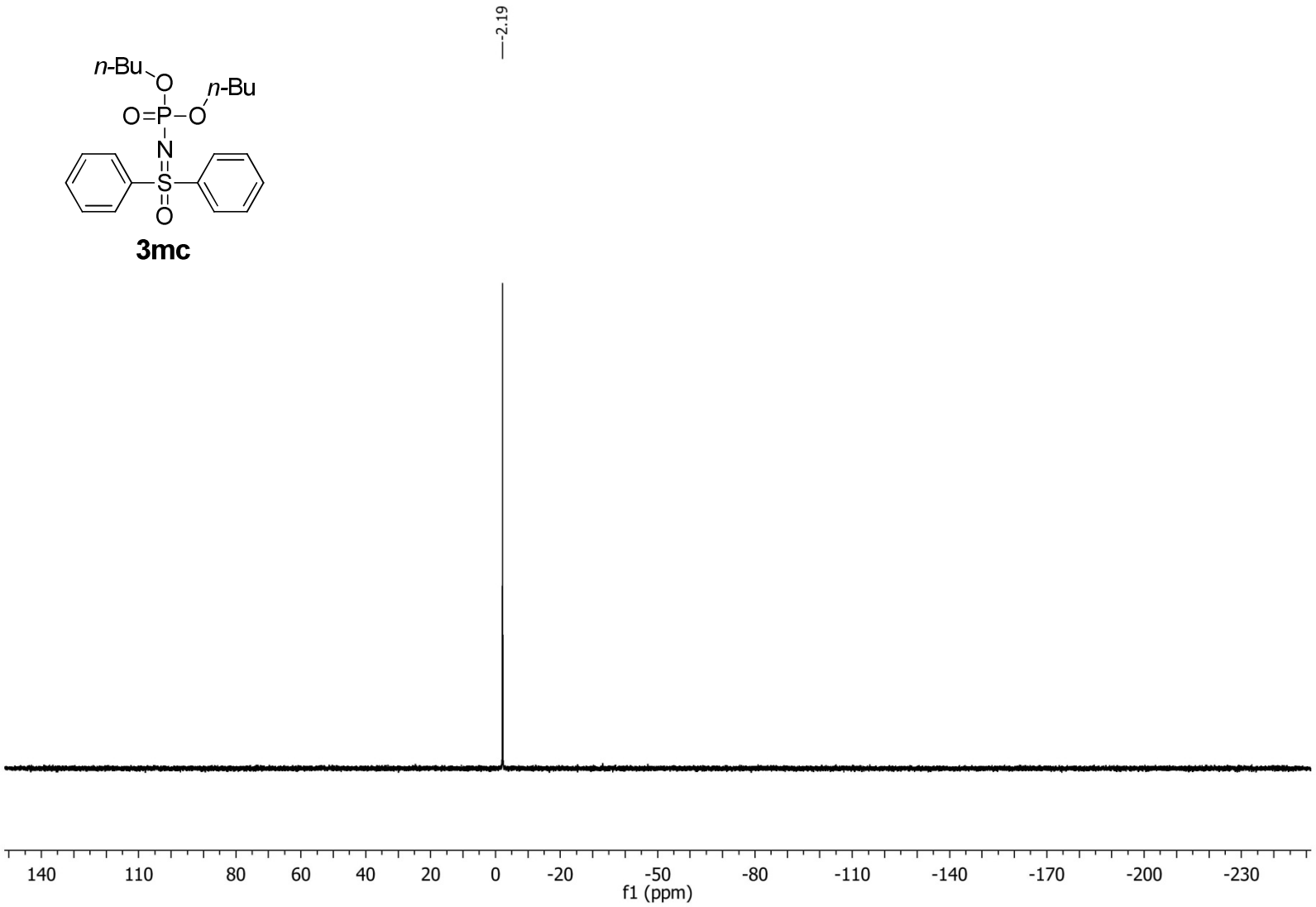


Figure S90. ^{31}P NMR for **3mc**

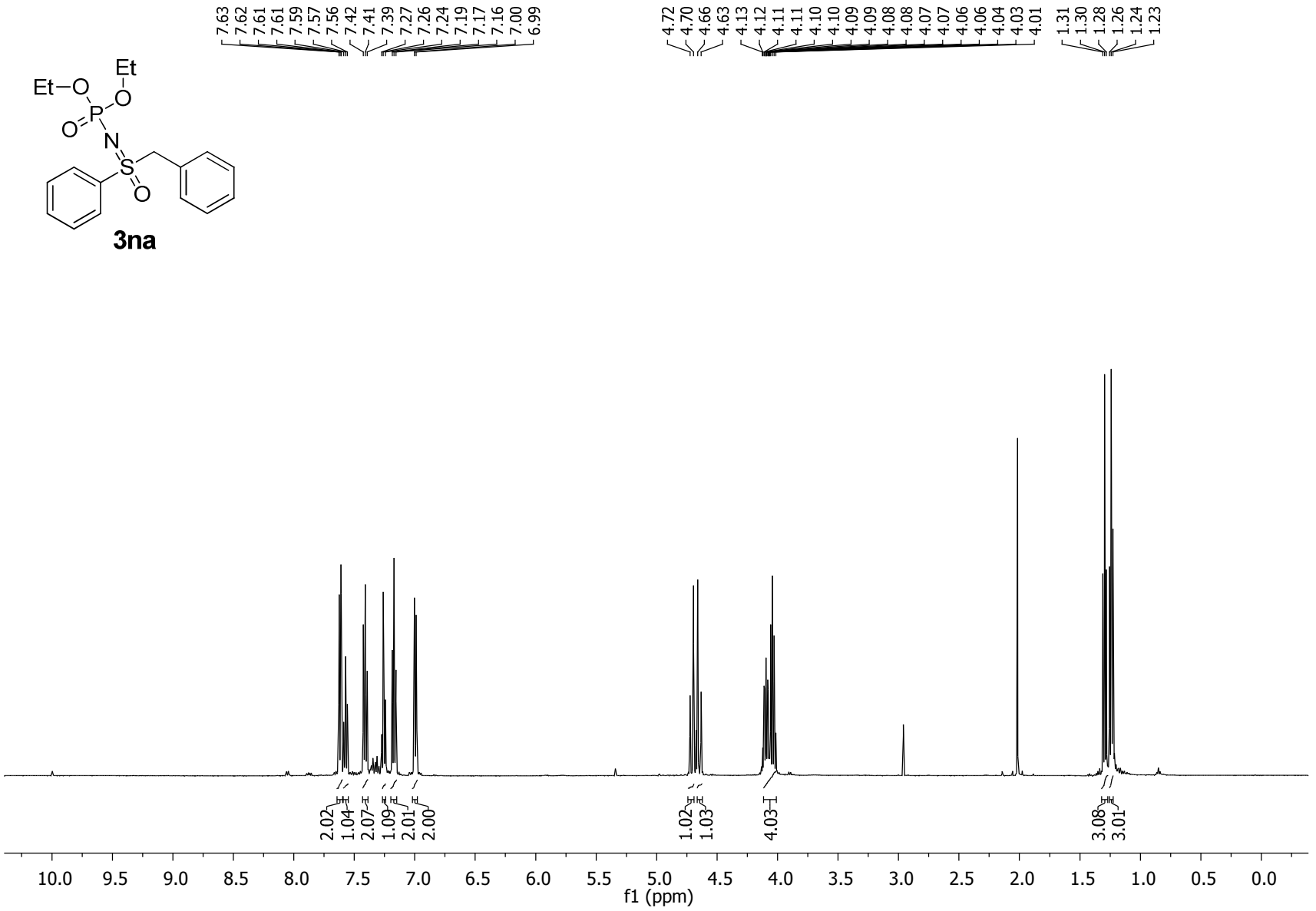


Figure S91. ^{1}H NMR for **3na**

