Electronic Supplementary Information

Regioselective Addition of Phosphites to Acyl Cyclopropanes and Following Rearrangements: A Facile Access to Enol Phosphates

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I. General Information

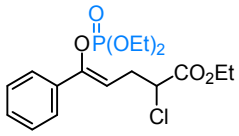
General procedures. All reactions were performed in oven-dried round-bottom flasks and tubes. Solvents were dried and freshly distilled before use. 4Å molecular sieves were freshly activated before use. Aldehydes and amines are purified either by distillation or recrystallization before use. Reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F-254 plates. TLC plates were normally visualized under UV irradiation (254 nm or 365 nm), stained with basic $KMnO_4$ or phosphomolybdic acid. Flash chromatography was performed using silica gel 60 (200−300 mesh).

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker Ascend 400 MHZ or 600 MHZ. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak ($CHCl_3$: δ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants in Hertz (Hz), and integration. HRMS was measured on a Bruker SolariX 7.0T spectrometer equipped with an ESI or APCI source.

Abbreviations used: TLC–thin layer chromatography; THF–tetrahydrofuran; PE–Petroleum Ethers; DCE–1,2-dichloroethane; NOE–Nuclear Overhauser Effect.

II. Reaction Condition Optimization

General procedure for the reaction condition optimization: To an oven-dried reaction tube charged with a magnetic stir bar were added ethyl 2-benzoyl-1-chlorocyclopropane-1-carboxylate **1a** (50.5 mg, 0.2 mmol) and diethyl phosphite **2a** (31 μL, 0.24 mmol). The reactants were dissolved in dried solvent (1 mL) under stirring, followed by the addition of a corresponding base (0.04-0.4 mmol). The reaction was kept stirring for indicated time till the consumption of **1a** (monitored by TLC). Water (5 mL) was added to quench the reaction and the mixture was extracted with EtOAc (3 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was then purified through silica gel column chromatography with petroleum ether/ethyl acetate as eluent to produce compound **3aa** as colorless oil. The results are summarized in **table 1**.



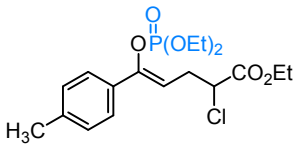
Ethyl (Z)-2-chloro-5-((diethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3aa**) Compound **3aa** was isolated through silica gel column chromatography as colorless liquid (71.1 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.40 – 7.31 (m, 3H), 5.66 (td, *J* = 7.3, 2.1 Hz, 1H), 4.46 (dd, *J* = 7.7, 6.3 Hz, 1H), 4.26 (qd, *J* = 7.1, 0.9 Hz, 2H), 4.17 – 3.99 (m, 4H), 3.16 – 3.06 (m, 1H), 3.01 (ddd, *J* = 15.2, 7.6, 2.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.24 (qd, *J* = 7.1, 1.0 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.2, 148.6 (d, *J* = 8.9 Hz), 134.9, 128.9, 128.3, 125.8, 111.0 (d, *J* = 6.6 Hz), 64.5 (d, *J* = 5.9 Hz), 62.1, 56.1 (d, *J* = 2.5 Hz), 31.7 (d, *J* = 1.5 Hz), 16.0 (d, *J* = 7.0 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -6.06; IR (KBr) *v* 2985, 2935, 2873, 1743, 1664, 1493, 1447, 1372, 1272, 1179, 1110, 1023, 886, 815, 767 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{24}ClO_6PNa$ $[M + Na]^+$ 413.0891, found 413.0905.

III. Cs_2CO_3 Promoted Cascade Reaction for Enol Phosphate Synthesis

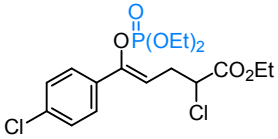
a. Preparation of the 2-aroyl-1-chlorocyclopropane-1-carboxylates substrates.

Substrate **1** and **5** are prepared according to a known procedure that was described in our previous publications.[1]

b. General procedure for the cascade reaction between 1 and 2 to prepare enol phosphate 3. To an oven-dried reaction tube charged with a magnetic stir bar and Cs_2CO_3 (70.6 mg, 0.2 mmol) under N_2 were added anhydrous CH_3CN (0.3 mL) and a dialkyl phosphite **2** (0.24 mmol) via syringes. The mixture was stirred at room temperature for 5 minutes before a corresponding aroyl cyclopropane derivative **1** or **5** (0.2 mmol, dissolved in 0.7 mL CH_3CN) was added via a syringe. The reaction was kept stirring for indicated time till the consumption of **1** or **5**. (monitored by TLC). Water (5 mL) was added to quench the reaction and the mixture was extracted with EtOAc (3 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was then purified through silica gel column chromatography with petroleum ether/ethyl acetate as eluent.

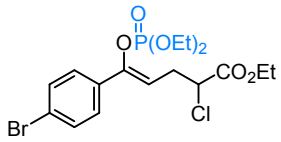


Ethyl (Z)-2-chloro-5-((diethoxyphosphoryl)oxy)-5-(p-tolyl)pent-4-enoate (**3ba**) was prepared from the reaction of **1b** and diethyl phosphite **2a** according to the general procedure. Compound **3ba** was isolated through silica gel column chromatography as colorless liquid (63.2 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.60 (td, J = 7.3, 2.1 Hz, 1H), 4.45 (dd, J = 7.7, 6.4 Hz, 1H), 4.25 (qd, J = 7.1, 0.9 Hz, 2H), 4.17 – 3.98 (m, 4H), 3.14 – 3.04 (m, 1H), 2.98 (dtd, J = 9.8, 7.5, 2.3 Hz, 1H), 2.35 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.28 – 1.23 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.2, 148.7 (d, J = 9.0 Hz), 138.8, 132.1, 129.0, 125.7, 110.0 (d, J = 6.6 Hz), 64.5 (d, J = 5.9 Hz), 62.1, 56.2 (d, J = 2.5 Hz), 31.7 (d, J = 1.4 Hz), 21.2, 16.0 (d, J = 6.9 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -6.02; IR (KBr) ν 2985, 2933, 2873, 1744, 1664, 1611, 1513, 1447, 1393, 1372, 1273, 1180, 1100, 1032, 984, 889, 861, 820, 757 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{26}ClO_6PNa$ $[M + Na]^+$ 427.1048, found 427.1048.

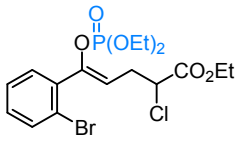


Ethyl (Z)-2-chloro-5-(4-chlorophenyl)-5-((diethoxyphosphoryl)oxy)pent-4-enoate (**3da**) was

prepared from the reaction of **1d** and diethyl phosphite **2a** according to the general procedure. Compound **3da** was isolated through silica gel column chromatography as colorless liquid (70.6 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.34 – 7.29 (m, 2H), 5.66 (td, *J* = 7.3, 2.1 Hz, 1H), 4.45 (dd, *J* = 7.7, 6.2 Hz, 1H), 4.25 (qd, *J* = 7.1, 1.1 Hz, 2H), 4.18 – 4.01 (m, 4H), 3.09 (dddd, *J* = 15.5, 7.4, 6.3, 2.2 Hz, 1H), 2.98 (dtd, *J* = 9.8, 7.5, 2.3 Hz, 1H), 1.30 (t, *J* = 5.3 Hz, 3H), 1.29 – 1.23 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 147.5 (d, *J* = 9.0 Hz), 134.7, 133.4, 128.5, 127.0, 111.5 (d, *J* = 6.5 Hz), 64.7 (d, *J* = 6.0 Hz), 62.2, 56.0 (d, *J* = 2.4 Hz), 31.7 (d, *J* = 1.4 Hz), 16.0 (d, *J* = 6.9 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -5.94; IR (KBr) *v* 2986, 2934, 2873, 1744, 1664, 1595, 1491, 1446, 1398, 1372, 1273, 1179, 1096, 1028, 888, 831, 769 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}Cl_2O_6PNa$ [M + Na]$^{+}$ 447.0502, found 447.0501.

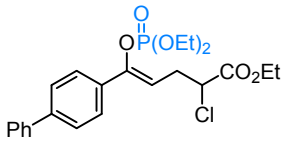


Ethyl (Z)-5-(4-bromophenyl)-2-chloro-5-((diethoxyphosphoryl)oxy)pent-4-enoate (**3ea**) was prepared from the reaction of **1e** and diethyl phosphite **2a** according to the general procedure. Compound **3ea** was isolated through silica gel column chromatography as colorless liquid (78.9 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.37 (m, 2H), 5.68 (td, *J* = 7.3, 2.1 Hz, 1H), 4.45 (dd, *J* = 7.7, 6.2 Hz, 1H), 4.25 (qd, *J* = 7.1, 0.9 Hz, 2H), 4.18 – 4.01 (m, 4H), 3.16 – 3.03 (m, 1H), 2.97 (dtd, *J* = 9.8, 7.5, 2.3 Hz, 1H), 1.30 (t, *J* = 5.3 Hz, 3H), 1.27 (td, *J* = 6.5, 1.9 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 147.6 (d, *J* = 8.9 Hz), 133.9, 131.5, 127.3, 123.0, 111.6 (d, *J* = 6.5 Hz), 64.7 (d, *J* = 5.9 Hz), 62.2, 56.0 (d, *J* = 2.4 Hz), 31.7 (d, *J* = 1.5 Hz), 16.0 (d, *J* = 6.8 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -5.94; IR (KBr) *v* 2985, 2935, 2872, 1744, 1663, 1589, 1487, 1446, 1396, 1372, 1273, 1180, 1101, 1071, 1028, 887, 826, 766 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}BrClO_6PNa$ [M + Na]$^{+}$ 490.9996, found 490.9997.

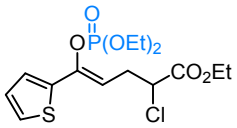


(Z)-4-(ethoxycarbonyl)-1-(2-bromophenyl)-4-chlorobut-1-enyl diethyl phosphate (**3fa**) was prepared from the reaction of **1f** and diethyl phosphite **2a** according to the general procedure.

Compound **3fa** was isolated through silica gel column chromatography as colorless liquid (79.8 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.20 (td, *J* = 7.7, 1.8 Hz, 1H), 5.36 (td, *J* = 7.2, 1.1 Hz, 1H), 4.47 (dd, *J* = 7.7, 6.4 Hz, 1H), 4.29 – 4.21 (m, 2H), 3.98 (dddt, *J* = 14.2, 10.0, 7.9, 7.2 Hz, 4H), 3.07 (dddd, *J* = 15.5, 7.3, 6.5, 1.9 Hz, 1H), 2.96 (dtd, *J* = 9.4, 7.5, 2.0 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.18 (qd, *J* = 7.1, 1.1 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 147.1 (d, *J* = 8.8 Hz), 136.6, 132.9, 131.7, 130.4, 127.1, 122.6, 115.2 (d, *J* = 7.6 Hz), 64.3 (d, *J* = 6.1 Hz), 62.2, 55.9 (d, *J* = 2.1 Hz), 31.3 (d, *J* = 1.0 Hz), 15.9 (dd, *J* = 7.1, 1.9 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -6.74; IR (KBr) *ν* 3062, 2985, 2935, 2872, 1744, 1682, 1589, 1562, 1471, 1434, 1394, 1372, 1280, 1179, 1100, 1031, 890, 861, 817, 765 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}BrClO_6PNa$ $[M + Na]^+$ 490.9996, found 490.9997.

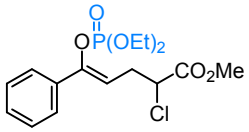


Ethyl (Z)-5-([1,1'-biphenyl]-4-yl)-2-chloro-5-((diethoxyphosphoryl)oxy)pent-4-enoate (**3ga**) was prepared from the reaction of **1g** and diethyl phosphite **2a** according to the general procedure. Compound **3ga** was isolated through silica gel column chromatography as colorless liquid (79.4 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 6H), 7.46 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.40 – 7.35 (m, 1H), 5.75 (td, *J* = 7.3, 2.1 Hz, 1H), 4.50 (dd, *J* = 7.7, 6.3 Hz, 1H), 4.34 – 4.24 (m, 2H), 4.22 – 4.05 (m, 4H), 3.20 – 3.11 (m, 1H), 3.05 (ddd, *J* = 15.2, 7.6, 2.3 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.30 – 1.25 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.2, 148.3 (d, *J* = 9.0 Hz), 141.6, 140.3, 133.8, 128.9, 127.6, 127.00, 126.98, 126.2, 111.0 (d, *J* = 6.5 Hz), 64.6 (d, *J* = 5.9 Hz), 62.2, 56.2 (d, *J* = 2.4 Hz), 31.8 (d, *J* = 1.3 Hz), 16.1 (d, *J* = 6.9 Hz), 14.1; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -5.92; IR (KBr) *ν* 3033, 2985, 2934, 1743, 1662, 1604, 1486, 1447, 1398, 1372, 1274, 1170, 1100, 1032, 889, 843, 818, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{28}ClO_6PNa$ $[M + Na]^+$ 489.1204, found 489.1201.

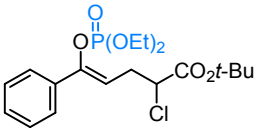


Ethyl (Z)-2-chloro-5-((diethoxyphosphoryl)oxy)-5-(thiophen-2-yl)pent-4-enoate (**3ha**) was

prepared from the reaction of **1h** and diethyl phosphite **2a** according to the general procedure. Compound **3ha** was isolated through silica gel column chromatography as yellow liquid (60.3 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 6.98 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.61 (td, *J* = 7.4, 2.4 Hz, 1H), 4.44 (dd, *J* = 7.6, 6.4 Hz, 1H), 4.29 – 4.22 (m, 2H), 4.23 – 4.08 (m, 4H), 3.13 – 3.02 (m, 1H), 2.97 (ddd, *J* = 15.2, 7.6, 2.3 Hz, 1H), 1.34 – 1.27 (m, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 143.3 (d, *J* = 9.1 Hz), 138.2, 127.3, 125.7, 125.6, 110.1 (d, *J* = 6.2 Hz), 64.8 (d, *J* = 5.9 Hz), 62.2, 55.9 (d, *J* = 2.6 Hz), 31.7 (d, *J* = 1.5 Hz), 16.1 (d, *J* = 6.9 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -6.01; IR (KBr) *ν* 3106, 2986, 2936, 2912, 1742, 1663, 1519, 1475, 1439, 1415, 1371, 1262, 1181, 1099, 1032, 863, 821, 713 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{22}ClO_6PSNa$ $[M + Na]^+$ 419.0454, found 419.0452.

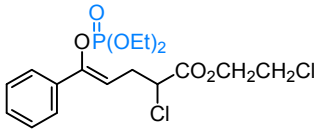


Methyl (*Z*)-2-chloro-5-((diethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3ja**) was prepared from the reaction of **1j** and diethyl phosphite **2a** according to the general procedure. Compound **3ja** was isolated through silica gel column chromatography as colorless liquid (62.5 mg, 83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.34 (q, *J* = 5.1 Hz, 3H), 5.66 (td, *J* = 7.3, 2.1 Hz, 1H), 4.49 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.19 – 3.97 (m, 4H), 3.81 (s, 3H), 3.12 (ddd, *J* = 13.7, 7.8, 2.1 Hz, 1H), 2.99 (dtd, *J* = 9.8, 7.5, 2.3 Hz, 1H), 1.28 – 1.21 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 148.6 (d, *J* = 9.0 Hz), 134.9, 128.9, 128.3, 125.8, 110.9 (d, *J* = 6.6 Hz), 64.6 (d, *J* = 5.9 Hz), 55.9 (d, *J* = 2.5 Hz), 53.0, 31.7 (d, *J* = 1.5 Hz), 16.0 (d, *J* = 6.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -6.04; IR (KBr) *ν* 2986, 2959, 2873, 1748, 1664, 1601, 1580, 1493, 1443, 1393, 1367, 1273, 1198, 1170, 1101, 1021, 984, 893, 805, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{22}ClO_6PNa$ $[M + Na]^+$ 399.0735, found 399.0736.

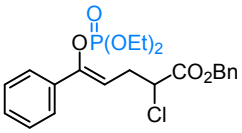


tert-butyl (Z)-2-chloro-5-((diethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3ka**) was prepared from the reaction of **1k** and diethyl phosphite **2a** according to the general procedure. Compound **3ka** was isolated through silica gel column chromatography as colorless liquid (66.2

mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.38 – 7.30 (m, 3H), 5.65 (td, *J* = 7.3, 2.1 Hz, 1H), 4.35 (dd, *J* = 7.4, 6.5 Hz, 1H), 4.18 – 3.98 (m, 4H), 3.11 – 2.92 (m, 2H), 1.49 (s, 9H), 1.28 – 1.20 (m, 6H);^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 148.4 (d, *J* = 9.1 Hz), 135.0, 128.8, 128.3, 125.7, 111.2 (d, *J* = 6.5 Hz), 82.7, 64.5 (d, *J* = 6.0 Hz), 57.2 (d, *J* = 2.3 Hz), 31.8 (d, *J* = 1.5 Hz), 27.8, 16.0 (d, *J* = 6.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -6.02; IR (KBr) *ν* 2983, 2934, 1739, 1664, 1602, 1579, 1478, 1394, 1369, 1274, 1154, 1101, 1035, 984, 888, 845, 817, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{28}ClO_6PNa$ $[M + Na]^+$ 441.1204, found 441.1210.

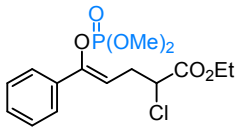


2-Chloroethyl (Z)-2-chloro-5-((diethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3la**) was prepared from the reaction of **1l** and diethyl phosphite **2a** according to the general procedure. Compound **3la** was isolated through silica gel column chromatography as yellow liquid (54.4 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.39 – 7.32 (m, 3H), 5.68 (td, *J* = 7.3, 2.1 Hz, 1H), 4.54 (dd, *J* = 7.5, 6.5 Hz, 1H), 4.50 – 4.42 (m, 2H), 4.18 – 4.00 (m, 4H), 3.78 – 3.70 (m, 2H), 3.21 – 3.09 (m, 1H), 3.04 (ddd, *J* = 15.2, 7.5, 2.3 Hz, 1H), 1.25 (qd, *J* = 7.0, 1.0 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.9, 148.7 (d, *J* = 9.0 Hz), 134.9, 128.9, 128.3, 125.8, 110.7 (d, *J* = 6.6 Hz), 65.4, 64.6 (d, *J* = 5.9 Hz), 55.8 (d, *J* = 2.5 Hz), 41.1, 31.7 (d, *J* = 1.5 Hz), 16.0 (d, *J* = 6.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -6.03; IR (KBr) *ν* 2985, 2935, 1803, 1750, 1665, 1628, 1601, 1493, 1447, 1391, 1273, 1169, 1101, 1033, 984, 893, 818, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}Cl_2O_6PNa$ $[M + Na]^+$ 447.0502, found 447.0500.

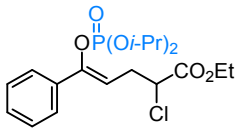


Benzyl (Z)-2-chloro-5-((diethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3ma**) was prepared from the reaction of **1m** and diethyl phosphite **2a** according to the general procedure. Compound **3ma** was isolated through silica gel column chromatography as colorless liquid (65.2 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.41 – 7.32 (m, 8H), 5.63 (td, *J* = 7.3, 2.2 Hz, 1H), 5.25 (s, 2H), 4.54 (dd, *J* = 7.5, 6.6 Hz, 1H), 4.18 – 3.96 (m, 4H), 3.18 – 3.09 (m, 1H),

3.04 (dtd, J = 9.8, 7.5, 2.3 Hz, 1H), 1.22 (tdd, J = 7.1, 2.7, 1.1 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.0, 148.6 (d, J = 9.0 Hz), 135.1, 134.9, 128.9, 128.6, 128.5, 128.3 (d, J = 1.8 Hz), 110.8 (d, J = 6.5 Hz), 67.7, 64.6 (d, J = 5.9 Hz), 56.1 (d, J = 2.6 Hz), 31.8 (d, J = 1.5 Hz), 16.0 (d, J = 7.0 Hz); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -6.02; IR (KBr) ν 3063, 3034, 2986, 2934, 1746, 1664, 1603, 1496, 1449, 1389, 1273, 1167, 1101, 1022, 984, 890, 818, 765 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{26}ClO_6PNa$ $[M + Na]^+$ 475.1048, found 475.1046.

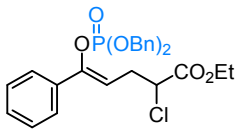


Ethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3ab**) was prepared from the reaction of **1a** and dimethyl phosphite **2b** according to the general procedure. Compound **3ab** was isolated through silica gel column chromatography as colorless liquid (67.5 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.40 – 7.32 (m, 3H), 5.67 (td, J = 7.3, 2.1 Hz, 1H), 4.45 (dd, J = 7.6, 6.2 Hz, 1H), 4.26 (qd, J = 7.1, 0.6 Hz, 2H), 3.73 (dd, J = 11.4, 4.1 Hz, 6H), 3.10 (dddd, J = 15.6, 7.5, 6.3, 2.2 Hz, 1H), 2.98 (dtd, J = 9.8, 7.5, 2.3 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.1, 148.4 (d, J = 8.9 Hz), 134.8, 129.0, 128.4, 125.7, 111.1 (d, J = 6.5 Hz), 62.2, 56.1 (d, J = 2.5 Hz), 54.9 (d, J = 6.0 Hz), 31.7 (d, J = 1.5 Hz), 14.0; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -3.64; IR (KBr) ν 3061, 2985, 2960, 2857, 1744, 1665, 1602, 1579, 1494, 1449, 1373, 1278, 1184, 1100, 1041, 955, 897, 853, 771 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{20}ClO_6PNa$ $[M + Na]^+$ 385.0578, found 385.0579.

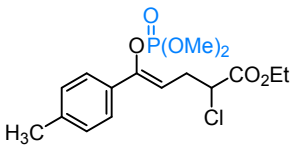


Ethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3ac**) was prepared from the reaction of **1a** and diisopropyl phosphite **2c** according to the general procedure. Compound **3ac** was isolated through silica gel column chromatography as yellow liquid (42.7 mg, 51% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.9, 1.7 Hz, 2H), 7.33 (dd, J = 7.3, 5.4 Hz, 3H), 5.66 (td, J = 7.3, 2.2 Hz, 1H), 4.64 (dt, J = 12.3, 6.2 Hz, 2H), 4.48 (dd, J = 7.8, 6.3 Hz, 1H), 4.26 (qd, J = 7.1, 0.9 Hz, 2H), 3.21 – 3.07 (m, 1H), 3.02 (ddd, J = 15.2, 7.6, 2.3 Hz, 1H), 1.38 – 1.28 (m, 9H), 1.18 (dd, J = 11.5, 6.2 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.2, 148.7

(d, J = 9.1 Hz), 135.1, 128.7, 128.2, 125.9, 110.8 (d, J = 6.6 Hz), 73.4 (d, J = 6.0 Hz), 62.1, 56.2 (d, J = 2.5 Hz), 31.8 (d, J = 1.5 Hz), 23.6 (d, J = 4.5 Hz), 23.4 (dd, J = 5.6, 4.0 Hz), 14.0; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -7.67; IR (KBr) ν 3062, 2983, 2934, 1744, 1663, 1494, 1466, 1450, 1380, 1271, 1180, 1145, 1104, 1002, 900, 860, 767 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{28}ClO_6PNa$ $[M + Na]^+$ 441.1204, found 441.1207.

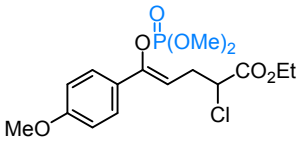


Ethyl (Z)-5-((bis(benzyloxy)phosphoryl)oxy)-2-chloro-5-phenylpent-4-enoate (**3ad**) was prepared from the reaction of **1a** and dibenzyl phosphite **2d** according to the general procedure. Compound **3ad** was isolated through silica gel column chromatography as colorless liquid (96.8 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.26 – 7.16 (m, 9H), 7.14 – 7.07 (m, 4H), 5.56 (td, J = 7.3, 2.0 Hz, 1H), 5.01 – 4.75 (m, 4H), 4.31 (dd, J = 7.6, 6.3 Hz, 1H), 4.11 (qd, J = 7.1, 2.5 Hz, 2H), 2.97 (ddd, J = 8.3, 7.7, 1.5 Hz, 1H), 2.88 (ddd, J = 15.3, 7.6, 2.3 Hz, 1H), 1.16 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.1, 148.5 (d, J = 9.1 Hz), 135.5 (d, J = 7.2 Hz), 134.8, 129.0, 128.6, 128.4, 127.9, 125.8, 111.2 (d, J = 6.6 Hz), 70.0 (d, J = 5.6 Hz), 62.2, 56.1 (d, J = 2.4 Hz), 31.8 (d, J = 1.4 Hz), 14.0; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -5.78; IR (KBr) ν 3064, 3035, 2981, 1743, 1664, 1602, 1496, 1454, 1375, 1276, 1213, 1180, 1100, 1015, 889, 806, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{28}ClO_6PNa$ $[M + Na]^+$ 537.1204, found 537.1204.

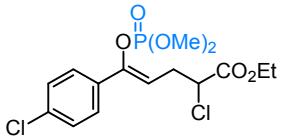


Ethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-(p-tolyl)pent-4-enoate (**3bb**) was prepared from the reaction of **1b** and dimethyl phosphite **2b** according to the general procedure. Compound **3bb** was isolated through silica gel column chromatography as colorless liquid (68.6 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.62 (td, J = 7.3, 2.0 Hz, 1H), 4.45 (dd, J = 7.6, 6.3 Hz, 1H), 4.33 – 4.19 (m, 2H), 3.74 (dd, J = 11.4, 3.7 Hz, 6H), 3.16 – 3.04 (m, 1H), 2.98 (ddd, J = 15.2, 7.5, 2.3 Hz, 1H), 2.36 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.2, 148.5 (d, J = 8.9 Hz), 139.0, 131.9,

129.1, 125.6, 110.1 (d, J = 6.5 Hz), 62.2, 56.2 (d, J = 2.5 Hz), 54.9 (d, J = 6.0 Hz), 31.7 (d, J = 1.5 Hz), 21.2, 14.0; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -3.63; IR (KBr) ν 2960, 2858, 1744, 1666, 1610, 1513, 1452, 1373, 1277, 1184, 1034, 900, 854, 822, 769 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{22}ClO_6PNa$ $[M + Na]^+$ 399.0735, found 399.0731.

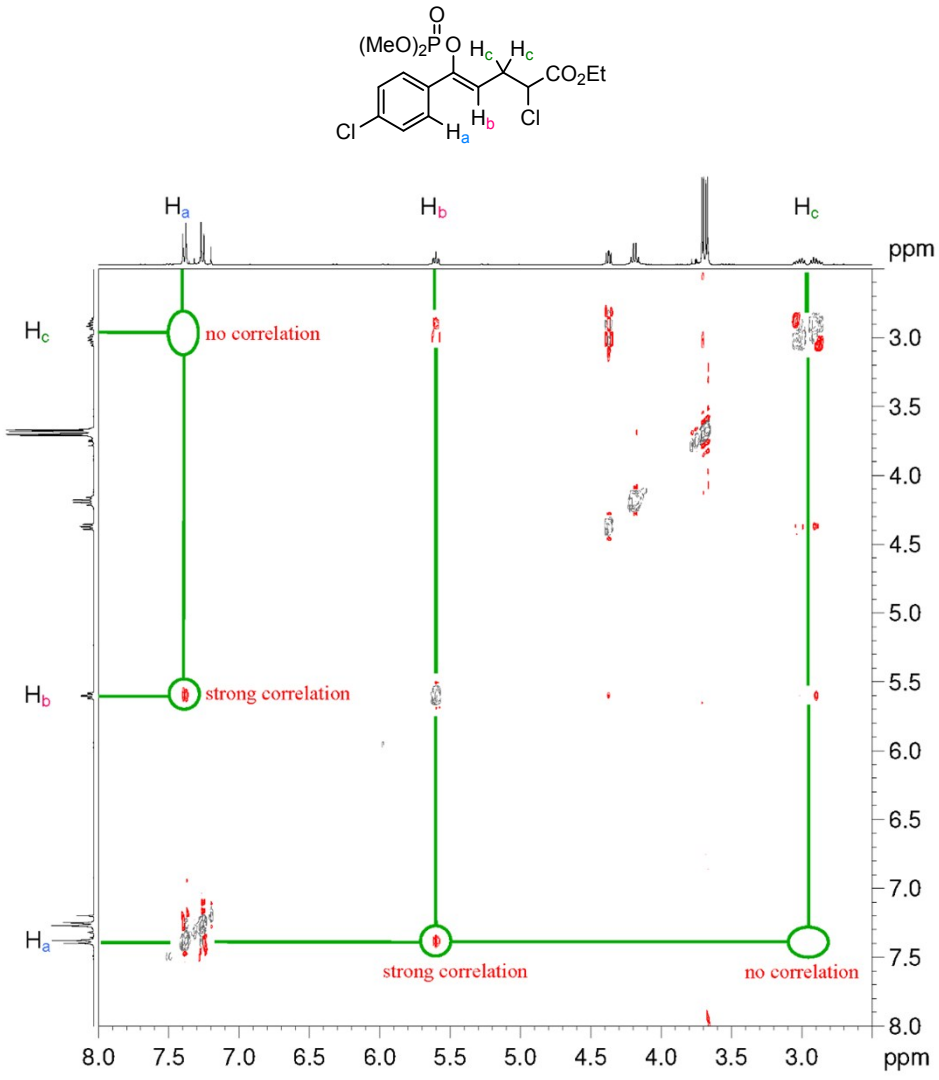


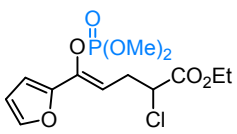
Ethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-(4-methoxyphenyl)pent-4-enoate (3cb) was prepared from the reaction of **1c** and dimethyl phosphite **2b** according to the general procedure. Compound **3cb** was isolated through silica gel column chromatography as colorless liquid (28.3 mg, 36% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 6.92 – 6.87 (m, 2H), 5.54 (td, J = 7.3, 2.0 Hz, 1H), 4.45 (dd, J = 7.6, 6.3 Hz, 1H), 4.27 (tt, J = 7.2, 3.6 Hz, 2H), 3.83 (s, 3H), 3.75 (dd, J = 11.4, 3.6 Hz, 6H), 3.17 – 3.02 (m, 1H), 2.96 (dtd, J = 9.7, 7.5, 2.3 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.2, 160.2 148.3 (d, J = 8.8 Hz), 127.4, 127.2, 113.8, 109.2 (d, J = 6.6 Hz), 62.2, 56.2 (d, J = 2.5 Hz), 55.3, 54.9 (d, J = 5.9 Hz), 31.7 (d, J = 1.5 Hz), 14.0; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -3.60; IR (KBr) ν 2960, 2854, 1743, 1667, 1607, 1577, 1513, 1463, 1372, 1255, 1181, 1099, 1034, 900, 852, 804, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{22}ClO_7PNa$ $[M + Na]^+$ 415.0684, found 415.0679.



Ethyl (Z)-2-chloro-5-(4-chlorophenyl)-5-((dimethoxyphosphoryl)oxy)pent-4-enoate (3db) was prepared from the reaction of **1d** and dimethyl phosphite **2b** according to the general procedure. Compound **3db** was isolated through silica gel column chromatography as colorless liquid (65.1 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.36 – 7.30 (m, 2H), 5.67 (td, J = 7.3, 2.1 Hz, 1H), 4.45 (dd, J = 7.6, 6.1 Hz, 1H), 4.32 – 4.20 (m, 2H), 3.76 (dd, J = 11.4, 4.0 Hz, 6H), 3.16 – 3.03 (m, 1H), 2.97 (dtd, J = 9.7, 7.5, 2.3 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.0, 147.4 (d, J = 8.8 Hz), 134.9, 133.2, 128.6, 127.0, 111.6 (d, J = 6.5 Hz), 62.2, 56.0 (d, J = 2.4 Hz), 55.0 (d, J = 6.0 Hz), 31.6 (d, J = 1.5 Hz), 14.0; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -3.57; IR (KBr) ν 2960, 2857, 1744, 1665, 1595, 1492, 1453,

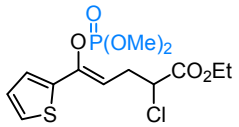
1401, 1373, 1279, 1184, 1095, 1033, 958, 897, 854, 785 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{19}Cl_2O_6PNa$ $[M + Na]^+$ 419.0189, found 419.0191. The geometry of the double bond was determined to be Z through NOE analysis with 3db as a representative: the aromatic hydrogen Ha shows strong correlation with olefin Hb, wheres the correlation between Ha and Hc is not observed.



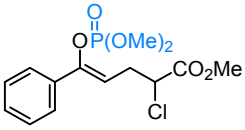


Ethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-(furan-2-yl)pent-4-enoate (3nb) was prepared from the reaction of **1n** and dimethyl phosphite **2b** according to the general procedure.

Compound **3nb** was isolated through silica gel column chromatography as yellow oil (69.8 mg, 99% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.0 Hz, 1H), 6.48 (d, *J* = 3.4 Hz, 1H), 6.34 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.69 (td, *J* = 7.6, 2.3 Hz, 1H), 4.35 (dd, *J* = 7.6, 6.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 11.4 Hz, 6H), 3.05 – 2.95 (m, 1H), 2.88 (ddd, *J* = 15.2, 7.6, 2.3 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 148.3, 143.0, 139.8 (d, *J* = 8.6 Hz), 111.4, 108.9 (d, *J* = 6.1 Hz), 108.5, 62.2, 55.9 (d, *J* = 2.5 Hz), 55.2 (d, *J* = 6.1 Hz), 31.1 (d, *J* = 1.5 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.39; IR (KBr) *ν* 3142, 2961, 2858, 1741, 1675, 1569, 1532, 1490, 1465, 1374, 1261, 1186, 1046, 858, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}ClO_7PNa$ $[M + Na]^+$ 375.0371, found 375.0369.

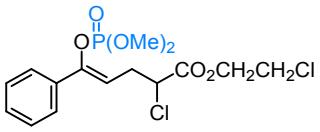


Ethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-(thiophen-2-yl)pent-4-enoate (**3hb**) was prepared from the reaction of **1h** and dimethyl phosphite **2b** according to the general procedure. Compound **3hb** was isolated through silica gel column chromatography as yellow oil (56.0 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 4.5 Hz, 2H), 6.99 (dd, *J* = 4.7, 4.0 Hz, 1H), 5.63 (td, *J* = 7.4, 2.3 Hz, 1H), 4.44 (dd, *J* = 7.6, 6.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.83 (dd, *J* = 11.4, 1.7 Hz, 6H), 3.16 – 3.02 (m, 1H), 2.95 (dtd, *J* = 9.8, 7.5, 2.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 143.2 (d, *J* = 9.0 Hz), 138.0, 127.4, 125.9, 125.6, 110.2 (d, *J* = 6.2 Hz), 62.2, 55.9 (d, *J* = 2.5 Hz), 55.1 (d, *J* = 6.0 Hz), 31.6 (d, *J* = 1.5 Hz), 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.63; IR (KBr) *ν* 3106, 2960, 2857, 1743, 1661, 1521, 1453, 1372, 1279, 1185, 1045, 855, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}ClO_6PSNa$ $[M + Na]^+$ 391.0142, found 391.0143.

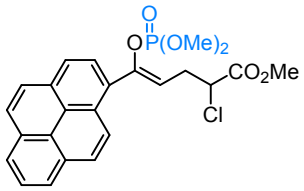


Methyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3jb**) was prepared from the reaction of **1j** and dimethyl phosphite **2b** according to the general procedure. Compound **3jb** was isolated through silica gel column chromatography as colorless oil (65.6 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.36 (dd, *J* = 7.7, 4.5 Hz, 3H), 5.66 (td, *J* = 7.3, 2.0 Hz, 1H), 4.48 (dd, *J* = 7.6, 6.2 Hz, 1H), 3.81 (s, 3H), 3.73 (dd, *J* =

11.4, 5.2 Hz, 6H), 3.11 (ddd, J = 13.6, 7.8, 2.1 Hz, 1H), 2.98 (dtd, J = 9.7, 7.5, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.6, 148.5 (d, J = 8.9 Hz), 134.8, 129.0, 128.4, 125.7, 111.0 (d, J = 6.5 Hz), 55.9 (d, J = 2.6 Hz), 54.9 (d, J = 6.0 Hz), 53.1, 31.7 (d, J = 1.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ -3.64; IR (KBr) ν 3061, 2985, 2960, 2846, 1743, 1658, 1603, 1579, 1489, 1432, 1373, 1277, 1184, 1101, 1044, 957, 898, 853, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{18}ClO_6PNa$ $[M + Na]^+$ 371.0422, found 371.0422.

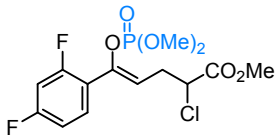


2-Chloroethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**3lb**) was prepared from the reaction of **1l** and dimethyl phosphite **2b** according to the general procedure. Compound **3lb** was isolated through silica gel column chromatography as yellow liquid (63.6 mg, 81% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.42 – 7.32 (m, 3H), 5.68 (qd, J = 7.5, 2.1 Hz, 1H), 4.58 – 4.50 (m, 1H), 4.49 – 4.42 (m, 2H), 3.83 – 3.80 (m, 2H), 3.73 (ddd, J = 11.3, 4.2, 2.7 Hz, 6H), 3.19 – 3.07 (m, 1H), 3.01 (tdd, J = 7.6, 6.4, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.8, 148.6 (d, J = 9.5 Hz), 134.7, 129.1, 128.4, 125.7, 110.8 (d, J = 6.6 Hz), 65.4, 55.8 (d, J = 2.5 Hz), 55.0 (d, J = 6.0 Hz), 53.1, 41.1, 31.6; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ -3.67; IR (KBr) ν 3062, 2960, 2858, 1803, 1749, 1666, 1629, 1494, 1449, 1276, 1177, 1042, 901, 854, 771 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{19}Cl_2O_6PNa$ $[M + Na]^+$ 419.0189, found 419.0190.



