Electronic Supplementary Material (ESI) for ChemComm.

Aerobic Oxidative C-H Phosphorylation of Quinoxalines under Catalyst-free Conditions

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Supporting Information

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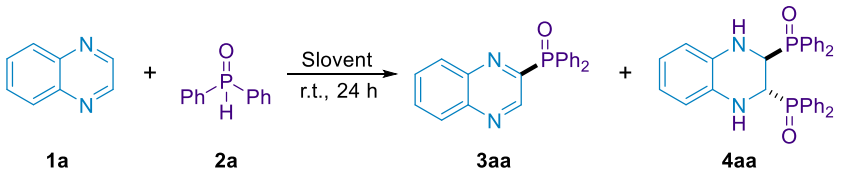
1. Reaction conditions optimization for the Phosphonation of Quinoxalines

Supplementary Table 1. Selected optimization studies [a]



1a **2a** **3aa** **4aa**

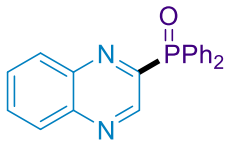
Entry	**1a**/**2a**	Solvent	Yield (%)	
			3aa	**4aa**
1	1/1.1	n-hexane	33	21
2	1/1.1	CCl_4	70	2
3	1/1.1	toluene	54	10
4	1/1.1	Et_2O	36	28
5	1/1.1	CH_2Cl_2	40	2
6	1/1.1	THF	40	10
7	1/1.1	EtOAc	53	14
8	1/1.1	EtOH	9	< 0.1
9	1/1.1	*i*-PrOH	15	< 0.1
10	1/1.1	MeOH	5	< 0.1
11	1/1.1	1,4-Dioxane	54	8
12	1/1.1	Actone	16	2
13	1/1.1	CH_3CN	49	25
14	1/1.1	DMF	16	2
15	1/1.1	DMSO	40	20
16	1/1.1	$CHCl_3$	10	< 0.1
17	1/1.1	1,2-dichlorethane	73	< 0.1
18	1/1.1	1-bromo-2-chlorethane	40	1
19[c]	1/1.1	1,2-dichlorethane	87	< 0.1
20[d]	1/1.1	1,2-dichlorethane	88	1
21[ce]	1/1.1	1,2-dichlorethane	92(90)	0
22[ce]	1/1.2	1,2-dichlorethane	92	0

[a]Reaction conditions: **1a** (0.1 mmol) and **2a** (0.11 mmol) in solvent(2 mL) under N_2 for 24 h. [b]Yield was determined by HPLC analysis. [c]Solvent (1 mL). [d]Solvent (0.5 mL) [e] under air.

2. Experimental Section and compound characterization

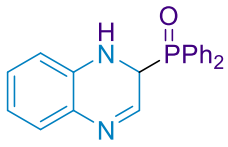
General information: Reagents and solvents were purchased from common commercial suppliers and were used without further purification. Column chromatography was generally performed on silica gel (200-300 mesh). Melting points were determined with a Büchi B-545 melting-point apparatus. 600MHz 1H NMR and 150MHz 13C NMR spectra were recorded on Varian VMS-600 spectrometers, respectively. The chemical shifts are reported in ppm (δ scale) relative to internal tetramethylsilane, and coupling constants are reported in hertz (Hz). High-resolution mass spectra (HRMS) were obtained on Agilent 6502 Q-TOF HPLC and mass spectrometry.

Synthesis of monophosphorylated product 3. A mixture of **quinoxalines 1** (0.2 mmol) and diarylphosphine oxides or diphenylphosphonate **2** (0.22 mmol), and 1,2-dichlorethane (2 mL) was stirred at room temperature for 24 h, and directly charged onto silica gel. The product was isolated using hexane/ethyl acetate (2/1~1:2) as eluent.



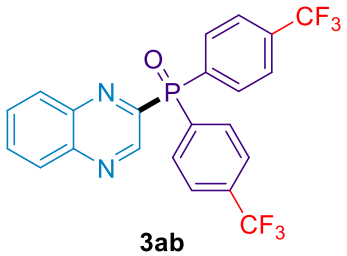
3aa

diphenyl(quinoxalin-2-yl)phosphine oxide (3aa). Yield, 91%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.25 – 8.19 (m, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.01 – 7.92 (m, 4H), 7.92 – 7.86 (m, 1H), 7.87 – 7.81 (m, 1H), 7.56 (td, *J* = 7.4, 1.0 Hz, 2H), 7.49 (td, *J* = 7.6, 3.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.54 (d, *J* = 124.0 Hz), 145.66 (d, *J* = 22.2 Hz), 142.43 (d, *J* = 17.1 Hz), 141.73, 132.38, 132.36, 132.33, 132.15 (2), 132.09 (2), 131.53, 130.99, 130.83, 130.24, 129.14, 128.62 (2), 128.53 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.46. HRMS (m/z) calcd for $C_{20}H_{16}N_2OP[M+H]^+$ 331.0966, found 331.0958.



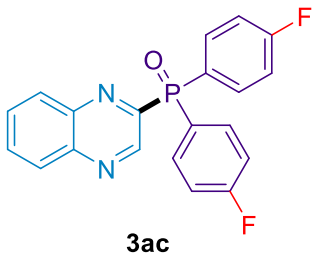
3aa'

(1,2-dihydroquinoxalin-2-yl)diphenylphosphine oxide (3aa'). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.45 (s, 1H), 8.16 (td, *J* = 8.5, 1.3 Hz, 2H), 7.94 (ddd, *J* = 14.1, 7.7, 6.4 Hz, 4H), 7.87 (dtd, *J* = 16.7, 6.9, 1.5 Hz, 2H), 7.73 – 7.66 (m, 5H), 7.65 (s, 1H), 3.54 – 3.32 (m, 1H).



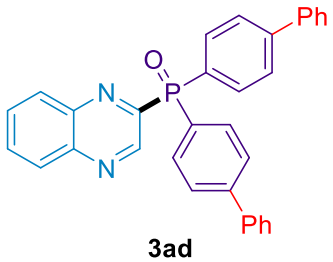
3ab

quinoxalin-2-ylbis(4-(trifluoromethyl)phenyl)phosphine oxide (3ab). Yield, 78%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 – 9.66 (m, 1H), 8.22 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.20 – 8.12 (m, 5H), 7.91 (m, 2H), 7.77 (dd, *J* = 8.4, 2.2 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.48 (d, *J* = 127.4 Hz), 146.20 (d, *J* = 22.4 Hz), 142.91 (d, *J* = 2.3 Hz), 142.11 (d, *J* = 17.5 Hz), 135.28 (d, *J* = 102.8 Hz), 134.73 – 133.93 (m), 132.61, 132.55 (2), 132.49 (2), 131.28, 130.04, 129.79 (d, *J* = 1.6 Hz), 125.66 – 125.55 (m), 125.52 (m), 134.30, 122.49; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 16.79; ^{19}F NMR (282 MHz, $CDCl_3$) δ -104.94 – -105.62 (m). HRMS (m/z) calcd for $C_{22}H_{14}F_6N_2OP[M+H]^+$ 467.467.0742, found 467.0738.



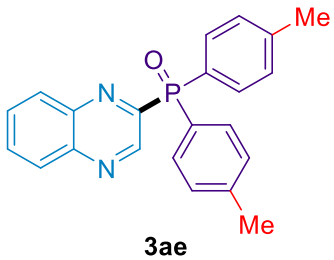
3ac

bis(4-fluorophenyl)(quinoxalin-2-yl)phosphine oxide (3ac). Yield, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.24 (dd, *J* = 8.3, 0.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.00 – 7.94 (m, 4H), 7.93 – 7.89 (m, 1H), 7.89 – 7.85 (m, 1H), 7.18 (tdd, *J* = 6.5, 4.4, 2.2 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.40 (dd, *J* = 254.6, 3.3 Hz), 151.93 (d, *J* = 126.5 Hz), 145.73 (d, *J* = 22.4 Hz), 142.28 (d, *J* = 17.2 Hz), 142.11, 134.70 (2), 134.64 (2), 134.63 (2), 134.57 (2), 132.47, 131.15, 130.09, 129.37, 127.10 (dd, *J* = 108.7, 3.3 Hz), 116.31 – 115.93 (4); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 18.94; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.30. HRMS (m/z) calcd for $C_{20}H_{14}F_2N_2OP[M+H]^+$ 367.0806, found 367.0800.



3ad

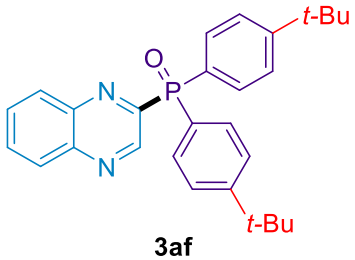
di([1,1'-biphenyl]-4-yl)(quinoxalin-2-yl)phosphine oxide (3ab). Yield, 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.21 (dd, *J* = 17.2, 8.2 Hz, 2H), 8.04 (dd, *J* = 11.6, 8.2 Hz, 4H), 7.86 (dt, *J* = 14.6, 7.0 Hz, 2H), 7.70 (dd, *J* = 7.9, 2.1 Hz, 4H), 7.62 – 7.54 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 4H), 7.36 (dd, *J* = 8.2, 6.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.15, 152.55 (d, *J* = 124.8 Hz), 145.86 (d, *J* = 22.2 Hz), 145.21 (d, *J* = 2.6 Hz), 142.46 (d, *J* = 17.0 Hz), 141.97, 139.81, 132.69 (2), 132.63 (2), 132.30, 131.00, 130.26, 129.80 (d, *J* = 106.4 Hz), 129.29, 128.96 (4), 128.24, 127.35(2), 127.29 (4), 127.27 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.43. HRMS (m/z) calcd for $C_{32}H_{24}N_2OP[M+H]^+$ 483.1621, found 483.1624.



3ae

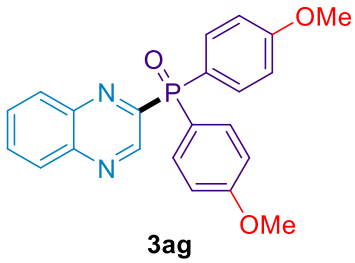
quinoxalin-2-yldi-p-tolylphosphine oxide (3ae). Yield, 60%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.17 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.85 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.81 (dd, *J* = 12.0, 8.1 Hz, 4H), 7.29 (dd, *J* = 8.0, 2.7 Hz, 4H), 2.40 (s, 6H); ^{13}C NMR (151

MHz, $CDCl_3$) δ 153.12 (d, *J* = 123.6 Hz), 145.40 (d, *J* = 22.3 Hz), 142.97 (d, *J* = 2.8 Hz), 142.54 (d, *J* = 16.9 Hz), 141.35, 132.31, 132.19 (2), 132.13 (2), 130.97, 130.26, 129.37 (2), 129.29 (2), 128.94, 127.92 (d, *J* = 107.8 Hz), 21.65, 21.64; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 21.41. HRMS (m/z) calcd for $C_{22}H_{20}N_2OP[M+H]^+$ 359.1308, found 359.1307.



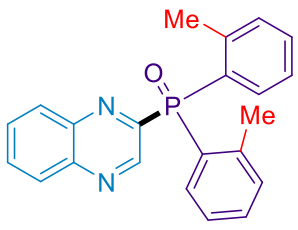
3af

bis(4-(tert-butyl)phenyl)(quinoxalin-2-yl)phosphine oxide (3af). Yield, 67%; ^1H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 11.9, 8.4 Hz, 6H), 7.50 (dd, *J* = 8.3, 2.6 Hz, 4H), 1.31 (s, 18H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.89, 155.87, 153.32 (d, *J* = 123.2 Hz), 145.22 (d, *J* = 22.4 Hz), 142.62 (d, *J* = 16.8 Hz), 141.09, 132.38, 132.04 (2), 131.97 (2), 131.02, 130.31, 128.80, 127.87 (d, *J* = 107.8 Hz), 125.67 (2), 125.59 (2), 35.05 (2), 31.05 (6); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.43. HRMS (m/z) calcd for $C_{28}H_{32}N_2OP[M+H]^+$ 443.2247, found 433.2252.



3ag

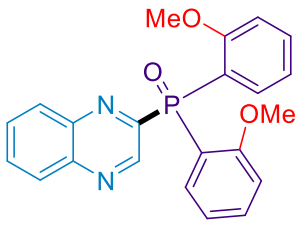
bis(4-(tert-butyl)phenyl)(quinoxalin-2-yl)phosphine oxide (3ag). Yield, 67%; ^1H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.31 – 8.24 (m, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.87 – 7.81 (m, 5H), 6.98 (dd, *J* = 8.8, 2.3 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.85, 162.83, 153.40 (d, *J* = 124.5 Hz), 145.20 (d, *J* = 22.3 Hz), 142.57 (d, *J* = 16.9 Hz), 141.12, 134.11 (2), 134.04 (2), 132.35, 131.02, 130.23, 128.82, 122.25 (d, *J* = 112.4 Hz), 114.24 (2), 114.15 (2), 55.36 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 21.54. HRMS (m/z) calcd for $C_{22}H_{20}N_2O_3P[M+H]^+$ 391.1206, found 391.1210.



3ah

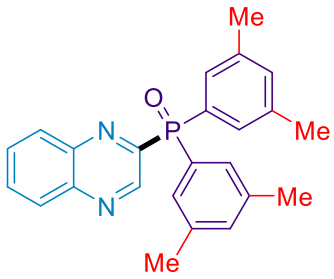
quinoxalin-2-yldi-o-tolylphosphine oxide (3ah). Yield, 56%; ^1H NMR (600 MHz, $CDCl_3$) δ 9.56 (s,

1H), 8.28 (dd, *J* = 8.4, 0.7 Hz, 1H), 8.16 – 8.08 (m, 1H), 7.91 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.85 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.47 (dd, *J* = 10.6, 4.4 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.31 (dd, *J* = 7.5, 4.5 Hz, 2H), 7.24 – 7.18 (m, 2H), 2.48 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.04 (d, *J* = 122.6 Hz), 146.20 (d, *J* = 22.9 Hz), 143.11 (d, *J* = 8.6 Hz), 142.29 (d, *J* = 17.0 Hz), 141.32, 133.08 (d, *J* = 12.0 Hz, 2C), 132.49 (d, *J* = 2.6 Hz, 2C), 132.40, 131.99 (d, *J* = 11.0 Hz, 2C), 131.00, 130.38, 129.38 (d, *J* = 103.0 Hz), 128.96, 125.62 (d, *J* = 12.9 Hz, 2C), 21.89 (d, *J* = 4.2 Hz, 2C); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 29.81. HRMS (m/z) calcd for $C_{22}H_{20}N_2OP[M+H]^+$ 359.1308, found 359.1310.



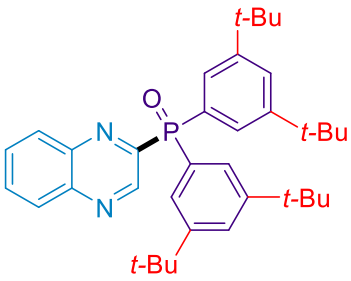
3ai

bis(2-methoxyphenyl)(quinoxalin-2-yl)phosphine oxide (3ai). Yield, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.37 – 8.31 (m, 2H), 7.95 – 7.85 (m, 2H), 7.75 (ddd, *J* = 14.3, 7.6, 1.6 Hz, 2H), 7.61 (dd, *J* = 11.6, 4.1 Hz, 2H), 7.13 (td, *J* = 7.5, 1.7 Hz, 2H), 6.95 (dd, *J* = 8.2, 5.6 Hz, 2H), 3.58 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.71 (d, *J* = 2.9 Hz, 2C), 155.60 (d, *J* = 131.4 Hz), 143.78 (d, *J* = 29.8 Hz), 143.33 (d, *J* = 17.2 Hz), 137.66, 135.08, 135.07, 134.86 (d, *J* = 7.9 Hz, 2C), 132.60, 131.16, 130.63, 126.87, 121.40 (d, *J* = 12.4 Hz, 2C), 117.71 (d, *J* = 109.1 Hz, 2C), 111.25 (d, *J* = 6.6 Hz, 2C), 55.56 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 18.47. HRMS (m/z) calcd for $C_{22}H_{20}N_2O_3P[M+H]^+$ 391.1206, found 391.1200.



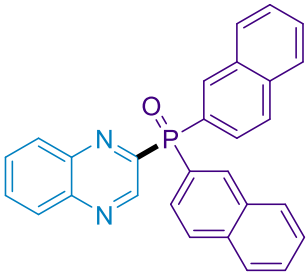
3aj

bis(3,5-dimethylphenyl)(quinoxalin-2-yl)phosphine oxide (3aj). Yield, 88%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.27 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.86 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.53 (s, 2H), 7.51 (s, 2H), 7.18 (s, 2H), 2.33 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.16 (d, *J* = 122.5 Hz), 145.40 (d, *J* = 22.3 Hz), 142.63 (d, *J* = 16.8 Hz), 141.25, 138.40 (2), 138.31 (2), 134.21 (d, *J* = 2.8 Hz), 132.34, 130.99, 130.76 (d, *J* = 104.2 Hz), 130.34, 129.69 (2), 129.62 (2), 128.88, 21.33 (4); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 21.87. HRMS (m/z) calcd for $C_{24}H_{24}N_2OP[M+H]^+$ 387.1621, found 387.1625.



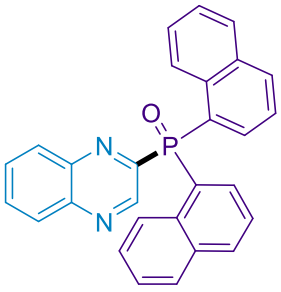
3ak

bis(3,5-di-tert-butylphenyl)(quinoxalin-2-yl)phosphine oxide (3ak). Yield, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.28 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.18 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.97 (d, *J* = 1.8 Hz, 2H), 7.95 (d, *J* = 1.8 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.60 (d, *J* = 0.9 Hz, 2H), 1.31 (s, 36H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.29 (d, *J* = 119.7 Hz), 151.08 (2), 151.00 (2), 144.99, 142.74, 140.90, 132.25, 131.14, 130.65, 129.97 (2), 128.76, 126.45 (2), 126.35 (2), 126.28 (2), 35.13 (4), 31.35 (12); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 19.20. HRMS (m/z) calcd for $C_{36}H_{48}N_2OP[M+H]^+$ 555.3499, found 555.3500.



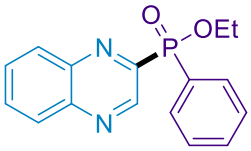
3am

di(naphthalen-2-yl)(quinoxalin-2-yl)phosphine oxide (3am). Yield, 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 2H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.90 – 7.83 (m, 1H), 7.81 – 7.75 (m, 1H), 7.69 (dd, *J* = 16.2, 7.1 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.39 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.99 (d, *J* = 124.3 Hz), 146.18 (d, *J* = 23.4 Hz), 142.30 (d, *J* = 17.2 Hz), 141.47, 134.11, 134.04, 133.90 (d, *J* = 9.6 Hz), 133.85 (2), 133.83 (2), 133.74 (d, *J* = 8.6 Hz), 132.39, 130.93, 130.41, 128.95 (2), 127.58 (d, *J* = 3.6 Hz), 127.30 (d, *J* = 5.2 Hz), 126.90 (2), 126.58 (2), 124.54, 124.44; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 30.62. HRMS (m/z) calcd for $C_{28}H_{20}N_2OP[M+H]^+$ 431.1308, found 431.1315.



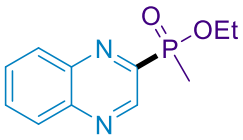
3an

di(naphthalen-1-yl)(quinoxalin-2-yl)phosphine oxide (3an). Yield, 85%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.58 (d, *J* = 14.2 Hz, 2H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.83 (m, 10H), 7.65 – 7.58 (m, 2H), 7.58 – 7.52 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.64 (d, *J* = 124.5 Hz), 145.80 (d, *J* = 22.3 Hz), 142.50 (d, *J* = 17.0 Hz), 141.81, 134.92 (d, *J* = 2.3 Hz), 134.39, 134.33, 132.47, 132.38, 131.04, 130.26, 129.18, 129.09 (2), 128.53 (2), 128.49, 128.41, 128.30 (d, *J* = 105.6 Hz), 127.85 (2), 127.03 (2), 126.83, 126.76 ; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 21.32. HRMS (m/z) calcd for $C_{28}H_{20}N_2OP[M+H]^+$ 431.1308, found 431.1311.



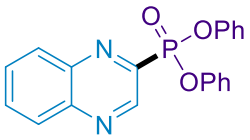
3ao

ethyl phenyl(quinoxalin-2-yl)phosphinate (3ao). Yield, 76%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.21 – 8.15 (m, 1H), 8.13 (dd, *J* = 8.3, 1.0 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.82 (dtd, *J* = 16.6, 6.9, 1.4 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.48 (td, *J* = 7.6, 3.7 Hz, 2H), 4.35 – 4.12 (m, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.68 (d, *J* = 161.6 Hz), 146.26 (d, *J* = 24.9 Hz), 142.81 (d, *J* = 2.4 Hz), 142.47 (d, *J* = 18.6 Hz), 132.90 (d, *J* = 2.8 Hz), 132.43 , 132.36, 132.02, 130.71, 130.32 (d, *J* = 0.9 Hz), 129.49 (d, *J* = 1.9 Hz), 129.39 (d, *J* = 140.0 Hz), 128.66, 128.57, 62.29 (d, *J* = 6.3 Hz), 16.56 (d, *J* = 6.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.30; HRMS (m/z) calcd for $C_{16}H_{16}N_2O_2P[M+H]^+$ 299.0945, found 299.0950.



3ap

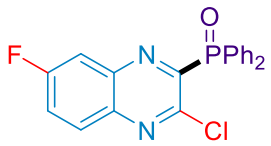
ethyl methyl(quinoxalin-2-yl)phosphinate (3ap). Yield, 67%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.25 – 8.11 (m, 2H), 7.97 – 7.72 (m, 2H), 4.29 – 4.14 (m, 1H), 4.04 – 3.91 (m, 1H), 1.92 (d, *J* = 15.1 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.29 (d, *J* = 152.0 Hz), 145.74 (d, *J* = 23.7 Hz), 143.07 (d, *J* = 2.4 Hz), 142.36 (d, *J* = 18.6 Hz), 132.06 (s), 130.86 (s), 130.07 (d, *J* = 1.0 Hz), 129.57 (d, *J* = 1.9 Hz), 61.63 (d, *J* = 6.5 Hz), 16.42 (d, *J* = 6.3 Hz), 13.67 (d, *J* = 104.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 39.24 (s); HRMS (m/z) calcd for $C_{11}H_{14}N_2O_2P[M+H]^+$ 237.0788, found 237.0797.



3aq

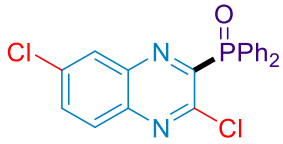
diphenyl quinoxalin-2-ylphosphonate (**3aq**). Yield, 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (s, 1H),

8.34 – 8.28 (m, 1H), 8.20 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.95-7.89 (m, 2H), 7.35 – 7.29 (m, 8H), 7.20 – 7.16 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.03 (d, *J* = 8.0 Hz), 147.00, 145.48, 146.31 (d, *J* = 29.7 Hz), 143.07 (d, *J* = 2.8 Hz), 142.42 (d, *J* = 22.5 Hz), 132.75, 131.22, 130.45 (d, *J* = 1.5 Hz), 129.86 (4), 129.53 (d, *J* = 2.3 Hz), 125.61 (2), 120.78 (2), 120.75 (2).^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 0.96. HRMS (m/z) calcd for $C_{20}H_{16}N_2O_3P[M+H]^+$ 363.0893, found 363.0890.



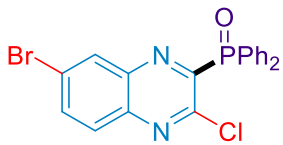
3ca

(3-chloro-7-fluoroquinoxalin-2-yl)diphenylphosphine oxide (3ca). Yield, 47%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 9.2, 5.4 Hz, 1H), 7.79 (dd, *J* = 12.2, 7.6 Hz, 4H), 7.69 – 7.64 (m, 1H), 7.64 – 7.58 (m, 3H), 7.53 (td, *J* = 7.5, 2.7 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.97 (d, *J* = 255.3 Hz), 151.36 (d, *J* = 126.7 Hz), 148.09, 140.66, 140.66, 139.13, 132.71 (d, *J* = 2.3 Hz), 132.14 (2), 132.08 (2), 130.43 (d, *J* = 9.8 Hz), 129.54 (d, *J* = 109.8 Hz), 128.72 (2), 128.64 (2), 123.73 (d, *J* = 26.2 Hz), 113.74 (d, *J* = 21.7 Hz), 110.08 (d, *J* = 209.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 29.46. HRMS (m/z) calcd for $C_{20}H_{14}ClFN_2OP[M+H]^+$ 383.0511, found 383.0510.



3da

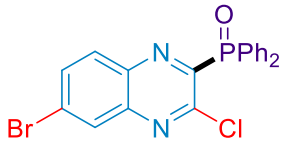
(3,7-dichloroquinoxalin-2-yl)diphenylphosphine oxide (3da). Yield, 81%; ^{1}H NMR (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 2.2 Hz, 1H), 7.83 – 7.75 (m, 5H), 7.61 (td, *J* = 7.5, 1.1 Hz, 2H), 7.52 (td, *J* = 7.7, 3.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.11 (d, *J* = 124.9 Hz), 149.02 (d, *J* = 21.3 Hz), 140.30, 140.03 (d, *J* = 15.8 Hz), 136.66, 134.03 (2), 132.46, 134.44, 132.07 (2), 132.01 (2), 130.22 (d, *J* = 109.2 Hz), 129.46 (d, *J* = 1.6 Hz), 128.87, 128.57 (2), 128.49 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 27.67. HRMS (m/z) calcd for $C_{20}H_{14}Cl_2N_2OP[M+H]^+$ 399.0215, found 399.0210.



3ea

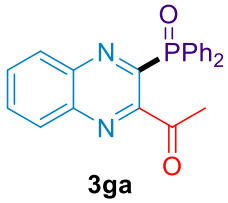
(7-bromo-3-chloroquinoxalin-2-yl)diphenylphosphine oxide (3ea). Yield, 54%;^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.9 Hz, 1H), 7.87 – 7.76 (m, 6H), 7.60 (dd, *J* = 10.7, 4.2 Hz, 2H), 7.51 (td, *J* = 7.7, 3.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.29 (d, *J* = 125.6 Hz), 149.81 (d, *J* = 21.2 Hz), 142.22, 138.63 (d, *J* = 15.7 Hz), 134.36, 132.41 (d, *J* = 2.7 Hz), 132.08 (2), 132.01 (2), 131.23,

130.64, 129.93, 128.56 (2), 128.48 (2), 127.76; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 27.59. HRMS (m/z) calcd for $C_{20}H_{14}BrClN_2OP[M+H]^+$ 442.9710, found 442.9705.



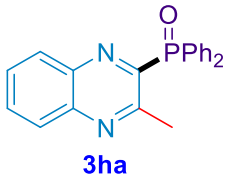
3fa

(6-bromo-3-chloroquinoxalin-2-yl)diphenylphosphine oxide (3fa). Yield, 59%;^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.9 Hz, 1H), 7.87 – 7.76 (m, 6H), 7.60 (dd, *J* = 10.7, 4.2 Hz, 2H), 7.51 (td, *J* = 7.7, 3.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.00 (d, *J* = 125.0 Hz), 149.10 (d, *J* = 21.6 Hz), 140.57, 140.27 (d, *J* = 15.7 Hz), 136.58 (2), 132.48, 132.46, 132.24, 132.08 (2), 132.01 (2), 130.12 (d, *J* = 109.2 Hz), 129.51, 128.60 (2), 128.51 (2), 124.76; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 27.87. HRMS (m/z) calcd for $C_{20}H_{14}BrClN_2OP[M+H]^+$ 442.9710, found 422.9715.



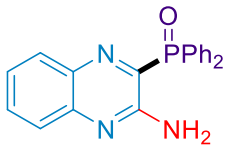
3ga

1-(3-(diphenylphosphoryl)quinoxalin-2-yl)ethan-1-one (**3ga**). Yield, 66%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.87 – 7.81 (m, 5H), 7.54 (td, *J* = 7.4, 1.3 Hz, 2H), 7.50 – 7.44 (m, 4H), 2.84 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.22, 170.15, 152.62 (d, *J* = 19.5 Hz), 149.91 (d, *J* = 122.9 Hz), 140.29 (d, *J* = 16.9 Hz), 139.03, 131.51, 131.34, 131.10 (2), 131.03 (2), 130.89, 130.87, 130.78, 130.62, 129.01, 128.65 (d, *J* = 1.8 Hz), 127.29 (2), 127.20 (2), 26.65; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 24.99. HRMS (m/z) calcd for $C_{22}H_{18}N_2O_2P[M+H]^+$ 373.1100, found 373.1109.



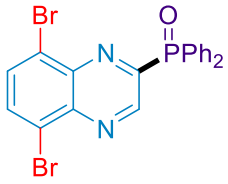
3ha

(3-methylquinoxalin-2-yl)diphenylphosphine oxide (**3ha**). Yield, 35%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.61 (dd, *J* = 11.3, 4.0 Hz, 1H), 7.56 (dd, *J* = 12.0, 7.3 Hz, 4H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.32 (td, *J* = 7.4, 0.9 Hz, 2H), 7.24 (td, *J* = 7.7, 3.0 Hz, 4H), 2.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.89 (d, *J* = 22.9 Hz), 152.42 (d, *J* = 123.5 Hz), 140.40 (d, *J* = 17.5 Hz), 139.24, 132.83, 132.27, 132.25, 132.17 (2), 132.11 (2), 131.16 (d, *J* = 106.2 Hz), 130.15, 130.05, 128.54 (2), 128.46 (2), 127.19, 22.75. ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 27.10. HRMS (m/z) calcd for $C_{21}H_{18}N_2OP[M+H]^+$ 345.1151, found 345.1153.



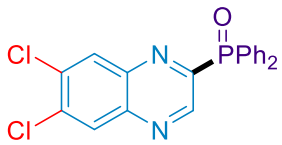
3ia

(3-aminoquinoxalin-2-yl)diphenylphosphine oxide (**3ia**). Yield, 89%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 4H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.59 (td, *J* = 7.4, 1.2 Hz, 2H), 7.50 (td, *J* = 7.7, 3.3 Hz, 4H), 7.43 (ddd, *J* = 8.3, 6.0, 2.3 Hz, 1H); ^{13}C ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.19 (d, *J* = 20.8 Hz), 141.85 (d, *J* = 124.9 Hz), 136.70 (d, *J* = 17.2 Hz), 133.23, 132.63, 132.61, 132.17 (d, *J* = 9.4 Hz), 132.16 (2), 132.10 (2), 130.67 (d, *J* = 106.6 Hz), 129.97, 128.65 (2), 128.57 (2), 125.68, 123.71; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 26.07. HRMS (m/z) calcd for $C_{20}H_{17}N_3OP[M+H]^+$ 346.1104, found 346.1102.



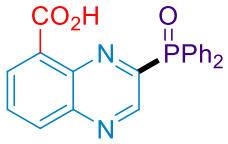
3ja

(5,8-dibromoquinoxalin-2-yl)diphenylphosphine oxide (**3ja**). Yield, 61%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.17 – 8.09 (m, 4H), 8.03 (m, 2H), 7.58 – 7.53 (m, 2H), 7.53 – 7.47 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.31 (d, *J* = 121.2 Hz), 147.44, 147.30, 141.31 (d, *J* = 2.3 Hz), 140.63 (d, *J* = 16.5 Hz), 135.17, 134.11, 132.39, 132.37, 132.13 (2), 132.06 (2), 131.05 (d, *J* = 105.2 Hz), 128.65 (2), 128.57 (2), 125.00, 124.15 (d, *J* = 2.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 17.38. HRMS (m/z) calcd for $C_{20}H_{14}Br_2N_2OP[M+H]^+$ 486.9205, found 486.9200.



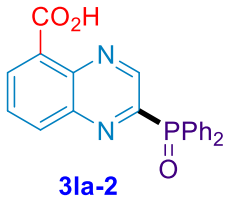
3ka

(6,7-dichloroquinoxalin-2-yl)diphenylphosphine oxide (**3ka**). Yield, 67%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.29 (d, *J* = 6.1 Hz, 2H), 7.96 – 7.85 (m, 4H), 7.61 – 7.53 (m, 2H), 7.50 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.74 (d, *J* = 121.2 Hz), 147.42, 147.28, 141.33 (d, *J* = 1.8 Hz), 140.70 (d, *J* = 17.4 Hz), 136.89, 135.76, 132.52, 132.50, 132.10 (2), 132.04 (2), 130.87 (d, *J* = 105.3 Hz), 130.52, 130.21 (d, *J* = 1.8 Hz), 128.68 (2), 128.60 (2)； ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 17.38. HRMS (m/z) calcd for $C_{20}H_{14}Cl_2N_2OP[M+H]^+$ 399.0215, found 399.0211.



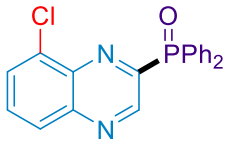
3la-1

3-(diphenylphosphoryl)quinoxaline-5-carboxylic acid (3la-1). Yield, 48%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.41 (s, 1H), 9.78 (s, 1H), 8.88 (d, *J* = 7.2 Hz, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.08 (t, *J* = 7.9 Hz, 1H), 7.81 (dd, *J* = 12.2, 7.7 Hz, 4H), 7.67 (t, *J* = 7.3 Hz, 2H), 7.57 (td, *J* = 7.5, 2.7 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.55 (d, *J* = 113.6 Hz), 147.70 (d, *J* = 19.4 Hz), 143.10, 138.71 (d, *J* = 14.1 Hz), 137.02, 135.10, 133.43, 133.41, 132.38, 132.02 (2), 131.95 (2), 129.33 (2), 129.24 (2), 129.02 (d, *J* = 106.7 Hz), 125.35; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 24.87. HRMS (m/z) calcd for $C_{21}H_{15}N_2O_3P[M+H]^+$ 375.0893, found 375.0899.



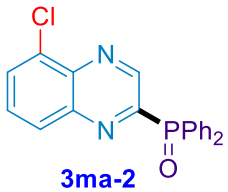
3la-2

2-(diphenylphosphoryl)quinoxaline-5-carboxylic acid (3la-2). Yield, 48%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.95 (dd, *J* = 7.3, 1.0 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.09 – 8.02 (m, 1H), 7.96 (dd, *J* = 12.0, 7.6 Hz, 4H), 7.60 (t, *J* = 7.3 Hz, 2H), 7.52 (td, *J* = 7.6, 2.8 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.55 (d, *J* = 113.6 Hz), 147.70 (d, *J* = 19.4 Hz), 143.10, 138.71 (d, *J* = 14.1 Hz), 137.02, 135.10, 133.43, 133.41, 132.38, 132.02 (2), 131.95 (2), 129.33 (2), 129.24 (2), 129.02 (d, *J* = 106.7 Hz), 125.35; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.26. HRMS (m/z) calcd for $C_{21}H_{15}N_2O_3P[M+H]^+$ 375.0893, found 375.0897.



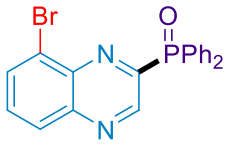
3ma-1

(8-chloroquinoxalin-2-yl)diphenylphosphine oxide (**3ma-1**). Yield, 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.10 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.97 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.96 – 7.91 (m, 4H), 7.76 (dd, *J* = 8.4, 7.6 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.49 (ddd, *J* = 7.4, 4.0, 2.4 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.44 (d, *J* = 122.2 Hz), 146.73 (d, *J* = 22.1 Hz), 143.07 (d, *J* = 17.0 Hz), 139.50 (d, *J* = 2.4 Hz), 133.60 (d, *J* = 2.3 Hz), 132.45, 132.43, 132.17 (2), 132.10 (2), 131.72, 131.04 (d, *J* = 105.2 Hz), 130.42, 129.28, 128.65 (2), 128.57 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.56. HRMS (m/z) calcd for $C_{20}H_{15}ClN_2OP[M+H]^+$ 365.0605, found 365.0600.



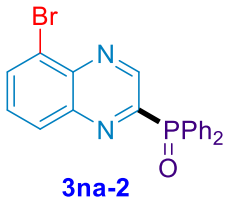
3ma-2

(5-chloroquinoxalin-2-yl)diphenylphosphine oxide (**3ma-2**). Yield, 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.12 (ddd, *J* = 11.0, 9.1, 4.1 Hz, 5H), 7.94 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.79 (dd, *J* = 8.3, 7.8 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.52 – 7.46 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.90 (d, *J* = 123.2 Hz), 146.82 (d, *J* = 21.5 Hz), 143.59 (d, *J* = 2.2 Hz), 138.97 (d, *J* = 16.6 Hz), 134.36, 132.29, 132.27, 132.09 (2), 132.03 (2), 131.60, 131.35 (d, *J* = 104.8 Hz), 130.57, 128.65 (d, *J* = 1.7 Hz), 128.61 (2), 128.53 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 17.65. HRMS (m/z) calcd for $C_{20}H_{15}ClN_2OP[M+H]^+$ 365.0605, found 365.0607.



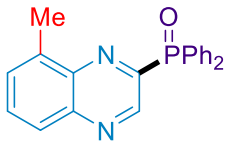
3na-1

(8-bromoquinoxalin-2-yl)diphenylphosphine oxide (3na-1). Yield, 91%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.18 (dd, *J* = 7.5, 1.1 Hz, 1H), 8.14 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.96 – 7.90 (m, 4H), 7.69 (dd, *J* = 8.3, 7.7 Hz, 1H), 7.57 (td, *J* = 7.4, 1.2 Hz, 2H), 7.49 (td, *J* = 7.6, 3.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.39 (d, *J* = 122.3 Hz), 147.00 (d, *J* = 22.2 Hz), 143.13 (d, *J* = 17.1 Hz), 140.40 (d, *J* = 2.2 Hz), 135.30, 132.46, 132.44, 132.17 (2), 132.10 (2), 131.01 (d, *J* = 105.3 Hz), 130.99, 130.04, 128.66 (2), 128.58 (2), 124.51 (d, *J* = 2.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.58. HRMS (m/z) calcd for $C_{20}H_{15}BrN_2OP[M+H]^+$ 409.0100, found 409.0110.



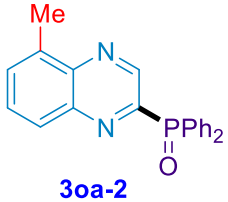
3na-2

(5-bromoquinoxalin-2-yl)diphenylphosphine oxide (3na-2). Yield, 91%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.16 (dt, *J* = 10.3, 4.7 Hz, 6H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.55 (td, *J* = 7.4, 1.3 Hz, 2H), 7.50 (ddd, *J* = 7.2, 5.4, 2.6 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.13 (d, *J* = 124.0 Hz), 146.77 (d, *J* = 21.4 Hz), 143.65, 139.85 (d, *J* = 16.6 Hz), 134.14, 132.32, 132.30, 132.17, 132.13 (2), 132.07(2), 131.21 (d, *J* = 104.9 Hz), 129.40, 128.63 (2), 128.55 (2), 125.41; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 17.48. HRMS (m/z) calcd for $C_{20}H_{15}BrN_2OP[M+H]^+$ 409.0100, found 409.0108.



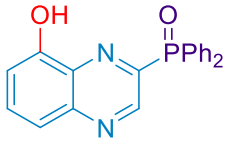
3oa-1

(8-methylquinoxalin-2-yl)diphenylphosphine oxide (**3oa-1**) Yield, 88%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.99 (dd, *J* = 7.6, 2.1 Hz, 1H), 7.98 – 7.92 (m, 4H), 7.74 – 7.68 (m, 2H), 7.55 (td, *J* = 7.4, 1.2 Hz, 2H), 7.48 (td, *J* = 7.6, 3.0 Hz, 4H), 2.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.56 (d, *J* = 124.9 Hz), 145.12 (d, *J* = 22.3 Hz), 142.43 (d, *J* = 17.0 Hz), 141.71, 138.02, 132.26, 132.25, 132.17 (2), 132.11 (2), 131.87, 131.80, 131.10, 130.51, 128.56 (2), 128.48 (2), 128.04, 17.29; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.71; HRMS (m/z) calcd for $C_{21}H_{18}N_2OP[M+H]^+$ 345.1151, found 345.1148.



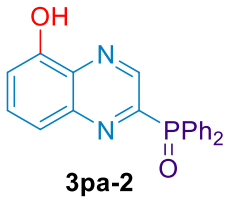
3oa-2

(5-methylquinoxalin-2-yl)diphenylphosphine oxide (3oa-2). Yield, 88%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 8.03 – 7.93 (m, 4H), 7.83 – 7.75 (m, 1H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.56 (td, *J* = 7.4, 1.3 Hz, 2H), 7.52 – 7.44 (m, 4H), 2.75 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.98 (d, *J* = 125.6 Hz), 145.10 (d, *J* = 22.4 Hz), 141.62 (d, *J* = 16.4 Hz), 138.57, 132.37, 132.29, 132.27, 132.12 (2), 132.06 (2), 131.46 (d, *J* = 104.9 Hz), 130.95, 128.54 (2), 128.46 (2), 126.78, 126.78, 17.11; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.20; HRMS (m/z) calcd for $C_{21}H_{18}N_2OP[M+H]^+$ 345.1151, found 345.1147.



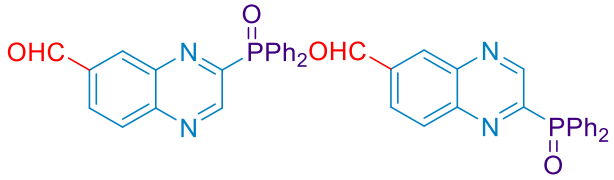
3pa-1

(8-hydroxyquinoxalin-2-yl)diphenylphosphine oxide (3pa-1). Yield, 60%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.00 – 7.93 (m, 4H), 7.77 – 7.72 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.49 (td, *J* = 7.6, 3.0 Hz, 4H), 7.33 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.13 (d, *J* = 124.4 Hz), 152.11, 143.75 (d, *J* = 22.6 Hz), 142.62 (d, *J* = 17.4 Hz), 132.41, 132.40, 132.15 (2), 132.08 (2), 131.99, 131.46, 130.76, 128.63 (2), 128.55 (2), 120.45, 112.77; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.73; HRMS (m/z) calcd for $C_{20}H_{16}N_2O_2P[M+H]^+$ 347.0944, found 347.0945.



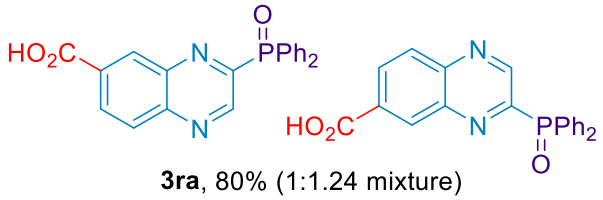
3pa-2

(5-hydroxyquinoxalin-2-yl)diphenylphosphine oxide (3pa-2). Yield, 60%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.82 (dt, *J* = 7.7, 7.0 Hz, 5H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 2H), 7.52 (td, *J* = 7.6, 2.9 Hz, 4H), 7.29 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.36, 149.14 (d, *J* = 122.1 Hz), 147.12 (d, *J* = 22.0 Hz), 143.00, 133.80, 132.71 (d, *J* = 2.4 Hz), 132.15 (2), 132.08 (2), 130.62 (d, *J* = 105.5 Hz), 128.93, 128.83 (2), 128.75 (2), 119.91, 112.02 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 23.42; HRMS (m/z) calcd for $C_{20}H_{16}N_2O_2P[M+H]^+$ 347.0944, found 347.0947.



3qa, 80% (1:1 mixture)

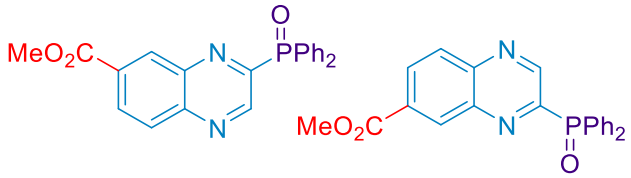
2 or 3-(diphenylphosphoryl)quinoxaline-6-carbaldehyde (3qa). Yield, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.29 (s, 1H), 9.75 (s, 1H), 8.65 (s, 1H)8.37 – 8.23 (m, 2H), 7.97 (dd, *J* = 11.9, 7.8 Hz, 4H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.51 (dd, *J* = 9.8, 4.9 Hz, 4H); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.27 (s, 1H), 9.75 (s, 1H), 8.64 (s, 1H)8.37 – 8.23 (m, 2H), 7.97 (dd, *J* = 11.9, 7.8 Hz, 4H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.51 (dd, *J* = 9.8, 4.9 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.98, 190.83, 148.51 (d, *J* = 21.5 Hz), 147.55 (d, *J* = 21.7 Hz), 145.43, 144.79 (d, *J* = 16.9 Hz), 142.48 (d, *J* = 2.1 Hz), 141.84 (d, *J* = 16.9 Hz), 138.27, 137.53, 135.21, 135.10, 132.60, 132.58, 132.17 (2), 132.15 (2), 132.10 (2), 132.09 (2), 131.46, 131.12, 131.06, 130.42, 130.37, 128.73 (2), 128.65 (2), 127.32; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.73 or 20.63; HRMS (m/z) calcd for $C_{21}H_{16}N_2O_2P[M+H]^+$ 359.0944, found 359.0948.



3ra, 80% (1:1.24 mixture)

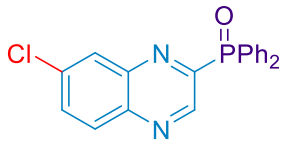
2 or 3-(diphenylphosphoryl)quinoxaline-6-carboxylic acid (3ra). Yield, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.94 (d, *J* = 1.7 Hz, 1H), 8.48 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.03 – 7.95 (m, 4H), 7.58 (dd, *J* = 10.4, 4.4 Hz, 2H), 7.51 (td, *J* = 7.6, 3.1 Hz, 4H) or ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.95 (d, *J* = 1.7 Hz, 1H), 8.44 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.04 – 7.94 (m, 4H), 7.58 (dd, *J* = 10.4, 4.4 Hz, 2H), 7.51 (td, *J* = 7.6, 3.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.21, 168.31, 154.33 (d, *J* = 122.4 Hz), 153.52 (d, *J* = 123.2 Hz), 147.95 (d, *J* = 21.5 Hz), 147.22 (d, *J* = 22.0 Hz), 144.45, 144.03 (d, *J* = 17.3 Hz), 141.89, 141.41 (d, *J* = 17.3 Hz), 133.46, 132.86, 132.62, 132.21, 132.17, 132.15, 132.11, 131.97, 131.69, 131.20 (d, *J* = 10.9 Hz), 130.89 (d,

J = 9.0 Hz), 130.49, 130.47, 130.18 (d, *J* = 8.9 Hz), 129.94, 128.74, 128.66; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 21.44 or 21.07; HRMS (m/z) calcd for $C_{21}H_{16}N_2O_3P[M+H]^+$ 375.0893, found 375.0890.



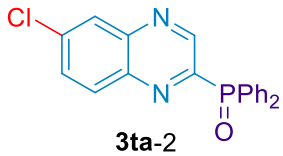
3sa, 80% (1:7.6 mixture)

methyl 2 or 3-(diphenylphosphoryl)quinoxaline-6-carboxylate (3sa). Yield, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.87 (d, *J* = 1.6 Hz, 1H), 8.40 (dd, *J* = 8.8, 1.7 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.97 (dt, *J* = 11.1, 7.0 Hz, 4H), 7.57 (dd, *J* = 10.7, 4.1 Hz, 2H), 7.50 (td, *J* = 7.6, 3.0 Hz, 4H), 4.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.82, 154.50 (d, *J* = 121.6 Hz), 147.22 (d, *J* = 21.8 Hz), 143.85 (d, *J* = 17.0 Hz), 141.94, 133.00, 132.49, 132.48, 132.19, 132.16, 132.10, 131.28, 130.58, 130.44, 130.17, 128.68, 128.60, 52.84; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.54 or 20.24; HRMS (m/z) calcd for $C_{22}H_{18}N_2O_3P[M+H]^+$ 389.1050, found 389.1055.



3ta-1

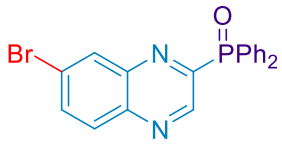
(7-chloroquinoxalin-2-yl)diphenylphosphine oxide (3ta-1). Yield, 98%; ^{1}H NMR (600 MHz, $CDCl_3$) δ9.61 (s, 1H), 8.18 (d, *J* = 2.2 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.95 – 7.90 (m, 4H), 7.77 (dd, *J* = 9.0, 2.2 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.50 (td, *J* = 7.6, 3.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ152.26 (d, *J* = 123.9 Hz), 147.18 (d, *J* = 22.0 Hz), 142.86, 140.71 (d, *J* = 16.8 Hz), 138.20, 132.55, 132.53, 132.15 (2), 132.08 (2), 132.03, 131.37, 131.24, 131.14 (d, *J* = 8.5 Hz), 130.41, 128.70 (2), 128.62 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 21.42. HRMS (m/z) calcd for $C_{20}H_{15}ClN_2OP[M+H]^+$ 365.0605, found 365.0609.



3ta-2

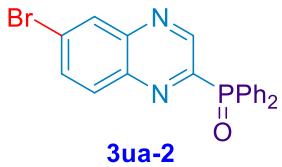
(6-chloroquinoxalin-2-yl)diphenylphosphine oxide (3ta-2). Yield, 98%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.17 (d, *J* = 2.3 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.98 – 7.90 (m, 4H), 7.80 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.57 (td, *J* = 7.4, 1.3 Hz, 2H), 7.52 – 7.46 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.51 (d, *J* = 122.5 Hz), 146.43 (d, *J* = 21.8 Hz), 142.34 (d, *J* = 17.3 Hz), 141.05, 136.83, 133.04, 132.45, 132.43, 132.12 (2), 132.06 (2), 131.38, 130.82 (d, *J* = 1.8 Hz), 130.68, 128.90, 128.65 (2), 128.57 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.48. HRMS (m/z) calcd for $C_{20}H_{15}ClN_2OP[M+H]^+$

365.0605, found 365.0608.



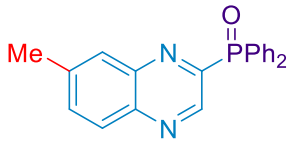
3ua-1

(7-bromoquinoxalin-2-yl)diphenylphosphine oxide (3ua-1). Yield, 98%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.37 (d, *J* = 2.1 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.97 – 7.87 (m, 5H), 7.57 (td, *J* = 7.4, 1.2 Hz, 2H), 7.49 (td, *J* = 7.6, 3.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.73 (d, *J* = 123.1 Hz), 147.18 (d, *J* = 21.9 Hz), 143.06, 140.93 (d, *J* = 17.1 Hz), 134.49, 132.43, 132.41, 132.14 (2), 132.08 (2), 131.91 (d, *J* = 1.6 Hz), 131.38, 131.10 (d, *J* = 105.3 Hz), 128.65 (2), 128.56 (2), 126.45； ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.60. HRMS (m/z) calcd for $C_{20}H_{15}BrN_2OP[M+H]^+$ 409.0100, found 409.0109.



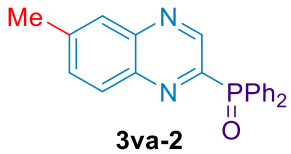
3ua-2

(6-bromoquinoxalin-2-yl)diphenylphosphine oxide (3ua-2). Yield, 98%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.94 (ddd, *J* = 9.0, 5.6, 4.5 Hz, 4H), 7.57 (td, *J* = 7.4, 1.2 Hz, 2H), 7.52 – 7.44 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.45 (d, *J* = 122.4 Hz), 146.61 (d, *J* = 21.7 Hz), 142.56 (d, *J* = 17.3 Hz), 141.36, 135.50, 132.44, 132.42, 132.31, 132.12 (2), 132.05 (2), 131.06 (d, *J* = 105.2 Hz), 130.90, 128.64 (2), 128.56 (2), 125.00； ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.41. HRMS (m/z) calcd for $C_{20}H_{15}BrN_2OP[M+H]^+$ 409.0100, found 409.0105.



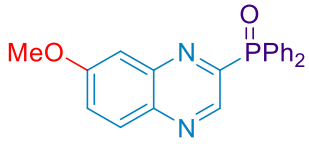
3va-1

(7-methylquinoxalin-2-yl)diphenylphosphine oxide (3va-1). Yield, 95%; ^{1}H ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.95 (m, 5H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 4H), 2.63 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.07 (d, *J* = 318.0 Hz), 146.40 (d, *J* = 22.4 Hz), 143.08, 142.88 (d, *J* = 62.2 Hz), 133.17, 132.22 (2), 132.16 (2), 132.10 (2), 129.72, 128.55 (2), 128.47 (2), 128.26, 29.70; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 19.00; HRMS (m/z) calcd for $C_{21}H_{18}N_2OP[M+H]^+$ 345.1151, found 345.1155.



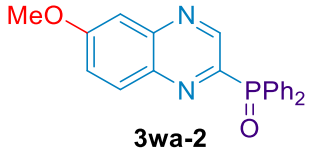
3va-2

(6-methylquinoxalin-2-yl)diphenylphosphine oxide (3va-2). Yield, 95%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 8.00 – 7.89 (m, 5H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.56 (dd, *J* = 10.6, 4.3 Hz, 2H), 7.48 (td, *J* = 8.0, 2.9 Hz, 4H), 2.61 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.22 (d, *J* = 124.8 Hz), 144.81 (d, *J* = 22.4 Hz), 142.52 (d, *J* = 17.1 Hz), 141.86, 140.29, 134.76, 132.29, 132.27, 132.12 (2), 132.06 (2), 131.34 (d, *J* = 105.0 Hz), 128.86, 128.56 (3), 128.48 (2), 116.35, 21.84; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 18.80; HRMS (m/z) calcd for $C_{21}H_{18}N_2OP[M+H]^+$ 345.1151, found 345.1150.



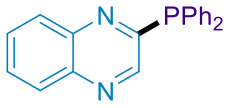
3wa-1

(7-methoxyquinoxalin-2-yl)diphenylphosphine oxide (3wa-1). Yield, 98%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.93 (dd, *J* = 11.8, 7.9 Hz, 4H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 5.9 Hz, 5H), 7.37 (s, 1H), 3.96 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.32, 151.70 (d, *J* = 125.1 Hz), 144.02 (d, *J* = 17.9 Hz), 143.88 (d, *J* = 22.7 Hz), 138.95 (d, *J* = 2.1 Hz), 132.25, 132.23, 132.13 (2), 132.07 (2), 131.38 (d, *J* = 104.8 Hz), 130.34 (d, *J* = 1.8 Hz), 128.55 (2), 128.46 (2), 125.92, 106.80, 55.94; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 19.40; HRMS (m/z) calcd for $C_{21}H_{18}N_2O_2P[M+H]^+$ 361.1100, found 361.1105.



3wa-2

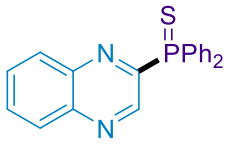
(6-methoxyquinoxalin-2-yl)diphenylphosphine oxide (3wa-2). Yield, 98%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.98 – 7.90 (m, 4H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.51 – 7.45 (m, 6H), 4.00 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.68, 146.08 (d, *J* = 23.1 Hz), 144.03, 132.23 (2), 132.17 (2), 132.11 (2), 131.29, 128.57 (2), 128.49 (2), 124.91, 105.98, 56.18; ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 19.17; HRMS (m/z) calcd for $C_{21}H_{18}N_2O_2P[M+H]^+$ 361.1100, found 361.1102.



6

2-(diphenylphosphaneyl)quinoxaline (6). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.25 (dd, *J* = 8.3, 0.9 Hz, 1H), 8.19 (dd, *J* = 8.3, 0.8 Hz, 1H), 8.00 – 7.93 (m, 4H), 7.93 – 7.88 (m, 1H), 7.88 – 7.83

(m, 1H), 7.57 (td, *J* = 7.4, 1.2 Hz, 2H), 7.49 (td, *J* = 7.6, 3.1 Hz, 4H).^{13}C NMR (151 MHz, $CDCl_3$) δ 152.63 (d, *J* = 124.0 Hz), 145.55 (d, *J* = 22.3 Hz), 142.49 (d, *J* = 17.0 Hz), 141.58, 132.40 (2), 132.38, 132.17 (2), 132.10 (2), 131.53, 131.05, 130.83, 130.26, 129.07, 128.63 (2), 128.55 (2). ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 20.48. HRMS (m/z) calcd for $C_{20}H_{16}N_2P[M+H]^+$ 315.1046, found 315.1045.



7

diphenyl(quinoxalin-2-yl)phosphine sulfide (7). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 8.14 – 8.09 (m, 1H), 8.00 – 7.93 (m, 4H), 7.92 – 7.87 (m, 1H), 7.86 – 7.81 (m, 1H), 7.56 – 7.52 (m, 2H), 7.50 – 7.44 (m, 4H); ^{13}C ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.84 (d, *J* = 104.7 Hz), 146.01 (d, *J* = 27.8 Hz), 141.51 (d, *J* = 16.2 Hz), 141.07, 132.53 (2), 132.46 (2), 132.36, 131.94, 131.92, 131.69, 131.12, 131.05, 130.23 (d, *J* = 1.3 Hz), 128.97 (d, *J* = 2.1 Hz), 128.54 (2), 128.45 (2); ^{31}P NMR (243 MHz, $CDCl_3$): δ (ppm) 35.74. HRMS (m/z) calcd for $C_{20}H_{16}N_2PS[M+H]^+$ 347.0766, found 347.0765.

