Supporting Information

Photocatalyst-Free Visible-Light-Promoted C(sp^2)-P Coupling:

Efficient Synthesis of Aryl Phosphonates

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Contents

1. General Information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Products were purified by column chromatography on 200-300 mesh silica gel, SiO_2. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured on a 400 MHz NMR spectrometer using $CDCl_3$ as the solvent. The chemical shifts are given in δ relative to TMS, and the coupling constants are given in Hertz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qui, quintet; sxt, sextet. The HRMS analyses were conducted using a TOF MS instrument with an EI source. Melting points were measured by a melting point instrument and were uncorrected.

2. Experimental section

2.1 General procedure for photochemical phosphorylation of aryl halides.

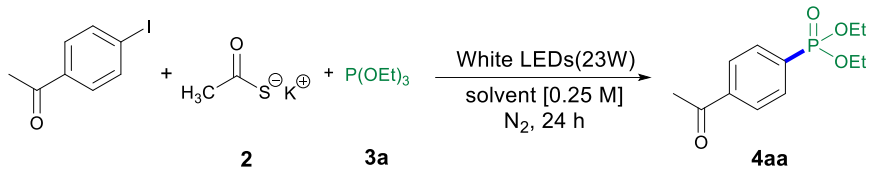
Aryl halide (0.5 mmol, 1.0 eq) **1** and potassium thioacetate **2** (1.0 mmol, 2,0 eq) were added to a 10 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3 times, and then trialkyl phosphite **3** (2.5 mmol, 5.0 eq) and CH_3CN (2.0 mL) were added. The mixture was placed on the magnetic stirrer under irradiation for 24h with white LEDs (4 × 23 w, 6500k) equipped with a cooling fan. When the reaction was completed, the reaction mixture was filtered and then the solvent was removed under reduced pressure. The residue was finally purified by silica gel column chromatography using hexane/ethyl acetate (10:1 to 1:1, v/v) as eluent to afford the pure product.

Larger-scale synthesis of 4aa. 4-Bromoacetophenone **1a** (995.3 mg, 5.0 mmol) and potassium thioacetate **2** (1.14g, 10.0 mmol) were added to a 50 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3

times, and then triethyl phosphite **3a** (4.15g, 25.0 mmol) and CH_3CN (20.0 mL) were added. The mixture was placed on the magnetic stirrer under irradiation for 24h with white LEDs (4 × 23 w, 6500k) equipped with a cooling fan. When the reaction was completed, the reaction mixture was filtered and then the solvent was removed under reduced pressure. The residue was finally purified by silica gel column chromatography using hexane/ethyl acetate (10:1 to 1:1, v/v) as eluent to afford the pure product **4aa** (871.2 mg, 68% yield).

2.2 Optimization studies of the phosphonylation of aryl iodides

Table S1: Solvent selection of the phosphonylation of aryl iodides[a]



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

entry	solvent	ratio (1a/3a)	yield[b](%)
1	**CH_3CN**	**1:5**	**73**
2	DMSO	1:5	44
3	DMF	1:5	36
4	DMA	1:5	30
5	THF	1:5	18
6	DCE	1:5	15
7	1,4-dioxane	1:5	trace

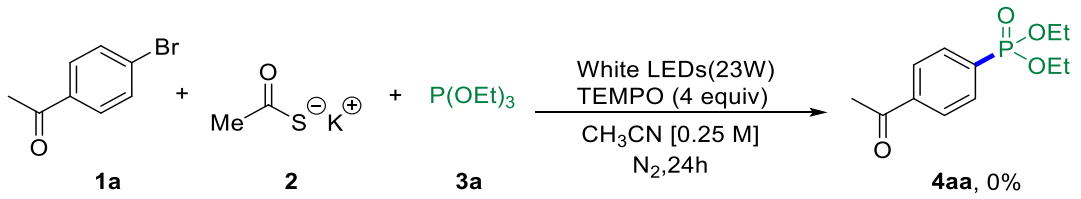
[a] Reaction conditions: 1a (0.5 mmol), 2 (1.0 mmol), 3a (2.5 mmol), solvent (2.0 mL), N_2, 24 h.

[b] Isolated yield.

2.3 Mechanism experiments.

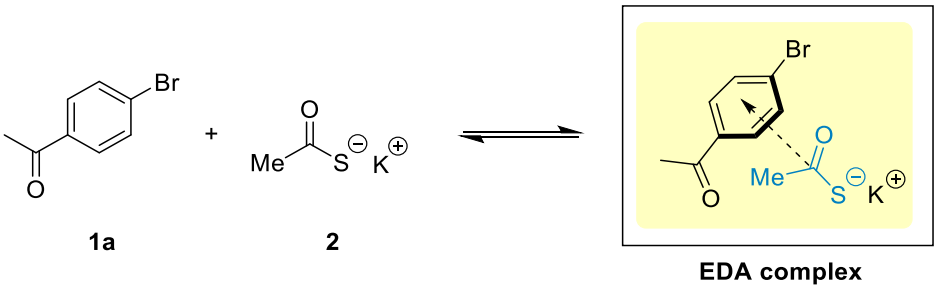
4-Bromoacetophenone **1a** (99.5 mg, 0.5 mmol), potassium thioacetate **2** (114.2 mg, 1.0 mmol) and TEMPO (234.4 mg, 1.5 mmol) were added to a 10 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3 times, and then triethyl phosphite **3a** (415.4mg, 2.5 mmol) and CH_3CN (2.0 mL) were added. The mixture was placed on the magnetic stirrer under irradiation for 24h with white LEDs (4 × 23 w,

6500k) equipped with a cooling fan. When the reaction was completed, products **4aa** and TEMPO-bound adduct could not be detected.



2.4 UV-Vis absorption spectra.

A. The UV-Vis absorption spectra of DMSO solutions of 4-bromoacetophenone **1a** (0.05 M), potassium thioacetate **2** (0.05 M), triethyl phosphite **3a** (0.05 M) and their mixtures (0.05 M) are shown in Figure S2. A bathochromic shift can be observed, indicating the formation of an EDA complex.



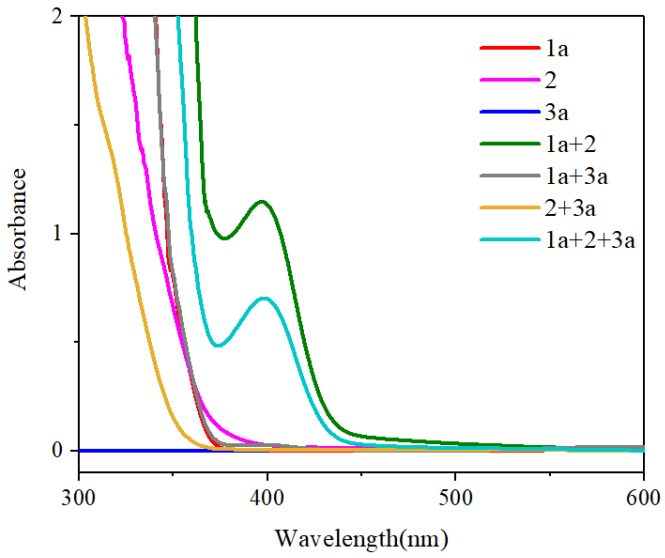


Fig S1, UV-Vis spectra of **1a**, **2**, **3a** and their mixtures for [0.05 M] solutions in DMSO

The following Fig S3 shows TLC analysis of UV-vis measure samples, and from left to right are 4-bromoacetophenone(**1a**), 4-bromoacetophenone/ potassium thioacetate/ triethyl phosphite(**1a/2/3a**) mixture in DMSO, co-spot of **1a/2/3a** mixture and diethyl (4-acetylphenyl)phosphonate, diethyl (4-acetylphenyl)phosphonate, potassium thioacetate, respectively.

Fig S2, TLC analysis of UV-vis measure samples

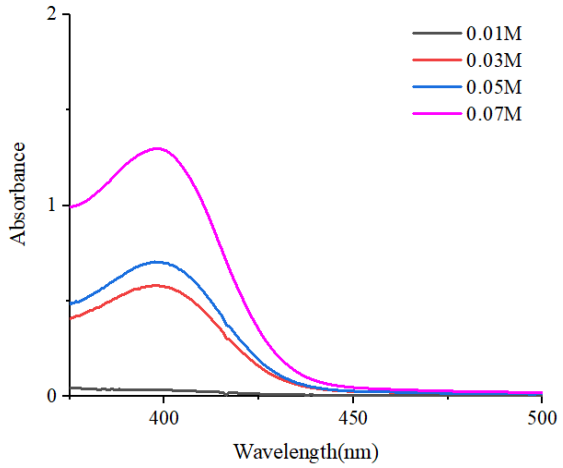


Fig S3, UV-Vis spectra of **1a**/**2**/**3a** mixture at different concentrations in DMSO

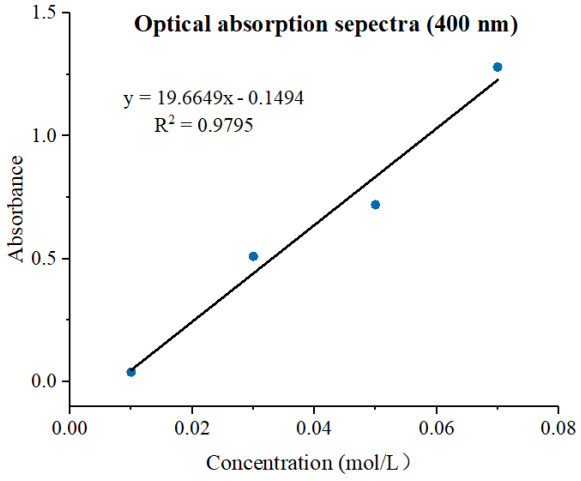


Fig S4, Plot of absorbance of **1a**/**2**/**3a** mixture as a function of concentrations. Path length =1 cm.

To evaluate the stoichiometry of the EDA complex, a Job's plot was constructed using UV-Vis spectroscopy. Absorption of different molar ratios of 4-bromoacetophenone (**1a**) and potassium thioacetate (**2**) in DMSO at a constant total concentration (0.1 M) at 400 nm was measured. The absorbance values were plotted against the molar fraction of **1a** in solution. Maximum absorbance was obtained for a 1:1 mixture, which indicates the stoichiometry of the EDA complex in solution.

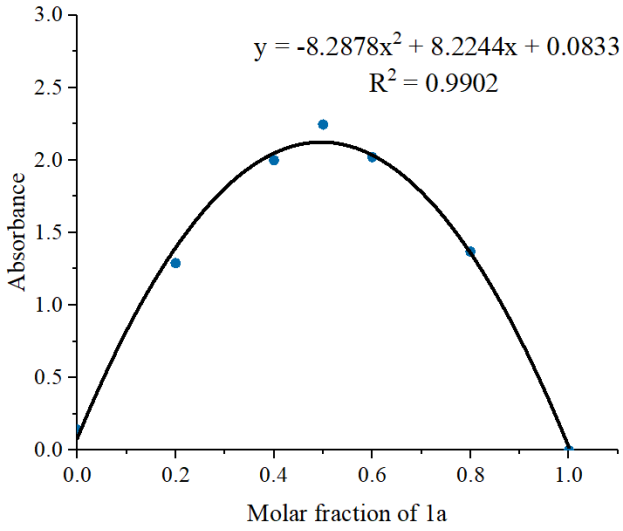


Fig S5, Job's plot for the EDA complex between **1a** and **2**

The color changes in CH_3CN are shown in the following Fig S7. The CH_3CN solution of **2** appears bright yellow and the CH_3CN solution of **1a/2** mixture appears orange yellow. In addition, the solution of **1a/2/3a** in CH_3CN appears light yellow, while the solutions of **1a**, **3a**, **2/3a** and **1a/3a** are colorless. There are many white crystals (possibly undissolved potassium thioacetate) in the solutions of **2**, **1a/2**, **2/3a** and **1a/2/3a**.

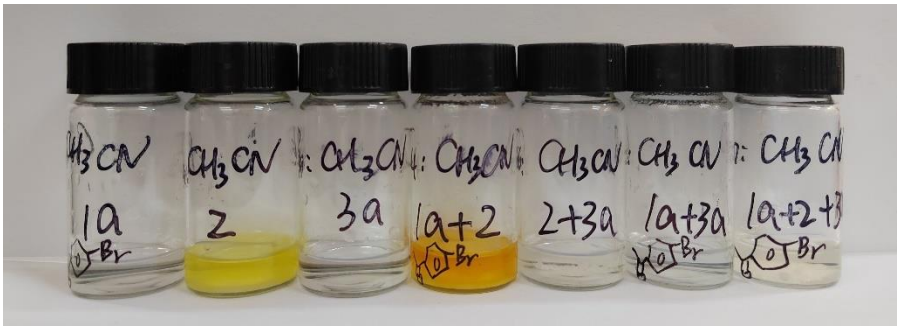
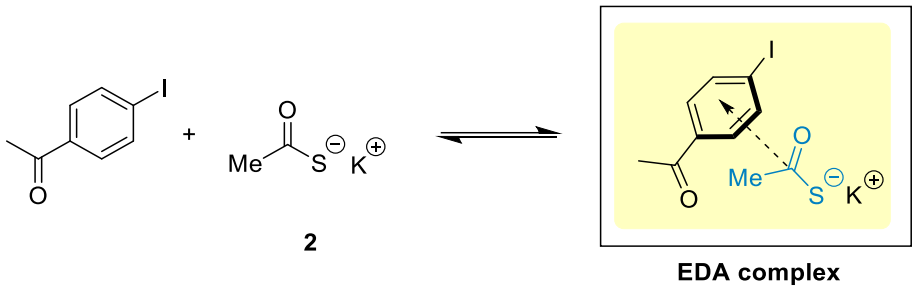


Fig S6, color changes of **1a**, **2**, **3a** and their mixtures in CH_3CN

B. The UV-Vis absorption spectra of 4-iodoacetophenone, potassium thioacetate **2**, triethyl phosphite **3a** and their mixtures were recorded for 0.05 M solutions in DMSO.



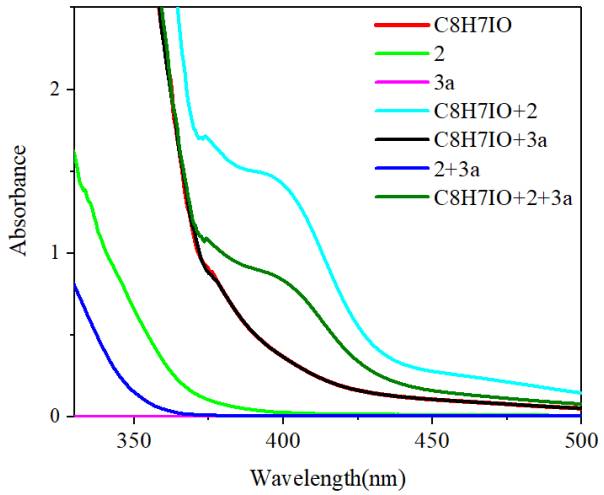


Fig S7, UV-Vis spectra of **C_8H_7IO**, **2**, **3a** and their mixtures for [0.05 M] solutions in DMSO

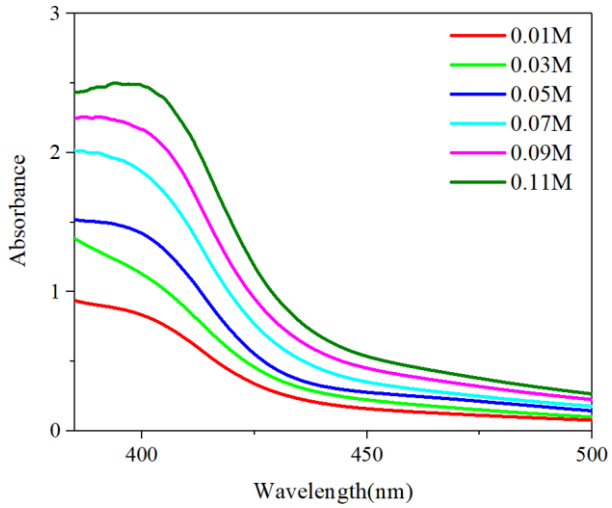


Fig S8, UV-Vis spectra of **C_8H_7IO /2/3a** mixture at different concentrations in DMSO

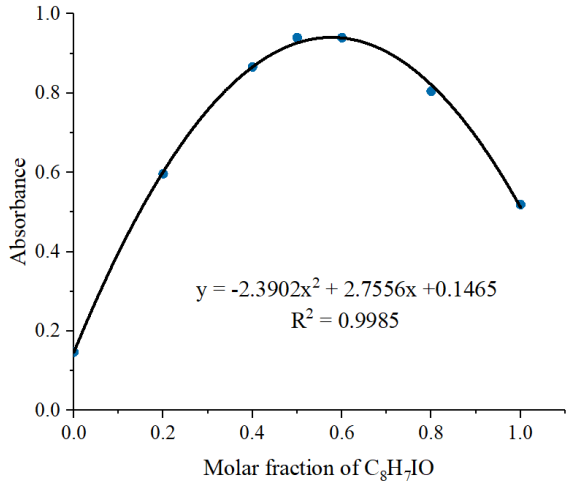


Fig S9, Job's plot for the EDA complex between **C_8H_7IO** and **2**

2.5 Light on-off experiments.

4-Bromoacetophenone **1a** (99.5 mg, 0.5 mmol) and potassium thioacetate **2** (114.2 mg, 1.0 mmol) were added to a 10 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3 times, and then triethyl phosphite **3a** (415.4mg, 2.5 mmol) and CH_3CN (2.0 mL) were added. The mixture was placed on the magnetic stirrer under irradiation with white LEDs (4 × 23 w, 6500k) equipped with a cooling fan. After 3 h of light irradiation, an aliquot (0.1 mL) was removed by a syringe from each vial and directly analyzed by ^{1}H-NMR using 1,3,5-trimethoxybenzene as an internal standard to obtain the yield of the phosphonate ester **4aa**. Thereafter, the light was switched off with continuous stirring for 3 h. Once again, an analytical sample solution was prepared (as mentioned earlier) and analyzed similarly, and the light was switched on for 3 h. This cycle was repeated and the yield of **4aa** with respect to time was plotted (Fig S4). The nature of the graph indicates that the process is dependent on light.

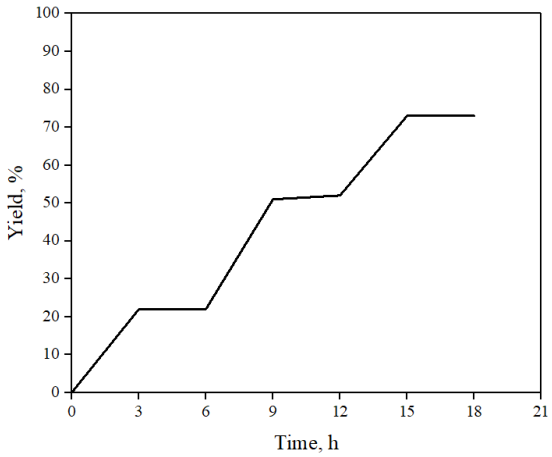
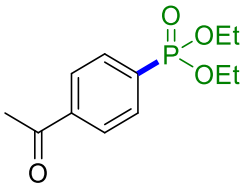
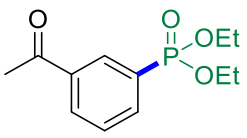


Fig S10, on-off experiment

3. Characterization data of products

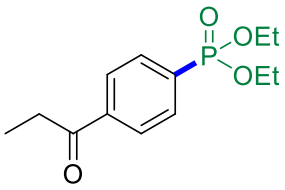


Diethyl (4-acetylphenyl)phosphonate (4aa). Colorless oil, 104 mg, yield: 81% for X=Br; 94 mg, yield: 73% for X=I; 10 mg, yield: 8% for X=Cl; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.93 – 7.86 (m, 2H), 4.19 – 4.00 (m, 4H), 2.60 (s, 3H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 139.9 (d, J = 3.2 Hz), 133.4 (d, J = 186.6 Hz), 132.1 (d, J = 10.1 Hz), 128.1 (d, J = 15.1 Hz), 62.5 (d, J = 5.5 Hz), 26.9, 16.4 (d, J = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.9. The spectral data were in accordance with the literature.[1]

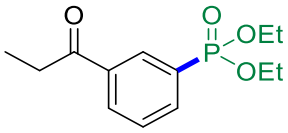


Diethyl (3-acetylphenyl)phosphonate (4ba). Yellow oil, 94 mg, Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 13.8 Hz, 1H), 8.10 (d, J = 9.7 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.57 – 7.52 (m,

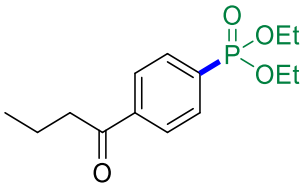
1H), 4.18 – 4.03 (m, 4H), 2.60 (s, 3H), 1.30 (t, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 137.2 (d, J = 13.9 Hz), 136.0 (d, J = 9.9 Hz), 131.9 (d, J = 3.0 Hz), 131.7 (d, J = 10.6 Hz), 129.5 (d, J = 189.4 Hz), 129.0 (d, J = 14.8 Hz), 62.5 (d, J = 5.6 Hz), 26.7, 16.4 (d, J = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.2. The spectral data were in accordance with the literature.[2]



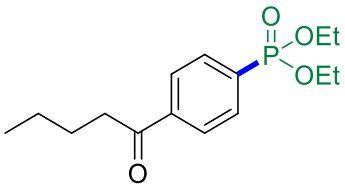
Diethyl (4-propionylphenyl)phosphonate (4ca). Yellow oil, 134 mg, Yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.1, 3.8 Hz, 2H), 7.85 (dd, J = 12.9, 7.9 Hz, 2H), 4.14 – 4.03 (m, 4H), 2.97 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.0 Hz, 6H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 139.8 (d, J = 3.3 Hz), 133.2 (d, J = 186.8 Hz), 132.2 (d, J = 10.1 Hz), 127.8 (d, J = 15.1 Hz), 62.5 (d, J = 5.6 Hz), 32.2, 16.4 (d, J = 6.3 Hz), 8.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.0. The spectral data were in accordance with the literature.[3]



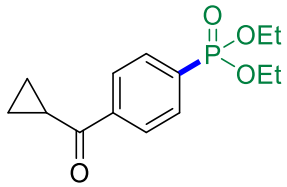
Diethyl (3-propionylphenyl)phosphonate (4da). Yellow oil, 97 mg, Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 13.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.97 (dd, J = 12.9, 7.5 Hz, 1H), 7.58 – 7.53 (m, 1H), 4.18 – 4.05 (m, 4H), 3.02 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.1 Hz, 6H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 137.0 (d, J = 13.7 Hz), 135.9 (d, J = 10.0 Hz), 131.7 (d, J = 3.0 Hz), 131.3 (d, J = 10.6 Hz), 129.4 (d, J = 189.3 Hz), 129.0 (d, J = 15.0 Hz), 62.4 (d, J = 5.6 Hz), 32.0, 16.4 (d, J = 6.4 Hz), 8.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.3; HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_{19}O_4P$ 270.1021, found 270.1018.



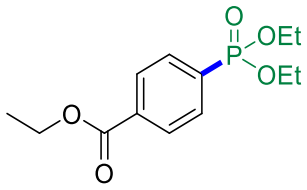
Diethyl (4-butyrylphenyl)phosphonate (4ea). Yellow oil, 107 mg, Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.9, 4.1 Hz, 2H), 7.87 (dd, *J* = 12.7, 8.2 Hz, 2H), 4.19 – 4.02 (m, 4H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.78 – 1.69 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 6H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 140.0 (d, *J* = 3.3 Hz), 133.1 (d, *J* = 186.8 Hz), 132.0 (d, *J* = 10.0 Hz), 127.8 (d, *J* = 15.1 Hz), 62.5 (d, *J* = 5.5 Hz), 40.8, 17.6, 16.4 (d, *J* = 6.3 Hz), 13.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.0. The spectral data were in accordance with the literature.[3]



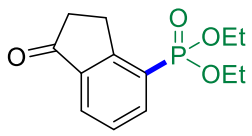
Diethyl (4-pentanoylphenyl)phosphonate (4fa). Yellow oil, 147 mg, Yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.3, 3.8 Hz, 2H), 7.88 (dd, *J* = 12.9, 7.9 Hz, 2H), 4.18 – 4.05 (m, 4H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.44 – 1.34 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 6H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 139.9 (d, *J* = 3.3 Hz), 133.1 (d, *J* = 186.8 Hz), 132.2 (d, *J* = 10.0 Hz), 127.8 (d, *J* = 15.1 Hz), 62.4 (d, *J* = 5.5 Hz), 40.8, 17.5, 16.3 (d, *J* = 6.3 Hz), 13.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.0; HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{23}O_4P$ 298.1334, found 298.1331.



Diethyl (4-(cyclopropanecarbonyl)phenyl)phosphonate (4ga). Colorless oil, 112 mg, Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.3, 3.8 Hz, 2H), 7.90 (dd, *J* = 12.9, 7.9 Hz, 2H), 4.21 – 4.04 (m, 4H), 2.68 – 2.62 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.27 – 1.23 (m, 2H), 1.09 – 1.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 141.0 (d, J = 3.2 Hz), 133.0 (d, J = 186.6 Hz), 132.1 (d, J = 10.0 Hz), 127.9 (d, J = 15.1 Hz), 62.5 (d, J = 5.5 Hz), 17.7, 16.4 (d, J = 6.4 Hz), 12.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.1; HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{19}O_4P$ 282.1021, found 282.1026.

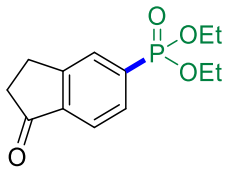


Ethyl 4-(diethoxyphosphoryl)benzoate (4ha). Colorless oil, 103 mg, Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.1, 3.8 Hz, 2H), 7.87 (dd, *J* = 13.0, 7.9 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.21 – 4.03 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 133.9 (d, *J* = 3.3 Hz), 133.1 (d, *J* = 186.5 Hz), 131.8 (d, *J* = 10.1 Hz), 129.4 (d, *J* = 15.1 Hz), 62.4 (d, *J* = 5.6 Hz), 61.5, 16.3 (d, *J* = 6.3 Hz), 14.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.1. The spectral data were in accordance with the literature.[1]

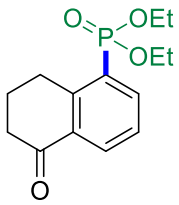


Diethyl (1-oxo-2,3-dihydro-1H-inden-4-yl)phosphonate (4ia). Colorless oil, 90 mg, Yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 13.7, 7.4 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.50

– 7.46 (m, 1H), 4.26 – 4.07 (m, 4H), 3.37 (t, *J* = 5.9 Hz, 2H), 2.72 (t, *J* = 8.0, 1.7 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 158.0 (d, *J* = 10.2 Hz), 138.9 (d, *J* = 10.7 Hz), 137.8 (d, *J* = 12.6 Hz), 127.8 (d, *J* = 3.2 Hz), 127.4 (d, *J* = 13.9 Hz), 127.0 (d, *J* = 189.5 Hz), 62.4 (d, *J* = 5.6 Hz), 36.0, 26.3 (d, *J* = 2.3 Hz), 16.4 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.2; HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_{17}O_4P$ 268.0864, found 268.0862.

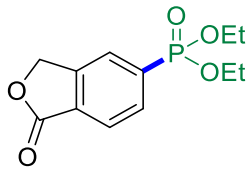


Diethyl (1-oxo-2,3-dihydro-1H-inden-5-yl)phosphonate (4ja). Colorless oil, 114 mg, Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 13.5 Hz, 1H), 7.81 – 7.70 (m, 2H), 4.20 – 4.03 (m, 4H), 3.16 (t, *J* = 7.0 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 154.6 (d, *J* = 16.1 Hz), 139.9 (d, *J* = 2.9 Hz), 135.0 (d, *J* = 183.8 Hz), 130.6 (d, *J* = 10.2 Hz), 130.3 (d, *J* = 10.5 Hz), 123.7 (d, *J* = 15.9 Hz), 62.5 (d, *J* = 5.6 Hz), 36.3, 25.8 (d, *J* = 1.5 Hz), 16.3 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.1; HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_{17}O_4P$ 268.0864, found 268.0863.

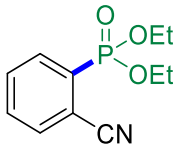


Diethyl (5-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)phosphonate (4ka). Colorless oil, 90 mg, Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.4 Hz, 1H), 8.08 (dd, *J* = 14.2, 7.6 Hz, 1H), 7.40 – 7.35 (m, 1H), 4.21 – 4.04 (m, 4H), 3.26 (t, *J* = 6.2 Hz, 2H), 2.65 (t, *J* = 6.6 Hz, 2H),

2.17 – 2.06 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 147.8 (d, *J* = 11.4 Hz), 138.7 (d, *J* = 10.2 Hz), 133.6 (d, *J* = 13.9 Hz), 131.7 (d, *J* = 3.0 Hz), 127.7 (d, *J* = 186.0 Hz), 126.3 (d, *J* = 15.2 Hz), 62.3 (d, *J* = 5.8 Hz), 38.8, 28.1 (d, *J* = 3.8 Hz), 22.7, 16.4 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.7; HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{19}O_4P$ 282.1021, found 282.1018.

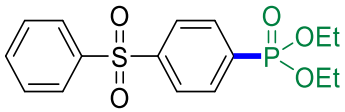


Diethyl (1-oxo-1,3-dihydroisobenzofuran-5-yl)phosphonate (4la). White solid, m.p. 64.8-66.2 ℃, 94 mg, Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.91 (m, 3H), 5.36 (s, 2H), 4.24 – 4.07 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.o, 146.3 (d, *J* = 16.8 Hz), 135.2 (d, *J* = 185.4 Hz), 132.1 (d, *J* = 10.5 Hz), 129.0 (d, *J* = 2.6 Hz), 125.9 (d, *J* = 11.0 Hz), 125.8 (d, *J* = 17.1 Hz), 69.7 (d, *J* = 2.4 Hz), 62.7 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.0; HRMS (EI) m/z: $[M]^+$ calcd for $C_{12}H_{15}O_5P$ 270.0657, found 270.0659.

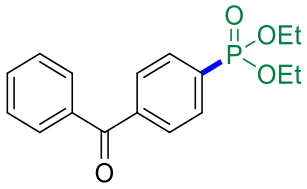


Diethyl (2-cyanophenyl)phosphonate (4ma). Colorless oil, 65 mg, Yield: 54% for X=Br; 63 mg, yield: 53% for X=I; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 14.2, 7.4 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.72 – 7.61 (m, 2H), 4.30 – 4.13 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6 (d, *J* = 3.3 Hz), 134.5 (d, *J* = 5.9 Hz), 132.5 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 187.8

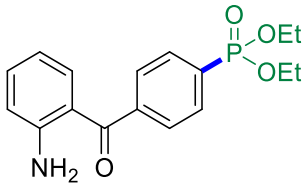
Hz), 132.3 (d, *J* = 14.1 Hz), 115.9 (d, *J* = 249.9 Hz), 63.2 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.6. The spectral data were in accordance with the literature.[1]



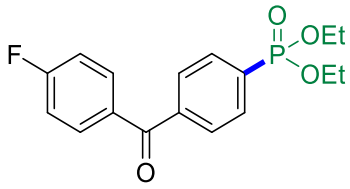
Diethyl (4-(phenylsulfonyl)phenyl)phosphonate (4na). Colorless oil, 138 mg, Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.3, 3.6 Hz, 2H), 7.91 (dd, *J* = 13.0, 7.9 Hz, 4H), 7.60 – 7.54 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 4.21 – 3.99 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (d, *J* = 3.5 Hz), 140.7, 134.2 (d, *J* = 187.2 Hz), 133.7, 132.6 (d, *J* = 10.2 Hz), 129.5, 127.9, 127.5 (d, *J* = 15.1 Hz), 62.6 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 6.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.5; HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{19}O_5PS$ 354.0691, found 354.0694.



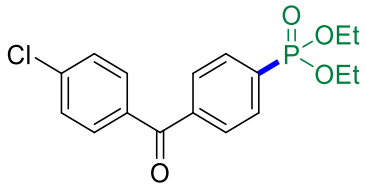
Diethyl (4-benzoylphenyl)phosphonate (4oa). Yellow oil, 156 mg, Yield: 98% for X=Br; 92 mg, yield: 58% for X=I; 11 mg, yield: 7% for X=Cl; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 12.9, 7.9 Hz, 2H), 7.82 (dd, *J* = 8.1, 3.9 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.20 – 4.06 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 140.9 (d, *J* = 3.2 Hz), 136.8, 133.0, 132.5 (d, *J* = 187.0 Hz), 131.7 (d, *J* = 10.0 Hz), 130.1, 129.6 (d, *J* = 15.0 Hz), 128.5, 62.4 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.0. The spectral data were in accordance with the literature.[4]



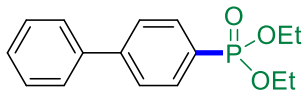
Diethyl (4-(2-aminobenzoyl)phenyl)phosphonate (4pa). Yellow solid, m.p. 122.7-124.3 ℃, 118 mg, Yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 13.1, 7.8 Hz, 2H), 7.69 (dd, *J* = 8.0, 3.9 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.27 (m, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.28 (s, 2H), 4.29 – 4.06 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 151.4, 143.8 (d, *J* = 3.2 Hz), 134.8, 134.5, 131.6 (d, *J* = 10.0 Hz), 130.9 (d, *J* = 187.7 Hz), 128.7 (d, *J* = 15.1 Hz), 117.3, 117.1, 115.6, 62.4 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.5; HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{20}NO_4P$ 333.1130, found 333.1133.



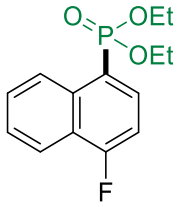
Diethyl (4-(4-fluorobenzoyl)phenyl)phosphonate (4qa). Colorless oil, 121 mg, Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 13.0, 7.9 Hz, 2H), 7.88 – 7.76 (m, 4H), 7.16 (t, *J* = 8.5 Hz, 2H), 4.23 – 4.07 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 165.7 (d, *J* = 255.3 Hz), 140.8 (d, *J* = 3.2 Hz), 133.0 (d, *J* = 3.0 Hz), 132.8 (d, *J* = 9.4 Hz), 132.6 (d, *J* = 187.1 Hz), 131.8 (d, *J* = 10.0 Hz), 129.5 (d, *J* = 15.0 Hz), 115.7 (d, *J* = 21.9 Hz), 62.5 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.9; HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{18}FO_4P$ 336.0927, found 336.0930.



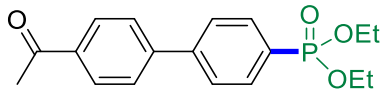
Diethyl (4-(4-chlorobenzoyl)phenyl)phosphonate (4ra). Colorless oil, 123 mg, Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 12.4, 7.5 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.27 (dd, *J* = 8.4, 1.3 Hz, 2H), 4.03 – 3.89 (m, 4H), 1.15 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 140.5 (d, *J* = 3.2 Hz), 139.6, 135.0, 132.8 (d, *J* = 187.3 Hz), 131.8 (d, *J* = 10.1 Hz), 131.5, 129.5 (d, *J* = 15.0 Hz), 128.9, 62.5 (d, *J* = 5.5 Hz), 16.3 (d, *J* = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.8; HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{18}ClO_4P$ 352.0631, found 352.0628.