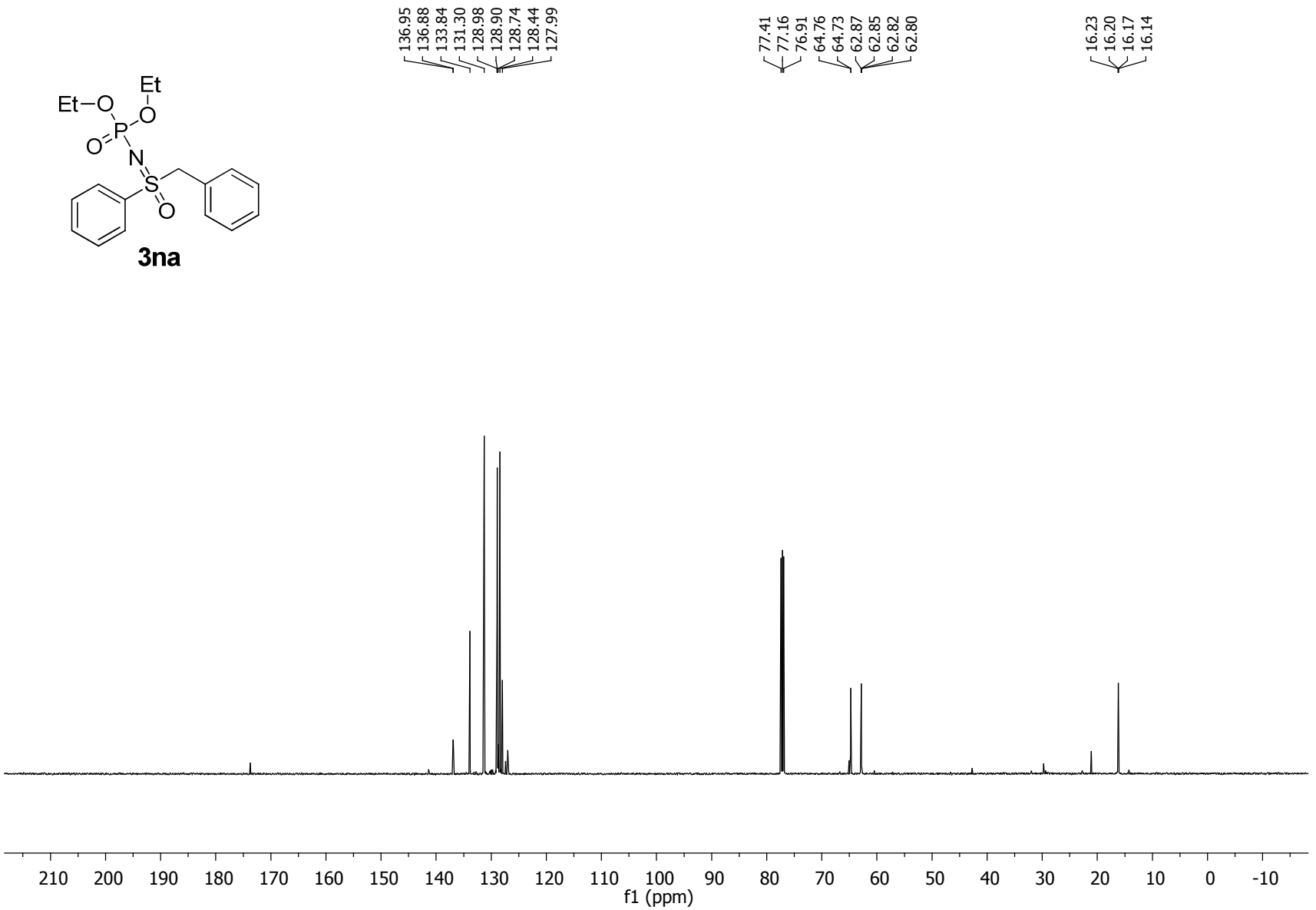


Figure S92. ^{13}C NMR for **3na**

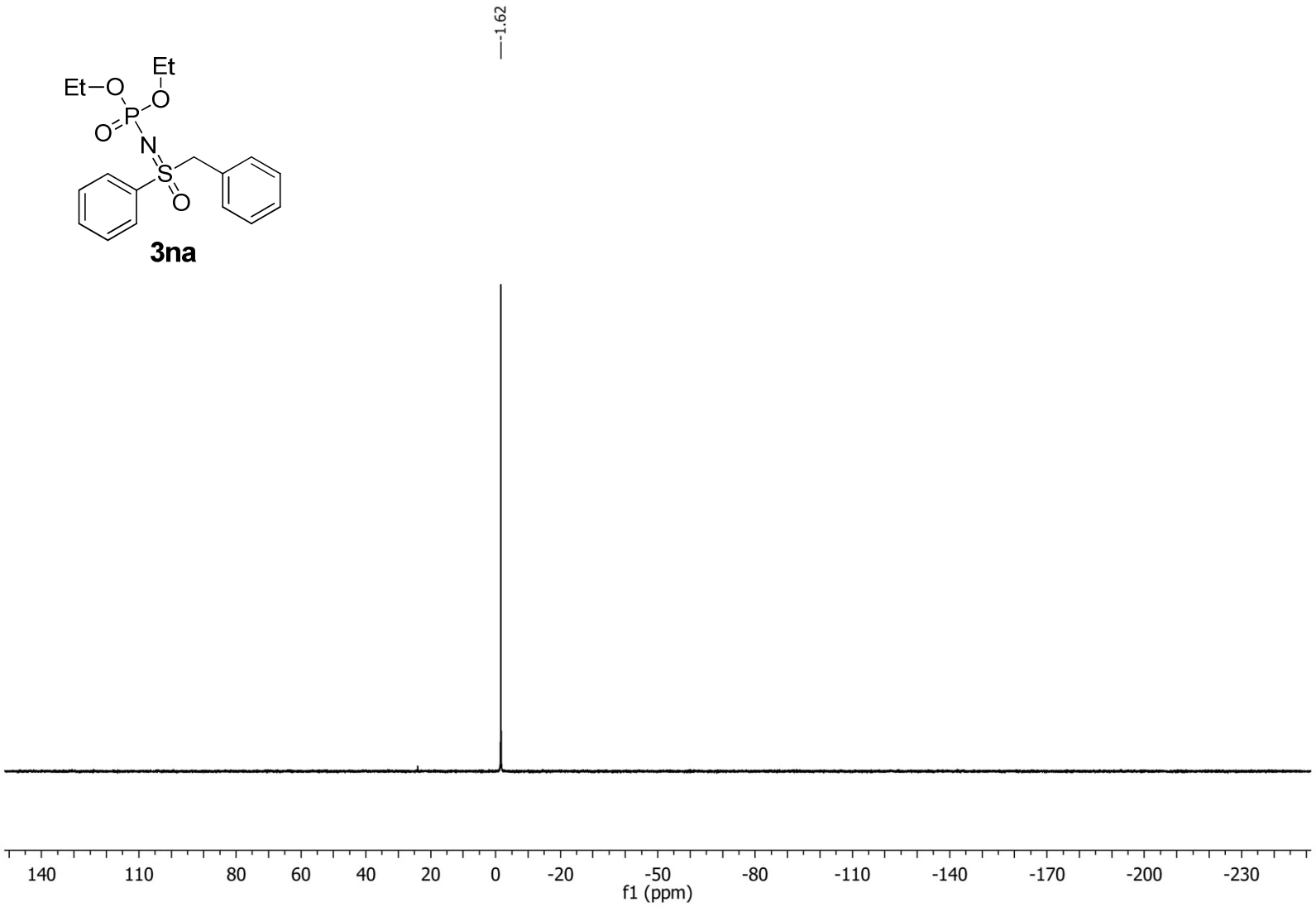


Figure S93. ^{31}P NMR for **3na**

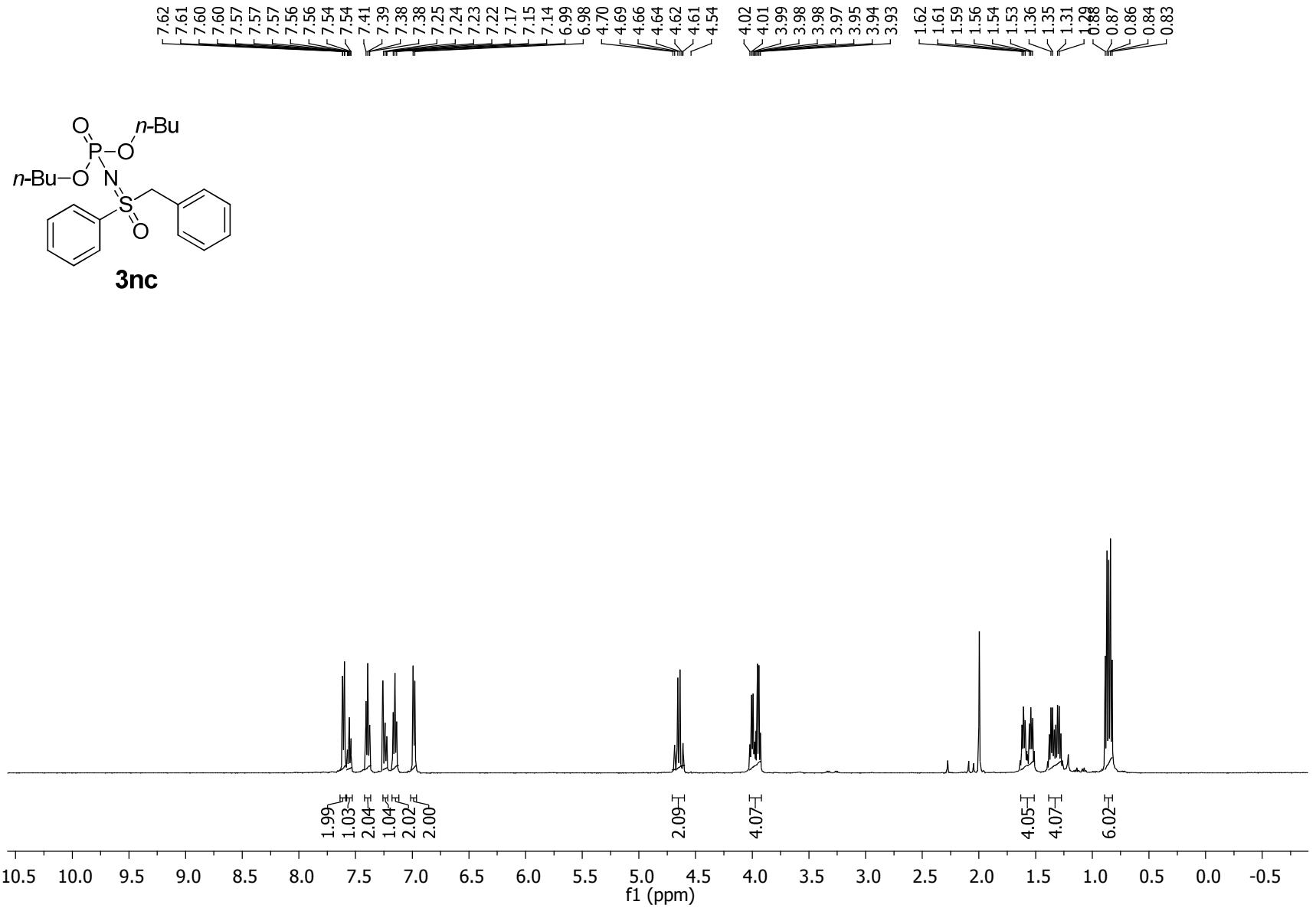


