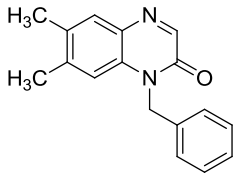
(Supporting Information)

Direct Phosphonation of Quinoxalin-2(1H)-ones under Transition-Metal-Free Conditions

Contents

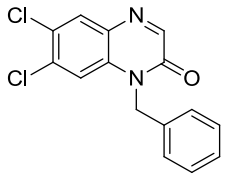
Ⅰ. General information

Commercial materials and solvents were used directly without further purification. All reactions were carried out under air unless otherwise stated. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All melting points were determined on a Beijing Science Instrument Dianguang Instrument Factory XT4B melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz, ^{31}P 162 MHz), using $CDCl_3$ and DMSO-d_6 as the solvents with tetramethylsilane (TMS) as the internal standard at room temperature. HRMSESI spectra were obtained on Agilent 6450 spectrometer, and HRMSEI spectra were obtained on Agilent Technologies 5973N. Quinoxalin-2(1H)-ones were prepared according to the literature.[1] Quinoxalin-2(1*H*)-ones **1a**,[1] **1h**,[2] **1i**,[3] **1j**,[4] **1o**,[5] are known compounds. Compounds **1l** and **1m** are new and their characterization data are as follows:



6, 7-Dimethyl-1-benzylquinoxalin-2(1*H*)-one (**1l**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.63 (s, 1H), 7.35–7.26 (m, 3H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.04 (s, 1H), 5.46 (s, 2H), 2.30 (d, *J* = 3.8 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 149.1, 141.0, 135.2, 132.8, 132.1, 130.6, 130.6, 128.9, 127.7, 126.8, 115.1, 45.4, 20.7, 19.1 ppm; HRMS (ESI, m/z): calculated for $C_{17}H_{16}N_2O$ $[M+H]^+$: 265.1341, found: 265.1337.



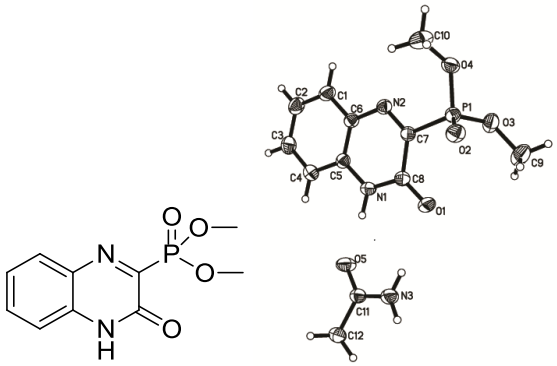
6, 7-Dichloro-1-benzylquinoxalin-2(1*H*)-one (**1m**)

^{1}H NMR (400 MHz, DMSO): δ 8.40 (s, 1H), 8.13 (s, 1H), 7.75 (s, 1H), 7.35–7.31 (m, 2H), 7.30–7.26 (m, 3H), 5.49 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 155.0, 153.1, 136.1, 134.2, 133.4, 133.3, 131.5, 129.7, 128.4, 127.7, 126.6, 117.7, 45.5 ppm; HRMS (ESI, m/z): calculated for $C_{15}H_{11}Cl_2N_2O$ $[M+H]^+$: 305.0248, found: 305.0243.

Ⅱ. General catalytic procedure

A reaction tube was charged with quinoxalin-2(1*H*)-one **1** (0.2 mmol), H-phosphonates **2** (0.6 mmol) or diphenylphosphine oxide **2** (0.3 mmol), $K_2S_2O_8$ (0.6 mmol), and CH_3CN (2 mL). The reaction mixture was stirred at 100 ℃ for 8 h and monitored by TLC. After completion of reaction, the resulting mixture was cooled to room temperature, filtered and concentrated under reduced pressure, and purified by column chromatography over silica gel with dichloromethane/methanol.

dimethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3a)



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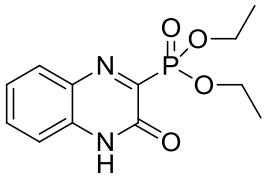
Primrose yellow solid: m.p. 170-172 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.80 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.42 – 7.33 (m, 2H), 3.88 (d, J = 11.1 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.5 (d, $J_{C\text{-}P}$ = 31.4 Hz), 153.8 (d, $J_{C\text{-}P}$ = 223.8 Hz), 133.5 (s), 133.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 25.3 Hz), 130.3 (s), 124.3 (s), 116.3 (s), 54.5 (d, $J_{C\text{-}P}$ = 6.3 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 9.4 (s). HRMS m/z (ESI) calculated for $C_{10}H_{11}N_2O_4P$ $(M+H)^+$ 255.0535, found 255.0530.

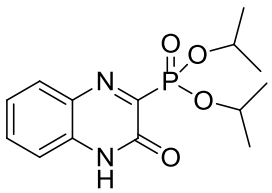
diethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3b)



Primrose yellow solid: m.p. 194-196 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.78 (s, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.42 – 7.31 (m, 2H), 4.26 (dq, J_1 = 14.2 Hz, J_2 = 7.1 Hz, 4H), 1.32 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.4 (d, $J_{C\text{-}P}$ = 31.4 Hz), 154.2 (d, $J_{C\text{-}P}$ = 222.9 Hz), 133.4 (s), 133.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 25.2 Hz), 130.3 (s), 124.3 (s), 116.3 (s), 63.8 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.8 (d, $J_{C\text{-}P}$ = 6.1 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 7.0 (s). HRMS m/z (ESI) calculated for $C_{12}H_{15}N_2O_4P$ $(M+H)^+$ 283.0848, found 283.0843.

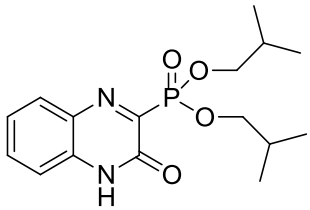
diisopropyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3c)



Primrose yellow solid: m.p. 191-196 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.74 (s, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.37 (dd, J_1 = 14.1, J_2 =7.4 Hz, 2H), 4.82 (dq, J_1 = 12.4, J_2 =6.2 Hz, 2H), 1.35 (dd, J_1 = 6.0 Hz, J_2 =4.7 Hz, 12H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.6 (d, $J_{C\text{-}P}$ = 223.5 Hz), 154.3 (d, $J_{C\text{-}P}$ = 31.4 Hz), 133.2 (s), 133.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.2 (s), 124.3 (s), 116.2 (s), 72.23 (d, $J_{C\text{-}P}$ = 6.2 Hz), 24.57 (d, $J_{C\text{-}P}$ = 3.2 Hz), 23.91 (d, $J_{C\text{-}P}$ = 6.0 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 5.3 (s). HRMS m/z (ESI) calculated for $C_{14}H_{29}N_2O_4P$ $(M+H)^+$ 311.1161, found 311.1157.

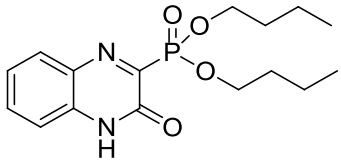
diisobutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3d)



White solid: m.p. 115-116 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.75 (s, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.40 – 7.32 (m, 2H), 3.98 (t, J = 6.8 Hz, 4H), 1.94 (td, J_1 = 13.3 Hz, J_2 = 6.6 Hz, 2H), 0.93 (d, J = 6.7 Hz, 12H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.4 (d, $J_{C\text{-}P}$ = 31.4 Hz), 154.3 (d, $J_{C\text{-}P}$ = 223.7 Hz), 133.4 (s), 133.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131. 9 (d, $J_{C\text{-}P}$ = 25.3 Hz), 130.3 (s), 124.3 (s), 116.3 (s), 73.4 (d, $J_{C\text{-}P}$ = 6.8 Hz), 29.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 19.0 (d, $J_{C\text{-}P}$ = 3.3 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 6.8 (s). HRMS m/z (ESI) calculated for $C_{16}H_{23}N_2O_4P$ $(M+H)^+$ 339.1474, found 339.1469.

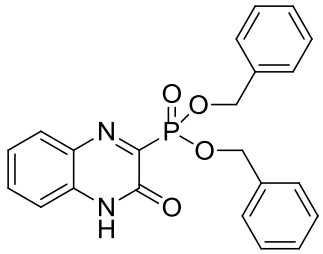
dibutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3e)



Pale green solid: m.p. 102-104 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.76 (s, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.40 – 7.31 (m, 2H), 4.19 (dd, J_1 = 13.9, J_2 = 6.5 Hz, 4H), 1.65 (dq, J_1 = 13.1 Hz, J_2 = 6.5 Hz, 4H), 1.45 – 1.34 (m, 4H), 0.90 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.4 (d, $J_{C\text{-}P}$ = 31.3 Hz), 154.2 (d, $J_{C\text{-}P}$ = 223.0 Hz), 133.4 (s), 133.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.9 (d, $J_{C\text{-}P}$ = 25.2 Hz), 130.2 (s), 124.3 (s), 116.3 (s), 67.3 (d, $J_{C\text{-}P}$ = 6.5 Hz), 32.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 18.7 (s), 13.9 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 7.0 (s). HRMS m/z (ESI) calculated for $C_{16}H_{23}N_2O_4P$ $(M+H)^+$ 339.1474, found 339.1470.

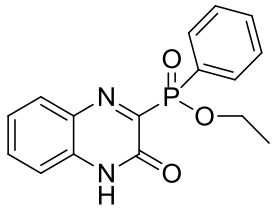
dibenzyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3f)



Pale green solid: m.p. 55-60 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.85 (s, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.67 (t, J_1 = 7.4 Hz, J_2 = 1H Hz), 7.45 (d, J = 6.8 Hz, 4H), 7.41 – 7.30 (m, 8H), 5.28 (d, J = 7.8 Hz, 4H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.55 (d, $J_{C\text{-}P}$ = 32.0 Hz), 153.8 (d, $J_{C\text{-}P}$ = 223.8 Hz), 137.00 (d, $J_{C\text{-}P}$ = 6.6 Hz), 133.54 (s), 133.22 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.04 (d, $J_{C\text{-}P}$ = 25.9 Hz), 130.33 (s), 128.84 (s), 128.63 (s), 128.33 (s), 124.36 (s), 116.32 (s), 68.91 (d, $J_{C\text{-}P}$ = 5.9 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 7.7 (s). HRMS m/z (ESI) calculated for $C_{22}H_{19}N_2O_4P$ $(M+H)^+$ 407.1161, found 407.1155.

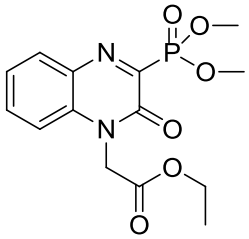
ethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)(phenyl)phosphinate (3g)



Yellow-green solid: m.p. 221-224 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.69 (s, 1H), 7.90 – 7.81 (m, 3H), 7.64 (dd, J_1 = 12.0 Hz, J_2 = 6.7 Hz, 2H), 7.53 (td, J_1 = 7.5 Hz, J_2 = 3.6 Hz, 2H), 7.35 (dd, J_1 = 11.8 Hz, J_2 = 7.9 Hz, 2H), 4.29 (dddd, J_1 = 17.5 Hz, J_2 = 14.7 Hz, J_3 = 10.2 Hz, J_4 = 7.7 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 156.5 (d, $J_{C\text{-}P}$ = 160.5 Hz), 154.3 (d, $J_{C\text{-}P}$ = 28.5 Hz), 133.3 (s), 133.3 (d, $J_{C\text{-}P}$ = 2.1 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.2 (s), 132.2 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 141.0 Hz), 130.4 (s), 128.8 (d, $J_{C\text{-}P}$ = 13.4 Hz), 124.3 (s), 116.3 (s), 62.4 (d, $J_{C\text{-}P}$ = 6.4 Hz), 17.0 (d, $J_{C\text{-}P}$ = 6.0 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 23.8 (s). HRMS m/z (ESI) calculated for $C_{16}H_{15}N_2O_3P$ $(M+H)^+$ 315.0899, found 315.0895.

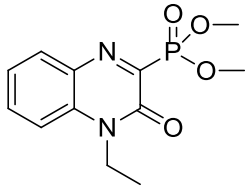
ethyl 2-(3-(dimethoxyphosphoryl)-2-oxoquinoxalin-1(2H)-yl)acetate (3h)



Cream solid solid: m.p. 95-99 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 8.00 (d, J = 7.9 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 5.13 (s, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.88 (d, J = 11.1 Hz, 6H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 167.6 (s), 153.6 (d, $J_{C\text{-}P}$ = 32.5 Hz), 152.0 (d, $J_{C\text{-}P}$ = 228.0 Hz), 134.0 (s), 133.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.5 (d, $J_{C\text{-}P}$ = 25.8 Hz), 131.5 (s), 124.9 (s), 115.5 (s), 62.0 (s), 54.7 (d, $J_{C\text{-}P}$ = 6.3 Hz), 44.1 (s), 14.5 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 8.7 (s). HRMS m/z (ESI) calculated for $C_{14}H_{17}N_2O_6P$ $(M+H)^+$ 341.0902, found 341.0898.

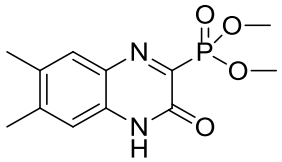
dimethyl (4-ethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3i)



Pale green solid: m.p. 104-106 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 7.96 (dd, J_1 = 8.0 Hz, J_2 =1.0 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.50 – 7.43 (m, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.88 (d, J = 11.0 Hz, 6H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 153.3 (d, $J_{C\text{-}P}$ = 2.3 Hz), 152.4 (d, $J_{C\text{-}P}$ = 259.9 Hz), 133.9 (s), 133.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 26.0 Hz), 131.6 (s), 124.4 (s), 115.4 (s), 54.7 (d, $J_{C\text{-}P}$ = 6.3 Hz), 37.4 (s), 12.7 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 9.3 (s). HRMS m/z (ESI) calculated for $C_{12}H_{15}N_2O_4P$ $(M+H)^+$ 283.0848, found 283.0845.

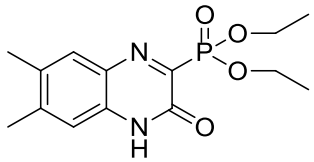
dimethyl (6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3j)



Green solid: m.p. 205-208 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.69 (s, 1H), 7.66 (s, 1H), 7.10 (s, 1H), 3.85 (d, J = 11.0 Hz, 6H), 2.32 (d, J = 15.4 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.7 (d, $J_{C\text{-}P}$ = 31.9 Hz), 152.0 (d, $J_{C\text{-}P}$ = 226.5 Hz), 143.8 (s), 133.4 (s), 131.3 (d, $J_{C\text{-}P}$ = 1.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 25.3 Hz), 129.9 (s), 116.1 (s), 54.5 (d, $J_{C\text{-}P}$ = 6.3 Hz), 20.5 (s), 19.3 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 10.0 (s). HRMS m/z (ESI) calculated for $C_{12}H_{15}N_2O_4P$ $(M+H)^+$ 283.0848, found 283.0843.

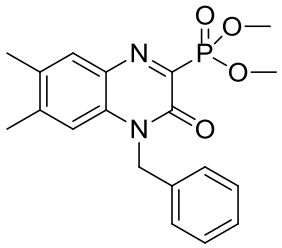
diethyl (6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3k)



Pale yellow solid: m.p. 127-132 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.65 (s, 1H), 7.64 (s, 1H), 7.10 (s, 1H), 4.29 – 4.19 (m, 4H), 2.32 (d, J = 14.5 Hz, 6H), 1.32 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.6 (d, $J_{C\text{-}P}$ = 31.7 Hz), 152.4 (d, $J_{C\text{-}P}$ = 226.3 Hz), 143.7 (s), 133.3 (s), 131.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.6 (d, $J_{C\text{-}P}$ = 25.6 Hz), 129.8 (d, $J_{C\text{-}P}$ = 0.6 Hz), 116.1 (s), 63.6 (d, $J_{C\text{-}P}$ = 6.2 Hz), 20.5 (s), 19.3 (s), 16.8 (d, $J_{C\text{-}P}$ = 6.1 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 7.6 (s).HRMS m/z (ESI) calculated for $C_{14}H_{19}N_2O_4P$ $(M+H)^+$ 311.1161, found 311.1157.

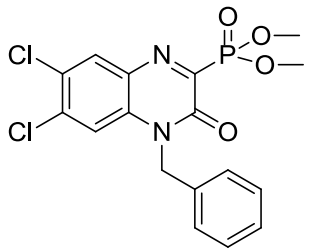
dimethyl (4-benzyl-6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3l)



Pale yellow solid: m.p. 125-127 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 7.75 (s, 1H), 7.41 (s, 1H), 7.34 (dd, J_1 = 10.3 Hz, J_1 = 4.4 Hz, 2H), 7.30 – 7.22 (m, 3H), 5.49 (s, 2H), 3.89 (d, J = 11.0 Hz, 6H), 2.31 (d, J = 11.6 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.1 (d, $J_{C\text{-}P}$ = 32.6 Hz), 150.7 (d, $J_{C\text{-}P}$ = 229.0 Hz), 144.3 (s), 136.1 (s), 133.8 (s), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.4 (d, $J_{C\text{-}P}$ = 26.0 Hz), 131.1 (s), 129.2 (s), 127.9 (s), 127.4 (s), 116.0 (s), 54.6 (d, $J_{C\text{-}P}$ = 6.4 Hz), 45.2 (s), 20.8 (s), 19.0 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 9.7 (s). HRMS m/z (ESI) calculated for $C_{19}H_{21}N_2O_4P$ $(M+H)^+$ 373.1317, found 373.1317.

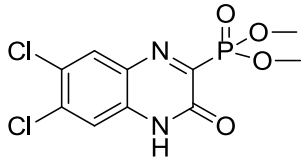
dimethyl (4-benzyl-6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3m)



Pale yellow solid: m.p. 223-228 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 8.31 (s, 1H), 7.86 (s, 1H), 7.36 (dd, J_1 = 10.1 Hz, J_2 = 4.4 Hz, 2H), 7.29 (dd, J_1 = 6.9 Hz, J_2 =3.5 Hz, 3H), 5.51 (s, 2H), 3.91 (d, J = 11.1 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 154.6 (d, J_{C-P} = 153.3 Hz), 153.3 (d, J_{C-P} = 40.9 Hz), 136.0 (s), 135.4 (s), 133.6 (d, J_{C-P} = 2.8 Hz), 132.3 (d, J = 26.0 Hz), 132.2 (d, J = 0.7 Hz), 129.3 (s), 128.1 (s), 127.3 (s), 126.8 (s), 117.5 (s), 54.9 (d, J_{C-P} = 6.3 Hz), 45.60 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 8.4 (s). HRMS m/z (ESI) calculated for $C_{17}H_{15}Cl_2N_2O_4P$ $(M+H)^+$ 413.0225, found 413.0219.

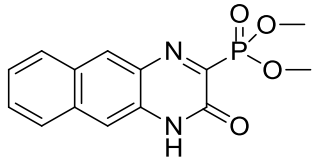
dimethyl (6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3n)



Pale yellow solid: m.p. 234-237 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.99 (s, 1H), 8.23 (s, 1H), 7.53 (s, 1H), 3.88 (d, J = 11.1 Hz, 1H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 155.6 (d, J_{C-P} = 223.4 Hz), 154.1 (d, J_{C-P} = 30.9 Hz), 135.4 (s), 133.1 (d, J_{C-P} = 2.9 Hz), 131.3 (d, J_{C-P} = 26.2 Hz), 131.3 (d, J_{C-P} = 1.0 Hz), 126.1 (d, J_{C-P} = 0.9 Hz), 117.5 (s), 54.7 (d, J_{C-P} = 6.3 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 8.9 (s). HRMS m/z (ESI) calculated for $C_{10}H_9Cl_2N_2O_4P$ $(M+H)^+$ 322.9755, found 322.9750.

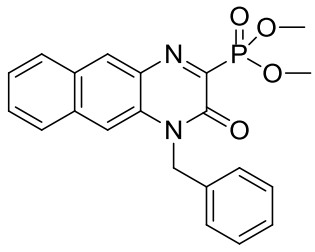
dimethyl (3-oxo-3,4-dihydrobenzo[g]quinoxalin-2-yl)phosphonate (3o)



Orange solid: m.p. 265-268 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.68 (s, 1H), 8.60 (s, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 3.91 (d, J = 11.0 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 155.4 (d, J_{C-P} = 193.0 Hz), 154.1 (s), 135.1 (s), 131.6 (d, J_{C-P} = 26.2 Hz), 130.5 (d, J_{C-P} = 1.9 Hz), 130.5 (s), 129.9 (s), 129.6 (s), 129.4 (s), 127.3 (s), 125.6 (s), 111.5 (s), 54.7 (d, J_{C-P} = 6.3 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 9.1 (s). HRMS m/z (ESI) calculated for $C_{14}H_{13}N_2O_4P$ $(M+H)^+$ 305.0691, found 305.0687.

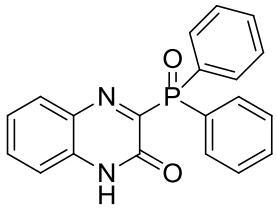
dimethyl (4-benzyl-3-oxo-3,4-dihydrobenzo[g]quinoxalin-2-yl)phosphonate (3p)



Orange solid: m.p. 95-97 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 8.69 (s, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 10.0 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.58 – 7.51 (m, 1H), 7.36 (qd, J_1 = 8.2 Hz, J_2 = 4.0 Hz, 4H), 7.29 – 7.24 (m, 1H), 5.57 (s, 2H), 3.95 (d, J = 11.1 Hz, 6H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 153.8 (d, J_{C-P} = 32.2 Hz), 153.6 (d, J_{C-P} = 225.6 Hz), 136.0 (s), 135.1 (s), 132.2 (d, J_{C-P} = 26.7 Hz), 131.7 (s), 130.9 (d, J_{C-P} = 2.7 Hz), 129.7 (s), 129.6 (s), 129.3 (s), 129.2 (s), 127.9 (s), 127.8 (s), 127.5 (s), 126.2 (s), 112.0 (s), 54.8 (d, J_{C-P} = 6.3 Hz), 45.4 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 8.9 (s). HRMS m/z (ESI) calculated for $C_{21}H_{19}N_2O_4P$ $(M+H)^+$ 395.1161, found 395.1157.

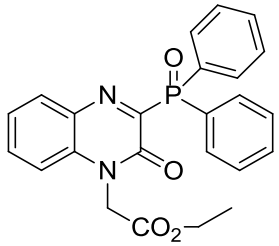
3-(diphenylphosphoryl)quinoxalin-2(1H)-one (3q)



Pale yellow solid: m.p. 279-284 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 12.72 (s, 1H), 7.85 – 7.76 (m, 4H), 7.71 (d, J = 8.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.59 (td, J_1 = 7.3 Hz, J_2 = 1.4 Hz, 2H), 7.52 (ddd, J_1 = 7.1 Hz, J_2 = 5.3 Hz, J_3 = 2.3 Hz, 4H), 7.38 – 7.29 (m, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 157.6 (d, $J_{C\text{-}P}$ = 126.4 Hz), 154.6 (d, $J_{C\text{-}P}$ = 24.9 Hz), 133.4 (s), 132.9 (s), 132.5 (d, $J_{C\text{-}P}$ = 20.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.8 (s), 131.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 130.4 (s), 128.8 (d, $J_{C\text{-}P}$ = 12.2 Hz), 124.2 (s), 116.3 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 21.9 (s). HRMS m/z (ESI) calculated for $C_{20}H_{15}N_2O_2P$ $(M+H)^+$ 347.0949, found 347.0945.