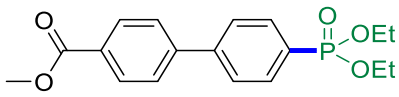
Diethyl [1,1'-biphenyl]-4-ylphosphonate (4sa). Colorless oil, 106 mg, Yield: 73% for X=Br; 101 mg, yield: 70% for X=I; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 12.7, 7.8 Hz, 2H), 7.68 (dd, *J* = 8.1, 3.9 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.49 – 7.42 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 4.23 – 4.04 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3 (d, *J* = 3.2 Hz), 140.0, 132.4 (d, *J* = 10.1 Hz), 129.0, 128.2, 127.3, 127.2 (d, *J* = 15.2 Hz), 126.9 (d, *J* = 190.0 Hz), 62.2 (d, *J* = 5.4 Hz), 16.4 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.0. The spectral data were in accordance with the literature.[1]



Diethyl (4-fluoronaphthalen-1-yl)phosphonate (4ta). Colorless oil, 107 mg, Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.5 Hz, 1H), 8.27 – 8.12 (m, 2H), 7.67 – 7.57 (m, 2H), 7.18 (t, *J* = 9.0 Hz, 1H), 4.25 – 4.01 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, *J* = 4.1 Hz), 160.8 (d, *J* = 4.1 Hz), 135.5 (t, *J* = 10.0 Hz), 134.7 (dd, *J* = 12.3, 5.3 Hz), 128.5, 126.7 (dd, *J* = 4.4, 2.5 Hz), 124.1 (dd, *J* = 15.8, 14.0 Hz), 121.2 (d, *J* = 6.4 Hz), 120.8 (dd, *J* = 186.8, 4.4 Hz), 108.6 (dd, *J* = 20.2, 17.6 Hz), 62.3 (d, *J* = 5.4 Hz), 16.4 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.3; HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{16}FO_3P$ 282.0821, found 282.0823.

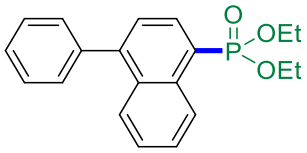


Diethyl (4'-acetyl-[1,1'-biphenyl]-4-yl)phosphonate (4ua). White solid, m.p. 96.5-97.4 ℃, 121 mg, Yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.90 (dd, *J* = 13.0, 7.8 Hz, 2H), 7.74 – 7.66 (m, 4H), 4.23 – 4.05 (m, 4H), 2.63 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 144.5, 143.8 (d, *J* = 3.1 Hz), 136.6, 132.5 (d, *J* = 10.2 Hz), 129.1, 127.5, 127.5, 127.3, 62.3 (d, *J* = 5.4 Hz), 26.8, 16.4 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{21}O_4P$ 332.1177, found 332.1174.

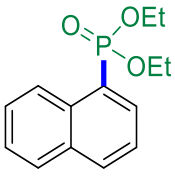


Methyl 4'-(diethoxyphosphoryl)-[1,1'-biphenyl]-4-carboxylate (4va). White solid, m.p. 81.6-82.4 ℃, 143 mg, Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.90

(dd, *J* = 13.0, 7.9 Hz, 2H), 7.74 – 7.63 (m, 4H), 4.22 – 4.05 (m, 4H), 3.93 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 144.1 (d, *J* = 39.9 Hz), 132.4 (d, *J* = 10.1 Hz), 130.2, 129.8, 128.0 (d, *J* = 189.4 Hz), 127.4, 127.3, 62.2 (d, *J* = 5.4 Hz), 52.2, 16.4 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{21}O_5P$ 348.1127, found 348.1125.

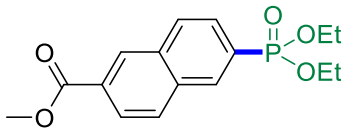


Diethyl (4-phenylnaphthalen-1-yl)phosphonate (4wa). White solid, 106 mg, Yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.29 (dd, *J* = 16.2, 7.3 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.52 – 7.44 (m, 7H), 4.28 – 4.10 (m, 7.2 Hz, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8 (d, *J* = 3.6 Hz), 140.0, 134.3 (d, *J* = 8.9 Hz), 133.2 (d, *J* = 11.3 Hz), 132.0 (d, *J* = 12.9 Hz), 129.9, 128.4, 127.9, 127.3, 127.0, 127.0 (d, *J* = 4.5 Hz), 126.4, 125.7 (d, *J* = 16.5 Hz), 123.9 (d, *J* = 183.8 Hz), 62.3 (d, *J* = 5.2 Hz), 16.5 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{21}O_3P$ 340.1228, found 340.1230.

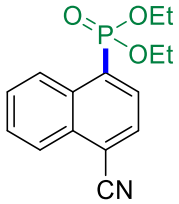


Diethyl naphthalen-1-ylphosphonate (4xa). Colorless oil, 74 mg, Yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.5 Hz, 1H), 8.23 (dd, *J* = 16.3, 7.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.56 – 7.48 (m, 2H), 4.25 – 4.02 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7 (d, *J* = 9.2 Hz), 133.6 (d, *J* = 3.7 Hz), 133.5, 132.7 (d, *J* = 10.9 Hz), 128.8 (d, *J* = 2.0 Hz), 127.4, 126.7 (d, *J* = 4.2 Hz), 126.4, 124.6 (d, *J* =

182.6 Hz), 124.5 (d, J = 16.7 Hz), 62.2 (d, J = 5.2 Hz), 16.3 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.2. The spectral data were in accordance with the literature.[1]

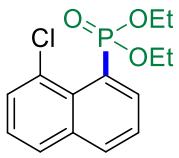


Methyl 6-(diethoxyphosphoryl)-2-naphthoate (4ya). White solid, m.p. 68.7-70.1 ℃, 156 mg, Yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.44 (d, J = 15.4 Hz, 1H), 8.11 (d, J = 8.7 Hz, 1H), 8.01 (dd, J = 8.6, 3.8 Hz, 1H), 7.96 (d, J = 8.6 Hz, 1H), 7.81 (t, J = 9.7 Hz, 1H), 4.26 – 4.06 (m, 4H), 3.97 (s, 3H), 1.33 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 134.3 (d, J = 16.6 Hz), 134.0 (d, J = 2.7 Hz), 133.6 (d, J = 10.0 Hz), 130.7, 129.7 (d, J = 14.2 Hz), 129.5, 129.2, 129.0, 127.3 (d, J = 9.7 Hz), 126.2, 62.4 (d, J = 5.4 Hz), 52.4, 16.4 (d, J = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.0; HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{19}O_5P$ 322.0970, found 322.0968.

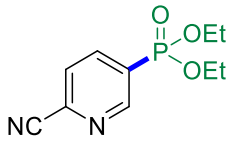


Diethyl (4-cyanonaphthalen-1-yl)phosphonate (4za). Colorless oil, 131 mg, Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 9.5 Hz, 1H), 8.33 – 8.21 (m, 2H), 7.94 (dd, J = 7.3, 3.2 Hz, 1H), 7.77 – 7.70 (m, 2H), 4.26 – 4.07 (m, 4H), 1.30 (t, J = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6 (d, J = 8.9 Hz), 132.4 (d, J = 5.9 Hz), 132.3 (d, J = 7.7 Hz), 131.0 (d, J = 181.5 Hz), 130.9 (d, J = 16.6 Hz), 128.9 (d, J = 1.5 Hz), 127.5 (d, J = 4.1 Hz), 125.9 (d, J = 1.4 Hz), 117.0 (d, J = 1.7 Hz), 115.2 (d, J = 3.9 Hz), 62.8 (d, J = 5.5 Hz), 16.3 (d, J = 6.3 Hz). ^{31}P NMR

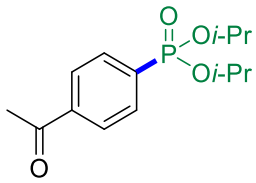
(162 MHz, $CDCl_3$) δ 16.0; HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{16}NO_3P$ 289.0868, found 289.0866.



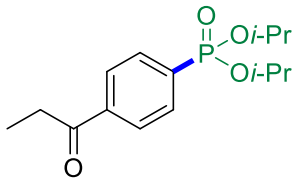
Diethyl (8-chloronaphthalen-1-yl)phosphonate (4ab). Colorless oil, 85 mg, Yield: 57%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 17.6, 7.3 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 4.27 – 4.14 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5 (d, *J* = 7.3 Hz), 136.3 (d, *J* = 11.7 Hz), 134.7 (d, *J* = 3.5 Hz), 131.5 (d, *J* = 9.0 Hz), 131.0, 130.8 (d, *J* = 5.6 Hz), 128.8 (d, *J* = 2.3 Hz), 126.3, 124.8 (d, *J* = 16.0 Hz), 124.0 (d, *J* = 187.5 Hz), 62.5 (d, *J* = 6.3 Hz), 16.3 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.2; HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{16}ClO_3P$ 298.0526, found 298.0527.



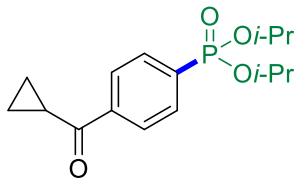
Diethyl (6-cyanopyridin-3-yl)phosphonate (4ac). Colorless oil, 105 mg, Yield: 88%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 6.1 Hz, 1H), 7.73 (dd, J = 13.3, 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 3.73 – 3.61 (m, 4H), 0.83 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2 (d, J = 12.2 Hz), 140.7 (d, J = 8.5 Hz), 136.7 (d, J = 2.4 Hz), 129.1 (d, J = 188.6 Hz), 128.0 (d, J = 12.0 Hz), 116.6 (d, J = 2.3 Hz), 63.3 (d, J = 5.8 Hz), 16.4 (d, J = 6.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.6; HRMS (EI) m/z: $[M]^+$ calcd for $C_{10}H_{13}N_2O_3P$ 240.0664, found 240.0567.



Diisopropyl (4-acetylphenyl)phosphonate (4af). Colorless oil, 90 mg, Yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.4, 2.6 Hz, 2H), 7.86 (dd, *J* = 13.2, 7.7 Hz, 2H), 4.74 – 4.59 (m, 2H), 2.58 (s, 3H), 1.32 (d, *J* = 6.2 Hz, 6H), 1.17 (d, *J* = 5.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 139.6 (d, *J* = 3.2 Hz), 134.9 (d, *J* = 187.2 Hz), 132.0 (d, *J* = 10.0 Hz), 127.9 (d, *J* = 15.0 Hz), 71.2 (d, *J* = 5.8 Hz), 26.8, 24.0 (d, *J* = 4.0 Hz), 23.8 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.6. The spectral data were in accordance with the literature.[5]

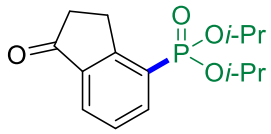


Diisopropyl (4-propionylphenyl)phosphonate (4ag). Colorless oil, 127 mg, Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.2, 3.7 Hz, 2H), 7.89 (dd, *J* = 12.8, 8.0 Hz, 2H), 4.77 – 4.64 (m, 2H), 3.01 (q, *J* = 7.2 Hz, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.22 (t, *J* = 5.9 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 139.5 (d, *J* = 3.1 Hz), 134.7 (d, *J* = 187.3 Hz), 132.0 (d, *J* = 9.9 Hz), 127.6 (d, *J* = 15.0 Hz), 71.2 (d, *J* = 5.7 Hz), 32.1, 24.0 (d, *J* = 4.0 Hz), 23.8 (d, *J* = 4.8 Hz), 8.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.7; HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{23}O_4P$ 298.1334, found 298.1332.

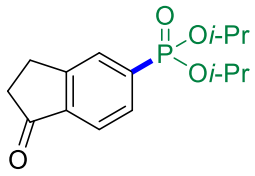


Diisopropyl (4-(cyclopropanecarbonyl)phenyl)phosphonate (4ah). Colorless oil, 140 mg, Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.7, 2.9 Hz, 2H), 7.90 (dd, *J* = 12.9, 7.9

Hz, 2H), 4.75 – 4.64 (m, 2H), 2.68 – (m, 1H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.24 (q, *J* = 3.9 Hz, 2H), 1.20 (d, *J* = 6.1 Hz, 6H), 1.06 (dd, *J* = 7.7, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 140.6 (d, *J* = 3.2 Hz), 134.5 (d, *J* = 187.2 Hz), 131.9 (d, *J* = 10.0 Hz), 127.6 (d, *J* = 15.0 Hz), 71.2 (d, *J* = 5.6 Hz), 24.0 (d, *J* = 4.0 Hz), 23.8 (d, *J* = 4.8 Hz), 17.6, 12.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.8; HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{23}O_4P$ 310.1334, found 310.1337.

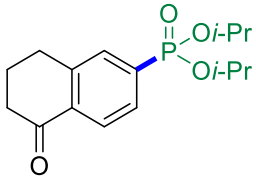


Diisopropyl (1-oxo-2,3-dihydro-1H-inden-4-yl)phosphonate (4ai). Colorless oil, 88 mg, Yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 13.8, 7.4 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.47 – 7.42 (m, 1H), 4.82 – 4.68 (m, 2H), 3.35 (t, *J* = 6.2 Hz, 2H), 2.69 (t, *J* = 6.5 Hz, 2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.22 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 157.8 (d, *J* = 10.0 Hz), 138.7 (d, *J* = 11.0 Hz), 137.6 (d, *J* = 12.6 Hz), 129.3, 127.5 (d, *J* = 3.3 Hz), 127.2 (d, *J* = 13.9 Hz), 71.2 (d, *J* = 5.8 Hz), 36.0, 26.2 (d, *J* = 2.2 Hz), 24.1 (d, *J* = 4.1 Hz), 23.9 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.9; HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{21}O_4P$ 296.1177, found 296.1175.

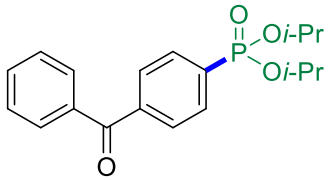


Diisopropyl (1-oxo-2,3-dihydro-1H-inden-5-yl)phosphonate (4aj). Colorless oil, 92 mg, Yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 13.4 Hz, 1H), 7.82 – 7.71 (m, 2H), 4.78 – 4.64 (m, 2H), 3.17 (t, *J* = 6.5 Hz, 2H), 2.71 (t, *J* = 6.5 Hz, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.22 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 154.5 (d, *J* = 16.1 Hz), 139.6 (d, *J* = 2.8 Hz), 136.6 (d, *J* = 184.5 Hz), 130.4 (d, *J* = 10.1 Hz), 130.3 (d, *J* = 10.3 Hz), 123.5 (d, *J* = 15.7 Hz),

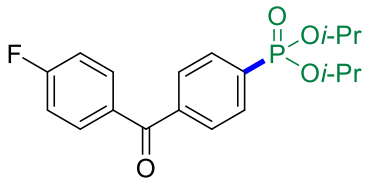
71.3 (d, J = 5.7 Hz), 36.3, 25.8 (d, J = 1.4 Hz), 24.0 (d, J = 4.0 Hz), 23.9 (d, J = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.9; HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{21}O_4P$ 296.1177, found 296.1179.



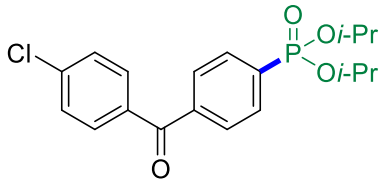
Diisopropyl (5-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)phosphonate (4ak). Colorless oil, 124 mg, Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 6.6 Hz, 1H), 8.14 (dd, J = 14.3, 7.5 Hz, 1H), 7.38 (td, J = 7.7, 3.5 Hz, 1H), 4.78 – 4.67 (m, 2H), 3.27 (t, J = 6.2 Hz, 2H), 2.66 (t, J = 6.5 Hz, 2H), 2.12 (p, J = 6.3 Hz, 2H), 1.37 (d, J = 6.2 Hz, 6H), 1.24 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7 (d, J = 2.6 Hz), 147.6 (d, J = 11.1 Hz), 138.7 (d, J = 10.3 Hz), 133.5 (d, J = 13.8 Hz), 131.4 (d, J = 2.9 Hz), 129.1 (d, J = 186.2 Hz), 126.1 (d, J = 15.2 Hz), 71.1 (d, J = 5.9 Hz), 38.8, 28.1 (d, J = 3.6 Hz), 24.1 (d, J = 4.1 Hz), 23.8 (d, J = 4.7 Hz), 22.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{23}O_4P$ 310.1334, found 310.1330.



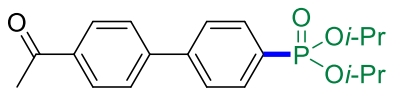
Diisopropyl (4-benzoylphenyl)phosphonate (4al). Colorless oil, 118 mg, Yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 12.6, 8.1 Hz, 2H), 7.85 – 7.76 (m, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.3 Hz, 2H), 4.80 – 4.65 (m, 2H), 1.38 (d, J = 6.2 Hz, 6H), 1.25 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 140.6 (d, J = 3.1 Hz), 136.9, 134.2 (d, J = 187.8 Hz), 132.9, 131.6 (d, J = 9.9 Hz), 130.1, 129.5 (d, J = 14.9 Hz), 128.5, 71.2 (d, J = 5.7 Hz), 24.1 (d, J = 4.0 Hz), 23.9 (d, J = 4.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.8. The spectral data were in accordance with the literature.[4]



Diisopropyl (4-(4-fluorobenzoyl)phenyl)phosphonate (4am). Colorless oil, 122 mg, Yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 12.9, 7.8 Hz, 2H), 7.87 – 7.75 (m, 4H), 7.16 (t, *J* = 8.4 Hz, 2H), 4.79 – 4.68 (m, 2H), 1.38 (d, *J* = 6.1 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 165.7 (d, *J* = 255.2 Hz), 140.5 (d, *J* = 3.0 Hz), 134.3 (d, *J* = 188.2 Hz), 133.2 (d, *J* = 3.0 Hz), 132.8 (d, *J* = 9.3 Hz), 131.7 (d, *J* = 9.9 Hz), 129.3 (d, *J* = 15.0 Hz), 115.7 (d, *J* = 22.0 Hz), 71.3 (d, *J* = 5.6 Hz), 24.1 (d, *J* = 3.9 Hz), 23.9 (d, *J* = 4.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.7; HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{22}FO_4P$ 364.1240, found 364.1242.

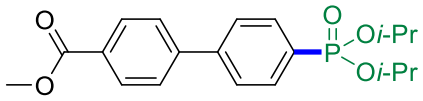


Diisopropyl (4-(4-chlorobenzoyl)phenyl)phosphonate (4an). Colorless oil, 137 mg, Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 12.9, 7.8 Hz, 2H), 7.80 (dd, *J* = 8.1, 3.7 Hz, 2H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 4.78 – 4.67 (m, 2H), 1.39 (d, *J* = 6.2 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 140.3 (d, *J* = 3.2 Hz), 139.6, 135.3, 134.6 (d, *J* = 187.9 Hz), 131.8 (d, *J* = 9.9 Hz), 131.6, 129.5 (d, *J* = 15.0 Hz), 128.9, 71.4 (d, *J* = 5.7 Hz), 24.2 (d, *J* = 4.0 Hz), 24.0 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.6; HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{22}ClO_4P$ 380.0944, found 380.0942.

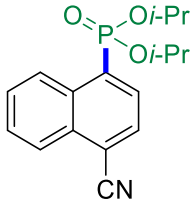


Diisopropyl (4'-acetyl-[1,1'-biphenyl]-4-yl)phosphonate (4ao). White solid, m.p. 65.8-66.4 °C, 114 mg, Yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.97 – 7.83 (m, 2H),

7.69 (d, *J* = 7.8 Hz, 4H), 4.75 – 4.68 (m, 2H), 2.63 (s, 3H), 1.38 (d, *J* = 5.8 Hz, 6H), 1.24 (d, *J* = 5.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 144.5, 143.4, 136.5, 132.4 (d, *J* = 9.3 Hz), 129.0, 127.5, 127.3, 127.1, 71.0, 26.7, 24.1, 23.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{25}O_4P$ 360.1490, found 360.1493.

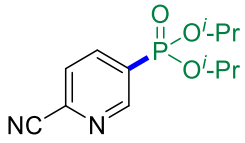


Methyl 4'-(diisopropoxyphosphoryl)-[1,1'-biphenyl]-4-carboxylate (4ap). White solid, m.p. 64.5-65.7 ℃, 117 mg, Yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.90 (dd, *J* = 12.9, 7.8 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 4H), 4.83 – 4.63 (m, *J* = 6.4 Hz, 2H), 3.94 (s, 3H), 1.39 (d, *J* = 6.1 Hz, 6H), 1.25 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 144.4, 143.5 (d, *J* = 3.0 Hz), 132.4 (d, *J* = 10.0 Hz), 130.2, 129.7 (d, *J* = 190.5 Hz), 129.8, 127.2, 127.1, 70.9 (d, *J* = 5.4 Hz), 52.2, 24.1 (d, *J* = 3.8 Hz), 23.9 (d, *J* = 4.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.2; HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{25}O_5P$ 376.1440, found 376.1444.

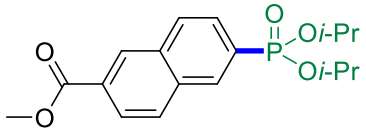


Diisopropyl (4-cyanonaphthalen-1-yl)phosphonate (4aq). White solid, m.p. 113.4-115.3 ℃, 111 mg, Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 9.3 Hz, 1H), 8.29 (dd, *J* = 15.9, 7.3 Hz, 2H), 7.95 (dd, *J* = 7.3, 3.1 Hz, 1H), 7.74 (td, *J* = 7.3, 6.6, 4.1 Hz, 2H), 4.83 – 4.70 (m, 2H), 1.41 (d, *J* = 6.2 Hz, 6H), 1.15 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5 (d, *J* = 181.7 Hz), 132.5 (d, *J* = 9.1 Hz), 132.4, 132.3 (d, *J* = 3.1 Hz), 131.0 (d, *J* = 16.7 Hz), 128.8, 128.6, 127.9 (d, *J* = 4.0 Hz), 125.9, 117.1, 114.9 (d, *J* = 3.8 Hz), 71.8 (d, *J* = 5.7 Hz), 24.1 (d, *J* = 4.1 Hz),

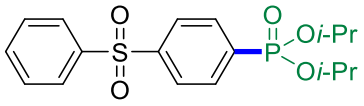
23.8 (d, *J* = 5.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.8; HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{20}NO_3P$ 317.1181, found 317.1179.



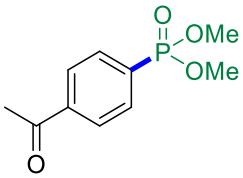
Diisopropyl (6-cyanopyridin-3-yl)phosphonate (4ar). Colorless oil, 76 mg, Yield: 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 6.1 Hz, 1H), 8.22 (dd, J = 13.3, 7.8 Hz, 1H), 7.75 (d, J = 10.6 Hz, 1H), 4.80 – 4.72 (m, 2H), 1.38 (d, J = 6.2 Hz, 6H), 1.24 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2 (d, J = 12.1 Hz), 140.5 (d, J = 8.4 Hz), 136.4 (d, J = 2.4 Hz), 130.6 (d, J = 189.0 Hz), 127.9 (d, J = 12.1 Hz), 116.7 (d, J = 2.2 Hz), 72.4 (d, J = 5.9 Hz), 24.1 (d, J = 4.3 Hz), 24.0 (d, J = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.3; HRMS (EI) m/z: $[M]^+$ calcd for $C_{12}H_{17}N_2O_3P$ 268.0977, found 268.0974.



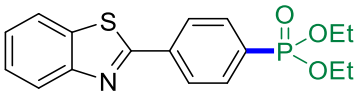
Methyl 6-(diisopropoxyphosphoryl)-2-naphthoate (4as). White solid, m.p. 99.3-100.4 ℃, 107 mg, Yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.45 (d, *J* = 15.3 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.03 – 7.95 (m, 2H), 7.86 – 7.76 (m, 1H), 4.79 – 4.68 (m, *J* = 6.4 Hz, 2H), 3.98 (s, 3H), 1.40 (d, *J* = 6.1 Hz, 6H), 1.22 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 134.5, 134.4, 134.0 (d, *J* = 2.5 Hz), 133.5 (d, *J* = 10.0 Hz), 130.8, 129.7, 129.5 (d, *J* = 4.6 Hz), 129.3, 127.5 (d, *J* = 9.4 Hz), 126.2, 71.2 (d, *J* = 5.4 Hz), 52.5, 24.2 (d, *J* = 3.8 Hz), 24.0 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.8; HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{23}O_5P$ 350.1283, found 350.1280.



Diisopropyl (4-(phenylsulfonyl)phenyl)phosphonate (4at). Colorless oil, 143 mg, Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.3, 3.5 Hz, 2H), 7.97 – 7.88 (m, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 4.73 – 4.65 (m, 2H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.20 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9 (d, *J* = 3.5 Hz), 140.8, 135.8 (d, *J* = 187.8 Hz), 133.7, 132.6 (d, *J* = 10.2 Hz), 129.5, 128.0, 127.45 (d, *J* = 15.1 Hz), 71.6 (d, *J* = 5.8 Hz), 24.1 (d, *J* = 4.1 Hz), 23.9 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{23}O_5PS$ 382.1004, found 382.1007.

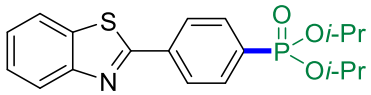


Dimethyl (4-acetylphenyl)phosphonate (4au). Colorless oil, 46 mg, Yield: 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.2, 3.8 Hz, 2H), 7.87 (dd, J = 12.9, 7.9 Hz, 2H), 3.75 (d, J = 11.1 Hz, 6H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 140.1 (d, J = 3.2 Hz), 132.3 (d, J = 10.1 Hz), 131.9 (d, J = 187.5 Hz), 128.2 (d, J = 15.1 Hz), 53.0 (d, J = 5.7 Hz), 26.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7. The spectral data were in accordance with the literature.[3]



Diethyl (4-(benzo[d]thiazol-2-yl)phenyl)phosphonate (4av). White solid, 160 mg, Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.2, 3.7 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 11.8, 7.6 Hz, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.24 – 4.05 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.0, 137.0 (d, *J* = 3.3 Hz), 135.2, 132.5 (d, *J* = 10.2 Hz), 130.9 (d, *J* = 188.3 Hz), 127.4 (d, *J* = 15.2 Hz), 126.7, 125.8, 123.6, 121.8, 62.4

(d, J = 5.5 Hz), 16.4 (d, J = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6. The spectral data were in accordance with the literature.[5]



Diisopropyl (4-(benzothiazol-2-yl)phenyl)phosphonate (4aw). White solid, m.p. 73.4-74.8 °C, 171 mg, Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.12 (m, 2H), 8.09 (d, J = 8.2 Hz, 1H), 7.99 – 7.88 (m, 3H), 7.51 (t, J = 7.7 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 4.72 (h, J = 6.4 Hz, 2H), 1.39 (d, J = 6.2 Hz, 6H), 1.24 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 154.1, 136.8, 135.2, 132.6 (d, J = 188.3 Hz), 132.5 (d, J = 10.1 Hz), 127.3 (d, J = 15.1 Hz), 126.6, 125.7, 123.6, 121.8, 71.1 (d, J = 5.5 Hz), 24.1 (d, J = 4.0 Hz), 23.9 (d, J = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.3; HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_3PS$ 375.1058, found 370.1056.

References

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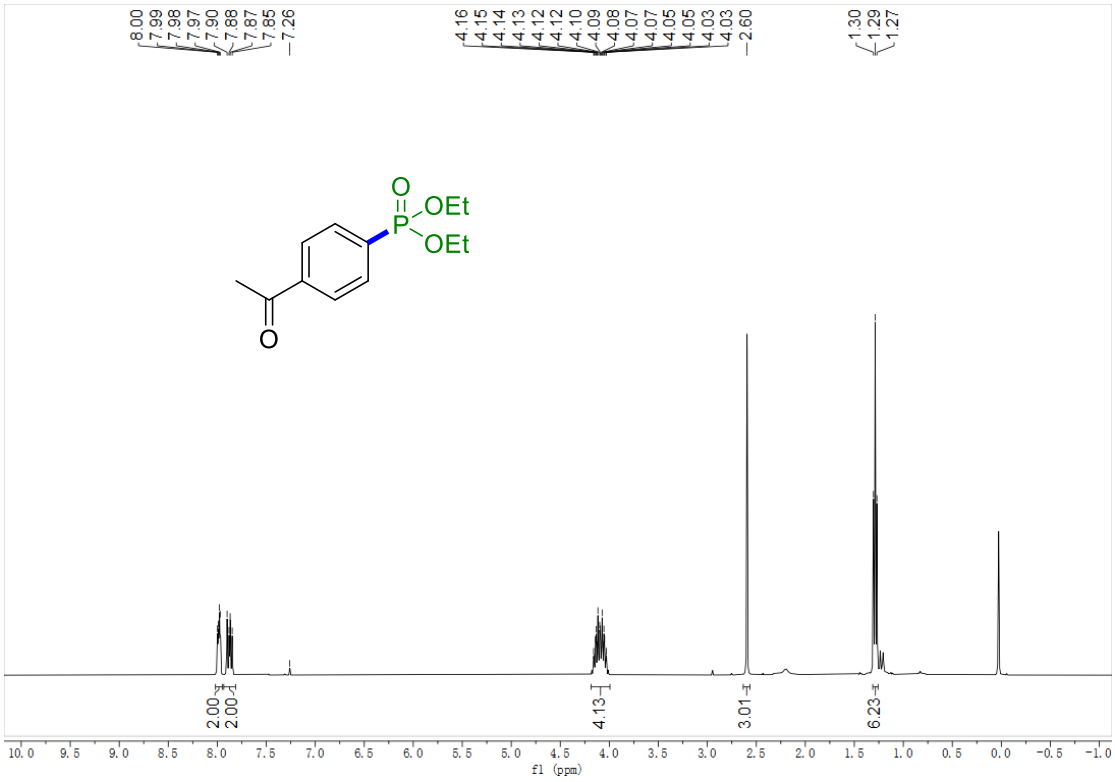
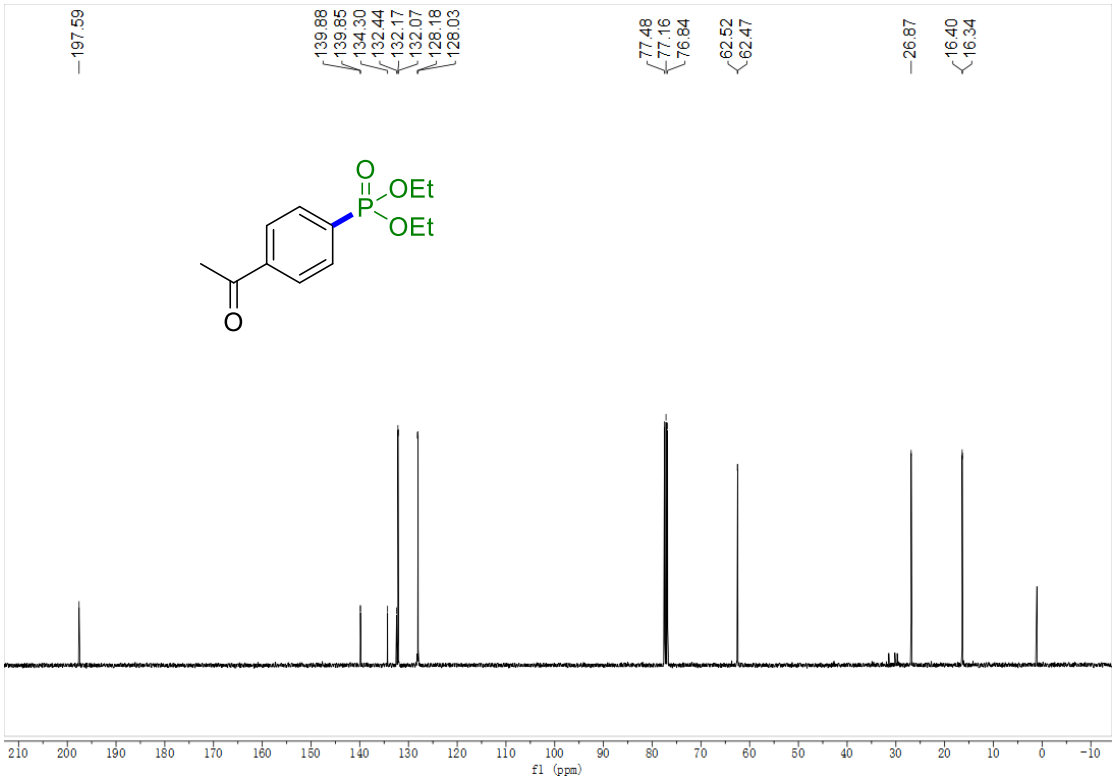
4. NMR spectrum

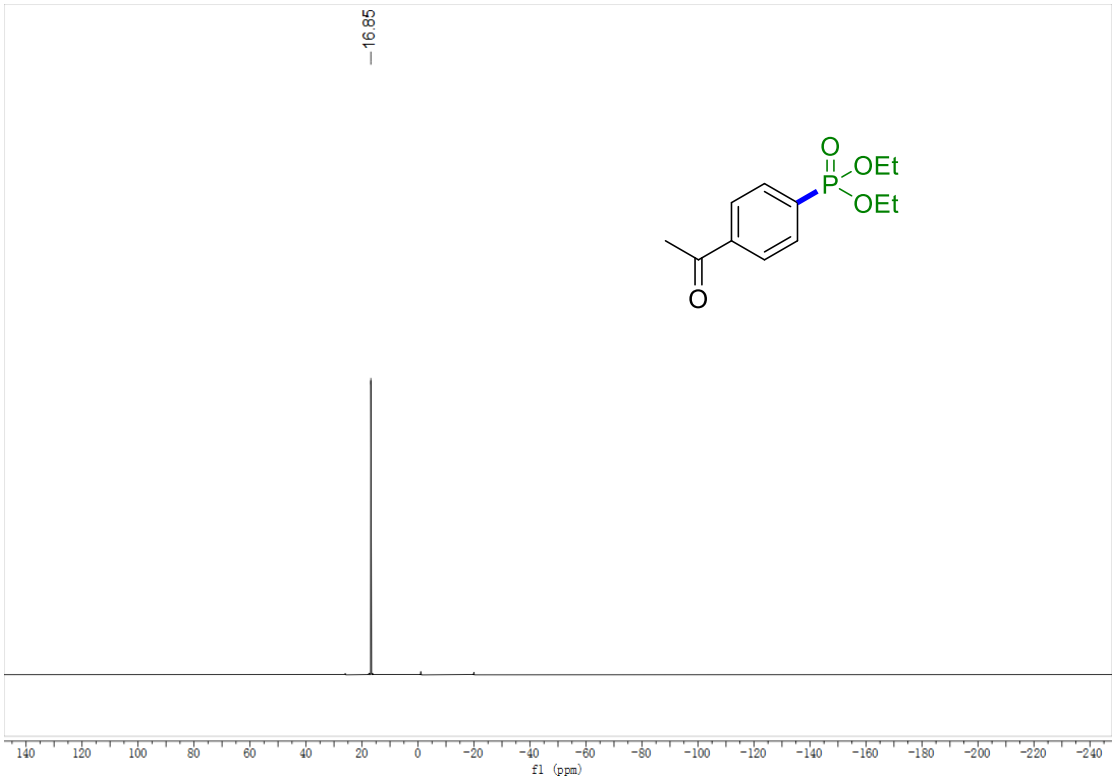
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aa**



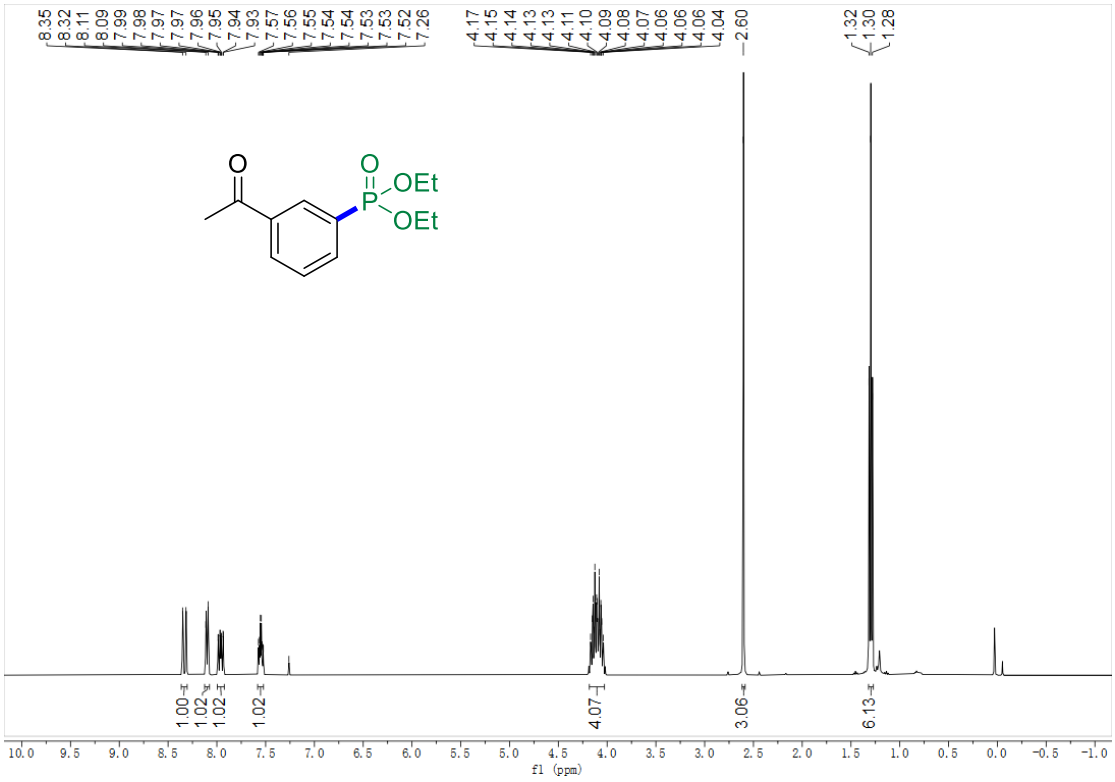
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4aa**