Ethyl (Z)-2-chloro-5-((dimethoxyphosphoryl)oxy)-5-(pyren-1-yl)pent-4-enoate (**3ob**) was prepared from the reaction of **1o** and dimethyl phosphite **2b** according to the general procedure. Compound **3ob** was isolated through silica gel column chromatography as yellow liquid (79.3 mg, 84% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 9.2 Hz, 1H), 8.08 (dd, J = 7.6, 1.6 Hz, 2H), 8.06 – 8.01 (m, 2H), 7.97 (dd, J = 8.4, 3.2 Hz, 2H), 7.94 – 7.87 (m, 2H), 5.47 (dd, J = 7.7, 6.9 Hz, 1H), 4.54 (dd, J = 7.5, 6.4 Hz, 1H), 3.75 (s, 3H), 3.29 (dd, J = 14.7, 11.4 Hz, 6H), 3.18 (ddd, J =

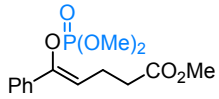
13.6, 7.4, 1.8 Hz, 1H), 3.09 (ddd, J = 14.9, 7.5, 1.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 168.6, 147.1 (d, J = 8.7 Hz), 130.9, 130.1, 129.7, 129.0, 128.0, 127.2, 126.3 (d, J = 9.8 Hz), 125.2, 124.5 (d, J = 11.5 Hz), 123.6, 123.5 (d, J = 6.9 Hz), 123.3, 114.6 (d, J = 7.5 Hz), 55.0 (d, J = 2.2 Hz), 53.5 (d, J = 6.1 Hz), 52.1, 30.7; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -3.86; IR (KBr) ν 3044, 2957, 2855, 1927, 1747, 1679, 1600, 1440, 1354, 1281, 1186, 1116, 1045, 914, 851, 772 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{22}ClO_6PNa$ $[M + Na]^+$ 495.0735, found 495.0739.



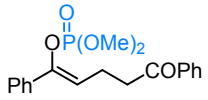
Methyl (Z)-2-chloro-5-(2,4-difluorophenyl)-5-((dimethoxyphosphoryl)oxy)pent-4-enoate (**3pb**) was prepared from the reaction of **1p** and dimethyl phosphite **2b** according to the general procedure. Compound **3pb** was isolated through silica gel column chromatography as colorless liquid (69.9 mg, 91% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 1H), 6.87 (t, J = 7.3 Hz, 1H), 6.84 – 6.77 (m, 1H), 5.57 (t, J = 7.3 Hz, 1H), 4.44 (t, J = 6.9 Hz, 1H), 3.82 – 3.75 (m, 3H), 3.74 – 3.67 (m, 6H), 3.11 – 3.00 (m, 1H), 3.00 – 2.90 (m, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 169.5, 163.0 (dd, J = 251.7, 12.0 Hz), 159.9 (dd, J = 254.0, 12.0 Hz), 142.3 (dd, J = 8.8, 3.0 Hz), 130.6 (dd, J = 9.8, 3.8 Hz), 119.4 (dd, J = 12.7, 4.2 Hz), 115.4 (t, J = 6.6 Hz), 111.3 (dd, J = 21.3, 3.7 Hz), 104.4 (t, J = 25.8 Hz), 55.6, 54.9 (d, J = 6.1 Hz), 53.1, 31.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ -3.95 (hept, J = 12.1 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -107.99 – -108.11 (m, 1F), -108.98 – -109.12 (m, 1F); IR (KBr) ν 3482, 3005, 2958, 2923, 2855, 1742, 1673, 1615, 1597, 1430, 1325, 1286, 1147, 1025, 972, 854, 777 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{17}F_2ClO_6P^+$ $[M+H]^+$ 385.0414, found 385.0413.

c. General procedure for the cascade reaction between 5 and 2b to prepare enol phosphate 6. To an oven-dried reaction tube charged with a magnetic stir bar were added a corresponding compound **5** (0.2 mmol) and dimethyl phosphite **2b** (22 μL, 0.24 mmol). The reactants were dissolved in dried acetonitrile (1 mL) under stirring, followed by the addition of Cs_2CO_3 (70.6 mg, 0.2 mmol). The reaction was kept stirring for 3 h. Water (5 mL) was added to quench the reaction and the mixture was extracted with EtOAc (3 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was then purified through silica

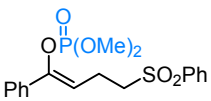
gel column chromatography with petroleum ether/ethyl acetate as eluent to afford compound **6** as colorless oil



Methyl (Z)-5-((dimethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**6a**) was prepared from the reaction of **5a** and dimethyl phosphite **2b** according to the general procedure. Compound **6a** was isolated through silica gel column chromatography as colorless oil (55.3 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.33 – 7.21 (m, 3H), 5.55 (td, *J* = 7.4, 2.0 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.61 (s, 3H), 2.71 – 2.52 (m, 2H), 2.44 (t, *J* = 7.4 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 145.7 (d, *J* = 8.9 Hz), 134.2, 127.6, 127.3, 124.5, 114.5 (d, *J* = 6.5 Hz), 53.8 (d, *J* = 6.0 Hz), 50.6, 32.3 (d, *J* = 2.1 Hz), 20.6 (d, *J* = 1.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.51; IR (KBr) *v* 3003, 2959, 2857, 1736, 1664, 1602, 1579, 1494, 1445, 1367, 1266, 1172, 1041, 904, 853, 800, 770 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{19}O_6PNa$ $[M + Na]^+$ 337.0811, found 337.0811.

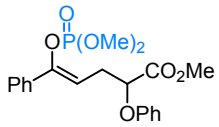


(Z)-Dimethyl (5-oxo-1,5-diphenylpent-1-en-1-yl) phosphate (**6b**) was prepared from the reaction of **5b** and dimethyl phosphite **2b** according to the general procedure. Compound **6b** was isolated through silica gel column chromatography as colorless oil (67.7 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.82 (m, 2H), 7.42 (ddd, *J* = 24.6, 14.4, 7.4 Hz, 5H), 7.31 – 7.17 (m, 3H), 5.65 (td, *J* = 7.6, 2.0 Hz, 1H), 3.64 (d, *J* = 11.3 Hz, 6H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.70 (qd, *J* = 7.4, 2.1 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 145.6 (d, *J* = 8.9 Hz), 135.8, 134.2, 132.1, 127.6, 127.5, 127.3, 127.1, 124.5, 115.2 (d, *J* = 6.5 Hz), 53.8 (d, *J* = 5.9 Hz), 36.8 (d, *J* = 2.2 Hz), 19.9; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.40; IR (KBr) *v* 3061, 2960, 2856, 1685, 1598, 1580, 1494, 1449, 1410, 1366, 1266, 1205, 1184, 1042, 901, 851, 798, 770 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{21}O_5PNa$ $[M + Na]^+$ 383.1019, found 383.1020.

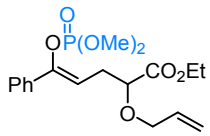


(Z)-Dimethyl (1-phenyl-4-(phenylsulfonyl)but-1-en-1-yl) phosphate (**6c**) was prepared from

the reaction of **5c** and dimethyl phosphite **2b** according to the general procedure. Compound **6c** was isolated through silica gel column chromatography as colorless oil (69.8 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.76 (m, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.28 – 7.21 (m, 3H), 5.47 (td, *J* = 7.7, 2.1 Hz, 1H), 3.58 (d, *J* = 11.4 Hz, 6H), 3.23 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.68 (ddd, *J* = 15.5, 7.8, 1.9 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.8 (d, *J* = 8.8 Hz), 138.1, 133.6, 132.7, 128.3, 127.9, 127.4, 127.1, 124.5, 111.4 (d, *J* = 6.5 Hz), 54.0 (d, *J* = 2.6 Hz), 53.8 (d, *J* = 6.0 Hz), 19.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.52; IR (KBr) *ν* 3063, 2960, 2856, 1714, 1583, 1493, 1448, 1406, 1285, 1185, 1145, 1085, 1043, 900, 853, 796, 768 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_6PSNa$ $[M + Na]^+$ 419.0689, found 419.0687.

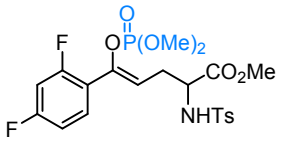


Methyl (Z)-5-((dimethoxyphosphoryl)oxy)-2-phenoxy-5-phenylpent-4-enoate (**6d**) was prepared from the reaction of **5d** and dimethyl phosphite **2b** according to the general procedure. Compound **6d** was isolated through silica gel column chromatography as colorless oil (69.9 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.46 – 7.21 (m, 5H), 7.05 – 6.81 (m, 3H), 5.77 (td, *J* = 7.4, 2.0 Hz, 1H), 4.82 (dd, *J* = 7.6, 5.1 Hz, 1H), 3.89 – 3.60 (m, 9H), 3.13 – 3.04 (m, 1H), 2.99 (ddd, *J* = 15.3, 7.6, 2.5 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 157.7, 148.0 (d, *J* = 9.0 Hz), 135.0, 129.6, 128.8, 128.4, 125.7, 121.9 (d, *J* = 7.7 Hz), 115.2, 111.2 (d, *J* = 6.6 Hz), 75.8, 54.9 (d, *J* = 6.0 Hz), 52.4, 29.8; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.50; IR (KBr) *ν* 3062, 3032, 2957, 2855, 1755, 1665, 1594, 1493, 1446, 1364, 1281, 1236, 1204, 1042, 895, 852, 758 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{23}O_7PNa$ $[M + Na]^+$ 429.1074, found 429.1071.



Ethyl (Z)-2-(allyloxy)-5-((dimethoxyphosphoryl)oxy)-5-phenylpent-4-enoate (**6e**) was prepared from the reaction of **5e** and dimethyl phosphite **2b** according to the general procedure. Compound **6e** was isolated through silica gel column chromatography as colorless oil (56.1 mg,

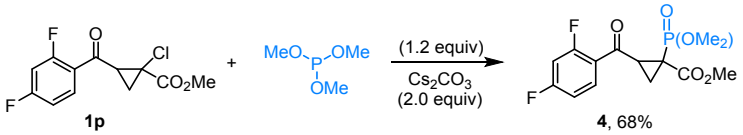
73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 17.9, 8.0, 1.5 Hz, 2H), 7.42 – 7.32 (m, 3H), 6.00 – 5.85 (m, 1H), 5.78 – 5.67 (m, 1H), 5.36 – 5.17 (m, 2H), 4.29 – 4.13 (m, 2H), 4.03 – 3.90 (m, 2H), 3.80 – 3.68 (m, 6H), 2.97 – 2.73 (m, 1H), 2.69 – 2.55 (m, 1H), 1.34 – 1.19 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.0, 147.5 (d, *J* = 9.1 Hz), 134.0, 128.6, 128.3, 125.6, 117.8, 111.9 (d, *J* = 6.7 Hz), 71.4 (d, *J* = 7.3 Hz), 61.0, 54.8 (d, *J* = 5.9 Hz), 31.1, 29.8, 14.2; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.53; IR (KBr) *v* 3061, 2983, 2959, 2858, 1744, 1665, 1579, 1494, 1449, 1374, 1276, 1191, 1110, 1043, 927, 906, 853, 771 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{25}O_7PNa$ $[M + Na]^+$ 407.1230, found 407.1231.



Methyl (Z)-5-(4-chlorophenyl)-5-((dimethoxyphosphoryl)oxy)-2-((4-methylphenyl)sulfonamide)pent-4-enoate (**6g**) was prepared from the reaction of **5g** and dimethyl phosphite **2b** according to the general procedure. Compound **6g** was isolated through silica gel column chromatography as colorless oil (46.3mg, 89% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.40 (td, *J* = 8.6, 6.3 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.86 (td, *J* = 8.1, 2.2 Hz, 1H), 6.80 (ddd, *J* = 11.0, 8.6, 2.6 Hz, 1H), 5.43 (td, *J* = 7.6, 1.6 Hz, 1H), 4.23 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.72 (d, *J* = 11.4 Hz, 3H), 3.68 (s, 3H), 3.68 (d, *J* = 11.4 Hz, 3H), 3.13 (dddd, *J* = 14.4, 7.0, 4.8, 1.9 Hz, 1H), 2.90 (dddd, *J* = 14.4, 10.4, 7.3, 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.0, 163.1 (dd, *J* = 252.0, 11.8 Hz), 159.9 (dd, *J* = 254.1, 12.0 Hz), 145.5, 142.5 (dd, *J* = 8.8, 3.0 Hz), 134.2, 130.7 (dd, *J* = 9.7, 3.9 Hz), 129.7, 129.3, 119.3 (dd, *J* = 13.0, 3.3 Hz), 114.9 (t, *J* = 6.8 Hz), 111.4 (dd, *J* = 21.4, 3.6 Hz), 104.4 (t, *J* = 25.9 Hz), 69.3, 55.0 – 54.9 (m), 53.0, 23.6, 21.7; ^{31}P NMR (243 MHz, $CDCl_3$) δ -3.99 (hept, *J* = 12.5, 11.8 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -107.82 (p, *J* = 8.2 Hz), -109.08 (q, *J* = 9.3 Hz); IR (KBr) *v* 3488, 3007, 2959, 2857, 1748, 1616, 1596, 1503, 1430, 1281, 1145, 1024, 853, 780 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{25}NO_8PS$ $[M + H]^+$ 520.1001,found 520.1002

IV. Mechanistic Related Control Experiments

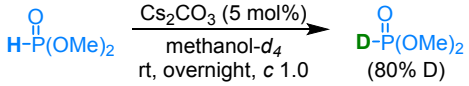
a. Cs_2CO_3 promoted reaction of 1d with trimethyl phosphite



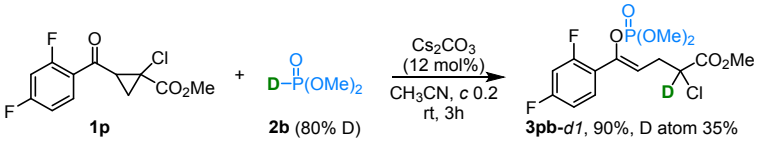
To an oven-dried reaction tube charged with a magnetic stir bar were added methyl 2-(2,4-difluorobenzoyl)-1-chlorocyclopropane-1-carboxylate **1p** (54.8 mg, 0.2 mmol) and trimethyl phosphite (28.4 μL, 0.24 mmol). The reactants were dissolved in dried acetonitrile (1 mL) under stirring, followed by the addition of Cs_2CO_3 (141.2 mg, 0.4 mmol). The reaction was kept stirring for 3 h. Water (5 mL) was added to quench the reaction and the mixture was extracted with EtOAc (3 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was then purified through silica gel column chromatography with petroleum ether/ethyl acetate as eluent to afford compound **4** as colorless oil (45.2 mg, 68% yield).

Methyl 2-(2,4-difluorobenzoyl)-1-(dimethoxyphosphoryl)cyclopropane-1-carboxylate (**4**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (td, *J* = 8.6, 6.5 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.91 (ddd, *J* = 11.0, 8.6, 2.4 Hz, 1H), 3.86 (d, *J* = 11.0 Hz, 3H), 3.83 (d, *J* = 11.0 Hz, 3H), 3.70 (s, 3H), 3.33 (dddd, *J* = 15.3, 8.6, 6.4, 2.3 Hz, 1H), 2.15 (dddd, *J* = 13.2, 5.9, 4.4, 1.1 Hz, 1H), 1.85 (ddd, *J* = 16.3, 8.6, 4.4 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.8 (t, *J* = 3.5 Hz), 166.7 (d, *J* = 5.5 Hz), 166.1 (dd, *J* = 258.0, 12.3 Hz), 162.7 (dd, *J* = 258.5, 12.7 Hz), 132.8 (dd, *J* = 10.7, 3.7 Hz), 122.4 (dd, *J* = 12.1, 3.5 Hz), 112.4 (dd, *J* = 21.5, 3.4 Hz), 105.0 (t, *J* = 26.3 Hz), 53.9 (dd, *J* = 6.2, 1.7 Hz), 53.1, 53.8 (d, *J* = 6.1 Hz), 31.3 (d, *J* = 180.7 Hz), 31.2 (dd, *J* = 9.0, 2.6 Hz), 18.2 (d, *J* = 3.8 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.79 – 22.32 (m); ^{19}F NMR (565 MHz, $CDCl_3$) δ -100.62 (dq, *J* = 14.6, 7.4 Hz), -105.30 (q, *J* = 10.9 Hz); IR (KBr) *v* 3481, 3100, 3015, 2959, 2855, 1737, 1681, 1611, 1489, 1432, 1305, 1252, 1208, 1147, 1102, 1031, 973, 875, 781 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{15}F_2O_6PNa$ $[M + Na]^+$ 371.0467, found 371.0467.

b. Deturated dimethylphosphite

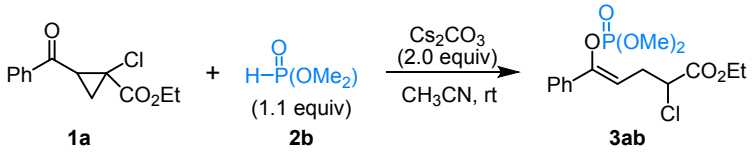


Deuturated dimethyl phosphite was prepared through the proton exchange between dimethyl phosphite and methanol-d4 with catalytic amount of cesium carbonate. After filtration and concentration *in vacuo*, the content was determined to be 80% by ^{1}H NMR.



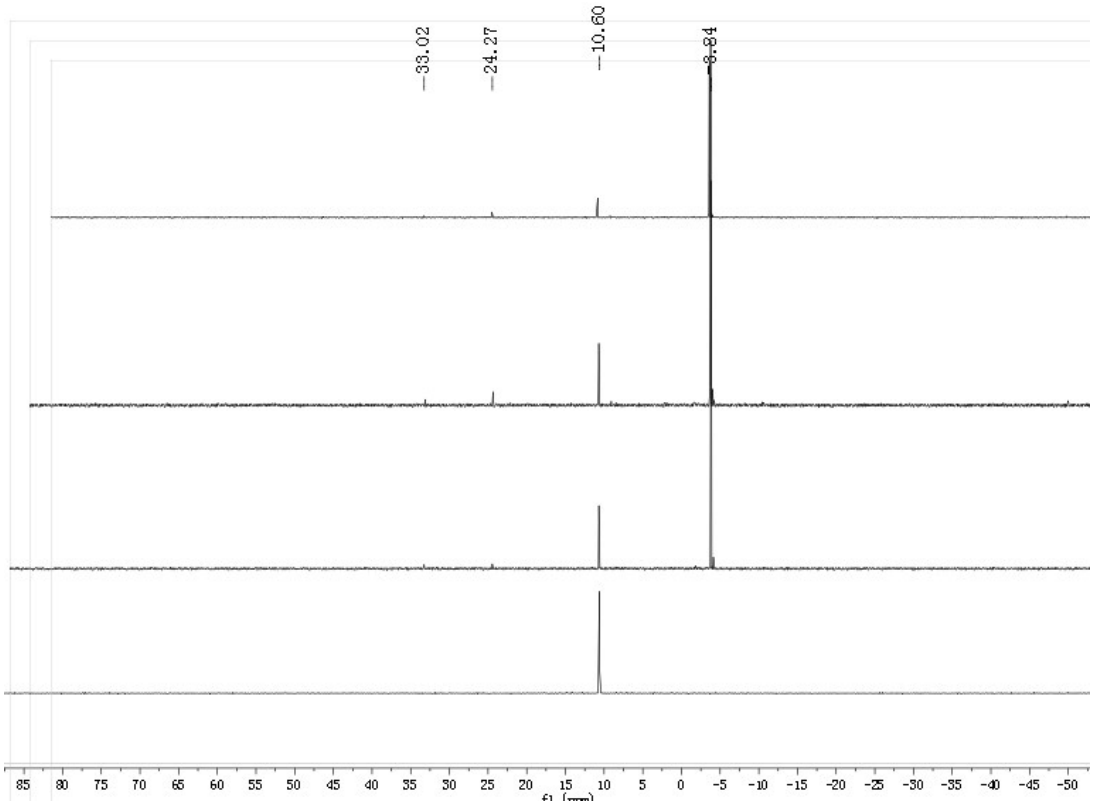
To an oven-dried reaction tube charged with a magnetic stir bar and anhydrous Cs_2CO_3 (6.5 mg) were added anhydrous acetonitrile (0.3 mL) and trimethyl phosphite-*d1* (28.5 μL, 0.24 mmol, 80% D-labelled). The mixture was stirred for 5 minutes at room temperature, followed by the addition of an solution of ethyl 2-(2,4-difluorobenzoyl)-1-chlorocyclopropane-1-carboxylate **1p** (53.3 mg, 0.2 mmol, dissolved in 0.7 mL of anhydrous acetonitrile). The reaction was kept stirring for 3 h and diluted with a 1:1 mixture hexanes/EtOAc. The insoluble salt was removed through filtration and the filtrate was concentrated *in vacuo*. The residue was then submitted for ^{1}H NMR analysis with trimethoxybenzene as an internal standard.

c. ^{31}P NMR monitoring of the reaction process.



To an oven-dried reaction tube charged with a magnetic stir bar were added ethyl 2-benzoyl-1-chlorocyclopropane-1-carboxylate **1a** (50.5 mg, 0.2 mmol), dimethyl phosphite **2b** (26 μL, 0.22 mmol) and anhydrous CH_3CN (1 mL). After 10 μL of reaction mixture was taken and diluted in $CDCl_3$ (0.5 mL) to make the first sample, Cs_2CO_3 (141.6 mg, 0.4 mmol) was added to start the reaction. Three additional aliquots (10 μL) were taken at 20, 40 and 60 min, respectively, filtered through a 0.45 μm nylon membrane and washed with $CDCl_3$ (0.5 mL). The samples obtained at different time point were immediately submitted for ^{31}P{^{1}H} NMR analysis and the stacked spectra were presented below. As we can see, other than the starting material **2b** (ppm 10.6), the final product **3ab** (ppm -3.84) was observed as the major species in the mixture. Only very limited

amount of other phosphor-related species (ppm 33.02, 24.27) were detected during the reaction process, which disappeared again as the reaction reached completion.

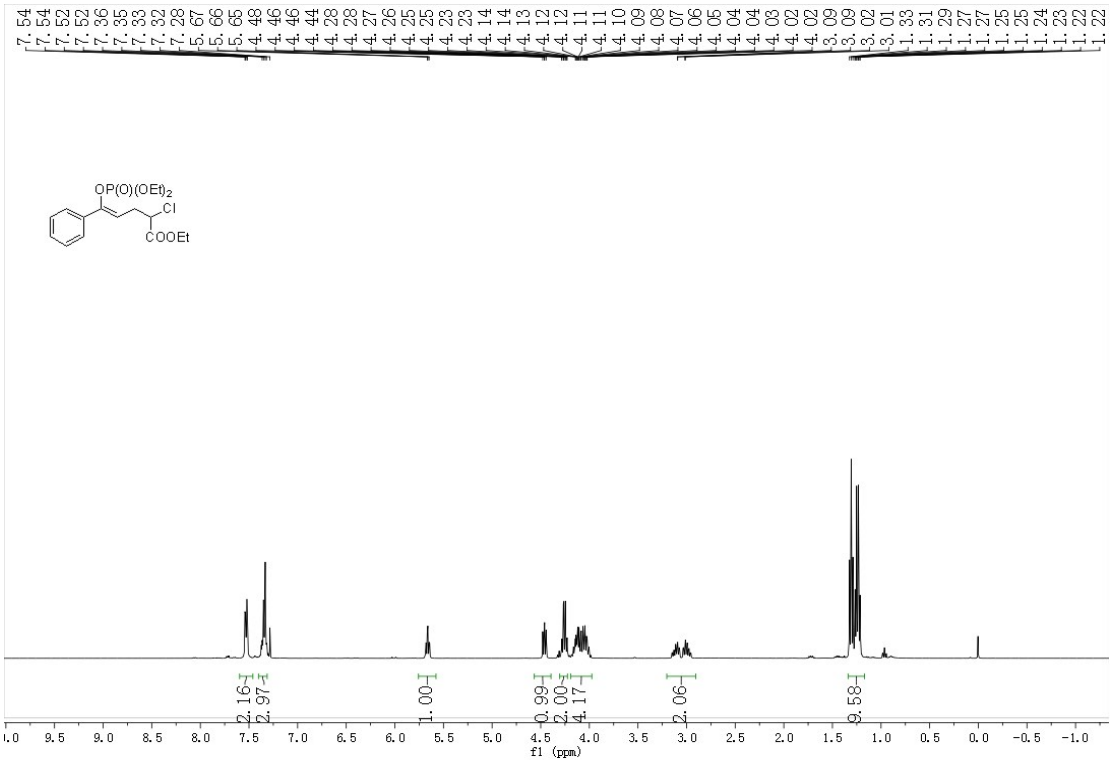


V. References

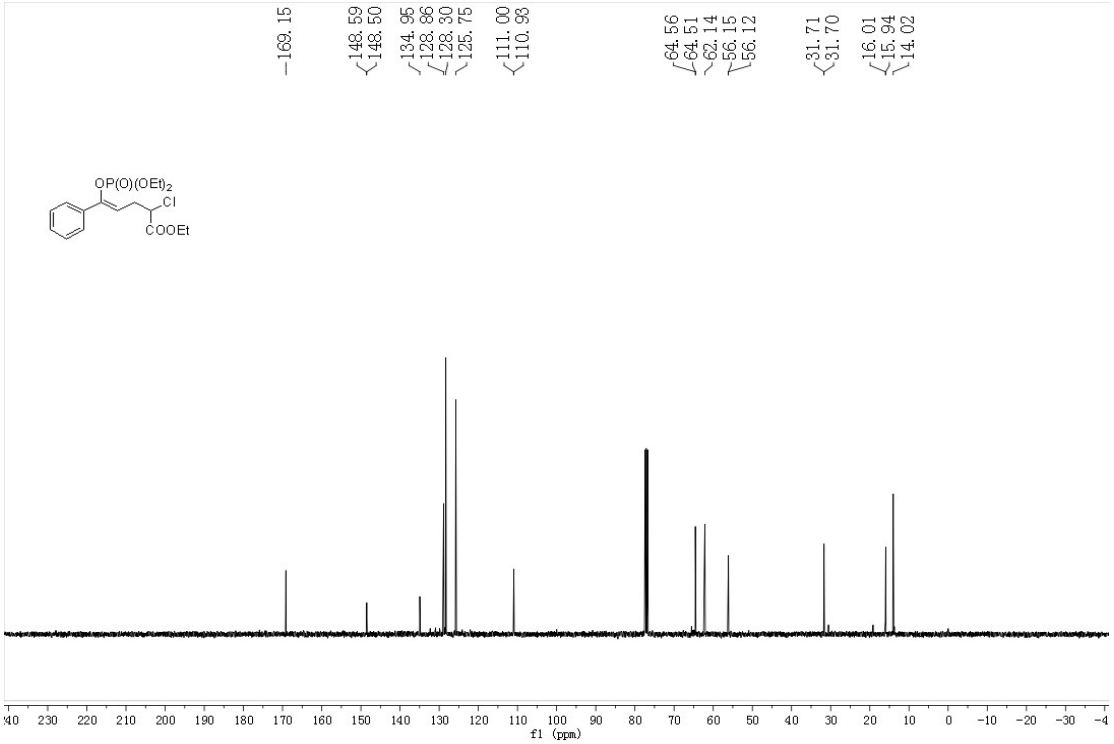
1. (a) M. Zhang, Y. Gong and W. Wang, *Eur. J. Org. Chem.*, 2013, **2013**, 7372-7381; (b) Y. Zhu, P. Xu and Y. Gong, *J. Org. Chem.*, 2016, **81**, 4829-4834; (c) Y. Zhu and Y. Gong, *Tetrahedron*, 2016, **72**, 3436-3442.

VI. NMR Spectra

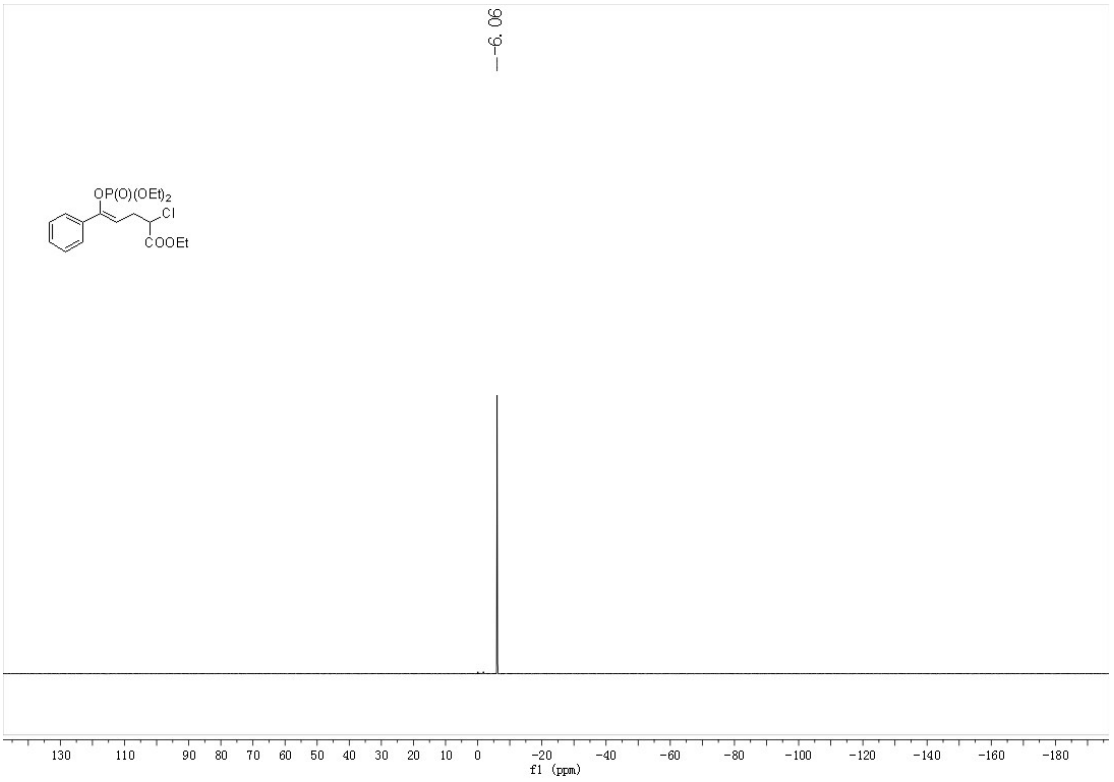
3aa ^{1}H NMR (400 MHz, $CDCl_3$)



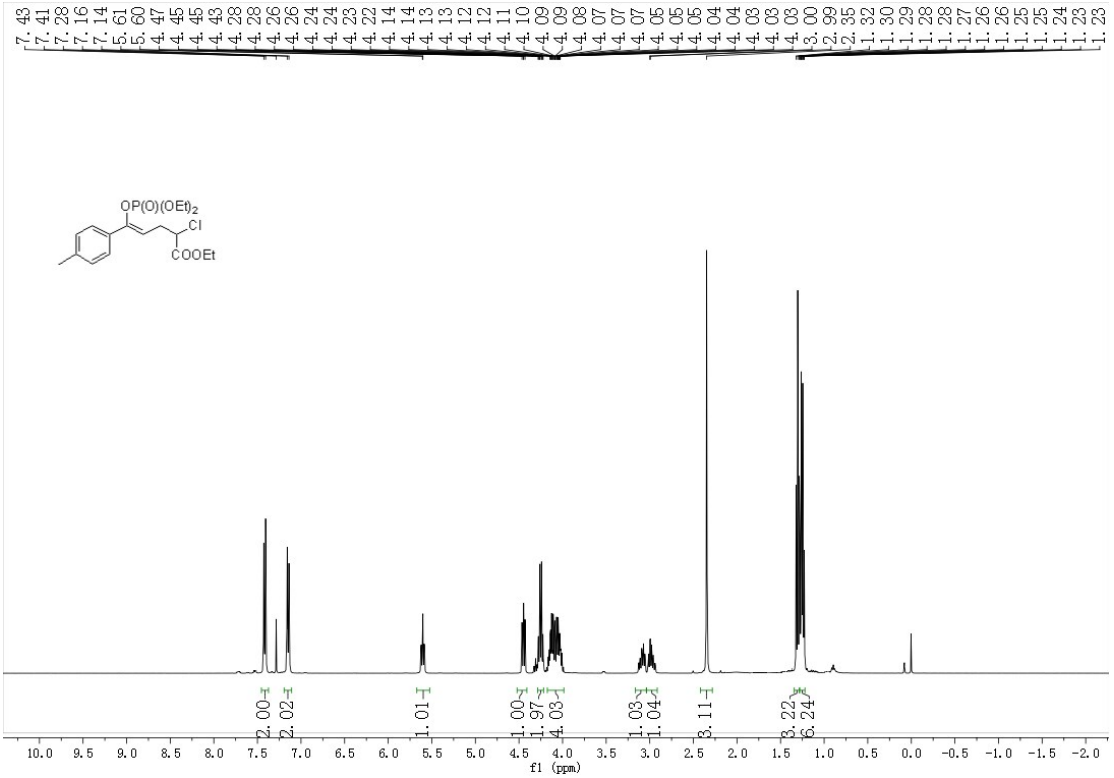
3aa $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



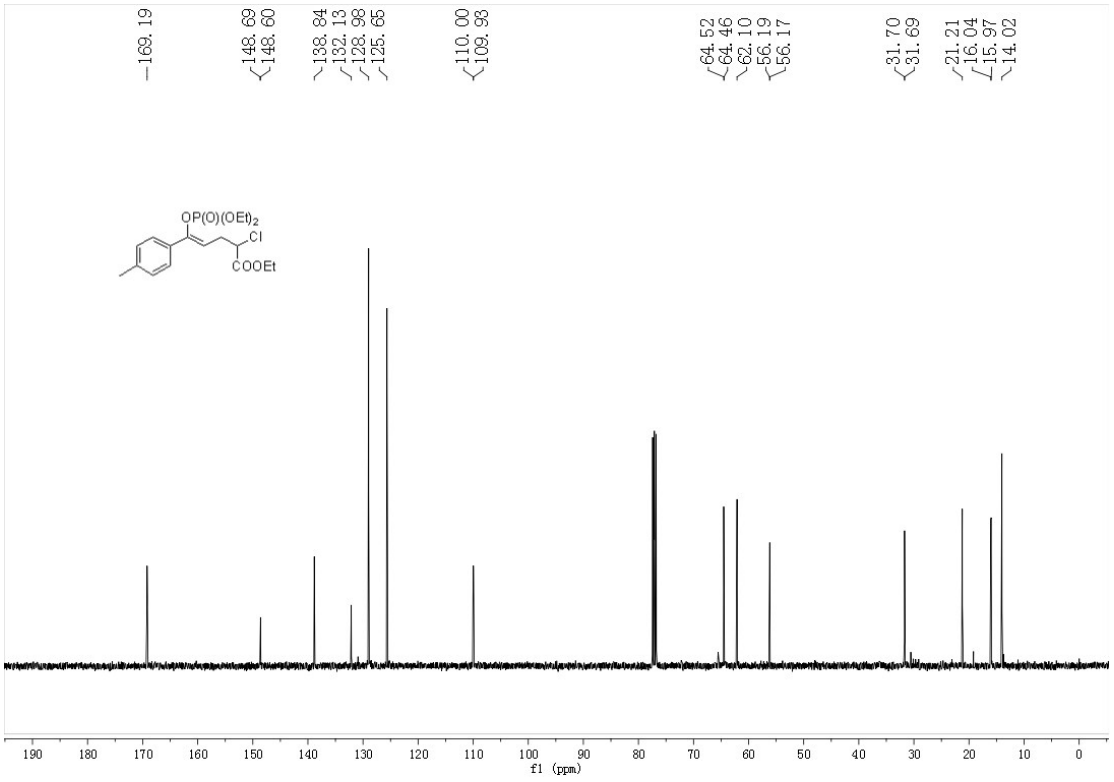
3aa $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



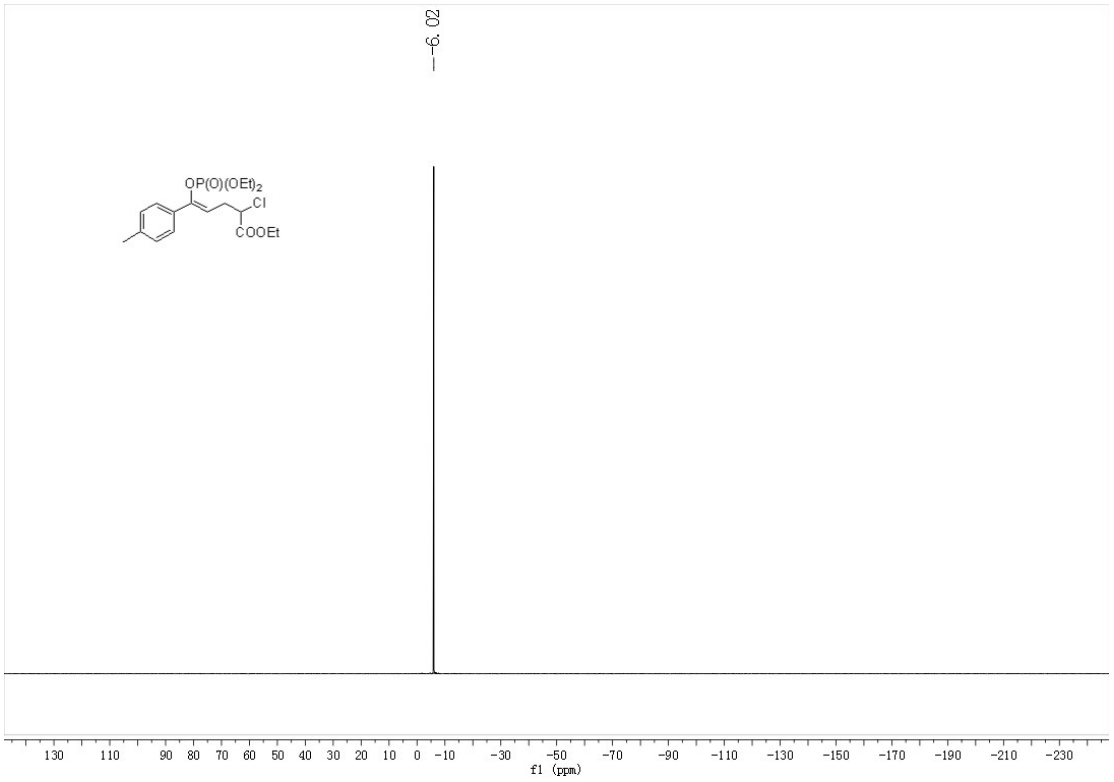
3ba ^{1}H NMR (400 MHz, $CDCl_3$)