Figure S94. ^{1}H NMR for **3nc**

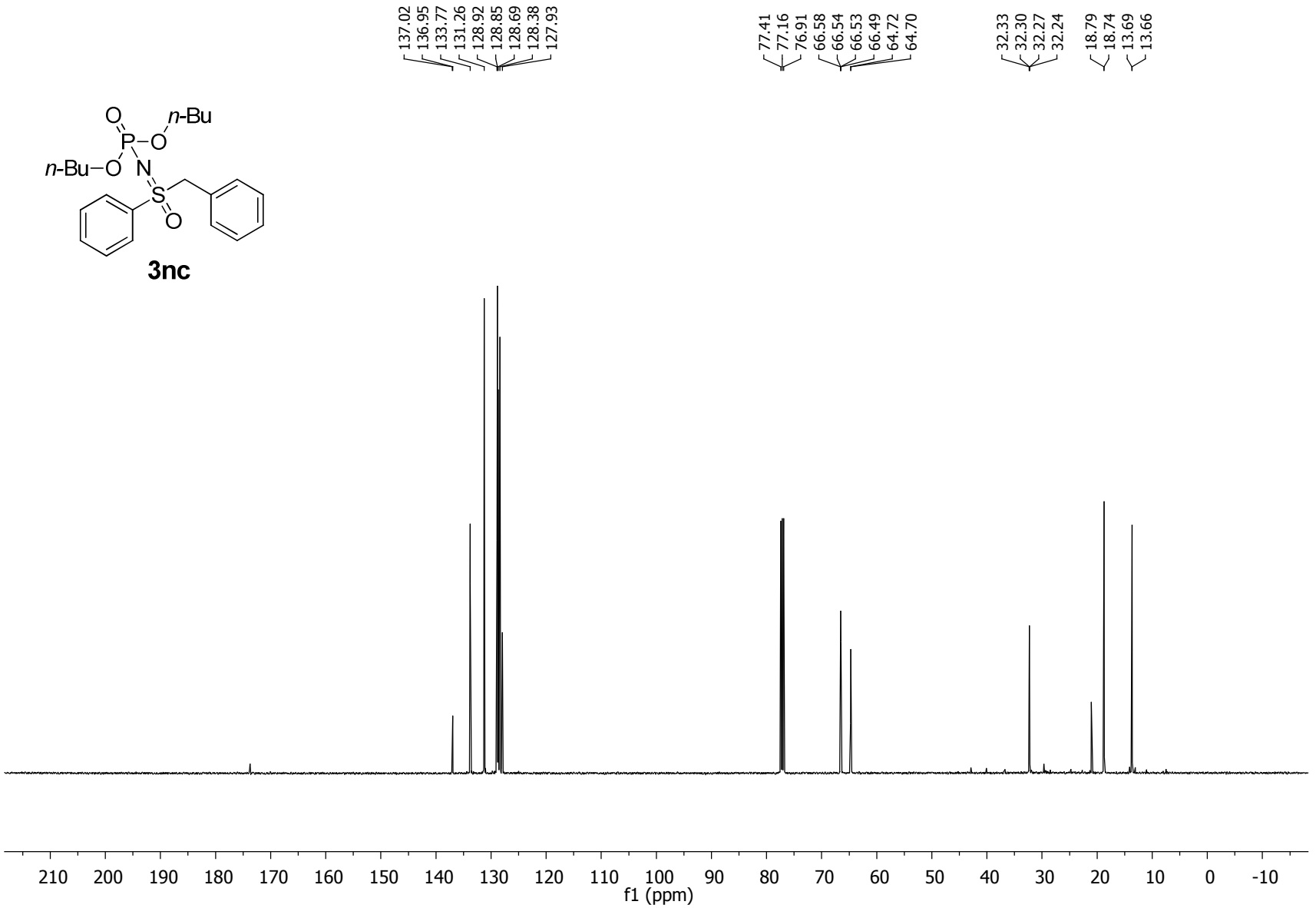


Figure S95. ^{13}C NMR for **3nc**

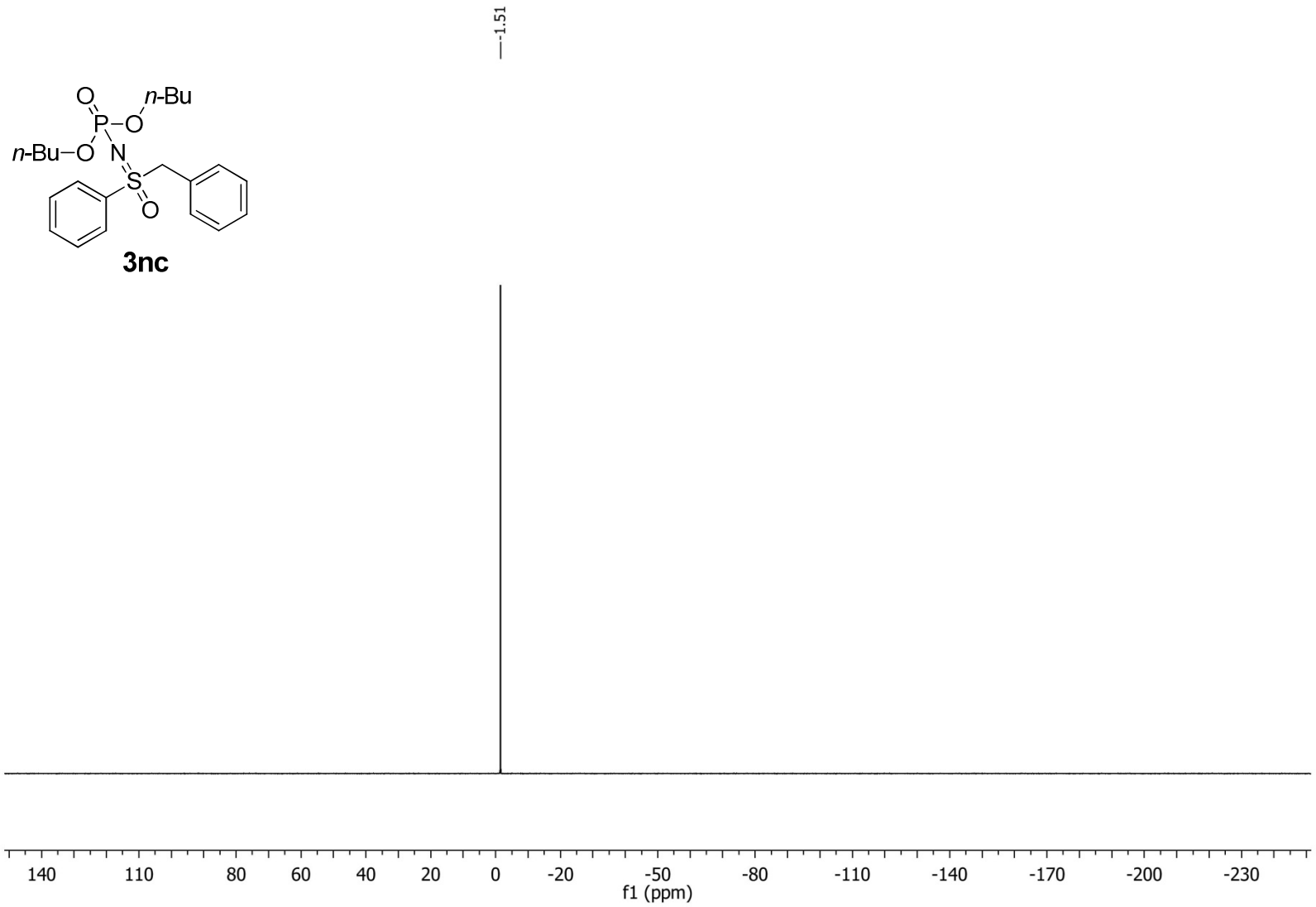