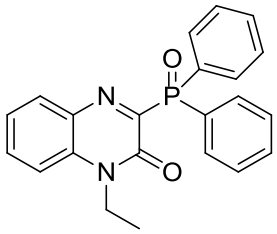
ethyl 2-(3-(diphenylphosphoryl)-2-oxoquinoxalin-1(2H)-yl)acetate (3r)



Pale green solid: m.p. 119-122 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 7.80 (ddd, J_1 = 21.1 Hz, J_2 = 10.1 Hz, J_3 = 4.3 Hz, 6H), 7.66 – 7.58 (m, 3H), 7.53 (ddd, J_1 = 7.2 Hz, J_2 = 5.3 Hz, J_3 = 2.3 Hz, 4H), 7.45 (t, J = 7.6 Hz, 1H), 5.08 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 167.6 (s), 155.9 (d, $J_{C\text{-}P}$ = 126.3 Hz), 153.7 (d, $J_{C\text{-}P}$ = 25.1 Hz), 134.0 (s), 133.8 (d, $J_{C\text{-}P}$ = 2.1 Hz), 132.9 (d, $J_{C\text{-}P}$ = 20.3 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.1 Hz), 132.0 (d, $J_{C\text{-}P}$ = 106.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 131.6 (s), 128.9 (d, $J_{C\text{-}P}$ = 12.2 Hz), 124.8 (s), 115.5 (s), 61.9 (s), 44.0 (s), 14.4 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 22.0 (s).HRMS m/z (ESI) calculated for $C_{24}H_{21}N_2O_4P$ $(M+H)^+$ 433.1317, found 433.1311.

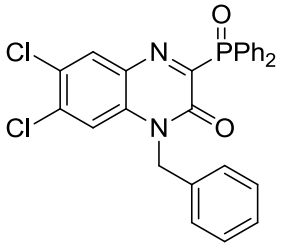
3-(diphenylphosphoryl)-1-ethylquinoxalin-2(1H)-one (3s)



Cream solid: m.p. 192-193 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 7.80 (dt, J_1 = 18.7 Hz, J_2 = 7.5 Hz, 6H), 7.72 (d, J = 8.2 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.52 (ddd, J_1 = 7.1 Hz, J_2 = 5.3 Hz, J_3 = 2.3 Hz, 4H), 7.42 (t, J = 7.4 Hz, 1H), 4.21 (q, J = 7.0 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 156.0 (d, $J_{C\text{-}P}$ = 127.2 Hz), 153.6 (d, $J_{C\text{-}P}$ = 24.9 Hz), 133.4 (d, $J_{C\text{-}P}$ = 2.0 Hz), 133.3 (d, $J_{C\text{-}P}$ = 101.8 Hz), 133.2 (d, $J_{C\text{-}P}$ = 20.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.8 (s), 131.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 131.6 (s), 128.8 (d, $J_{C\text{-}P}$ = 12.2 Hz), 124.3 (s), 115.4 (s), 37.3 (s), 12.8 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 22.3 (s). HRMS m/z (ESI) calculated for $C_{22}H_{19}N_2O_2P$ $(M+H)^+$ 375.1262, found 375.1258.

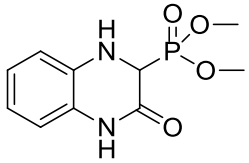
1-benzyl-6,7-dichloro-3-(diphenylphosphoryl)quinoxalin-2(1H)-one (3t)



Cream solid: m.p. 243-244 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 8.04 (s, 1H), 7.89 (s, 1H), 7.87 (s, 1H), 7.85 (d, J = 1.4 Hz, 1H), 7.84 (s, 1H), 7.82 (d, J = 1.3 Hz, 1H), 7.61 (td, J_1 = 7.3 Hz, J_2 = 1.3 Hz, 2H), 7.54 (ddd, J_1 = 7.1 Hz, J_2 = 5.3 Hz, J_3 = 2.3 Hz, 4H), 7.35 – 7.25 (m, 3H), 7.22 (d, J = 7.0 Hz, 2H), 5.45 (s, 2H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 158.3 (d, J_{C-P} = 124.4 Hz), 153.7 (d, J_{C-P} = 24.3 Hz), 136.0 (s), 135.4 (s), 133.7 (d, J_{C-P} = 2.0 Hz), 132.7 (d, J_{C-P} = 20.9 Hz), 132.4 (d, J_{C-P} = 2.5 Hz), 132.4 (s), 131.8 (d, J_{C-P} = 9.7 Hz), 131.7 (d, J_{C-P} = 75.5 Hz), 129.2 (s), 128.9 (d, J_{C-P} = 12.3 Hz), 128.0 (s), 127.3 (s), 126.7 (s), 117.4 (s), 45.3 (s). ^{31}P NMR (162 MHz, d_6-DMSO) δ 22.3 (s). HRMS m/z (ESI) calculated for $C_{24}H_{21}N_2O_3P$ $(M+H)^+$ 505.0639, found 505.0634.

(S)-dimethyl (3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)phosphonate (4a)



White solid: m.p. 184-187 ℃

^{1}H NMR (400 MHz, d_6-DMSO) δ 10.47 (s, 1H), 6.80 – 6.74 (m, 2H), 6.71 (d, J = 7.3 Hz, 1H), 6.62 – 6.56 (m, 1H), 6.30 (d, J = 1.7 Hz, 1H), 4.49 (dd, J_1 = 14.6 Hz, J_2 =2.1 Hz, 1H), 3.66 (d, J = 10.7 Hz, 3H), 3.53 (d, J = 10.7 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 162.3 (s), 133.1 (s), 125.9 (s), 123.5 (s), 118.4 (s), 115.2 (s), 113.9 (s), 55.2 (d, J_{C-P} = 132.6 Hz), 53.50 (dd, J_{1C-P} = 18.2 Hz, J_{2C-P} =6.8 Hz). ^{31}P NMR (162 MHz, d_6-DMSO) δ 21.7 (s). HRMS m/z (EI) calculated for $C_{10}H_{13}N_2O_4P$ $(M)^+$ 256.0613, found 256.0619.

Ⅲ. References

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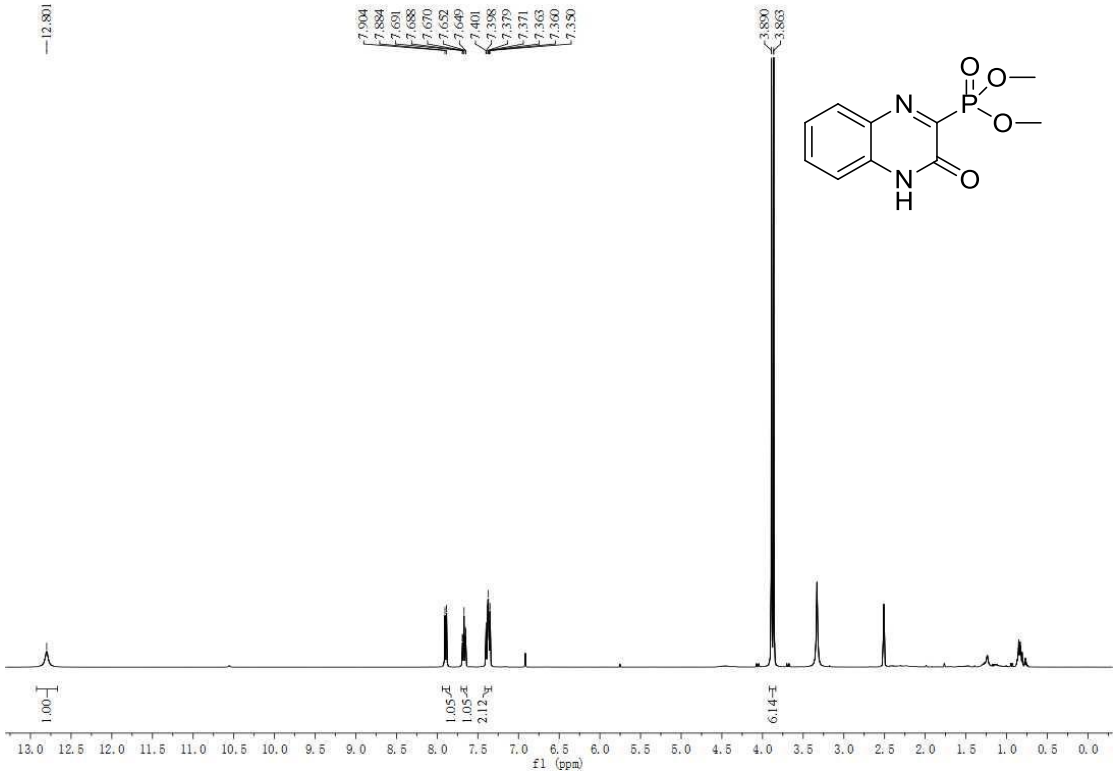
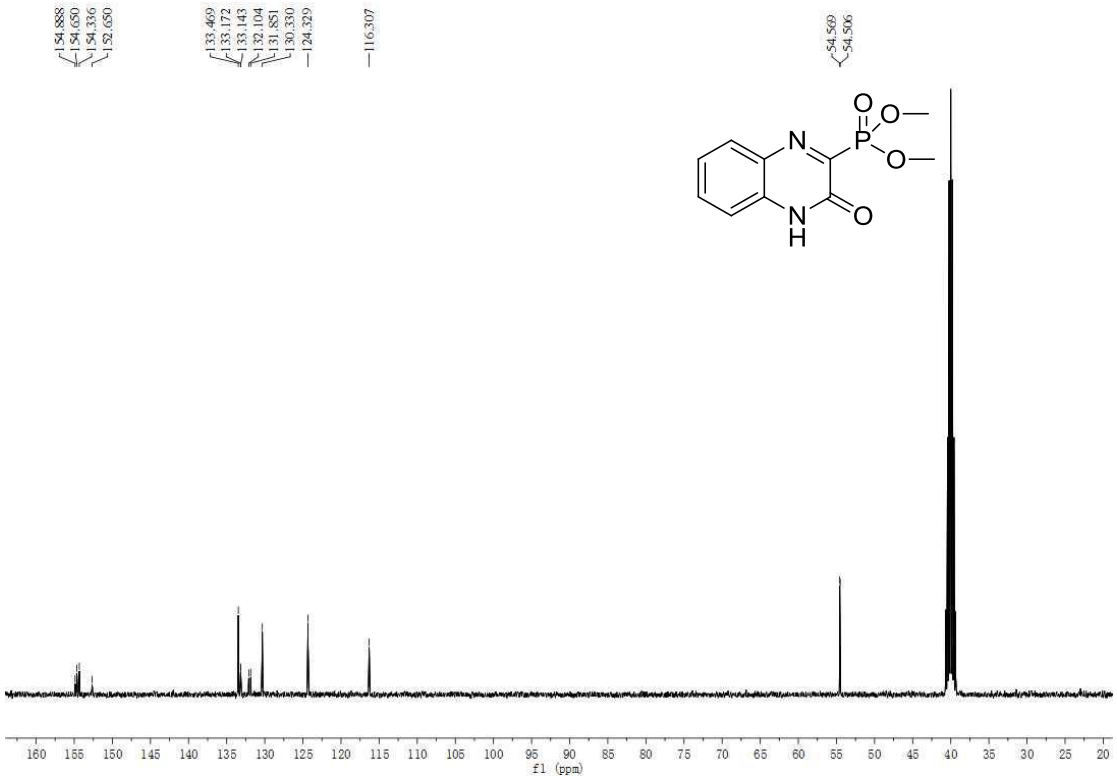
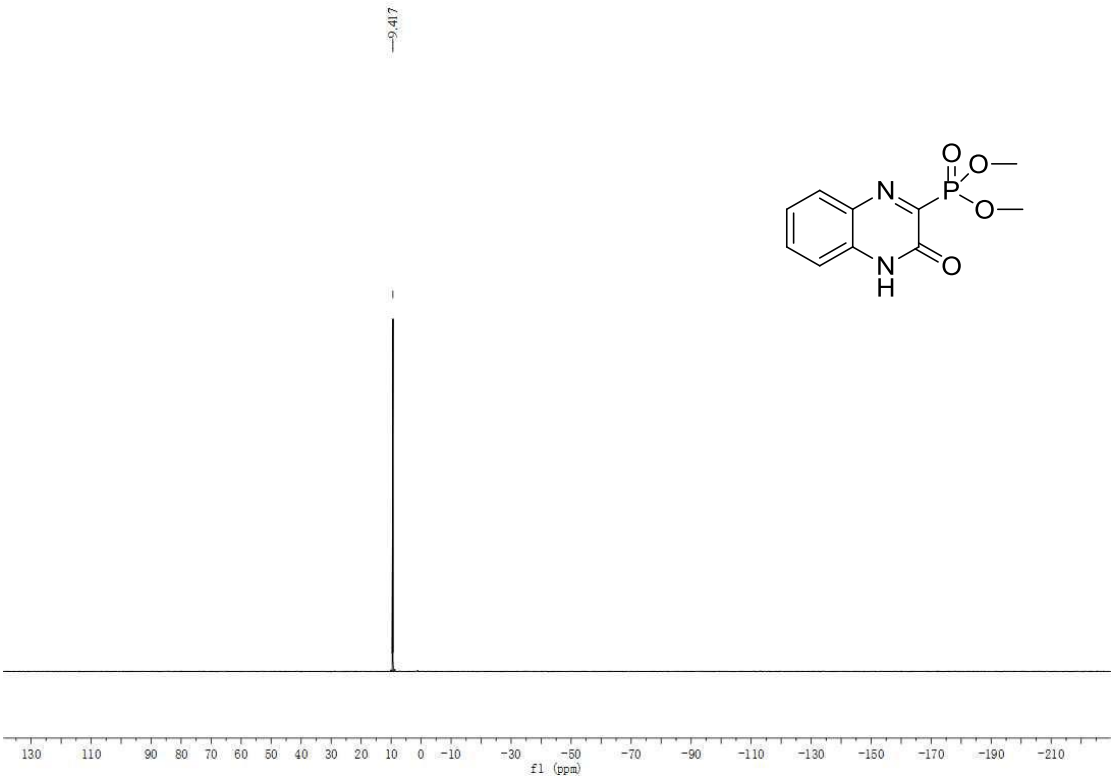
Ⅳ. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of products

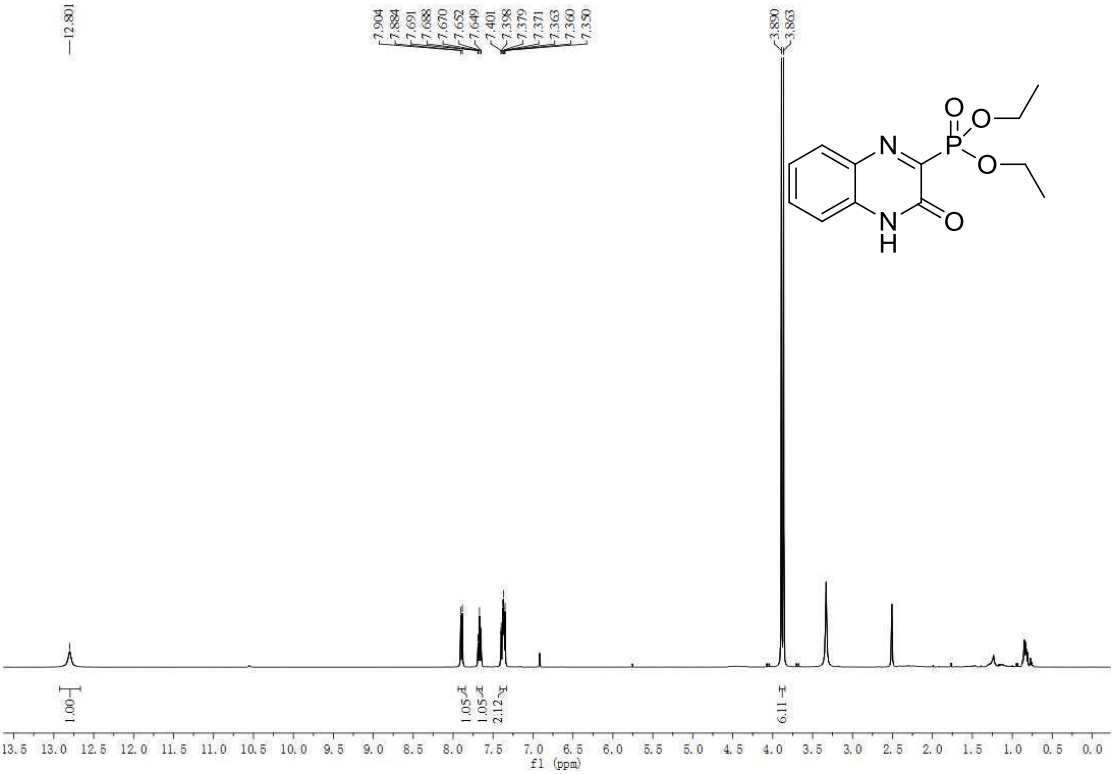
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3a

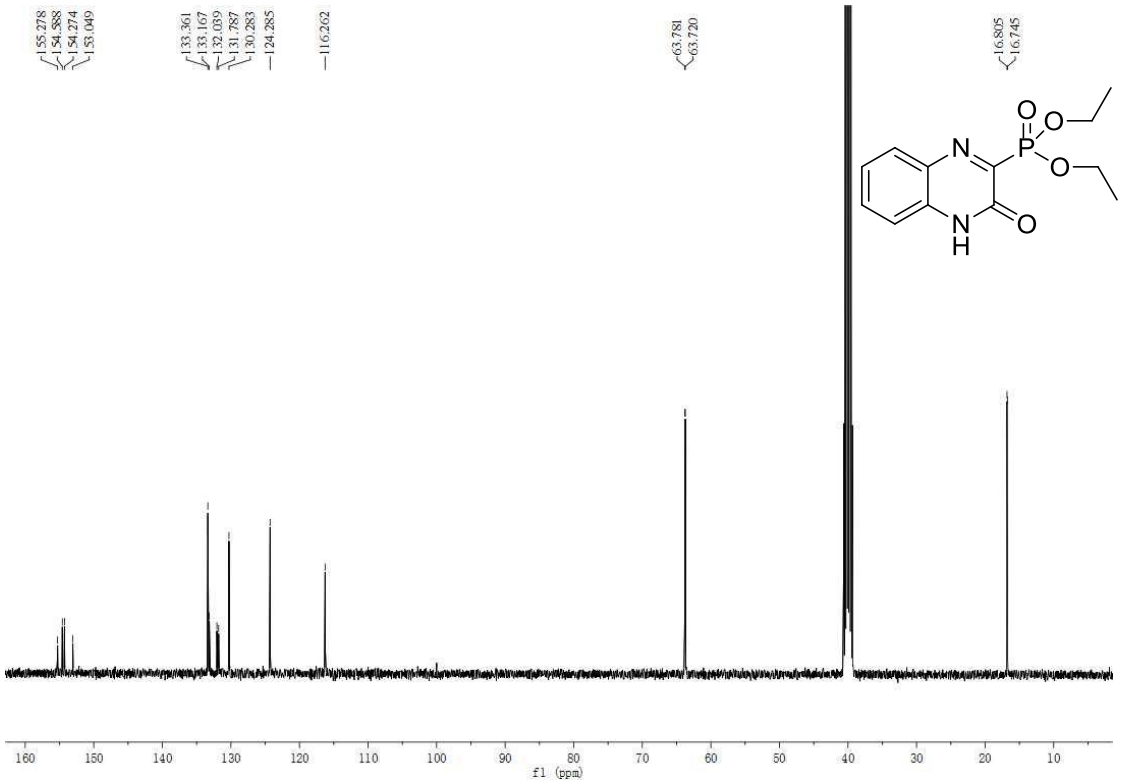






^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3b

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16.805
16.745
O
O
P
O
N
N
H
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60
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20
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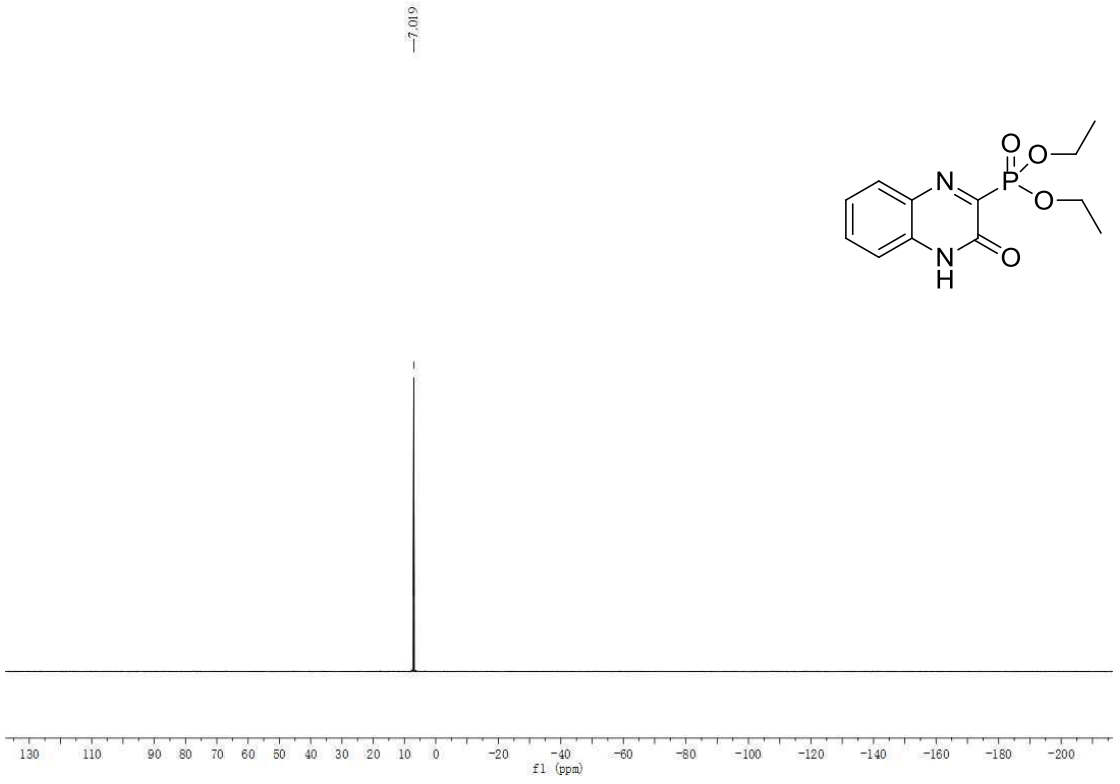
f1 (ppm)


