Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

Supporting Information for:

Direct Regioselective Phosphonation of Heteroaryl *N*-oxides with H-phosphonates under Metal and External Oxidant Free Conditions

Hui Wang[a], Xiuling Cui*[a,b], Yu Pei[a], Qianqian Zhang[a], Jie Bai[a], Donghui Wei[a] and Yangjie Wu*[a]

[a] *Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou, 450052, P.R. China*

[b] *Xiamen Key Laboratory of Ocean and Gene Drugs, School of Biomedical Sciences and Institute of Molecular Medicine of Huaqiao University & Engineering Research Center of Molecular Medicine of Chinese Education Ministry, Fujian, Xiamen, 361021, P.R. China*

E-mail: cuixl@zzu.edu.cn; wyj@zzu.edu.cn

Table of Contents

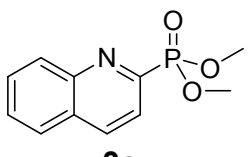
I. General experimental

Unless otherwise noted all commercial materials were used without further purification. The solvents were purified and dried according to standard methods. The dimethyl, diethyl and dibenzyl H-phosphonates were all purchased from Acros. Other H-phosphonates were prepared according to the literature procedure.[1] The silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All of the heteroaryl N-oxides were synthesized according to the literature.[2] The NMR spectra were recorded on a Bruker DPX-400 spectrometer. Chemical shifts were reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR (400 MHz), chloroform-*d* (δ 77.00) for ^{13}C NMR (100 MHz) and H_3PO_4 as external standard for ^{31}P NMR (162 MHz). High resolution mass spectra (HRMS) were recorded on an Agilent 6450 spectrometer with micromass MS software using electrospray ionisation (ESI). Melting points were recorded on a XT4A melting point apparatus and were uncorrected. The DFT calculations were performed using the Gaussian 09 program[3]. All structures were optimized and at the B3LYP[4-6]/6-31G(d, p) level, and the corresponding vibrational frequencies were calculated at the same level.

II. General procedure for the Phosphonation of Heteroaryl *N*-oxides

A mixture of quinoline *N*-oxide (72.5 mg, 0.5 mmol) and dimethyl H-phosphonate (138 uL, 1.5 mmol) in xylene (2.0 ml) in a sealed tube was stirred at 100 °C for 20 h. After cooling to room temperature, the mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether=3/1, v/v) to afford the desired product **3a**.

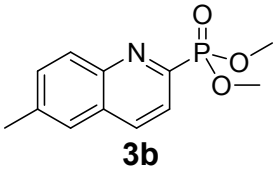
III. Experimental data for the described substances



3a

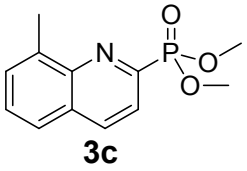
Dimethyl quinolin-2-ylphosphonate (3a)[7] Colorless oil (89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.11-8.04 (m, 2 H), 7.80 (dd, *J* = 8.3, 4.7 Hz, 1 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.57 (t, *J* = 7.7 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 3.76 (d, *J* = 11.0 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz,

$CDCl_3$): δ = 151.45 (d, J = 224.7 Hz), 147.96 (d, J = 25.9 Hz), 136.15 (d, J = 11.9 Hz), 130.09, 128.38 (d, J = 3.4 Hz), 128.28, 127.58 (d, J = 1.6 Hz), 123.13 (d, J = 26.6 Hz), 53.45 (d, J = 6.2 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 13.4 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{13}NO_3P$ [$M+H^+$]: 238.0628, found: 238.0630.



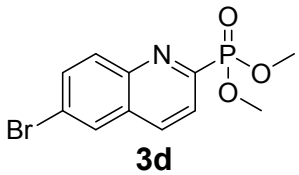
3b

Dimethyl (6-methylquinolin-2-yl)phosphonate (3b) Colorless oil (76% yield): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.14-8.07 (m, 2 H), 7.91-7.87 (m, 1 H), 7.54 (d, J = 6.5 Hz, 2 H), 3.87 (d, J = 10.9 Hz, 6 H), 2.49 (s, 3 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ = 150.49 (d, J = 225.5 Hz), 146.96 (d, J = 25.9 Hz), 138.77, 135.50 (d, J = 12 Hz), 132.67, 130.01, 128.74 (d, J = 3.4 Hz), 126.45 (d, J = 1.6 Hz), 123.49 (d, J = 26.7 Hz), 53.58 (d, J = 6.1 Hz), 21.73 ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 13.7 ppm. **HRMS** (EI^+): calculated for $C_{12}H_{15}NO_3P$ [$M+H^+$]: 252.0784, found: 252.0788.



3c

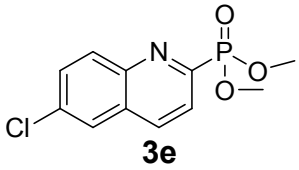
Dimethyl (8-methylquinolin-2-yl)phosphonate (3c) Colorless oil (72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.21 (dd, J = 8.3, 6.0 Hz, 1 H), 7.93 (dd, J = 8.3, 4.5 Hz, 1 H), 7.66 (d, J = 8.1 Hz, 1 H), 7.60 (d, J = 6.9 Hz, 1 H), 7.49 (t, J = 7.7 Hz, 1 H), 3.96 (d, J = 10.8 Hz, 6 H), 2.81 (s, 3 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ = 150.64 (d, J = 226.0 Hz), 147.17 (d, J = 25.2 Hz), 138.23 (d, J = 1.2 Hz), 136.45 (d, J = 11.8 Hz), 130.27, 128.62 (d, J = 3.5 Hz), 128.31, 125.72 (d, J = 1.3 Hz), 123.03 (d, J = 27.2 Hz), 54.02 (d, J = 6.3 Hz), 17.91 ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 12.8 ppm. **HRMS** (EI^+): calculated for $C_{12}H_{15}NO_3P$ [$M+H^+$]: 252.0784, found: 252.0787.



3d

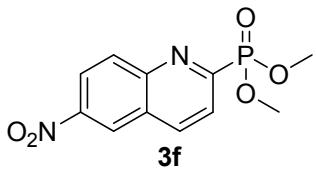
Dimethyl (6-bromoquinolin-2-yl)phosphonate (3d) Orange oil (72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.14 (dd, J = 5.7, 8.3 Hz, 1 H), 8.05 (d, J = 9.0 Hz, 1 H), 7.97 (d, J = 2.1 Hz, 1 H), 7.93 (dd, J = 4.7, 8.4 Hz, 1 H), 7.77 (dd, J = 2.2, 9.0 Hz, 1 H), 3.88 (d, J = 10.8 Hz, 6 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ = 152.05 (d, J = 225.3 Hz), 146.50 (d, J = 26.0 Hz), 135.12 (d, J = 11.7 Hz), 133.68, 131.82, 129.58 (d, J = 1.5 Hz), 129.37 (d, J = 3.4 Hz), 123.98 (d, J = 26.4 Hz), 122.56, 53.54 (d, J = 6.2 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 12.8 ppm.

HRMS (EI^+): calculated for $C_{11}H_{12}N_2O_5P$ [$M+H^+$]: 315.9733, found: 315.9737.



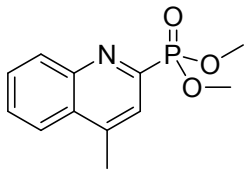
3e

Dimethyl (6-chloroquinolin-2-yl)phosphonate (**3e**) Orange oil (74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ =8.18-8.12 (m, 2 H), 7.95 (dd, *J* = 4.6, 8.4 Hz, 1 H), 7.80 (d, *J* = 2.2 Hz, 1 H), 7.66 (dd, *J* = 2.2, 9.0 Hz, 1 H), 3.89 (dd, *J* =10.9 Hz, 6 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): *δ* = 151.88 (d, *J* = 225.6 Hz), 146.37 (d, *J* = 26.0 Hz), 135.28 (d, *J* = 11.7 Hz), 134.29, 131.83, 131.22, 129.99 (d, *J* = 3.4 Hz), 126.22 (d, *J* = 1.5 Hz), 124.07 (d, *J* = 26.4 Hz), 53.59 (d, *J* = 6.1 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): *δ* = 12.8 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{12}ClNO_3P$ [$M+H^+$]: 272.0238, found: 272.0245.



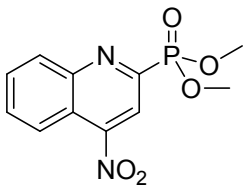
3f

Dimethyl (6-nitroquinolin-2-yl)phosphonate (3f) Yellow solid (50% yield). m.p. 129-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.81 (d, *J* = 2.4 Hz, 1 H), 8.52-8.46 (m, 2 H), 8.37 (d, *J* = 9.3 Hz, 1 H), 8.12-8.08 (dd, *J* = 8.4, 4.7 Hz, 1 H), 3.95 (d, *J* = 10.9 Hz, 6 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): *δ* = 156.14 (d, *J* = 224.0 Hz), 149.76 (d, *J* = 25.8 Hz), 146.63, 138.38 (d, *J* = 11.4 Hz), 132.38, 127.45 (d, *J* = 3.4 Hz), 124.93 (d, *J* = 25.8 Hz), 124.51 (d, *J* = 1.49 Hz), 123.65, 54.00 (d, *J* = 6.3 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): *δ* = 11.5 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{12}N_2O_5P$ [$M+H^+$]: 283.0478, found: 283.0480.



3g

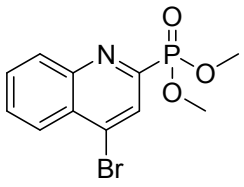
Dimethyl (4-methylquinolin-2-yl)phosphonate (3g) Colorless oil (68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.19 (d, *J* = 8.4, 1 H), 7.96 (dd, *J* = 8.3, 0.7 Hz, 1 H), 7.79 (dd, *J* = 5.2, 0.4 Hz, 1 H), 7.73-7.67 (m, 1 H), 7.61-7.56 (m, 1 H), 3.87 (d, *J* = 10.9 Hz, 6 H), 2.69 (s, 3 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): *δ* = 151.04 (d, *J* = 223.2 Hz), 147.92 (d, *J* = 26.3 Hz), 145.05 (d, *J* = 11.8 Hz), 131.00, 129.85, 128.64 (d, *J* = 3.2 Hz), 128.23, 124.17 (dd, *J* = 1.6 Hz), 123.75 (d, *J* = 1.1 Hz), 53.60 (t, *J* = 6.0 Hz), 18.73 (d, *J* = 3.7 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): *δ* = 13.9 ppm. **HRMS** (EI^+): calculated for $C_{12}H_{15}NO_3P$ [$M+H^+$]: 252.0784, found: 252.0788.



3h

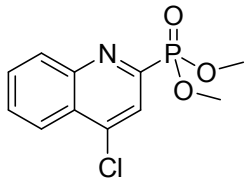
Dimethyl (4-nitroquinolin-2-yl)phosphonate (3h) Yellow oil (22%

yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.79 (dd, J = 8.9, 1.5 Hz, 1 H), 8.73 (d, J = 8.3 Hz, 1 H), 8.60 (d, J = 9.1 Hz, 1 H), 7.95-7.86 (m, 2 H), 4.05 (d, J = 11.6 Hz, 6 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ = 143.75 (d, J = 7.5 Hz), 139.74 (d, J = 11.8 Hz), 136.59 (d, J = 219.4 Hz), 133.45, 132.20, 125.16, 123.68 (d, J = 1.6 Hz), 123.50 (d, J = 11.9 Hz), 120.82, 55.29 (d, J = 6.1 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 6.4 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{12}N_2O_5P$ [M+H$^+$]: 283.0478, found: 283.0479.



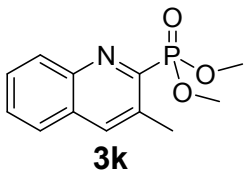
3i

Dimethyl (4-bromoquinolin-2-yl)phosphonate (3i) Orange oil (32% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.27-8.20 (m, 3 H), 7.84-7.79 (m, 1 H), 7.75-7.70 (m, 1 H), 3.93 (d, J = 10.8 Hz, 6 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ = 152.04 (d, J = 225.7 Hz), 149.21 (d, J = 27.1 Hz), 135.32 (d, J = 17.3 Hz), 131.53, 131.29, 130.20 128.78 (d, J = 3.1 Hz), 127.69 (d, J = 27.3 Hz), 127.23, 54.25 (d, J = 6.2 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 11.6 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{12}BrNO_3P$ [M+H$^+$]: 315.9733, found: 315.9735.



3j

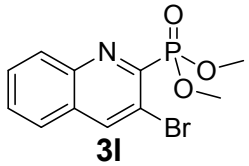
Dimethyl (4-chloroquinolin-2-yl)phosphonate (3j) Colorless oil (39% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.24-8.21 (m, 2 H), 8.03 (dd, J = 5.4, 2.1 Hz, 1 H), 7.82-7.77 (m, 1 H), 7.70 (t, J = 8.1 Hz, 1 H), 3.91 (d, J = 11.1 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.76 (d, J = 226.3 Hz), 149.07 (d, J = 27.4 Hz), 143.46 (d, J = 17.6 Hz), 131.13, 130.81, 129.56, 126.93 (d, J = 3.1 Hz), 124.12, 123.58 (d, J = 27.5 Hz), 53.86 (d, J = 6.2 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 11.9 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{12}ClNO_3P$ [M+H$^+$]: 272.0238, found: 272.0241.



3k

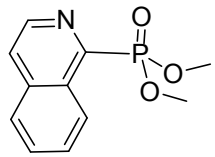
Dimethyl (3-methylquinolin-2-yl)phosphonate (3k) White solid (83% yield): m.p. 79-80 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.5 Hz, 1 H), 7.88 (d, J = 6.8 Hz, 1 H), 7.64 (d, J = 8.2 Hz, 1 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 3.90 (d, J = 11.0 Hz, 6 H), 2.67 (s, 3 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.52 (d, J = 222.8 Hz), 145.86 (d, J = 26.0 Hz), 136.92 (d, J = 12.1 Hz), 133.38 (d, J = 28.3 Hz), 130.03 (d, J = 1.4 Hz), 129.13, 128.64 (d, J = 3.5 Hz), 128.46, 126.83 (d, J = 1.7 Hz), 53.69 (d, J = 6.6 Hz), 19.41 ppm. **^{31}P NMR** (162 MHz,

$CDCl_3$): δ = 14.0 ppm. **HRMS** (EI^+): calculated for $C_{12}H_{15}NO_3P$ [M+H^+]: 252.0784, found: 252.0789.



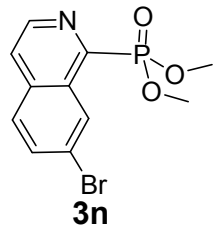
3l

Dimethyl (3-bromoquinolin-2-yl)phosphonate (3l) White solid (85% yield). m.p. 152-153 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 6.0 Hz, 1 H), 8.15 (d, J = 8.4 Hz, 1 H), 7.78-7.73 (m, 2 H), 7.66-7.61 (m, 1 H), 4.02 (d, J = 11.1 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.83 (d, J = 235.7 Hz), 145.66 (d, J = 24.2 Hz), 139.95 (d, J = 9.4 Hz), 130.45, 130.33 (d, J = 1.2 Hz), 129.53, 129.29 (d, J = 3.3 Hz), 126.64, 117.94 (d, J = 25.4 Hz), 54.25 (t, J = 6.1 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 11.7 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{12}BrNO_3P$ [M+H^+]: 315.9733, found: 315.9737.



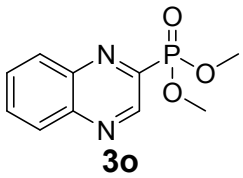
3m

Dimethyl isoquinolin-1-ylphosphonate (3m)[8] Colorless oil (92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.84 (d, J = 8.5 Hz, 1 H), 8.64 (d, J = 5.6 Hz, 1 H), 7.83-7.79 (m, 1 H), 7.75 (dd, J = 5.4, 2.6 Hz, 1 H), 7.70-7.61 (m, 2 H), 3.89 (d, J = 11.0 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.36 (d, J = 222.6 Hz), 142.06 (d, J = 25.5 Hz), 136.01 (d, J = 10.5 Hz), 130.66, 130.95 (d, J = 29.0 Hz), 128.59, 127.28 (d, J = 2.3 Hz), 126.86, 123.90 (d, J = 4.1 Hz), 53.71 (t, J = 6.1 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 13.2 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{13}NO_3P$ [M+H^+]: 238.0628, found: 238.0634.



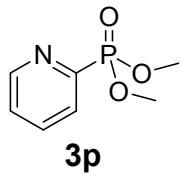
3n

Dimethyl (7-bromoisoquinolin-1-yl)phosphonate (3n) Light yellow solid (80% yield). m. p. 84-85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.08 (s, 1 H), 8.70 (d, J = 5.6 Hz, 1 H), 7.80-7.71 (m, 3 H), 3.92 (d, J = 11.0 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.86 (d, J = 223.9 Hz), 142.74 (d, J = 24.9 Hz), 134.81, 134.68, 131.01 (d, J = 29.0 Hz), 129.41, 129.13 (d, J = 2.5 Hz), 123.92 (d, J = 4.2 Hz), 123.16, 54.2 (d, J = 6.3 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 12.4 ppm. **HRMS** (EI^+): calculated for $C_{11}H_{12}BrNO_3P$ [M+H^+]: 315.9733, found: 315.9735.



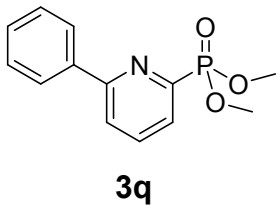
3o

Dimethyl quinoxalin-2-ylphosphonate (3o)[9] Orange oil (74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.18 (s, 1 H), 8.12 (dd, J = 8.0, 1.8 Hz, 1 H), 8.05-8.01 (m, 1 H), 7.79-7.71 (m, 2 H), 3.87 (d, J = 11.0 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 147.00 (d, J = 222.4 Hz), 146.09 (d, J = 27.7 Hz), 143.03 (d, J = 2.6 Hz), 142.17 (d, J = 21.4 Hz), 132.16, 130.88, 130.16 (d, J = 1.3 Hz), 129.46 (d, J = 2.1 Hz), 53.85 (t, J = 5.4 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 11.0 ppm. **HRMS** (EI^+): calculated for $C_{10}H_{12}N_2O_3P$ [M+H$^+$]: 239.0580, found: 239.0581.



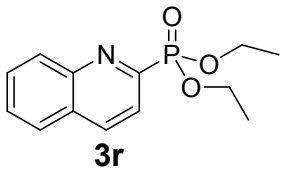
3p

Dimethyl pyridin-2-ylphosphonate (3p)[10] Colorless oil (48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 4.8 Hz, 1 H), 7.90 (t, J = 7.7 Hz, 1 H), 7.79-7.72 (m, 1 H), 7.41-7.36 (m, 1 H), 3.80 (d, J = 10.9 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.79 (d, J = 226.7 Hz), 150.56 (d, J = 22.8 Hz), 136.19 (d, J = 12.4 Hz), 128.38 (d, J = 25.2 Hz), 126.23 (d, J = 4.0 Hz), 53.44 (d, J = 6.1 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 13.7 ppm. **HRMS** (EI^+): calculated for $C_7H_{11}NO_3P$ [M+H$^+$]: 188.0471, found: 188.0473.



3q

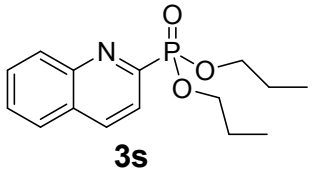
Dimethyl (6-phenylpyridin-2-yl)phosphonate (3q) Colorless oil (26% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.06-8.03 (m, 2 H), 7.90-7.85 (m, 3 H), 7.51-7.41 (m, 3 H), 3.84 (d, J = 10.8 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.94 (d, J = 22.6 Hz), 151.01 (d, J = 226.4 Hz), 138.25, 136.95 (d, J = 12.6 Hz), 129.62, 128.85 (d), 127.06 (d), 126.56 (d, J = 25.4 Hz), 122.81 (d, J = 4.0 Hz), 53.83 (d, J = 6.2 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 13.2 ppm. **HRMS** (EI^+): calculated for $C_{13}H_{15}NO_3P$ [M+H$^+$]: 264.0784, found: 264.0790.



3r

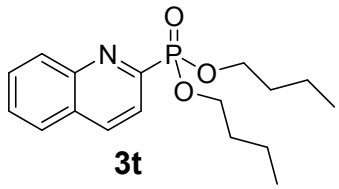
Diethyl quinolin-2-ylphosphonate (3r)[10] Colorless oil (79% yield). **^{1}H NMR** (400 MHz, CDCl3): δ = 8.19 (t, J = 8.1 Hz, 2 H), 7.93 (dd, J = 8.4, 4.6 Hz, 1 H), 7.77 (d, J = 8.2 Hz, 1 H), 7.72-7.67 (m, 1 H), 7.54 (t, J = 7.2 Hz, 1 H), 4.31-4.16 (m, 4 H), 1.31 (t, J = 9.5 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 152.62 (d, J = 223.7 Hz), 148.08 (d, J = 25.8 Hz), 136.10

(d, J = 11.7 Hz), 130.27, 130.02, 128.42 (d, J = 3.4 Hz), 128.21, 127.59 (d, J = 1.5 Hz), 123.18 (d, J = 26.5 Hz), 63.02 (d, J = 6.0 Hz), 16.25 (d, J = 6.1 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 10.9 ppm. **HRMS** (EI^+): calculated for $C_{13}H_{17}NO_3P$ [$M+H^+$]: 266.0941, found: 266.0944.



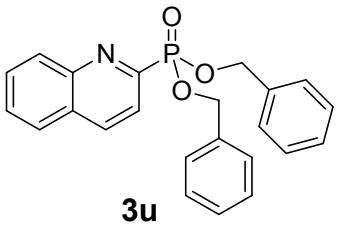
3s

Dipropyl quinolin-2-ylphosphonate (3s) Colorless oil (61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.25 (t, J = 8.3 Hz, 2 H), 7.97 (dd, J = 8.4, 4.6 Hz, 1 H), 7.83 (d, J = 8.2 Hz, 1 H), 7.78-7.72 (m, 1 H), 7.61 (t, J = 7.4 Hz, 1 H), 4.24-4.11 (m, 4 H), 1.76-1.68 (m, 4 H), 0.93 (t, J = 7.4 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 152.80 (d, J = 224.0 Hz), 148.22 (d, J = 25.9 Hz), 136.13 (d, J = 11.7 Hz), 130.46 (d, J = 1.2 Hz), 130.13, 128.55 (d, J = 3.4 Hz), 128.32, 127.72 (d, J = 1.6 Hz), 123.34 (d, J = 26.3 Hz), 68.63 (d, J = 6.3 Hz), 67.25 (d, J = 6.0 Hz), 23.86 (d, J = 6.2 Hz), 23.77 (d, J = 6.2 Hz), 10.04 ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 10.9 ppm. **HRMS** (EI^+): calculated for $C_{15}H_{21}NO_3P$ [$M+H^+$]: 294.1254, found: 294.1261.



3t

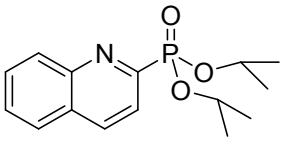
Dibutyl quinolin-2-ylphosphonate (3t) Colorless oil (53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.15 (t, J = 8.0 Hz, 2 H), 7.88 (dd, J = 8.3, 4.5 Hz, 1 H), 7.73 (d, J = 8.2 Hz, 1 H), 7.67-7.62 (m, 1 H), 7.49 (t, J = 7.2 Hz, 1 H), 4.20-4.07 (m, 4 H), 1.65-1.57 (m, 4 H), 1.36-1.26 (m, 4 H), 0.79 (t, J = 7.4 Hz, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 152.75 (d, J = 223.7 Hz), 148.14 (d, J = 25.9 Hz), 136.07 (d, J = 11.6 Hz), 130.33 (d, J = 1.1 Hz), 130.07, 128.46 (d, J = 3.4 Hz), 128.24, 127.68 (d, J = 1.5 Hz), 123.25 (d, J = 26.3 Hz), 66.76 (d, J = 6.2 Hz), 32.43 (d, J = 6.1 Hz) 18.63 , 13.52 ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 10.8 ppm. **HRMS** (EI^+): calculated for $C_{17}H_{25}NO_3P$ [$M+H^+$]: 322.1567, found: 322.1574.



3u

Dibenzyl quinoline-2-ylphosphonate (3u) Orange oil (82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26-8.19 (m, 2 H), 7.94 (dd, J = 8.3, 4.7 Hz, 1 H), 7.83 (d, J = 8.2 Hz, 1 H), 7.80-7.74 (m, 1 H), 7.62 (t, J = 7.2 Hz, 1 H), 7.42-7.38 (m, 4 H), 7.34-7.27 (m, 1 H), 5.28 (d, J = 7.8 Hz, 4 H) ppm. **^{13}C NMR**

(100 MHz, $CDCl_3$): δ = 152.30 (d, J = 225.6 Hz), 148.05 (d, J = 26.3 Hz), 136.11 (d, J = 11.9 Hz), 135.98 (d, J = 6.5 Hz), 130.29 (d, J = 1.2 Hz), 130.12, 128.47 (d, J = 3.3 Hz), 128.37, 128.34, 128.26, 127.95, 127.62 (d, J = 1.6 Hz), 123.14 (d, J = 26.8 Hz), 68.50 (d, J = 6.0 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 11.2 ppm. **HRMS** (EI^+): calculated for $C_{23}H_{21}NO_3P$ [$M+H^+$]: 390.1254, found: 390.1263.



3v

Diisopropyl quinolin-2-ylphosphonate (3v) Colorless oil (44% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.16-8.12 (m, 2 H), 7.88 (dd, J = 8.4, 4.5 Hz, 1 H), 7.77 (d, J = 8.3 Hz, 1 H), 7.67-7.62 (m, 1 H), 7.49 (t, J = 7.4 Hz, 1 H), 4.86-4.74 (m, 4 H), 1.31 (d, J = 6.3 Hz, 6 H), 1.21 (d, J = 6.2 Hz, 6 H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ = 154.22 (d, J = 224.2 Hz), 148.45 (d, J = 25.9 Hz), 136.29 (d, J = 11.5 Hz), 130.70 (d, J = 1.2 Hz), 130.32, 128.73 (d, J = 3.4 Hz), 128.47, 127.99 (d, J = 1.6 Hz), 123.55 (d, J = 26.3 Hz), 72.13 (d, J = 6.0 Hz), 24.39 (d, J = 3.9 Hz), 24.13 (d, J = 4.9 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 9.0 ppm. **HRMS** (EI^+): calculated for $C_{15}H_{21}NO_3P$ [$M+H^+$]: 294.1254, found: 294.1258.

IV. References

1 P. N. Kapoor, L. M. Venanzi, *Helv. Chim. Acta.*, 1977, **60**, 2824.

2 L.-C. Campeau, D. R. Stuart, J.-P. Leclerc, M. Bertrand-Laperle, E. Villemure, H.-Y. Sun, S. Lasserre, N. Guimond, M. Lecavallier, K. Fagnou, *J. Am. Chem. Soc.*, 2009, **131**, 3291.

3 G. W. Trucks, M. J. Frisch, 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 , *Revision C*. 01; **2010**.

4 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

5 C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785.

6 B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.

7 C.-B. Xiang, Y.-J. Bian, X.-R. Mao, Z.-Z. Huang, *J. Org. Chem.*, 2012, **77**, 7706.

8 H. Mirko, G. Wolfgang, G. Helmar, A. Ernst, *Synthesis*, 1999, **12**, 2071.

9 S. Dahbi, E. Methnani, P. Bisseret, *Tetrahedron Lett.*, 2010, **51**, 5516.

10 Y.-L. Zhao, G.-J. Wu, F.-S. Han, *Chem. Commun.*, 2012, **48**, 5868.

V. Cartesian coordinates of the optimized structures

1a

C	-2.69626800	0.37864300	0.00000400
C	-1.70228200	1.33208100	0.00000000
C	-0.33178300	0.95874900	-0.00000100
C	-0.03311200	-0.43242200	-0.00000400
C	-1.05189300	-1.40329200	-0.00000400
C	-2.36985200	-0.99753600	0.00000200
H	0.51026800	2.96221000	0.00000400
H	-3.73849900	0.68317700	0.00000900
H	-1.95029600	2.38959000	0.00000300
C	0.72977000	1.89995600	-0.00000200
H	-0.75684200	-2.44461300	-0.00001300
H	-3.16284600	-1.73875900	0.00000400
C	2.29531500	0.05946000	0.00000100
C	2.02466700	1.43386700	0.00000300
H	3.29021800	-0.36434200	0.00000200
H	2.86842400	2.11552900	0.00001100
O	1.57387700	-2.11461900	0.00001300
N	1.30874100	-0.86612300	-0.00001600

2a

P	0.01727900	0.53826100	0.27788600
H	-0.24682400	0.56201800	1.66360600
O	-1.43599600	0.30789700	-0.36970000
O	0.71746800	-0.90553700	0.06321800
O	0.74816200	1.70851400	-0.24850800
C	-2.21682100	-0.84776200	-0.02668300

H	-3.19348500	-0.71133400	-0.49199900
H	-1.74405200	-1.75625800	-0.40782000
H	-2.34655900	-0.93184800	1.05911600
C	2.14167300	-0.99186500	-0.13720500
H	2.32597500	-1.91374100	-0.69084100
H	2.50358700	-0.13277800	-0.70525400
H	2.65599500	-1.03921500	0.82815900

2a-1

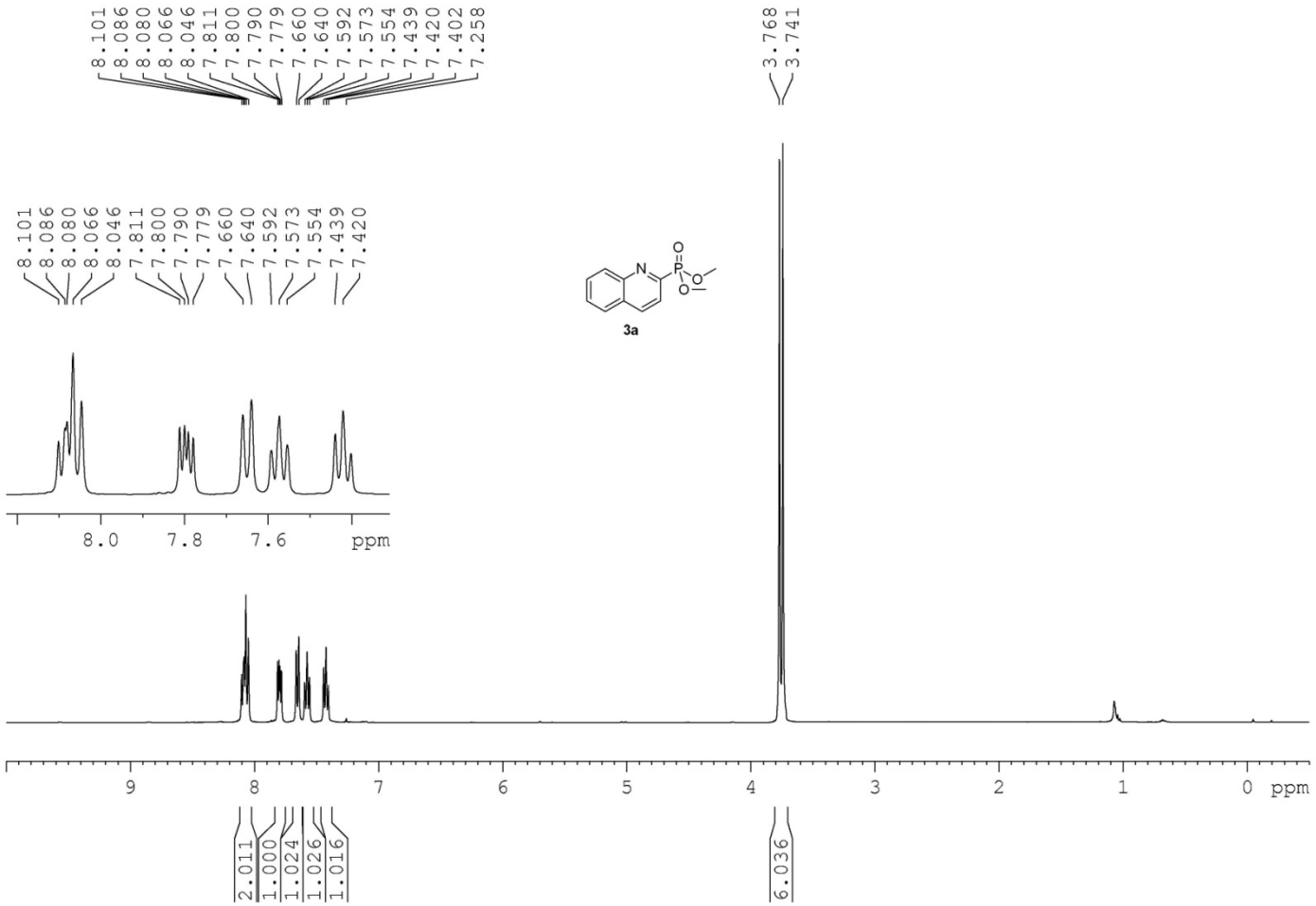
P	0.00377400	0.40178600	0.47410900
O	-1.43333900	0.24010300	-0.31537400
O	0.82643800	-0.76295100	-0.36435600
C	-2.23636400	-0.89660500	0.00948400
H	-3.23629600	-0.70719500	-0.38608100
H	-1.83091900	-1.80353500	-0.45081500
H	-2.30882800	-1.04983400	1.09481000
C	2.18016800	-1.01205700	0.01601900
H	2.45973000	-1.98556400	-0.39238800
H	2.84713600	-0.24637300	-0.39522900
H	2.30093500	-1.03857900	1.10746700
O	0.54725700	1.74152600	-0.33282200
H	0.52596900	2.50685200	0.25799800

