Supporting Information

Metal-free phosphonation of heteroarene N-oxides with trialkyl phosphite at room temperature

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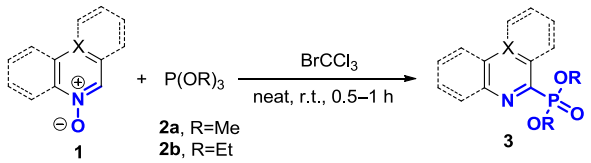
1 General experimental details

Unless otherwise noted, commercially available reagents were used as received. All solvents for chromatographic separations were distilled before use. Column chromatography was carried out with 200−300 mesh silica gel. The thin-layer chromatography (TLC) was performed on glass-backed silica plates. UV light, I_2, and solutions of 2,4-dinitrophenylhydrazine and potassium permanganate were used to visualize products. Concentrating a solution under reduced pressure refers to distillation using a rotary evaporator attached to a vacuum pump (3 – 10 mmHg). Products obtained as solids or high boiling oils were dried under vacuum (1 – 3 mmHg). Melting points (uncorrected) were recorded on an X-6 microscope melting point detector (Beijing Focus Instrument Co., Ltd). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AV 600 NMR spectrometer at 298 K. The chemical shifts (δ) of ^{1}H and ^{13}C were internally referenced by the residual solvent signals relative to tetramethylsilane ($CDCl_3$ at 7.26 ppm for ^{1}H, and at 77.00 ppm for ^{13}C). $^{31}P\{^{1}H\}$ NMR spectra were not calibrated via referencing the phosphorus-containing standard, but indirectly referenced via the deuterium lock signal of deuterated solvents using the respective reference frequencies ratio as recommended.[1] Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration). FT-IR spectra were determined on a Bruker TENSOR-27 FT-IR Spectrometer (Bruker) using a KBr pellet method in the wavelength range of 4000 – 400 cm^{-1}. High-resolution mass spectrometry (HRMS) for accurate mass measurements was performed on a Waters Synapt-G2 mass spectrometer or an Agilent LCMS TOF 6224 mass spectrometer. All the known products were confirmed by comparison with spectroscopic analysis of the authentic samples. The yields in the text refer to isolated yields of compounds (average of two runs).

2. General procedure for the phosphonation of heteroaryl *N*-oxides



In a typical run, to the mixture of isoquinoline *N*-oxide **1** (1.0 mmol) and $P(OMe)_3$ (**2a**, 350 μL, 3.0 mmol) was slowly added $CBrCl_3$ (300 μL, 3.0 mmol) with continual stirring at room temperature. Note that the reactions are mild exothermic. It should be careful for the scale up of the reactions. After **1** was completely consumed as monitored by TLC (typically, for 30 min to 1 h), the mixture was diluted with ethyl acetate (10 mL) and saturated aqueous Na_2CO_3 (10 mL) in sequence, and then extracted. The organic extract was sequentially washed with saturated aqueous Na_2CO_3 (10 mL × 2), water (10 mL × 2) and brine (10 mL × 2), dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica column chromatography (petroleum ether/EtOAc mixture as eluent). The isolated products were confirmed by ^1H, ^{13}C and ^{31}P NMR. The exact time for each reaction is shown in Table 2.

Dimethyl isoquinolin-1-ylphosphonate (3a):[2] Yellow oil (192 mg, 81% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.5 Hz, 1H), 8.71 (d, *J* = 5.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.81 (dd, *J* = 5.1, 2.3 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 3.95 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.6 (d, *J* = 224.0 Hz), 142.1 (d, *J* = 25.6 Hz), 136.1 (d, *J* = 10.7 Hz), 130.6, 130.1 (d, *J* = 29.4 Hz), 128.6, 127.3 (d, *J* = 2.4 Hz), 127.0, 123.8 (d, *J* = 4.2 Hz), 53.7 (d, *J* = 6.3 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.7.

Dimethyl (4-bromoisoquinolin-1-yl)phosphonate (3b): Yellow solid (262 mg, 83% yield); m.p. 101 – 104 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.6 Hz, 1H), 8.88 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.85 (t, *J* = 7.3 Hz, 1H), 7.76 (t, *J* = 7.3 Hz, 1H), 3.93 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.9 (d, *J* = 224.7 Hz), 143.9 (d, *J* = 25.9 Hz), 134.9 (d, *J* = 11.6 Hz), 131.9, 131.0 (d, *J* = 30.6 Hz), 129.5, 127.4, 126.6 (d, *J* = 1.4 Hz), 123.8 (d, *J* = 4.1 Hz), 53.8 (d, *J* = 6.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.1. HRMS (ESI-TOF) calcd for $C_{11}H_{11}BrNO_3P$ $[M+H]^+$: 315.9733. Found: 315.9730.

Dimethyl (5-bromoisoquinolin-1-yl)phosphonate (3c): Yellow solid (291 mg, 92% yield); m.p. 57 – 59 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, *J* = 8.6 Hz, 1H), 8.82 (d, *J* = 5.7 Hz, 1H), 8.21 (d, *J* =

5.1 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 3.95 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2 (d, *J* = 224.6 Hz), 143.4 (d, *J* = 25.5 Hz), 135.2 (d, *J* = 11.3 Hz), 134.4, 131.1 (d, *J* = 30.4 Hz), 128.8, 126.8, 122.6, 122.1, 53.9 (d, *J* = 6.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.9. IR ($\nu_{P=O}$): 1248 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{11}H_{11}BrNO_3P$ $[M+H]^+$: 315.9733. Found: 315.9729.

Dimethyl (5,8-dibromoisoquinolin-1-yl)phosphonate (3d): Yellow solid (363 mg, 92% yield); m.p. 123 – 126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 5.4 Hz, 1H), 8.21 (d, *J* = 5.3 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 3.96 (d, *J* = 11.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5 (d, *J* = 235.0 Hz), 142.3 (d, *J* = 25.0 Hz), 137.5 (d, *J* = 9.7 Hz), 135.6, 134.2, 130.9 (d, *J* = 28.3 Hz), 122.4 (d, *J* = 4.8 Hz), 122.3, 119.3, 53.9 (d, *J* = 7.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.7. IR ($\nu_{P=O}$): 1244 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{11}H_{10}Br_2NO_3P$ $[M+H]^+$: 393.8838. Found: 393.8840.

Dimethyl (4,7-dichloroisoquinolin-1-yl)phosphonate (3e): Yellow solid (187 mg, 61% yield); m.p. 114 – 117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 5.4 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 3.95 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.3 (d, *J* = 227.0 Hz), 149.3 (d, *J* = 27.9 Hz), 143.6 (d, *J* = 17.6 Hz), 137.4, 130.5, 129.6, 125.6, 125.5 (d, *J* = 3.1 Hz), 123.8 (d, *J* = 27.3 Hz), 54.0 (d, *J* = 6.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.8. HRMS (ESI-TOF) calcd for $C_{11}H_{10}Cl_2NO_3P$ $[M+H]^+$: 305.9848. Found: 305.9845.

Dimethyl (5-nitroisoquinolin-1-yl)phosphonate (3f): Yellow solid (183 mg, 65% yield); m.p. 103 – 105 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.39 (d, *J* = 8.6 Hz, 1H), 8.92 (d, *J* = 6.0 Hz, 1H), 8.63 (dd, *J* = 5.9, 1.8 Hz, 1H), 8.56 (d, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 8.1 Hz, 1H), 3.98 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.0 (d, *J* = 225.2 Hz), 145.4, 145.1 (d, *J* = 24.7 Hz), 134.1, 130.1 (d, *J* = 30.4 Hz), 128.5 (d, *J* = 11.4 Hz), 128.4, 127.0, 118.6 (d, *J* = 4.2 Hz), 54.1 (d, *J* = 6.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.1. IR ($\nu_{P=O}$): 1262 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{11}H_{11}N_2O_5P$ $[M+H]^+$: 283.0478. Found: 283.0485.

Dimethyl (4-iodoquinolin-2-yl)phosphonate (3g): Yellow solid (327 mg, 90% yield); m.p. 112 – 115 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.88 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 3.94 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7 (d, *J* = 223.9 Hz), 150.3 (d, *J* = 25.5 Hz), 137.4 (d, *J* = 11.3 Hz), 132.3, 131.6, 130.8 (d, *J* = 30.4 Hz), 129.6, 127.7, 102.1, 53.9 (d, *J* = 6.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.1. IR ($\nu_{P=O}$): 1275 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{11}H_{11}INO_3P$ $[M+H]^+$: 363.9594. Found: 363.9589.

Dimethyl quinolin-2-ylphosphonate (3h):[2] Yellow oil (142mg, 60% yield).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 – 8.24 (m, 2H), 8.00 (dd, *J* = 8.2, 4.7 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 3.94 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7 (d, *J* = 226.5 Hz), 148.2 (d, *J* = 26.0 Hz), 136.3 (d, *J* = 12.0 Hz), 130.4, 130.3, 128.6 (d, *J* = 3.4 Hz), 128.5, 127.7, 123.4 (d, *J* = 26.8 Hz), 53.6 (d, *J* = 6.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.8.

Dimethyl (3-iodoquinolin-2-yl)phosphonate (3i): Light yellow solid (320 mg, 88% yield); m.p. 165 – 167 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.6 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 4.04 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.4 (d, *J* = 237.9 Hz), 147.4 (d, *J* = 10.6 Hz), 145.8 (d, *J* = 24.5 Hz), 130.6, 130.3, 129.5, 129.3, 126.5, 89.1 (d, *J* = 28.8 Hz), 54.2 (d, *J* = 6.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.0. IR ($\nu_{P=O}$): 1291 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{11}H_{11}INO_3P$ $[M+H]^+$: 363.9594. Found: 363.9591.

Dimethyl (3-bromoquinolin-2-yl)phosphonate (3j):[2] Light yellow solid (224 mg, 71% yield).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.9 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 4.04 (d, *J* = 11.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.0 (d, *J* = 237.3 Hz), 145.7 (d, *J* = 24.3 Hz), 139.9 (d, *J* = 9.4 Hz), 130.38 (d, *J* = 7.1 Hz), 130.35, 129.5, 129.3 (d, *J* = 3.4 Hz), 126.6, 118.0 (d, *J* = 25.5 Hz), 54.2 (d, *J* = 6.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.1.

Dimethyl (6-bromoquinolin-2-yl)phosphonate (3k):[2] Light yellow solid (205 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.2, 5.7 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 1.9 Hz, 1H), 7.99 (dd, *J* = 8.4, 4.7 Hz, 1H), 7.84 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.93 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4 (d, *J* = 226.9 Hz), 146.8 (d, *J* = 26.2 Hz), 135.2 (d, *J* = 11.8 Hz), 133.9, 132.1 (d, *J* = 0.8 Hz), 129.8 (d, *J* = 1.3 Hz), 129.6 (d, *J* = 3.4 Hz), 124.2 (d, *J* = 26.6 Hz), 122.8, 53.7 (d, *J* = 6.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.3.

Dimethyl (4-methylquinolin-2-yl)phosphonate (3l):[2] Yellow solid (108 mg, 43% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 5.0 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 3.93 (d, *J* = 10.9 Hz, 6H), 2.76 (s, 3H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2 (d, *J* = 224.7 Hz), 148.0 (d, *J* = 26.7 Hz), 145.0 (d, *J* = 12.1 Hz), 131.1, 129.81, 128.7 (d, *J* = 3.4 Hz), 128.2, 124.2 (d, *J* = 26.7 Hz), 123.7, 53.6 (d, *J* = 6.2 Hz), 18.7. ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.3.

Dimethyl (6-methoxyquinolin-2-yl)phosphonate (3m): Yellow solid (131 mg, 49% yield); m.p.

75 – 78 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (t, *J* = 7.9 Hz, 2H), 7.95 (dd, *J* = 8.2, 4.8 Hz, 1H), 7.43 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.09 (d, *J* = 2.1 Hz, 1H), 3.96 (s, 3H), 3.92 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 148.6 (d, *J* = 228.6 Hz), 144.7 (d, *J* = 26.1 Hz), 134.7 (d, *J* = 12.1 Hz), 131.9, 130.2, 124.0 (d, *J* = 27.1 Hz), 123.5, 104.7, 55.6, 53.5 (d, *J* = 6.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.6. IR ($\nu_{P=O}$): 1234 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{12}H_{14}NO_4P$ $[M+Na]^+$: 290.0558. Found: 290.0559.

Dimethyl (8-methoxyquinolin-2-yl)phosphonate (3n): Yellow oil (80 mg, 30% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.3, 5.8 Hz, 1H), 8.00 (dd, *J* = 8.3, 4.6 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 4.07 (s, 3H), 3.96 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 150.4 (d, *J* = 229.3 Hz), 140.5 (d, *J* = 25.7 Hz), 136.0 (d, *J* = 11.9 Hz), 129.9 (d, *J* = 3.5 Hz), 128.9, 124.0 (d, *J* = 27.3 Hz), 119.4 (d, *J* = 1.4 Hz), 108.6, 56.19, 53.7 (d, *J* = 6.3 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.8. IR ($\nu_{P=O}$): 1260 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{12}H_{14}NO_4P$ $[M+H]^+$: 268.0739 . Found: 268.0736.

Dimethyl (8-ethoxyquinolin-2-yl)phosphonate (3o): Yellow oil (93 mg, 33% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.1, 6.0 Hz, 1H), 7.96 (dd, *J* = 8.3, 4.5 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 4.29 (q, *J* = 6.9 Hz, 2H), 4.01 (d, *J* = 10.7 Hz, 6H), 1.58 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 150.7 (d, *J* = 229.6 Hz), 140.5 (d, *J* = 25.8 Hz), 135.9 (d, *J* = 11.8 Hz), 129.9 (d, *J* = 3.5 Hz), 128.9, 123.6 (d, *J* = 27.4 Hz), 119.3, 109.9, 64.7, 54.0 (d, *J* = 6.5 Hz), 14.7. ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.2. IR ($\nu_{P=O}$): 1261 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{16}NO_4P$ $[M+H]^+$: 282.0895. Found: 282.0896.

Dimethyl quinoxalin-2-ylphosphonate (3p):[2] Light yellow solid (202 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 8.18 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.90 (t, *J* = 7.6 Hz, 1H), 7.87 (t, *J* = 7.5 Hz, 1H), 3.98 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2 (d, *J* = 224.3 Hz), 146.2 (d, *J* = 27.9 Hz), 143.2 (d, *J* = 2.7 Hz), 142.3 (d, *J* = 21.4 Hz), 132.2, 130.9, 130.3 (d, *J* = 1.4 Hz), 129.6 (d, *J* = 2.2 Hz), 53.9 (d, *J* = 6.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.7.

Dimethyl 1,10-phenanthrolin-2-ylphosphonate (3q): Yellow oil (101 mg, 35% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.24 (d, *J* = 3.1 Hz, 1H), 8.40 – 8.32 (m, 1H), 8.30 – 8.23 (m, 2H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.68 (dd, *J* = 7.9, 4.3 Hz, 1H), 4.02 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.6 (d, *J* = 229.3 Hz), 150.9, 146.5 (d, *J* = 24.5 Hz), 146.2, 136.05 (d, *J* = 11.9 Hz), 136.03, 129.6 (d, *J* = 3.6 Hz), 129.1, 128.8, 126.15 (d, *J* = 1.4 Hz), 126.1 (d, *J* = 27.0 Hz), 123.5,

53.8 (d, *J* = 6.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.86. IR ($\nu_{P=O}$): 1241 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{13}N_2O_3P$ $[M+Na]^+$: 311.0562. Found: 311.0562.

Compounds **3r**–**3w** were obtained in analogous fashion to **3a** from the corresponding *N*-oxide with **2b**.

Diethyl isoquinolin-1-ylphosphonate (3r):[3] Yellow oil (64 mg, 24% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 5.2 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.79 (s, 1H), 7.74 (dd, *J* = 7.4 Hz, 1H), 7.69 (dd, *J* = 10.4, 4.6 Hz, 1H), 4.36 – 4.27 (m, 4H), 1.38 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5 (d, *J* = 222.9 Hz), 142.1 (d, *J* = 25.5 Hz), 136.1 (d, *J* = 10.5 Hz), 130.5, 129.9 (d, *J* = 29.8 Hz), 128.4, 127.2 (d, *J* = 2.2 Hz), 127.1, 123.6 (d, *J* = 4.0 Hz), 63.2 (d, *J* = 6.2 Hz), 16.3 (d, *J* = 6.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.5.

Diethyl (4-bromoisoquinolin-1-yl)phosphonate (3s): Yellow oil (165 mg, 48% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (d, *J* = 8.6 Hz, 1H), 8.89 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 4.34 – 4.27 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9 (d, *J* = 223.0 Hz), 144.0 (d, *J* = 25.8 Hz), 134.9 (d, *J* = 11.5 Hz), 131.8, 131.0 (d, *J* = 30.3 Hz), 129.3, 127.6, 126.6, 123.6, 63.4 (d, *J* = 6.2 Hz), 16.4 (d, *J* = 6.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 9.8. IR ($\nu_{P=O}$): 1245 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{13}H_{15}BrNO_3P$ $[M+H]^+$： 344.0046. Found: 344.0044.

Diethyl (6-methoxyquinolin-2-yl)phosphonate (3t):[3] Yellow oil (100 mg, 34% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (t, *J* = 8.4 Hz, 2H), 7.95 (dd, *J* = 8.3, 4.7 Hz, 1H), 7.42 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 4.36 – 4.22 (m, 4H), 3.95 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 149.8 (d, *J* = 227.6 Hz), 144.6 (d, *J* = 26.1 Hz), 134.5 (d, *J* = 12.0 Hz), 132.0, 130.0, 123.9 (d, *J* = 26.8 Hz), 123.3, 104.7, 63.0 (d, *J* = 6.0 Hz), 55.6, 16.4 (d, *J* = 6.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.25.

Diethyl quinolin-2-ylphosphonate (3u):[2] Yellow oil (90 mg, 34% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (t, *J* = 6.9 Hz, 2H), 8.01 (dd, *J* = 7.5, 4.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 4.37 – 4.25 (m, 4H), 1.39 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9 (d, *J* = 225.4 Hz), 148.3 (d, *J* = 26.3 Hz), 136.1 (d, *J* = 11.8 Hz), 130.5, 130.1, 128.6, 128.3, 127.7, 123.4 (d, *J* = 26.6 Hz), 63.2 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 6.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.5.

Diethyl (8-methoxyquinolin-2-yl)phosphonate (3v): Yellow oil (115 mg, 39% yield).^{1}H NMR

(600 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.2, 5.8 Hz, 1H), 7.99 (dd, *J* = 8.3, 4.5 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 4.34 (dd, *J* = 15.0, 7.4 Hz, 4H), 4.07 (s, 3H), 1.40 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 151.4 (d, *J* = 228.2 Hz), 140.4 (d, *J* = 25.4 Hz), 135.8 (d, *J* = 12.0 Hz), 129.8, 128.7, 123.9 (d, *J* = 27.1 Hz), 119.3, 108.6, 63.3 (d, *J* = 6.2 Hz), 56.2, 16.4 (d, *J* = 6.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.7. IR ($\nu_{P=O}$): 1260 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{18}NO_4P$ $[M+Na]^+$: 318.0871. Found: 318.0873.

Diethyl (8-ethoxyquinolin-2-yl)phosphonate (3w): Yellow oil (121 mg, 39% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.1, 5.9 Hz, 1H), 7.95 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 4.39 (p, *J* = 7.1 Hz, 4H), 4.28 (dd, *J* = 13.8, 6.9 Hz, 2H), 1.58 (t, *J* = 6.9 Hz, 3H), 1.43 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 151.5 (d, *J* = 228.6 Hz), 140.4 (d, *J* = 25.7 Hz), 135.8 (d, *J* = 11.6 Hz), 129.8 (d, *J* = 3.4 Hz), 128.7, 123.6 (d, *J* = 27.2 Hz), 119.3, 109.8, 64.7, 63.5 (d, *J* = 6.4 Hz), 16.4 (d, *J* = 6.2 Hz), 14.72. ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.3. IR ($\nu_{P=O}$): 1259 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{15}H_{20}NO_4P$ $[M+Na]^+$: 332.1028. Found: 332.1029.

3 The ^{31}P NMR spectra of the reaction mixtures

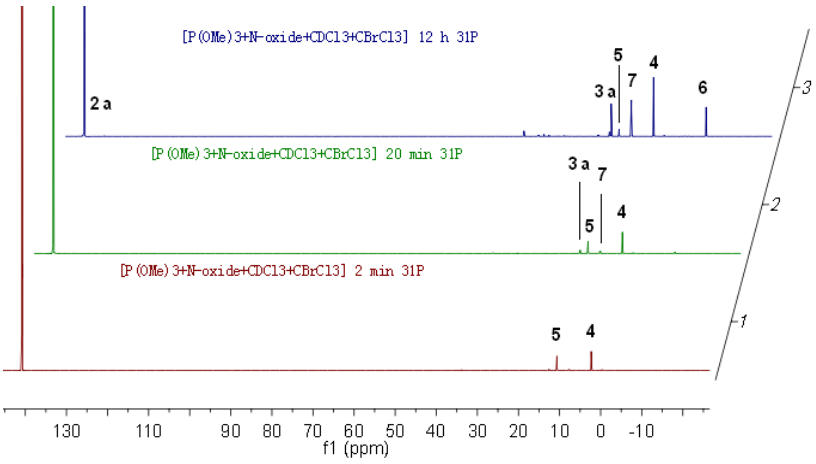


Figure S1. The stacked ^{31}P {^1H} NMR spectra of the reaction mixture of **1a** for monitoring the reaction progress in a solvent.

Note: *From bottom to top*, 1 (red bronze), 2 min after the addition of $CBrCl_3$; 2 (green), 20 min after the addition of $CBrCl_3$, and it is same with the spectrum shown in Figure S2 (see below); 3 (blue), 12 h after the addition of $CBrCl_3$. The bold codes above the peaks denote the assignment

of each peak to the related molecule in the text as well as in Figure S2. The reaction solvent was $CDCl_3$. The spectra were recorded at 298 K.

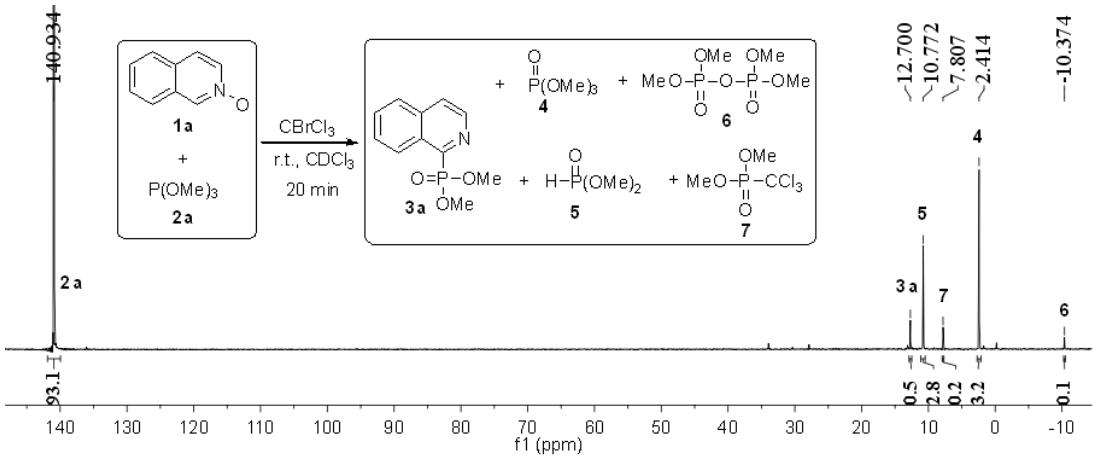


Figure S2. The $^{31}P\ \{^1H\}$ NMR spectrum of the reaction mixture of **1a** in a solvent 20 min after the addition of $CBrCl_3$.

Note: The reaction solvent was $CDCl_3$. The spectrum was recorded at 298 K. The bold codes above the peaks denote the assignment of each peak to the related molecule in the inserted box.

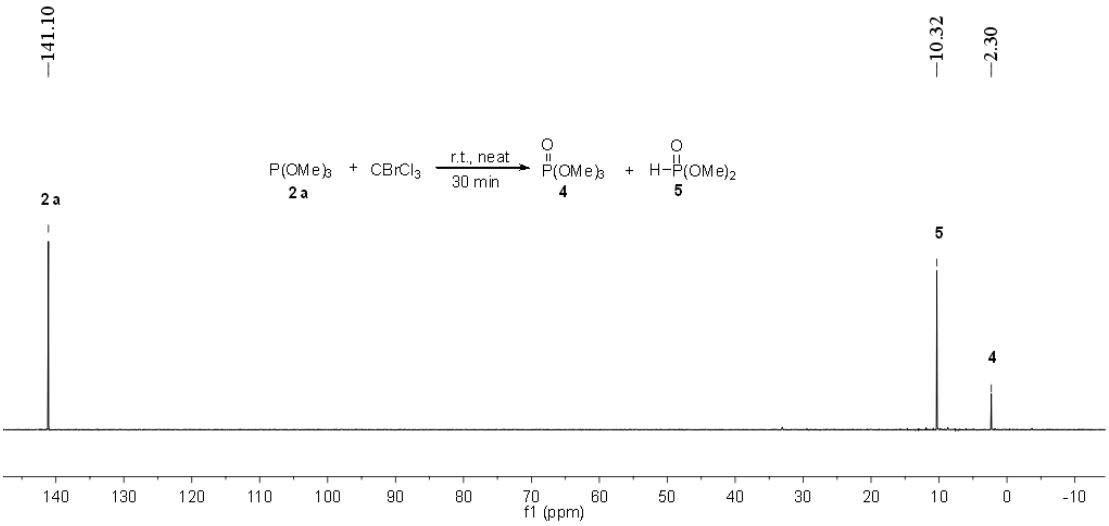


Figure S3. The $^{31}P\ \{^1H\}$ NMR spectrum of the reaction mixture of **2a** with $CBrCl_3$ in the absence of solvent.

Note: The spectrum was recorded with $CDCl_3$ as solvent at 298 K. The bold codes above the peaks denote the assignment of each peak to the related molecule in the inserted equation.

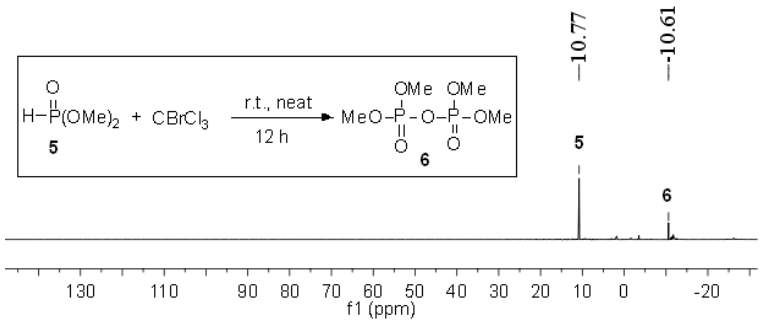


Figure S4. The ^{31}P {^{1}H} NMR spectrum of the reaction mixture of **5** with $CBrCl_3$ in the absence of solvent.

Note: The spectrum was recorded with $CDCl_3$ as solvent at 298 K. The bold codes above the peaks denote the assignment of each peak to the related molecule in the inserted equation.

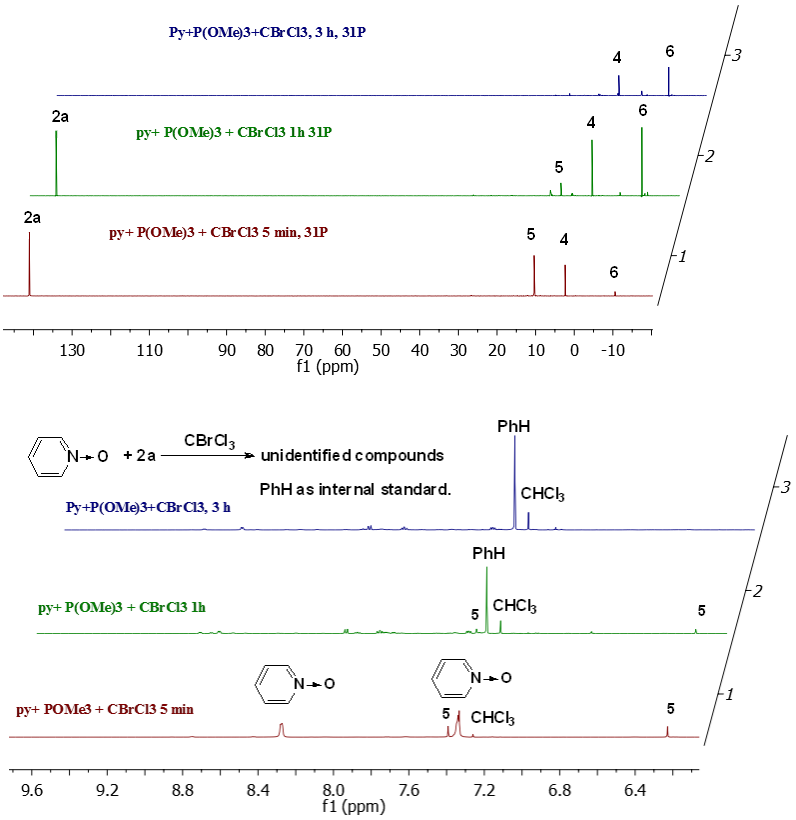
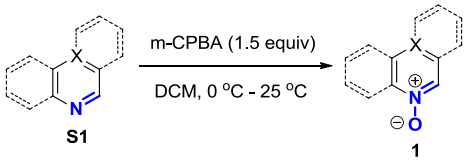


Figure S5. The stacked ^{31}P {^{1}H} and ^{1}H NMR spectra of the reaction mixture of **1a** with pyridine *N*-oxide for monitoring the reaction progress.

Note: Top, ^{31}P {^{1}H} NMR spectra; bottom, ^{1}H NMR spectra. 1 (red bronze), 5 min after the addition of $CBrCl_3$; 2 (green), 1 h after the addition of $CBrCl_3$; 3 (blue), 3 h after the addition of $CBrCl_3$. The bold codes above the peaks denote the assignment of each peak to the related

molecule in the text as well as in Figure S2. Trace of benzene was employed as internal standard. The spectra were recorded with $CDCl_3$ as solvent at 298 K. The ^{31}P {^1H} NMR spectra indicated that **2a** was mainly converted to trimethyl phosphate (**4**) and tetramethyl diphosphate (**6**). As the ^1H NMR spectra shown, pyridine *N*-oxide was fully transformed into a complicated mixture, but the desired compound did not yield.

4 Syntheses of the substrates



The syntheses of heteroarene *N*-oxides were realized through the classic oxidation of *N*-heteroarene by peroxy acids.[4–8] Typically, a solution of *N*-heteroarene **S1** (5.0 mmol) was dissolved in DCM (25 mL) and cooled to 0 °C. Then 3-chloroperbenzoic acid (*m*-CPBA, 1.52 g, 7.5 mmol, 85% purity) was added to the solution in portions. The mixture was stirred at 25 °C overnight, quenched with a saturated aqueous $NaHCO_3$ solution (50 mL), extracted with DCM (30 mL × 3), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product.

The substrates **1** were prepared according to the above procedure. **1a**,[4] **1b**,[5] **1c**,[6] **1f**,[6] **1h**,[6] **1i**,[7] **1j**,[6] **1k**,[4] **1l**,[4] **1m**,[4] **1n**,[8] **1o**,[6] **1p**,[6] and **1q**[6] were reported previously. Characterization data of the new substrates are as follows.

5,8-dibromoisoquinoline 2-oxide (1d): Light yellow solid (1.24 g, 82% yield); m.p. 188 – 190 °C.^1H NMR (600 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.22 (d, *J* = 7.3 Hz, 1H), 8.04 (d, *J* = 7.3 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.26 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.79, 136.25, 133.78, 132.43, 129.99, 128.75, 123.99, 121.16, 118.23. HRMS (ESI-TOF) cald for $C_9H_5Br_2NO$ $[M+H]^+$: 301.8811. Found: 301.8809.

4,7-dichloroisoquinoline 2-oxide (1e): Light yellow solid (0.84 g, 79% yield); m.p. 157 – 159 °C.^1H NMR (600 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.42 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.38 (s, 1H). The resolution of ^{13}C NMR spectrum was difficult due to the severe broadening of

peaks. HRMS (ESI-TOF) calcd for $C_9H_5Cl_2NO$ $[M+H]^+$: 213.9821. Found: 213.9818.

4-iodoisoquinoline 2-oxide (1g): Yellow solid (1.08 g, 80% yield); m.p. 165 – 167 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.63 (s, 1H), 7.95 (s, 1H), 7.66 (s, 3H). The resolution of ^{13}C NMR spectrum was difficult due to the severe broadening of peaks. HRMS (ESI-TOF) calcd for C_9H_6INO $[M+Na]^+$: 293.9392. Found: 293.9392.