7.019
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H
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0
-20
-40
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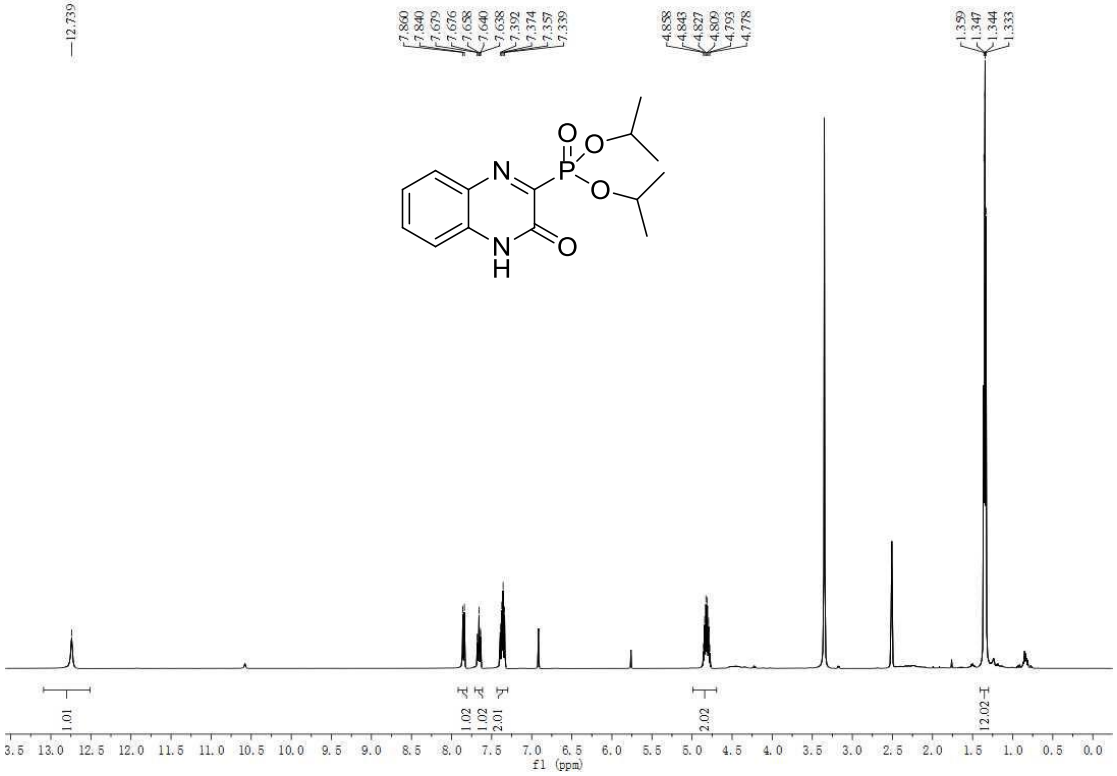
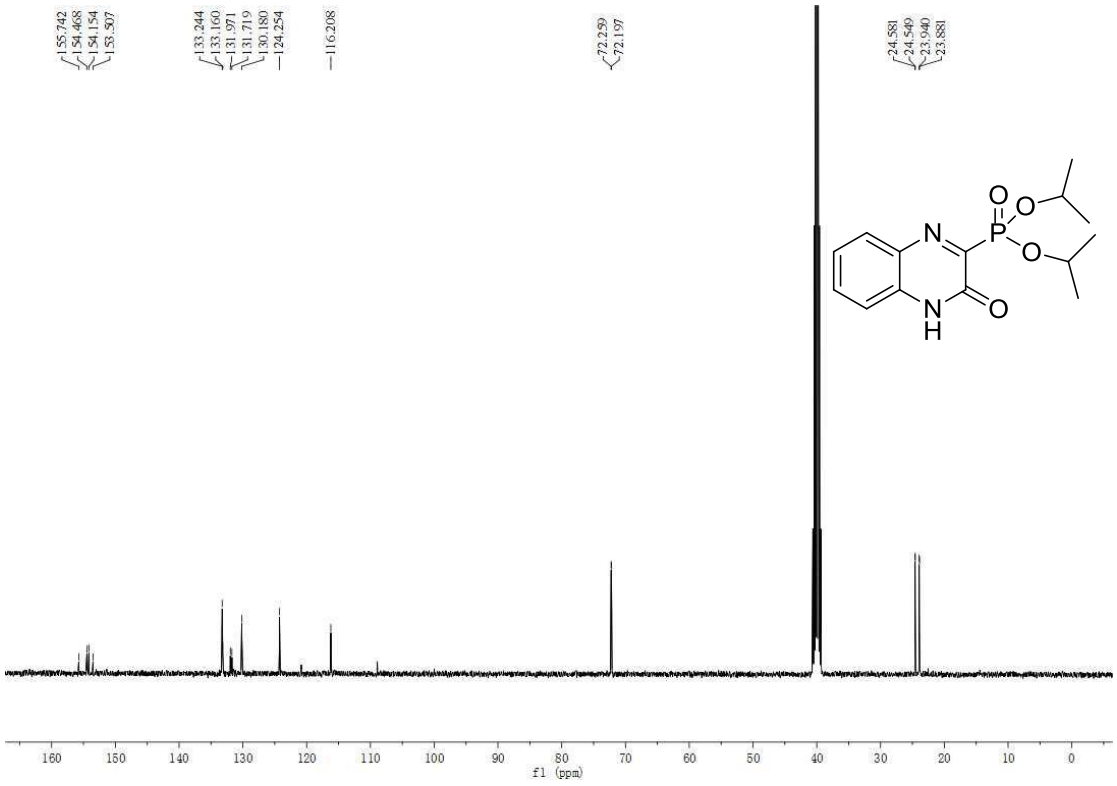
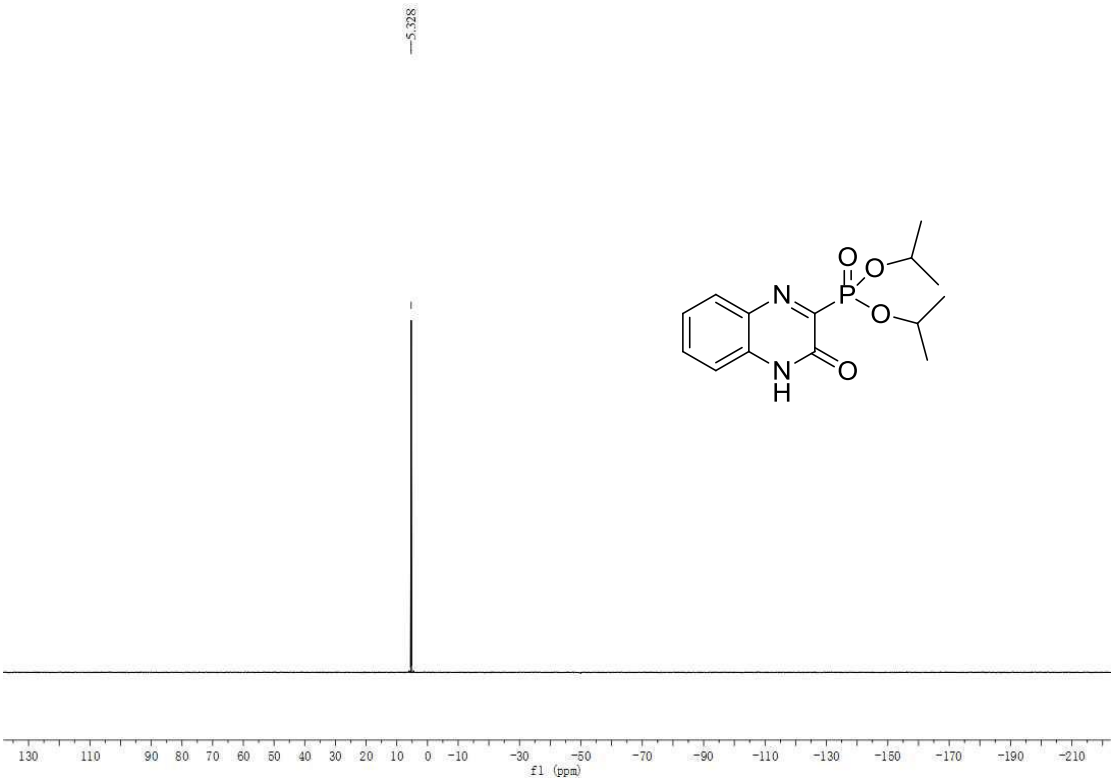
f1 (ppm)

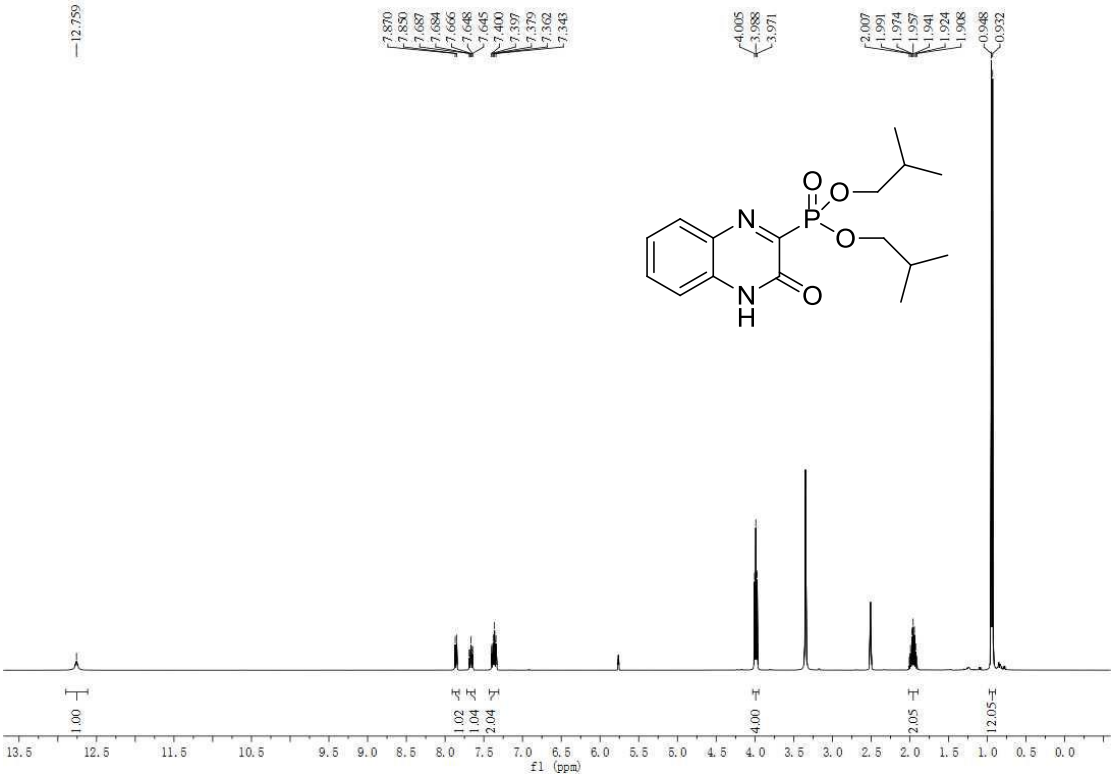
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3c

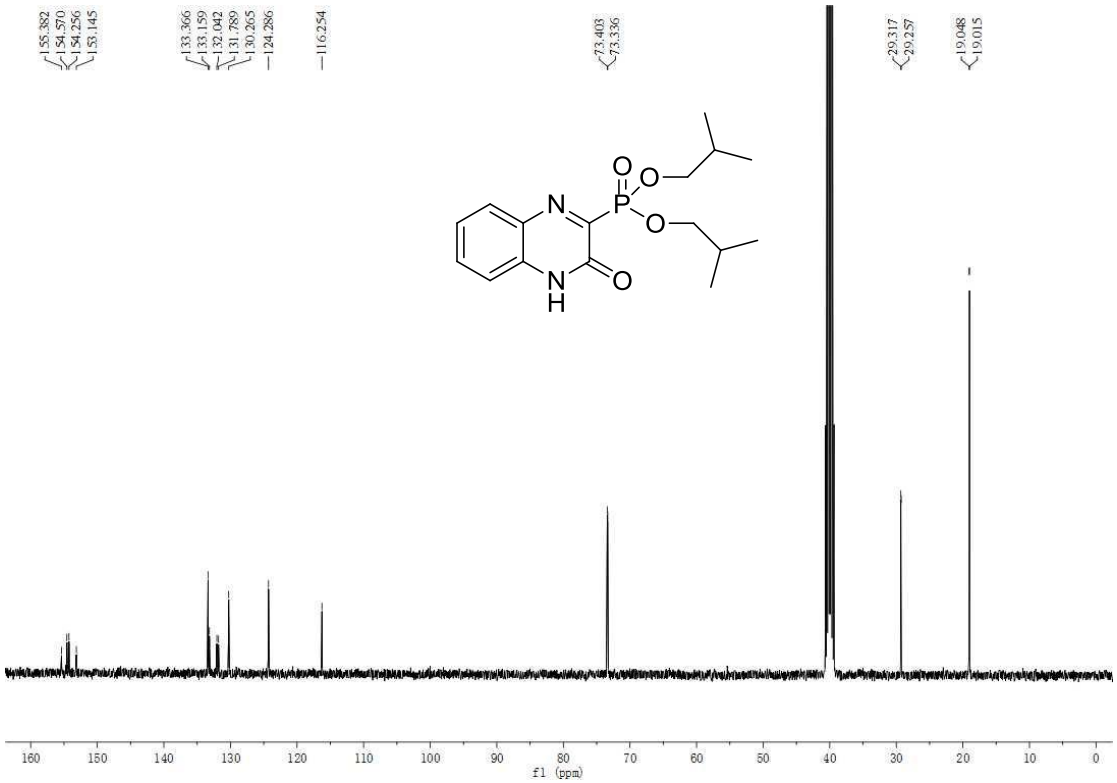






^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3d

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19.015
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N
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H
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90
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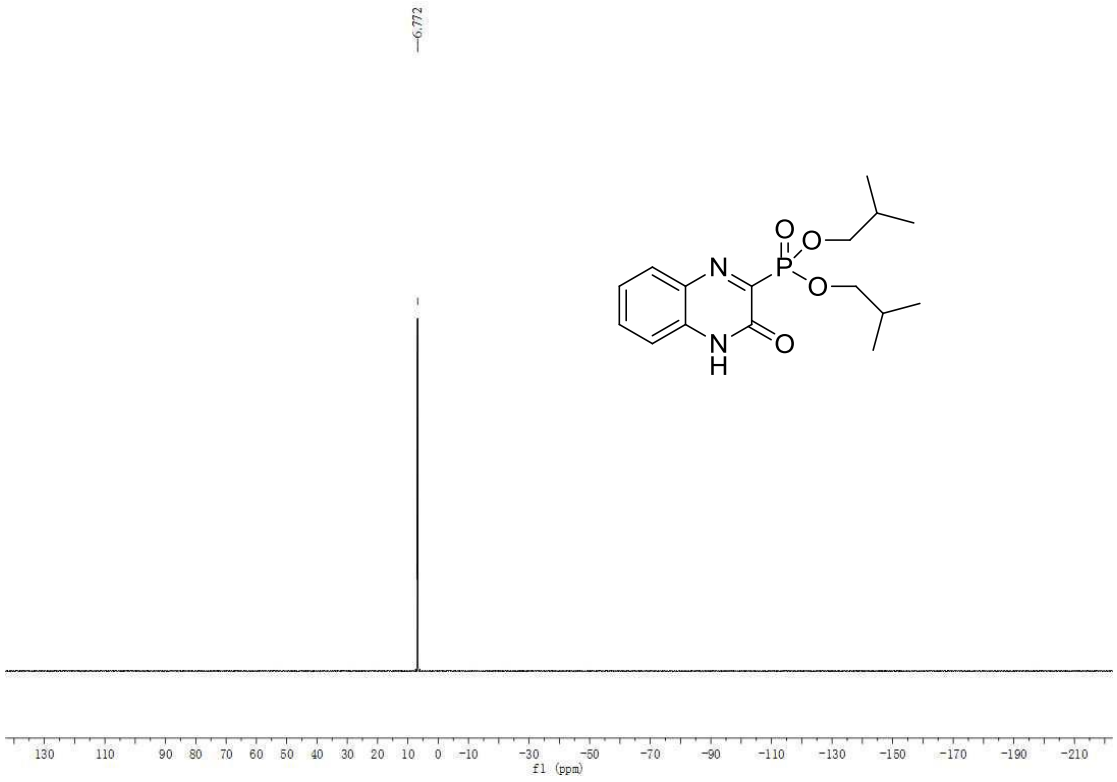
f1 (ppm)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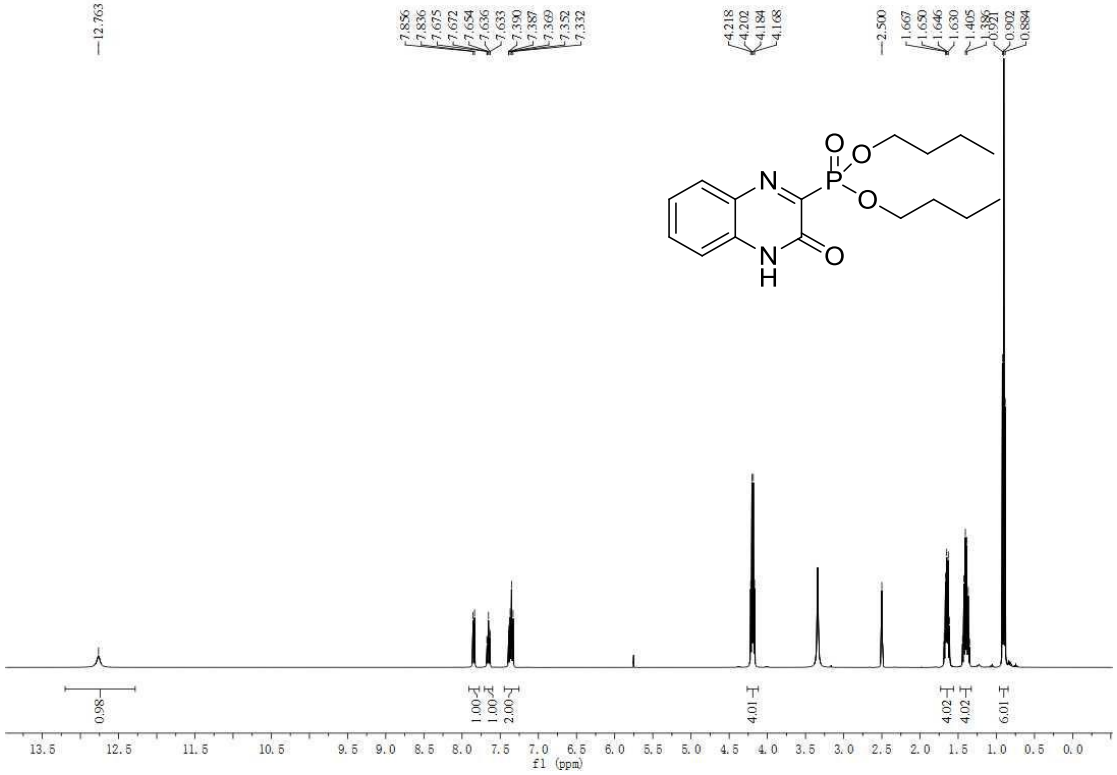
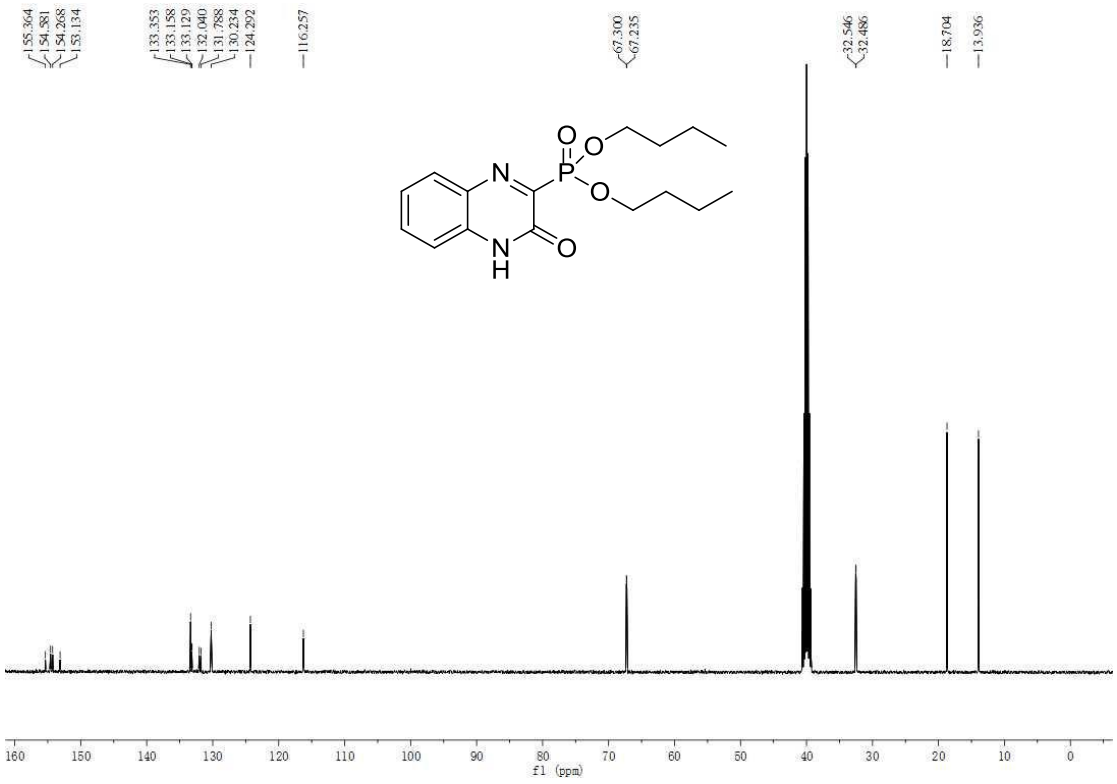
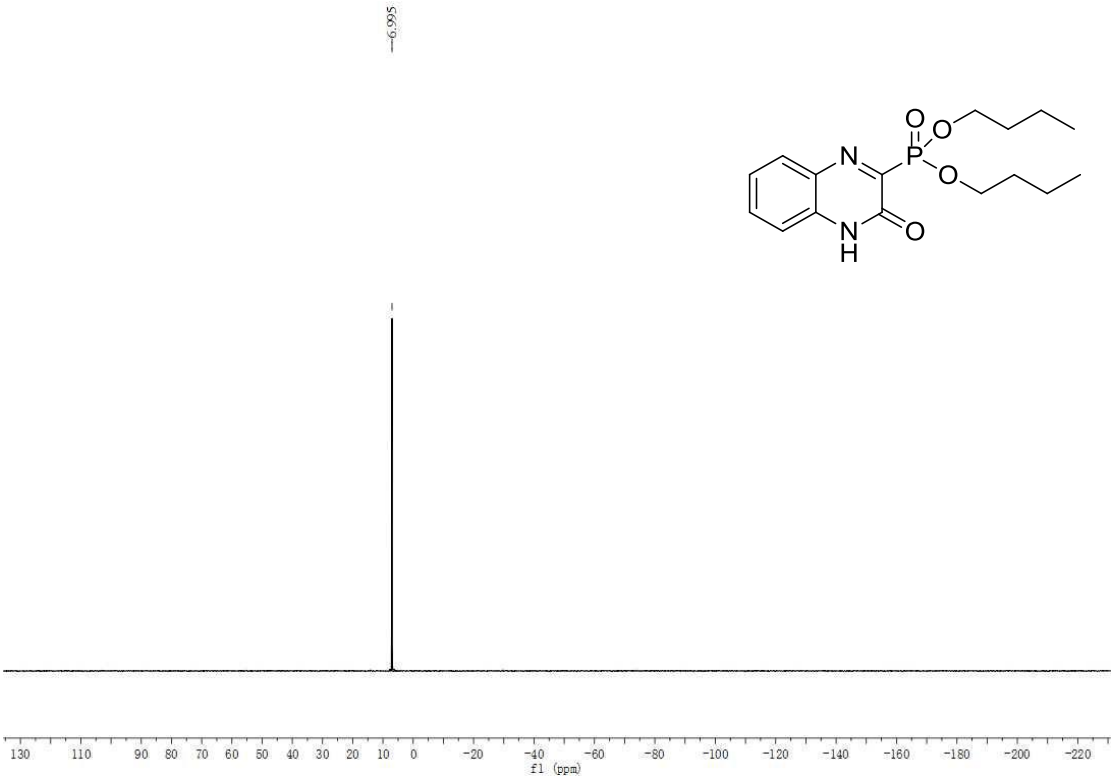
-210
f1 (ppm)