E

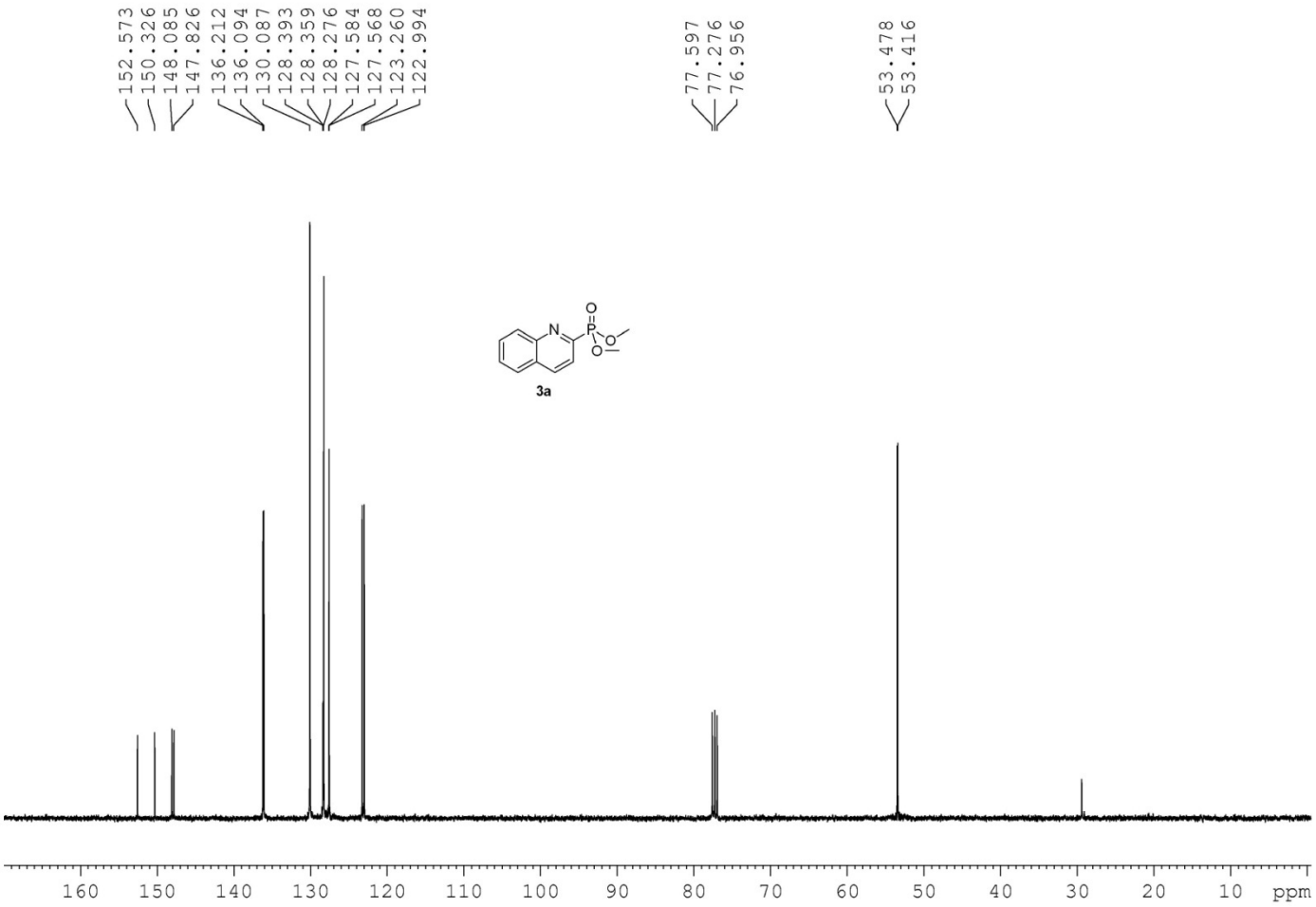
C	-4.66460200	-0.36769000	0.25773300
C	-3.69376700	-1.33358700	-0.00655500
C	-2.34777700	-0.98748000	-0.15756900
C	-1.97040700	0.36933500	-0.02062700
C	-2.94279900	1.34204100	0.23822300
C	-4.28140400	0.96811400	0.37259300
H	-1.61976800	-3.00086800	-0.60986100
H	-5.70503500	-0.65466400	0.37033400
H	-3.97699400	-2.37750800	-0.11425000
C	-1.32186100	-1.96096000	-0.50748200
H	-2.64215000	2.37585600	0.35358200
H	-5.02455500	1.73281000	0.57863400
C	0.41440100	-0.17306700	-0.63422500
C	-0.05650000	-1.59961400	-0.74800700
H	0.69175700	-2.32031900	-1.05869100
N	-0.61178000	0.71894400	-0.09198300
P	1.93026500	-0.13367200	0.45794800
O	2.43032600	1.39558000	0.59538200
O	2.96549000	-0.83090600	-0.59494800
C	2.84706100	2.19426500	-0.52227800
H	3.44275700	3.01196500	-0.11287700
H	3.45708000	1.61202400	-1.21931500

H	1.97204100	2.60179000	-1.03363600
C	4.15227700	-1.46447400	-0.07756200
H	4.89738600	-0.71262300	0.20116600
H	3.90981000	-2.07532300	0.79496600
H	4.54784600	-2.08954900	-0.87964000
O	1.81662400	-0.79243100	1.77774100
H	0.73461200	0.18730100	-1.63019200
O	-0.38428000	2.05490500	-0.48555300
H	-0.78930800	2.14309800	-1.37199800
	H_2O		
O	0.00000000	0.00000000	0.11918900
H	0.00000000	0.75928700	-0.47675500
H	0.00000000	-0.75928700	-0.47675500
	3a		
C	-4.49717900	-0.27360400	-0.05464900
C	-3.77271500	0.89470900	-0.11546700
C	-2.35474700	0.85598700	-0.08480100
C	-1.69569700	-0.41975500	0.01212300
C	-2.47131200	-1.60770800	0.07436700
C	-3.84344600	-1.53059900	0.04045700
H	-2.02168900	2.99326500	-0.21631700
H	-5.58149400	-0.23949500	-0.07925800
H	-4.27381200	1.85514300	-0.18807000
C	-1.54911600	2.01805400	-0.14450900
H	-1.95221100	-2.55717200	0.14672800
H	-4.43879600	-2.43664400	0.08679500
C	0.36280700	0.60531200	-0.01271100
C	-0.17487700	1.90946600	-0.11260000
H	0.46997300	2.77880100	-0.15716400
N	-0.34008900	-0.51874400	0.04900700
P	2.12038600	0.26495300	-0.03501800
O	2.69035100	-0.24046700	-1.40982800
O	2.53666500	-0.83771900	1.00616800
C	2.48312700	-1.59307700	-1.94086600
H	2.97319900	-1.59077900	-2.91185200
H	2.94738200	-2.31634100	-1.27097300
H	1.41451500	-1.78281700	-2.04579200
C	2.02805400	-0.94052800	2.37607000
H	2.60706100	-1.74037400	2.83266100
H	2.19554400	-0.00254800	2.90787300
H	0.96975700	-1.19727200	2.34095800
O	2.82380800	1.66157000	0.21760000
H	3.76943000	1.71653800	0.00062900

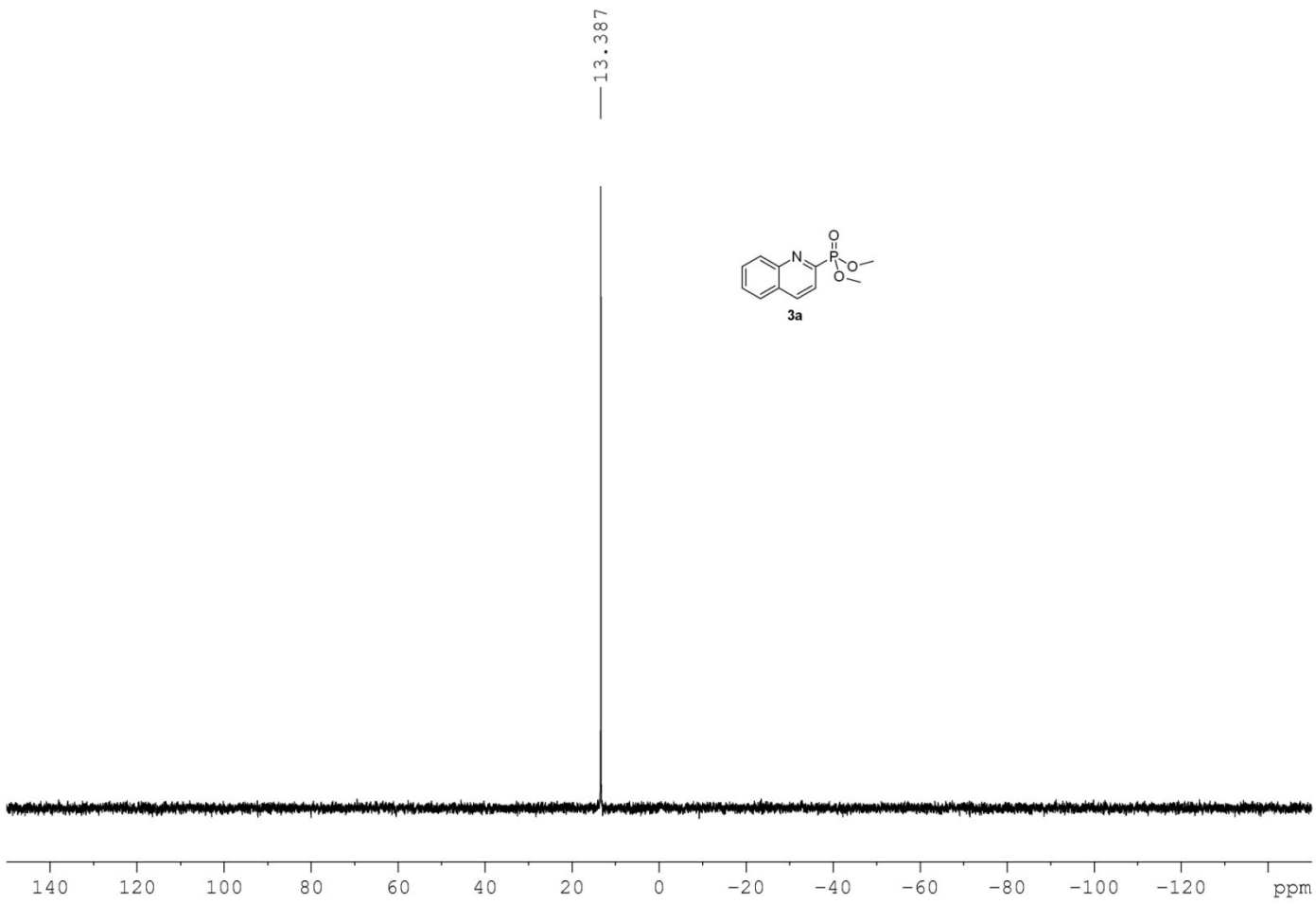
VI. ^{1}H, ^{13}C and ^{31}P NMR spectra of products.



