

C3-H Methylene phosphorylation of Azaarenes Enabled by Catalyst-controlled Regioselective Cyclizative Rearrangement

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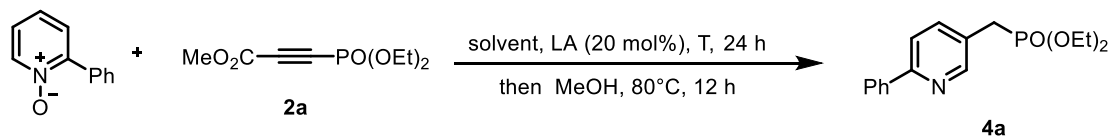
1. General information

NMR spectra were recorded on Bruker AV 400 MHz spectrometer. Chemical shifts are given in ppm. ^{19}F NMR and ^{31}P NMR spectra are calibrated using absolute referencing to the ^1H NMR spectrum, as suggested by IUPAC. (Harris et al., 2001). The spectra are calibrated to the residual ^1H and ^{13}C signals of the solvents. Signal multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), and combinations thereof (e.g., dd, dt). Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus.

Materials and Methods: Unless otherwise noted, starting materials were purchased from commercial sources Adamas-Beta®, Leyan, Shanghai Bide pharmatech Co. Ltd., Shanghai Haohong Scientific Co. Ltd, J&K®, Macklin, Aladdin®, Energy chemical, and used without any purification. More sensitive compounds were stored in a desiccator or in a glove box if required. Solvents were purchased in HPLC quality, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Reactions were monitored by thin layer chromatography (TLC) using Xinnuo TLC silica gel 60 F254. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (230- 400 mesh). Zinc bromide (Cat No. 1042696) was purchased from Leyan, Shanghai, China.

2. Optimization of the reaction conditions

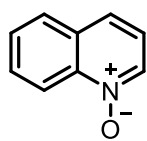
Table S1: Condition optimization for *meta*-C-H methylenephosponylation of pyridines^a



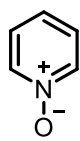
Entry	T (°C)	Solvent	LA	Yield (%) ^b
1	90	dioxane	ZnBr ₂	56
2	90	THF	ZnBr ₂	56
3	90	EtOH	ZnBr ₂	45
4	90	DCE	ZnBr ₂	48
5	90	MeCN	ZnBr ₂	46
6	90	MTBE	ZnBr ₂	37
7	90	DMF	ZnBr ₂	trace
8	90	DMSO	ZnBr ₂	trace
9	90	PhCF ₃	ZnBr ₂	50
10	90	PhCH ₃	ZnBr ₂	53
11	90	PhCl	ZnBr ₂	60
12	90	PhCl	Mg(OTf) ₂	56
13	90	PhCl	Sc(OTf) ₃	52
14	90	PhCl	Ni(OTf) ₂	47
15	90	PhCl	Cu(OTf) ₂	10
16	100	PhCl	ZnBr₂	64
17 ^c	100	PhCl	ZnBr ₂	62

^aReaction conditions: 2-phenylpyridine *N*-oxide (0.1 mmol, 1 equiv), **2a** (0.2 mmol, 2 equiv), LA (0.02 mmol, 20 mol%), solvent (1 mL), 90 °C, 24 h, then add MeOH (0.5 mL), 80 °C, 12 h. ^bIsolated yield. ^cZnBr₂ (0.04 mmol, 40 mol%).

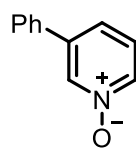
Table S2: Failed substrates



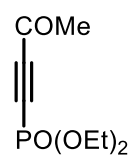
NR



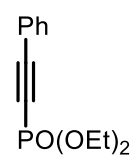
NR



trace

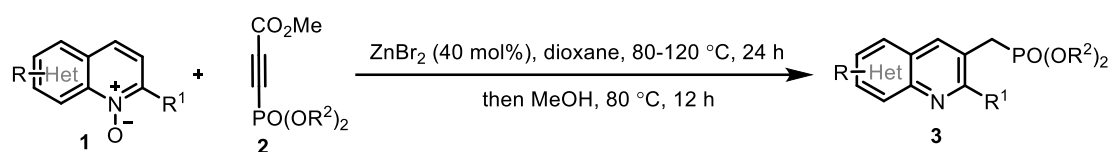


14% yield



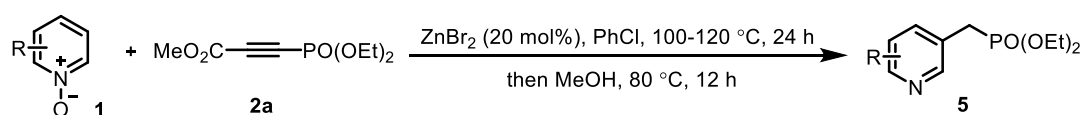
NR

3. General procedure for *meta*-C–H methylenephosphonylation of azaarenes

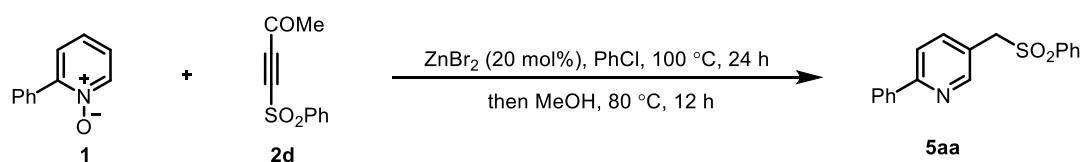


Procedure A: A mixture of azaarene **1** (0.1 mmol, 1.0 equiv), alkyne **2** (0.15 mmol, 1.5 equiv) and ZnBr₂ (0.04 mmol, 40 mol%) was dissolved in dioxane (1 mL) and stirred at indicated temperature (T₁) for 24 h. After cooling to room temperature, MeOH (0.5 mL) was added to the above reaction mixture, and the reaction was stirred at 80 °C for 12 h. When the reaction was completed and cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using PE/EtOAc as eluent to afford product **3**.

Procedure B: An oven-dried vial was charged with azaarene **1ap** (0.1 mmol, 1.0 equiv), alkyne **2a** (0.15 mmol, 1.5 equiv), and ZnBr₂ (0.04 mmol, 40 mol%), then the mixture was stirred in dioxane (1 mL) at 120 °C for 24 h. Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using PE/EtOAc as eluent to afford product **3ap**.

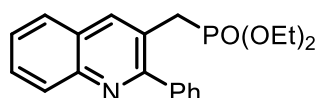


Procedure C: A mixture of azaarene **1** (0.1 mmol, 1.0 equiv), alkyne **2a** (0.2 mmol, 2.0 equiv) and ZnBr₂ (0.02 mmol, 20 mol%) was dissolved in PhCl (1 mL) and stirred at indicated temperature (T₂) for 24 h. After cooling to room temperature, MeOH (0.5 mL) was added to the above reaction mixture, and the reaction was stirred at 80 °C for 12 h. When the reaction was completed and cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using PE/EtOAc as eluent to afford product **5**.



Procedure D: A mixture of azaarene **1** (0.1 mmol, 1.0 equiv), alkyne **2d** (0.2 mmol, 2.0 equiv) and ZnBr₂ (0.02 mmol, 20 mol%) was dissolved in PhCl (1 mL) and stirred at 100 °C for 24 h. After cooling to room temperature, MeOH (0.5 mL) was added to the above reaction mixture, and the reaction was stirred at 80 °C for 12 h. When the reaction was completed and cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using PE/EtOAc as eluent to afford product **5aa**.

diethyl ((2-phenylquinolin-3-yl)methyl)phosphonate (3a)



Following procedure A: T₁ = 80 °C, 29.6 mg, yellow oil, 83% yield.

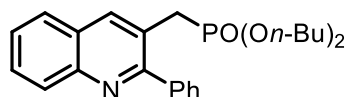
¹H NMR (400 MHz, Chloroform-*d*) 8.41 (d, *J* = 3.4 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 6.8, 1H), 7.66 – 7.60 (m, 2H), 7.57 – 7.42 (m, 4H), 4.02 – 3.92 (m, 4H), 3.37 (d, *J* = 22.2 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.4 (d, *J* = 7.4 Hz), 146.9 (d, *J* = 2.5 Hz), 140.3, 138.1 (d, *J* = 6.1 Hz), 129.7 (d, *J* = 1.5 Hz), 129.4 (d, *J* = 1.5 Hz), 129.3, 128.6, 128.5, 127.4 (d, *J* = 1.3 Hz), 127.3 (d, *J* = 3.2 Hz), 126.9, 123.6 (d, *J* = 8,7 Hz), 62.3 (d, *J* = 6.7 Hz), 30.0 (d, *J* = 139.2 Hz), 16.5 (d, *J* = 6.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₃NO₃P⁺ 356.1410; Found 356.1422.

dibutyl ((2-phenylquinolin-3-yl)methyl)phosphonate (3b)



Following procedure A: T₁ = 80 °C, 32.9 mg, colorless oil, 80% yield.

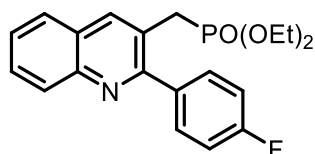
¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 3.4 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.66 (m, 1H), 7.63 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.56 – 7.40 (m, 4H), 3.94 – 3.85 (m, 4H), 3.37 (d, *J* = 22.2 Hz, 2H), 1.59 – 1.47 (m, 4H), 1.31 – 1.22 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.3 (d, $J = 7.5$ Hz), 146.9 (d, $J = 2.5$ Hz), 140.3, 138.1 (d, $J = 6.0$ Hz), 129.7 (d, $J = 1.6$ Hz), 129.4 (d, $J = 1.4$ Hz), 129.3, 128.6, 128.5, 127.3 (d, $J = 1.3$ Hz), 127.2 (d, $J = 3.2$ Hz), 126.8, 123.6 (d, $J = 8.5$ Hz), 66.0 (d, $J = 7.0$ Hz), 32.5 (d, $J = 6.0$ Hz), 29.8 (d, $J = 139.3$ Hz), 18.7, 13.6.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{31}\text{NO}_3\text{P}^+$ 412.2042; Found: 412.2042.

diethyl ((2-(4-fluorophenyl)quinolin-3-yl)methyl)phosphonate (3c)



Following procedure A: $T_1 = 80$ °C, 26.8 mg, yellow oil, 72% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, $J = 3.5$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H), 7.87 – 7.80 (m, 1H), 7.75 – 7.60 (m, 3H), 7.54 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 7.24 – 7.13 (m, 2H), 4.04 – 3.96 (m, 4H), 3.33 (d, $J = 22.2$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H).

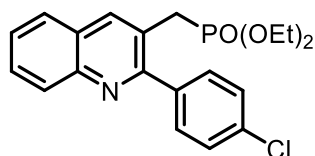
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0 (d, $J = 248.7$ Hz), 159.3 (d, $J = 7.1$ Hz), 146.9 (d, $J = 2.4$ Hz), 138.2 (d, $J = 5.9$ Hz), 136.3 (d, $J = 3.5$ Hz), 131.3 (d, $J = 8.3$ Hz), 129.9 (d, $J = 1.5$ Hz), 129.3 (d, $J = 1.5$ Hz), 127.4 (d, $J = 1.4$ Hz), 127.3 (d, $J = 3.2$ Hz), 127.0, 123.5 (d, $J = 8.7$ Hz), 115.5 (d, $J = 21.6$ Hz), 62.4 (d, $J = 6.8$ Hz), 30.1 (d, $J = 139.5$ Hz), 16.5 (d, $J = 5.9$ Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.4.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.8.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{FNO}_3\text{P}^+$ 374.1316; Found: 374.1323.

diethyl ((2-(4-chlorophenyl)quinolin-3-yl)methyl)phosphonate (3d)



Following procedure A: $T_1 = 80$ °C, 28.5 mg, yellow oil, 73% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, $J = 3.5$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H), 7.85 (s, 1H), 7.73 – 7.68 (m, 1H), 7.64 – 7.58 (m, 2H), 7.57 – 7.52 (m, 1H), 7.51 – 7.45

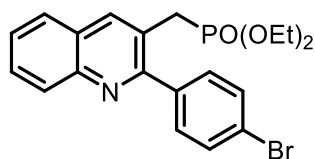
(m, 2H), 4.05 – 3.95 (m, 4H), 3.32 (d, $J = 22.2$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.1 (d, $J = 7.2$ Hz), 146.9 (d, $J = 2.5$ Hz), 138.7, 138.3 (d, $J = 6.1$ Hz), 134.7, 130.9, 129.9 (d, $J = 1.5$ Hz), 129.4 (d, $J = 1.6$ Hz), 128.8, 127.4 (d, $J = 1.4$ Hz), 127.3 (d, $J = 3.2$ Hz), 127.1, 123.4 (d, $J = 8.6$ Hz), 62.4 (d, $J = 6.9$ Hz), 30.1 (d, $J = 139.6$ Hz), 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.7.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{ClNO}_3\text{P}^+$ 390.1020; Found: 390.1025.

diethyl ((2-(4-bromophenyl)quinolin-3-yl)methyl)phosphonate (3e)



Following procedure A: $T_1 = 80$ °C, 33.3 mg, yellow oil, 76% yield.

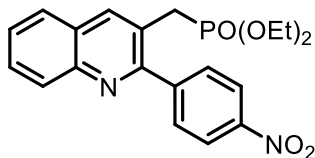
^1H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, $J = 3.5$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.70 (t, $J = 7.7$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.58 – 7.50 (m, 3H), 4.04 – 3.96 (m, 4H), 3.32 (d, $J = 22.2$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.1 (d, $J = 7.3$ Hz), 146.9 (d, $J = 2.5$ Hz), 139.2, 138.3 (d, $J = 6.1$ Hz), 131.7, 131.1, 129.9 (d, $J = 1.5$ Hz), 129.3 (d, $J = 1.5$ Hz), 127.4 (d, $J = 1.3$ Hz), 127.3 (d, $J = 3.2$ Hz), 127.1, 123.3 (d, $J = 8.6$ Hz), 123.0, 62.4 (d, $J = 6.8$ Hz), 30.0 (d, $J = 139.5$ Hz), 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.7.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{BrNO}_3\text{P}^+$ 434.0515; Found: 434.0513.

diethyl ((2-(4-nitrophenyl)quinolin-3-yl)methyl)phosphonate (3f)



Following procedure A: $T_1 = 80$ °C, 26.3 mg, white solid, 65% yield. M.p = 90 – 92 °C.

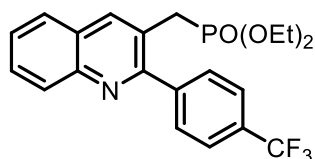
^1H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, $J = 3.5$ Hz, 1H), 8.39 – 8.30 (m, 2H), 8.10 (d, $J = 8.5$ Hz, 1H), 7.90 – 7.86 (m, 3H), 7.74 (t, $J = 7.7$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 4.06 – 3.97 (m, 4H), 3.29 (d, $J = 22.2$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.9 (d, *J* = 7.0 Hz), 147.9, 146.9 (d, *J* = 2.5 Hz), 146.7, 138.7 (d, *J* = 6.0 Hz), 130.7, 130.3 (d, *J* = 1.5 Hz), 129.4 (d, *J* = 1.6 Hz), 127.6, 127.5, 127.47 (d, *J* = 1.4 Hz), 123.7, 123.1 (d, *J* = 8.6 Hz), 62.5 (d, *J* = 6.8 Hz), 30.1 (d, *J* = 140.0 Hz), 16.5 (d, *J* = 5.9 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.3.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂N₂O₅P⁺ 401.1261; Found: 401.1262.

diethyl ((2-(4-(trifluoromethyl)phenyl)quinolin-3-yl)methyl)phosphonate (3g)



Following procedure A: T₁ = 80 °C, 27.9 mg, yellow oil, 66% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 3.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.81 – 7.70 (m, 5H), 7.57 (t, *J* = 7.5 Hz, 1H), 4.05 – 3.97 (m, 4H), 3.32 (d, *J* = 22.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 6H).

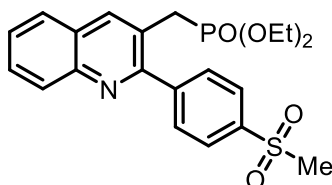
¹³C NMR (101 MHz, Chloroform-*d*) δ 158.8 (d, *J* = 7.2 Hz), 146.9 (d, *J* = 2.5 Hz), 143.9, 138.4 (d, *J* = 6.1 Hz), 130.6 (q, *J* = 32.7 Hz), 130.1, 129.9, 129.4, 127.5, 127.4, 127.3, 125.6 (q, *J* = 3.5 Hz), 124.2 (q, *J* = 271.1 Hz), 123.3 (d, *J* = 8.7 Hz), 62.4 (d, *J* = 6.9 Hz), 30.1 (d, *J* = 139.8 Hz), 16.5 (d, *J* = 5.9 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.6.

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.5.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₂F₃NO₃P⁺ 424.1284; Found: 424.1281.

diethyl ((2-(4-(methylsulfonyl)phenyl)quinolin-3-yl)methyl)phosphonate (3h)



Following procedure A: T₁ = 80 °C, 30.6 mg, white solid, 70% yield. M.p = 134 – 135 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 3.4 Hz, 1H), 8.10 – 8.07 (m, 3H),

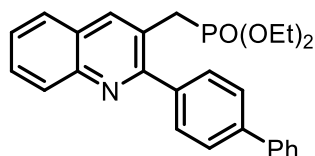
7.95 – 7.88 (m, 2H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.76 – 7.70 (m, 1H), 7.60 – 7.56 (m, 1H), 4.06 – 3.95 (m, 4H), 3.28 (d, $J = 22.2$ Hz, 2H), 3.09 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 158.2 (d, $J = 7.2$ Hz), 146.9 (d, $J = 2.5$ Hz), 145.8, 140.4, 138.6 (d, $J = 6.0$ Hz), 130.6, 130.2 (d, $J = 1.5$ Hz), 129.4 (d, $J = 1.5$ Hz), 127.7, 127.5, 127.48, 127.47, 123.2 (d, $J = 8.6$ Hz), 62.5 (d, $J = 6.7$ Hz), 44.7, 30.0 (d, $J = 139.9$ Hz), 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform- d) δ 25.3.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_5\text{P}^+$ 434.1186; Found: 434.1187.

diethyl ((2-([1,1'-biphenyl]-4-yl)quinolin-3-yl)methyl)phosphonate (3i)



Following procedure A: $T_1 = 80$ °C, 31.2 mg, yellow oil, 72% yield.

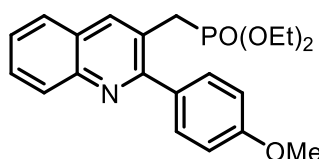
^1H NMR (400 MHz, Chloroform- d) δ 8.43 (d, $J = 3.5$ Hz, 1H), 8.14 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.69 (d, $J = 33.1$ Hz, 7H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.38 (t, $J = 7.3$ Hz, 1H), 4.05 – 3.97 (m, 4H), 3.44 (d, $J = 22.2$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 160.0 (d, $J = 7.3$ Hz), 147.0 (d, $J = 2.5$ Hz), 141.4, 140.8, 139.2, 138.2 (d, $J = 6.0$ Hz), 129.8, 129.76, 129.4, 129.0, 127.6, 127.4, 127.36, 127.3, 127.2, 126.9, 123.6 (d, $J = 8.7$ Hz), 62.3 (d, $J = 6.8$ Hz), 30.1 (d, $J = 139.2$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform- d) δ 25.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_3\text{P}^+$ 432.1723; Found: 432.1722.

diethyl ((2-(4-methoxyphenyl)quinolin-3-yl)methyl)phosphonate (3j)



Following procedure A: $T_1 = 80$ °C, 23.1 mg, yellow oil, 60% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.38 (d, $J = 3.4$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H),

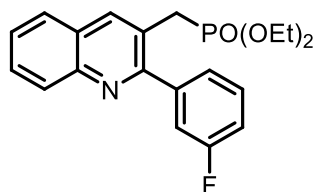
7.82 (d, $J = 8.1$ Hz, 1H), 7.68 (ddt, $J = 8.3, 7.0, 1.2$ Hz, 1H), 7.62 – 7.57 (m, 2H), 7.52 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 7.05 – 6.99 (m, 2H), 4.03 – 3.87 (m, 4H), 3.87 (s, 3H), 3.39 (d, $J = 22.2$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.1 (d, $J = 7.3$ Hz), 159.9, 147.0 (d, $J = 2.5$ Hz), 138.1 (d, $J = 6.0$ Hz), 132.8, 130.8, 129.6 (d, $J = 1.5$ Hz), 129.3 (d, $J = 1.5$ Hz), 127.4 (d, $J = 1.4$ Hz), 127.1 (d, $J = 3.2$ Hz), 126.7, 123.6 (d, $J = 8.5$ Hz), 114.0, 62.3 (d, $J = 6.8$ Hz), 55.5, 30.0 (d, $J = 139.2$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.1.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_4\text{P}^+$ 386.1516; Found: 386.1515.

diethyl ((2-(3-fluorophenyl)quinolin-3-yl)methyl)phosphonate (3k)



Following procedure A: $T_1 = 80$ °C, 27.5 mg, yellow oil, 73% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, $J = 3.5$ Hz, 1H), 8.11 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.71 (ddt, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.56 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.50 – 7.34 (m, 3H), 7.20 – 7.08 (m, 1H), 4.07 – 3.94 (m, 4H), 3.34 (d, $J = 22.2$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H).

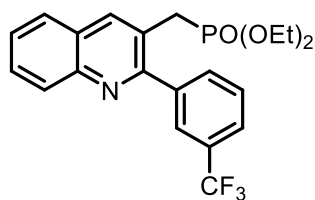
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.8 (d, $J = 246.9$ Hz), 158.9 (dd, $J = 7.1, 2.3$ Hz), 146.8 (d, $J = 2.5$ Hz), 142.4 (d, $J = 7.4$ Hz), 138.4 (d, $J = 6.0$ Hz), 130.2 (d, $J = 8.3$ Hz), 129.9 (d, $J = 1.5$ Hz), 129.4 (d, $J = 1.5$ Hz), 127.4 (d, $J = 1.3$ Hz), 127.38 (d, $J = 3.1$ Hz), 127.1, 125.1 (d, $J = 2.9$ Hz), 123.4 (d, $J = 8.7$ Hz), 116.7 (d, $J = 22.2$ Hz), 115.5 (d, $J = 21.0$ Hz), 62.4 (d, $J = 6.8$ Hz), 30.0 (d, $J = 139.6$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.7.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.6.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{FNO}_3\text{P}^+$ 374.1316; Found: 374.1320.

diethyl ((2-(3-(trifluoromethyl)phenyl)quinolin-3-yl)methyl)phosphonate (3l)



Following procedure A: $T_1 = 80\text{ }^\circ\text{C}$, 28.4 mg, yellow oil, 67% yield.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.41 (d, $J = 3.5$ Hz, 1H), 8.11 (d, $J = 8.5$ Hz, 1H), 7.99 (s, 1H), 7.89 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 7.63 (t, $J = 7.7$ Hz, 1H), 7.57 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 4.09 – 3.94 (m, 4H), 3.30 (d, $J = 22.2$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H).

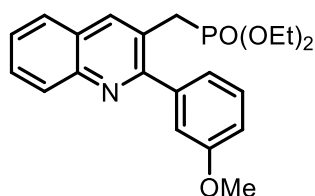
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 158.7 (d, $J = 7.1$ Hz), 146.9 (d, $J = 2.6$ Hz), 141.0, 138.5 (d, $J = 6.1$ Hz), 132.8, 131.0 (q, $J = 32.5$ Hz), 130.1, 129.4, 129.1, 127.5, 127.4, 127.3, 126.5 (q, $J = 3.9$ Hz), 125.3 (d, $J = 3.8$ Hz), 124.2 (q, $J = 273.4$ Hz), 123.4 (d, $J = 8.7$ Hz), 62.4 (d, $J = 6.8$ Hz), 30.1 (d, $J = 139.6$ Hz), 16.4 (d, $J = 6.0$ Hz).

$^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62.5.

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{F}_3\text{NO}_3\text{P}^+$ 424.1284; Found: 424.1289.

diethyl ((2-(3-methoxyphenyl)quinolin-3-yl)methyl)phosphonate (3m)



Following procedure A: $T_1 = 80\text{ }^\circ\text{C}$, 28.7 mg, yellow oil, 74% yield.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.40 (d, $J = 3.5$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.70 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.54 (ddd, $J = 8.0, 6.9, 1.2$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 1H), 7.22 – 7.16 (m, 2H), 6.99 (ddd, $J = 8.3, 2.6, 1.1$ Hz, 1H), 4.06 – 3.93 (m, 4H), 3.86 (s, 3H), 3.37 (d, $J = 22.2$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 6H).

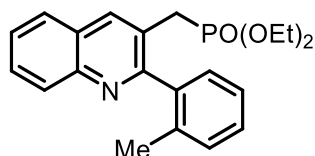
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 160.2 (d, $J = 7.4$ Hz), 159.7, 146.8 (d, $J = 2.5$ Hz), 141.5, 138.1 (d, $J = 6.0$ Hz), 129.8 (d, $J = 1.5$ Hz), 129.7, 129.4 (d, $J = 1.7$ Hz), 127.4, 127.3 (d, $J = 3.2$ Hz), 126.9, 123.5 (d, $J = 8.5$ Hz), 121.7, 114.7, 114.61, 62.3 (d,

$J = 6.8$ Hz), 55.5, 29.9 (d, $J = 139.3$ Hz), 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_4\text{P}^+$ 386.1516; Found: 386.1525.

diethyl ((2-(*o*-tolyl)quinolin-3-yl)methyl)phosphonate (3n)



Following procedure A: $T_1 = 120$ °C, 14.2 mg, yellow oil, 38% yield.

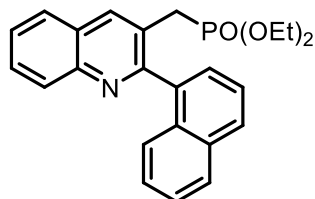
^1H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, $J = 3.3$ Hz, 1H), 8.11 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.70 (t, $J = 7.7$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.37 – 7.28 (m, 4H), 4.00 – 3.90 (m, 4H), 3.31 – 3.01 (m, 2H), 2.09 (s, 3H), 1.26 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.8 (d, $J = 8.0$ Hz), 146.9 (d, $J = 2.3$ Hz), 139.5, 137.5 (d, $J = 5.9$ Hz), 136.0, 130.6, 129.7 (d, $J = 1.4$ Hz), 129.3 (d, $J = 1.3$ Hz), 129.2, 128.6, 127.5 (d, $J = 1.3$ Hz), 127.4 (d, $J = 3.0$ Hz), 126.8, 126.0, 124.3 (d, $J = 8.4$ Hz), 62.2, 29.4 (d, $J = 139.9$ Hz), 19.7, 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_3\text{P}^+$ 370.1567; Found: 370.1566.

diethyl ((2-(naphthalen-1-yl)quinolin-3-yl)methyl)phosphonate (3o)



Following procedure A: $T_1 = 120$ °C, 14.8 mg, yellow oil, 36% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, $J = 3.3$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.97 – 7.92 (m, 3H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.62 – 7.58 (m, 3H), 7.50 – 7.46 (m, 1H), 7.41 – 7.33 (m, 2H), 3.95 – 3.74 (m, 4H), 3.19 (dd, $J = 22.6, 15.6$ Hz, 1H), 3.02 (dd, $J = 21.5, 15.6$ Hz, 1H), 1.18 – 1.11 (m, 6H).

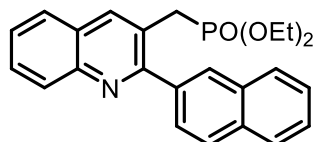
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7 (d, $J = 8.0$ Hz), 147.0 (d, $J = 2.4$ Hz), 137.7 (d, $J = 5.9$ Hz), 137.3, 133.8, 131.8, 129.8, 129.5, 129.0, 128.5, 127.6, 127.5 (d,

$J = 2.9$ Hz), 127.4, 127.1, 126.7, 126.2, 125.5, 125.2 (d, $J = 8.3$ Hz), 62.2 (d, $J = 6.8$ Hz), 62.15 (d, $J = 6.8$ Hz), 29.8 (d, $J = 139.6$ Hz), 16.4 (d, $J = 6.1$ Hz), 16.39 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.8.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{P}^+$ 406.1567; Found: 406.1568.

diethyl ((2-(naphthalen-2-yl)quinolin-3-yl)methyl)phosphonate (3p)



Following procedure A: $T_1 = 80$ °C, 27.9 mg, yellow oil, 68% yield.

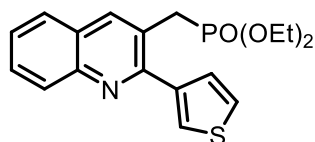
^1H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, $J = 3.4$ Hz, 1H), 8.16 – 8.14 (m, 2H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.95 – 7.87 (m, 3H), 7.80 – 7.68 (m, 2H), 7.61 – 7.49 (m, 3H), 4.06 – 3.88 (m, 4H), 3.42 (d, $J = 22.2$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.3 (d, $J = 7.3$ Hz), 147.0 (d, $J = 2.5$ Hz), 138.2 (d, $J = 6.1$ Hz), 137.7, 133.2, 133.18, 129.8 (d, $J = 1.5$ Hz), 129.4 (d, $J = 1.5$ Hz), 128.8, 128.5, 128.3, 127.8, 127.4 (d, $J = 1.3$ Hz), 127.3 (d, $J = 3.2$ Hz), 127.0, 126.9, 126.6, 126.5, 123.7 (d, $J = 8.5$ Hz), 62.3 (d, $J = 6.7$ Hz), 30.1 (d, $J = 139.3$ Hz), 16.4 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{P}^+$ 406.1567; Found: 406.1564.

diethyl ((2-(thiophen-3-yl)quinolin-3-yl)methyl)phosphonate (3q)



Following procedure A: $T_1 = 80$ °C, 24.5 mg, yellow oil, 67% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, $J = 3.5$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 7.86 – 7.78 (m, 2H), 7.73 – 7.65 (m, 1H), 7.56 – 7.50 (m, 2H), 7.44 (dd, $J = 5.0, 3.0$ Hz, 1H), 4.11 – 3.95 (m, 4H), 3.45 (d, $J = 22.2$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 6H).

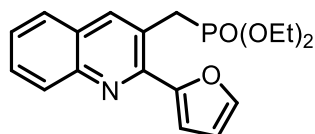
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.6 (d, $J = 7.1$ Hz), 147.0 (d, $J = 2.6$ Hz),

141.1, 138.3 (d, $J = 6.1$ Hz), 129.7 (d, $J = 1.6$ Hz), 129.32, 129.3, 127.3 (d, $J = 1.4$ Hz), 127.1 (d, $J = 3.3$ Hz), 126.8, 125.9, 125.83, 123.6 (d, $J = 8.7$ Hz), 62.4 (d, $J = 6.8$ Hz), 30.2 (d, $J = 139.4$ Hz), 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3\text{PS}^+$ 362.0974; Found: 362.0978.

diethyl ((2-(furan-2-yl)quinolin-3-yl)methyl)phosphonate (3r)



Following procedure A: $T_1 = 80$ °C, 13.1 mg, yellow oil, 37% yield.

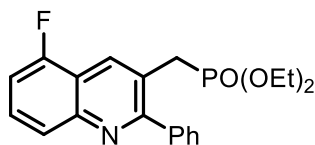
^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, $J = 3.6$ Hz, 1H), 8.08 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.71 – 7.62 (m, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.25 (s, 1H), 6.60 (dd, $J = 3.5, 1.8$ Hz, 1H), 4.05 – 3.91 (m, 4H), 3.80 (d, $J = 22.2$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.0, 148.6 (d, $J = 5.9$ Hz), 147.0 (d, $J = 2.5$ Hz), 143.6, 139.4 (d, $J = 6.6$ Hz), 129.9 (d, $J = 1.6$ Hz), 129.3 (d, $J = 1.5$ Hz), 127.3 (d, $J = 1.5$ Hz), 127.0 (d, $J = 3.2$ Hz), 126.9, 122.8 (d, $J = 9.8$ Hz), 112.6, 112.0, 62.3 (d, $J = 6.9$ Hz), 30.7 (d, $J = 139.0$ Hz), 16.4 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.7.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_4\text{P}^+$ 346.1203; Found: 346.1205.

diethyl ((5-fluoro-2-phenylquinolin-3-yl)methyl)phosphonate (3s)



Following procedure A: $T_1 = 80$ °C, 23.9 mg, colorless oil, 64% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, $J = 3.5$ Hz, 1H), 7.92 (d, $J = 8.5$ Hz, 1H), 7.67 – 7.58 (m, 3H), 7.53 – 7.43 (m, 3H), 7.20 – 7.17 (m, 1H), 4.06 – 3.94 (m, 4H), 3.40 (d, $J = 22.3$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 6H).

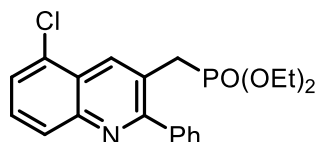
¹³C NMR (101 MHz, Chloroform-*d*) δ 161.3 (d, *J* = 6.9 Hz), 157.6 (d, *J* = 255.8 Hz), 147.6 (t, *J* = 2.7 Hz), 139.9, 131.4 (dd, *J* = 6.1, 4.1 Hz), 129.3, 129.1 (d, *J* = 9.0 Hz), 128.7, 128.6, 125.3 (dd, *J* = 4.2, 1.5 Hz), 124.2 (dd, *J* = 9.0, 2.5 Hz), 118.1 (dd, *J* = 16.0, 3.4 Hz), 110.3 (d, *J* = 19.2 Hz), 62.3 (d, *J* = 6.8 Hz), 30.2 (d, *J* = 139.2 Hz), 16.4 (d, *J* = 6.2 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -122.9.

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.3.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂FNO₃P⁺ 374.1316; Found: 374.1315.

diethyl ((5-chloro-2-phenylquinolin-3-yl)methyl)phosphonate (3t)



Following procedure A: T₁ = 80 °C, 25 mg, colorless oil, 64% yield.

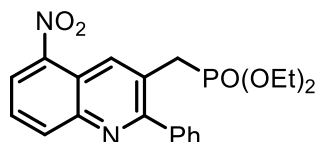
¹H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 3.5 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.66 (dt, *J* = 6.1, 1.5 Hz, 2H), 7.65 – 7.56 (m, 2H), 7.55 – 7.41 (m, 3H), 4.05 – 3.98 (m, 4H), 3.42 (d, *J* = 22.3 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.2 (d, *J* = 7.0 Hz), 147.5 (d, *J* = 2.6 Hz), 139.7, 135.0 (d, *J* = 6.0 Hz), 130.9 (d, *J* = 1.7 Hz), 129.4, 129.3, 128.8, 128.7, 128.65, 126.8, 125.4 (d, *J* = 3.3 Hz), 125.0 (d, *J* = 9.1 Hz), 62.4 (d, *J* = 6.7 Hz), 30.3 (d, *J* = 139.1 Hz), 16.5 (d, *J* = 6.2 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂ClNO₃P⁺ 390.1020; Found: 390.1025.

diethyl ((5-nitro-2-phenylquinolin-3-yl)methyl)phosphonate (3u)



Following procedure A: T₁ = 80 °C, 22.7 mg, yellow solid, 56% yield. M.p = 76 – 77 °C.

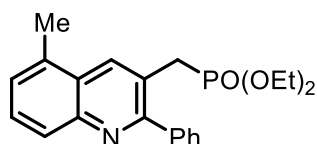
¹H NMR (400 MHz, Chloroform-*d*) δ 9.18 (d, *J* = 3.5 Hz, 1H), 8.41 (dd, *J* = 15.2, 8.1 Hz, 2H), 7.77 (t, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.47 (m, 3H), 4.08 – 4.01 (m, 4H), 3.45 (d, *J* = 22.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.8 (d, *J* = 6.8 Hz), 147.0 (d, *J* = 2.5 Hz), 145.0, 139.2, 136.7 (d, *J* = 1.6 Hz), 134.0 (d, *J* = 6.1 Hz), 129.3, 129.1, 128.8, 127.8 (d, *J* = 9.2 Hz), 127.6 (d, *J* = 1.5 Hz), 124.9, 120.2 (d, *J* = 3.5 Hz), 62.5 (d, *J* = 6.7 Hz), 30.7 (d, *J* = 138.5 Hz), 16.4 (d, *J* = 6.2 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 24.6.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂N₂O₅P⁺ 401.1261; Found: 401.1264.

diethyl ((5-methyl-2-phenylquinolin-3-yl)methyl)phosphonate (3v)



Following procedure A: T₁ = 80 °C, 27.3 mg, yellow oil, 74% yield.

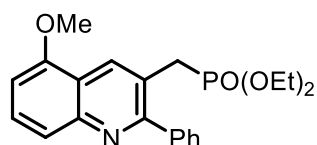
¹H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 3.4 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.49 (dd, *J* = 8.0, 6.6 Hz, 2H), 7.48 – 7.39 (m, 1H), 7.36 (d, *J* = 7.0 Hz, 1H), 4.04 – 3.89 (m, 4H), 3.40 (d, *J* = 22.2 Hz, 2H), 2.73 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.8 (d, *J* = 7.3 Hz), 147.2 (d, *J* = 2.6 Hz), 140.3, 134.8 (d, *J* = 6.0 Hz), 134.3 (d, *J* = 1.4 Hz), 129.4 (d, *J* = 1.5 Hz), 129.36, 128.6, 128.4, 127.7 (d, *J* = 1.5 Hz), 127.2, 126.6 (d, *J* = 3.2 Hz), 123.0 (d, *J* = 8.8 Hz), 62.2 (d, *J* = 6.8 Hz), 30.2 (d, *J* = 139.1 Hz), 18.8, 16.5 (d, *J* = 6.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₅NO₃P⁺ 370.1567; Found: 370.1571.

diethyl ((5-methoxy-2-phenylquinolin-3-yl)methyl)phosphonate (3w)



Following procedure A: T₁ = 80 °C, 24.5 mg, yellow oil, 63% yield.

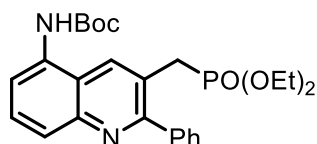
¹H NMR (400 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 3.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.63 – 7.54 (m, 1H), 7.53 – 7.44 (m, 2H), 7.47 – 7.39 (m, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.01 (s, 3H), 4.01 – 3.91 (m, 4H), 3.38 (d, *J* = 22.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.5 (d, *J* = 7.2 Hz), 155.0, 147.7 (d, *J* = 2.6 Hz), 140.3, 133.1 (d, *J* = 5.8 Hz), 129.7 (d, *J* = 1.5 Hz), 129.4, 128.5, 128.4, 122.6 (d, *J* = 8.9 Hz), 121.5 (d, *J* = 1.5 Hz), 119.8 (d, *J* = 3.2 Hz), 104.3, 62.3 (d, *J* = 6.8 Hz), 55.9, 30.1 (d, *J* = 139.1 Hz), 16.4 (d, *J* = 6.3 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₅NO₄P⁺ 386.1516; Found: 386.1515.

***tert*-butyl (3-((diethoxyphosphoryl)methyl)-2-phenylquinolin-5-yl)carbamate (3x)**



Following procedure A: T₁ = 80 °C, 27.6 mg, white solid, 58% yield. M.p = 186 – 187 °C.

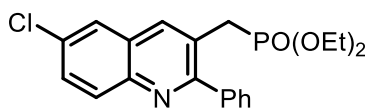
¹H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 3.4 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.37 (m, 4H), 4.03 – 3.89 (m, 4H), 3.39 (d, *J* = 22.3 Hz, 2H), 1.56 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.1 (d, *J* = 7.3 Hz), 153.6, 147.3 (d, *J* = 2.5 Hz), 140.0, 133.0, 131.7 (d, *J* = 5.9 Hz), 129.8, 129.3, 128.6, 125.6, 123.0 (d, *J* = 8.8 Hz), 120.8, 119.2, 81.0, 62.4 (d, *J* = 6.8 Hz), 30.0 (d, *J* = 139.1 Hz), 28.5, 16.4 (d, *J* = 6.2 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₅H₃₂N₂O₅P⁺ 471.2043; Found: 471.2051.

diethyl ((6-chloro-2-phenylquinolin-3-yl)methyl)phosphonate (3y)



Following procedure A: $T_1 = 80\text{ }^\circ\text{C}$, 29 mg, yellow oil, 74% yield.

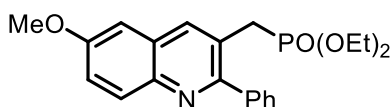
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.31 (d, $J = 3.4$ Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 1H), 7.82 (d, $J = 2.3$ Hz, 1H), 7.66 – 7.57 (m, 3H), 7.54 – 7.40 (m, 3H), 4.01 – 3.91 (m, 4H), 3.36 (d, $J = 22.3$ Hz, 2H), 1.21 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 160.6 (d, $J = 7.3$ Hz), 145.2 (d, $J = 2.3$ Hz), 139.9, 137.1 (d, $J = 6.1$ Hz), 132.5 (d, $J = 1.4$ Hz), 131.1 (d, $J = 1.5$ Hz), 130.7 (d, $J = 1.5$ Hz), 129.3, 128.7, 128.6, 127.8 (d, $J = 3.1$ Hz), 126.0 (d, $J = 1.4$ Hz), 124.8 (d, $J = 8.7$ Hz), 62.4 (d, $J = 6.8$ Hz), 30.0 (d, $J = 139.1$ Hz), 16.5 (d, $J = 6.1$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{ClNO}_3\text{P}^+$ 390.1020; Found: 390.1019.

diethyl ((6-methoxy-2-phenylquinolin-3-yl)methyl)phosphonate (3z)



Following procedure A: $T_1 = 80\text{ }^\circ\text{C}$, 24.1 mg, white solid, 62% yield. M.p = 72 – 73 $^\circ\text{C}$.

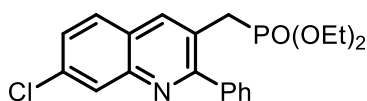
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.31 (d, $J = 3.4$ Hz, 1H), 8.00 (d, $J = 9.2$ Hz, 1H), 7.60 (d, $J = 7.4$ Hz, 2H), 7.48 (t, $J = 7.4$ Hz, 2H), 7.46 – 7.38 (m, 1H), 7.34 (dd, $J = 9.3$, 2.8 Hz, 1H), 7.09 (d, $J = 2.8$ Hz, 1H), 4.01 – 3.93 (m, 4H), 3.93 (s, 3H), δ 3.34 (d, $J = 22.2$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 158.1, 157.8 (d, $J = 7.5$ Hz), 143.1 (d, $J = 2.5$ Hz), 140.3, 136.8 (d, $J = 5.9$ Hz), 130.8 (d, $J = 1.5$ Hz), 129.4, 128.5, 128.3, 128.2, 123.7 (d, $J = 8.5$ Hz), 122.6 (d, $J = 1.5$ Hz), 104.6, 62.3 (d, $J = 6.8$ Hz), 55.7, 29.9 (d, $J = 139.0$ Hz), 16.5 (d, $J = 5.9$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 26.1.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_4\text{P}^+$ 386.1516; Found: 386.1518.

diethyl ((7-chloro-2-phenylquinolin-3-yl)methyl)phosphonate (3aa)



Following procedure A: $T_1 = 80\text{ }^\circ\text{C}$, 25.8 mg, yellow oil, 66% yield.

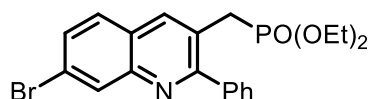
¹H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 3.4 Hz, 1H), 8.11 (d, *J* = 2.1 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.54 – 7.41 (m, 4H), 4.02 – 3.93 (m, 4H), 3.35 (d, *J* = 22.2 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.3 (d, *J* = 7.3 Hz), 147.2 (d, *J* = 2.5 Hz), 139.9, 137.9 (d, *J* = 6.1 Hz), 135.5 (d, *J* = 1.8 Hz), 129.3, 128.7, 128.65, 128.6, 128.4 (d, *J* = 1.5 Hz), 127.9, 125.6 (d, *J* = 3.2 Hz), 123.9 (d, *J* = 8.6 Hz), 62.4 (d, *J* = 6.8 Hz), 29.9 (d, *J* = 139.2 Hz), 16.5 (d, *J* = 6.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.6.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂ClNO₃P⁺ 390.1020; Found: 390.1030.

diethyl ((7-bromo-2-phenylquinolin-3-yl)methyl)phosphonate (3ab)



Following procedure A: T₁ = 80 °C, 30.9 mg, yellow oil, 71% yield.

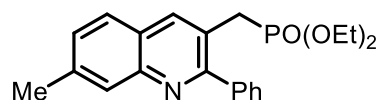
¹H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 3.4 Hz, 1H), 8.31 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.54 – 7.41 (m, 3H), 4.06 – 3.88 (m, 4H), 3.35 (d, *J* = 22.3 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.3 (d, *J* = 7.3 Hz), 147.4 (d, *J* = 2.5 Hz), 139.8, 138.0 (d, *J* = 6.0 Hz), 131.7 (d, *J* = 1.5 Hz), 130.4, 129.3, 128.7, 128.68 (d, *J* = 1.3 Hz), 128.6, 125.8 (d, *J* = 3.2 Hz), 124.1 (d, *J* = 8.5 Hz), 123.7 (d, *J* = 1.9 Hz), 62.4 (d, *J* = 6.8 Hz), 30.0 (d, *J* = 139.2 Hz), 16.5 (d, *J* = 5.9 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.5.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂BrNO₃P⁺ 434.0515; Found: 434.0521.

diethyl ((7-methyl-2-phenylquinolin-3-yl)methyl)phosphonate (3ac)



Following procedure A: T₁ = 80 °C, 27.8 mg, yellow oil, 75% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 3.4 Hz, 1H), 7.90 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.53 – 7.34 (m, 4H), 4.05 – 3.87 (m, 4H), 3.35 (d,

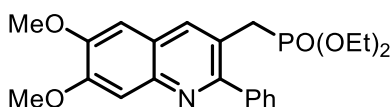
$J = 22.1$ Hz, 2H), 2.55 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2 (d, $J = 7.3$ Hz), 147.1 (d, $J = 2.4$ Hz), 140.4, 140.0 (d, $J = 1.5$ Hz), 137.8 (d, $J = 5.9$ Hz), 129.3, 129.1, 128.5, 128.4, 128.35, 127.0 (d, $J = 1.4$ Hz), 125.3 (d, $J = 3.2$ Hz), 122.5 (d, $J = 8.7$ Hz), 62.2 (d, $J = 6.7$ Hz), 29.9 (d, $J = 139.3$ Hz), 22.0, 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.1.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_3\text{P}^+$ 370.1567; Found: 370.1562.

diethyl ((6,7-dimethoxy-2-phenylquinolin-3-yl)methyl)phosphonate (3ad)



Following procedure A: $T_1 = 80$ °C, 22.7 mg, yellow oil, 54% yield.

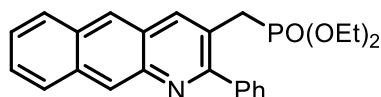
^1H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, $J = 3.2$ Hz, 1H), 7.63 – 7.55 (m, 2H), 7.52 – 7.37 (m, 4H), 7.08 (s, 1H), 4.03 (s, 3H), 4.00 (s, 3H), 4.00 – 3.90 (m, 4H), 3.32 (d, $J = 22.0$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.0 (d, $J = 7.8$ Hz), 152.8, 150.2, 144.0 (d, $J = 2.4$ Hz), 140.6, 136.3 (d, $J = 5.7$ Hz), 129.4, 128.5, 128.2, 123.0 (d, $J = 3.1$ Hz), 121.4 (d, $J = 8.4$ Hz), 108.0, 104.7, 62.3 (d, $J = 6.8$ Hz), 56.3, 56.2, 29.8 (d, $J = 139.3$ Hz), 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.4.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_5\text{P}^+$ 416.1621; Found: 416.1627.

diethyl ((2-phenylbenzo[*g*]quinolin-3-yl)methyl)phosphonate (3ae)



Following procedure A: $T_1 = 80$ °C, 20.6 mg, yellow oil, 50% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.56 (d, $J = 3.9$ Hz, 1H), 8.42 (s, 1H), 8.10 – 8.00 (m, 2H), 7.72 – 7.64 (m, 2H), 7.60 – 7.34 (m, 5H), 4.05 – 3.89 (m, 4H), 3.42 (d, $J = 22.4$ Hz, 2H), 1.21 (t, $J = 7.1$ Hz, 6H).

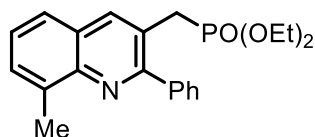
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4 (d, $J = 7.2$ Hz), 143.4 (d, $J = 2.3$ Hz),

140.3, 138.2 (d, $J = 7.0$ Hz), 134.2 (d, $J = 1.7$ Hz), 132.1 (d, $J = 1.4$ Hz), 129.3, 128.7, 128.65, 128.62, 128.3, 127.4 (d, $J = 1.5$ Hz), 126.3, 126.2, 126.18, 125.7 (d, $J = 3.4$ Hz), 123.2 (d, $J = 9.1$ Hz), 62.4 (d, $J = 6.8$ Hz), 30.1 (d, $J = 139.4$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{P}^+$ 406.1567; Found: 406.1566.

diethyl ((8-methyl-2-phenylquinolin-3-yl)methyl)phosphonate (3af)



Following procedure A: $T_1 = 80$ °C, 20.5 mg, yellow oil, 55% yield.

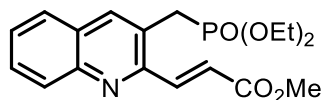
^1H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, $J = 3.4$ Hz, 1H), 7.75 – 7.64 (m, 3H), 7.58 – 7.39 (m, 5H), 4.06 – 3.95 (m, 2H), 3.99 – 3.88 (m, 2H), 3.42 (d, $J = 22.2$ Hz, 2H), 2.79 (s, 3H), 1.21 (t, $J = 7.0$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.7 (d, $J = 7.3$ Hz), 146.1 (d, $J = 2.4$ Hz), 140.8, 138.3 (d, $J = 6.0$ Hz), 137.5 (d, $J = 1.5$ Hz), 129.8, 129.6 (d, $J = 1.5$ Hz), 128.4, 128.3, 127.1 (d, $J = 3.1$ Hz), 126.6, 125.3 (d, $J = 1.4$ Hz), 123.0 (d, $J = 8.6$ Hz), 62.3 (d, $J = 6.7$ Hz), 30.0 (d, $J = 139.0$ Hz), 18.0, 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.1.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_3\text{P}^+$ 370.1567; Found: 370.1567.

methyl (*E*)-3-(3-((diethoxyphosphoryl)methyl)quinolin-2-yl)acrylate (3ag)



Following procedure A: $T_1 = 80$ °C, 18.2 mg, white solid, 44% yield. M.p = 68 – 70 °C.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.10 (m, 2H), 8.06 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.69 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.53 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.27 (d, $J = 15.1$ Hz, 1H), 4.05 – 4.02 (m, 4H), 3.85 (s, 3H), 3.45 (d, $J = 21.9$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 6H).

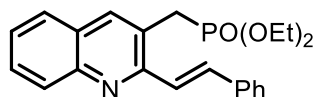
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 151.7 (d, $J = 5.3$ Hz), 147.3 (d, $J = 2.7$

Hz), 140.3, 138.6 (d, $J = 6.8$ Hz), 130.0 (d, $J = 1.6$ Hz), 129.8 (d, $J = 1.6$ Hz), 128.3 (d, $J = 3.2$ Hz), 127.6, 127.3, 124.9 (d, $J = 9.6$ Hz), 124.86, 62.6 (d, $J = 6.9$ Hz), 52.0, 30.4 (d, $J = 139.8$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.3.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_5\text{P}^+$ 364.1308, Found: 364.1308.

diethyl (*E*)-((2-styrylquinolin-3-yl)methyl)phosphonate (3ah)



Following procedure A: $T_1 = 80$ °C, 12.5 mg, yellow oil, 32% yield.

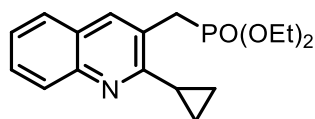
^1H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.06 (m, 2H), 8.00 (d, $J = 15.5$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.70 – 7.61 (m, 4H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.40 (dd, $J = 8.3$, 6.7 Hz, 2H), 7.33 (dd, $J = 8.3$, 6.2 Hz, 1H), 4.09 – 4.02 (m, 4H), 3.49 (d, $J = 21.8$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.5 (d, $J = 5.0$ Hz), 147.4 (d, $J = 2.6$ Hz), 138.3 (d, $J = 7.0$ Hz), 137.1, 136.2, 129.7 (d, $J = 1.7$ Hz), 129.2 (d, $J = 1.6$ Hz), 128.9, 128.7, 127.6, 127.5 (d, $J = 3.4$ Hz), 127.3, 126.4, 124.5, 123.9 (d, $J = 9.7$ Hz), 62.6 (d, $J = 6.9$ Hz), 30.8 (d, $J = 139.6$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_3\text{P}^+$ 382.1567, Found: 382.1570.

diethyl ((2-cyclopropylquinolin-3-yl)methyl)phosphonate (3ai)



Following procedure A: $T_1 = 80$ °C, MeOH (0.5 mL) and CH_3COOH (6.0 mg, 0.1 mmol) were added, 7.9 mg, yellow oil, 24% yield.

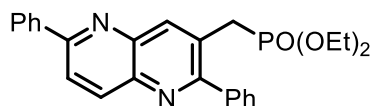
^1H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, $J = 3.7$ Hz, 1H), 7.92 (d, $J = 8.5$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.60 (dd, $J = 8.4$, 6.8 Hz, 1H), 7.42 (t, $J = 7.3$ Hz, 1H), 4.15 – 3.97 (m, 4H), 3.52 (d, $J = 21.9$ Hz, 2H), 2.46 – 2.39 (m, 1H), 1.25 (t, $J = 7.0$ Hz, 8H), 1.08 – 1.03 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.4 (d, *J* = 5.3 Hz), 147.0, 137.0 (d, *J* = 6.9 Hz), 129.1, 128.7, 127.2 (d, *J* = 1.5 Hz), 126.7 (d, *J* = 3.3 Hz), 125.7, 124.6 (d, *J* = 9.7 Hz), 62.5 (d, *J* = 6.9 Hz), 30.3 (d, *J* = 139.9 Hz), 16.6 (d, *J* = 6.1 Hz), 15.0, 9.5.

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.8.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₇H₂₃NO₃P⁺ 320.1410, Found: 320.1421.

diethyl ((2,6-diphenyl-1,5-naphthyridin-3-yl)methyl)phosphonate (3aj)



Following procedure A: T₁ = 80 °C, 28.5 mg, yellow solid, 65% yield. M.p = 124 – 126 °C.

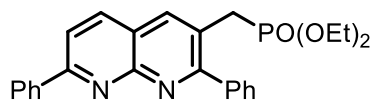
¹H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 3.4 Hz, 1H), 8.46 (d, *J* = 8.9, 1H), 8.21 – 8.17 (m, 2H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.57 – 7.45 (m, 6H), 4.09 – 3.95 (m, 4H), 3.44 (d, *J* = 22.4 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.8 (d, *J* = 6.9 Hz), 158.3, 142.7 (d, *J* = 3.3 Hz), 141.6 (d, *J* = 2.5 Hz), 139.8, 139.3 (d, *J* = 5.9 Hz), 139.1, 137.8, 129.9, 129.4, 129.1, 128.8, 128.7, 127.9 (d, *J* = 9.0 Hz), 127.8, 122.6, 62.4 (d, *J* = 6.6 Hz), 30.5 (d, *J* = 138.7 Hz), 16.5 (d, *J* = 5.9 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₅H₂₆N₂O₃P⁺ 433.1676, Found: 433.1675.

diethyl ((2,7-diphenyl-1,8-naphthyridin-3-yl)methyl)phosphonate (3ak)



Following procedure A: T₁ = 80 °C, 18.6 mg, yellow solid, 43% yield. M.p = 92 – 94 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 3.4 Hz, 1H), 8.35 – 8.25 (m, 3H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.71 – 7.43 (m, 6H), 4.04 – 3.88 (m, 4H), 3.43 (d, *J* = 22.3 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 6H).

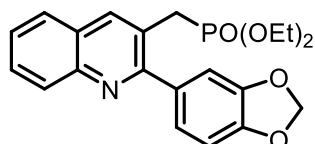
¹³C NMR (101 MHz, Chloroform-*d*) δ 163.9 (d, *J* = 7.5 Hz), 160.8 (d, *J* = 1.4 Hz),

154.8 (d, $J = 2.6$ Hz), 139.7, 138.8 (d, $J = 5.9$ Hz), 138.7, 137.4, 130.2, 129.5, 128.9, 128.7, 128.4, 128.1, 124.6 (d, $J = 8.5$ Hz), 120.6 (d, $J = 3.2$ Hz), 120.1, 62.4 (d, $J = 6.9$ Hz), 29.9 (d, $J = 139.1$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.6.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_3\text{P}^+$ 433.1676, Found: 433.1682.

diethyl ((2-(benzo[*d*][1,3]dioxol-5-yl)quinolin-3-yl)methyl)phosphonate (3al)



Following procedure A: $T_1 = 80$ °C, 29.2 mg, yellow oil, 73% yield.

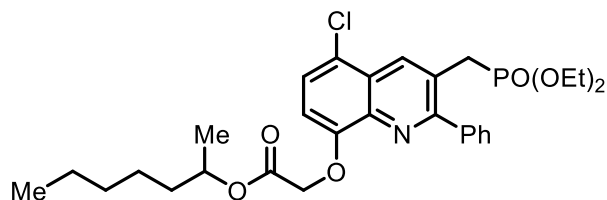
^1H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, $J = 3.5$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.69 (t, $J = 7.7$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.12 (d, $J = 9.5$ Hz, 2H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.02 (s, 2H), 4.04 – 3.97 (m, 4H), 3.39 (d, $J = 22.2$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8 (d, $J = 7.4$ Hz), 147.9, 147.8, 146.8 (d, $J = 2.5$ Hz), 138.1 (d, $J = 5.9$ Hz), 134.2, 129.7, 129.3, 127.4, 127.2 (d, $J = 3.2$ Hz), 126.8, 123.5 (d, $J = 8.4$ Hz), 123.3, 110.1, 108.4, 101.3, 62.3 (d, $J = 6.8$ Hz), 30.0 (d, $J = 139.3$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_5\text{P}^+$ 400.1308; Found: 400.1308.

heptan-2-yl 2-((5-chloro-3-((diethoxyphosphoryl)methyl)-2-phenylquinolin-8-yl)oxy)acetate (3am)



Following procedure A: $T_1 = 120$ °C, 19.2 mg, yellow oil, 34% yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, $J = 3.5$ Hz, 1H), 7.73 – 7.65 (m, 2H), 7.52 – 7.41 (m, 4H), 6.90 (d, $J = 8.4$ Hz, 1H), 5.02 – 4.96 (m, 1H), 4.93 (s, 2H), 4.07 –

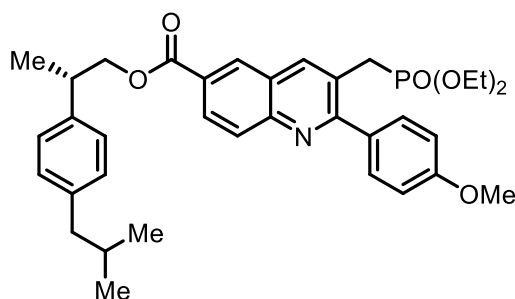
3.96 (m, 4H), 3.44 (d, $J = 22.3$ Hz, 2H), 1.61 – 1.40 (m, 2H), 1.27 – 1.18 (m, 15H), 0.87 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 168.6, 159.9 (d, $J = 7.0$ Hz), 153.2, 139.8, 139.5 (d, $J = 2.8$ Hz), 135.3 (d, $J = 6.0$ Hz), 129.8, 128.7, 128.5, 126.3, 126.2, 125.6 (d, $J = 9.1$ Hz), 123.3, 110.8, 72.7, 67.0, 62.4 (d, $J = 6.8$ Hz), 35.8, 31.7, 30.3 (d, $J = 138.8$ Hz), 25.1, 22.6, 20.0, 16.5 (d, $J = 6.2$ Hz), 14.1.

^{31}P NMR (162 MHz, Chloroform- d) δ 25.1.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{38}\text{ClNO}_6\text{P}^+$ 562.2120, Found: 562.2123.

(*R*)-2-(4-isobutylphenyl)propyl 3-((diethoxyphosphoryl)methyl)-2-(4-methoxyphenyl)quinoline-6-carboxylate (3an)



Following procedure A: $T_1 = 80$ °C, 28.4 mg, yellow oil, 47% yield.

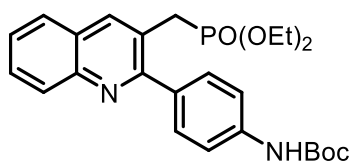
^1H NMR (400 MHz, Chloroform- d) δ 8.54 (d, $J = 1.9$ Hz, 1H), 8.45 (d, $J = 3.4$ Hz, 1H), 8.25 – 8.16 (m, 1H), 8.11 (d, $J = 8.9$ Hz, 1H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 7.7$ Hz, 2H), 7.12 (d, $J = 7.7$ Hz, 2H), 7.04 (d, $J = 8.3$ Hz, 2H), 4.54 – 4.37 (m, 2H), 4.51 – 4.40 (m, 4H), 3.88 (s, 3H), 3.42 (d, $J = 22.3$ Hz, 2H), 3.31 – 3.25 (m, 1H), 2.45 (d, $J = 7.2$ Hz, 2H), 1.92 – 1.78 (m, 1H), 1.43 (d, $J = 7.0$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 6H), 0.89 (d, $J = 6.6$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 166.2, 162.2 (d, $J = 7.1$ Hz), 160.2, 148.7 (d, $J = 2.5$ Hz), 140.3, 140.27, 139.3 (d, $J = 6.1$ Hz), 132.3, 130.8, 130.5, 129.6, 129.4, 129.1, 128.3, 127.2, 126.2 (d, $J = 3.2$ Hz), 124.7 (d, $J = 8.6$ Hz), 114.1, 70.5, 62.4 (d, $J = 6.8$ Hz), 55.5, 45.1, 38.8, 30.3, 30.1 (d, $J = 139.1$ Hz), 22.5, 22.49, 18.2, 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform- d) δ 25.7.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{43}\text{NO}_6\text{P}^+$ 604.2823, Found: 604.2825.

diethyl ((2-(p-tolyl)quinolin-3-yl)methyl)phosphonate (3ao)



Following procedure A: $T_1 = 80\text{ }^\circ\text{C}$, 35.2 mg, yellow solid, 74% yield. M.p = 193 – 195 $^\circ\text{C}$.

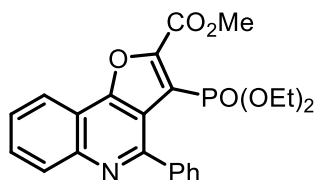
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.41 (d, $J = 3.4$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.68 (t, $J = 7.7$ Hz, 1H), 7.59 (d, $J = 8.5$ Hz, 2H), 7.55 – 7.46 (m, 3H), 6.86 (s, 1H), 4.03 – 3.93 (m, 4H), 3.37 (d, $J = 22.2$ Hz, 2H), 1.52 (s, 9H), 1.21 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 159.9 (d, $J = 7.5$ Hz), 152.8, 146.9, 138.8, 138.2 (d, $J = 6.1$ Hz), 134.7, 130.2, 129.7, 129.3, 127.4, 127.2 (d, $J = 3.2$ Hz), 126.7, 123.6 (d, $J = 8.3$ Hz), 118.3, 80.8, 62.3 (d, $J = 6.8$ Hz), 29.9 (d, $J = 139.3$ Hz), 28.5, 16.5 (d, $J = 5.9$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 26.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_5\text{P}^+$ 471.2043; Found: 471.2045.

methyl 3-(diethoxyphosphoryl)-4-phenylfuro[3,2-*c*]quinoline-2-carboxylate (3ap)



Following procedure B, 14.2 mg, white solid, 32% yield. M.p = 104 – 106 $^\circ\text{C}$.

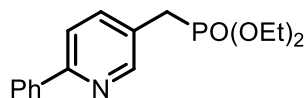
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.39 (d, $J = 8.1$ Hz, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 7.85 – 7.78 (m, 3H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.56 – 7.45 (m, 3H), 4.08 (s, 3H), 3.94 – 3.78 (m, 4H), 1.14 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 159.7, 156.8 (d, $J = 13.8$ Hz), 156.6, 152.0 (d, $J = 22.6$ Hz), 146.2, 140.7, 130.3, 129.8, 129.4, 129.2, 128.3, 127.5, 120.5, 118.2 (d, $J = 9.9$ Hz), 115.4, 113.8 (d, $J = 211.4$ Hz), 62.7 (d, $J = 6.0$ Hz), 53.5, 16.2 (d, $J = 6.8$ Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 8.0.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₃H₂₃NO₆P⁺ 440.1258, Found: 440.1267.

diethyl ((6-phenylpyridin-3-yl)methyl)phosphonate (5a)



Following procedure C: T₂ = 100 °C, 19.6 mg, white solid, 64% yield.

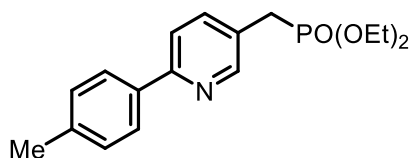
¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 – 8.54 (m, 1H), 8.02 – 7.94 (m, 2H), 7.77 – 7.67 (m, 2H), 7.50 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 4.10 – 4.03 (m, 4H), 3.17 (d, *J* = 21.6 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.2 (d, *J* = 3.9 Hz), 150.5 (d, *J* = 7.6 Hz), 139.1 (d, *J* = 1.5 Hz), 138.1 (d, *J* = 5.7 Hz), 129.1, 128.9, 126.9, 126.3 (d, *J* = 9.3 Hz), 120.4 (d, *J* = 3.1 Hz), 62.5 (d, *J* = 6.7 Hz), 30.9 (d, *J* = 140.0 Hz), 16.5 (d, *J* = 5.9 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₂₁NO₃P⁺ 306.1254, Found: 306.1248.

diethyl ((6-(*p*-tolyl)pyridin-3-yl)methyl)phosphonate (5b)



Following procedure C: T₂ = 100 °C, 17.9 mg, yellow oil, 56% yield.

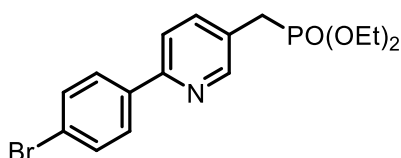
¹H NMR (400 MHz, Chloroform-*d*) δ 8.56 – 8.52 (m, 1H), 7.91 – 7.84 (m, 2H), 7.72 (dt, *J* = 8.3, 2.4 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.10 – 4.02 (m, 4H), 3.15 (d, *J* = 21.5 Hz, 2H), 2.40 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.2 (d, *J* = 3.8 Hz), 150.4 (d, *J* = 7.6 Hz), 139.1, 138.0 (d, *J* = 5.7 Hz), 136.3 (d, *J* = 1.5 Hz), 129.6, 126.8, 126.0 (d, *J* = 9.3 Hz), 120.1 (d, *J* = 3.1 Hz), 62.5 (d, *J* = 6.7 Hz), 30.8 (d, *J* = 140.0 Hz), 21.4, 16.5 (d, *J* = 6.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.3.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₇H₂₃NO₃P⁺ 320.1410, Found: 320.1411.

diethyl ((6-(4-bromophenyl)pyridin-3-yl)methyl)phosphonate (5c)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 25.3 mg, yellow oil, 65% yield.

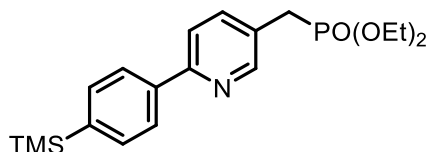
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.55 (t, $J = 2.5$ Hz, 1H), 7.88 – 7.83 (m, 2H), 7.74 (dt, $J = 8.3, 2.4$ Hz, 1H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.60 – 7.56 (m, 2H), 4.12 – 4.00 (m, 4H), 3.16 (d, $J = 21.6$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 155.0 (d, $J = 3.9$ Hz), 150.6 (d, $J = 7.4$ Hz), 138.2 (d, $J = 5.7$ Hz), 138.0 (d, $J = 1.7$ Hz), 132.0, 128.5, 126.8 (d, $J = 9.2$ Hz), 123.5, 120.1 (d, $J = 3.0$ Hz), 62.5 (d, $J = 6.8$ Hz), 30.9 (d, $J = 139.9$ Hz), 16.5 (d, $J = 5.9$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{20}\text{BrNO}_3\text{P}^+$ 384.0359, Found: 384.0360.

diethyl ((6-(4-silylphenyl)pyridin-3-yl)methyl)phosphonate (5d)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 21.4 mg, white solid, 56% yield. M.p = 62 – 64 $^\circ\text{C}$.

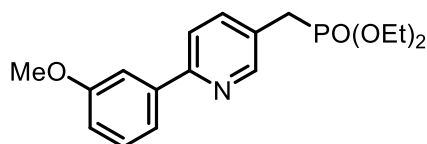
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.57 (t, $J = 2.5$ Hz, 1H), 7.99 – 7.93 (m, 2H), 7.74 (dt, $J = 8.2, 2.3$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.64 – 7.60 (m, 2H), 4.10 – 4.03 (m, 4H), 3.16 (d, $J = 21.6$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H), 0.29 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 156.2 (d, $J = 3.8$ Hz), 150.5 (d, $J = 7.5$ Hz), 141.6, 139.3 (d, $J = 1.5$ Hz), 138.0 (d, $J = 5.7$ Hz), 133.9, 126.4 (d, $J = 9.1$ Hz), 126.1, 120.4 (d, $J = 3.1$ Hz), 62.5 (d, $J = 6.8$ Hz), 30.9 (d, $J = 140.0$ Hz), 16.5 (d, $J = 6.0$ Hz), -1.0.

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_3\text{PSi}^+$ 378.1649, Found: 378.1654.

diethyl ((6-(3-methoxyphenyl)pyridin-3-yl)methyl)phosphonate (5e)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 20.6 mg, yellow oil, 61% yield.

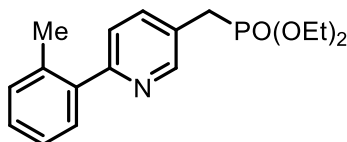
^1H NMR (400 MHz, Chloroform-*d*) δ 8.56 (t, $J = 2.5$ Hz, 1H), 7.74 (dt, $J = 8.3, 2.4$ Hz, 1H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.56 (t, $J = 2.1$ Hz, 1H), 7.52 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 1H), 6.98 – 6.93 (m, 1H), 4.10 – 4.02 (m, 4H), 3.88 (s, 3H), 3.16 (d, $J = 21.6$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 156.0 (d, $J = 3.9$ Hz), 150.4 (d, $J = 7.5$ Hz), 140.6 (d, $J = 1.5$ Hz), 138.0 (d, $J = 5.7$ Hz), 129.9, 126.5 (d, $J = 9.2$ Hz), 120.5 (d, $J = 3.0$ Hz), 119.3, 115.2, 112.0, 62.5 (d, $J = 6.8$ Hz), 55.5, 30.9 (d, $J = 140.0$ Hz), 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{P}^+$ 336.1359, Found: 336.1360.

diethyl ((6-(*o*-tolyl)pyridin-3-yl)methyl)phosphonate (5f)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 15.1 mg, yellow oil, 47% yield.

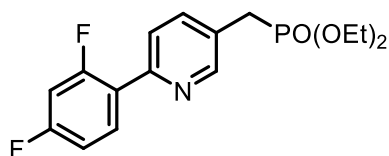
^1H NMR (400 MHz, Chloroform-*d*) δ 8.57 (t, $J = 2.5$ Hz, 1H), 7.74 (dt, $J = 8.1, 2.4$ Hz, 1H), 7.38 (td, $J = 7.0, 6.2, 1.7$ Hz, 2H), 7.30 – 7.25 (m, 3H), 4.12 – 4.04 (m, 4H), 3.18 (d, $J = 21.6$ Hz, 2H), 2.35 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.7 (d, $J = 3.8$ Hz), 150.0 (d, $J = 7.5$ Hz), 140.1, 137.5 (d, $J = 5.6$ Hz), 135.9, 130.9, 129.7, 128.4, 126.0, 125.8 (d, $J = 9.1$ Hz), 123.9 (d, $J = 3.0$ Hz), 62.5 (d, $J = 6.7$ Hz), 30.9 (d, $J = 140.0$ Hz), 20.4, 16.5 (d, $J = 6.0$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.3.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{P}^+$ 320.1410, Found: 320.1410.

diethyl ((6-(2,4-difluorophenyl)pyridin-3-yl)methyl)phosphonate (5g)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 17.2 mg, yellow oil, 50% yield.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.58 (d, $J = 2.4$ Hz, 1H), 8.02 – 7.96 (m, 1H), 7.77 – 7.67 (m, 2H), 6.99 (td, $J = 8.2, 2.4$ Hz, 1H), 6.90 (ddd, $J = 11.3, 8.8, 2.5$ Hz, 1H), 4.12 – 4.03 (m, 4H), 3.17 (d, $J = 21.6$ Hz, 2H), 1.28 (t, $J = 7.0$ Hz, 6H).

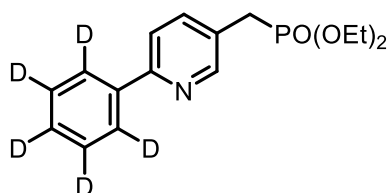
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 163.4 (dd, $J = 251.9, 12.2$ Hz), 160.8 (dd, $J = 252.7, 11.3$ Hz), 151.2 (t, $J = 2.8$ Hz), 150.6 (d, $J = 7.3$ Hz), 137.8 (d, $J = 5.8$ Hz), 132.1 (dd, $J = 9.5, 4.5$ Hz), 126.8 (d, $J = 9.2$ Hz), 124.0 (dd, $J = 9.6, 3.0$ Hz), 123.6 – 123.3 (m), 112.0 (dd, $J = 21.1, 3.6$ Hz), 104.5 (t, $J = 26.3$ Hz), 62.5 (d, $J = 6.8$ Hz), 30.9 (d, $J = 140.0$ Hz), 16.5 (d, $J = 5.9$ Hz).

$^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -109.2 (d, $J = 8.4$ Hz, 1F), -112.7 (d, $J = 8.5$ Hz, 1F).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{19}\text{F}_2\text{NO}_3\text{P}^+$ 342.1065, Found: 342.1069.

diethyl ((6-(phenyl-*d*5)pyridin-3-yl)methyl)phosphonate (5h)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 16.4 mg, yellow oil, 52% yield.

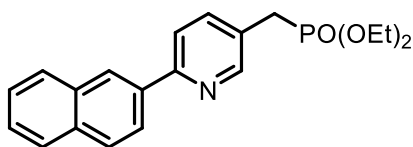
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.57 (t, $J = 2.5$ Hz, 1H), 7.75 (dt, $J = 8.2, 2.4$ Hz, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), 4.13 – 4.00 (m, 4H), 3.17 (d, $J = 21.6$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 156.2 (d, $J = 3.8$ Hz), 150.5 (d, $J = 7.5$ Hz), 138.9, 138.1 (d, $J = 5.7$ Hz), 128.6, 128.3, 126.8, 126.3 (d, $J = 9.2$ Hz), 120.4 (d, $J = 3.0$ Hz), 62.5 (d, $J = 6.7$ Hz), 30.9 (d, $J = 140.0$ Hz), 16.5 (d, $J = 6.0$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}D_5NO_3P^+$ 311.1567, Found: 311.1570.

diethyl ((6-(naphthalen-2-yl)pyridin-3-yl)methyl)phosphonate (5i)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 22.2 mg, white solid, 62% yield. M.p = 71 – 73 $^\circ\text{C}$.

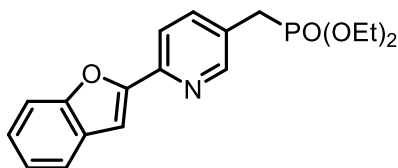
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.62 (d, $J = 2.5$ Hz, 1H), 8.47 (d, $J = 1.8$ Hz, 1H), 8.12 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.94 (d, $J = 6.8$, 2H), 7.88 – 7.83 (m, 2H), 7.79 (dt, $J = 8.2, 2.4$ Hz, 1H), 7.52 – 7.48 (m, 2H), 4.15 – 4.03 (m, 4H), 3.19 (d, $J = 21.6$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 156.0 (d, $J = 3.9$ Hz), 150.6 (d, $J = 7.5$ Hz), 138.1 (d, $J = 5.8$ Hz), 136.3 (d, $J = 1.6$ Hz), 133.7, 133.6, 128.8, 128.6, 127.8, 126.7, 126.44, 126.4 (d, $J = 9.2$ Hz), 126.3, 124.6, 120.6 (d, $J = 3.1$ Hz), 62.5 (d, $J = 6.7$ Hz), 30.9 (d, $J = 140.0$ Hz), 16.5 (d, $J = 6.0$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}NO_3P^+$ 356.1410, Found: 356.1412.

diethyl ((6-(benzofuran-2-yl)pyridin-3-yl)methyl)phosphonate (5j)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 18.5 mg, yellow solid, 53% yield. M.p = 50 – 52 $^\circ\text{C}$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.55 (d, $J = 2.5$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.77 (dt, $J = 8.2, 2.5$ Hz, 1H), 7.63 (d, $J = 7.7$ Hz, 1H), 7.56 (d, $J = 8.2$ Hz, 1H), 7.40 (s, 1H), 7.35 – 7.30 (m, 1H), 7.27 – 7.22 (m, 1H), 4.13 – 3.99 (m, 4H), 3.17 (d, $J = 21.7$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H).

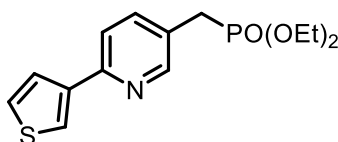
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 155.4, 154.9 (d, $J = 2.2$ Hz), 150.7 (d, $J = 7.5$ Hz), 148.0 (d, $J = 3.9$ Hz), 138.0 (d, $J = 5.9$ Hz), 128.9, 127.3 (d, $J = 9.3$ Hz), 125.3,

123.3, 121.8, 119.7 (d, $J = 3.1$ Hz), 111.6, 104.9, 62.5 (d, $J = 6.8$ Hz), 31.1 (d, $J = 139.9$ Hz), 16.5 (d, $J = 5.9$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.8.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_4\text{P}^+$ 346.1203, Found: 346.1207.

diethyl ((6-(thiophen-3-yl)pyridin-3-yl)methyl)phosphonate (5k)



Following procedure C: $T_2 = 100$ °C, 16.8 mg, yellow oil, 54% yield.

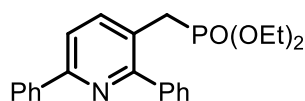
^1H NMR (400 MHz, Chloroform-*d*) δ 8.49 (t, $J = 2.6$ Hz, 1H), 7.87 (dd, $J = 3.2, 1.3$ Hz, 1H), 7.70 (dt, $J = 8.2, 2.4$ Hz, 1H), 7.64 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.58 (d, $J = 8.1$ Hz, 1H), 7.39 (dd, $J = 5.1, 3.0$ Hz, 1H), 4.09 – 4.02 (m, 4H), 3.14 (d, $J = 21.6$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.3 (d, $J = 3.9$ Hz), 150.4 (d, $J = 7.6$ Hz), 141.9 (d, $J = 1.6$ Hz), 138.0 (d, $J = 5.8$ Hz), 126.5, 126.3, 126.0 (d, $J = 9.4$ Hz), 123.6, 120.1 (d, $J = 3.2$ Hz), 62.5 (d, $J = 6.7$ Hz), 30.9 (d, $J = 140.1$ Hz), 16.5 (d, $J = 5.9$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{PS}^+$ 312.0818, Found: 312.0822.

diethyl ((2,6-diphenylpyridin-3-yl)methyl)phosphonate (5l)



Following procedure C: $T_2 = 120$ °C, 28.6 mg, colorless oil, 75% yield.

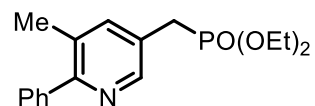
^1H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.04 (m, 2H), 7.99 (dd, $J = 8.2, 2.5$ Hz, 1H), 7.73 – 7.65 (m, 3H), 7.52 – 7.36 (m, 6H), 4.07 – 3.94 (m, 4H), 3.29 (d, $J = 22.2$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0 (d, $J = 8.5$ Hz), 155.5 (d, $J = 3.6$ Hz), 140.3, 139.5 (d, $J = 4.6$ Hz), 139.1 (d, $J = 1.5$ Hz), 129.6, 129.0, 128.8, 128.4, 128.3, 127.1, 123.8 (d, $J = 8.7$ Hz), 118.9 (d, $J = 3.2$ Hz), 62.3 (d, $J = 6.8$ Hz), 29.8 (d, $J = 138.9$ Hz), 16.5 (d, $J = 6.0$ Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 26.1.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₅NO₃P⁺ 382.1567, Found: 382.1571.

diethyl ((5-methyl-6-phenylpyridin-3-yl)methyl)phosphonate (5m)



Following procedure C: T₂ = 100 °C, 11.6 mg, yellow oil, 36% yield.

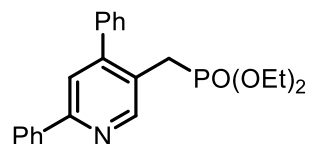
¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (t, *J* = 2.4 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 – 7.48 (m, 2H), 7.44 (ddt, *J* = 8.0, 6.3, 1.1 Hz, 2H), 7.41 – 7.35 (m, 1H), 4.13 – 4.05 (m, 4H), 3.14 (d, *J* = 21.5 Hz, 2H), 2.35 (d, *J* = 0.9 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.4 (d, *J* = 3.8 Hz), 147.7 (d, *J* = 7.3 Hz), 140.3, 139.9 (d, *J* = 5.8 Hz), 130.8 (d, *J* = 3.0 Hz), 129.1, 128.3, 128.1, 126.2 (d, *J* = 9.0 Hz), 62.5 (d, *J* = 6.8 Hz), 30.6 (d, *J* = 139.9 Hz), 20.1, 16.5 (d, *J* = 6.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.5.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₇H₂₃NO₃P⁺ 320.1410, Found: 320.1415.

diethyl ((4,6-diphenylpyridin-3-yl)methyl)phosphonate (5n)



Following procedure C: T₂ = 100 °C, 18.9 mg, colorless oil, 49% yield.

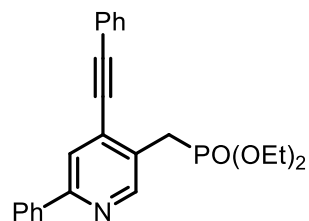
¹H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 2.6 Hz, 1H), 8.04 – 7.96 (m, 2H), 7.63 (s, 1H), 7.51 – 7.39 (m, 8H), 4.08 – 3.95 (m, 4H), 3.23 (d, *J* = 22.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.9 (d, *J* = 3.8 Hz), 151.6 (d, *J* = 5.0 Hz), 150.9 (d, *J* = 7.4 Hz), 139.0 (d, *J* = 1.6 Hz), 138.8, 129.1, 128.9, 128.7, 128.4, 127.0, 124.0 (d, *J* = 9.1 Hz), 121.8 (d, *J* = 2.9 Hz), 62.3 (d, *J* = 6.8 Hz), 27.9 (d, *J* = 139.8 Hz), 16.5 (d, *J* = 6.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.5.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₅NO₃P⁺ 382.1567, Found: 382.1560.

diethyl ((6-phenyl-4-(phenylethynyl)pyridin-3-yl)methyl)phosphonate (5o)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 18.1 mg, yellow oil, 44% yield.

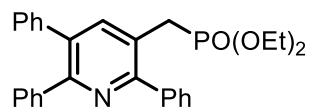
^1H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, $J = 2.7$ Hz, 1H), 8.03 – 7.98 (m, 2H), 7.84 (s, 1H), 7.63 – 7.57 (m, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.37 (m, 4H), 4.16 – 4.06 (m, 4H), 3.50 (d, $J = 22.0$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.9 (d, $J = 3.9$ Hz), 151.1 (d, $J = 5.5$ Hz), 138.6 (d, $J = 1.8$ Hz), 132.4 (d, $J = 7.0$ Hz), 132.0, 129.5, 129.3, 128.9, 128.7, 127.3 (d, $J = 9.9$ Hz), 127.0, 122.6 (d, $J = 3.1$ Hz), 122.2, 97.7, 85.8 (d, $J = 2.5$ Hz), 62.5 (d, $J = 6.7$ Hz), 29.5 (d, $J = 139.4$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{P}^+$ 406.1567, Found: 406.1573.

diethyl ((2,5,6-triphenylpyridin-3-yl)methyl)phosphonate (5p)



Following procedure C: $T_2 = 120\text{ }^\circ\text{C}$, 20.6 mg, white solid, 45% yield. M.p = 107 – 109 $^\circ\text{C}$.

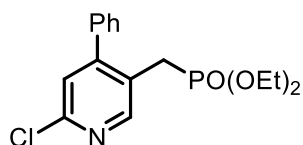
^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, $J = 2.6$ Hz, 1H), 7.74 – 7.69 (m, 2H), 7.48 (dd, $J = 8.2, 6.6$ Hz, 2H), 7.43 – 7.40 (m, 3H), 7.29 – 7.25 (m, 3H), 7.25 – 7.19 (m, 5H), 4.08 – 3.96 (m, 4H), 3.33 (d, $J = 22.1$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.7 (d, $J = 8.4$ Hz), 155.3 (d, $J = 3.6$ Hz), 141.4 (d, $J = 4.7$ Hz), 140.0, 139.92, 139.6, 134.5 (d, $J = 3.1$ Hz), 130.2, 129.7, 129.66, 128.44, 128.4, 128.3, 127.9, 127.87, 127.3, 123.8 (d, $J = 8.7$ Hz), 62.3 (d, $J = 6.7$ Hz), 29.7 (d, $J = 139.0$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{29}NO_3P^+$ 458.1880, Found: 458.1883.

diethyl ((6-chloro-4-phenylpyridin-3-yl)methyl)phosphonate (5q)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, MeOH (0.5 mL) and Et_3N (0.15 mmol) were added, 12.9 mg, yellow oil, 38% yield.

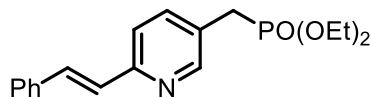
1H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, $J = 2.7$ Hz, 1H), 7.51 – 7.38 (m, 5H), 7.24 (s, 1H), 4.06 – 3.93 (m, 4H), 3.14 (d, $J = 22.1$ Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.1 (d, $J = 7.3$ Hz), 151.5 (d, $J = 5.1$ Hz), 150.0 (d, $J = 4.0$ Hz), 137.3, 128.87, 128.9, 125.0 (d, $J = 2.7$ Hz), 124.8 (d, $J = 8.8$ Hz), 62.4 (d, $J = 6.8$ Hz), 27.5 (d, $J = 140.2$ Hz), 16.5 (d, $J = 6.1$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}ClNO_3P^+$ 340.0864, Found: 340.0864.

diethyl (*E*-((6-styrylpyridin-3-yl)methyl)phosphonate (5r)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 8.2 mg, yellow oil, 24% yield.

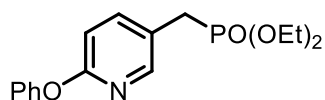
1H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, $J = 2.6$ Hz, 1H), 7.66 (dt, $J = 8.1, 2.5$ Hz, 1H), 7.62 (d, $J = 16.4$ Hz, 1H), 7.57 – 7.56 (m, 2H), 7.39 – 7.35 (m, 3H), 7.32 – 7.27 (m, 1H), 7.16 (d, $J = 16.1$ Hz, 1H), 4.13 – 4.00 (m, 4H), 3.14 (d, $J = 21.6$ Hz, 2H), 1.27 (t, $J = 7.0$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.4 (d, $J = 4.0$ Hz), 150.4 (d, $J = 7.6$ Hz), 137.9 (d, $J = 5.8$ Hz), 136.7, 132.9 (d, $J = 1.8$ Hz), 128.8, 128.5, 127.6 (d, $J = 2.3$ Hz), 127.2, 126.3 (d, $J = 9.4$ Hz), 121.9 (d, $J = 3.1$ Hz), 62.5 (d, $J = 6.9$ Hz), 31.0 (d, $J = 140.0$ Hz), 16.5 (d, $J = 5.9$ Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}NO_3P^+$ 332.1410, Found: 332.1418.

diethyl ((6-phenoxy)pyridin-3-yl)methyl)phosphonate (5s)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, MeOH (0.5 mL) and Et_3N (0.15 mmol) were added, 15.4 mg, yellow oil, 47% yield.

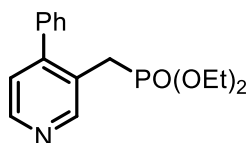
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.06 (d, $J = 2.8$ Hz, 1H), 7.68 (dt, $J = 8.5, 2.4$ Hz, 1H), 7.42 – 7.34 (m, 2H), 7.22 – 7.17 (m, 1H), 7.15 – 7.05 (m, 2H), 6.86 (d, $J = 8.5$ Hz, 1H), 4.09 – 4.02 (m, 4H), 3.07 (d, $J = 21.1$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 163.0 (d, $J = 3.2$ Hz), 154.3, 148.2 (d, $J = 8.0$ Hz), 140.9 (d, $J = 5.1$ Hz), 129.8, 124.8, 122.4 (d, $J = 9.1$ Hz), 121.2, 111.4 (d, $J = 2.8$ Hz), 62.4 (d, $J = 6.8$ Hz), 30.1 (d, $J = 141.0$ Hz), 16.5 (d, $J = 6.0$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_4\text{P}^+$ 322.1203, Found: 322.1212.

diethyl ((4-phenylpyridin-3-yl)methyl)phosphonate (5t)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, MeOH (0.5 mL) and Et_3N (0.15 mmol) were added, 9.8 mg, yellow oil, 32% yield.

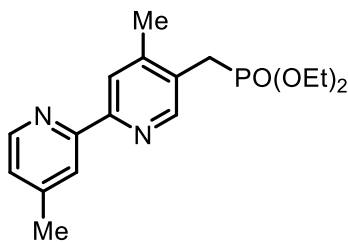
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.76 – 8.69 (m, 1H), 8.52 (d, $J = 4.4$ Hz, 1H), 7.50 – 7.38 (m, 5H), 7.21 (d, $J = 5.0$ Hz, 1H), 4.05 – 3.92 (m, 4H), 3.20 (d, $J = 22.2$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 151.7 (d, $J = 4.8$ Hz), 150.2 (d, $J = 7.5$ Hz), 148.0 (d, $J = 3.7$ Hz), 138.4, 129.1, 128.7, 128.4, 125.6 (d, $J = 8.9$ Hz), 124.9 (d, $J = 2.7$ Hz), 62.3 (d, $J = 6.7$ Hz), 28.0 (d, $J = 140.2$ Hz), 16.5 (d, $J = 6.1$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.4.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{P}^+$ 306.1254, Found: 306.1255.

diethyl ((4,4'-dimethyl-[2,2'-bipyridin]-5-yl)methyl)phosphonate (5u)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, no ZnBr_2 was added, 18.4 mg, yellow oil, 55% yield.

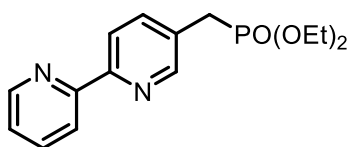
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.50 – 8.45 (m, 2H), 8.20 (s, 2H), 7.12 (d, $J = 5.0$ Hz, 1H), 4.08 – 4.01 (m, 4H), 3.22 (d, $J = 22.0$ Hz, 2H), 2.51 – 2.47 (m, 3H), 2.43 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 155.8, 154.7, 150.6 (d, $J = 5.7$ Hz), 149.0, 148.4, 147.5 (d, $J = 5.9$ Hz), 127.2 (d, $J = 9.6$ Hz), 124.8, 122.8 (d, $J = 3.3$ Hz), 122.0, 62.4 (d, $J = 6.9$ Hz), 28.7 (d, $J = 140.2$ Hz), 21.3, 19.7, 16.5 (d, $J = 6.0$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.3.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_3\text{P}^+$ 335.1519, Found: 335.1516.

diethyl ((2,2'-bipyridin)-5-ylmethyl)phosphonate (5v)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, no ZnBr_2 was added, 16.7 mg, yellow oil, 54% yield.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.69 – 8.64 (m, 1H), 8.55 (d, $J = 2.6$ Hz, 1H), 8.34 (t, $J = 7.3$ Hz, 2H), 7.82 – 7.76 (m, 2H), 7.29 (ddd, $J = 7.5, 4.8, 1.1$ Hz, 1H), 4.10 – 3.99 (m, 4H), 3.18 (d, $J = 21.7$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 6H).

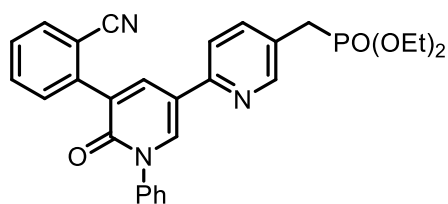
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 155.8, 154.8 (d, $J = 3.8$ Hz), 150.0 (d, $J = 7.4$ Hz), 149.2, 138.1 (d, $J = 5.8$ Hz), 137.0, 128.1 (d, $J = 9.1$ Hz), 123.7, 121.1, 120.8 (d, $J = 3.1$ Hz), 62.4 (d, $J = 6.8$ Hz), 31.0 (d, $J = 139.8$ Hz), 16.4 (d, $J = 6.1$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 24.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_3\text{P}^+$ 307.1206, Found: 307.1210.

diethyl ((5'-(2-cyanophenyl)-6'-oxo-1'-phenyl-1',6'-dihydro-[2,3'-bipyridin]-5-

yl)methyl)phosphonate (5w)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 26.5 mg, yellow solid, 53% yield. M.p = 70 – 72 $^\circ\text{C}$.

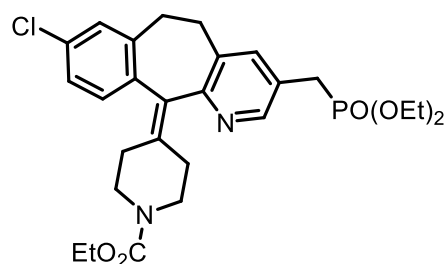
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.46 (d, $J = 2.4$ Hz, 1H), 8.32 – 8.26 (m, 2H), 7.80 – 7.70 (m, 3H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.58 – 7.49 (m, 5H), 7.44 (t, $J = 7.6$ Hz, 2H), 4.09 – 4.02 (m, 4H), 3.14 (d, $J = 21.6$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 160.5, 151.7 (d, $J = 3.7$ Hz), 150.5 (d, $J = 7.5$ Hz), 141.0, 140.4, 138.9, 138.4 (d, $J = 5.8$ Hz), 138.0, 133.3, 132.4, 131.2, 129.5, 129.1, 128.9, 128.4, 126.8, 126.5 (d, $J = 9.4$ Hz), 118.7, 118.6 (d, $J = 3.0$ Hz), 118.0, 112.6, 62.5 (d, $J = 6.8$ Hz), 30.8 (d, $J = 140.0$ Hz), 16.5 (d, $J = 6.0$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 24.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}_4\text{P}^+$ 500.1734, Found: 500.1733.

ethyl 4-(8-chloro-3-((diethoxyphosphoryl)methyl)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (5x)



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 30.8 mg, yellow solid, 57% yield. M.p = 126 – 127 $^\circ\text{C}$.

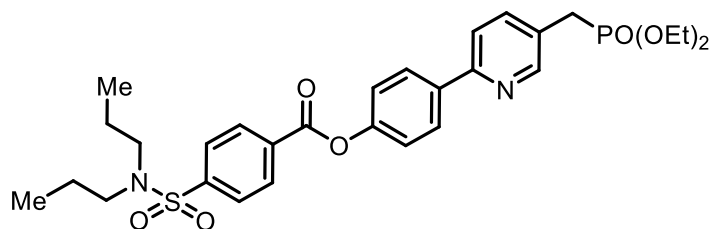
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.28 (t, $J = 2.3$ Hz, 1H), 7.44 (s, 1H), 7.18 – 7.06 (m, 3H), 4.16 – 4.01 (m, 6H), 3.80 (s, 2H), 3.41 – 3.27 (m, 2H), 3.16 – 3.09 (m, 2H), 3.05 (d, $J = 21.5$ Hz, 2H), 2.90 – 2.73 (m, 2H), 2.50 – 2.43 (m, 1H), 2.34 – 2.27 (m, 3H), 1.27 – 1.23 (m, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.6, 155.4 (d, *J* = 3.7 Hz), 147.4 (d, *J* = 7.3 Hz), 139.7, 139.0 (d, *J* = 5.9 Hz), 137.9 (d, *J* = 5.1 Hz), 133.9, 133.3 (d, *J* = 3.0 Hz), 133.0, 130.5, 129.0, 126.4 (d, *J* = 8.8 Hz), 126.3, 62.4 (d, *J* = 6.8 Hz), 62.3 (d, *J* = 6.8 Hz), 61.4, 44.9, 44.86, 31.6 (d, *J* = 2.8 Hz), 30.9, 30.6, 30.56 (d, *J* = 140.1 Hz), 29.8, 16.5 (d, *J* = 6.0 Hz), 14.8.

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.2.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₇H₃₅ClN₂O₅P⁺ 533.1967, Found: 533.1963.

4-(5-((diethoxyphosphoryl)methyl)pyridin-2-yl)phenyl **4-(*N,N*-dipropylsulfamoyl)benzoate (5y)**



Following procedure C: T₂ = 100 °C, 31.1 mg, white solid, 52% yield. M.p = 69 – 71 °C.

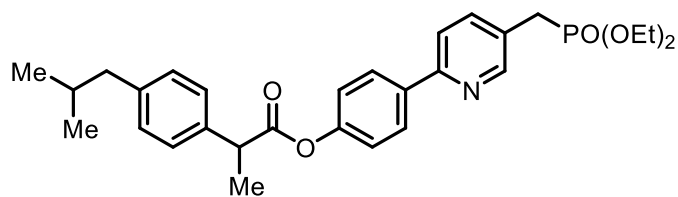
¹H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 2.6 Hz, 1H), 8.37 – 8.30 (m, 2H), 8.09 – 8.04 (m, 2H), 7.98 – 7.92 (m, 2H), 7.76 (dt, *J* = 8.3, 2.4 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 4.11 – 4.03 (m, 4H), 3.17 (d, *J* = 22.1 Hz, 2H), 3.14 – 3.08 (m, 4H), 1.62 – 1.50 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 6H), 0.88 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 163.9, 155.1 (d, *J* = 3.8 Hz), 151.4, 150.6 (d, *J* = 7.5 Hz), 145.1, 138.2 (d, *J* = 5.8 Hz), 137.2, 132.8, 130.9, 128.2, 127.3, 126.6 (d, *J* = 9.3 Hz), 121.9, 120.3 (d, *J* = 3.0 Hz), 62.5 (d, *J* = 6.8 Hz), 50.0, 30.8 (d, *J* = 140.0 Hz), 22.0, 16.5 (d, *J* = 6.0 Hz), 11.3.

³¹P NMR (162 MHz, Chloroform-*d*) δ 25.1.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₉H₃₈N₂O₇PS⁺ 589.2132, Found: 589.2132.

4-(5-((diethoxyphosphoryl)methyl)pyridin-2-yl)phenyl **2-(4-isobutylphenyl)propanoate (5z)**



Following procedure C: $T_2 = 100\text{ }^\circ\text{C}$, 27.9 mg, white solid, 54% yield. M.p = 89 – 91 $^\circ\text{C}$.

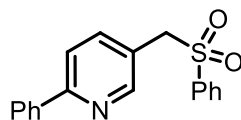
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.56 – 8.52 (m, 1H), 7.98 – 7.93 (m, 2H), 7.73 (dt, $J = 8.2, 2.4$ Hz, 1H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.33 – 7.29 (m, 2H), 7.17 – 7.13 (m, 2H), 7.12 – 7.08 (m, 2H), 4.10 – 4.02 (m, 4H), 3.95 (q, $J = 7.1$ Hz, 1H), 3.15 (d, $J = 21.6$ Hz, 2H), 2.47 (d, $J = 7.2$ Hz, 2H), 1.92 – 1.85 (m, 1H), 1.61 (d, $J = 7.1$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 6H), 0.91 (d, $J = 6.6$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 173.2, 155.3 (d, $J = 3.9$ Hz), 151.7, 150.5 (d, $J = 7.4$ Hz), 141.0, 138.1 (d, $J = 5.8$ Hz), 137.3, 136.6 (d, $J = 1.5$ Hz), 129.7, 127.9, 127.3, 126.4 (d, $J = 9.1$ Hz), 121.8, 120.2 (d, $J = 3.0$ Hz), 62.5 (d, $J = 6.7$ Hz), 45.4, 45.2, 30.8 (d, $J = 140.0$ Hz), 30.3, 22.5, 18.7, 16.5 (d, $J = 5.9$ Hz).

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 25.1.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{37}\text{NO}_5\text{P}^+$ 510.2404, Found: 510.2406.

2-phenyl-5-((phenylsulfonyl)methyl)pyridine (5aa)



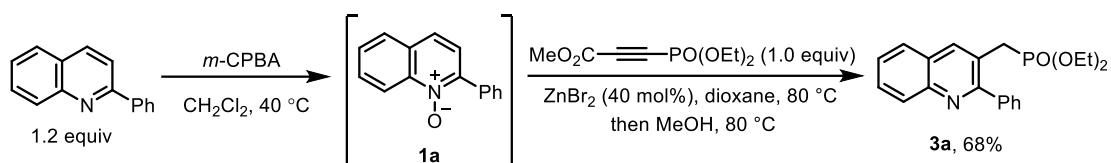
Following procedure D, 16.5 mg, white solid, 53% yield. M.p = 181 – 183 $^\circ\text{C}$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.16 (d, $J = 2.2$ Hz, 1H), 7.92 – 7.86 (m, 2H), 7.65 – 7.52 (m, 5H), 7.45 – 7.34 (m, 5H), 4.28 (s, 2H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 157.7, 151.1, 139.0, 138.4, 137.5, 134.2, 129.5, 129.3, 128.9, 128.6, 127.0, 122.7, 120.3, 59.9.

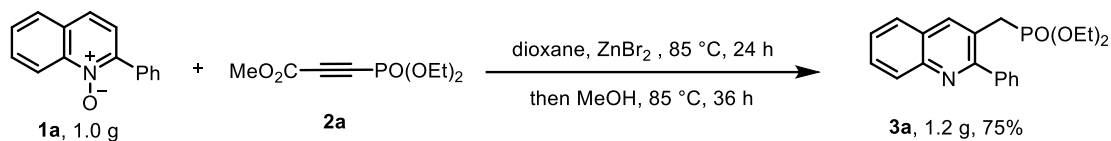
HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_2\text{S}^+$ 310.0896, Found: 310.0910.

4. One-pot synthesis of **3a** from 2-phenylquinoline and gram-scale reaction.



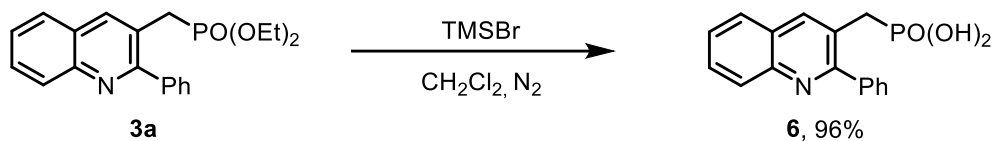
To a solution of 2-phenylquinoline (24.6 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) was added *m*-CPBA (31.1 mg, 0.36 mmol), and the mixture was stirred at $40\text{ }^\circ\text{C}$ for 36 h.

