Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Stereoselective Synthesis of Vinyl-phosphonates through Aromatic Aza-Claisen Rearrangement of α-Aminophosphonates

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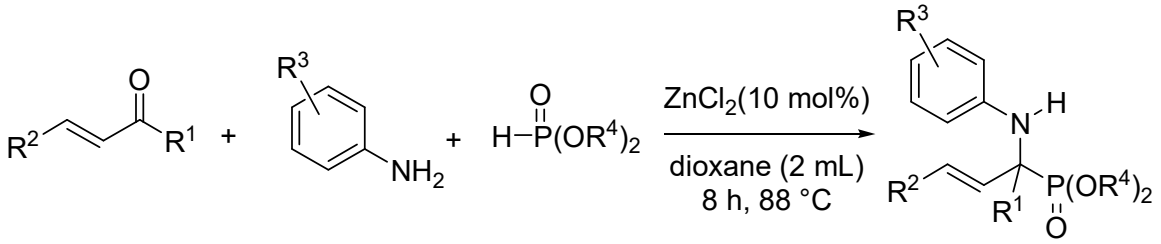
General: All chemicals were commercial products. NMR spectra were obtained with a 400 MHz Bruker Avance instrument with the chemical shifts being reported as δ ppm and couplings expressed in Hertz. The chemical shift data for each signal on ^{1}H NMR are given in units of δ relative to $CHCl_3$ (δ=7.26) for $CDCl_3$ solution. For ^{13}C NMR spectra, the chemical shifts in $CDCl_3$ and DMSO are recorded relative to the $CDCl_3$ resonance (δ=77.0) and DMSO resonance (δ=40.45). Silica gel column chromatography was carried out with Silica gel 100 (Merck No. 10184). Merck Silica-gel 60 F254 plates (No. 5744) were used for the preparative TLC. Melting points are uncorrected. X-Ray crystal data was collected by a Bruker SMART APEX II diffractometer. The structure was solved by a direct method using SHLEXS-97 (Scheldrik,1997) and refined with a full matrix laser-squares method.

2n: Molecular formula= $C_{20}H_{25}ClNO_3P$,MW=393.33,space group=*P*-1, *a*=8.617 (2) Å, *b*=9.976 (3) Å, *c*=13.012 (3) Å, *V*=979.49 (4) $Å^3$, *T*=90 K, *Z*=2, D_x=1.335 Mg/m^3, (Mo-K_α)=0.71073 Å, R=0.029 over independent reflections (5582), α=75.004(1), β=89.623(1), γ=65.828(1). Crystallographic data and structure factors for the single crystal X-ray diffraction analysis reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication No. CCDC: 2236285, copies of these data can be obtained, free of charge, upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:+44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

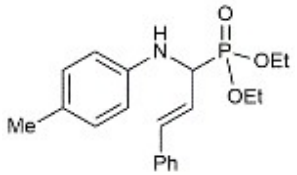
2u: Molecular formula= $C_{21}H_{28}NO_4P$,MW=389.41,space group=*P*-1, *a*=9.838 (2) Å, *b*=9.658 (3) Å, *c*=10.988 (3) Å, *V*=1020.13 (4) $Å^3$, *T*=90 K, *Z*=2, D_x=1.268 Mg/m^3, (Mo-K_α)=0.71073 Å, R=0.034 over independent reflections (5955), α=90, β=102.287 (1), γ=90. Crystallographic data and structure factors for the single crystal X-ray diffraction analysis reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication No. CCDC: 2236286, copies of these data can be obtained, free of charge, upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:+44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

General procedure for the synthesis of 1-aminophosphonate 1:



Aldehyde (10 mmol) was added to a mixture of amine (10 mmol) and diethyl phosphite (10 mmol) in dioxane (2 mL). $ZnCl_2$ (10 mol%) was added to the mixture and the reaction mixture was stirred at 88 °Cfor 8 h without using any inert gas.The completion of the reaction was monitored by TLC.Ethyl acetate (10 mL) was added to the reaction mixture and the solution was washed with NaOH (5%, 2 x 5 mL) and dried over sodium sulfate. The solvent was evaporated and the crude product was purified by a short column chromatography with *n*-Hexane-EtOAc (5:5) to give compound **1**as the viscous oil or white solid. All products gave satisfactory spectral data in accord with the assigned structures.

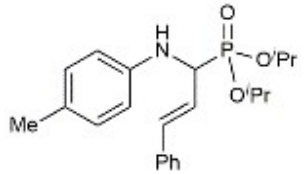
(E)-diethyl (3-phenyl-1-(p-tolylamino)allyl)phosphonate (1a):



Yellow waxy solid(95%, 341mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.28 (m, 4H), 7.28 – 7.22 (m, 1H), 6.96 – 6.86 (m, 2H), 6.80 – 6.66 (m, 3H), 6.28 (ddd, *J* = 16.0, 6.5, 4.8 Hz, 1H), 5.75 (dd, *J* = 9.8, 4.9 Hz, 1H), 4.68 (dddd, *J* = 24.9, 9.8, 6.4, 1.5 Hz, 1H), 4.18 – 4.00 (m, 4H), 2.15 (s, 3H), 1.22 (dt, *J* = 11.6, 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 145.4 (d, *J* = 12.1 Hz), 136.6 (d, *J* = 2.0 Hz), 131.9 (d, *J* = 12.1 Hz), 129.6, 129.2, 128.1, 126.6, 125.6,

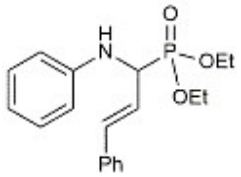
125.0 (d, J = 2.0 Hz), 113.8, 62.9 (d, J = 7.0Hz), 62.5 (d, J = 7.0 Hz), 52.3 (d, J = 155.5 Hz), 20.5, 16.8 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.85.HRMS (ESI): Calcd for $C_{20}H_{26}NO_3NaP$ $[M + Na]^+$: 382.1548, Found: 382.1543.

(E)-diisopropyl (3-phenyl-1-(p-tolylamino)allyl)phosphonate (1b):



Orange viscous liquid (95%, 367mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 6.90 (d, J = 8.2 Hz, 2H), 6.80 – 6.67 (m, 3H), 6.27 (ddd, J = 16.0, 6.5, 4.9 Hz, 1H), 5.71 – 5.58 (m, 1H), 4.75 – 4.62 (m, 2H), 4.62 – 4.49 (m, 1H), 2.15 (d, J = 3.4 Hz, 3H), 1.28 (t, J = 6.3 Hz, 6H), 1.24 – 1.15 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 145.5 (d, J = 12.1 Hz), 136.7 (d, J = 3.0 Hz), 131.8 (d, J = 13.1 Hz), 129.6, 129.1, 128.0, 126.5, 125.6, 125.2, 113.8, 71.4 (d, J = 7.0 Hz), 70.9 (d, J = 7.0 Hz), 52.9 (d, J = 156.5 Hz), 24.4 (d, J = 3.0 Hz), 24.3 (d, J = 3.0 Hz), 24.1(d, J = 5.0 Hz), 23.9 (d, J = 5.0 Hz), 20.5. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 21.13.HRMS(ESI): Calcd for$C_{22}H_{30}NO_3NaP$ $[M + Na]^+$: 410.1861, Found:.

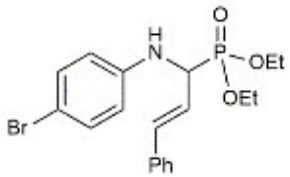
(E)-diethyl (3-phenyl-1-(phenylamino)allyl)phosphonate (1c):



Yellow waxy solid (94%, 324mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.31 (m, 4H), 7.26 (t, J = 7.1 Hz, 1H), 7.15 – 7.03 (m, 2H), 6.89 – 6.79 (m, 2H), 6.73 (ddd, J = 16.0, 4.9, 1.4 Hz, 1H), 6.59 (tt, J = 7.2, 1.1 Hz, 1H), 6.28 (ddd, J = 16.0, 6.4, 4.8 Hz, 1H), 5.94 (dd, J = 9.6, 4.8 Hz, 1H), 4.73 (dddd, J = 24.7, 9.7, 6.4, 1.5 Hz, 1H), 4.18 – 3.99 (m, 4H), 1.29 – 1.14 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 147.7 (d, J = 11.1 Hz), 136.6 (d, J = 3.0 Hz), 132.0 (d, J =

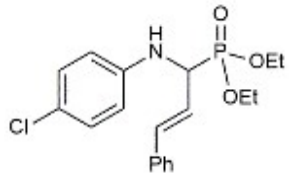
13.1 Hz), 129.2, 129.2, 128.1, 126.6, 124.9 (d, J = 3.0 Hz), 117.2, 113.7, 62.9 (d, J = 7.0Hz), 62.5 (d, J = 7.0 Hz), 52.1 (d, J = 155.5 Hz), 16.8 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ: 22.70. HRMS (ESI): Calcd for $C_{19}H_{24}NO_3NaP$ $[M + Na]^+$: 368.1391, Found: 368.1391.

(E)-diethyl (1-((4-bromophenyl)amino)-3-phenylallyl)phosphonate (1d):

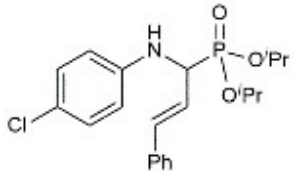


Yellow solid (91%, 384mg, M.P. 115-118 ℃).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.30 (m, 4H), 7.30 – 7.19 (m, 3H), 6.89 – 6.79 (m, 2H), 6.72 (ddd, J = 16.0, 4.8, 1.4 Hz, 1H), 6.34 – 6.21 (m, 2H), 4.74 (dddd, J = 24.6, 9.6, 6.3, 1.5 Hz, 1H), 4.09 (ddqt, J = 10.4, 8.7, 7.1, 3.4 Hz, 4H), 1.29 – 1.15 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 147.1 (d, J = 10.1 Hz), 136.5 (d, J = 3.0 Hz), 132.1 (d, J = 12.1 Hz), 131.7, 129.2, 128.2, 126.6, 124.4 (d, J = 3.0 Hz), 115.7, 107.9, 62.9 (d, J = 7.0 Hz), 62.6 (d, J = 7.0 Hz), 52.0 (d, J = 154.5 Hz), 16.8 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.35. HRMS (ESI): Calcd for $C_{19}H_{23}NO_3BrNaP$ $[M + Na]^+$: 446.0497, Found: 446.0493.

(E)-diethyl (1-((4-chlorophenyl)amino)-3-phenylallyl)phosphonate (1e):

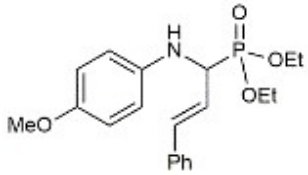


Yellow solid (91%, 344mg, M.P. 108-110 ℃).^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.28 (m, 3H), 7.23 – 7.12 (m, 3H), 7.10 (dd, J = 8.4, 2.5 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 5.60 – 5.47 (m, 1H), 5.20 – 4.45 (m, 3H), 4.15 – 4.08 (m, 4H), 1.33 (td, J = 7.1, 2.0 Hz, 6H).^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 146.7 (d, J = 11.1 Hz), 136.5 (d, J = 3.0 Hz), 132.1 (d, J = 12.1 Hz), 129.2, 128.8, 128.2, 126.6, 124.4 (d, J = 3.0 Hz), 120.5, 115.1, 62.9 (d, J = 7.0 Hz), 62.6 (d, J = 7.0 Hz), 52.1 (d, J = 154.5 Hz), 16.7 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.40.HRMS(ESI): Calcd for$C_{19}H_{23}NO_3ClNaP$ $[M + Na]^+$: 402.1001, Found: 402.0998.



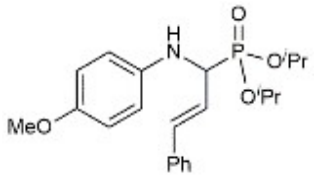
(E)-diisopropyl (1-((4-chlorophenyl)amino)-3-phenylallyl)phosphonate (1f): Yellow solid (82%, 333mg, M.P. 98-101 ℃).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 – 7.30 (m, 4H), 7.25 (t, J = 7.0 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.91 – 6.86 (m, 2H), 6.77 – 6.67 (m, 1H), 6.27 (ddd, J = 16.0, 6.4, 4.8 Hz, 1H), 6.20 (dd, J = 9.6, 4.9 Hz, 1H), 4.75 – 4.57 (m, 3H), 1.28 (dd, J = 7.7, 6.1 Hz, 6H), 1.19 (dd, J = 26.9, 6.2 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 146.9 (d, J = 11.1 Hz), 136.6 (d, J = 3.0 Hz), 132.0 (d, J = 12.1 Hz), 129.2, 128.8, 128.1, 126.6, 124.6 (d, J = 3.0 Hz), 120.4, 115.1, 71.4 (d, J = 7.0 Hz), 71.0 (d, J = 7.0 Hz), 52.6 (d, J = 157.5 Hz), 24.4 (d, J = 3.0 Hz), 24.3 (d, J = 3.0 Hz), 24.1 (d, J = 5.0 Hz), 23.9 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 20.71. HRMS (ESI): Calcd for $C_{21}H_{27}ClNO_3NaP$ $[M + Na]^+$: 430.1315, Found: 430.1313.

(E)-diethyl (1-((4-methoxyphenyl)amino)-3-phenylallyl)phosphonate (1g):



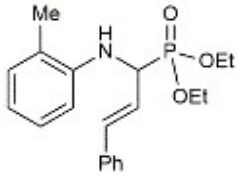
White solid(96%, 360mg, M.P. 108-110 ℃).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.30 (m, 4H), 7.30 – 7.21 (m, 1H), 6.85 – 6.76 (m, 2H), 6.76 – 6.66 (m, 3H), 6.26 (ddd, J = 16.0, 6.5, 4.8 Hz, 1H), 5.53 (dd, J = 9.8, 5.0 Hz, 1H), 4.63 (dddd, J = 24.9, 9.8, 6.5, 1.5 Hz, 1H), 4.17 – 3.99 (m, 4H), 3.64 (s, 3H), 1.22 (dt, J = 8.4, 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.8, 141.7 (d, J = 12.1 Hz), 136.6 (d, J = 3.0 Hz), 132.0 (d, J = 12.1 Hz), 129.1, 128.1, 126.6, 125.2 (d, J = 2.0 Hz), 115.0, 114.8, 62.9 (d, J = 7.0 Hz), 62.5 (d, J = 7.0 Hz), 55.6, 53.0 (d, J = 154.5 Hz), 16.8 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.94. HRMS (ESI): Calcd for $C_{20}H_{26}NO_4NaP$ $[M + Na]^+$: 398.1497, Found:398.1497.

(E)-diisopropyl (1-((4-methoxyphenyl)amino)-3-phenylallyl)phosphonate (1h):



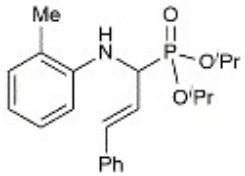
Lemon solid (95%, 383mg, 110-113 ℃).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 – 7.30 (m, 4H), 7.28 – 7.21 (m, 1H), 6.83 – 6.77 (m, 2H), 6.75 – 6.66 (m, 3H), 6.25 (ddd, J = 16.0, 6.5, 4.8 Hz, 1H), 5.44 (dd, J = 9.8, 5.2 Hz, 1H), 4.67 (ddp, J = 15.4, 7.4, 6.2 Hz, 2H), 4.51 (dddd, J = 25.4, 9.8, 6.5, 1.4 Hz, 1H), 3.64 (s, 3H), 1.32 – 1.15 (m, 12H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.7, 141.8 (d, J = 13.1 Hz), 136.7 (d, J = 3.0 Hz), 131.9 (d, J = 12.1 Hz), 129.2, 128.0, 126.5, 125.4, 114.9, 114.7, 71.3 (d, J = 7.0 Hz), 70.8 (d, J = 7.0 Hz), 55.6, 53.5 (d, J = 156.5 Hz), 24.4 (d, J = 3.0 Hz), 24.3 (d, J = 4.0 Hz), 24.1 (d, J = 5.0 Hz), 23.9 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 21.24. HRMS (ESI): Calcd for $C_{22}H_{30}NO_4NaP$ $[M + Na]^+$: 426.1810, Found: 426.1807.

(E)-diethyl (3-phenyl-1-(o-tolylamino)allyl)phosphonate (1i):



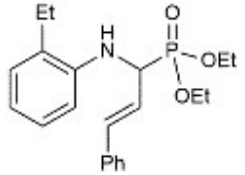
Yellow waxy solid (95%, 341mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 (dd, J = 8.0, 1.4 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.30 – 7.22 (m, 1H), 7.08 – 6.98 (m, 2H), 6.80 – 6.69 (m, 2H), 6.61 (td, J = 7.4, 1.1 Hz, 1H), 6.36 (ddd, J = 16.0, 6.8, 4.8 Hz, 1H), 4.78 (dddd, J = 24.4, 8.5, 6.8, 1.4 Hz, 1H), 4.52 (dd, J = 9.4, 5.9 Hz, 1H), 4.20 – 4.00 (m, 4H), 2.21 (s, 3H), 1.22 (q, J = 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 144.9 (d, J = 11.1 Hz), 136.6 (d, J = 4.0 Hz), 132.1 (d, J = 12.1 Hz), 130.4, 129.1, 128.2, 127.1, 126.7, 124.9 (d, J = 3.0 Hz), 123.2, 117.9, 111.8, 63.0 (d, J = 6.0 Hz), 62.8, (d, J = 7.0 Hz) , 52.5 (d, J = 153.5 Hz), 17.8, 16.7 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.80. HRMS (ESI): Calcd for $C_{20}H_{26}NO_3NaP$ $[M + Na]^+$: 382.1548, Found: 382.1547.

(E)-diisopropyl (3-phenyl-1-(o-tolylamino)allyl)phosphonate (1j):



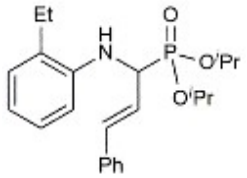
Orange waxy solid (93%, 360mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.08 – 6.98 (m, 2H), 6.78 – 6.70 (m, 2H), 6.61 (td, J = 7.3, 1.1 Hz, 1H), 6.35 (ddd, J = 16.0, 6.6, 4.8 Hz, 1H), 4.76 – 4.60 (m, 3H), 4.45 (dd, J = 9.1, 6.7 Hz, 1H), 2.22 (s, 3H), 1.32 – 1.17 (m, 12H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 145.0 (d, J = 11.1 Hz), 136.6 (d, J = 3.0 Hz), 132.0 (d, J = 12.1 Hz), 130.4, 129.1, 128.1, 127.2, 126.7, 125.1 (d, J = 4.0 Hz), 122.9, 117.8, 111.6, 71.5 (d, J = 7.0 Hz), 71.2 (d, J = 7.0 Hz), 52.9 (d, J = 154.5 Hz), 24.4 (d, J = 4.0 Hz), 24.3 (d, J = 3.0 Hz), 24.0 (d, J = 5.0 Hz), 23.9 (d, J = 5.0 Hz), 17.7. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 20.98. HRMS (ESI): Calcd for $C_{22}H_{30}NO_3NaP$ $[M + Na]^+$: 410.1816, Found: .

(E)-diethyl (1-((2-ethylphenyl)amino)-3-phenylallyl)phosphonate (1k):



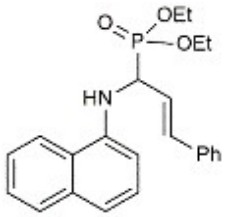
White waxy solid (95%, 354mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.30 – 7.22 (m, 1H), 7.11 – 6.97 (m, 2H), 6.82 – 6.69 (m, 2H), 6.66 (td, J = 7.4, 1.1 Hz, 1H), 6.36 (ddd, J = 16.0, 6.7, 4.8 Hz, 1H), 4.78 (dddd, J = 24.3, 8.4, 6.7, 1.4 Hz, 1H), 4.56 (dd, J = 9.1, 6.5 Hz, 1H), 4.20 – 4.00 (m, 4H), 2.59 (qd, J = 7.5, 4.7 Hz, 2H), 1.32 – 1.14 (m, 9H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 144.2 (d, J = 11.1 Hz), 136.6 (d, J = 3.0 Hz), 132.2 (d, J = 13.1 Hz), 129.1, 128.6, 128.4, 128.2, 127.1, 126.7, 124.9 (d, J = 4.0 Hz), 118.1, 112.0, 62.9 (d, J = 7.0 Hz), 62.8 (d, J = 7.0 Hz), 52.5 (d, J = 152.5 Hz), 23.9, 16.7 (d, J = 5.0 Hz), 13.5. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.86. HRMS (ESI): Calcd for $C_{21}H_{28}NO_3NaP$ $[M + Na]^+$: 396.1704, Found: 396.1700 .

(E)-diisopropyl (1-((2-ethylphenyl)amino)-3-phenylallyl)phosphonate (1l):



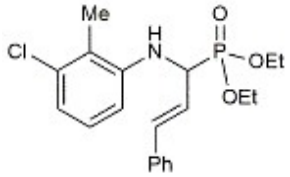
Yellow waxy solid (94%, 377mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (d, J = 7.3 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.08 – 6.98 (m, 2H), 6.78 – 6.68 (m, 2H), 6.65 (td, J = 7.4, 1.1 Hz, 1H), 6.34 (ddd, J = 16.0, 6.6, 4.8 Hz, 1H), 4.76 – 4.59 (m, 3H), 4.48 (dd, J = 8.8, 7.2 Hz, 1H), 2.58 (qd, J = 7.5, 2.4 Hz, 2H), 1.30 – 1.19 (m, 15H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 144.3 (d, J = 11.1 Hz), 136.6 (d, J = 3.0 Hz), 132.0 (d, J = 12.1 Hz), 129.1, 128.5, 128.4, 128.1, 127.1, 126.7, 125.1 (d, J = 4.0 Hz), 118.0, 111.8, 71.4 (d, J = 7.0 Hz), 71.3 (d, J = 7.0 Hz), 52.8 (d, J = 154.5 Hz), 24.3 (d, J = 5.0 Hz), 24.3 (d, J = 5.0 Hz), 24.0 (d, J = 5.0 Hz), 23.9 (d, J = 5.0 Hz), 13.5. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 21.03. HRMS (ESI): Calcd for $C_{23}H_{32}NO_3NaP$ $[M + Na]^+$: 424.2017, Found: .

(E)-diethyl (1-(naphthalen-1-ylamino)-3-phenylallyl)phosphonate (1m):



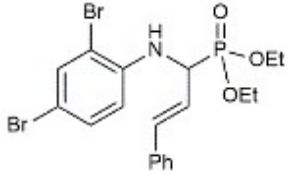
Yellow waxy solid (91%, 359mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 – 8.25 (m, 1H), 7.86 – 7.79 (m, 1H), 7.53 – 7.46 (m, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.34 (td, J = 7.5, 5.2 Hz, 3H), 7.29 – 7.22 (m, 2H), 6.91 – 6.81 (m, 2H), 6.51 (ddd, J = 16.1, 7.0, 4.9 Hz, 1H), 5.99 (dd, J = 9.0, 4.3 Hz, 1H), 4.95 (dddd, J = 23.2, 8.5, 6.9, 1.3 Hz, 1H), 4.21 – 4.05 (m, 4H), 1.22 (dt, J = 23.1, 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 142.6 (d, J = 12.1 Hz), 136.7 (d, J = 3.0 Hz), 134.5, 132.4 (d, J = 12.1 Hz), 129.1, 128.5, 128.2, 126.9, 126.7, 126.2, 124.9, 124.5 (d, J = 3.0 Hz), 124.1, 122.0, 117.8, 106.3, 63.0 (d, J = 7.0 Hz), 62.7 (d, J = 7.0 Hz), 53.2 (d, J = 155.5 Hz), 16.8 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.47.

(E)-diethyl (1-((3-chloro-2-methylphenyl)amino)-3-phenylallyl)phosphonate (1n):



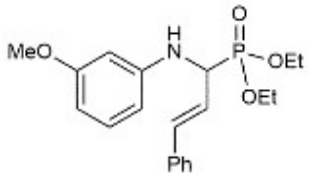
Orange waxy solid (92%, 361mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (d, J = 7.2 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.31 – 7.22 (m, 1H), 7.03 (t, J = 8.1 Hz, 1H), 6.85 – 6.69 (m, 3H), 6.37 (ddd, J = 16.0, 6.6, 4.8 Hz, 1H), 4.89 (dd, J = 9.4, 4.8 Hz, 1H), 4.80 (dddd, J = 23.7, 9.3, 6.5, 1.4 Hz, 1H), 4.20 – 4.01 (m, 4H), 2.30 (s, 3H), 1.22 (q, J = 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 146.6 (d, J = 11.1 Hz), 136.5 (d, J = 4.0 Hz), 133.9, 132.3 (d, J = 12.1 Hz), 129.1, 128.2, 127.6, 126.7, 124.4 (d, J = 4.0 Hz), 120.9, 118.5, 111.0, 63.0 (d, J = 7.0 Hz), 62.8 (d, J = 7.0 Hz), 52.9 (d, J = 153.5 Hz), 16.7 (d, J = 6.0 Hz), 14.1. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.37. HRMS (ESI): Calcd for $C_{20}H_{25}ClNO_3NaP$ $[M + Na]^+$: 416.1158, Found: 416.1156.

(E)-diethyl (1-((2,4-dibromophenyl)amino)-3-phenylallyl)phosphonate (1o):



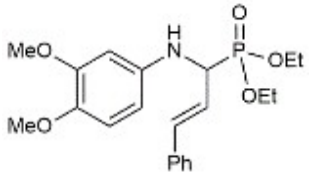
Orange waxy solid (80%, 400mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, J = 2.3 Hz, 1H), 7.46 – 7.30 (m, 5H), 7.30 – 7.22 (m, 1H), 6.91 (d, J = 8.9 Hz, 1H), 6.69 (ddd, J = 16.0, 4.9, 1.2 Hz, 1H), 6.31 (ddd, J = 16.0, 6.6, 4.8 Hz, 1H), 5.06 (dd, J = 9.0, 7.0 Hz, 1H), 4.94 (dddd, J = 24.5, 8.5, 6.5, 1.4 Hz, 1H), 4.22 – 4.04 (m, 4H), 1.24 (t, J = 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 143.1 (d, J = 12.1 Hz), 136.2 (d, J = 3.0 Hz), 134.2, 132.6 (d, J = 12.1 Hz), 131.6, 129.1, 128.4, 126.8, 123.7 (d, J = 4.0 Hz), 115.1, 110.5, 108.9, 63.2 (d, J = 6.0 Hz), 63.1 (d, J = 7.0 Hz), 52.2 (d, J = 151.5 Hz), 16.8 (d, J = 5.0 Hz), 16.7 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 21.71. HRMS (ESI): Calcd for $C_{19}H_{22}Br_2NO_3NaP$ $[M + Na]^+$: 523.9602, Found: 523.9600.

(E)-diethyl (1-((3-methoxyphenyl)amino)-3-phenylallyl)phosphonate (1p):



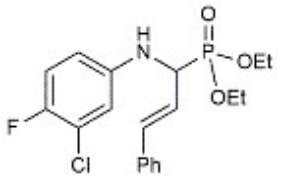
Orange viscous liquid (94%, 352mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.30 (m, 4H), 7.29 – 7.22 (m, 1H), 7.04 – 6.96 (m, 1H), 6.75 (ddd, J = 16.0, 4.9, 1.3 Hz, 1H), 6.51 – 6.40 (m, 2H), 6.29 (ddd, J = 16.0, 6.5, 4.8 Hz, 1H), 6.23 – 6.16 (m, 1H), 5.98 (dd, J = 9.6, 4.8 Hz, 1H), 4.74 (dddd, J = 24.8, 9.6, 6.4, 1.5 Hz, 1H), 4.19 – 4.00 (m, 4H), 3.68 (s, 3H), 1.23 (dt, J = 9.8, 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 160.6, 149.1 (d, J = 11.1 Hz), 136.6 (d, J = 3.0 Hz), 131.9 (d, J = 13.1 Hz), 129.9, 129.2, 128.1, 126.6, 124.9, 106.5, 102.8, 99.6, 62.9 (d, J = 7.0 Hz), 62.6 (d, J = 7.0 Hz), 55.1, 52.1 (d, J = 154.5 Hz), 16.8 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.66. HRMS (ESI): Calcd for $C_{20}H_{26}NO_4NaP$ $[M + Na]^+$: 398.1497, Found: 398.1494.

(E)-diethyl (1-((3,4-dimethoxyphenyl)amino)-3-phenylallyl)phosphonate (1q):



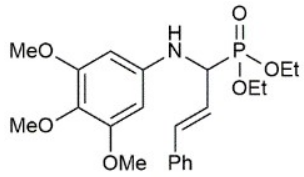
Dark viscous liquid (96%, 388mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 6.80 – 6.68 (m, 2H), 6.64 (d, J = 2.6 Hz, 1H), 6.36 – 6.22 (m, 2H), 5.54 (dd, J = 9.7, 5.1 Hz, 1H), 4.68 (dddd, J = 24.9, 9.7, 6.5, 1.4 Hz, 1H), 4.10 (dddd, J = 11.7, 7.2, 3.3, 1.7 Hz, 4H), 3.72 (s, 3H), 3.63 (s, 3H), 1.28 – 1.21 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 150.1, 142.6 (d, J = 12.1 Hz), 141.3, 136.7 (d, J = 3.0 Hz), 132.0 (d, J = 12.1 Hz), 129.1, 128.1, 126.6, 125.2(d, J = 3.0 Hz), 114.3, 104.4, 100.5, 62.8 (d, J = 6.0 Hz), 62.5 (d, J = 7.0 Hz), 56.8, 55.7, 52.9 (d, J = 154.5 Hz), 16.8 (d, J = 5.0 Hz), 16.7 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.95. HRMS (ESI): Calcd for $C_{21}H_{28}NO_5NaP$ $[M + Na]^+$: 428.1603, Found: 428.1602.

(E)-diethyl (1-((3-chloro-4-fluorophenyl)amino)-3-phenylallyl)phosphonate (1r):



White solid (93%, 369mg, M.P. 110-113 ℃).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.31 (m, 4H), 7.31 – 7.22 (m, 1H), 7.13 (t, J = 9.1 Hz, 1H), 7.03 (dd, J = 6.4, 2.8 Hz, 1H), 6.83 (ddd, J = 9.1, 3.9, 2.9 Hz, 1H), 6.73 (ddd, J = 16.0, 4.9, 1.4 Hz, 1H), 6.34 – 6.20 (m, 2H), 4.79 (dddd, J = 24.7, 9.8, 6.3, 1.5 Hz, 1H), 4.18 – 4.00 (m, 4H), 1.22 (dt, J = 11.9, 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 148.8 (d, J = 236.3 Hz), 145.3 (d, J = 11.1 Hz), 136.5 (d, J = 3.0 Hz), 132.1 (d, J = 12.1 Hz), 129.2, 128.2, 126.6, 124.3 (d, J = 3.0 Hz), 119.6 (d, J = 18.1 Hz), 117.0 (d, J = 21.2 Hz), 114.2, 113.3 (d, J = 6.0 Hz), 62.9 (d, J = 6.0 Hz), 62.6 (d, J = 7.0 Hz), 52.1 (d, J = 154.5 Hz), 16.7 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.32. HRMS (ESI): Calcd for C19H22NO3FNaPCl [M + Na]$^{+}$: 420.0908, Found: 420.0905.

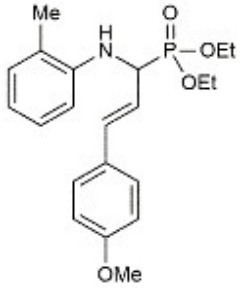
(E)-diethyl (3-phenyl-1-((3,4,5-trimethoxyphenyl)amino)allyl)phosphonate (1s):



1s

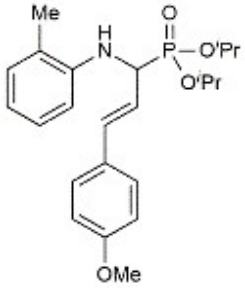
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (d, J = 7.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.29 – 7.22 (m, 1H), 6.80 (ddd, J = 16.0, 4.7, 1.2 Hz, 1H), 6.29 (ddd, J = 16.0, 6.7, 5.0 Hz, 1H), 6.23 (s, 2H), 5.71 (t, J = 6.6 Hz, 1H), 4.80 (dt, J = 24.8, 6.9 Hz, 1H), 4.18 – 4.07 (m, 4H), 3.73 (s, 6H), 3.56 (s, 3H), 1.25 (td, J = 7.1, 3.0 Hz, 6H).^{13}C NMR (101 MHz, DMSO-d_6) δ 153.75, 144.39(d, J = 11.1 Hz), 136.73(d, J = 3.0 Hz), 132.25(d, J = 12.1 Hz), 129.72, 129.19, 128.15, 126.64, 125.18(d, J = 3.0 Hz), 91.83, 62.89(d, J = 7.0 Hz), 62.59(d, J = 7.0 Hz), 60.55, 56.04, 52.57(d, J = 154.5 Hz), 16.80(d, J = 5.0 Hz), 16.76(d, J = 4.0 Hz),.^{31}P NMR (162 MHz, DMSO-d_6) δ 22.89 ppm.

(E)-diethyl (3-(4-methoxyphenyl)-1-(o-tolylamino)allyl)phosphonate (1t):



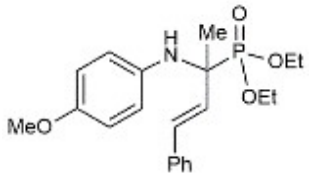
White waxy solid (95%, 369mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (d, J = 8.5 Hz, 2H), 7.04 (t, J = 8.1 Hz, 2H), 6.96 – 6.87 (m, 2H), 6.77 (d, J = 8.0 Hz, 1H), 6.70 (dd, J = 15.8, 4.9 Hz, 1H), 6.62 (td, J = 7.4, 1.1 Hz, 1H), 6.20 (ddd, J = 16.0, 6.9, 4.9 Hz, 1H), 4.81 – 4.66 (m, 1H), 4.51 (dd, J = 9.3, 6.0 Hz, 1H), 4.18 – 4.03 (m, 4H), 3.75 (s, 3H), 2.22 (s, 3H), 1.22 (q, J = 6.9 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 159.4, 145.0 (d, J = 11.1 Hz), 131.8 (d, J = 13.1 Hz), 130.4, 129.3 (d, J = 3.0 Hz), 128.0, 127.1, 123.1, 122.2 (d, J = 3.0 Hz), 117.8, 114.5, 111.7, 62.9 (d, J = 7.0 Hz), 62.7 (d, J = 7.0 Hz), 55.5, 52.6 (d, J = 154.5 Hz), 17.8, 16.7 (d, J = 5.05 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 23.02.

(E)-diisopropyl (3-(4-methoxyphenyl)-1-(o-tolylamino)allyl)phosphonate (1u):



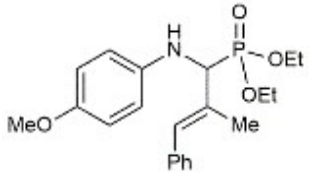
Yellow waxy solid (84%, 350mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (d, J = 8.5 Hz, 2H), 7.04 (t, J = 8.1 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.80 – 6.66 (m, 2H), 6.66 – 6.58 (m, 1H), 6.21 (ddd, J = 16.0, 6.8, 4.8 Hz, 1H), 4.78 – 4.56 (m, 3H), 4.46 (dd, J = 9.1, 6.7 Hz, 1H), 3.75 (s, 3H), 2.23 (s, 3H), 1.29 (dd, J = 6.2, 4.4 Hz, 6H), 1.21 (dd, J = 9.3, 6.2 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 159.4, 145.1 (d, J = 12.1 Hz), 131.7 (d, J = 13.1 Hz), 130.4, 129.3 (d, J = 3.0 Hz), 127.9, 127.2, 122.8, 122.4 (d, J = 4.0 Hz), 117.7, 114.5, 111.6, 71.4 (d, J = 7.0 Hz), 71.1 (d, J = 8.0 Hz), 55.4, 53.0 (d, J = 154.5 Hz), 24.3 (d, J = 4.0 Hz), 24.3 (d, J = 4.0 Hz), 23.9 (d, J = 5.0 Hz), 23.9 (d, J = 4.0 Hz), 17.7. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 21.26.

(E)-diethyl (2-((4-methoxyphenyl)amino)-4-phenylbut-3-en-2-yl)phosphonate (1v):



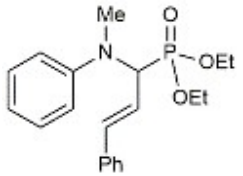
Red viscous oil (87%, 338mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 6.97 – 6.90 (m, 2H), 6.75 – 6.62 (m, 3H), 6.51 (dd, J = 16.3, 6.6 Hz, 1H), 4.85 (d, J = 7.7 Hz, 1H), 4.17 – 4.07 (m, 4H), 1.62 (d, J = 15.8 Hz, 3H), 1.26 (q, J = 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.2, 139.2 (d, J = 13.1 Hz), 136.9 (d, J = 4.0 Hz), 131.2 (d, J = 10.1 Hz), 130.8 (d, J = 6.0 Hz), 129.1, 128.1, 126.7, 120.4, 114.2, 63.1 (d, J = 9.0 Hz), 63.0 (d, J = 8.0 Hz), 58.2 (d, J = 153.5 Hz), 55.5, 20.9, 16.8 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 25.39. HRMS (ESI): Calcd for $C_{21}H_{28}NO_4NaP$ $[M + Na]^+$: 412.1654, Found:412.1652.

(E)-diethyl (1-((4-methoxyphenyl)amino)-2-methyl-3-phenylallyl)phosphonate (1w):



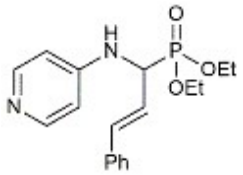
Orange viscous oil (93%, 361mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (t, J = 7.6 Hz, 2H), 7.27 – 7.19 (m, 3H), 6.86 – 6.79 (m, 2H), 6.76 – 6.70 (m, 3H), 5.67 (dd, J = 10.0, 7.3 Hz, 1H), 4.47 (dd, J = 25.4, 9.9 Hz, 1H), 4.19 – 4.02 (m, 4H), 3.64 (s, 3H), 1.94 (dd, J = 3.3, 1.3 Hz, 3H), 1.24 (dt, J = 9.4, 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.8, 141.6 (d, J = 16.1 Hz), 137.5 (d, J = 2.0 Hz), 134.0 (d, J = 3.0 Hz), 129.2 (d, J = 12.1 Hz), 129.0 (d, J = 2.0 Hz), 128.7, 127.0, 115.1, 114.7, 62.8 (d, J = 6.0 Hz), 62.6 (d, J = 7.0 Hz), 58.3 (d, J = 151.5 Hz), 55.6, 16.8 (d, J = 6.0 Hz), 16.7 (d, J = 6.0 Hz), 16.0. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 23.20. HRMS (ESI): Calcd for $C_{21}H_{28}NO_4NaP$ $[M + Na]^+$: 412.1654, Found: 412.1650.

(E)-diethyl (1-(methyl(phenyl)amino)-3-phenylallyl)phosphonate (1y):



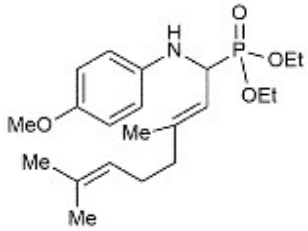
White waxy solid (94%, 337mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 – 7.45 (m, 2H), 7.38 – 7.20 (m, 5H), 6.97 – 6.90 (m, 2H), 6.82 – 6.68 (m, 2H), 6.46 (dt, J = 15.9, 7.2 Hz, 1H), 5.04 (ddd, J = 25.3, 7.0, 1.4 Hz, 1H), 4.14 – 3.99 (m, 4H), 3.06 (d, J = 0.9 Hz, 3H), 1.18 (dt, J = 21.9, 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 149.85 (d, J = 7.07 Hz), 136.5, 134.0 (d, J = 13.1 Hz), 129.4, 129.1, 128.4, 126.9, 121.8, 117.6, 113.7, 62.5 (d, J = 7.0 Hz), 62.3 (d, J = 7.0 Hz), 58.4 (d, J = 154.5 Hz), 34.8, 16.7 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.22. HRMS (ESI): Calcd for $C_{20}H_{26}NO_3NaP$ $[M + Na]^+$: 382.1548, Found: 382.1547 .

(E)-diethyl (3-phenyl-1-(pyridin-4-ylamino)allyl)phosphonate (1z):



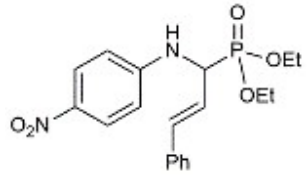
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 (dd, J = 8.0, 1.4 Hz, 2H), 7.36 (dd, J = 8.4, 6.8 Hz, 2H), 7.34 – 7.21 (m, 1H), 6.74 (ddd, J = 15.9, 5.0, 1.7 Hz, 1H), 6.35 (ddd, J = 15.9, 6.0, 4.8 Hz, 1H), 6.03 (dd, J = 12.5, 5.9 Hz, 1H), 4.63 (dtd, J = 15.5, 6.0, 1.7 Hz, 1H), 4.17 – 3.98 (m, 4H), 1.25 (t, J = 7.0 Hz, 6H).^{13}C NMR (101 MHz, DMSO-d_6) δ 136.7 (d, J = 3.0 Hz), 131.0 (d, J =13.1 Hz), 129.1, 128.1, 126.7 (d, J = 2.0 Hz), 126.4 (d, J = 3.0 Hz), 67.8 (d, J = 163.6 Hz), 62.6 (d, J = 7.0 Hz),62.3 (d, J = 6.0 Hz), 16.8 (d, J = 6.0 Hz), 16.8 (d, J = 5.0 Hz).^{31}P NMR (162 MHz, DMSO-d_6) δ 21.8 ppm. HRMS (ESI): Calcd for $C_{18}H_{23}N_2O_3NaP$ $[M + Na]^+$: 369.1344.

(E)-diethyl (1-((4-methoxyphenyl)amino)-3,7-dimethylocta-2,6-dien-1-yl)phosphonate (1aa):



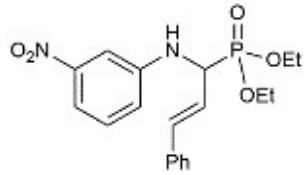
Orange viscous oil (92%, 364 mg) (mixure of two geometric isomers); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.76 – 6.62 (m, 5H), 6.60 – 6.53 (m, 1H), 5.22 (ddd, J = 9.0, 7.0, 4.3 Hz, 1H), 5.17 – 5.01 (m, 2H), 4.46 – 4.31 (m, 1H), 4.13 – 3.96 (m, 4H), 3.64 (d, J = 3.8 Hz, 4H), 2.22 – 1.97 (m, 4H), 1.77 – 1.69 (m, 3H), 1.65 – 1.54 (m, 6H), 1.26 – 1.16 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.81, 151.15, 142.76, 142.12, 142.01, 139.92, 139.79, 139.66, 131.54, 131.30, 124.40, 124.08, 121.22, 121.13, 121.10, 115.43, 114.93, 114.84, 114.67, 62.65, 62.58, 62.52, 62.27, 62.24, 62.20, 62.17, 55.63, 55.60, 51.81, 51.72, 50.21, 50.15, 39.61, 32.62, 26.35, 26.23, 26.20, 25.82, 23.47, 17.91, 17.86, 17.07, 16.82, 16.77. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 24.33, 24.25HRMS (ESI): Calcd for $C_{21}H_{34}NO_4NaP$ [M + Na]$^{+}$: 418.2123, Found: 418.2123 .

(E)-diethyl (1-((4-nitrophenyl)amino)-3-phenylallyl)phosphonate (1bb):



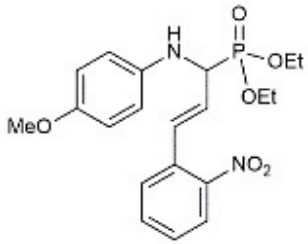
Red viscous liquid (78%, 304 mg) (the compound quickly converted to other product during NMR analysis) ^{1}H NMR of the mixyure (400 MHz, DMSO-d_6) δ 8.18 – 8.01 (m, 2H), 7.69 (dd, J = 9.5, 3.8 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H), 7.40 – 7.16 (m, 4H), 7.00 (d, J = 9.0 Hz, 1H), 6.87 – 6.65 (m, 2H), 5.12 – 4.97 (m, 1H), 4.20 – 3.95 (m, 4H), 3.37 (dd, J = 7.3, 2.8 Hz, 1H), 1.22 (dt, J = 19.2, 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 154.07, 153.99, 152.81, 144.14, 143.87, 138.42, 137.94, 137.18, 136.37, 132.75, 132.63, 129.25, 129.16, 129.12, 128.92, 128.44, 127.11, 126.97, 126.76, 126.38, 126.30, 123.32, 113.13, 63.11 (d, J = 7.0 Hz), 62.94 (d, J = 6.0 Hz), 62.49 (d, J = 5.0 Hz), 51.76 (d, J = 154.5 Hz), 34.08 (d, J = 14.1 Hz), 16.78 (d, J = 7.0 Hz), 16.61 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 21.33, 13.01 ppm; HRMS (ESI): Calcd for $C_{19}H_{23}N_2O_5NaP$ [M + Na]$^{+}$: 413.1242, Found: 413.1242 .

(E)-diethyl (1-((3-nitrophenyl)amino)-3-phenylallyl)phosphonate (1cc):



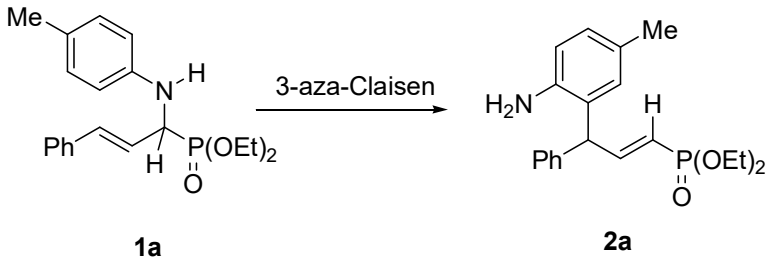
Red viscous oil (84%, 327mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (t, J = 2.3 Hz, 1H), 7.45 – 7.23 (m, 8H), 6.88 (dd, J = 9.4, 4.5 Hz, 1H), 6.77 (ddd, J = 16.0, 4.9, 1.4 Hz, 1H), 6.30 (ddd, J = 16.0, 6.3, 4.9 Hz, 1H), 4.95 (dddd, J = 24.0, 9.4, 6.3, 1.5 Hz, 1H), 4.20 – 4.00 (m, 4H), 1.22 (dt, J = 16.1, 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 149.1, 149.0 (d, J = 10.1 Hz), 136.4 (d, J = 3.0 Hz), 132.2 (d, J = 12.1 Hz), 130.3, 129.2, 128.3, 126.7, 123.9 (d, J = 3.0 Hz), 119.6, 111.3, 107.5, 62.9 (d, J = 7.0 Hz), 62.7 (d, J = 7.0 Hz), 51.8 (d, J = 154.5 Hz), 16.7 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.00. HRMS (ESI): Calcd for $C_{19}H_{23}N_2O_5NaP$ $[M + Na]^+$: 413.1242, Found: 413.1239.

(E)-diethyl (1-((4-methoxyphenyl)amino)-3-(2-nitrophenyl)allyl)phosphonate (1dd):



Red viscous liquid (90%, 378mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 – 7.88 (m, 1H), 7.66 (dd, J = 6.6, 1.4 Hz, 2H), 7.48 (ddd, J = 8.5, 6.5, 2.3 Hz, 1H), 7.13 – 7.04 (m, 1H), 6.88 – 6.83 (m, 2H), 6.78 – 6.72 (m, 2H), 6.38 (ddd, J = 15.7, 6.5, 4.8 Hz, 1H), 5.58 (s, 1H), 4.75 (dd, J = 25.4, 6.3 Hz, 1H), 4.13 (dddd, J = 13.8, 8.9, 7.0, 4.7 Hz, 4H), 3.65 (s, 3H), 1.25 (dt, J = 10.3, 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.0, 148.0, 141.5 (d, J = 11.1 Hz), 133.7, 131.3, 131.3 (d, J = 4.0 Hz), 129.1, 128.5, 126.6 (d, J = 13.1 Hz), 124.6, 115.1, 114.7, 63.0 (d, J = 7.0 Hz), 62.6 (d, J = 7.0 Hz), 55.6, 53.3 (d, J = 153.5 Hz), 16.7 (d, J = 5.0 Hz), 16.6 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 22.17. HRMS (ESI): Calcd for $C_{20}H_{25}N_2O_6NaP$ $[M + Na]^+$: 443.1348, Found: 443.1348 .

*Table S1.*Aza-Claisen rearrangement of aminophosphonate **1a** in various conditions



1a **2a**

Entry	Additive	Solvent	*T*(°C)	Time (h)	Yield of **2a**%[a]
1	-	H_2O	reflux	24	-
2	-	EtOH	reflux	24	-
3	-	CH_3CN	reflux	24	-
4	-	1,4-Dioxane	100	24	-
5	-	DMF	100	24	-
6	-	DMSO	100	24	-
7	-	Toluene	100	24	-
8	$BF_3.OEt_2$	Toluene	rt	24	-[b]
9	$ZnCl_2$	DMF	100	24	-[b]
10	AcOH (2 mL)	-	reflux	24	10
11	HCl (2 mL, 36%)	-	reflux	24	-[c]
12	HCl (2 mL, 36%)	-	rt	24	45
13	HCl (2 mL, 36%)	-	rt	12	58
14	HCl (2 mL, 36%)	-	rt	6	58

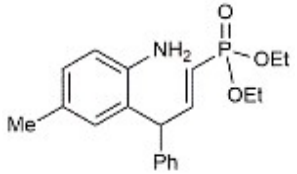
15	HCl (1 mL, 36%)	EtOH (1 mL)	rt	12	58
16	HCl (2 mL, 36%)	EtOH (1 mL)	rt	12	67
17	HCl (2 mL, 36%)	EtOH (1 mL)	rt	24	63
18	$MeSO_3H$ (2 mL, 98%)	-	rt	24	48
19	$MeSO_3H$ (2 mL, 98%)	-	reflux	24	36
20	$MeSO_3H/P_2O_5$ (1 mL/0.2 g)	-	70	24	70
21	$MeSO_3H/P_2O_5$ (1 mL/0.2 g)	-	100	24	65
22	TFA (0.2 mL)	CH_2Cl_2(2 mL)	rt	24	-
23	TFA (0.2 mL)	EtOH (2 mL)	rt	24	-
24	TFA (1 mL)	-	rt	12	58
25	TFA (1 mL)	-	50	12	66
26	TFA (1 mL)	-	reflux	4	83
27	TFA (1 mL)	-	reflux	8	83

[a]Yields refers to the isolated product**2a**after short column chromatography for the reaction of **1a** (1 mmol). [b] Reactions carried out in the presence 3 equiv of additive. [c]Hydrolyzed product (phosphonate to phosphonic acid) was detected.

General procedure for the Aza-Claisen rearrangement of 1-aminophosphonate 1 in TFA: 1-Aminophosphonate **1** (1 mmol) was added to a TFA (1 mL). The reaction mixture was stirred at refluxfor 1-4 h without using any inert gas.The completion of the reaction was monitored by TLC.Ethyl acetate (10 mL) was added to the reaction mixture and the solution was washed with NaOH (10 %, 2 x 5 mL) and dried over sodium sulfate. The solvent was evaporated and the crude product was purified by a short column chromatography with *n*-Hexane-EtOAc (5:5 to 1:20) to give the compound **2**as the viscous oil or white solid. All products gave satisfactory spectral data in accord with the assigned structures.

General procedure for the Aza-Claisen rearrangement of 1-aminophosphonate 1 in HCl:EtOH: 1-Aminophosphonate **1** (1 mmol) was added to a mixture of HCl (37%) in EtOH (2:1 v:v, 2 mL). The reaction mixture was stirred at rtfor 1-4 h without using any inert gas.The completion of the reaction was monitored by TLC.Ethyl acetate (10 mL) was added to the reaction mixture and the solution was washed with NaOH (10 %, 2 x 5 mL) and dried over sodium sulfate. The solvent was evaporated and the crude product was purified by a short column chromatography with *n*-Hexane-EtOAc (5:5 to 1:20) to give the compound **2**as the viscous oil or white solid. All products gave satisfactory spectral data in accord with the assigned structures.

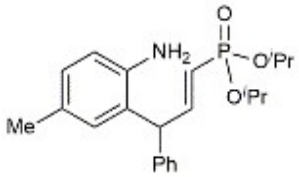
(E)-diethyl (3-(2-amino-5-methylphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2a):



White waxy solid (83%, 298mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (dd, J = 8.1, 6.8 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.24 – 7.20 (m, 2H), 7.08 – 6.99 (m, 1H), 6.97 (dd, J = 6.6, 2.1 Hz, 1H), 6.90 (dd, J = 8.1, 6.1 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 5.63 (ddt, J = 20.6, 17.0, 1.9 Hz, 1H), 5.21 (d, J = 6.9 Hz, 1H), 3.98 (dddd, J = 8.5, 7.1, 6.3, 3.6 Hz, 4H), 2.22 (d, J = 19.5 Hz, 3H), 1.23 (td, J = 7.1, 3.9 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.3 (d, J = 6.0 Hz), 141.0, 129.8, 129.1, 129.1, 129.0, 129.0, 128.8, 128.8, 128.7, 127.3, 118.2 (d, J = 183.8 Hz), 61.7 (d, J = 5.0

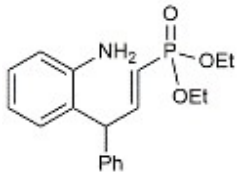
Hz), 47.9 (d, J = 21.2 Hz), 20.9, 16.6 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.73. HRMS (ESI): Calcd for $C_{20}H_{26}NO_3NaP$ [M + Na]$^+$: 382.1548, Found: 382.1544.

(E)-diisopropyl (3-(2-amino-5-methylphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2b):



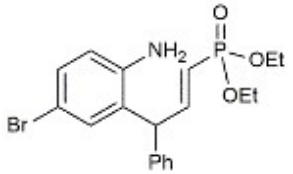
Dark orangewaxy solid (77%, 298mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (dd, J = 8.2, 6.9 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.21 – 7.15 (m, 2H), 7.04 – 6.91 (m, 1H), 6.80 (dd, J = 8.1, 2.0 Hz, 1H), 6.66 – 6.56 (m, 2H), 5.60 – 5.46 (m, 1H), 5.05 (d, J = 6.7 Hz, 1H), 4.69 (s, 2H, NH_2), 4.52 (dpd, J = 8.1, 6.2, 4.1 Hz, 2H), 2.13 (s, 3H), 1.27 – 1.20 (m, 12H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.0 (d, J = 6.0 Hz), 143.8, 141.4, 132.1, 132.0, 129.1, 129.0, 129.0, 128.8, 128.4, 127.1, 125.0, 125.0, 119.1 (d, J = 184.8 Hz), 116.0, 70.0 (d, J = 6.0 Hz), 48.2 (d, J = 22.2 Hz), 24.1 (d, J = 4.0 Hz), 24.1 (d, J = 4.0 Hz), 20.7. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 16.00. HRMS (ESI): Calcd for $C_{22}H_{30}NO_3NaP$ [M + Na]$^+$: 410.1861, Found: 410.1858.

(E)-diethyl (3-(2-aminophenyl)-3-phenylprop-1-en-1-yl)phosphonate(2c):



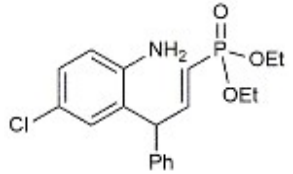
Whitewaxy solid (91%, 314mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.24 (m, 2H), 7.24 – 7.20 (m, 2H), 7.16 – 7.10 (m, 1H), 7.04 – 6.93 (m, 2H), 6.85 (t, J = 7.5 Hz, 1H), 5.66 – 5.54 (m, 1H), 5.21 (d, J = 6.8 Hz, 1H), 3.98 (dqd, J = 8.4, 7.1, 2.9 Hz, 4H), 1.22 (td, J = 7.1, 2.9 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, Chloroform-d) δ 152.9 (d, J = 6.0 Hz), 139.1, 129.5, 129.0, 128.9, 128.8, 128.8, 128.8, 128.7, 128.3, 127.4, 118.5 (d, J = 187.8Hz), 62.0 (d, J = 5.0 Hz), 49.4 (d, J = 22.2 Hz), 16.3 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.73.HRMS(ESI):Calcd for$C_{19}H_{24}NO_3NaP$ [M + Na]$^+$: 368.1391, Found: 368.1388.

(E)-diethyl (3-(2-amino-5-bromophenyl)-3-phenylprop-1-en-1-yl)phosphonate (2d):



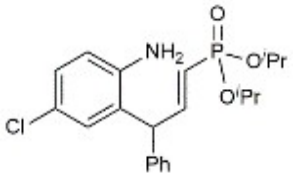
Whitewaxy solid (91%, 385mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.34 (m, 2H), 7.33 – 7.25 (m, 1H), 7.24 – 7.16 (m, 2H), 7.16 – 7.09 (m, 1H), 7.07 – 6.90 (m, 1H), 6.89 – 6.82 (m, 1H), 6.70 – 6.60 (m, 1H), 5.67 – 5.51 (m, 1H), 5.20 (s, 2H, NH_2), 5.09 (dt, J = 6.8, 1.8 Hz, 1H), 4.05 – 3.93 (m, 4H), 1.23 (td, J = 7.0, 2.1 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.7 (d, J = 6.0 Hz), 145.8, 140.6, 130.9, 130.5, 129.2, 128.8, 127.4, 127.1, 118.2 (d, J = 183.8 Hz), 117.6, 107.1, 61.7 (d, J = 6.0 Hz), 48.1 (d, J = 21.2 Hz), 16.6 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.60.HRMS(ESI):Calcd for$C_{19}H_{23}BrNO_3NaP$ [M + Na]$^{+}$: 446.0497, Found: 446.0494.

(E)-diethyl (3-(2-amino-5-chlorophenyl)-3-phenylprop-1-en-1-yl)phosphonate(2e):



Dark orangewaxy solid (94%, 356mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 3H), 7.23 – 7.12 (m, 3H), 7.10 (dd, J = 8.4, 2.5 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 5.60 – 5.47 (m, 1H), 5.20 – 4.45 (m, 3H, NH_2 + CH), 4.17 – 4.06 (m, 5H), 1.33 (td, J = 7.1, 2.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, Chloroform-*d*) δ 152.1 (d, J = 6.0 Hz), 140.7, 138.5, 129.1, 128.9, 128.9, 128.8, 128.0, 127.6, 125.2, 119.0, 118.9 (d, J = 186.8 Hz), 62.0 (d, J = 6.0 Hz), 49.7 (d, J = 22.2 Hz), 16.3 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, Chloroform-*d*) δ 17.98.HRMS(ESI): Calcd for$C_{19}H_{23}ClNO_3NaP$ [M + Na]$^{+}$: 402.1001, Found: 402.0996.

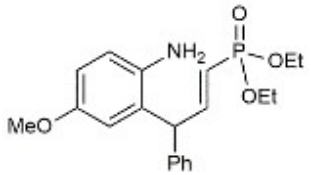
(E)-diisopropyl (3-(2-amino-5-chlorophenyl)-3-phenylprop-1-en-1-yl)phosphonate (2f):



White solid(82%, 333mg, M.P. 91-94 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.34 (m, 2H), 7.32 – 7.26 (m, 1H), 7.22 – 7.15 (m, 2H), 7.04 – 6.87 (m, 2H), 6.75 – 6.65 (m, 2H), 5.54 (ddd, J = 20.2, 16.9, 1.4 Hz, 1H), 5.18 (s, 2H, NH_2), 5.09 (dt, J = 6.8, 1.9 Hz, 1H), 4.52 (dpd, J = 8.2, 6.2, 3.9 Hz, 2H), 1.23 (ddd, J = 11.3, 6.1, 3.0 Hz, 12H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.0 (d, J = 6.0 Hz), 145.4, 140.6, 129.1, 128.8,

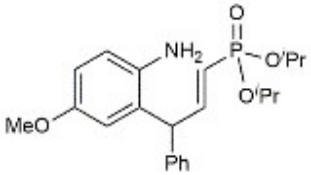
128.1, 127.6, 127.4, 126.6, 119.7 (d, J = 184.8 Hz), 119.6, 117.0, 70.1 (d, J = 5.0 Hz), 47.9 (d, J = 22.2 Hz), 24.1 (d, J = 4.0 Hz), 24.1 (d, J = 4.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 15.63.HRMS(ESI): Calcd for$C_{21}H_{27}ClNO_3NaP$ [M + Na]$^+$: 430.1315, Found: 430.1312.

(E)-diethyl (3-(2-amino-5-methoxyphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2g):



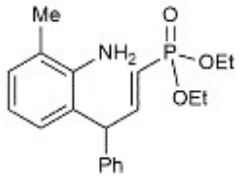
White waxy solid (95%, 356mg),^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 7.24 – 7.14 (m, 3H), 6.72 (dd, J = 8.6, 2.8 Hz, 1H), 6.67 (d, J = 8.5 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 5.52 (ddd, J = 20.3, 17.2, 1.8 Hz, 1H), 4.90 (dt, J = 5.4, 2.2 Hz, 1H), 4.18 – 4.05 (m, 4H), 3.75 (s, 3H), 3.28 (s, 2H, NH_2), 1.33 (td, J = 7.1, 2.7 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, Chloroform-d) δ 153.0, 152.8 (d, J = 6.0 Hz), 139.2, 137.7, 128.9, 128.8, 127.8, 127.3, 118.4 (d, J = 186.8 Hz), 117.8, 115.4, 112.8, 61.7 (d, J = 6.0 Hz), 55.6, 50.2 (d, J = 21.2 Hz), 16.3 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, Chloroform-d) δ 18.24.HRMS(ESI): Calcd for$C_{20}H_{26}NO_4NaP$ [M + Na]$^+$: 398.1497, Found: 398.1494.

(E)-diisopropyl (3-(2-amino-5-methoxyphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2h):



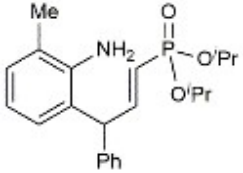
Dark orangewaxy solid(96%, 386mg);^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (t, J = 7.5 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.22 – 7.17 (m, 2H), 6.99 (ddd, J = 21.2, 16.9, 6.7 Hz, 1H), 6.70 – 6.63 (m, 2H), 6.45 – 6.40 (m, 1H), 5.55 (ddd, J = 20.4, 17.0, 1.5 Hz, 1H), 5.08 (dt, J = 6.7, 2.0 Hz, 1H), 4.52 (dpd, J = 8.1, 6.2, 3.6 Hz, 4H, NH_2 + OCH), 3.61 (s, 3H), 1.23 (ddd, J = 11.5, 6.2, 3.7 Hz, 12H). ^{13}C {^{1}H} NMR (101 MHz, Chloroform-d) δ 157.4 (d, J = 5.0 Hz), 156.1, 145.9, 144.8, 133.8, 133.6, 131.9, 131.2, 124.1 (d, J = 184.8 Hz), 121.6, 119.6, 117.8, 74.8 (d, J = 6.0 Hz), 60.3, 53.3 (d, J = 21.2 Hz), 28.9 (d, J = 3.0 Hz), 28.8 (d, J = 4.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 15.90.HRMS(ESI): Calcd for$C_{20}H_{30}NO_4NaP$ [M + Na]$^+$:426.1810, Found:426.1808.

(E)-diethyl (3-(2-amino-3-methylphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2i):



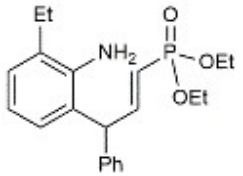
Whitewaxy solid (92%, 330mg).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.34 (m, 2H), 7.30 – 7.25 (m, 1H), 7.22 – 7.19 (m, 2H), 7.09 – 6.96 (m, 2H), 6.80 (dd, J = 7.7, 1.6 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), 5.64 – 5.51 (m, 1H), 5.45 – 5.18 (m, 1H), 3.98 (dddd, J = 10.6, 7.1, 4.9, 3.5 Hz, 4H), 2.18 (s, 3H), 1.23 (td, J = 7.0, 3.3 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.6 (d, J = 6.0 Hz), 141.2, 129.5, 129.2, 129.0, 128.9, 128.6, 128.5, 127.2, 127.0, 126.9, 117.9 (d, J = 184.8 Hz), 61.6 (d, J = 6.0 Hz), 48.2 (d, J = 21.2 Hz), 18.6, 16.6 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.79.HRMS(ESI): Calcd for$C_{20}H_{26}NO_3NaP$ $[M + Na]^+$: 382.1548, Found: 382.1545.

(E)-diisopropyl (3-(2-amino-3-methylphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2j):



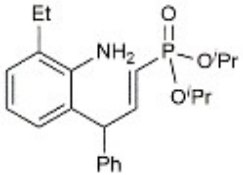
Dark orangewaxy solid (85%, 329mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (dd, J = 8.1, 6.8 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.23 – 7.18 (m, 2H), 7.02 (ddd, J = 21.2, 16.9, 6.5 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.73 (dd, J = 7.7, 1.5 Hz, 1H), 6.54 (t, J = 7.5 Hz, 1H), 5.54 (ddd, J = 20.5, 17.0, 1.5 Hz, 1H), 5.18 (dt, J = 6.6, 1.9 Hz, 1H), 4.78 – 4.48 (m, 4H, NH_2 + 2OCH), 2.11 (s, 3H), 1.23 (ddd, J = 12.1, 6.2, 3.9 Hz, 12H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.1 (d, J = 6.0 Hz), 143.9, 141.5, 129.1, 128.9, 128.9, 127.1, 126.5, 124.6, 122.4, 119.1 (d, J = 184.8 Hz), 116.4, 70.0 (d, J = 6.0 Hz), 48.5 (d, J = 21.2 Hz), 24.1 (d, J = 4.0 Hz), 24.0 (d, J = 4.0 Hz), 18.6. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 16.03.HRMS(ESI): Calcd for$C_{22}H_{30}NO_3NaP$ $[M + Na]^+$: 410.1816, Found: 410.1859.

(E)-diethyl (3-(2-amino-3-ethylphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2k):



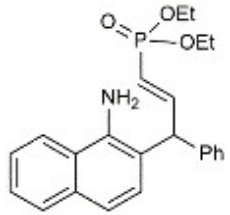
Whitewaxy solid (96%, 358mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (t, J = 7.5 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.23 – 7.17 (m, 2H), 7.10 – 6.95 (m, 1H), 6.92 (dd, J = 7.5, 1.4 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 5.62 – 5.46 (m, 1H), 5.21 – 5.12 (m, 1H), 4.63 (s, 2H, NH_2), 4.02 – 3.92 (m, 4H), 2.48 (tt, J = 7.4, 3.4 Hz, 2H), 1.22 (td, J = 7.0, 3.4 Hz, 6H), 1.14 (dd, J = 8.1, 6.7 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 154.0 (d, J = 6.0 Hz), 143.3, 141.4, 129.0, 128.9, 128.0, 127.2, 127.1, 126.5, 124.7, 117.5 (d, J = 183.8 Hz), 116.6, 61.6 (d, J = 6.0 Hz), 48.6 (d, J = 22.2 Hz), 24.3, 16.6 (d, J = 6.0 Hz), 13.6. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.99.HRMS(ESI): Calcd for$C_{21}H_{28}NO_3NaP$ $[M + Na]^+$: 396.1704, Found: 396.1700.

(E)-diisopropyl (3-(2-amino-3-ethylphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2l):



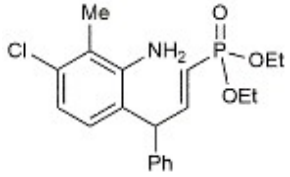
Dark orange waxy solid (89%, 357mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.07 – 6.89 (m, 2H), 6.71 (dd, J = 7.7, 1.5 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 5.52 (dd, J = 20.5, 16.9 Hz, 1H), 5.17 (d, J = 6.6 Hz, 1H), 4.95 – 4.45 (m, 4H, NH_2 + 2OCH), 2.55 – 2.43 (m, 2H), 1.23 (ddd, J = 12.3, 6.3, 3.8 Hz, 12H), 1.15 (t, J = 7.4 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.2 (d, J = 6.0 Hz), 143.3, 141.5, 129.0, 128.9, 128.0, 127.1, 127.0, 126.4, 124.8, 119.0 (d, J = 184.3 Hz), 116.6, 70.0 (d, J = 6.0 Hz), 48.5 (d, J = 21.2 Hz), 24.3, 24.1 (d, J = 4.0 Hz), 24.0 (d, J = 4.0 Hz), 13.6. ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 16.00.HRMS(ESI): Calcd for$C_{23}H_{32}NO_3NaP$ $[M + Na]^+$: 424.2018, Found: 424.2015.

(E)-diethyl (3-(1-aminonaphthalen-2-yl)-3-phenylprop-1-en-1-yl)phosphonate (2m):



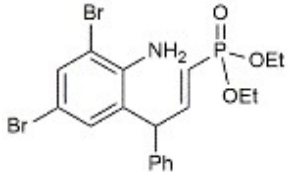
Pale brownviscous oil [method (HCl:EtOH) 85%, 335mg]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 – 8.18 (m, 1H), 7.77 – 7.71 (m, 1H), 7.46 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.10 (m, 5H), 7.05 (d, J = 8.5 Hz, 1H), 6.50 – 4.90 (m, 4H, NH_2, 2×CH), 4.06 – 3.96 (m, 4H), 1.24 (td, J = 7.0, 6.2 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.7 (d, J = 5.0 Hz), 141.9, 141.4, 133.5, 129.0, 128.9, 128.2, 127.3, 127.1, 125.9, 124.6, 123.6, 122.9, 118.0, 117.7 (d, J = 183.8 Hz), 116.3, 61.6 (d, J = 6.0 Hz), 48.3 (d, J = 21.2 Hz), 16.6 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 18.06.

(E)-diethyl (3-(2-amino-4-chloro-3-methylphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2n):



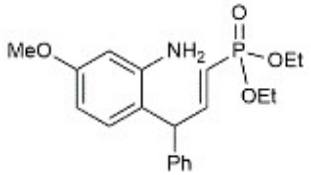
White solid (95%, 373mg); M.P. 88-91 ℃; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.27 – 7.14 (m, 3H), 6.91 – 6.79 (m, 2H), 5.50 (ddd, J = 20.1, 17.2, 1.7 Hz, 1H), 4.81 (dt, J = 5.2, 2.3 Hz, 1H), 4.18 – 4.05 (m, 4H), 3.63 (s, 2H, NH_2), 2.23 (s, 3H), 1.33 (td, J = 7.1, 2.5 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, Chloroform-d) δ 152.6 (d, J = 7.0 Hz), 143.6, 139.0, 133.7, 129.0, 128.7, 127.5, 127.1, 123.6, 120.5, 118.9, 118.6 (d, J = 187.8 Hz), 61.8 (d, J = 6.0 Hz), 50.2 (d, J = 22.2 Hz), 16.3 (d, J = 6.0 Hz), 14.0. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 18.13. HRMS (ESI): Calcd for $C_{20}H_{25}ClNO_3NaP$ $[M + Na]^+$: 416.1158, Found: 416.1159.

(E)-diethyl (3-(2-amino-3,5-dibromophenyl)-3-phenylprop-1-en-1-yl)phosphonate (2o):



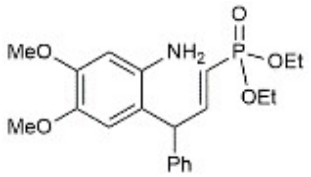
Yellow solid (94%, 470mg, M.P. 87-90 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (d, J = 2.3 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.40 – 7.30 (m, 3H), 7.30 – 7.24 (m, 1H), 6.90 (d, J = 8.9 Hz, 1H), 6.67 (ddd, J = 16.0, 4.9, 1.2 Hz, 1H), 6.30 (ddd, J = 15.9, 6.5, 4.8 Hz, 1H), 5.04 (dd, J = 9.0, 6.8 Hz, 1H), 4.93 (dddd, J = 24.3, 8.5, 6.5, 1.4 Hz, 1H), 4.18 – 4.06 (m, 4H), 1.24 (t, J = 7.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 143.1 (d, J = 12.1 Hz), 136.2 (d, J = 2.0 Hz), 134.2, 132.7, 132.6, 131.6, 129.2, 128.4, 126.8, 123.7 (d, J = 5.0 Hz), 115.1, 108.9 (d, J = 162.6 Hz), 63.2 (d, J = 6.0 Hz), 63.1 (d, J = 6.0 Hz), 52.1 (d, J = 51.5Hz), 16.8 (d, J = 5.0 Hz), 16.7 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 21.72.HRMS(ESI): Calcd for$C_{19}H_{22}Br_2NO_3NaP$ $[M + Na]^+$: 523.9602, Found: 523.9602.

(E)-diethyl (3-(2-amino-6-methoxyphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2p):



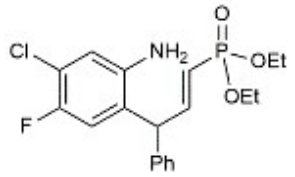
White waxy solid (75%, 281mg);^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.32 (m, 2H), 7.28 – 7.23 (m, 1H), 7.19 – 7.14 (m, 2H), 7.04 – 6.90 (m, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.26 (d, J = 2.6 Hz, 1H), 6.16 (dd, J = 8.5, 2.6 Hz, 1H), 5.52 (ddd, J = 21.0, 17.0, 1.5 Hz, 1H), 5.00 (dt, J = 6.6, 1.9 Hz, 1H), 4.97 (s, 2H, NH_2), 3.97 (dqd, J = 8.3, 7.1, 3.1 Hz, 4H), 3.66 (s, 3H), 1.22 (td, J = 7.0, 2.5 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 159.3, 154.0 (d, J = 6.0 Hz), 147.5, 141.6, 129.6, 128.9, 128.8, 127.0, 117.6, 117.2 (d, J = 184.8 Hz), 102.5, 100.8, 61.6 (d, J = 5.0 Hz), 55.0, 47.8 (d, J = 21.2 Hz), 16.6 (d, J = 5.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 18.08;HRMS(ESI): Calcd for$C_{20}H_{26}NO_4NaP$ $[M + Na]^+$: 398.1497, Found: 398.1494.

(E)-diethyl (3-(6-amino-2,3-dimethoxyphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2q):

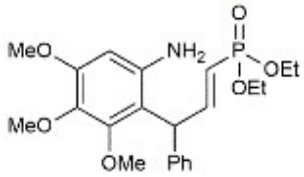


Whitewaxy solid (97%, 393mg);^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.33 (m, 2H), 7.29 – 7.21 (m, 3H), 7.07 (ddd, J = 21.3, 17.0, 6.8 Hz, 1H), 6.48 (d, J = 3.5 Hz, 2H), 5.65 (ddd, J = 21.0, 17.0, 1.4 Hz, 1H), 5.08 (dt, J = 7.0, 1.9 Hz, 1H), 4.05 – 3.98 (m, 4H), 3.71 (s, 3H), 3.60 (s, 3H), 1.24 (td, J = 7.0, 3.6 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.8 (d, J = 5.0 Hz), 149.4, 141.6, 140.9, 140.6, 128.9, 128.8, 127.0, 117.6 (d, J = 184.8 Hz), 116.5, 115.2, 101.7, 61.6 (d, J = 6.0 Hz), 57.3, 55.7, 48.3 (d, J = 22.2 Hz), 16.5 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 18.04;HRMS(ESI): Calcd for$C_{21}H_{28}NO_5NaP$ $[M + Na]^+$: 428.1603, Found: 428.1598.

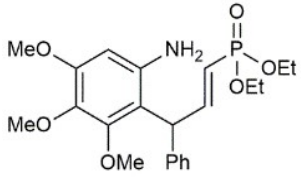
(E)-diethyl (3-(6-amino-2-chloro-3-fluorophenyl)-3-phenylprop-1-en-1-yl)phosphonate (2r):



Whitewaxy solid (91%, 361mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 7.00 (ddd, J = 21.1, 17.0, 6.9 Hz, 1H), 6.82 (d, J = 6.8 Hz, 1H), 6.76 (d, J = 10.5 Hz, 1H), 5.64 (ddd, J = 20.4, 17.0, 1.4 Hz, 1H), 5.20 (s, 2H), 5.09 (d, J = 6.9 Hz, 1H), 4.03 – 3.94 (m, 4H), 1.23 (td, J = 7.3, 1.5 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.2 (d, J = 6.0 Hz), 148.2 (d, J = 234.3 Hz), 143.9, 140.4, 129.2, 128.8, 127.5, 125.3 (d, J = 5.0 Hz), 118.4 (d, J = 183.8 Hz), 118.0 (d, J = 18.1Hz), 116.4 (d, J = 22.2 Hz), 115.8, 61.7 (d, J = 5.0 Hz), 47.9 (d, J = 22.2 Hz), 16.6 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.49;HRMS(ESI):Calcd for$C_{19}H_{22}ClFNO_3NaP$ $[M + Na]^+$: 420.0908, Found: 420.0906.



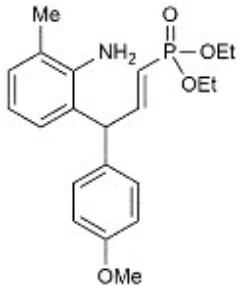
(E)-diethyl (3-(6-amino-2,3,4-trimethoxyphenyl)-3-phenylprop-1-en-1-yl)phosphonate (2s):



2s

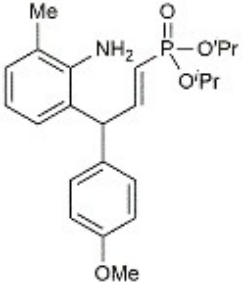
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 (t, J = 7.6 Hz, 2H), 7.23 (dt, J = 7.8, 2.3 Hz, 1H), 7.18 – 7.12 (m, 2H), 6.21 (s, 1H), 5.83 (ddd, J = 21.5, 17.0, 1.2 Hz, 1H), 5.15 (d, J = 7.7 Hz, 1H), 4.74 (s, 2H), 4.00 (ddq, J = 9.6, 8.4, 7.0 Hz, 4H), 3.73 (s, 3H), 3.63 (s, 3H), 3.41 (s, 3H), 1.24 (dt, J = 9.8, 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.11(d, J = 5.0 Hz), 153.07, 152.47, 142.92, 142.58, 133.56, 128.78, 127.53, 126.59, 117.25(d, J = 183.8 Hz), 111.01, 96.12, 61.58(d, J = 6.0 Hz), 61.55(d, J = 6.0 Hz), 60.45(d, J = 28.2 Hz), 55.74, 45.31(d, J = 23.2 Hz), 16.65(d, J = 6.0 Hz), 16.62(d, J = 5.0 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 18.34.

(E)-diethyl (3-(2-amino-3-methylphenyl)-3-(4-methoxyphenyl)prop-1-en-1-yl)phosphonate (2t):



Yellow viscous oil (87%, 338mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.09 (dd, J = 9.3, 2.6 Hz, 2H), 7.06 – 6.96 (m, 1H), 6.94 – 6.87 (m, 2H), 6.79 – 6.69 (m, 2H), 6.60 (d, J = 8.0 Hz, 1H), 5.63 (ddd, J = 21.1, 16.9, 1.4 Hz, 1H), 4.88 – 4.72 (m, 3H, NH_2+CH), 3.97 (dq, J = 8.4, 7.0 Hz, 4H), 3.74 (s, 3H), 2.04 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 158.2, 155.2 (d, J = 5.0 Hz), 145.7, 134.9, 130.1, 129.5, 126.6, 121.6, 116.8 (d, J = 183.8 Hz), 114.5, 114.3, 61.5 (d, J = 6.0 Hz), 55.4, 53.1 (d, J = 21.2 Hz), 18.0, 16.6 (d, J = 6.0 Hz); ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 18.25 ppm.

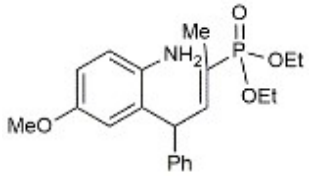
(E)-diisopropyl (3-(2-amino-3-methylphenyl)-3-(4-methoxyphenyl)prop-1-en-1-yl)phosphonate (2u):



Yellow viscous liquid (85%, 354mg) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.11 – 7.05 (m, 2H), 7.05 – 6.86 (m, 3H), 6.78 – 6.67 (m, 2H), 6.60 (d, J = 8.1 Hz, 1H), 5.59 (ddd, J = 20.7, 16.9, 1.4 Hz, 1H), 5.05 – 4.65 (m, 3H, NH_2+CH), 4.51 (dp, J = 8.1, 6.2 Hz, 2H), 3.73 (s, 3H), 2.04 (s, 3H), 1.23

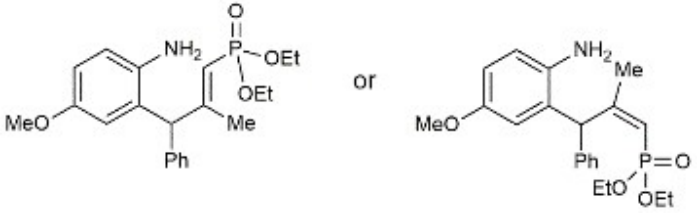
(dd, *J* = 12.5, 6.2 Hz, 12H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 158.2, 154.4 (d, *J* = 6.0 Hz), 145.7, 134.9, 130.1, 129.5, 126.6, 121.6, 118.3 (d, *J* = 183.8 Hz), 114.5, 114.3, 69.9 (d, *J* = 5.0 Hz), 55.4, 52.9 (d, *J* = 22.2 Hz), 24.1 (d, *J* = 4.0 Hz), 24.0 (d, *J* = 5.0 Hz); 18.0.^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 16.32 ppm.

(E)-diethyl (4-(2-amino-5-methoxyphenyl)-4-phenylbut-2-en-2-yl)phosphonate (2v):



Whites solid (92%, 358mg, M.P. 141-144 ℃). ^{1}H NMR (400 MHz, DMSO-d6) δ 7.38 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 6.88 – 6.72 (m, 1H), 6.68 – 6.59 (m, 2H), 6.59 – 6.52 (m, 1H), 5.14 (dd, J = 9.1, 3.2 Hz, 1H), 4.45 (d, J = 4.6 Hz, 2H), 4.04 – 3.89 (m, 4H), 3.66 – 3.58 (m, 3H), 1.86 – 1.75 (m, 3H), 1.27 – 1.18 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.5, 147.3 (d, *J* = 10.1 Hz), 142.7, 140.0, 129.0, 128.2, 127.7, 126.9, 125.2 (d, *J* = 175.7 Hz), 117.0, 114.4, 112.9, 61.6 (d, *J* = 5.0 Hz), 55.6, 43.8 (d, *J* = 19.1 Hz), 16.6 (d, *J* = 6.0 Hz), 13.3(d, *J* = 10.1 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 20.63 ppm;HRMS(ESI): Calcd for$C_{21}H_{28}NO_4NaP$ $[M + Na]^+$: 412.1654, Found: 412.1649.

(E and Z)-diethyl (3-(2-amino-5-methoxyphenyl)-2-methyl-3-phenylprop-1-en-1-yl)phosphonate (2w and 2x):

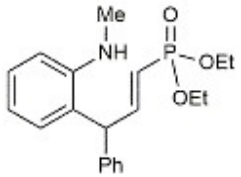


2v: Whitewaxy solid(95%, 365mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.14 – 7.09 (m, 2H), 6.68 – 6.60 (m, 2H), 6.16 (d, *J* = 2.6 Hz, 1H), 6.00 (s, 1H), 5.91 (dq, *J* = 17.7, 1.2 Hz, 1H), 4.78 (s, 2H, NH_2), 4.01 – 3.92 (m, 2H), 3.80 – 3.70 (m, 2H), 3.53 (s, 3H), 1.78 (dd, *J* = 1.4, 0.7 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 160.9 (d, *J* = 7.0Hz), 150.6, 141.7, 141.2, 128.8, 128.7, 126.8, 125.4, 116.4, 116.1 (d, *J* = 183.8 Hz), 116.0, 113.2, 61.5 (d, *J* = 6.0 Hz), 61.4 (d, *J* = 5.0 Hz), 55.6, 48.0 (d, *J* = 6.0 Hz), 23.8 (d, *J* = 23.2 Hz), 16.5 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 7.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 16.72.HRMS(ESI): Calcd for$C_{21}H_{28}NO_4NaP$ $[M + Na]^+$: 412.1654, Found: 412.1650.

2w: White solid(95%, 365mg, M.P. 127-130 ℃),^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.25 (m, 1H), 7.17 – 7.10 (m, 2H), 6.70 – 6.62 (m, 2H), 6.26 – 6.19 (m, 1H), 5.04 – 4.94 (m, 2H), 4.48 (s, 2H, NH_2), 3.99 – 3.88 (m, 4H), 3.58 (s, 3H), 2.10 – 2.04 (m, 3H), 1.21

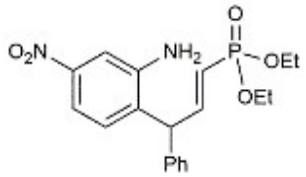
(td, *J* = 7.0, 5.0 Hz, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 163.1 (d, *J* = 8.0 Hz), 151.1, 140.5, 140.5, 129.6, 129.0, 127.3, 126.0, 116.8, 115.2, 114.0 (d, *J* = 186.8 Hz), 112.9, 61.2 (d, *J* = 6.0 Hz), 61.1 (d, *J* = 6.0 Hz), 55.5, 54.9 (d, *J* = 21.2 Hz), 21.1 (d, *J* = 7.0 Hz), 16.6 (d, *J* = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.80.HRMS(ESI): Calcd for$C_{21}H_{28}NO_4NaP$ $[M + Na]^+$: 412.1654, Found: 412.1652.

(E)-diethyl (3-(2-(methylamino)phenyl)-3-phenylprop-1-en-1-yl)phosphonate (2y):



Dark orangewaxysolid (96%, 344mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 – 7.32 (m, 2H), 7.30 – 7.24 (m, 1H), 7.21 – 7.16 (m, 2H), 7.13 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.00 (ddd, *J* = 21.2, 17.0, 6.5 Hz, 1H), 6.81 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.64 – 6.54 (m, 2H), 5.50 (ddd, *J* = 20.8, 17.0, 1.5 Hz, 1H), 5.17 (d, *J* = 5.3 Hz, 1H), 5.12 (dt, *J* = 6.7, 1.9 Hz, 1H), 3.97 (dqd, *J* = 8.4, 7.2, 4.0 Hz, 4H), 2.71 (d, *J* = 3.0 Hz, 3H), 1.24 – 1.19 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.8 (d, *J* = 5.0 Hz), 147.1, 141.1, 129.2, 129.0, 128.6, 128.3, 127.2, 125.3, 117.6 (d, *J* = 183.7 Hz), 116.1, 110.2, 61.6 (d, *J* = 5.0 Hz), 47.8 (d, *J* = 21.2 Hz), 30.6, 16.6 (d, *J* = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.89.HRMS(ESI):Calcd for$C_{20}H_{26}NO_3NaP$ $[M + Na]^+$: 382.1548, Found: 382.1543.

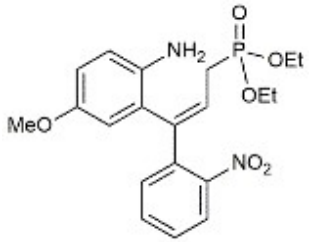
(E)-diethyl (3-(2-amino-4-nitrophenyl)-3-phenylprop-1-en-1-yl)phosphonate (2cc):



Dark orangewaxy solid (43%, 167mg).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.44 (t, *J* = 2.3 Hz, 1H), 7.41 (dd, *J* = 6.9, 2.0 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.24 (m, 1H), 7.08 – 6.87 (m, 2H), 5.97 (ddd, *J* = 18.9, 17.1, 1.6 Hz, 1H), 5.19 – 5.09 (m, 1H), 4.12 – 4.00 (m, 4H), 1.32 – 1.26 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, Chloroform-*d*) δ 150.6 (d, *J* = 6.0 Hz), 149.2, 147.3, 138.5, 129.7, 129.2, 128.6,

127.4, 119.5, 117.3 (d, J = 187.8 Hz), 112.7, 107.4, 62.1 (d, J = 5.0 Hz), 62.0 (d, J = 5.0 Hz), 60.4 (d, J = 22.2 Hz), 16.3 (d, J = 6.0 Hz), 16.2 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 17.69.HRMS(ESI): Calcd for$C_{19}H_{23}N_2O5NaP$ [M + Na]$^+$: 413.1242, Found:.

(E)-diethyl (3-(2-amino-5-methoxyphenyl)-3-(2-nitrophenyl)allyl)phosphonate(3dd):



Orange viscous liquid (72%, 302.5 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (dd, J = 8.2, 1.3 Hz, 1H), 7.63 (td, J = 7.6, 1.4 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.33 (dd, J = 7.9, 1.4 Hz, 1H), 6.68 (dd, J = 3.3, 1.5 Hz, 2H), 6.59 (dq, J = 2.2, 1.3, 0.9 Hz, 1H), 5.37 (s, 1H), 4.62 (d, J = 4.4 Hz, 1H), 4.02 – 3.91 (m, 5H), 3.59 (s, 3H), 2.13 (dd, J = 17.4, 6.6 Hz, 2H), 1.21 – 1.16 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.1, 149.4, 144.7, 138.0, 133.8, 131.5, 130.2, 124.4, 114.0, 111.8, 110.6, 63.4 (d, J = 3.0 Hz), 61.6 (d, J = 7.0 Hz), 61.5 (d, J = 7.0 Hz), 55.7, 50.0 (d, J = 13.1 Hz) 31.1 (d, J = 136.3 Hz), 16.5 (d, J = 6.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, DMSO-d_6) δ 28.27 ppm; HRMS(ESI):Calcd for$C_{20}H_{25}N_2O_6NaP$ [M + Na]$^+$: 443.1348, Found: 443.1347.