5 The experiments for the mechanism investigations

A. The records of NMR spectra for the reaction mixture of 1c with 2a

The reaction procedure was described above as the general procedure for the phosphonation. After **1c** was completely consumed as monitored by TLC (about 30 min), a 60 μL aliquot of the mixture was transferred to a NMR tube, diluted with $CDCl_3$ (0.5 mL), and submitted to record ^{1}H, ^{31}P and ^{13}C NMR spectra. The ^{31}P NMR spectrum is shown in Figures 1. Characterization data of the identified compounds are as follows. $P(OMe)_3$ **(2a)**,[9] ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.52 (d, *J* = 10.7 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 48.9 (d, *J* = 10.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 141.2. Trimethyl phosphate (**4**),[10] ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 (d, *J* = 11.0 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 54.2 (d, *J* = 5.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 2.4. Dimethyl hydrophosphonate (**5**),[11] ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.76 (d, *J* = 698.0 Hz, 1H), 3.79 (d, *J* = 11.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 51.9 (d, *J* = 5.8 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 10.5. Tetramethyl diphosphate (**6**),[12] ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.82 (d, *J* = 11.2 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 55.3 (d, *J* = 4.5 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −10.5. CH_3OH,[13] ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 50.1. $CHCl_3$,[14] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26; ^{13}C NMR (151 MHz, $CDCl_3$) δ 77.2. $CBrCl_3$,[15] ^{13}C NMR (151 MHz, $CDCl_3$) δ 67.5. CH_3Br,[16] ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.56 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 9.8.

B. Monitoring the progress of the deoxygenative phosphonation in a solvent

A NMR tube (5×180 mm) was charged with the mixture of isoquinoline *N*-oxide (**1a**, 48 mg, 0.33 mmol) and $P(OMe)_3$ (**2a**, 117 μL, 1.0 mmol) in $CDCl_3$ (400 μL), and $CBrCl_3$ (100 μL, 1.0 mmol)

was added dropwise with shaking at room temperature. After the addition was complete, the mixture was thoroughly shaken for a moment, and submitted to record its ^{1}H and ^{31}P NMR spectra. The first ^{31}P NMR spectrum was recorded at 2 min after the addition. Then the sample was continually shaken for 20 min, and submitted to record its ^{1}H and ^{31}P NMR spectra again. After the sample was placed at room temperature for 12 h, the spectra were recorded once more. The ^{31}P NMR spectra are shown in Figures S2 and S3. The identified compounds included **3a**, **4**–**7** and CH_3Br. Dimethyl (trichloromethyl)phosphonate (**7**) was parallelly prepared according to the literature,[17] and its characterization data are as follows. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.07 (d, *J* = 10.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 88.4 (d, *J* = 199.7 Hz), 57.0 (d, *J* = 6.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 7.6.

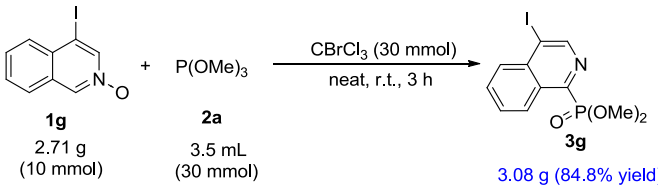
C. Control experiment shown in Equation 3

$CBrCl_3$ (300 μL, 3.0 mmol) was slowly added dropwise to $P(OMe)_3$ (**2a**, 350 μL, 3.0 mmol) with continual stirring at room temperature. After the addition was complete, a 60 μL aliquot of the mixture was transferred to a NMR tube, diluted with $CDCl_3$ (0.5 mL), and submitted to record ^{1}H and ^{31}P NMR spectra. 30 min later, another 60 μL aliquot of the mixture was transferred to a NMR tube, diluted with $CDCl_3$ (0.5 mL), and submitted to record the NMR spectra. The spectra of the two samples were similar, and a ^{31}P NMR spectrum was shown in Figure S3. 3.5 h later, the spectra of the reaction mixture indicated that **2a** had been completely consumed.

D. Control experiment shown in Equation 4

$CBrCl_3$ (300 μL, 3.0 mmol) was added dropwise to dimethyl hydrogenphosphonate (**3**, 275 μL, 3.0 mmol). The mixture was continually stirred at room temperature for 12 h. A 60 μL aliquot of the mixture was transferred to a NMR tube, diluted with $CDCl_3$ (0.5 mL), and submitted to record ^{1}H and ^{31}P NMR spectra. The ^{31}P NMR spectrum is shown in Figure S4, which indicates that **3** has partially converted to **6**.

6 The experiment for the scale up of reaction



1g
2.71 g
(10 mmol)

2a
3.5 mL
(30 mmol)

3g
3.08 g (84.8% yield)

In a 250 mL flask, $CBrCl_3$ (3.0 mL, 30 mmol) was slowly added with continual stirring to the suspension of isoquinoline *N*-oxide **1g** (2.71g, 10 mmol) and $P(OMe)_3$ (**2a**, 3.50 mL, 30 mmol). Note that the reaction is mild exothermic. The reaction flask was cooled with water bath to keep the temperature not exceeding 35 ^{o}C during the addition. The water bath was removed after the addition was complete (about 5 min). The mixture was continually stirred at ambient temperature until **1g** was completely consumed as monitored by TLC (about 3 hours). The mixture was submitted to the workup and purifications according to the above-mentioned general procedure. The product (**3g**) was isolated as a yellow solid (3.08 g, 84.8% yield).

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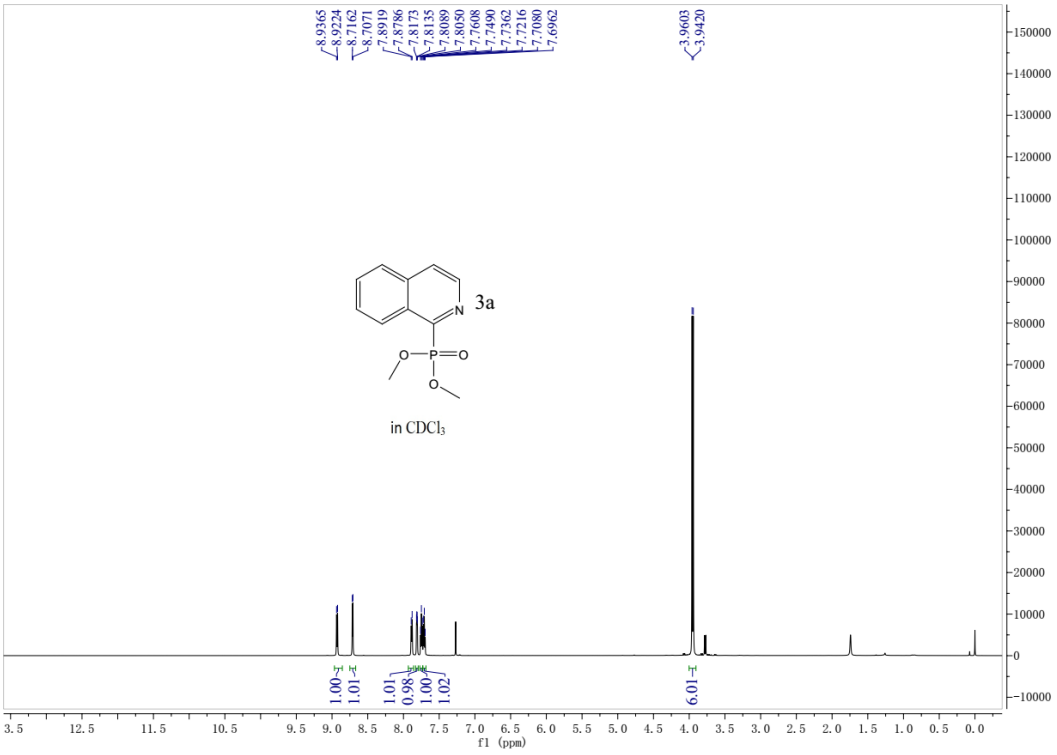
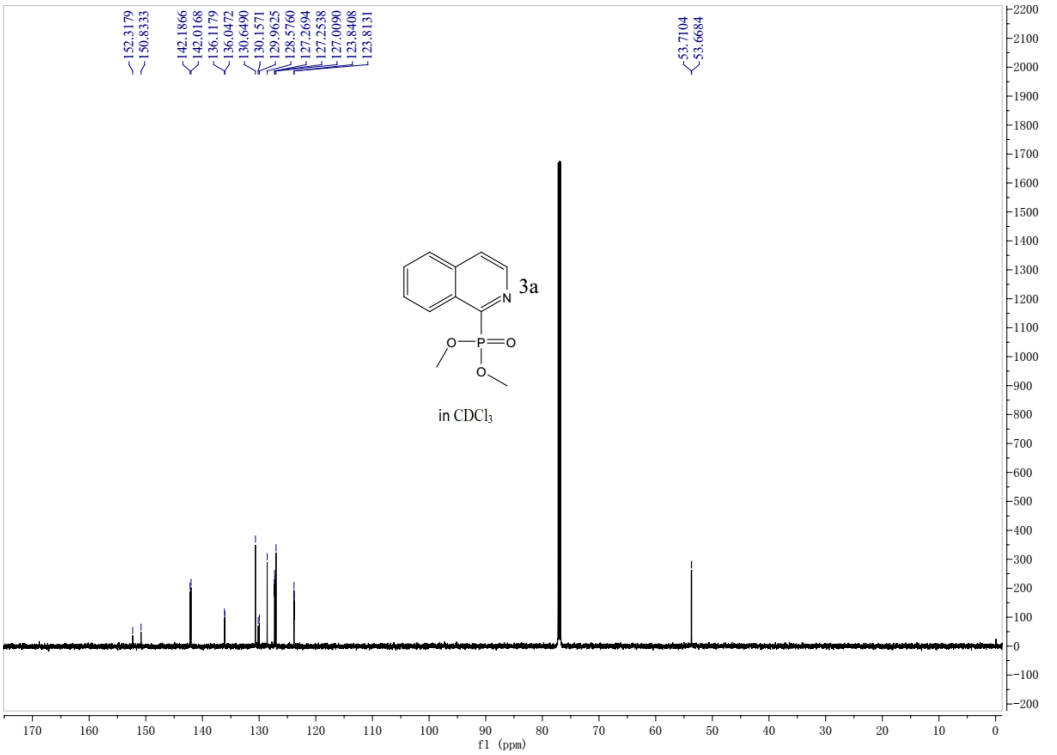
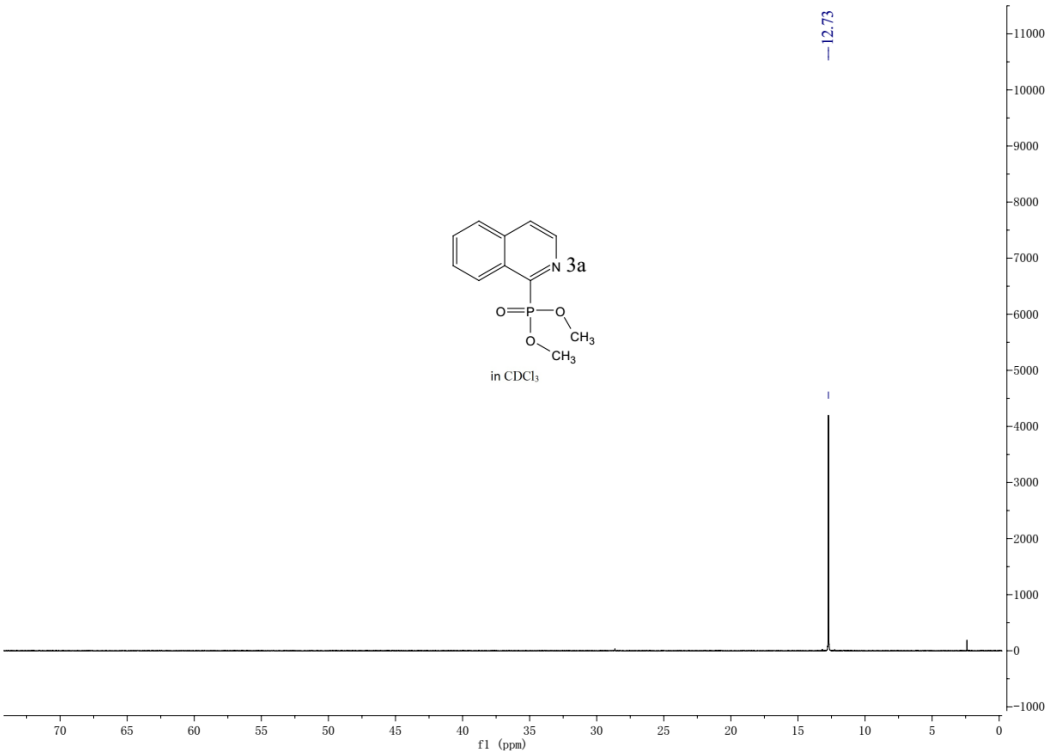
Appendix. NMR & MS spectra of new compounds



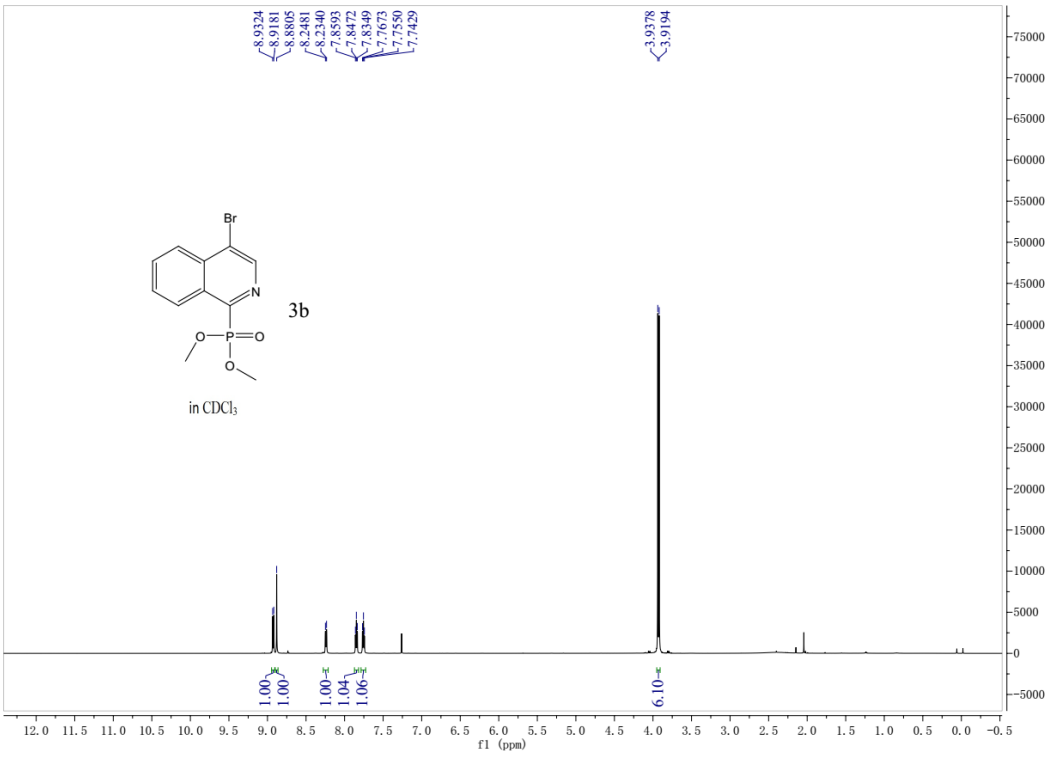
^{1}H NMR spectrum of compound **3a**



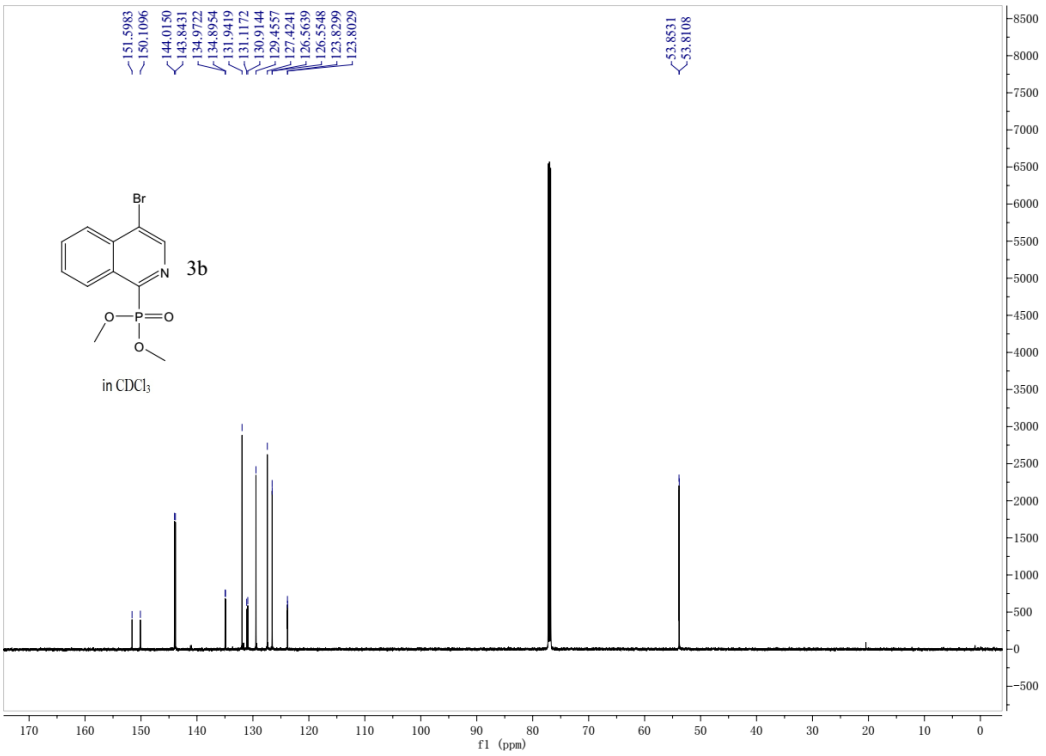
^{13}C NMR spectrum of compound **3a**



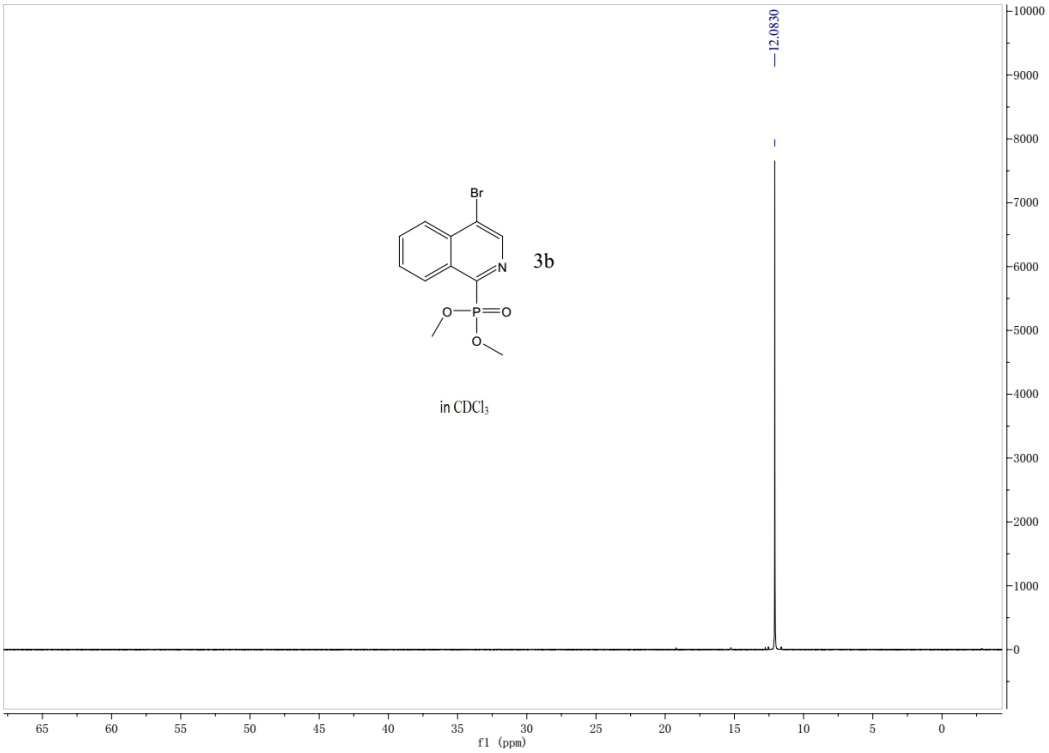
^{31}P NMR spectrum of compound **3a**



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

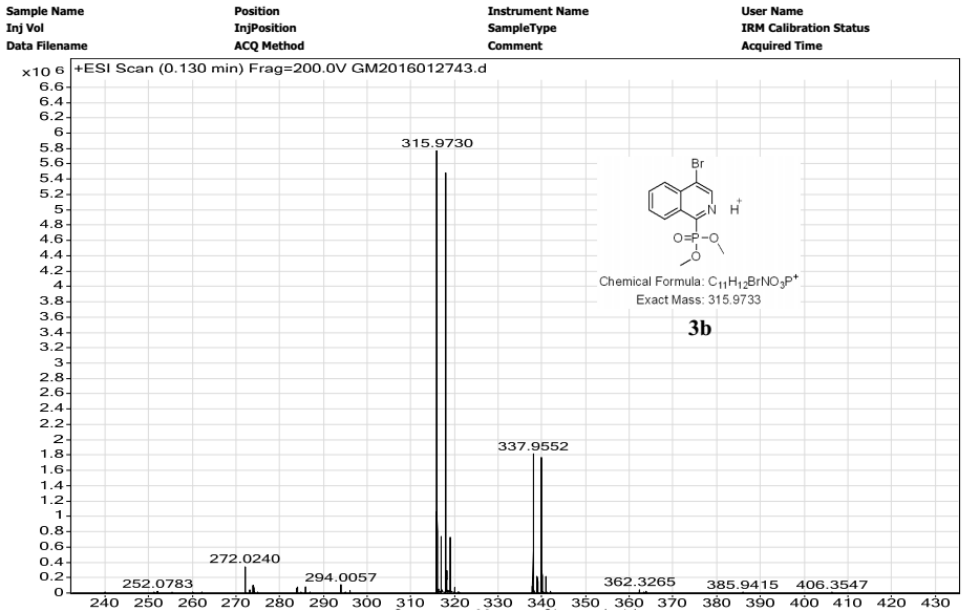


^{13}C NMR spectrum of compound **3b**

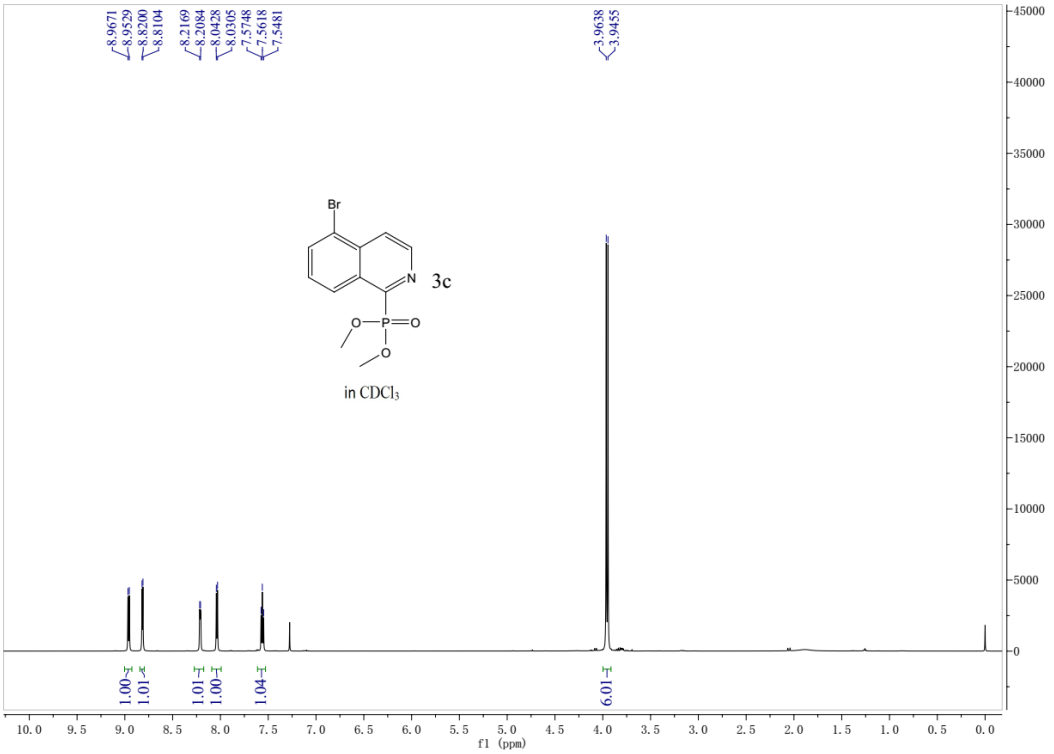


^{31}P NMR spectrum of compound

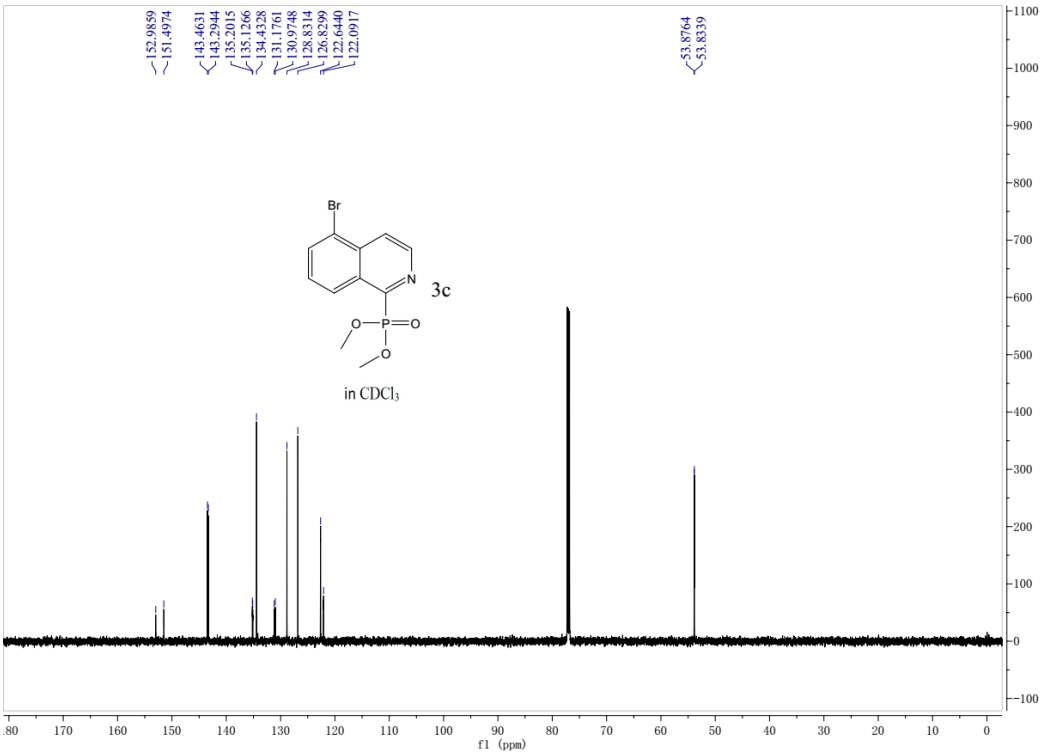
3b



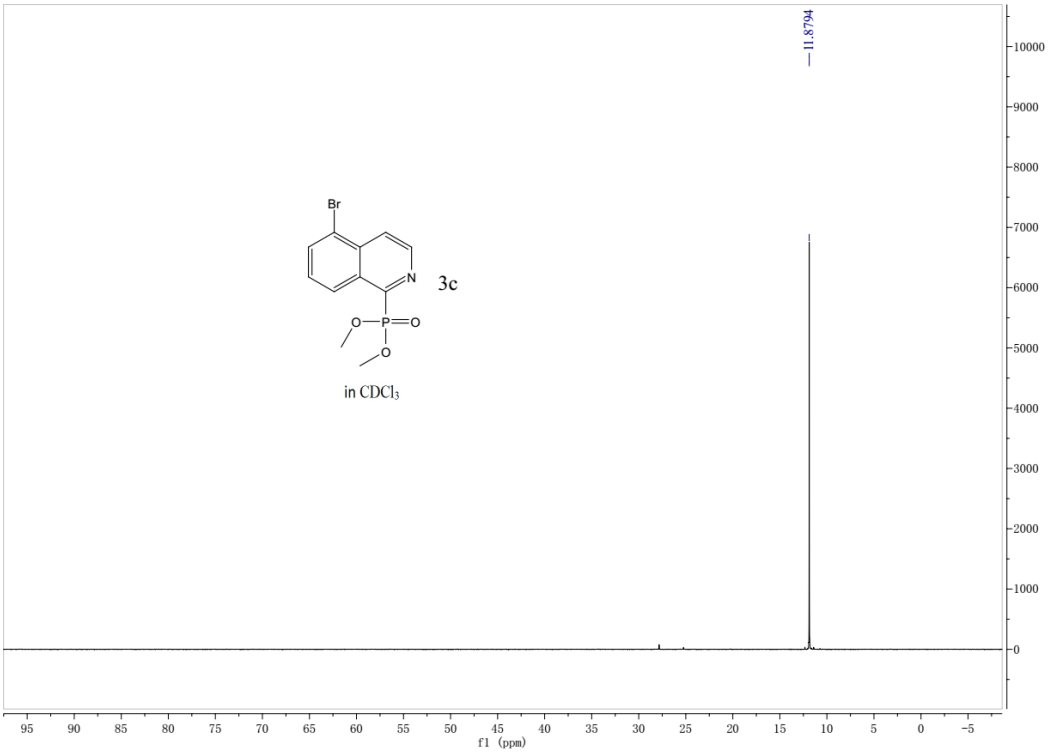
HRMS (ESI-TOF) spectrum of compound **3b**