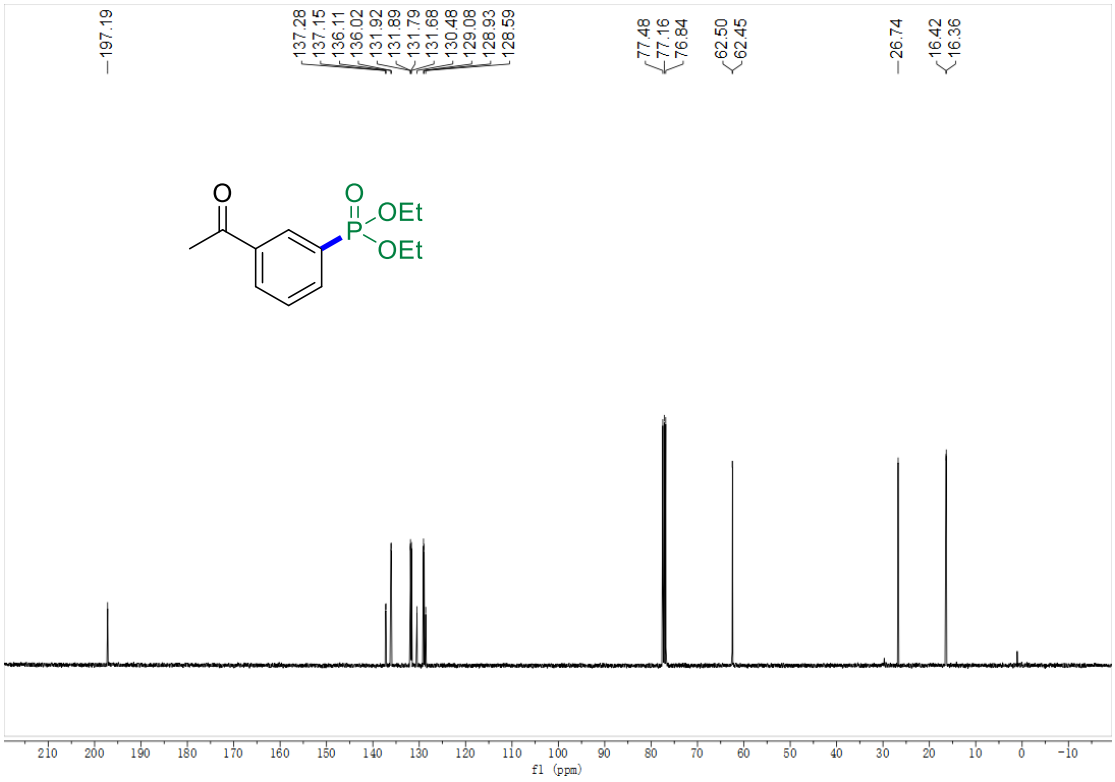
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4aa**



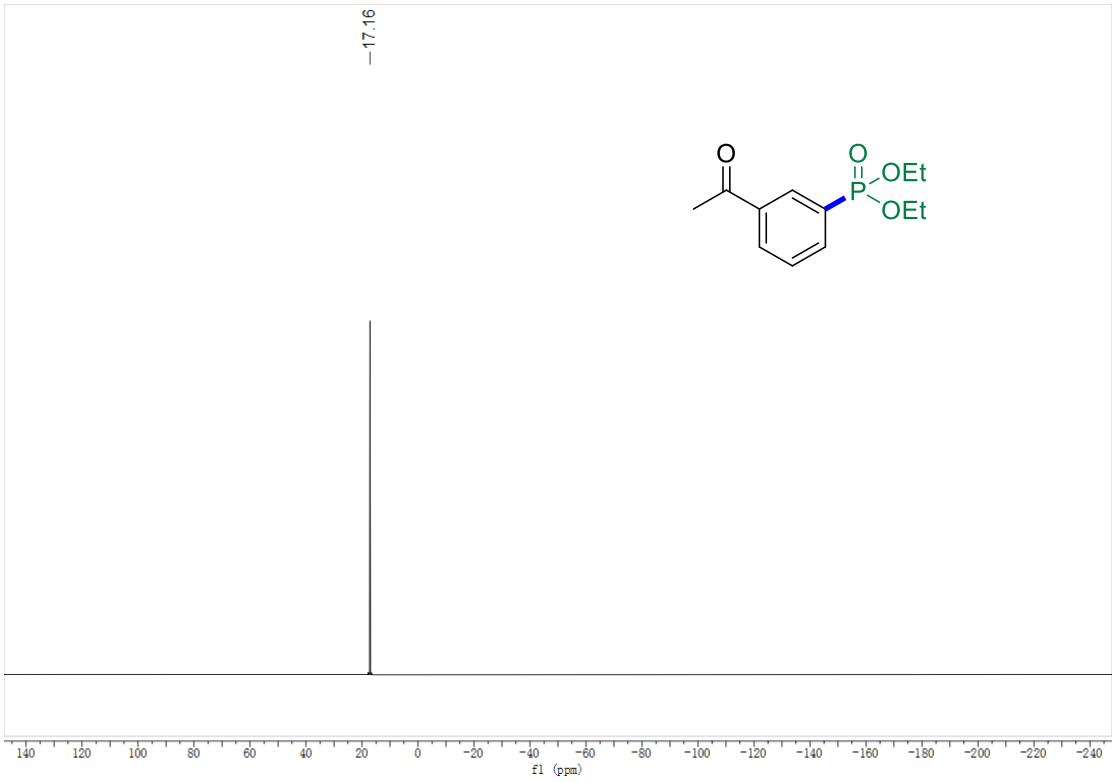
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ba**



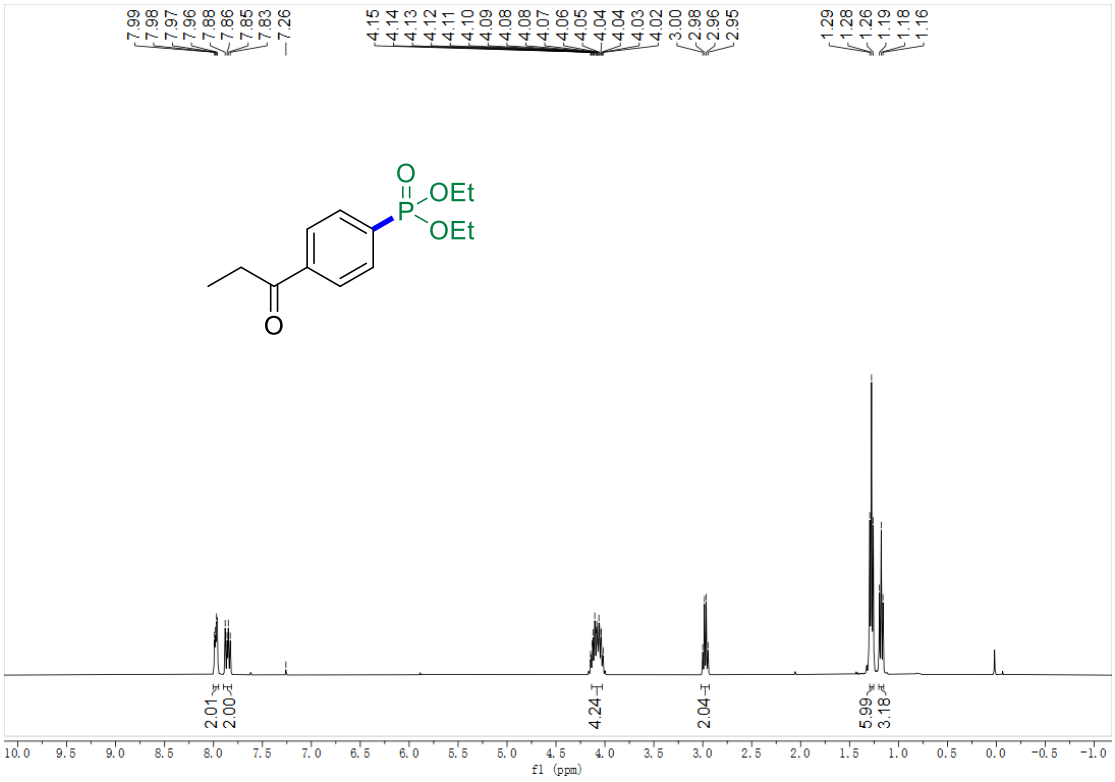
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ba**



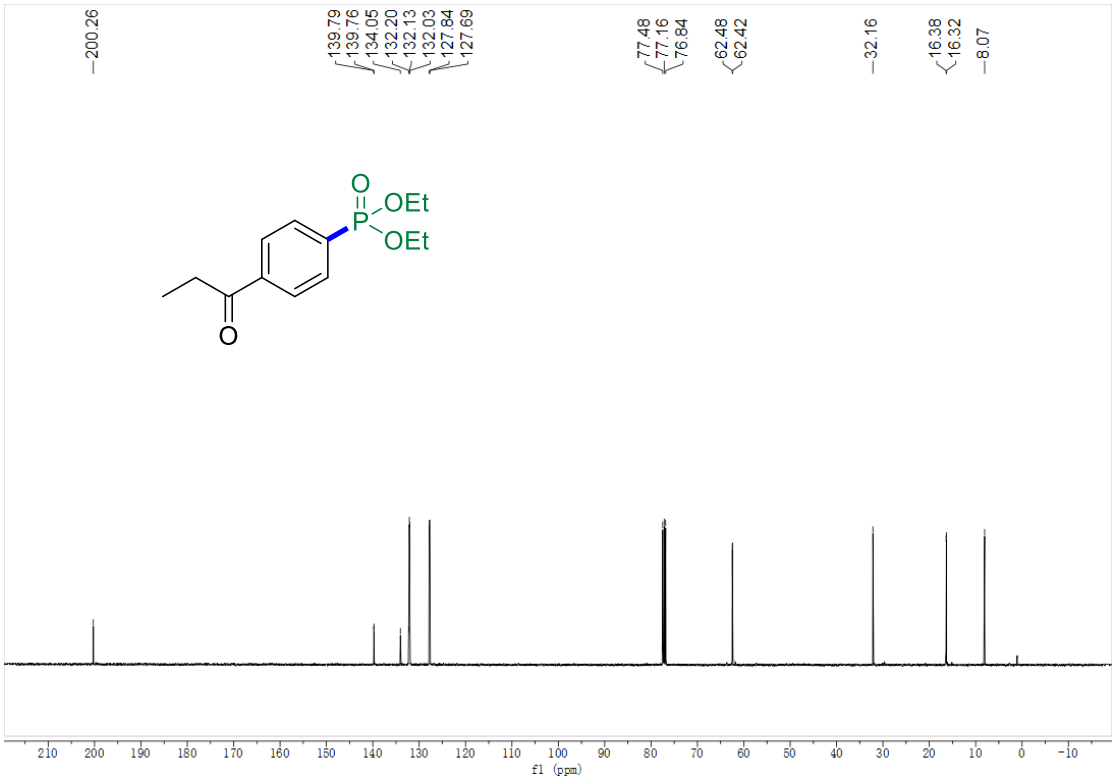
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ba**



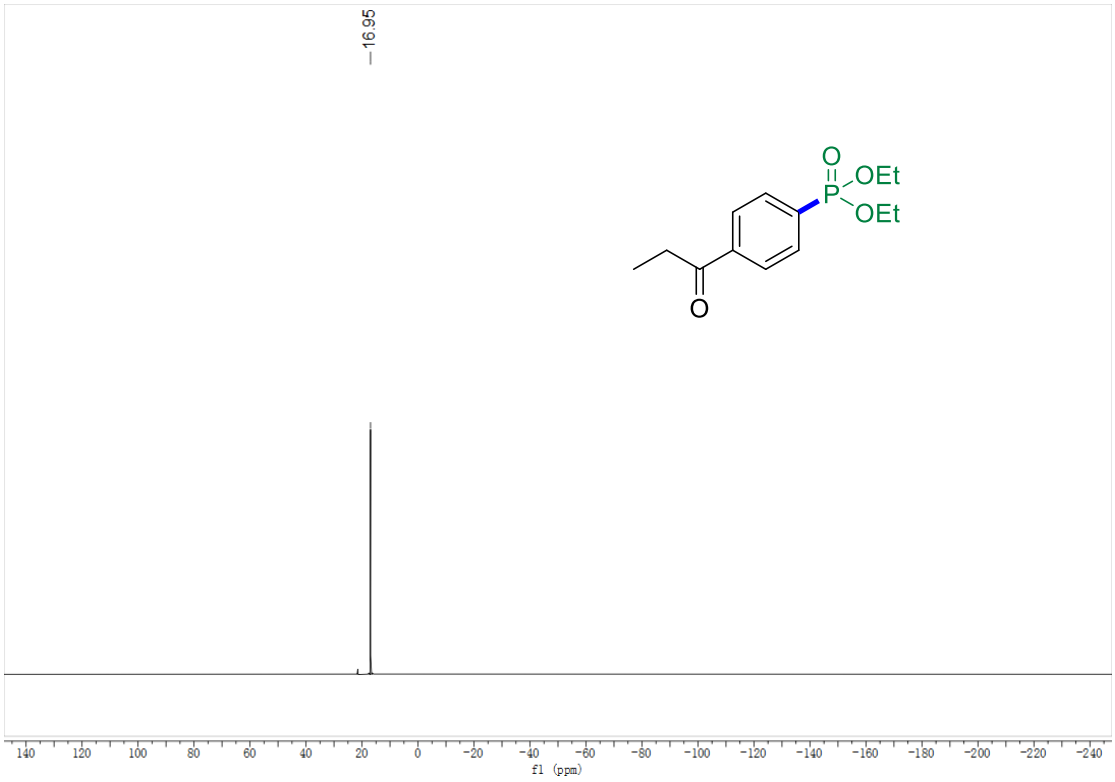
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ca**



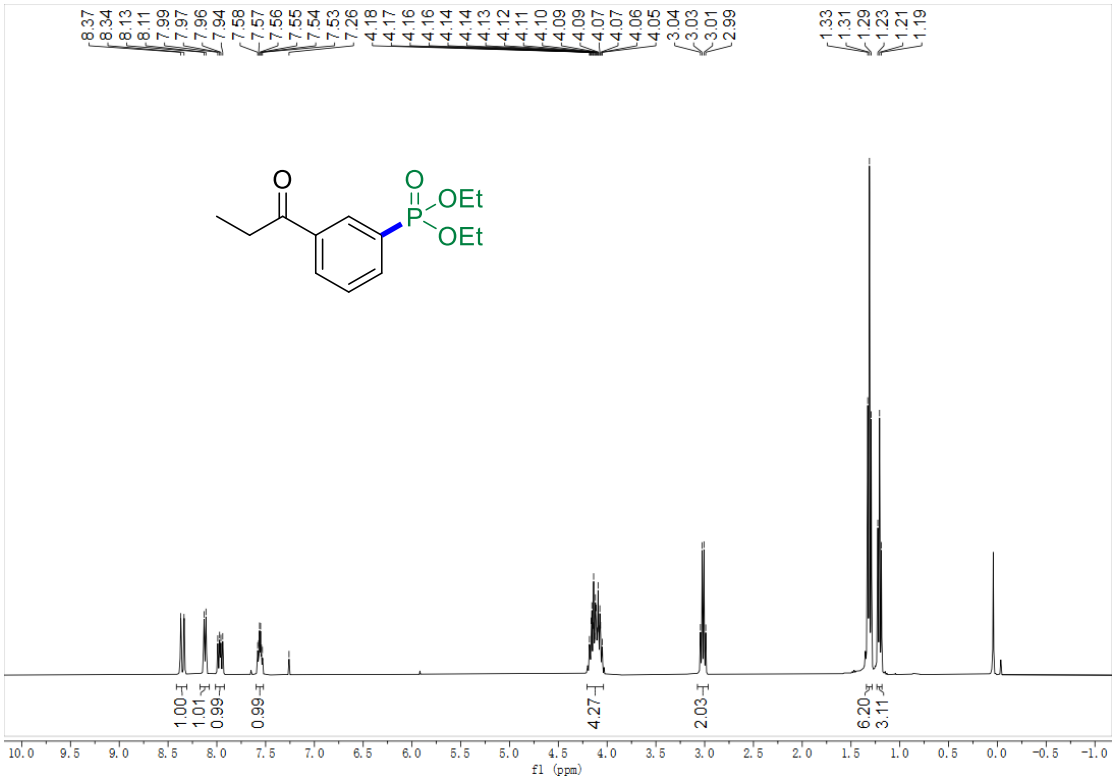
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ca**



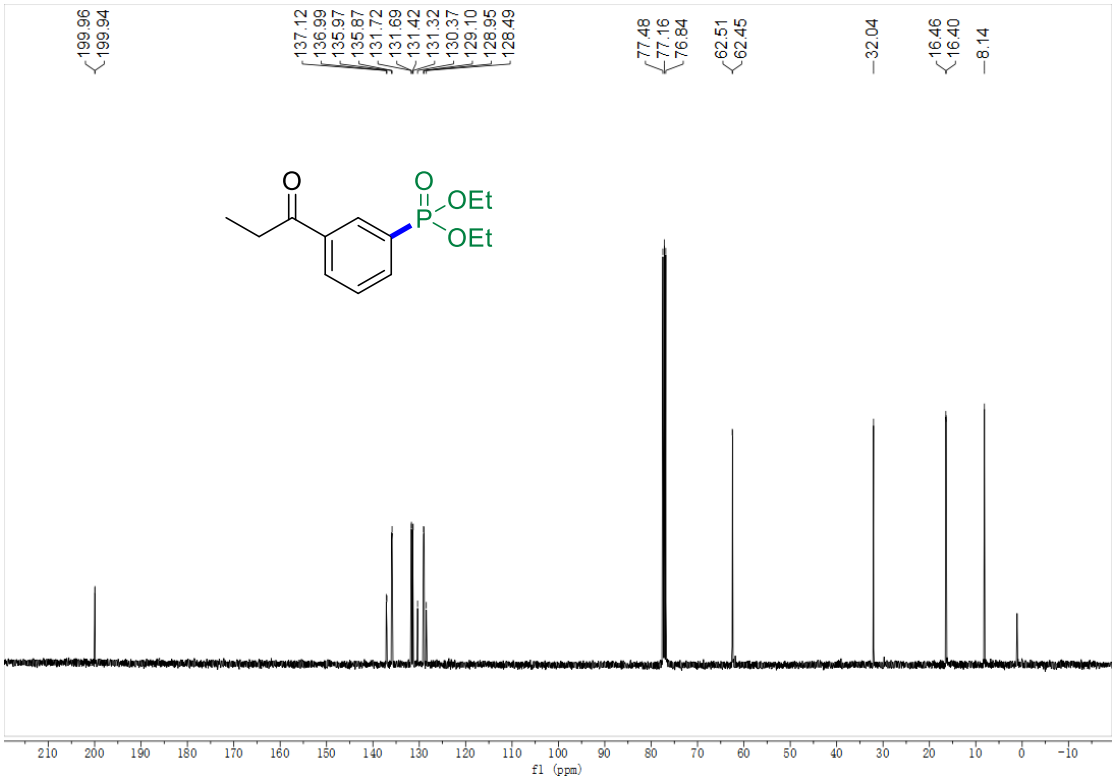
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ca**



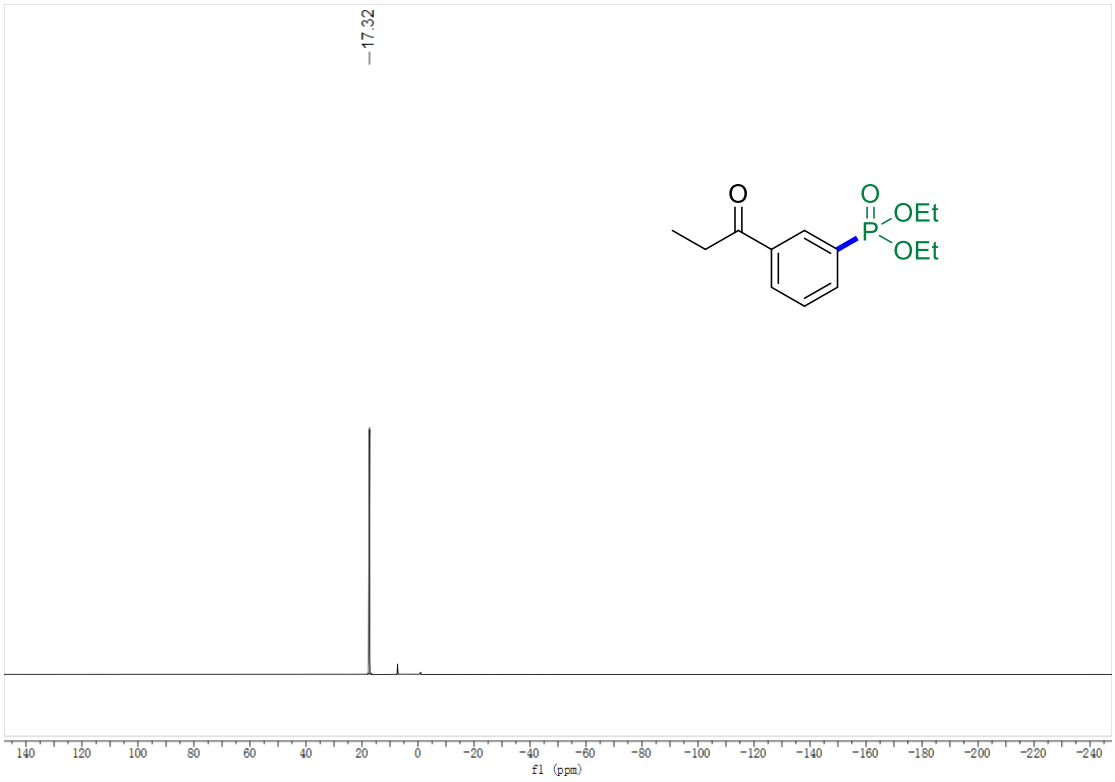
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4da**



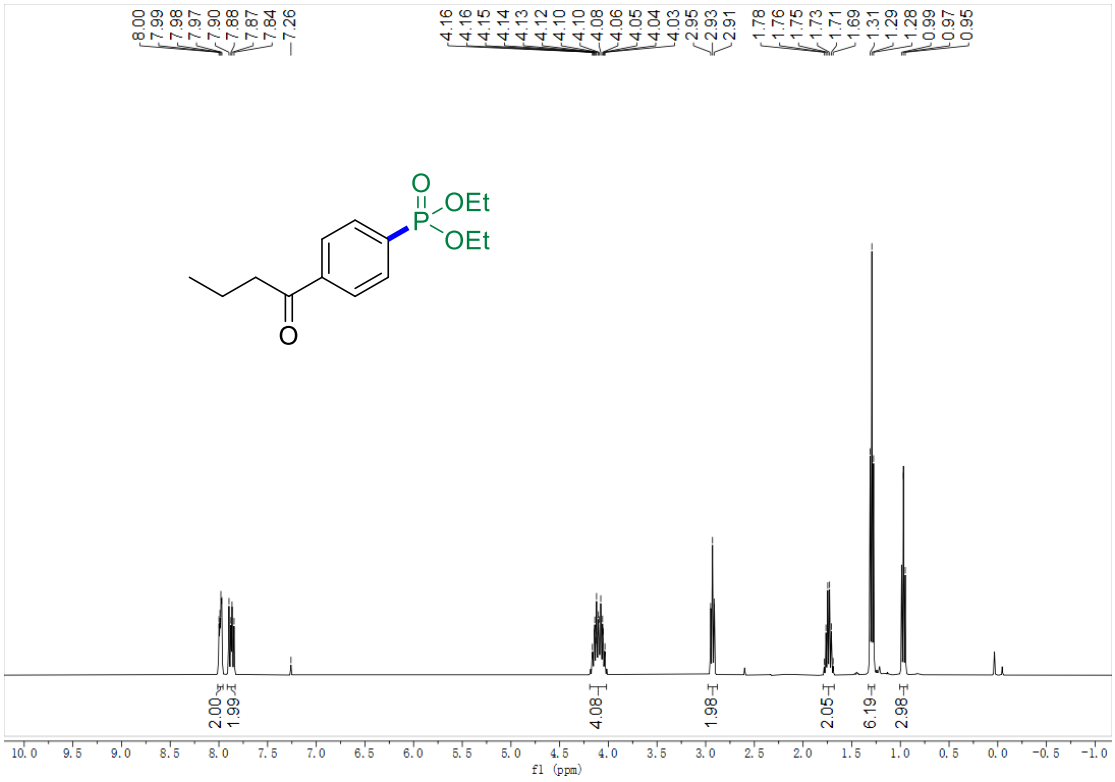
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4da**



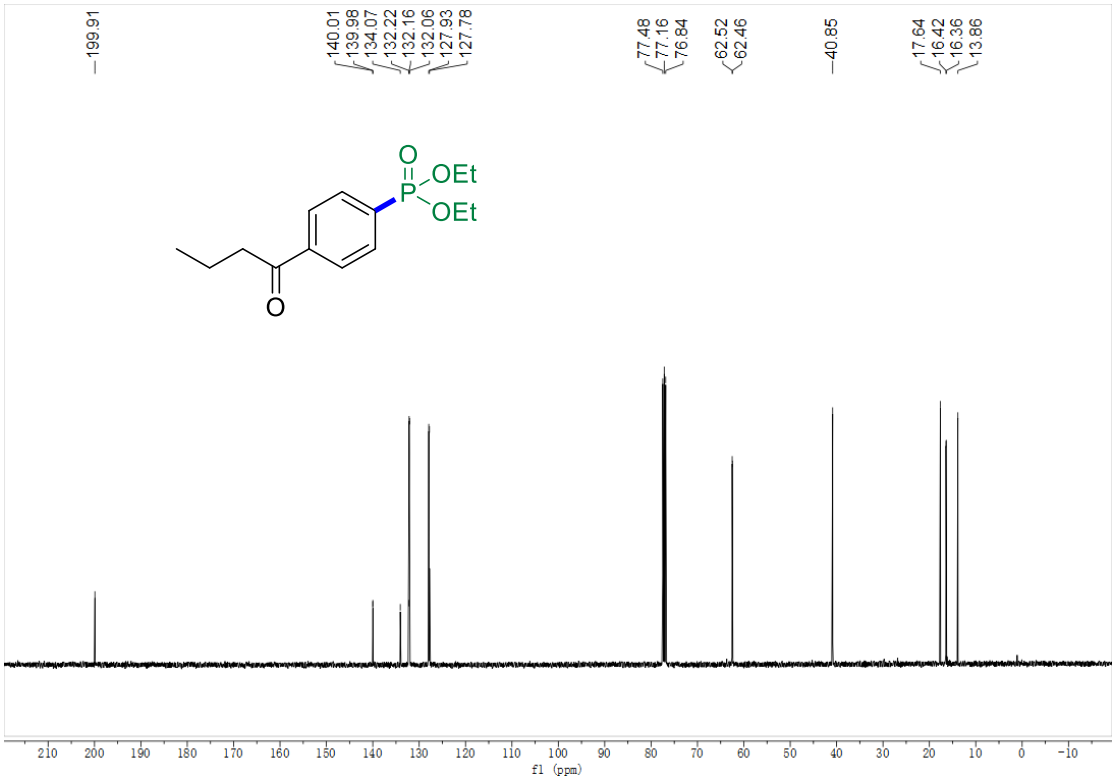
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4da**



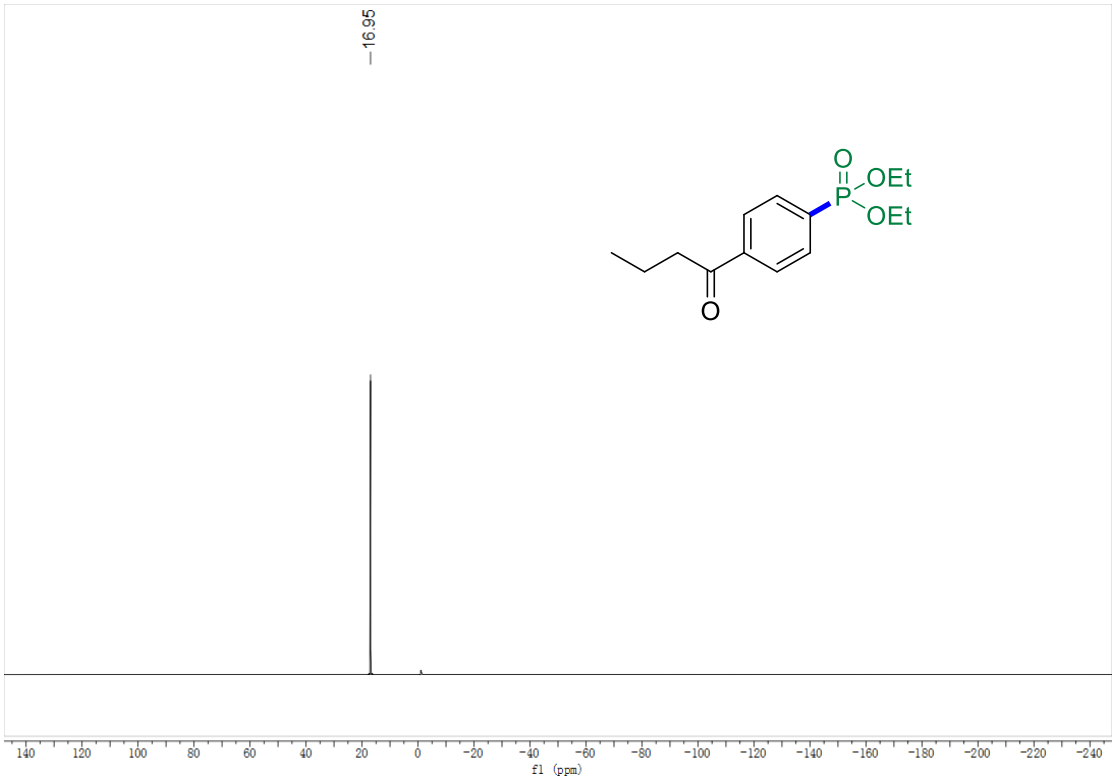
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ea**



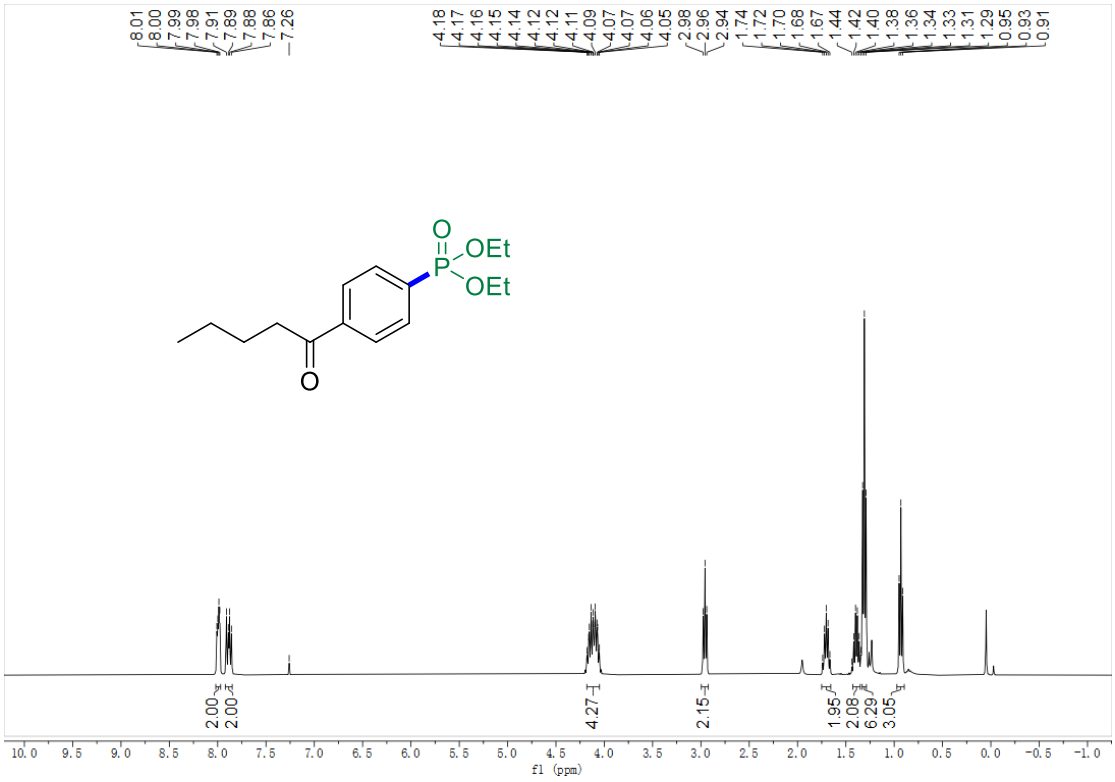
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ea**



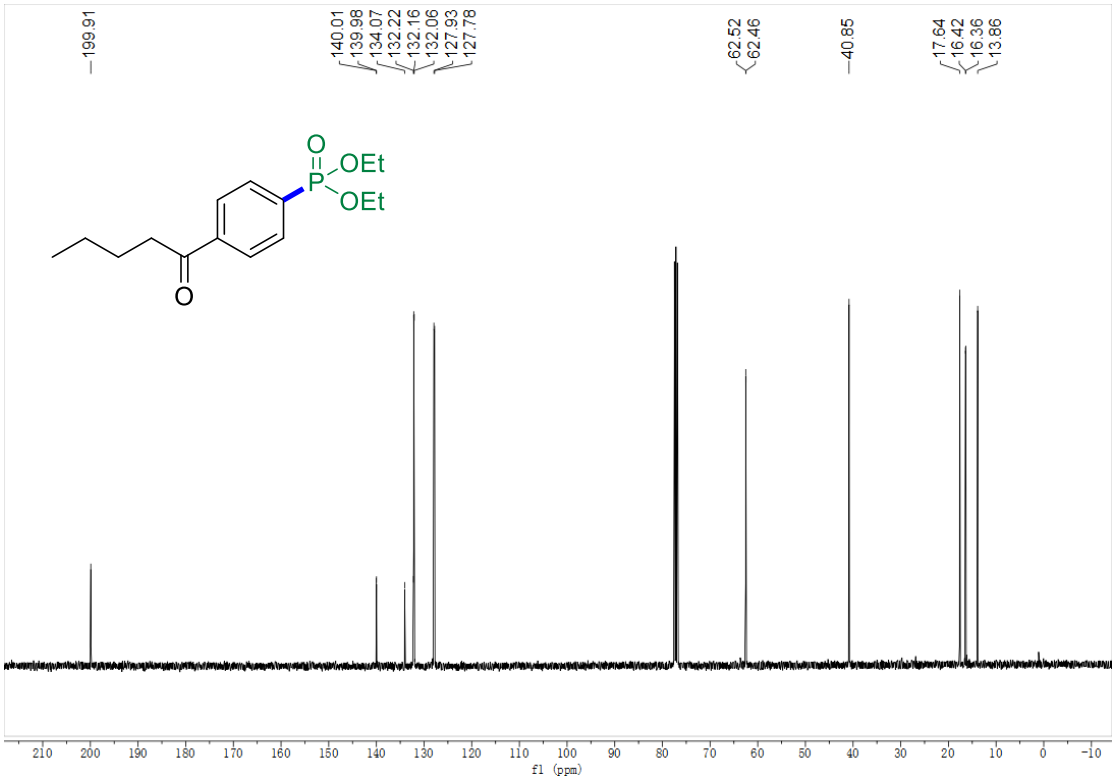
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ea**