The solvent was then removed in vacuo, to the residue were added alkyne **2a** (22.1 mg, 0.10 mmol), ZnBr_2 (9.0 mg, 0.04 mmol), and dioxane (1 mL). The reaction mixture was stirred at $80\text{ }^\circ\text{C}$ for 24 h, followed by the addition of MeOH (0.5 mL) and stirring for another 12 h. After the reaction was completed, the solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel using PE/EtOAc (v/v = 2:1) as eluent to provide **3a** as yellow oil (24.2 mg, 68% yield).



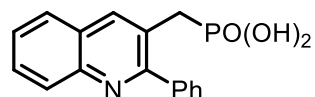
An oven-dried flask was charged with **1a** (1.0 g, 4.52 mmol), **2a** (1.5 g, 6.78 mmol), ZnBr_2 (0.4 g, 1.8 mmol) and dioxane (45 mL). The mixture was stirred at $85\text{ }^\circ\text{C}$ for 24 h. Then MeOH (20 mL) was added and the reaction was allowed to proceed for an additional 36 h. Upon completion of the reaction, the solvent was removed and product **3a** was obtained as yellow oil (1.2 g, 75% yield) by column chromatography on silica gel using PE/EtOAc (v/v = 2:1) as eluent.

5. Synthetic applications



Prepared according to the reported method.^[1] To a solution of **3a** (36.0 mg, 0.1 mmol) in CH₂Cl₂ (1 mL) was added dropwise a solution of bromotrimethylsilane (TMSBr, 76.5 mg, 0.5 mmol) in CH₂Cl₂ (1 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure, and the residue was treated with MeOH (1 mL) and stirred for an additional 1 h. After solvent removal under reduced pressure, the resulting solid was washed with cold EtOAc to afford the desired product **6**.

((2-phenylquinolin-3-yl)methyl)phosphonic acid (**6**)



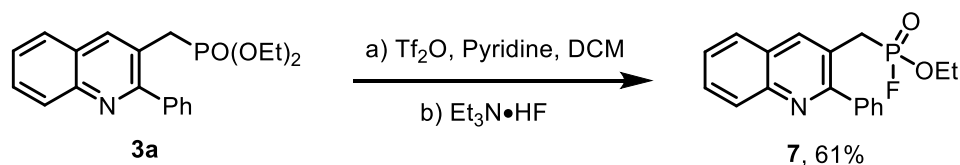
28.8 mg, white solid, 96% yield. M.p = 275 -278 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 9.28 (d, *J* = 3.1 Hz, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.6 Hz, 1H), 8.19 (t, *J* = 7.8 Hz, 1H), 8.02 (t, *J* = 7.7 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.80 – 7.70 (m, 3H), 3.46 (d, *J* = 21.7 Hz, 2H).

¹³C NMR (101 MHz, Methanol-*d*₄) δ 156.4 (d, *J* = 6.6 Hz), 148.0 (d, *J* = 5.2 Hz), 137.2 (d, *J* = 1.9 Hz), 135.0, 131.5, 131.0, 130.0, 129.6, 129.0, 128.6, 128.2 (d, *J* = 8.1 Hz), 128.0 (d, *J* = 3.0 Hz), 119.7, 30.1 (d, *J* = 135.7 Hz).

³¹P NMR (162 MHz, Methanol-*d*₄) δ 20.4.

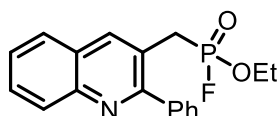
HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₅NO₃P⁺ 300.0784, Found: 300.0789.



Prepared according to the reported method.^[2] Trifluoromethanesulfonic anhydride (Tf₂O, 93.1 mg, 0.33 mmol) was added to a stirred solution of compound **3a** (39.1 mg, 0.11 mmol) in CH₂Cl₂ (1 mL) at room temperature, and the resulting mixture was stirred

for 5 minutes. Subsequently, pyridine (34.8 mg, 0.44 mmol) was introduced to the reaction system, and stirring was continued for an additional 5 minutes. Upon the addition of triethylamine trihydrofluoride (Et₃N·3HF, 17.7 mg, 0.11 mmol), the reaction mixture was allowed to react for 15 minutes at room temperature. Thereafter, Na₂CO₃ (35.0 mg, 0.33 mmol) and methanol (MeOH, 1 mL) were added sequentially, and the resulting solution was stirred for a further 15 minutes at room temperature to complete the reaction. Finally, the crude product was purified by column chromatography on silica gel using PE/EtOAc (v/v = 1:2) as the eluent, affording the target product **7**.

ethyl ((2-phenylquinolin-3-yl)methyl)phosphonofluoridate (7**)**



22.9 mg, yellow oil, 61% yield.

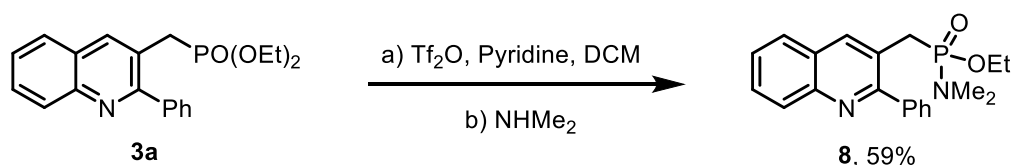
¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 3.6 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.74 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.60 – 7.45 (m, 6H), 4.22 – 4.14 (m, 2H), 3.59 – 3.49 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.2 (d, *J* = 7.9 Hz), 147.1 (d, *J* = 2.7 Hz), 139.9, 138.2 (d, *J* = 6.6 Hz), 130.2 (d, *J* = 1.7 Hz), 129.5 (d, *J* = 1.6 Hz), 129.1, 128.8, 128.7, 127.4 (d, *J* = 1.4 Hz), 127.2 (d, *J* = 3.3 Hz), 127.15 (d, *J* = 1.3 Hz), 121.5 (d, *J* = 9.2 Hz), 64.2 (d, *J* = 7.3 Hz), 28.8 (dd, *J* = 143.9, 24.8 Hz), 16.4 (d, *J* = 5.7 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.6 (d, *J* = 1078.6 Hz, 1F).

³¹P NMR (162 MHz, Chloroform-*d*) δ 24.3 (d, *J* = 1078.4 Hz, 1P).

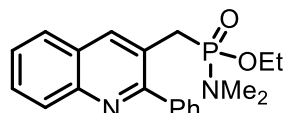
HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₈H₁₈FNO₂P⁺ 330.1054, Found: 330.1053.



Compound **3a** (35.6 mg, 0.1 mmol) was dissolved in CH₂Cl₂ (1 mL) followed by the addition of Tf₂O (84.6 mg, 0.3 mmol), the reaction was stirred for 10 min at room temperature. After adding pyridine (31.6 mg, 0.4 mmol), the mixture was stirred for a

further 10 min. Then a 2M solution of dimethylamine in THF (0.25 mL, 0.5 mmol) was added and the resulting solution was stirred at 50 °C for 1 h. Upon completion of the reaction, the solvent was removed under reduced pressure. The resulting residue was then purified by column chromatography on silica gel using CH₂Cl₂/MeOH (v/v =100:1) as the eluent to give the target product **8**.

ethyl *N,N*-dimethyl-*P*-((2-phenylquinolin-3-yl)methyl)phosphonamidite (8**)**



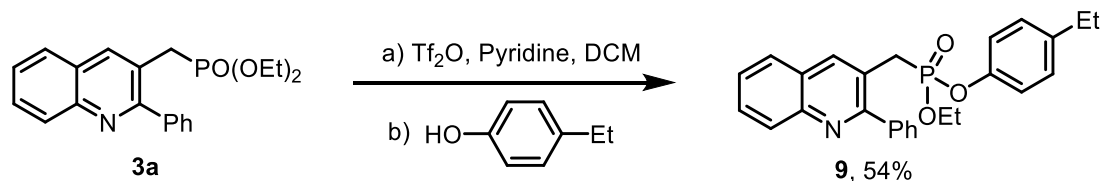
21.0 mg, yellow oil, 59% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 3.3 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.57 – 7.41 (m, 4H), 3.99 – 3.91 (m, 1H), 3.85 – 3.76 (m, 1H), 3.42 – 3.22 (m, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.2 (d, *J* = 6.7 Hz), 146.8 (d, *J* = 2.5 Hz), 140.5, 138.3 (d, *J* = 5.8 Hz), 129.5, 129.4, 129.35, 128.5, 128.4, 127.5, 127.4 (d, *J* = 3.1 Hz), 126.7, 124.4 (d, *J* = 7.9 Hz), 59.9 (d, *J* = 6.9 Hz), 36.1 (d, *J* = 4.3 Hz), 29.7 (d, *J* = 126.6 Hz), 16.3 (d, *J* = 6.8 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 30.7.

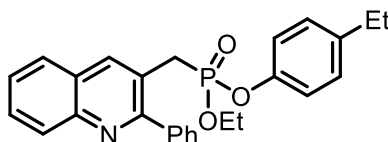
HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₄N₂O₂P⁺ 355.1570, Found: 355.1572.



To a stirring solution of compound **3a** (35.6 mg, 0.1 mmol) in CH₂Cl₂ (1 mL) was added Tf₂O (84.6 mg, 0.3 mmol). After stirring for 10 min at room temperature, pyridine (31.6 mg, 0.4 mmol) was added, and the mixture was stirred for an additional 10 min. Subsequently, 4-ethylphenol was added, and the reaction was allowed to proceed for 15 min. Thereafter, Na₂CO₃ (35.0 mg, 0.33 mmol) and MeOH (1 mL) were added sequentially, and the mixture was heated at 50 °C for 3 h. After completion of the

reaction, the crude product was purified by column chromatography on silica gel (PE/EtOAc, v/v = 3:1) to afford product **9**.

ethyl (4-ethylphenyl) ((2-phenylquinolin-3-yl)methyl)phosphonate (9**)**



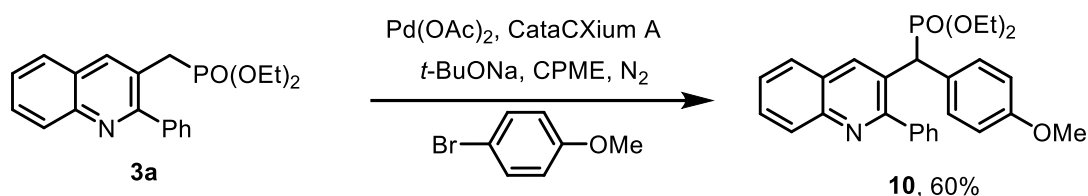
23.6 mg, yellow oil, 54% yield.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.45 (d, $J = 3.5$ Hz, 1H), 8.14 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.64 – 7.52 (m, 3H), 7.47 (q, $J = 7.2$, 6.7 Hz, 3H), 7.07 (d, $J = 8.2$ Hz, 2H), 6.97 – 6.90 (m, 2H), 4.10 – 4.01 (m, 2H), 3.53 (d, $J = 22.2$ Hz, 2H), 2.58 (q, $J = 7.6$ Hz, 2H), 1.22 – 1.14 (m, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 160.4 (d, $J = 7.6$ Hz), 148.4 (d, $J = 8.8$ Hz), 146.9 (d, $J = 2.5$ Hz), 141.0 (d, $J = 1.4$ Hz), 140.1, 138.2 (d, $J = 6.2$ Hz), 129.8, 129.4, 129.3, 129.1, 128.6, 128.5, 127.4 (d, $J = 1.5$ Hz), 127.3 (d, $J = 3.2$ Hz), 126.9, 123.1 (d, $J = 8.7$ Hz), 120.2 (d, $J = 4.3$ Hz), 63.2 (d, $J = 7.1$ Hz), 30.0 (d, $J = 139.8$ Hz), 28.2, 16.4 (d, $J = 5.9$ Hz), 15.7.

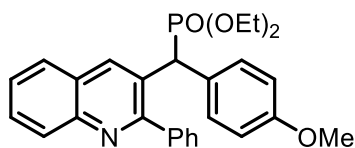
$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 22.7.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_3\text{P}^+$ 432.1723, Found: 432.1729.



Prepared according to the reported method.^[3] $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol) and CataCXium A (7.2 mg, 0.02 mmol) were dissolved in methoxycyclopentane (CPME 1 mL) and stirred for 1 h at room temperature under N_2 . *t*-BuONa (28.8 mg, 0.3 mmol), **3a** (35.5 mg, 0.1 mmol), and 1-bromo-4-methoxybenzene (37.4 mg, 0.2 mmol) were added, and the mixture was heated at 80 °C for 12 h. The mixture was extracted with EtOAc (3 \times 5 mL), dried over anhydrous Na_2SO_4 , and concentrated. The residue was purified by column chromatography (PE/EtOAc, v/v = 1:1) afforded the product **10**.

diethyl ((4-methoxyphenyl)(2-phenylquinolin-3-yl)methyl)phosphonate (10)



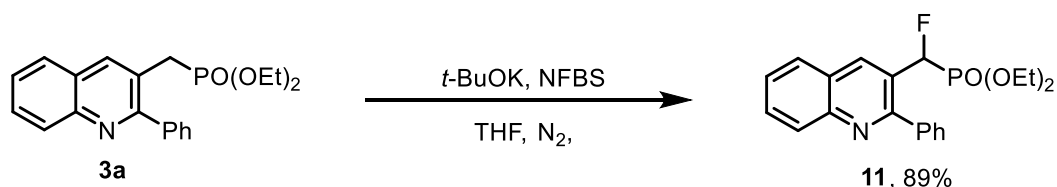
27.8 mg, white solid, 60% yield. M.p = 120 – 121 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 2.3 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.38 – 7.35 (m, 2H), 7.20 – 7.13 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.69 (d, *J* = 25.6 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.94 – 3.82 (m, 2H), 3.75 (s, 3H), 3.73 – 3.62 (m, 1H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.2 (d, *J* = 12.1 Hz), 159.2 (d, *J* = 2.5 Hz), 146.9 (d, *J* = 1.4 Hz), 140.6, 137.5 (d, *J* = 5.7 Hz), 131.0, 130.9, 130.2, 129.6, 129.59, 129.3, 128.8, 128.4, 128.1 (d, *J* = 6.1 Hz), 127.7 (d, *J* = 1.5 Hz), 127.1, 114.4 (d, *J* = 2.0 Hz), 63.5 (d, *J* = 7.1 Hz), 62.9 (d, *J* = 7.3 Hz), 55.6, 45.7 (d, *J* = 140.1 Hz), 16.7 (d, *J* = 5.9 Hz), 16.7 (d, *J* = 5.7 Hz).

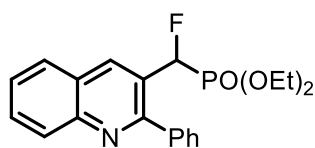
³¹P NMR (162 MHz, Chloroform-*d*) δ 25.4.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₇H₂₉NO₄P⁺ 462.1829, Found: 462.1834.



Prepared according to the reported method^[4]. To a solution of **3a** (35.6 mg, 0.1 mmol) in THF (1 mL) was added *t*-BuOK (22.4 mg, 0.2 mmol), and the mixture was stirred at -40 °C for 0.5 h under N₂. Subsequently, *N*-fluorobis(phenylsulfonyl)amine (NFBS, 78.8 mg, 0.25 mmol) was added. After stirring for an additional 15 min, the reaction mixture was quenched with water, and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EtOAc, v/v = 4:1) to afford product **11**.

diethyl (fluoro(2-phenylquinolin-3-yl)methyl)phosphonate (11)



34.9 mg, yellow oil, 89% yield.

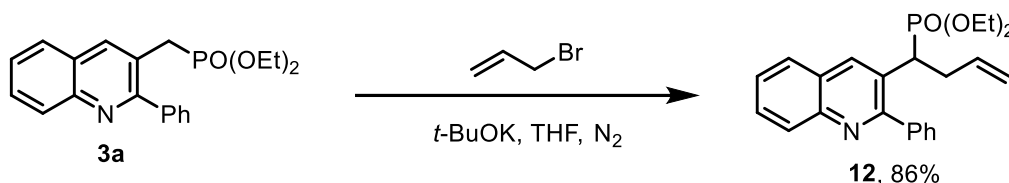
¹H NMR (400 MHz, Chloroform-*d*) δ 8.82 (t, $J = 1.9$ Hz, 1H), 8.16 (d, $J = 8.5$ Hz, 1H), 7.95 (d, $J = 8.2$ Hz, 1H), 7.78 (t, $J = 7.7$ Hz, 1H), 7.71 – 7.64 (m, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.54 – 7.46 (m, 3H), 5.98 (dd, $J = 44.3, 7.9$ Hz, 1H), 4.27 – 4.18 (m, 2H), 4.13 – 3.93 (m, 2H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.20 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.2 (dd, $J = 8.8, 3.2$ Hz), 148.1 (t, $J = 2.2$ Hz), 139.2, 138.6 (t, $J = 4.8$ Hz), 131.1, 129.5, 128.9, 128.7, 128.4, 127.2, 126.9 (d, $J = 2.1$ Hz), 124.9 (d, $J = 17.6$ Hz), 85.8 (dd, $J = 180.4, 173.7$ Hz), 64.0 (d, $J = 6.7$ Hz), 63.4 (d, $J = 6.8$ Hz), 16.6 (d, $J = 5.6$ Hz), 16.4 (d, $J = 5.7$ Hz).

¹⁹F NMR (377 MHz, Chloroform-*d*) δ -188.1 (d, $J = 93.2$ Hz).

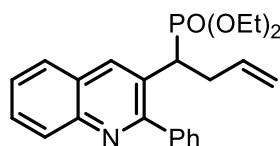
³¹P NMR (162 MHz, Chloroform-*d*) δ 15.4 (d, $J = 93.3$ Hz).

HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{20}H_{22}FNO_3P^+$ 374.1316, Found: 374.1313.



To a solution of **3a** (35.6 mg, 0.1 mmol) in THF was added *t*-BuOK (22.4 mg, 0.2 mmol) at -40 °C. After stirring for 30 min under N₂, 3-bromoprop-1-ene (24.2 mg, 0.2 mmol) was added. The mixture was stirred for a further 15 min, then extracted with EtOAc three times. The organic layer was dried over Na₂SO₄ and concentrated. Purification by column chromatography (PE/EtOAc, v/v = 1:1) afforded the product **12**.

diethyl (1-(2-phenylquinolin-3-yl)but-3-en-1-yl)phosphonate (12)



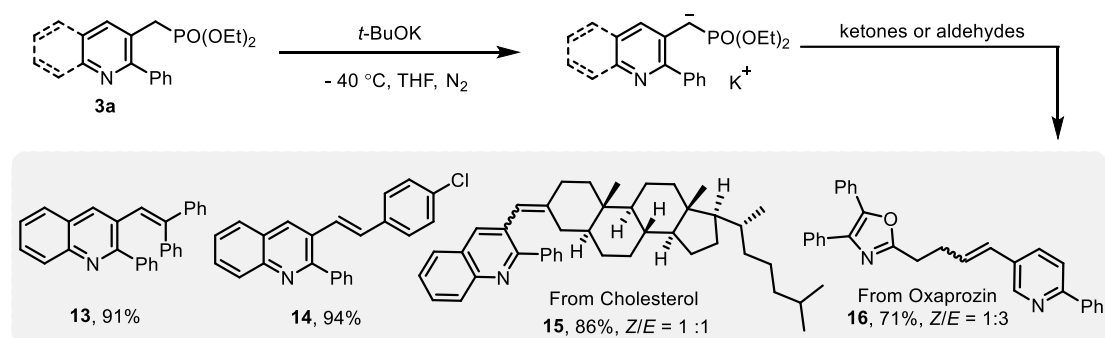
34.2 mg, colorless oil, 86% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 3.2 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.58 – 7.51 (m, 3H), 7.49 – 7.40 (m, 3H), 5.54 – 5.44 (m, 1H), 4.90 – 4.82 (m, 2H), 4.08 – 3.99 (m, 2H), 3.96 – 3.86 (m, 1H), 3.85 – 3.75 (m, 1H), 3.60 (ddd, *J* = 22.4, 10.9, 4.3 Hz, 1H), 2.92 – 2.61 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.2 (d, *J* = 8.3 Hz), 146.6 (d, *J* = 2.1 Hz), 140.3, 136.5 (d, *J* = 5.4 Hz), 134.5, 134.4, 129.8 (d, *J* = 1.4 Hz), 129.4 (d, *J* = 1.2 Hz), 129.3, 128.5, 128.3, 127.7, 127.4 (d, *J* = 2.8 Hz), 126.7, 117.8, 62.7 (d, *J* = 7.2 Hz), 62.2 (d, *J* = 7.2 Hz), 39.0 (d, *J* = 139.1 Hz), 36.0 (d, *J* = 2.7 Hz), 16.5 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 5.7 Hz).

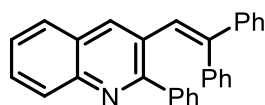
³¹P NMR (162 MHz, Chloroform-*d*) δ 28.1.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₃H₂₇NO₃P⁺ 396.1723, Found: 396.1721.



General procedure: *t*-BuOK (22.4 mg, 0.2 mmol) was added to a solution of **3a** (42.6 mg, 0.12 mmol) in THF (1 mL) at -40 °C. After stirring for 1 h under N₂, the corresponding ketone or aldehyde (0.1 mmol) was added. The mixture was warmed to room temperature and stirred for 3 h. Water was added, and the mixture was extracted with EtOAc. The combined organic layers were concentrated and purified by column chromatography (PE/EtOAc, 40:1 to 10:1) to give the *meta*-alkenyl azaarene.

3-(2,2-diphenylvinyl)-2-phenylquinoline (**13**)



35 mg, white solid, 91% yield. M.p = 190 – 192 °C.

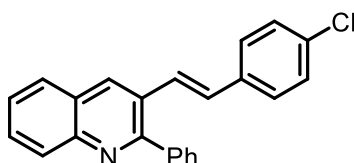
¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.77 – 7.72 (m, 2H),

7.68 (s, 1H), 7.59 (t, $J = 6.92$ Hz, 1H), 7.44 – 7.33 (m, 5H), 7.24 – 7.22 (m, 8H), 7.16 – 7.14 (m, 2H), 6.91 (s, 1H).

^{13}C NMR (101 MHz, Chloroform- d) δ 159.5, 146.8, 144.1, 142.9, 140.4, 139.7, 137.9, 130.7, 130.0, 129.7, 129.5, 129.3, 128.7, 128.6, 128.4, 128.37, 128.1, 127.9, 127.6, 127.59, 126.9, 126.4, 125.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{22}\text{N}^+$ 384.1747, Found: 384.1745.

(*E*)-3-(4-chlorostyryl)-2-phenylquinoline (14)



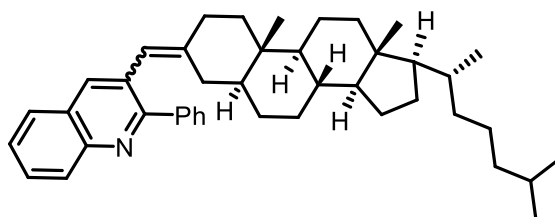
32.2 mg, white solid, 94% yield. M.p = 165 – 166 °C.

^1H NMR (400 MHz, Chloroform- d) δ 8.42 (s, 1H), 8.16 (d, $J = 8.5$ Hz, 1H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.73 – 7.69 (m, 3H), 7.57 – 7.46 (m, 4H), 7.33 (q, $J = 8.4$ Hz, 4H), 7.15 (q, $J = 16.2$ Hz, 2H).

^{13}C NMR (101 MHz, Chloroform- d) δ 158.9, 147.5, 140.0, 135.7, 133.7, 133.1, 129.9, 129.87, 129.8, 129.76, 129.5, 129.1, 128.8, 128.5, 128.0, 127.6, 127.5, 127.3, 126.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{17}\text{ClN}^+$ 342.1044, Found: 342.1047.

3-(((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-3*H*-cyclopenta[*a*]phenanthren-3-ylidene)methyl)-2-phenylquinoline (15)



50.6 mg, a mixture of isomers ($Z/E = 1:1$, determined by ^1H NMR analysis of the mixture), white solid, 86% yield. M.p = 133 – 136 °C.

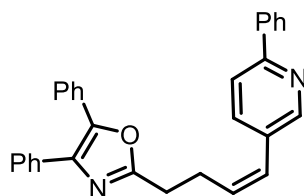
^1H NMR (400 MHz, Chloroform- d) δ 8.16 (s, 1H), 8.14 (s, 1H), 7.97 (d, $J = 3.4$ Hz, 2H), 7.80 (d, $J = 8.2$ Hz, 2H), 7.77 – 7.70 (m, 4H), 7.67 (t, $J = 7.6$ Hz, 2H), 7.53 – 7.40 (m, 8H), 6.15 (s, 1H), 6.12 (s, 1H), 2.65 (d, $J = 14.3$ Hz, 1H), 2.40 – 2.28 (m, 2H), 2.25

– 2.14 (m, 2H), 2.11 – 1.43 (m, 19H), 1.40 – 0.98 (m, 38H), 0.92 – 0.85 (m, 24H), 0.67 (d, $J = 2.8$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform- d) δ 159.4, 159.37, 146.9, 144.1, 144.0, 140.8, 140.7, 137.1, 137.06, 130.36, 130.3, 130.0, 129.99, 129.4, 129.1, 128.4, 128.36, 128.1, 127.3, 127.26, 127.23, 127.21, 126.5, 120.4, 120.1, 56.6, 56.59, 56.4, 54.5, 54.49, 48.1, 47.1, 42.7, 40.2, 39.9, 39.8, 39.6, 39.3, 36.5, 36.4, 36.3, 35.9, 35.6, 35.5, 33.0, 32.5, 32.1, 32.0, 29.1, 28.9, 28.4, 28.1, 25.6, 24.34, 24.3, 24.0, 23.0, 22.7, 21.3, 21.2, 18.81, 18.8, 12.2, 12.0, 11.9.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{43}\text{H}_{58}\text{N}^+$ 588.4564, Found: 588.4569.

(Z)-4,5-diphenyl-2-(4-(6-phenylpyridin-3-yl)but-3-en-1-yl)oxazole (16-Z)



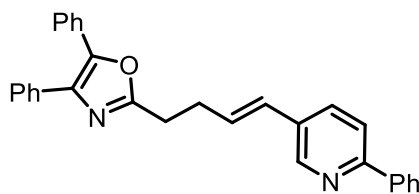
8.0 mg, yellow oil, 18% yield.

^1H NMR (400 MHz, Chloroform- d) δ 8.63 (d, $J = 2.0$ Hz, 1H), 8.03 – 7.95 (m, 2H), 7.71 – 7.66 (m, 2H), 7.66 – 7.61 (m, 2H), 7.56 – 7.52 (m, 2H), 7.50 – 7.46 (m, 2H), 7.44 – 7.29 (m, 7H), 6.51 (d, $J = 11.8$ Hz, 1H), 5.92 (dt, $J = 11.7, 7.2$ Hz, 1H), 3.07 – 3.00 (m, 2H), 2.95 (dd, $J = 8.1, 6.4$ Hz, 2H).

^{13}C NMR (101 MHz, Chloroform- d) δ 162.5, 155.6, 149.8, 145.5, 139.1, 136.7, 135.3, 132.7, 132.6, 131.4, 129.1, 129.01, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 126.9, 126.6, 120.1, 28.4, 26.4.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_2\text{O}^+$ 429.1961, Found: 429.1958.

(E)-4,5-diphenyl-2-(4-(6-phenylpyridin-3-yl)but-3-en-1-yl)oxazole (16-E)



22.8 mg, white solid, 53% yield. M.p = 116 – 118 °C.

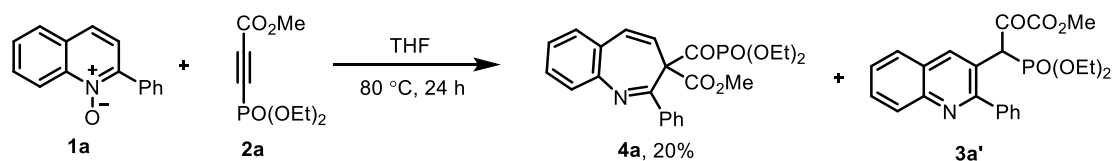
^1H NMR (400 MHz, Chloroform- d) δ 8.64 (d, $J = 2.3$ Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 2H),

7.76 (dd, $J = 8.3, 2.3$ Hz, 1H), 7.67 (dd, $J = 9.7, 7.7$ Hz, 3H), 7.62 – 7.56 (m, 2H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.43 – 7.30 (m, 7H), 6.55 (d, $J = 16.0$ Hz, 1H), 6.44 (dt, $J = 15.7, 6.6$ Hz, 1H), 3.08 (t, $J = 7.6$ Hz, 2H), 2.84 (q, $J = 7.2$ Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.7, 156.0, 148.1, 145.4, 139.2, 135.2, 133.5, 132.6, 131.5, 130.7, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.2, 128.0, 127.8, 126.8, 126.5, 120.4, 30.7, 28.2.

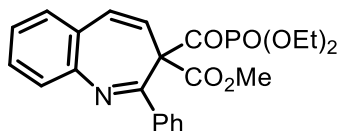
HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_2\text{O}^+$ 429.1961, Found: 429.1962.

6. Mechanistic studies



A mixture of *N*-oxide **1a** (22.1 mg, 0.1 mmol), alkyne **2a** (33.0 mg, 0.15 mmol) was dissolved in THF (1 mL) and stirred at 80 °C for 24 h. Upon cooling to room temperature, the volatiles were removed under reduced pressure. Purification of the crude residue by column chromatography on silica gel (eluent: PE/EtOAc = 2:1) yielded product **4a** and **3a'**. ¹H and ³¹P NMR analysis revealed **3a'** exists as a mixture of ketone and enolate tautomers with a ratio of 1:0.6.

methyl 3-((diethoxyphosphoryl)carbonyl)-2-phenyl-3H-benzo[*b*]azepine-3-carboxylate (4a)



8.8 mg, yellow oil, 20% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.29 (m, 7H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 10.1 Hz, 1H), 6.57 (d, *J* = 10.1 Hz, 1H), 4.05 – 3.86 (m, 2H), 3.84 – 3.74 (m, 1H), 3.58 – 3.48 (m, 1H), 3.48 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.5 (d, *J* = 176.6 Hz), 167.6 (d, *J* = 3.0 Hz), 153.2 (d, *J* = 5.9 Hz), 146.0, 139.7 (d, *J* = 2.9 Hz), 131.7, 130.3, 129.1, 128.4, 128.1, 128.0, 127.9, 125.1, 124.8, 121.2 (d, *J* = 2.3 Hz), 71.9 (d, *J* = 56.6 Hz), 64.3 (d, *J* = 8.0 Hz), 63.8 (d, *J* = 6.6 Hz), 53.3, 16.3 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 6.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ -5.3.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₃H₂₅NO₆P⁺ 442.1414; Found 442.1424.

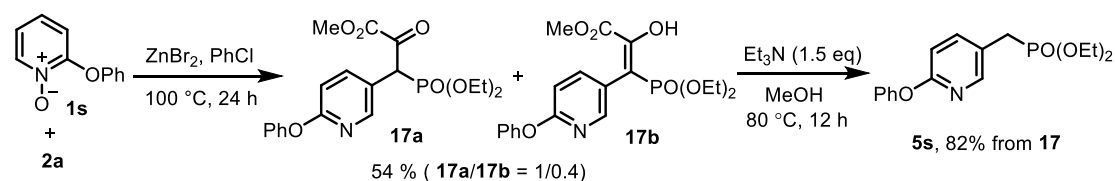
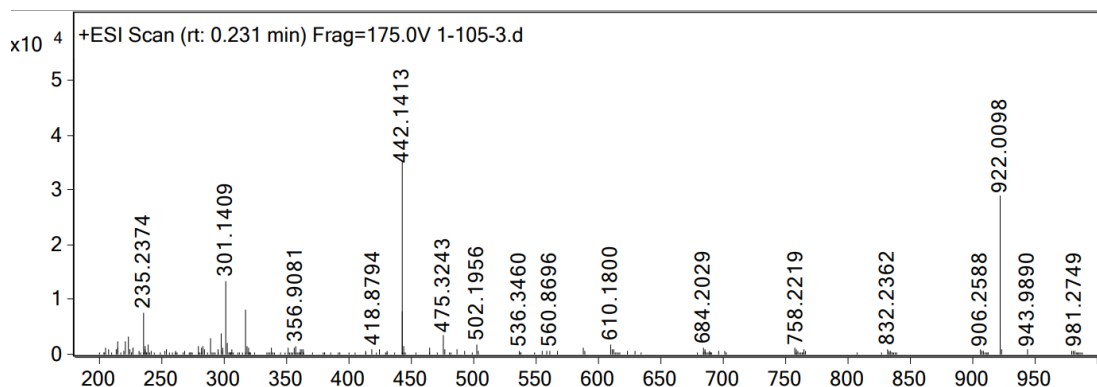
3a', a tautomeric mixture of ketone and enolate with a ratio of 1:0.6, 2 mg, yellow oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 11.85 (s, 1H, enolate), 8.68 (d, *J* = 3.0 Hz, 1H, ketone), 8.19 – 8.08 (m, 1H, ketone, 1H enolate), 8.00 – 7.90 (m, 1H, ketone, 1H

enolate), 7.81 – 7.69 (m, 2H, ketone, 2H enolate), 7.62 – 7.34 (m, 5H, ketone, 6H enolate), 5.92 (d, $J = 25.9$ Hz, 1H, ketone), 4.13 – 3.81 (m, 4H, ketone, 4H enolate), 3.80 (s, 3H, ketone), 3.53 (s, 3H, enolate), 1.28 – 1.24 (m, 6H, ketone), 1.19 (t, $J = 7.1$ Hz, 6H, enolate).

^{31}P NMR (162 MHz, Chloroform- d) δ 20.7 (s, enolate), 16.7 (s, ketone)

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_6\text{P}^+$ 442.1414, Found: 442.1413.



A mixture of *N*-oxide **1s** (0.1 mmol, 18.7 mg), alkyne **2a** (0.2 mmol, 44.0 mg) and ZnBr_2 (0.02 mmol, 4.51 mg) was dissolved in PhCl (1 mL), then the mixture was stirred at 100 °C until **1s** was completely consumed monitored by thin layer chromatography (TLC). After 24 h, the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using MeOH/DCM (v/v = 1:50) as eluent to afford **17** as yellow oil (22.0 mg, 54% yield).

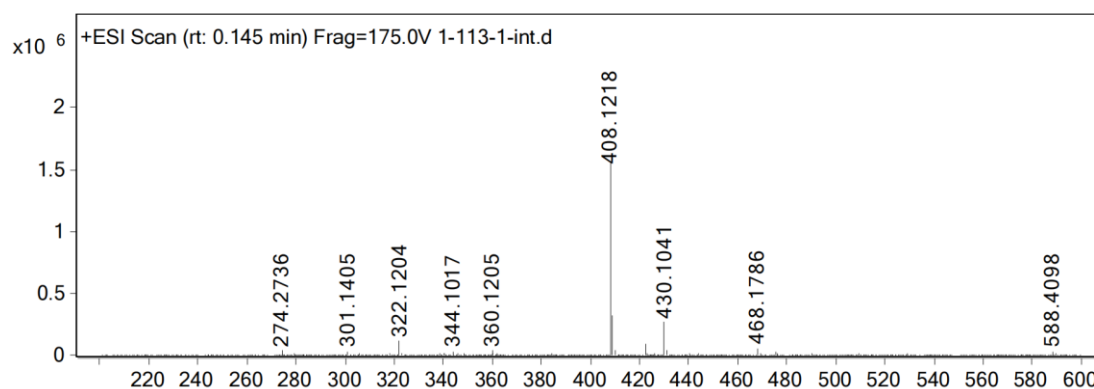
An oven-dried vial was charged with the **17** (20.4 mg, 0.05 mmol), Et_3N (7.6 mg, 0.08 mmol) and MeOH (0.5 mL), then the solution was reacted at 80 °C for 12 h. After the reaction was completed, the solvent was removed and the crude product was purified by column chromatography (PE/EtOAc = 1:4) to yield **5s** as yellow oil (13.3 mg, 82% yield from **17**).

17, a tautomeric mixture of ketone **17a** and enolate **17b** with a ratio of 1:0.4, ^1H NMR

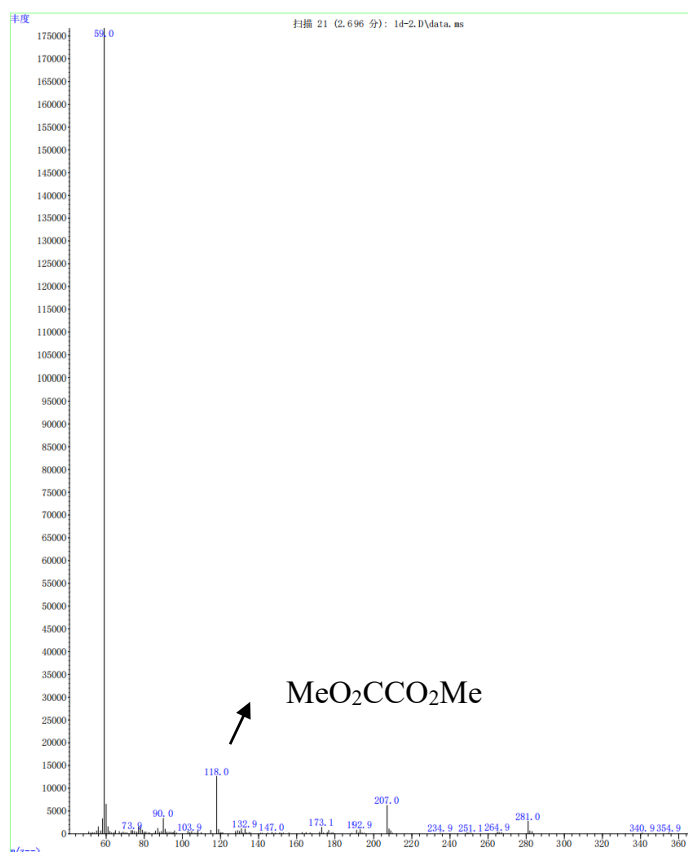
(400 MHz, Chloroform-*d*) δ 11.86 (s, 1H, **17b**), 8.18 (t, $J = 2.6$ Hz, 1H, **17a**), 7.99 – 7.94 (m, 1H, **17a**, 1H, **17b**), 7.53 – 7.48 (m, 1H, **17b**), 7.43 – 7.35 (m, 2H, **17a**, 2H, **17b**), 7.23 – 7.11 (m, 3H, **17a**, 3H, **17b**), 6.92 (d, $J = 8.6$ Hz, 1H, **17a**), 6.86 (d, $J = 8.5$ Hz, 1H, **17b**), 5.46 (d, $J = 26.1$ Hz, 1H, **17a**), 4.14 – 4.05 (m, 4H, **17a**, 4H, **17b**), 3.90 (s, 3H, **17a**), 3.65 (s, 3H, **17b**), 1.29 – 1.22 (m, 6H, **17a**, 6H, **17b**).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.7 (s, **17b**), 16.1 (s, **17a**).

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_7\text{P}^+$ 408.1207, Found: 408.1218.



Detection of byproduct $\text{MeO}_2\text{CCO}_2\text{Me}$ by GC-MS analysis of the crude reaction mixture under standard conditions



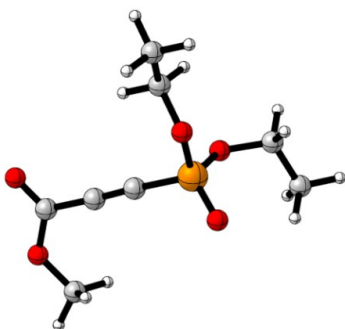
7. Density functional theory (DFT) studies

Computational Methods

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package.^[5] For the geometry optimization, the B3LYP functional^[6,7] with Grimme's third generation empirical dispersion correction including Becke-Johanson damping was used,^[8,9] which is denoted as B3LYP-D3BJ. The def2svp^[10] basis sets was used for all geometry optimizations performed. Hessian calculation were performed to confirm the stationary points; minima with no imaginary frequency. Solvent effects were considered based on SMD model in 1,4-dioxane for the geometry optimization and single-point energy calculation.^[11] The Hirshfeld charge was used for computing charges on the atoms with Multiwfn 3.8 program.^[12-14]

Cartesian coordinates (Å) of optimized structures

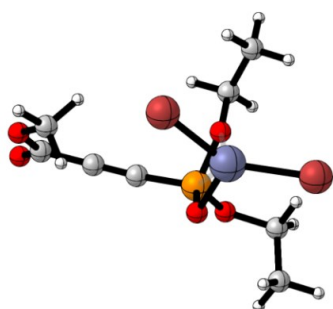
2a



C	-1.87860200	0.20003500	-0.14488300
C	-0.69814600	0.01642300	0.07803800
P	0.99105600	-0.25442000	0.52888000
O	1.19311200	-1.10482000	1.72410600
C	-3.28098300	0.47218700	-0.44795500
O	-3.62202900	1.47205800	-1.02708200
O	-4.16818100	-0.44346500	-0.04974800
C	-3.74187100	-1.62442800	0.64171900
O	1.55323000	-0.79588800	-0.88034400

C	2.81575000	-2.88111000	-0.66156600
C	2.87099800	-1.39686300	-0.95240200
O	1.60140000	1.21936500	0.72038800
C	2.16352500	3.49372600	0.22073000
C	1.56052900	2.21922200	-0.32084200
H	-4.65756400	-2.18420300	0.86912700
H	-3.08444200	-2.24046700	0.00936600
H	-3.22369900	-1.37369700	1.57979500
H	3.81769100	-3.32286000	-0.78546800
H	2.47767000	-3.05988700	0.36940500
H	2.12580400	-3.38775700	-1.35430900
H	3.21885700	-1.19709800	-1.97642500
H	3.55290700	-0.87759500	-0.25874100
H	2.14484800	4.27387700	-0.55651600
H	1.59478400	3.85602400	1.09079700
H	3.20823000	3.33407400	0.52955800
H	2.11873300	1.84725700	-1.19535800
H	0.51289000	2.37547500	-0.63003300

2a-ZnBr₂ (18)

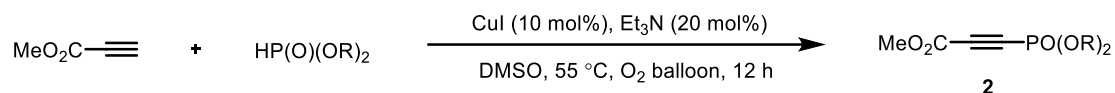


C	-3.32862500	1.07425800	-0.16778700
C	-2.16106500	1.40761800	-0.13420000
P	-0.42238000	1.43751200	-0.13928600

O	0.18395300	0.62779900	-1.26260100
C	-4.71999100	0.61861600	-0.22217900
O	-5.64516700	1.38146800	-0.12237200
O	-4.88240100	-0.69196300	-0.38911500
C	-3.74592100	-1.57274400	-0.48748600
O	-0.03743900	2.96929200	-0.07279900
C	1.82393900	3.58296400	-1.55617400
C	1.37882700	3.36638100	-0.13022000
O	0.06251000	0.70147100	1.19581900
C	0.45300800	0.06182900	3.45790100
C	-0.24070900	1.06443800	2.56913500
H	-4.16062000	-2.57720400	-0.63178500
H	-3.11108200	-1.31067700	-1.34577900
H	-3.14690400	-1.55312600	0.43381600
H	2.85948500	3.95850800	-1.55477800
H	1.80279200	2.64077000	-2.12211300
H	1.18571900	4.32372300	-2.06151300
H	1.42220000	4.28756200	0.46571900
H	1.98565300	2.59388700	0.36766700
H	0.25187500	0.29767700	4.51415600
H	0.09020000	-0.95547000	3.24716900
H	1.54056600	0.08399500	3.29097500
H	0.11437200	2.09231800	2.74198000
H	-1.33481300	1.04291600	2.69752200
Br	3.43175300	-0.24269500	-0.11304500
Br	-0.13823000	-2.77995300	-0.15099800
Zn	1.24515200	-0.94065200	-0.44925400

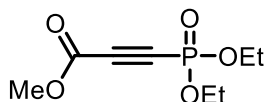
8. Substrates preparation and characterization.

The *N*-oxide compounds were prepared according to previous literature reported by our group.^[15-17] Alkynes **2** were prepared according to literature procedures with some modifications.^[18]



The corresponding phosphite ester (1 mmol, 139 mg), CuI (19 mg, 0.1 mmol), Et₃N (21 mg, 0.2 mmol) were dissolved in anhydrous DMSO (6 mL), then the mixture was purged with O₂ balloon for 3 min. Subsequently, a solution of methyl propiolate (1.2 mmol, 101 mg) in anhydrous DMSO (3 mL) was added dropwise at 55 °C under an oxygen atmosphere. The resulting system was stirred at 55 °C for 12 h while maintaining the oxygen atmosphere. Upon completion of the reaction, the mixture was extracted with saturated brine, dried over anhydrous Na₂SO₄, concentrated in vacuo. The residue was purified by column chromatography on silica gel using PE/EtOAc (v/v = 6:1) as eluent to afford alkyne product **2**.

methyl 3-(diethoxyphosphoryl)propiolate (**2a**)



122 mg, yellow oil, 55% yield.

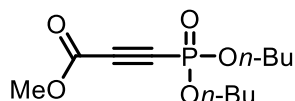
¹H NMR (400 MHz, Chloroform-*d*) δ 4.21 – 4.13 (m, 4H), 3.79 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 152.1 (d, *J* = 6.0 Hz), 86.5 (d, *J* = 46.6 Hz), 74.1, 64.3 (d, *J* = 5.7 Hz), 53.6, 16.2 (d, *J* = 6.9 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ -9.8.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₈H₁₄O₅P⁺ 221.0573, Found: 221.0577.

methyl 3-(dibutoxyphosphoryl)propiolate (**2b**)



139 mg, yellow oil, 50% yield.

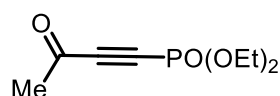
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 4.18 – 4.09 (m, 4H), 3.83 (s, 3H), 1.77 – 1.63 (m, 4H), 1.49 – 1.36 (m, 4H), 0.94 (t, $J = 7.4$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 152.1 (d, $J = 5.9$ Hz), 86.5 (d, $J = 46.4$ Hz), 74.0, 67.9 (d, $J = 6.1$ Hz), 53.5, 32.2 (d, $J = 6.9$ Hz), 18.7, 13.6.

$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ -9.4.

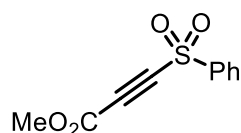
HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_5\text{P}^+$ 277.1199, Found: 277.1196.

diethyl (3-oxobut-1-yn-1-yl)phosphonate (2c)



The diethyl (3-oxobut-1-yn-1-yl)phosphonate **2c** was synthesized according to literature procedures^[19]. Yellow liquid, $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 4.26 – 4.11 (m, 4H), 2.40 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 182.4 (d, $J = 4.2$ Hz), 92.5 (d, $J = 43.0$ Hz), 77.5 (d, $J = 277.9$ Hz), 64.1 (d, $J = 5.7$ Hz), 32.4, 16.0 (d, $J = 6.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ -9.1. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_8\text{H}_{14}\text{O}_4\text{P}^+$ 205.0624, Found: 205.0616.

methyl 3-(phenylsulfonyl)propiolate (2d)



The methyl 3-(phenylsulfonyl)propiolate **2d** was synthesized according to literature procedures^[20-21]. Yellow liquid, $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.07 – 7.99 (m, 2H), 7.78 – 7.72 (m, 1H), 7.63 (dd, $J = 8.5, 7.3$ Hz, 2H), 3.82 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 151.4, 139.7, 135.3, 129.8, 128.1, 79.5, 79.4, 53.9. **HRMS (ESI)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_9\text{O}_4\text{S}^+$ 225.0216, Found: 225.0220.

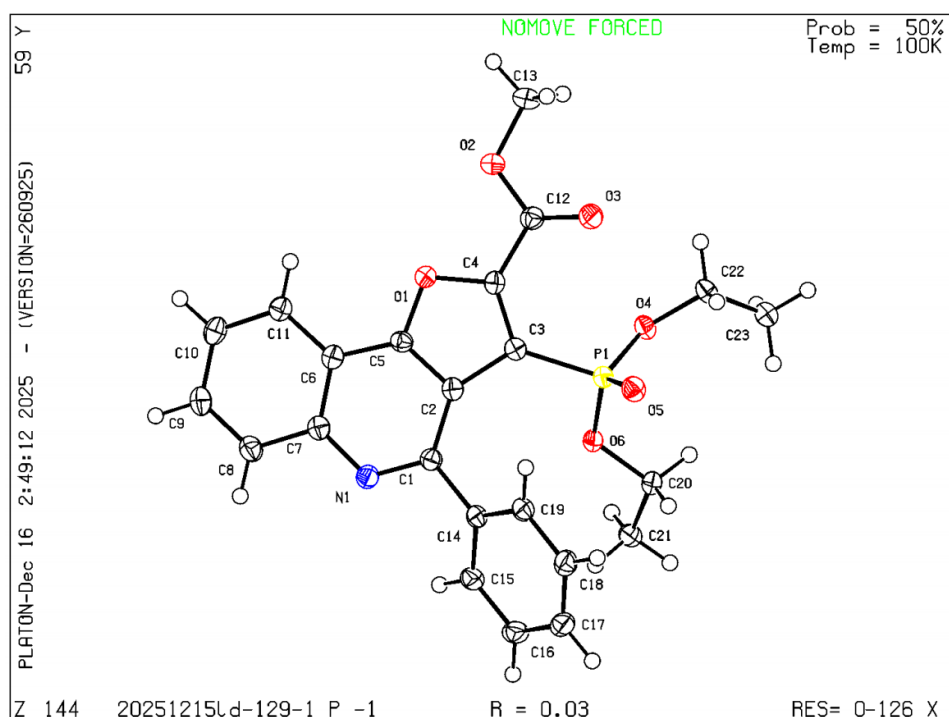
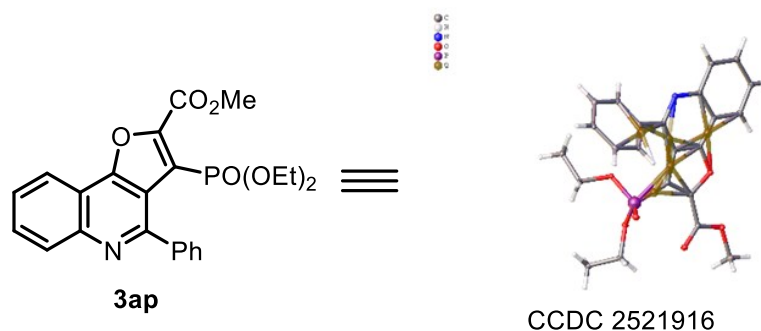
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10. Crystallographic data

Table 2 Crystallographic data for **3ap**



Bond precision:	C-C = 0.0020 Å	Wavelength=1.54184	
Cell:	a=7.3493(4)	b=8.8307(5)	c=16.1540(9)
	alpha=76.690(5)	beta=84.882(4)	gamma=86.571(5)
Temperature:	Temperature:		
	Calculated	Reported	
Volume	1015.32(10)	1015.32(10)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C23 H22 N O6 P	C23 H22 N O6 P	

Sum formula	C23 H22 N O6 P	C23 H22 N O6 P
Mr	439.39	439.38
Dx (g·cm ⁻³)	1.437	1.437
Z	2	2
Mu (mm ⁻¹)	1.568	1.568
F000	460.0	460.0
F000'	462.02	
h,k,lmax	9, 11, 20	9, 11, 20
Nref	4200	3947
Tmin,Tmax	0.778, 0.828	0.922, 1.000
Tmin'	0.778	

Correction method= # Reported T Limits: Tmin=0.922 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.940

Theta(max) = 75.480

R(reflections)= 0.0347(3525)

wR2(reflections) = 0.0952(3947)

S = 1.072

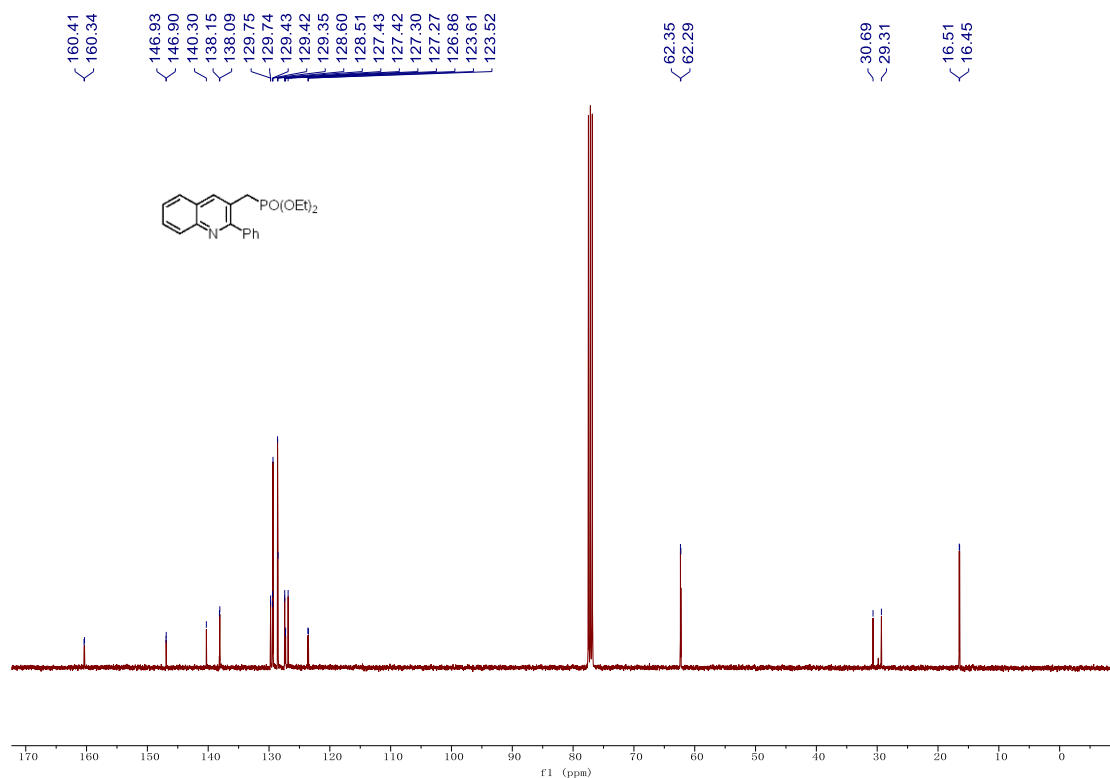
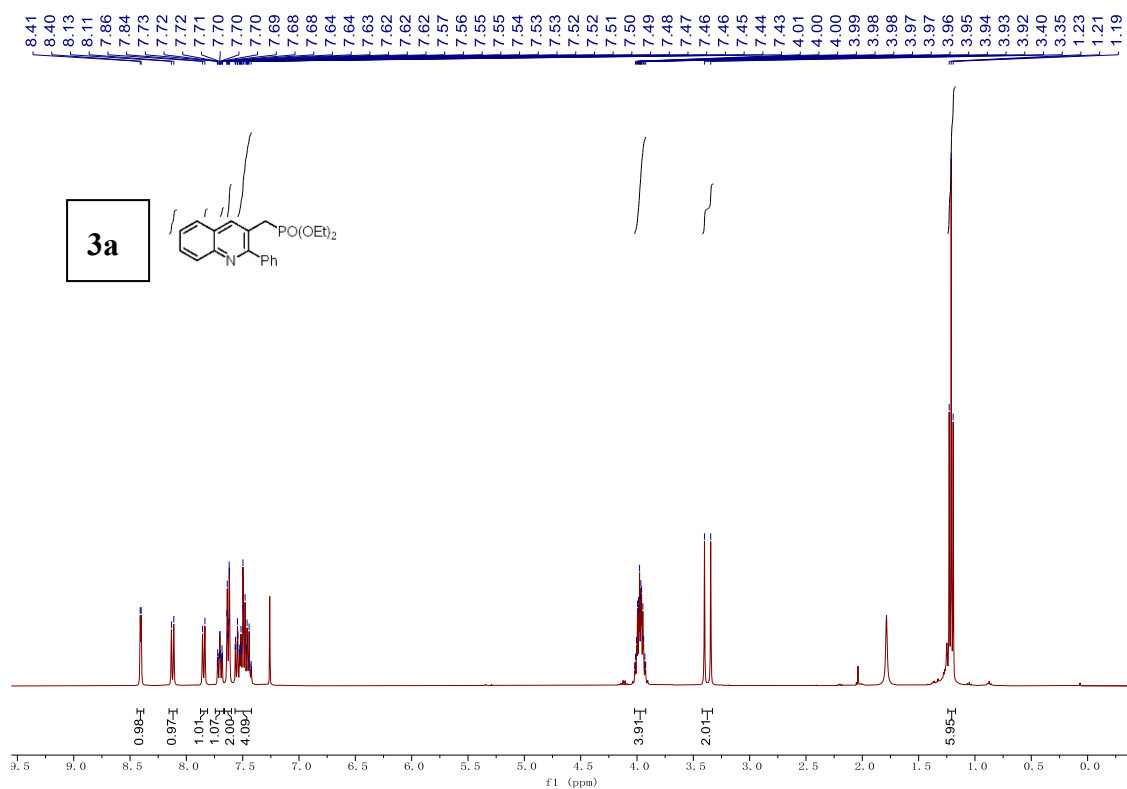
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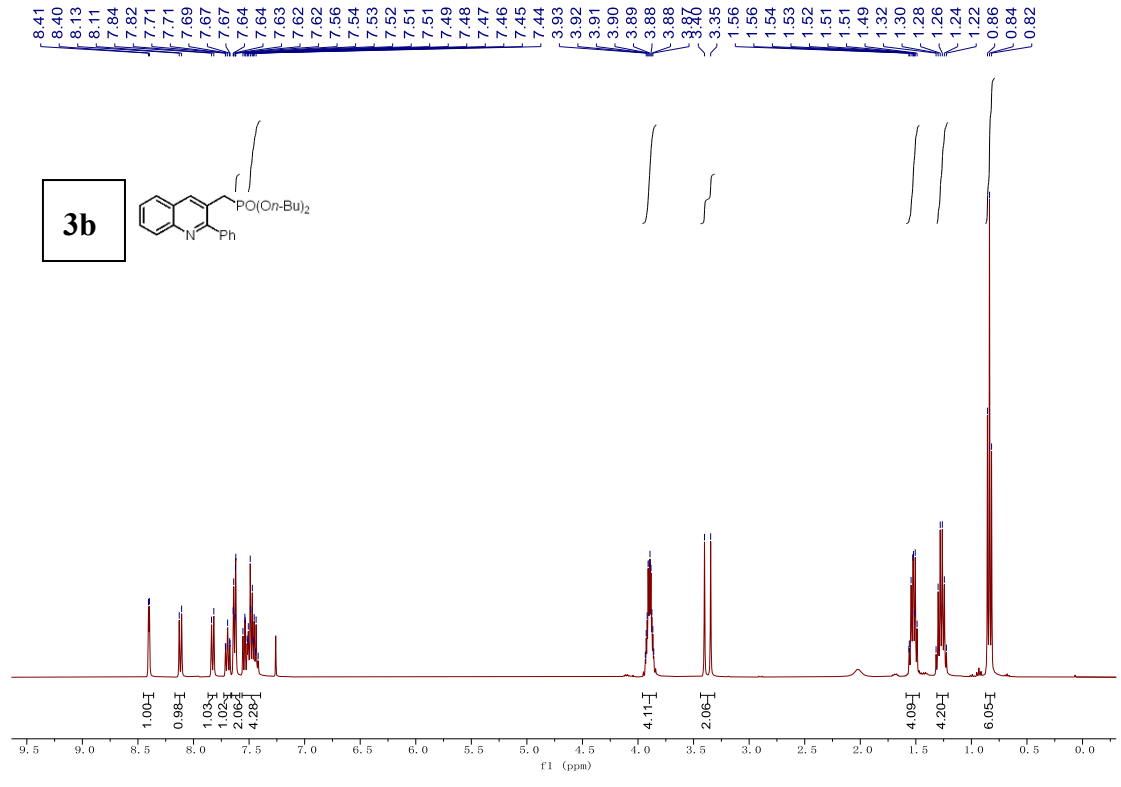
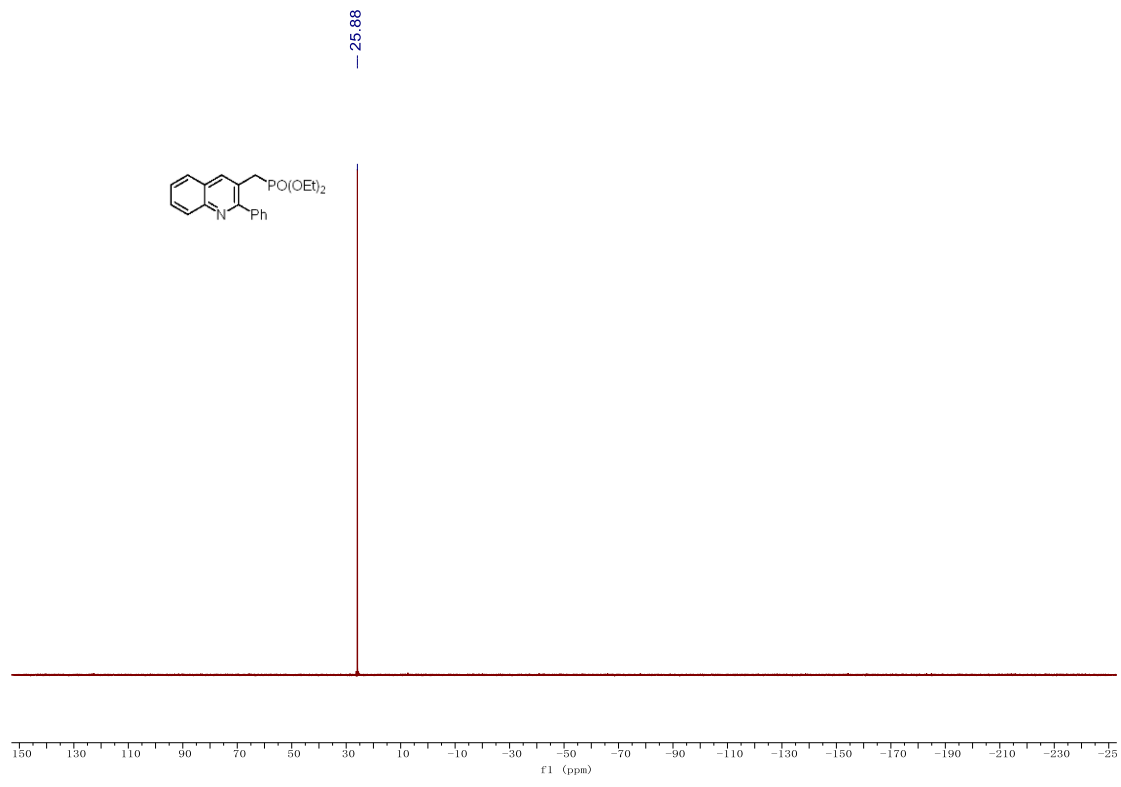
CCDC#2521916 contains the supplementary crystallographic data for this structure.

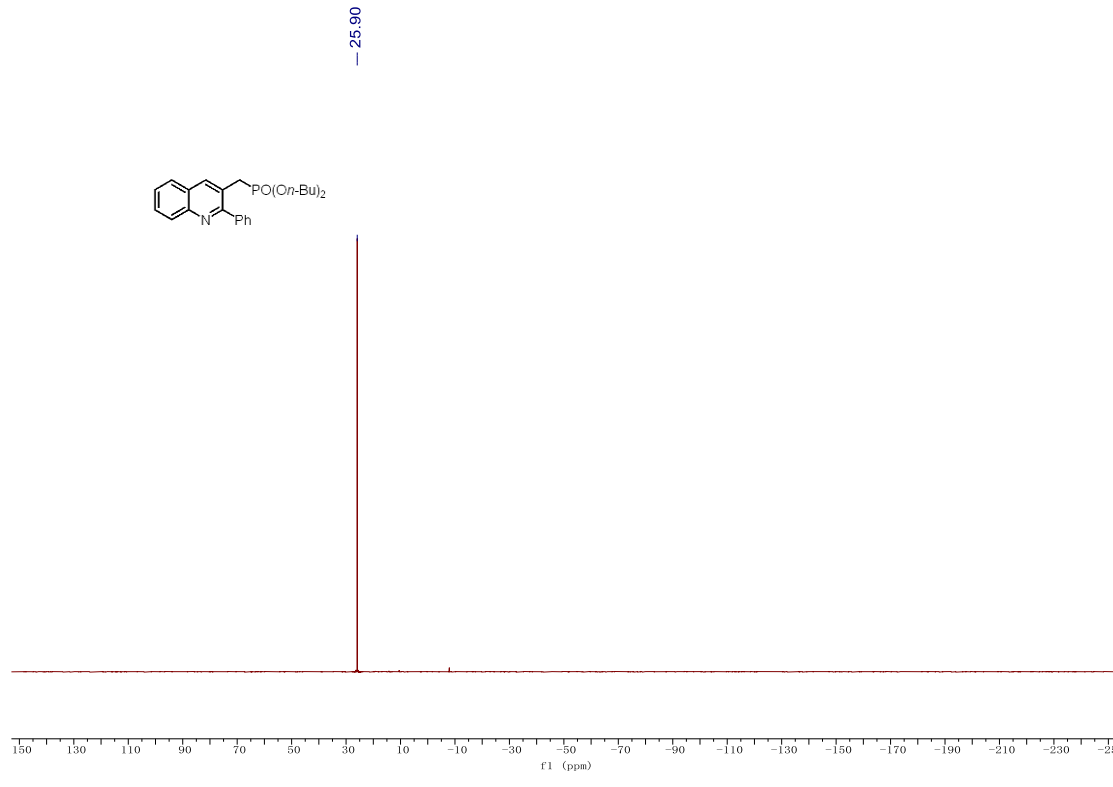
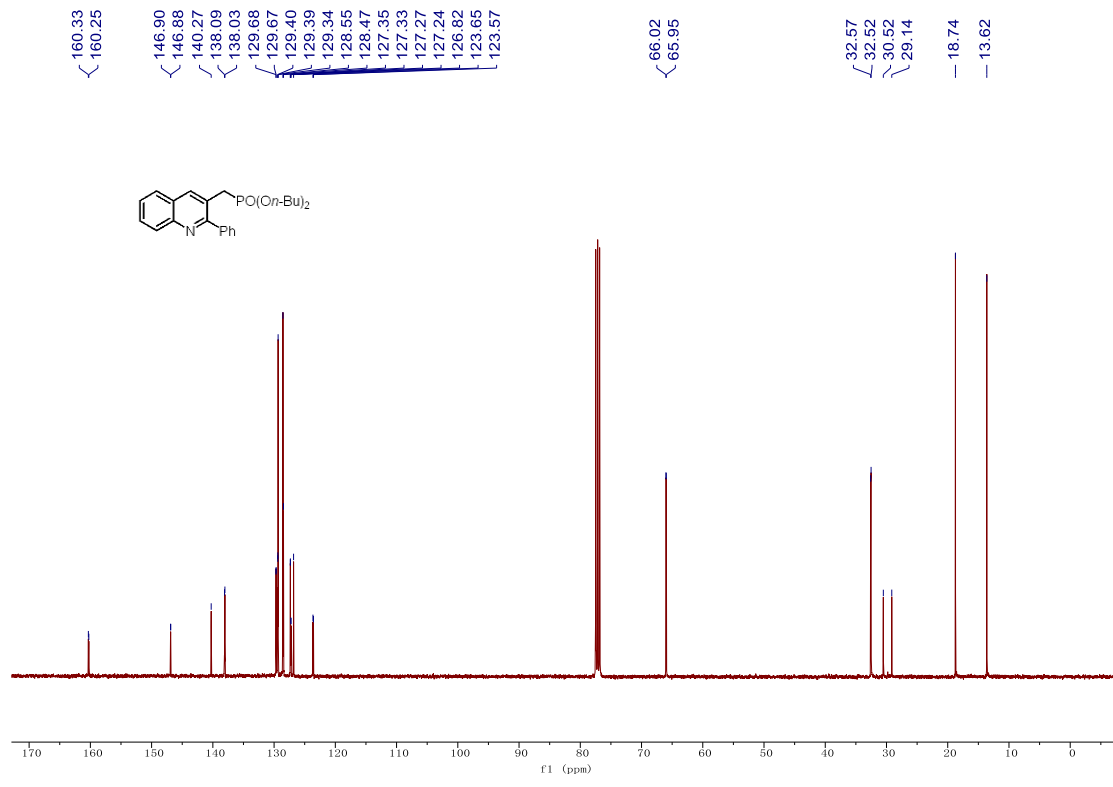
The data can be Cambridge obtained free of charge from the Crystallographic Data

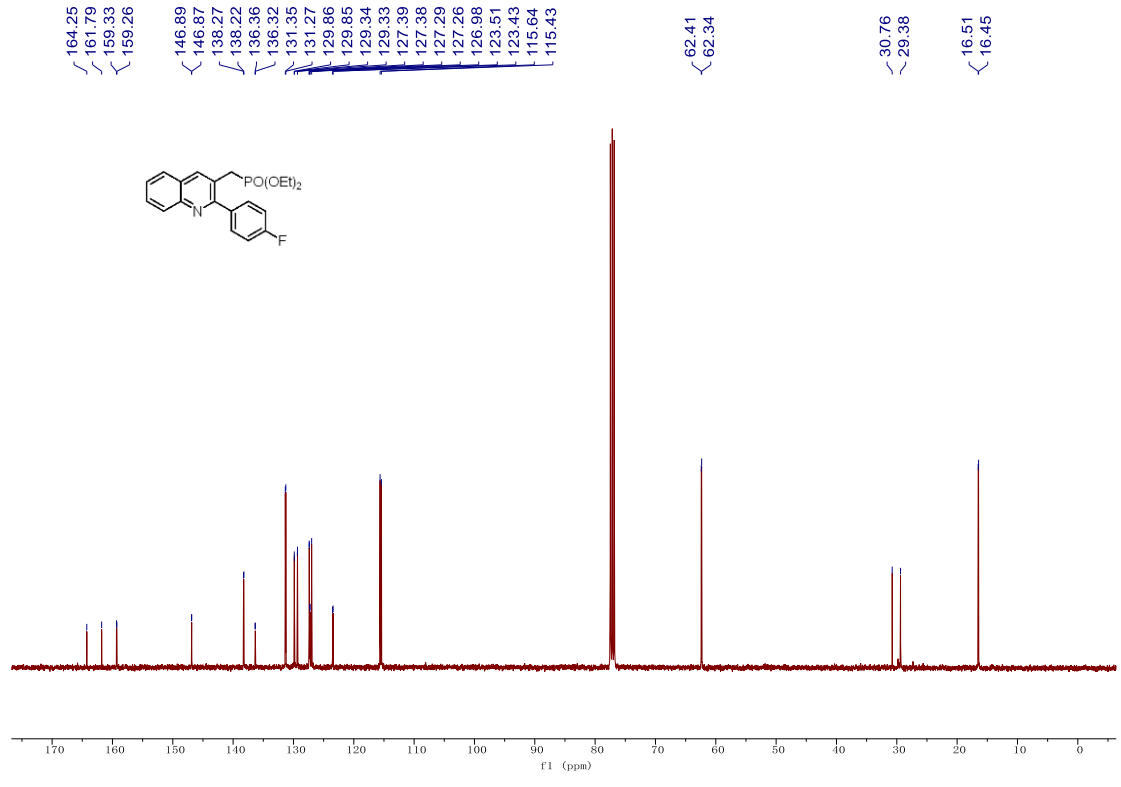
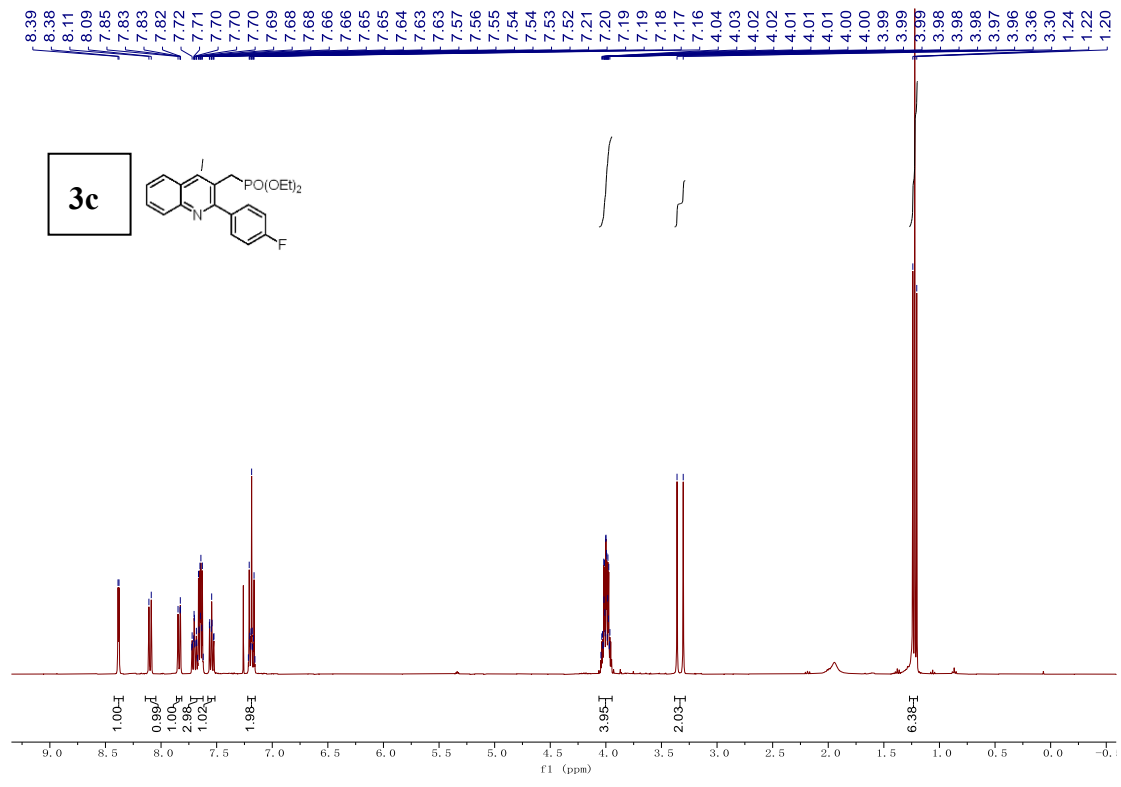
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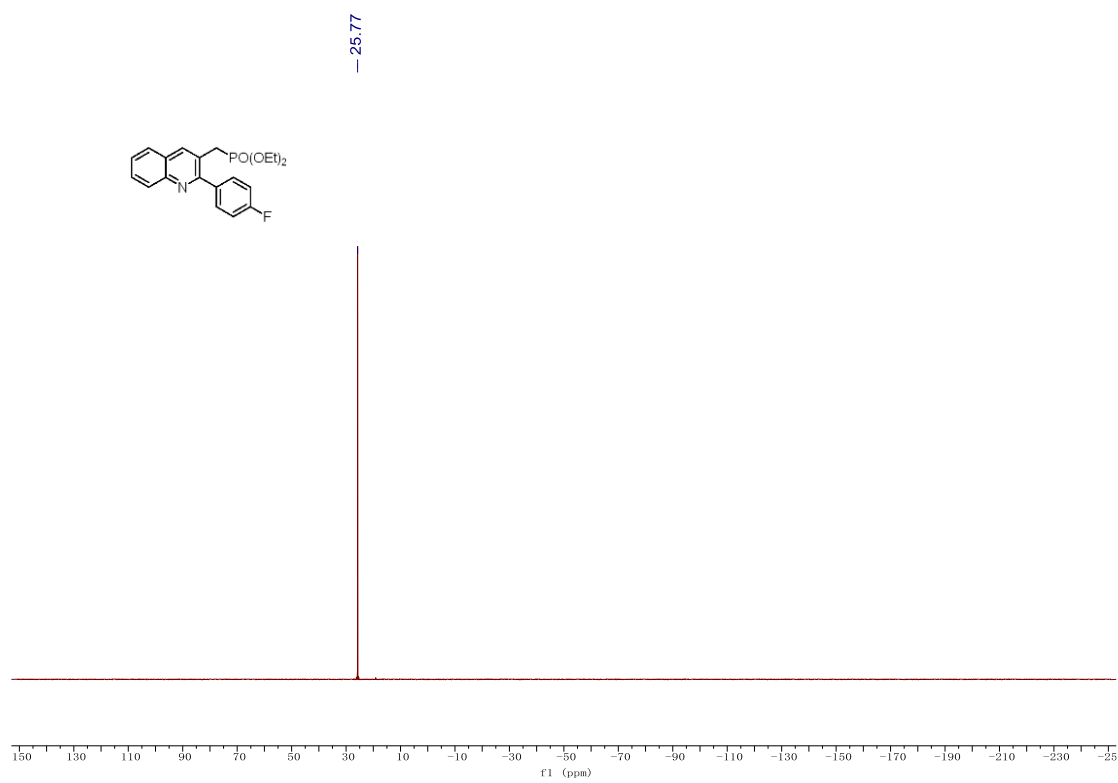
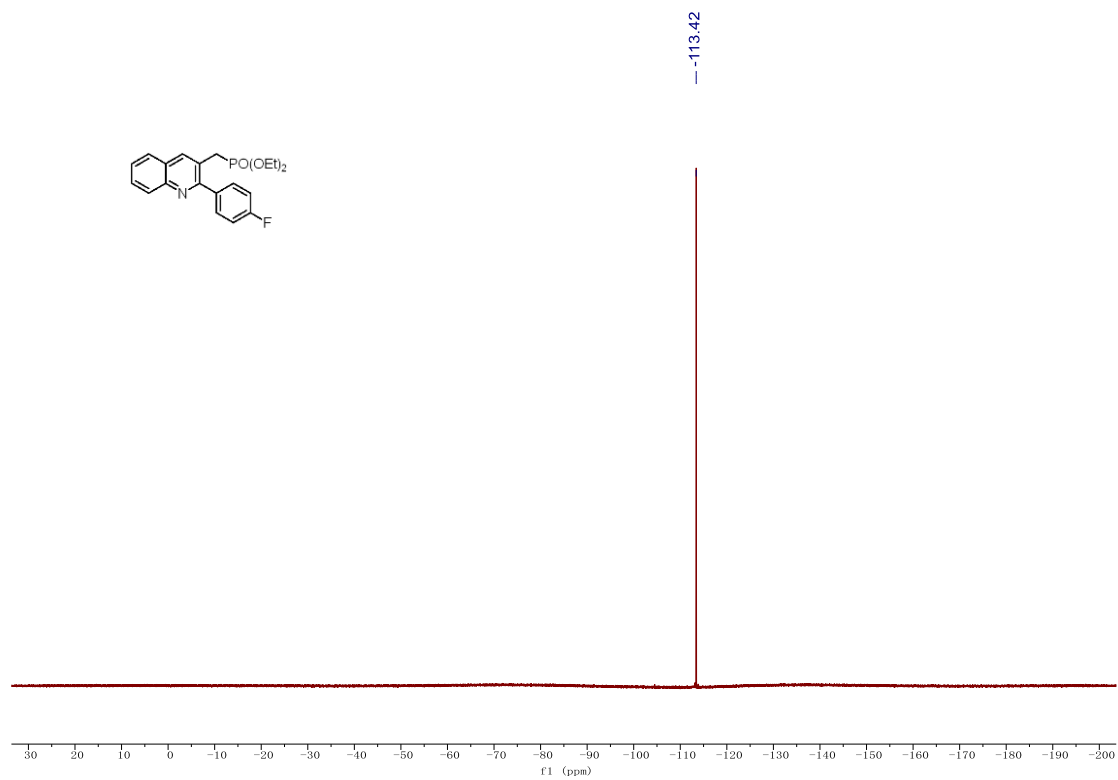
11. Copies of NMR spectra

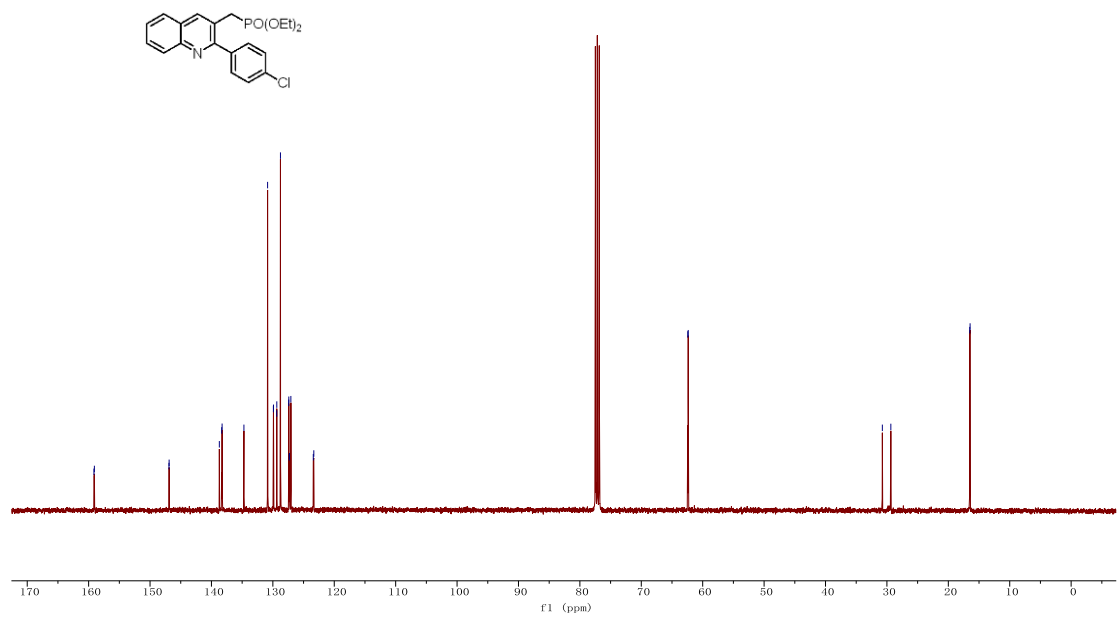
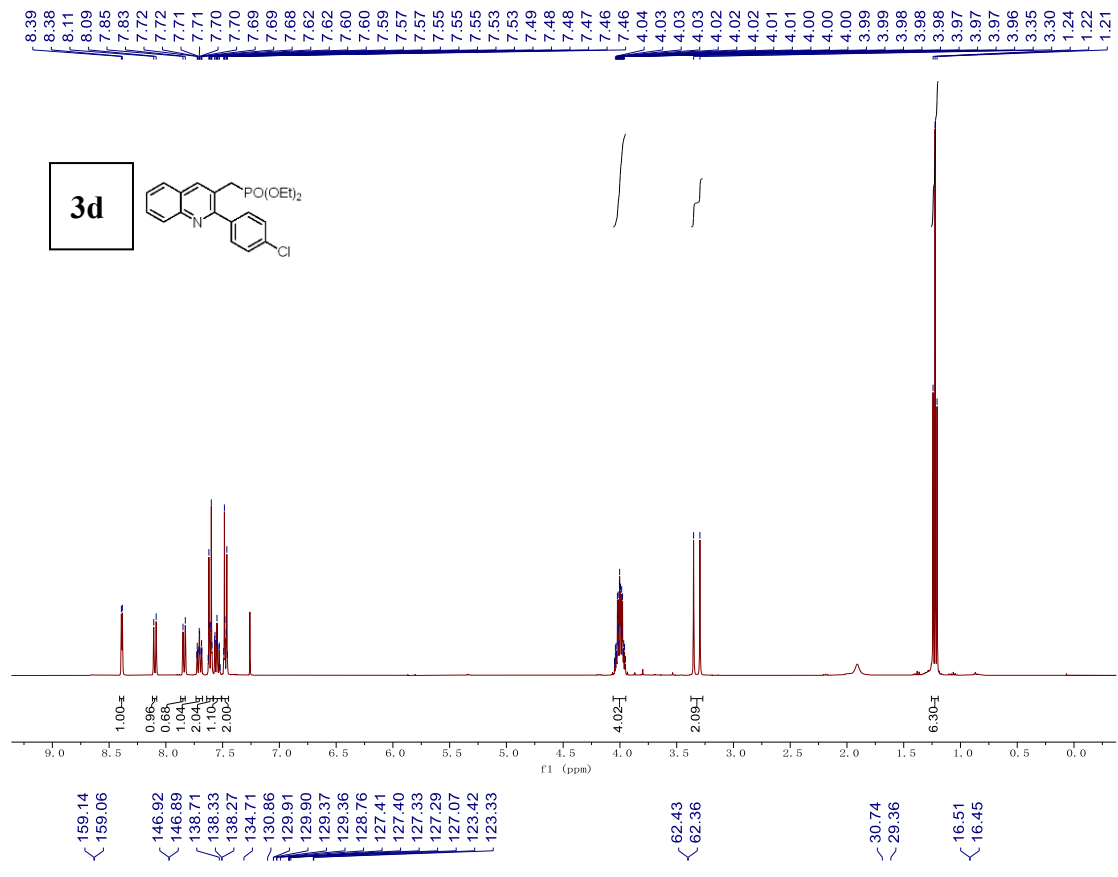


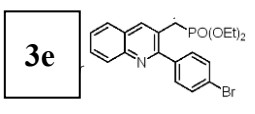
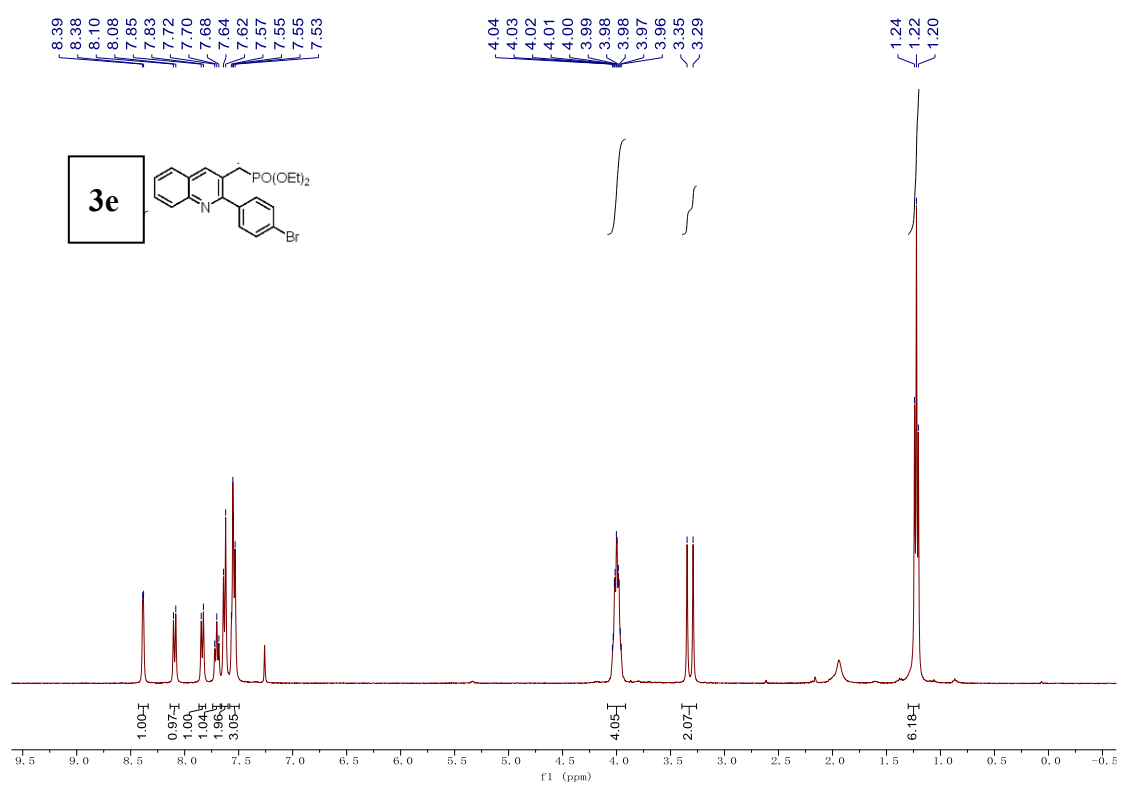
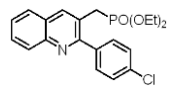
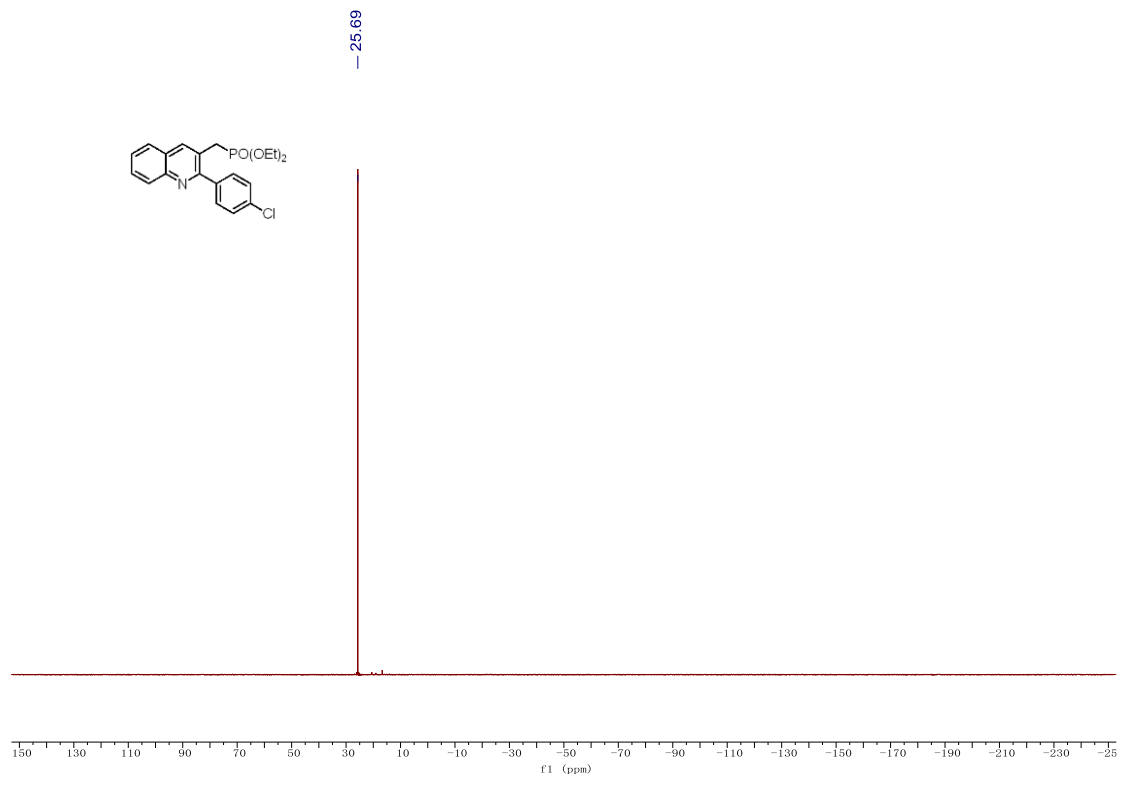


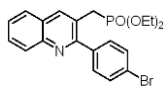
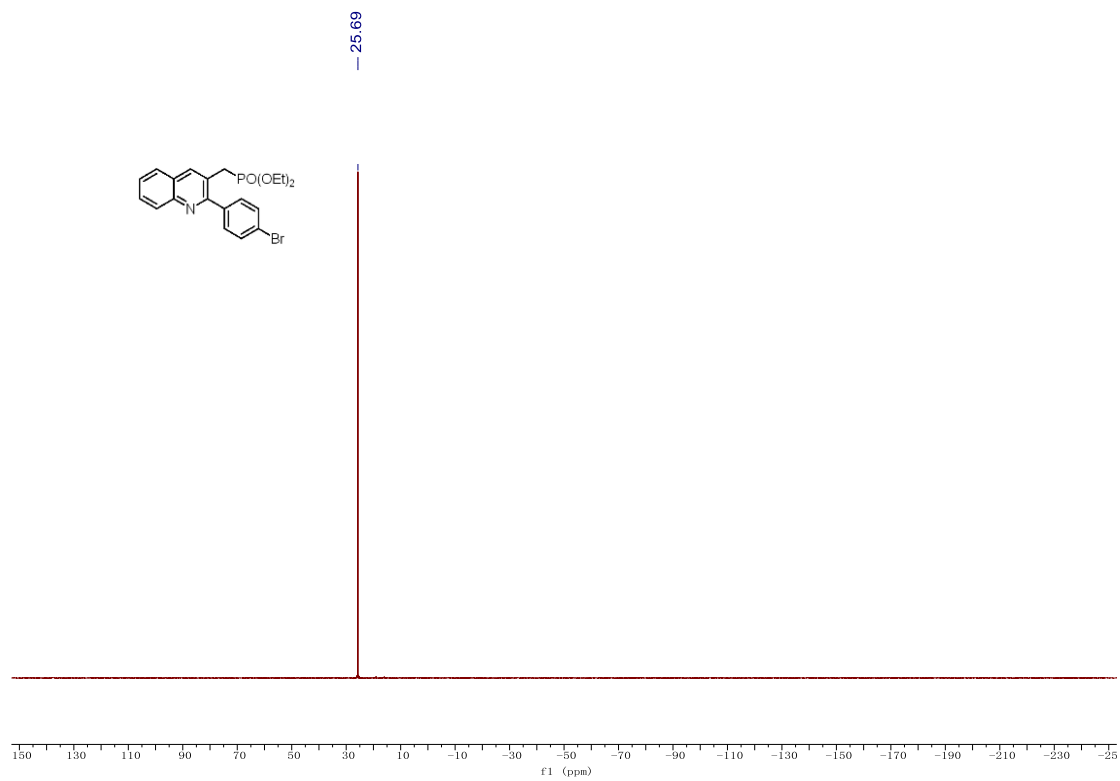
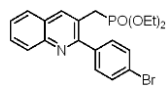
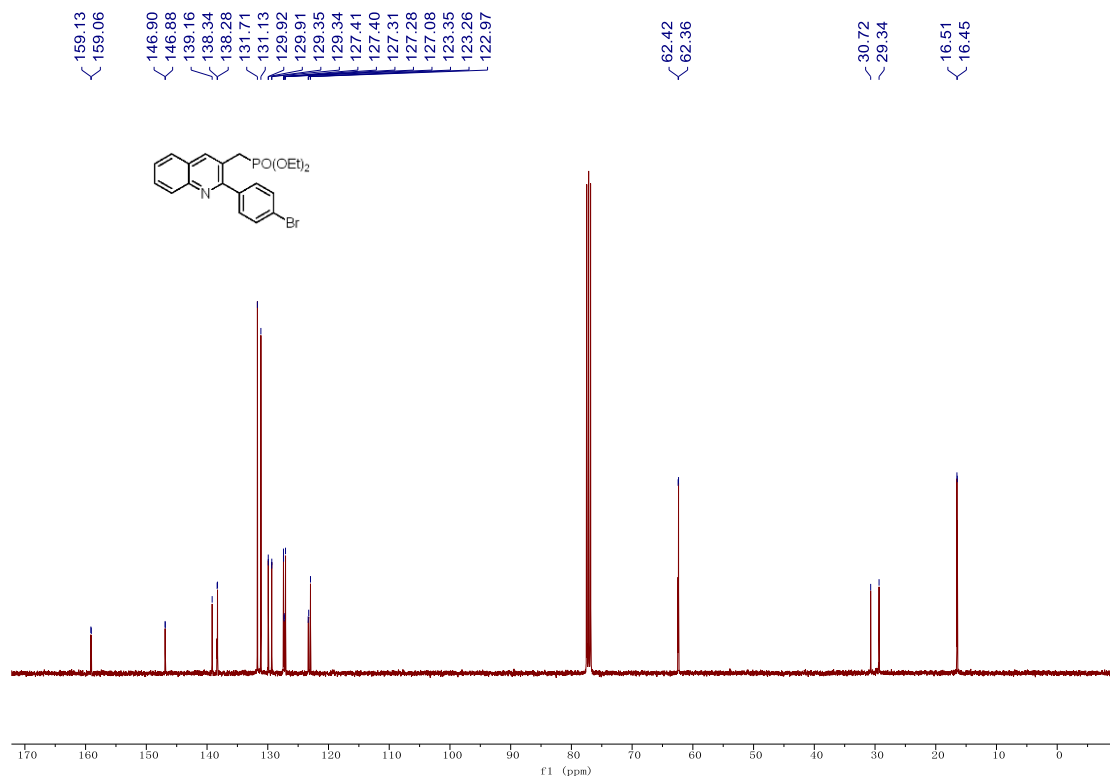


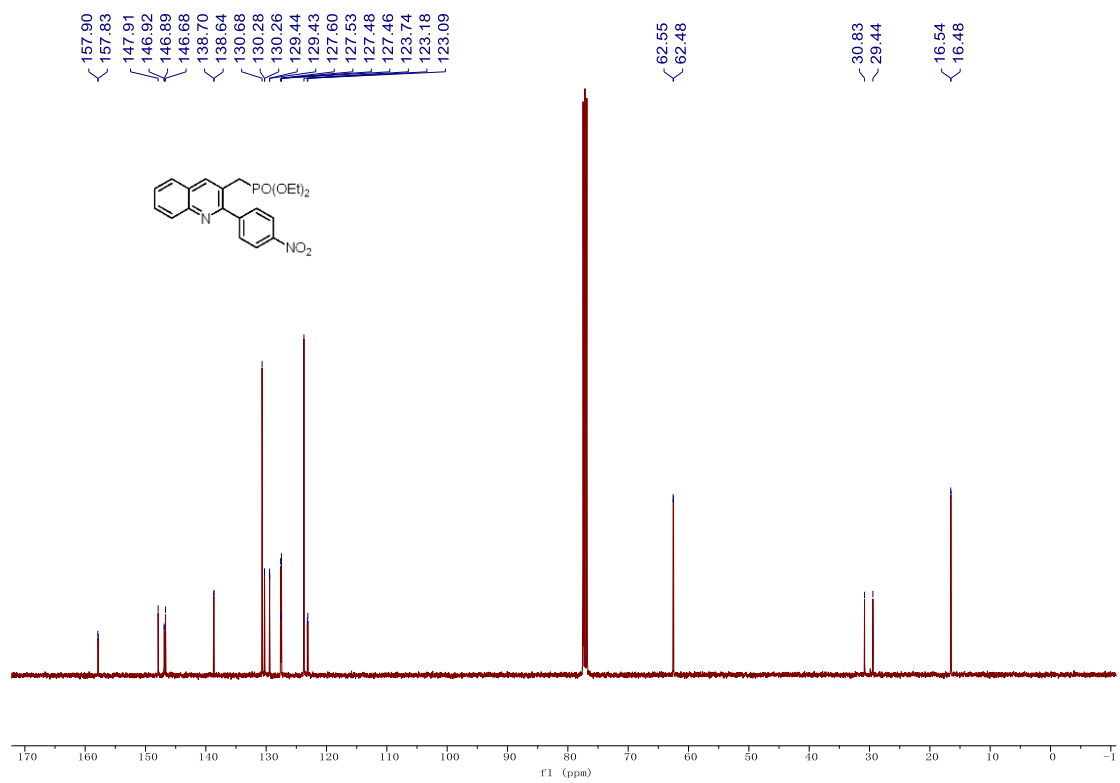
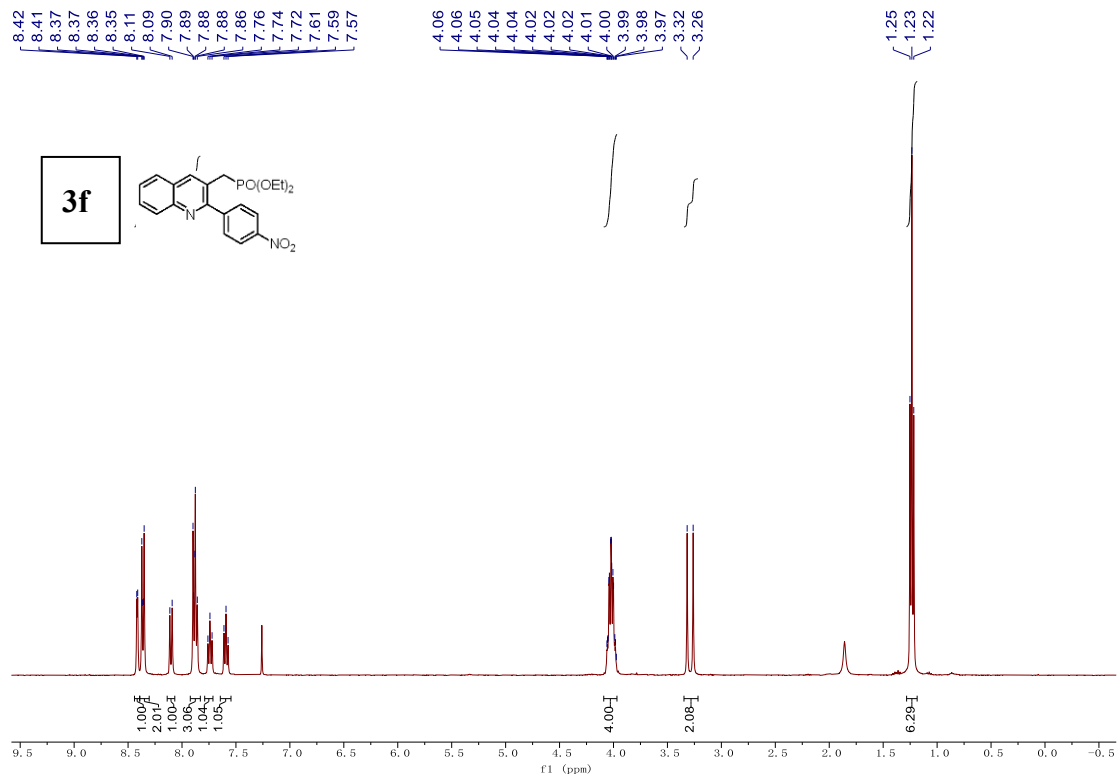