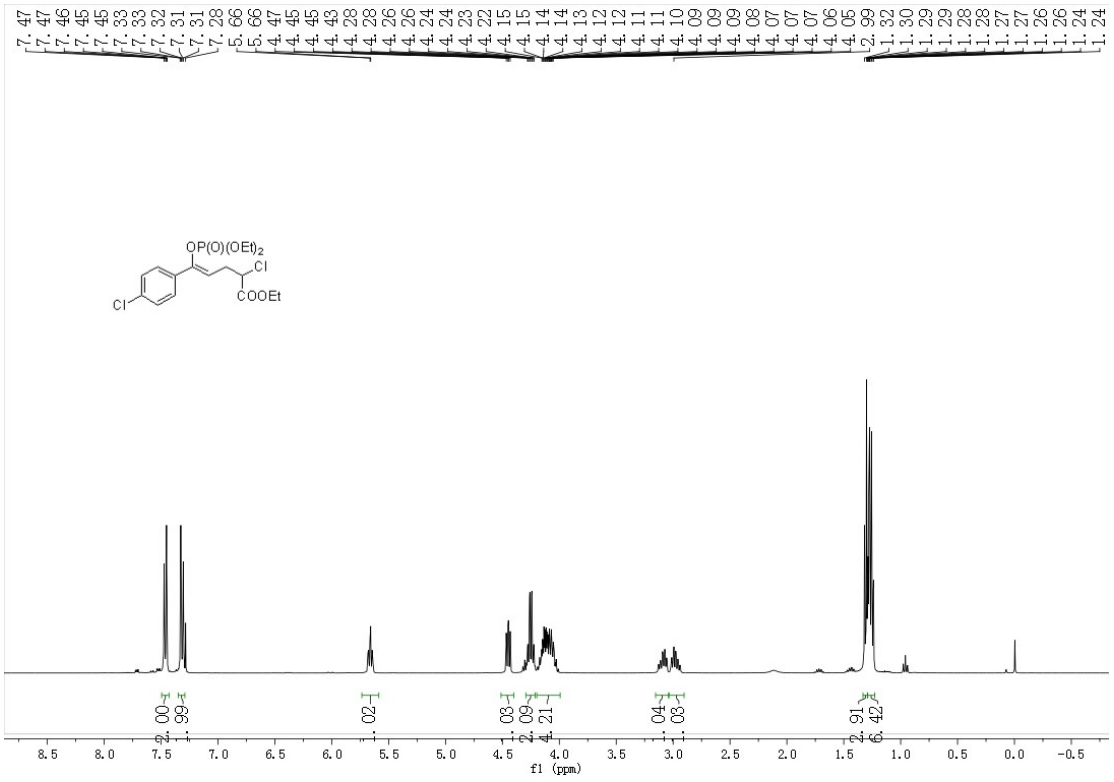
3ba $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



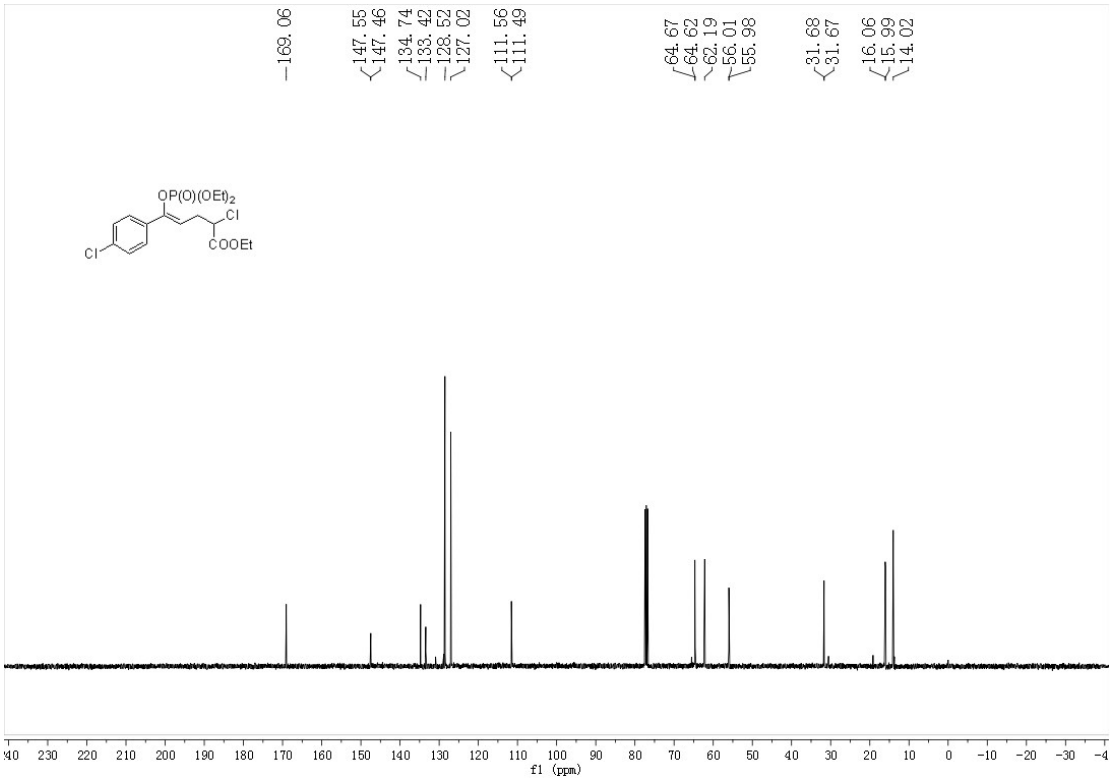
3ba $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



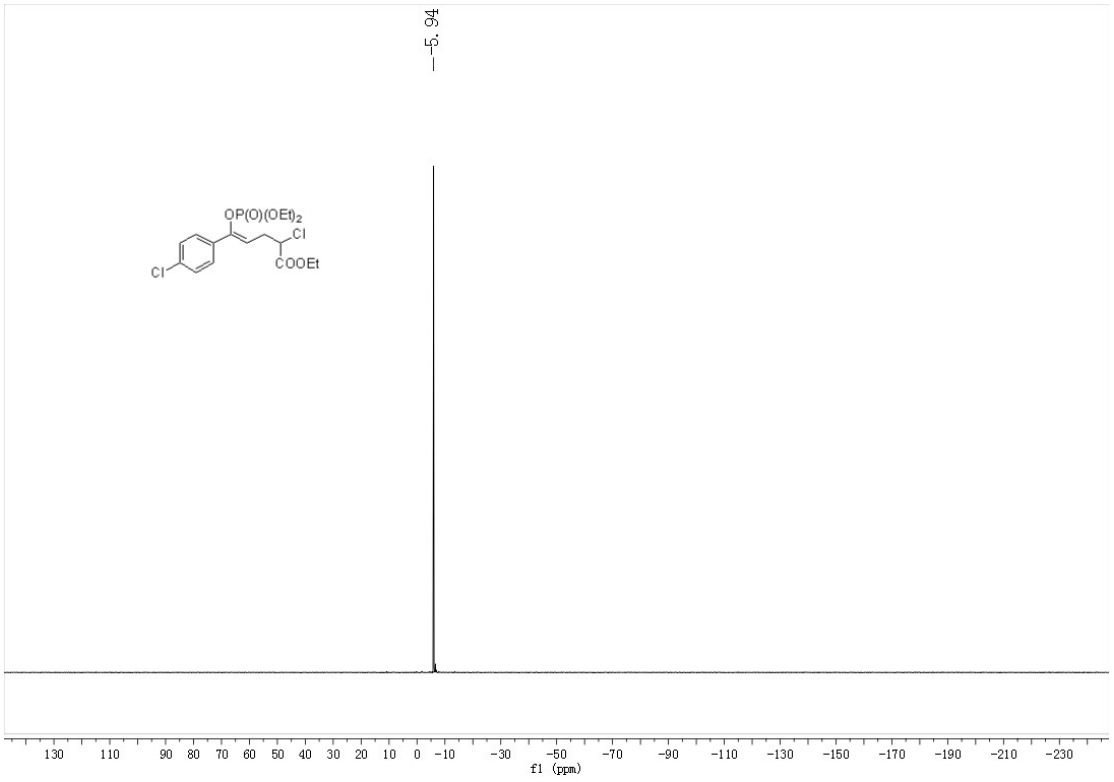
3da ^{1}H NMR (400 MHz, $CDCl_3$)



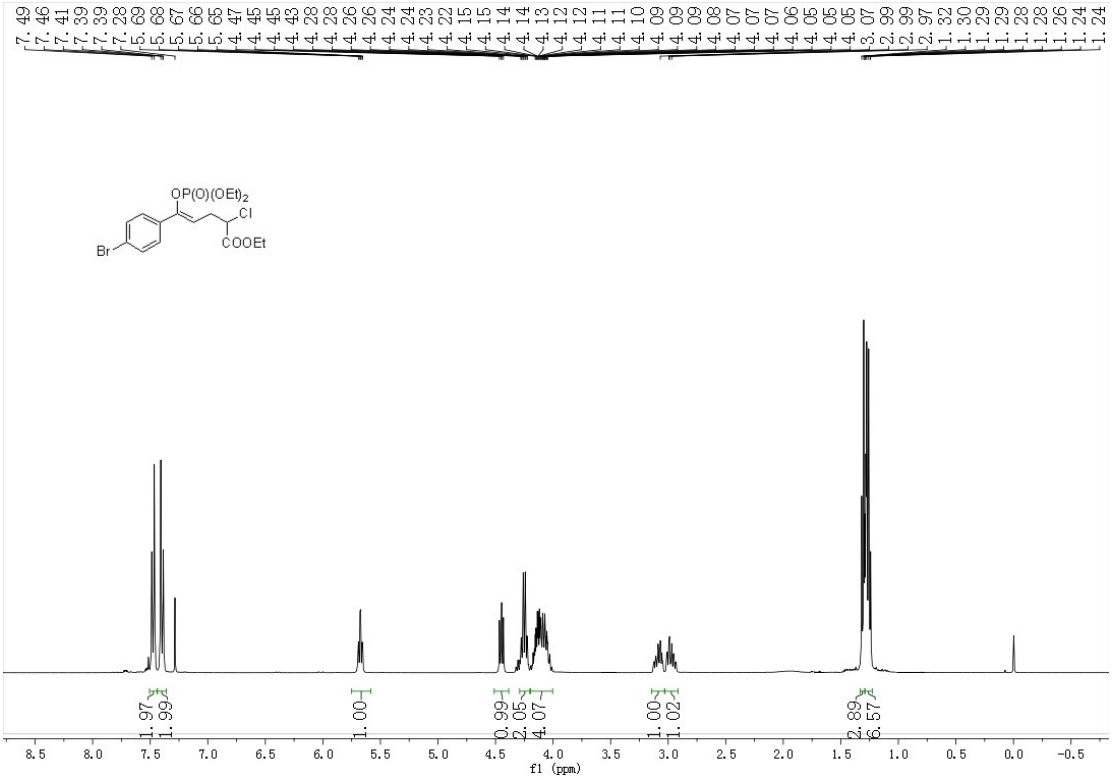
3da $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



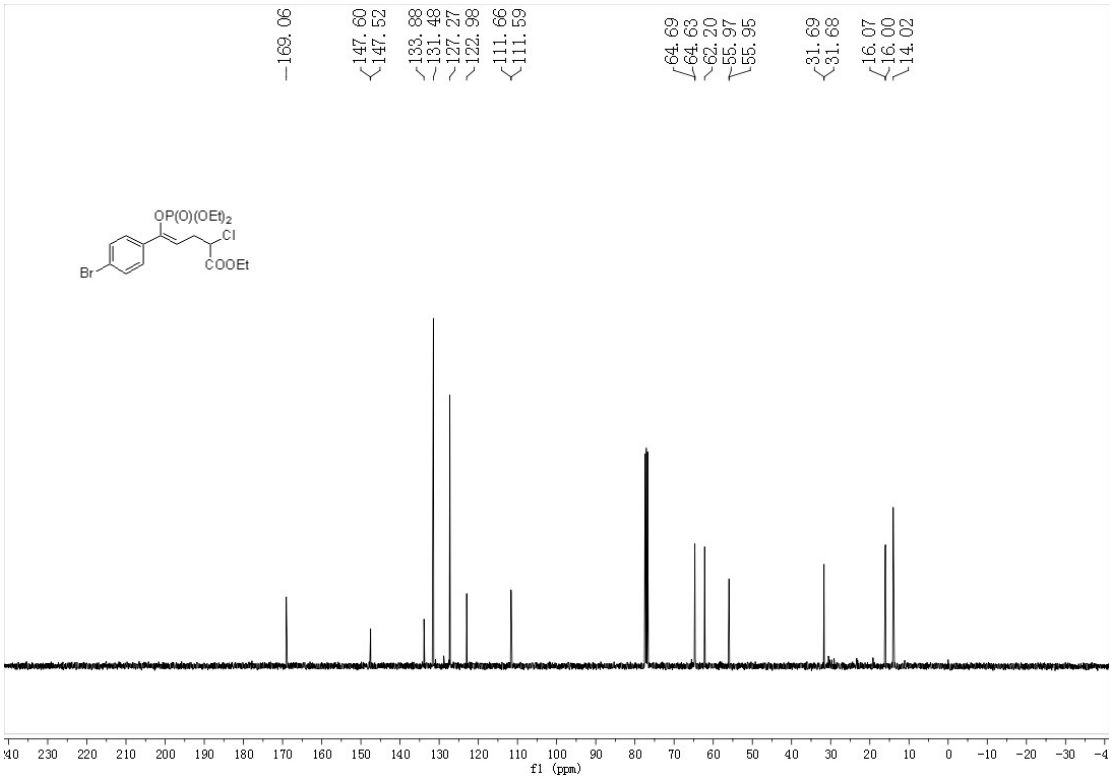
3da $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



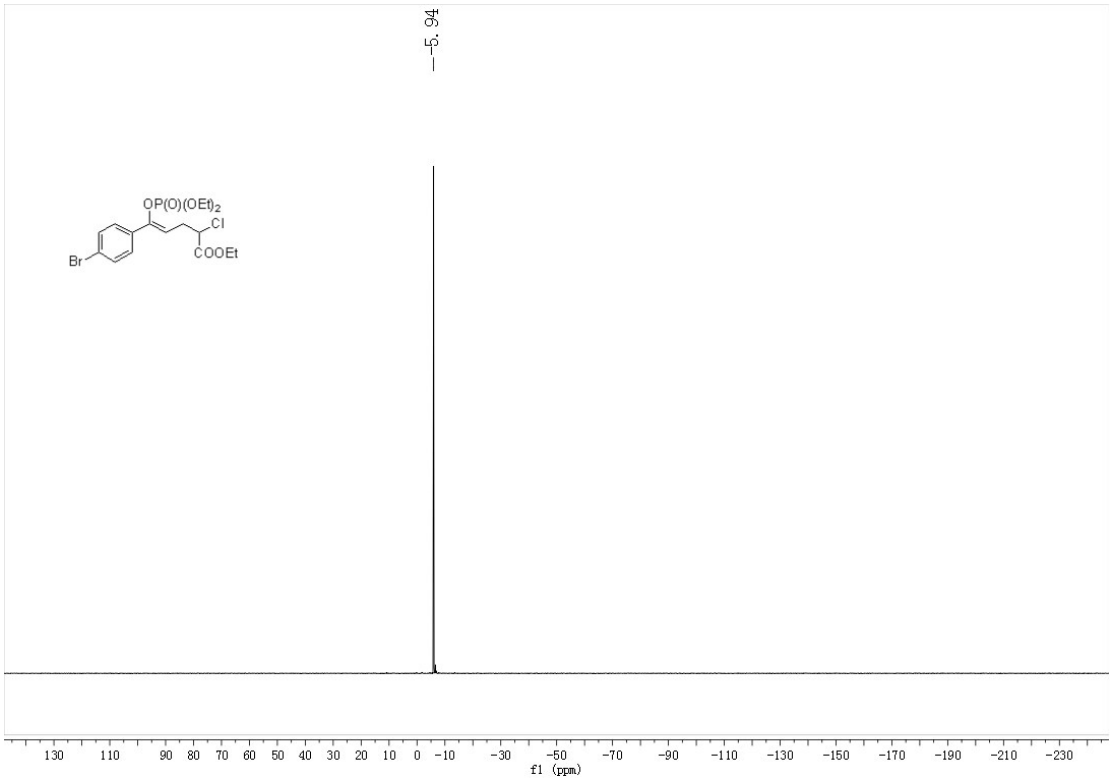
3ea ^{1}H NMR (400 MHz, $CDCl_3$)



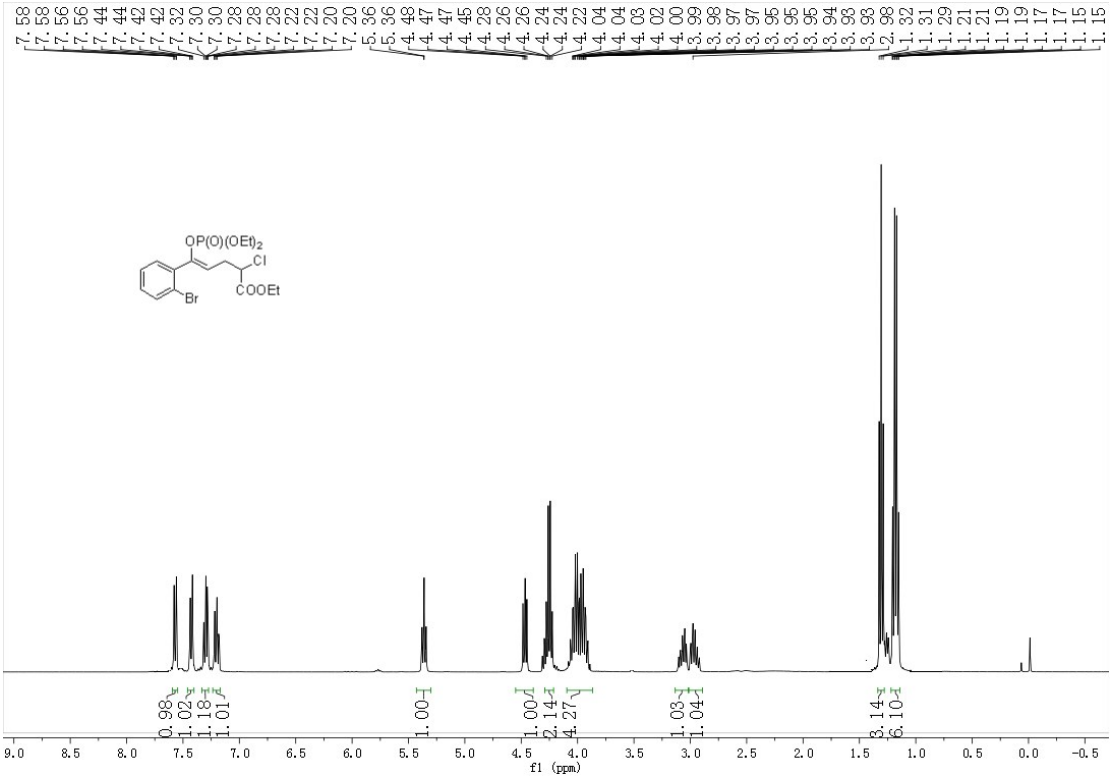
3ea $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



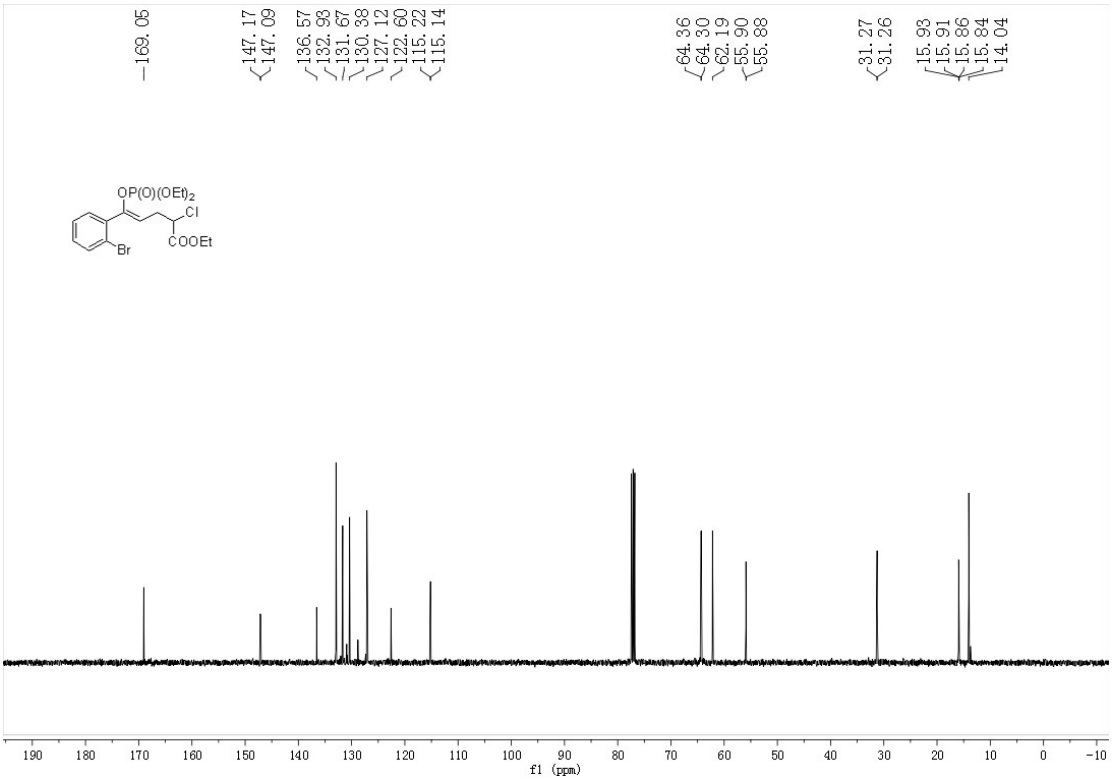
3ea $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



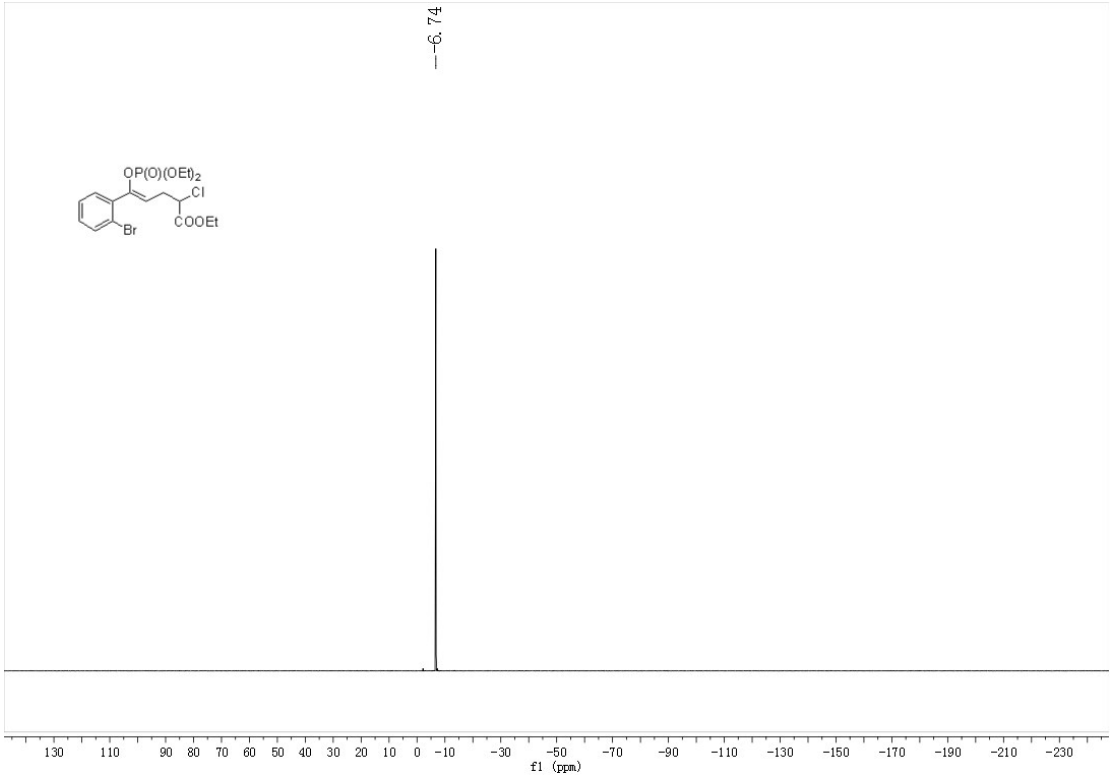
3fa ^{1}H NMR (400 MHz, $CDCl_3$)



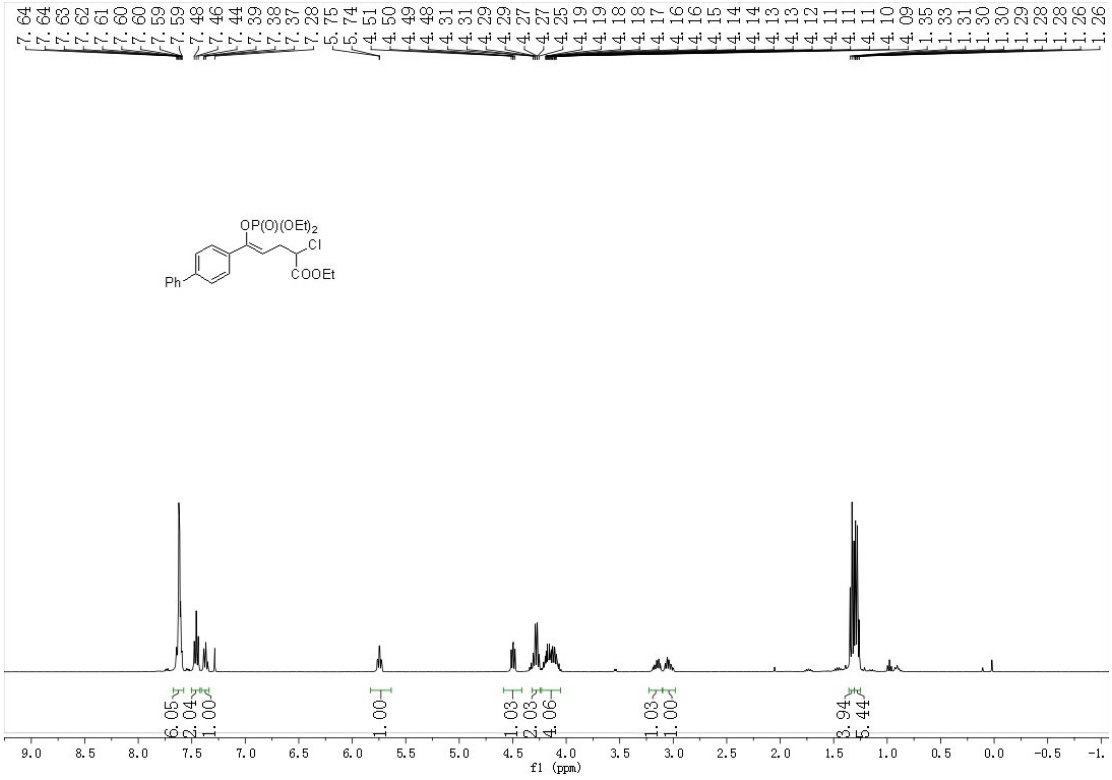
3fa $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



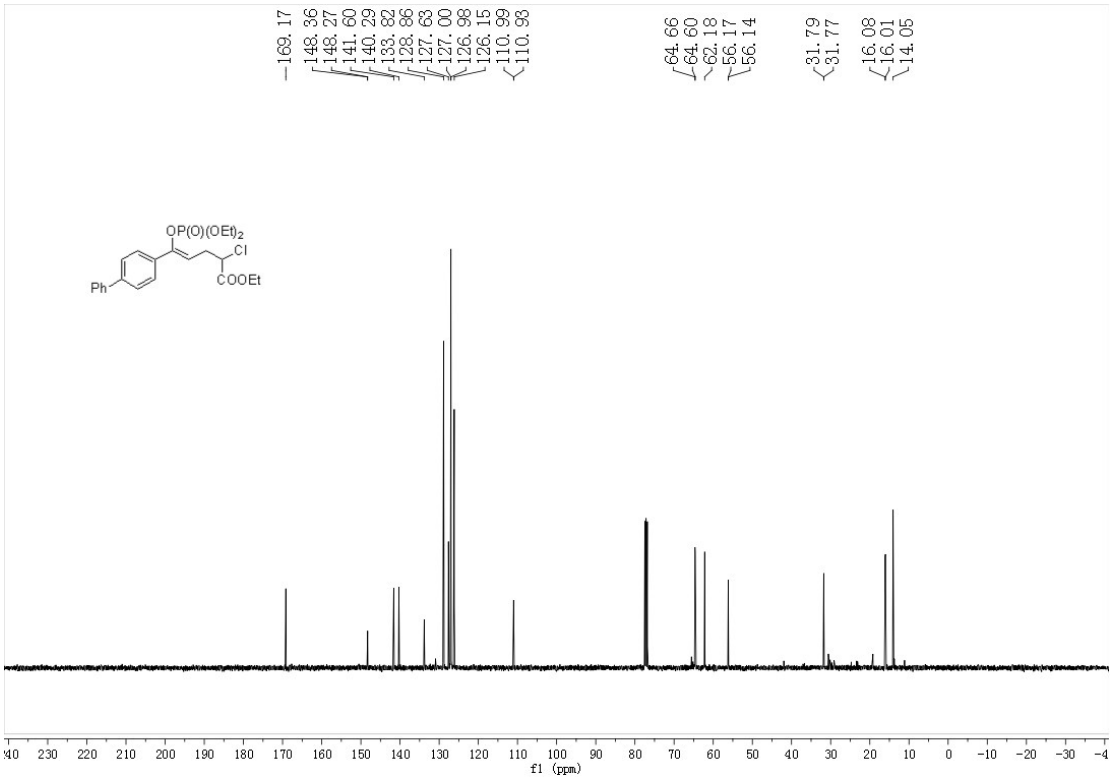
3fa $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



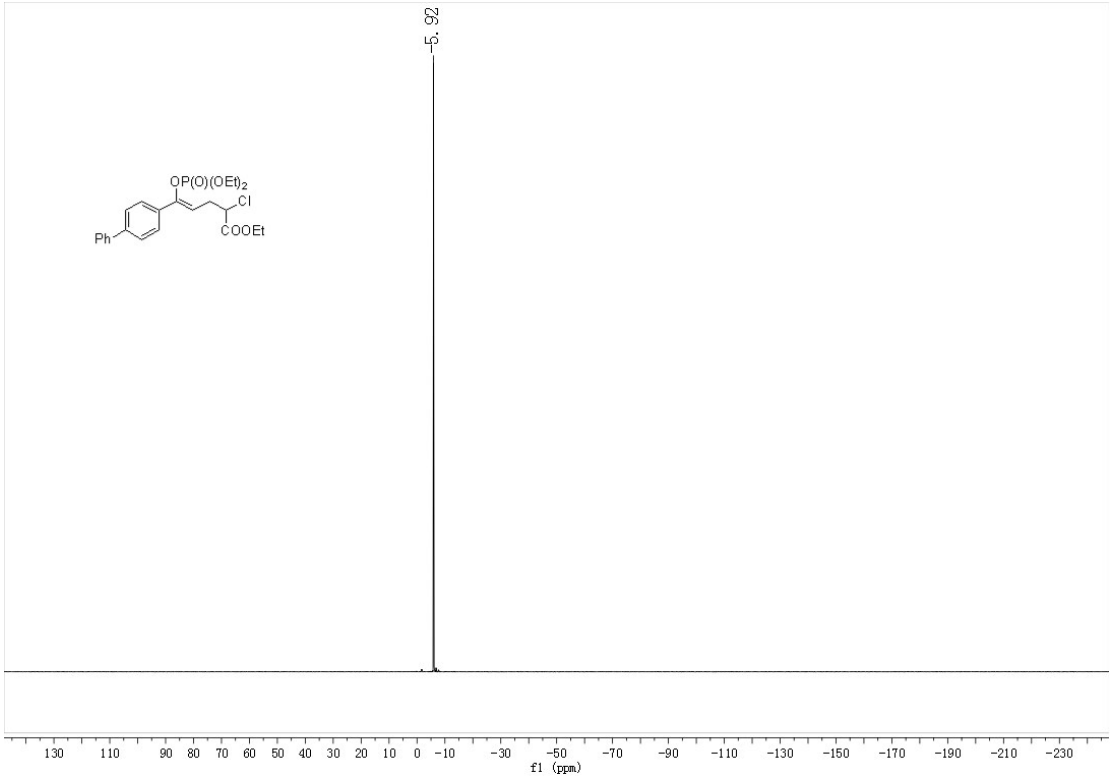
3ga ^{1}H NMR (400 MHz, $CDCl_3$)



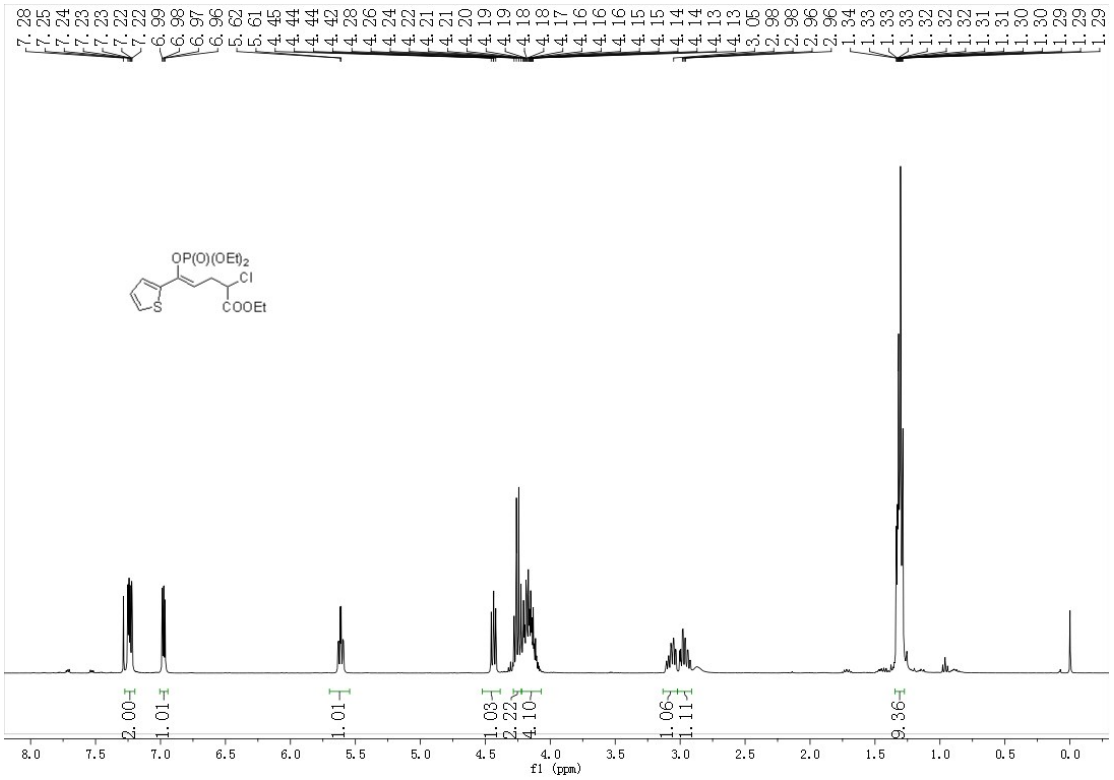
3ga $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



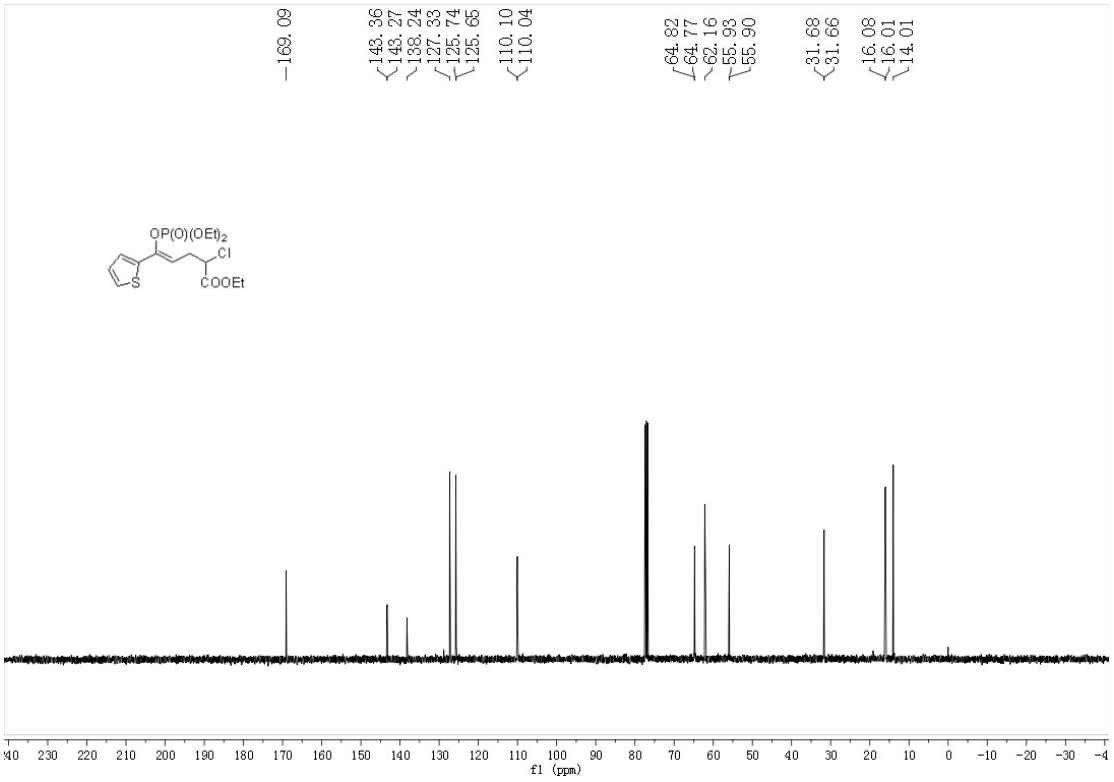
3ga $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



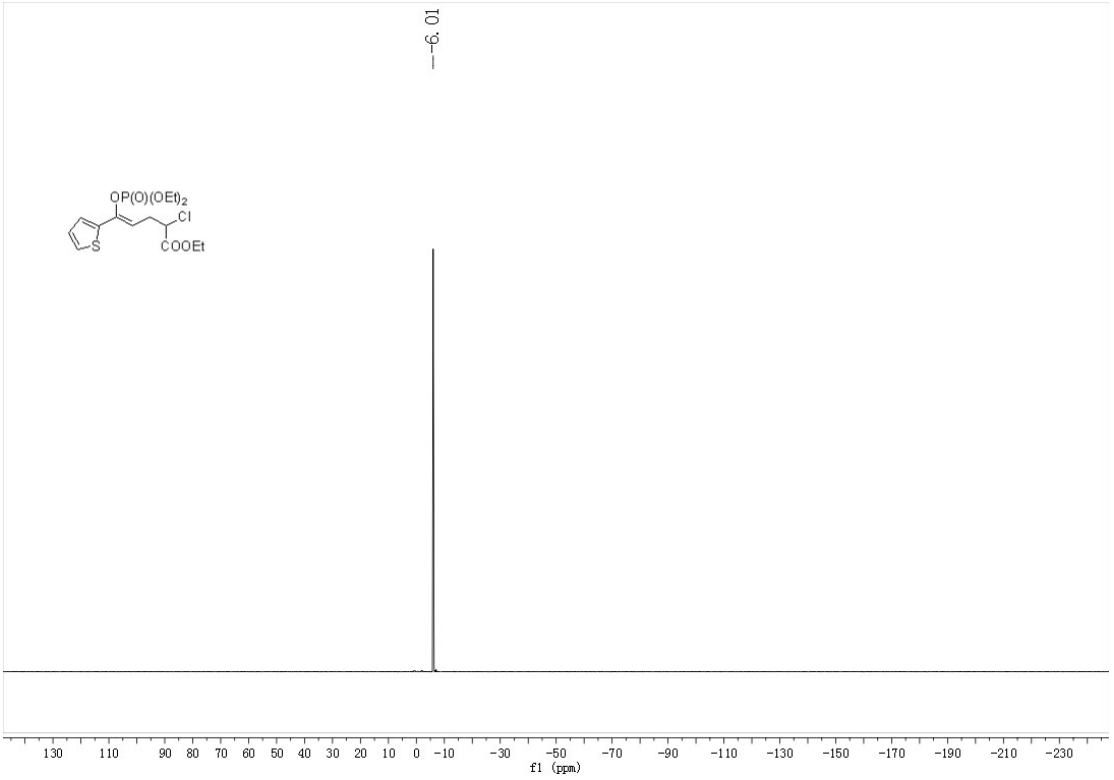
3ha ^{1}H NMR (400 MHz, $CDCl_3$)