3. NMR spectrum of **3**, **6** and **7**

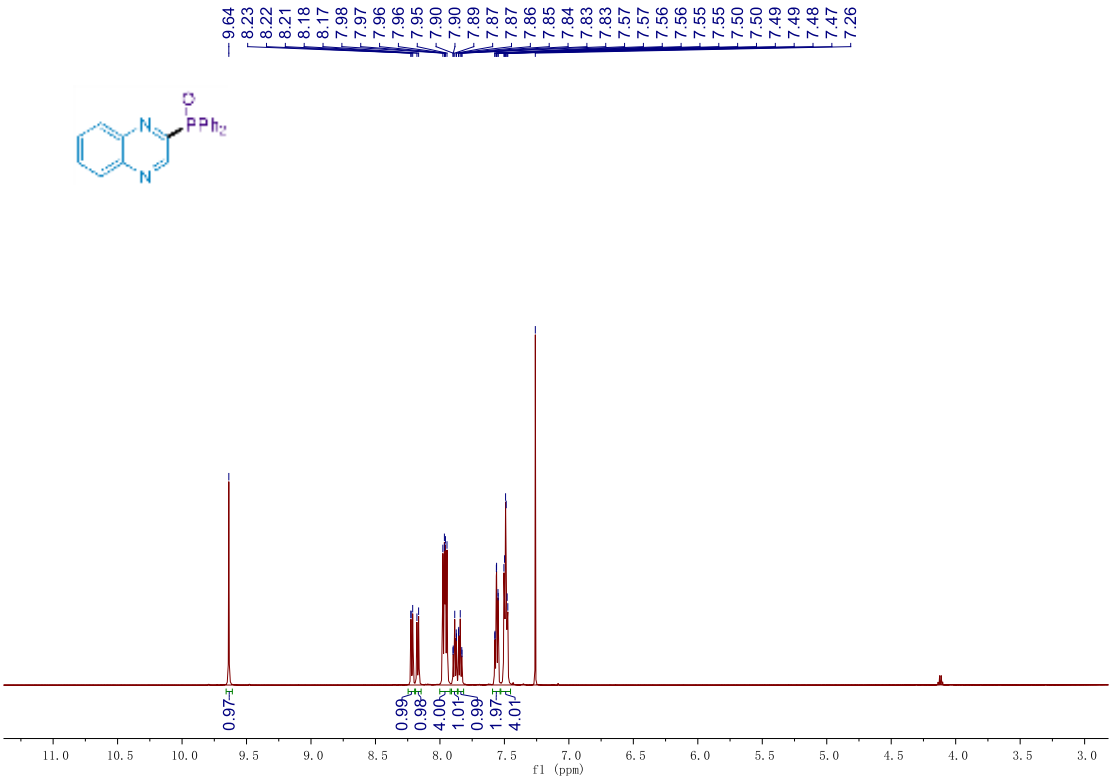


Fig.S 1 ^{1}H NMR of compound **3aa**

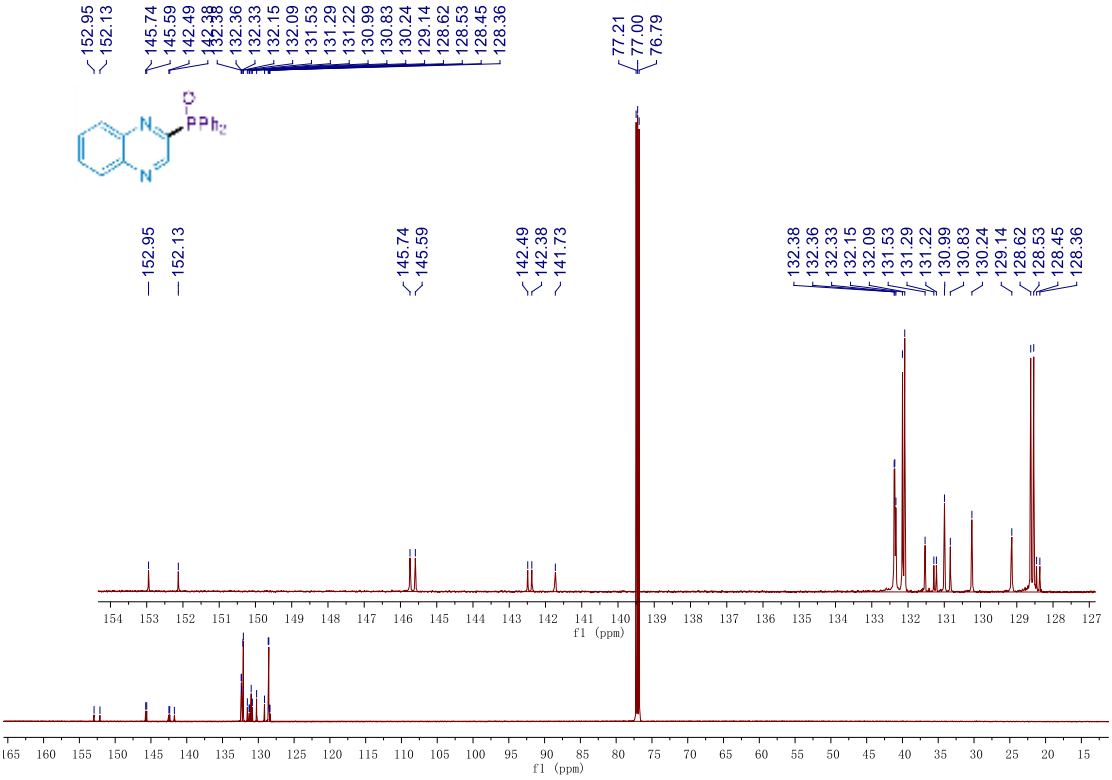


Fig.S 2 ^{13}C NMR of compound **3aa**

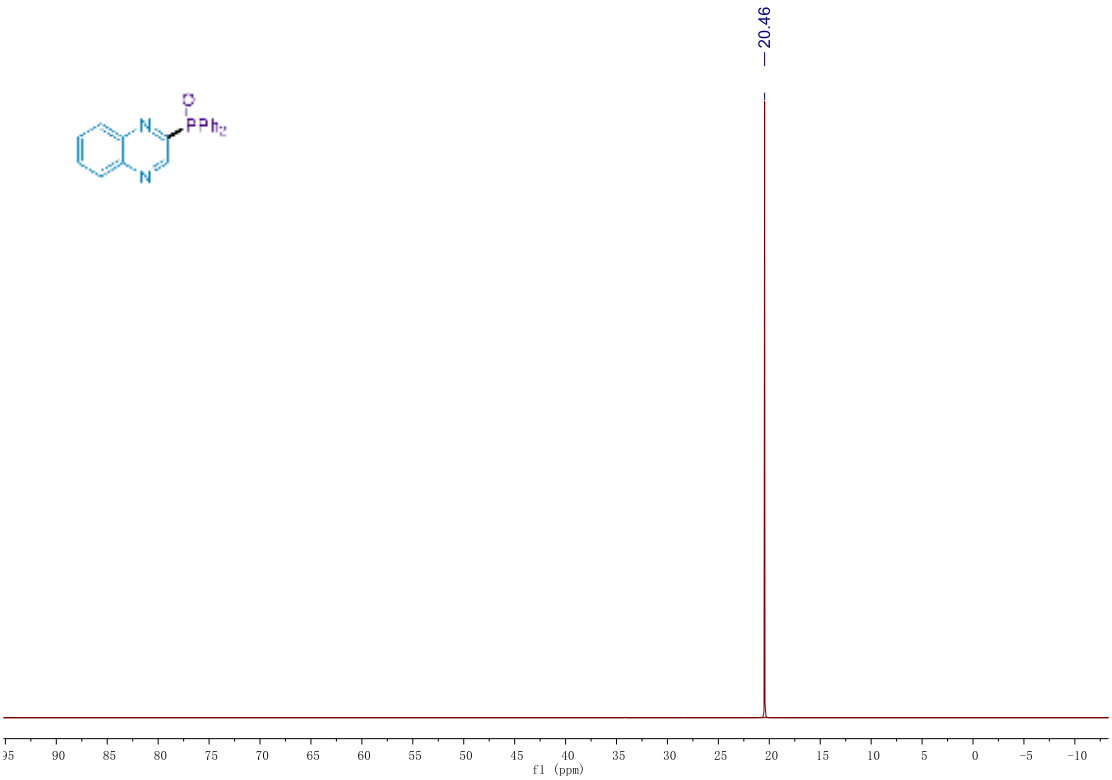


Fig.S 3 ^{31}P NMR of compound **3aa**

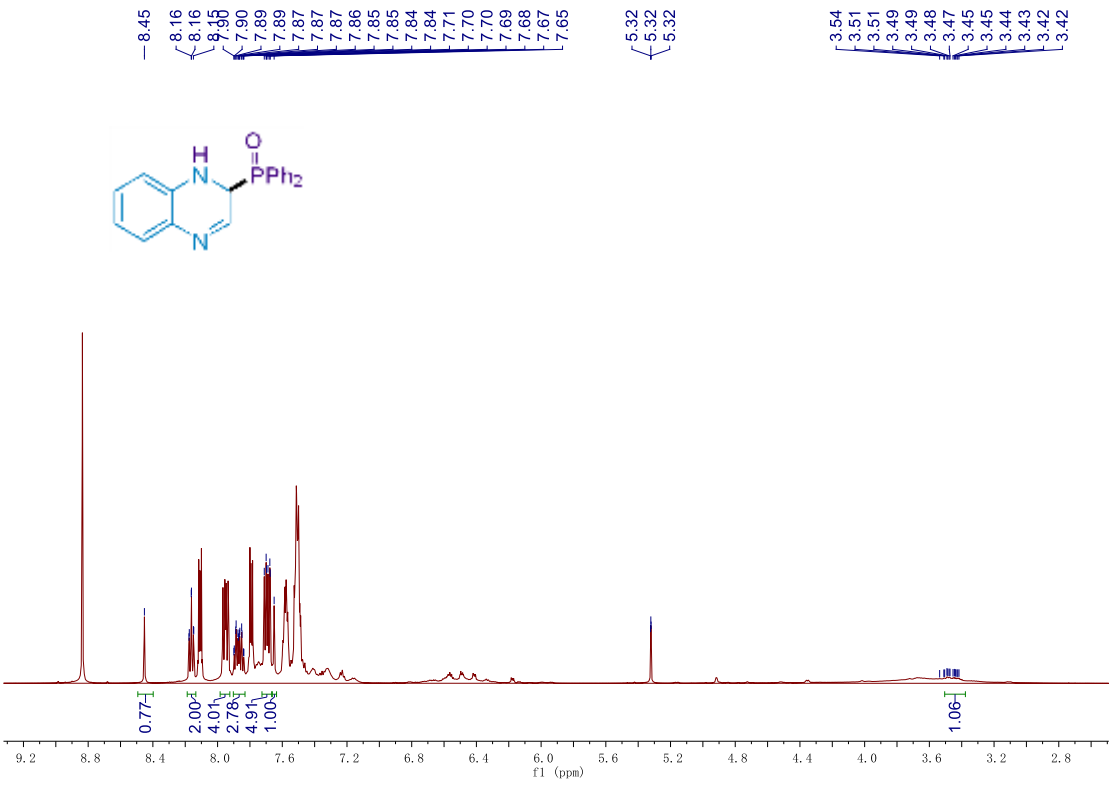


Fig.S 4 ^{1}H NMR of compound **3aa'**

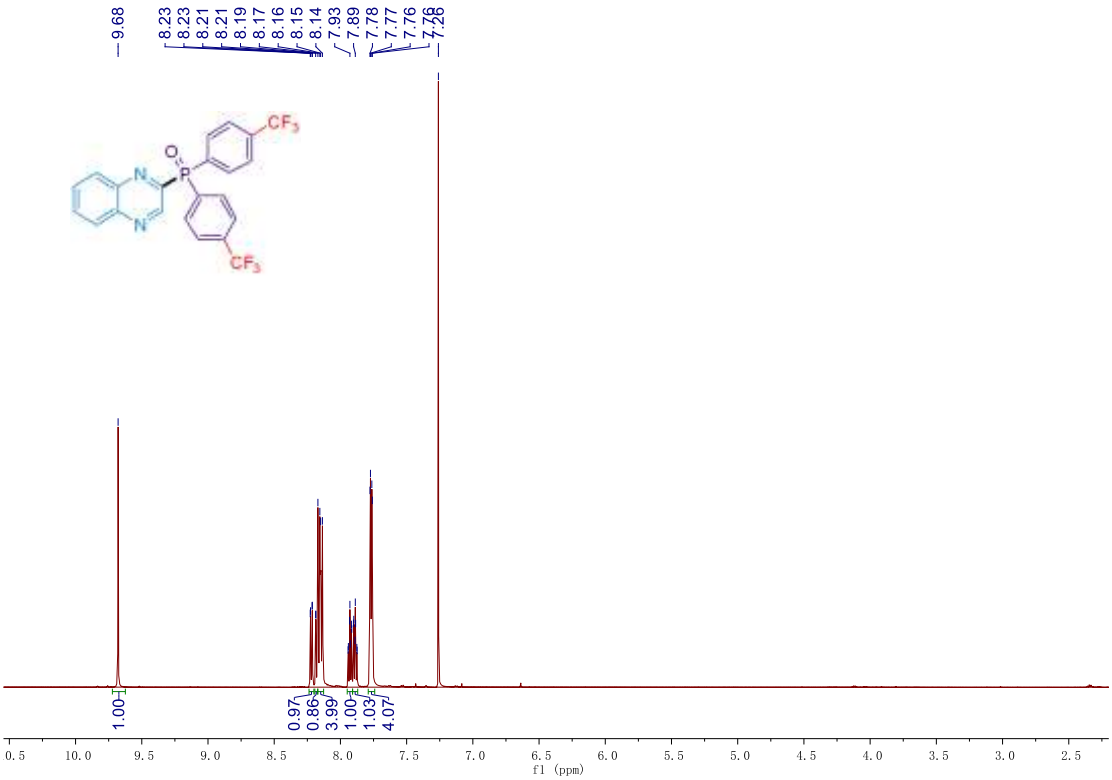


Fig.S 5 ^{1}H NMR of compound **3ab**

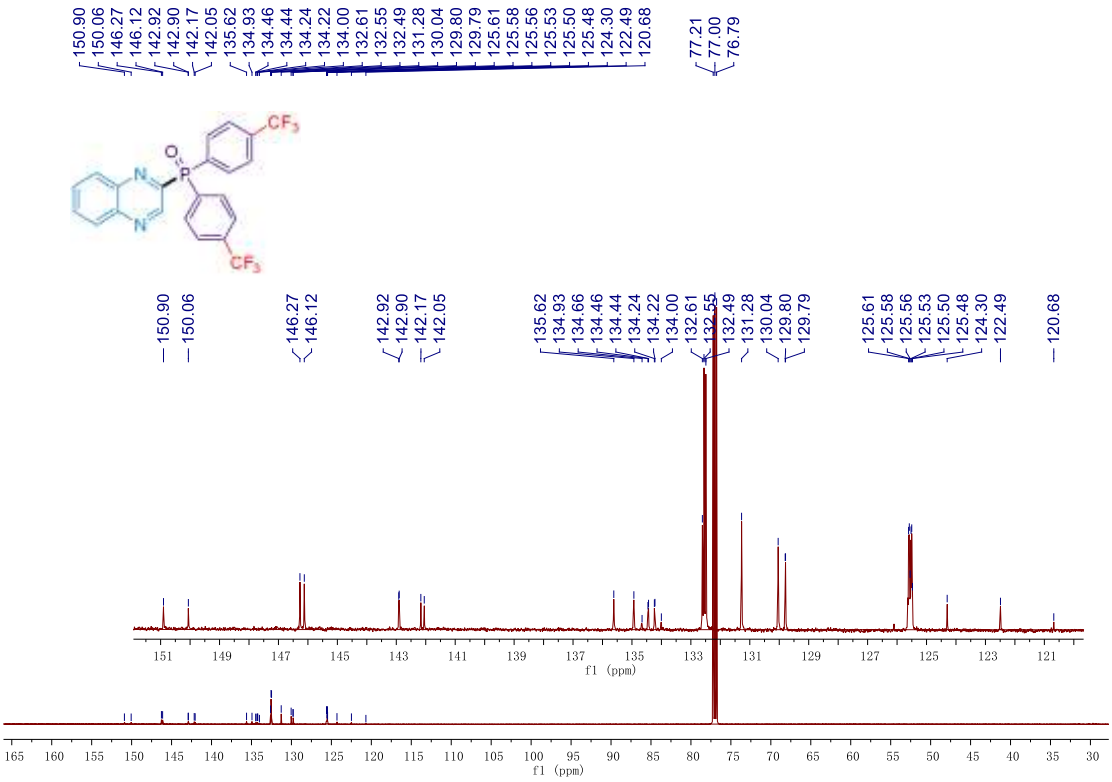


Fig.S 6 ^{13}C NMR of compound **3ab**

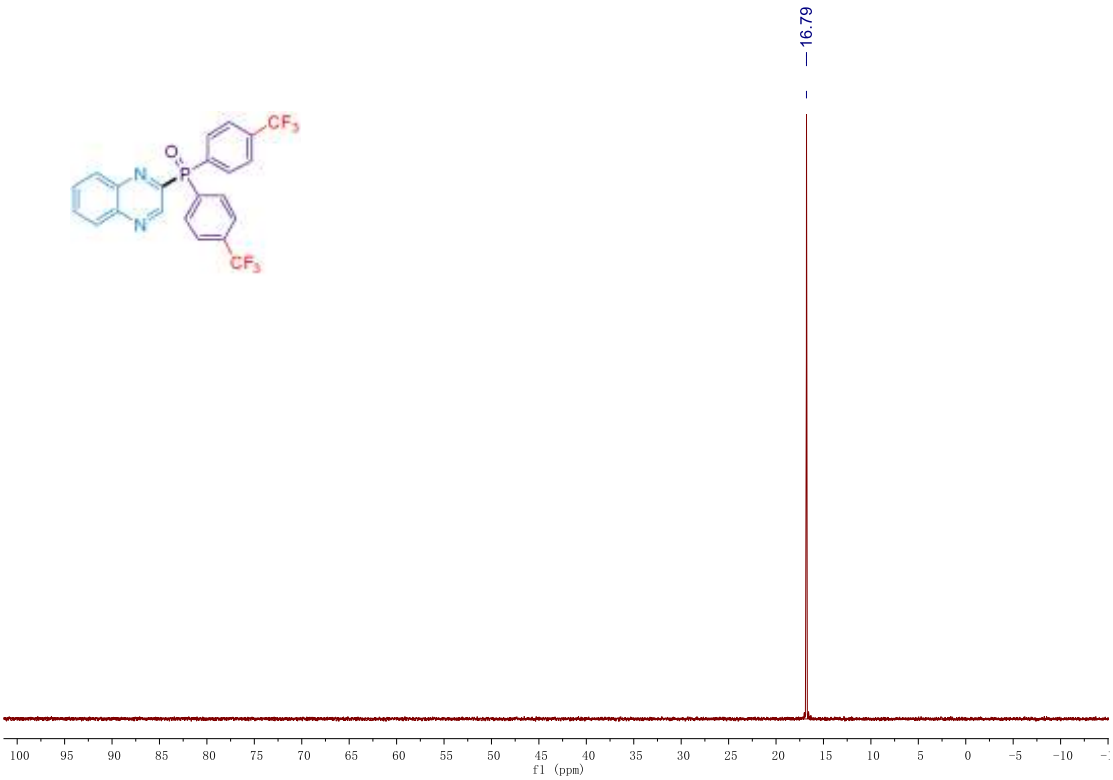


Fig.S 7 ^{31}P NMR of compound **3ab**

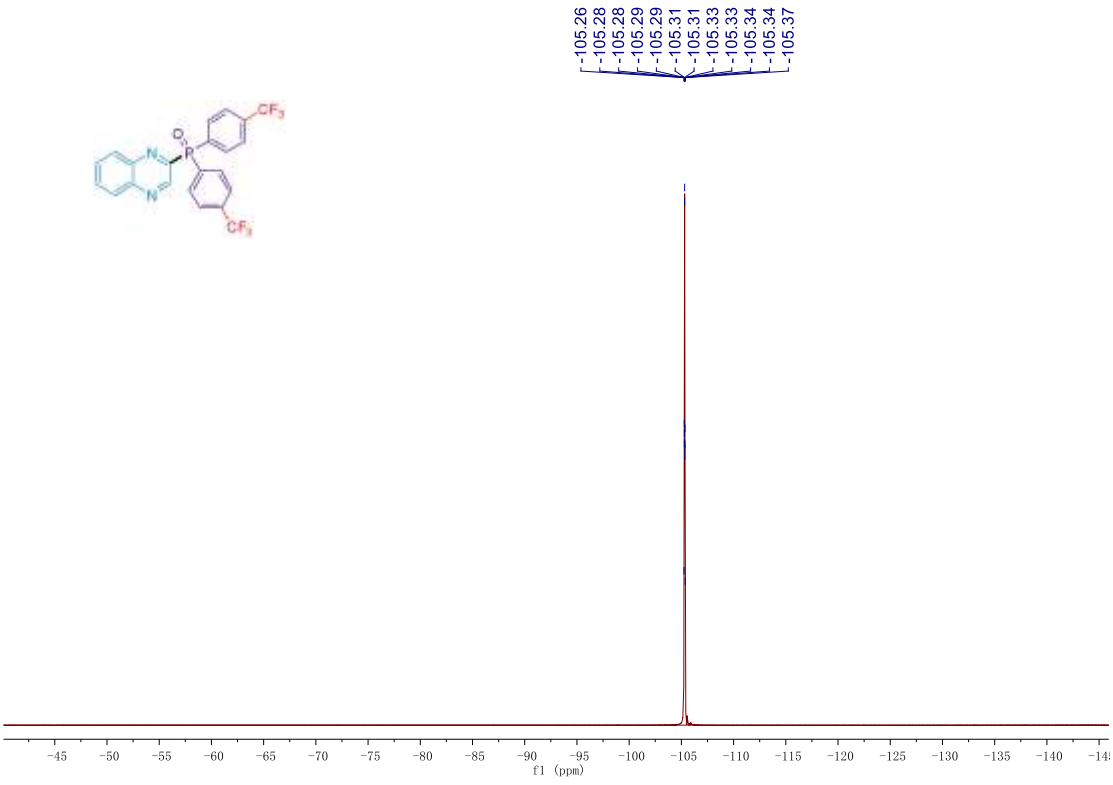


Fig.S 8 ^{19}F NMR of compound **3ab**

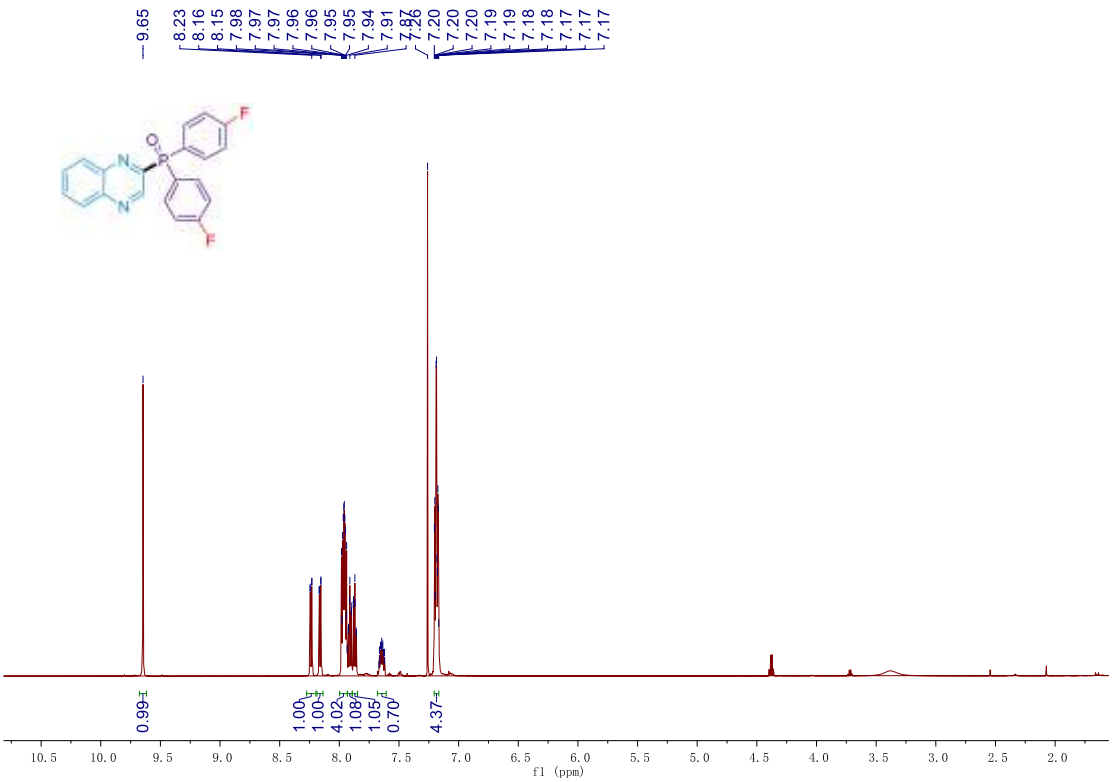


Fig.S 9 ^{1}H NMR of compound **3ac**

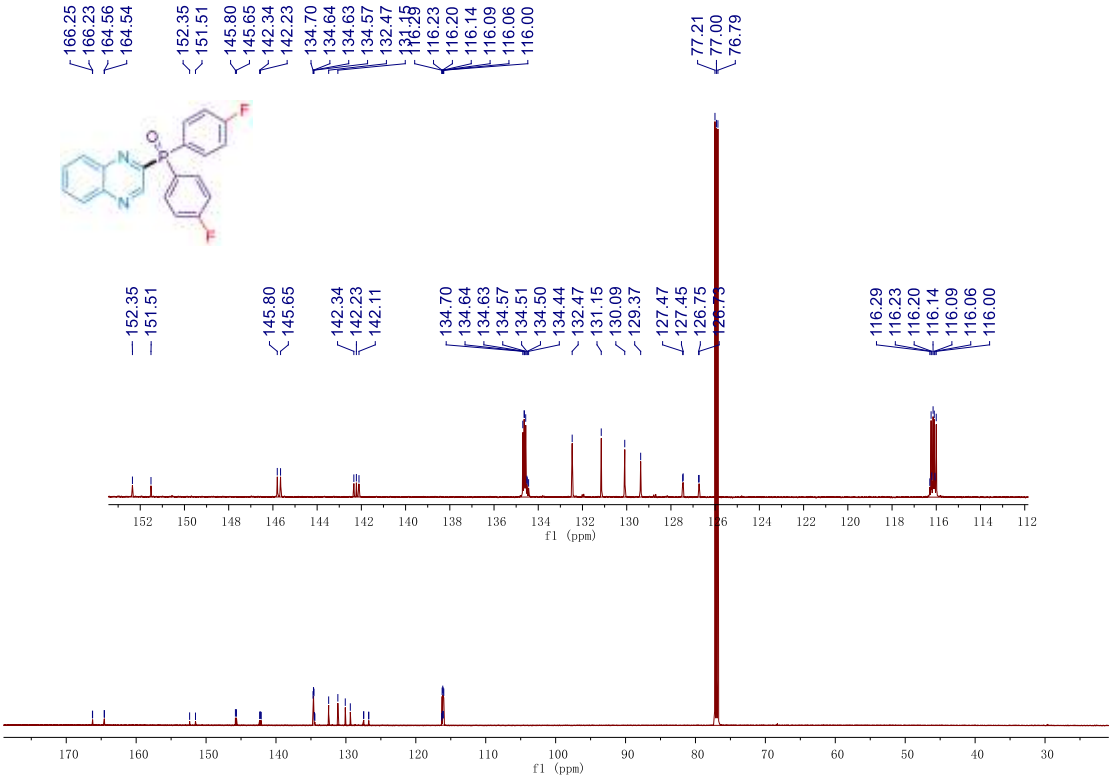


Fig.S 10 ^{13}C NMR of compound **3ac**

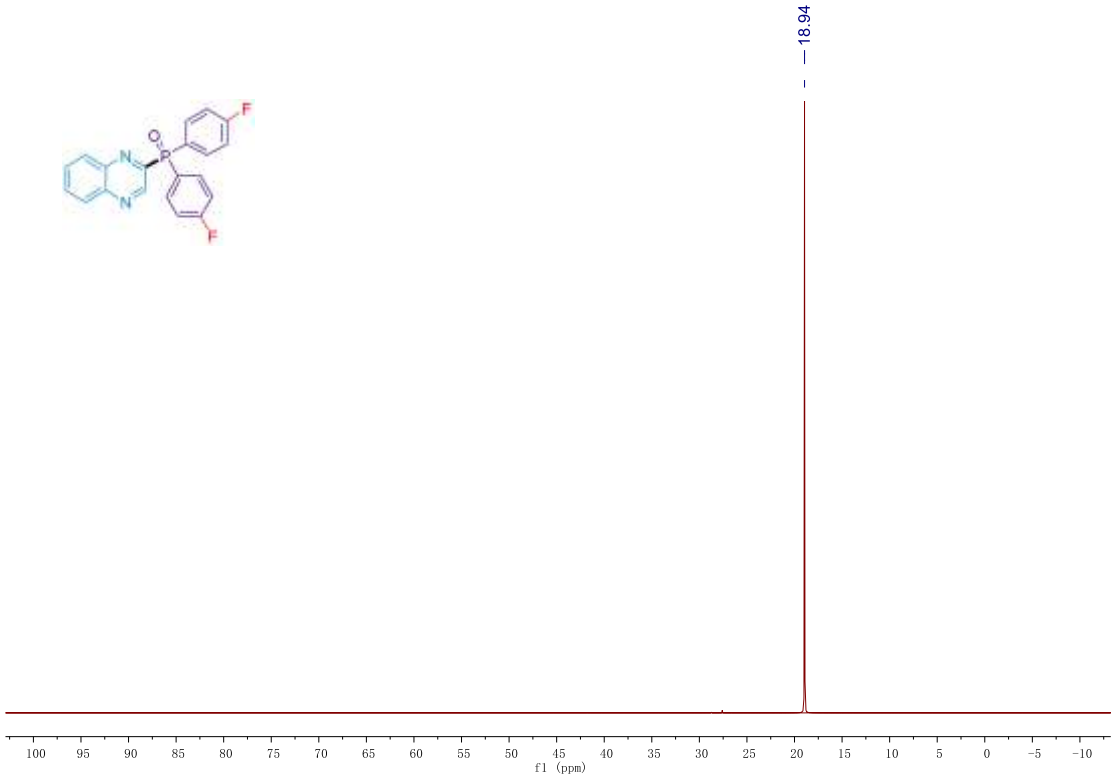


Fig.S 11 ^{31}P NMR of compound **3ac**

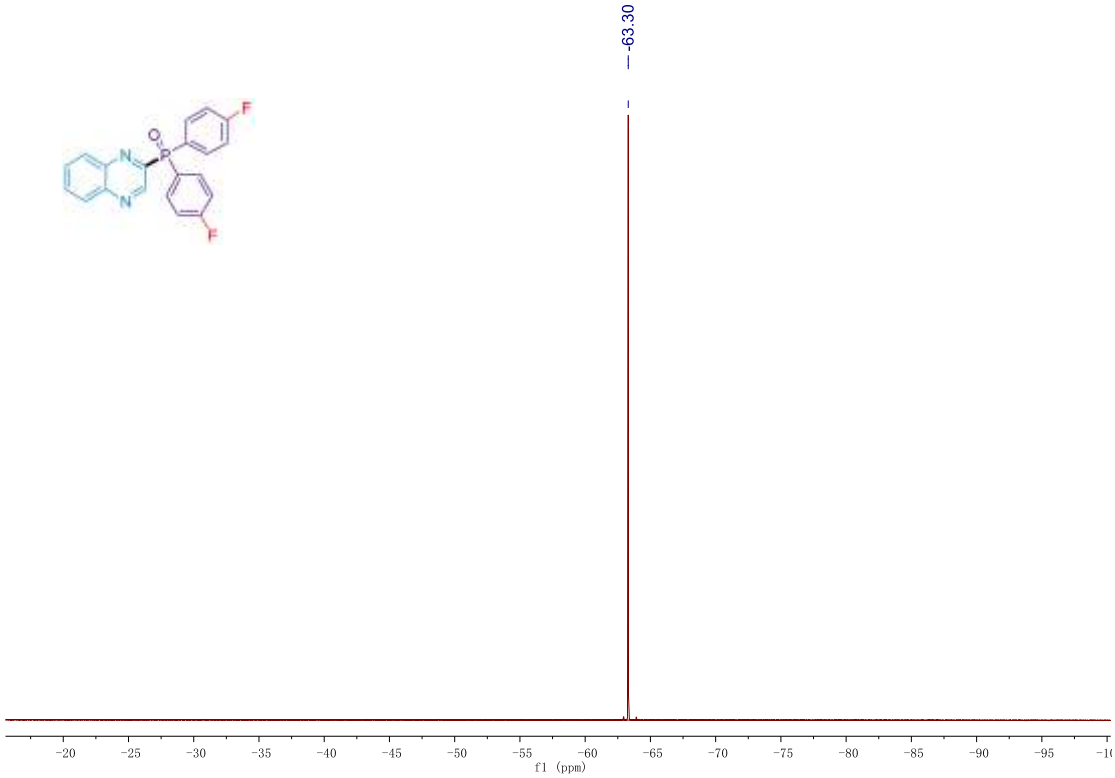


Fig.S 12 ^{19}F NMR of compound **3ac**

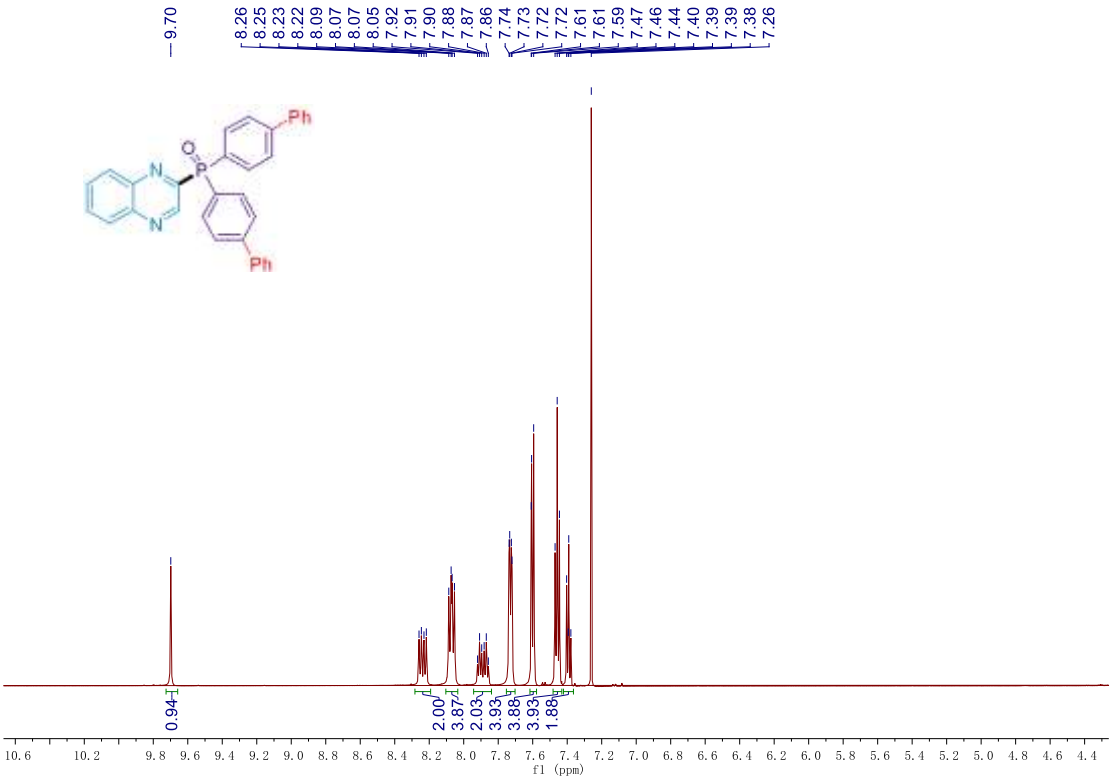


Fig.S 13 ^{1}H NMR of compound **3ad**

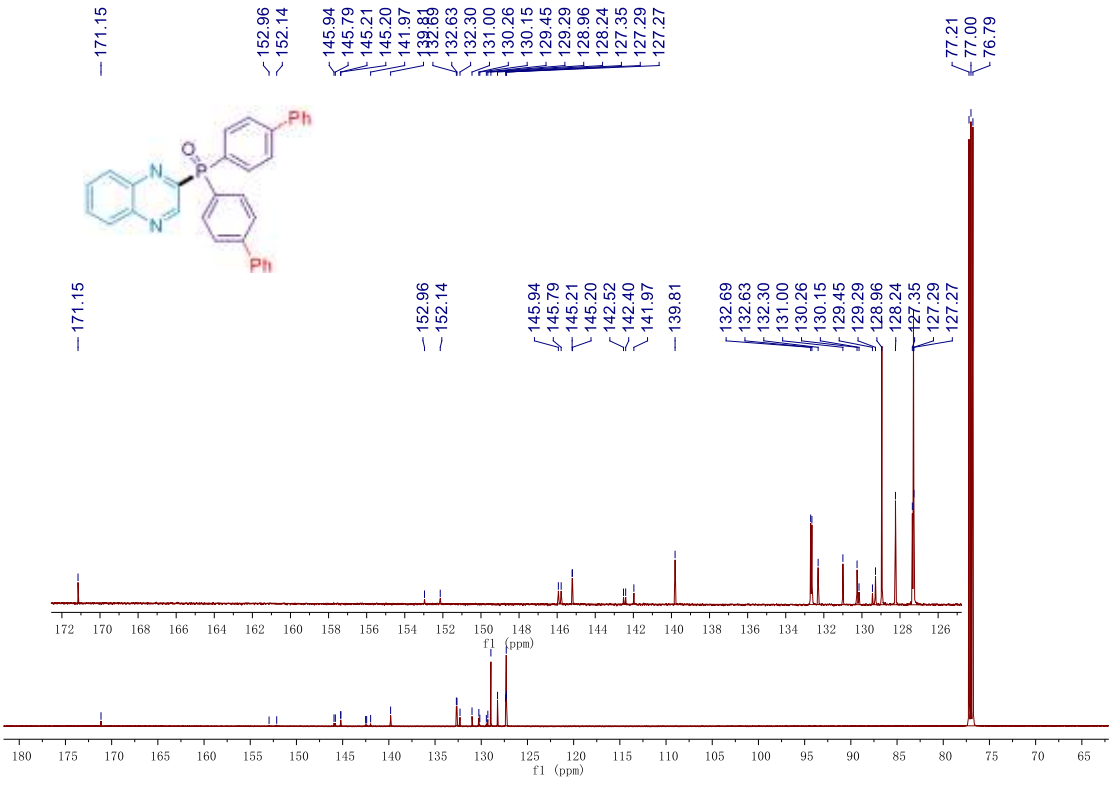


Fig.S 14 ^{13}C NMR of compound **3ad**

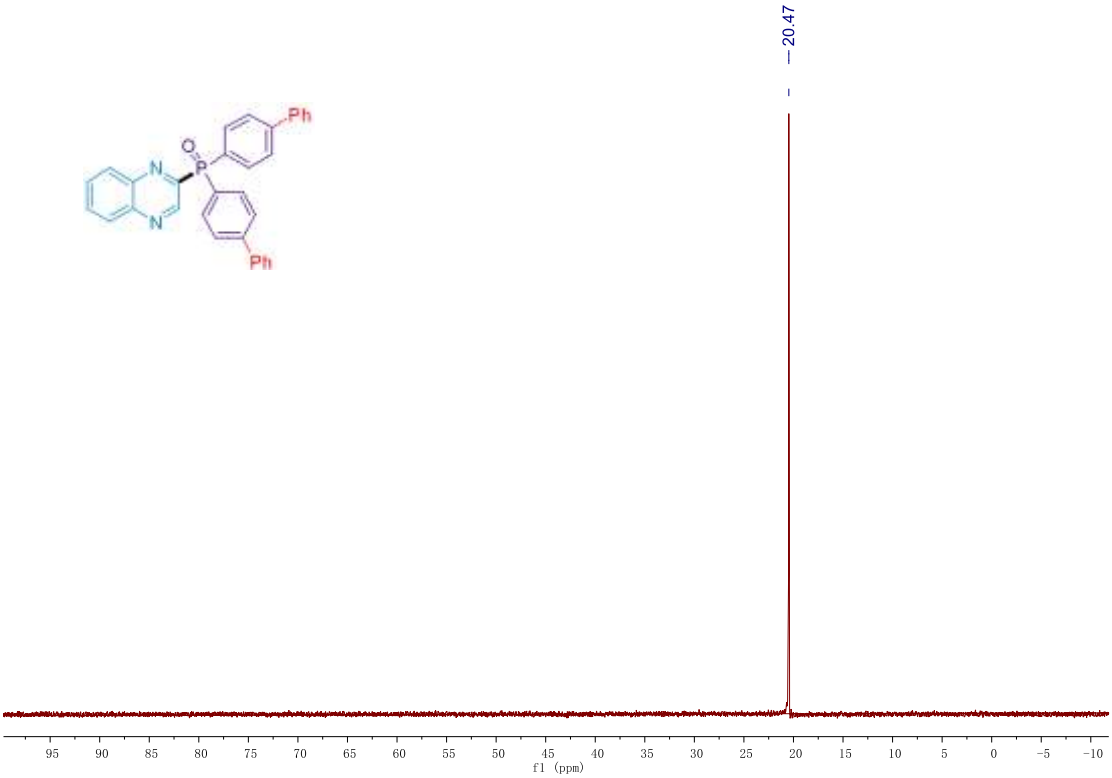


Fig.S 15 ^{31}P NMR of compound **3ad**

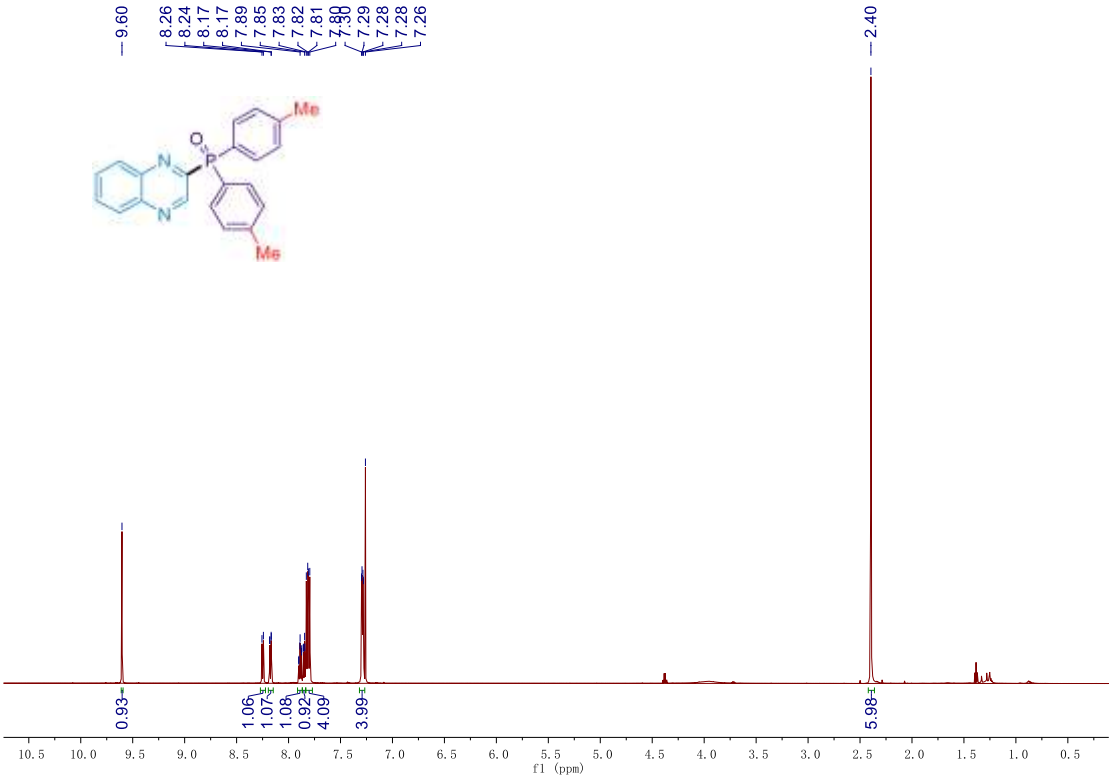


Fig.S 16 ^{1}H NMR of compound **3ae**

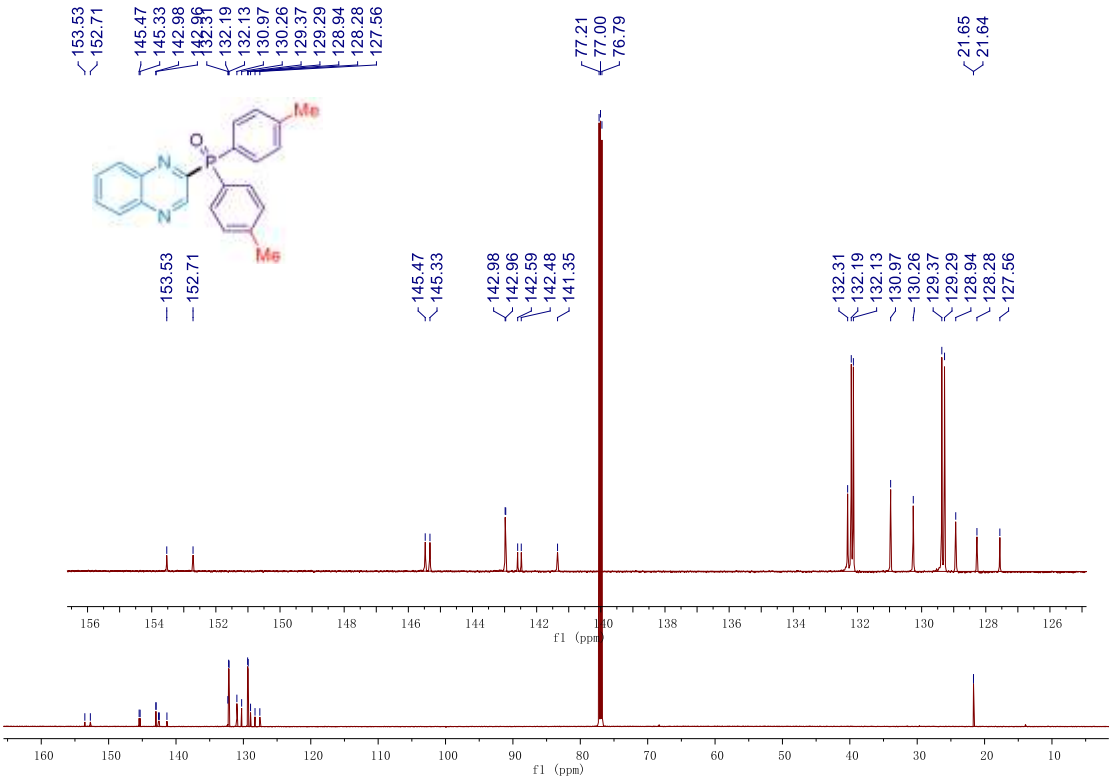


Fig.S 17 ^{13}C NMR of compound **3ae**

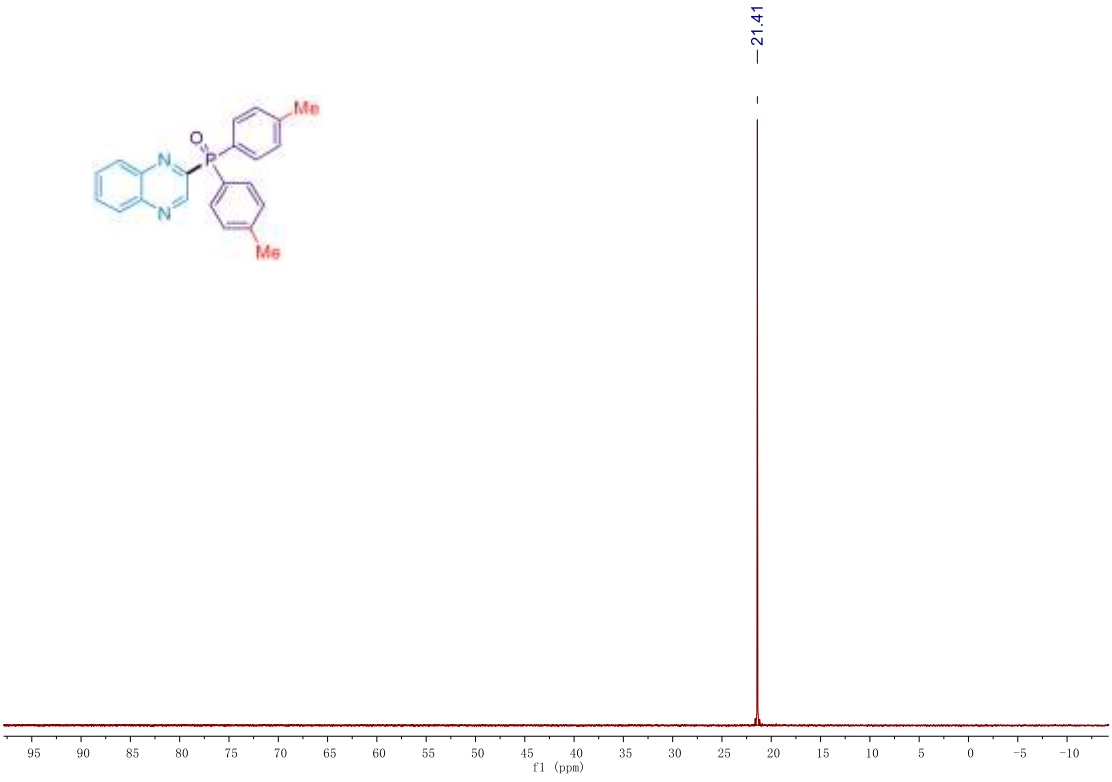


Fig.S 18 ^{31}P NMR of compound **3ae**

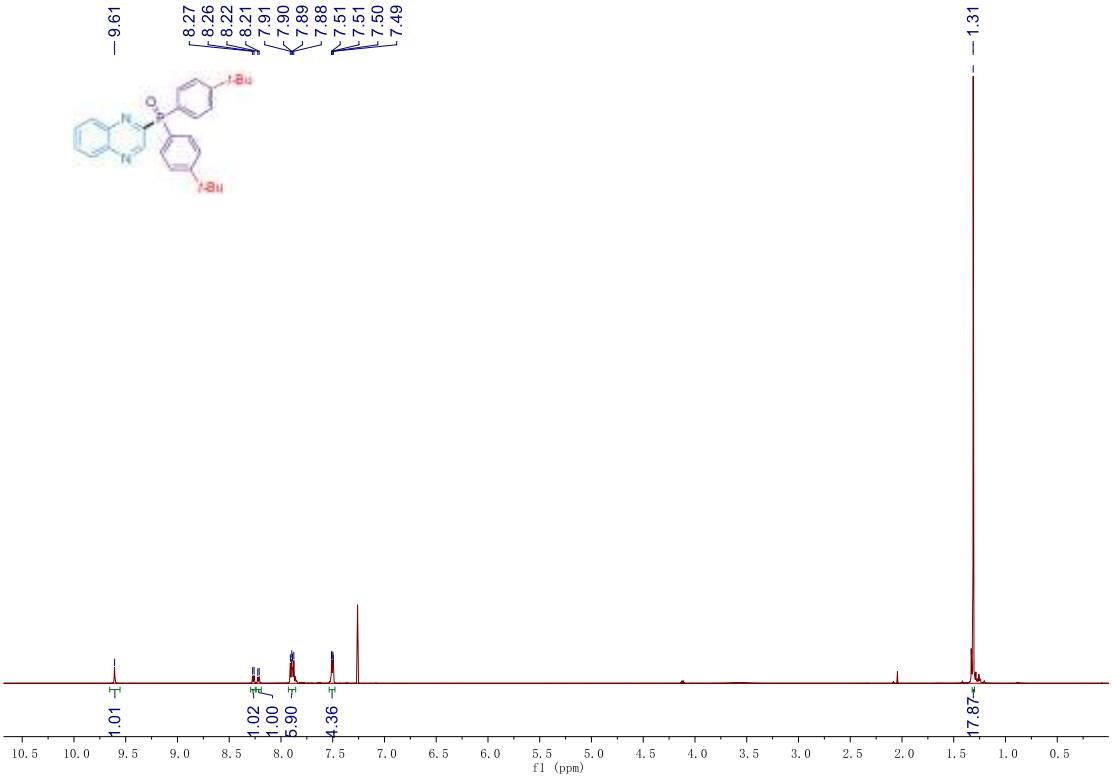


Fig.S 19 ^{1}H NMR of compound **3af**

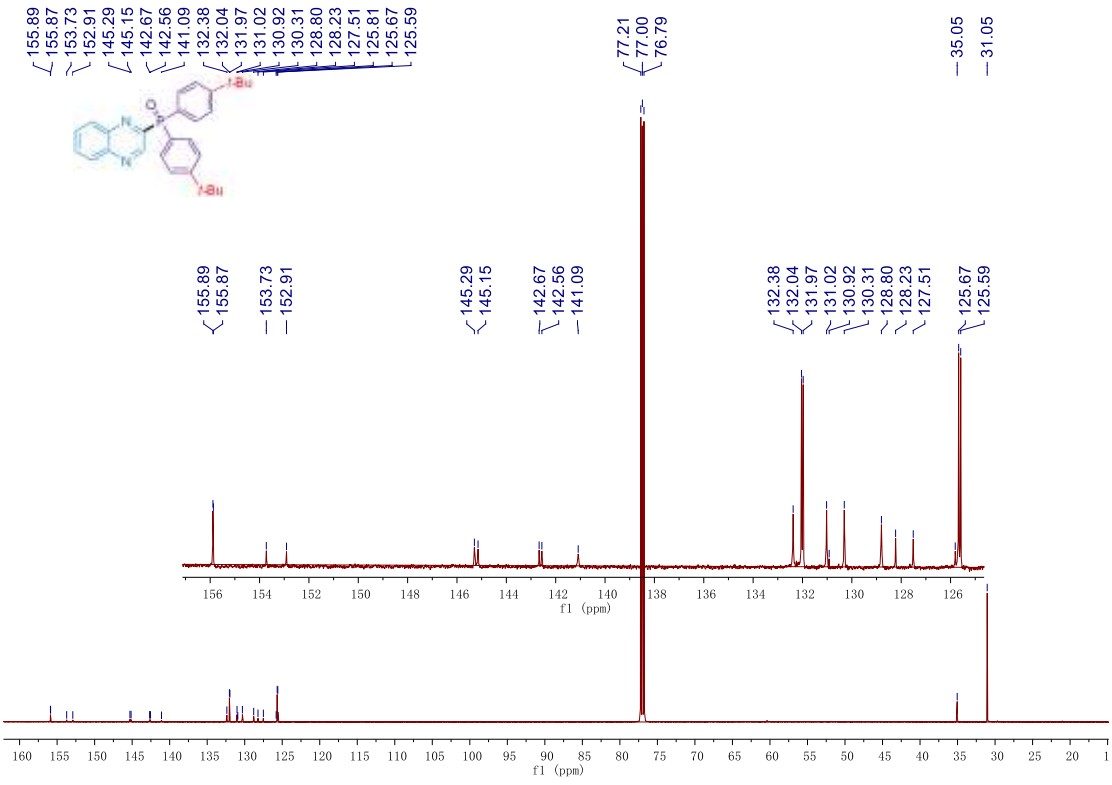


Fig.S 20 ^{13}C NMR of compound **3af**

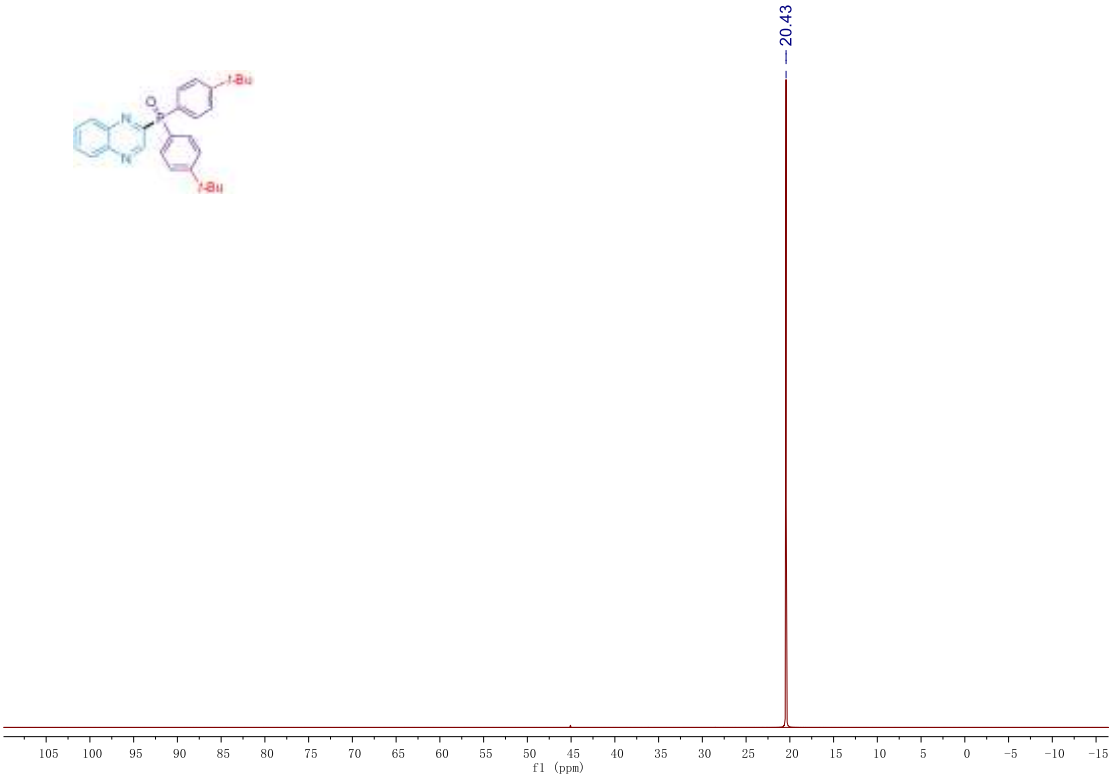


Fig.S 21 ^{31}P NMR of compound **3af**