Figure S96. ^{31}P NMR for **3nc**

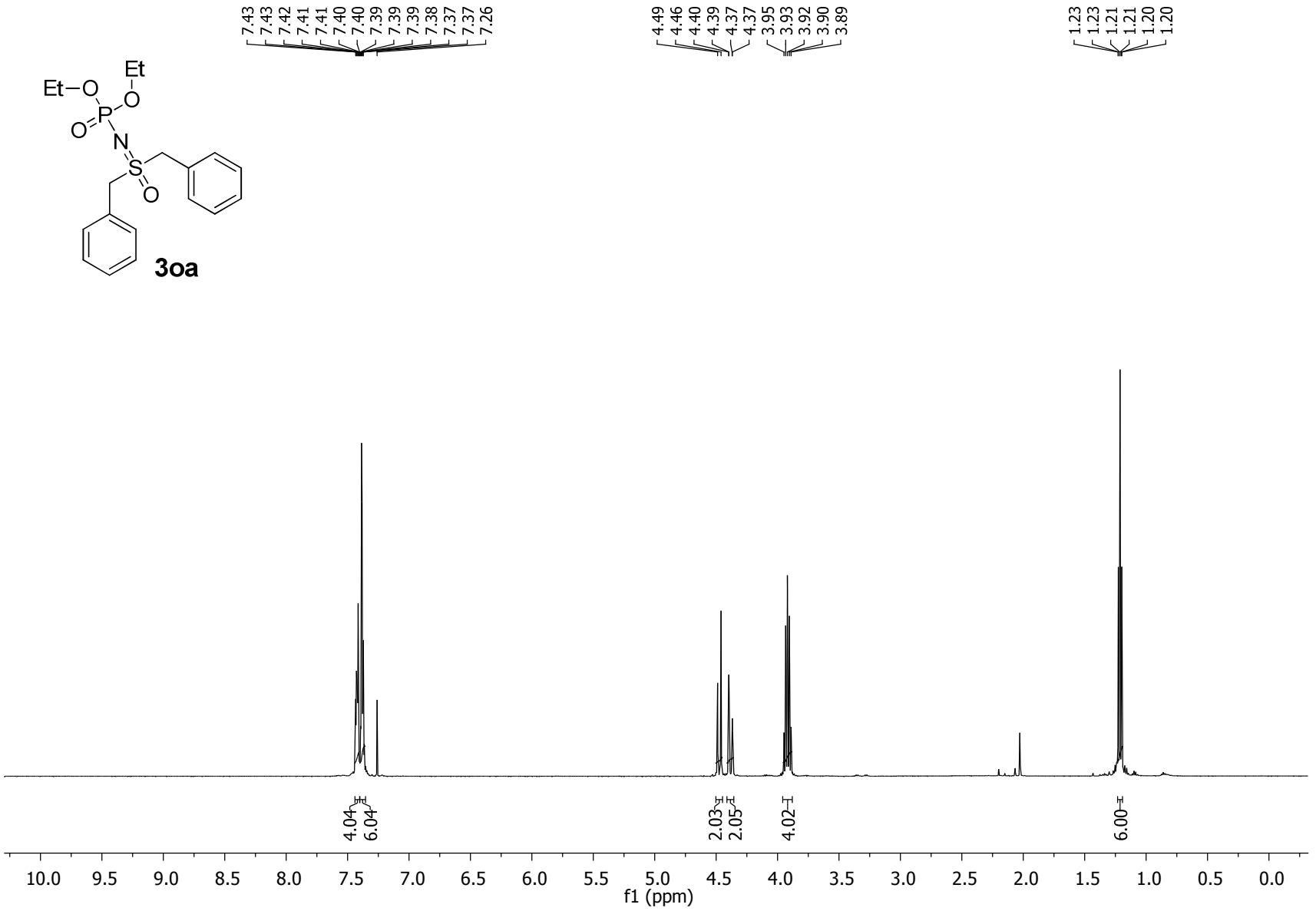


Figure S97. ^{1}H NMR for **3oa**

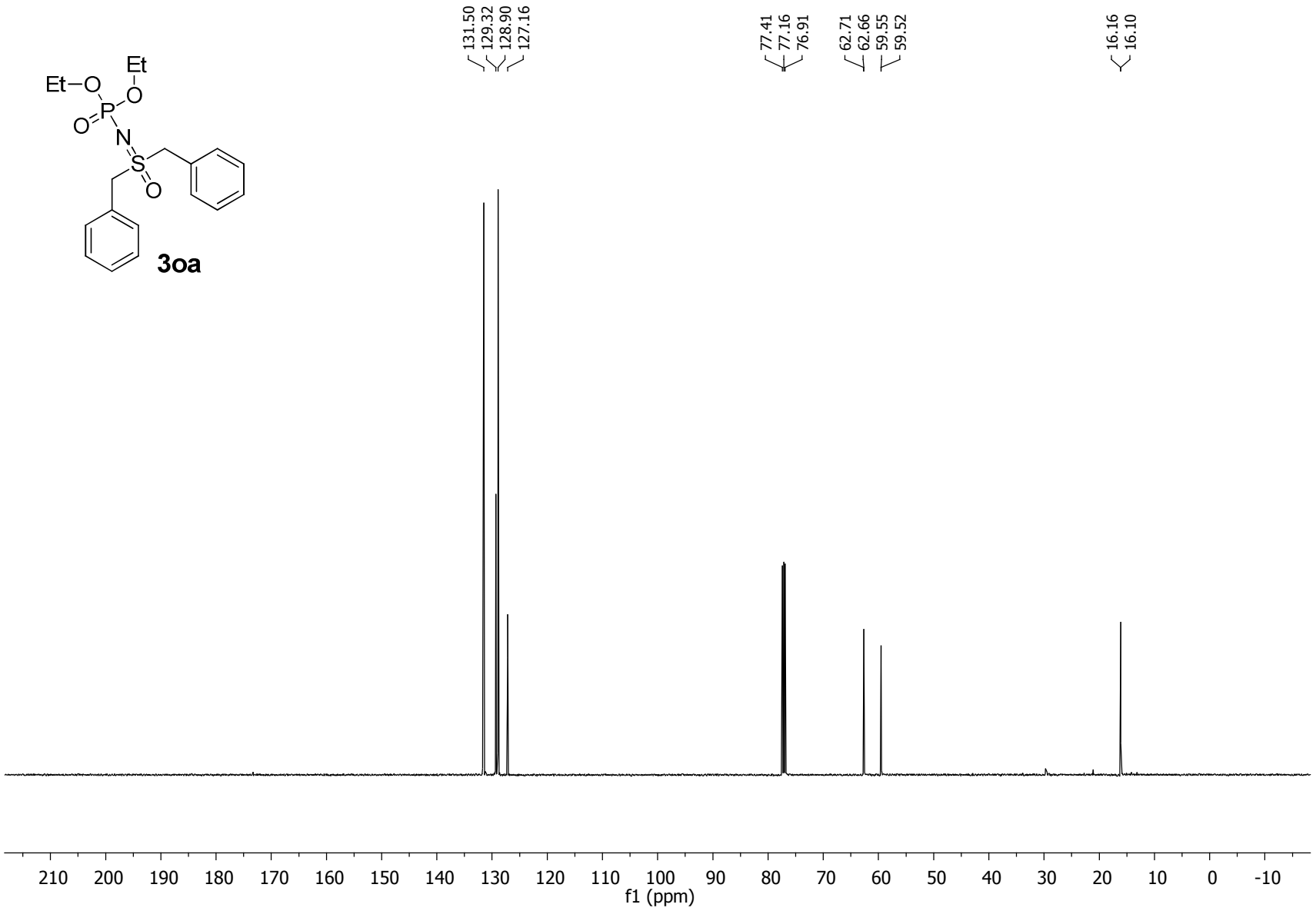