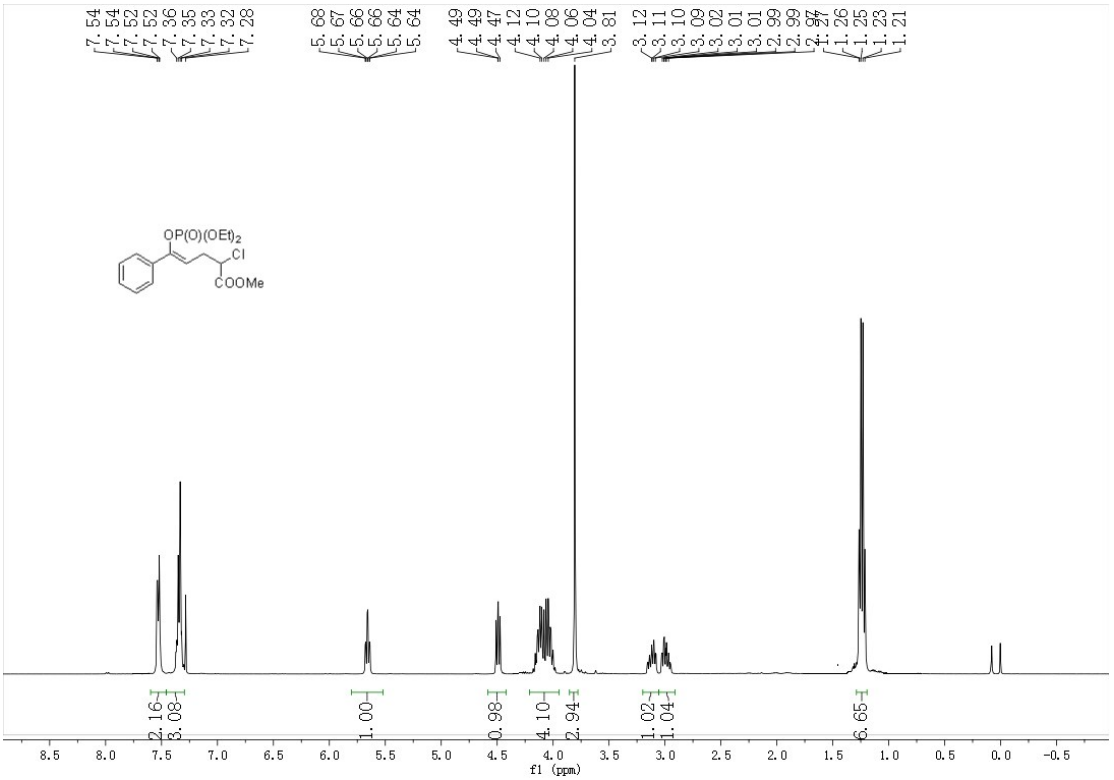
3ha $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3ha $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



3ja ^{1}H NMR (400 MHz, $CDCl_3$)



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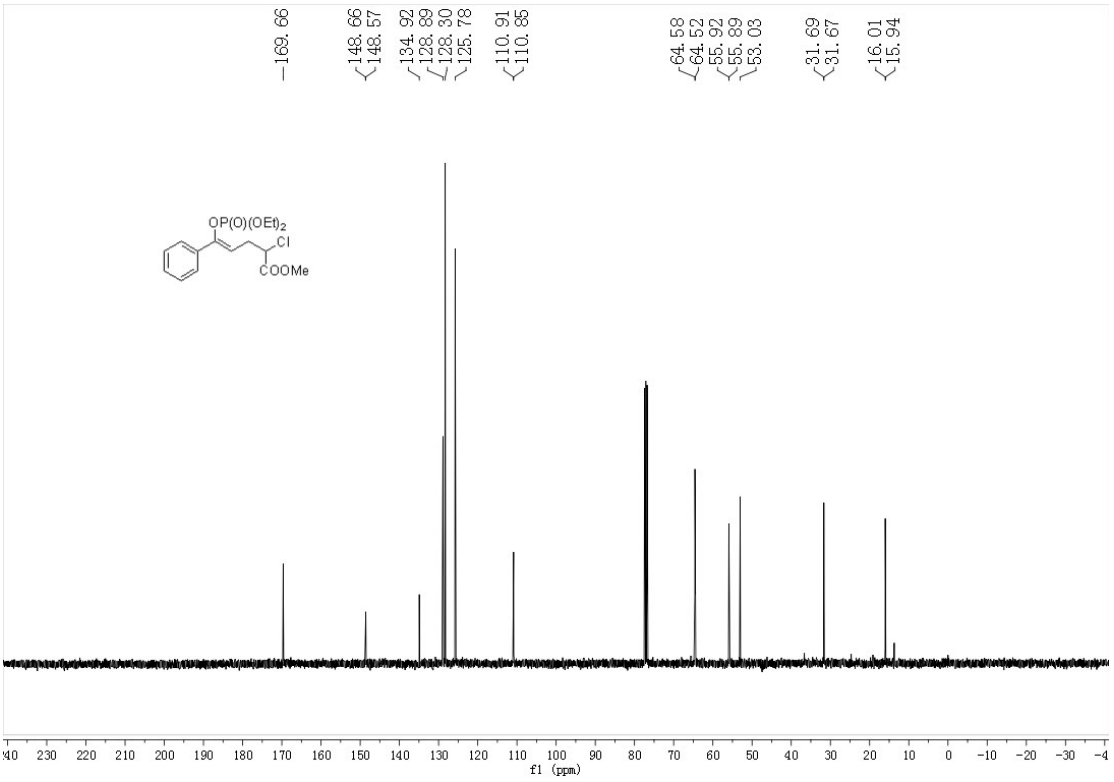

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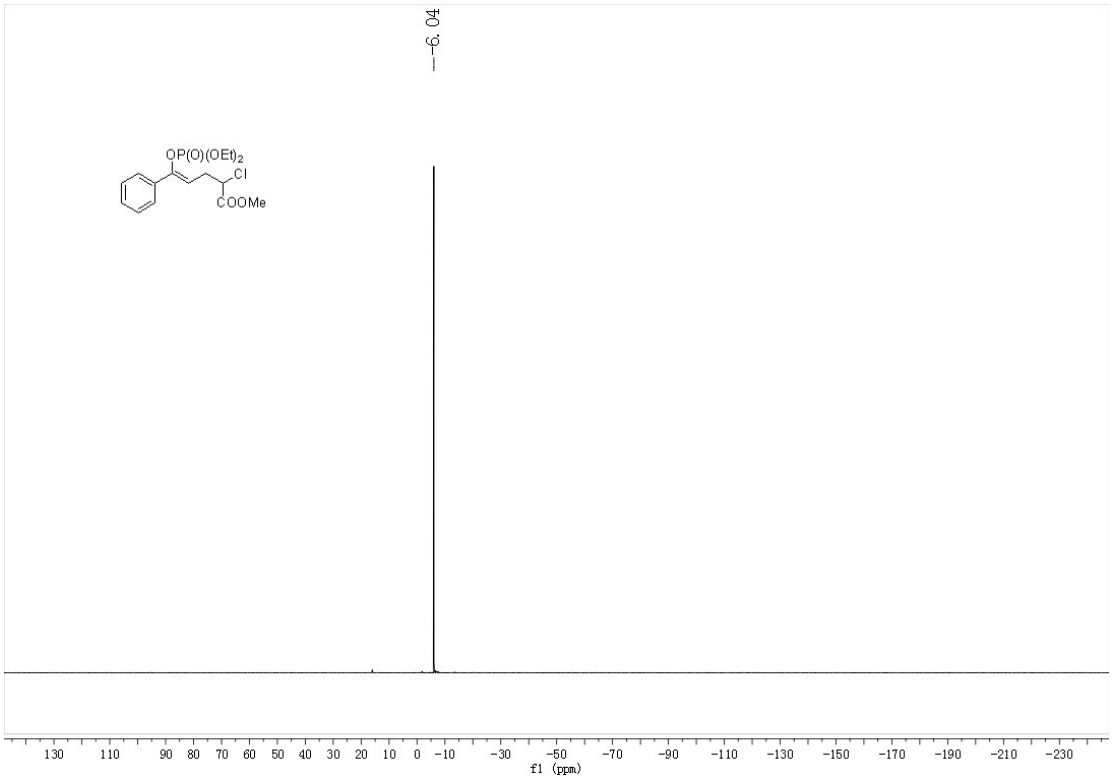

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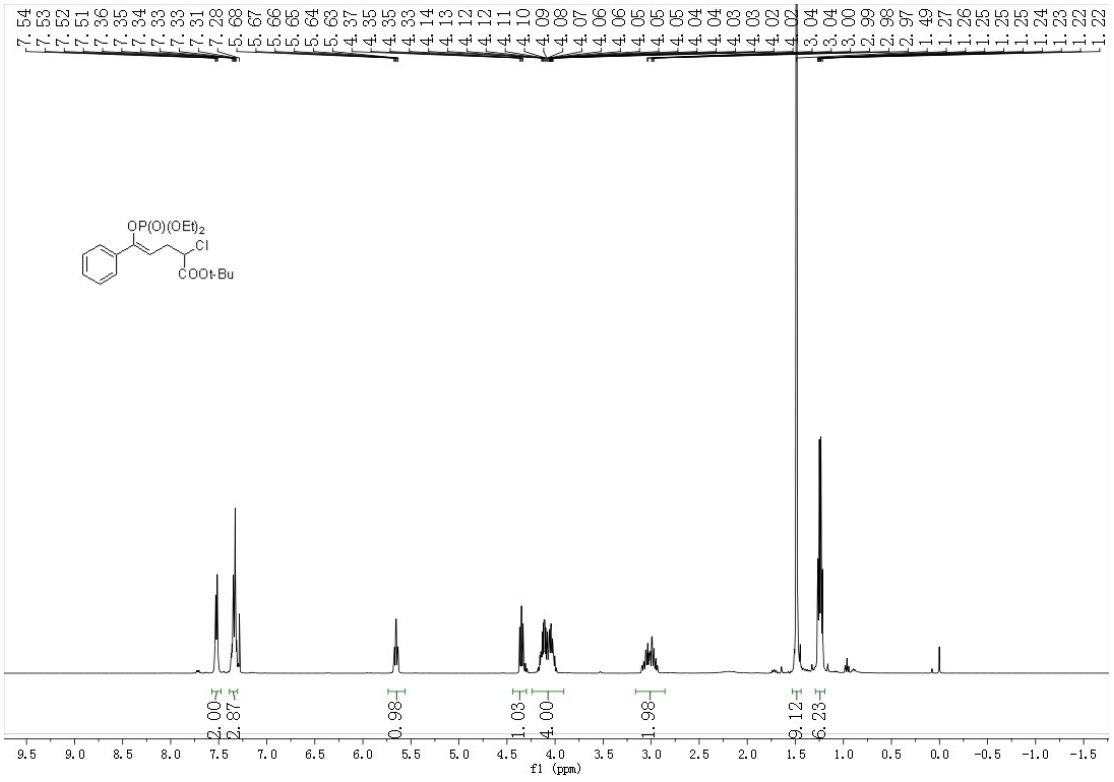

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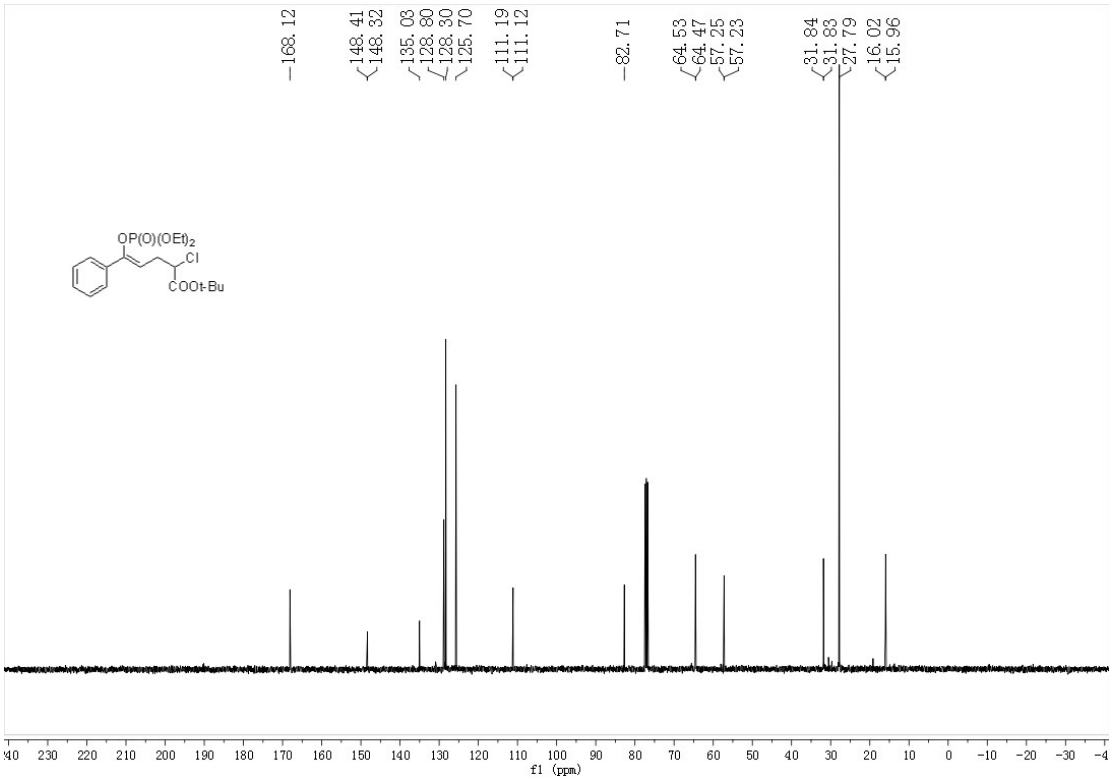
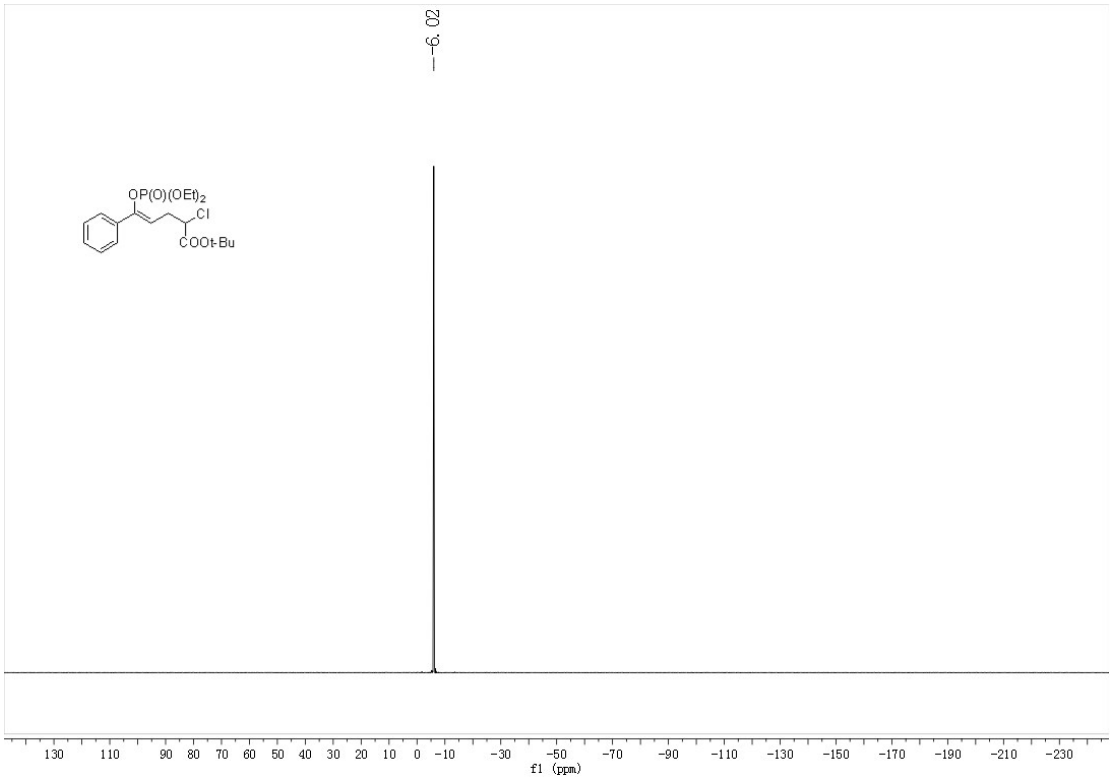


3ka $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



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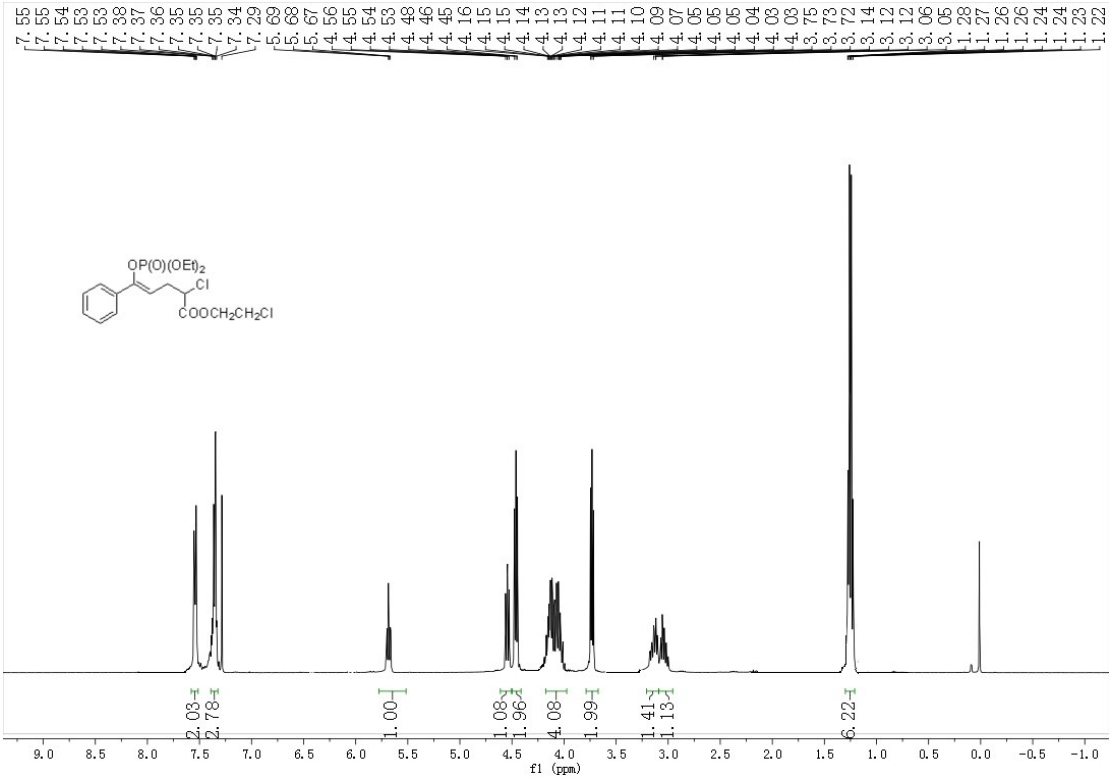

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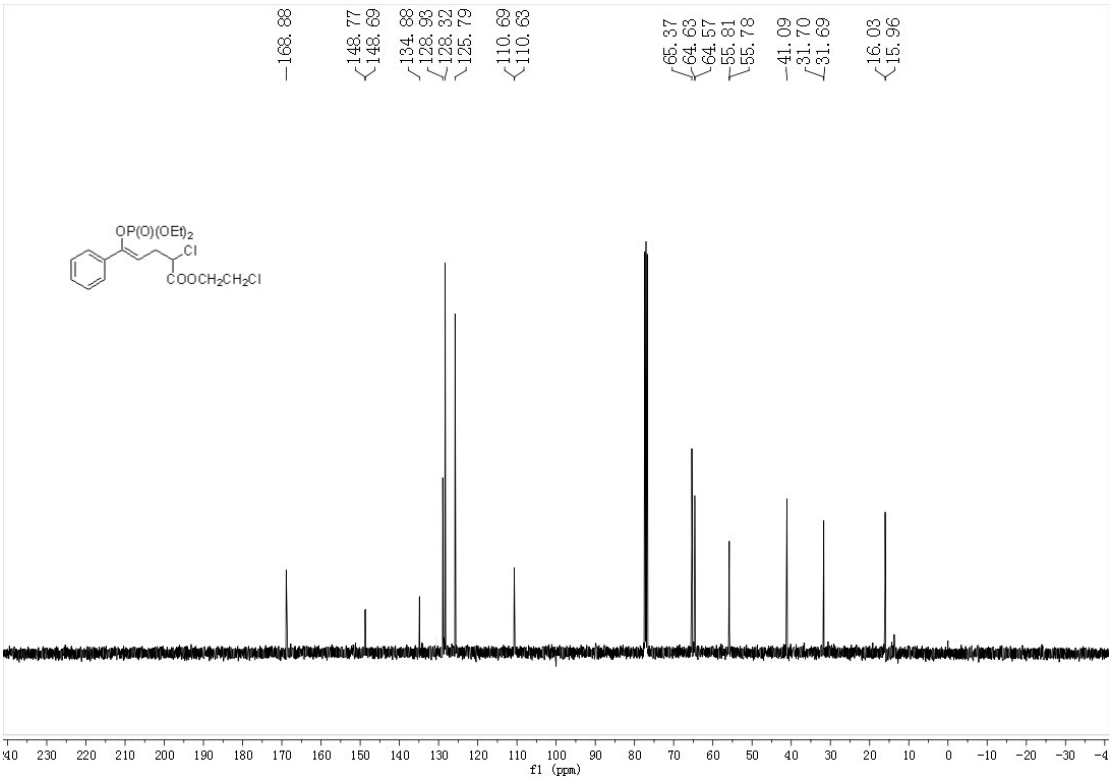

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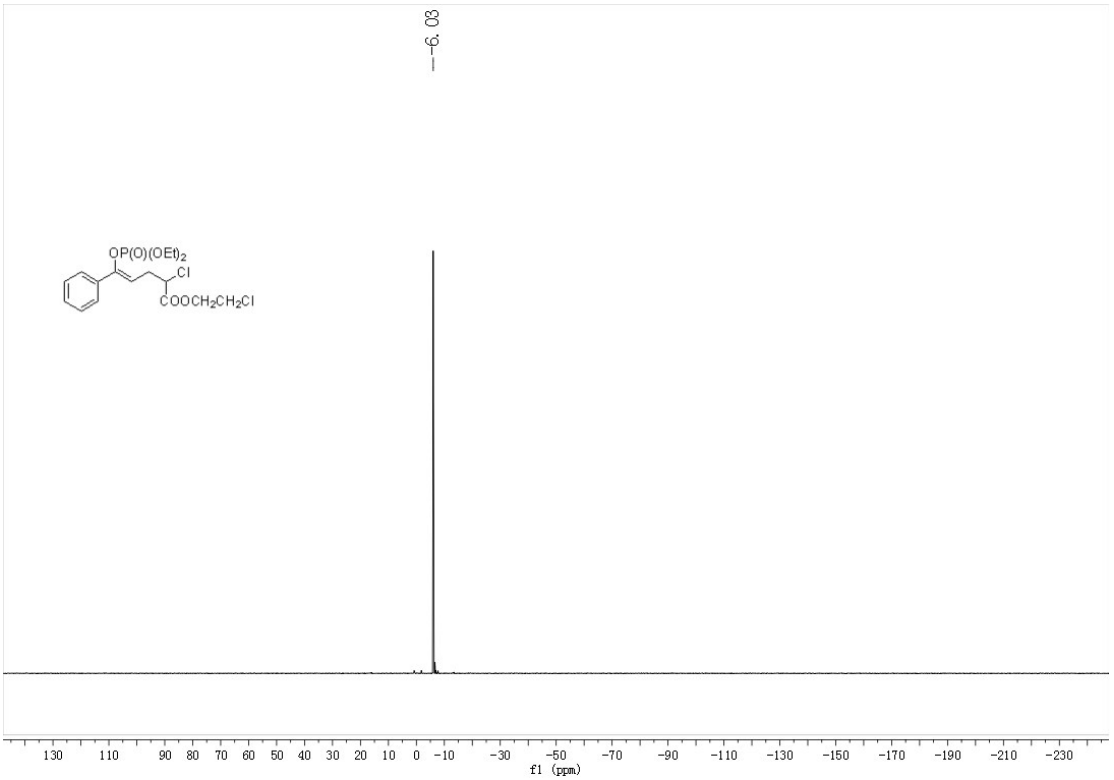
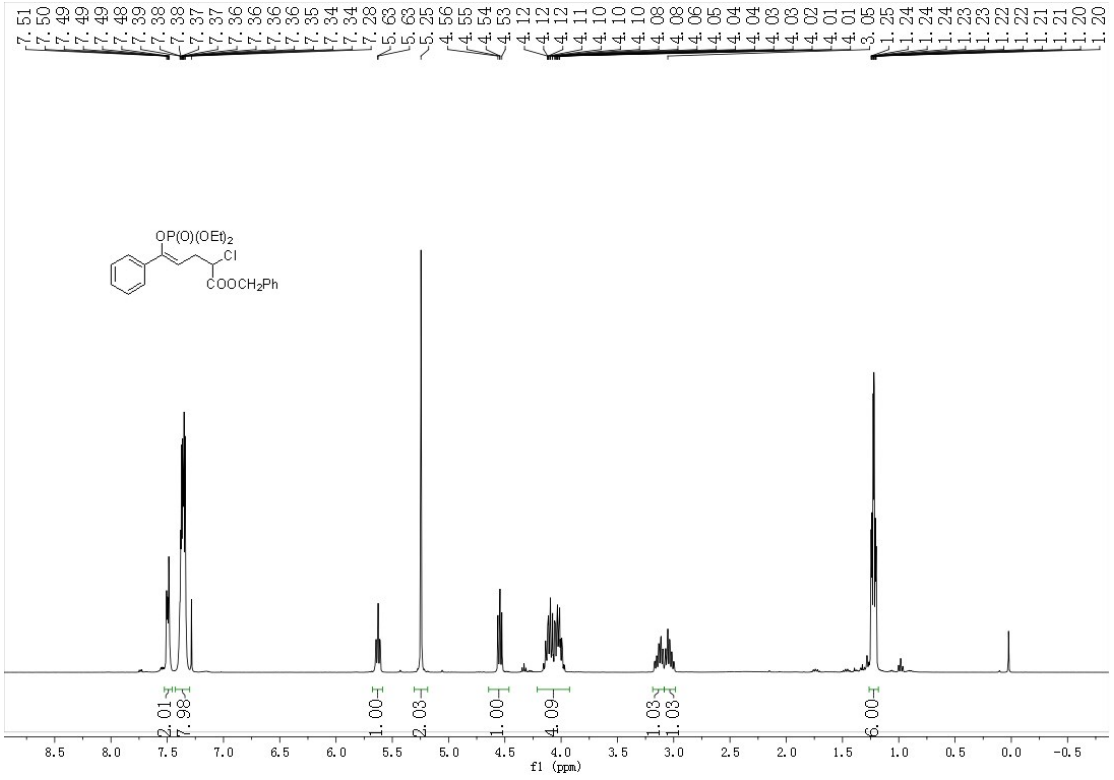


3ma ^{1}H NMR (400 MHz, $CDCl_3$)



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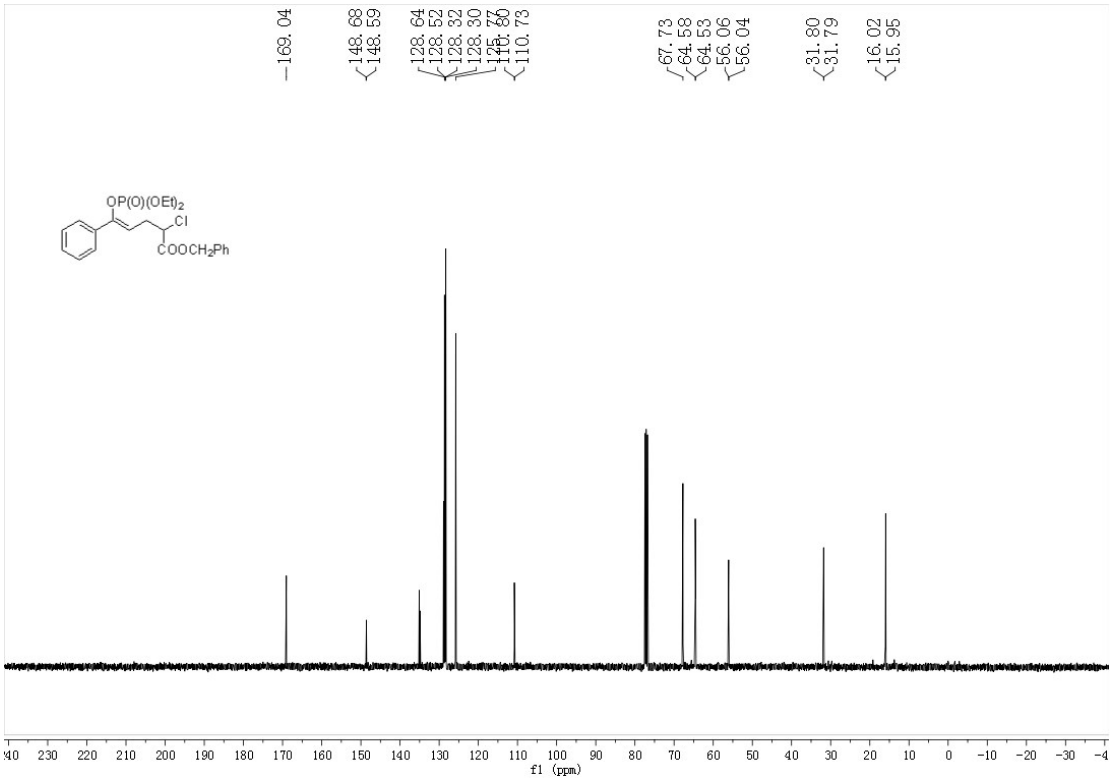
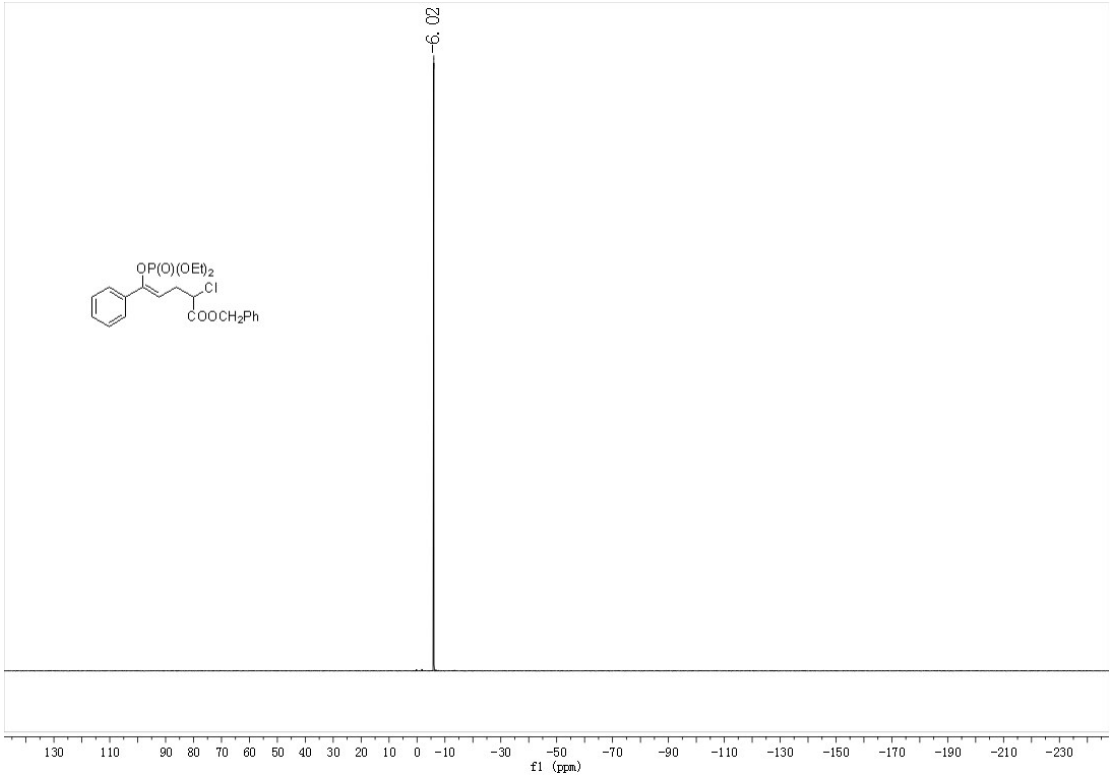
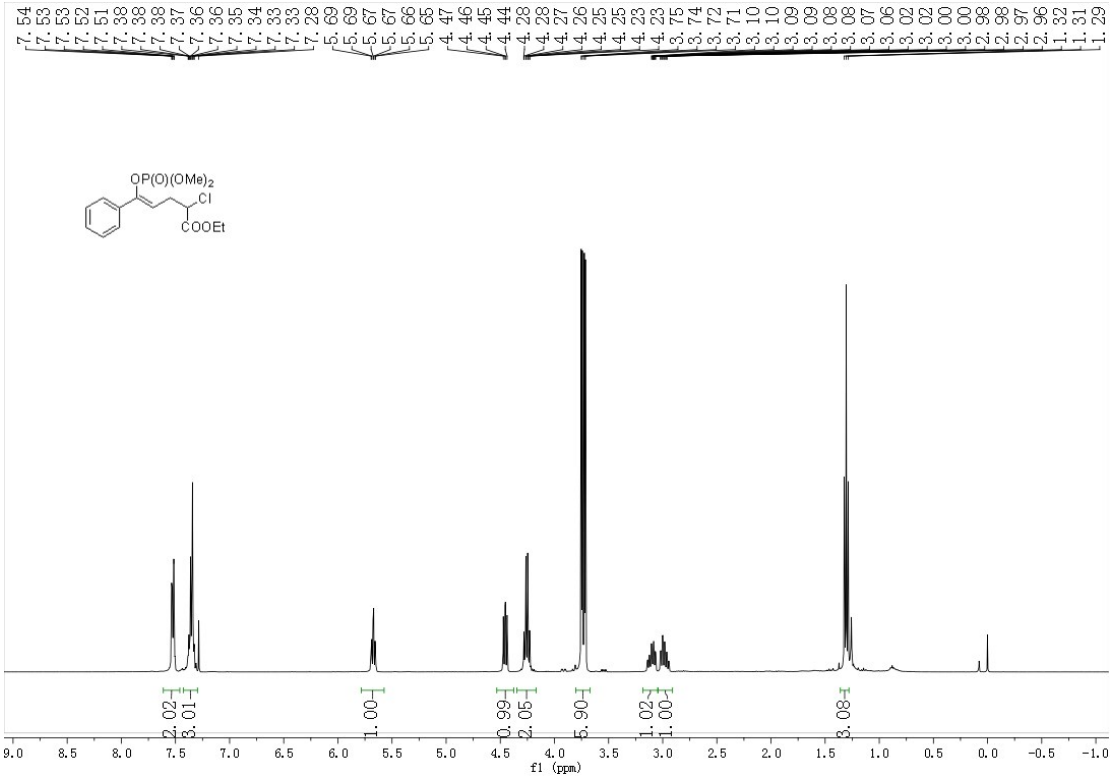


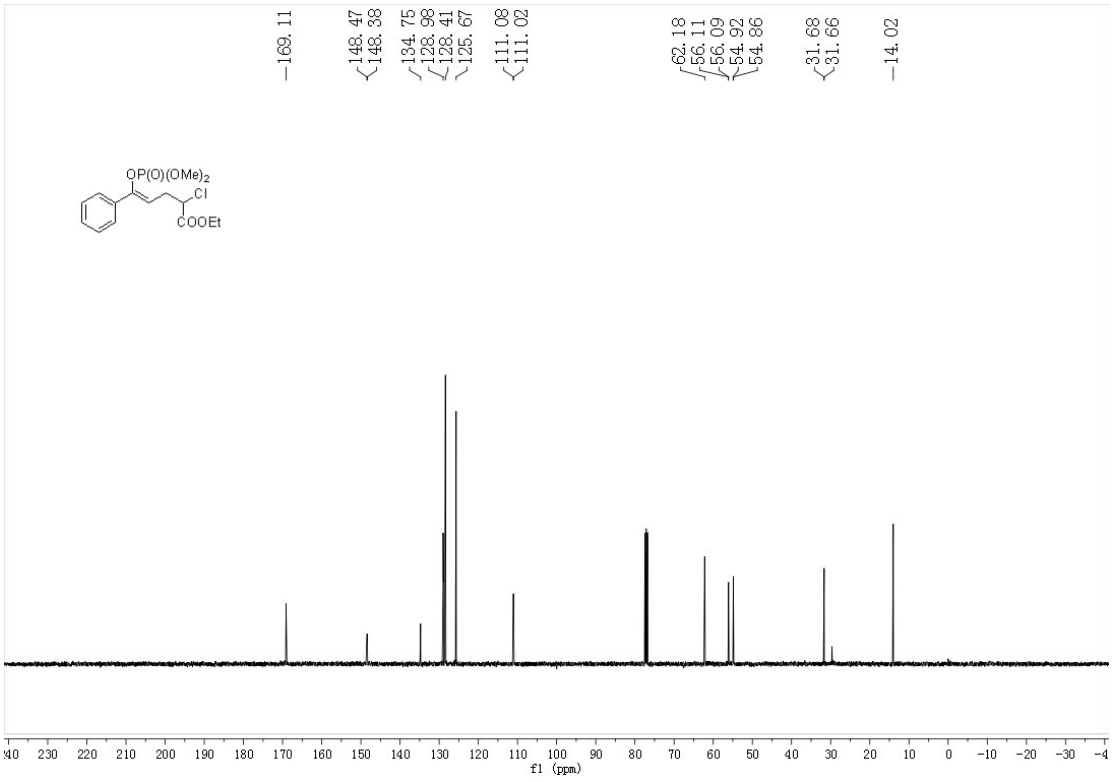
3ma $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