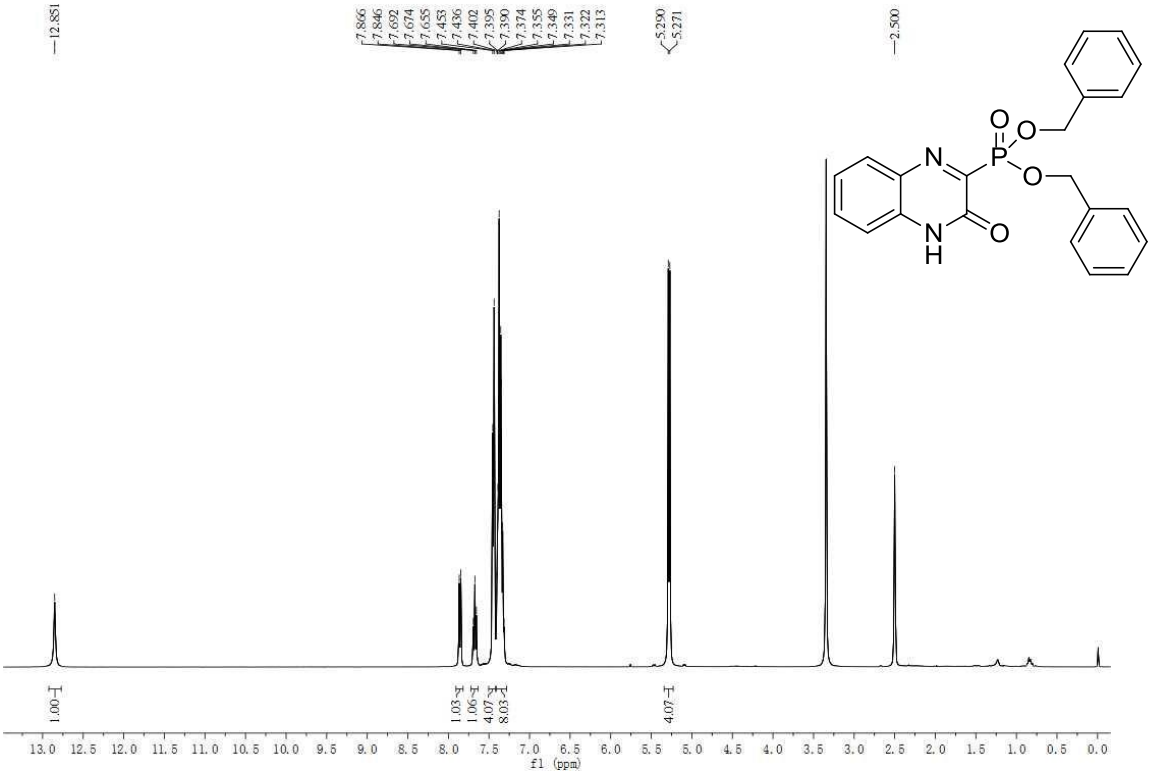
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3e

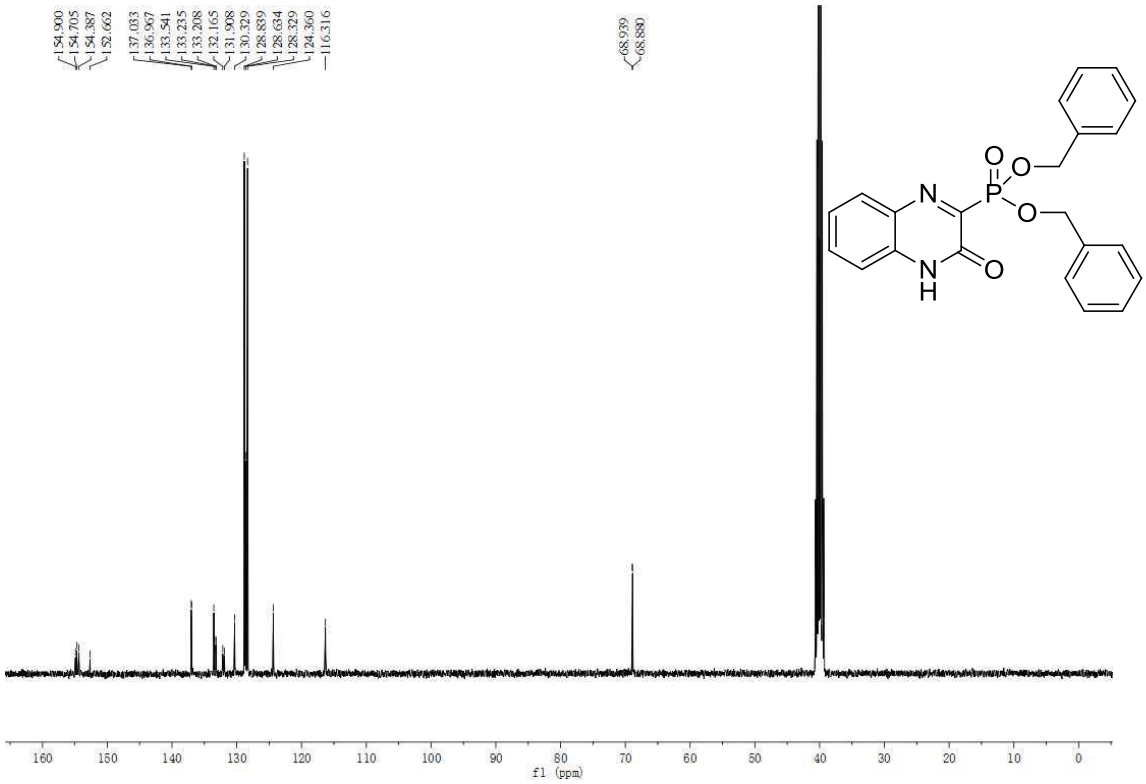


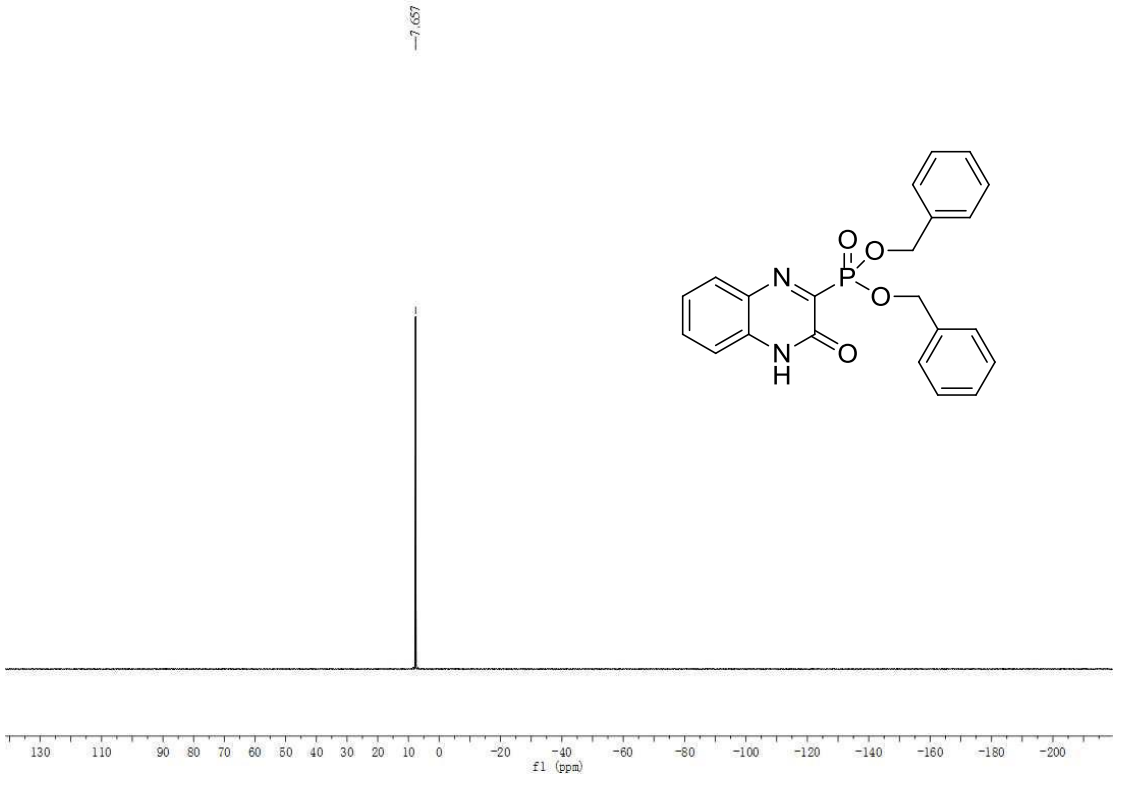




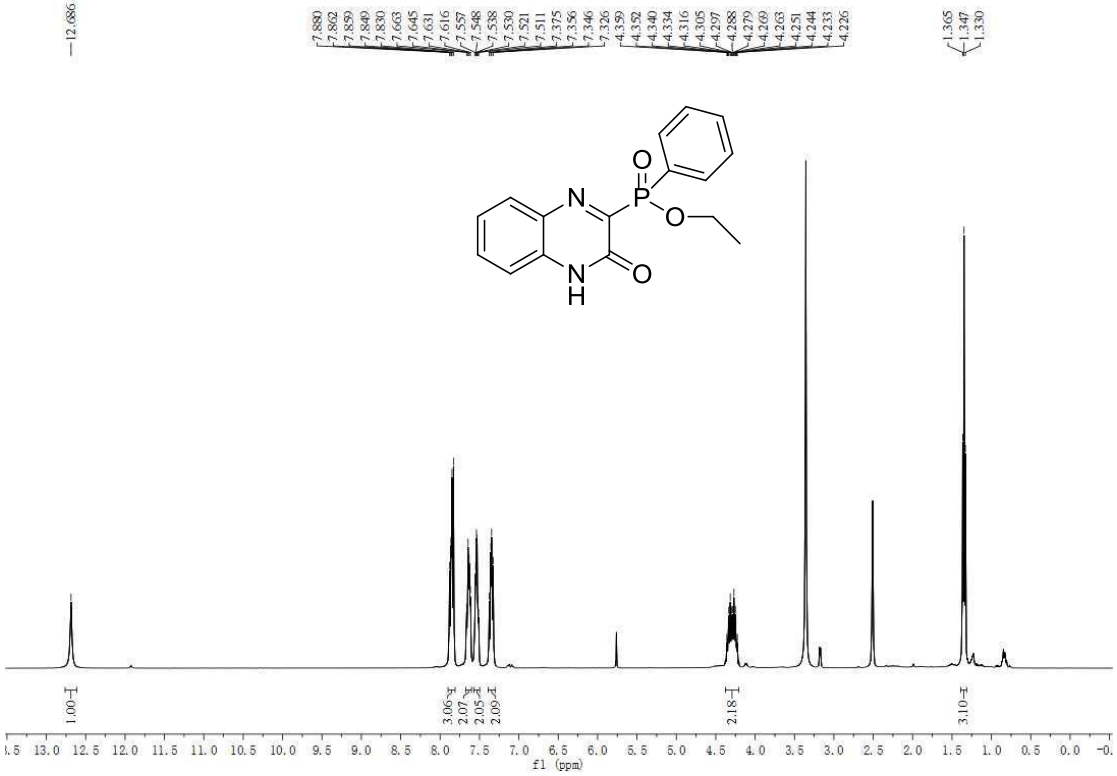
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3f

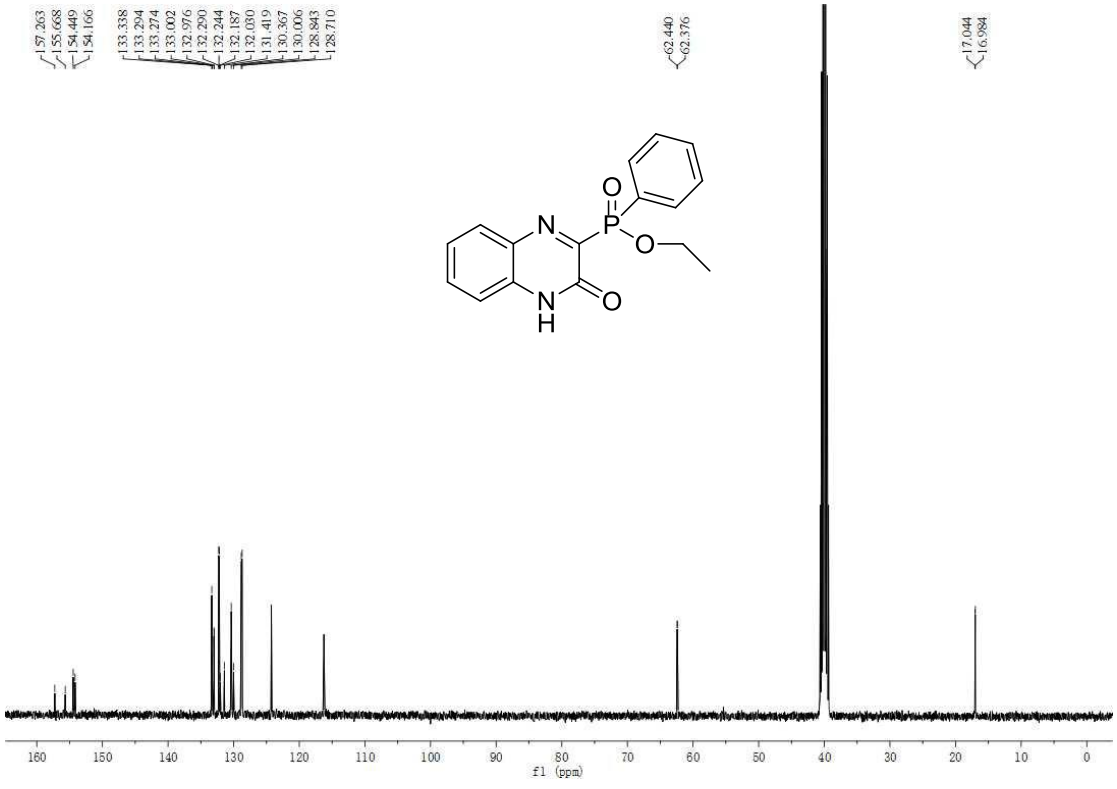


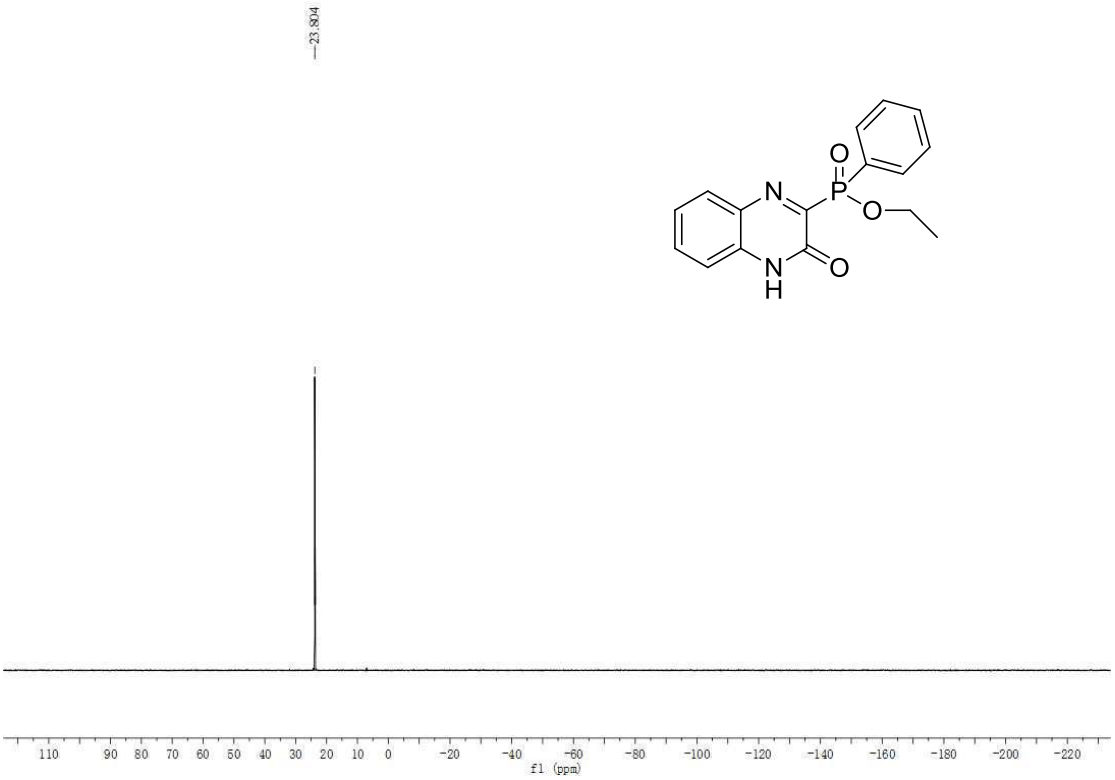

154.900
154.705
154.387
152.662
137.033
136.967
133.541
133.235
133.208
132.165
131.908
130.329
128.839
128.634
128.329
124.360
116.316
68.939
68.880
O
O
P
O
N
N
H
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.657
O
O
P
O
N
N
H
O
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

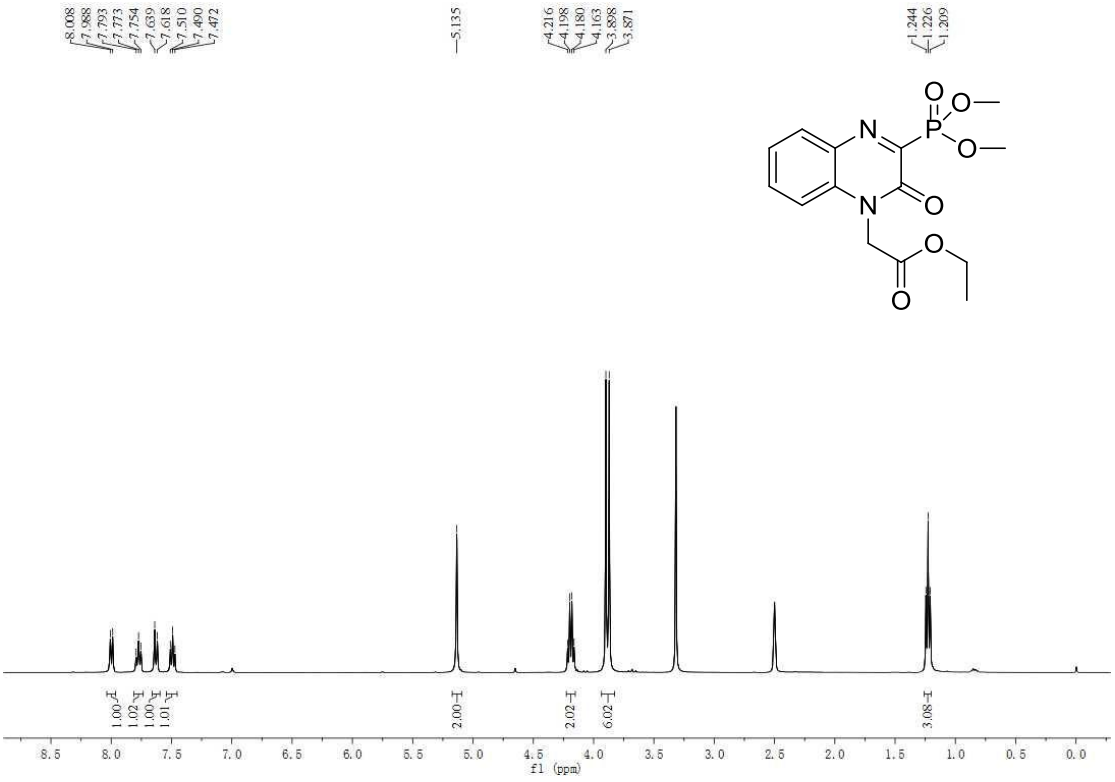
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3g