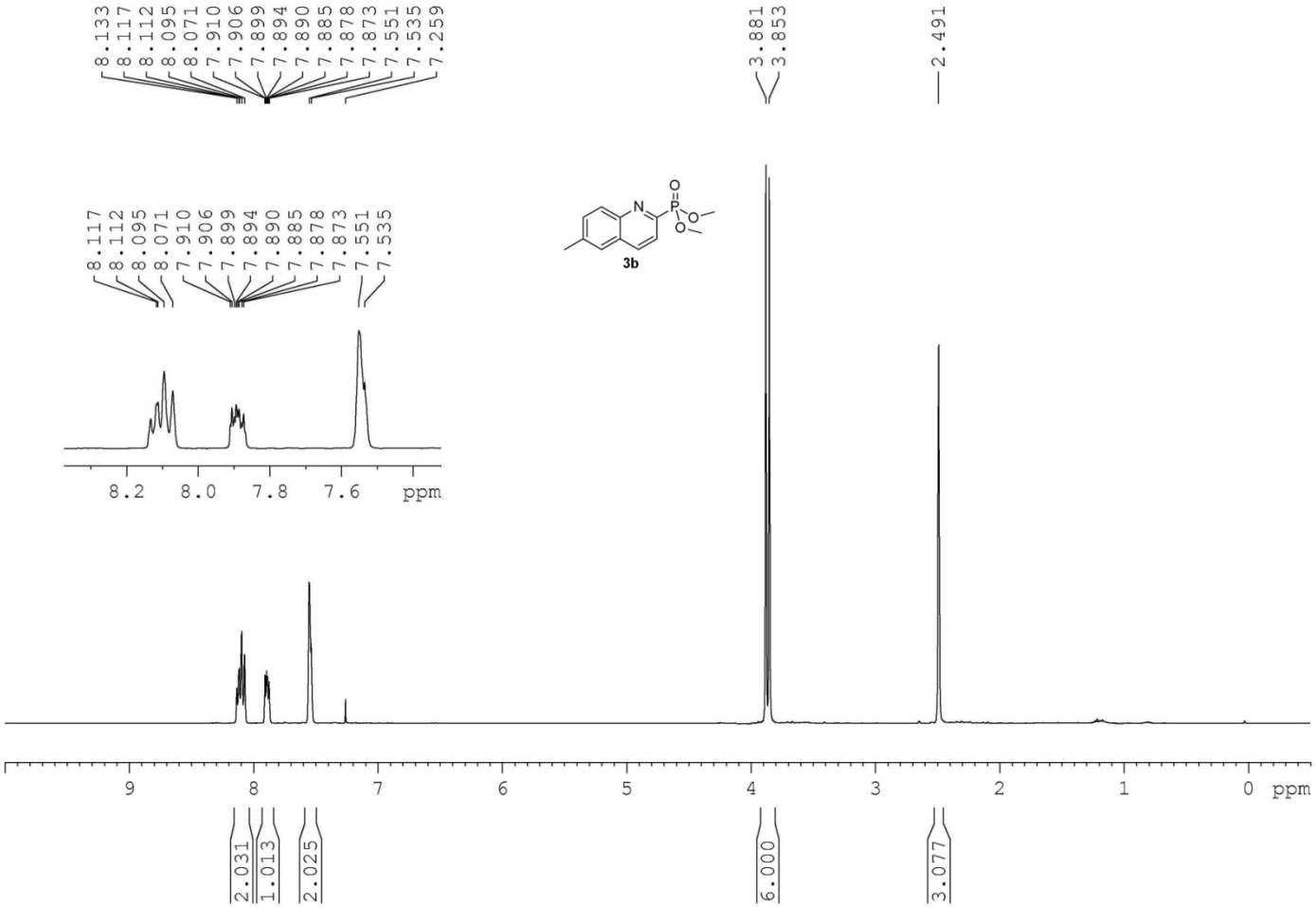
^{1}H NMR spectrum of compound **3a**



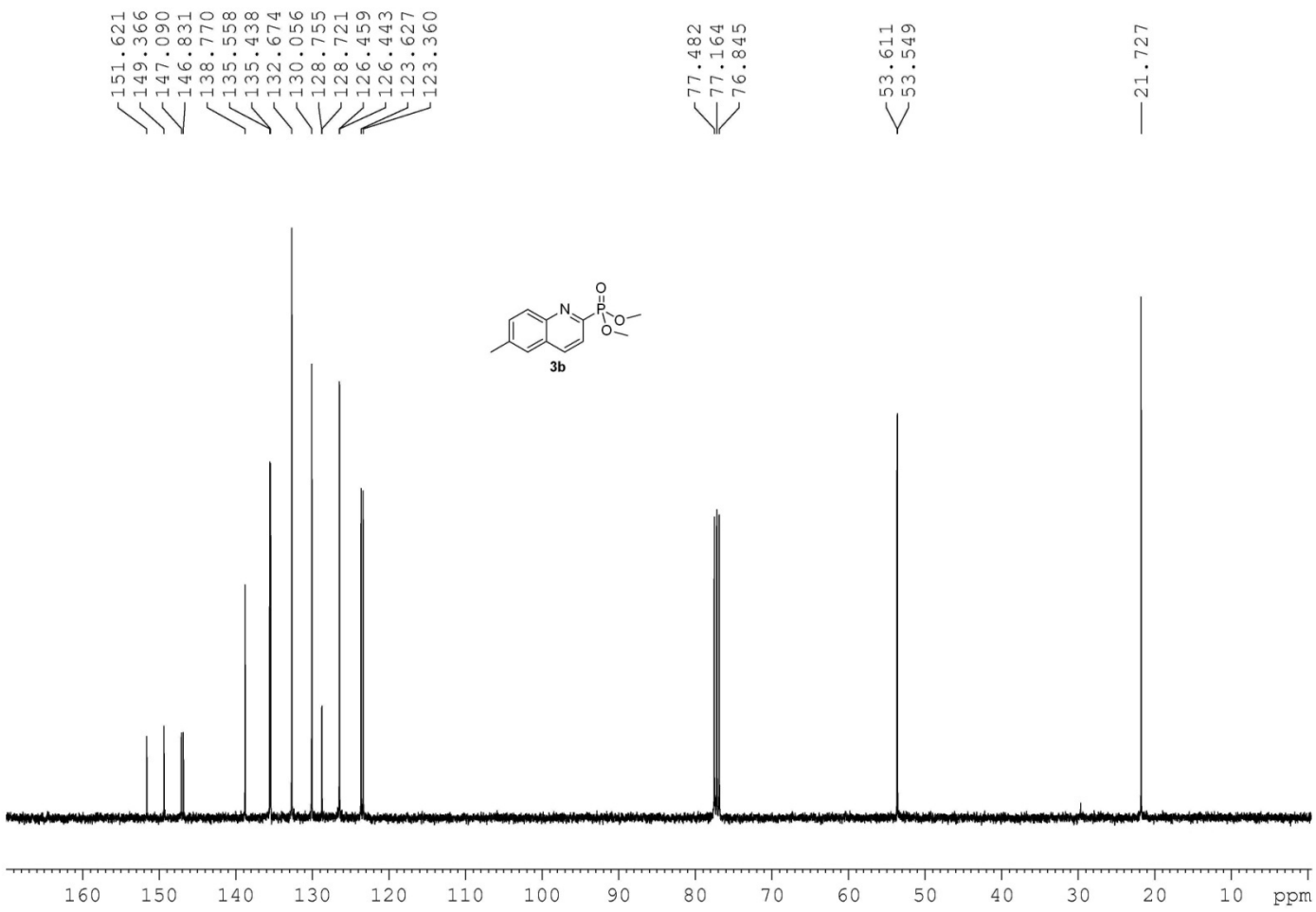
^{13}C NMR spectrum of compound **3a**



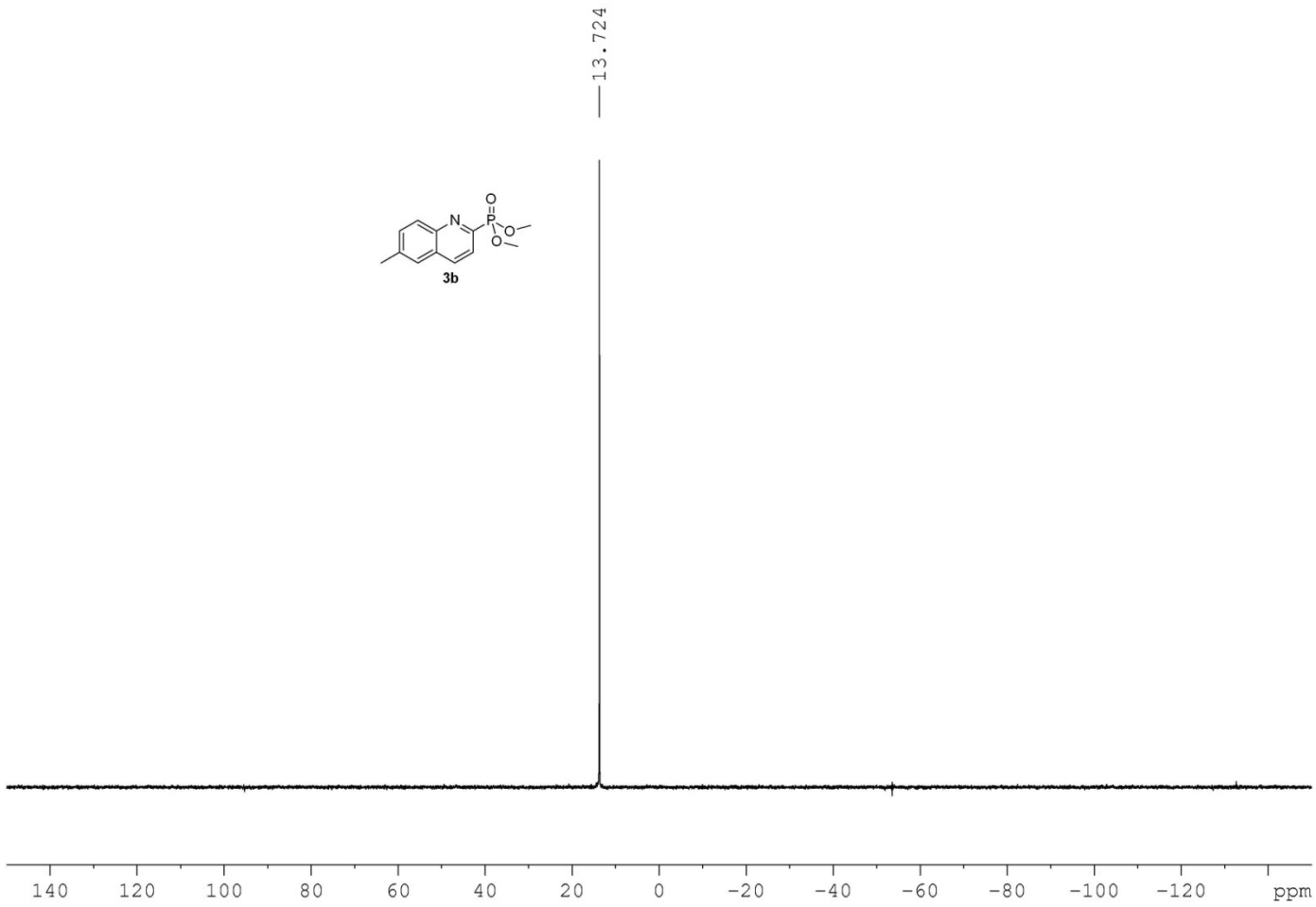
^{31}P NMR spectrum of compound **3a**



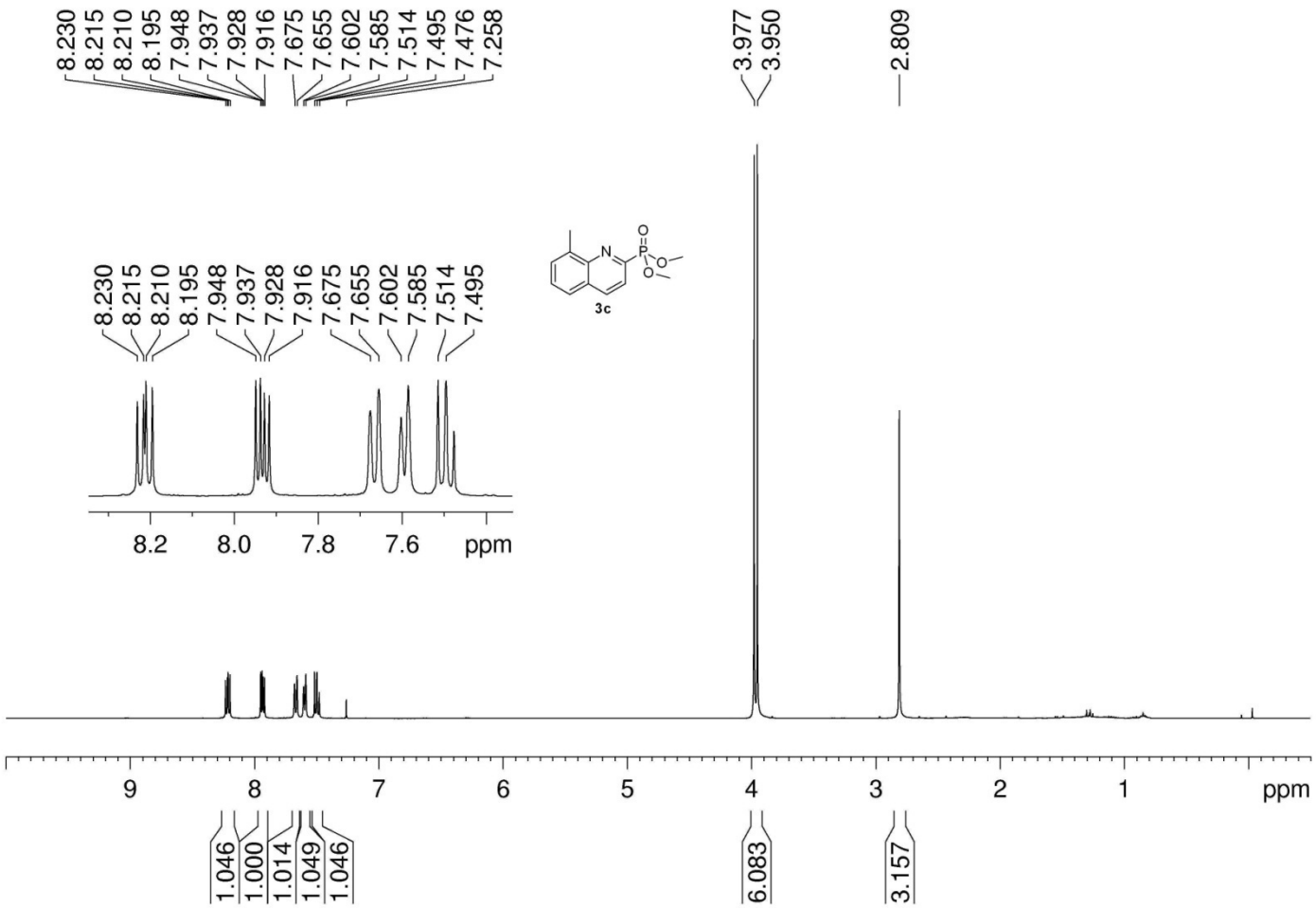
^{1}H NMR spectrum of compound **3b**



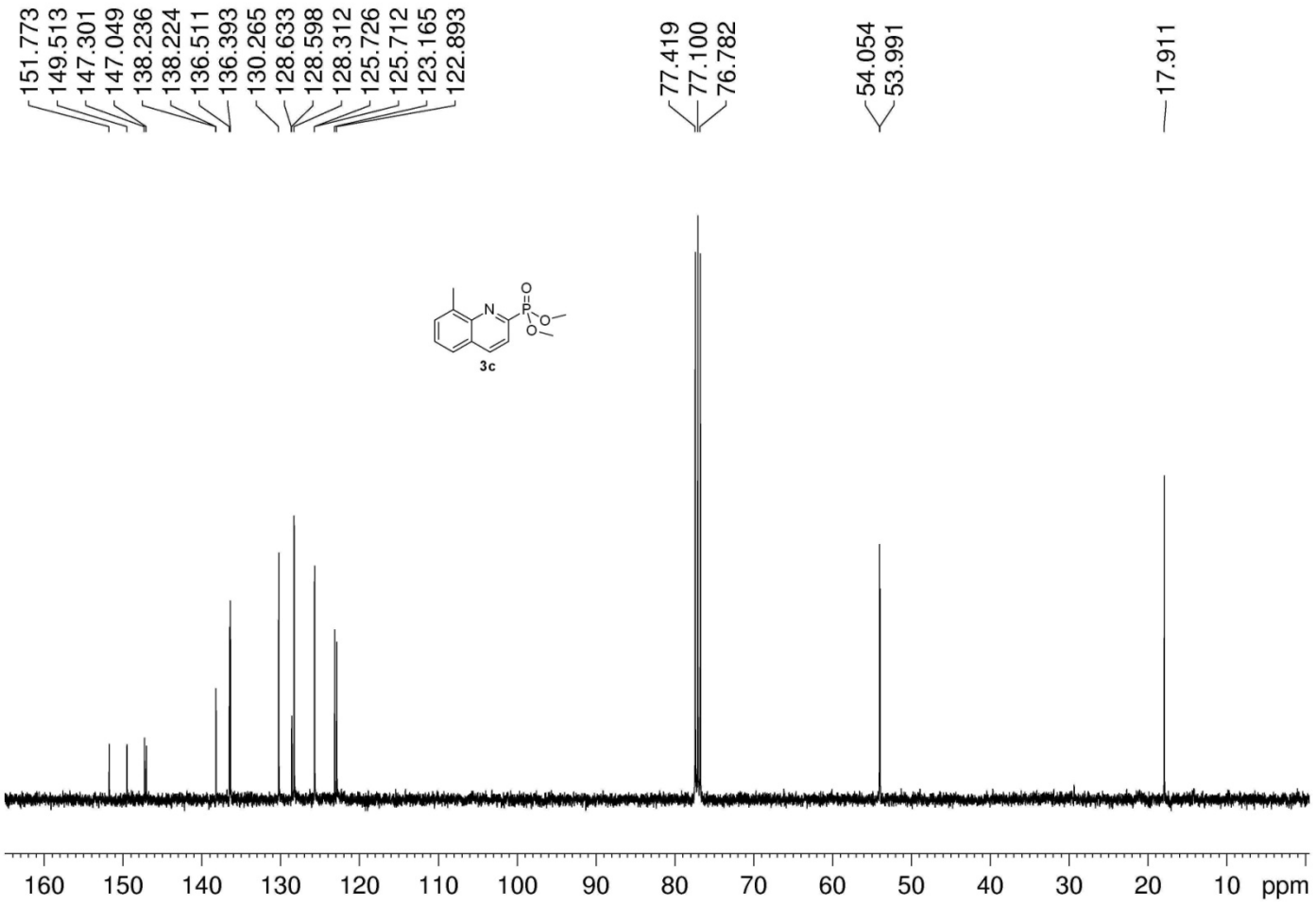
^{13}C NMR spectrum of compound **3b**



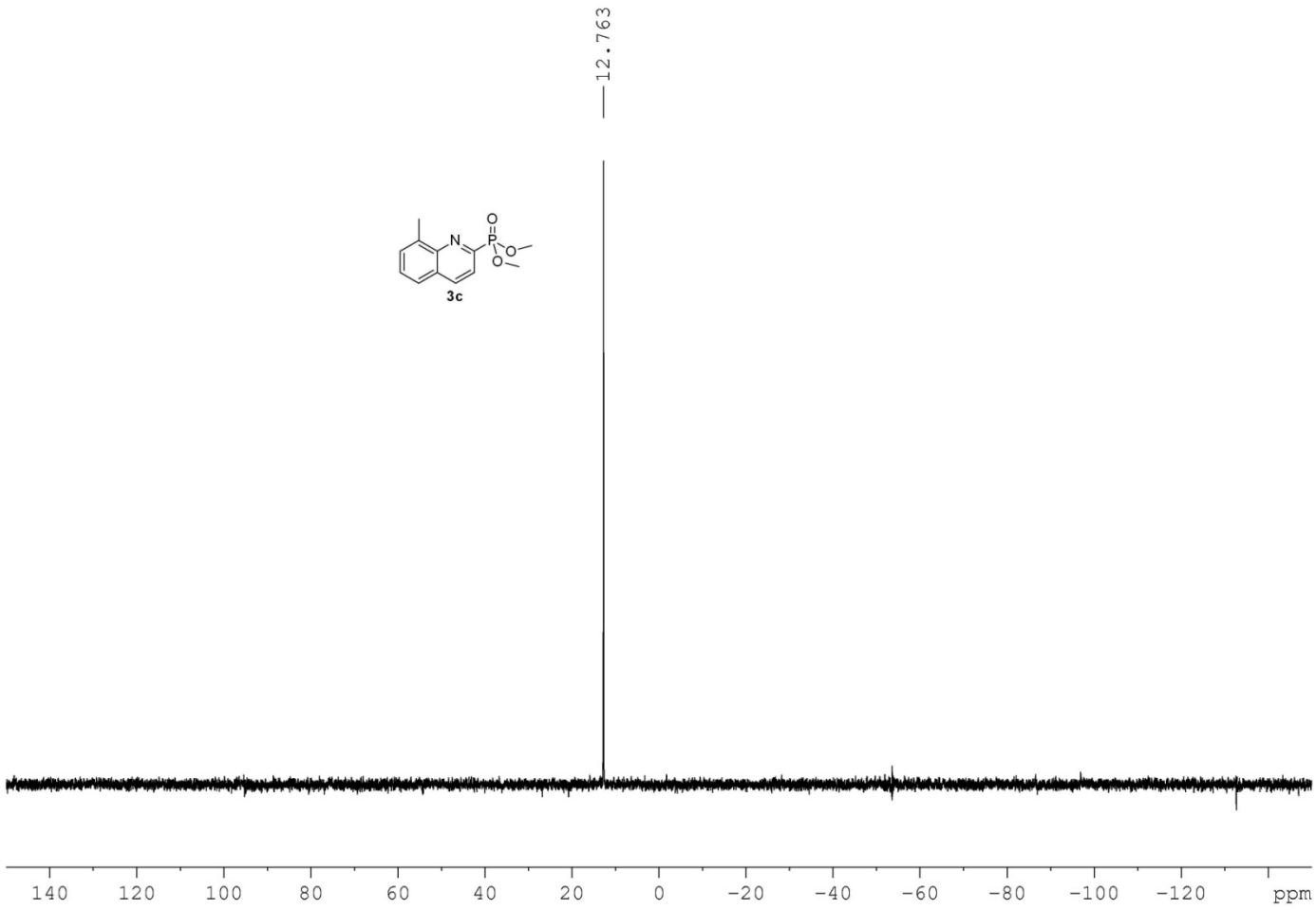
^{31}P NMR spectrum of compound **3b**



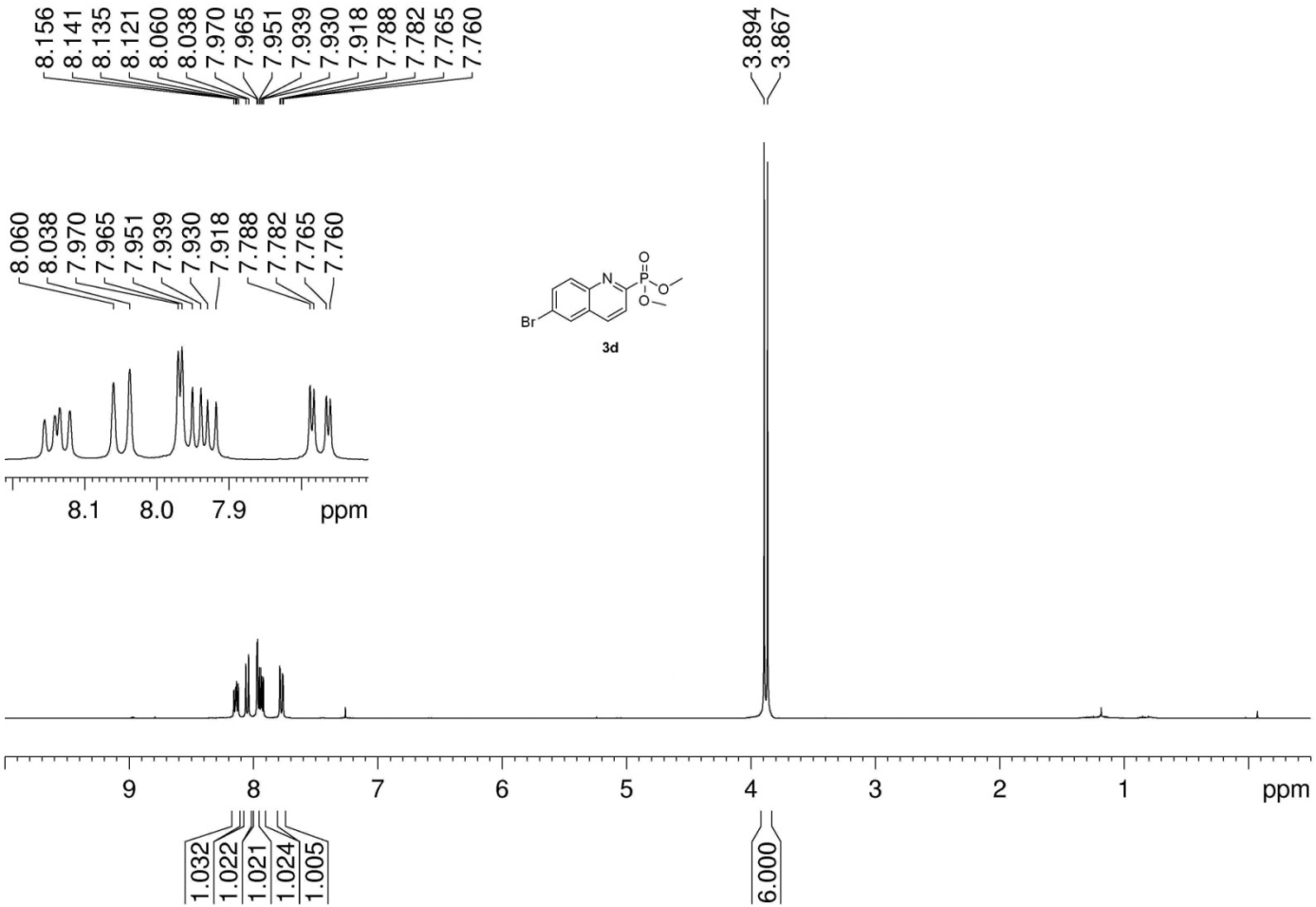
^{1}H NMR spectrum of compound **3c**



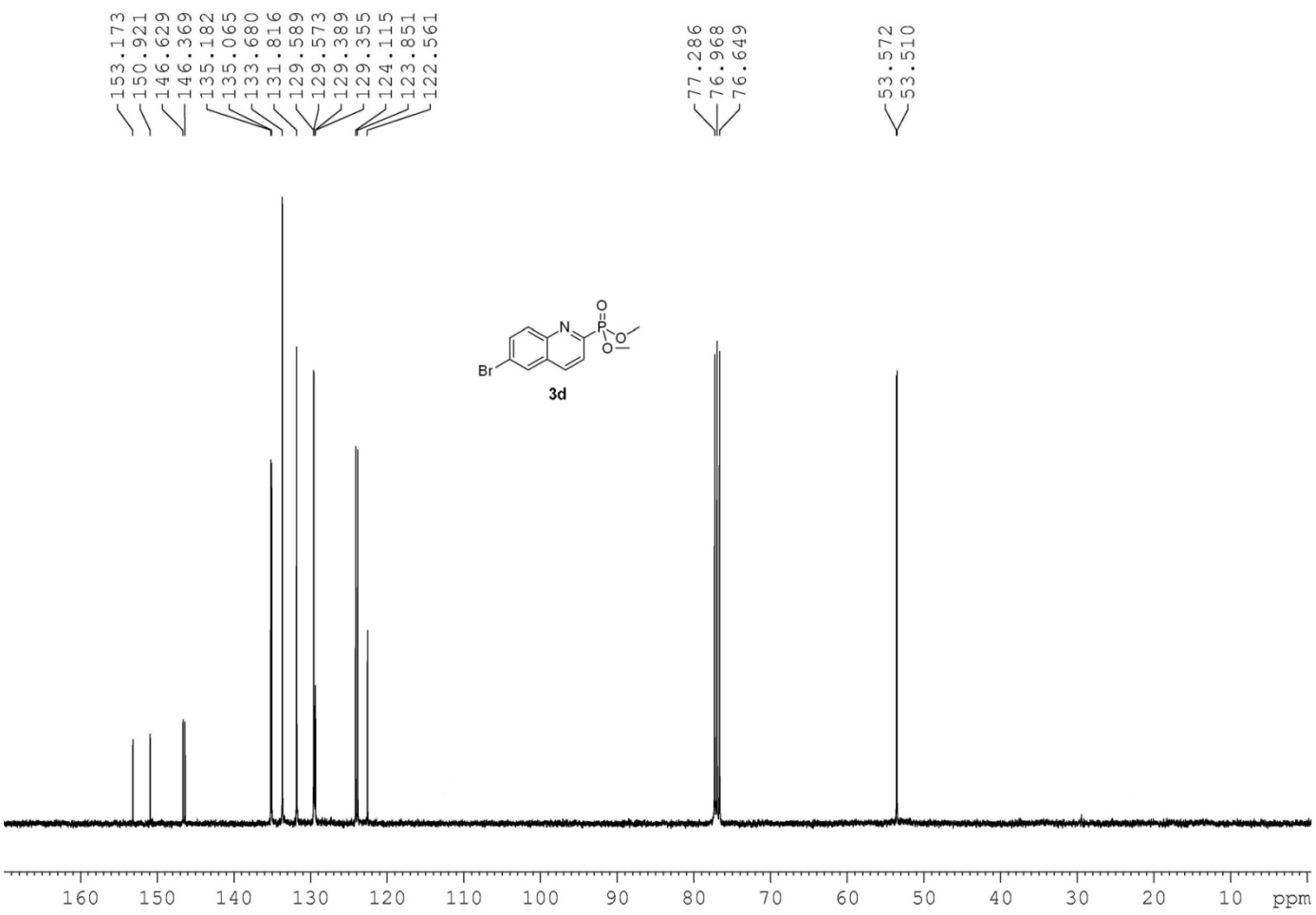
^{13}C NMR spectrum of compound **3c**



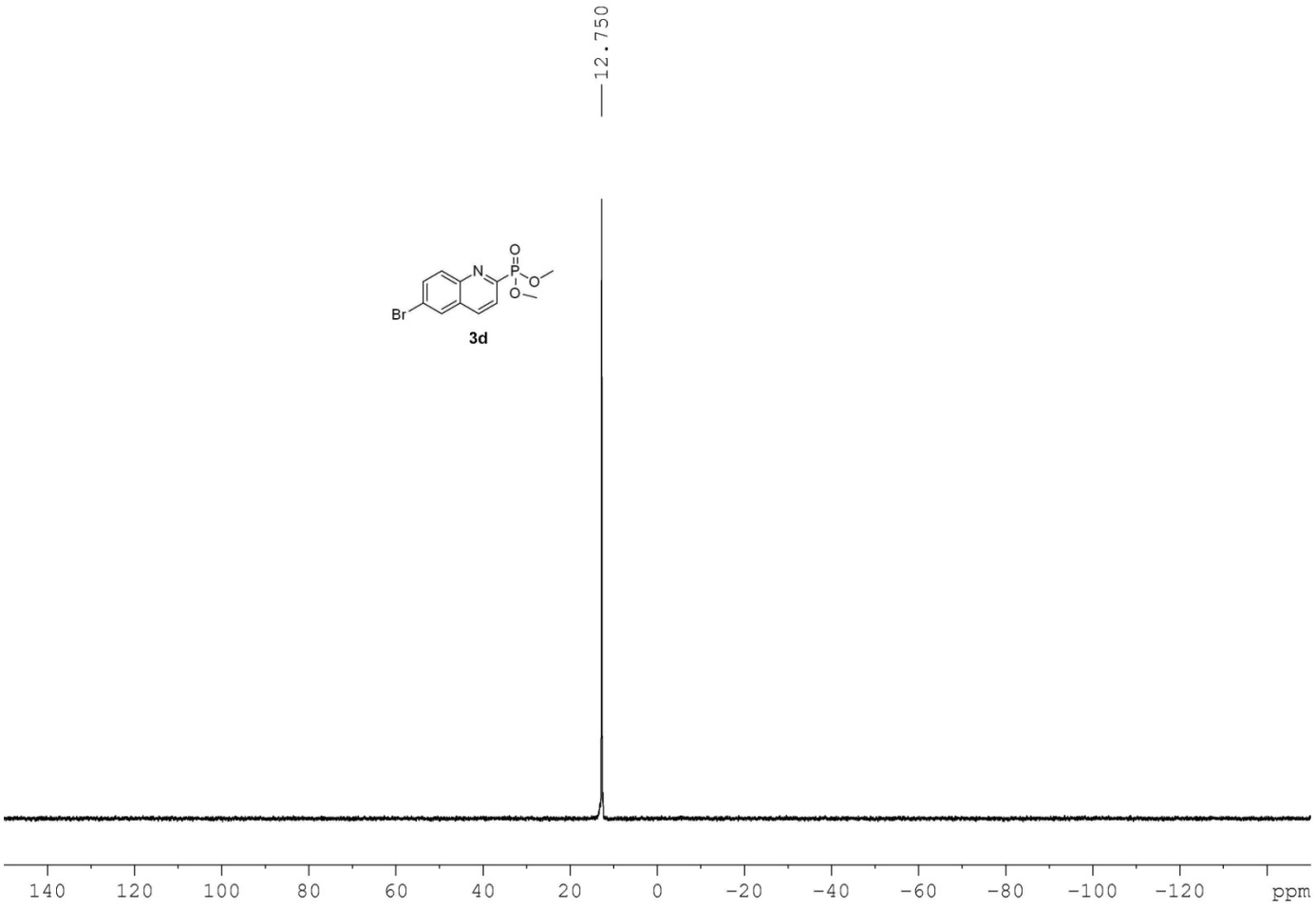
^{31}P NMR spectrum of compound **3c**



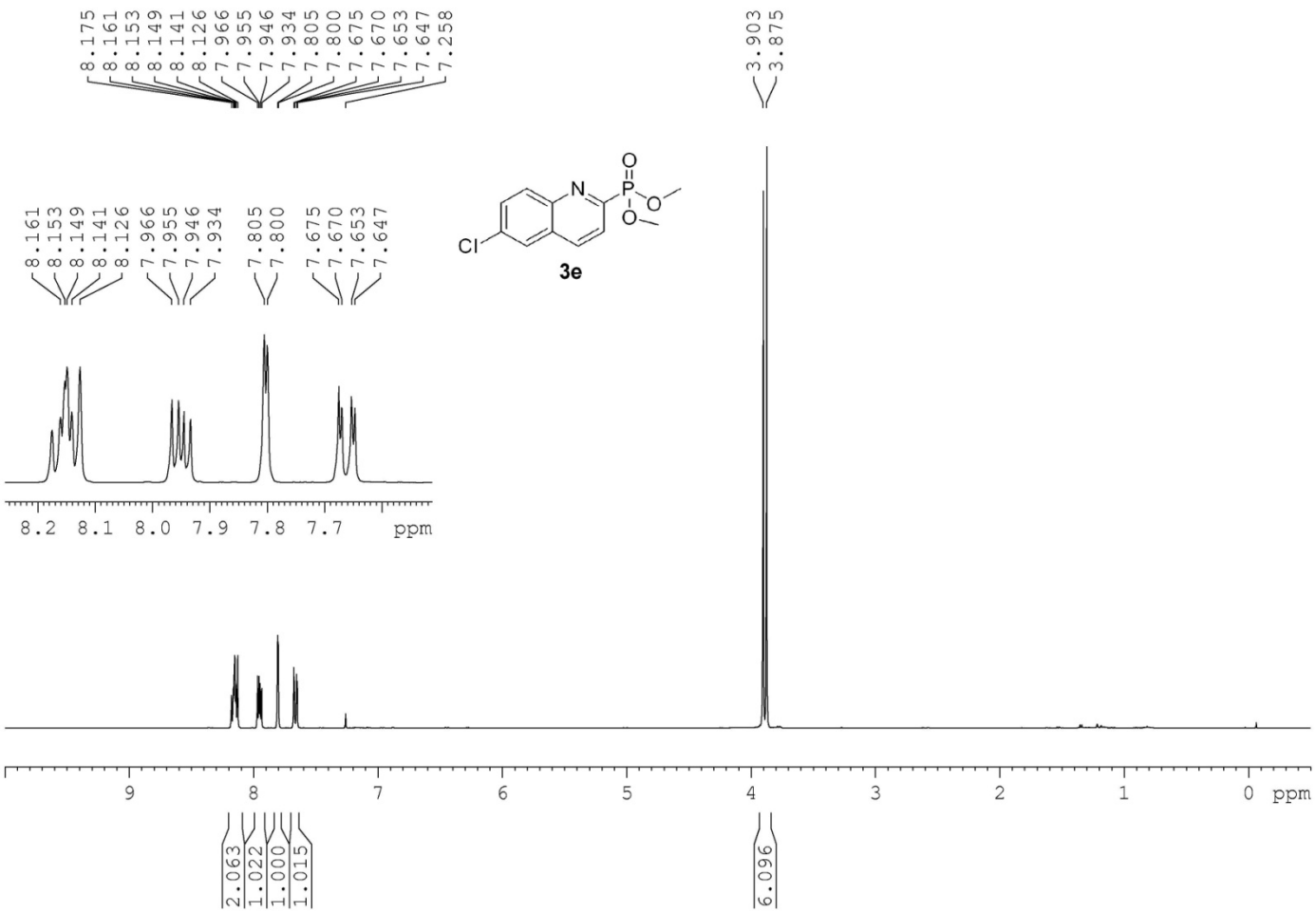
^{1}H NMR spectrum of compound **3d**



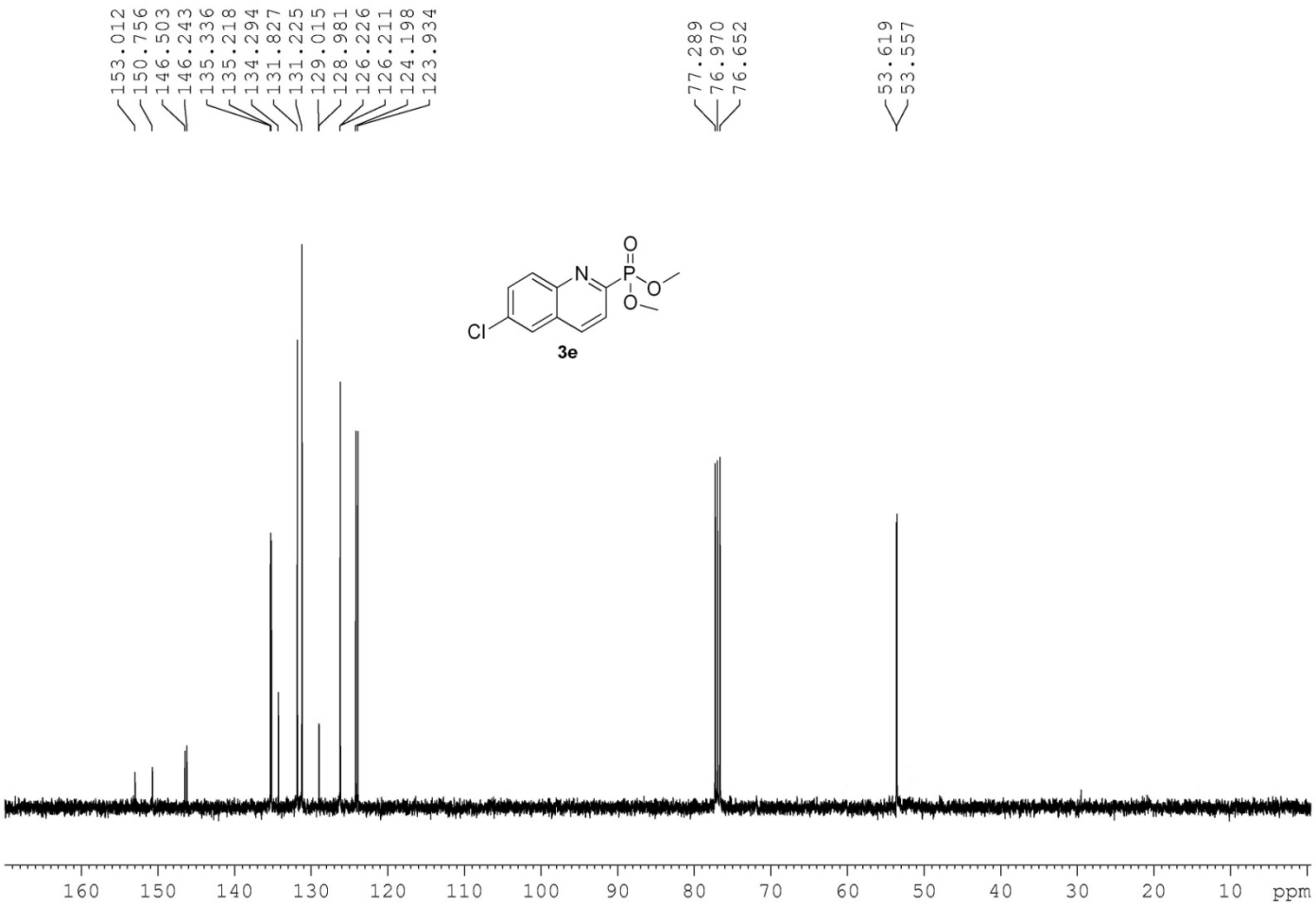
^{13}C NMR spectrum of compound **3d**