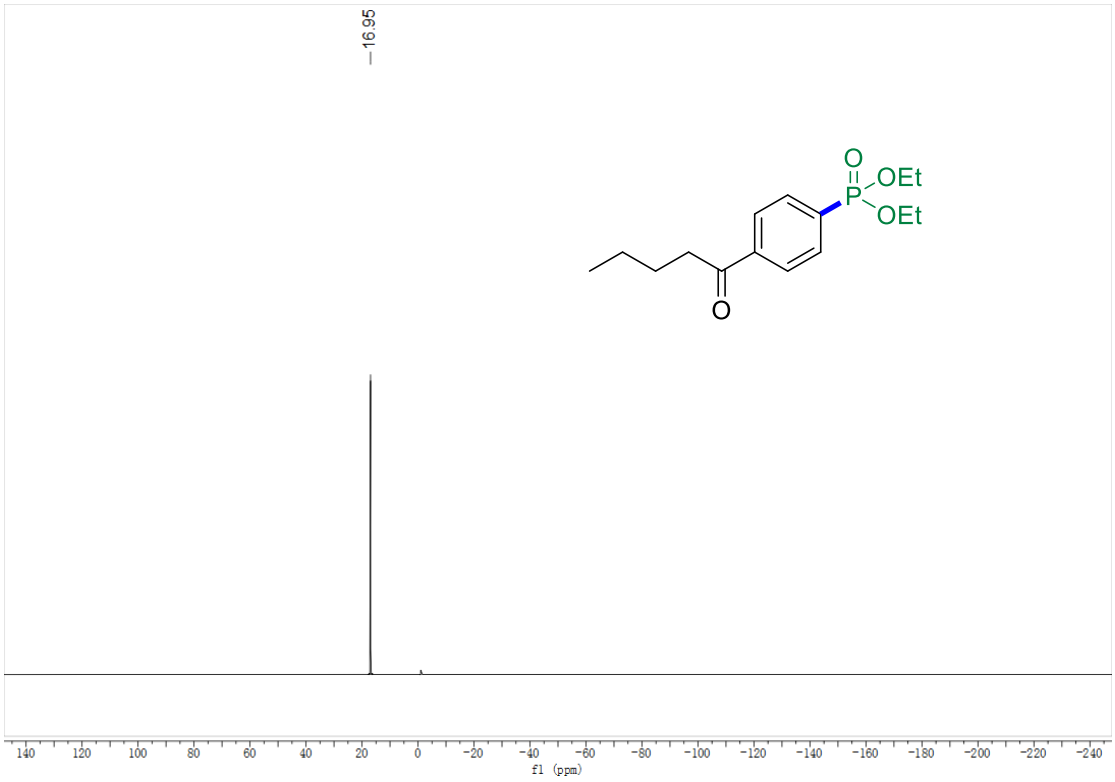
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4fa**



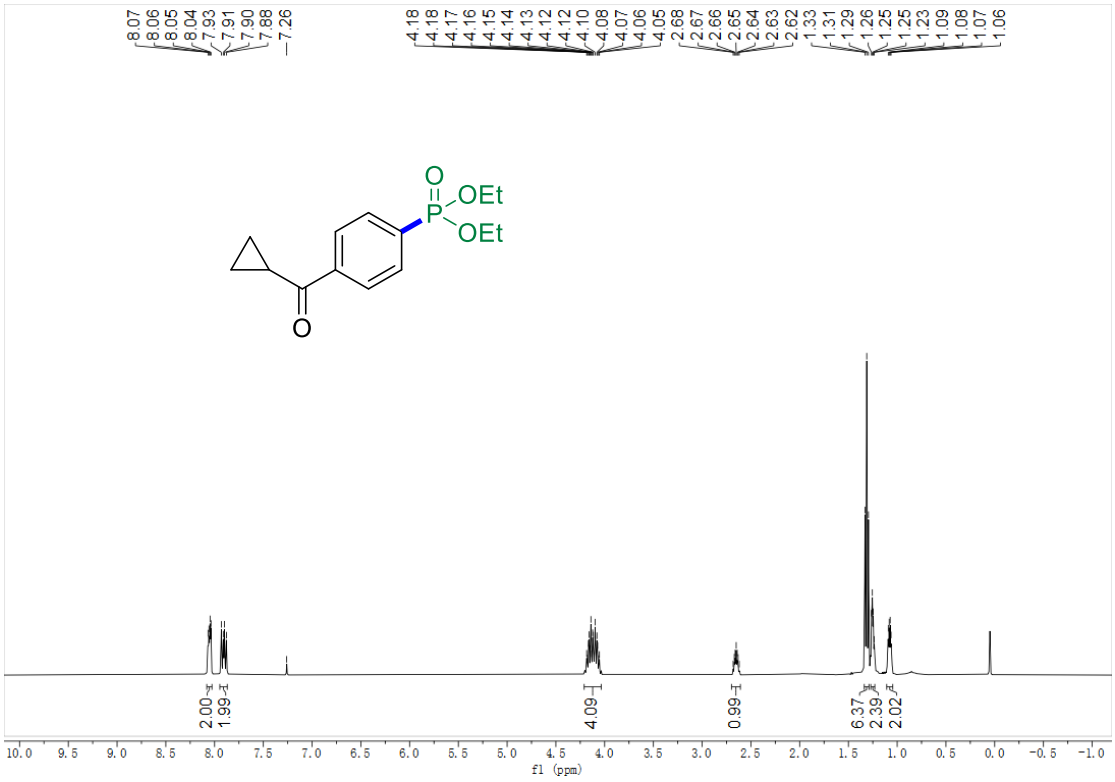
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4fa**



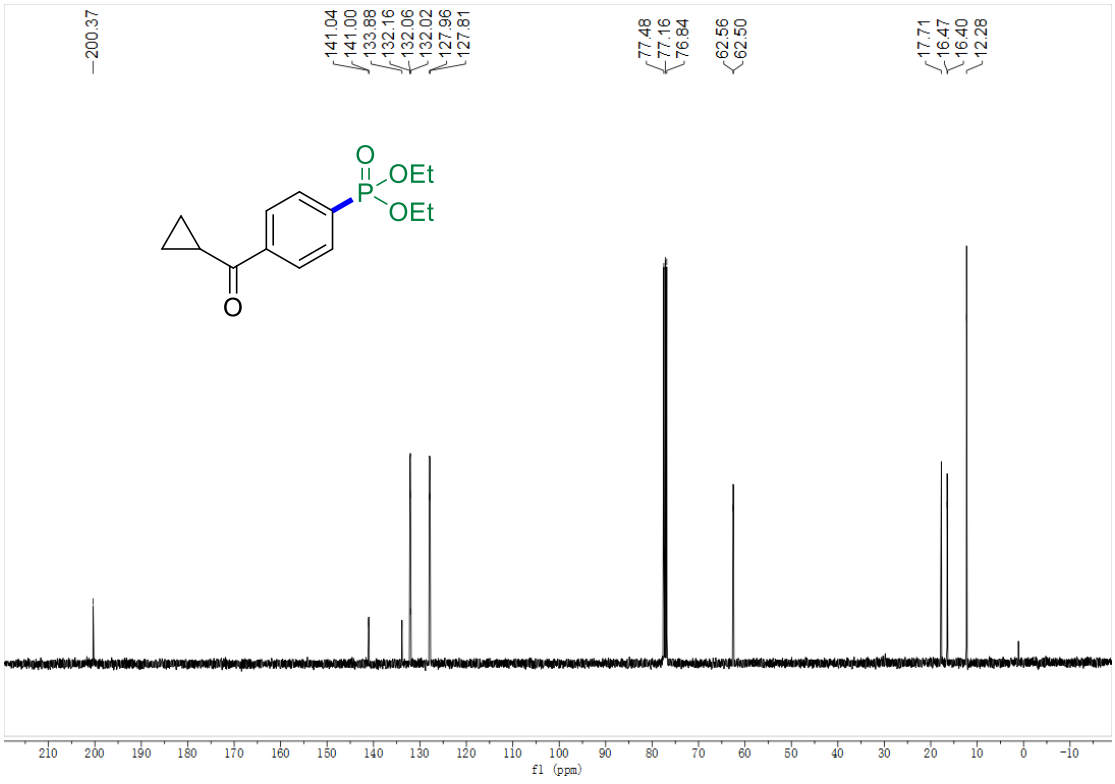
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4fa**



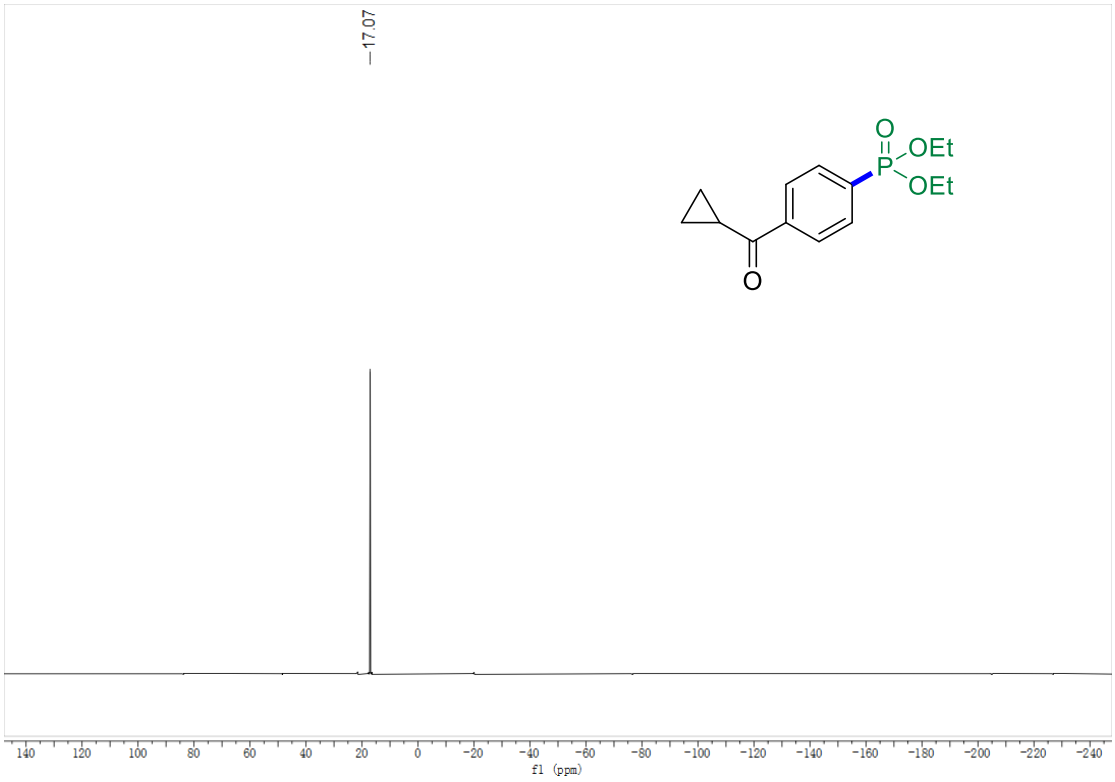
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ga**



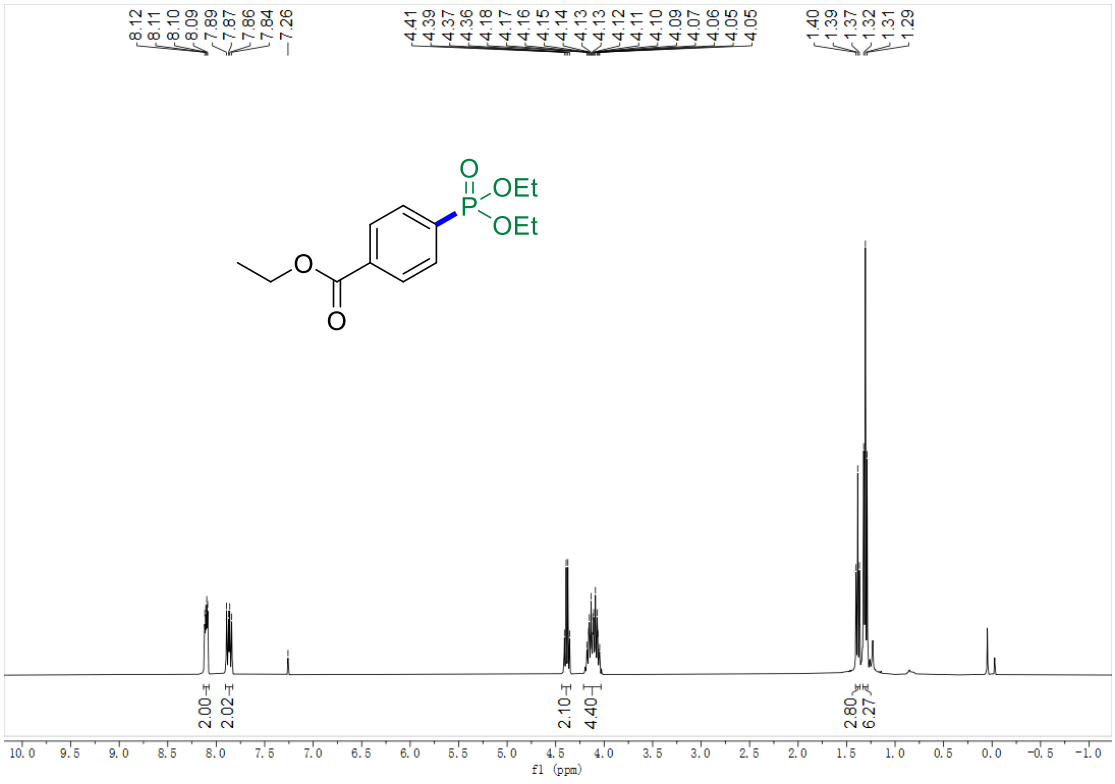
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ga**



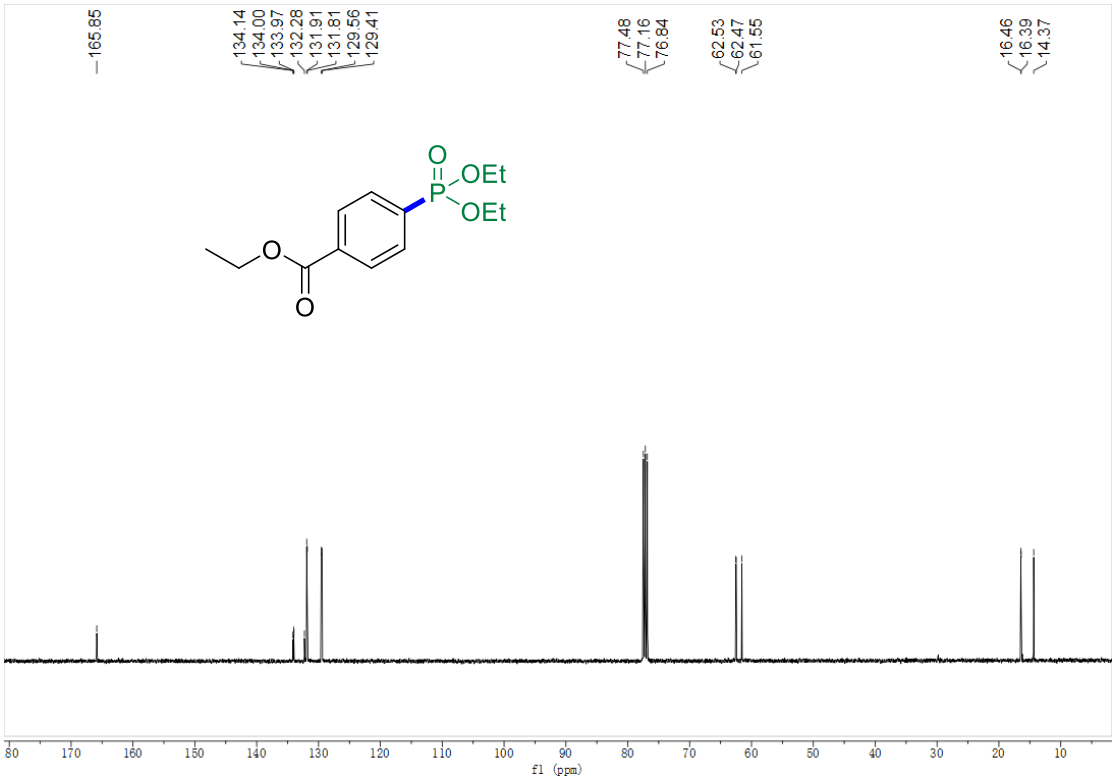
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ga**



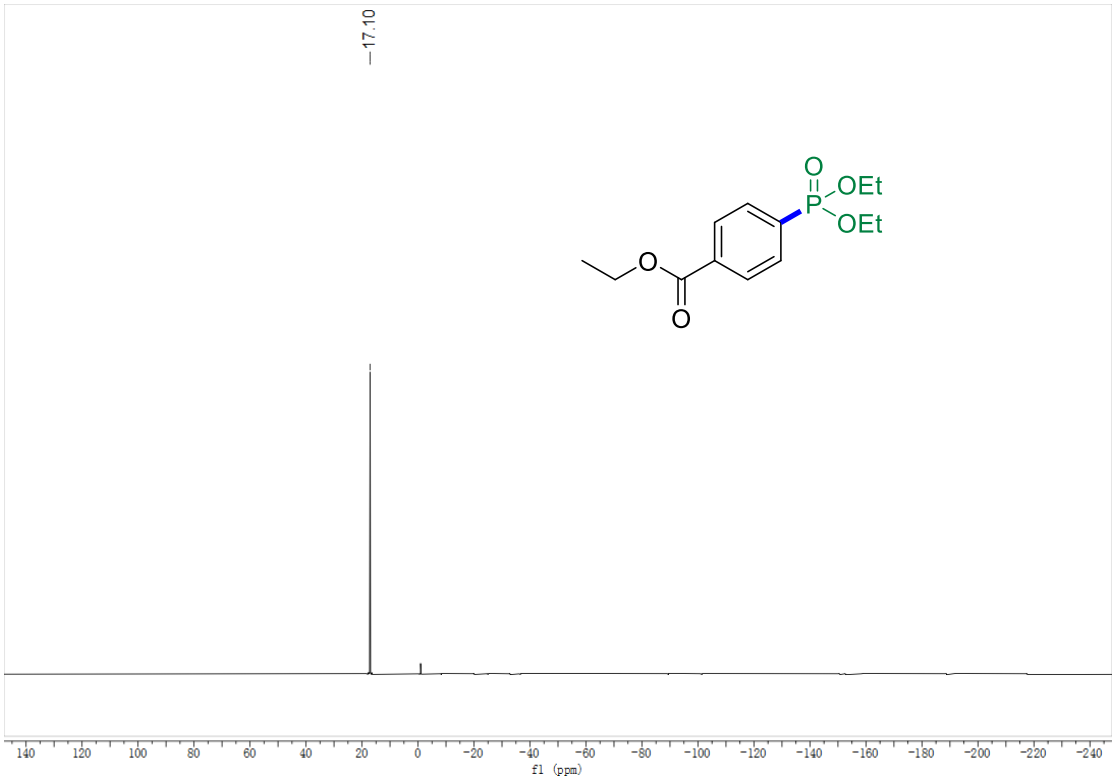
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ha**



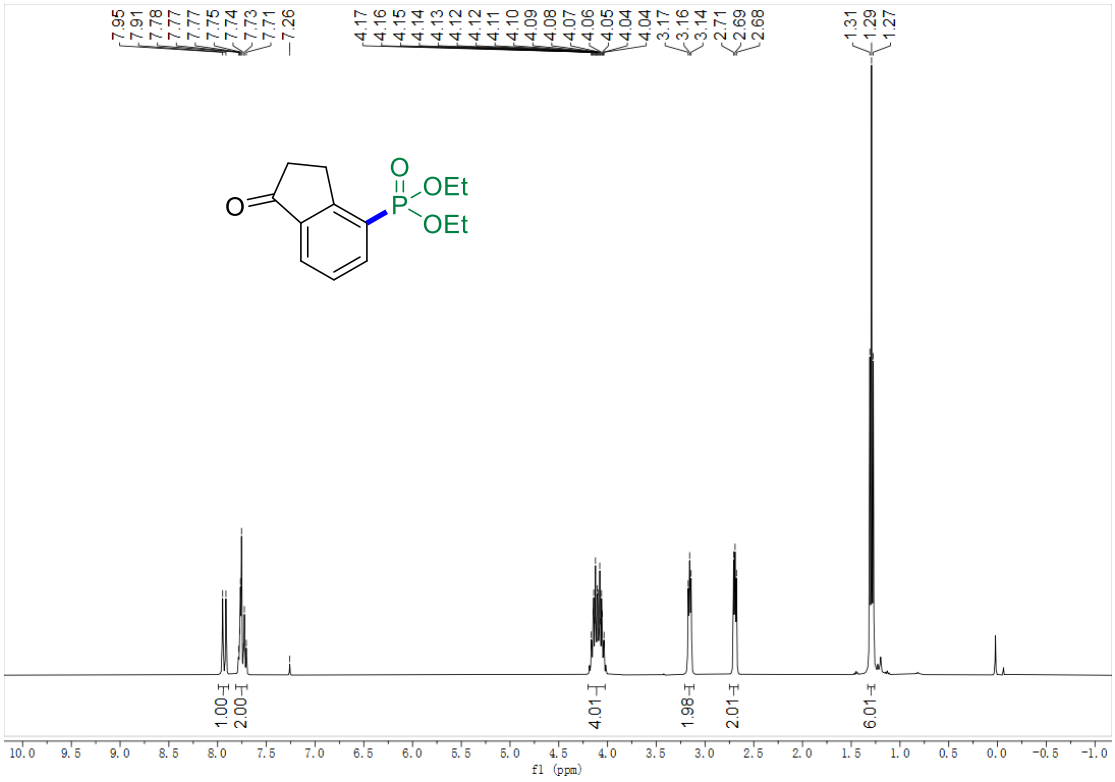
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ha**



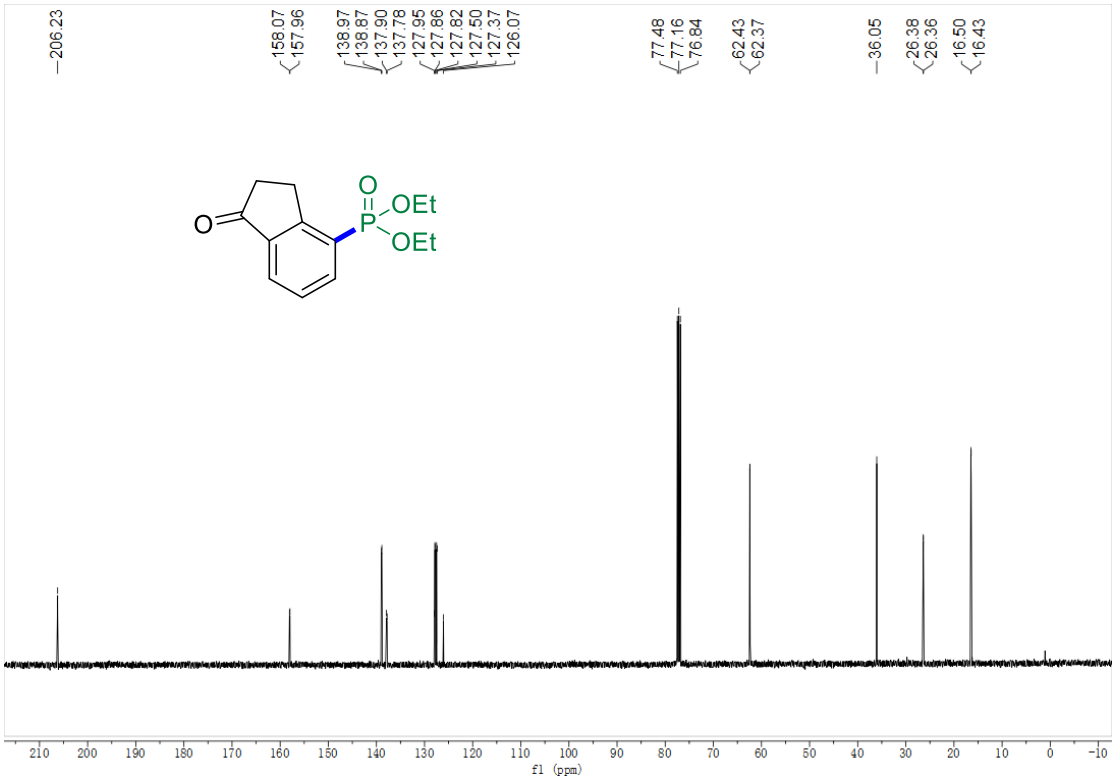
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ha**



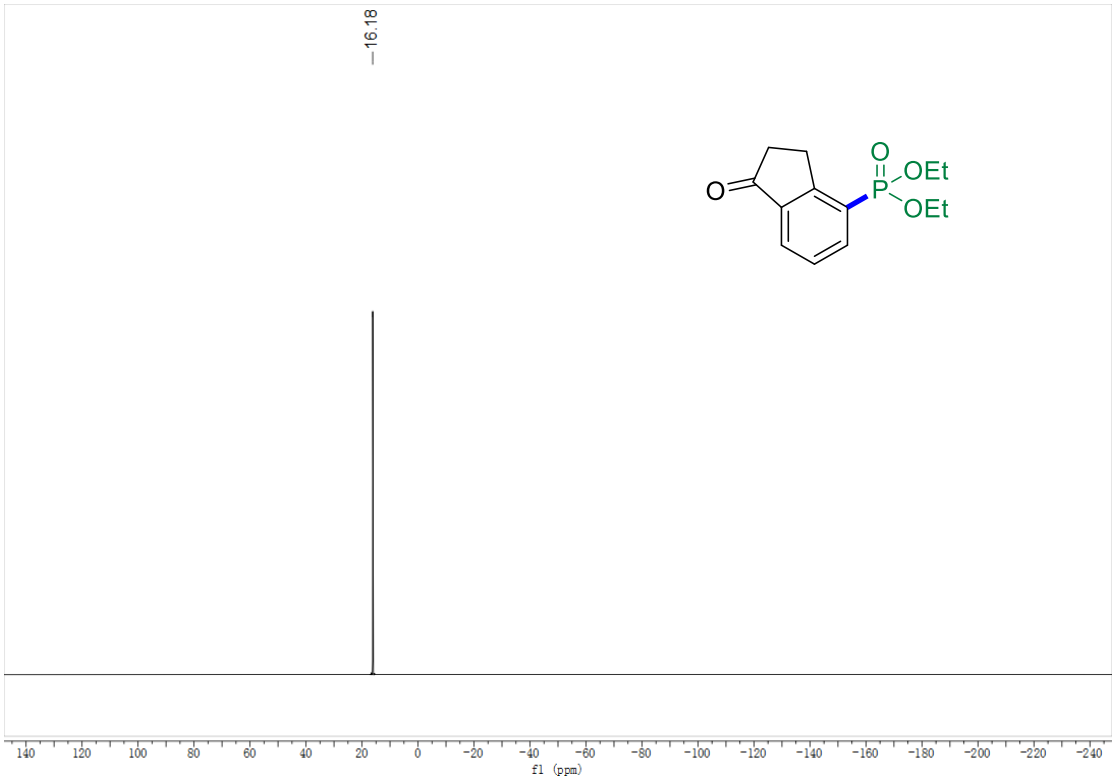
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ia**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ia**



^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ia**



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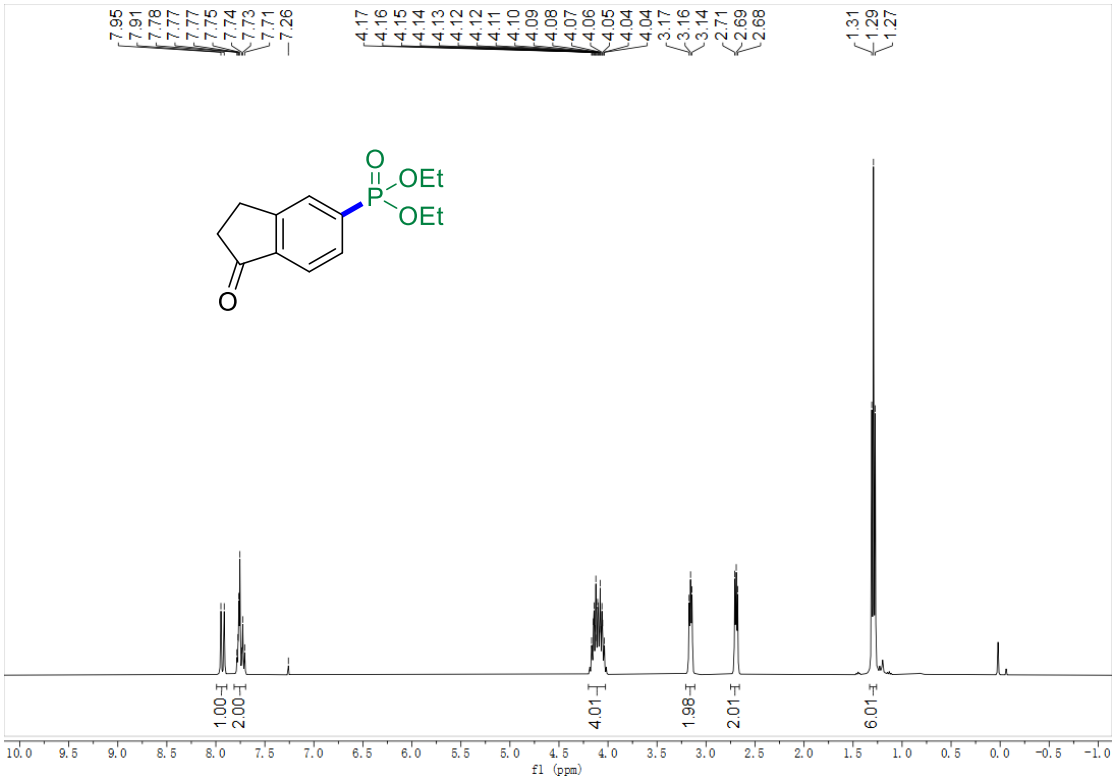
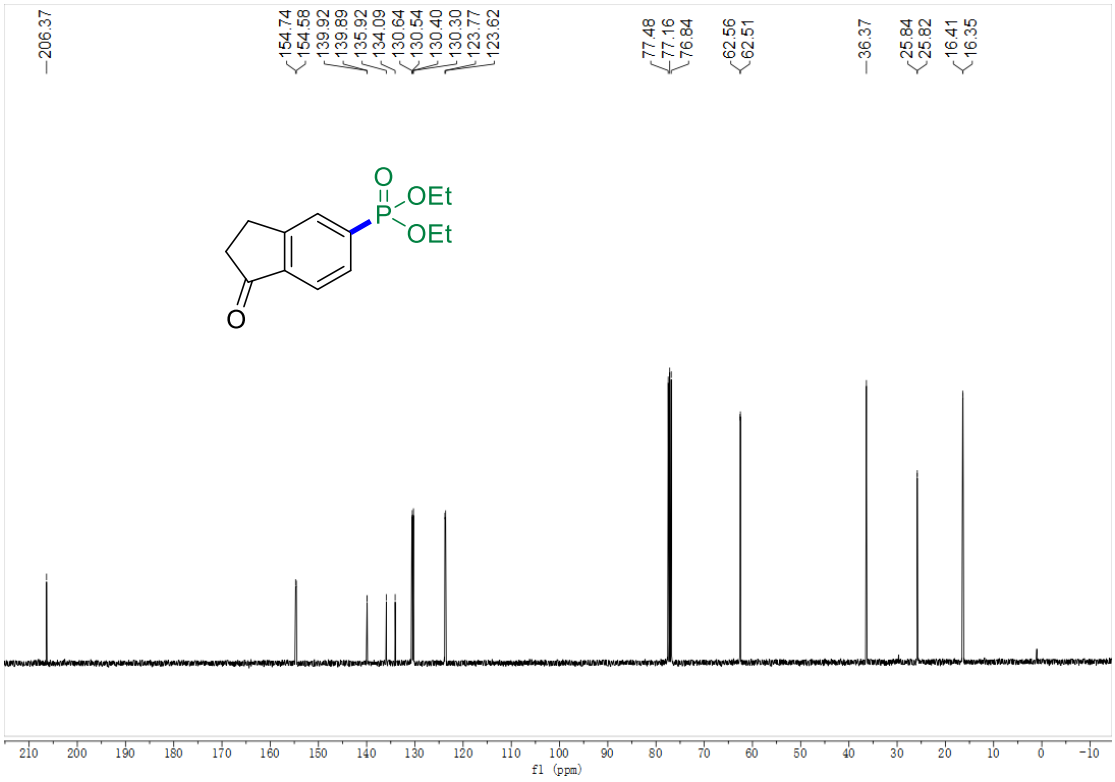
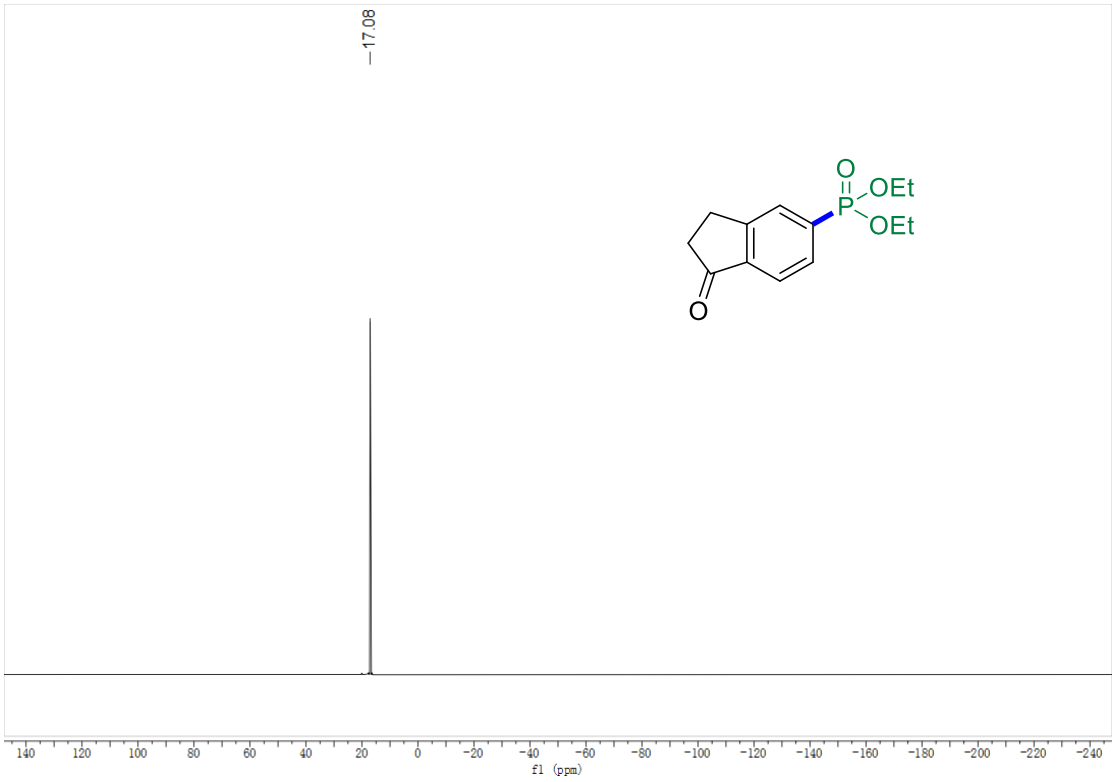