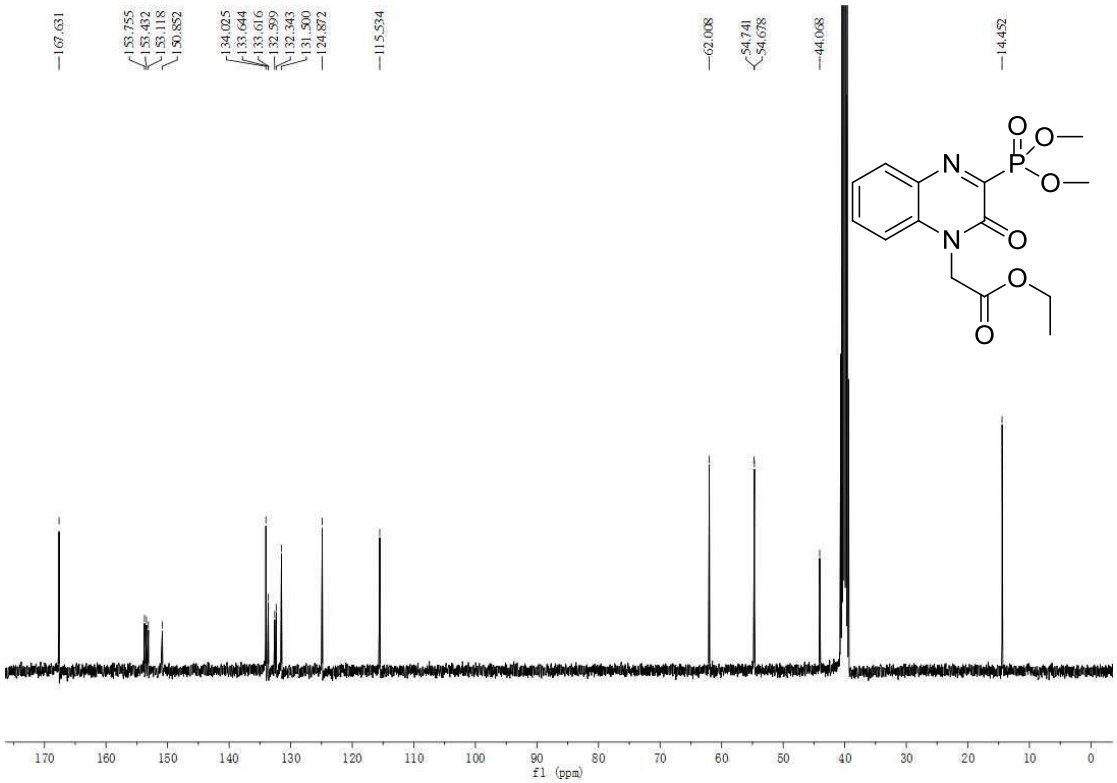


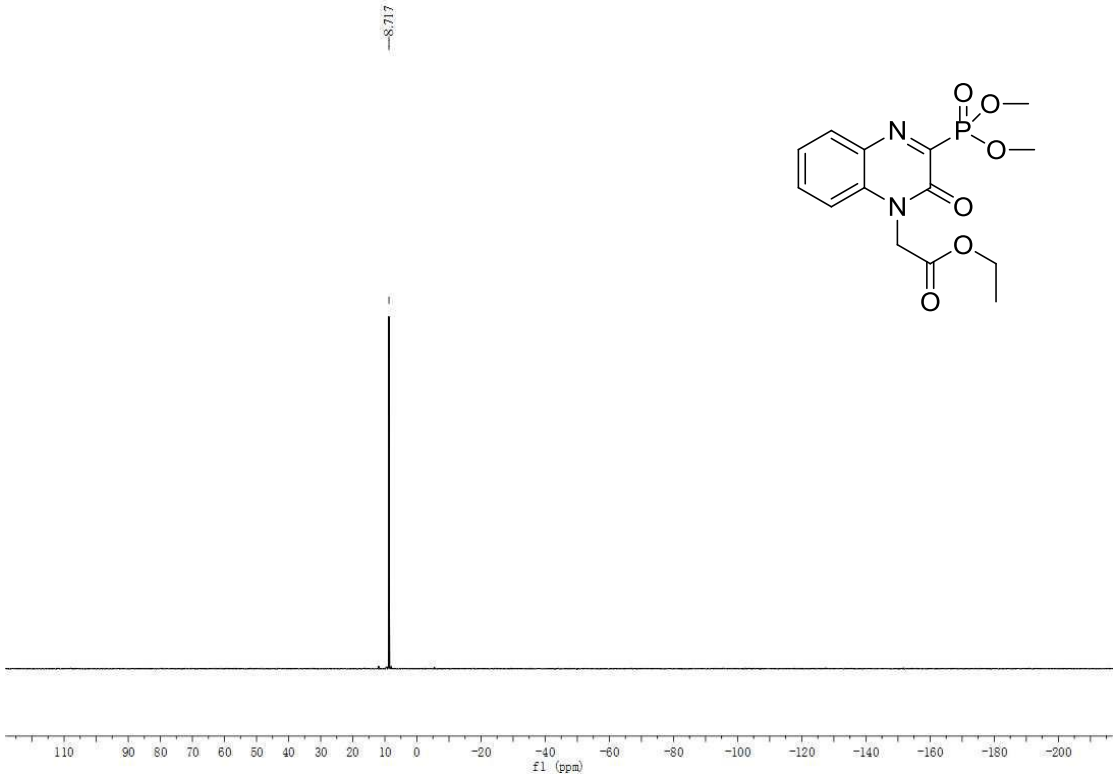




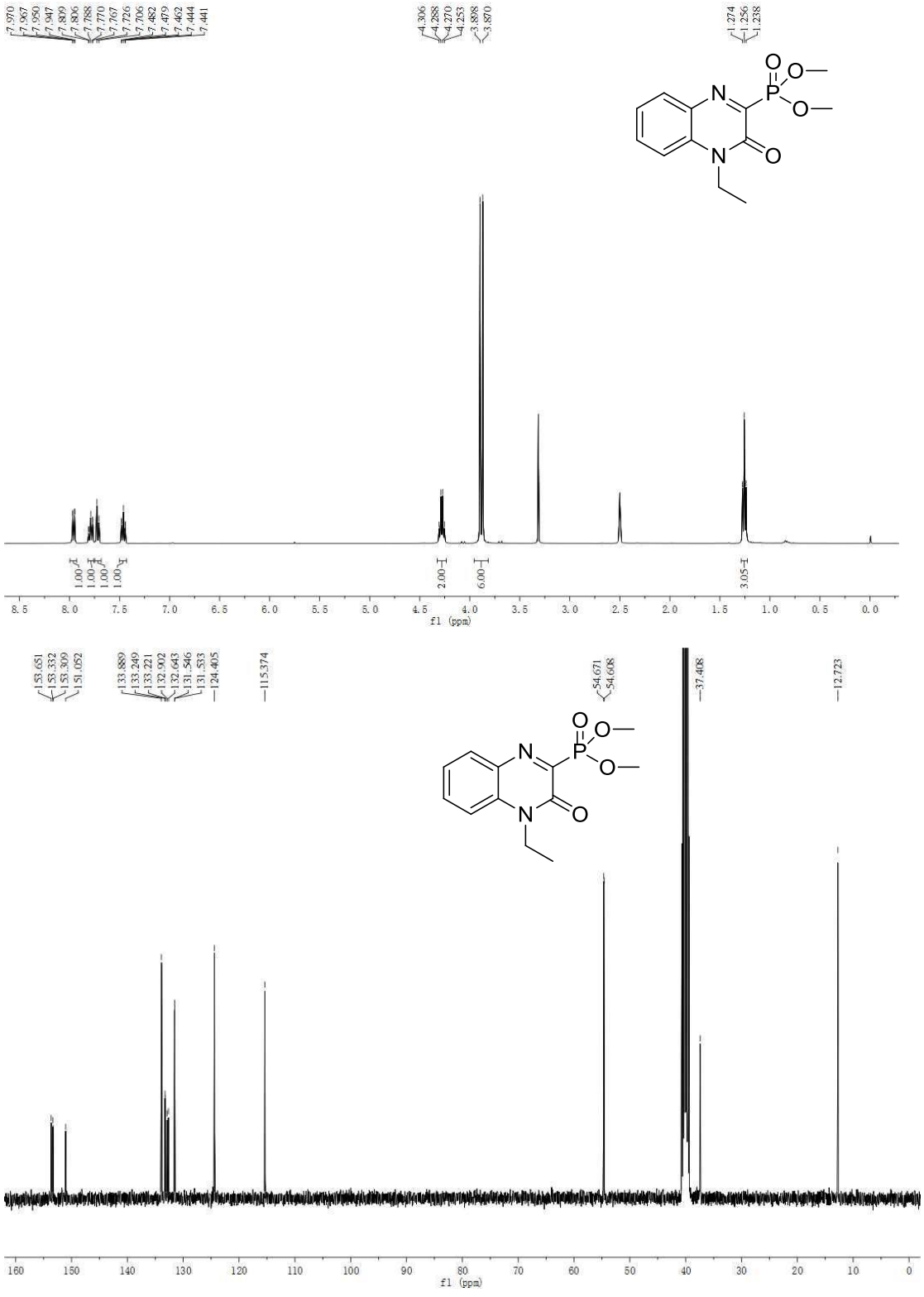
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3h

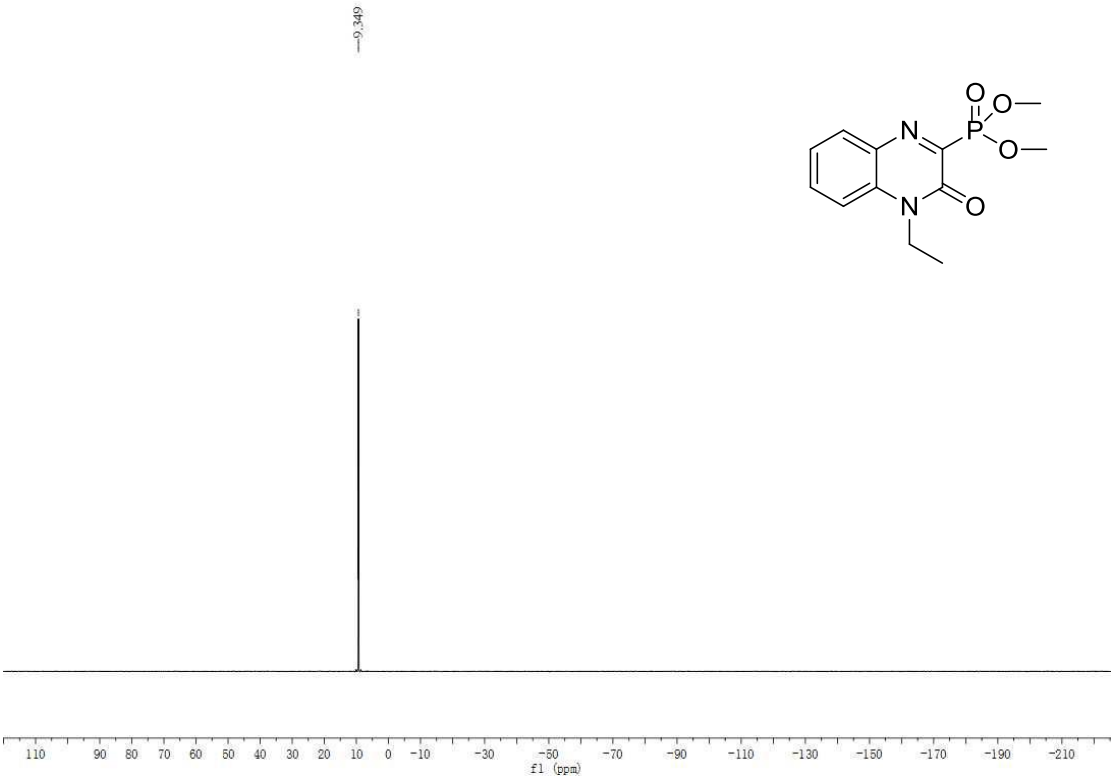



167.631
153.755
153.432
153.118
150.852
134.025
133.644
133.616
132.599
132.343
131.500
124.872
115.534
62.008
54.741
54.678
44.068
14.452
f1 (ppm)

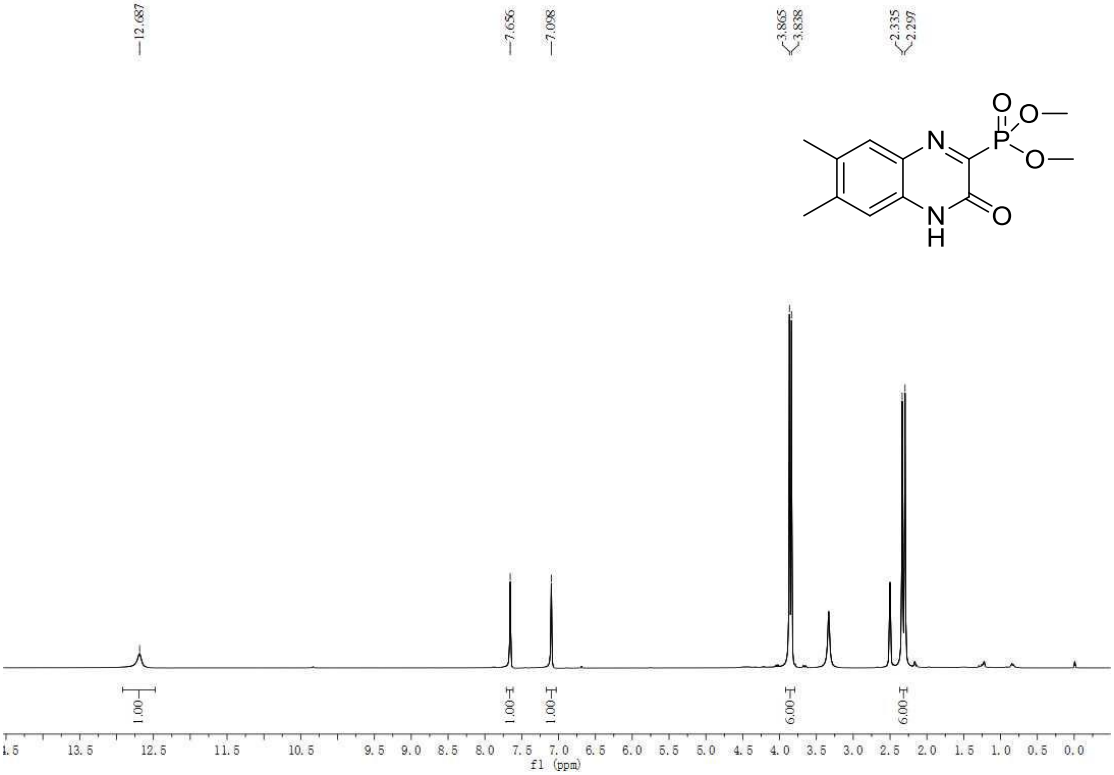

8.717
f1 (ppm)

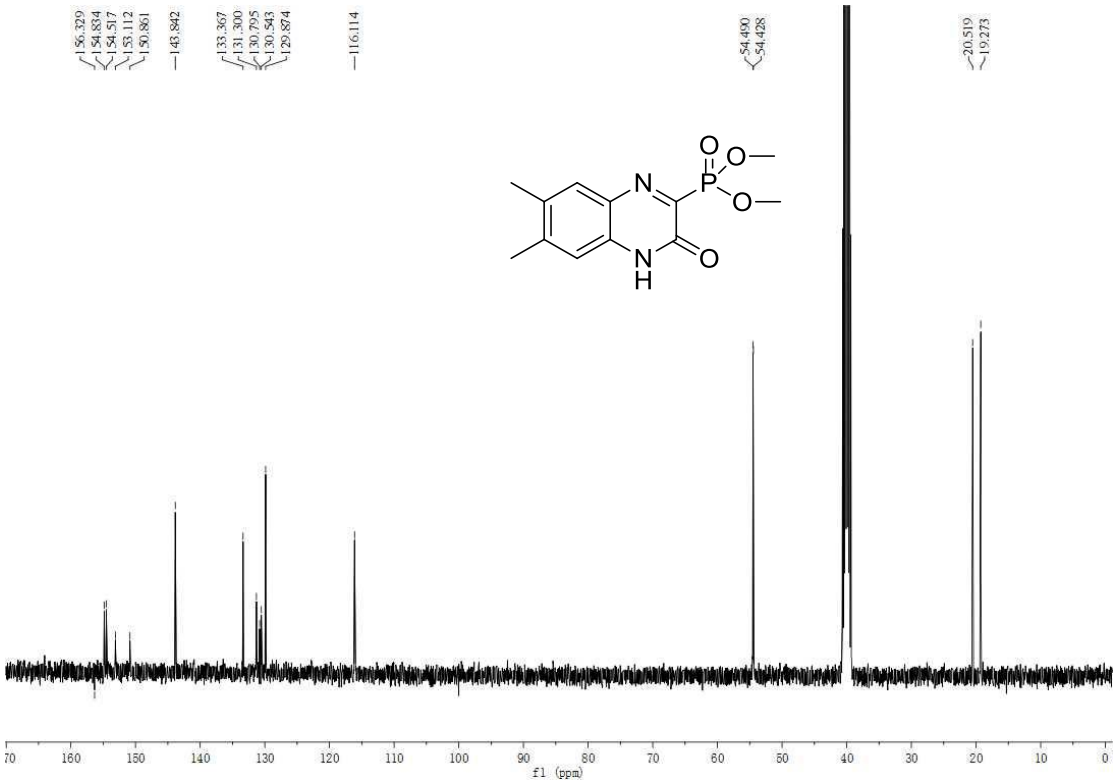
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3i





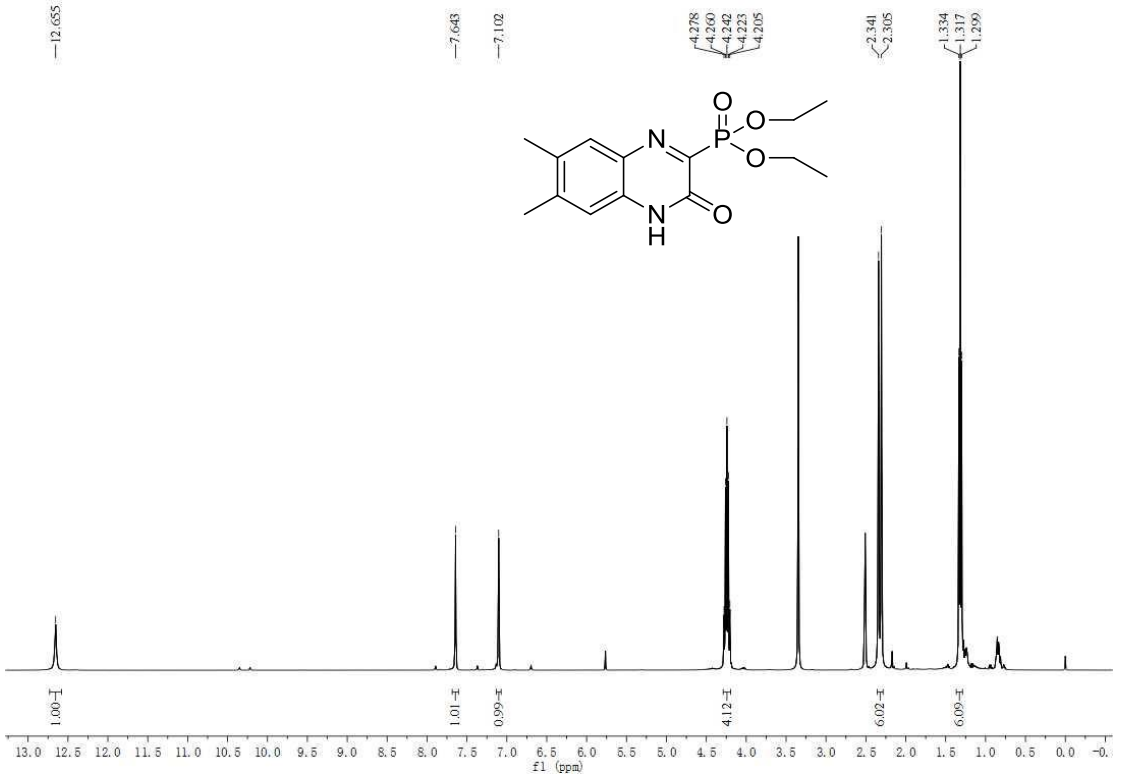
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3j

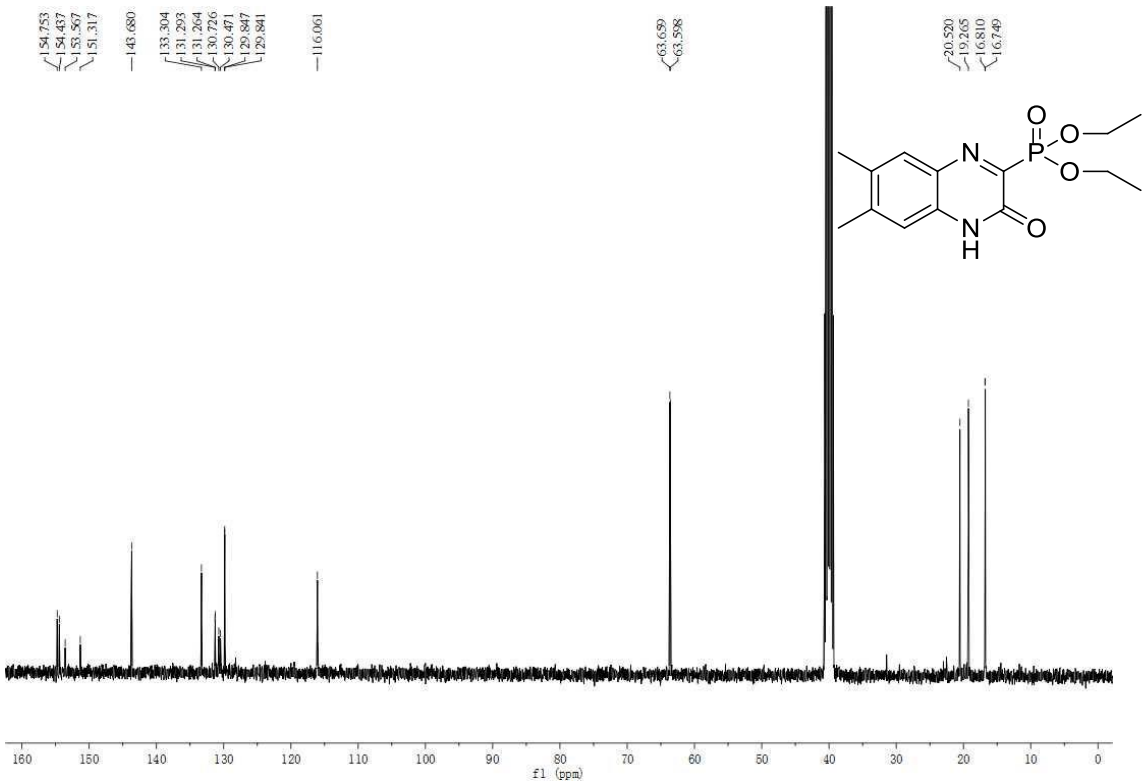


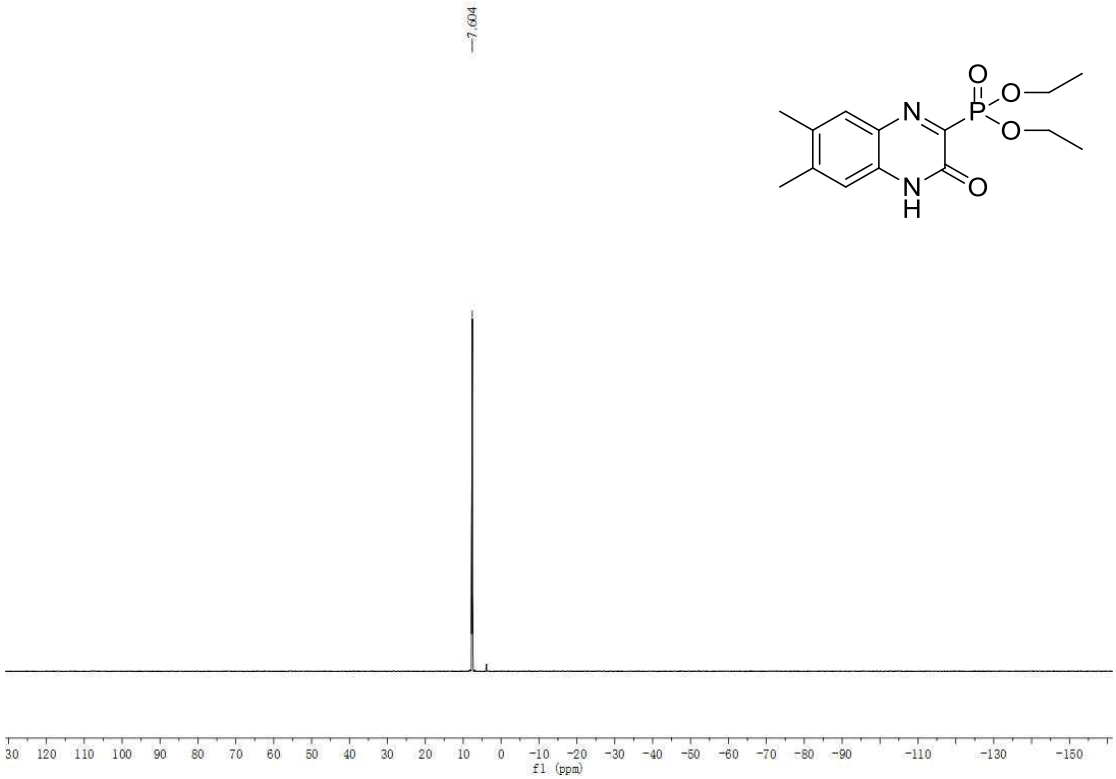

156.329
154.834
154.517
153.112
150.861
143.842
133.367
131.300
130.795
130.543
129.874
116.114
54.490
54.428
20.519
19.273
f1 (ppm)


10.031
f1 (ppm)