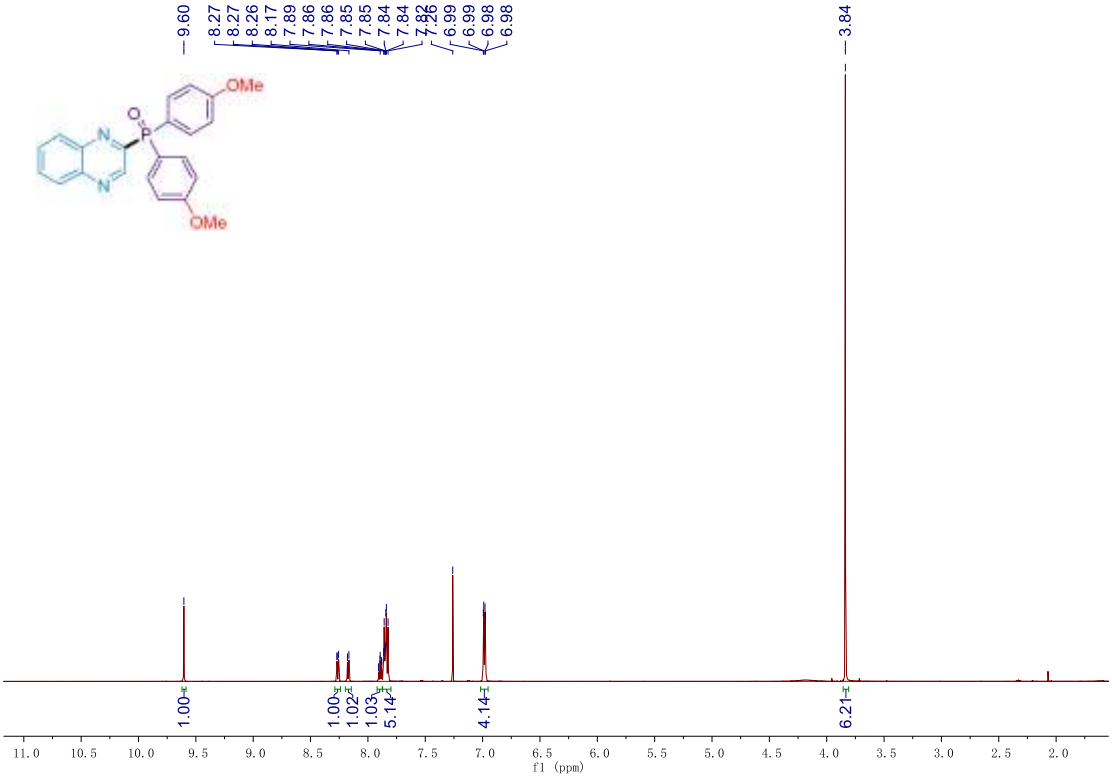


Fig.S 22 ^{1}H NMR of compound **3ag**

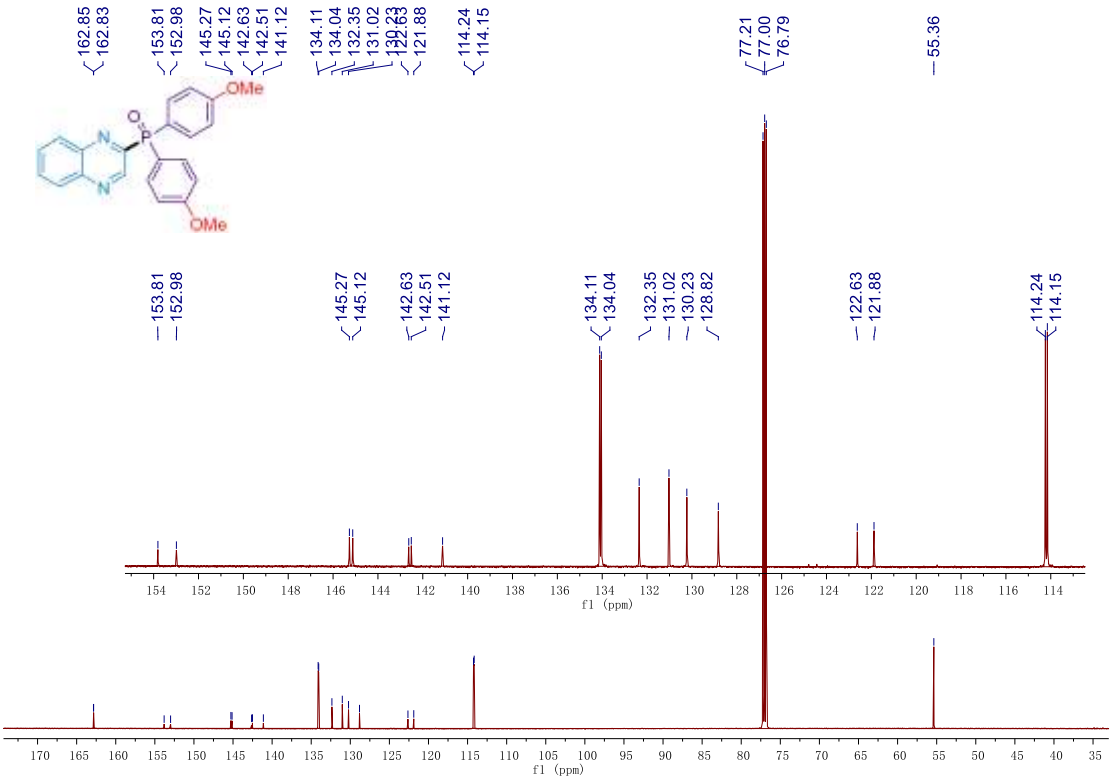


Fig.S 23 ^{13}C NMR of compound **3ag**

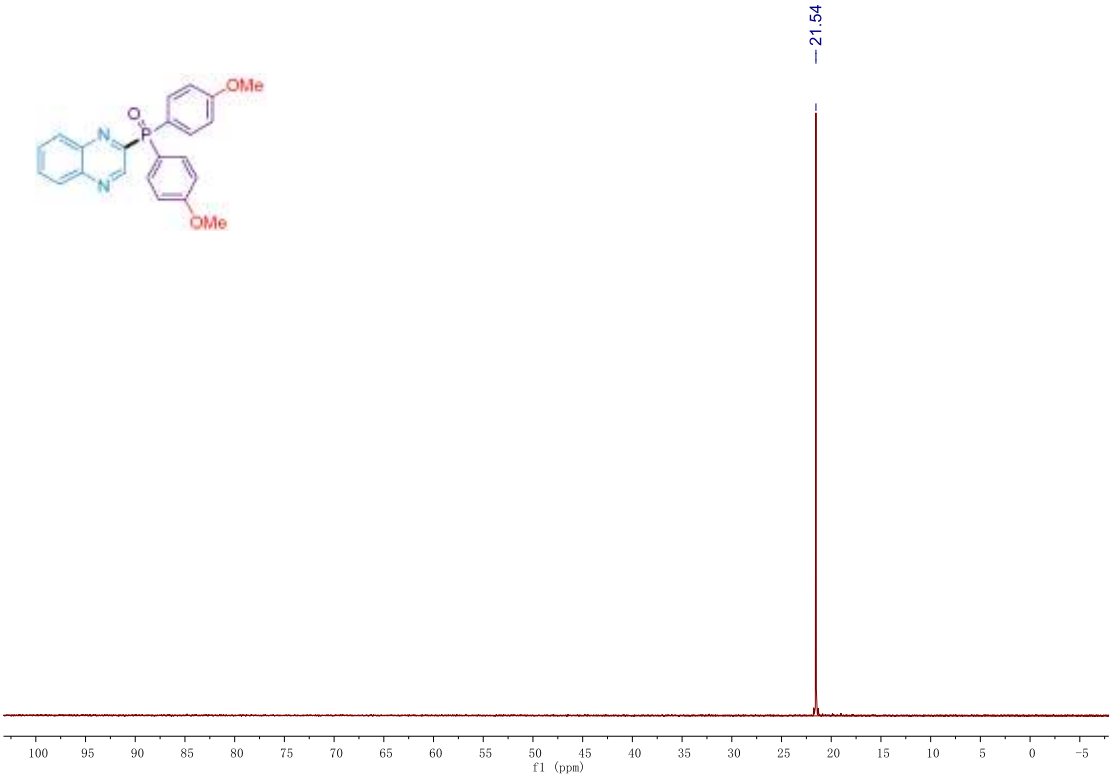


Fig.S 24 ^{31}P NMR of compound **3ag**

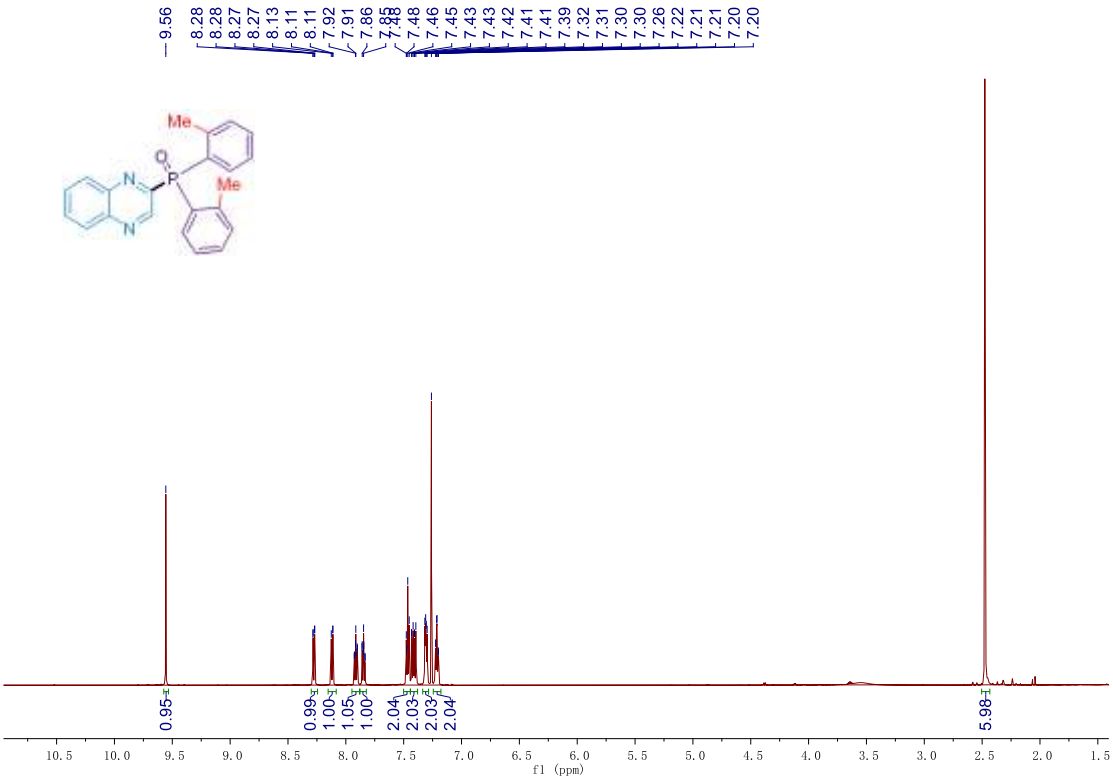


Fig.S 25 ^{1}H NMR of compound **3ah**

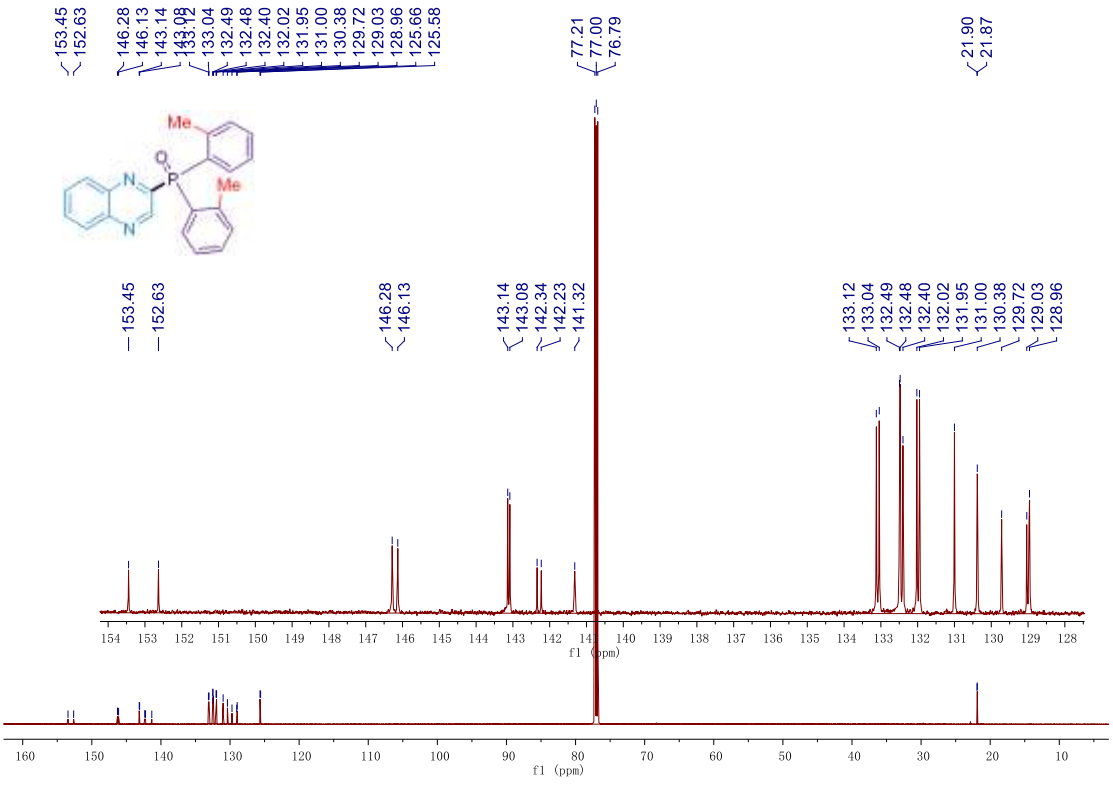


Fig.S 26 ^{13}C NMR of compound **3ah**

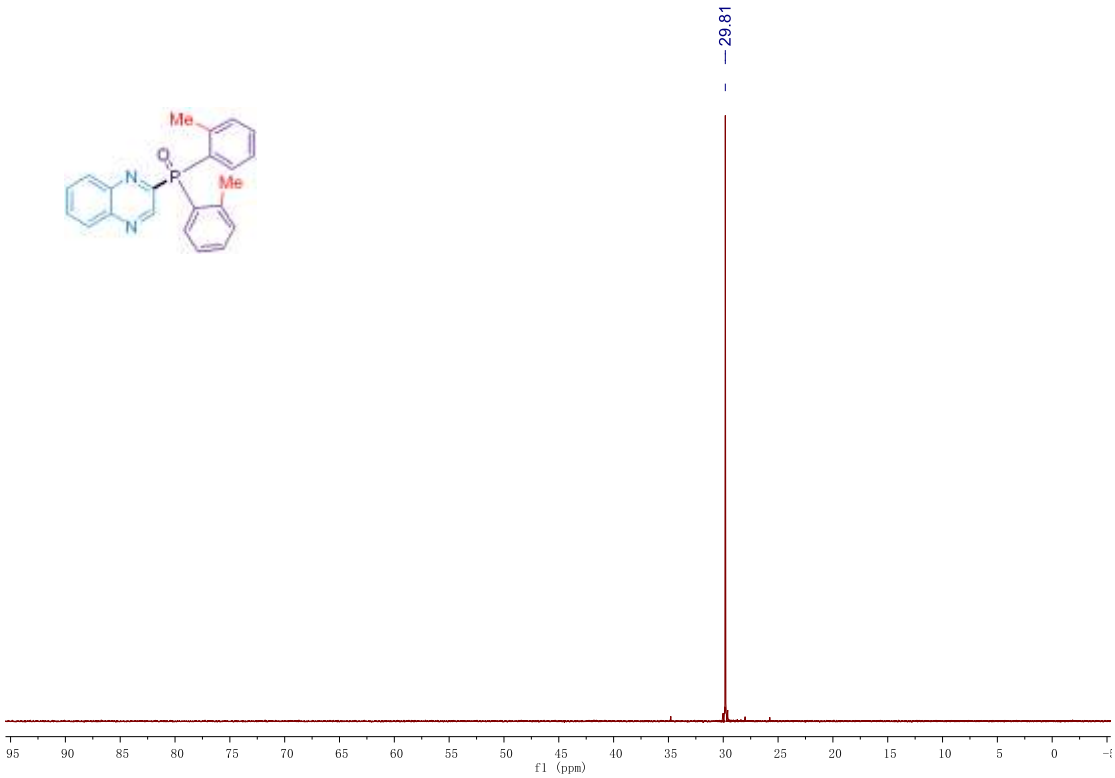


Fig.S 27 ^{31}P NMR of compound **3ah**

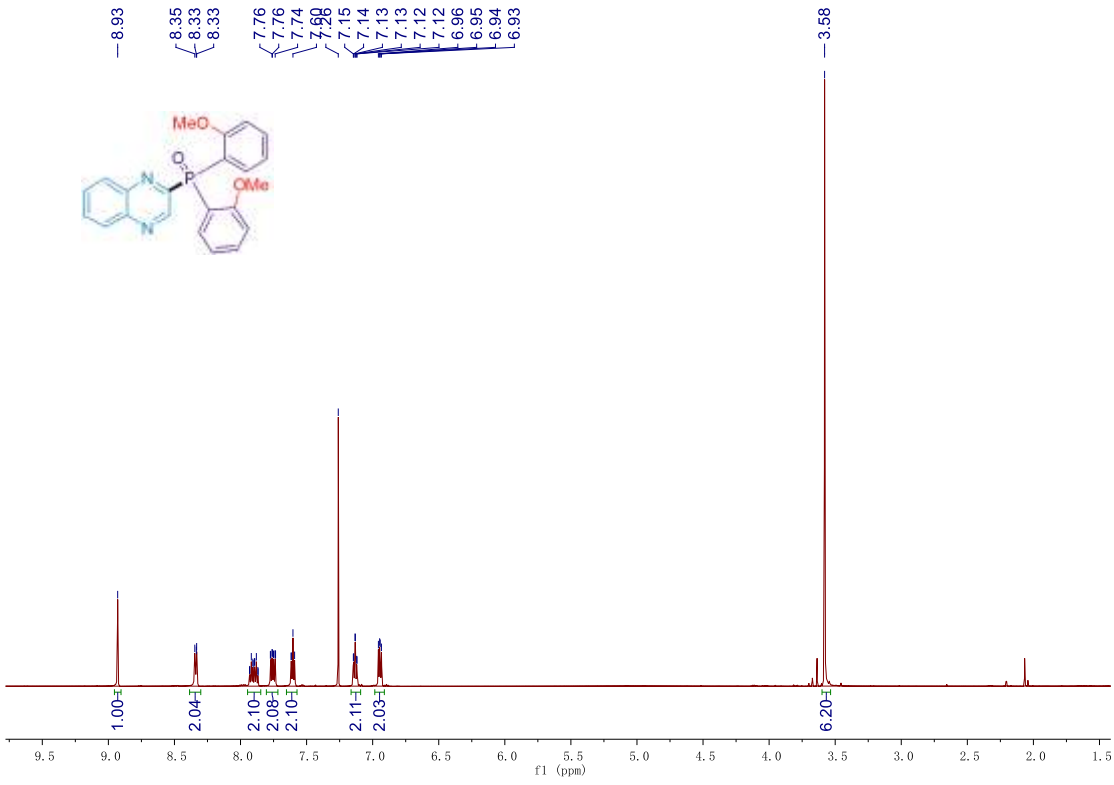


Fig.S 28 ^{1}H NMR of compound **3ai**

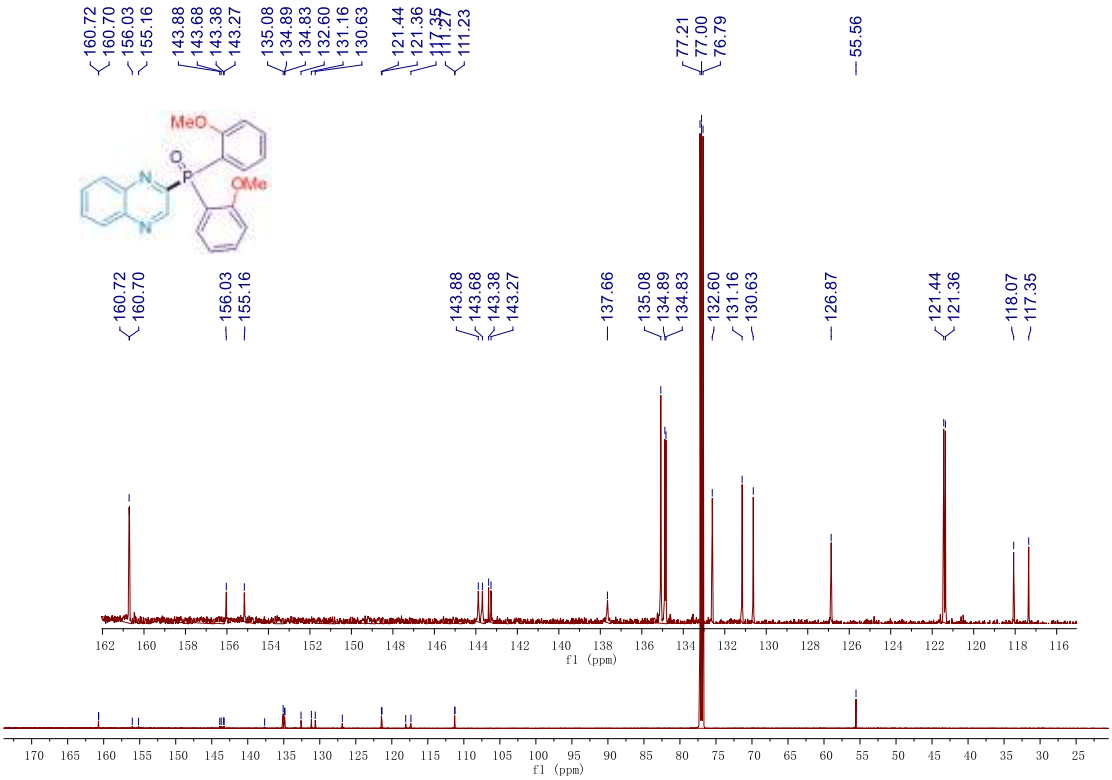


Fig.S 29 ^{13}C NMR of compound **3ai**

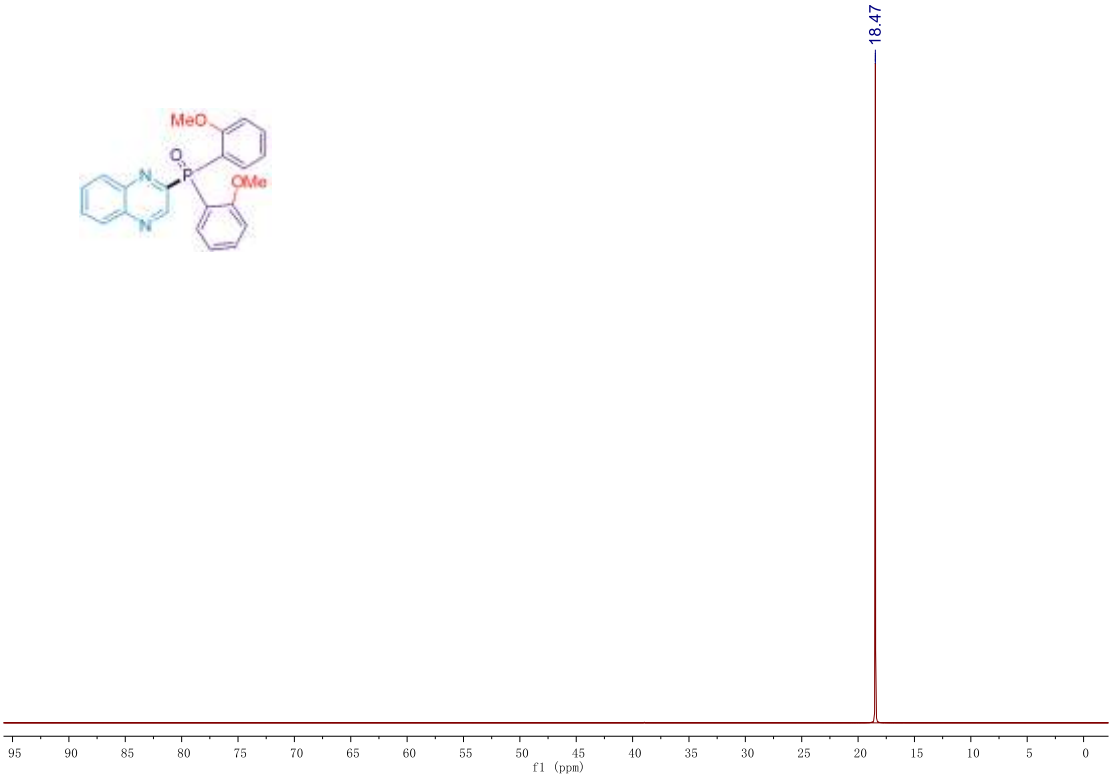


Fig.S 30 ^{31}P NMR of compound **3ai**

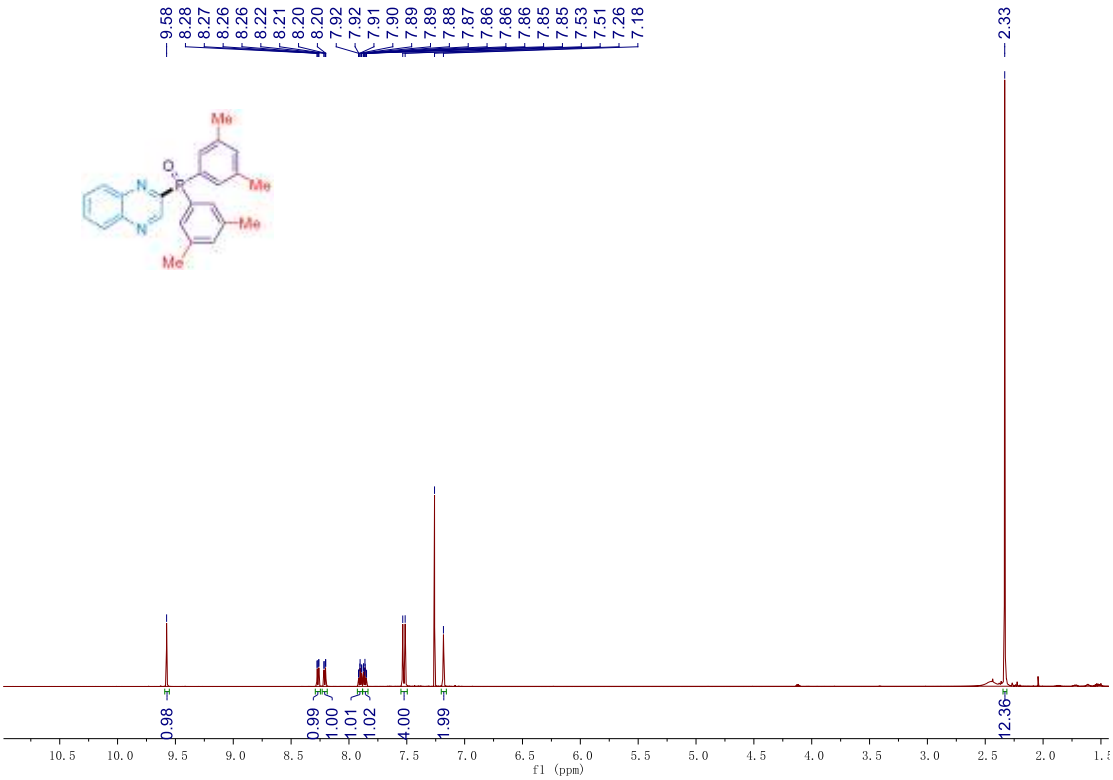


Fig.S 31 ^{1}H NMR of compound **3aj**

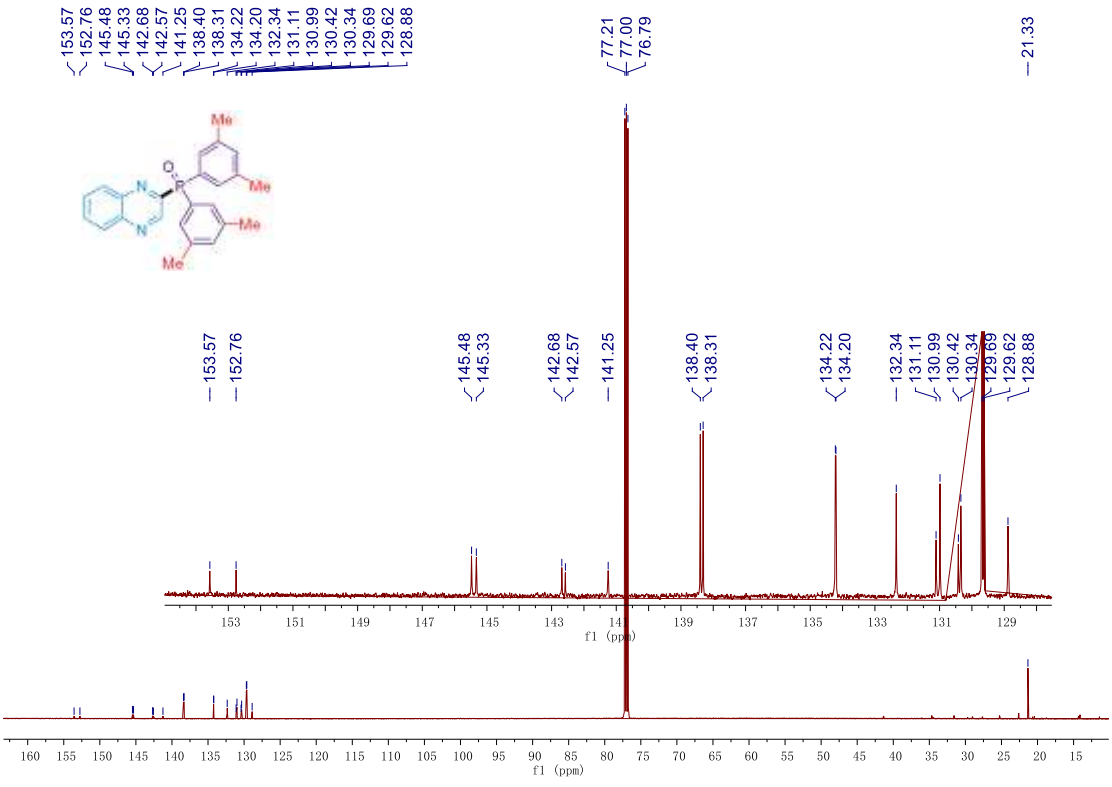


Fig.S 32 ^{13}C NMR of compound **3aj**

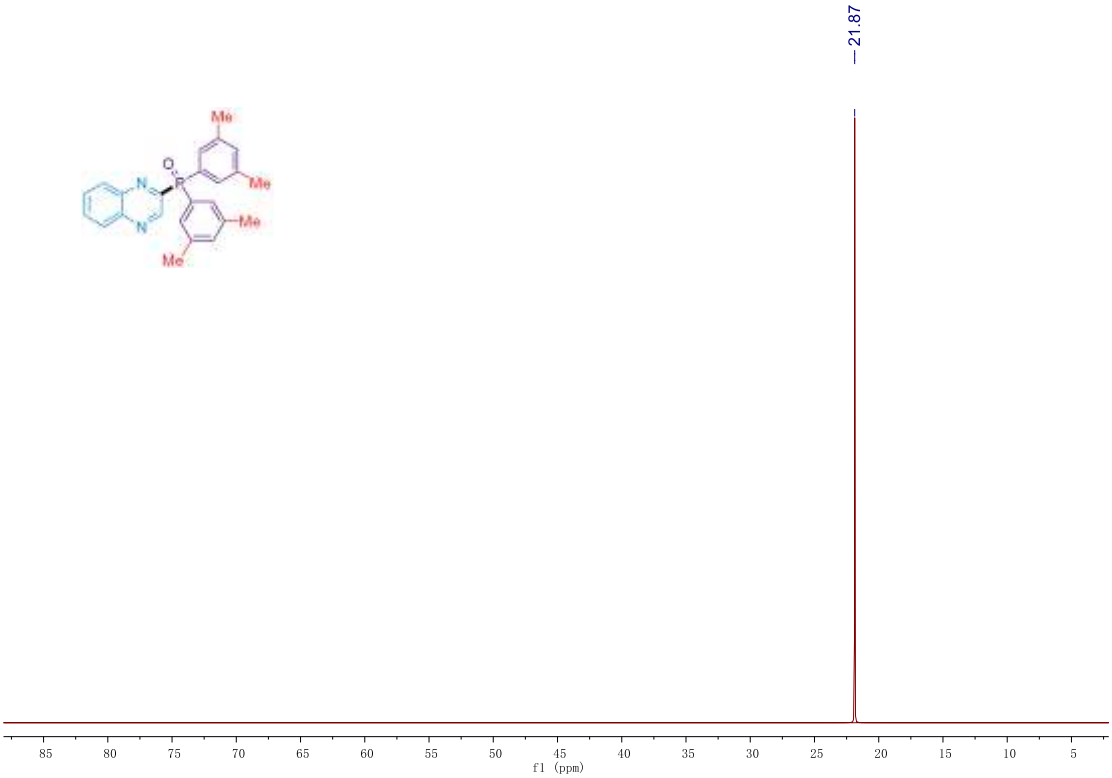


Fig.S 33 ^{31}P NMR of compound **3aj**

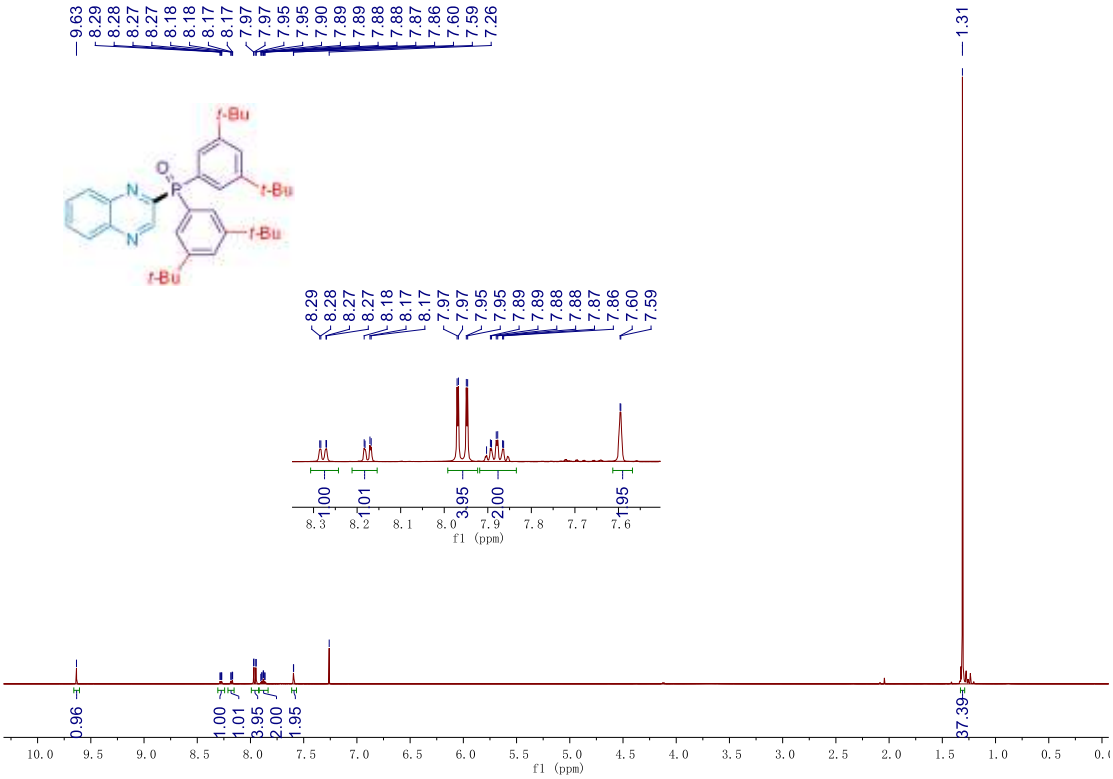


Fig.S 34 ^{1}H NMR of compound **3ak**

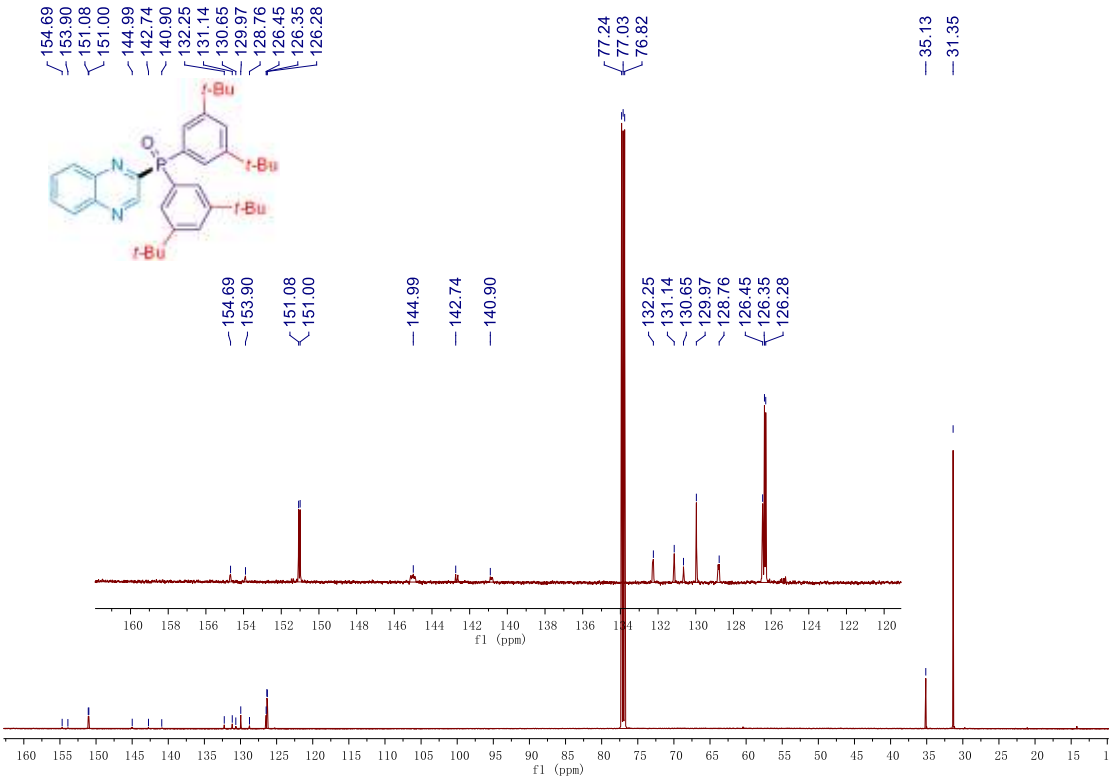


Fig.S 35 ^{13}C NMR of compound **3ak**

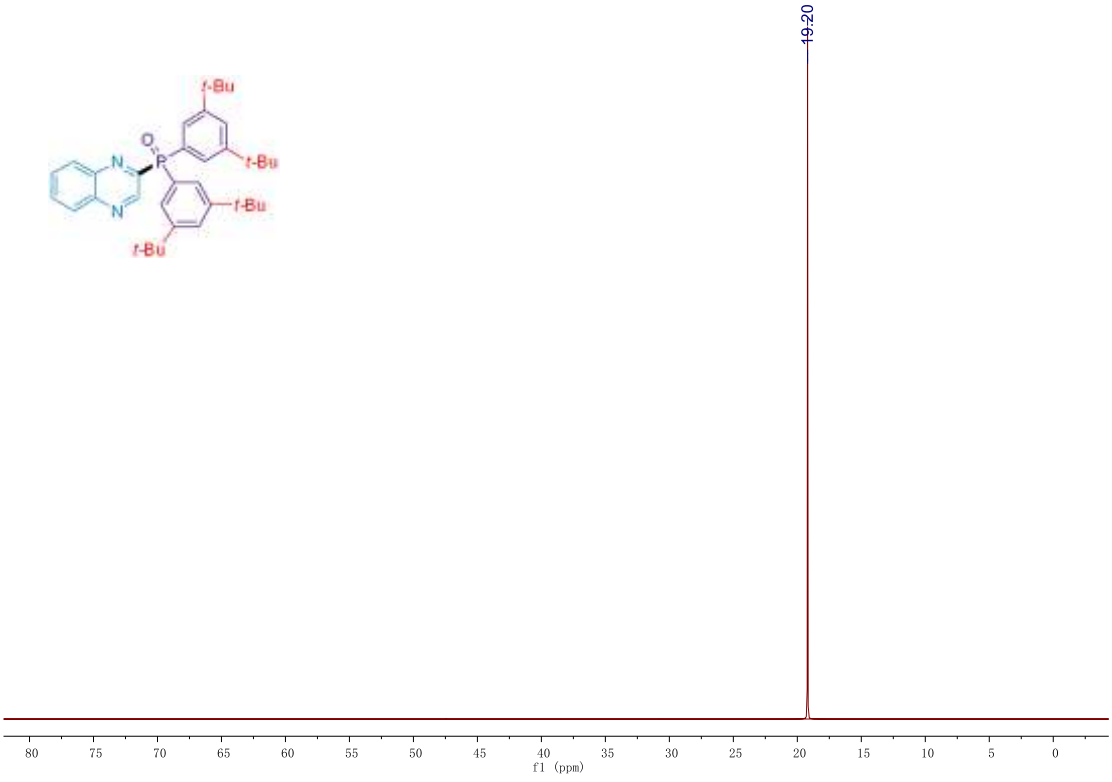


Fig.S 36 ^{31}P NMR of compound **3ak**

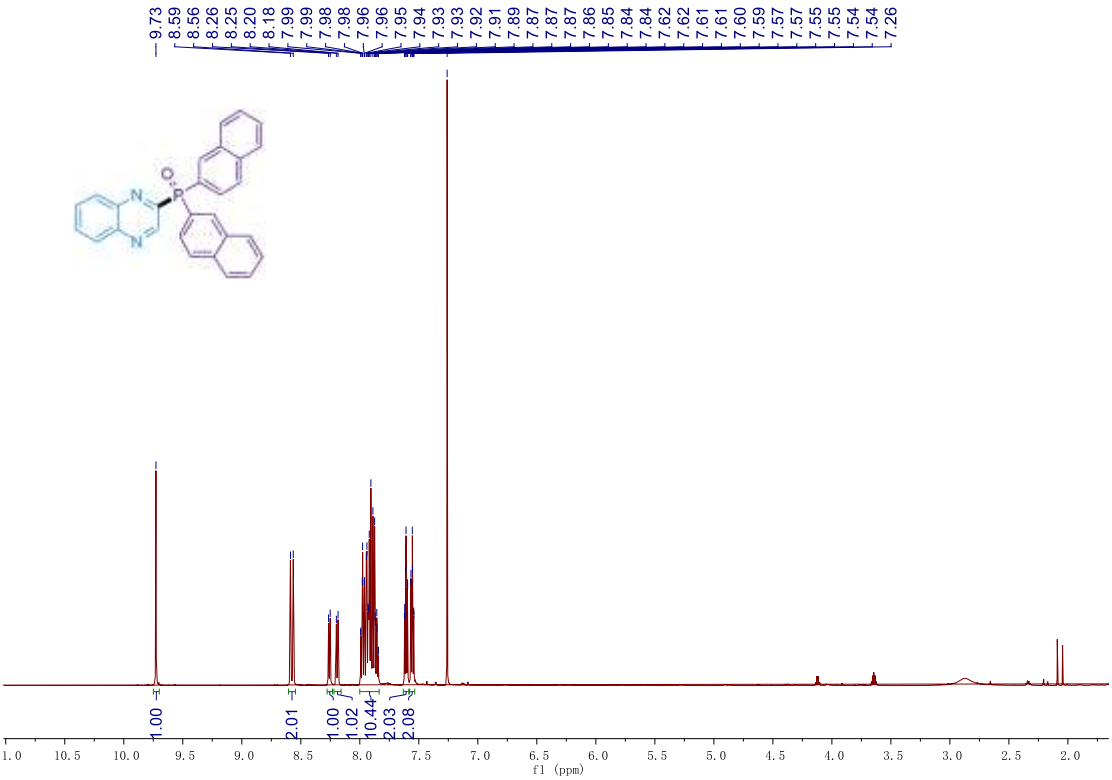


Fig.S 37 ^{1}H NMR of compound **3am**

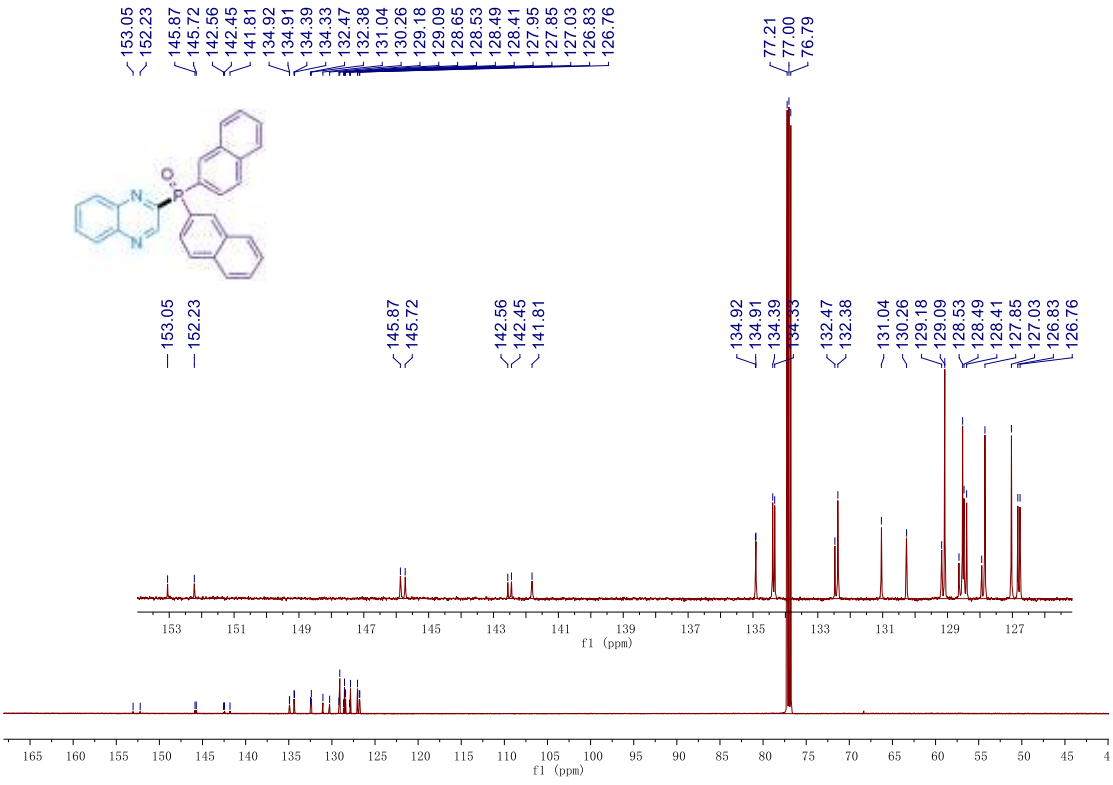


Fig.S 38 ^{13}C NMR of compound **3am**

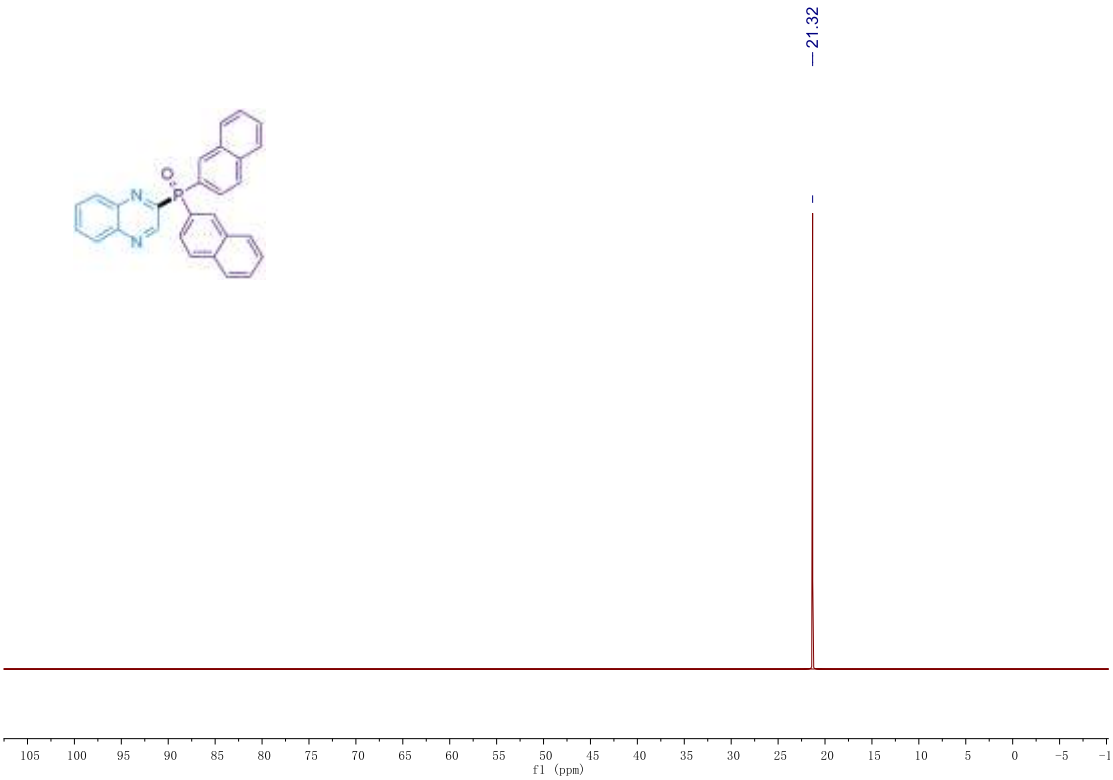


Fig.S 39 ^{31}P NMR of compound **3am**

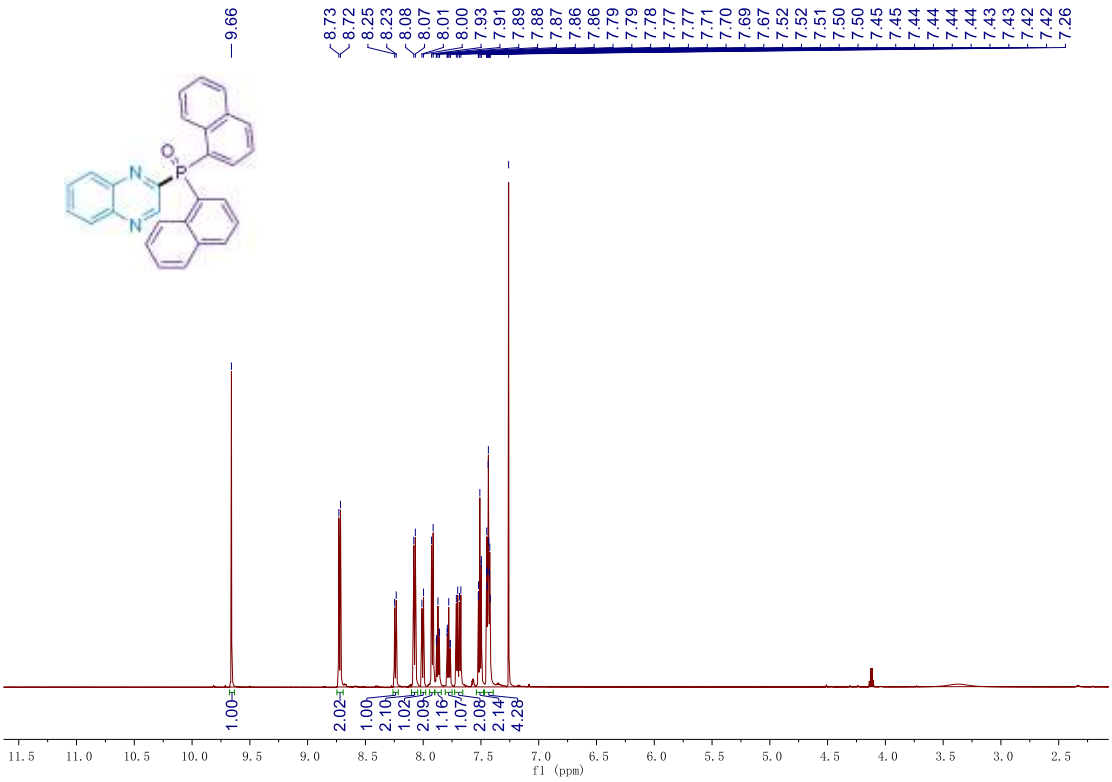


Fig.S 40 ^{1}H NMR of compound **3an**

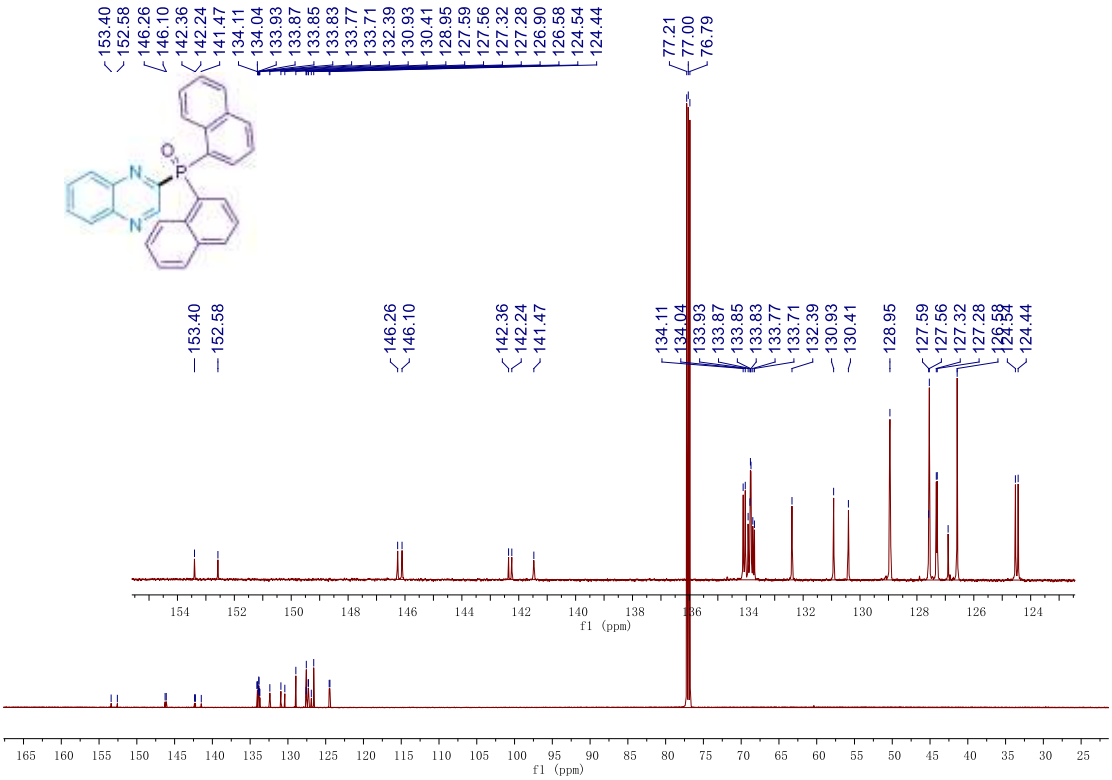


Fig.S 41 ^{13}C NMR of compound **3an**

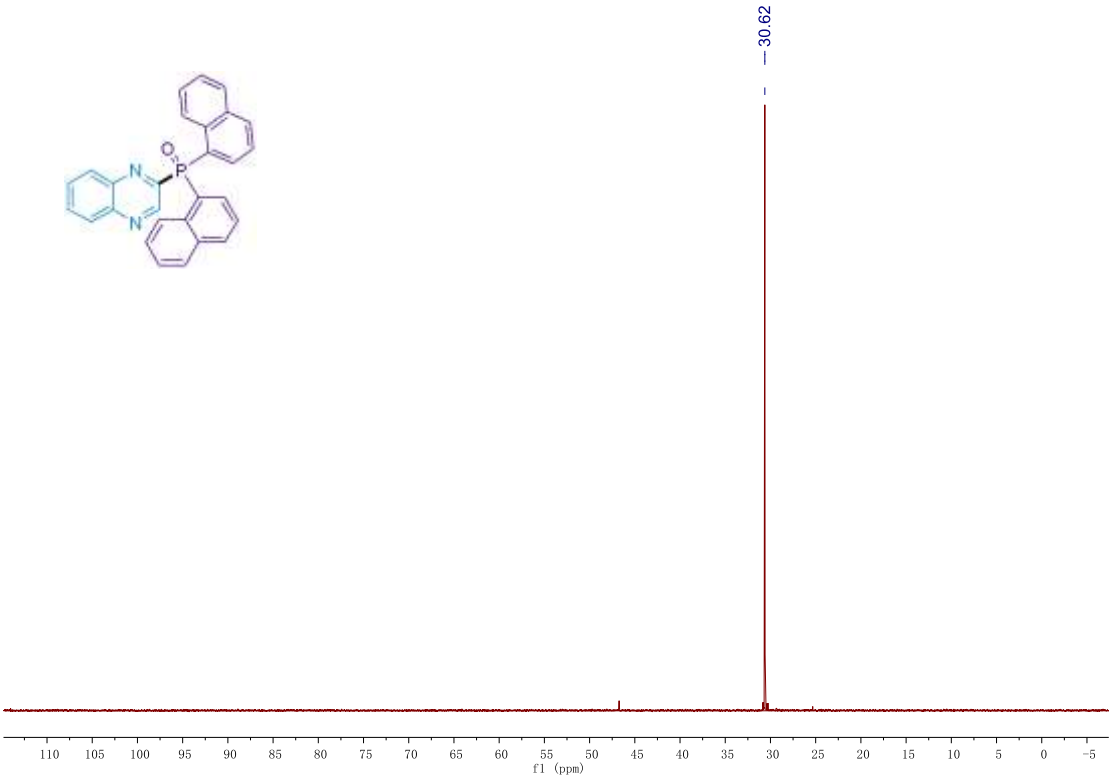


Fig.S 42 ^{31}P NMR of compound **3an**