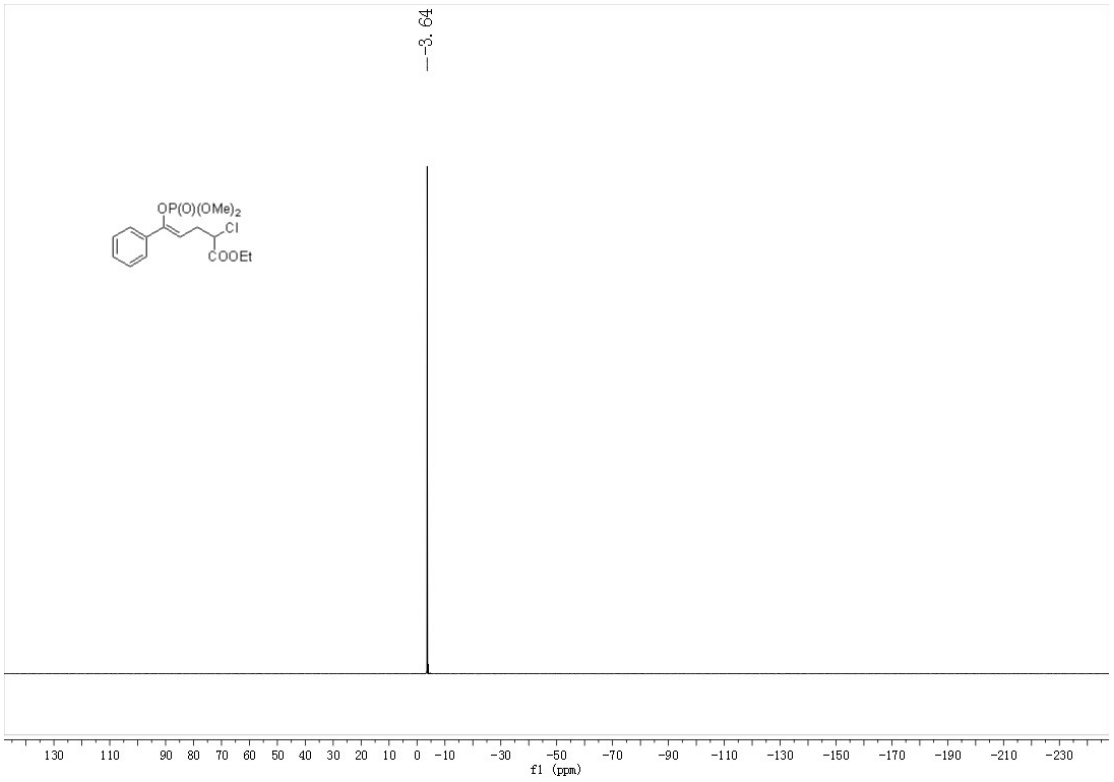
3ab ^{1}H NMR (400 MHz, $CDCl_3$)



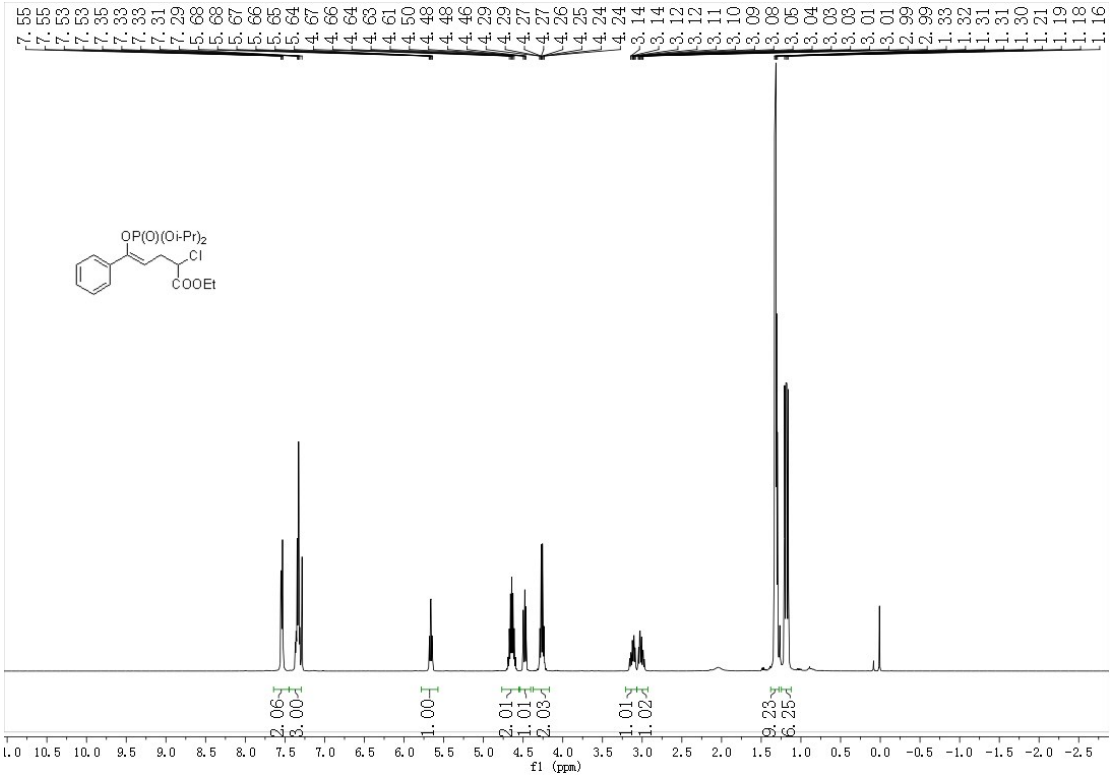
3ab $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



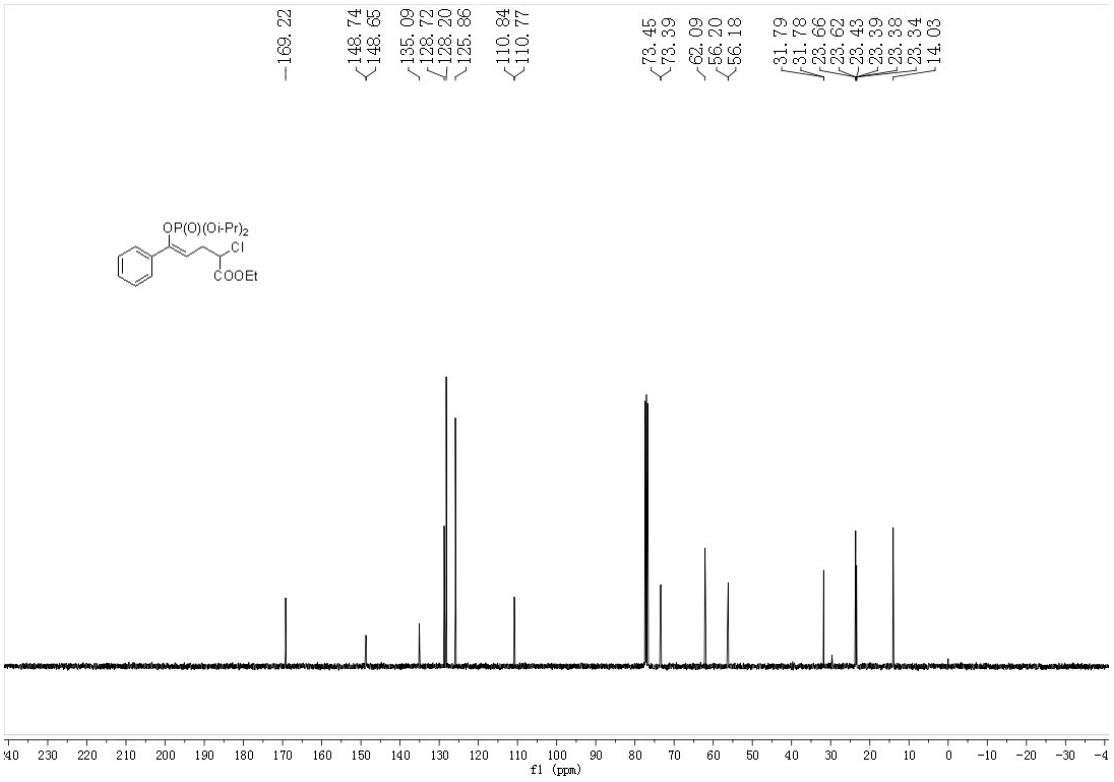
3ab $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



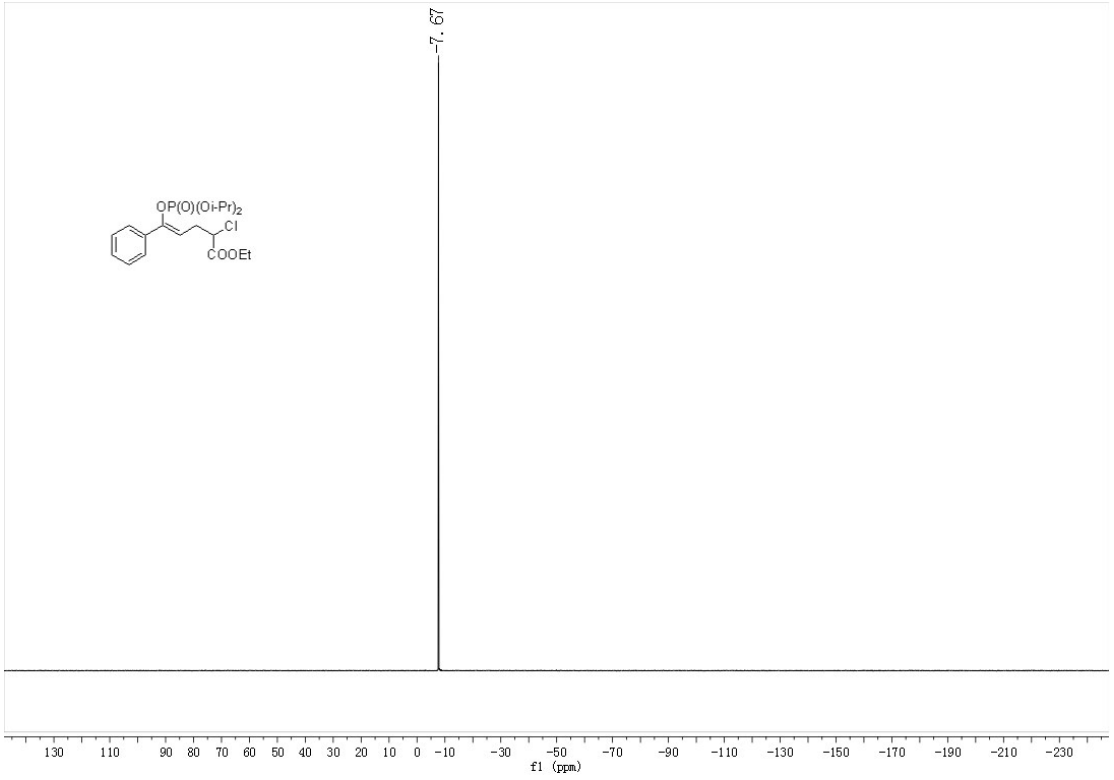
3ac ^{1}H NMR (400 MHz, $CDCl_3$)



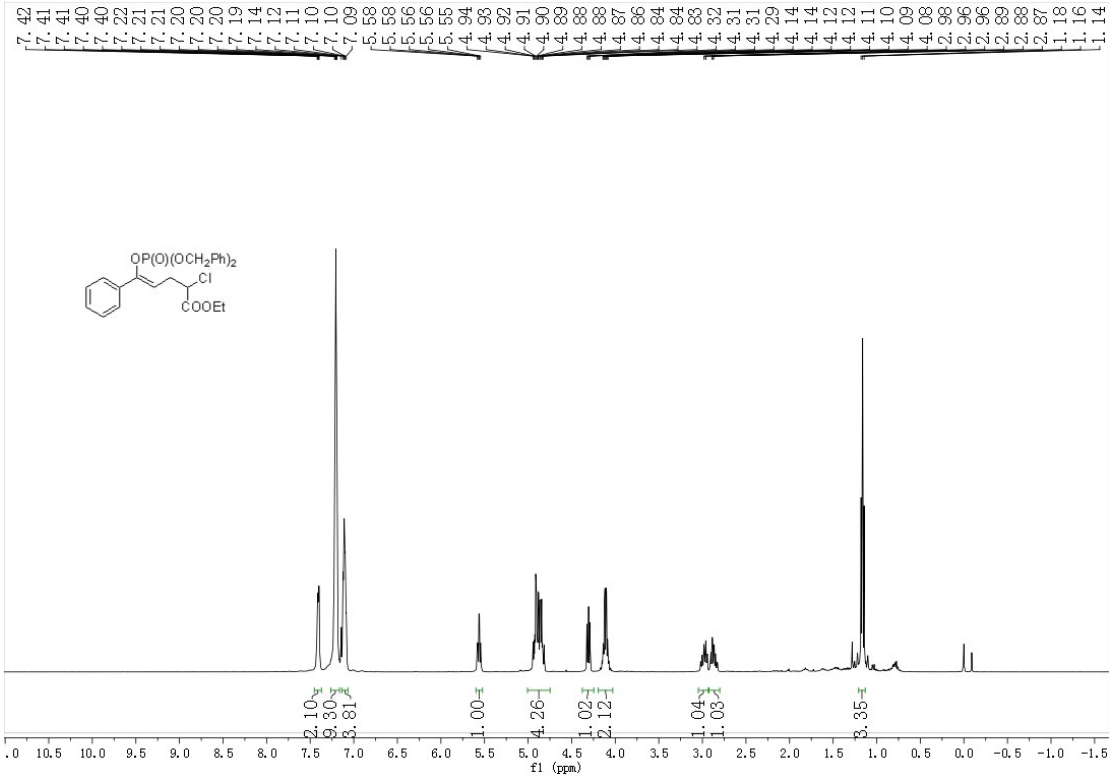
3ac $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



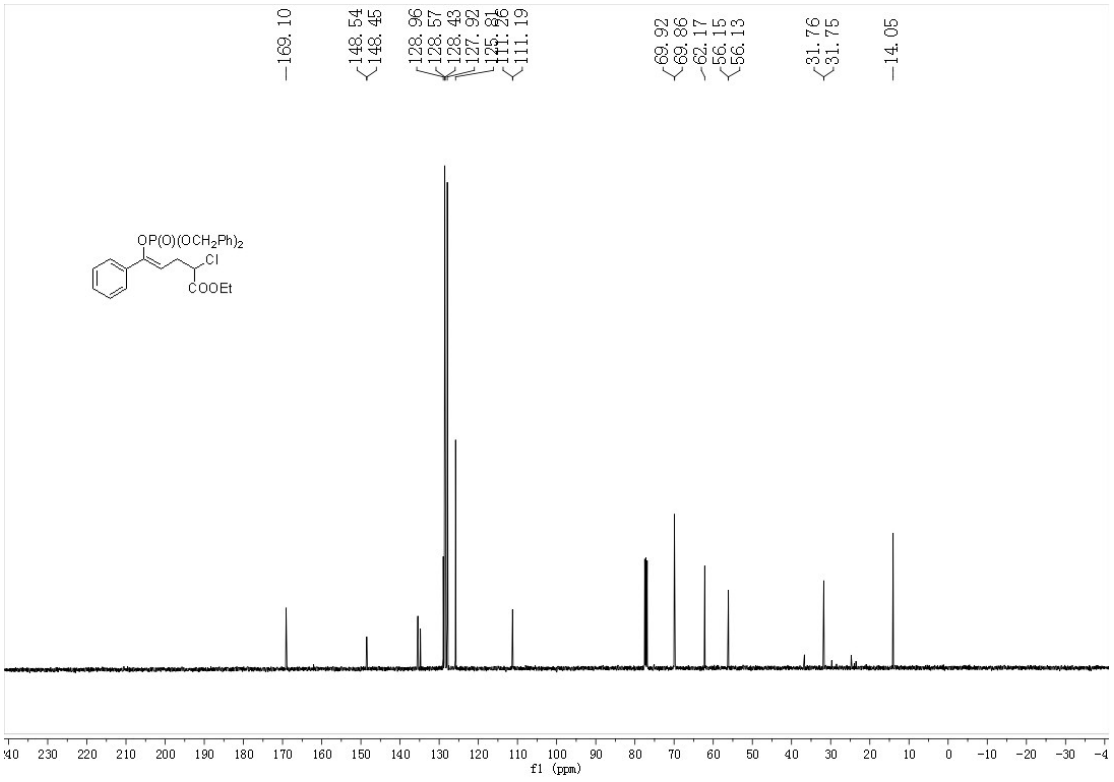
3ac $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



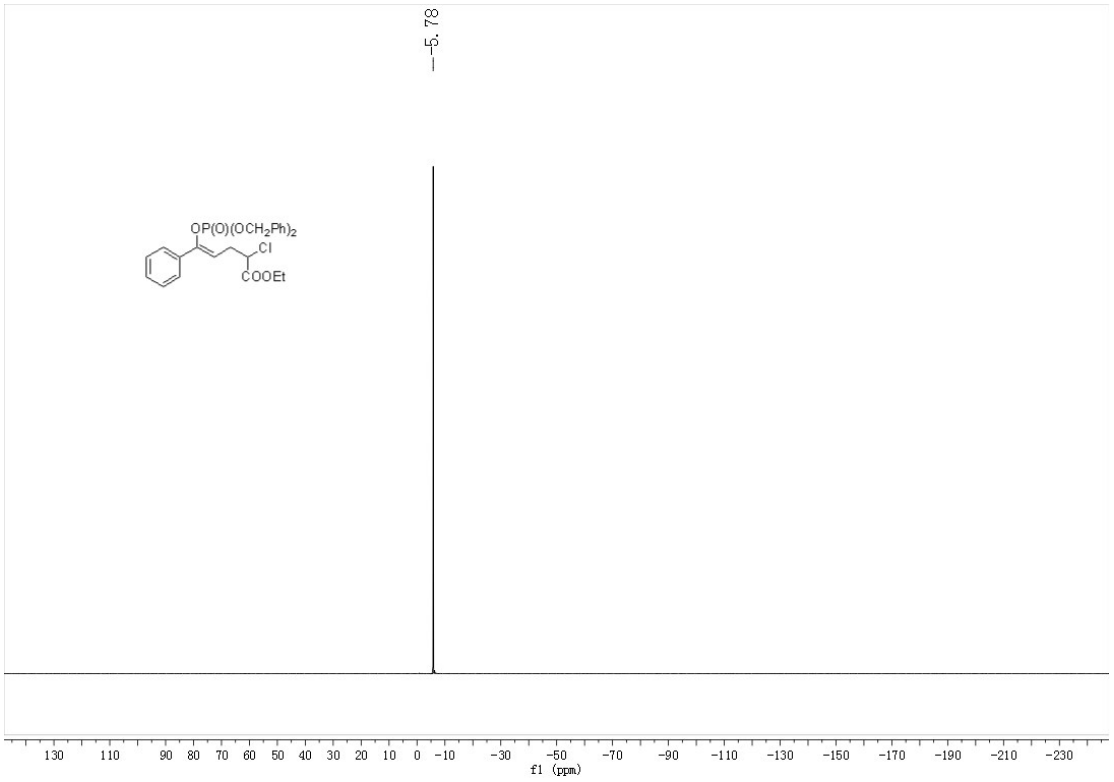
3ad ^{1}H NMR (400 MHz, $CDCl_3$)



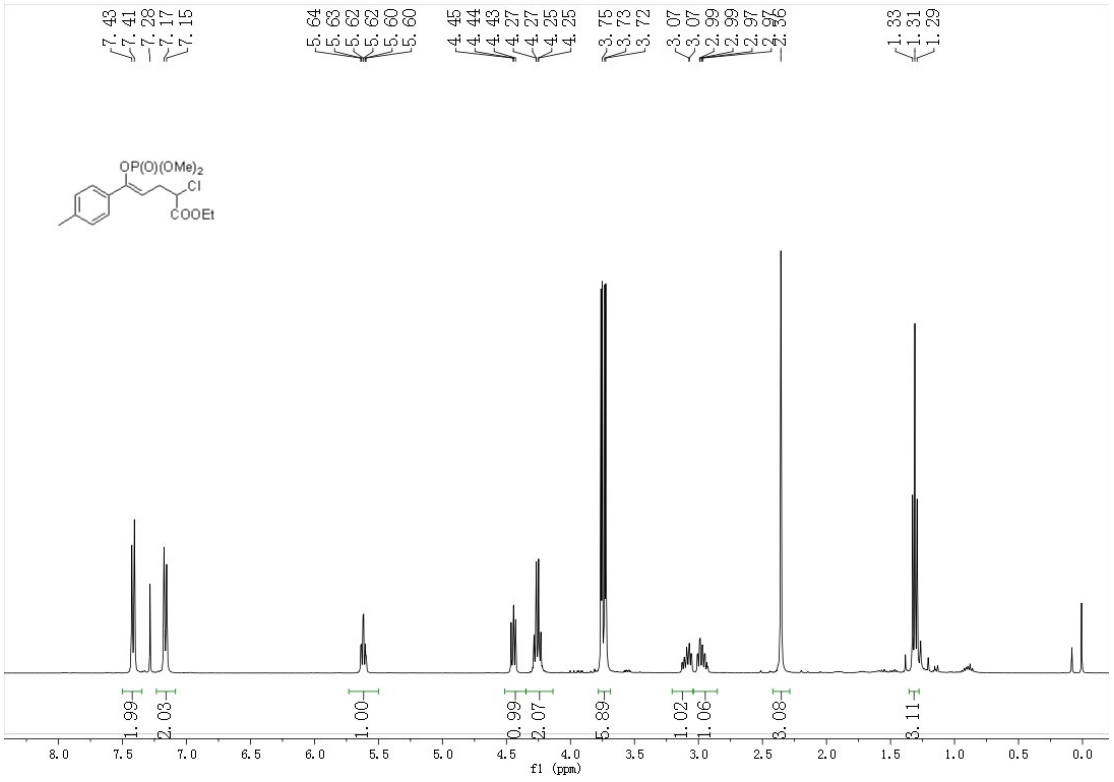
3ad $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



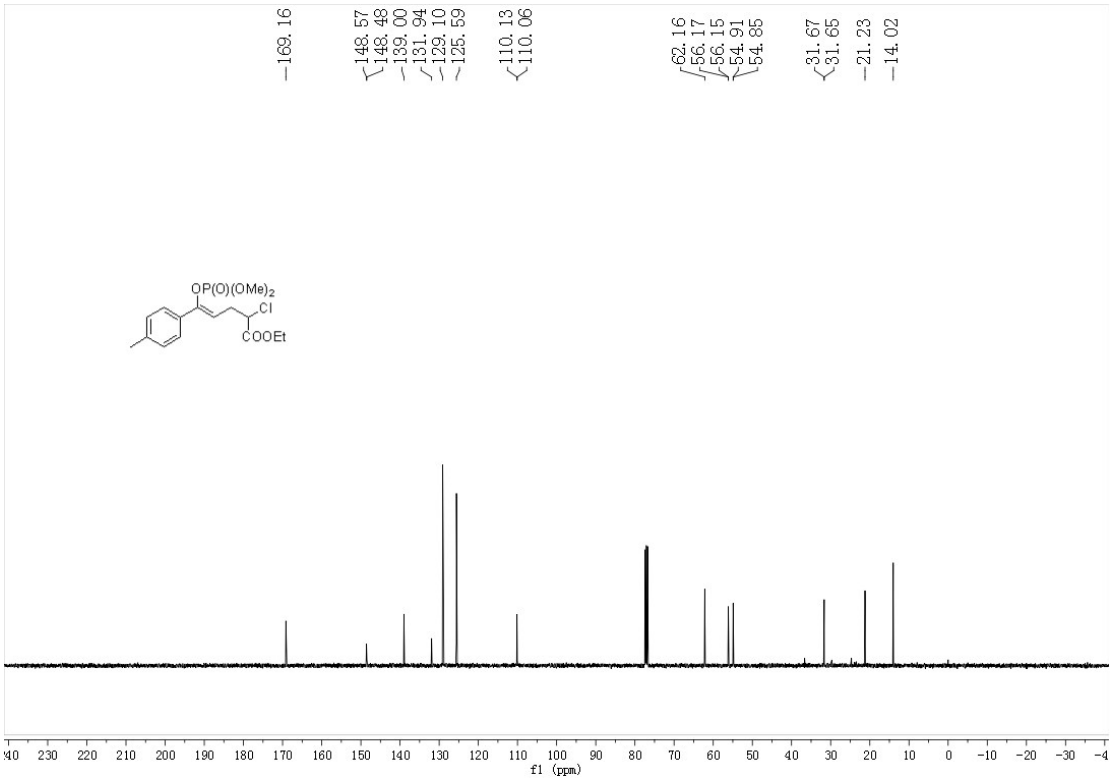
3ad $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



3bb ^{1}H NMR (400 MHz, $CDCl_3$)



3bb $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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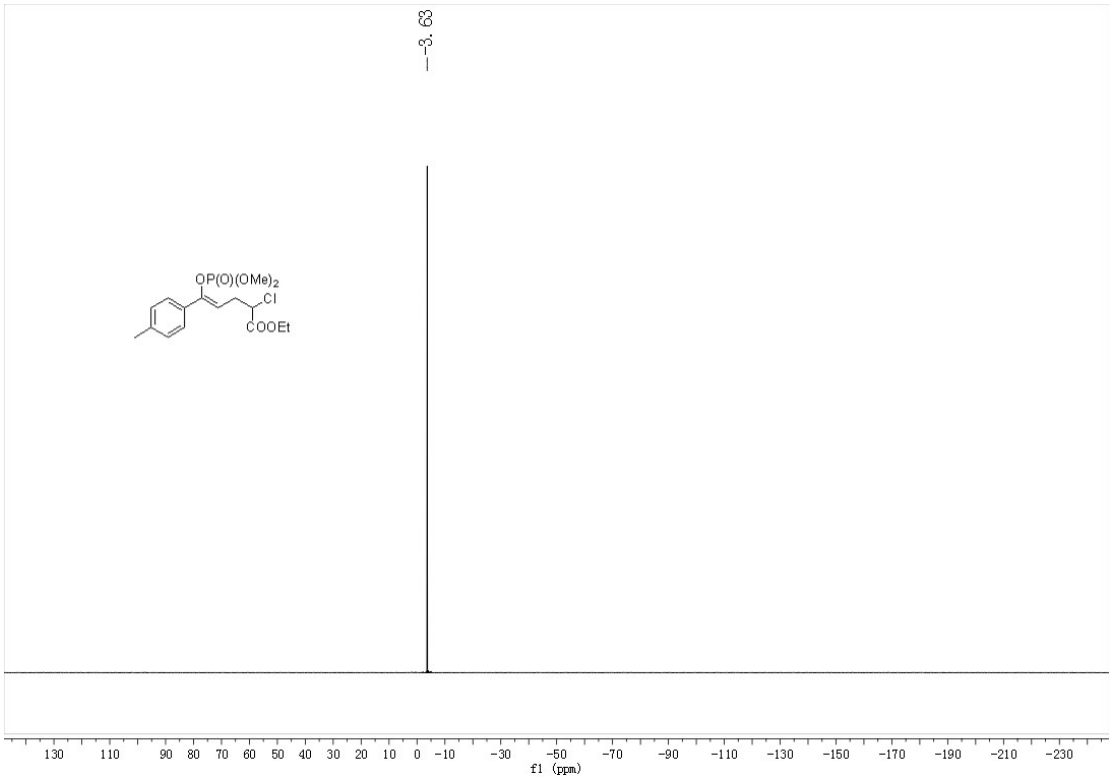
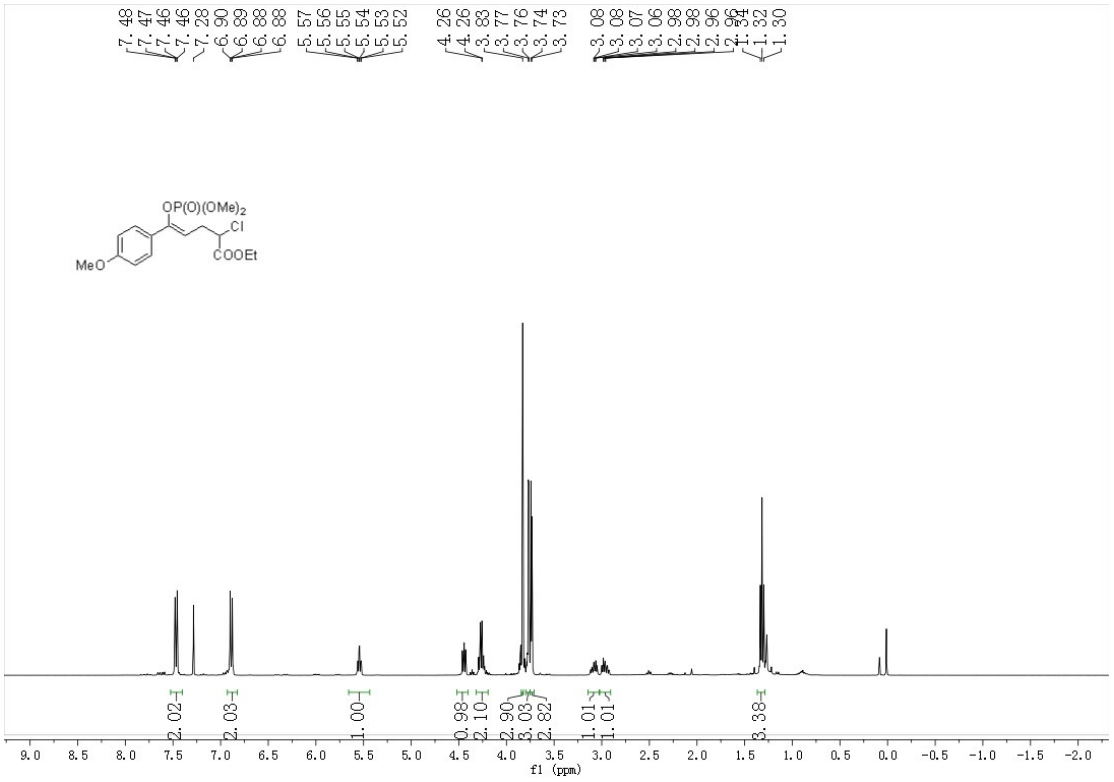
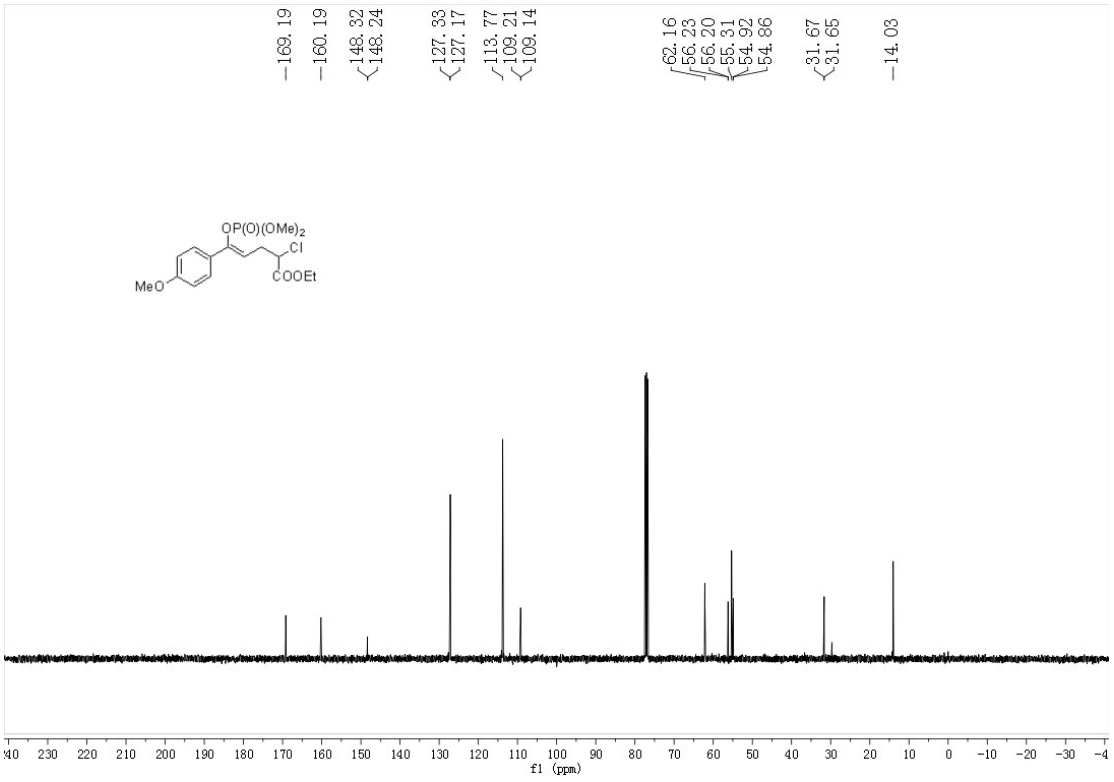


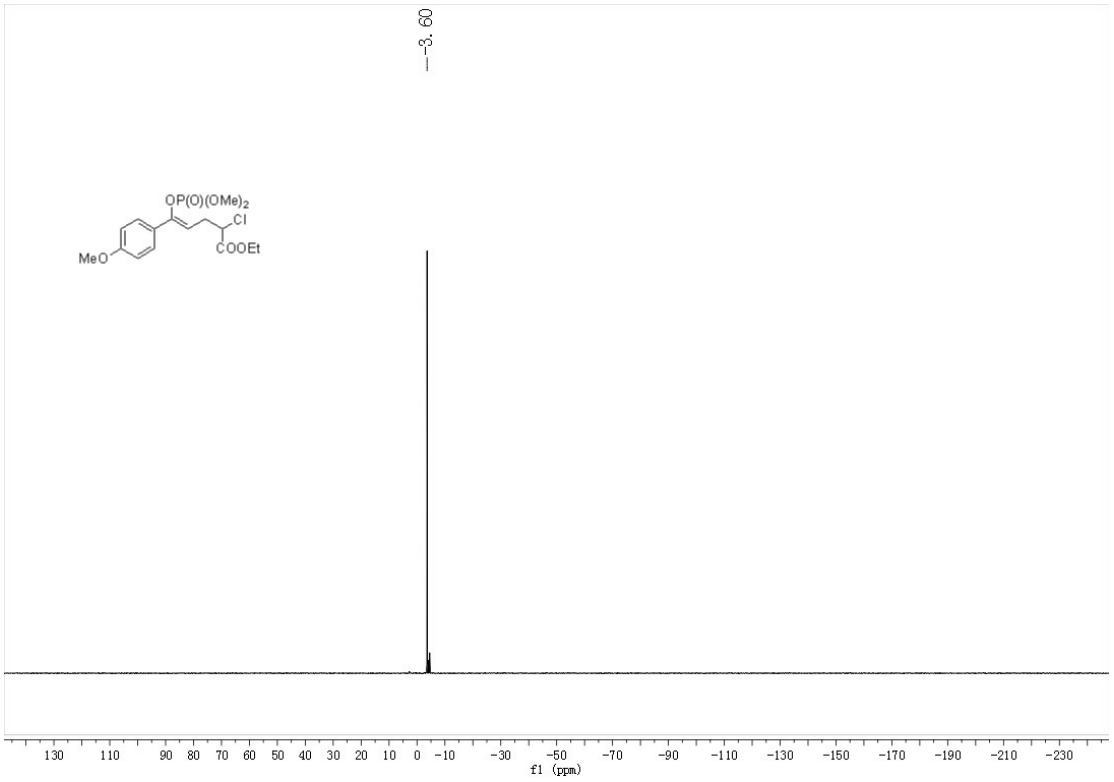
3cb ^{1}H NMR (400 MHz, $CDCl_3$)



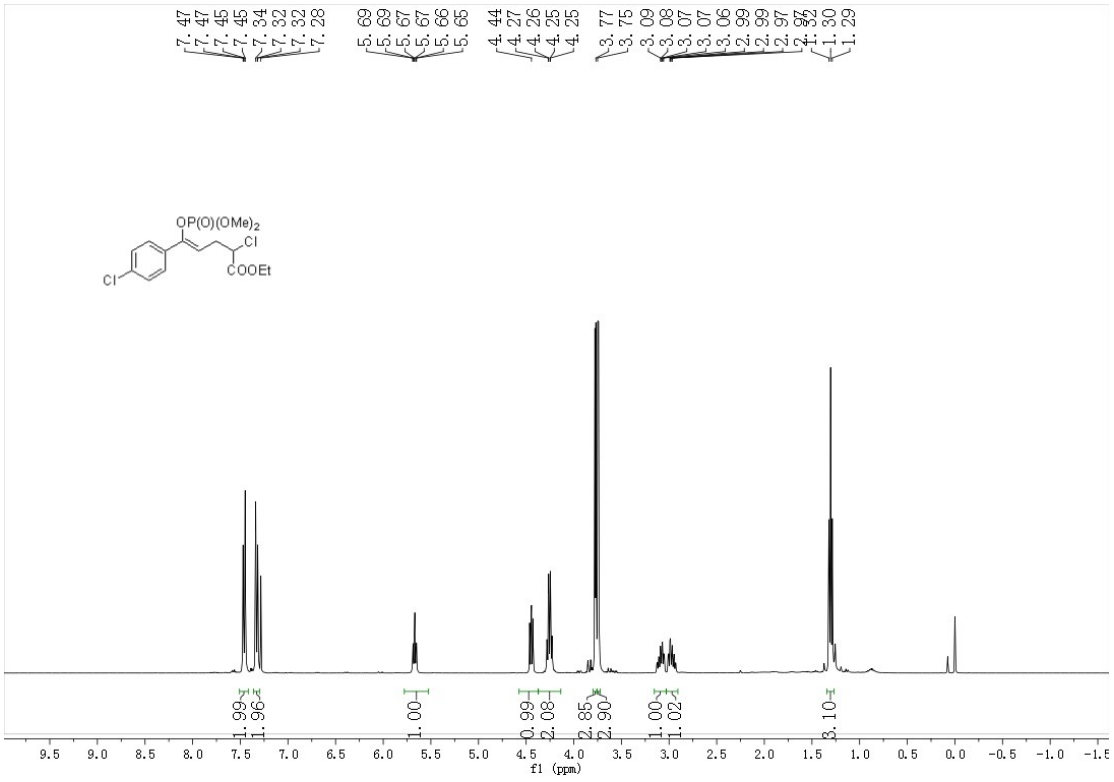
3cb $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