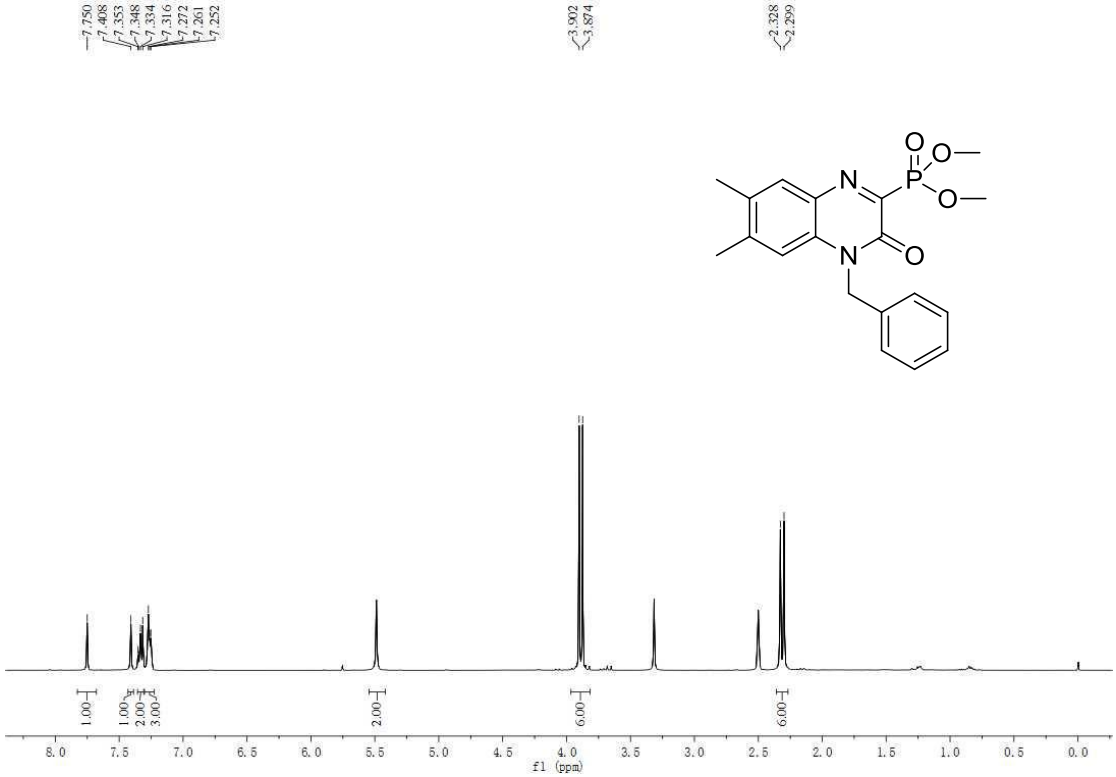
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3k

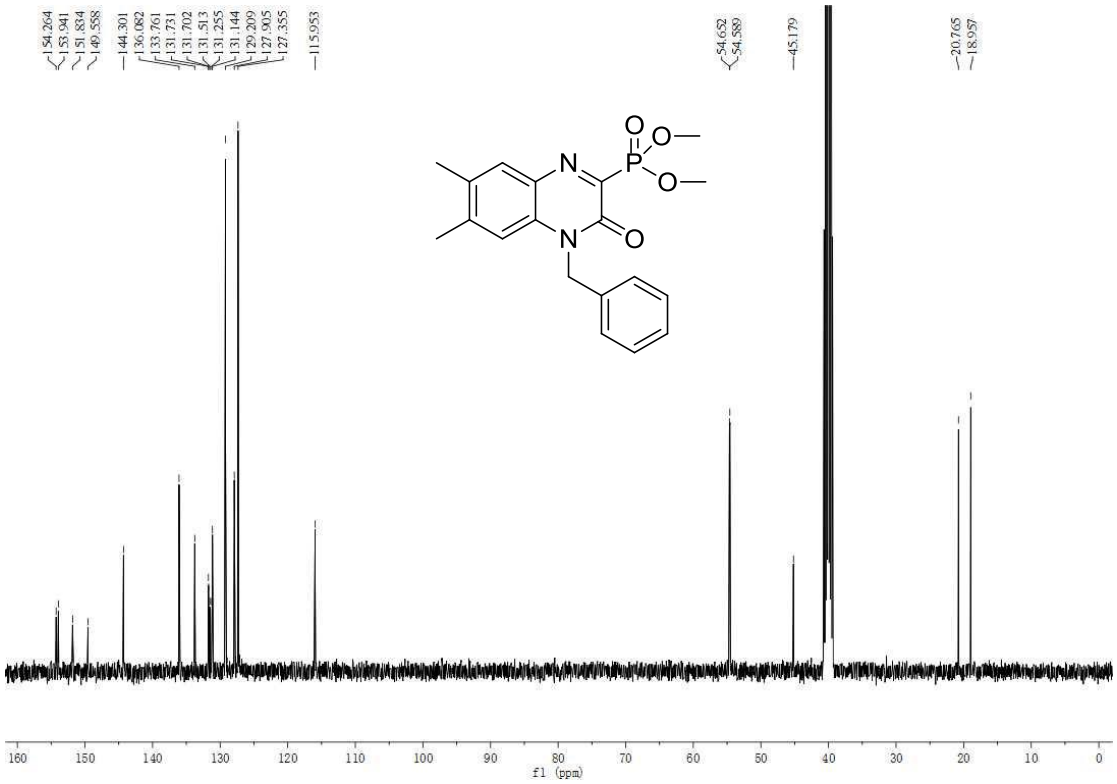


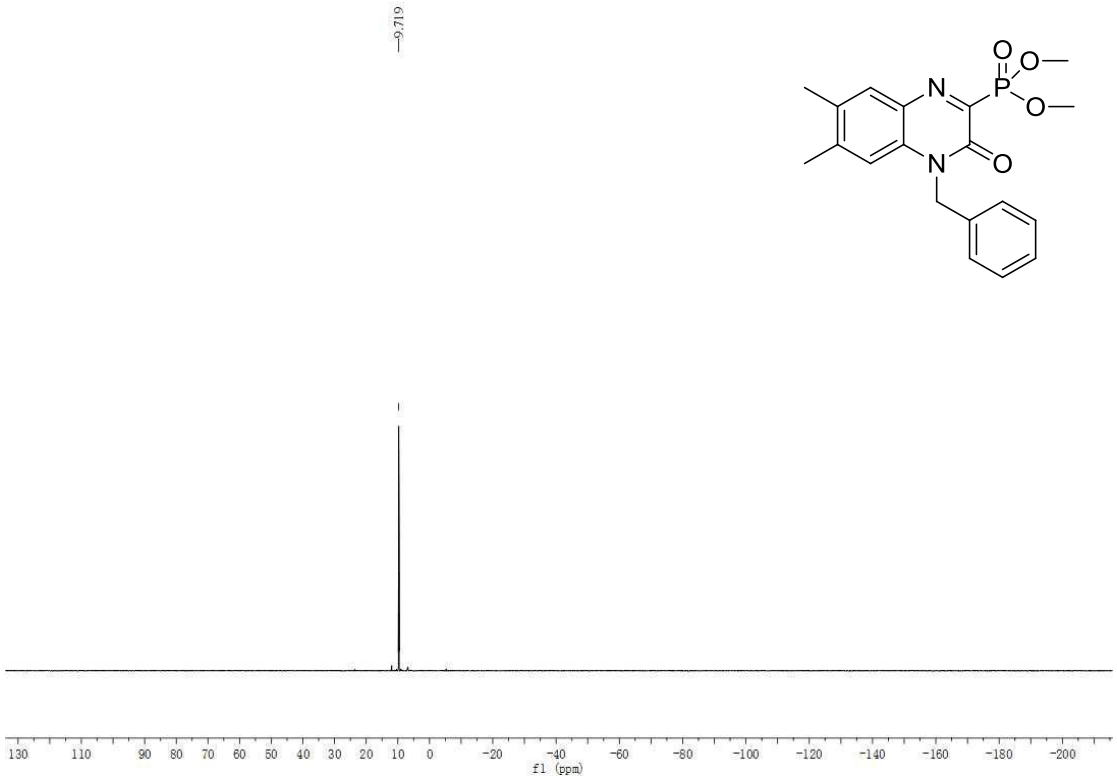




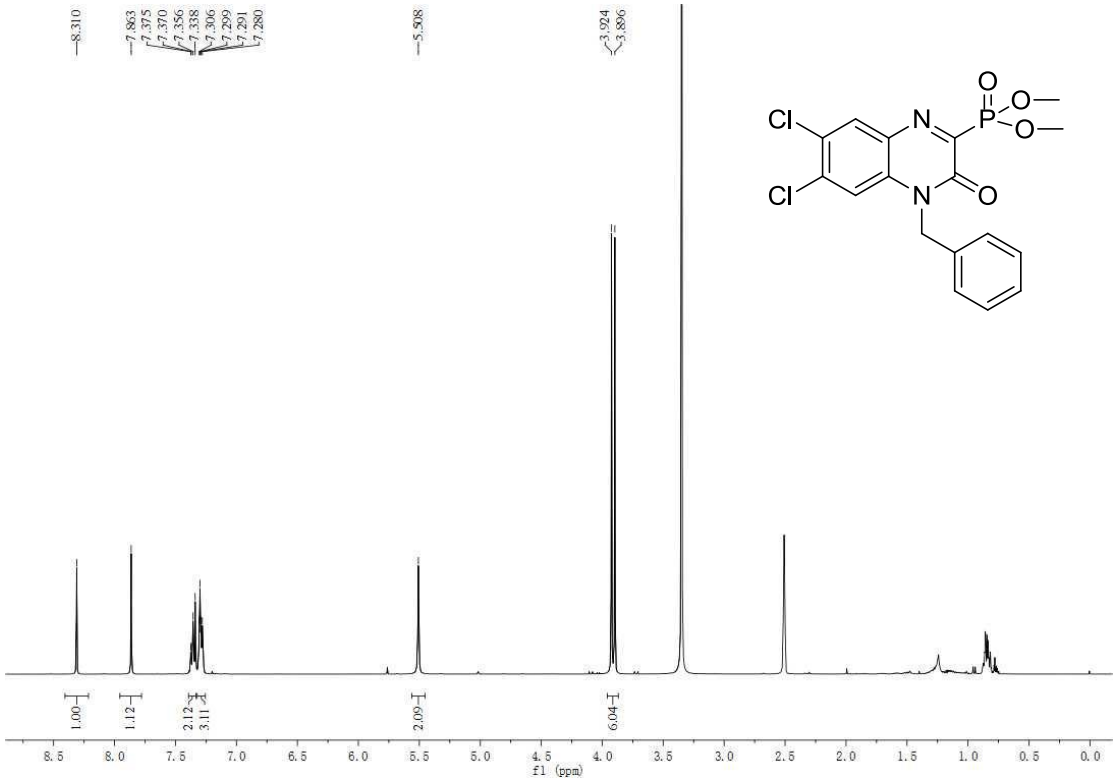
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3l

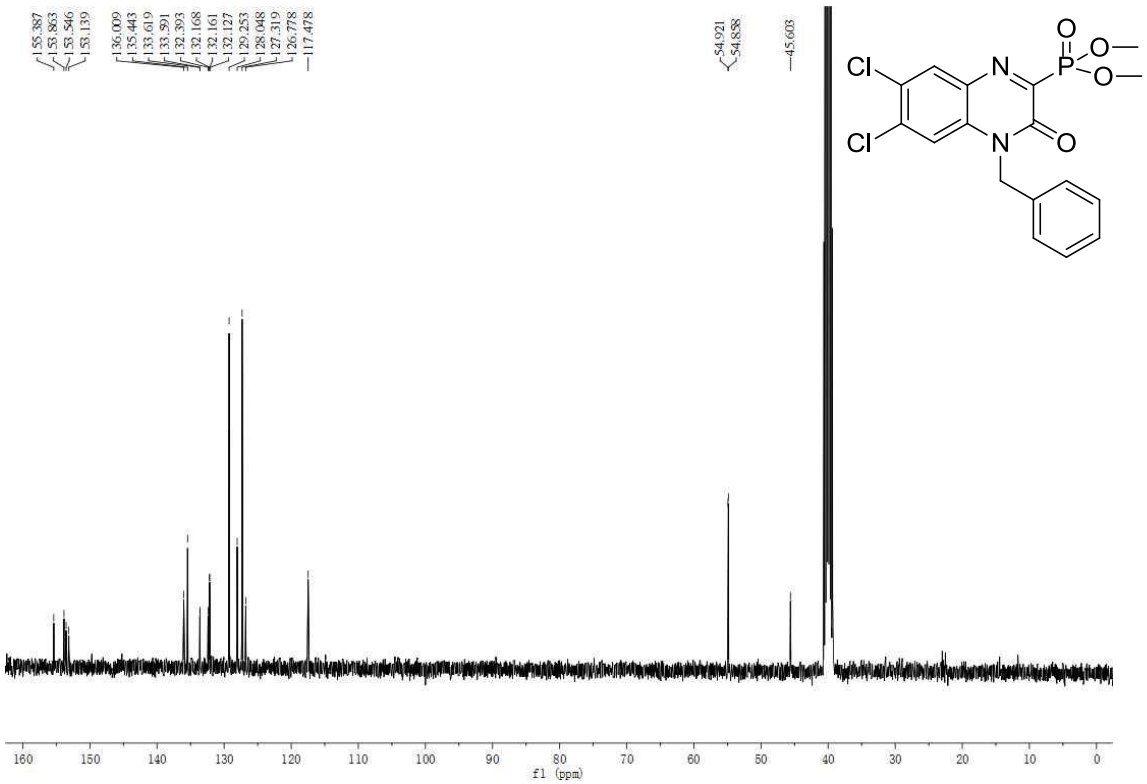



154.264
153.941
151.834
149.558
144.301
136.082
133.761
131.731
131.702
131.513
131.255
131.144
129.209
127.905
127.355
115.953
54.652
54.589
45.179
20.765
18.957
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

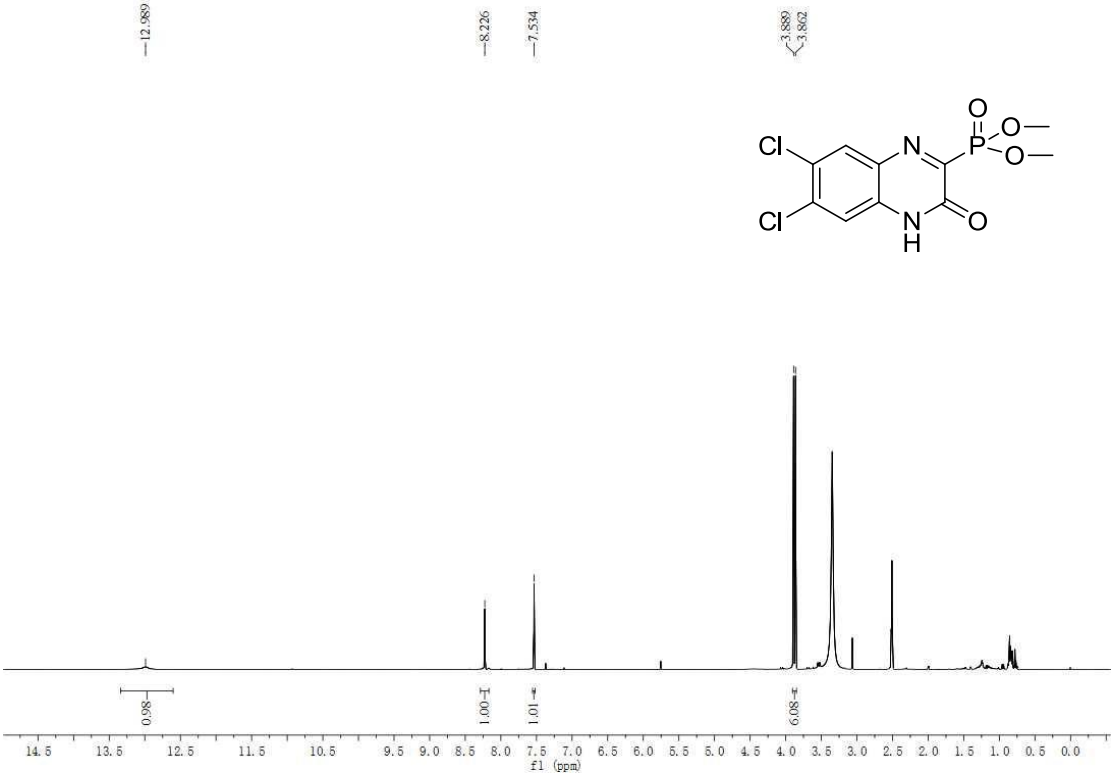

9.719
130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

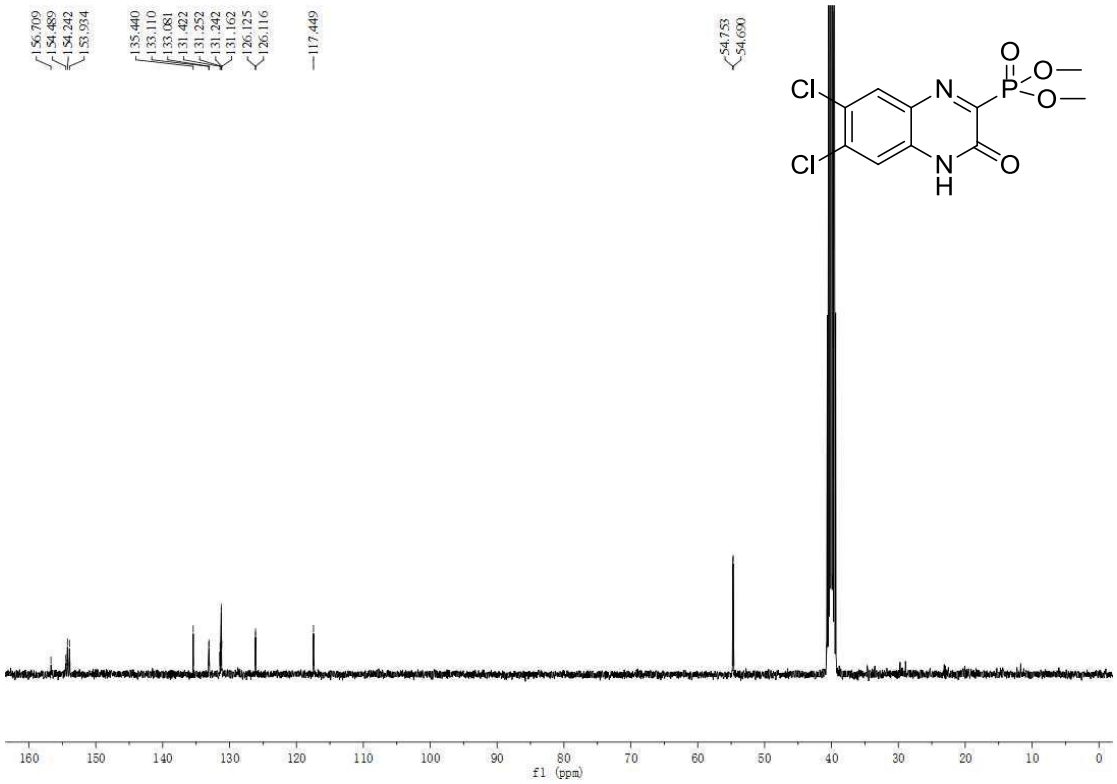
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3m

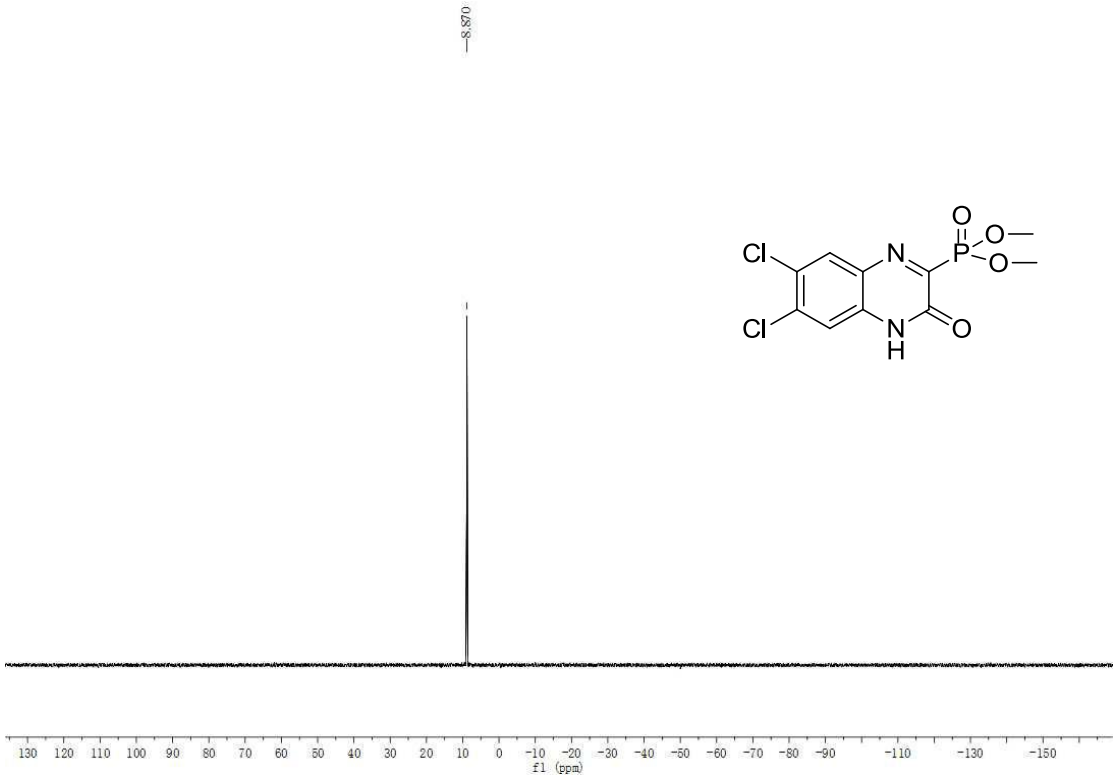




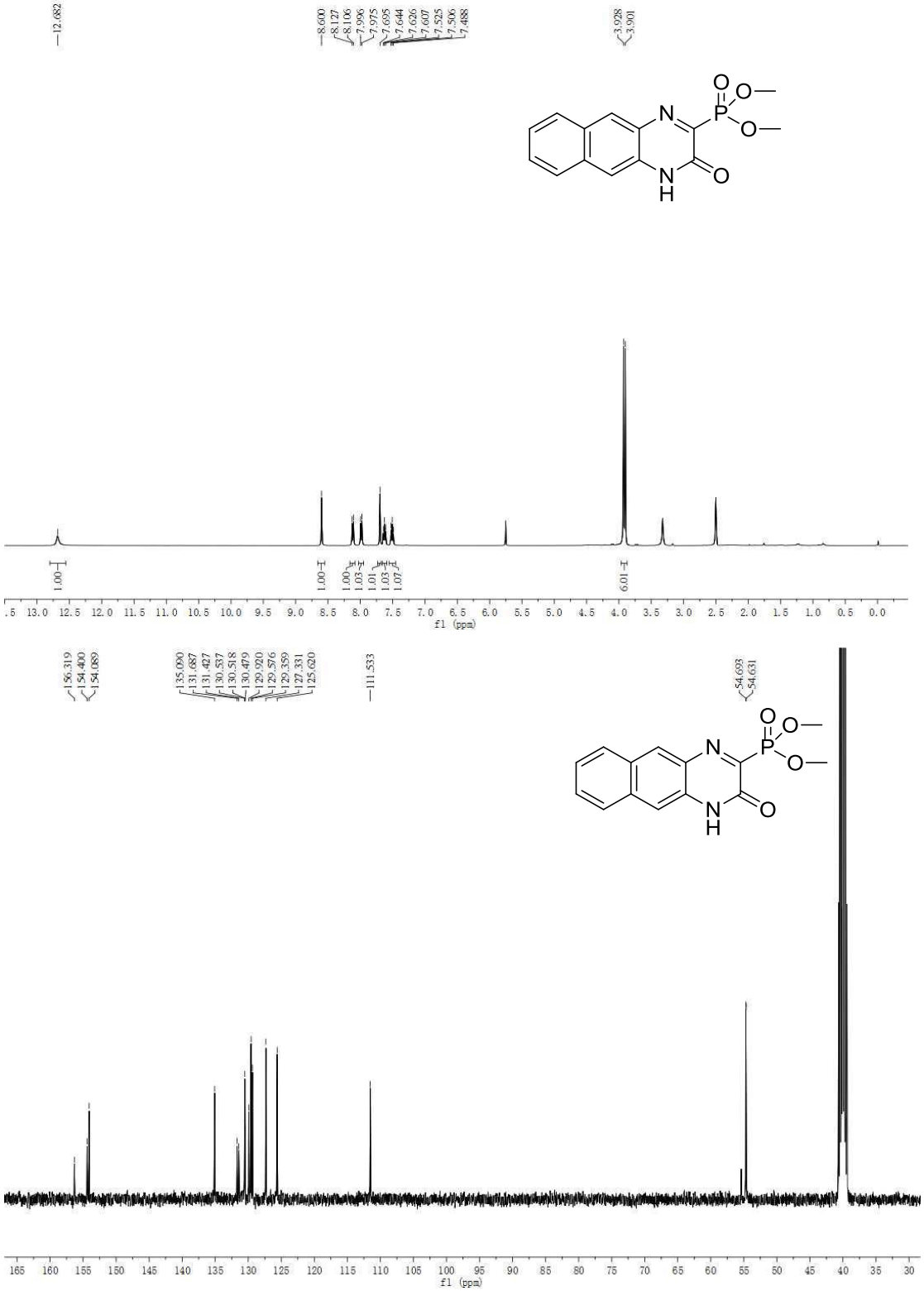
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3n