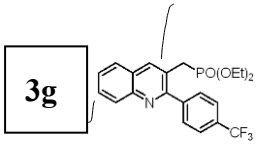
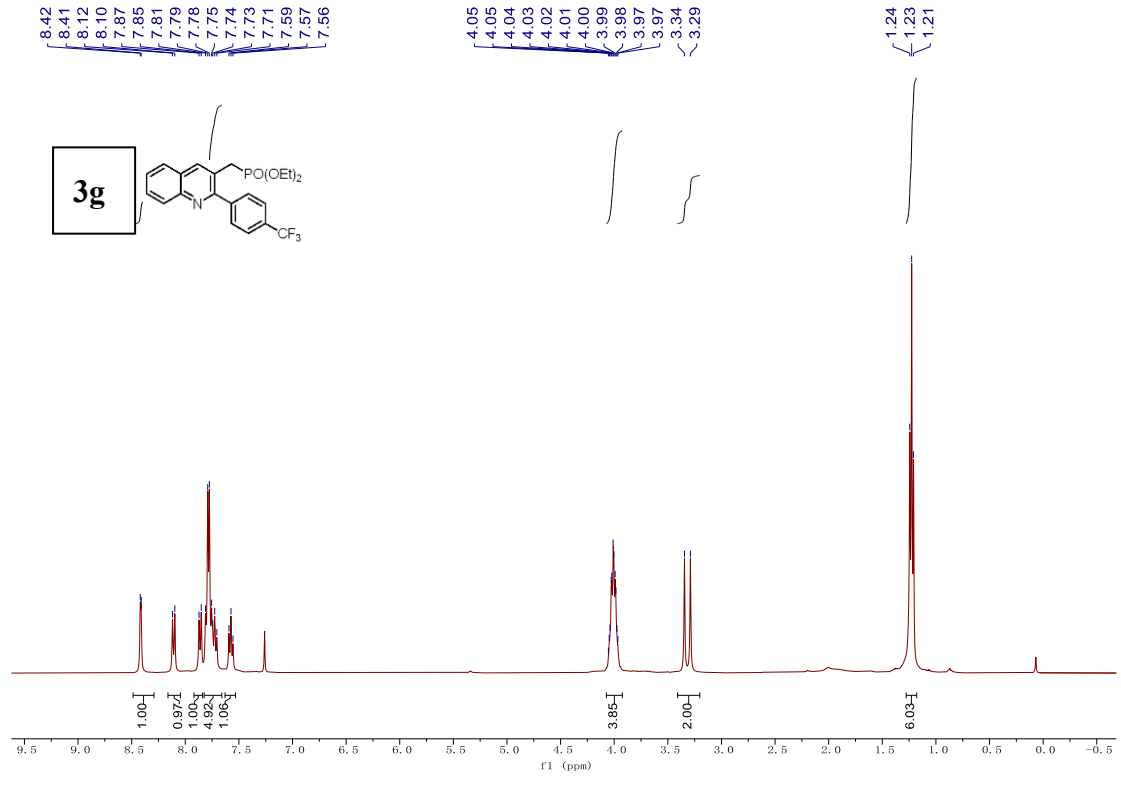
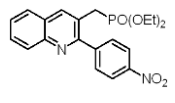
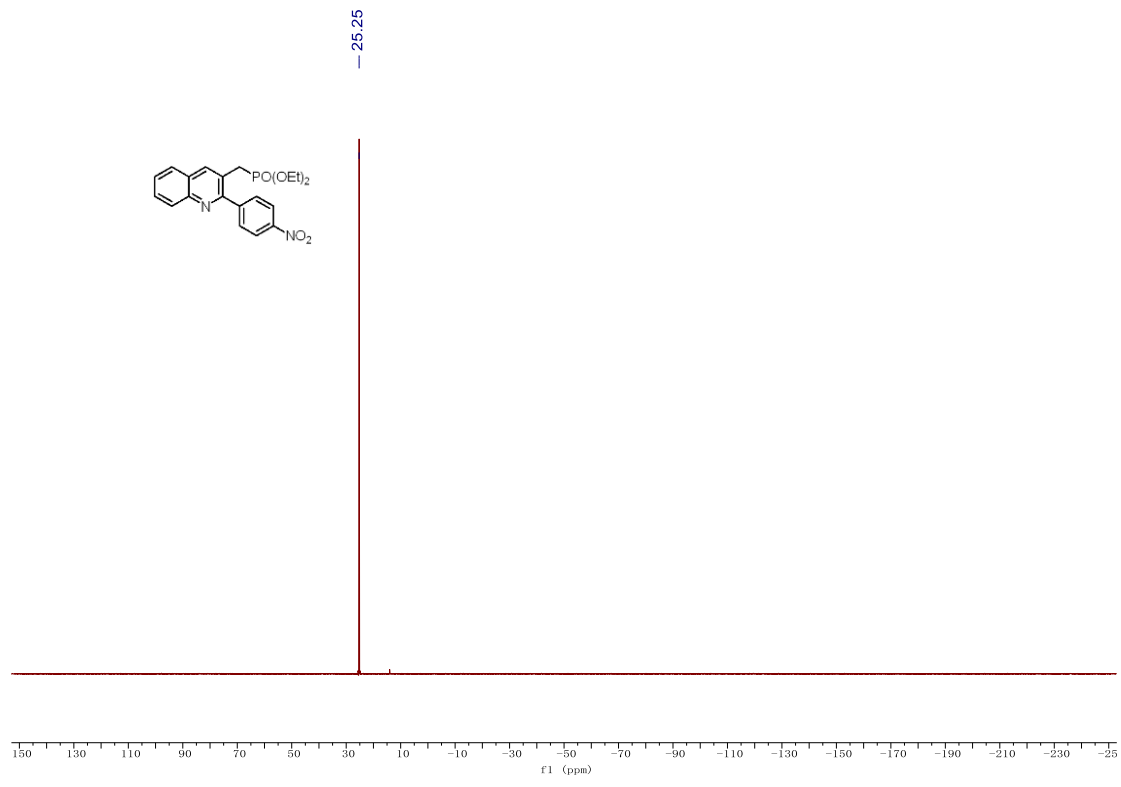


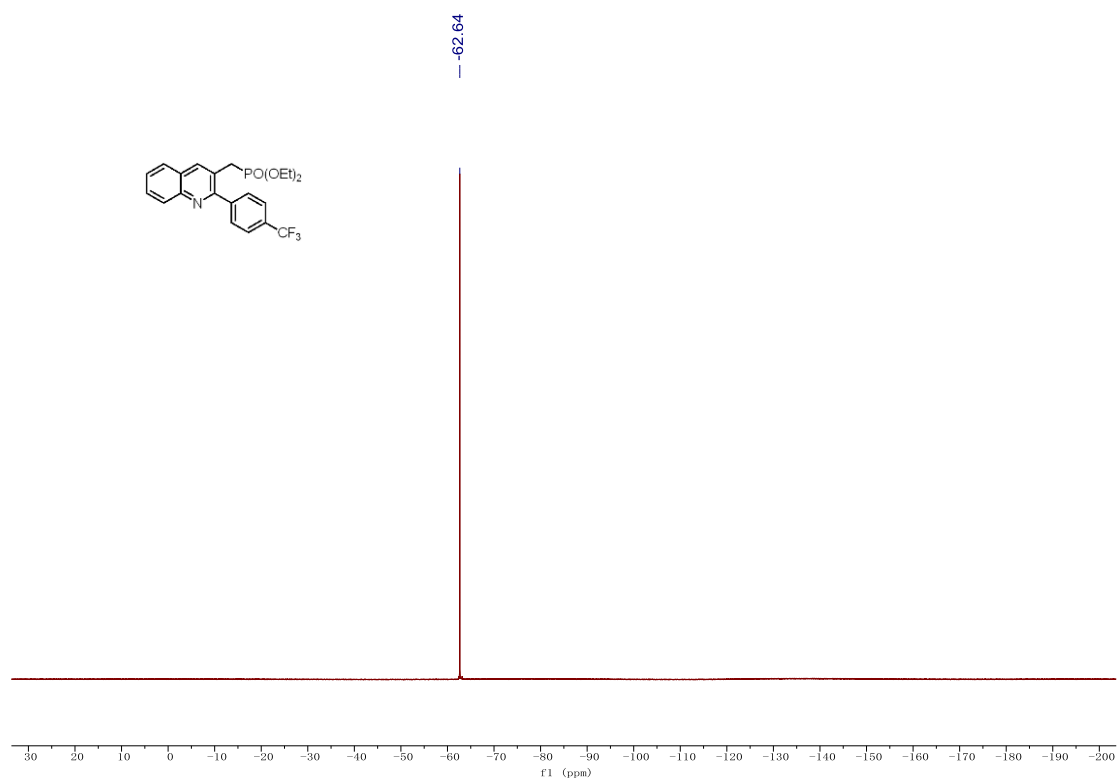
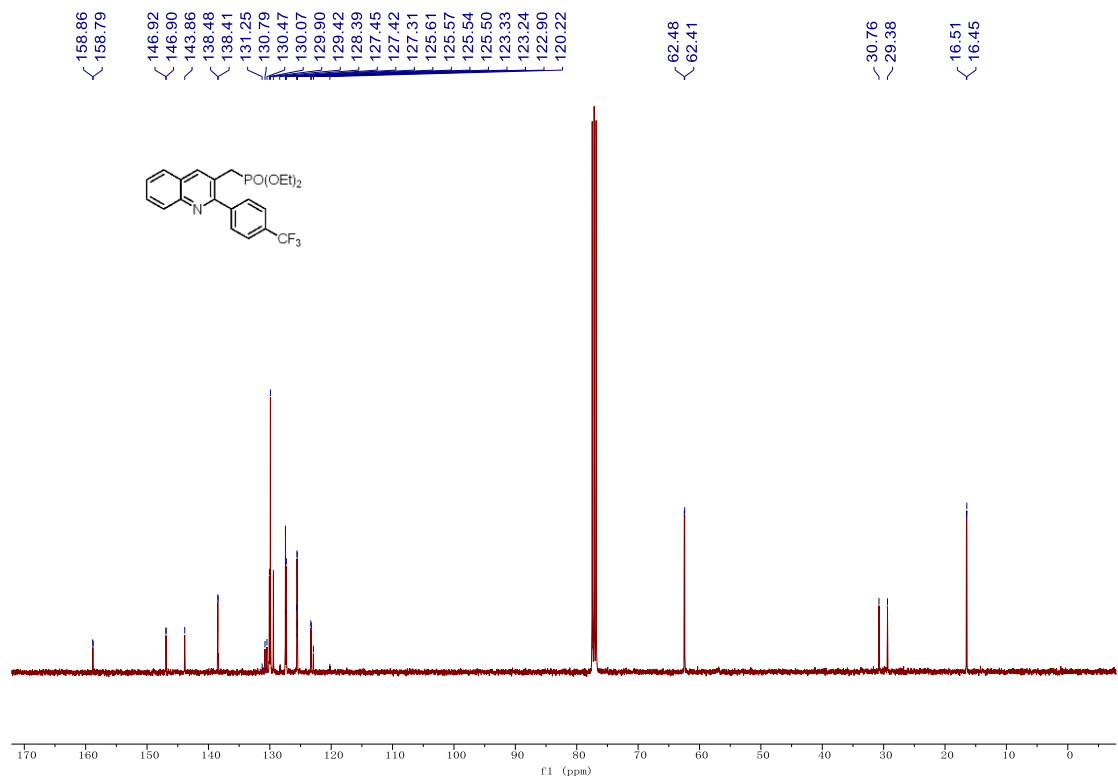


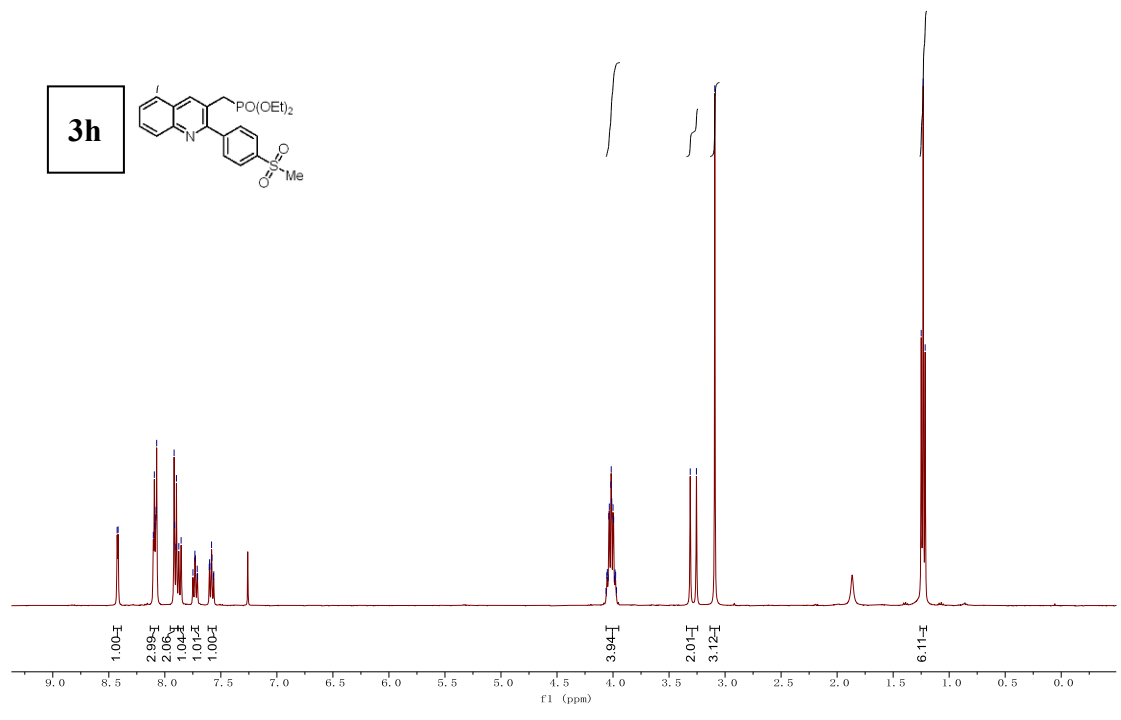
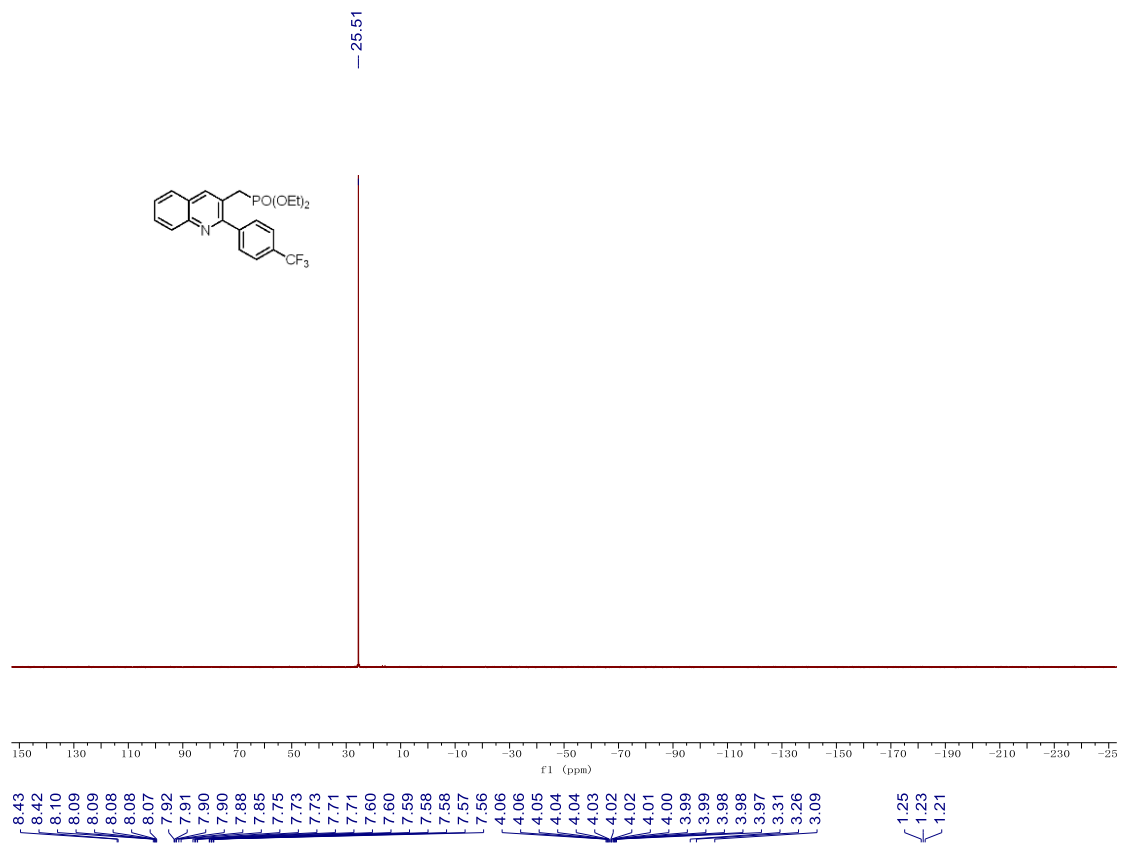


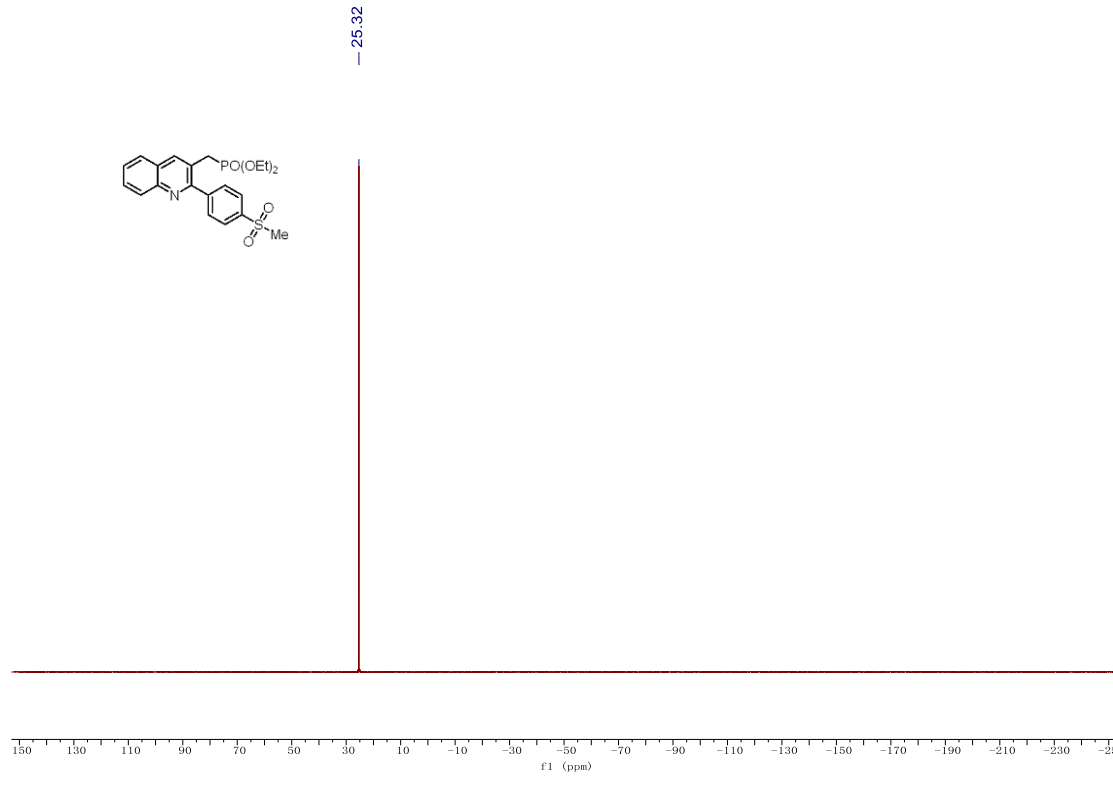
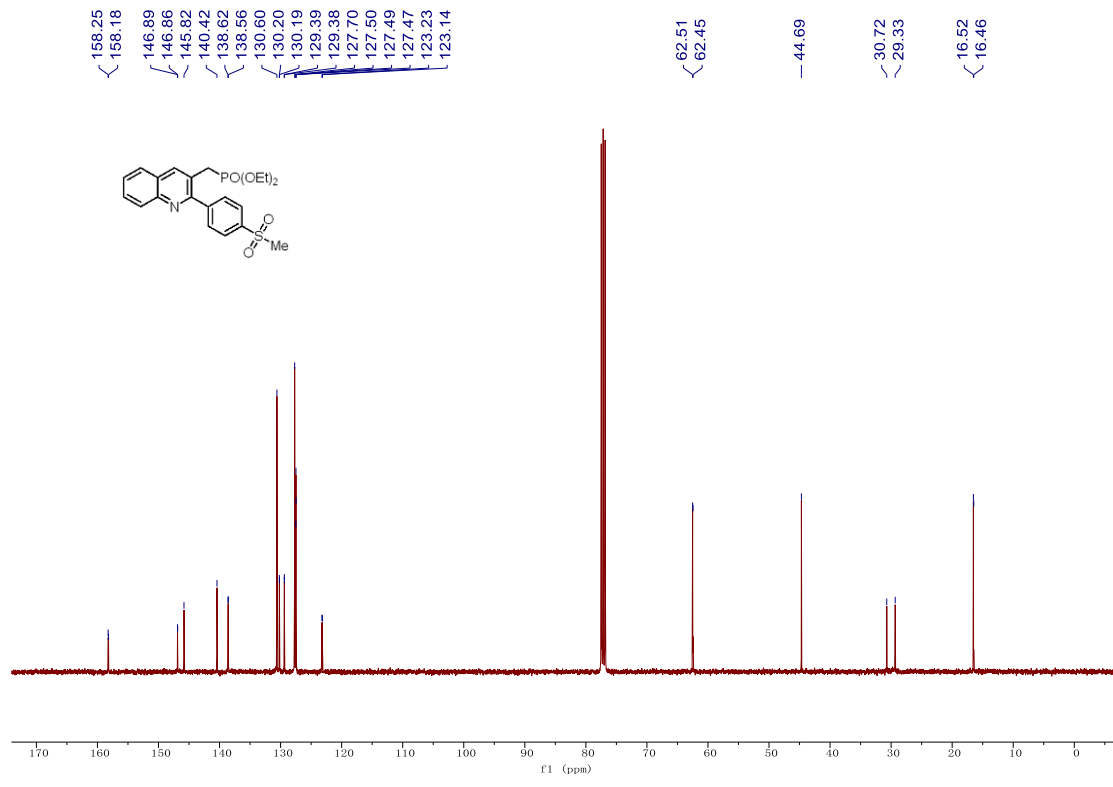


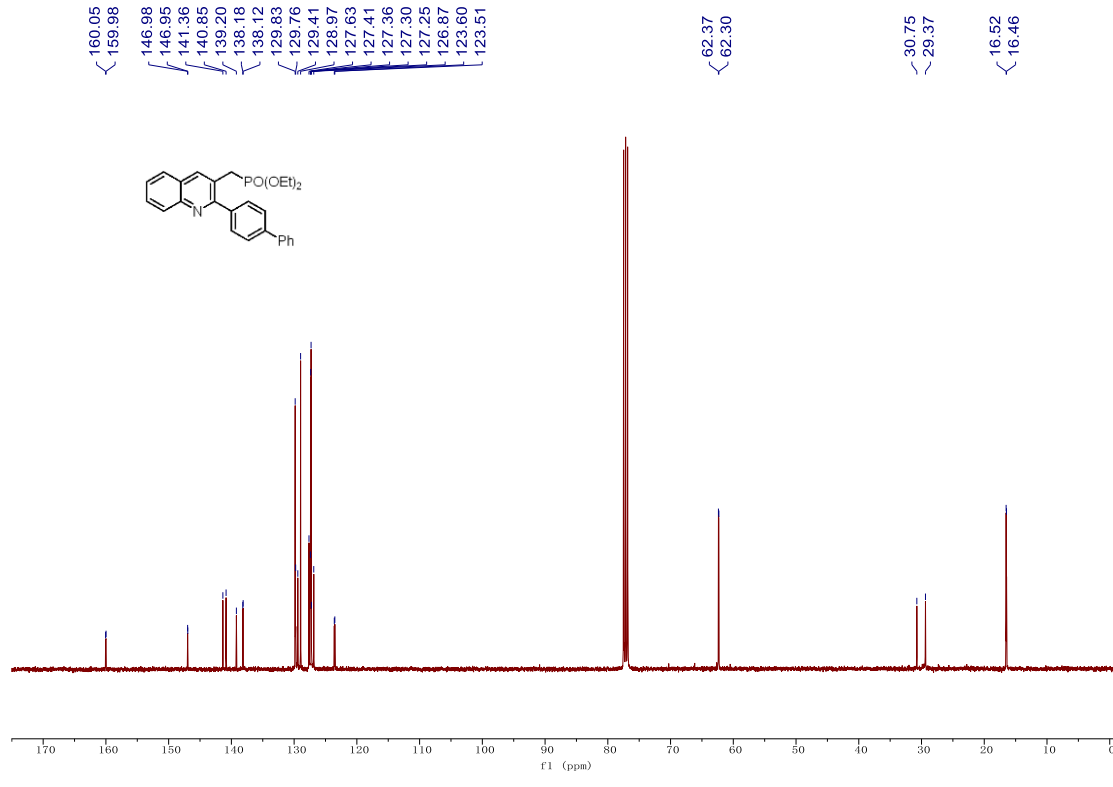
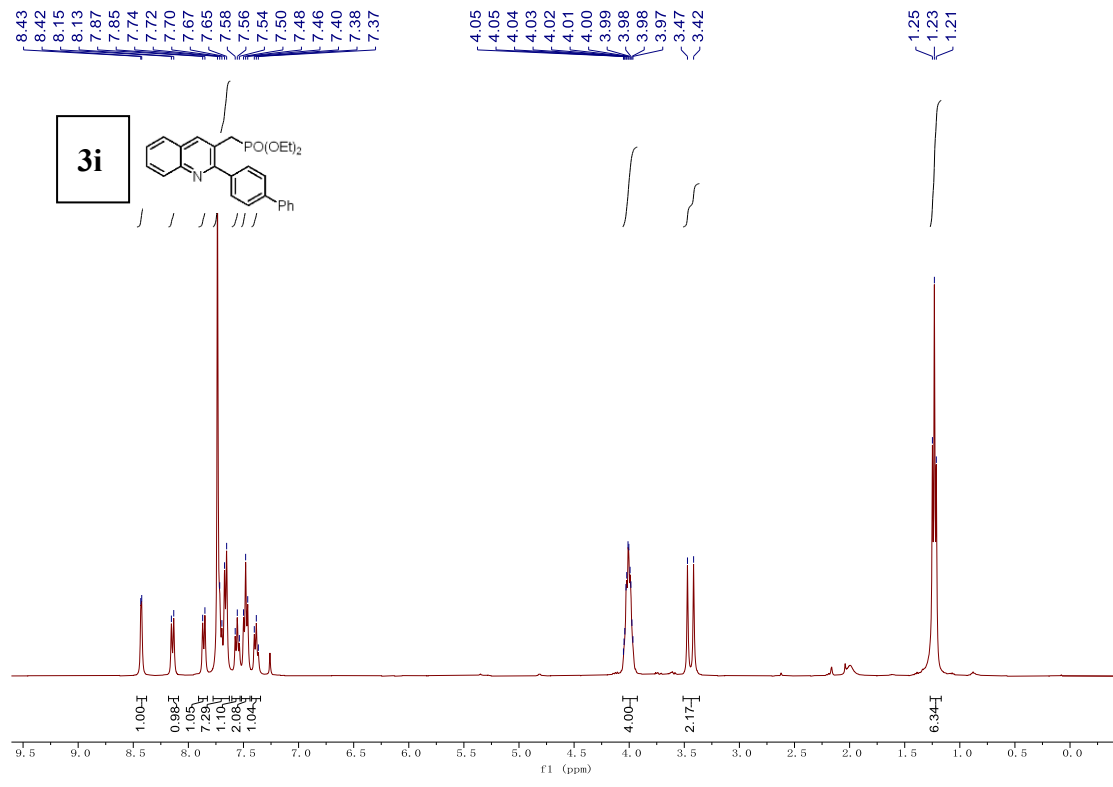


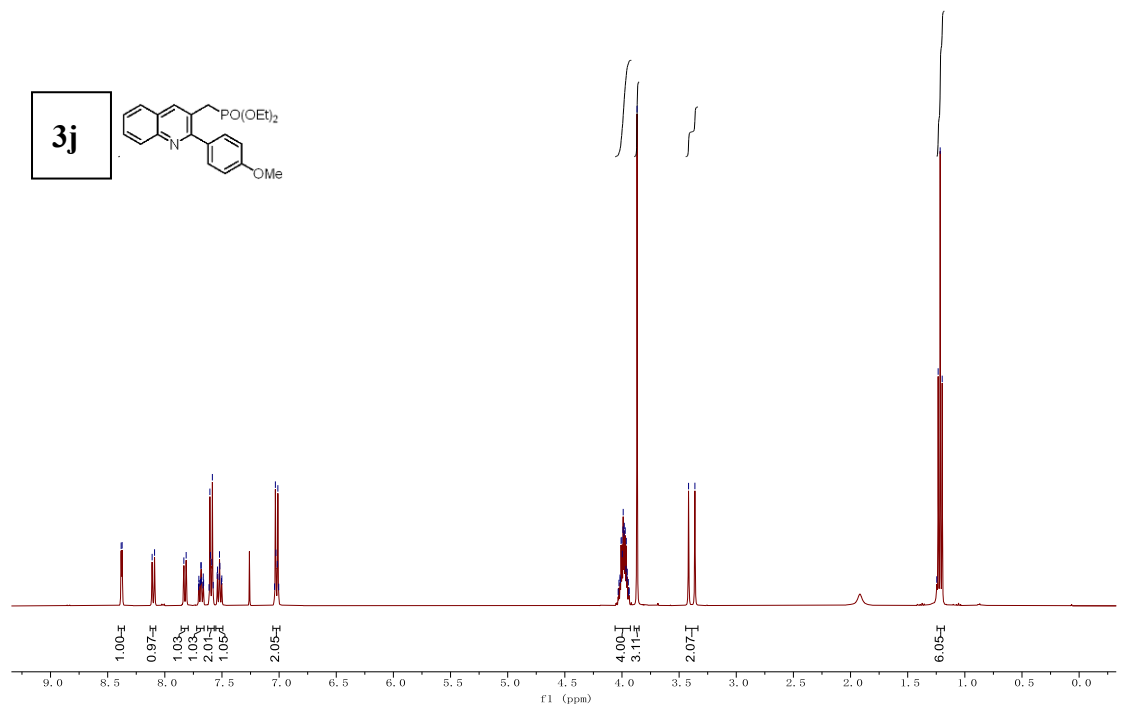
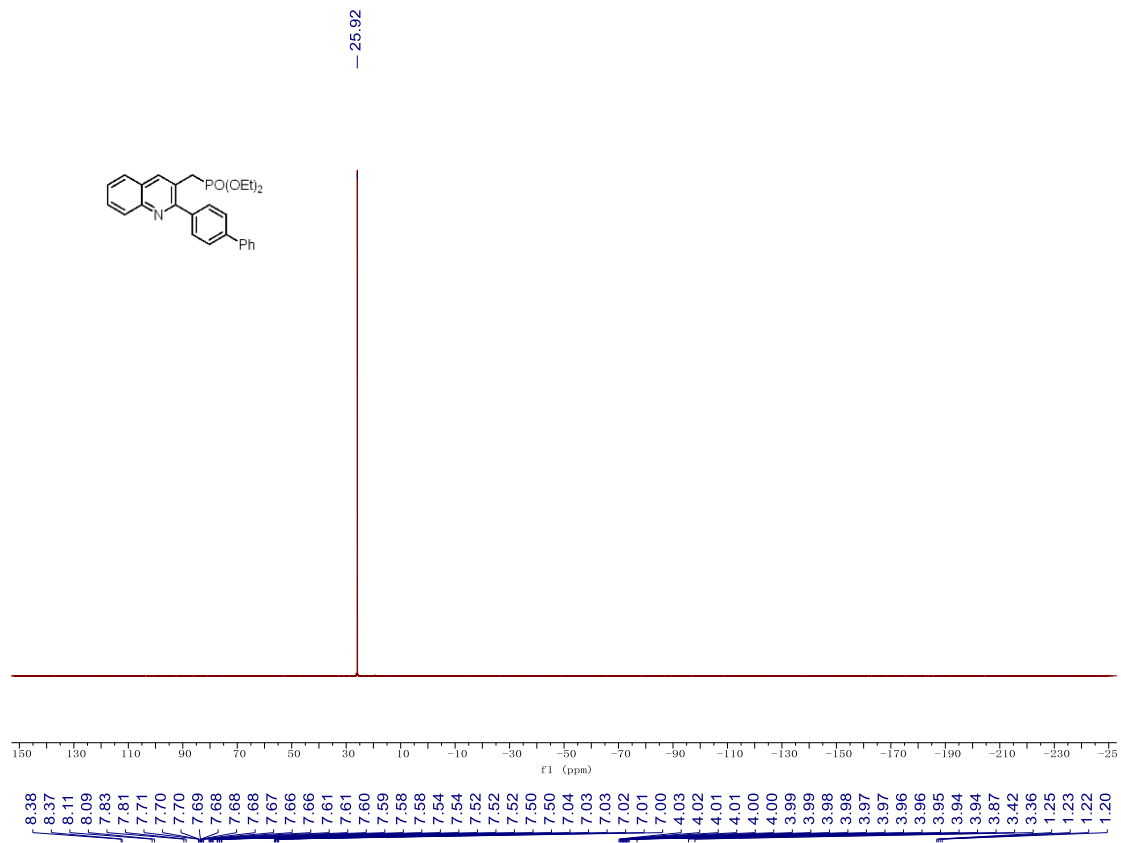


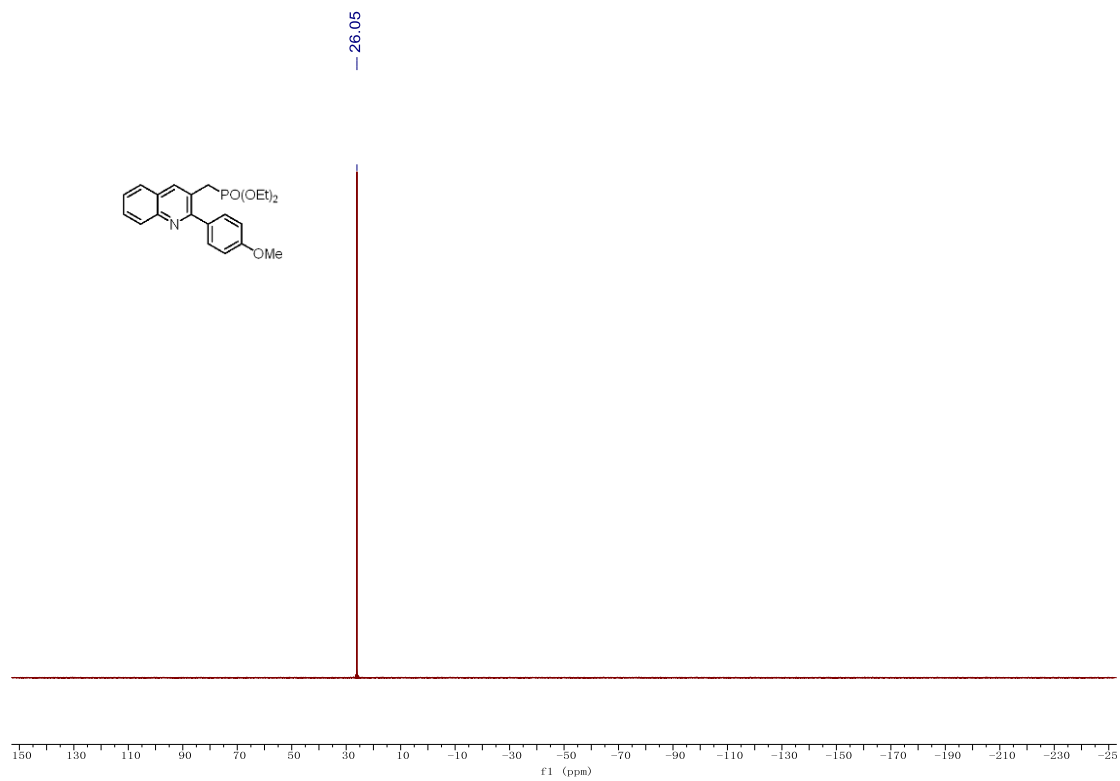
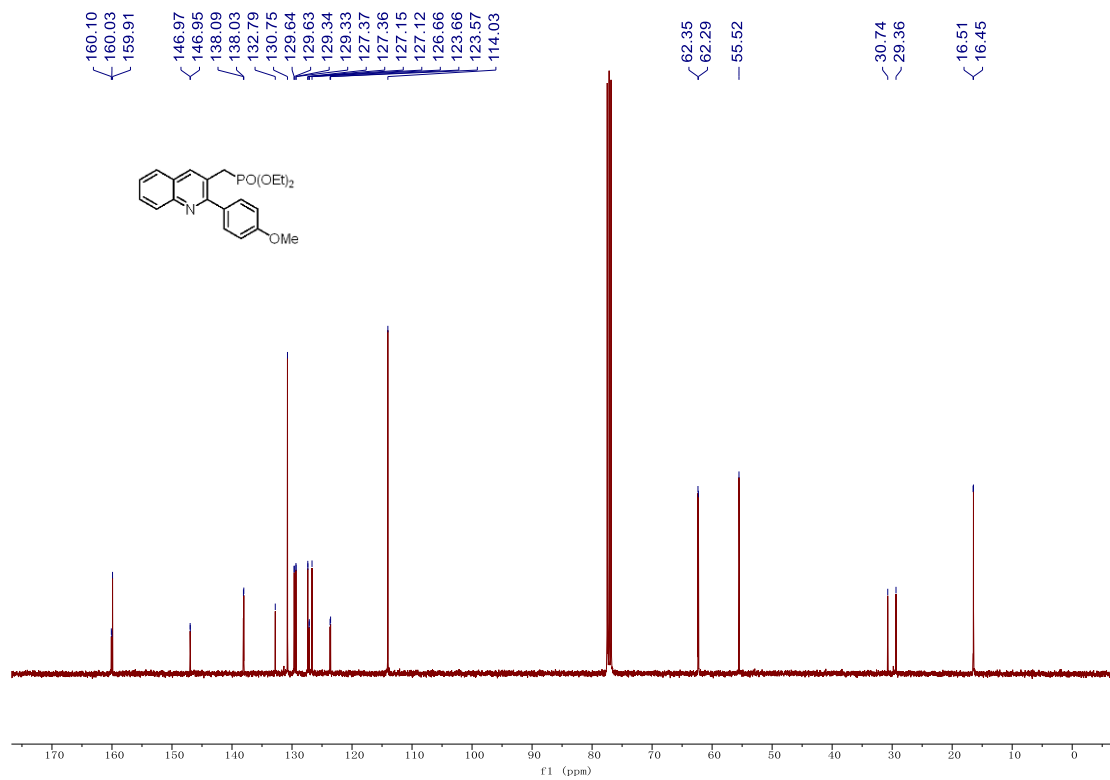


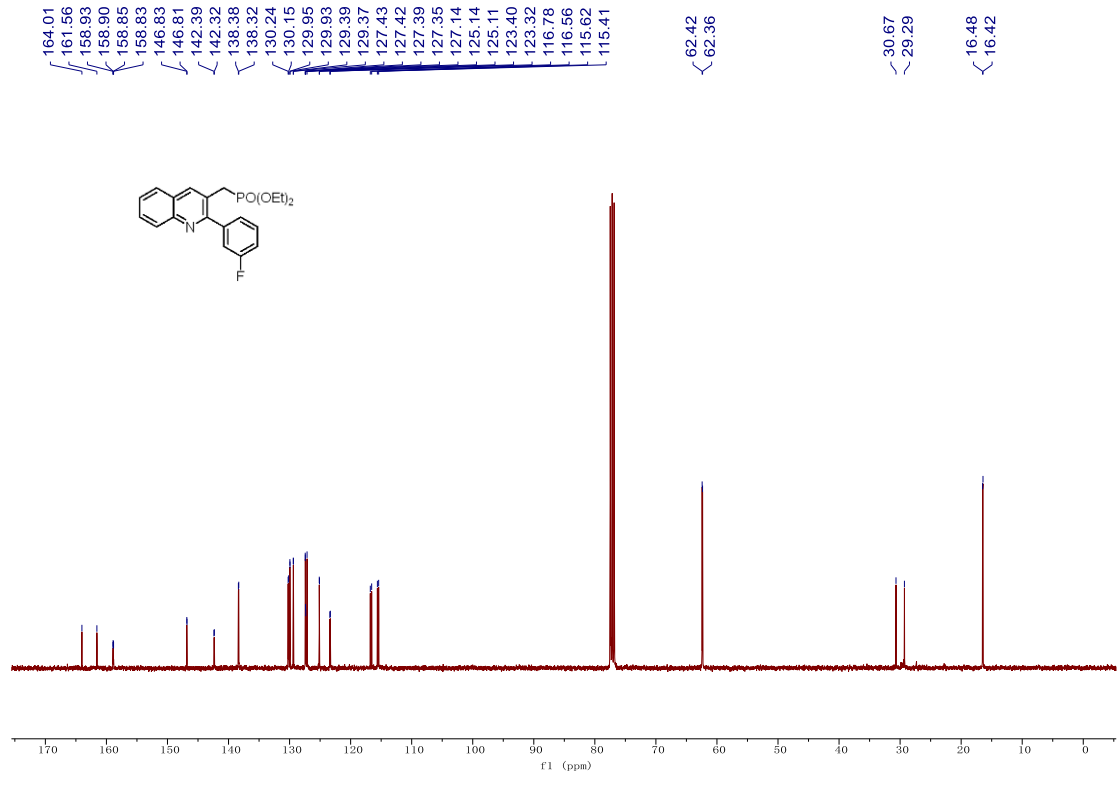
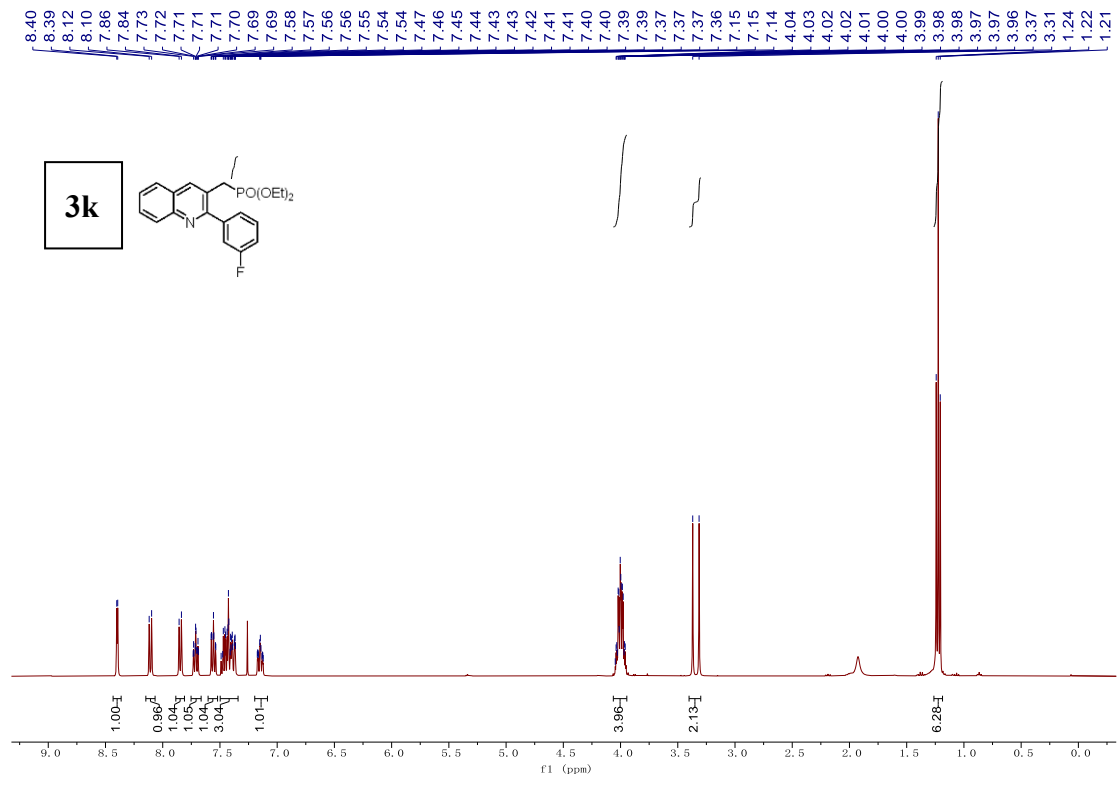


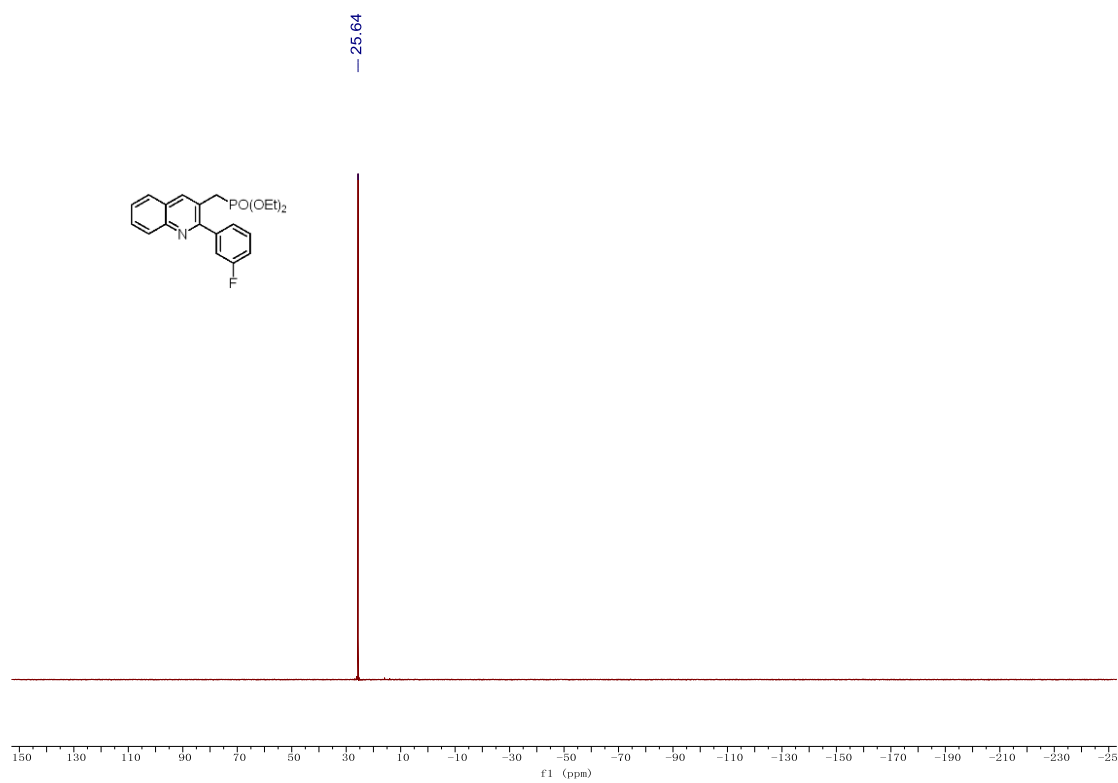
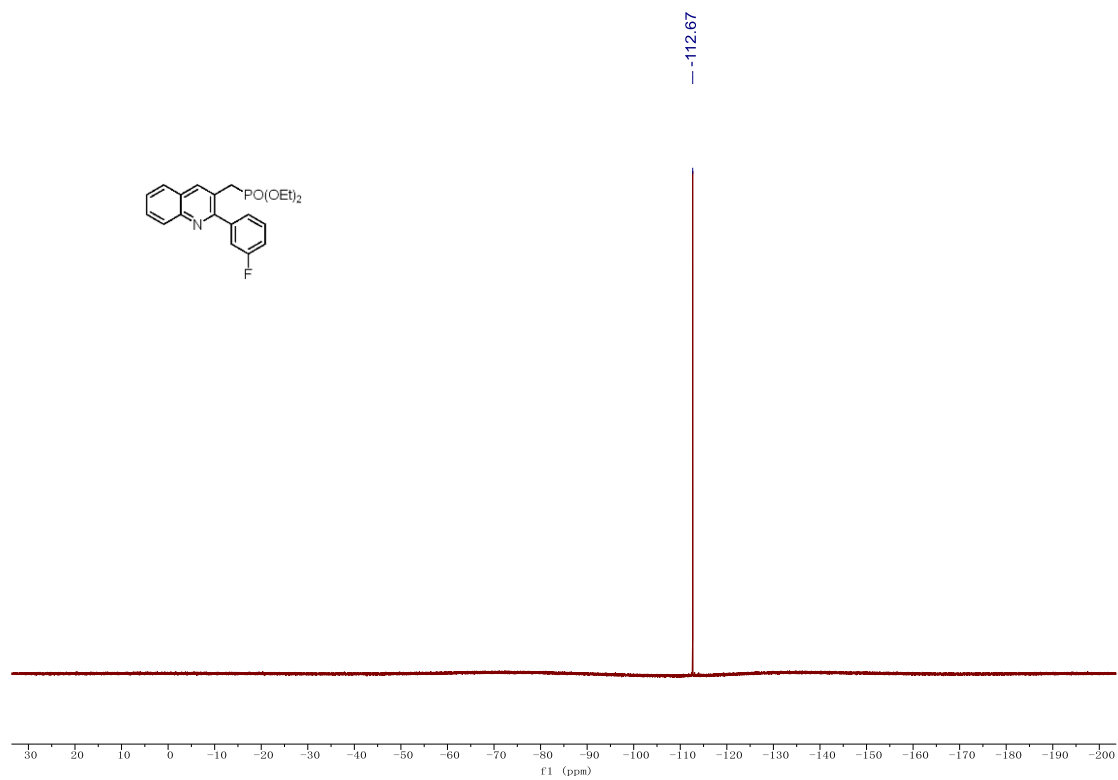


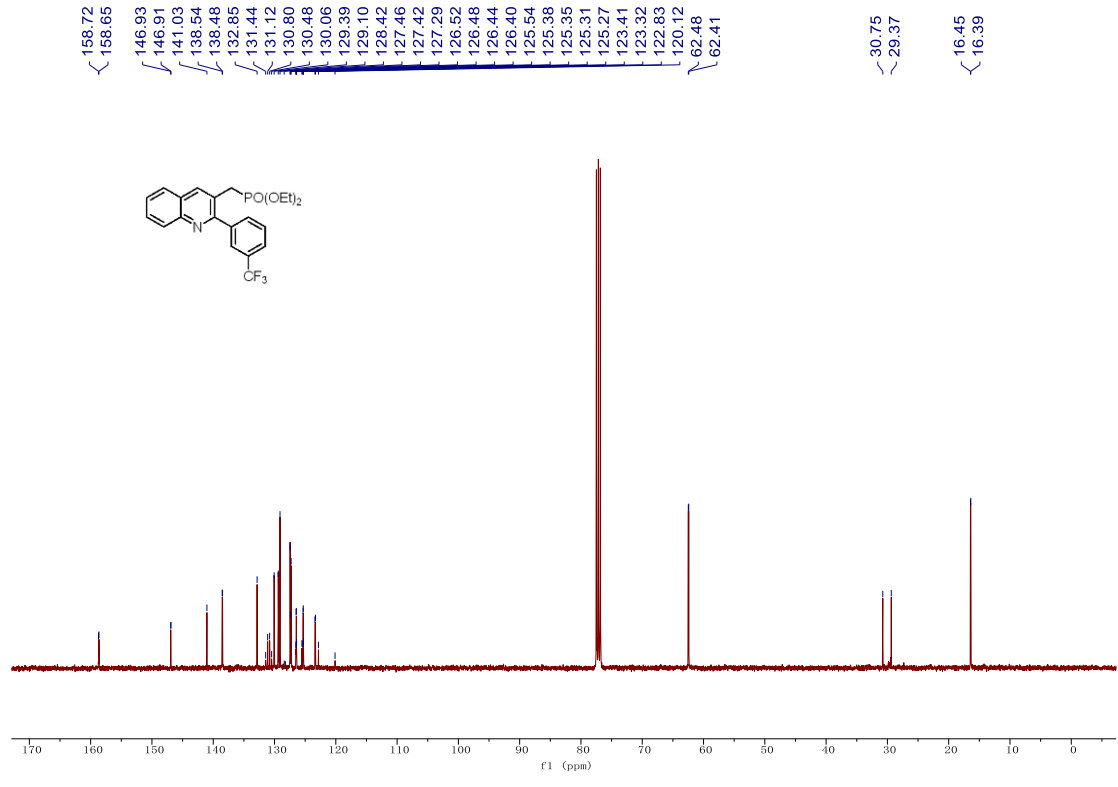
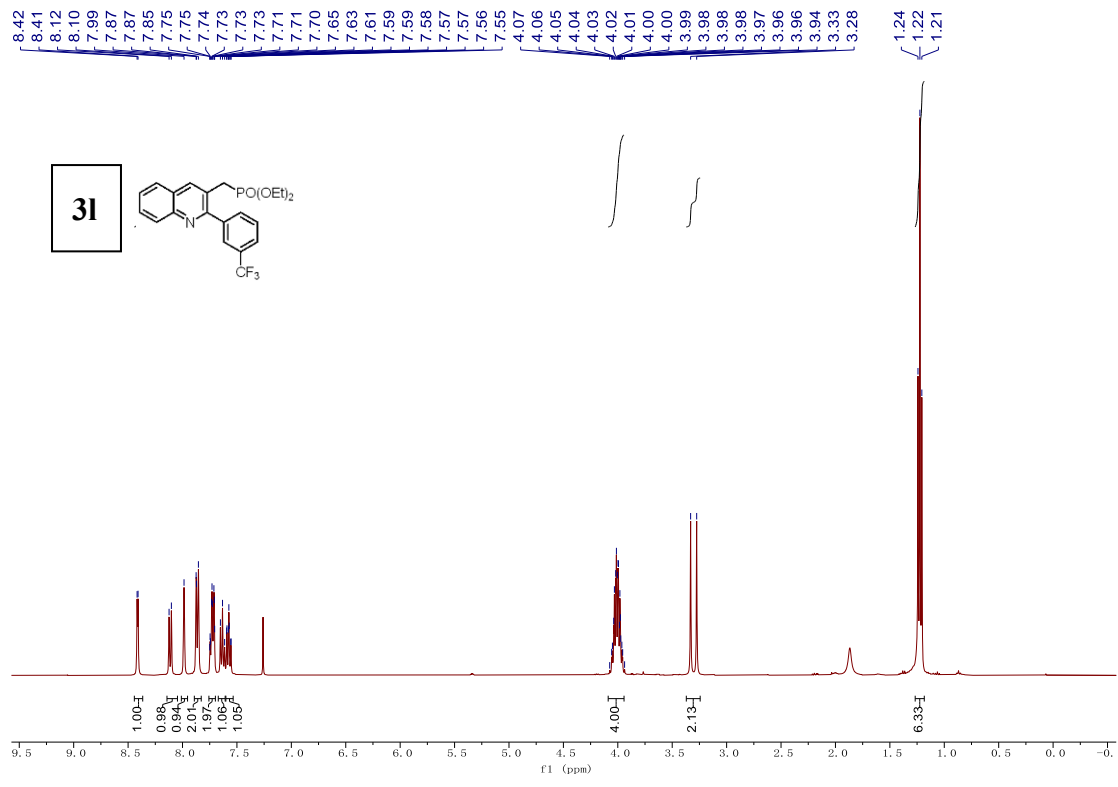


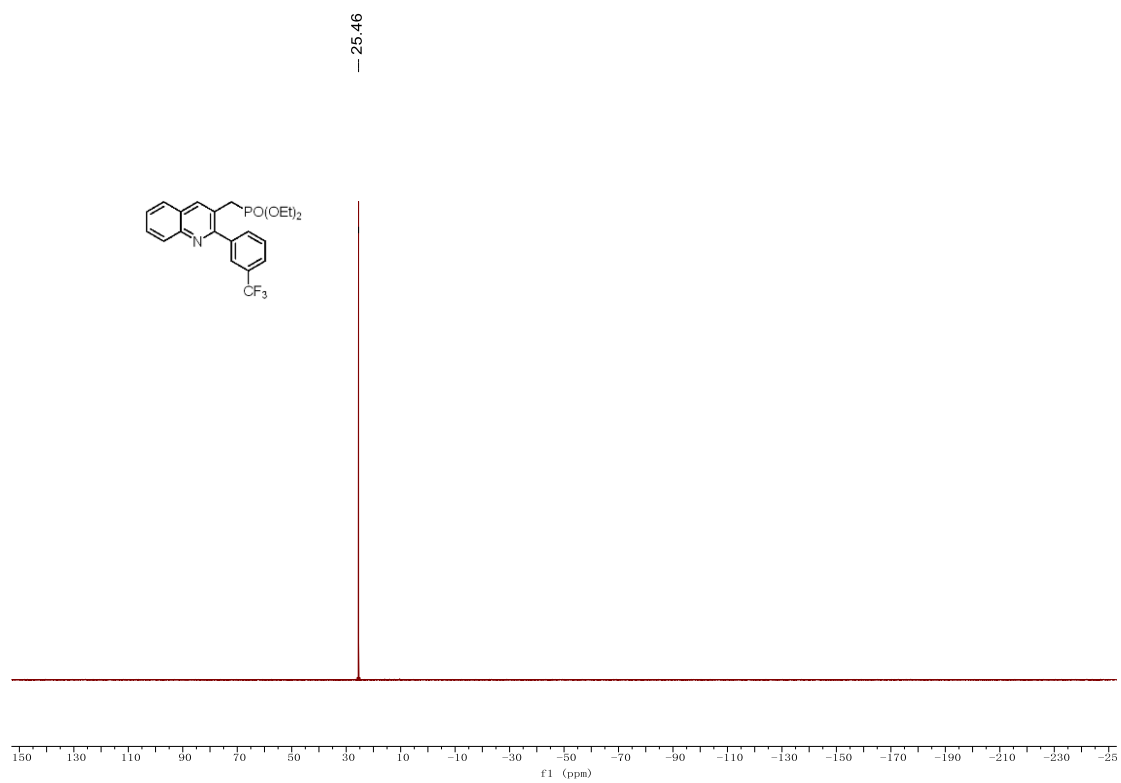
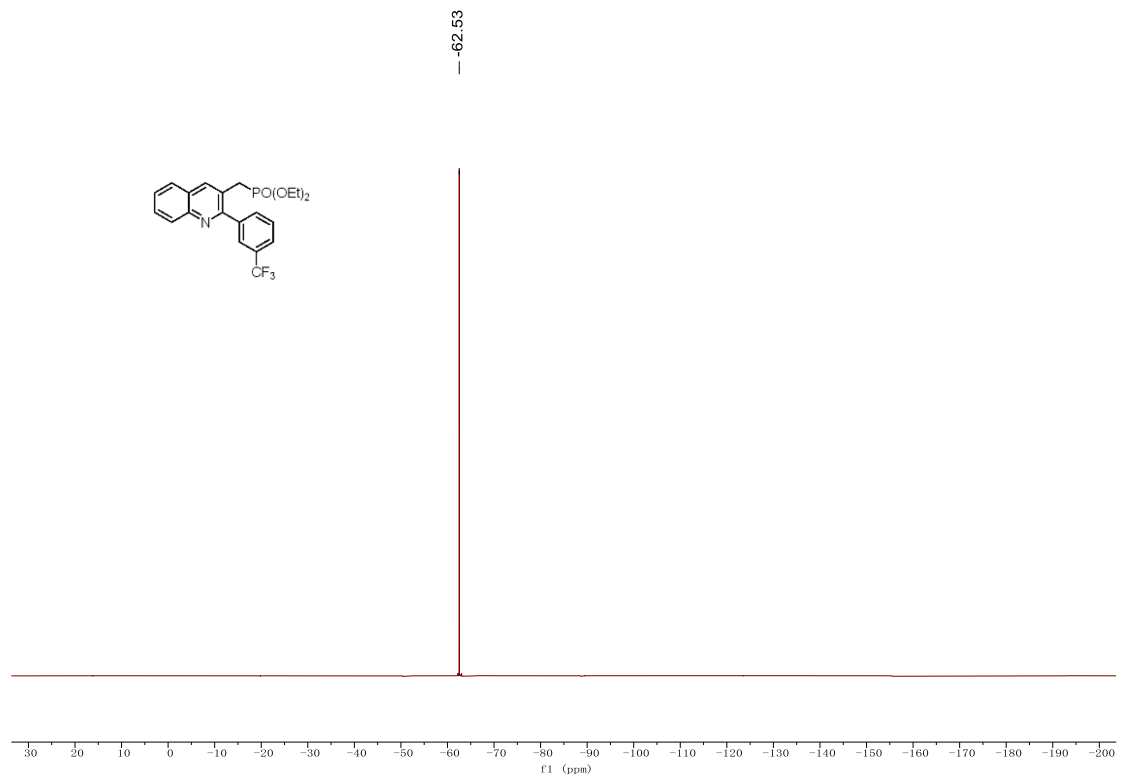


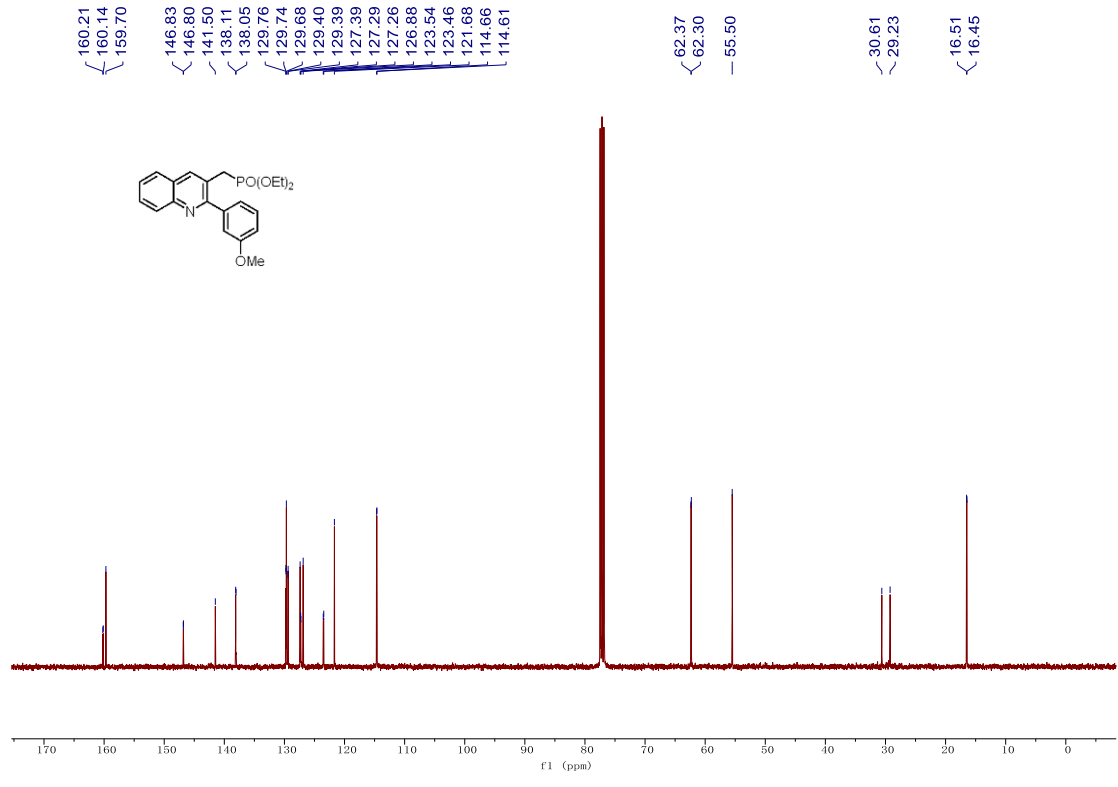
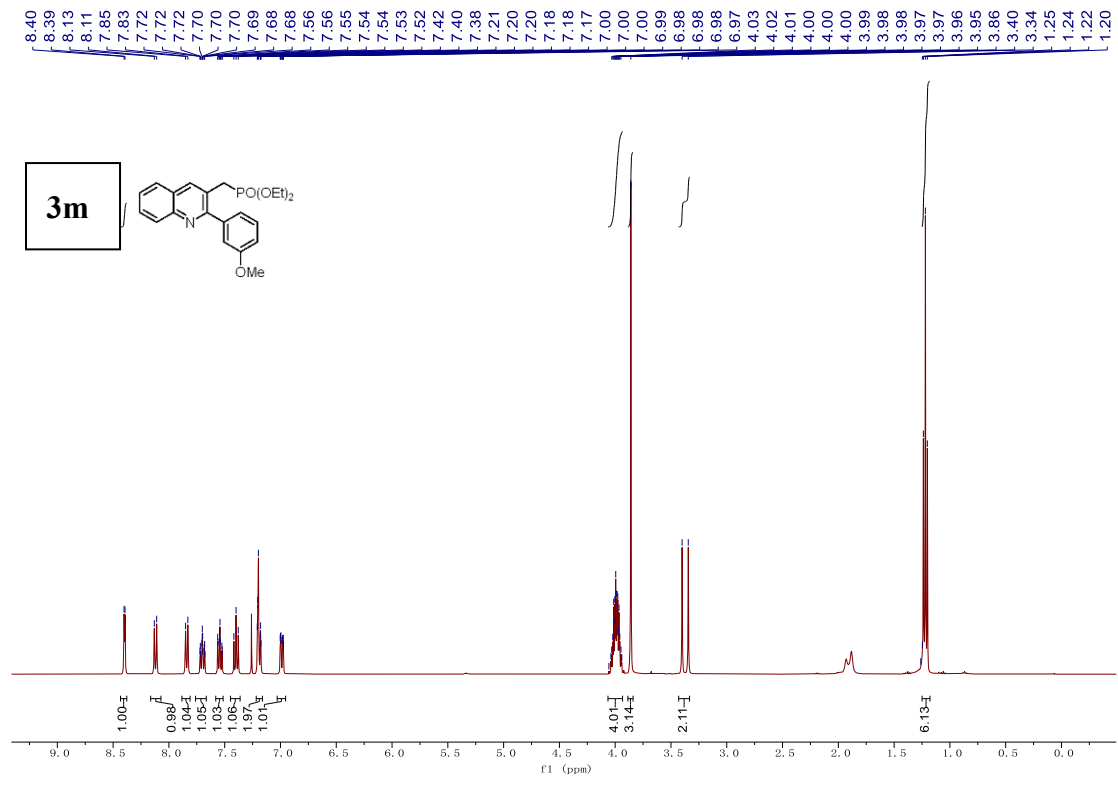


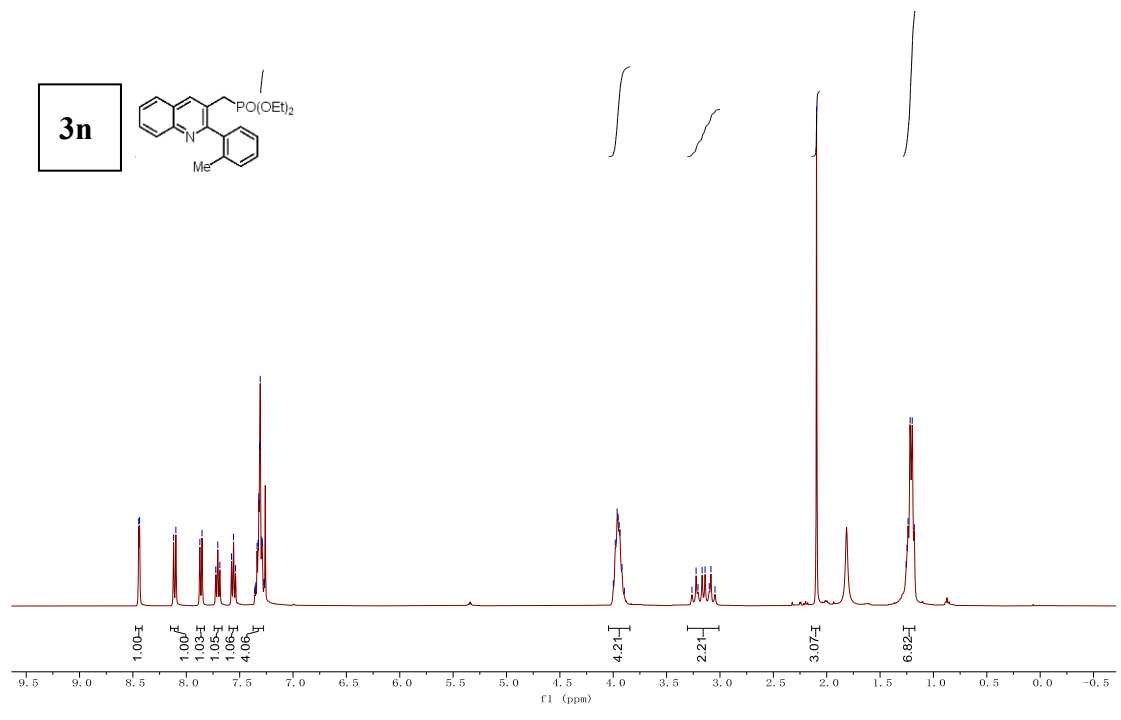
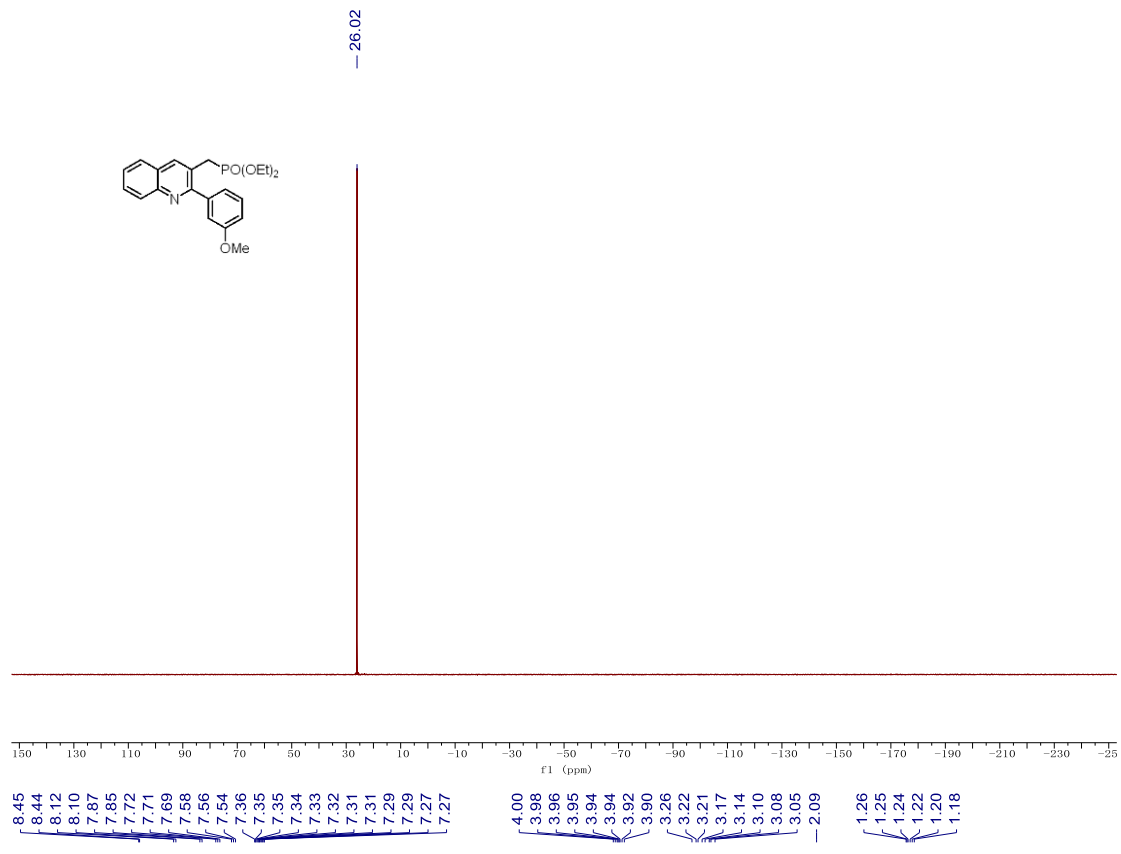


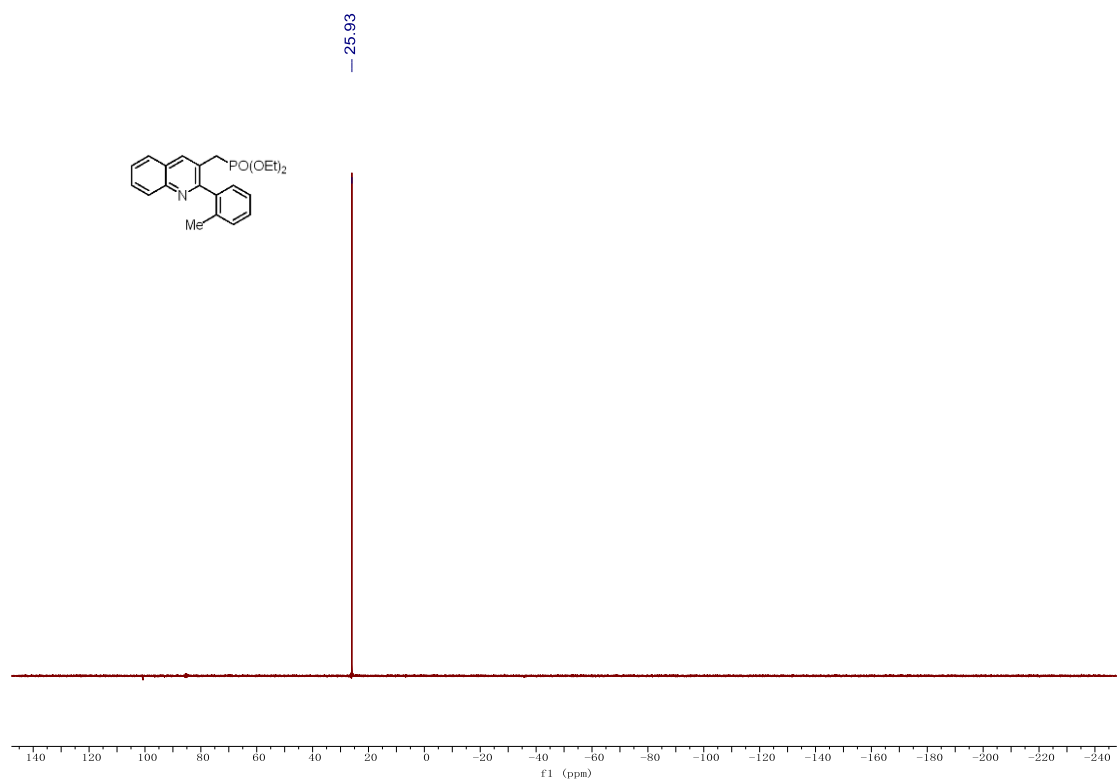
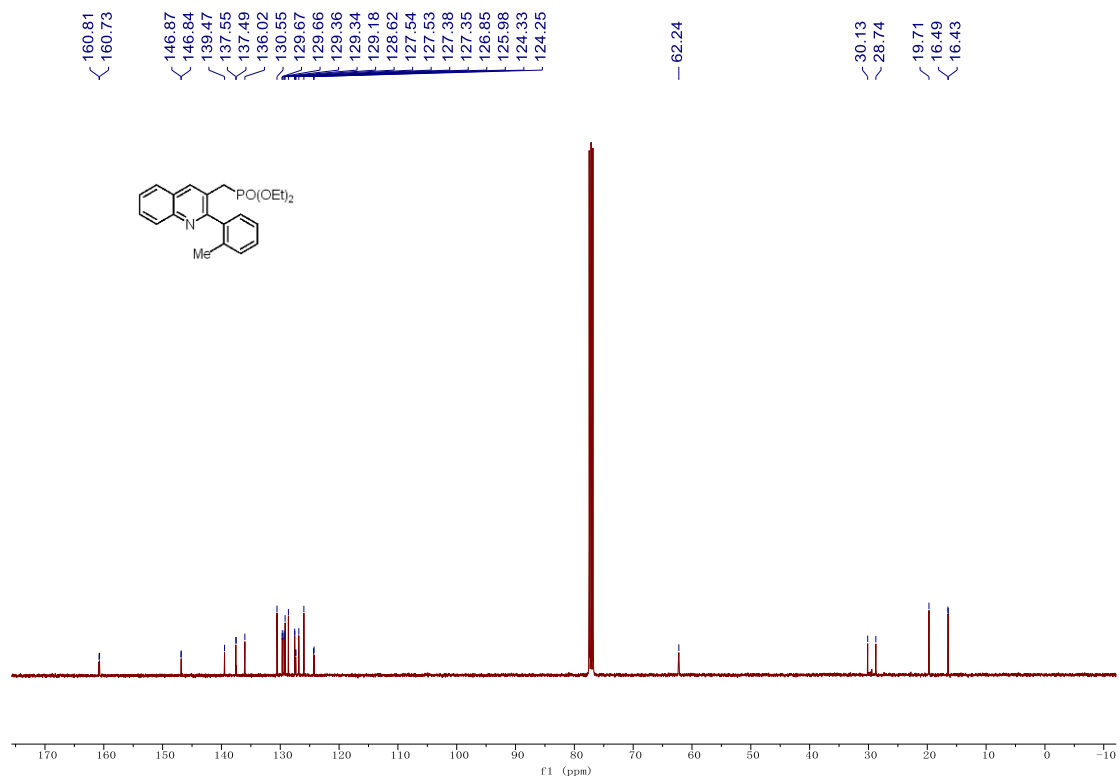


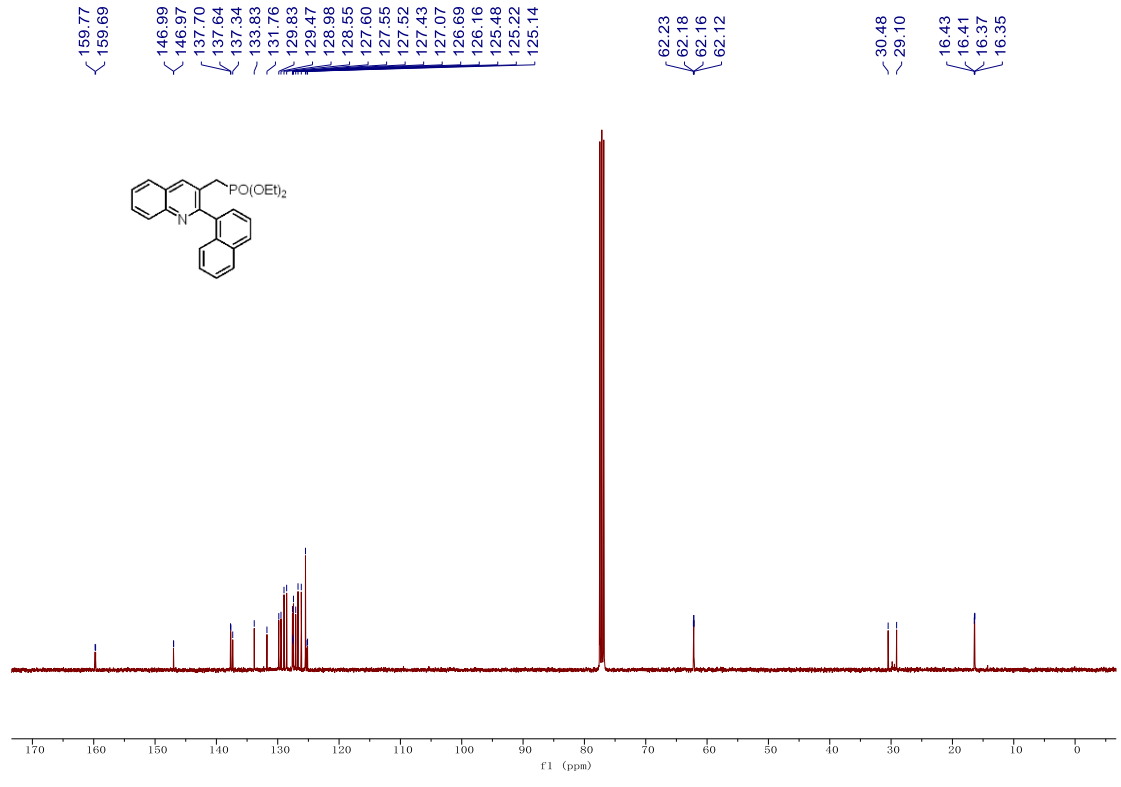
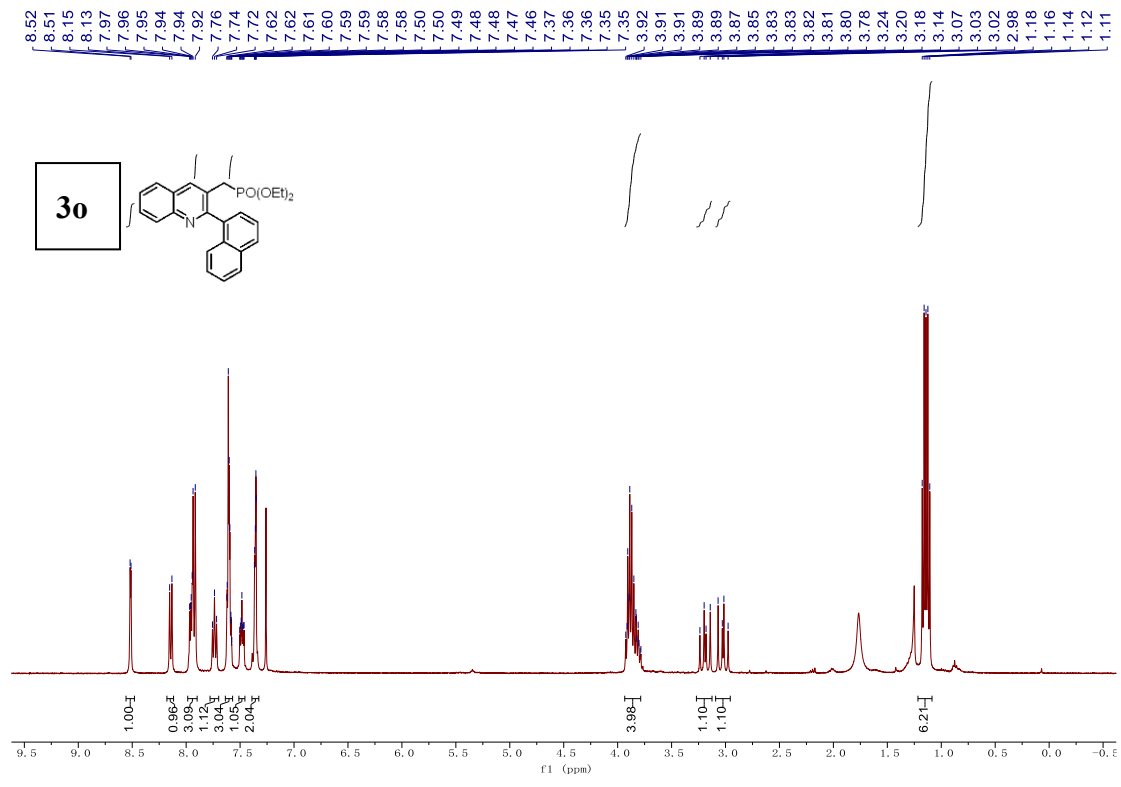


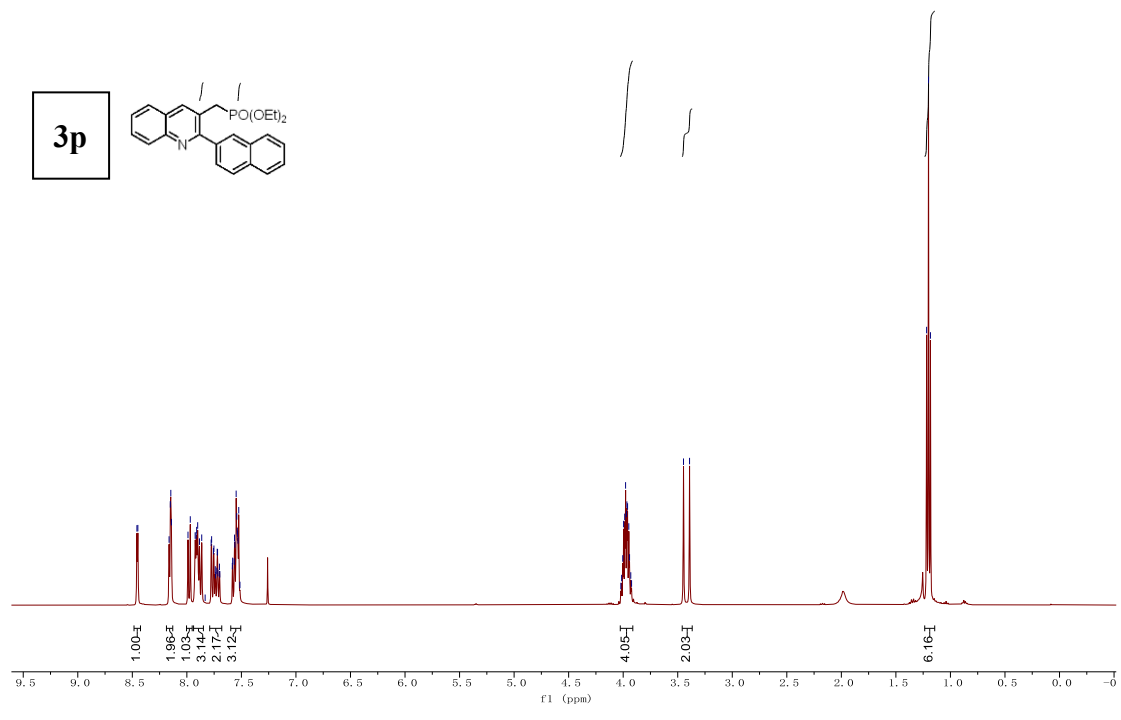
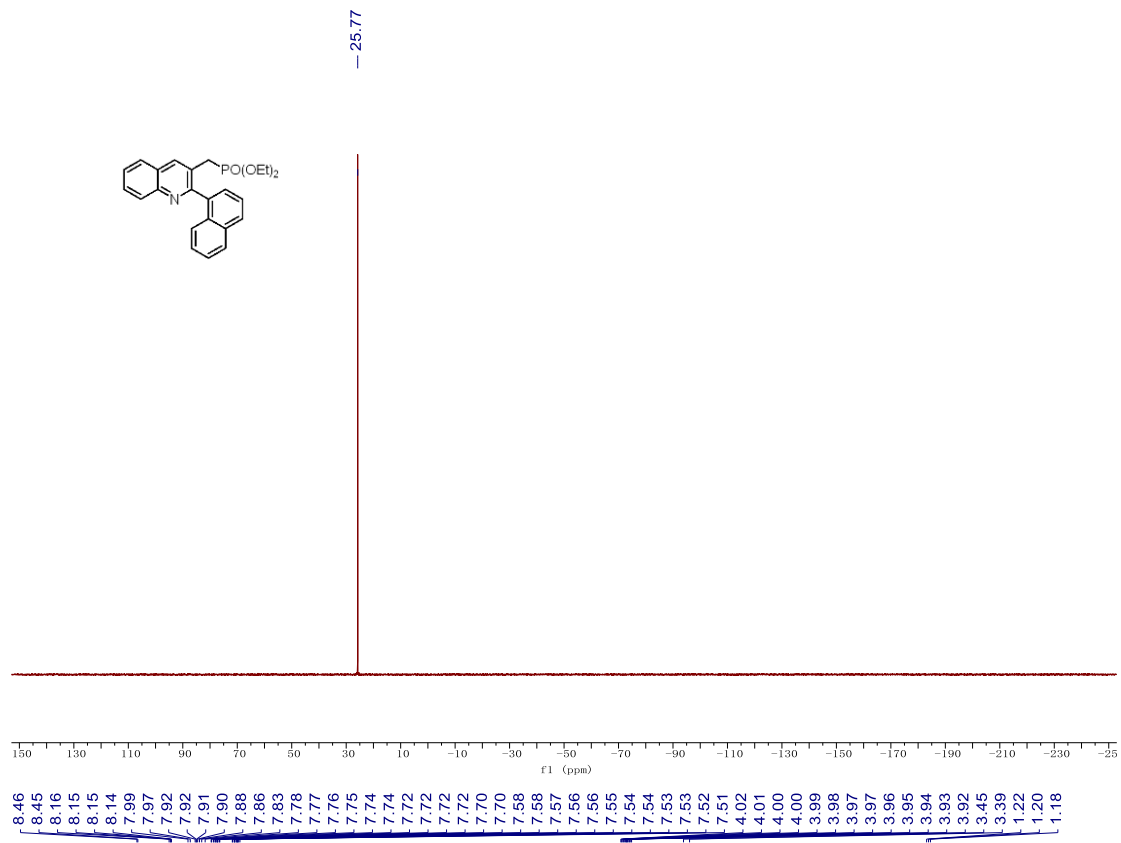


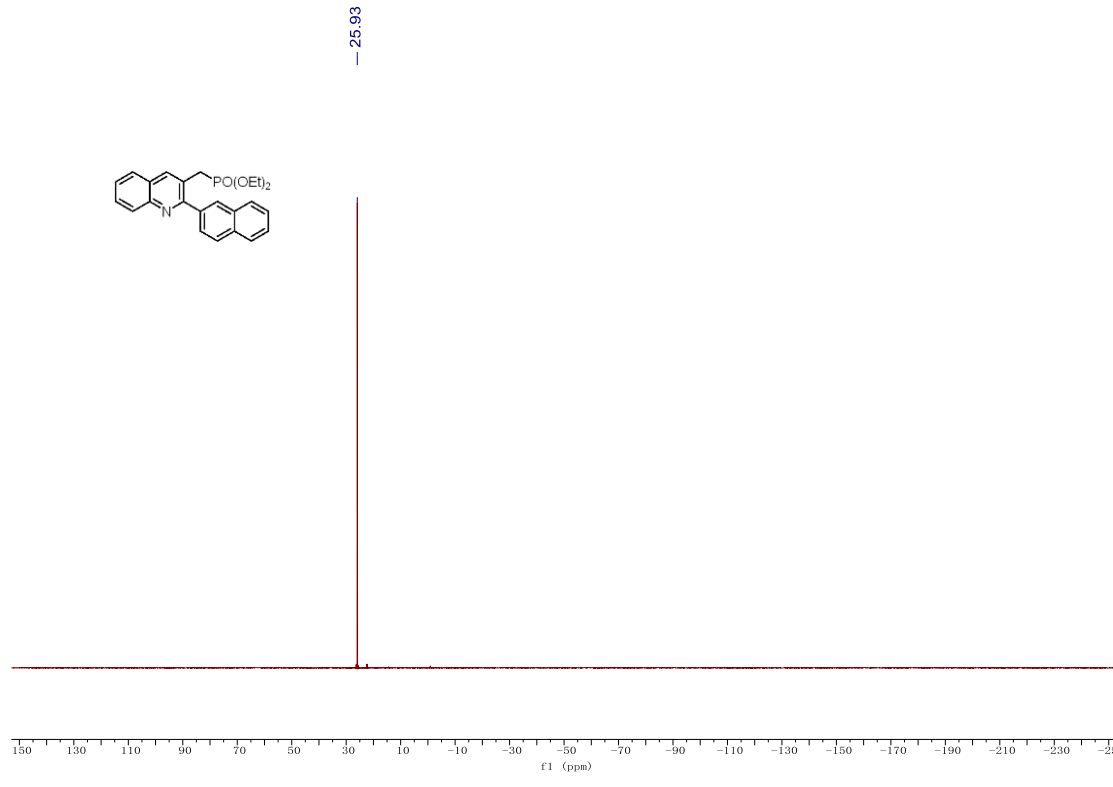
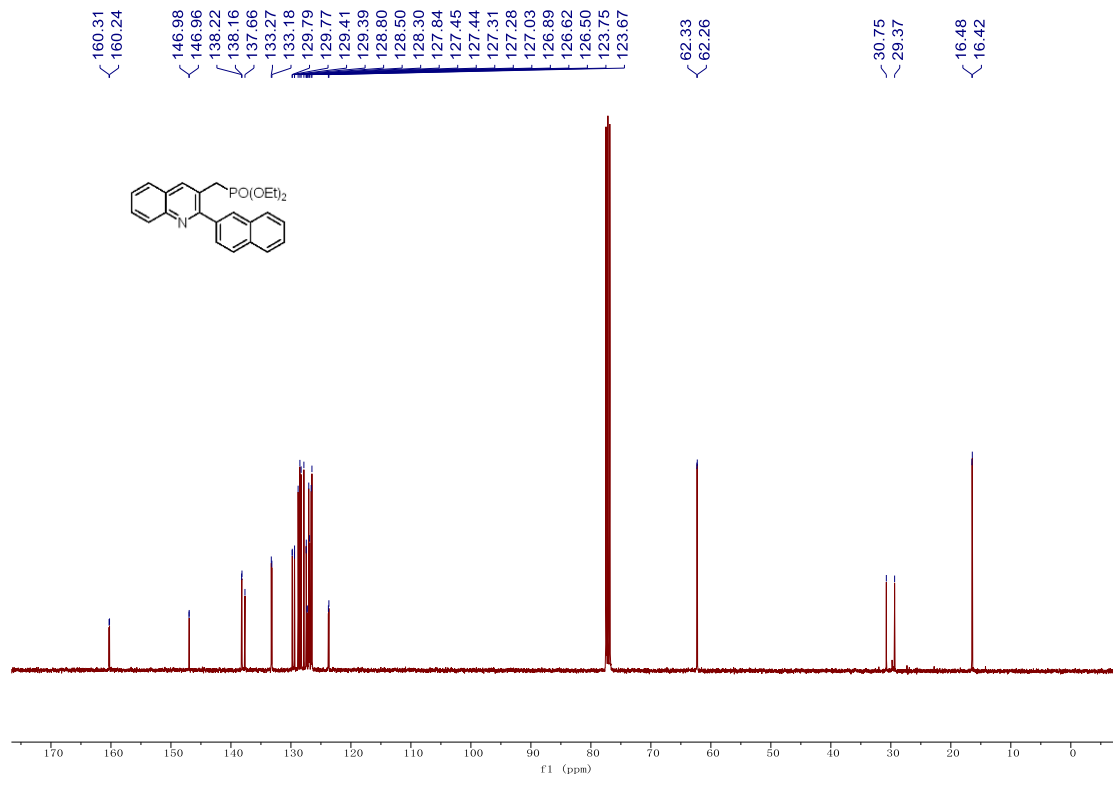


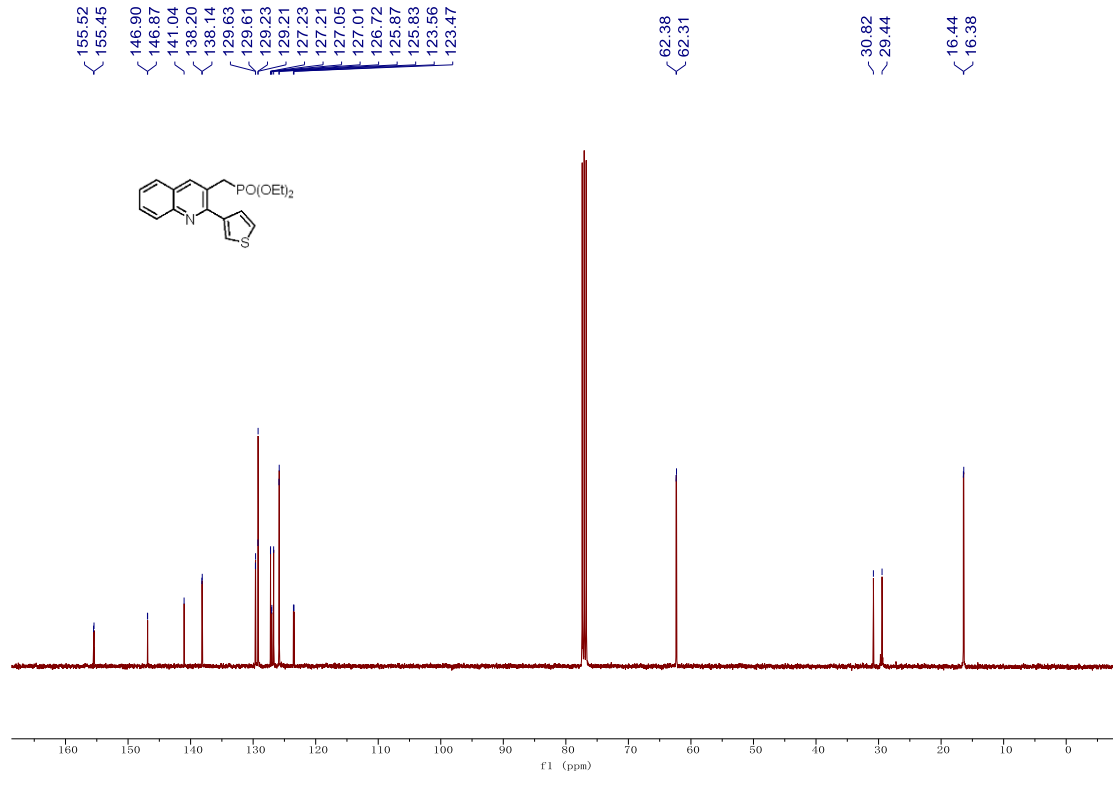
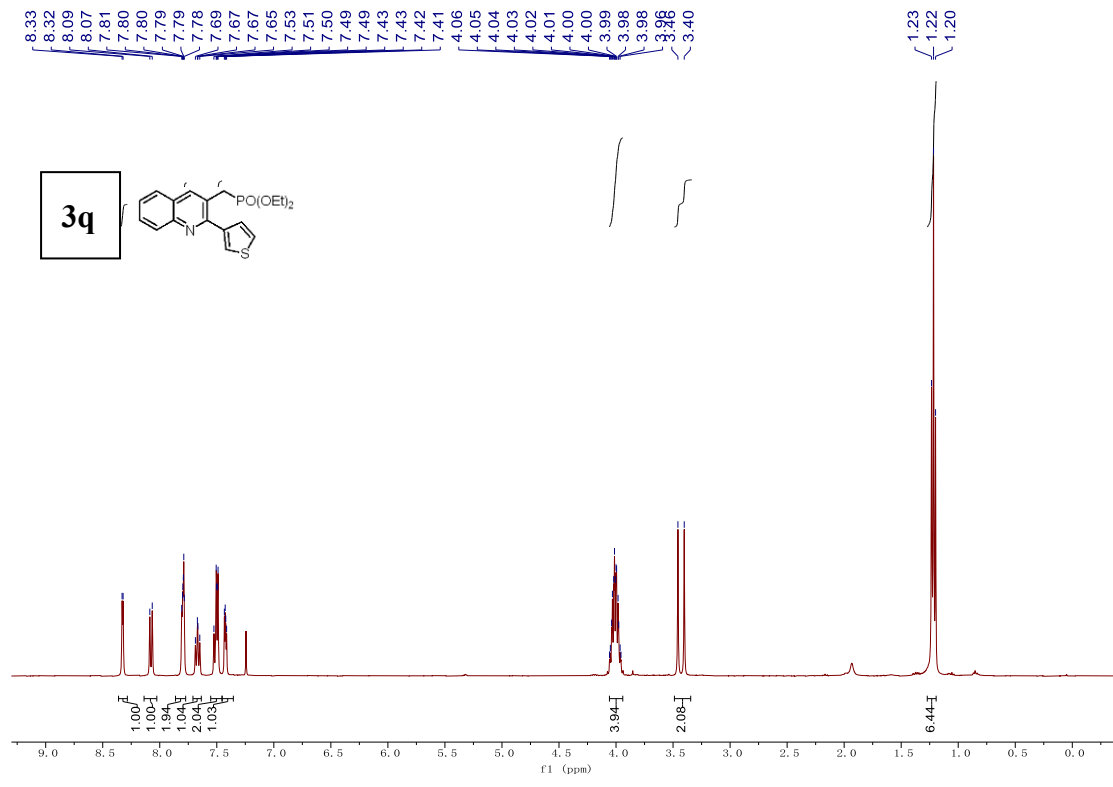


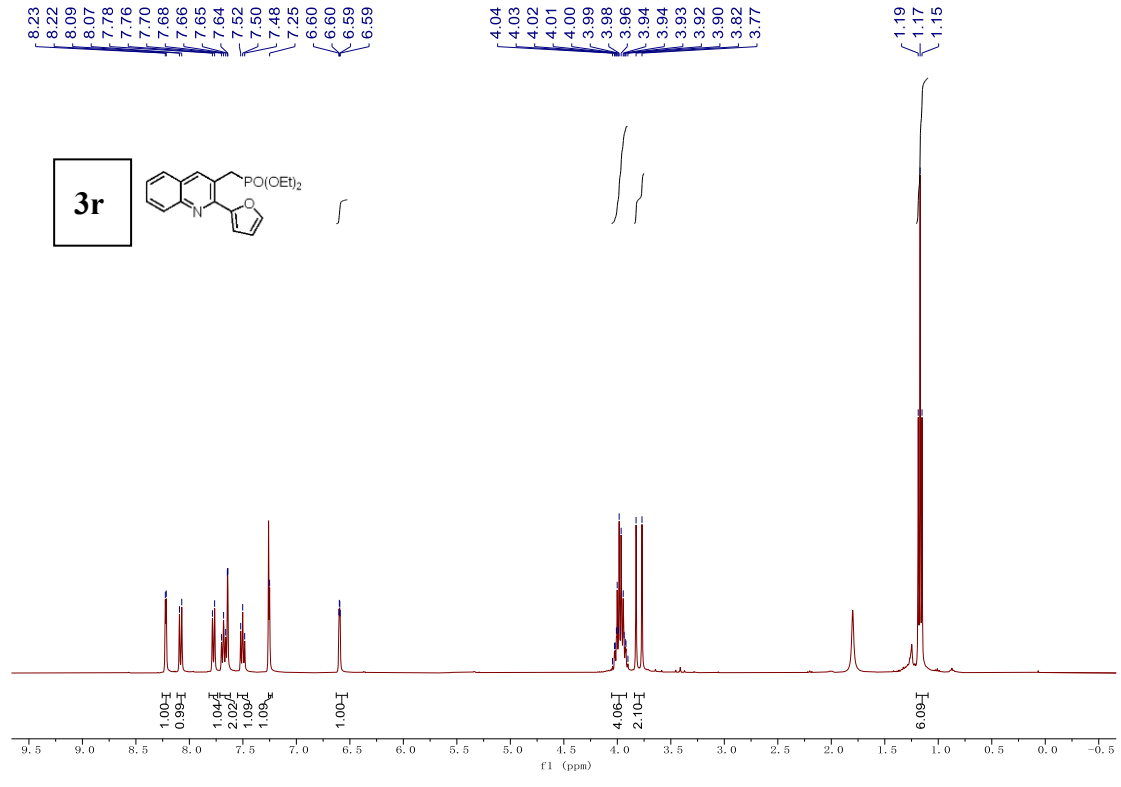
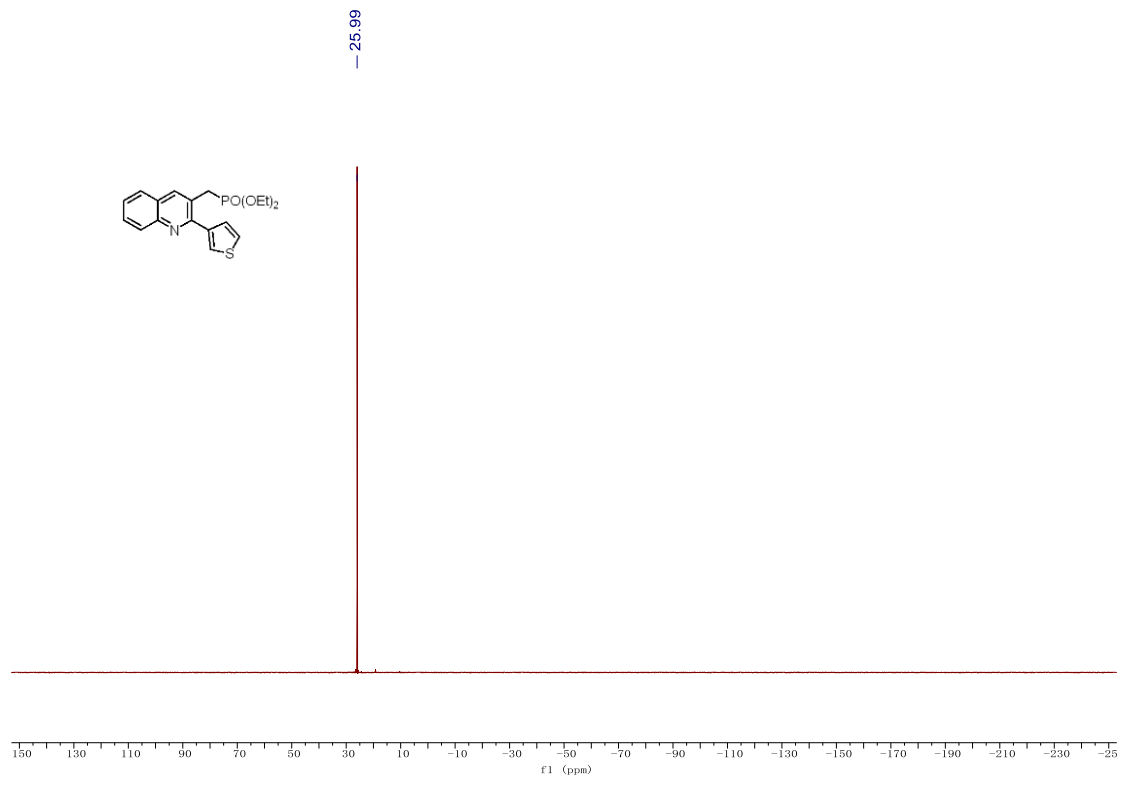