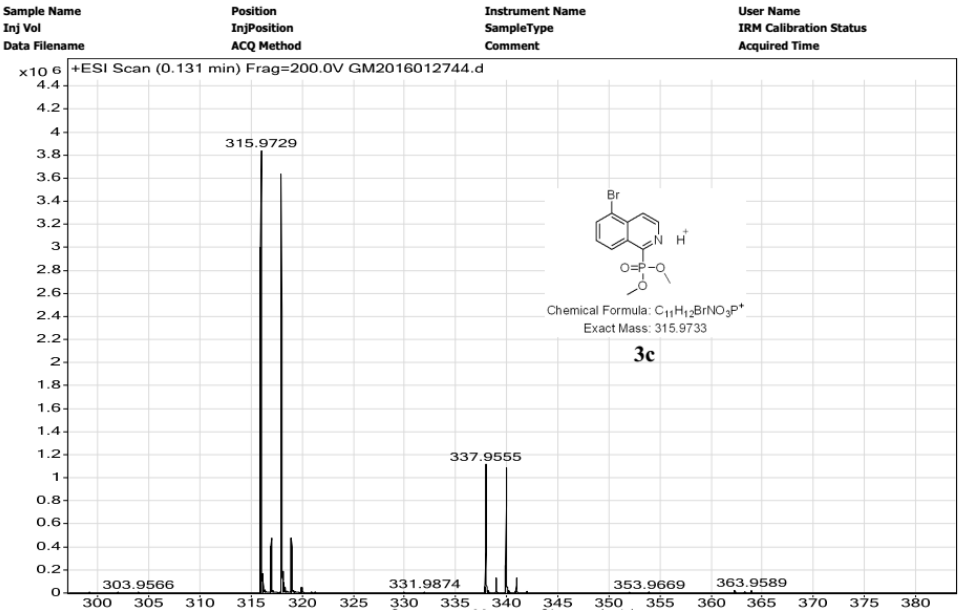
^{1}H NMR spectrum of compound **3c**



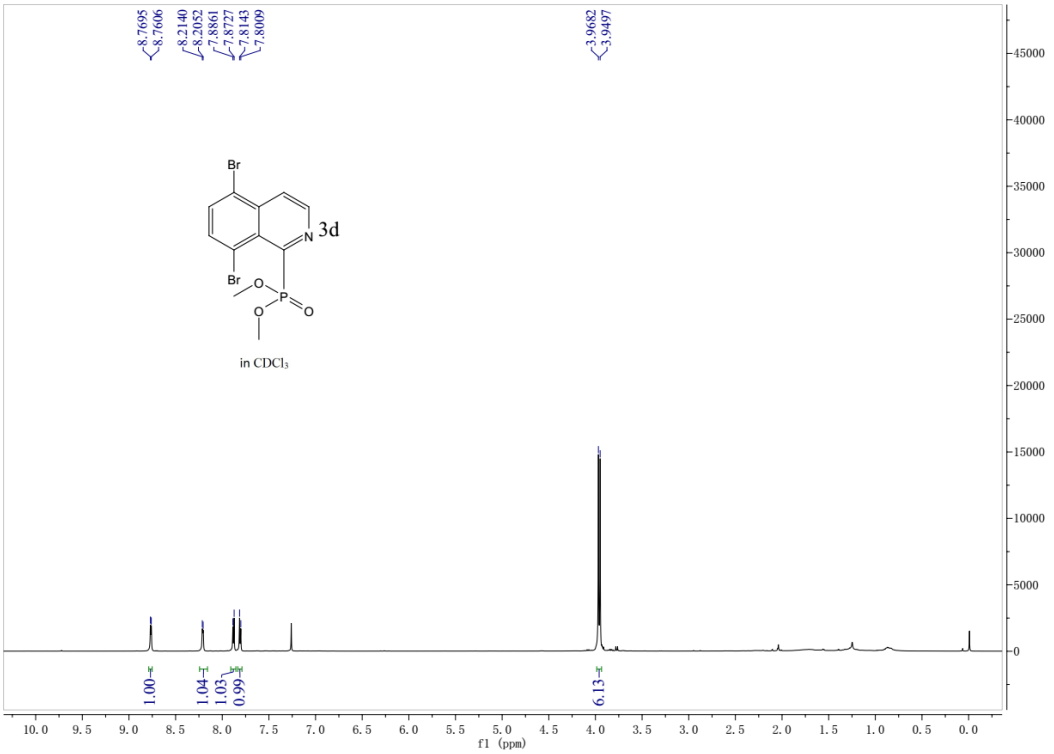
^{13}C NMR spectrum of compound **3c**



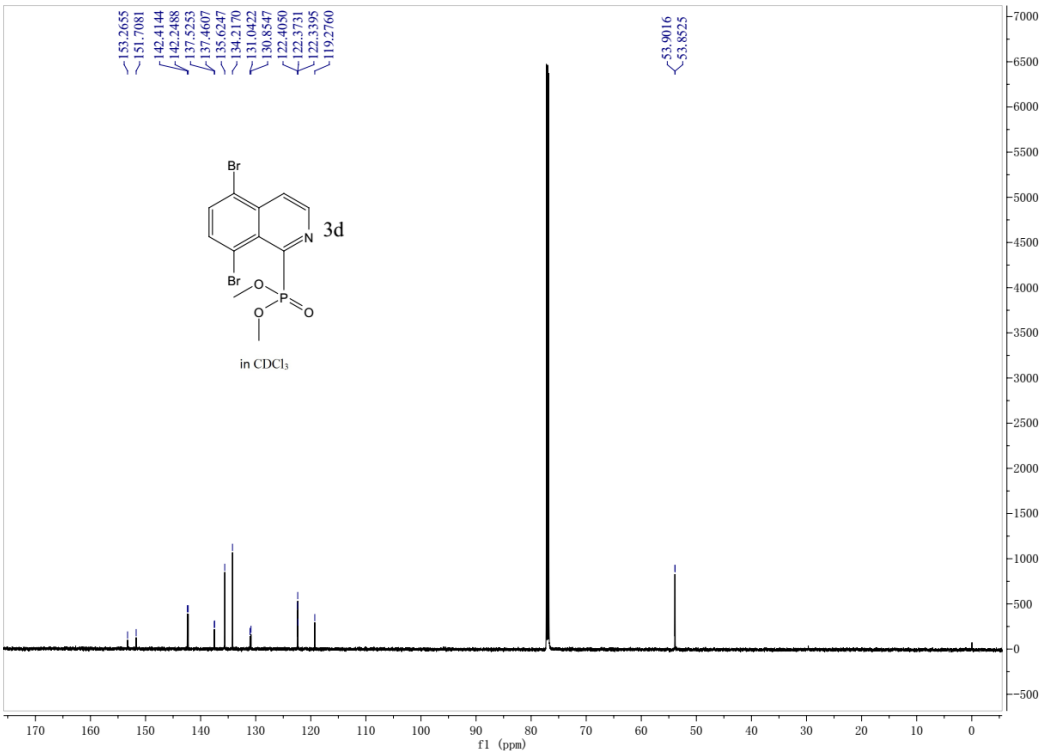
^{31}P NMR spectrum of compound **3c**



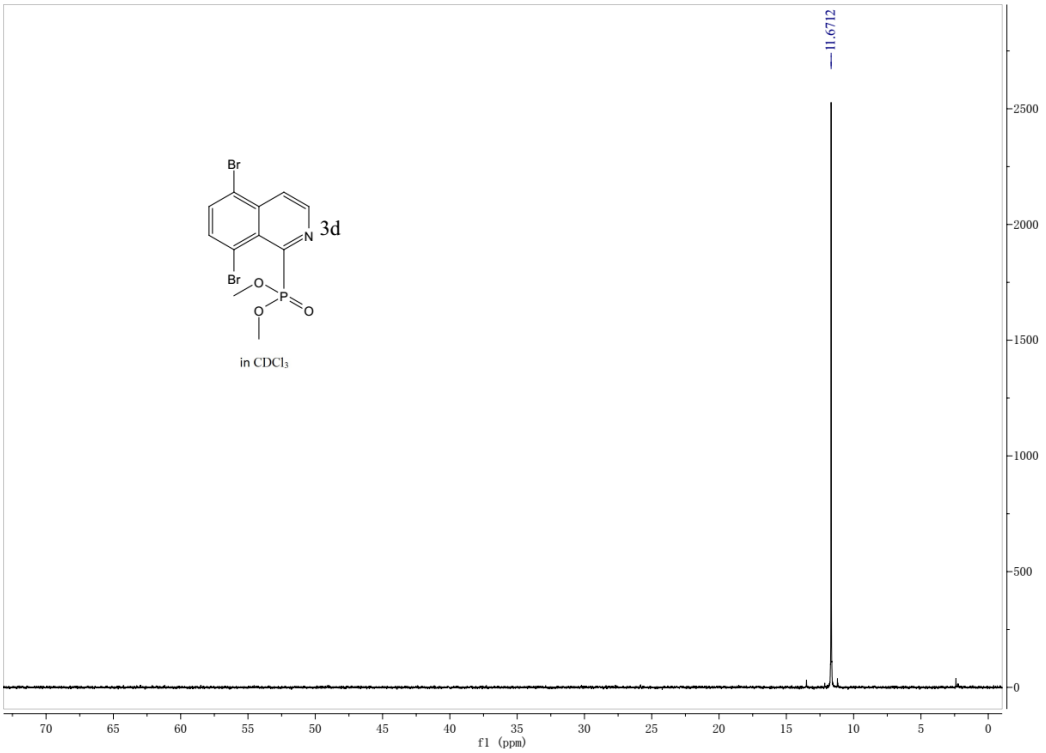
HRMS (ESI-TOF) spectrum of compound **3c**



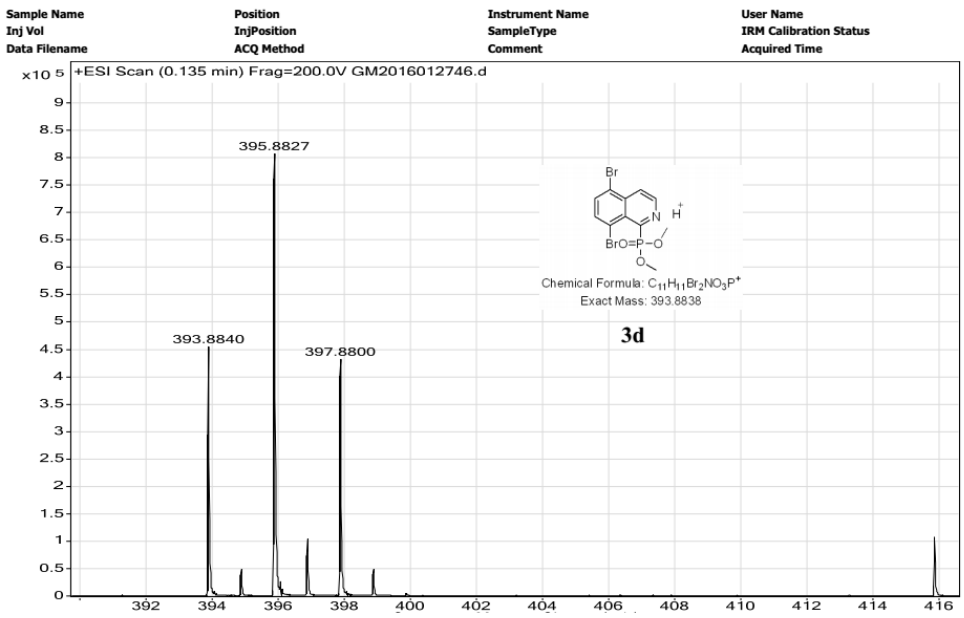
^{1}H NMR spectrum of compound **3d**



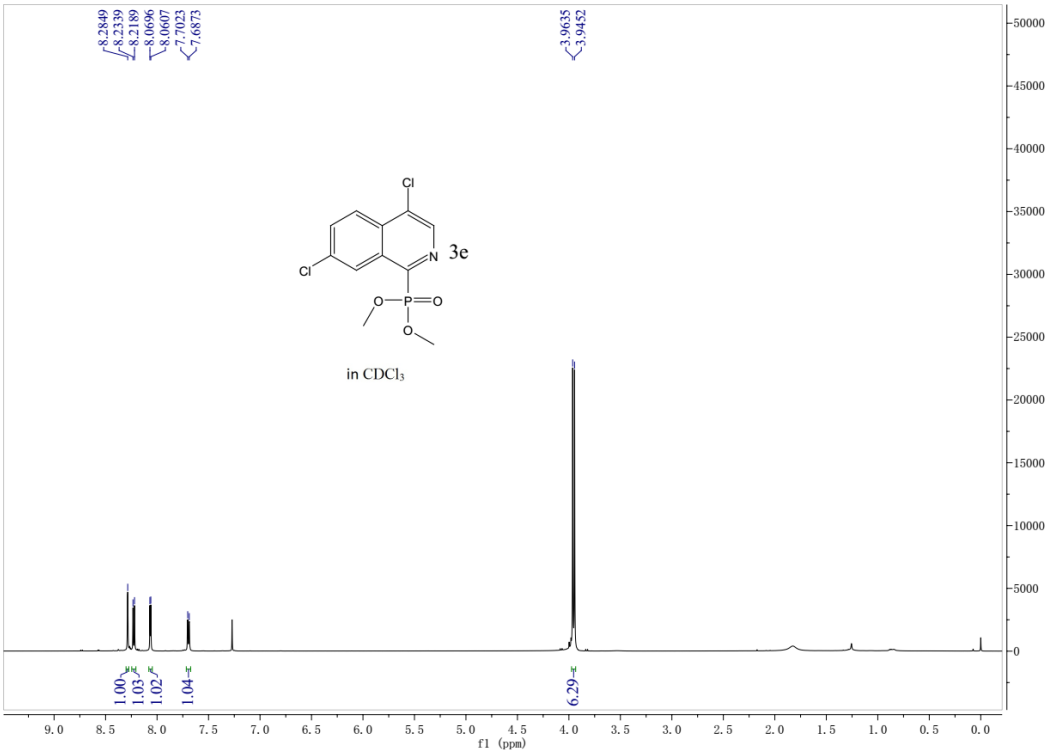
^{13}C NMR spectrum of compound **3d**



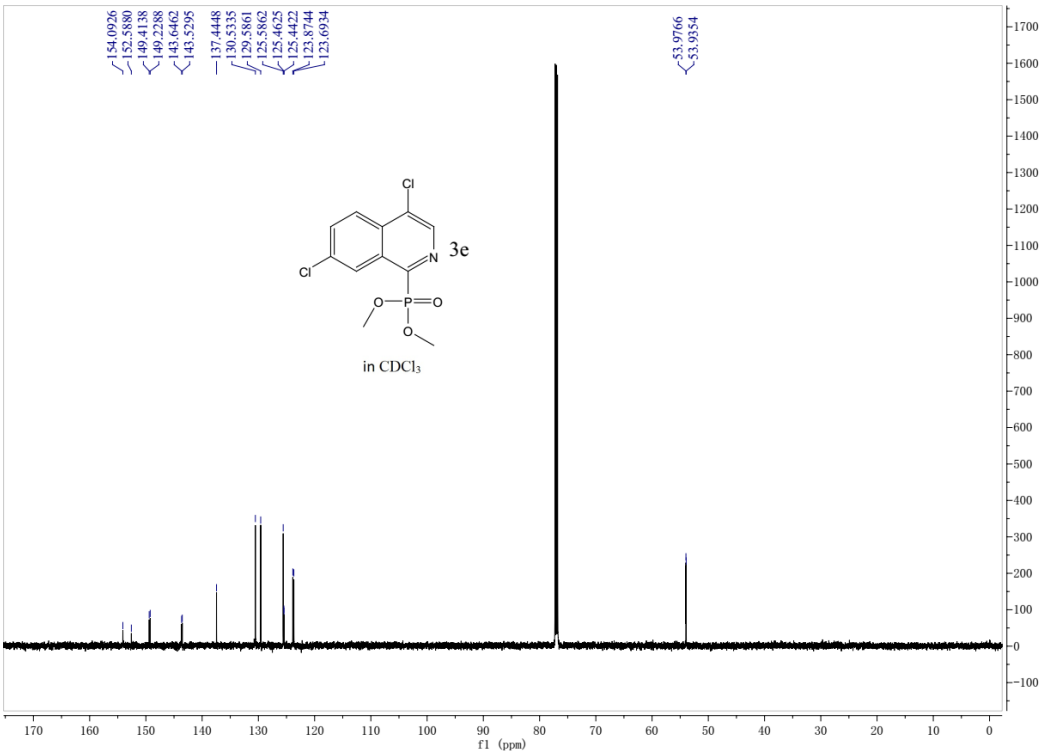
^{31}P NMR spectrum of compound **3d**



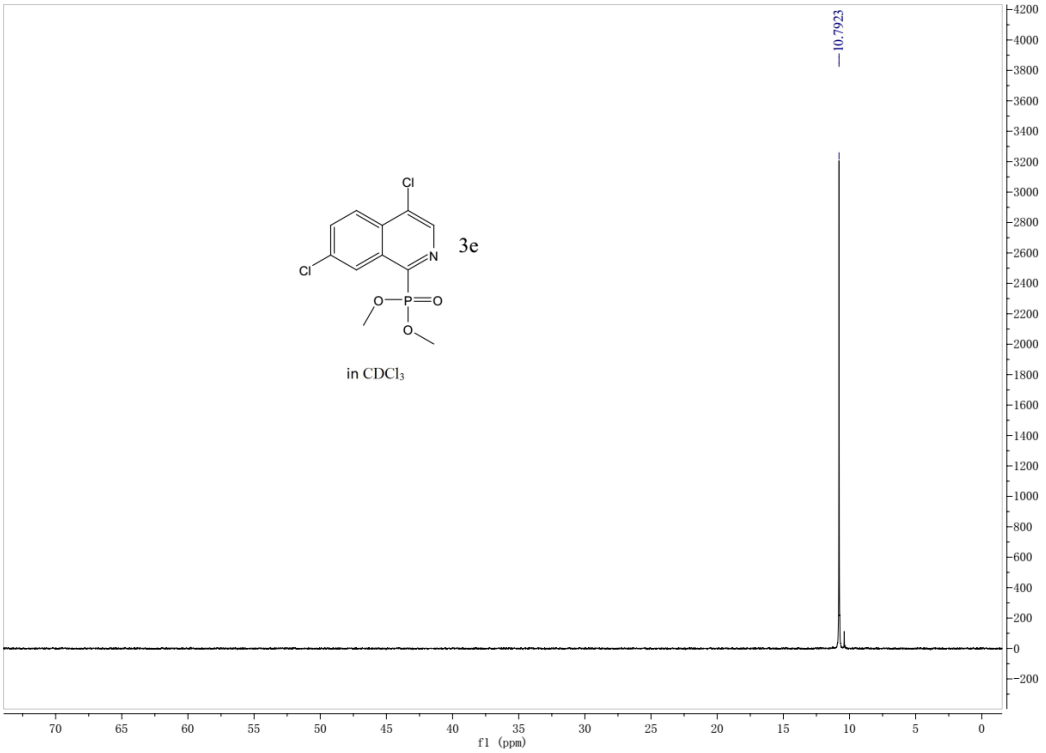
HRMS (ESI-TOF) spectrum of compound **3d**



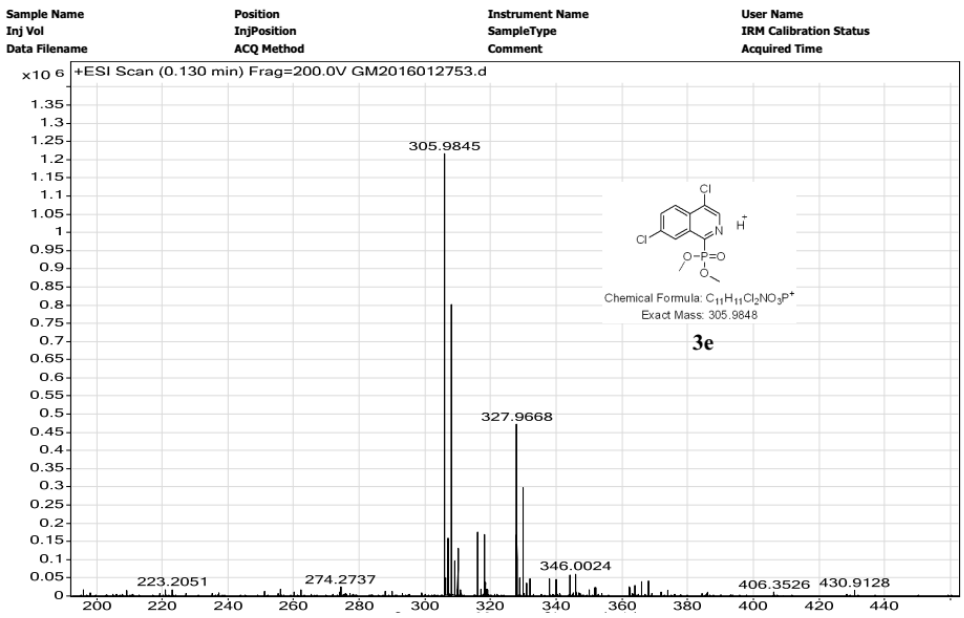
^{1}H NMR spectrum of compound **3e**



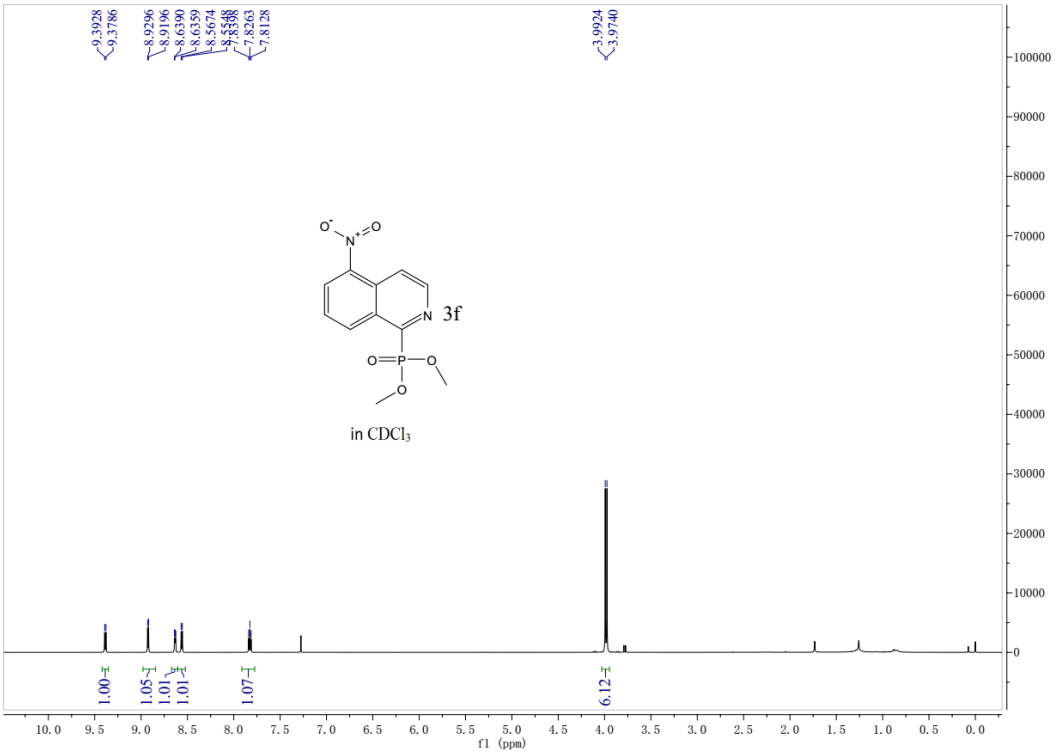
^{13}C NMR spectrum of compound **3e**



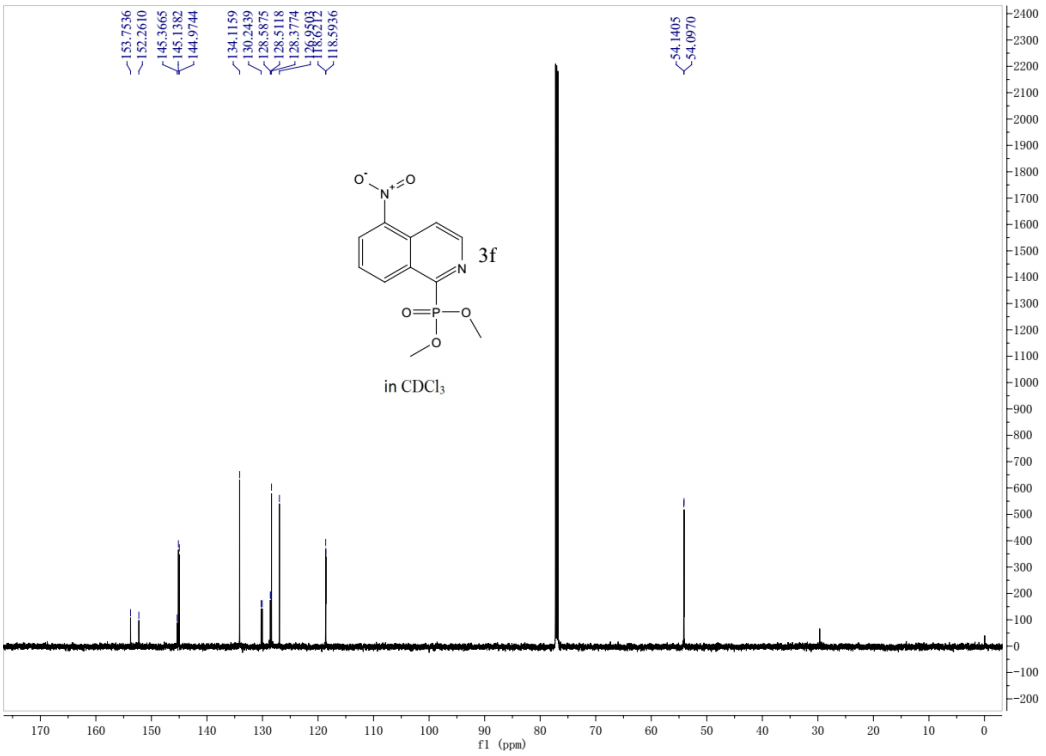
^{31}P NMR spectrum of compound **3e**



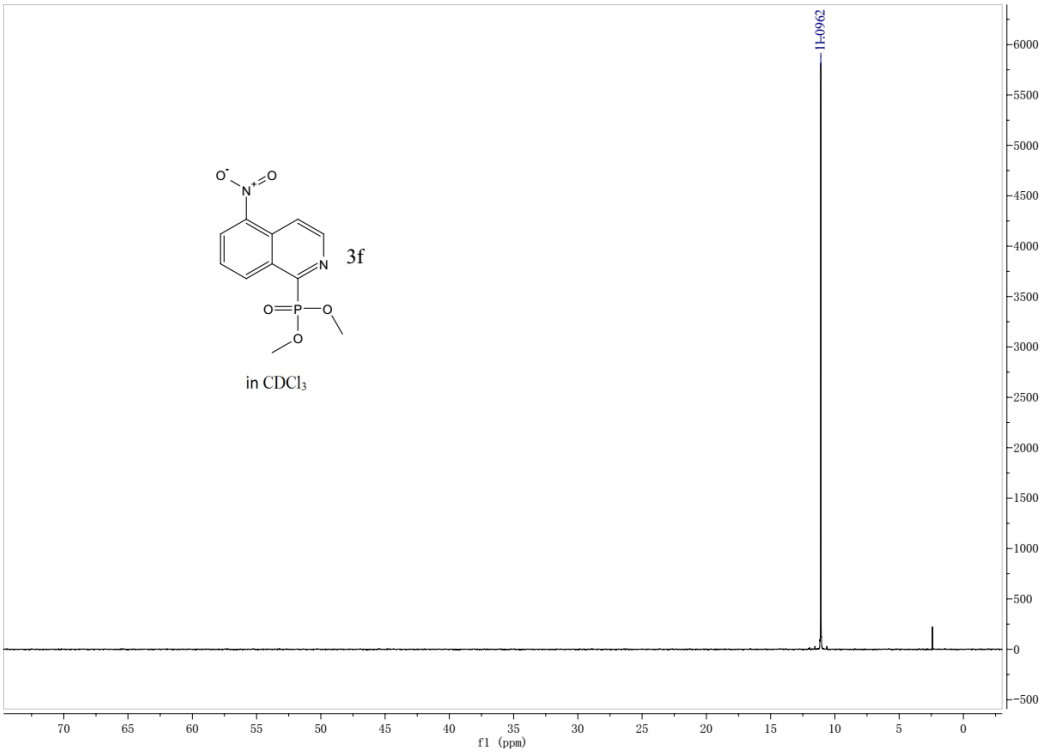
HRMS (ESI-TOF) spectrum of compound **3e**



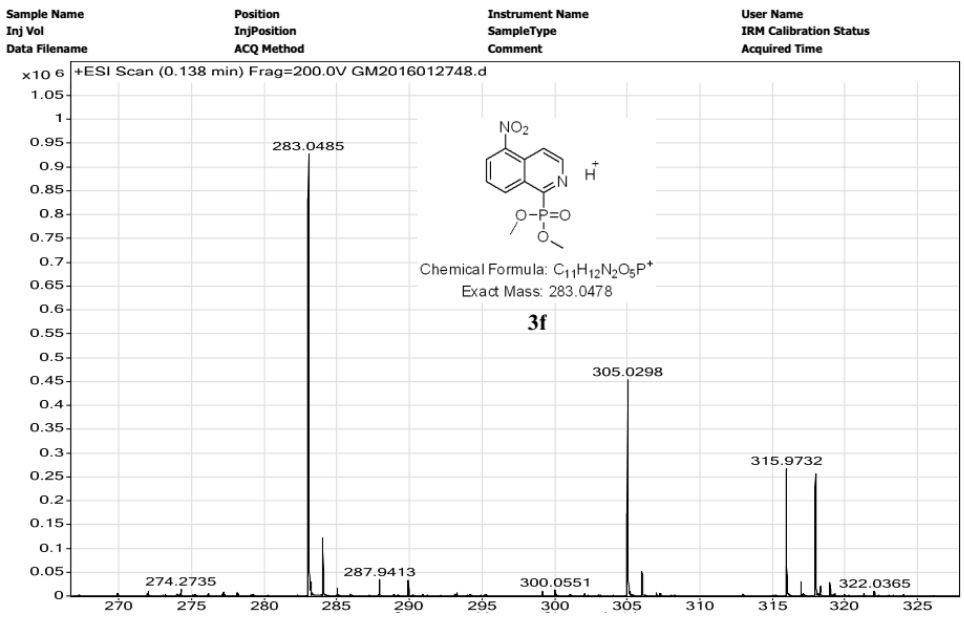
^{1}H NMR spectrum of compound **3f**



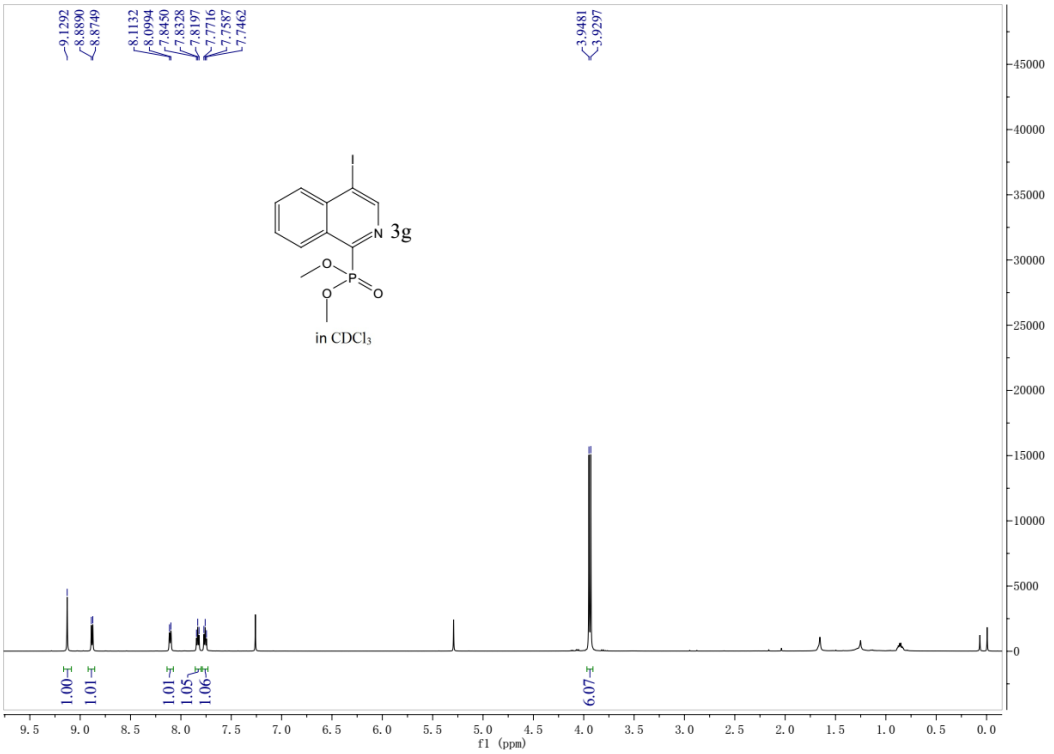
^{13}C NMR spectrum of compound **3f**



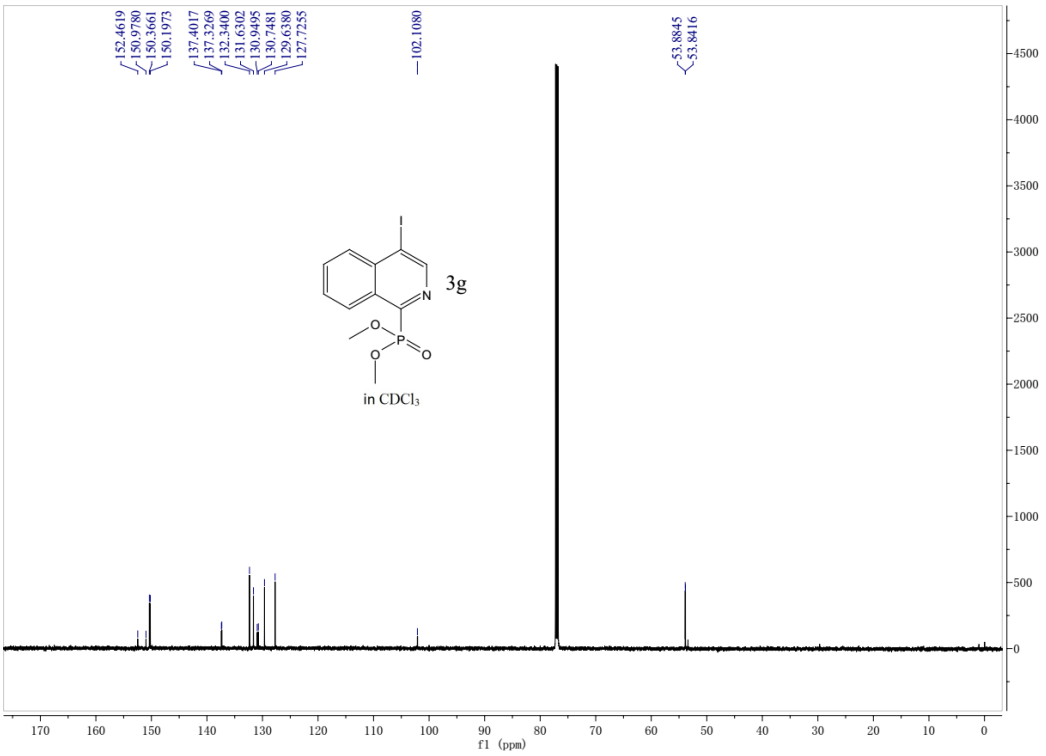
^{31}P NMR spectrum of compound **3f**



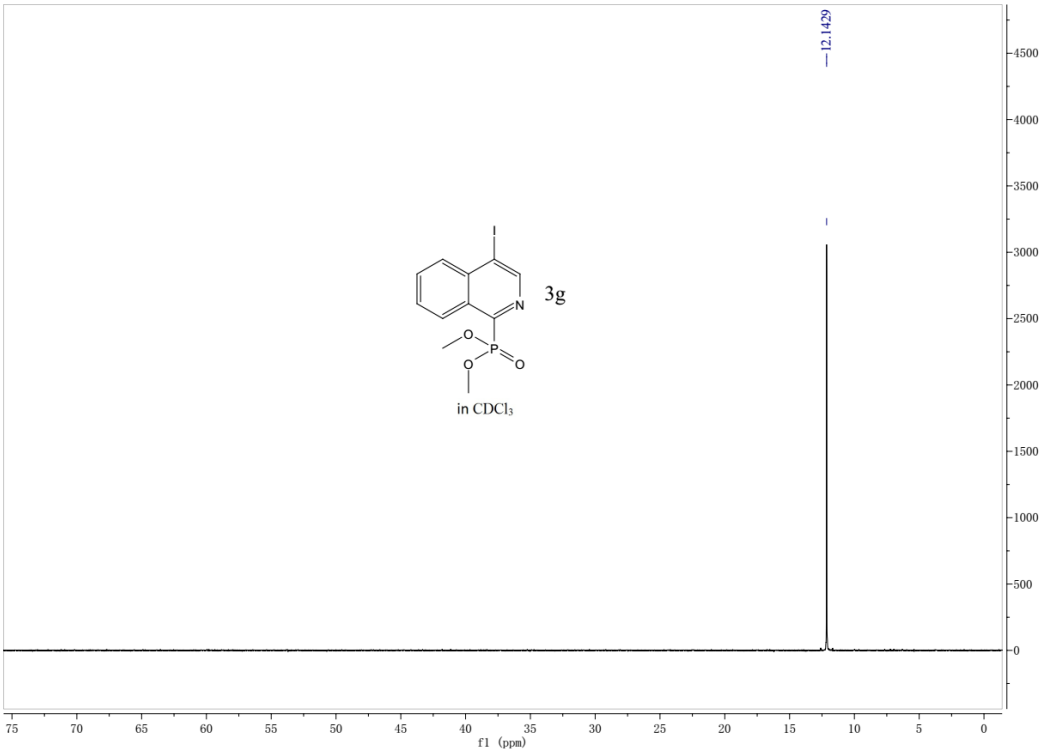
HRMS (ESI-TOF) spectrum of compound **3f**