Figure S98. ^{13}C NMR for **3oa**

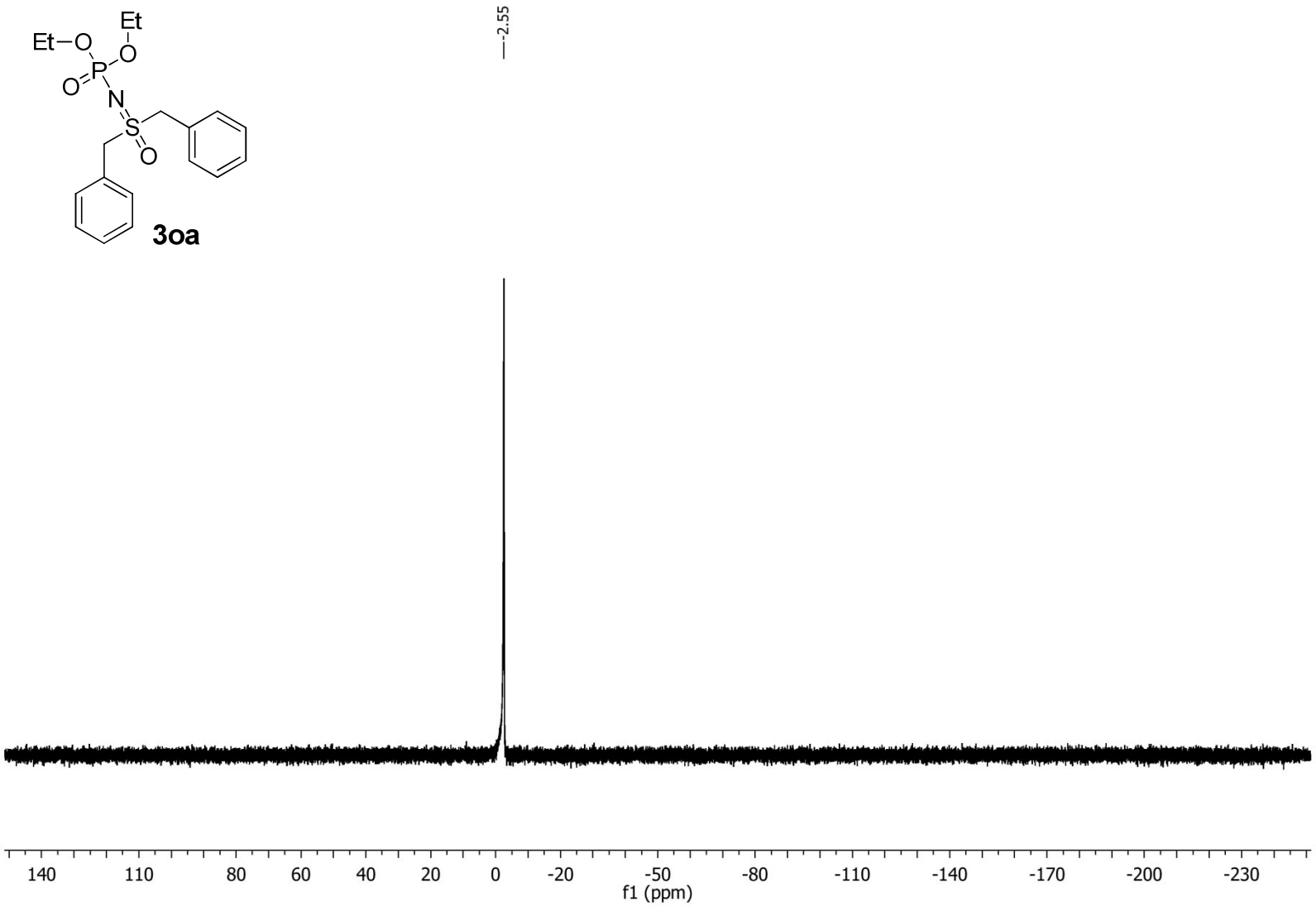


Figure S99. ^{31}P NMR for **3oa**

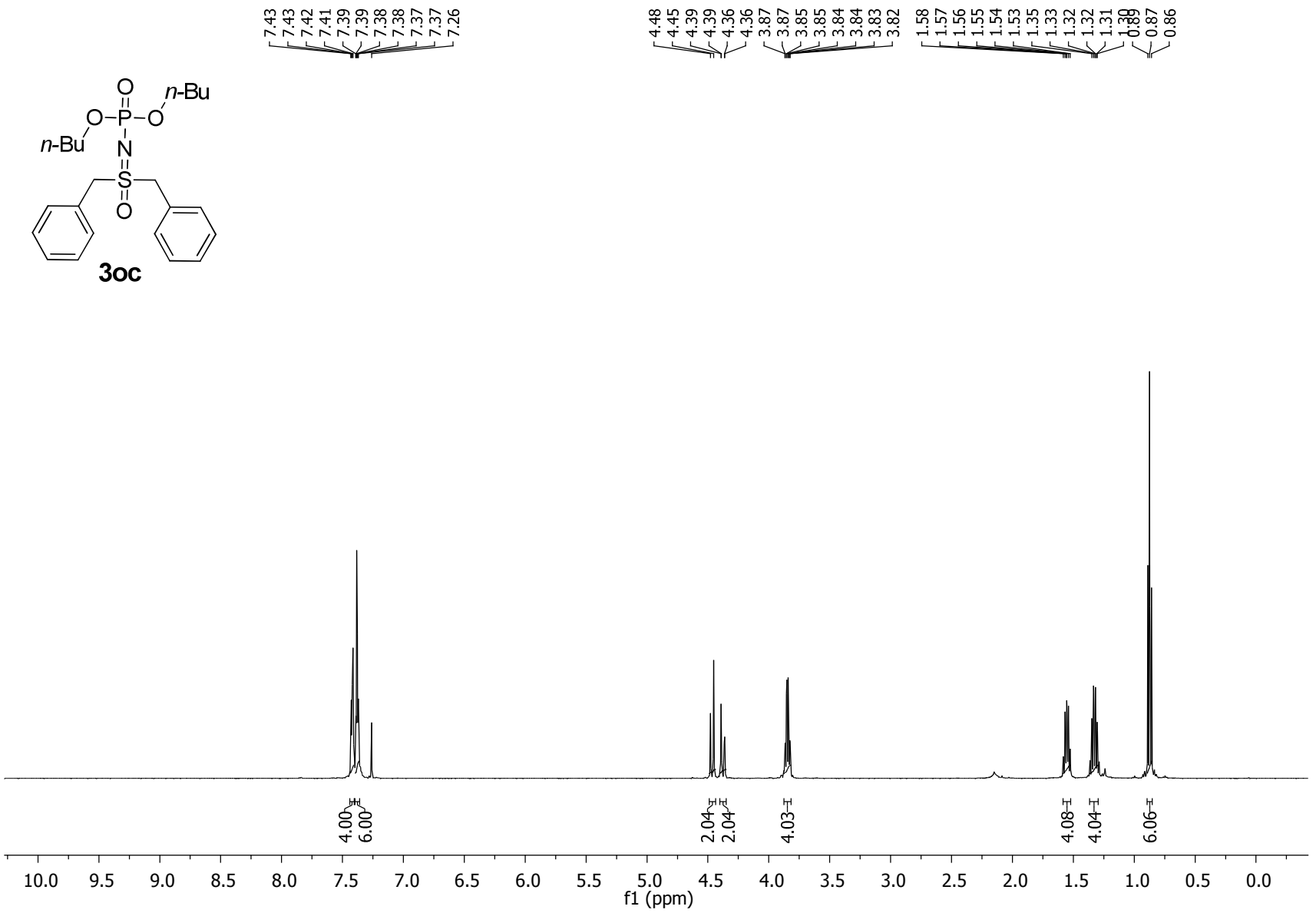


Figure S100. ^{1}H NMR for **3oc**