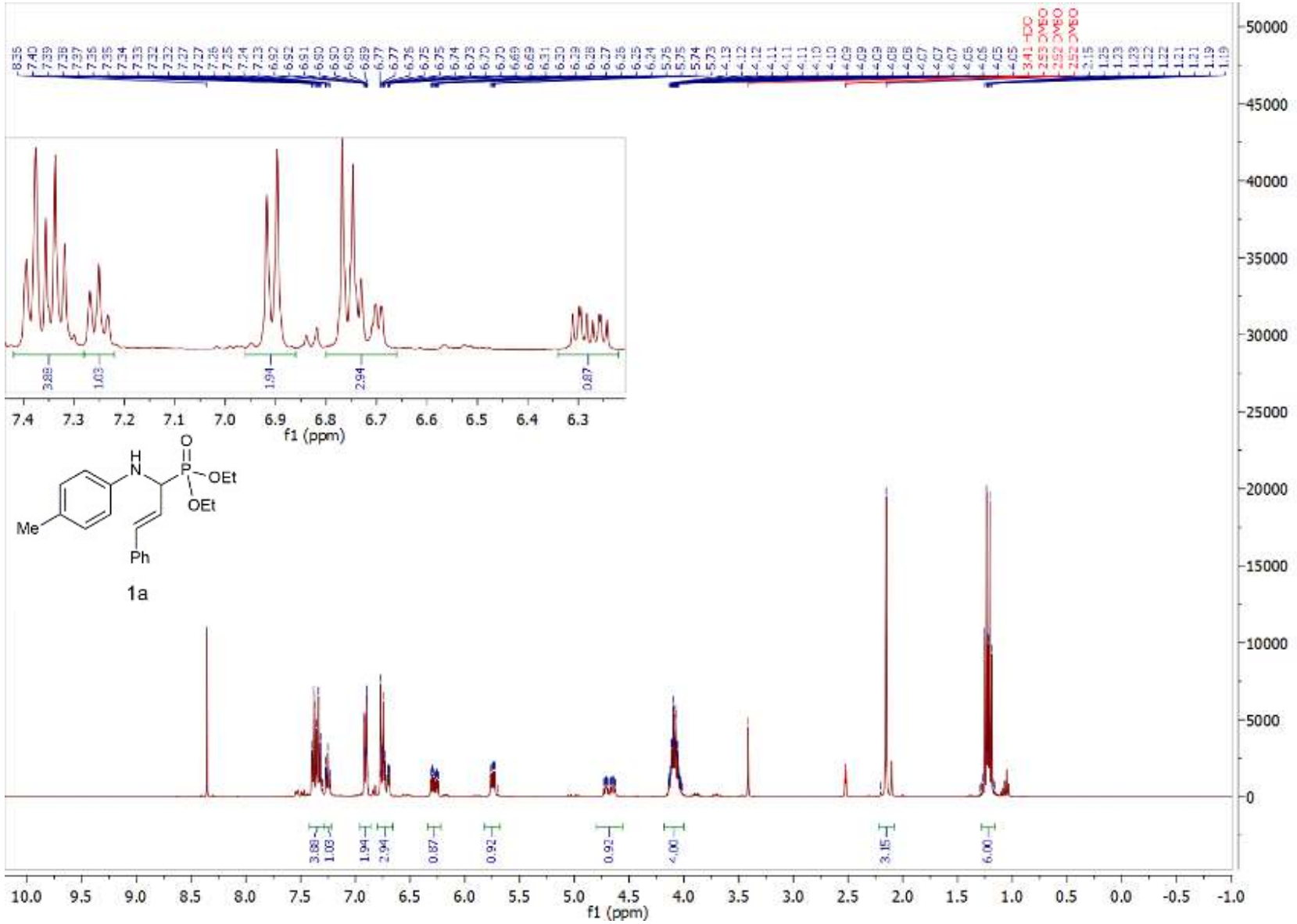


Figure S1: ^{1}H NMR Spectra of 1a

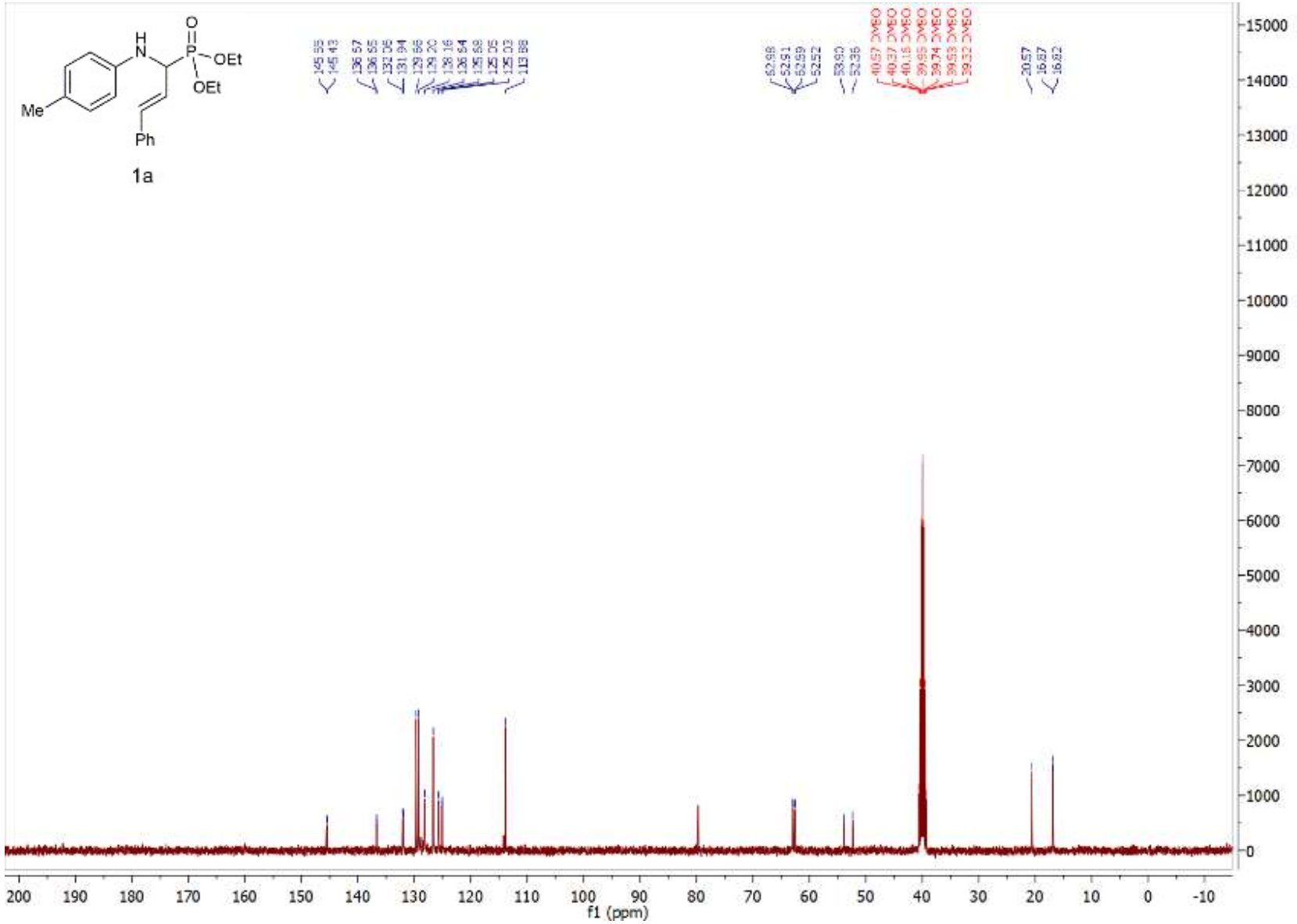


Figure S2: ^{13}C NMR Spectra of 1a

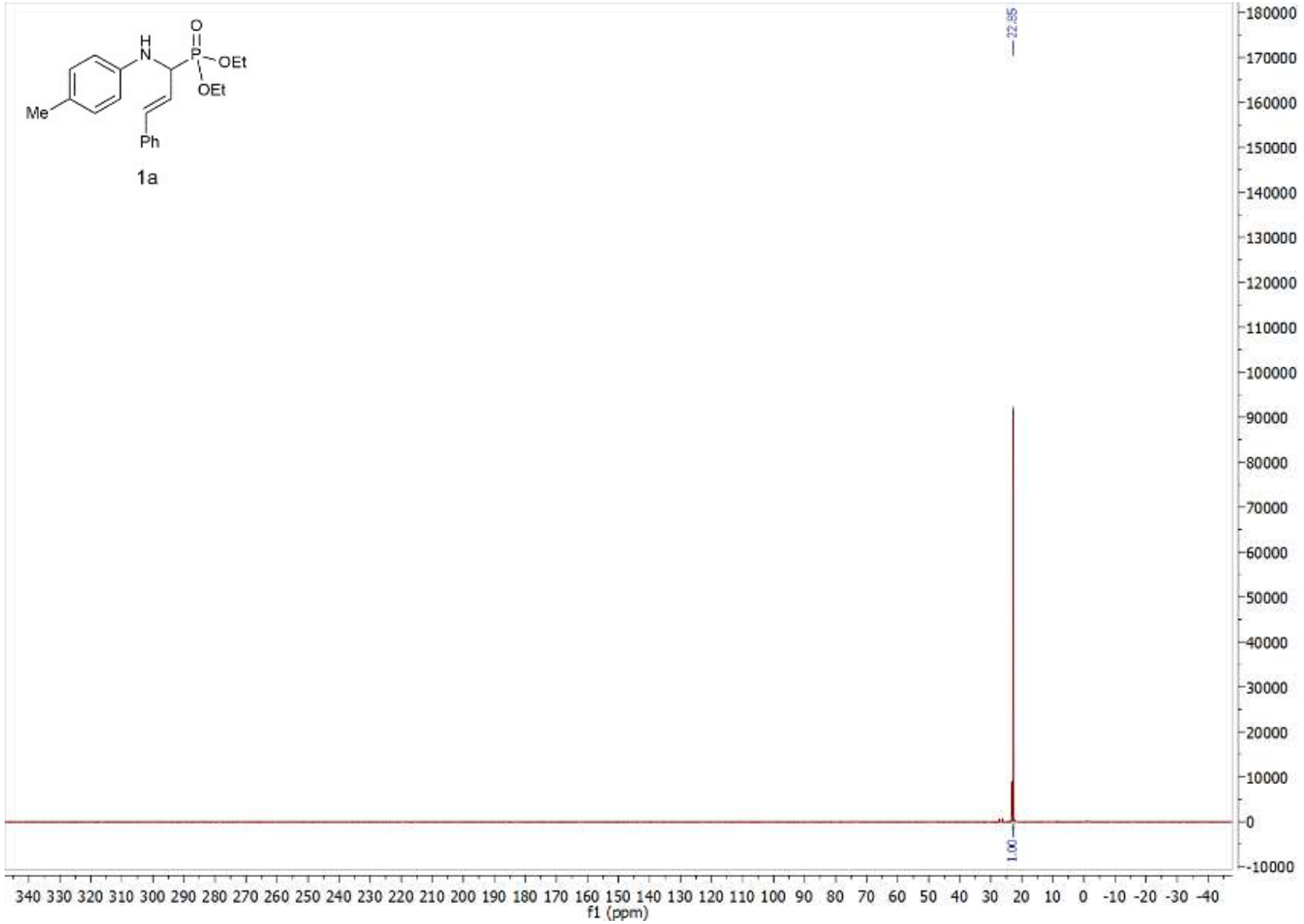


Figure S3: ^{31}P NMR Spectra of 1a

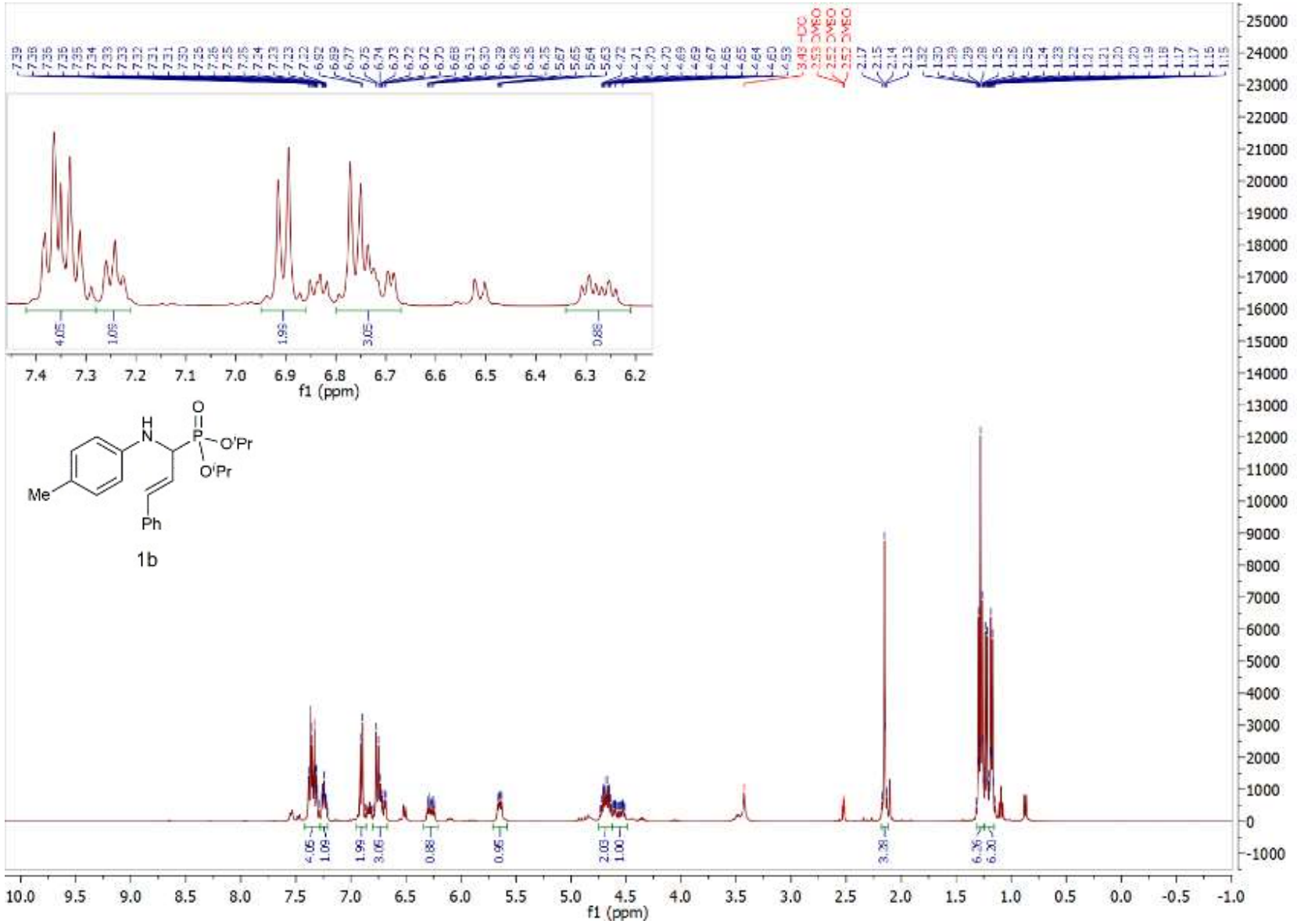


Figure S4: ^{1}H NMR Spectra of 1b

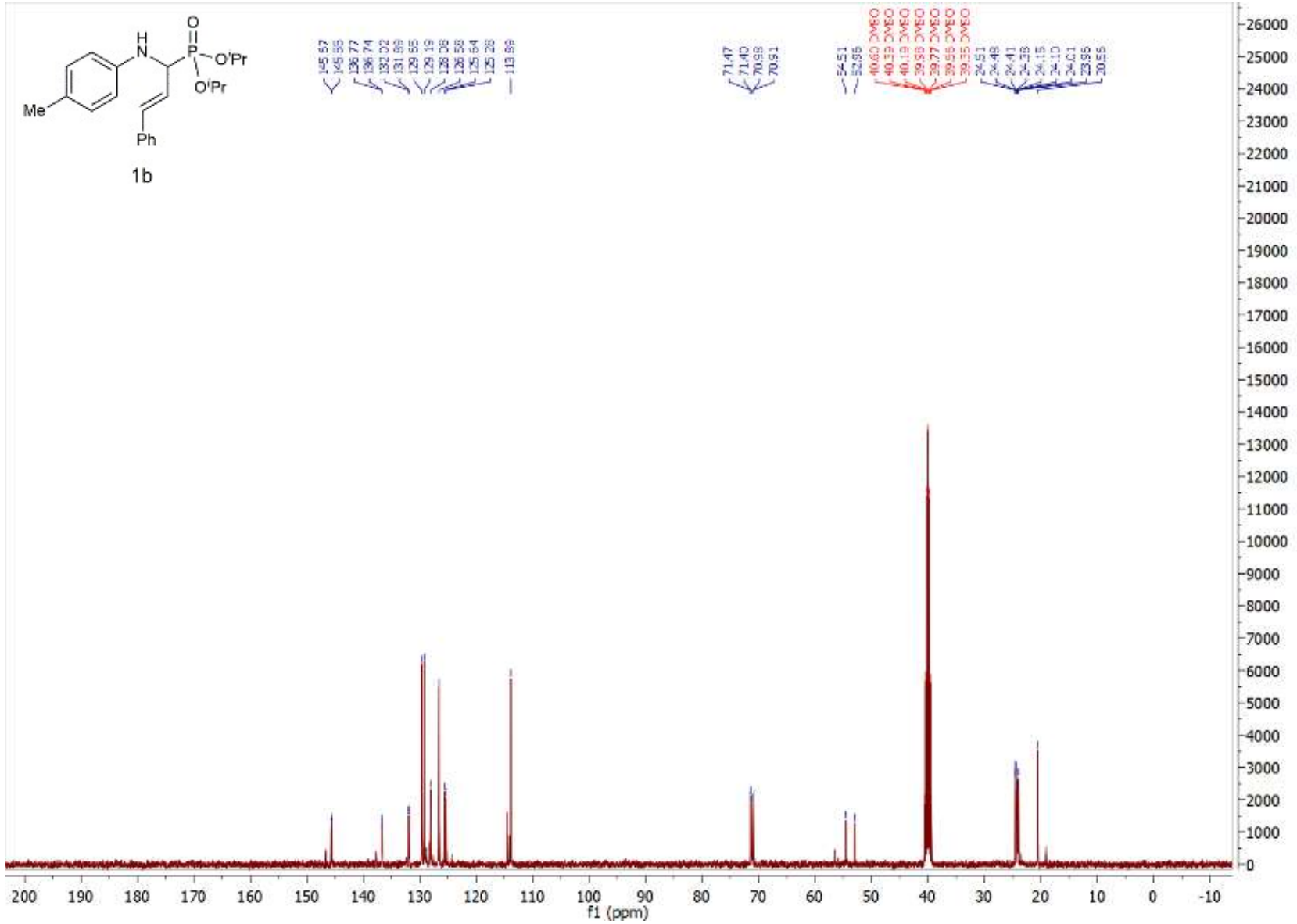


Figure S5: ^{13}C NMR Spectra of 1b

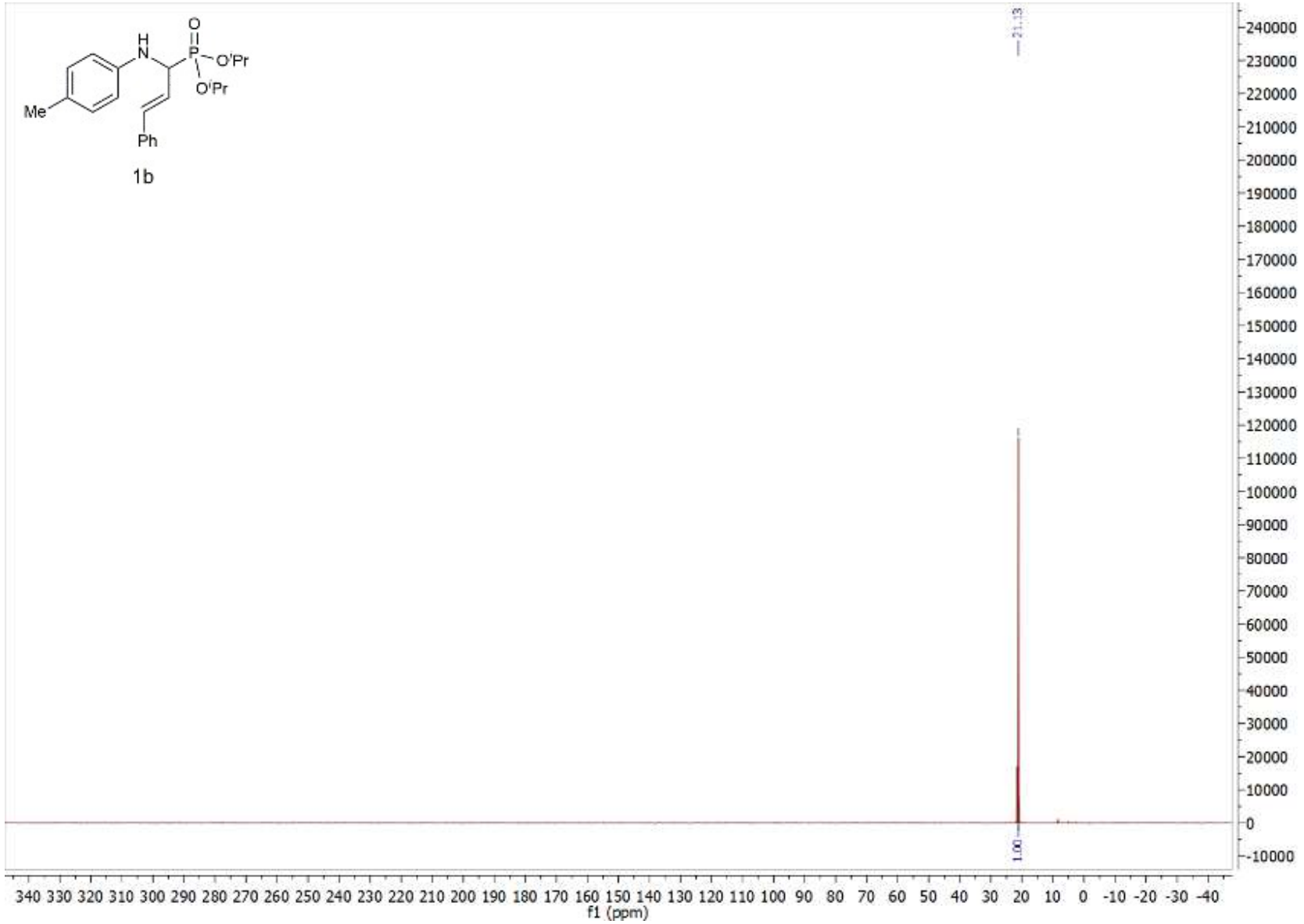


Figure S6: ^{31}P NMR Spectra of 1b

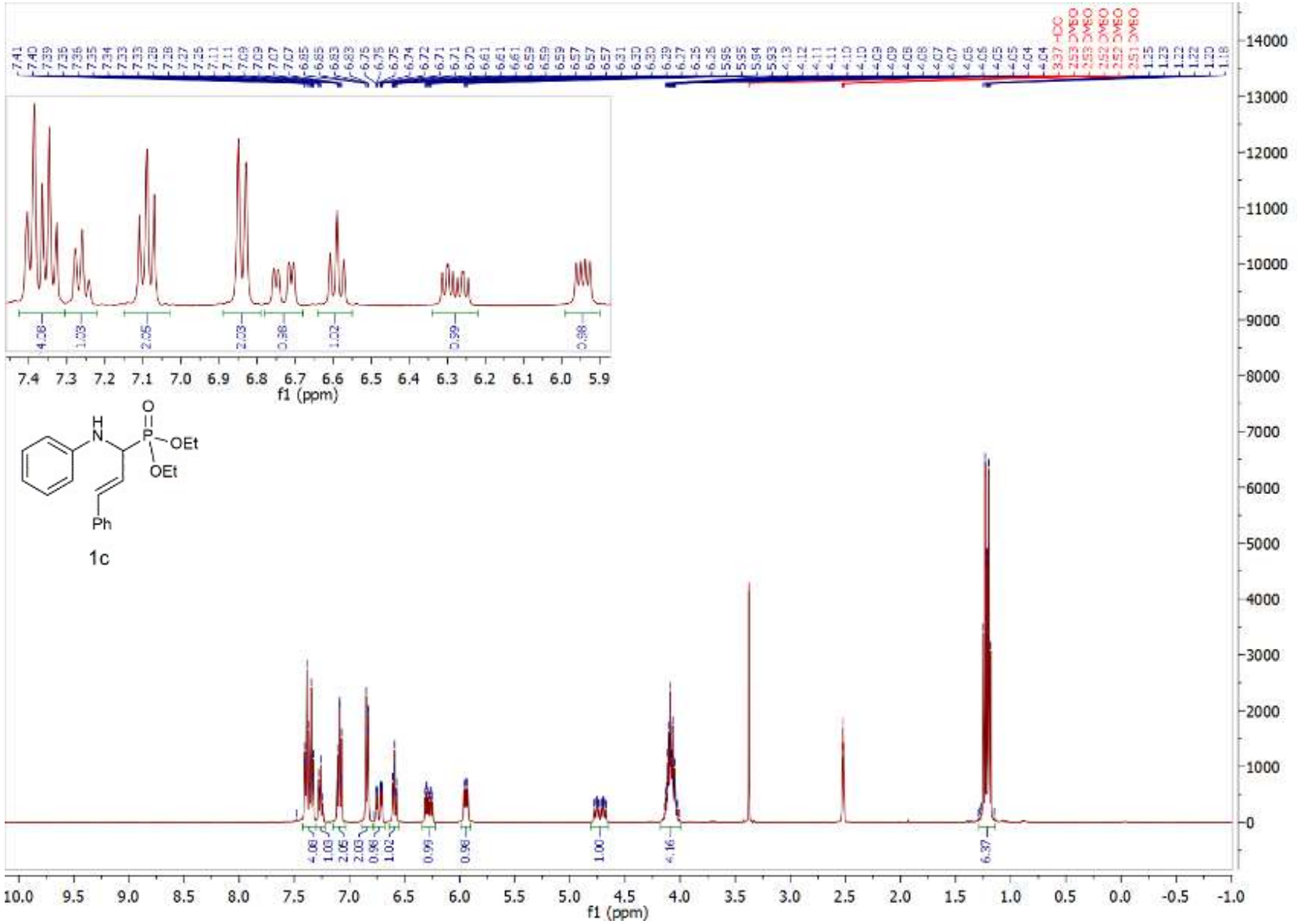


Figure S7: ^{1}H NMR Spectra of 1c

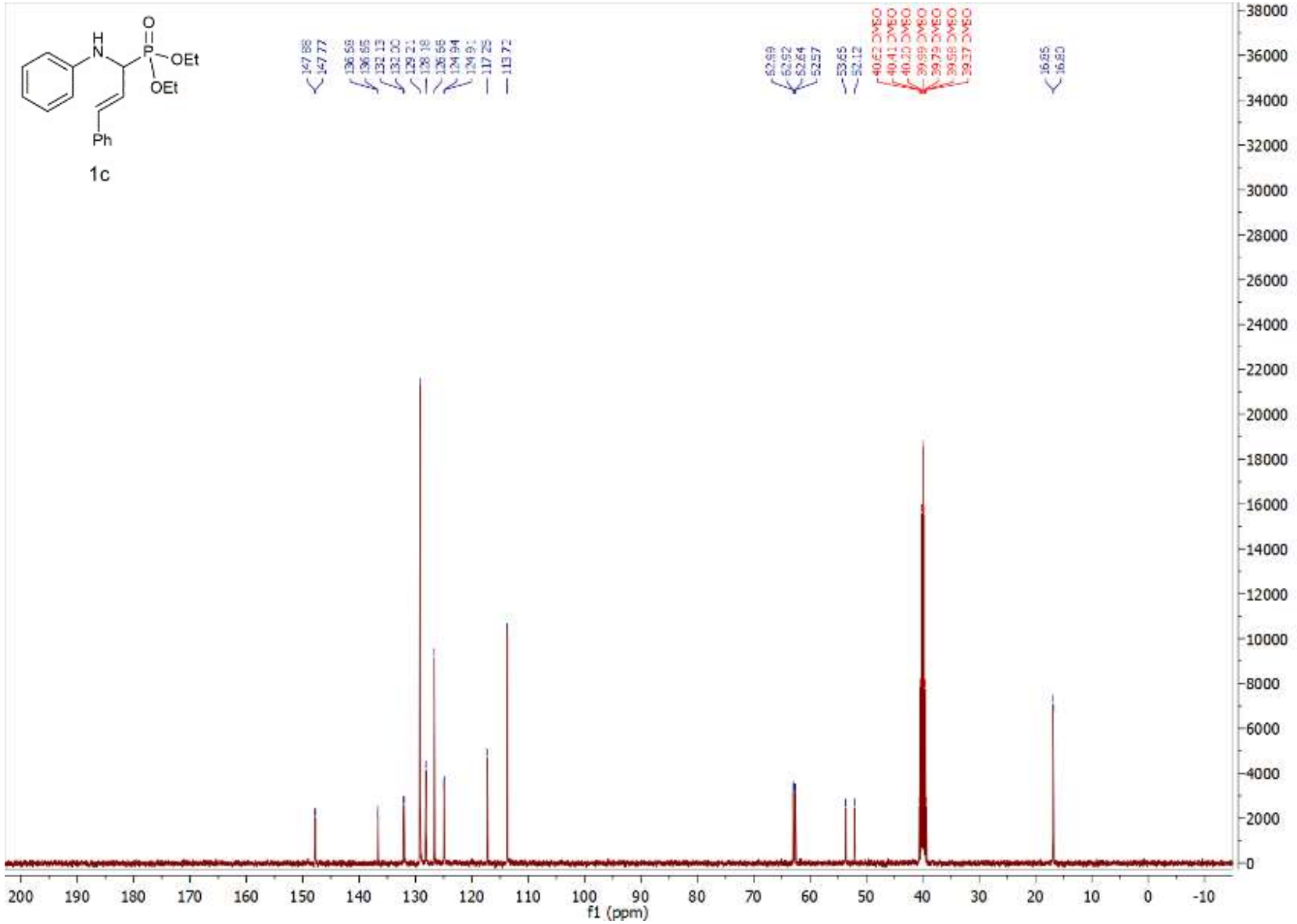


Figure S8: ^{13}C NMR Spectra of 1c

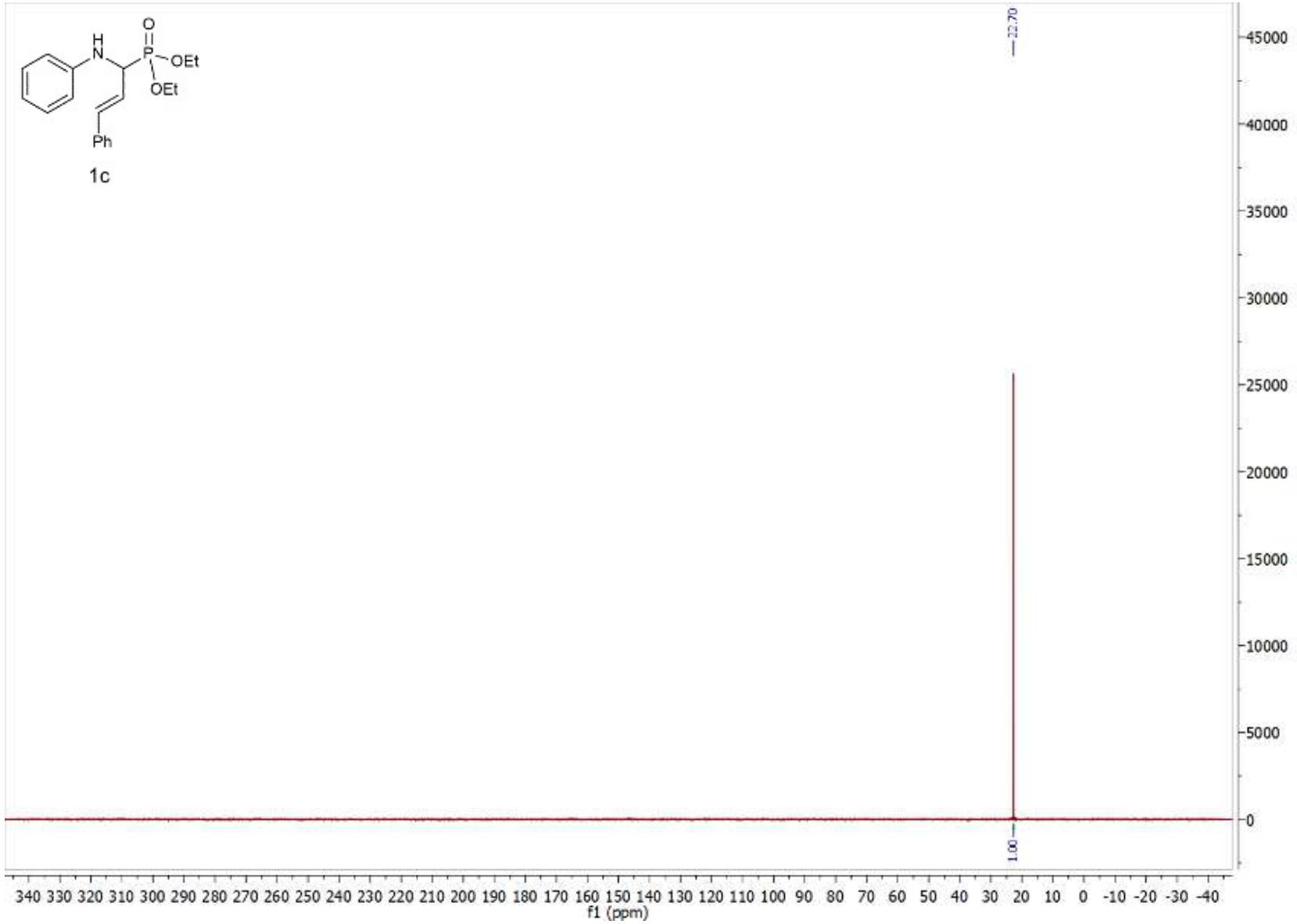


Figure S9: ^{31}P NMR Spectra of 1c

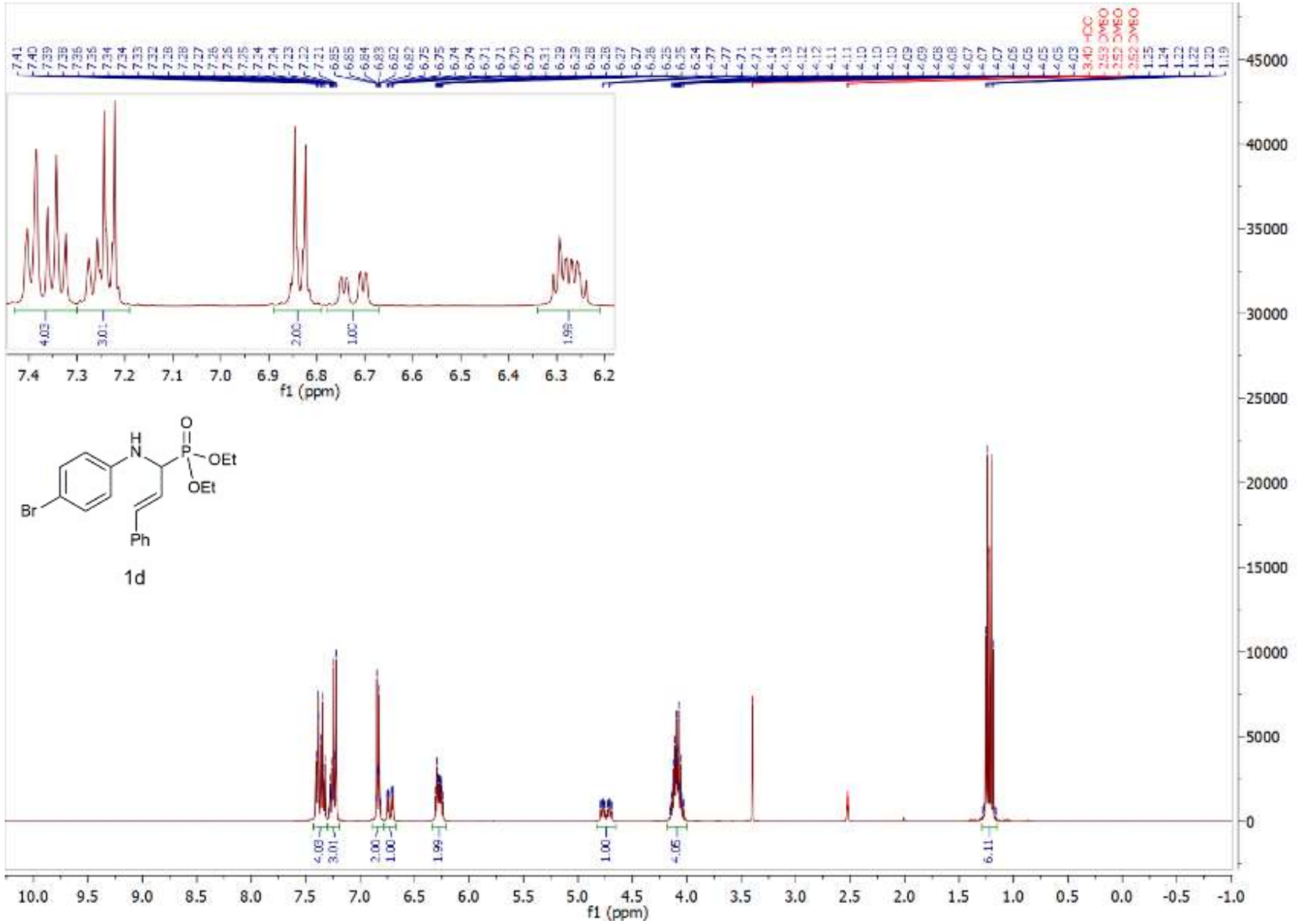


Figure S10: ^{1}H NMR Spectra of 1d

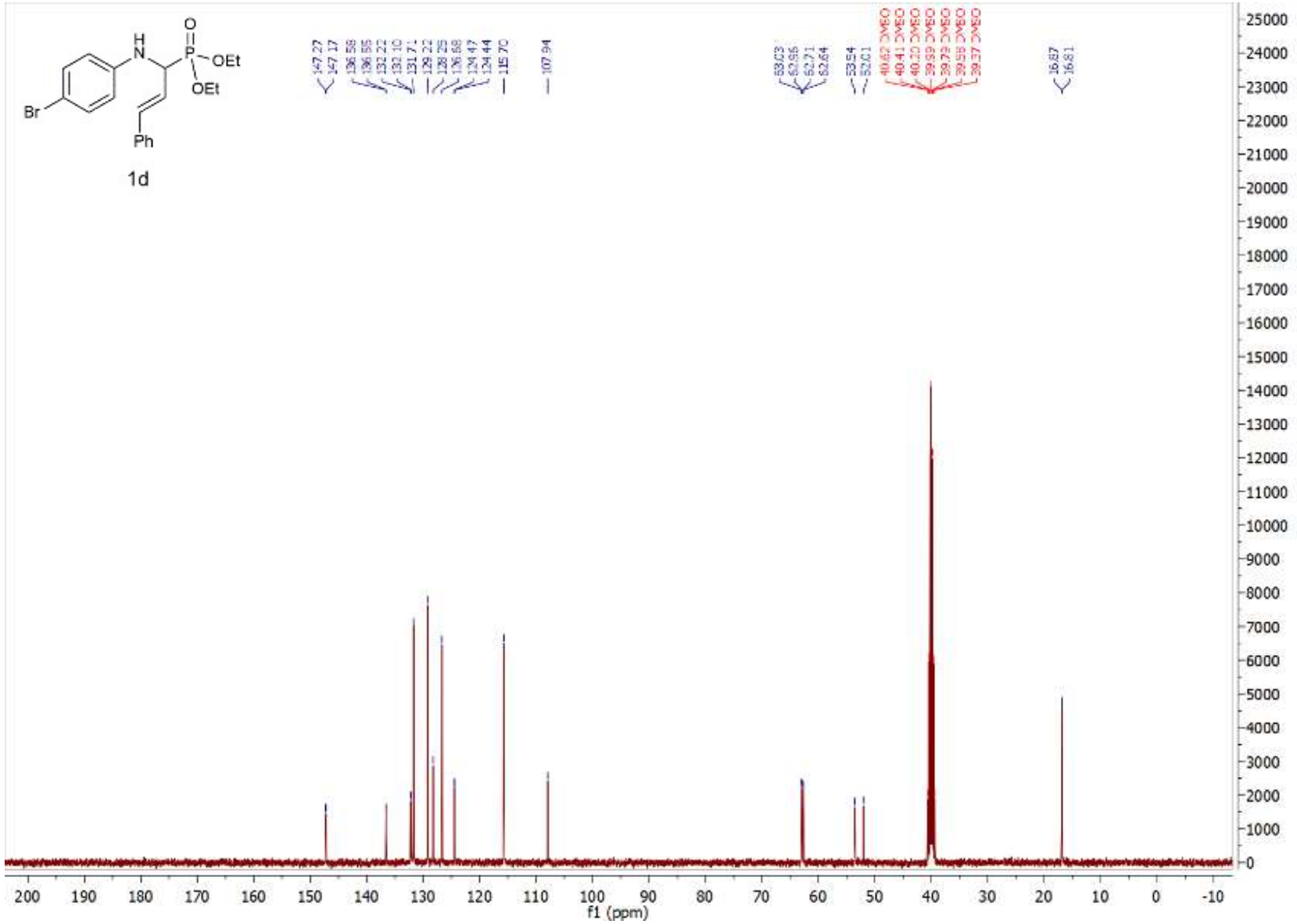


Figure S11: ^{13}C NMR Spectra of 1d

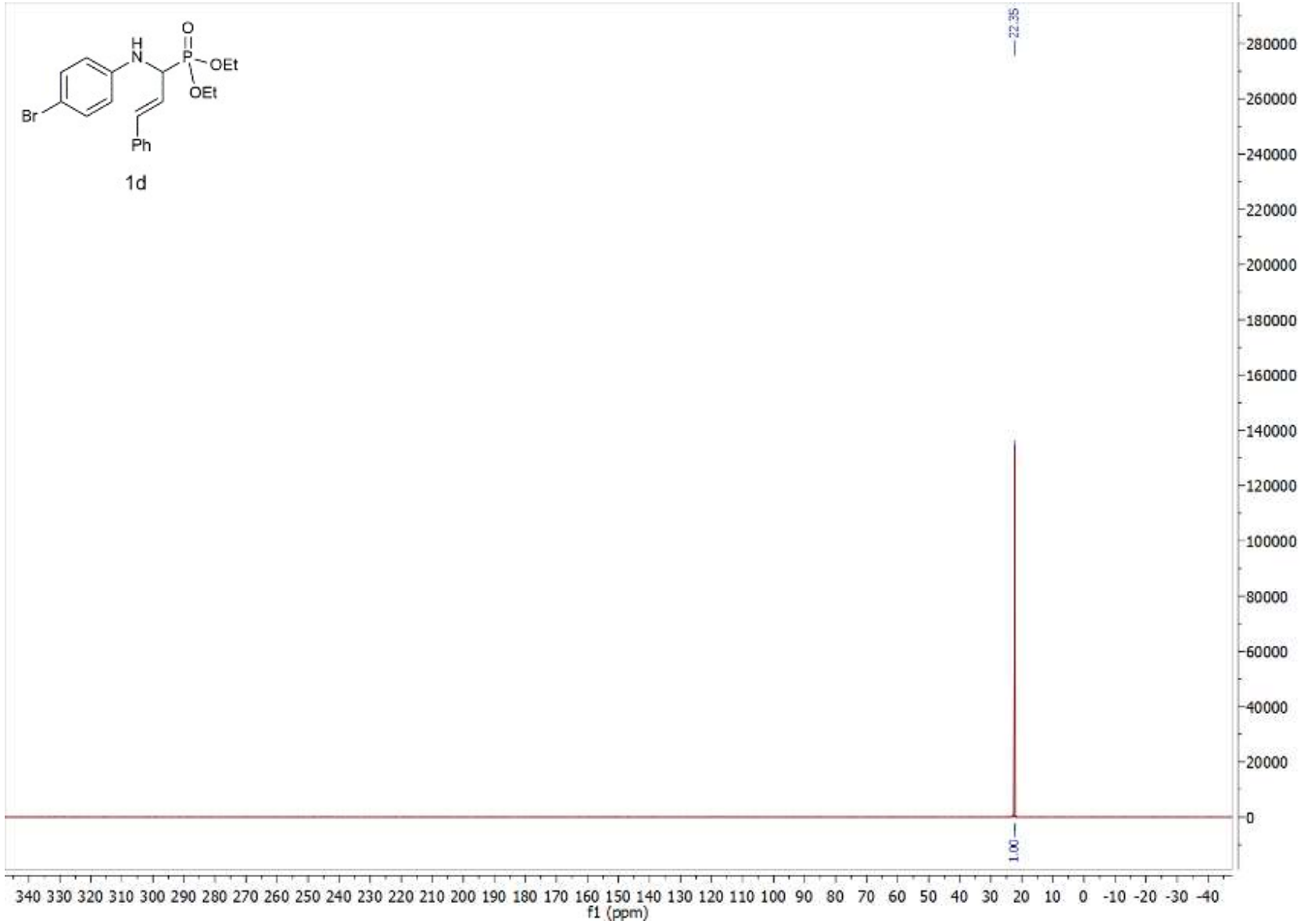


Figure S12: ^{31}P NMR Spectra of 1d

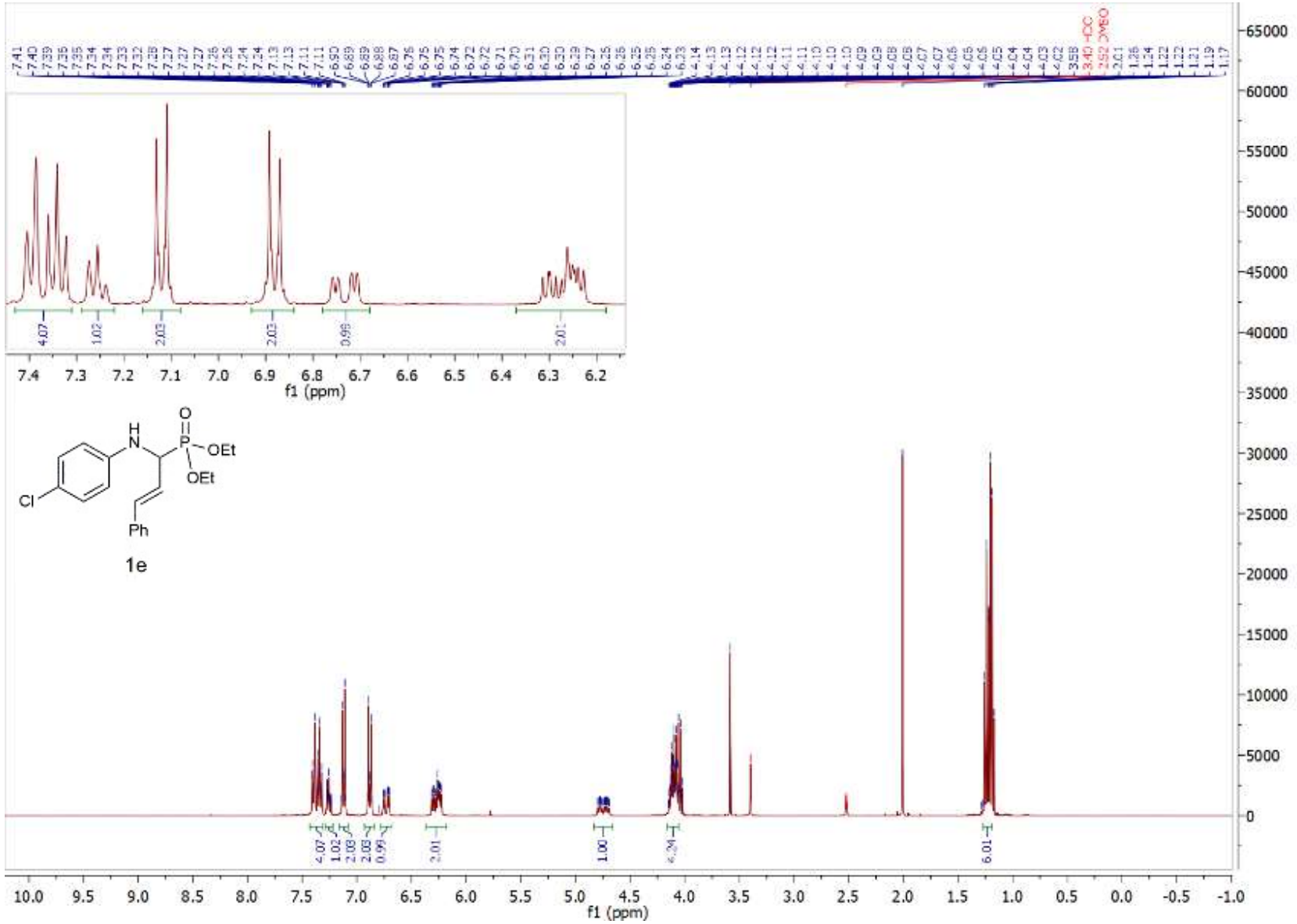


Figure S13: ^{1}H NMR Spectra of 1e

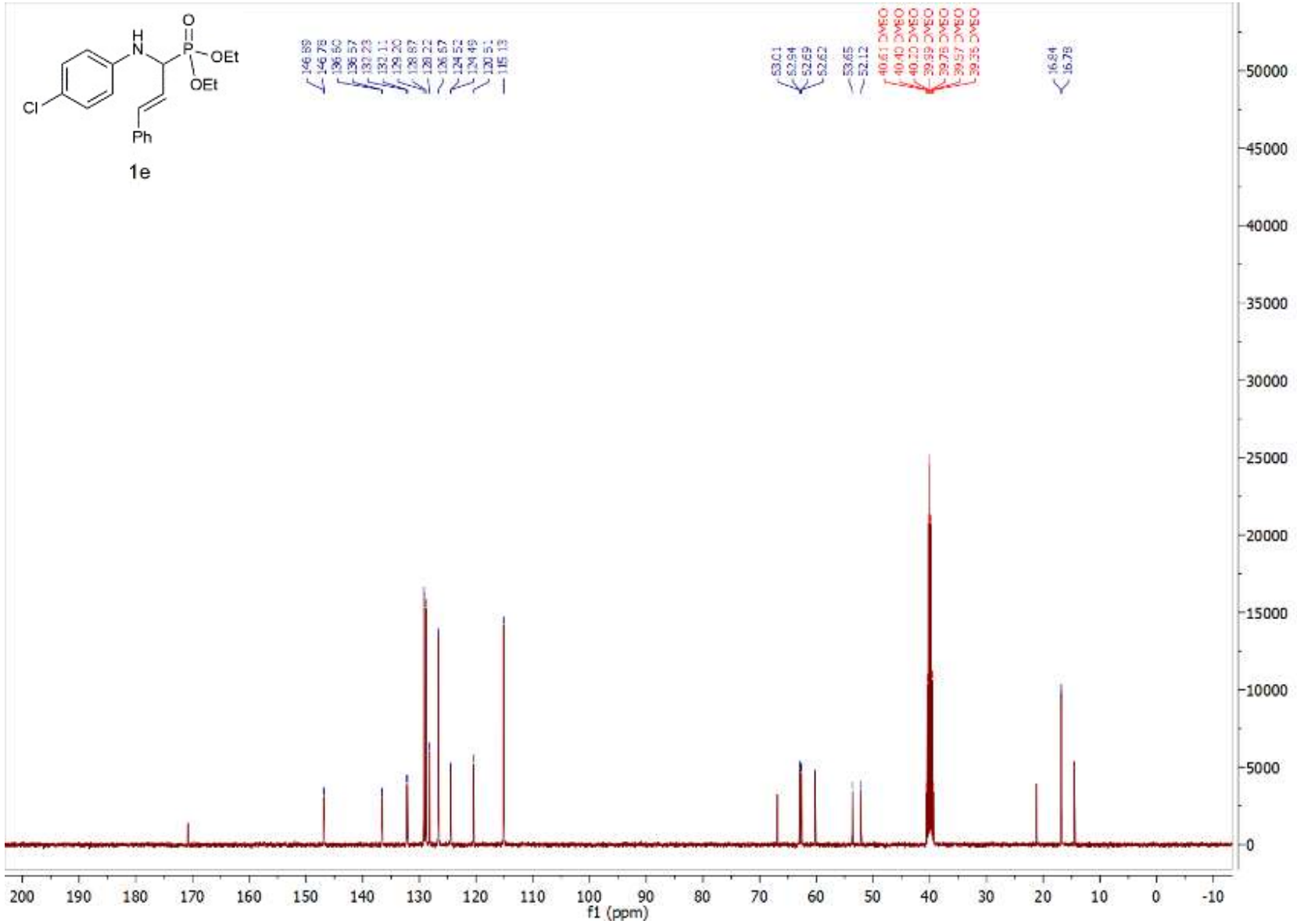


Figure S14: ^{13}C NMR Spectra of 1e

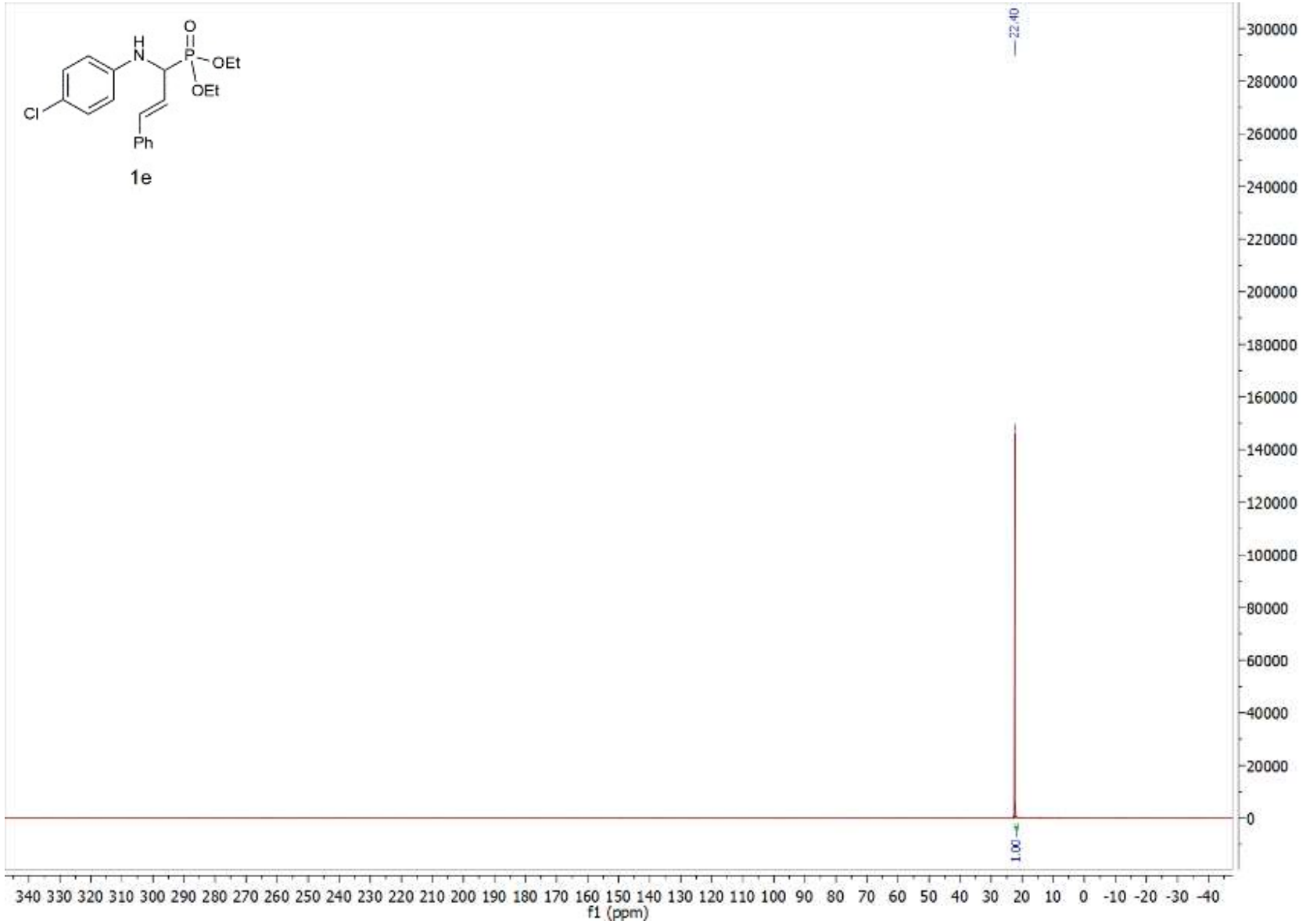


Figure S15: ^{31}P NMR Spectra of 1e

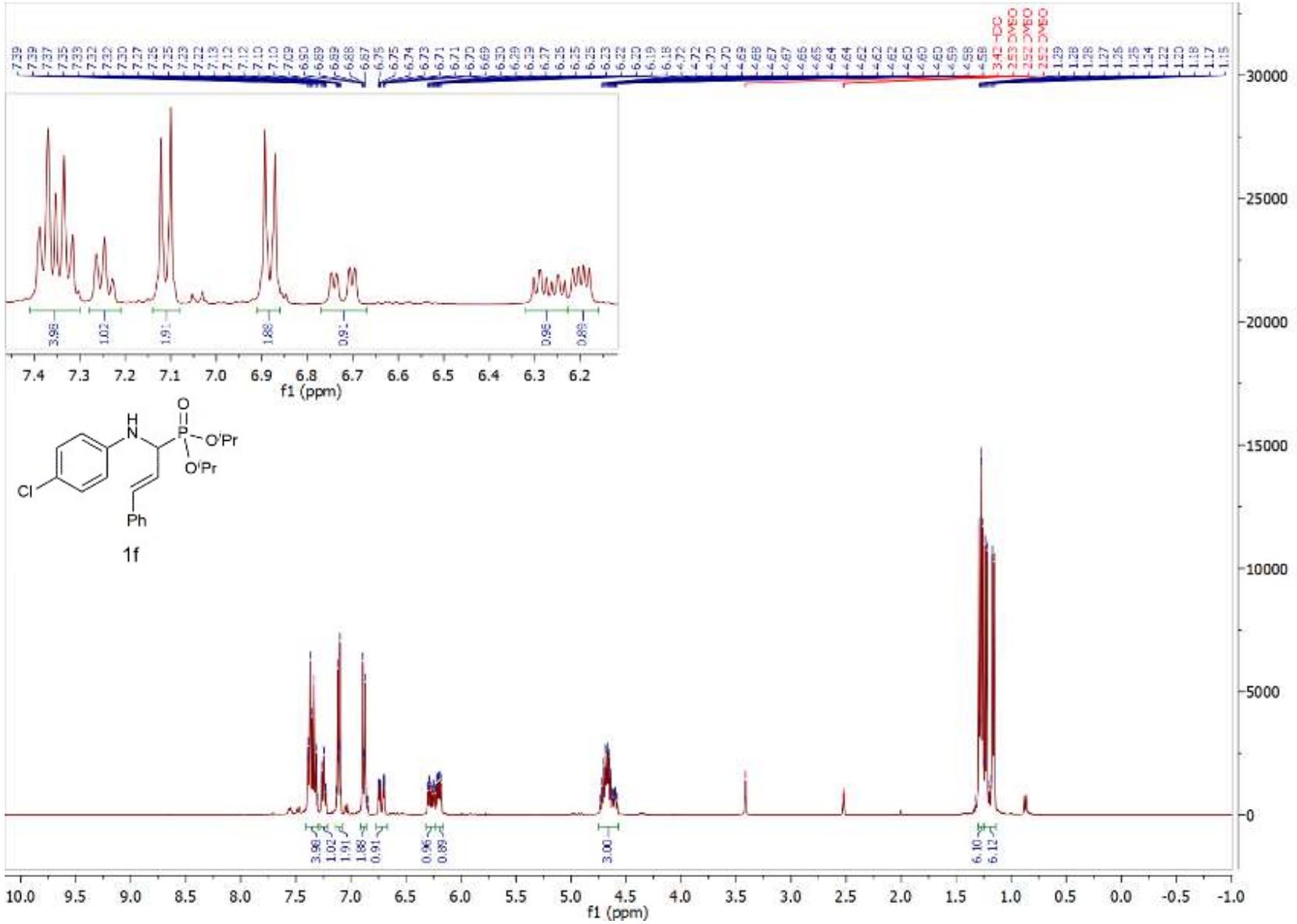


Figure S16: ^{1}H NMR Spectra of 1f

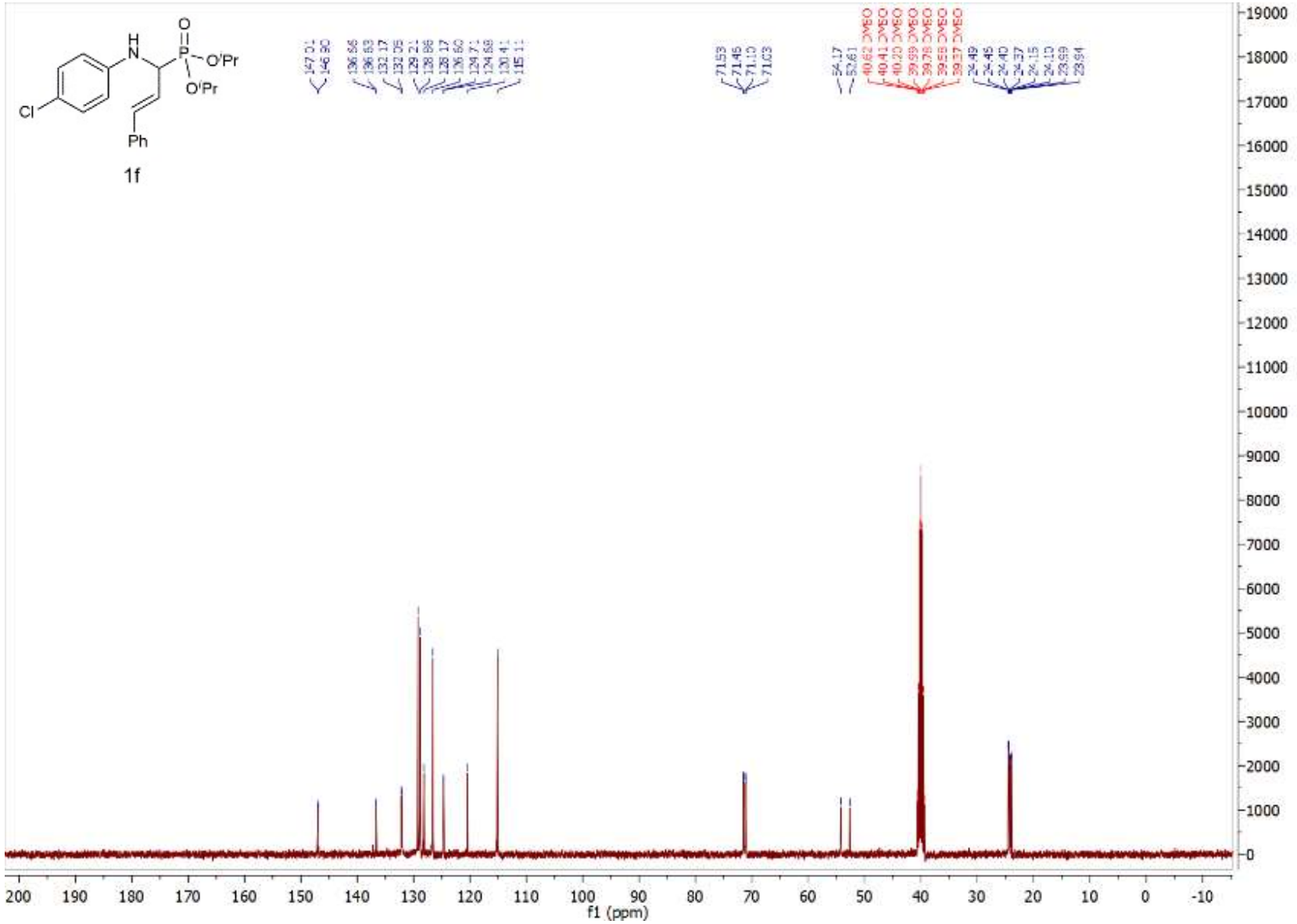


Figure S17: ^{13}C NMR Spectra of 1f

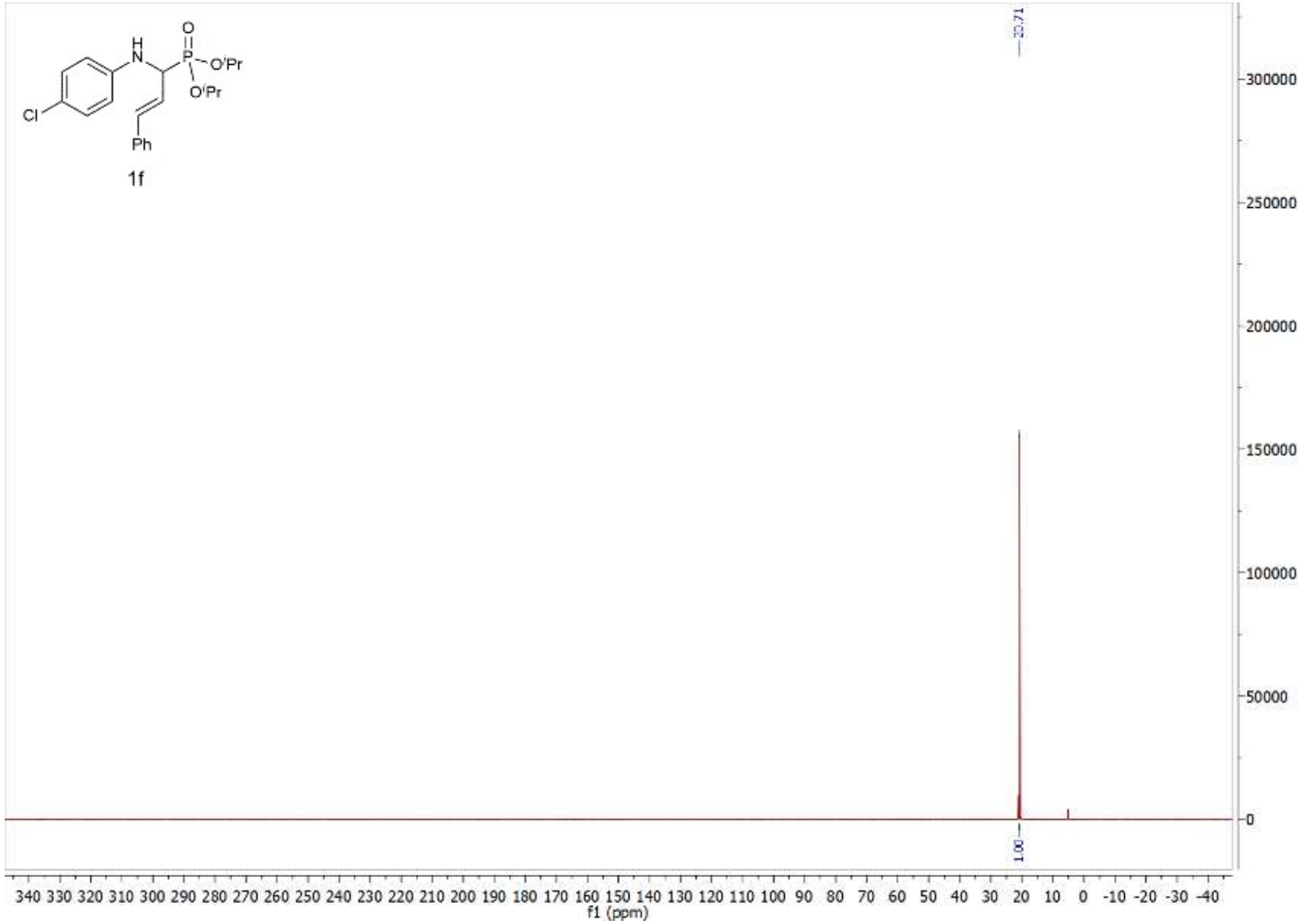


Figure S18: ^{31}P NMR Spectra of 1f

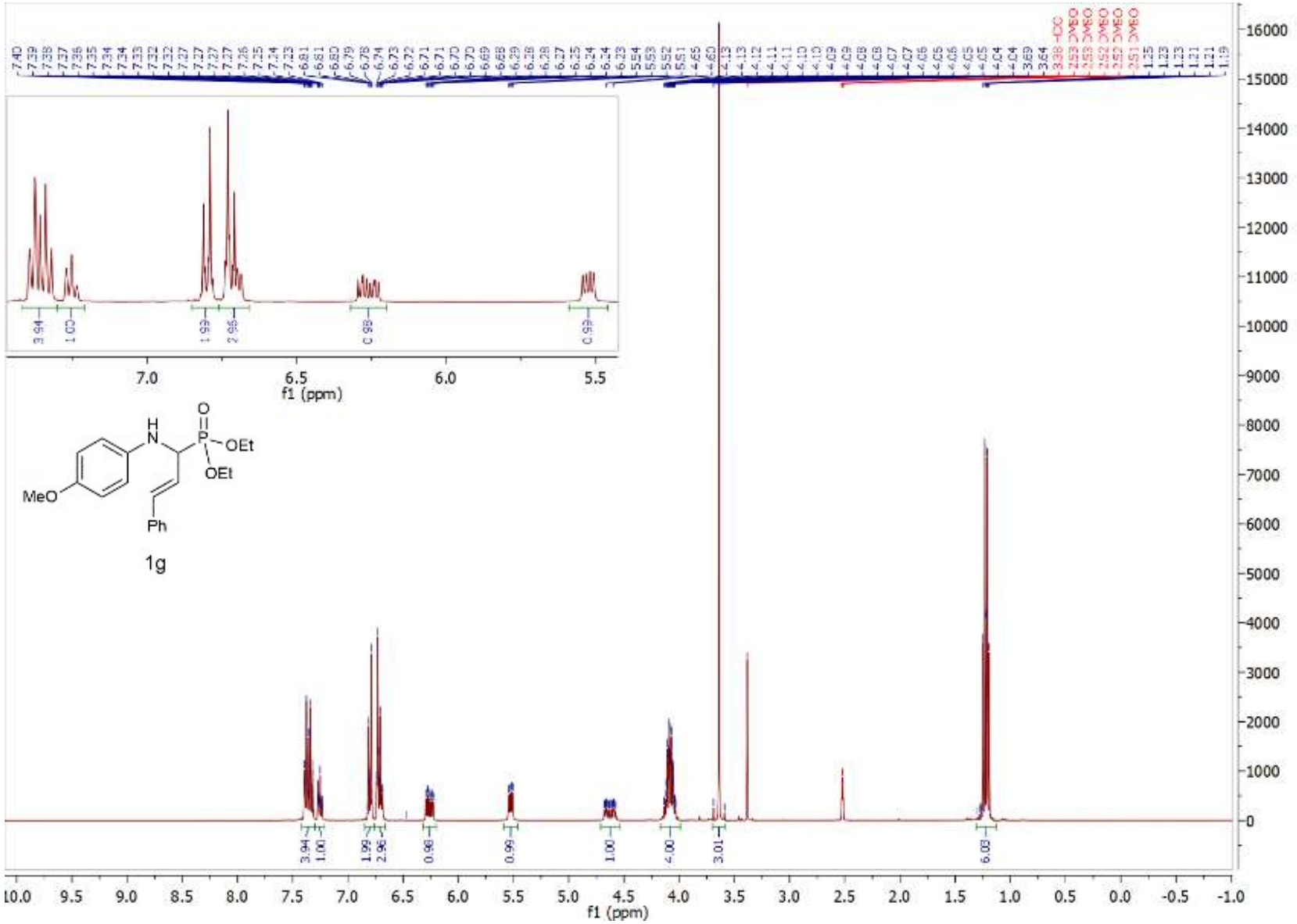


Figure S19: ^{1}H NMR Spectra of 1g

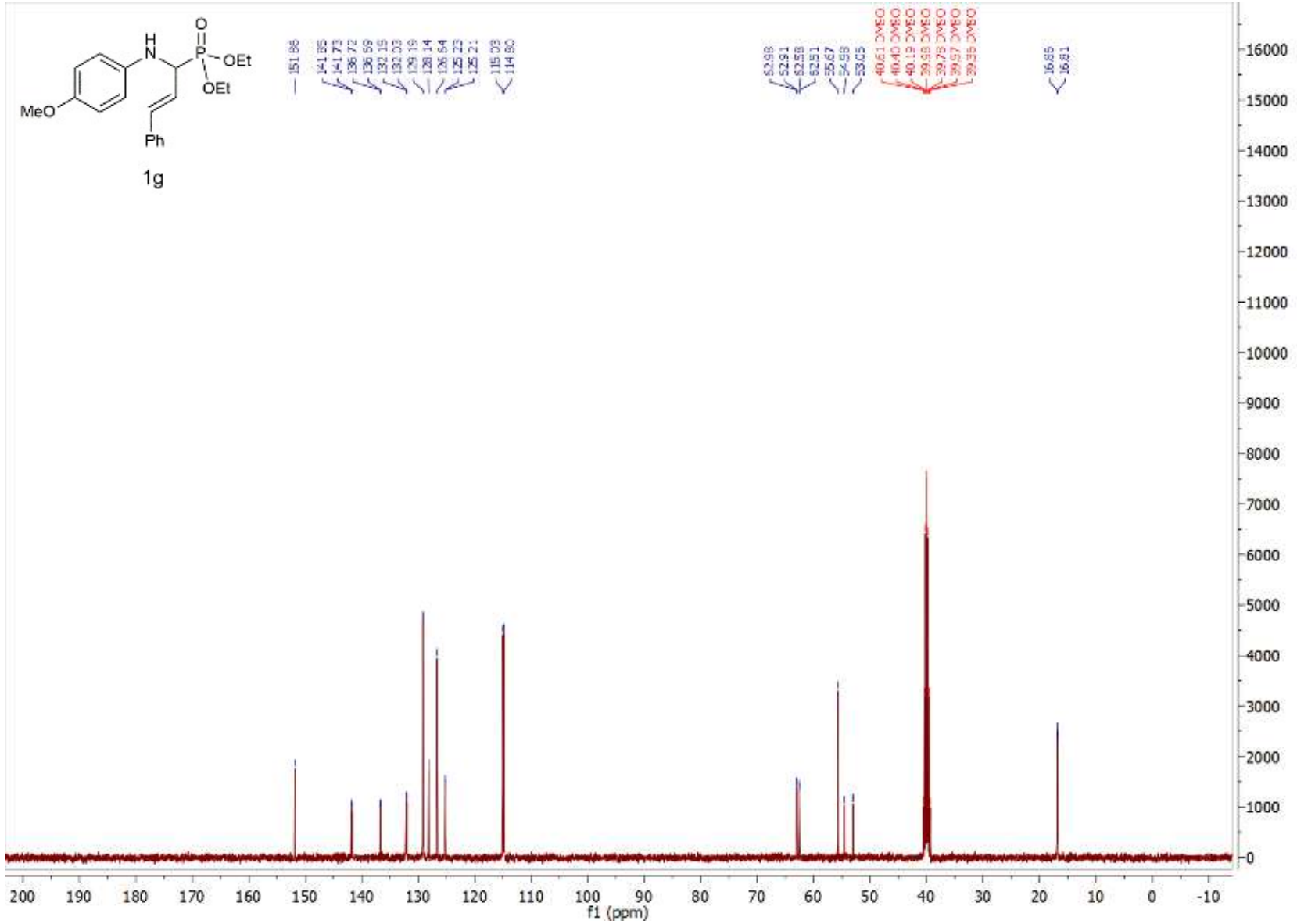


Figure S20: ^{13}C NMR Spectra of 1g

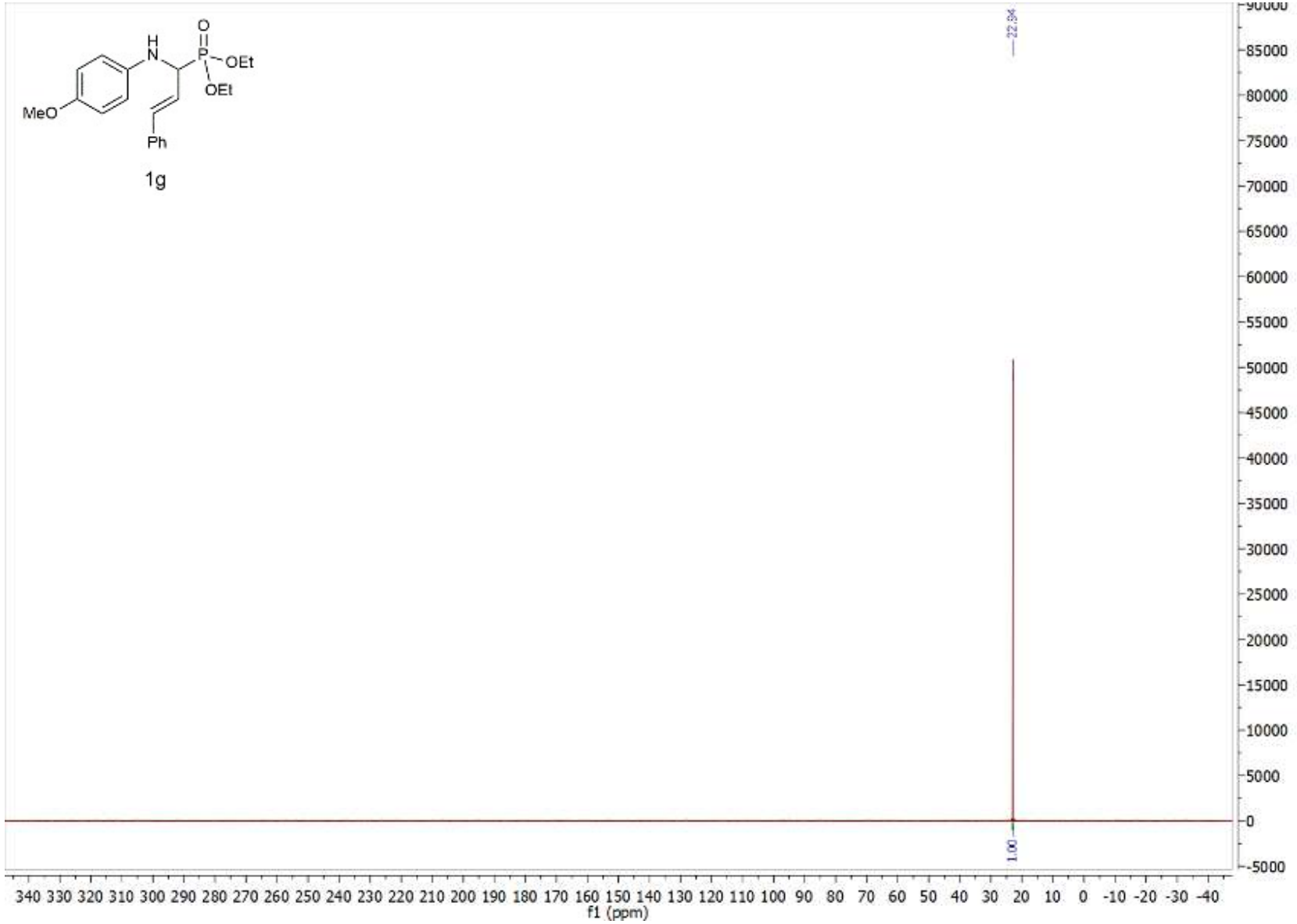


Figure S21: ^{31}P NMR Spectra of 1g

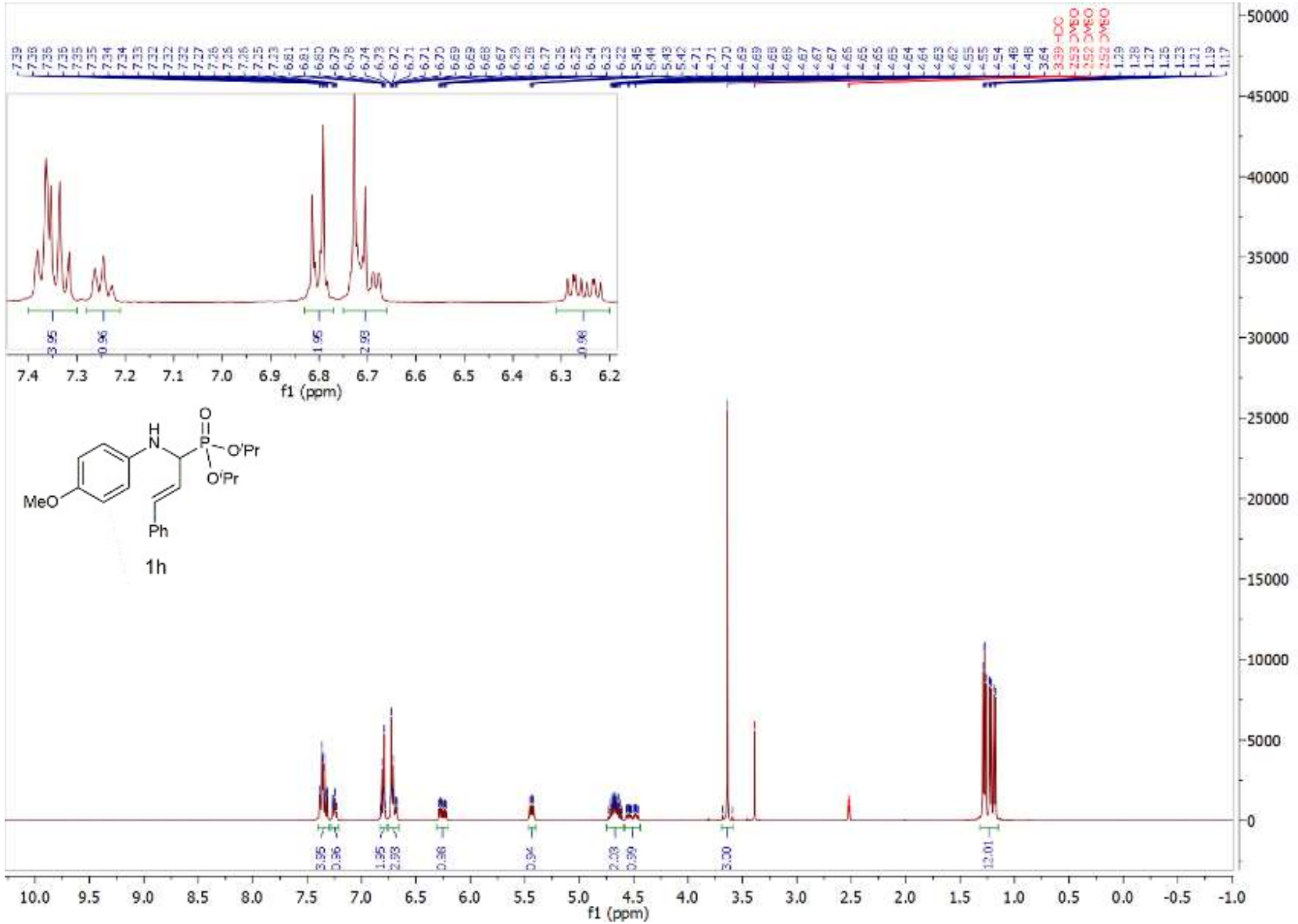


Figure S22: ^{1}H NMR Spectra of 1h

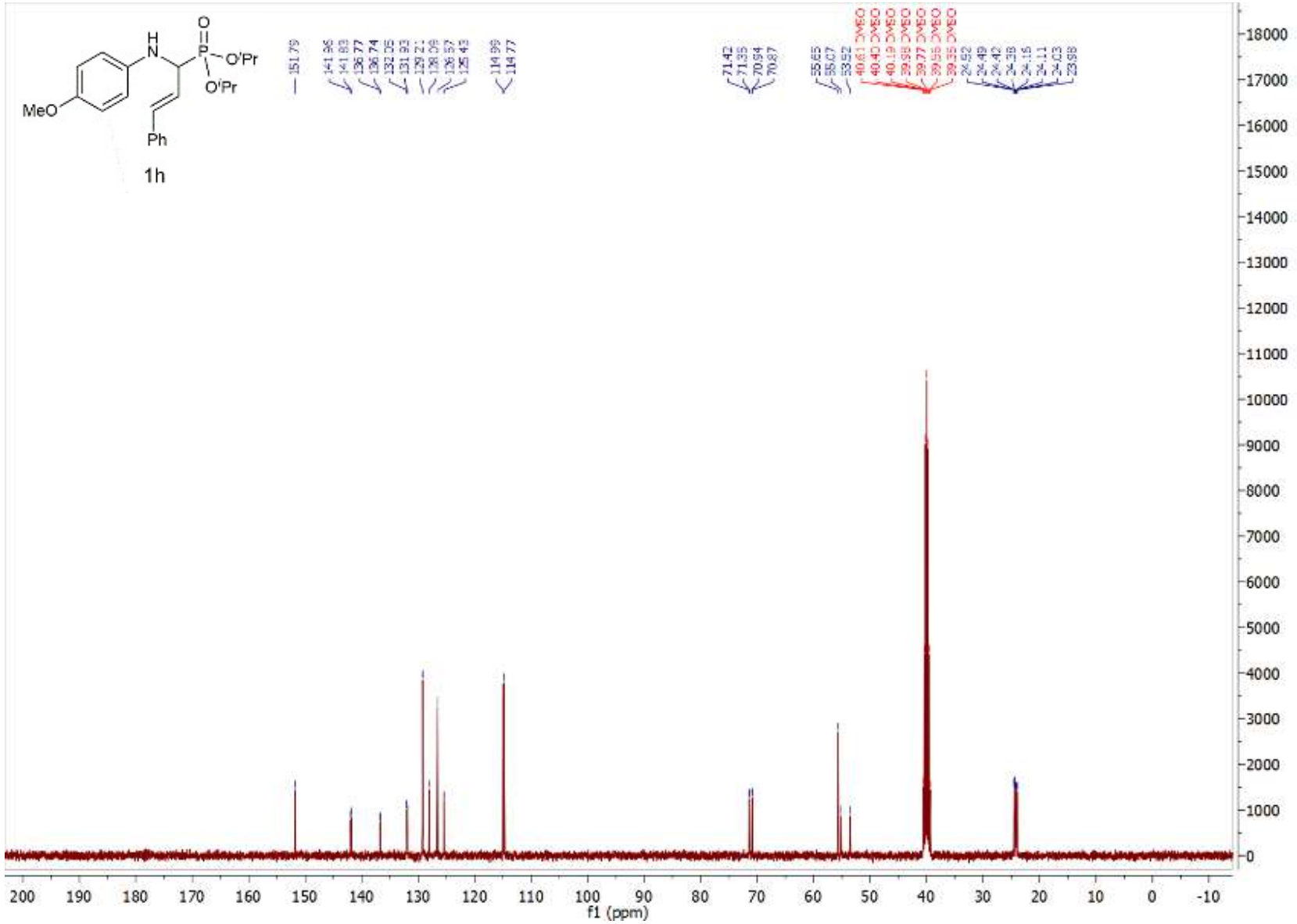


Figure S23: ^{13}C NMR Spectra of 1h

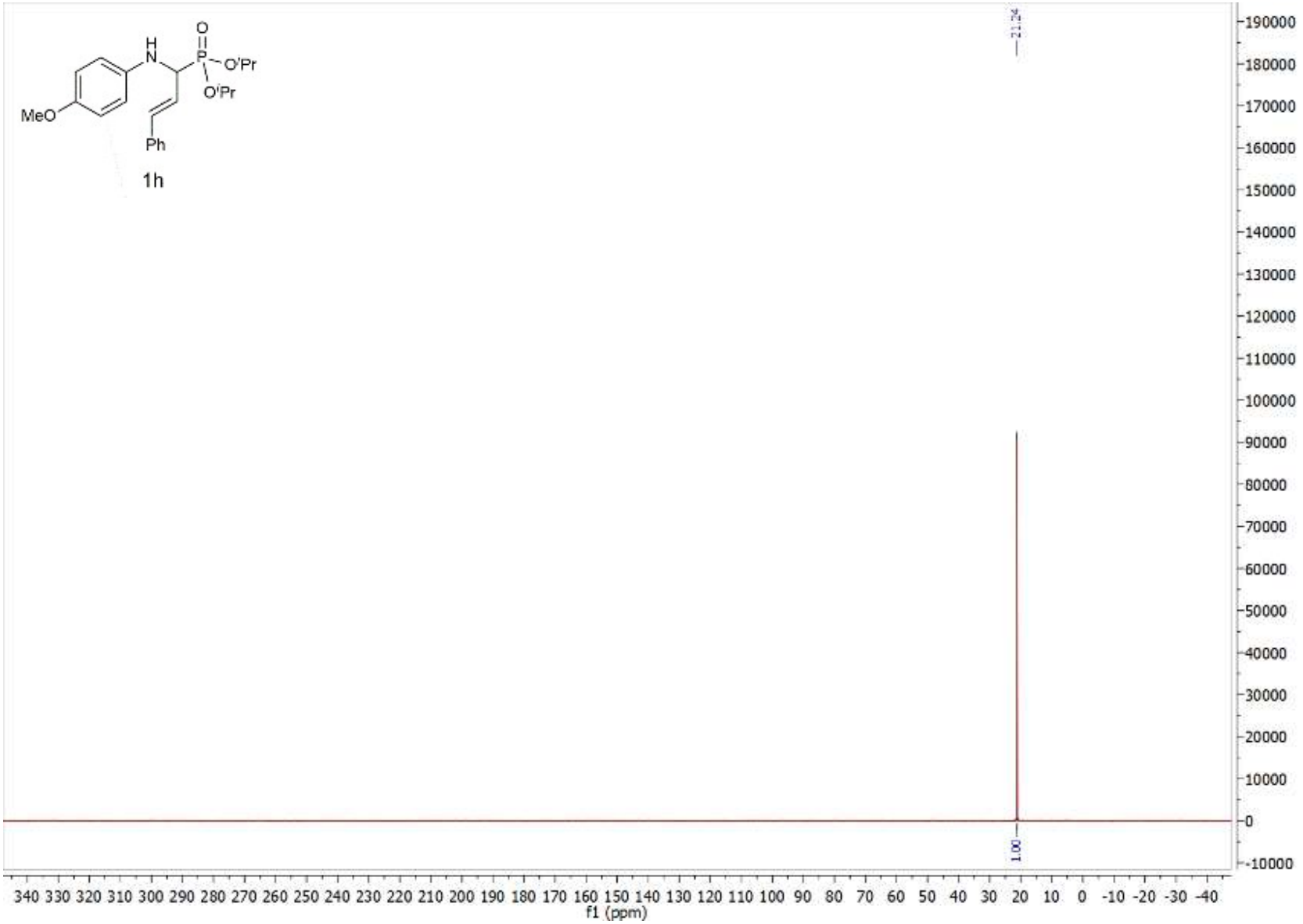


Figure S24: ^{31}P NMR Spectra of 1h

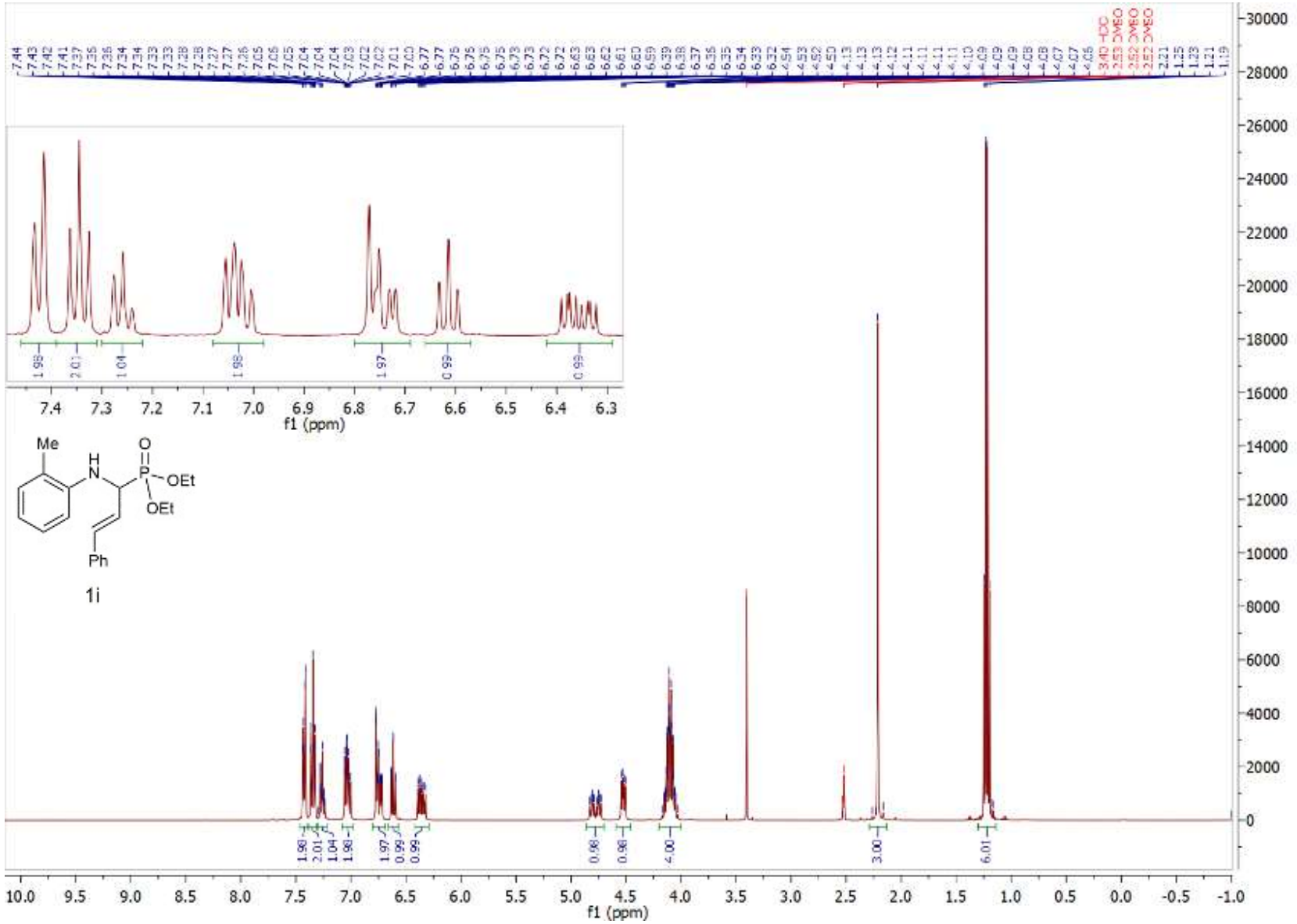


Figure S25: ^{1}H NMR Spectra of 1i

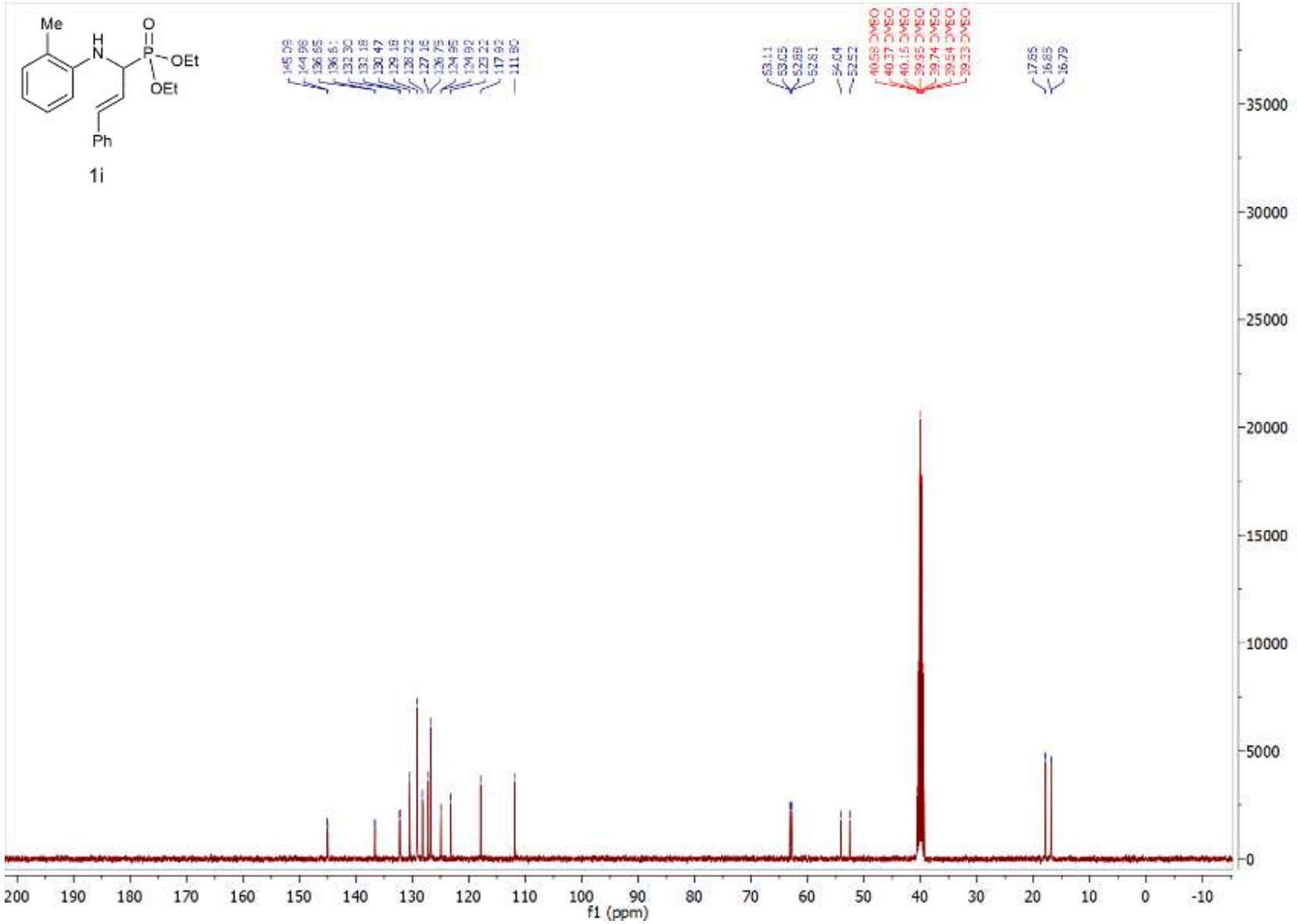


Figure S26: ^{13}C NMR Spectra of 1i

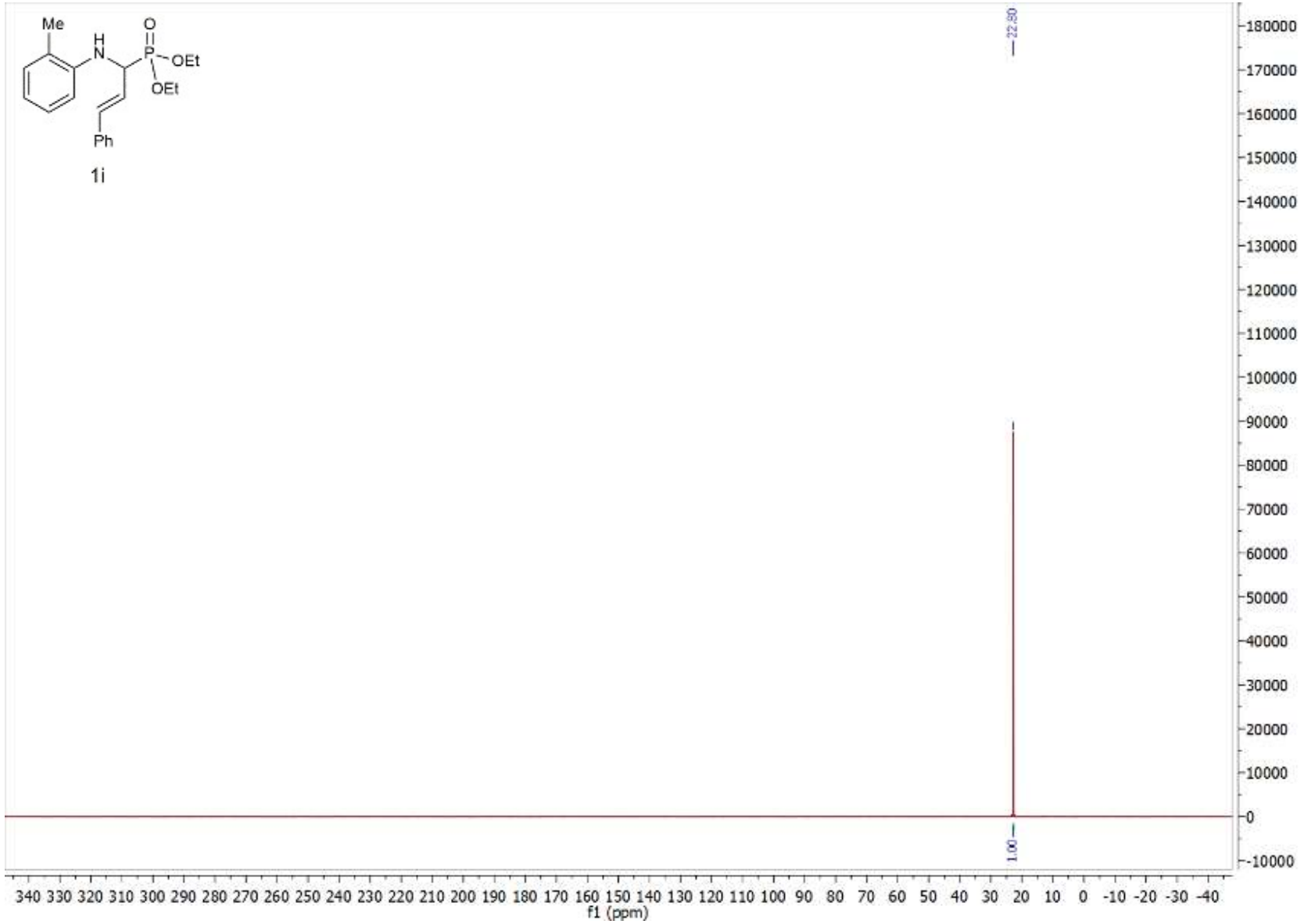


Figure S27: ^{31}P NMR Spectra of 1i

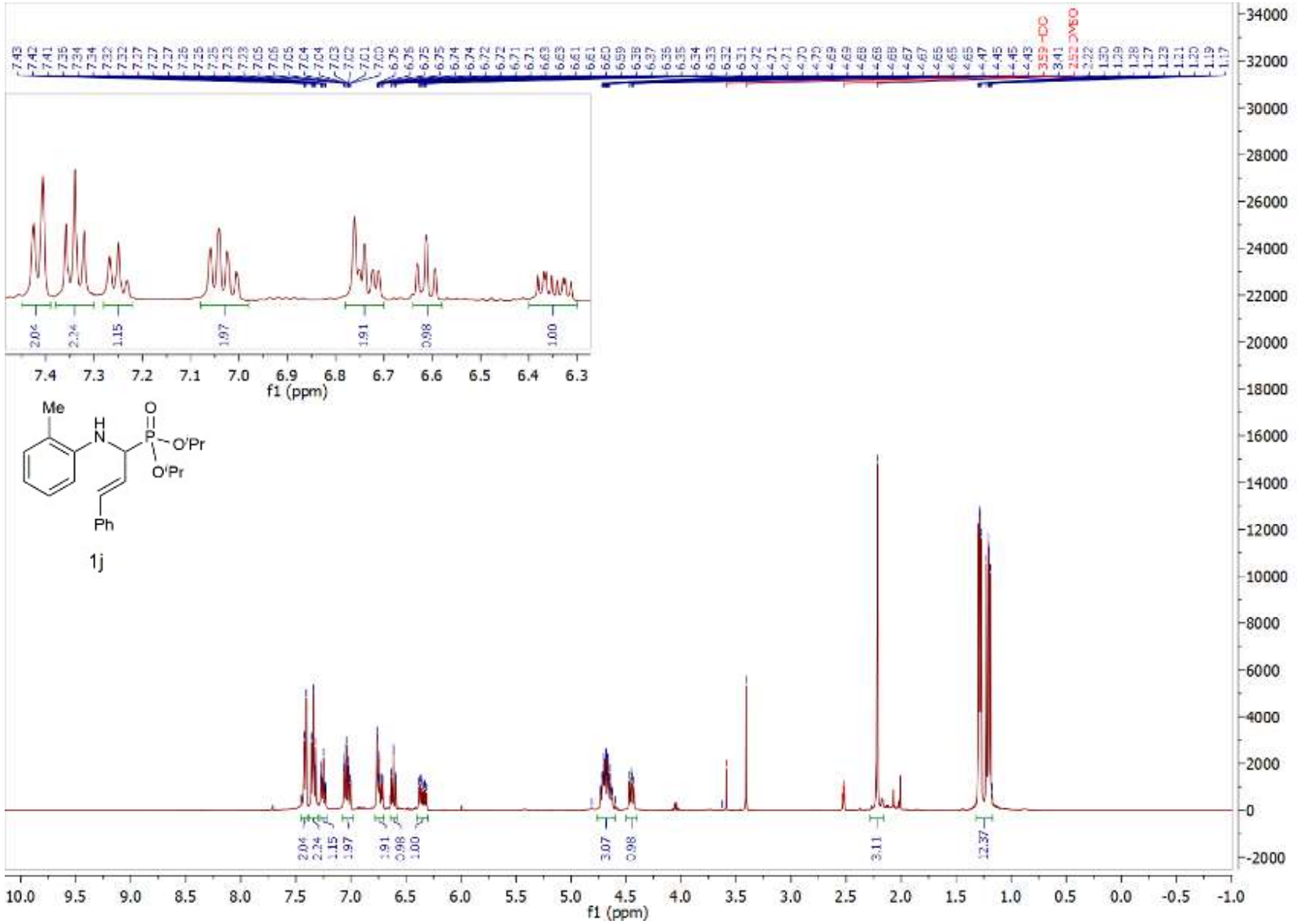


Figure S28: ^{1}H NMR Spectra of 1j

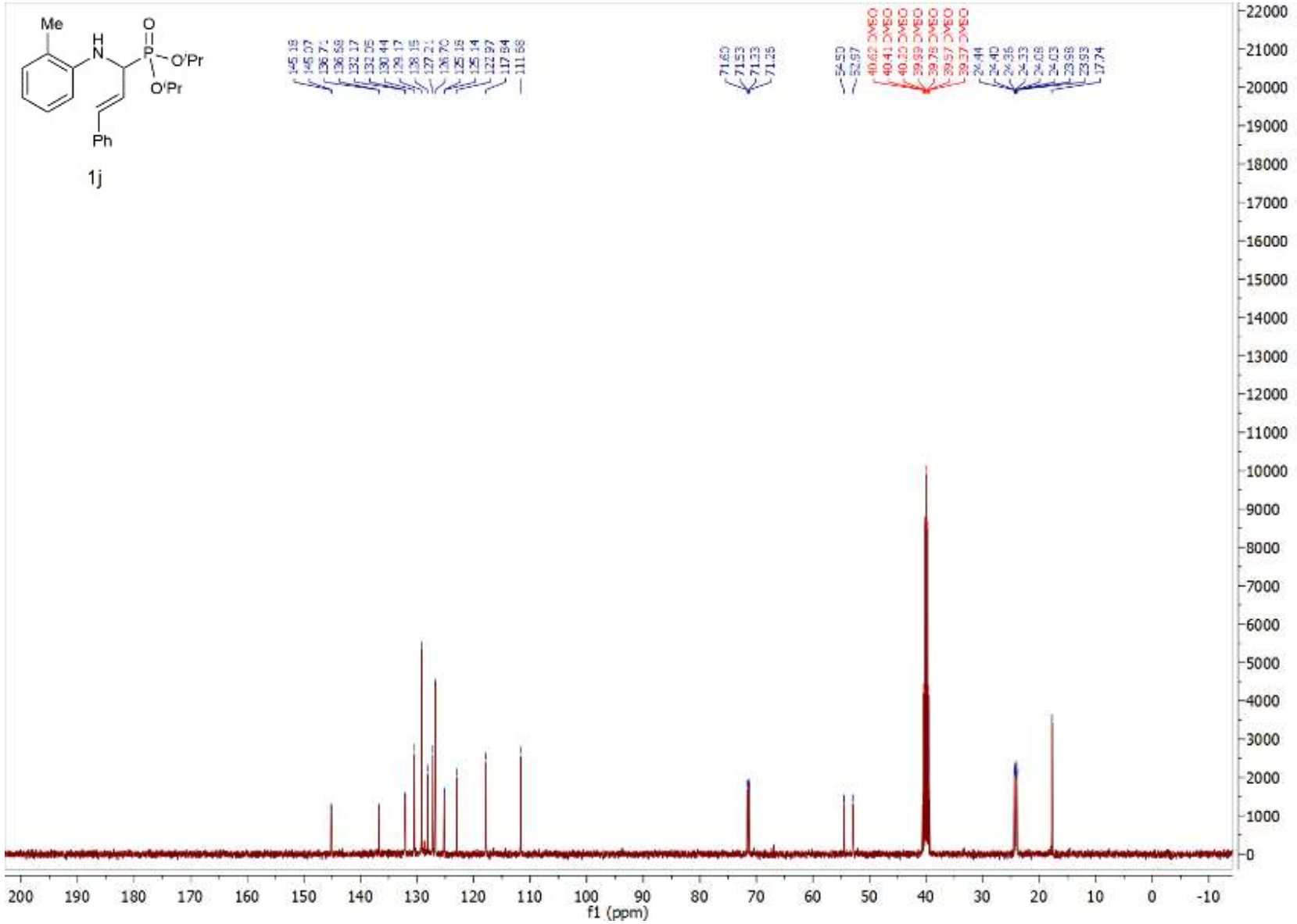


Figure S29: ^{13}C NMR Spectra of 1j