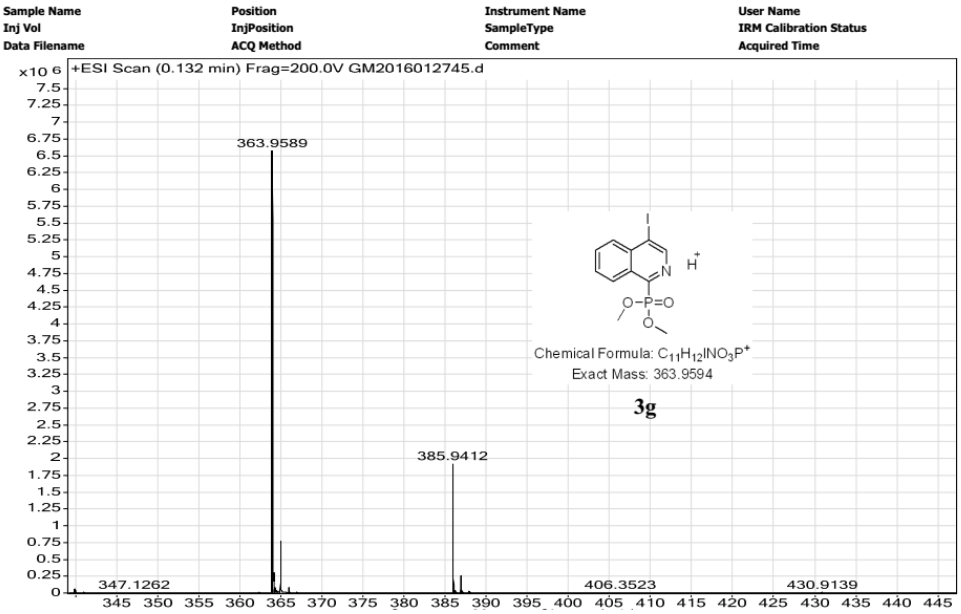
^{1}H NMR spectrum of compound **3g**



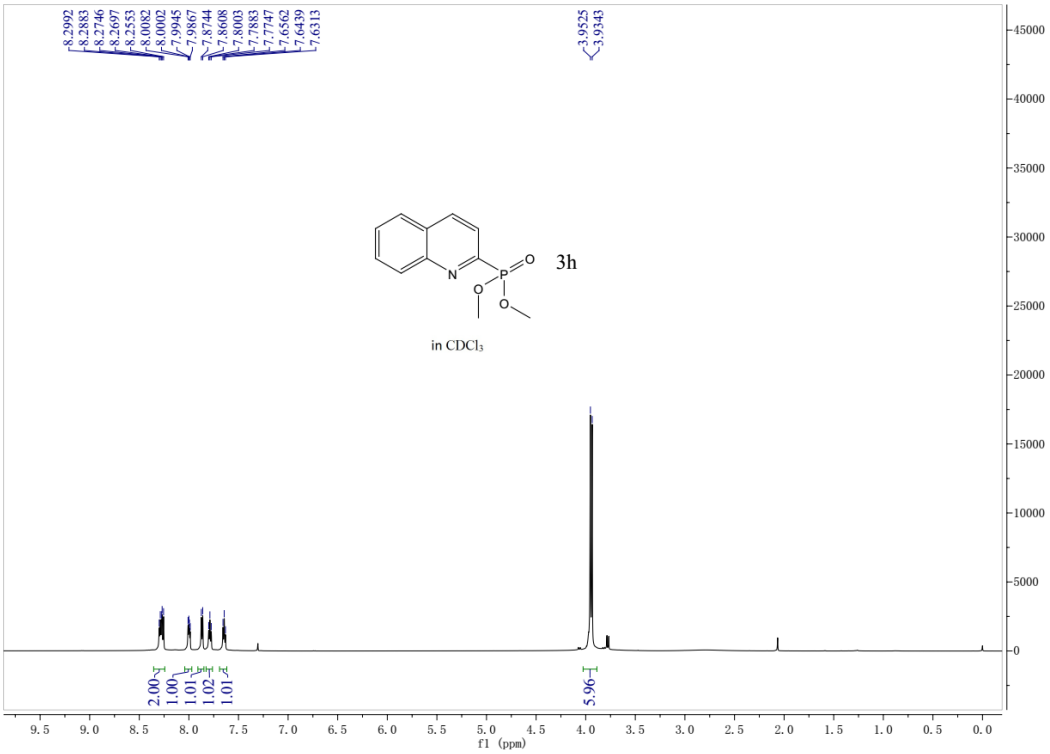
^{13}C NMR spectrum of compound **3g**



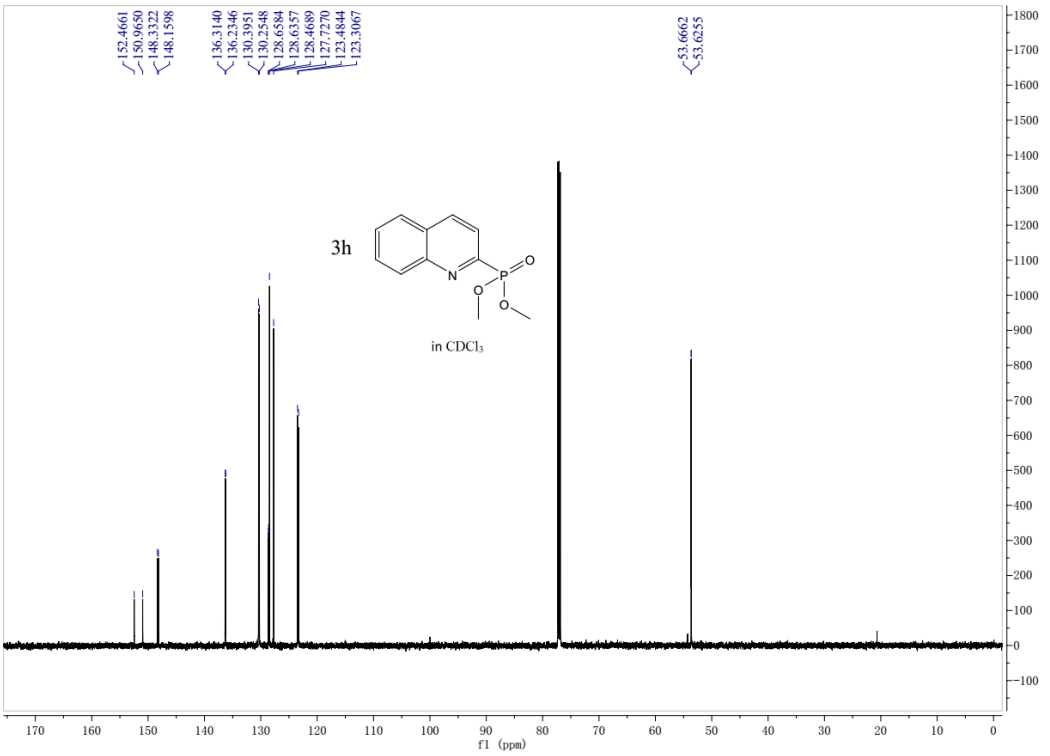
^{31}P NMR spectrum of compound **3g**



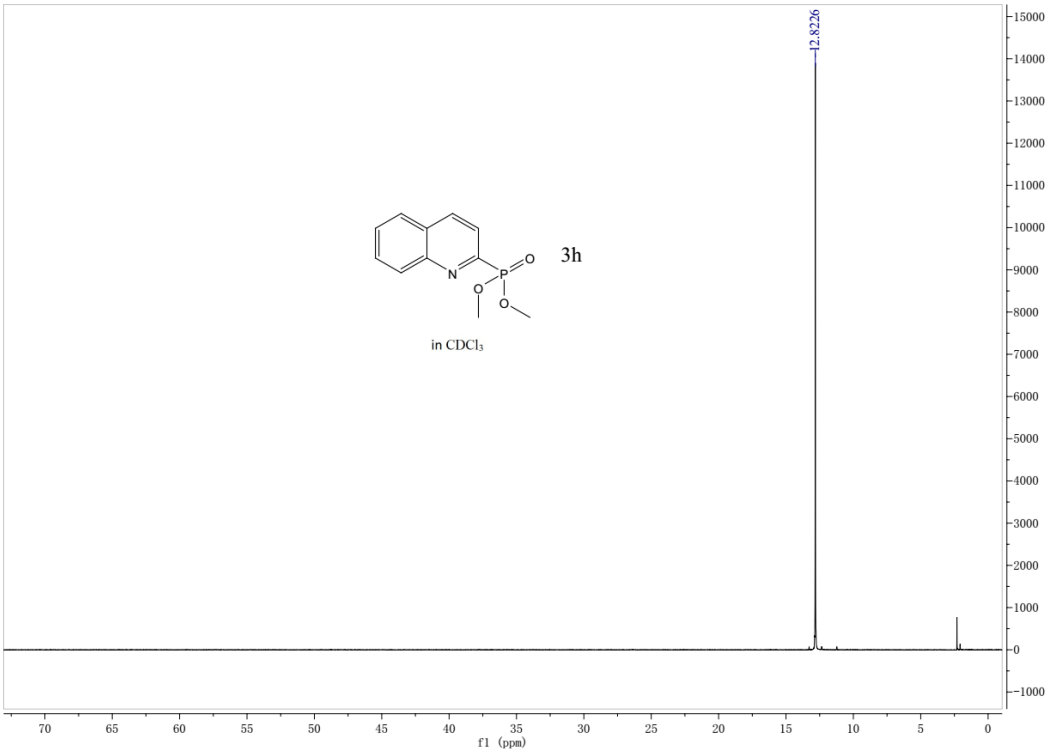
HRMS (ESI-TOF) spectrum of compound **3g**



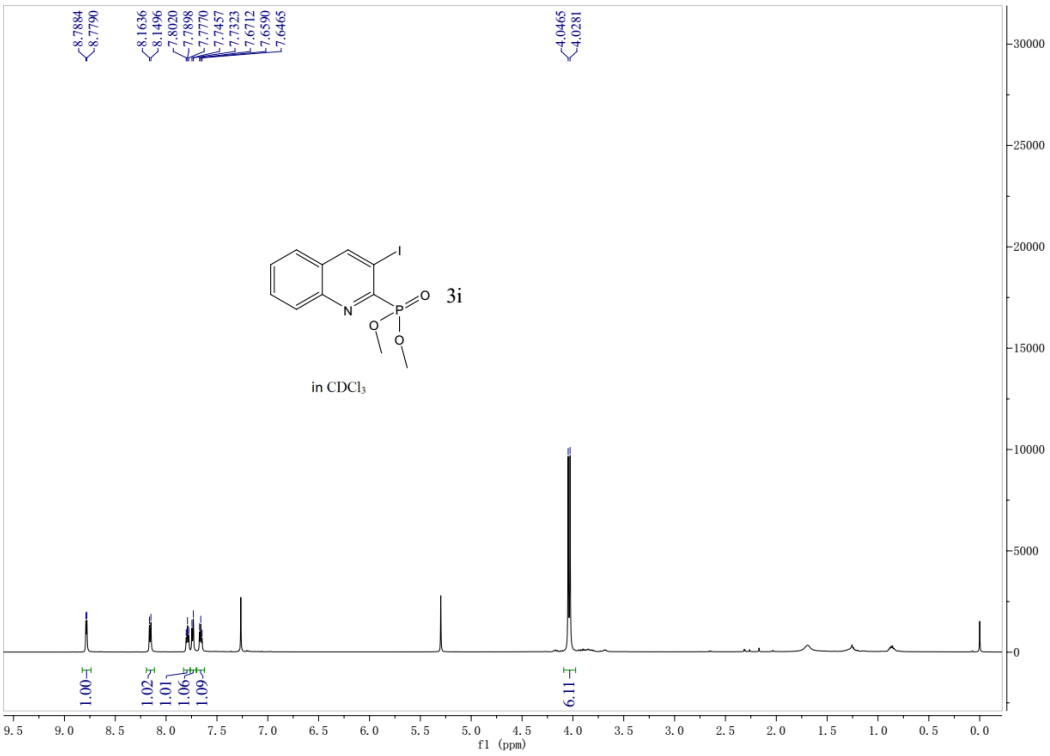
^{1}H NMR spectrum of compound **3h**



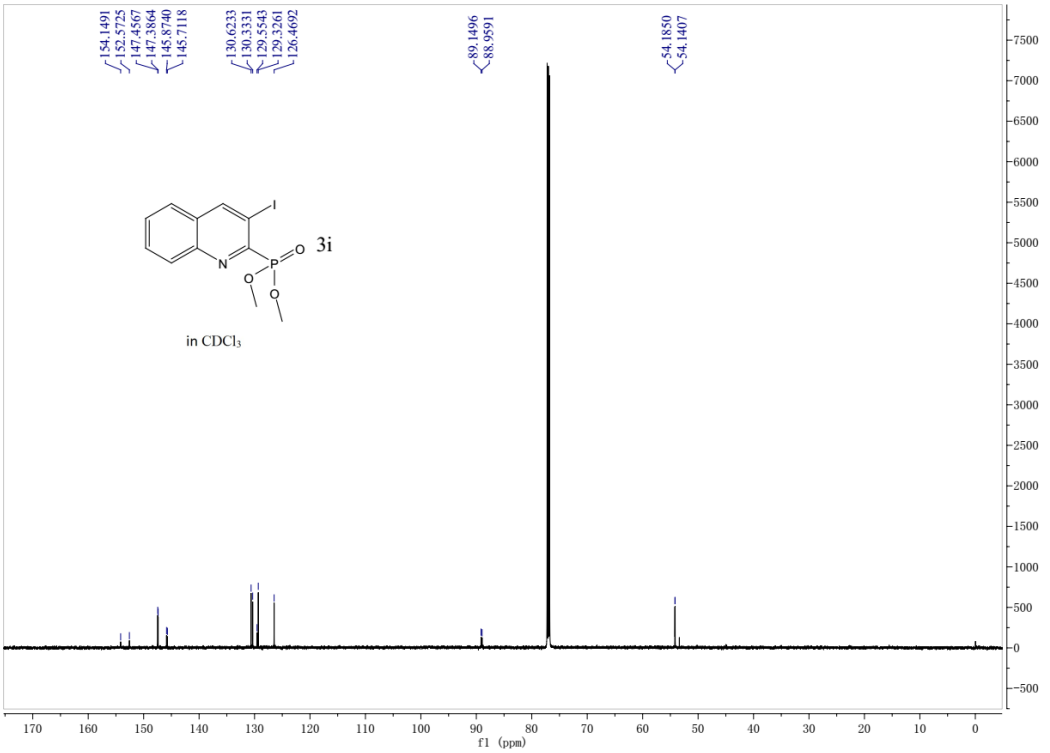
^{13}C NMR spectrum of compound **3h**



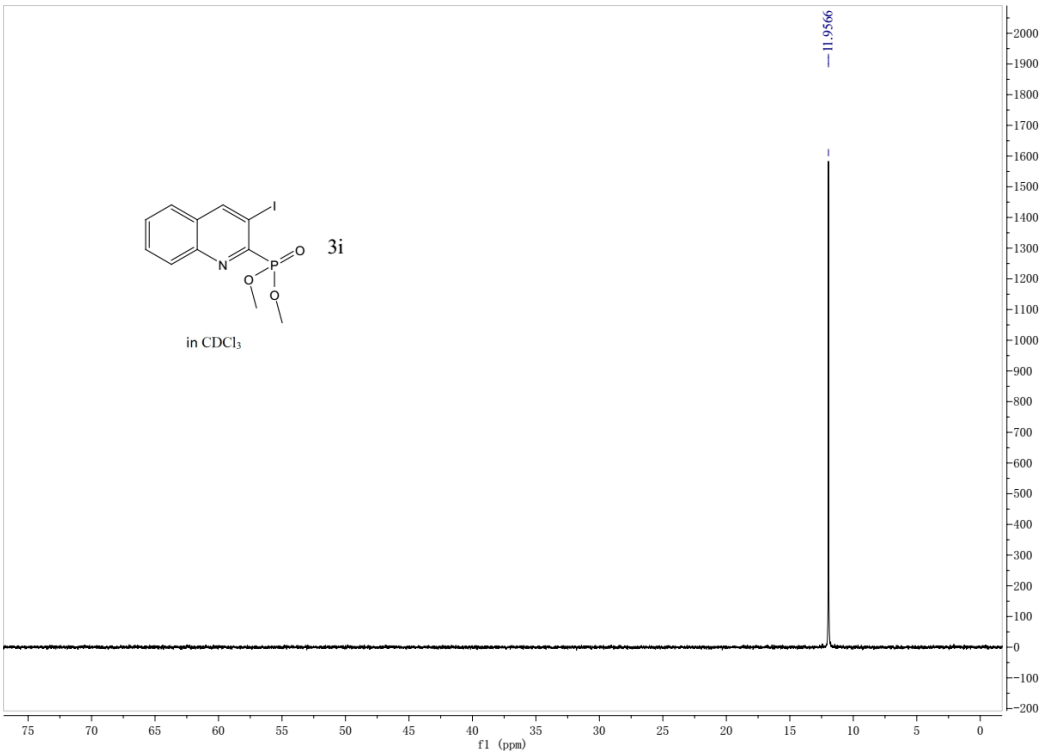
^{31}P NMR spectrum of compound **3h**



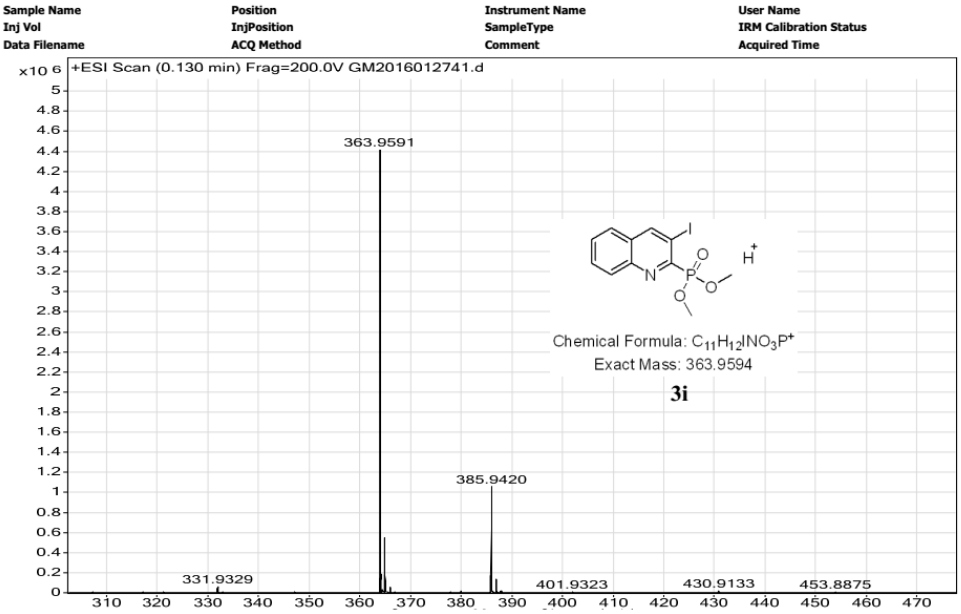
^{1}H NMR spectrum of compound **3i**



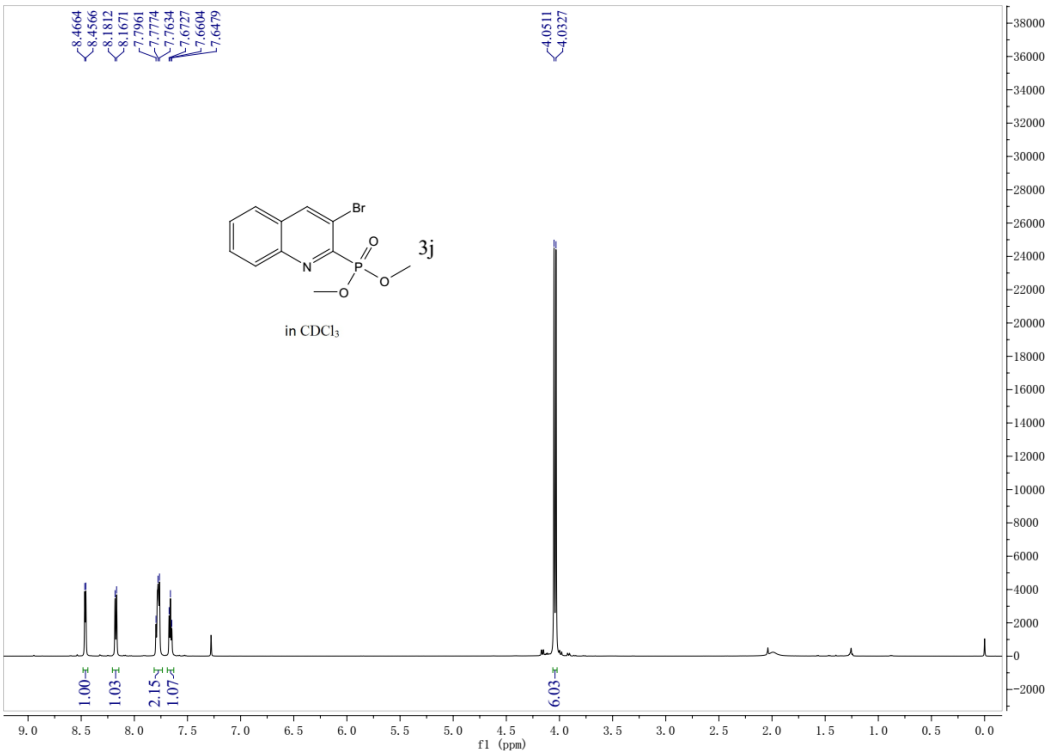
^{13}C NMR spectrum of compound **3i**



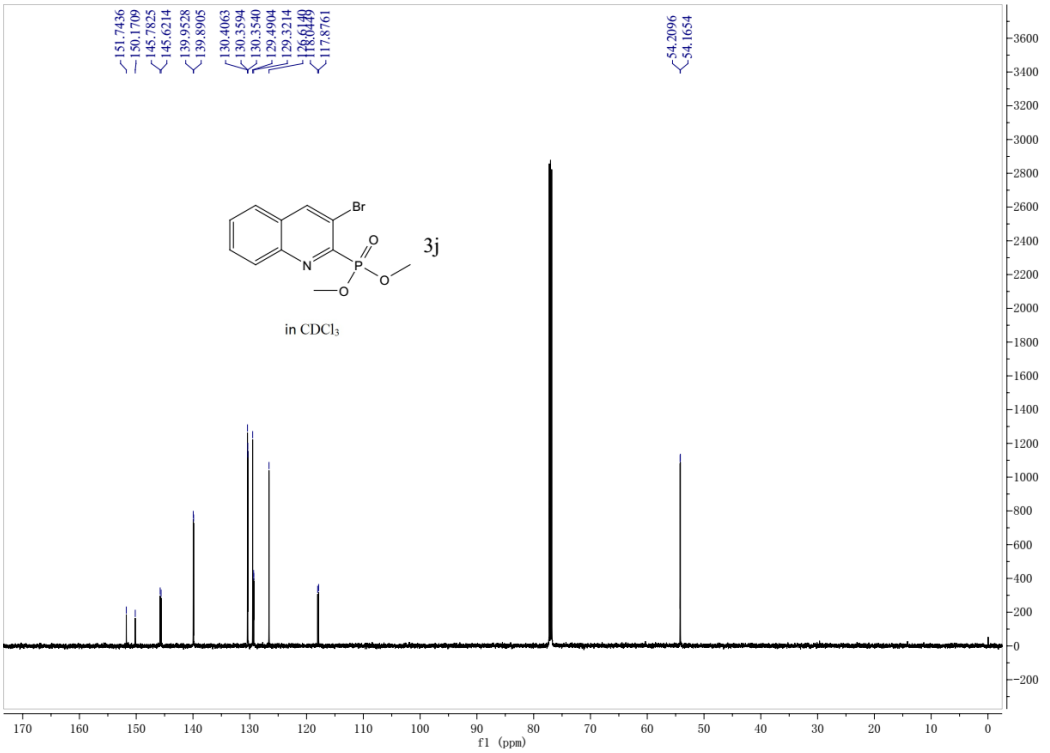
^{31}P NMR spectrum of compound **3i**



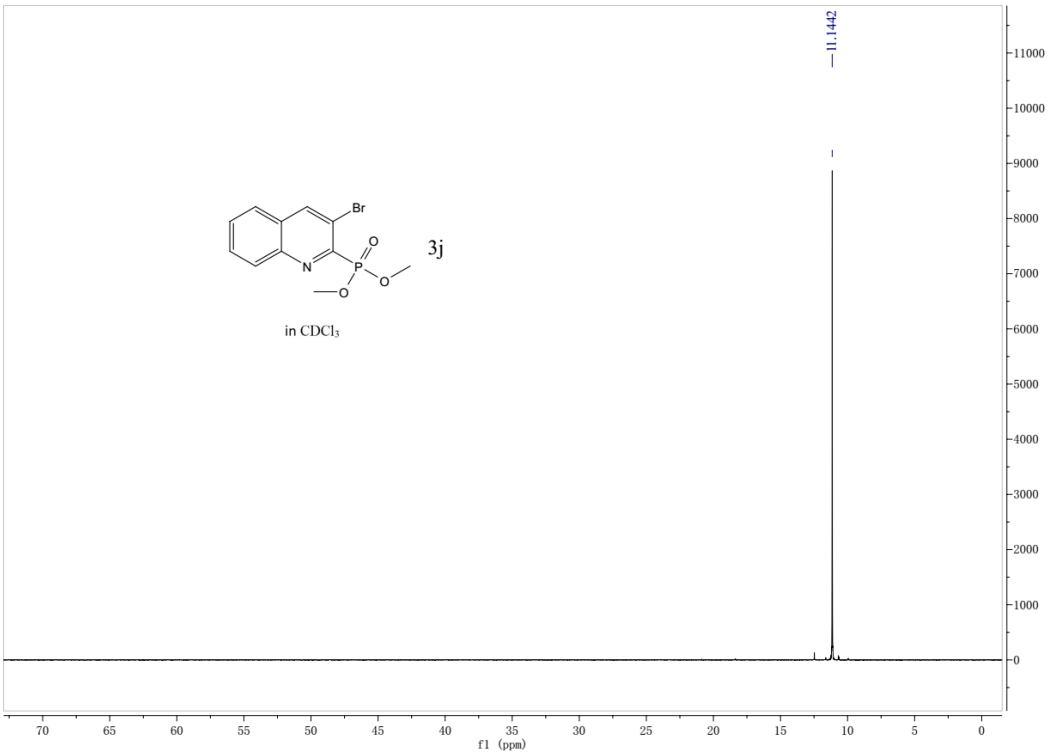
HRMS (ESI-TOF) spectrum of compound **3i**