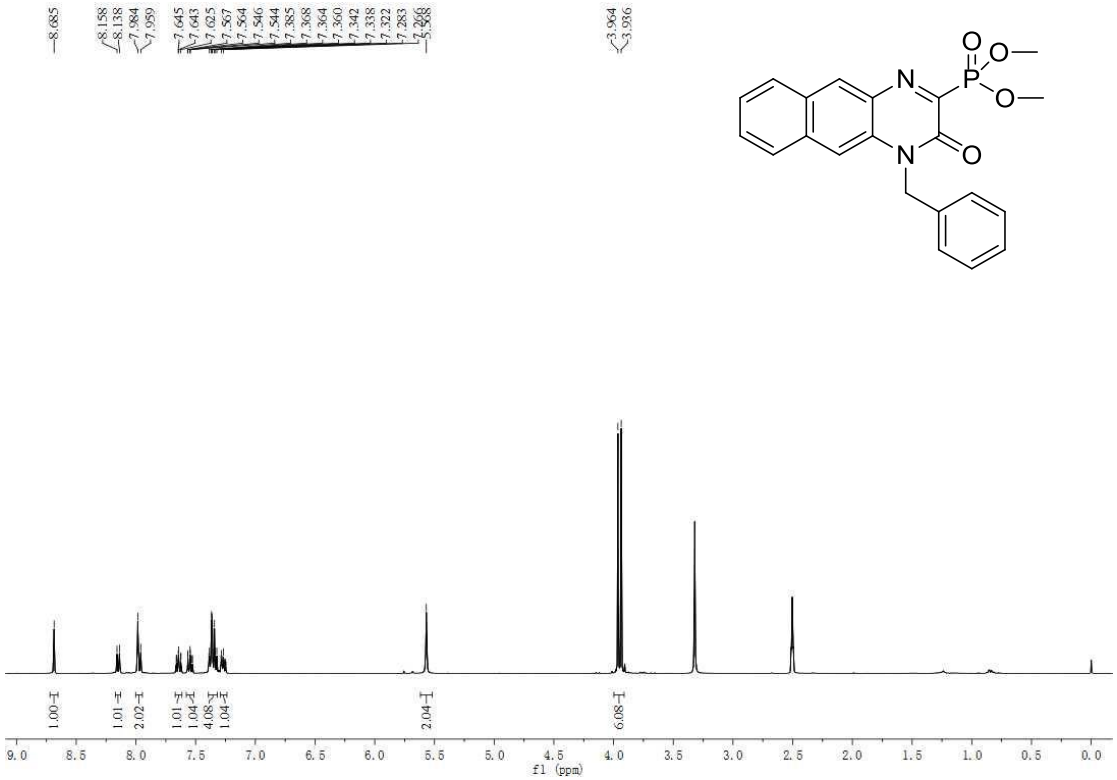

156.709
154.489
154.242
153.934
135.440
133.110
133.081
131.422
131.252
131.242
131.162
126.125
126.116
117.449
54.753
54.690
Cl
Cl
N
P
O
O
O
N
H
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

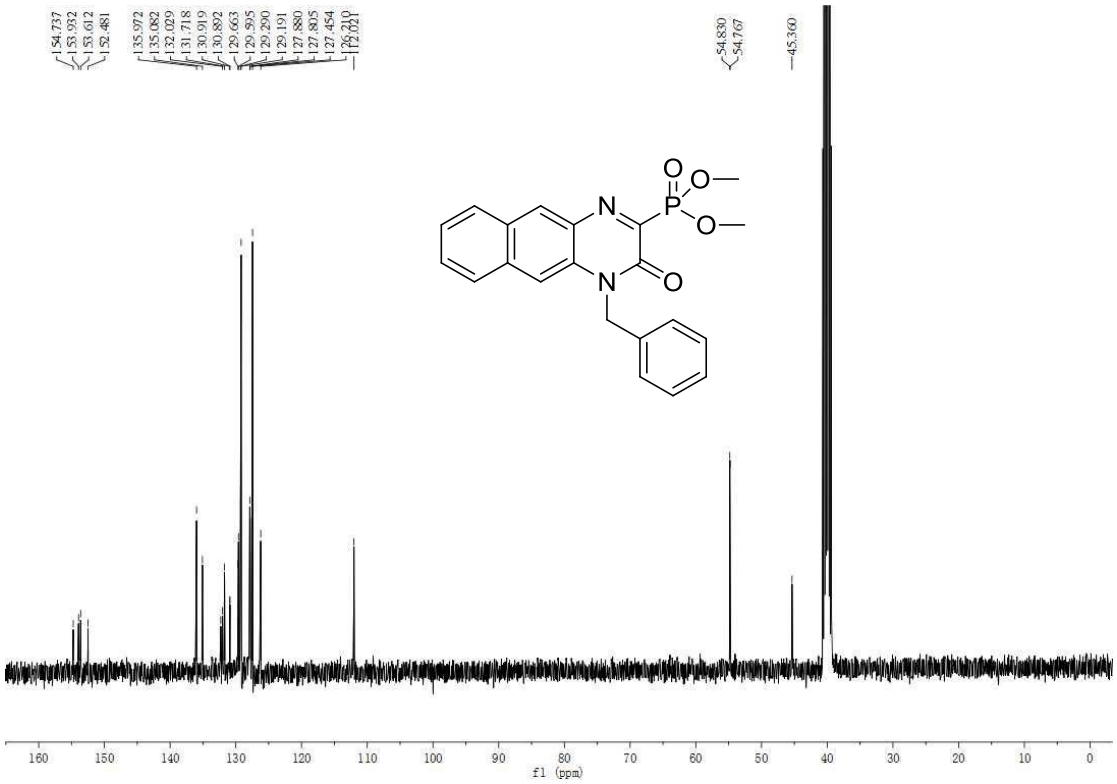

8.870
Cl
Cl
N
P
O
O
O
N
H
O
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
f1 (ppm)

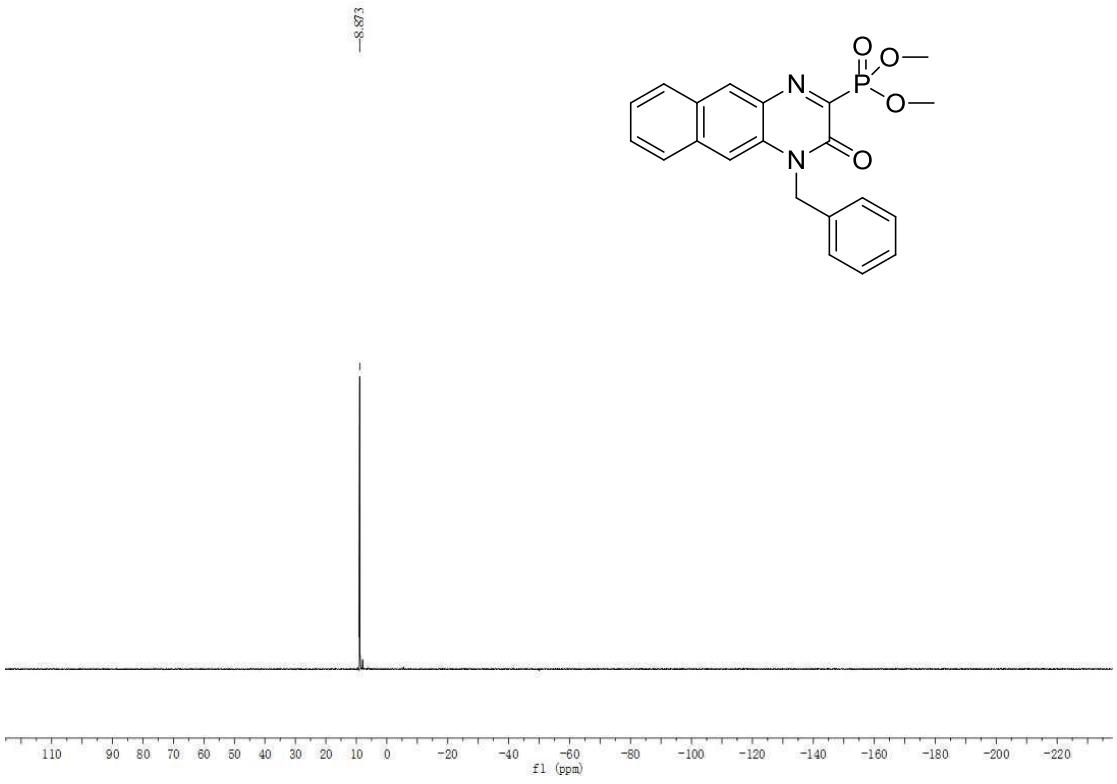
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3o



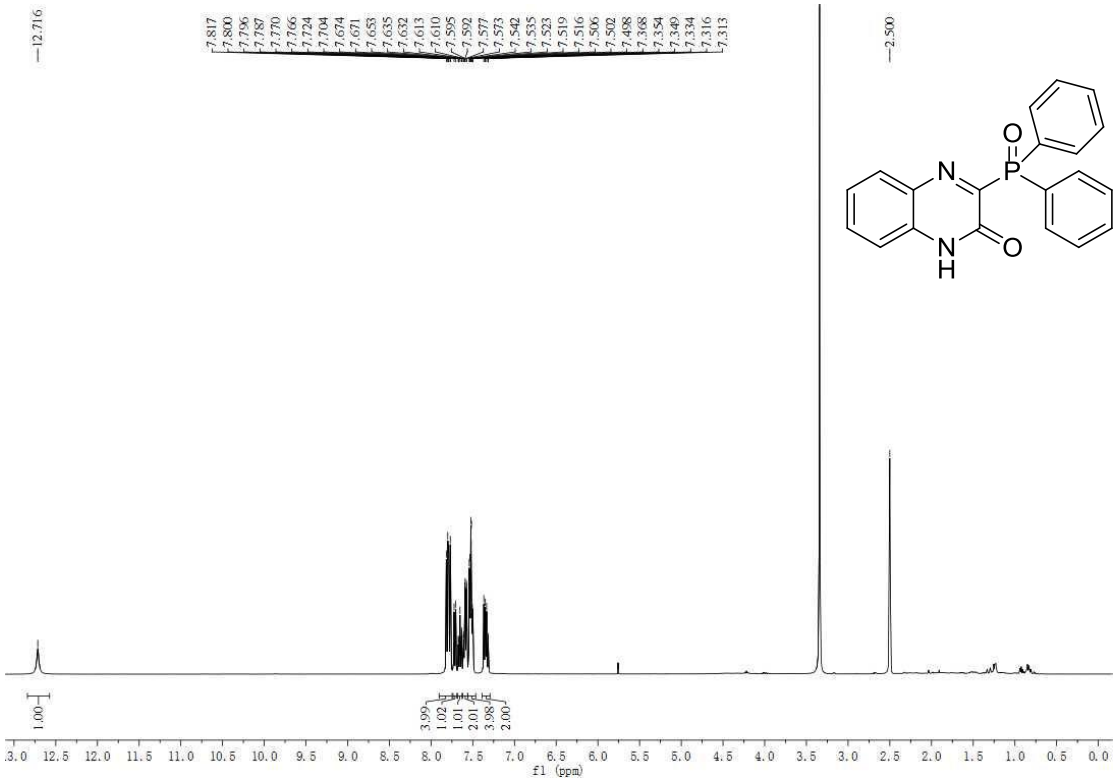
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3p

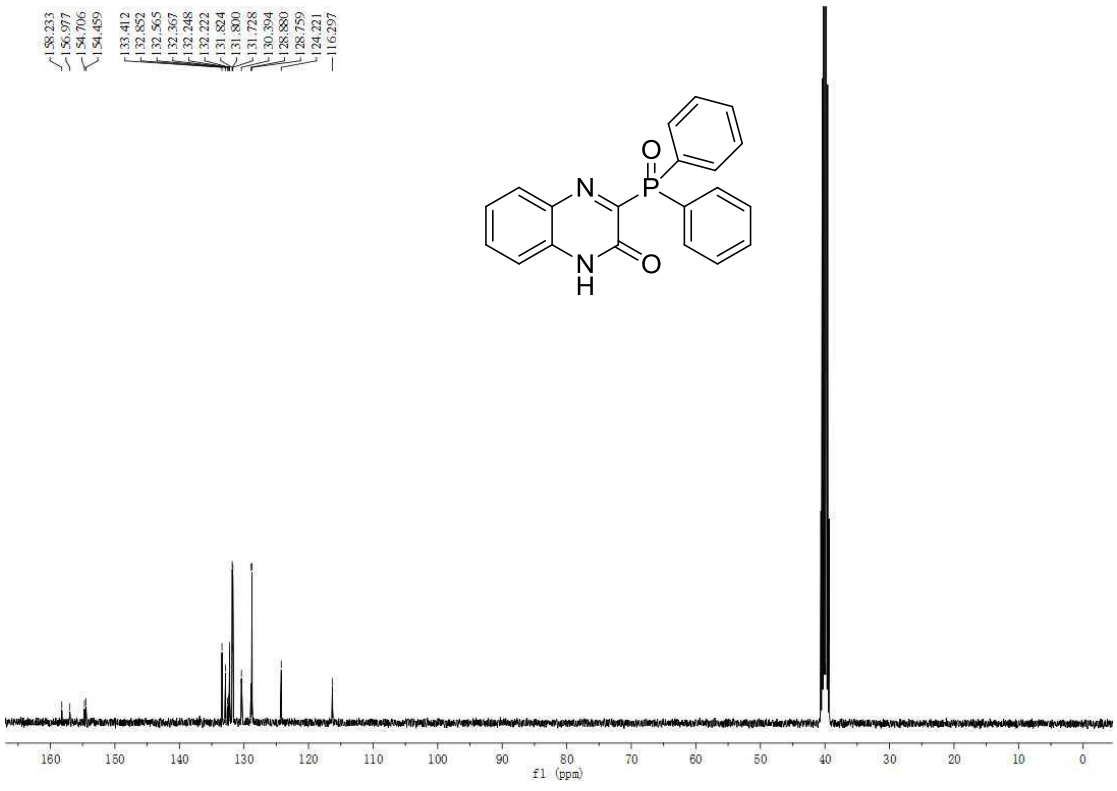


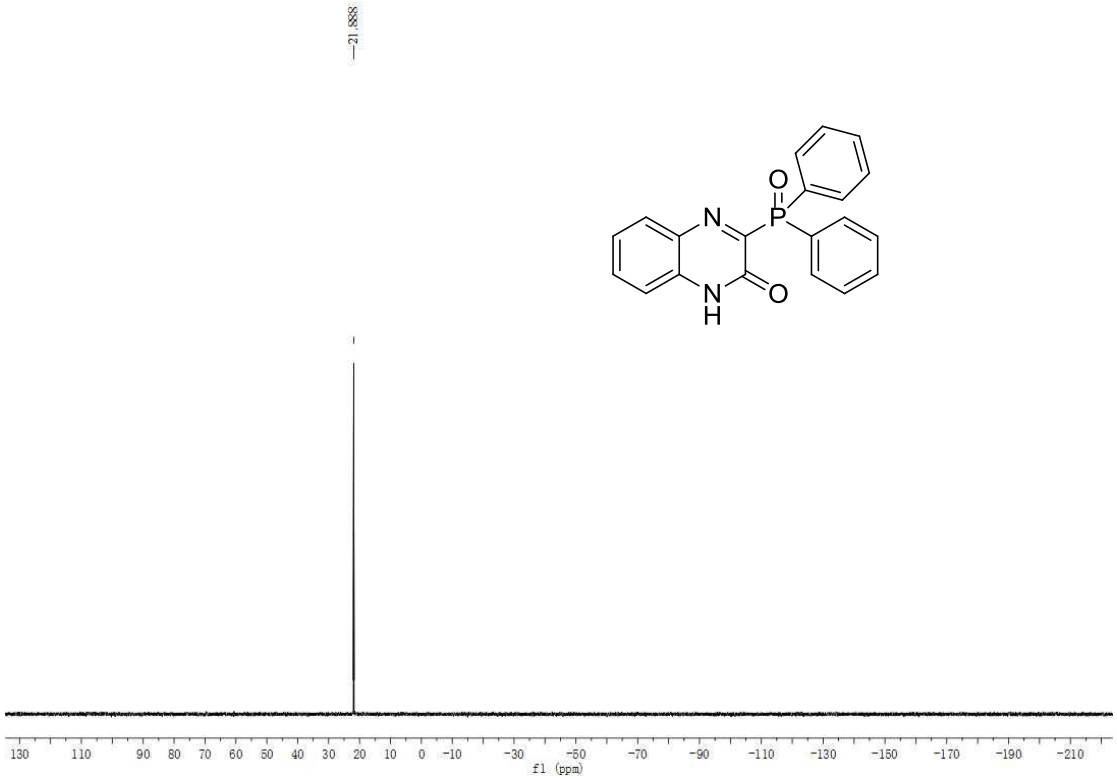

154.737
153.932
153.612
152.481
135.972
135.082
132.029
131.718
130.919
130.892
129.663
129.595
129.290
129.191
127.880
127.805
127.454
126.210
122.021
54.830
54.767
45.360
O
O
P
O
N
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.873
O
O
P
O
N
N
O
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

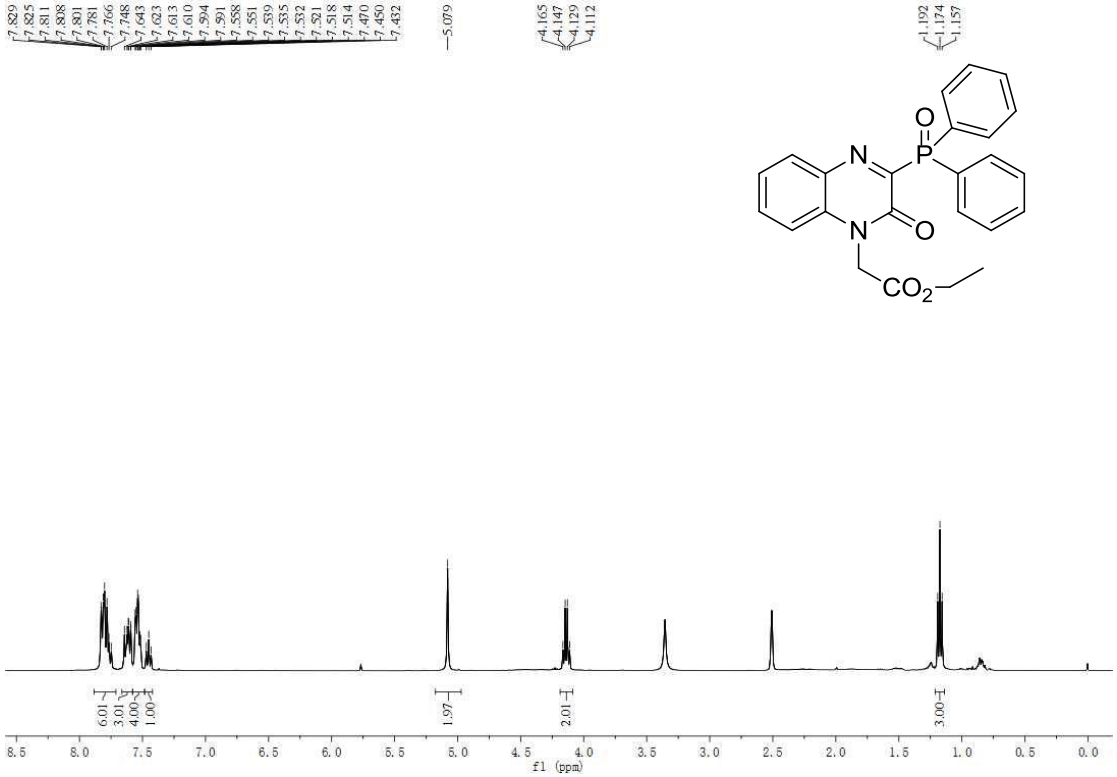
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3q