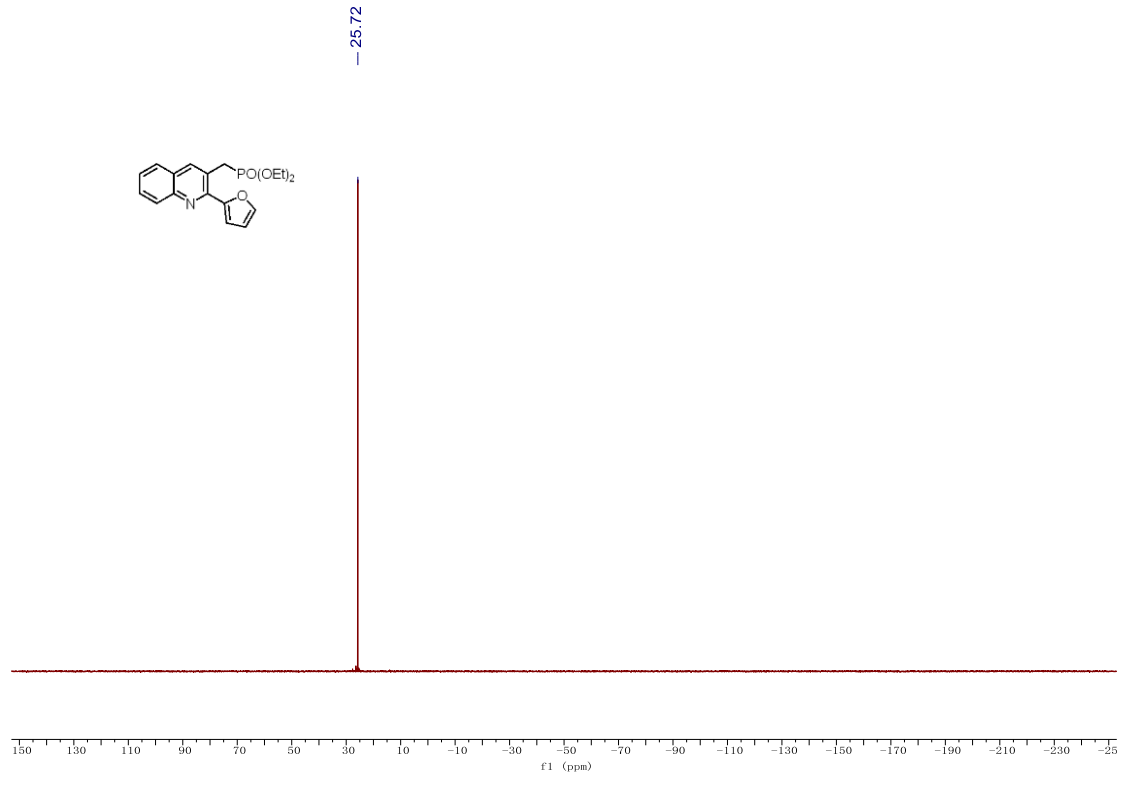
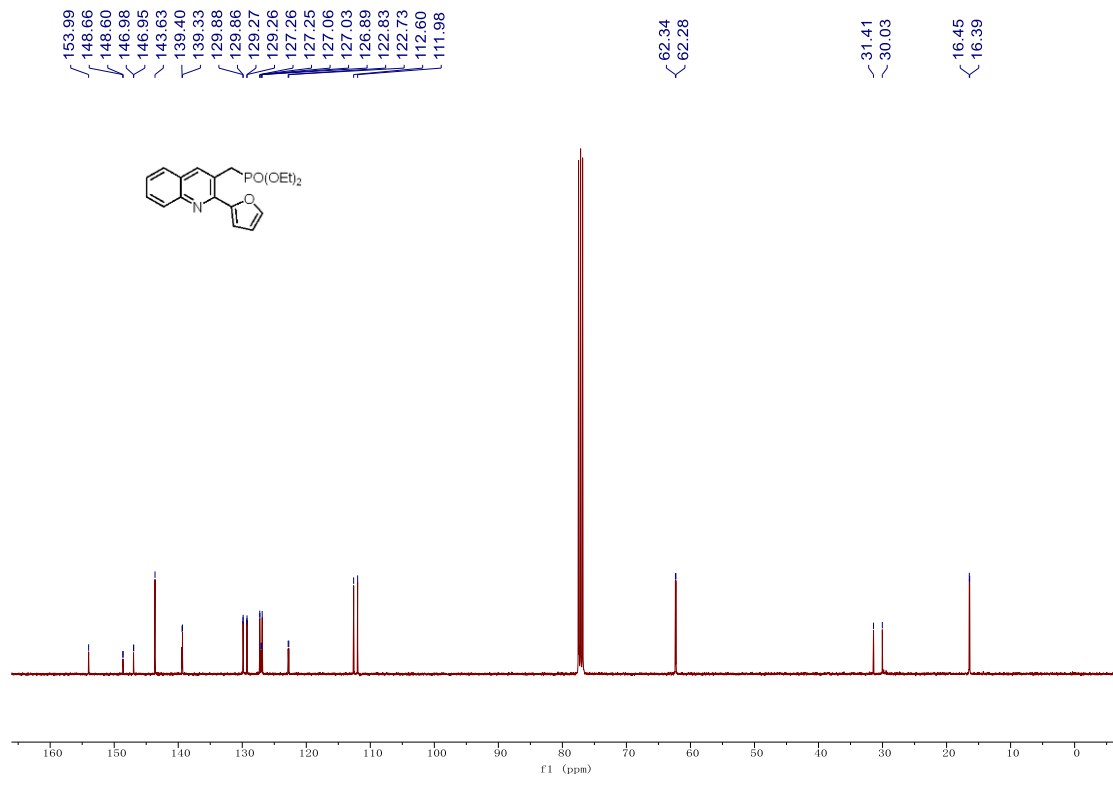


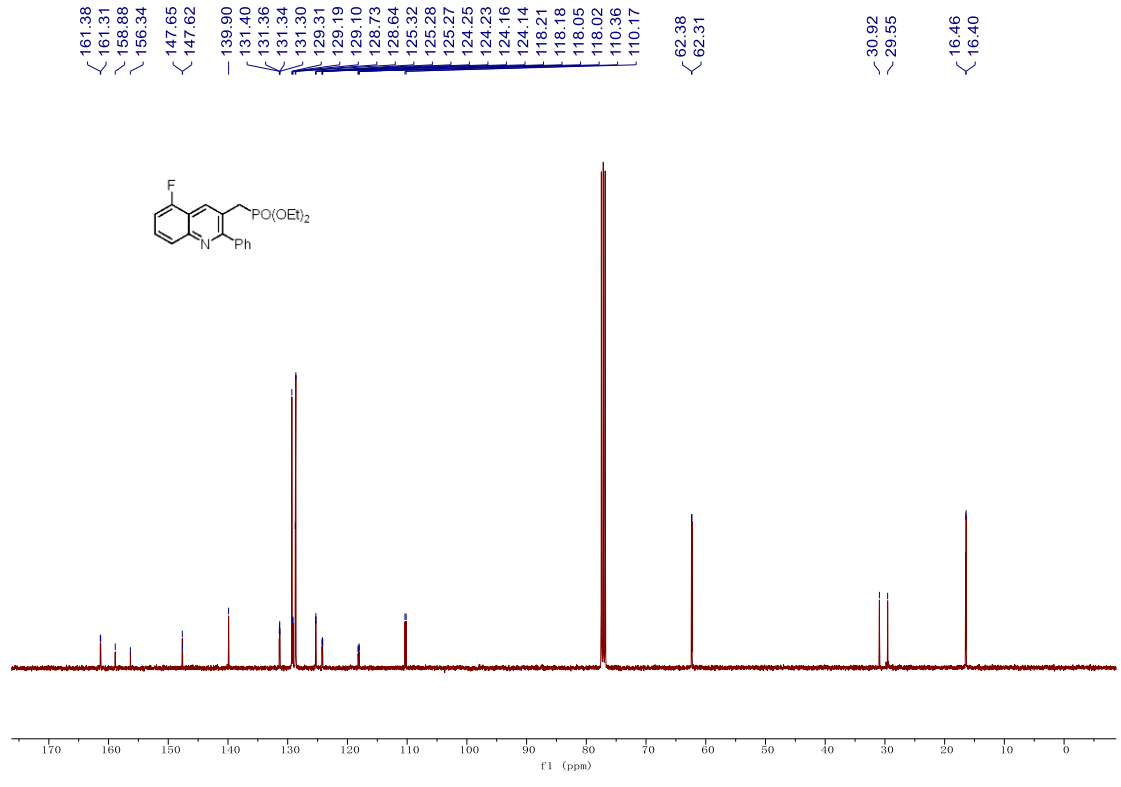
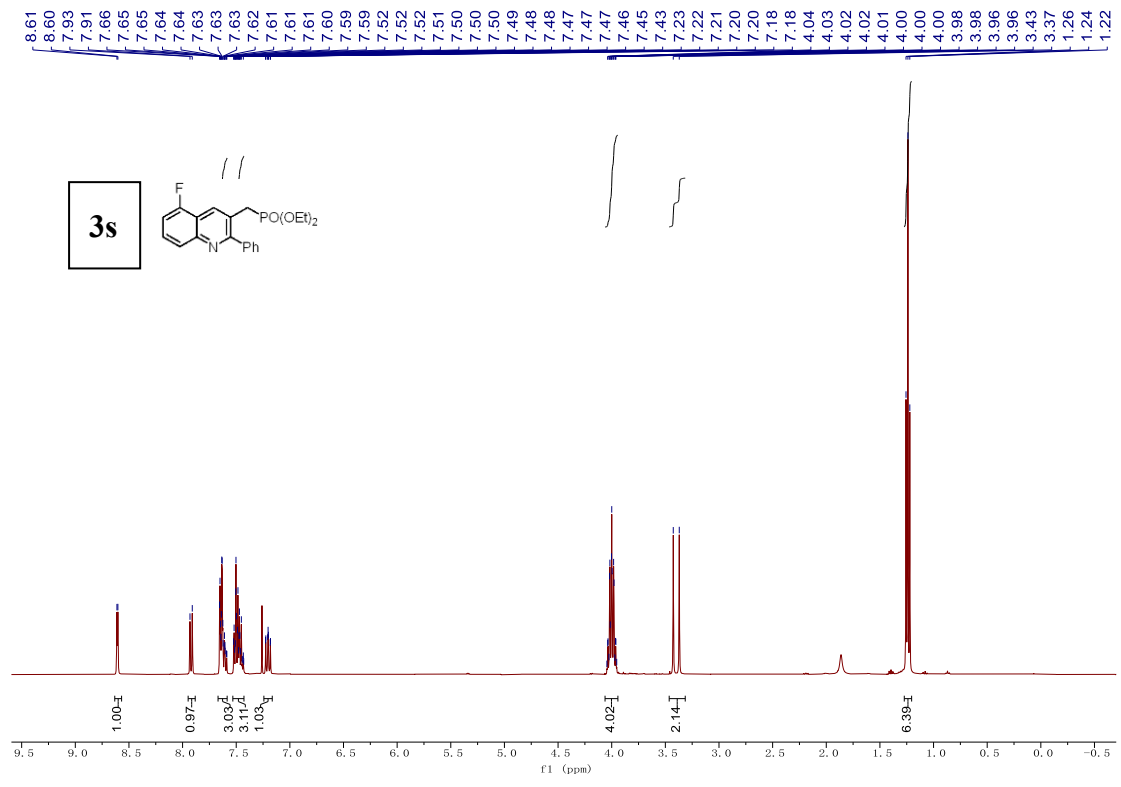


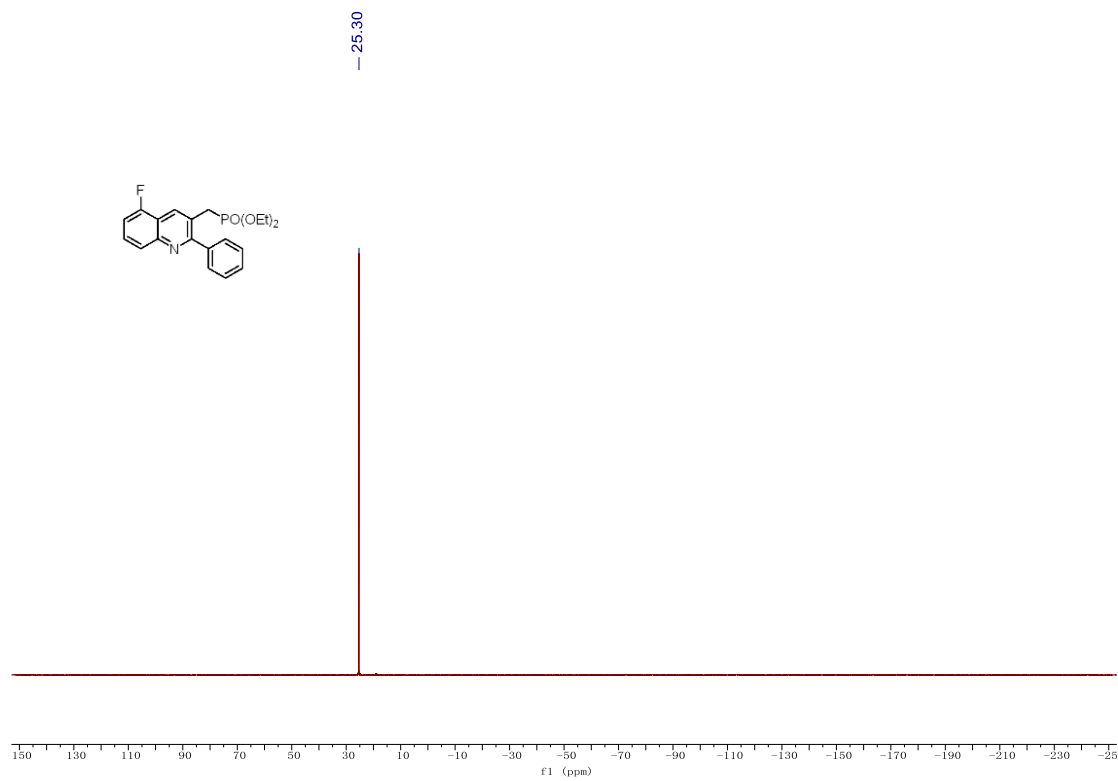
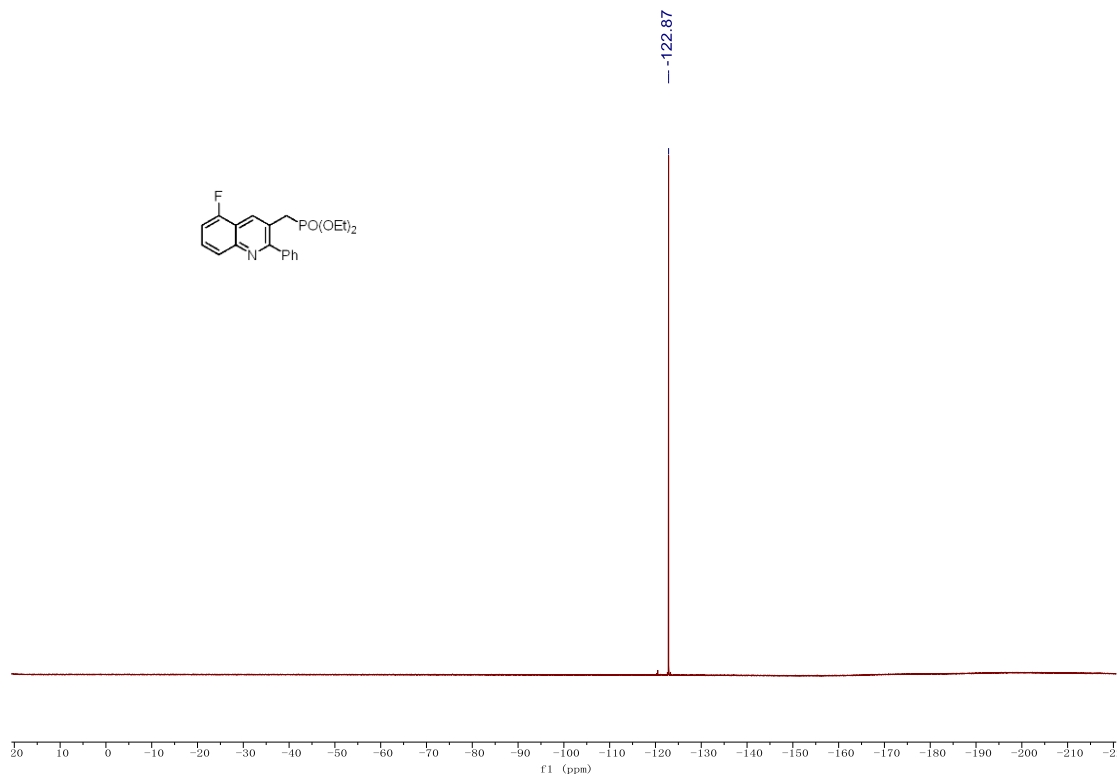


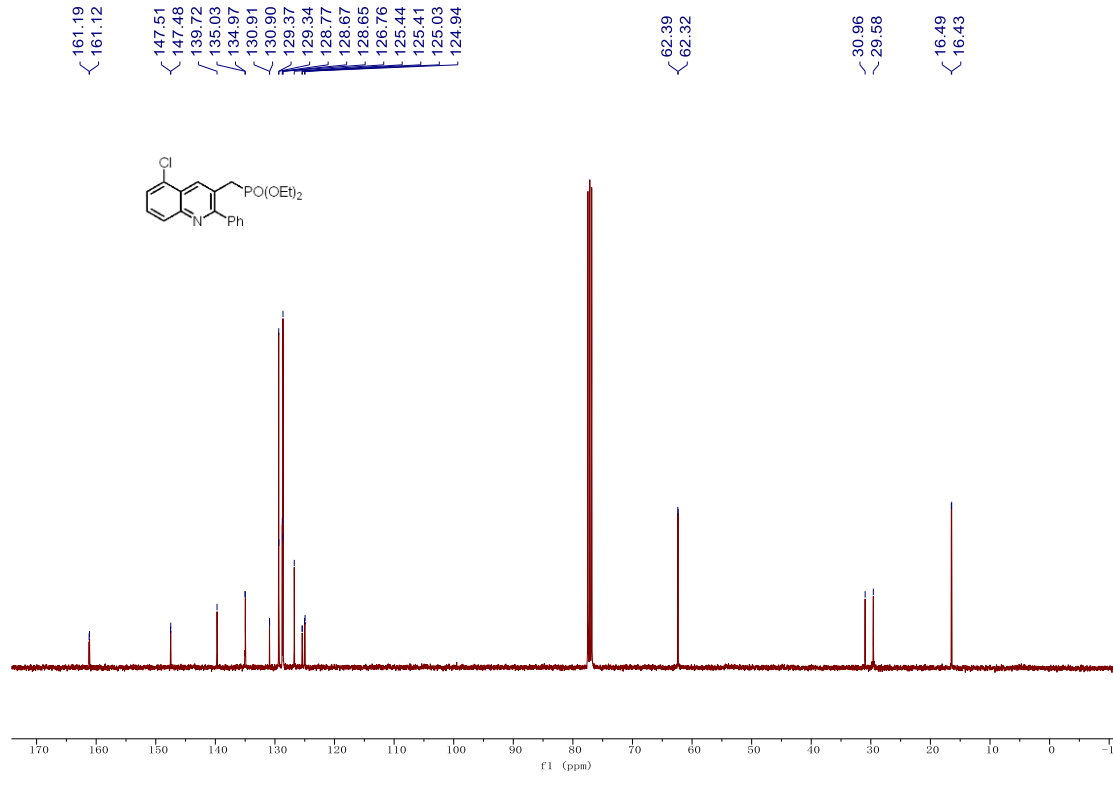
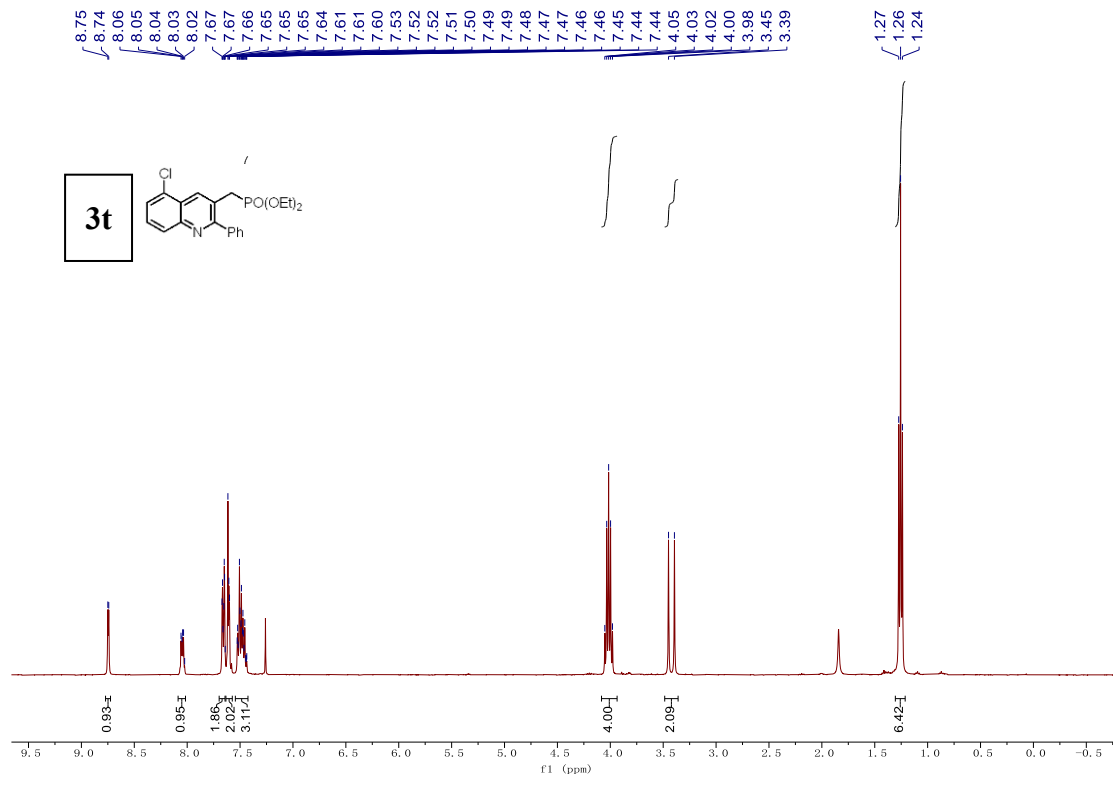


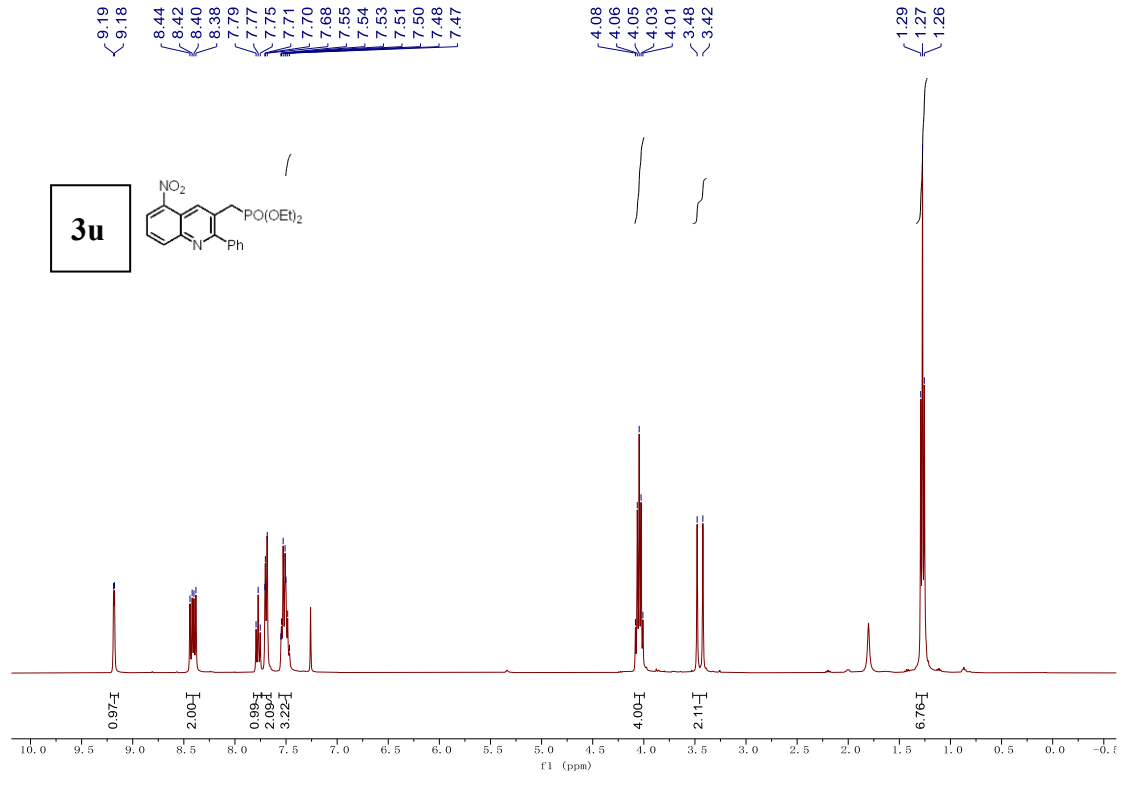
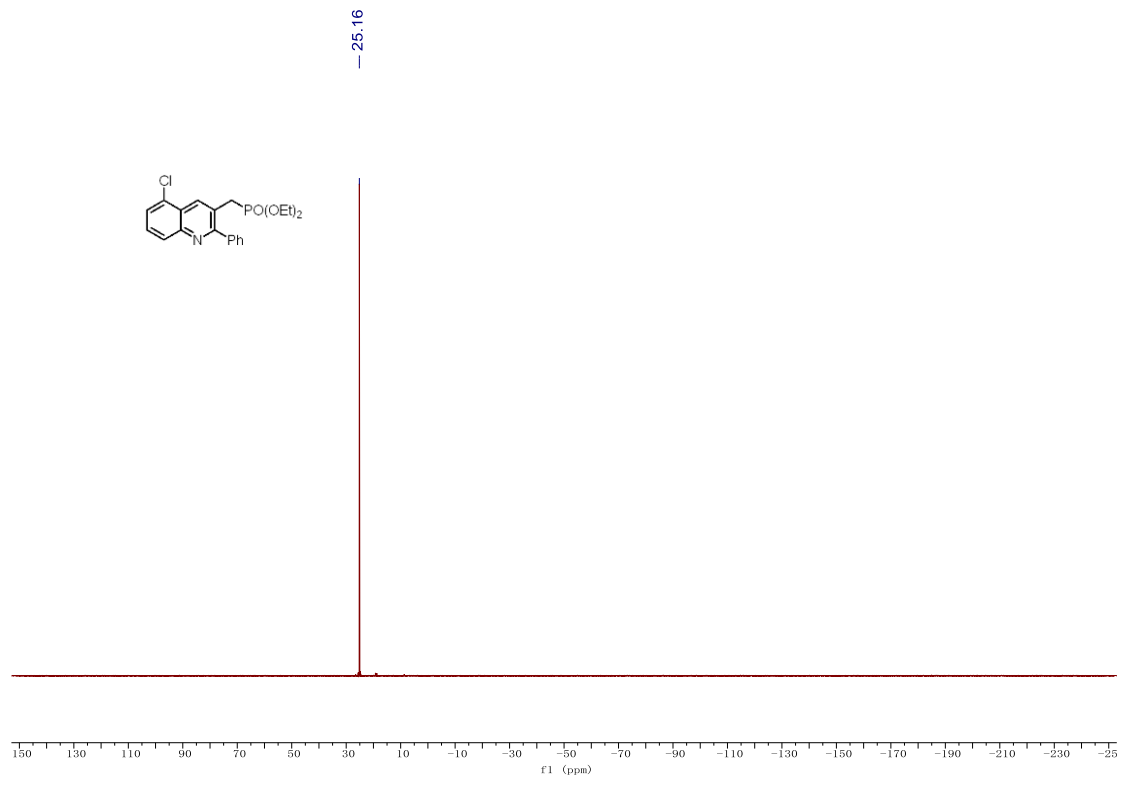


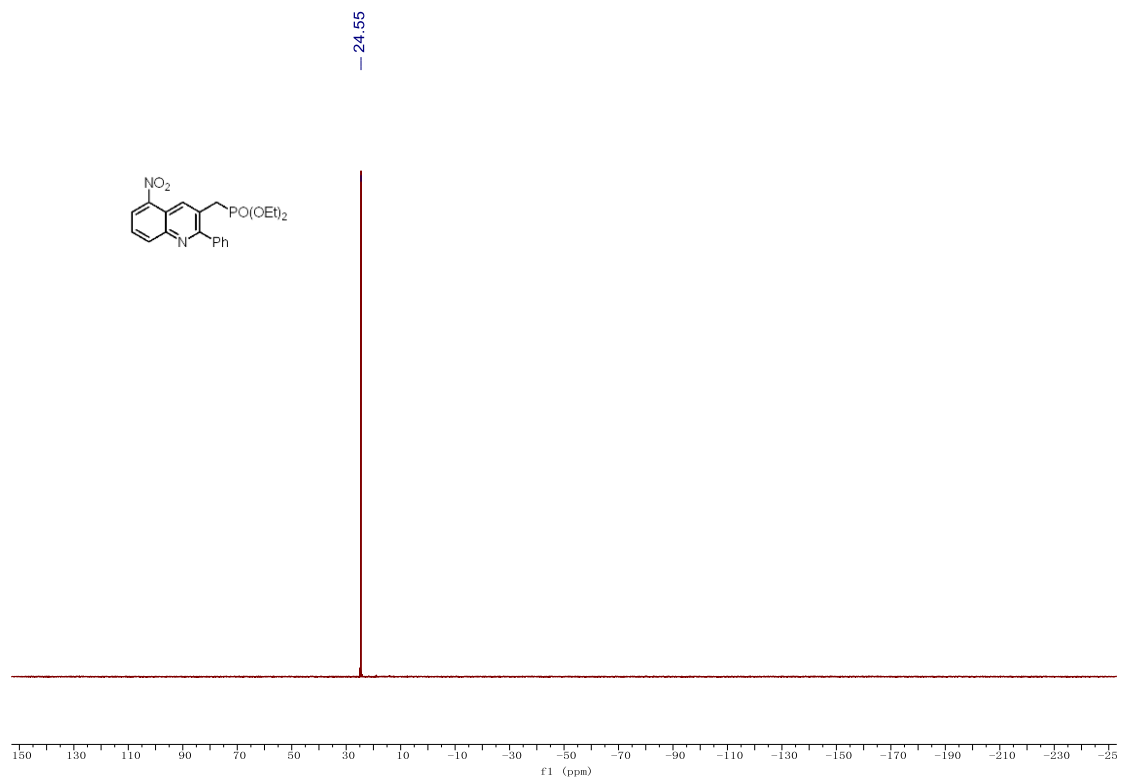
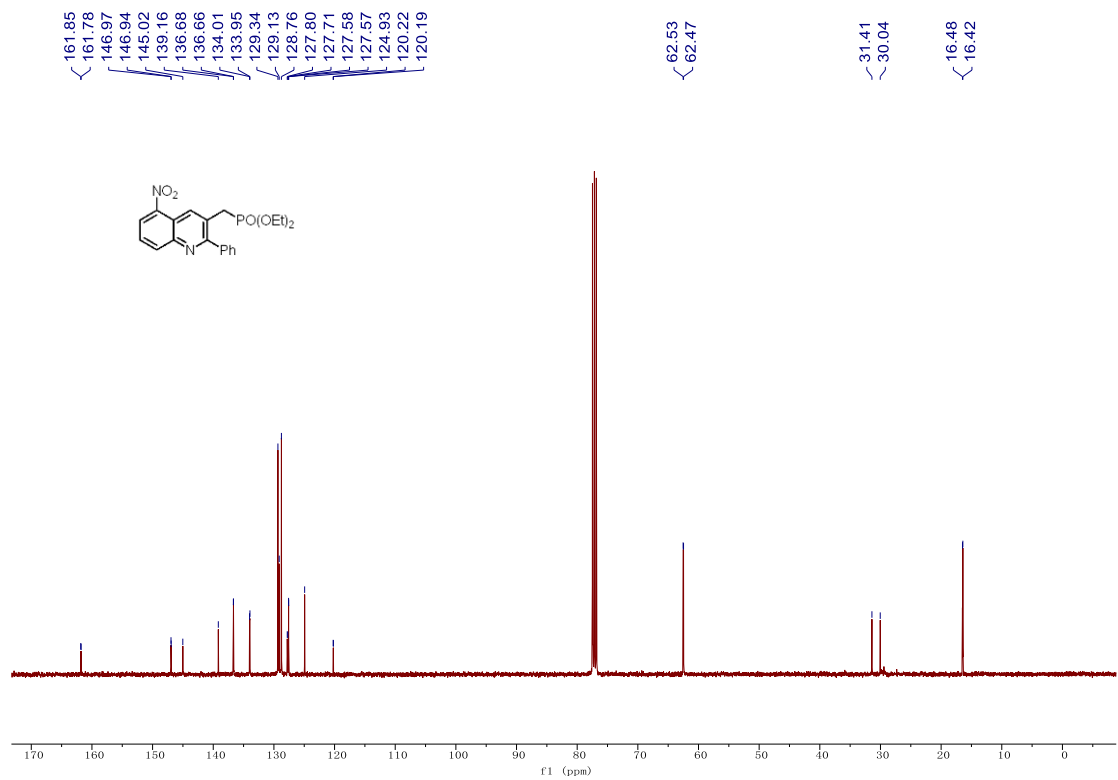


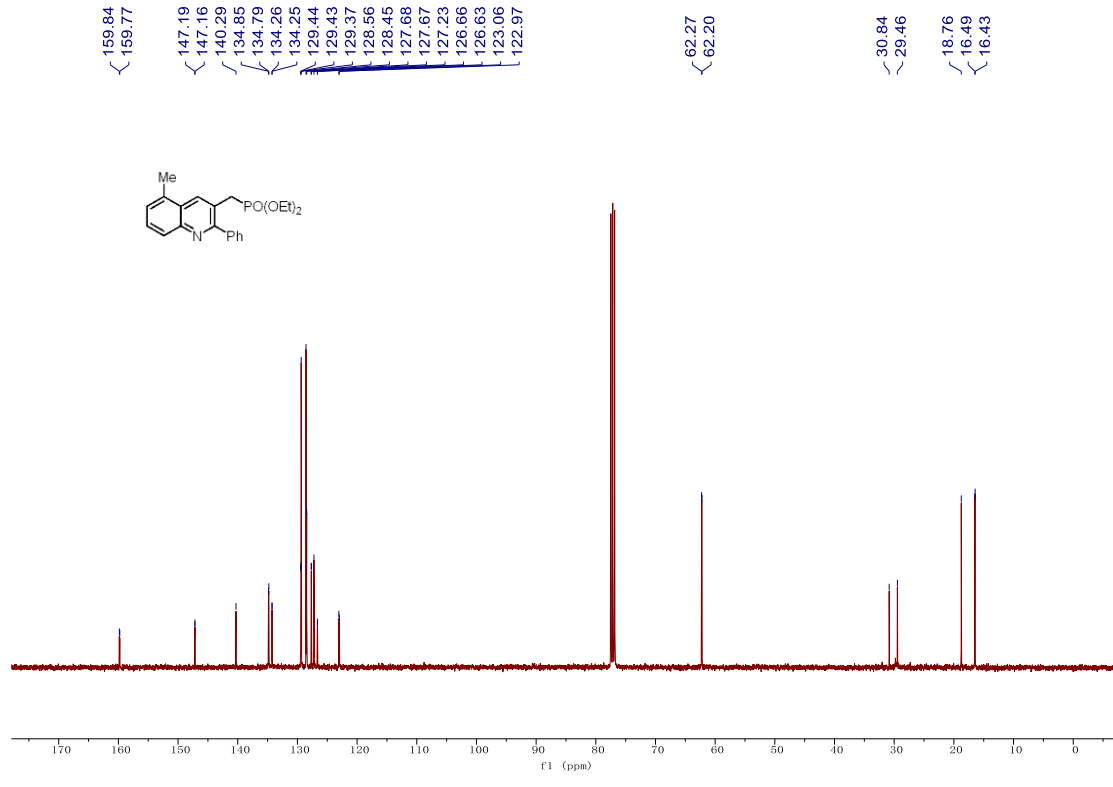
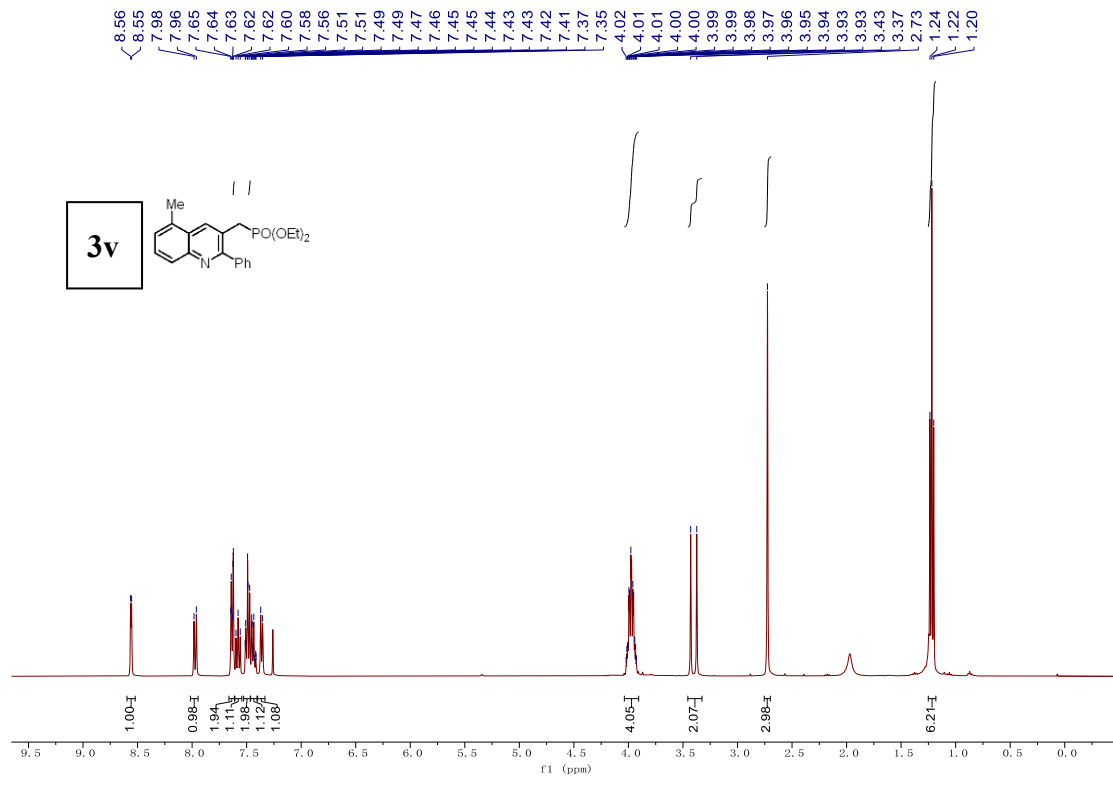


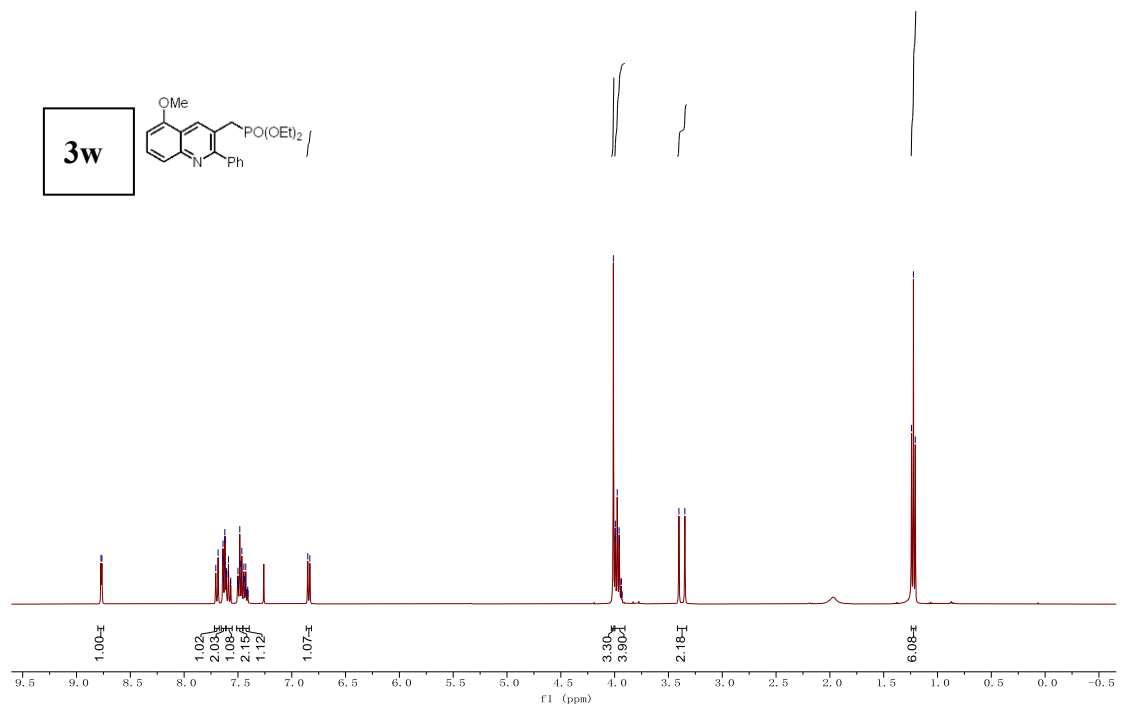
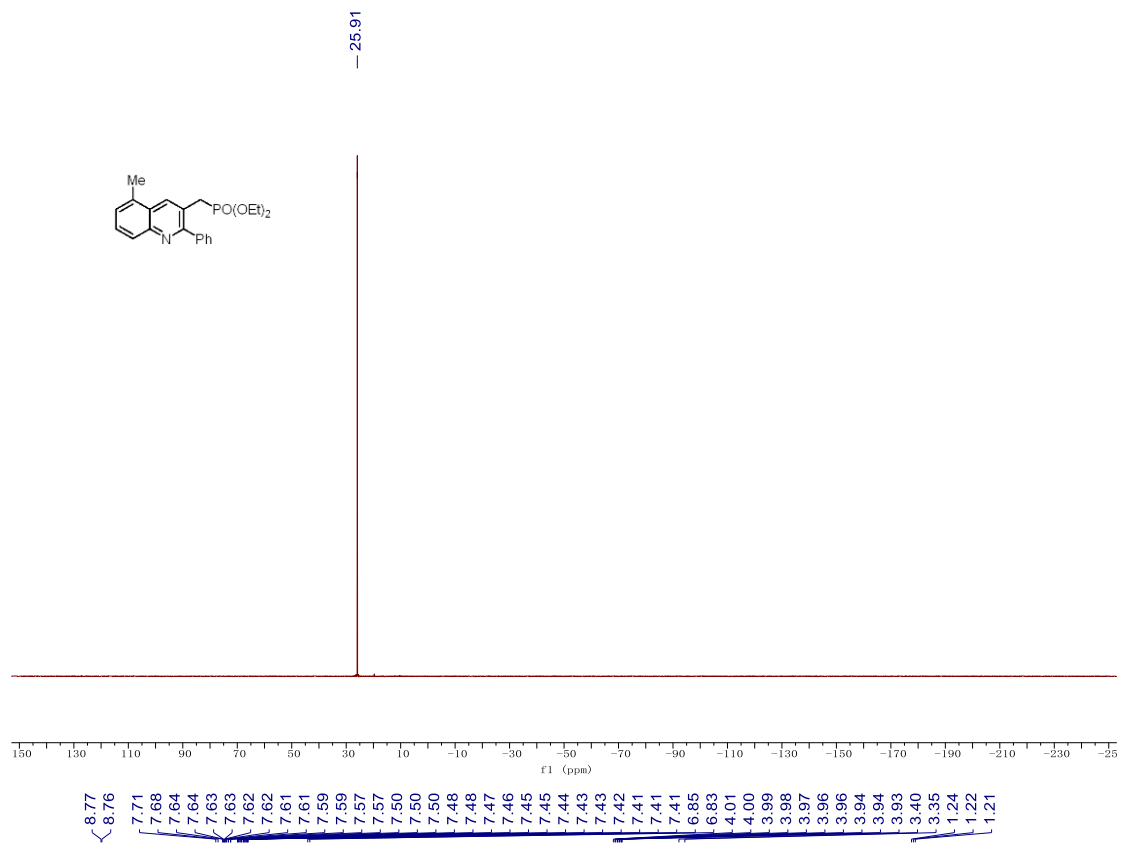


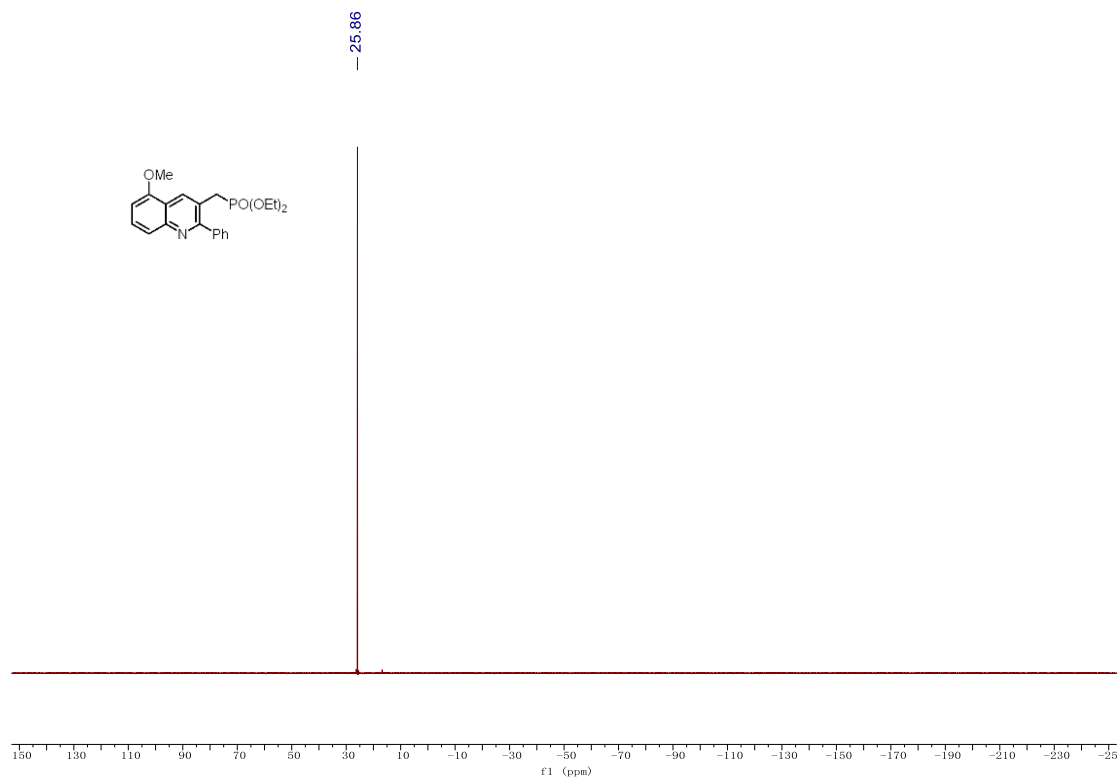
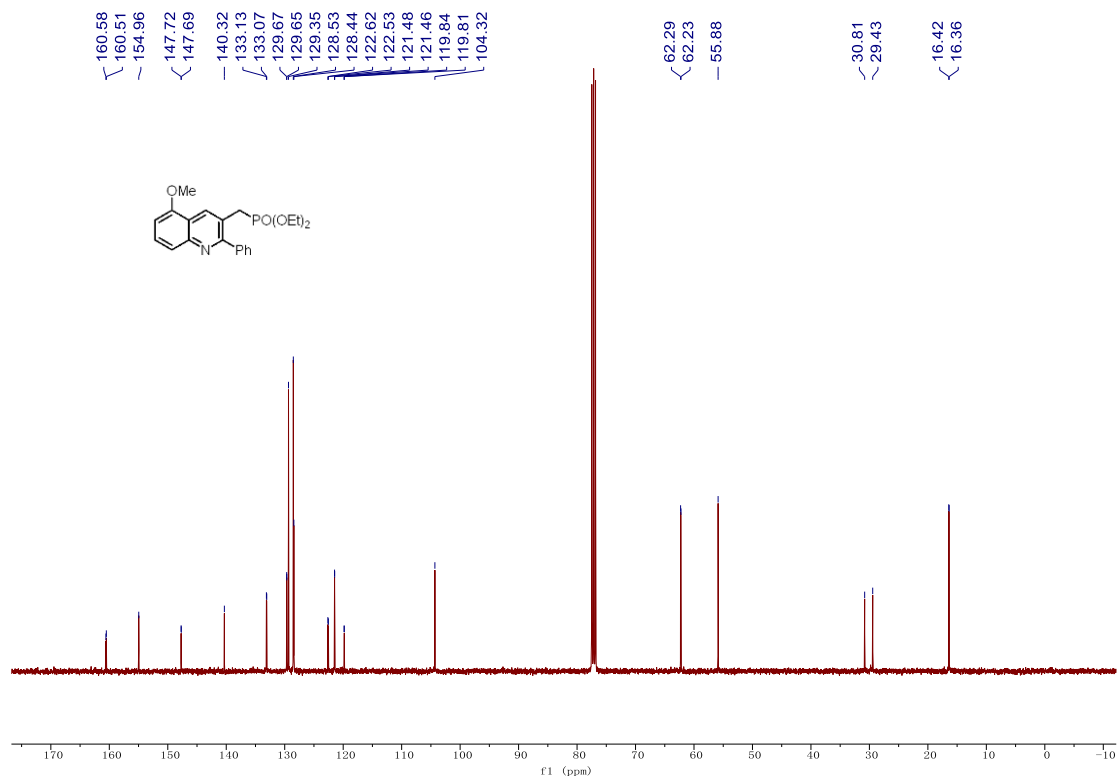


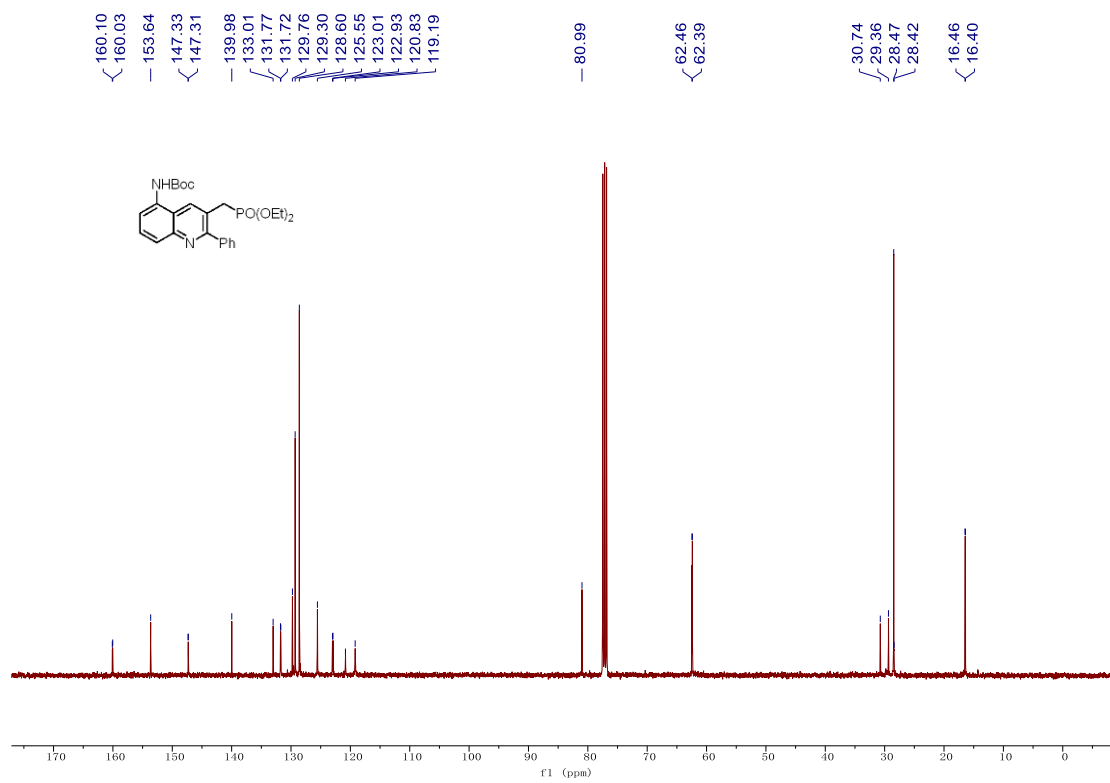
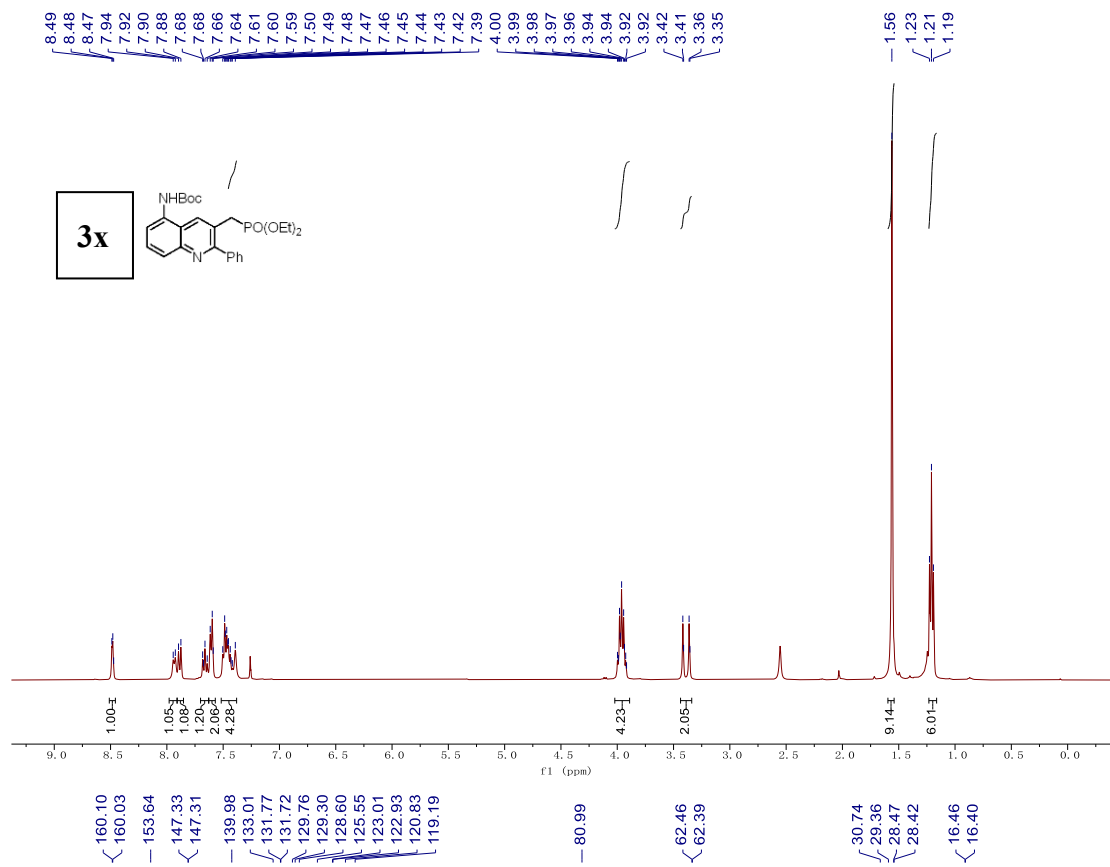


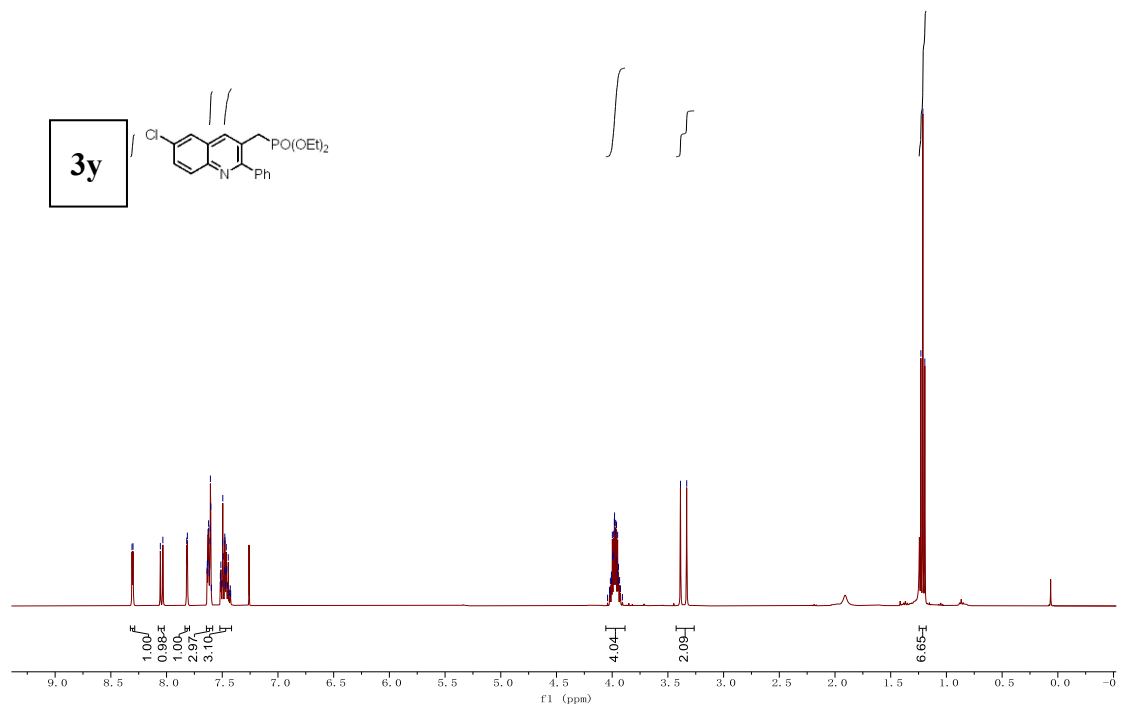
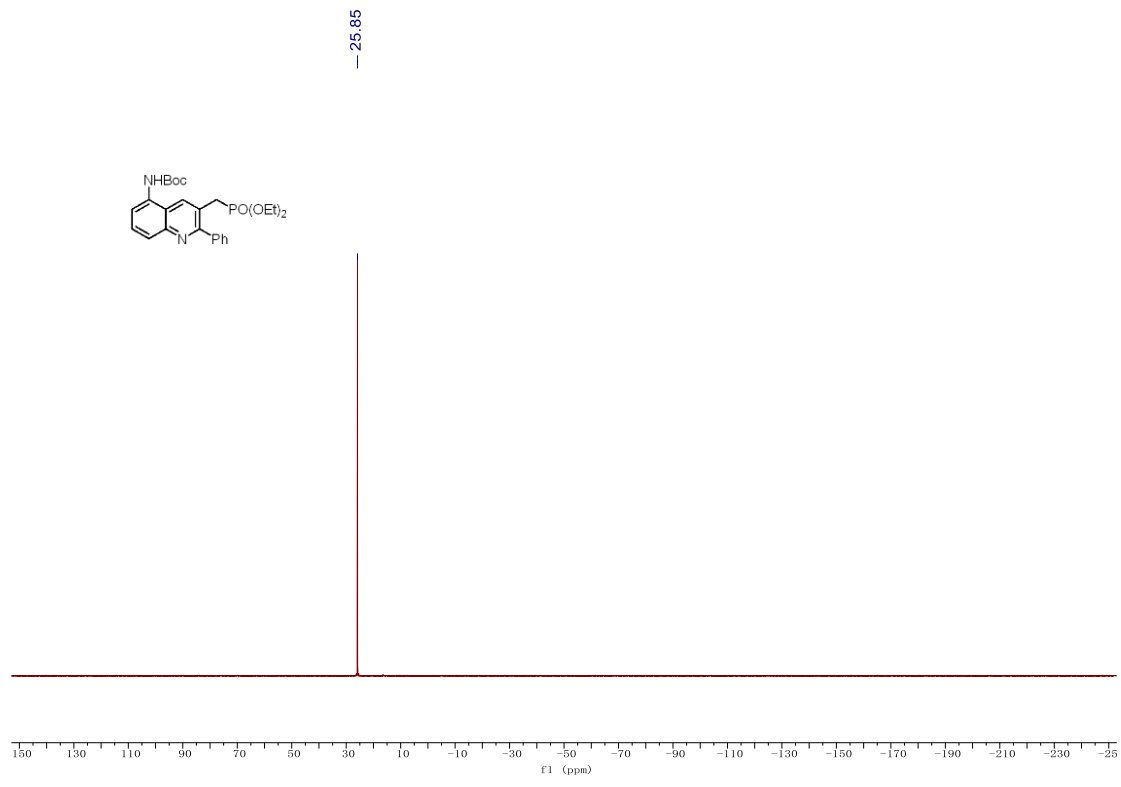


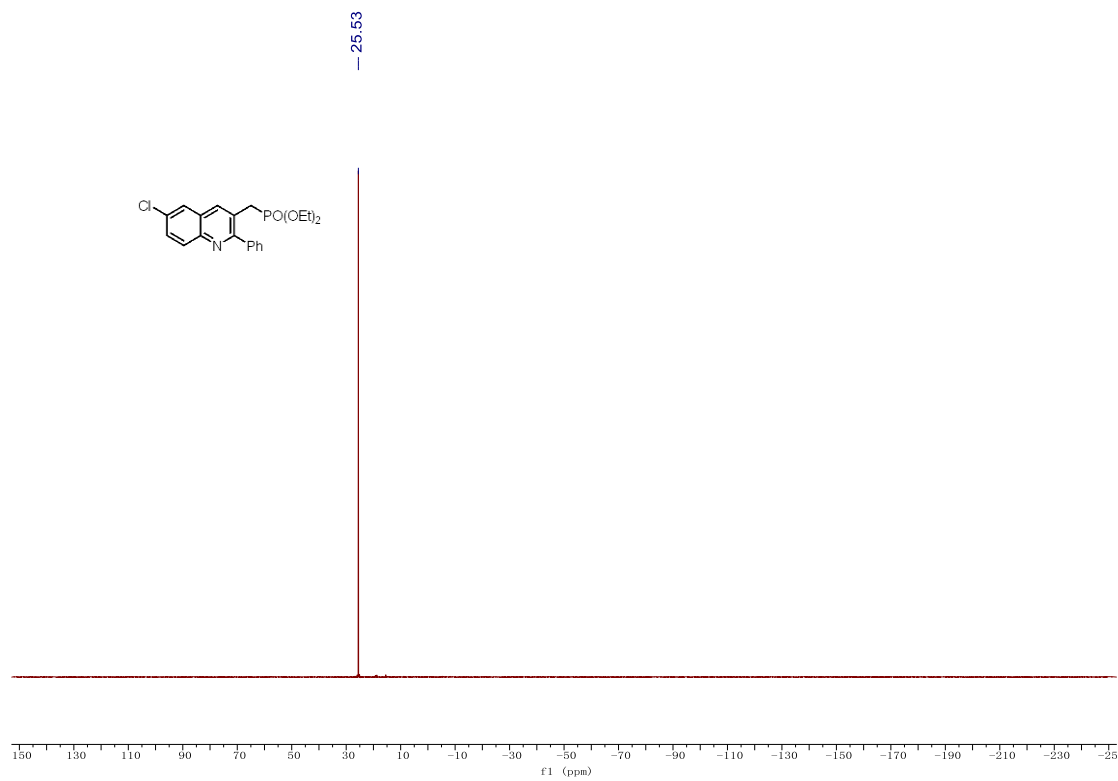
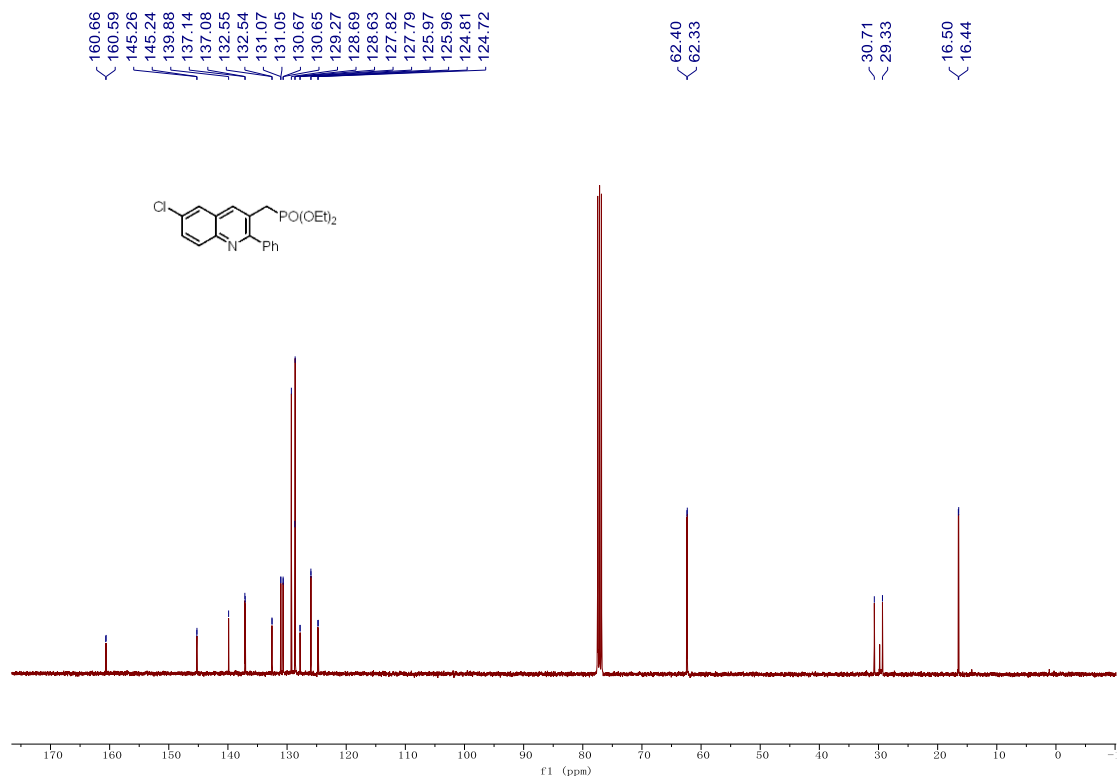


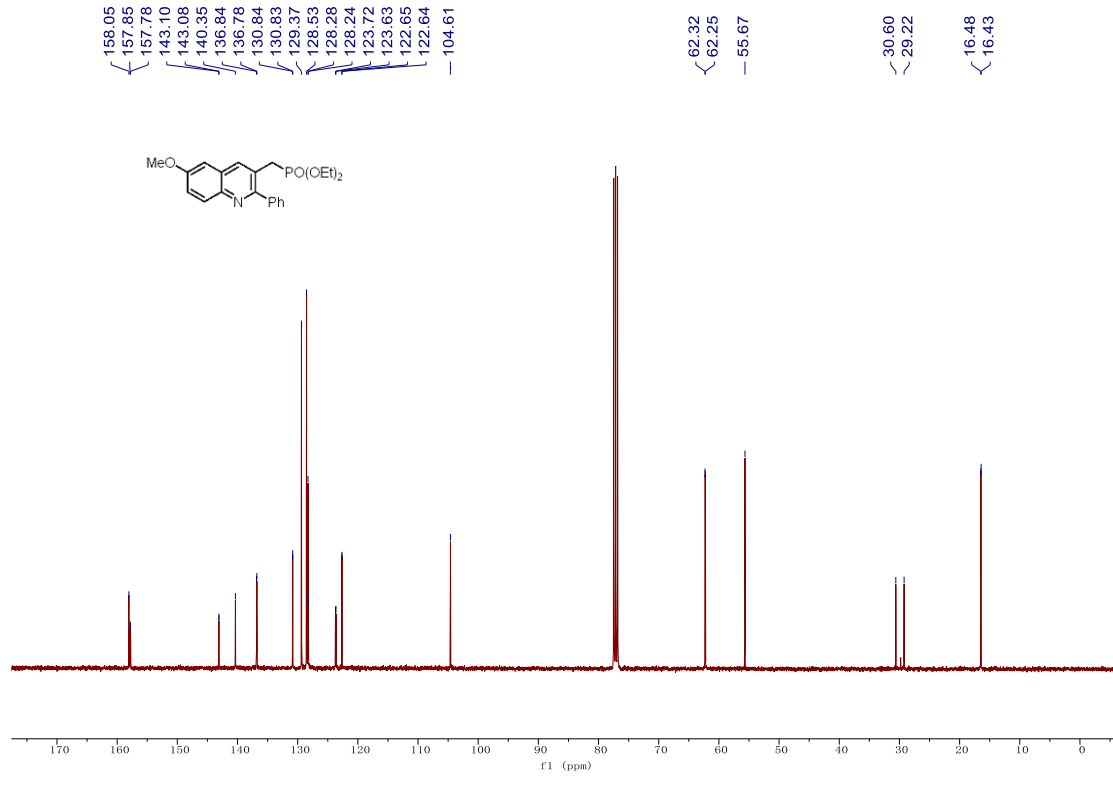
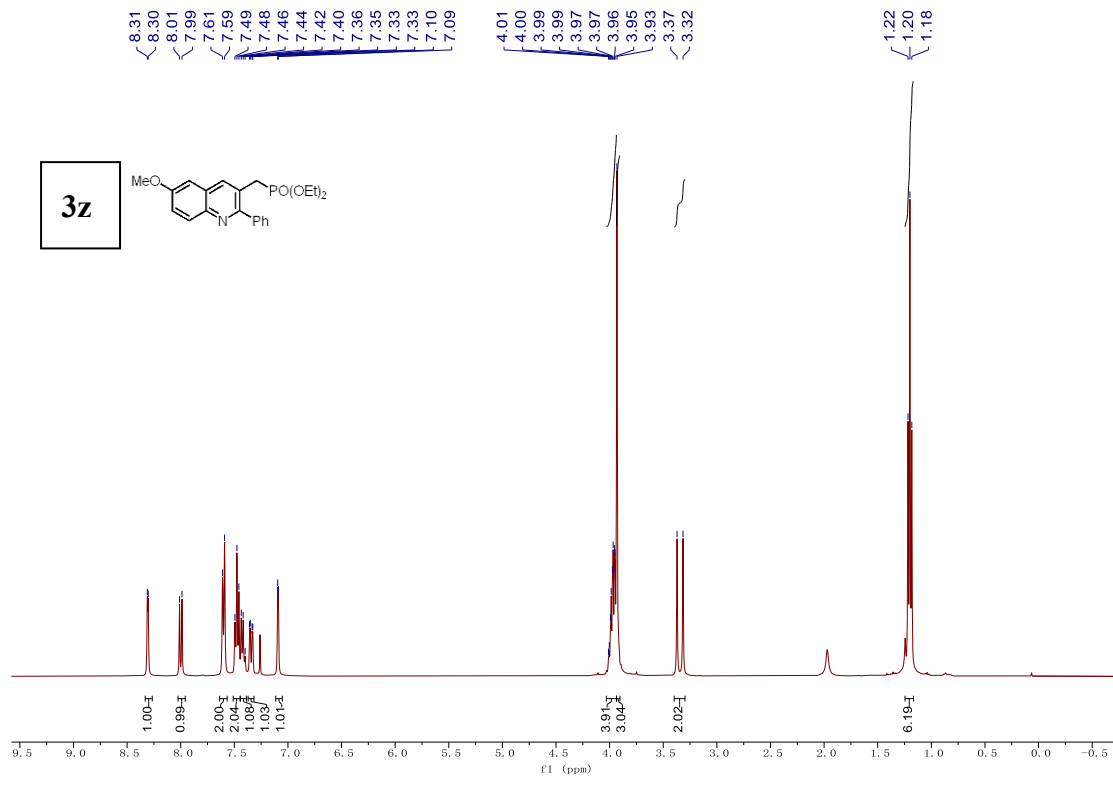


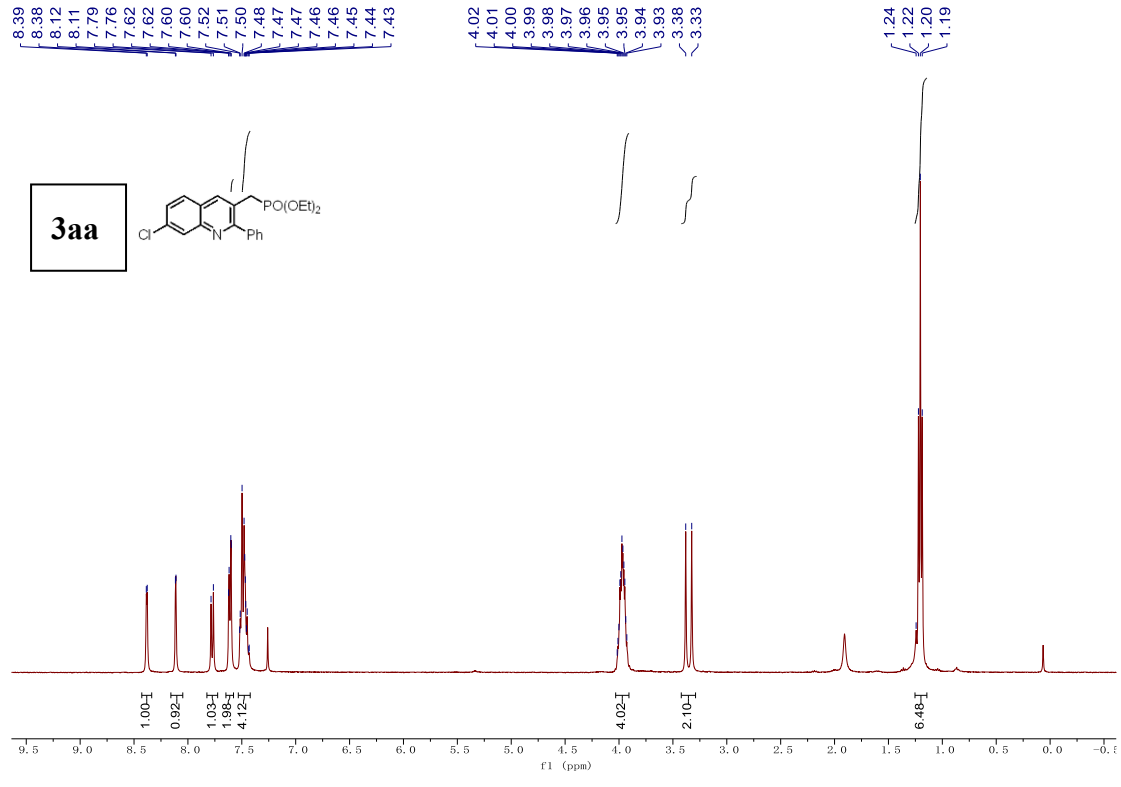
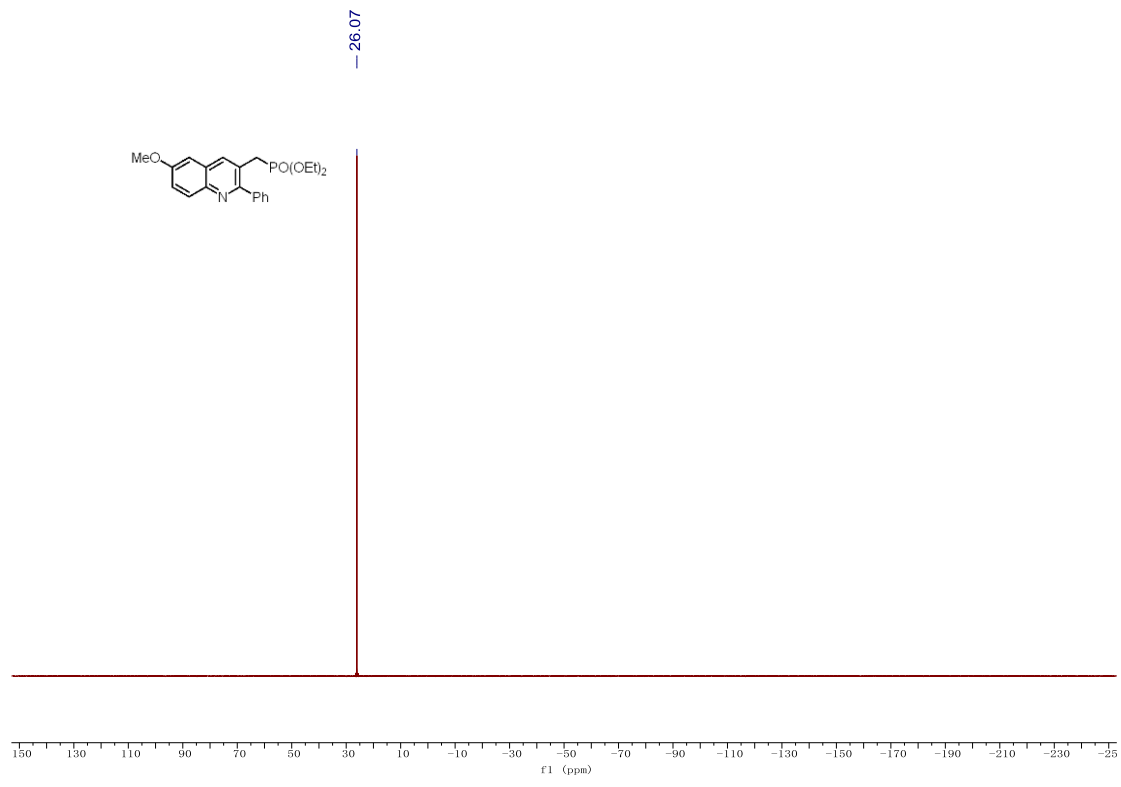


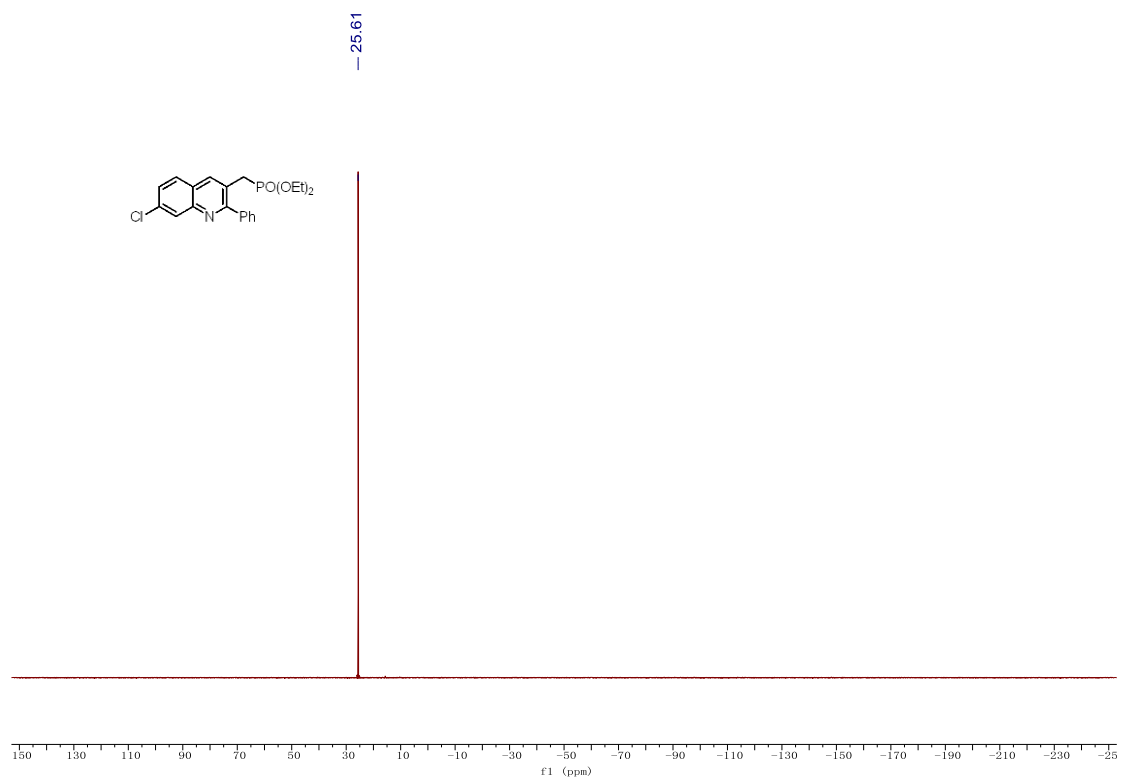
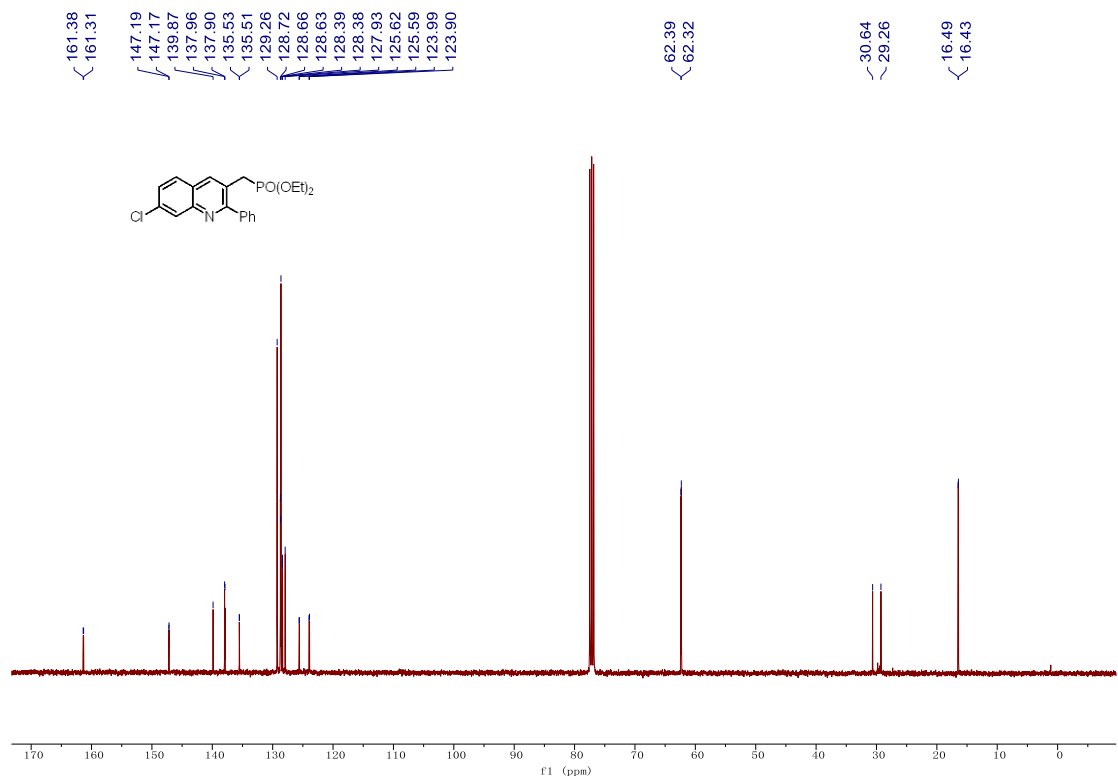


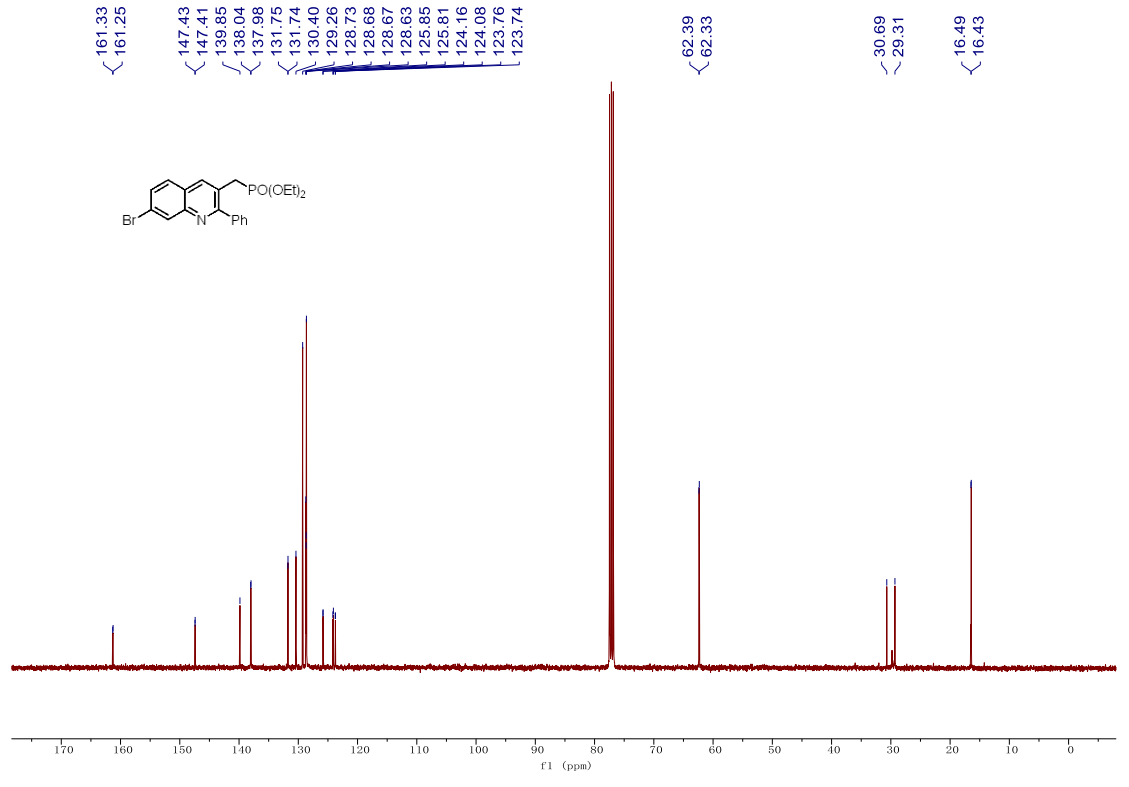
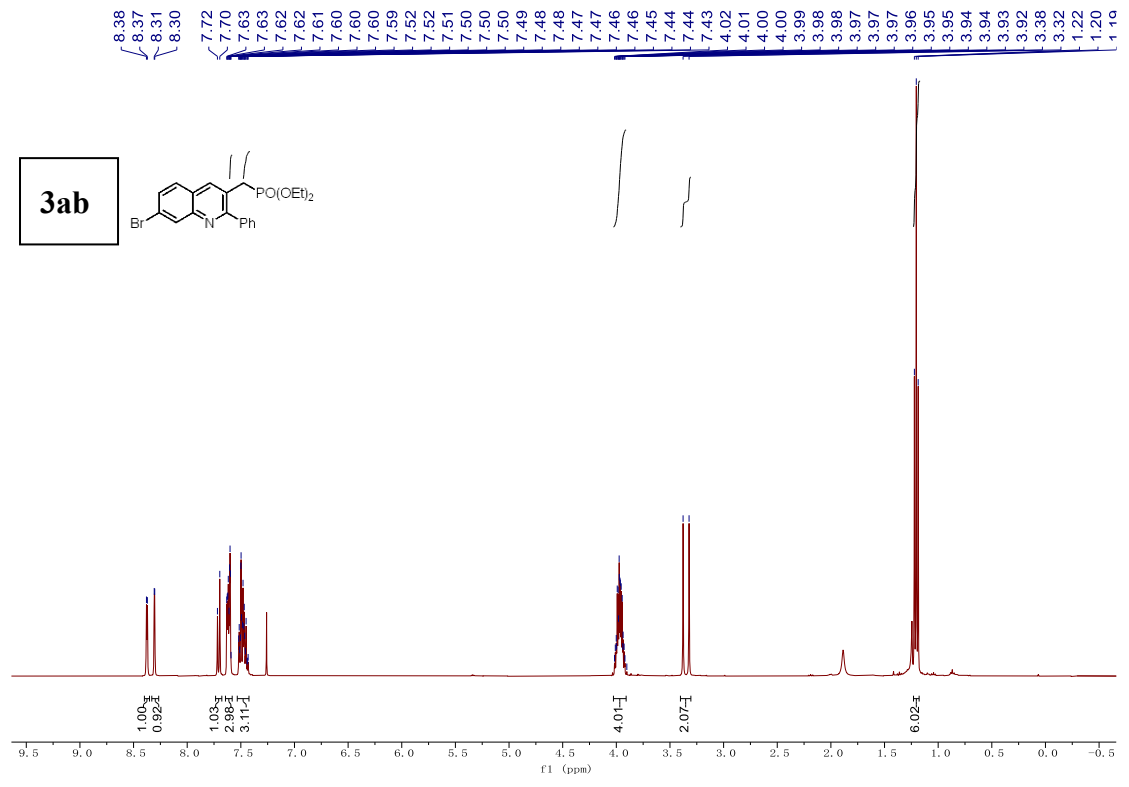


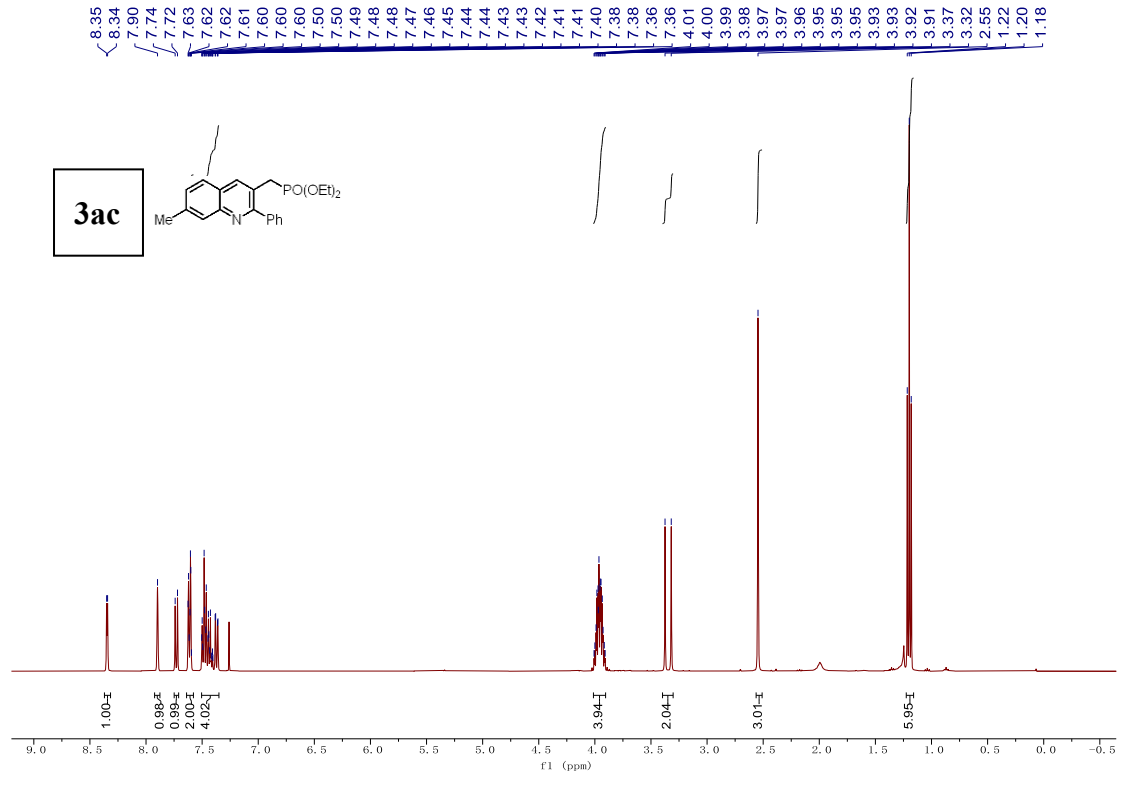
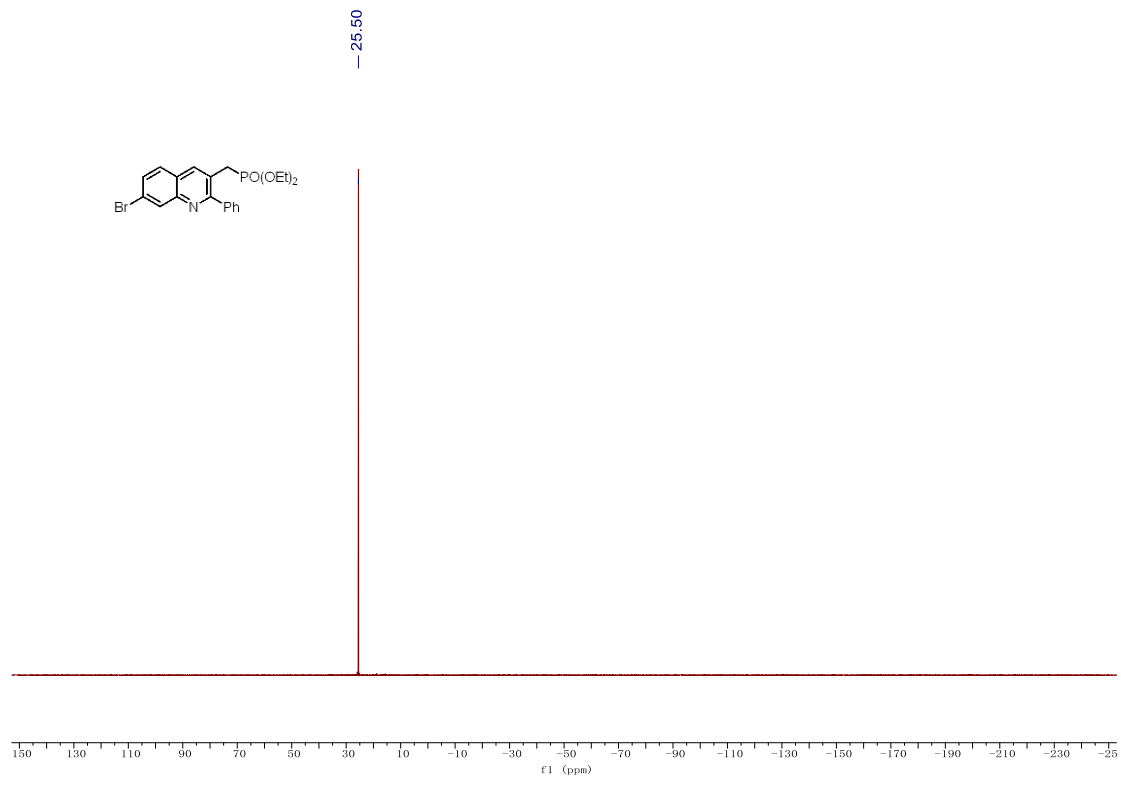


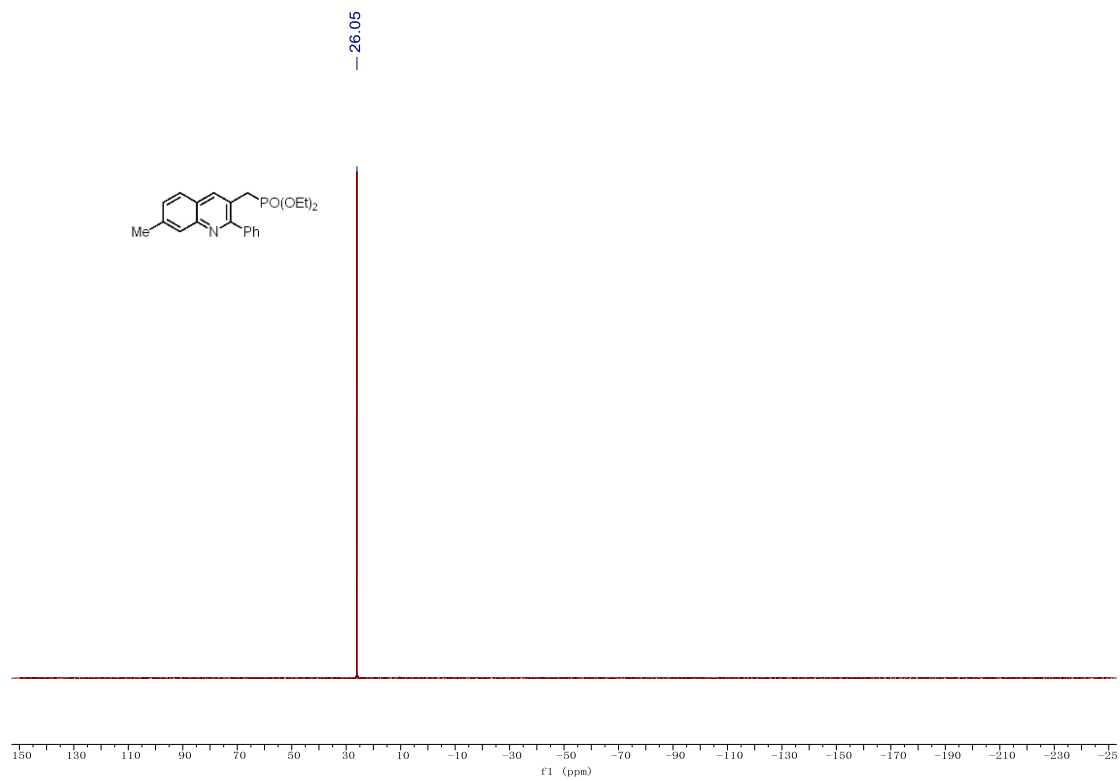
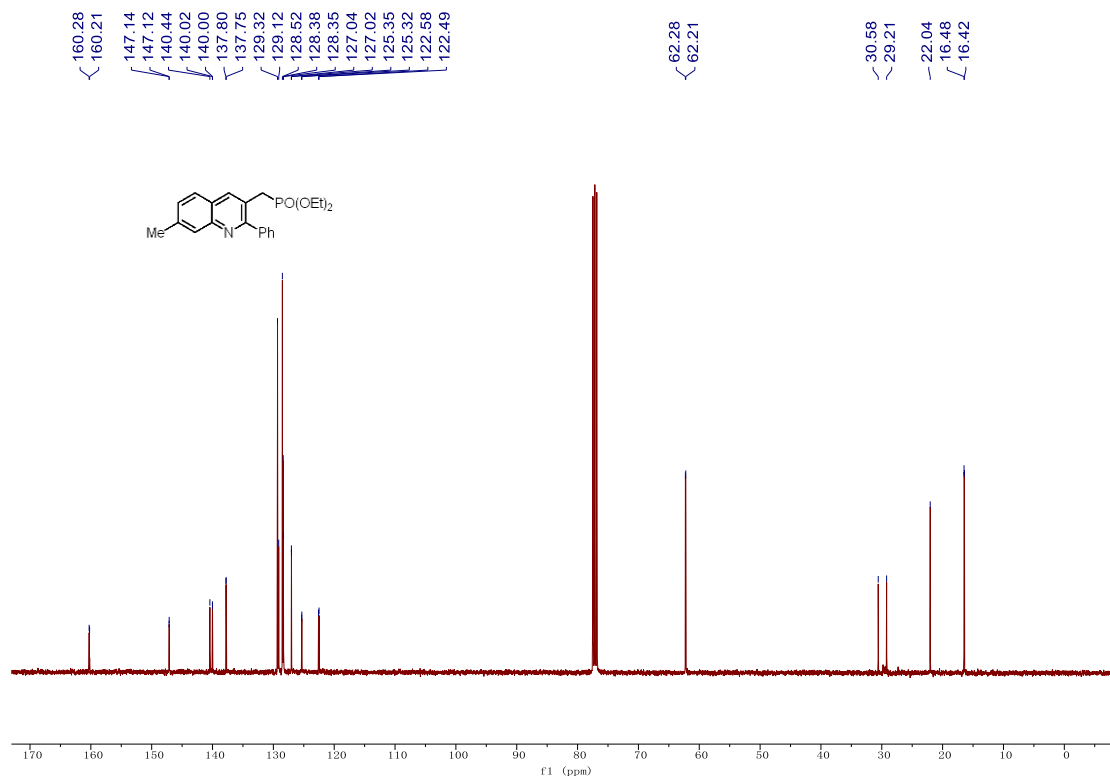