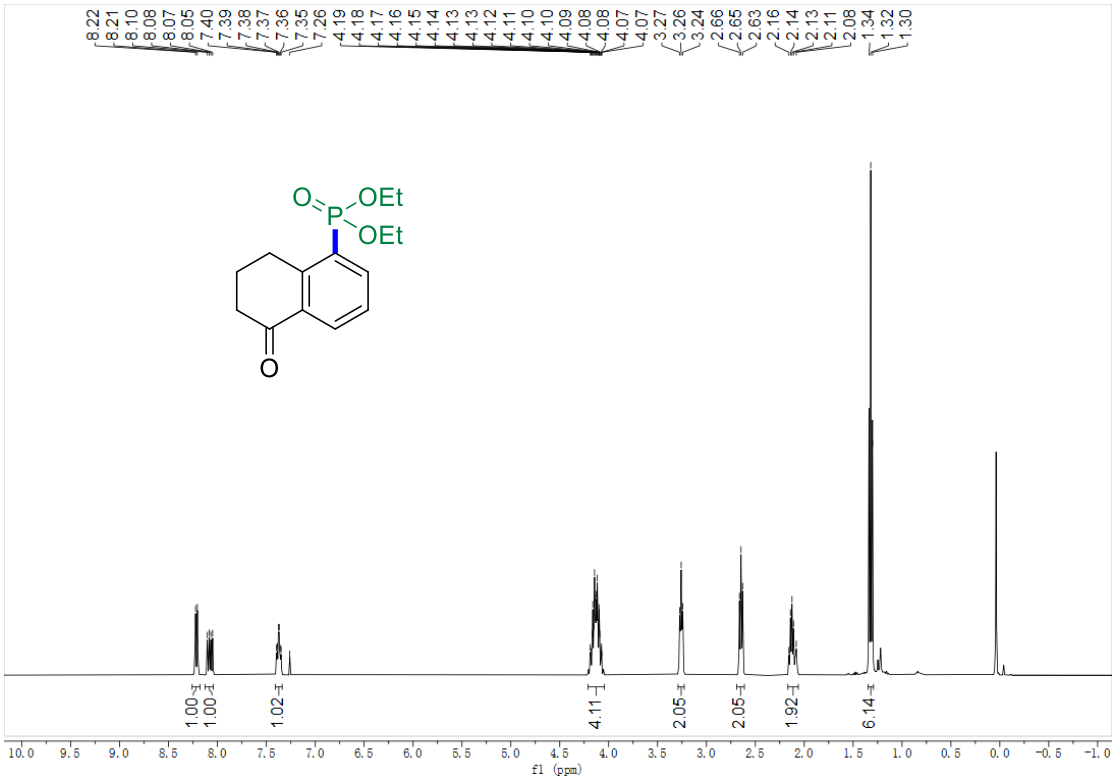
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ja**



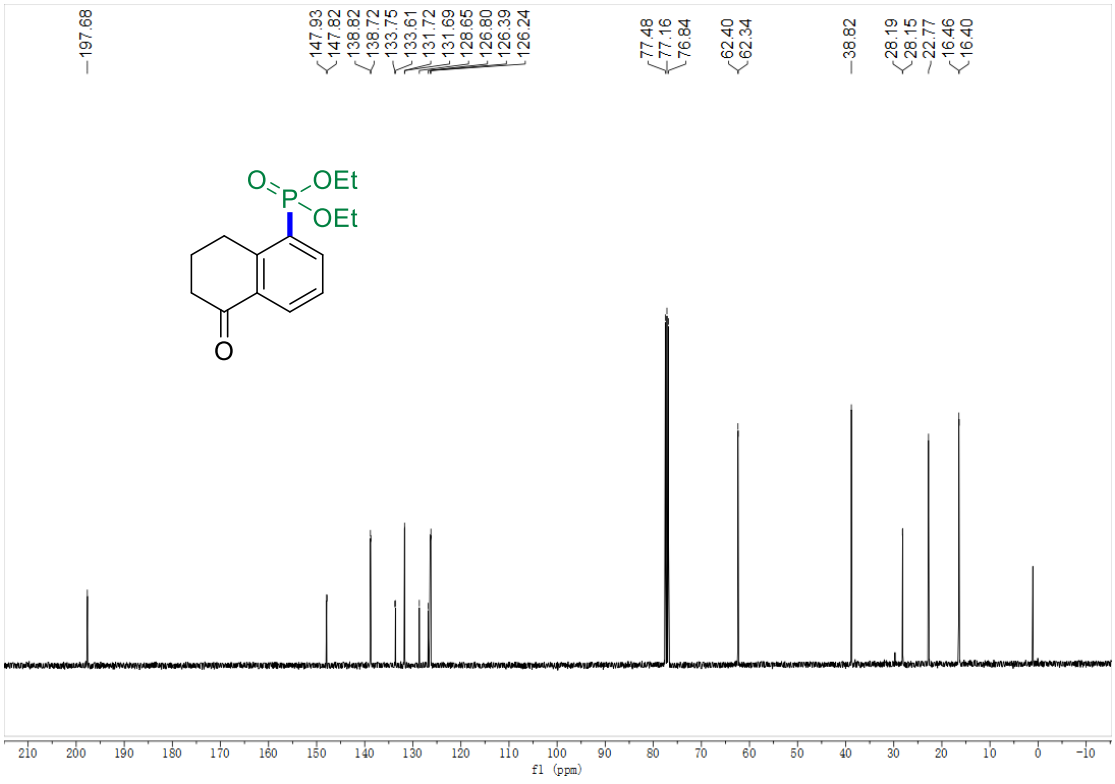
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ja**



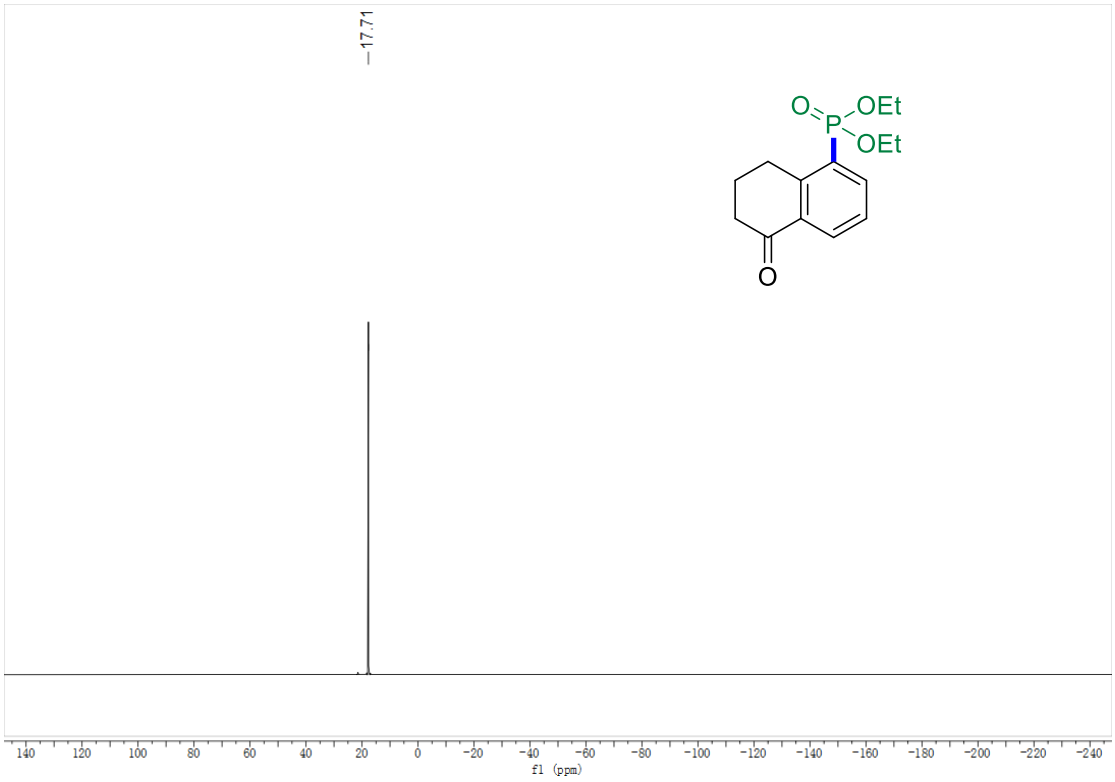
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ka**



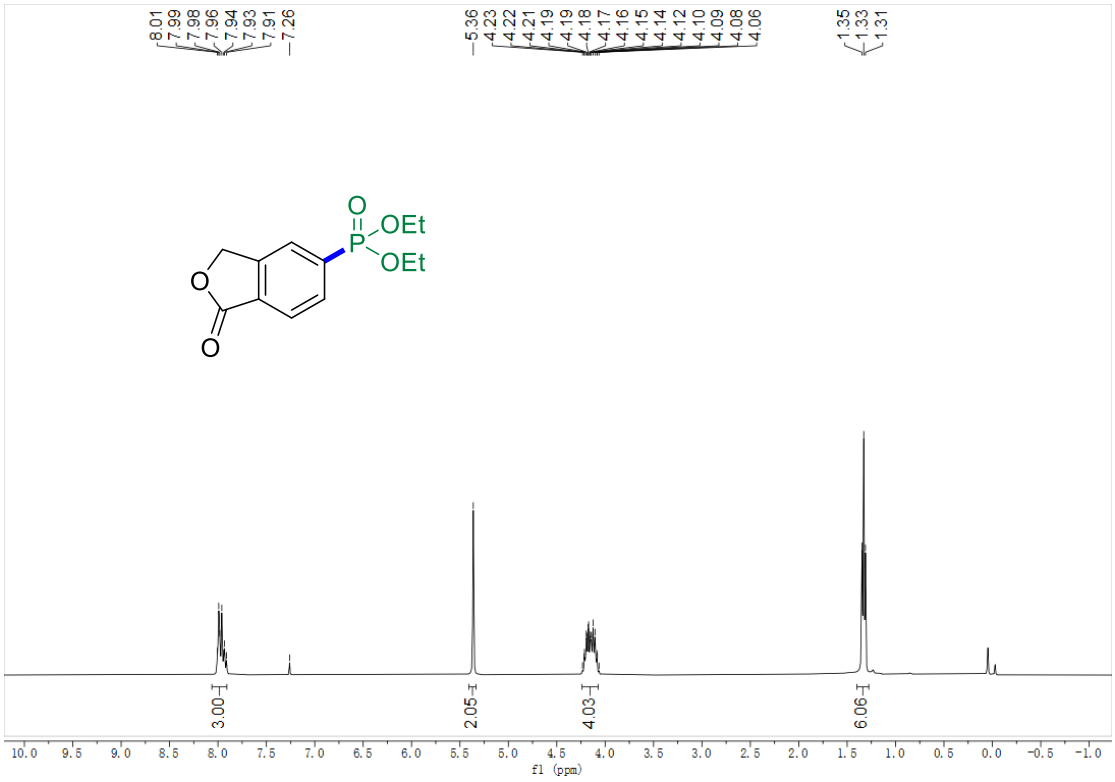
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ka**



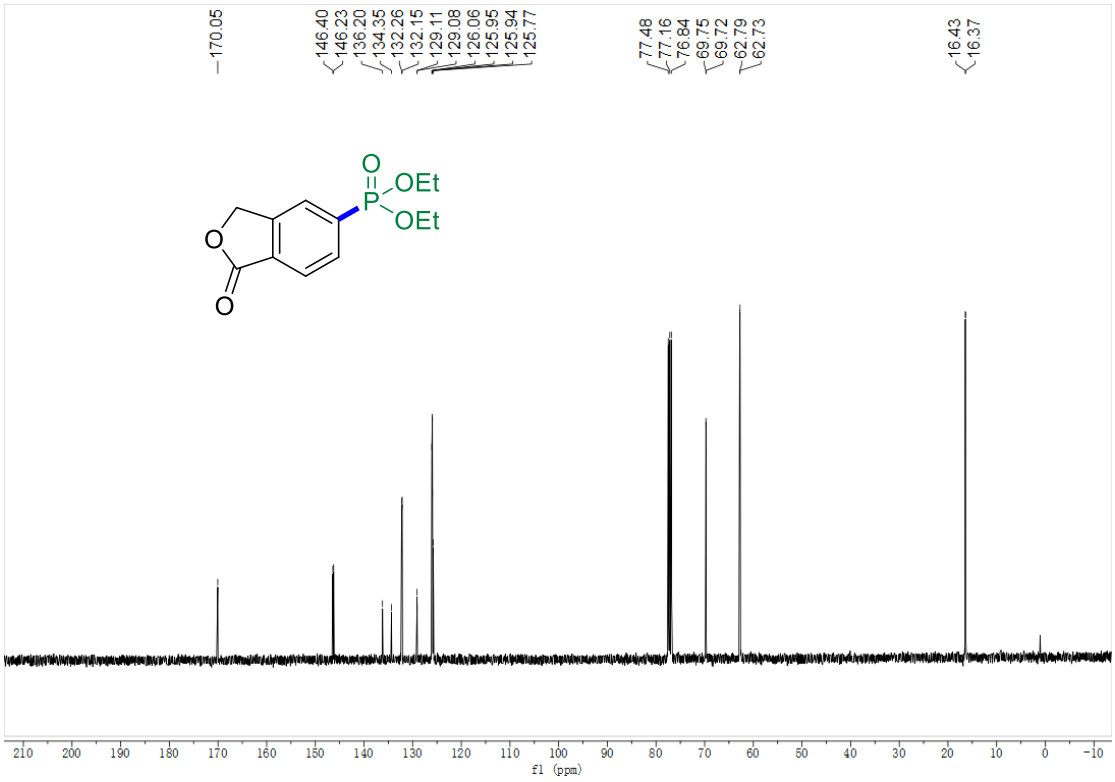
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ka**



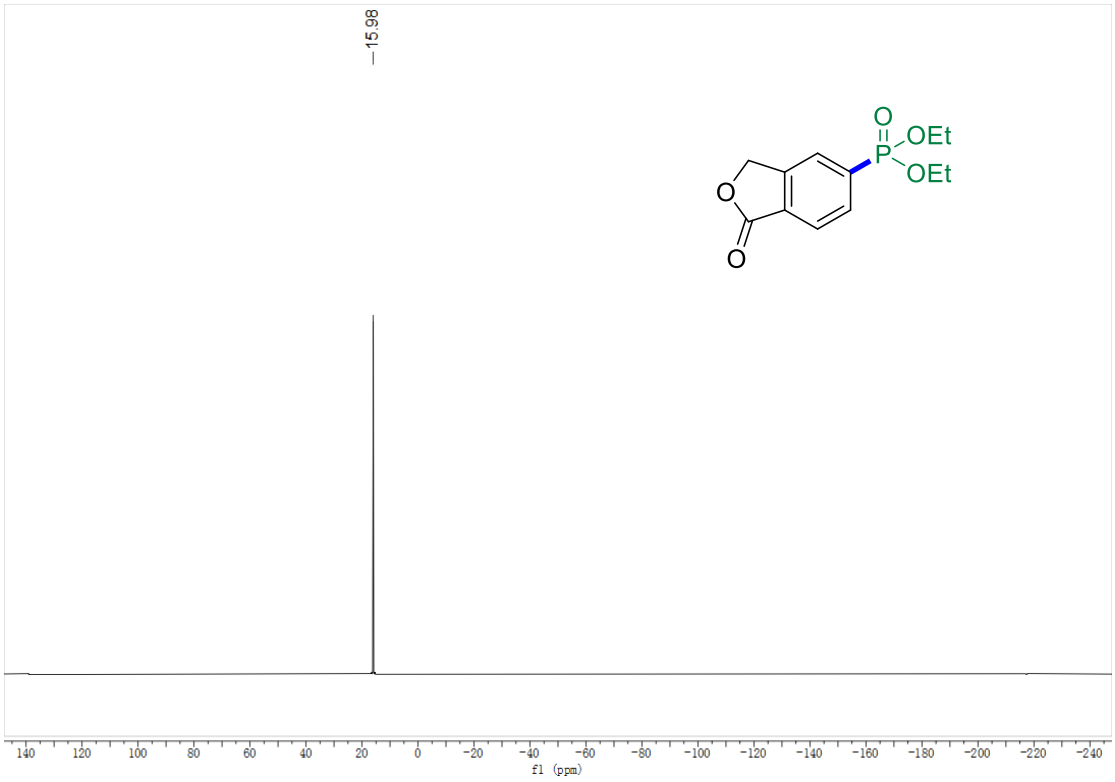
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4la**



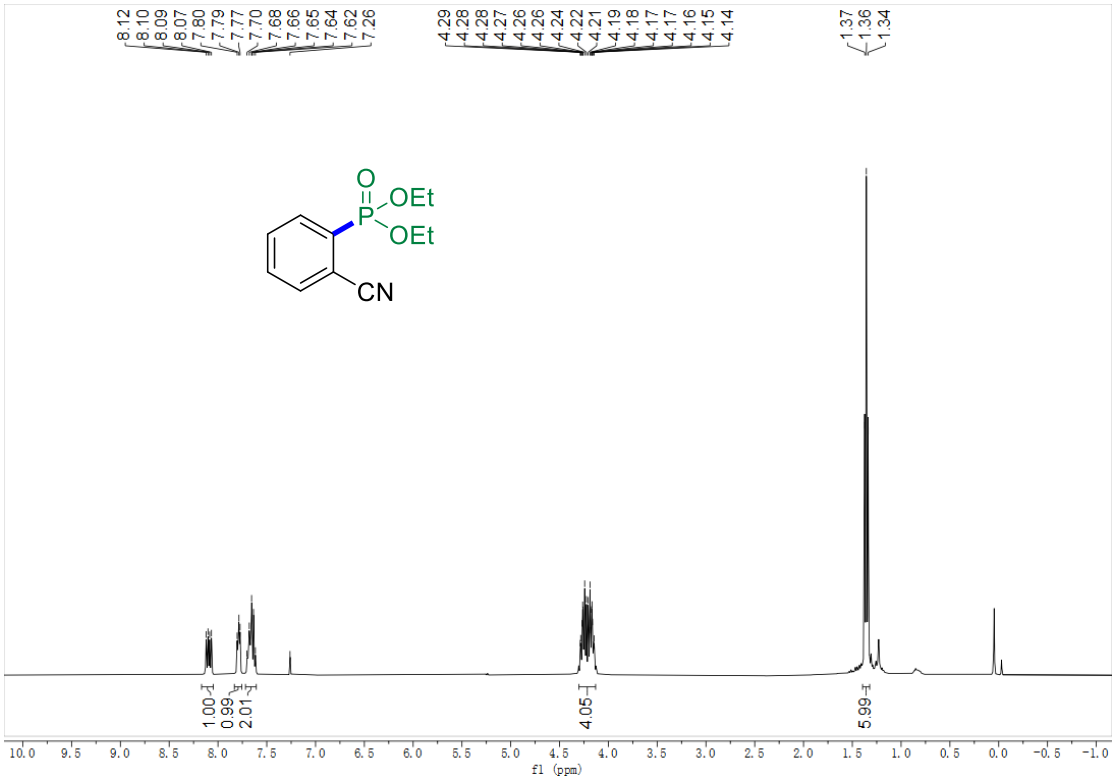
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4la**



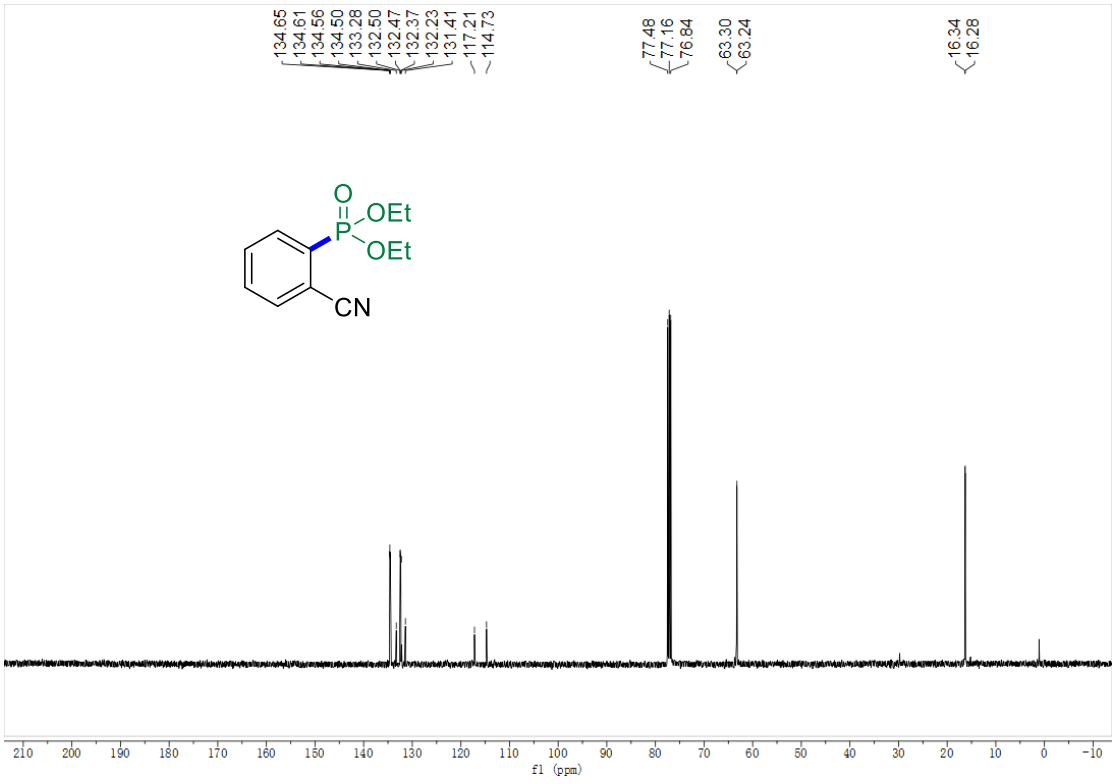
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4la**



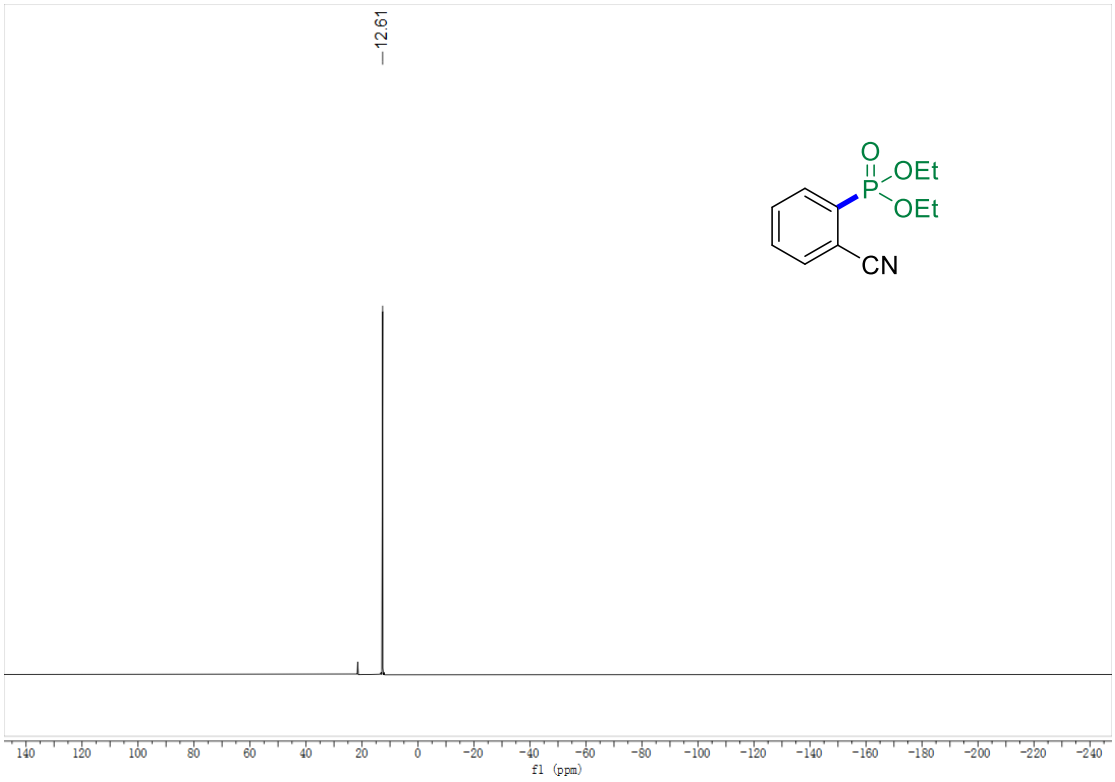
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ma**



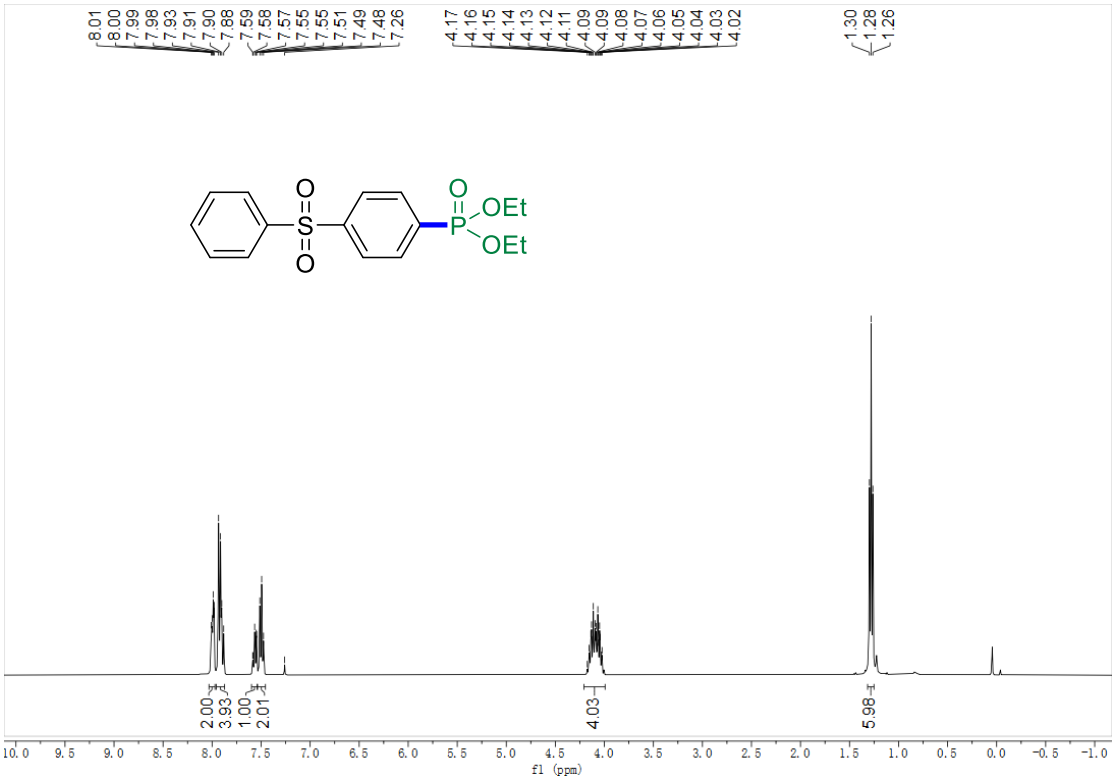
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ma**



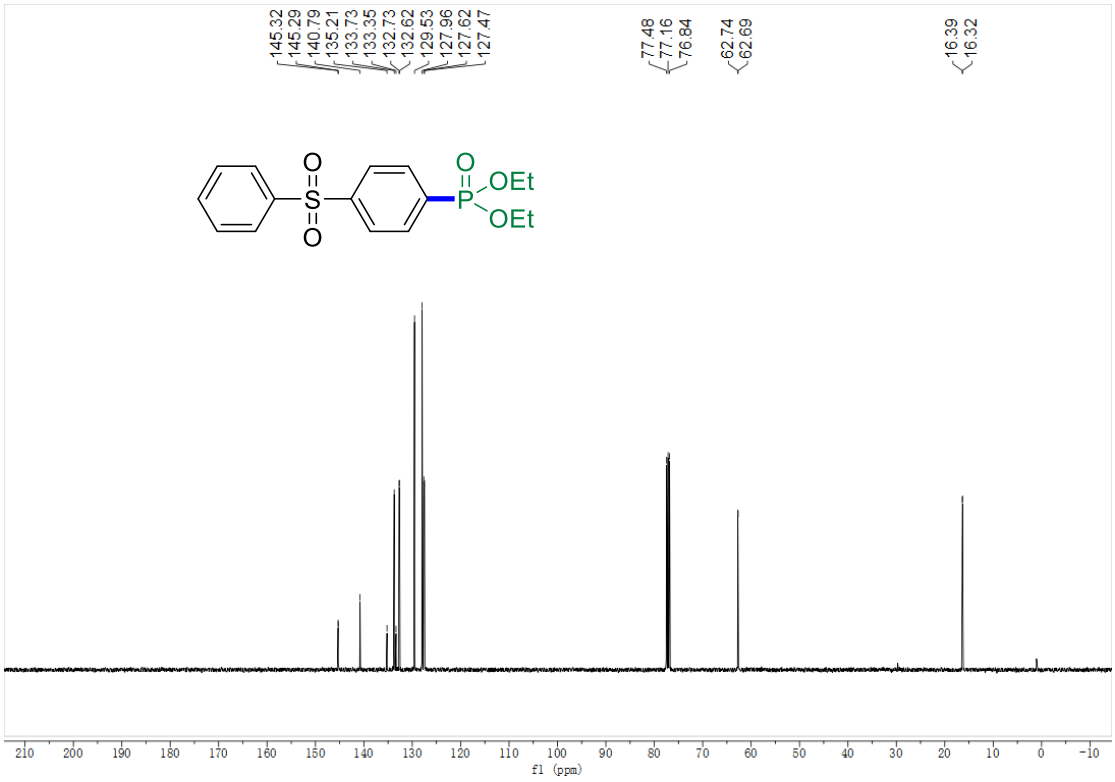
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ma**



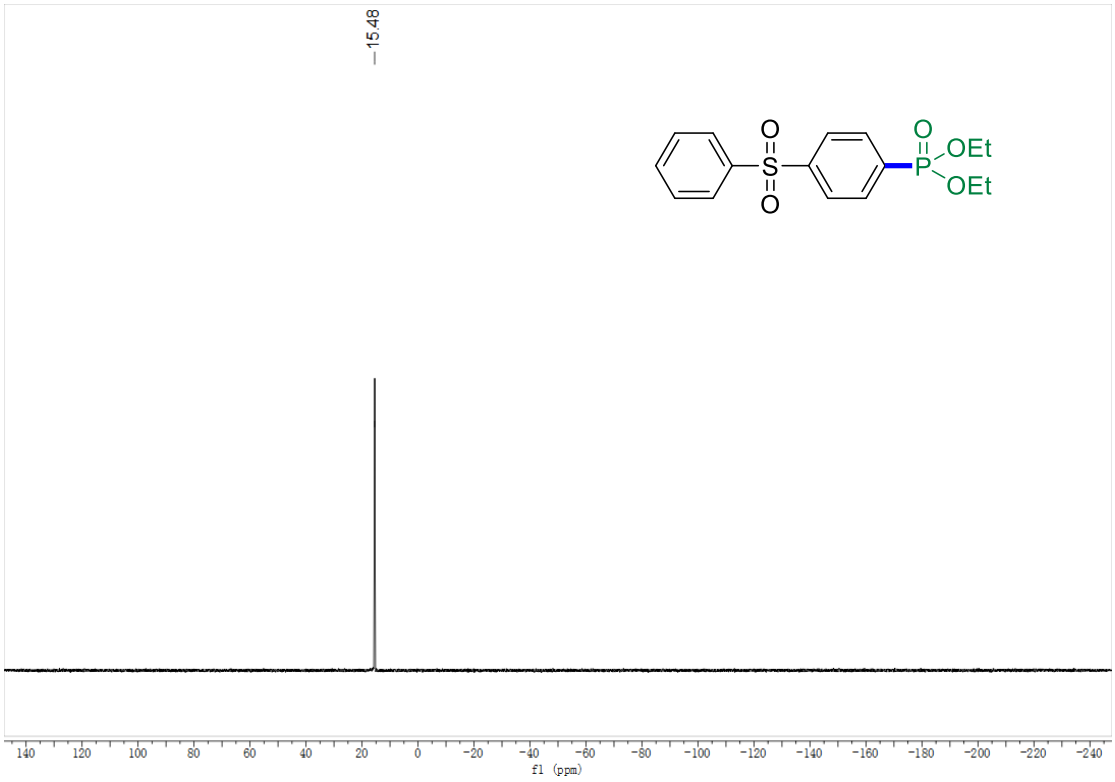
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4na**



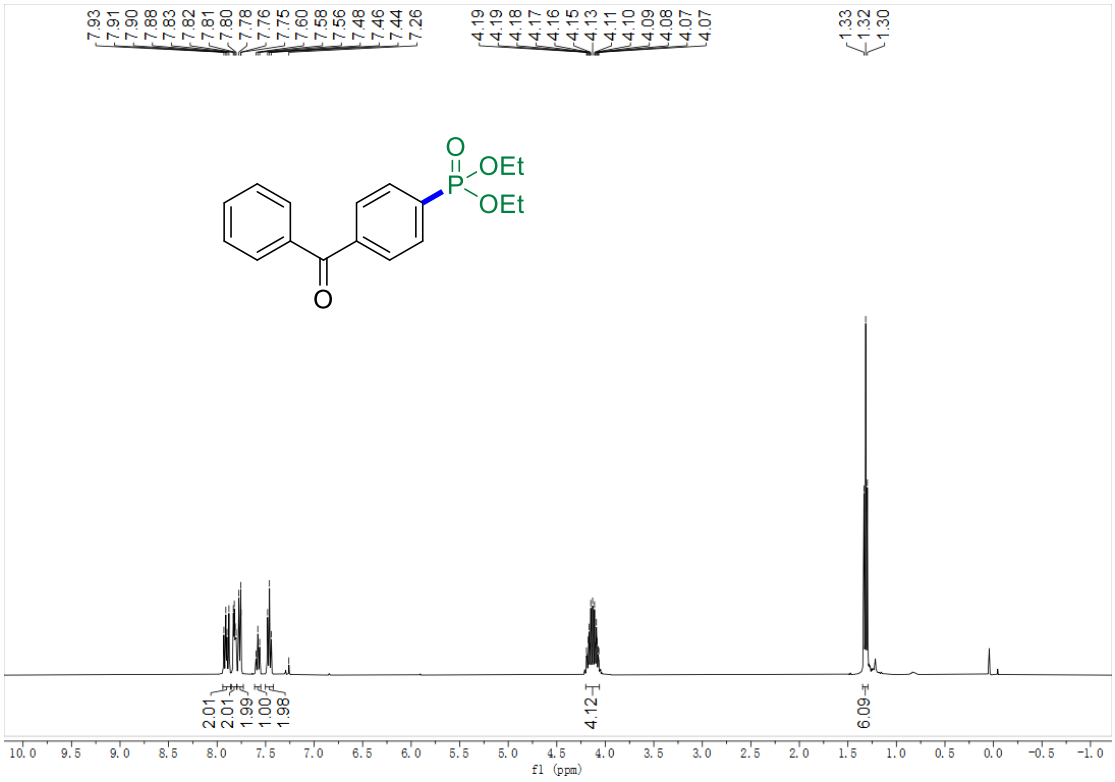
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4na**