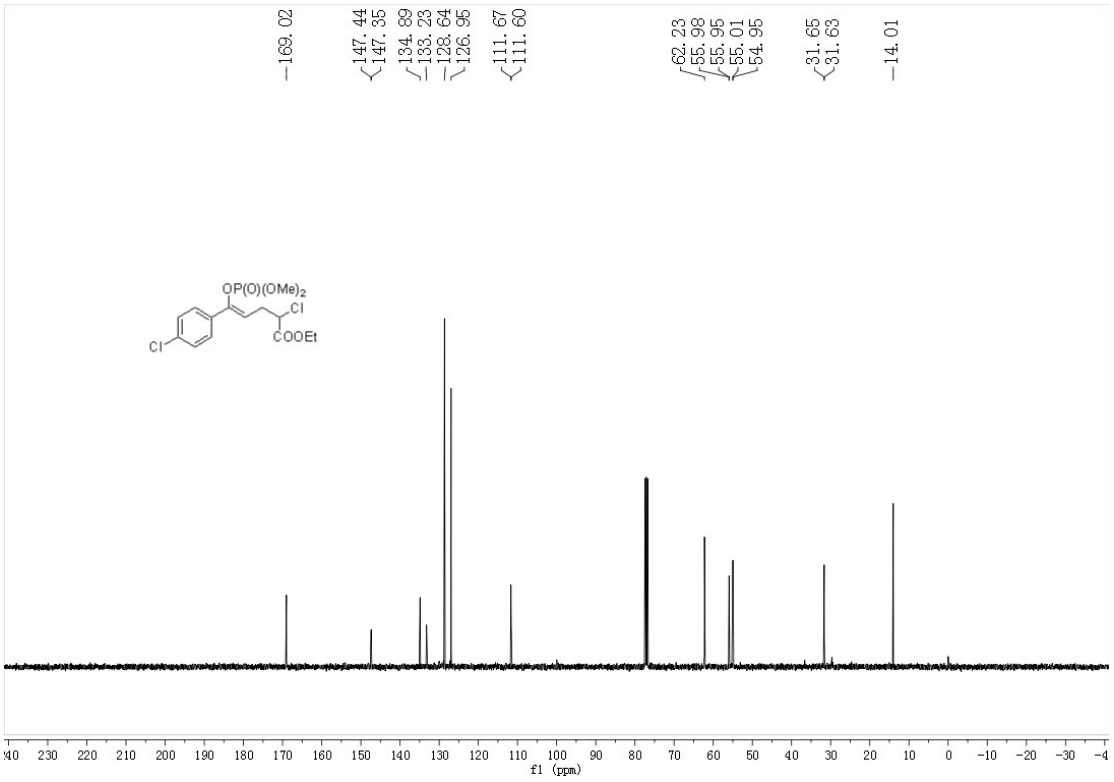
3cb $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



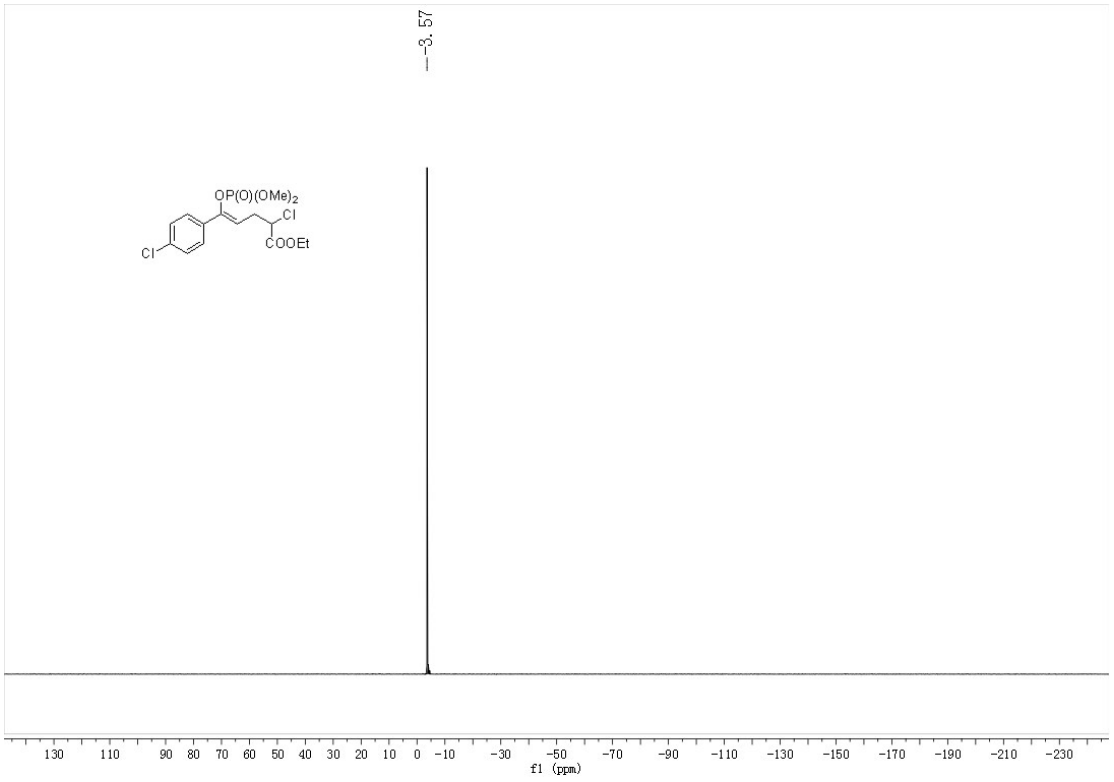
3db ^{1}H NMR (400 MHz, $CDCl_3$)



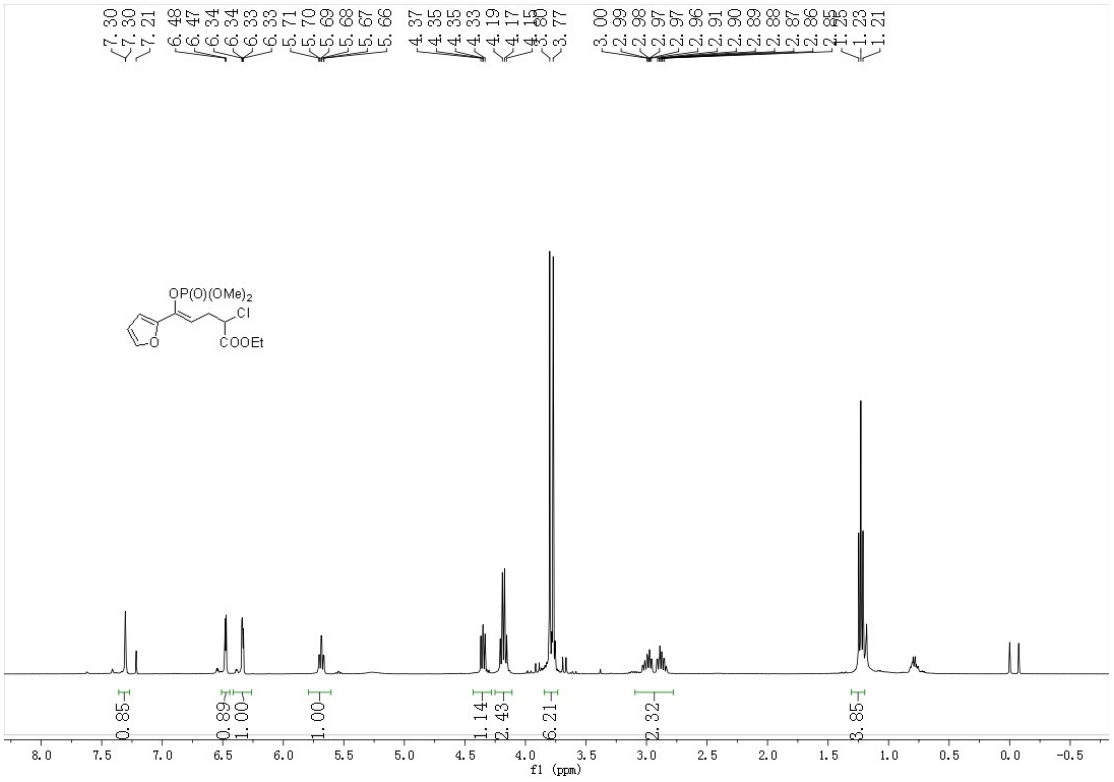
3db $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



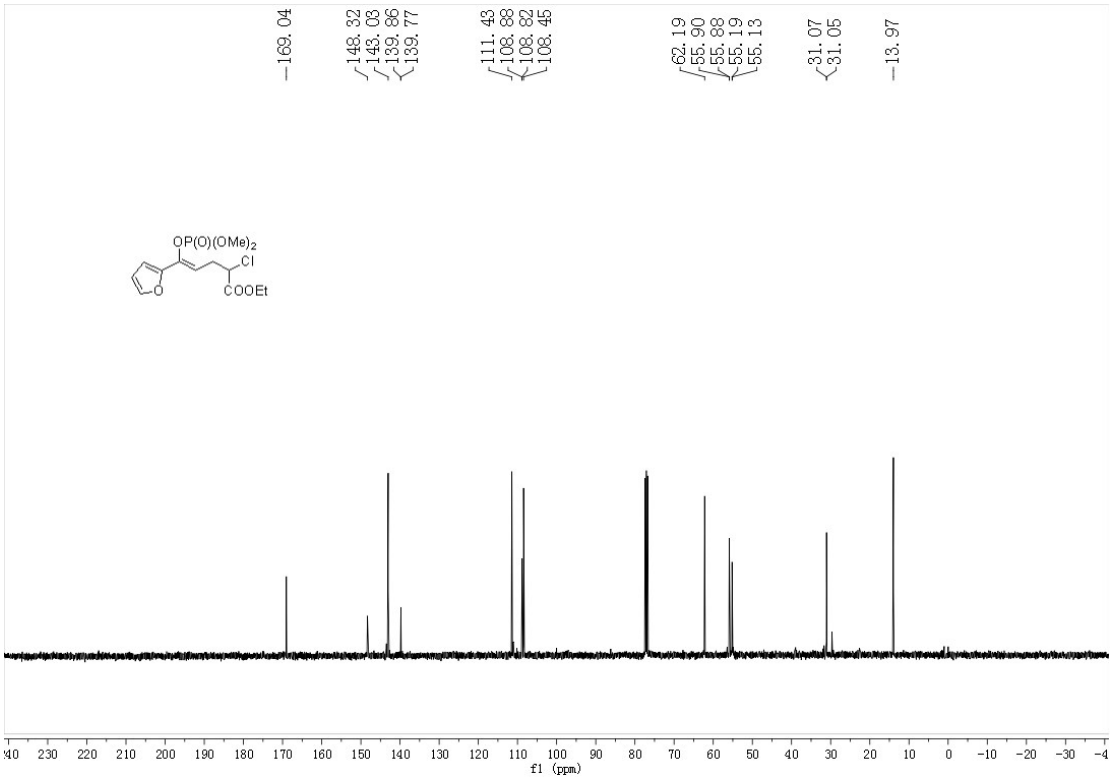
3db $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



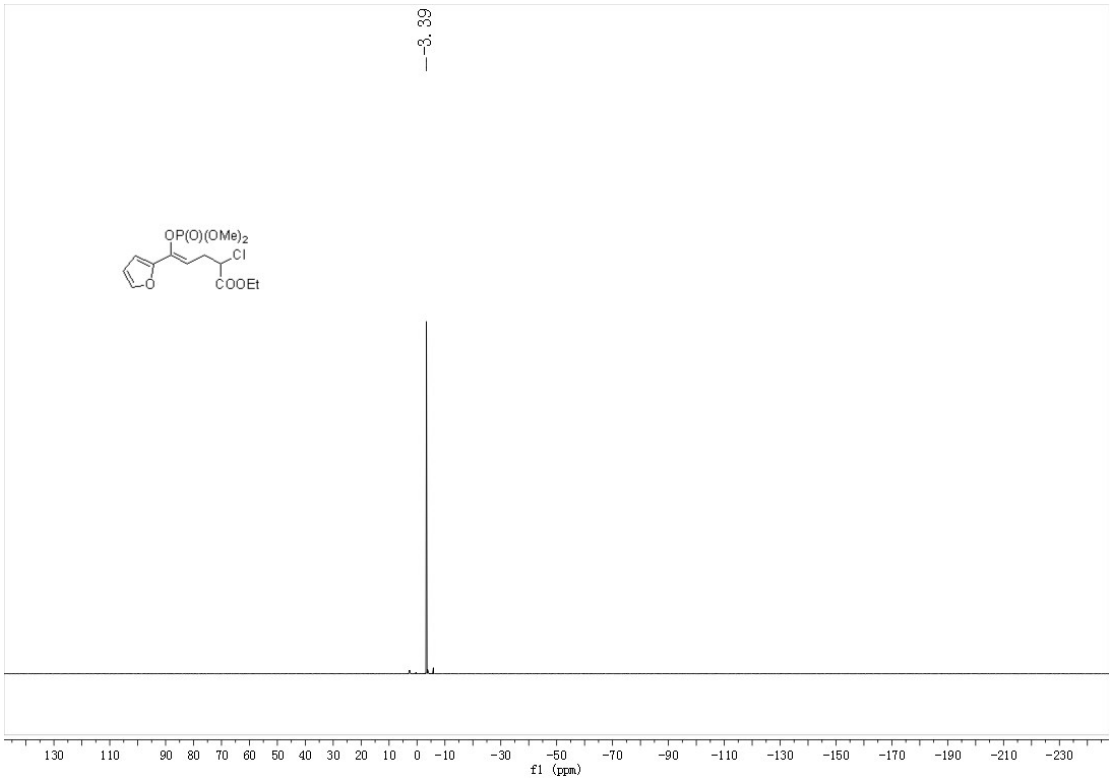
3nb ^{1}H NMR (400 MHz, $CDCl_3$)



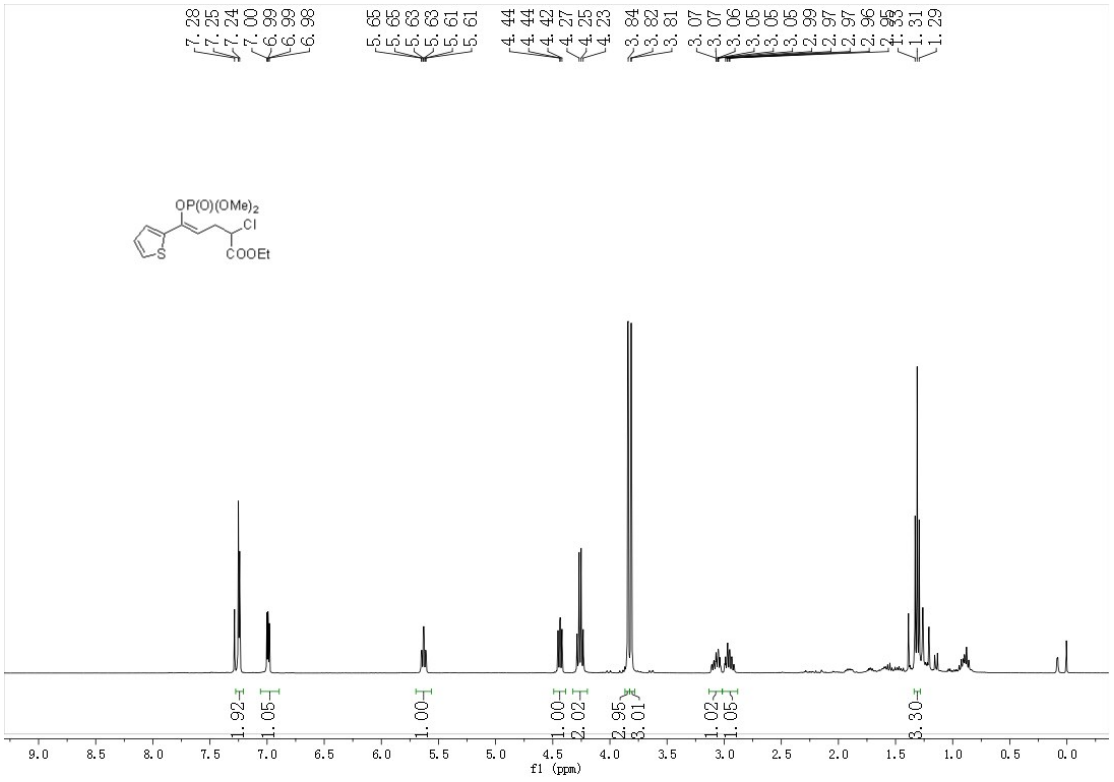
3nb $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



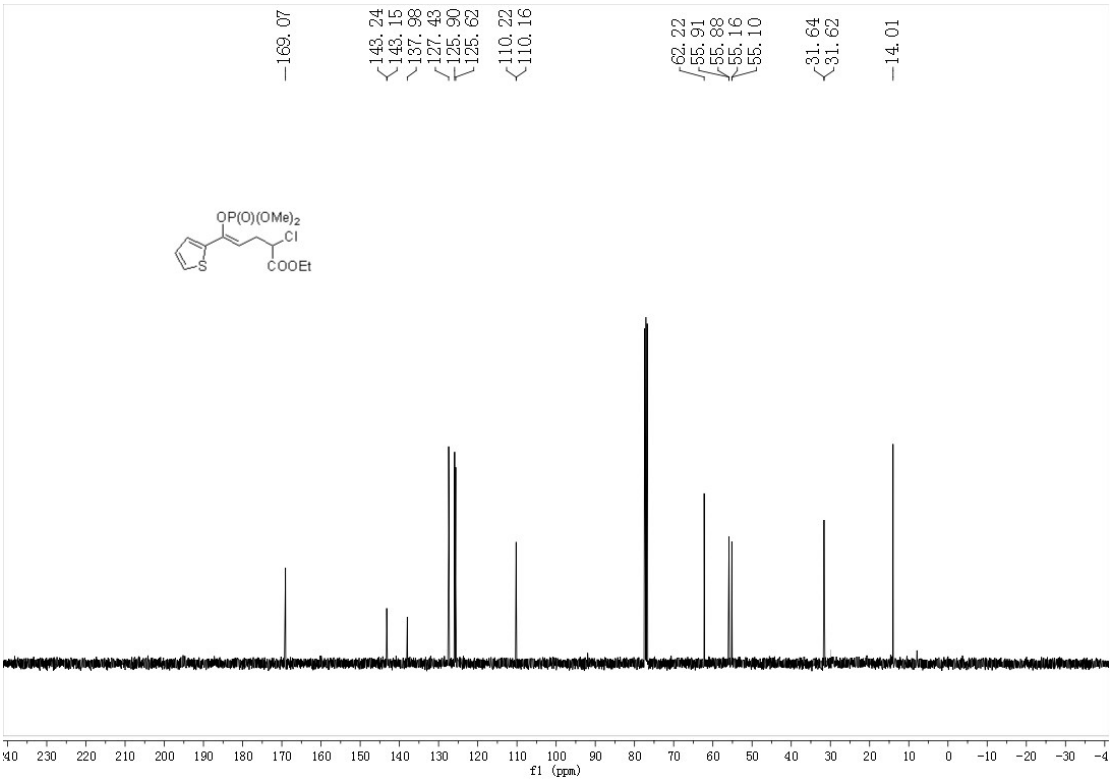
3nb $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



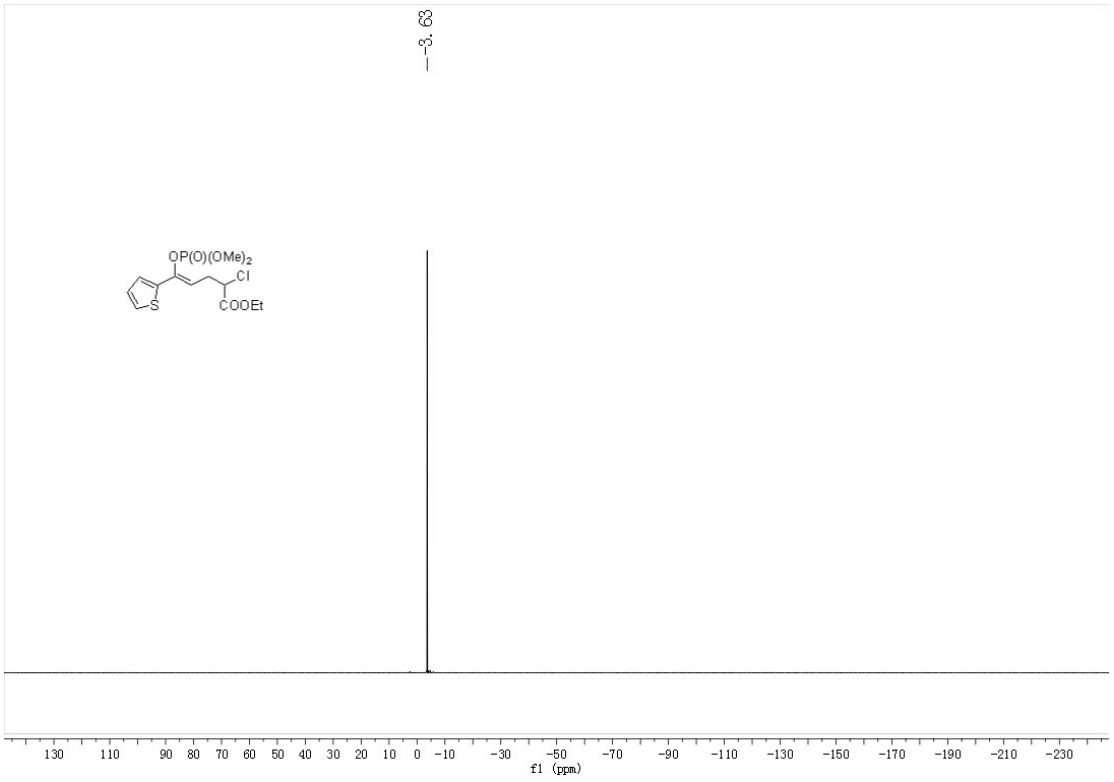
3hb ^{1}H NMR (400 MHz, $CDCl_3$)



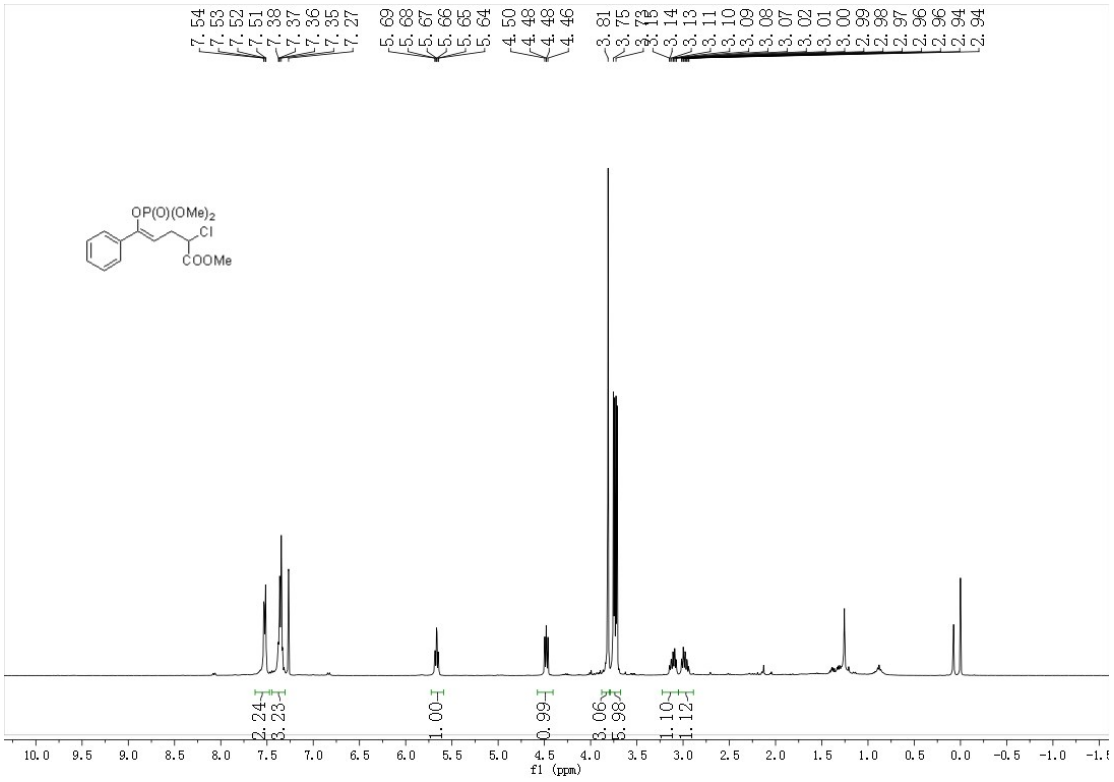
3hb $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



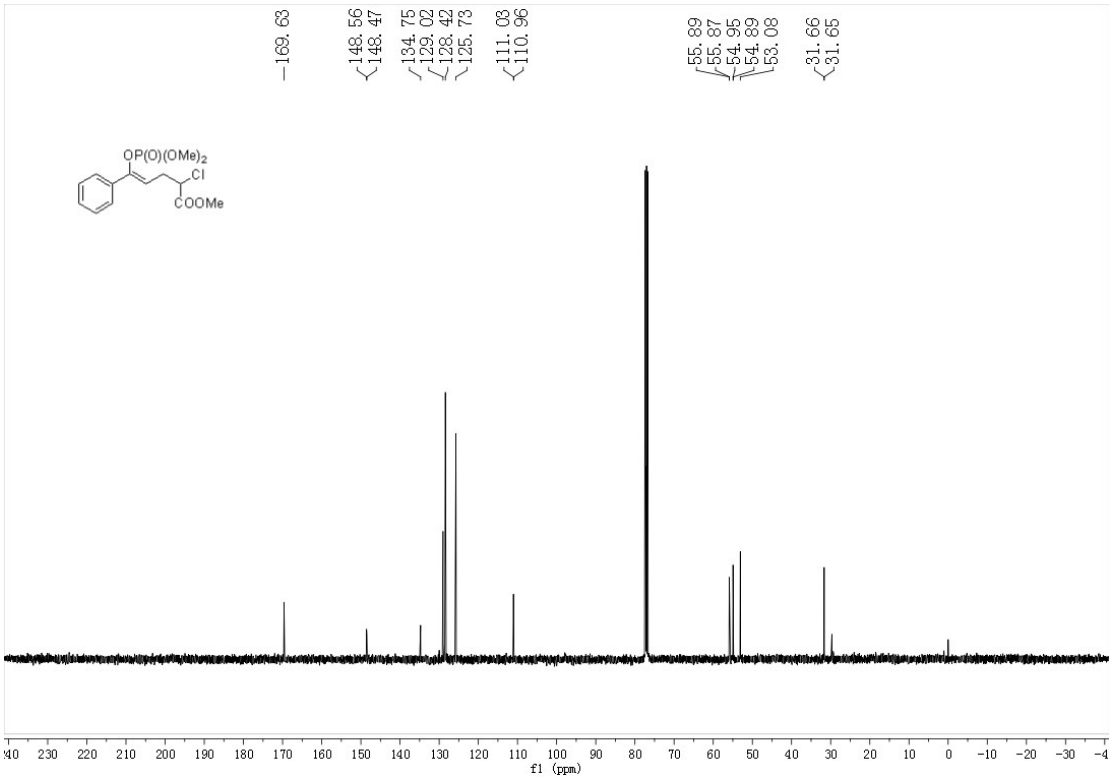
3hb $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



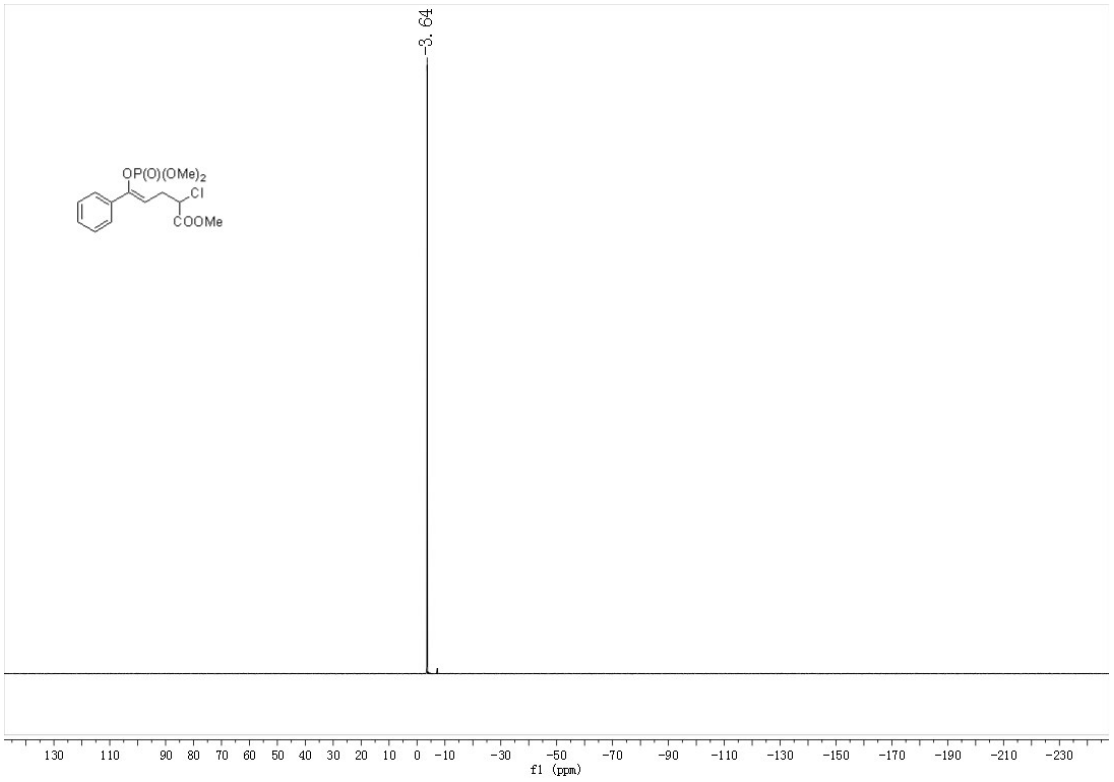
3jb ^{1}H NMR (400 MHz, $CDCl_3$)



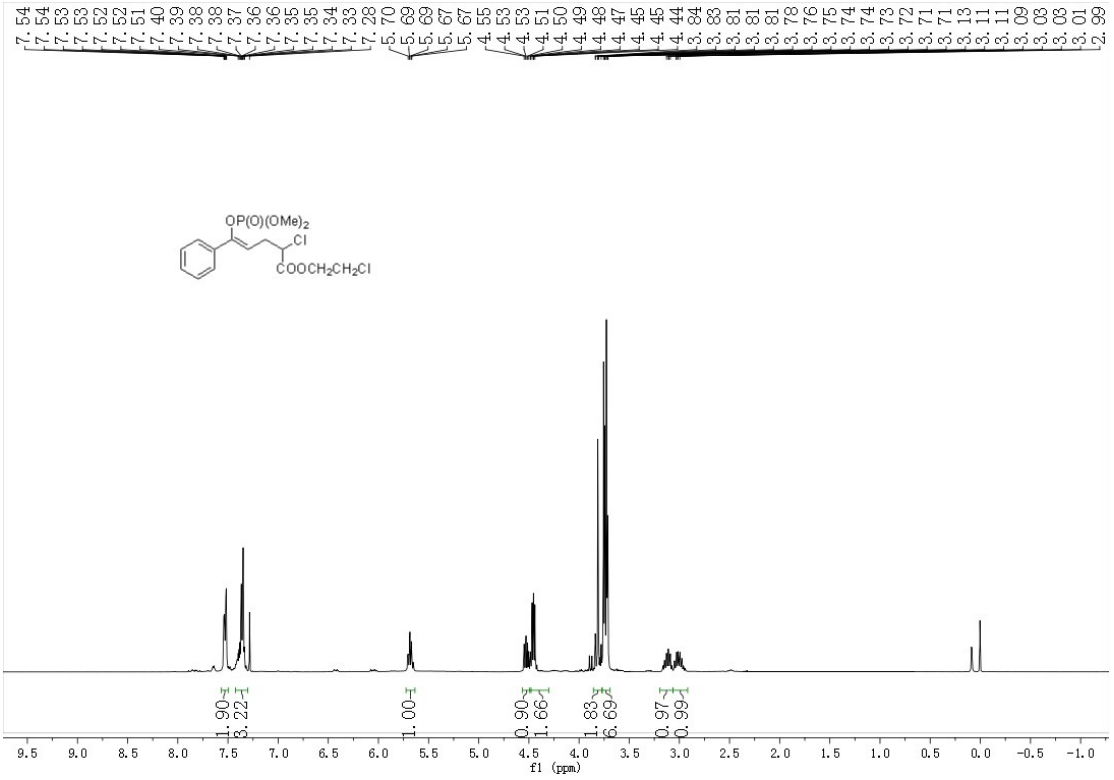
3jb $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



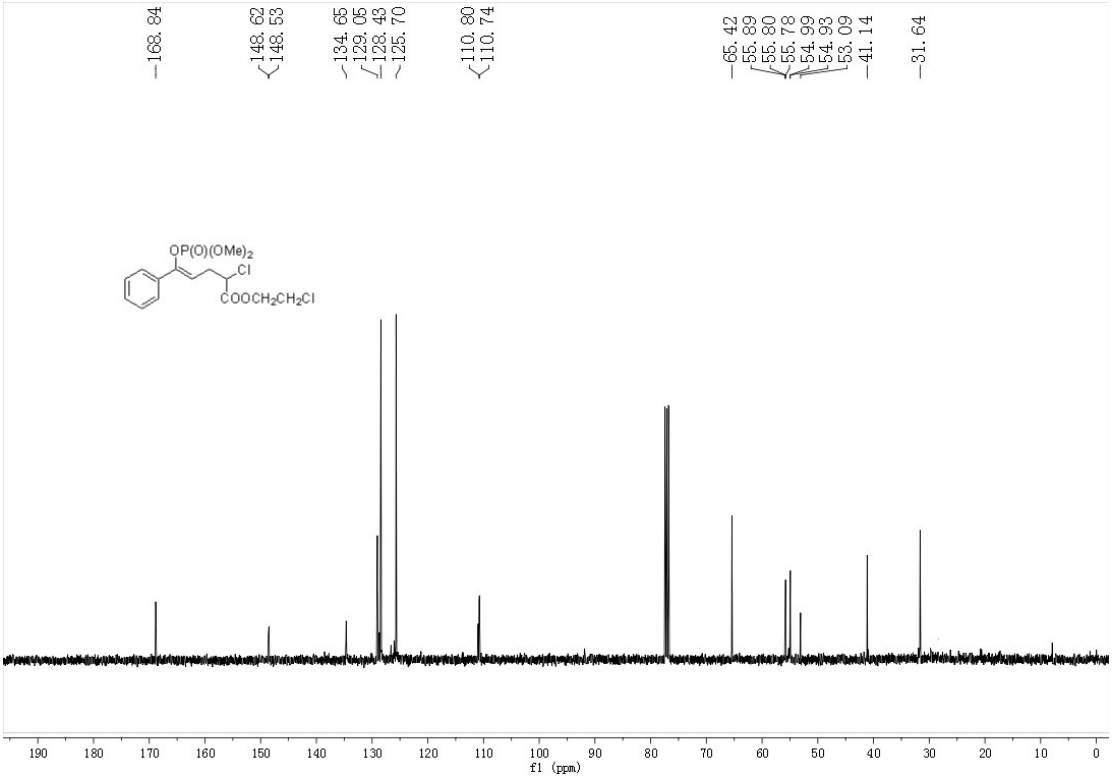
3jb $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



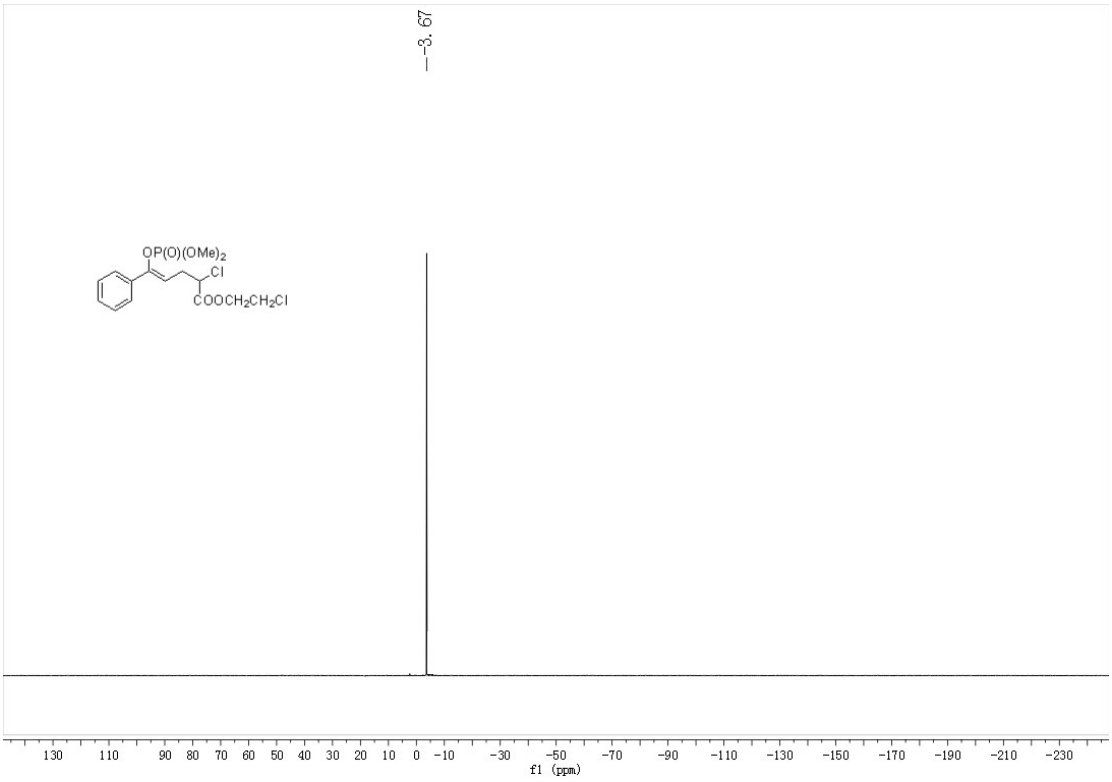
3lb ^{1}H NMR (400 MHz, $CDCl_3$)