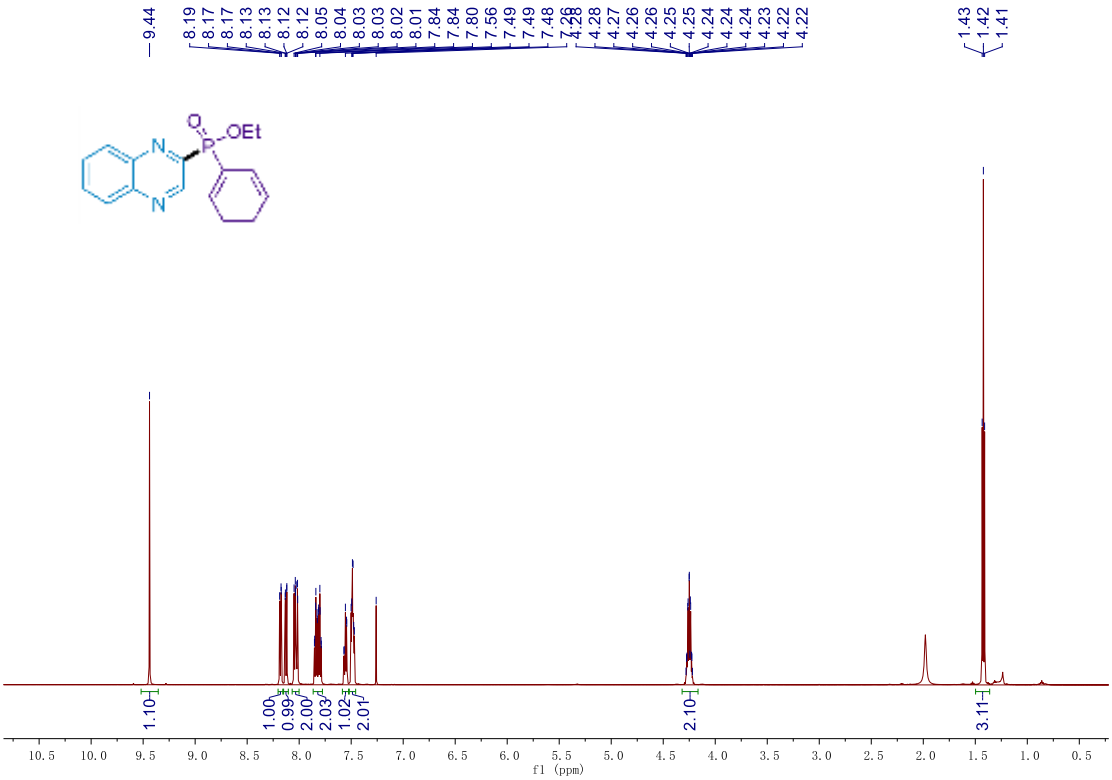


Fig.S 43 ^{1}H NMR of compound **3ao**

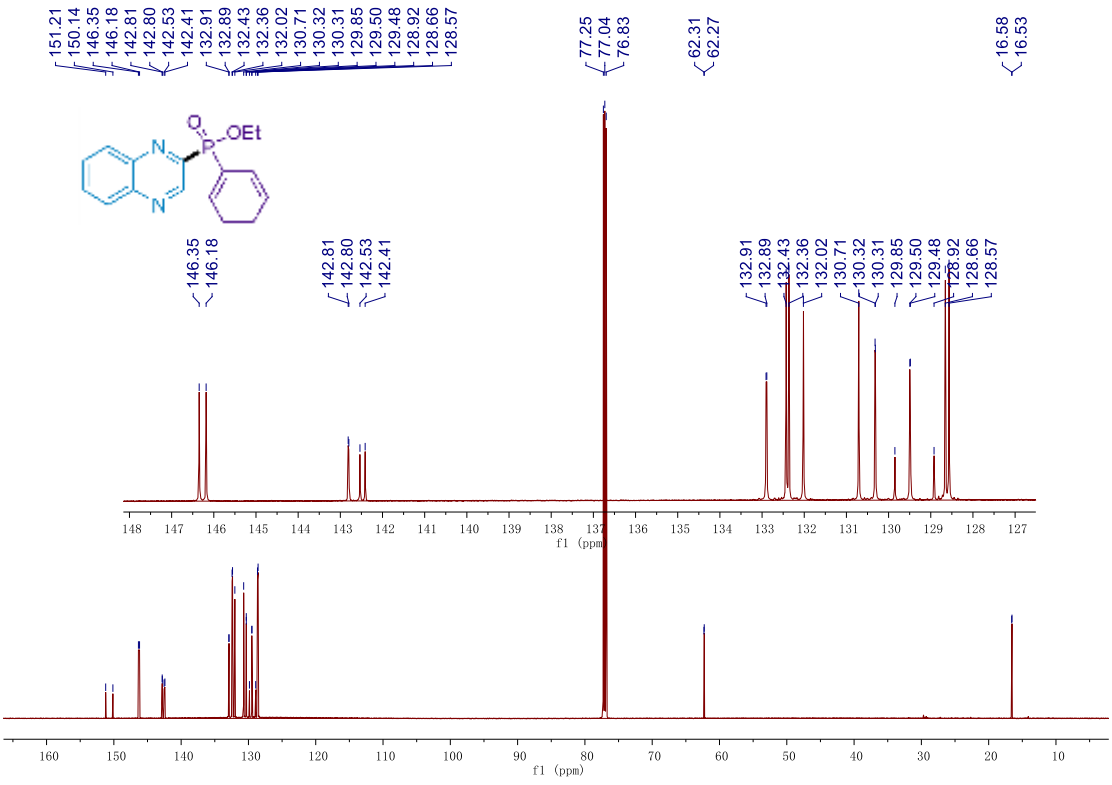


Fig.S 44 ^{13}C NMR of compound **3ao**

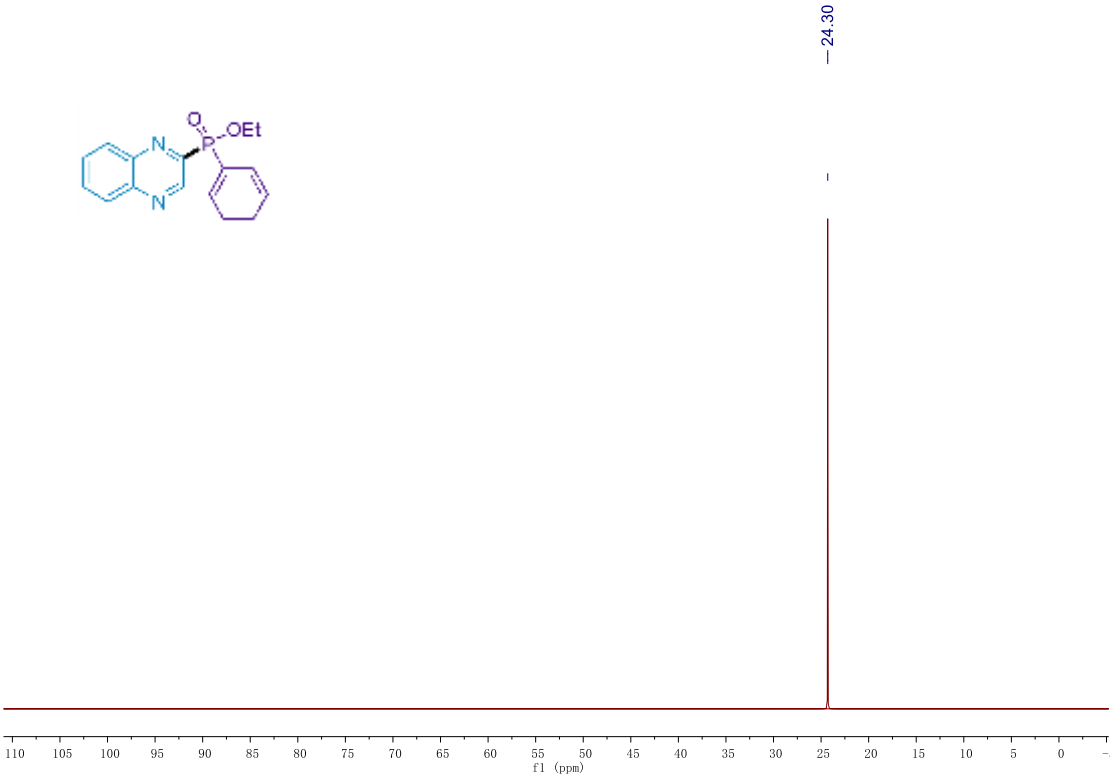


Fig.S 45 ^{31}P NMR of compound **3ao**

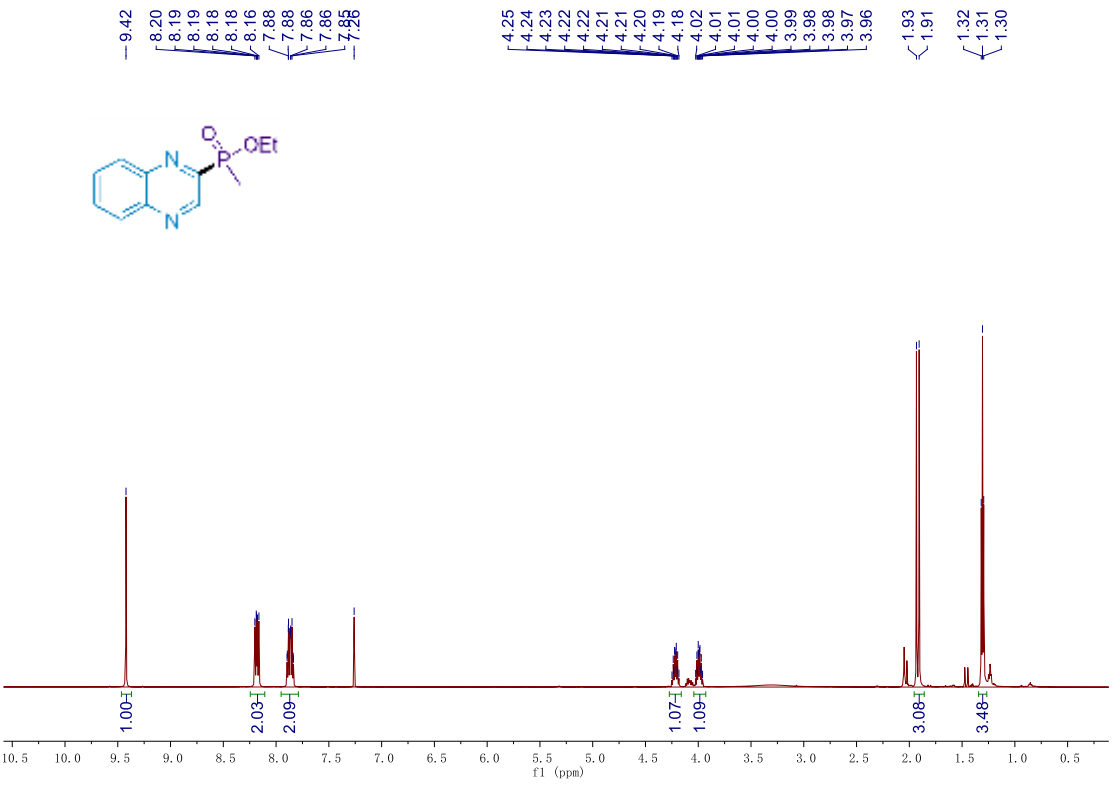


Fig.S 46 ^{1}H NMR of compound **3ap**

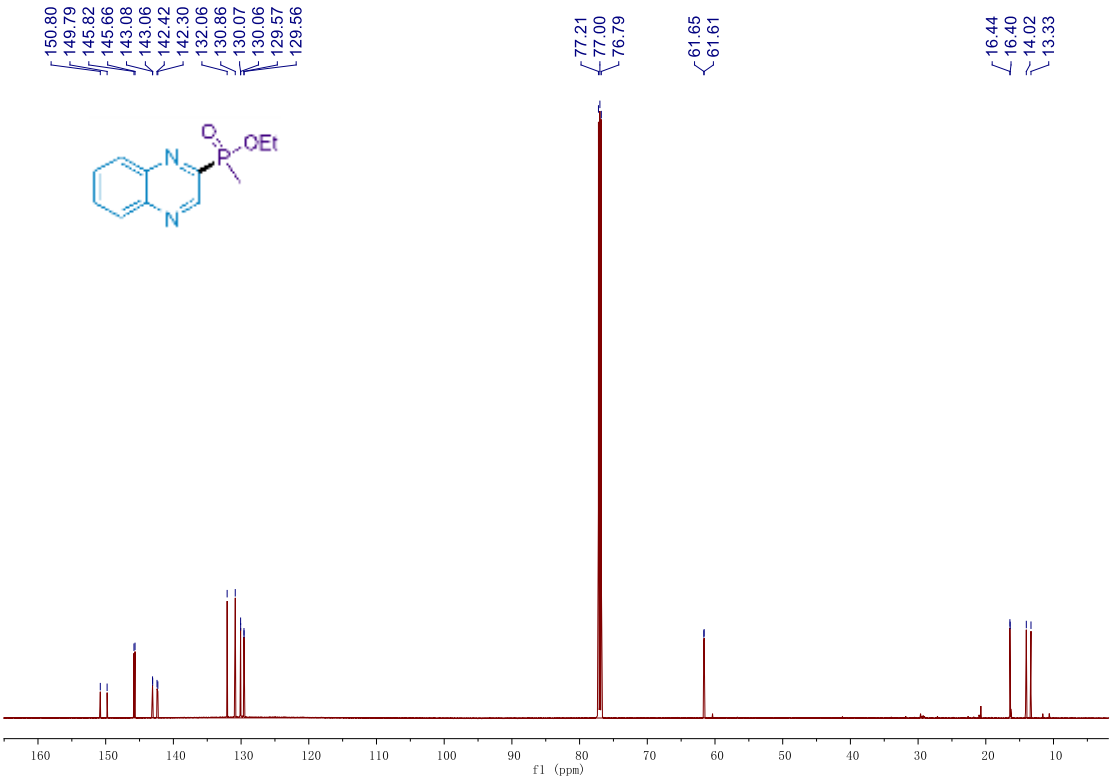


Fig.S 47 ^{13}C NMR of compound **3ap**

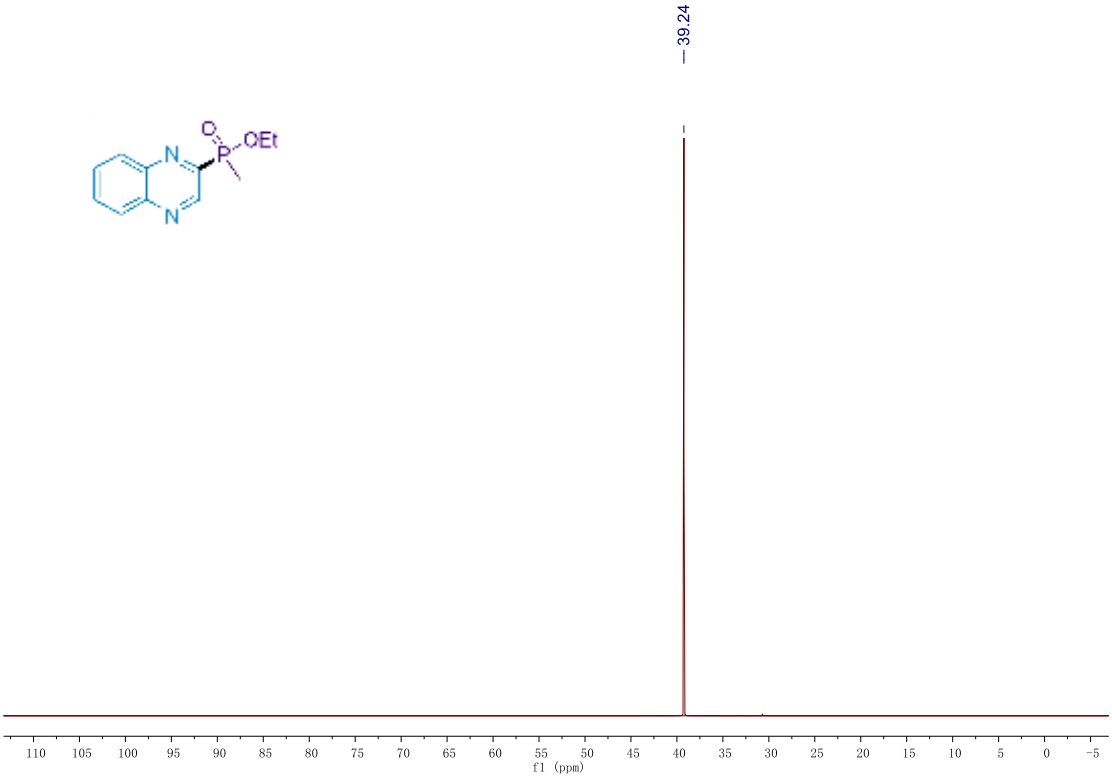


Fig.S 48 ^{31}P NMR of compound **3ap**

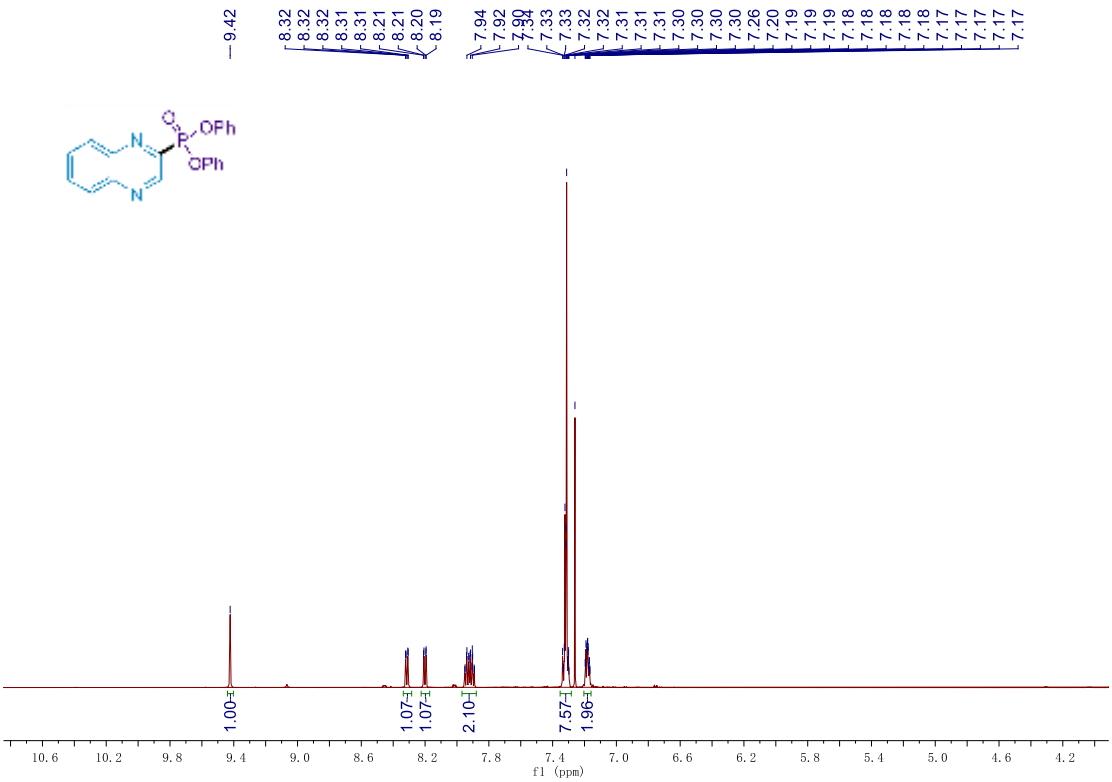


Fig.S 49 ^{1}H NMR of compound **3aq**

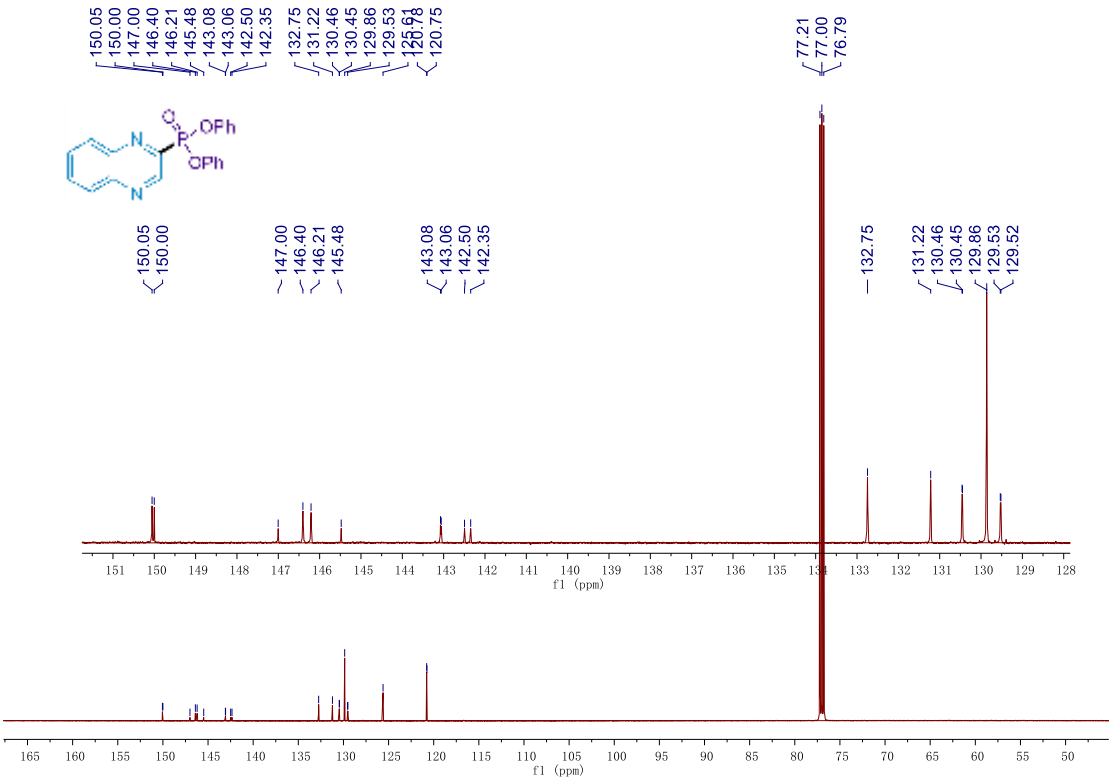


Fig.S 50 ^{13}C NMR of compound **3aq**

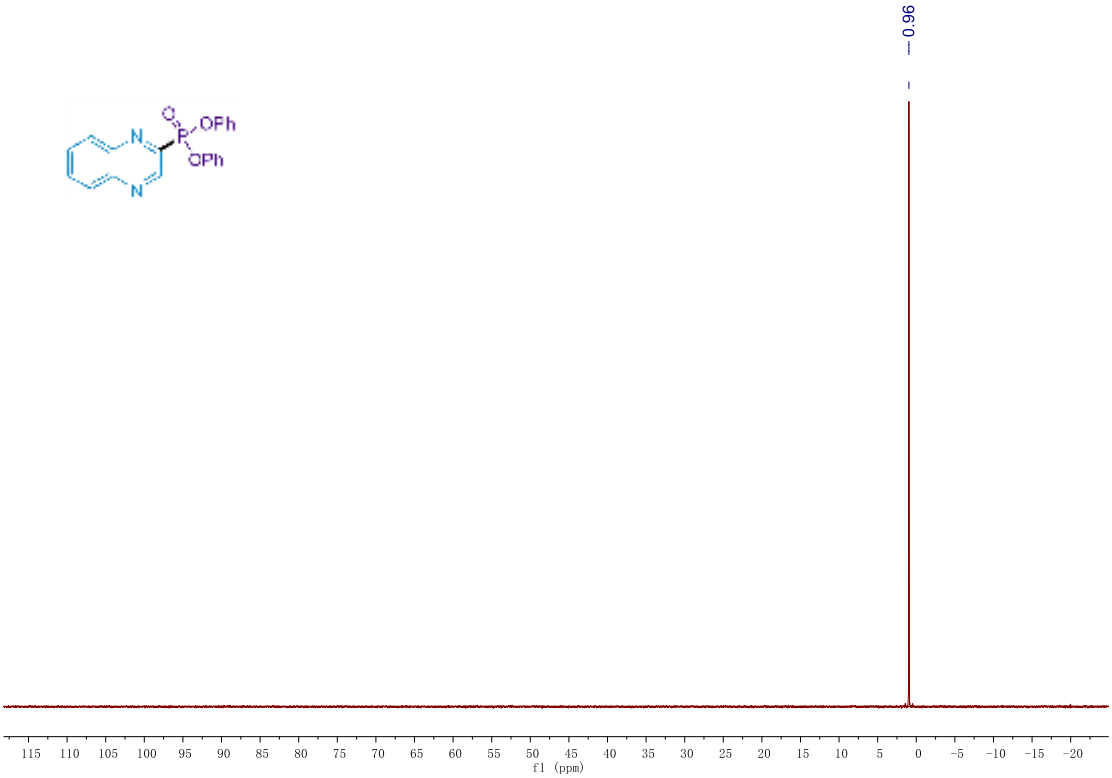


Fig.S 51 ^{31}P NMR of compound **3aq**

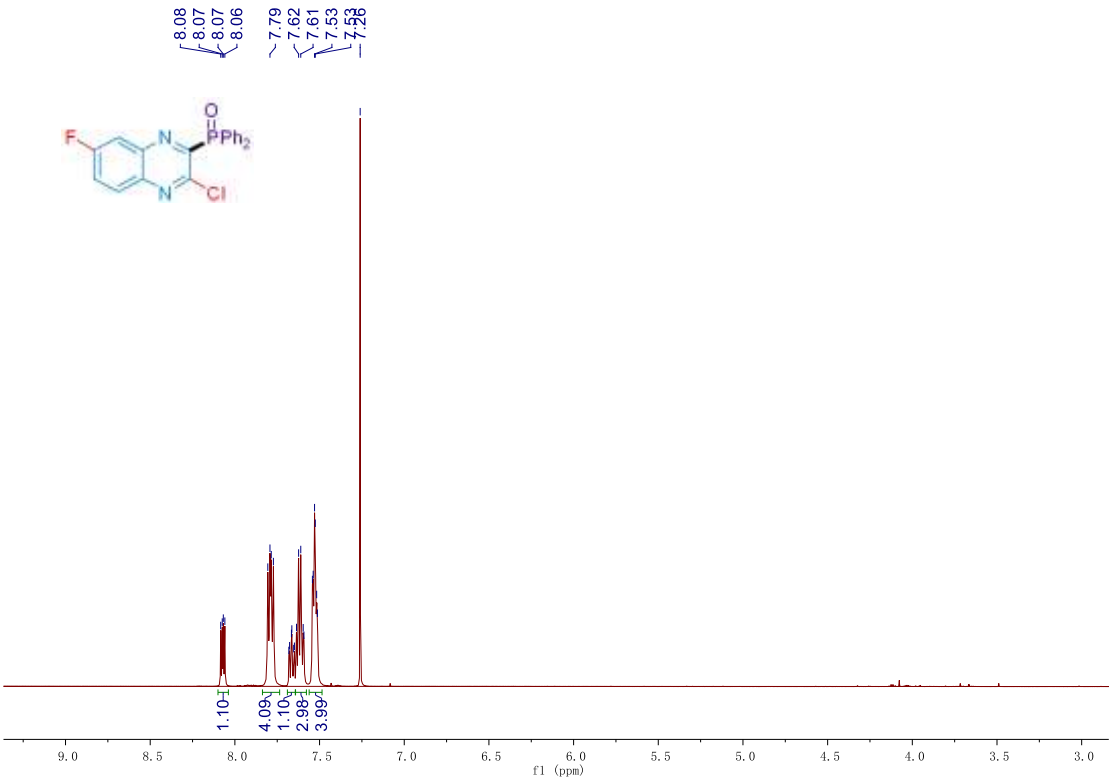


Fig.S 52 ^{1}H NMR of compound **3ca**

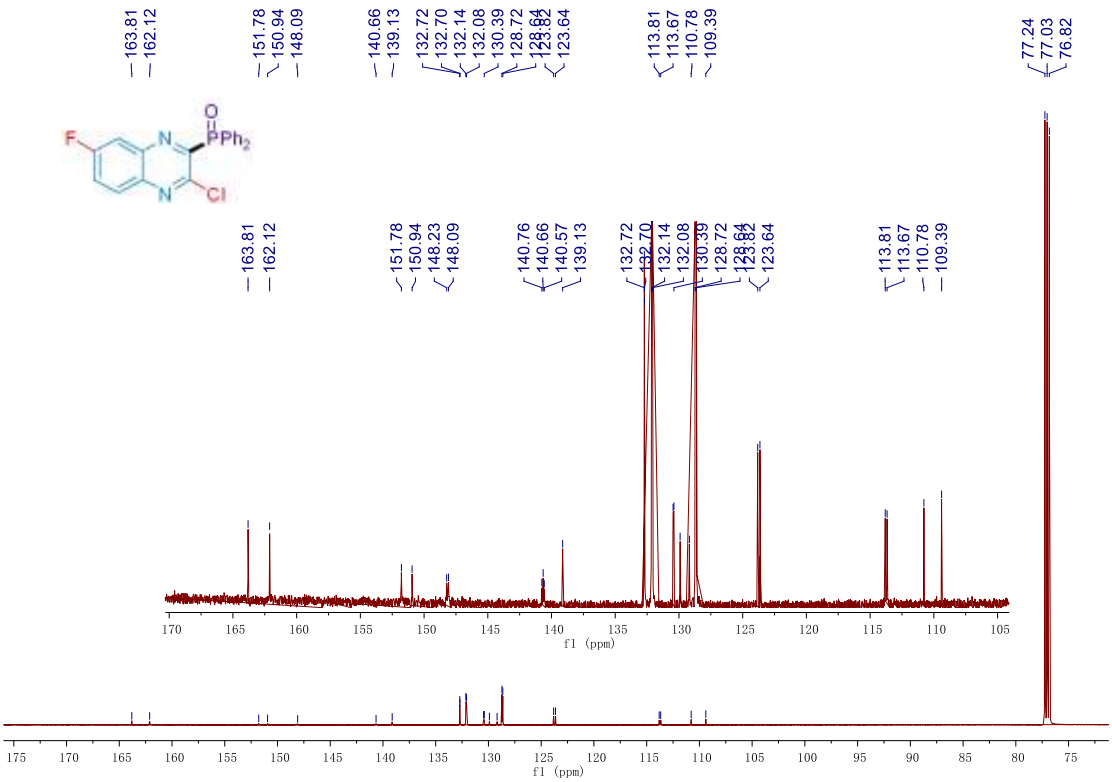


Fig.S 53 ^{13}C NMR of compound **3ca**

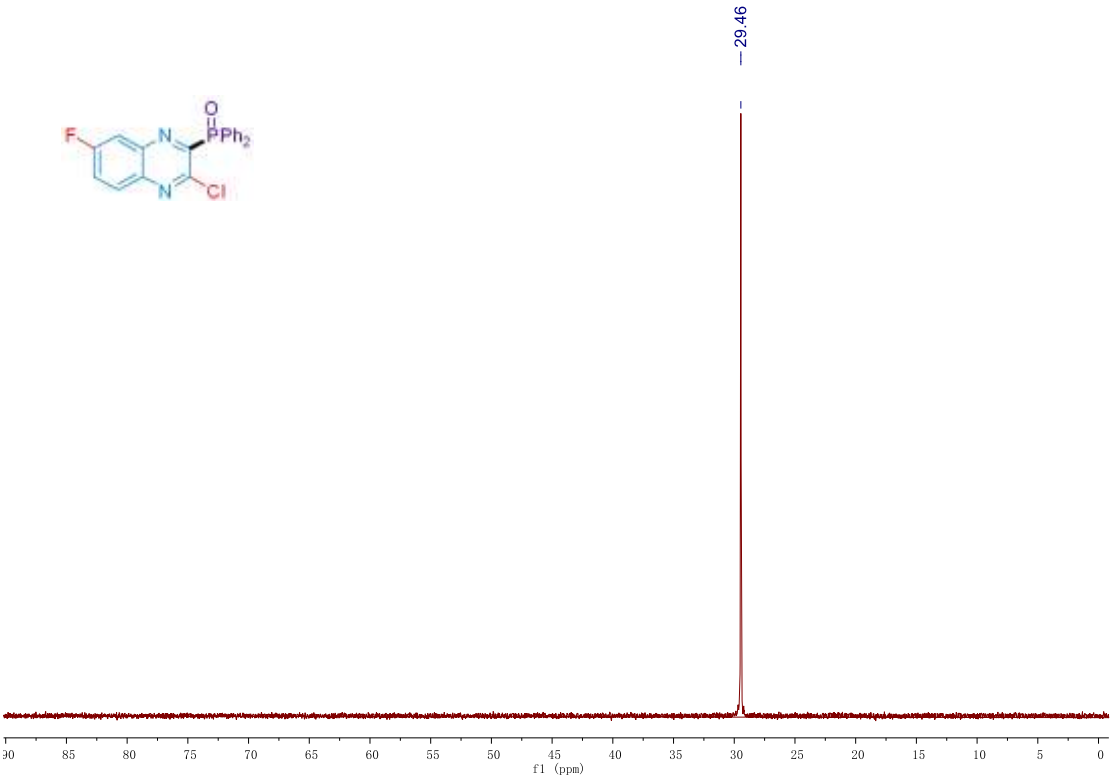


Fig.S 54 ^{31}P NMR of compound **3ca**

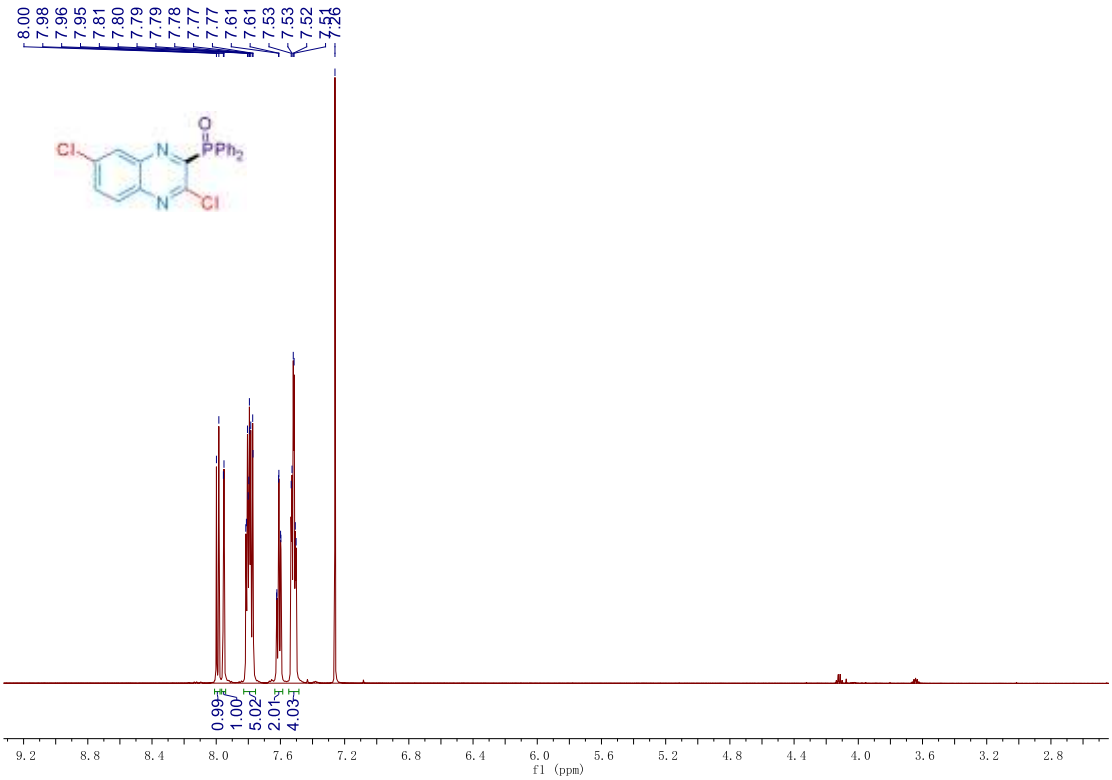


Fig.S 55 ^{1}H NMR of compound **3da**

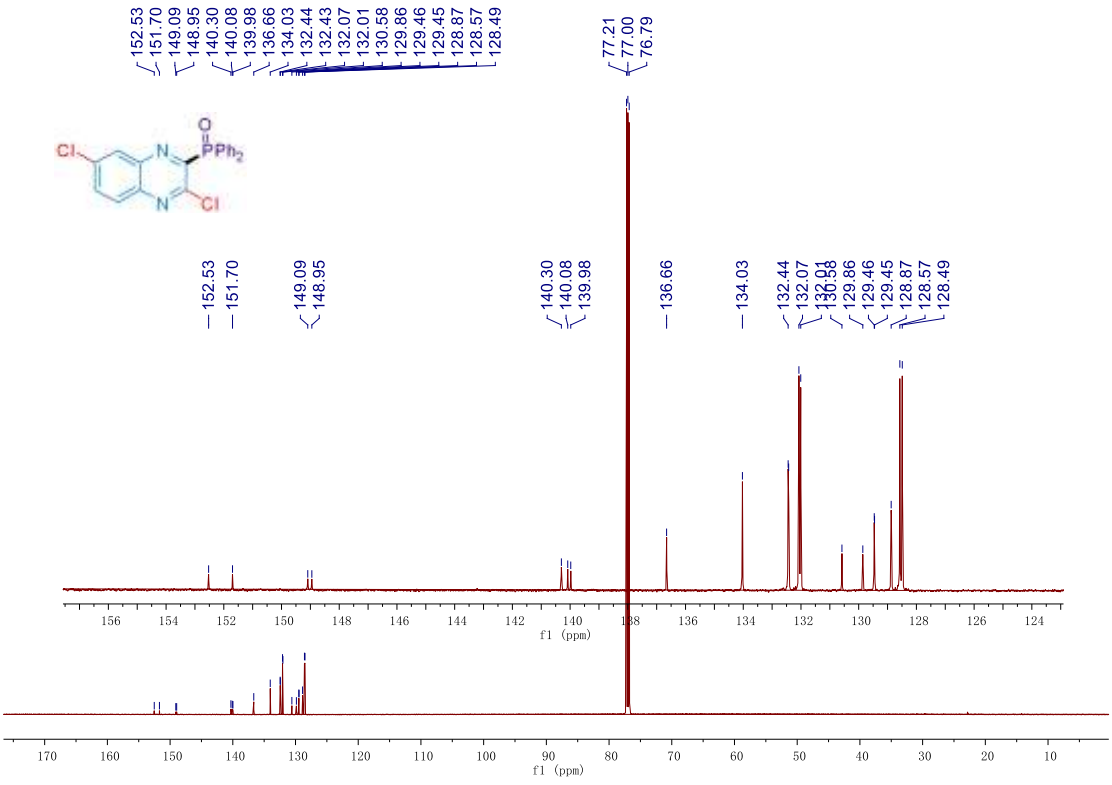


Fig.S 56 ^{13}C NMR of compound **3da**

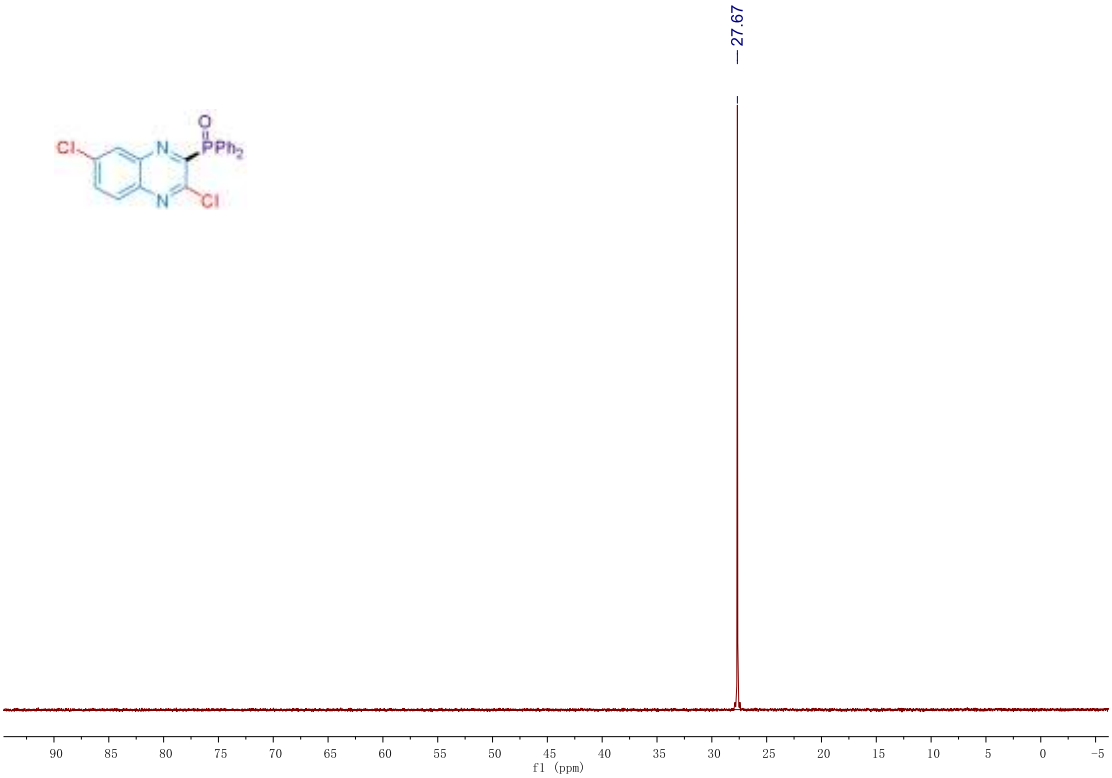


Fig.S 57 ^{31}P NMR of compound **3da**

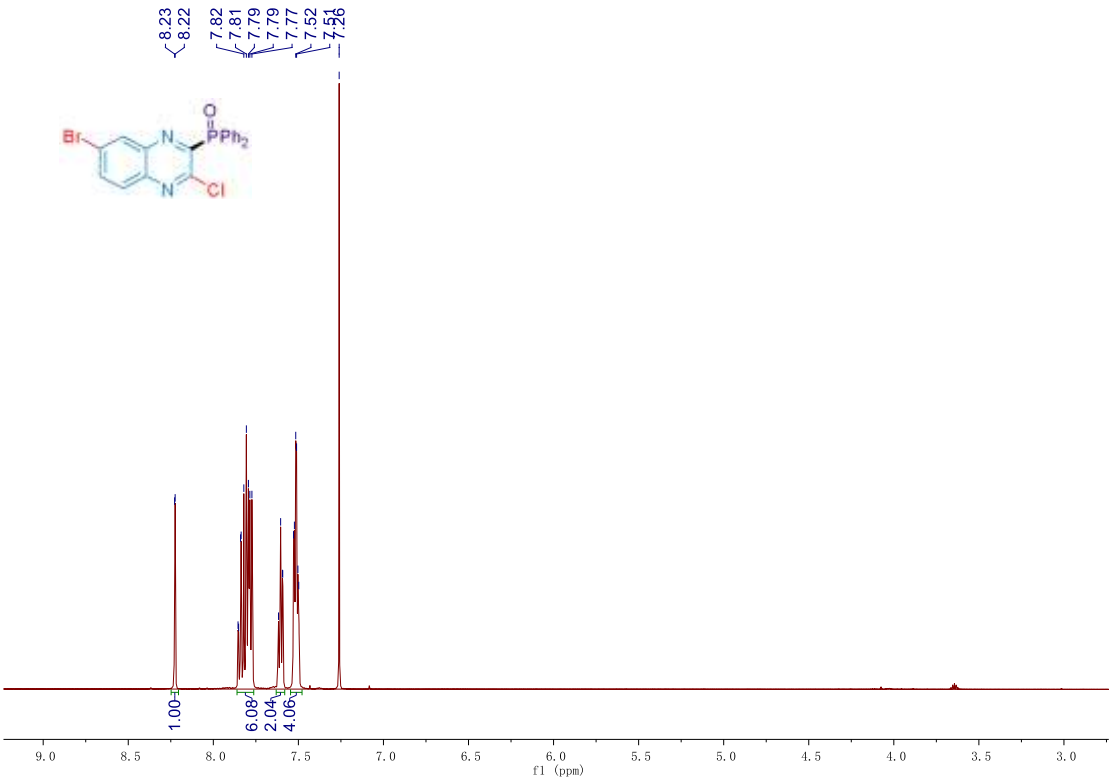


Fig.S 58 ^{1}H NMR of compound **3ea**

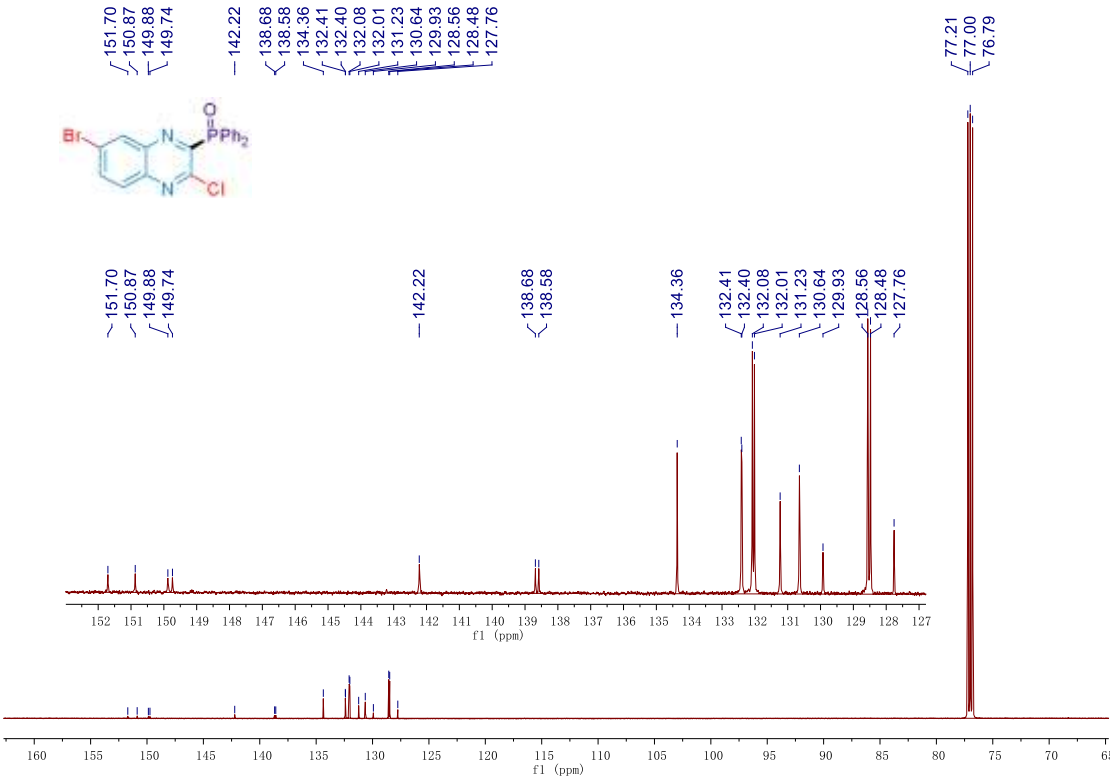


Fig.S 59 ^{13}C NMR of compound **3ea**

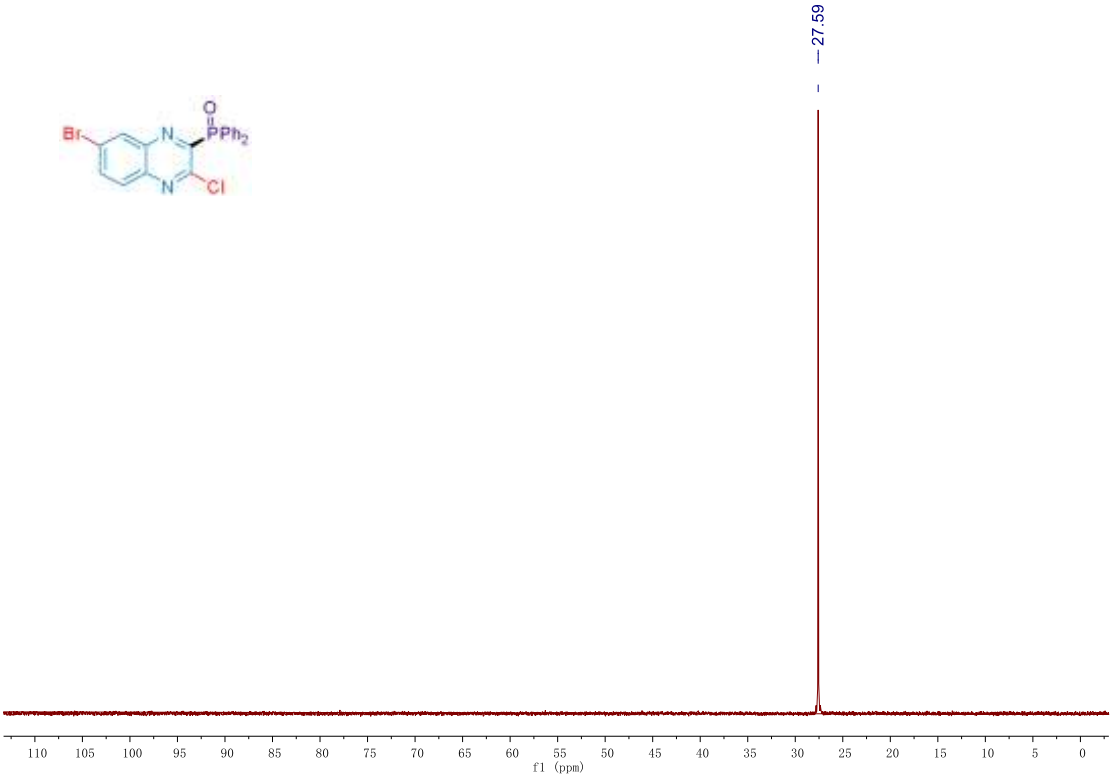


Fig.S 60 ^{31}P NMR of compound **3ea**

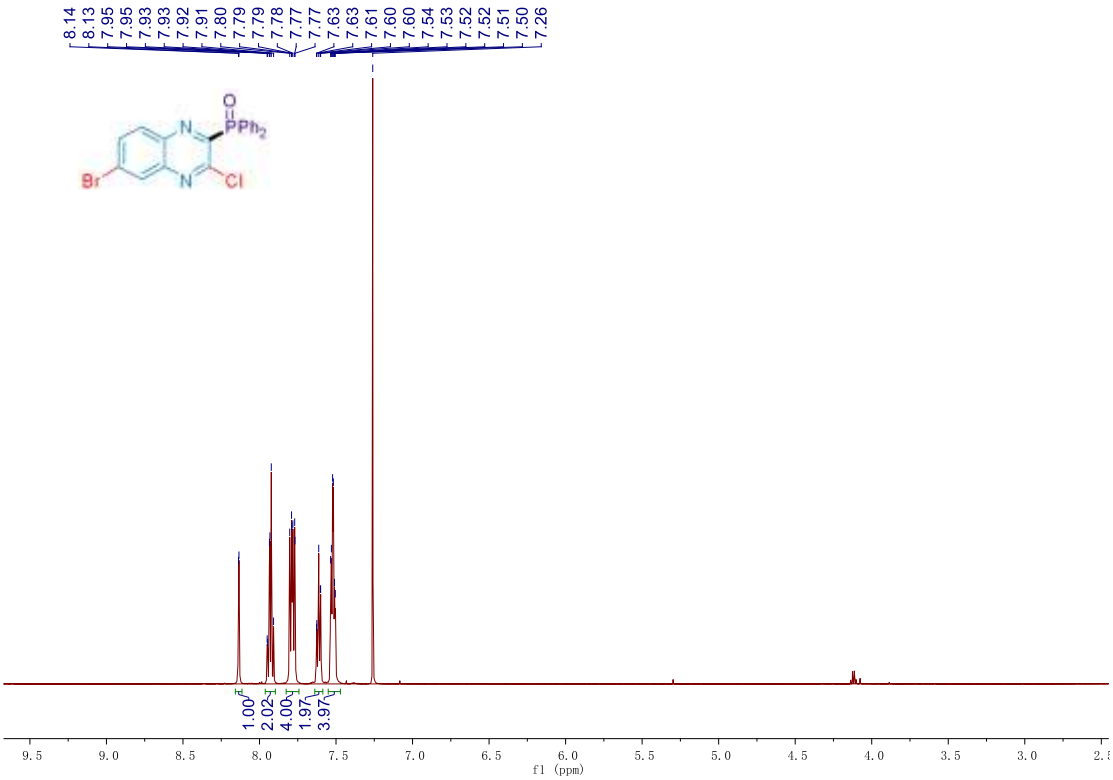


Fig.S 61 ^{1}H NMR of compound **3fa**

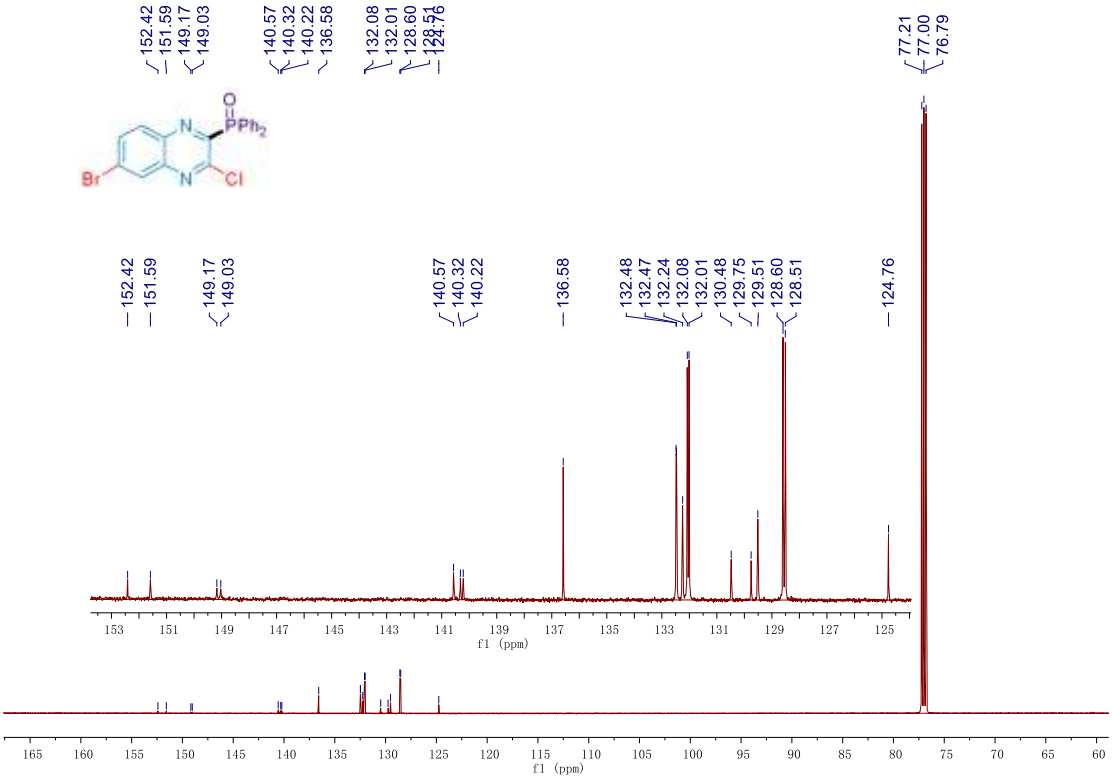


Fig.S 62 ^{13}C NMR of compound **3fa**

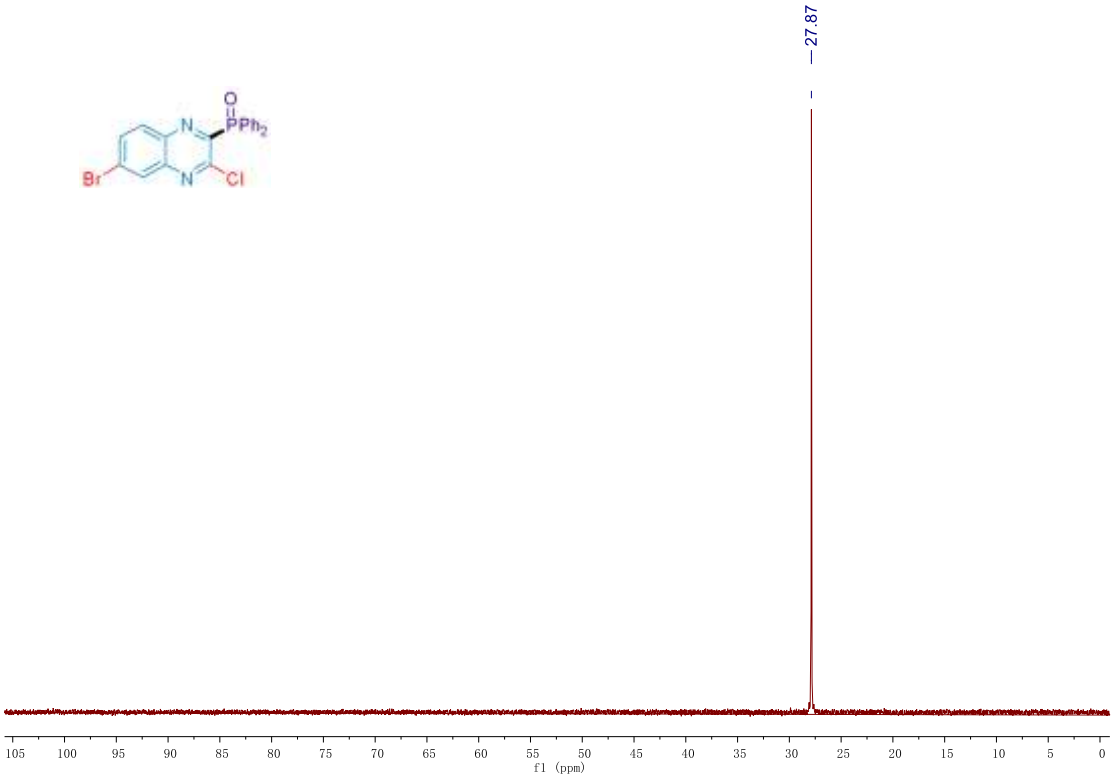


Fig.S 63 ^{31}P NMR of compound **3fa**

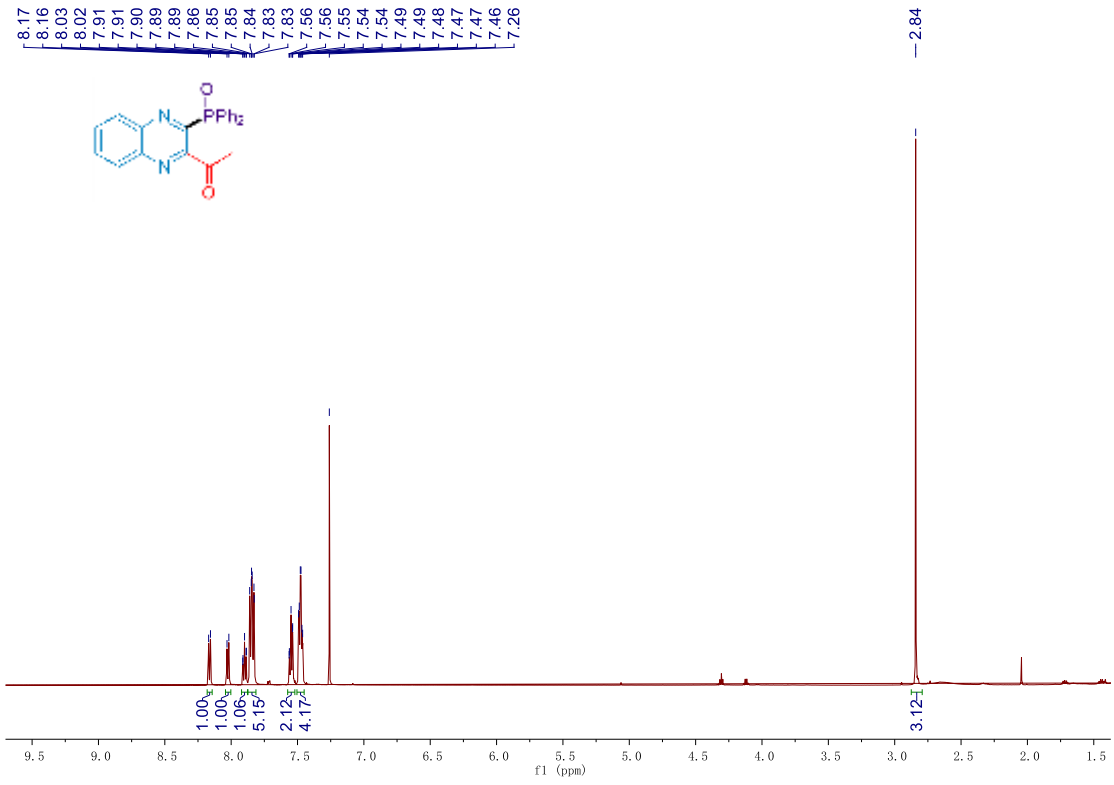