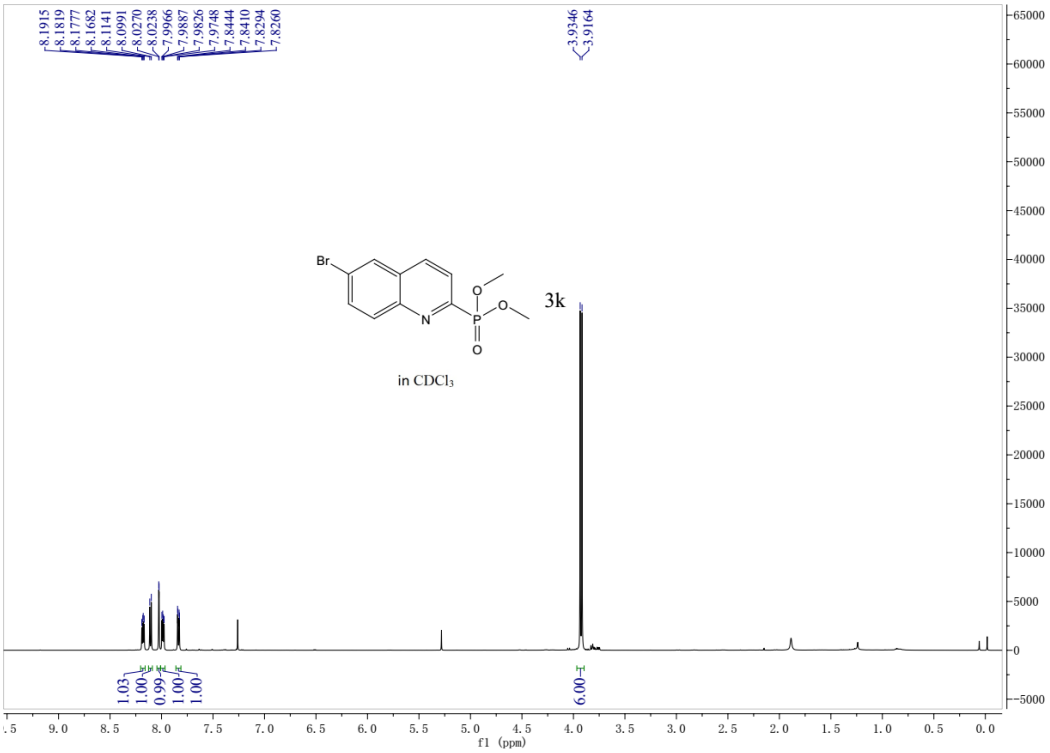
^{1}H NMR spectrum of compound **3j**



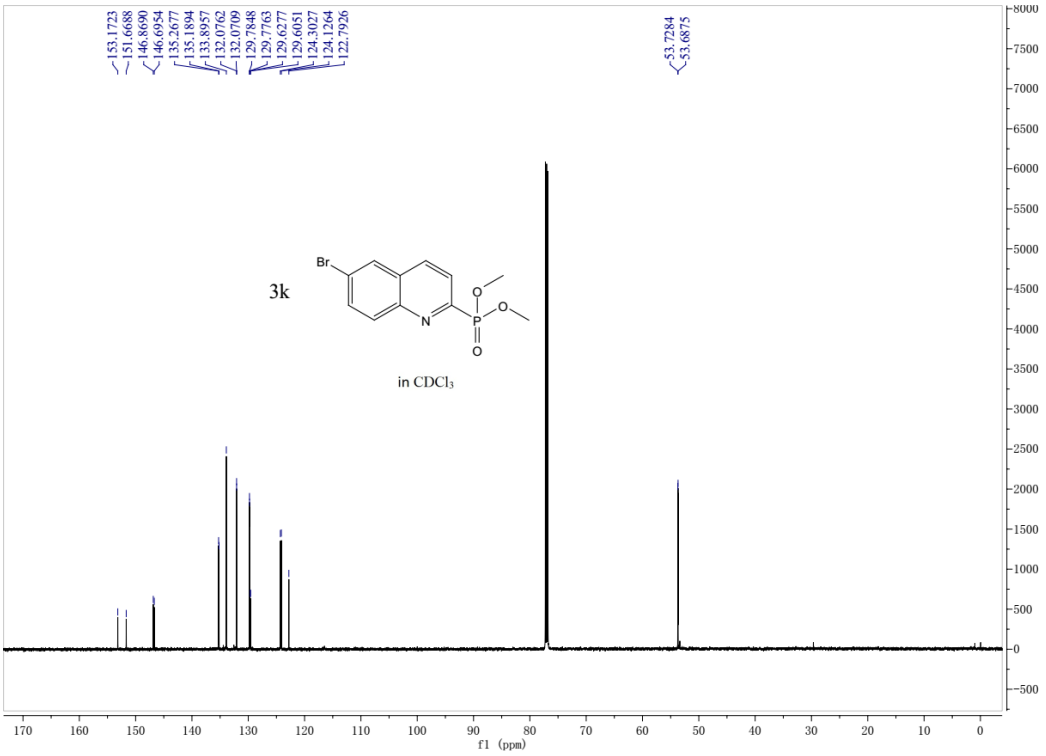
^{13}C NMR spectrum of compound **3j**



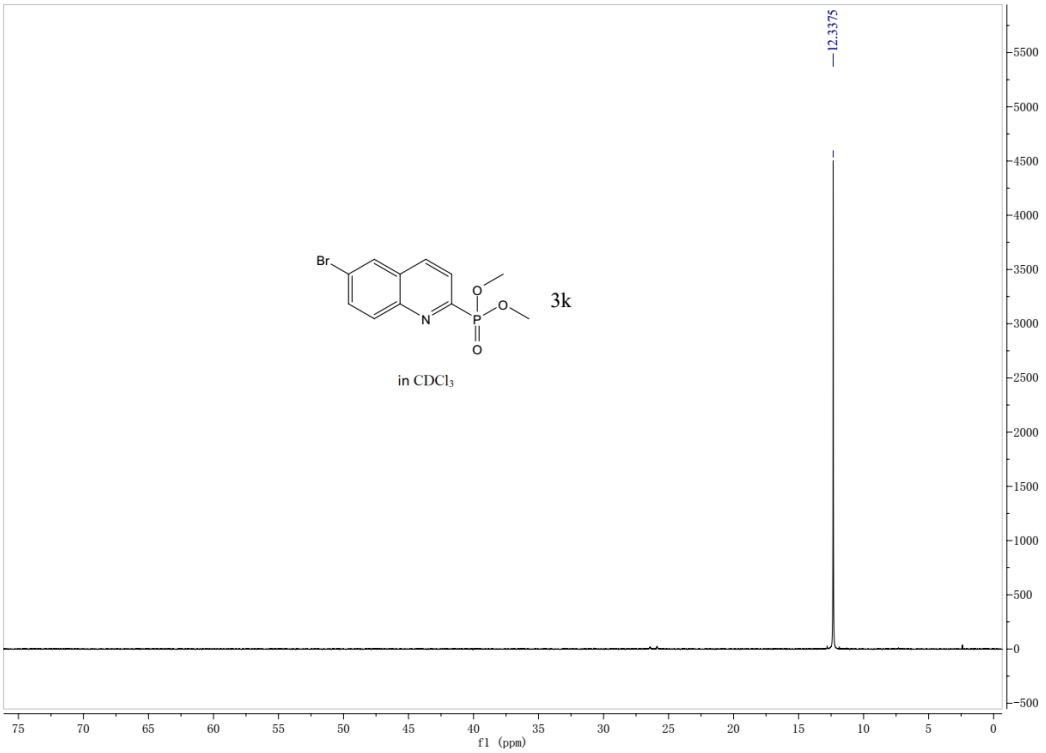
^{31}P NMR spectrum of compound **3j**



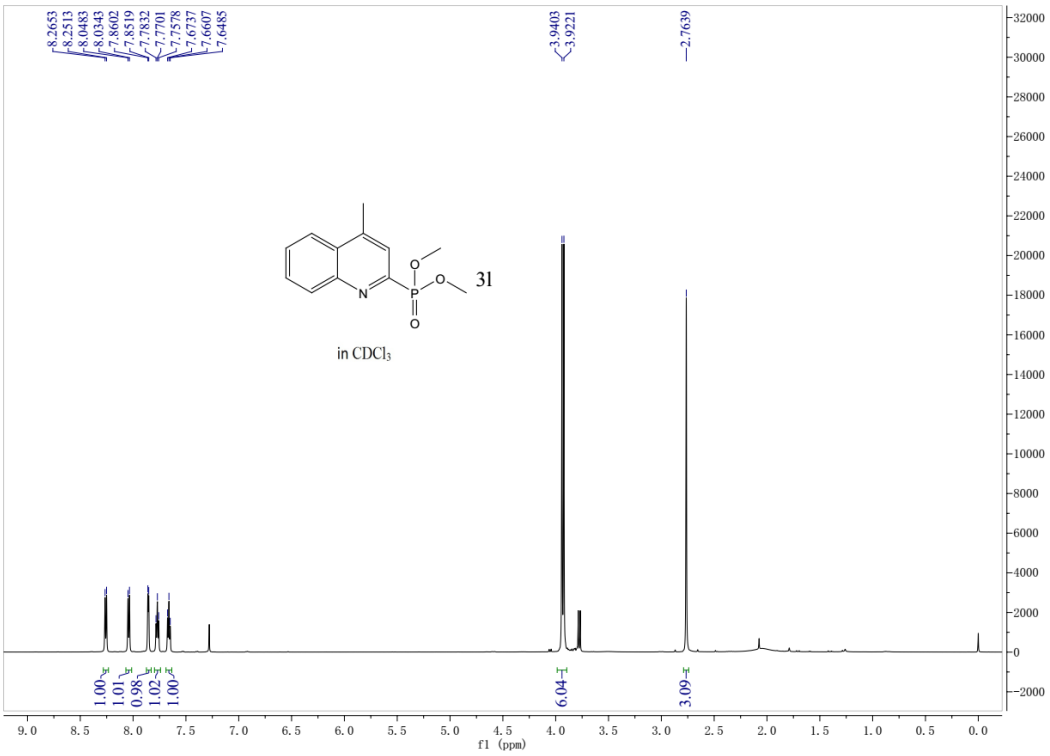
^{1}H NMR spectrum of compound **3k**



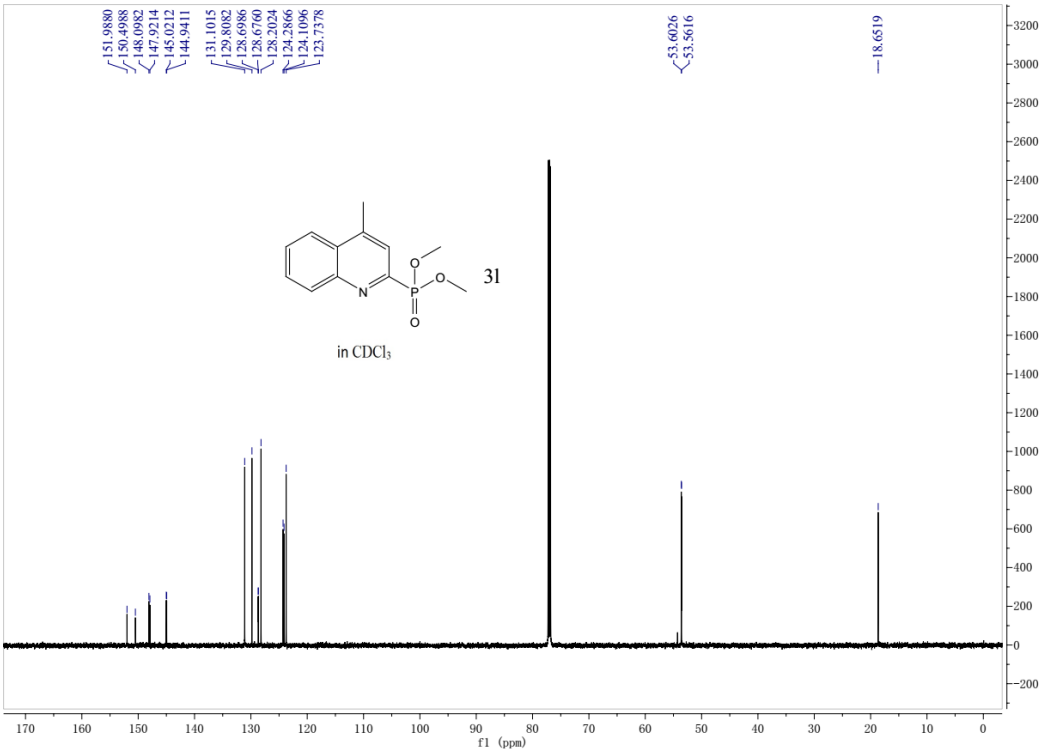
^{13}C NMR spectrum of compound **3k**



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

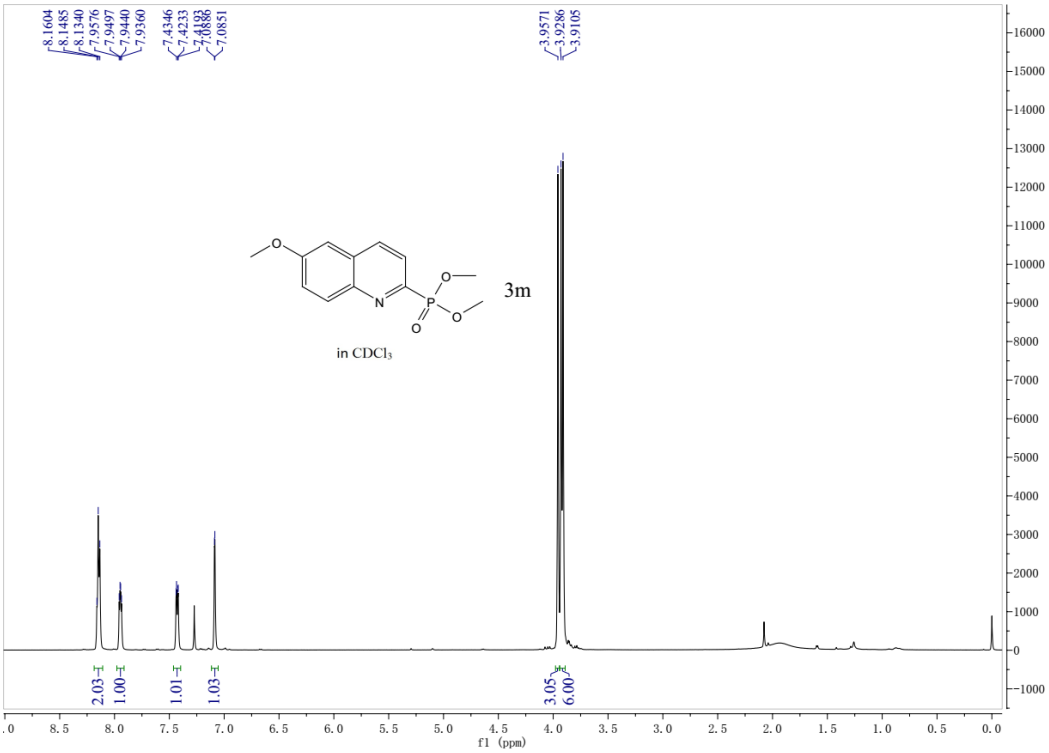


^{1}H NMR spectrum of compound **3l**

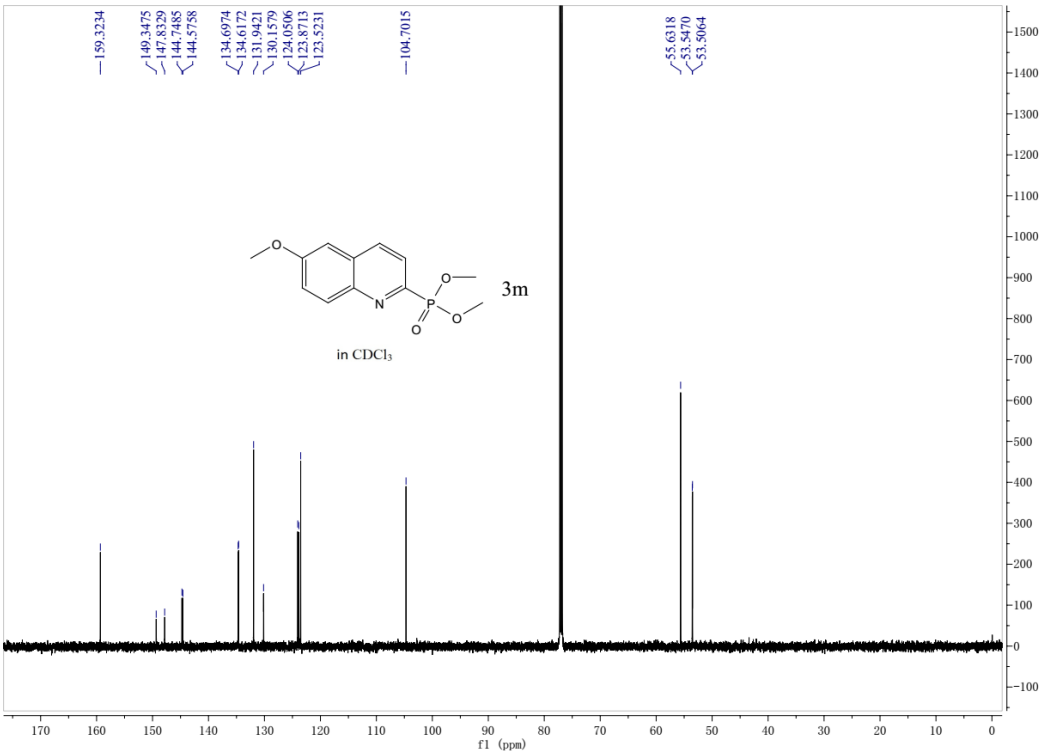


^{13}C NMR spectrum of compound **3l**

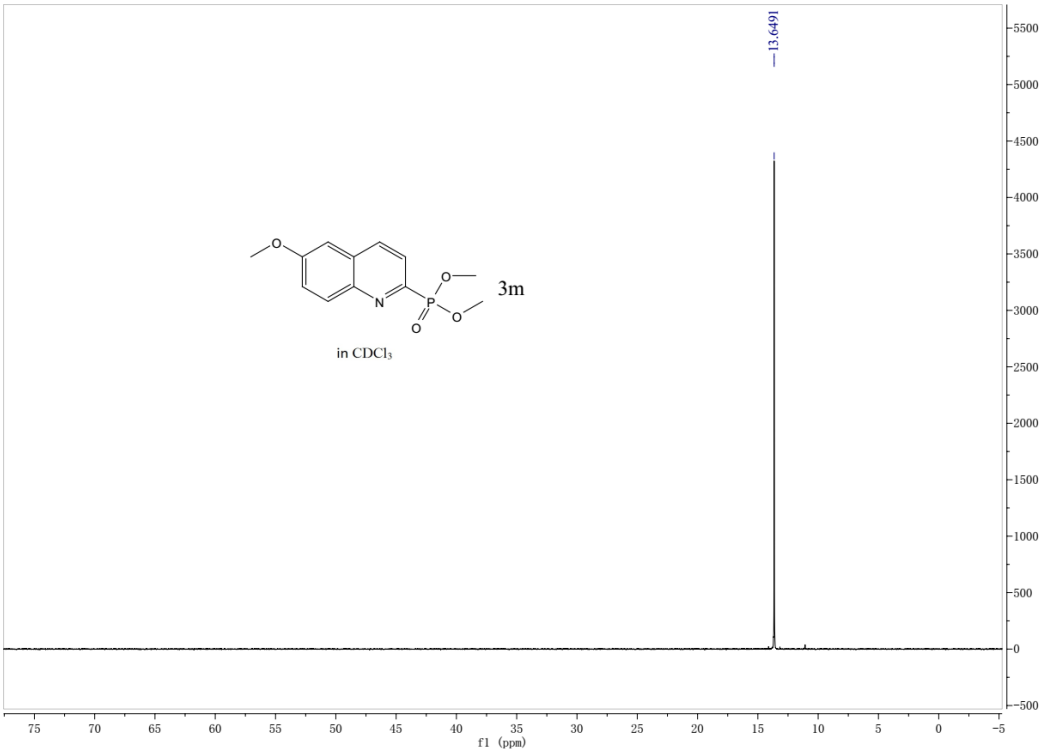
^{31}P NMR spectrum of compound **3l**



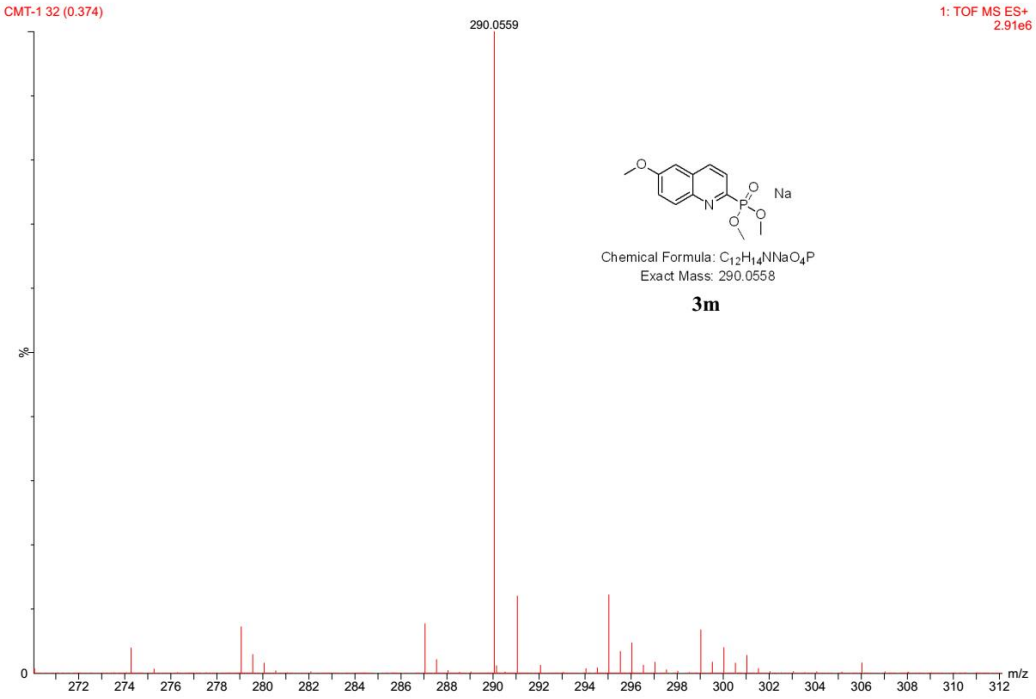
^{1}H NMR spectrum of compound **3m**



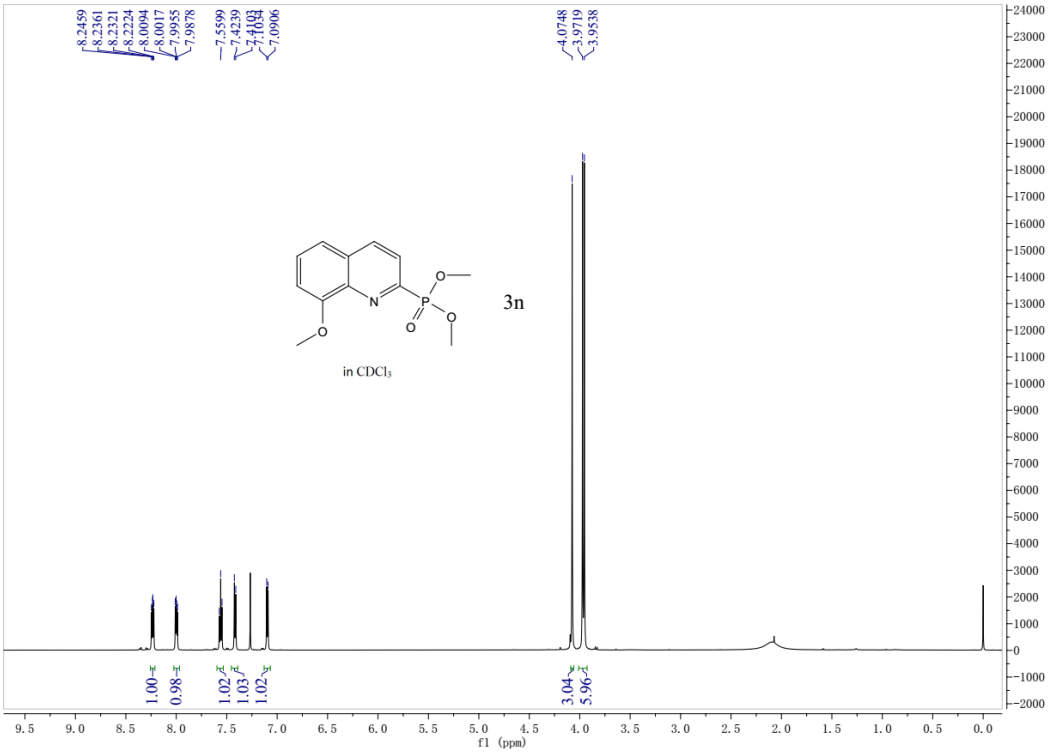
^{13}C NMR spectrum of compound **3m**



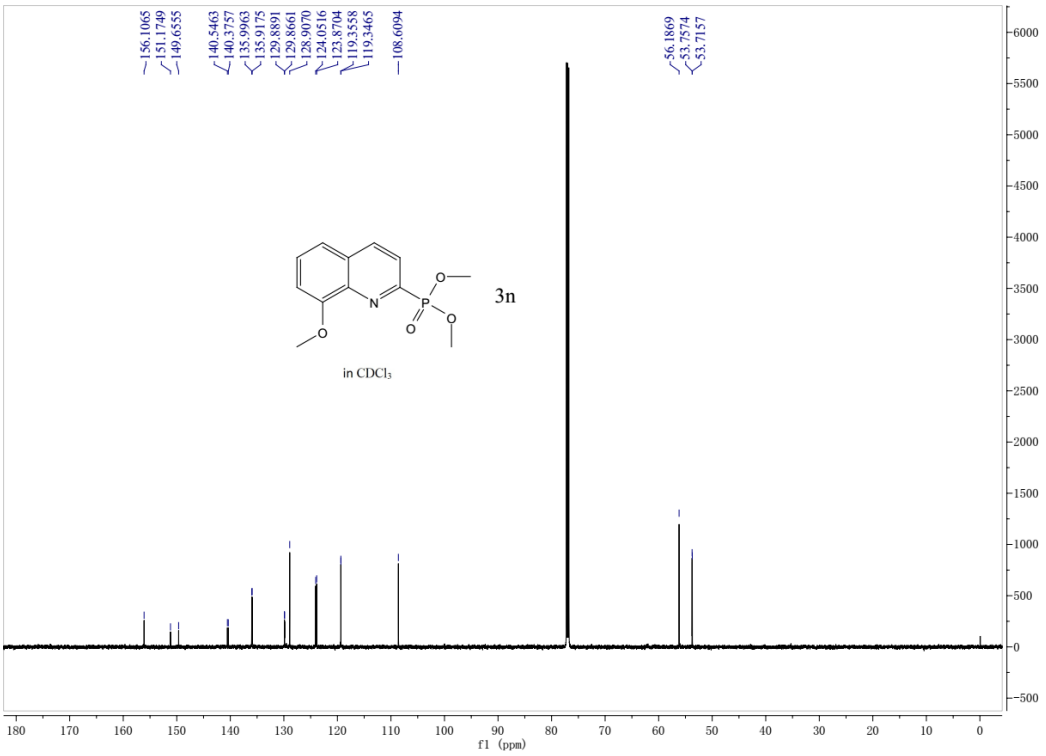
^{31}P NMR spectrum of compound **3m**



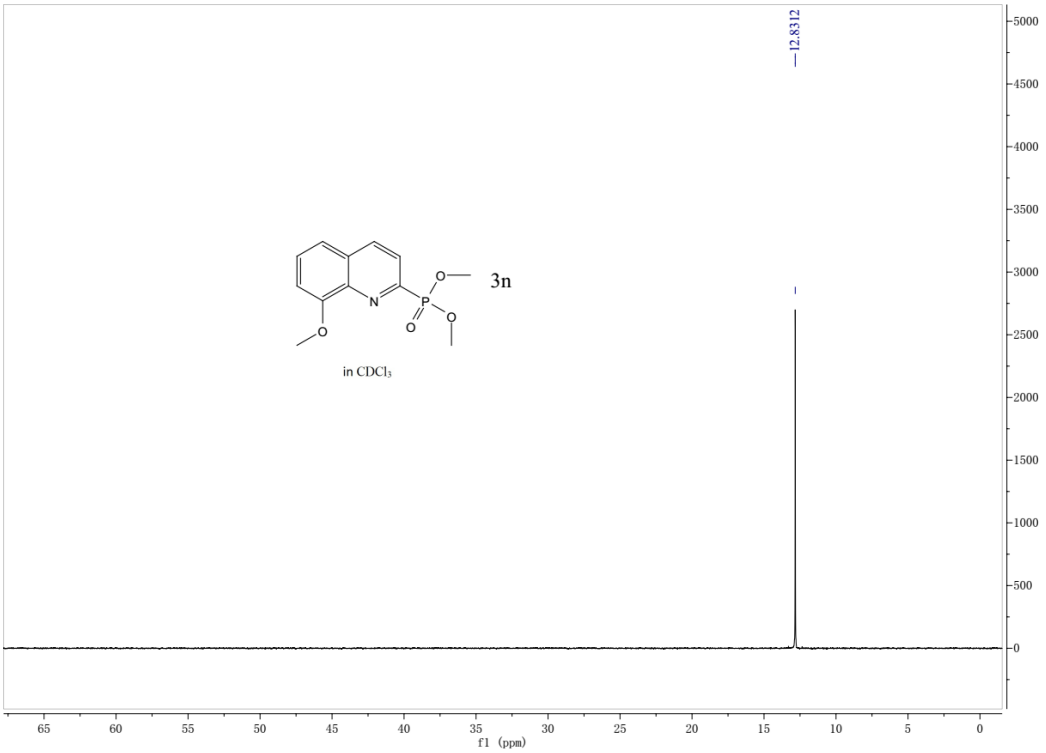
HRMS (ESI-TOF) spectrum of compound **3m**



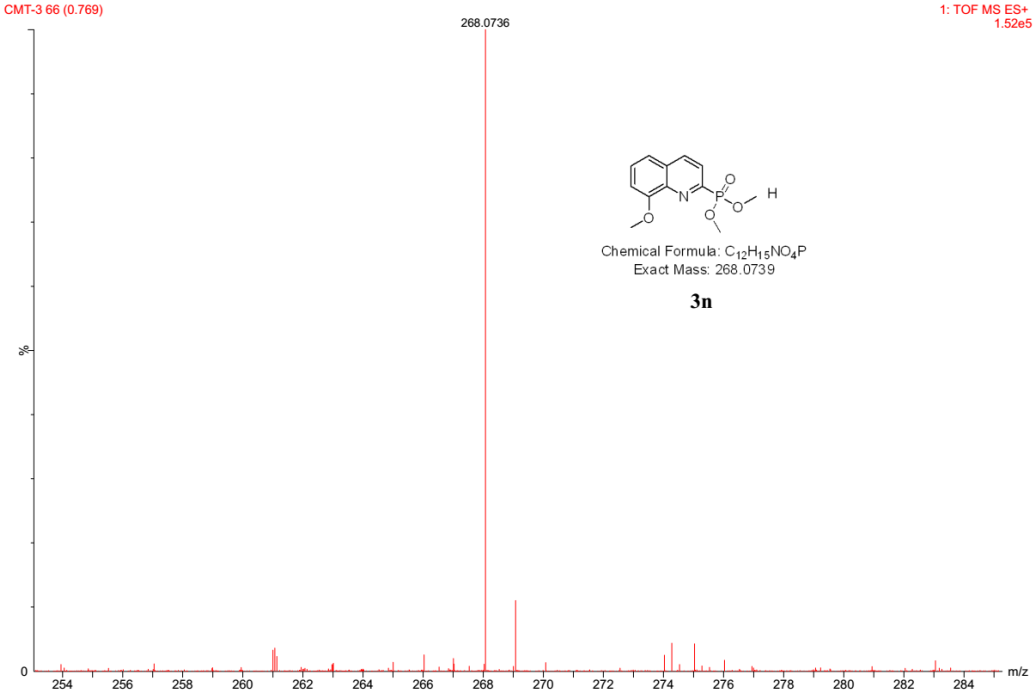
^{1}H NMR spectrum of compound **3n**



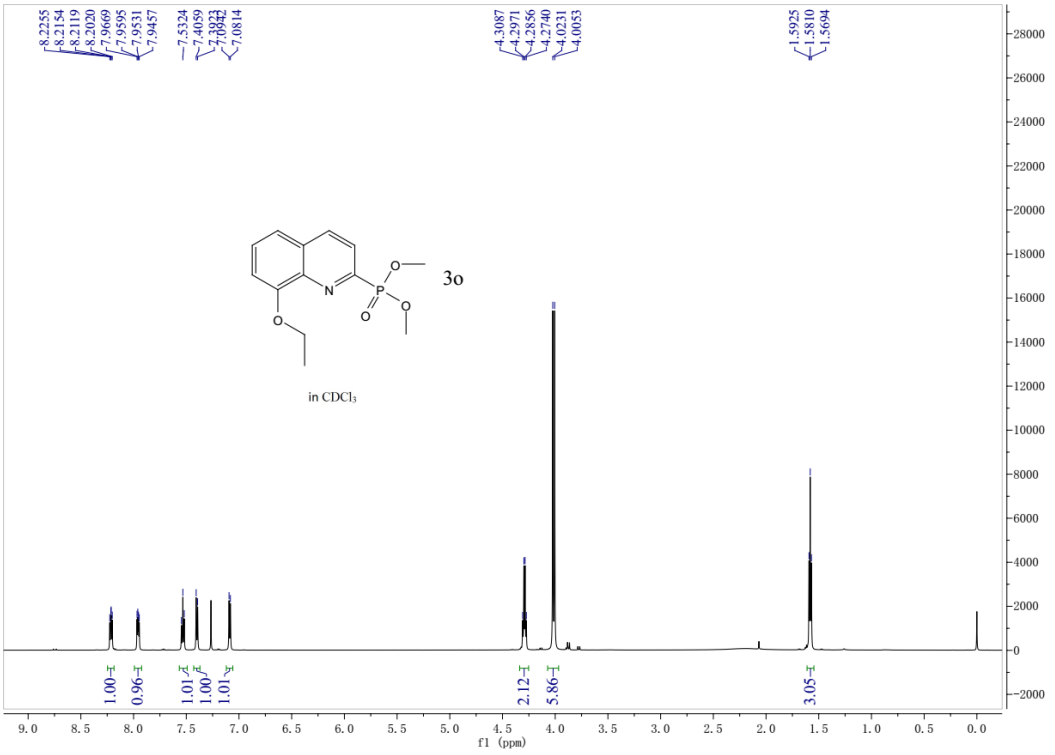
^{13}C NMR spectrum of compound **3n**



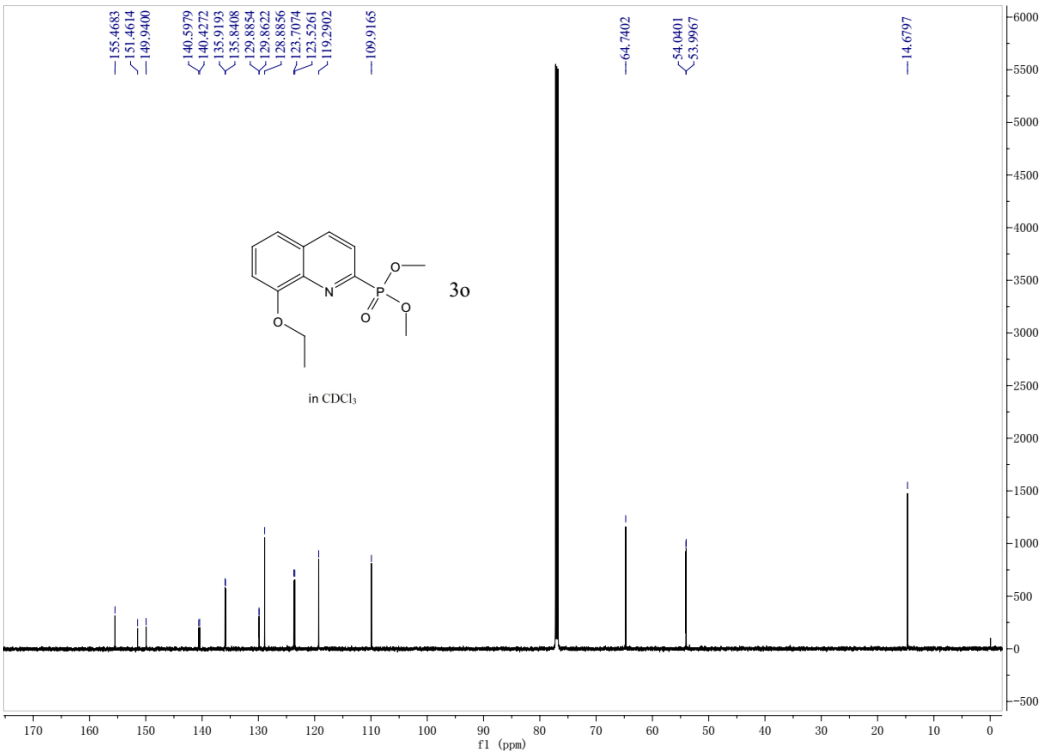
^{31}P NMR spectrum of compound **3n**



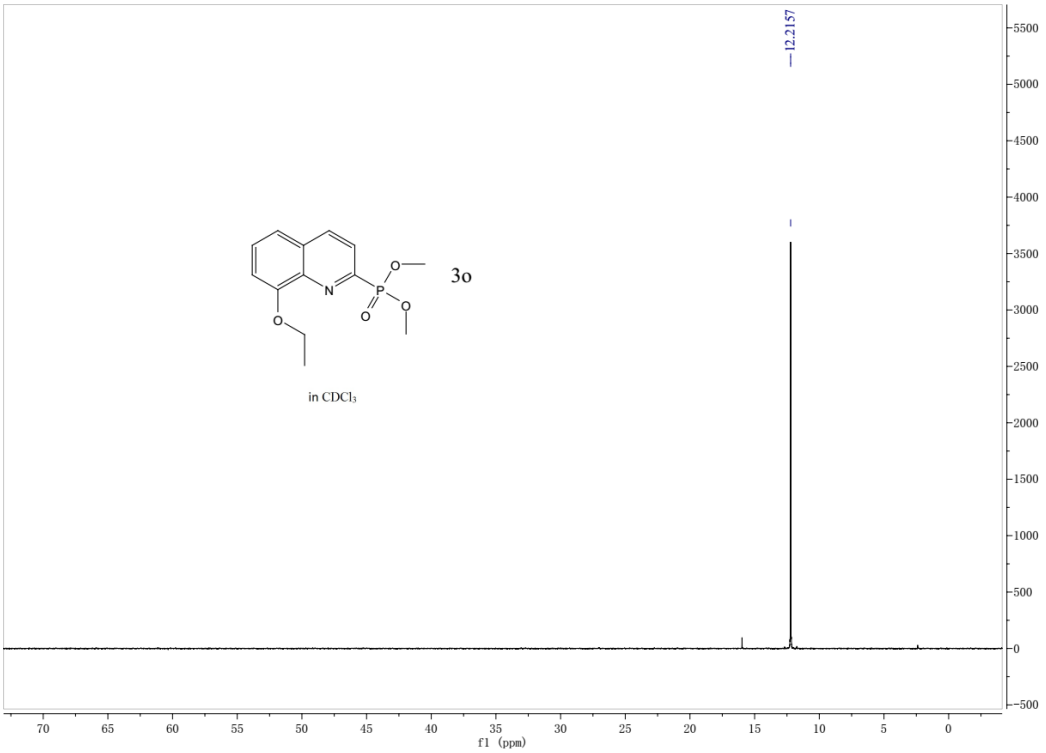
HRMS (ESI-TOF) spectrum of compound **3n**