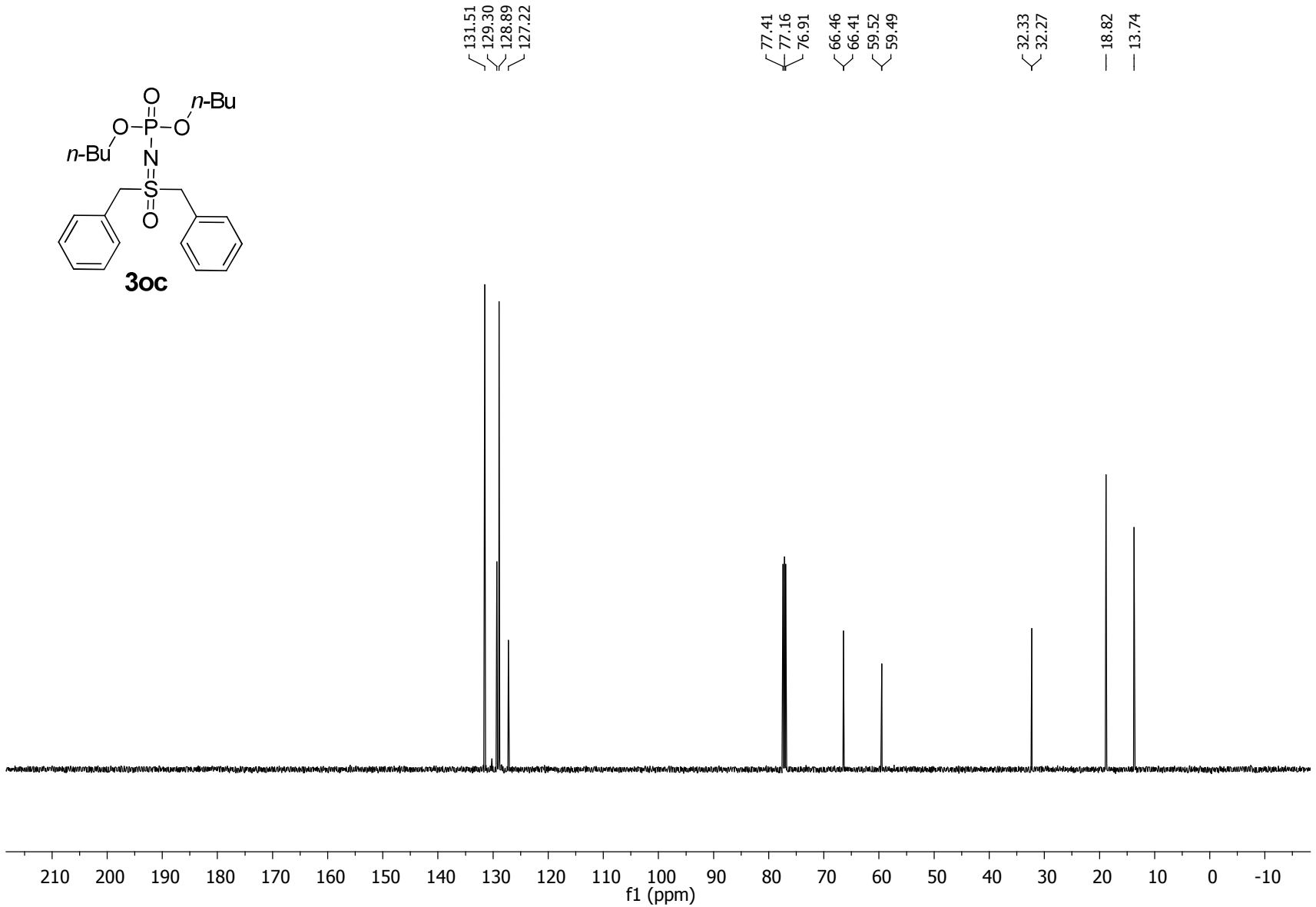


Figure S101. ^{13}C NMR for **3oc**

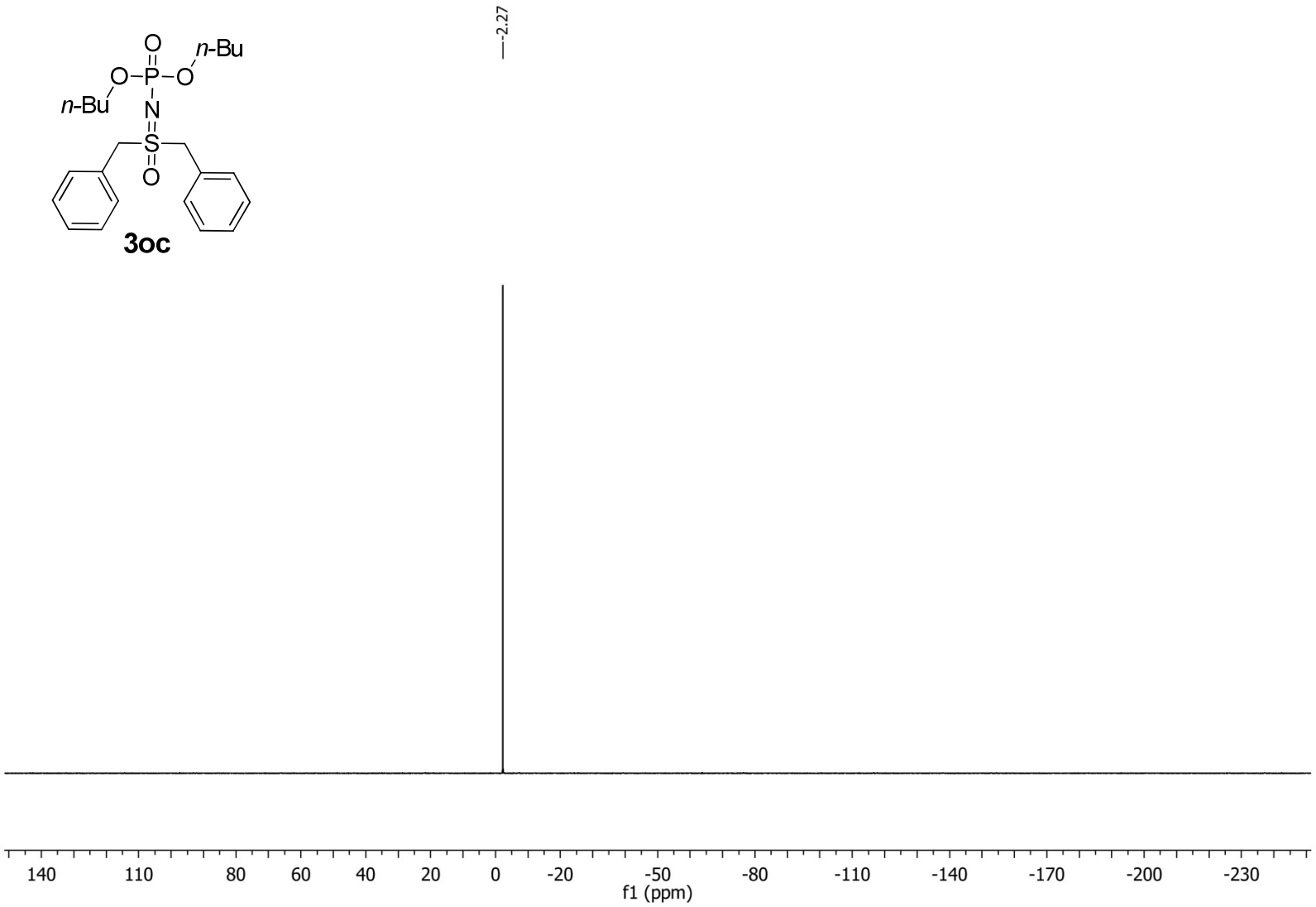
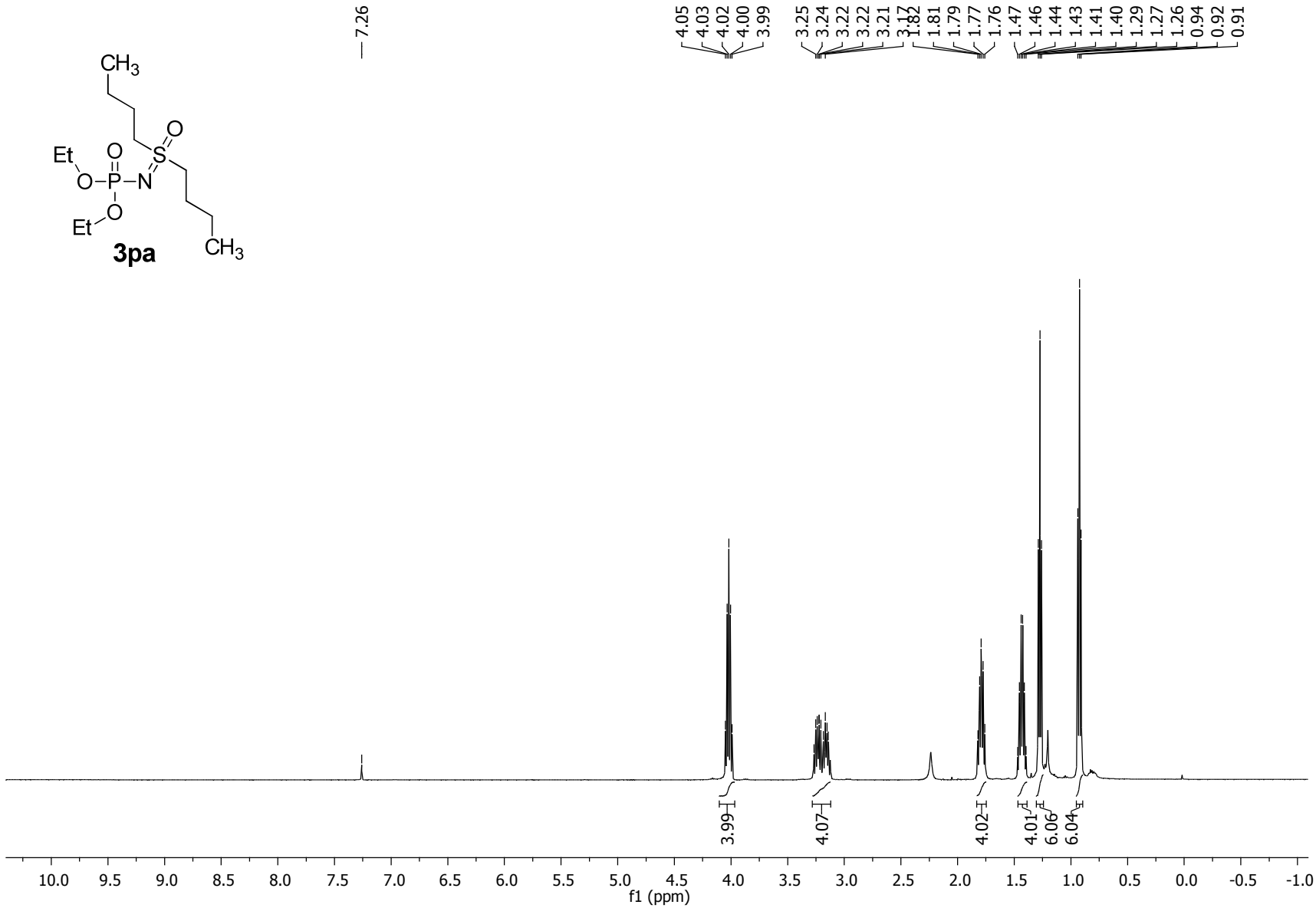