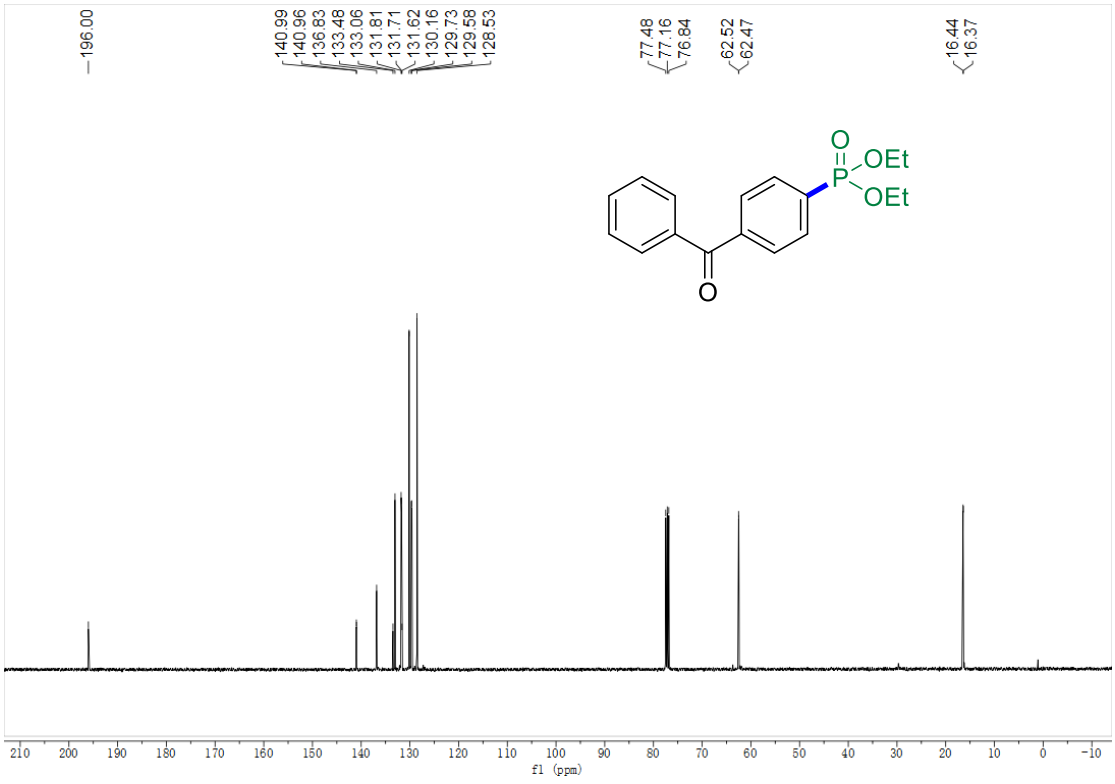
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4na**



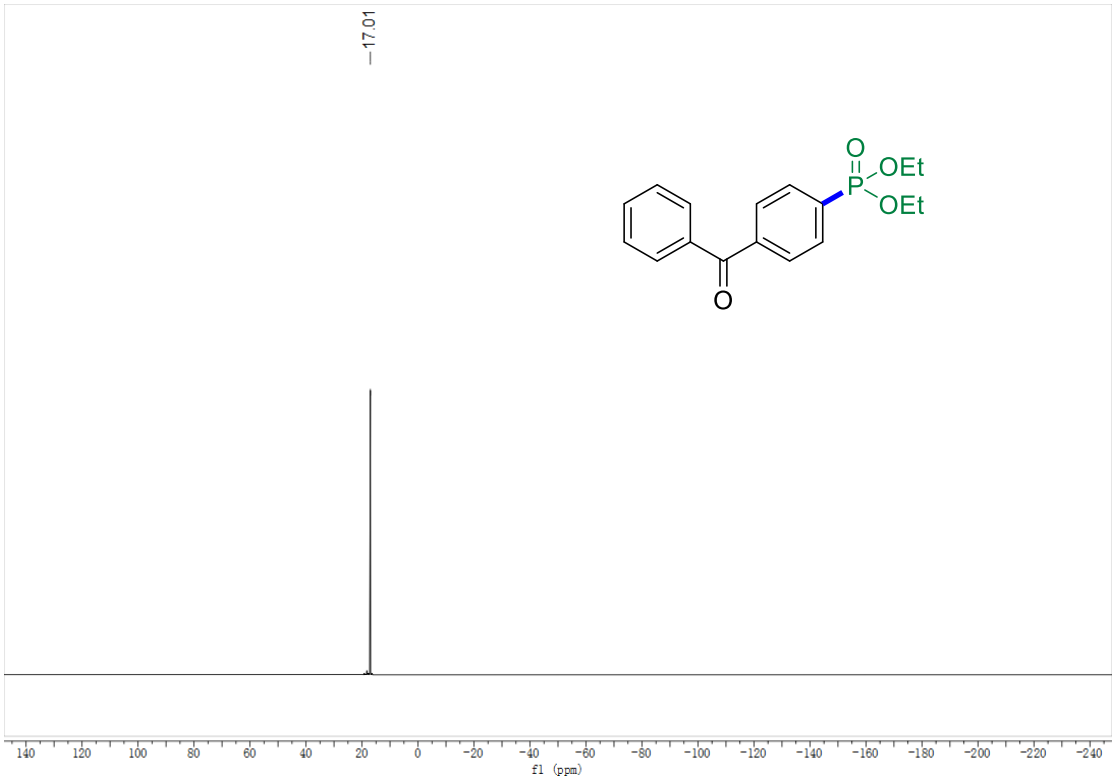
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4oa**



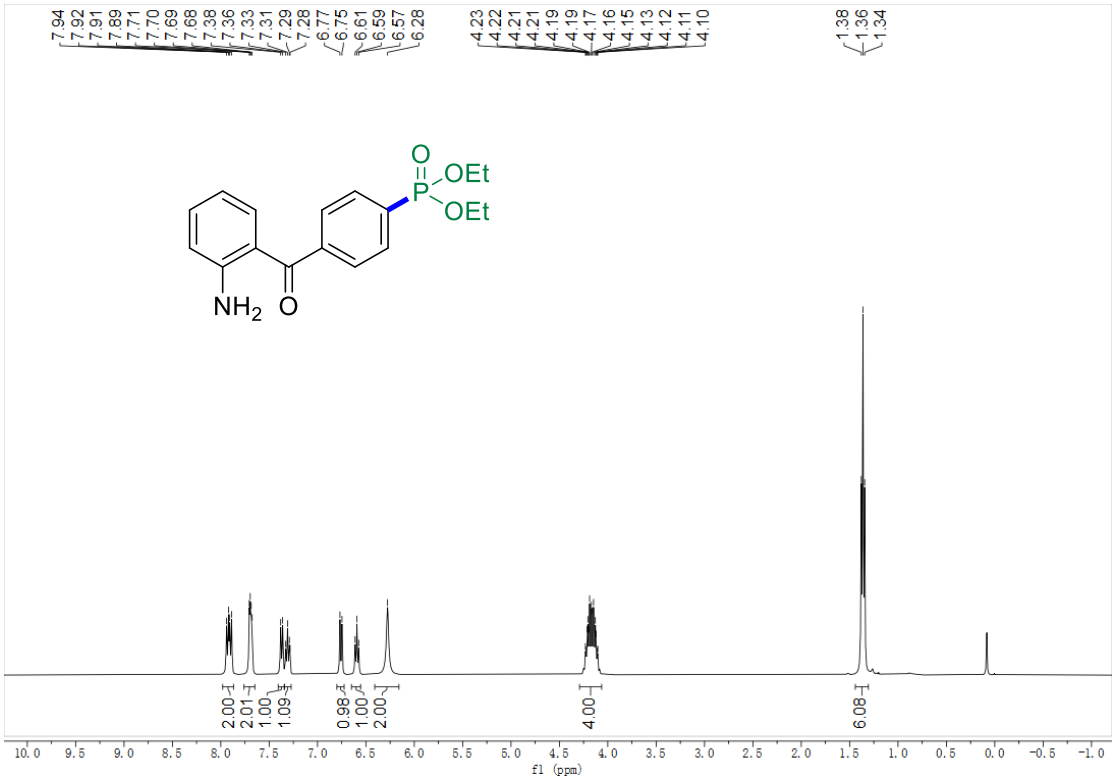
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4oa**



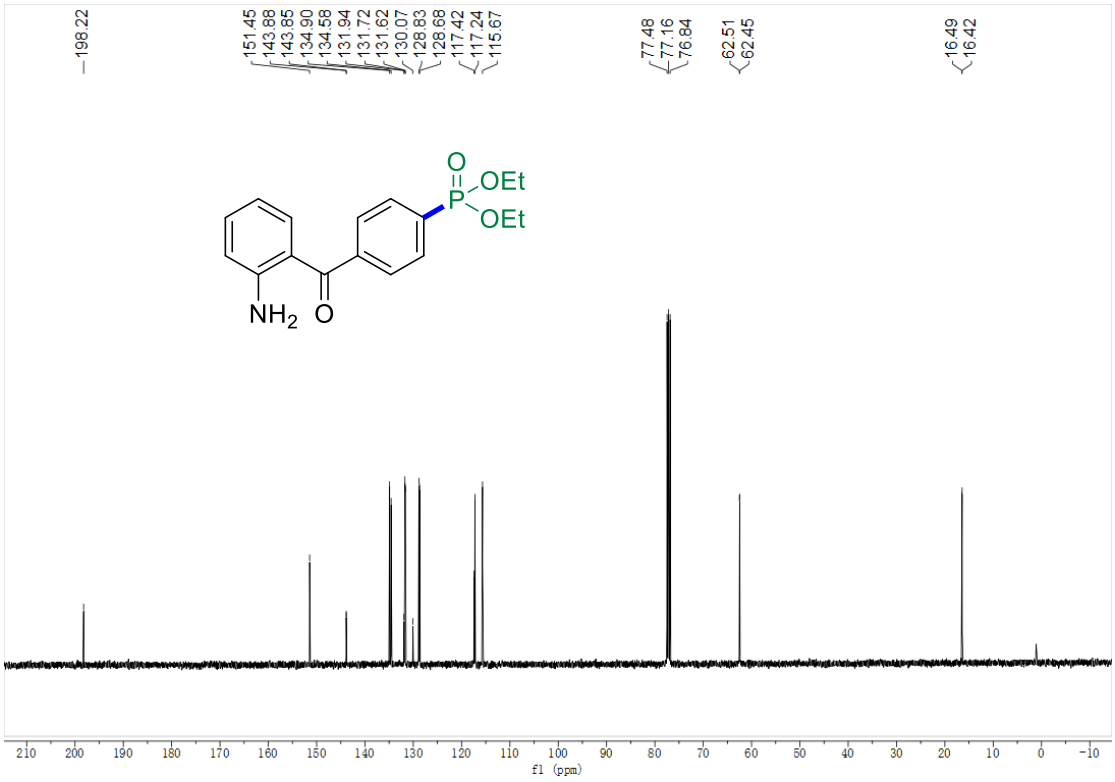
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4oa**



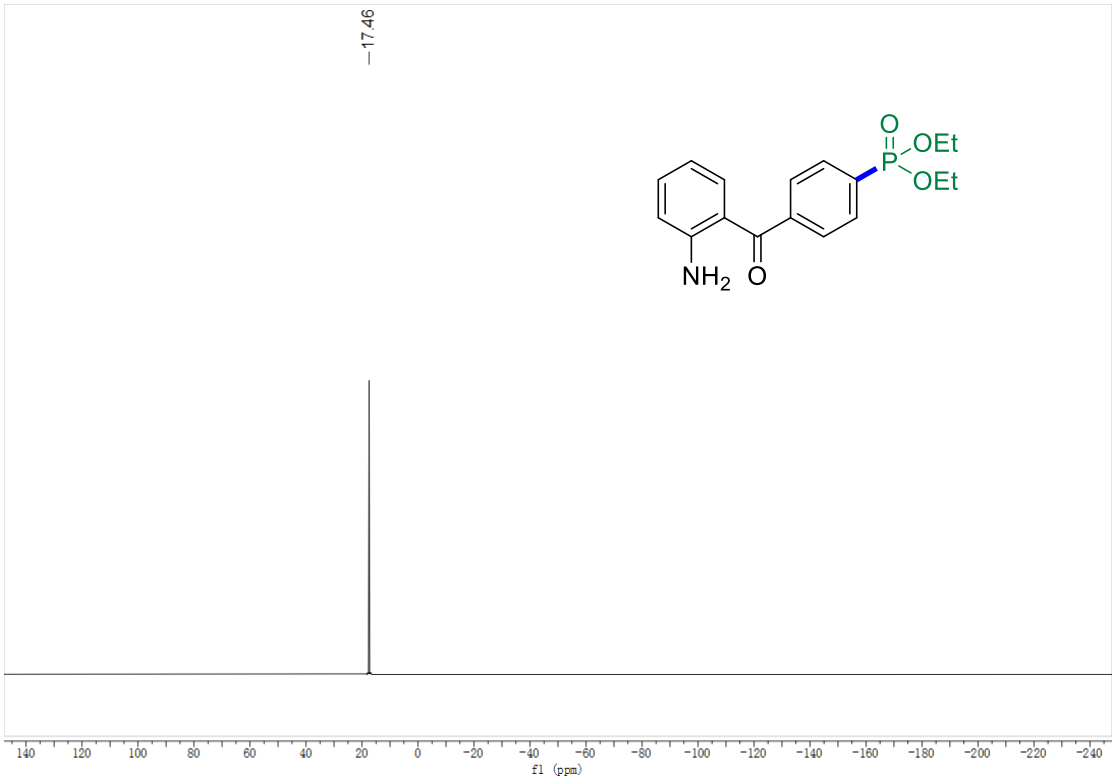
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4pa**



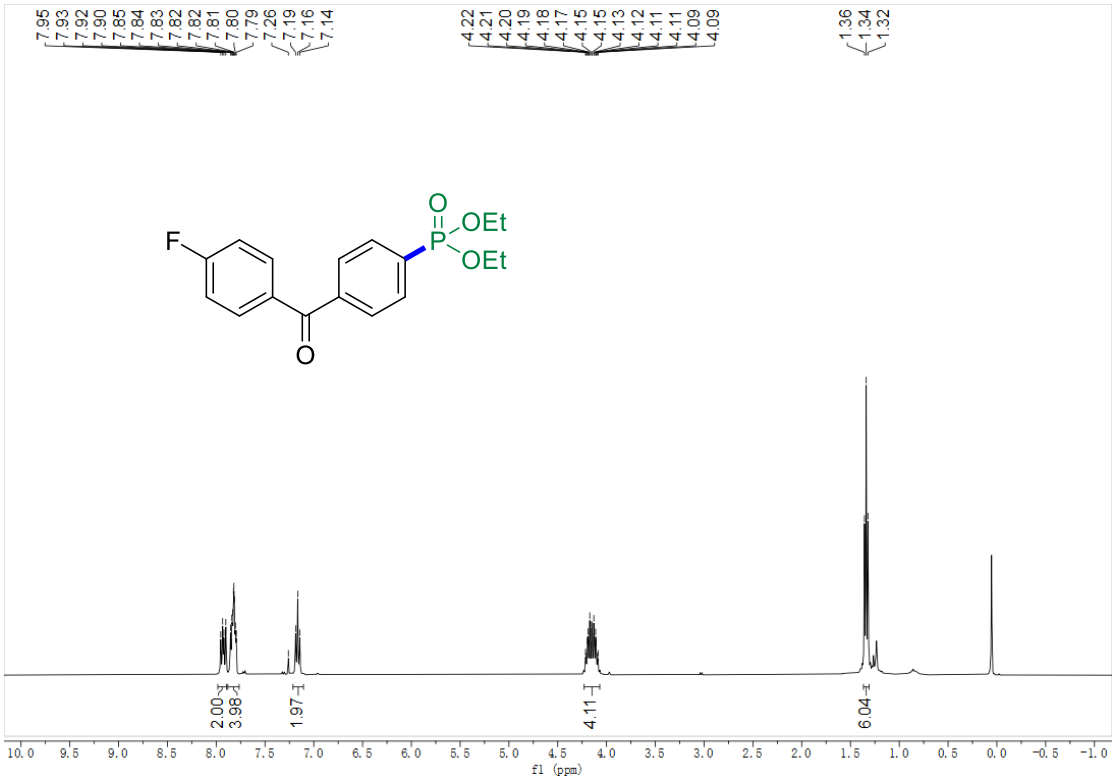
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4pa**



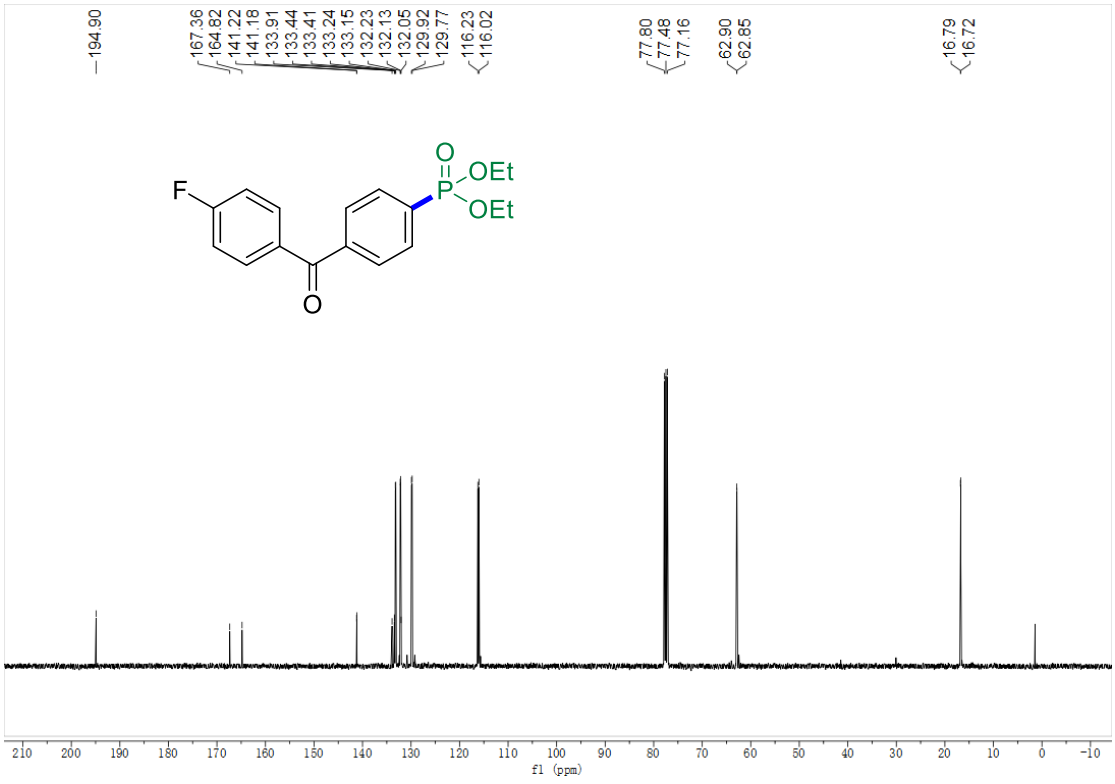
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4pa**



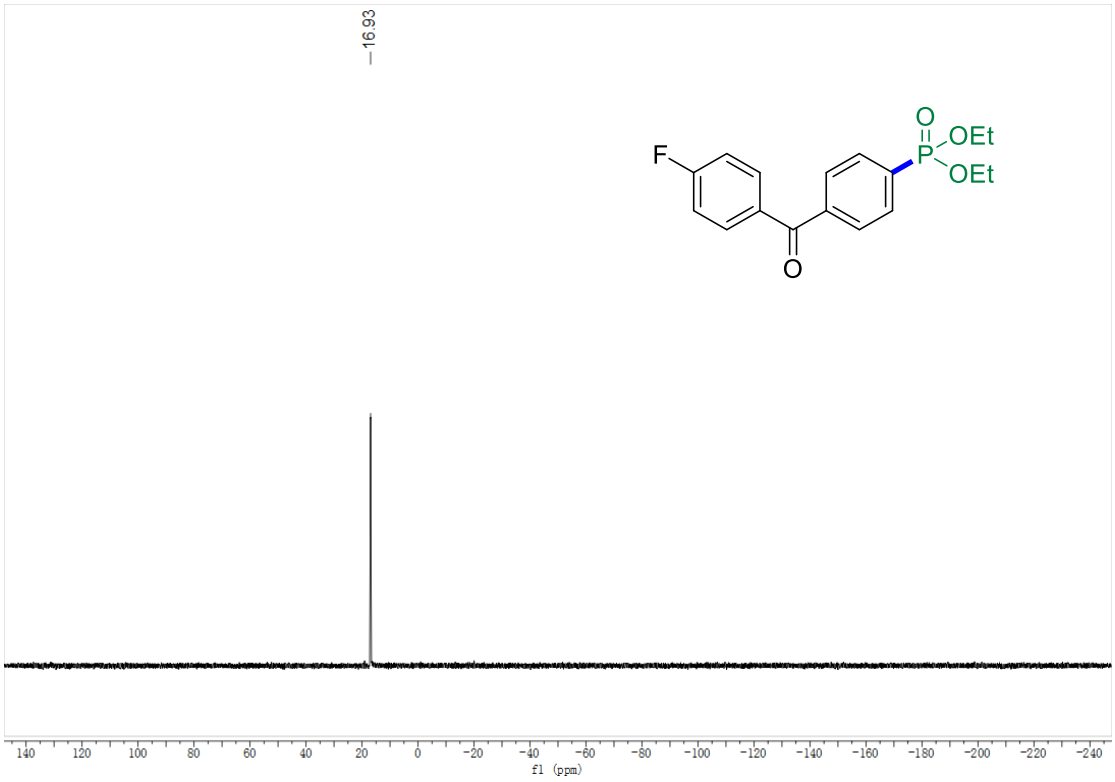
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4qa**



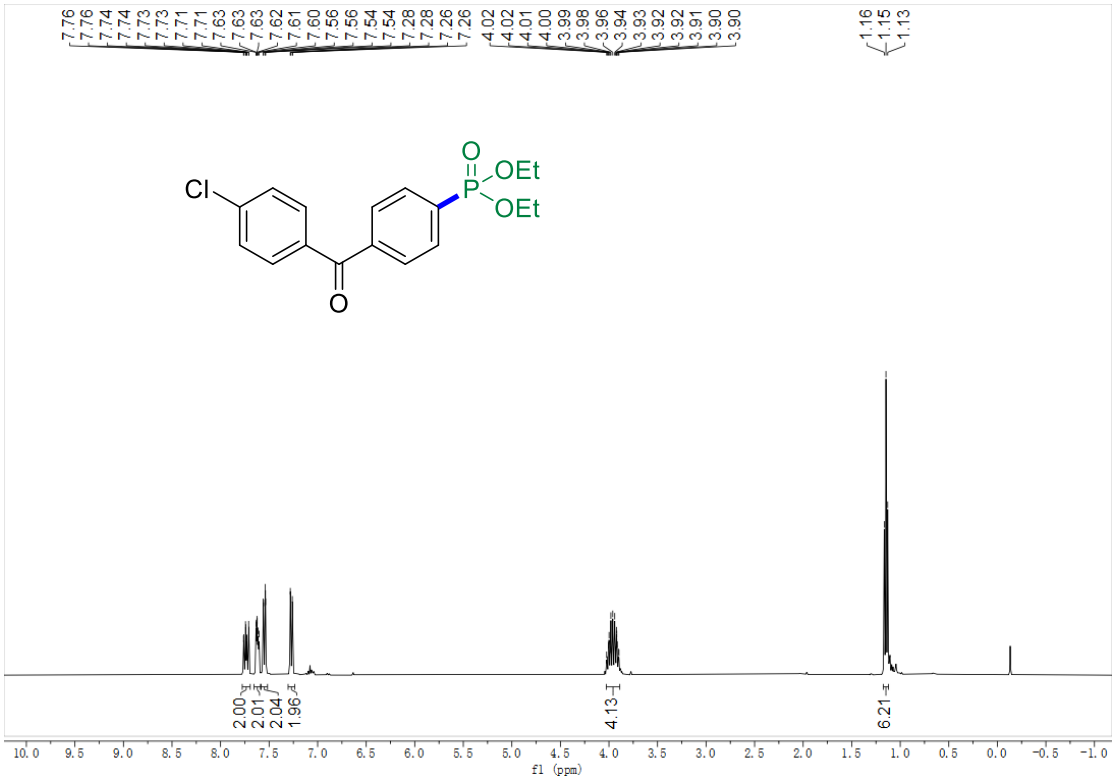
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4qa**



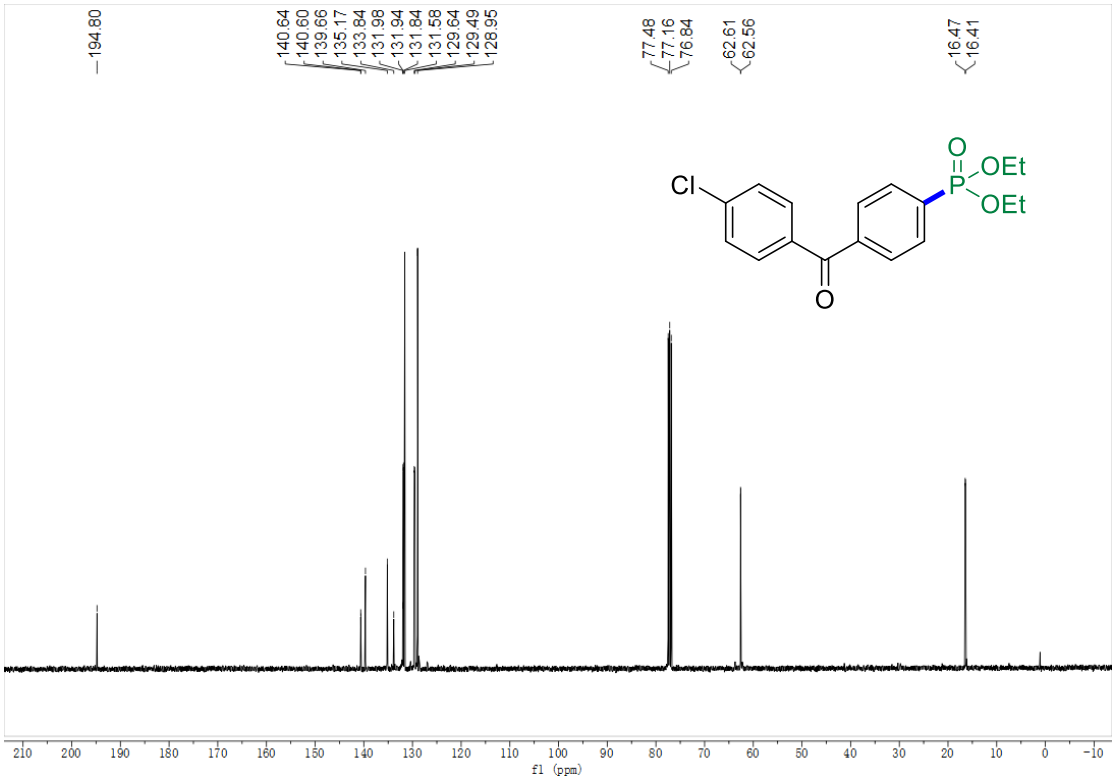
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4qa**



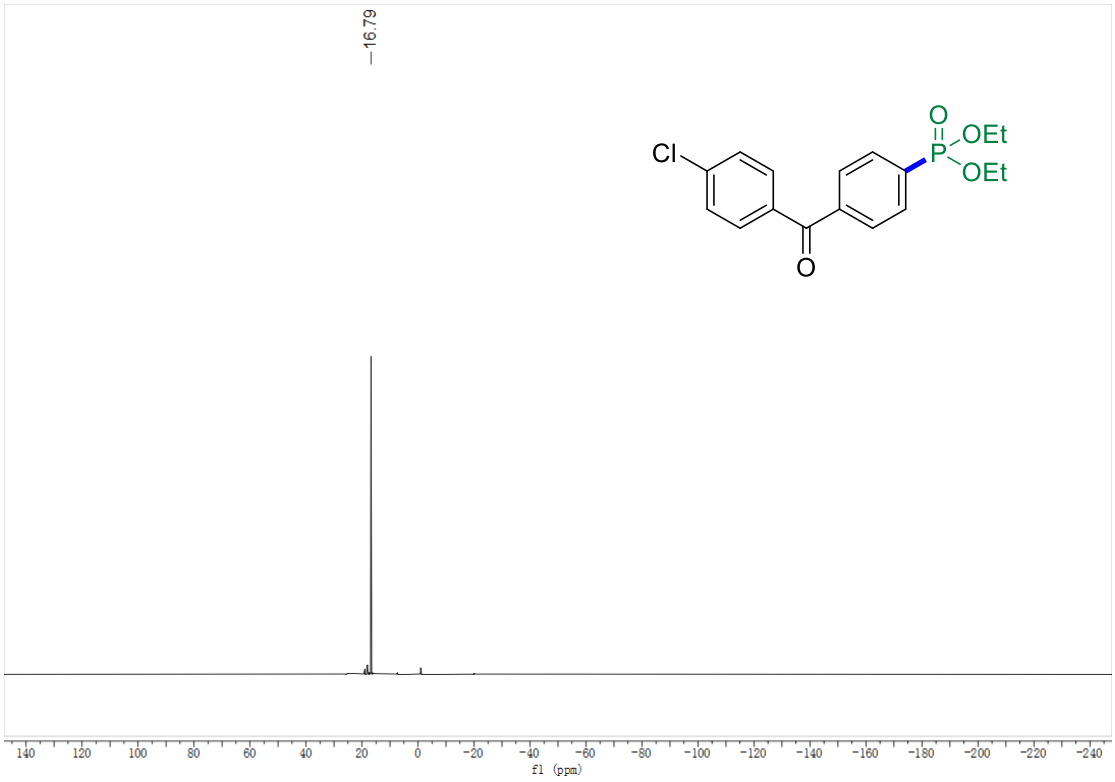
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ra**



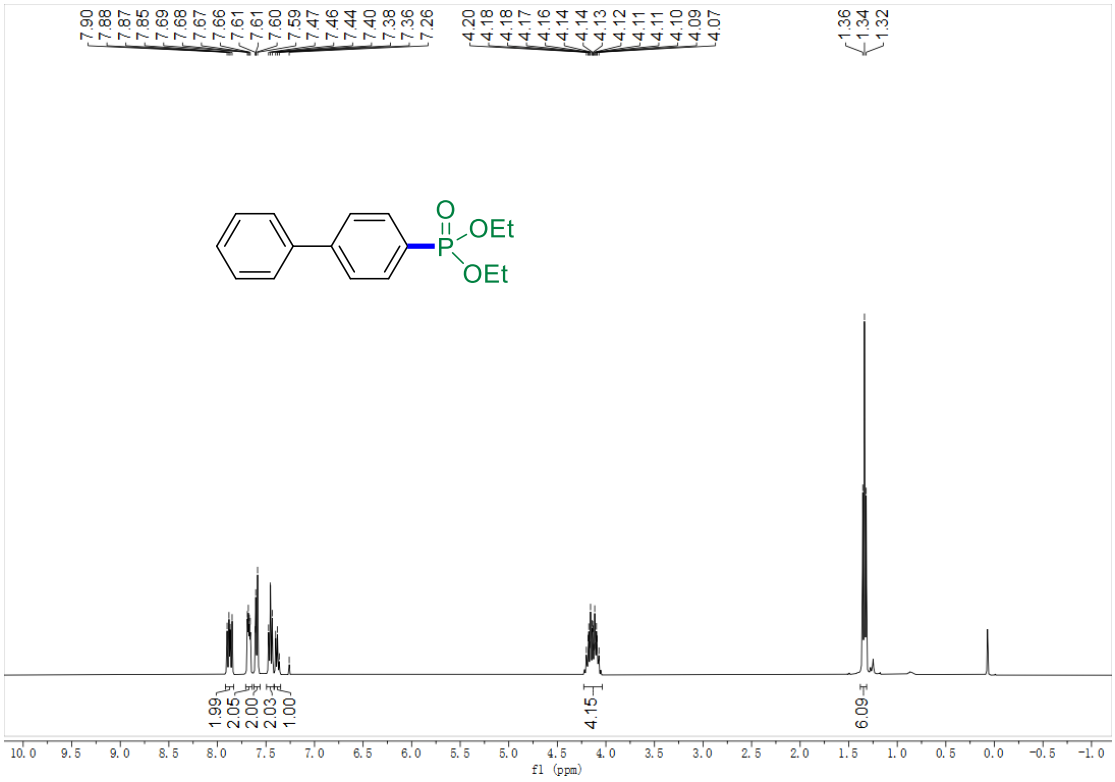
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ra**



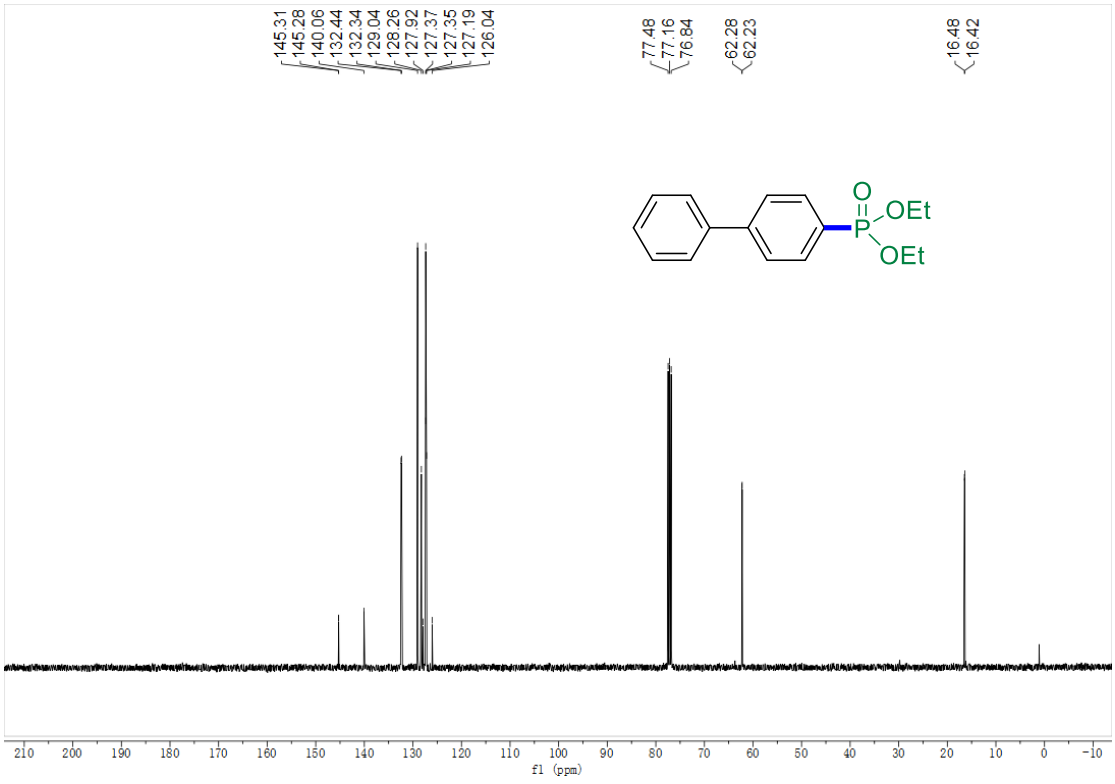
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ra**



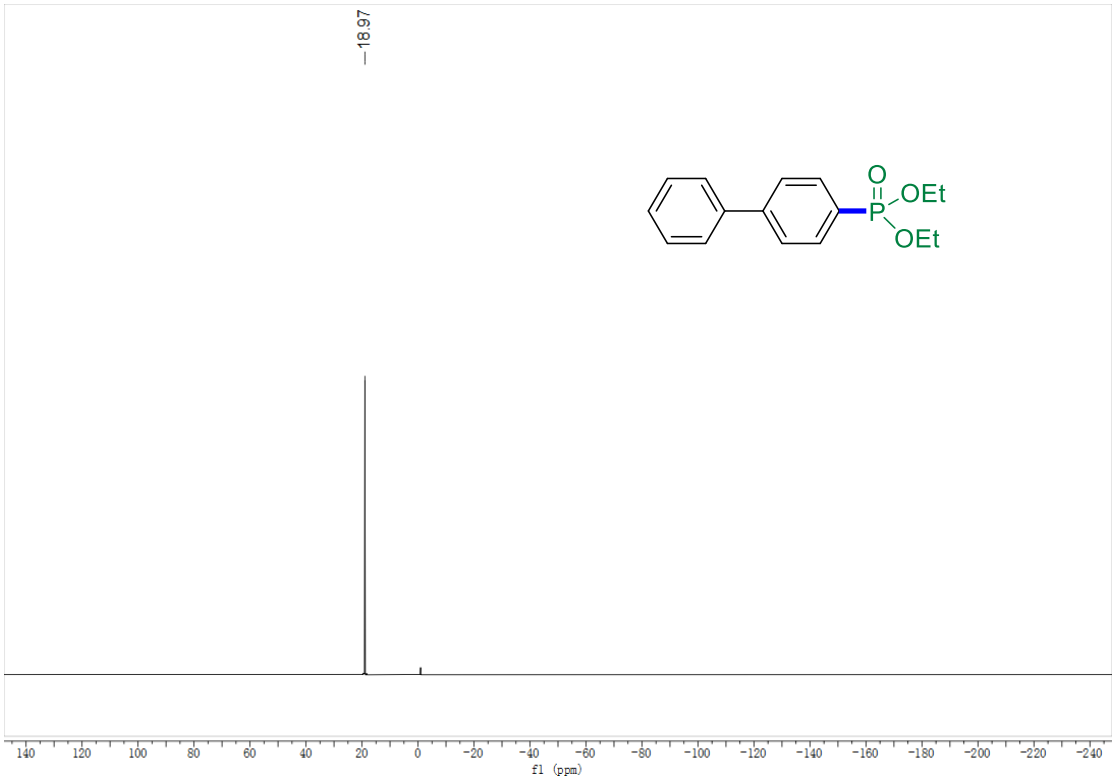
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4sa**