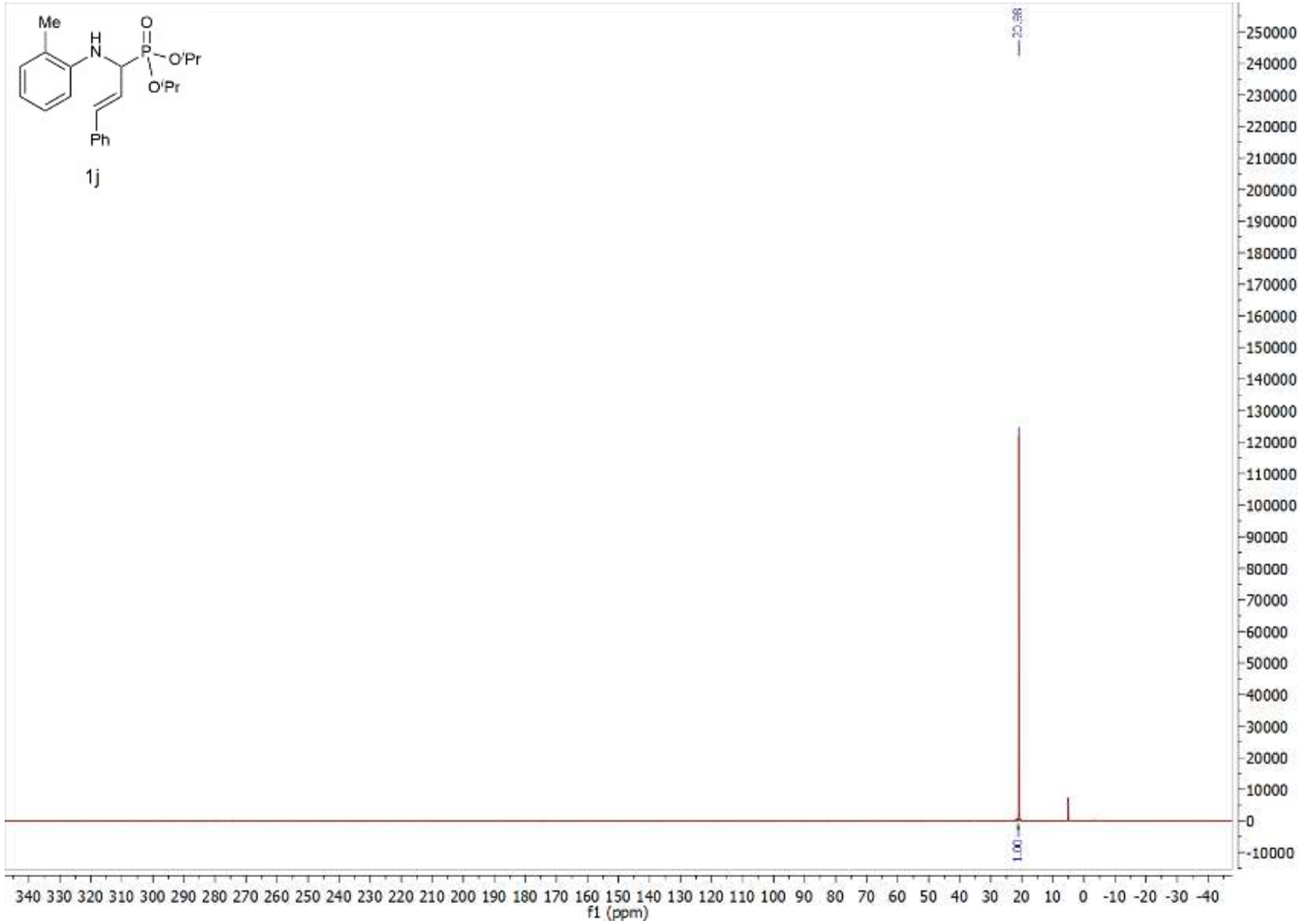


Figure S30: ^{31}P NMR Spectra of 1j

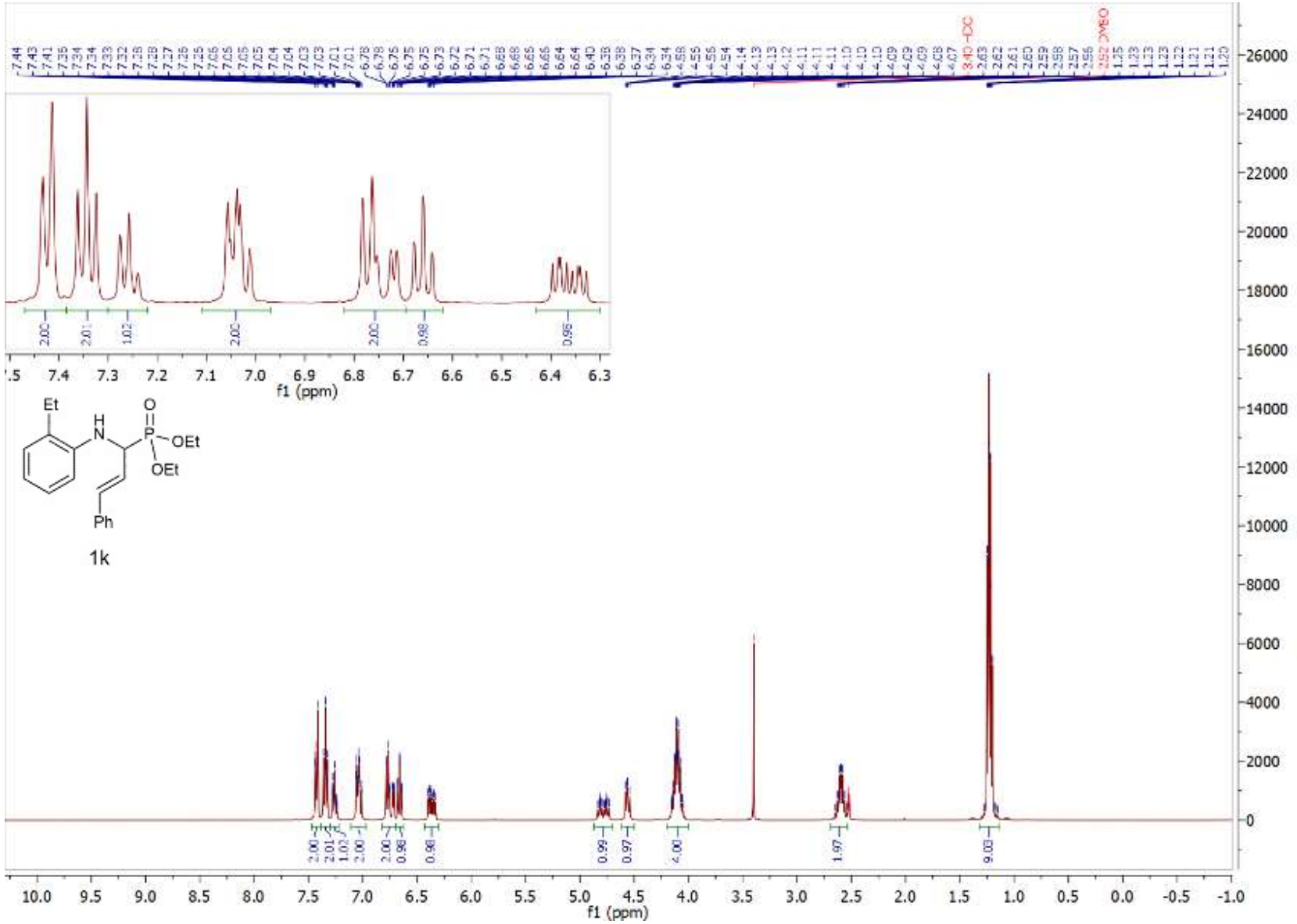


Figure S31: ^{1}H NMR Spectra of 1k

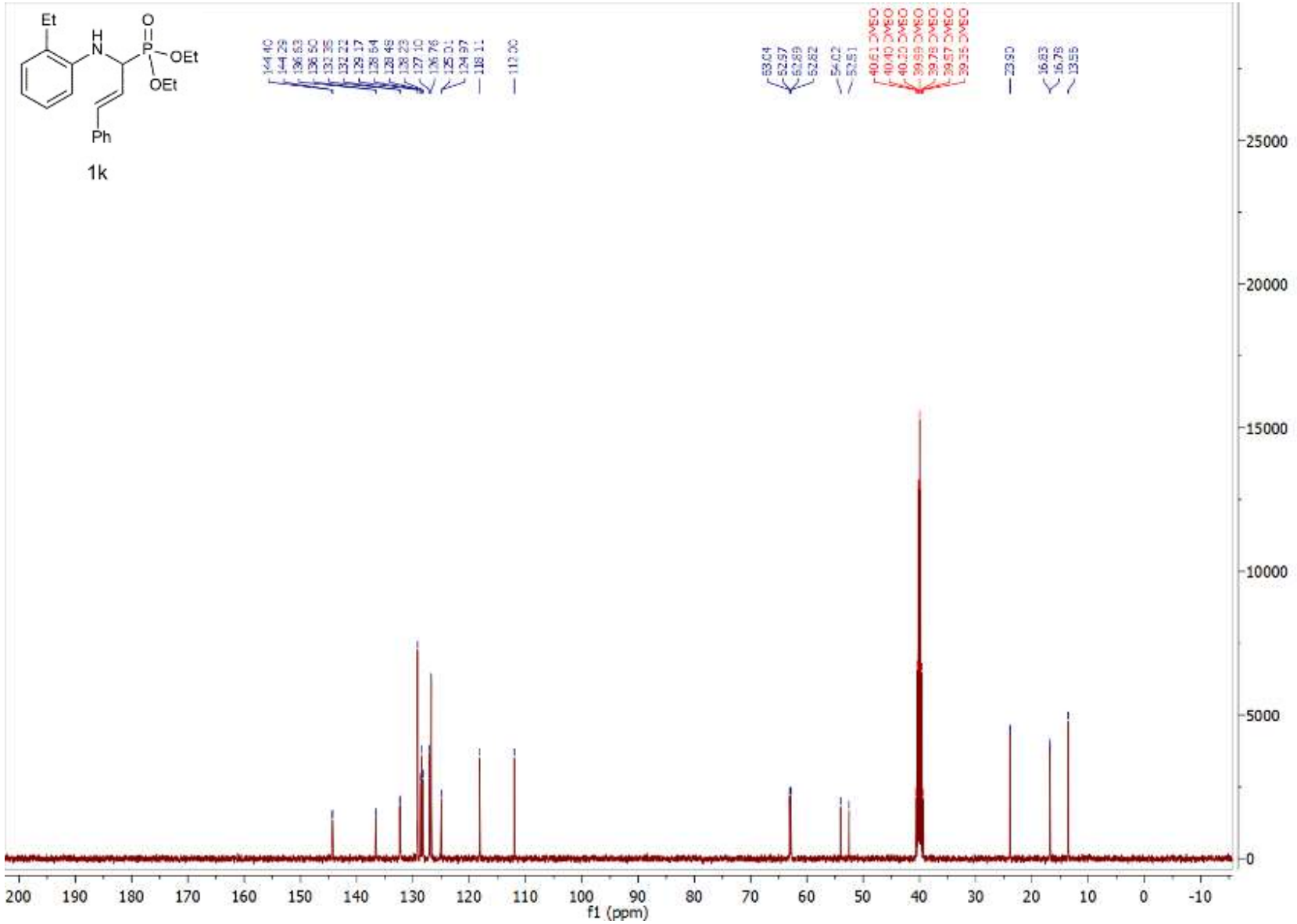


Figure S32: ^{13}C NMR Spectra of 1k

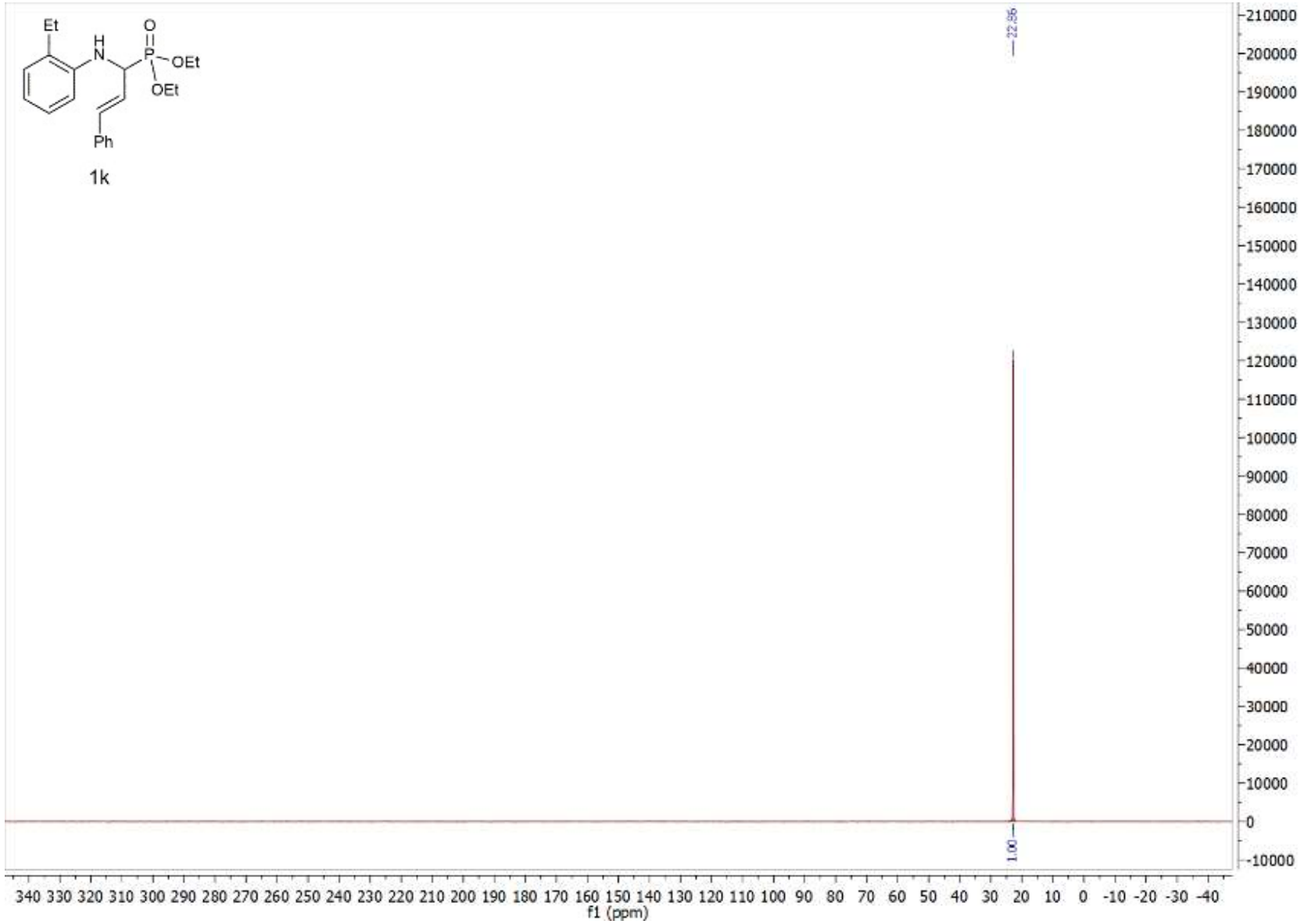


Figure S33: ^{31}P NMR Spectra of 1k

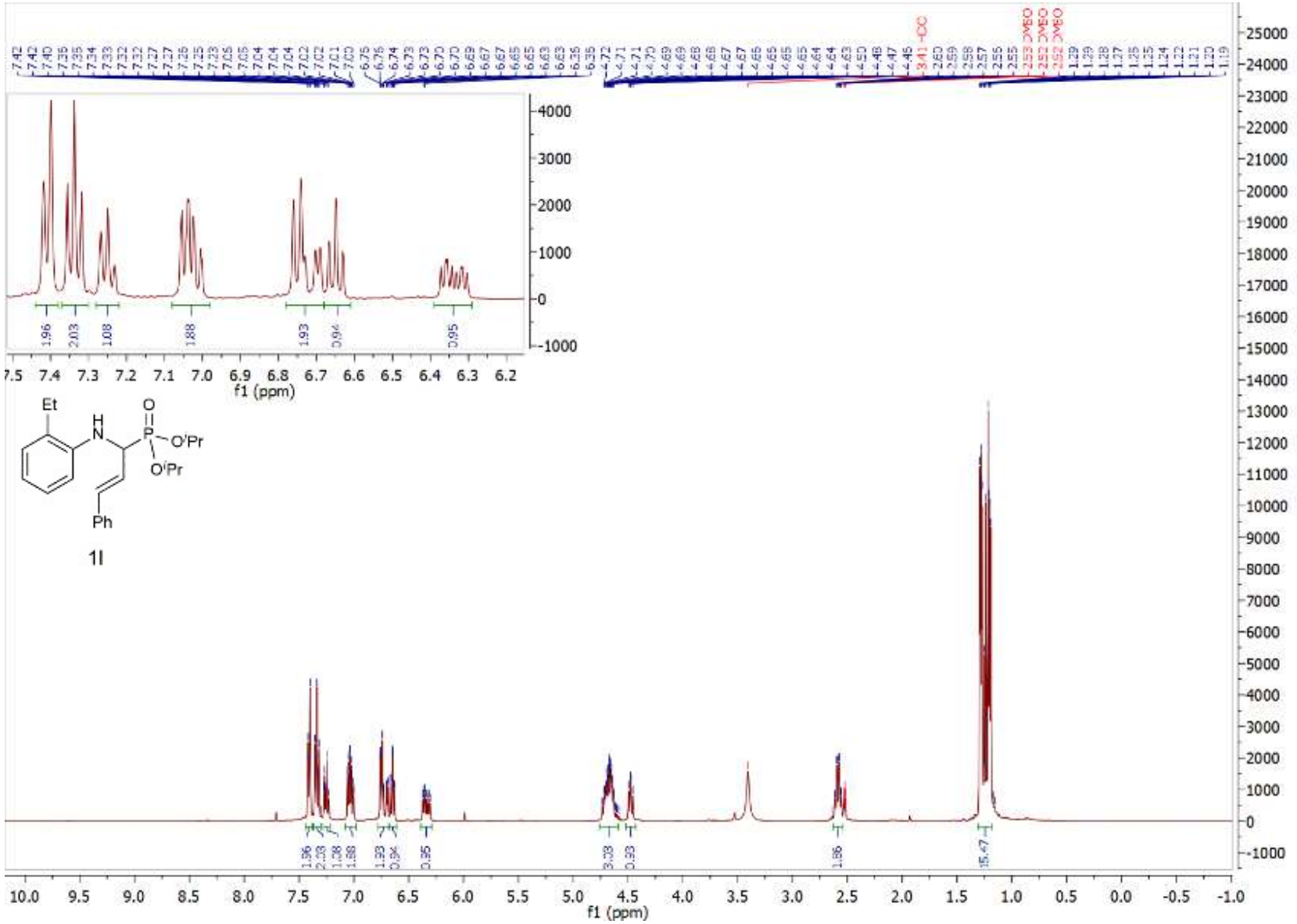


Figure S34: ^{1}H NMR Spectra of 1l

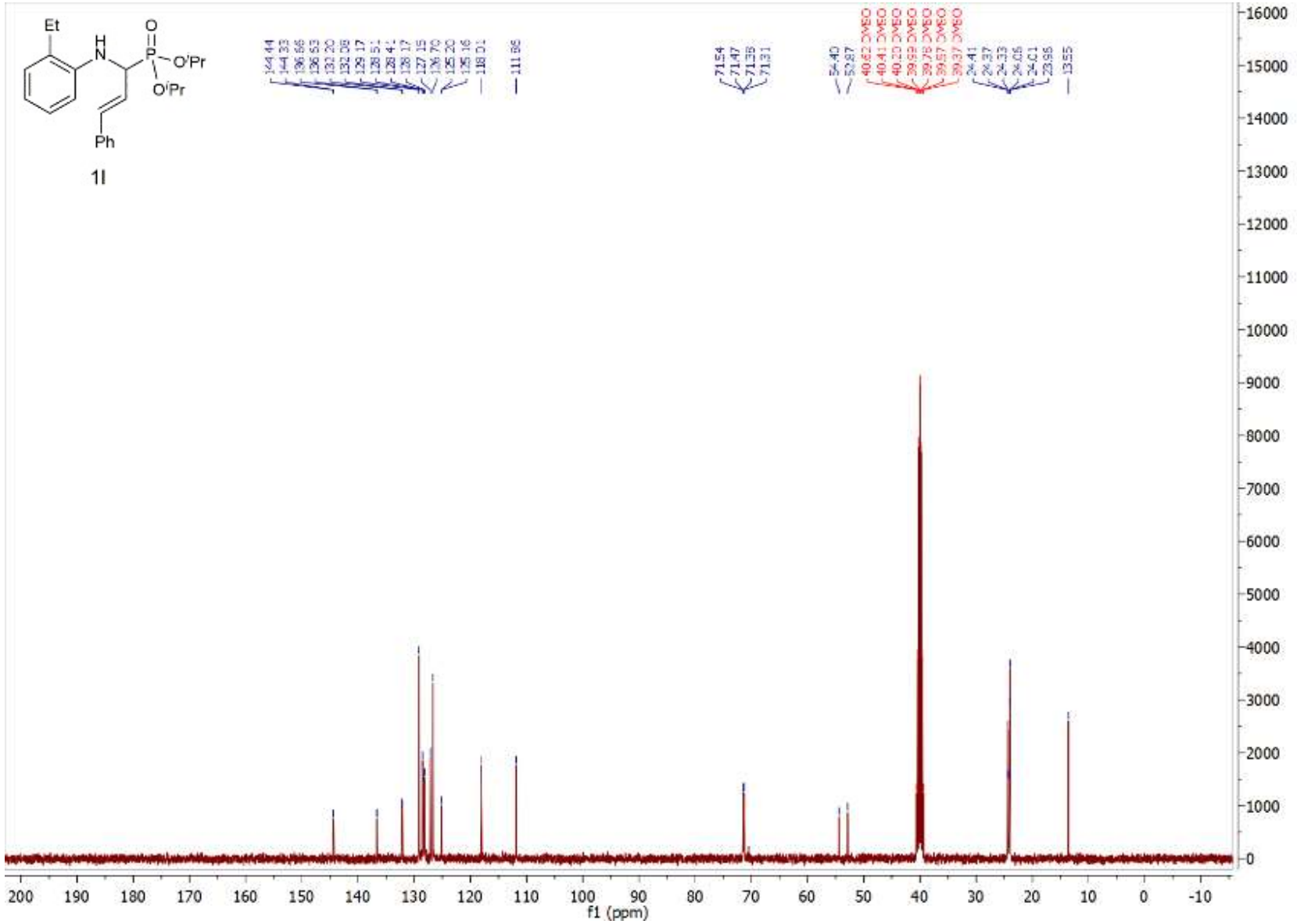


Figure S35: ^{13}C NMR Spectra of 1l

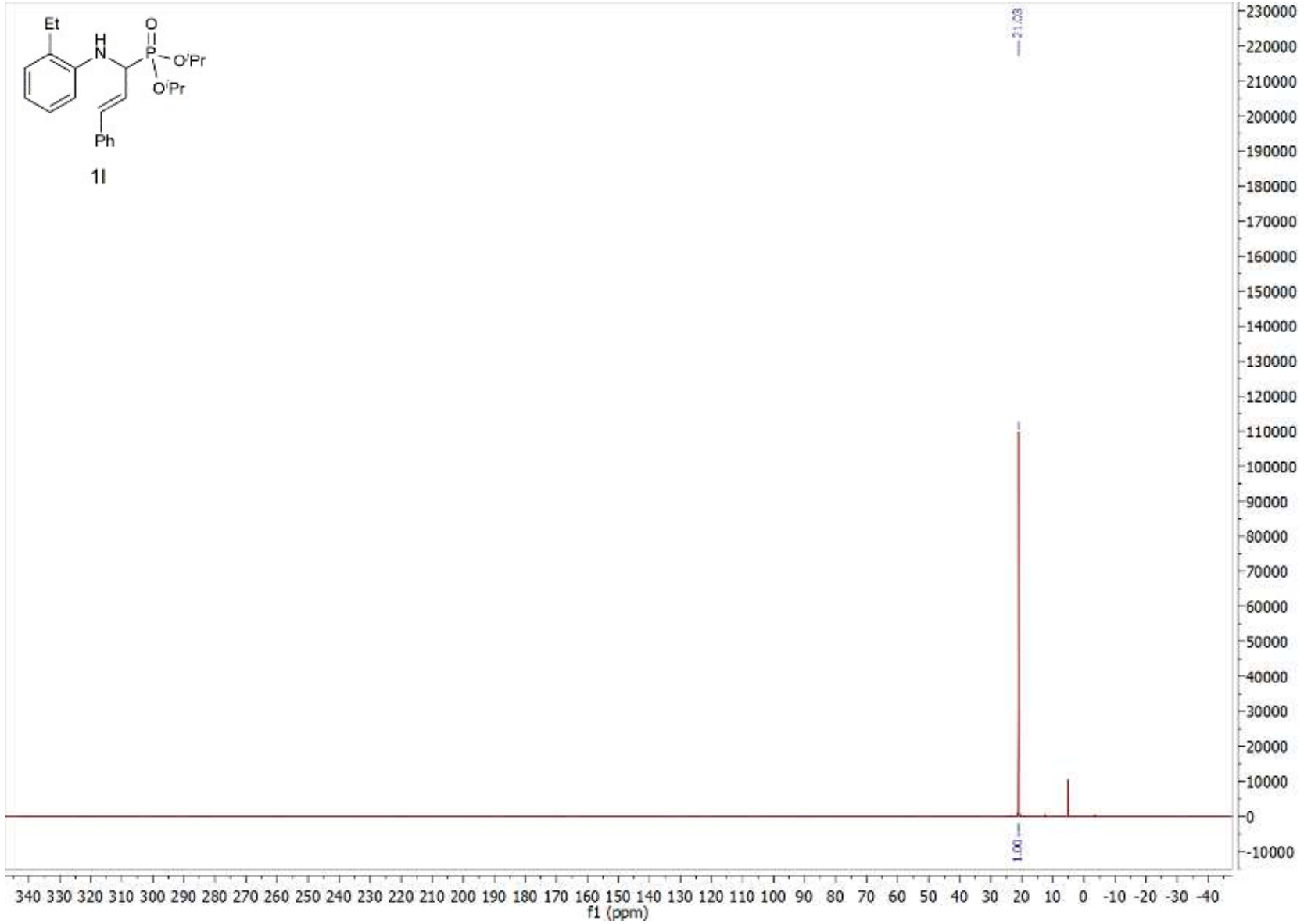


Figure S36: ^{31}P NMR Spectra of 1l

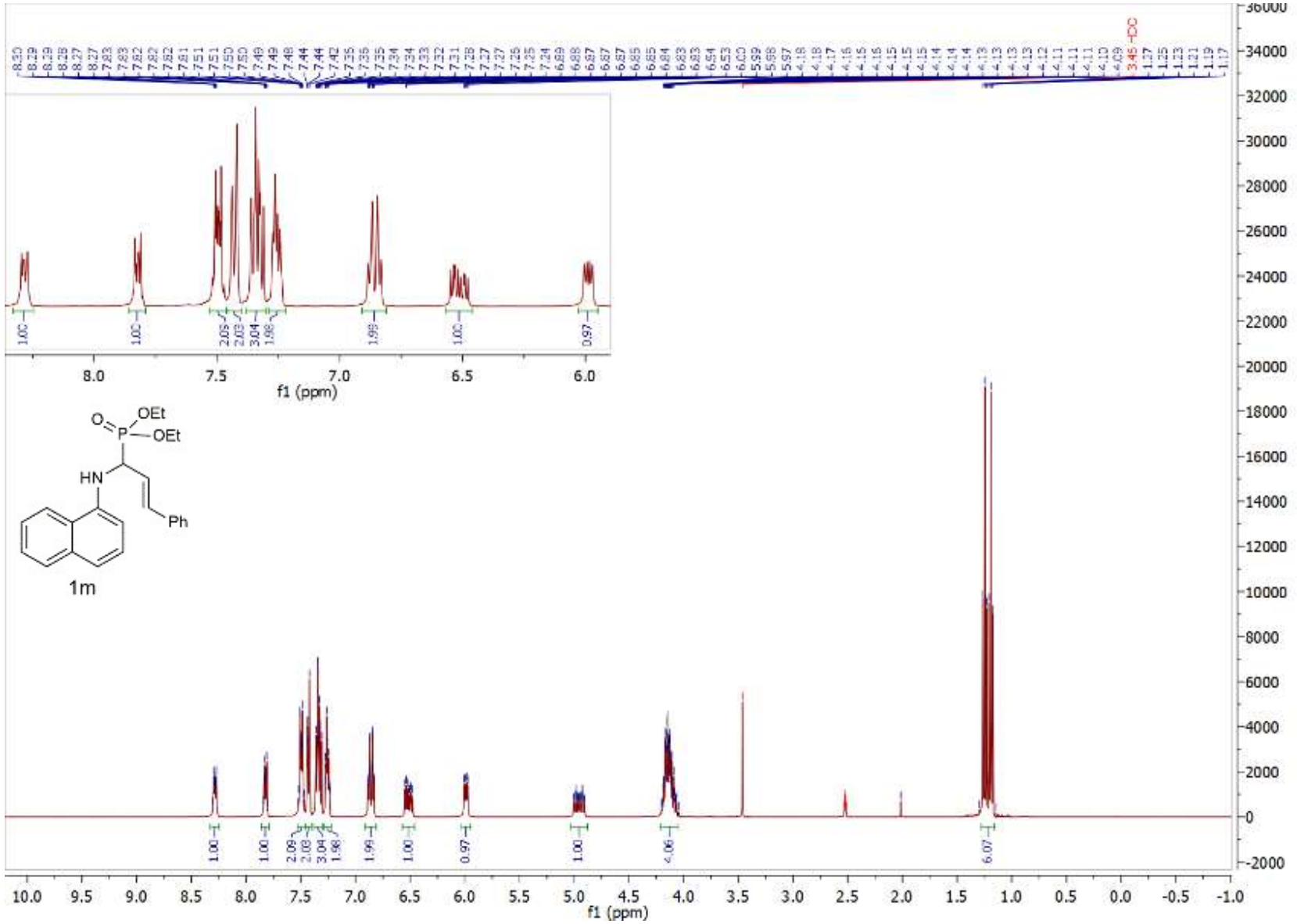


Figure S37: ^{1}H NMR Spectra of 1m

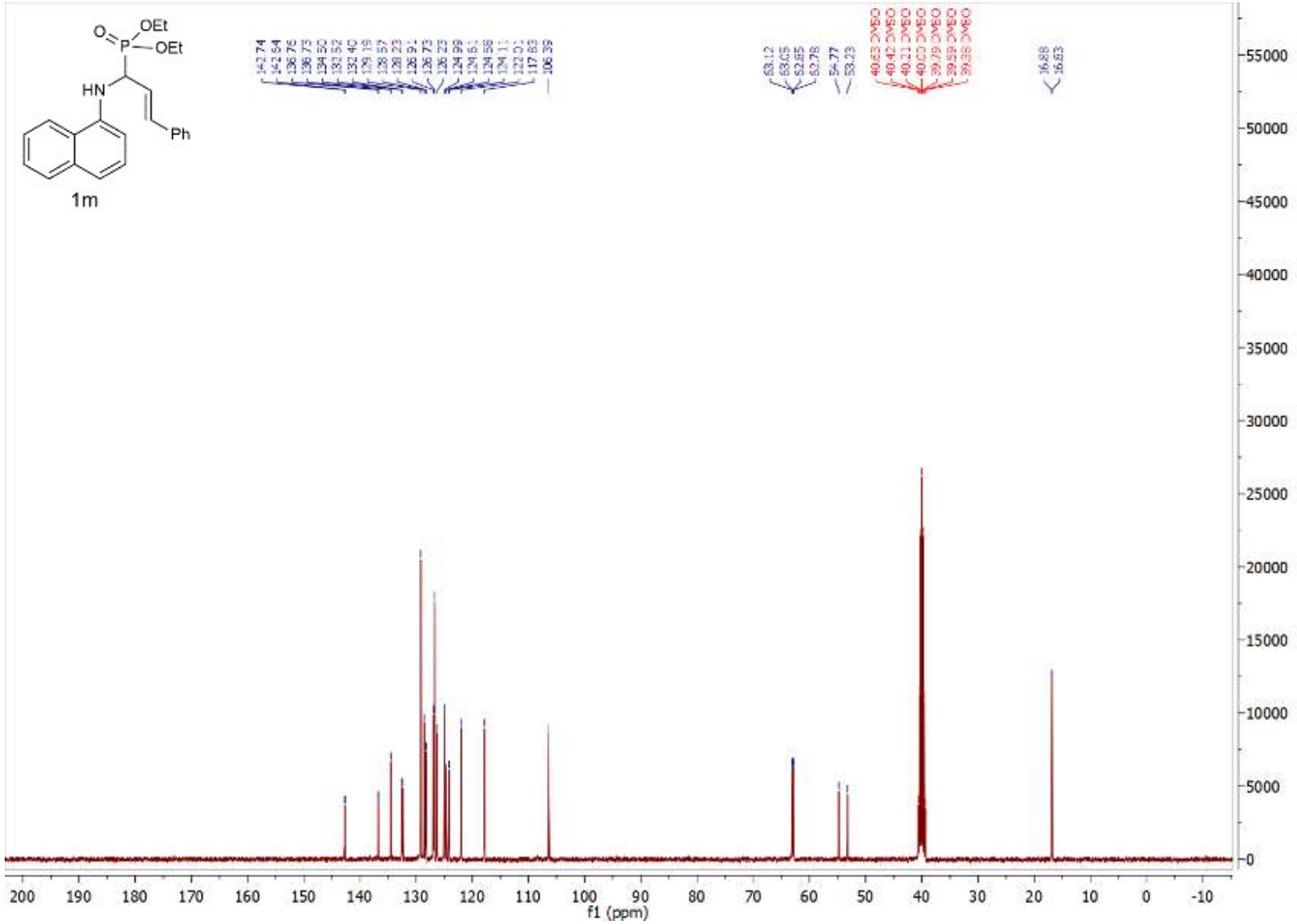


Figure S38: ^{13}C NMR Spectra of 1m

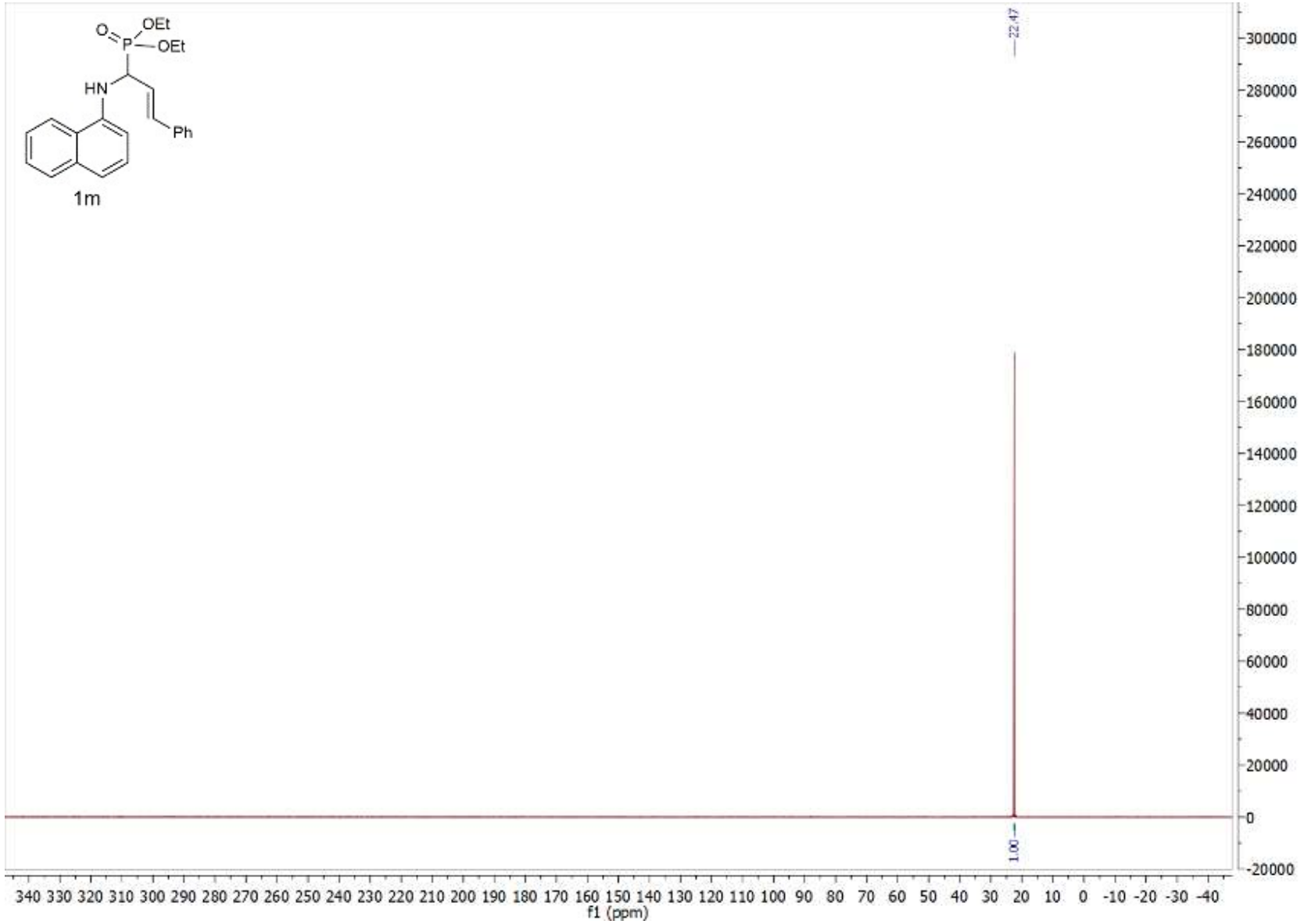


Figure S39: ^{31}P NMR Spectra of 1m

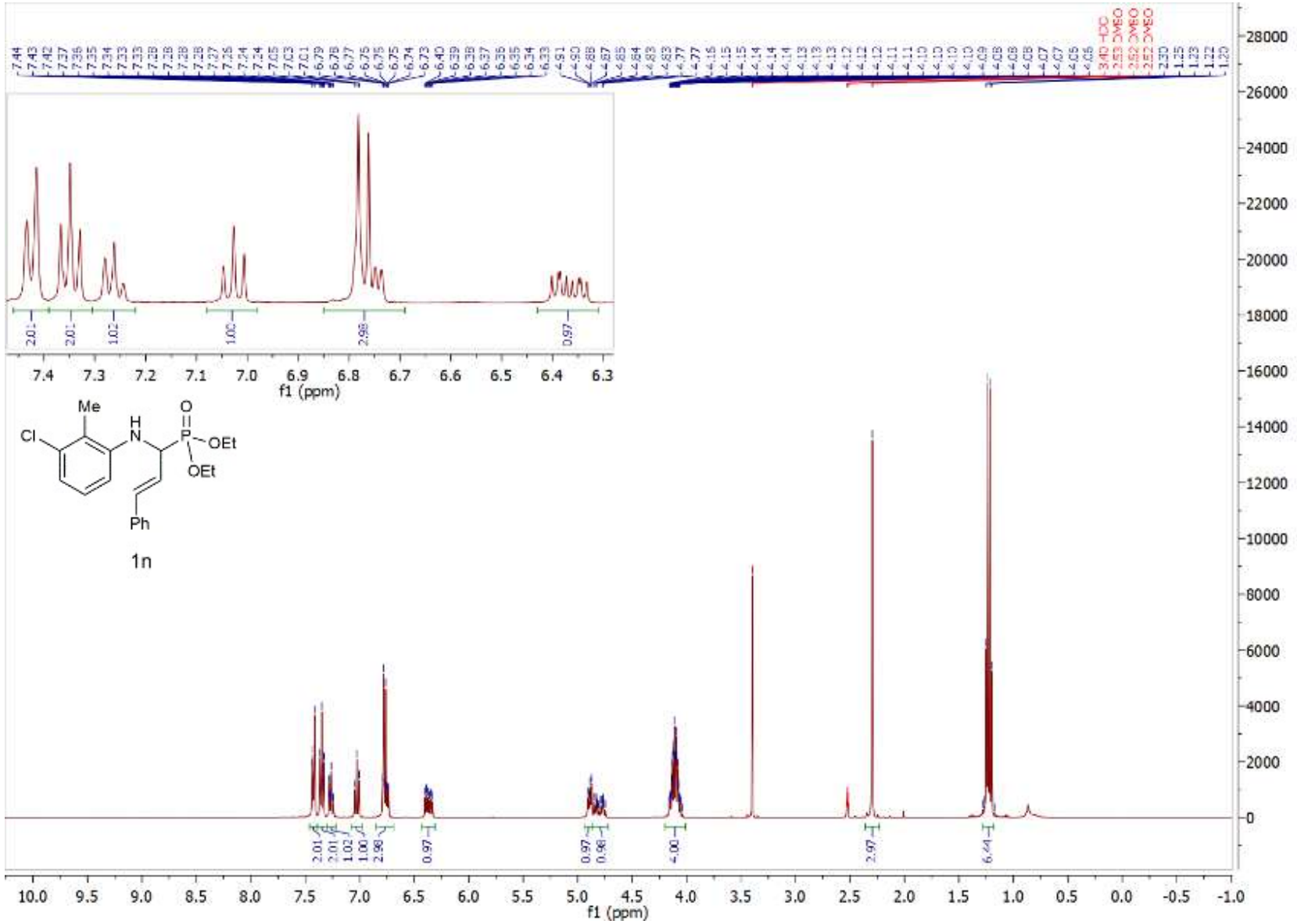


Figure S40: ^{1}H NMR Spectra of 1n

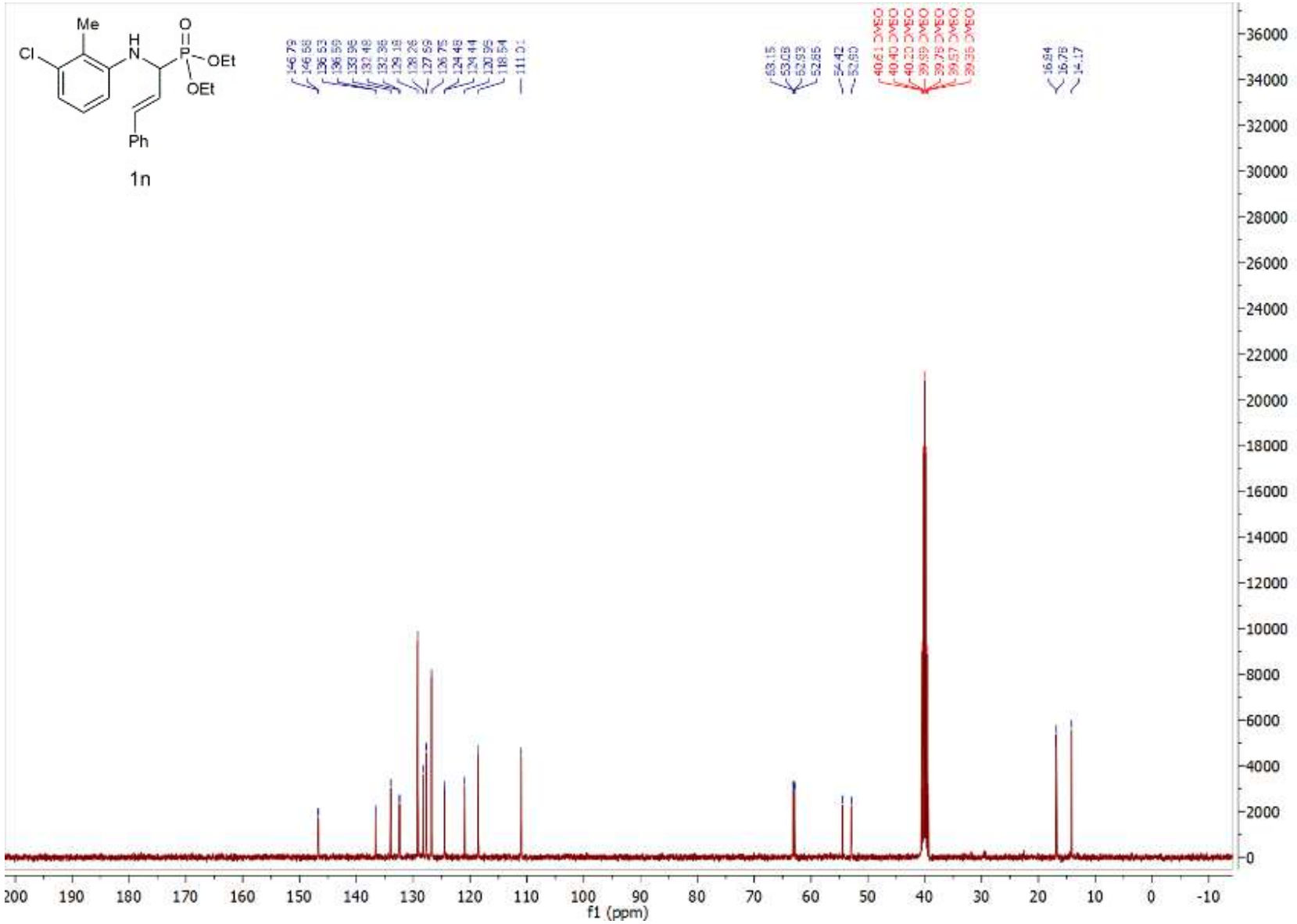


Figure S41: ^{13}C NMR Spectra of 1n

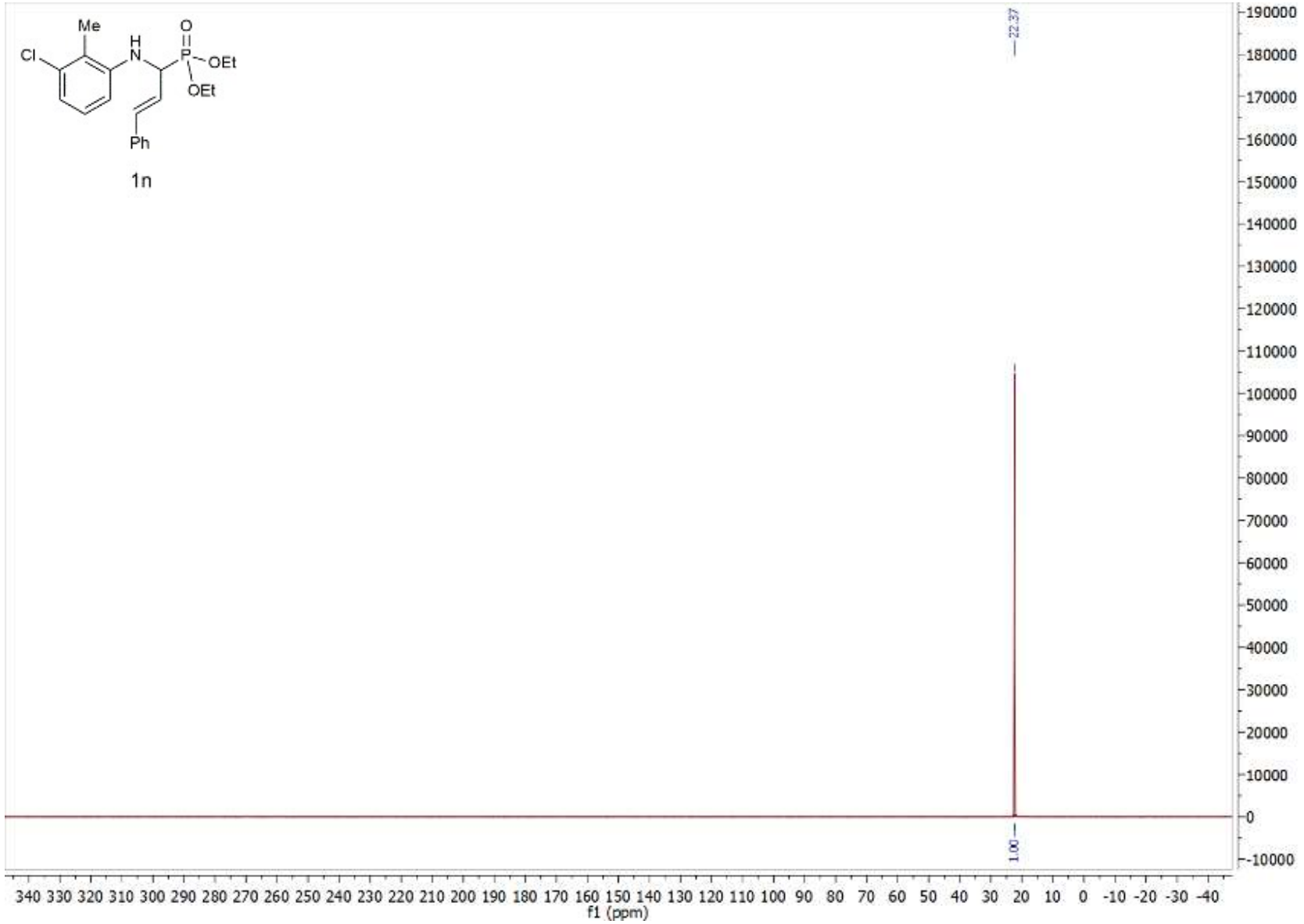


Figure S42: ^{31}P NMR Spectra of 1n

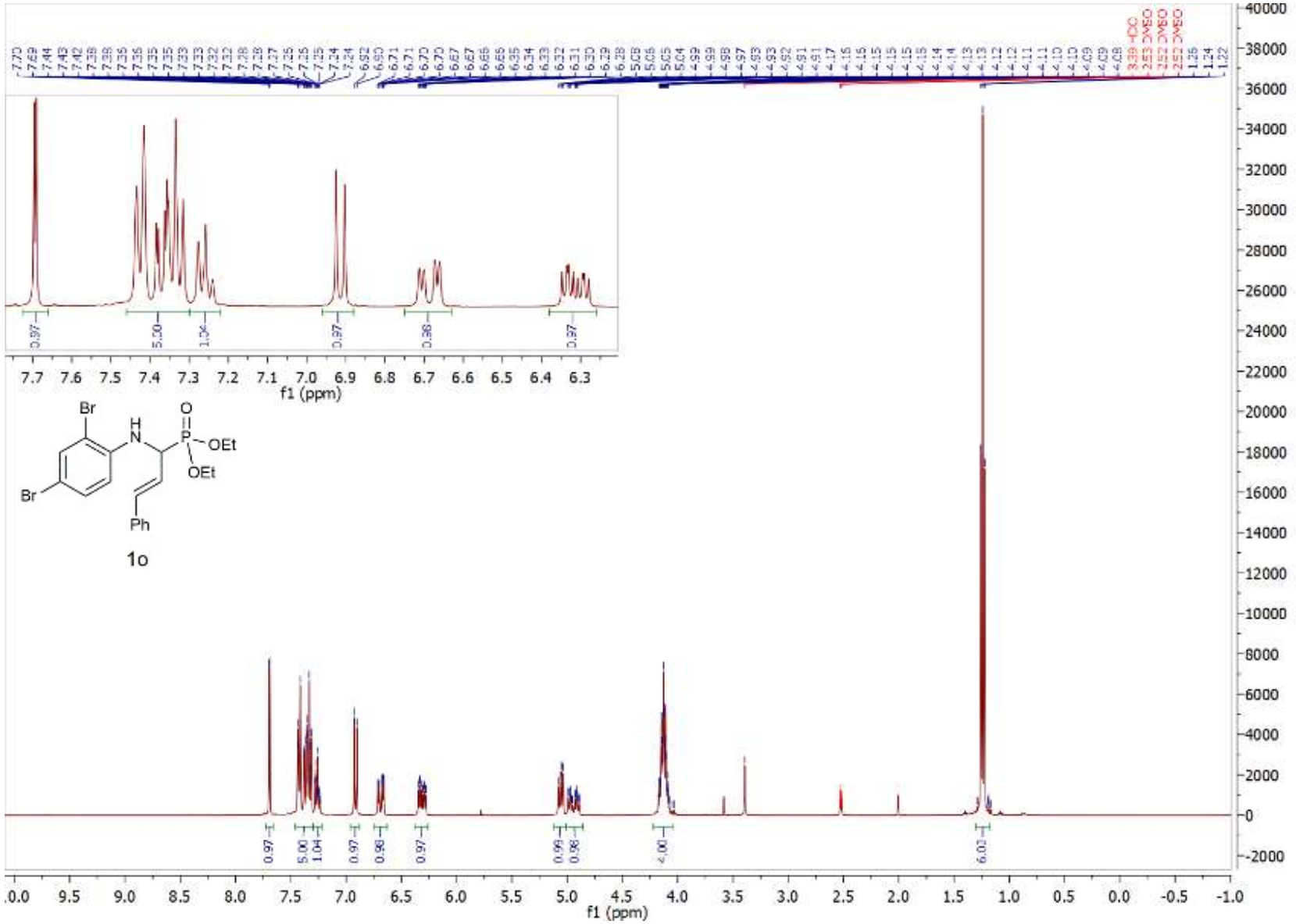


Figure S43: ^{1}H NMR Spectra of 1o

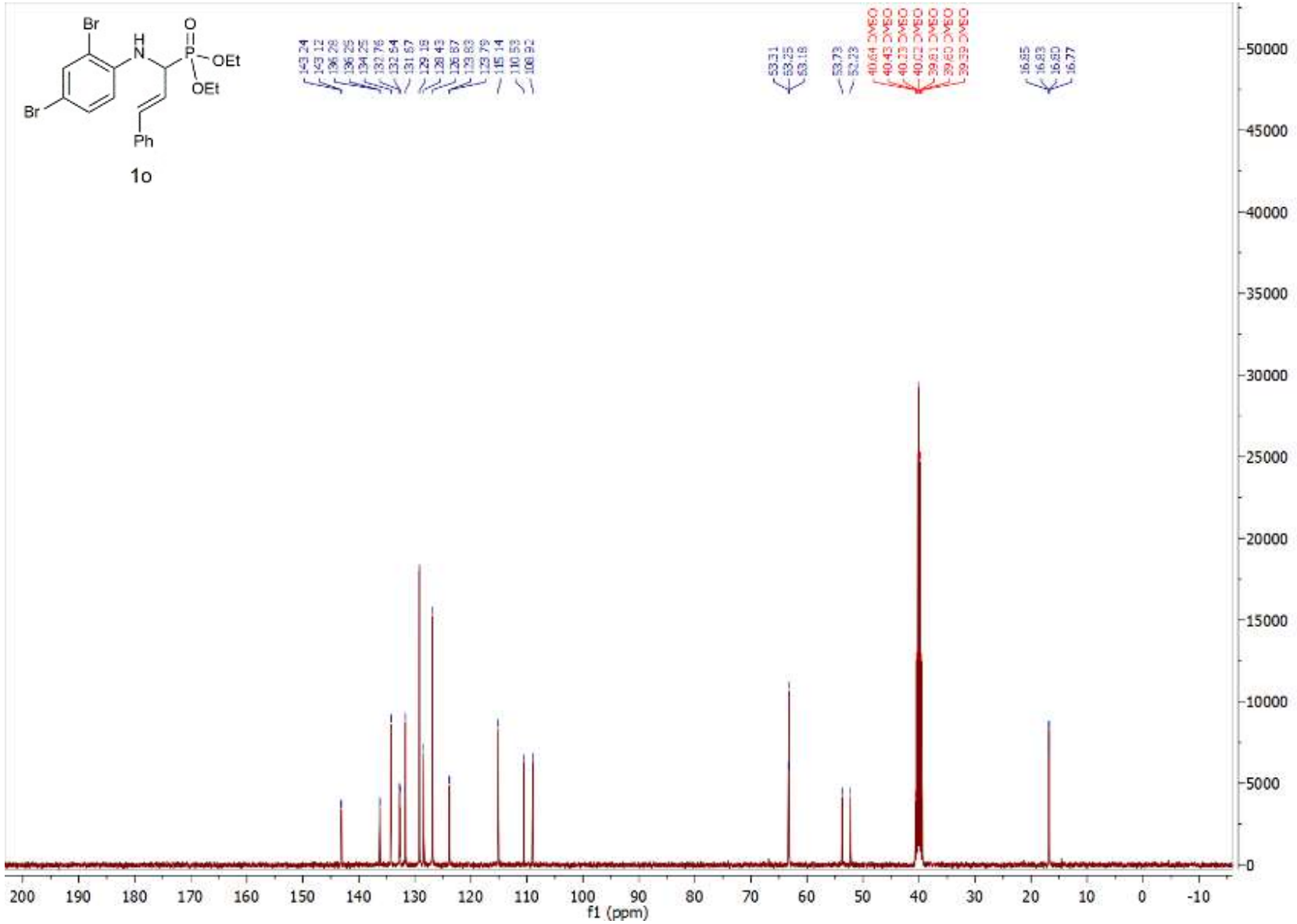


Figure S44: ^{13}C NMR Spectra of 1o

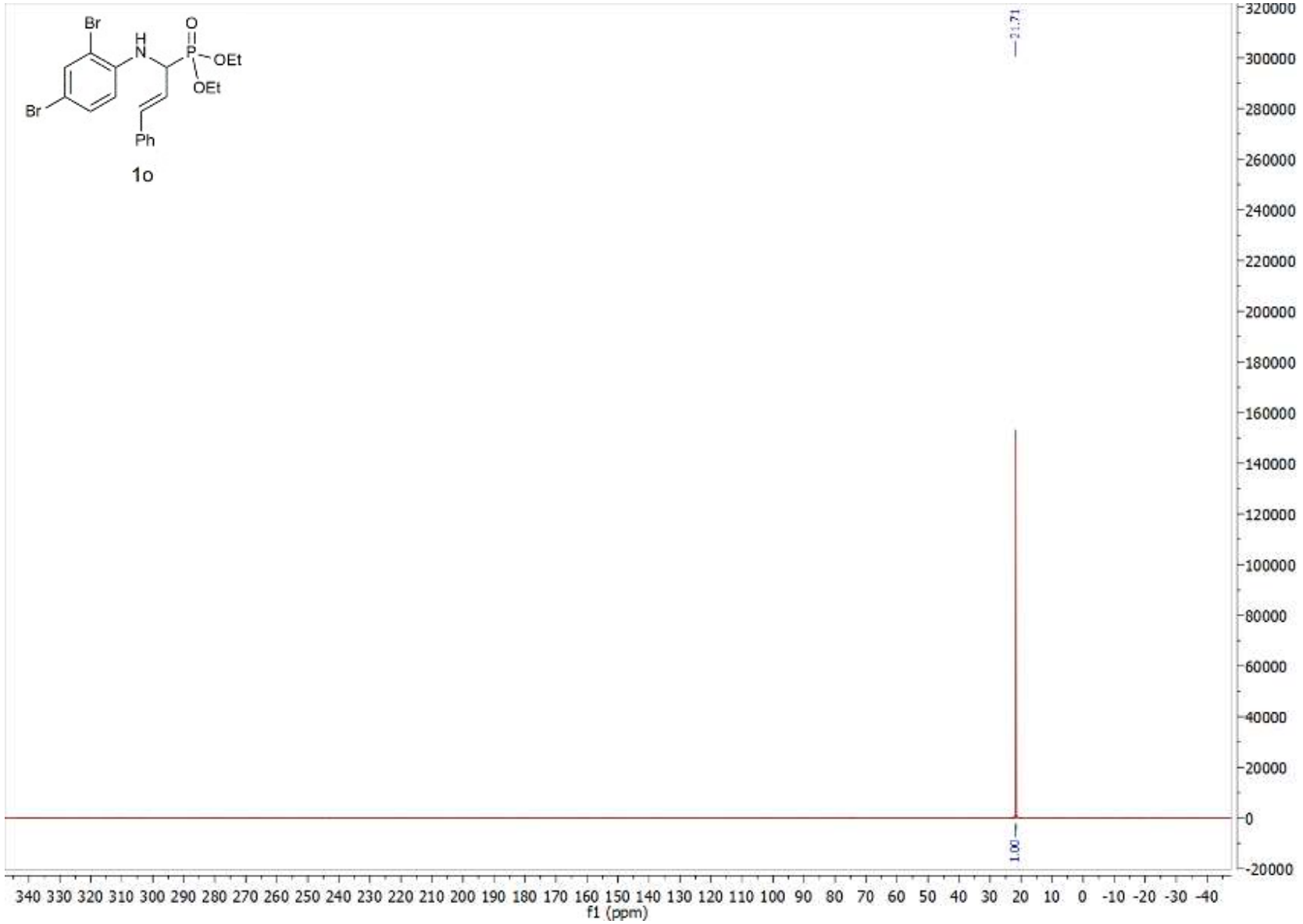


Figure S45: ^{31}P NMR Spectra of 1o

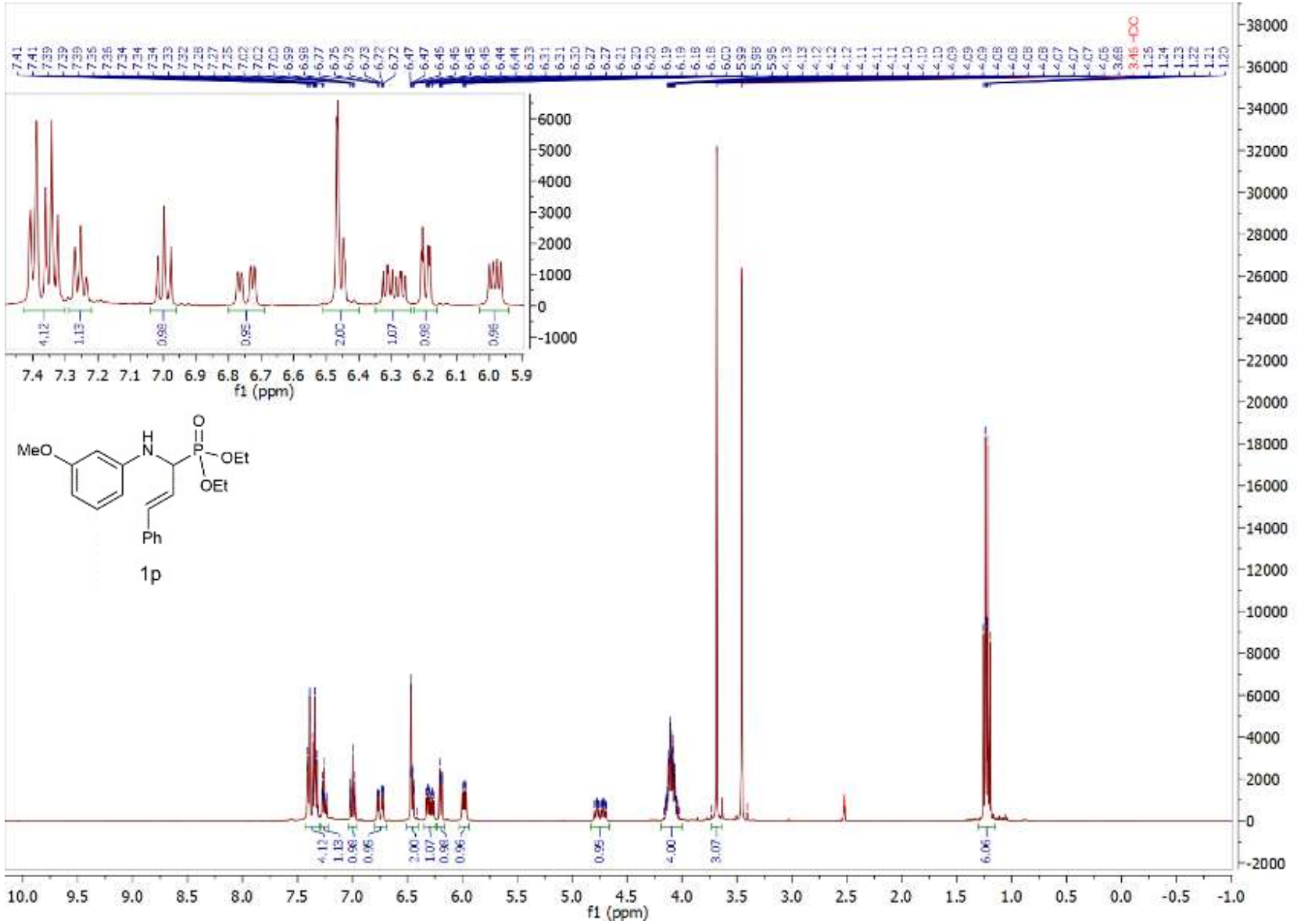


Figure S46: ^{1}H NMR Spectra of 1p

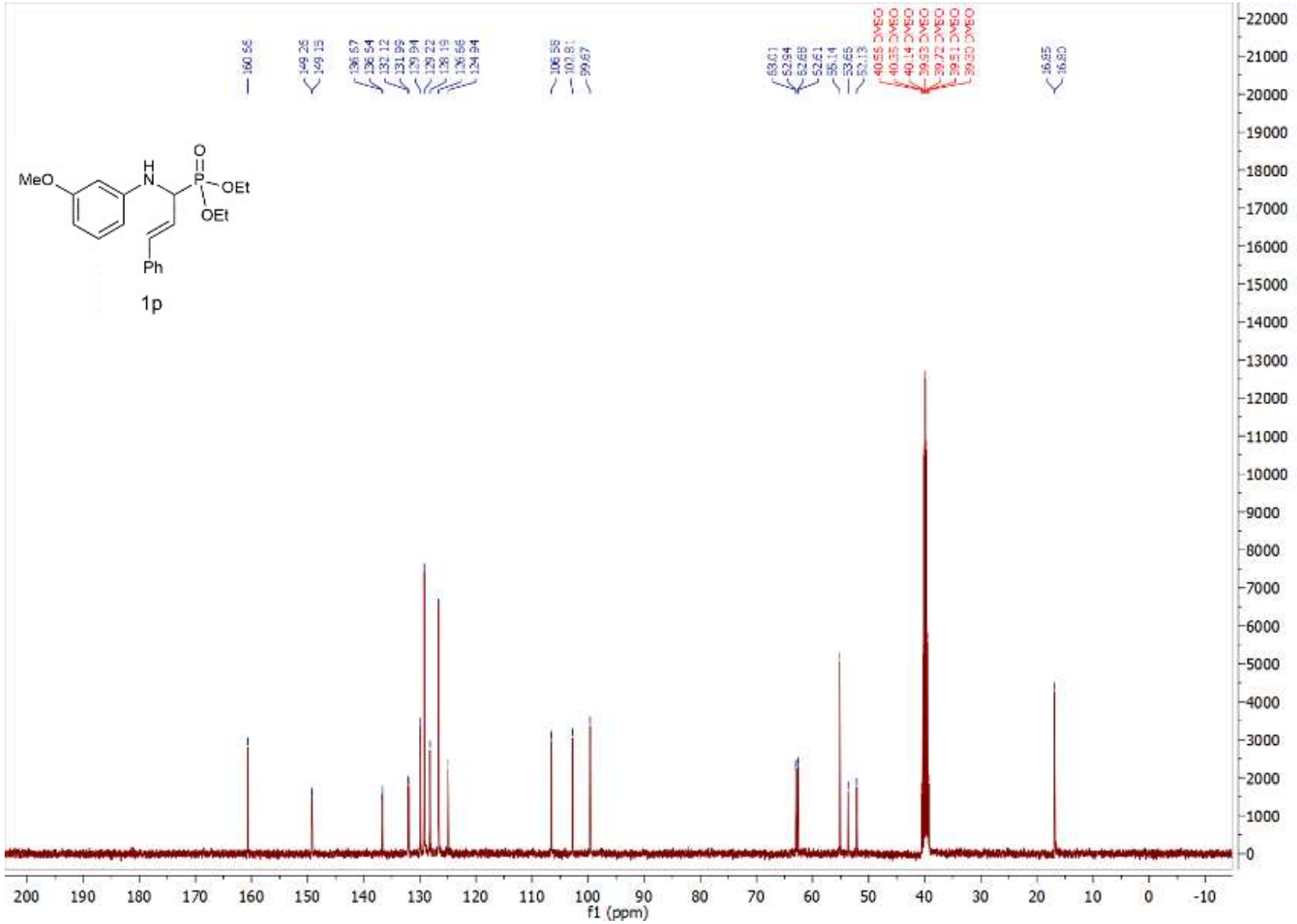


Figure S47: ^{13}C NMR Spectra of 1p

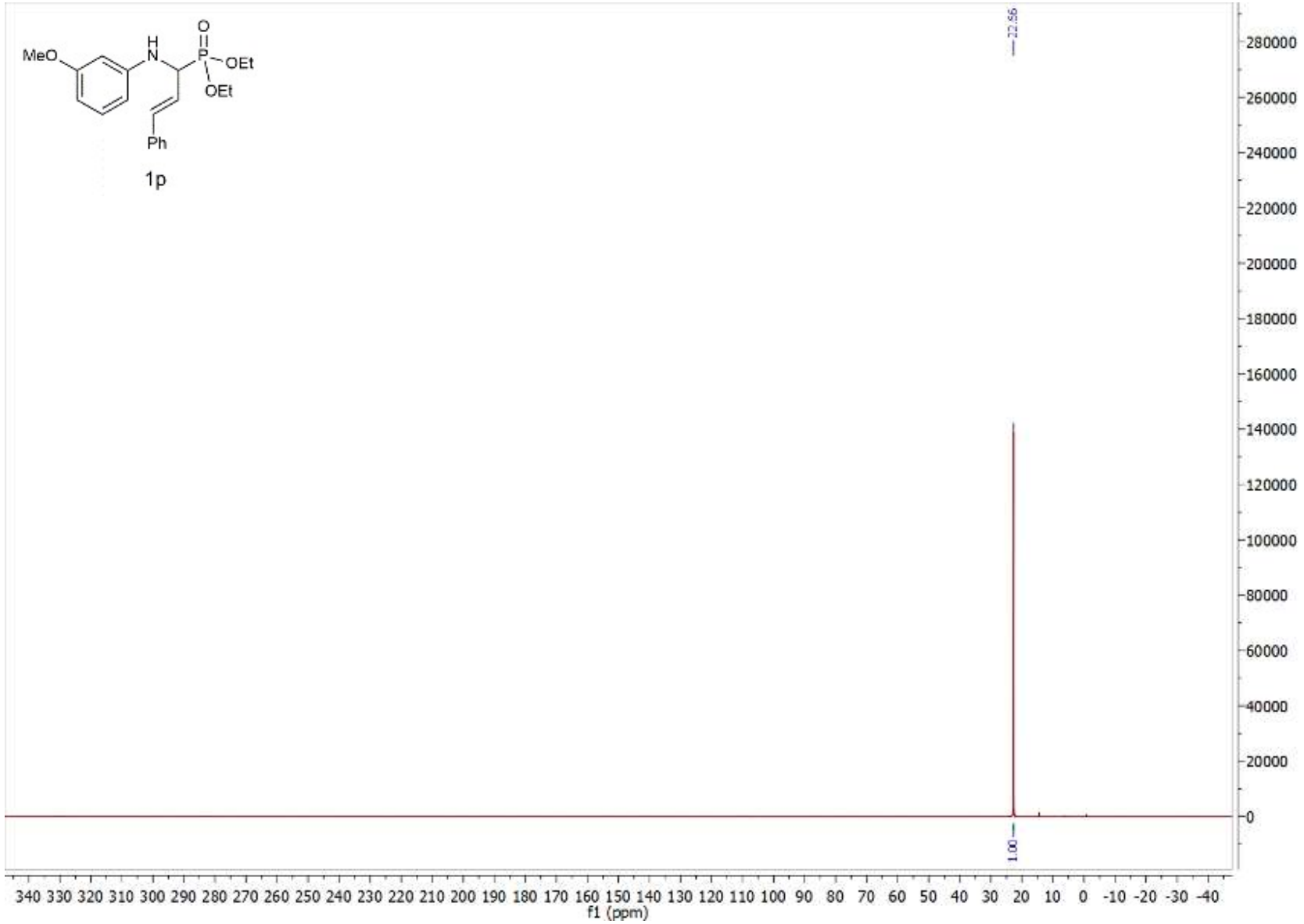


Figure S48: ^{31}P NMR Spectra of 1p

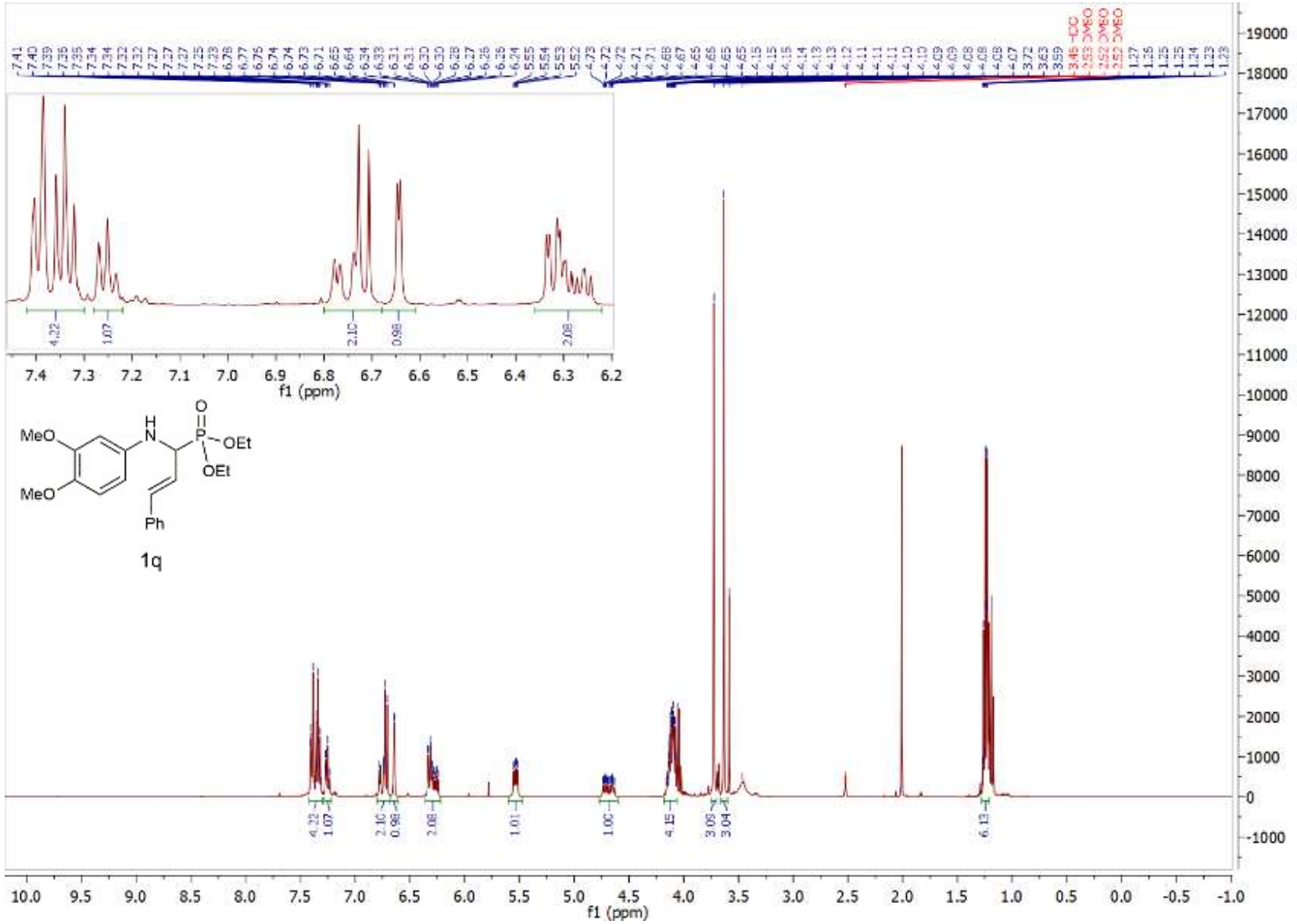


Figure S49: ^{1}H NMR Spectra of 1q

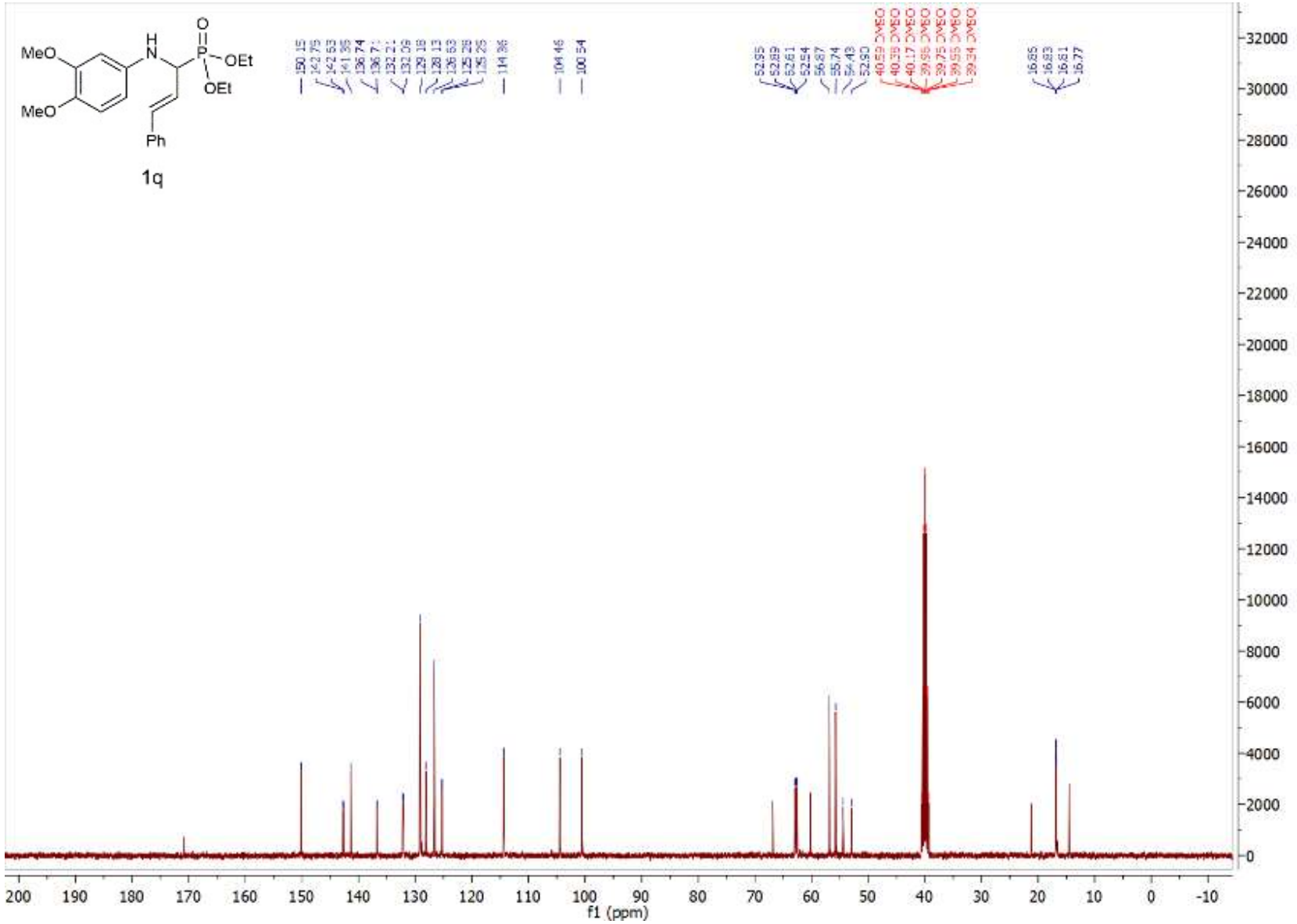


Figure S50: ^{13}C NMR Spectra of q

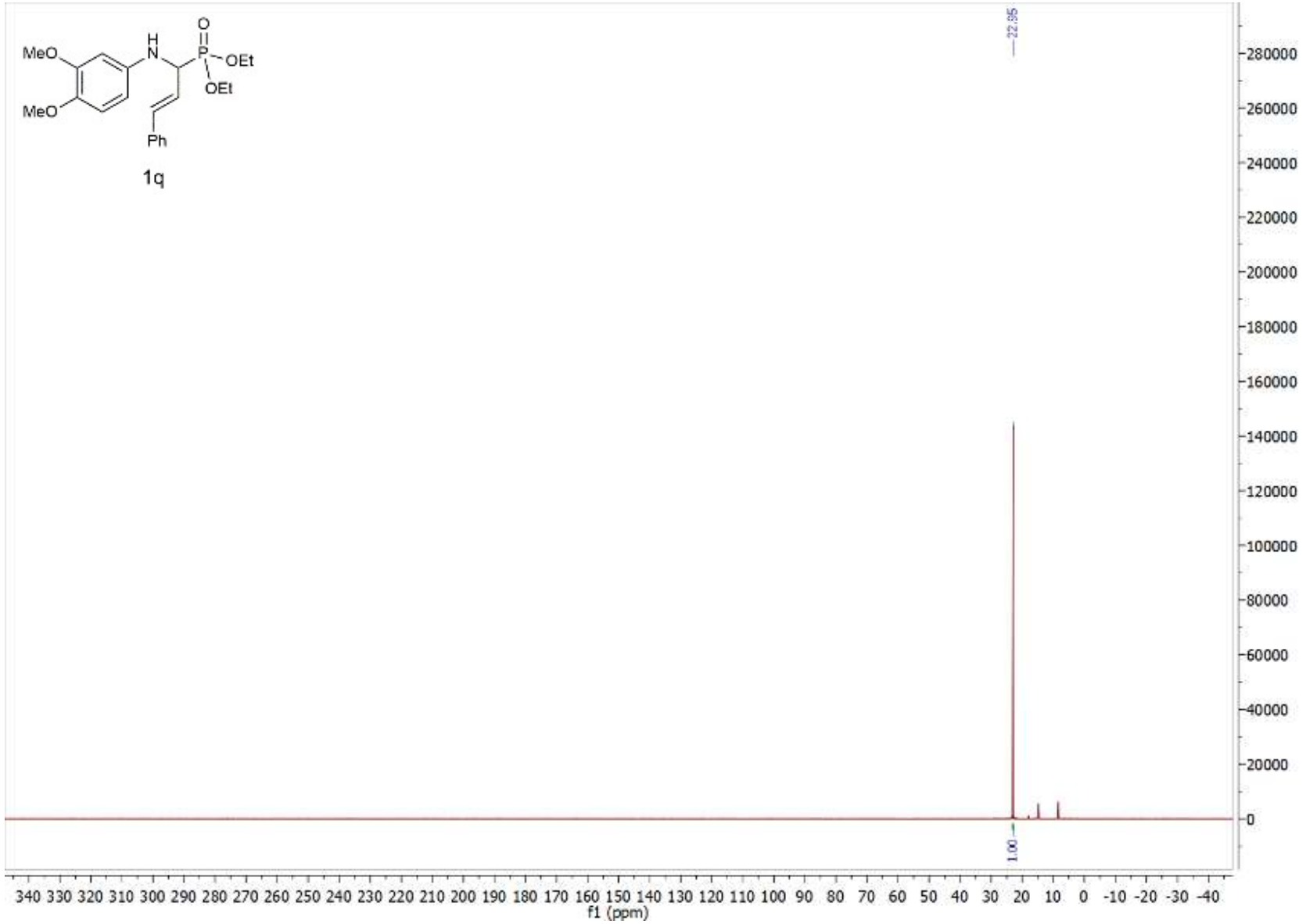


Figure S51: ^{31}P NMR Spectra of 1q

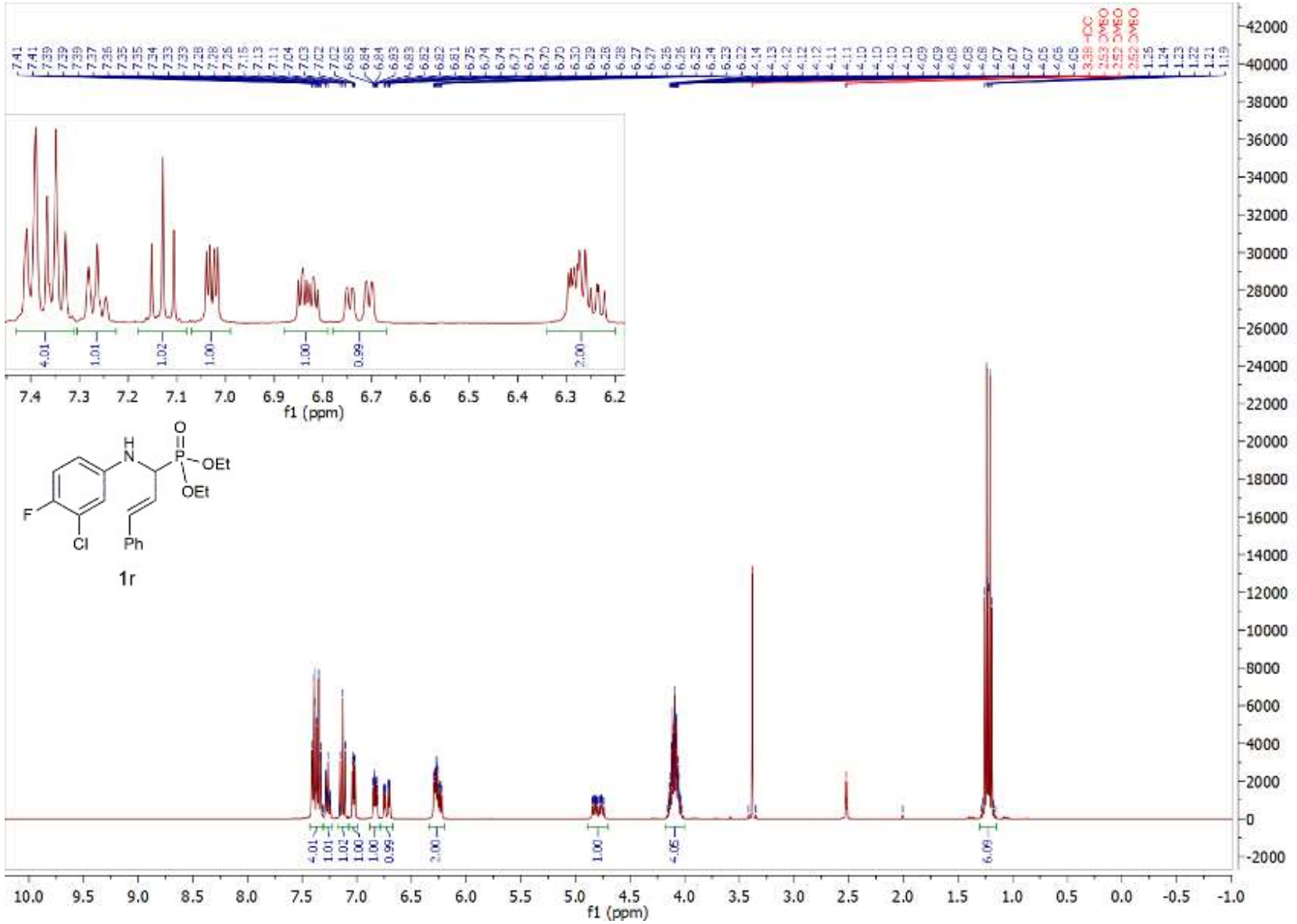


Figure S52: ^{1}H NMR Spectra of 1r

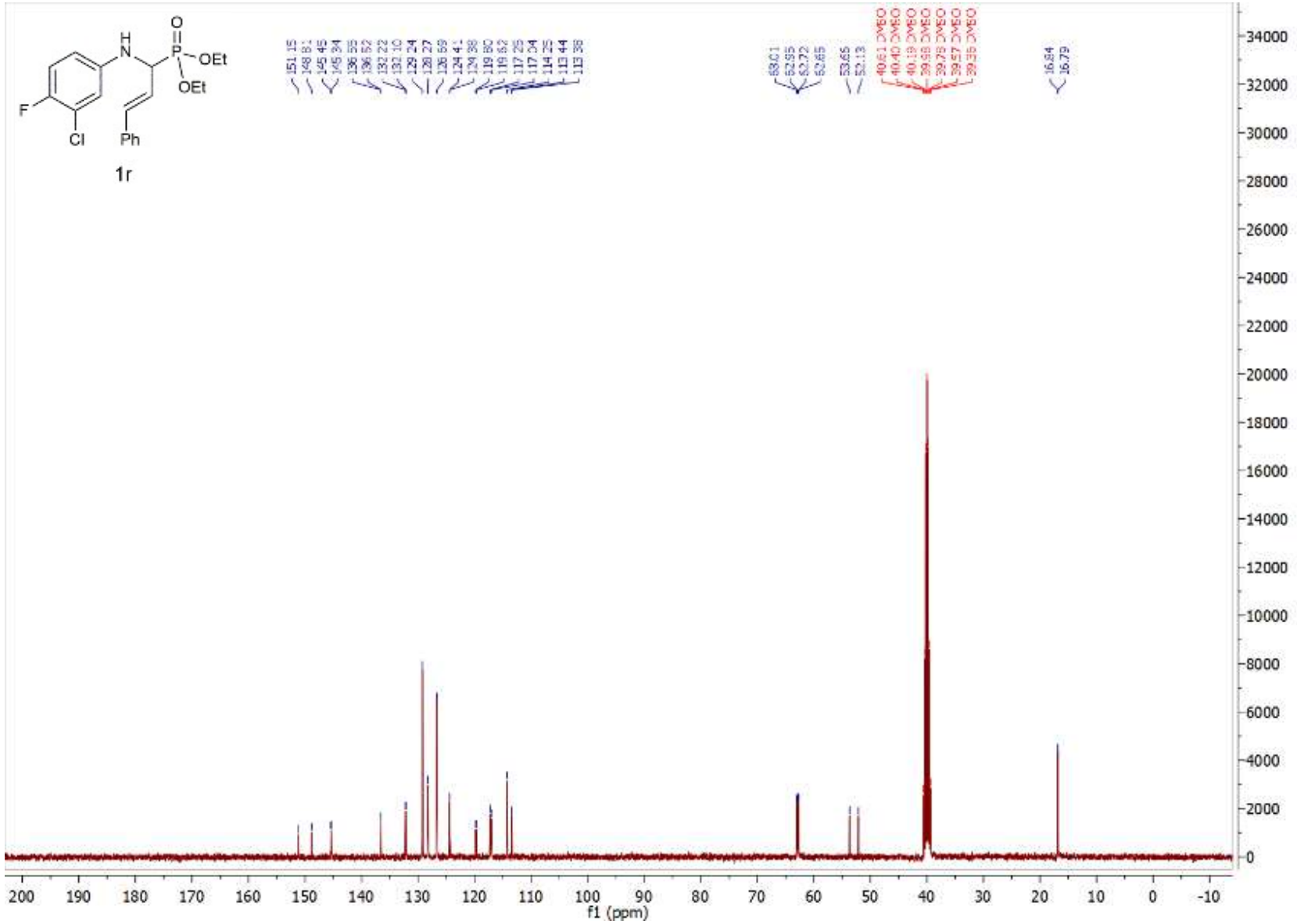


Figure S53: ^{13}C NMR Spectra of 1r

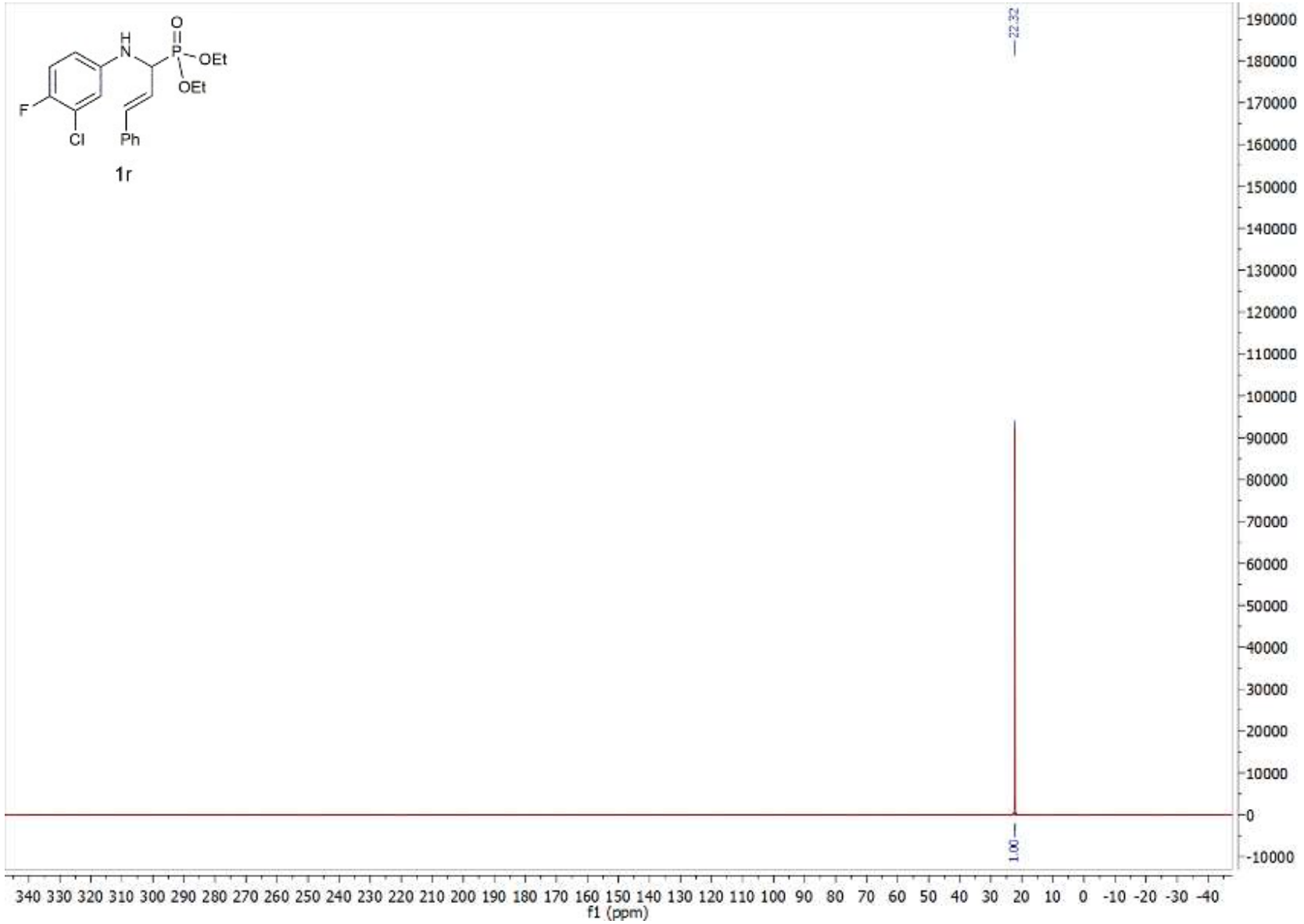


Figure S54: ^{31}P NMR Spectra of 1r

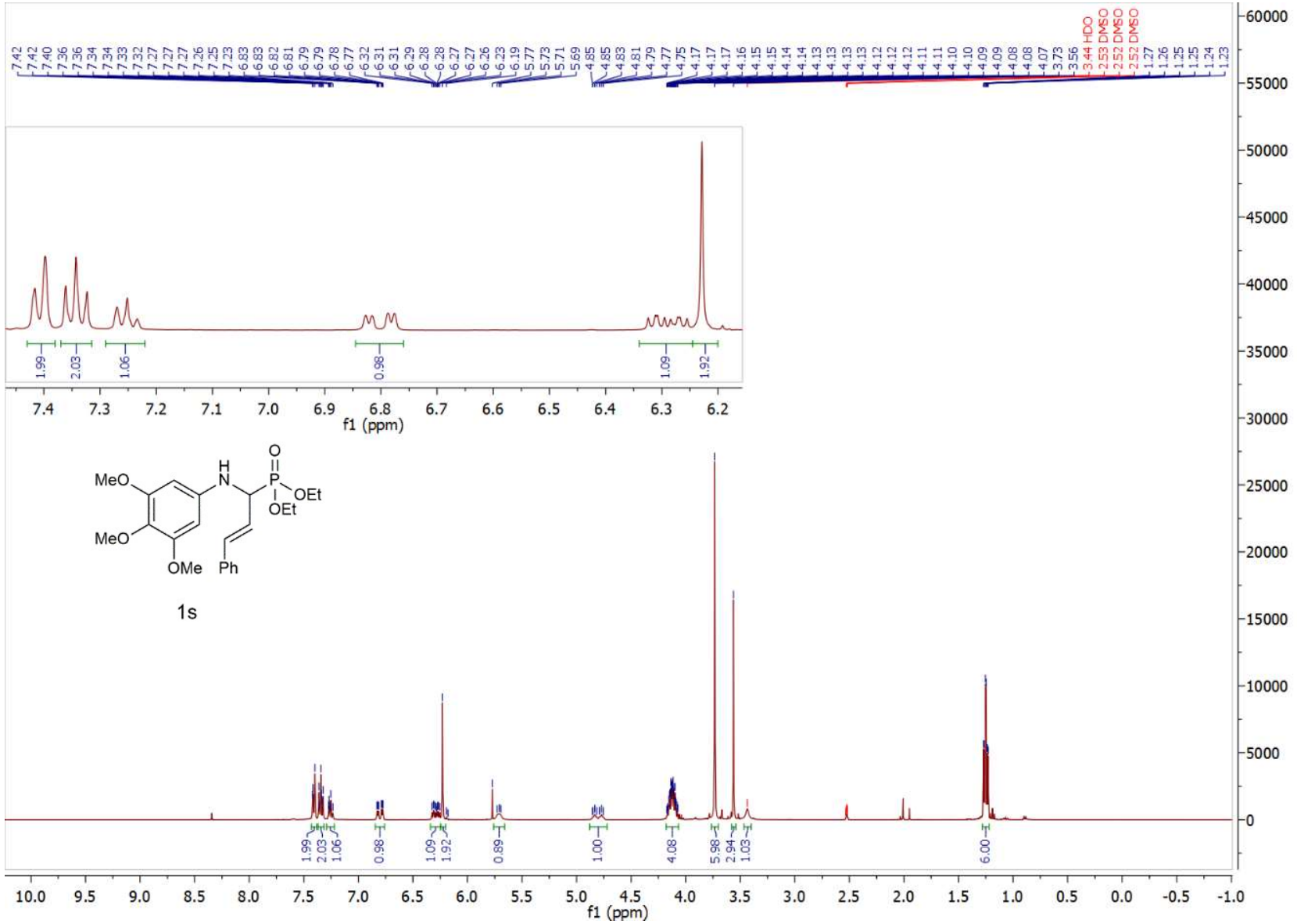


Figure S55: ^{1}H NMR Spectra of 1s

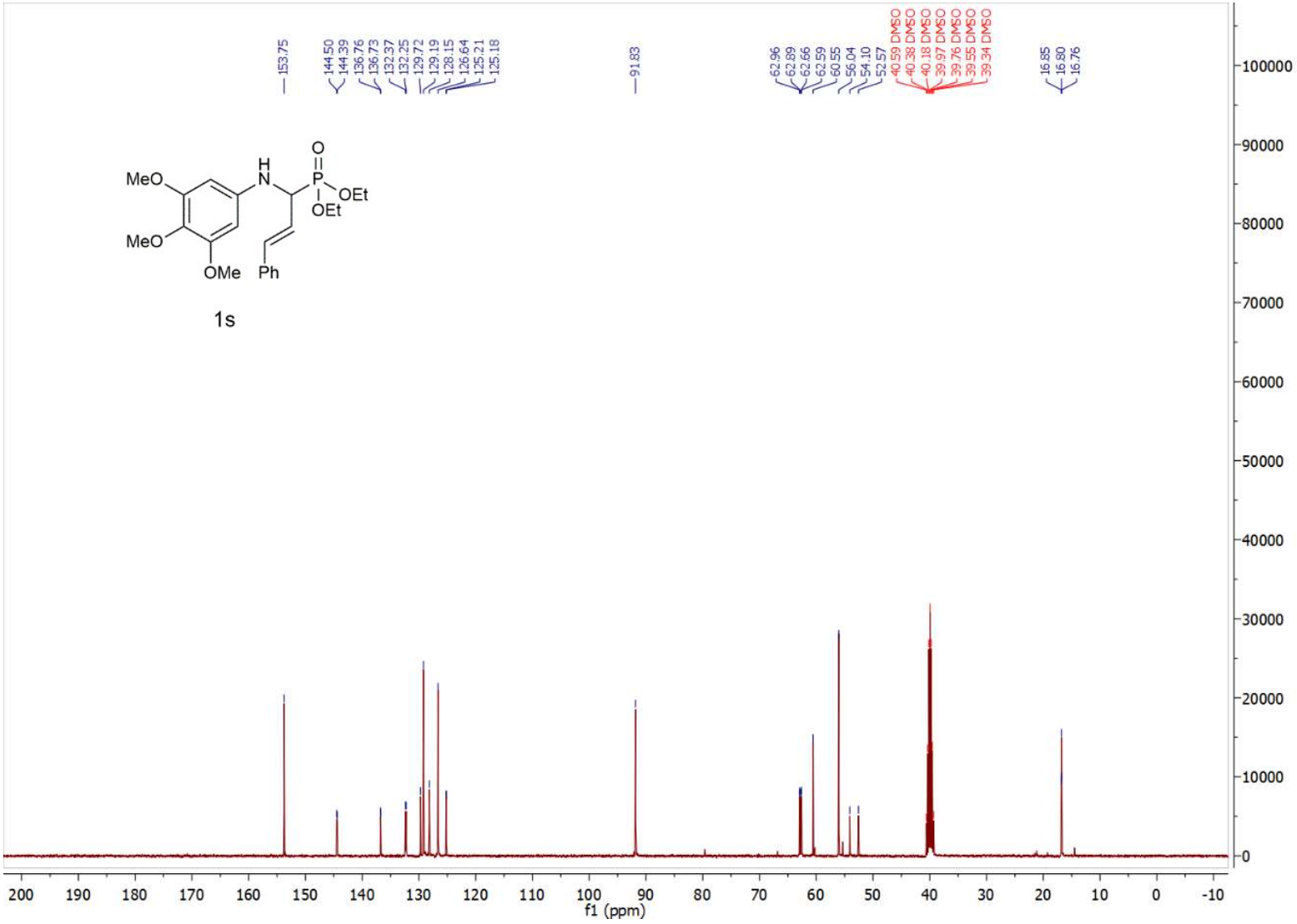


Figure S56: ^{13}C NMR Spectra of 1s

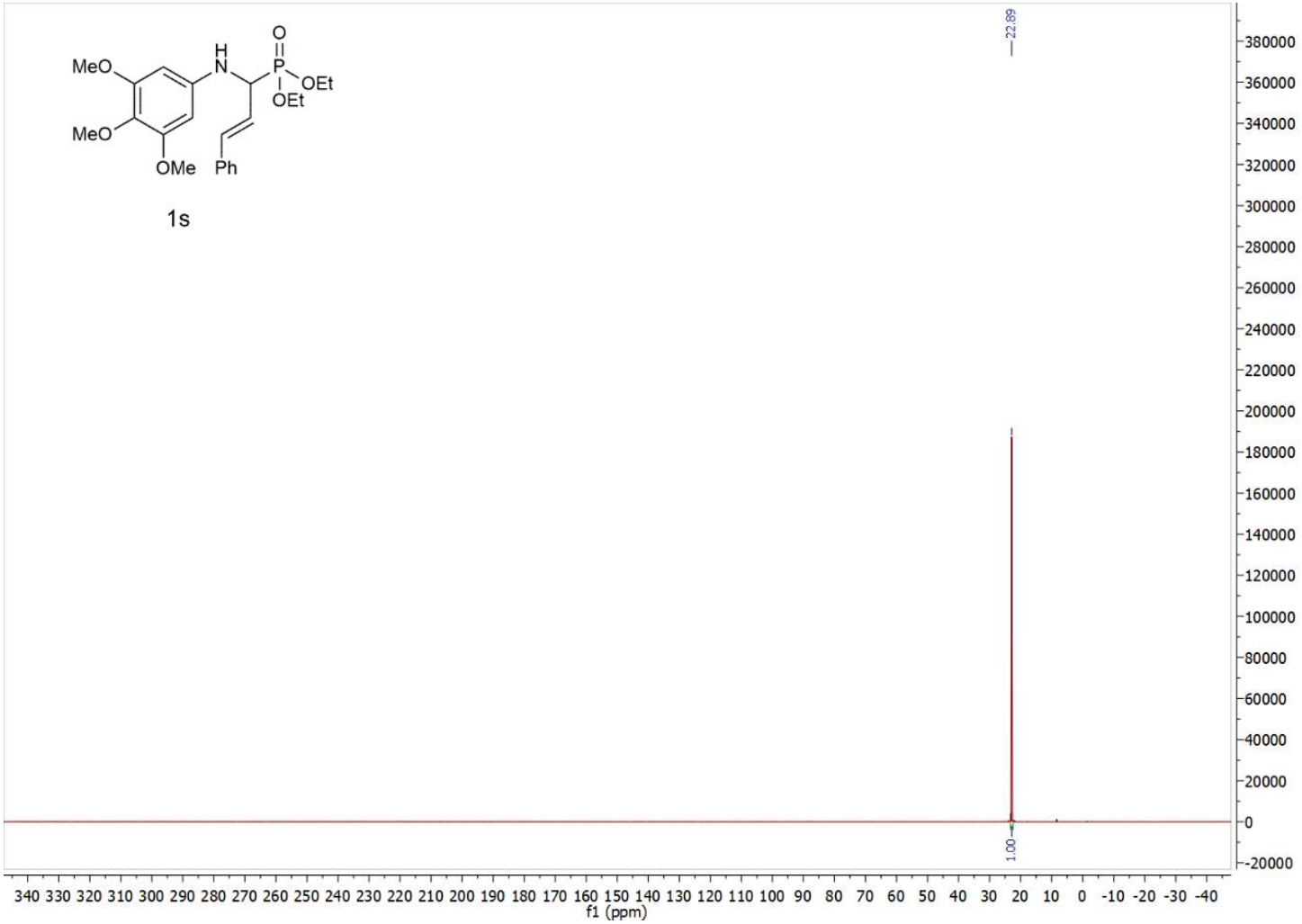


Figure S57: ^{31}P NMR Spectra of 1s

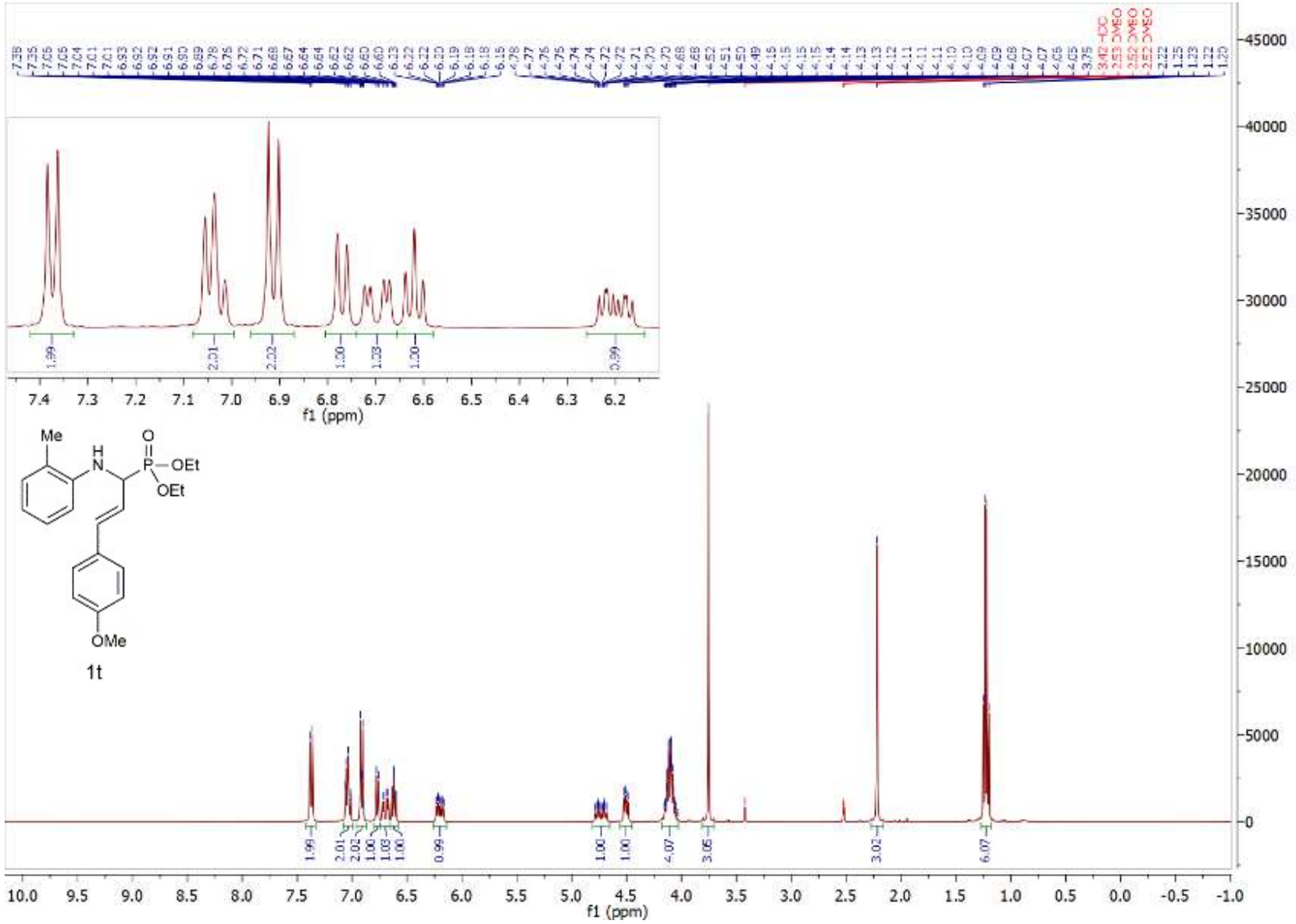

Me
H
N
O
P
OEt
OEt
OMe
1t
f1 (ppm)