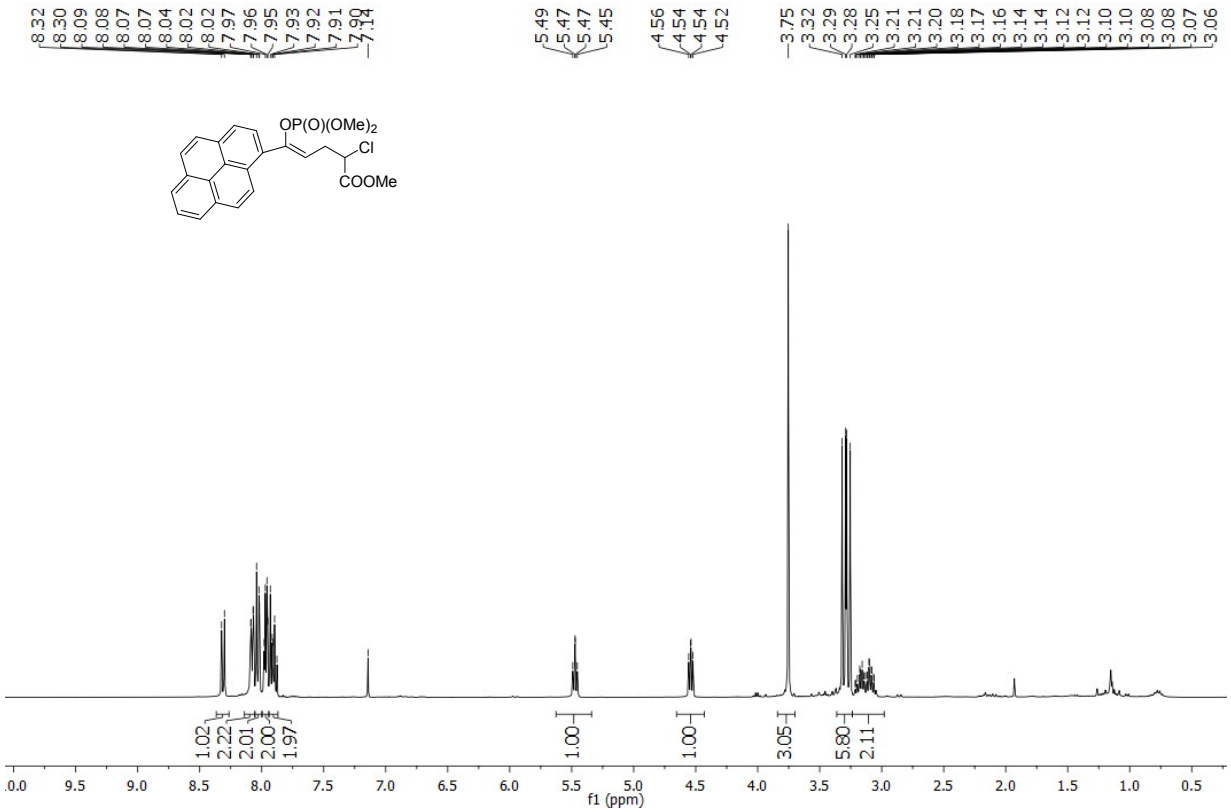
3lb $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



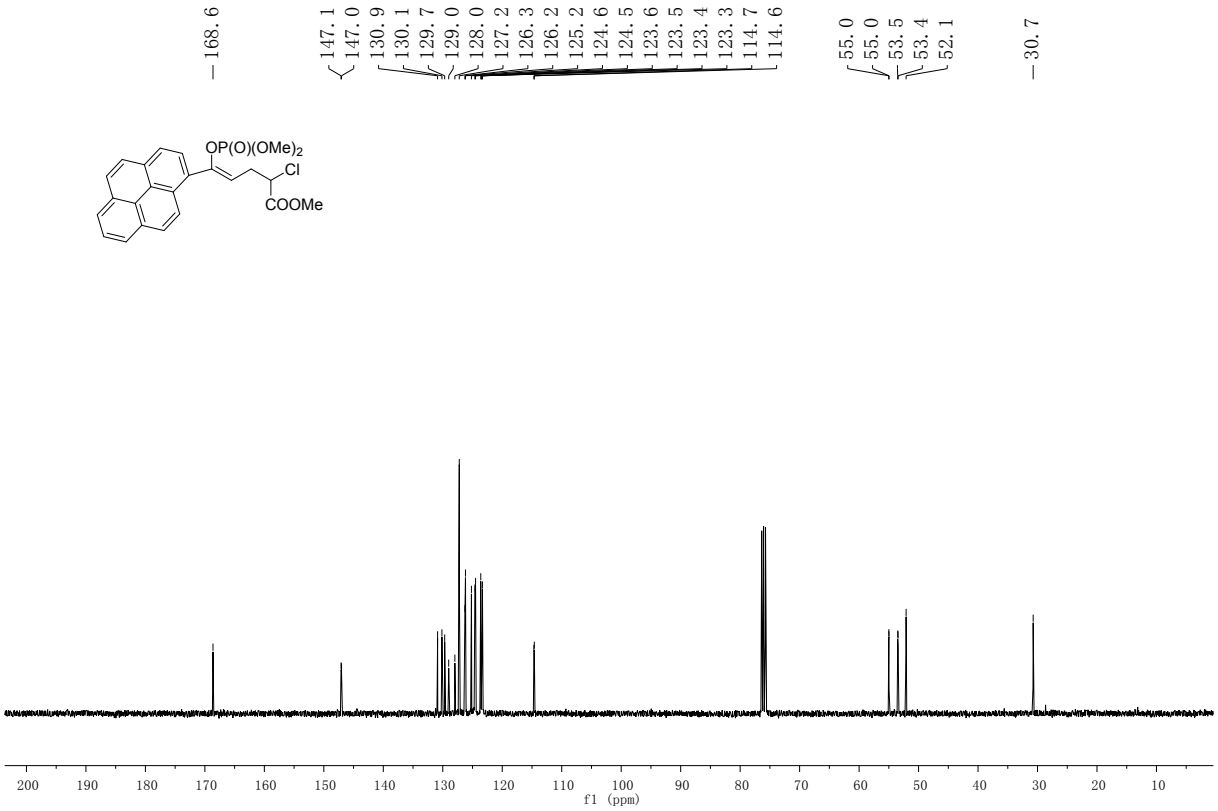
3lb $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



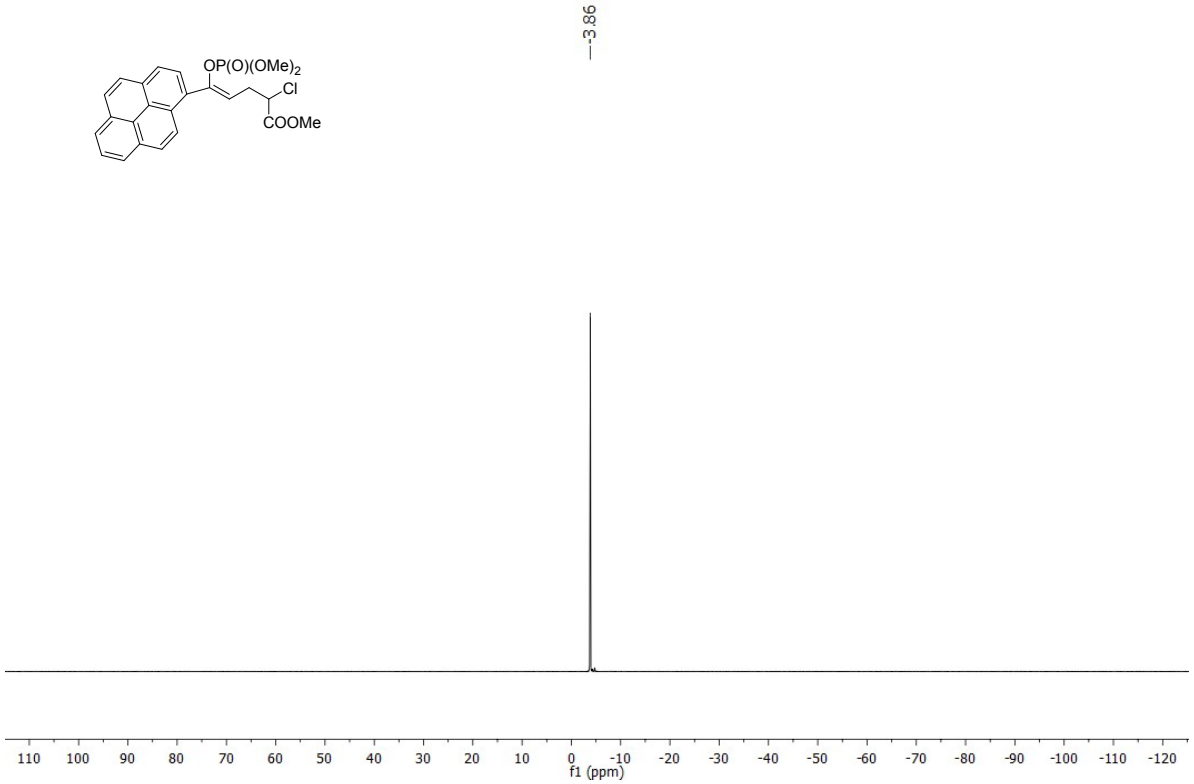
3ob ^{1}H NMR (400 MHz, $CDCl_3$)



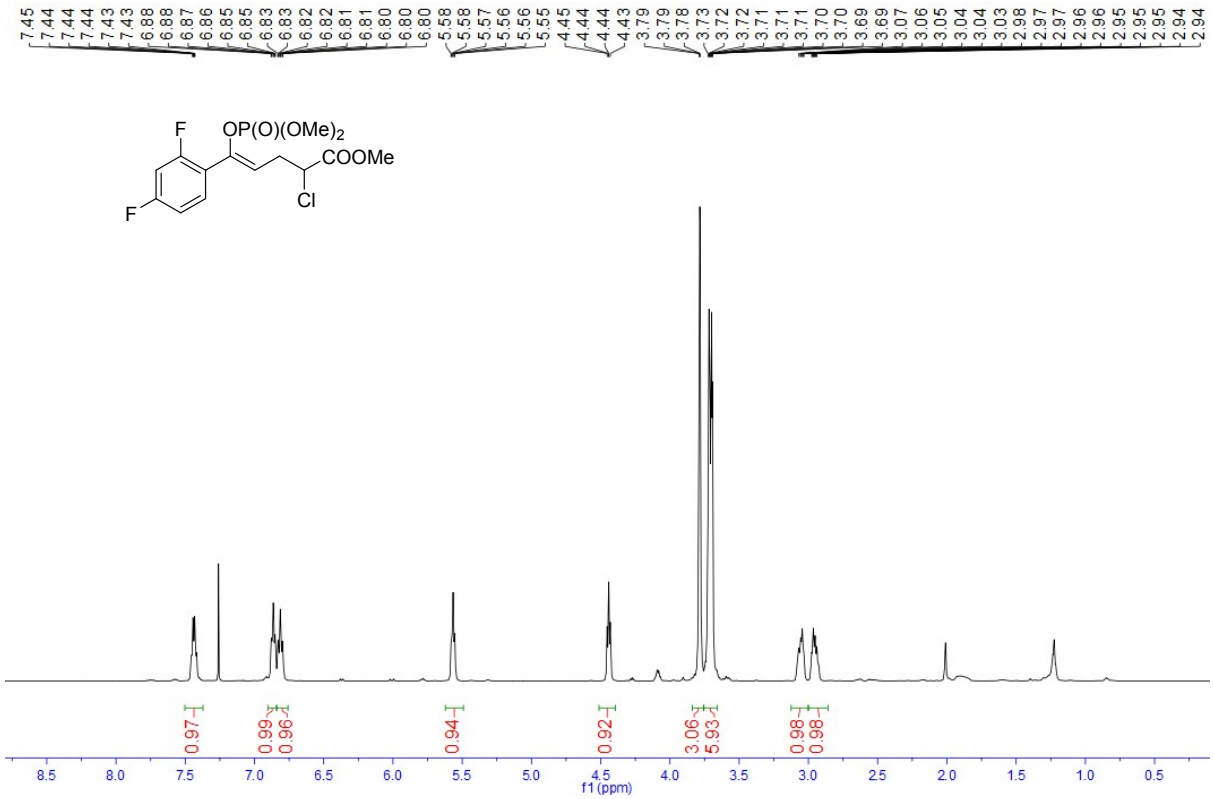
3ob $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



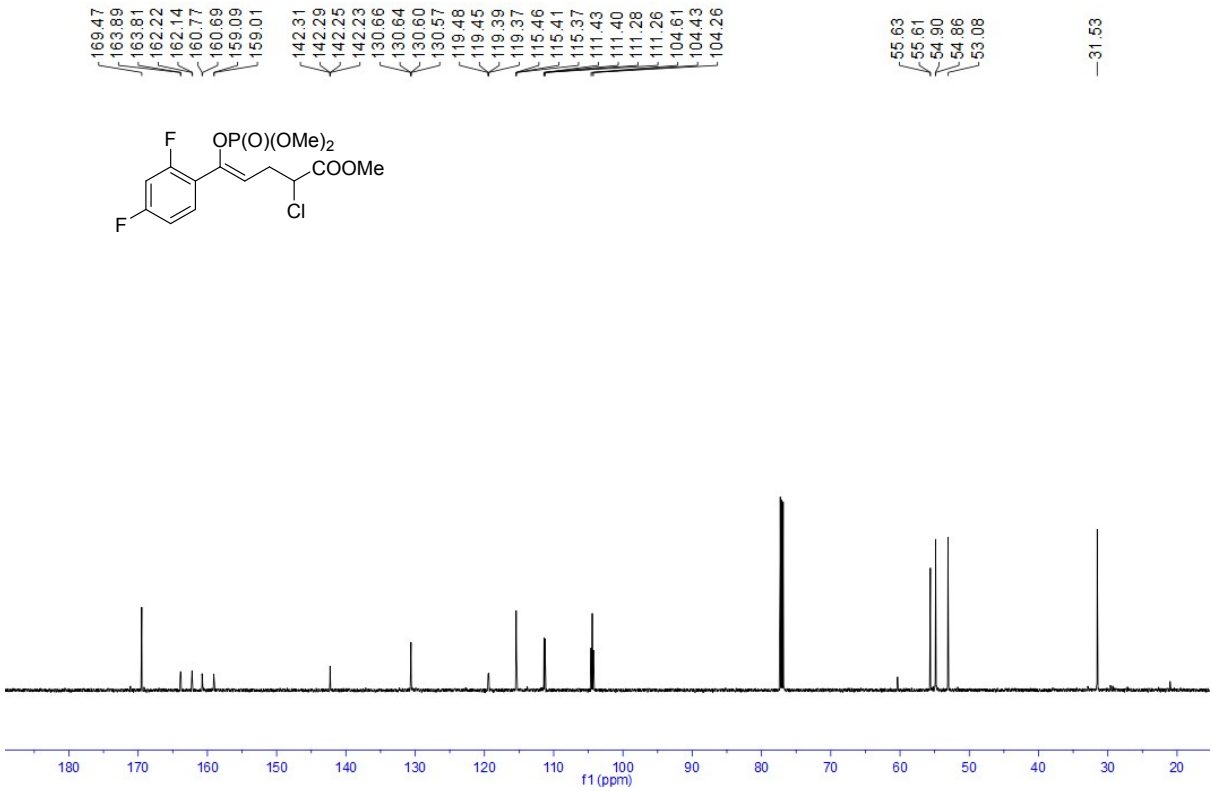
3ob $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



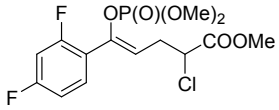
3pb ^{1}H NMR (600 MHz, $CDCl_3$)



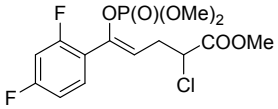
3pb $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



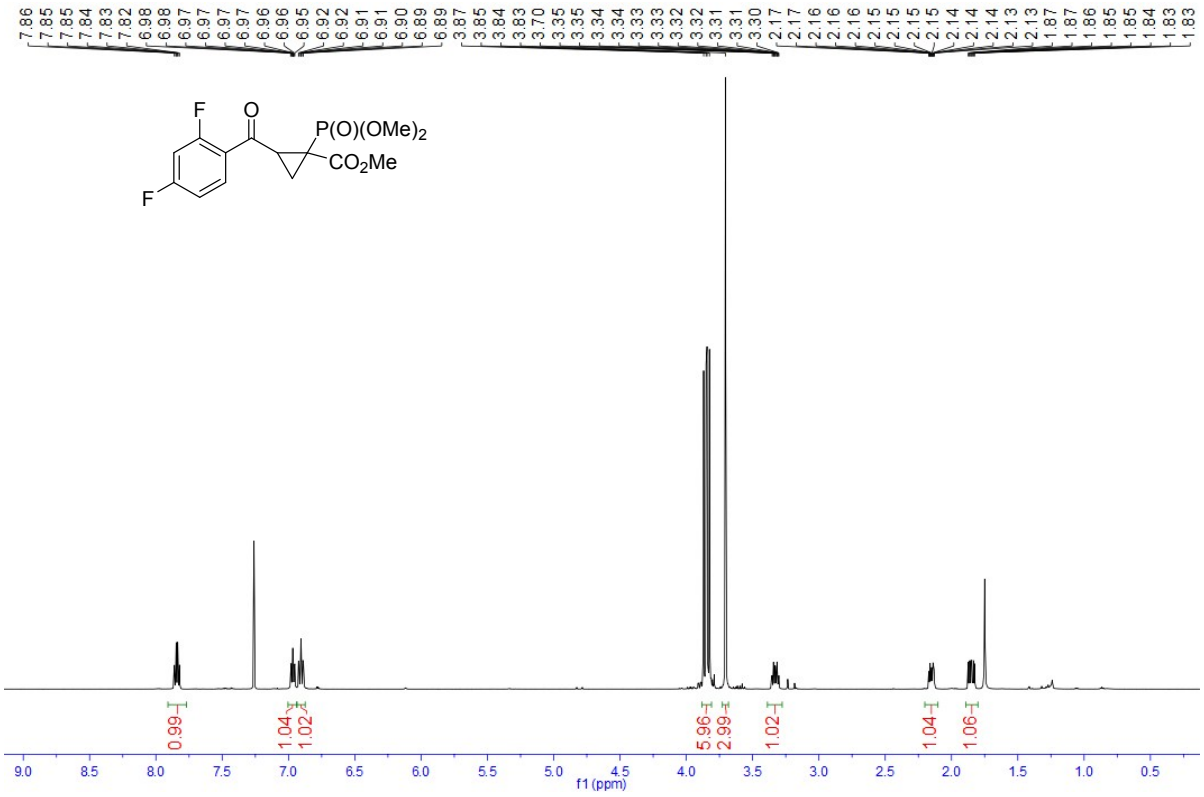
3pb ^{31}P NMR (243 MHz, $CDCl_3$)



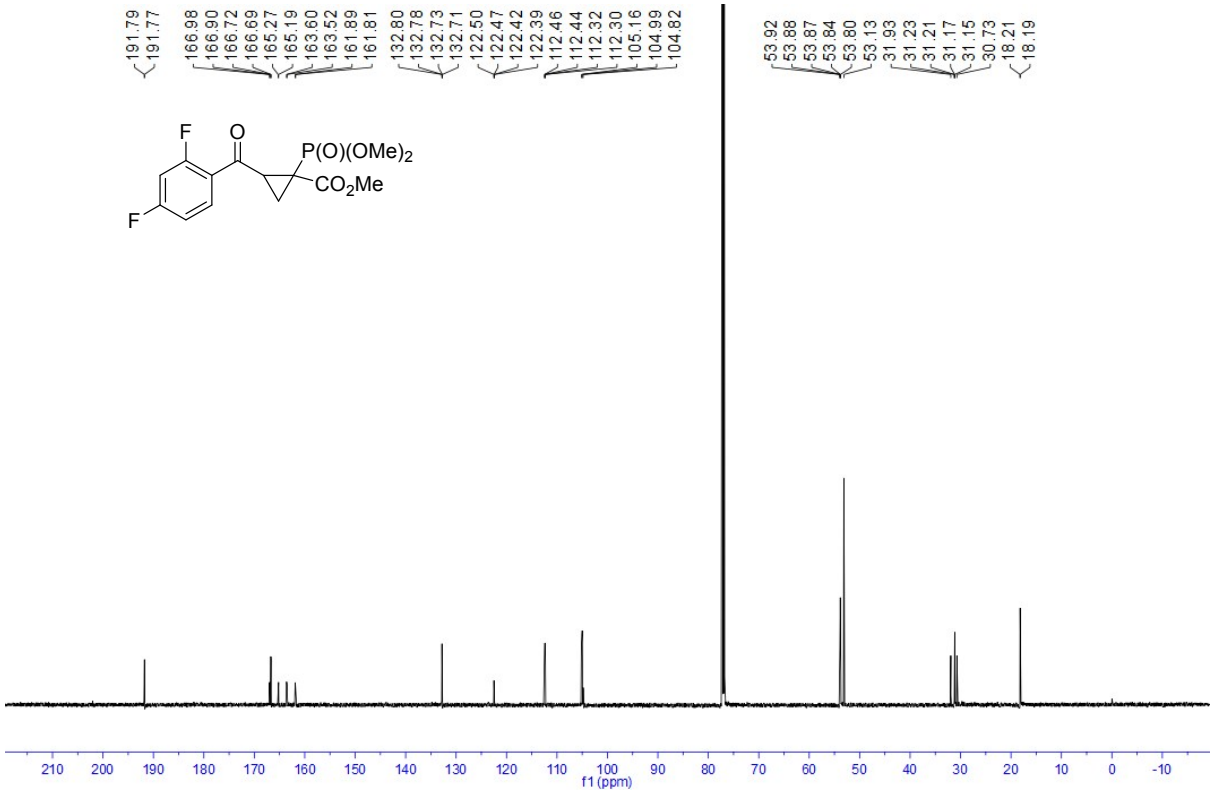
3pb ^{19}F NMR (565 MHz, $CDCl_3$)



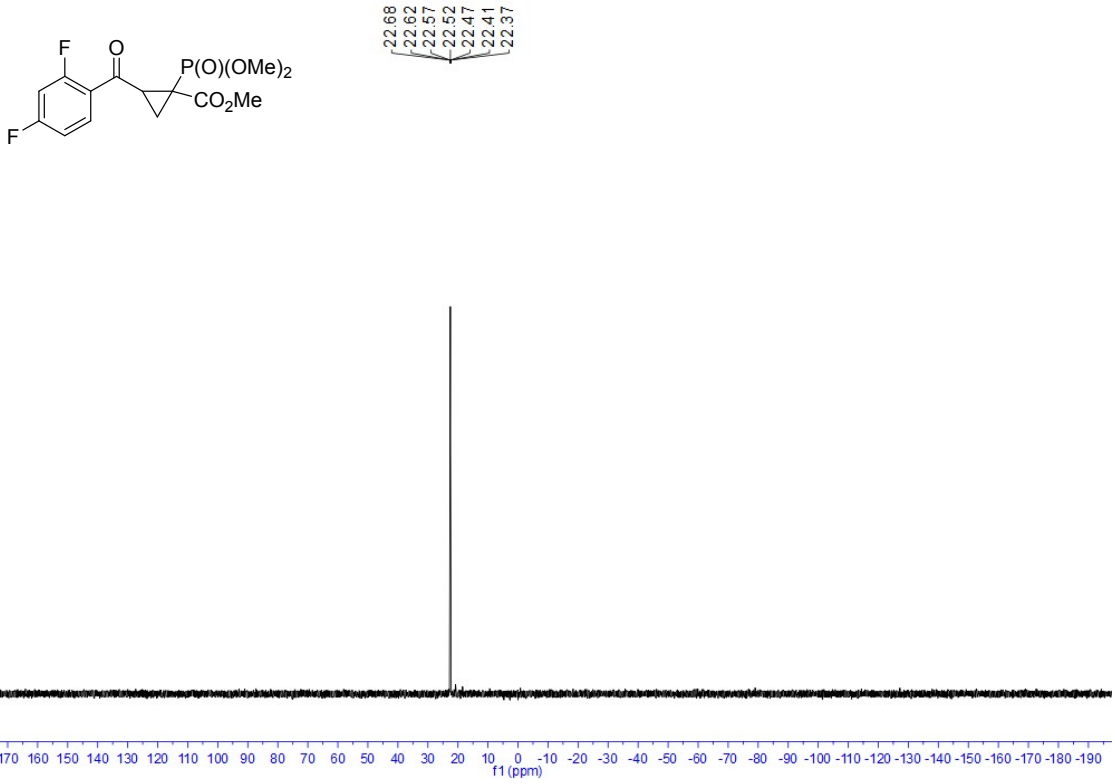
4 ^{1}H NMR (600 MHz, $CDCl_3$)



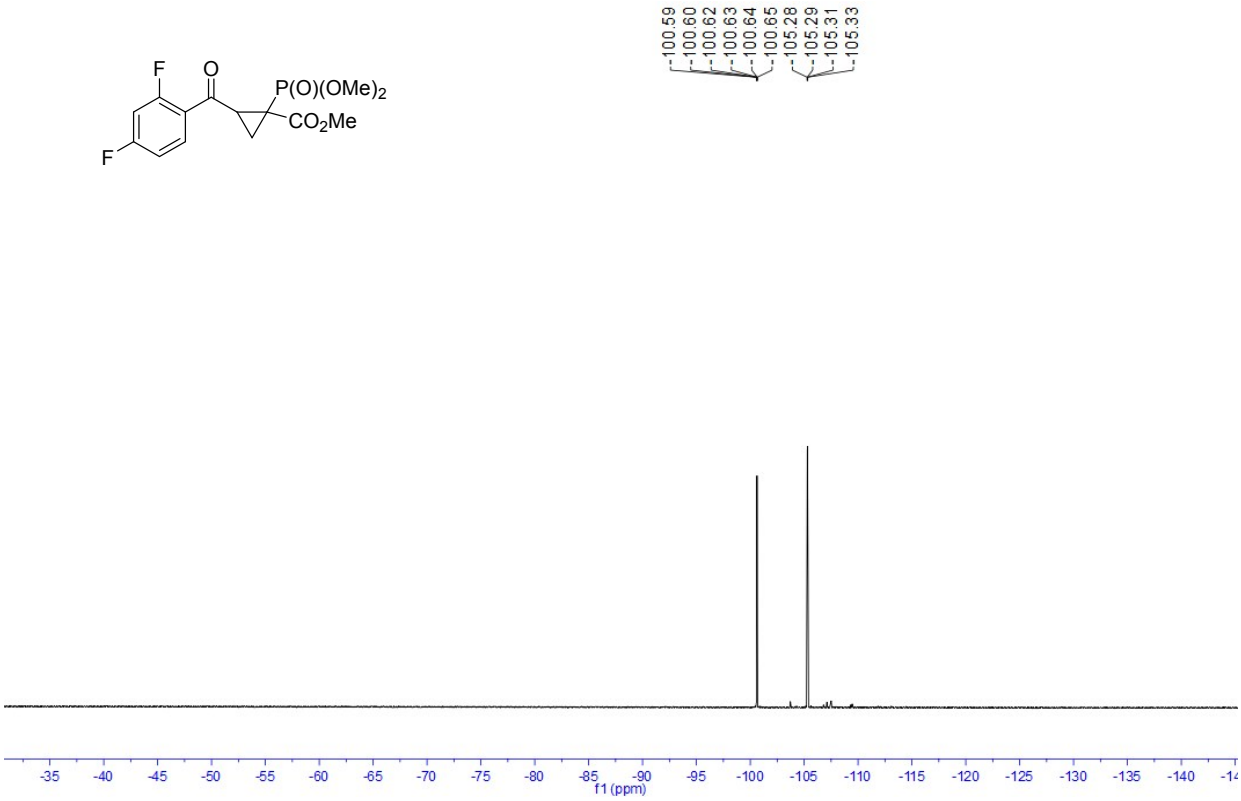
4 ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



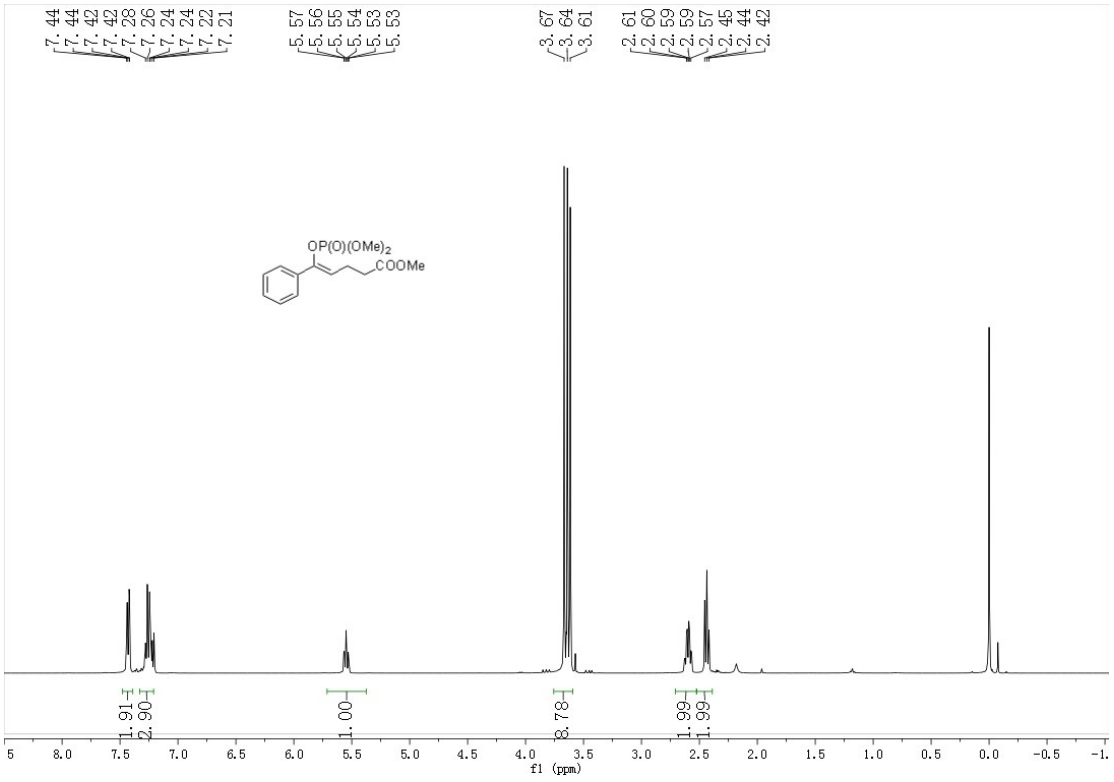
4 ^{31}P NMR (243 MHz, $CDCl_3$)



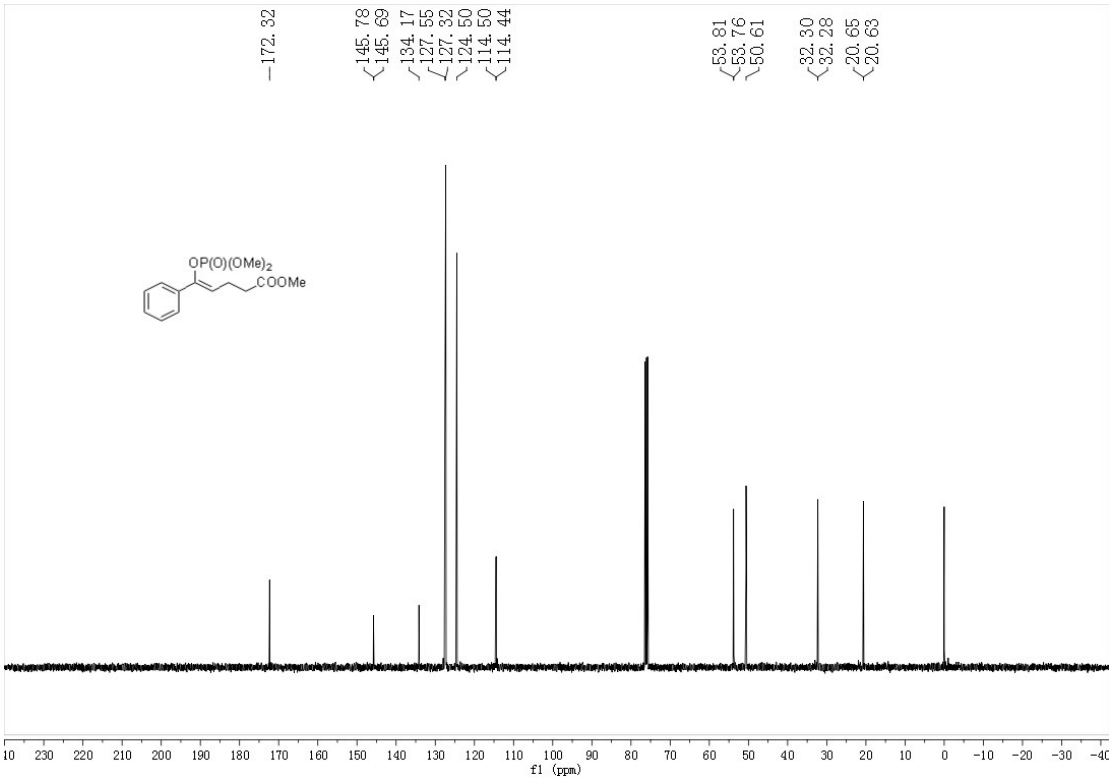
4 ^{19}F NMR (565 MHz, $CDCl_3$)



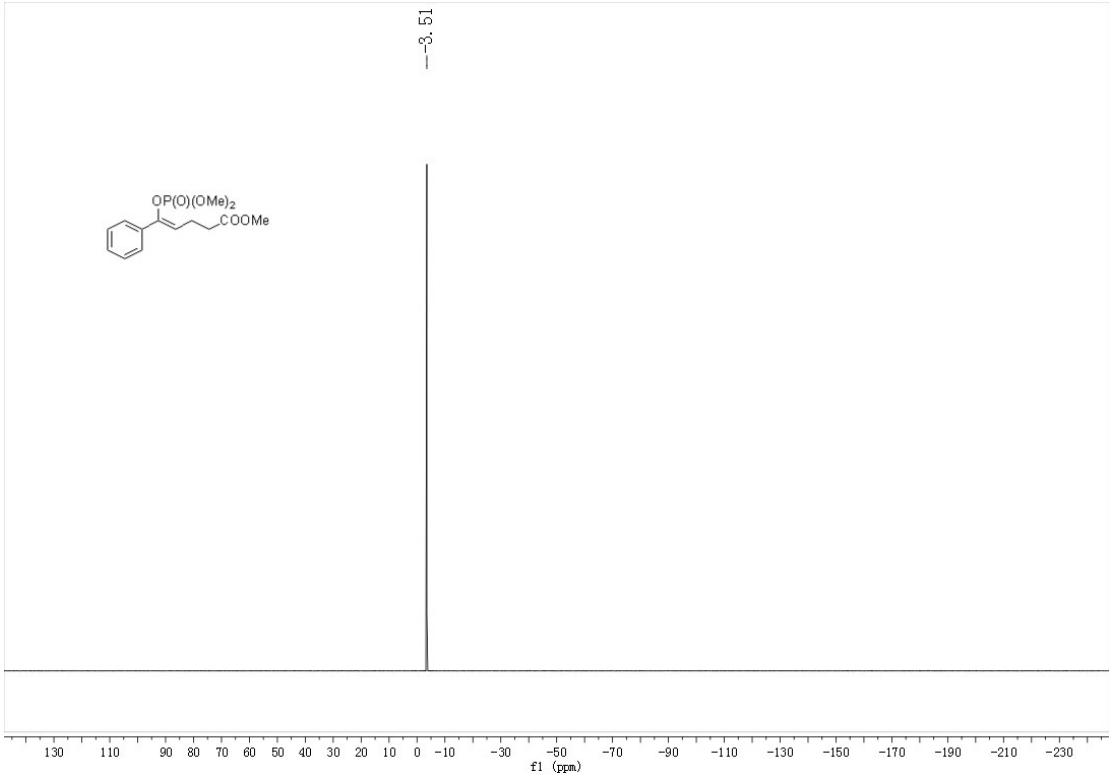
6a ^{1}H NMR (400 MHz, $CDCl_3$)



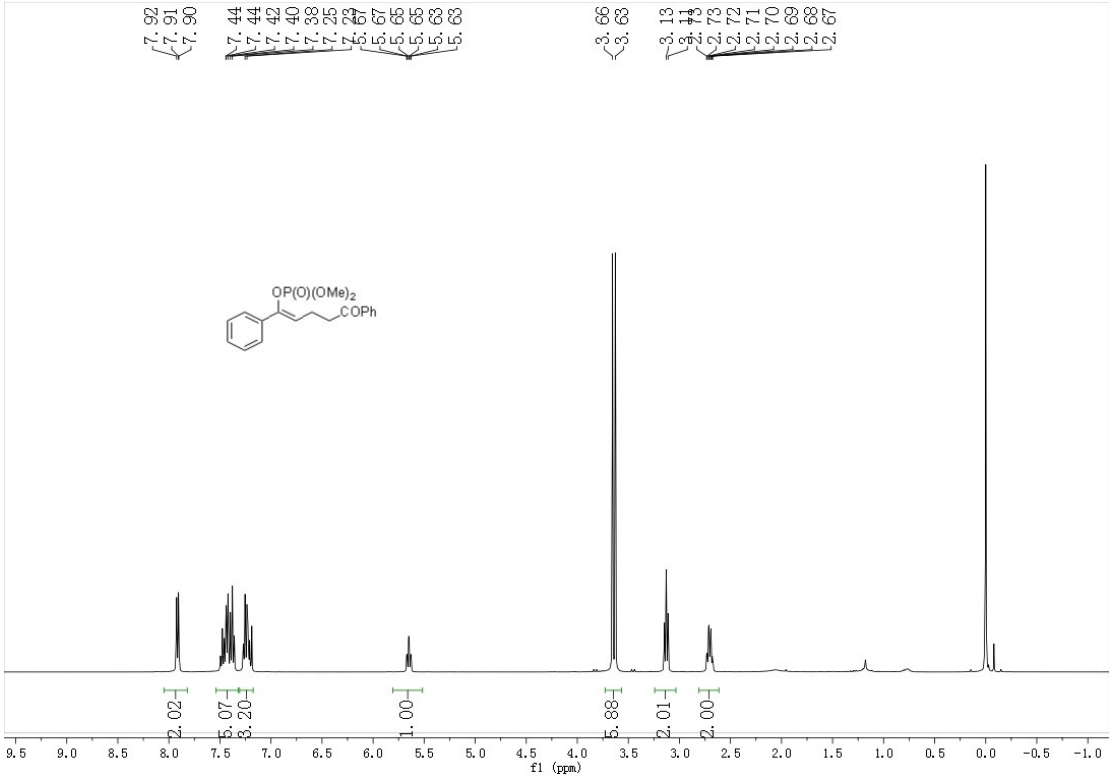
6a $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