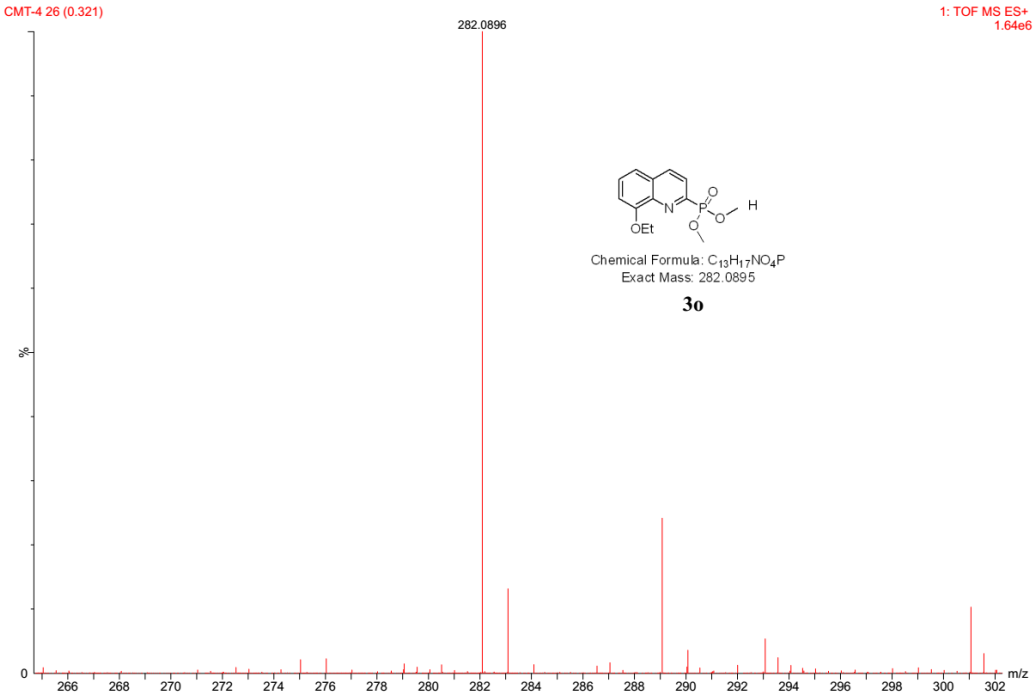
^{1}H NMR spectrum of compound **3o**



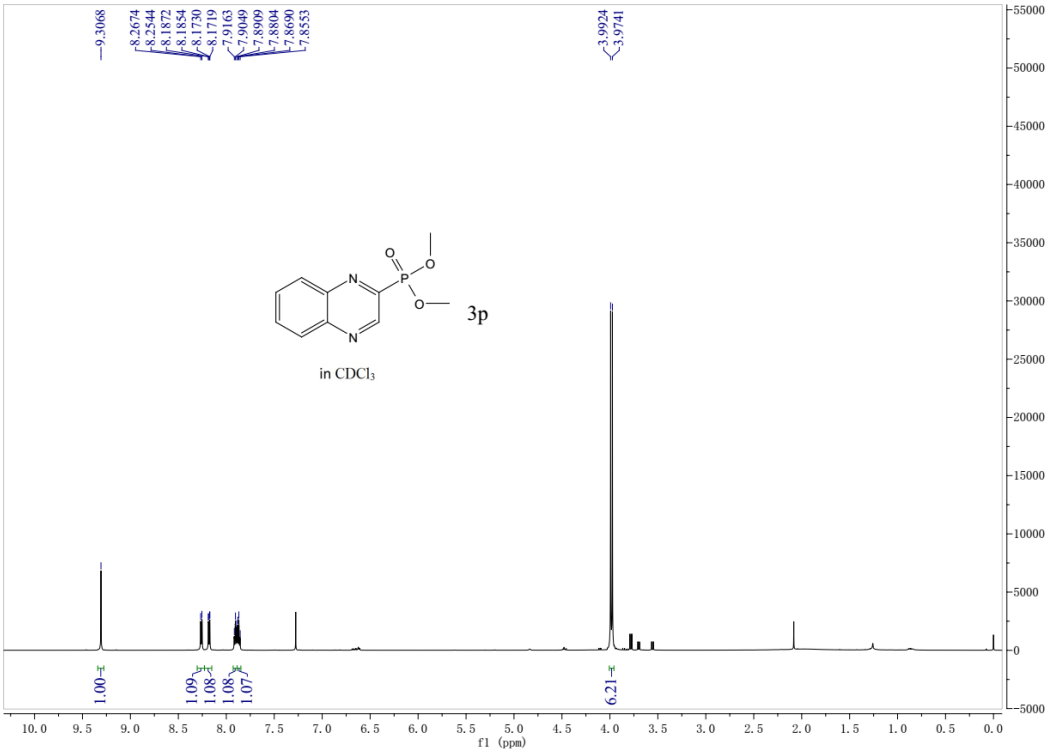
^{13}C NMR spectrum of compound **3o**



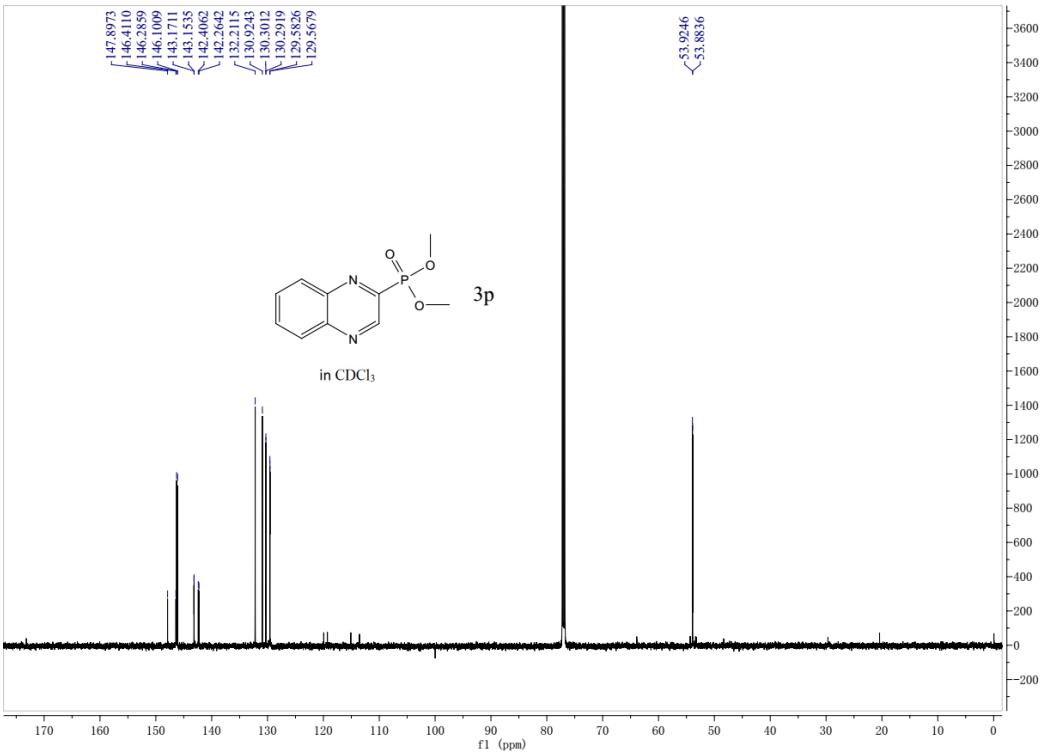
^{31}P NMR spectrum of compound **3o**



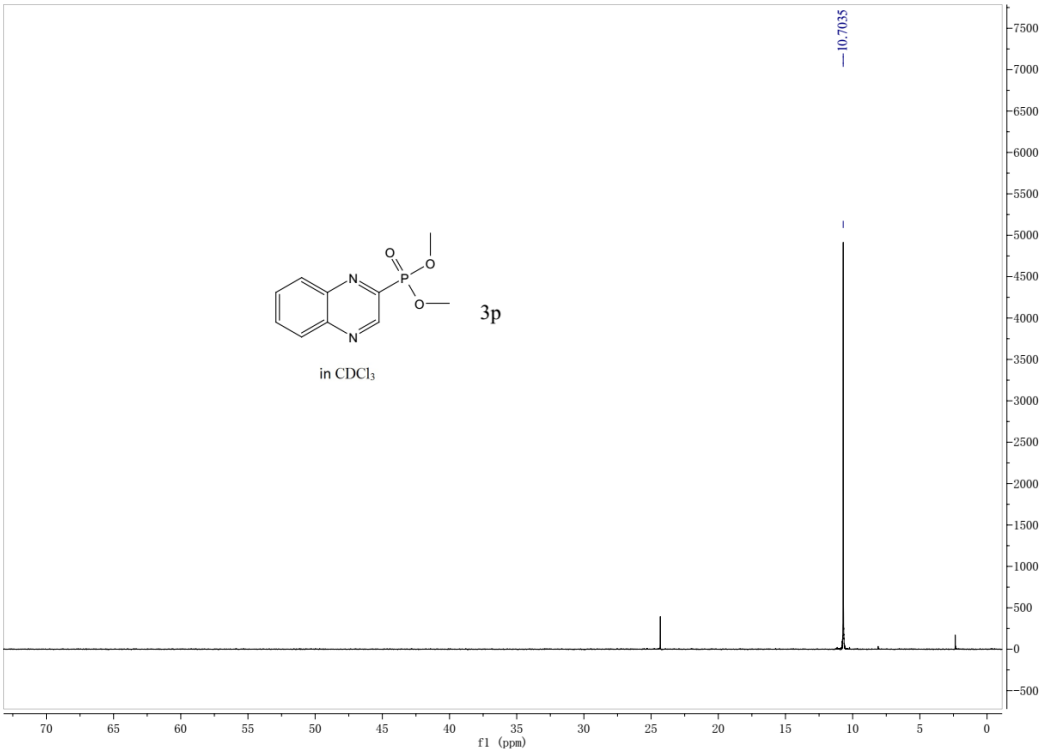
HRMS (ESI-TOF) spectrum of compound **3o**



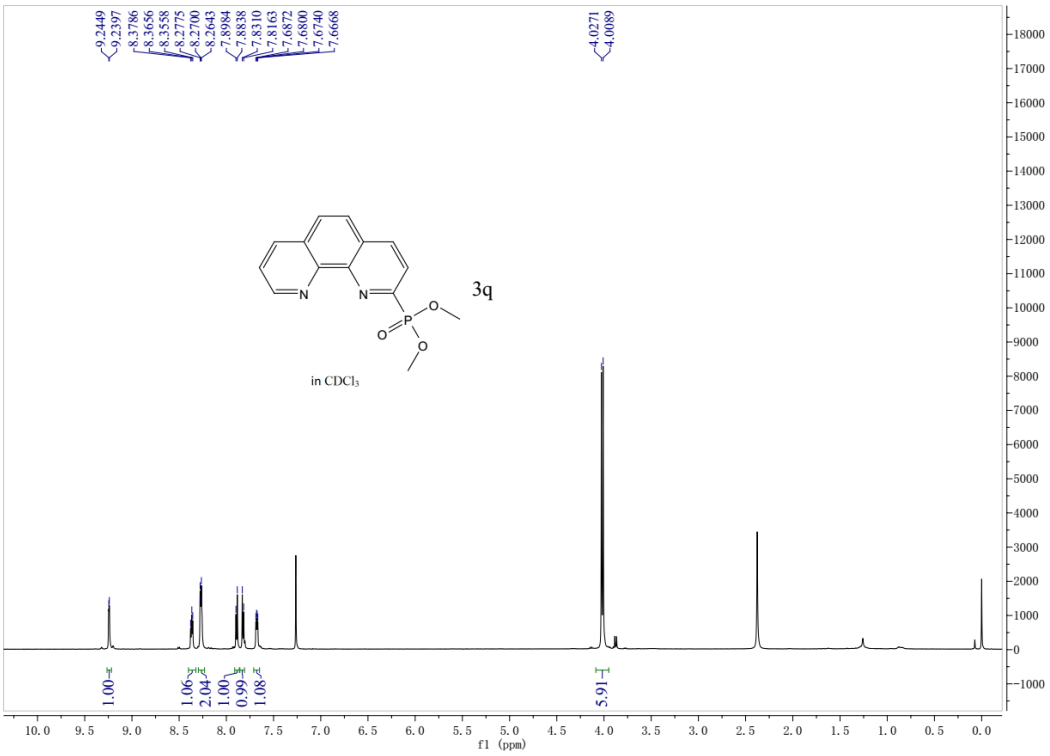
^{1}H NMR spectrum of compound **3p**



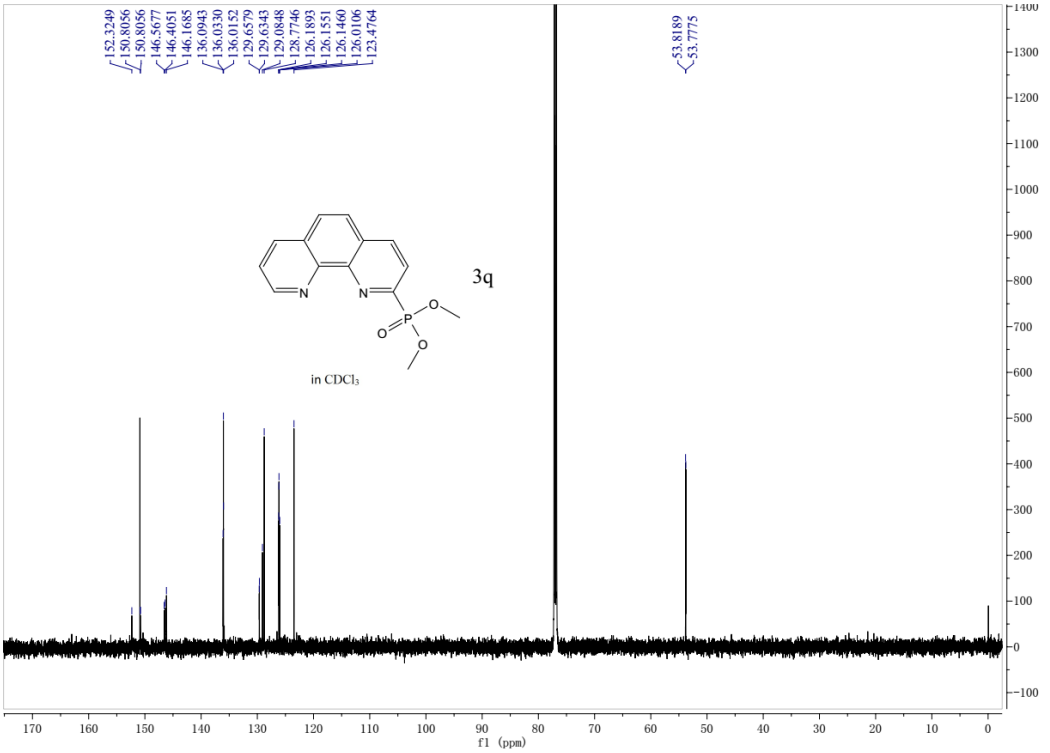
^{13}C NMR spectrum of compound **3p**



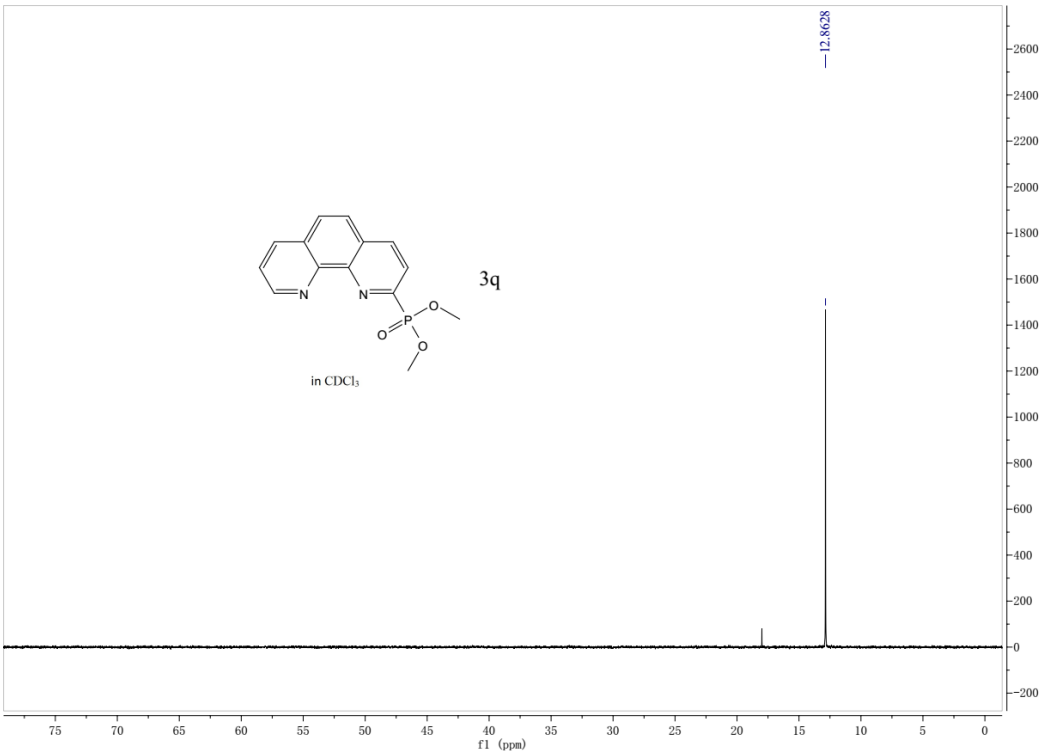
^{31}P NMR spectrum of compound **3p**



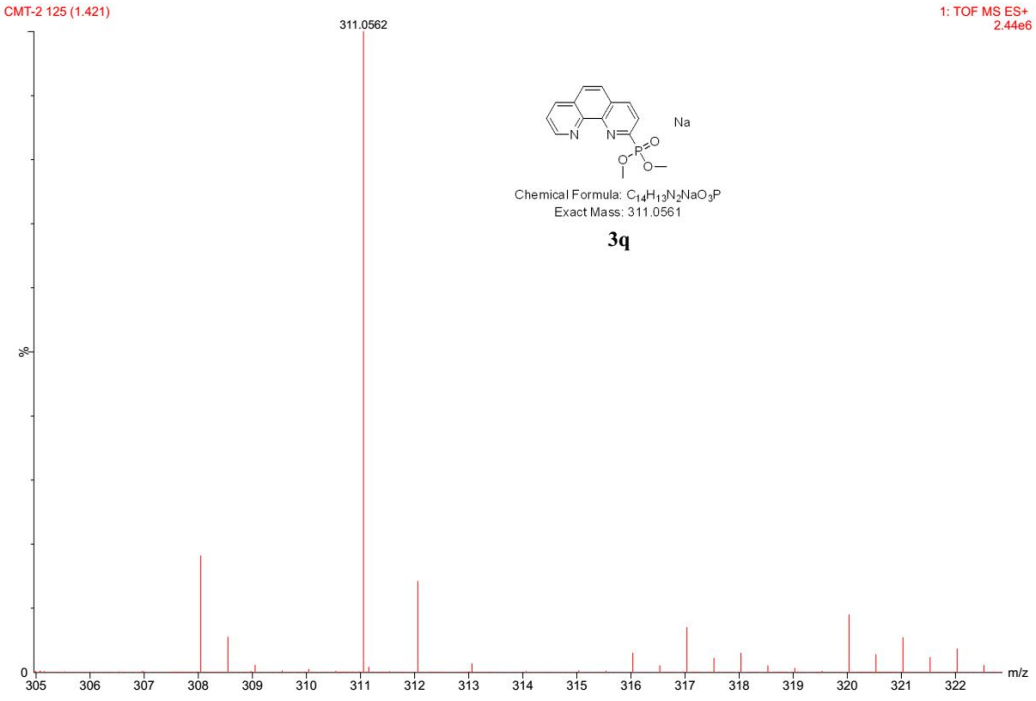
^{1}H NMR spectrum of compound **3q**



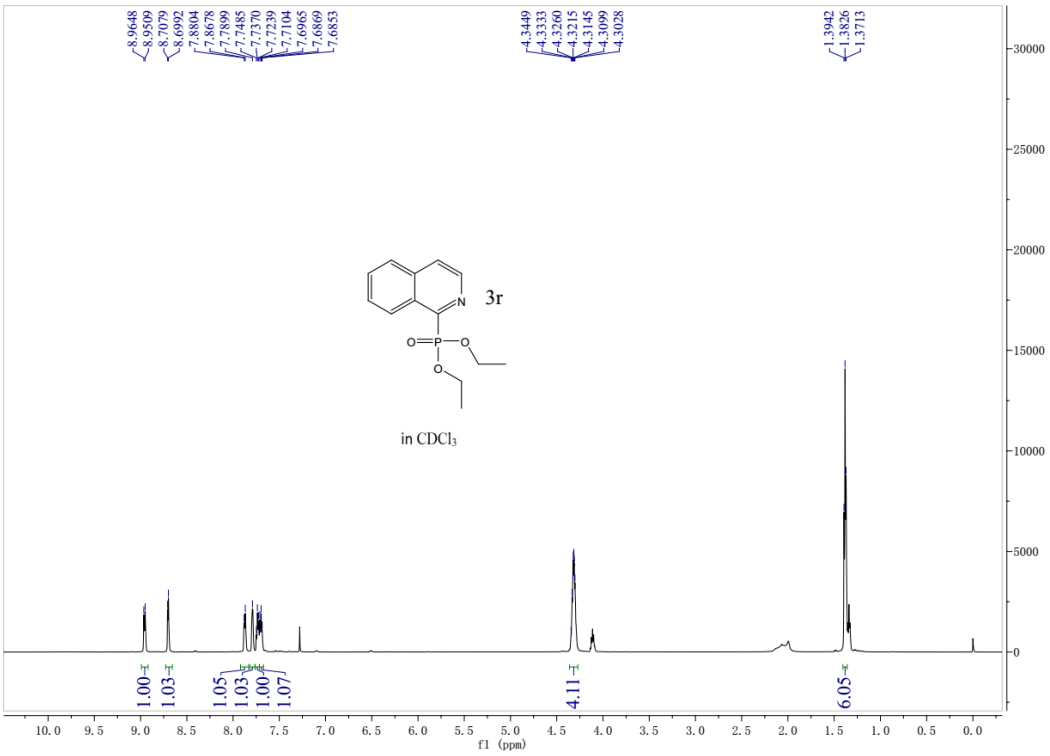
^{13}C NMR spectrum of compound **3q**



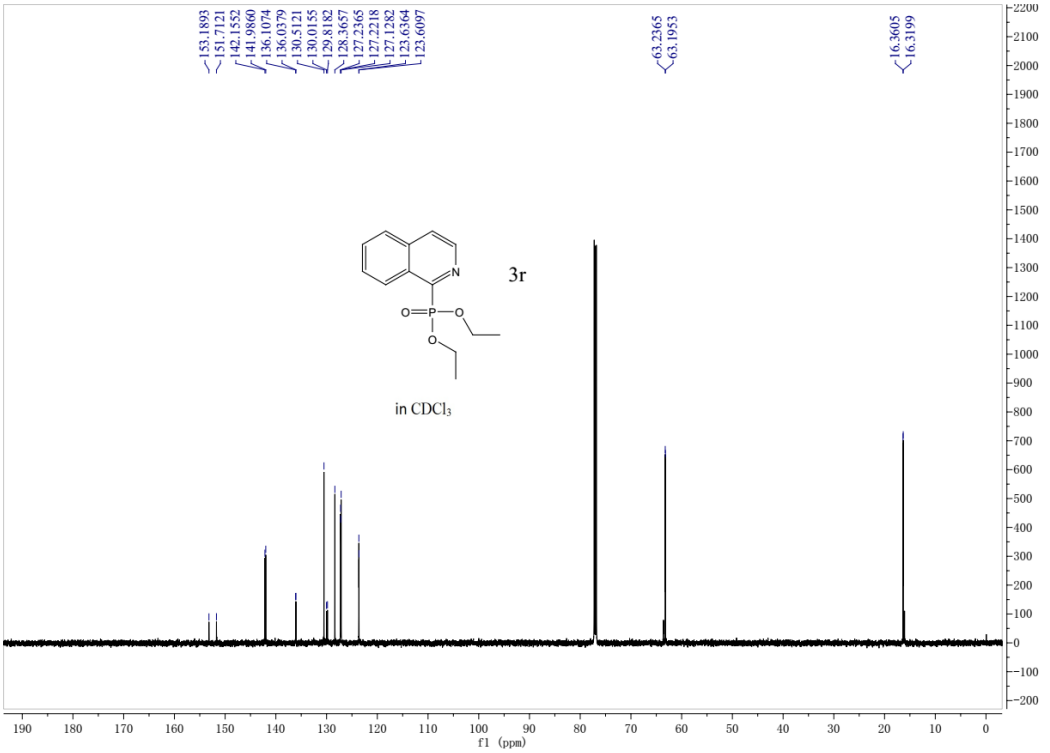
^{31}P NMR spectrum of compound **3q**



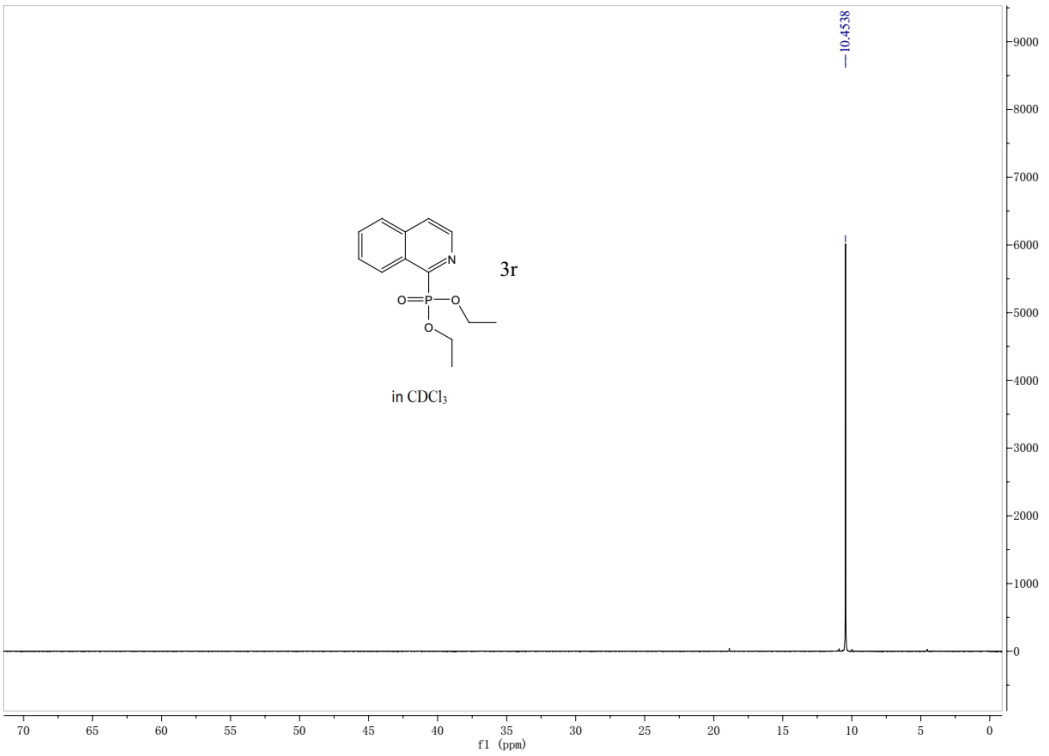
HRMS (ESI-TOF) spectrum of compound **3q**