Figure S58: ^{1}H NMR Spectra of 1t

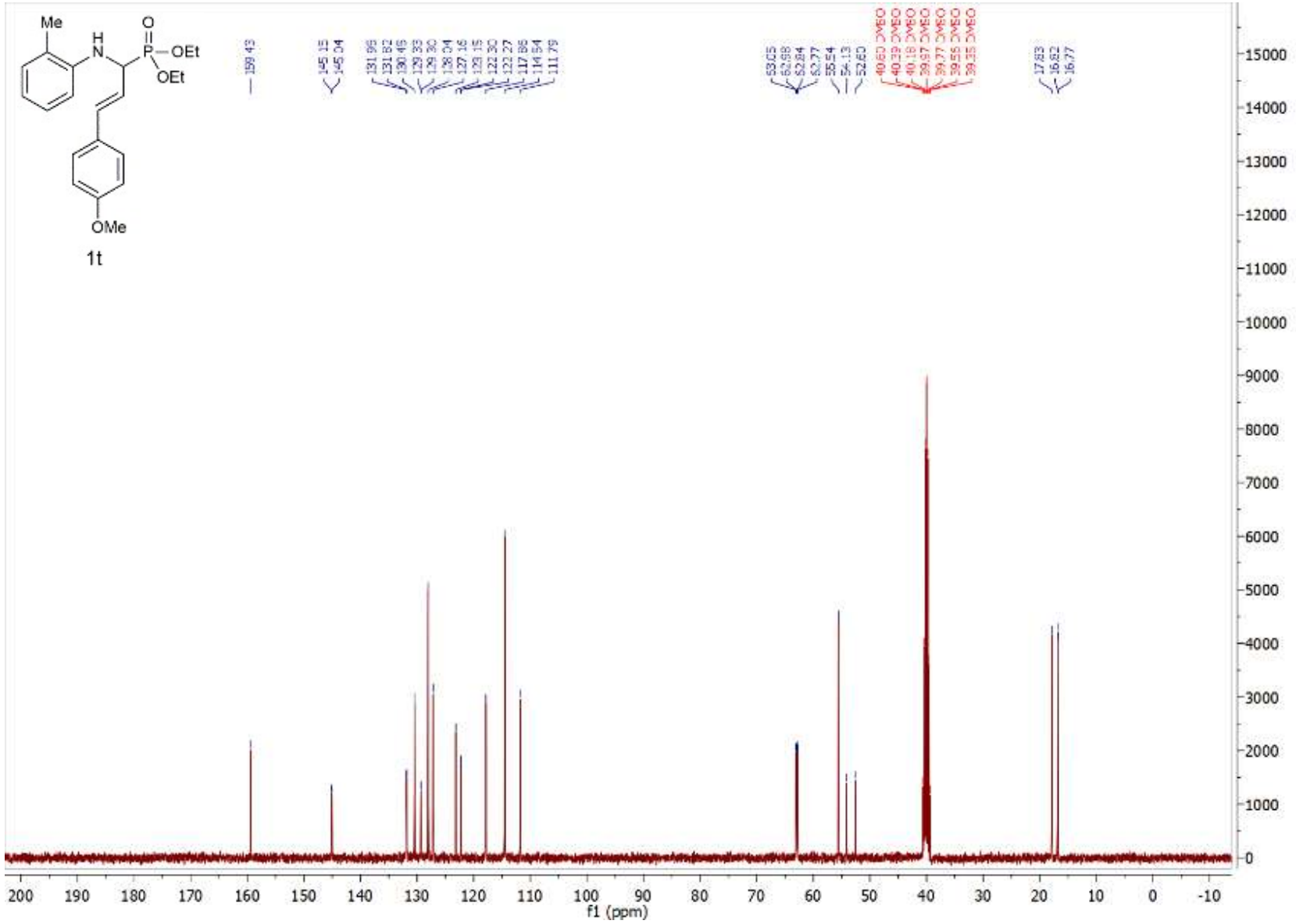


Figure S59: ^{13}C NMR Spectra of 1t

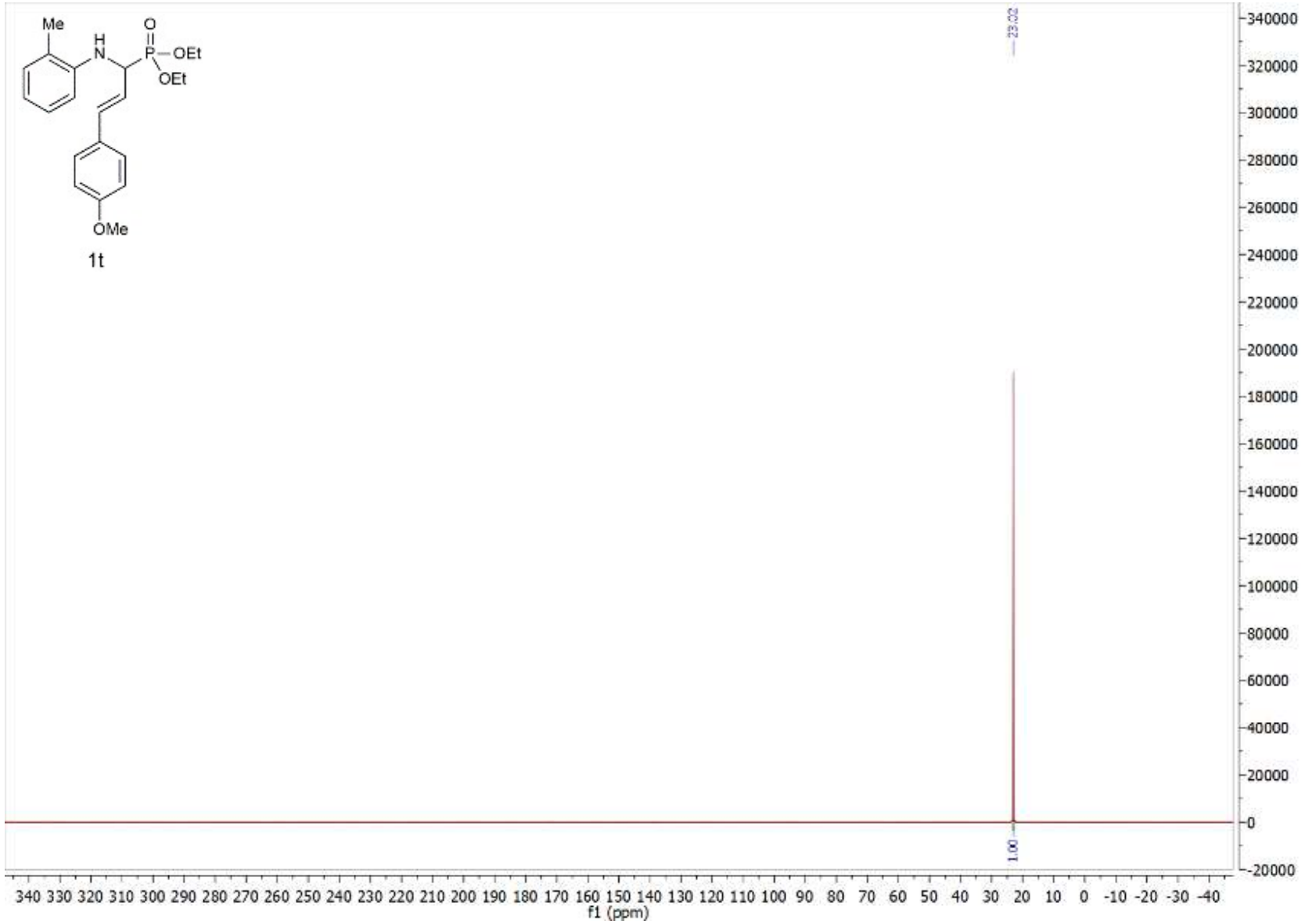


Figure S60: ^{31}P NMR Spectra of 1t

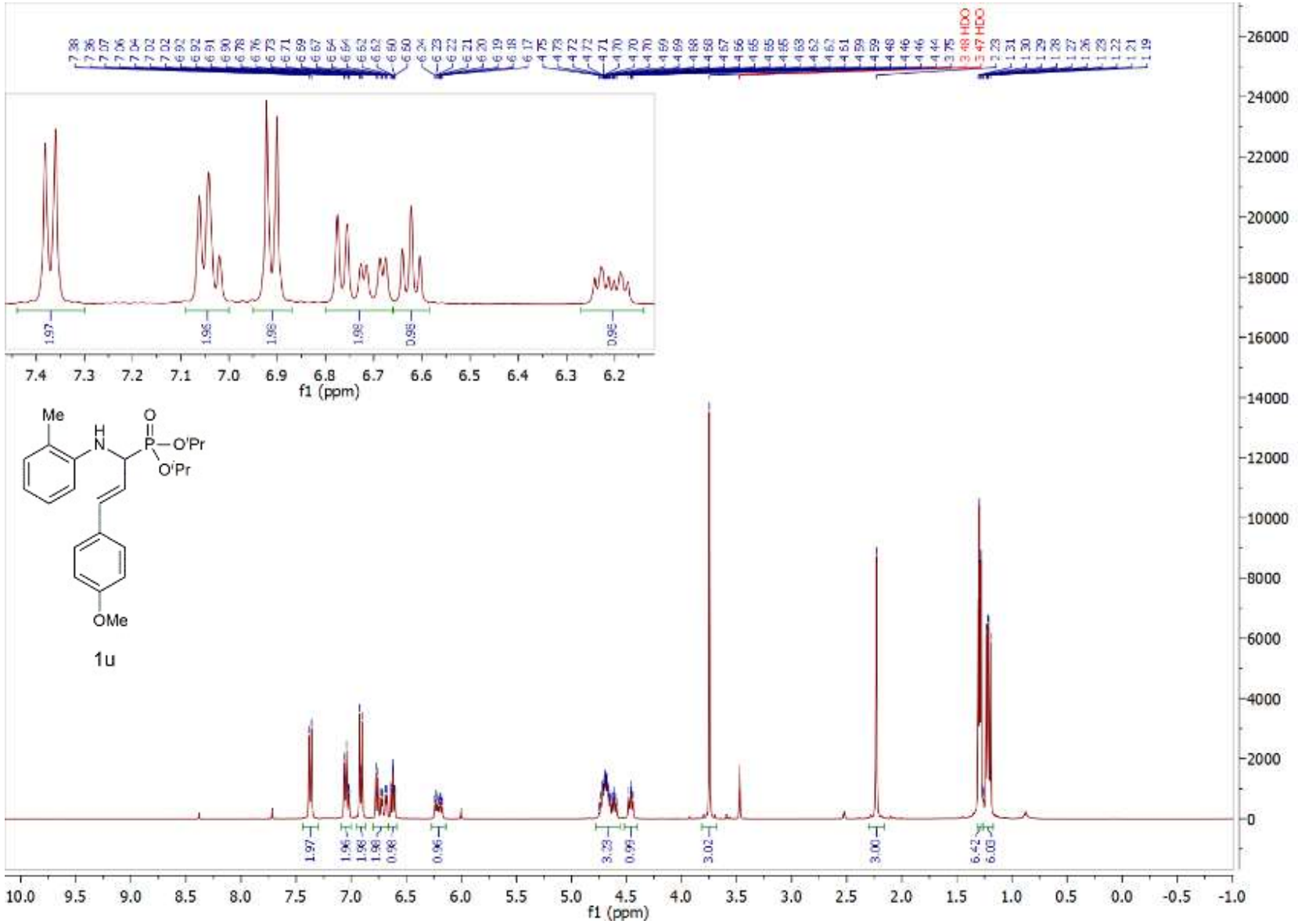


Figure S61: ^{1}H NMR Spectra of 1u

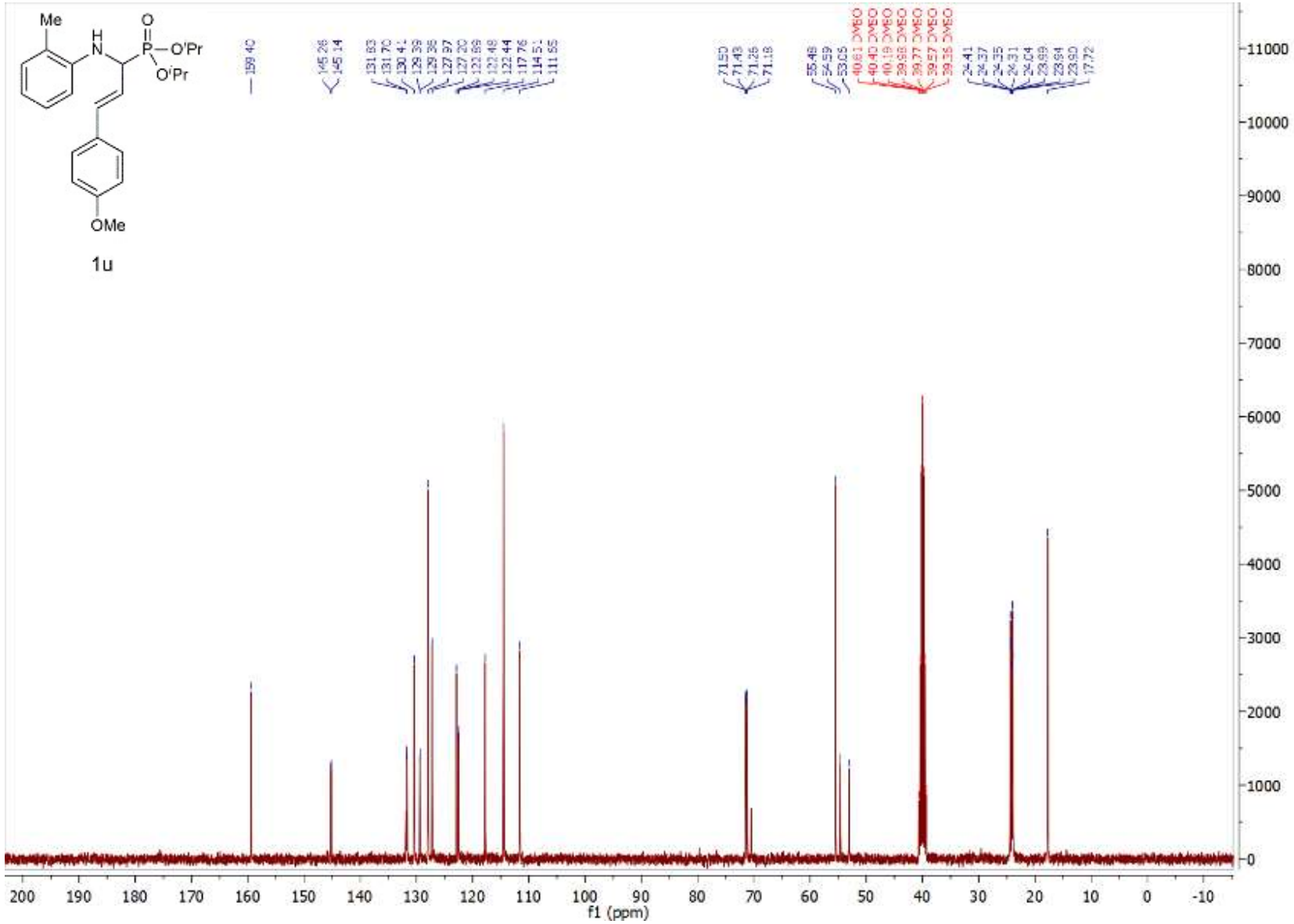


Figure S62: ^{13}C NMR Spectra of 1u

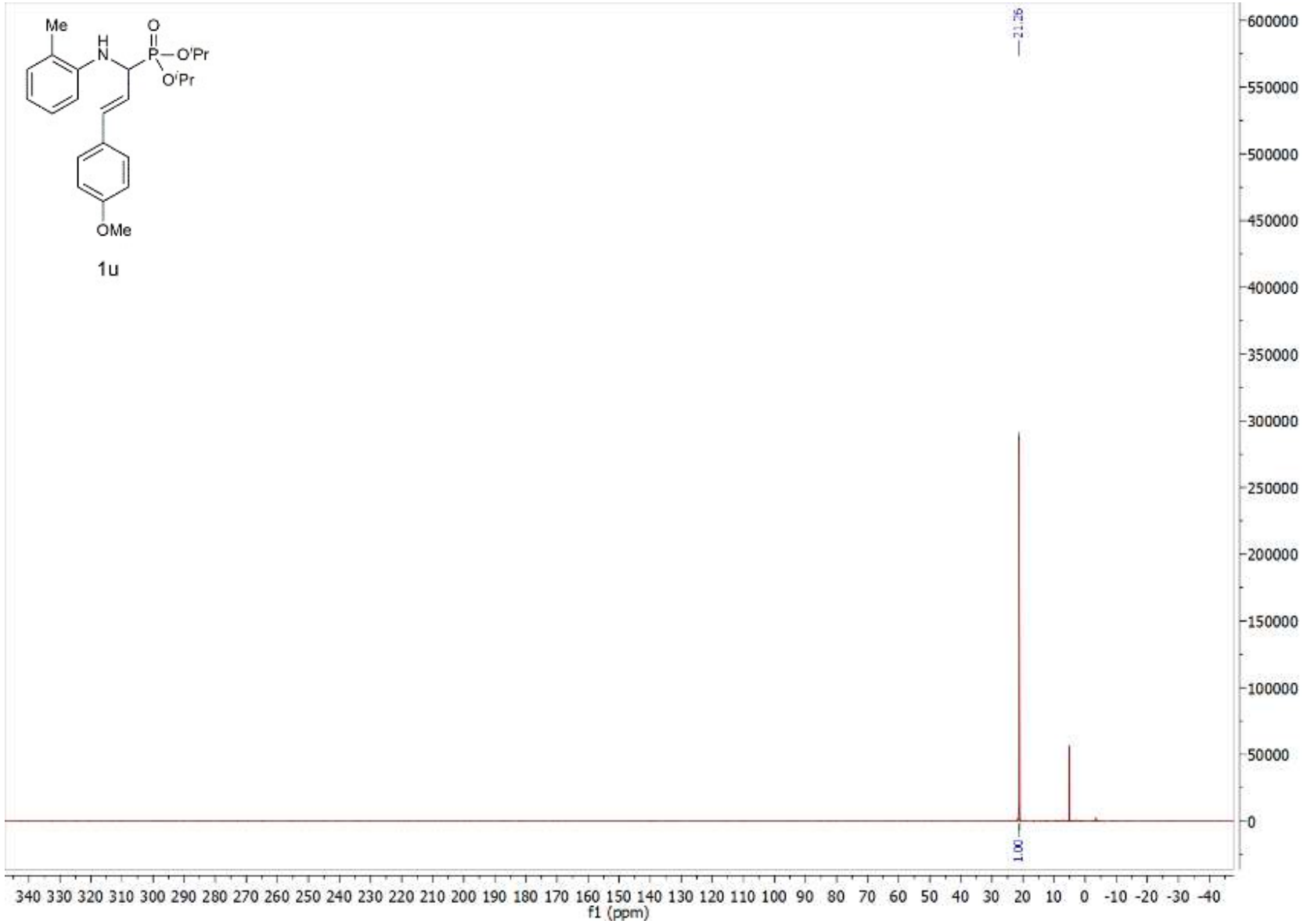


Figure S63: ^{31}P NMR Spectra of 1u

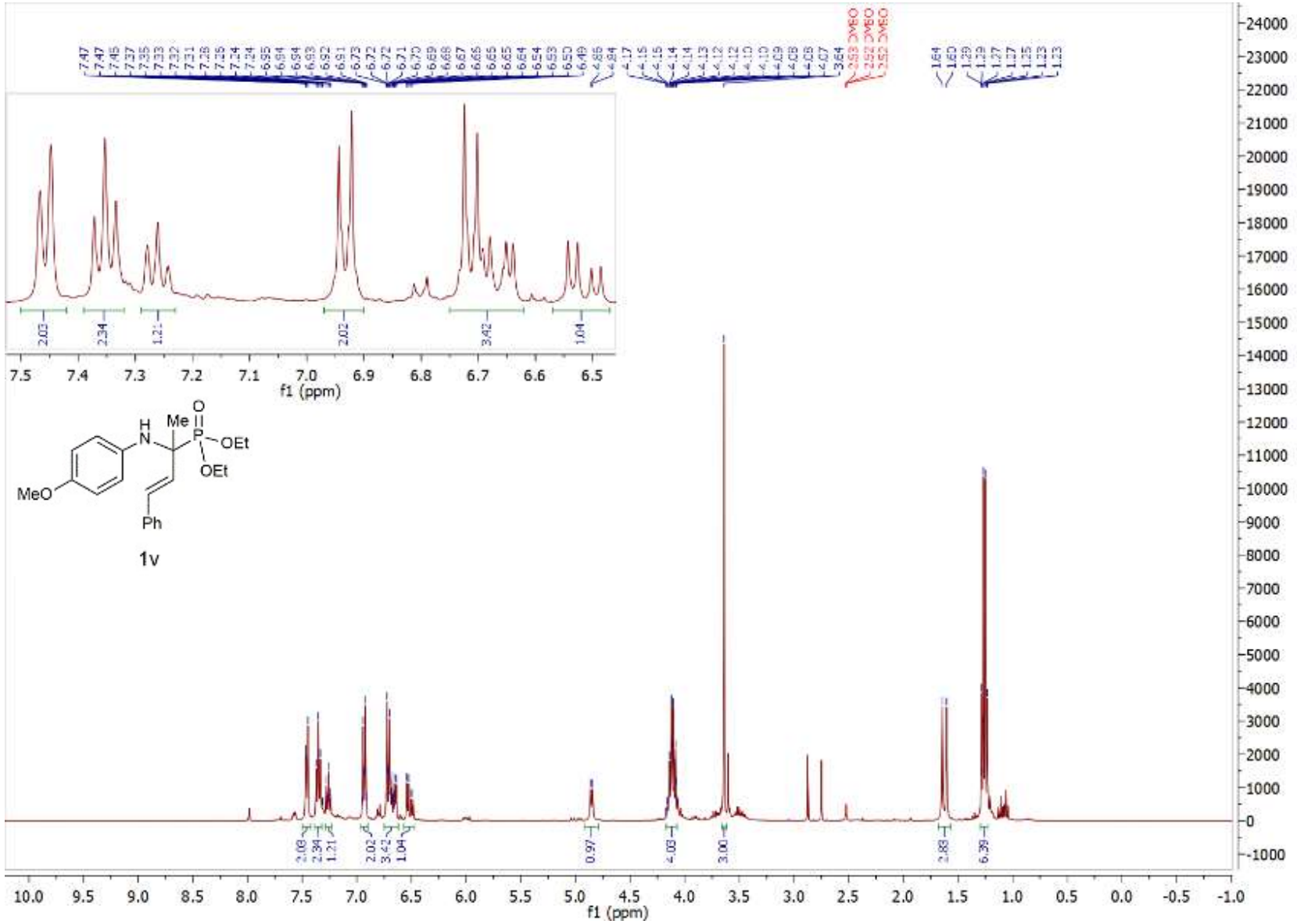


Figure S64: ^{1}H NMR Spectra of 1v

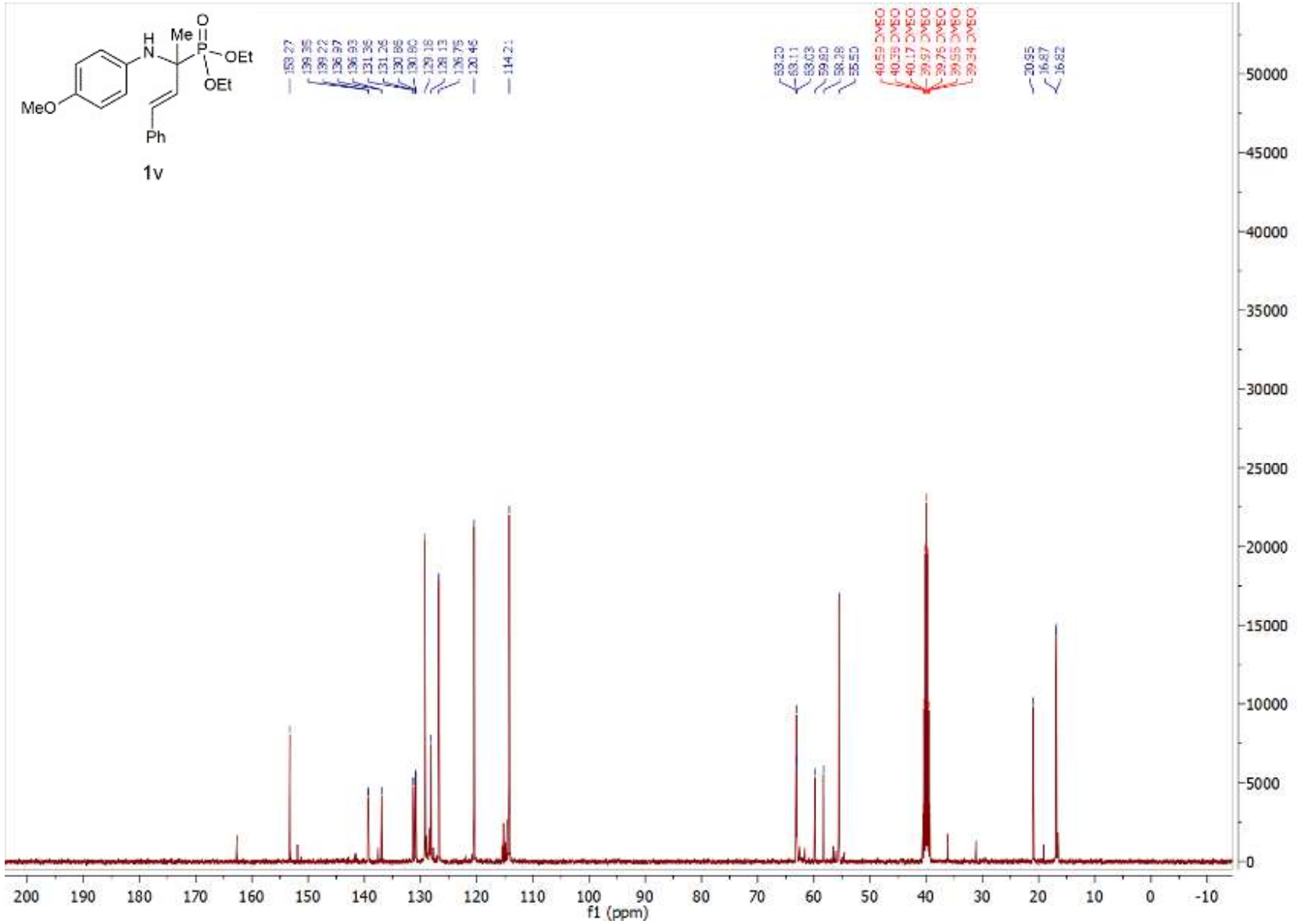


Figure S65: ^{13}C NMR Spectra of 1v

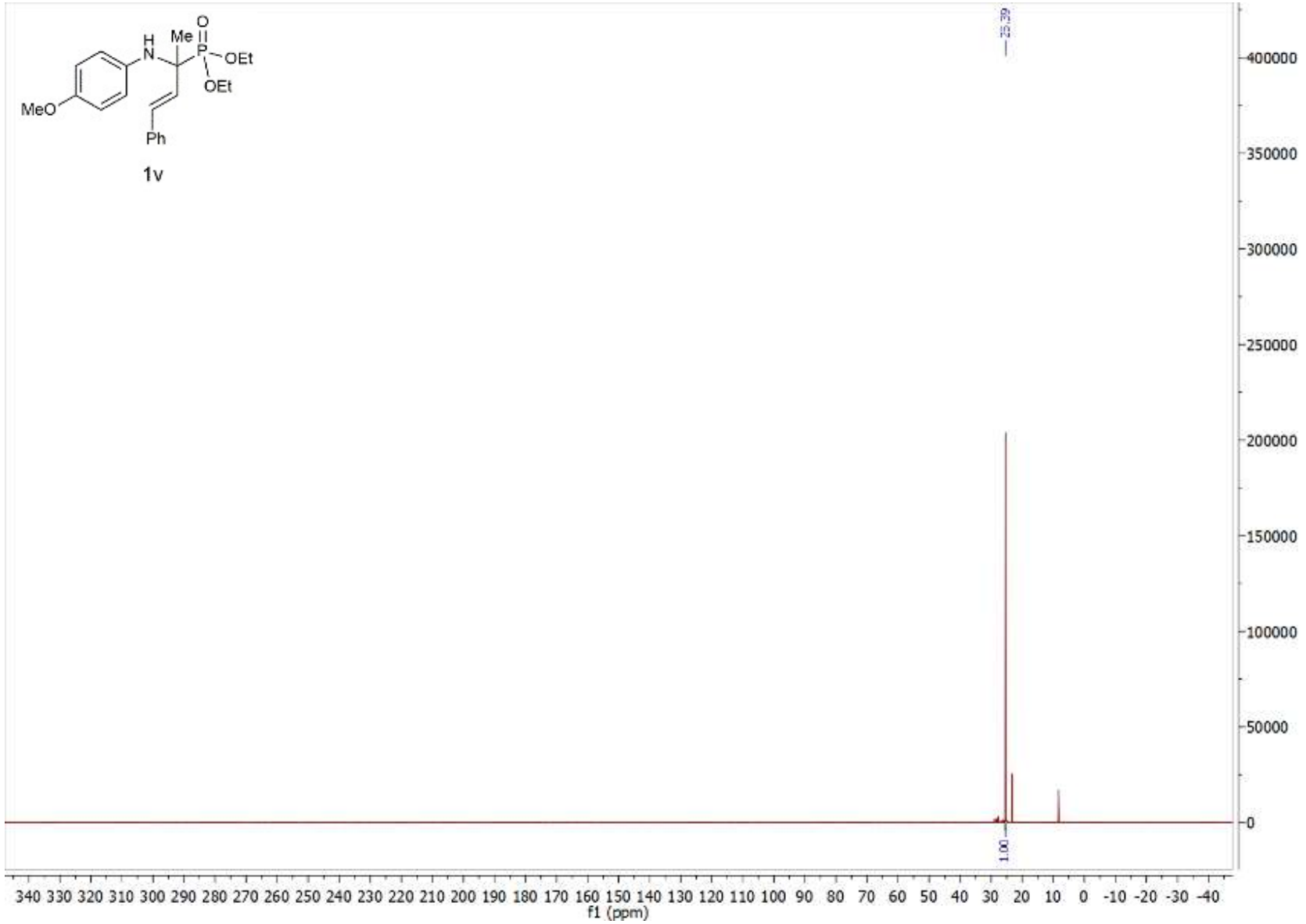


Figure S66: ^{31}P NMR Spectra of 1v

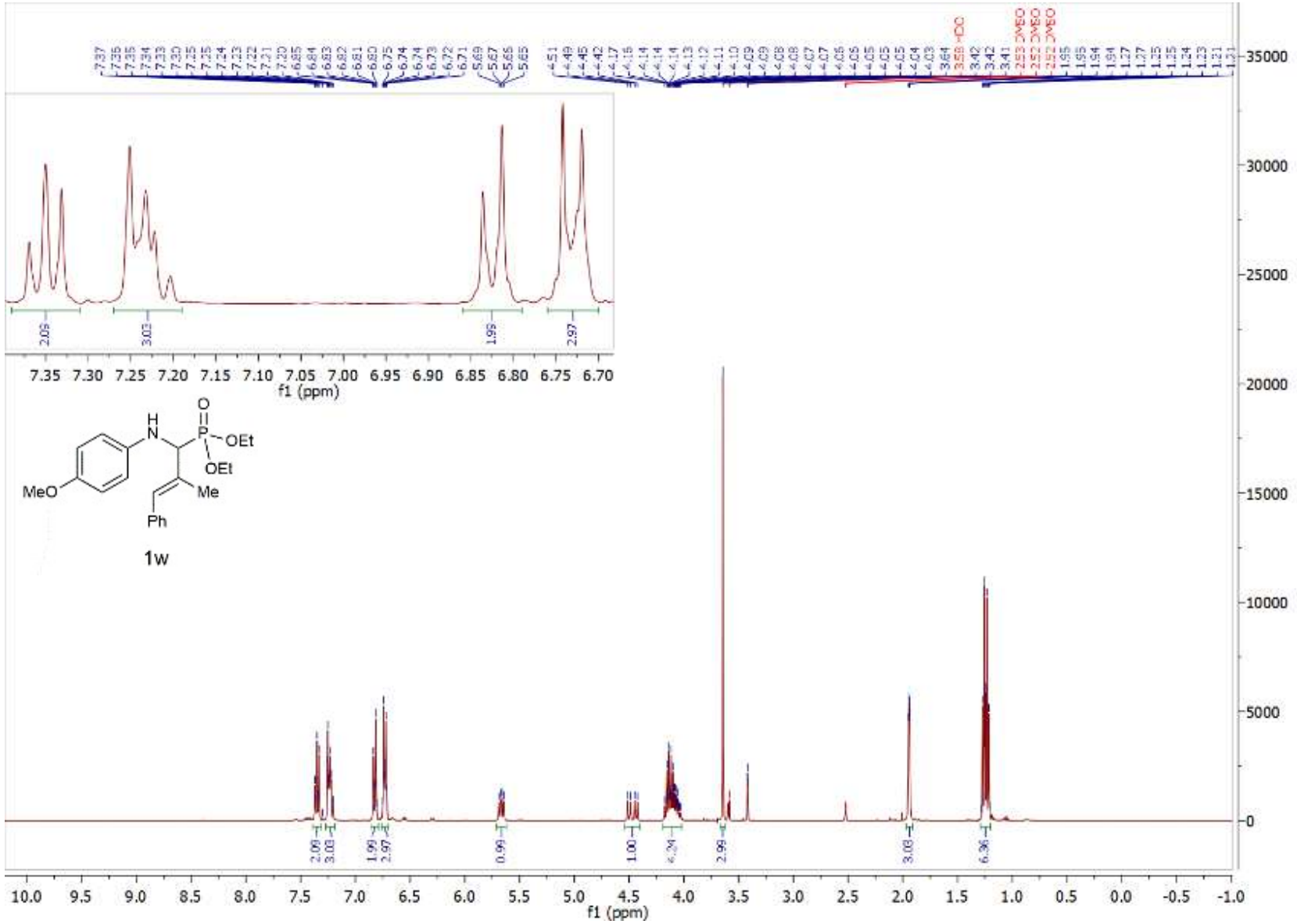


Figure S67: ^{1}H NMR Spectra of 1w

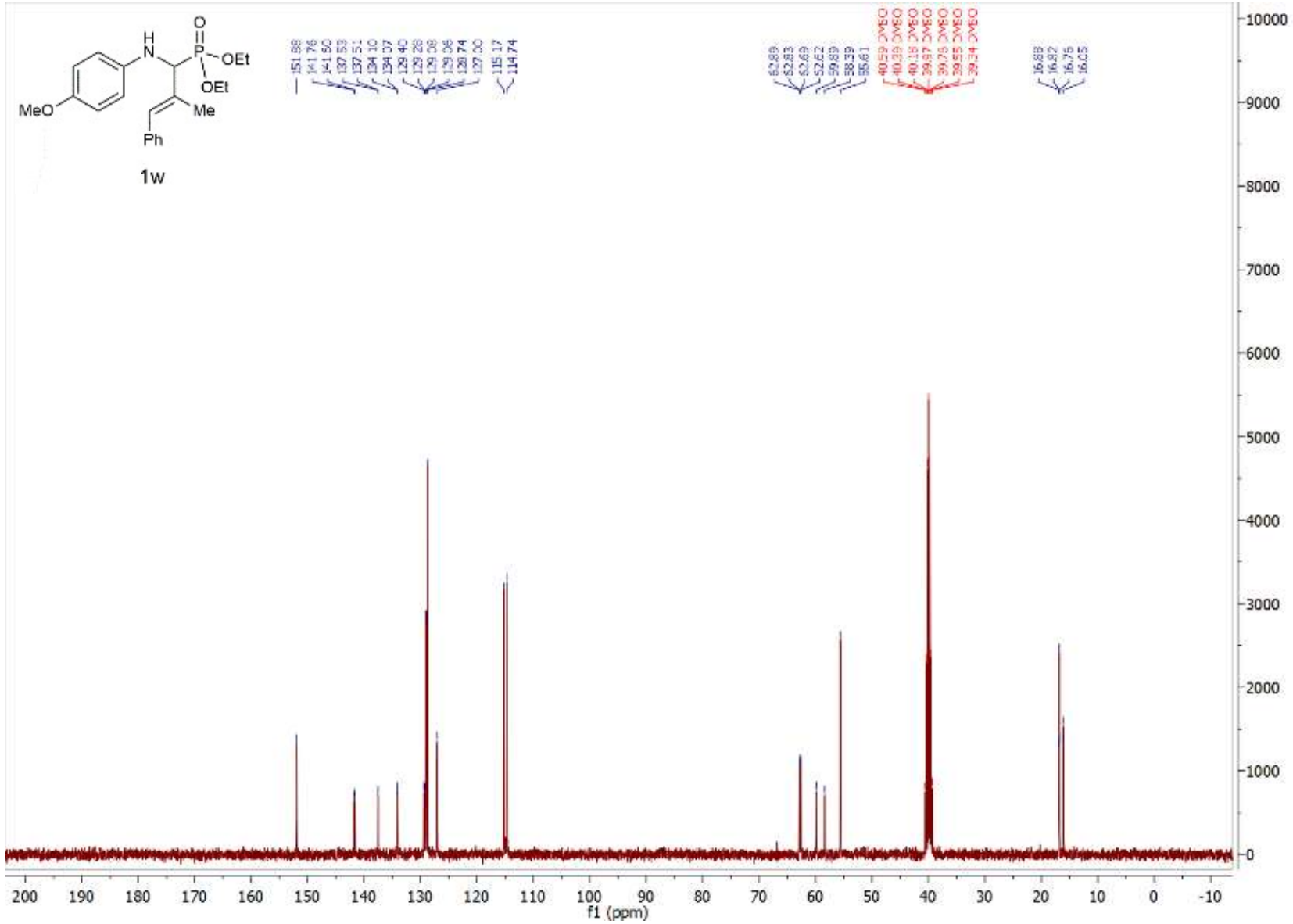


Figure S68: ^{13}C NMR Spectra of 1w

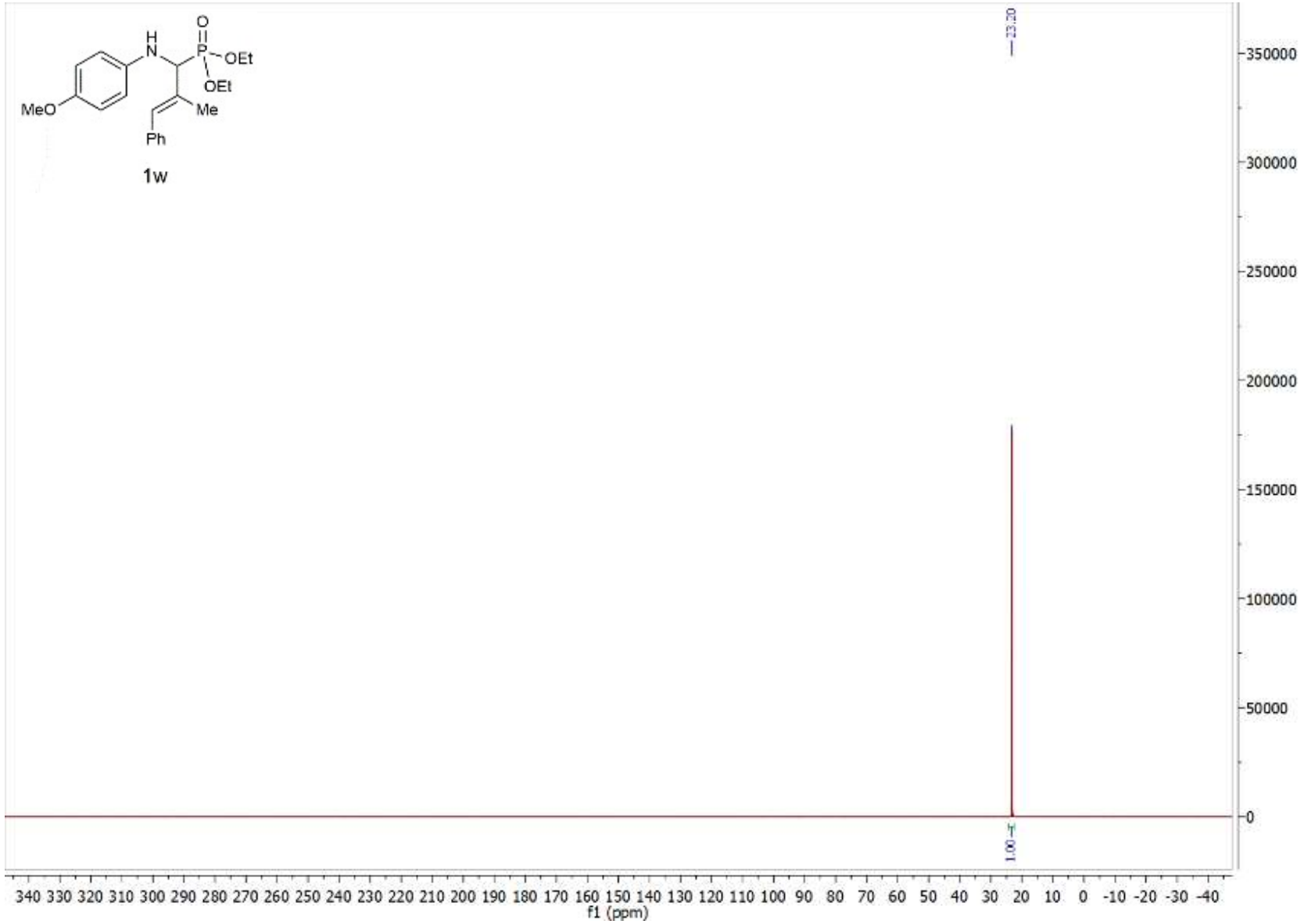


Figure S69: ^{31}P NMR Spectra of 1w

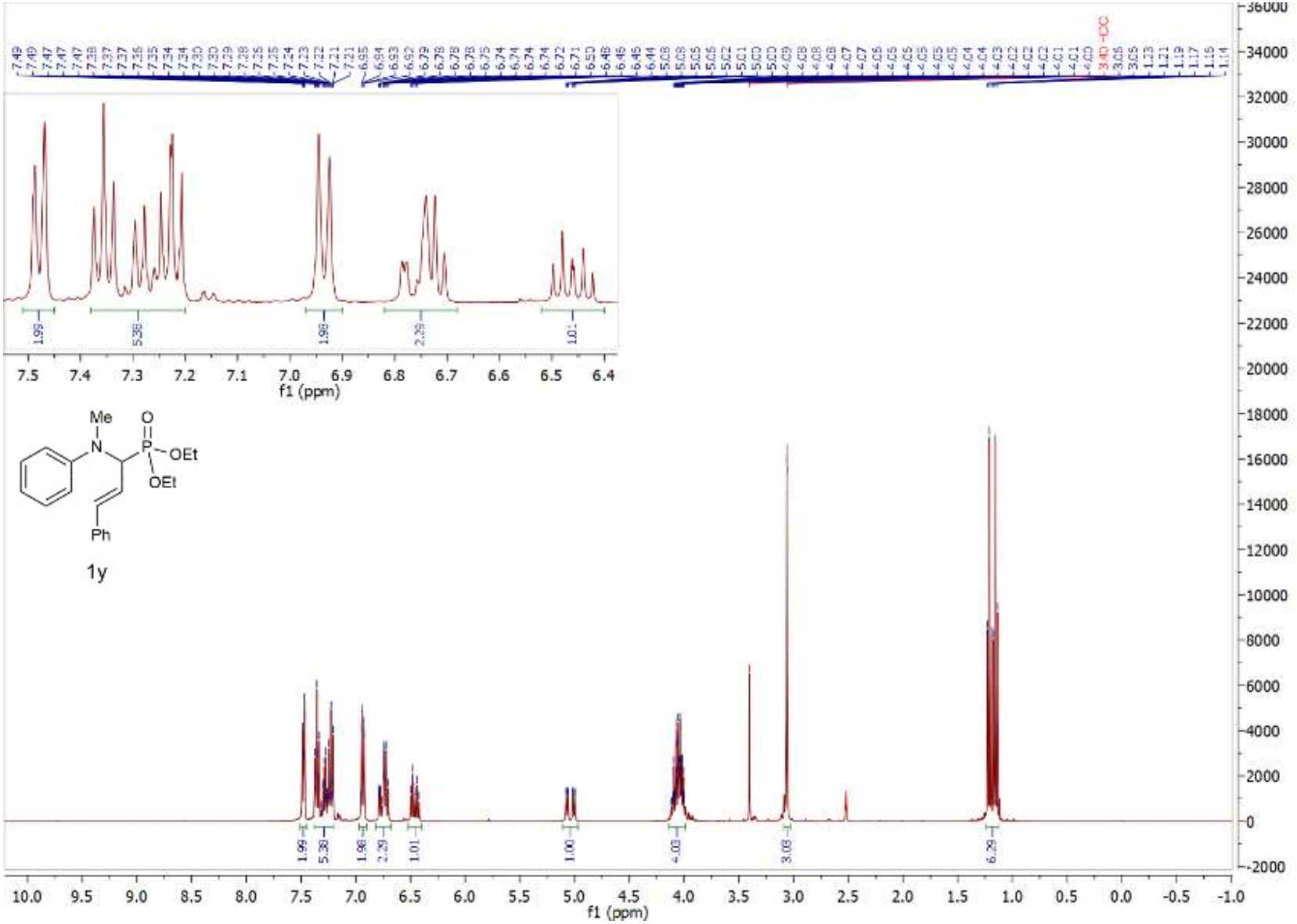


Figure S70: ^{1}H NMR Spectra of 1y

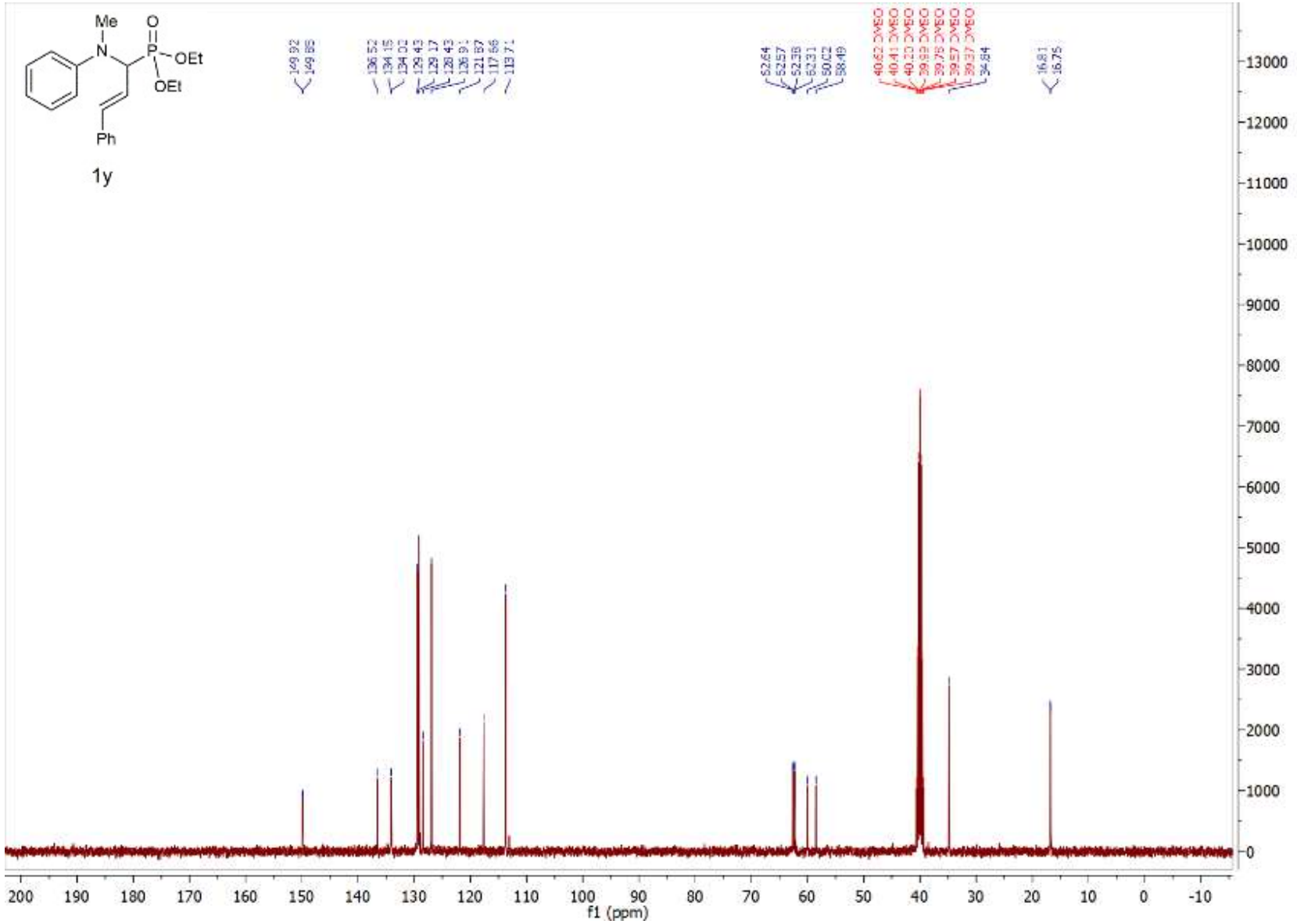


Figure S71: ^{13}C NMR Spectra of 1y

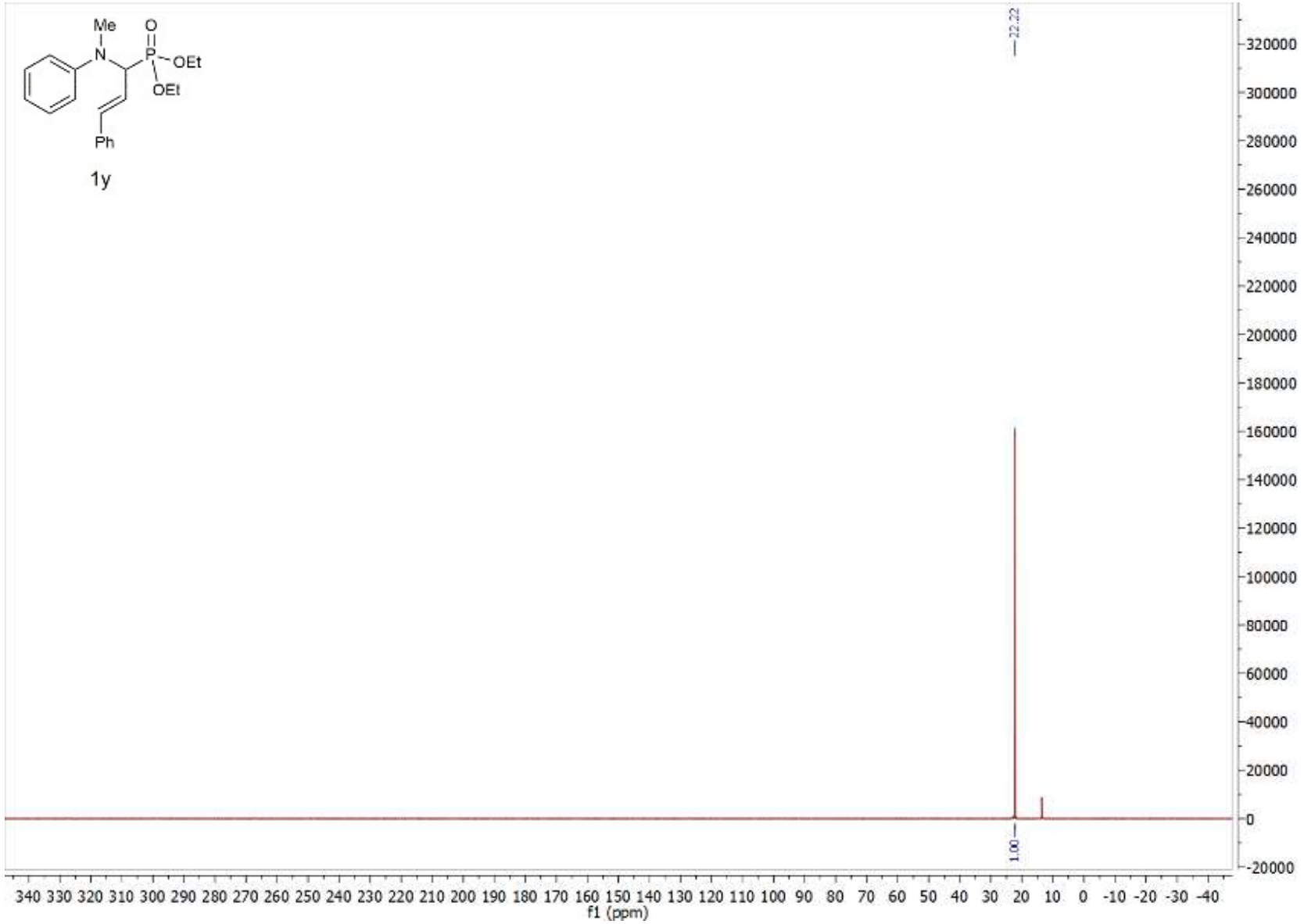


Figure S72: ^{31}P NMR Spectra of 1y

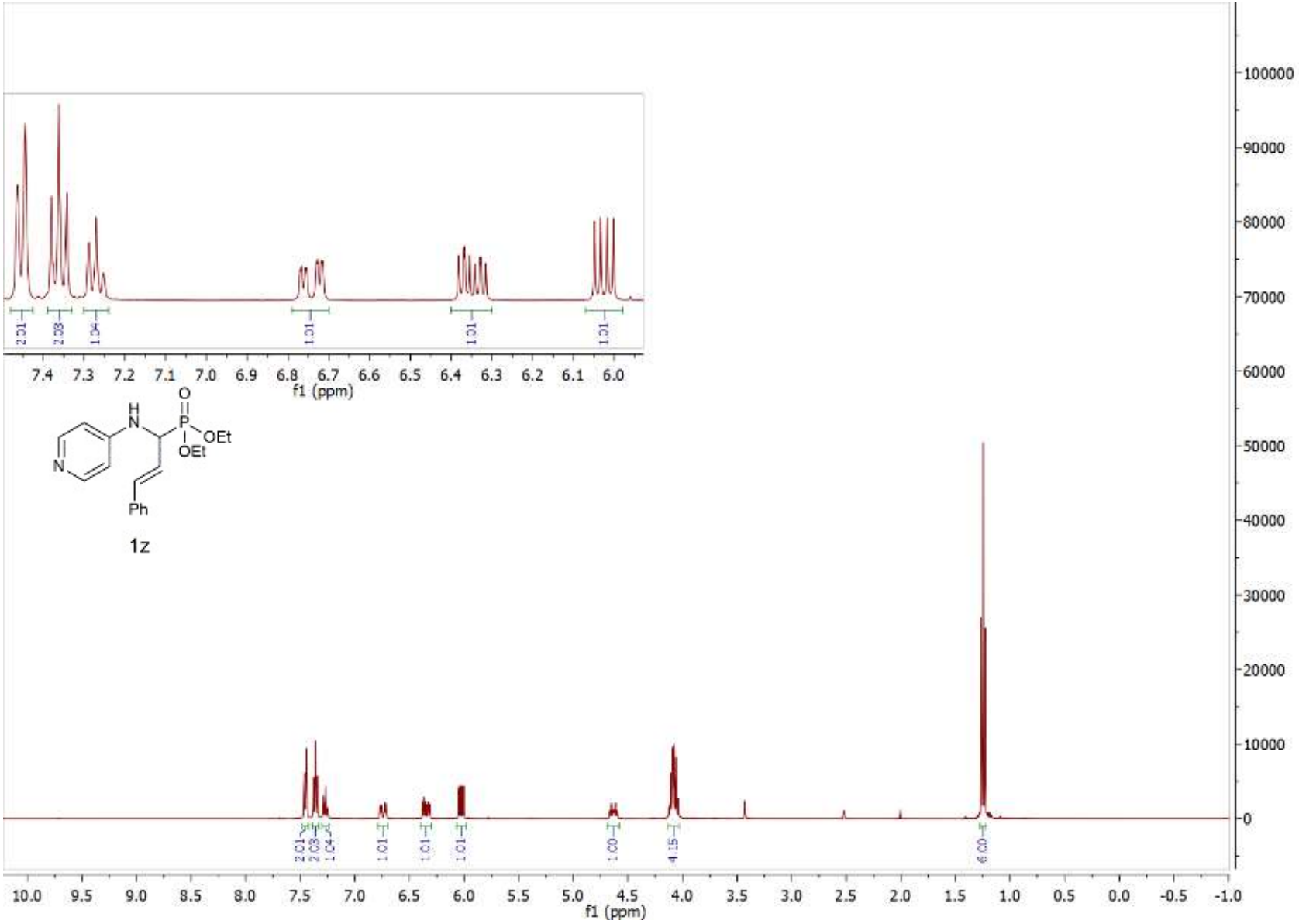


Figure S73: ^{1}H NMR Spectra of 1z

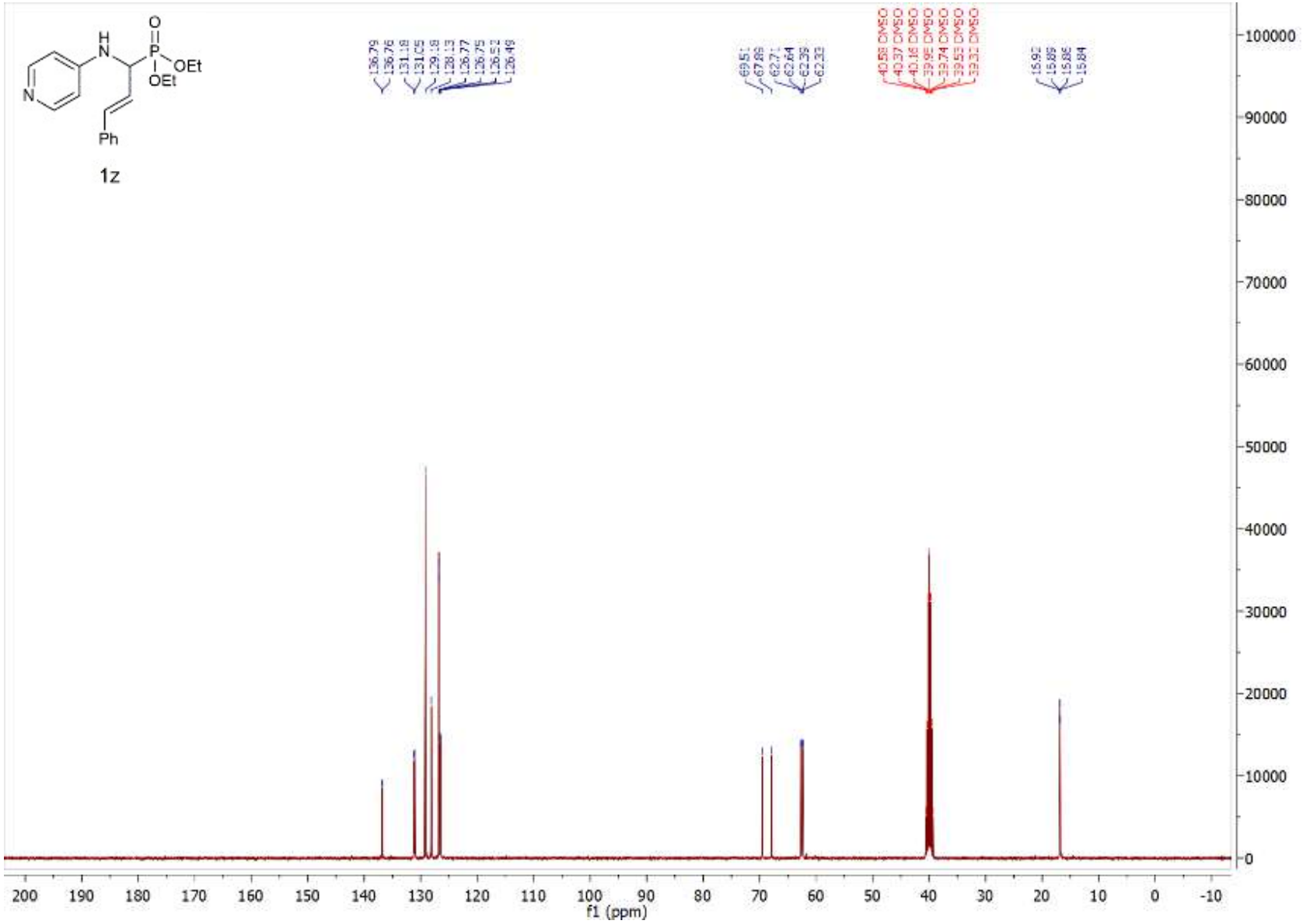


Figure S74: ^{13}C NMR Spectra of 1z

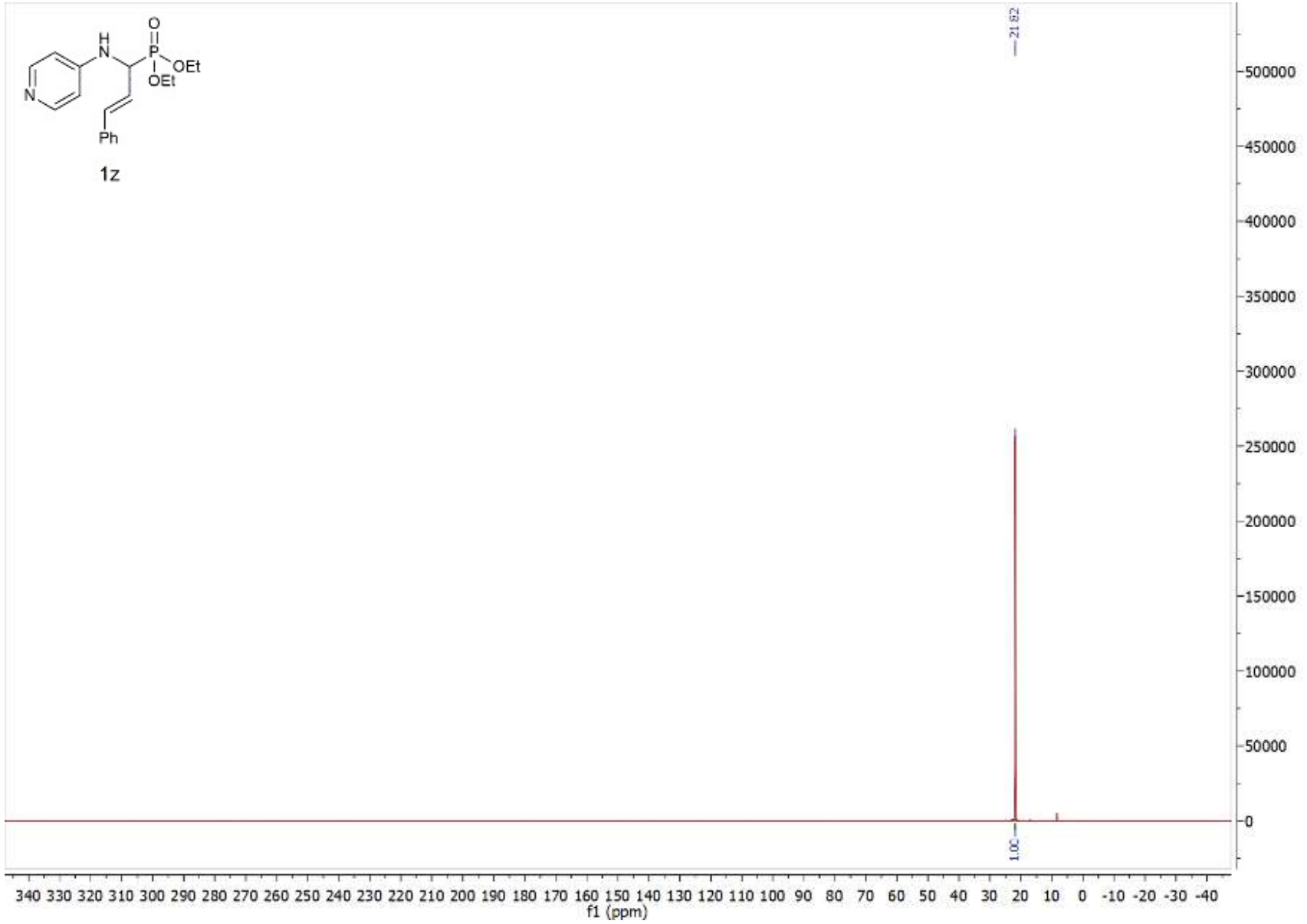


Figure S75: ^{31}P NMR Spectra of 1z

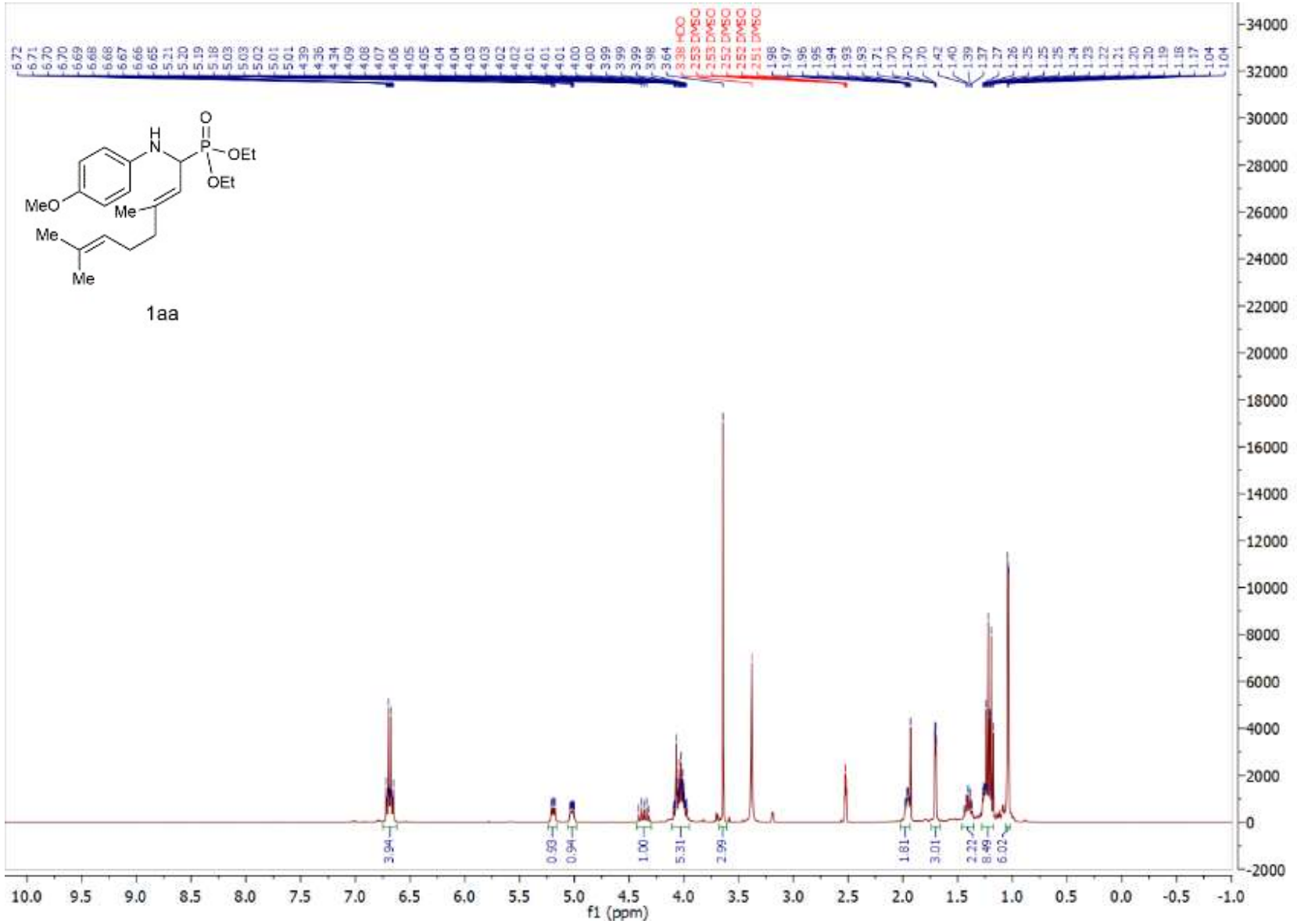


Figure S76: ^{1}H NMR Spectra of 1aa

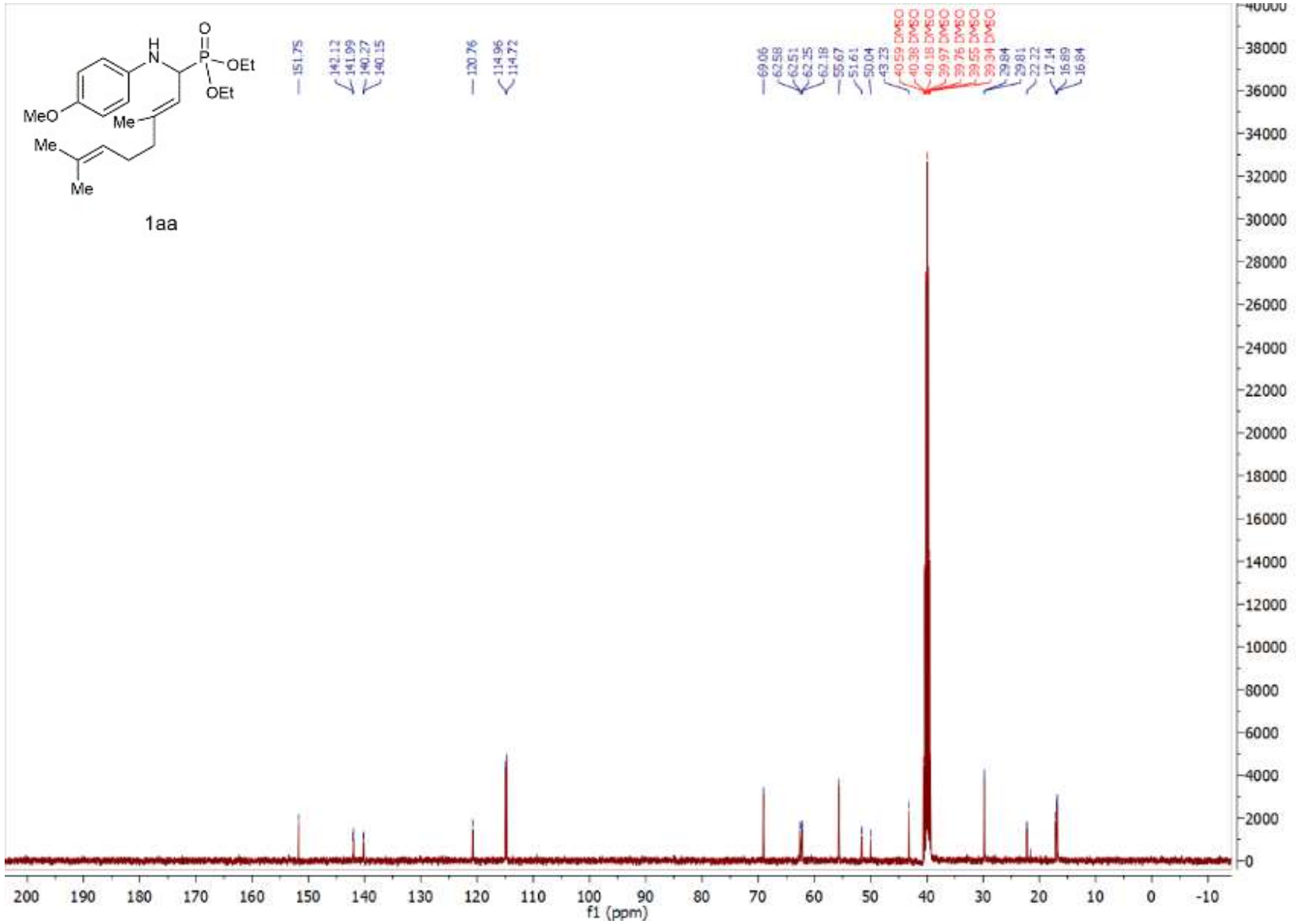


Figure S77: ^{13}C NMR Spectra of 1aa

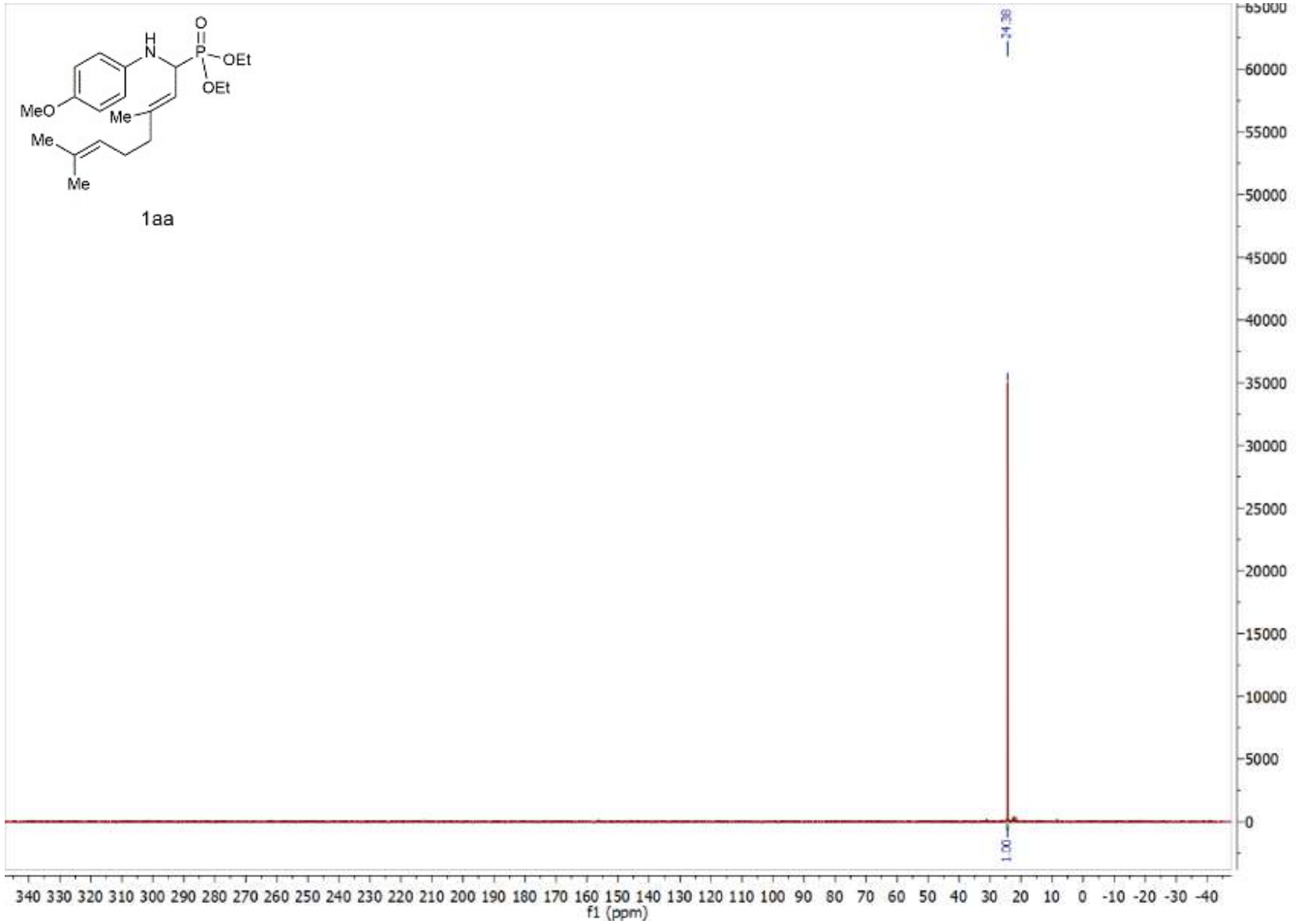


Figure S78: ^{31}P NMR Spectra of 1aa

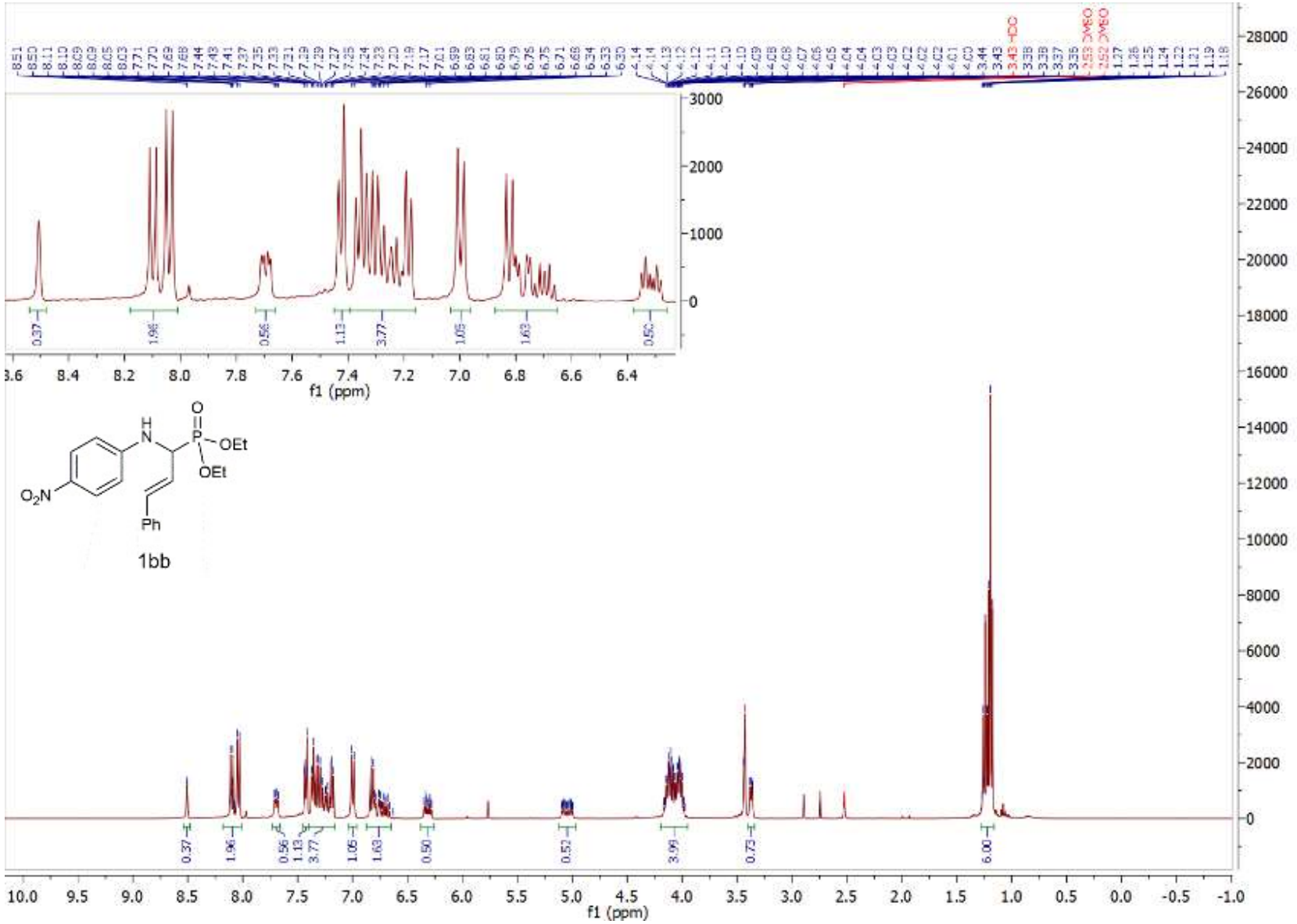


Figure S79: ^{1}H NMR Spectra of 1bb

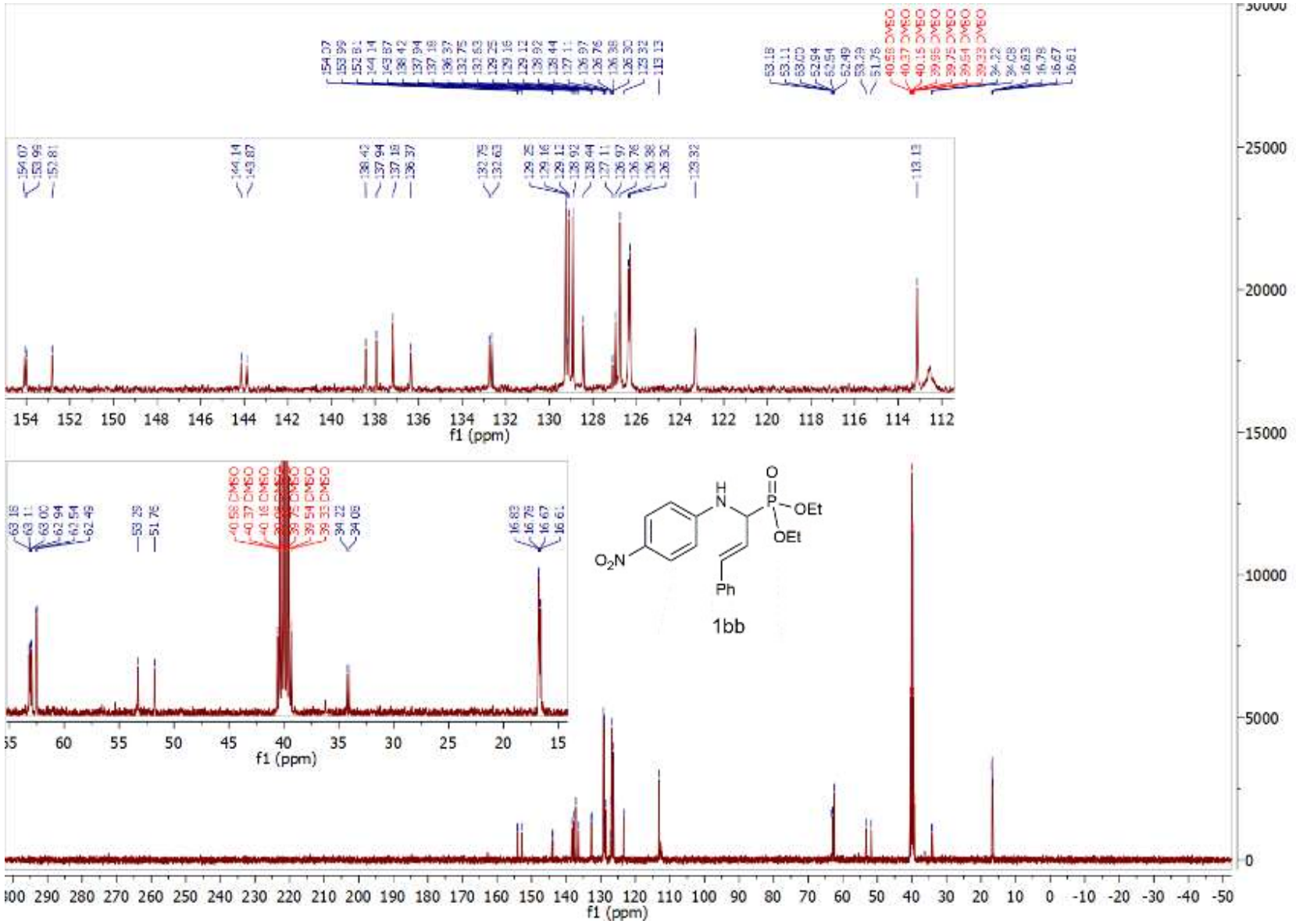


Figure S80: ^{13}C NMR Spectra of 1bb

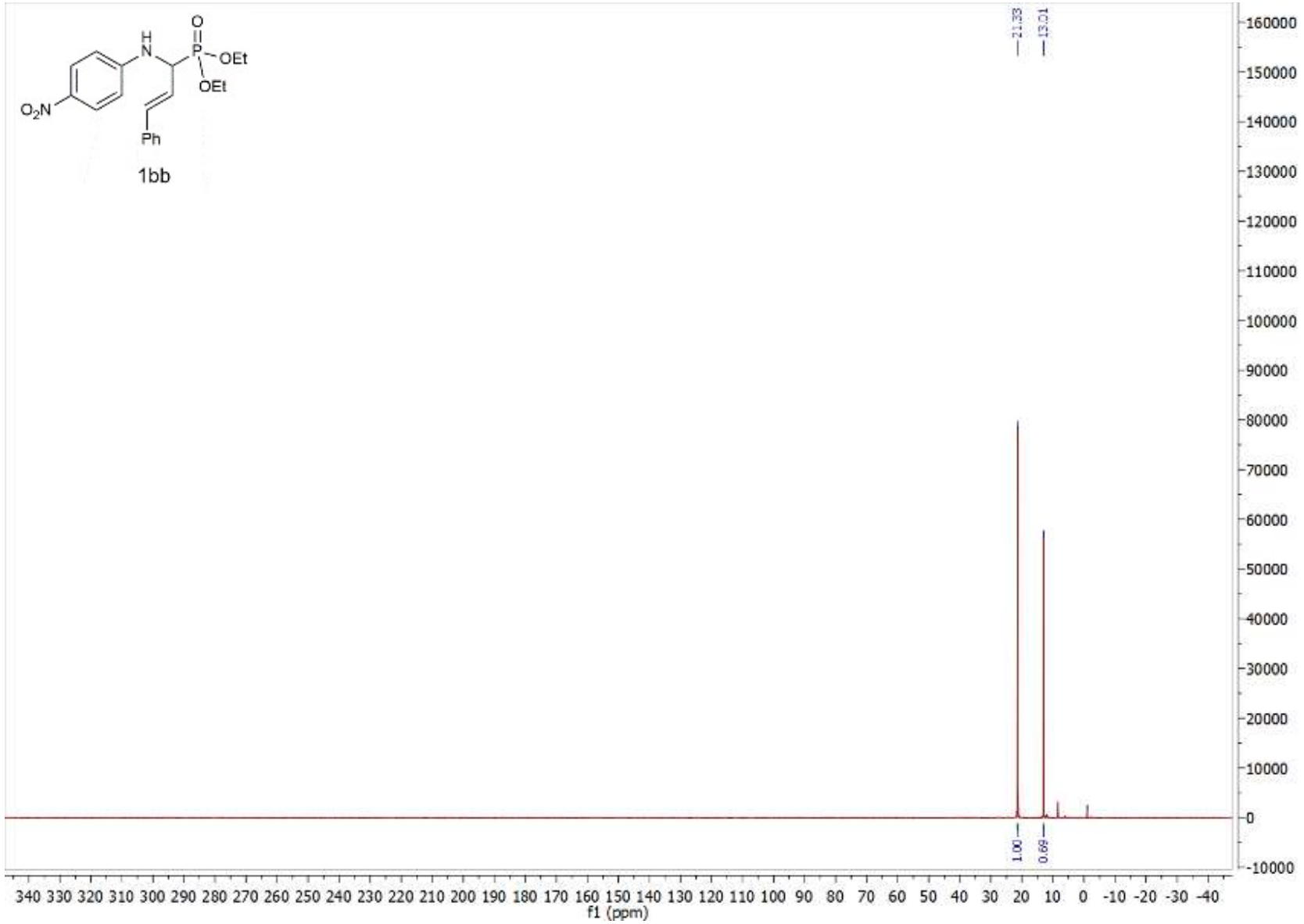


Figure S81: ^{31}P NMR Spectra of 1bb

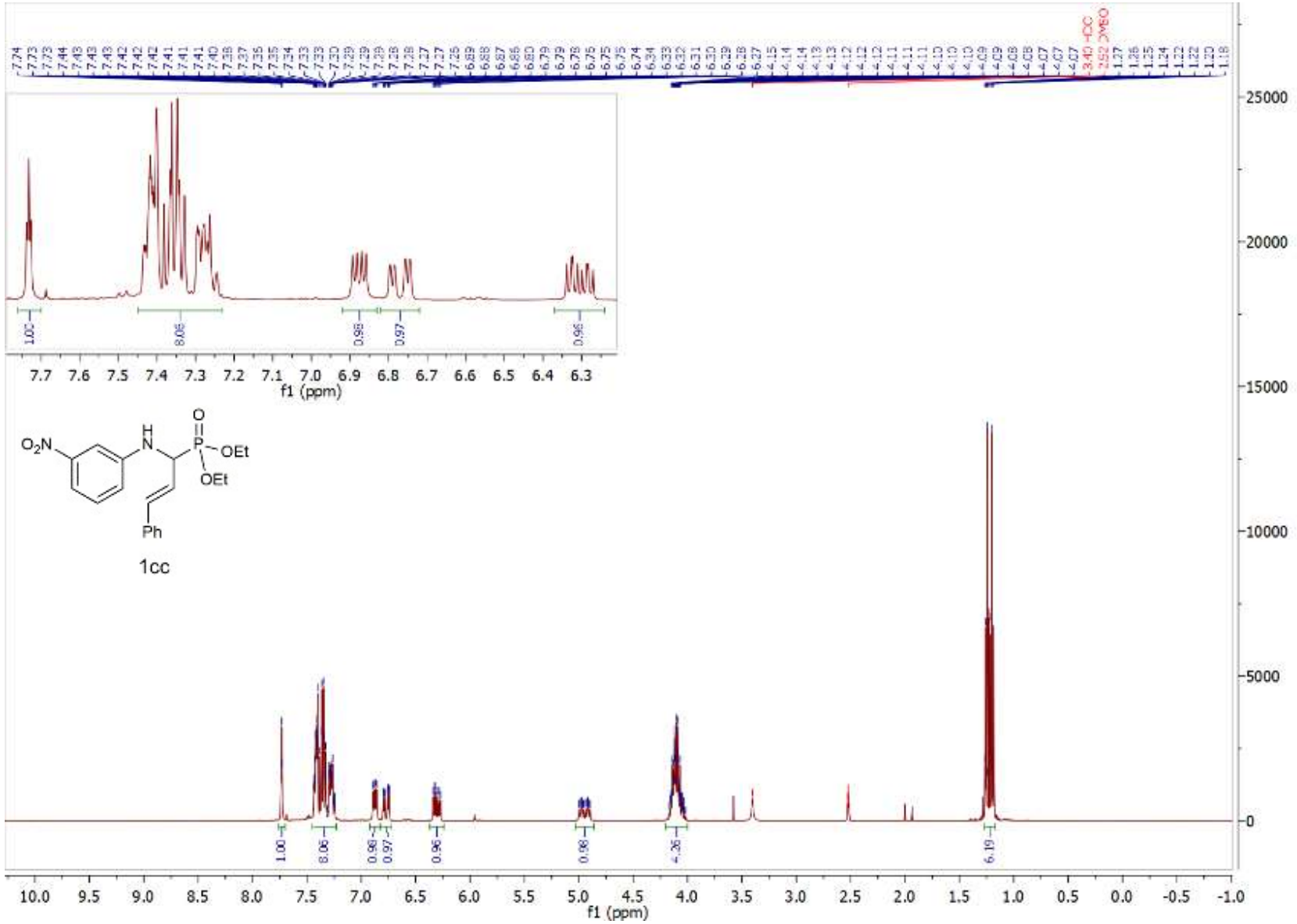


Figure S82: ^{1}H NMR Spectra of 1cc

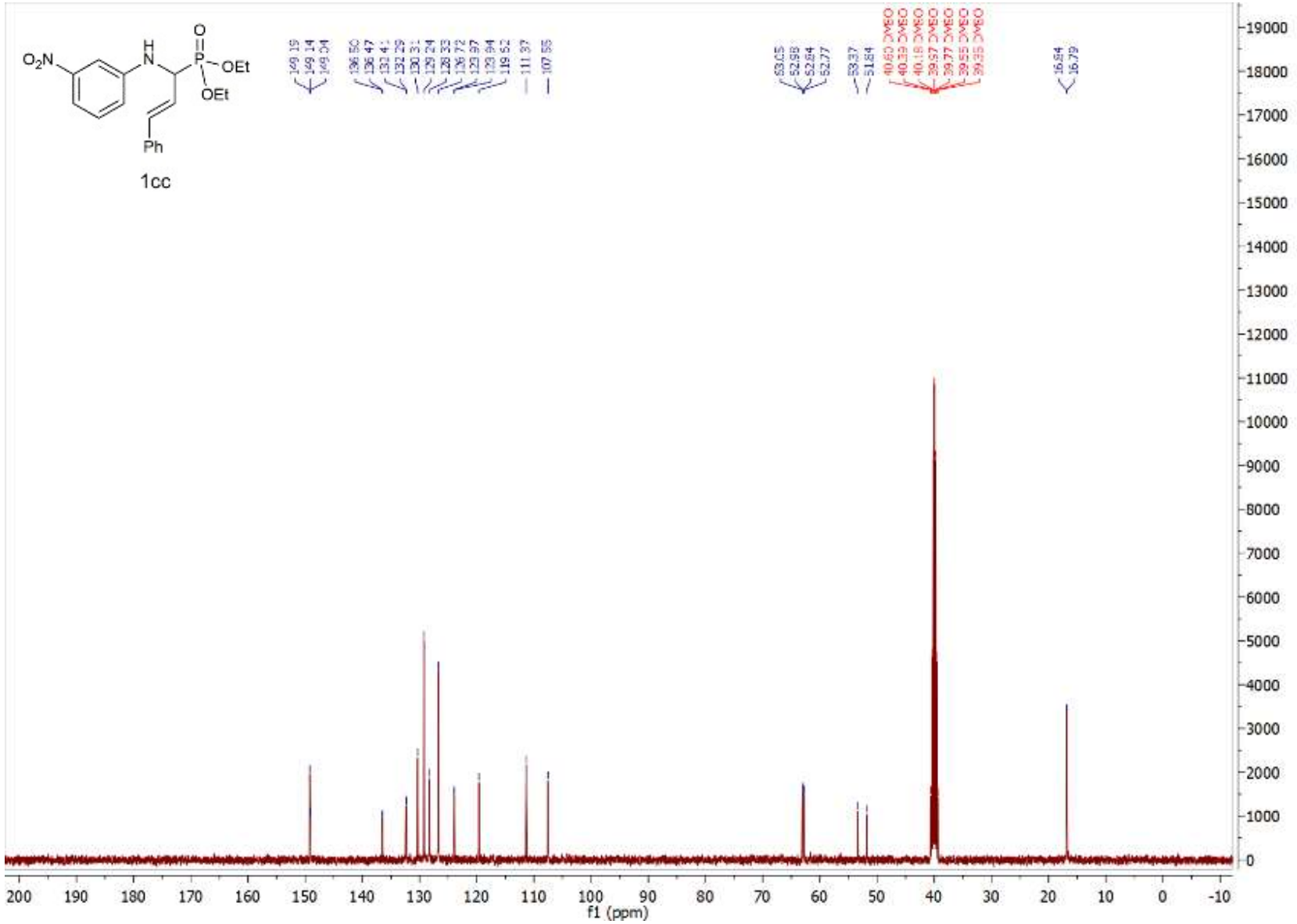


Figure S83: ^{13}C NMR Spectra of 1cc

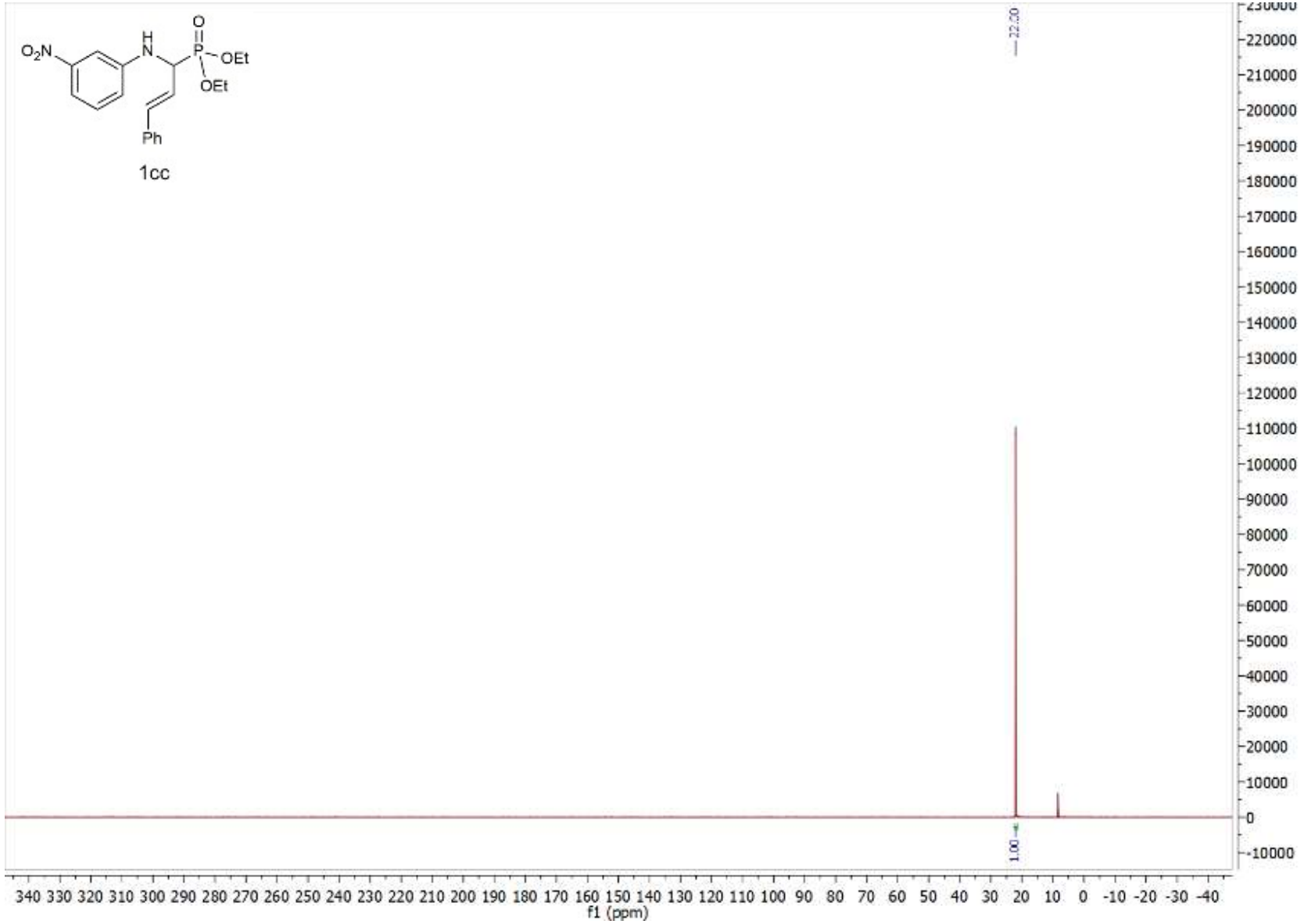


Figure S84: ^{31}P NMR Spectra of 1cc

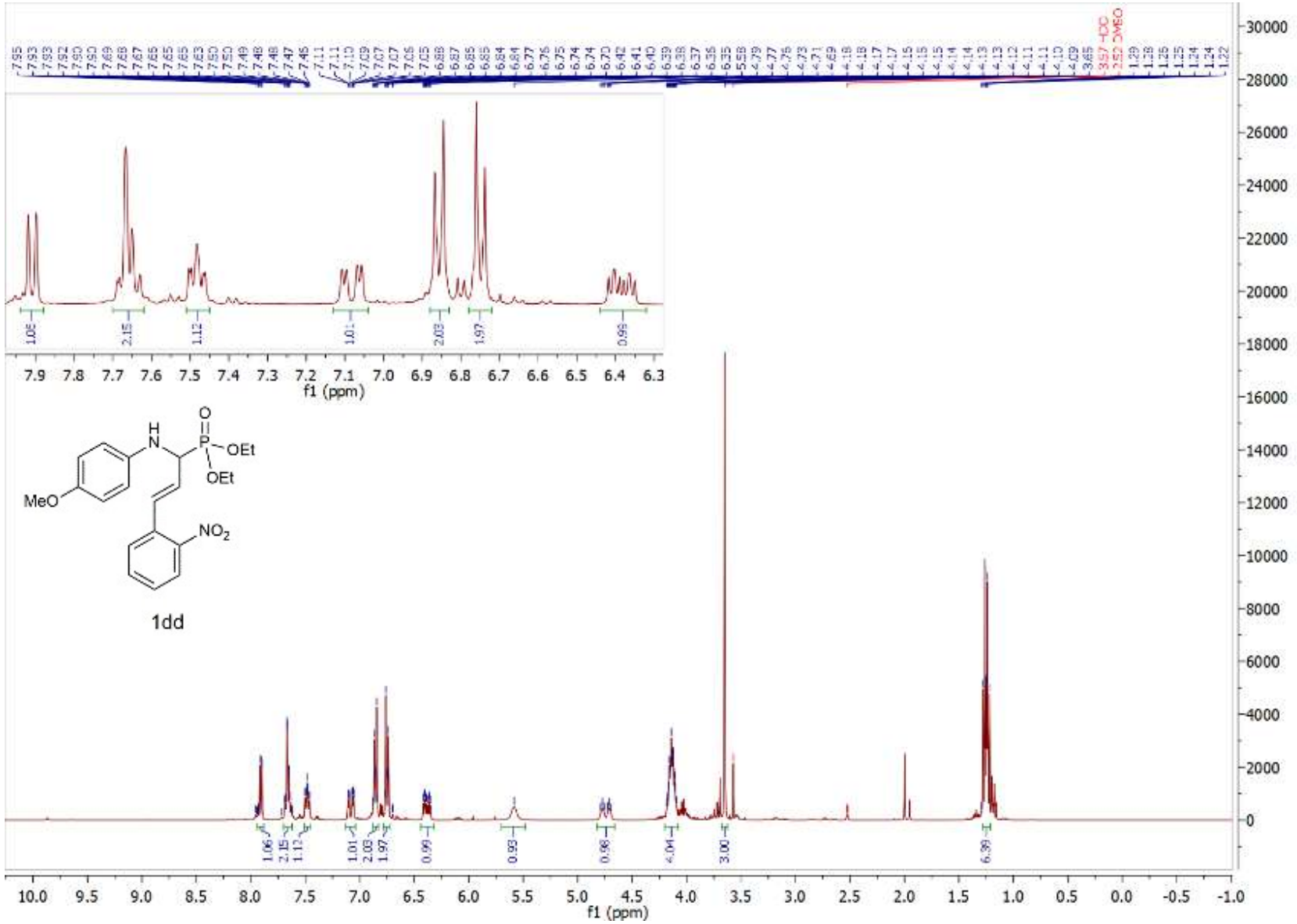


Figure S85: ^{1}H NMR Spectra of 1dd

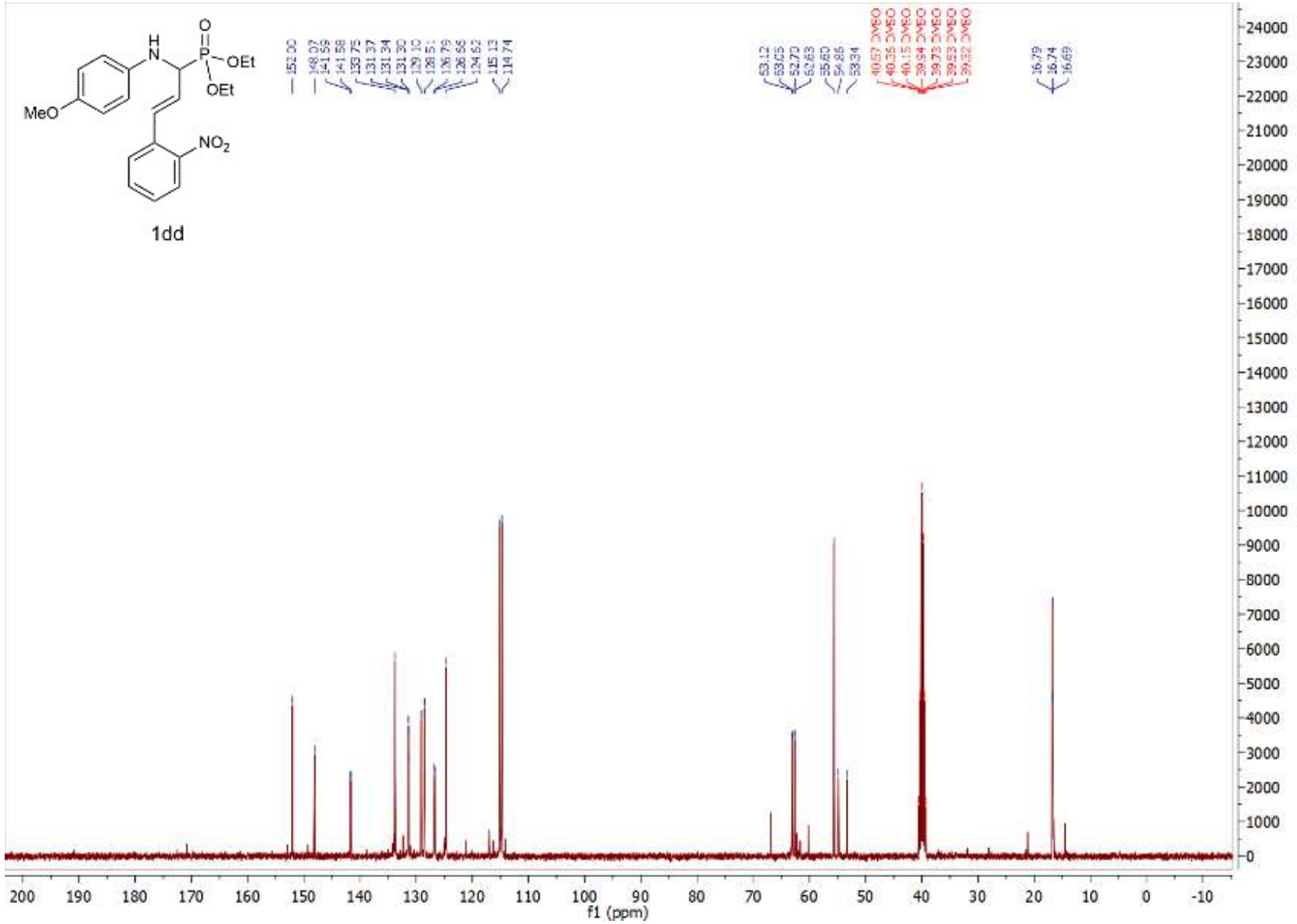


Figure S86: ^{13}C NMR Spectra of 1dd

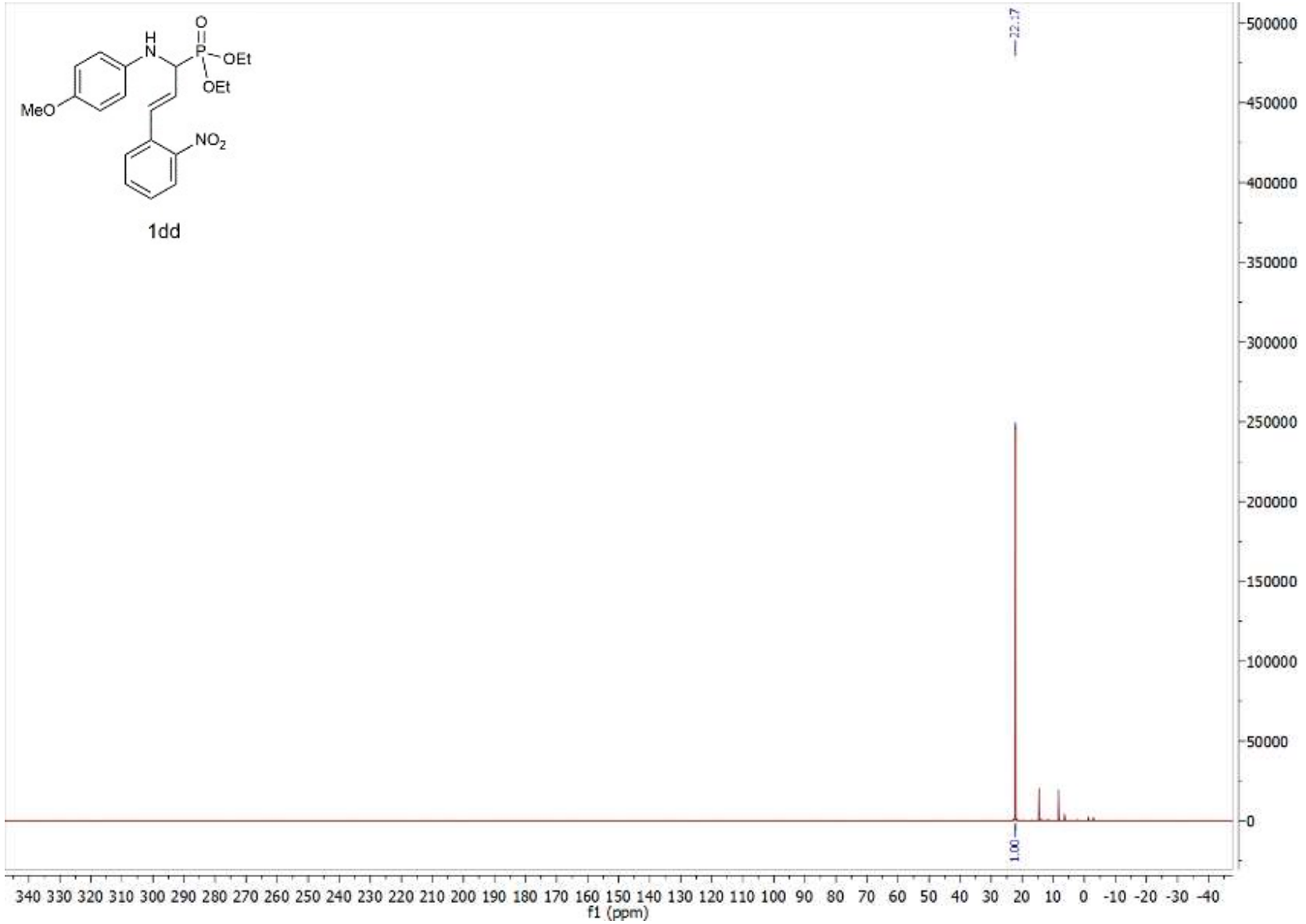


Figure S87: ^{31}P NMR Spectra of 1dd

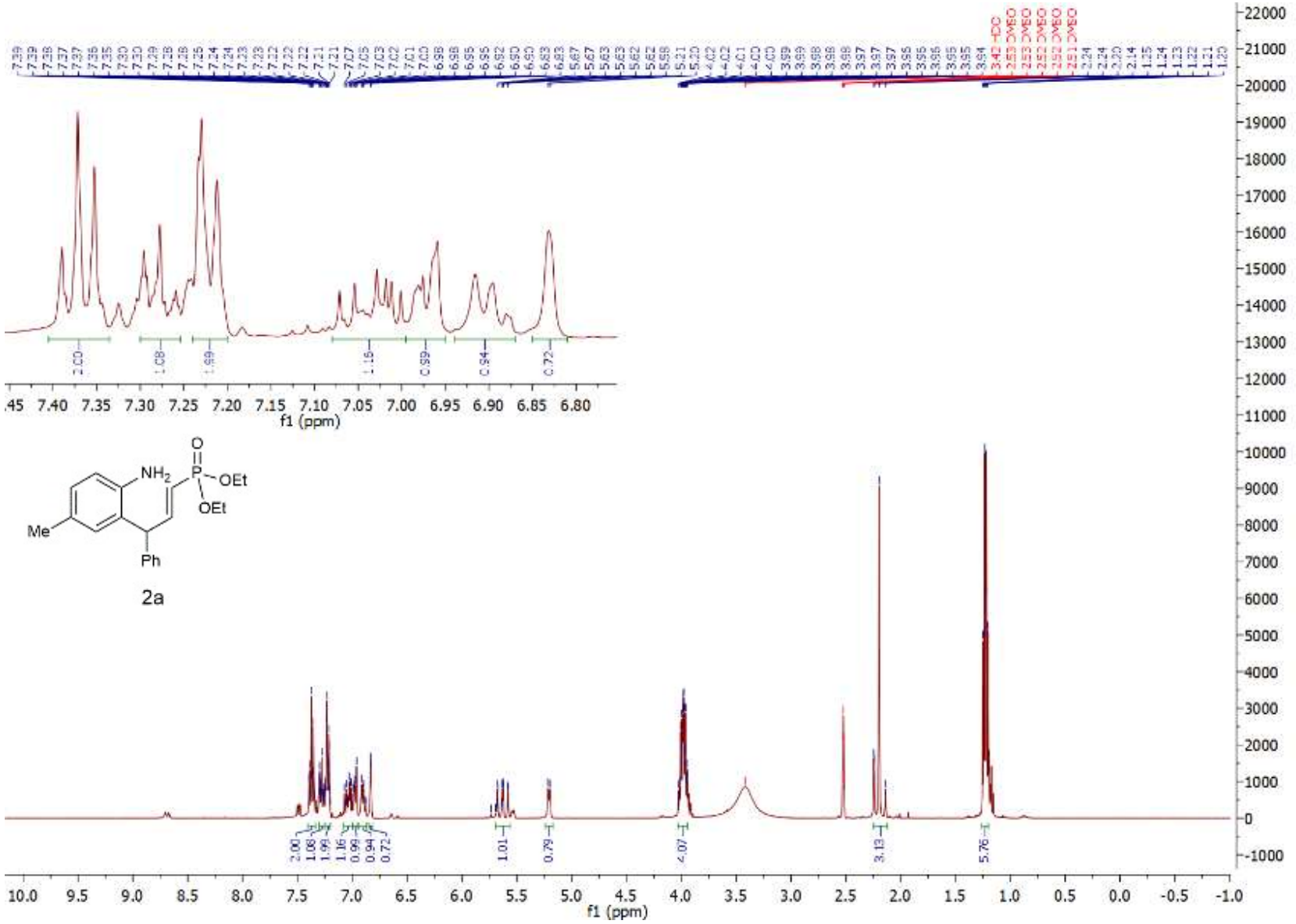


Figure S88: ^{1}H NMR Spectra of 2a

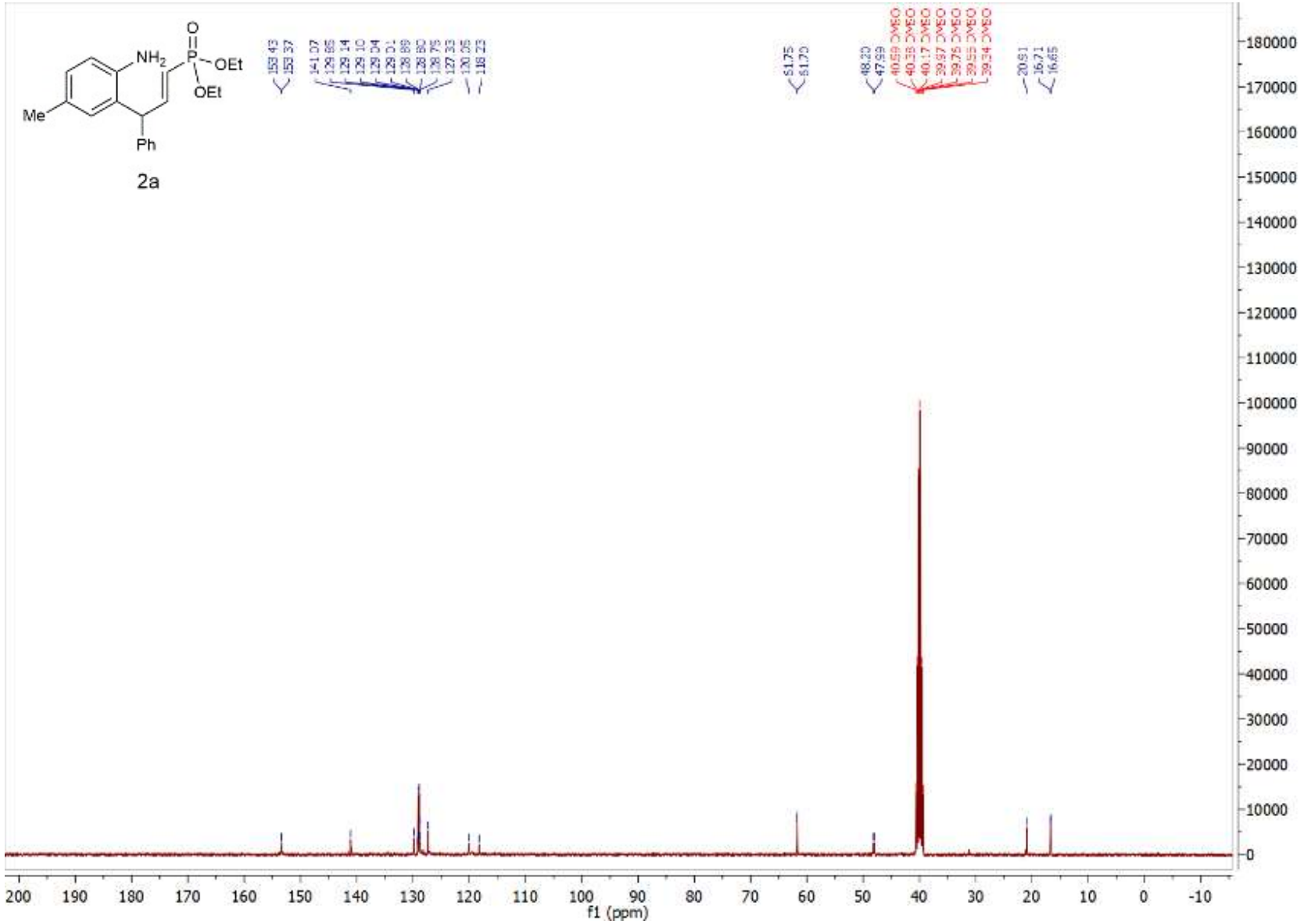


Figure S89: ^{13}C NMR Spectra of 2a

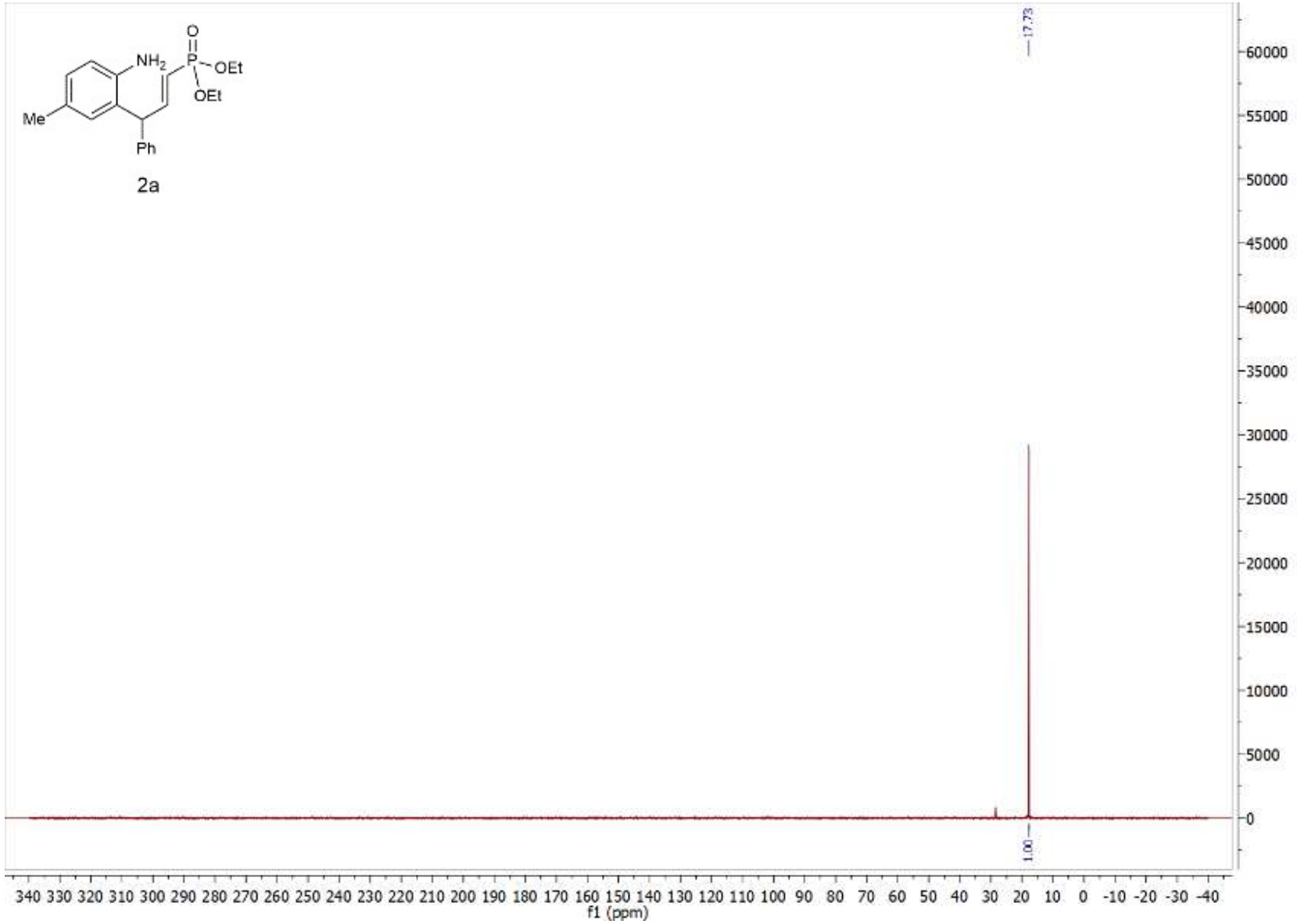


Figure S90: ^{31}P NMR Spectra of 2a

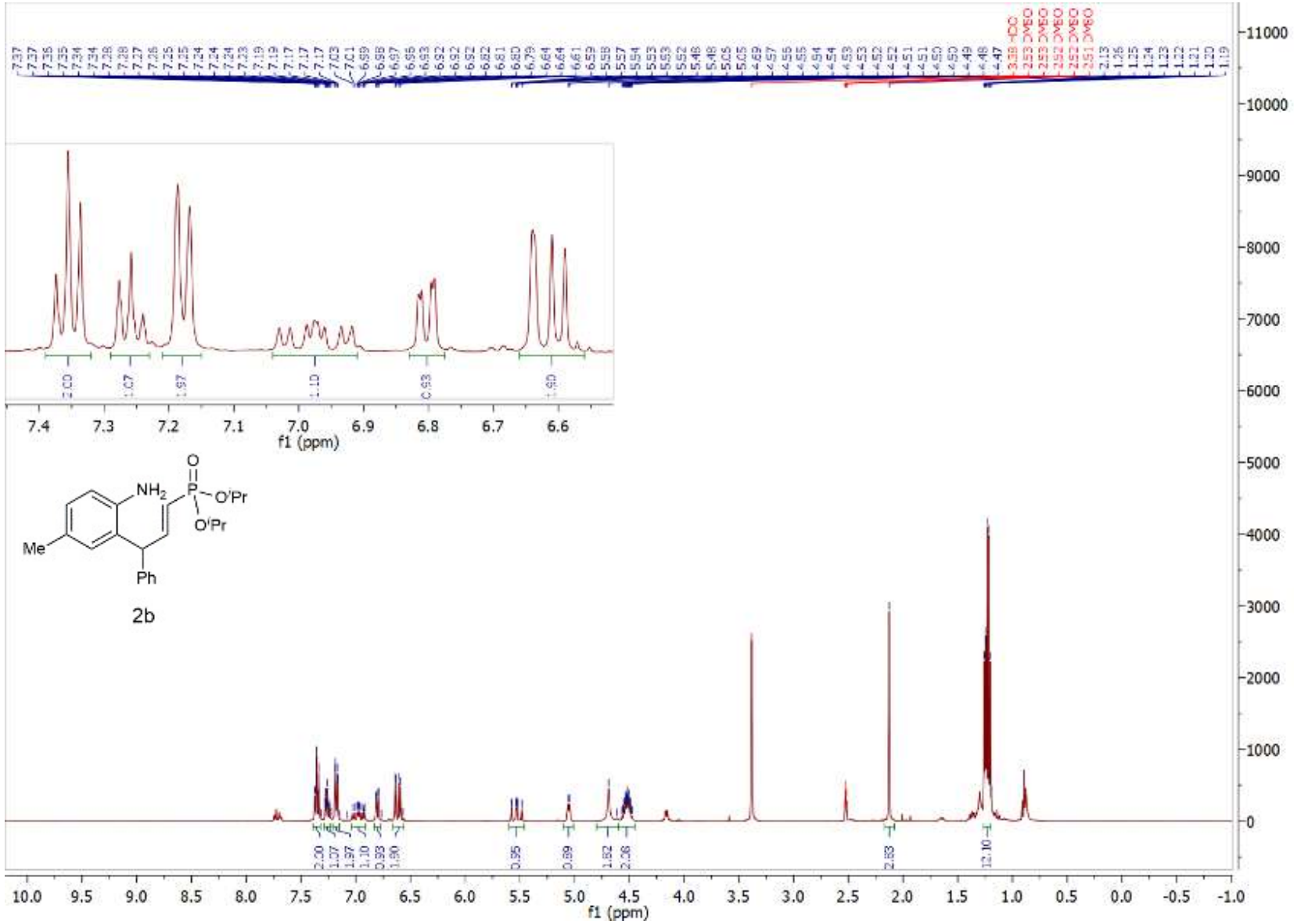


Figure S91: ^{1}H NMR Spectra of 2b

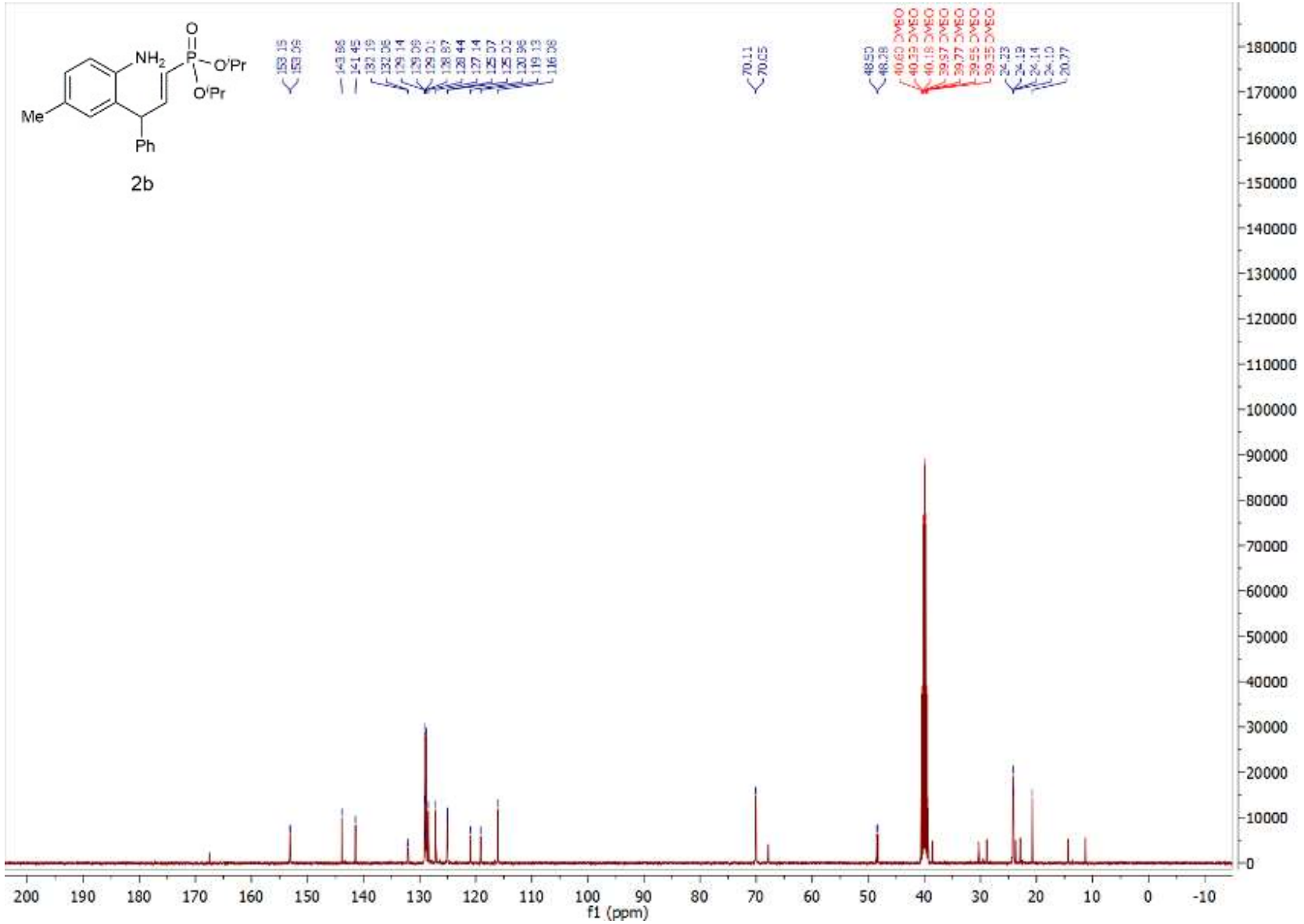


Figure S92: ^{13}C NMR Spectra of 2b

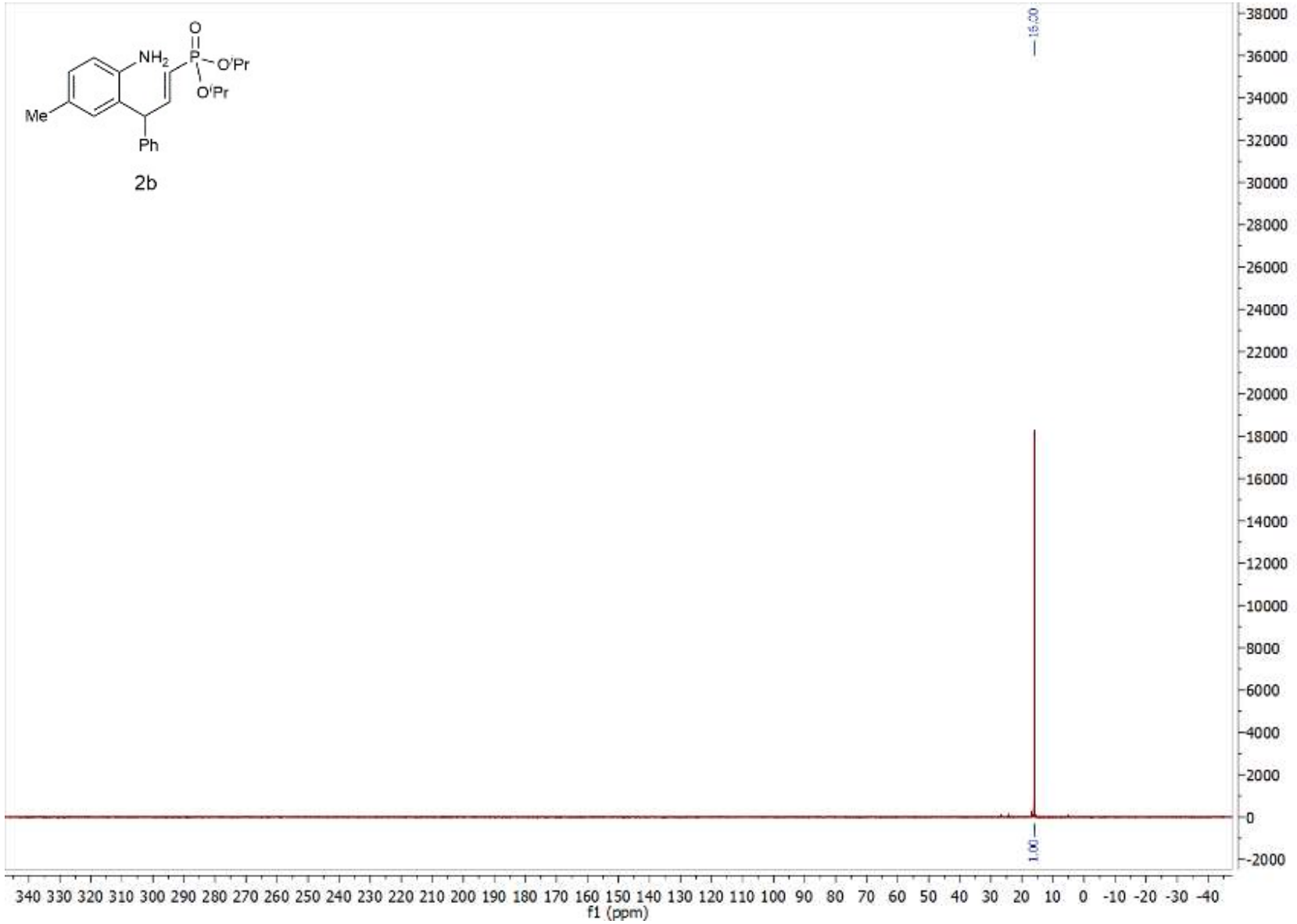


Figure S93: ^{31}P NMR Spectra of 2b

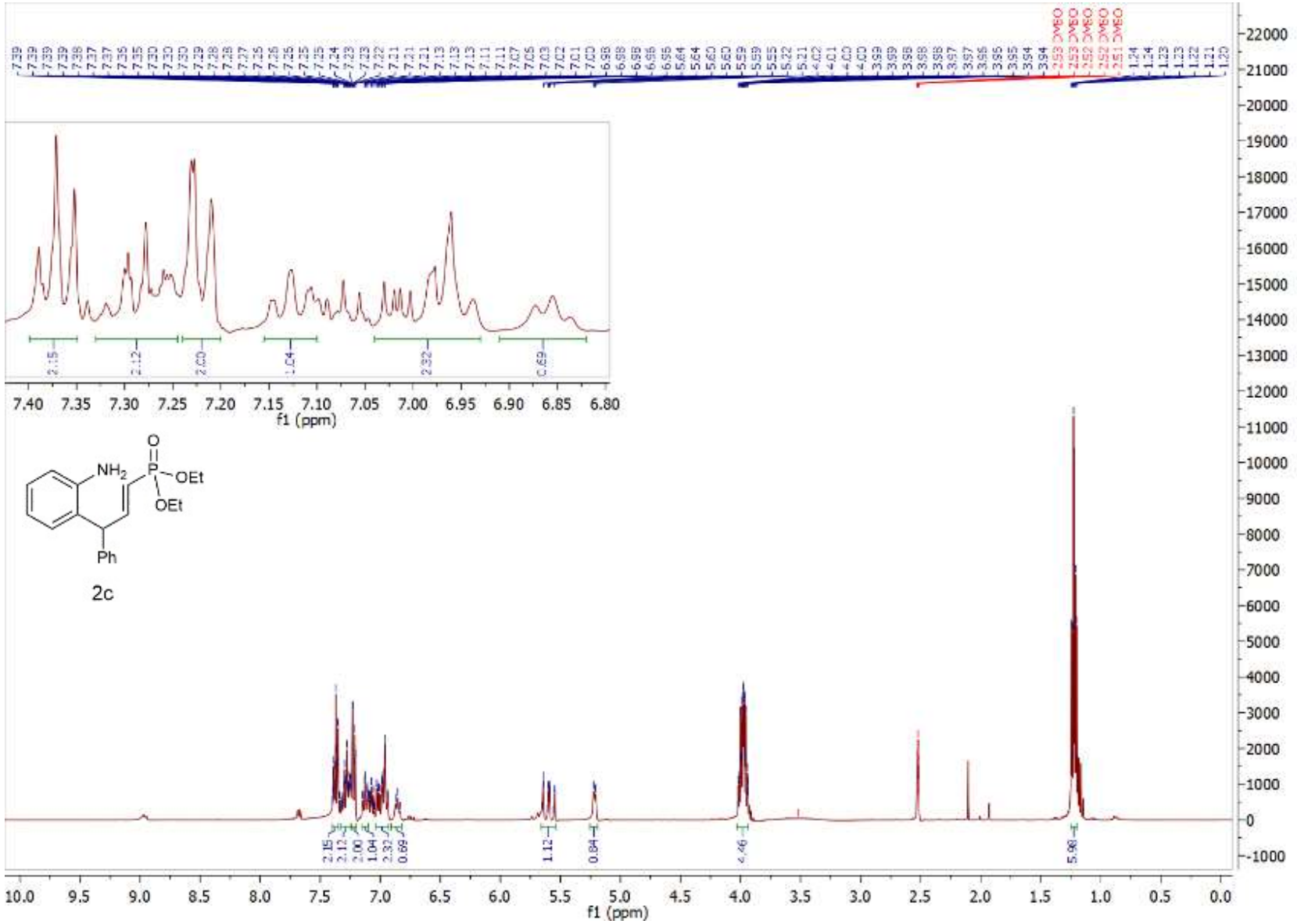


Figure S94: ^{1}H NMR Spectra of 2c

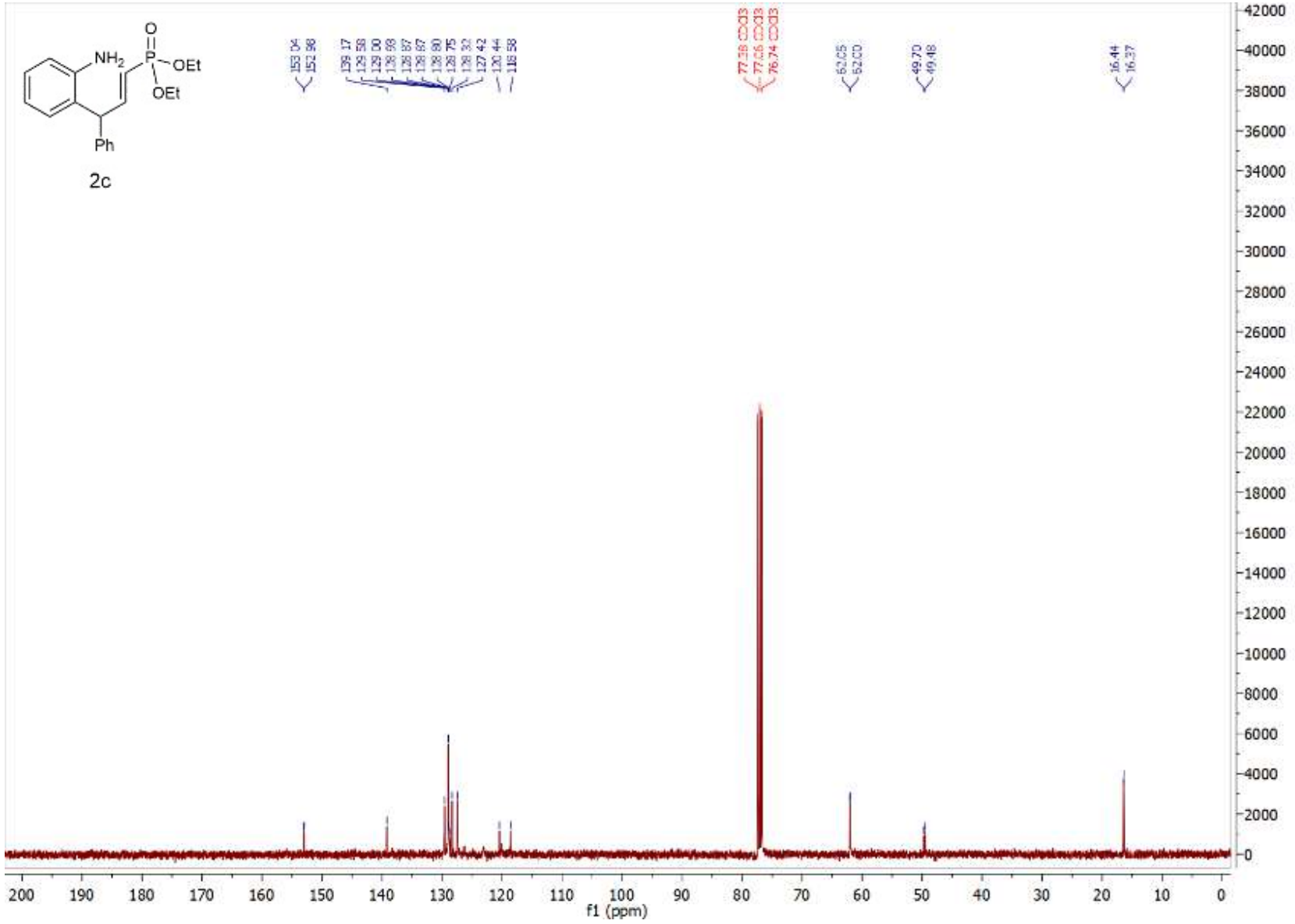


Figure S95: ^{13}C NMR Spectra of 2c

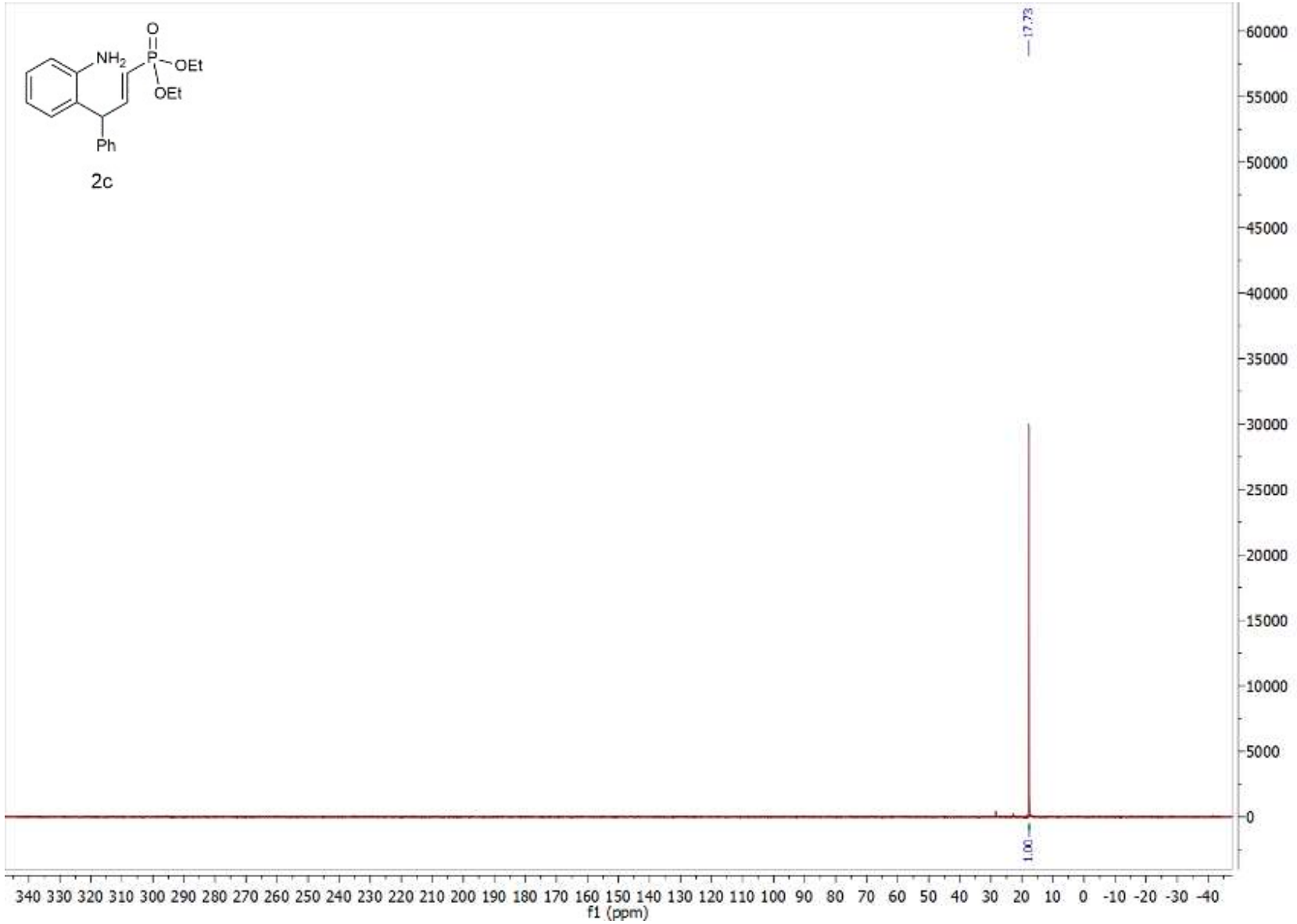


Figure S96: ^{31}P NMR Spectra of 2c

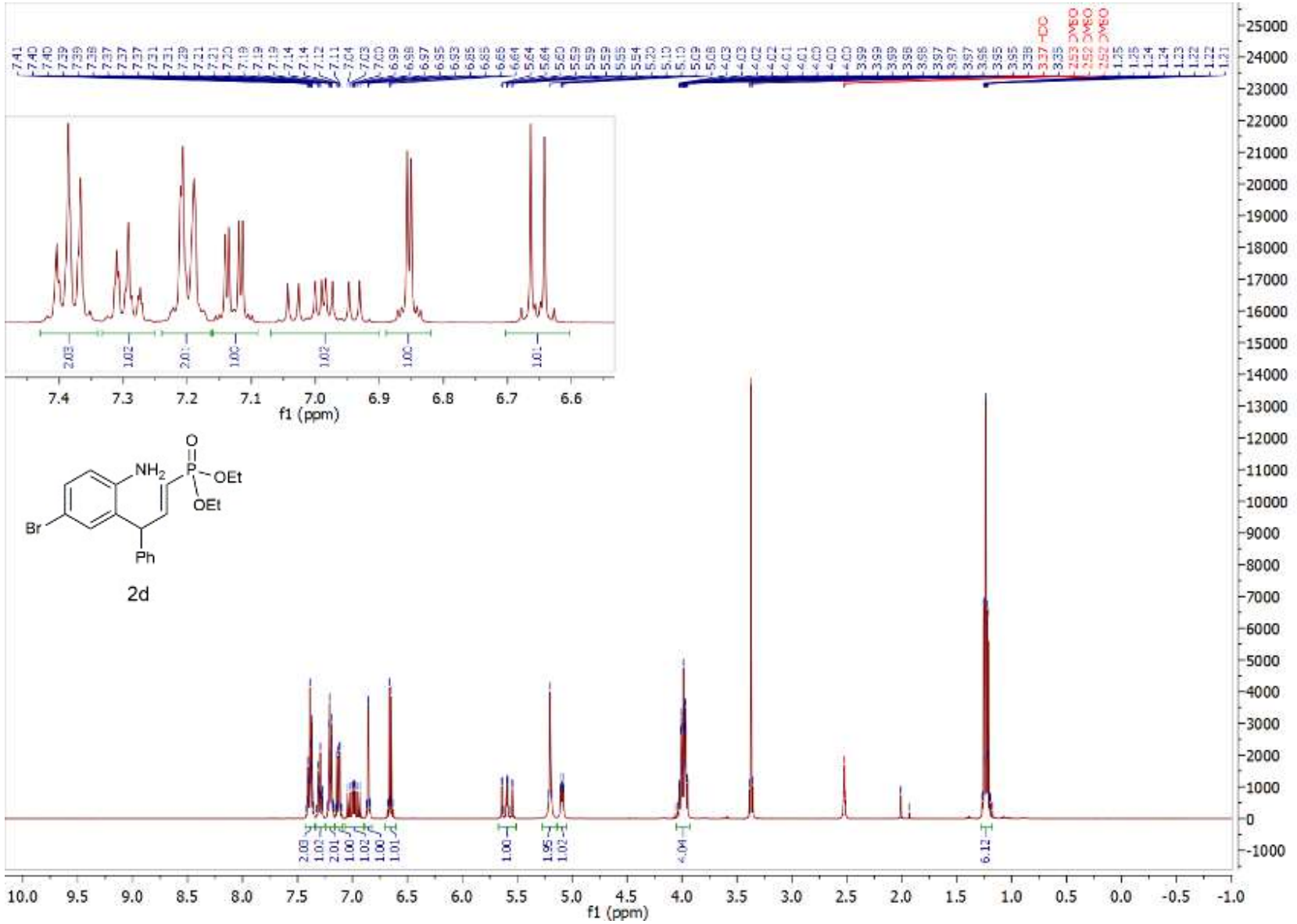


Figure S97: ^{1}H NMR Spectra of 2d

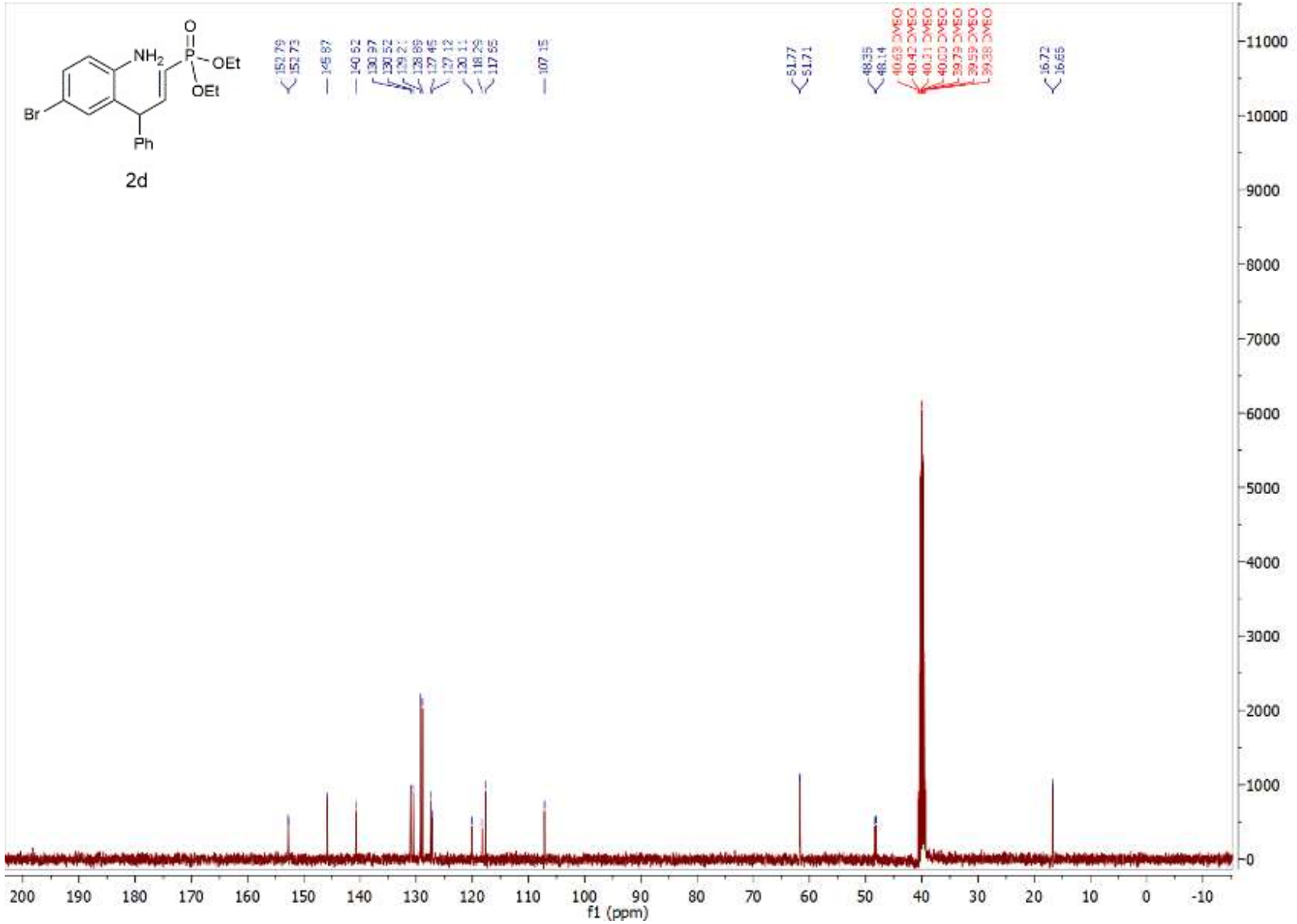


Figure S98: ^{13}C NMR Spectra of 2d

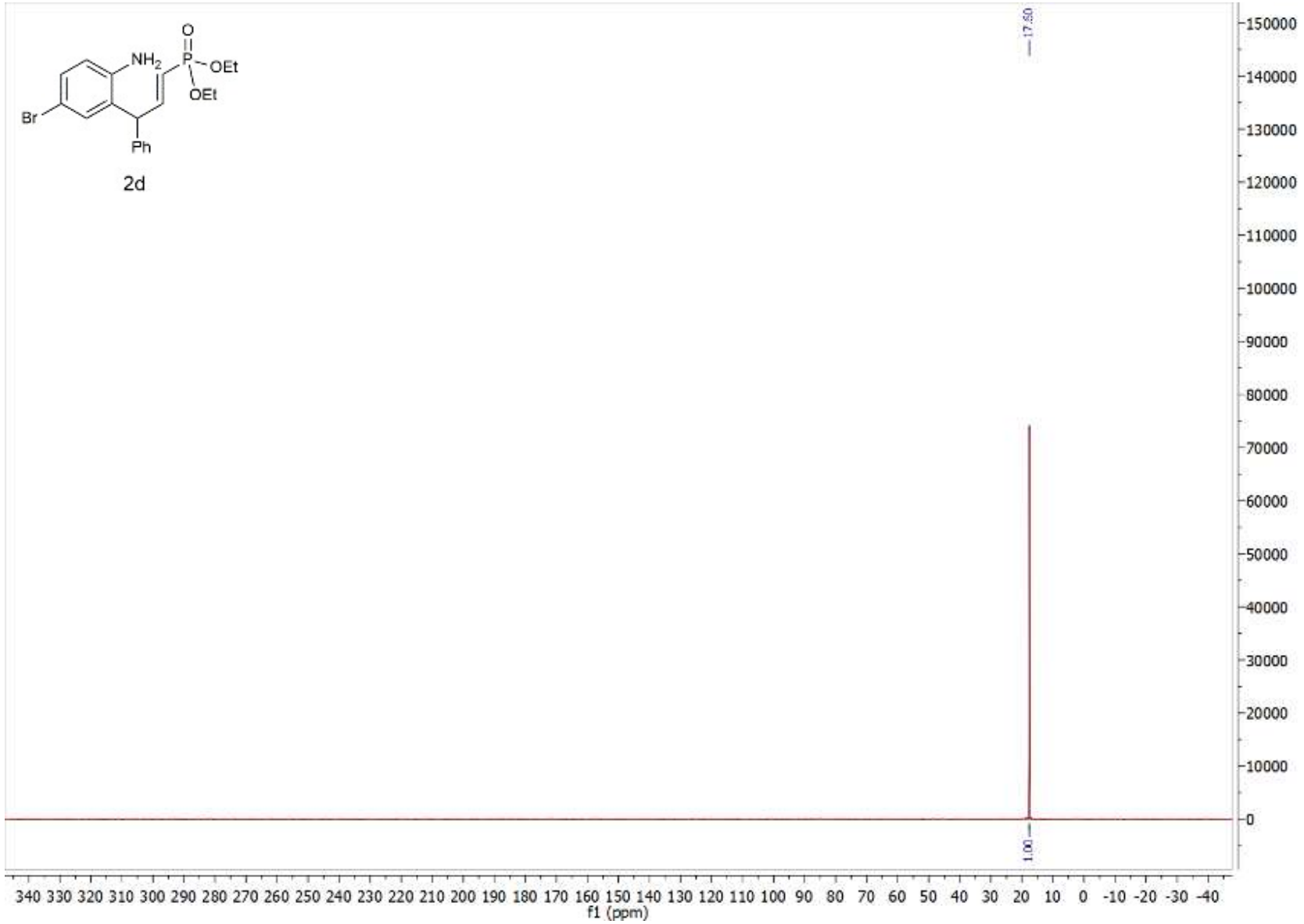


Figure S99: ^{31}P NMR Spectra of 2d

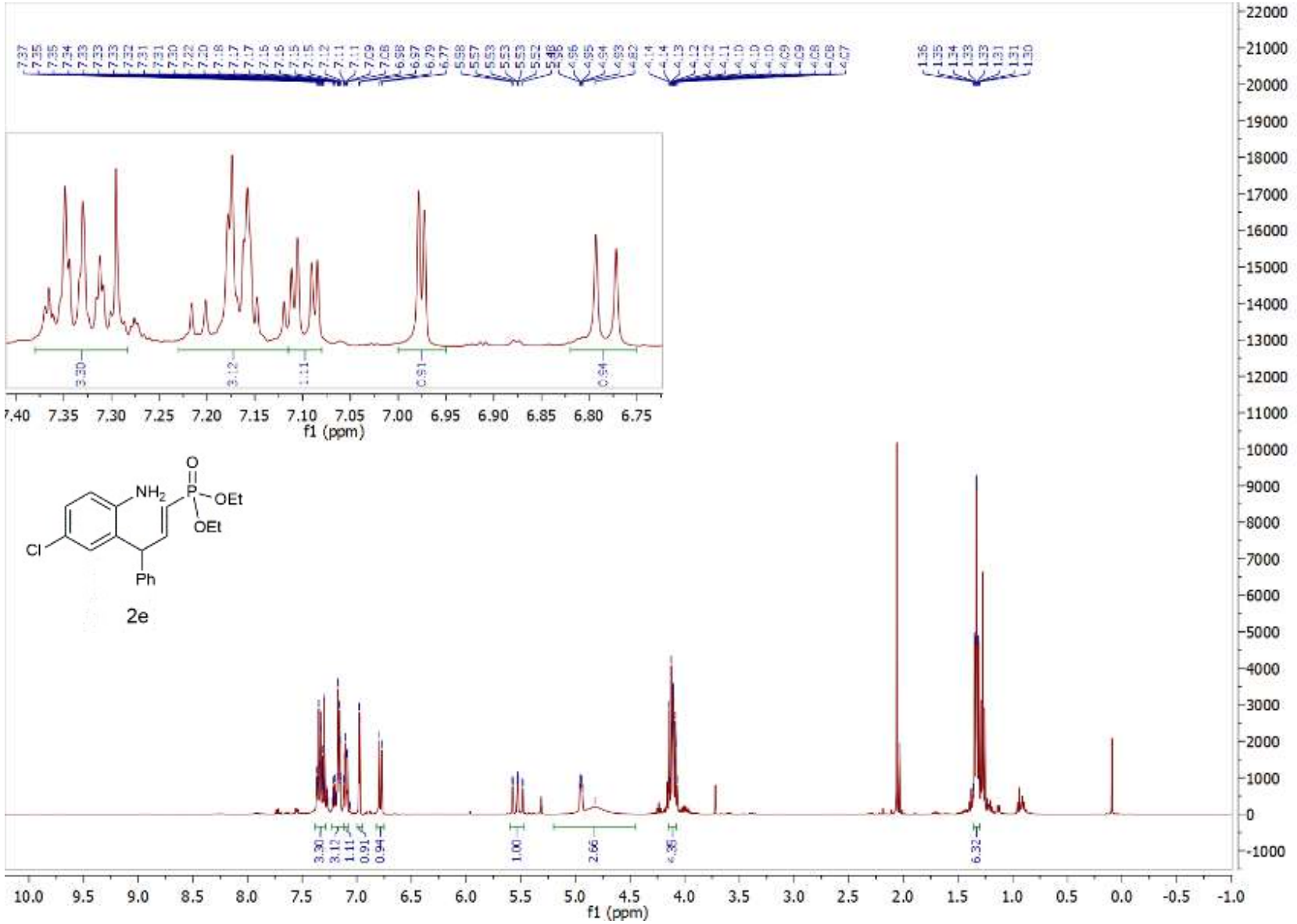


Figure S100: ^{1}H NMR Spectra of 2e

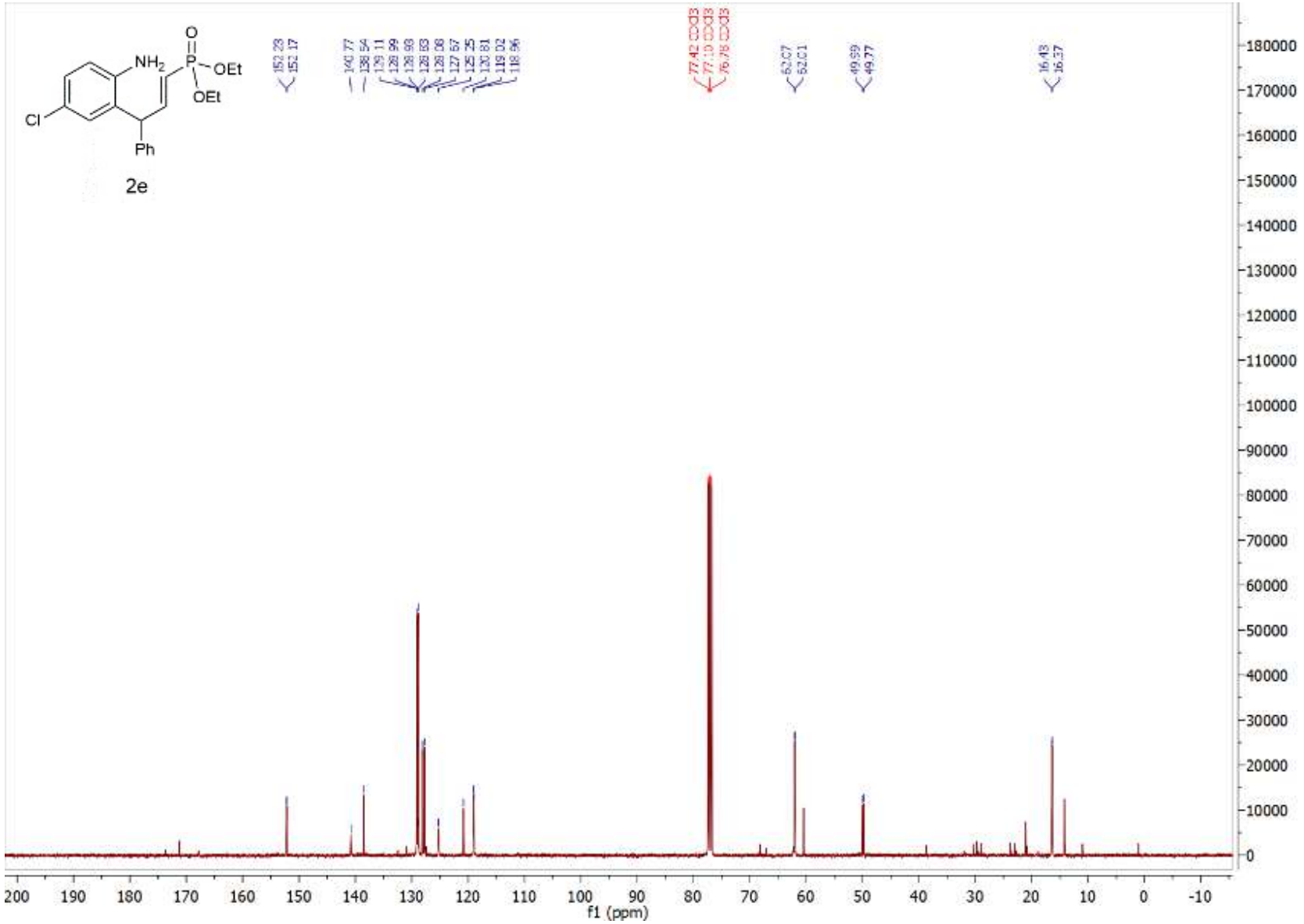


Figure S101: ^{13}C NMR Spectra of 2e

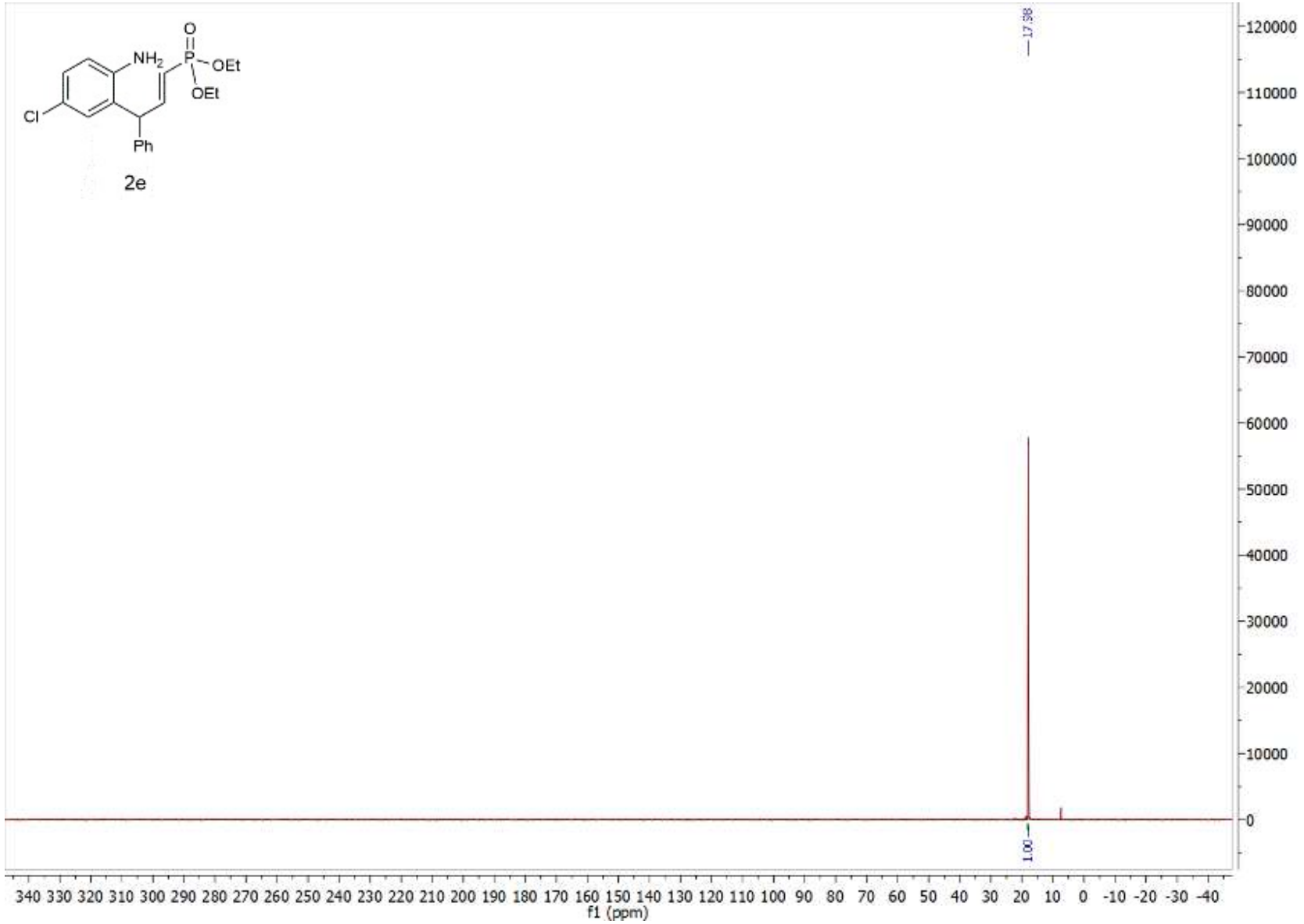


Figure S102: ^{31}P NMR Spectra of 2e

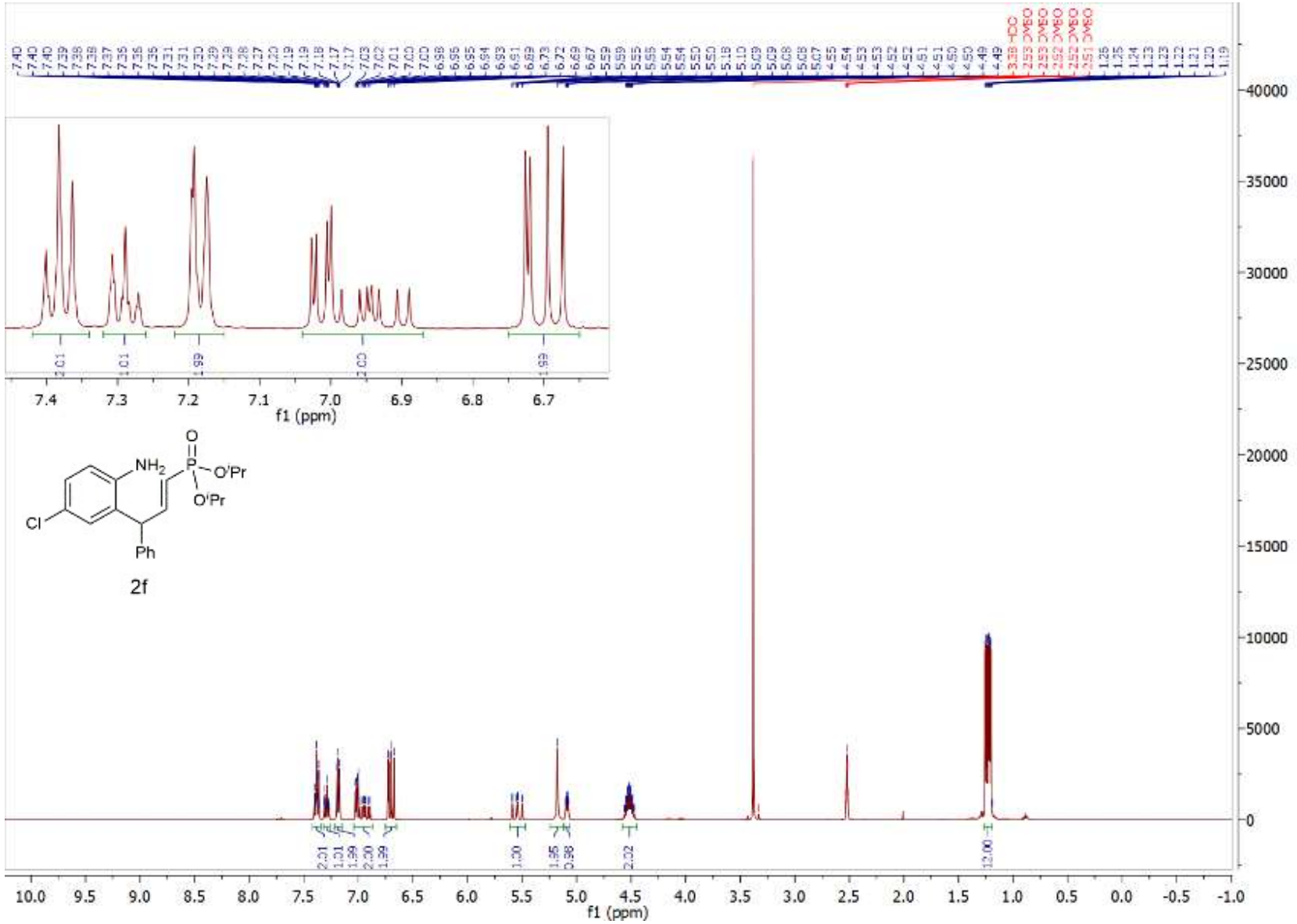


Figure S103: ^{1}H NMR Spectra of 2f

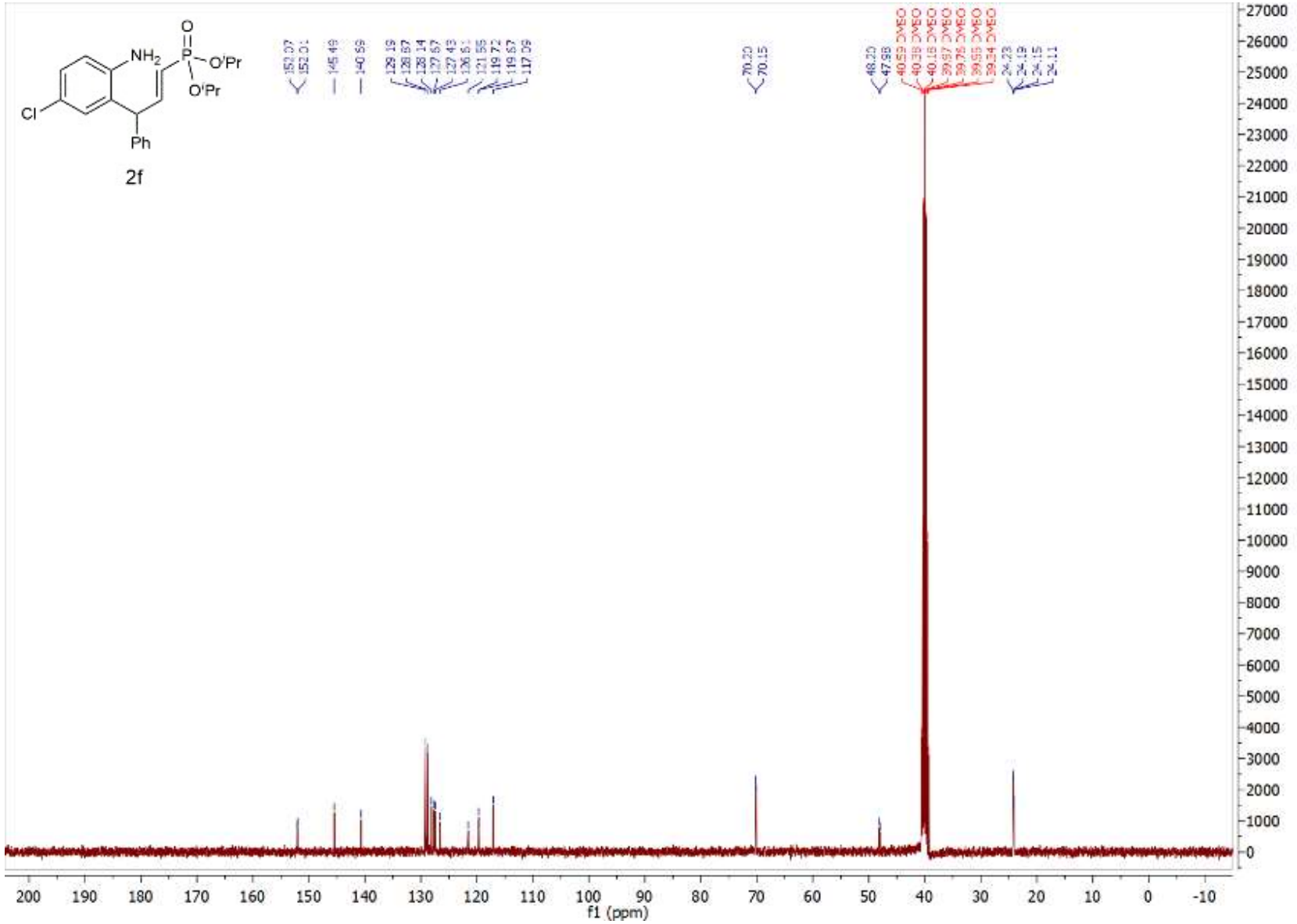


Figure S104: ^{13}C NMR Spectra of 2f

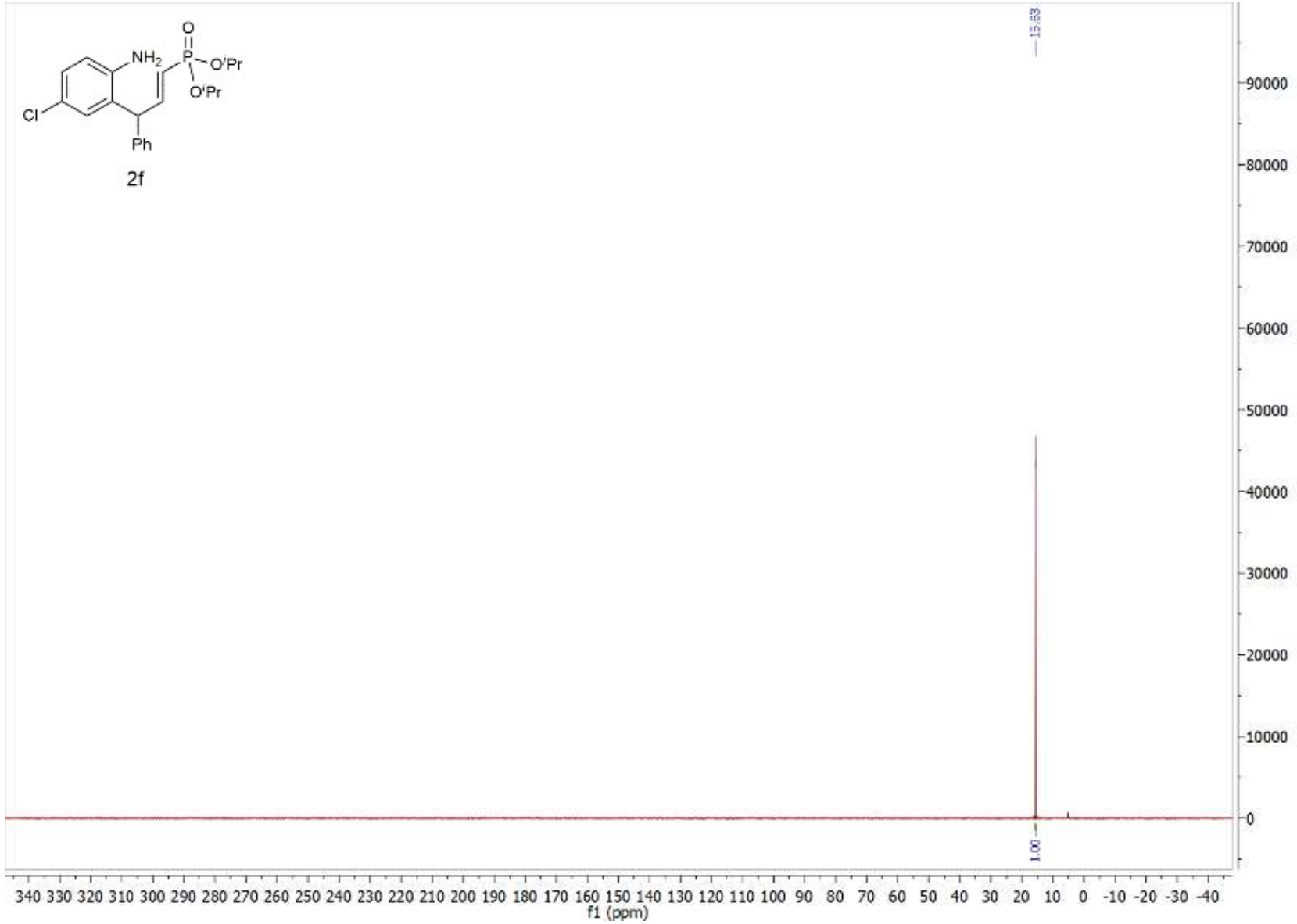


Figure S105: ^{31}P NMR Spectra of 2f

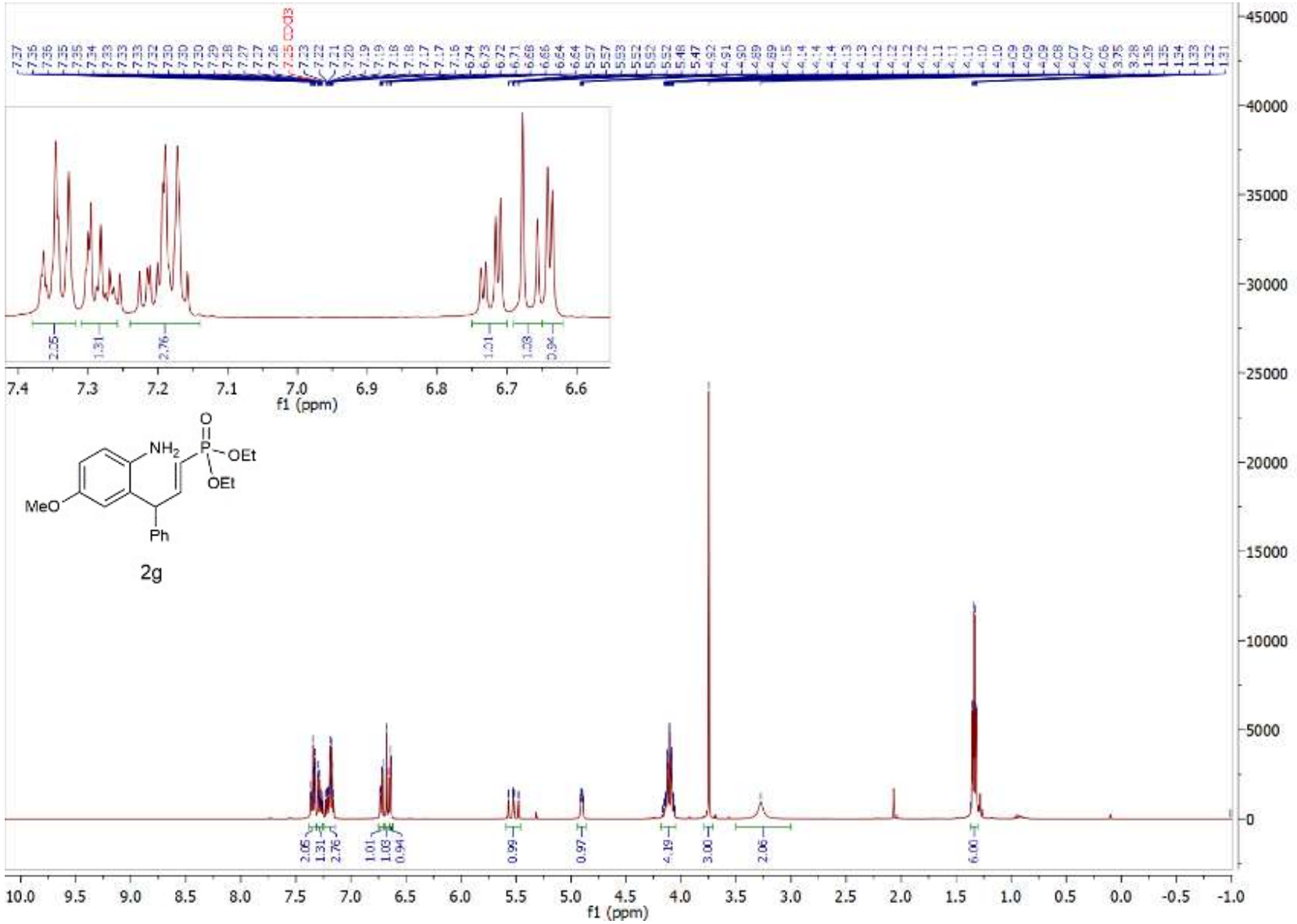


Figure S106: ^{1}H NMR Spectra of 2g

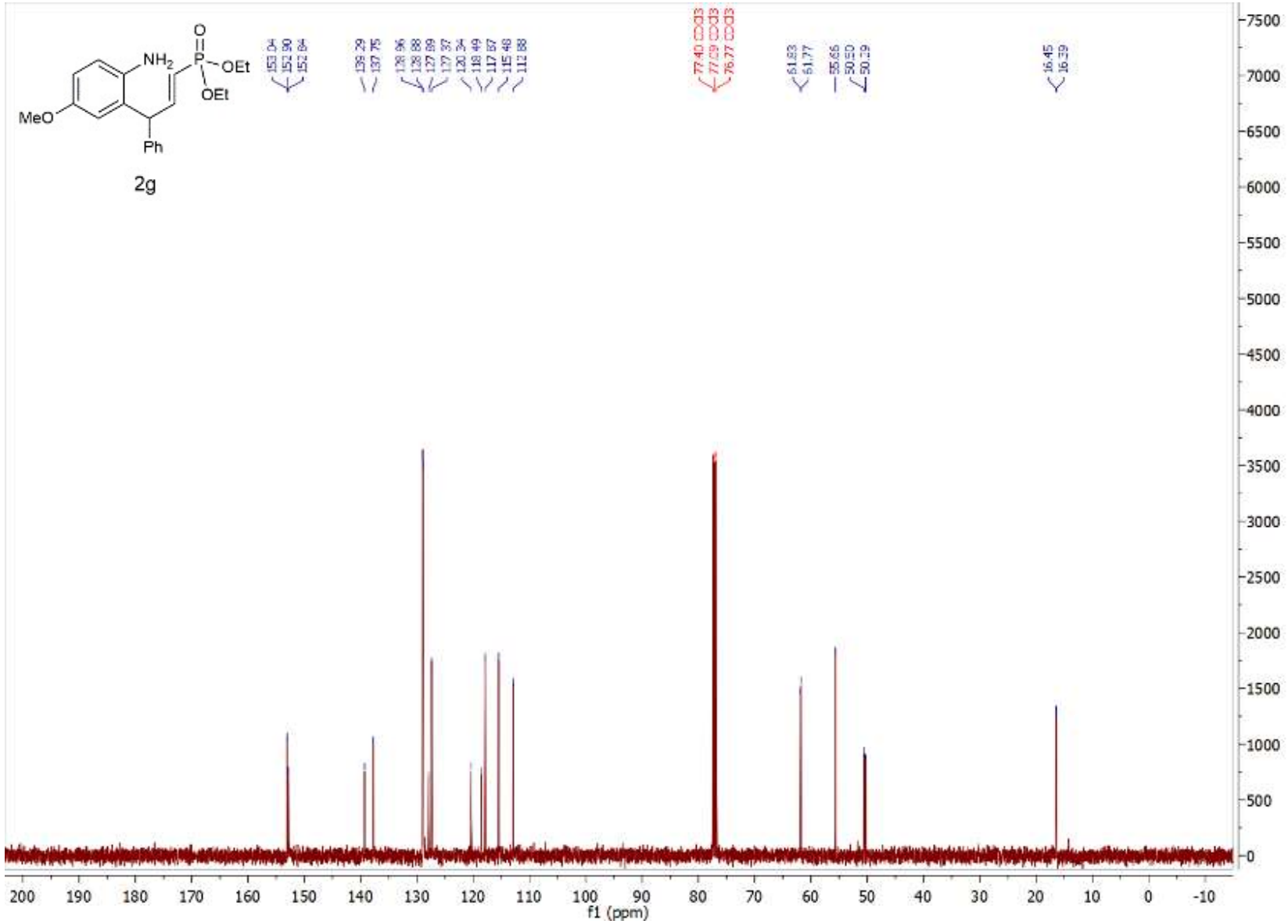


Figure S107: ^{13}C NMR Spectra of 2g

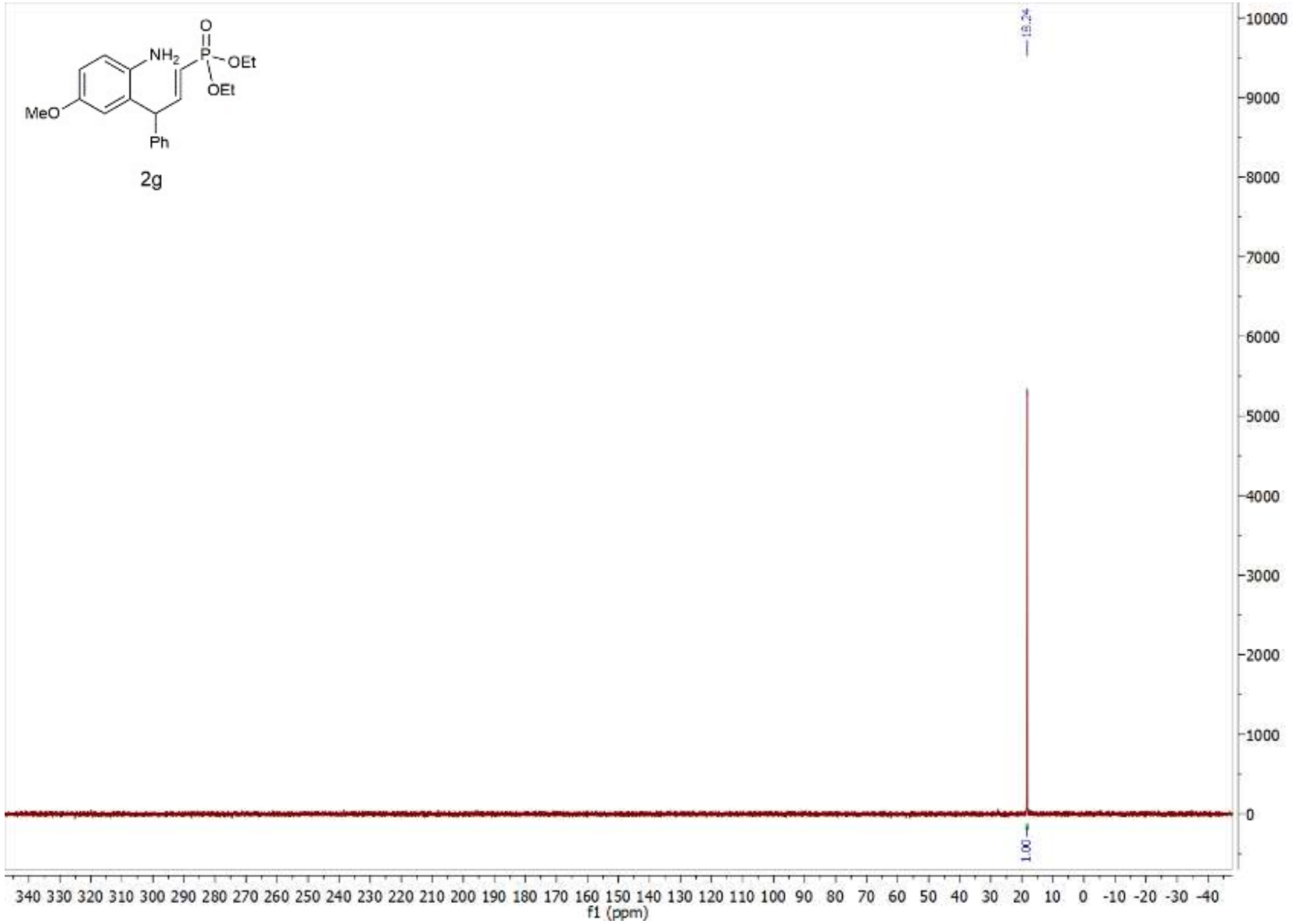


Figure S108: ^{31}P NMR Spectra of 2g

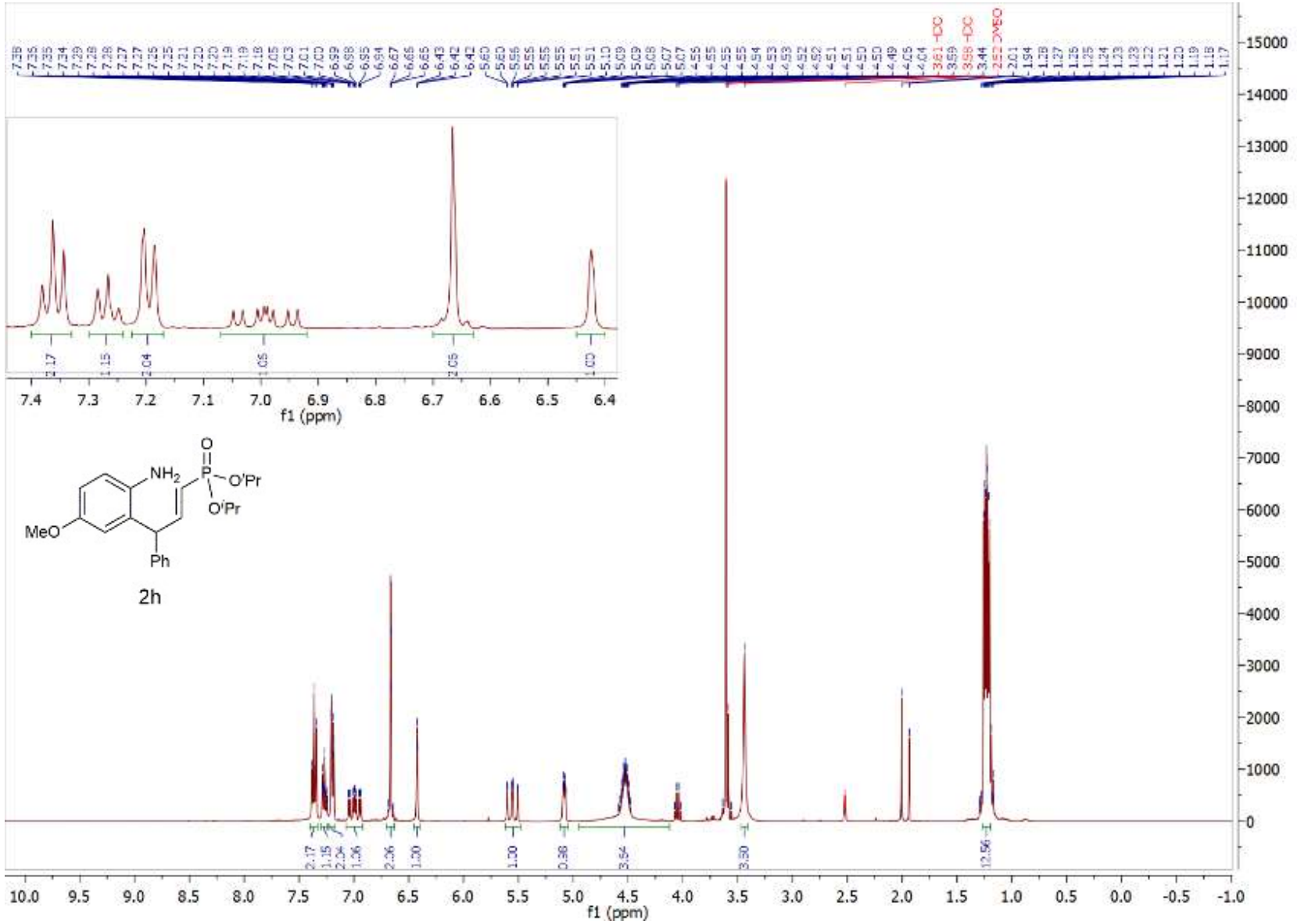


Figure S109: ^{1}H NMR Spectra of 2h

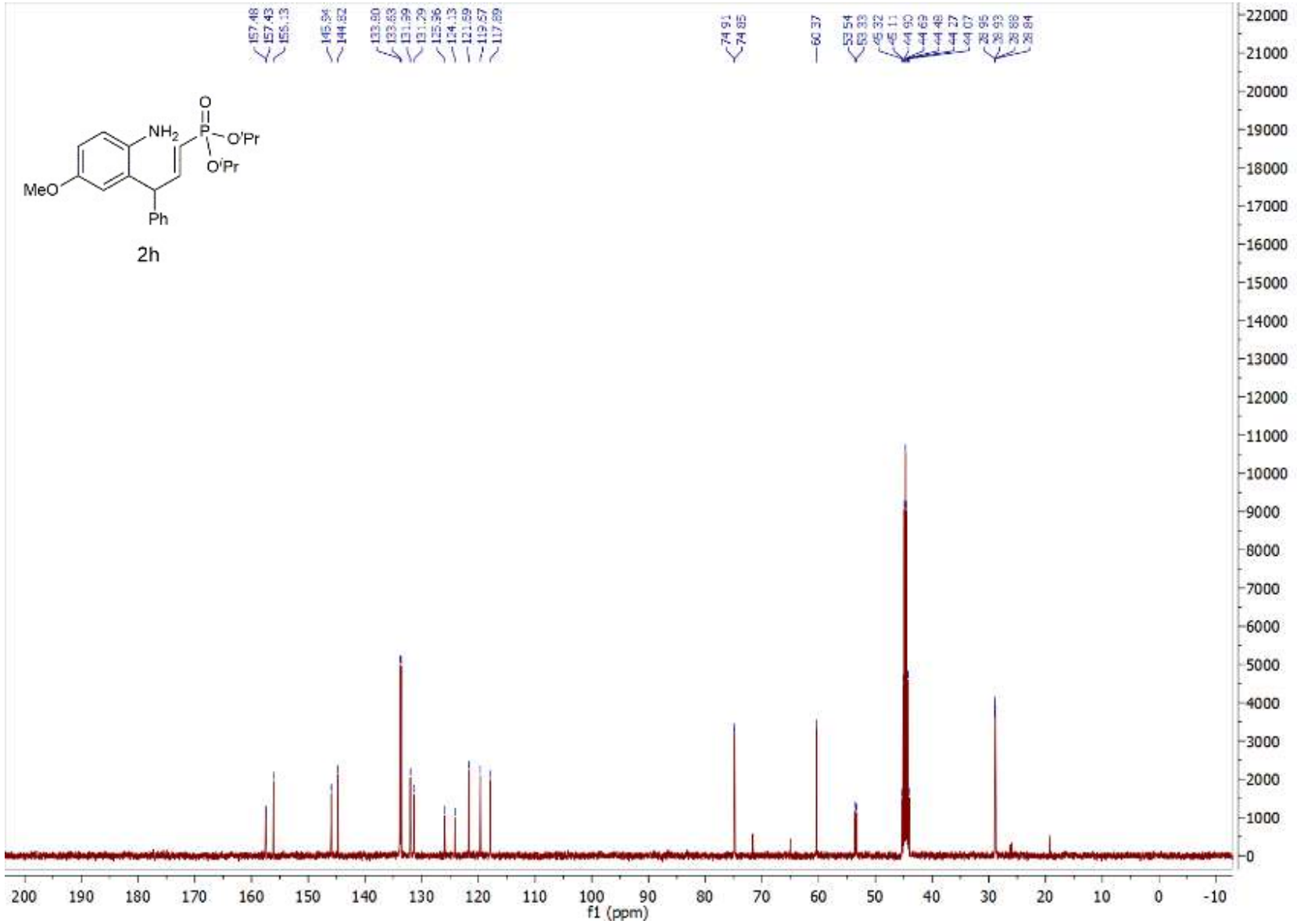


Figure S110: ^{13}C NMR Spectra of 2h

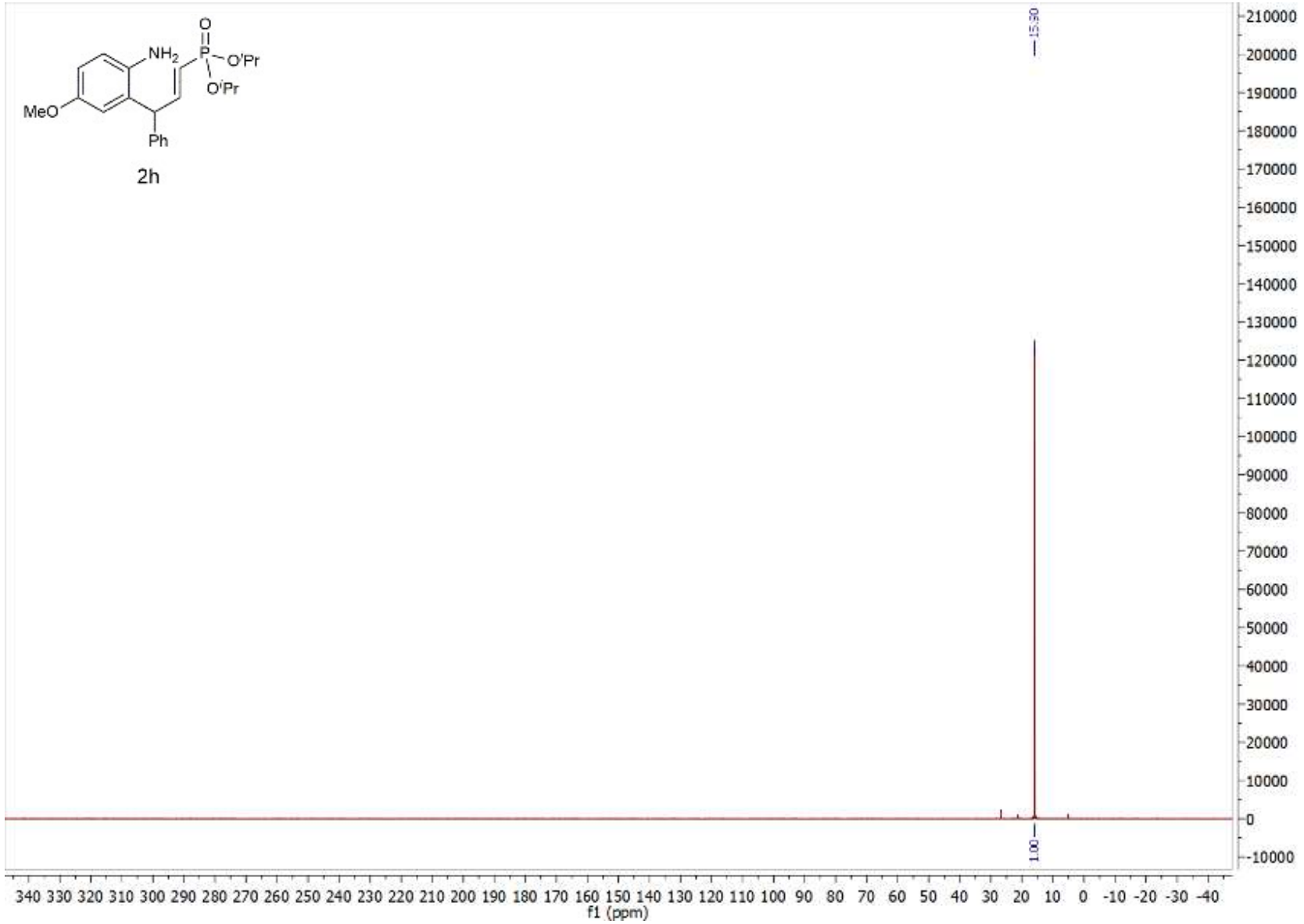


Figure S111: ^{31}P NMR Spectra of 2h

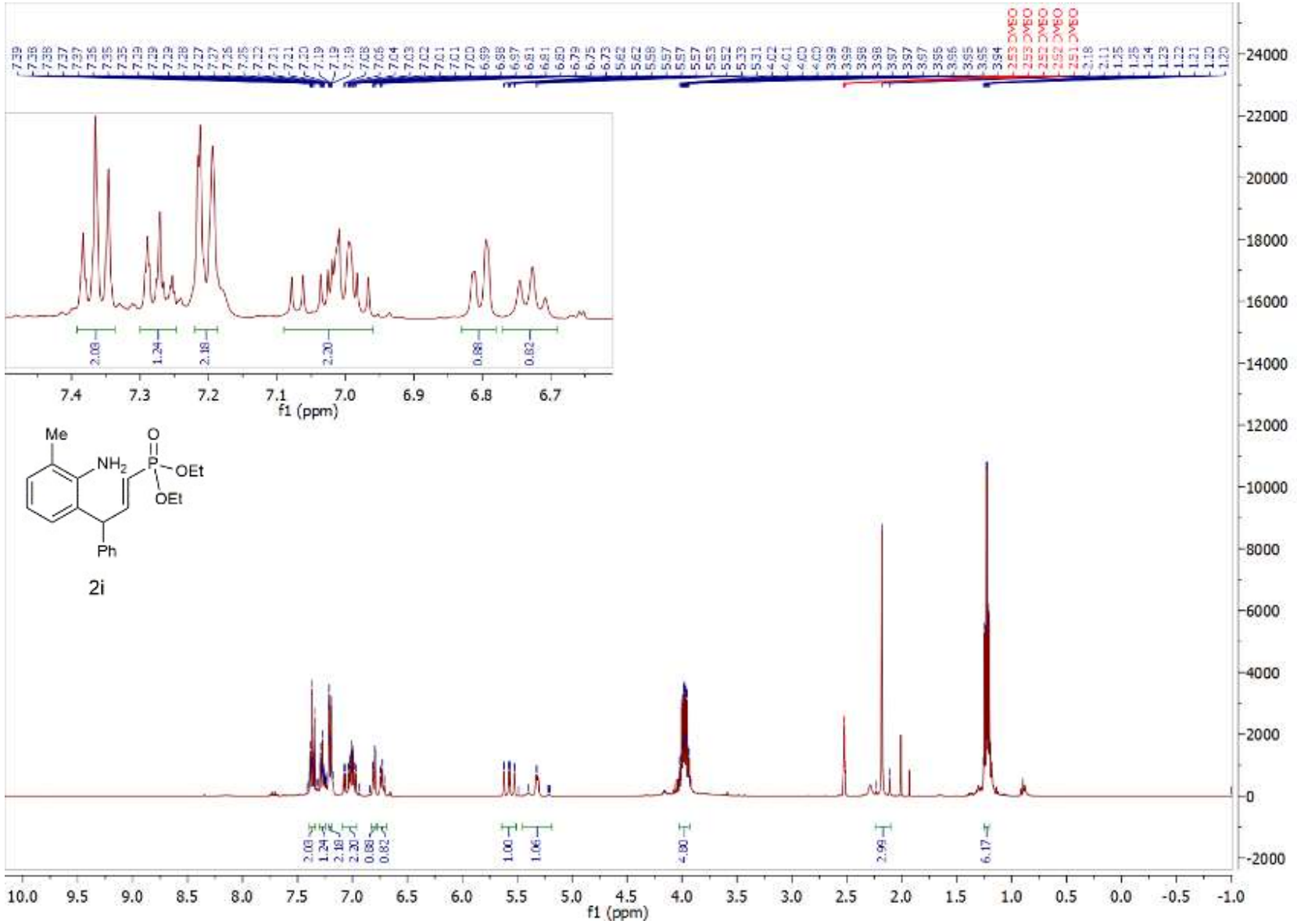


Figure S112: ^{1}H NMR Spectra of 2i

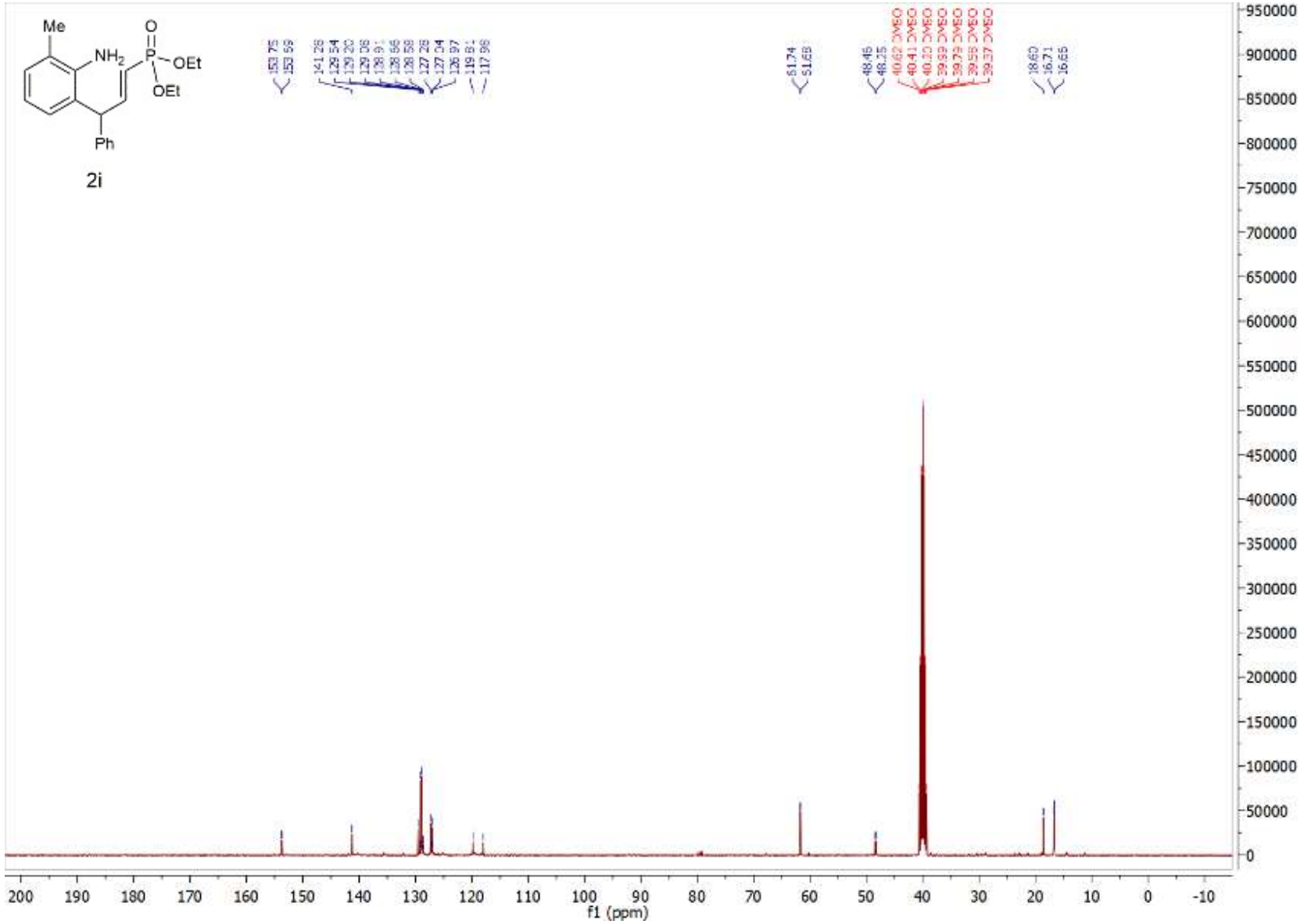


Figure S113: ^{13}C NMR Spectra of 2i

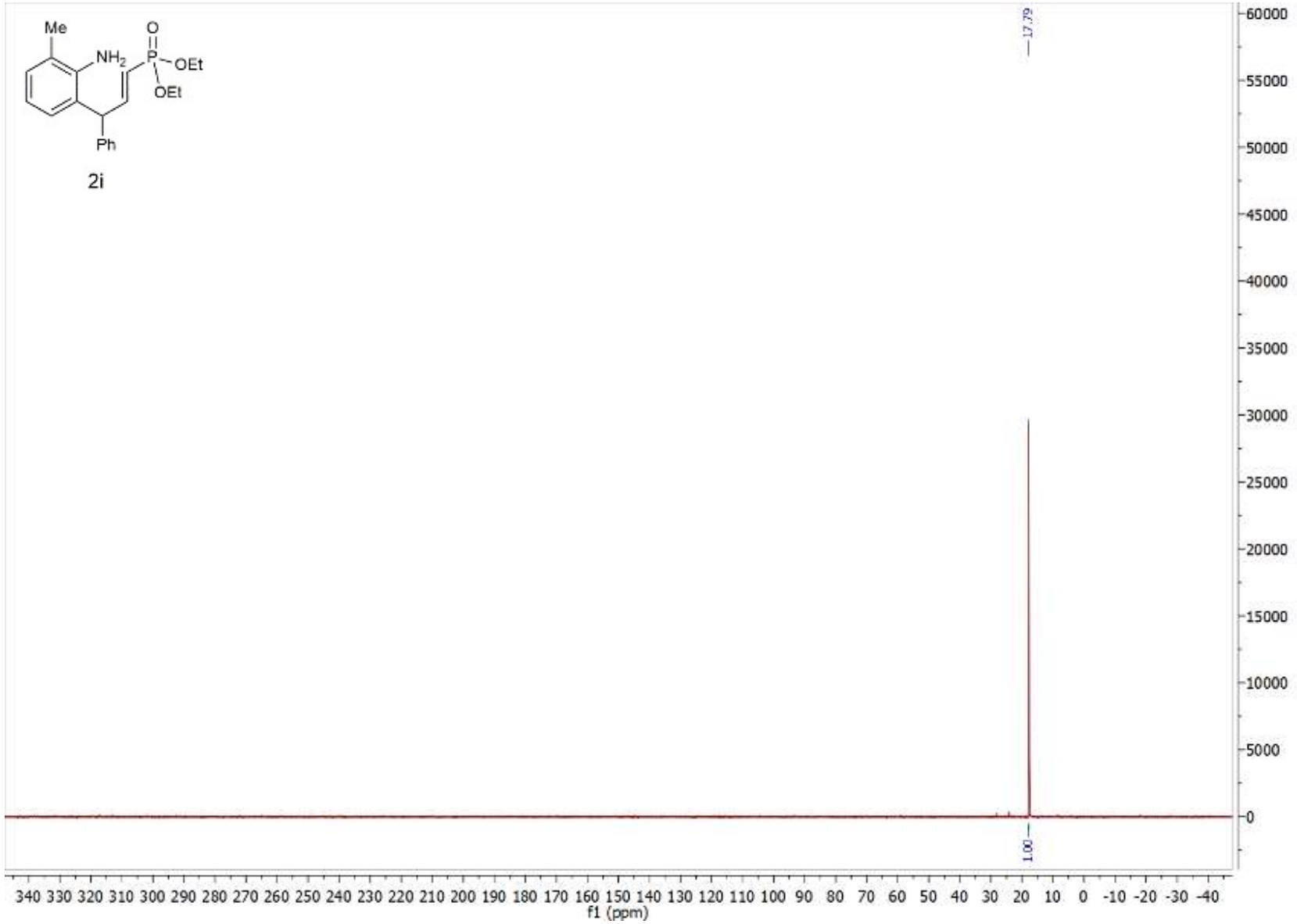


Figure S114: ^{31}P NMR Spectra of 2i

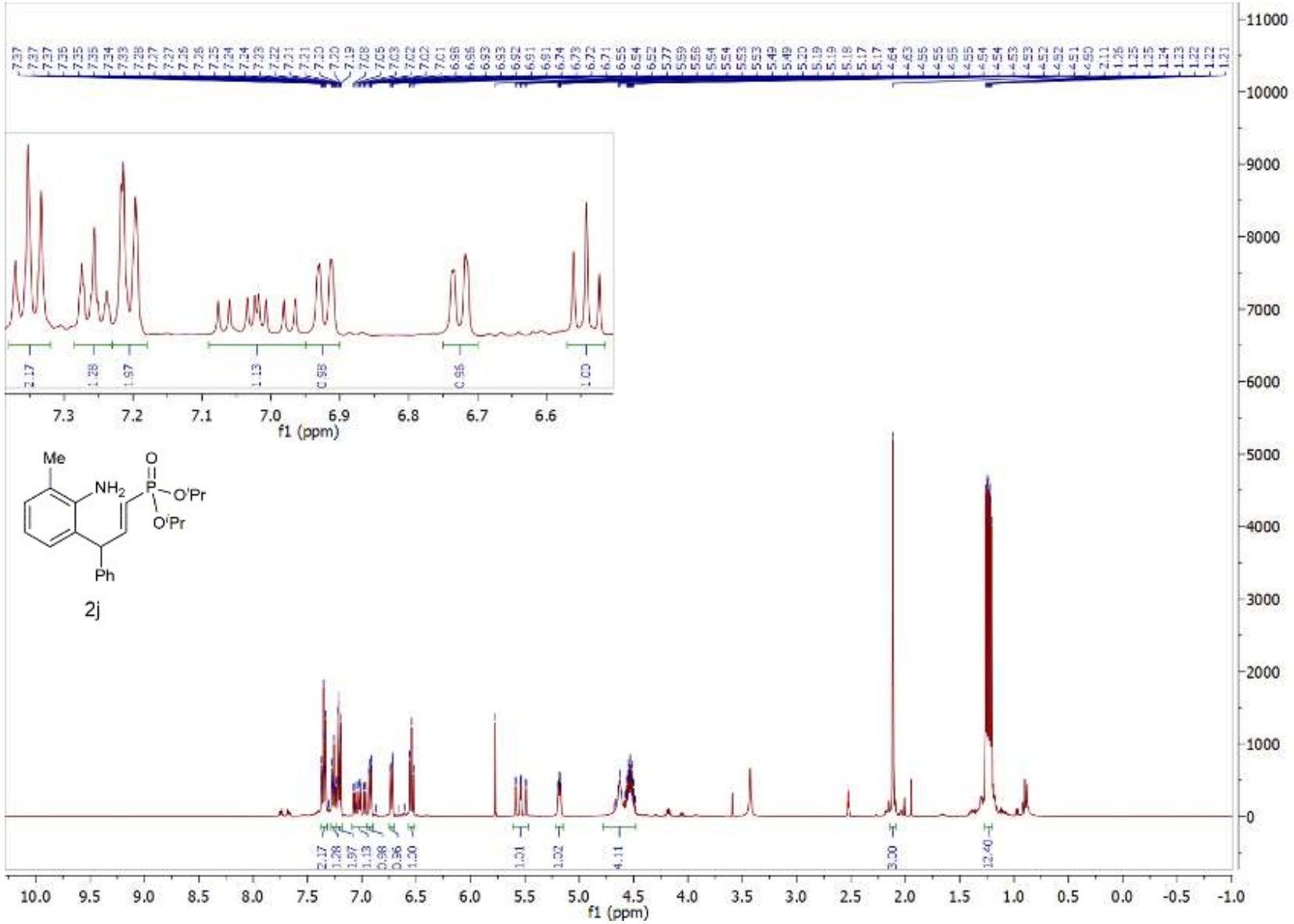


Figure S115: ^{1}H NMR Spectra of 2j

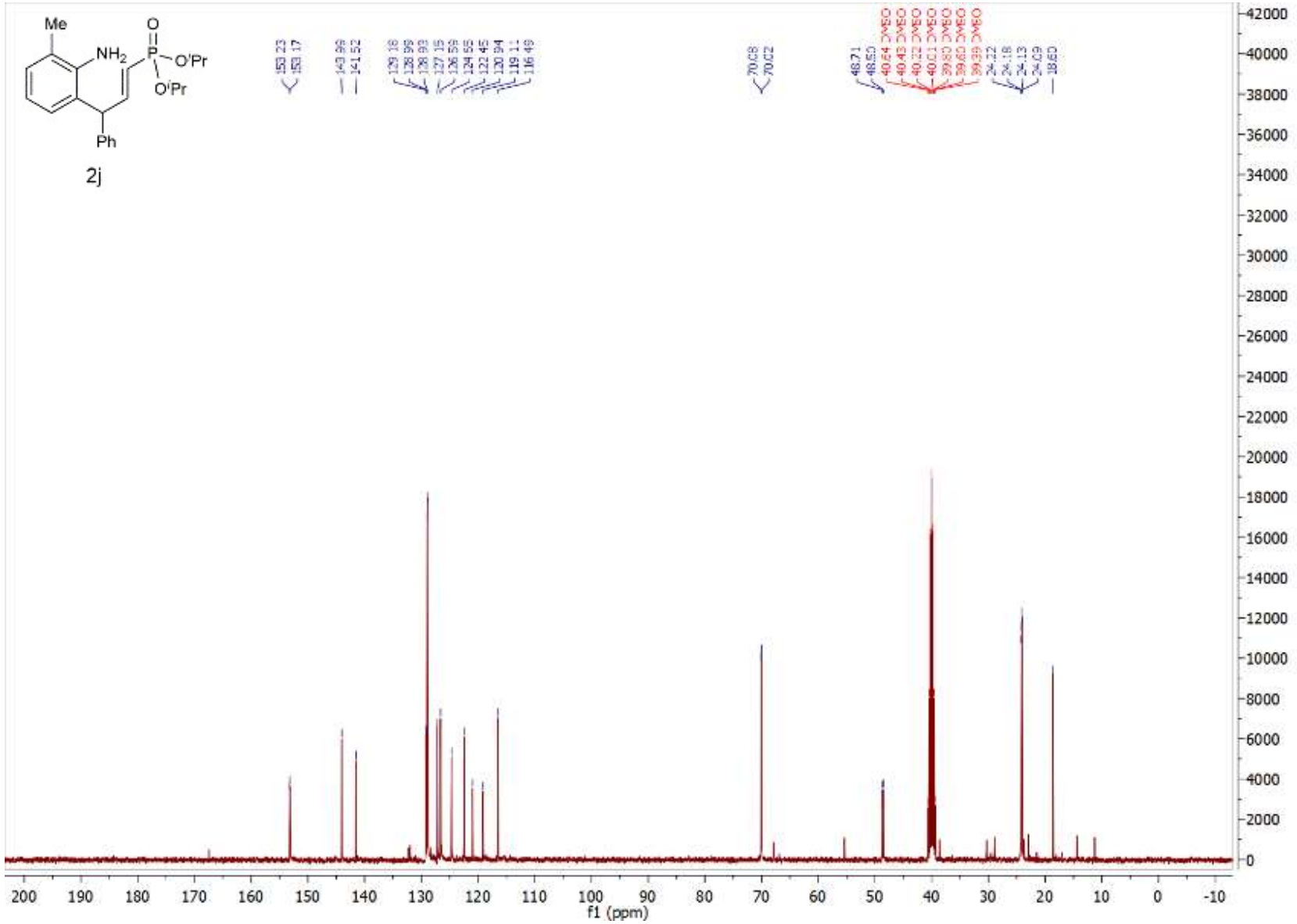


Figure S116: ^{13}C NMR Spectra of 2j

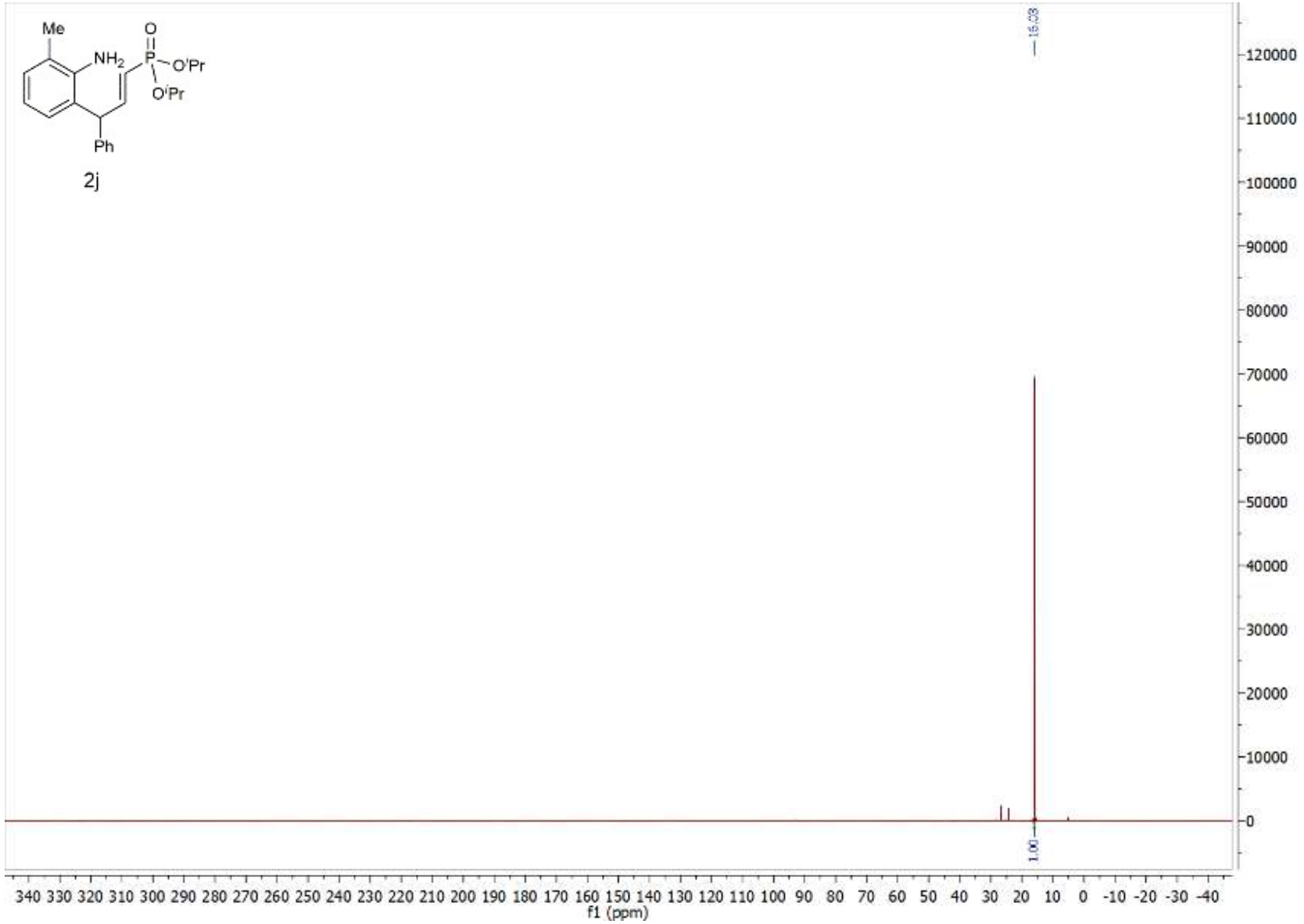


Figure S117: ^{31}P NMR Spectra of 2j

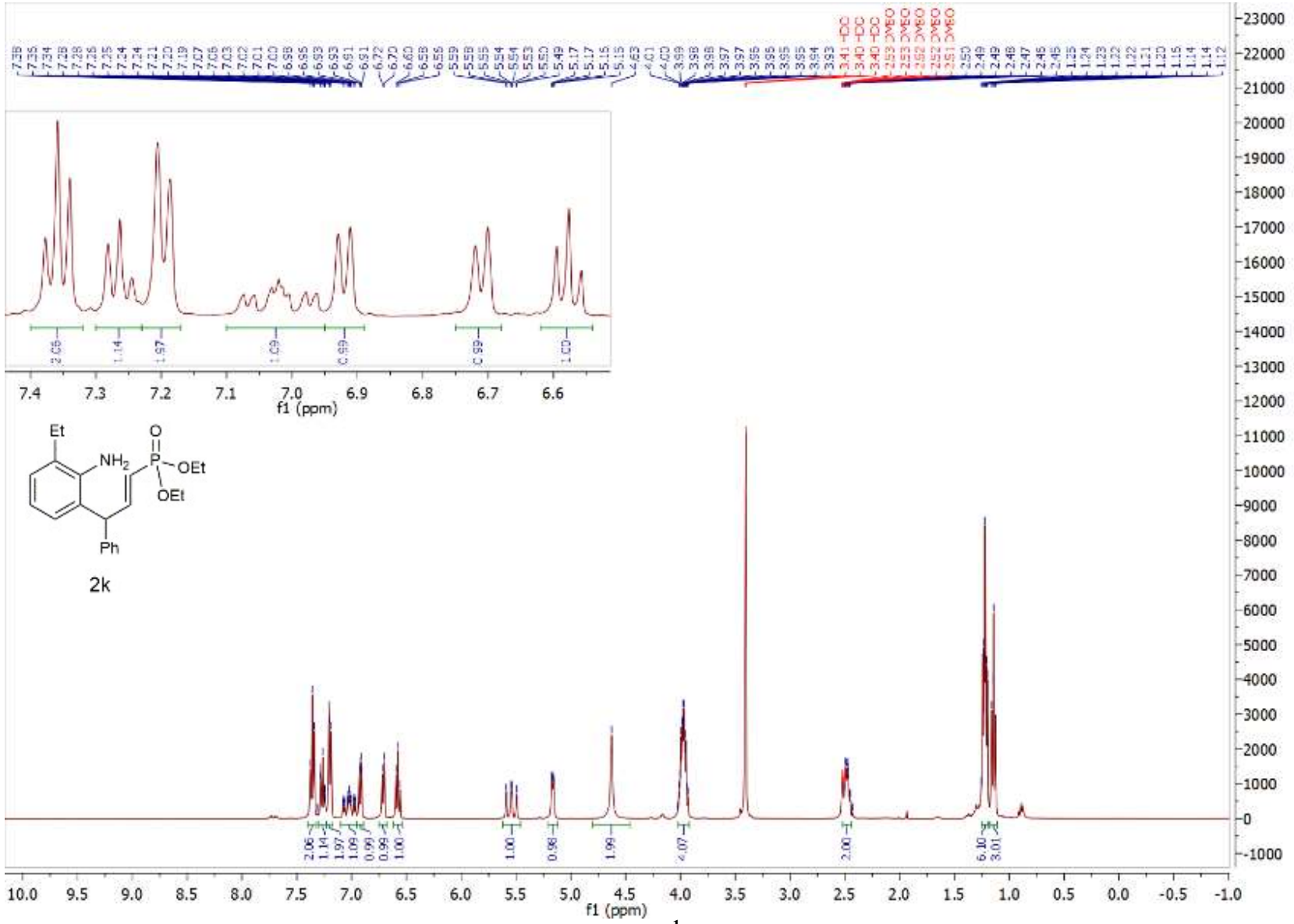


Figure S118: ^{1}H NMR Spectra of 2k

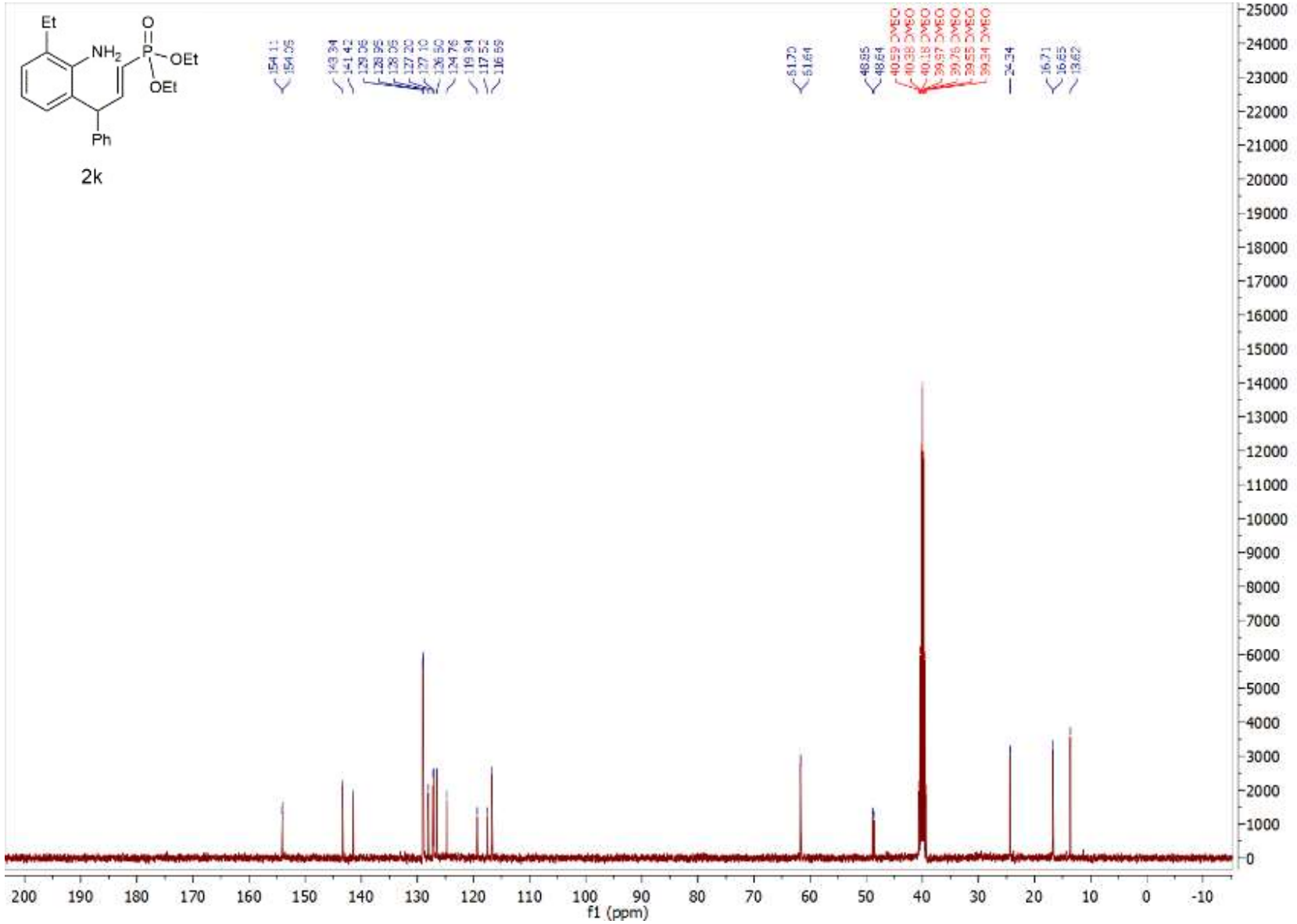


Figure S119: ^{13}C NMR Spectra of 2k

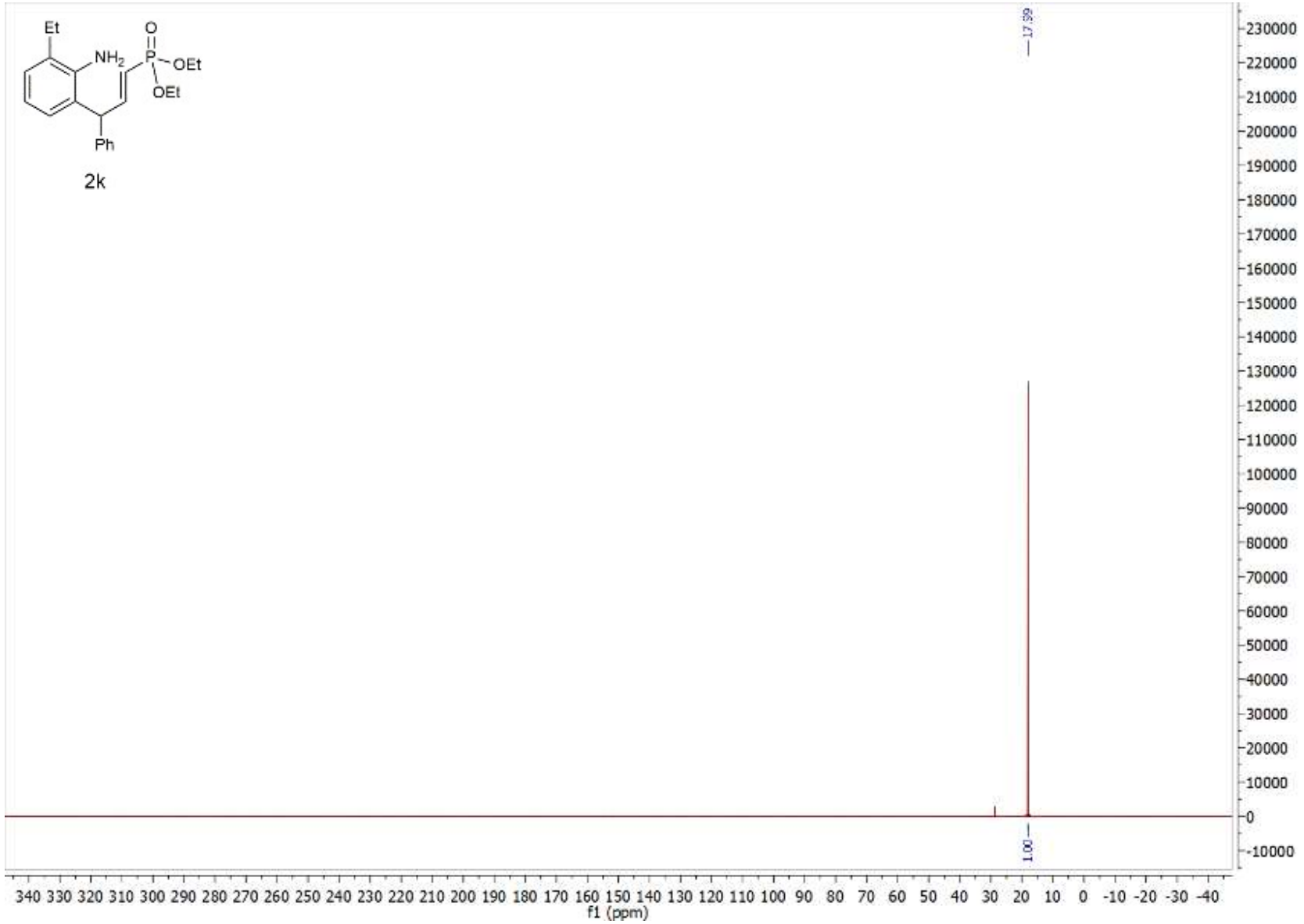


Figure S120: ^{31}P NMR Spectra of 2k

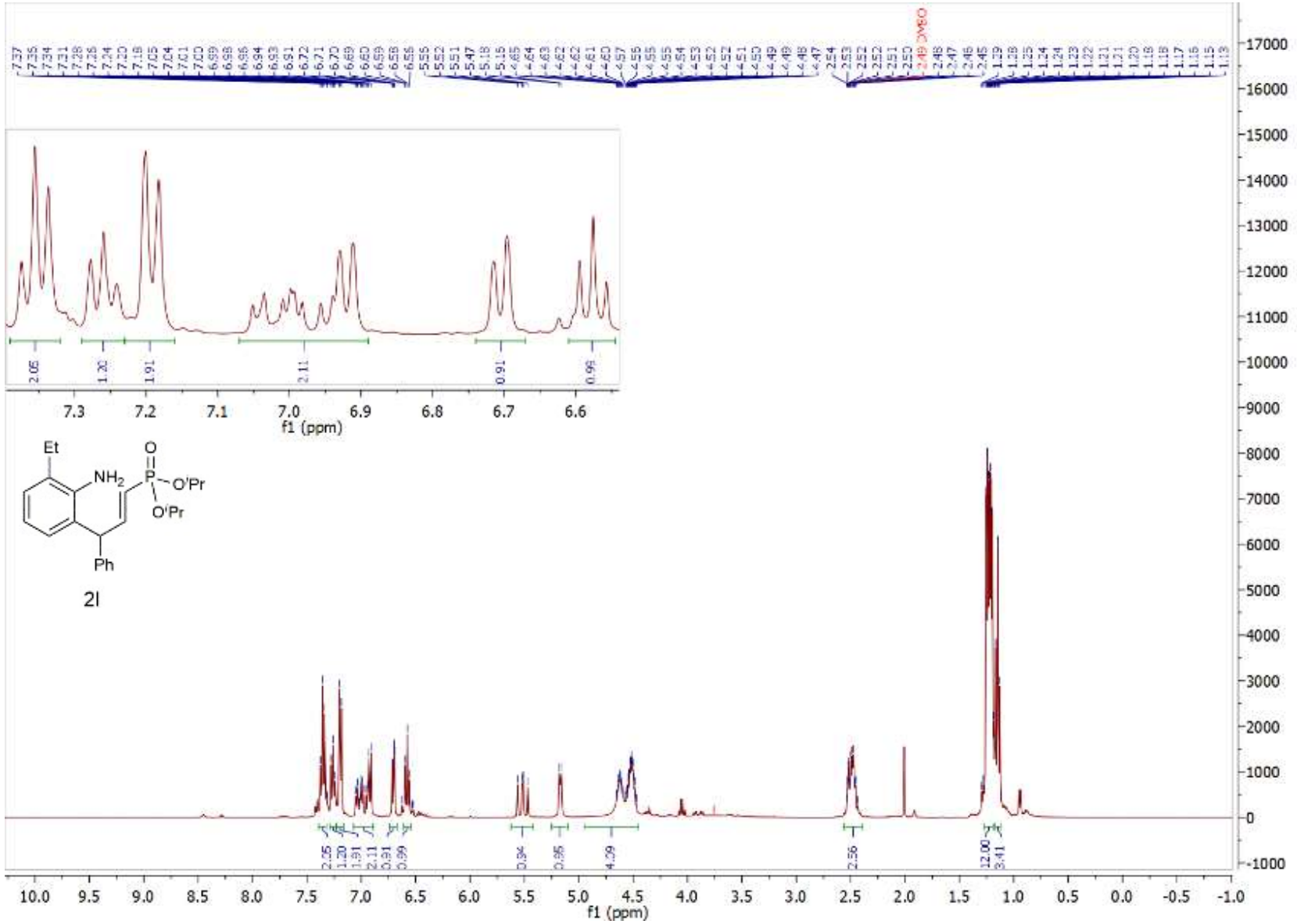


Figure S121: ^{1}H NMR Spectra of 2l

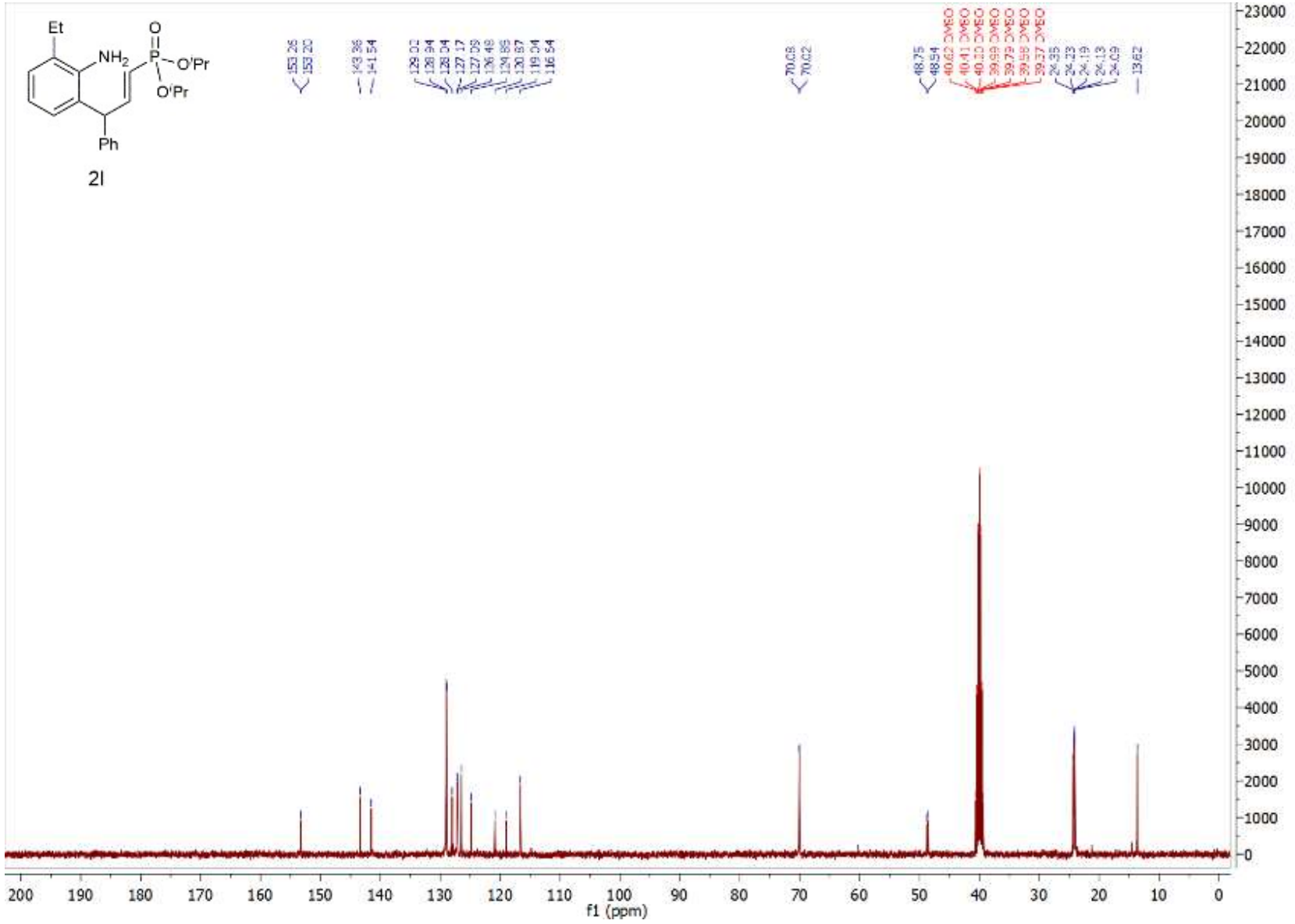


Figure S122: ^{13}C NMR Spectra of 2l

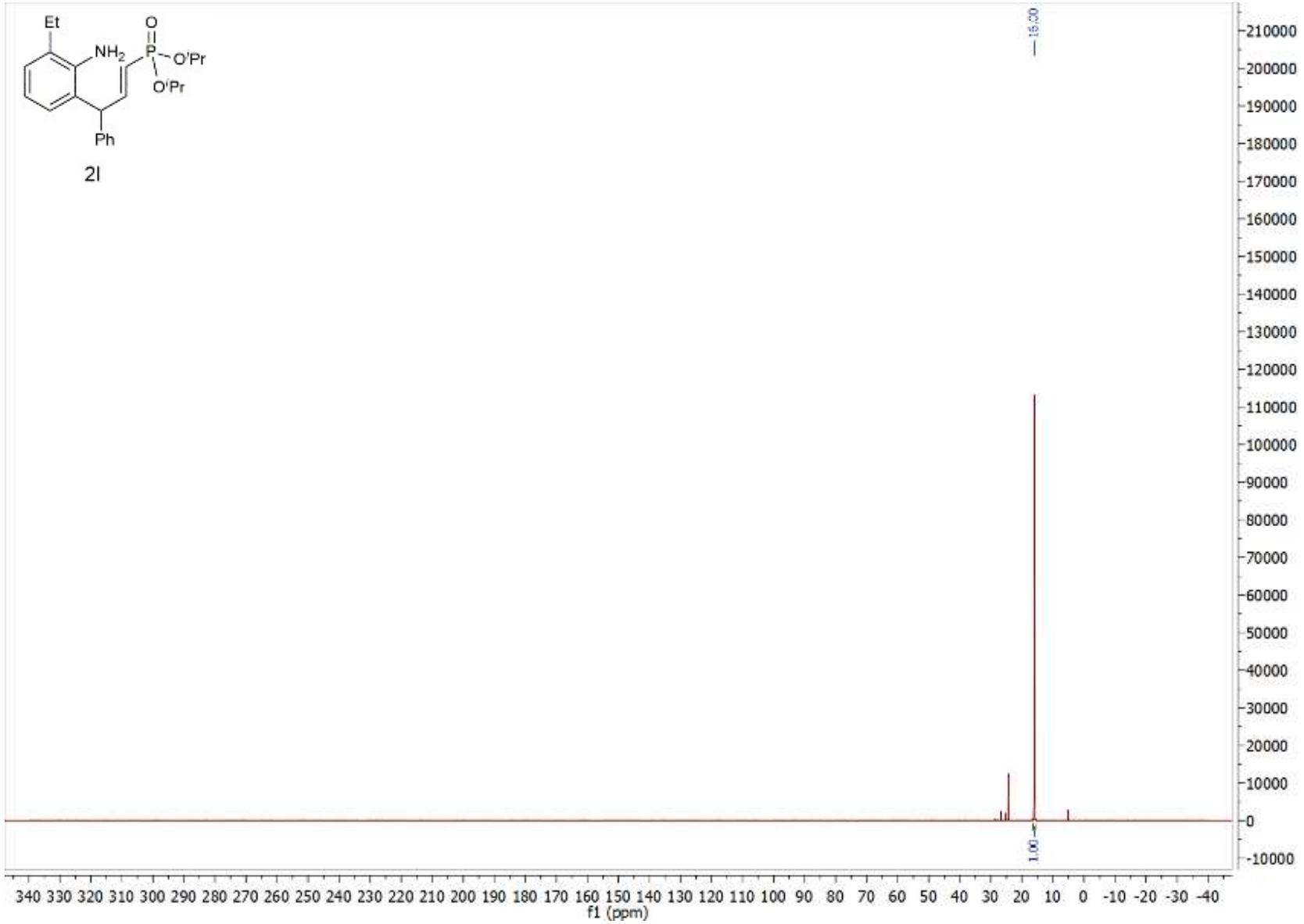


Figure S123: ^{31}P NMR Spectra of 2l

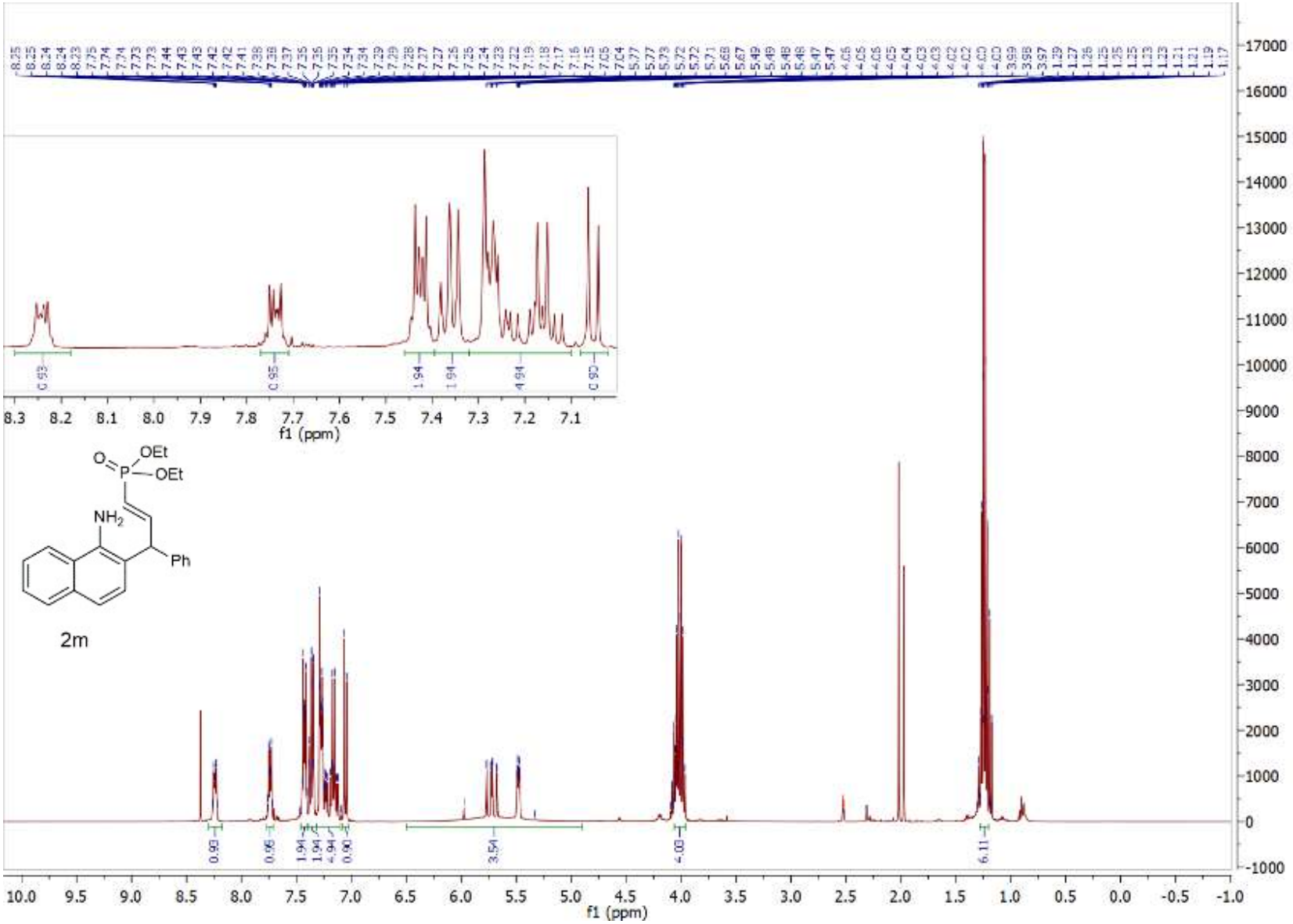


Figure S124: ^{1}H NMR Spectra of 2m

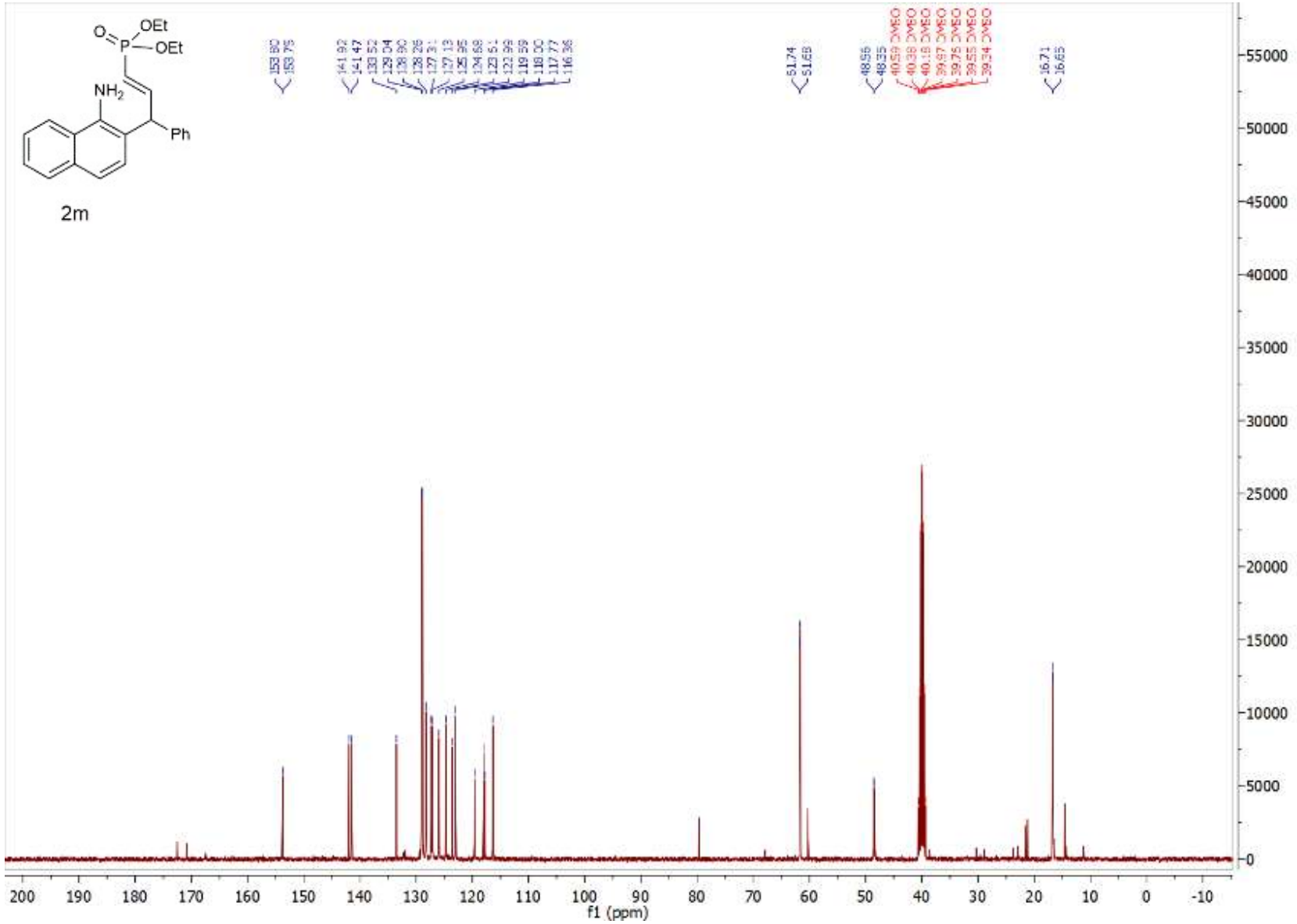


Figure S125: ^{13}C NMR Spectra of 2m

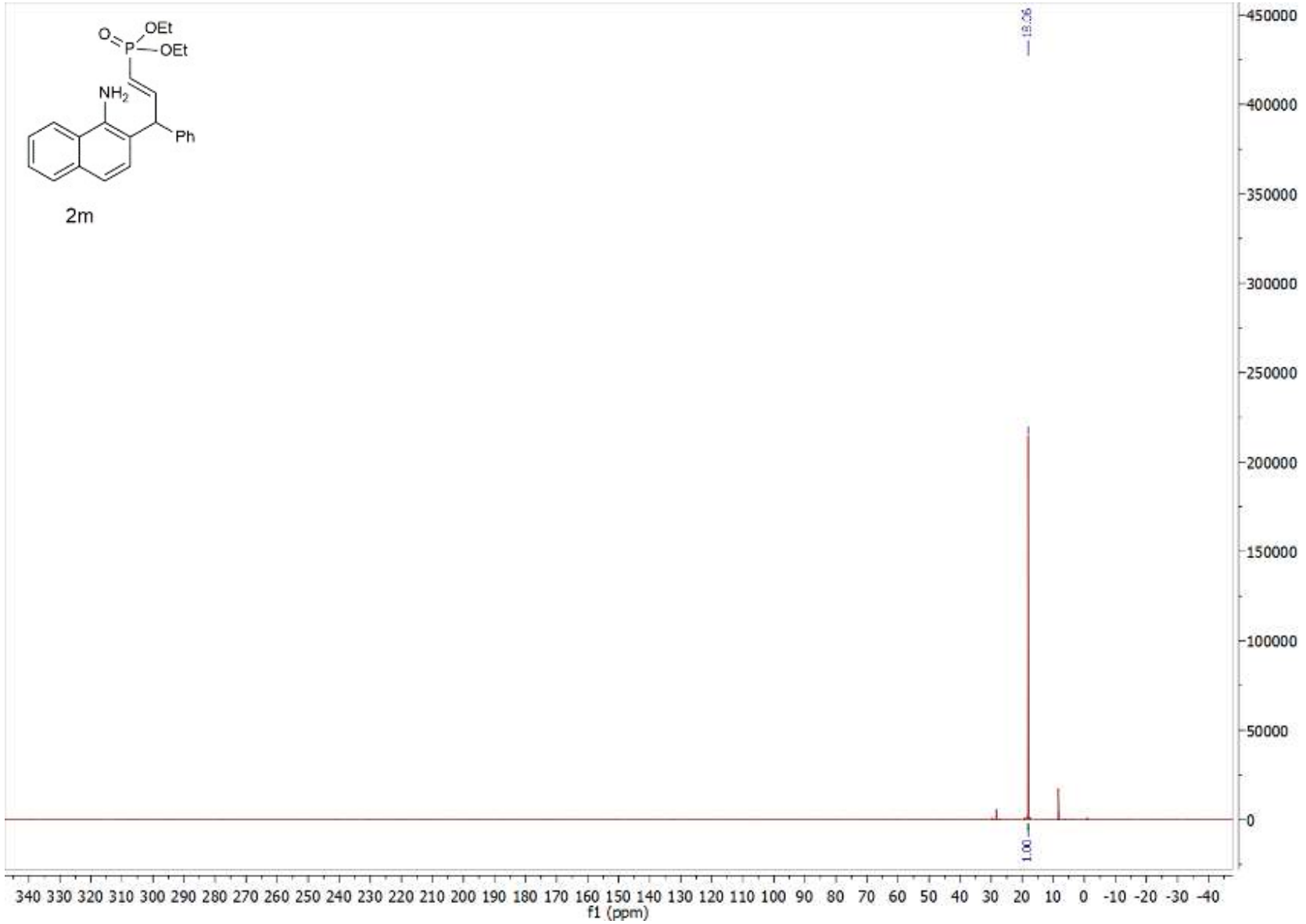


Figure S126: ^{31}P NMR Spectra of 2m

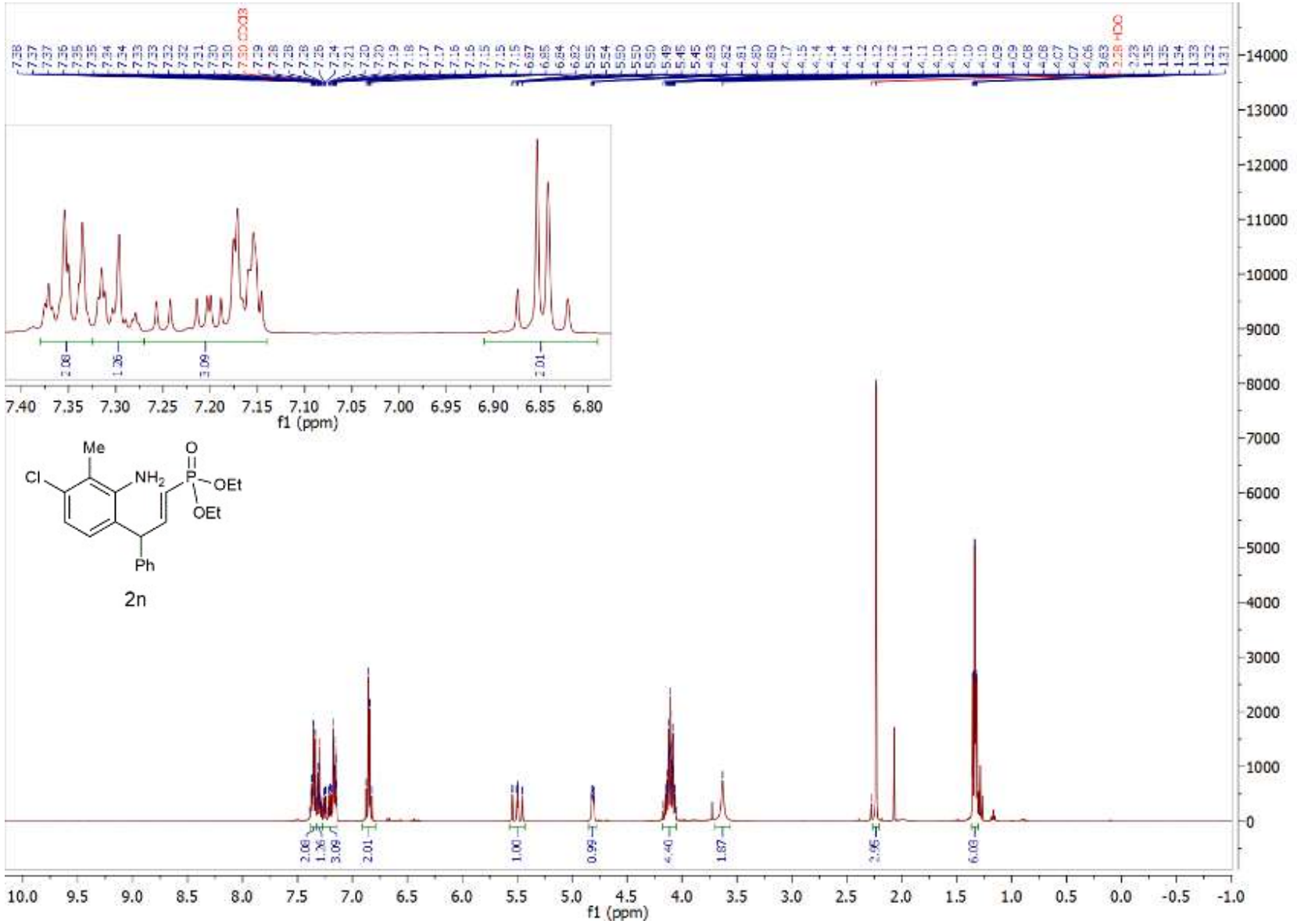


Figure S127: ^{1}H NMR Spectra of 2n

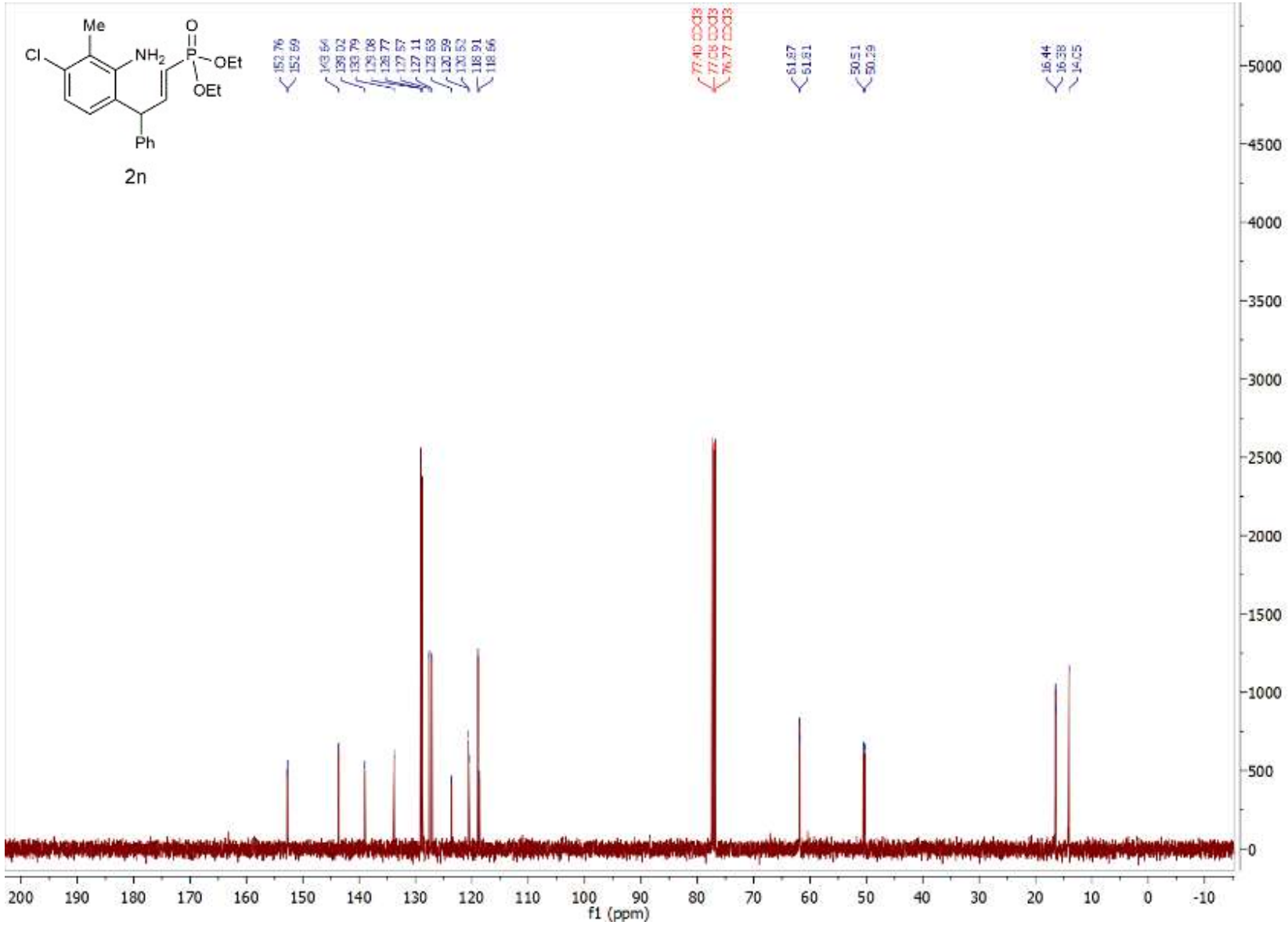


Figure S128: ^{13}C NMR Spectra of 2n

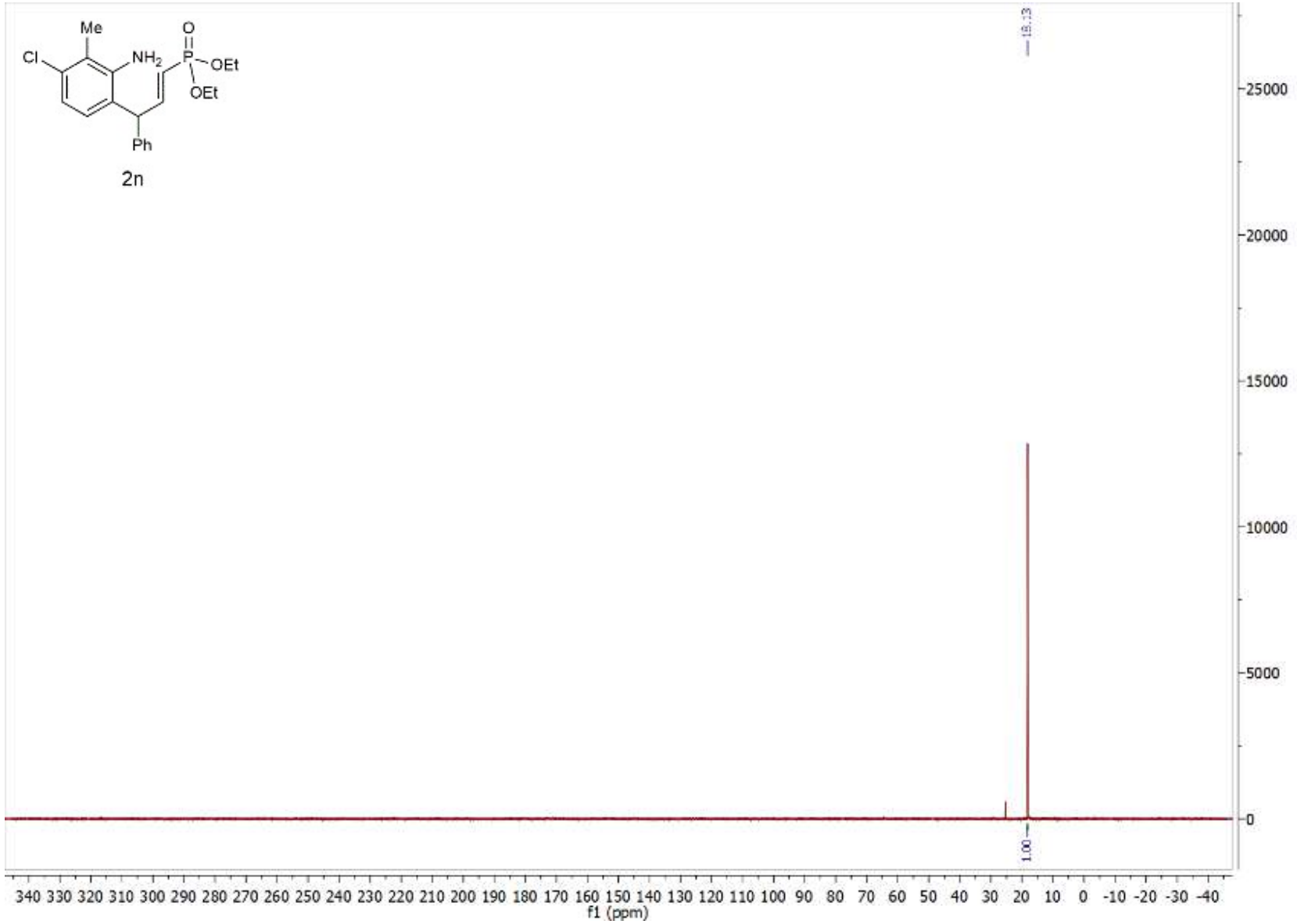


Figure S129: ^{31}P NMR Spectra of 2n

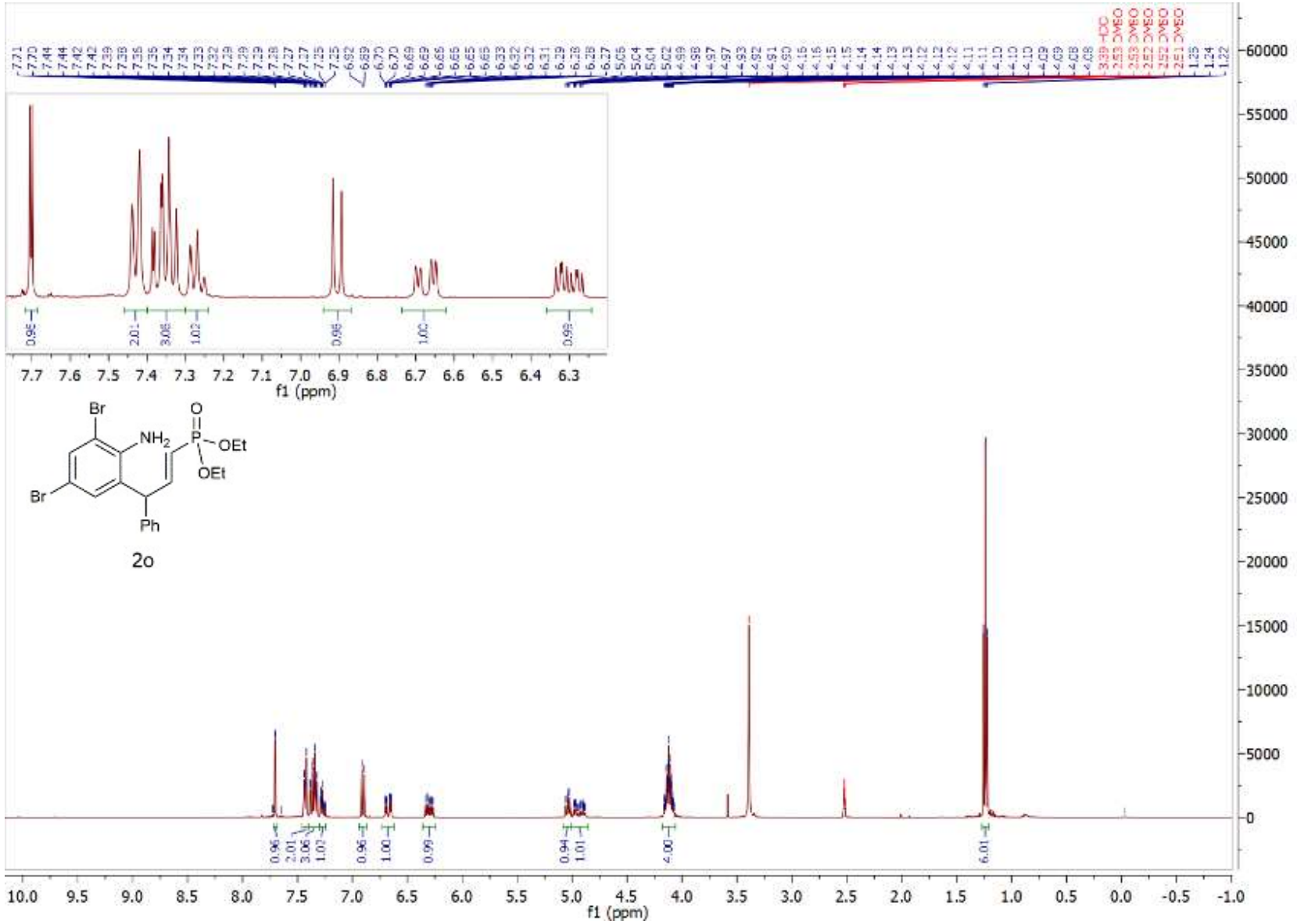


Figure S130: ^{1}H NMR Spectra of 2o

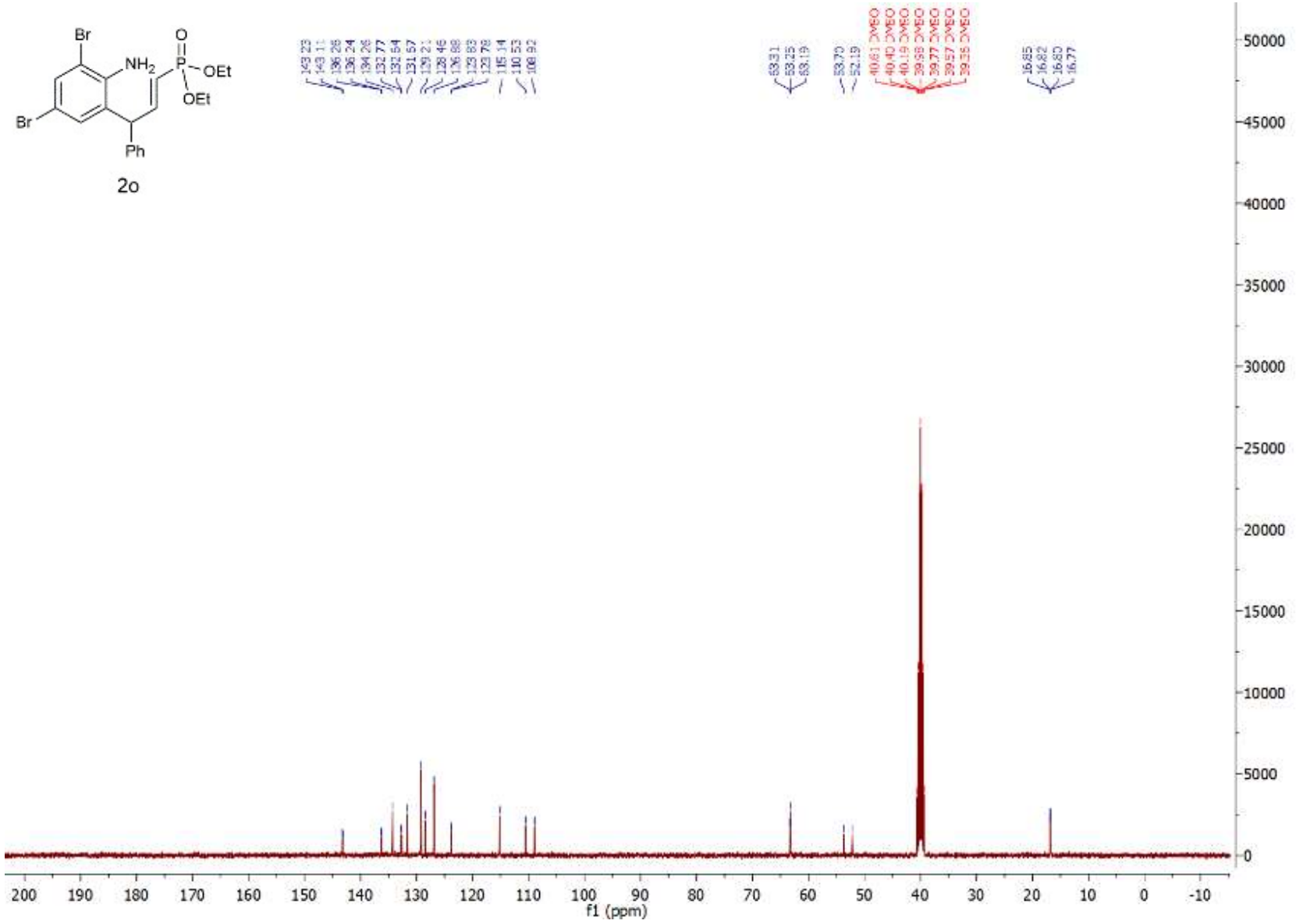


Figure S131: ^{13}C NMR Spectra of 2o

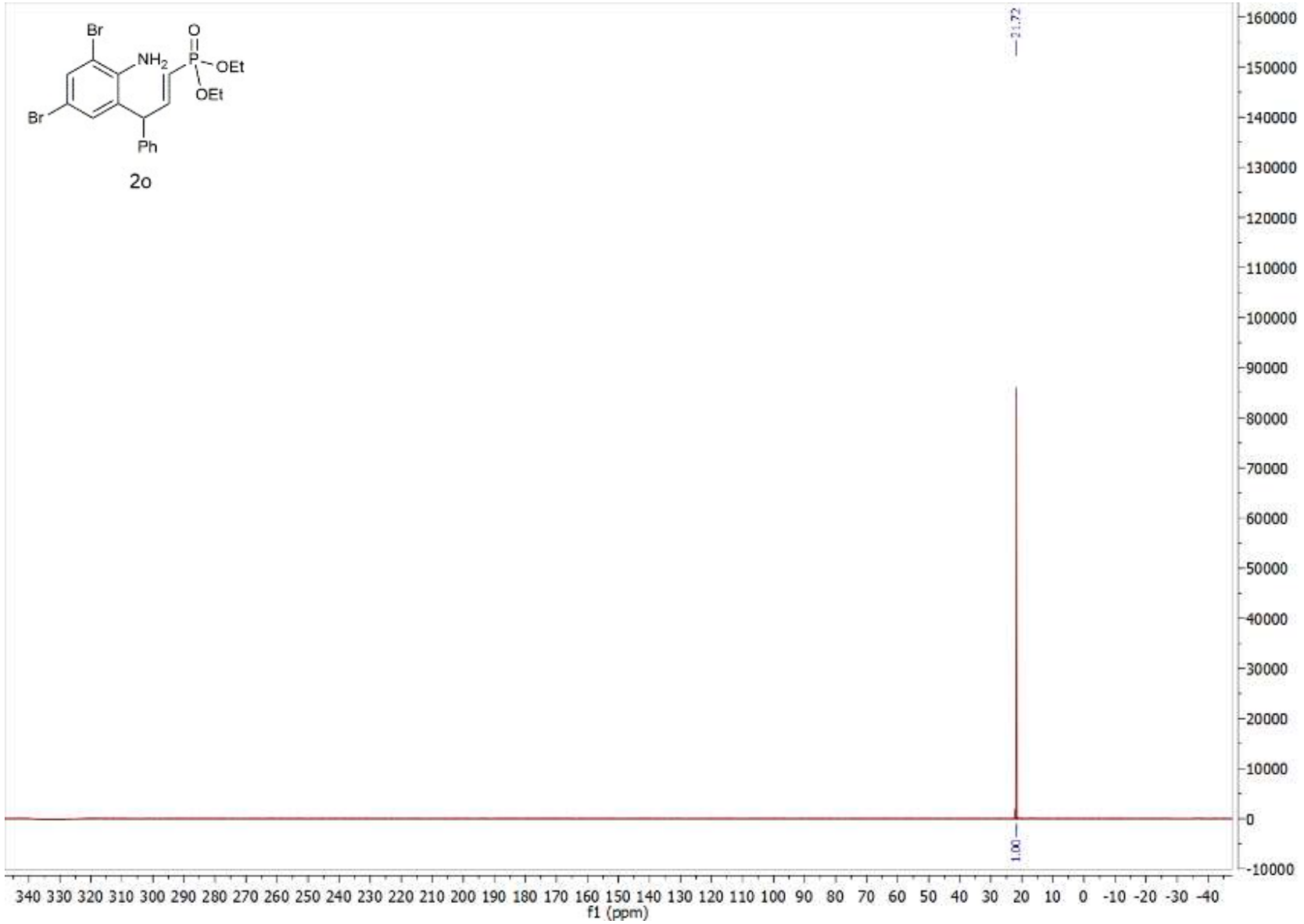


Figure S132: ^{31}P NMR Spectra of 2o

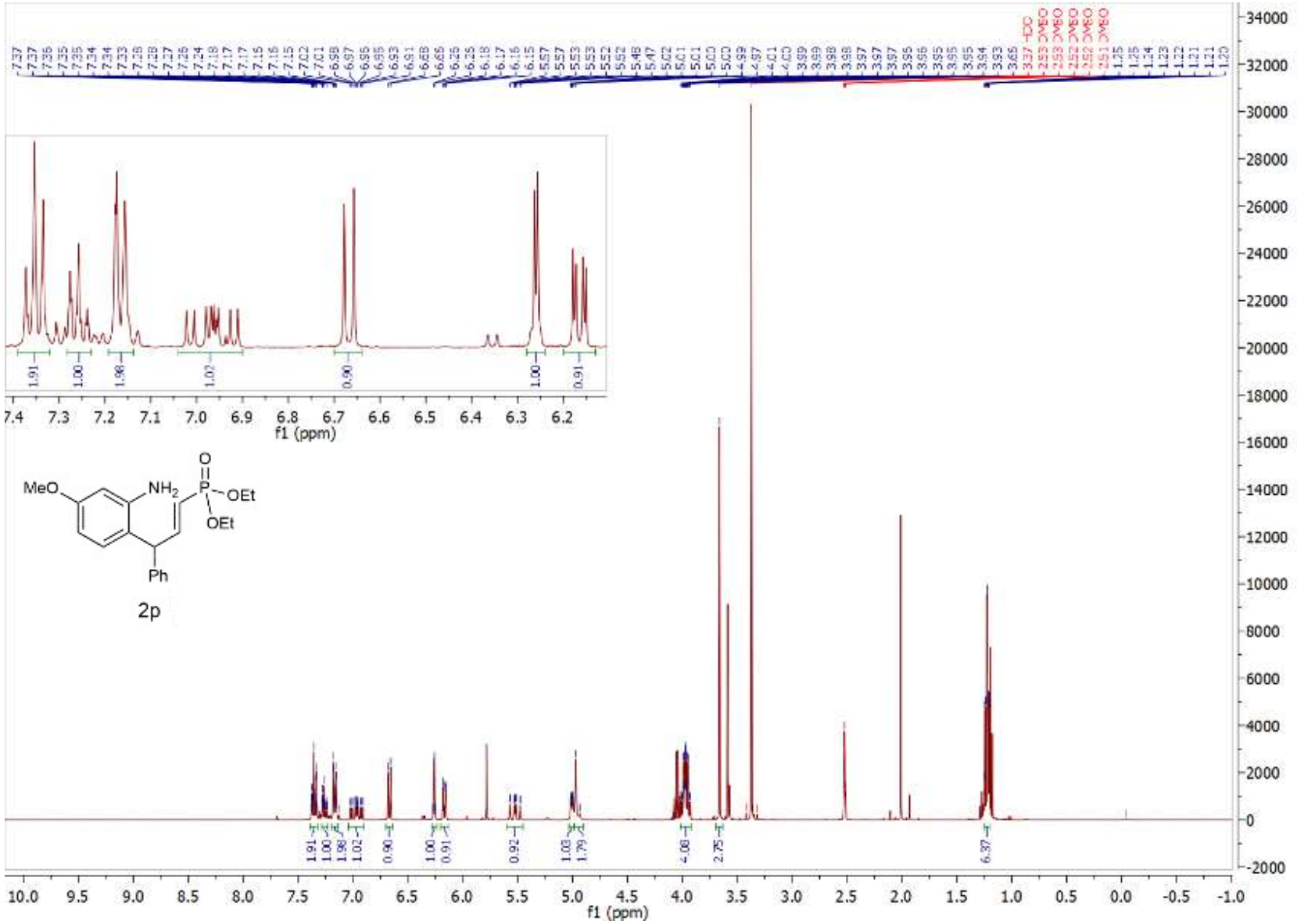


Figure S133: ^{1}H NMR Spectra of 2p

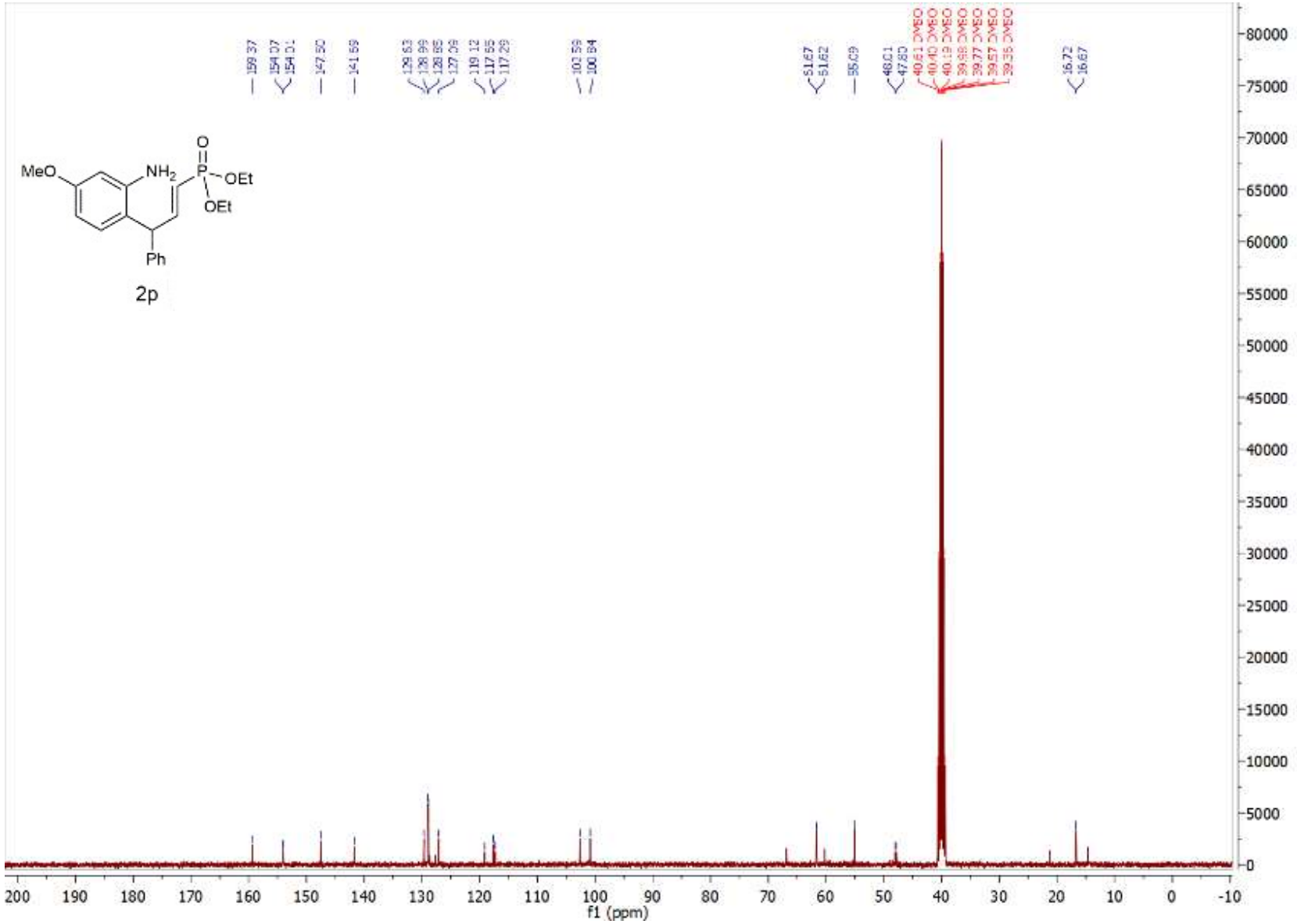


Figure S134: ^{13}C NMR Spectra of 2p

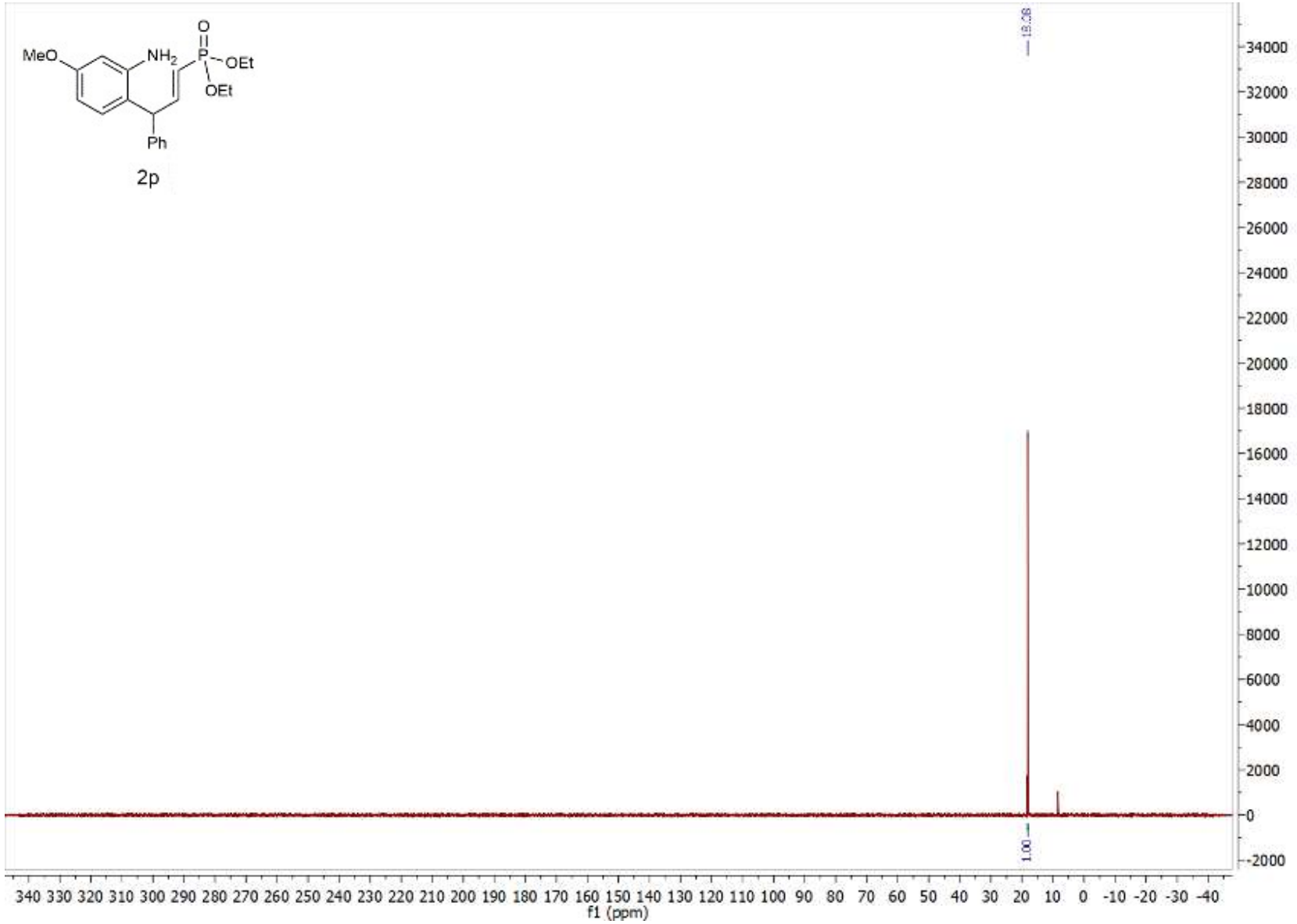


Figure S135: ^{31}P NMR Spectra of 2p

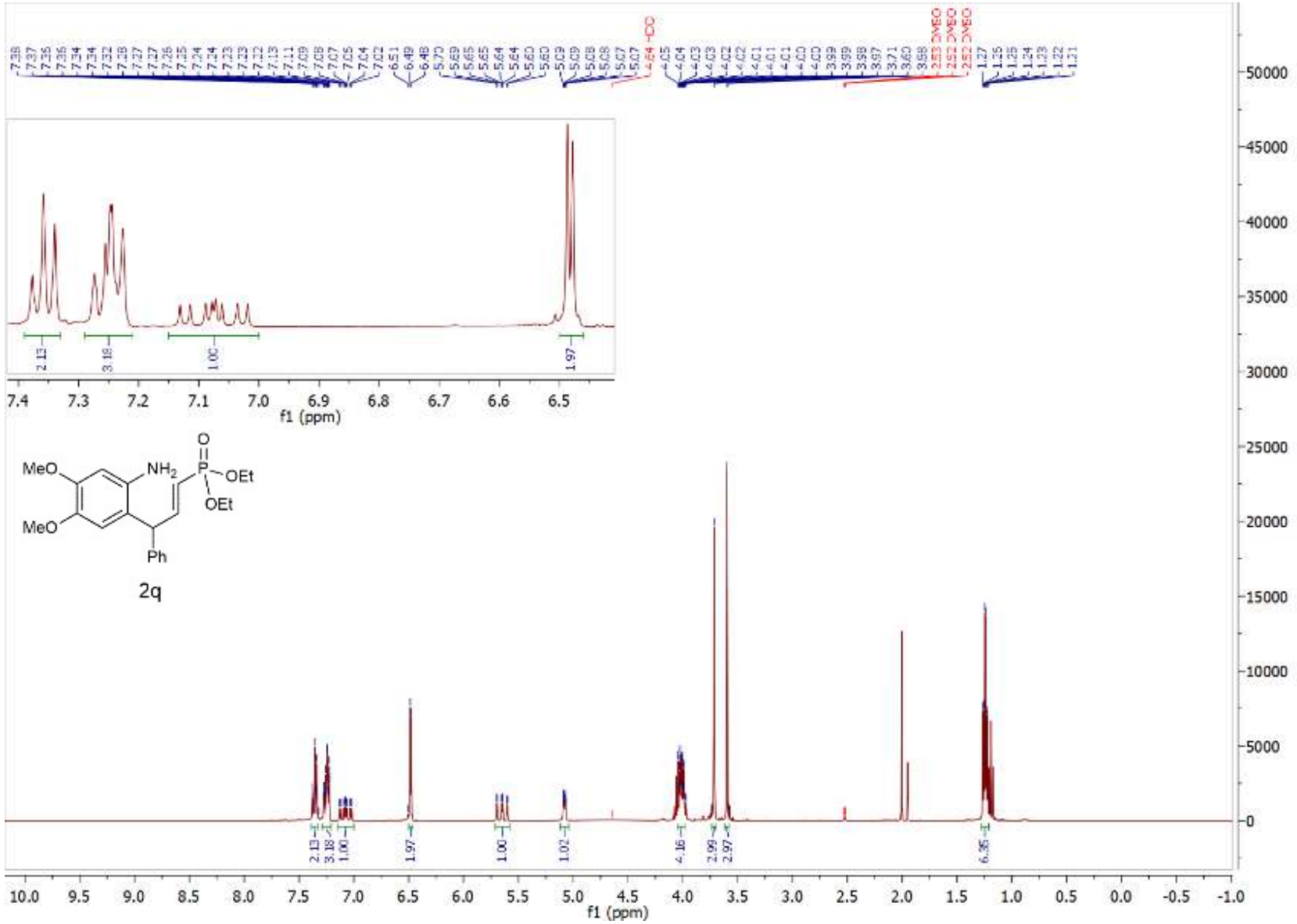


Figure S136: ^{1}H NMR Spectra of 2q

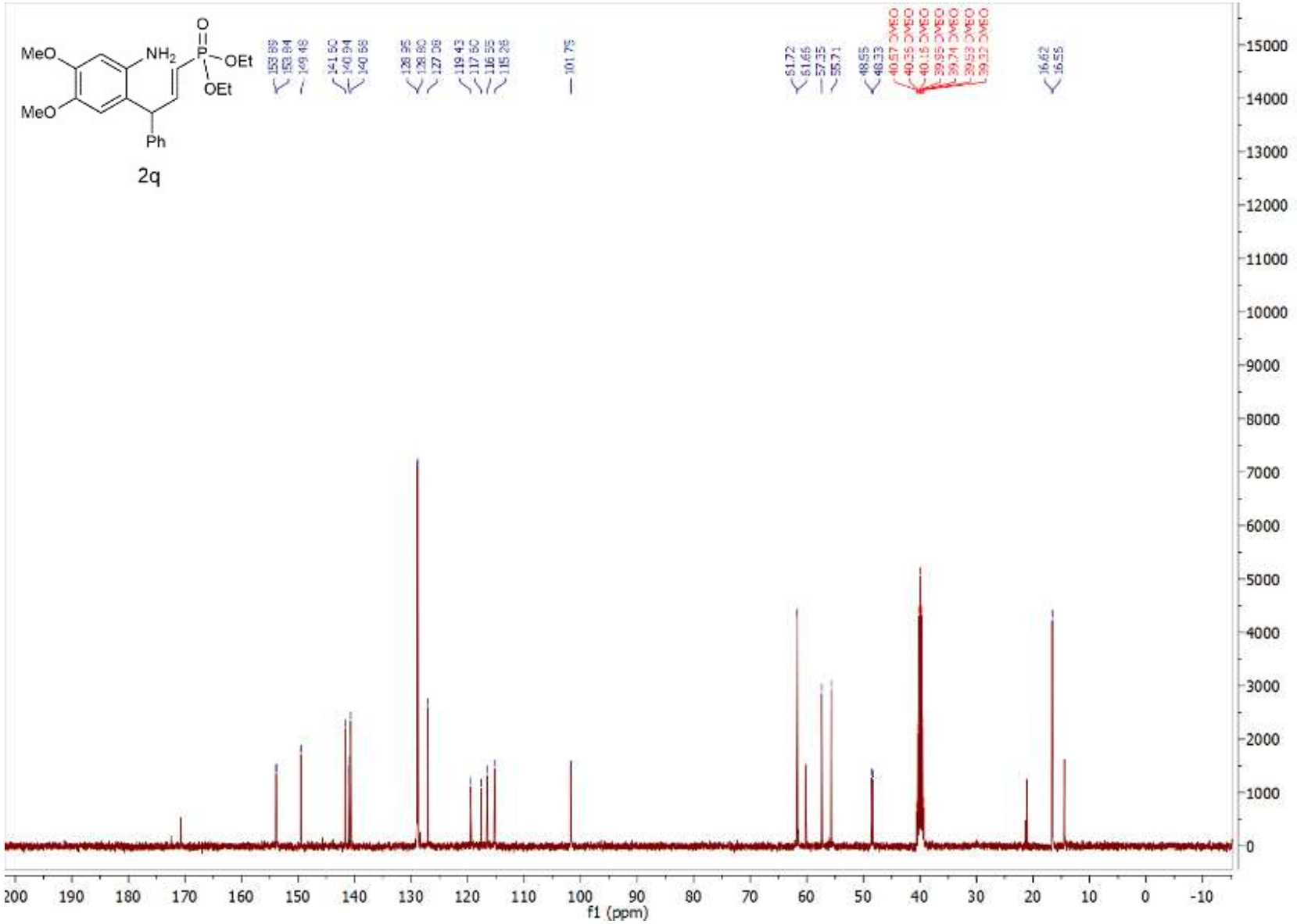


Figure S137: ^{13}C NMR Spectra of 2q

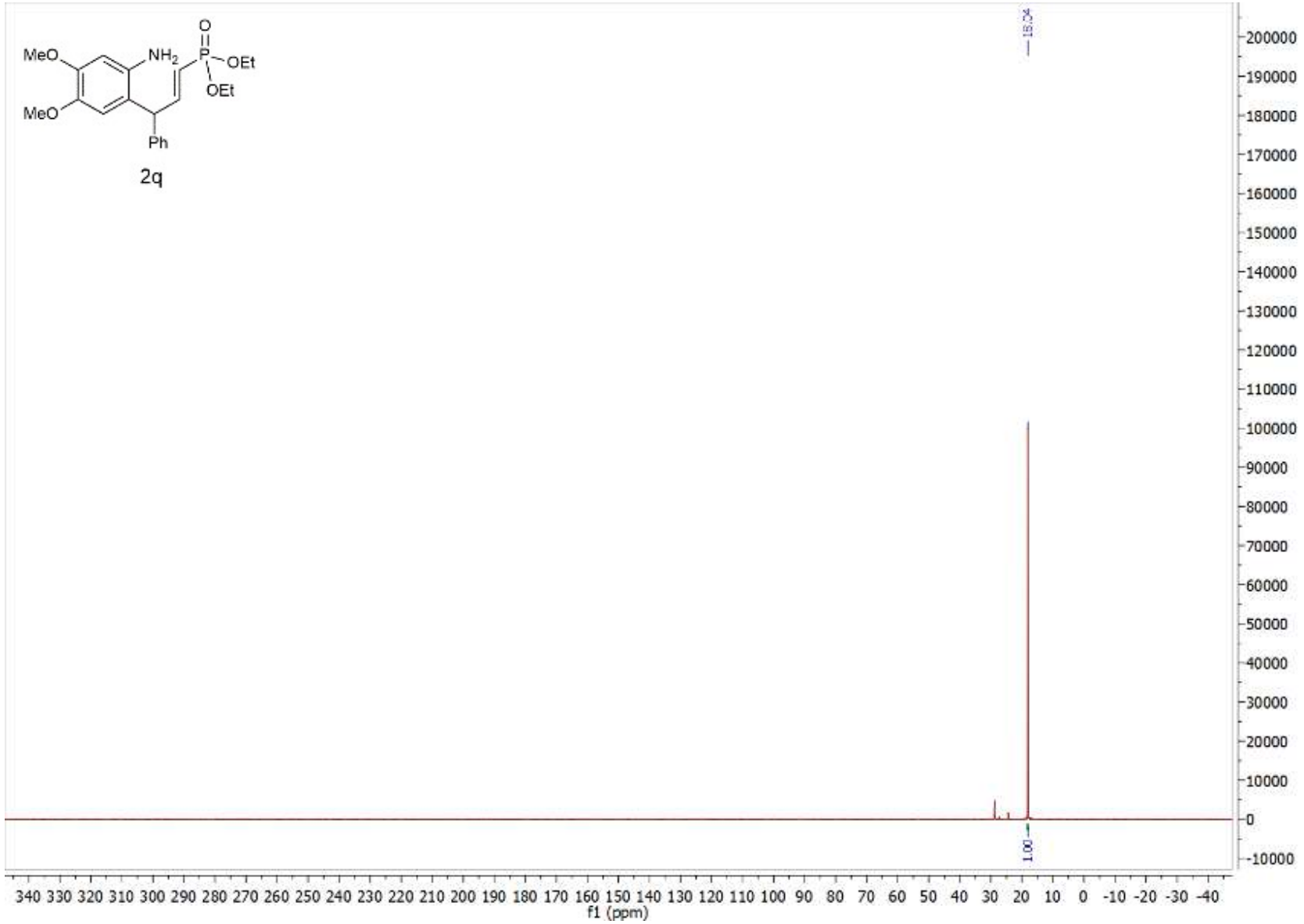


Figure S138: ^{31}P NMR Spectra of 2q

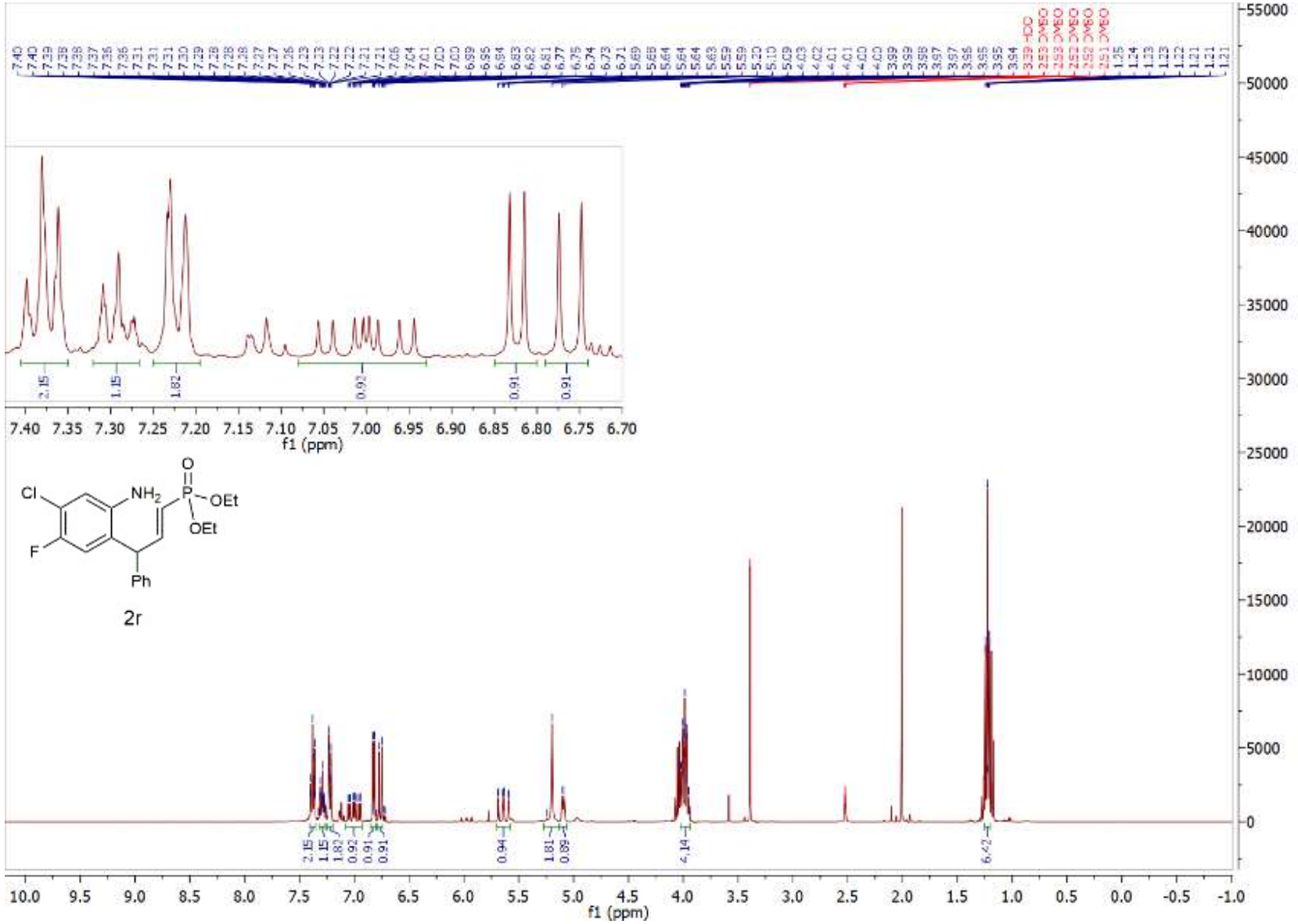


Figure S139: ^{1}H NMR Spectra of 2r

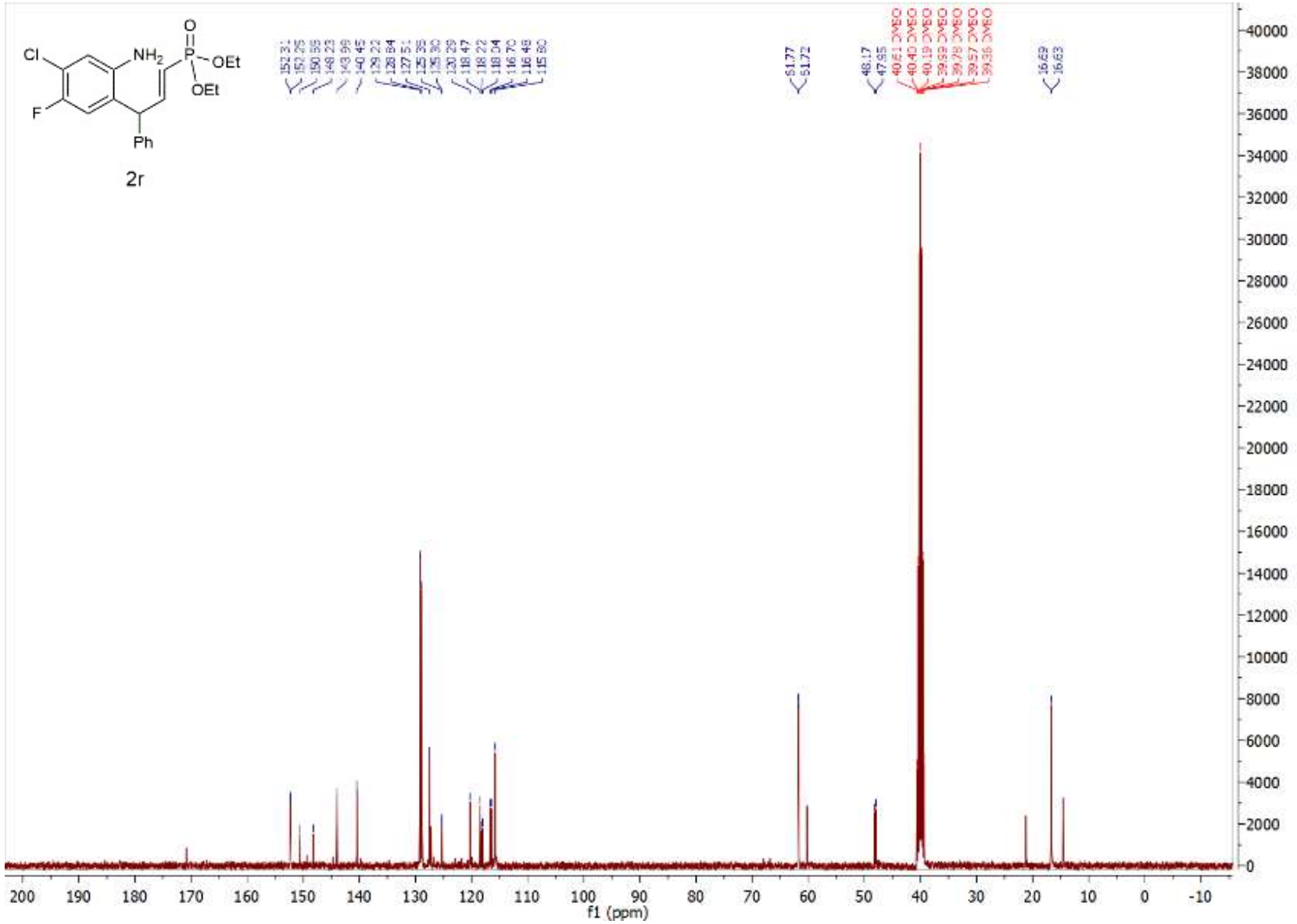


Figure S140: ^{13}C NMR Spectra of 2r

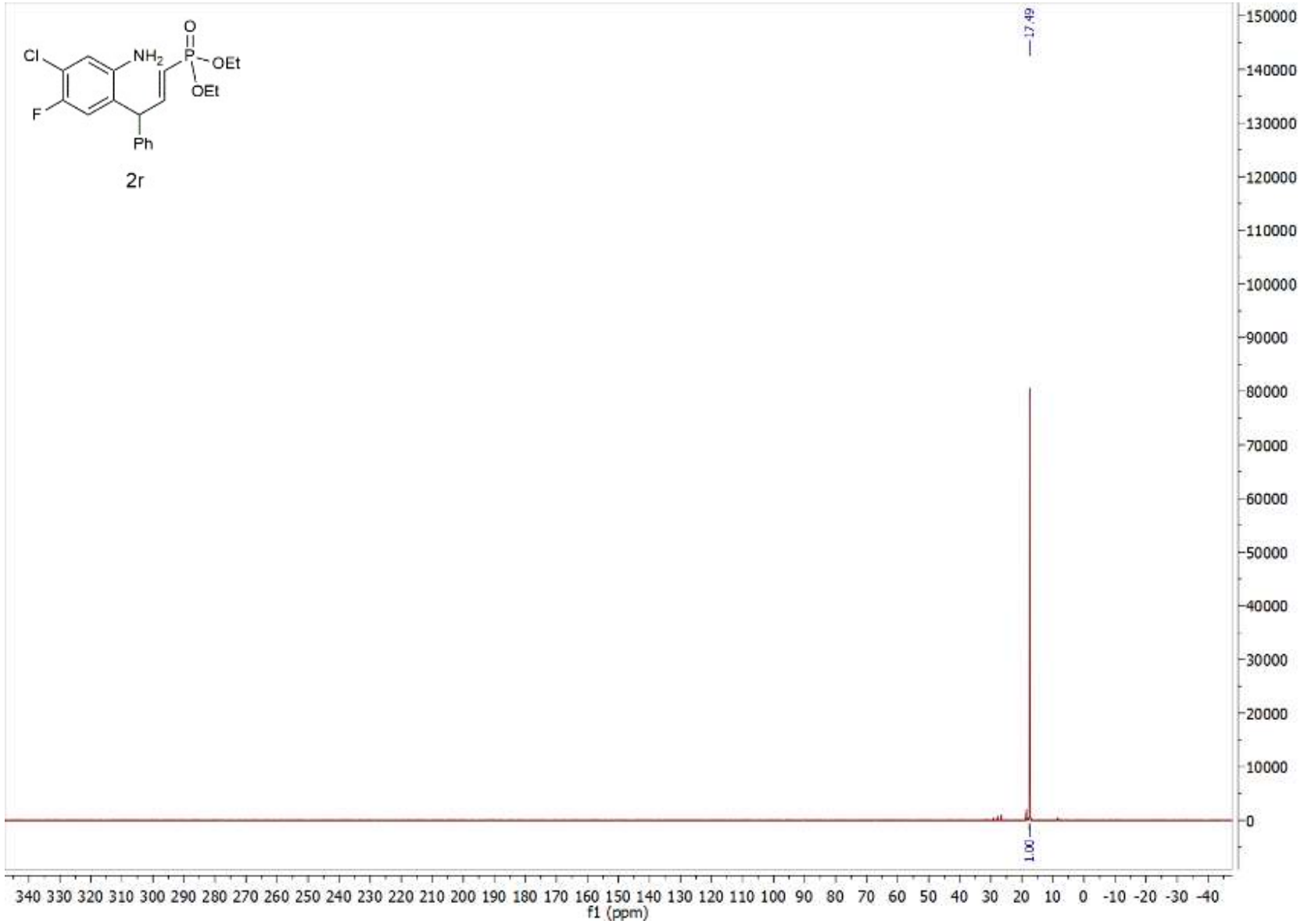


Figure S141: ^{31}P NMR Spectra of 2r

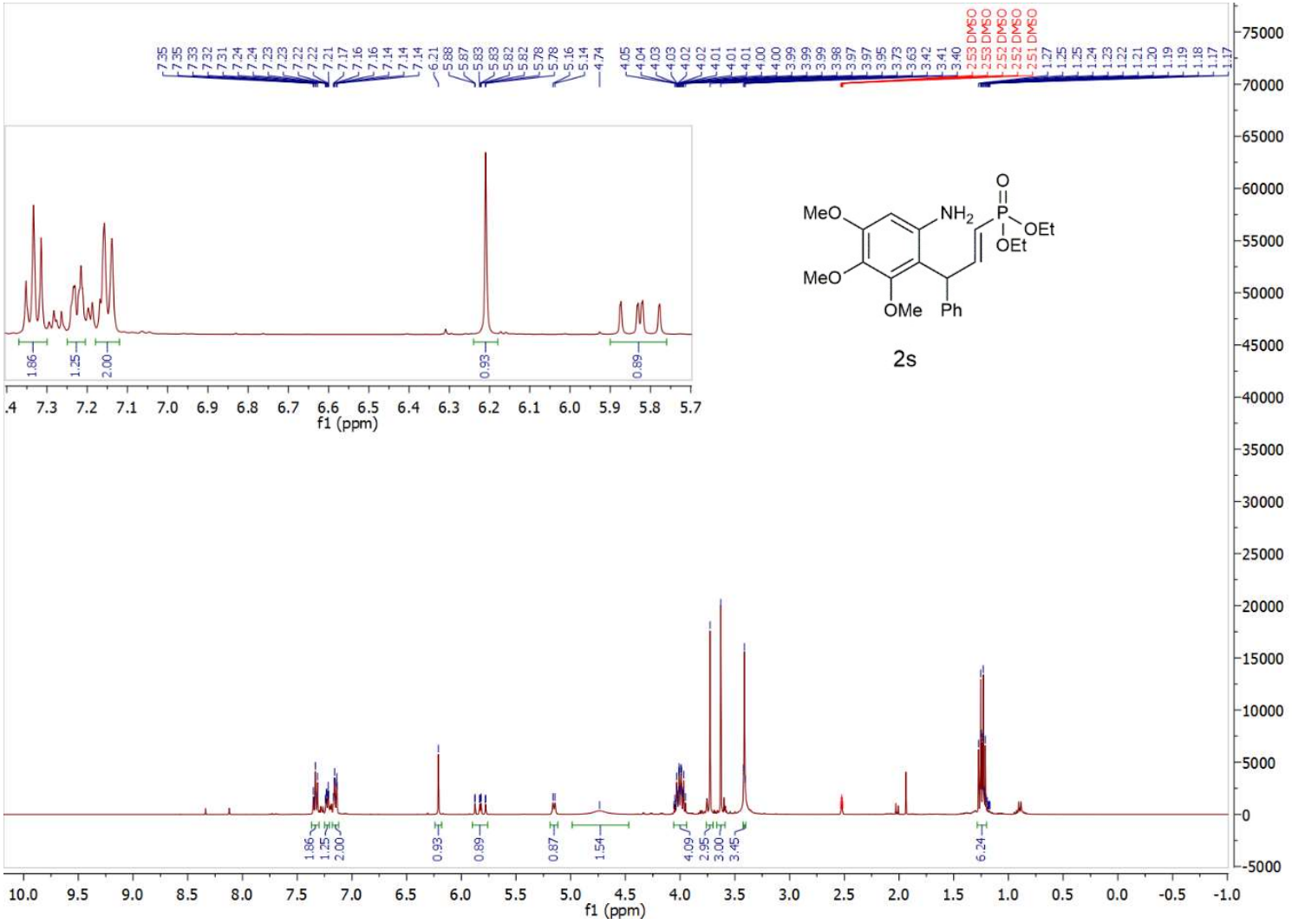


Figure S142: ^{1}H NMR Spectra of 2s

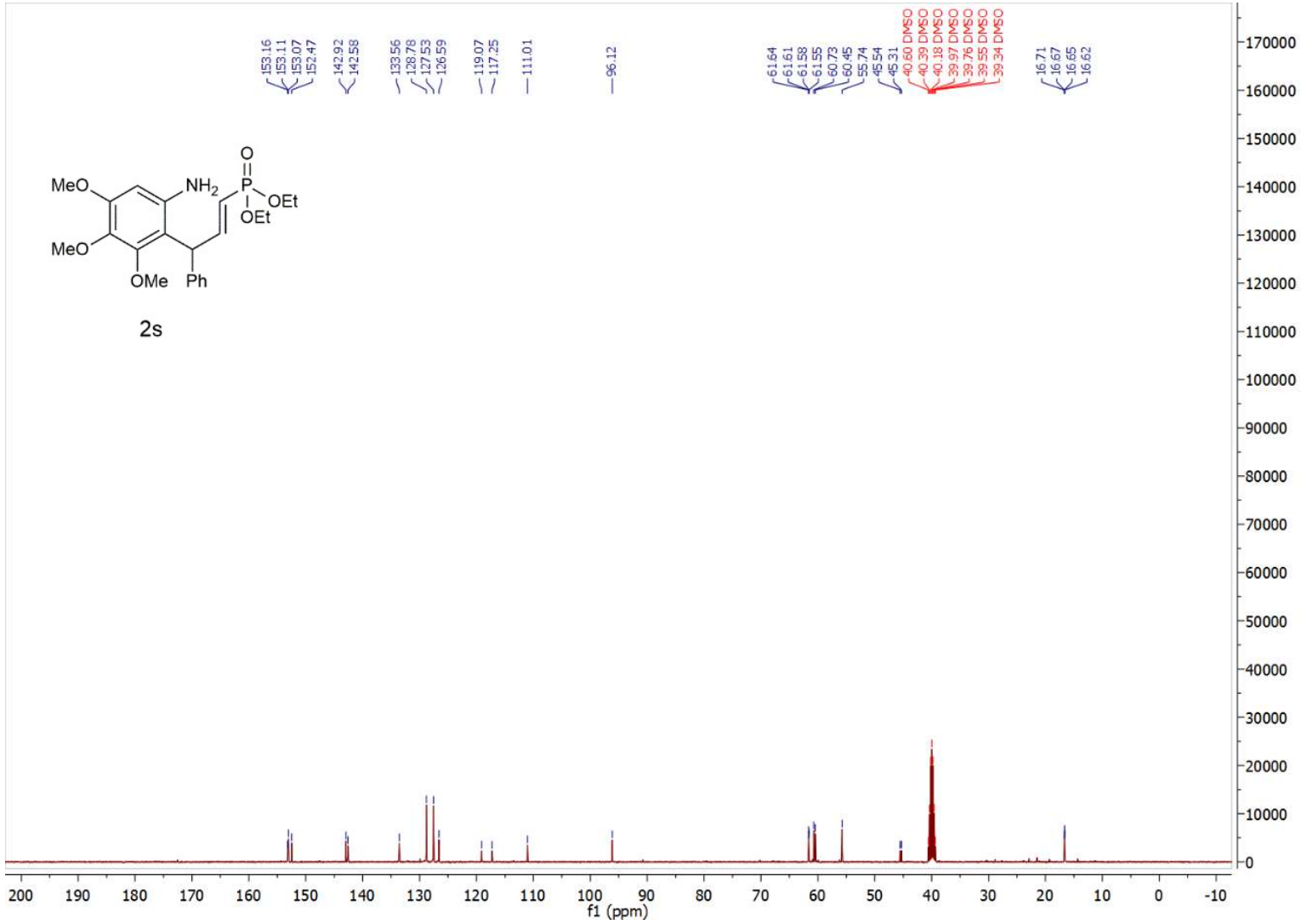


Figure S143: ^{13}C NMR Spectra of 2s

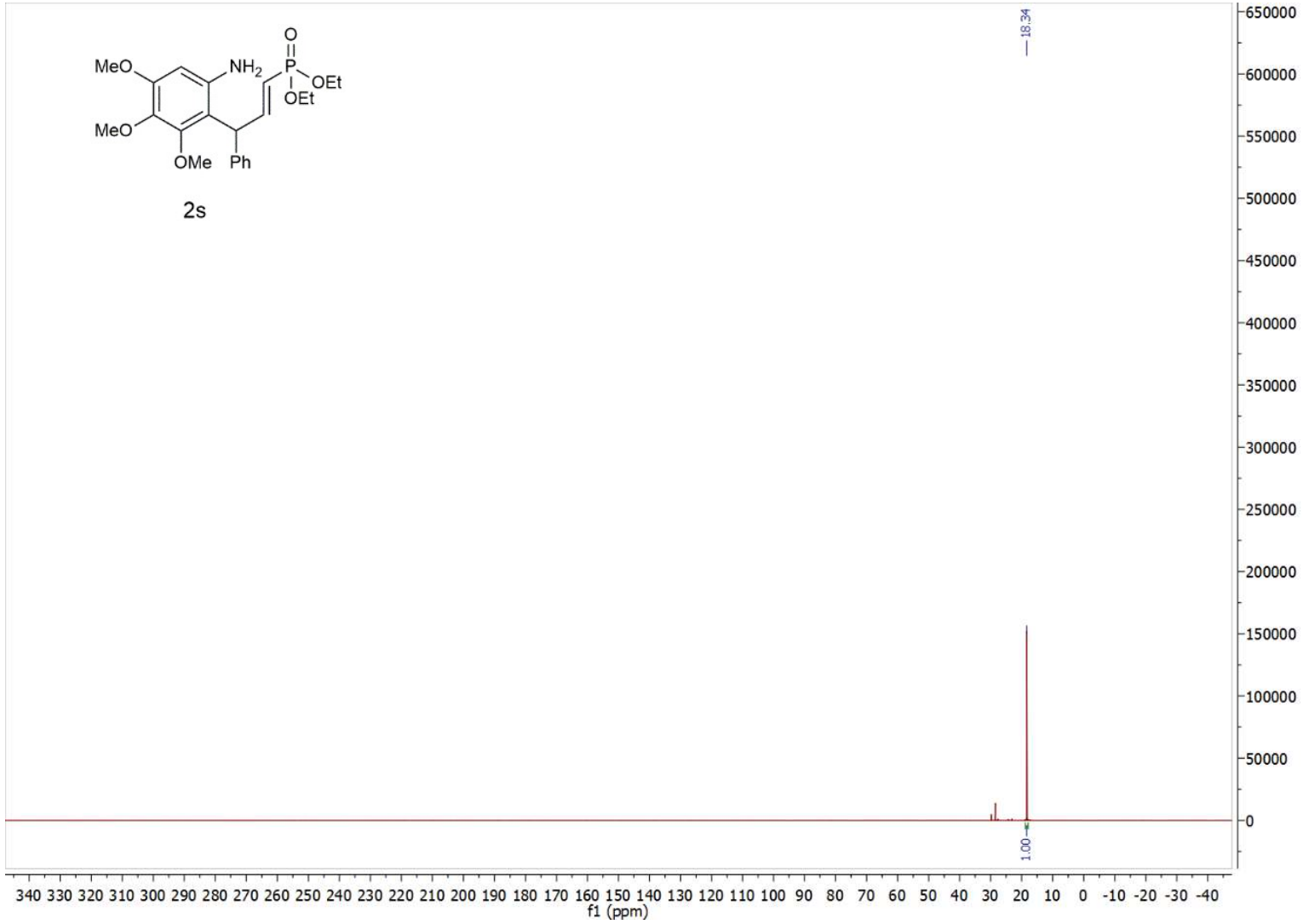


Figure S144: ^{31}P NMR Spectra of 2s

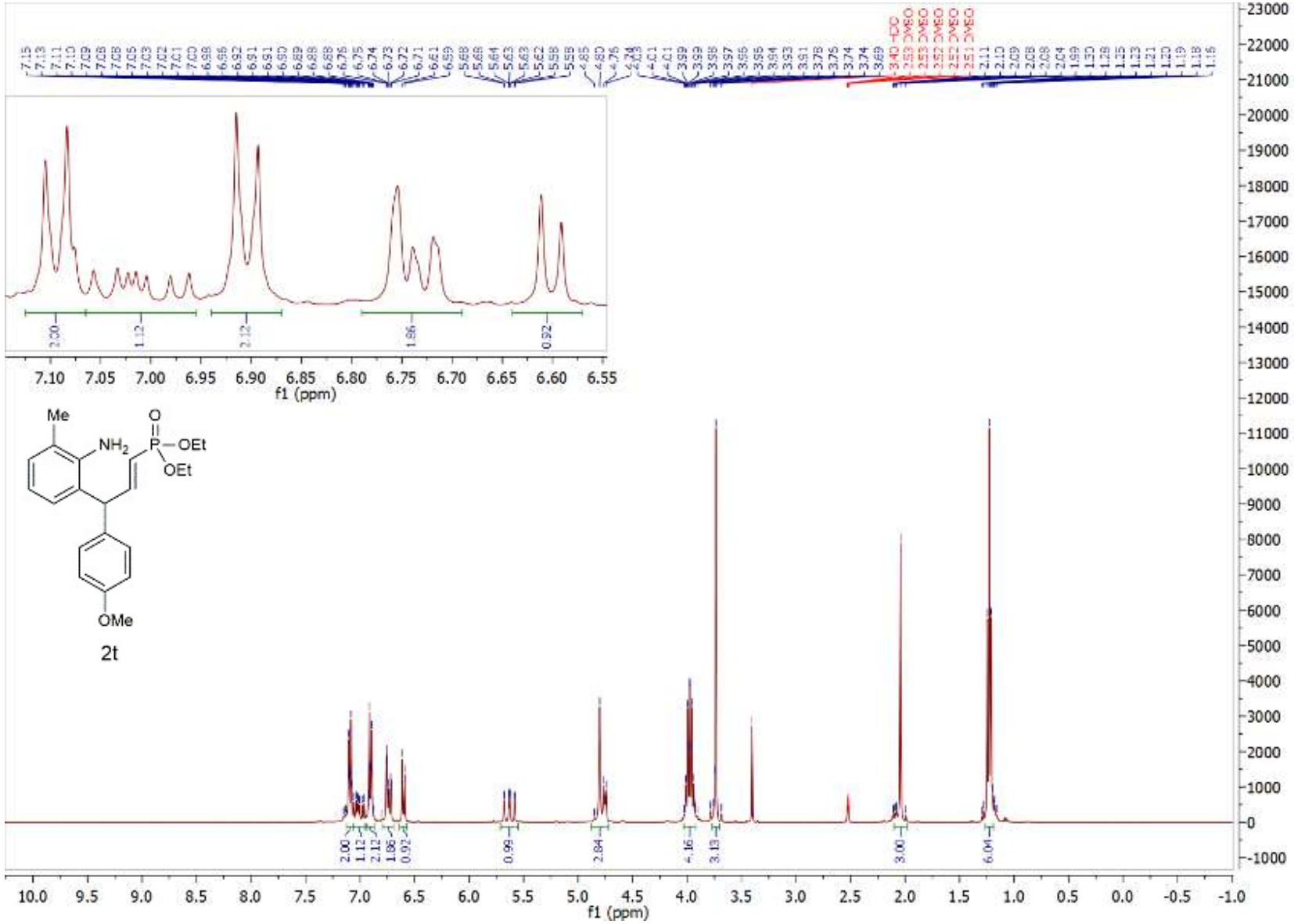


Figure S145: ^{1}H NMR Spectra of 2t

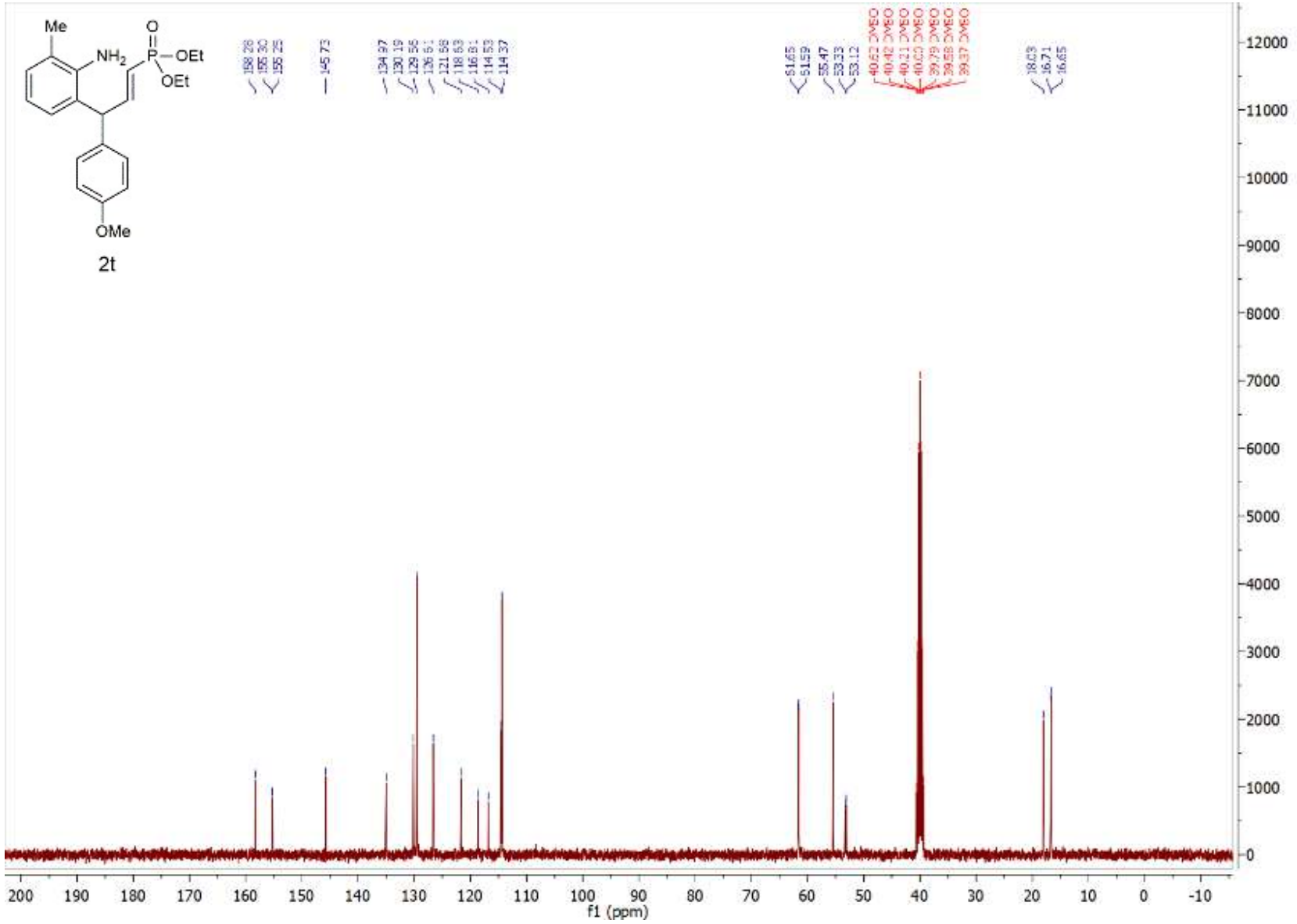


Figure S146: ^{13}C NMR Spectra of 2t

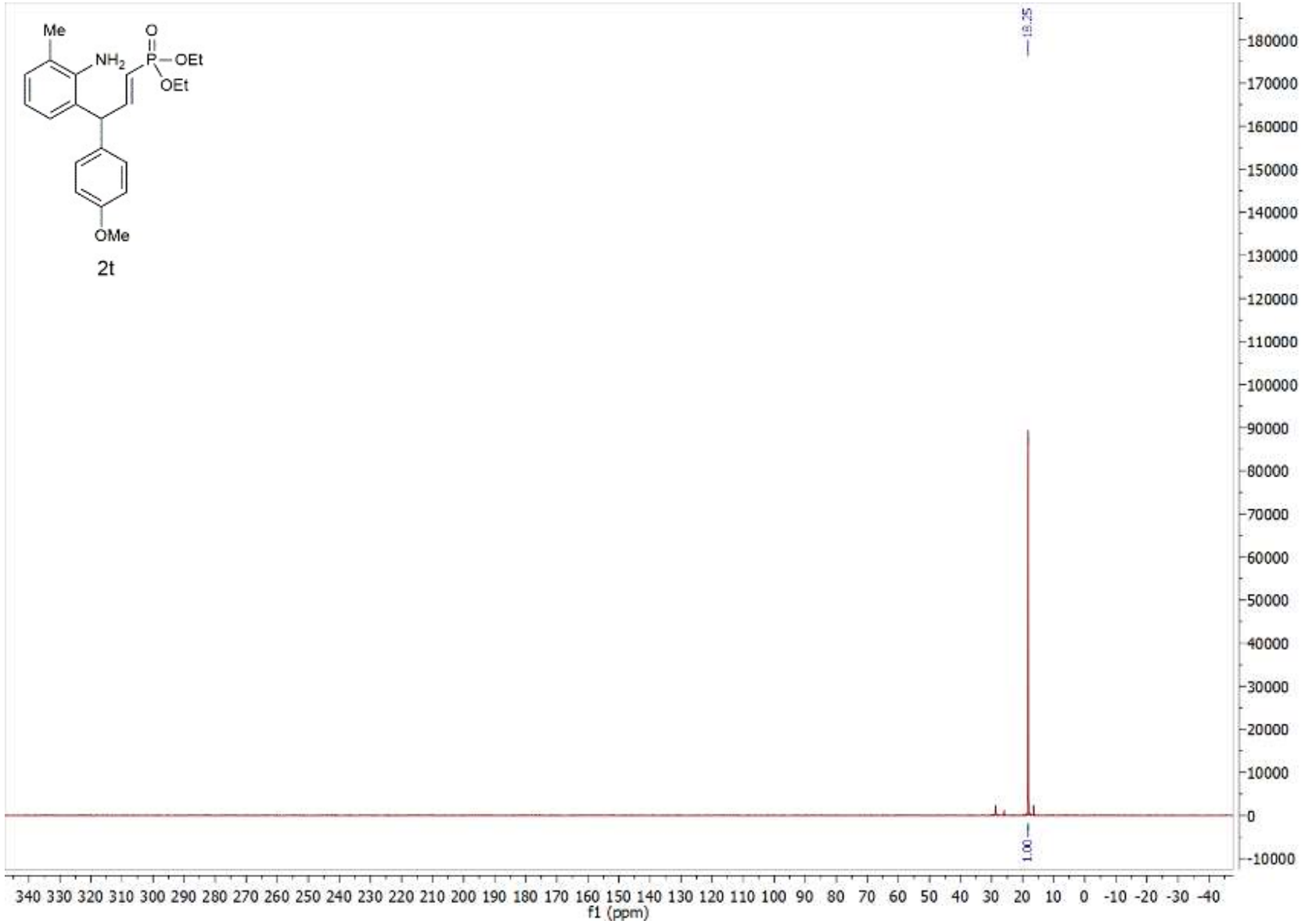


Figure S147: ^{31}P NMR Spectra of 2t

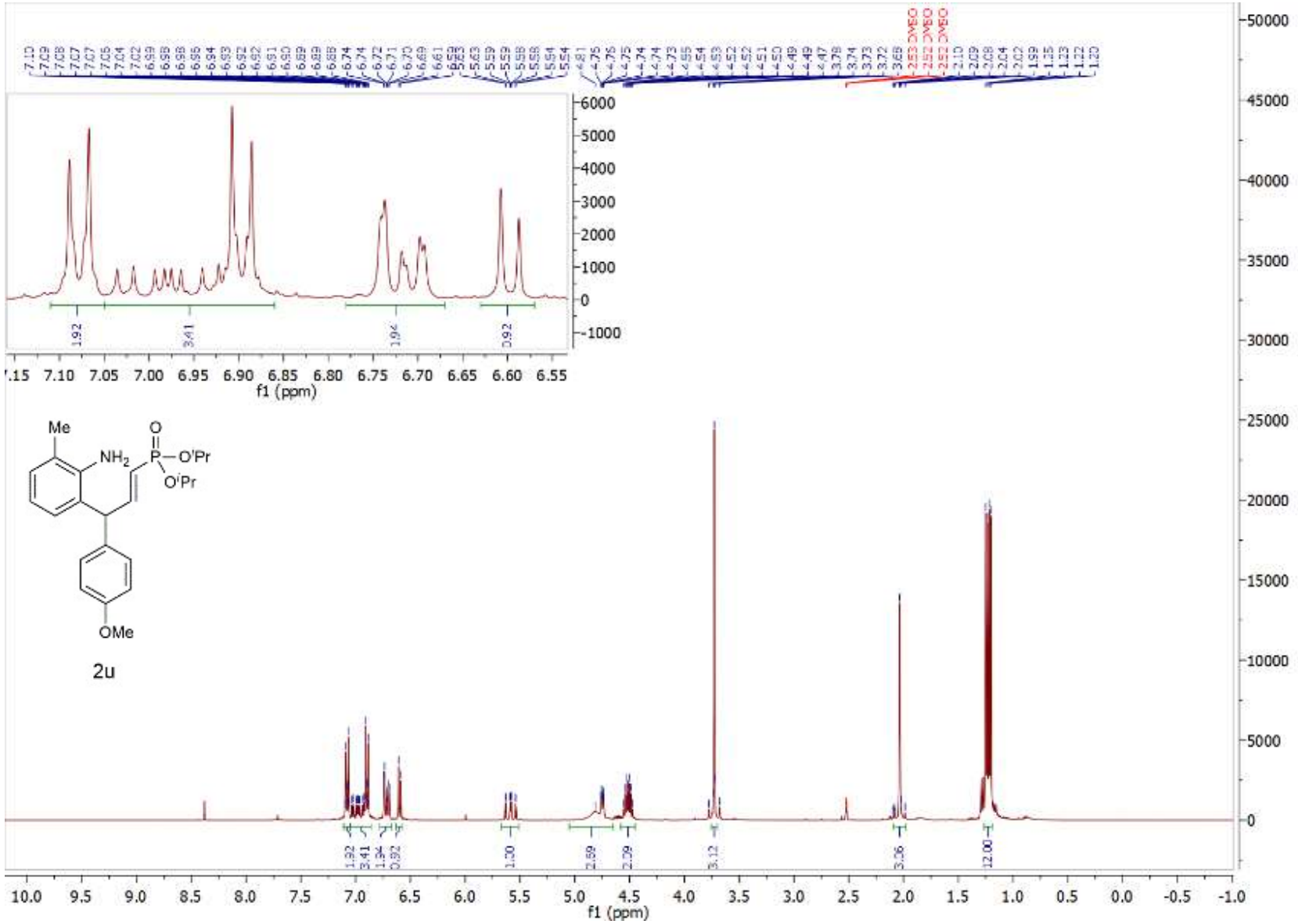


Figure S148: ^{1}H NMR Spectra of 2u

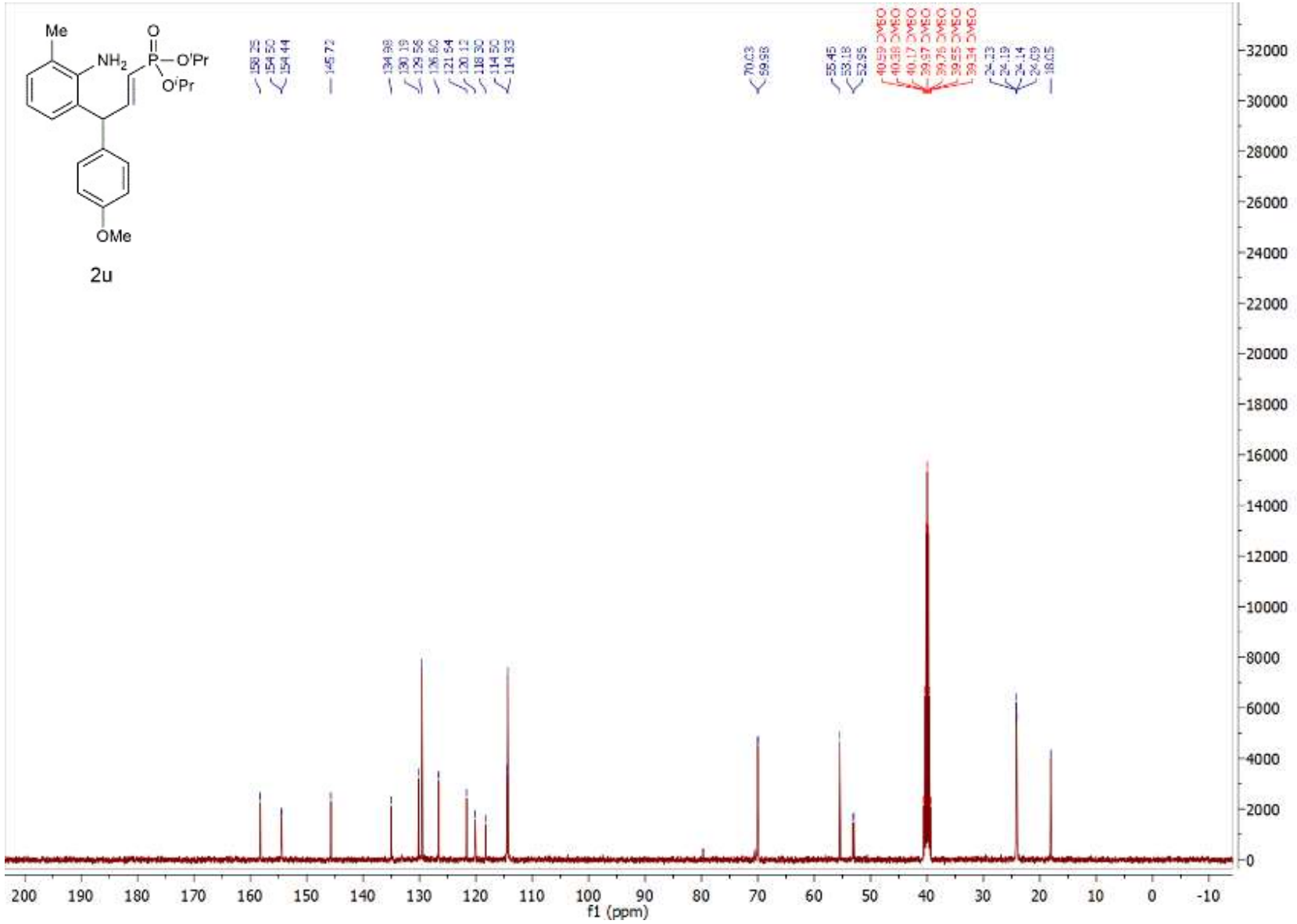