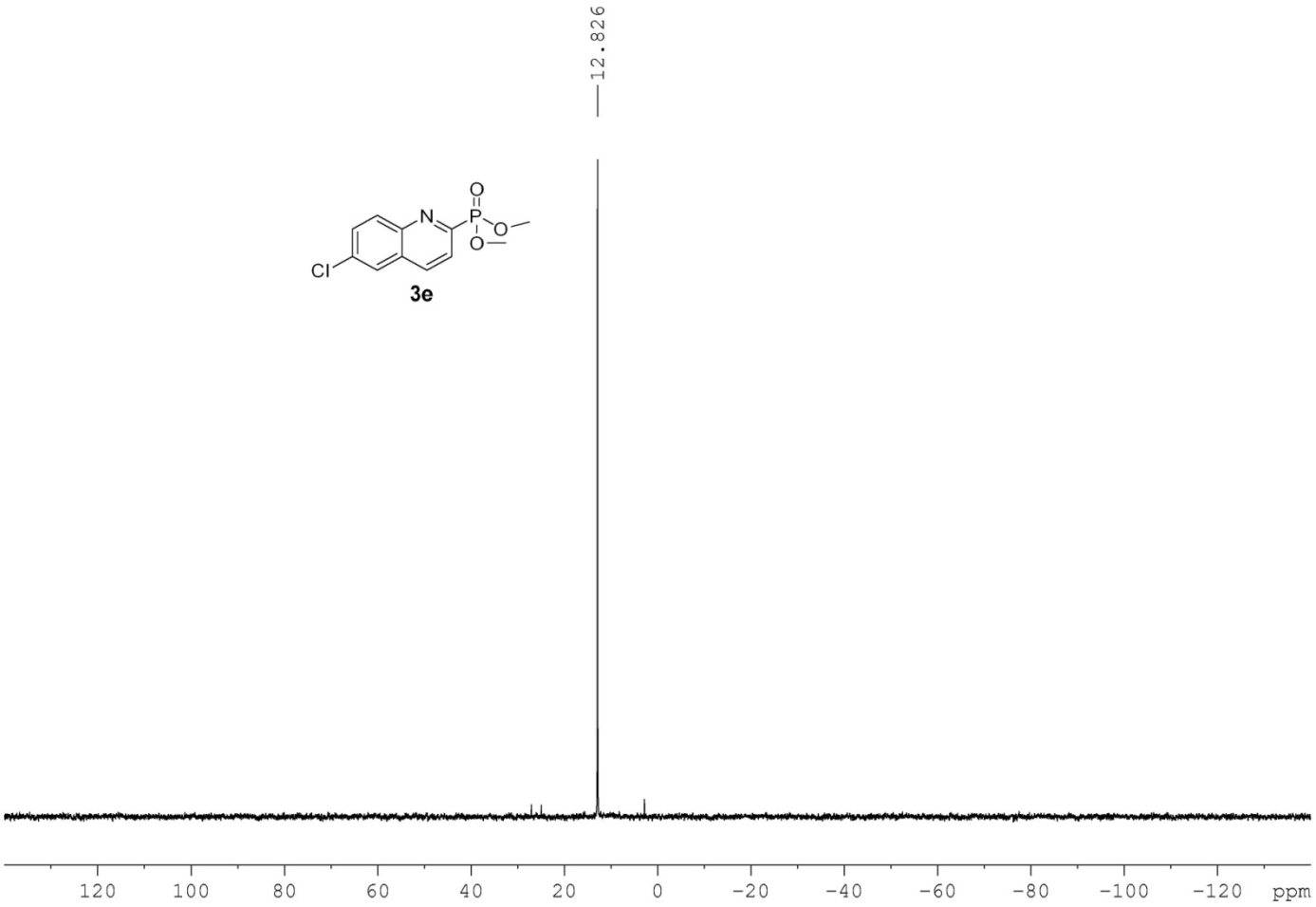
^{31}P NMR spectrum of compound **3d**



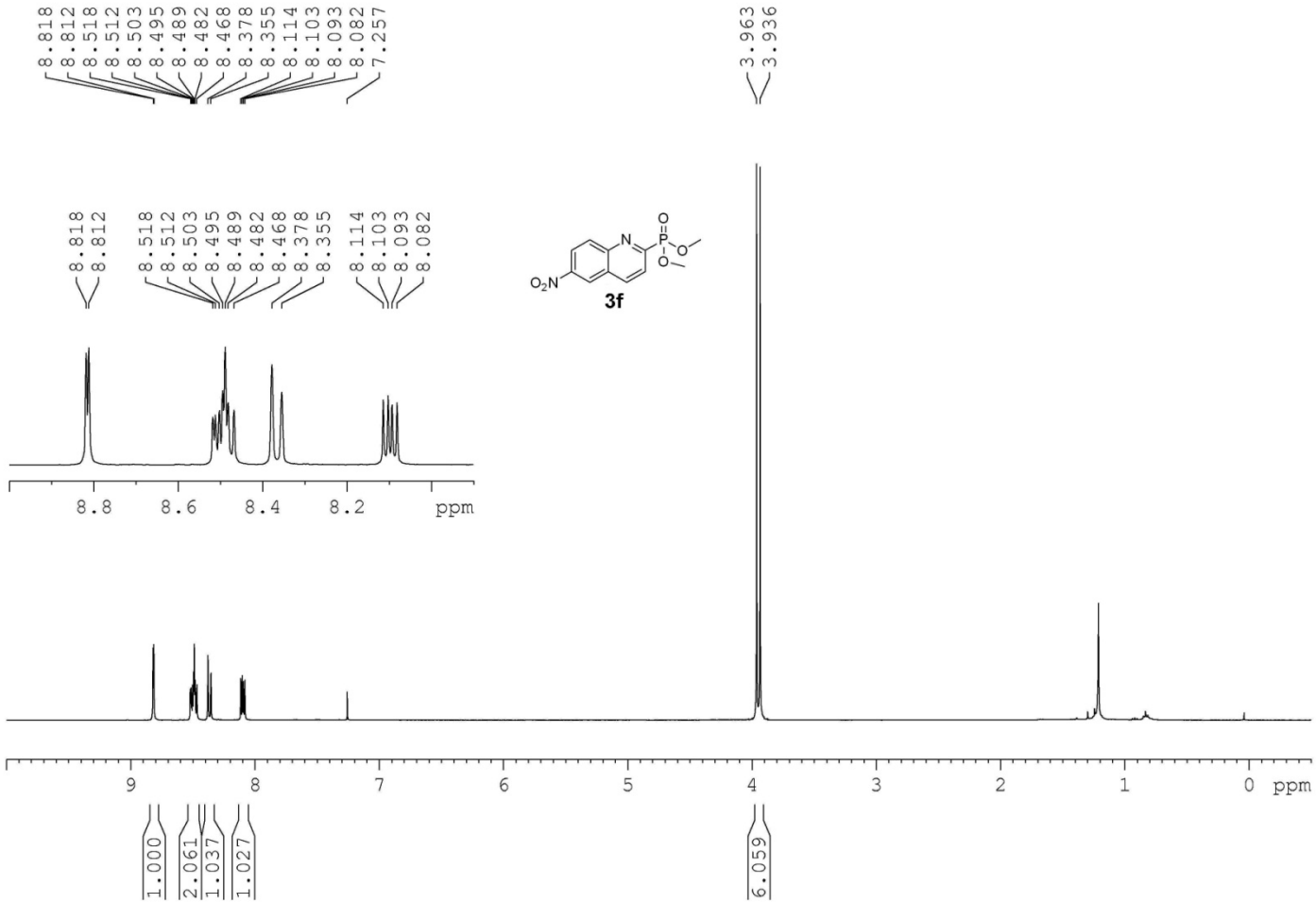
^{1}H NMR spectrum of compound **3e**



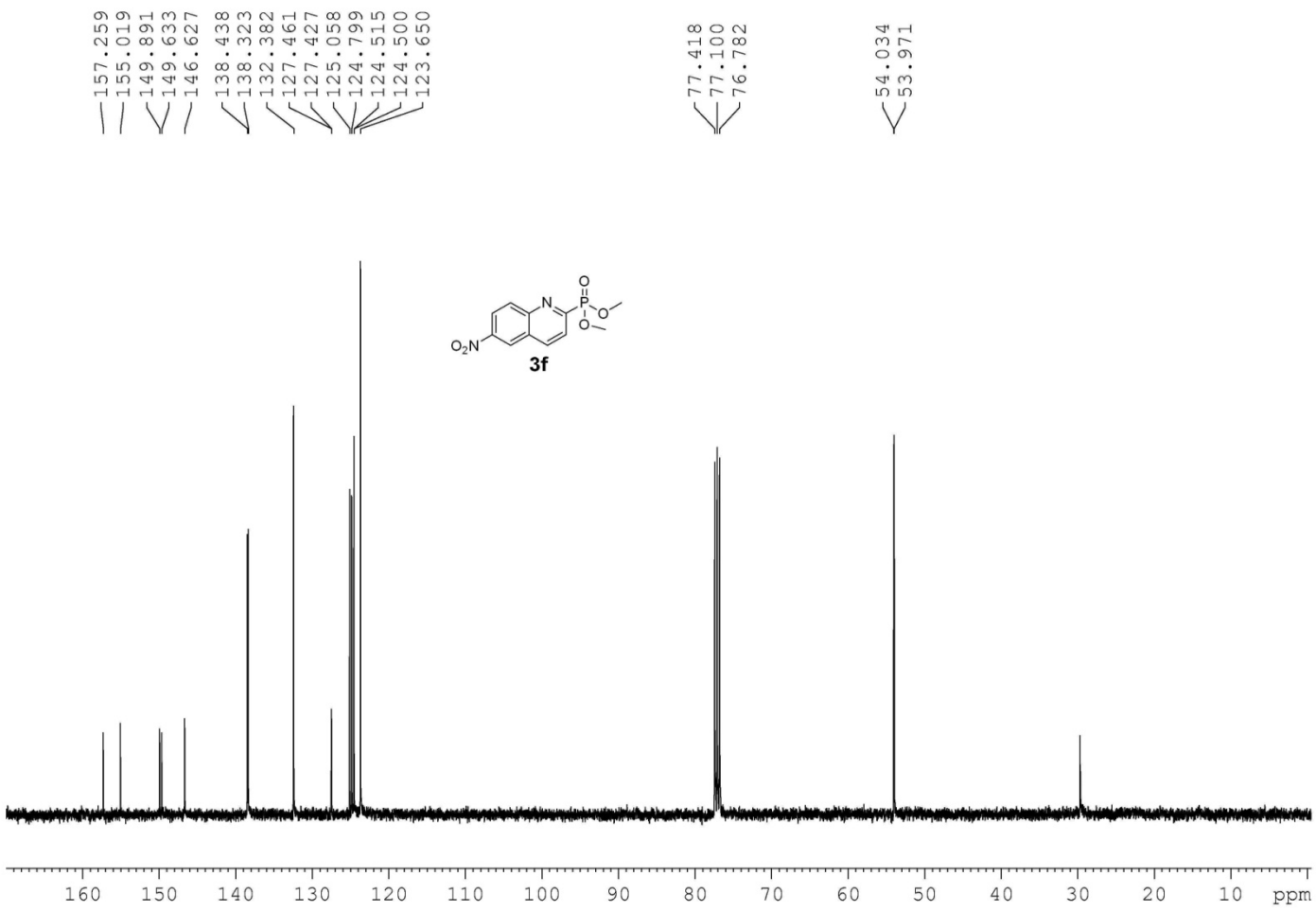
^{13}C NMR spectrum of compound **3e**



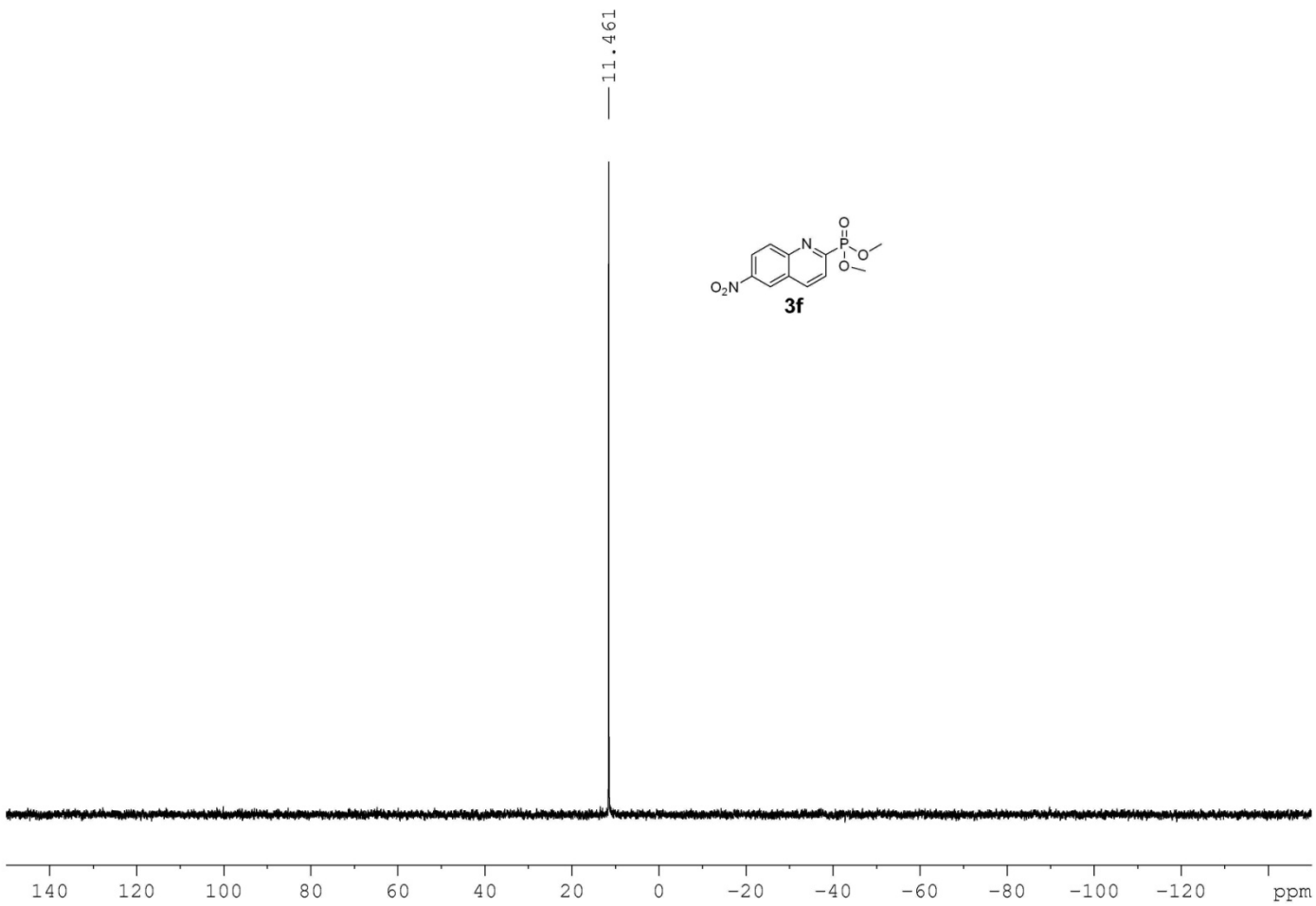
^{31}P NMR spectrum of compound **3e**



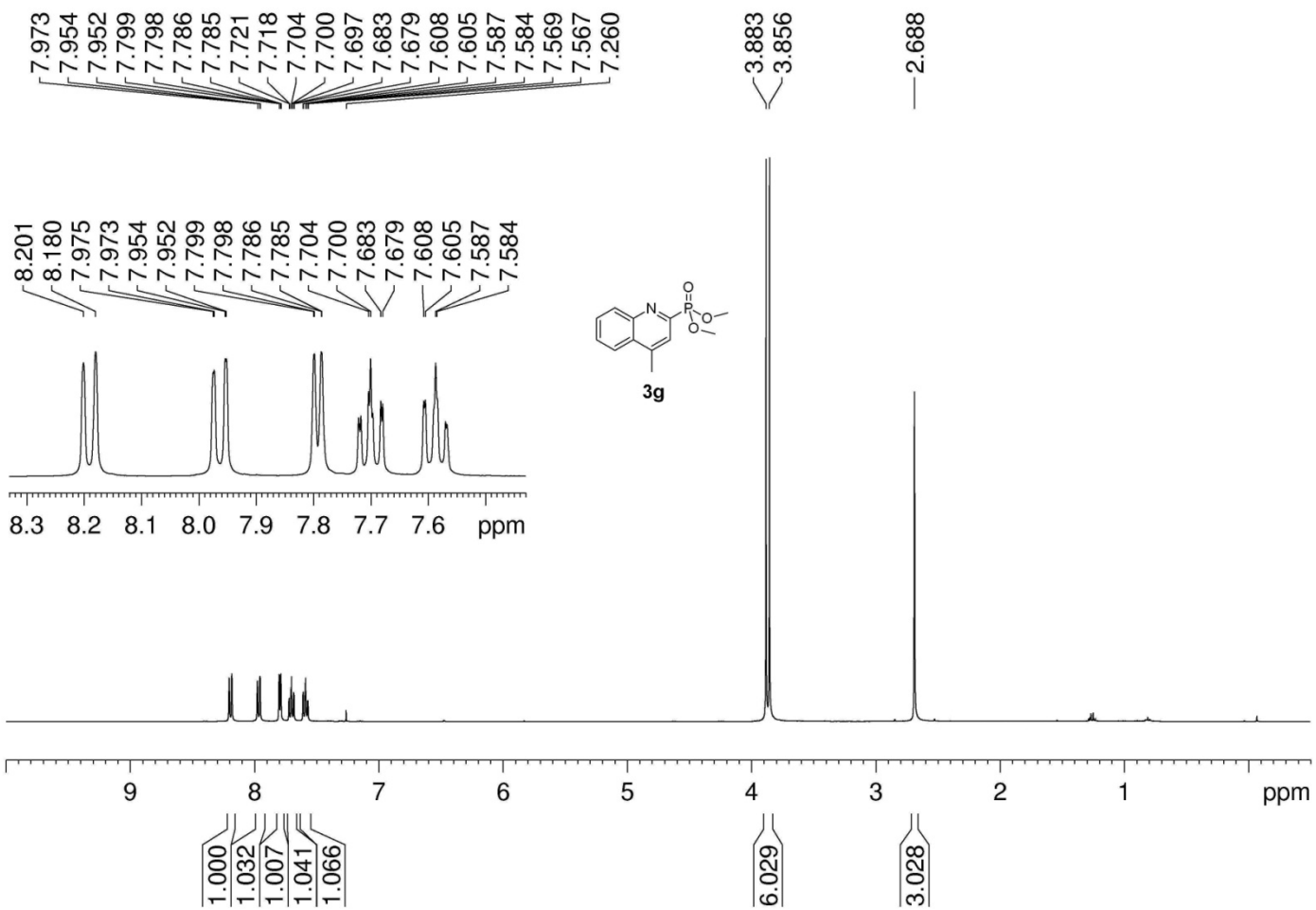
^{1}H NMR spectrum of compound **3f**



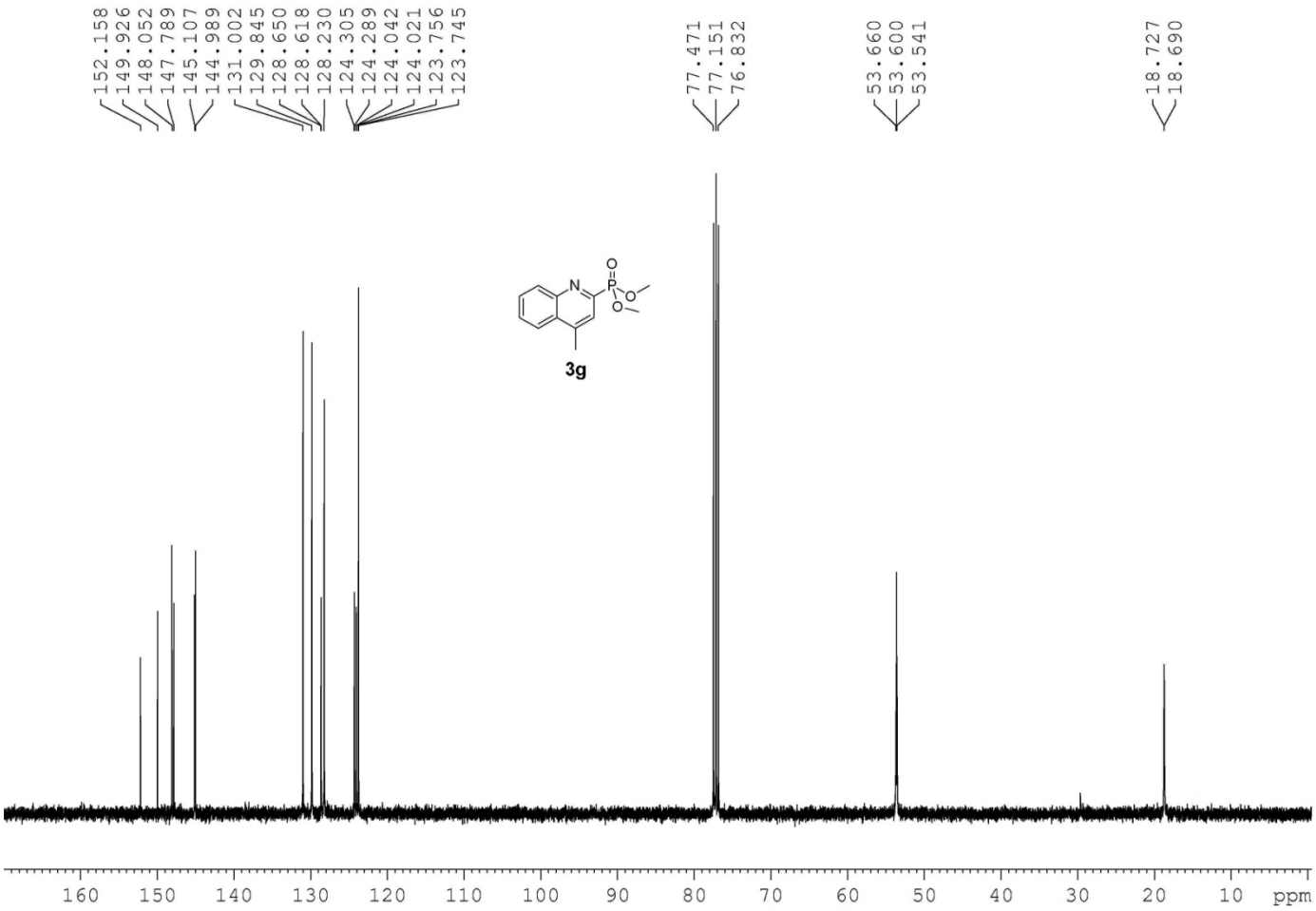
^{13}C NMR spectrum of compound **3f**



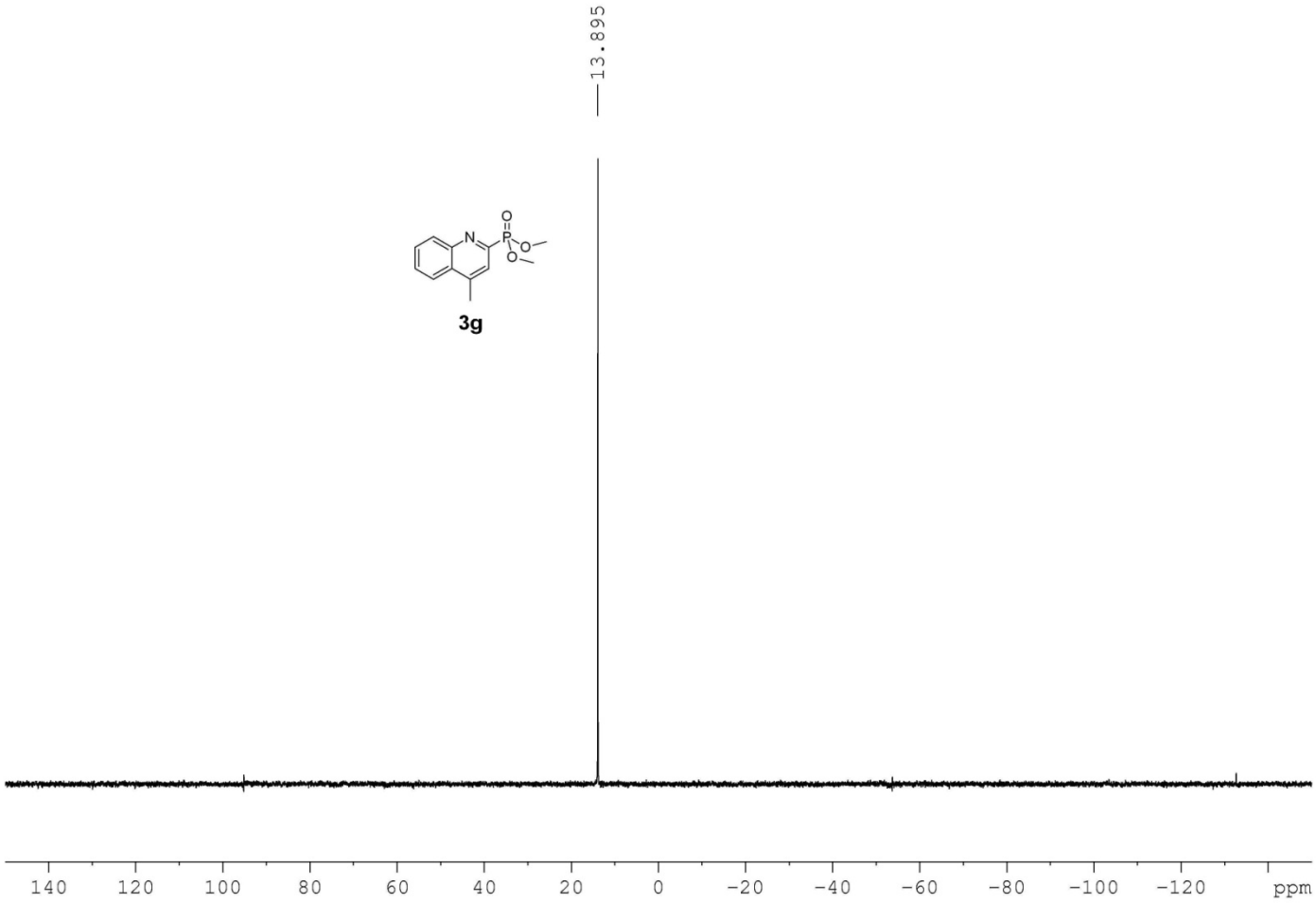
^{31}P NMR spectrum of compound **3f**



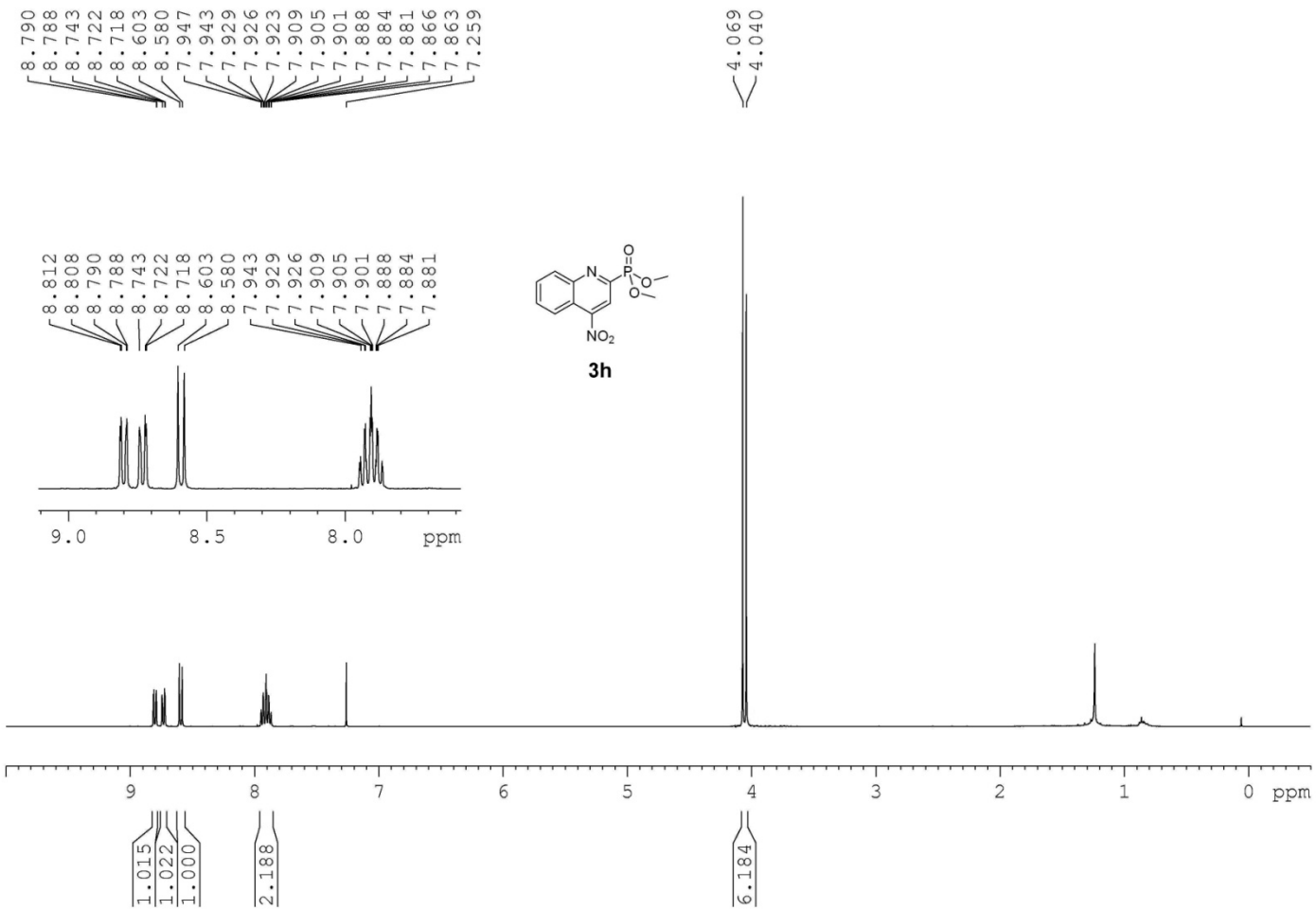
^{1}H NMR spectrum of compound **3g**



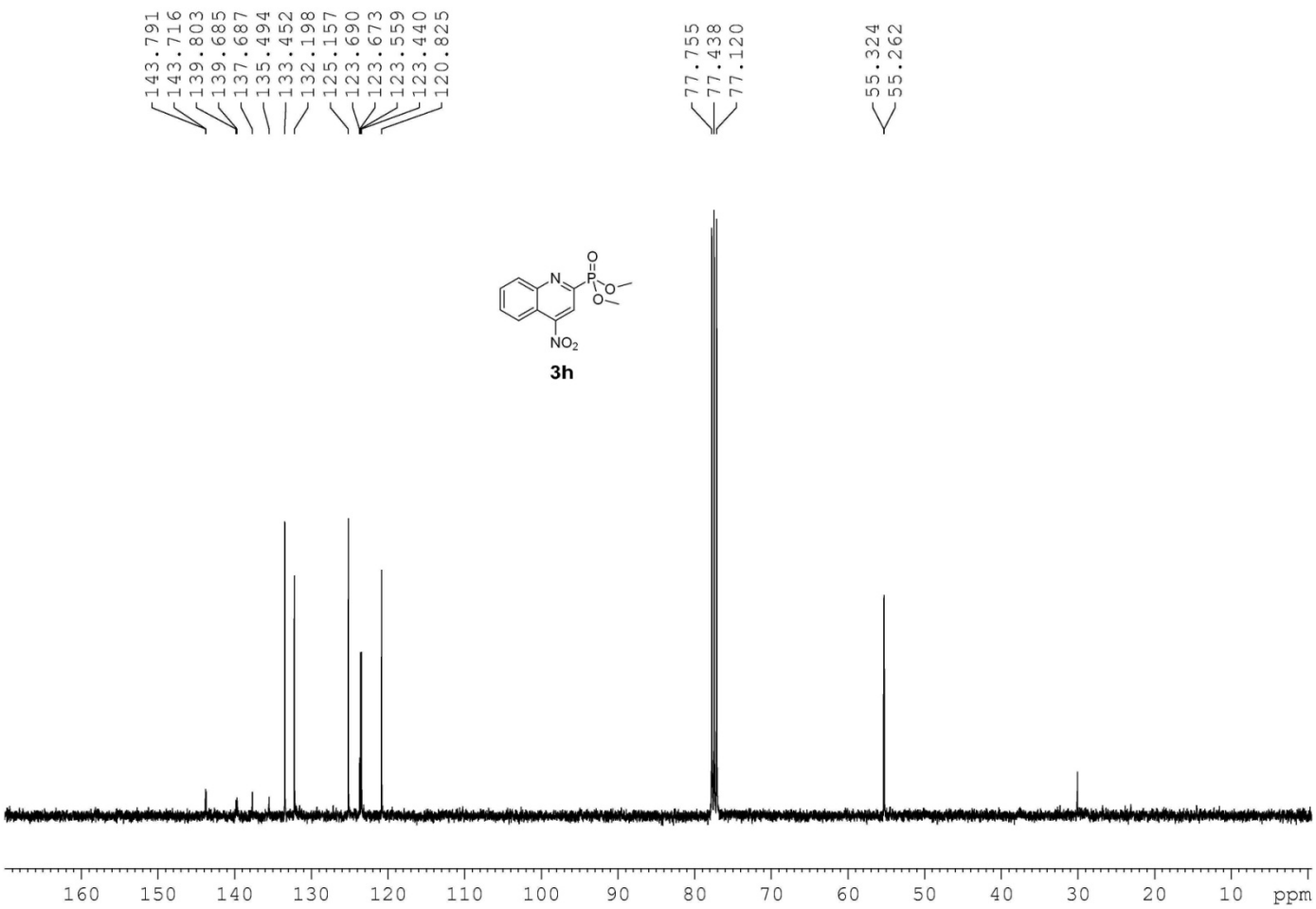
^{13}C NMR spectrum of compound **3g**



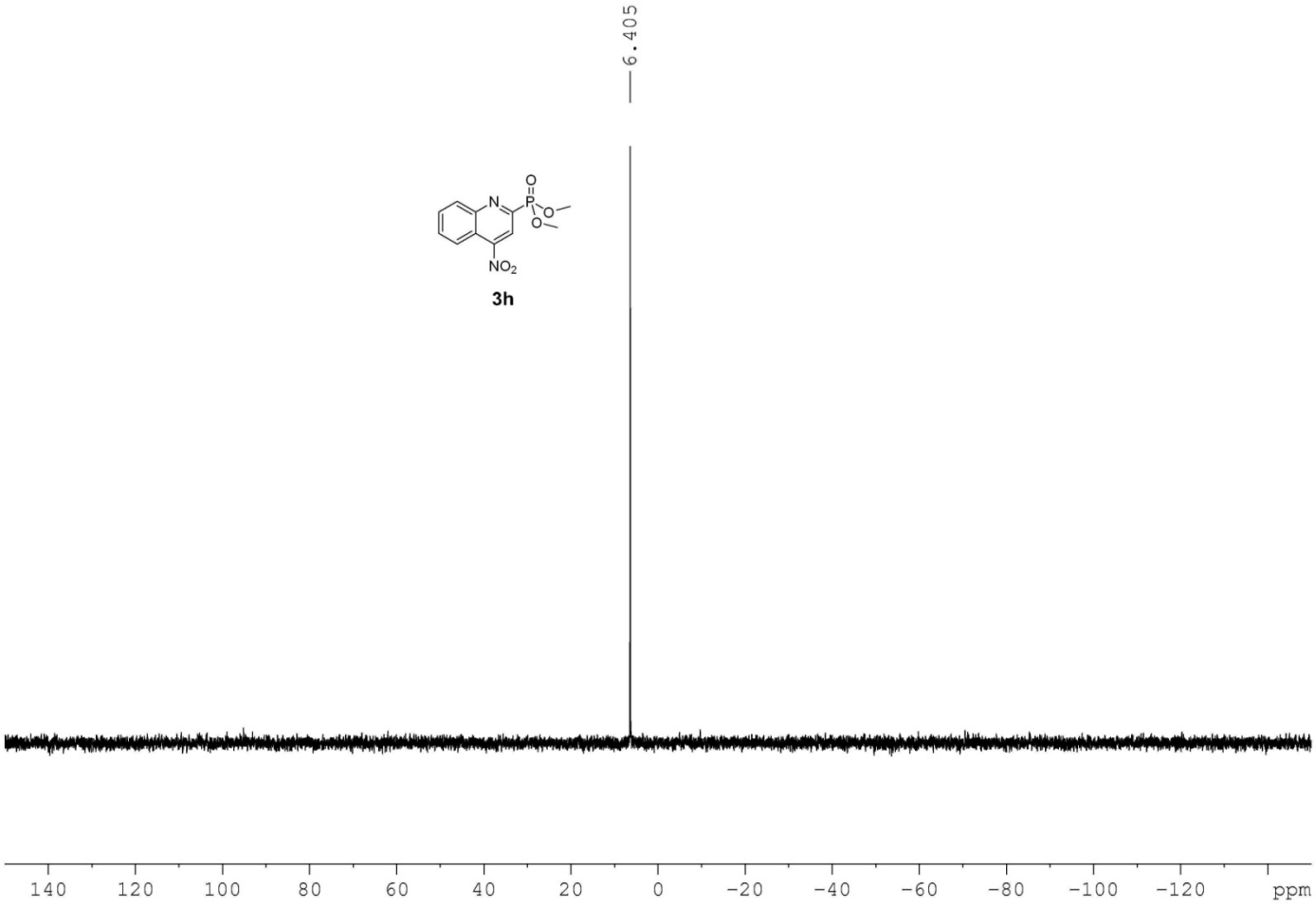
^{31}P NMR spectrum of compound **3g**



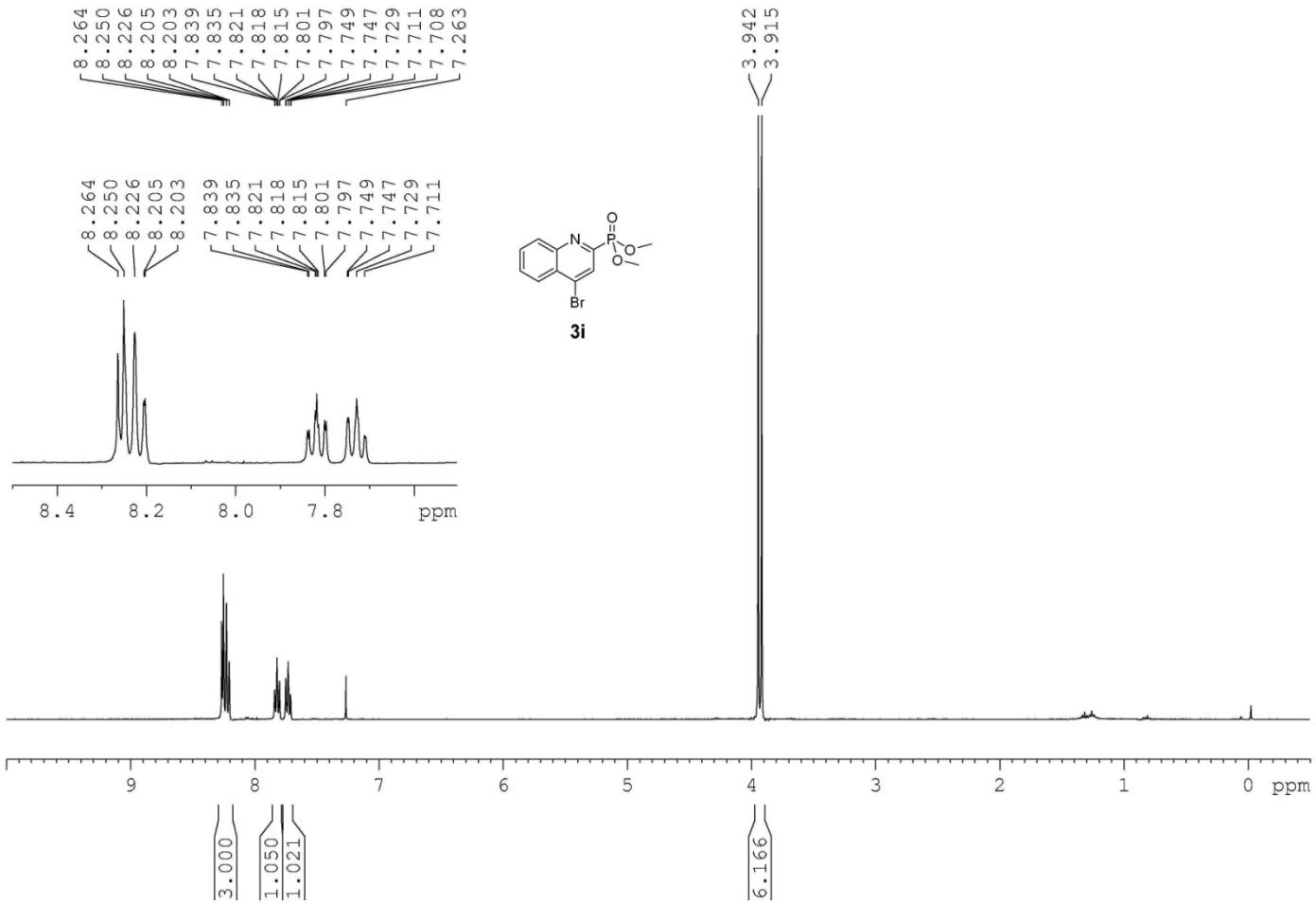