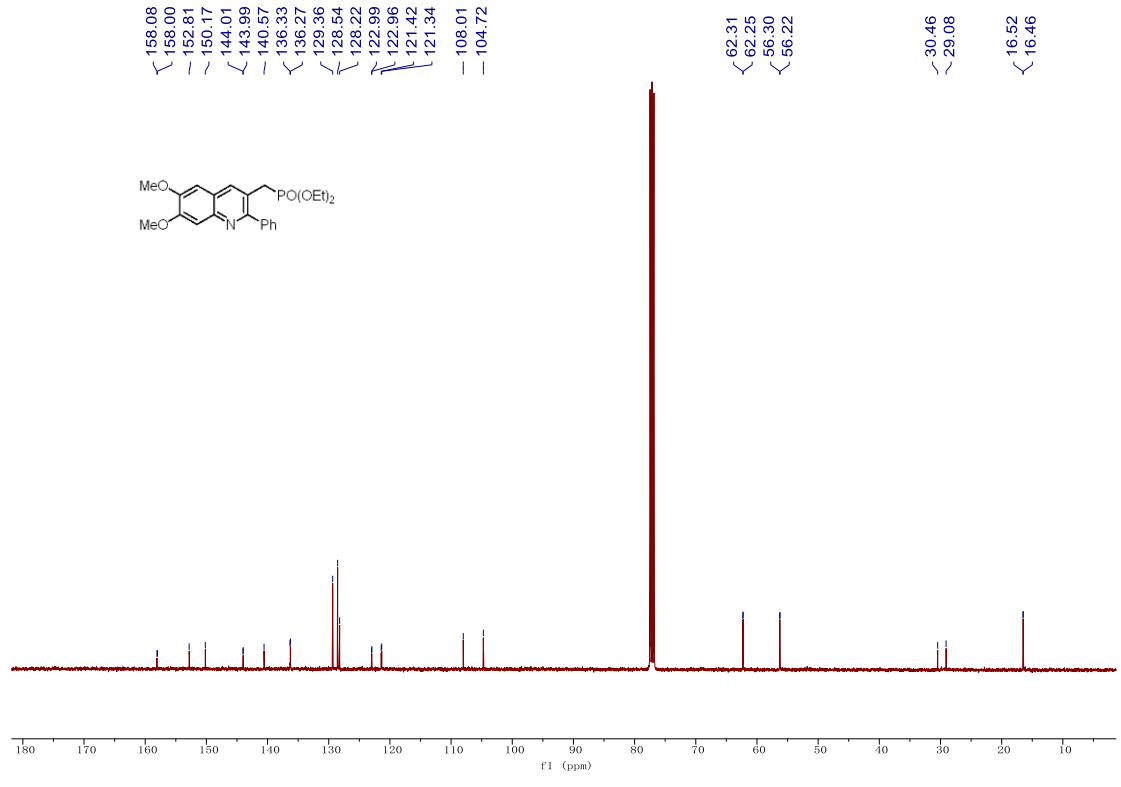
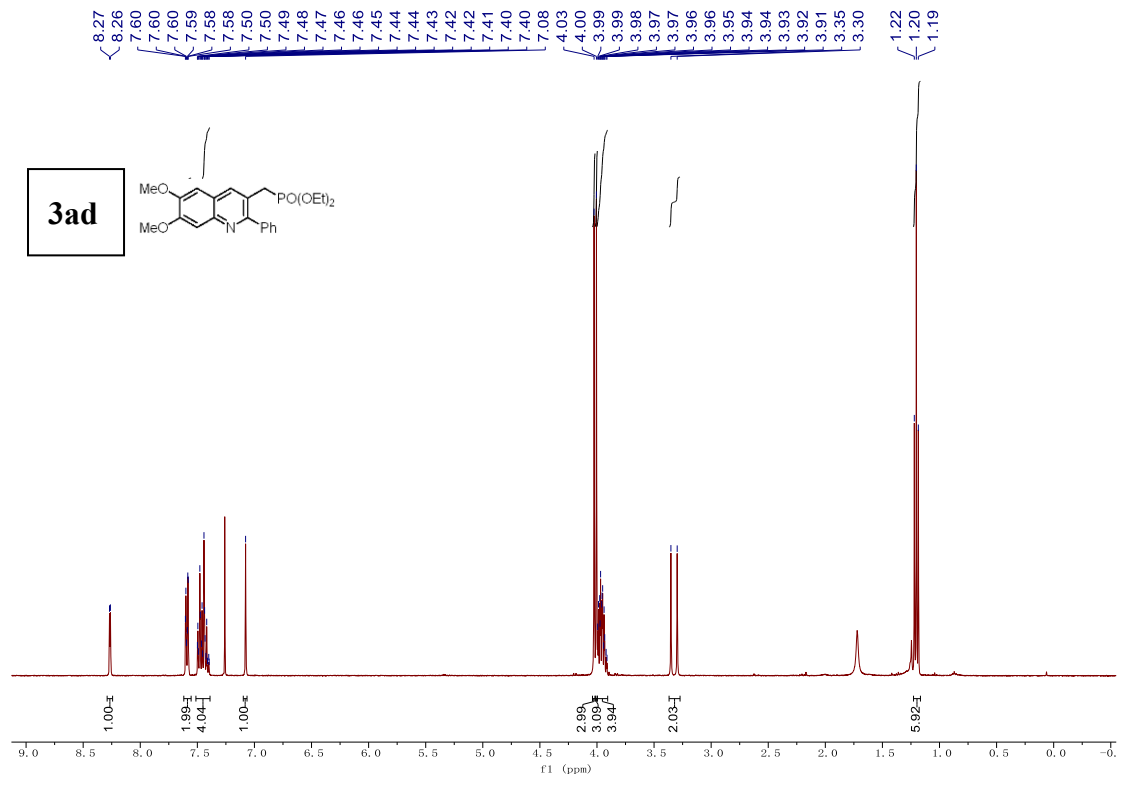


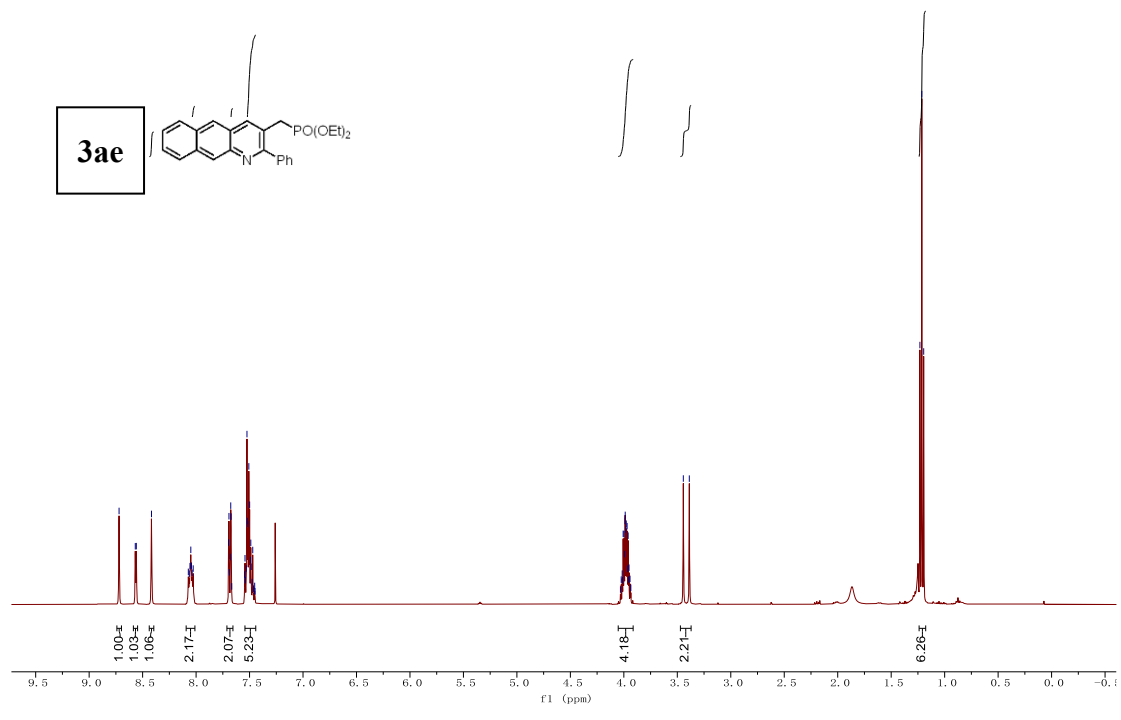
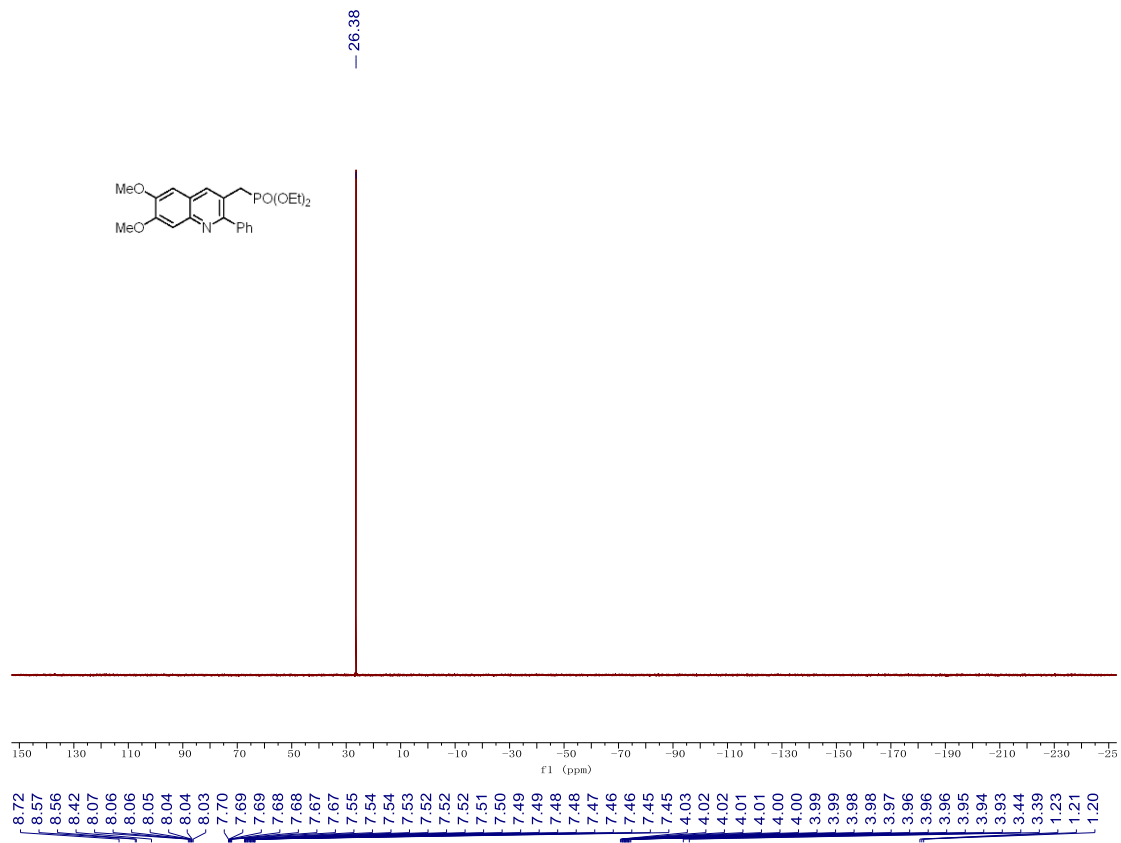


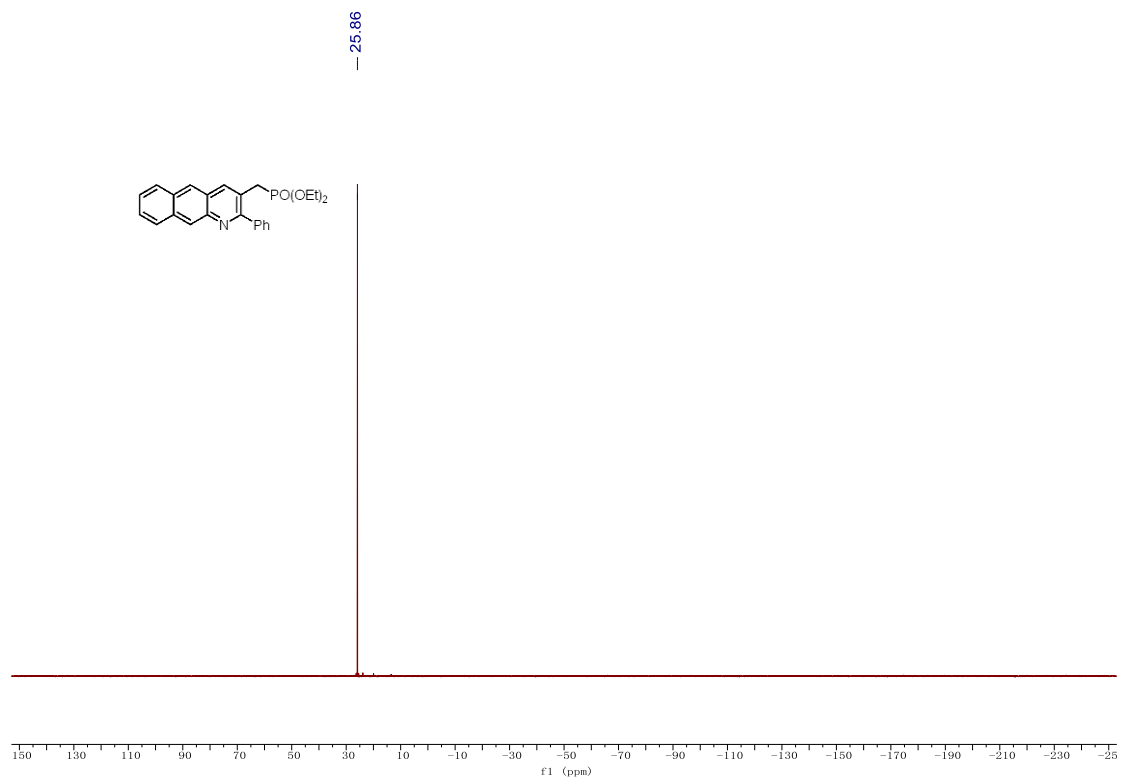
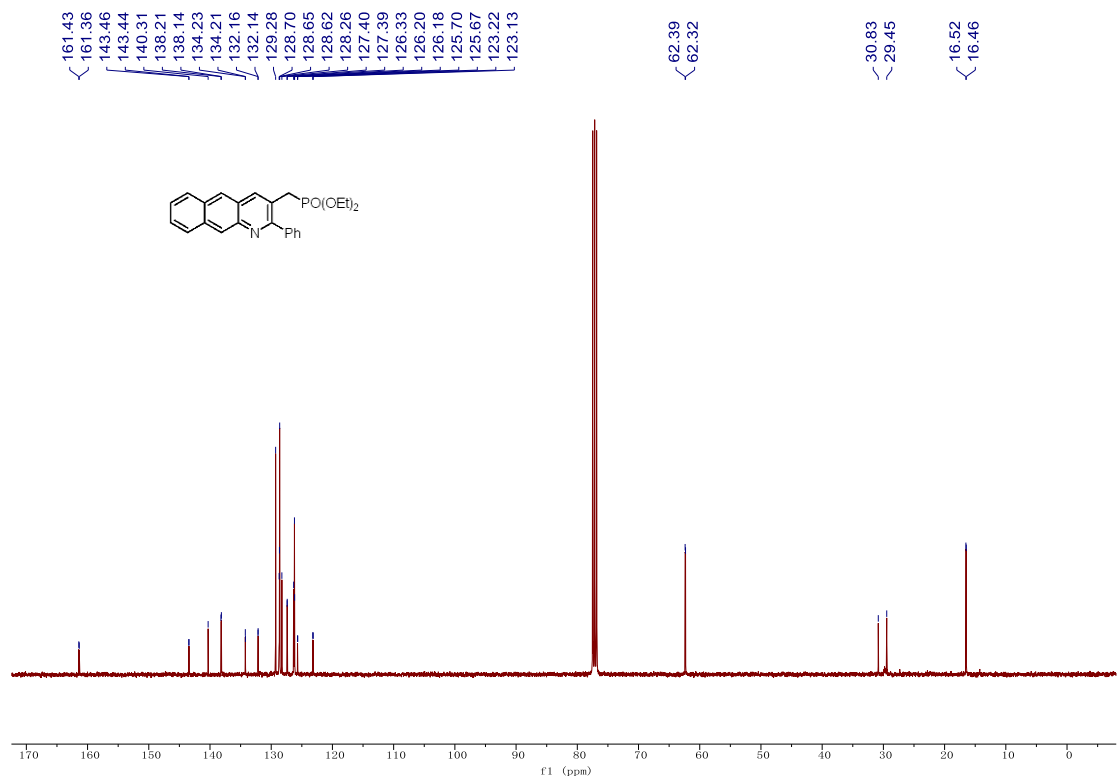


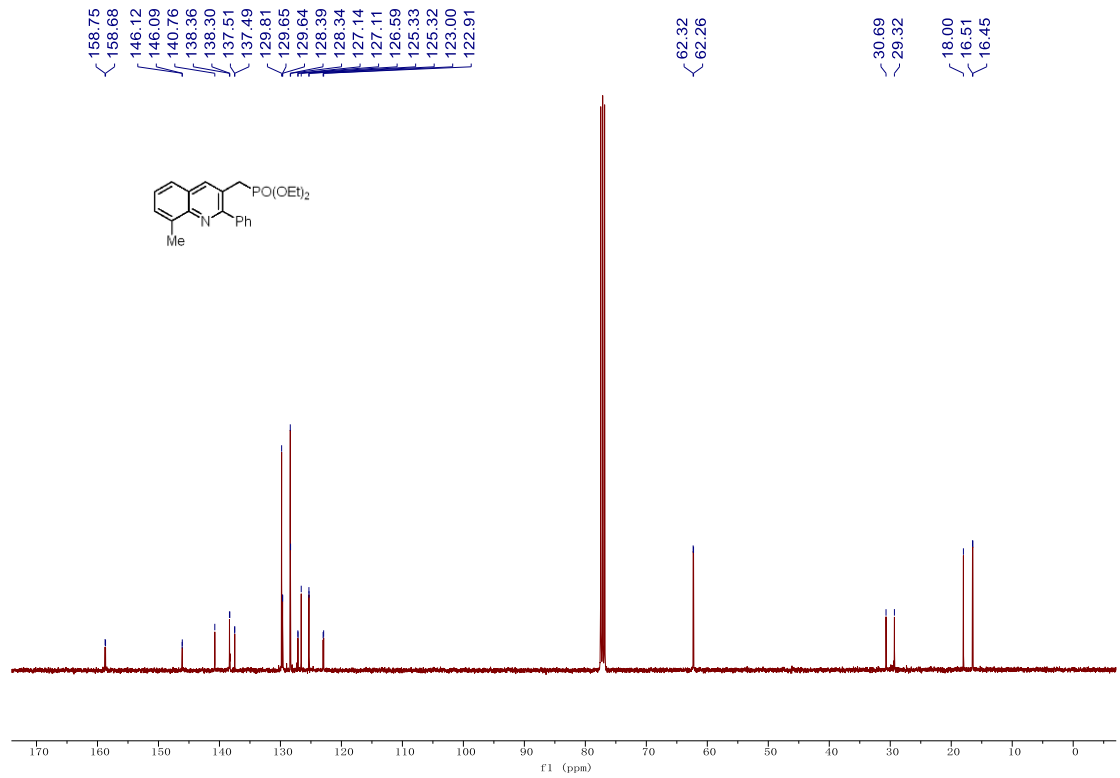
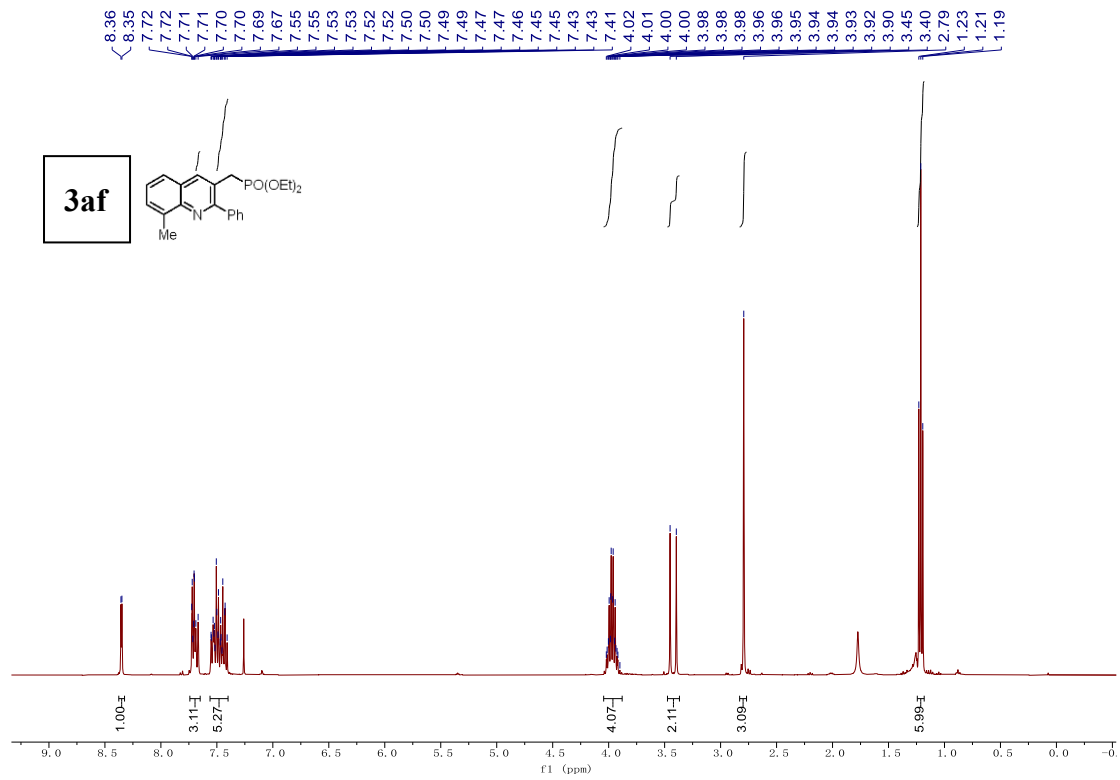


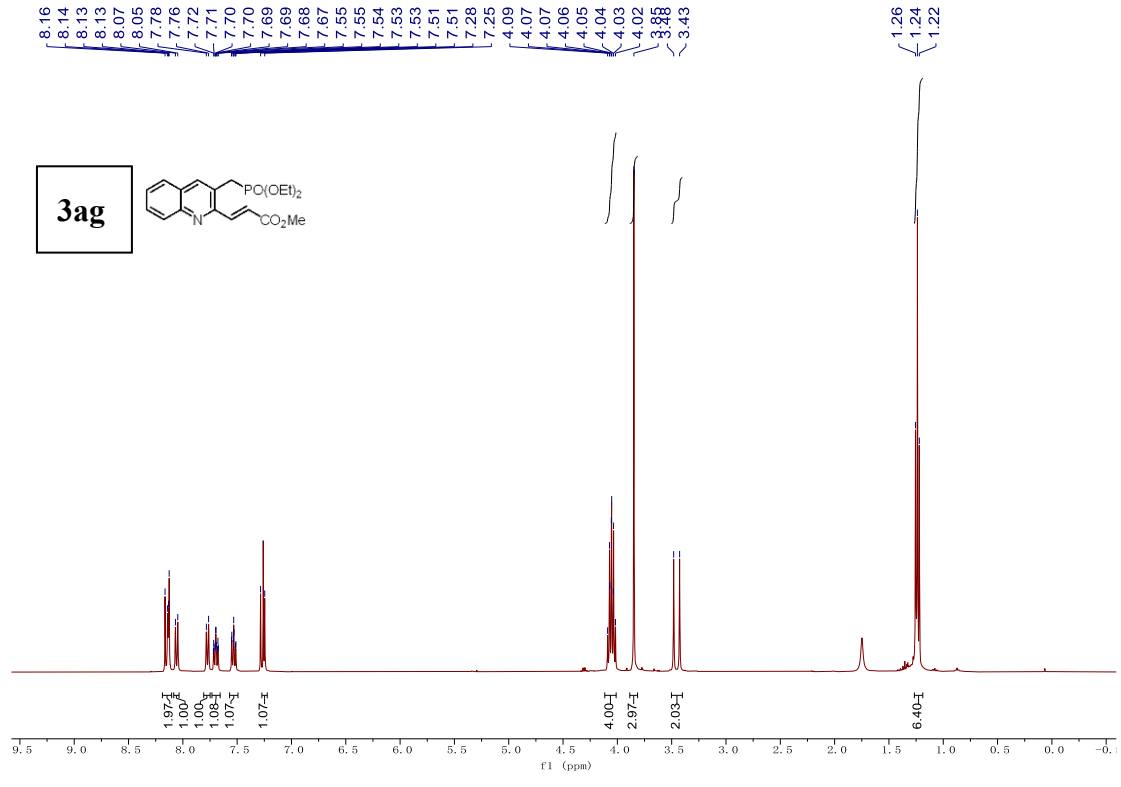
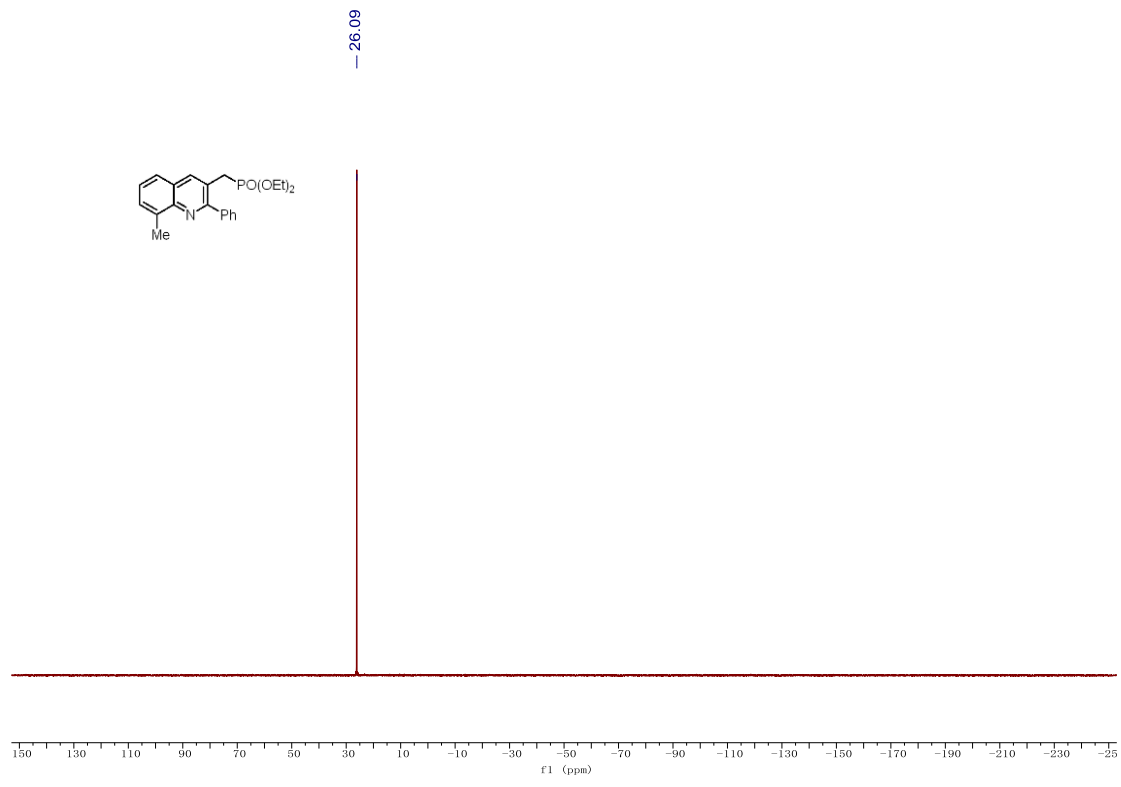


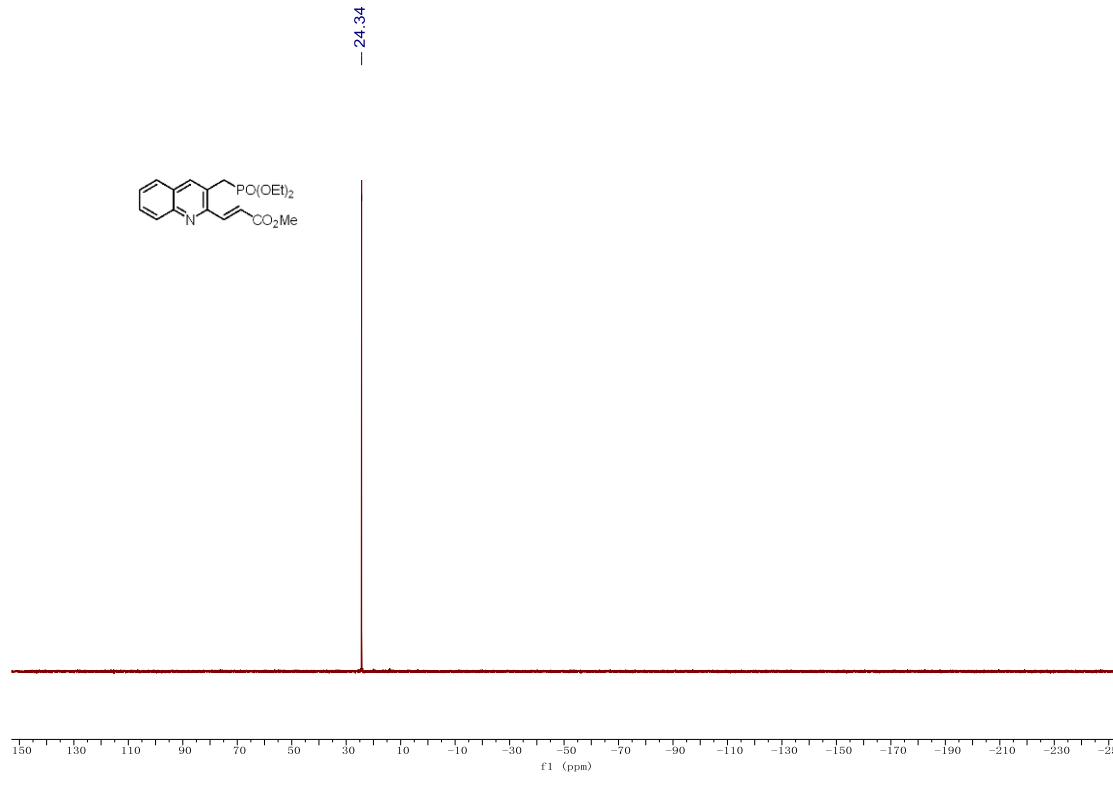
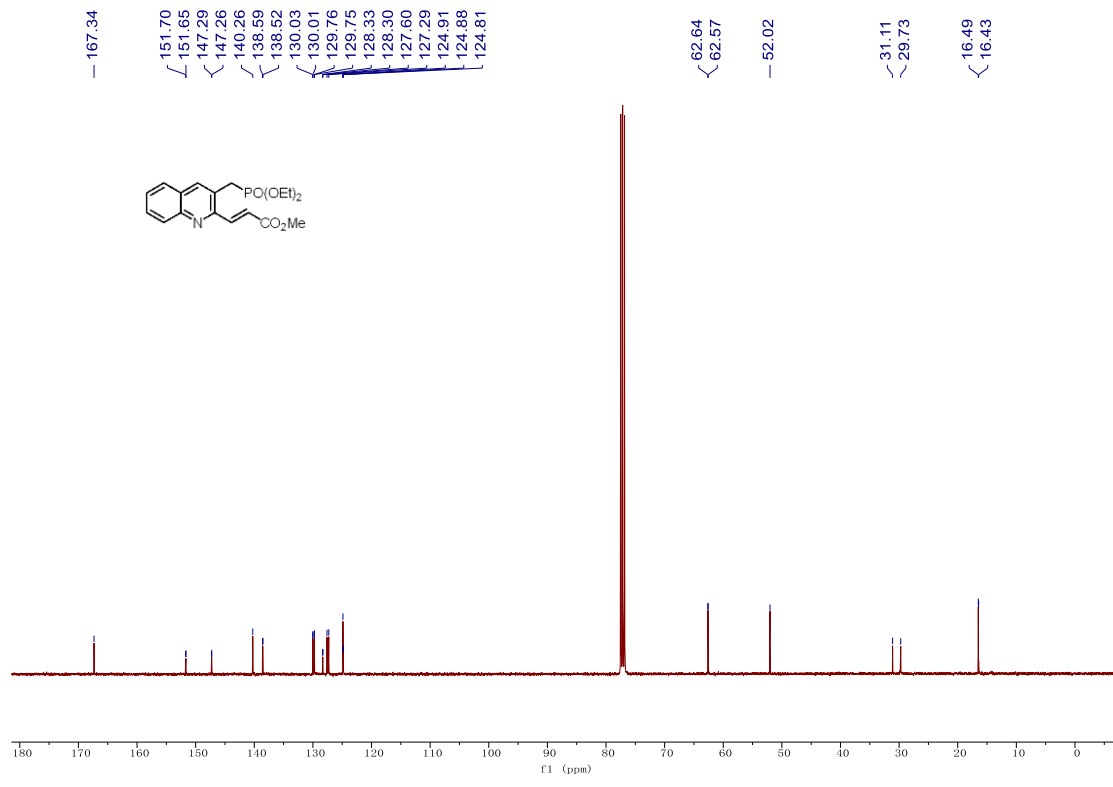


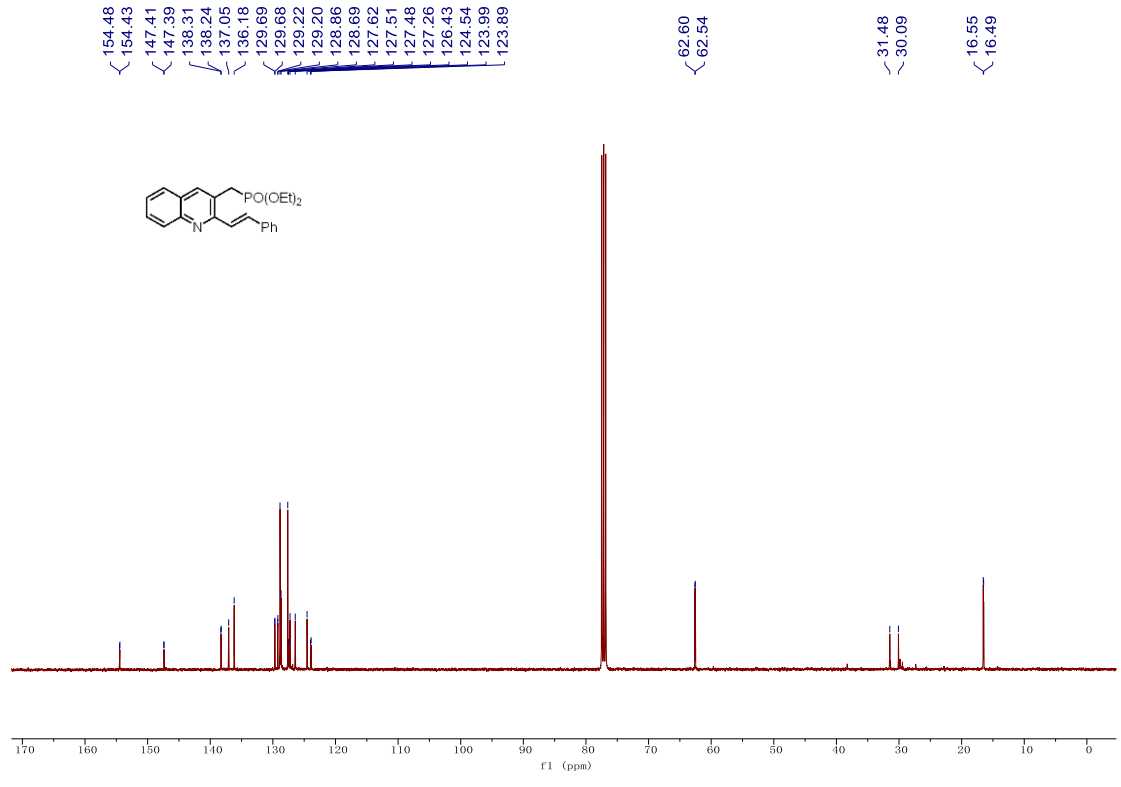
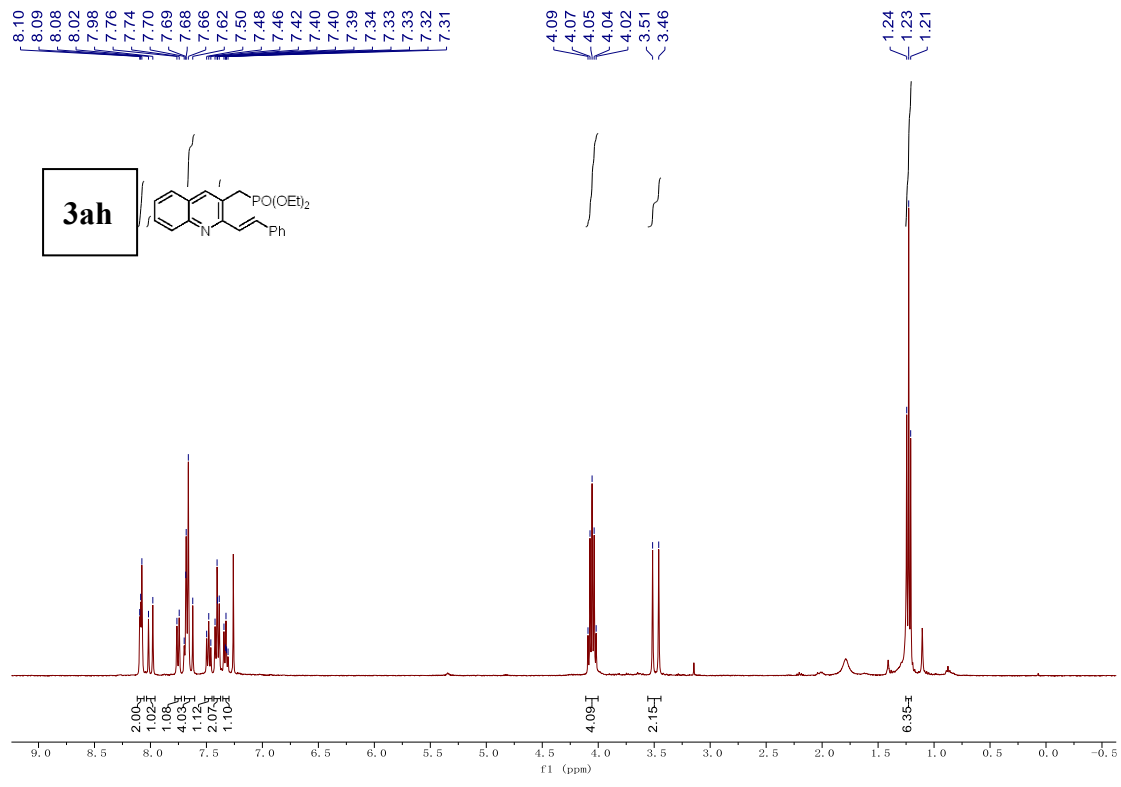


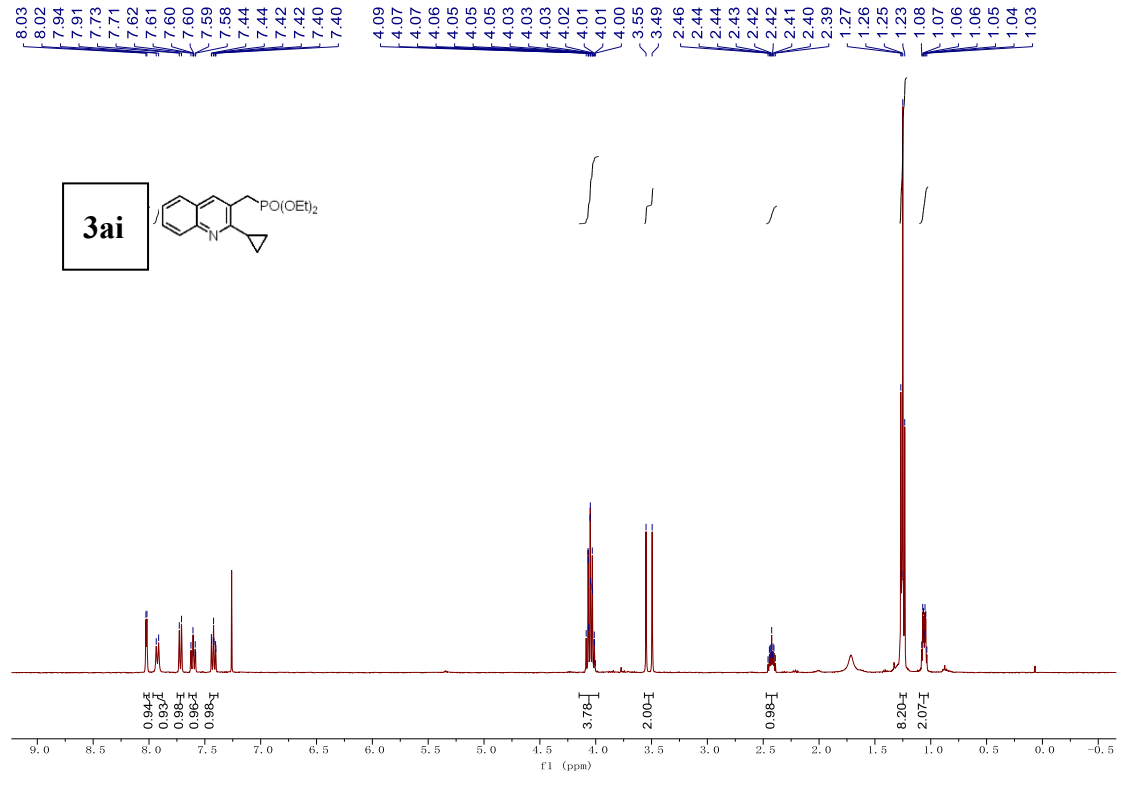
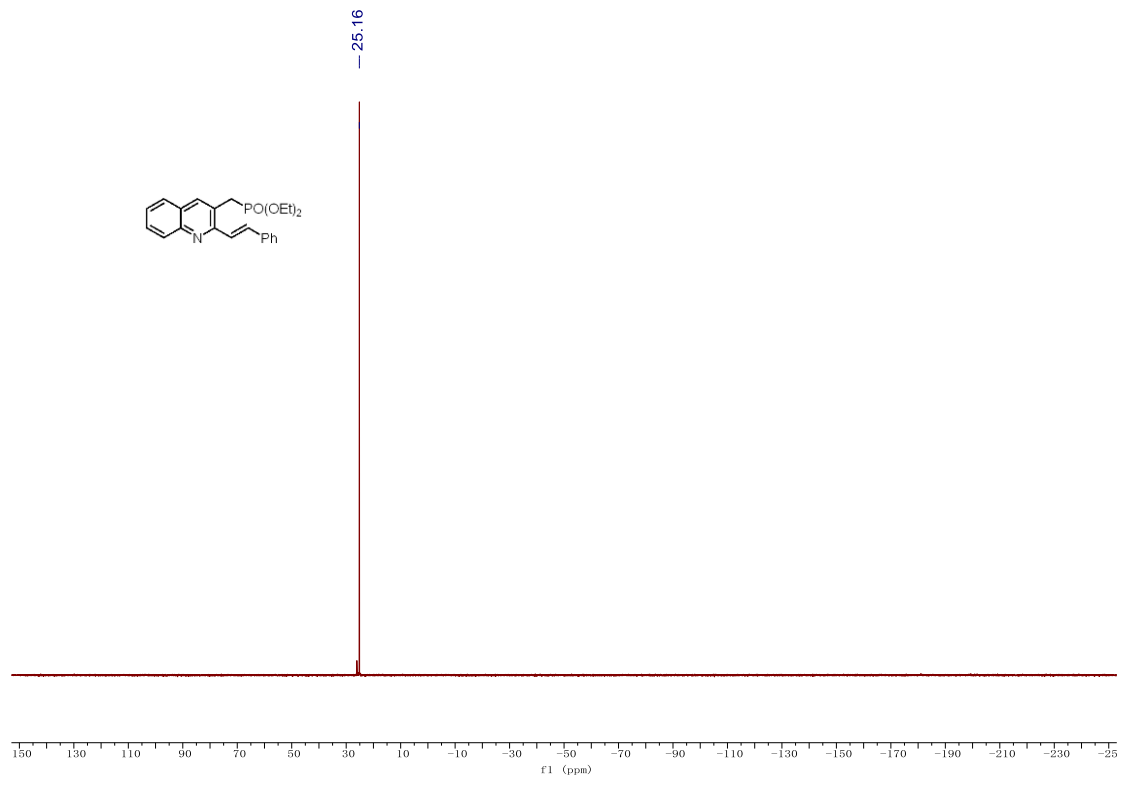


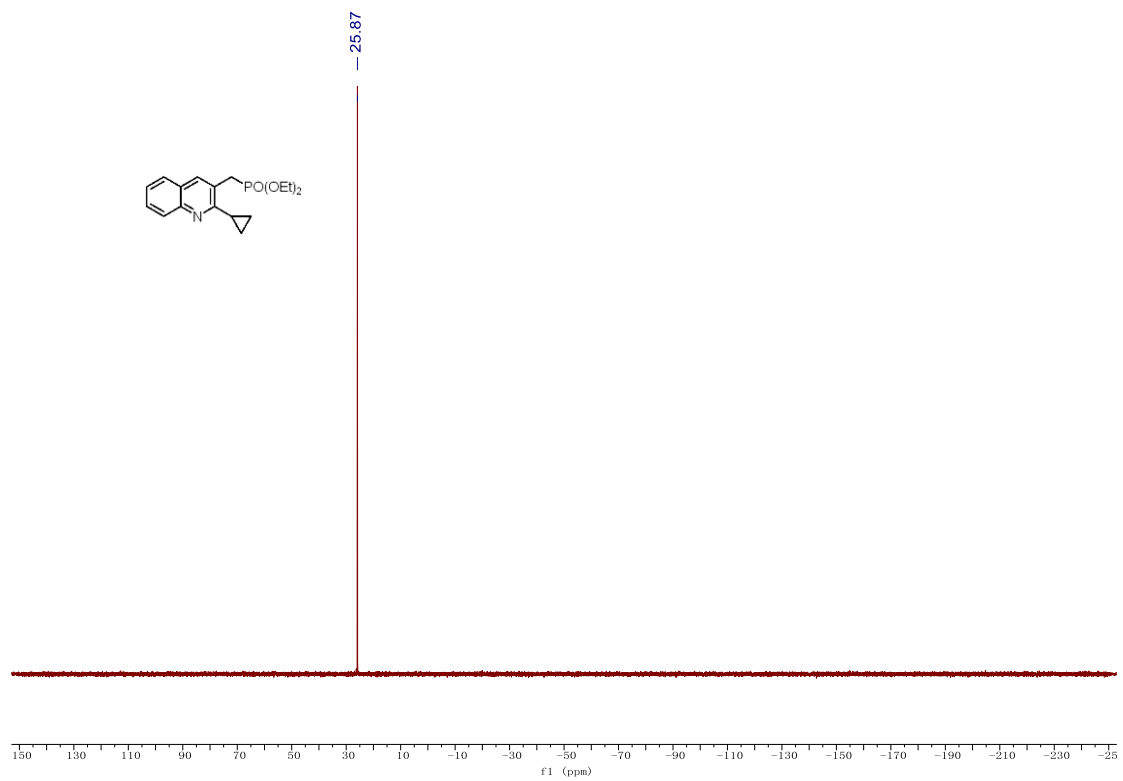
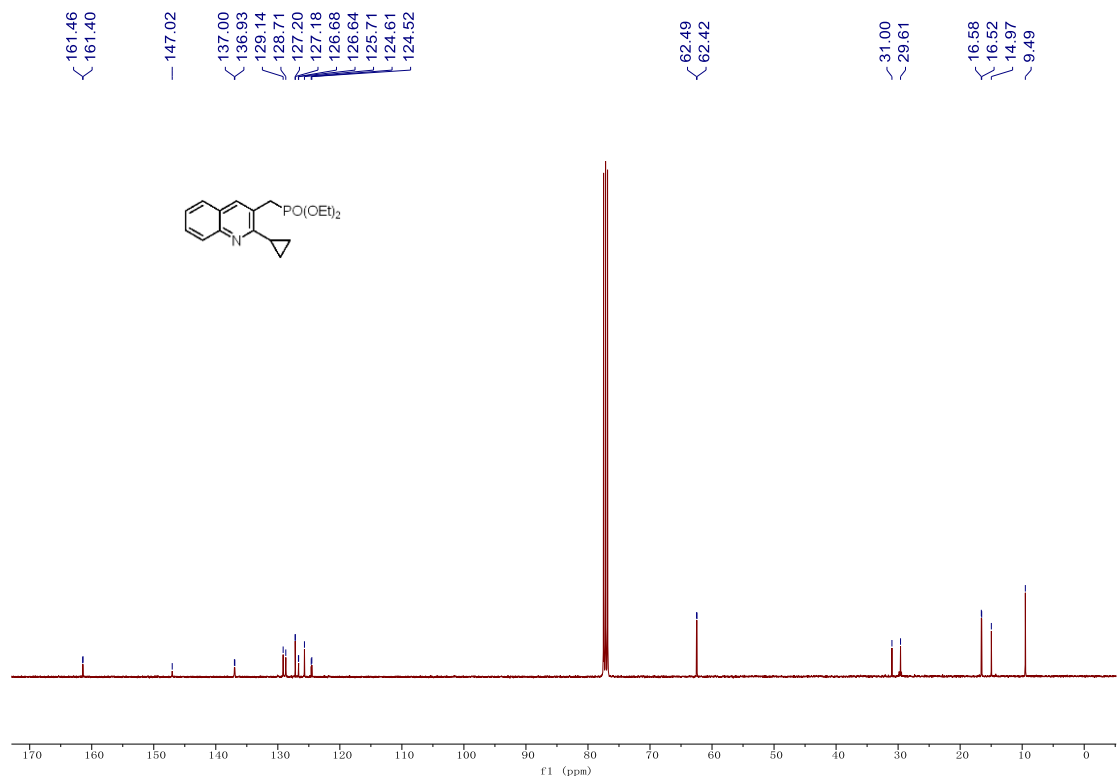


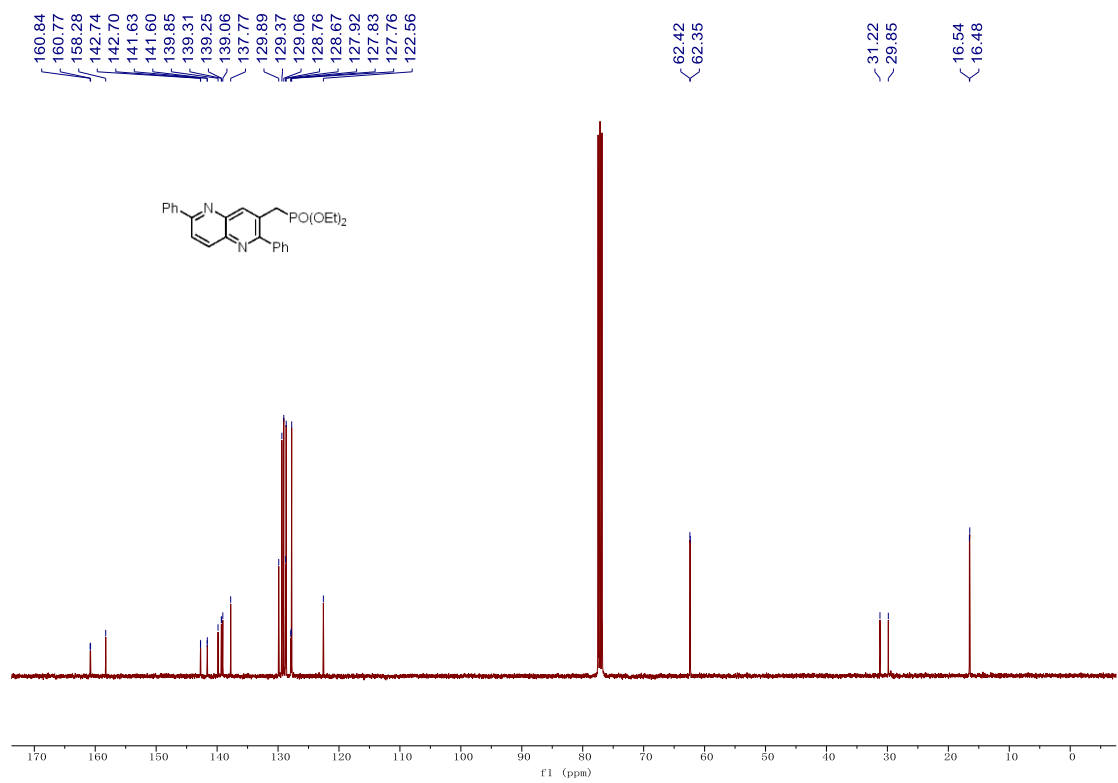
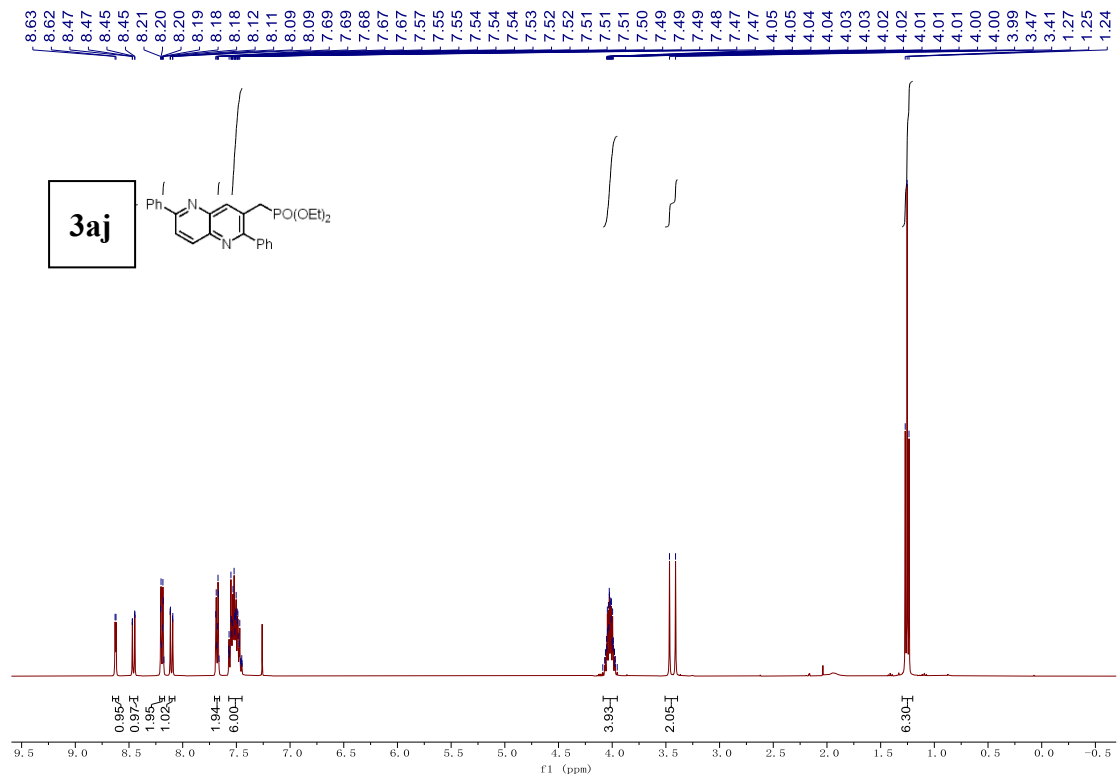


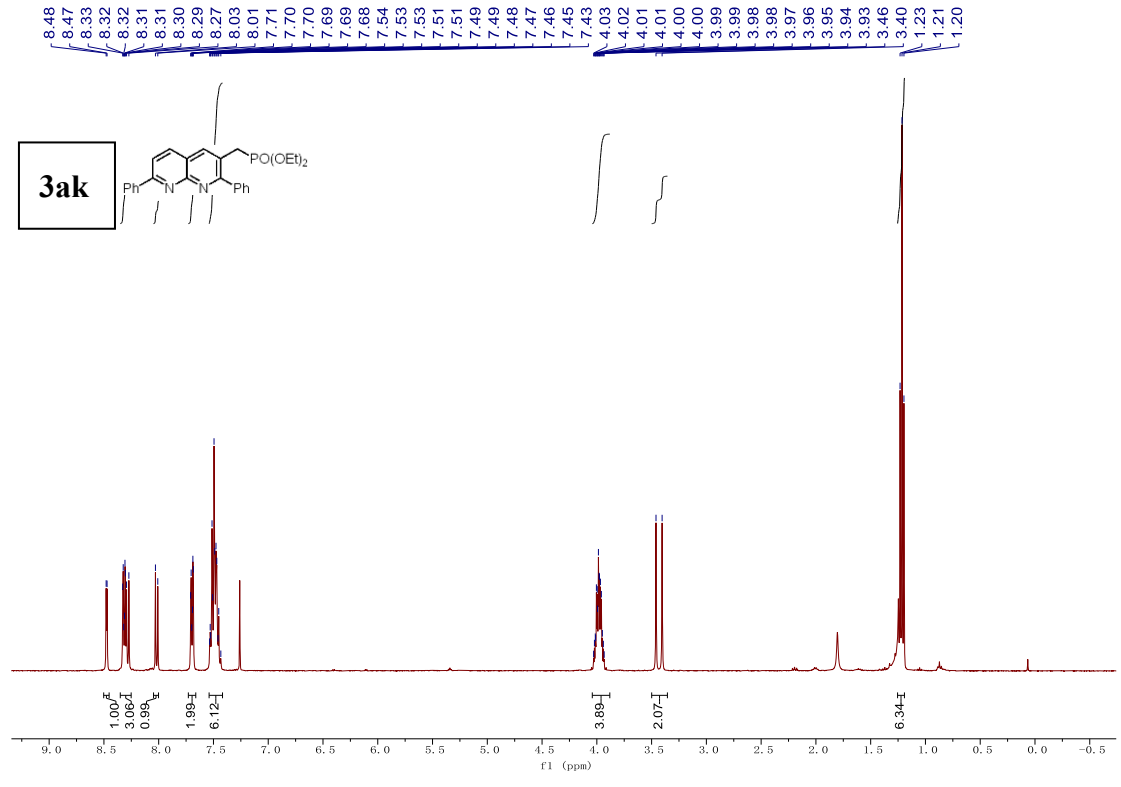
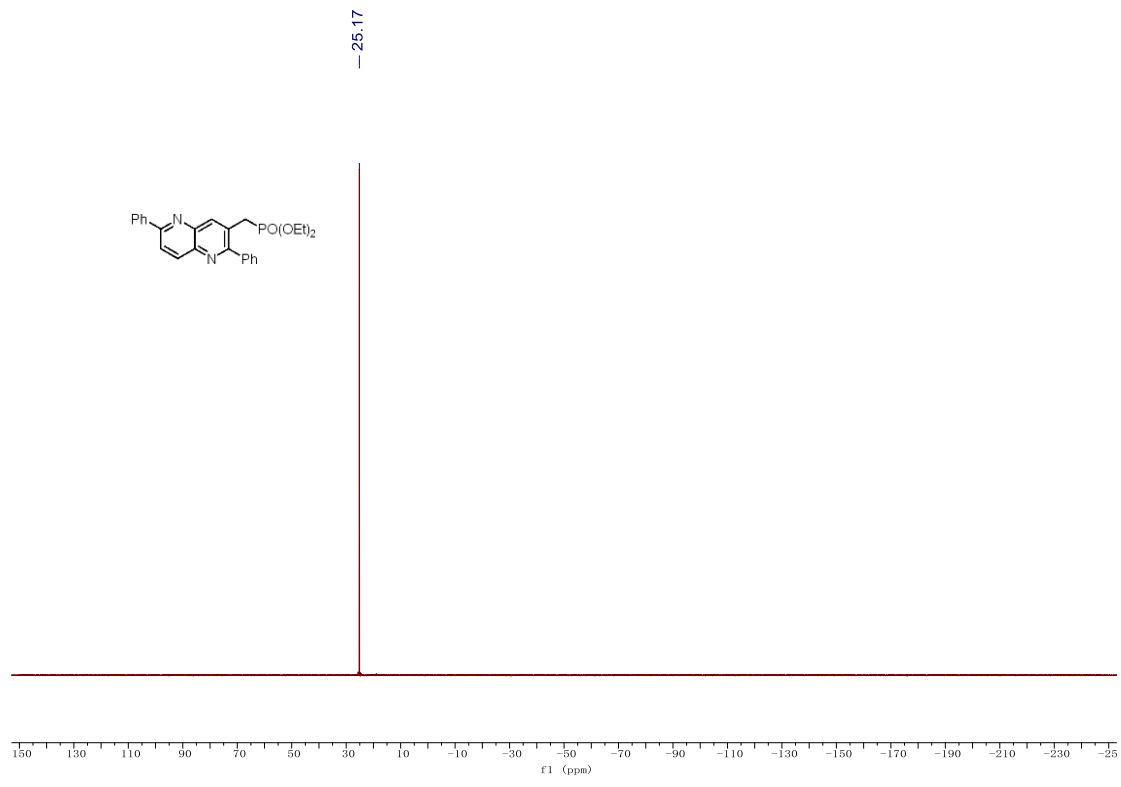


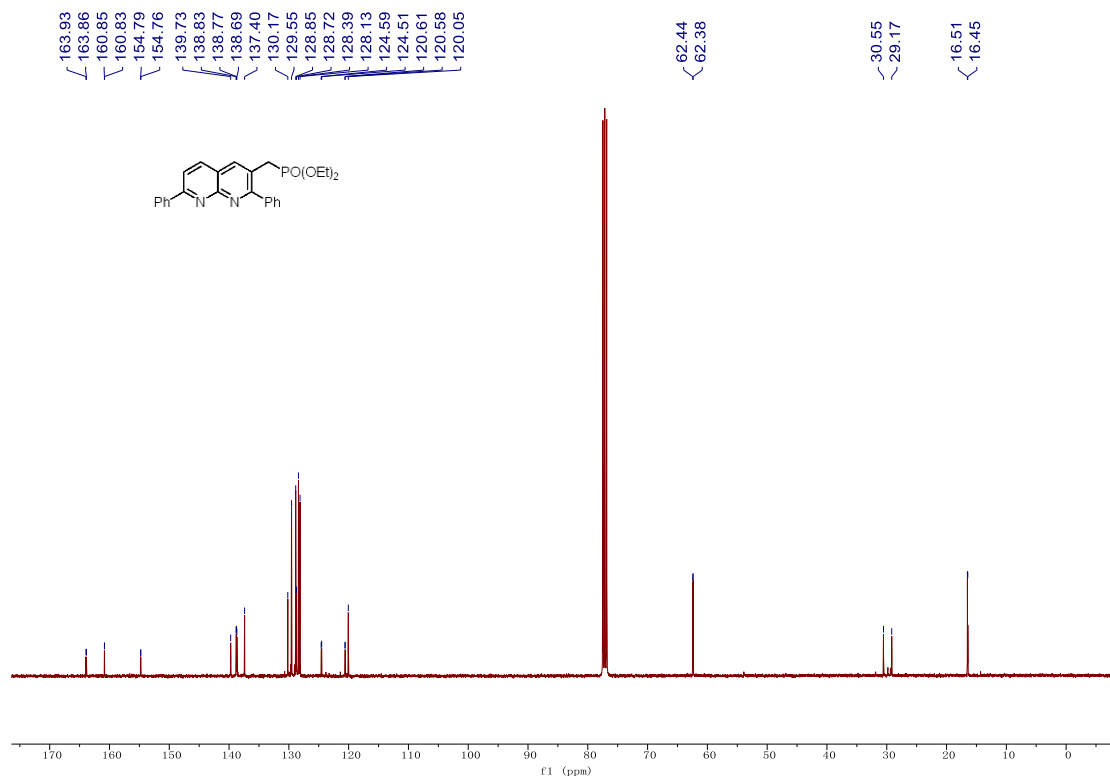




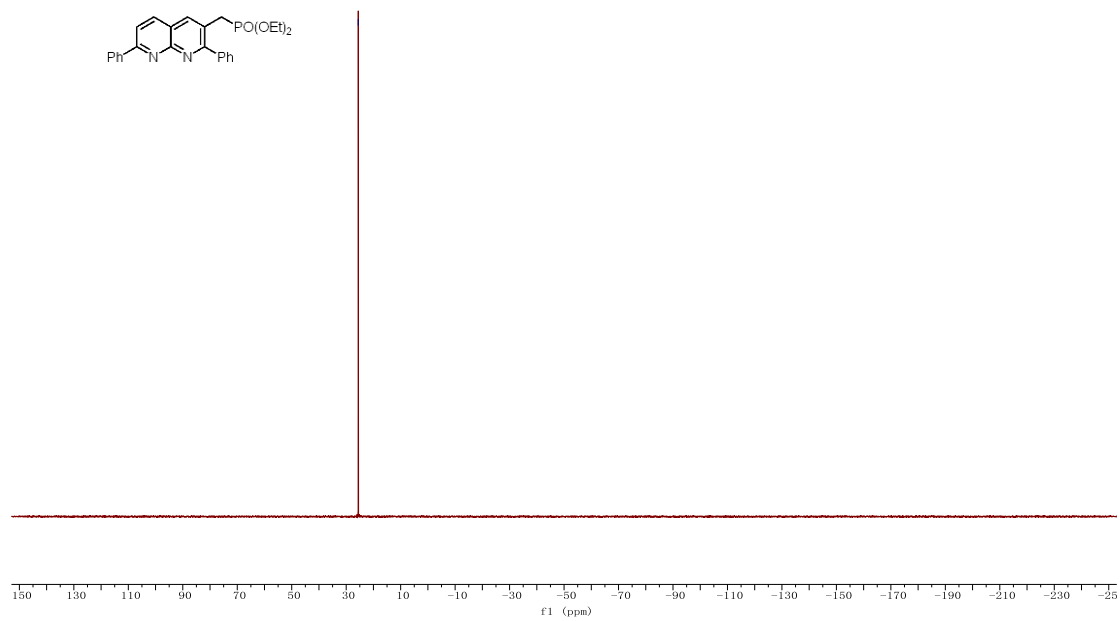


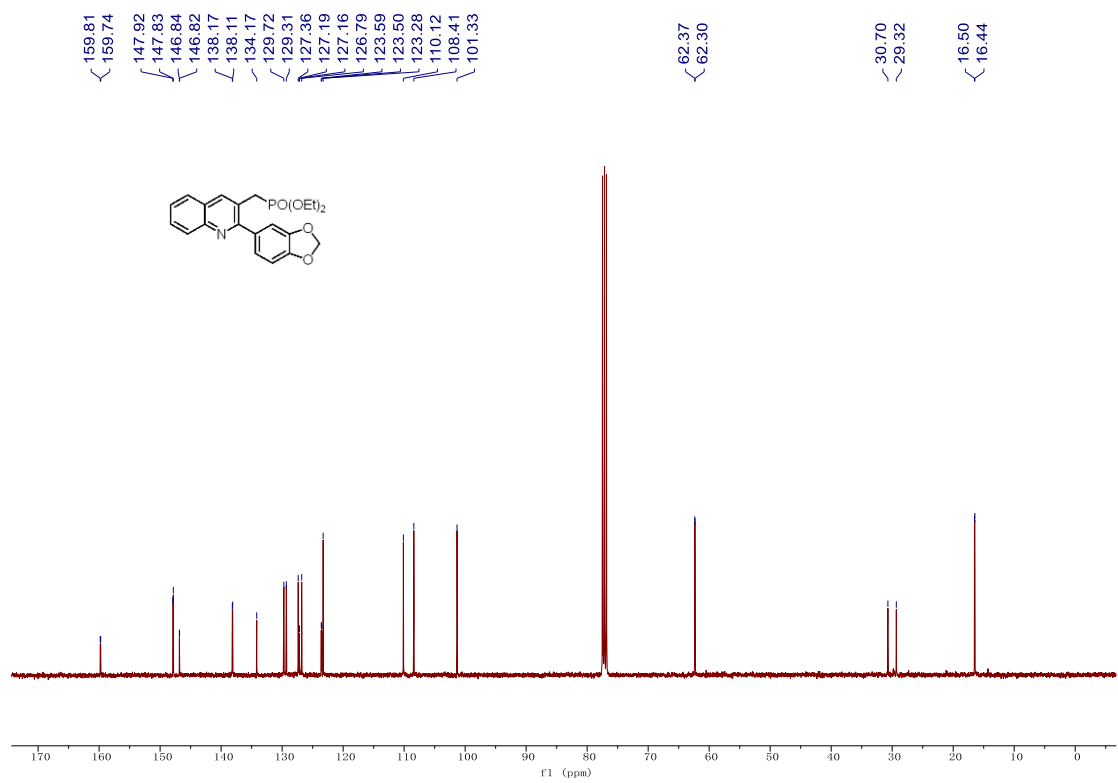
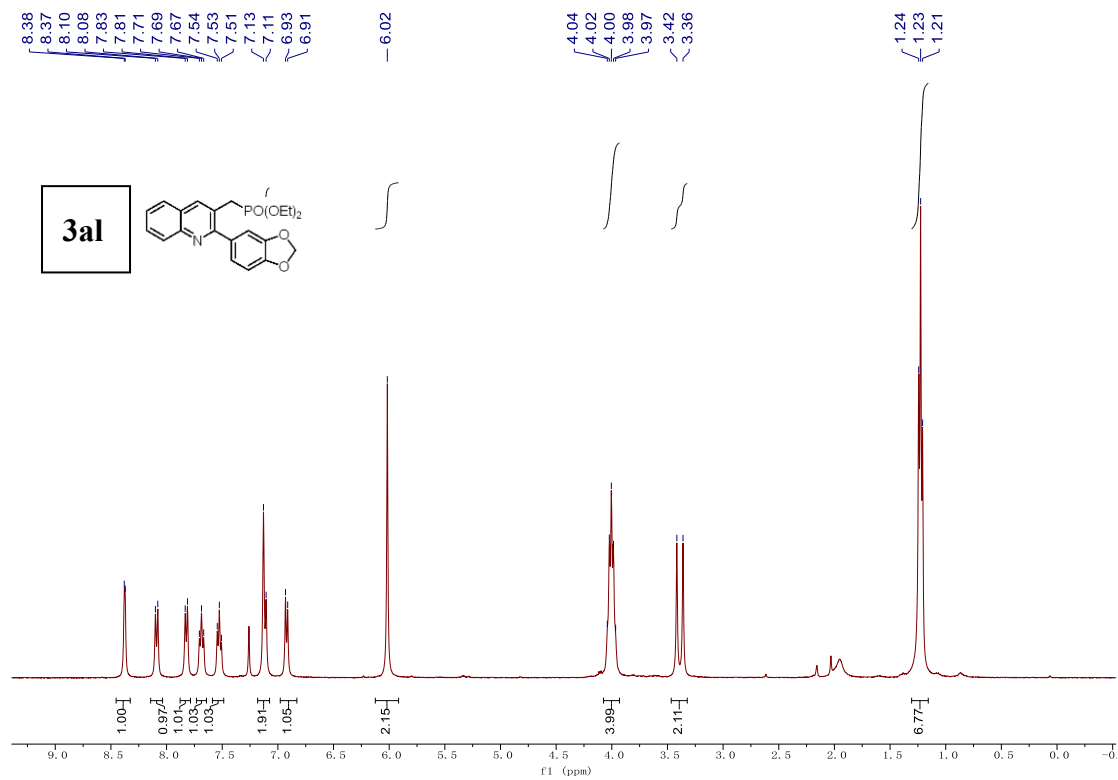


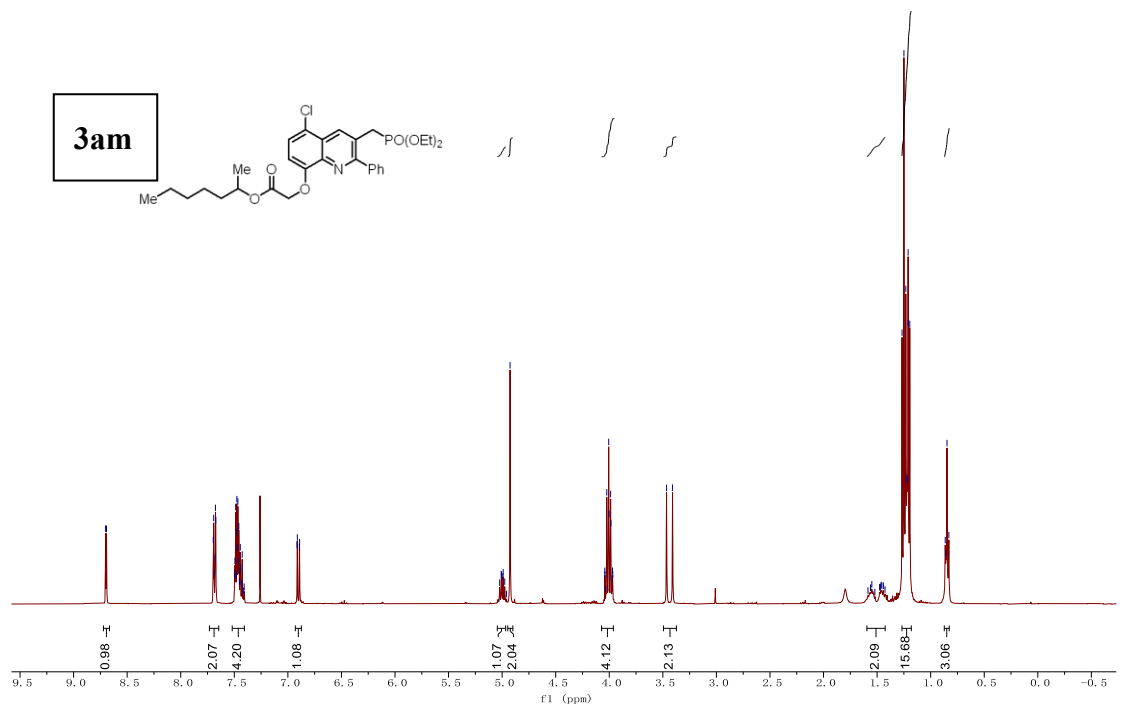
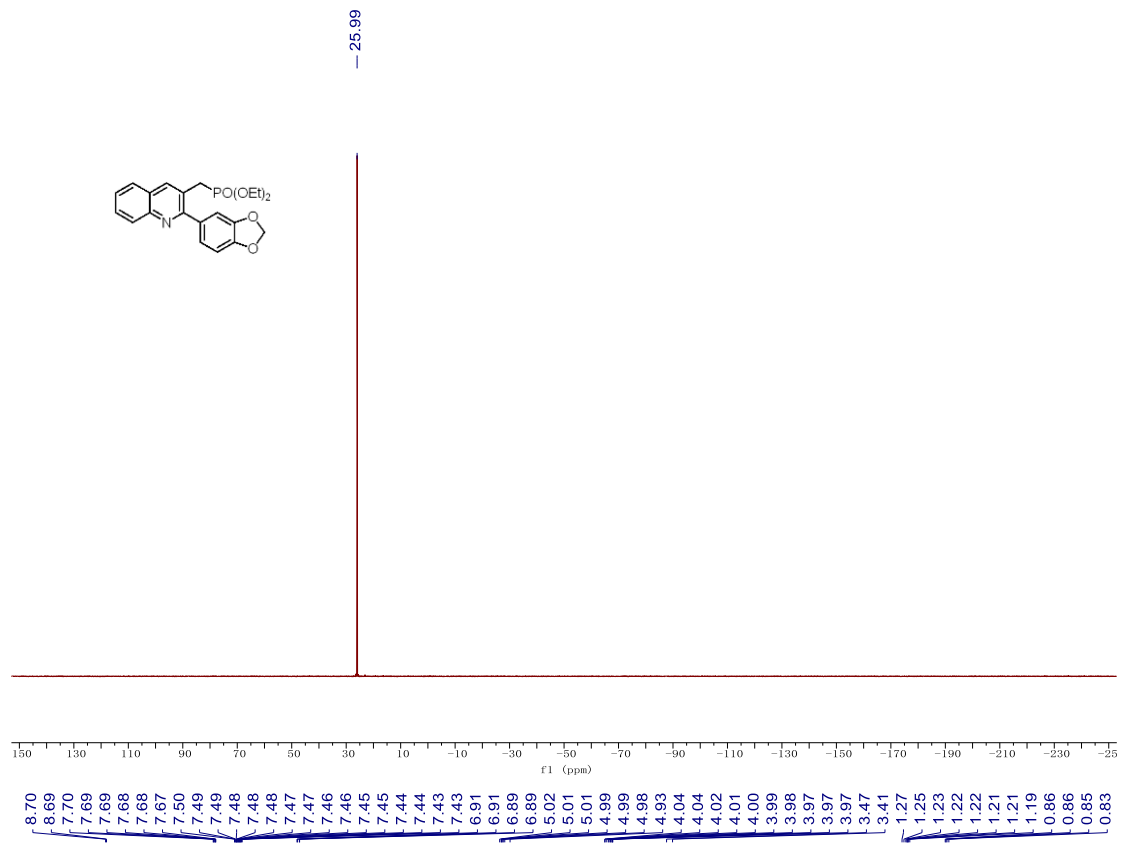


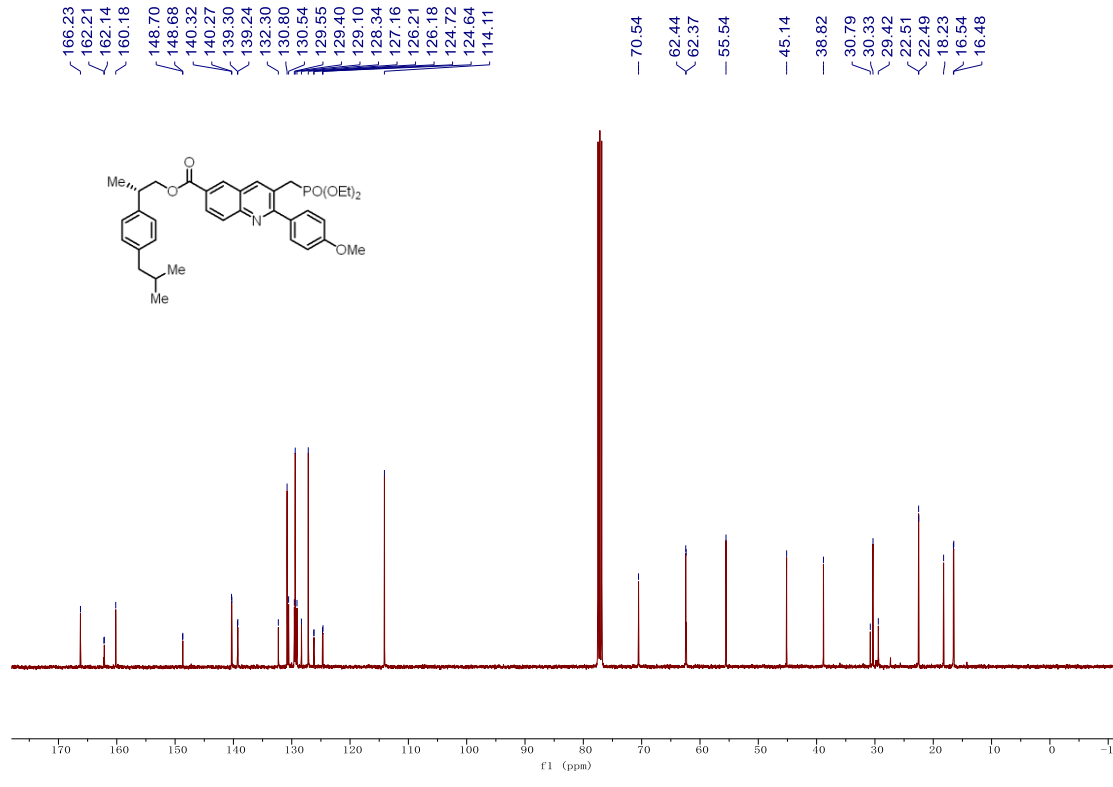
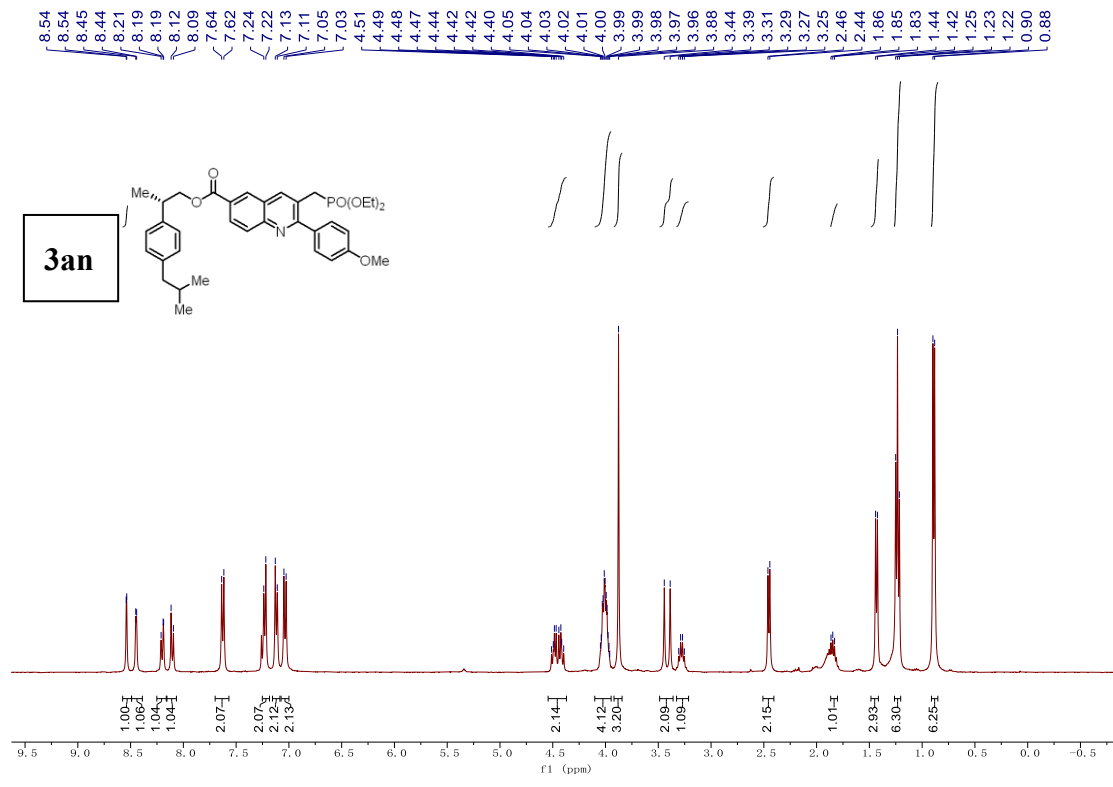


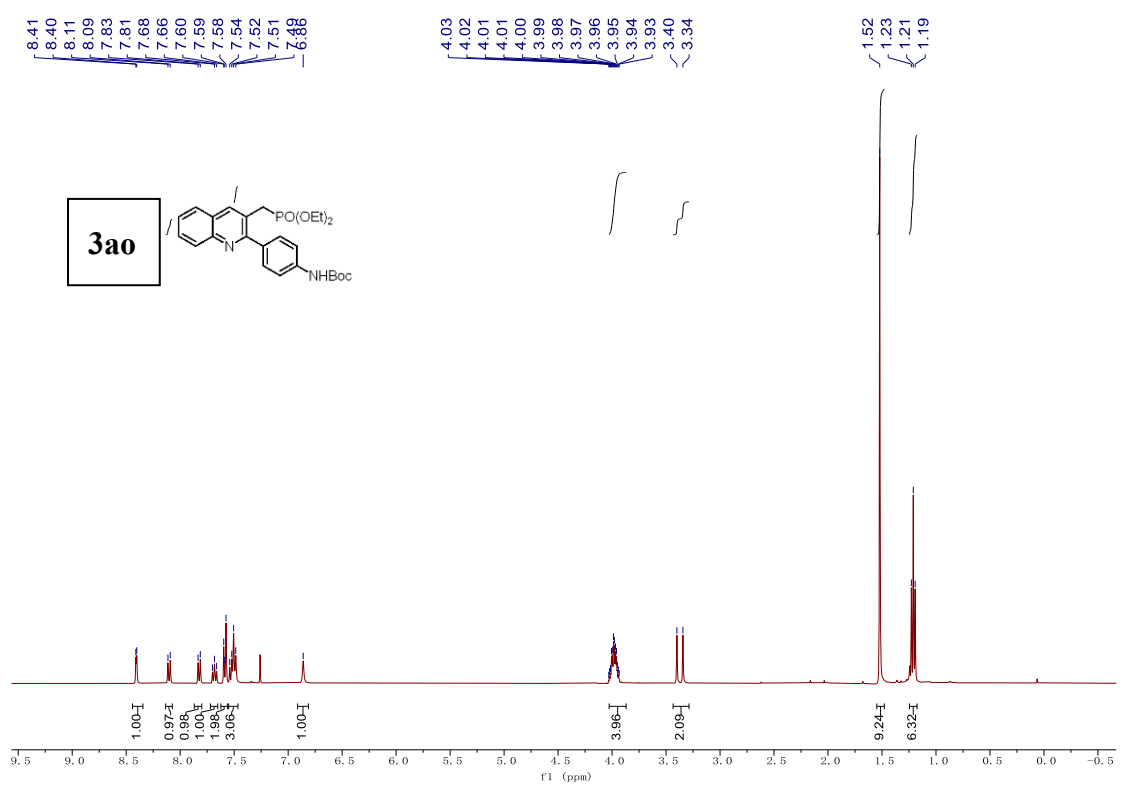
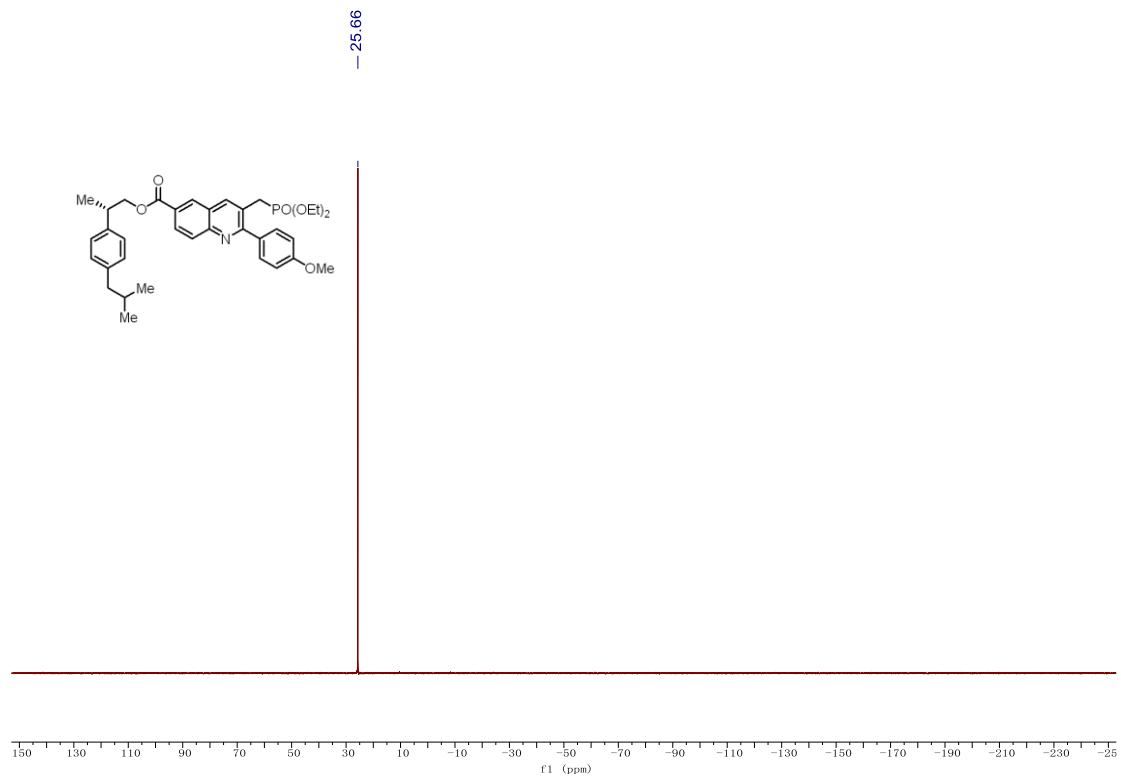
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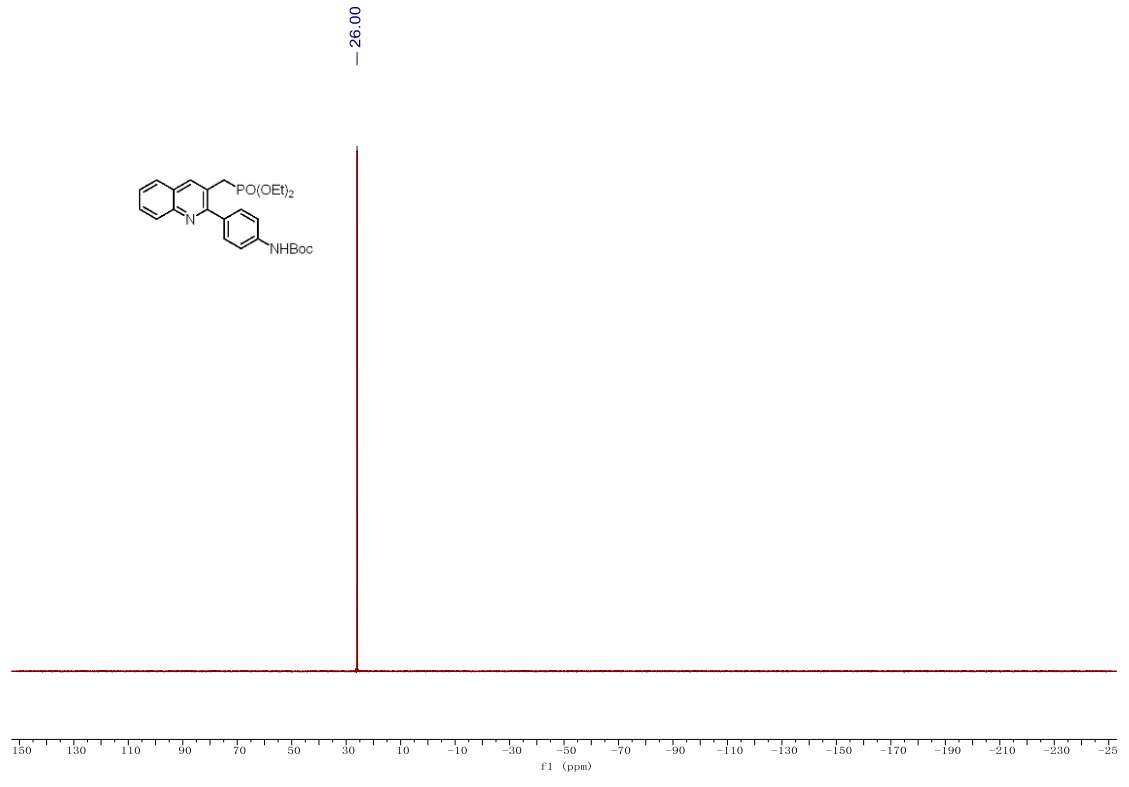
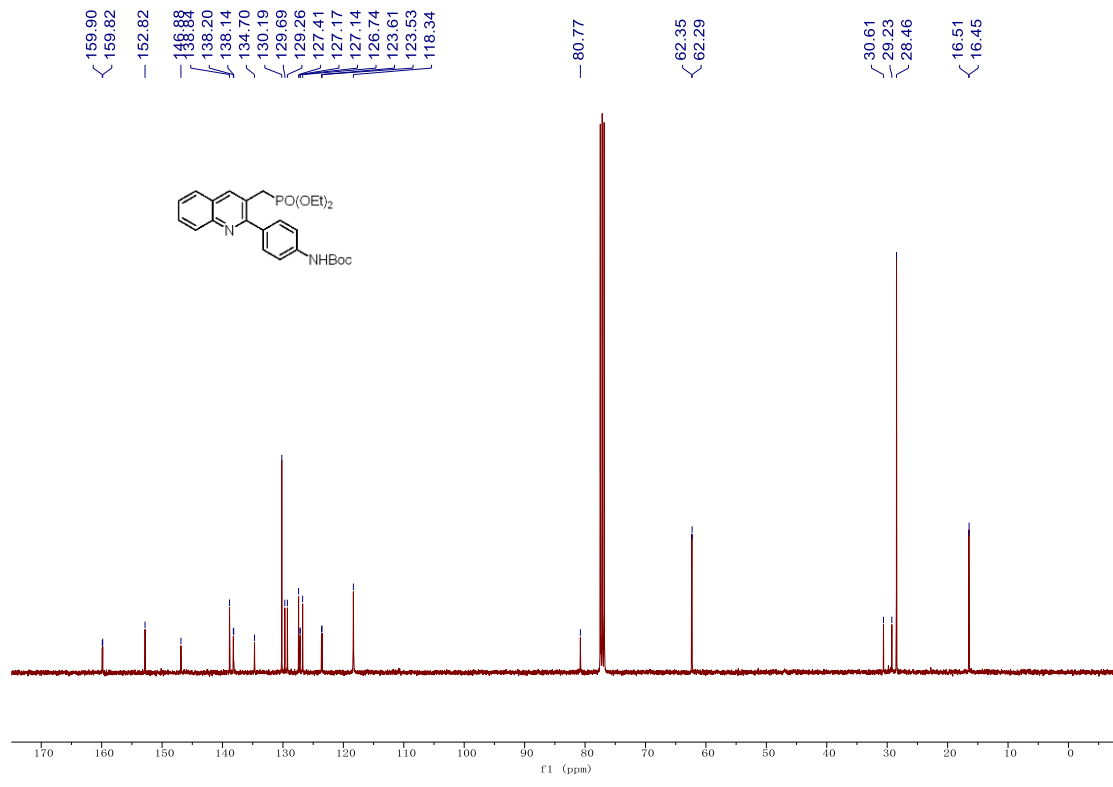


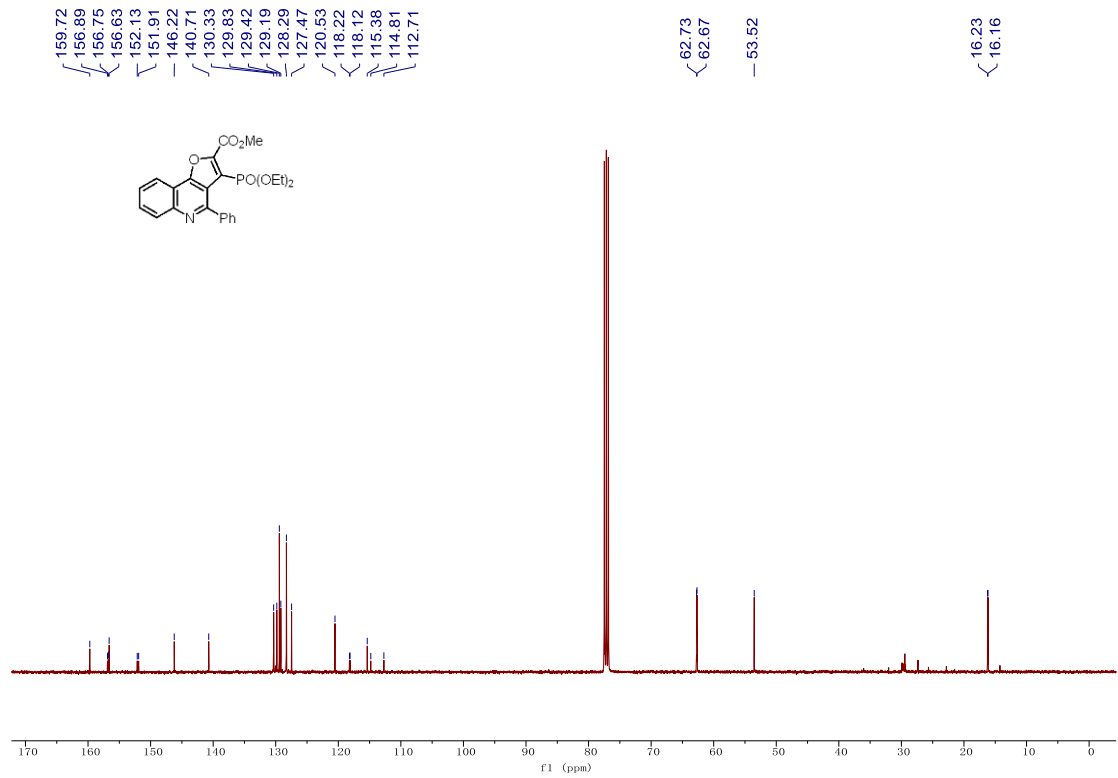
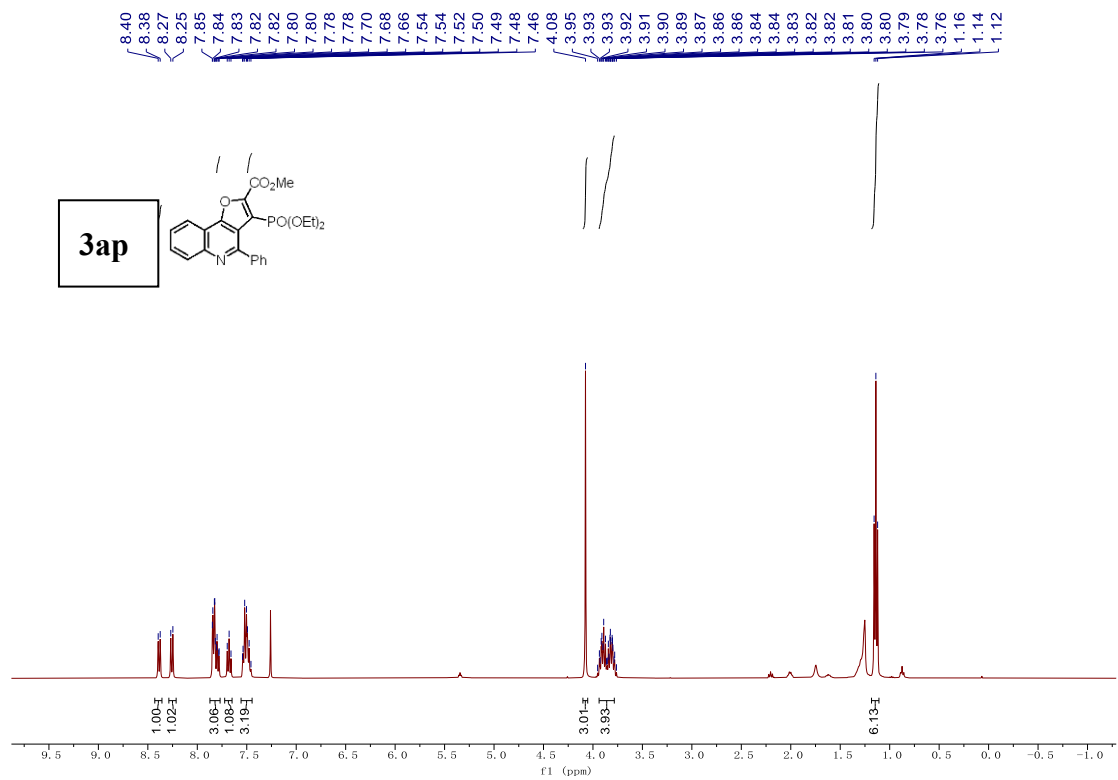


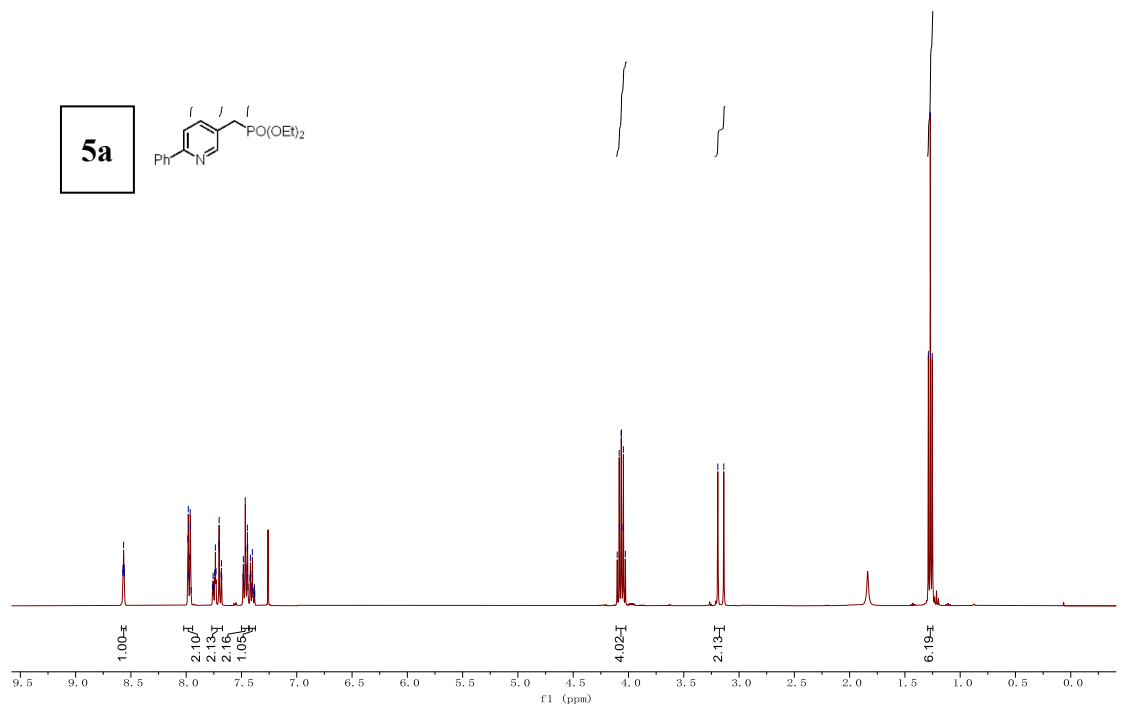
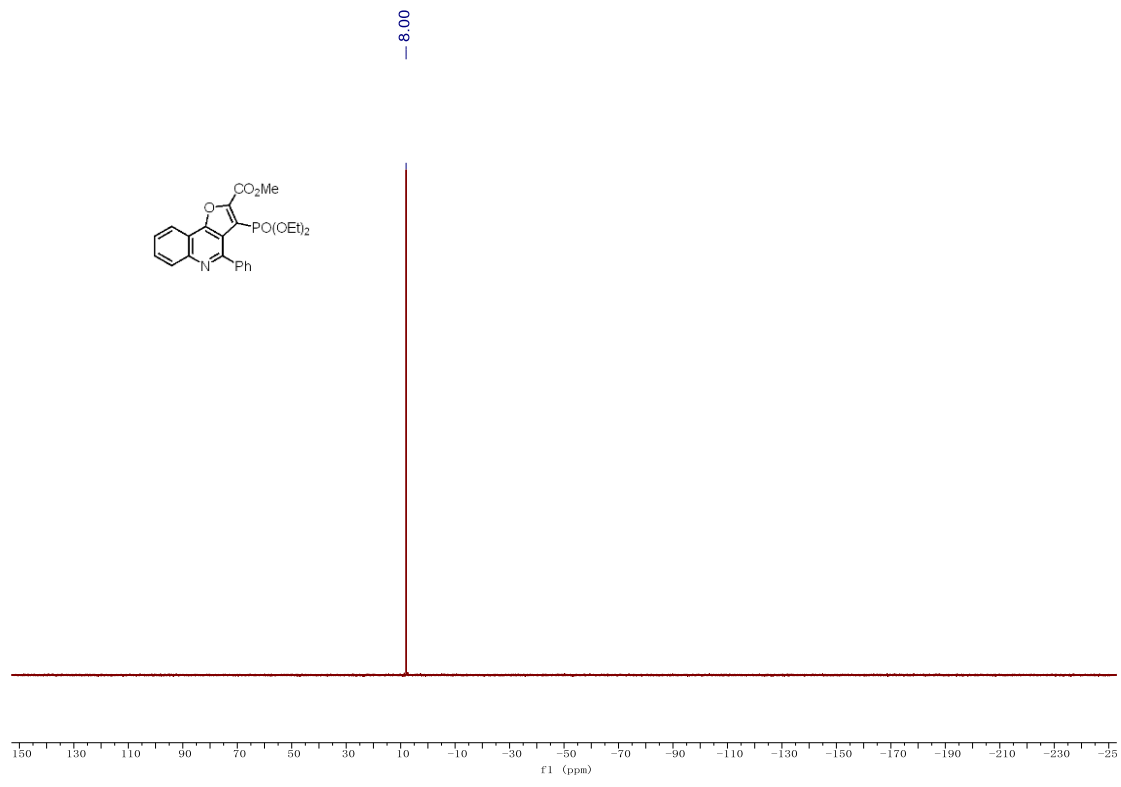