Figure S149: ^{13}C NMR Spectra of 2u

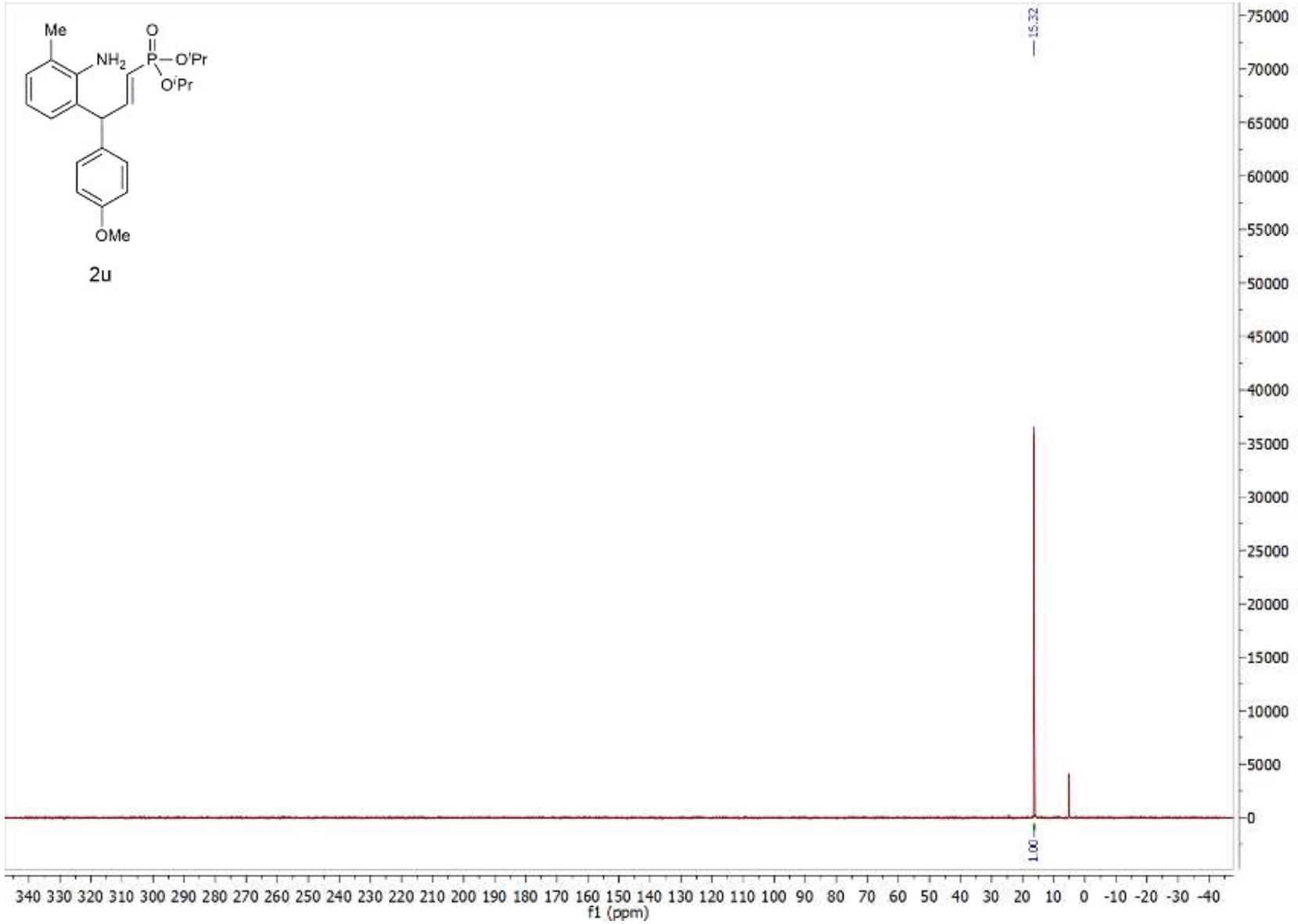


Figure S150: ^{31}P NMR Spectra of 2u

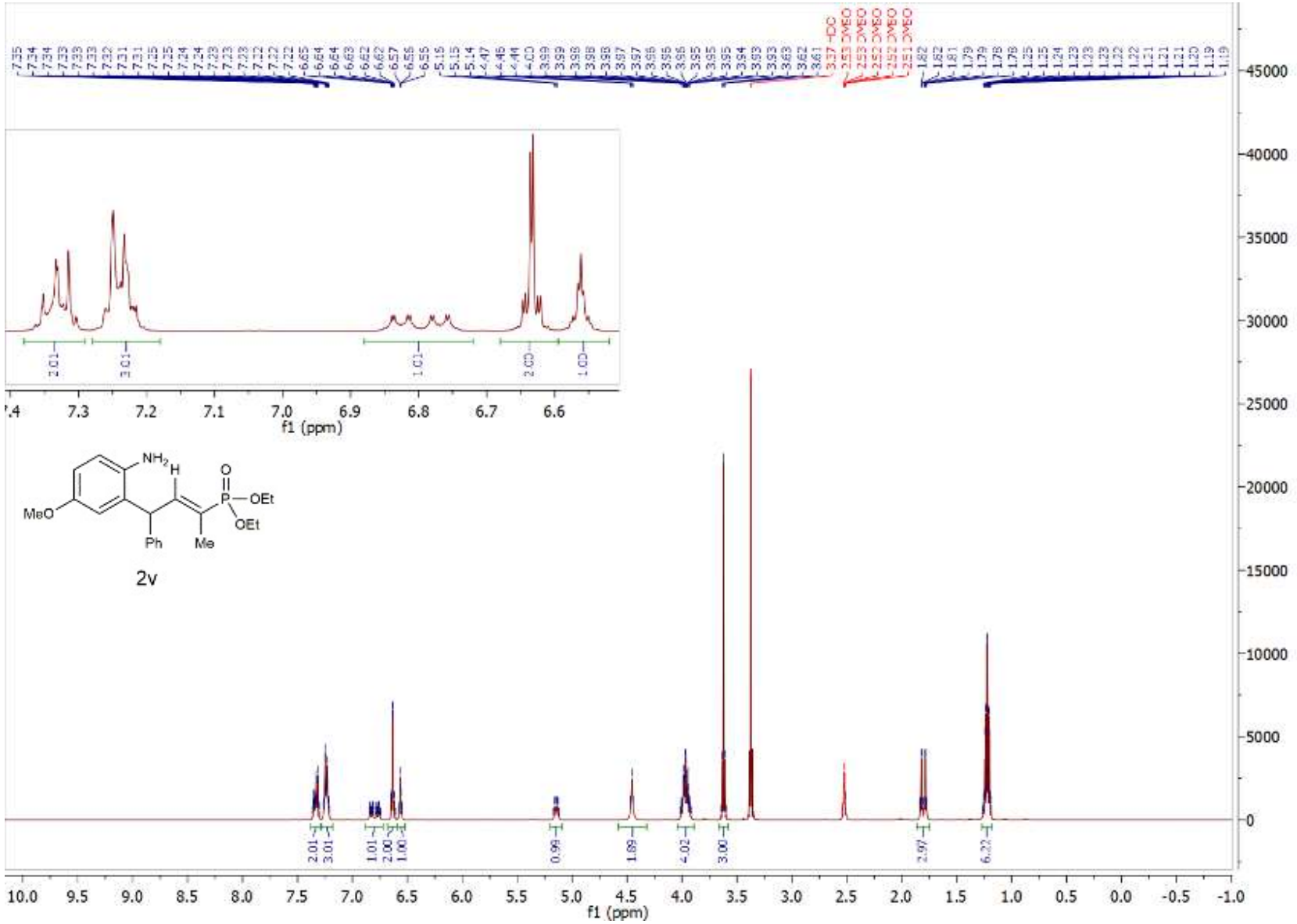


Figure S151: ^{1}H NMR Spectra of 2v

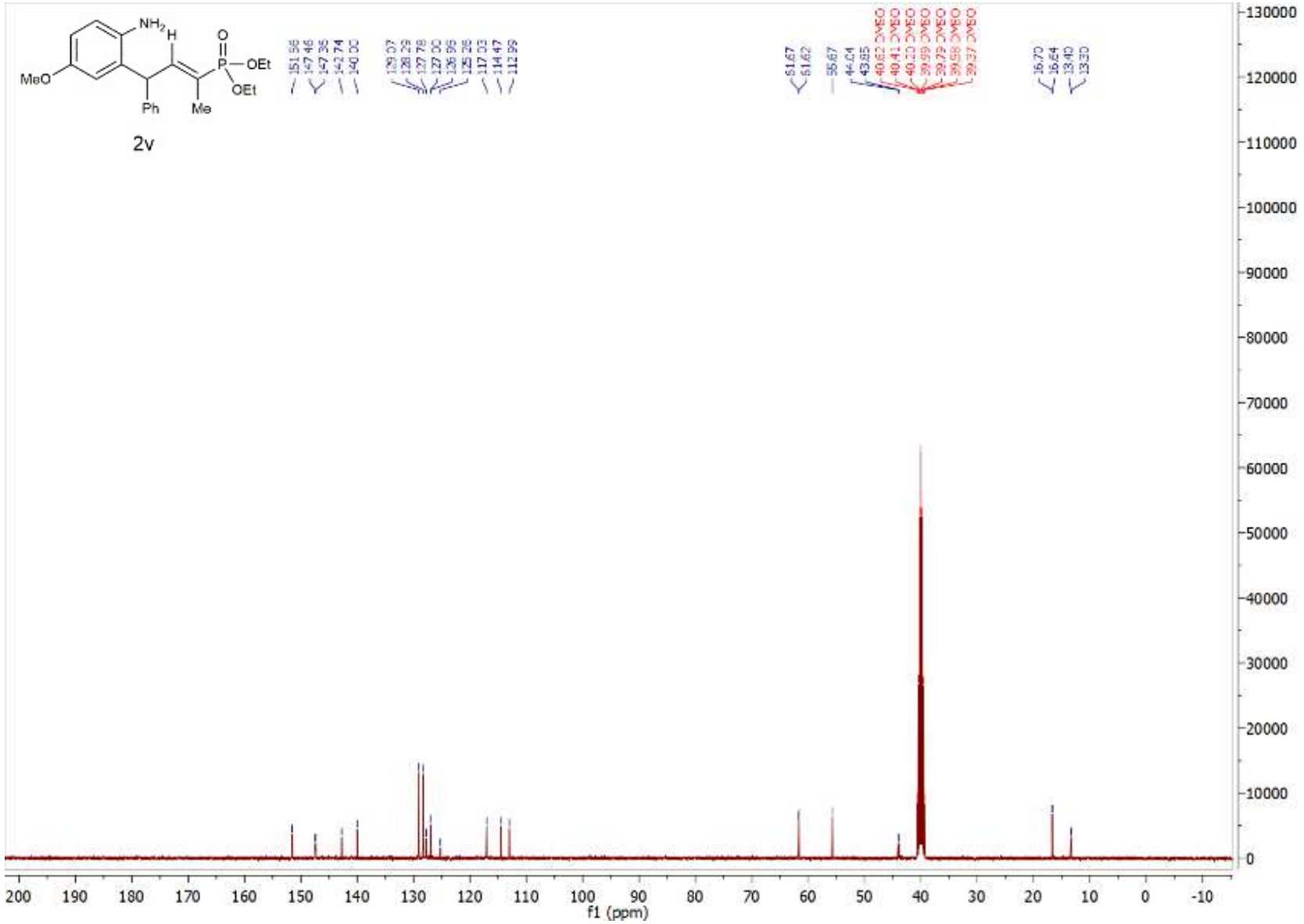


Figure S152: ^{13}C NMR Spectra of 2v

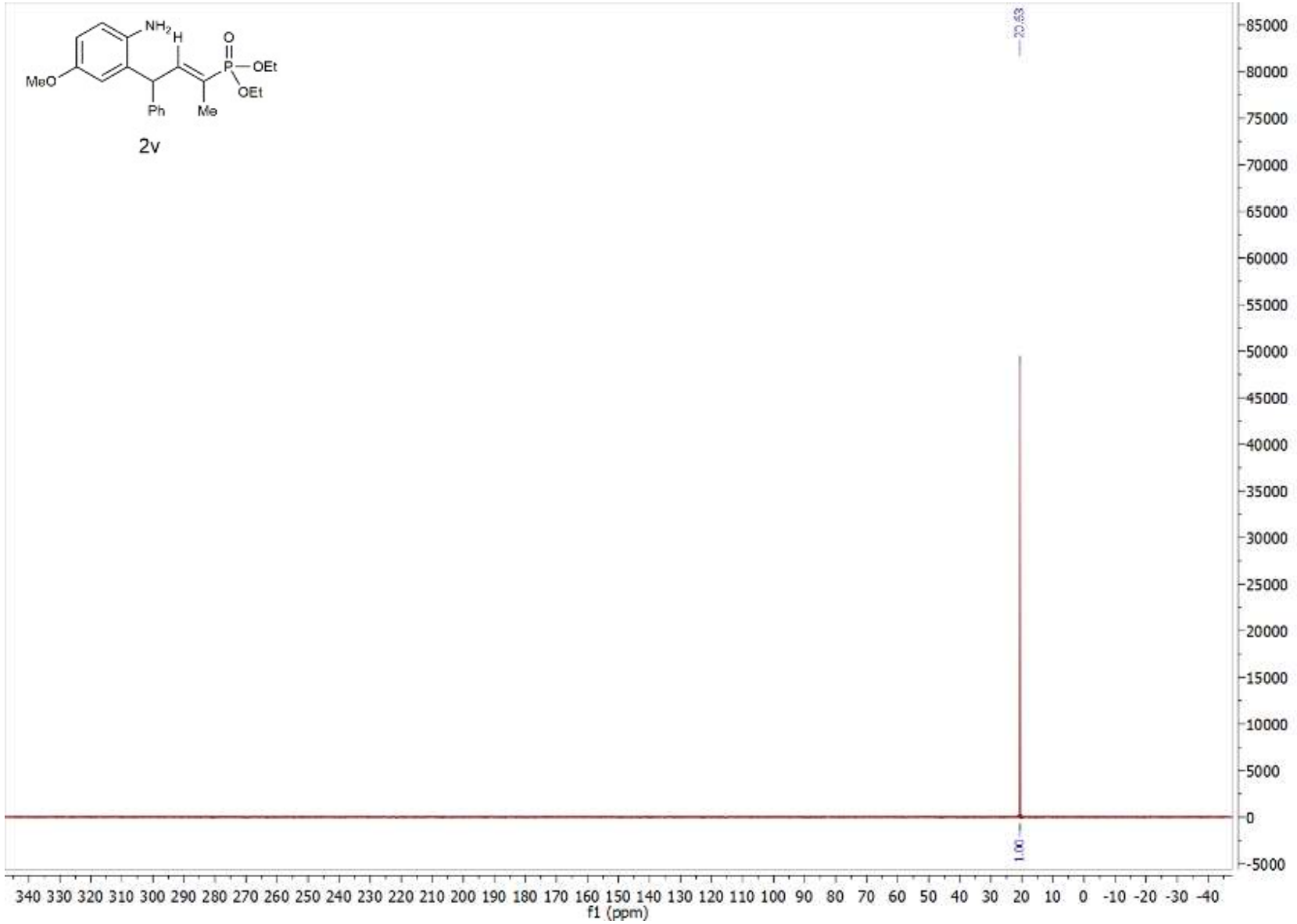


Figure S153: ^{31}P NMR Spectra of 2v

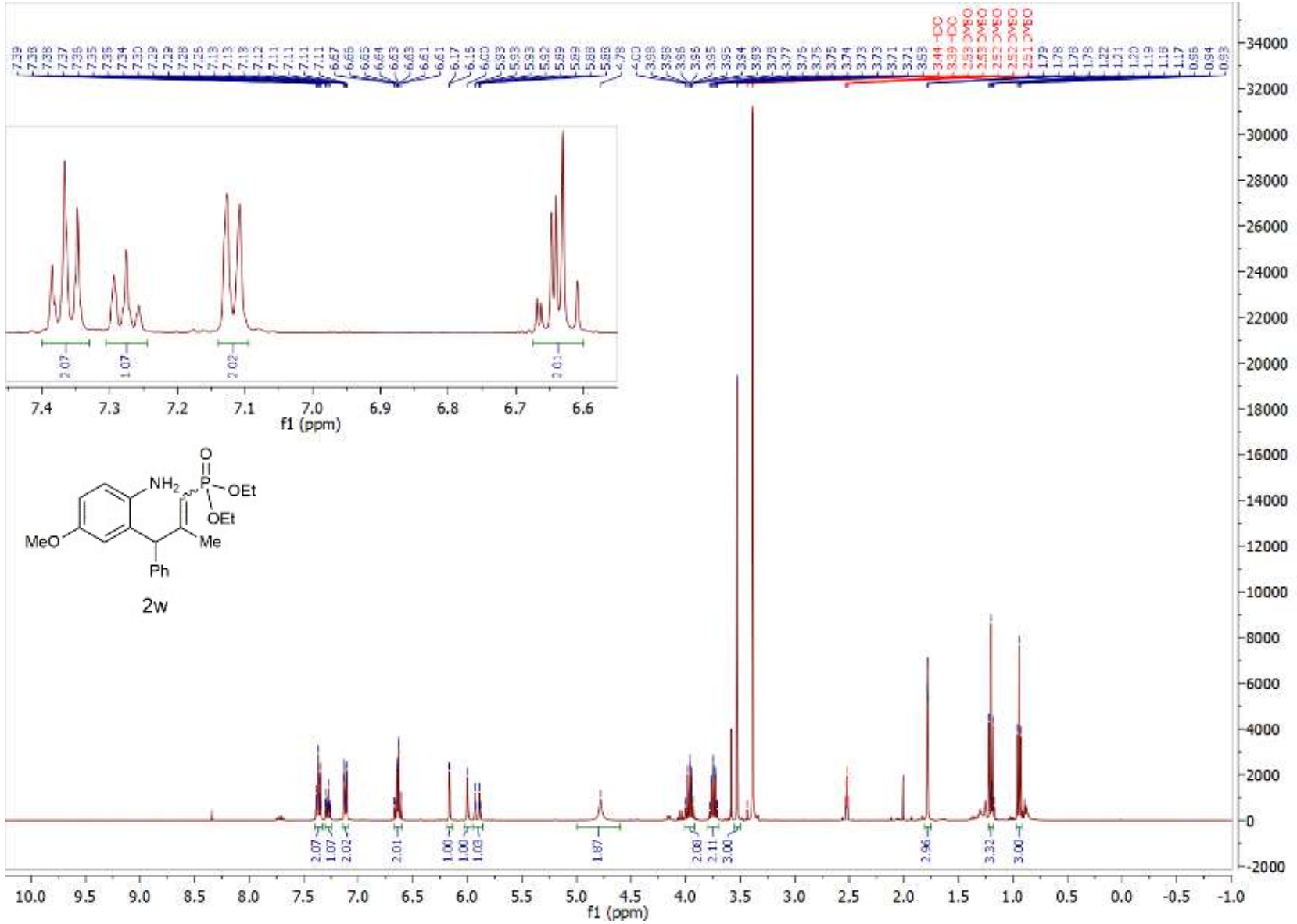


Figure S154: ^{1}H NMR Spectra of 2w

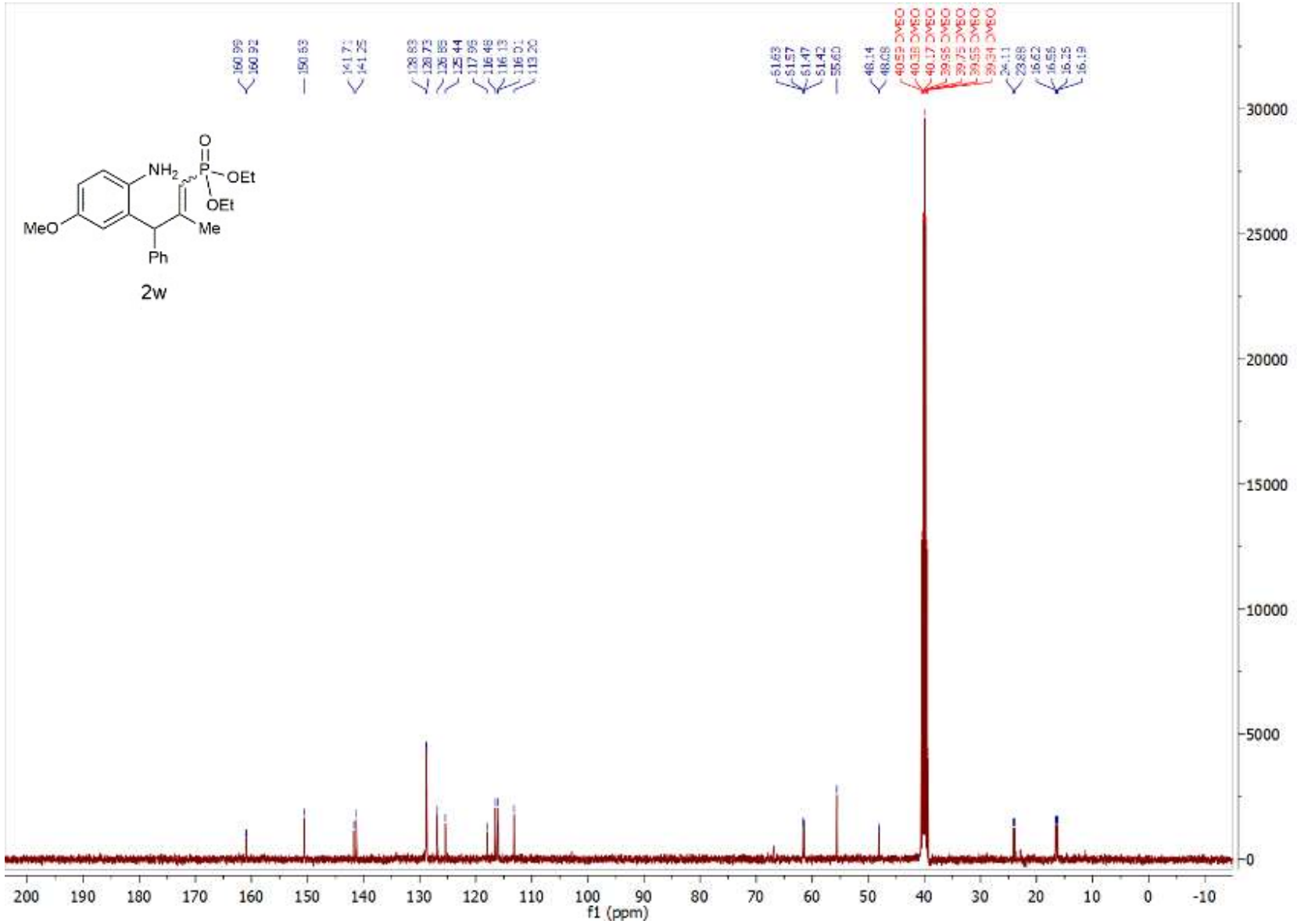


Figure S155: ^{13}C NMR Spectra of 2w

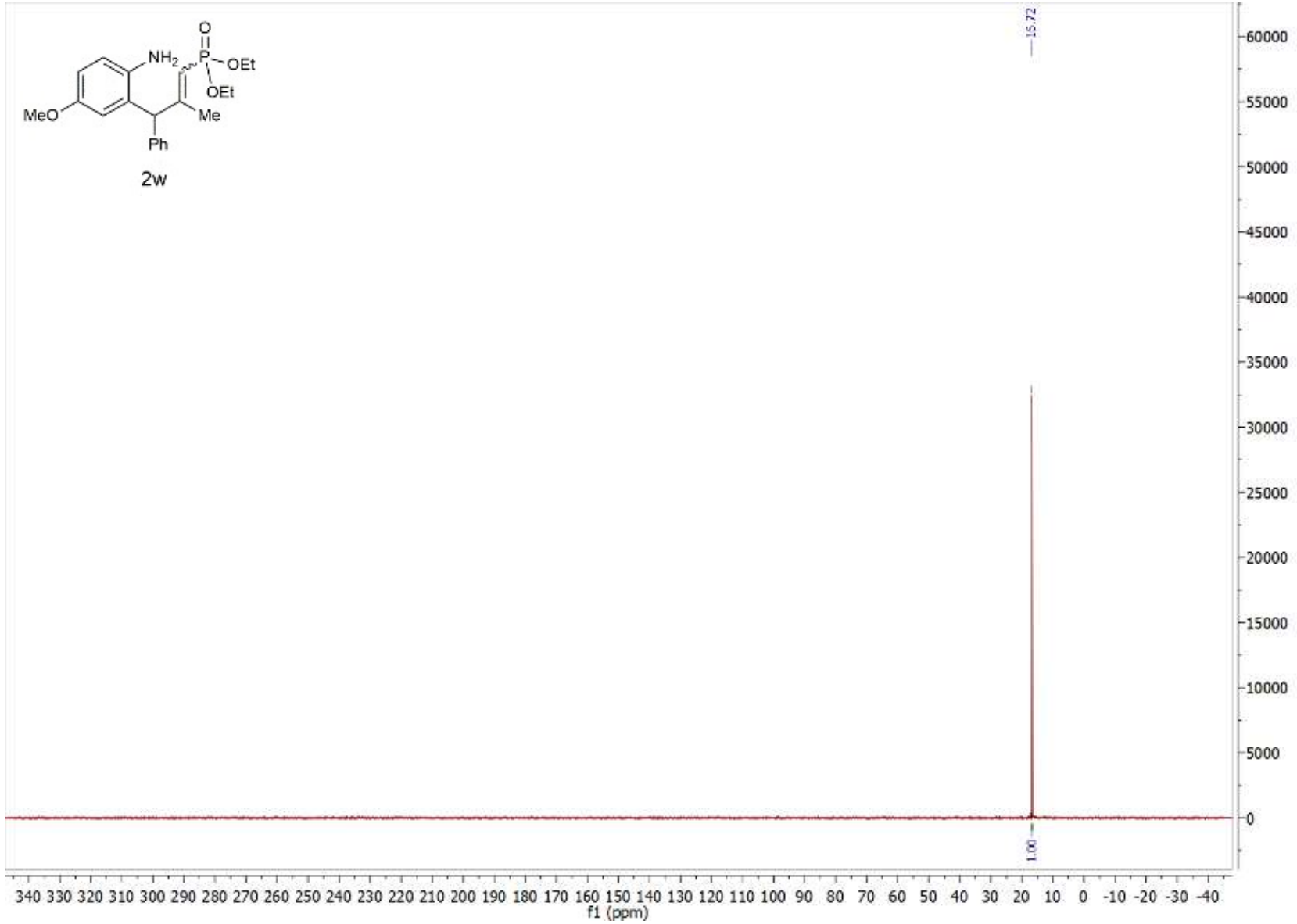


Figure S156: ^{31}P NMR Spectra of 2w

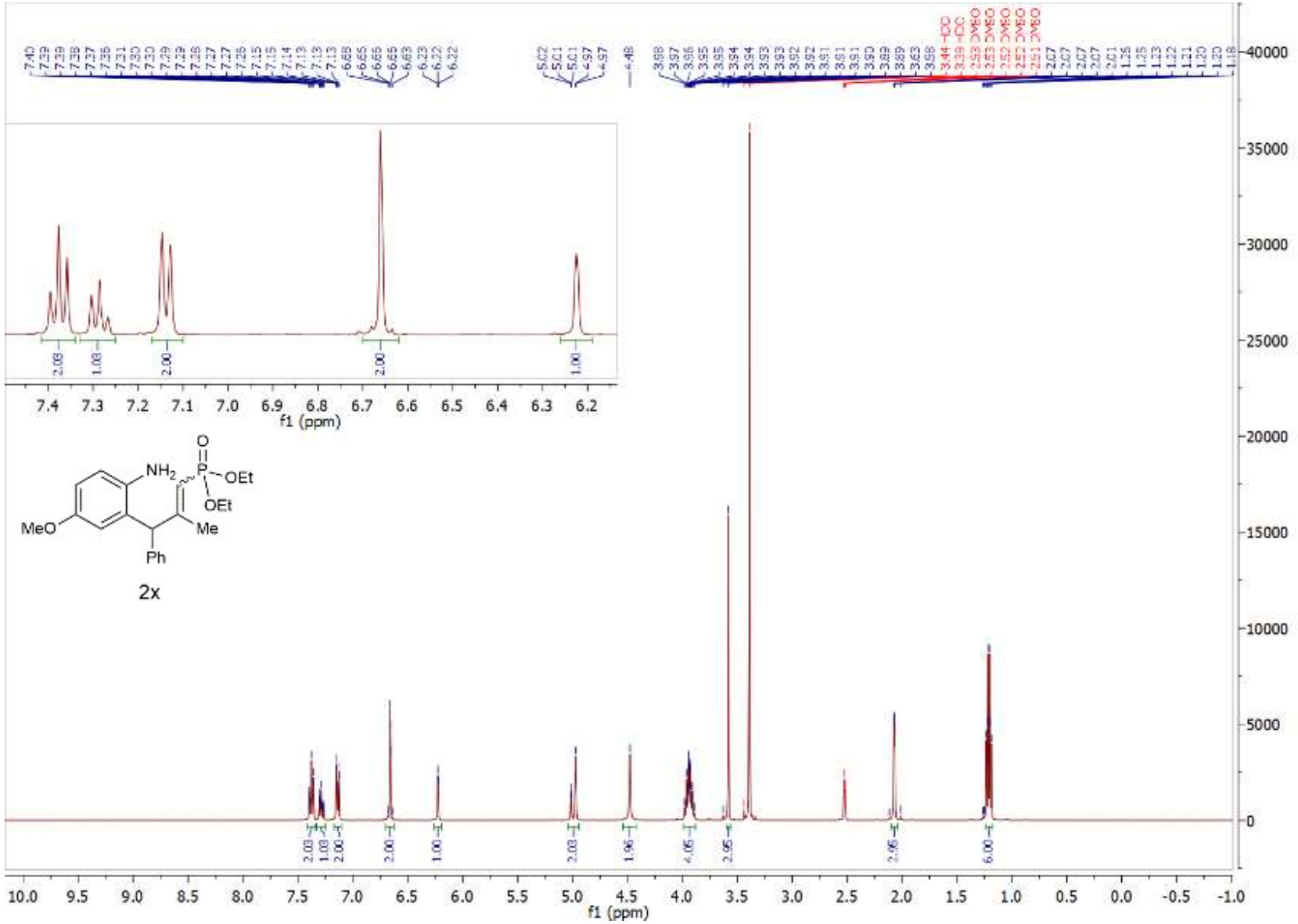


Figure S157: ^{1}H NMR Spectra of 2x

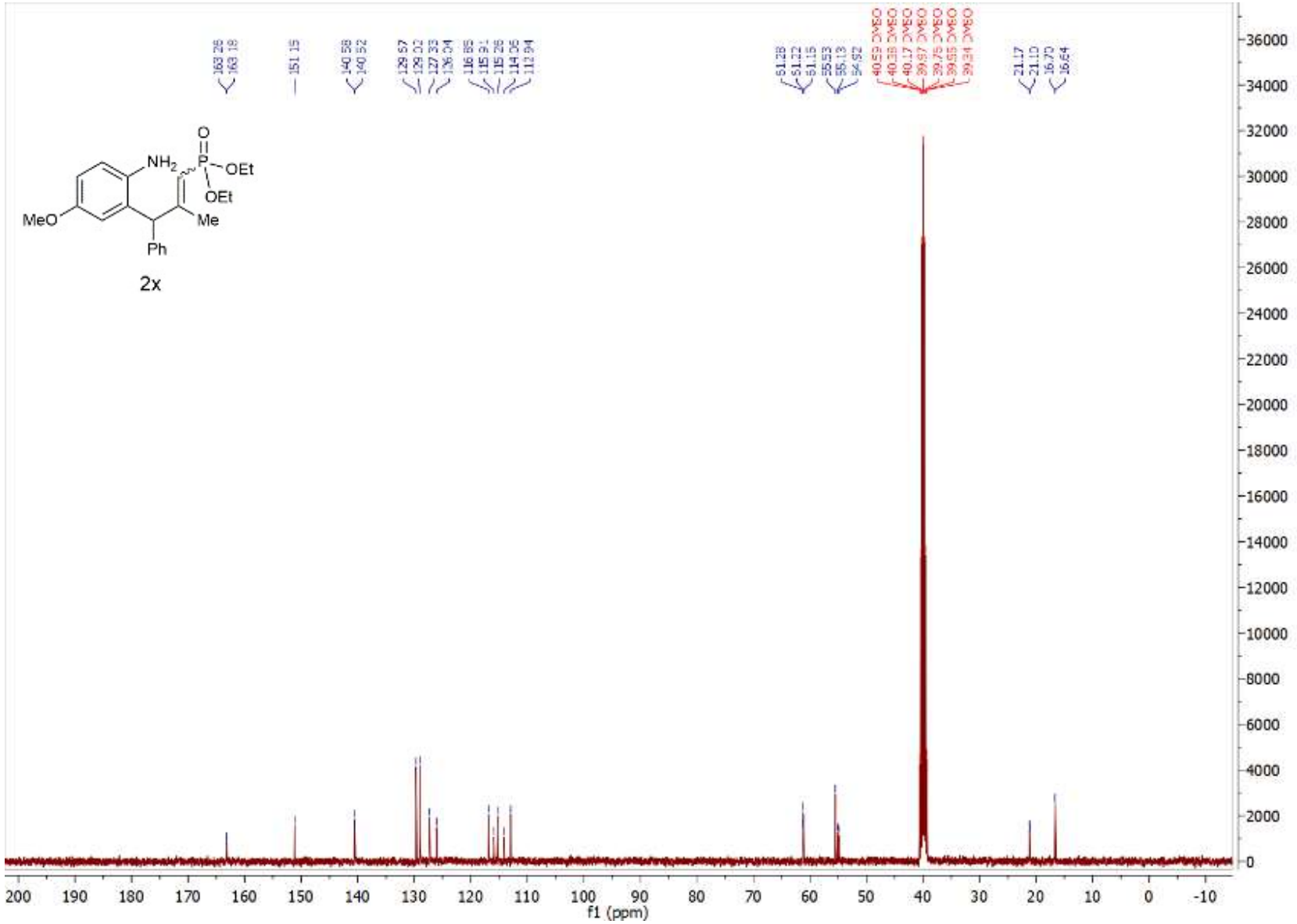


Figure S158: ^{13}C NMR Spectra of 2x

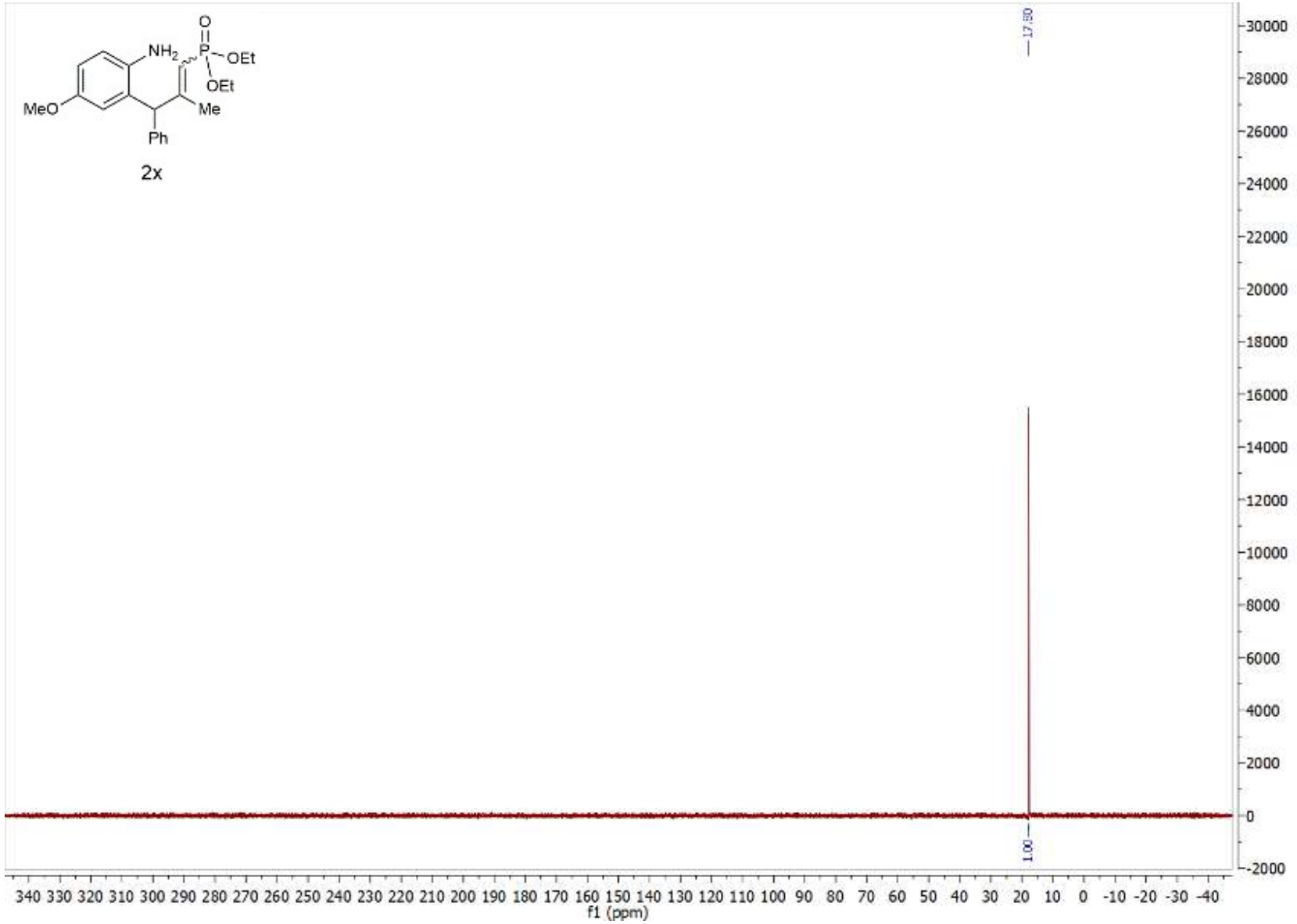


Figure S159: ^{31}P NMR Spectra of 2x

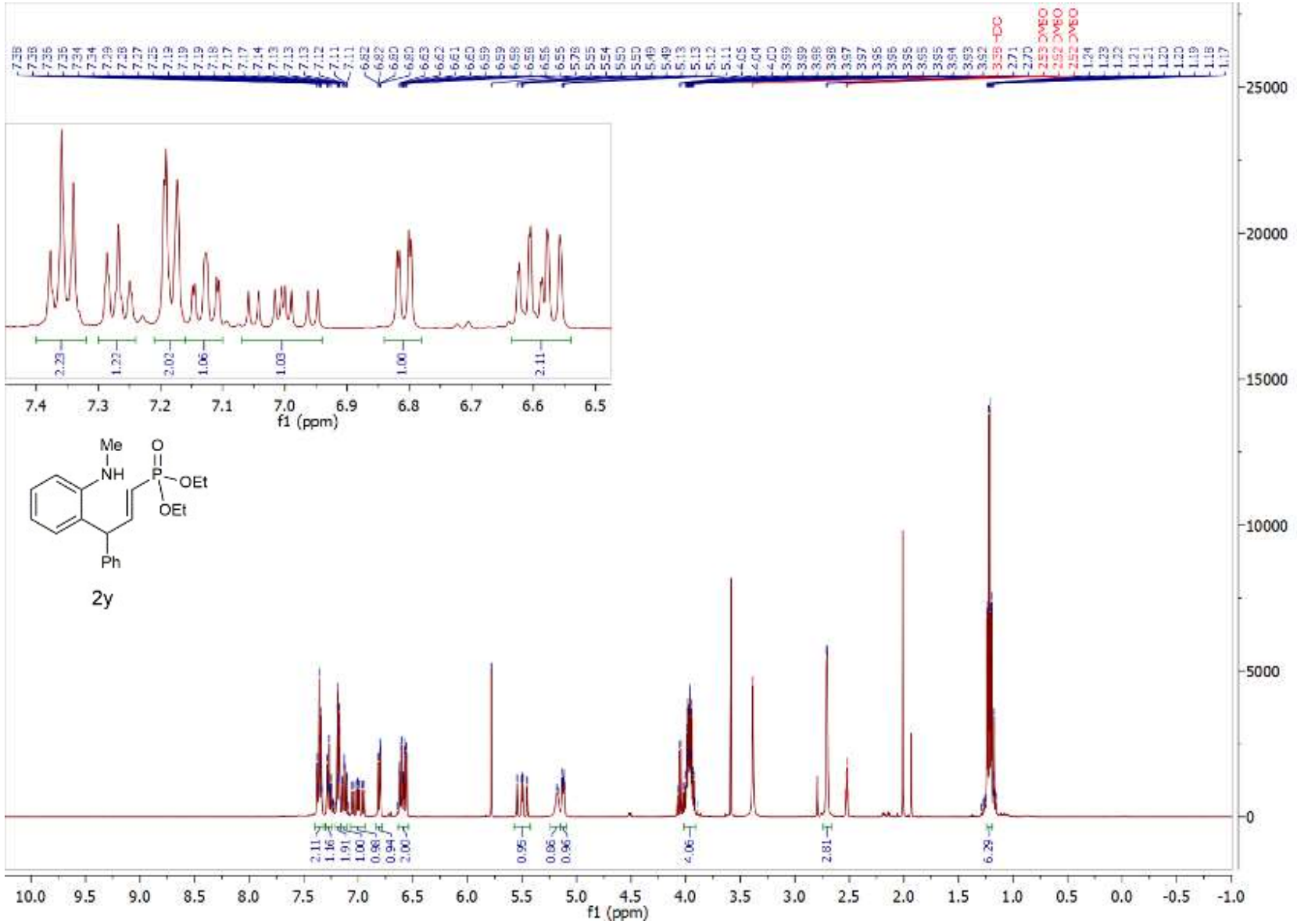


Figure S160: ^{1}H NMR Spectra of 2y

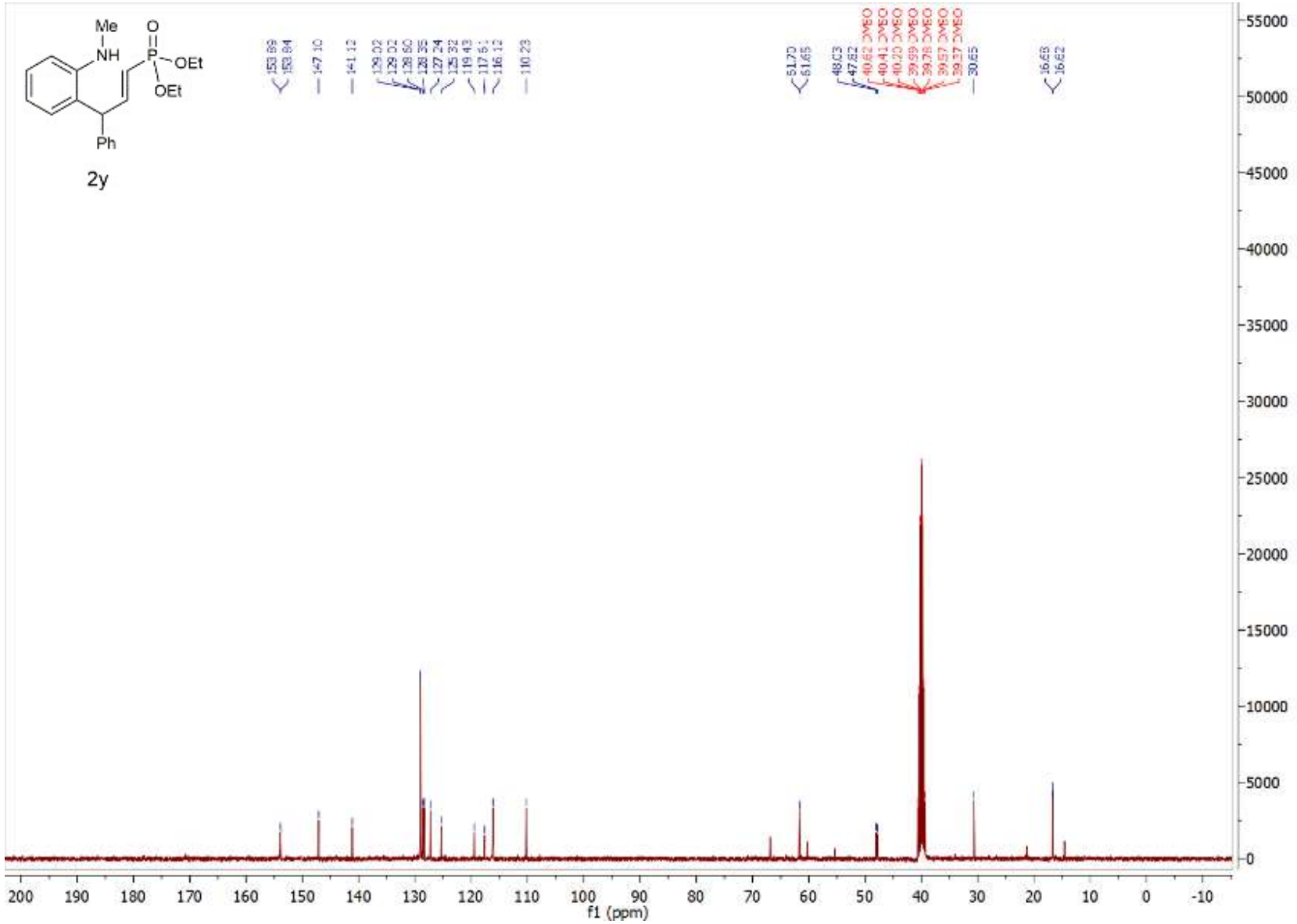


Figure S161: ^{13}C NMR Spectra of 2y

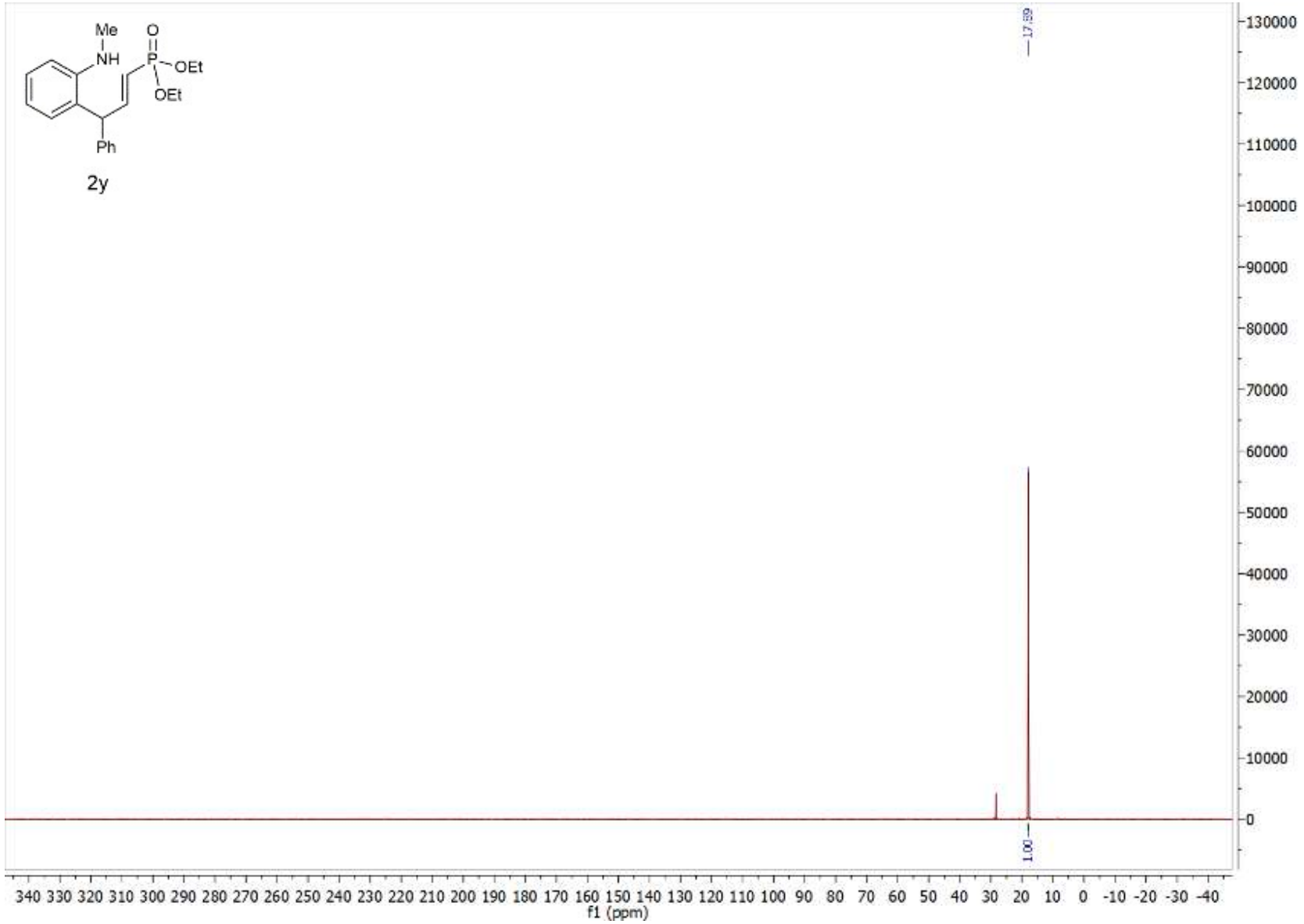


Figure S162: ^{31}P NMR Spectra of 2y

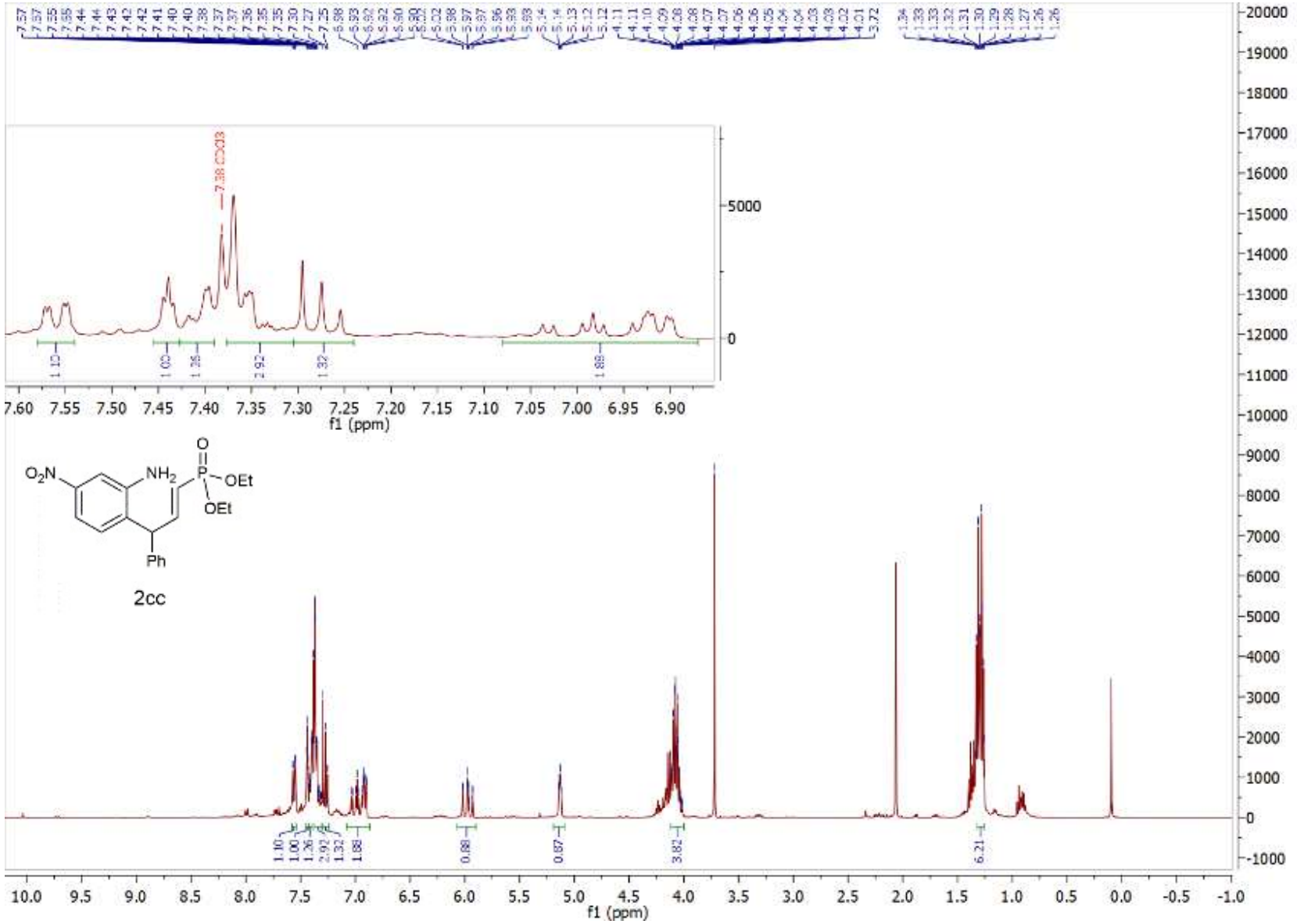


Figure S163: ^{1}H NMR Spectra of 2cc

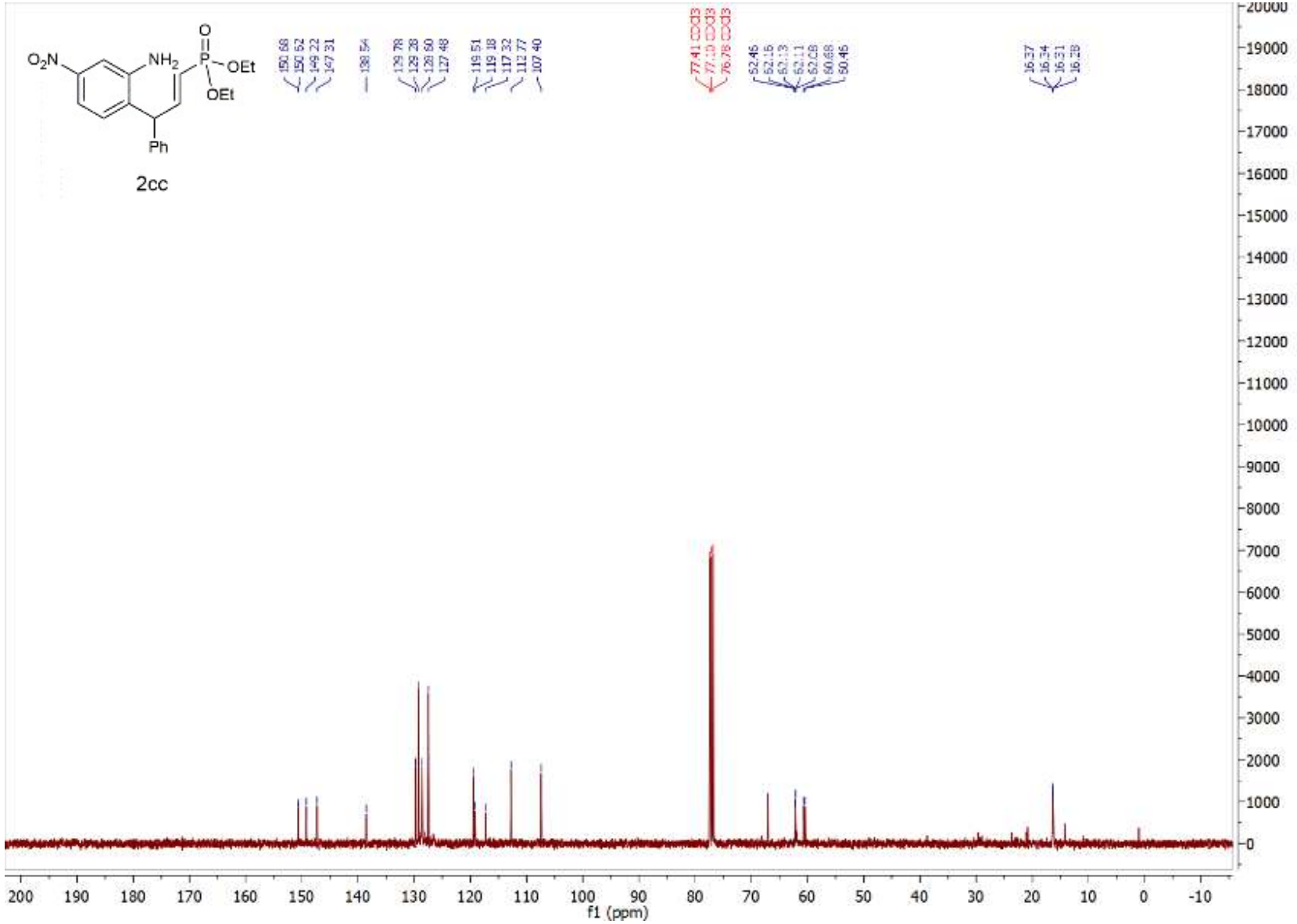


Figure S164: ^{13}C NMR Spectra of 2cc

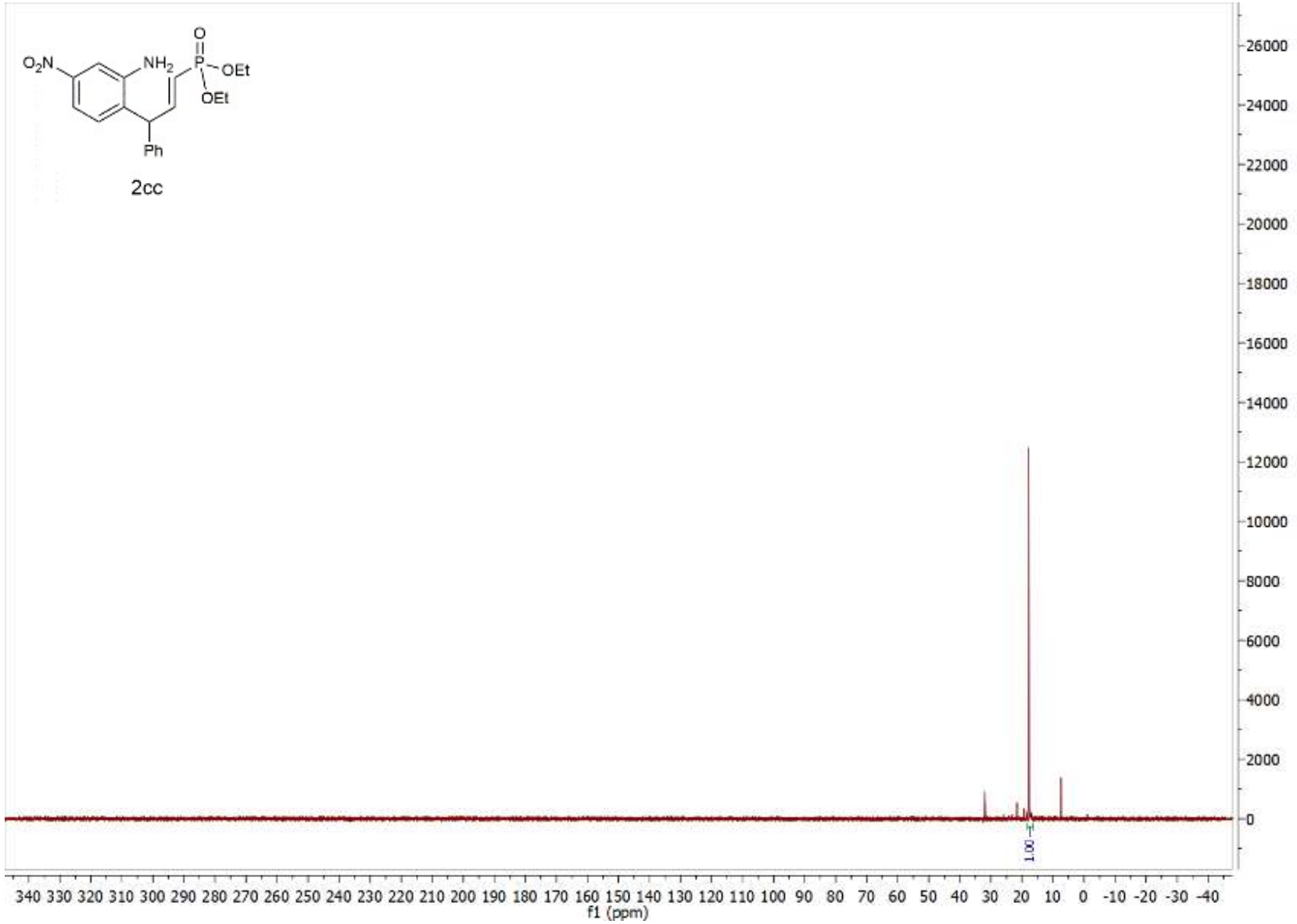


Figure S165: ^{31}P NMR Spectra of 2cc

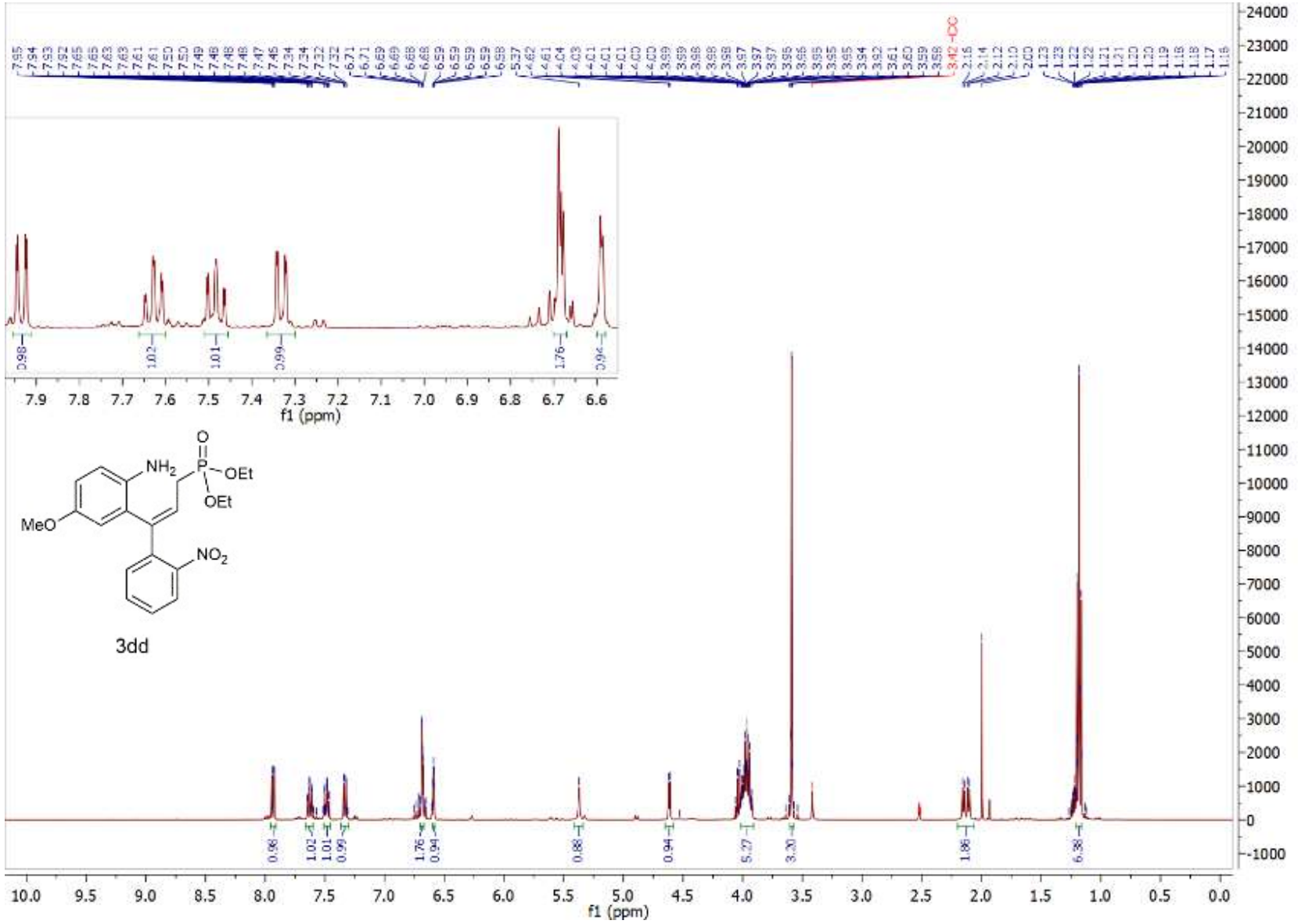


Figure S166: ^{1}H NMR Spectra of 3dd

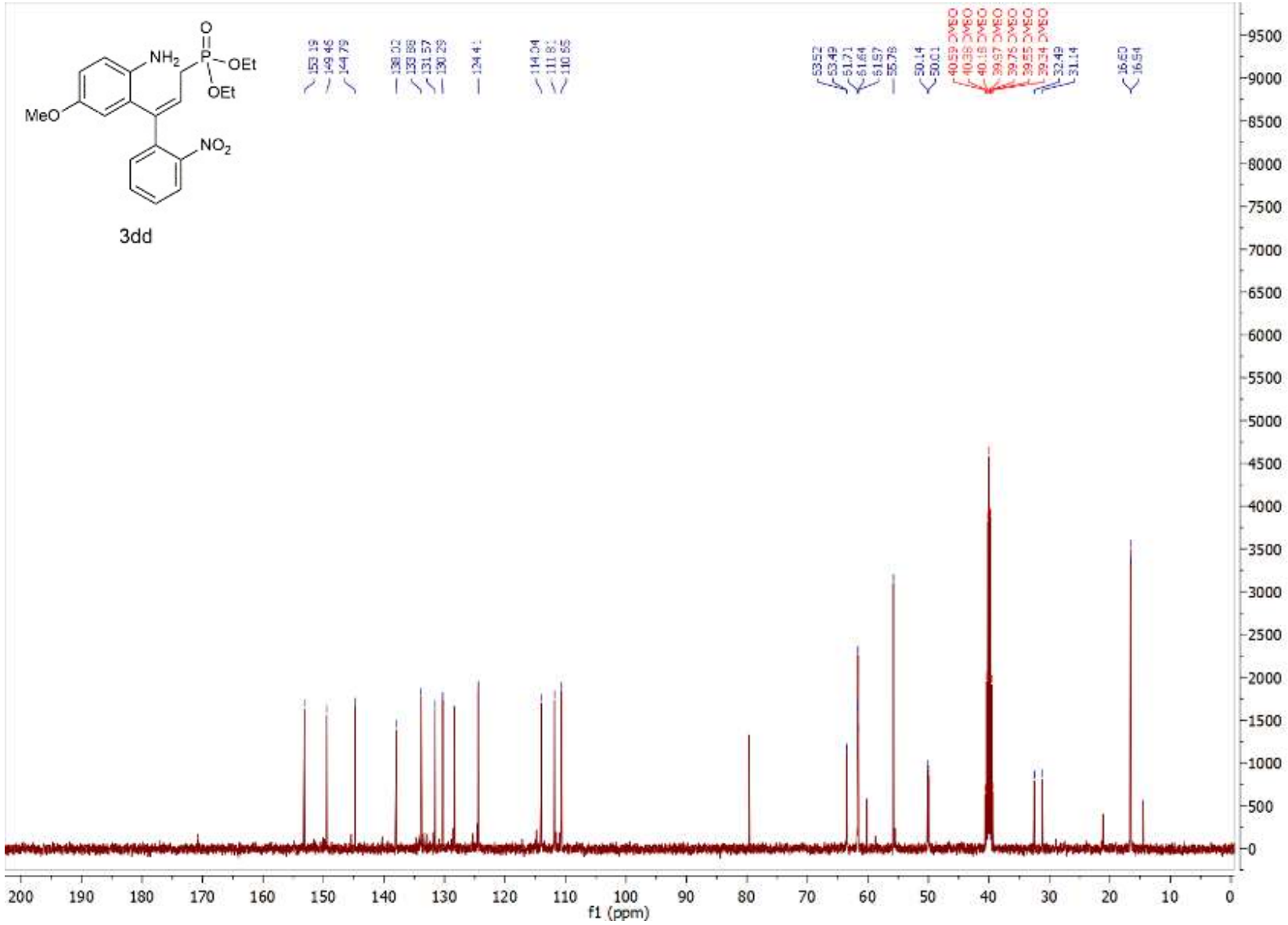


Figure S167: ^{13}C NMR Spectra of 3dd

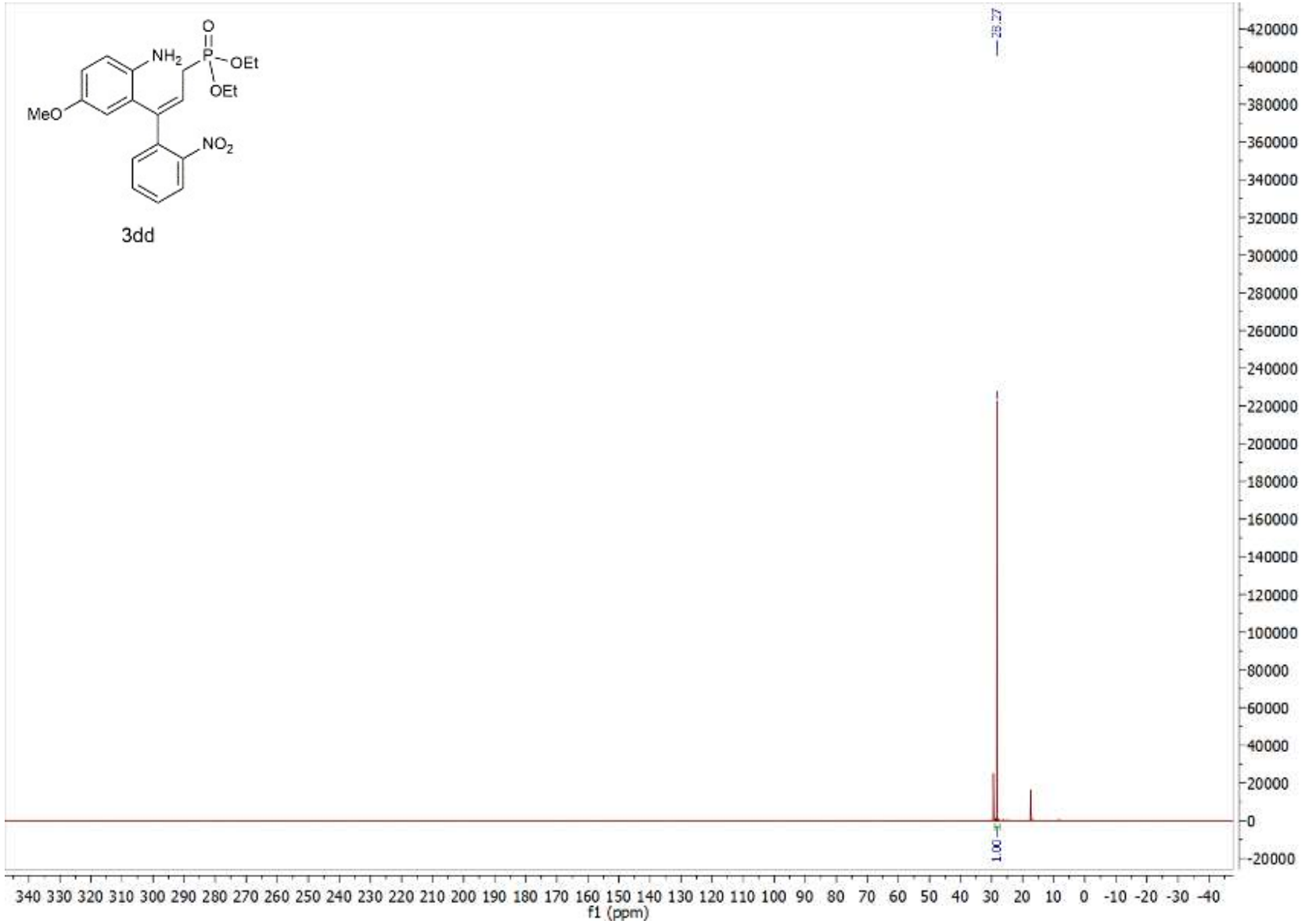


Figure S168: ^{31}P NMR Spectra of 3dd

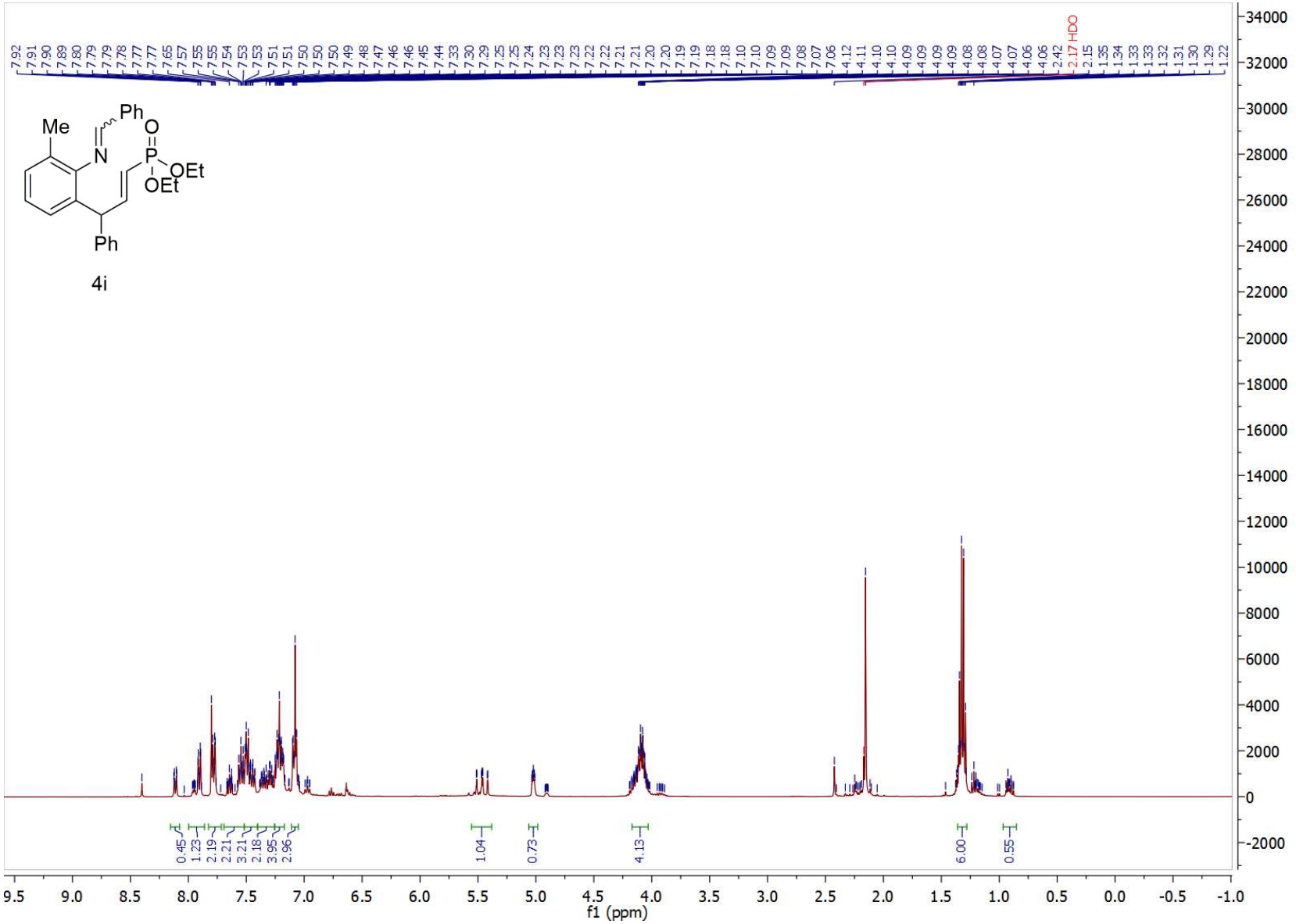


Figure S169: ^{1}H NMR Spectra of the reaction mixture of 4i

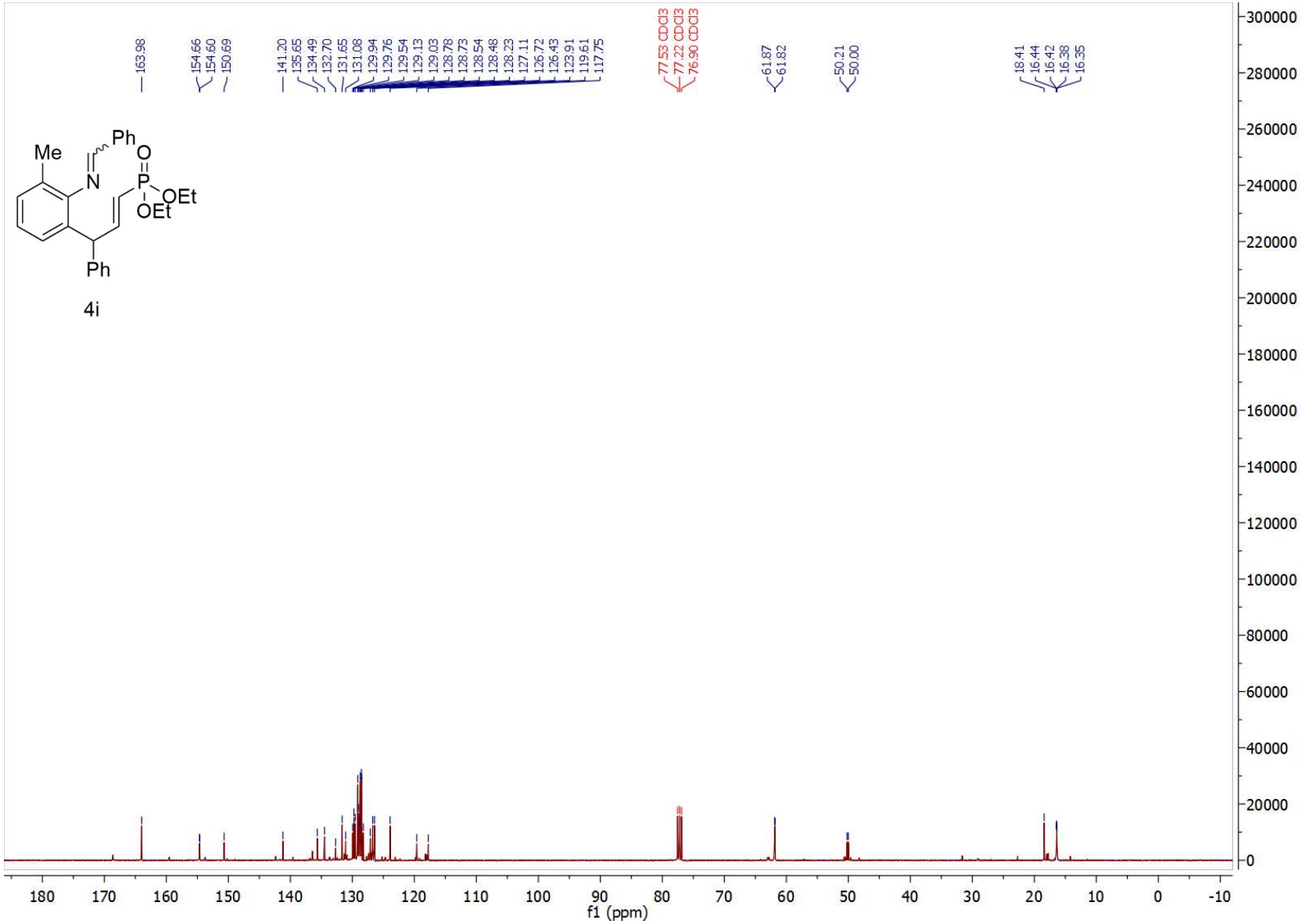


Figure S170: ^{13}C NMR Spectra of the reaction mixture of 4i

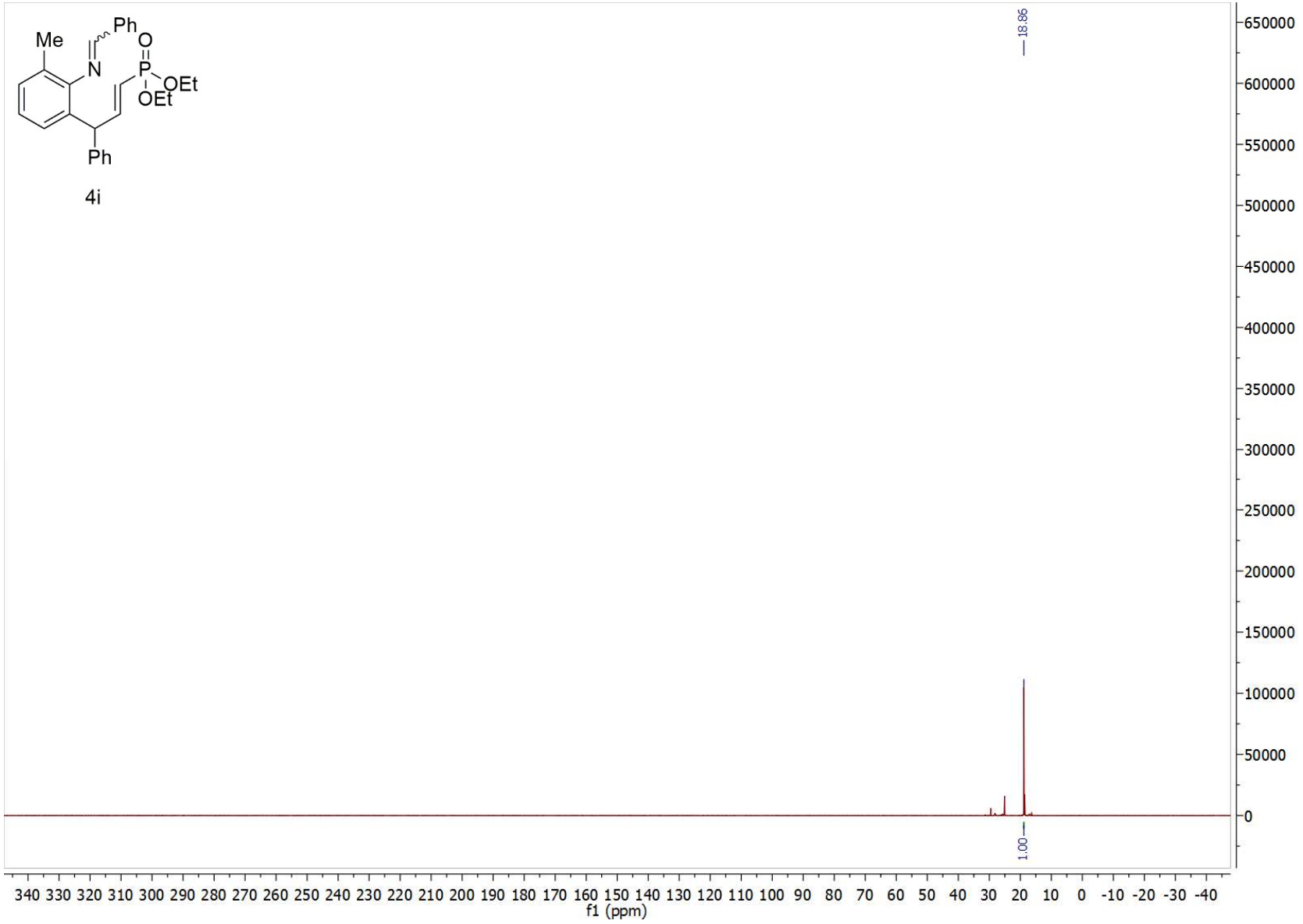
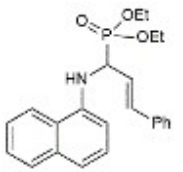


Figure S171: ^{31}P NMR Spectra of the reaction mixture of 4i

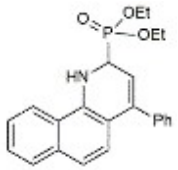
DFT calculations

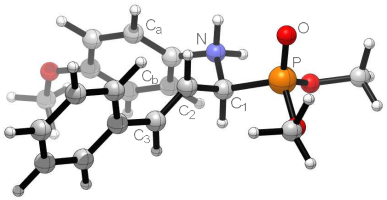
All calculations were conducted by using a *Gaussian 09* program package, revision D.01.[i]Molecular geometries were optimized with 'opt=tight' and 'int=ultrafine' keywordsand characterized by frequency analysis using a hybrid density functional (M06-2X)[ii]with 6-31+G(d,p) basis set as implemented in *Gaussian*09. Polarizable continuum model (PCM) parameters of trifluoroacetic acid are not available, therefore the parameters of acetic acid were applied. Single imaginary frequency was obtained in all transition states, which were supported by the intrinsic reaction coordinate (IRC) calculations using the local quadratic approximation (lqa) algorithm. Each geometry of reaction intermediates was obtained by structural optimization of the IRC geometries.Gibbs free energies *G* are calculated at 298 K.

Geometry and energy of starting material

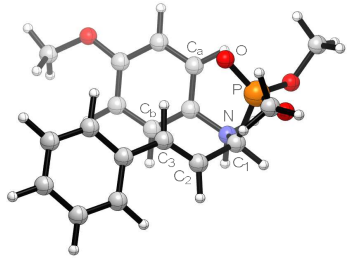


&





SM-1a (0 kcal mol^{-1})



SM-1b (+1.5 kcal mol^{-1})

SM-1a

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.177994	-0.665134	0.158974
2	1	0.944191	-0.899636	1.200823
3	6	0.648055	0.669867	-0.243427
4	1	0.892032	1.006556	-1.250213
5	6	-0.047500	1.436781	0.607263
6	1	-0.287113	1.032785	1.591170

SM-1b

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.614953	0.603272	1.284233
2	1	2.312335	1.052355	1.997403
3	6	0.365405	1.422585	1.185513
4	1	0.185735	2.104127	2.011917
5	6	-0.512667	1.291511	0.177400
6	1	-0.286500	0.585516	-0.621512

7	6	-0.538750	2.795692	0.340518	7	6	-1.792950	1.998440	0.036816
8	6	-1.511410	3.337990	1.191275	8	6	-2.643407	1.615834	-1.009877
9	6	-0.064485	3.570021	-0.729690	9	6	-2.202214	3.025741	0.901517
10	6	-2.021380	4.614243	0.964641	10	6	-3.879263	2.234424	-1.186271
11	1	-1.872716	2.750964	2.031338	11	1	-2.329447	0.825608	-1.687036
12	6	-0.571430	4.845220	-0.953361	12	6	-3.433374	3.645586	0.722960
13	1	0.717285	3.185486	-1.378094	13	1	-1.557057	3.351497	1.711540
14	6	-1.554200	5.369198	-0.109959	14	6	-4.276573	3.250455	-0.319368
15	1	-2.778399	5.019227	1.628104	15	1	-4.527040	1.926192	-2.000388
16	1	-0.193623	5.437082	-1.780722	16	1	-3.737738	4.441538	1.394811
17	1	-1.945317	6.366049	-0.285837	17	1	-5.236548	3.738043	-0.455083
18	6	-0.891482	-1.917172	-0.544074	18	6	0.365940	-1.635748	1.154506
19	6	-1.408758	-2.685234	0.486036	19	6	-0.969383	-1.555912	1.518410
20	6	-1.716205	-1.219462	-1.423380	20	6	0.788773	-2.451373	0.106988
21	6	-2.790515	-2.774319	0.646572	21	6	-1.918038	-2.300836	0.821716
22	1	-0.755575	-3.225603	1.165465	22	1	-1.286976	-0.913833	2.334622
23	6	-3.088338	-1.306313	-1.265880	23	6	-0.150949	-3.193329	-0.586525
24	1	-1.298032	-0.615883	-2.223267	24	1	1.837279	-2.506703	-0.170080
25	6	-3.633321	-2.081758	-0.230451	25	6	-1.508643	-3.118195	-0.238449
26	1	-3.188742	-3.382968	1.447964	26	1	-2.958248	-2.231797	1.112439
27	1	-3.760479	-0.780712	-1.934482	27	1	0.143634	-3.839082	-1.405770
28	8	-4.979054	-2.101731	-0.161450	28	8	-2.345163	-3.873017	-0.978068
29	6	-5.588886	-2.873588	0.866609	29	6	-3.735177	-3.827548	-0.677605
30	1	-5.291974	-2.507908	1.854517	30	1	-4.126188	-2.812619	-0.800747

31	1	-6.661483	-2.746448	0.736041	31	1	-4.214605	-4.494402	-1.391187
32	1	-5.328062	-3.931586	0.764689	32	1	-3.924526	-4.180496	0.340866
33	15	2.993224	-0.731081	-0.106152	33	15	2.576296	0.464347	-0.278478
34	8	3.269966	-2.202957	0.431537	34	8	3.673355	-0.566301	0.259910
35	8	3.623084	0.220261	0.994861	35	8	3.342635	1.856008	-0.347031
36	8	3.354982	-0.442734	-1.514549	36	8	1.849085	0.079100	-1.507884
37	6	4.605123	-2.759490	0.355735	37	6	4.731167	-1.007514	-0.624733
38	1	4.517993	-3.792695	0.682605	38	1	5.291527	-1.758647	-0.073320
39	1	4.966510	-2.714801	-0.672640	39	1	4.299685	-1.440505	-1.528757
40	1	5.266848	-2.206376	1.023782	40	1	5.374229	-0.161203	-0.870946
41	6	4.000468	1.579153	0.665827	41	6	2.935505	2.871413	-1.294152
42	1	3.103463	2.193670	0.564767	42	1	2.007838	3.336603	-0.955834
43	1	4.604086	1.928034	1.500424	43	1	3.740994	3.602169	-1.308602
44	1	4.579328	1.590352	-0.257745	44	1	2.800861	2.428392	-2.280806
45	1	1.027333	-2.672368	-0.412067	45	1	1.057218	-0.685401	2.834834
46	1	0.814653	-1.635682	-1.665119	46	1	2.257761	-1.293521	1.892533
47	7	0.568846	-1.790356	-0.678457	47	7	1.352789	-0.804230	1.859756

E(RM062X) = -1396.19932694	E(RM062X) = -1396.19714601
Zero-point correction= 0.392871 (Hartree/Particle)	Zero-point correction= 0.392763 (Hartree/Particle)
Sum of electronic and thermal Energies= -1395.781725	Sum of electronic and thermal Energies= -1395.779710
Sum of electronic and thermal Enthalpies= -1395.780781	Sum of electronic and thermal Enthalpies= -1395.778765
Sum of electronic and thermal Free Energies= -1395.864841	Sum of electronic and thermal Free Energies= -1395.862432

Geometry and energy for a reaction path to give (*E*)-product

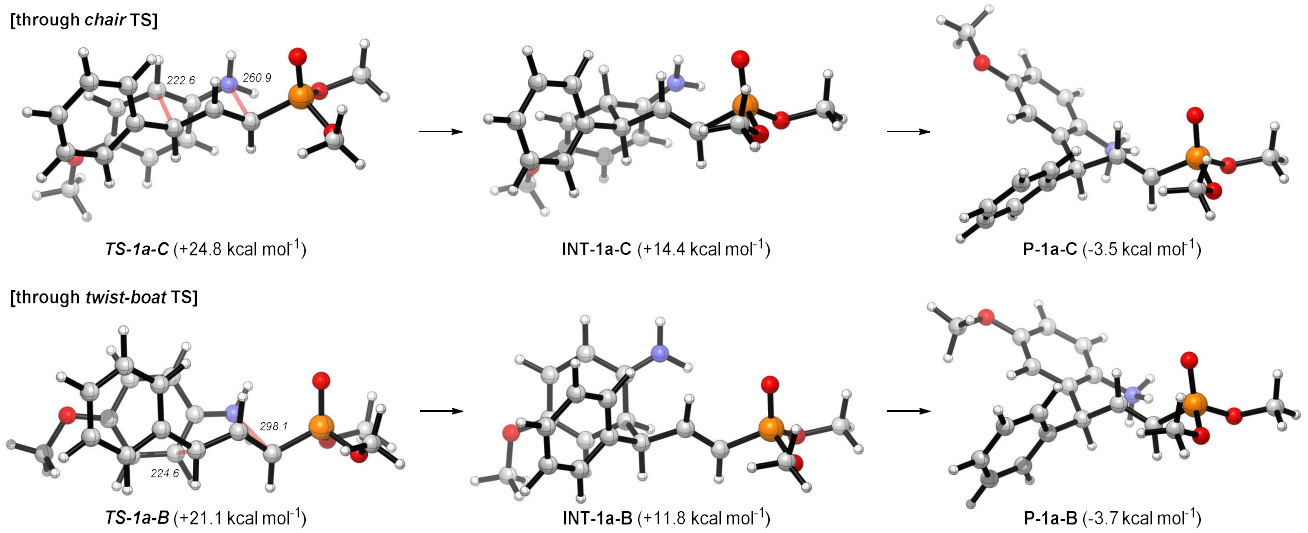


Figure S1. Reaction profilesfor step 1. Free energy differences are shown in kcal mol^{-1}. Interatomic distances are shown in pm.

TS-1a-C ***TS-1a-B***

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.726616	0.003826	0.467168	1	6	-1.990552	0.359834	-0.841747
2	1	1.476025	-0.764496	1.196385	2	1	-1.996738	0.090573	-1.897065
3	6	0.785782	0.853714	-0.007324	3	6	-0.859037	0.715229	-0.207492
4	1	1.084123	1.636888	-0.700830	4	1	-0.915007	0.955175	0.852841
5	6	-0.599322	0.676495	0.313621	5	6	0.434517	0.681762	-0.851890