^{1}H NMR spectrum of compound **3h**



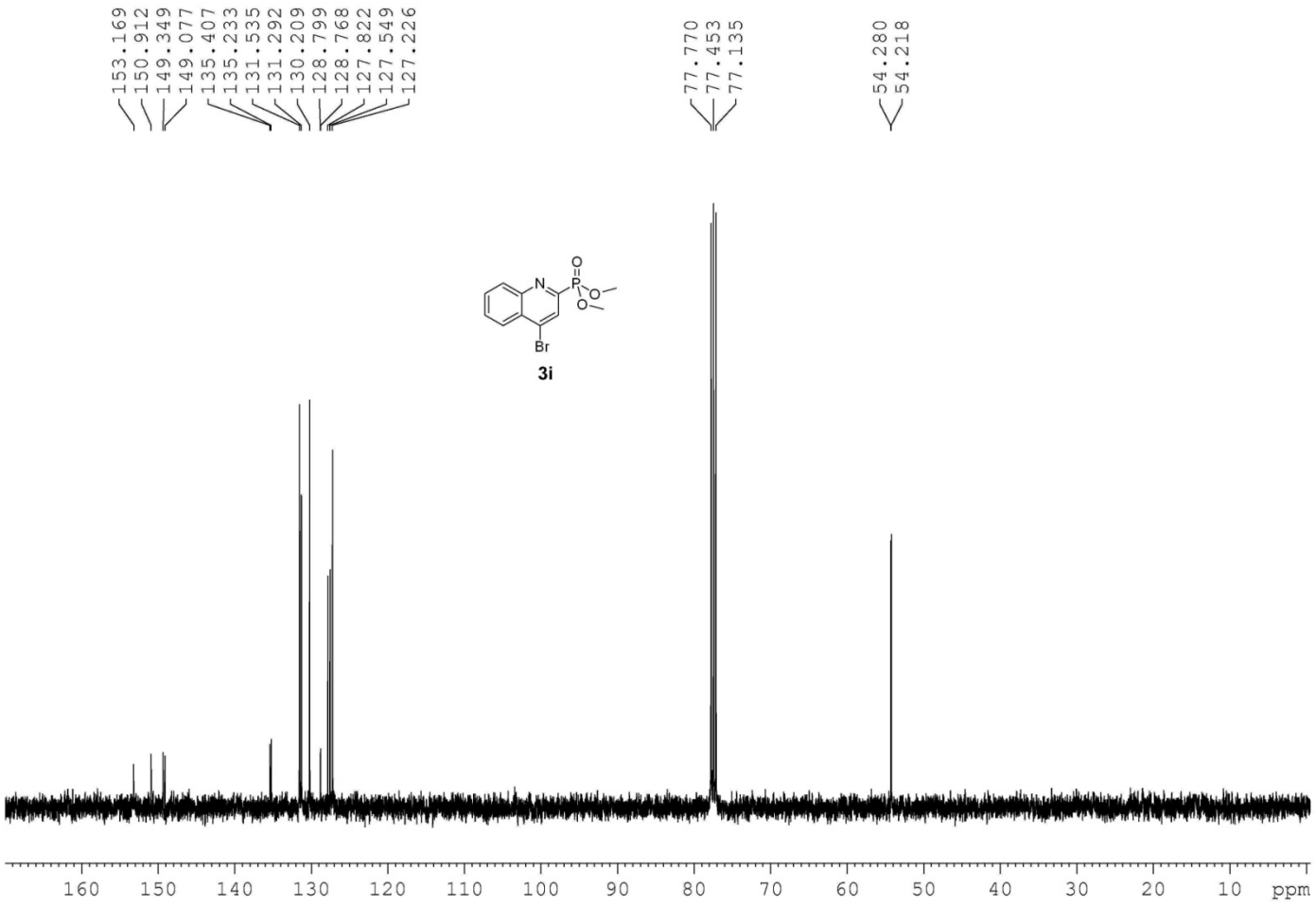
^{13}C NMR spectrum of compound **3h**



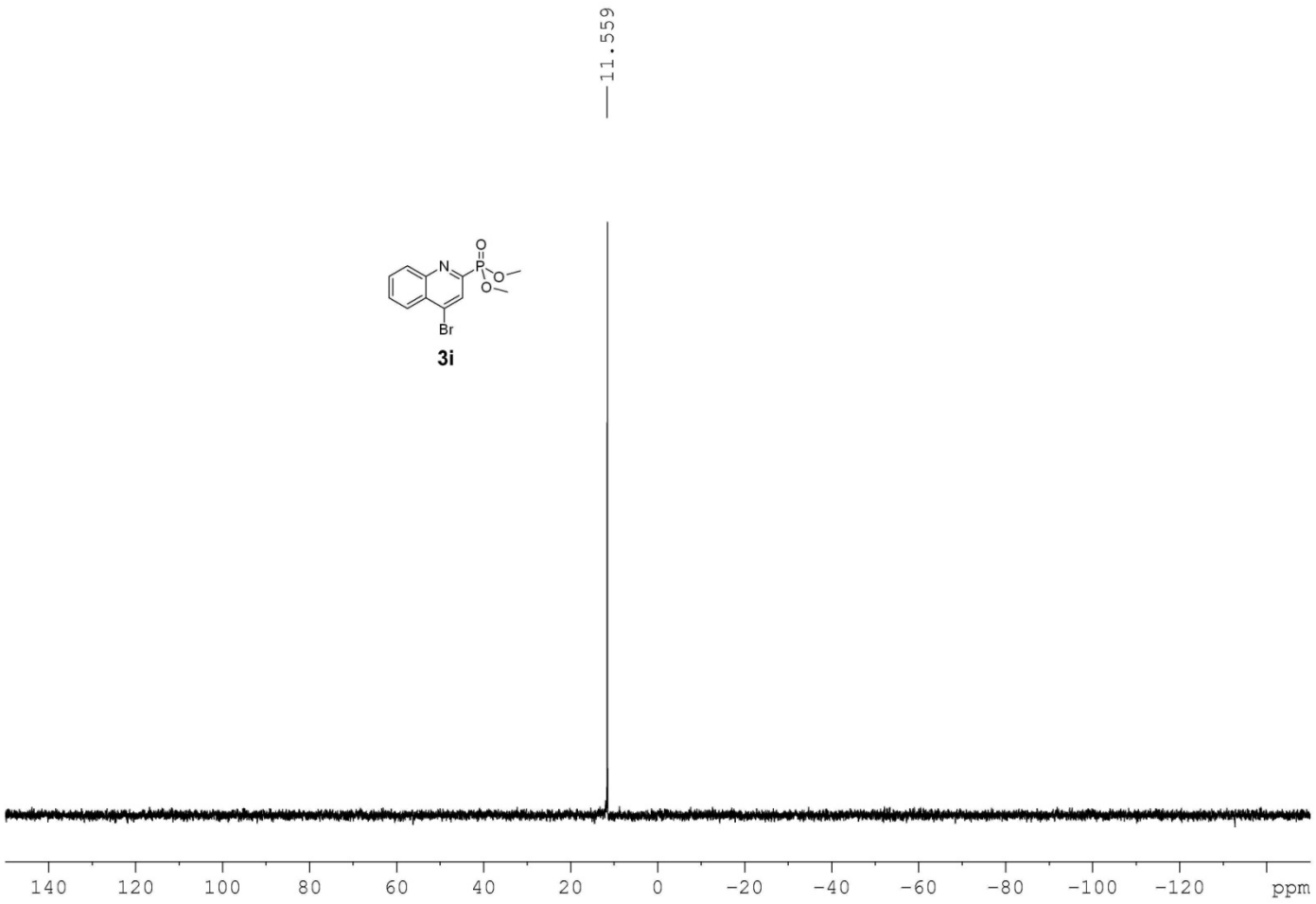
^{31}P NMR spectrum of compound **3h**



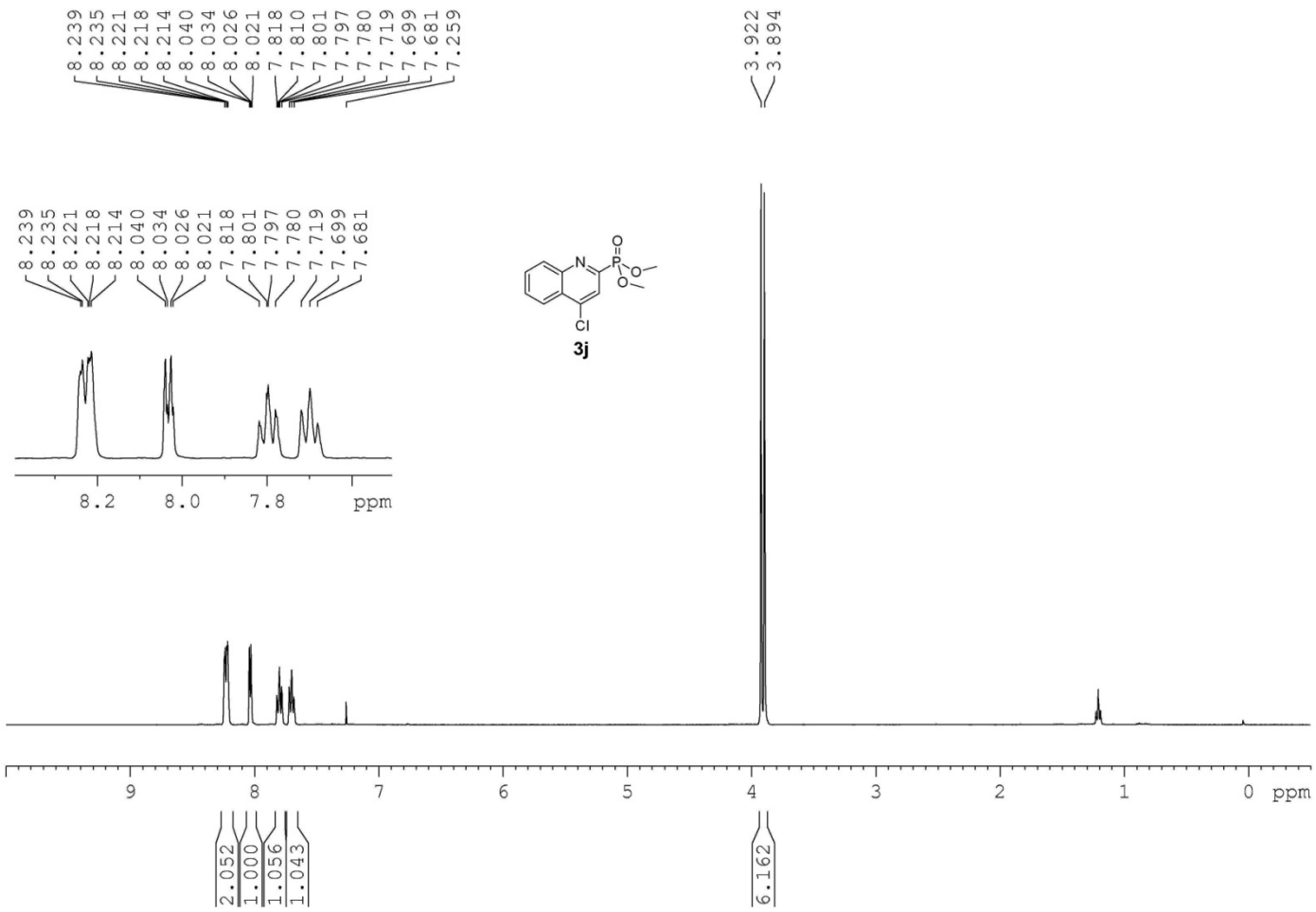
^{1}H NMR spectrum of compound **3i**



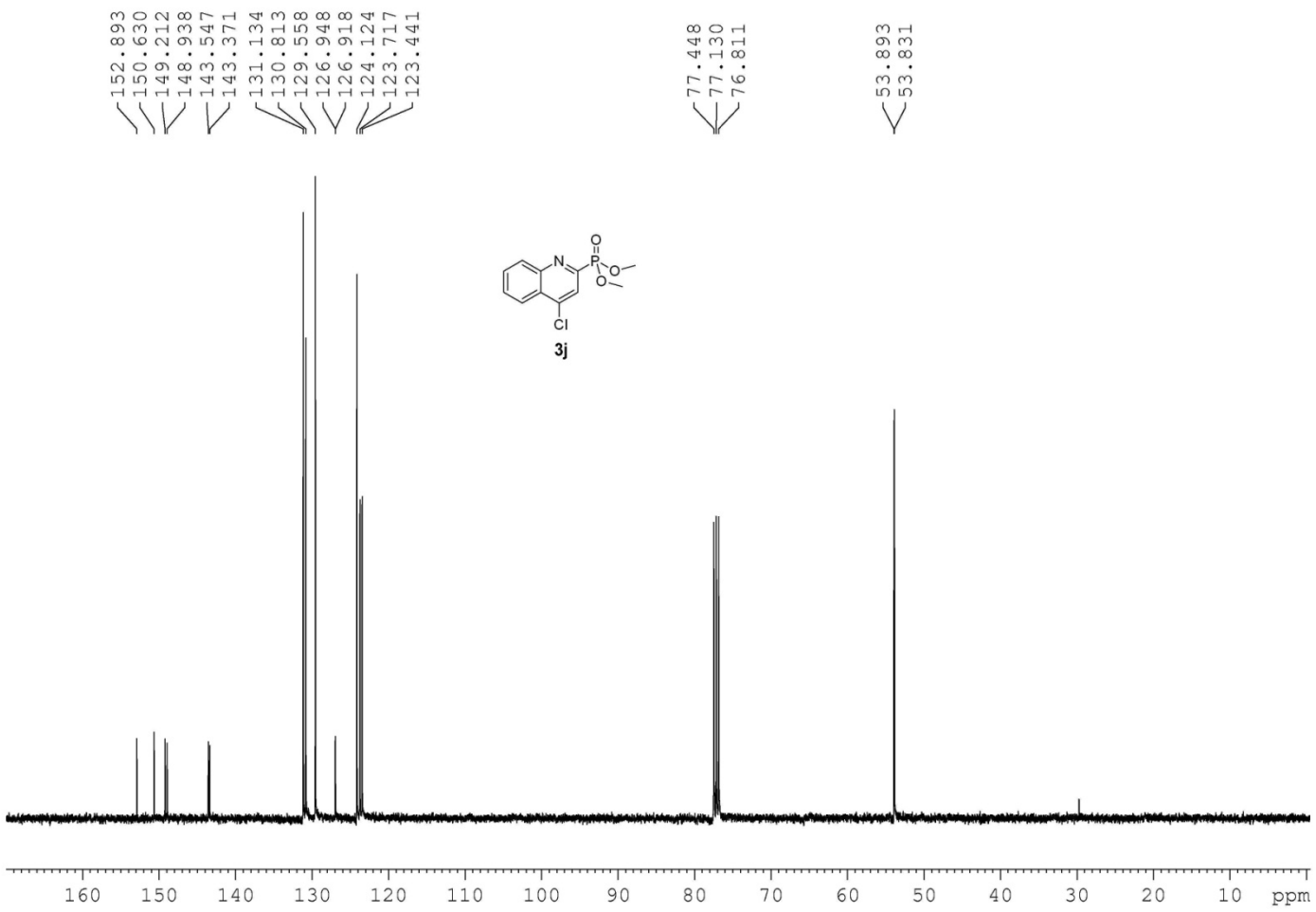
^{13}C NMR spectrum of compound **3i**



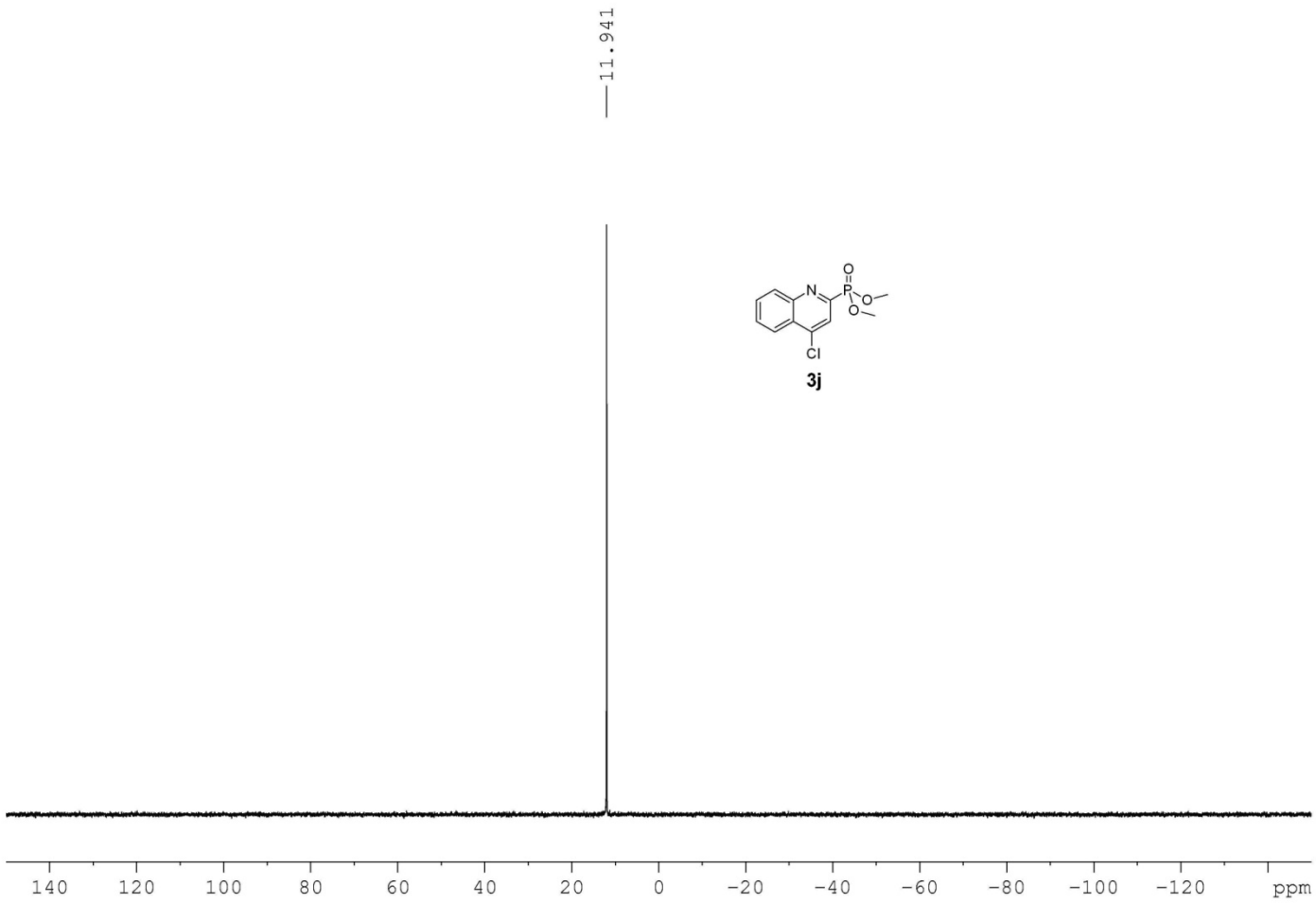
^{31}P NMR spectrum of compound **3i**



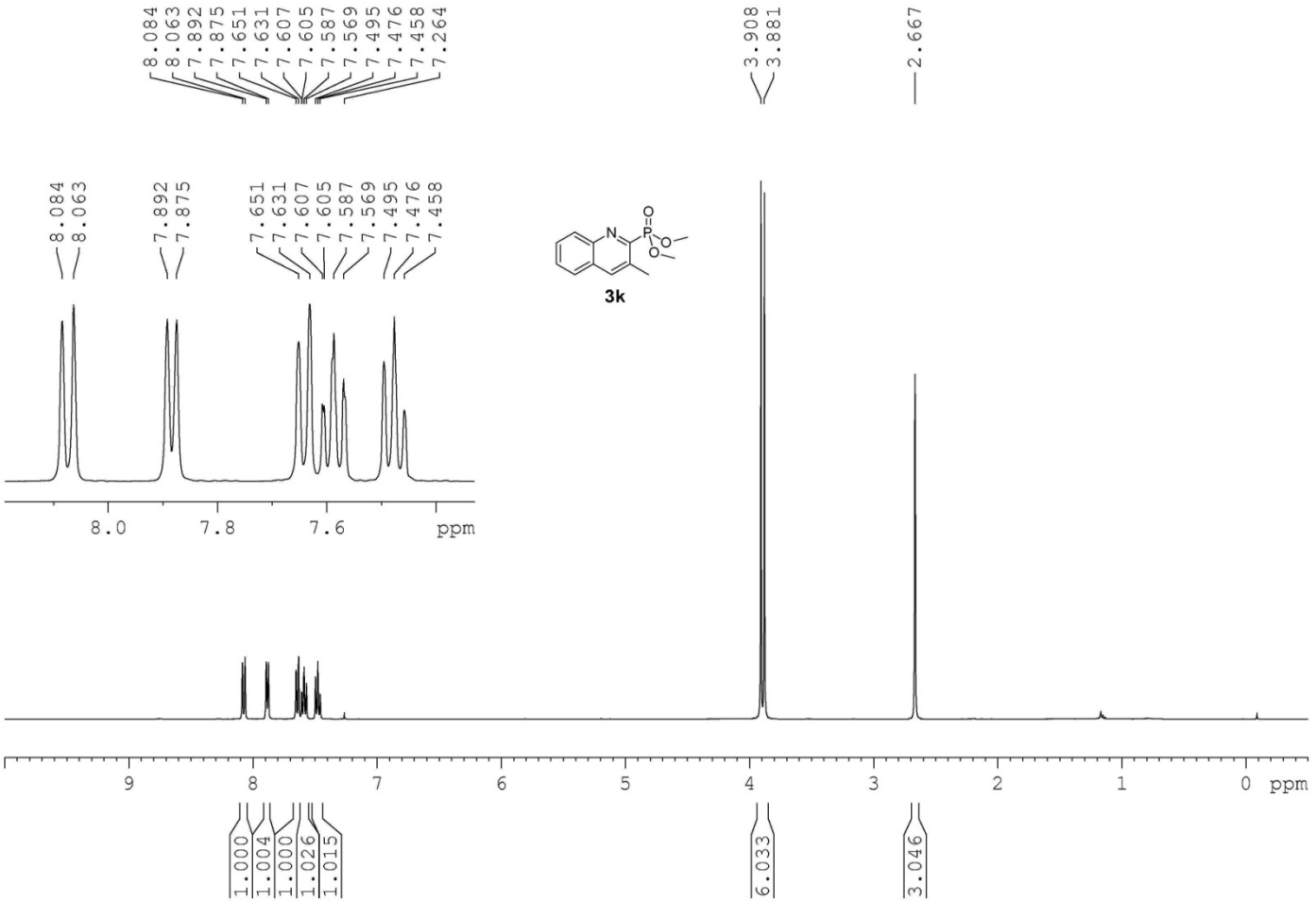
^{1}H NMR spectrum of compound **3j**



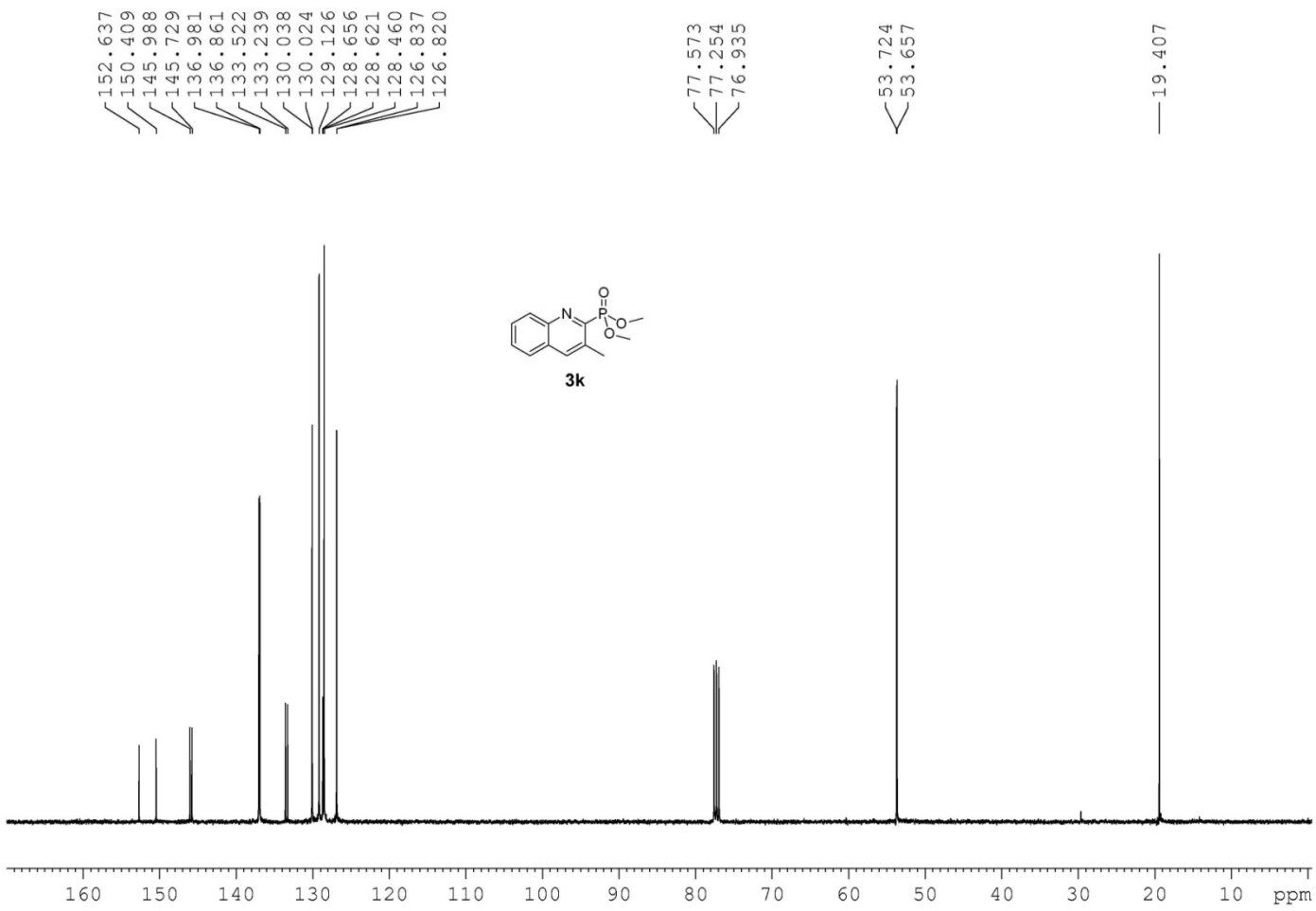
^{13}C NMR spectrum of compound **3j**



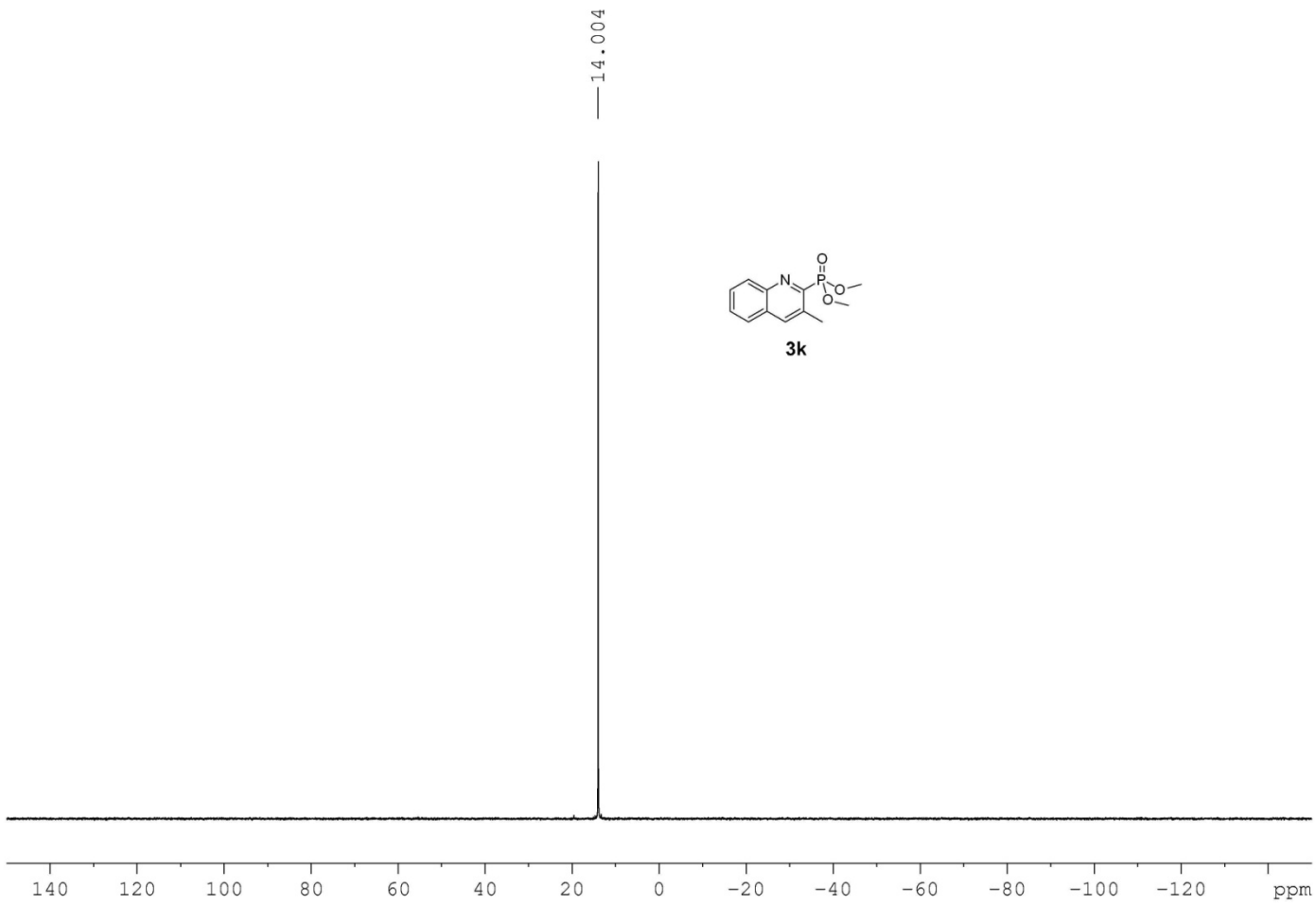
^{31}P NMR spectrum of compound **3j**



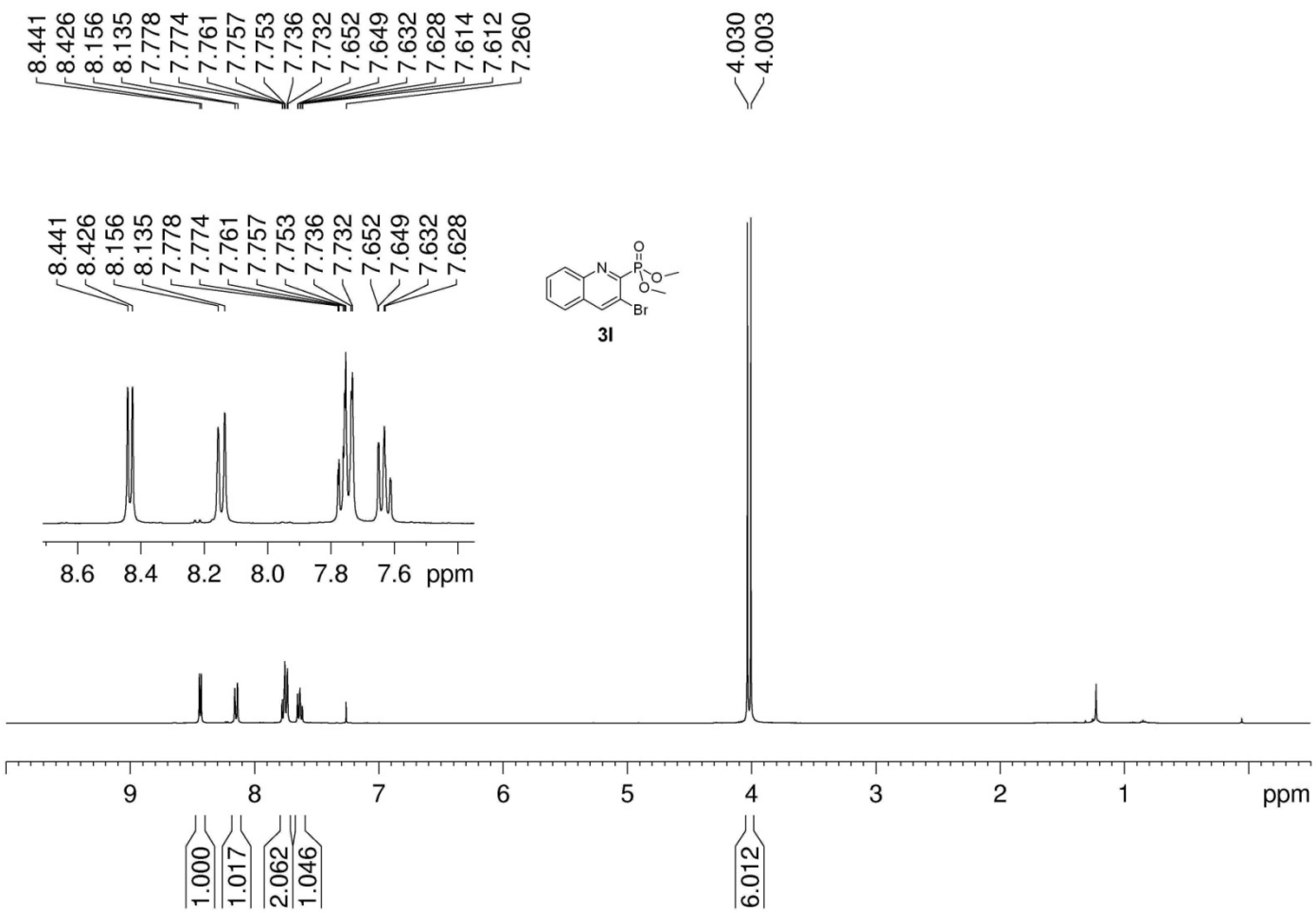
^{1}H NMR spectrum of compound **3k**



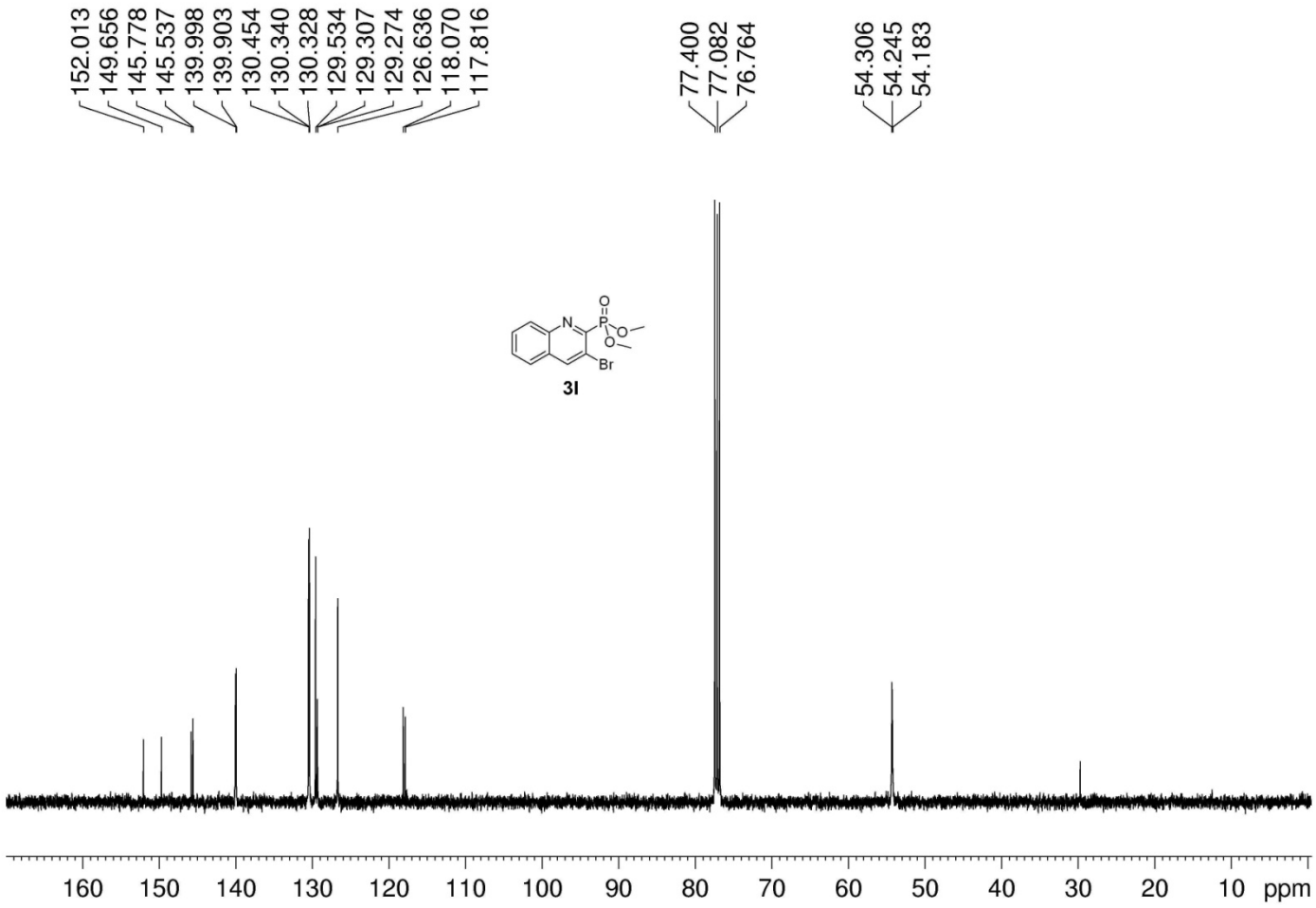
^{13}C NMR spectrum of compound **3k**