Fig.S 64 ^{1}H NMR of compound **3ga**

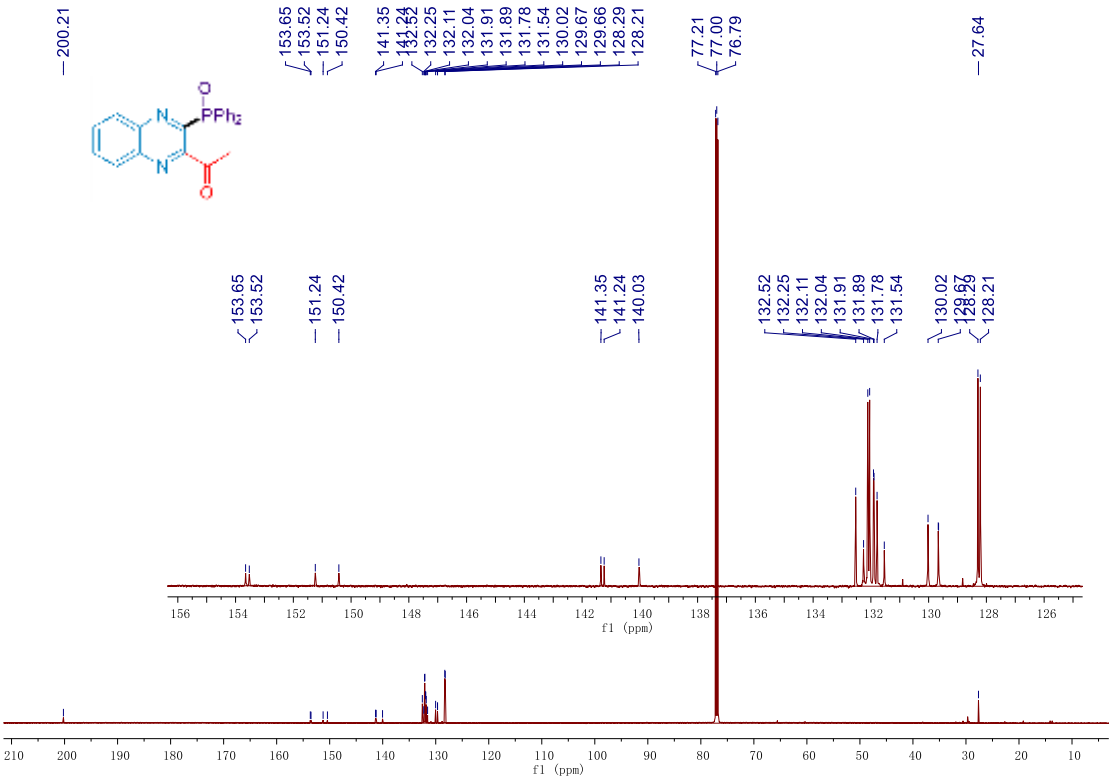


Fig.S 65 ^{13}C NMR of compound **3ga**

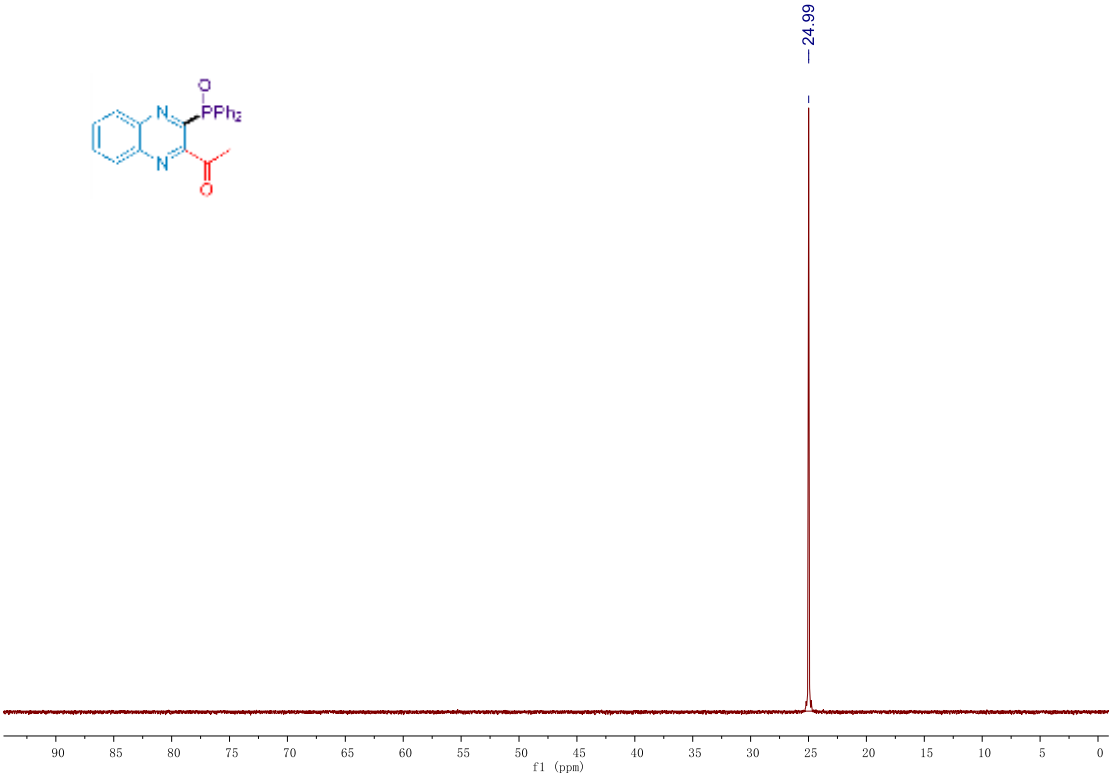


Fig.S 66 ^{31}P NMR of compound **3ga**

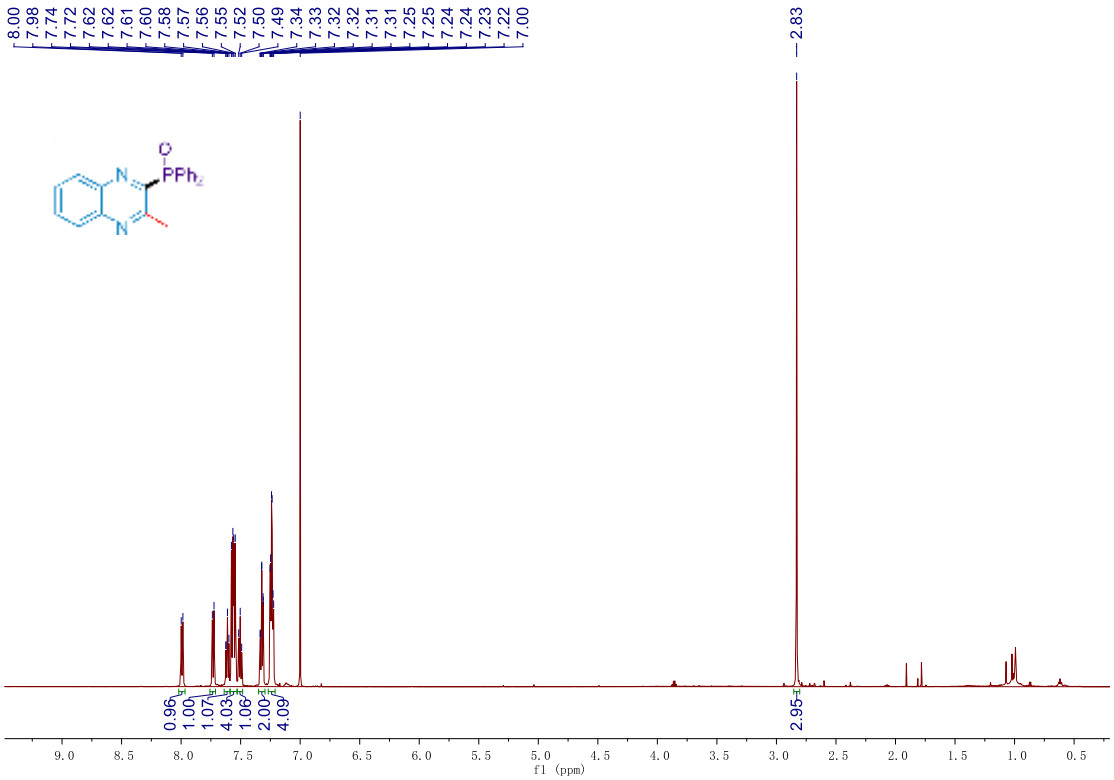


Fig.S 67 ^{1}H NMR of compound **3ha**

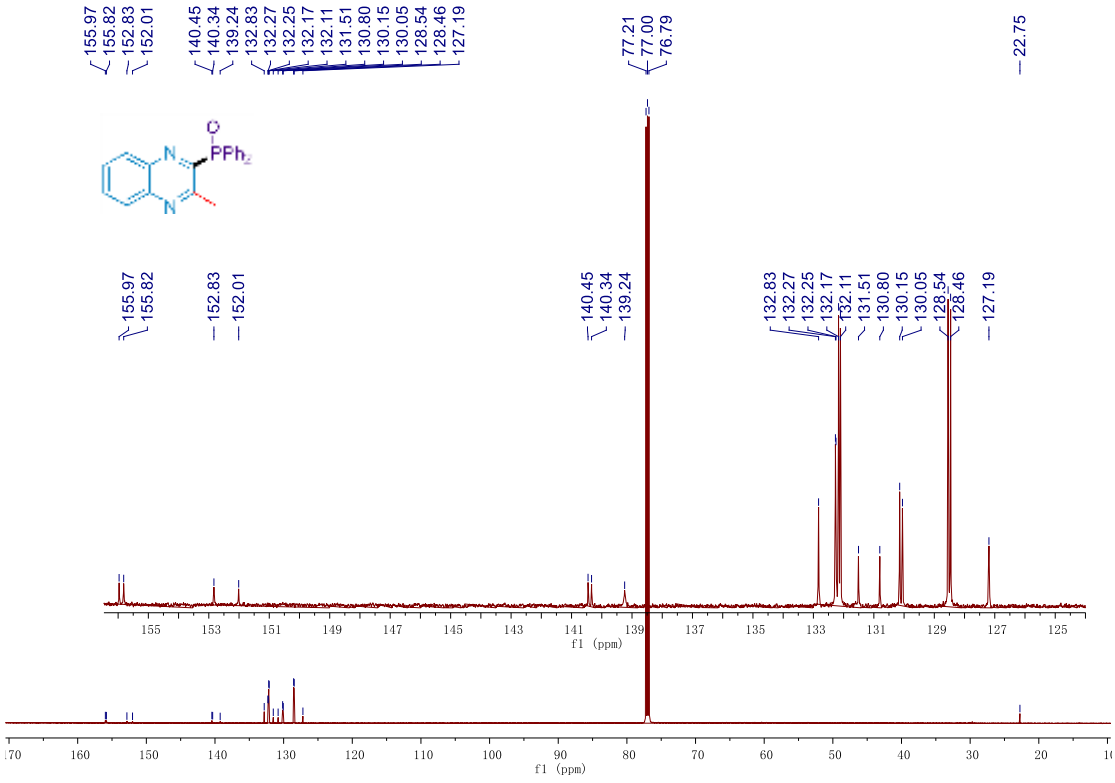


Fig.S 68 ^{13}C NMR of compound **3ha**

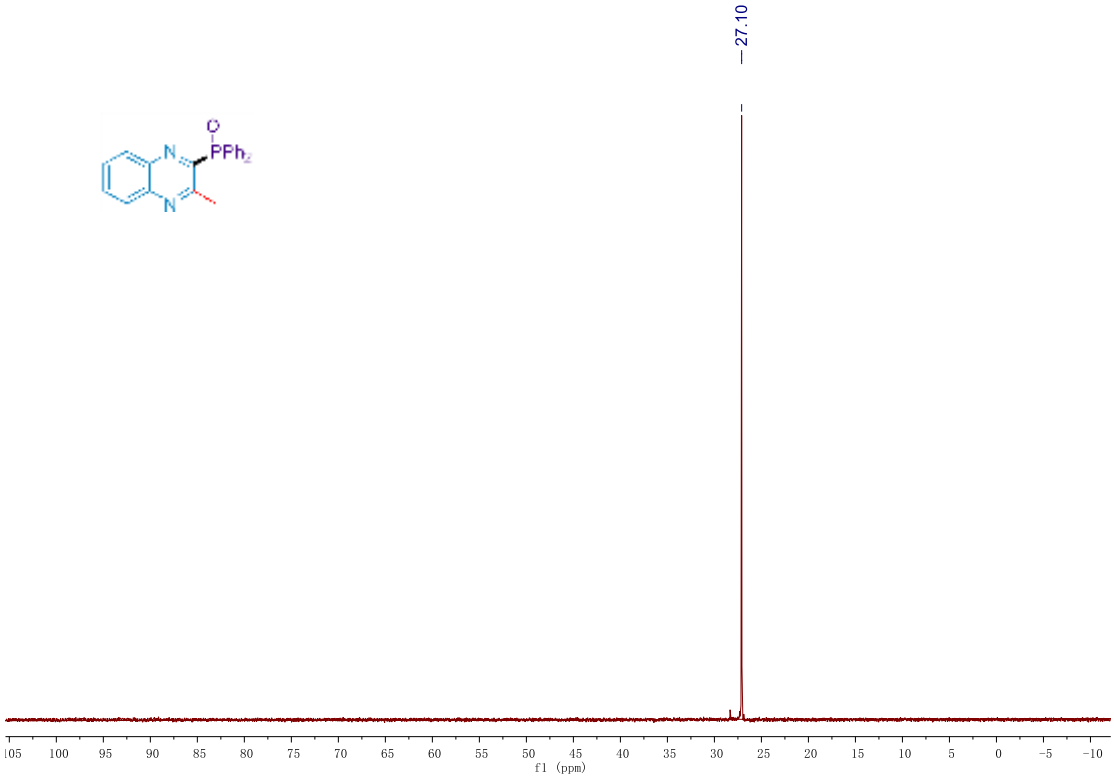


Fig.S 69 ^{31}P NMR of compound **3ha**

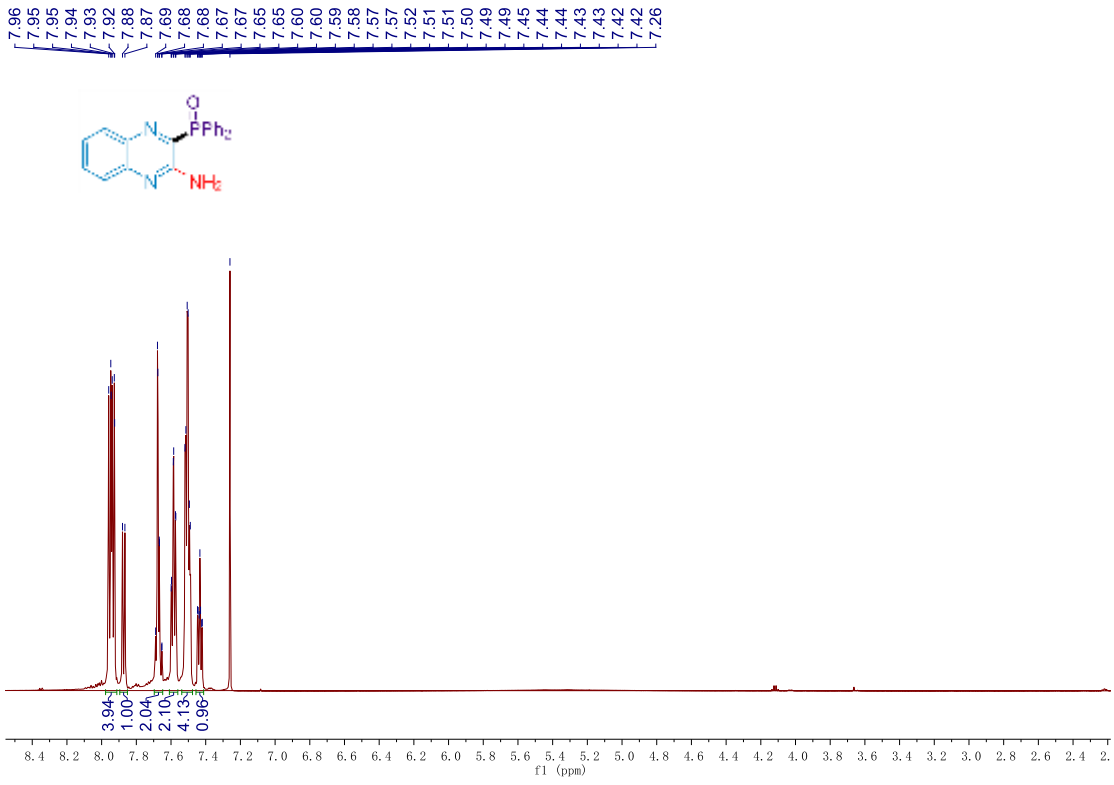


Fig.S 70 ^{1}H NMR of compound **3ia**

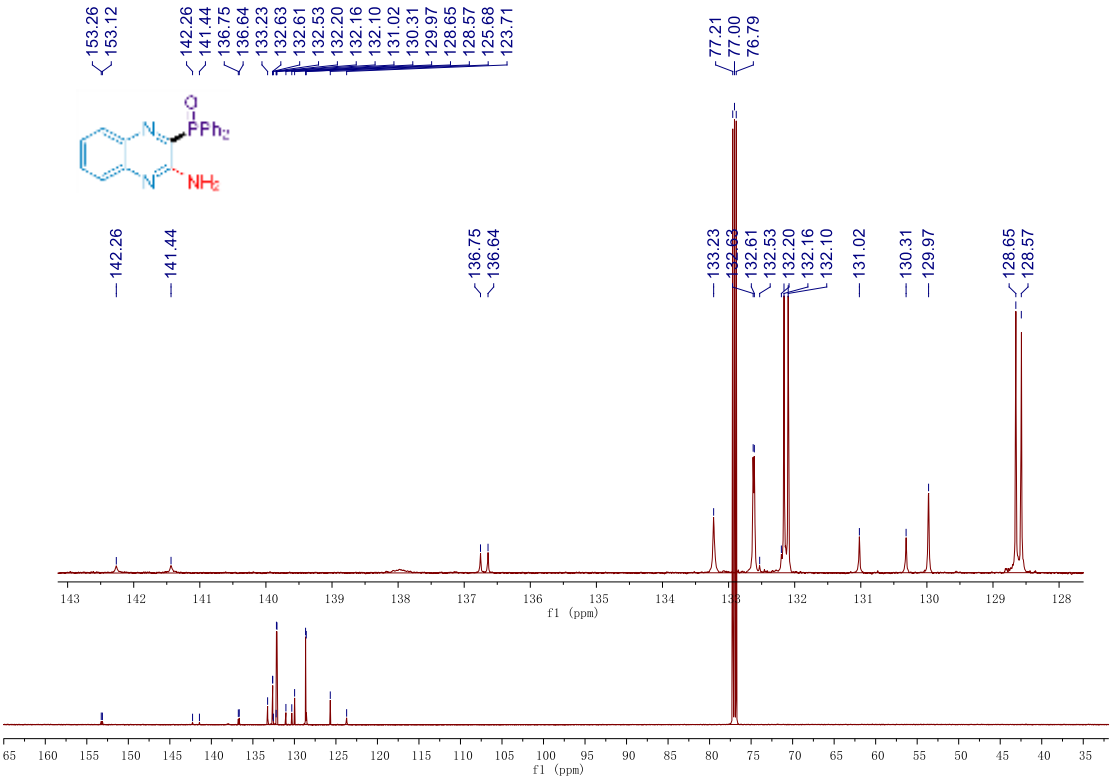


Fig.S 71 ^{13}C NMR of compound **3ia**

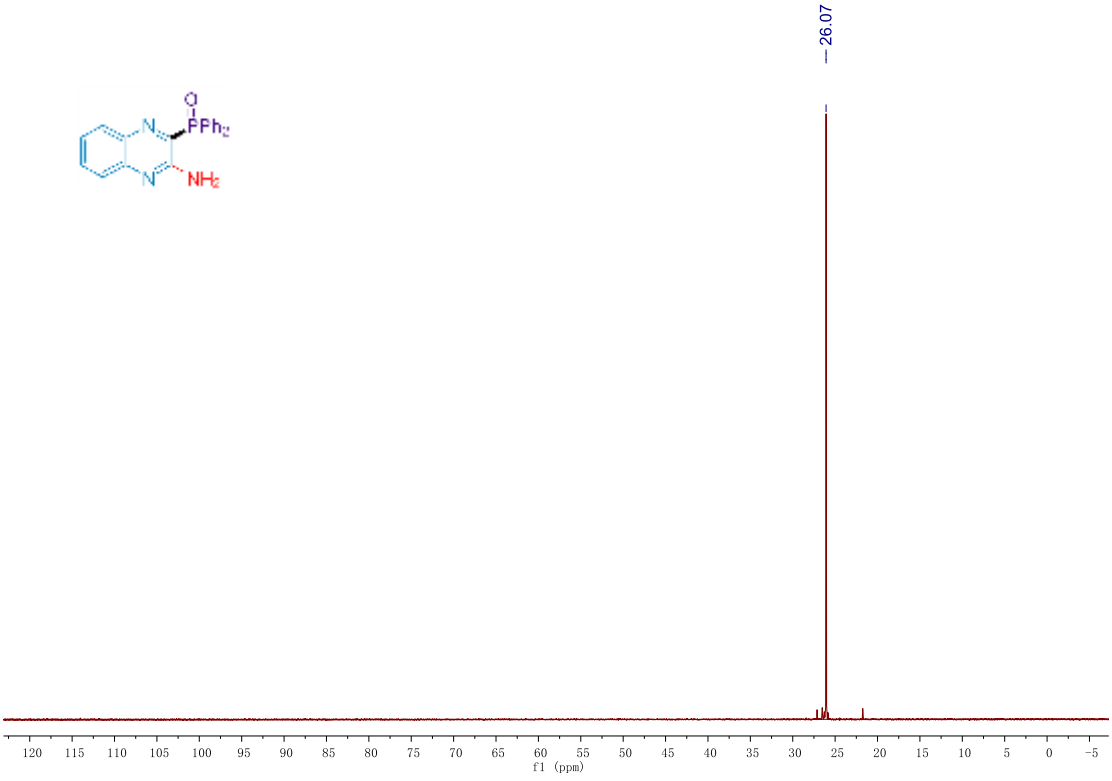


Fig.S 72 ^{31}P NMR of compound **3ia**

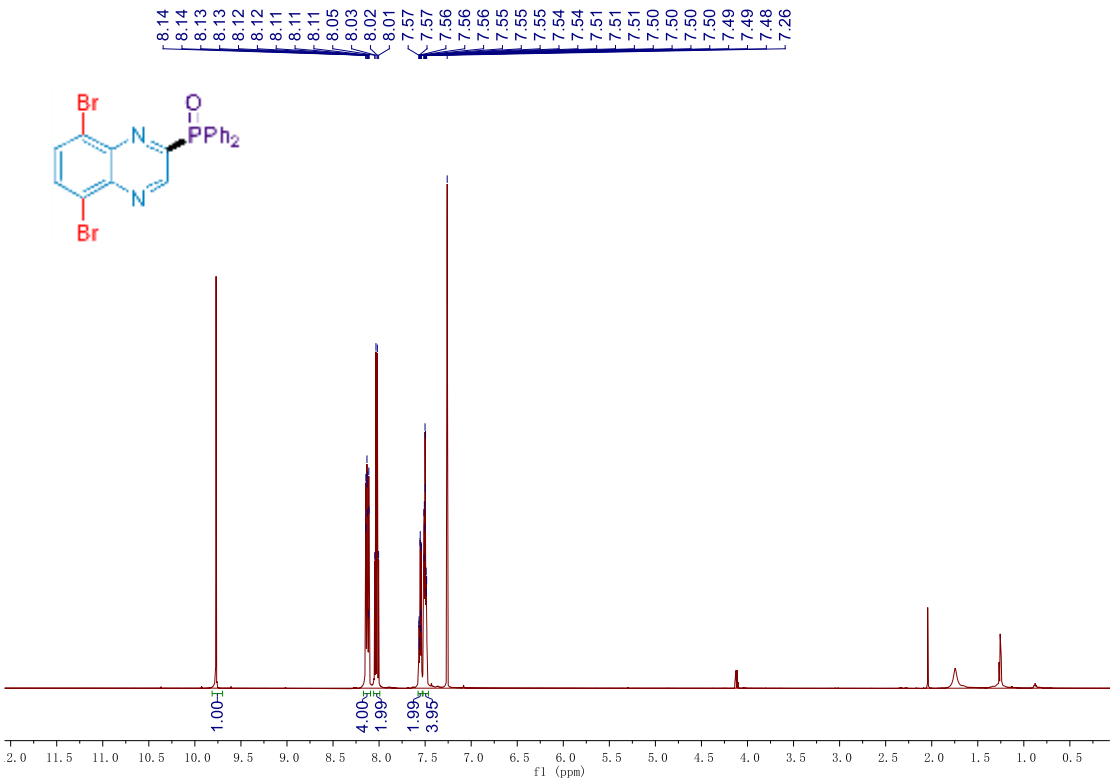


Fig.S 73 ^{1}H NMR of compound **3ja**

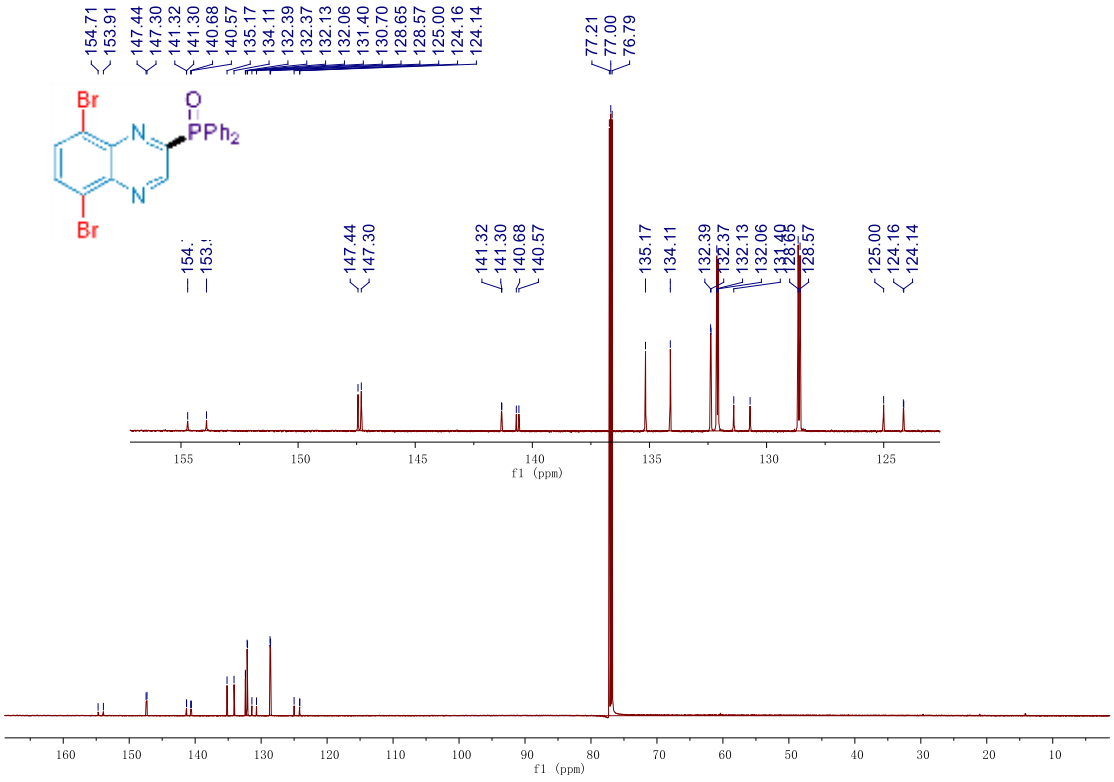


Fig.S 74 ^{13}C NMR of compound **3ja**

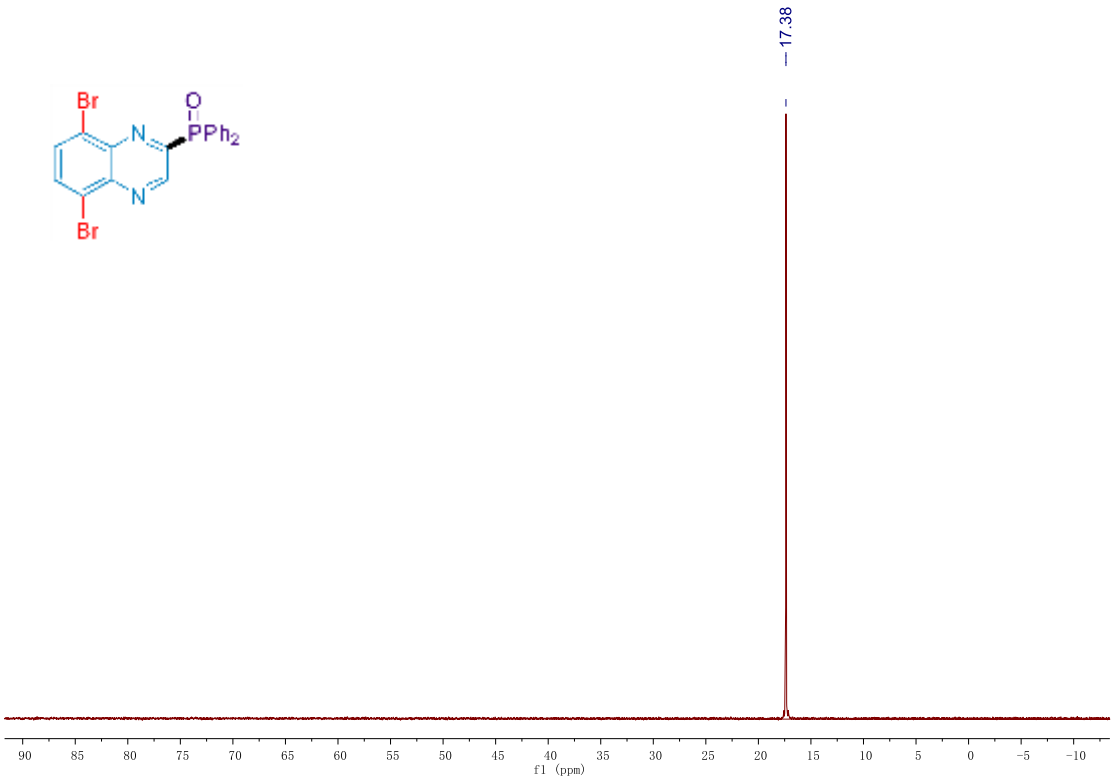


Fig.S 75 ^{31}P NMR of compound **3ja**

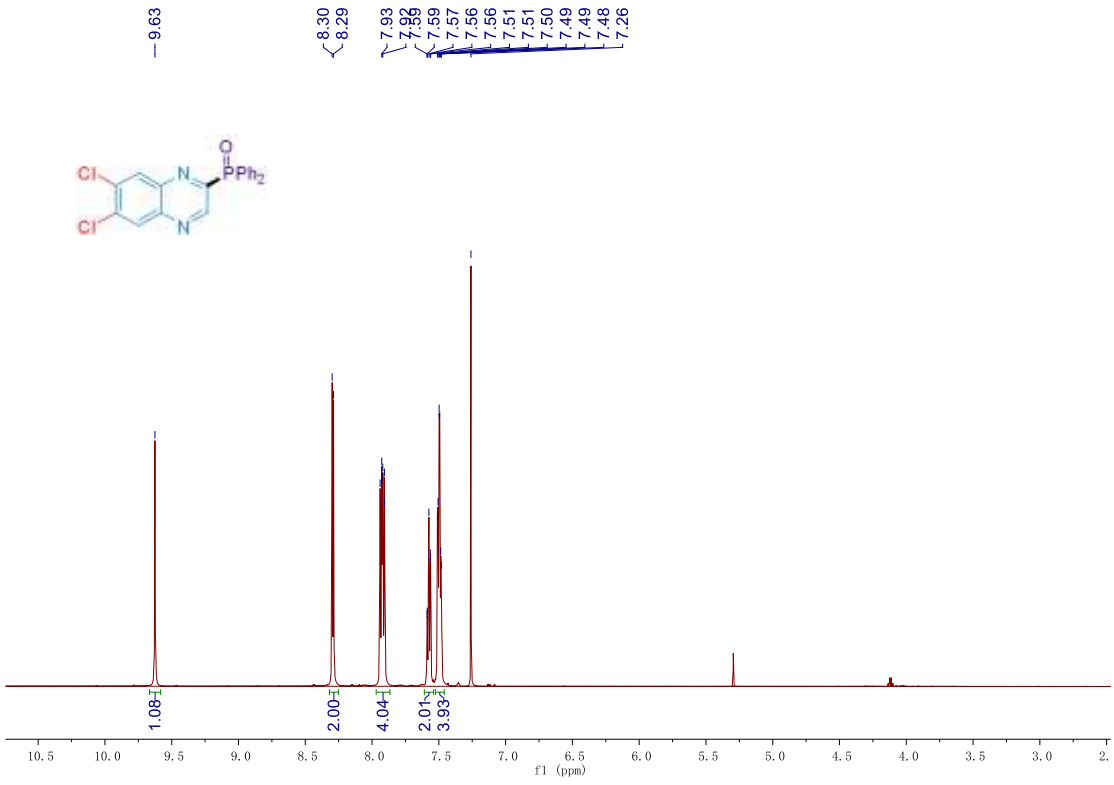


Fig.S 76 ^{1}H NMR of compound **3ka**

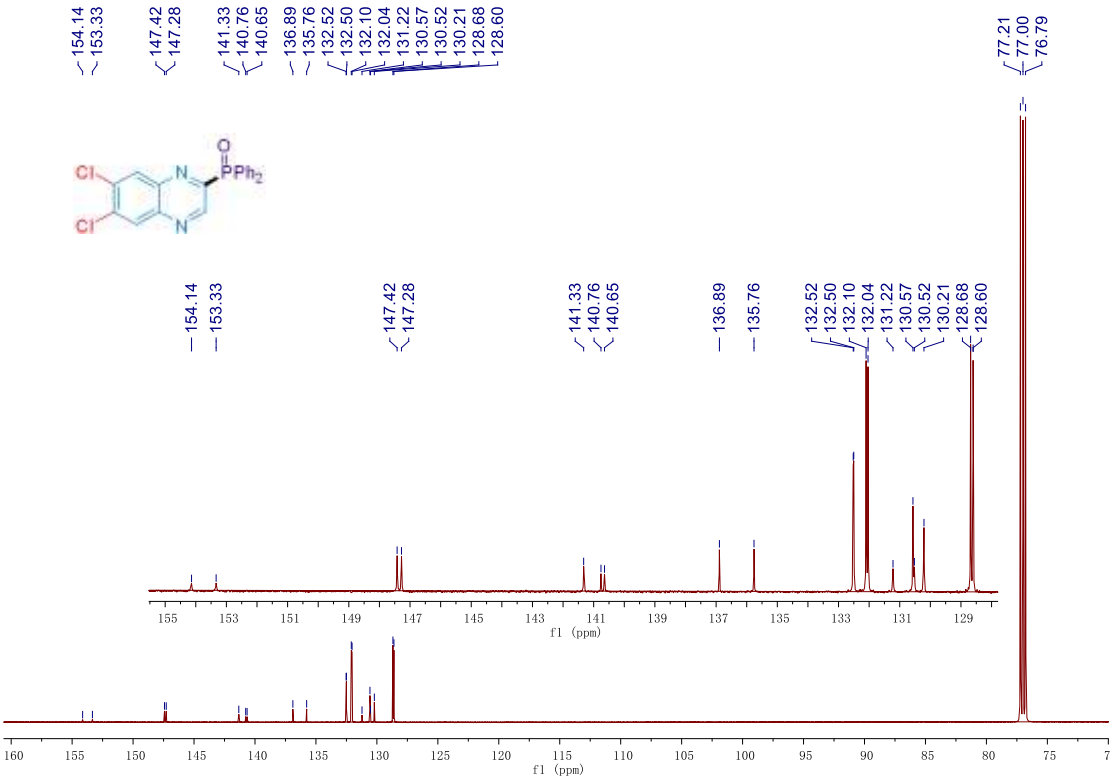


Fig.S 77 ^{13}C NMR of compound **3ka**

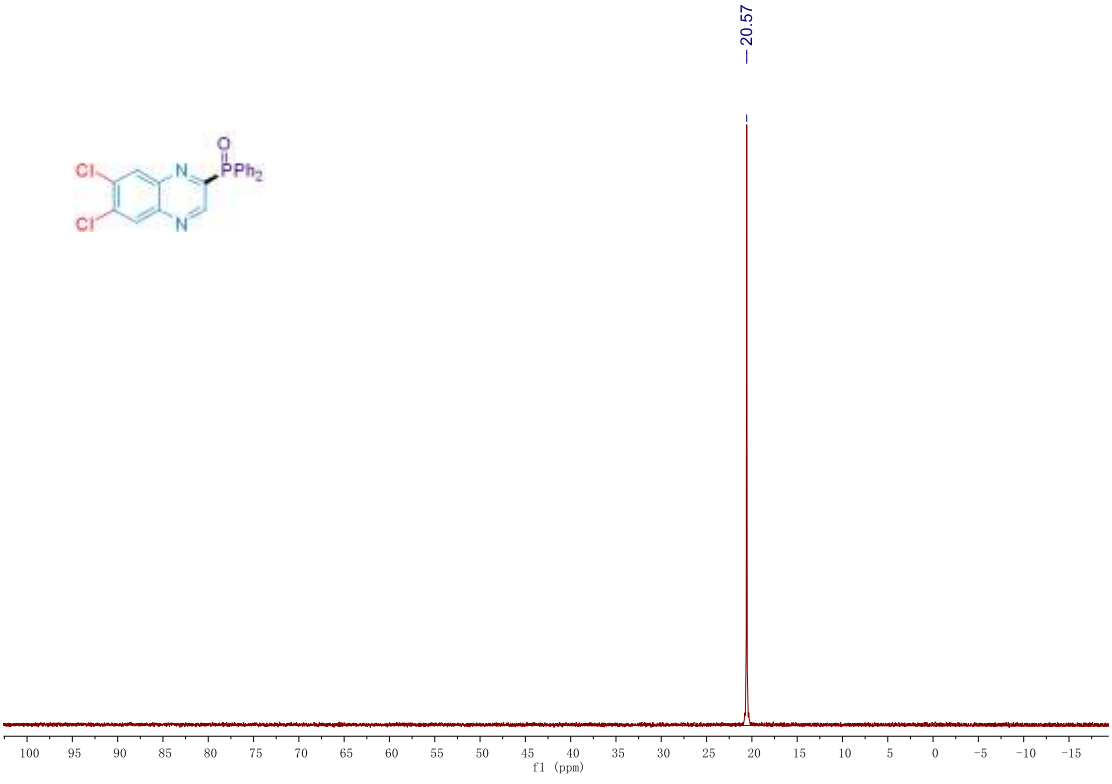


Fig.S 78 ^{31}P NMR of compound **3ka**

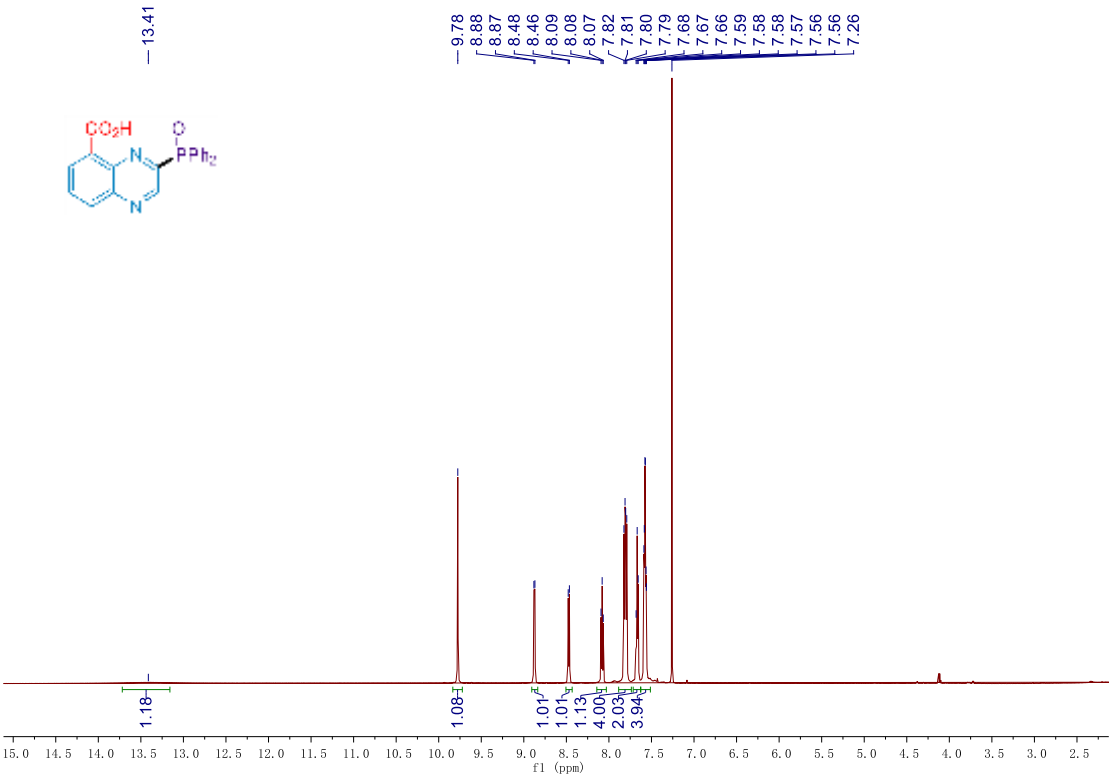


Fig.S 79 ^{1}H NMR of compound **3la-1**

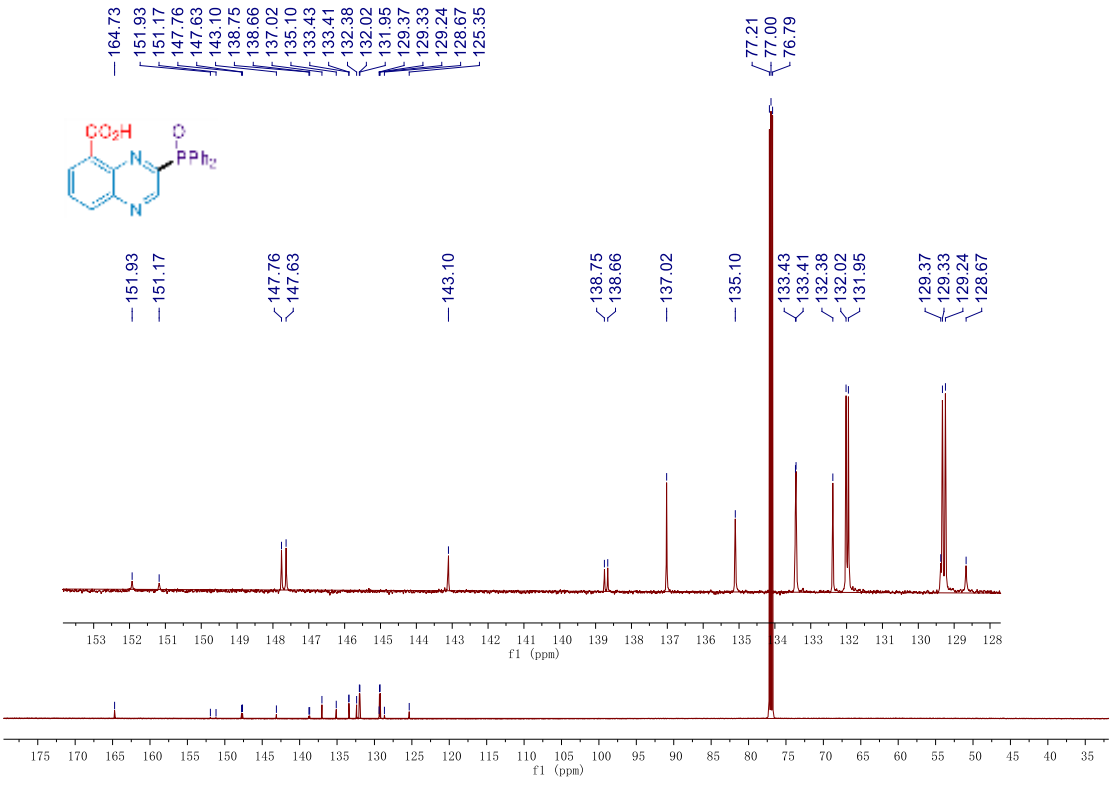


Fig.S 80 ^{13}C NMR of compound **3la-1**

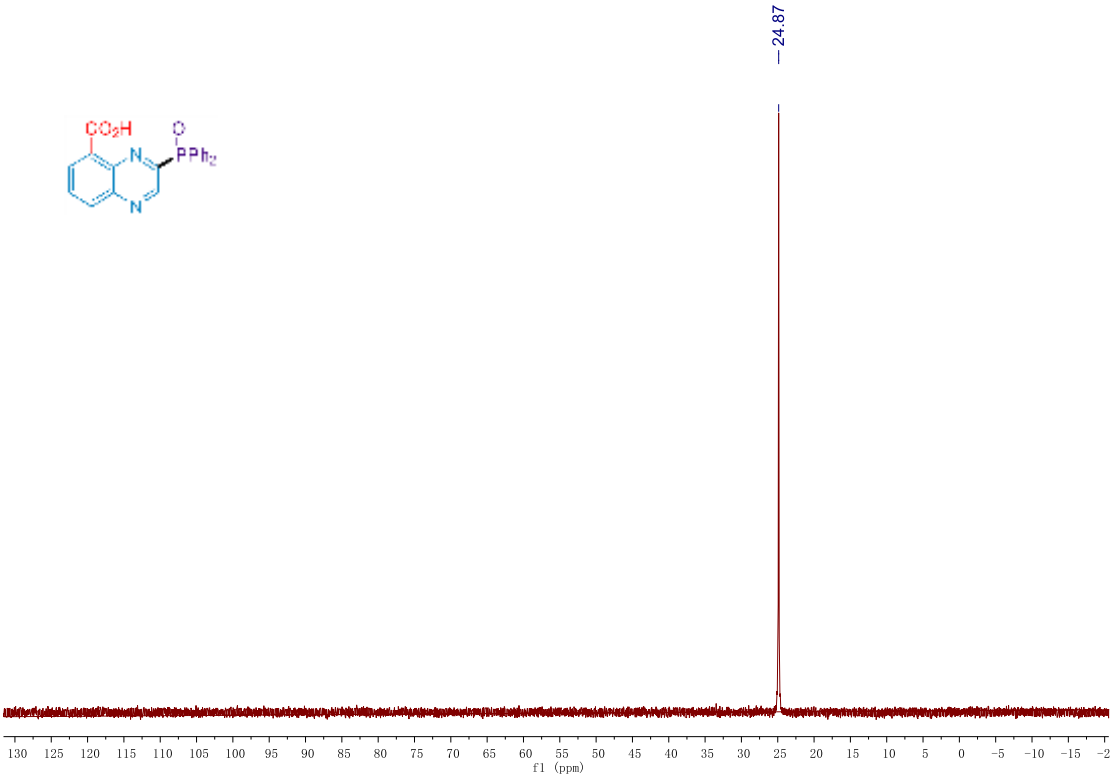


Fig.S 81 ^{31}P NMR of compound **3la-1**

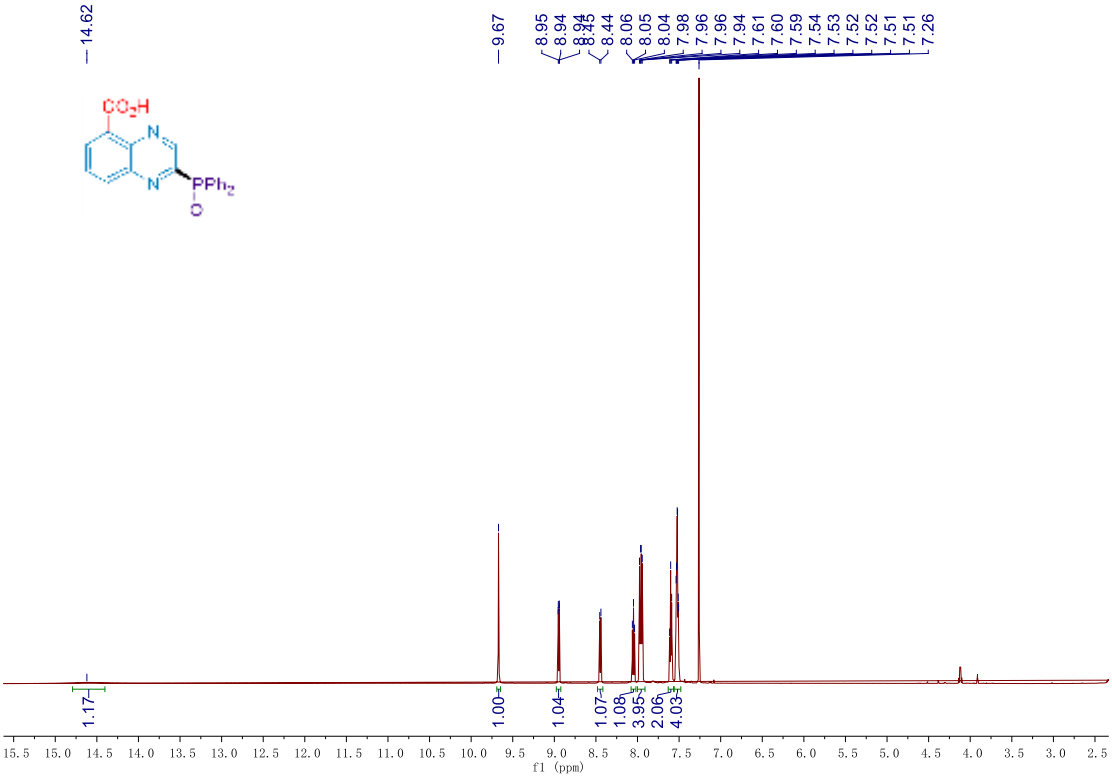


Fig.S 82 ^{1}H NMR of compound **3la-2**

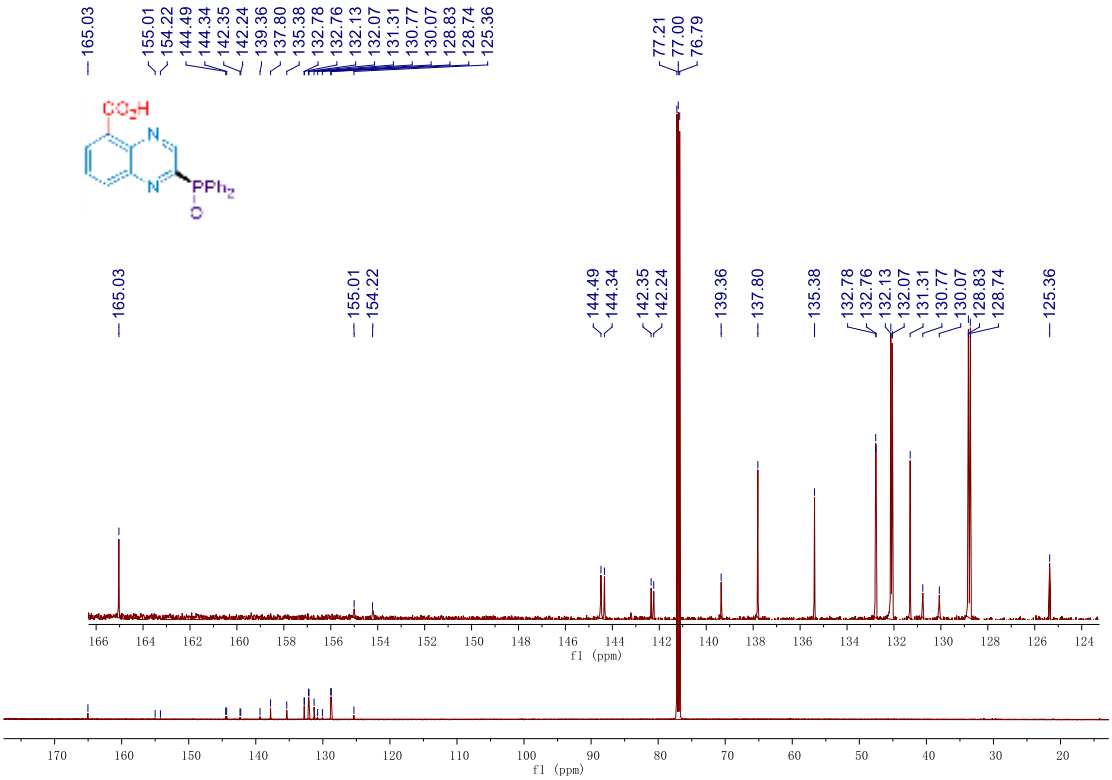


Fig.S 83 ^{13}C NMR of compound **3la-2**

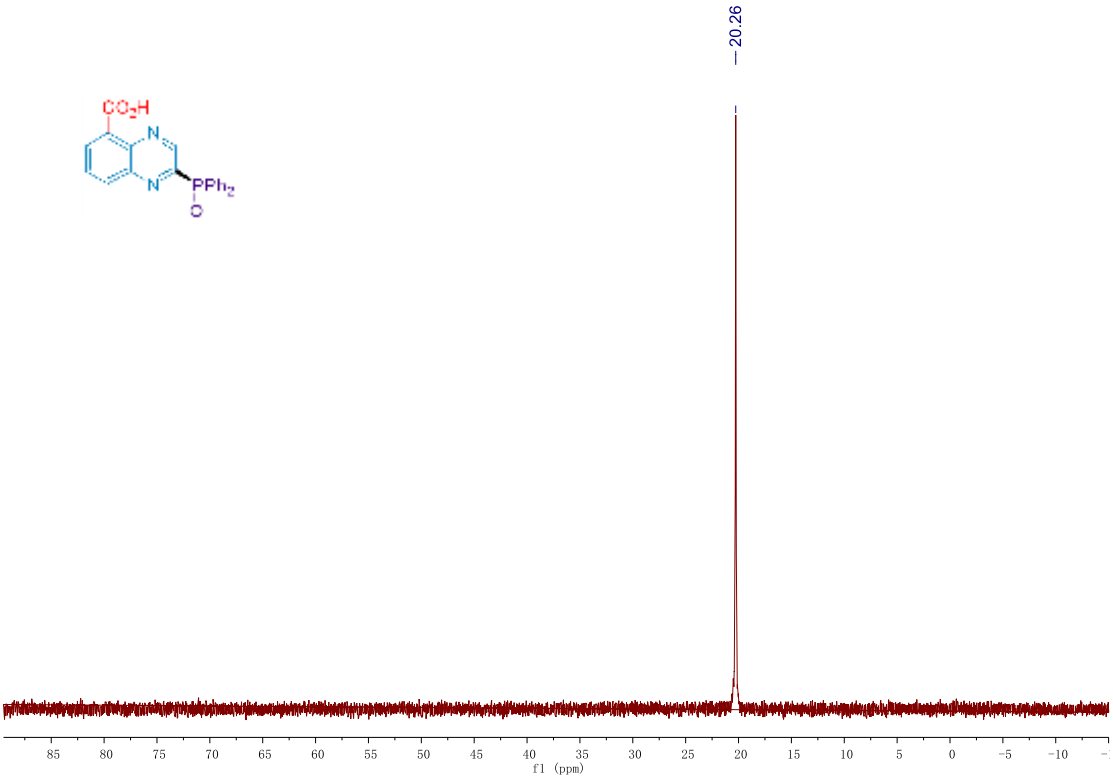


Fig.S 84 ^{31}P NMR of compound **3la-2**

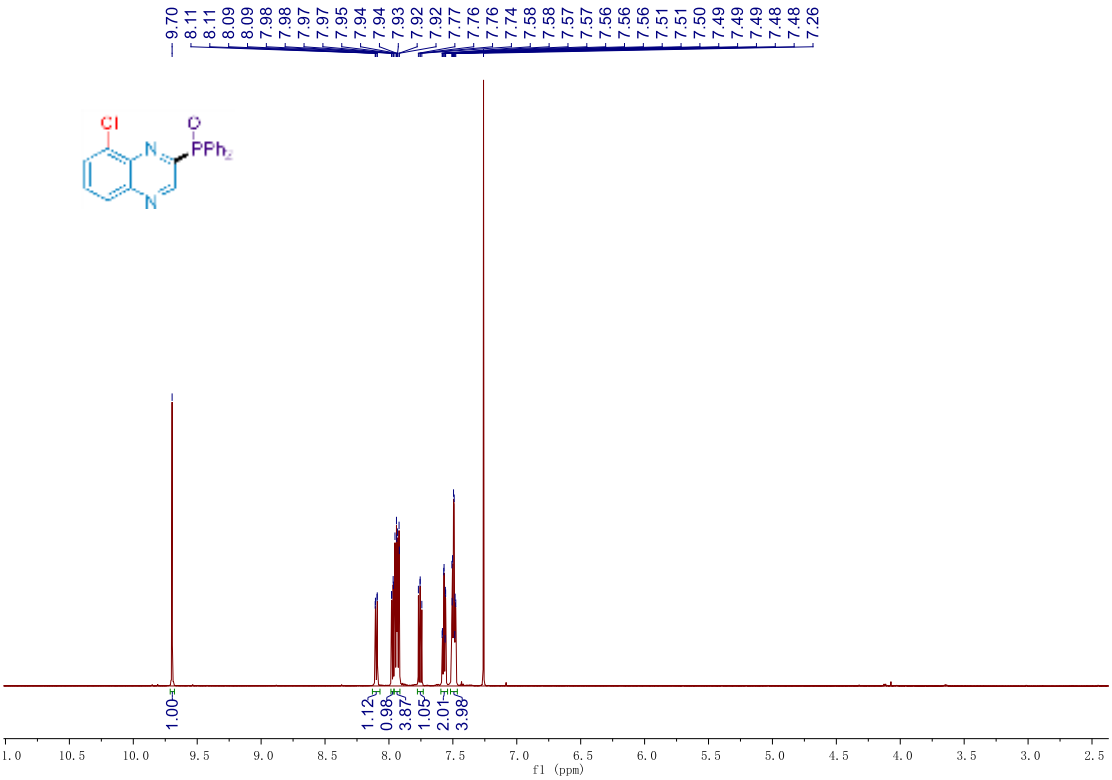