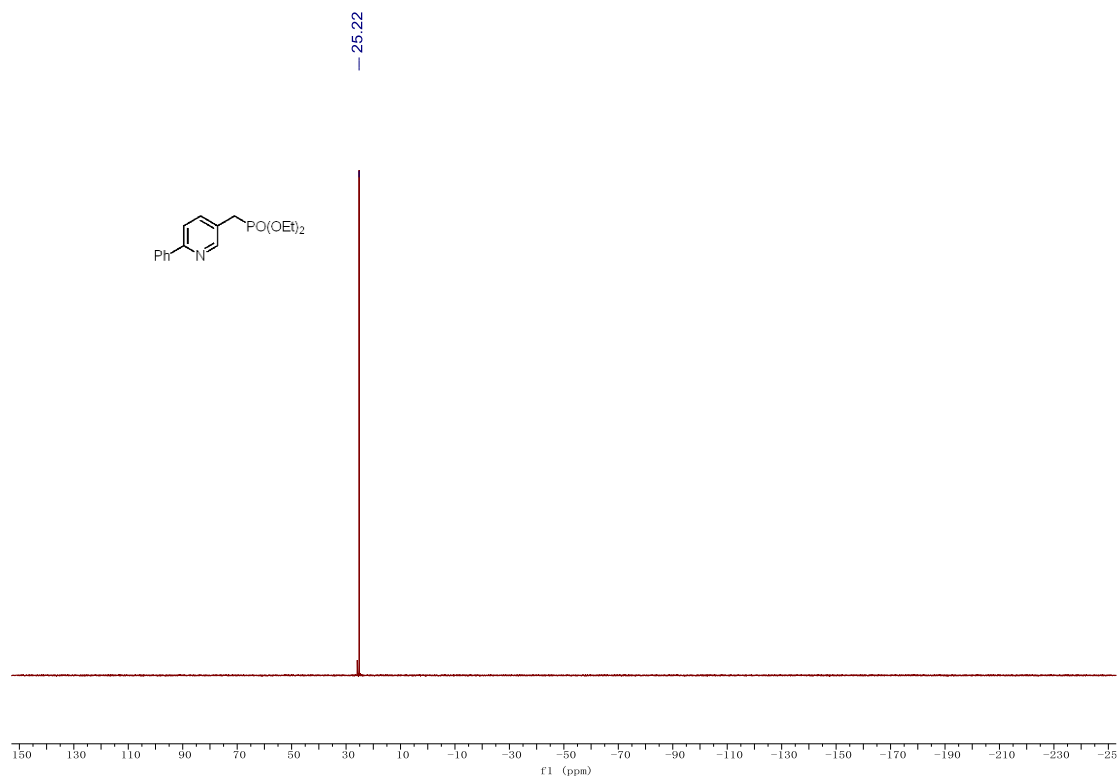
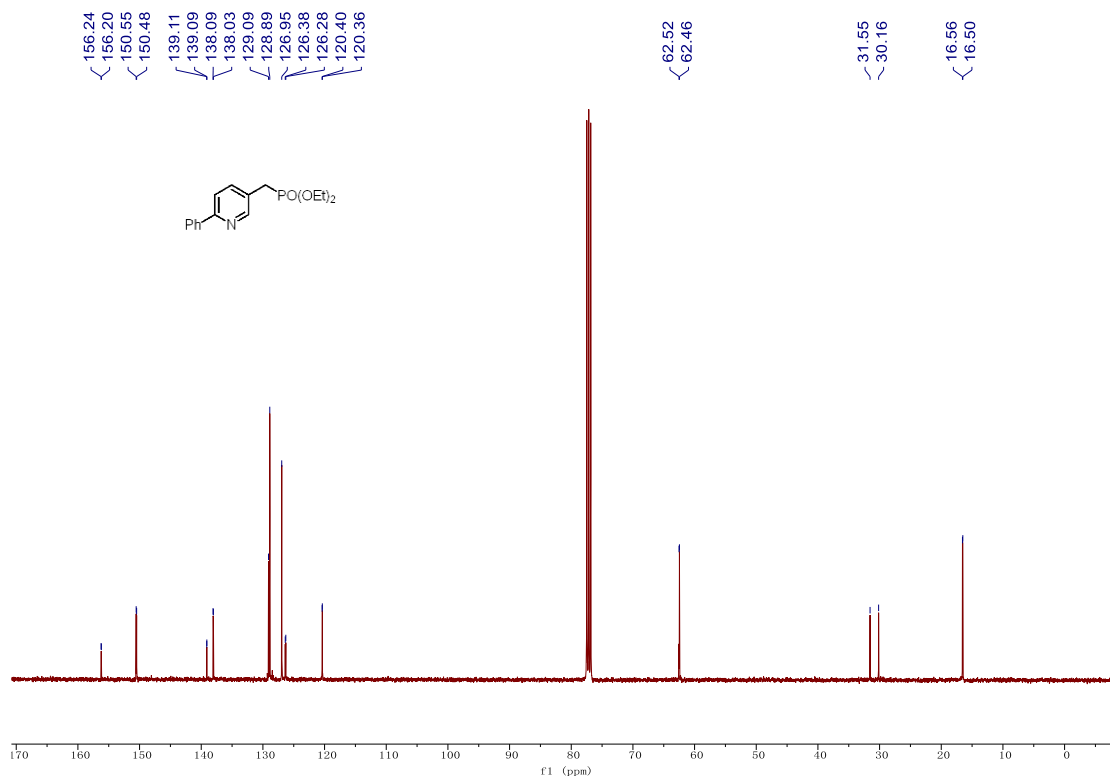


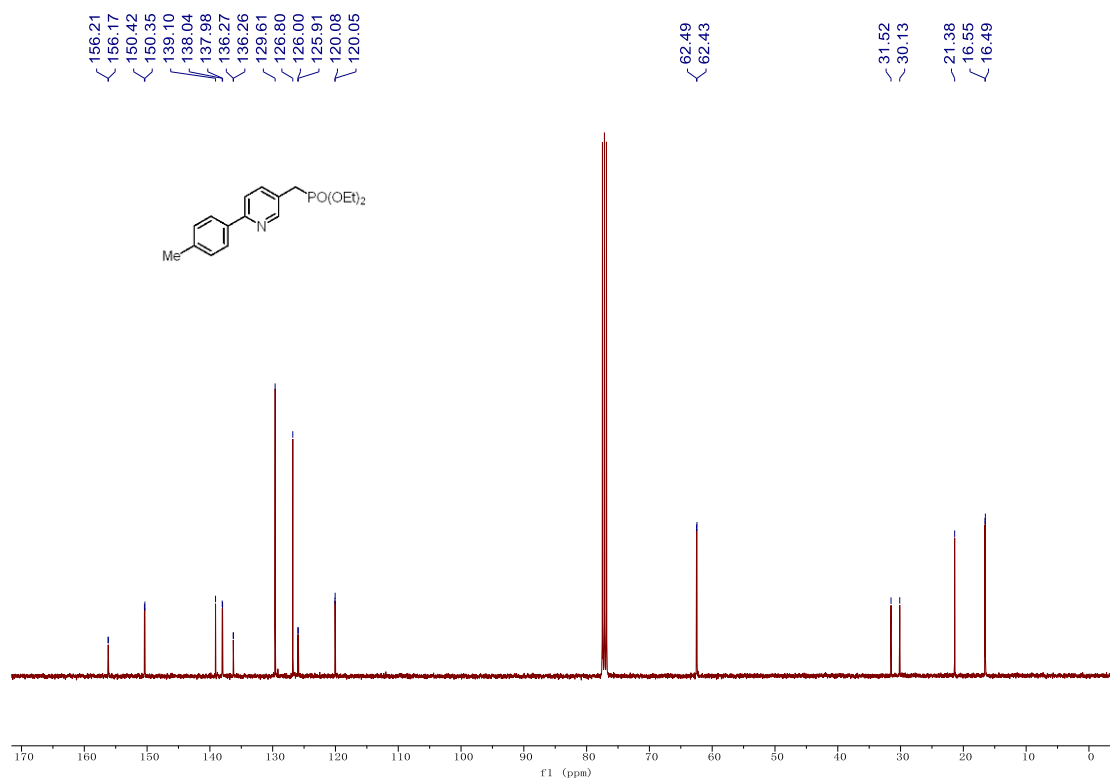
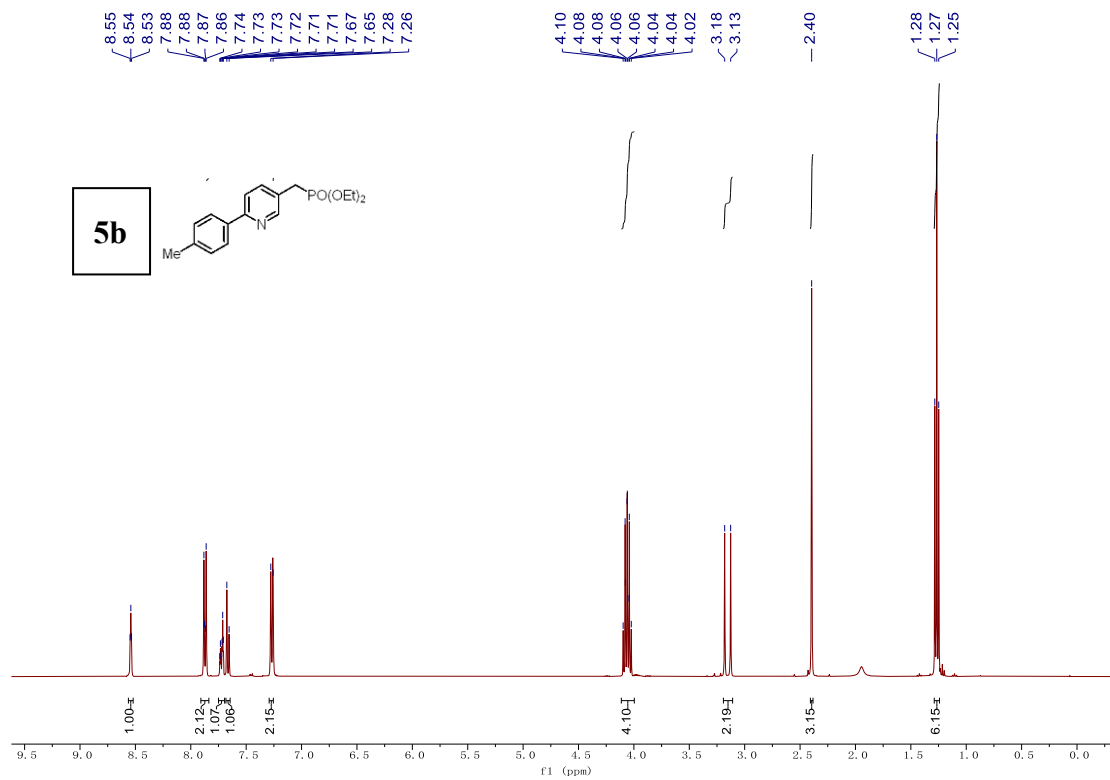


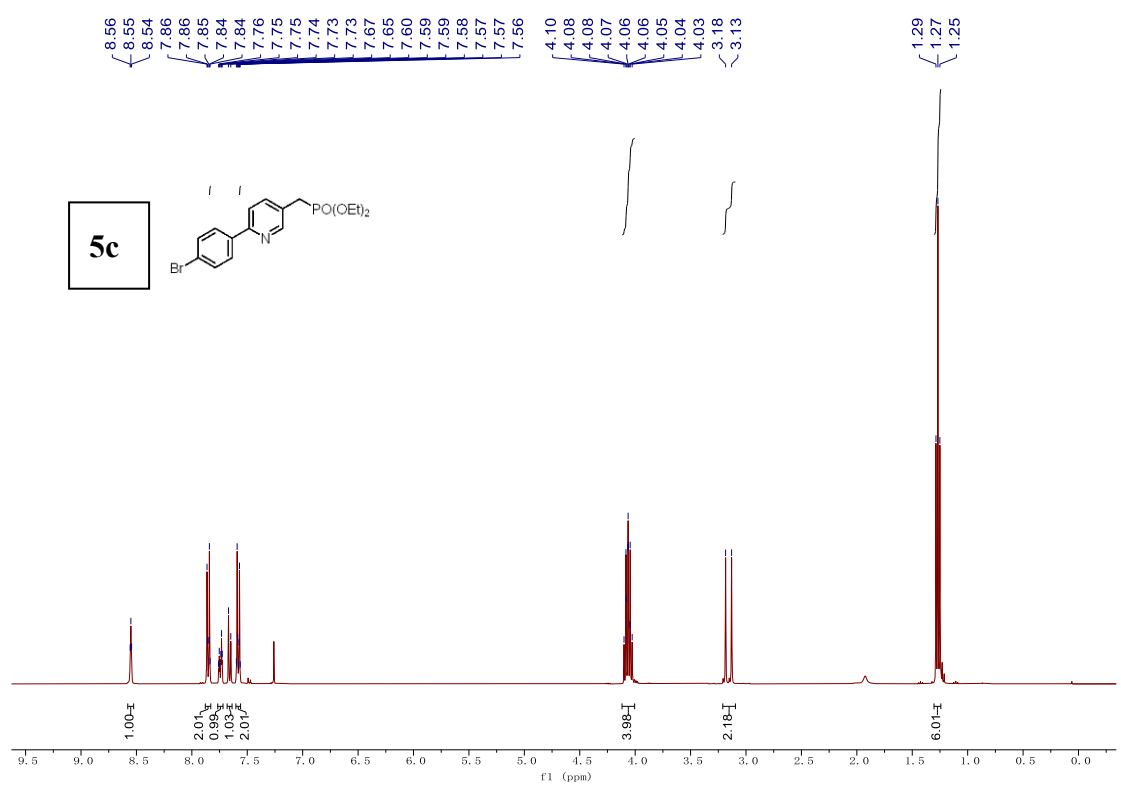
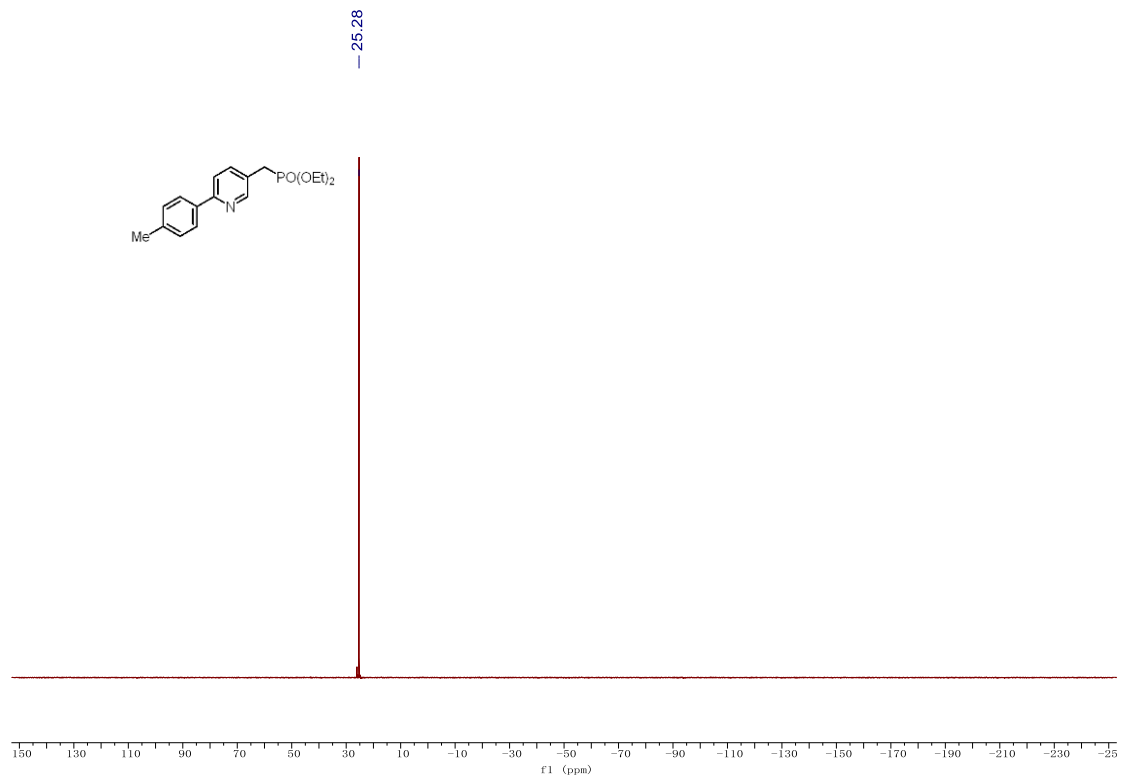


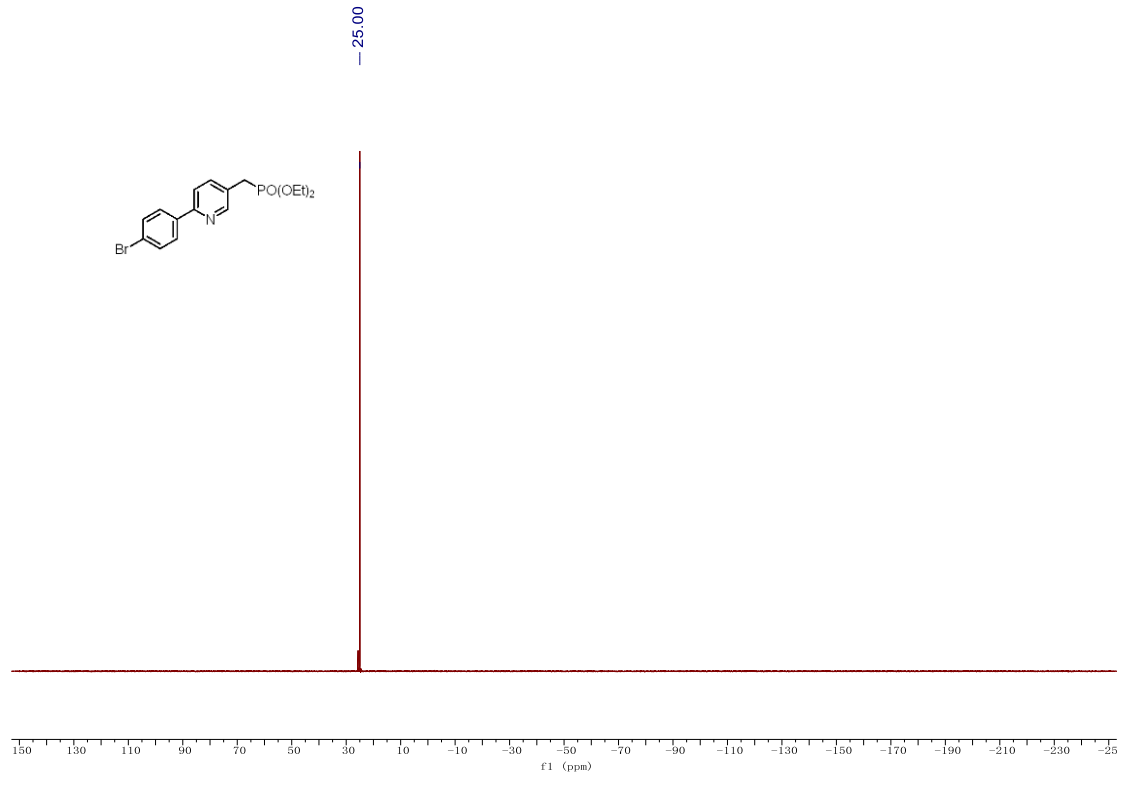
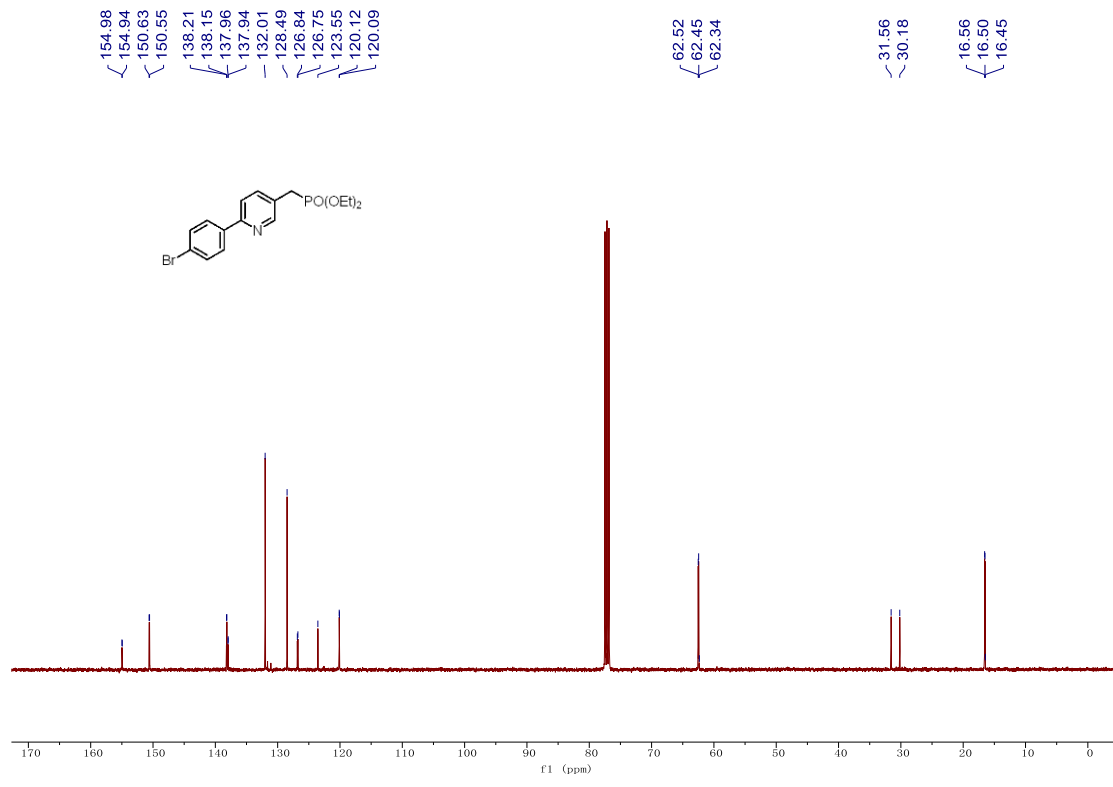


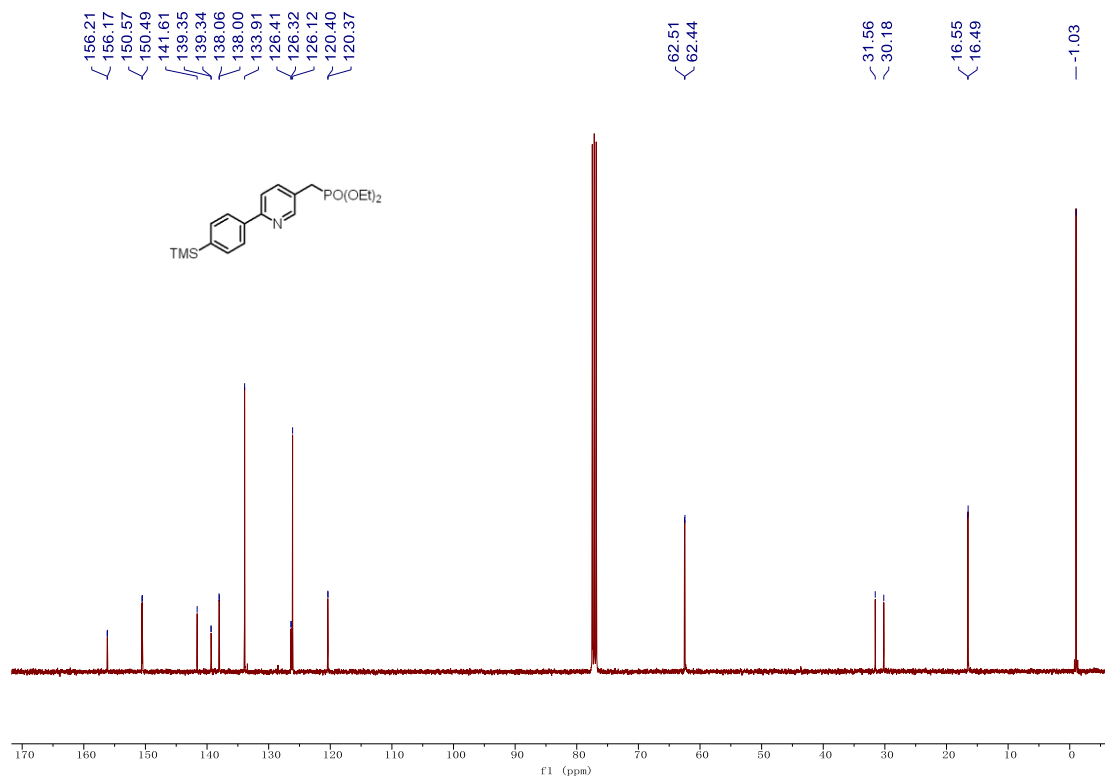
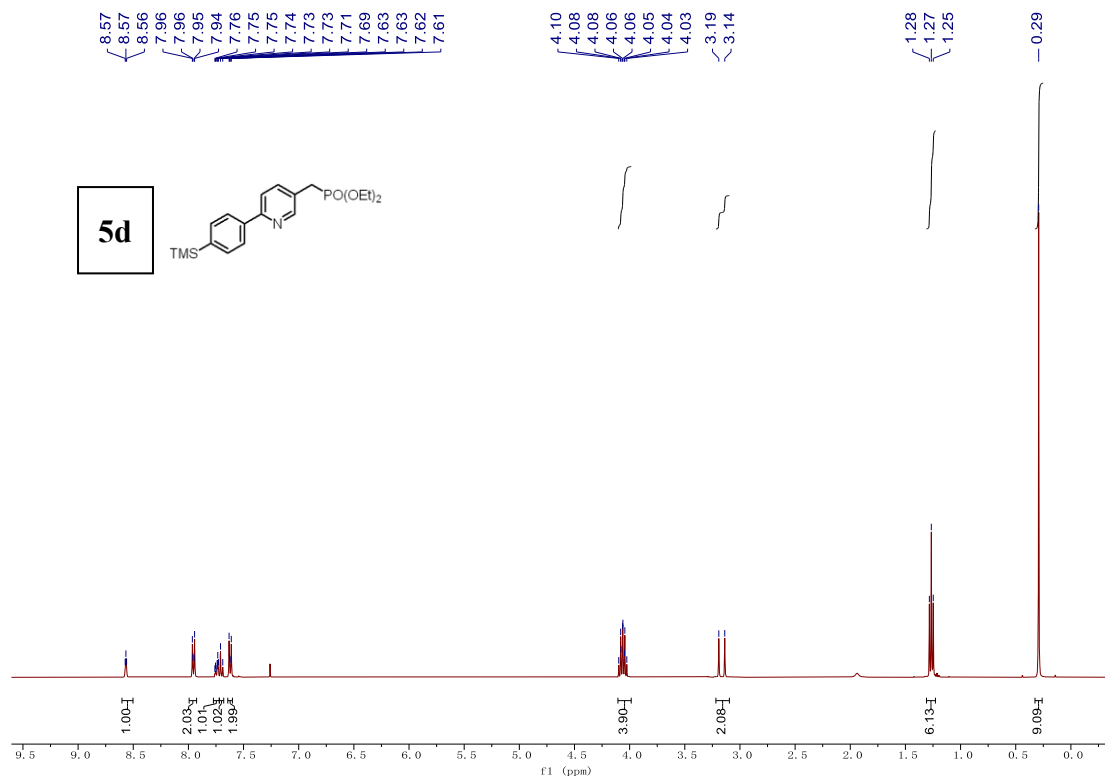


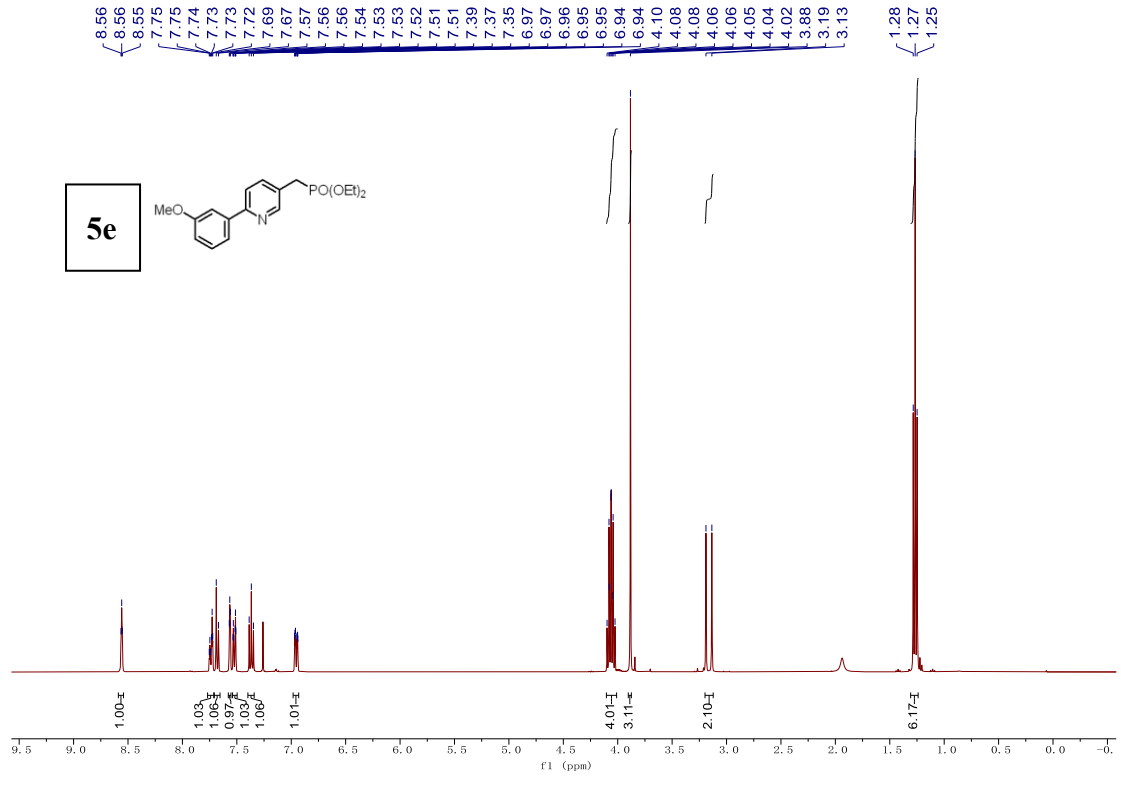
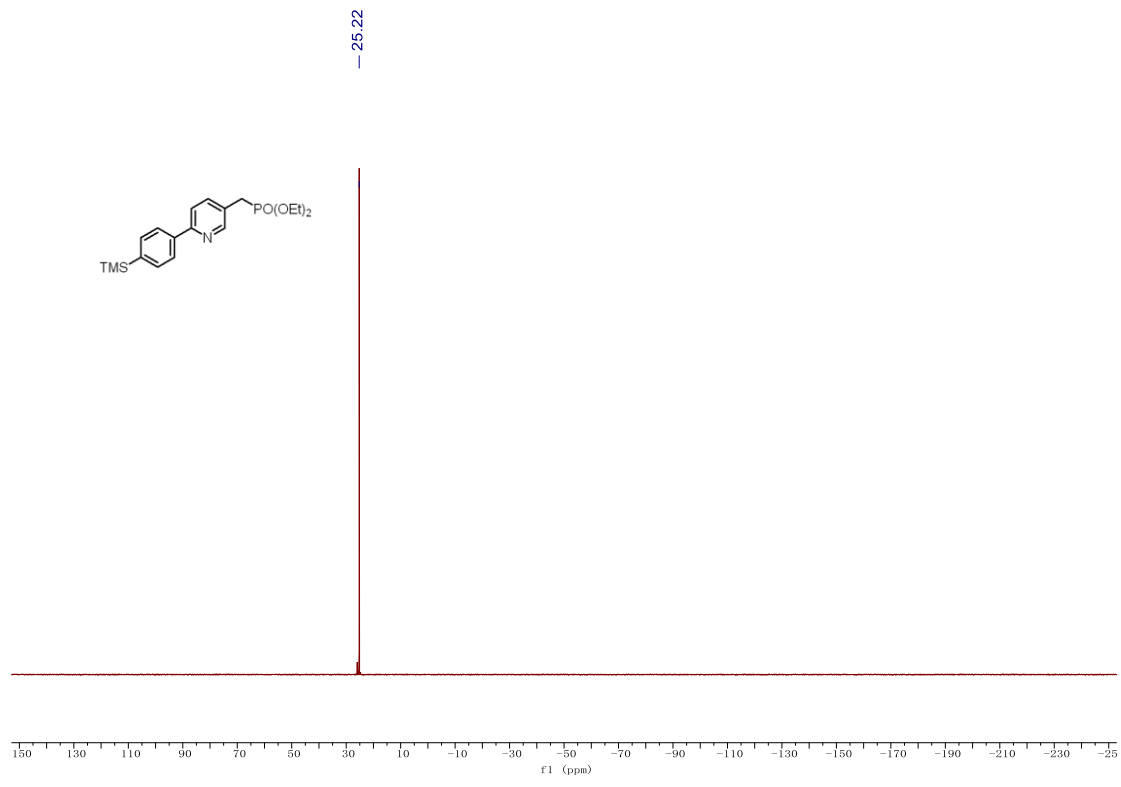


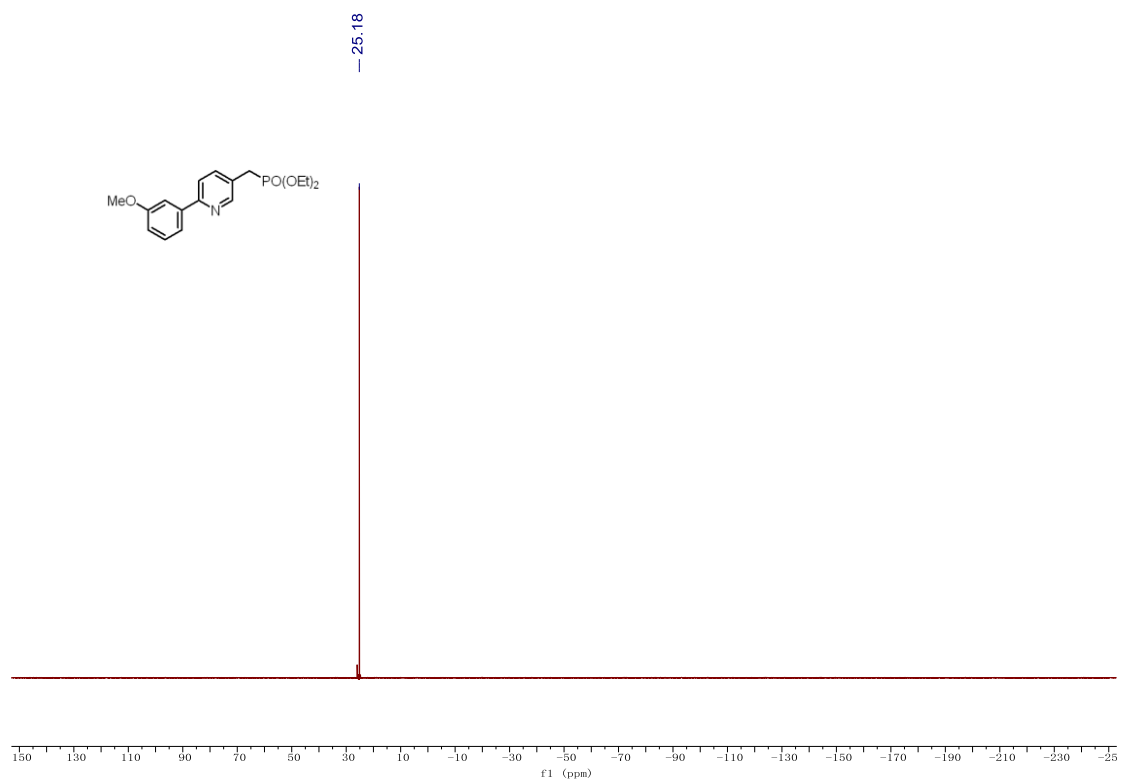
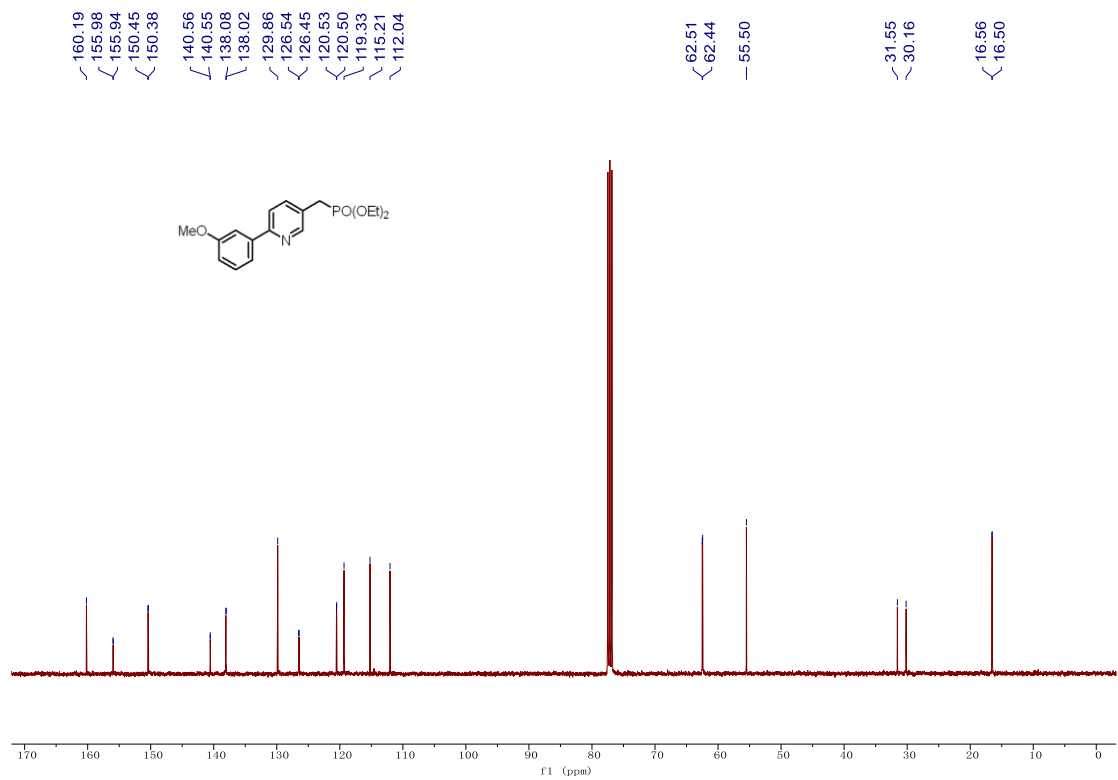


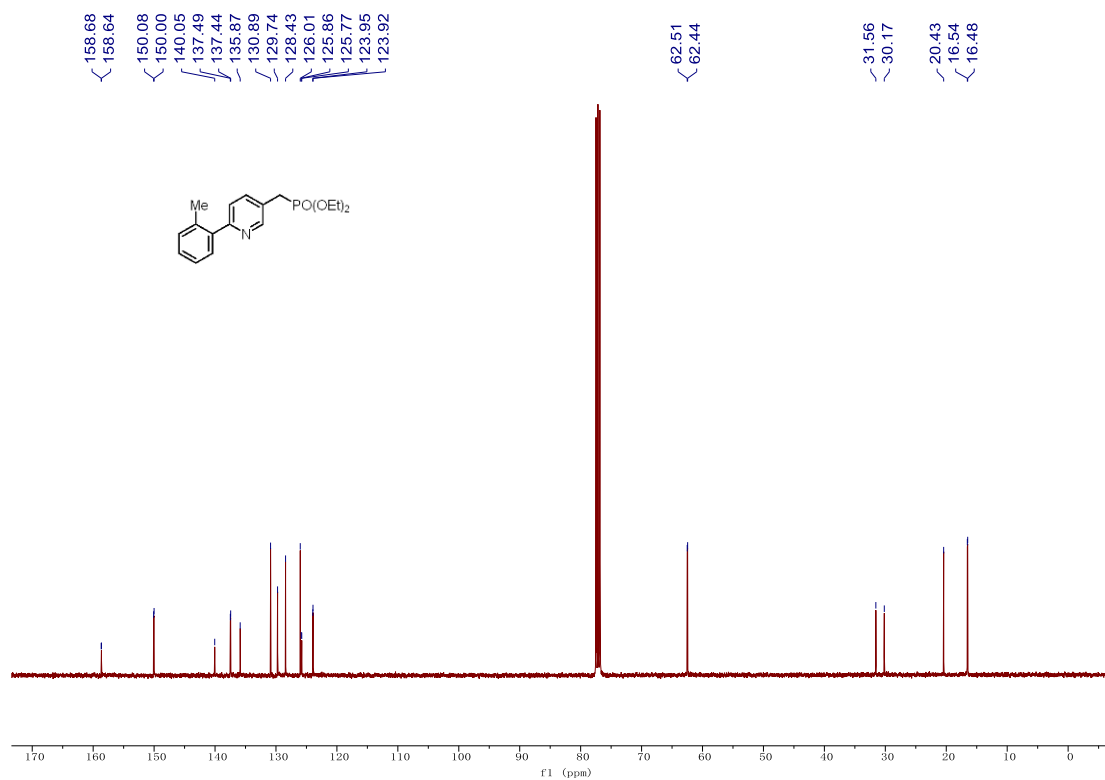
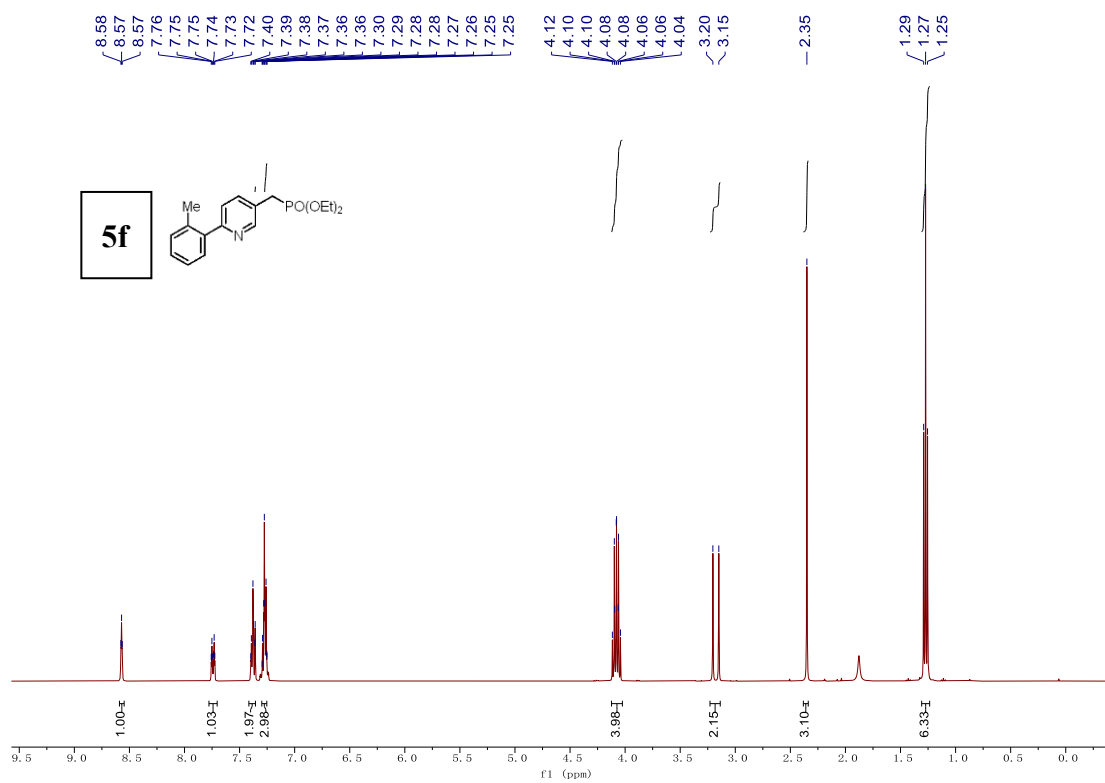


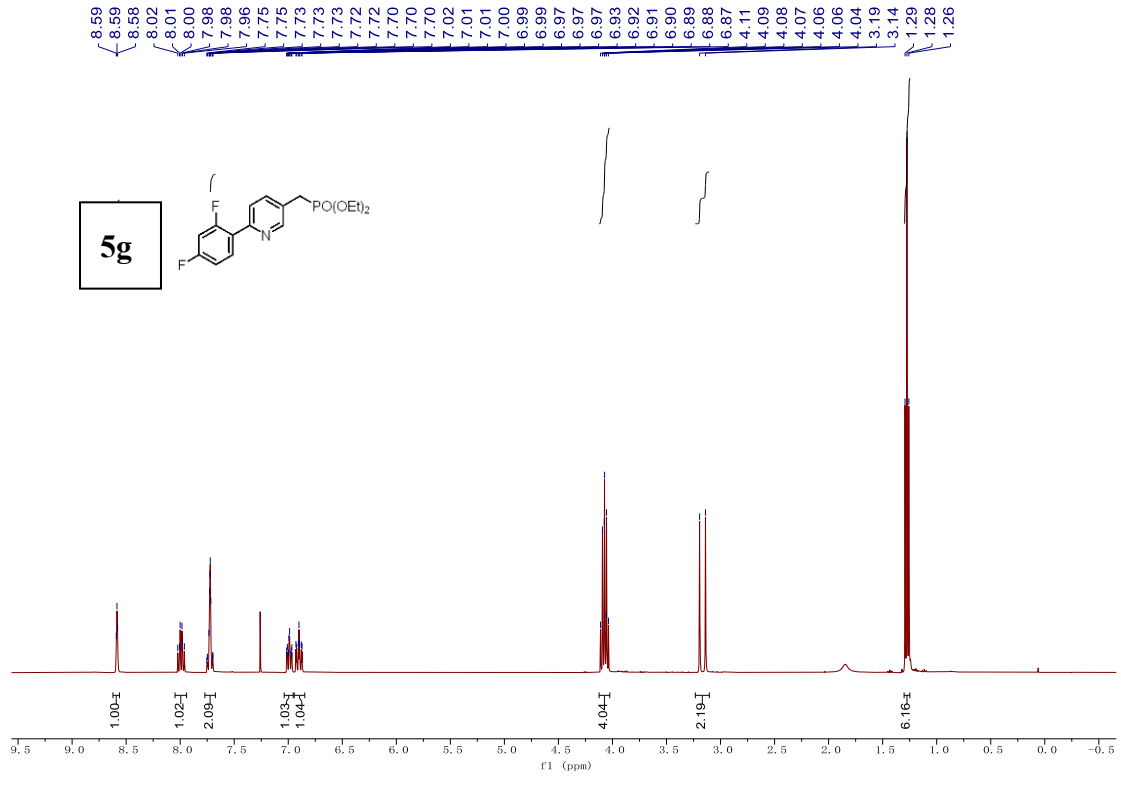
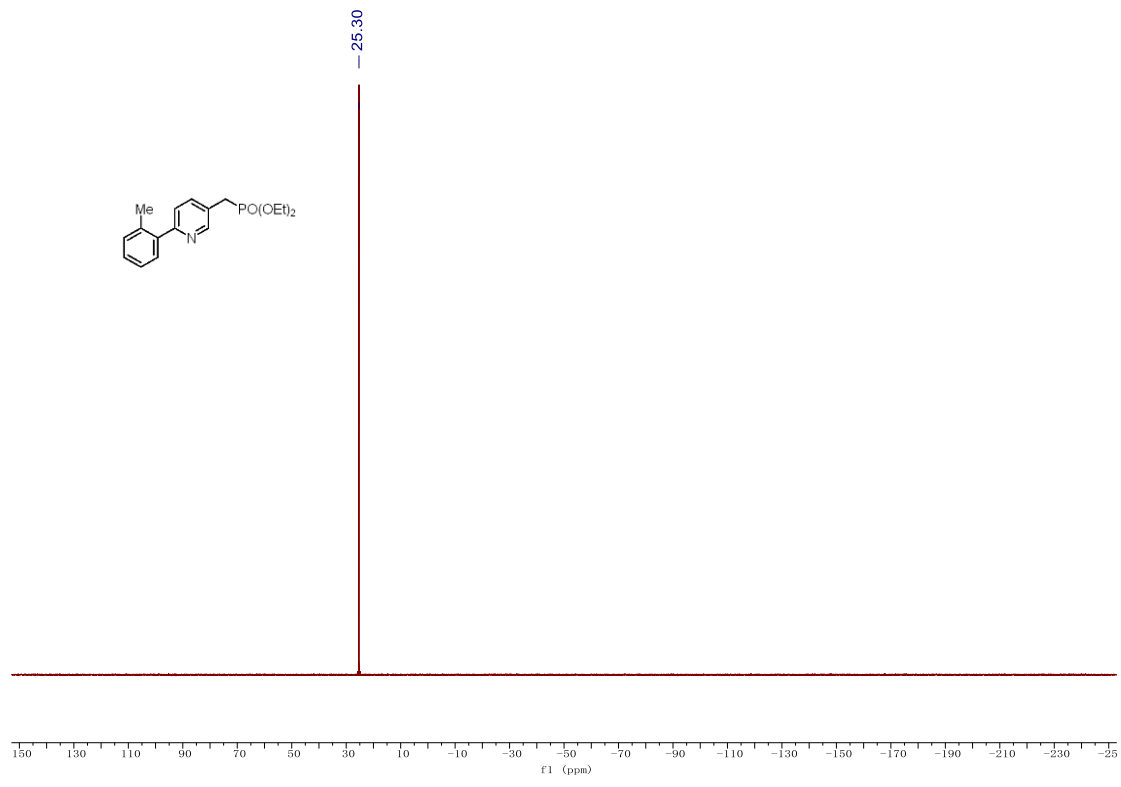


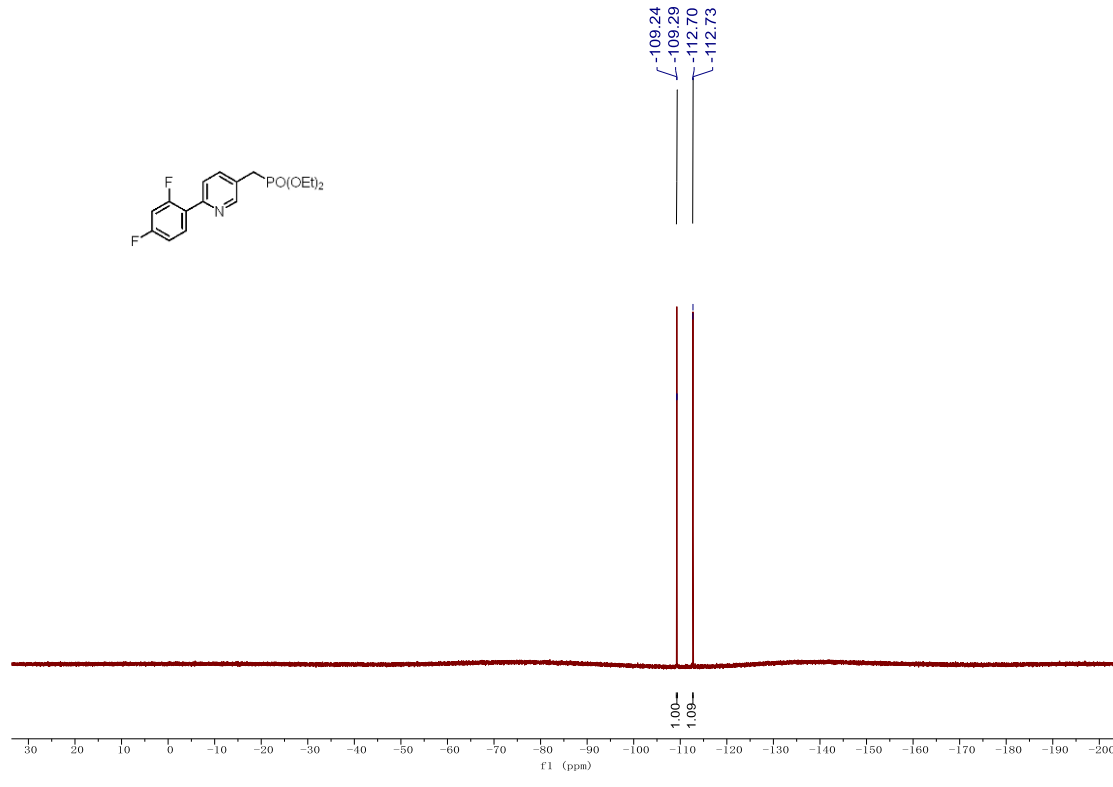
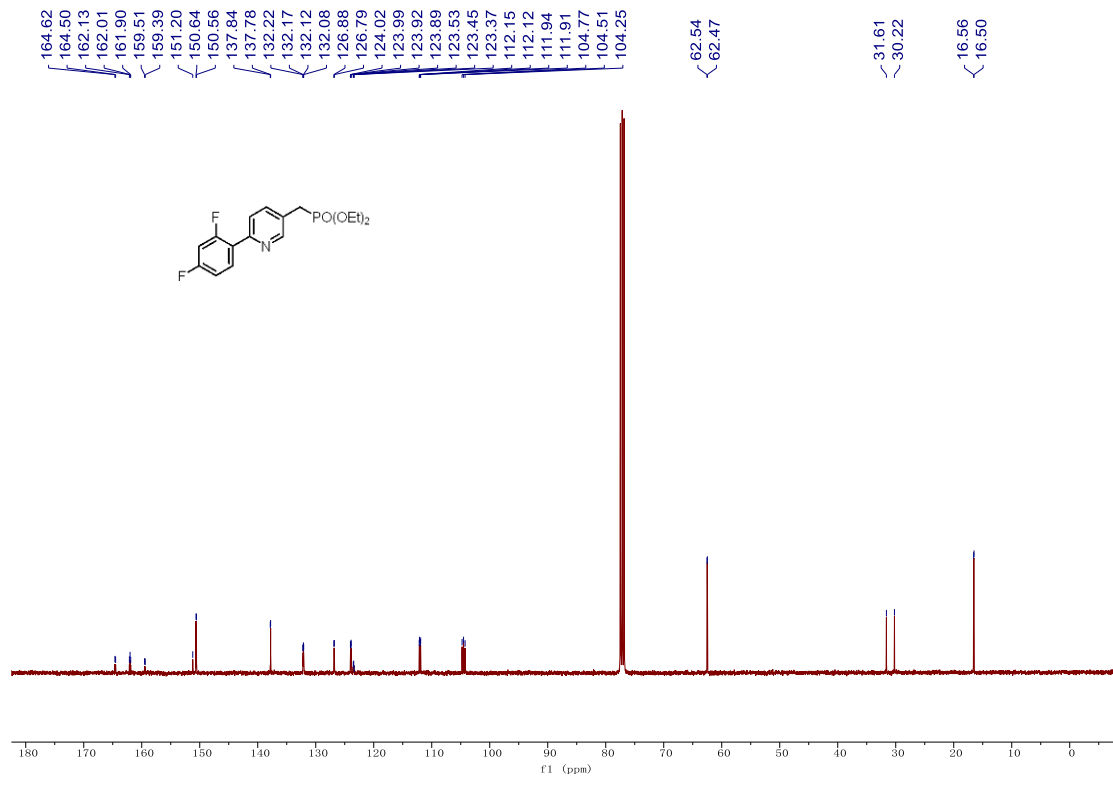


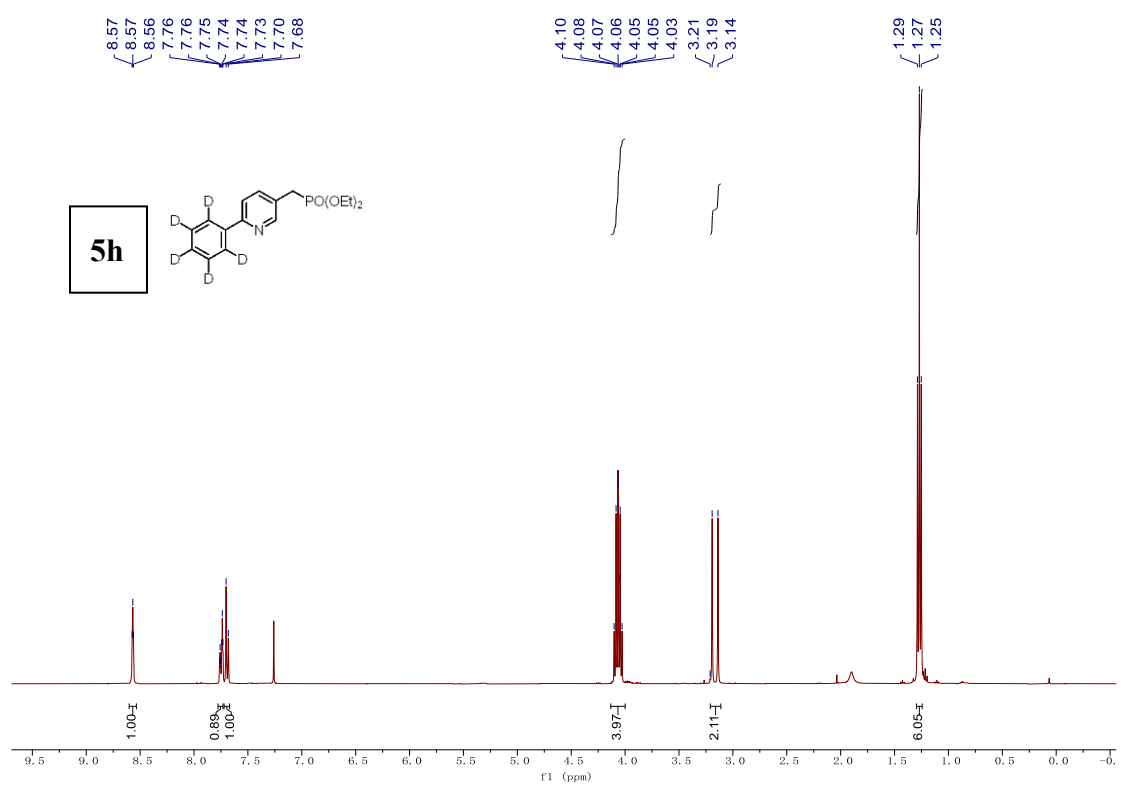
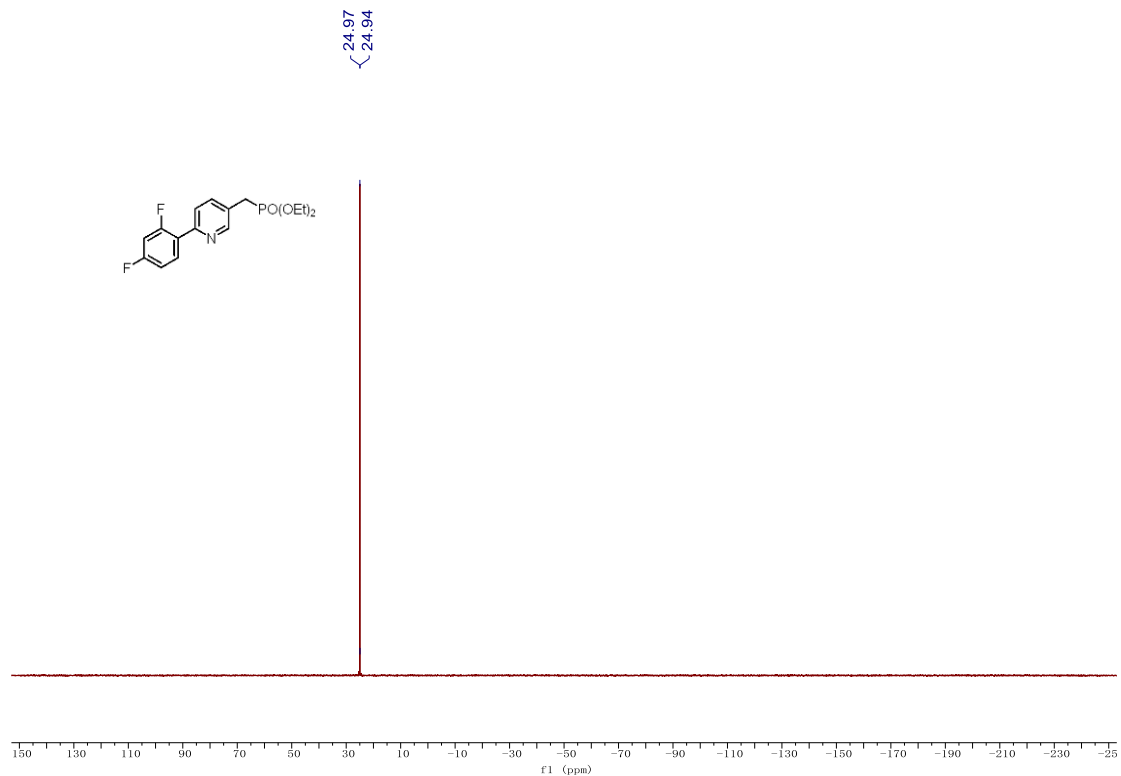


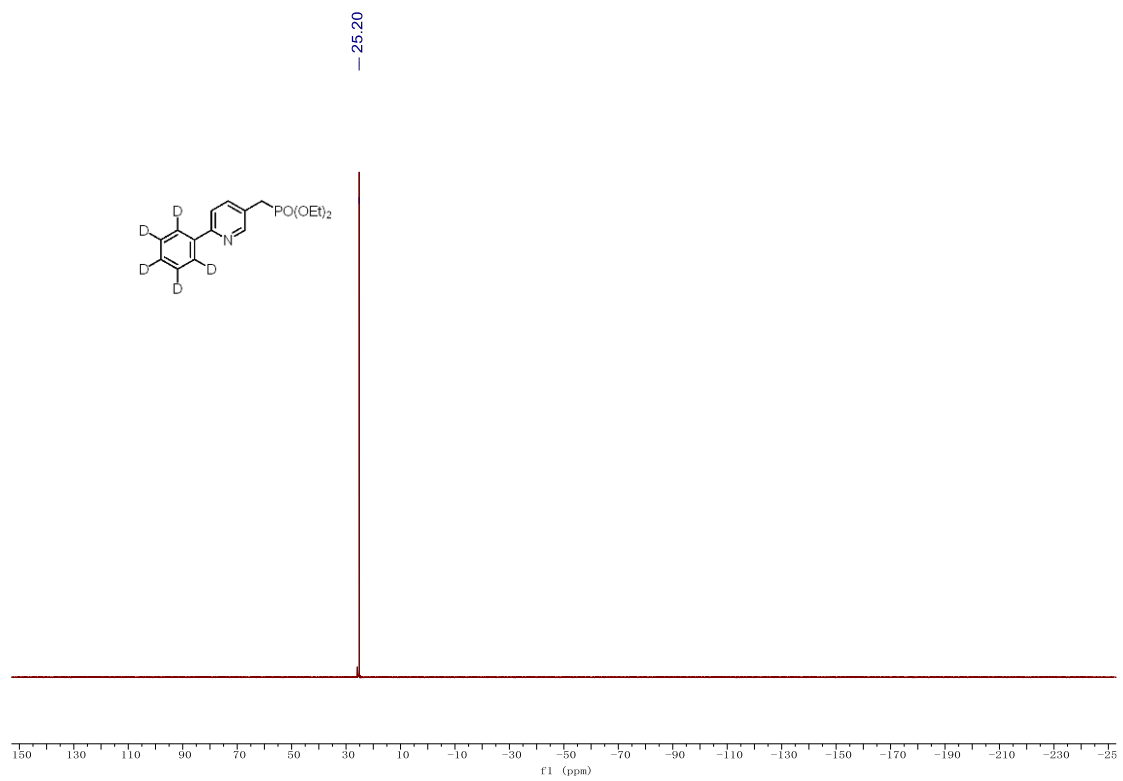
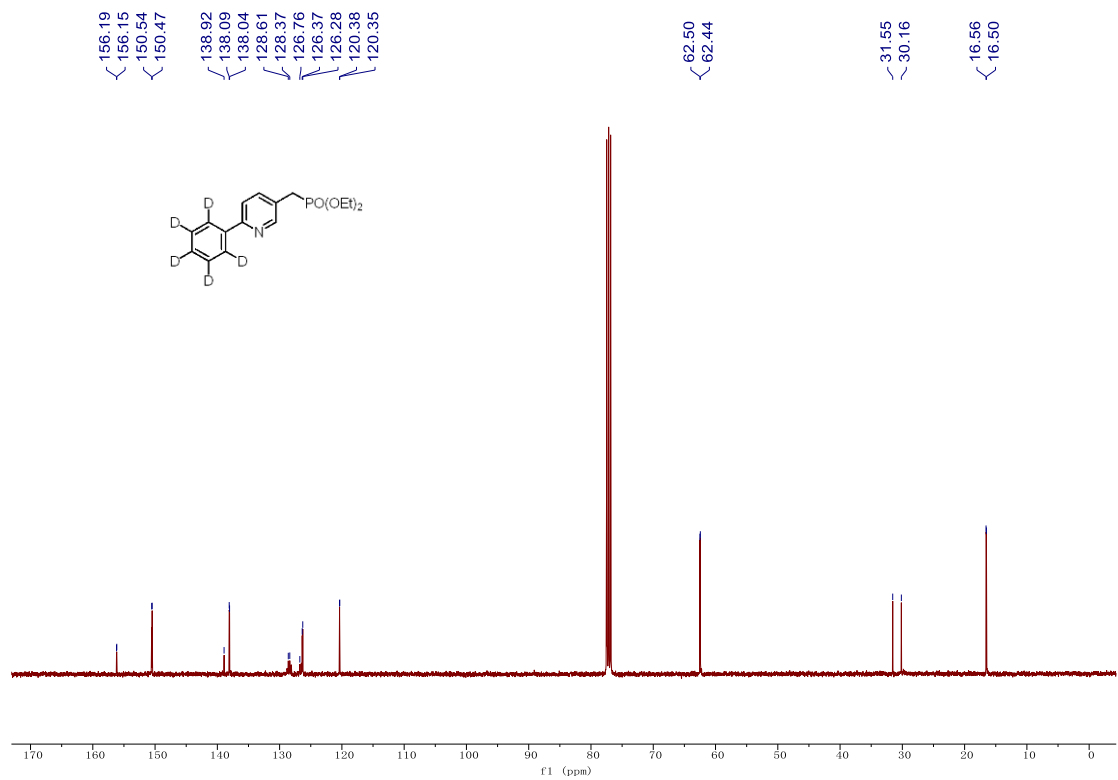


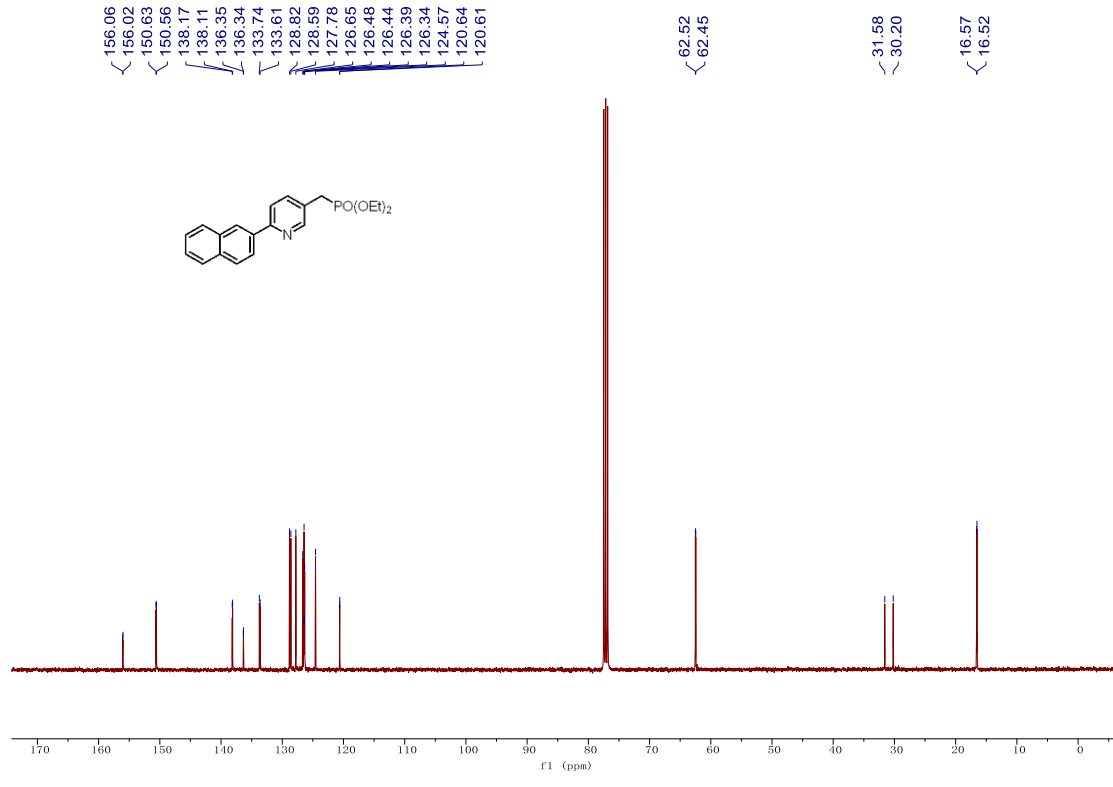
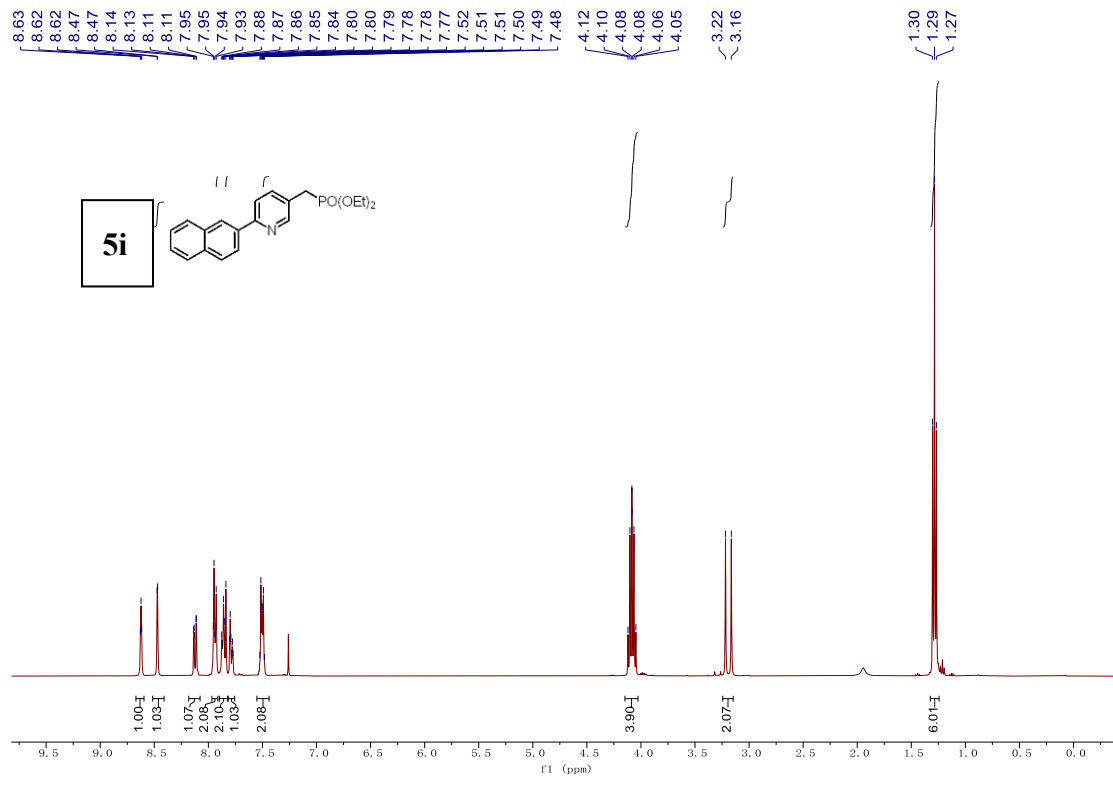


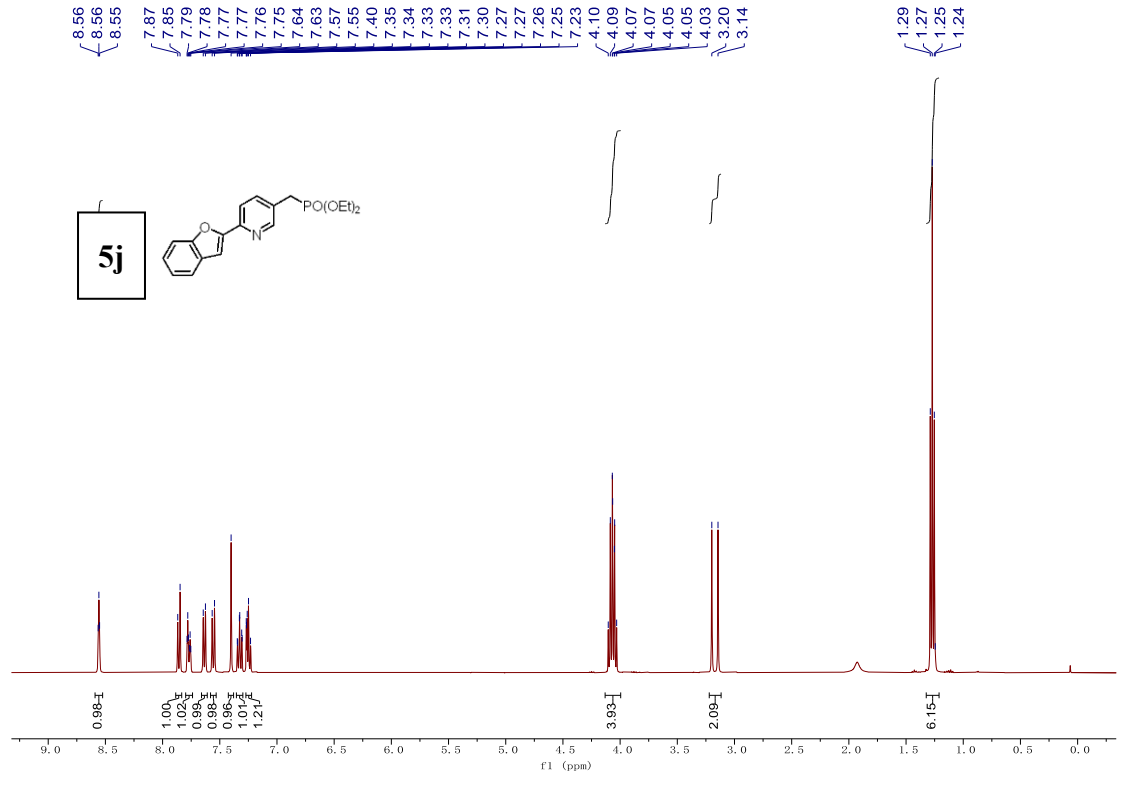
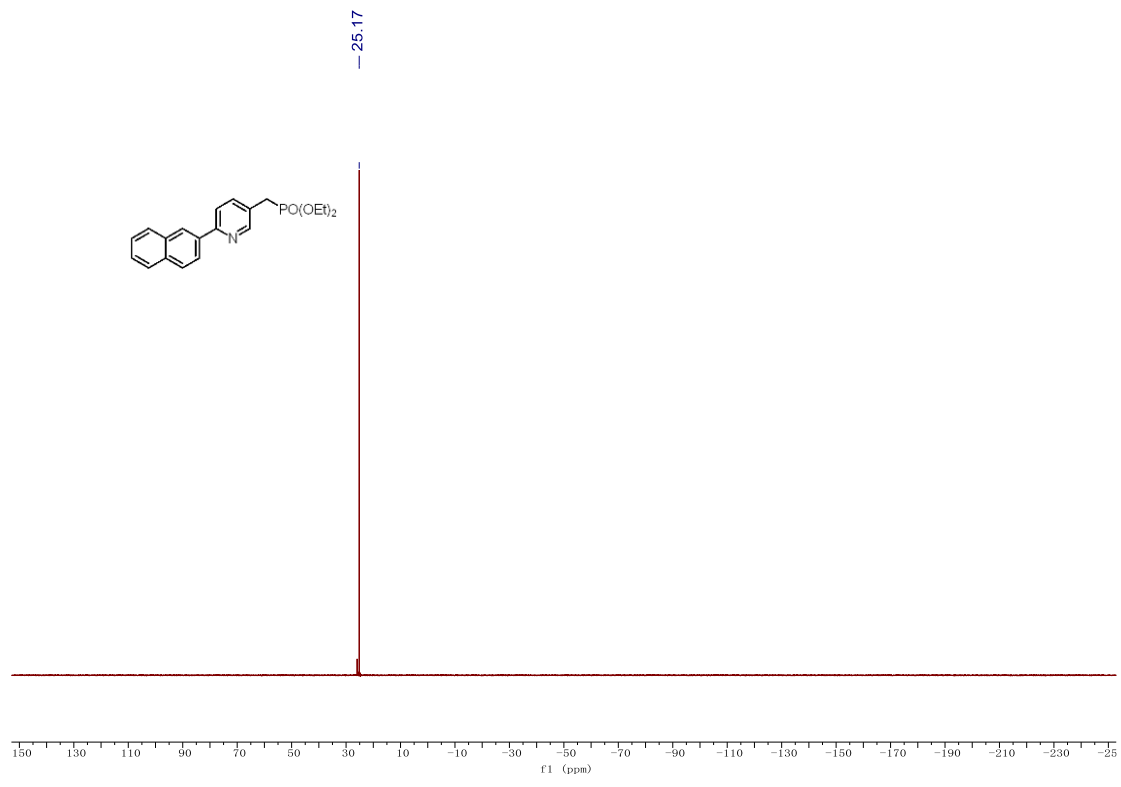


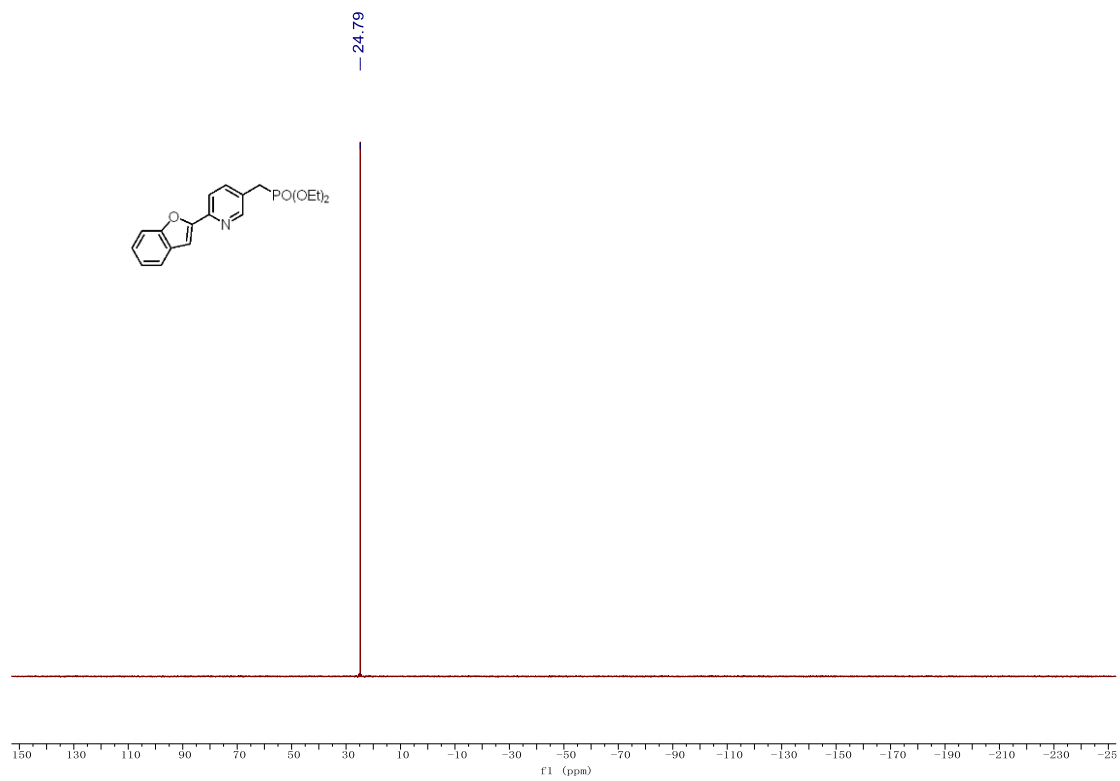
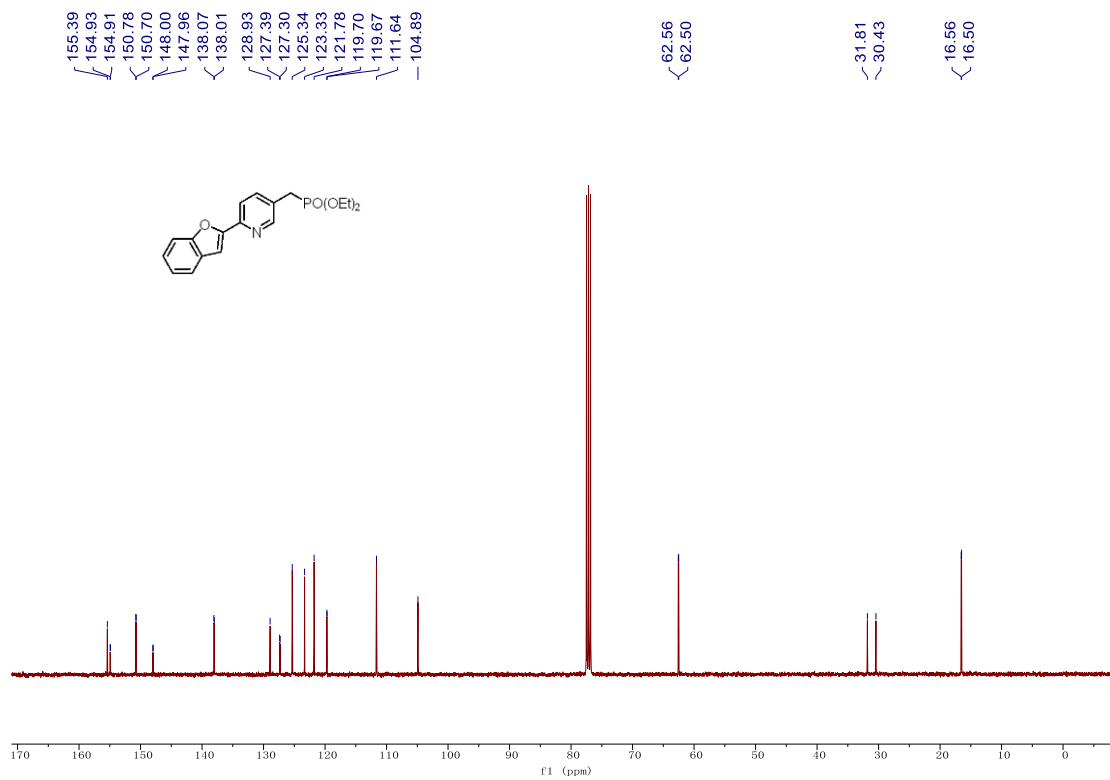


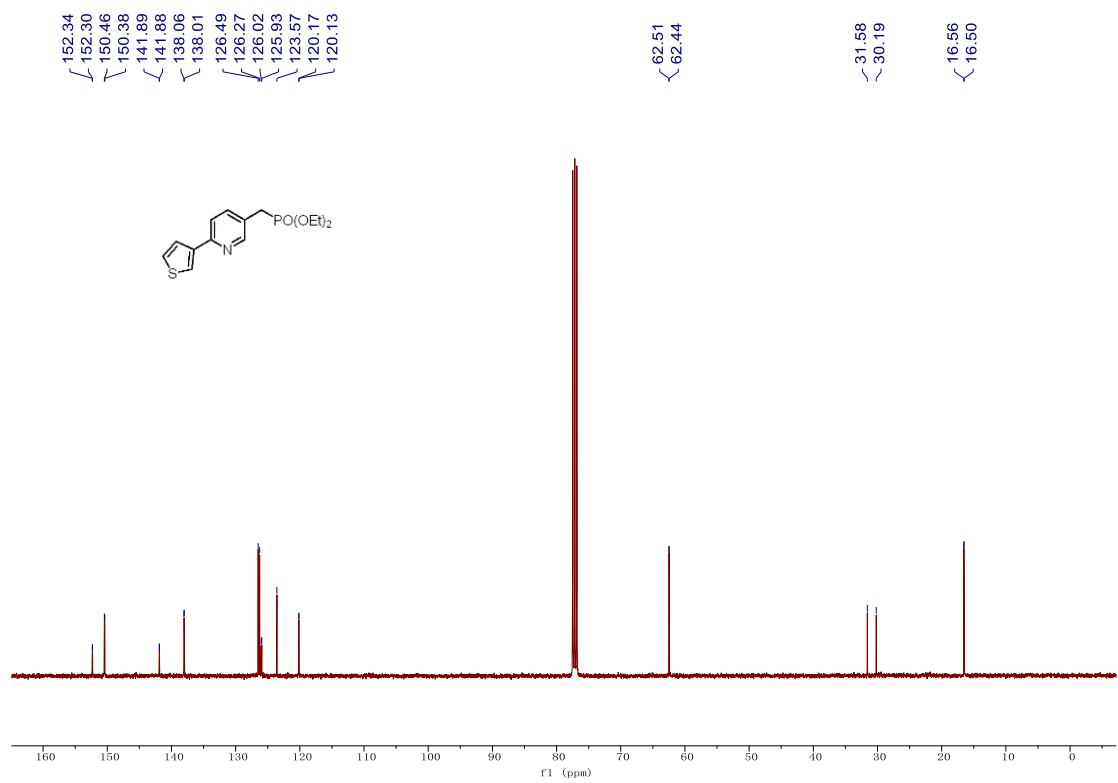
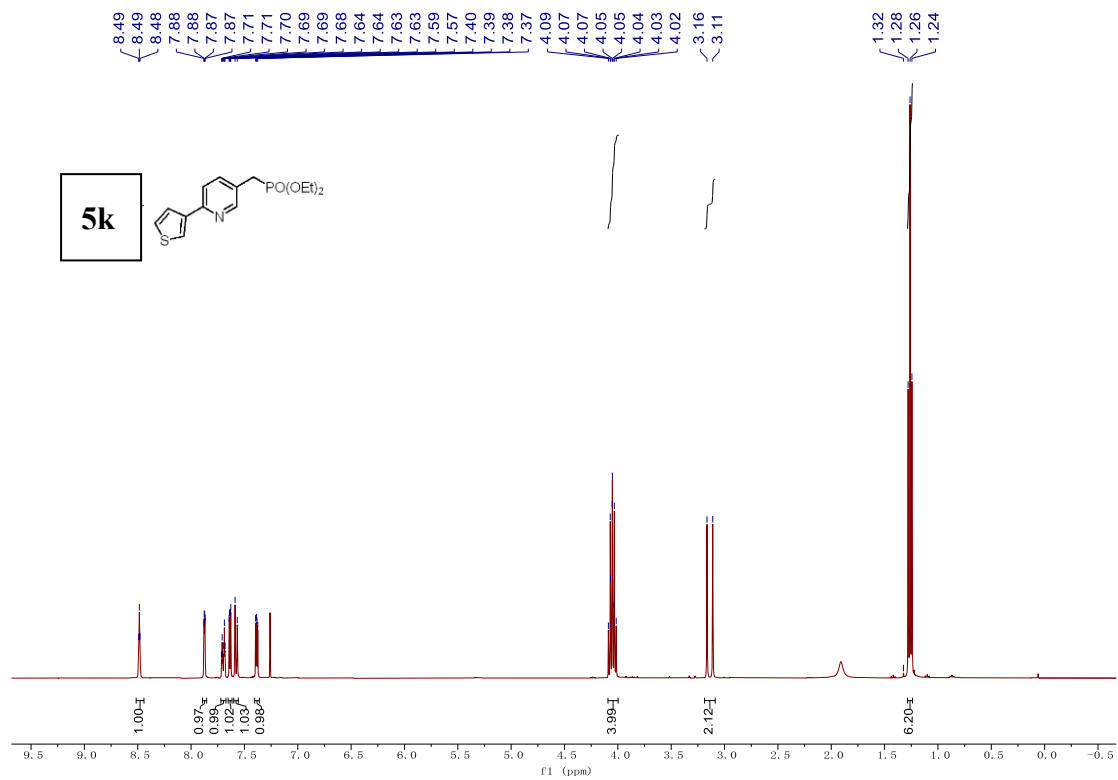


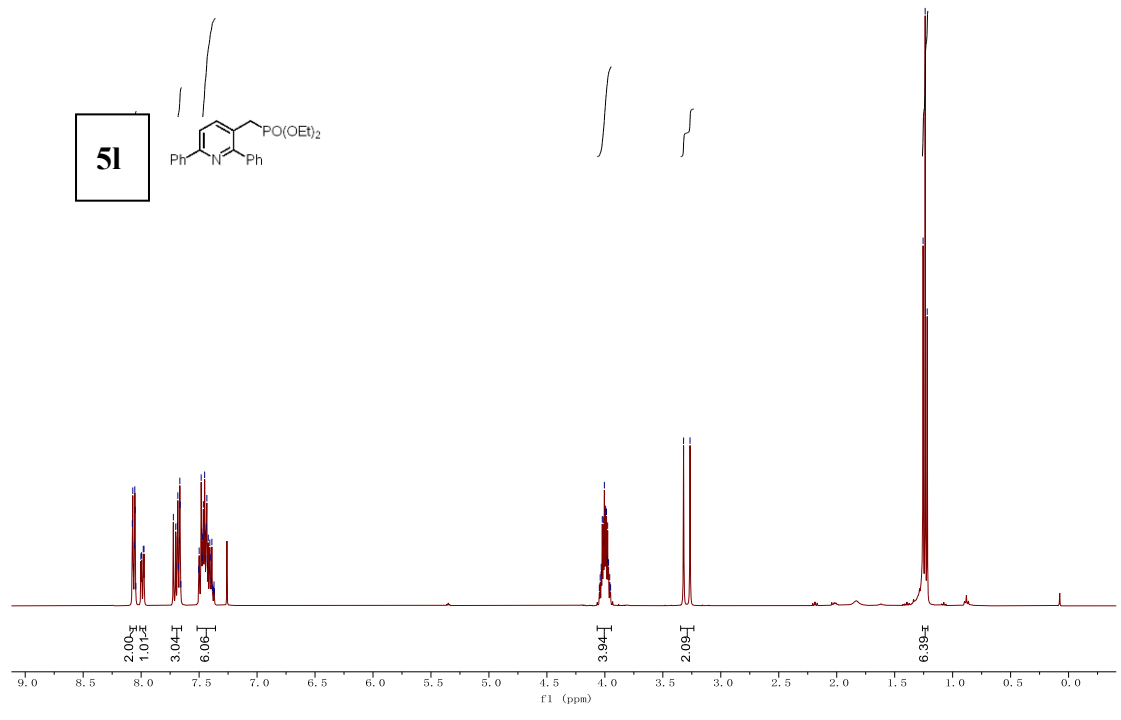
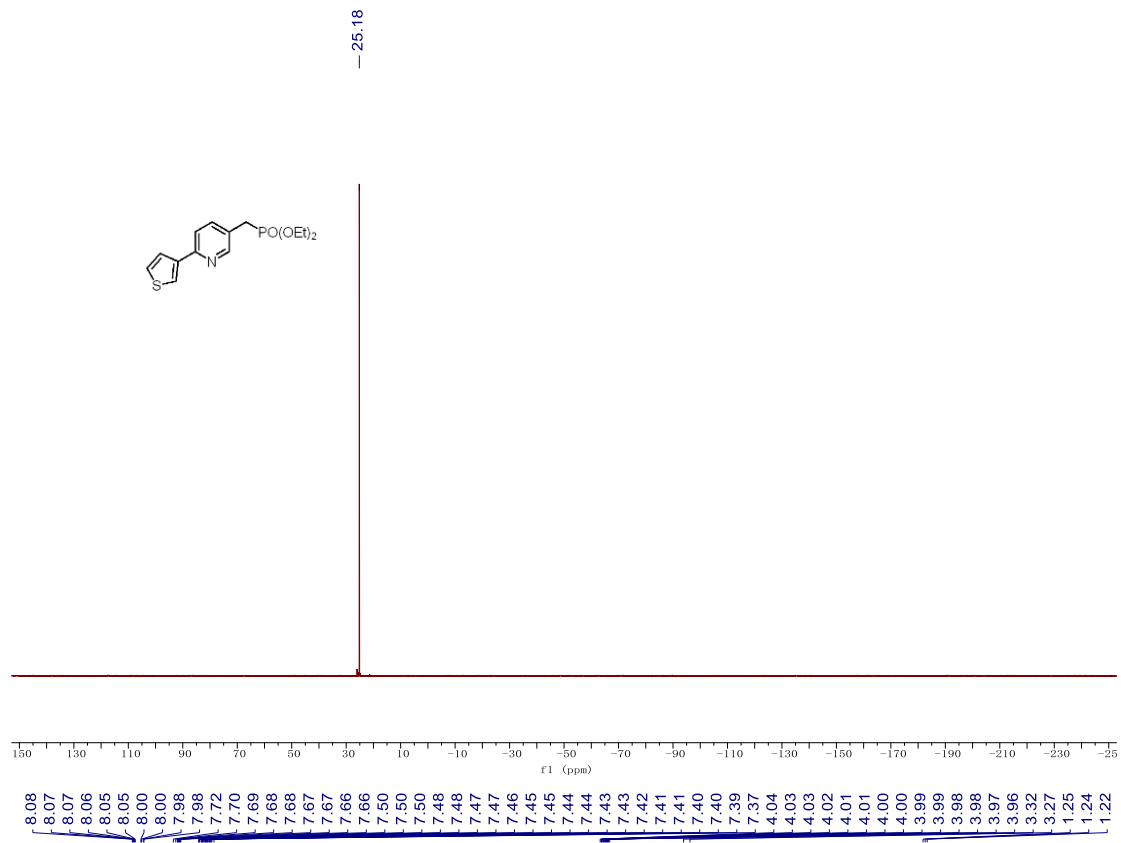


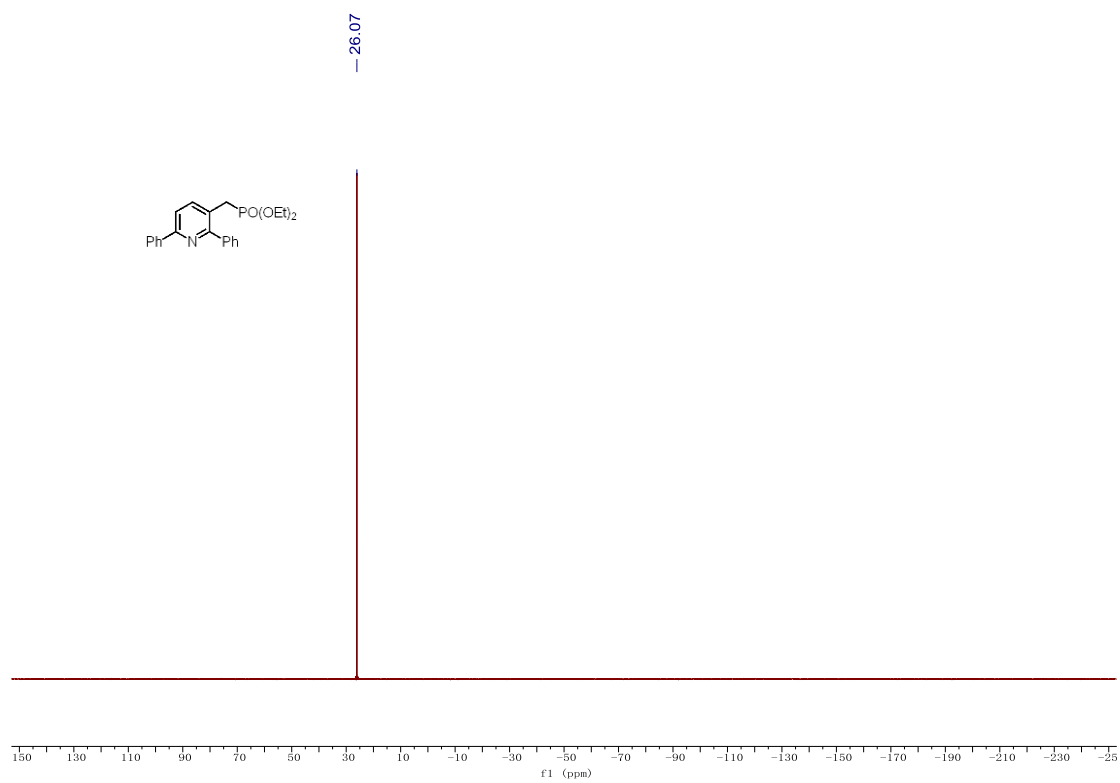
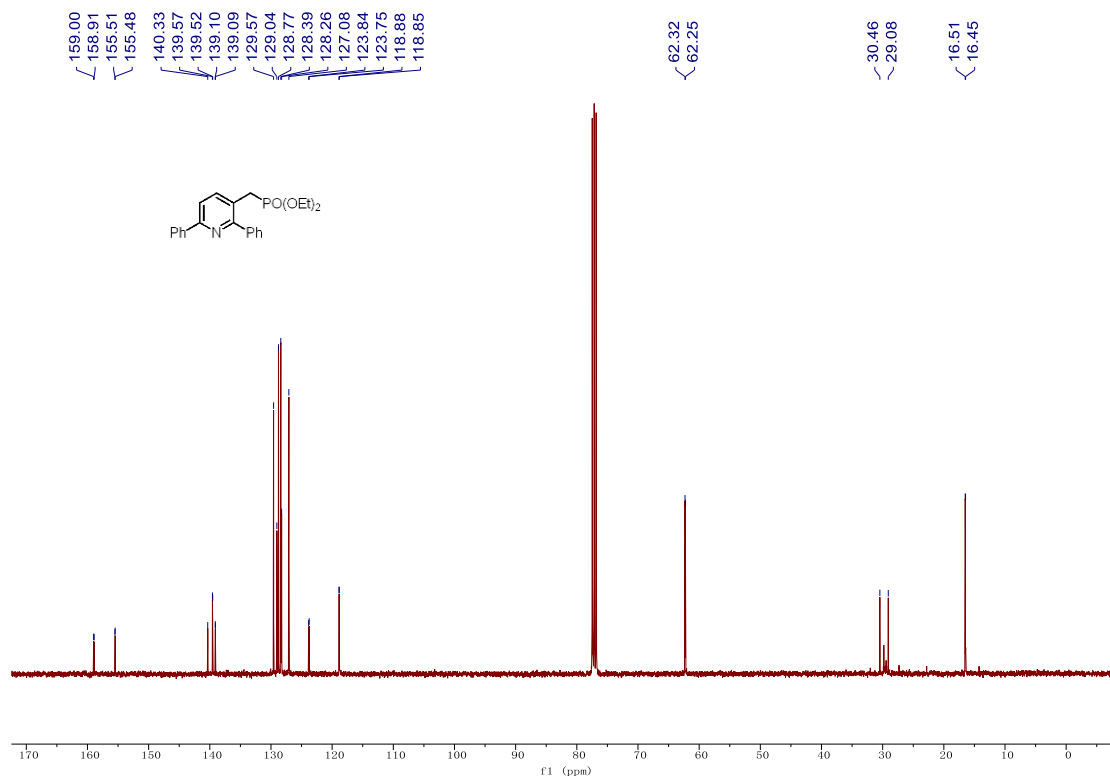


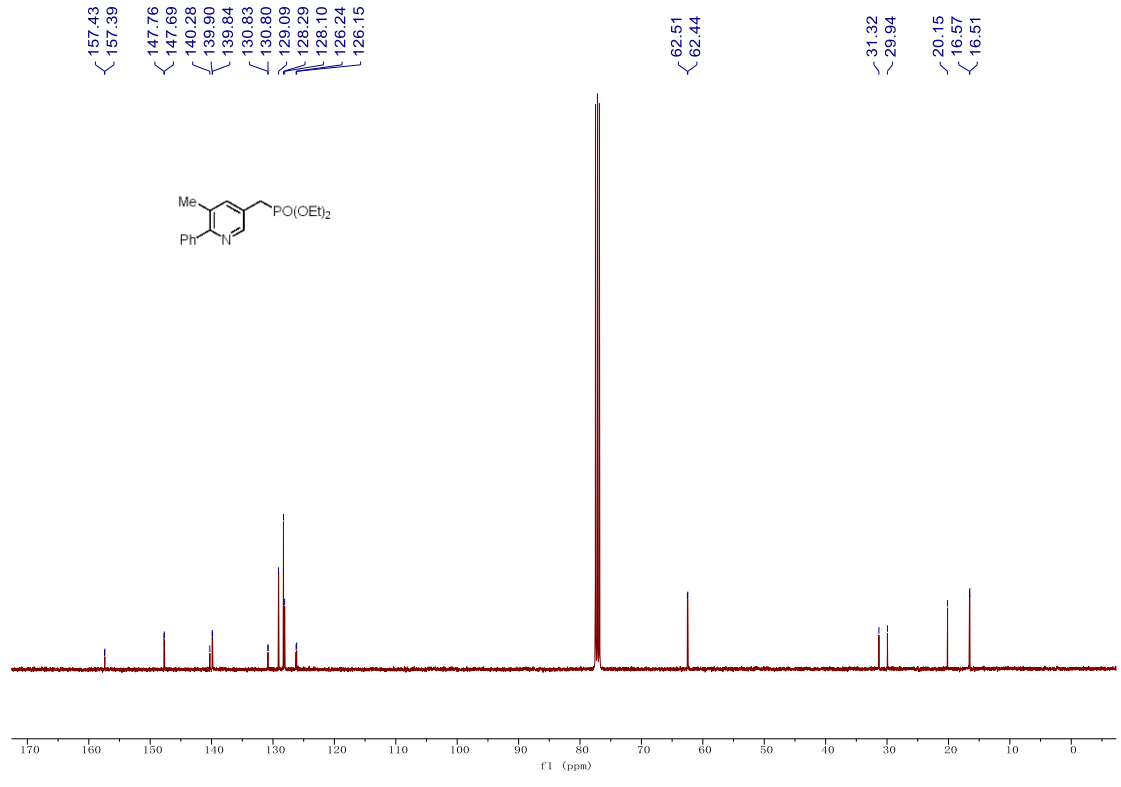
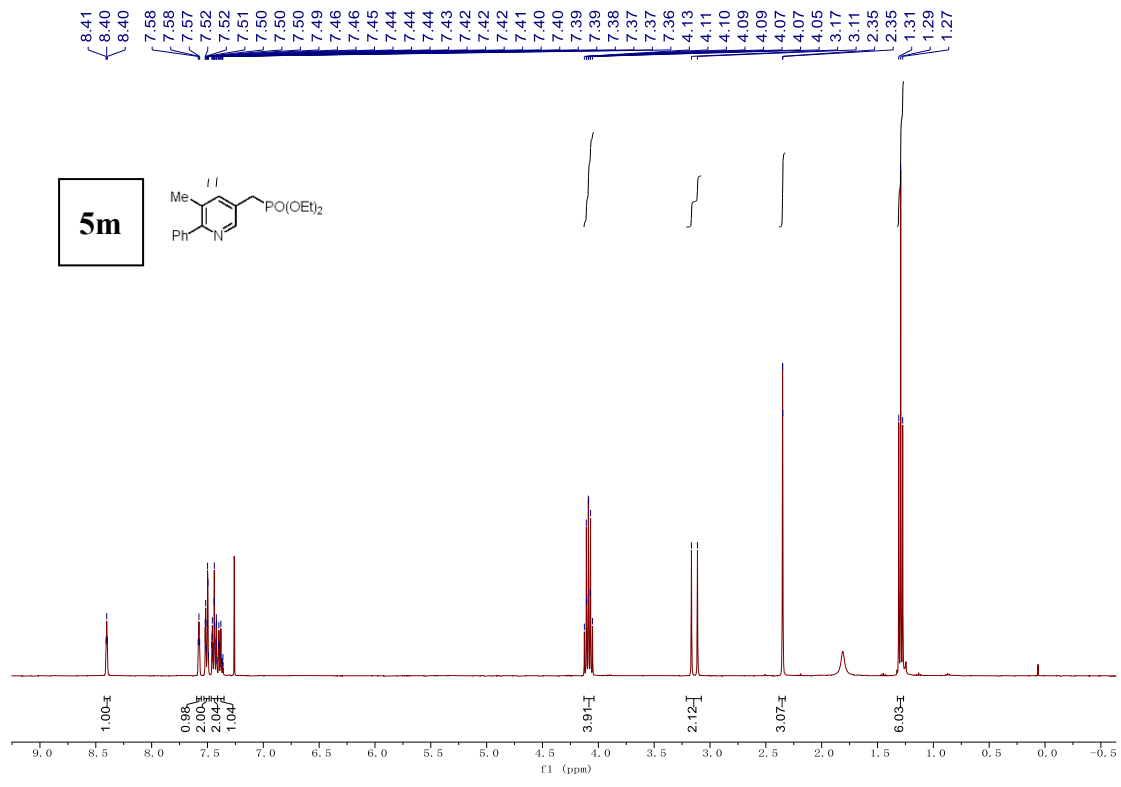