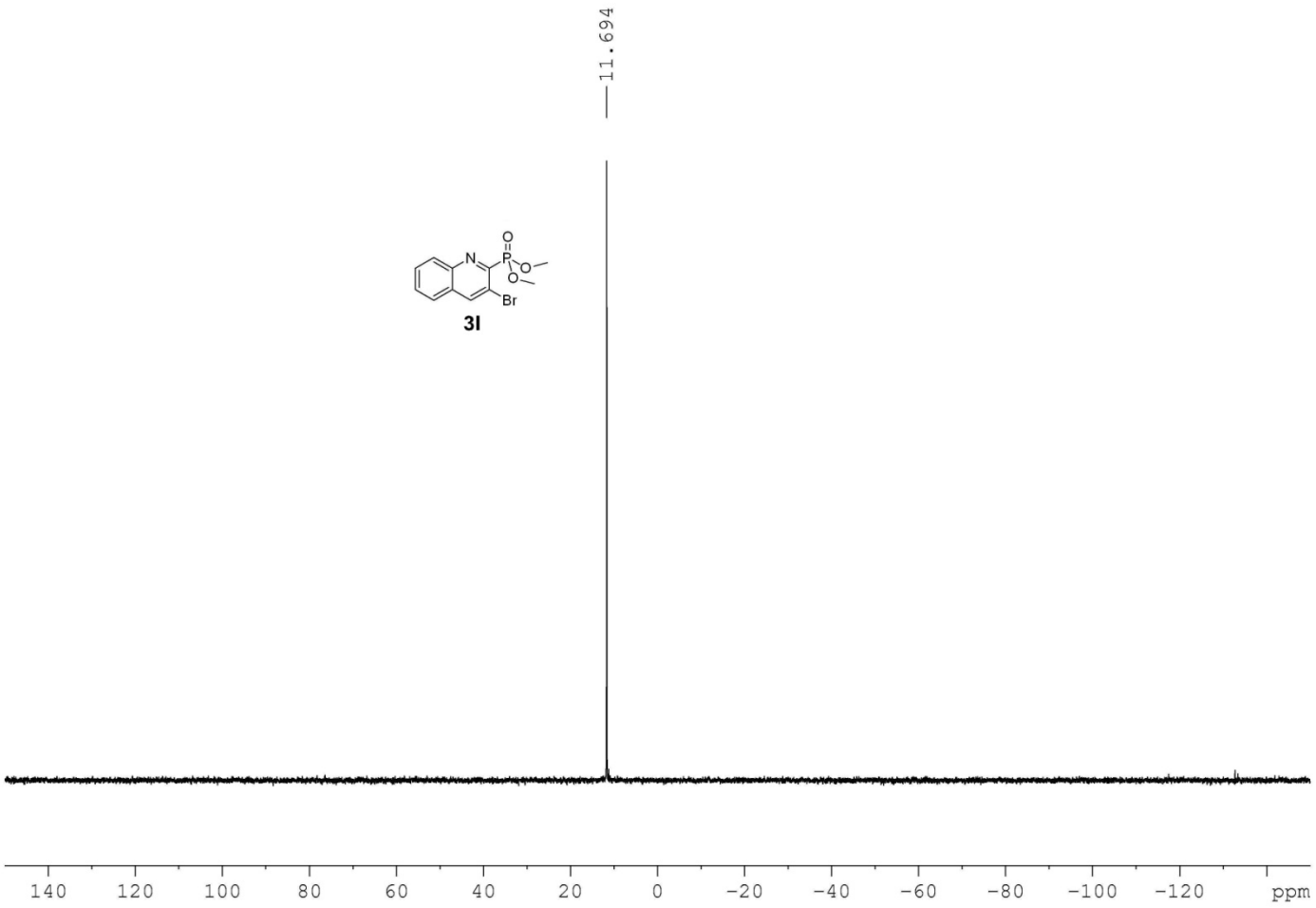
^{31}P NMR spectrum of compound **3k**



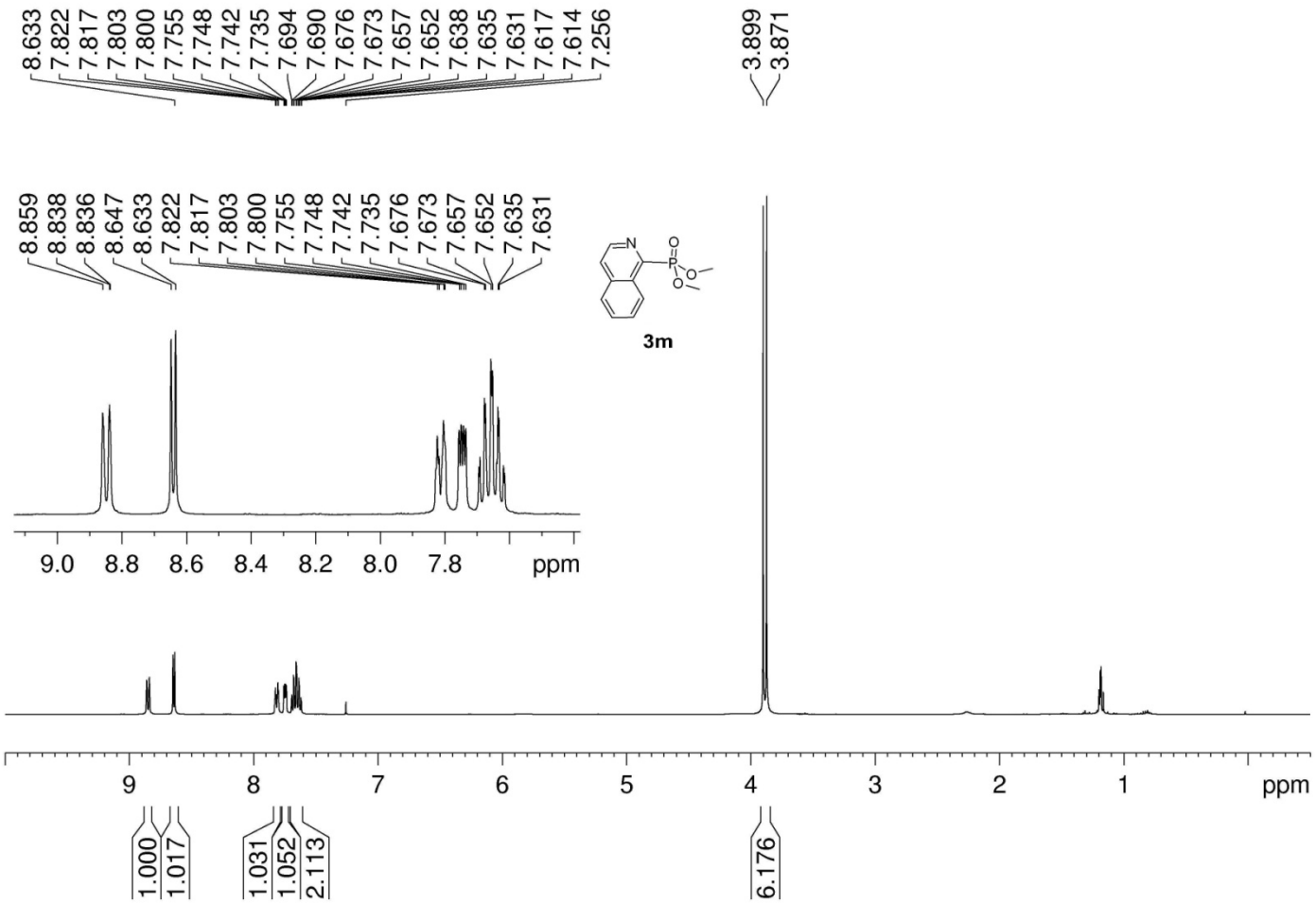
^{1}H NMR spectrum of compound **3l**



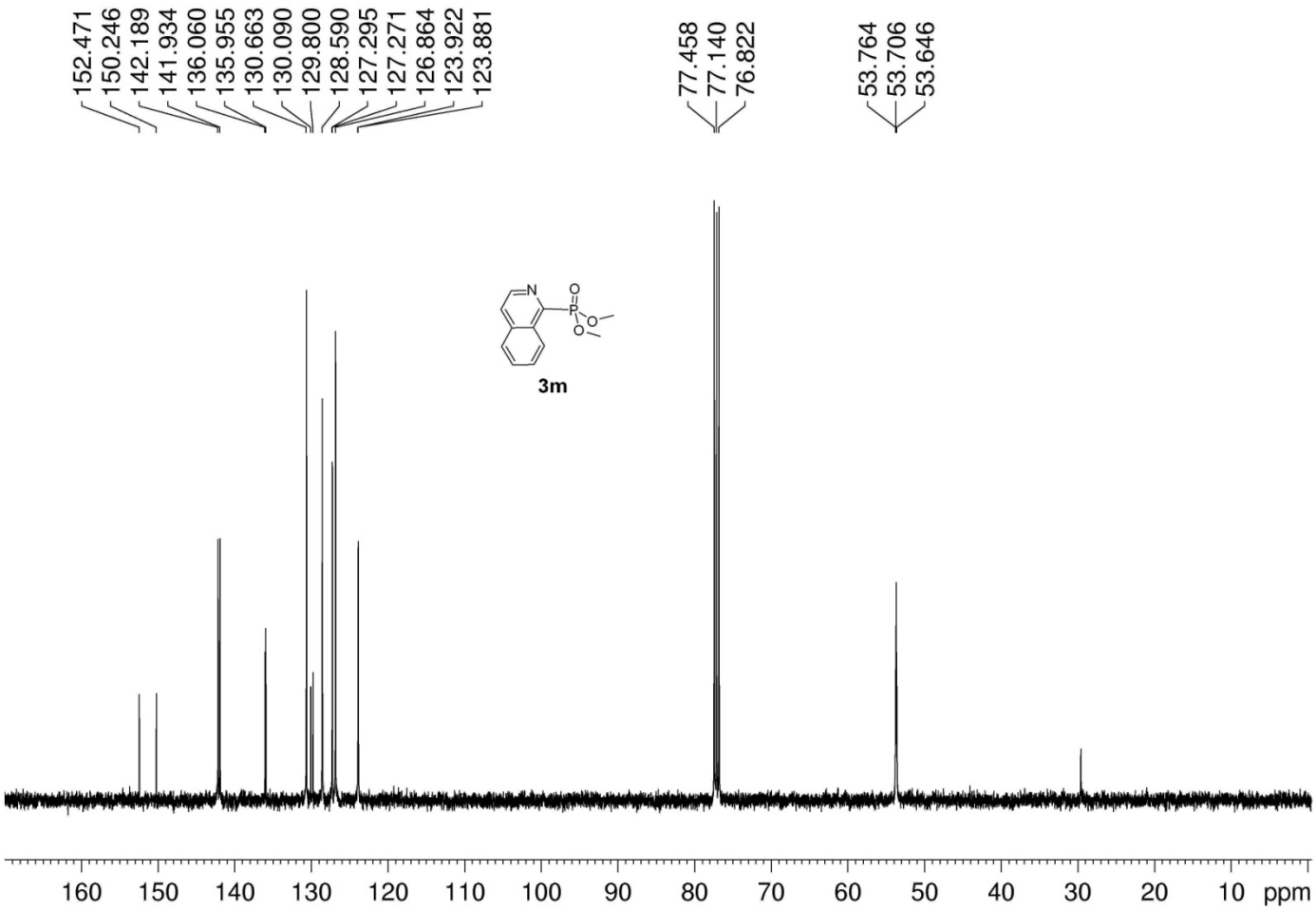
^{13}C NMR spectrum of compound **3l**



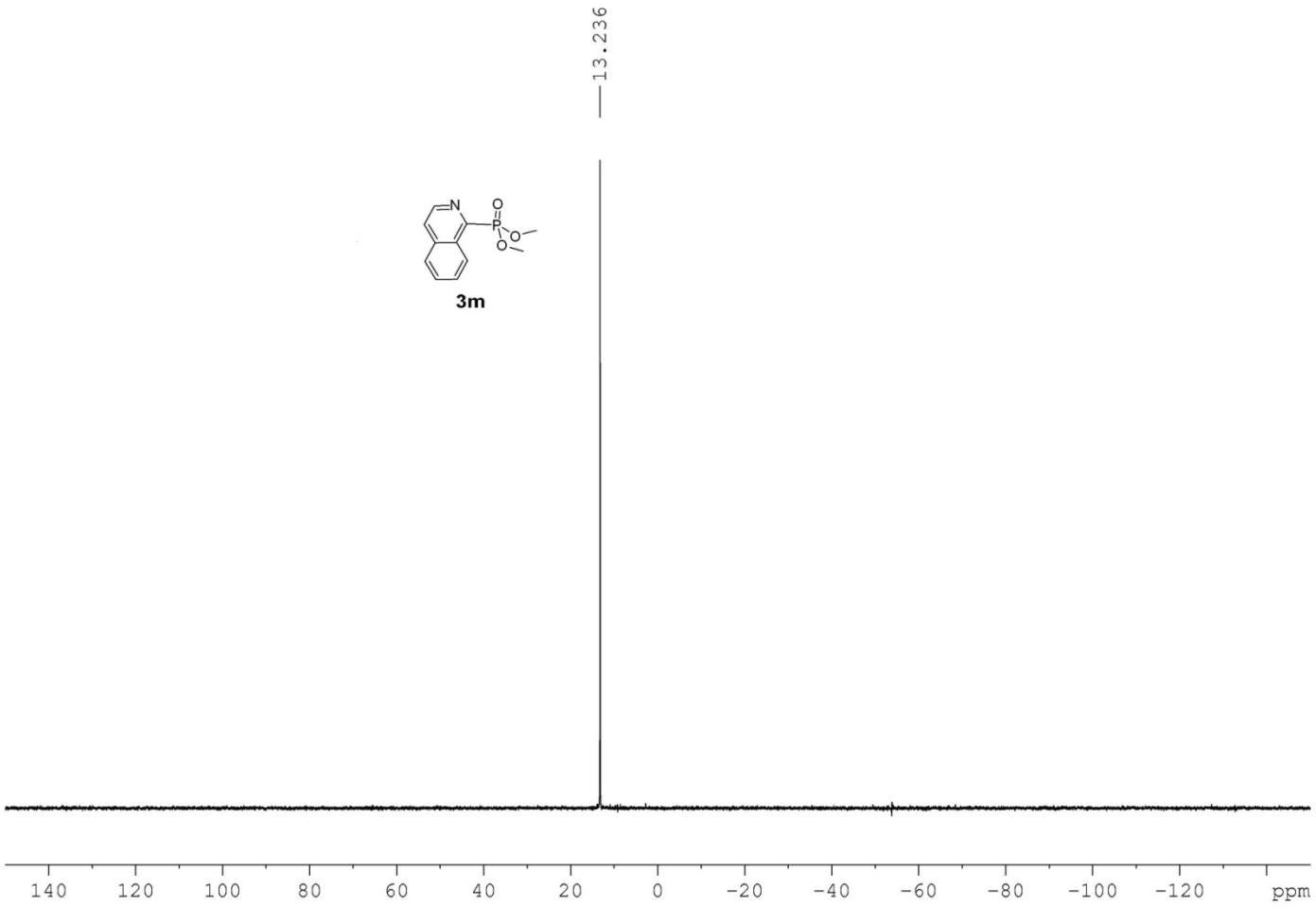
^{31}P NMR spectrum of compound **3l**



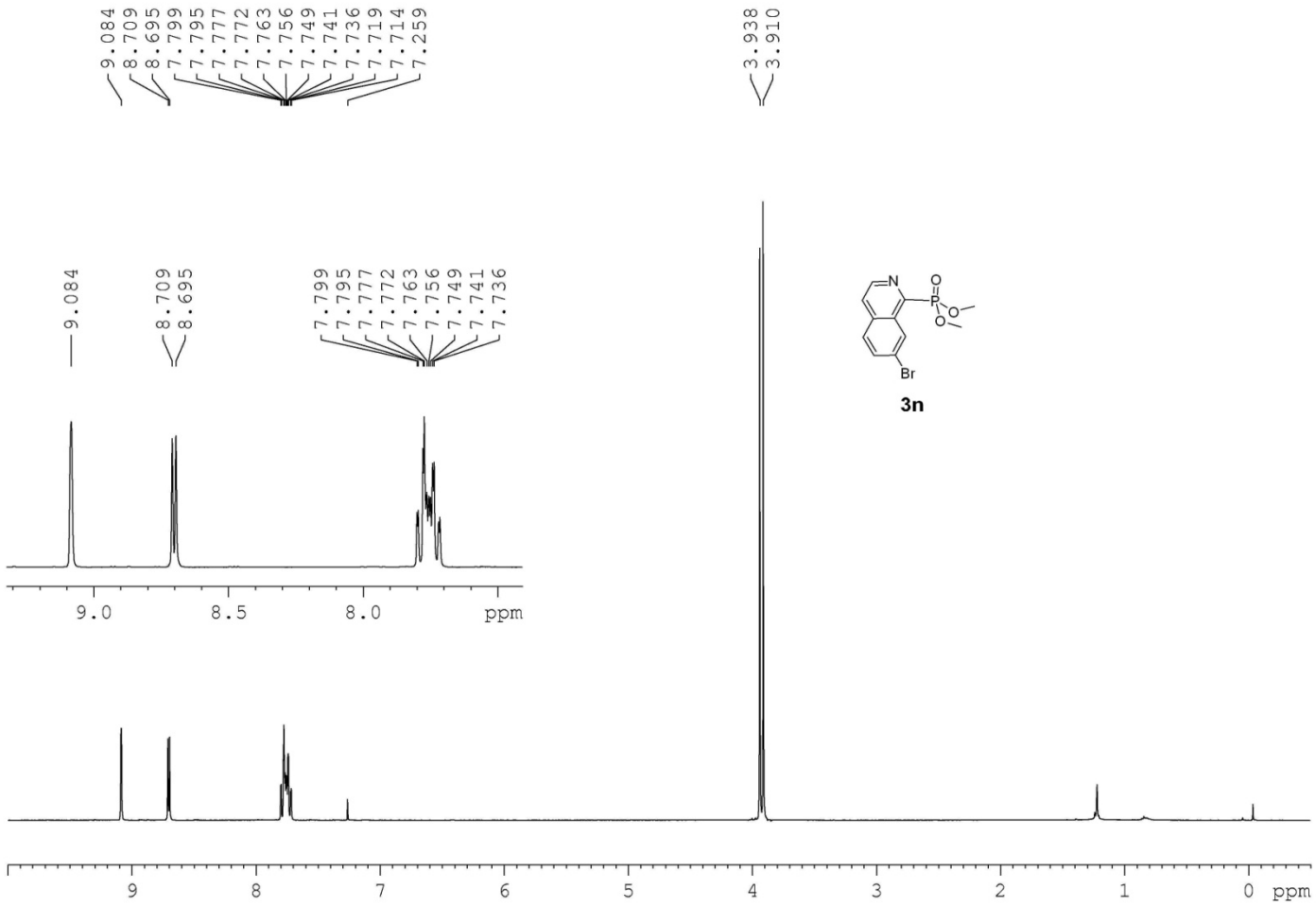
^{1}H NMR spectrum of compound **3m**



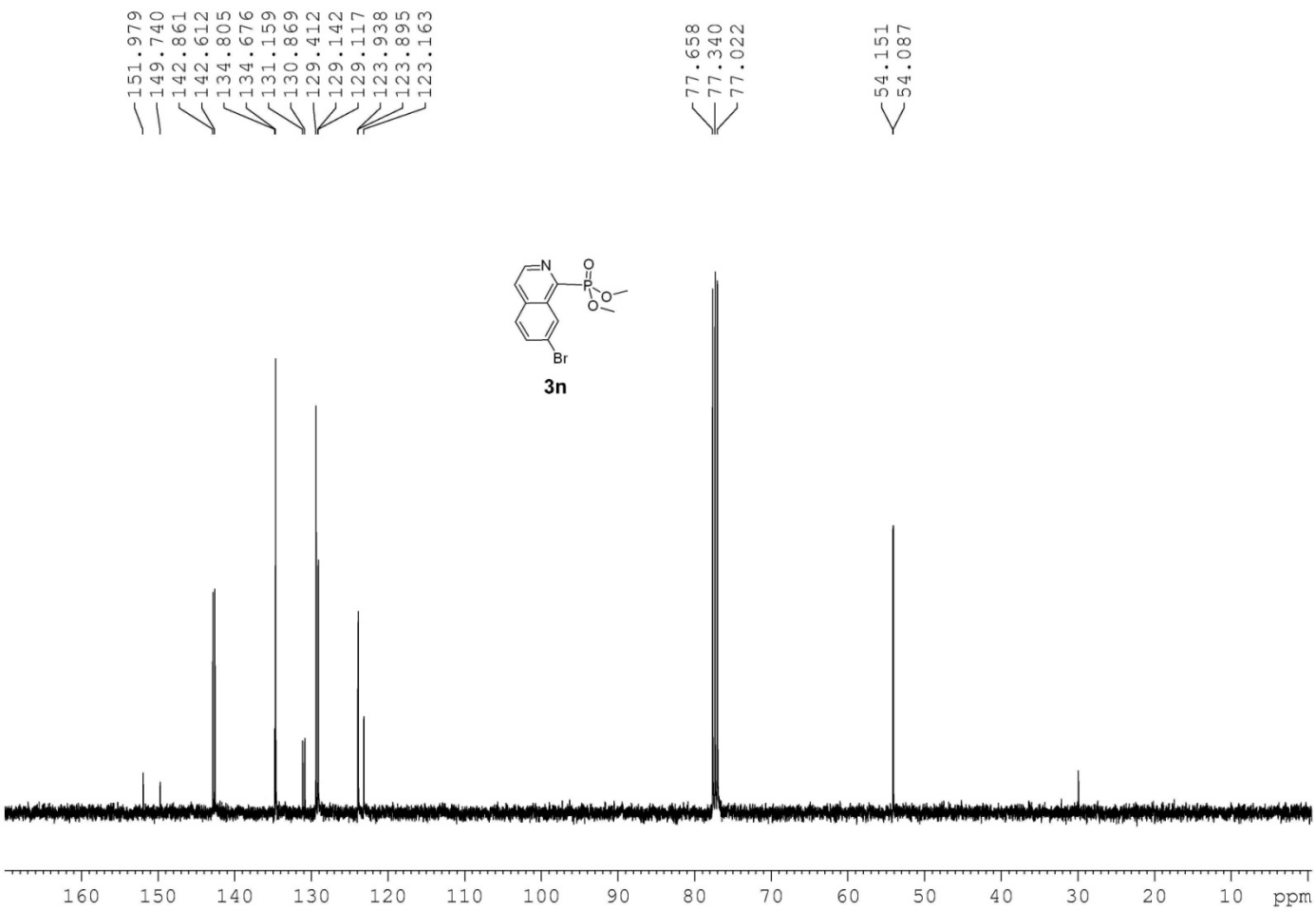
^{13}C NMR spectrum of compound **3m**



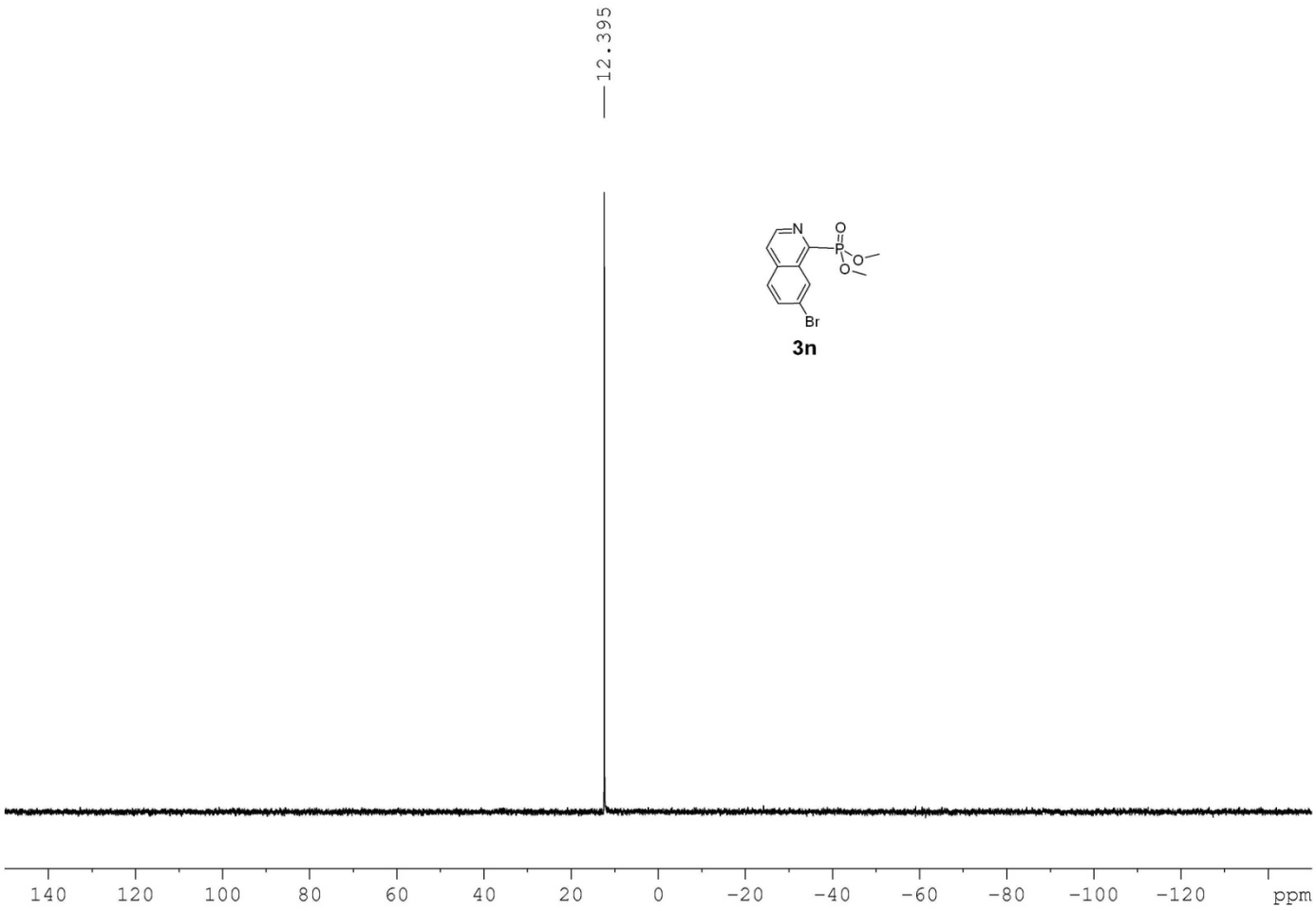
^{31}P NMR spectrum of compound **3m**



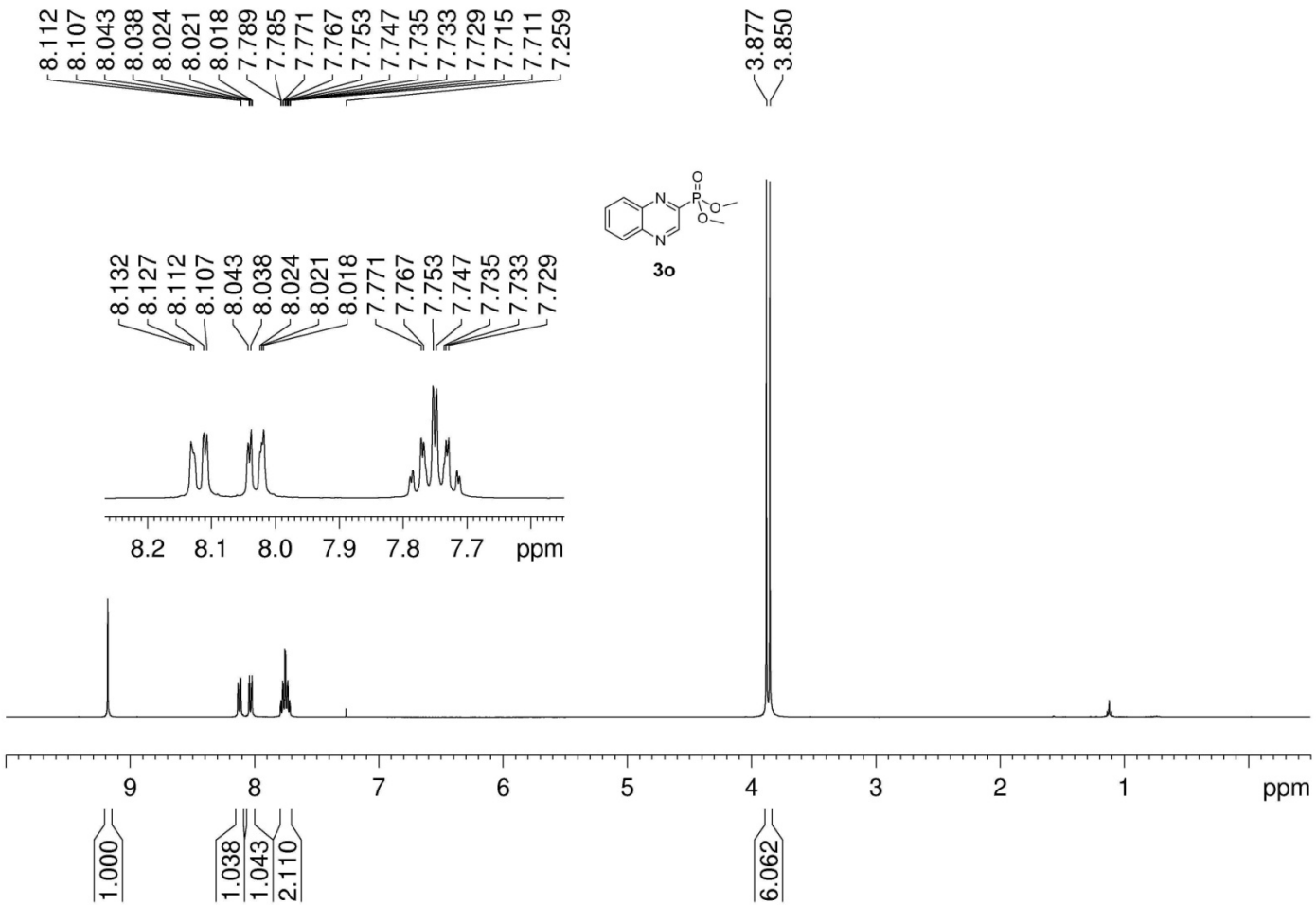
^{1}H NMR spectrum of compound **3n**



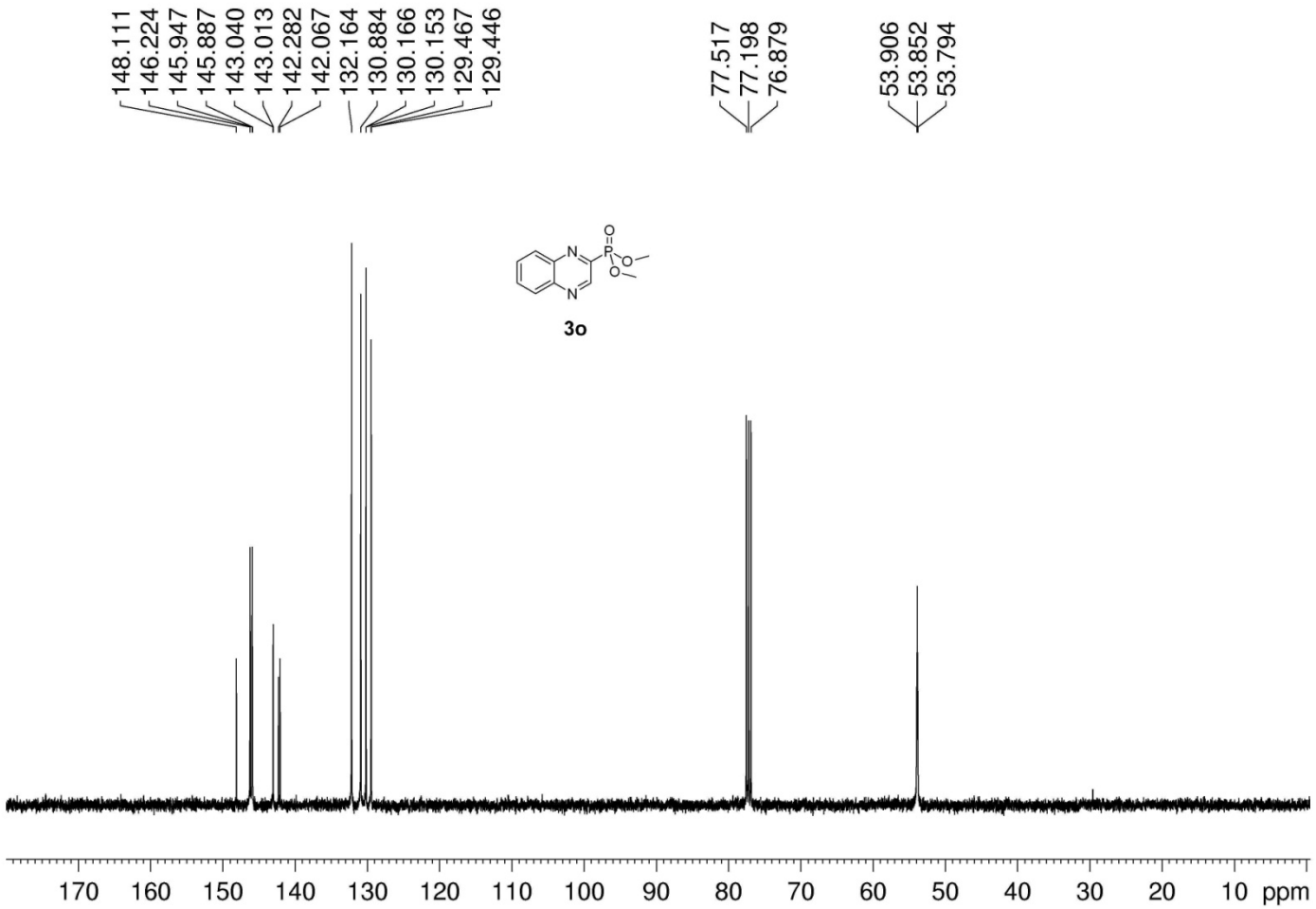
^{13}C NMR spectrum of compound **3n**



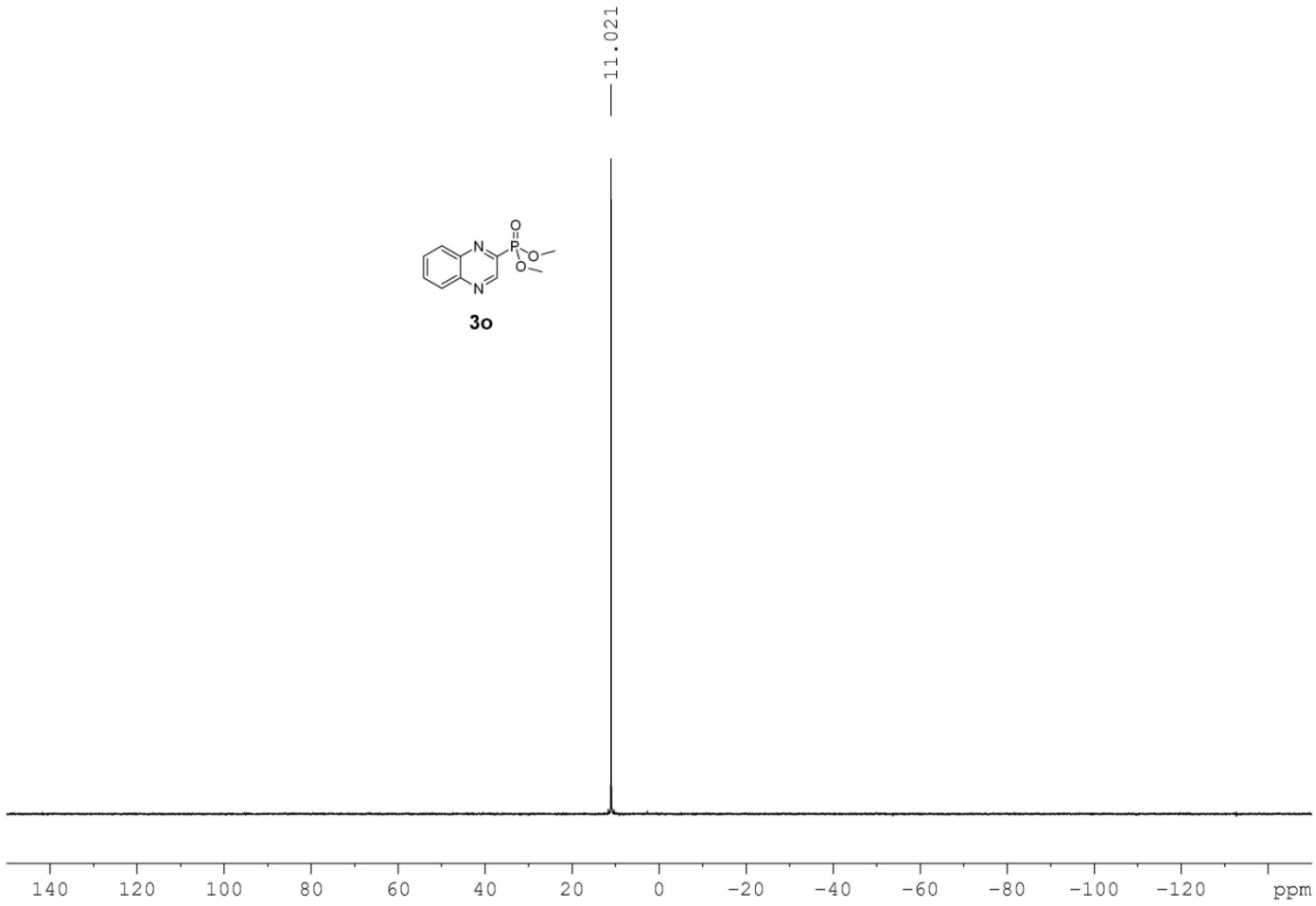
^{31}P NMR spectrum of compound **3n**



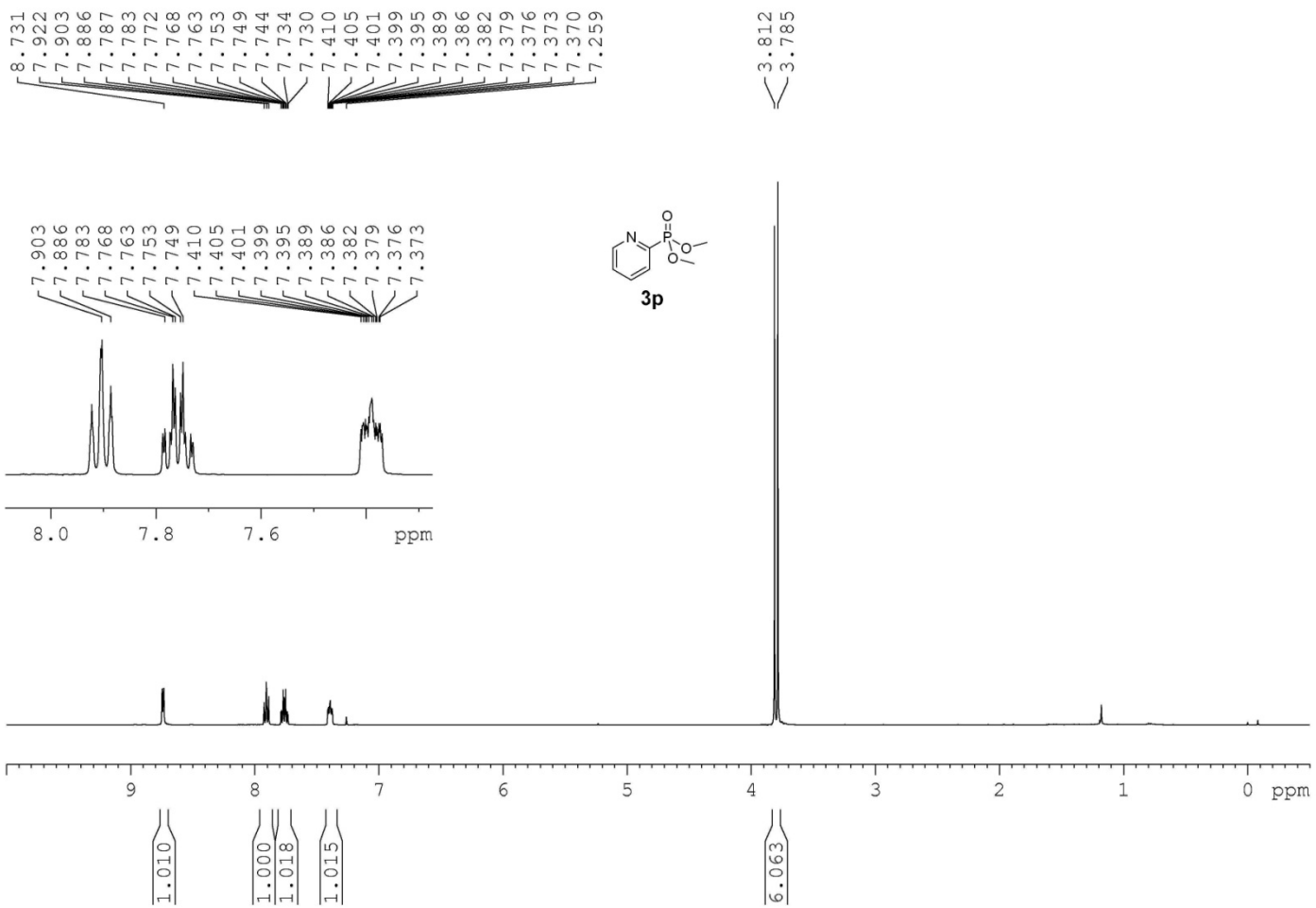
^{1}H NMR spectrum of compound **3o**