Figure S102. ^{31}P NMR for **3oc**



3pa

Figure S103. ^{1}H NMR for **3pa**

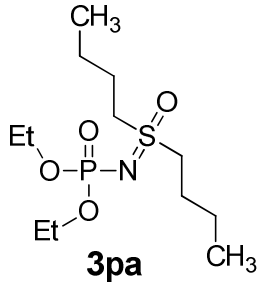


Figure S104. ^{13}C NMR for **3pa**

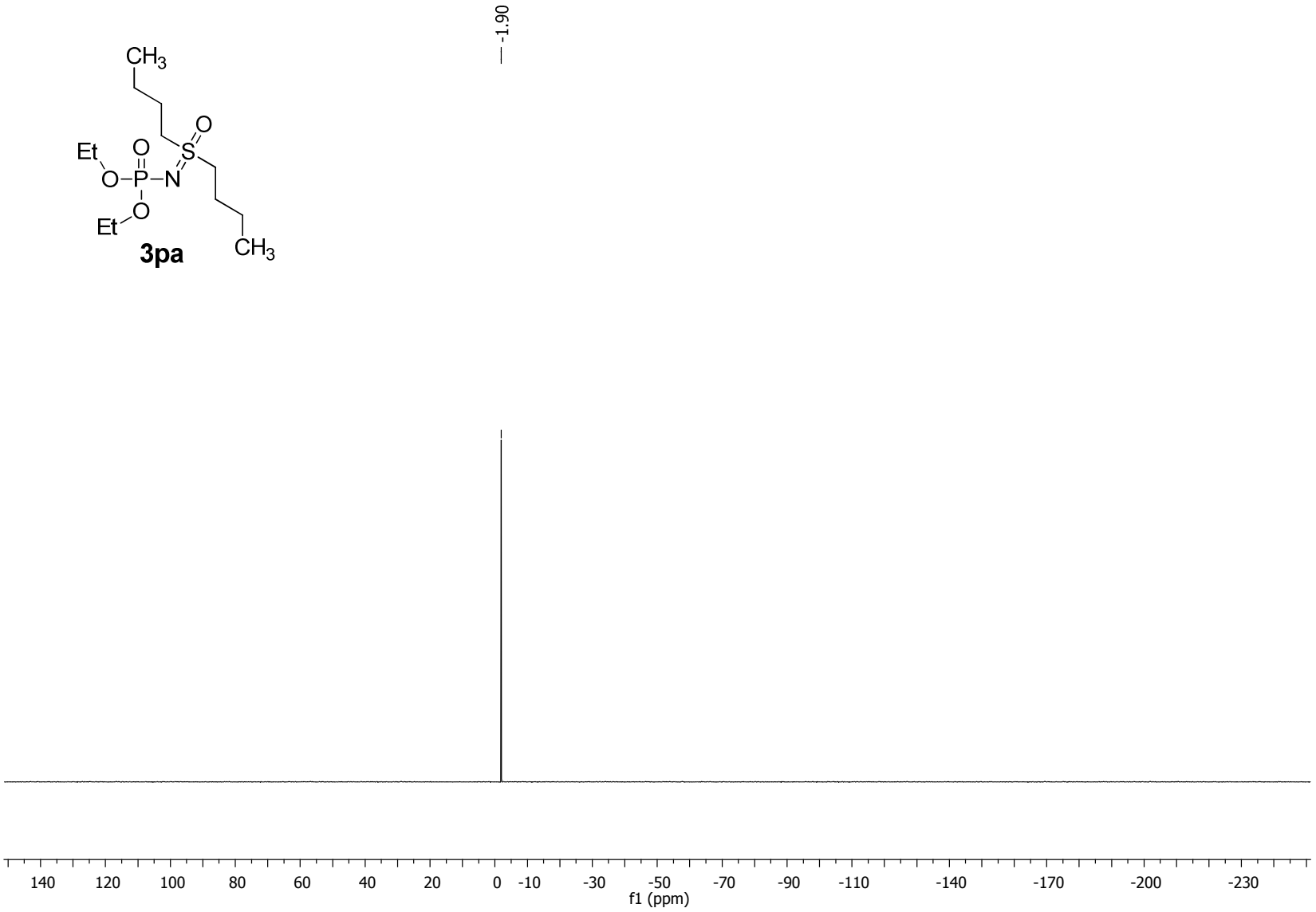


Figure S105. ^{31}P NMR for **3pa**

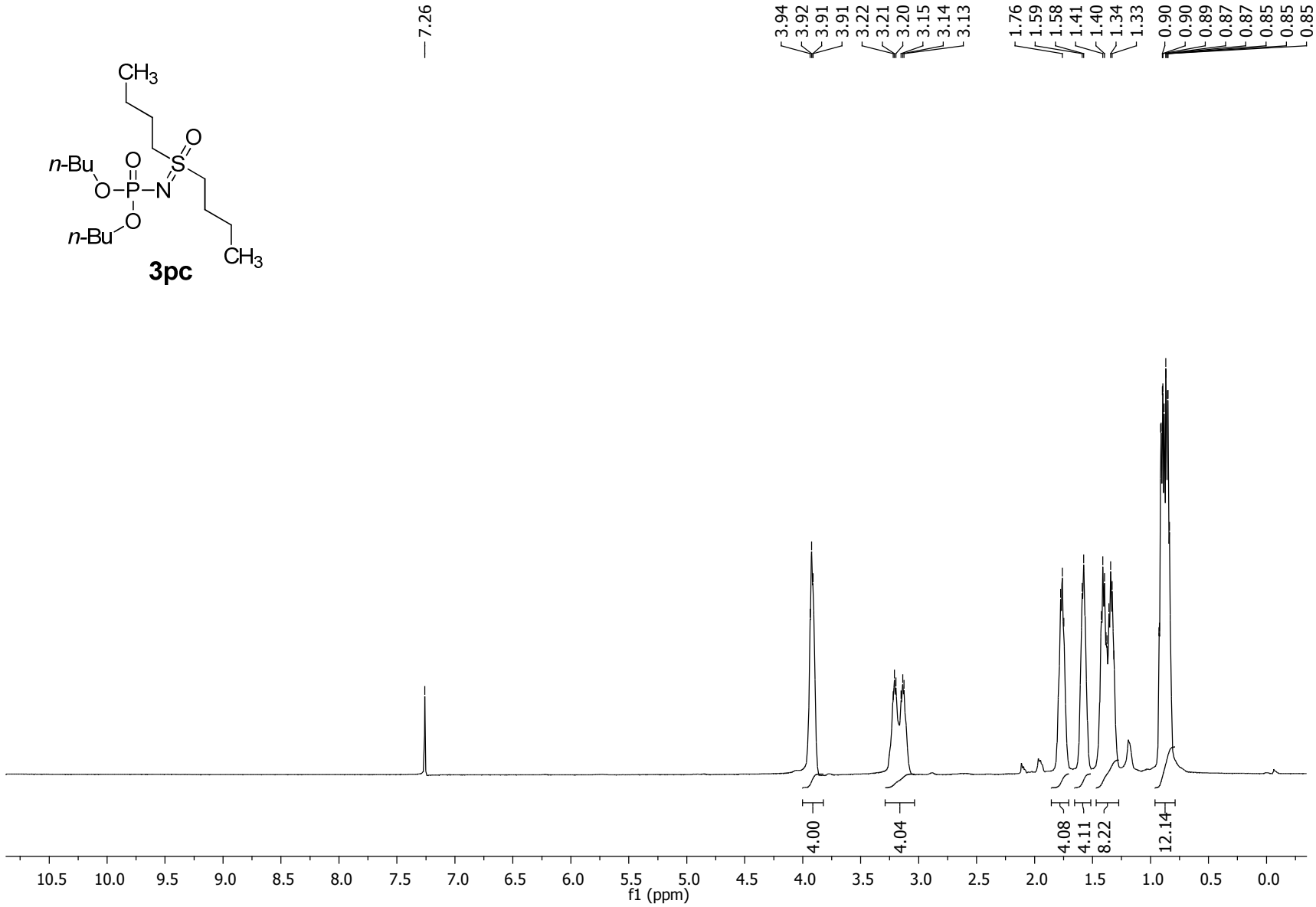


Figure S106. ^{1}H NMR for **3pc**

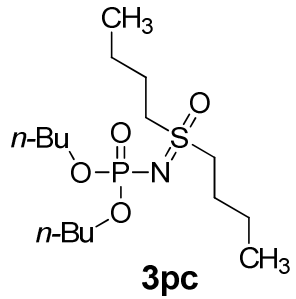