Fig.S 85 ^{1}H NMR of compound **3ma-1**

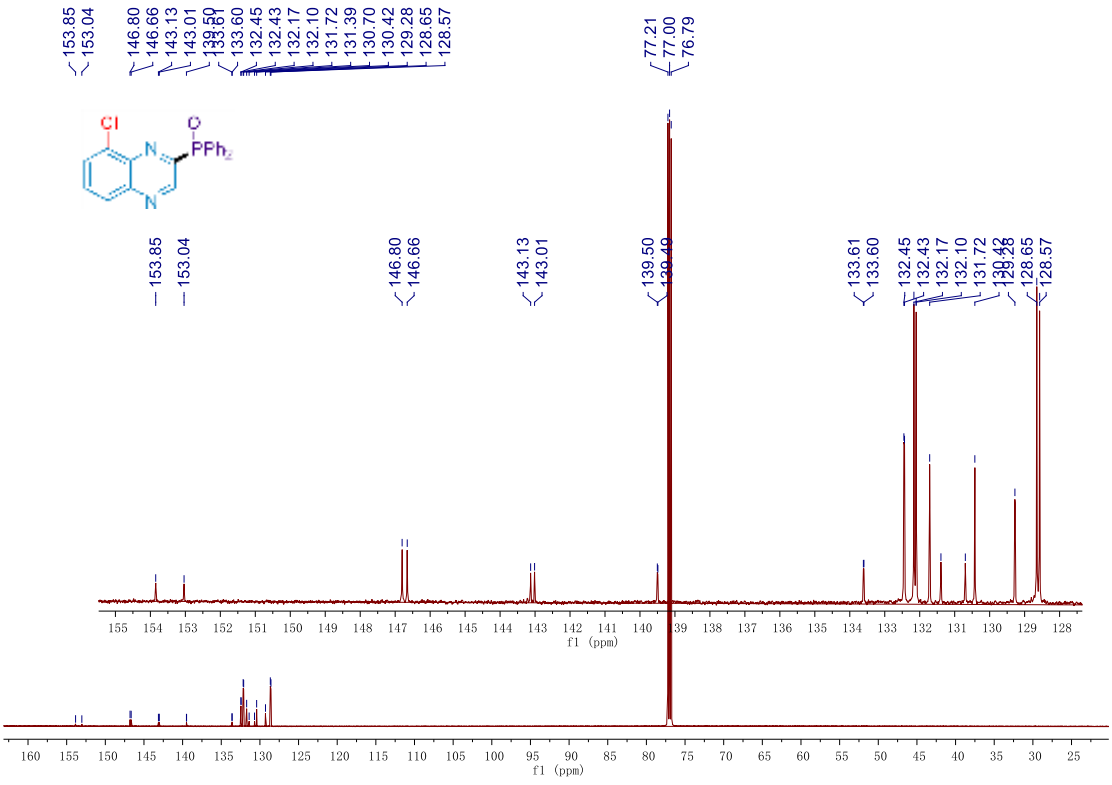


Fig.S 86 ^{13}C NMR of compound **3ma-1**

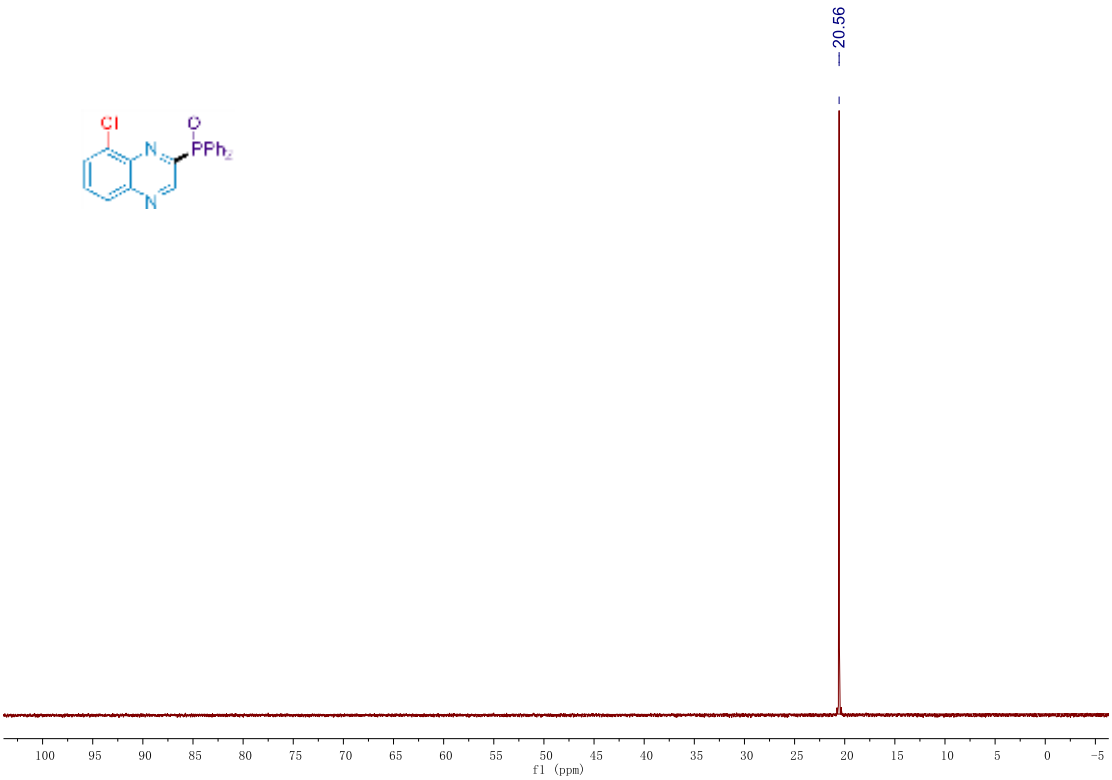


Fig.S 87 ^{31}P NMR of compound **3ma-1**

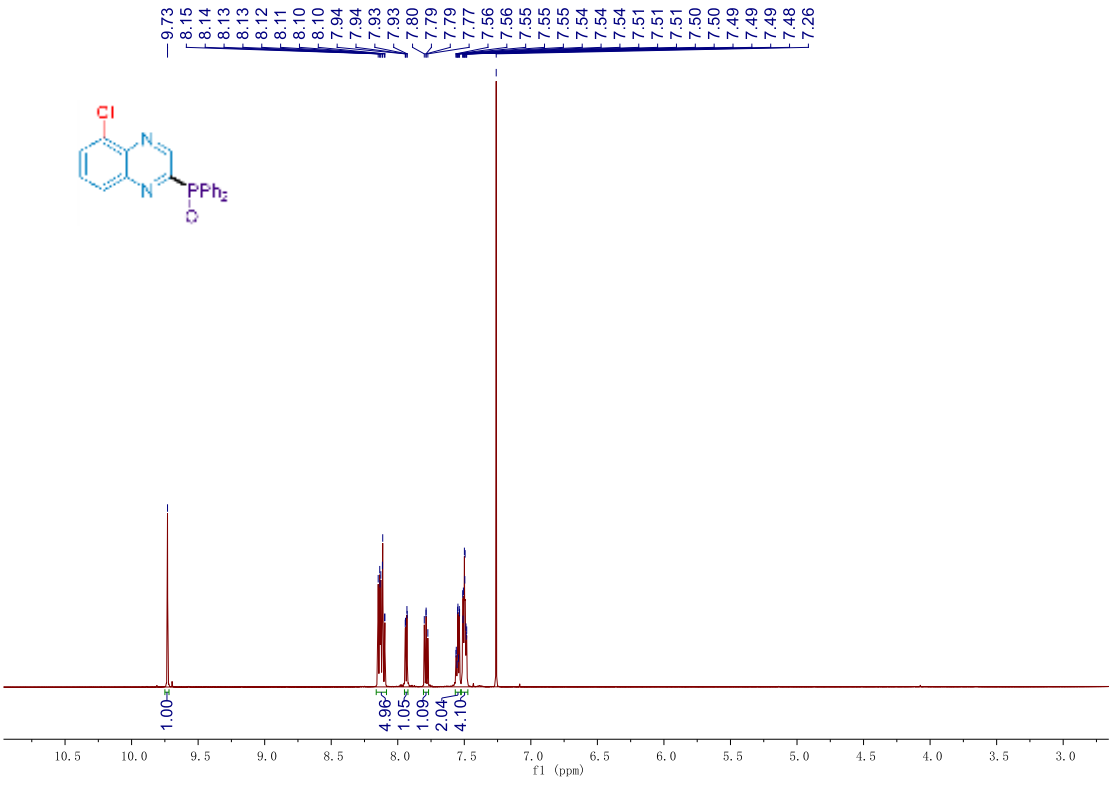


Fig.S 88 ^{1}H NMR of compound **3ma-2**

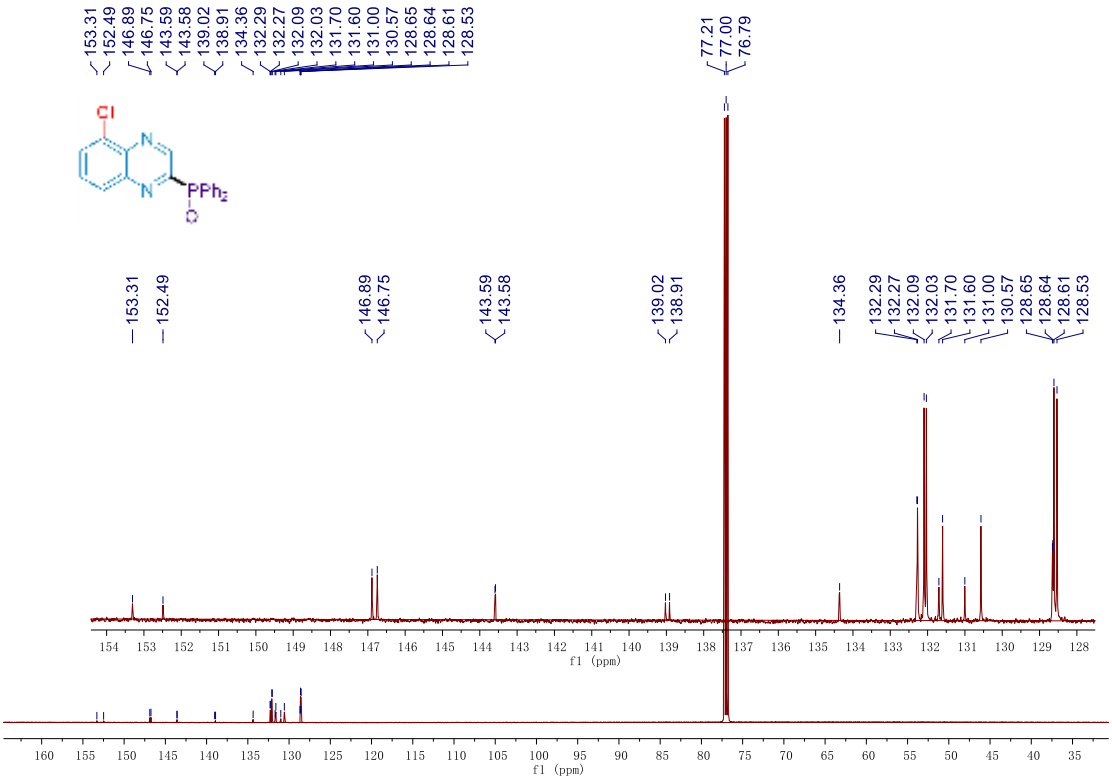


Fig.S 89 ^{13}C NMR of compound **3ma-2**

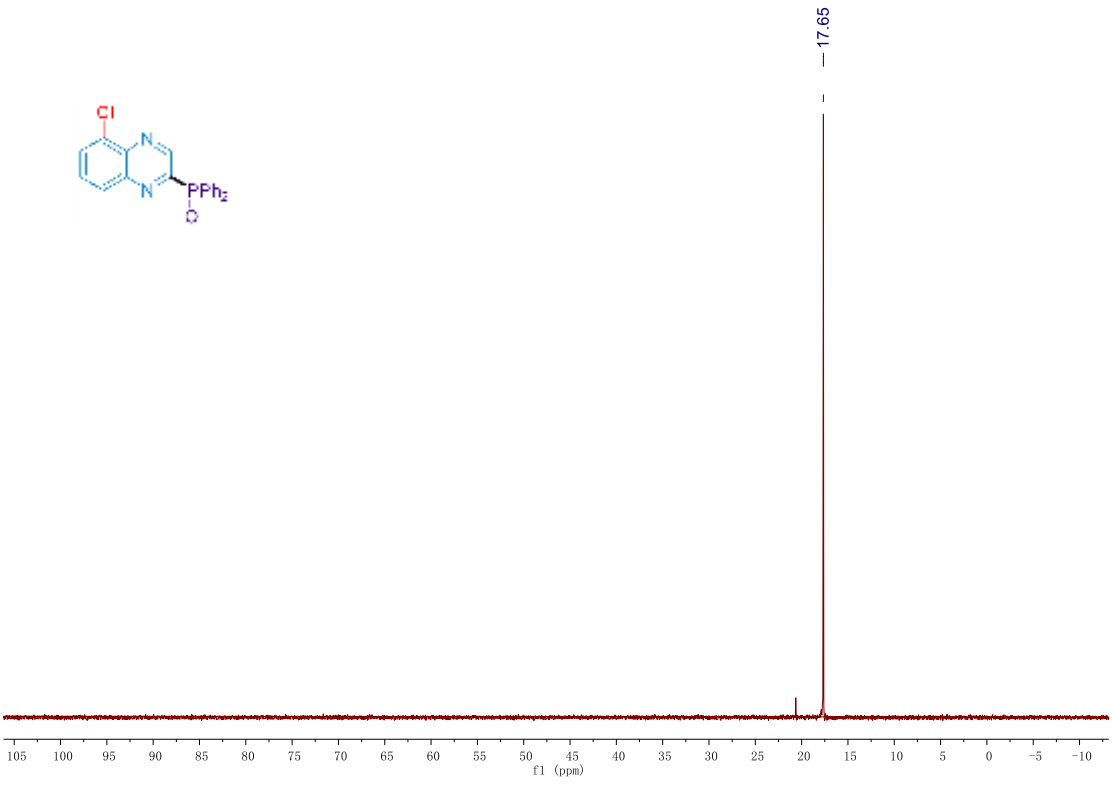


Fig.S 90 ^{31}P NMR of compound **3ma-2**

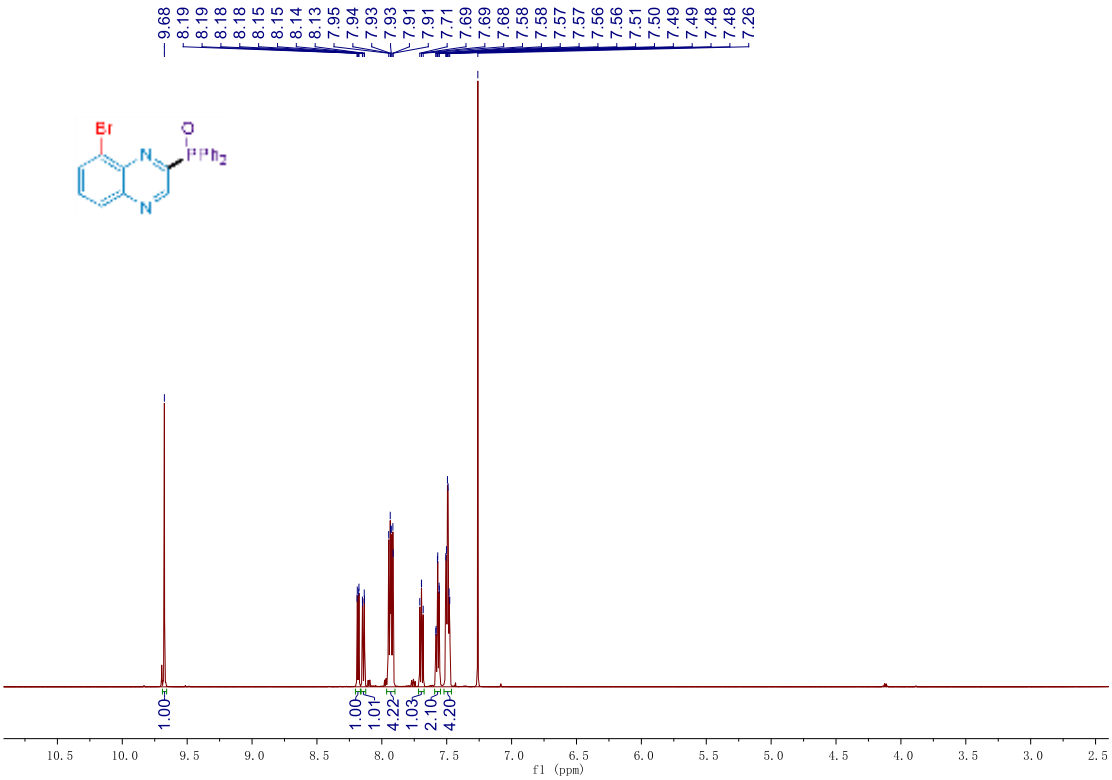


Fig.S 91 ^{1}H NMR of compound **3na-1**

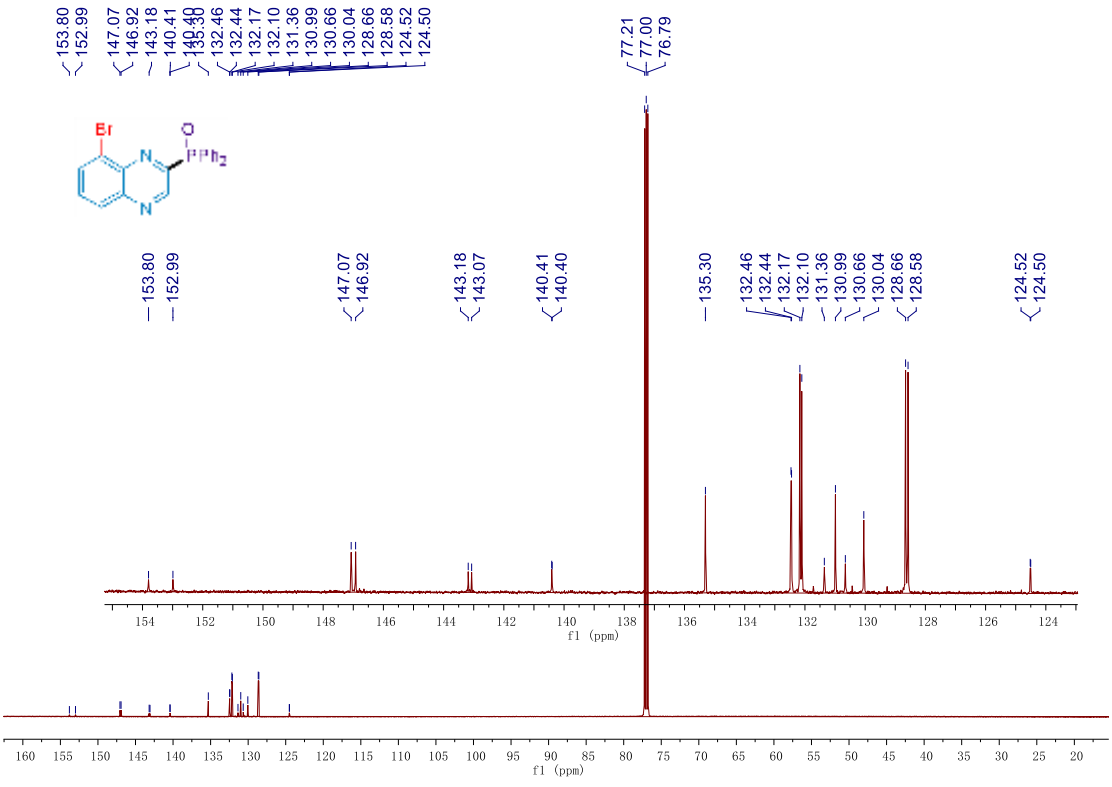


Fig.S 92 ^{13}C NMR of compound **3na-1**

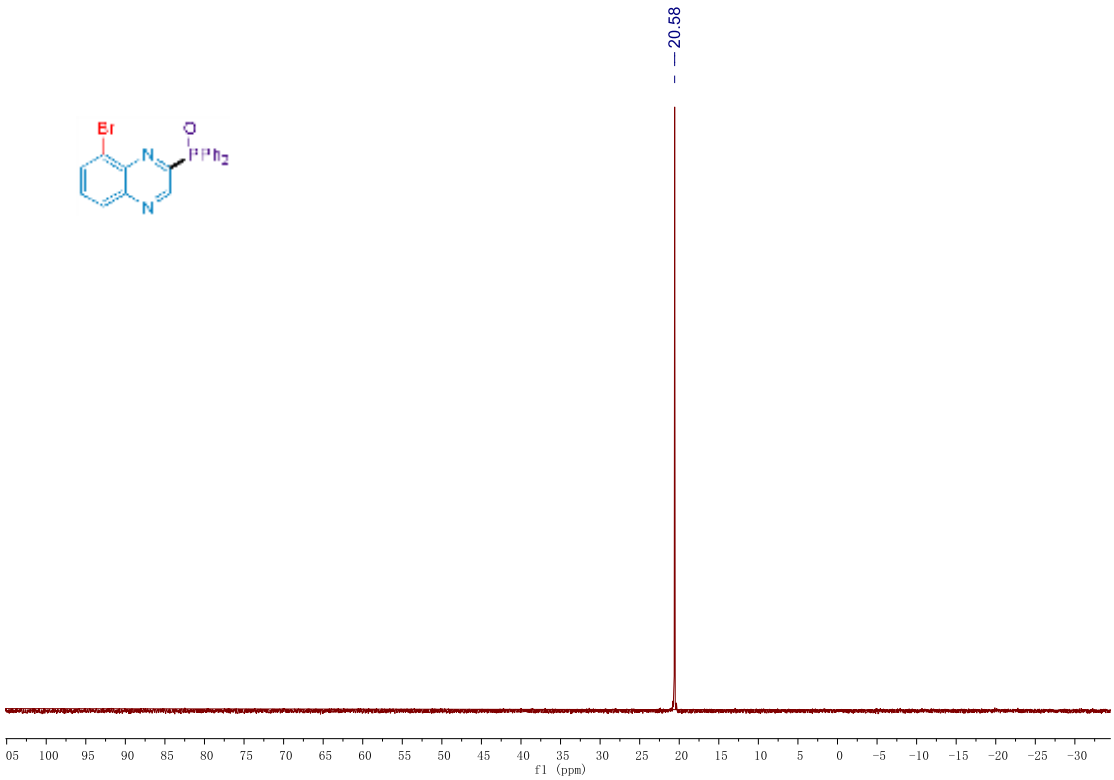


Fig.S 93 ^{31}P NMR of compound **3na-1**

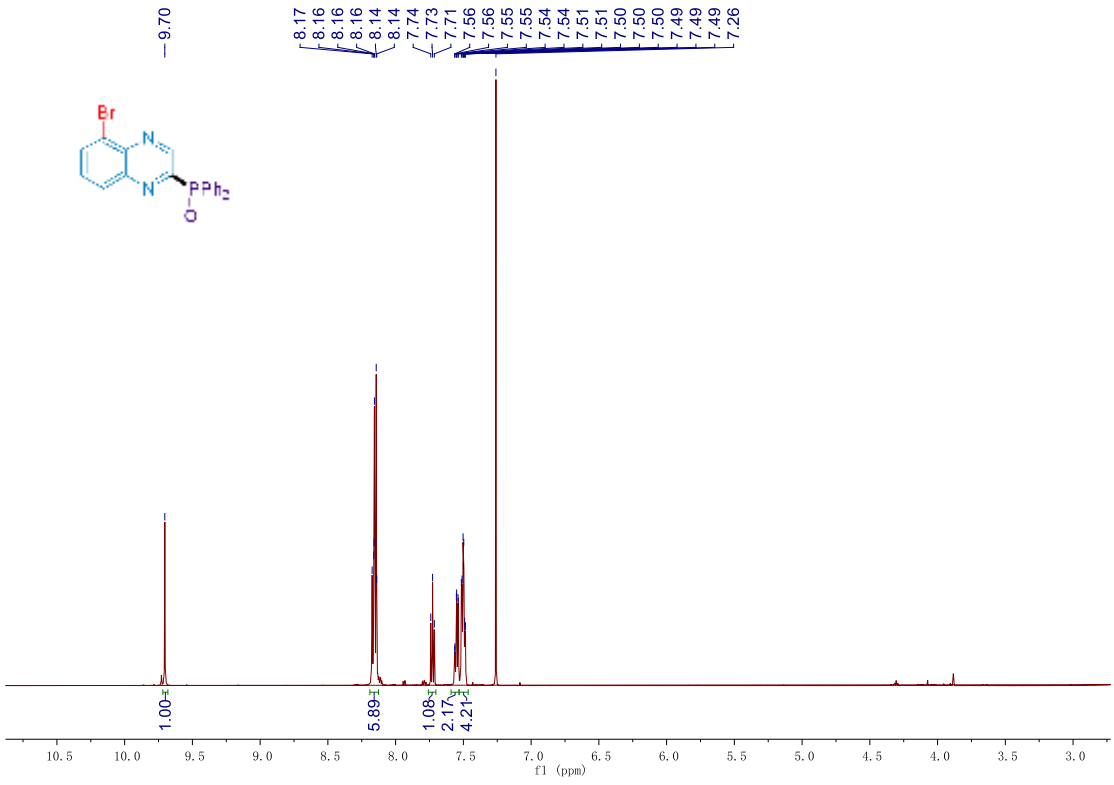


Fig.S 94 ^{1}H NMR of compound **3na-2**

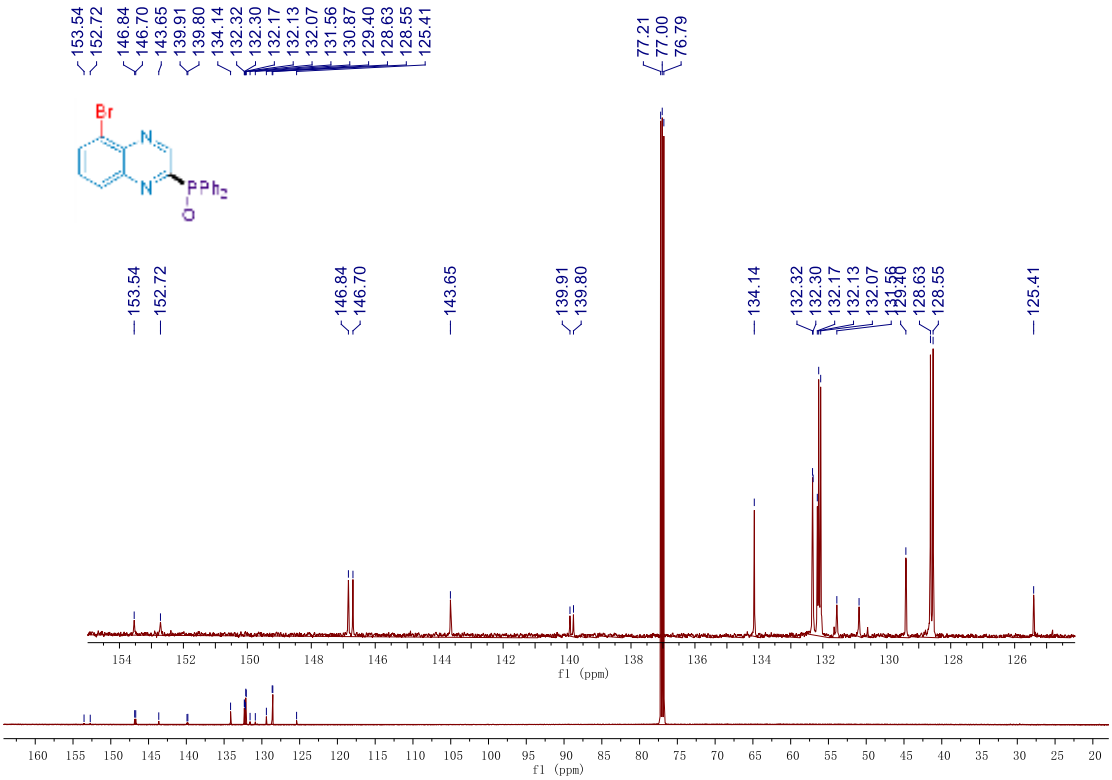


Fig.S 95 ^{13}C NMR of compound **3na-2**

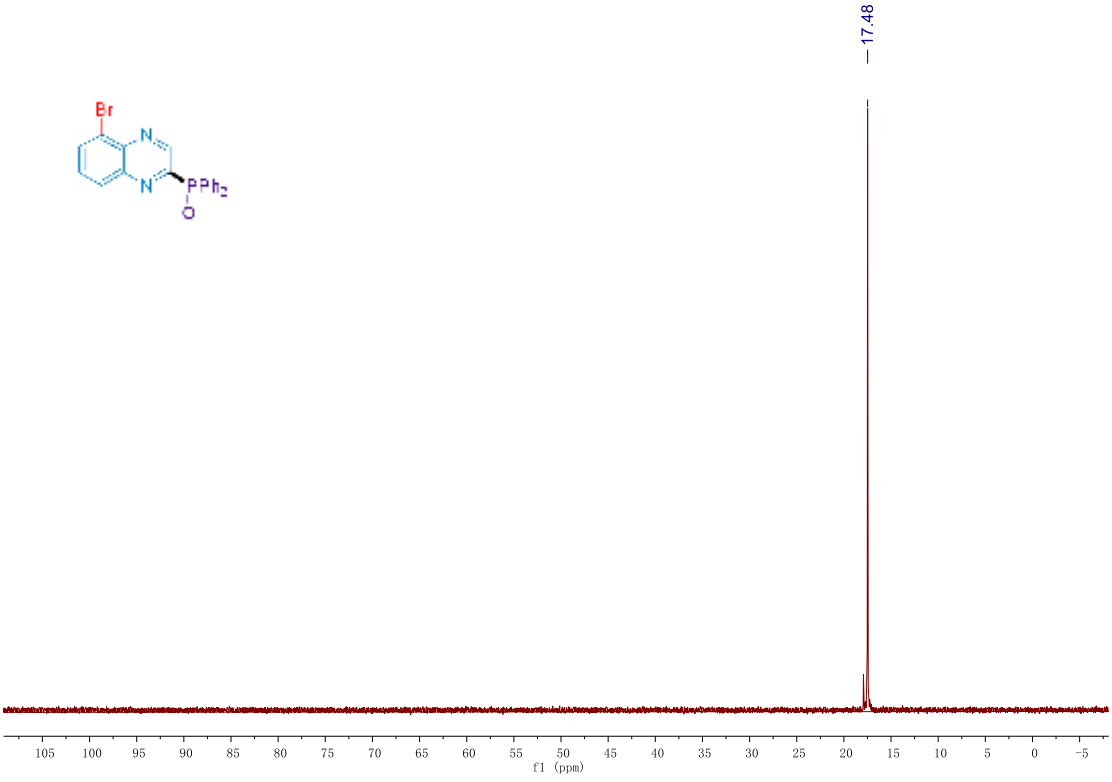


Fig.S 96 ^{31}P NMR of compound **3na-2**

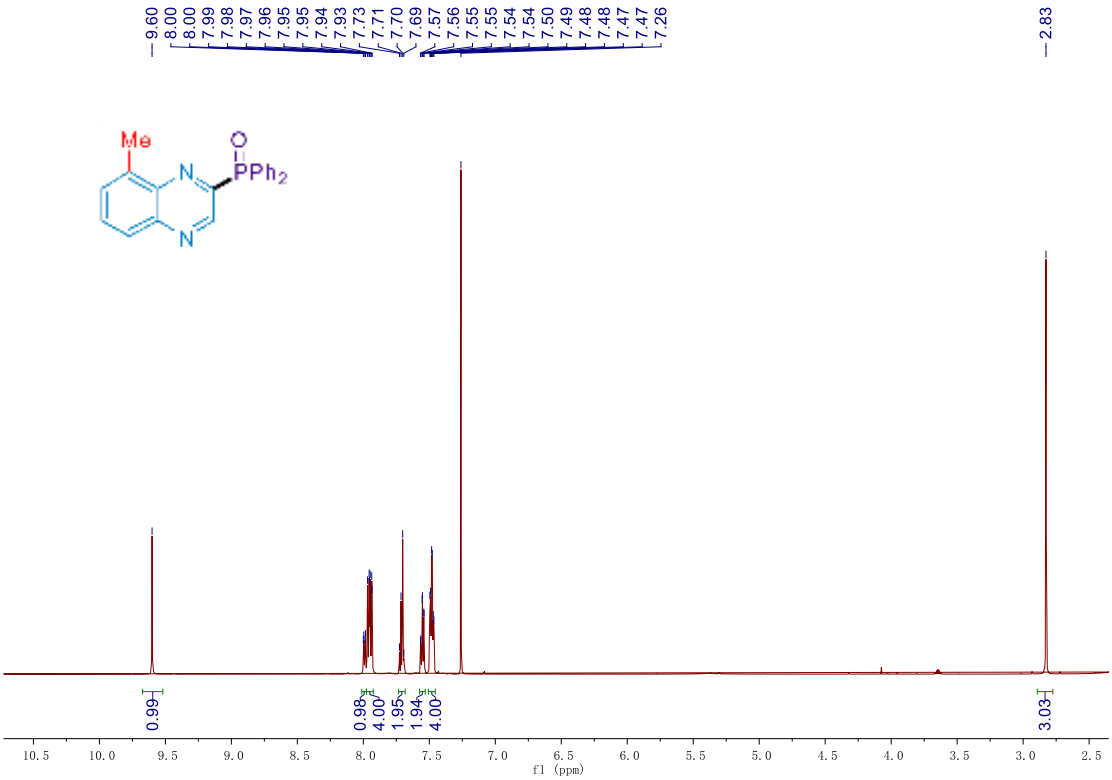


Fig.S 97 ^{1}H NMR of compound **3oa-1**

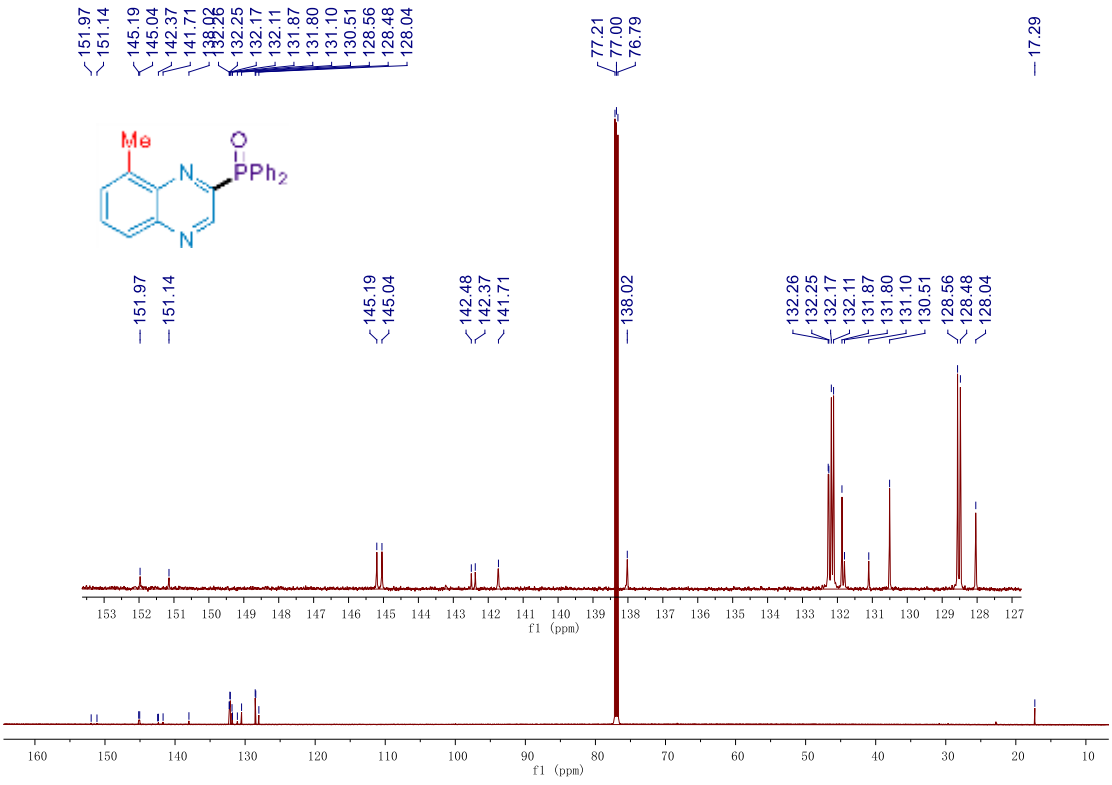


Fig.S 98 ^{13}C NMR of compound **3oa-1**

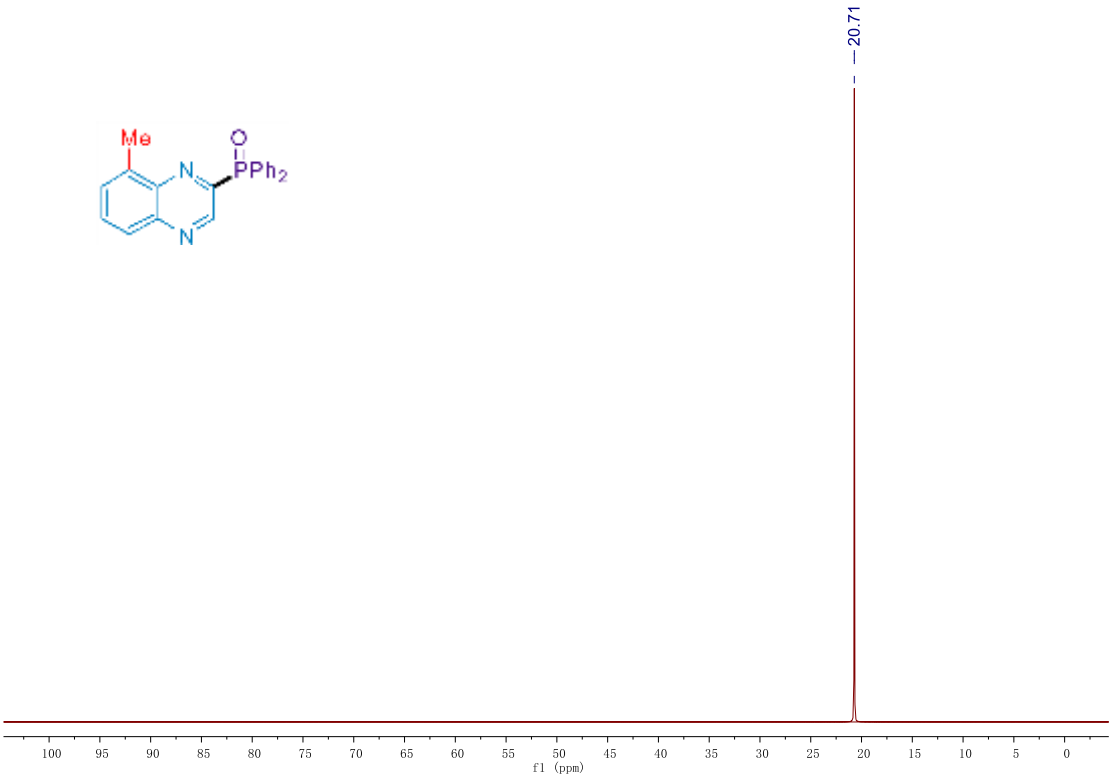


Fig.S 99 ^{31}P NMR of compound **3oa-1**

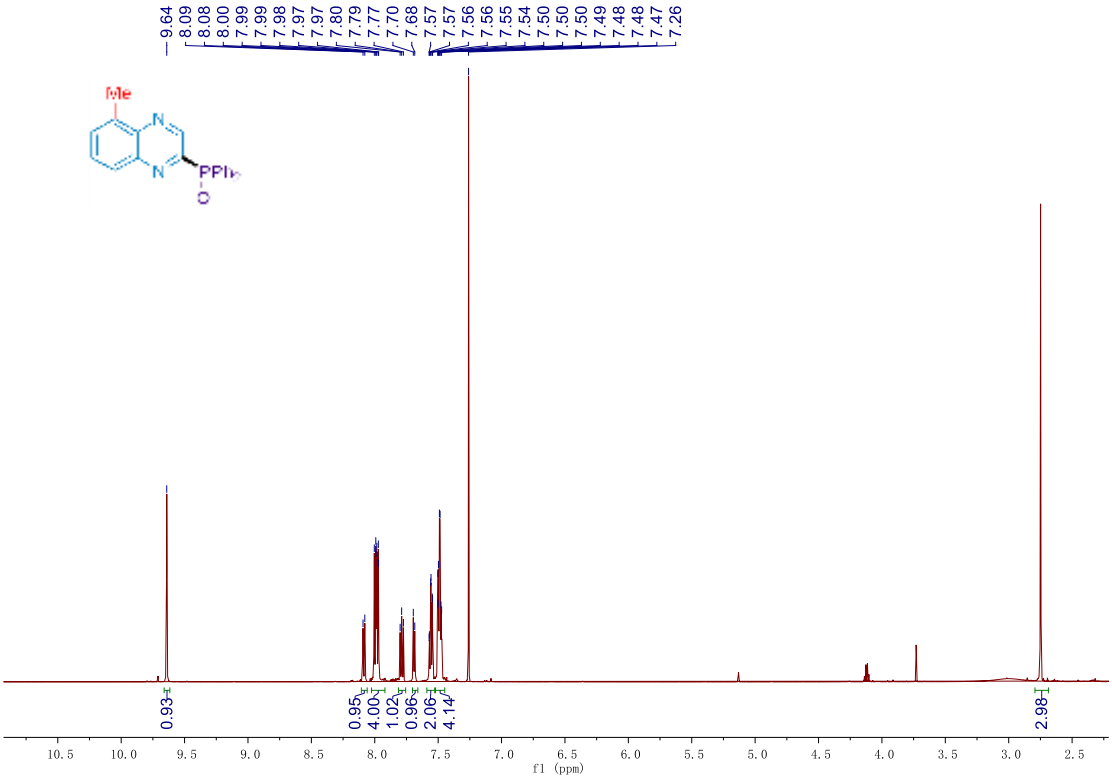


Fig.S 100 ^{1}H NMR of compound **3oa-2**

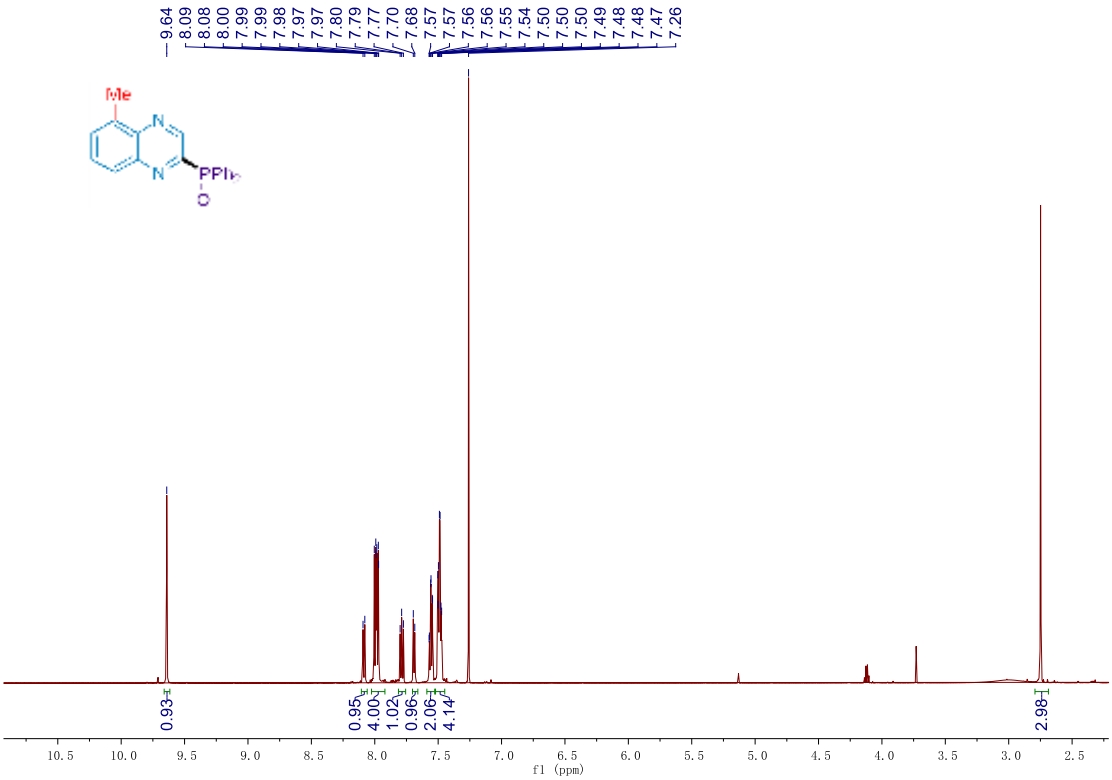


Fig.S 101 ^{13}C NMR of compound **3oa-2**

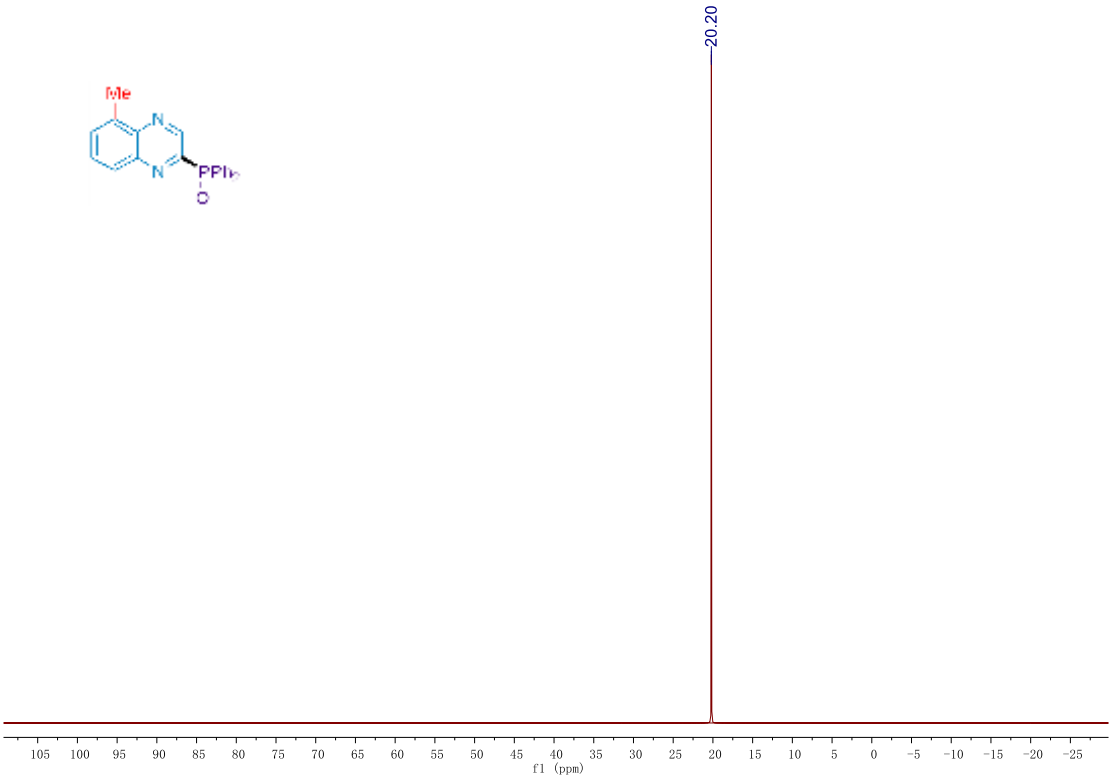


Fig.S 102 ^{31}P NMR of compound **3oa-2**

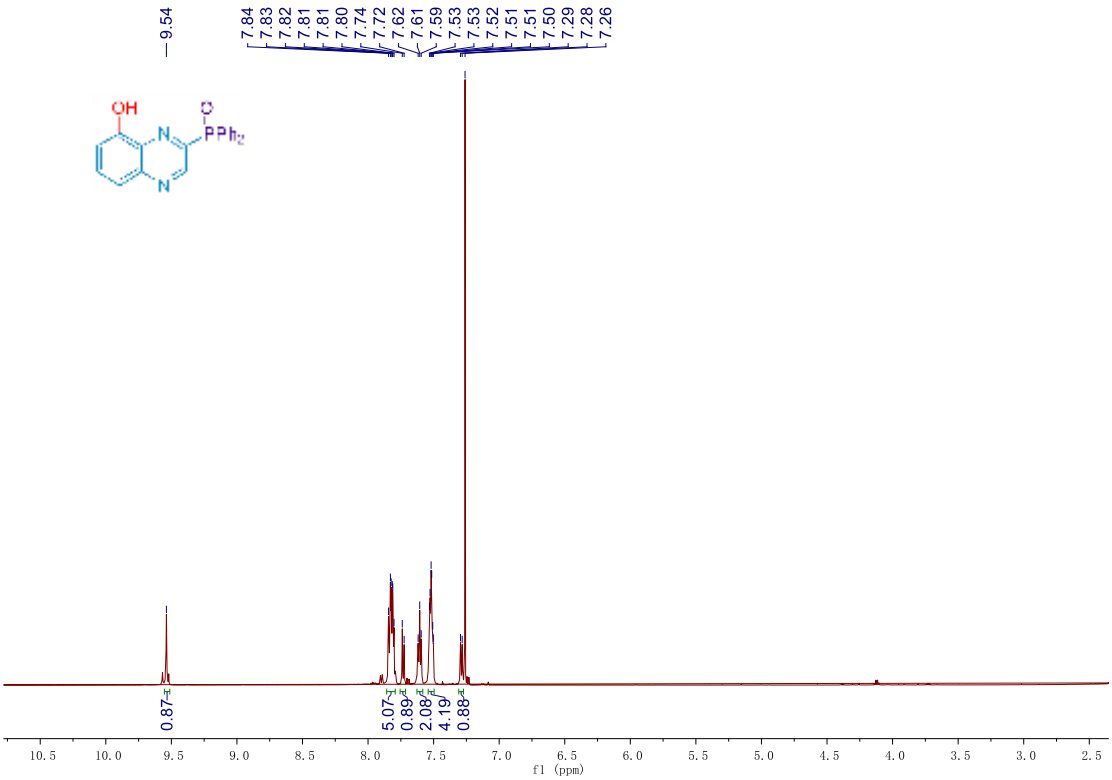


Fig.S 103 ^{1}H NMR of compound **3pa-1**

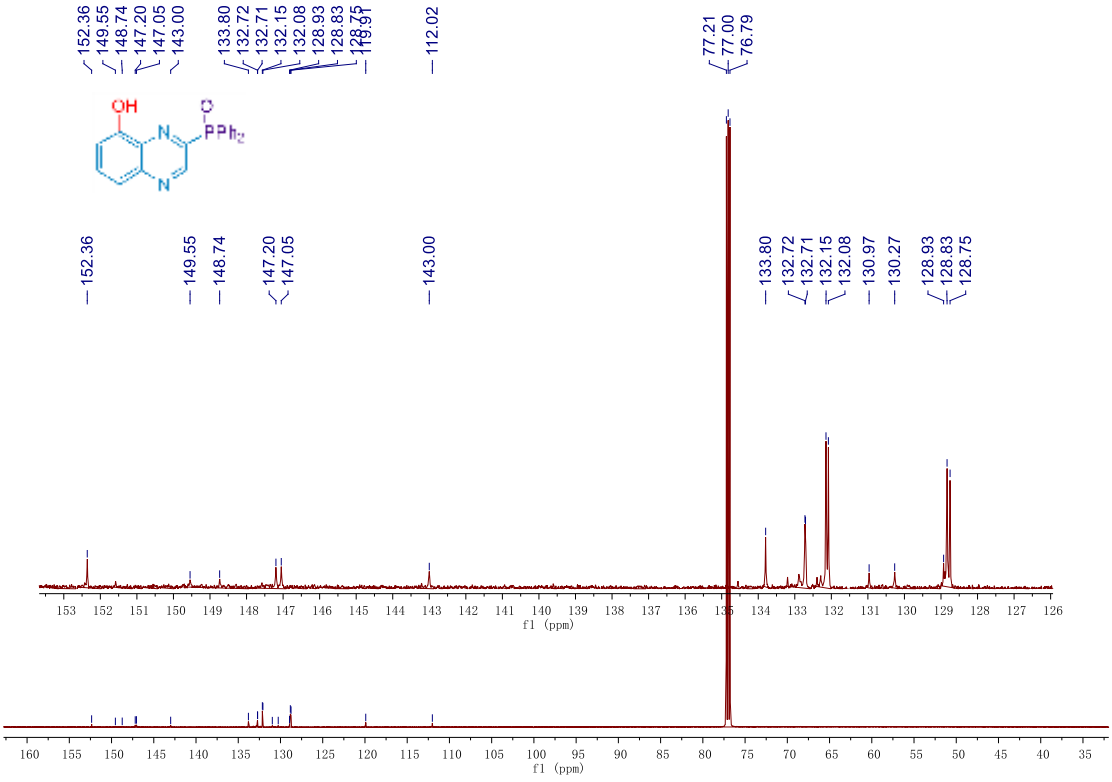


Fig.S 104 ^{13}C NMR of compound **3pa-1**

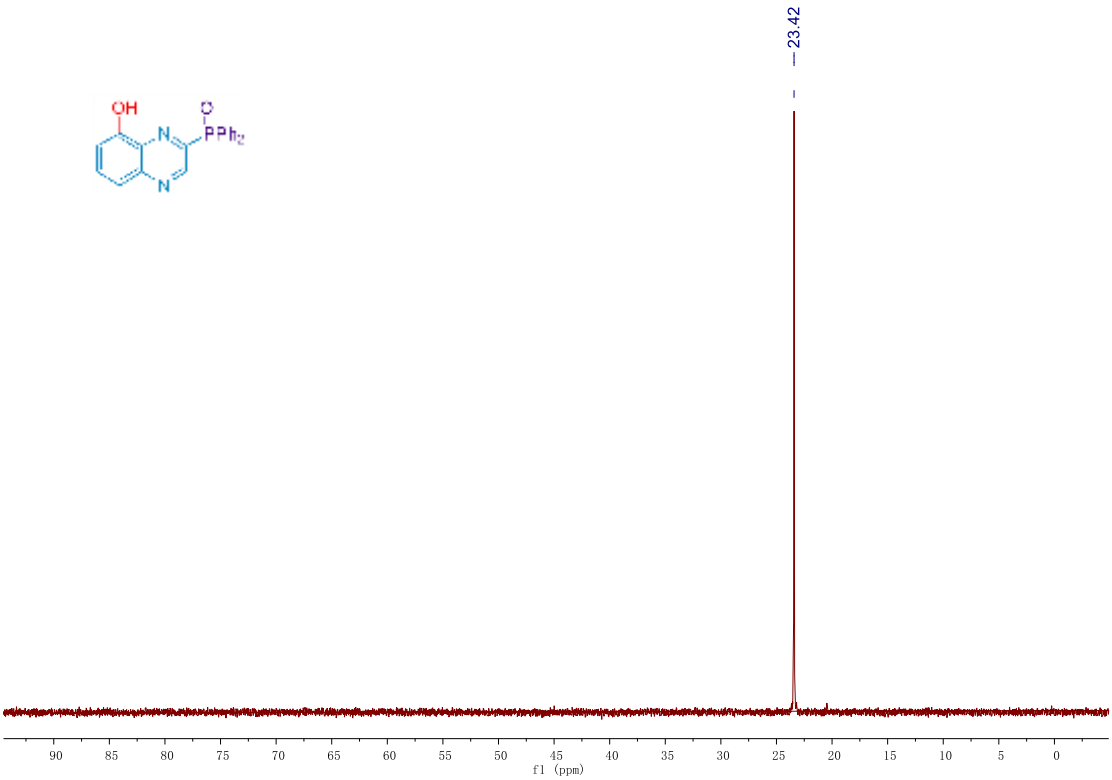


Fig.S 105 ^{31}P NMR of compound **3pa-1**

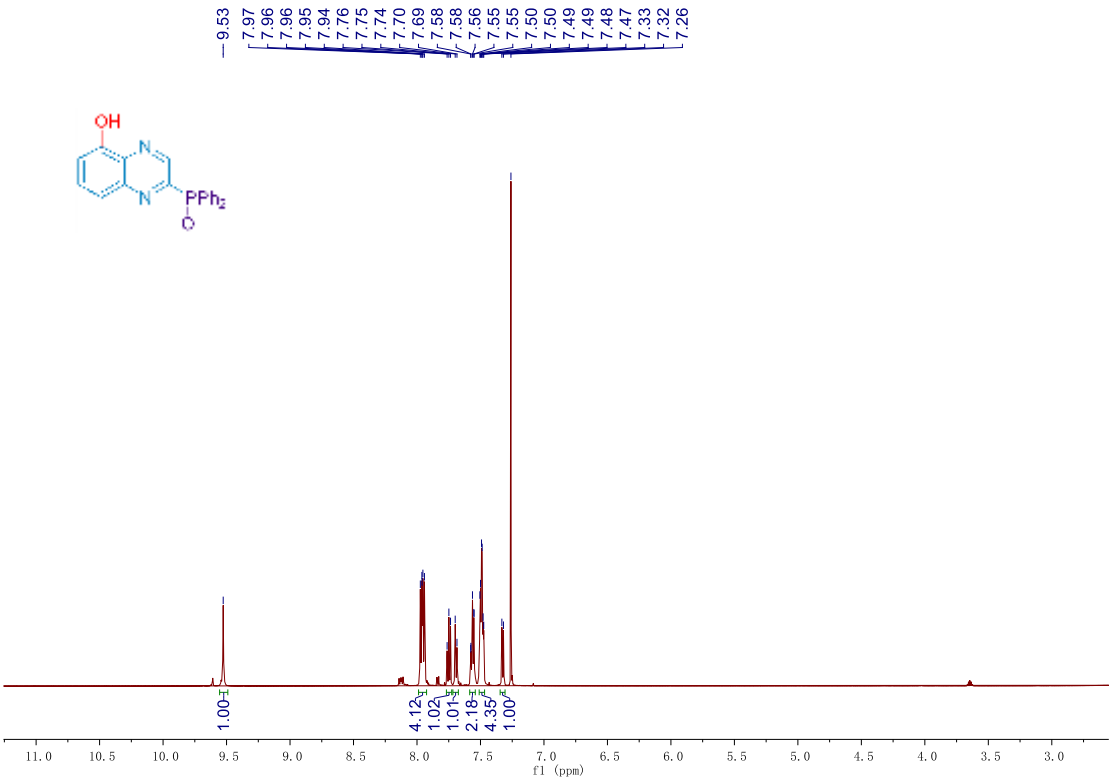