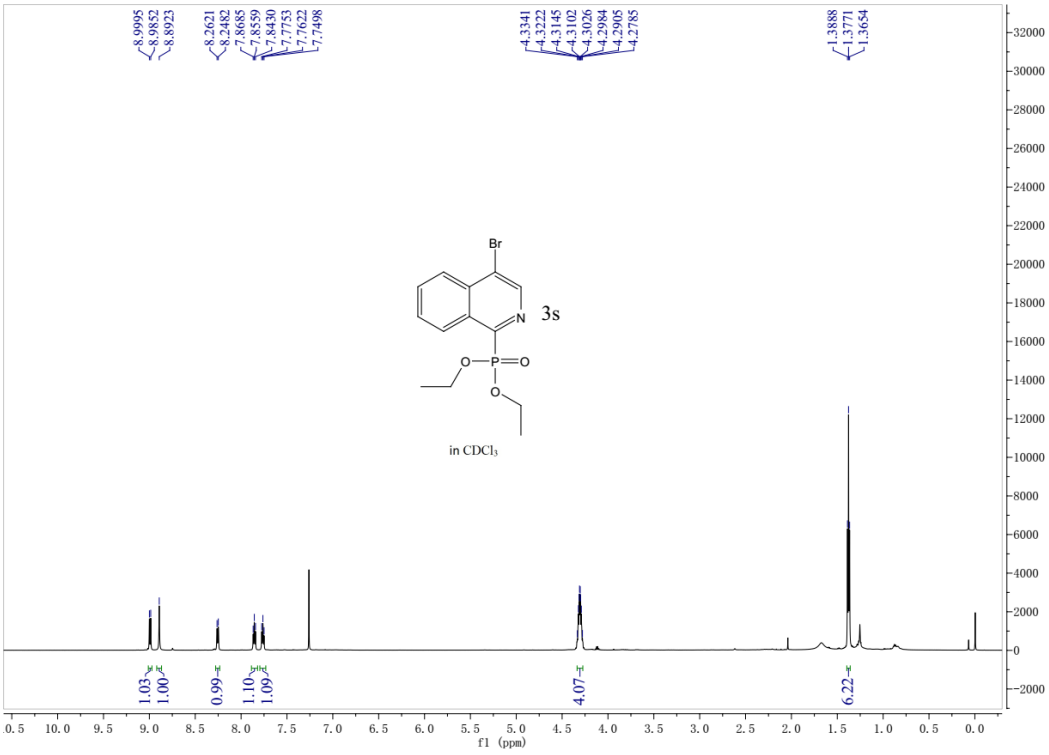
^{1}H NMR spectrum of compound **3r**



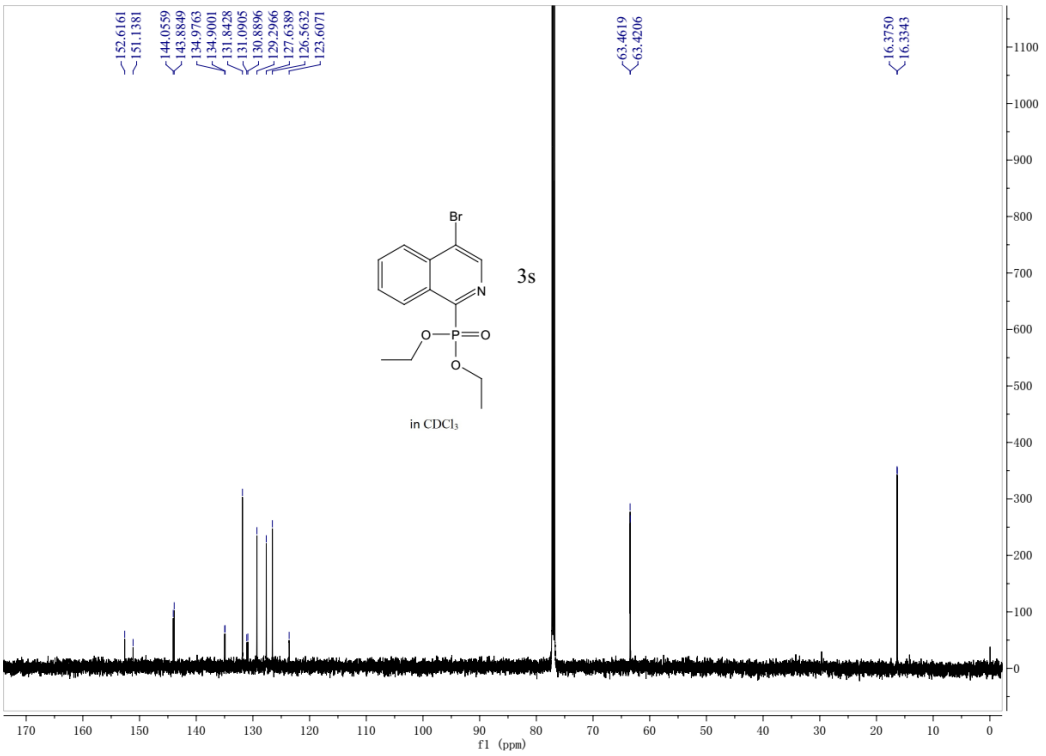
^{13}C NMR spectrum of compound **3r**



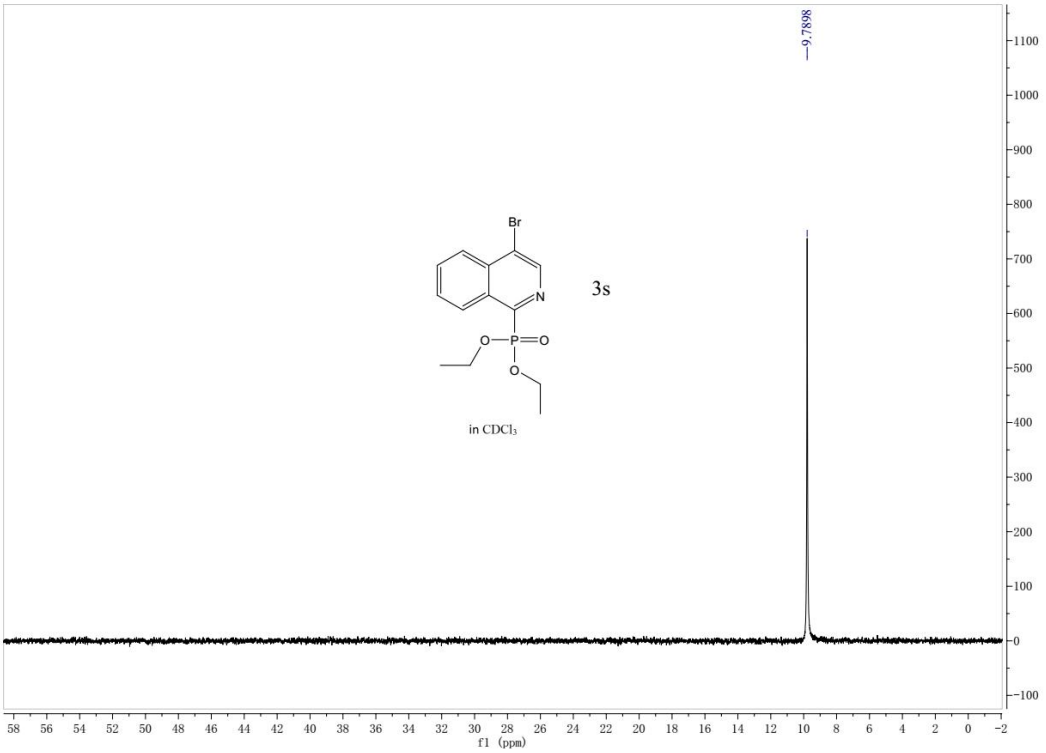
^{31}P NMR spectrum of compound **3r**



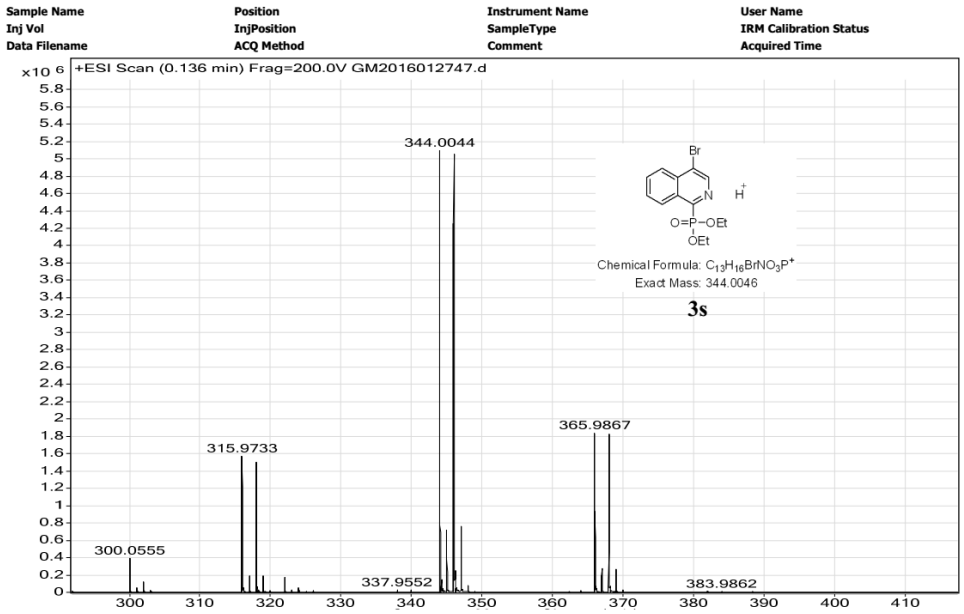
^{1}H NMR spectrum of compound **3s**



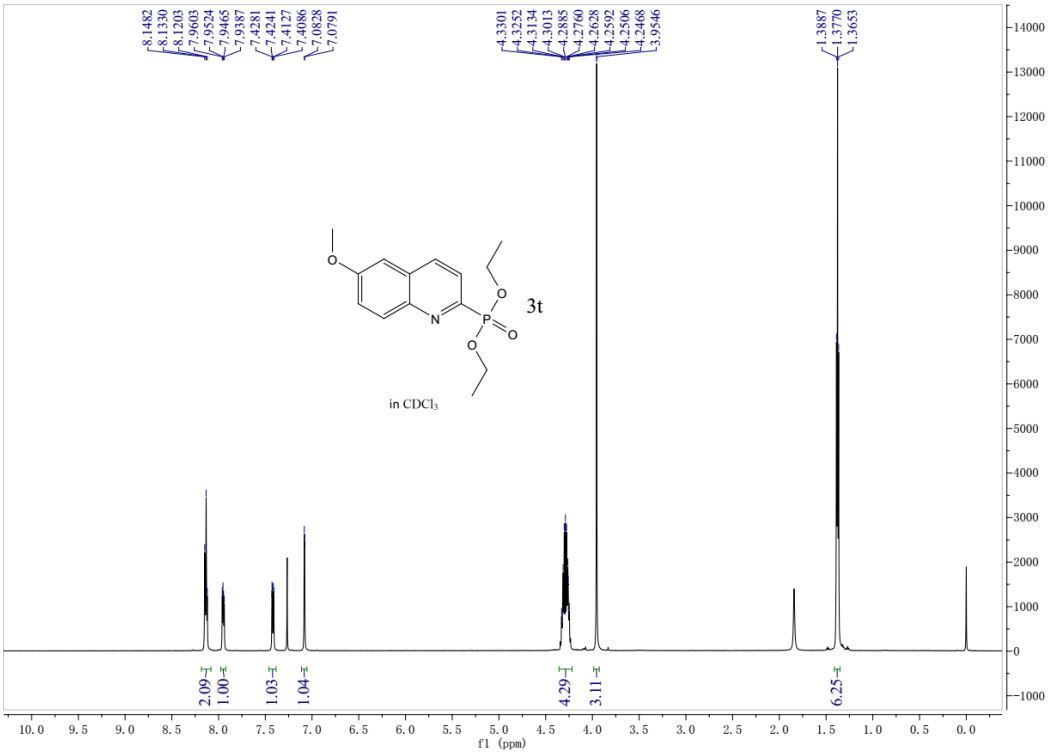
^{13}C NMR spectrum of compound **3s**



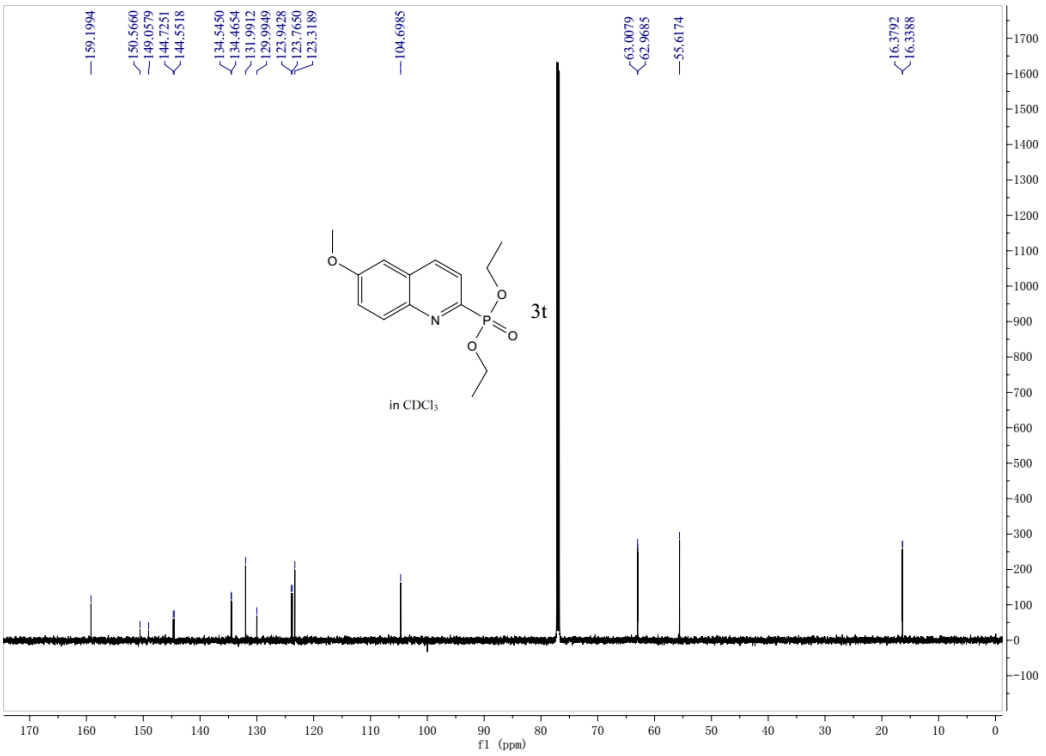
^{31}P NMR spectrum of compound **3s**



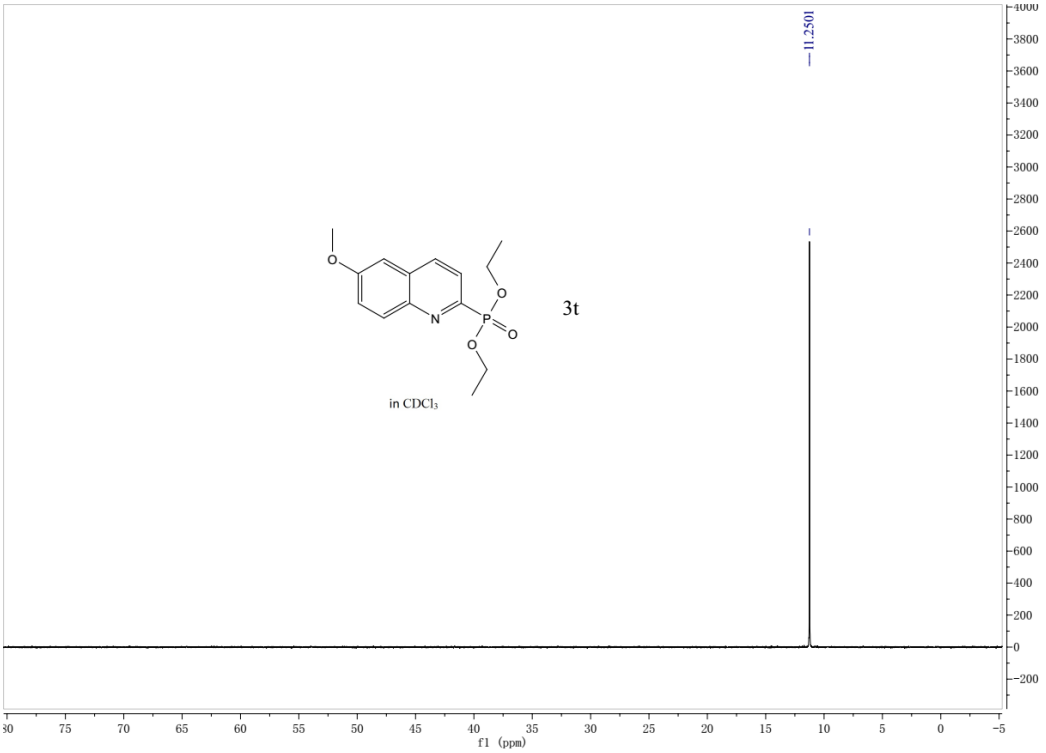
HRMS (ESI-TOF) spectrum of compound **3s**