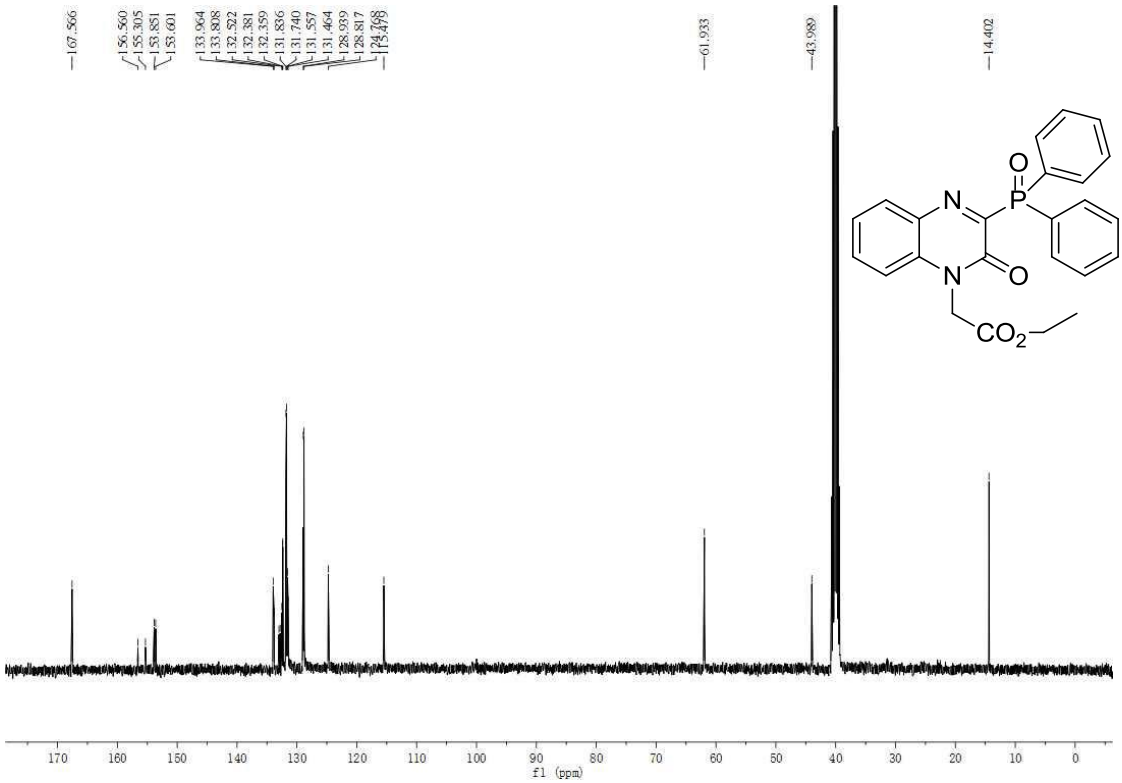






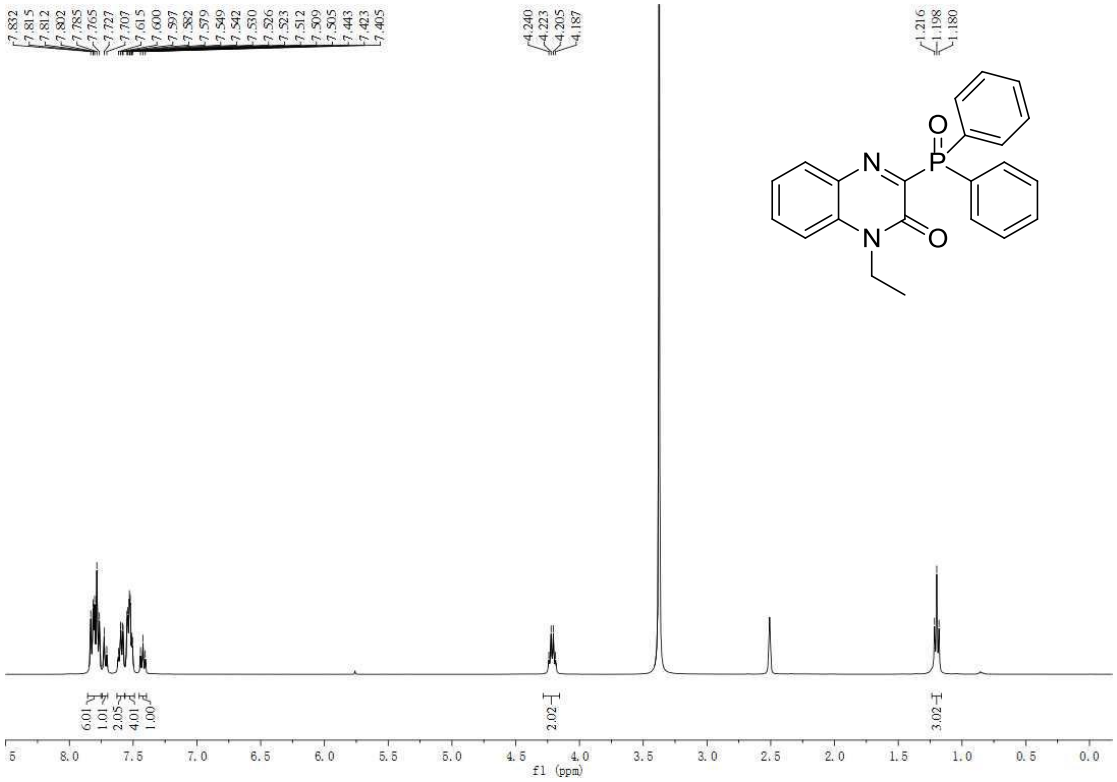
^{1}H NMR , ^{13}C NMR and ^{31}P NMR spectra of 3r

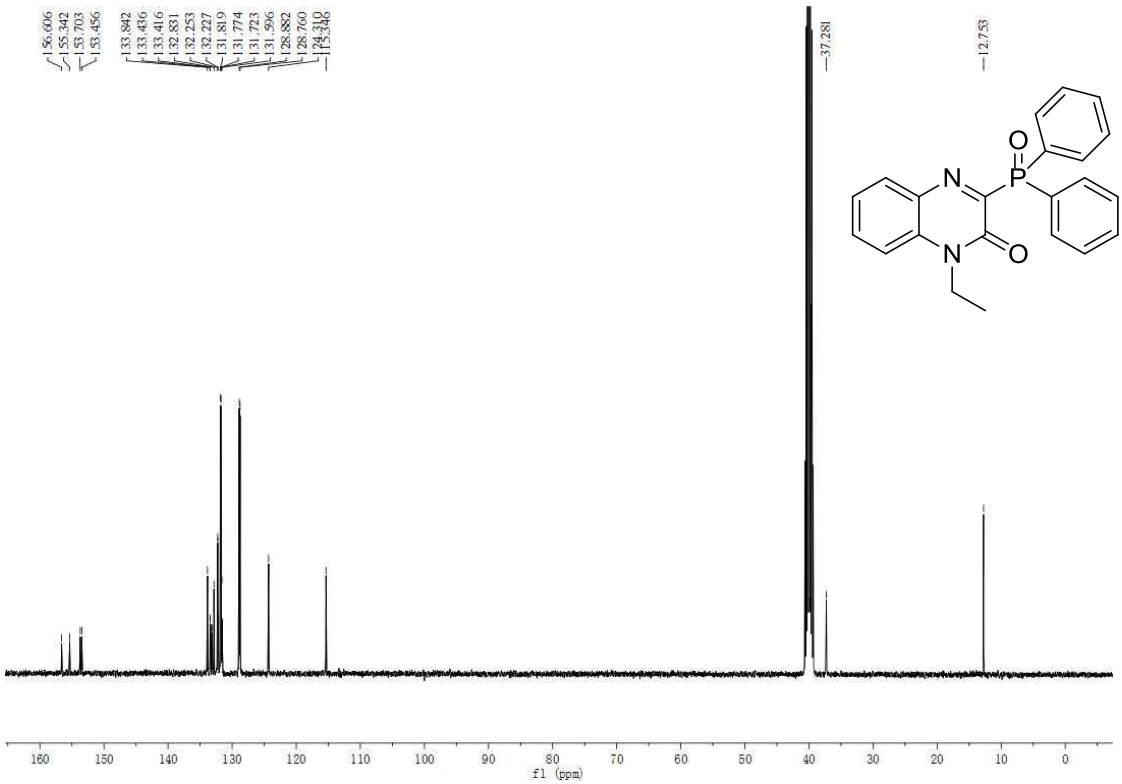



167.566
156.560
155.305
153.851
153.601
133.964
133.808
132.522
132.381
132.359
131.836
131.740
131.557
131.464
128.939
128.817
124.768
124.478
61.933
43.989
14.402
O
P
N
N
O
CO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

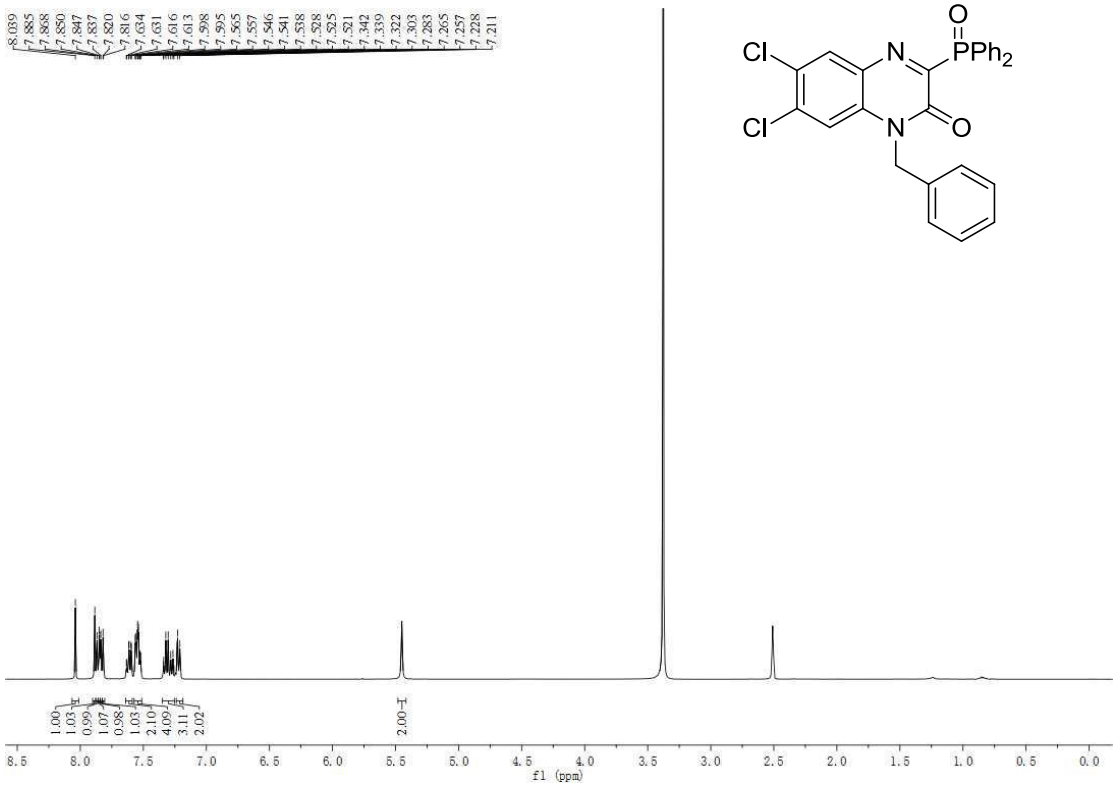

21.981
O
P
N
N
O
CO2
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
f1 (ppm)

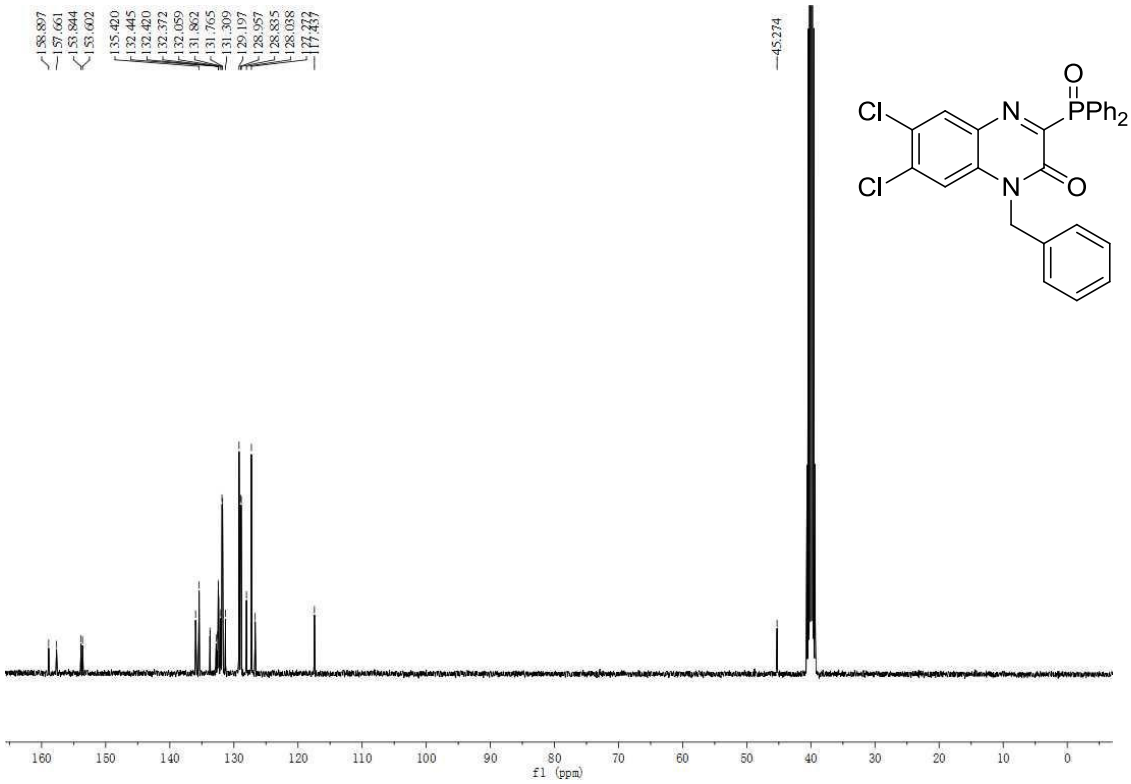
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3s

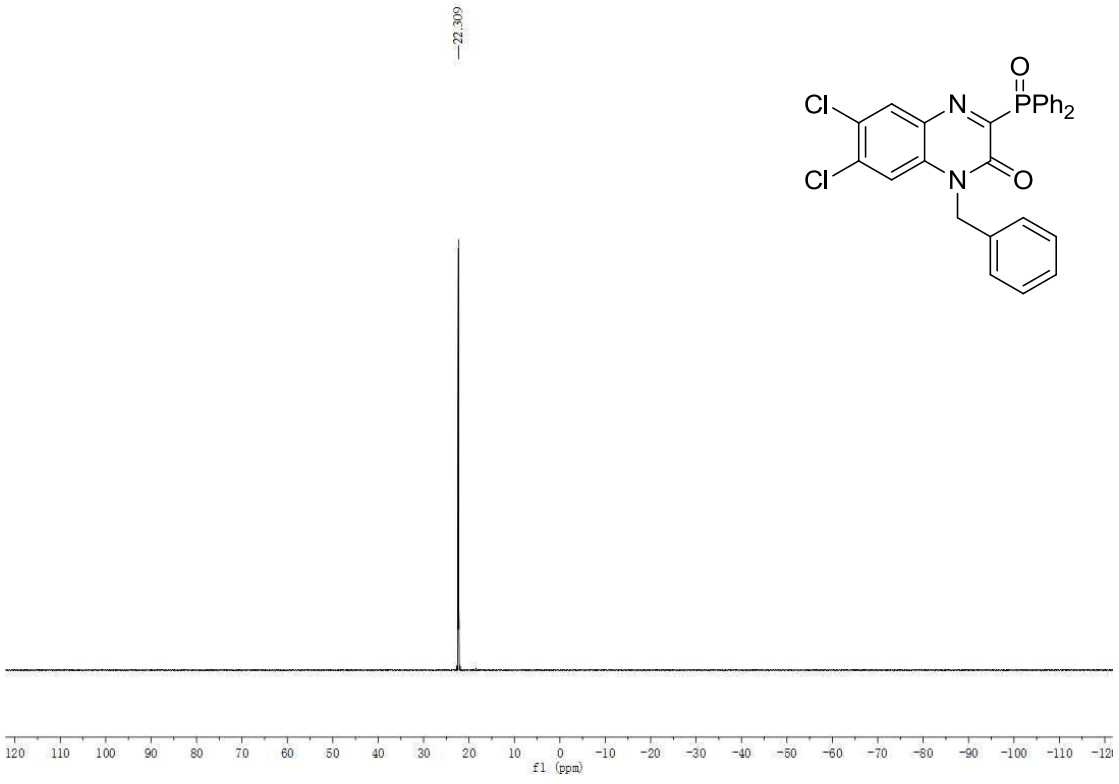




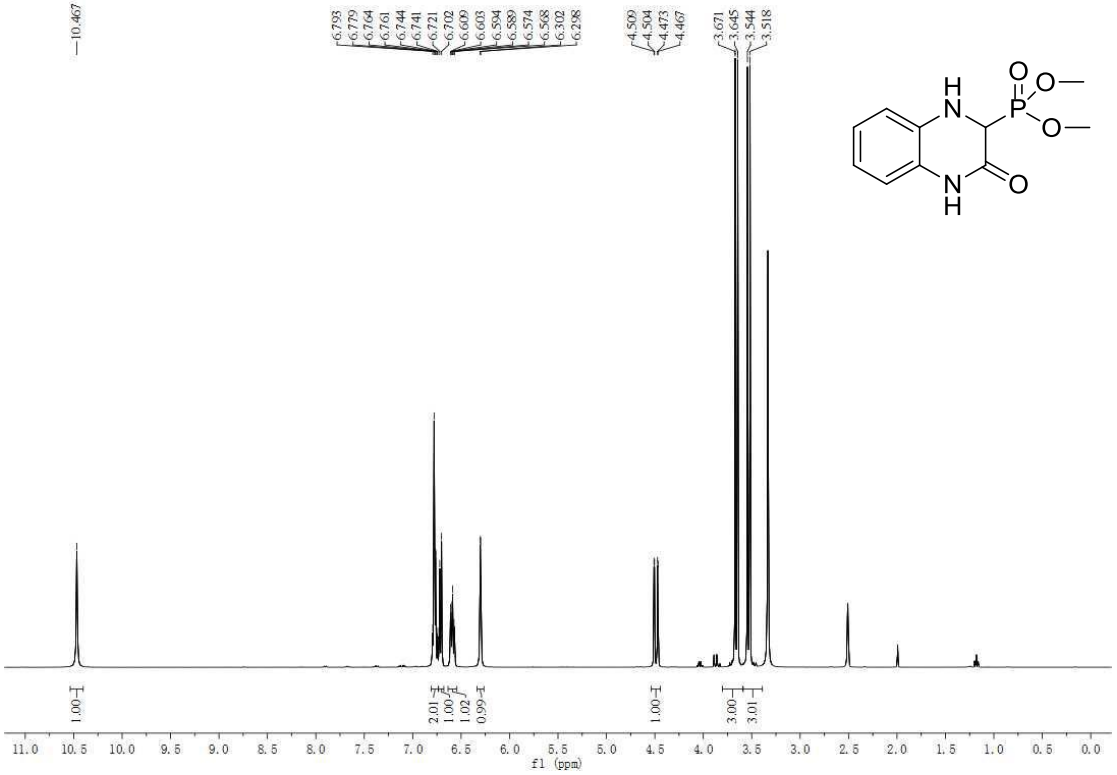
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 3t

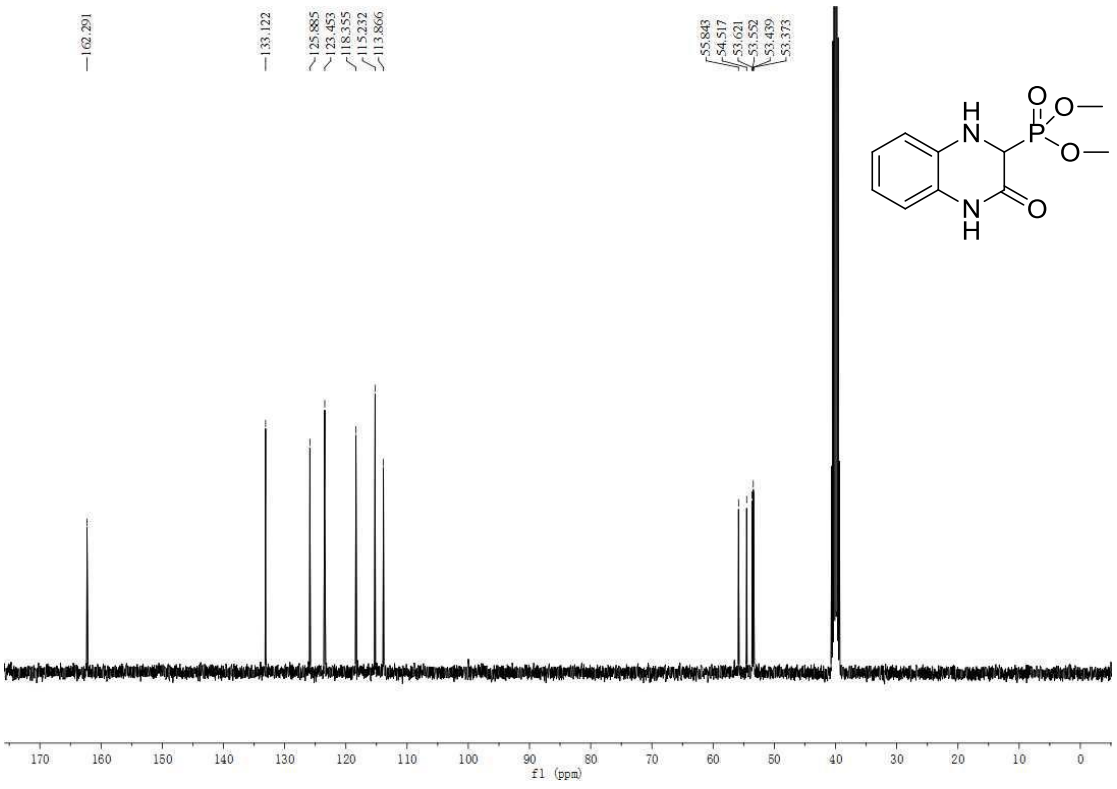


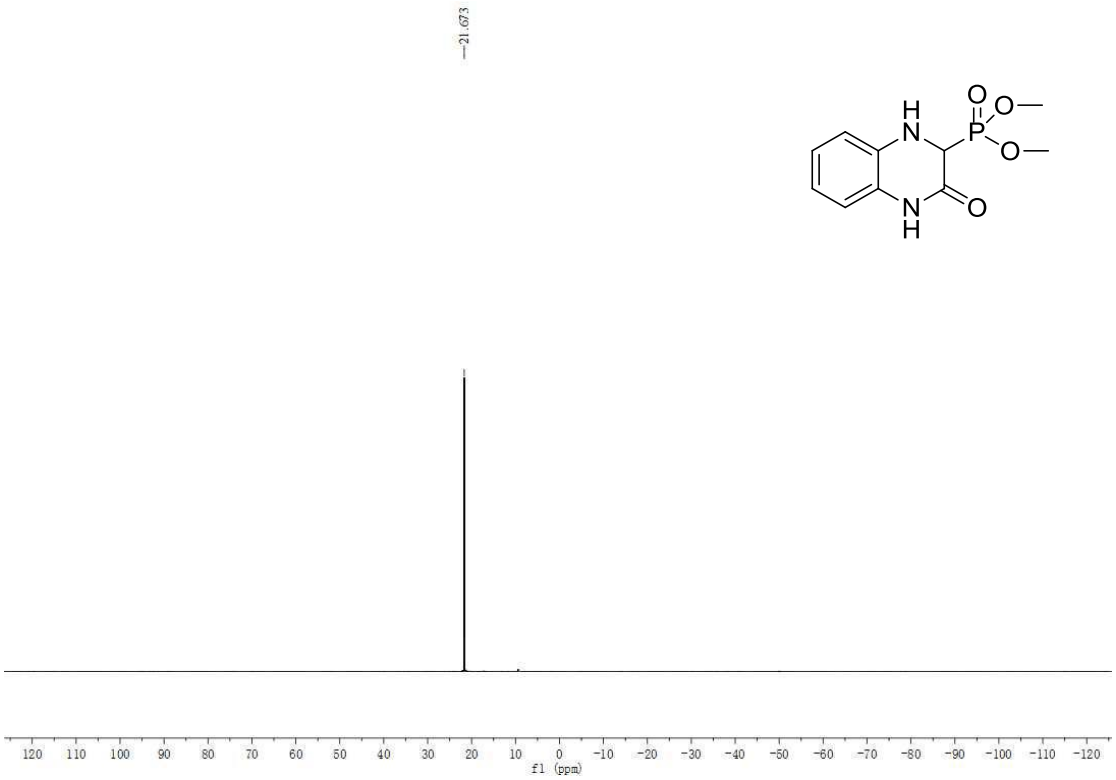

158.897
157.661
153.844
153.602
135.420
132.445
132.420
132.372
132.059
131.862
131.765
131.309
129.197
128.957
128.835
128.038
77.432
45.274
Cl
Cl
N
PPh2
O
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


22.309
Cl
Cl
N
PPh2
O
N
O
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of 4a






21.673
H
N
O
P
O
O
N
H
O
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)