6	1	-0.817110	-0.007371	1.133662	6	1	0.411887	0.646033	-1.939516
7	6	-1.596120	1.722090	0.095629	7	6	1.611160	1.304880	-0.280897

8	6	-2.737642	1.732451	0.913848	8	6	2.680294	1.632032	-1.139888
9	6	-1.458426	2.698008	-0.905771	9	6	1.749684	1.562114	1.096998
10	6	-3.714191	2.708008	0.748414	10	6	3.837715	2.214542	-0.644303
11	1	-2.850439	0.972508	1.682588	11	1	2.584893	1.432415	-2.204404
12	6	-2.440698	3.666053	-1.074398	12	6	2.911612	2.145397	1.590980
13	1	-0.595834	2.694181	-1.565222	13	1	0.954724	1.302755	1.788322
14	6	-3.567490	3.674296	-0.247625	14	6	3.956347	2.468678	0.725041
15	1	-4.588500	2.713488	1.390331	15	1	4.648719	2.469802	-1.318350
16	1	-2.331540	4.414497	-1.851911	16	1	3.004317	2.341597	2.653651
17	1	-4.330938	4.433492	-0.382754	17	1	4.862629	2.920175	1.115346
18	6	-0.347817	-1.846445	-0.761366	18	6	0.311752	-1.817489	0.312482
19	6	-0.853952	-2.752263	0.211449	19	6	0.918752	-1.509602	-0.948684
20	6	-1.207691	-0.806184	-1.230755	20	6	1.114396	-1.704510	1.487094
21	6	-2.181103	-2.726233	0.552488	21	6	2.334069	-1.479701	-1.065002
22	1	-0.191044	-3.490984	0.650431	22	1	0.327004	-1.681228	-1.843344
23	6	-2.599651	-0.884478	-0.961357	23	6	2.454053	-1.486831	1.363087
24	1	-0.874963	-0.192300	-2.063002	24	1	0.658109	-1.824226	2.464233
25	6	-3.083628	-1.799929	-0.058921	25	6	3.092103	-1.405687	0.078454
26	1	-2.543135	-3.437899	1.285268	26	1	2.773222	-1.401993	-2.051601
27	1	-3.277612	-0.167154	-1.410779	27	1	3.085734	-1.402613	2.242009
28	8	-4.408104	-1.772790	0.208196	28	8	4.428190	-1.268466	0.133505
29	6	-4.959645	-2.787247	1.040835	29	6	5.130418	-1.212240	-1.102503
30	1	-4.560545	-2.721607	2.057608	30	1	4.796599	-0.353113	-1.694450
31	1	-6.031366	-2.600339	1.060662	31	1	6.181223	-1.097946	-0.845322

32	1	-4.769030	-3.781373	0.624709	32	1	4.982807	-2.137242	-1.669165
33	15	3.453127	0.192396	0.007851	33	15	-3.525405	0.225802	0.068729
34	8	3.833201	-1.318571	-0.342618	34	8	-3.920638	-1.288895	-0.262840
35	8	4.274701	0.420465	1.362283	35	8	-4.646847	1.028163	-0.745915
36	8	3.677280	1.219115	-1.038539	36	8	-3.411797	0.600321	1.500585
37	6	5.209762	-1.635457	-0.646608	37	6	-5.215155	-1.780472	0.146150
38	1	5.221321	-2.683625	-0.937141	38	1	-5.222468	-2.843482	-0.085140
39	1	5.563644	-1.013915	-1.471338	39	1	-5.352581	-1.629729	1.218850
40	1	5.826471	-1.482617	0.240509	40	1	-5.997200	-1.266655	-0.415101
41	6	4.459401	1.762998	1.852012	41	6	-4.834992	2.429534	-0.471644
42	1	3.498198	2.190314	2.149259	42	1	-3.934981	2.990642	-0.737386
43	1	5.110647	1.680671	2.719634	43	1	-5.666954	2.750679	-1.094959
44	1	4.925188	2.380916	1.083417	44	1	-5.070977	2.575734	0.583196
45	1	1.559921	-2.616784	-0.801306	45	1	-1.541563	-2.318564	-0.431036
46	1	1.255437	-1.383706	-1.954602	46	1	-1.426905	-2.288719	1.286102
47	7	0.937238	-1.893175	-1.140215	47	7	-0.974483	-2.157322	0.390603

E(RM062X) = -1396.15735540	E(RM062X) = -1396.16414796
Zero-point correction = 0.388789 (Hartree/Particle)	Zero-point correction= 0.389129 (Hartree/Particle)
Sum of electronic and thermal Energies= -1395.743894	Sum of electronic and thermal Energies= -1395.750500
Sum of electronic and thermal Enthalpies = -1395.742950	Sum of electronic and thermal Enthalpies= -1395.749556
Sum of electronic and thermal Free Energies = -1395.825251	Sum of electronic and thermal Free Energies= -1395.831232

INT-1a-C	**INT-1a-B**

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.749854	-0.305070	0.530293	1	6	-2.054174	-0.246434	-0.822207
2	1	1.487200	-0.724159	1.499902	2	1	-1.973524	-0.575062	-1.856878
3	6	0.836431	0.234869	-0.279652	3	6	-0.985458	0.089004	-0.094430
4	1	1.161546	0.648685	-1.236477	4	1	-1.146979	0.427249	0.928545
5	6	-0.626758	0.323284	0.046204	5	6	0.429288	0.014881	-0.603674
6	1	-0.796676	-0.054971	1.059995	6	1	0.395948	-0.011785	-1.697266
7	6	-1.105588	1.763262	-0.027555	7	6	1.278982	1.196729	-0.175873
8	6	-1.676734	2.359109	1.098679	8	6	2.108153	1.817243	-1.115681
9	6	-0.990067	2.503614	-1.208767	9	6	1.274363	1.676918	1.138338
10	6	-2.126412	3.678234	1.047993	10	6	2.924009	2.886527	-0.751983
11	1	-1.775193	1.787265	2.017671	11	1	2.115311	1.458806	-2.142168
12	6	-1.441856	3.820431	-1.260913	12	6	2.089325	2.746741	1.505487
13	1	-0.548853	2.060404	-2.098522	13	1	0.635629	1.224664	1.893446
14	6	-2.010676	4.410952	-0.131954	14	6	2.917340	3.352908	0.562085
15	1	-2.569038	4.130056	1.929782	15	1	3.560330	3.356119	-1.495063
16	1	-1.348017	4.384878	-2.182912	16	1	2.072676	3.107585	2.528765
17	1	-2.361984	5.436713	-0.173353	17	1	3.549383	4.187300	0.848064
18	6	-1.049475	-2.002324	-0.816428	18	6	1.156470	-1.574483	1.249097
19	6	-1.770319	-2.909097	0.022682	19	6	1.108052	-1.392785	-0.234165
20	6	-1.509945	-0.585946	-0.936980	20	6	2.387364	-1.390936	1.956683
21	6	-3.007854	-2.567039	0.466023	21	6	2.439778	-1.453523	-0.909867
22	1	-1.345649	-3.880261	0.251687	22	1	0.439016	-2.151000	-0.656652

23	6	-2.943250	-0.383554	-0.573598	23	6	3.538152	-1.290678	1.249727
24	1	-1.322388	-0.225069	-1.955244	24	1	2.388098	-1.381974	3.041377
25	6	-3.640121	-1.304996	0.121148	25	6	3.582265	-1.362014	-0.202189
26	1	-3.545555	-3.278089	1.084348	26	1	2.427544	-1.478136	-1.993306
27	1	-3.390751	0.578611	-0.797634	27	1	4.487753	-1.174874	1.764320
28	8	-4.902355	-1.011933	0.517168	28	8	4.839179	-1.325706	-0.688293
29	6	-5.762835	-2.076249	0.916420	29	6	4.977241	-1.350434	-2.103434
30	1	-5.471684	-2.476362	1.892029	30	1	4.474259	-0.486559	-2.551213
31	1	-6.755246	-1.636524	0.993978	31	1	6.045394	-1.303137	-2.303106
32	1	-5.776094	-2.874006	0.167156	32	1	4.561987	-2.277065	-2.513077
33	15	3.467859	-0.329005	0.030500	33	15	-3.684486	-0.117566	-0.092191
34	8	3.904684	-1.806305	0.446577	34	8	-4.374884	-1.463403	-0.595748
35	8	4.287422	0.548230	1.096219	35	8	-4.496319	0.983602	-0.932231
36	8	3.685196	0.073979	-1.383155	36	8	-3.662276	0.133522	1.372474
37	6	5.287091	-2.189819	0.300489	37	6	-5.762870	-1.694930	-0.280300
38	1	5.337353	-3.246388	0.555113	38	1	-5.993237	-2.694309	-0.643200
39	1	5.613347	-2.037539	-0.730407	39	1	-5.916739	-1.643990	0.799534
40	1	5.906127	-1.608062	0.985807	40	1	-6.385663	-0.956926	-0.789105
41	6	4.361362	1.971567	0.901361	41	6	-4.363649	2.366765	-0.560586
42	1	3.362272	2.413734	0.957012	42	1	-3.325689	2.692641	-0.675275
43	1	4.979214	2.357930	1.709591	43	1	-5.001658	2.927238	-1.241024
44	1	4.816731	2.194663	-0.064708	44	1	-4.689172	2.510767	0.470713
45	1	0.407006	-3.327687	-1.303919	45	1	-0.818752	-2.036447	1.413027
46	1	0.559900	-1.777541	-2.045093	46	1	0.046381	-1.944322	2.907492

47	7	0.037362	-2.391073	-1.429439	47	7	0.057966	-1.866976	1.895860

E(RM062X) = -1396.17467136	E(RM062X) = -1396.18152765
Zero-point correction = 0.390637 (Hartree/Particle)	Zero-point correction = 0.391995 (Hartree/Particle)
Sum of electronic and thermal Energies = -1395.759075	Sum of electronic and thermal Energies = -1395.764981
Sum of electronic and thermal Enthalpies = -1395.758131	Sum of electronic and thermal Enthalpies = -1395.764037
Sum of electronic and thermal Free Energies = -1395.841952	Sum of electronic and thermal Free Energies = -1395.846101

P-1a-C

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.993237	-0.085281	0.670756
2	1	2.155324	0.100750	1.732656
3	6	0.788702	0.046795	0.104827
4	1	0.685317	-0.134937	-0.965744
5	6	-0.470228	0.406530	0.861430
6	1	-0.249964	0.348334	1.936269
7	6	-0.925042	1.835097	0.592827
8	6	-1.768396	2.451673	1.522972
9	6	-0.553506	2.534834	-0.556708
10	6	-2.237417	3.744284	1.306712
11	1	-2.062240	1.912155	2.420313