Fig.S 106 ^{1}H NMR of compound **3pa-2**

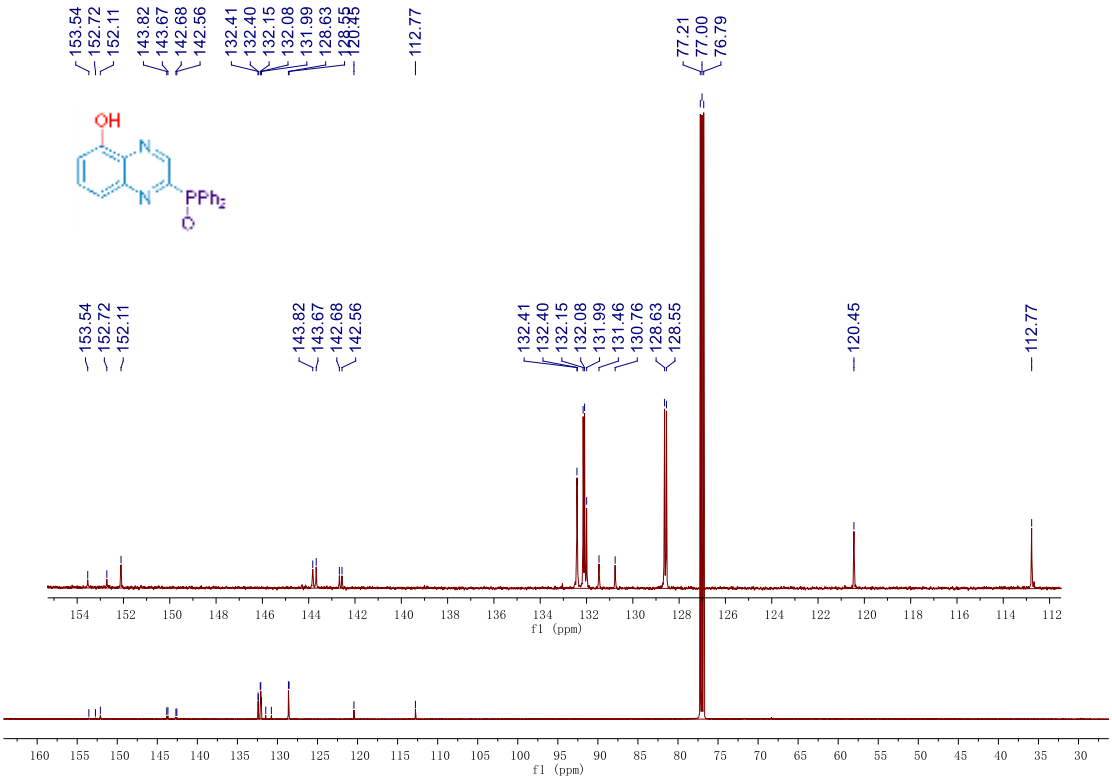


Fig.S 107 ^{13}C NMR of compound **3pa-2**

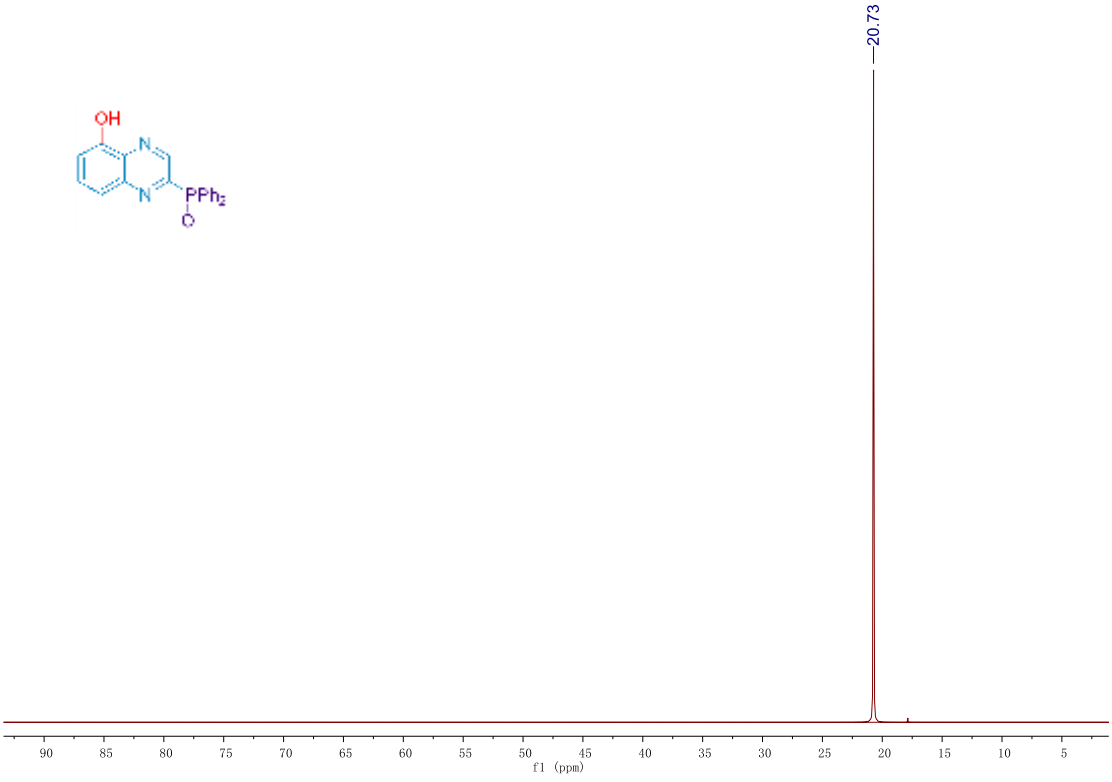


Fig.S 108 ^{31}P NMR of compound **3pa-2**

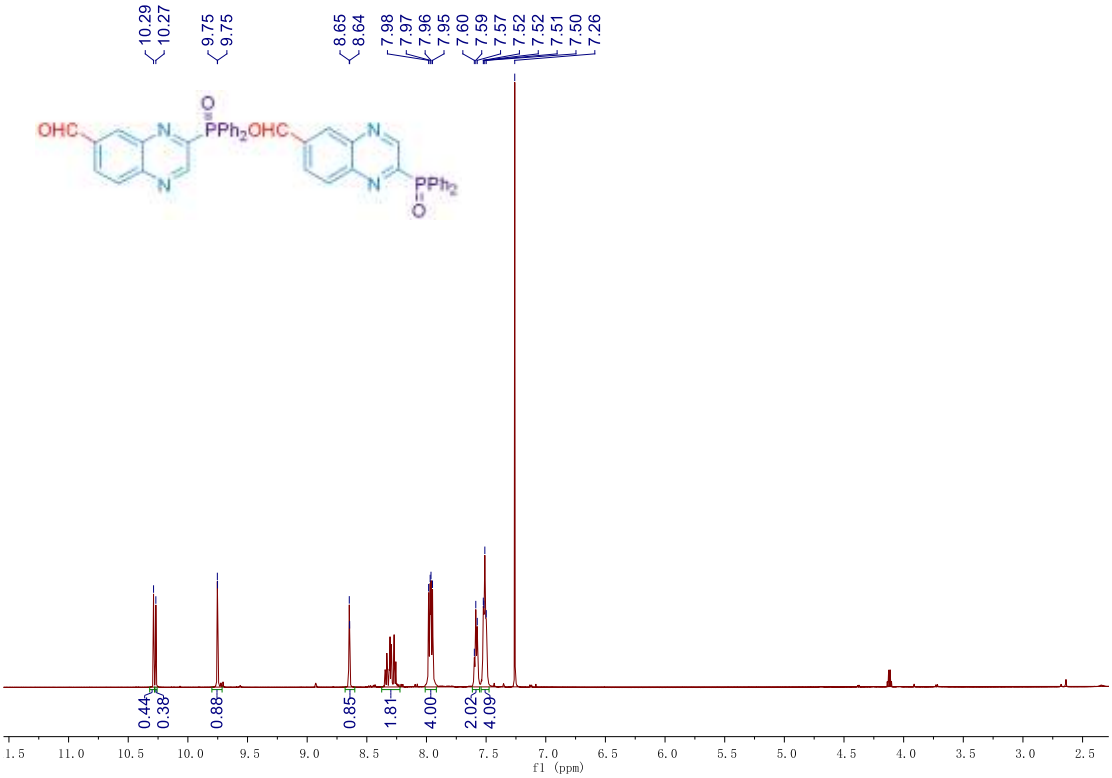


Fig.S 109 ^{1}H NMR of compound **3qa**

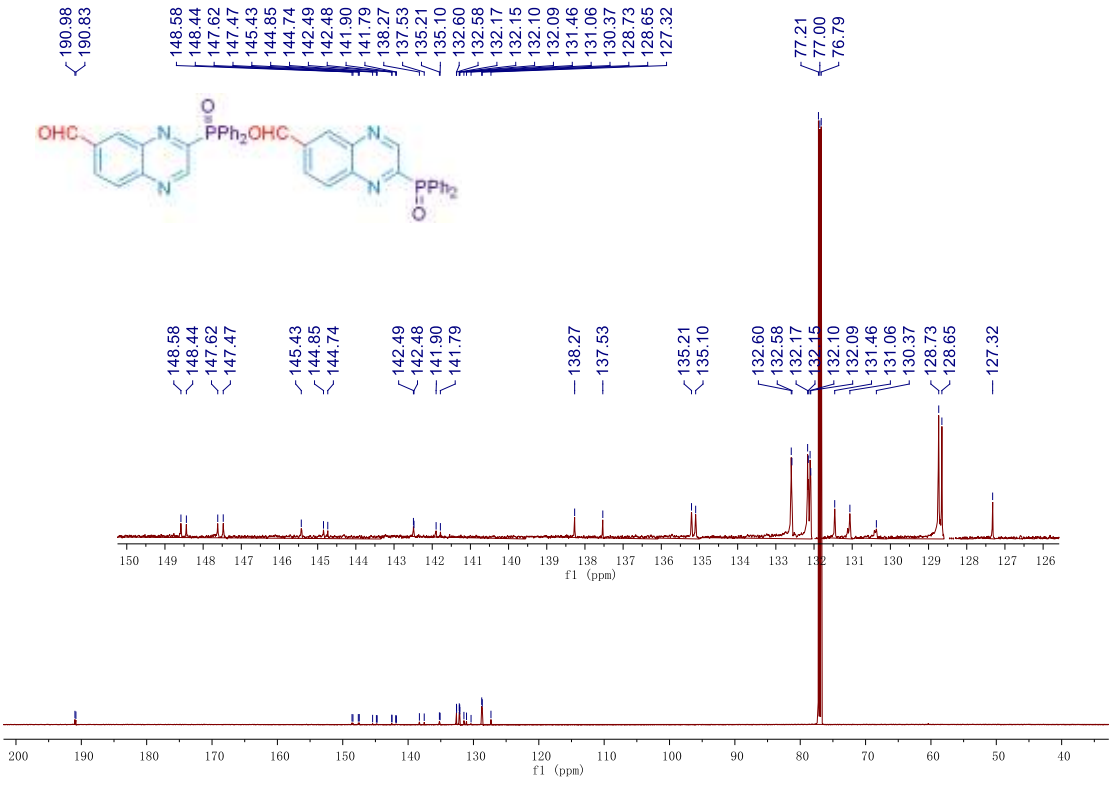


Fig.S 110 ^{13}C NMR of compound **3qa**

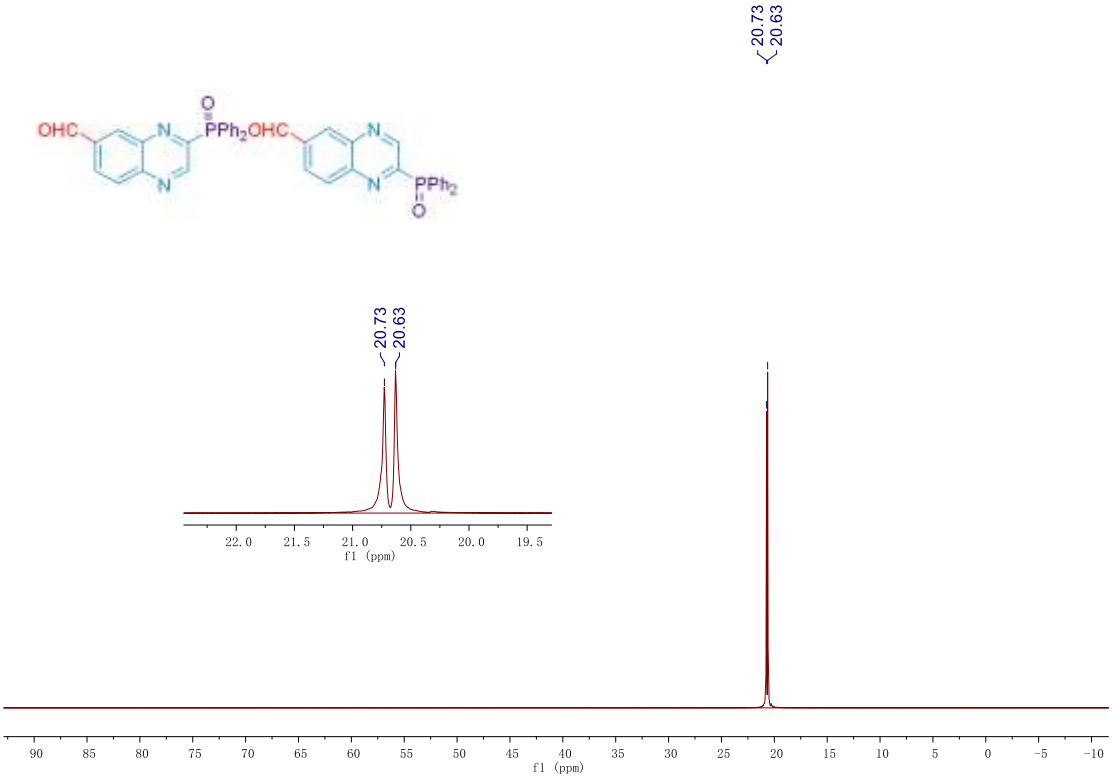


Fig.S 111 ^{31}P NMR of compound **3qa**

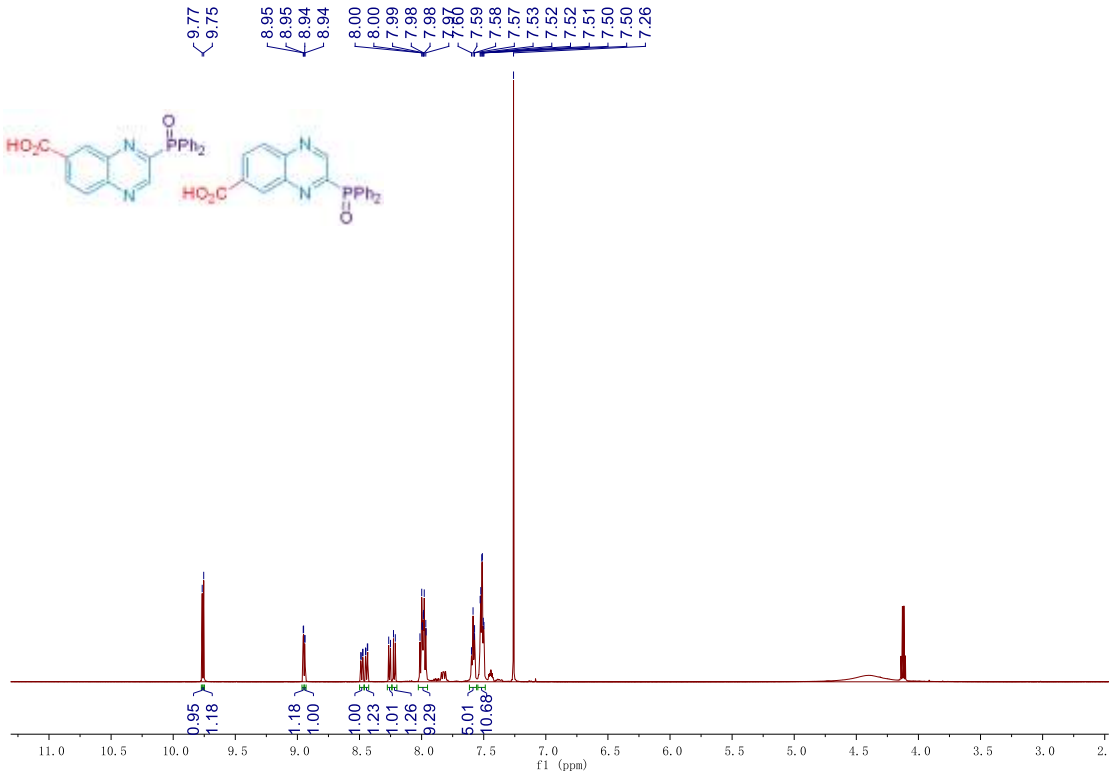


Fig.S 112 ^{1}H NMR of compound **3ra**

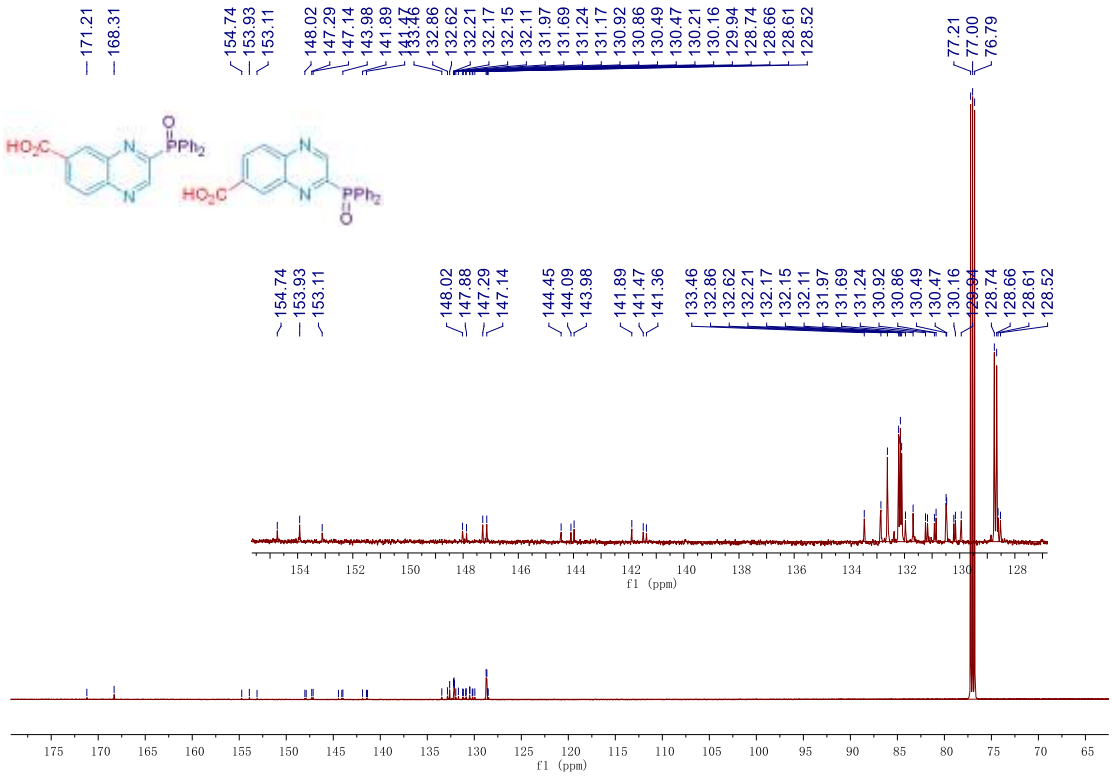


Fig.S 113 ^{13}C NMR of compound **3ra**

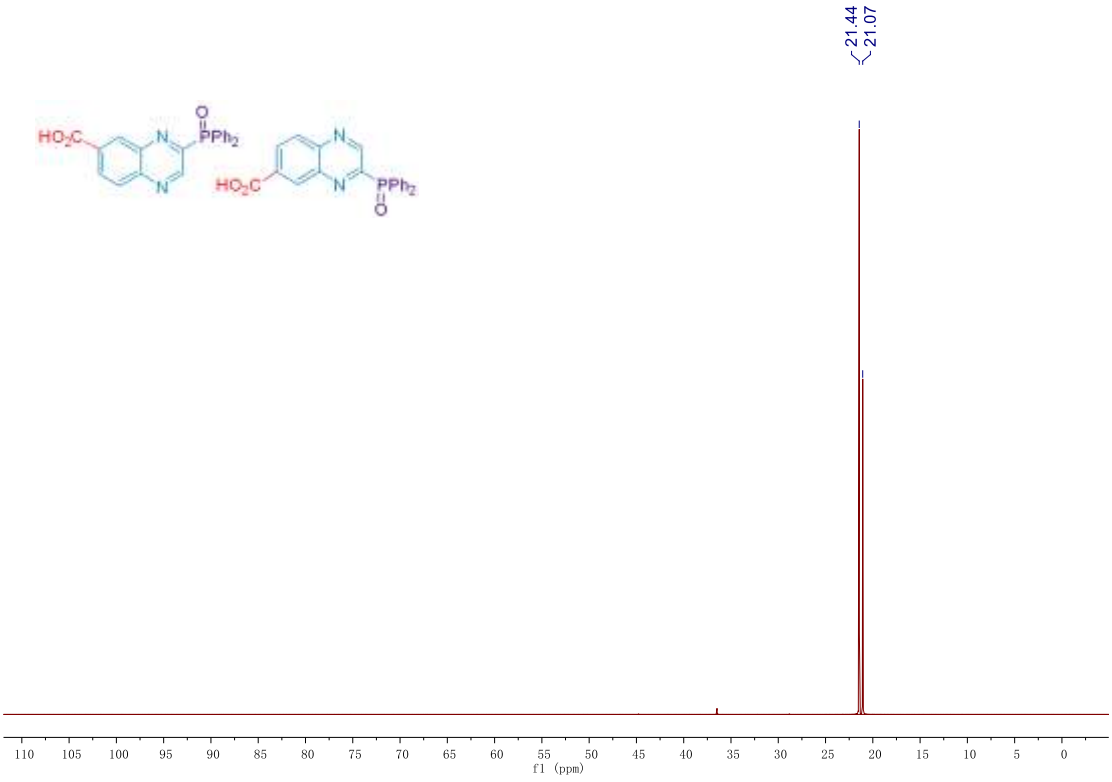


Fig.S 114 ^{31}P NMR of compound **3ra**

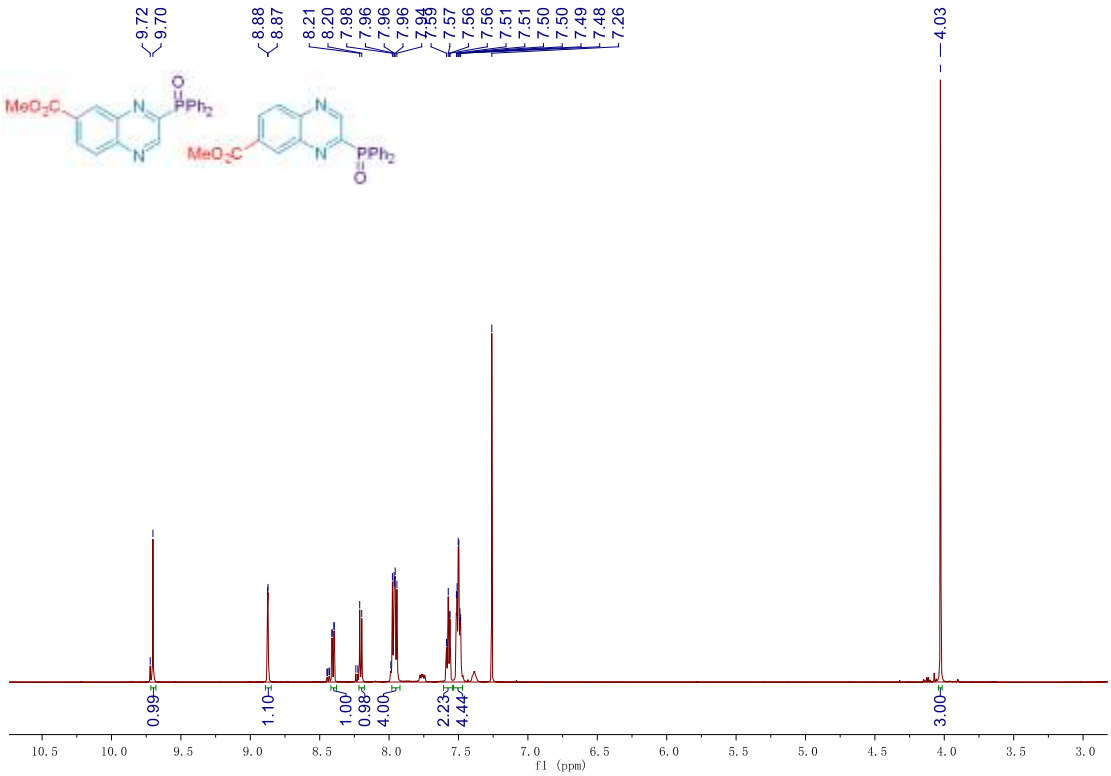


Fig.S 115 ^{1}H NMR of compound **3sa**

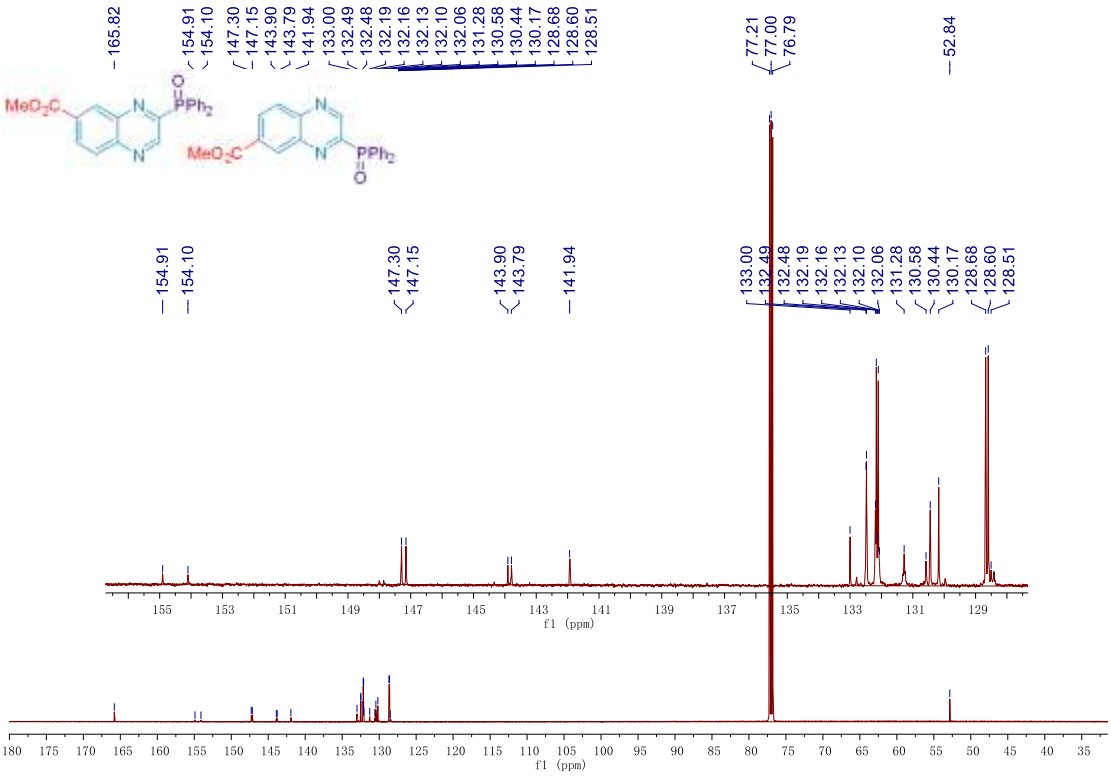


Fig.S 116 ^{13}C NMR of compound **3sa**

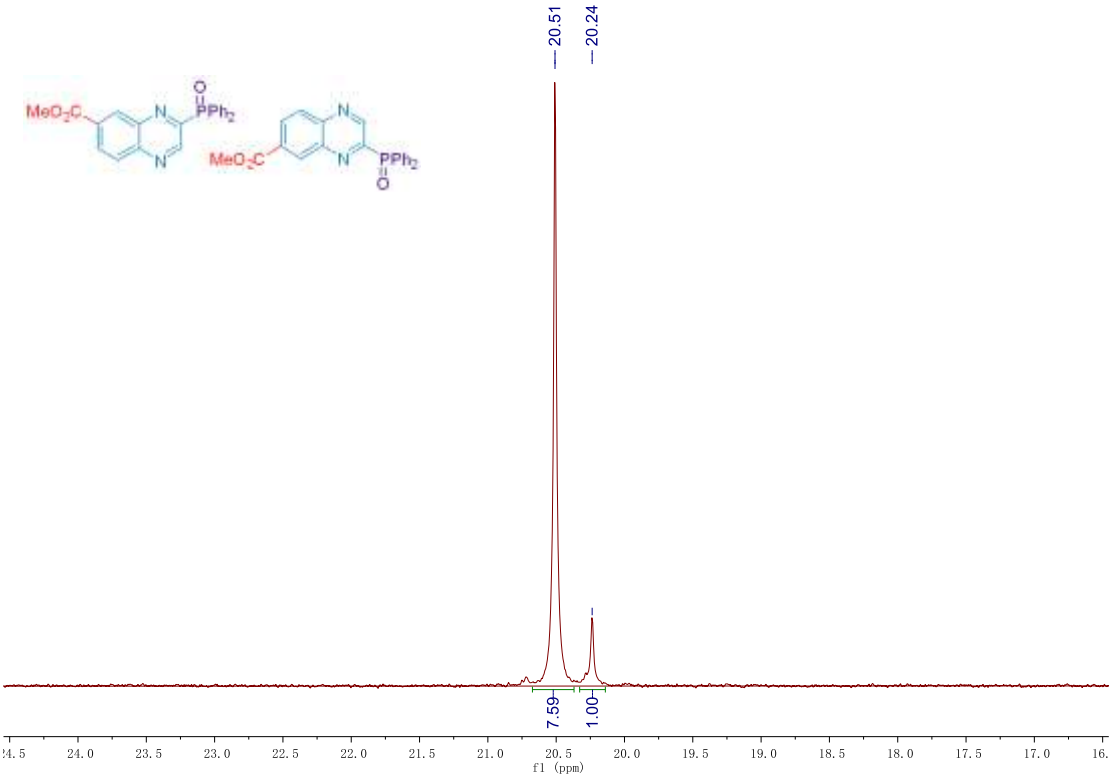


Fig.S 117 ^{31}P NMR of compound **3sa**

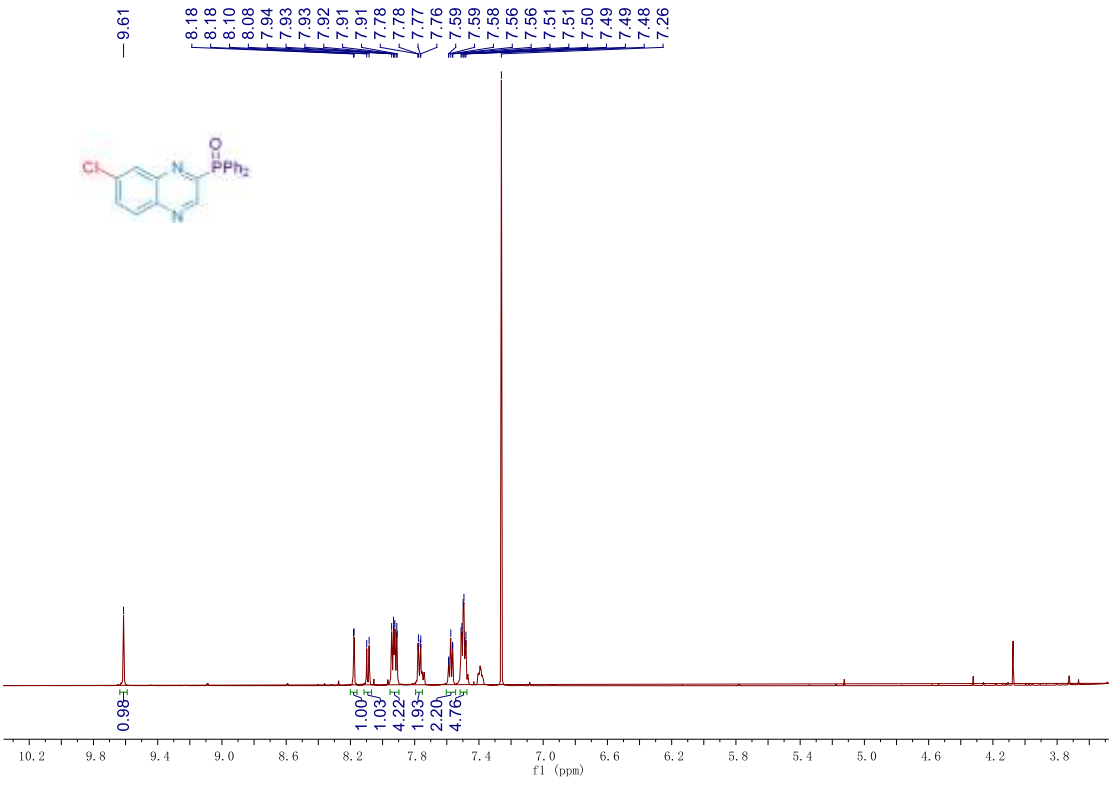


Fig.S 118 ^{1}H NMR of compound **3ta-1**

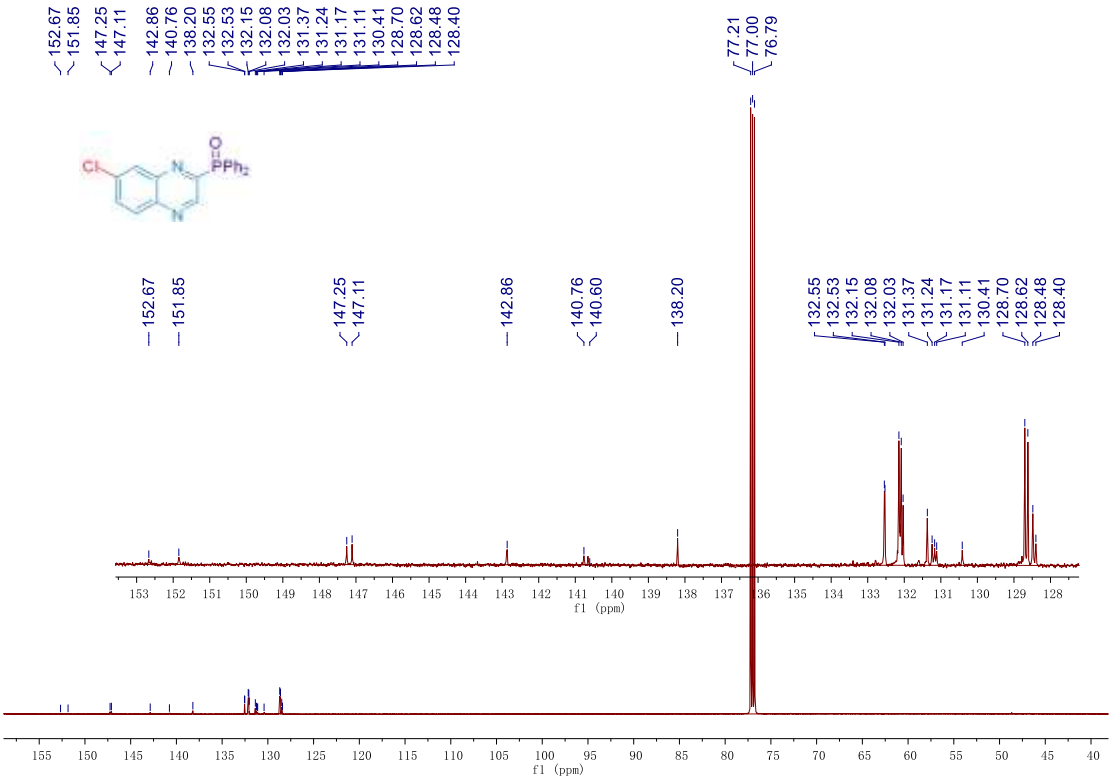


Fig.S 119 ^{13}C NMR of compound **3ta-1**

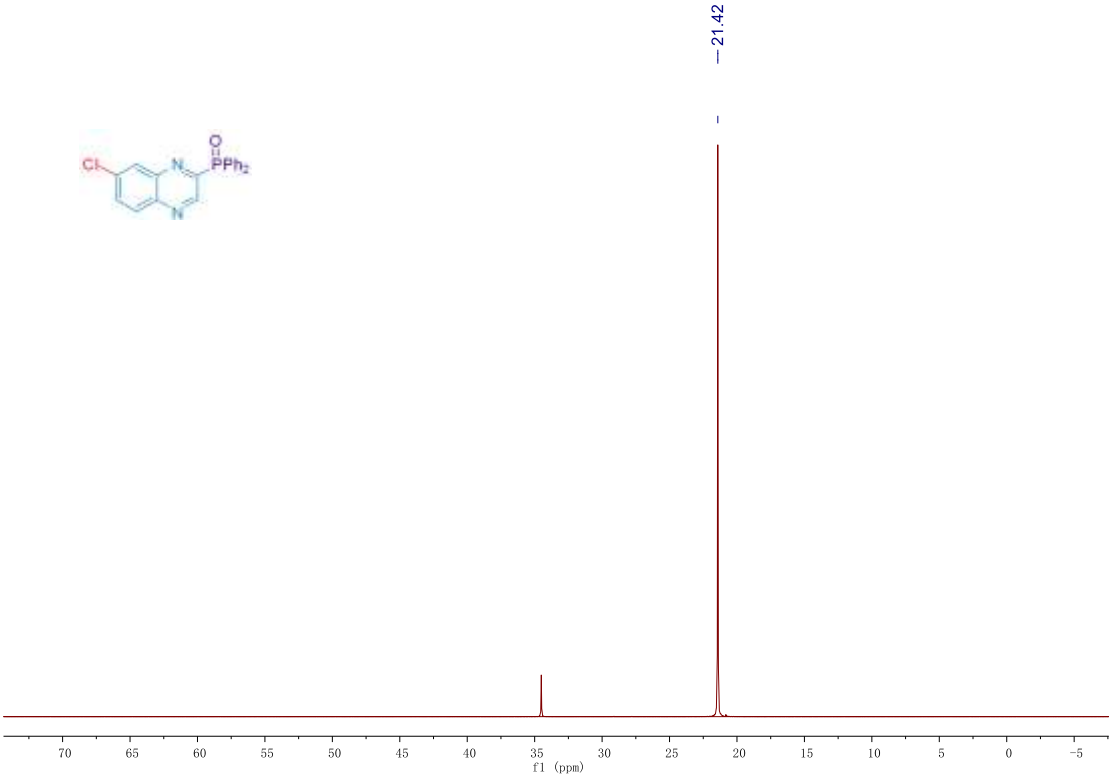


Fig.S 120 ^{31}P NMR of compound **3ta-1**

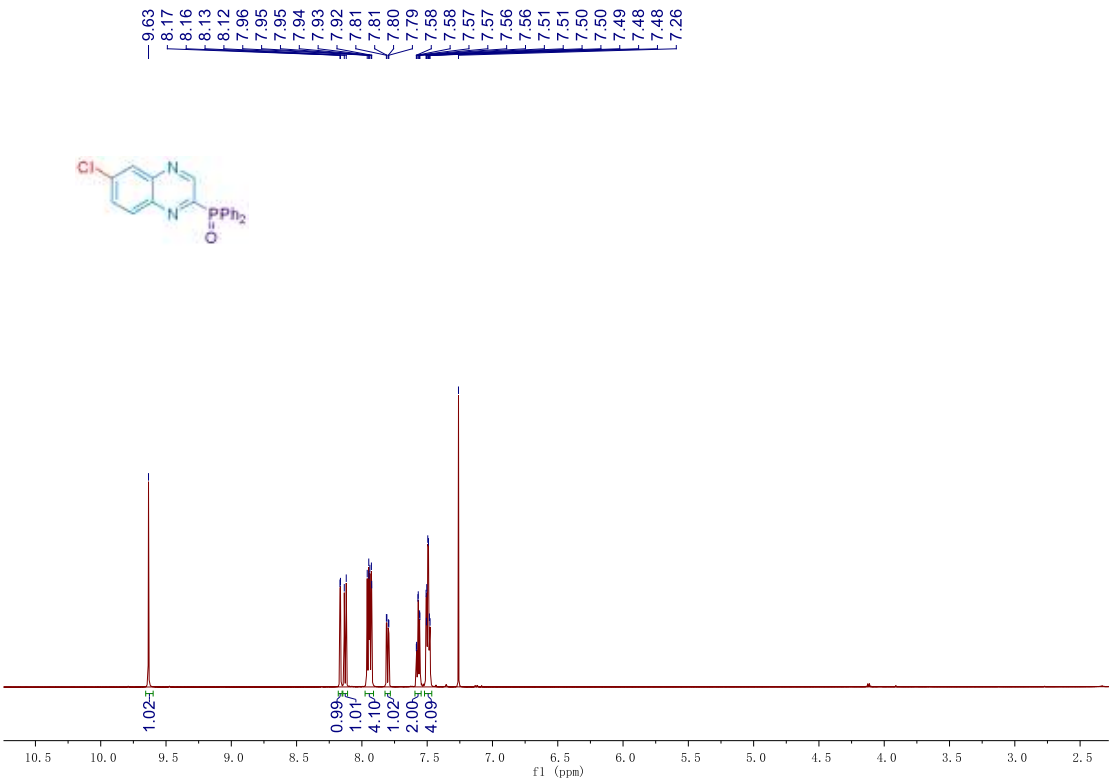


Fig.S 121 ^{1}H NMR of compound **3ta-2**

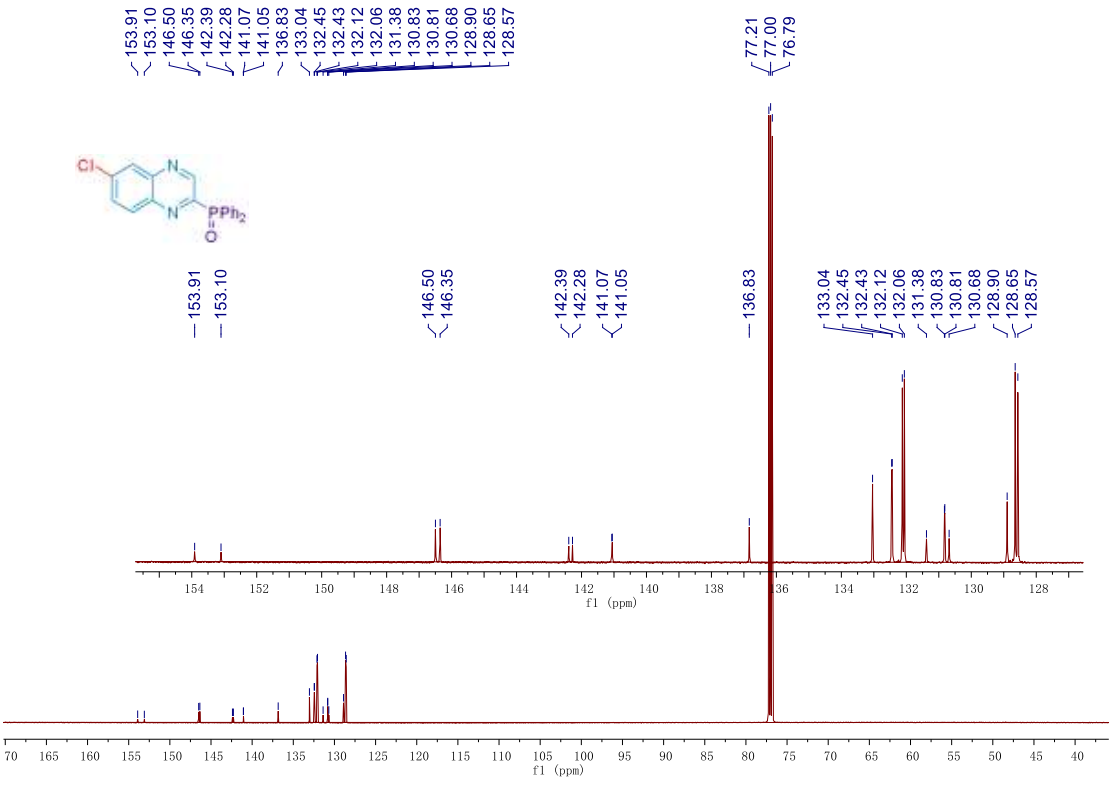


Fig.S 122 ^{13}C NMR of compound **3ta-2**

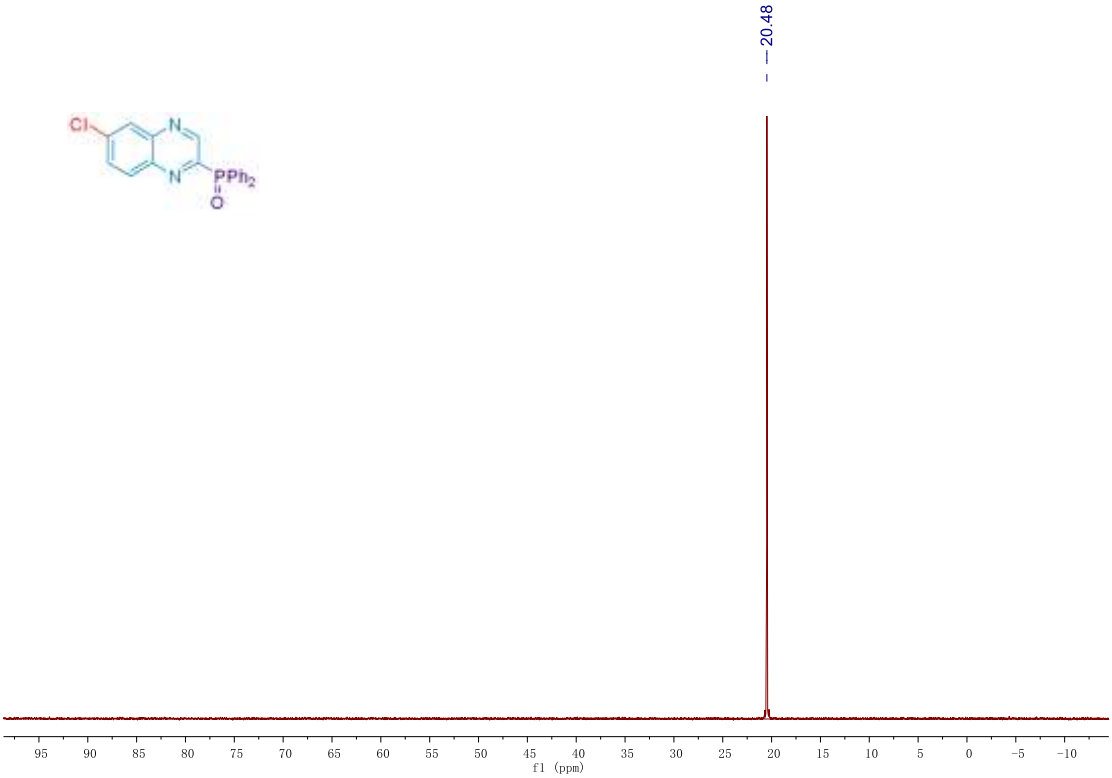


Fig.S 123 ^{31}P NMR of compound **3ta-2**

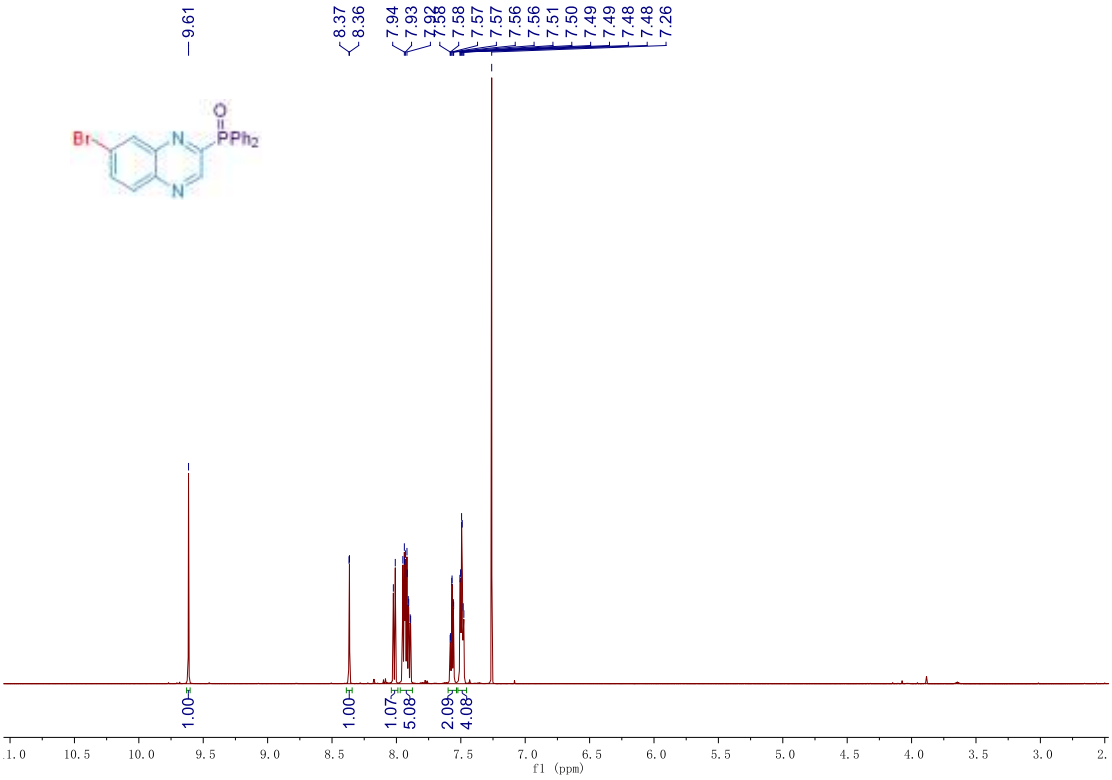


Fig.S 124 ^{1}H NMR of compound **3ua-1**

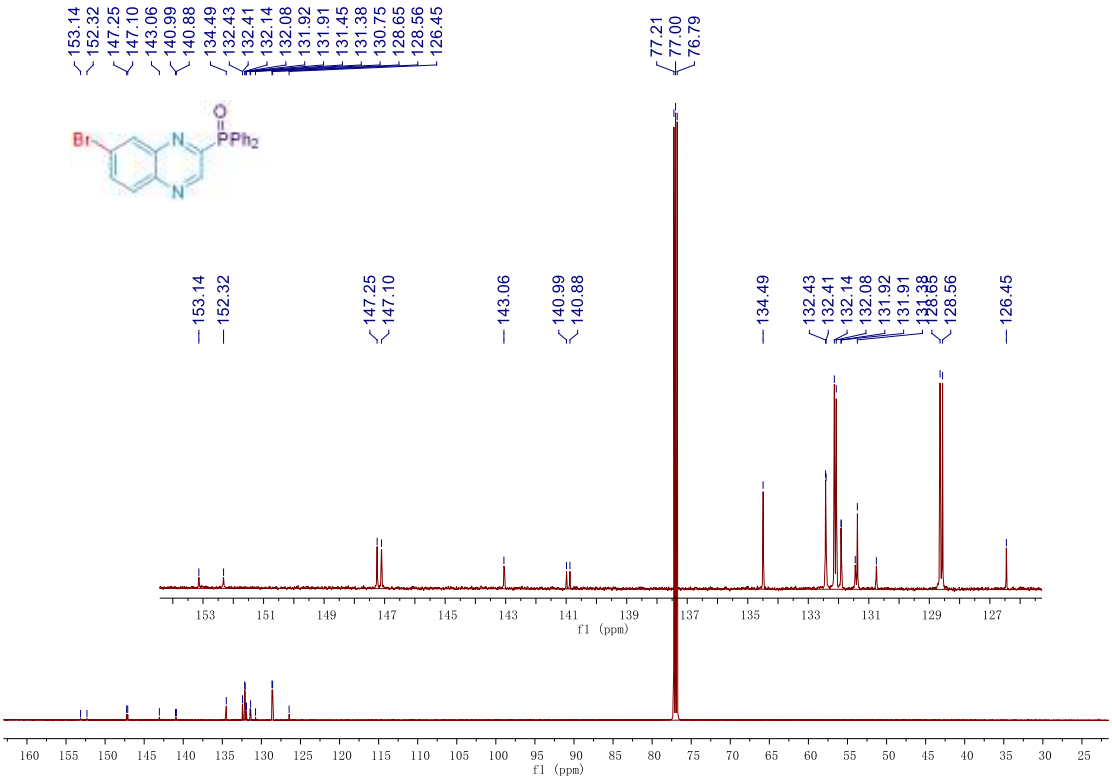


Fig.S 125 ^{13}C NMR of compound **3ua-1**

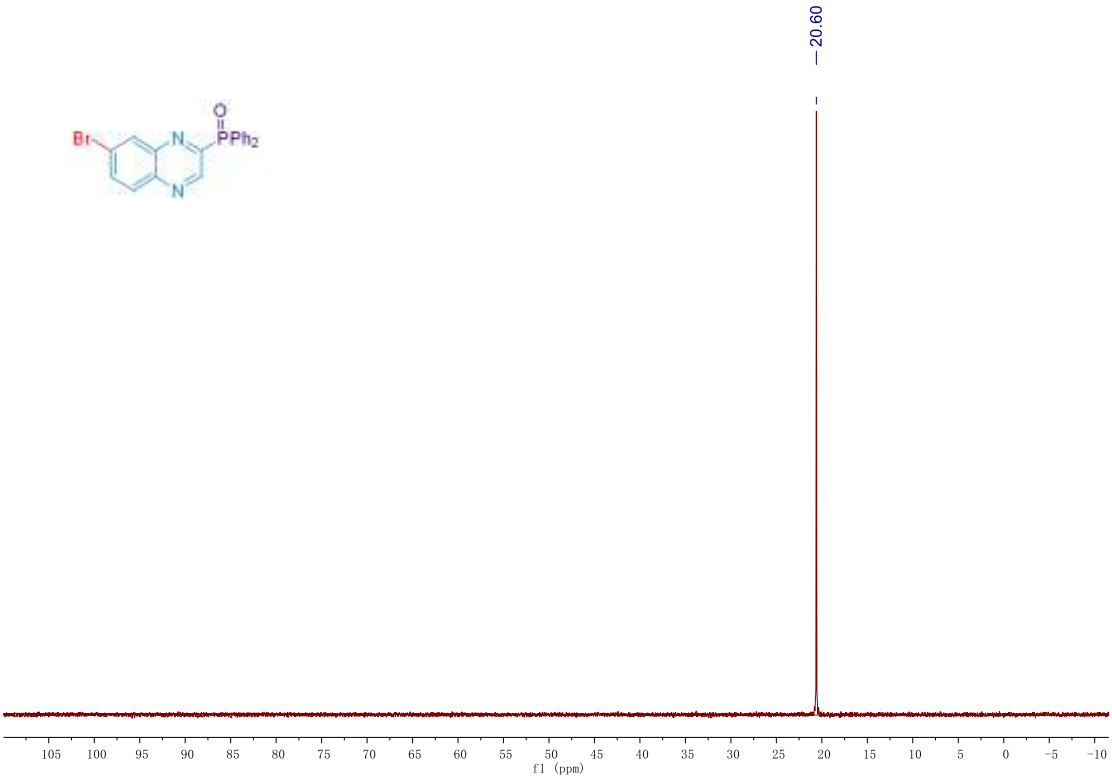


Fig.S 126 ^{31}P NMR of compound **3ua-1**