Figure S107. ^{13}C NMR for **3pc**

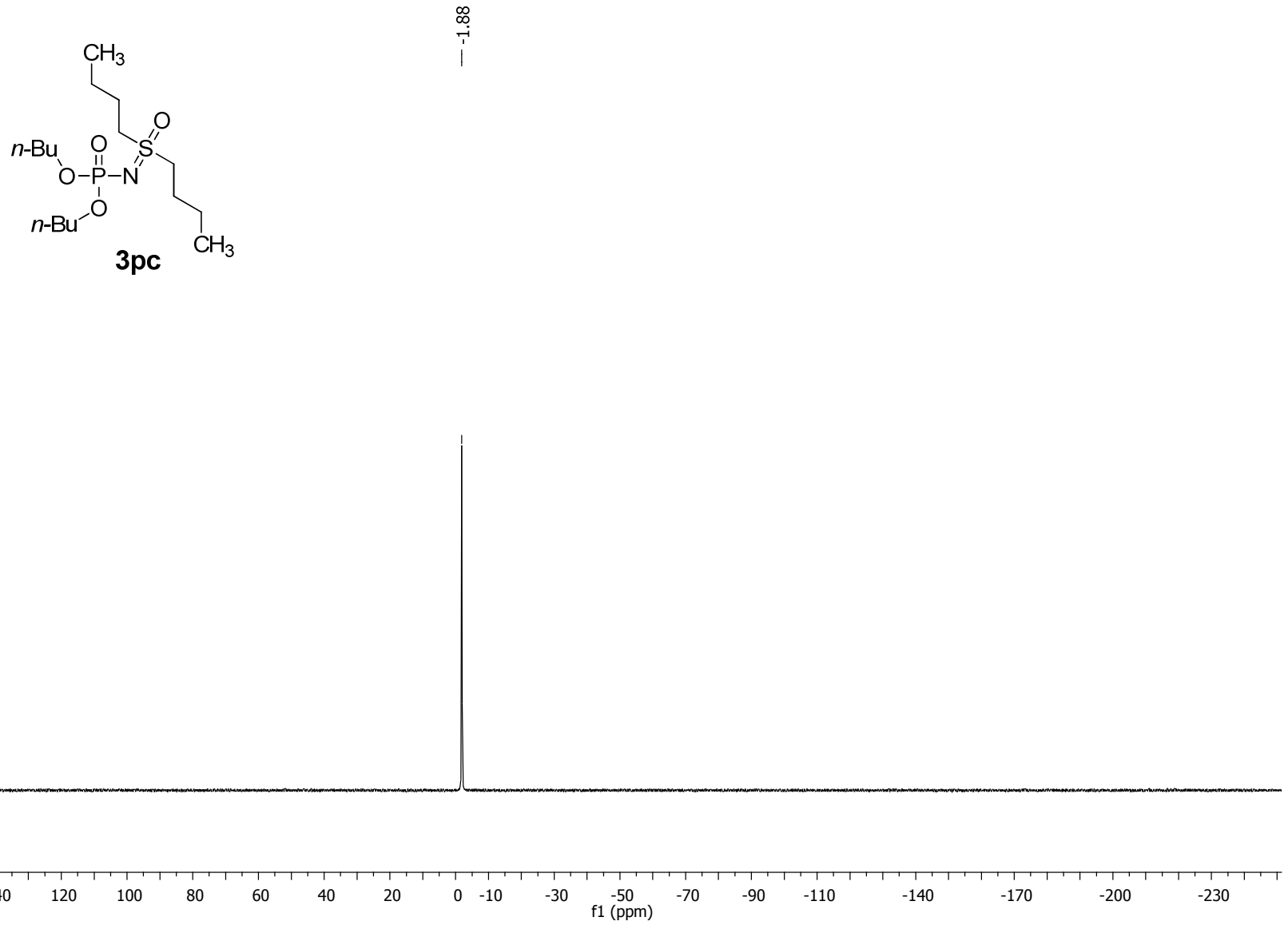


Figure S108. ^{31}P NMR for **3pc**

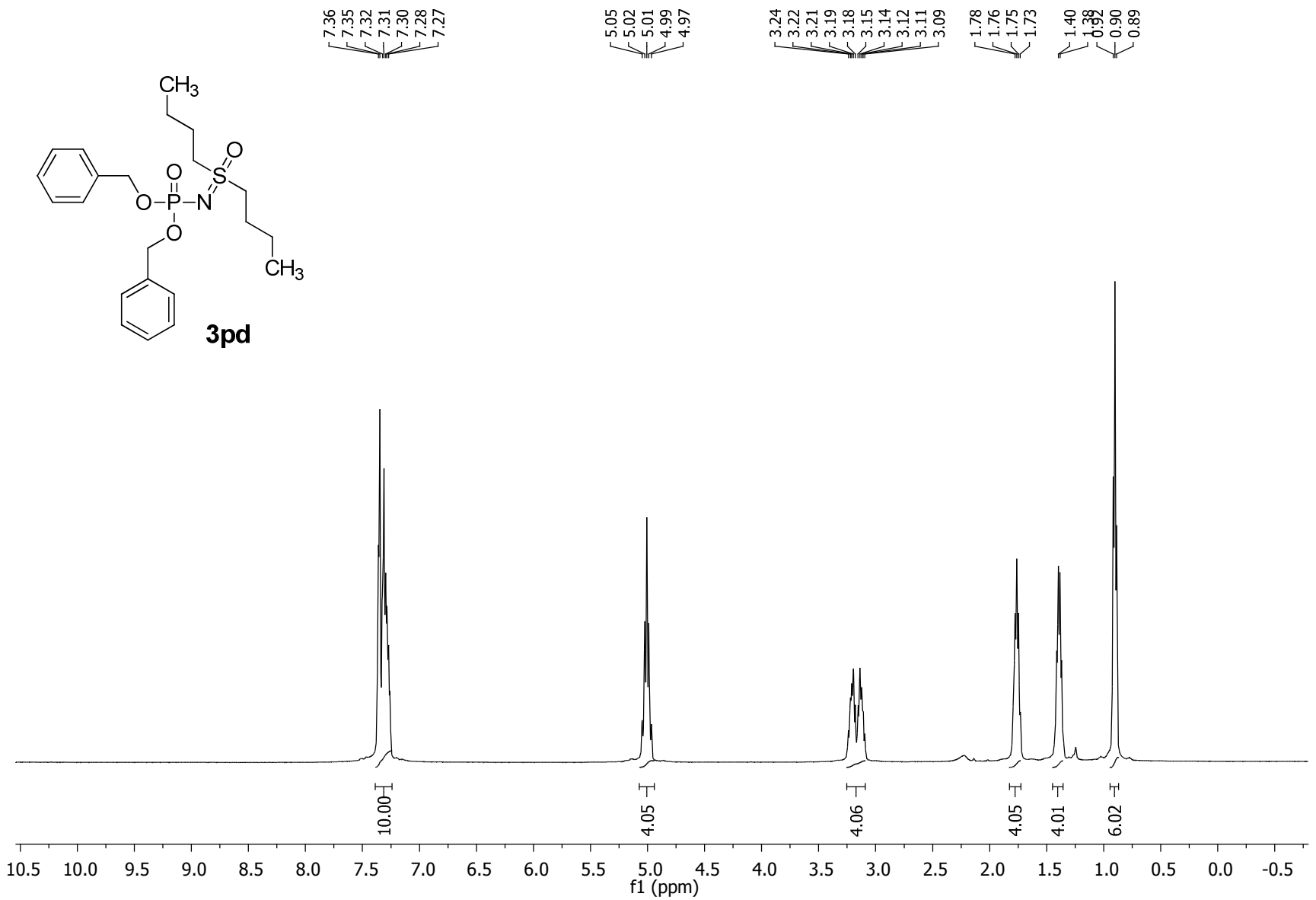


Figure S109. ^{1}H NMR for **3pd**

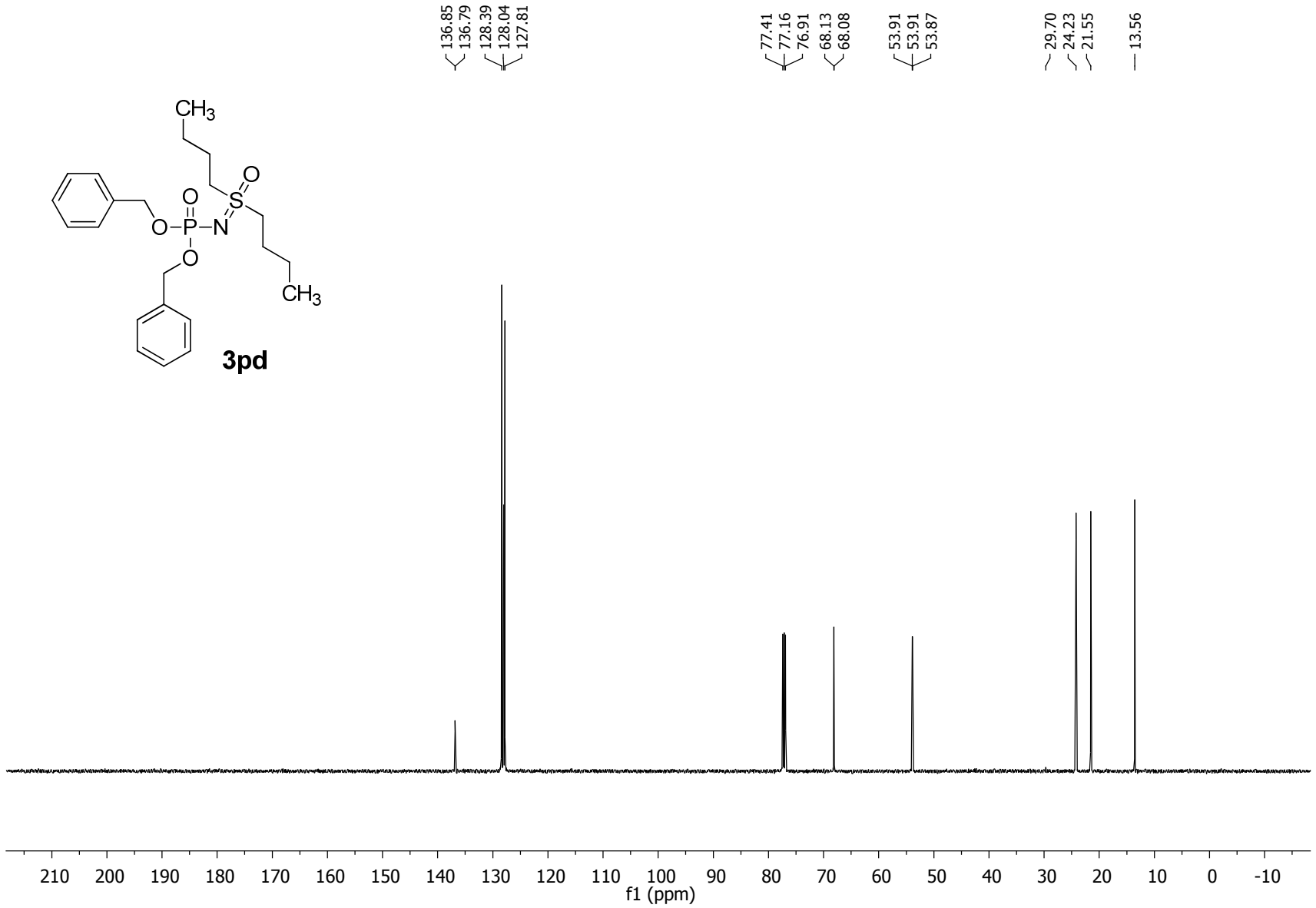


Figure S110. ^{13}C NMR for **3pd**

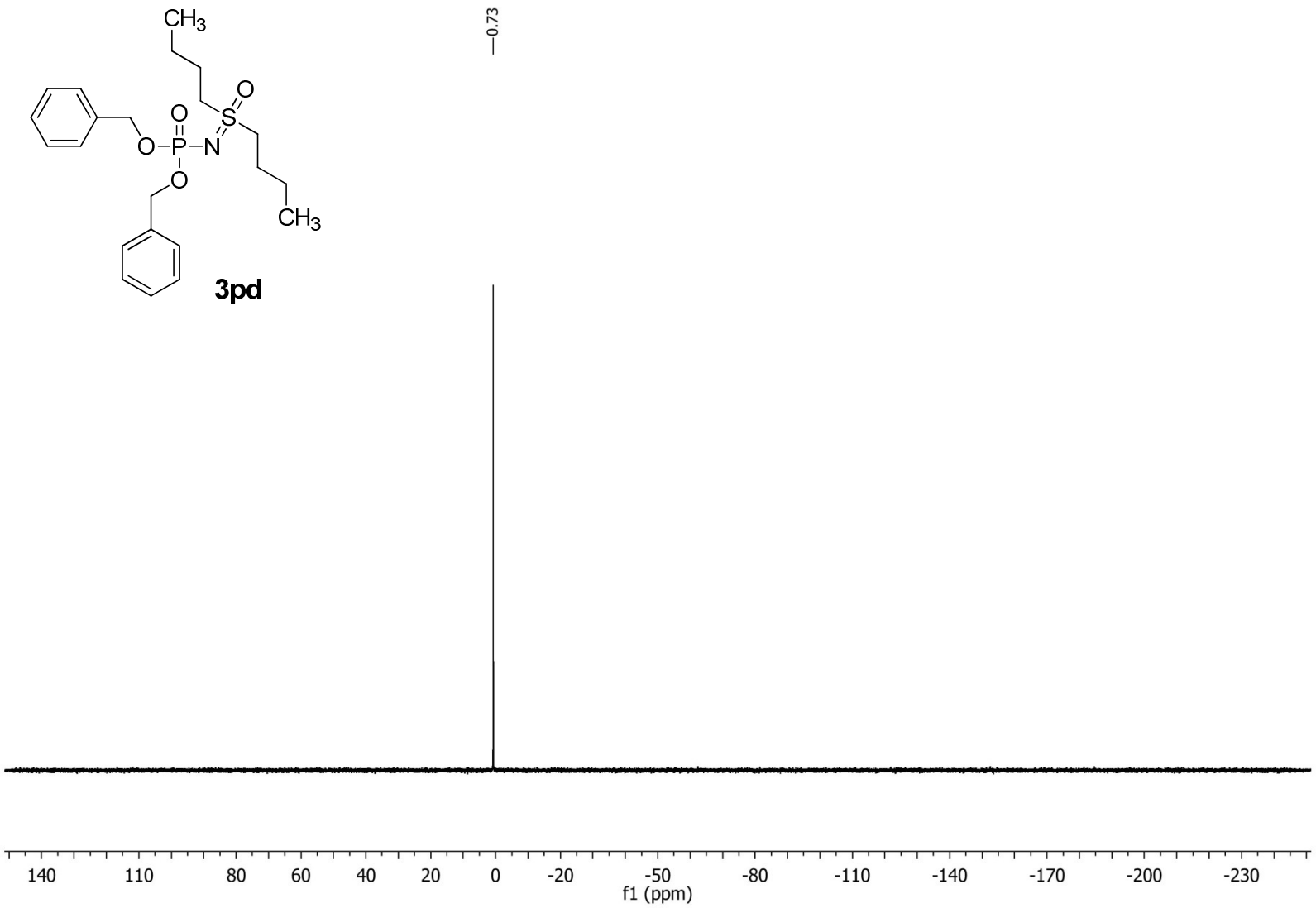


Figure S111. ^{31}P NMR for **3pd**