12	6	-1.023541	3.831474	-0.774495
13	1	0.103755	2.080559	-1.292119

P-1a-B

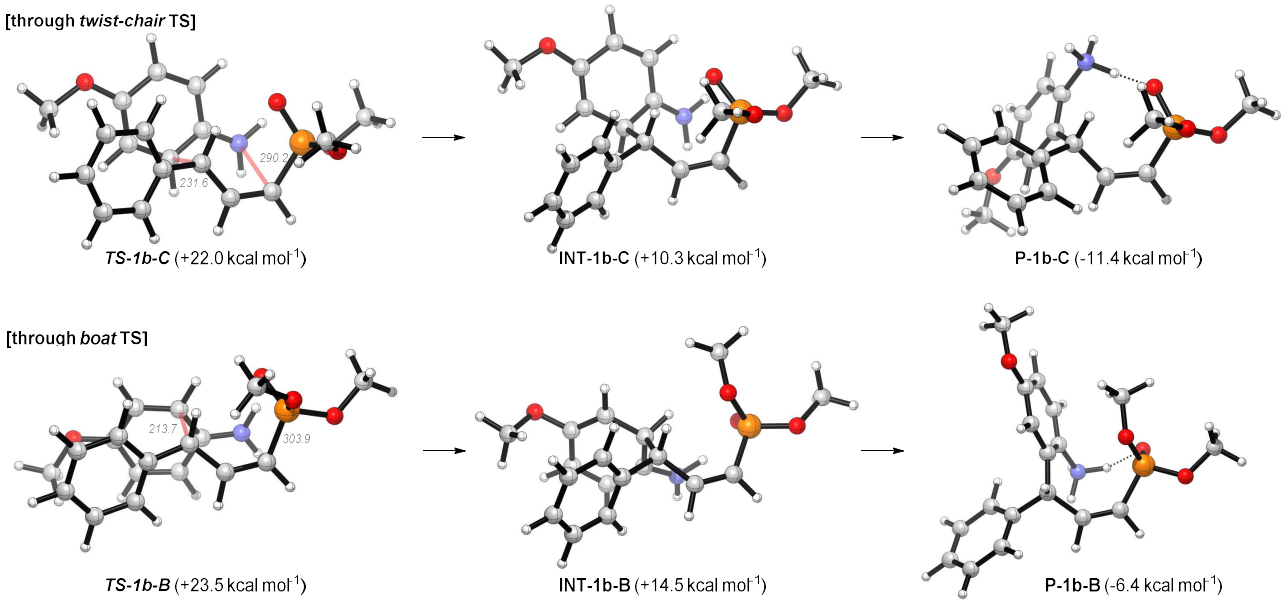
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.005823	-0.197091	-0.453460
2	1	-2.248546	-0.034940	-1.503335
3	6	-0.751928	-0.105684	0.002764
4	1	-0.564541	-0.262762	1.065637
5	6	0.447136	0.194338	-0.871367
6	1	0.135674	0.094110	-1.919987
7	6	0.916919	1.632590	-0.698818
8	6	1.459424	2.303234	-1.798103
9	6	0.856199	2.286288	0.535641
10	6	1.938015	3.605731	-1.668068
11	1	1.511179	1.801654	-2.761271
12	6	1.334307	3.589918	0.666478
13	1	0.443403	1.783571	1.405634

14	6	-1.865957	4.438139	0.153788	14	6	1.876814	4.252286	-0.433860
15	1	-2.889649	4.210666	2.038037	15	1	2.354657	4.115208	-2.530954
16	1	-0.727355	4.364371	-1.672303	16	1	1.281167	4.086239	1.630098
17	1	-2.229419	5.446299	-0.016389	17	1	2.246522	5.267254	-0.330970
18	6	-1.425928	-1.956200	0.974378	18	6	1.369215	-2.183630	-0.890038
19	6	-2.361291	-2.928036	0.667613	19	6	1.549843	-0.832545	-0.591572
20	6	-1.547505	-0.629916	0.532910	20	6	2.337642	-3.143768	-0.614796
21	6	-3.468801	-2.604534	-0.112781	21	6	2.757001	-0.461330	0.005047
22	1	-2.244221	-3.944307	1.032418	22	1	0.107000	-2.416238	-2.547541
23	6	-2.651058	-0.321520	-0.248082	23	6	3.528758	-2.762334	-0.024018
24	1	0.620598	-2.035641	1.386843	24	1	2.166271	-4.188269	-0.858267
25	6	-3.610516	-1.293343	-0.573852	25	6	3.742612	-1.413504	0.286943
26	1	-4.194973	-3.372246	-0.345761	26	1	2.919542	0.582102	0.241039
27	1	-2.797977	0.687318	-0.618719	27	1	4.300707	-3.488374	0.202765
28	8	-4.634817	-0.863265	-1.335159	28	8	4.926981	-1.119424	0.857375
29	6	-5.644196	-1.800508	-1.693329	29	6	5.197462	0.237398	1.193220
30	1	-6.139041	-2.196750	-0.801213	30	1	4.468683	0.610940	1.919367
31	1	-6.361740	-1.247514	-2.295700	31	1	6.191072	0.239402	1.636325
32	1	-5.221287	-2.619709	-2.282963	32	1	5.191015	0.867837	0.298497
33	15	3.414499	-0.469439	-0.349756	33	15	-3.349365	-0.472721	0.699341
34	8	4.158825	-1.576913	0.524424	34	8	-4.249056	-1.525535	-0.090574
35	8	4.421316	0.772449	-0.207980	35	8	-4.273944	0.837857	0.641296
36	8	3.071572	-0.819362	-1.751054	36	8	-2.900694	-0.839623	2.066160
37	6	5.426229	-2.088667	0.062246	37	6	-5.509527	-1.932271	0.481754

38	1	5.703116	-2.881970	0.753278	38	1	-5.902510	-2.708278	-0.171606
39	1	5.323144	-2.490493	-0.947665	39	1	-5.354661	-2.331211	1.486186
40	1	6.174549	-1.294315	0.082558	40	1	-6.193377	-1.082054	0.509821
41	6	4.210898	1.915780	-1.055834	41	6	-3.928556	1.956388	1.477851
42	1	3.220933	2.345570	-0.873340	42	1	-2.941139	2.342733	1.206755
43	1	4.979348	2.638687	-0.789503	43	1	-4.683196	2.718451	1.293918
44	1	4.306359	1.627480	-2.103699	44	1	-3.938505	1.656852	2.526850
45	1	-0.317422	-1.940462	2.754495	45	1	-0.711265	-2.204530	-1.116215
46	1	-0.220122	-3.357135	1.915593	46	1	0.015181	-3.648618	-1.459805
47	7	-0.269058	-2.339146	1.809350	47	7	0.122515	-2.633022	-1.544500

E(RM062X) = -1396.20642113	E(RM062X) = -1396.20633956
Zero-point correction = 0.393160 (Hartree/Particle)	Zero-point correction = 0.393542 (Hartree/Particle)
Sum of electronic and thermal Energies = -1395.788439	Sum of electronic and thermal Energies = -1395.787979
Sum of electronic and thermal Enthalpies = -1395.787494	Sum of electronic and thermal Enthalpies = -1395.787035
Sum of electronic and thermal Free Energies = -1395.870391	Sum of electronic and thermal Free Energies = -1395.870764

X.3.Geometry and energy for a reaction path to give (*Z*)-product



TS-1b-C

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.072383	0.827043	1.321512
2	1	2.702171	1.106002	2.164301
3	6	0.743713	1.079883	1.391990
4	1	0.369112	1.544726	2.301484
5	6	-0.204936	0.731817	0.365913
6	1	0.215396	0.307154	-0.541748
7	6	-1.491476	1.378133	0.196878

TS-1b-B

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.121415	0.057686	1.424294
2	1	2.582995	-0.144046	2.387378
3	6	0.792044	0.270552	1.365228
4	1	0.242258	0.182080	2.299049
5	6	0.013272	0.622749	0.184059
6	1	0.589545	1.008674	-0.653567
7	6	-1.293025	1.256624	0.362952

8	6	-2.120791	1.249014	-1.054914	8	6	-1.756715	2.129159	-0.638646
9	6	-2.146206	2.087315	1.222258	9	6	-2.136898	0.966821	1.448197
10	6	-3.367067	1.825961	-1.284978	10	6	-3.018177	2.699572	-0.556420
11	1	-1.615760	0.705017	-1.848717	11	1	-1.115439	2.352145	-1.487980
12	6	-3.389201	2.657291	0.990186	12	6	-3.406274	1.538400	1.527221
13	1	-1.689944	2.186640	2.201937	13	1	-1.817806	0.288410	2.232314
14	6	-4.001046	2.530118	-0.263304	14	6	-3.851045	2.398565	0.526381
15	1	-3.839581	1.725389	-2.256290	15	1	-3.358881	3.374614	-1.334254
16	1	-3.888034	3.204820	1.782762	16	1	-4.047338	1.306277	2.371574
17	1	-4.972341	2.981876	-0.437285	17	1	-4.841201	2.838326	0.587923
18	6	0.147715	-1.869195	0.657442	18	6	-0.162276	-2.026631	-0.006465
19	6	-0.918524	-1.235584	1.357619	19	6	-1.274838	-2.388849	0.814039
20	6	-0.105254	-2.343697	-0.672239	20	6	-0.384561	-1.070179	-1.058214
21	6	-2.252807	-1.365548	0.899017	21	6	-2.533191	-1.998342	0.454029
22	1	-0.750127	-0.924476	2.384173	22	1	-1.118346	-3.009465	1.690494
23	6	-1.378890	-2.342551	-1.151549	23	6	-1.711921	-0.854981	-1.520581
24	1	0.719272	-2.720328	-1.267026	24	1	0.445814	-0.893924	-1.734119
25	6	-2.480677	-1.876405	-0.356487	25	6	-2.775369	-1.247281	-0.750942
26	1	-3.053053	-0.973546	1.513554	26	1	-3.365622	-2.291206	1.083866
27	1	-1.597629	-2.713714	-2.147596	27	1	-1.885867	-0.269363	-2.416071
28	8	-3.682220	-1.993795	-0.948355	28	8	-4.012832	-0.908503	-1.163227
29	6	-4.813203	-1.519594	-0.225314	29	6	-5.133400	-1.280482	-0.367441
30	1	-4.702264	-0.453004	-0.001266	30	1	-5.071145	-0.827958	0.627717
31	1	-5.671430	-1.676063	-0.875294	31	1	-6.004856	-0.889873	-0.888878

32	1	-4.940478	-2.086267	0.702652	32	1	-5.213779	-2.368657	-0.285566
33	15	2.987838	0.267889	-0.121513	33	15	3.237519	0.117051	0.023847
34	8	4.078131	-0.683392	0.550593	34	8	4.509130	-0.628567	0.616447
35	8	3.885392	1.522116	-0.555155	35	8	3.785398	1.610871	-0.142107
36	8	2.184694	-0.312504	-1.230608	36	8	2.649045	-0.448869	-1.226555
37	6	5.197185	-1.133670	-0.244313	37	6	5.703666	-0.733018	-0.187968
38	1	5.738952	-1.845274	0.374819	38	1	6.385124	-1.372739	0.368059
39	1	4.840818	-1.622887	-1.153380	39	1	5.468026	-1.184915	-1.153482
40	1	5.836039	-0.285153	-0.493213	40	1	6.141194	0.257089	-0.324662
41	6	3.319619	2.505056	-1.442139	41	6	2.997909	2.598650	-0.827868
42	1	3.005529	2.031432	-2.373383	42	1	2.158880	2.909033	-0.197704
43	1	2.468818	2.999793	-0.964340	43	1	3.655479	3.448247	-1.000141
44	1	4.107198	3.231195	-1.632062	44	1	2.640113	2.203275	-1.781313
45	1	1.500862	-1.832767	2.198341	45	1	1.247776	-3.141597	0.966945
46	1	2.120688	-2.415107	0.699099	46	1	1.811875	-2.244325	-0.421316
47	7	1.360230	-1.983457	1.209056	47	7	1.053044	-2.510595	0.201346

E(RM062X) = -1396.16364934	E(RM062X) = -1396.16204068
Zero-point correction = 0.388604 (Hartree/Particle)	Zero-point correction = 0.389116 (Hartree/Particle)
Sum of electronic and thermal Energies = -1395.750578	Sum of electronic and thermal Energies = -1395.748672
Sum of electronic and thermal Enthalpies = -1395.749633	Sum of electronic and thermal Enthalpies = -1395.747728
Sum of electronic and thermal Free Energies = -1395.829788	Sum of electronic and thermal Free Energies = -1395.827395

INT-1b-C	**INT-1b-B**

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.993925	-1.093720	1.222560	1	6	2.168091	1.260728	1.117922
2	1	-2.637751	-1.627808	1.917488	2	1	2.693466	1.761213	1.926808