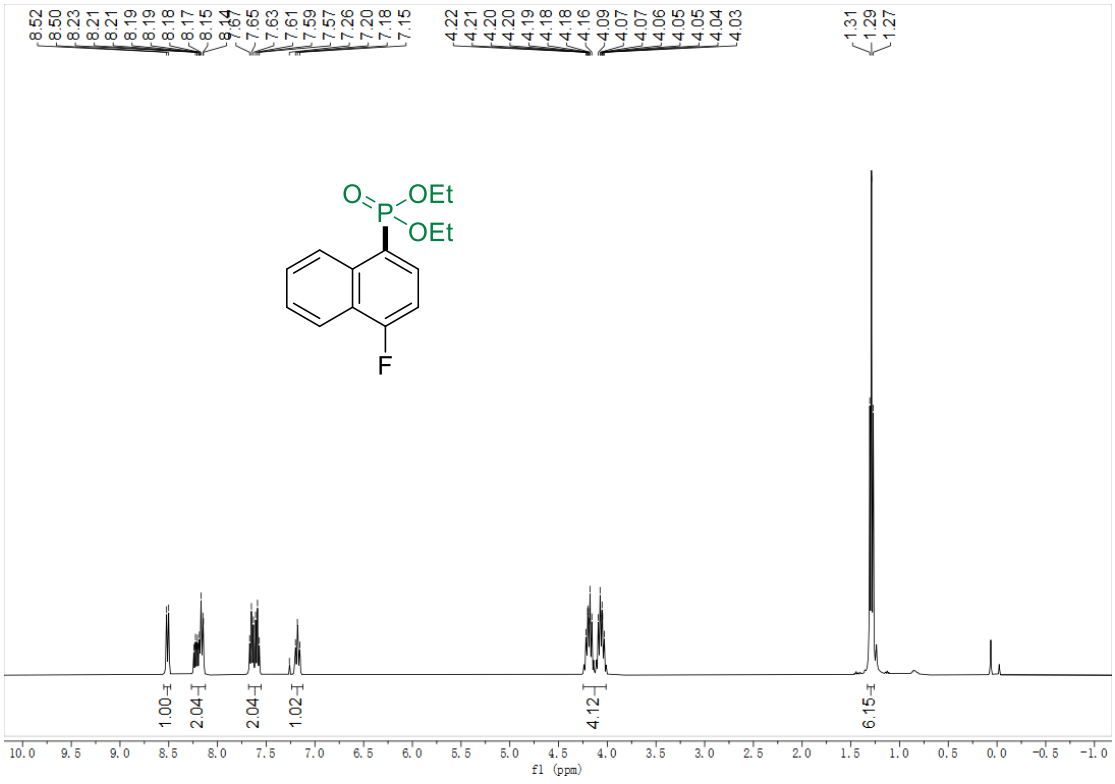
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4sa**



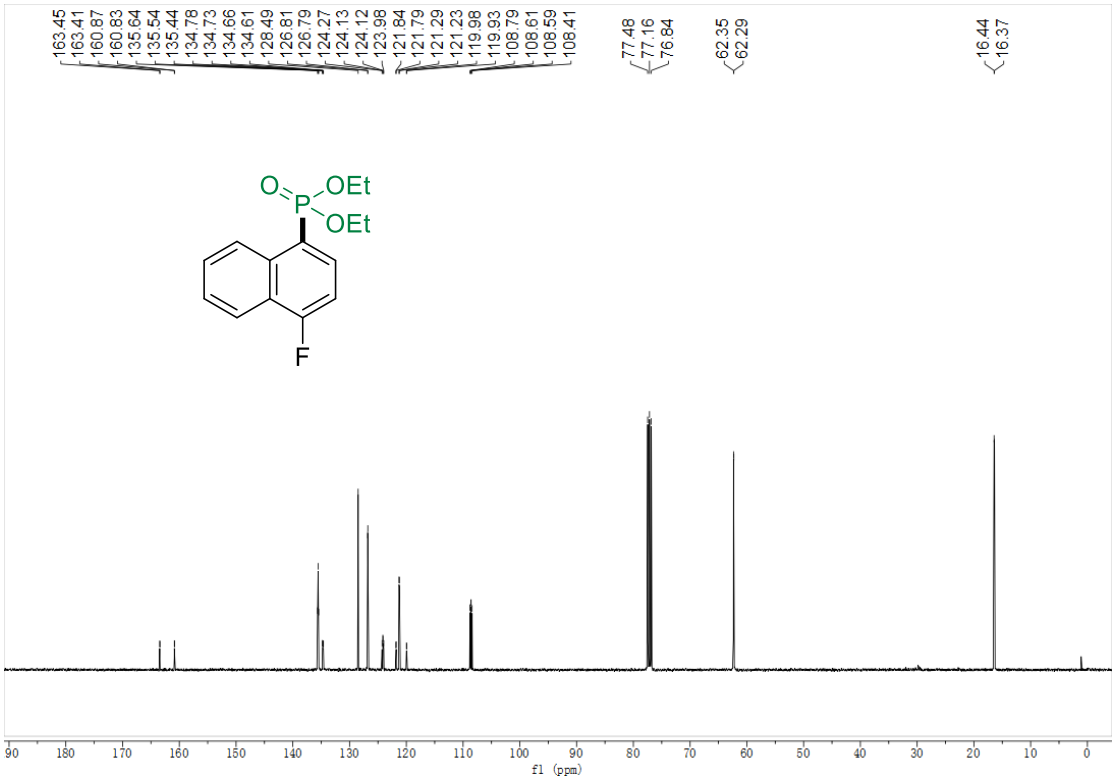
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4sa**



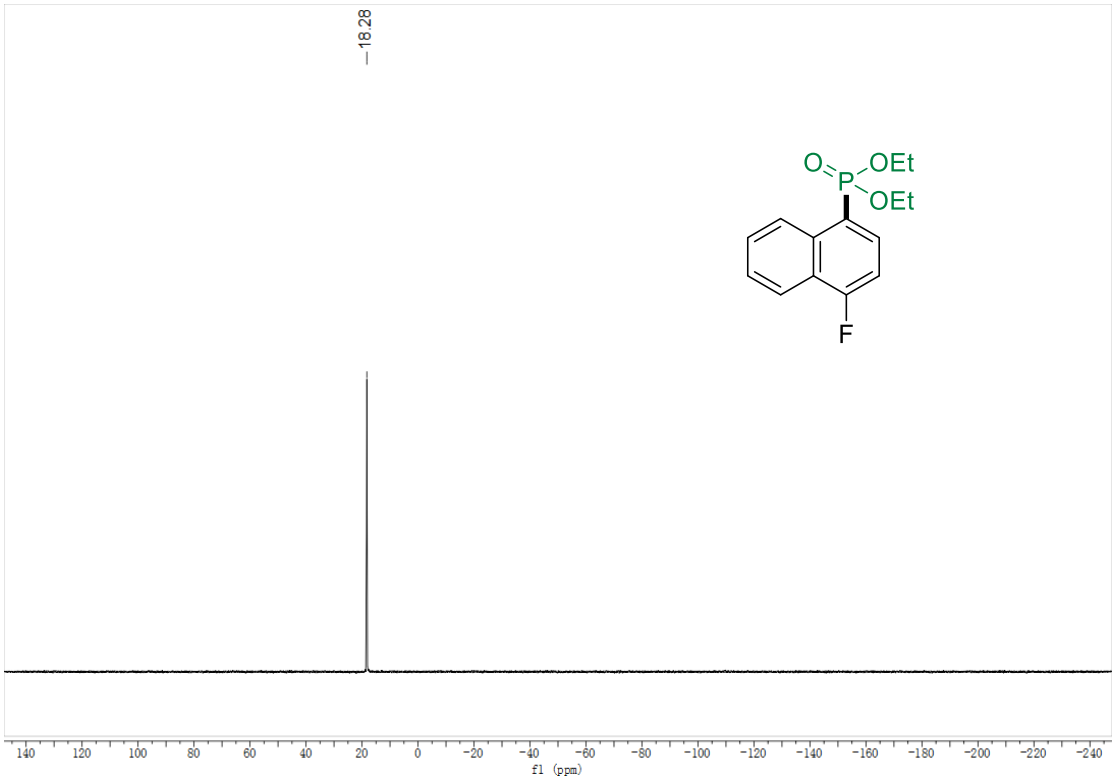
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ta**



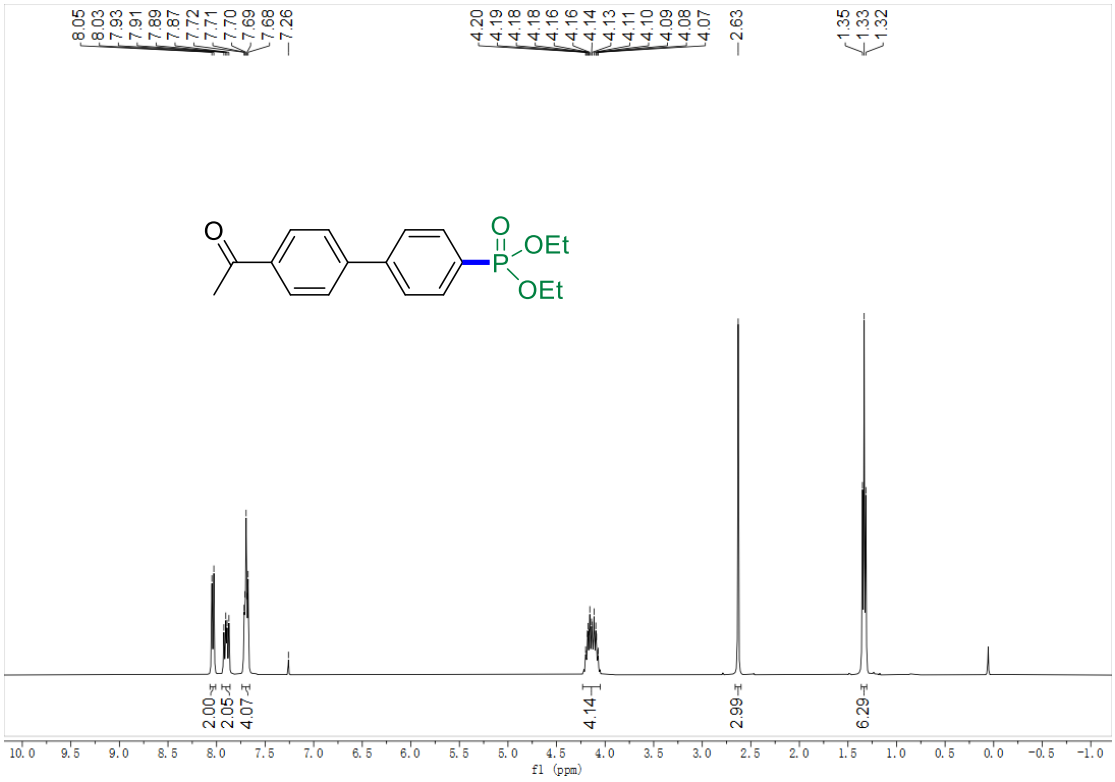
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ta**



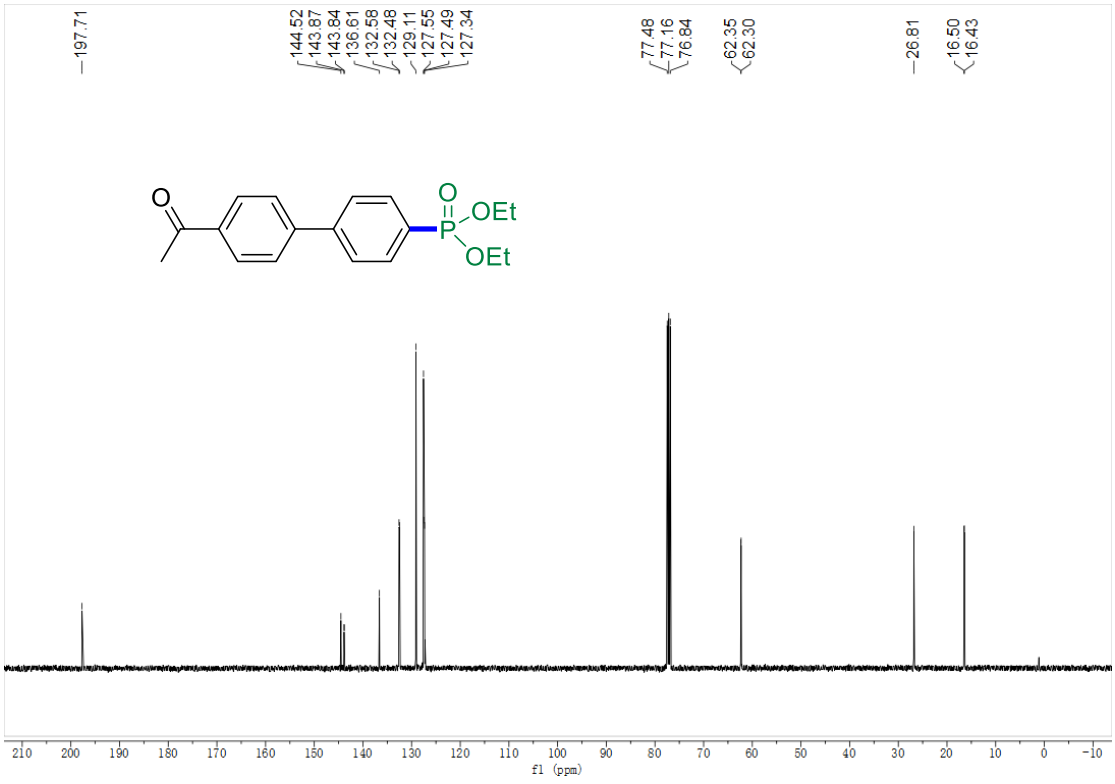
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ta**



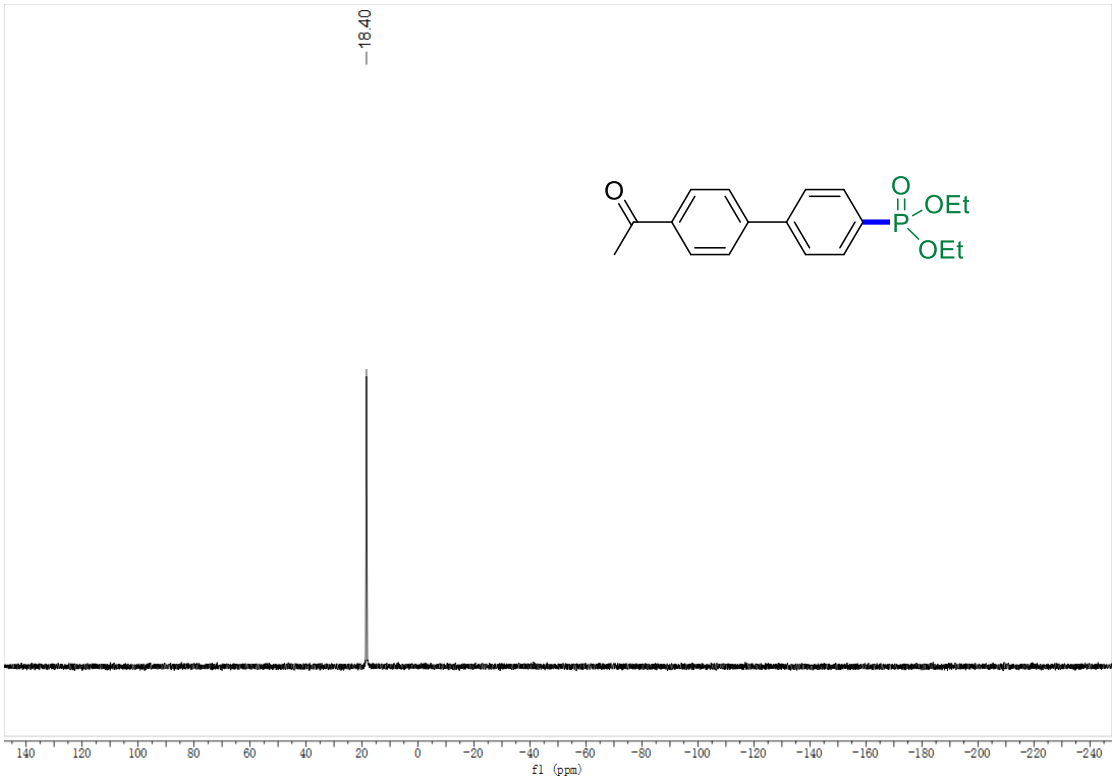
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ua**



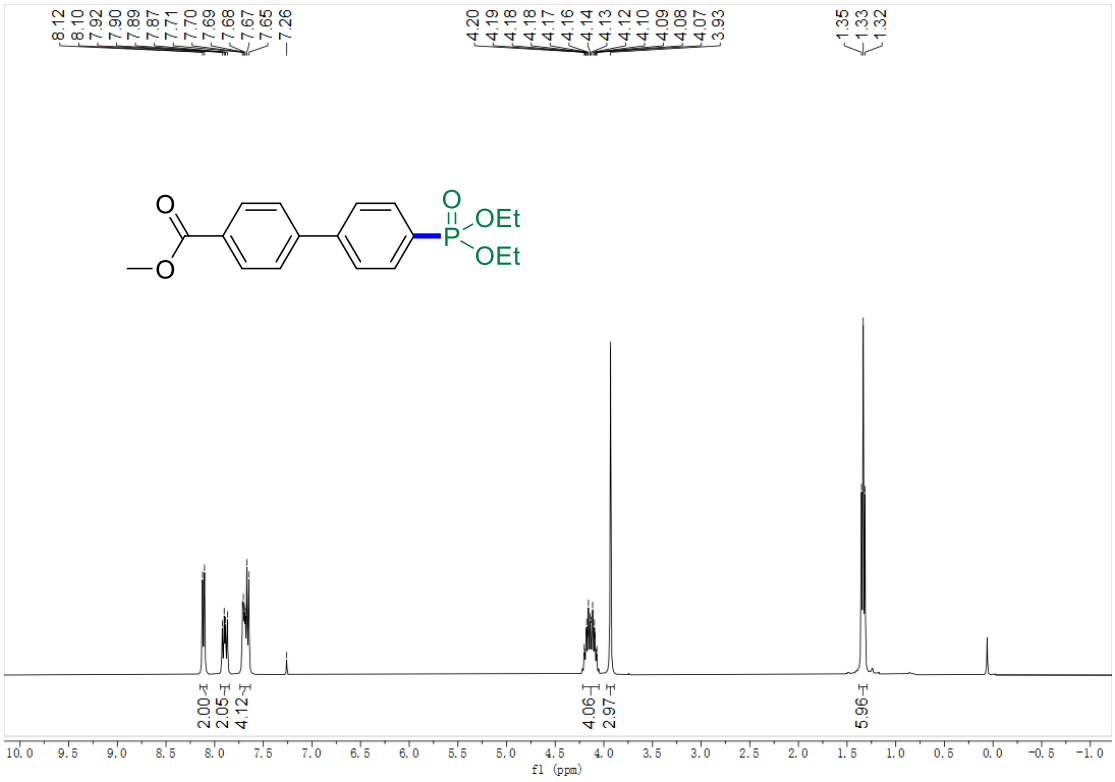
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ua**



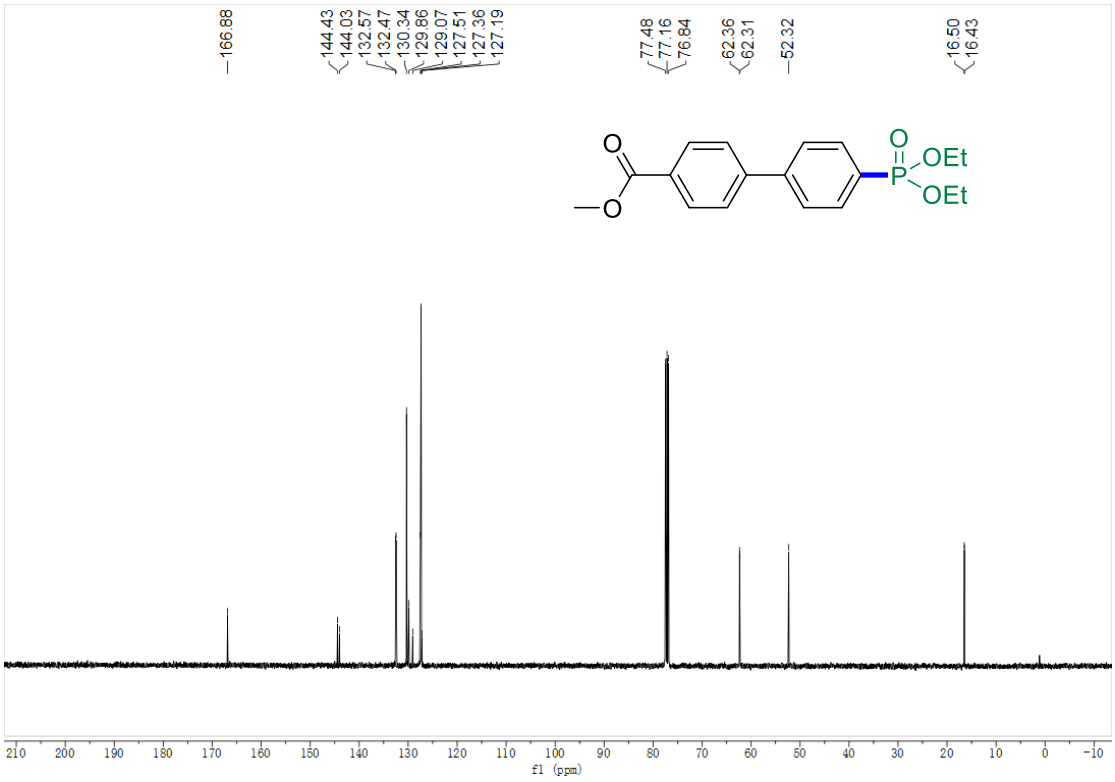
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ua**



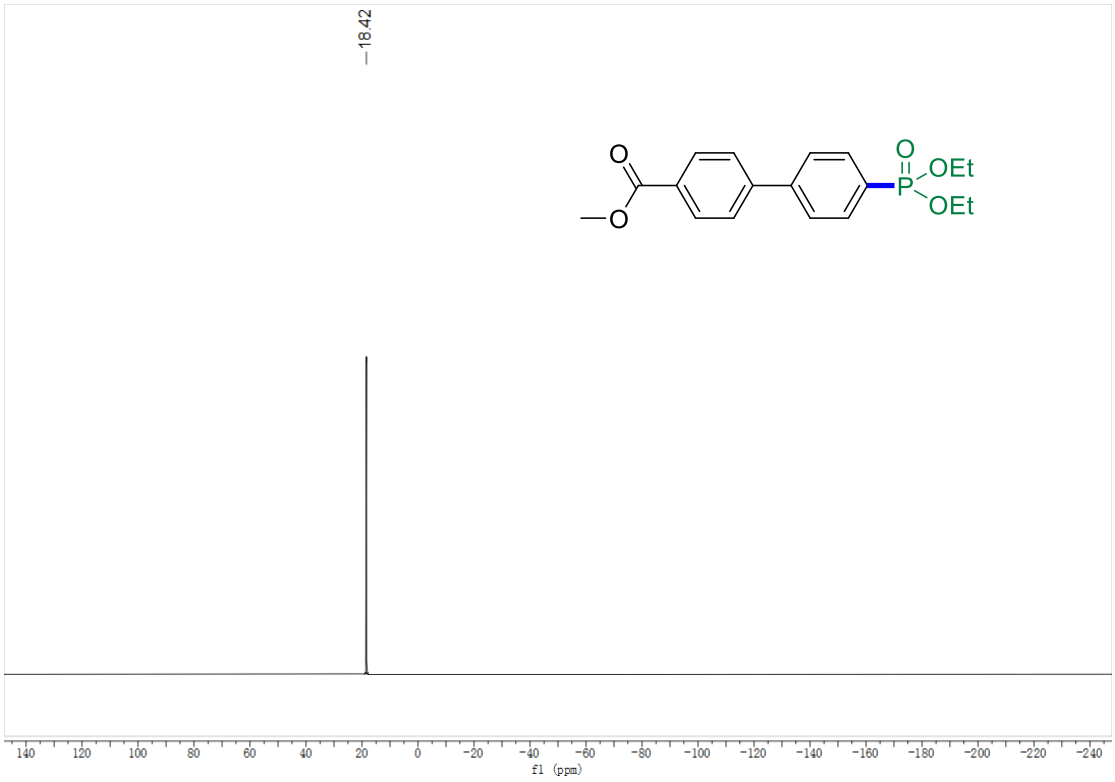
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4va**



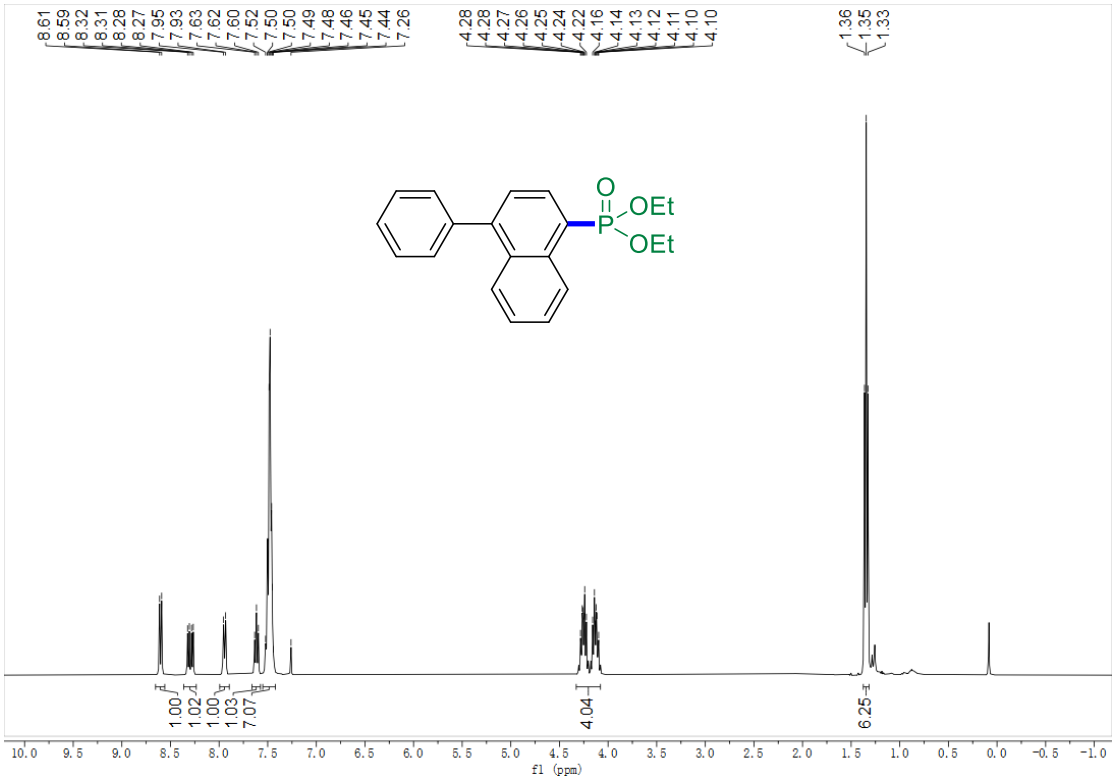
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4va**



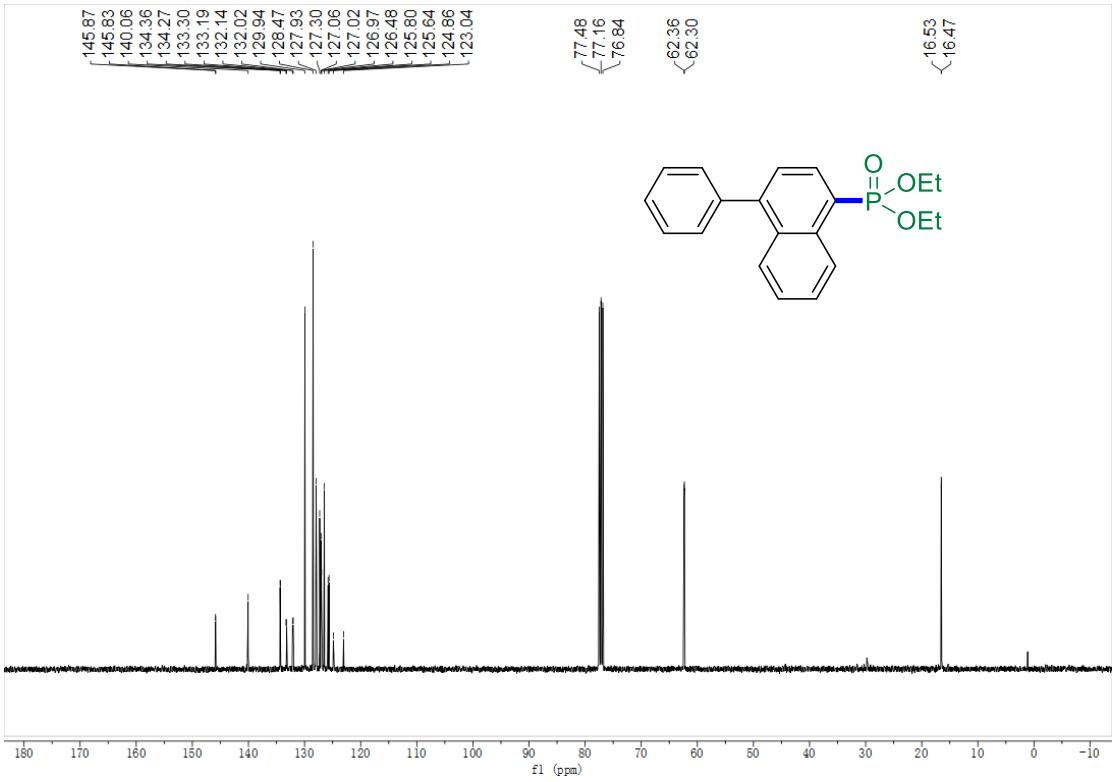
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4va**



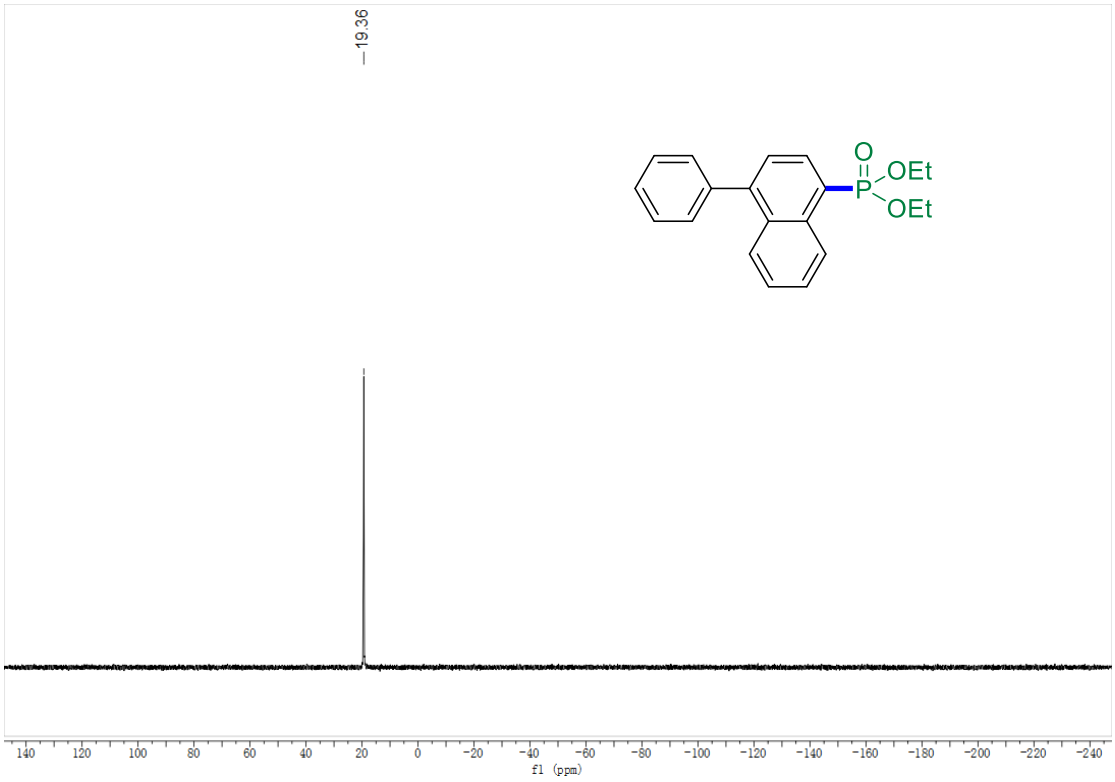
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4wa**



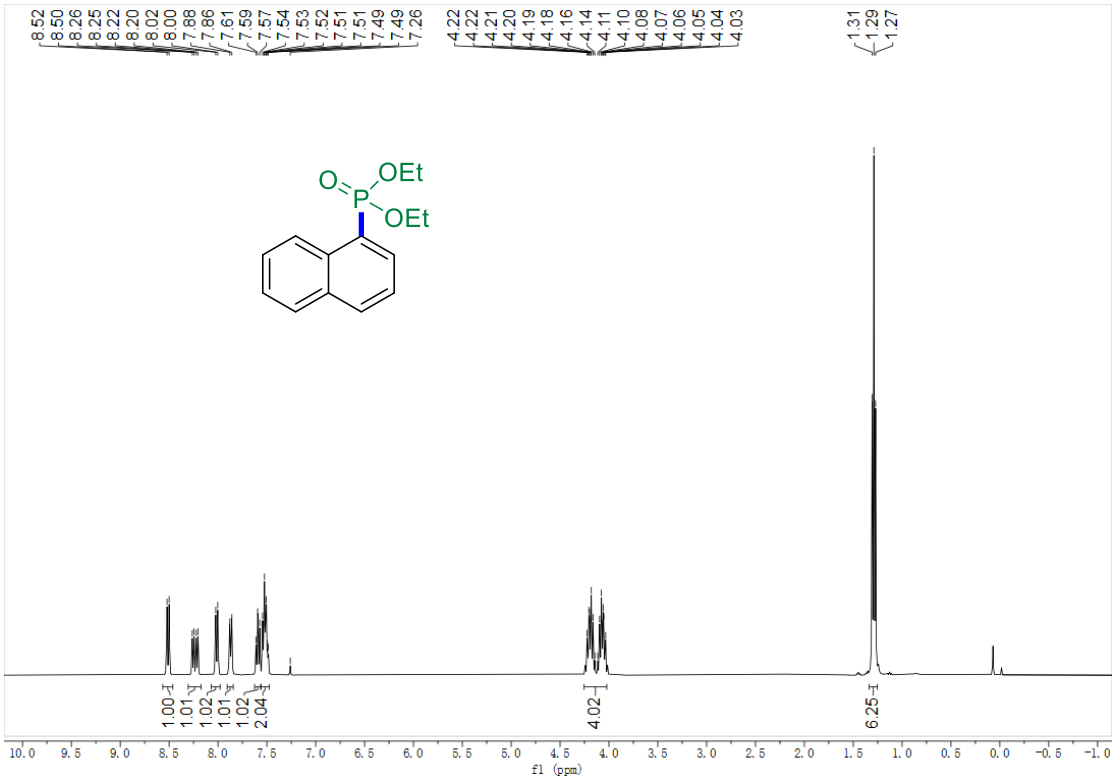
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4wa**