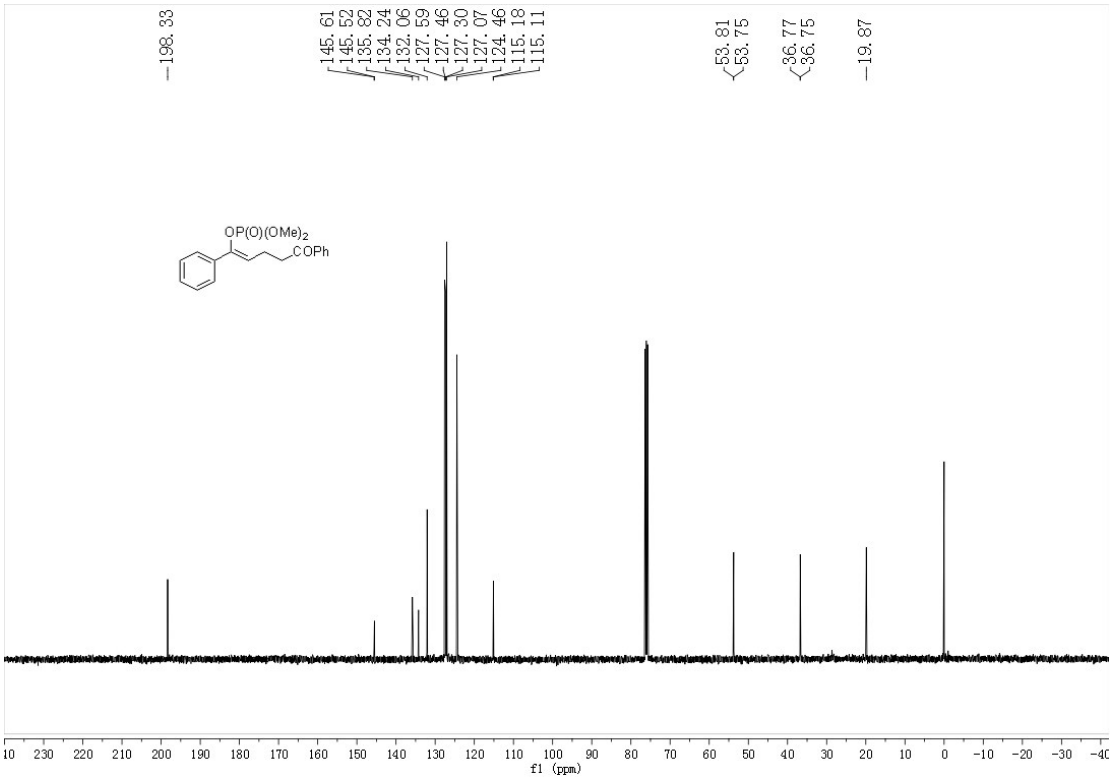
6a $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



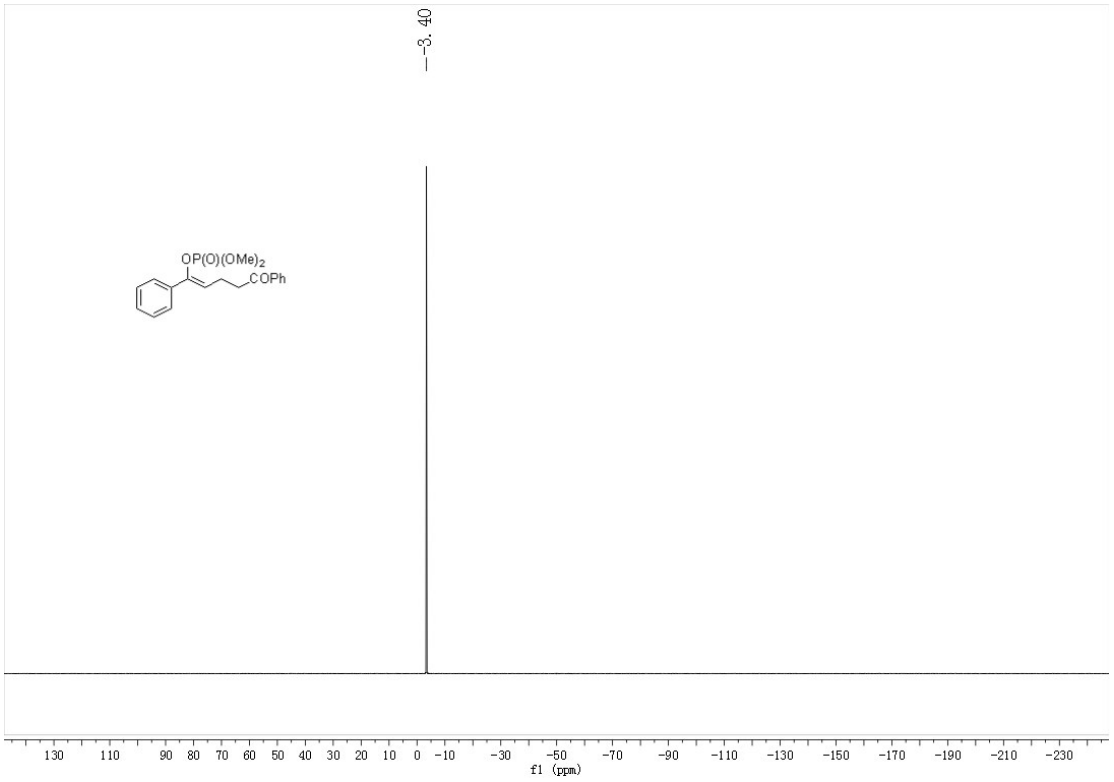
6b ^{1}H NMR (400 MHz, $CDCl_3$)



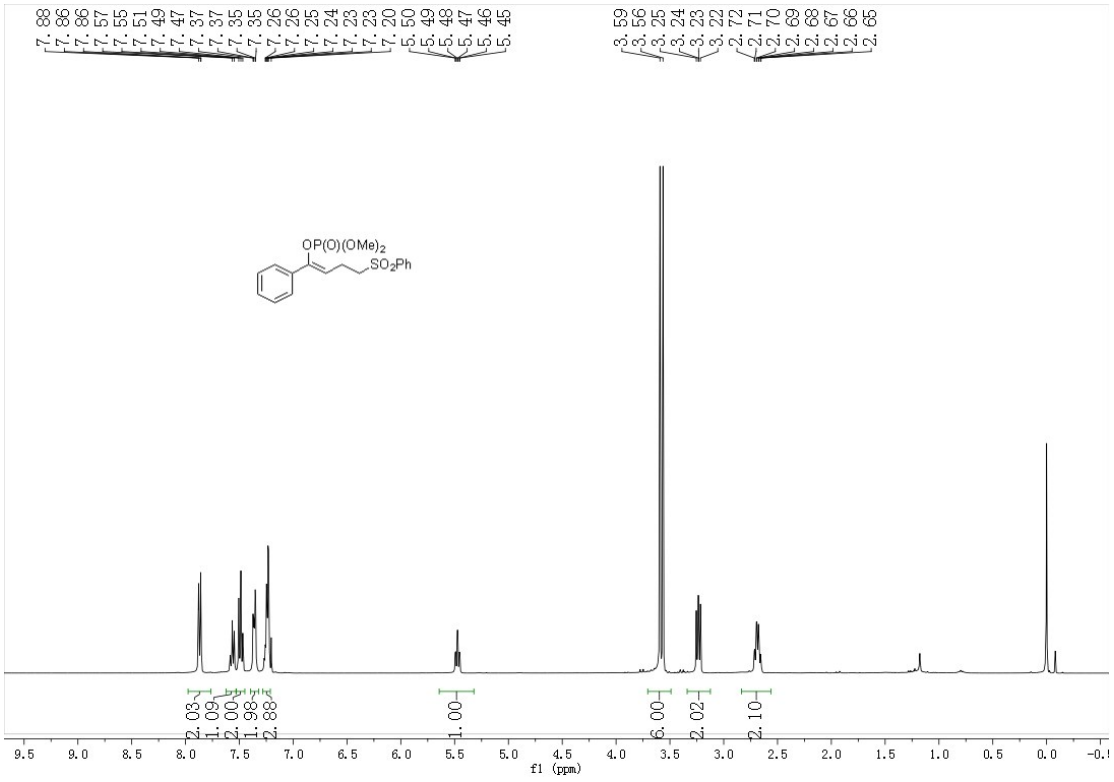
6b $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



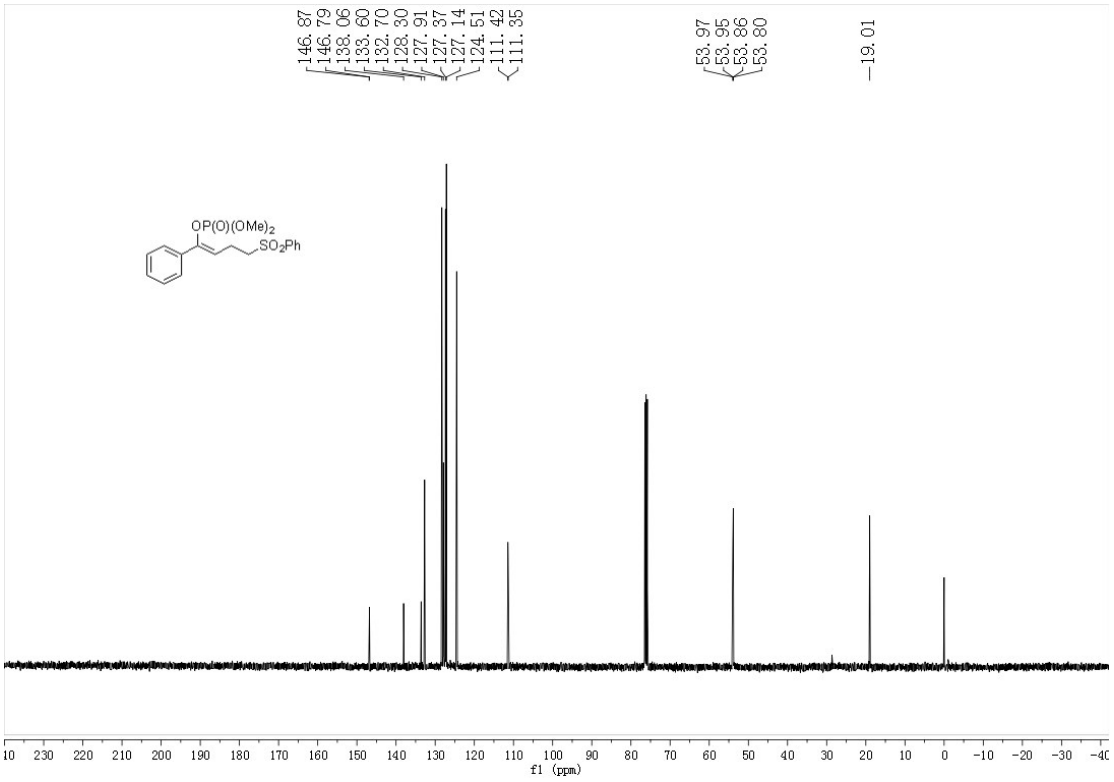
6b $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



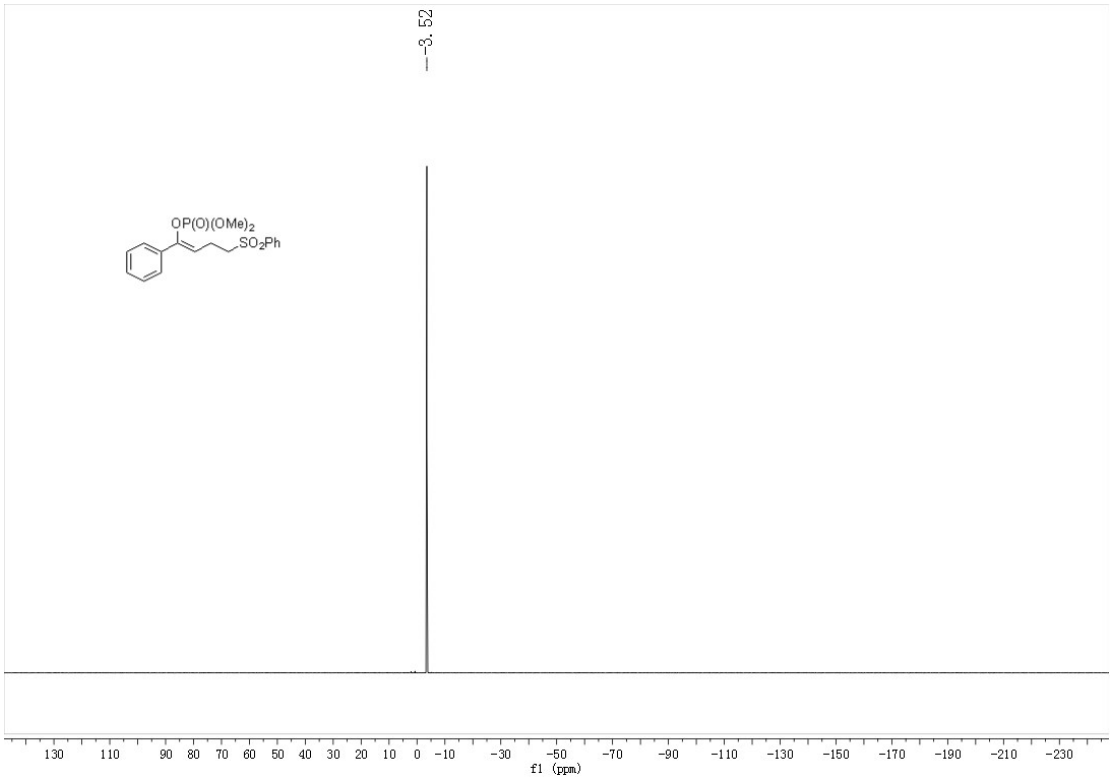
6c ^{1}H NMR (400 MHz, $CDCl_3$)



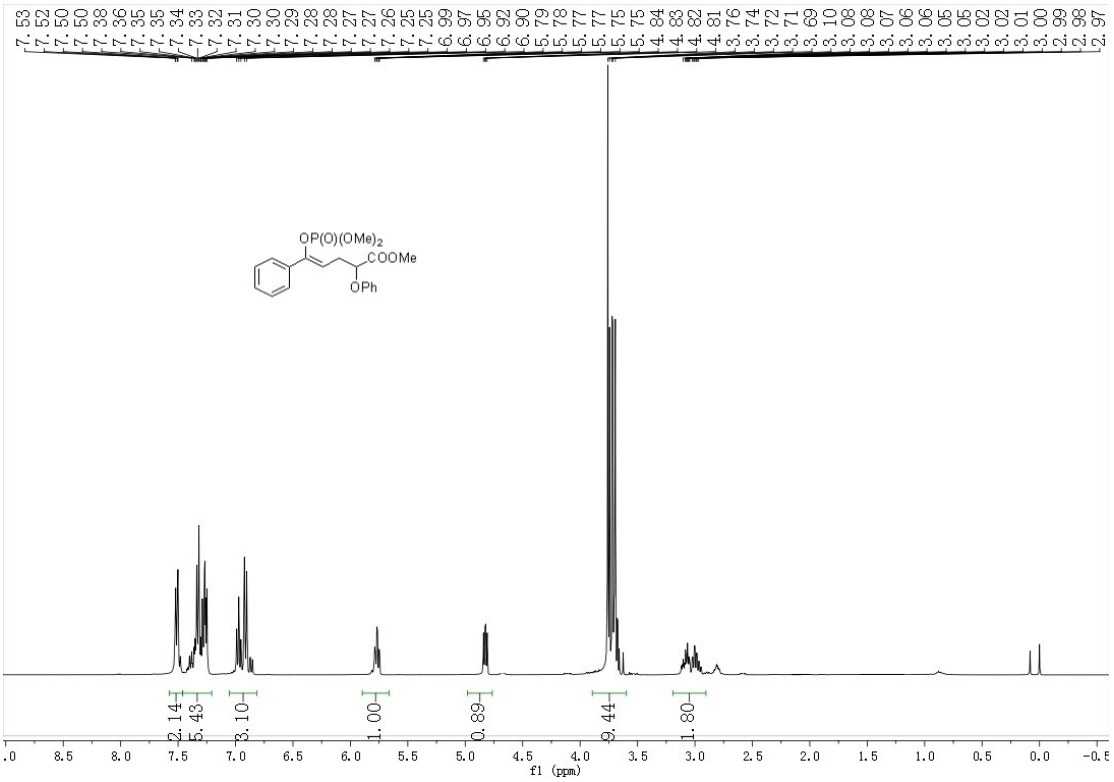
6c $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



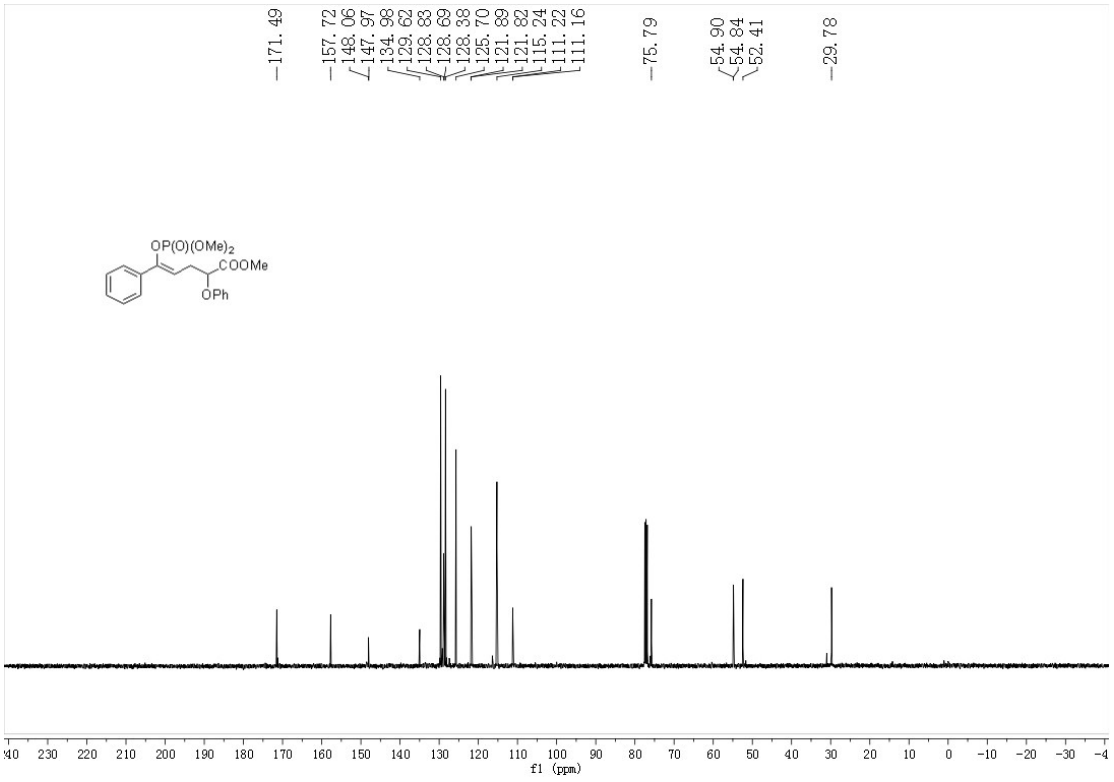
6c $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



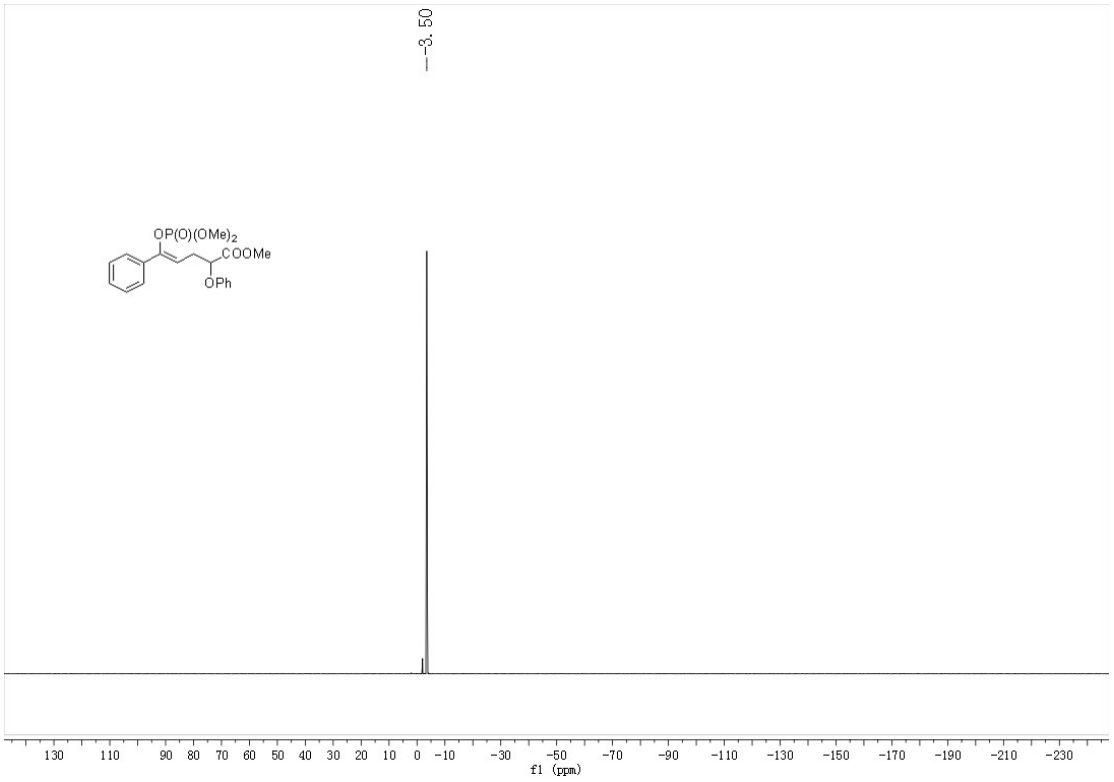
6d ^{1}H NMR (400 MHz, $CDCl_3$)



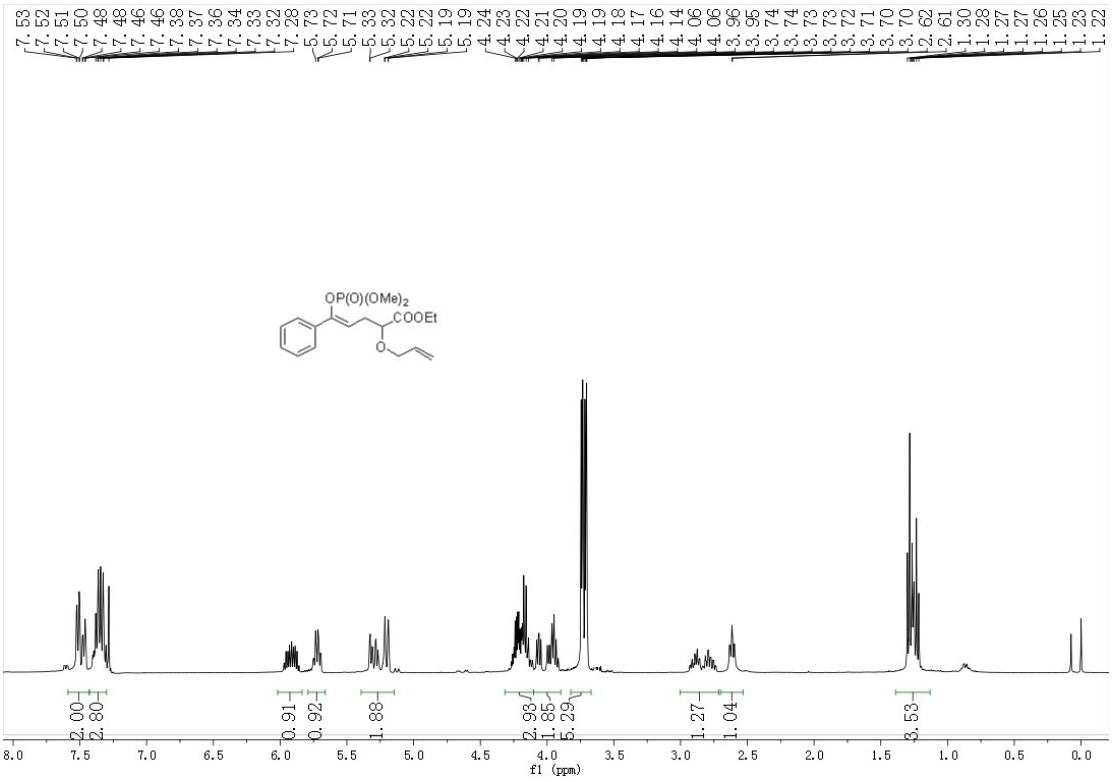
6d $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



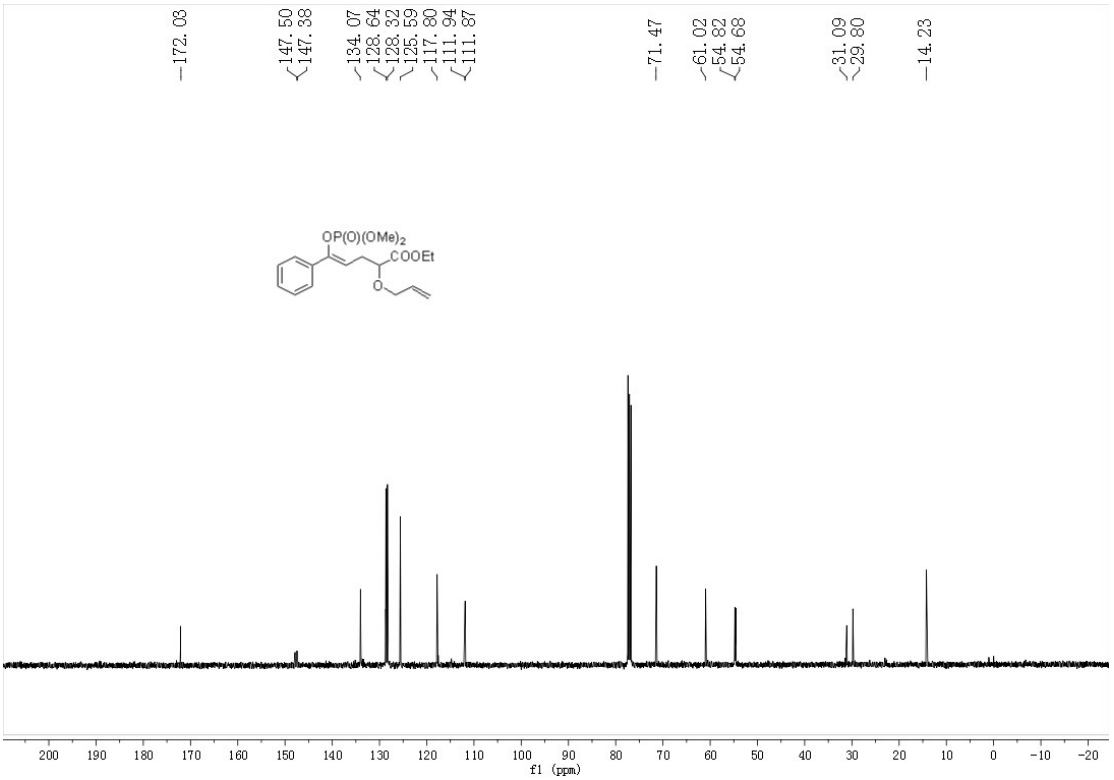
6d $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



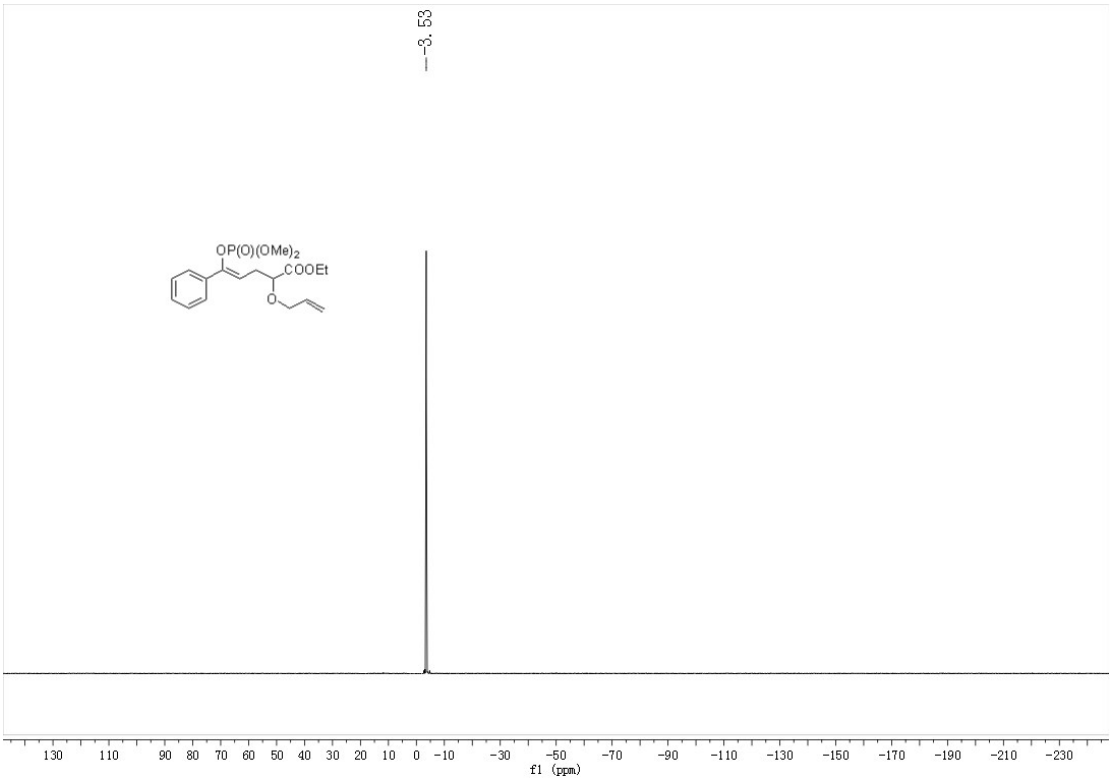
6e ^{1}H NMR (400 MHz, $CDCl_3$)



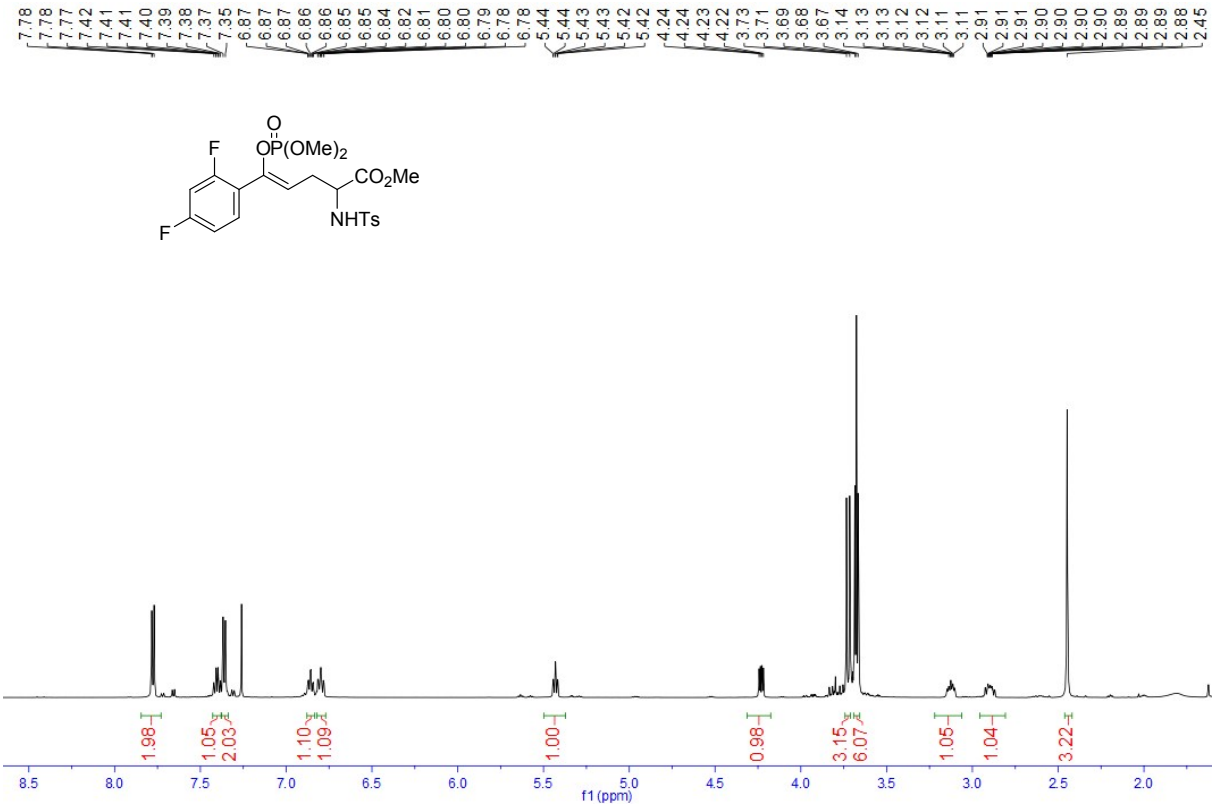
6e $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



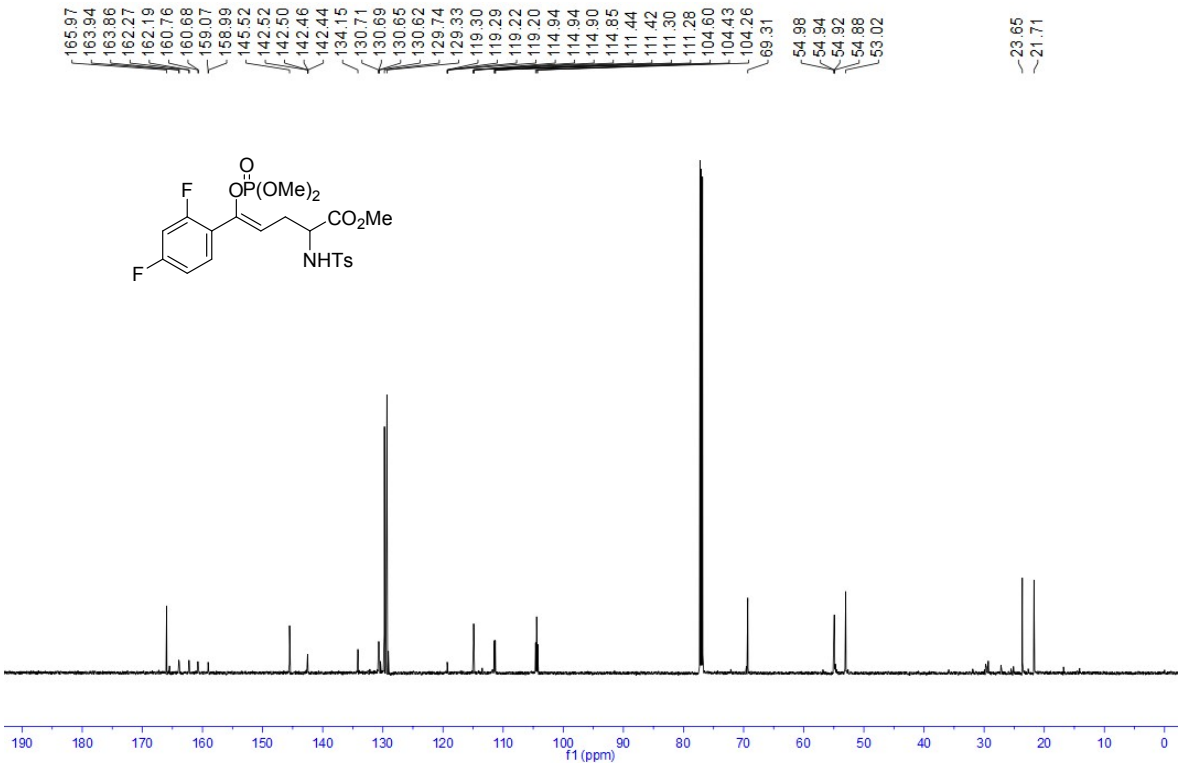
6e $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



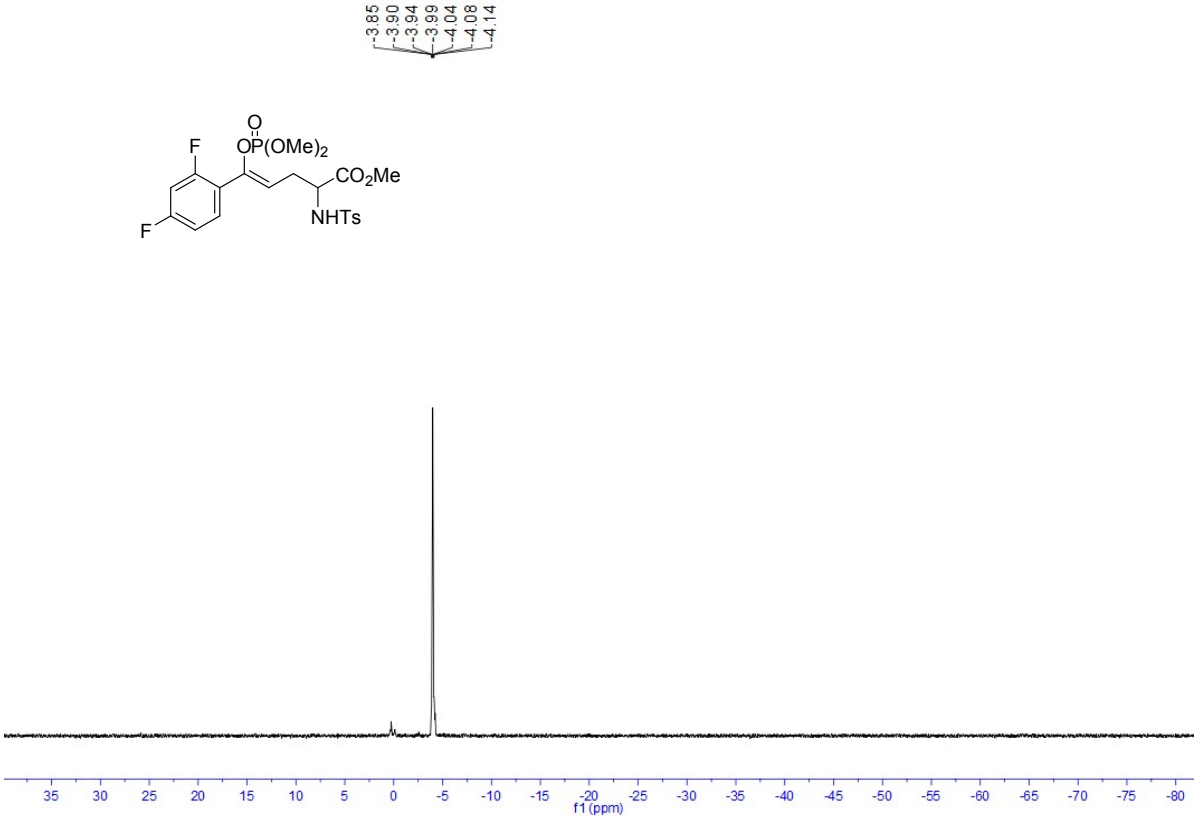
6g ^{1}H NMR (600 MHz, $CDCl_3$)



6g $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



6g ^{31}P NMR (243 MHz, $CDCl_3$)



6g ^{19}F NMR (565 MHz, $CDCl_3$)