3	6	-0.674682	-1.051775	1.446586	3	6	0.832406	1.318832	1.065486
4	1	-0.304454	-1.544734	2.346157	4	1	0.338025	1.887184	1.851047
5	6	0.386463	-0.426456	0.578090	5	6	-0.092957	0.752347	0.008107
6	1	-0.023313	-0.161150	-0.399726	6	1	0.310596	1.033591	-0.969807
7	6	1.528713	-1.407615	0.377267	7	6	-1.483457	1.347074	0.128531
8	6	1.886988	-1.781385	-0.919872	8	6	-2.067227	1.960409	-0.983829
9	6	2.244440	-1.931575	1.458999	9	6	-2.201924	1.299954	1.327275
10	6	2.942395	-2.667327	-1.136331	10	6	-3.348979	2.502852	-0.907483
11	1	1.342749	-1.369138	-1.765995	11	1	-1.513605	2.015935	-1.917958
12	6	3.302345	-2.812443	1.244330	12	6	-3.489064	1.829942	1.403982
13	1	1.989933	-1.650874	2.478672	13	1	-1.760686	0.851822	2.214975
14	6	3.652882	-3.183864	-0.054411	14	6	-4.066915	2.430370	0.285384
15	1	3.209084	-2.949882	-2.149671	15	1	-3.785197	2.979672	-1.779466
16	1	3.852316	-3.209213	2.091533	16	1	-4.035686	1.782228	2.340329
17	1	4.475383	-3.871885	-0.220356	17	1	-5.066152	2.849073	0.347266
18	6	-0.175864	1.945690	1.131177	18	6	-0.254850	-1.519659	1.244837
19	6	0.934942	0.945414	1.202614	19	6	-1.540803	-1.977015	1.692982
20	6	-0.206664	2.917127	0.074454	20	6	-0.116854	-0.859154	-0.092511
21	6	2.165998	1.352881	0.452293	21	6	-2.529932	-2.113068	0.777300
22	1	1.180631	0.753237	2.254393	22	1	-1.668869	-2.298536	2.721061

23	6	0.902353	3.102411	-0.673200	23	6	-1.204439	-1.218307	-1.051598
24	1	-1.104476	3.504623	-0.080190	24	1	0.859075	-1.141472	-0.500235
25	6	2.127261	2.345233	-0.456683	25	6	-2.347562	-1.777770	-0.627988
26	1	3.051853	0.752668	0.615399	26	1	-3.486972	-2.531418	1.077570
27	1	0.917520	3.848910	-1.461750	27	1	-1.085886	-0.927866	-2.091807
28	8	3.141033	2.757131	-1.246913	28	8	-3.362679	-2.081443	-1.489475
29	6	4.364626	2.040454	-1.140968	29	6	-4.479602	-1.192439	-1.374910
30	1	4.209801	0.982641	-1.380581	30	1	-4.169643	-0.168805	-1.609445
31	1	5.041718	2.490956	-1.863451	31	1	-5.224141	-1.537411	-2.090566
32	1	4.779404	2.135527	-0.132062	32	1	-4.902958	-1.220902	-0.364454
33	15	-2.819242	-0.365644	-0.193266	33	15	3.182616	0.245251	0.063319
34	8	-4.270562	-0.085997	0.398592	34	8	4.619895	0.904806	0.213999
35	8	-3.118414	-1.560846	-1.221632	35	8	2.645912	0.534438	-1.415716
36	8	-2.107247	0.789591	-0.805738	36	8	3.130720	-1.214237	0.408482
37	6	-5.297532	0.420106	-0.479463	37	6	5.788093	0.200788	-0.258282
38	1	-6.155582	0.636875	0.153096	38	1	6.645223	0.762140	0.106293
39	1	-4.955073	1.332059	-0.972831	39	1	5.799599	-0.813907	0.142760
40	1	-5.556799	-0.339454	-1.218885	40	1	5.795164	0.182061	-1.350146
41	6	-2.035605	-2.039568	-2.036602	41	6	2.758888	-0.431461	-2.481752
42	1	-1.616833	-1.221584	-2.627029	42	1	1.860955	-0.327073	-3.090670
43	1	-1.260884	-2.489701	-1.405998	43	1	3.641819	-0.202106	-3.079322
44	1	-2.455966	-2.799427	-2.692156	44	1	2.826218	-1.443114	-2.075747
45	1	-1.137249	1.242383	2.777107	45	1	0.749757	-2.104970	2.894300
46	1	-1.941138	2.520430	1.935240	46	1	1.750998	-1.501951	1.583242

47	7	-1.135984	1.908054	2.012873	47	7	0.812879	-1.683380	1.973448

E(RM062X) = -1396.18462710	E(RM062X) = -1396.17829086
Zero-point correction = 0.391376 (Hartree/Particle)	Zero-point correction = 0.390920 (Hartree/Particle)
Sum of electronic and thermal Energies = -1395.768850	Sum of electronic and thermal Energies = -1395.763027
Sum of electronic and thermal Enthalpies = -1395.767906	Sum of electronic and thermal Enthalpies = -1395.762083
Sum of electronic and thermal Free Energies = -1395.848381	Sum of electronic and thermal Free Energies = -1395.841791

P-1b-C

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.325018	-0.824920	1.773472
2	1	-1.471849	-1.079284	2.819988
3	6	-0.087209	-0.653856	1.298549
4	1	0.740240	-0.763256	2.000090
5	6	0.322030	-0.291521	-0.112261
6	1	-0.552743	-0.369386	-0.764264
7	6	1.372325	-1.246662	-0.676944
8	6	2.107911	-0.867869	-1.806041
9	6	1.573543	-2.517263	-0.134034
10	6	3.028809	-1.740371	-2.378103
11	1	1.960768	0.120190	-2.236323
12	6	2.501727	-3.391890	-0.703987
13	1	1.007923	-2.837955	0.736604

P-1b-B

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.116130	1.550537	0.414809
2	1	2.905884	2.192942	0.797768
3	6	0.867599	2.031757	0.422443
4	1	0.767495	3.047414	0.802521
5	6	-0.452995	1.476379	-0.093424
6	1	-0.451262	1.760015	-1.155287
7	6	-1.613575	2.257396	0.544858
8	6	-1.732798	3.620303	0.242885
9	6	-2.542777	1.679736	1.411823
10	6	-2.746377	4.390076	0.804136
11	1	-1.030477	4.082254	-0.447525
12	6	-3.558487	2.452915	1.980610
13	1	-2.508067	0.617600	1.636330

14	6	3.231229	-3.006530	-1.825159	14	6	-3.662358	3.807707	1.682432
15	1	3.591730	-1.431380	-3.253063	15	1	-2.825178	5.442426	0.551090
16	1	2.650307	-4.374167	-0.267107	16	1	-4.272569	1.985519	2.651017
17	1	3.953141	-3.685556	-2.266957	17	1	-4.455014	4.405254	2.120461
18	6	0.112227	2.200155	-0.687310	18	6	-0.512891	-0.879114	1.011386
19	6	0.809480	1.155228	-0.090454	19	6	-0.912946	-2.207298	0.981373
20	6	0.569318	3.516486	-0.609846	20	6	-0.714648	-0.022546	-0.078680
21	6	1.997123	1.453261	0.590201	21	6	-1.551607	-2.731381	-0.137457
22	1	-1.611591	2.812160	-1.636191	22	1	-0.724652	-2.849392	1.837043
23	6	1.734860	3.804368	0.073924	23	6	-1.347481	-0.563648	-1.194623
24	1	0.012857	4.316728	-1.088780	24	1	1.234471	-0.674389	2.041659
25	6	2.460477	2.765946	0.677247	25	6	-1.764968	-1.898810	-1.240076
26	1	2.556771	0.636964	1.033754	26	1	-1.860204	-3.768640	-0.136795
27	1	2.106564	4.819922	0.147716	27	1	-1.539165	0.059323	-2.063151
28	8	3.592276	3.130745	1.314279	28	8	-2.355370	-2.290486	-2.387290
29	6	4.370503	2.114851	1.935226	29	6	-2.817213	-3.634044	-2.475785
30	1	4.721743	1.387377	1.196496	30	1	-3.571780	-3.835981	-1.709204
31	1	5.222149	2.624260	2.381362	31	1	-3.262982	-3.729863	-3.463571
32	1	3.794951	1.607063	2.715640	32	1	-1.985209	-4.338172	-2.376727
33	15	-2.825380	-0.701257	0.815850	33	15	2.712311	-0.066173	-0.043810
34	8	-3.917270	-0.419045	1.924375	34	8	4.244819	0.254041	-0.326571
35	8	-3.223709	-2.161075	0.301045	35	8	2.050671	-0.440590	-1.445438
36	8	-2.787219	0.289170	-0.315146	36	8	2.493808	-1.118104	1.007886
37	6	-5.304399	-0.285006	1.540981	37	6	5.118922	-0.816806	-0.737516

38	1	-5.837443	-0.002350	2.445542	38	1	6.129350	-0.416392	-0.698398
39	1	-5.407612	0.493742	0.783316	39	1	5.024954	-1.663982	-0.054751
40	1	-5.674825	-1.239991	1.165415	40	1	4.878431	-1.115689	-1.760407
41	6	-2.501177	-2.724138	-0.808723	41	6	1.697546	-1.804124	-1.759956
42	1	-2.606432	-2.085953	-1.688560	42	1	1.034590	-1.751951	-2.621795
43	1	-1.444048	-2.846737	-0.548755	43	1	2.595772	-2.371587	-2.011343
44	1	-2.943405	-3.699771	-0.997547	44	1	1.186519	-2.264628	-0.911911
45	1	-1.803546	1.286842	-0.938480	45	1	-0.115210	-0.919134	3.048541
46	1	-0.910910	1.519235	-2.365108	46	1	0.132681	0.569745	2.384318
47	7	-1.115760	1.936793	-1.451482	47	7	0.215893	-0.435810	2.209467

E(RM062X) = -1396.22156014	E(RM062X) = -1396.21104617
Zero-point correction = 0.392797 (Hartree/Particle)	Zero-point correction = 0.392337 (Hartree/Particle)
Sum of electronic and thermal Energies = -1395.804823	Sum of electronic and thermal Energies = -1395.794586
Sum of electronic and thermal Enthalpies = -1395.803879	Sum of electronic and thermal Enthalpies = -1395.793642
Sum of electronic and thermal Free Energies = -1395.883027	Sum of electronic and thermal Free Energies = -1395.875117

References

[i]. For *Gaussian 09*, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[ii]. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.***2008**, *120*: 215.