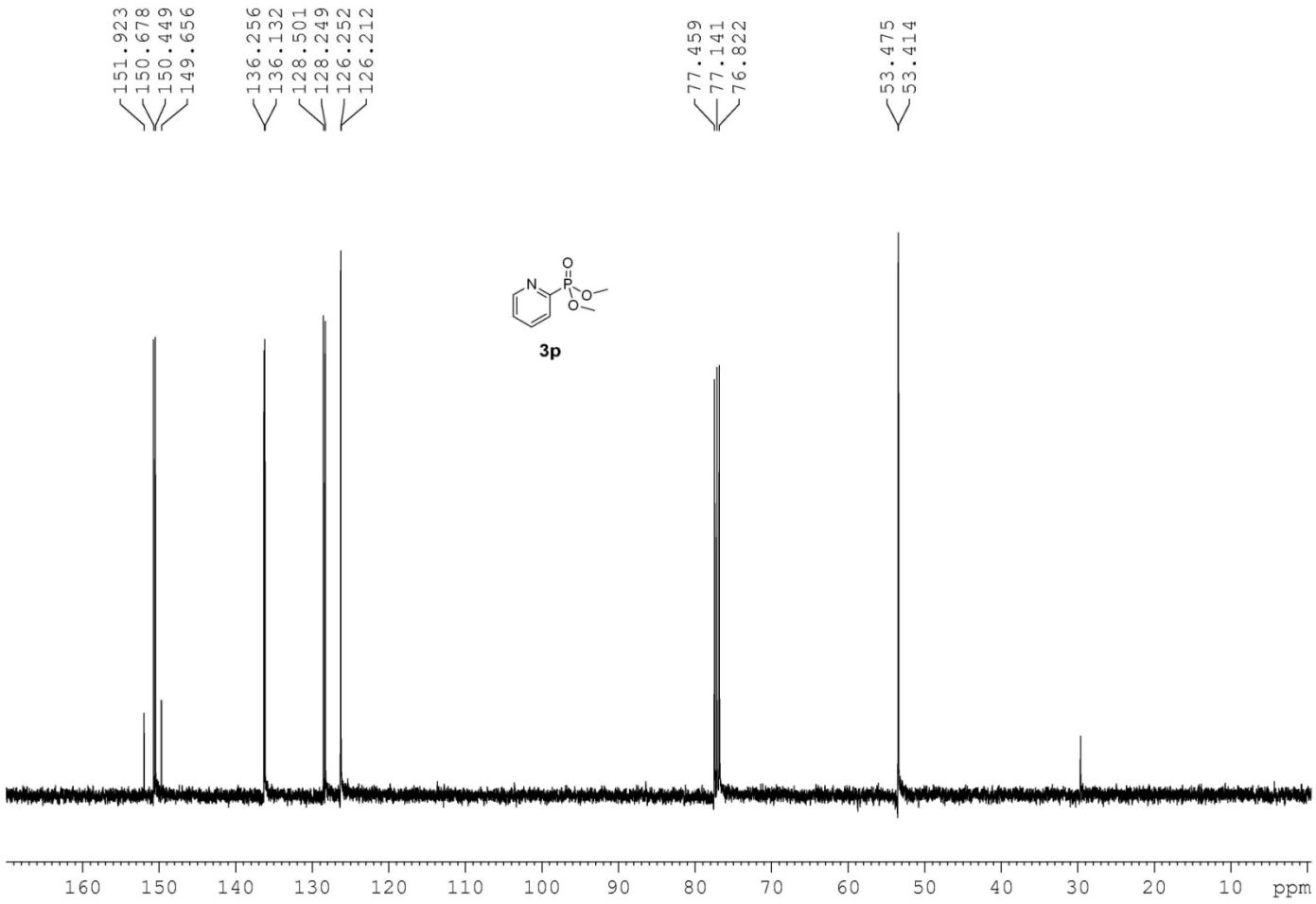
^{13}C NMR spectrum of compound **3o**



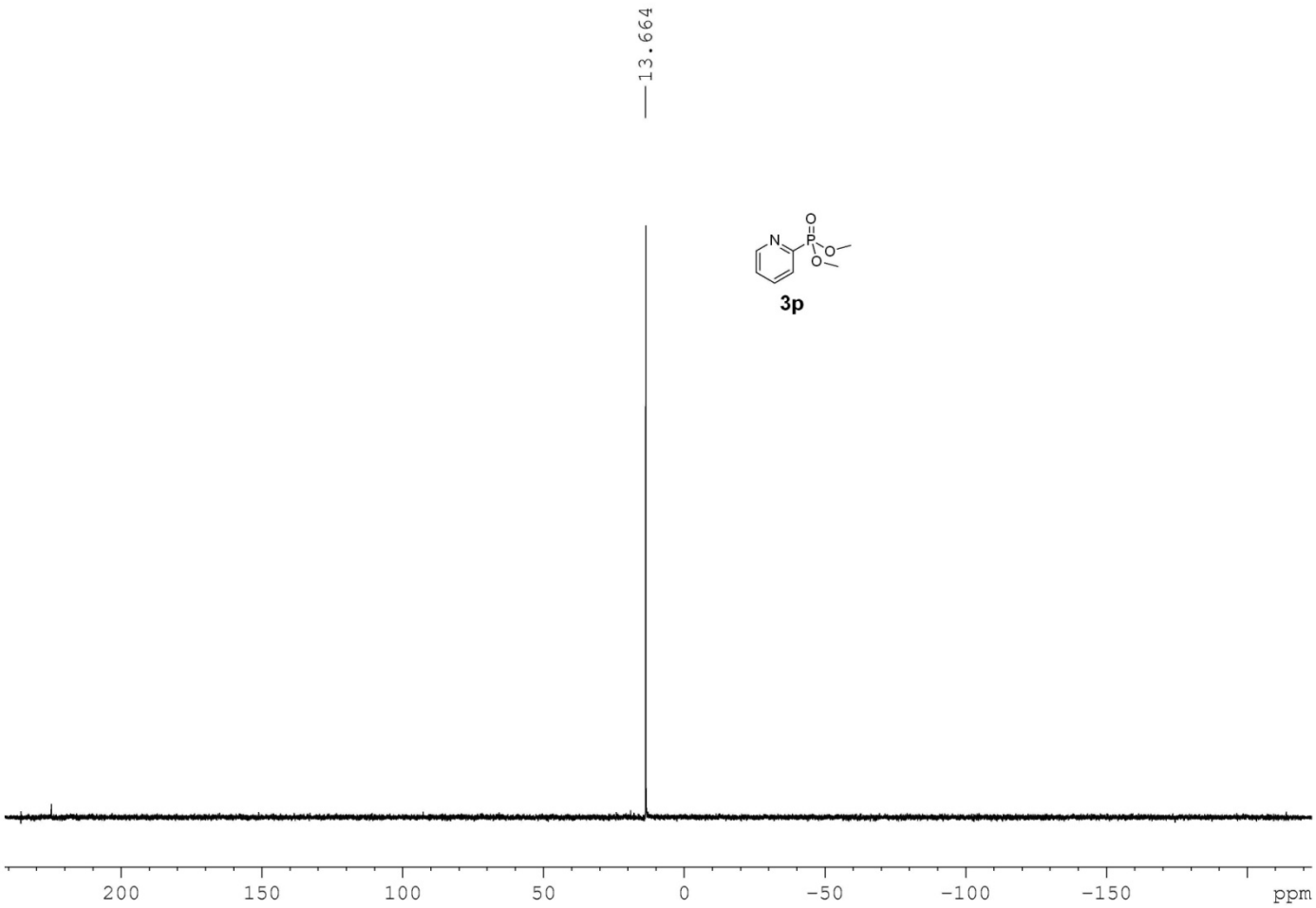
^{31}P NMR spectrum of compound **3o**



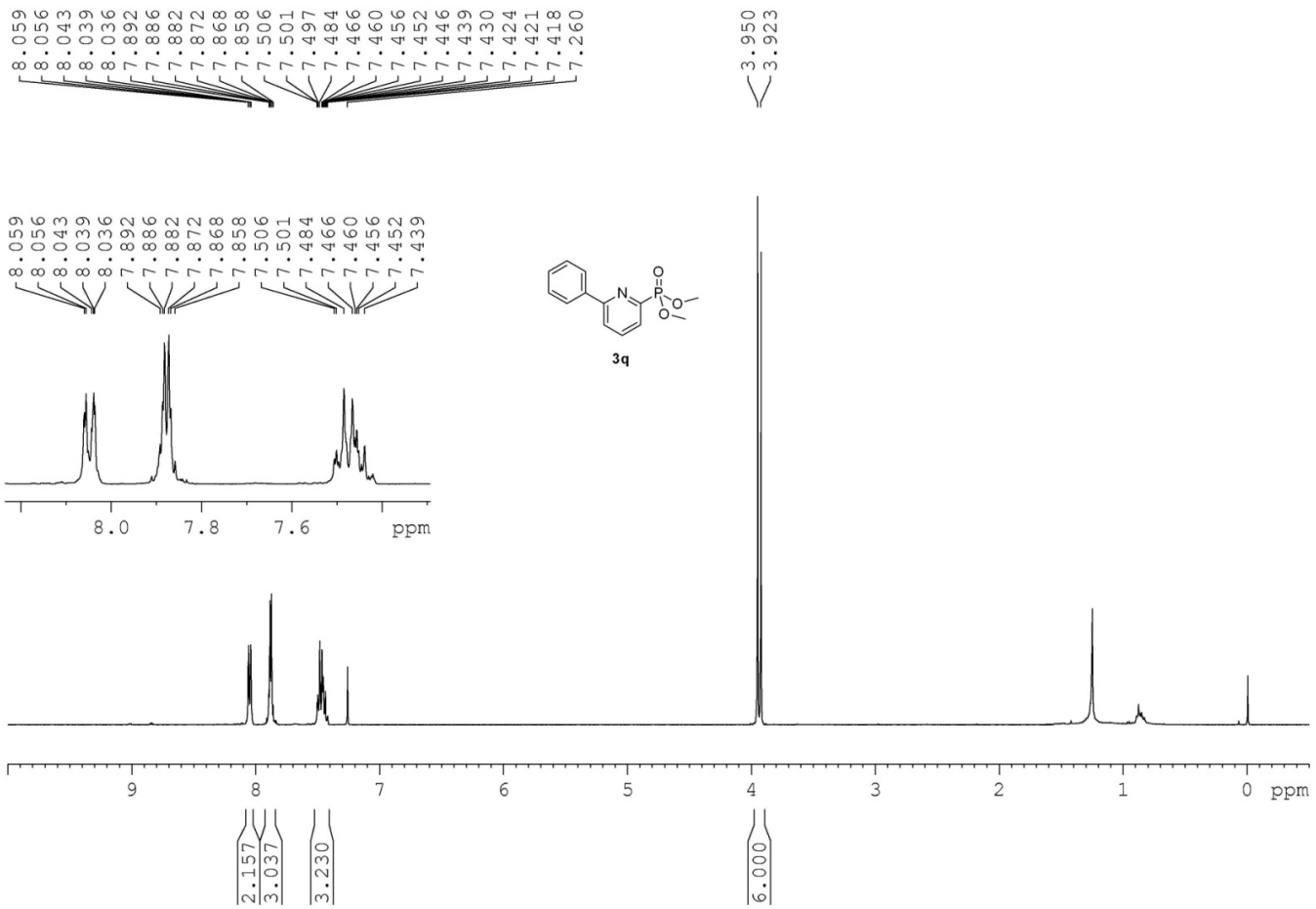
^{1}H NMR spectrum of compound **3p**



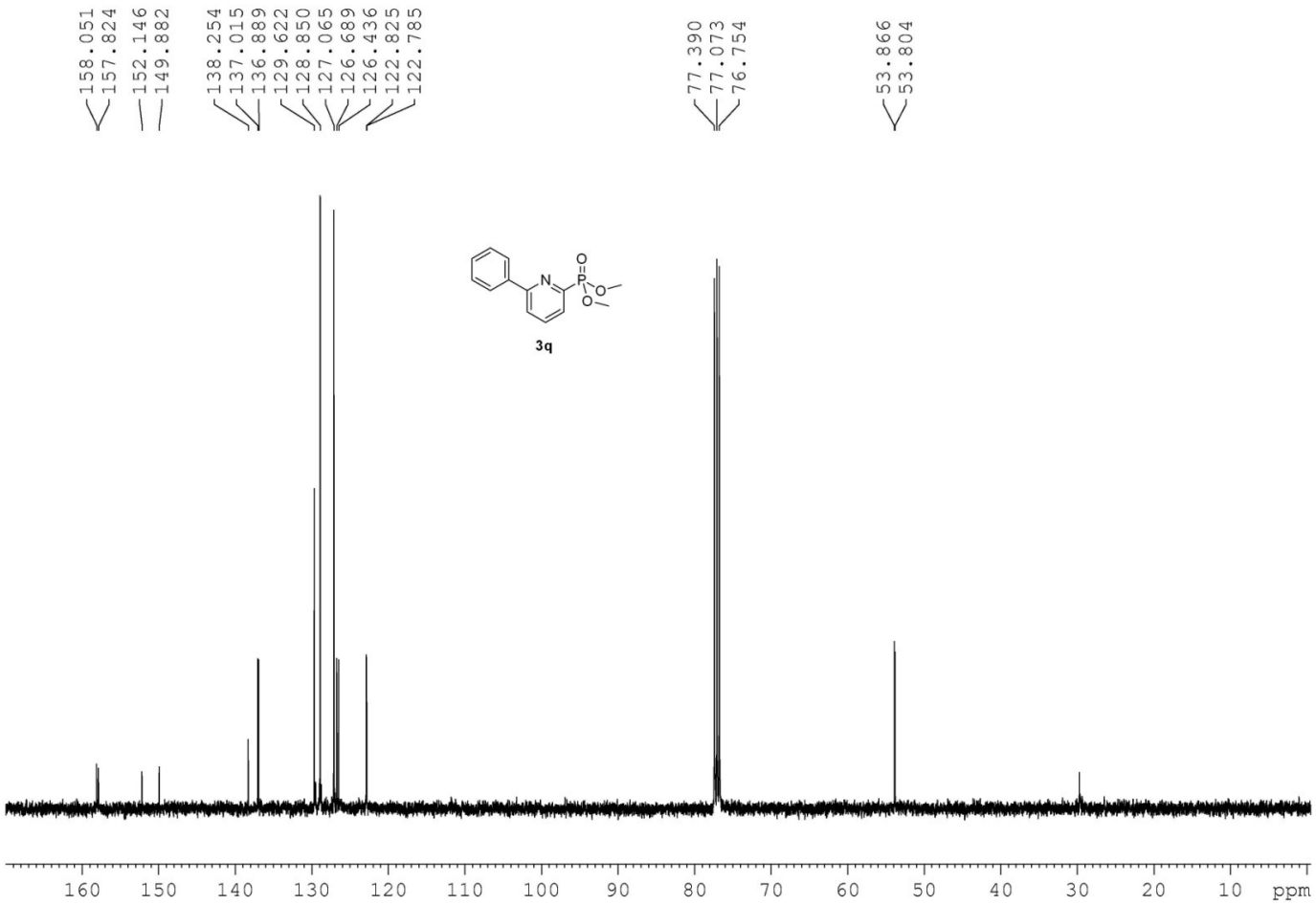
^{13}C NMR spectrum of compound **3p**



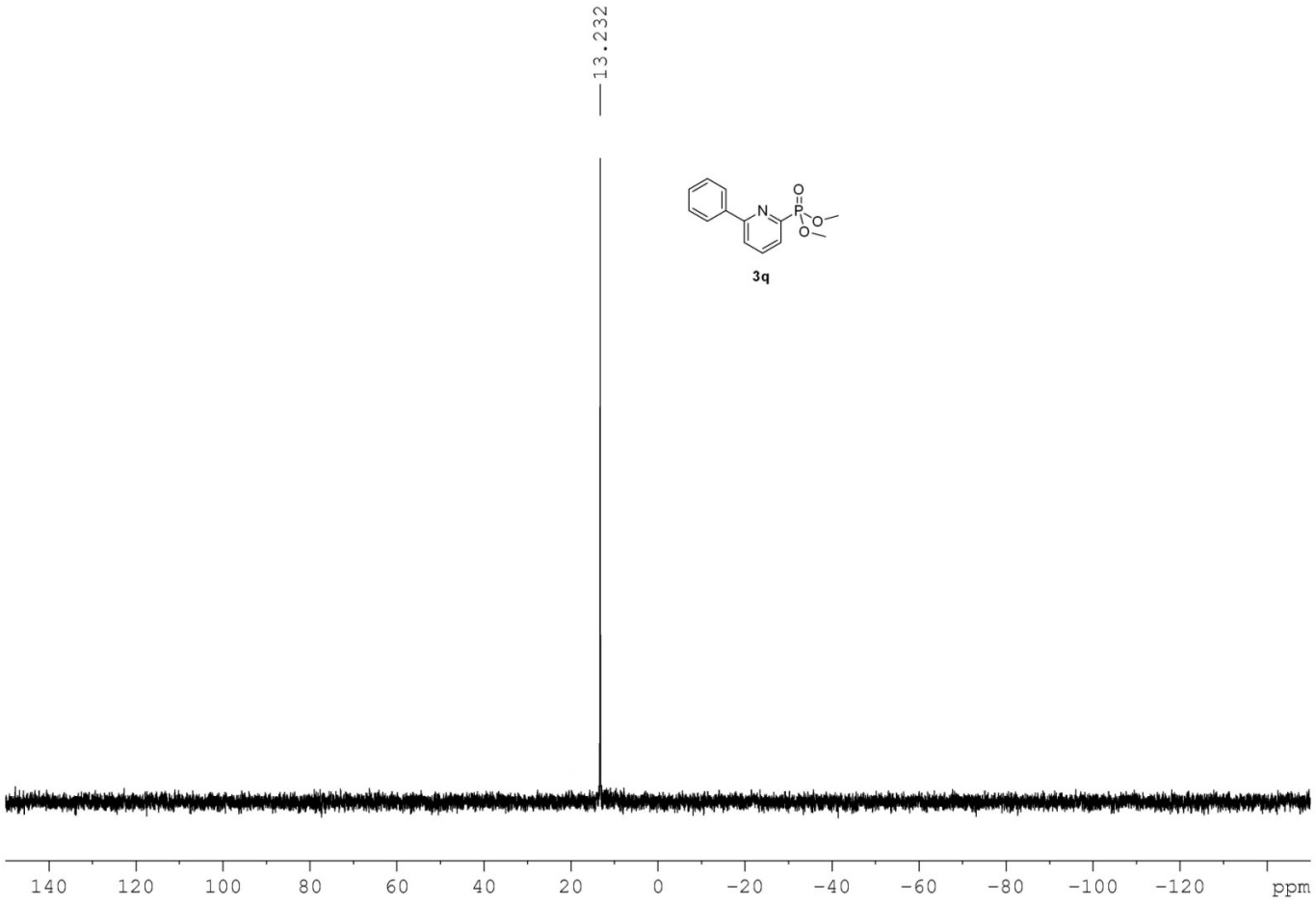
^{31}P NMR spectrum of compound **3p**



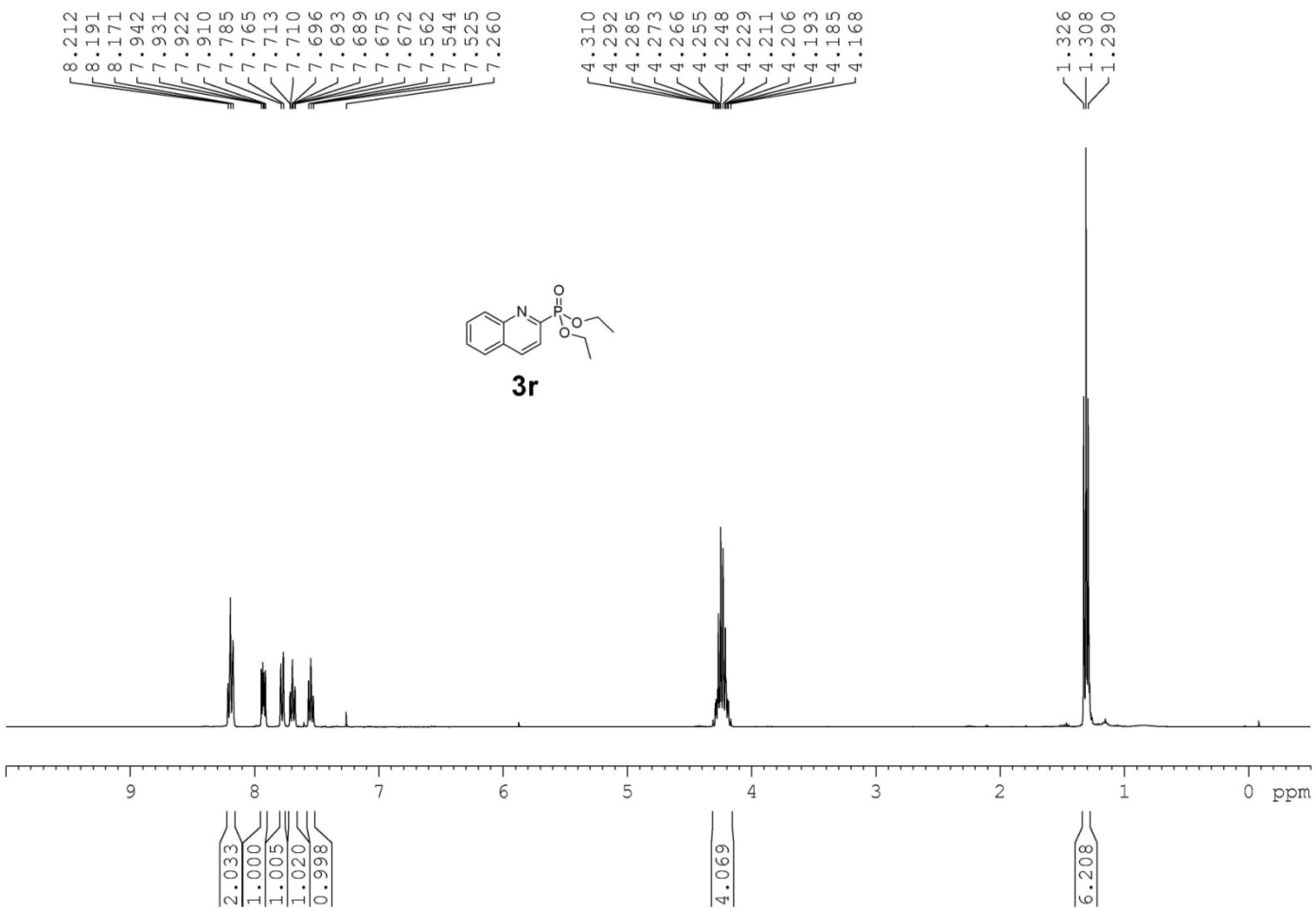
^{1}H NMR spectrum of compound **3q**



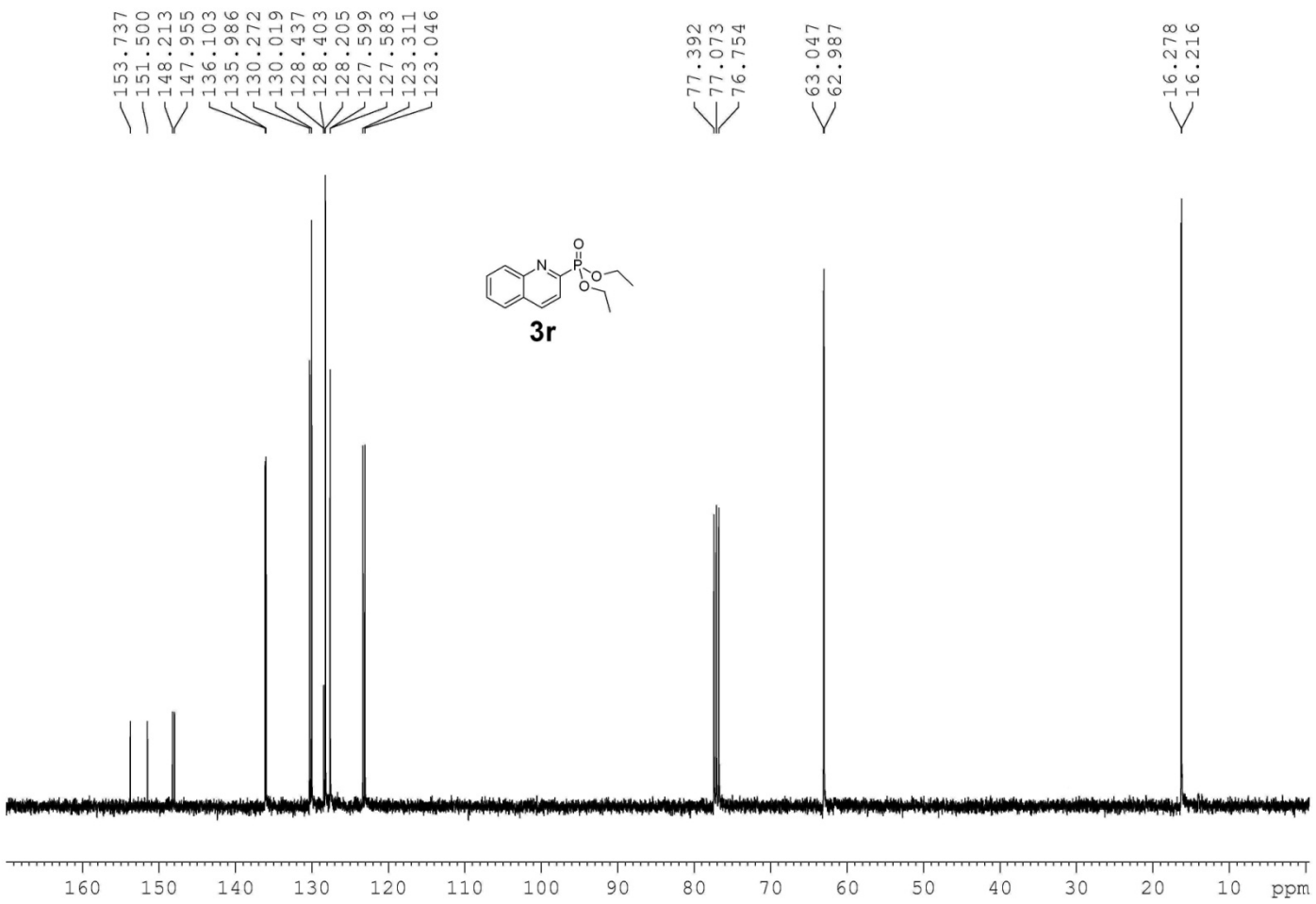
^{13}C NMR spectrum of compound **3q**



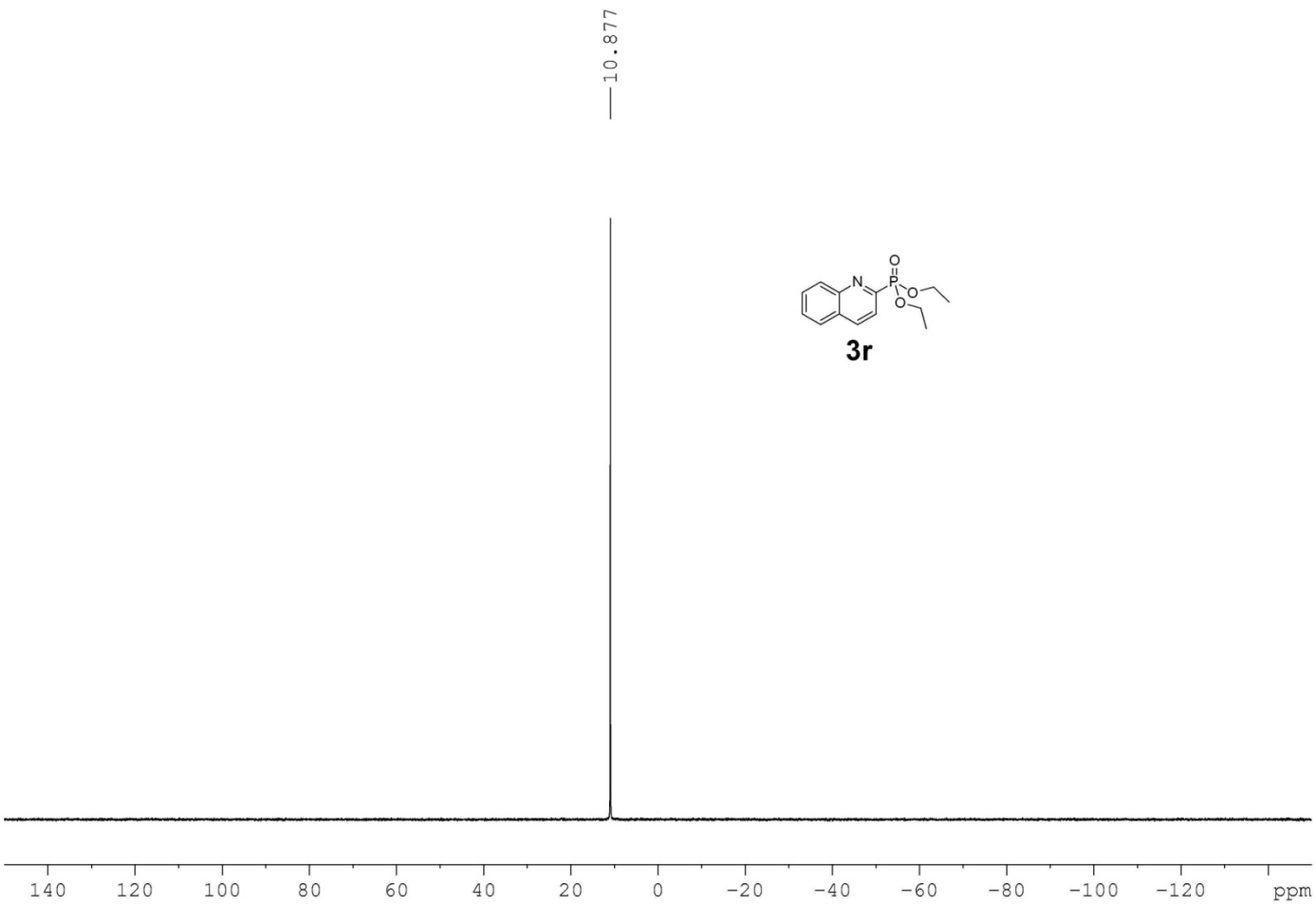
^{31}P NMR spectrum of compound **3q**



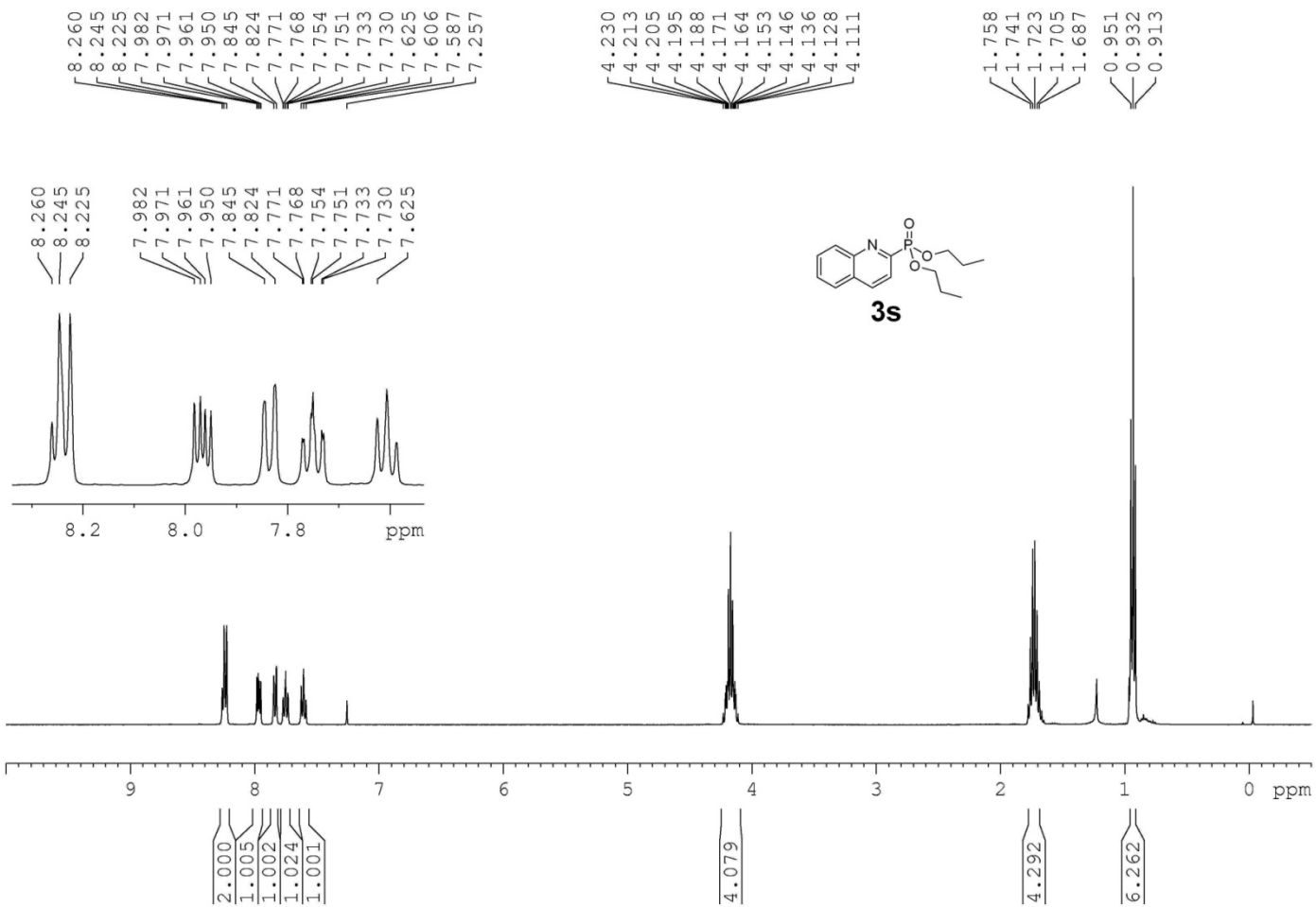
^{1}H NMR spectrum of compound **3r**



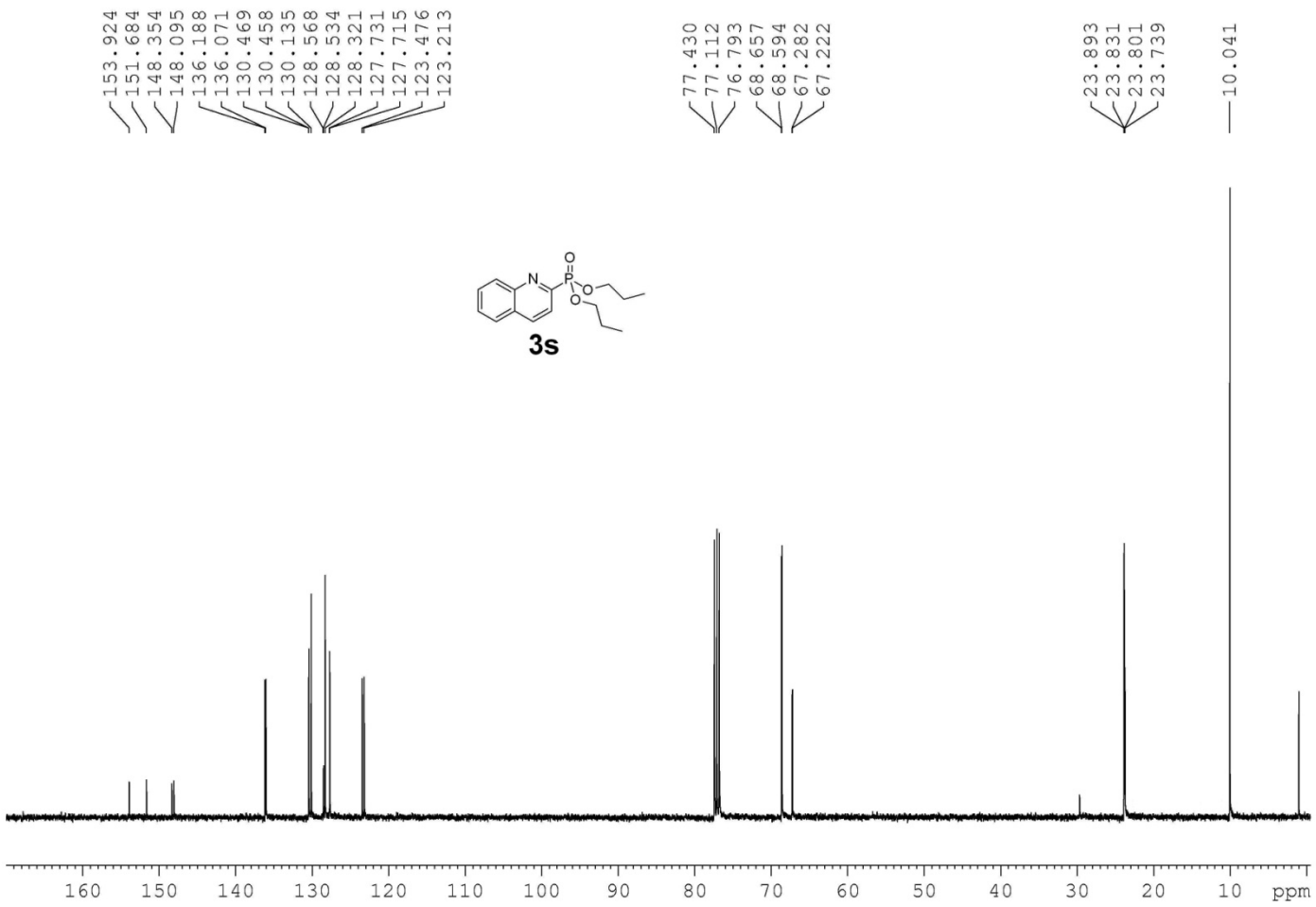
^{13}C NMR spectrum of compound **3r**



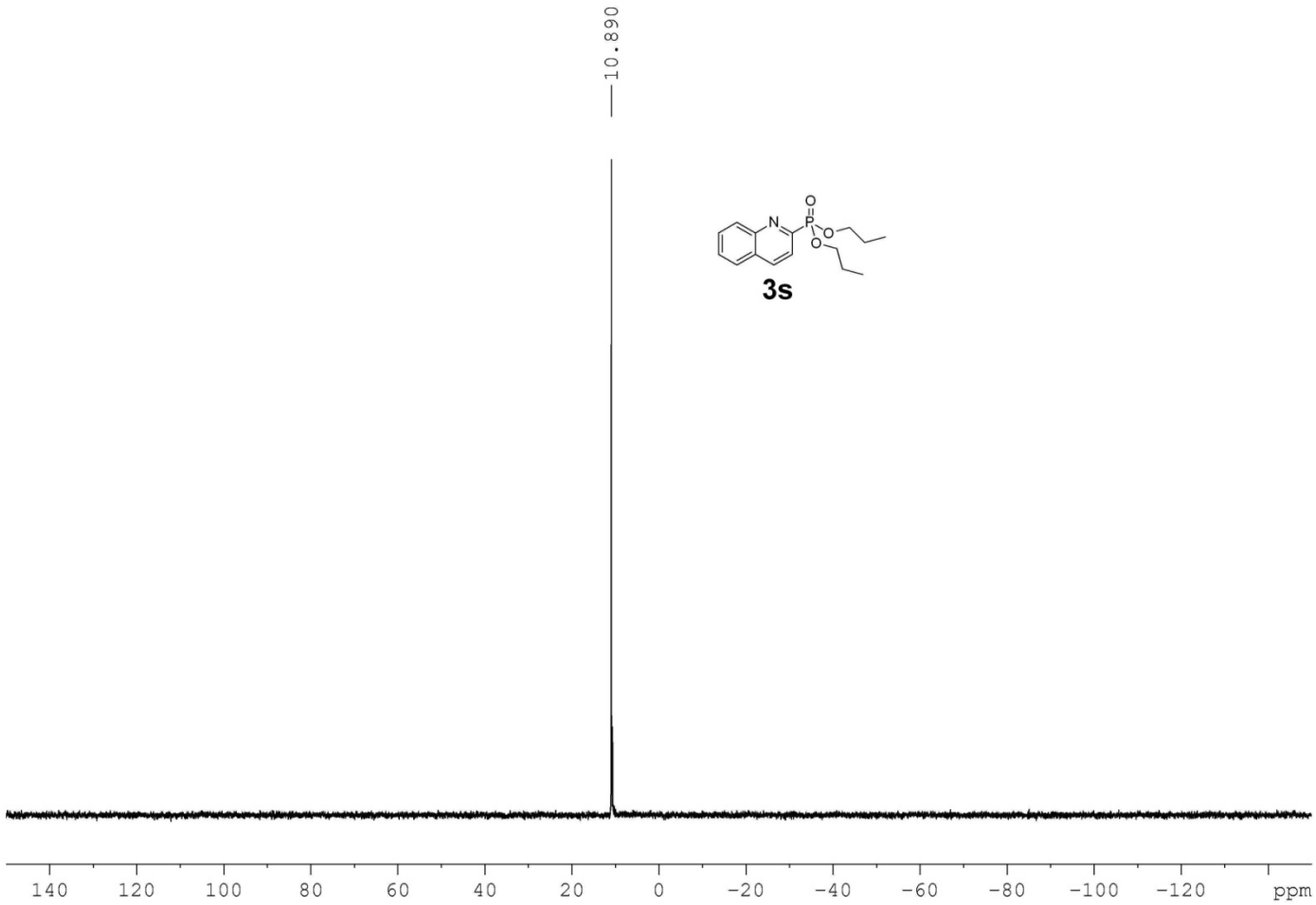