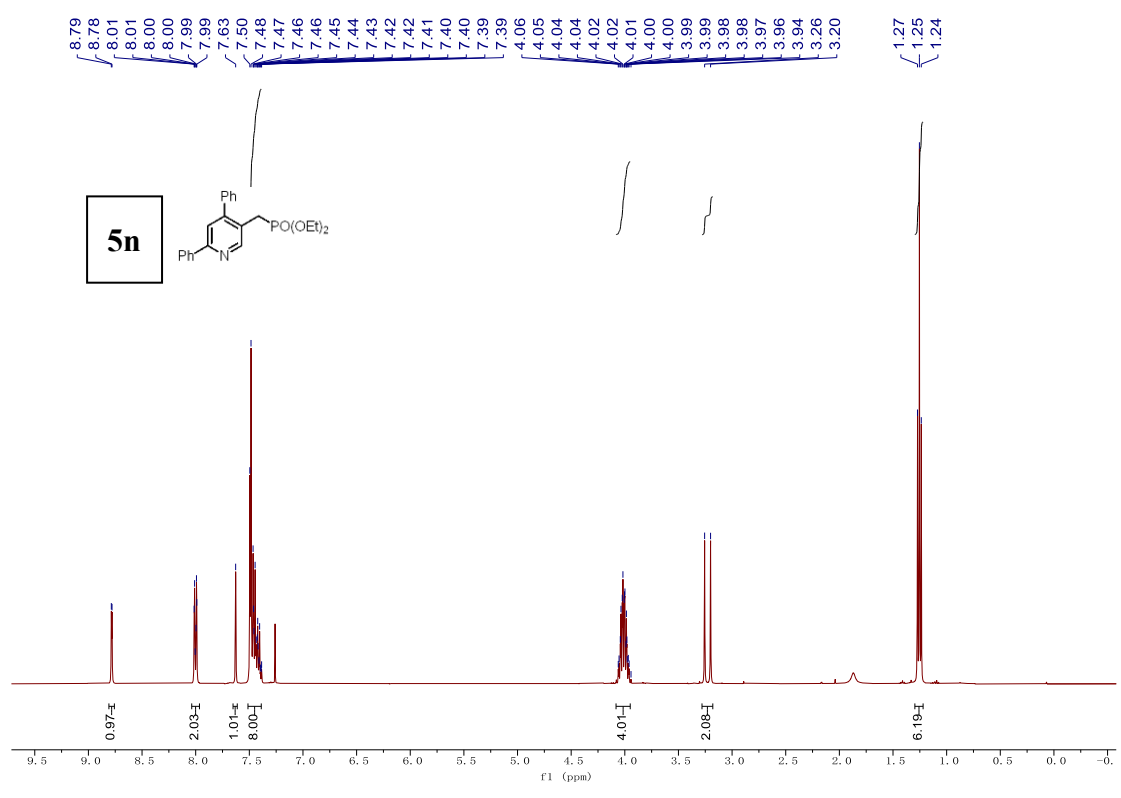
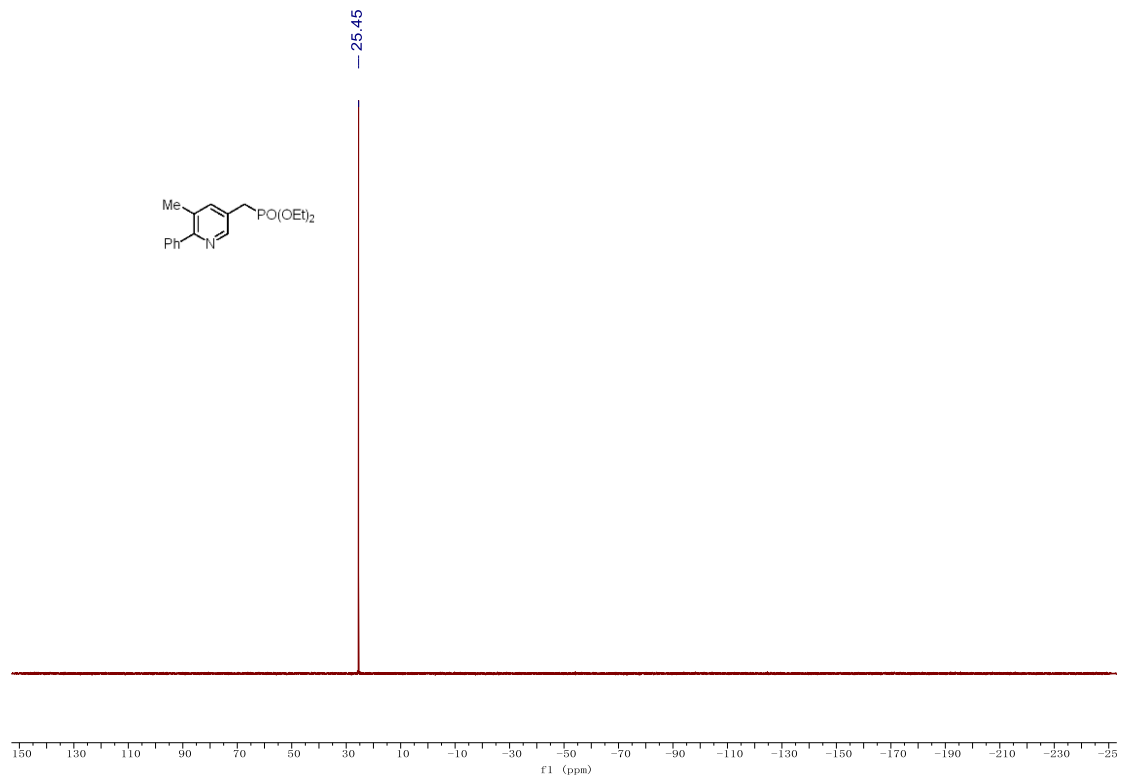


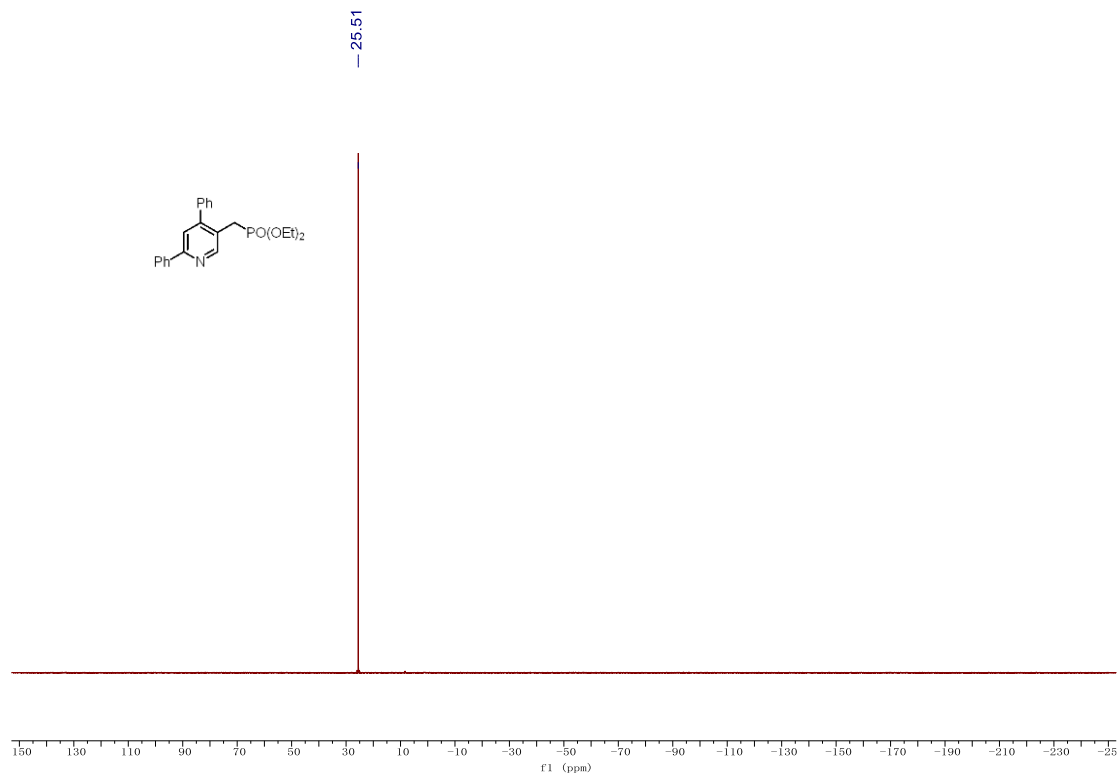
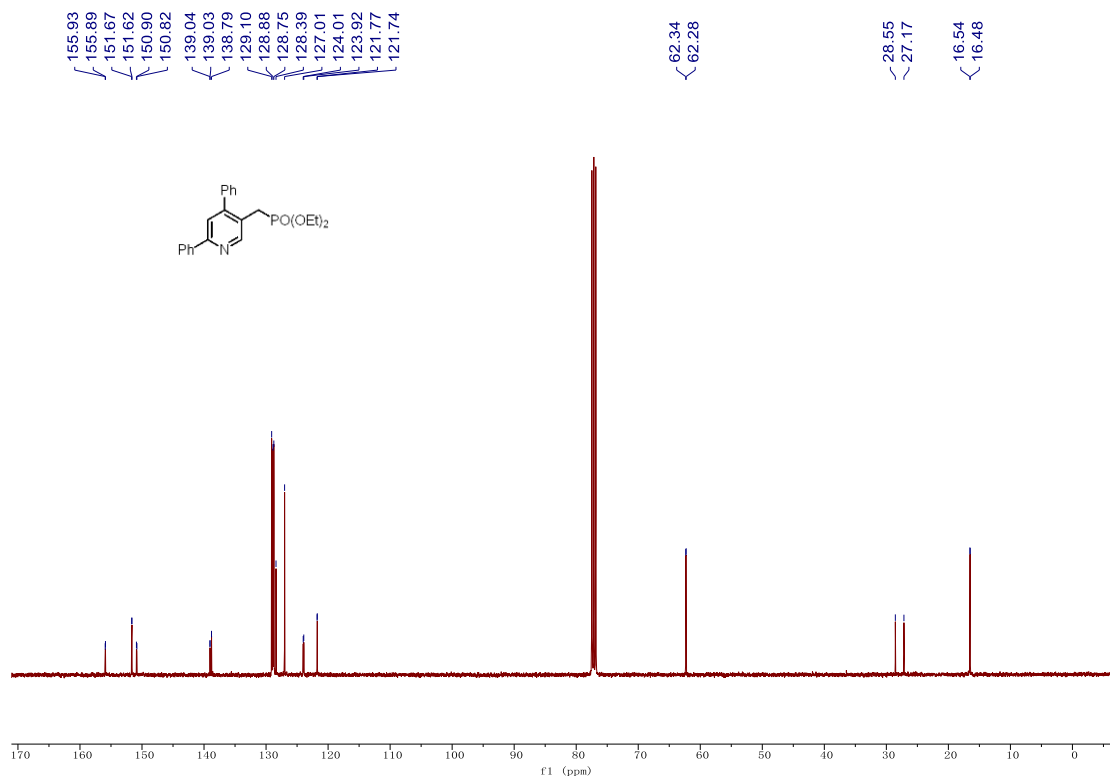


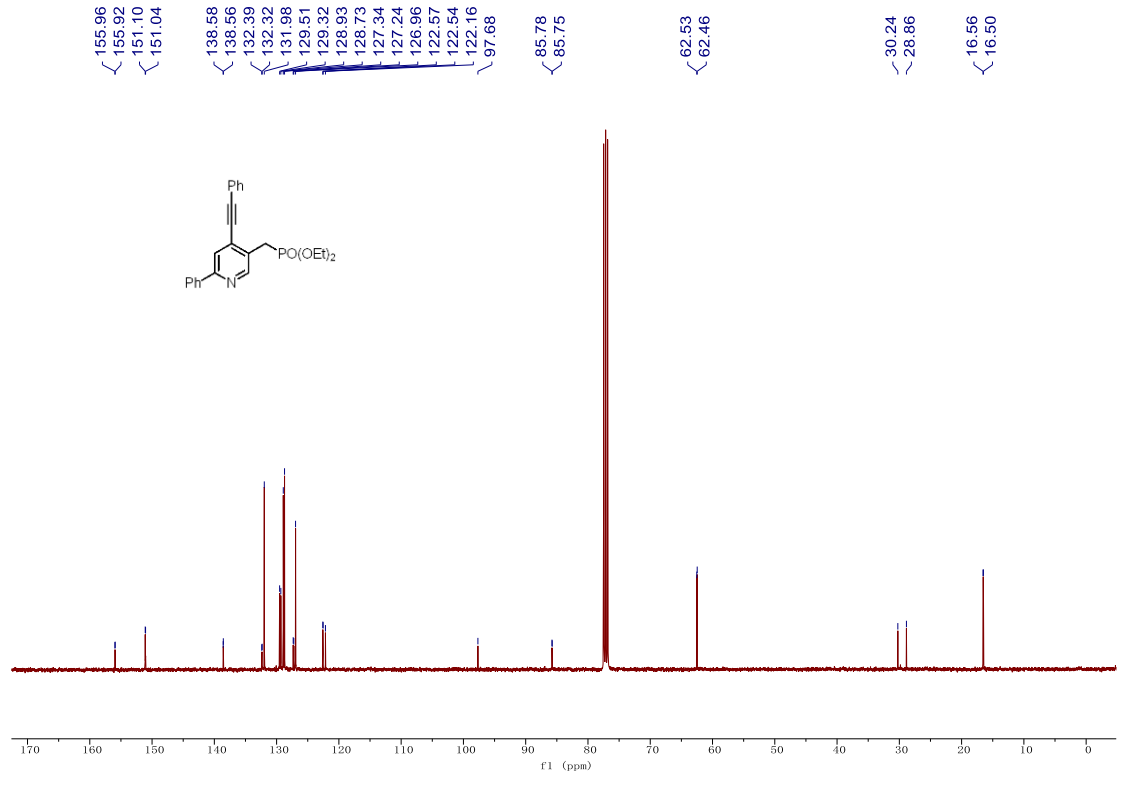
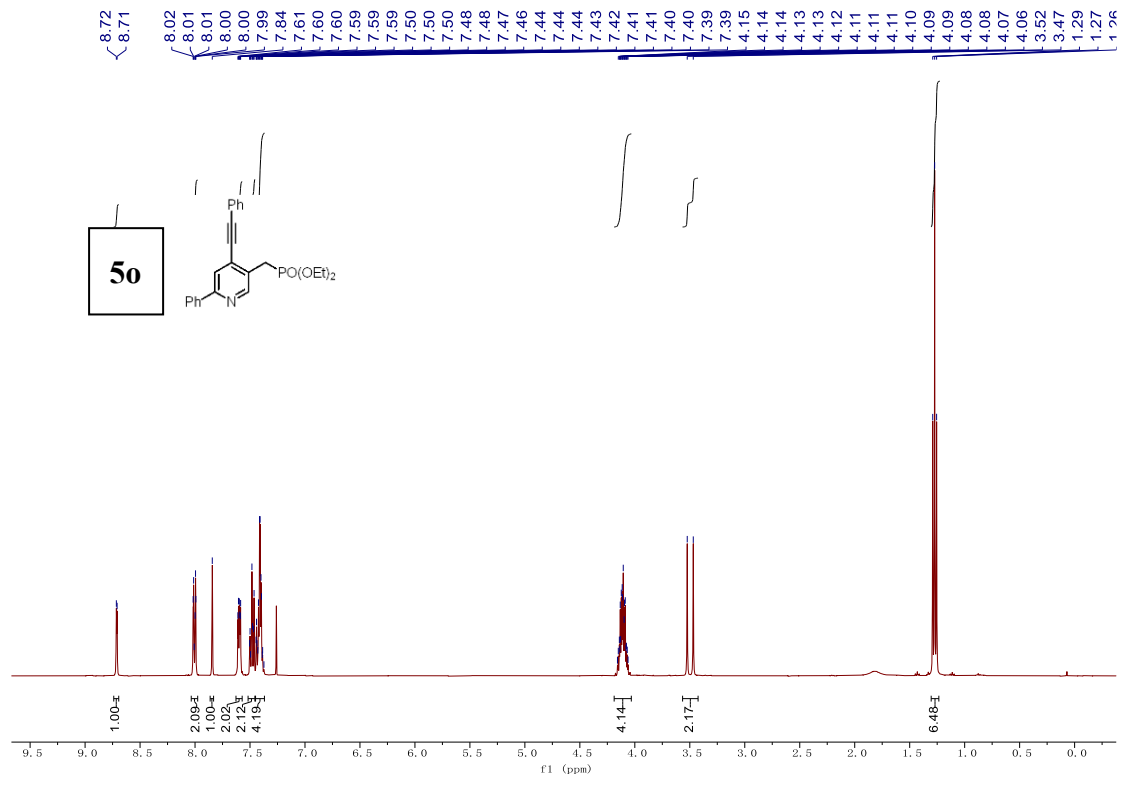


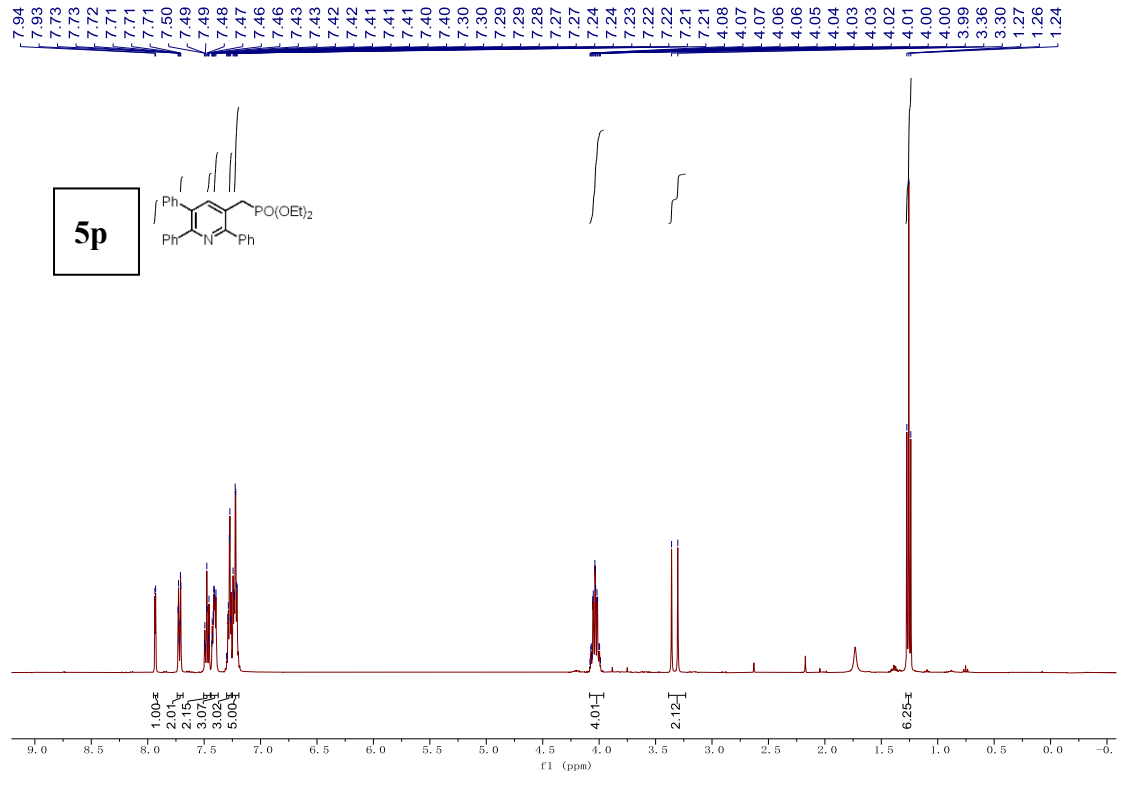
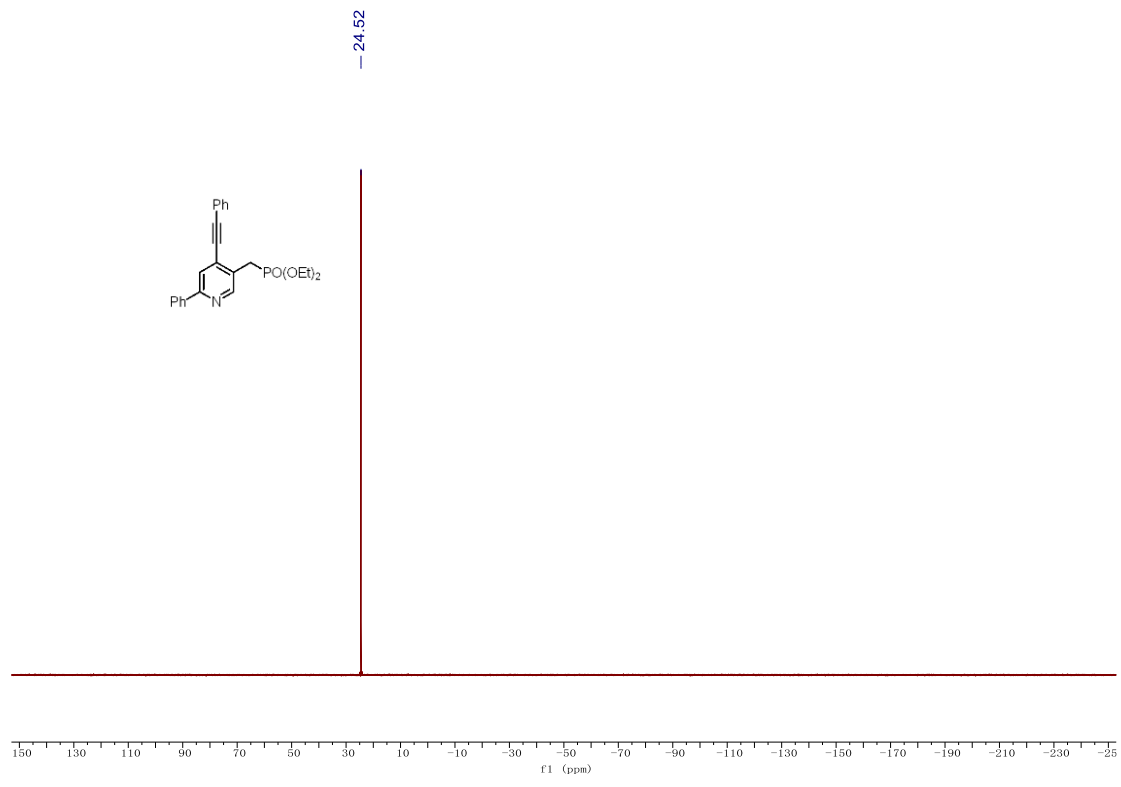


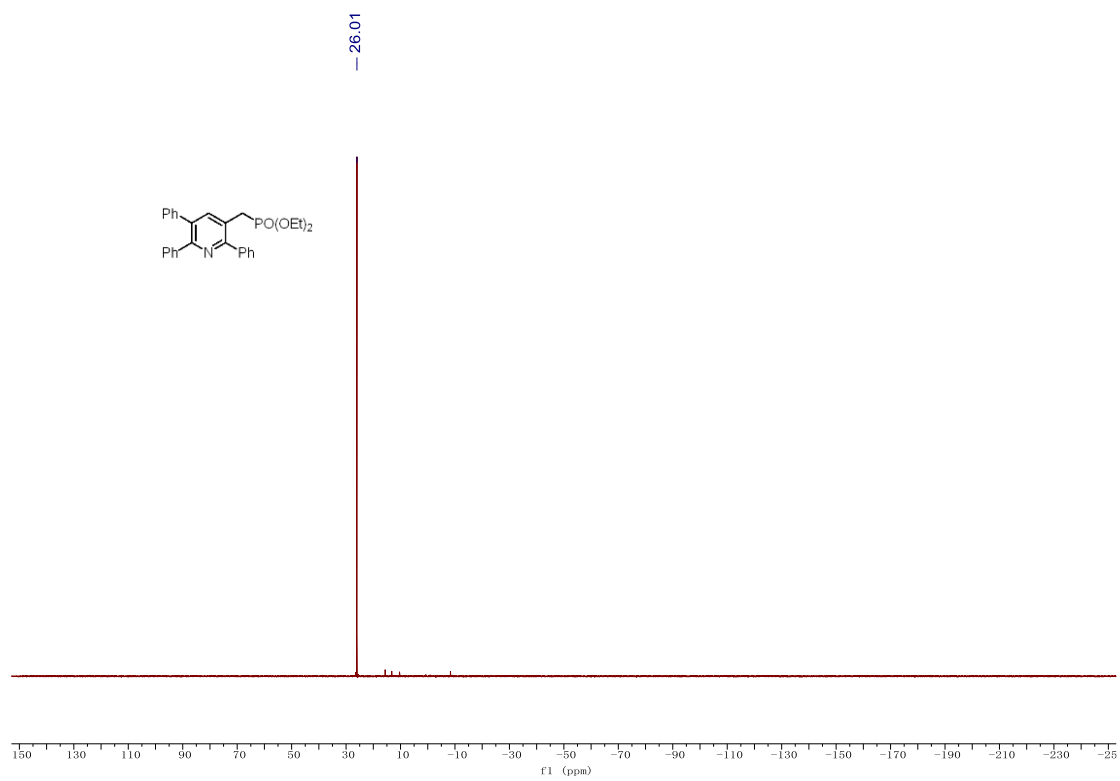
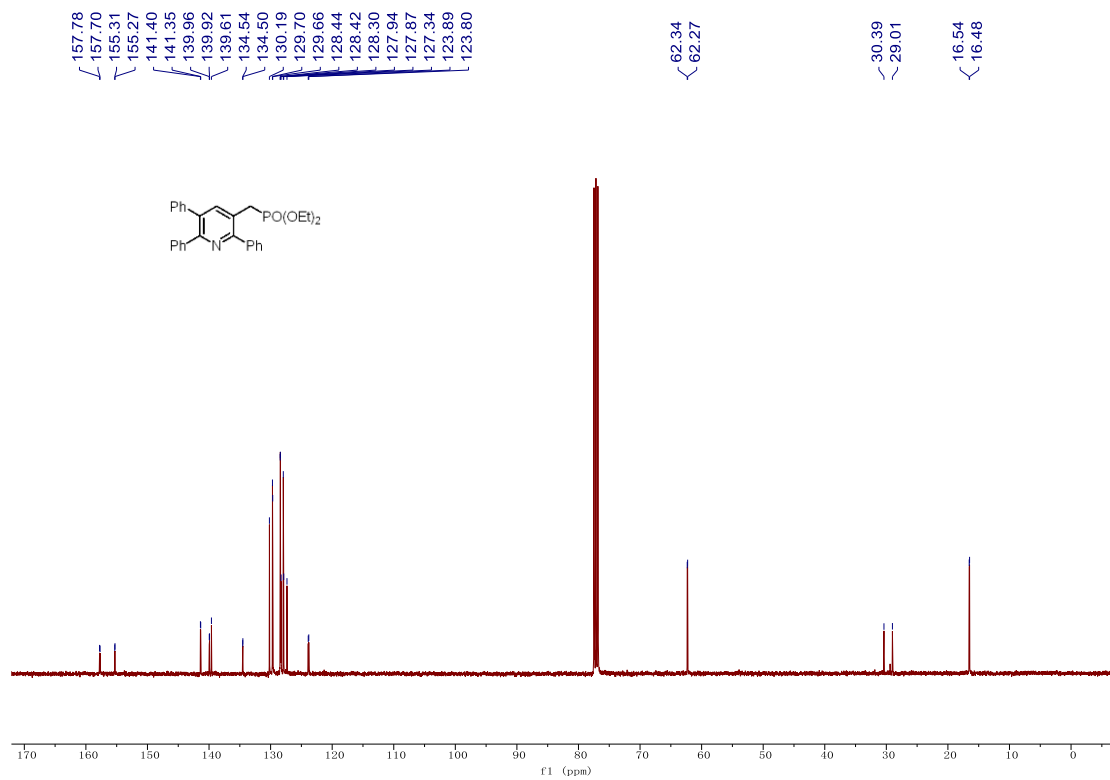


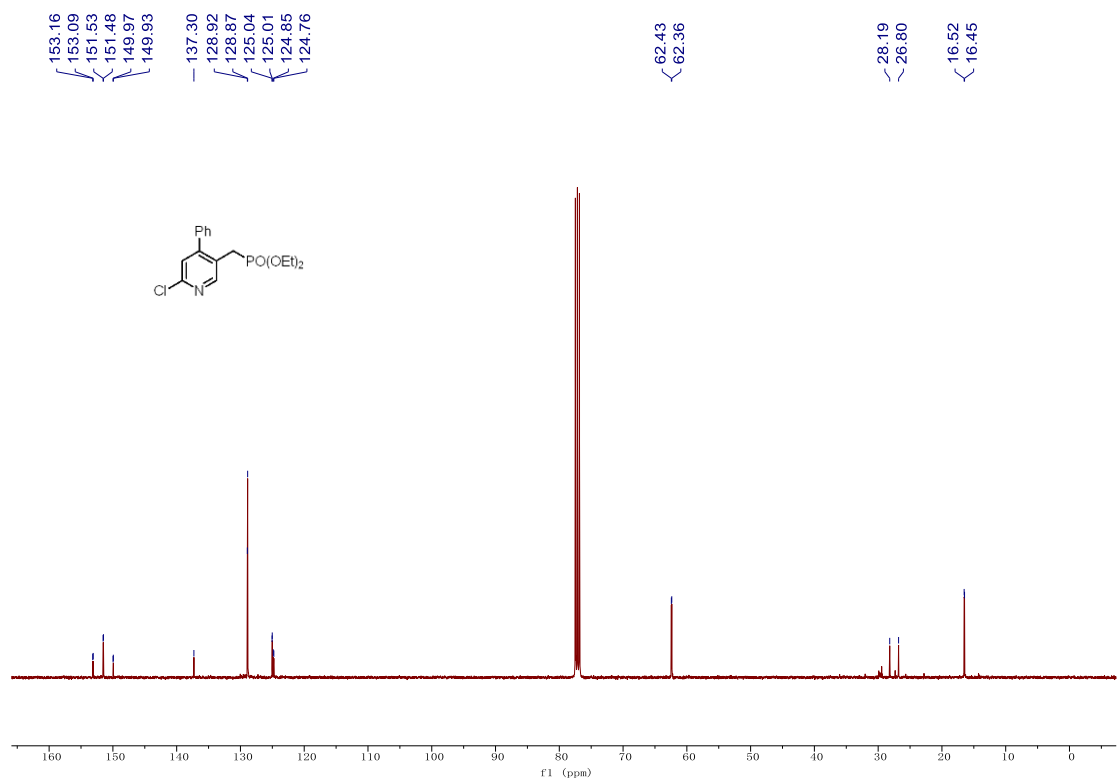
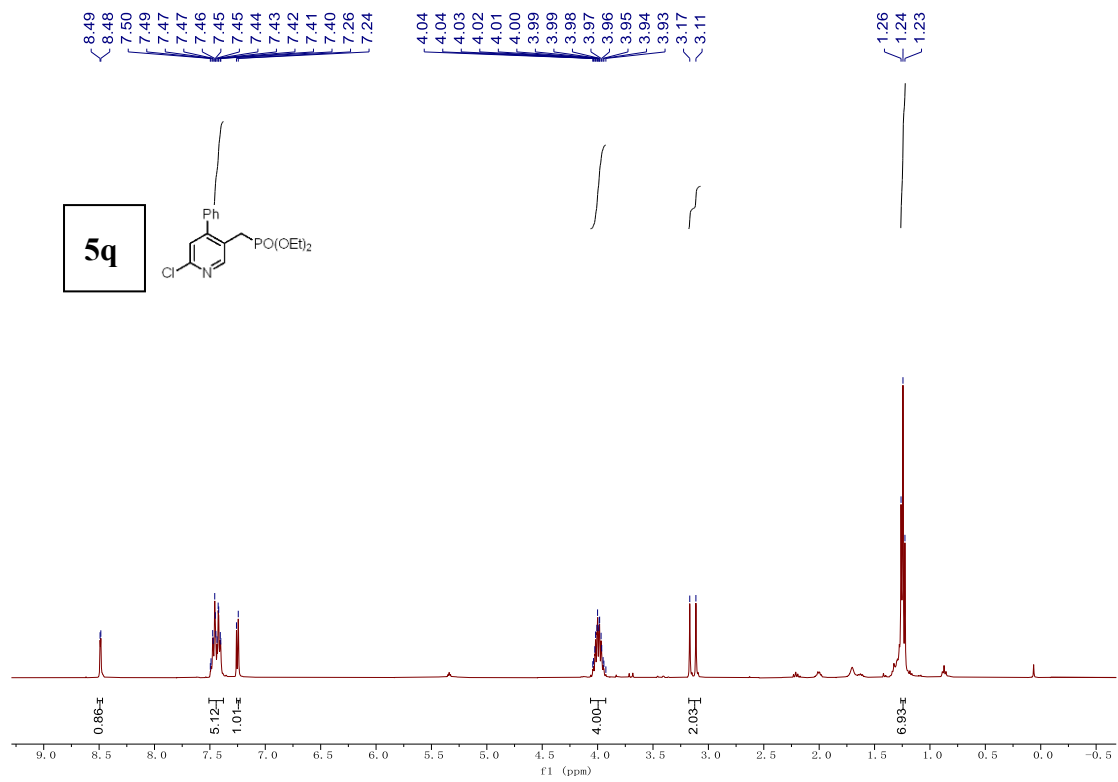


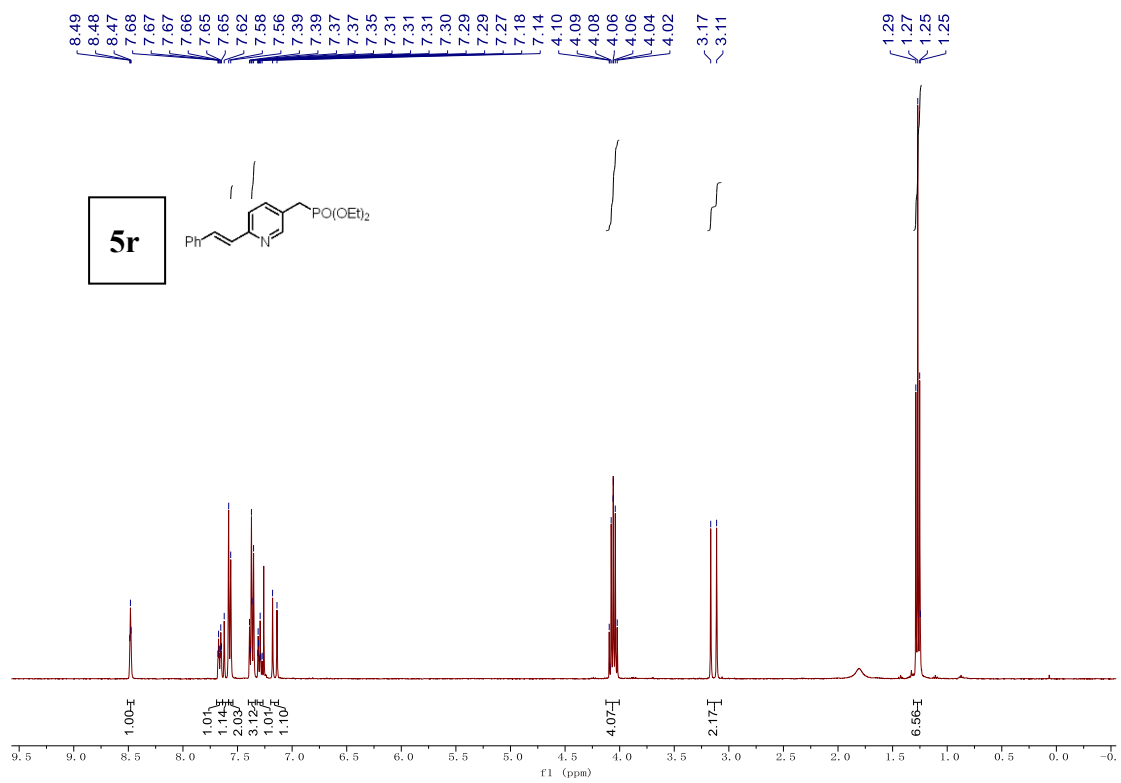
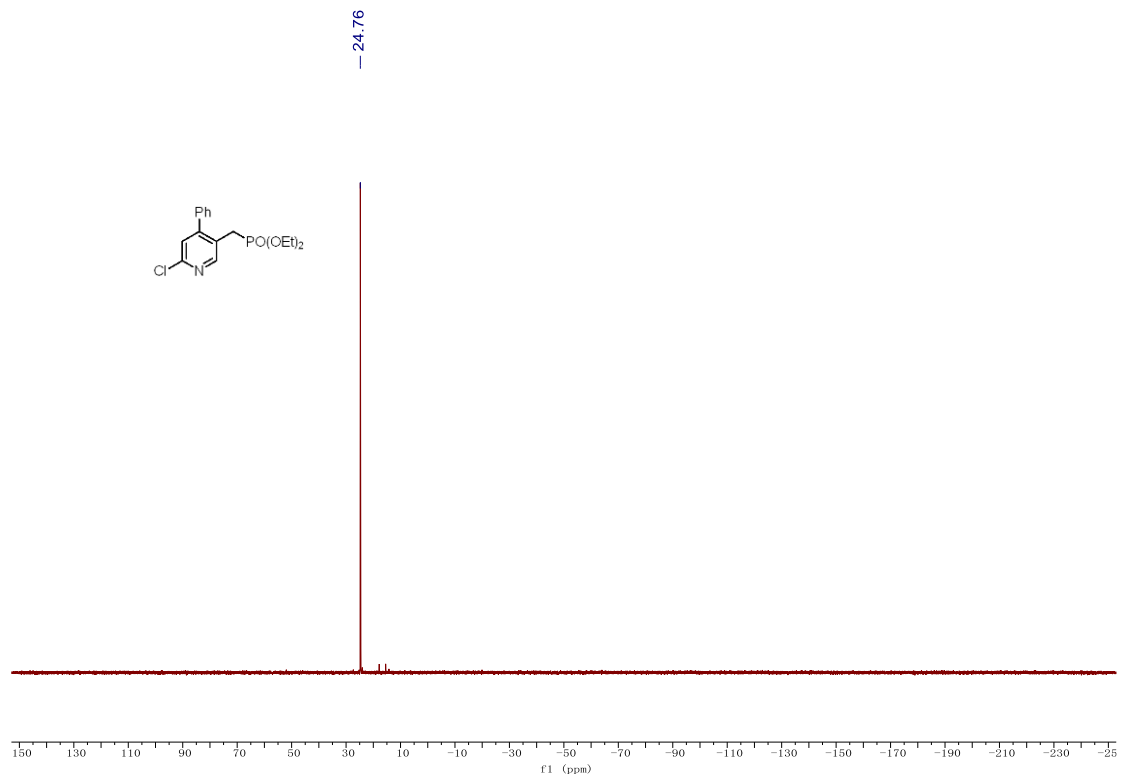


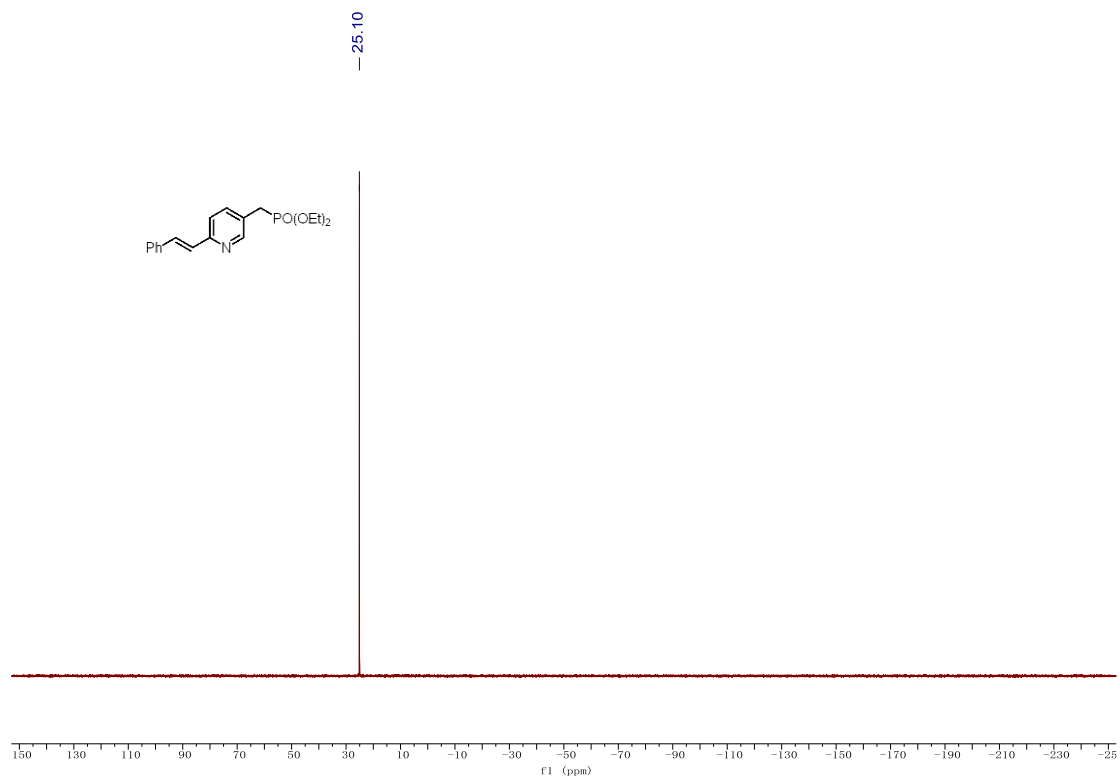
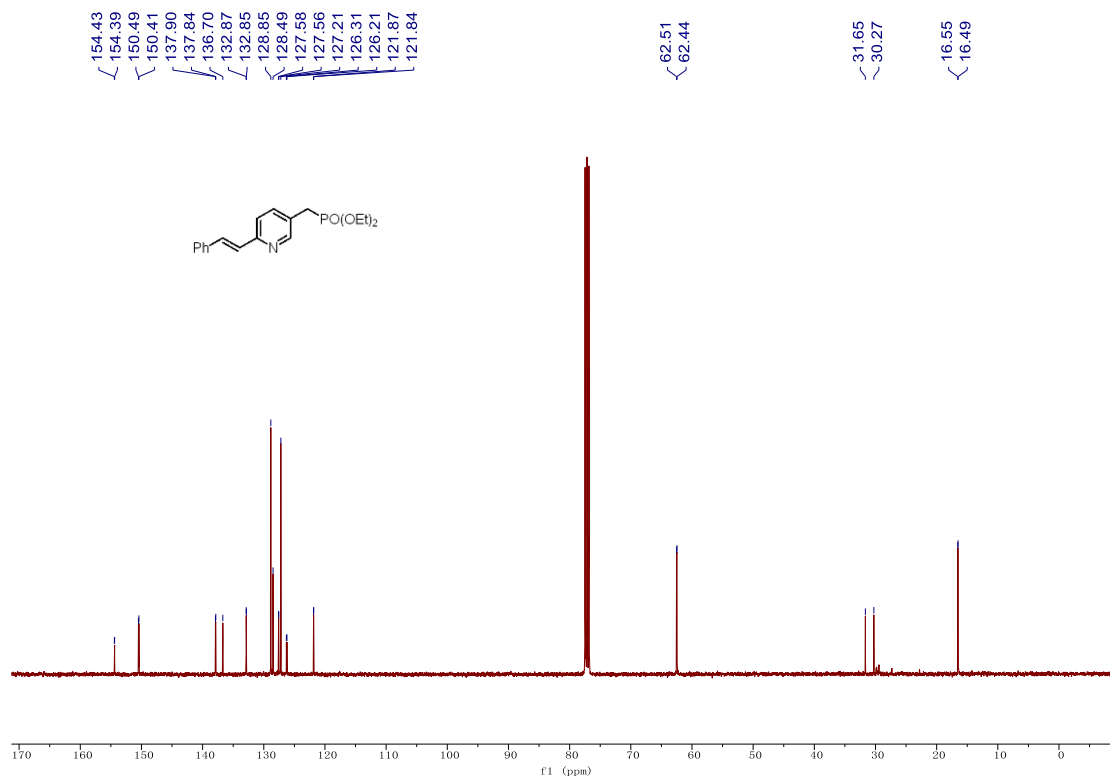


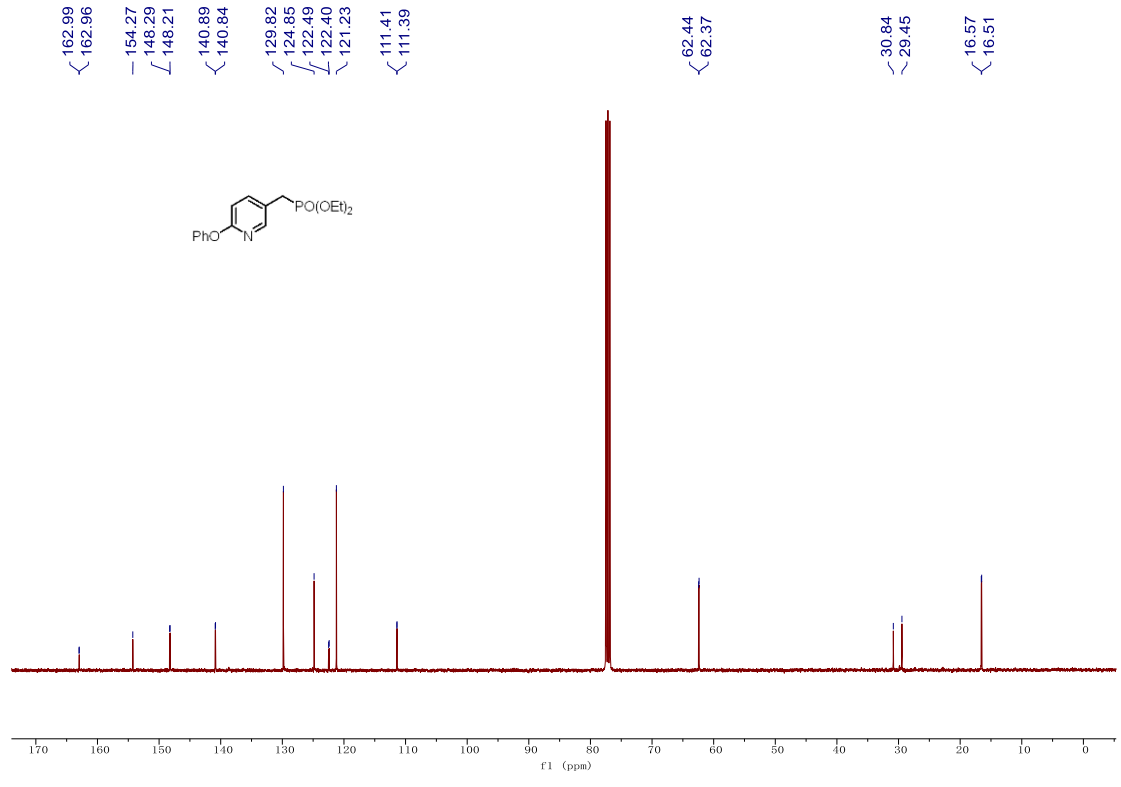
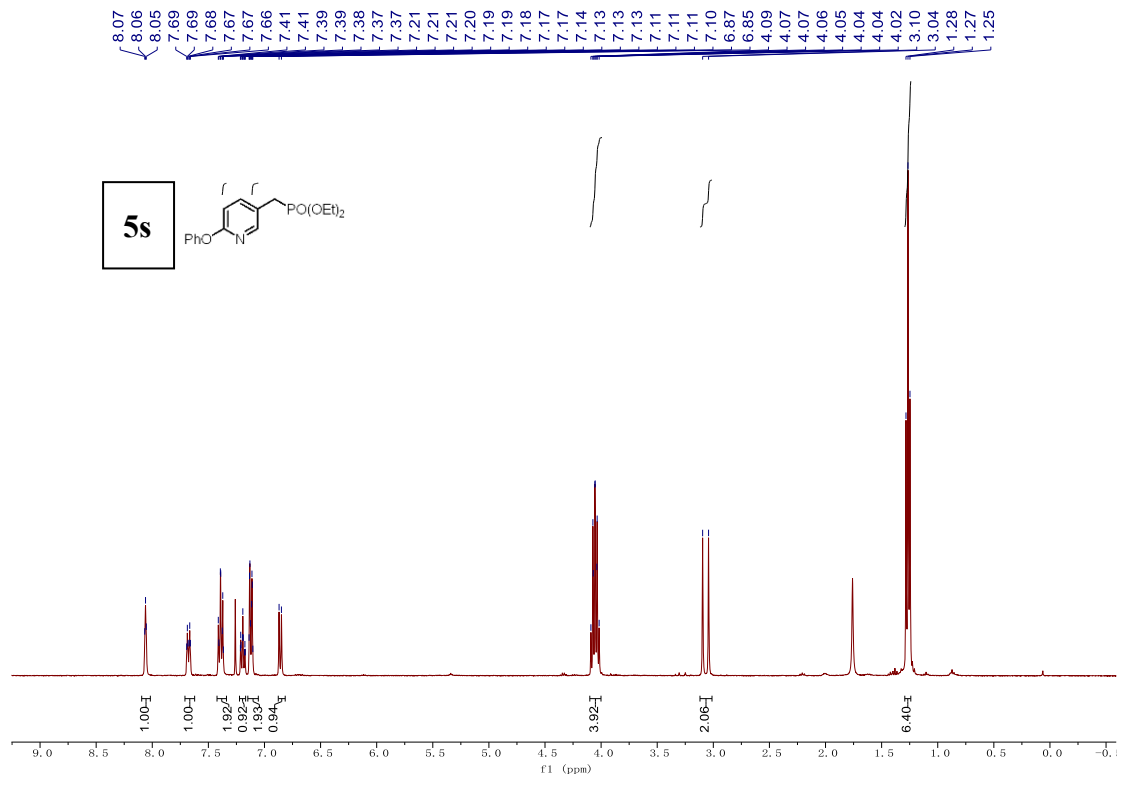


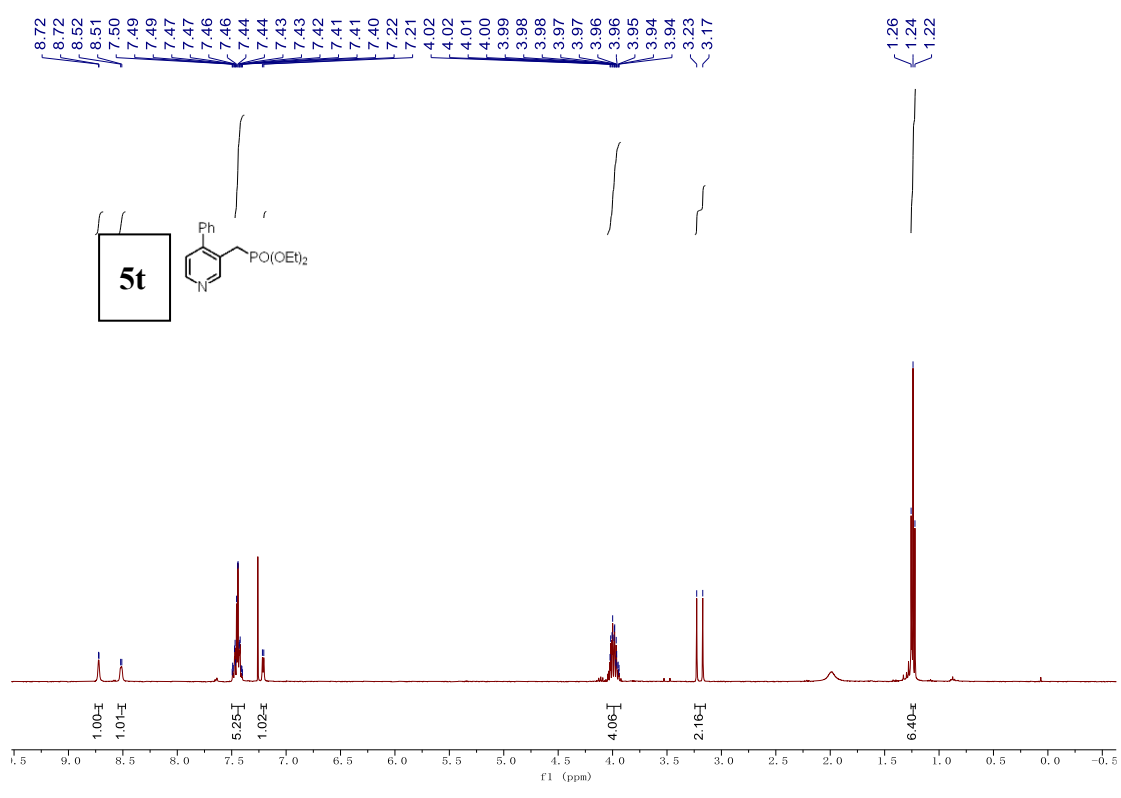
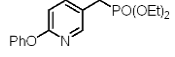
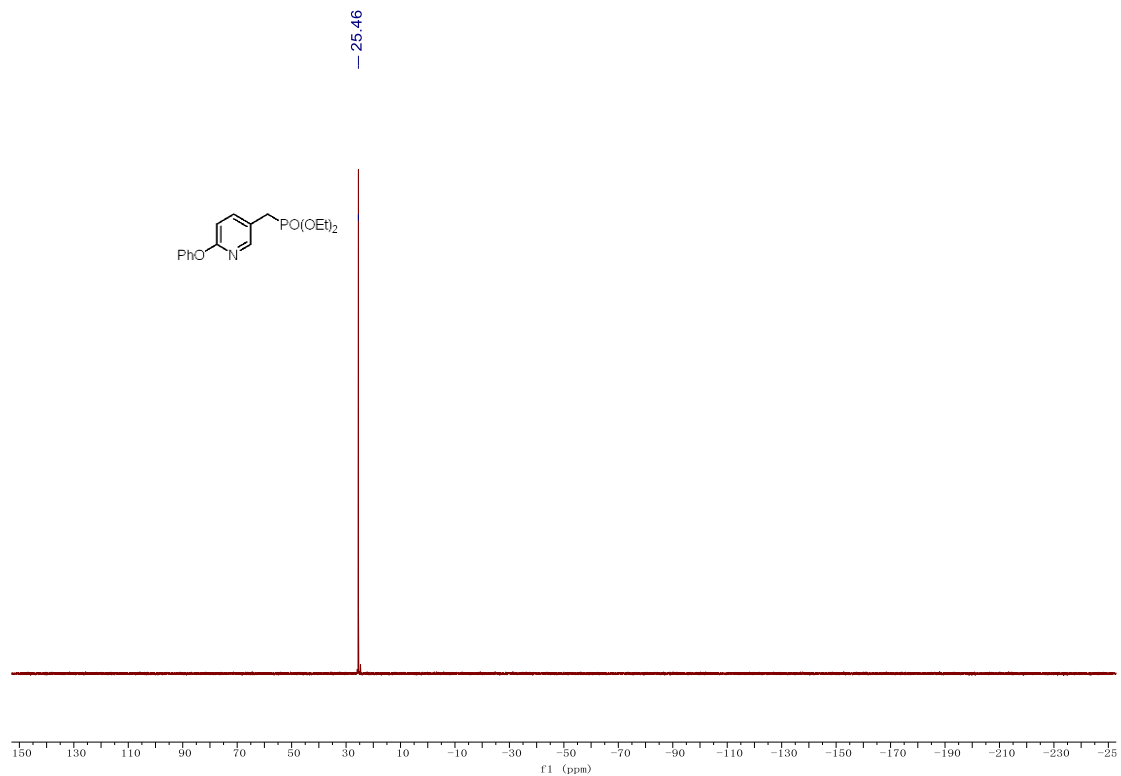


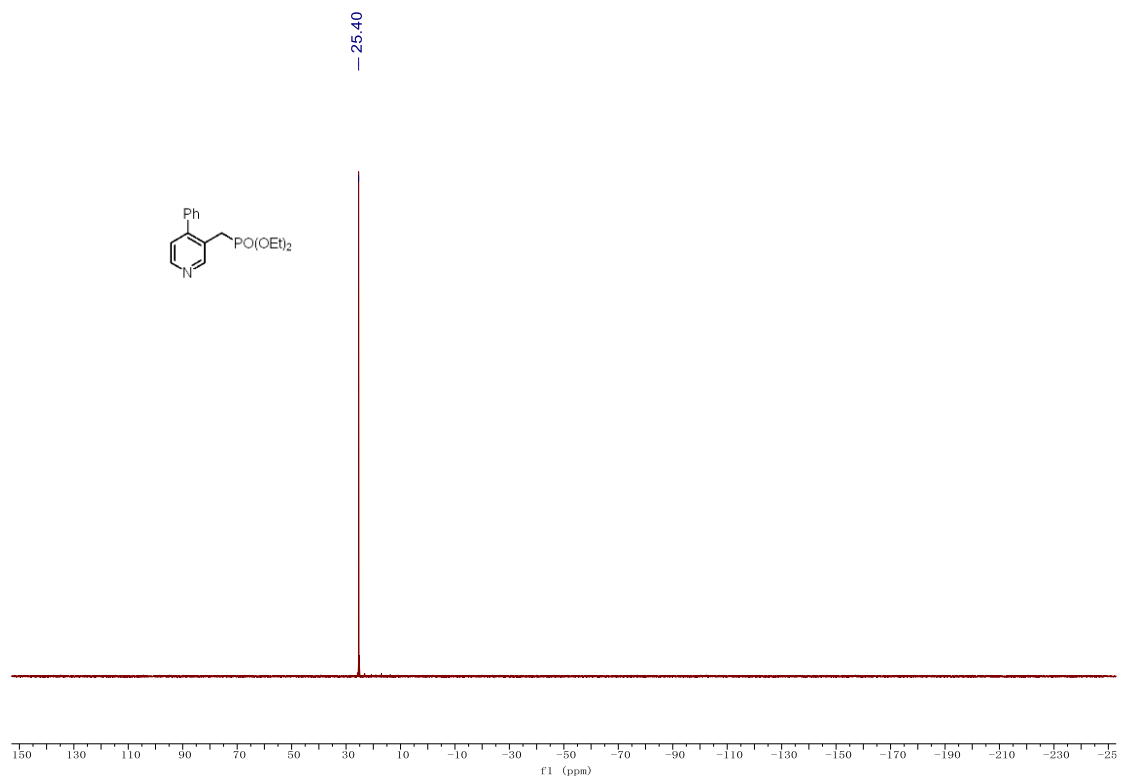
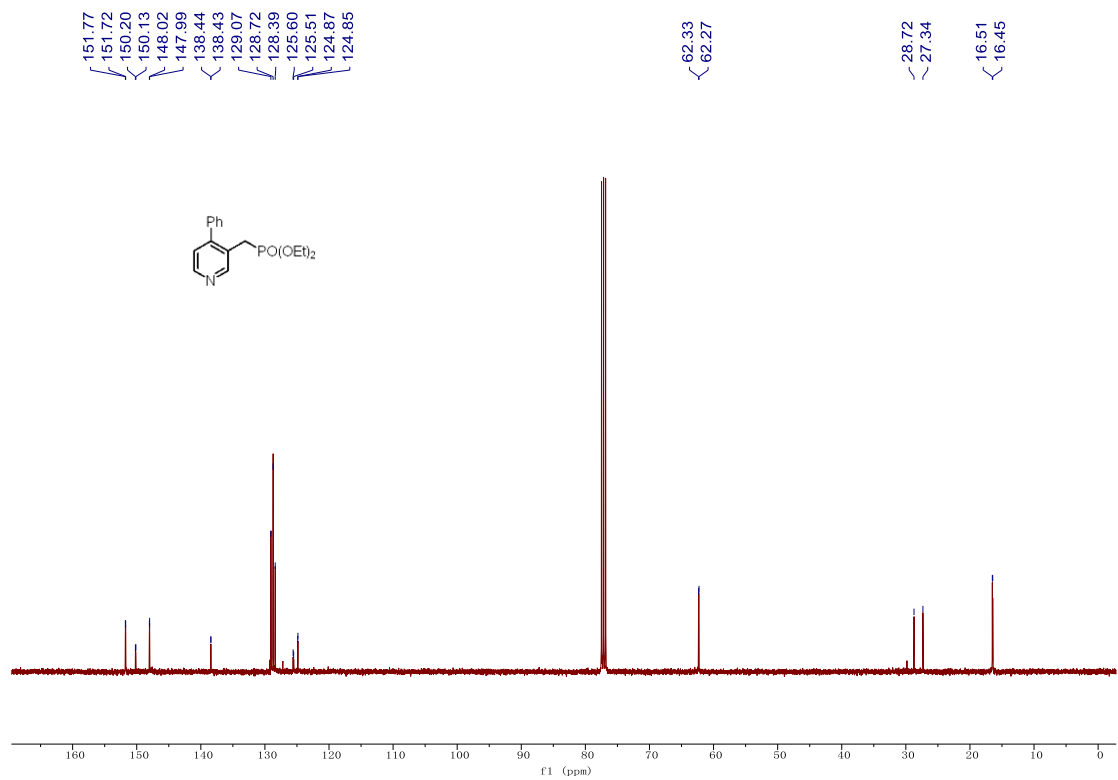


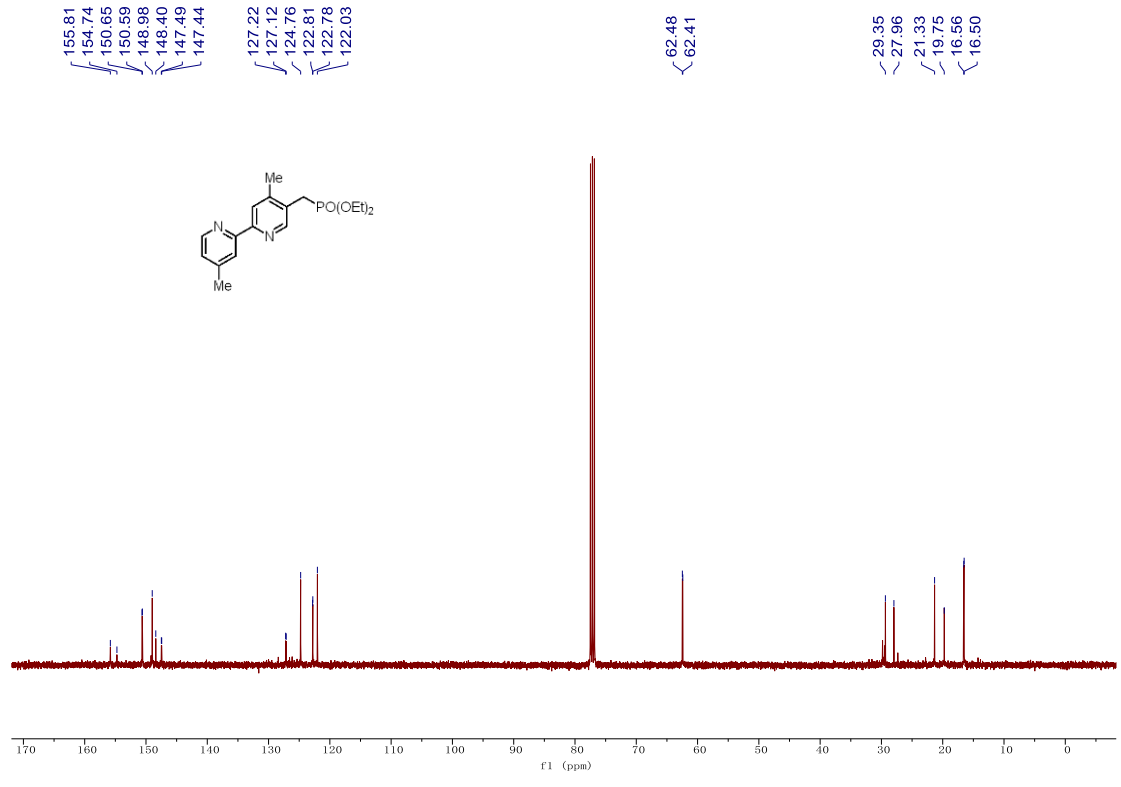
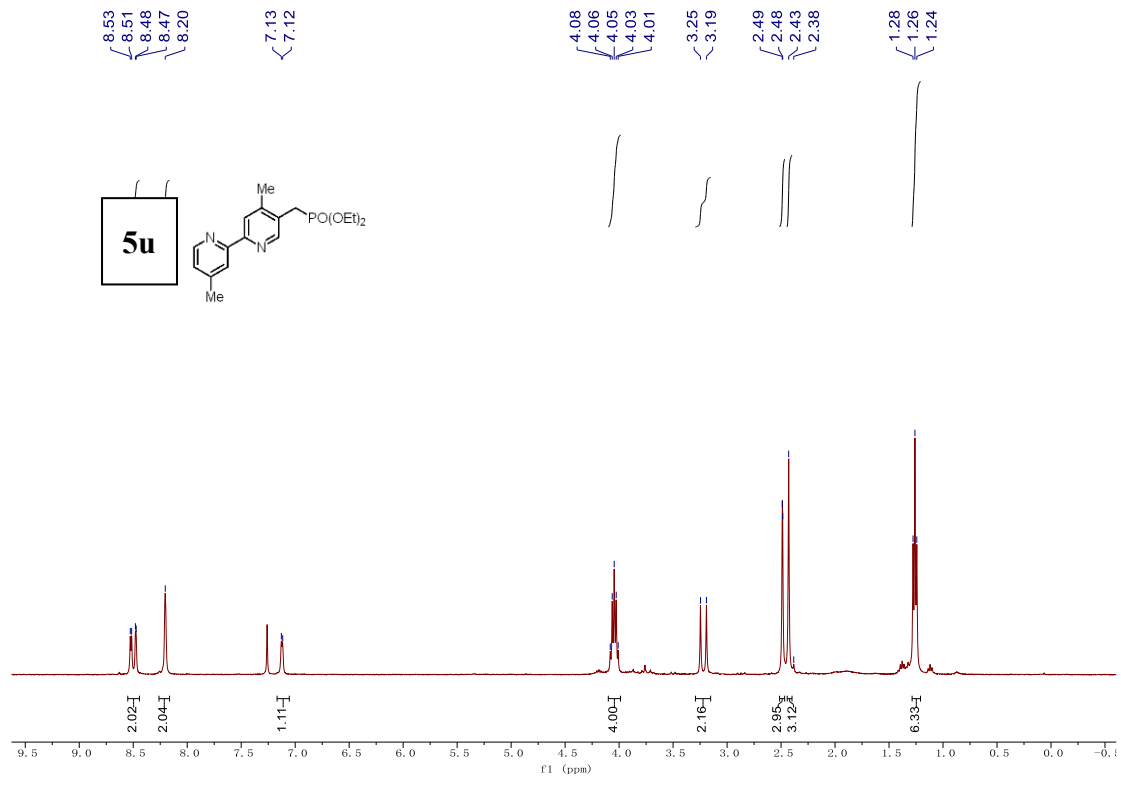


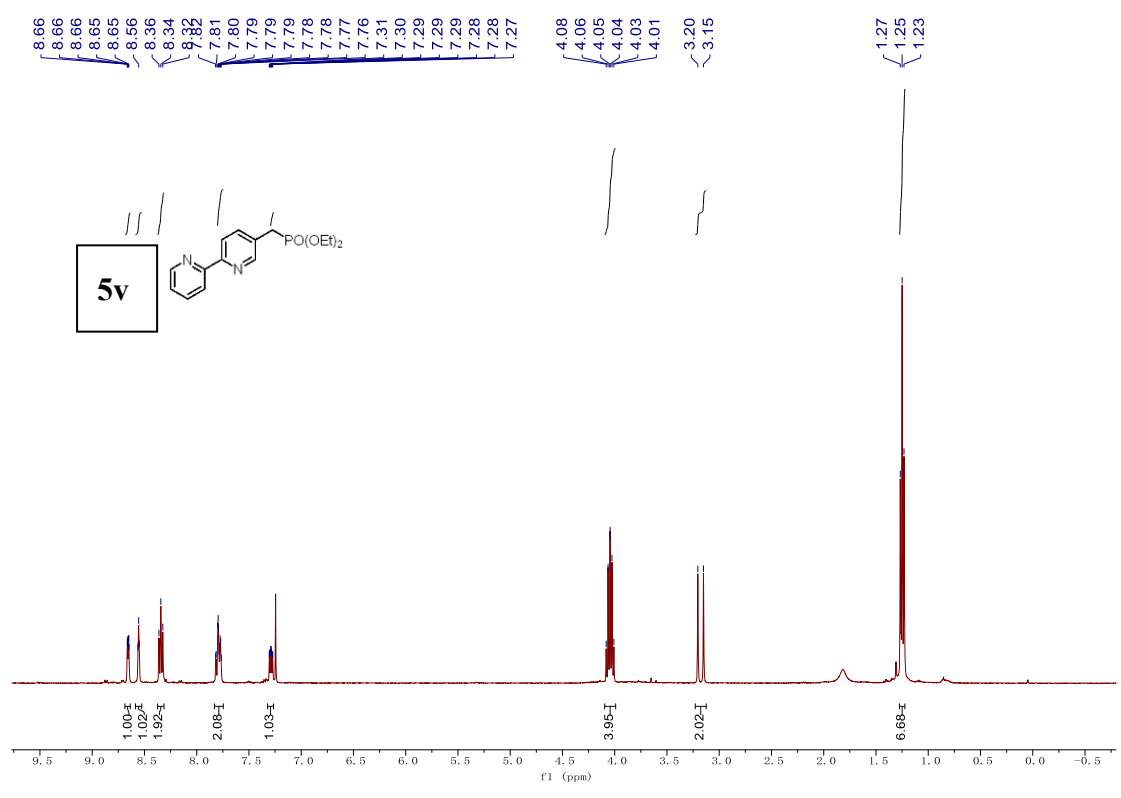
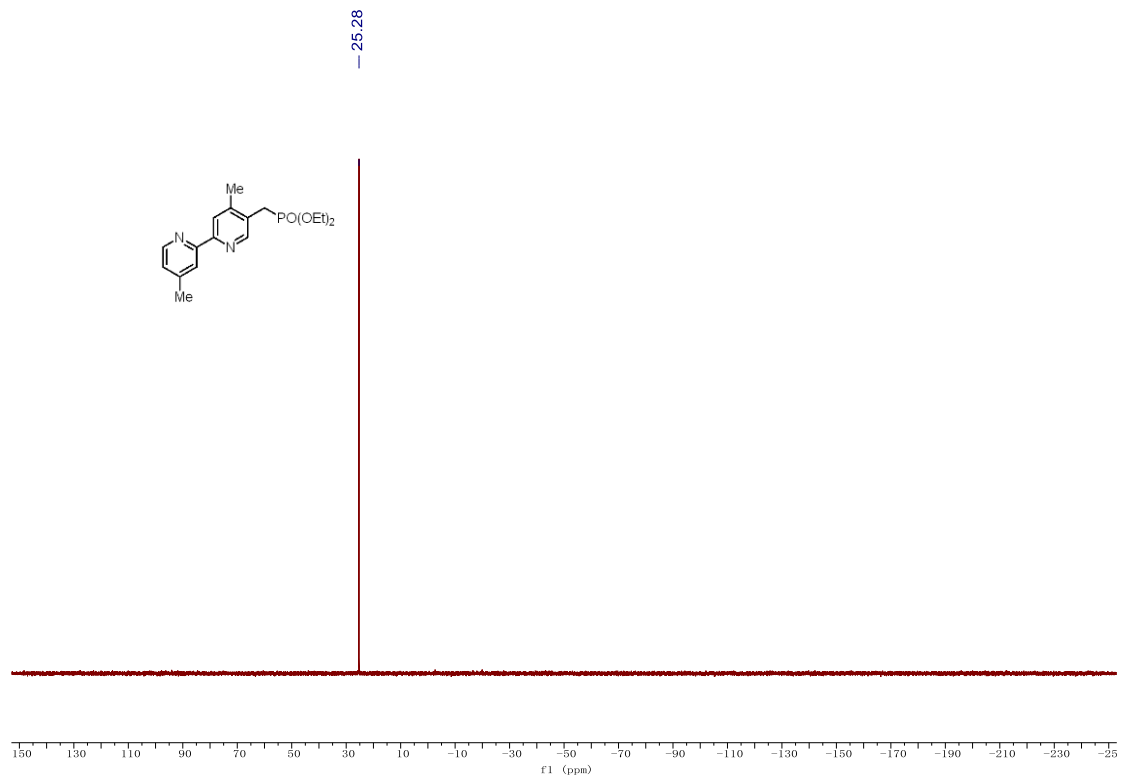


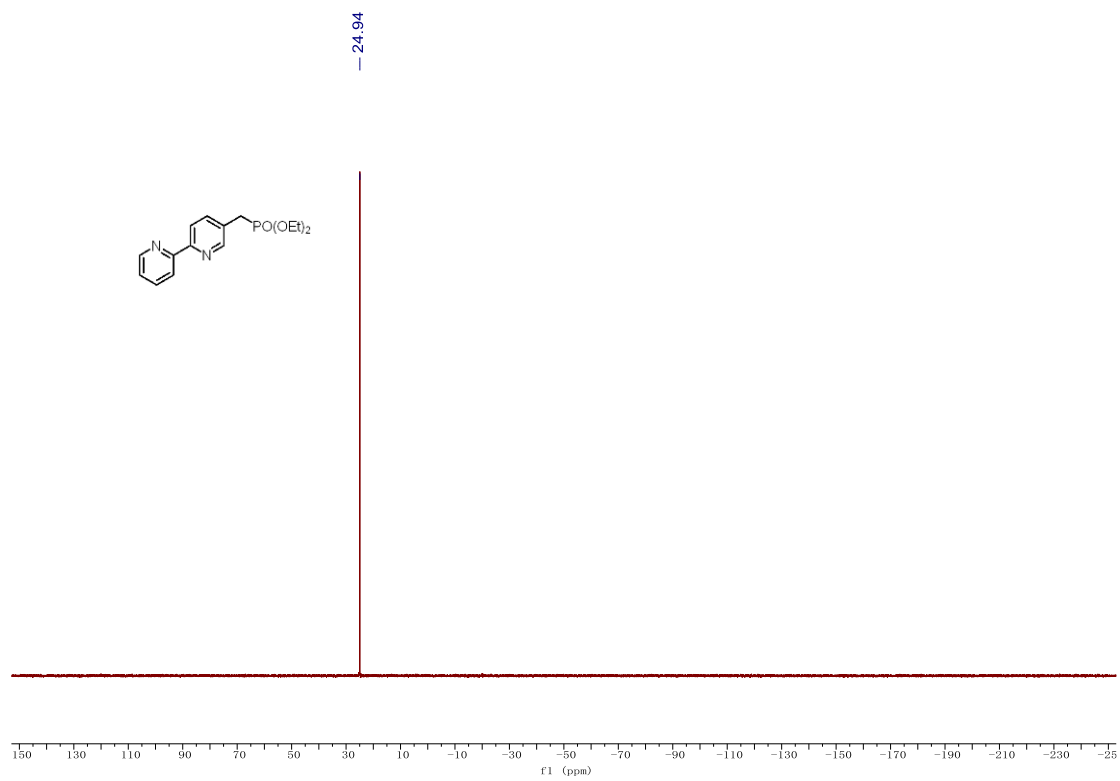
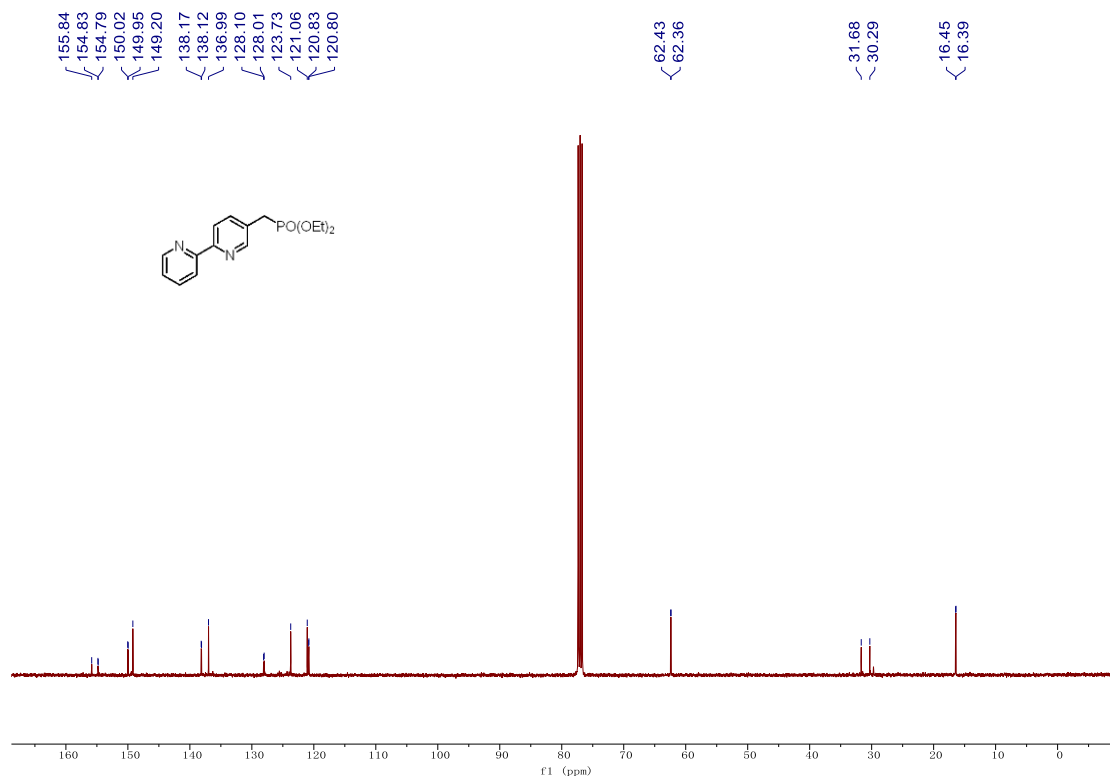


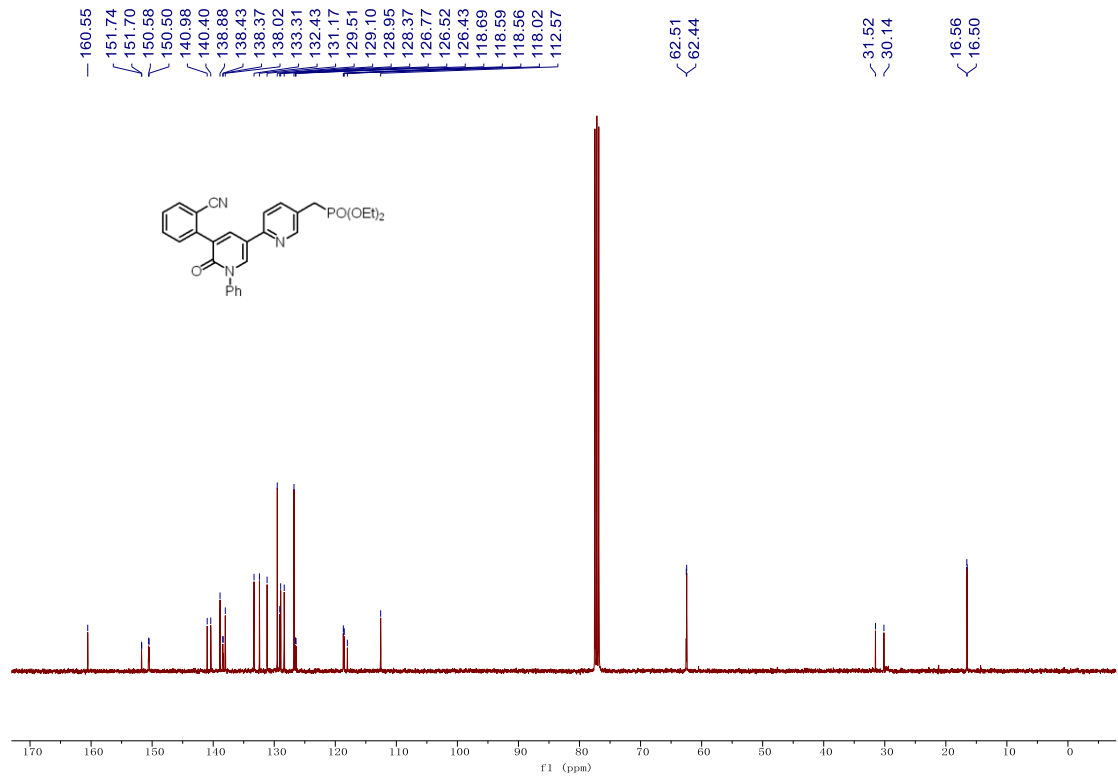
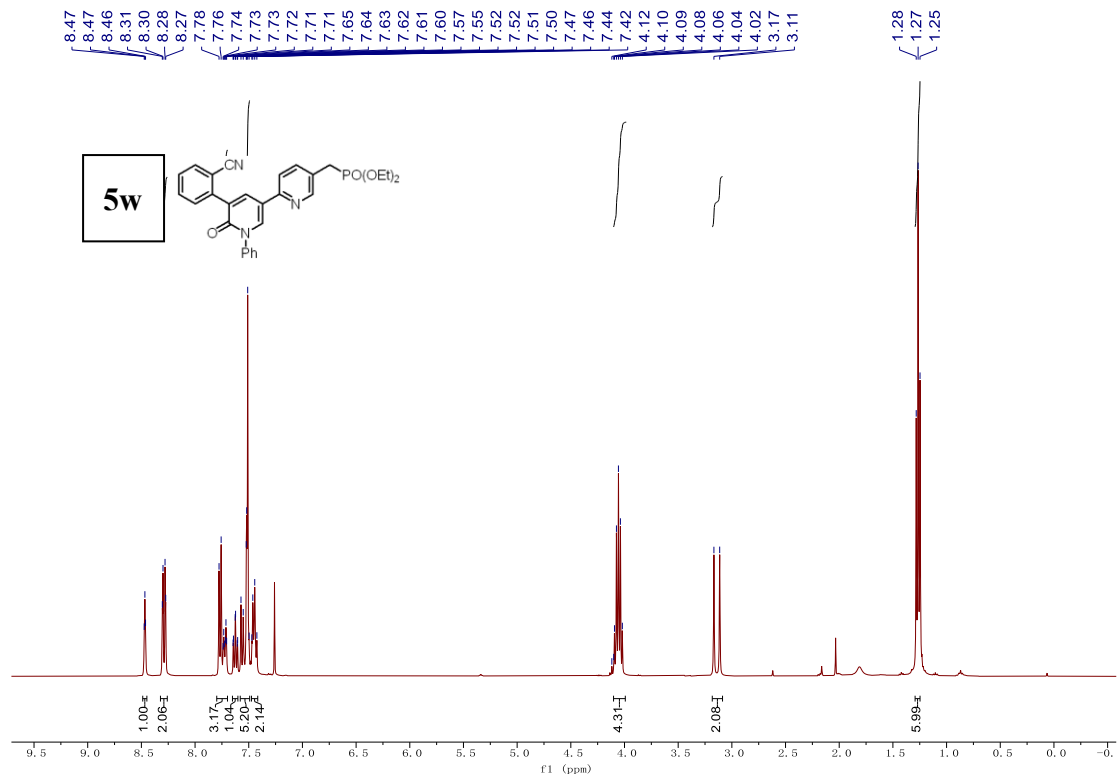


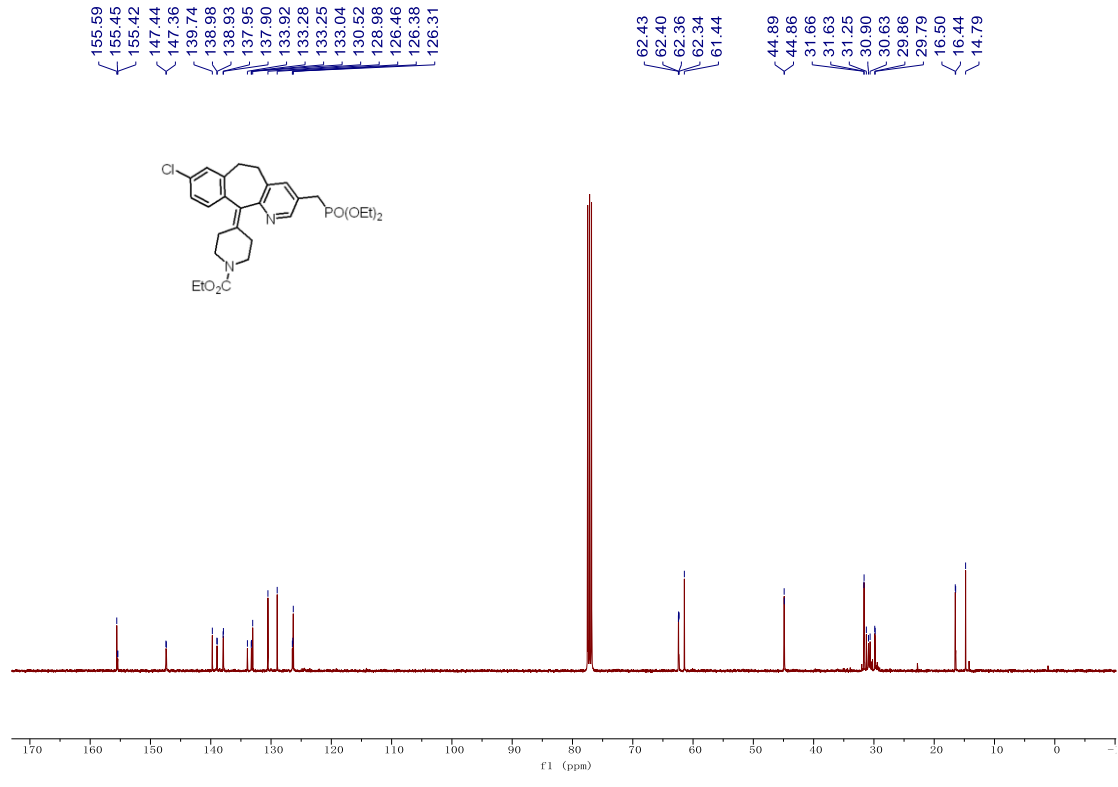
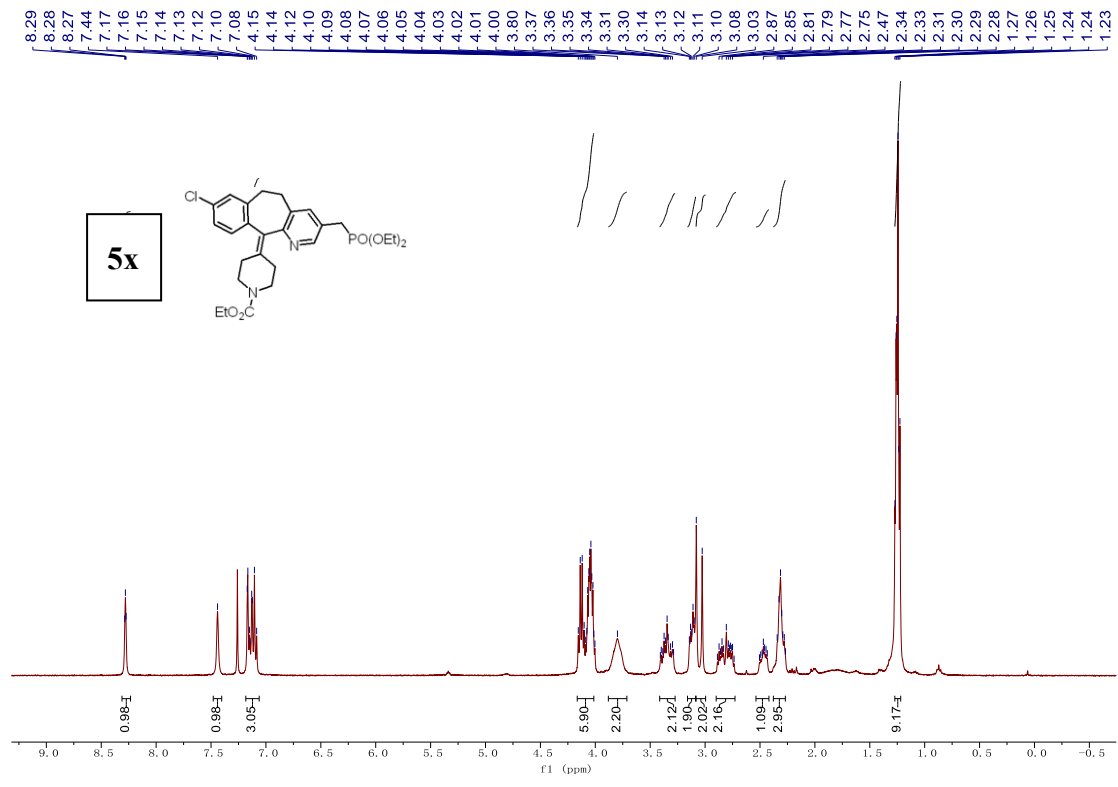


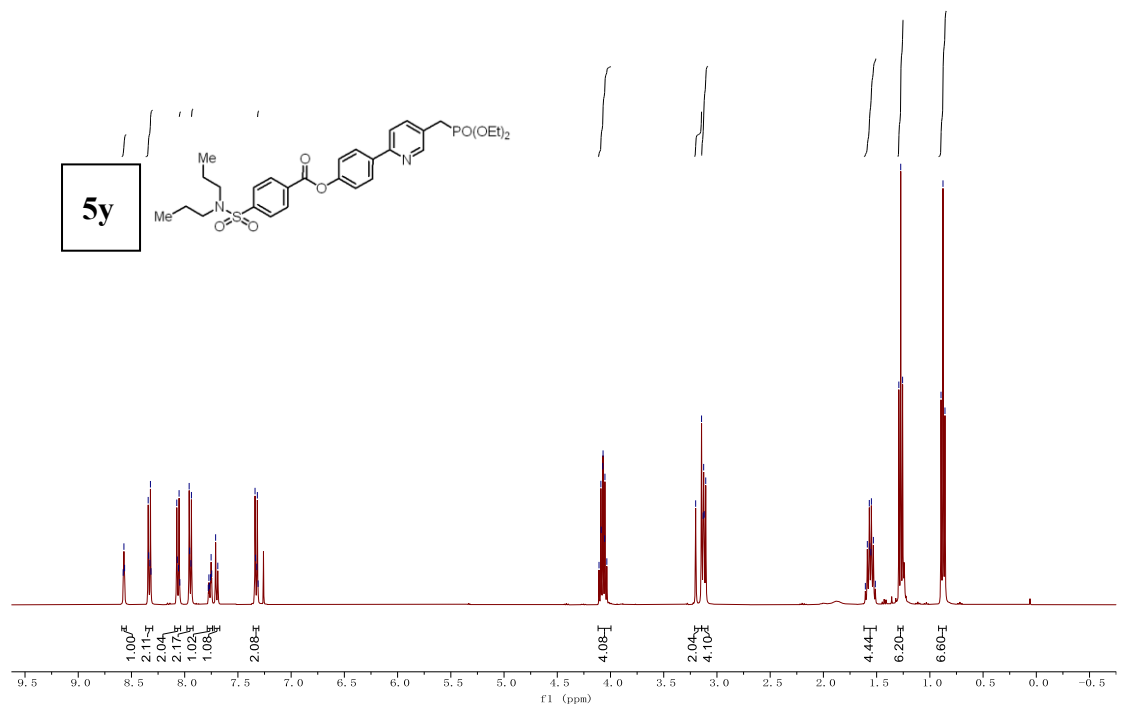
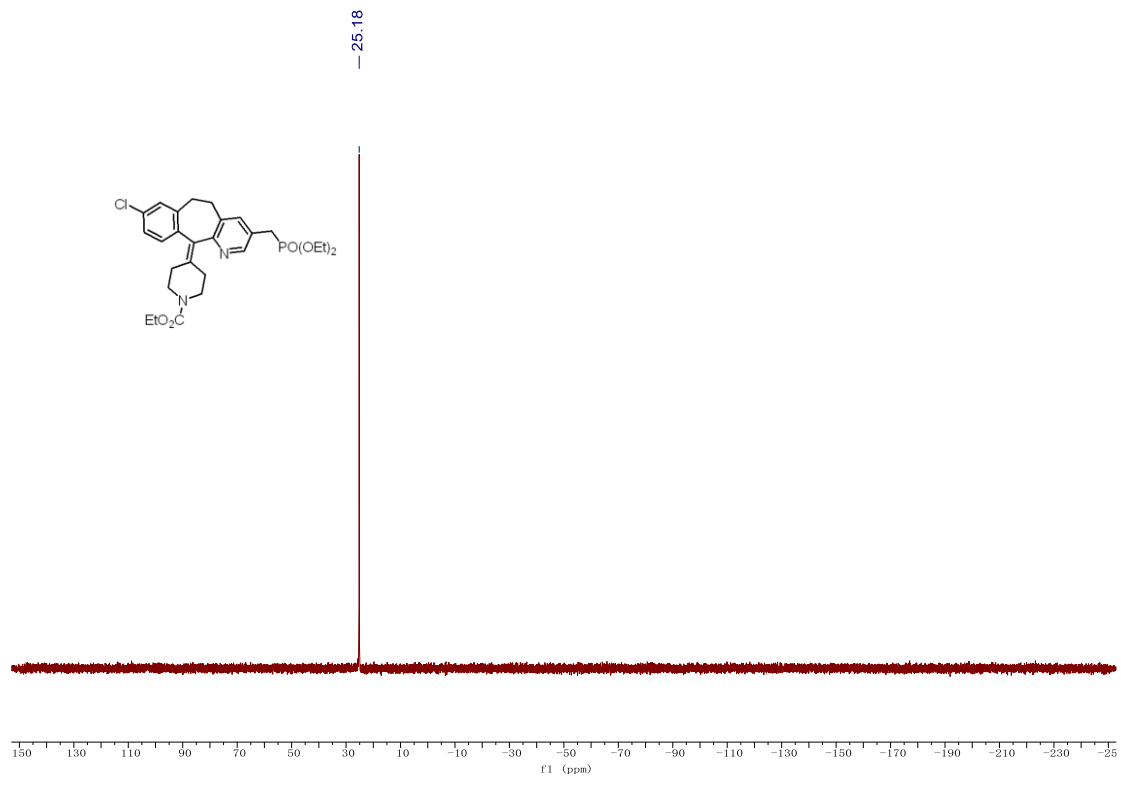


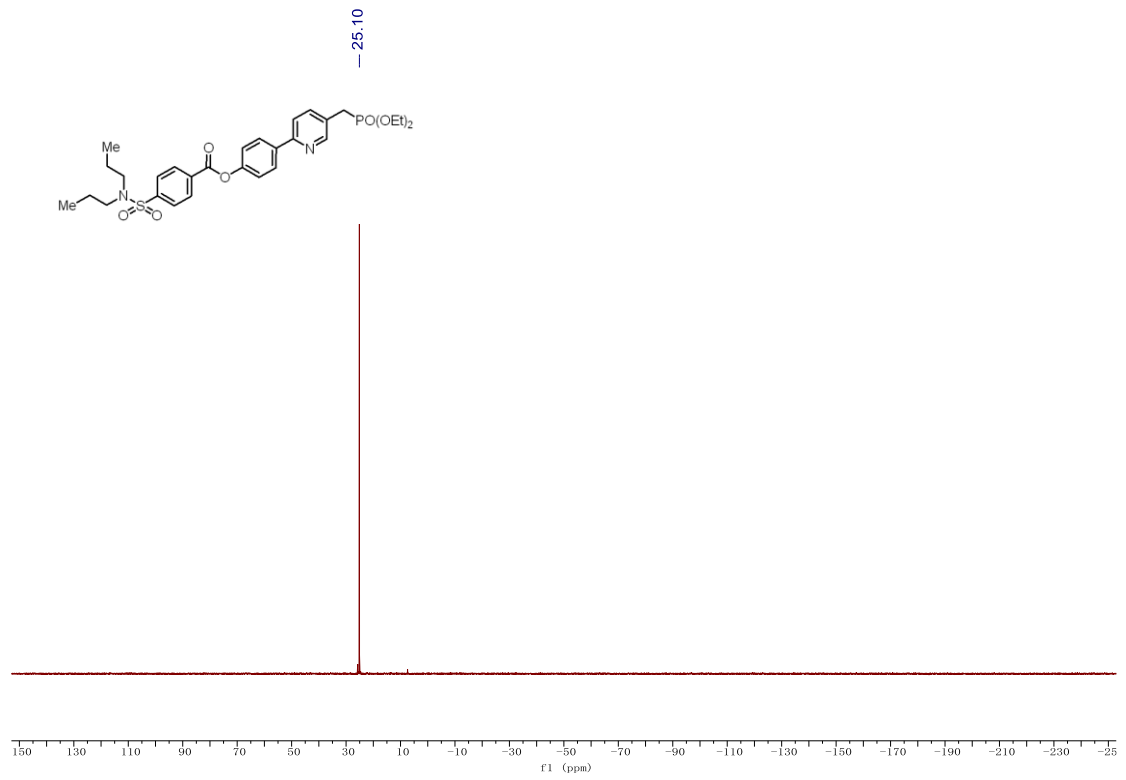
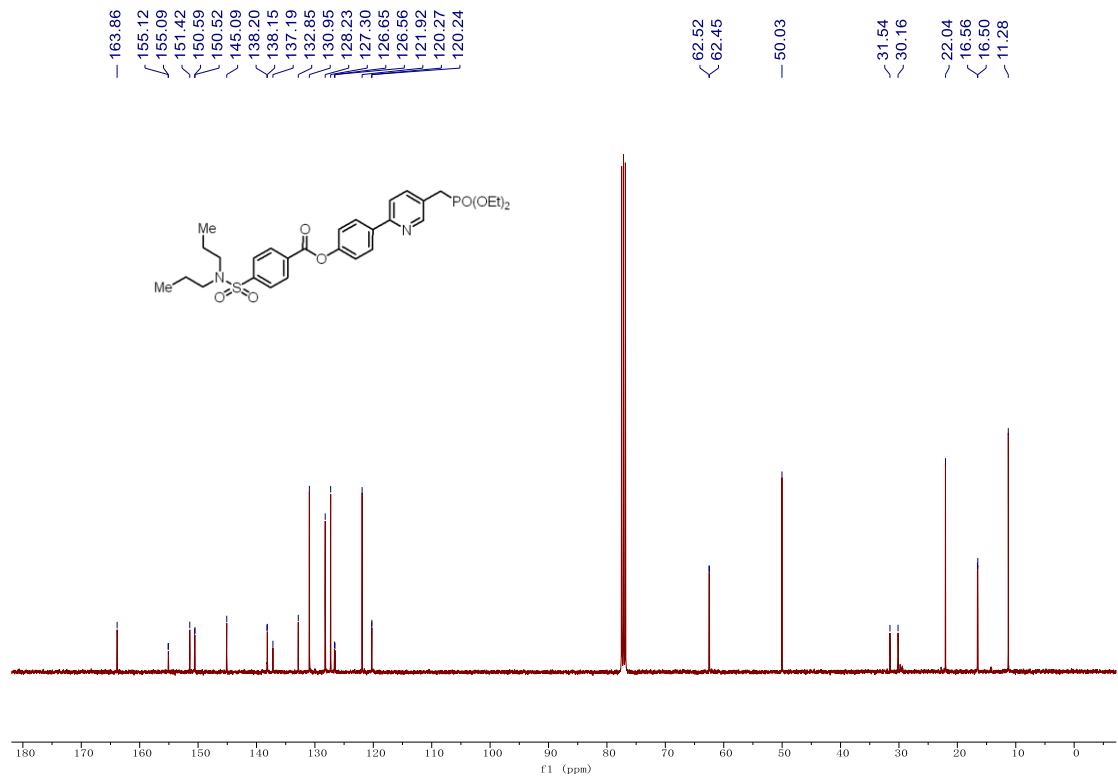


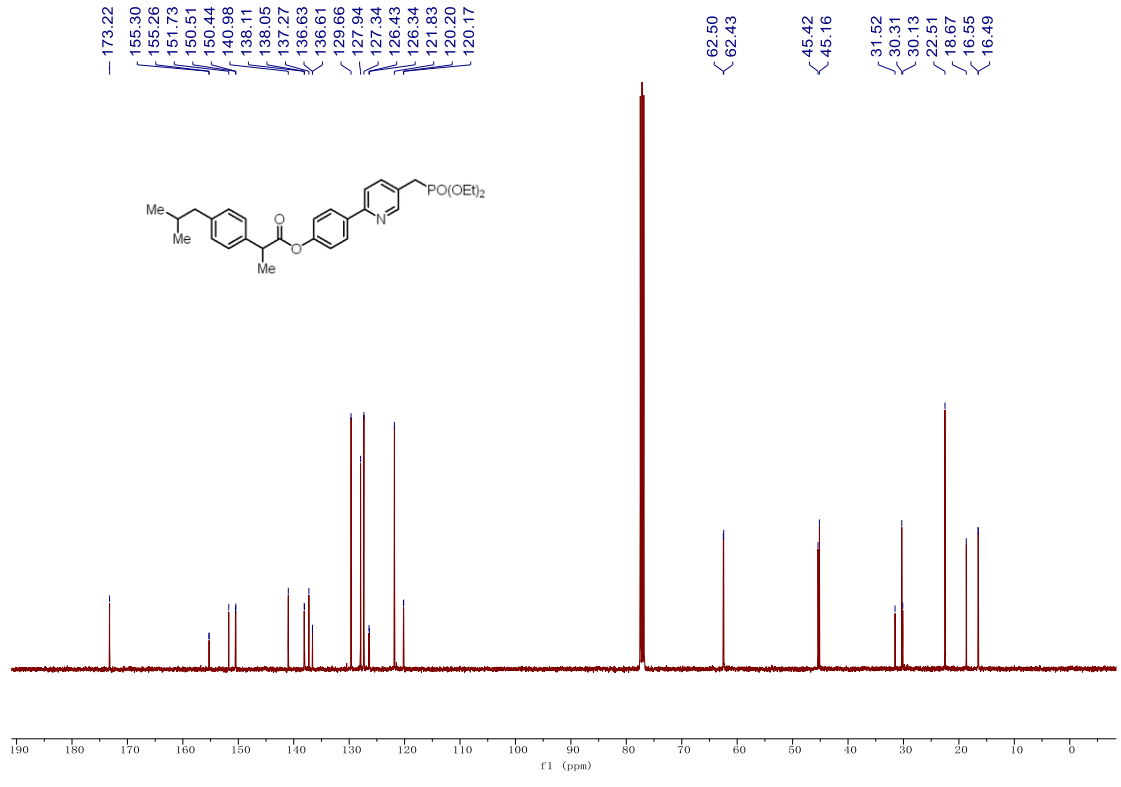
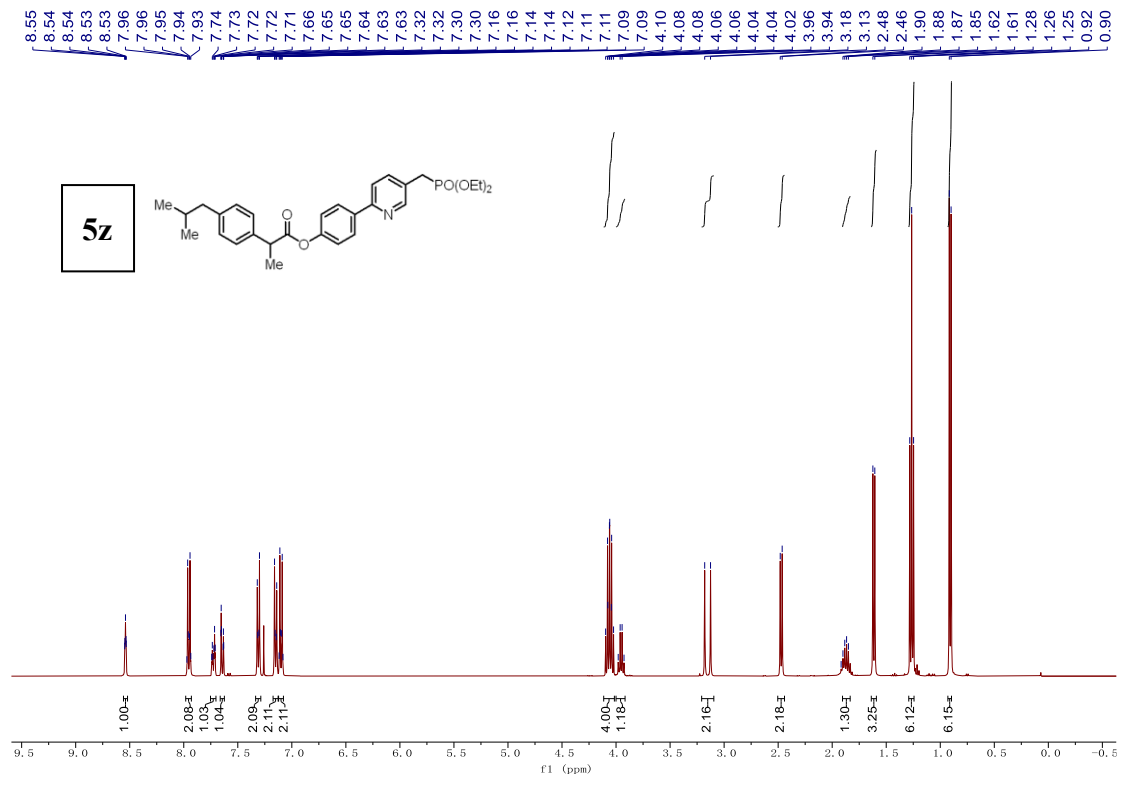