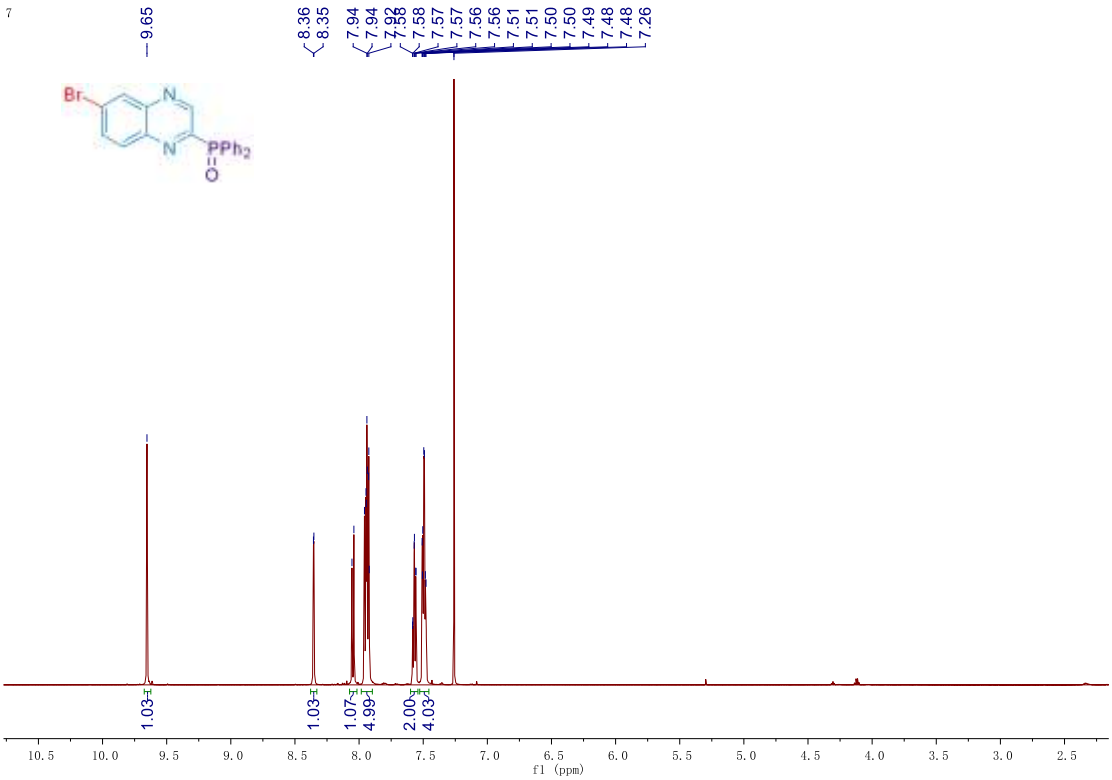


Fig.S 127 ^{1}H NMR of compound **3ua-2**

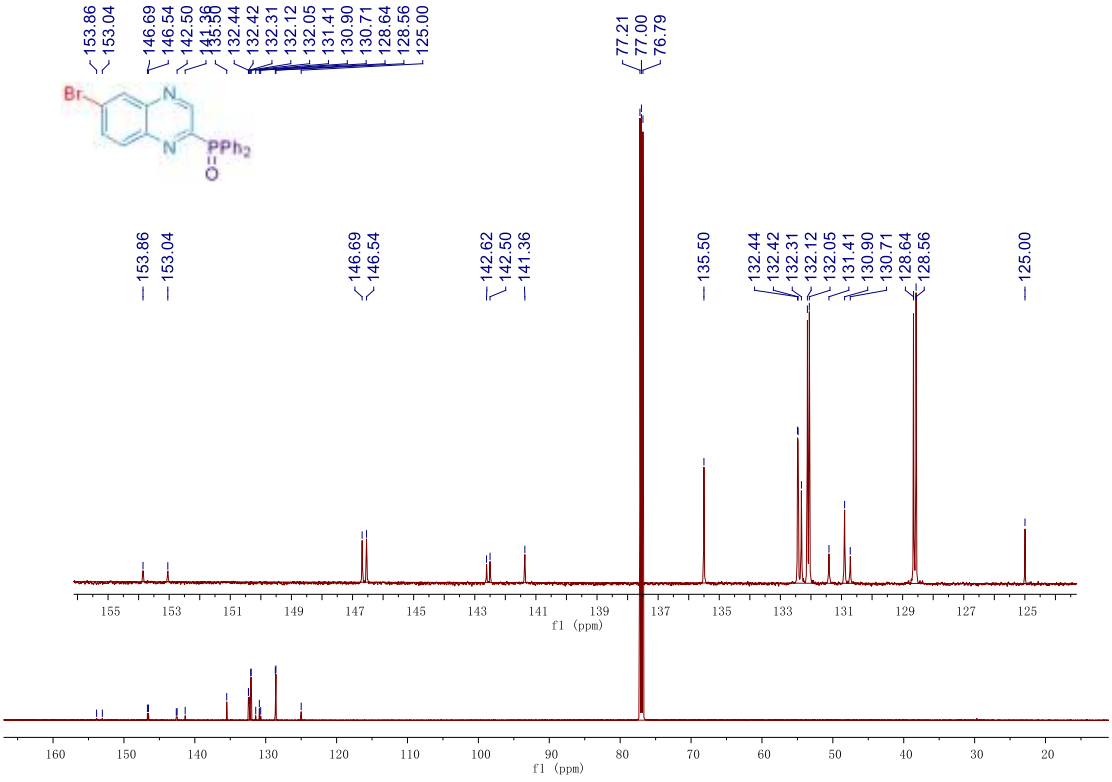


Fig.S 128 ^{13}C NMR of compound **3ua-2**

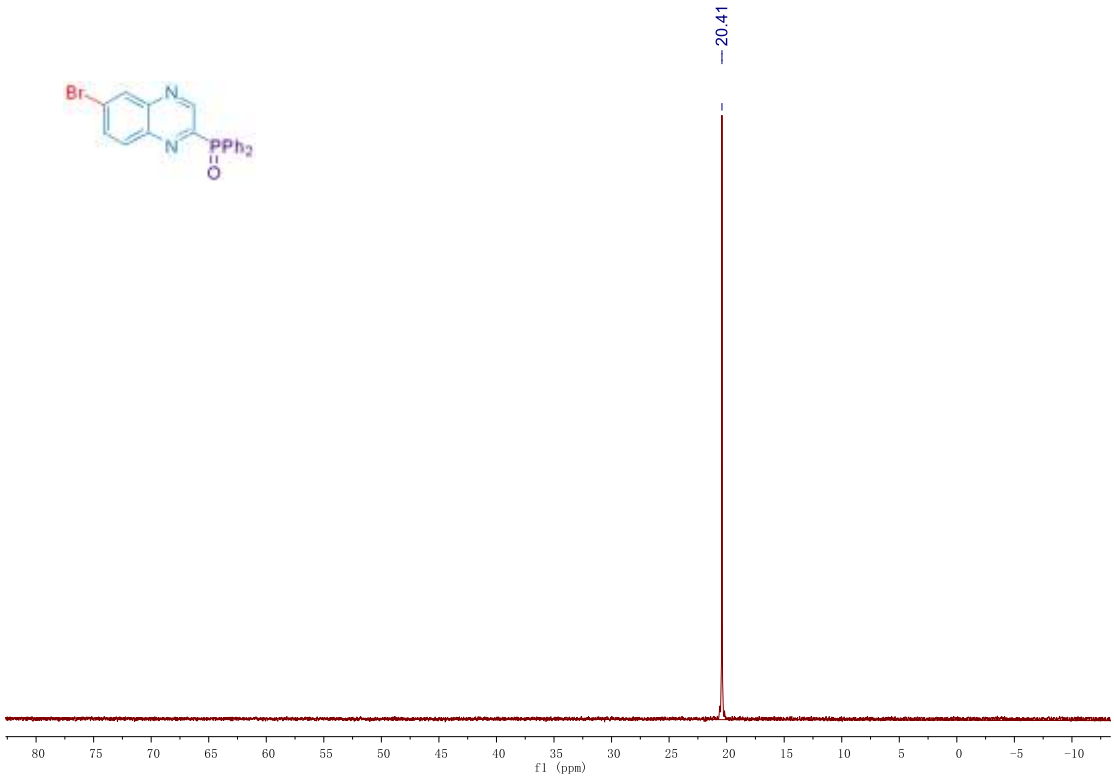


Fig.S 129 ^{31}P NMR of compound **3ua-2**

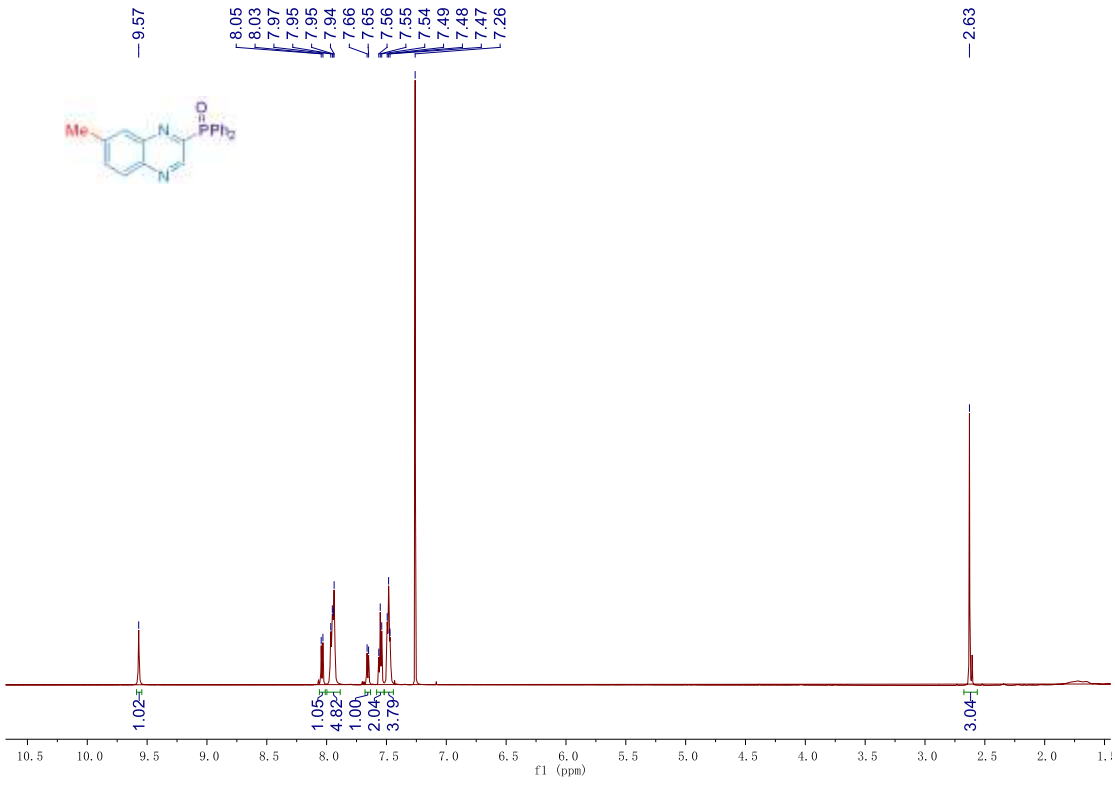


Fig.S 130 ^{1}H NMR of compound **3va-1**

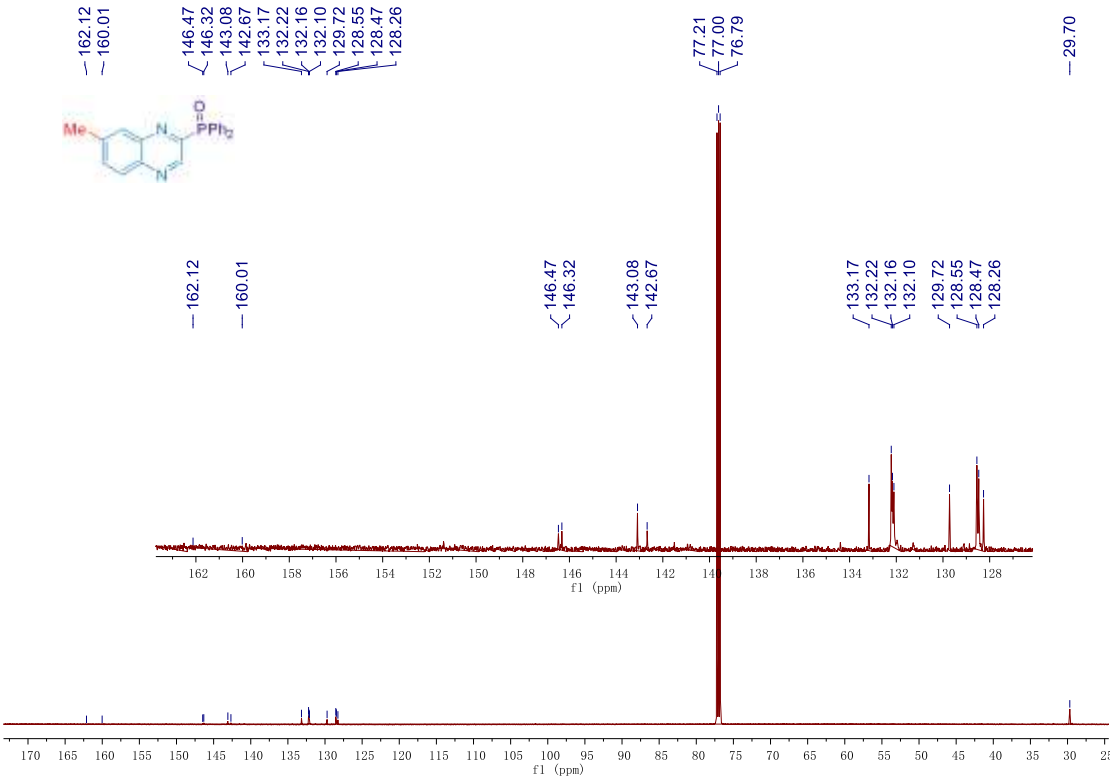


Fig.S 131 ^{13}C NMR of compound **3va-1**

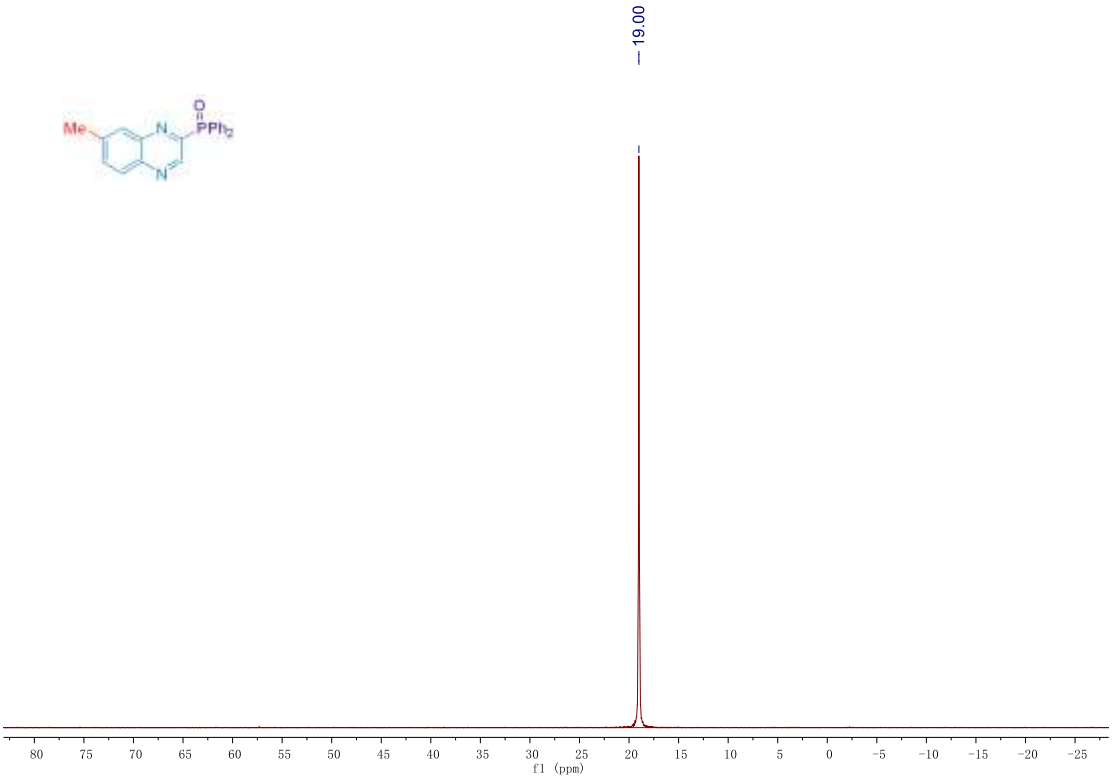


Fig.S 132 ^{31}P NMR of compound **3va-1**

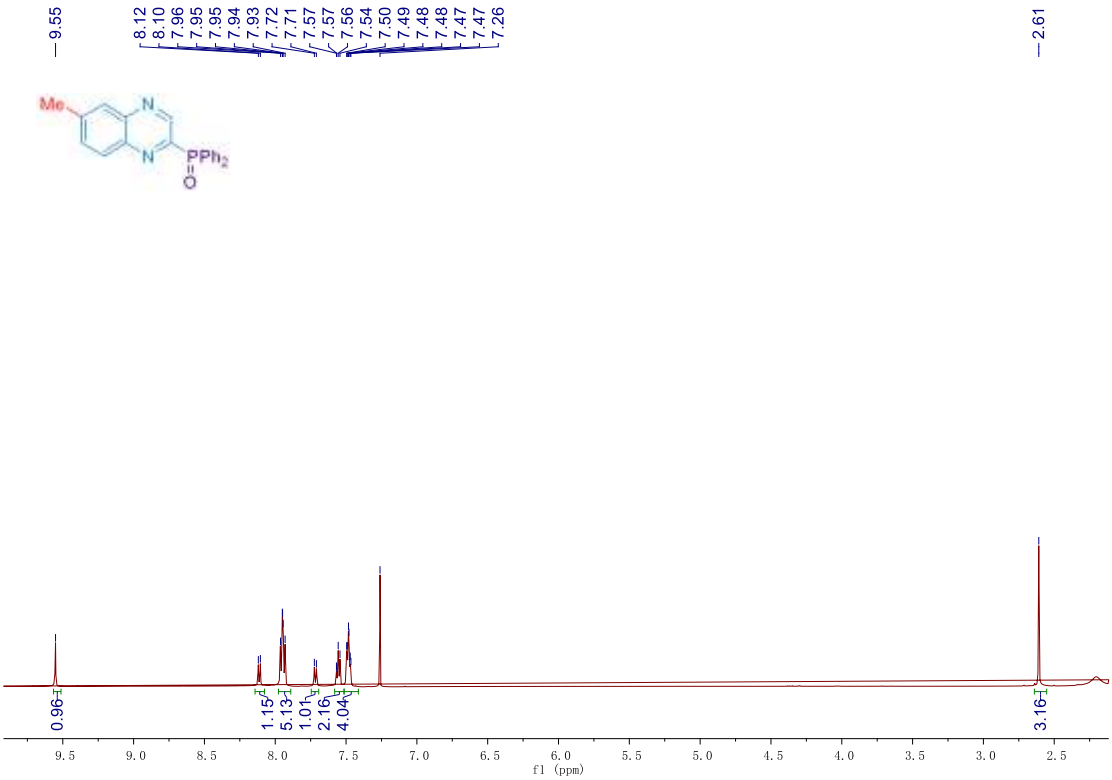


Fig.S 133 ^{1}H NMR of compound **3va-2**

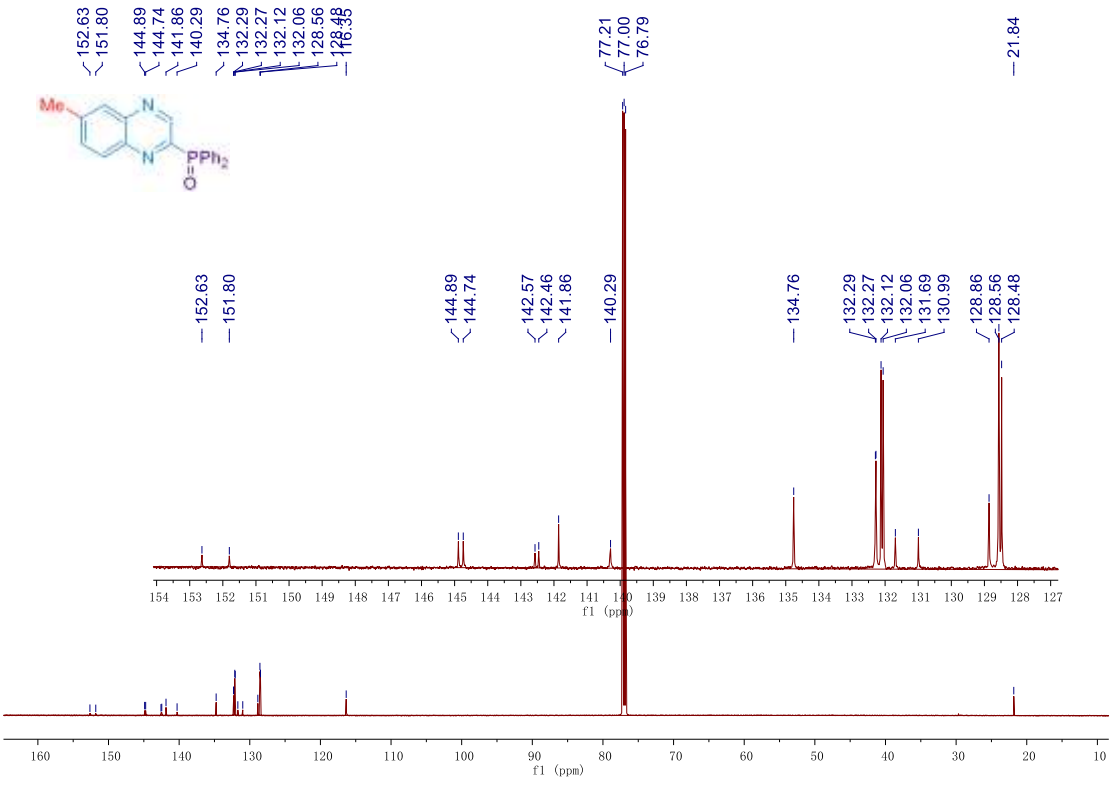


Fig.S 134 ^{13}C NMR of compound **3va-2**

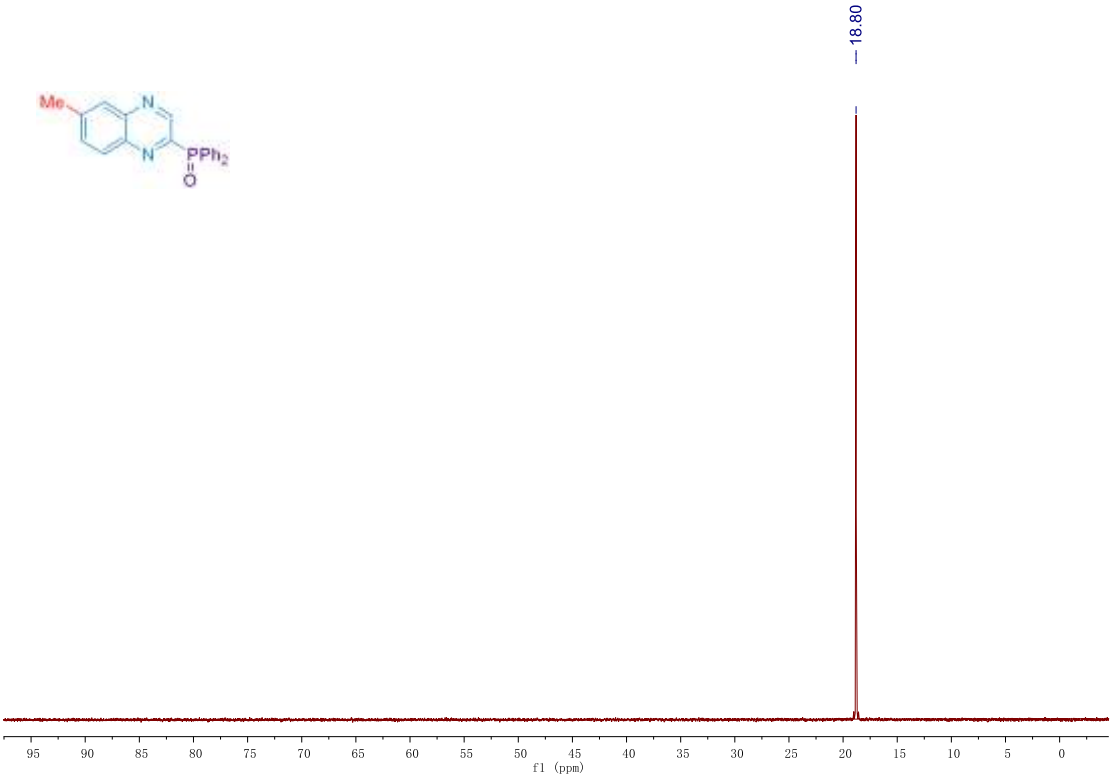


Fig.S 135 ^{31}P NMR of compound **3va-2**

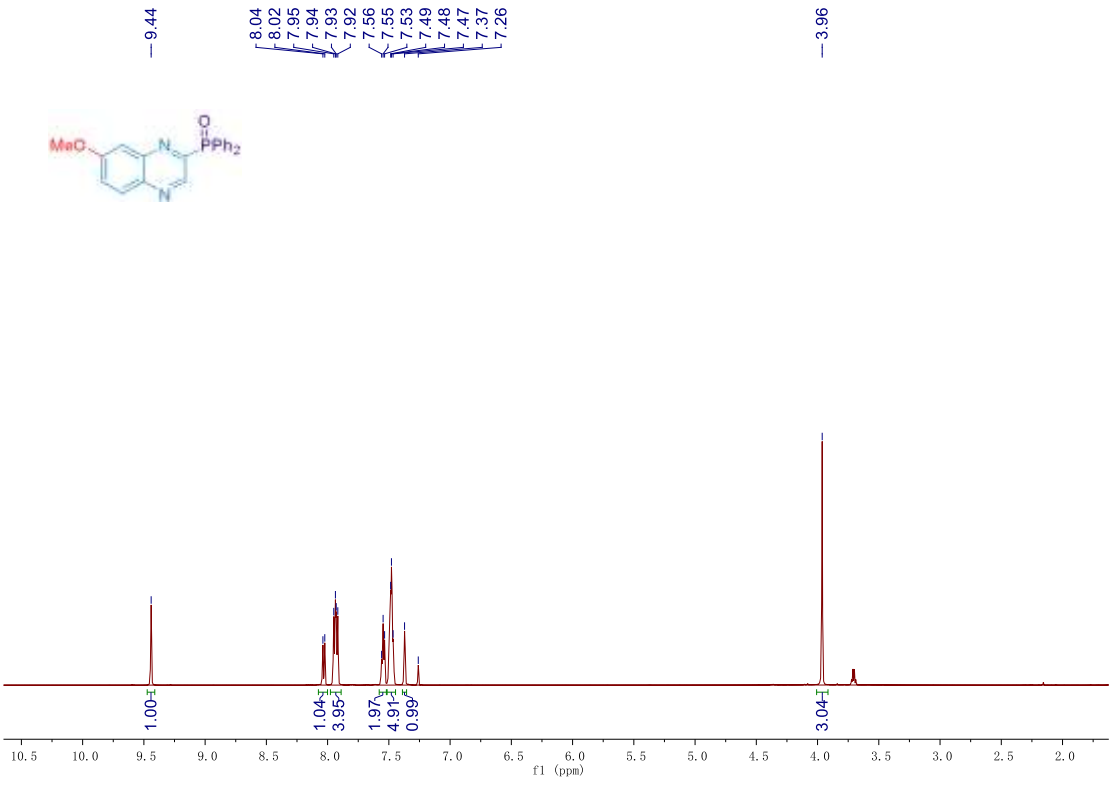


Fig.S 136 ^{1}H NMR of compound **3wa-1**

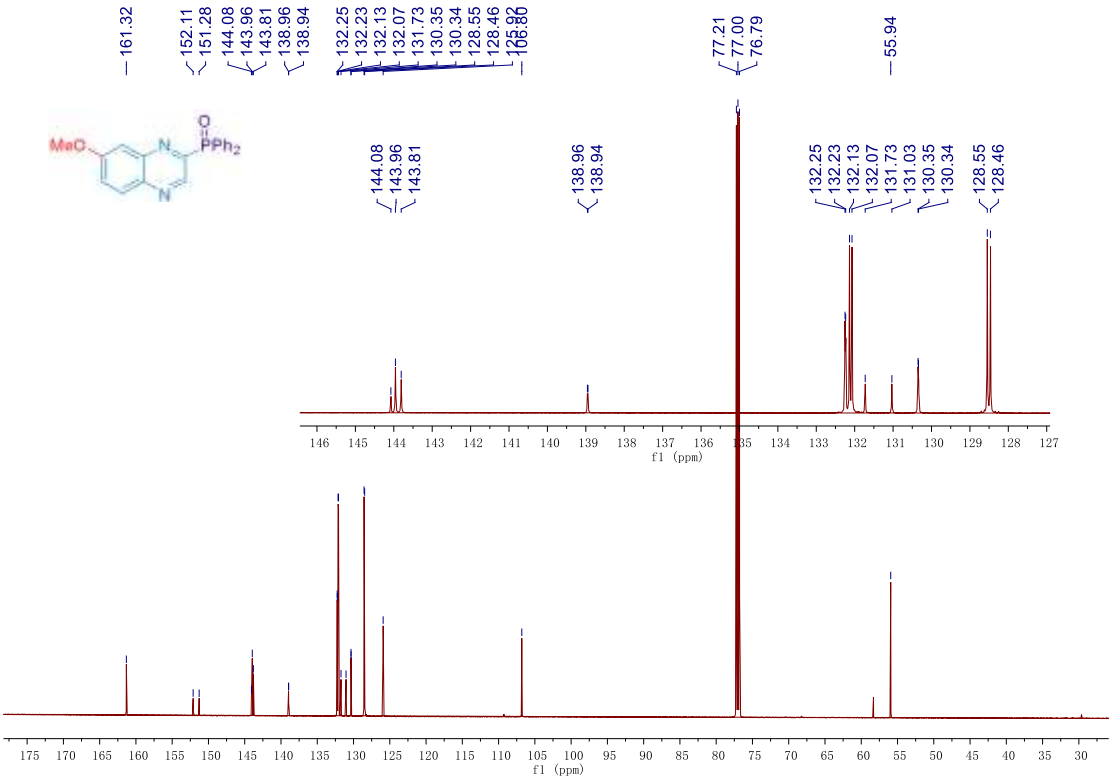


Fig.S 137 ^{13}C NMR of compound **3wa-1**

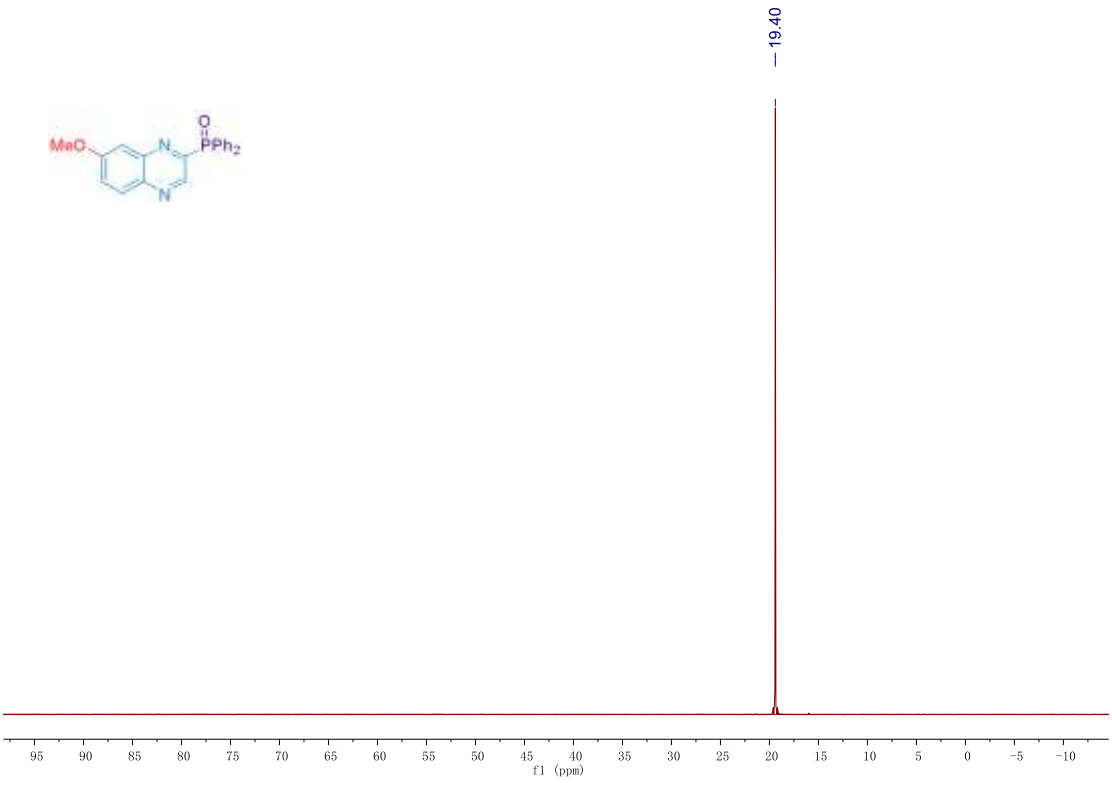


Fig.S 138 ^{31}P NMR of compound **3wa-1**

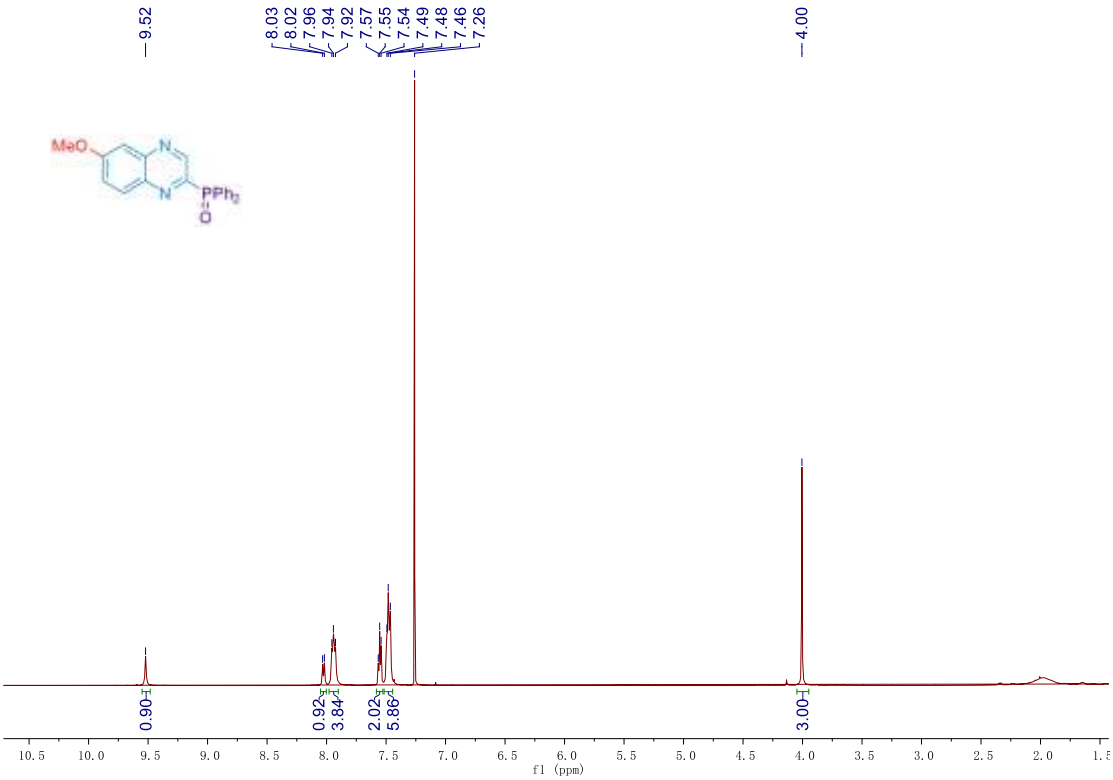


Fig.S 139 ^{1}H NMR of compound **3wa-2**

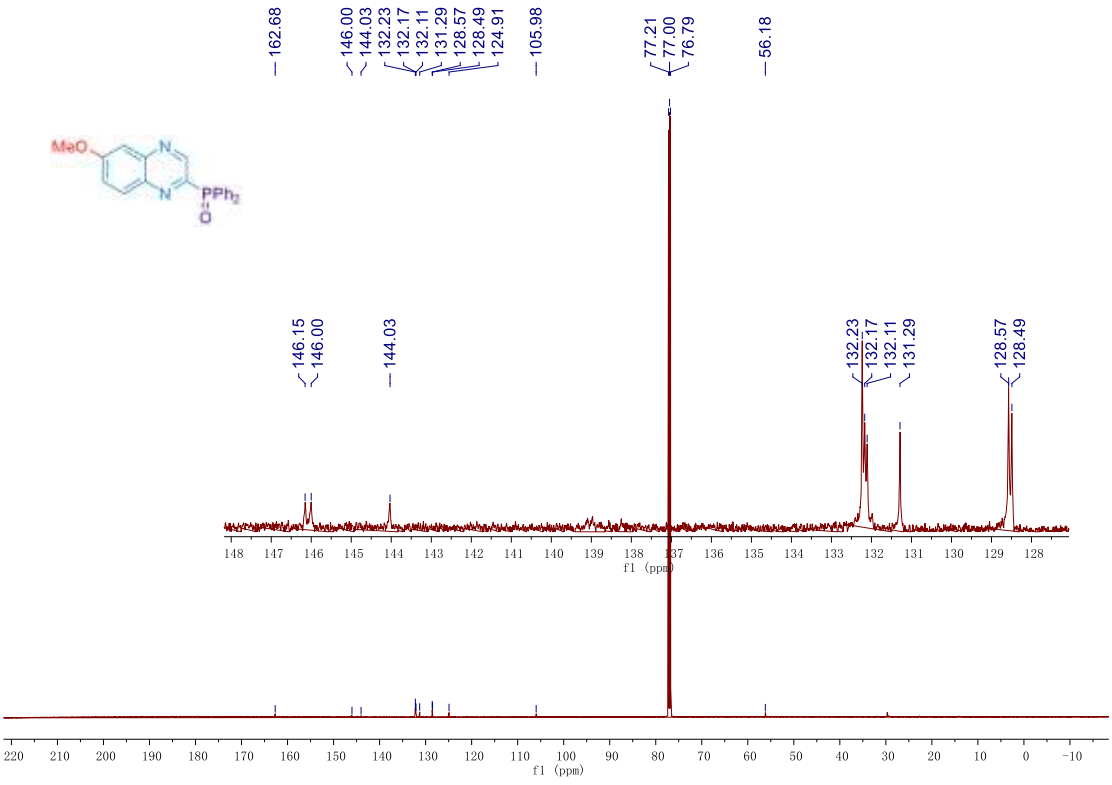


Fig.S 140 ^{13}C NMR of compound **3wa-2**

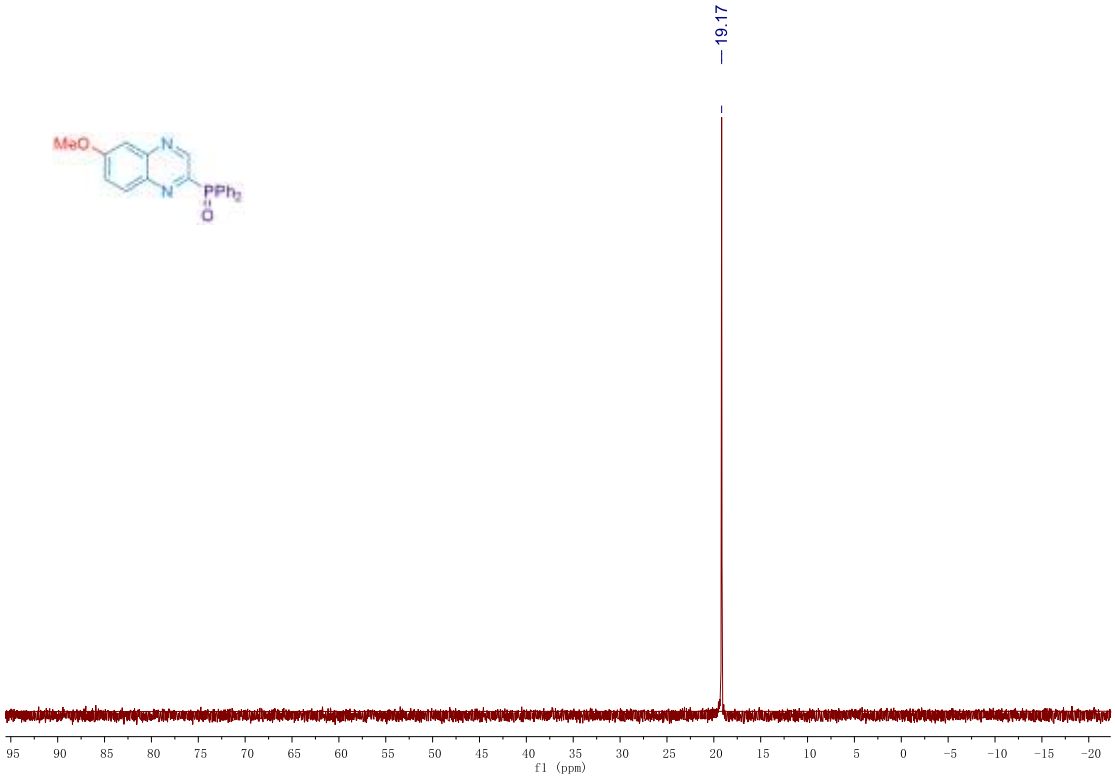


Fig.S 141 ^{31}P NMR of compound **3wa-2**

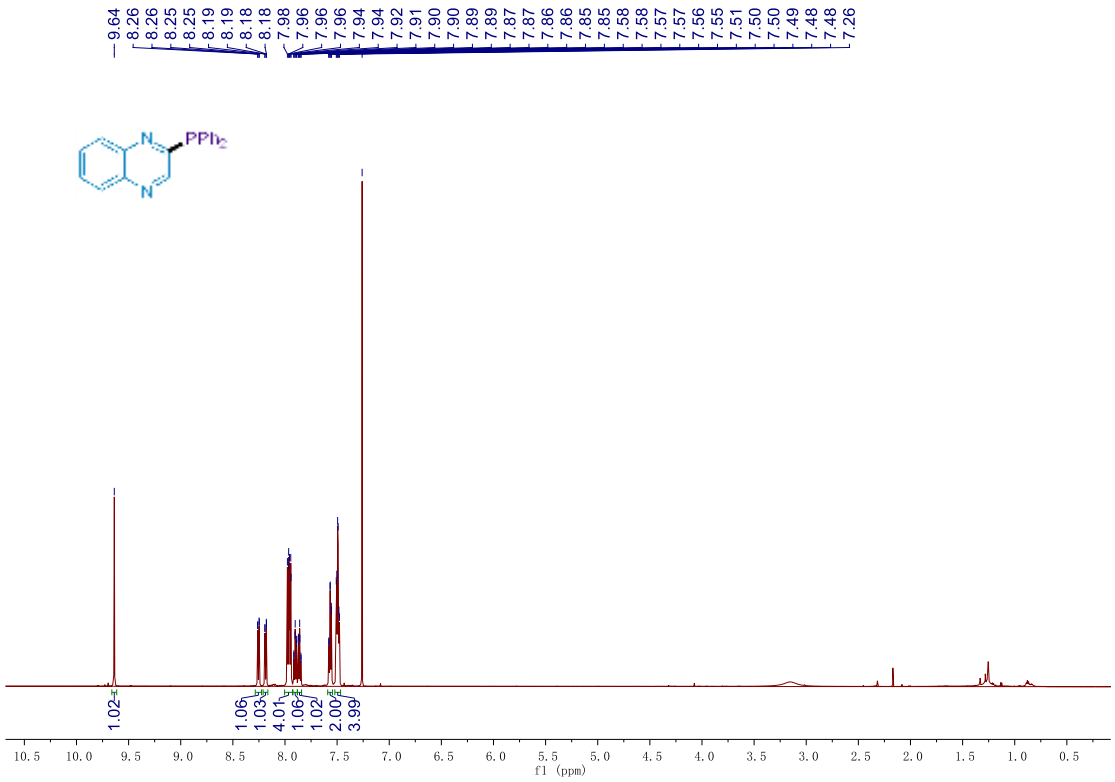


Fig.S 142 ^{1}H NMR of compound **6**

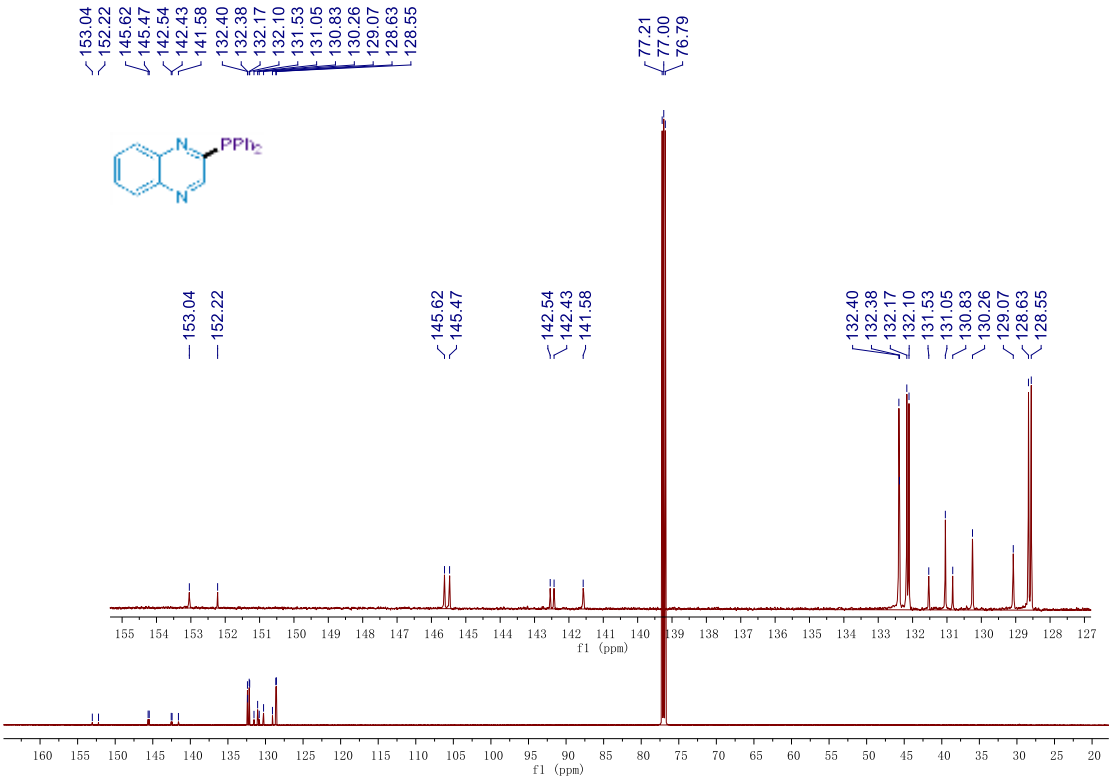


Fig.S 143 ^{13}C NMR of compound **6**

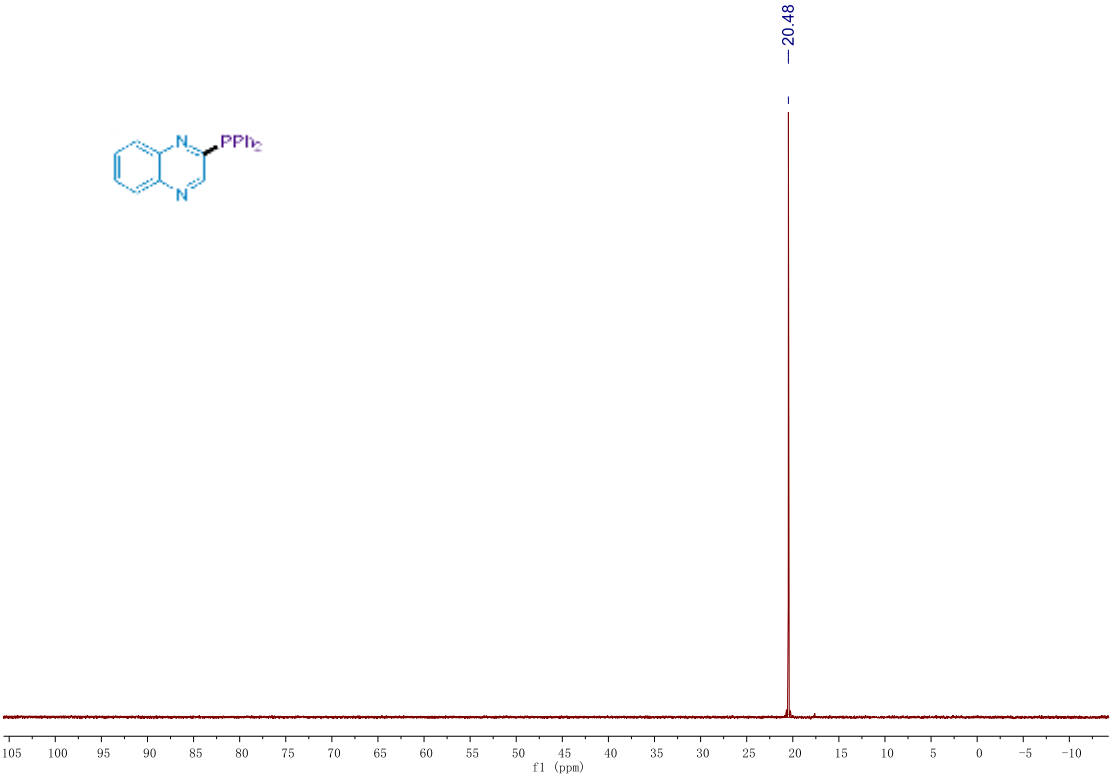


Fig.S 144 ^{31}P NMR of compound **6**

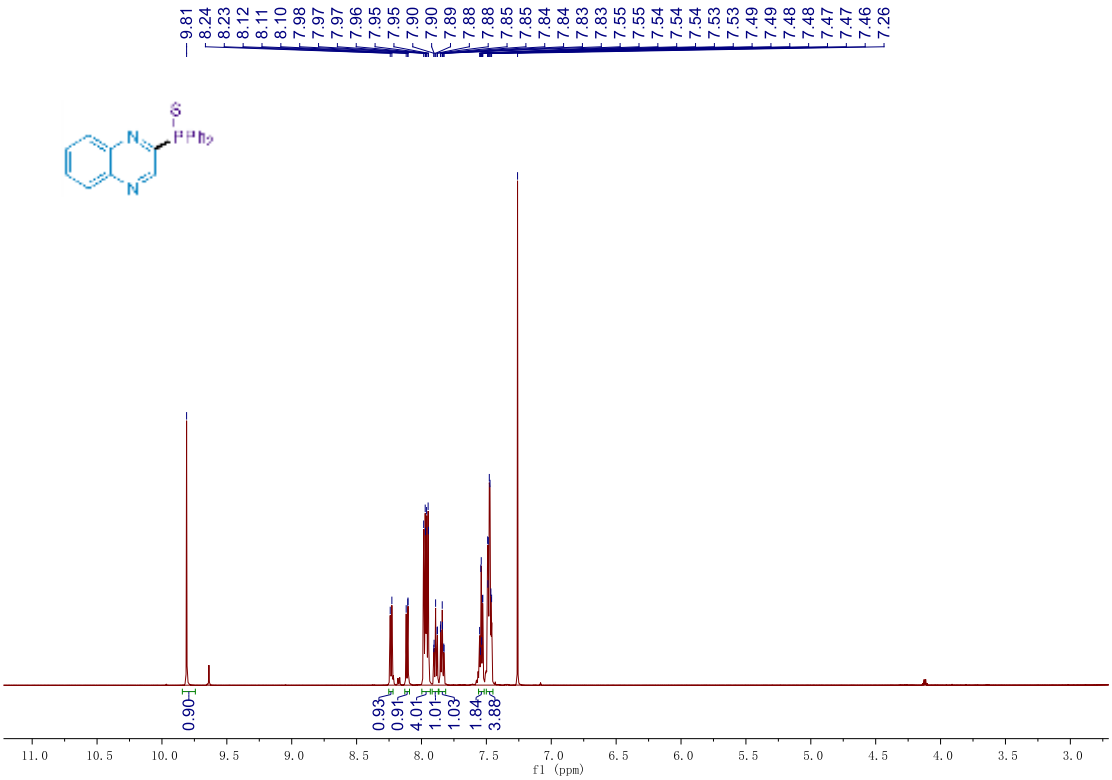


Fig.S 145 ^{1}H NMR of compound **7**

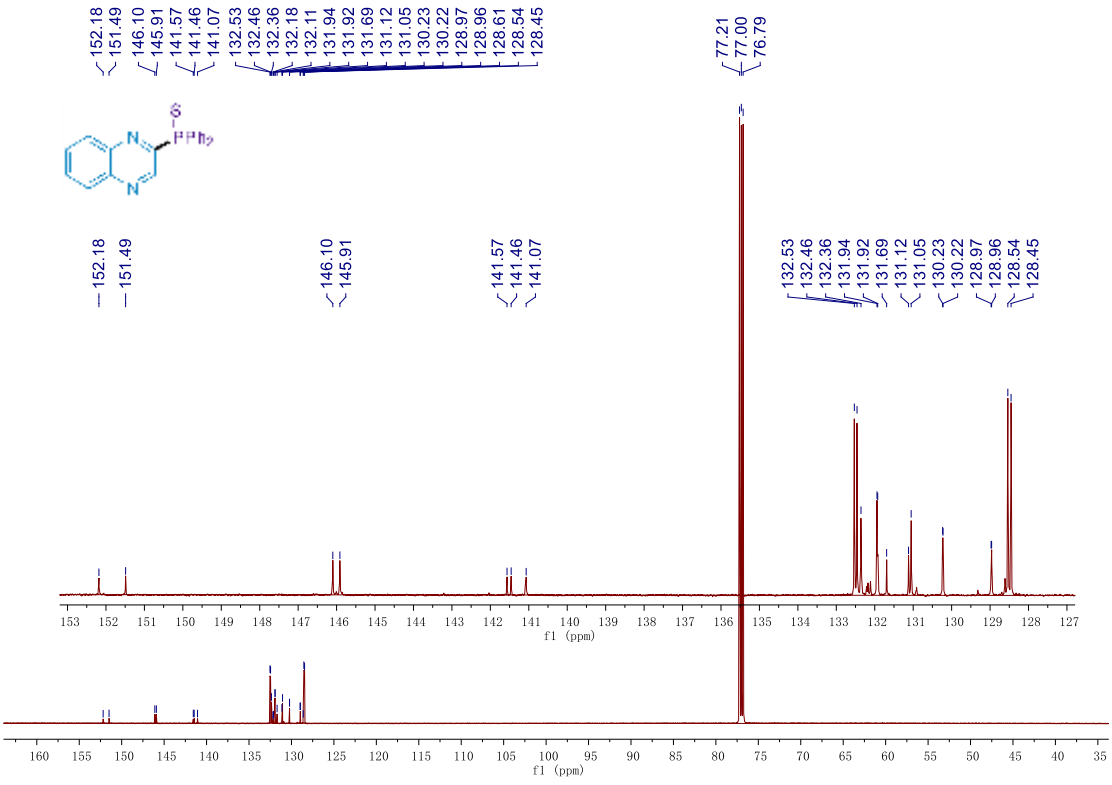


Fig.S 146 ^{13}C NMR of compound **7**

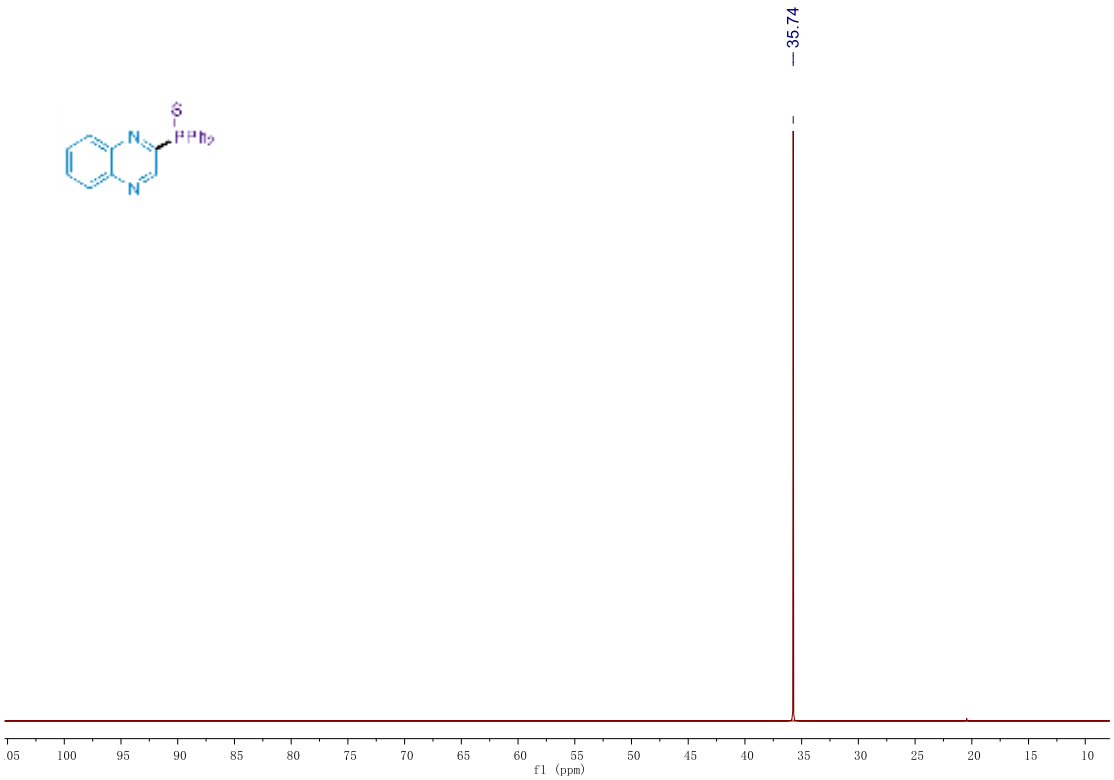


Fig.S 147 ^{31}P NMR of compound **7**