^{31}P NMR spectrum of compound **3r**



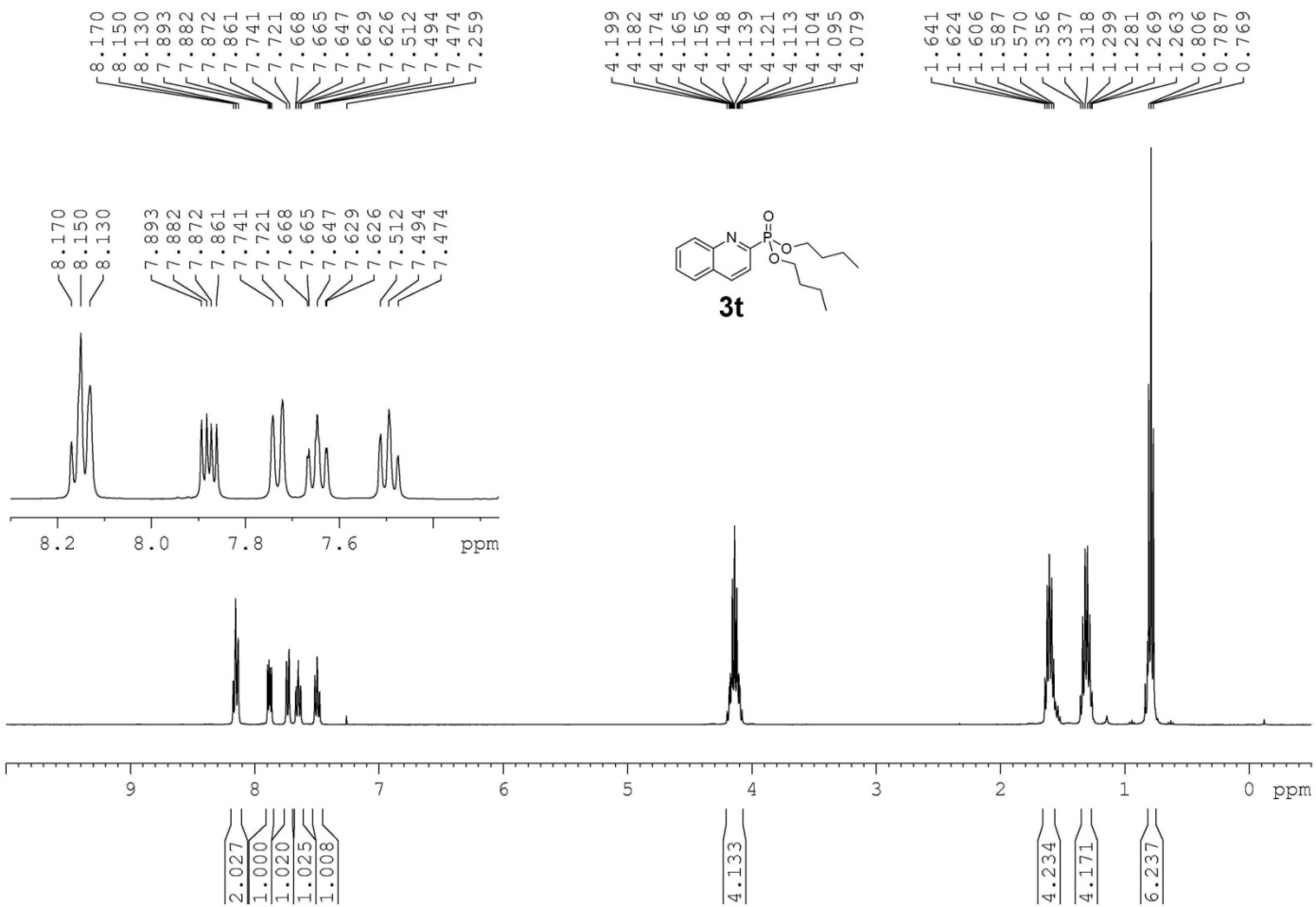
^{1}H NMR spectrum of compound **3s**



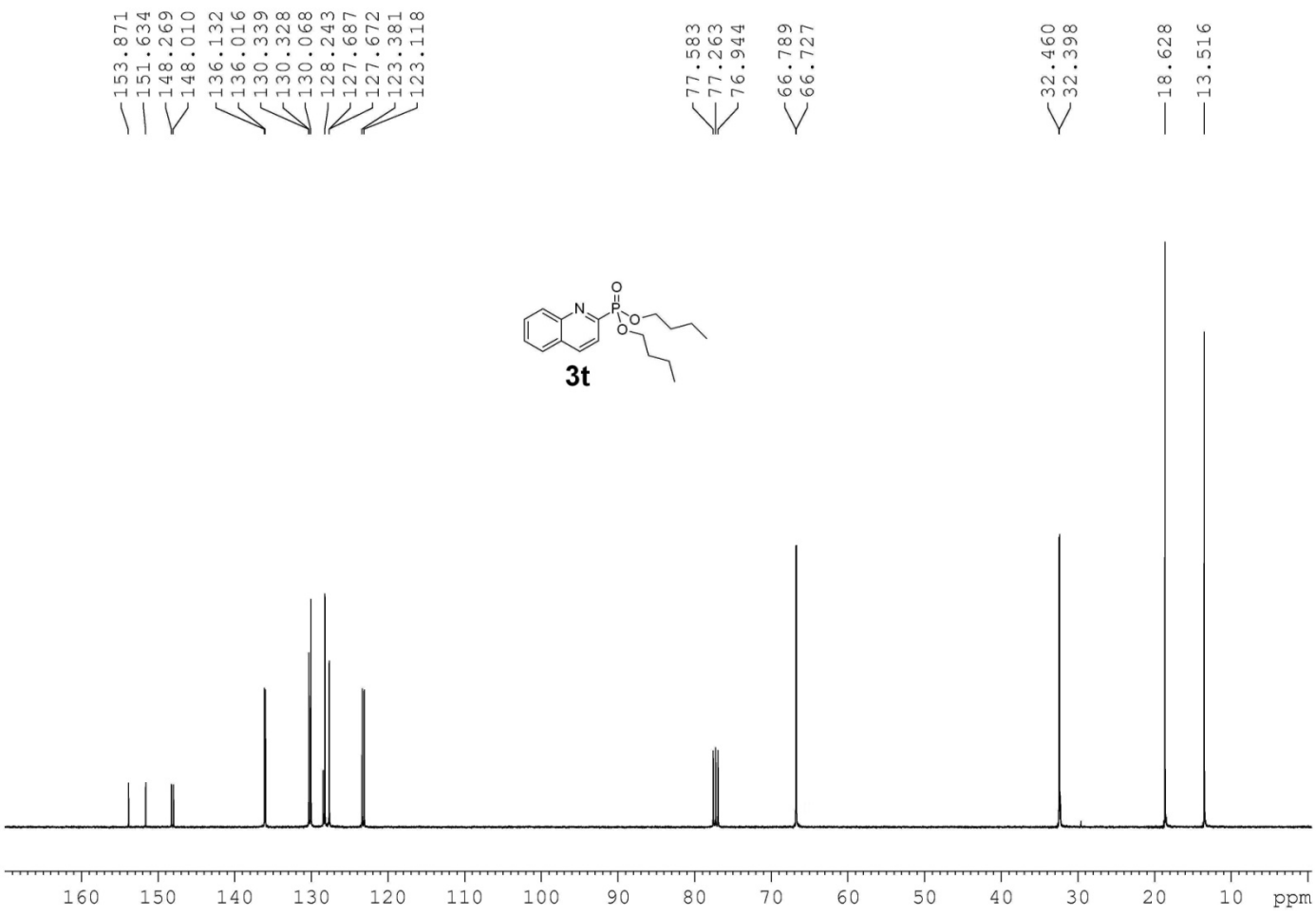
^{13}C NMR spectrum of compound **3s**



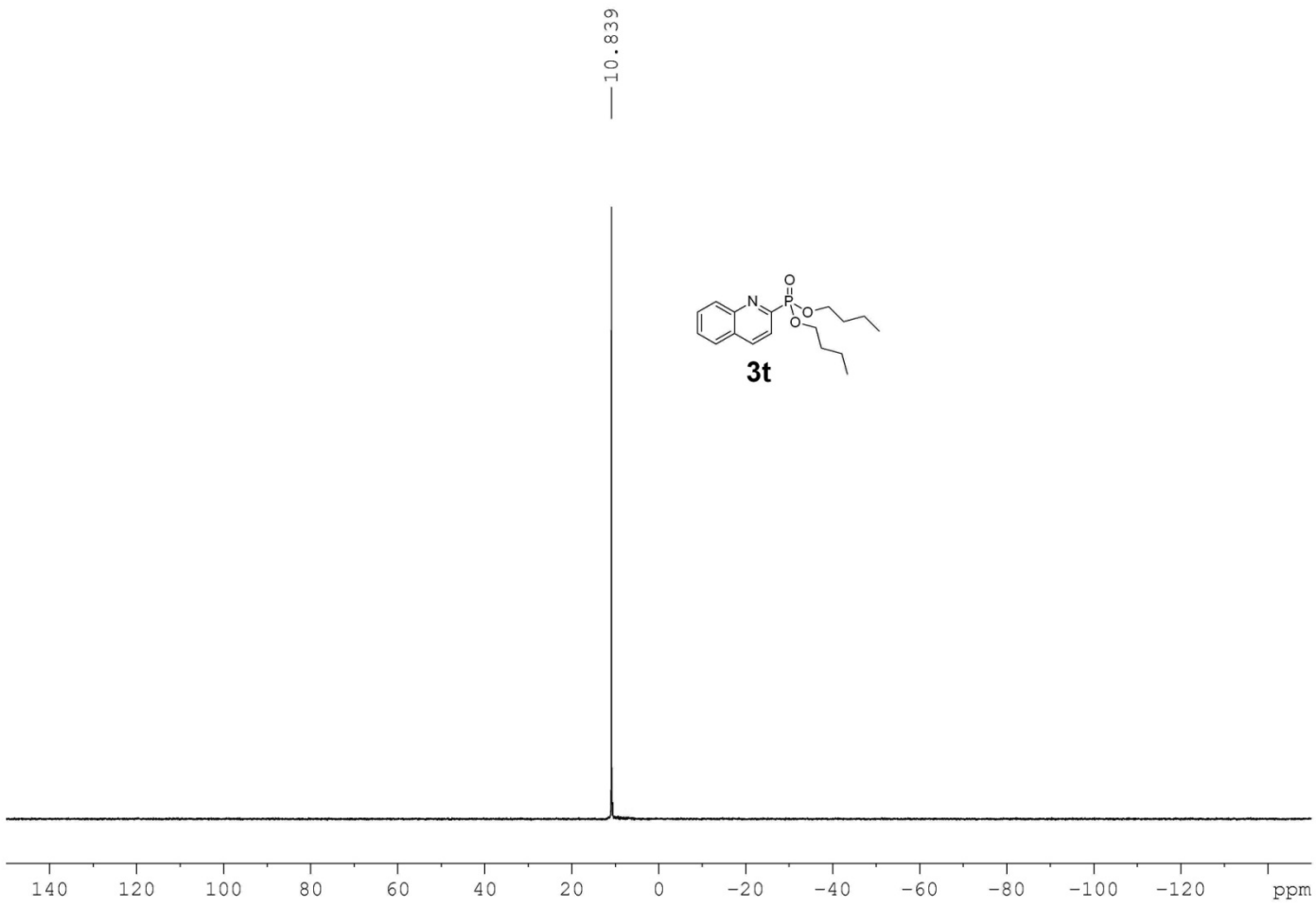
^{31}P NMR spectrum of compound **3s**



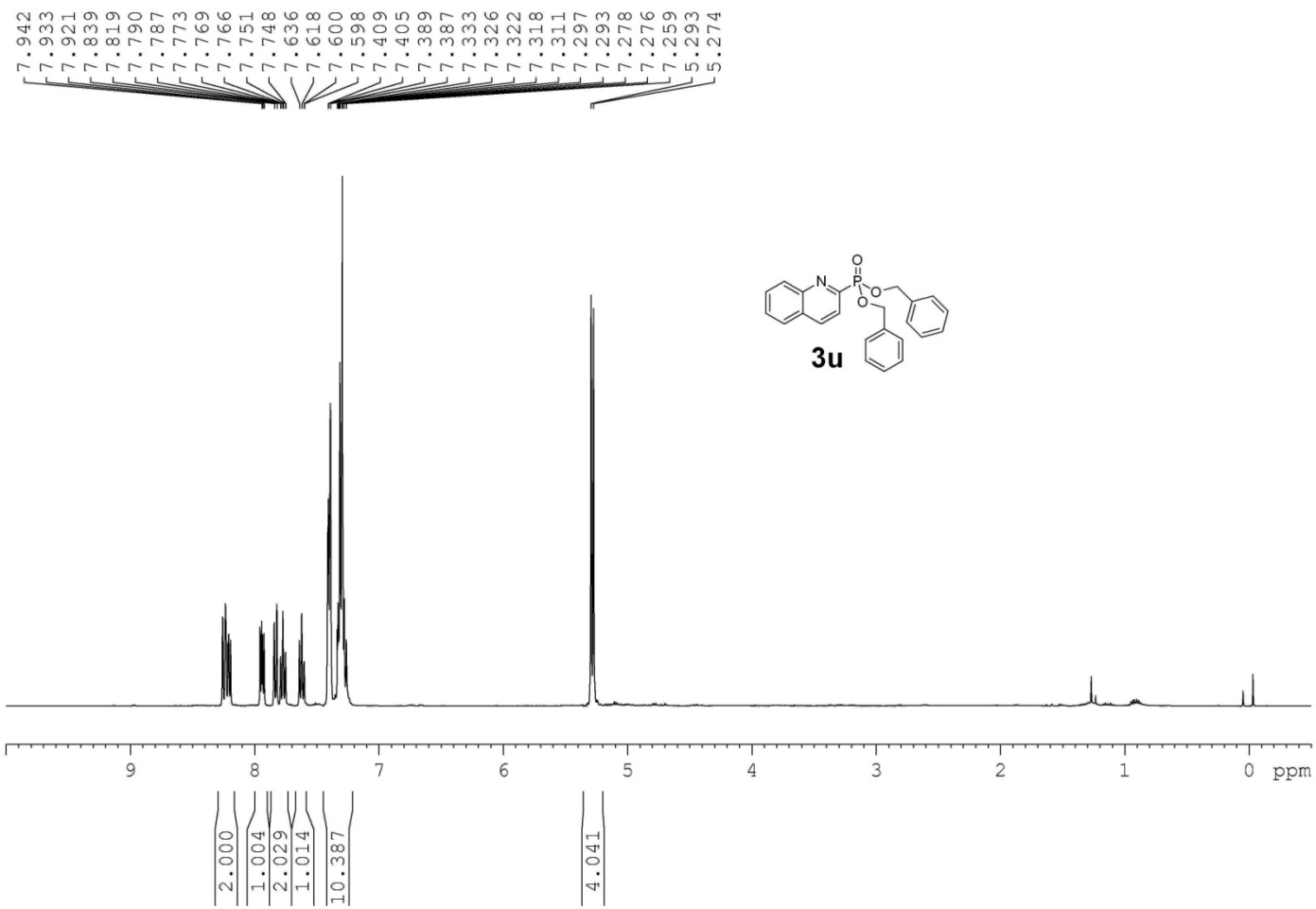
^{1}H NMR spectrum of compound **3t**



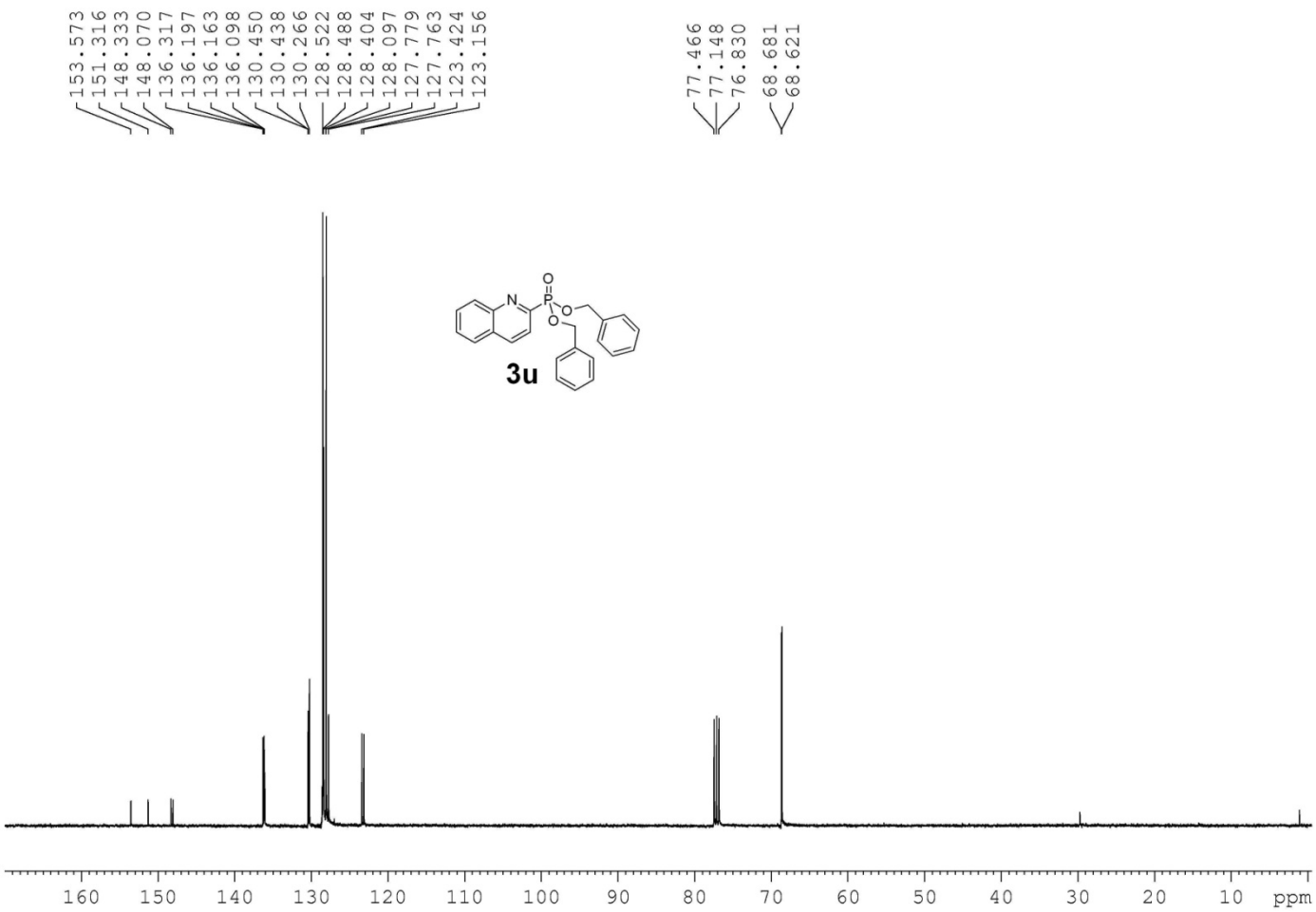
^{13}C NMR spectrum of compound **3t**



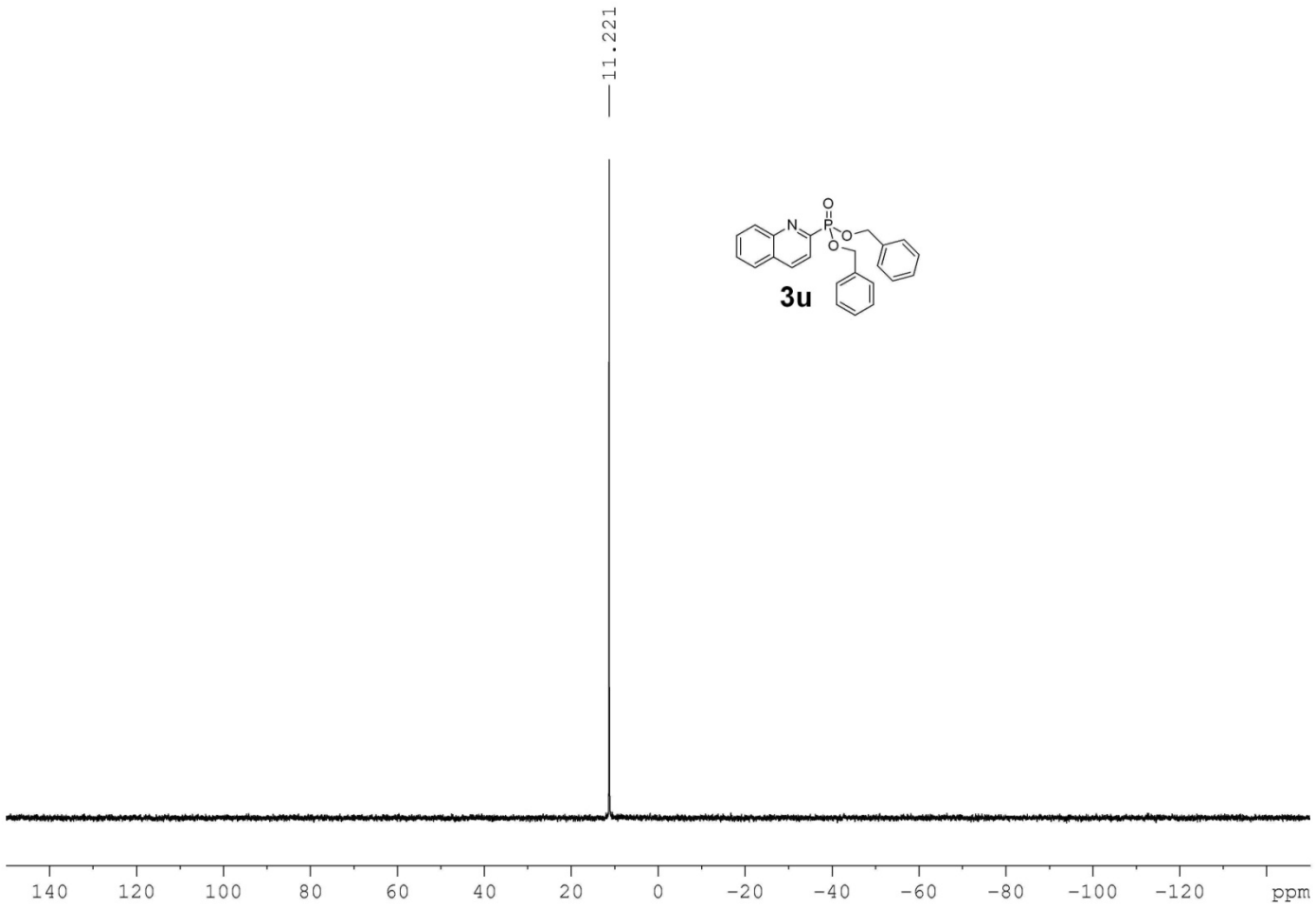
^{31}P NMR spectrum of compound **3t**



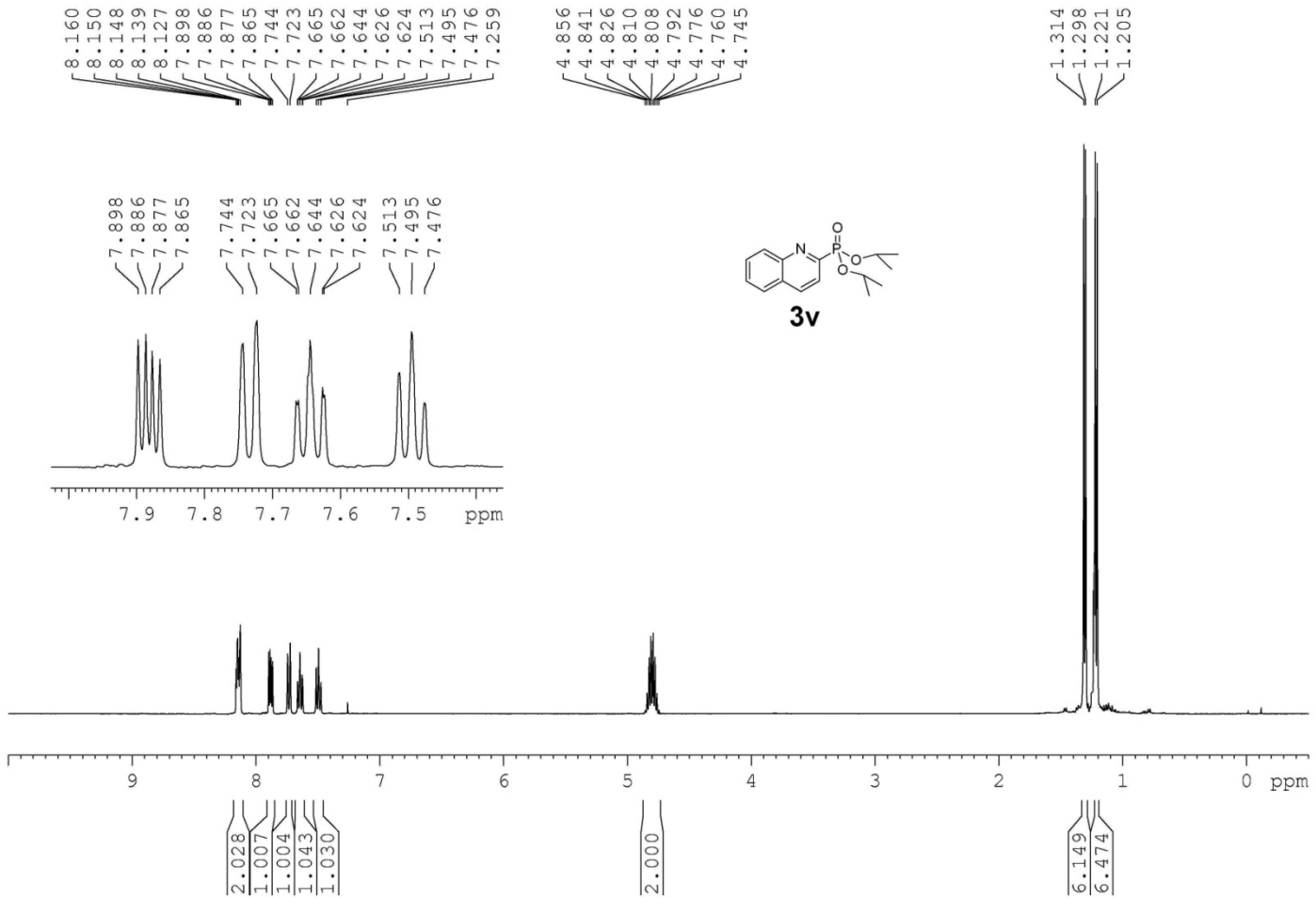
^{1}H NMR spectrum of compound **3u**



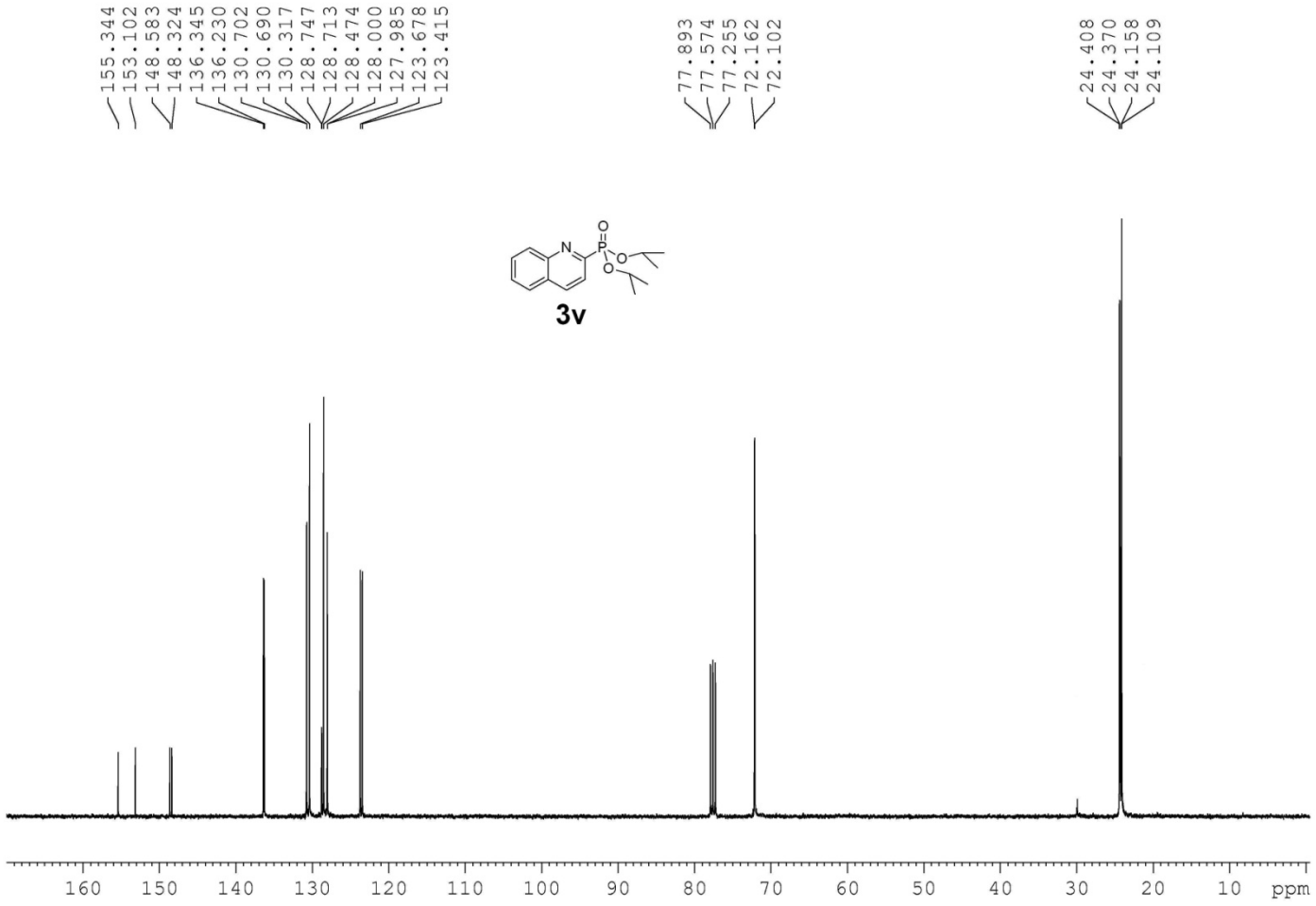
^{13}C NMR spectrum of compound **3u**



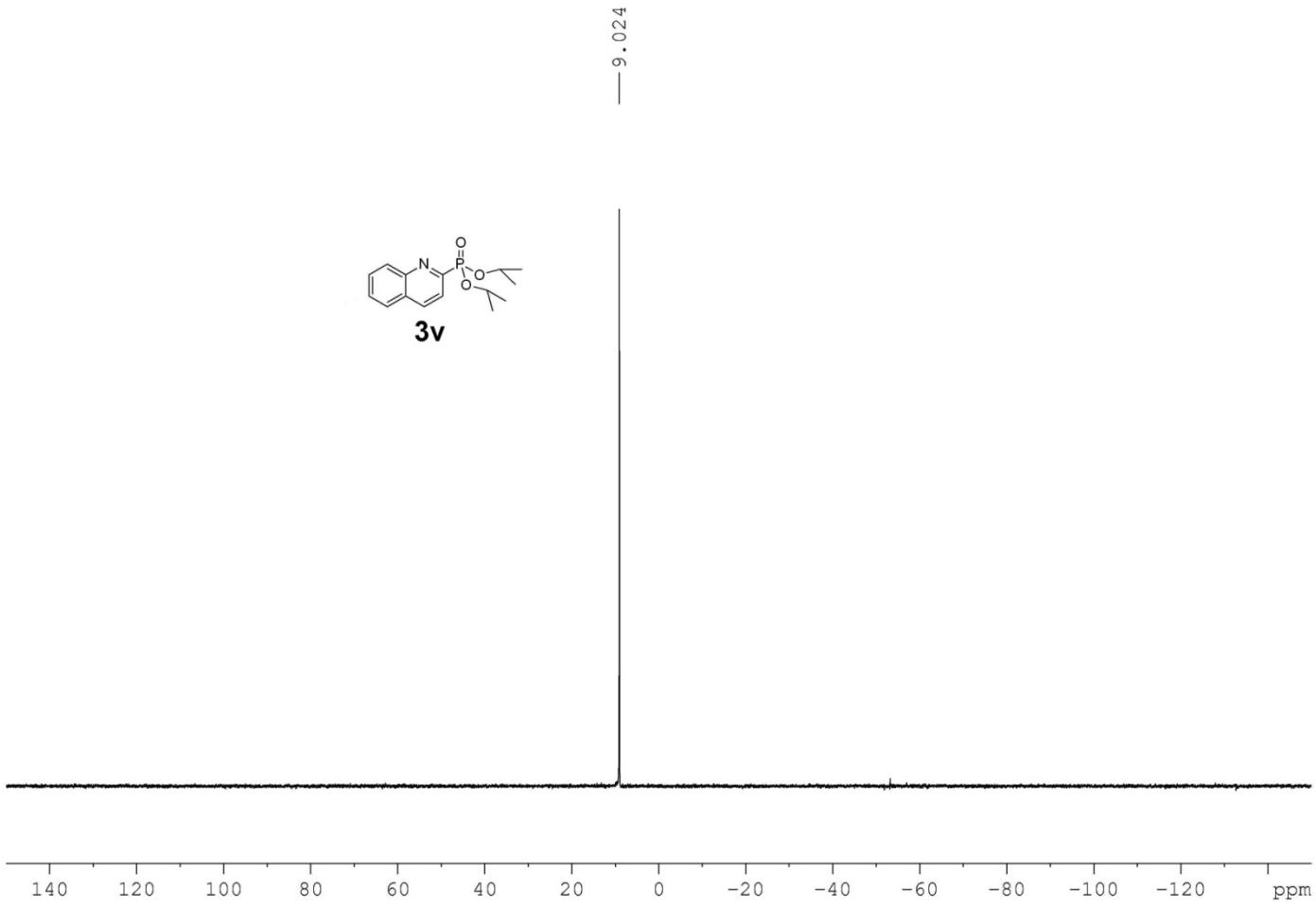
^{31}P NMR spectrum of compound **3u**



^{1}H NMR spectrum of compound **3v**



^{13}C NMR spectrum of compound **3v**



^{31}P NMR spectrum of compound **3v**