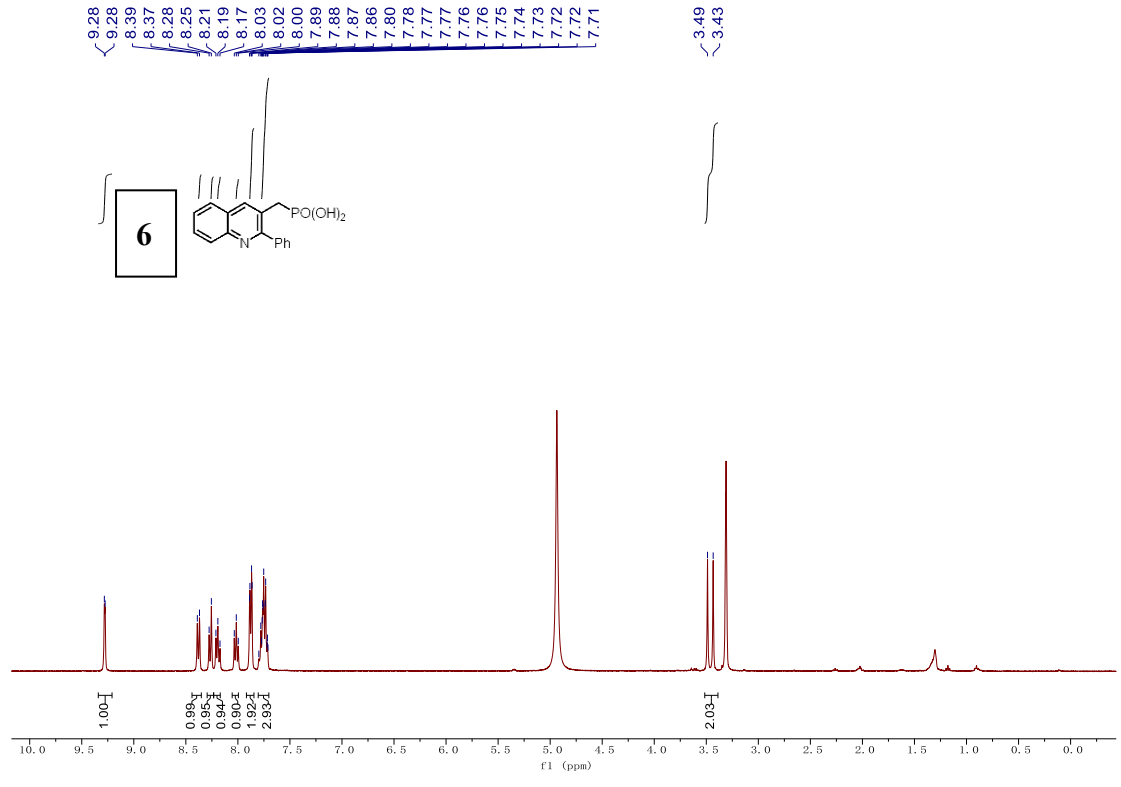
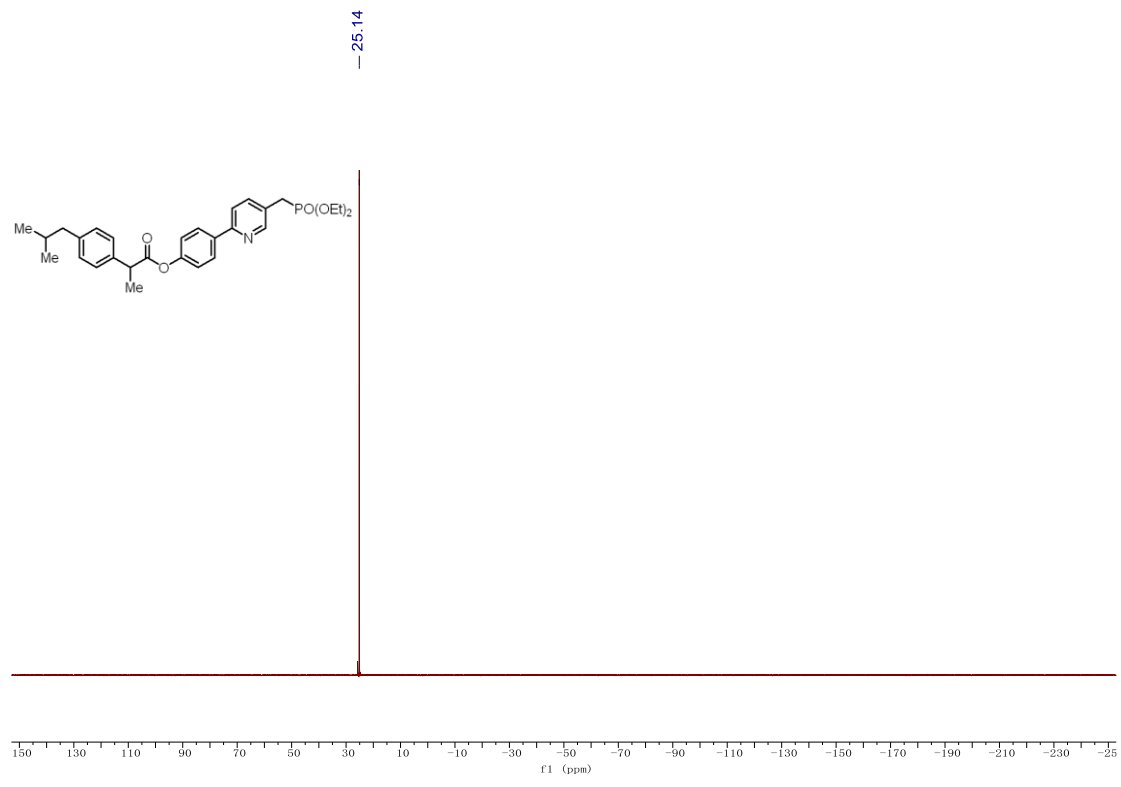


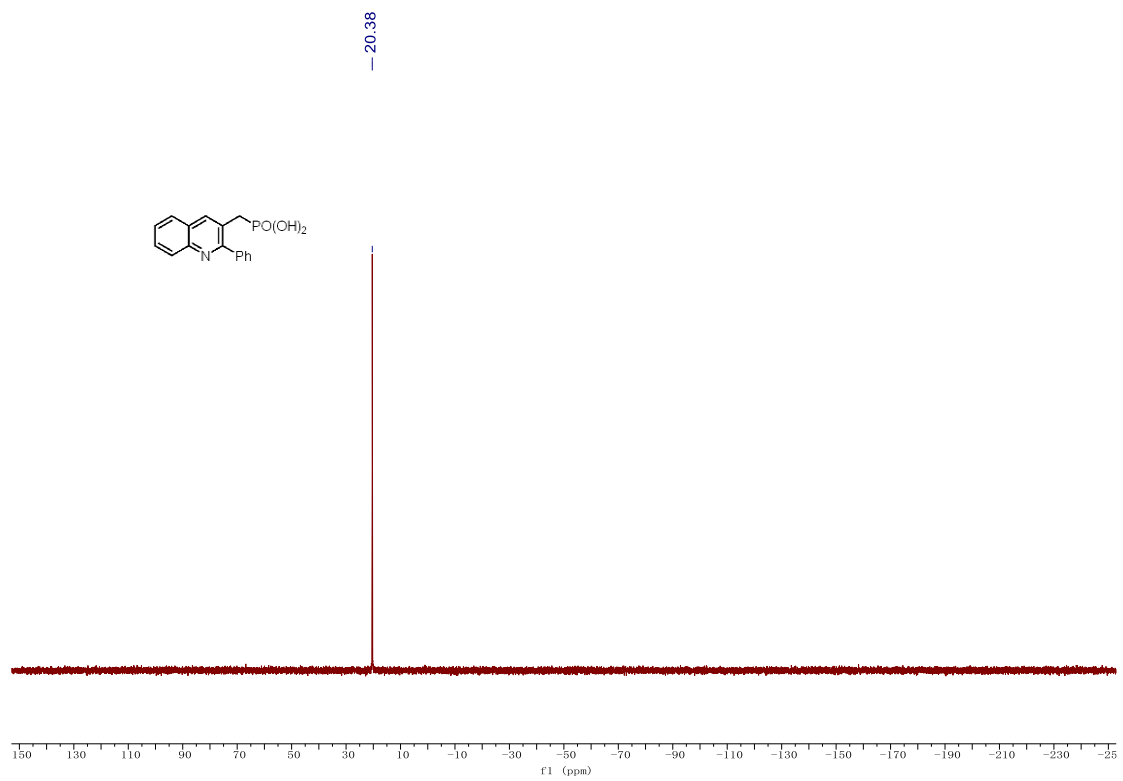
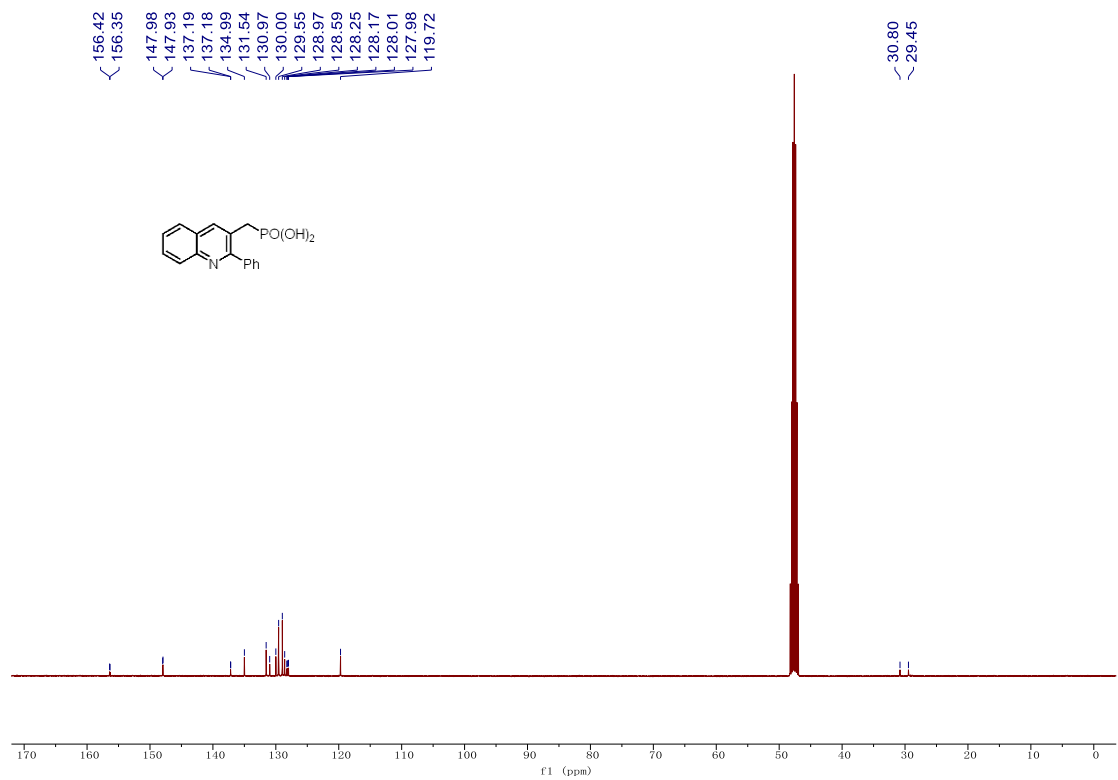


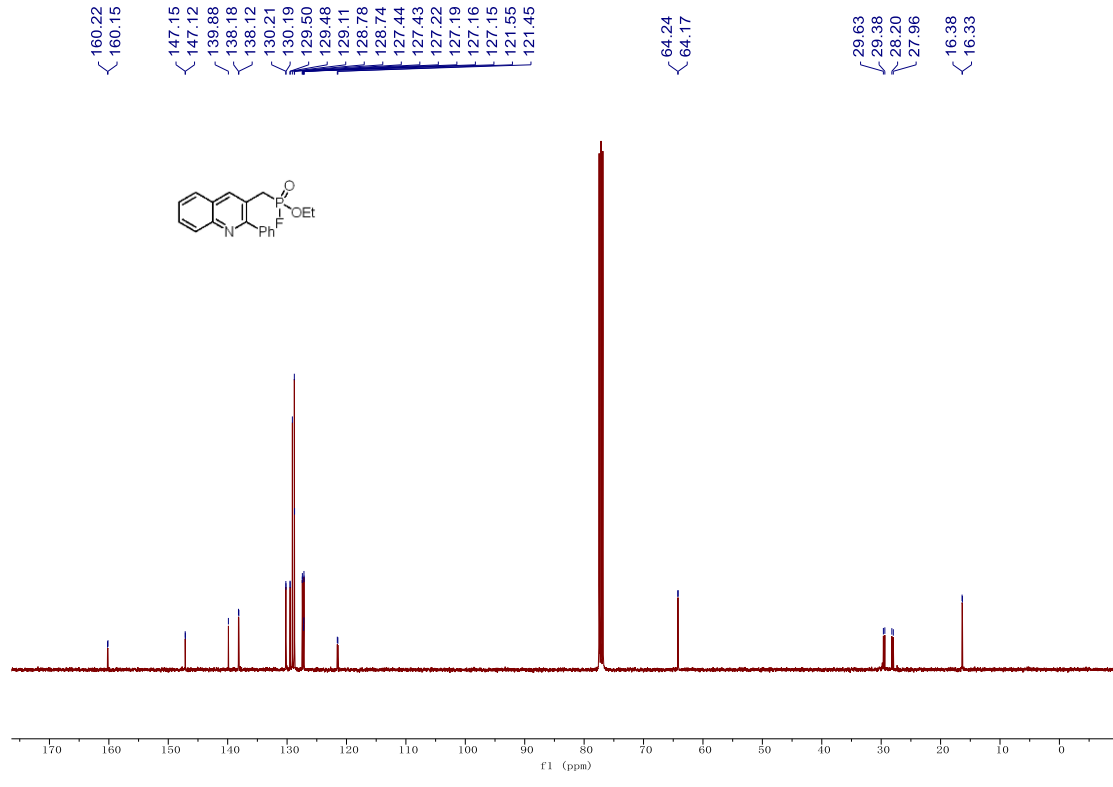
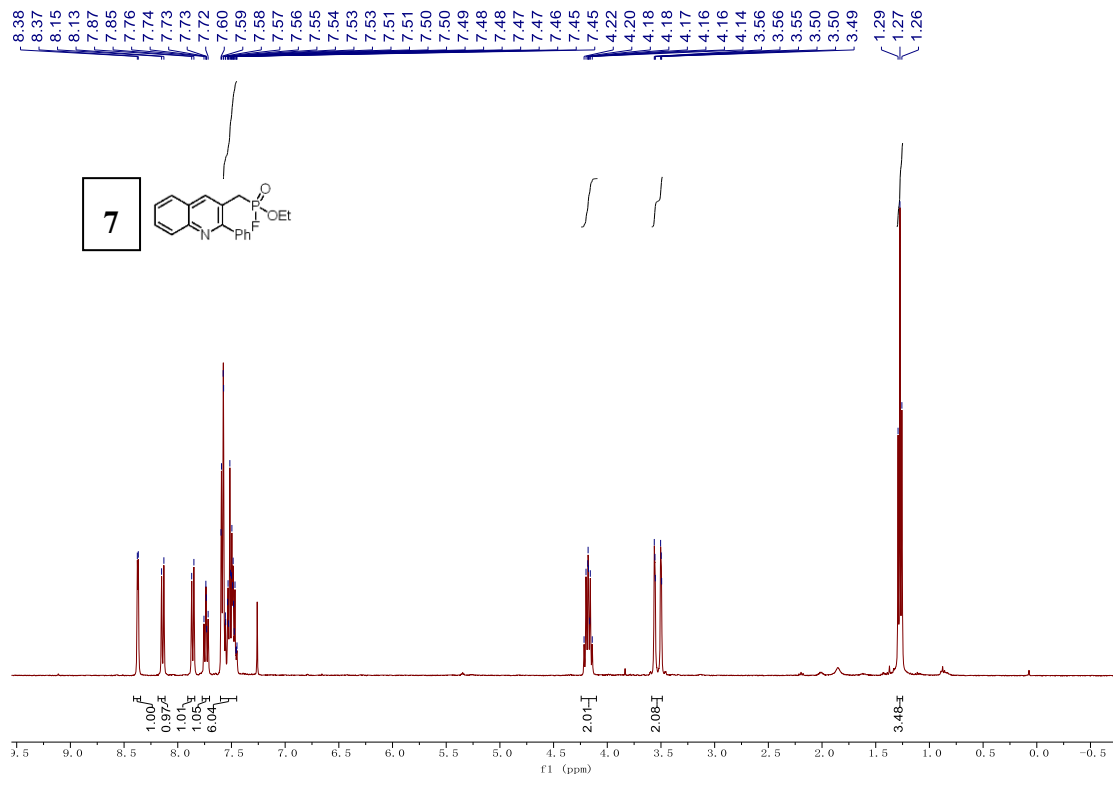


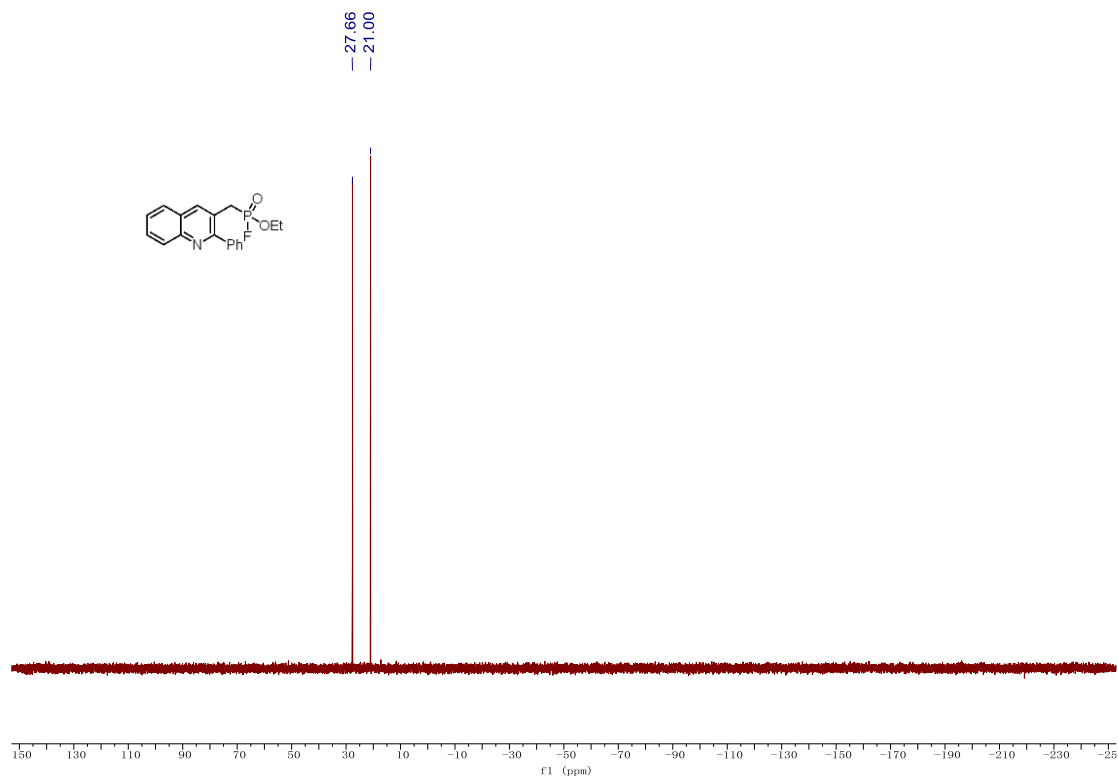
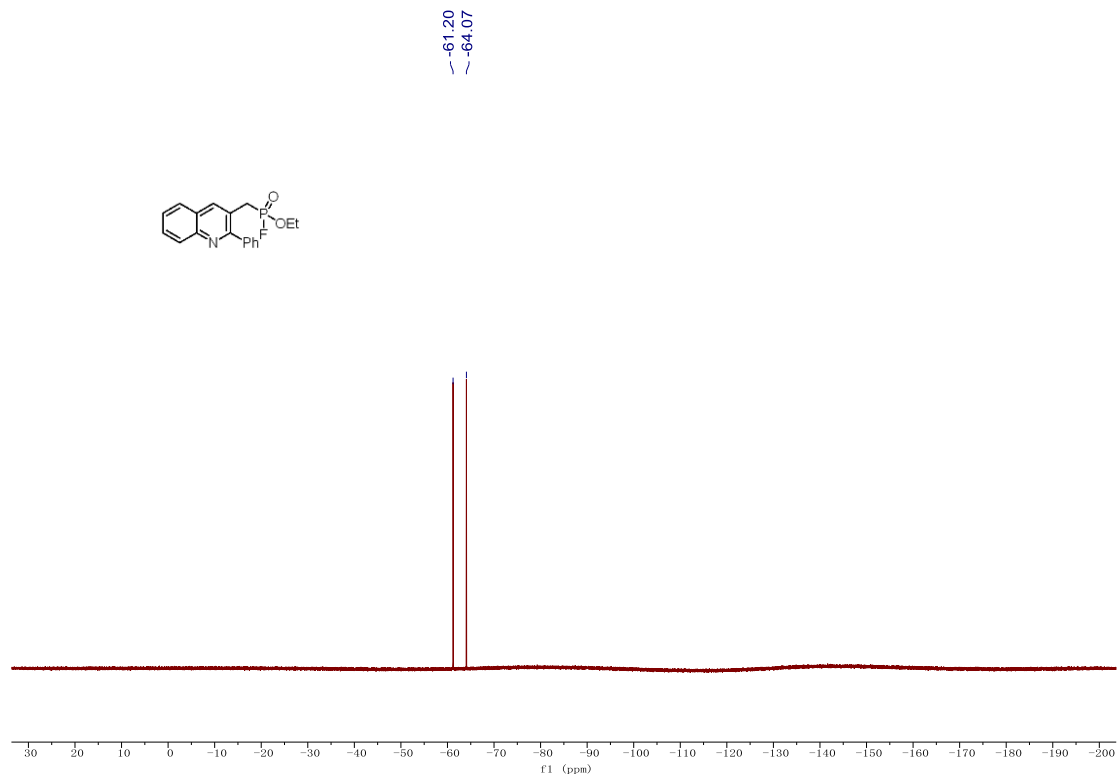


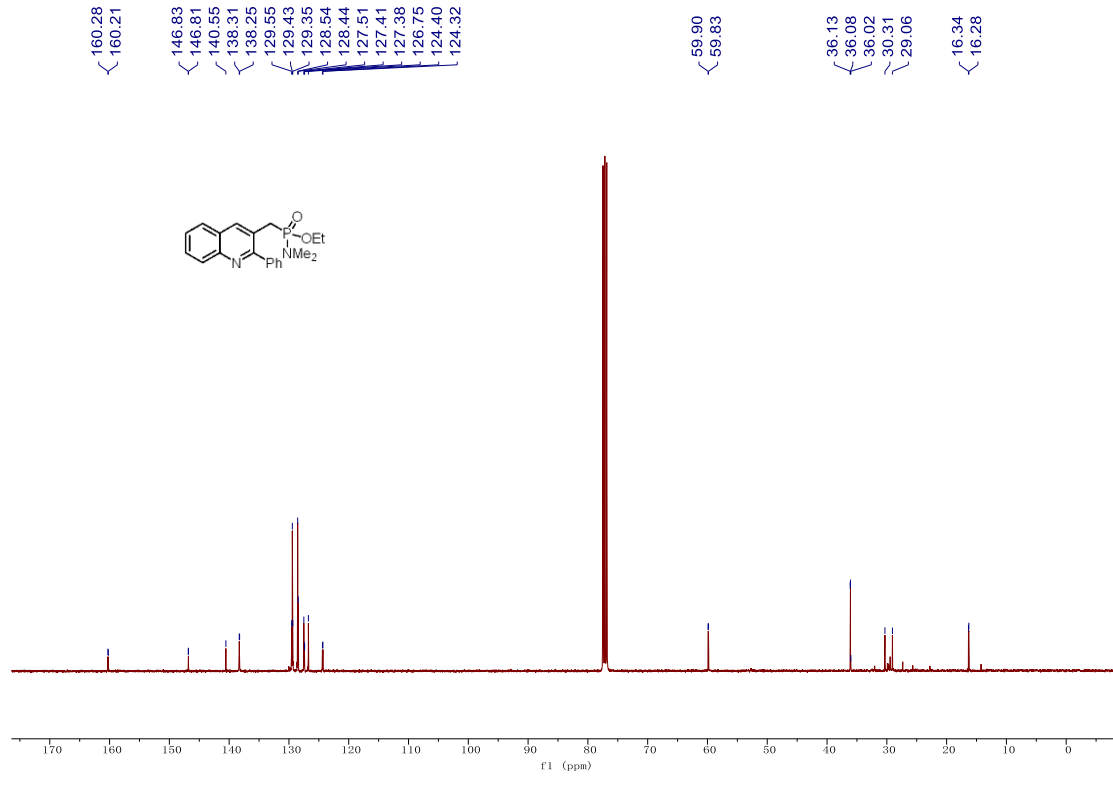
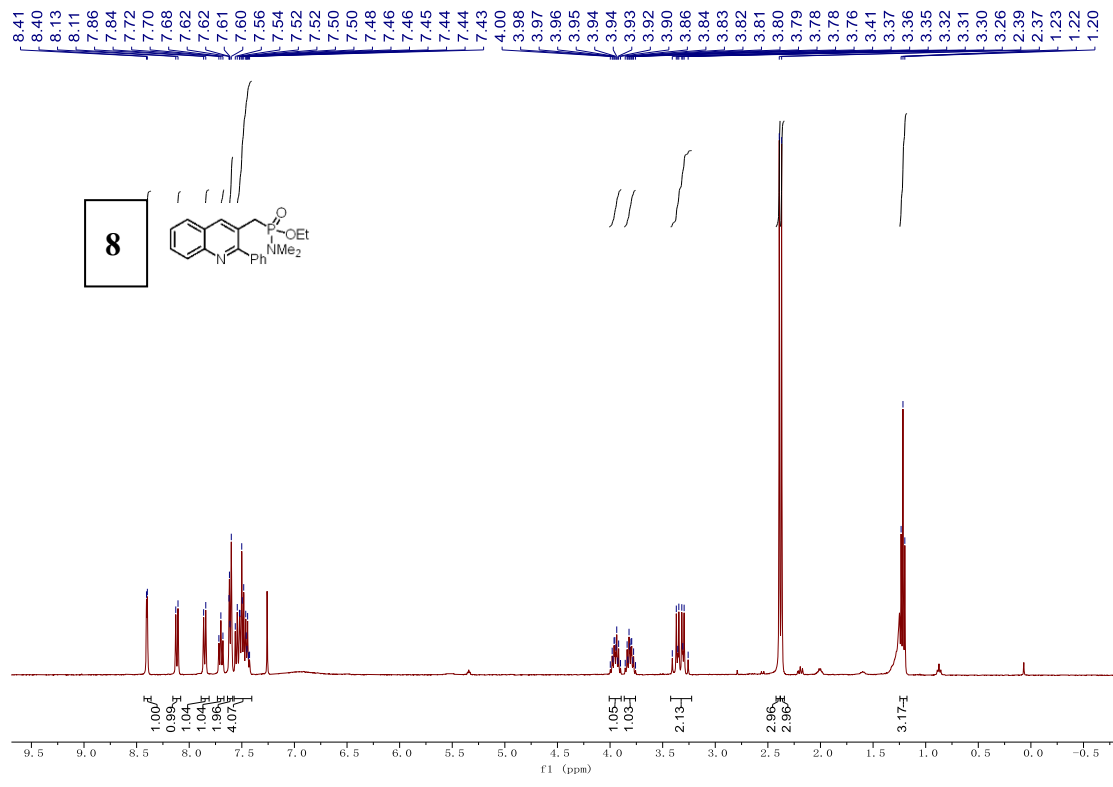


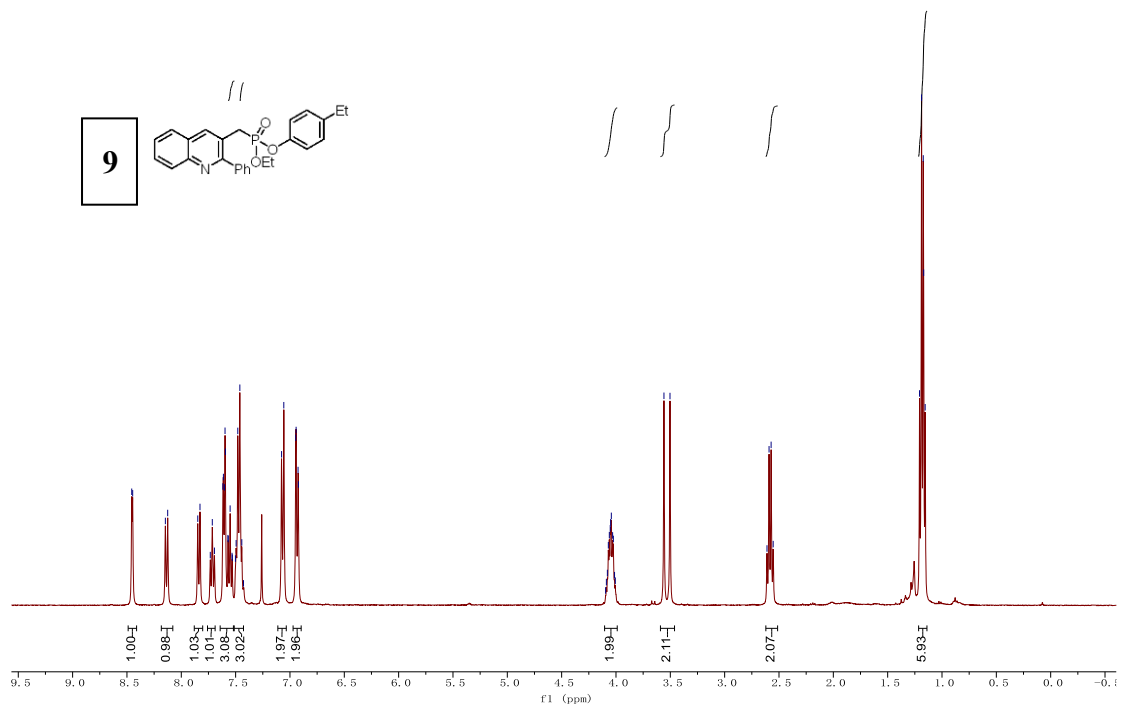
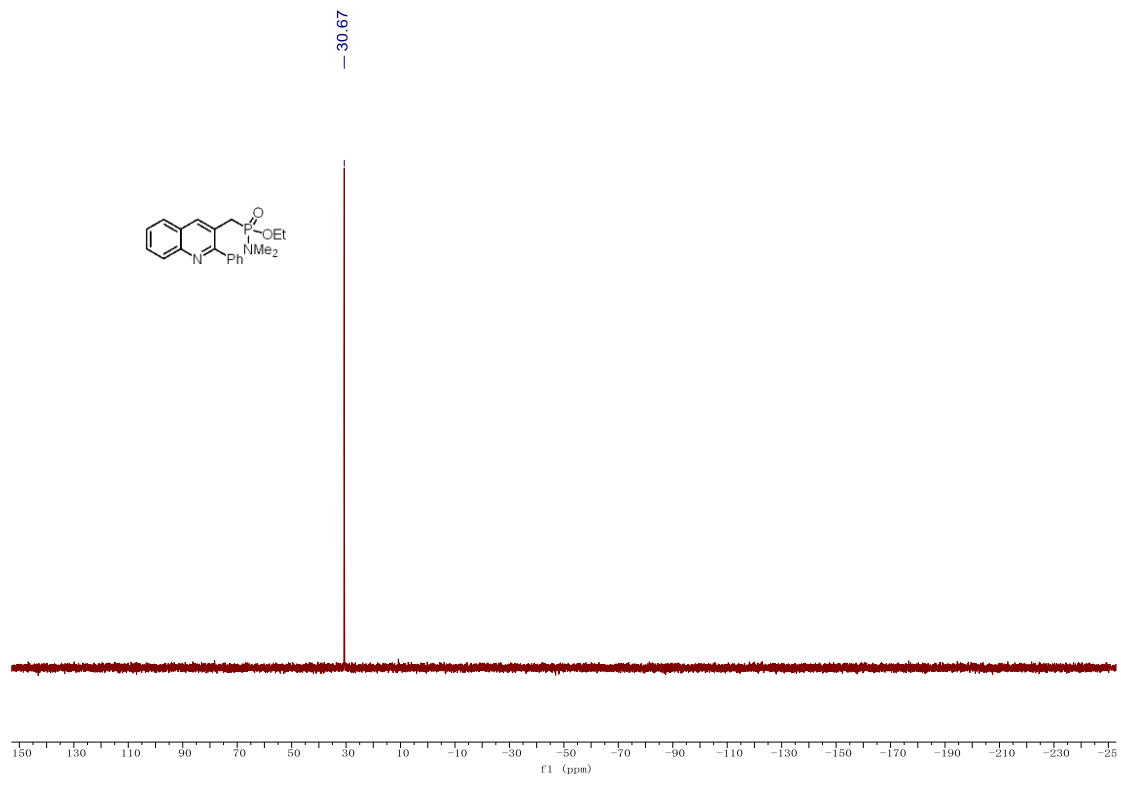


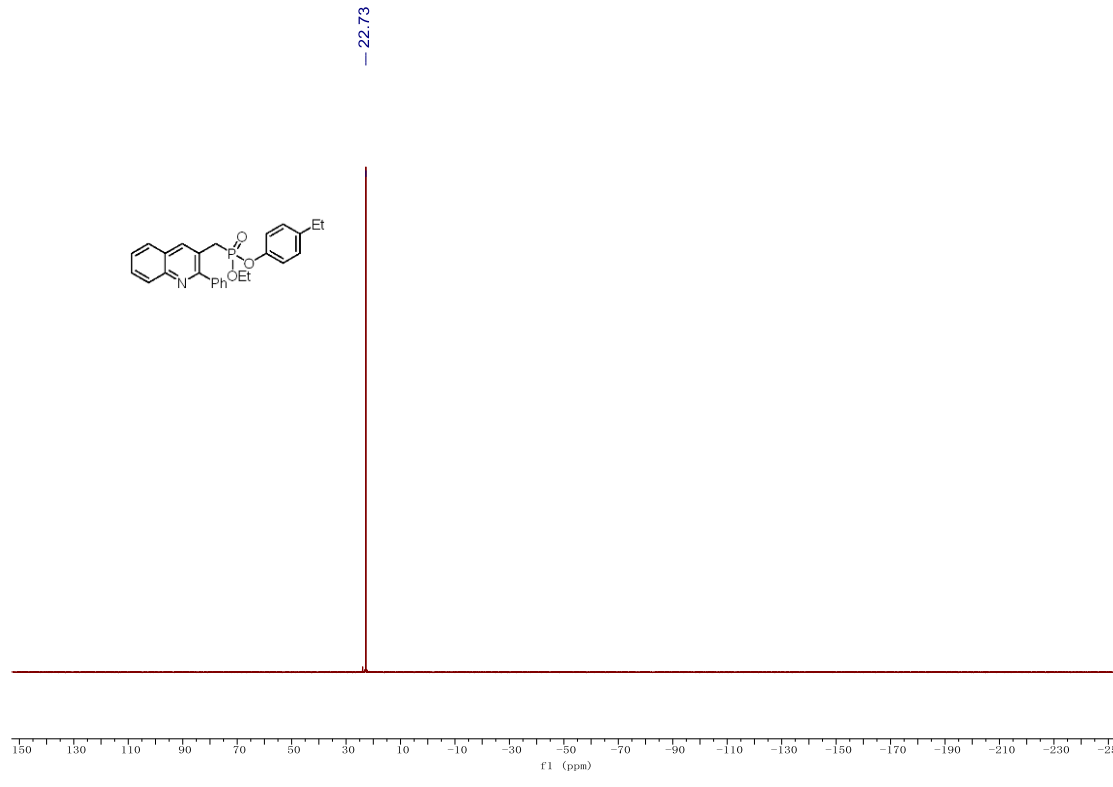
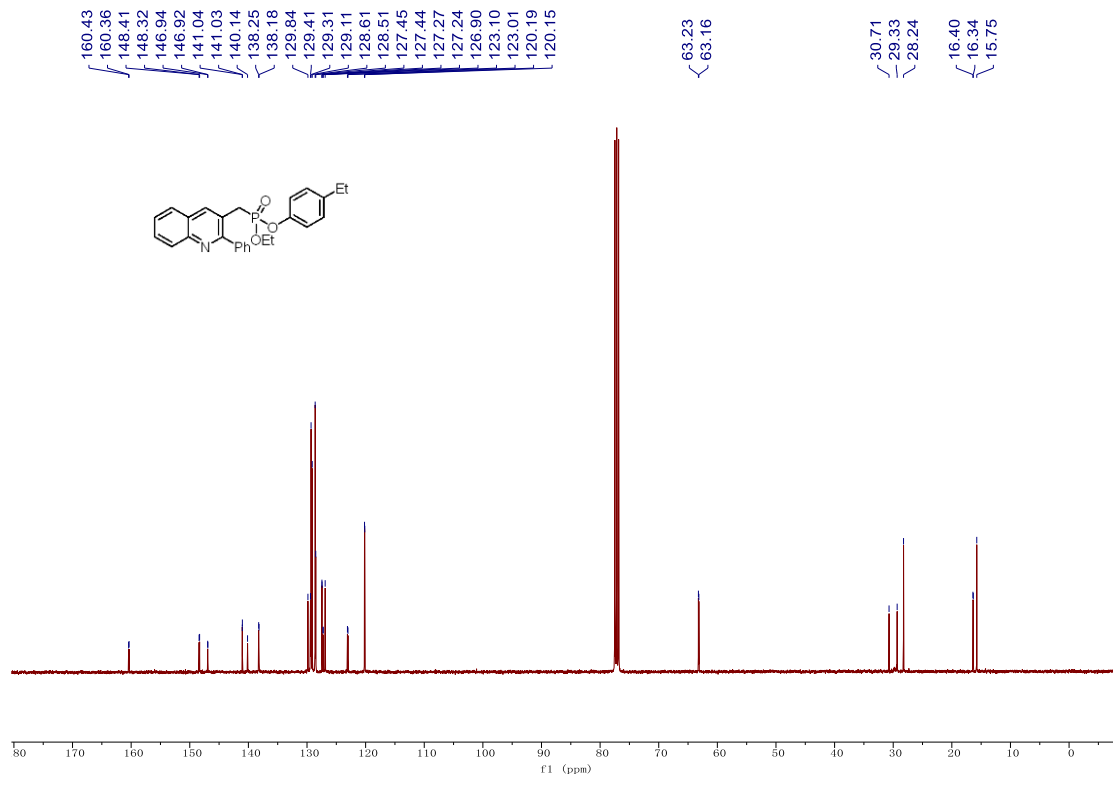


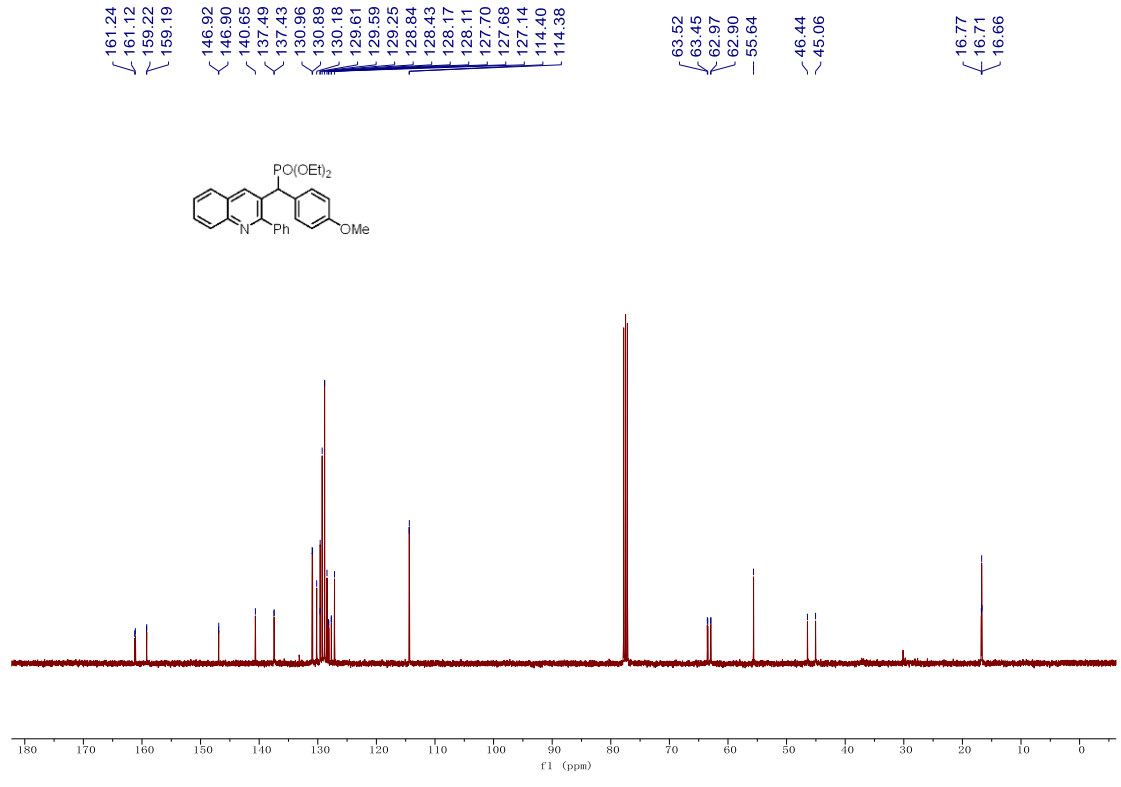
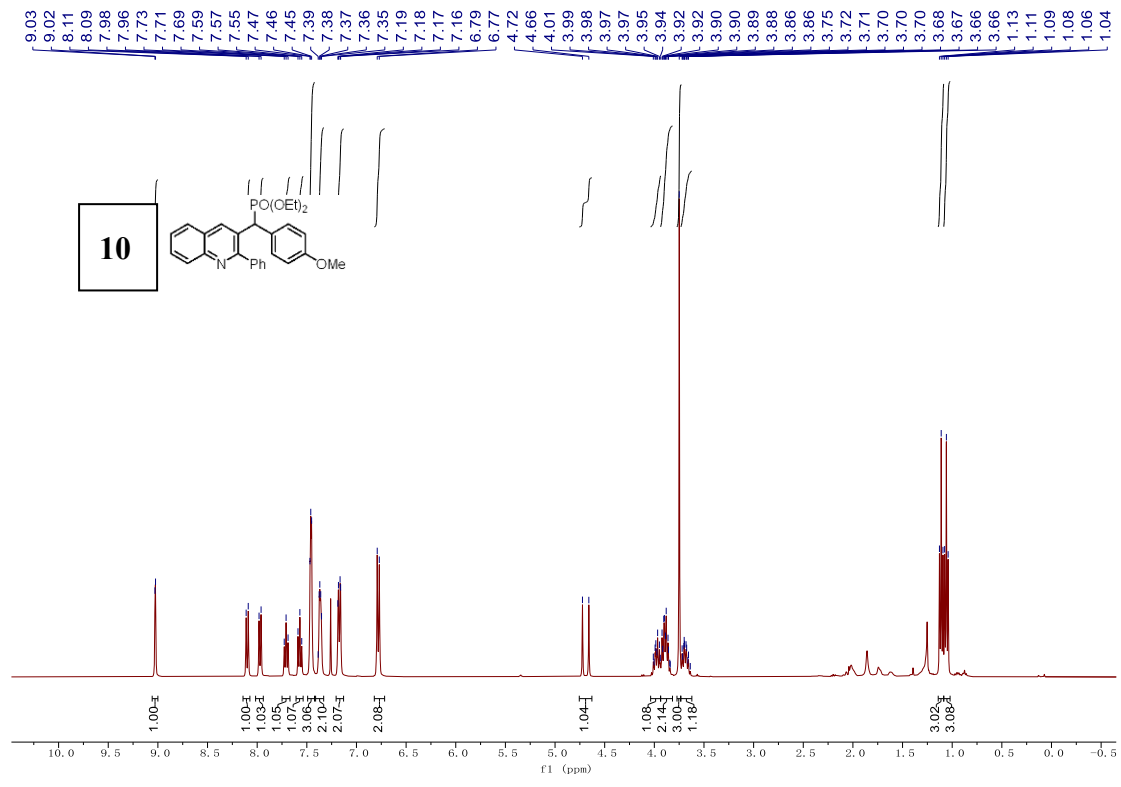


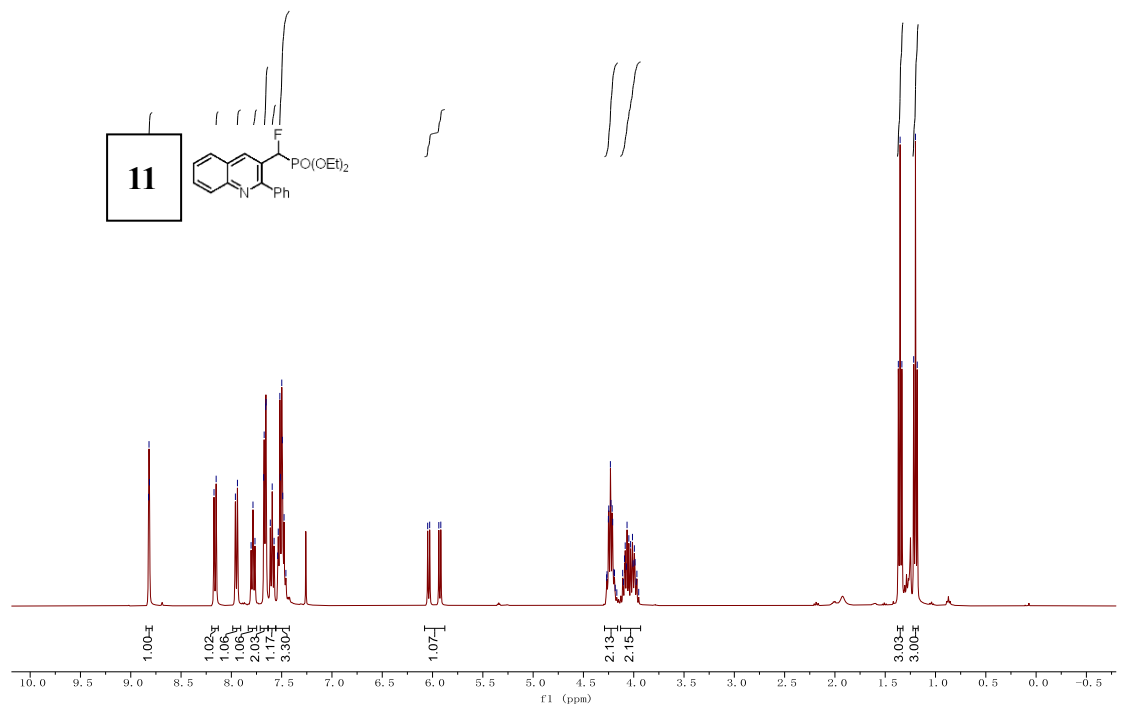
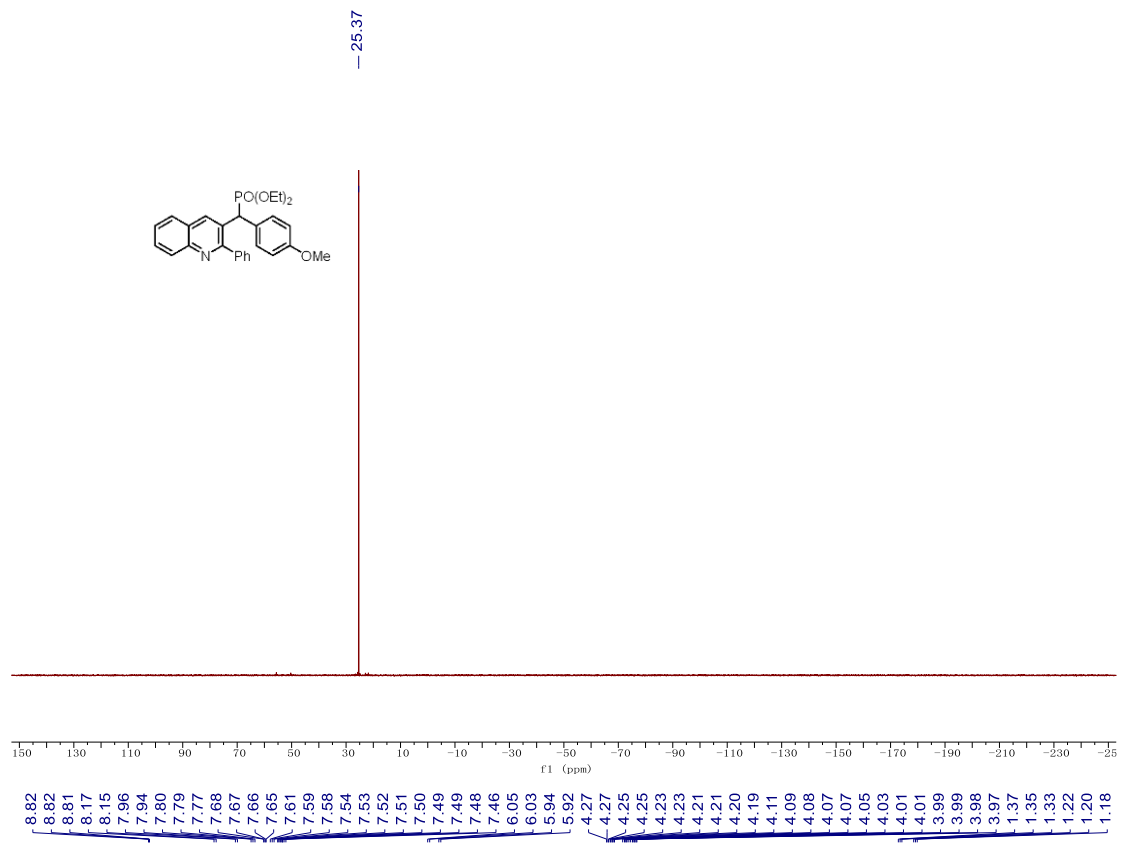


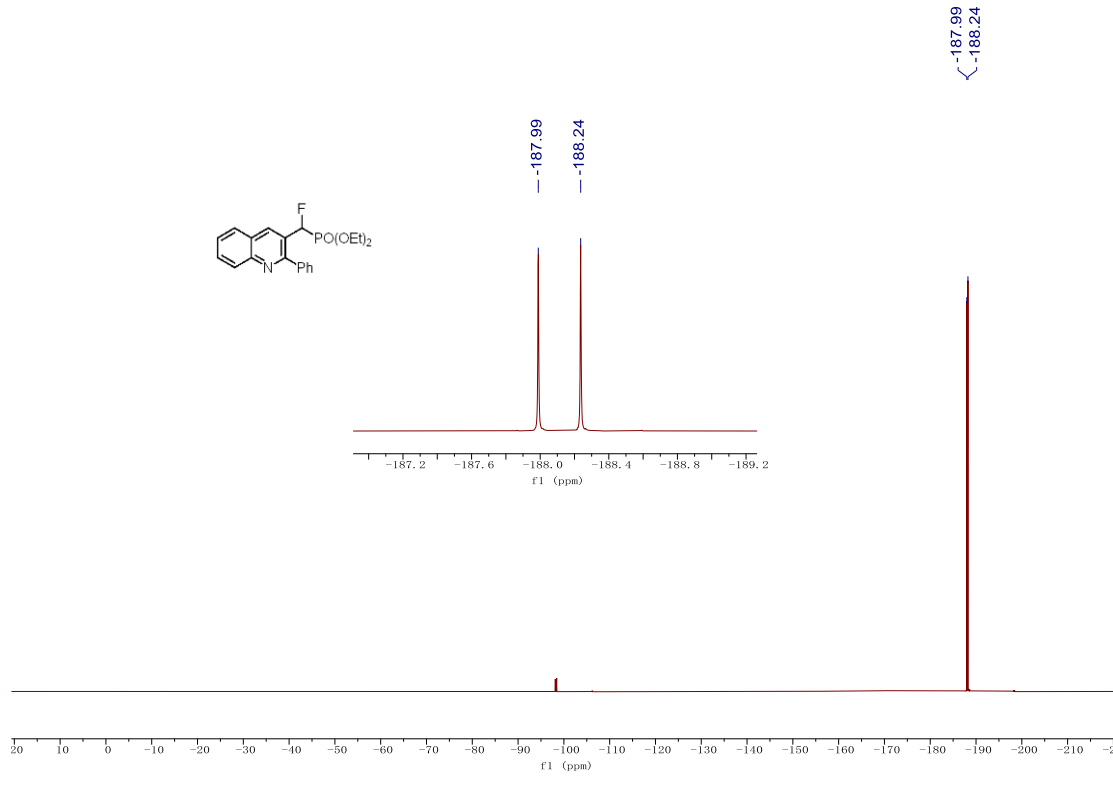
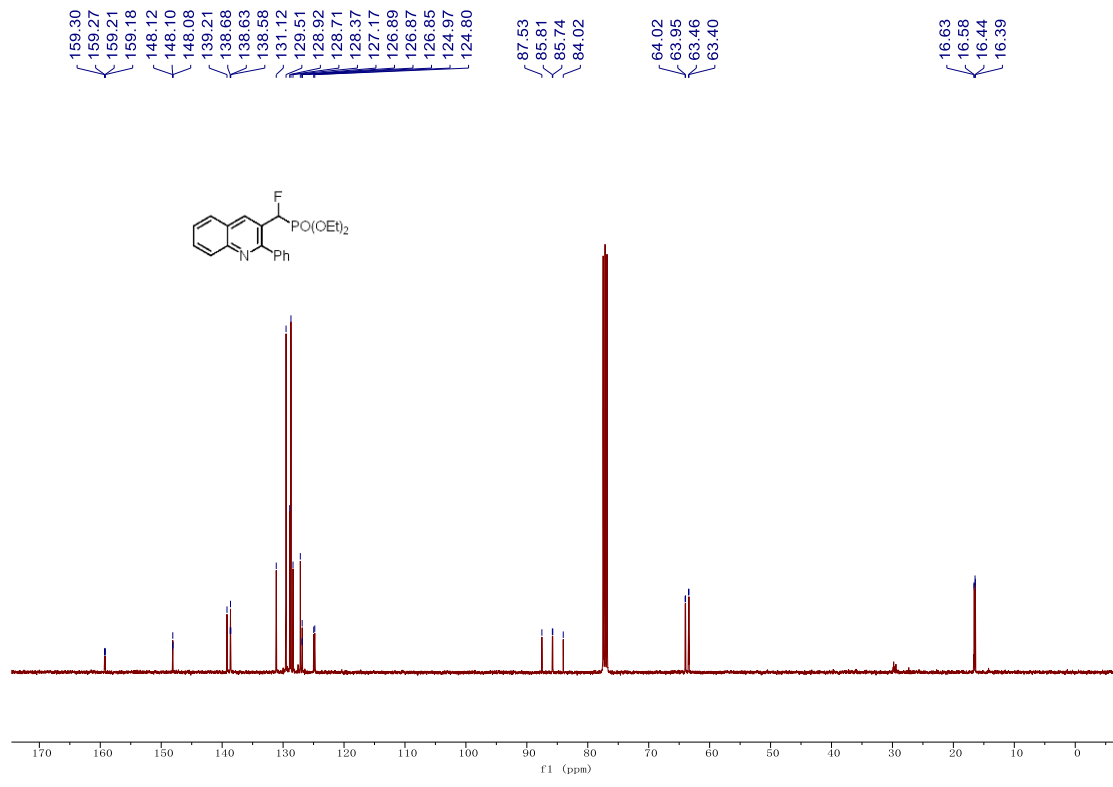


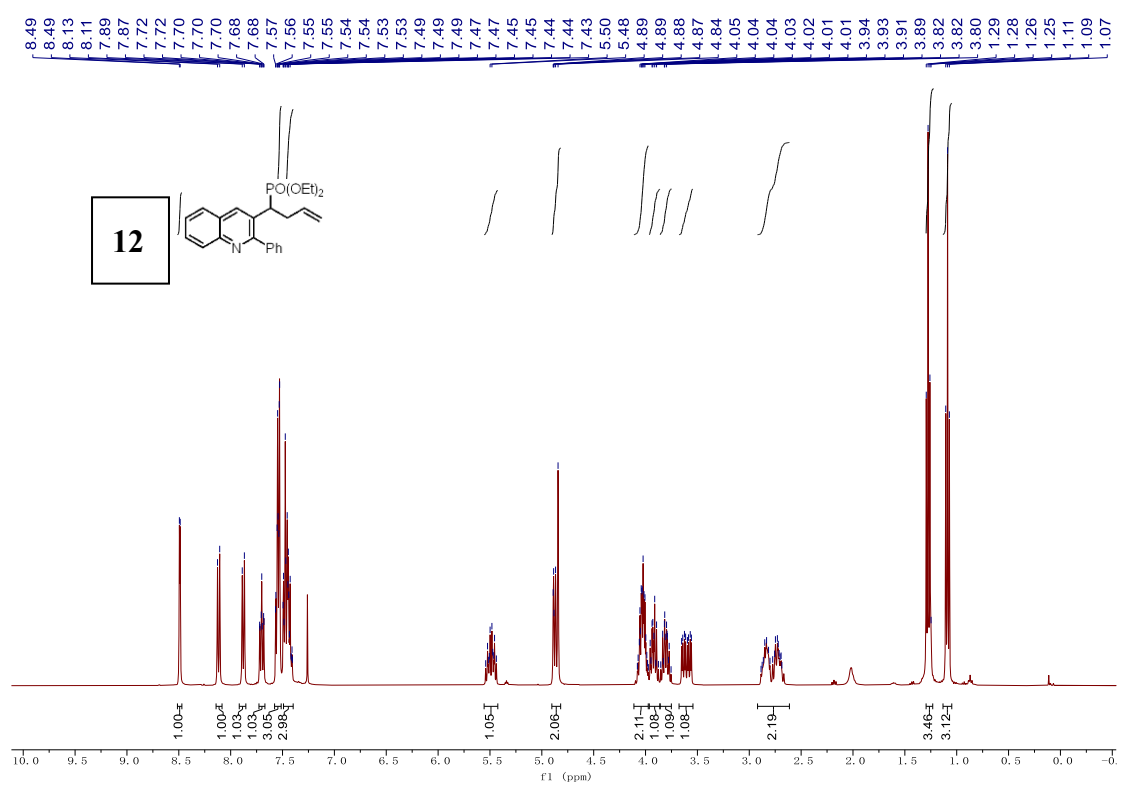
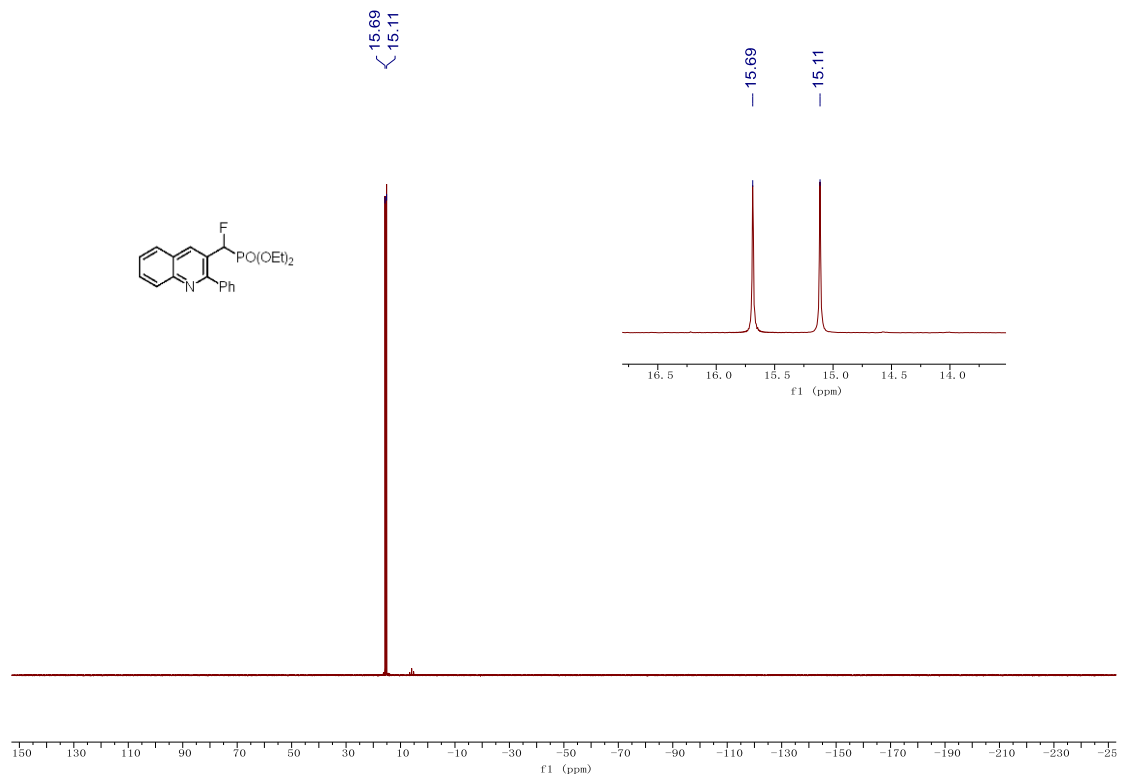


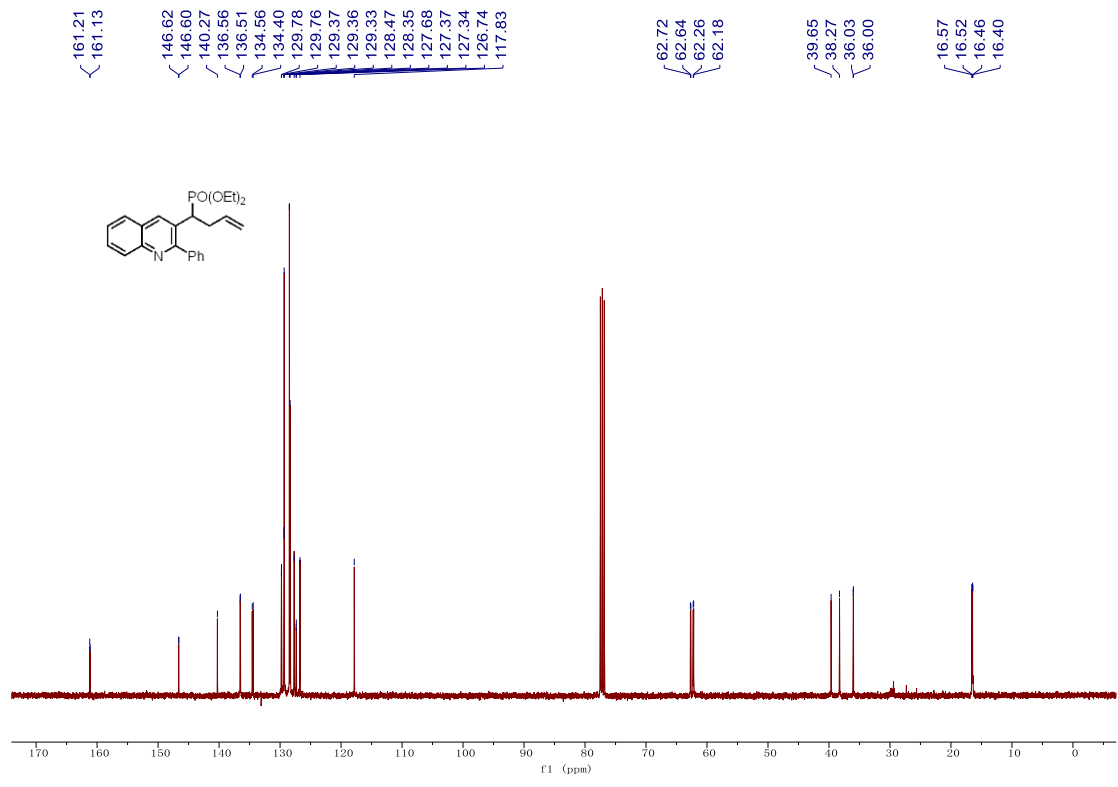




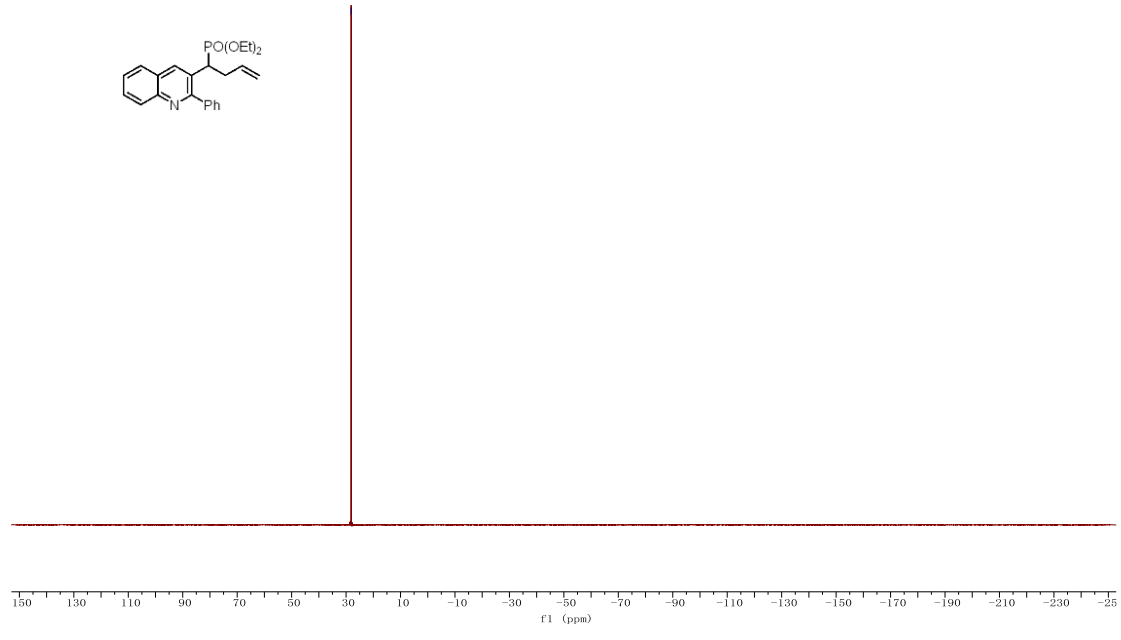


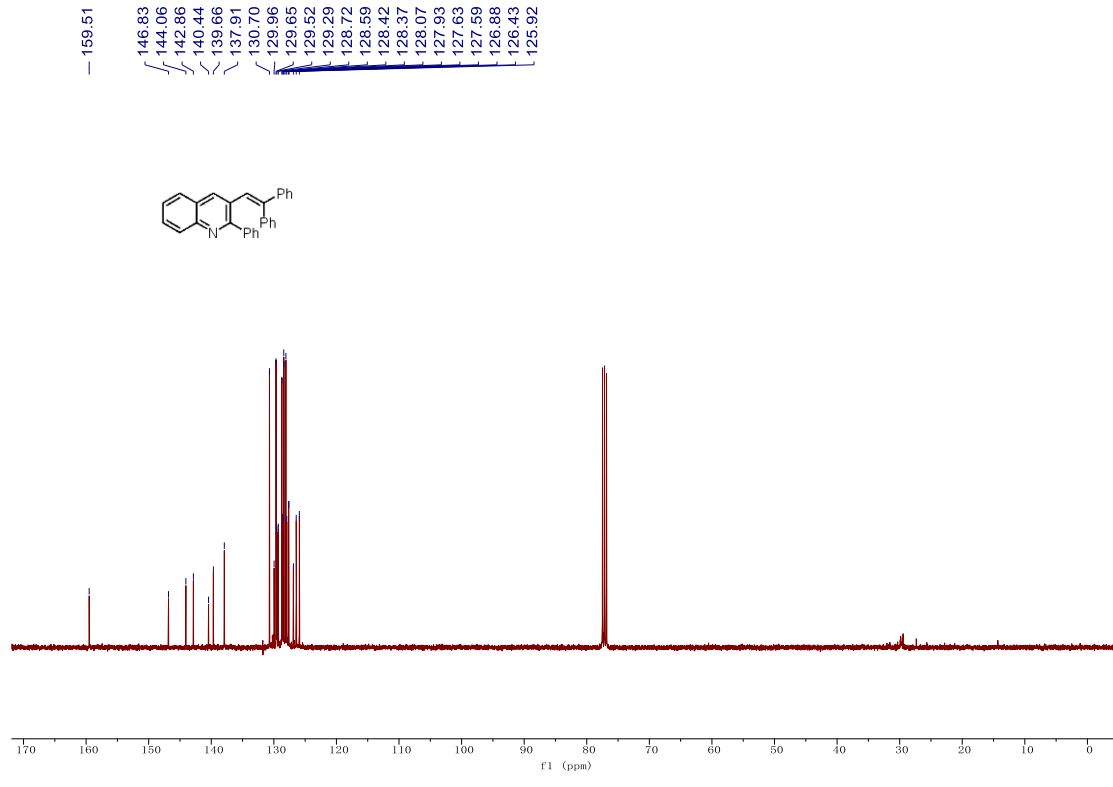
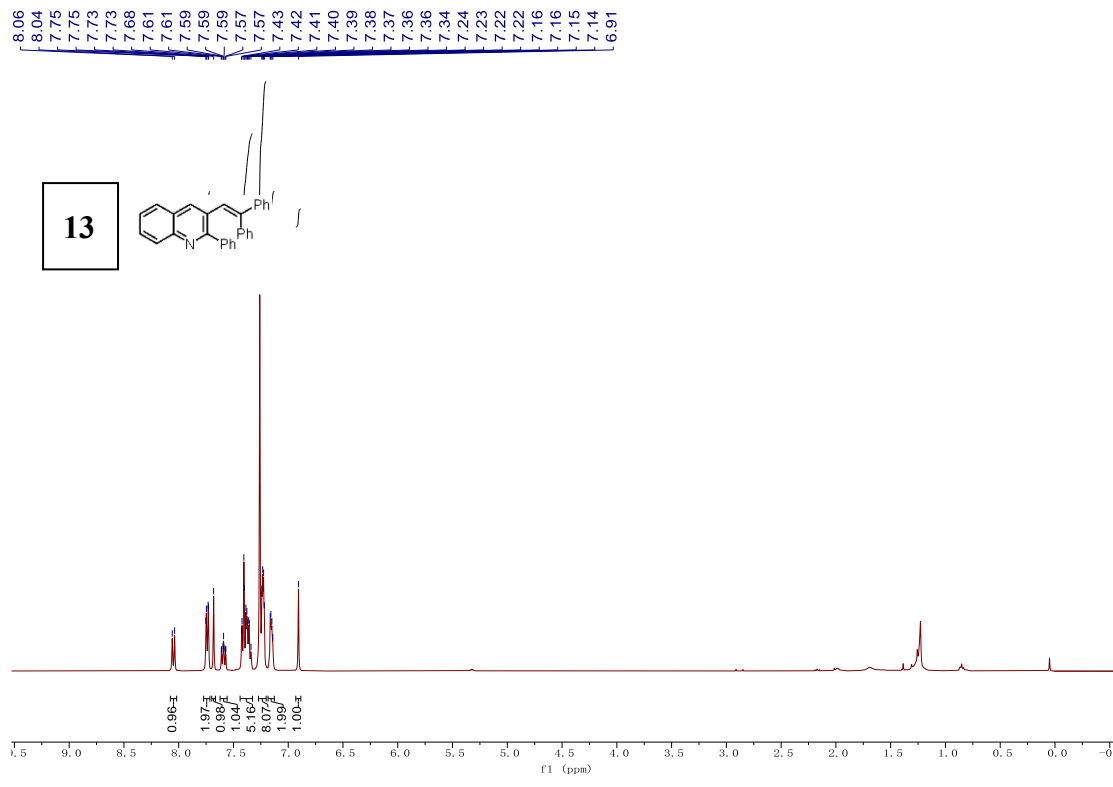






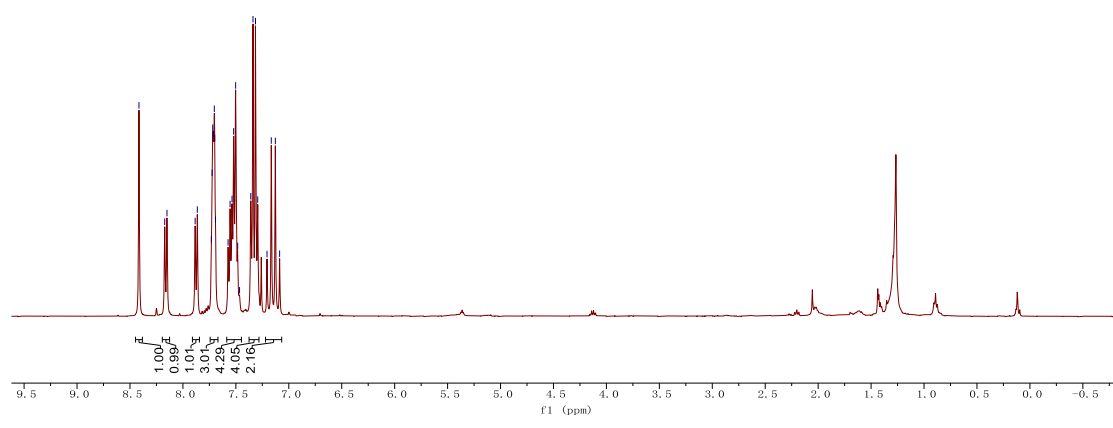
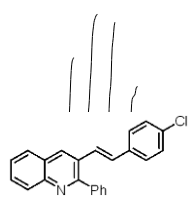
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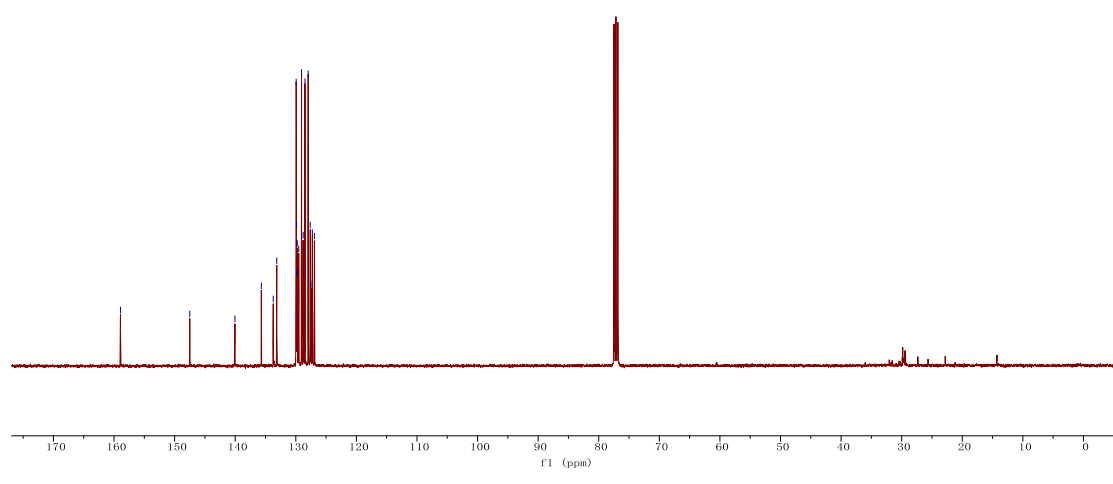
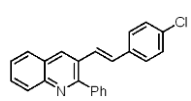


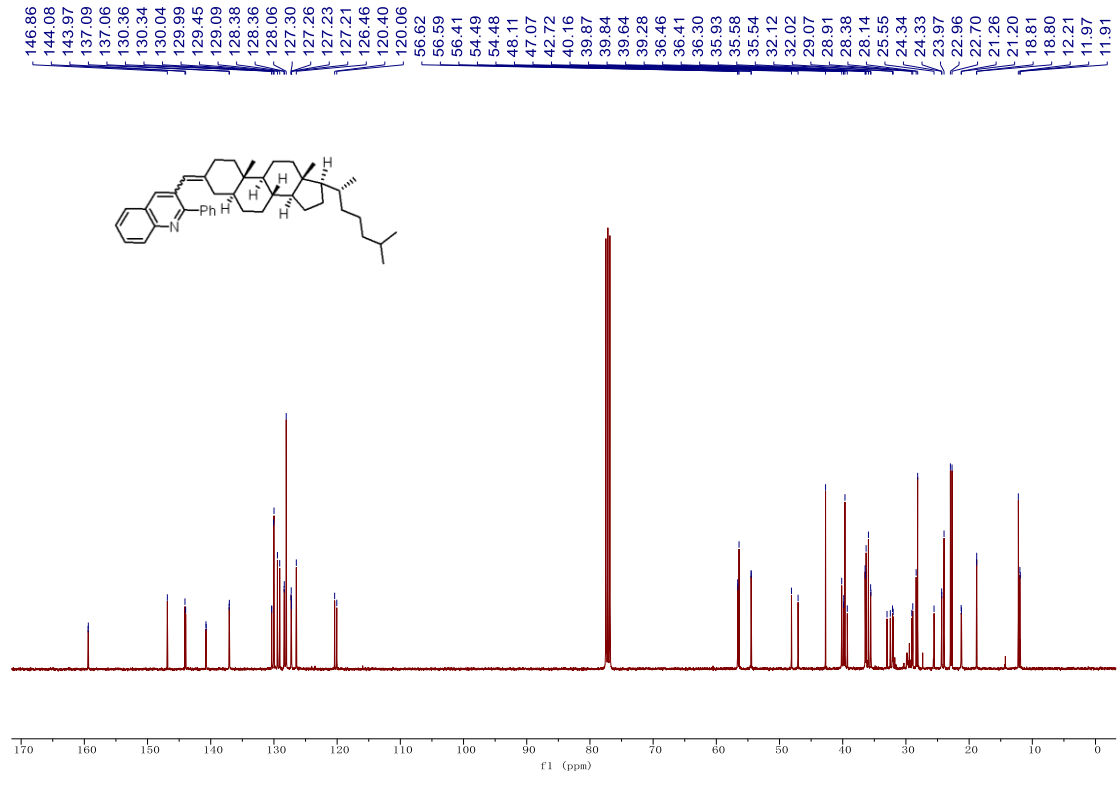
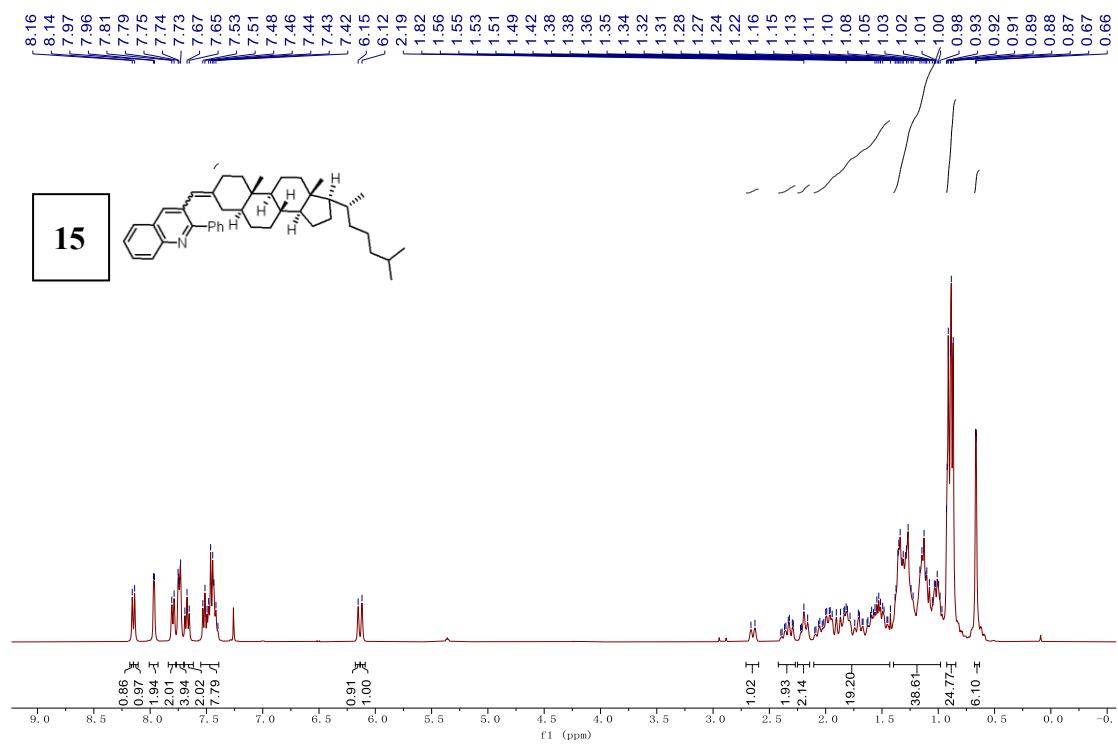
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7.71
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7.13
7.09

14



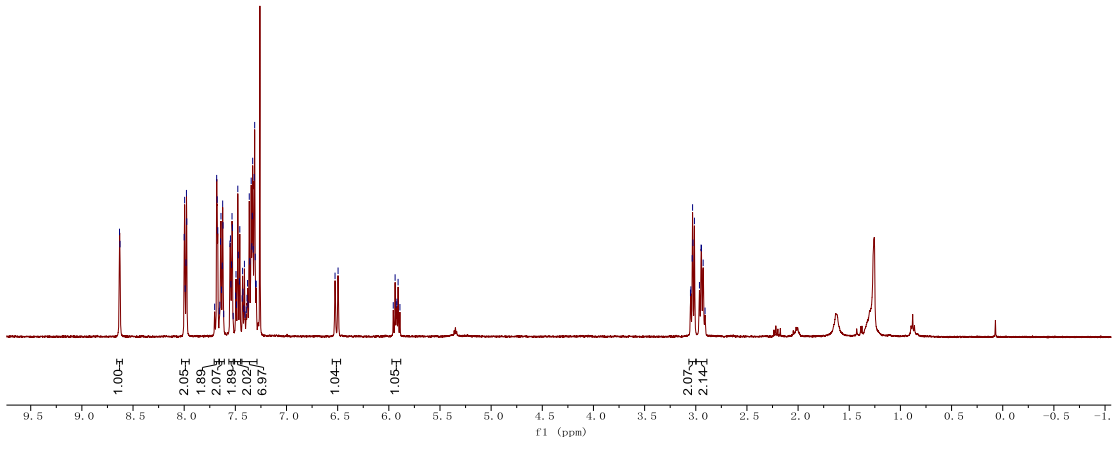
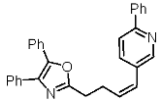
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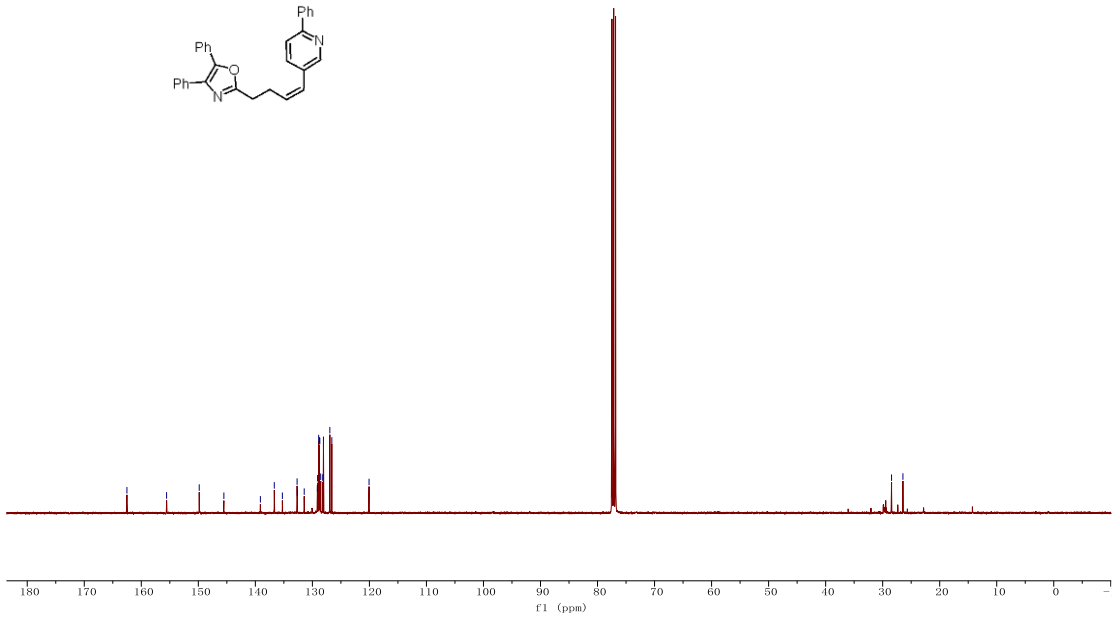
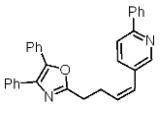
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2.93

16-Z

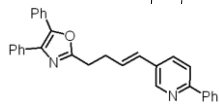


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120.06

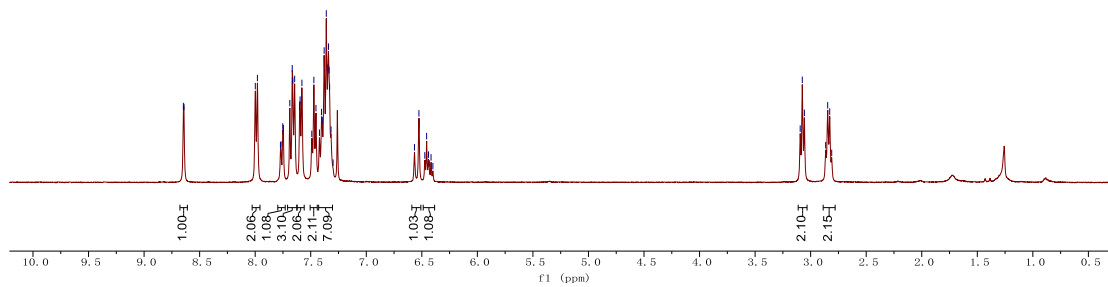
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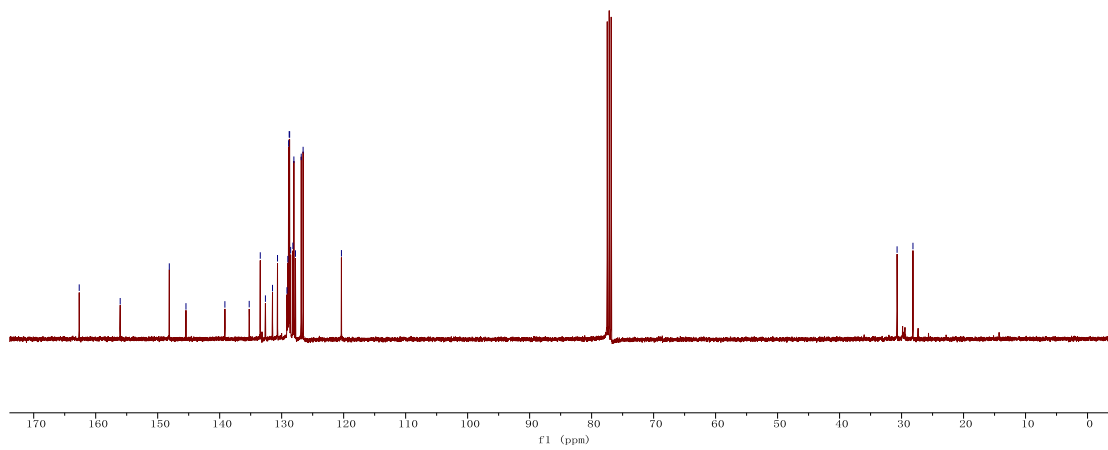
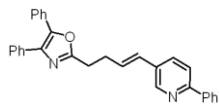
16-E

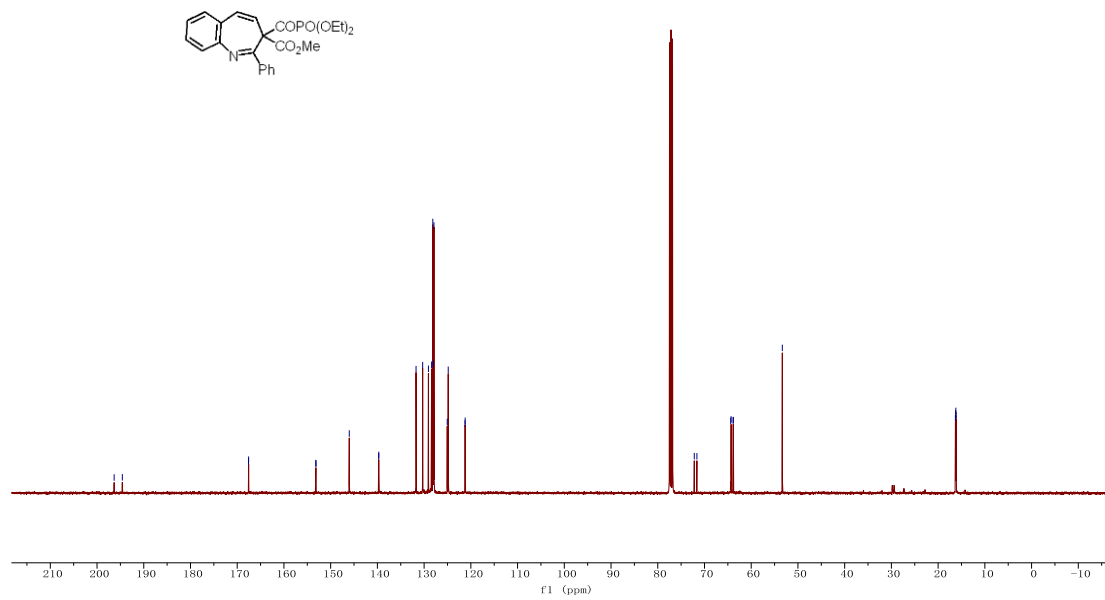
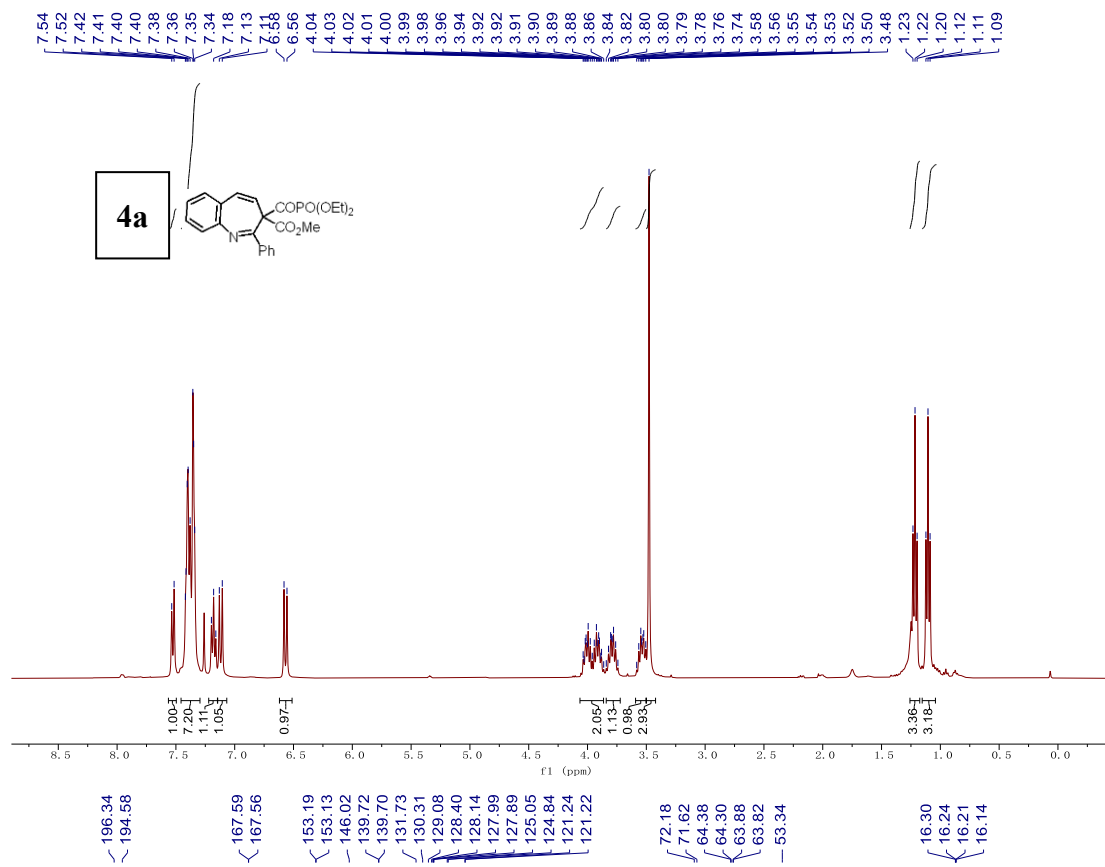


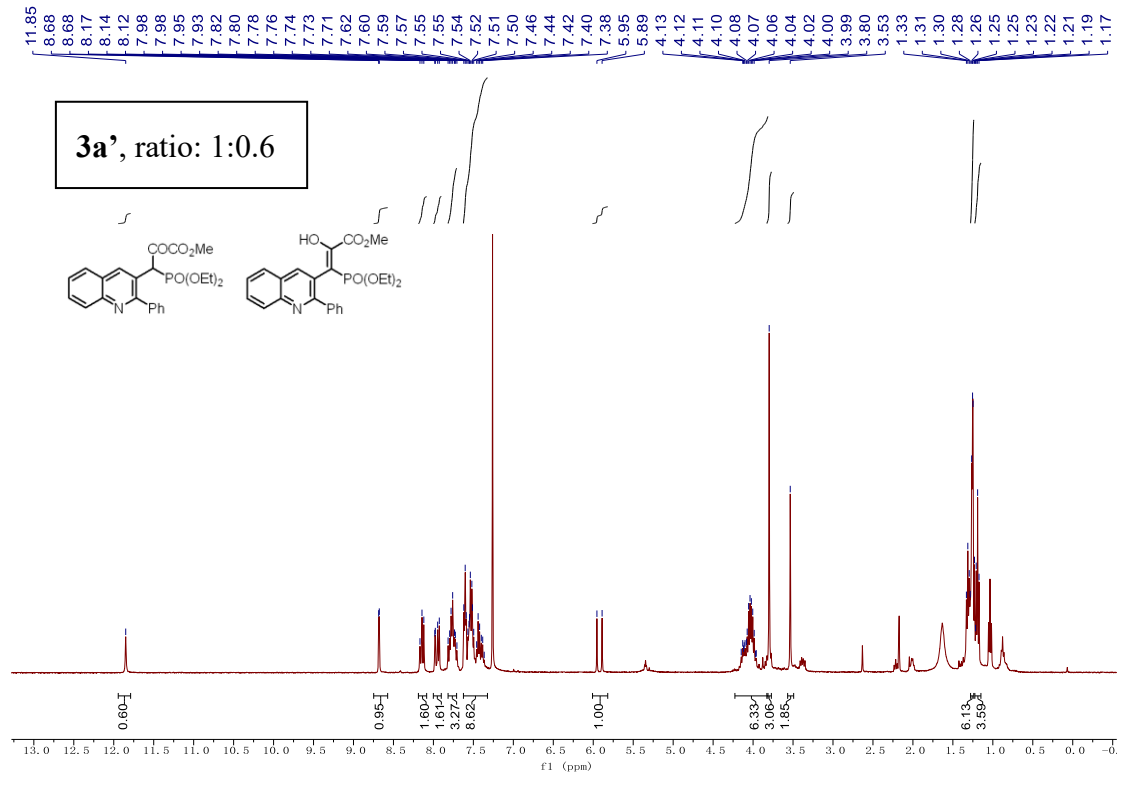
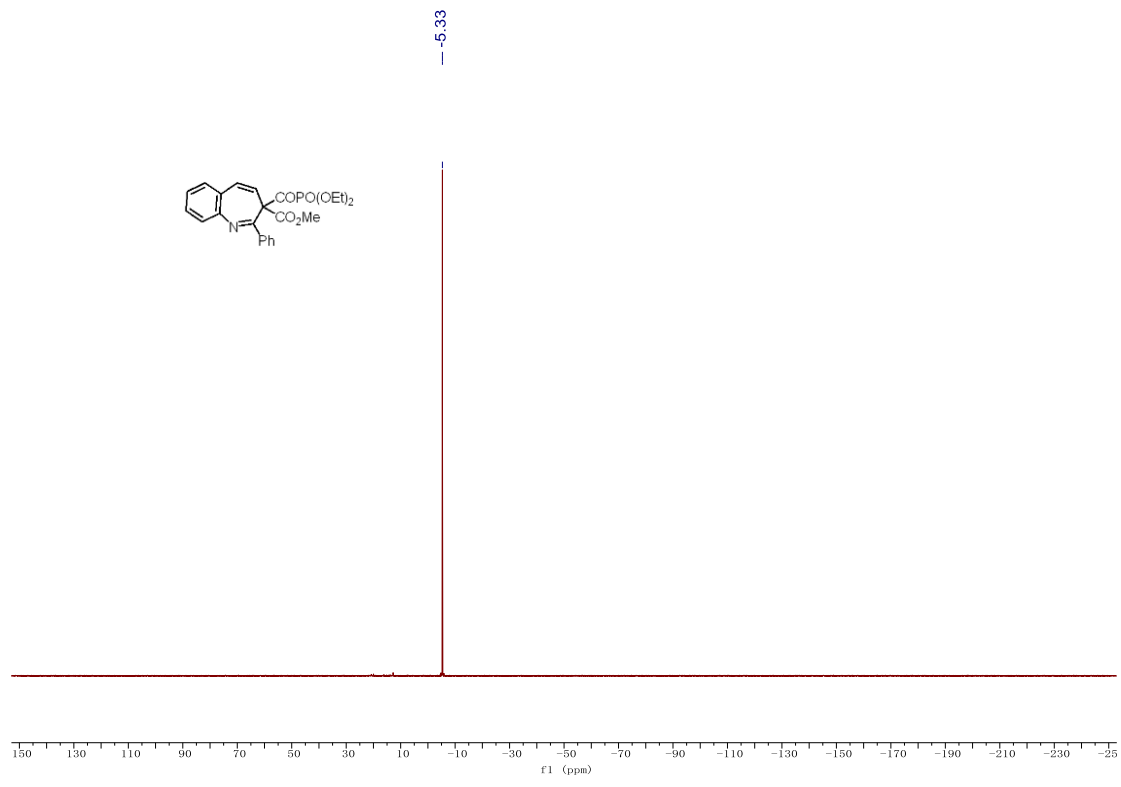
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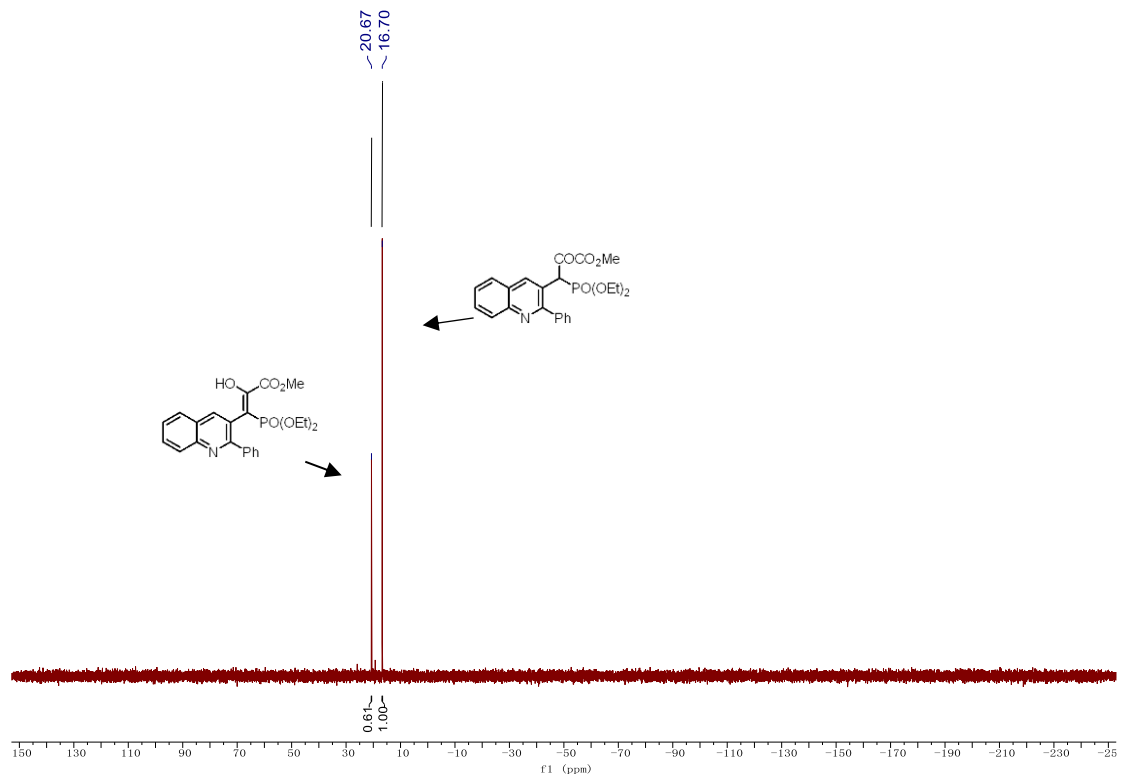


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17a, 17b ratio: 1:0.4