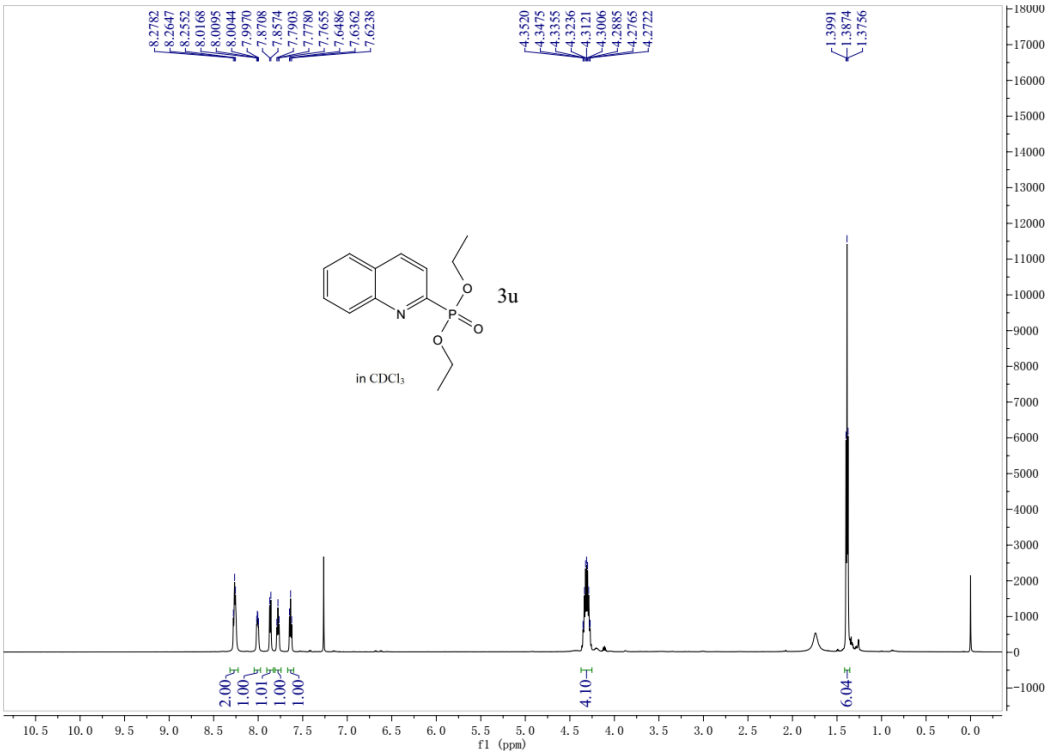
^{1}H NMR spectrum of compound **3t**



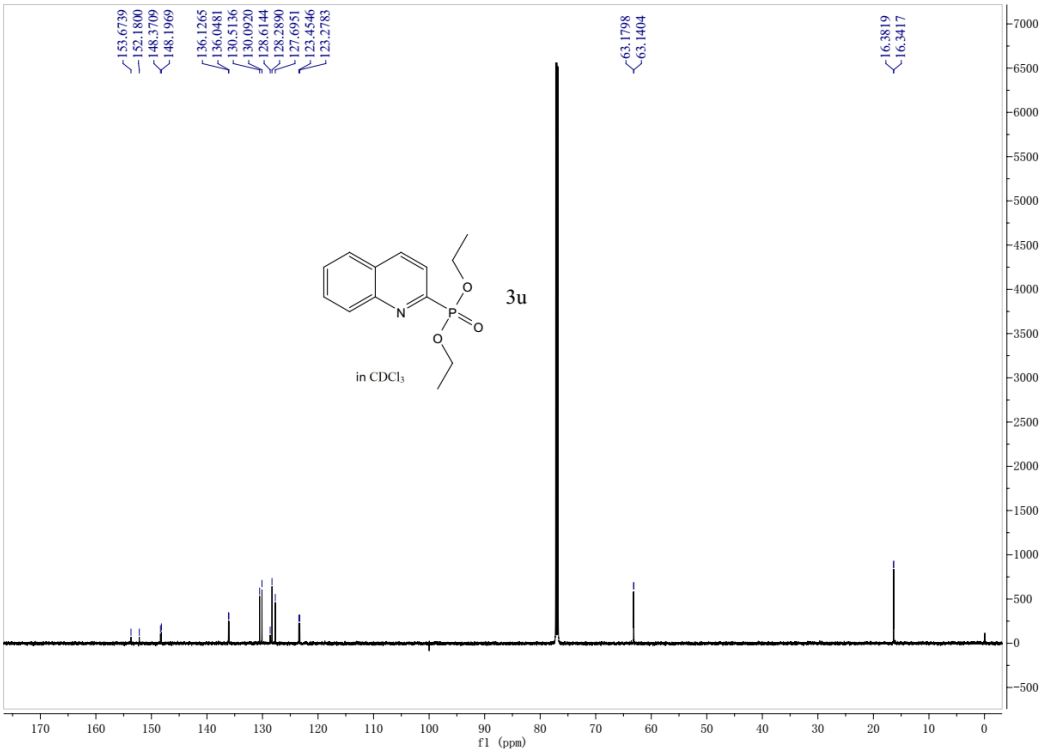
^{13}C NMR spectrum of compound **3t**



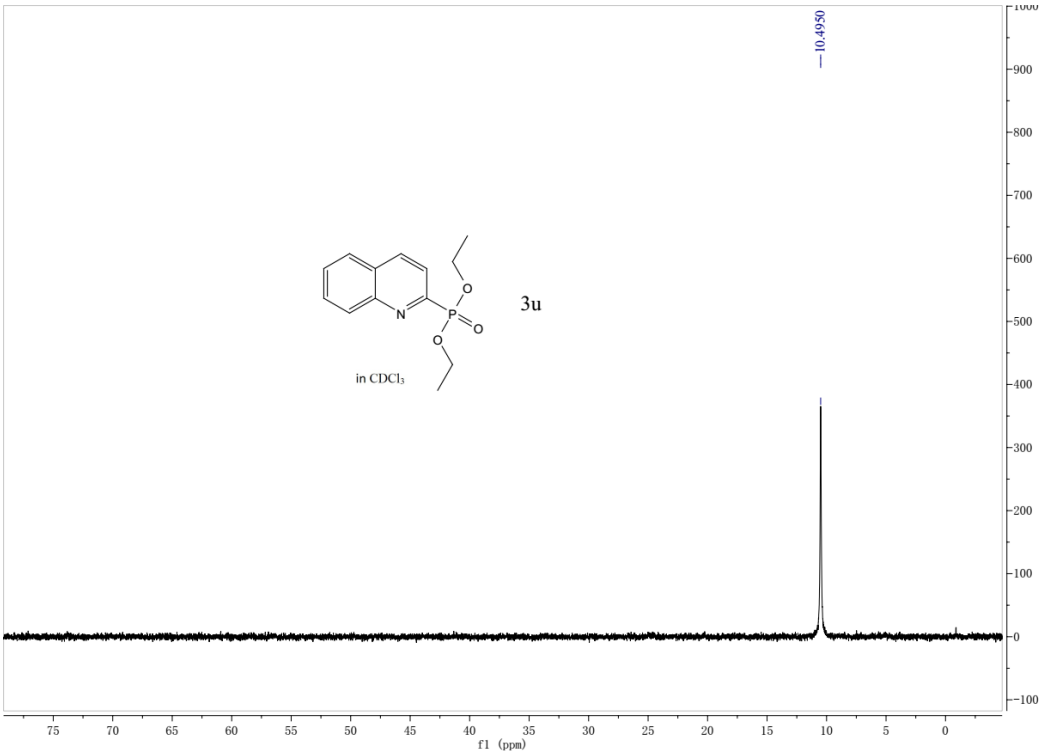
^{31}P NMR spectrum of compound **3t**



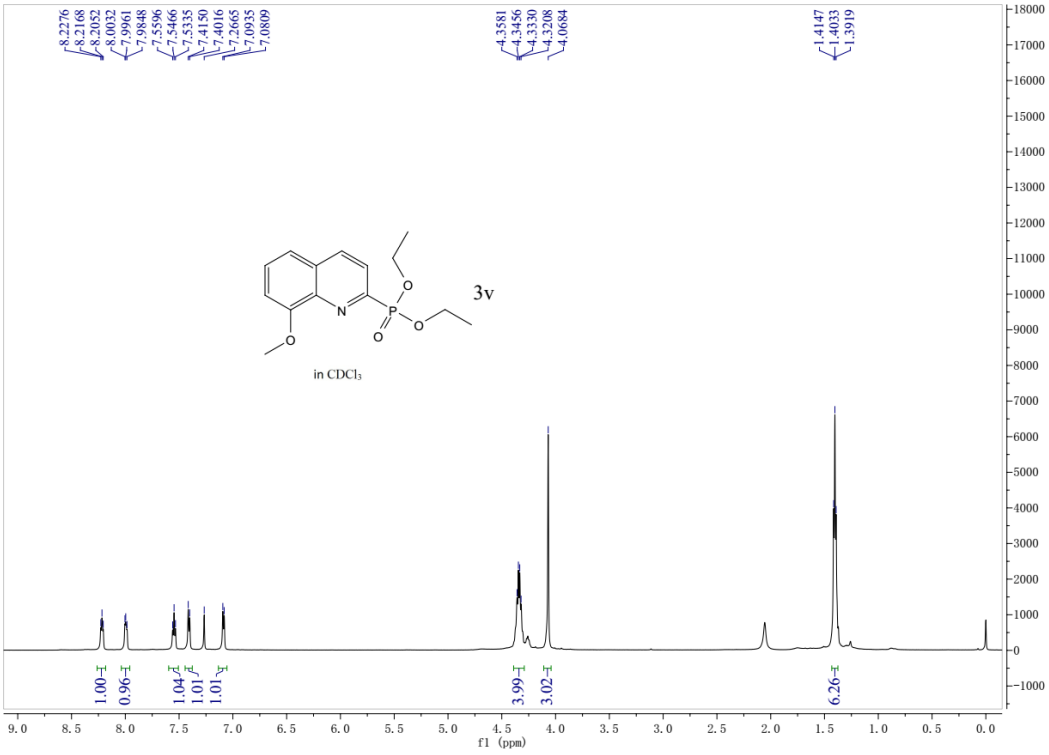
^{1}H NMR spectrum of compound **3u**



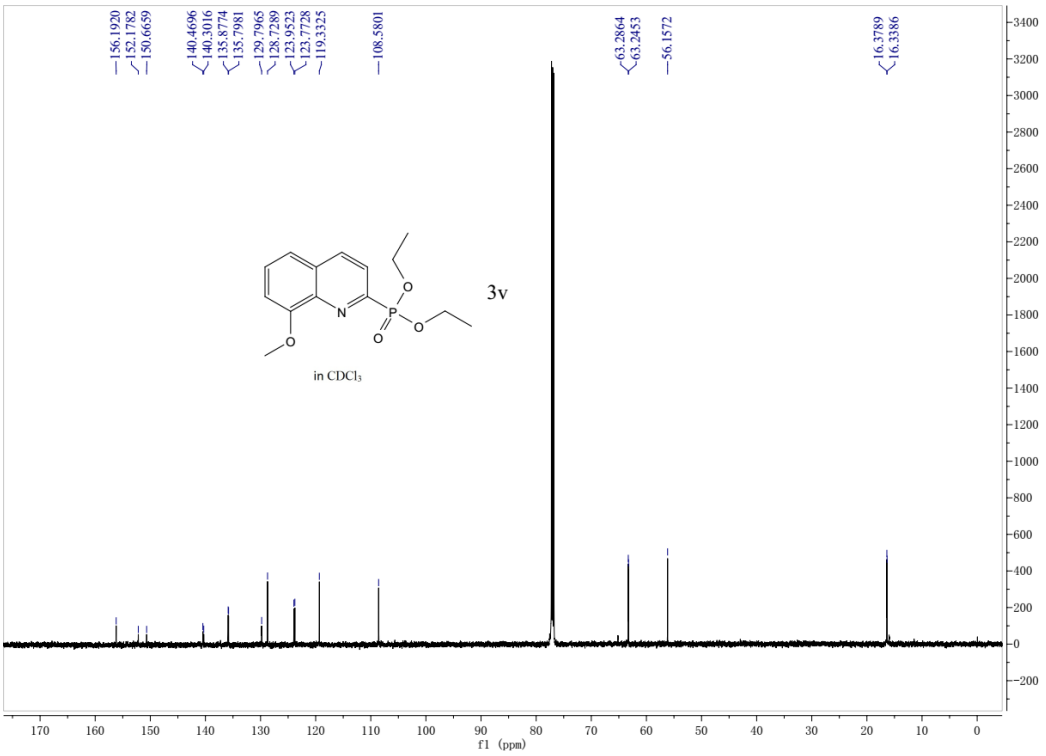
^{13}C NMR spectrum of compound **3u**



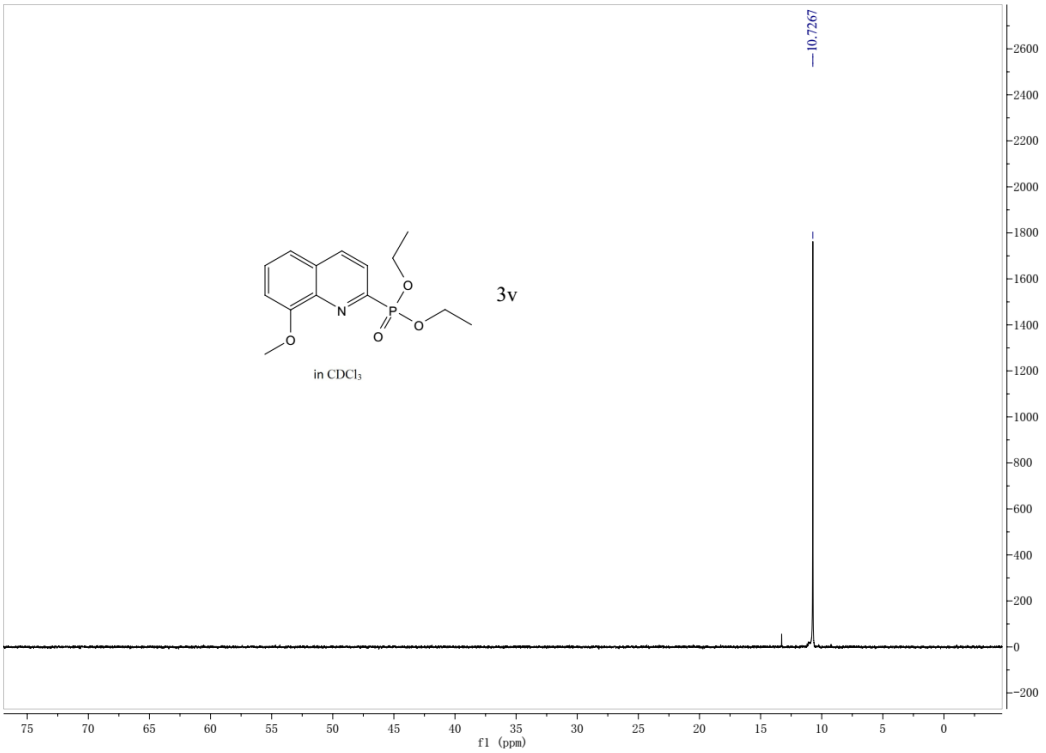
^{31}P NMR spectrum of compound **3u**



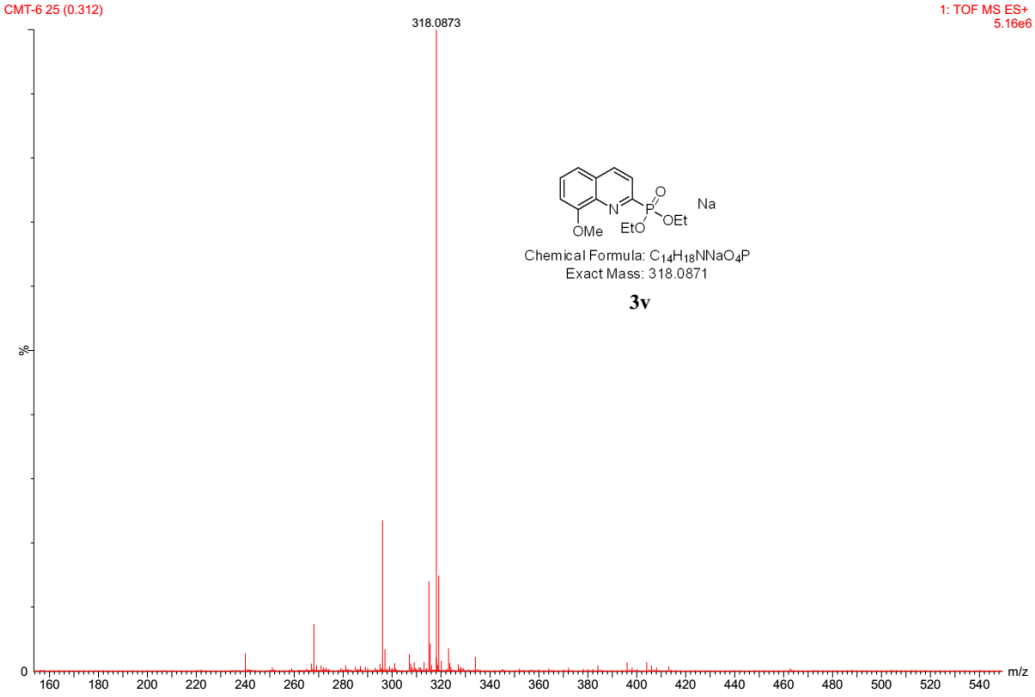
^{1}H NMR spectrum of compound **3v**



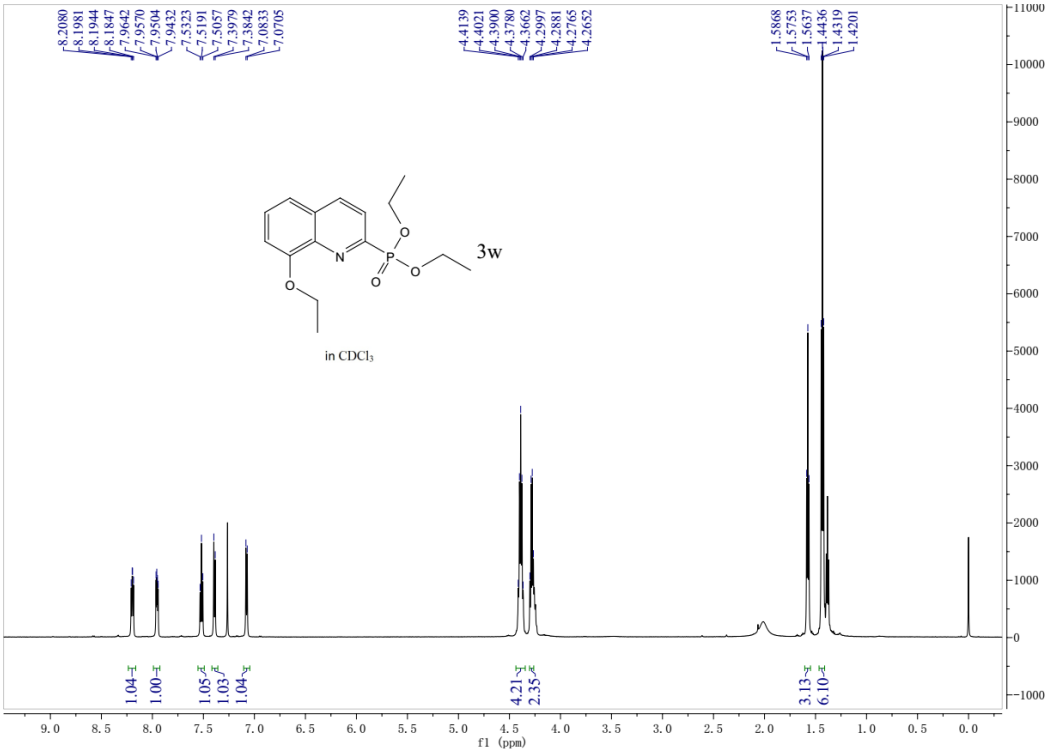
^{13}C NMR spectrum of compound **3v**



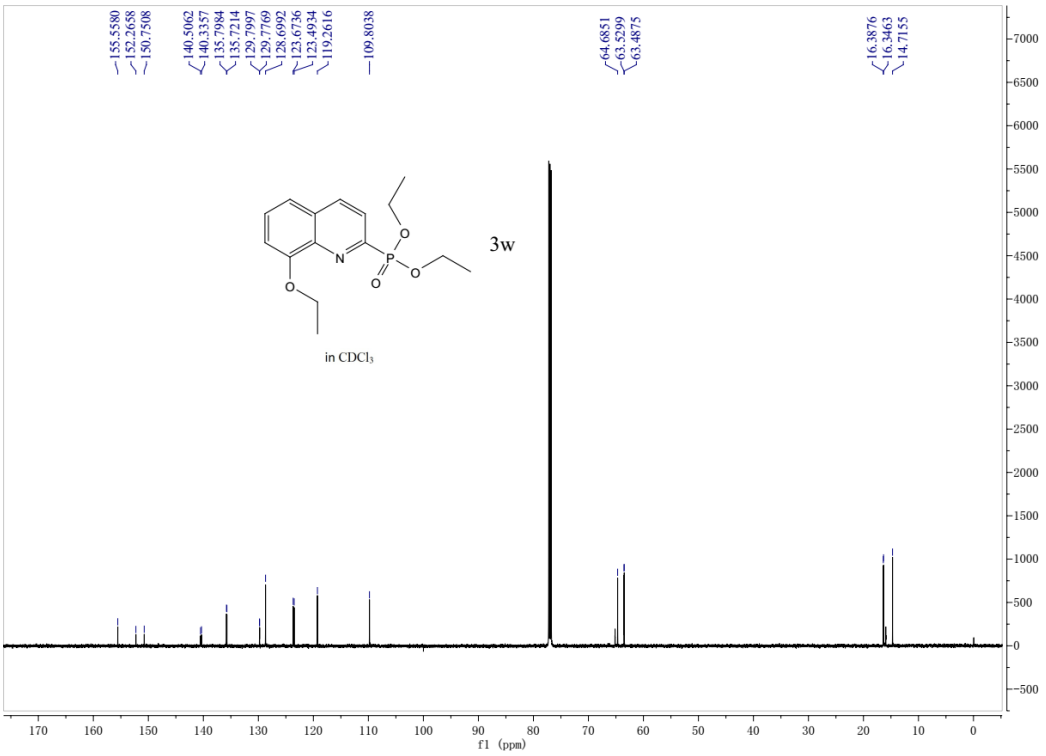
^{31}P NMR spectrum of compound **3v**



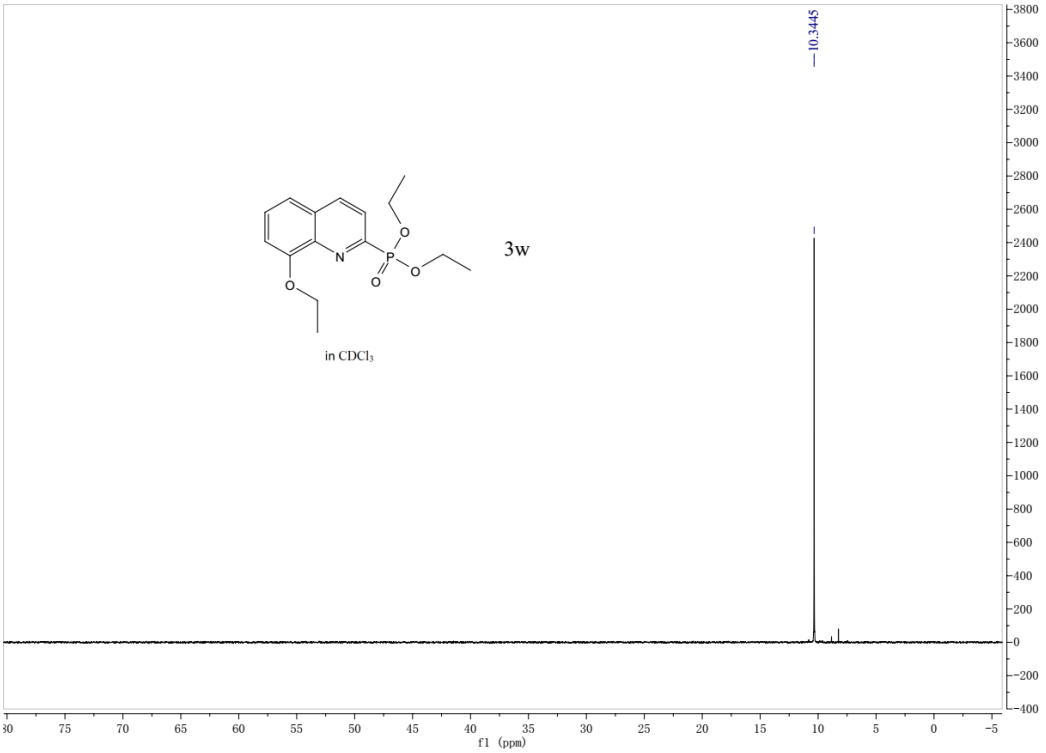
HRMS (ESI-TOF) spectrum of compound **3v**



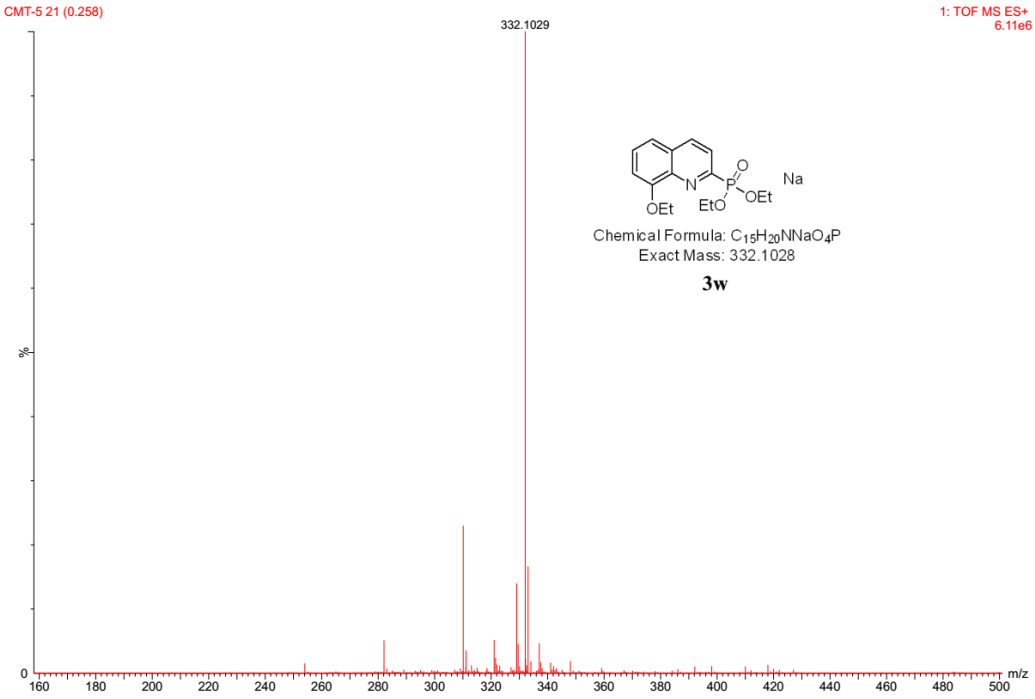
^{1}H NMR spectrum of compound **3w**



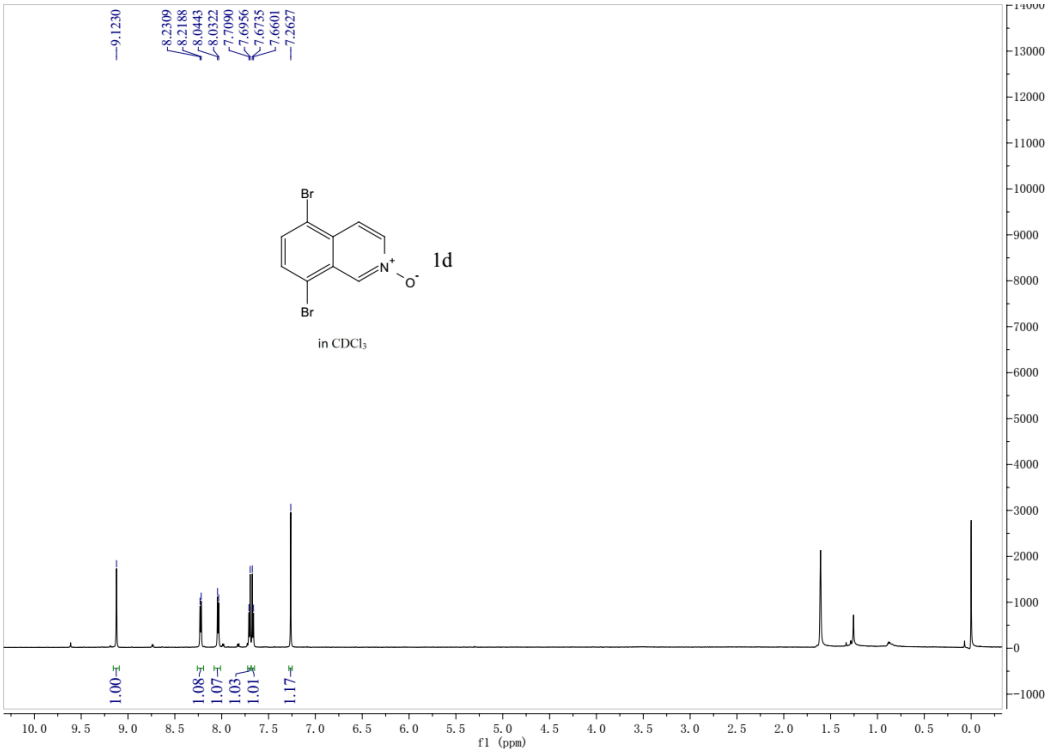
^{13}C NMR spectrum of compound **3w**



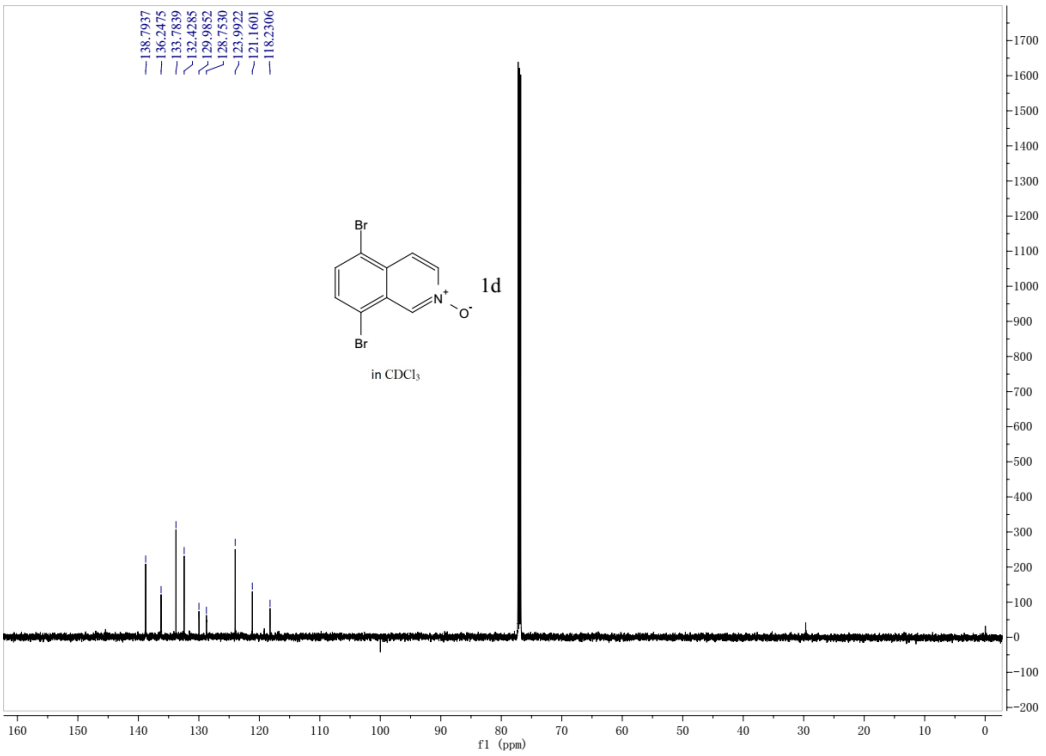
^{31}P NMR spectrum of compound **3w**



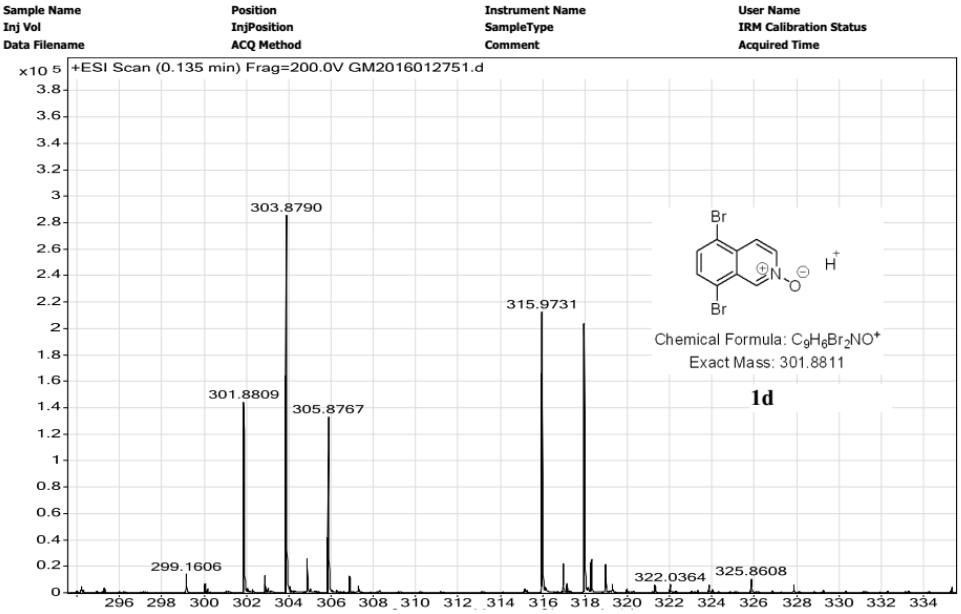
HRMS (ESI-TOF) spectrum of compound **3w**



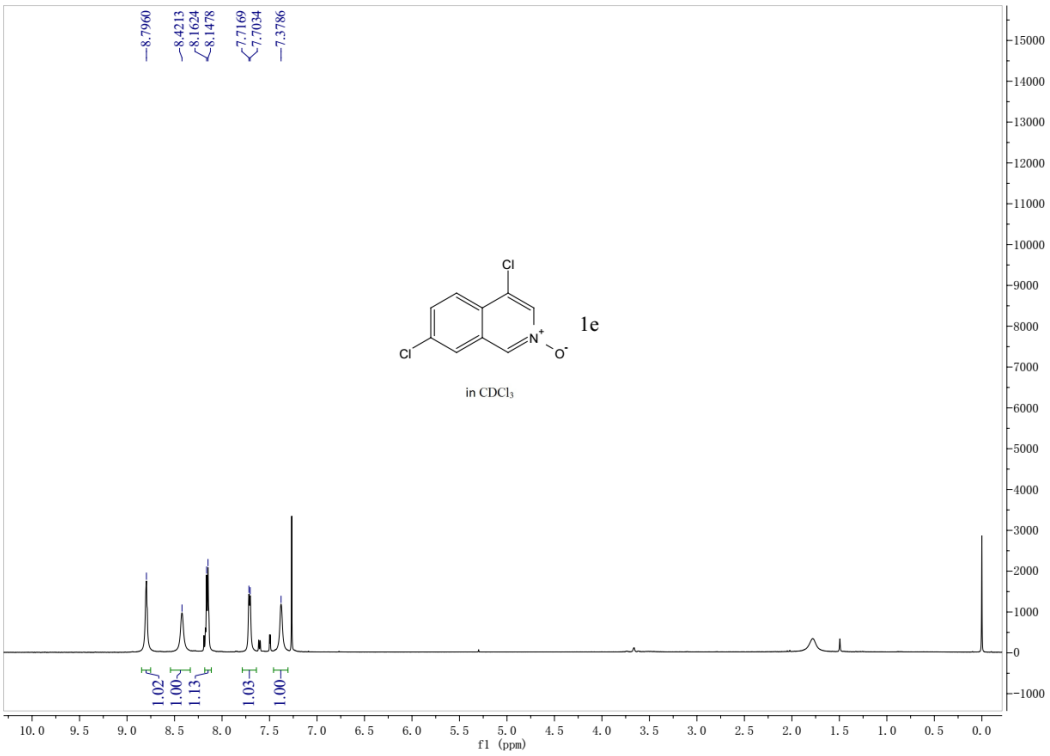
^{1}H NMR spectrum of compound **1d**



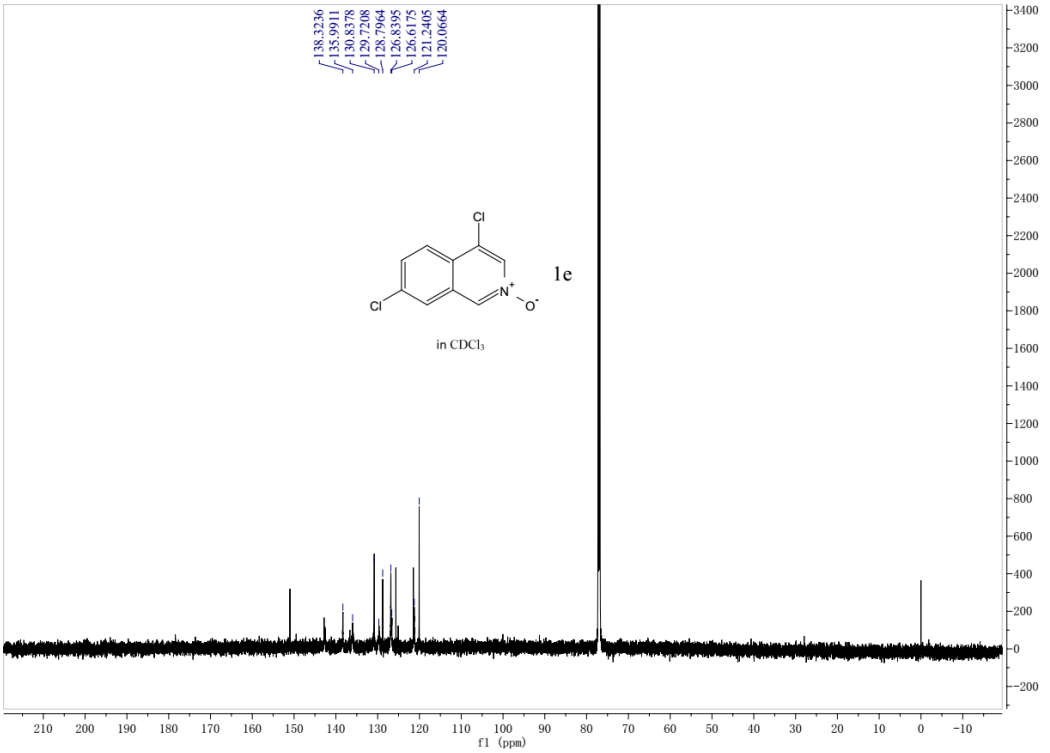
^{13}C NMR spectrum of compound **1d**



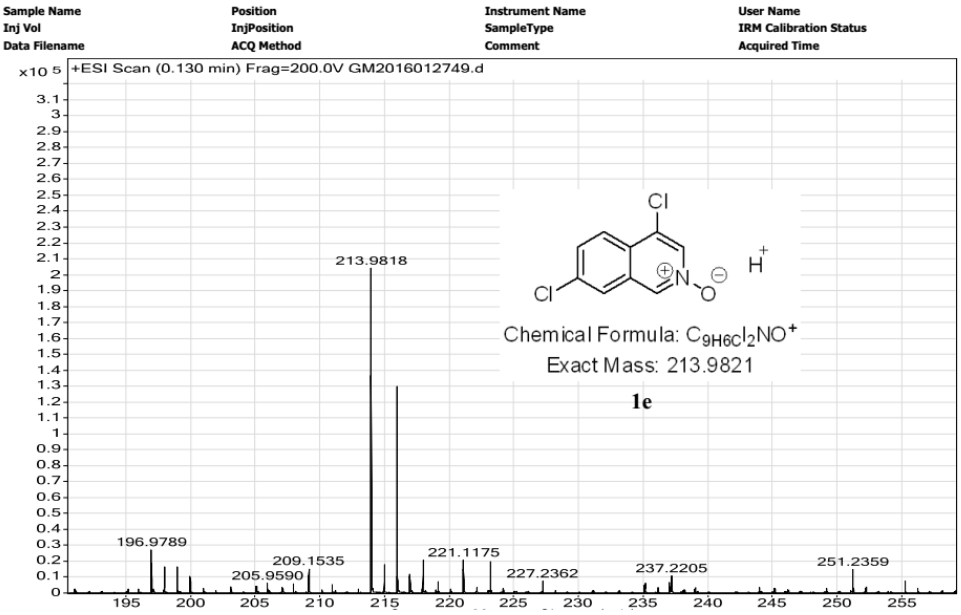
HRMS (ESI-TOF) spectrum of compound **1d**



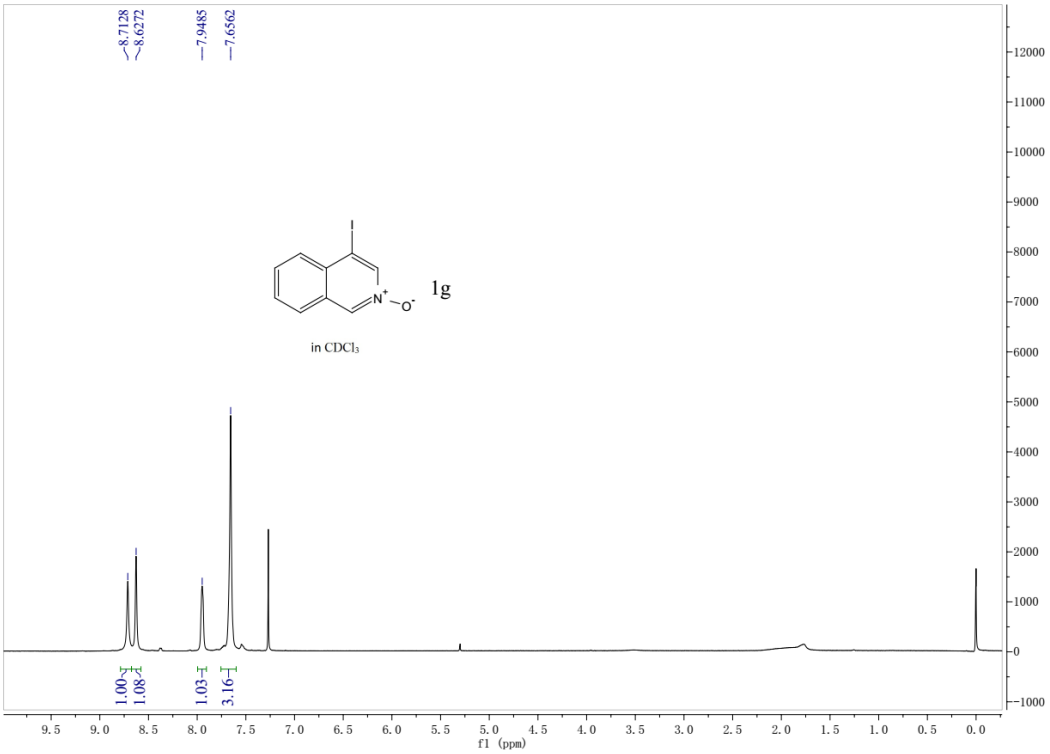
^{1}H NMR spectrum of compound **1e**



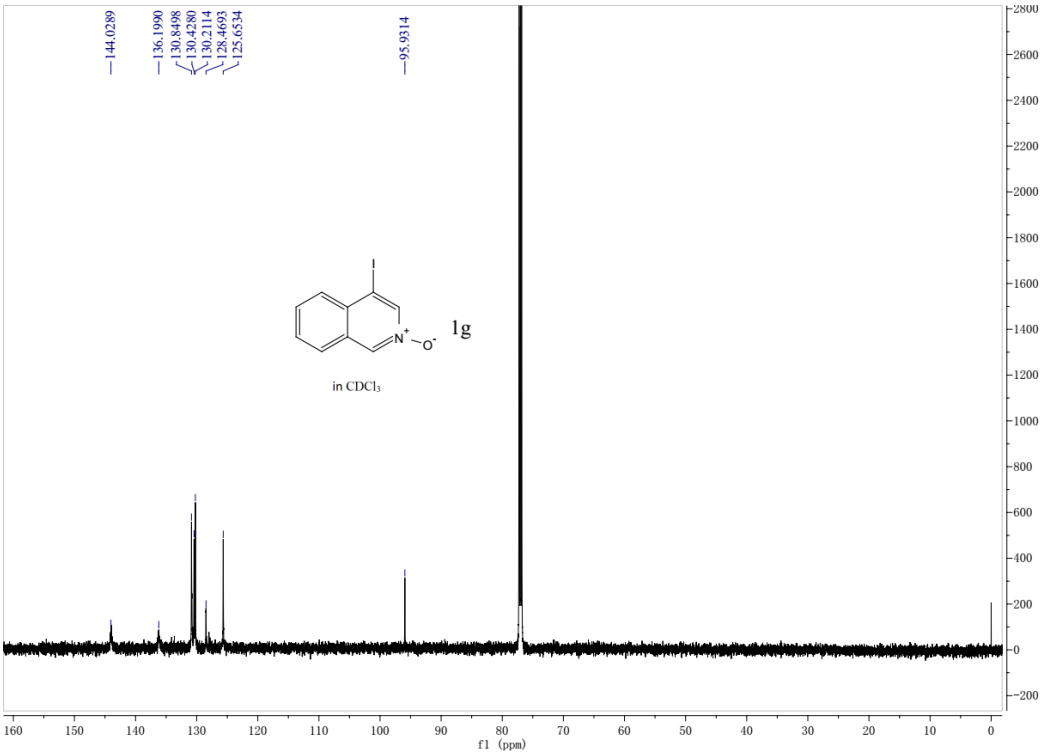
^{13}C NMR spectrum of compound **1e**



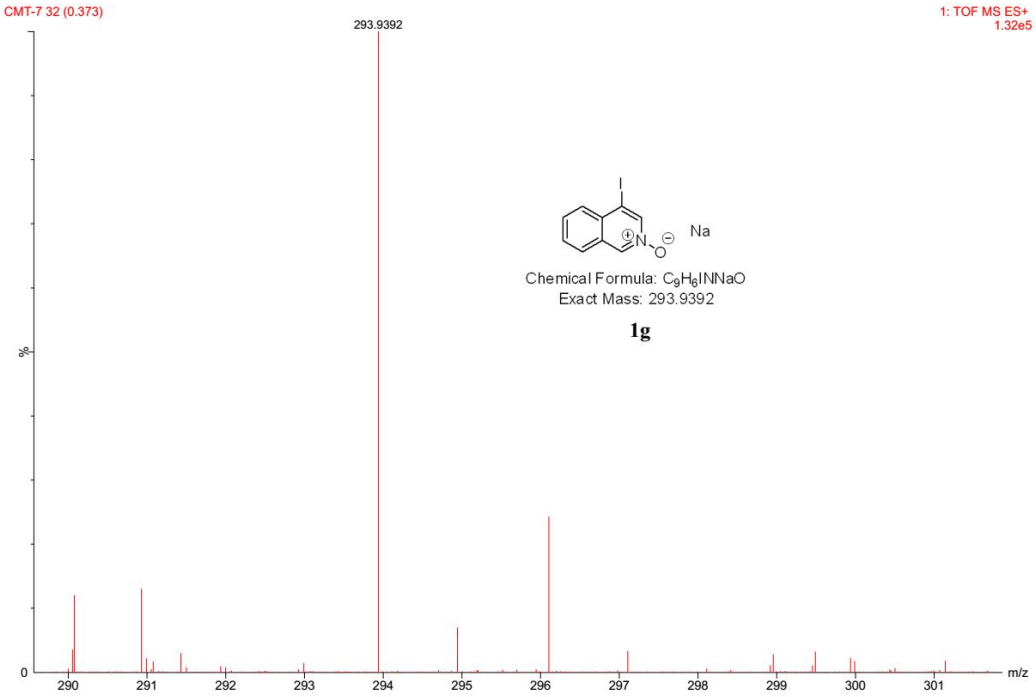
HRMS (ESI-TOF) spectrum of compound **1e**



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



^{13}C NMR spectrum of compound **1g**



HRMS (ESI-TOF) spectrum of compound **1g**