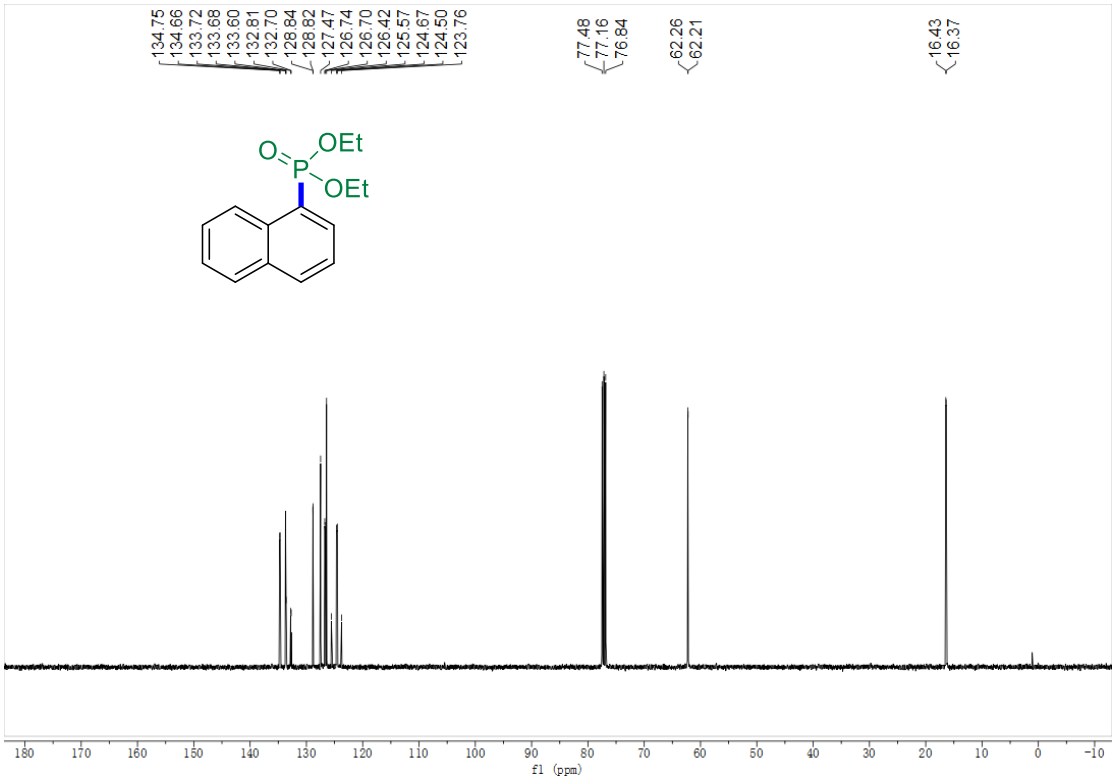
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4wa**



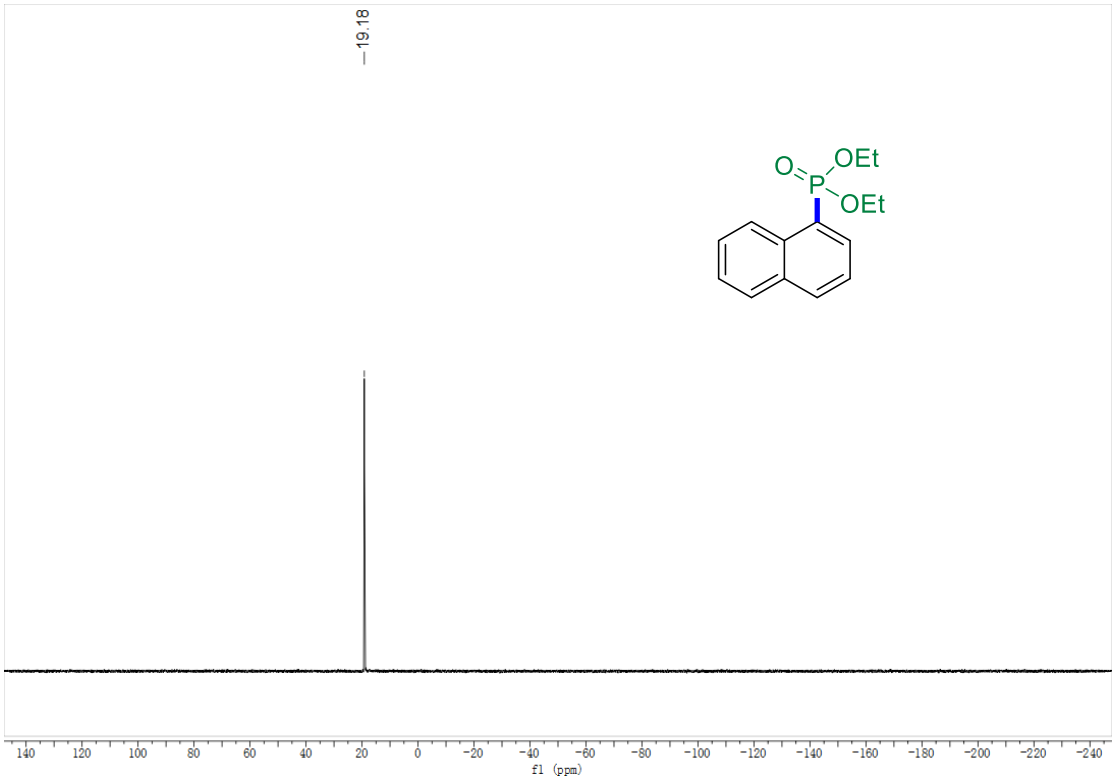
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4xa**



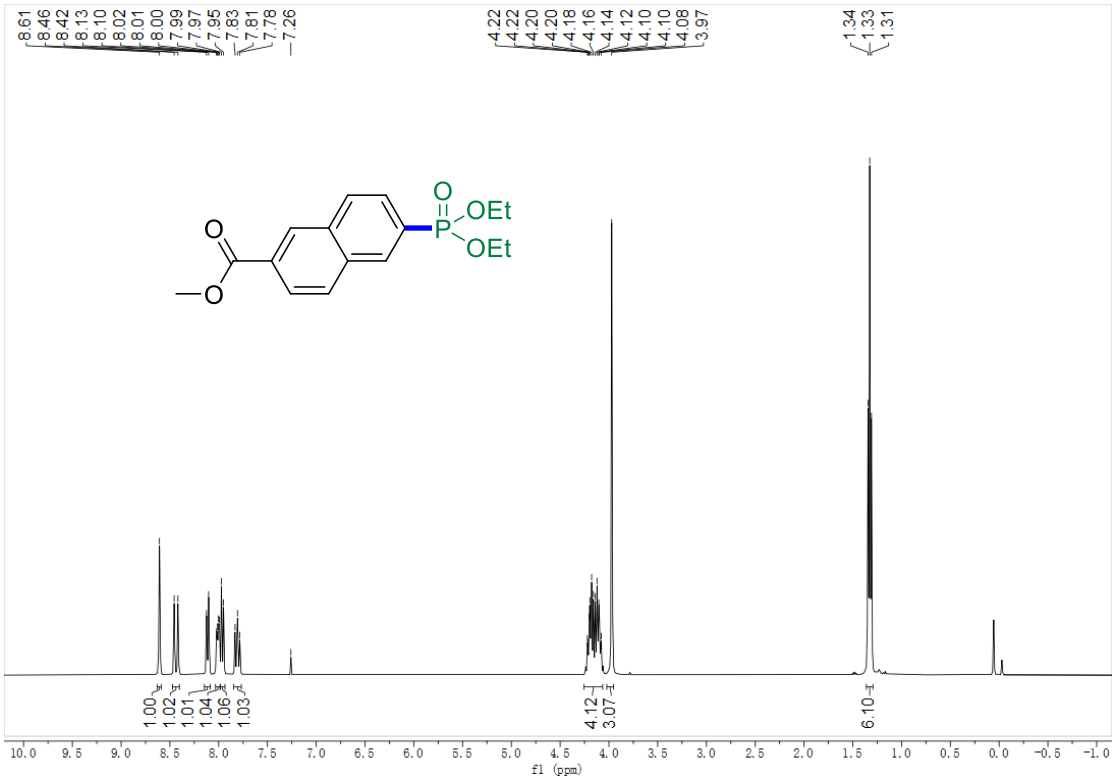
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4xa**



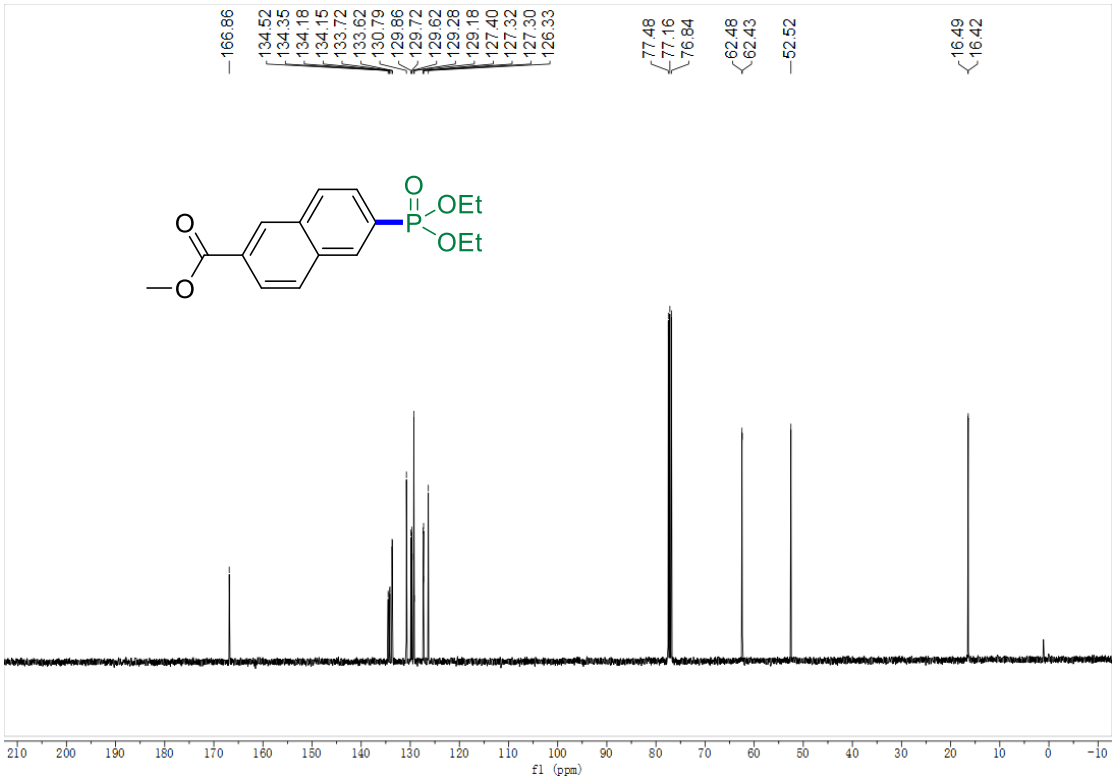
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4xa**



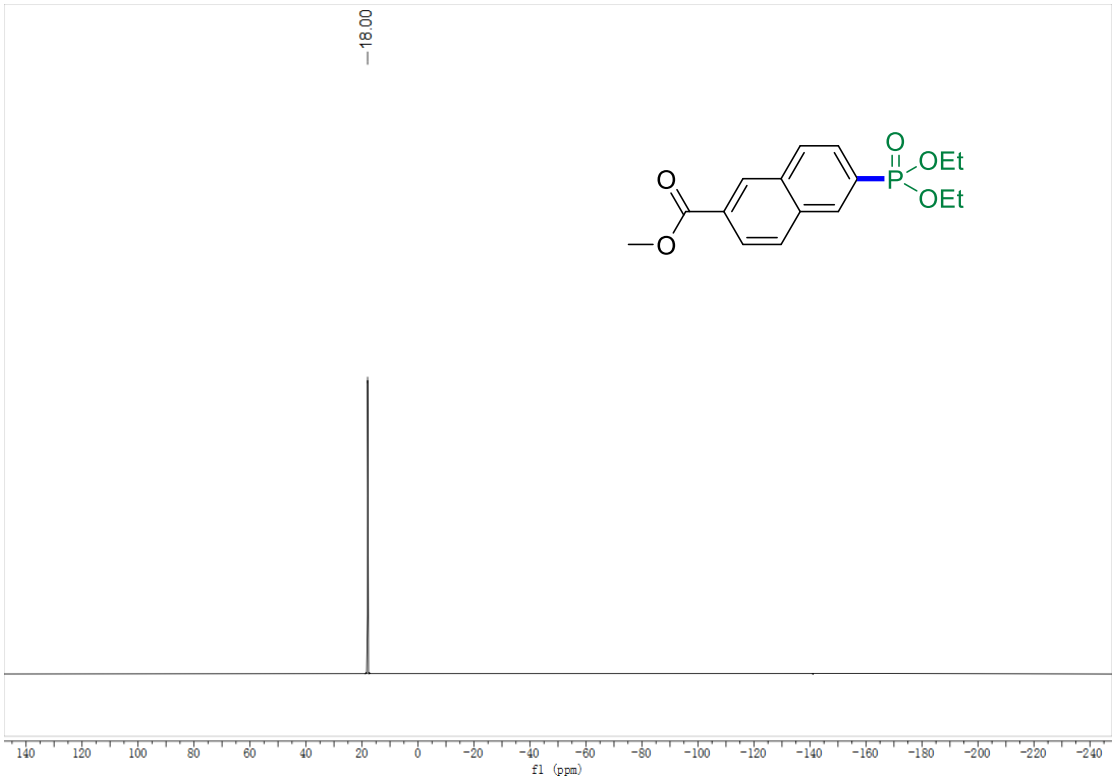
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ya**



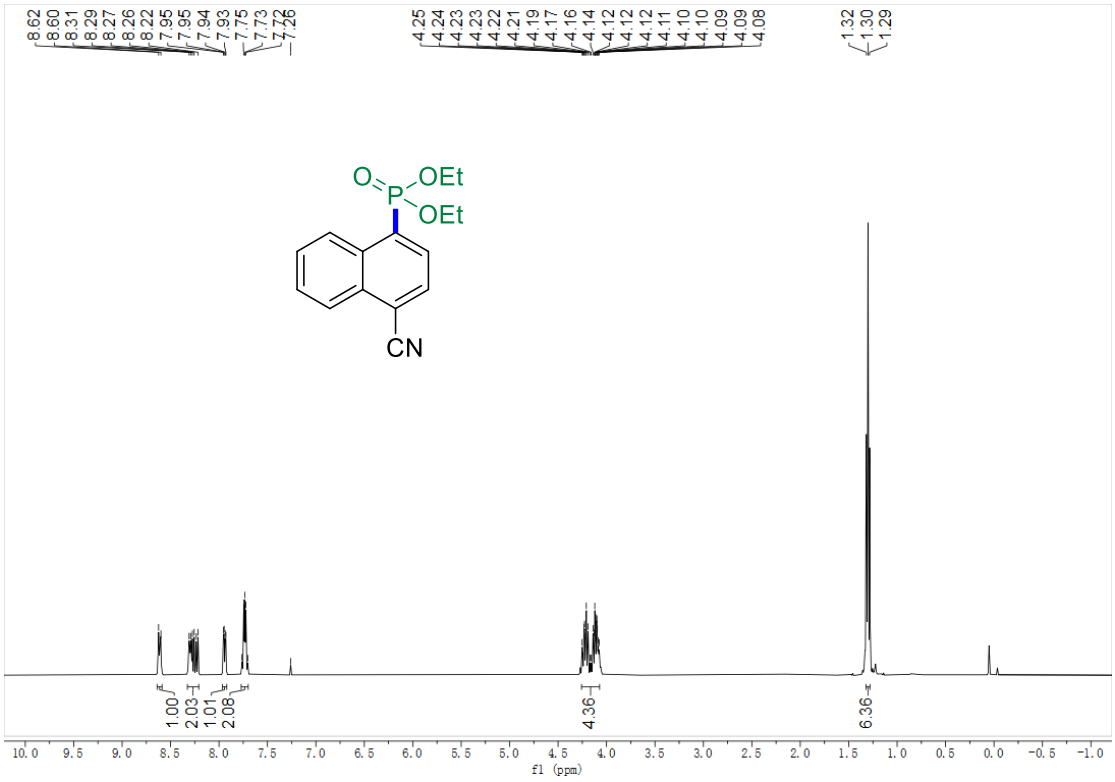
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ya**



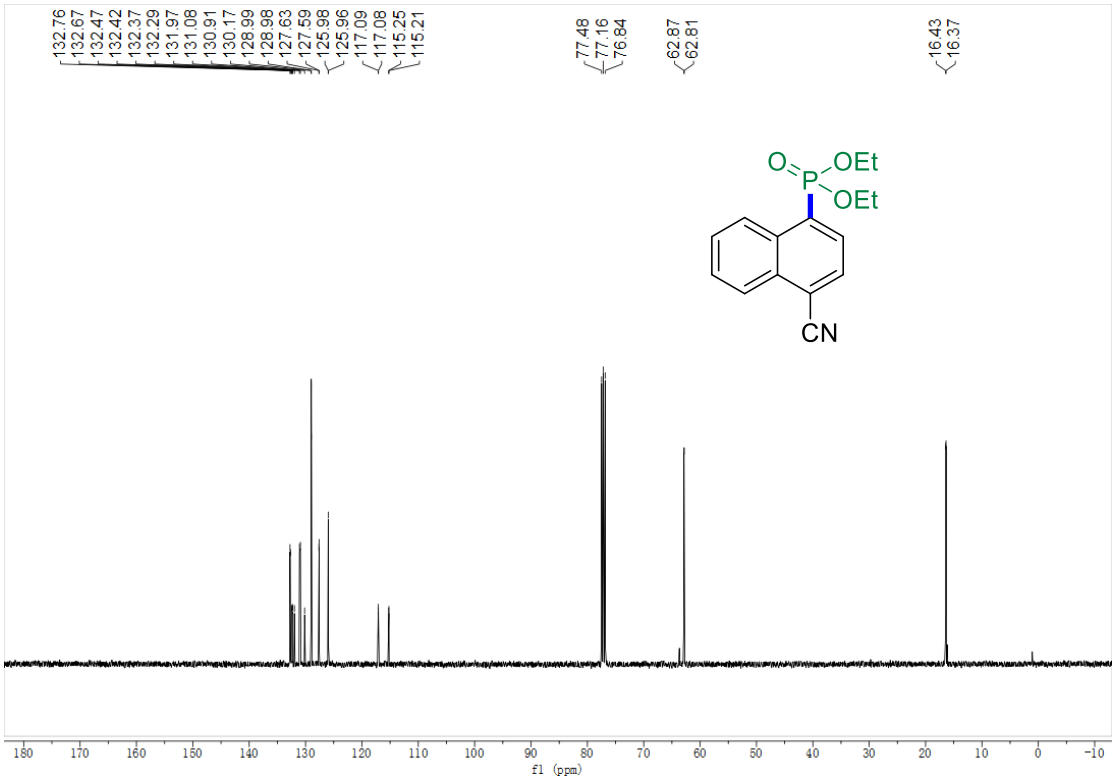
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ya**



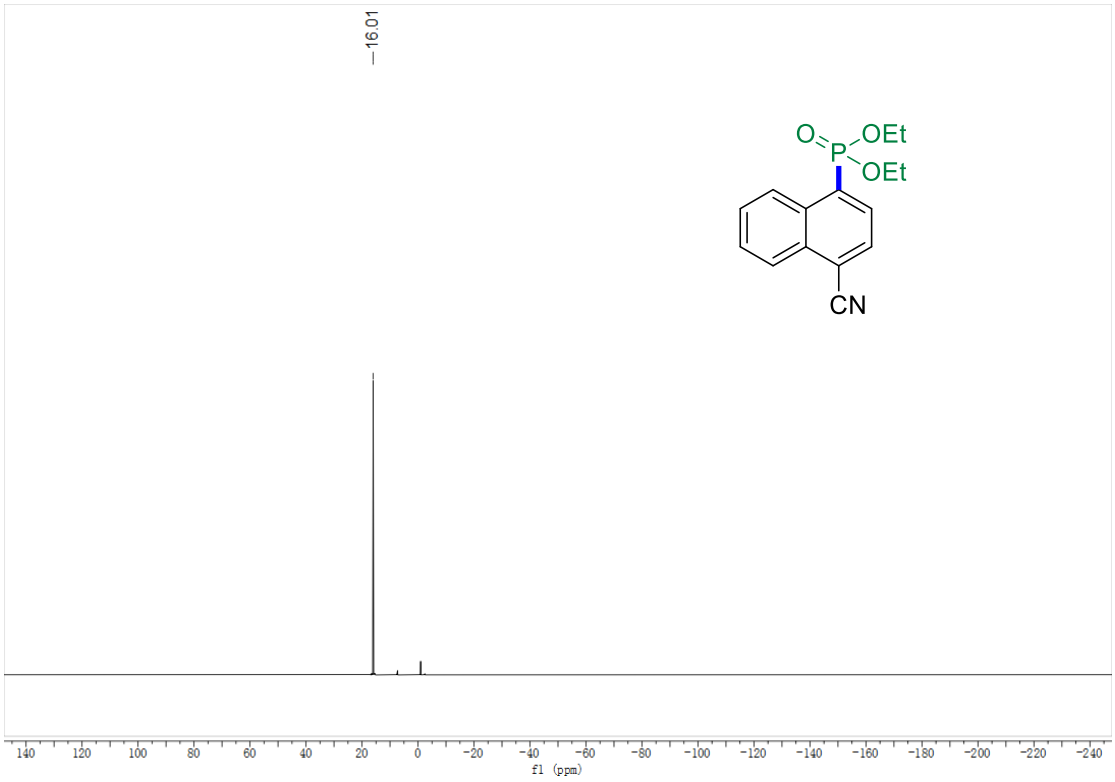
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4za**



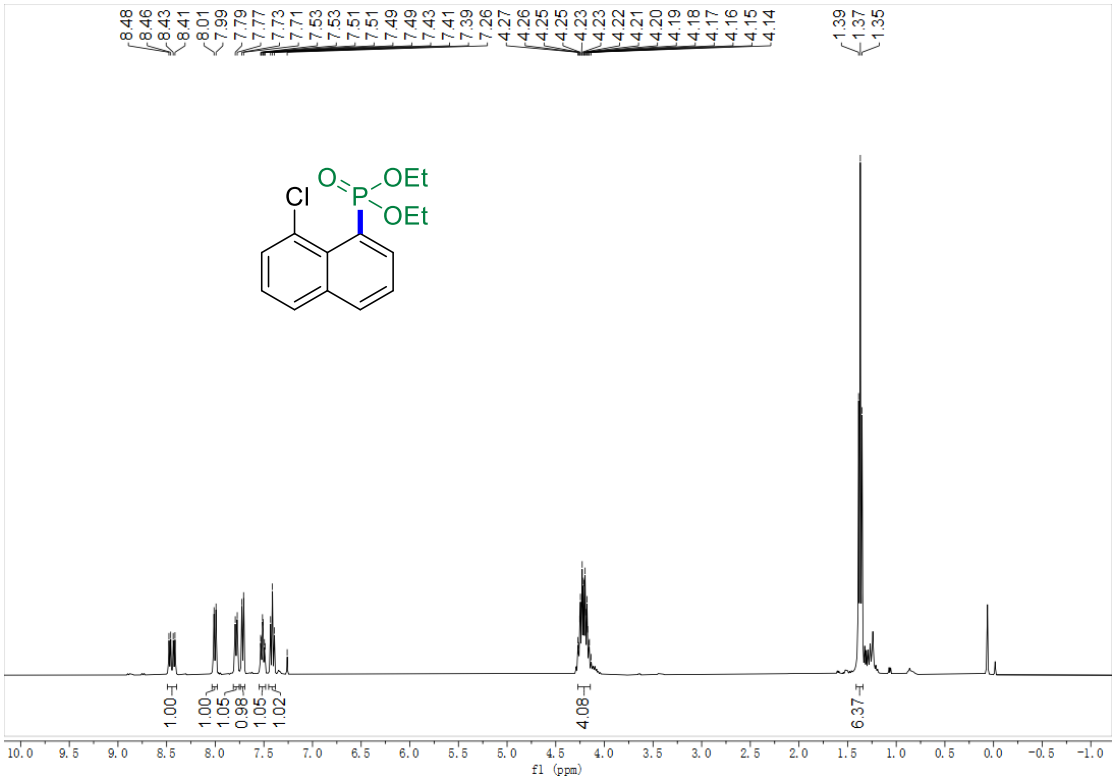
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4za**



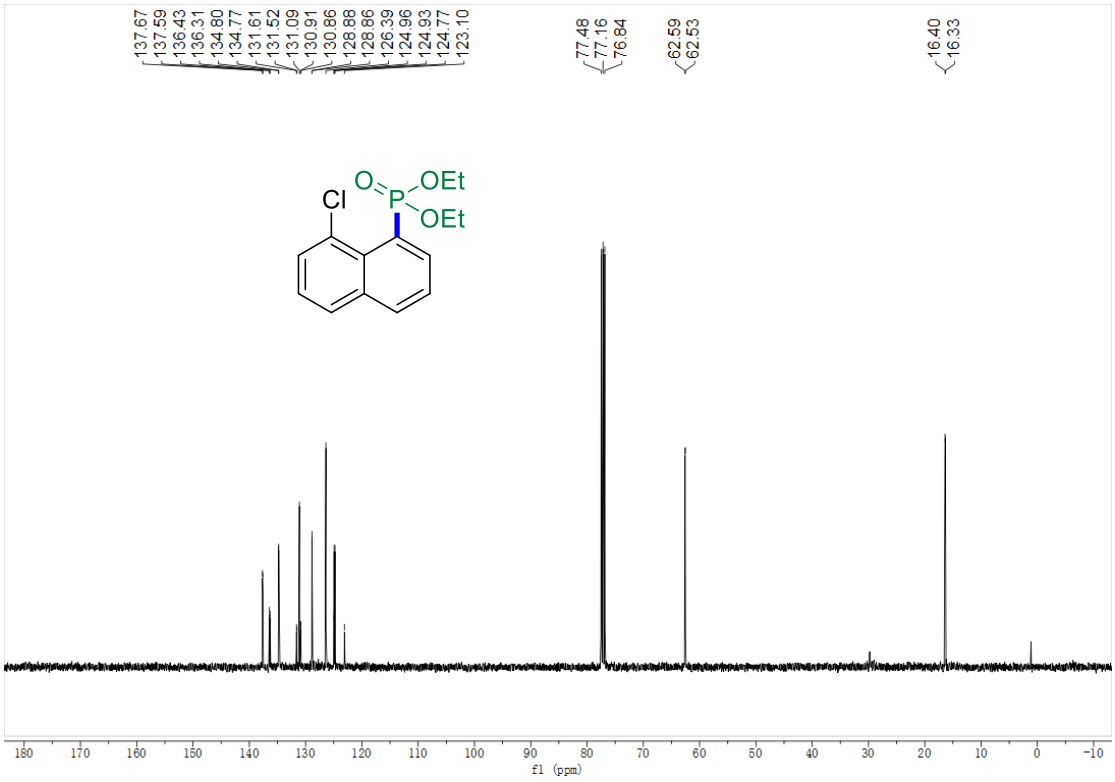
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4za**



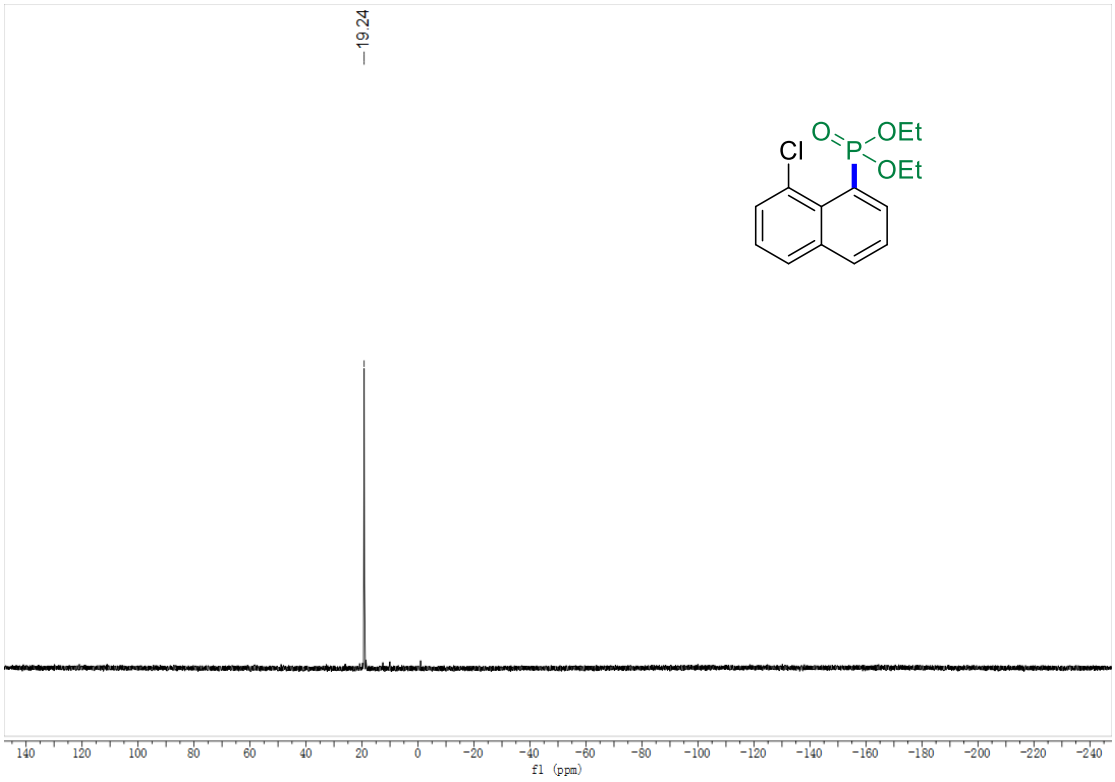
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ab**



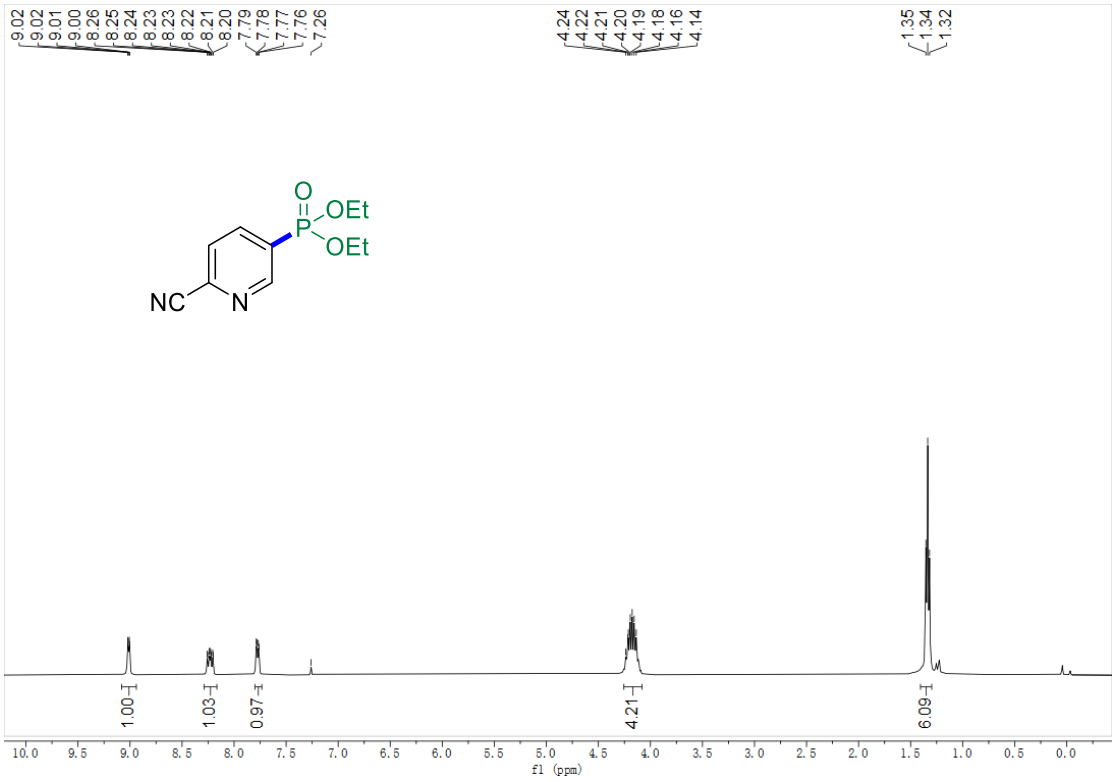
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ab**



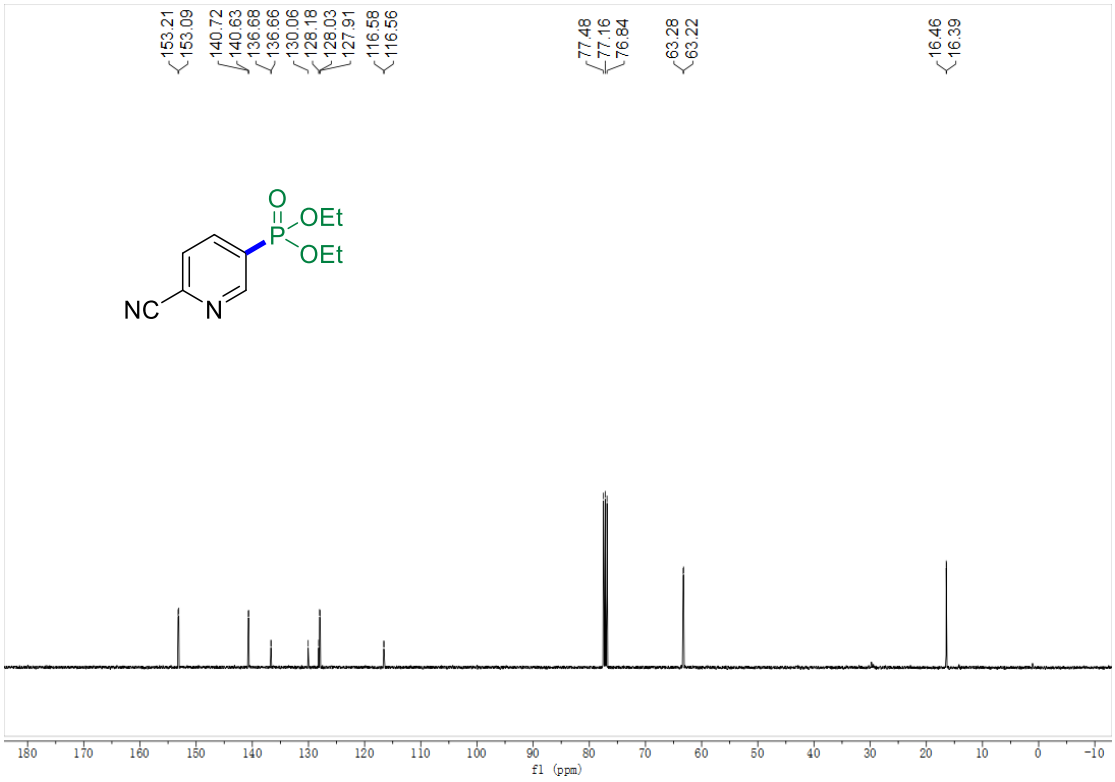
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ab**



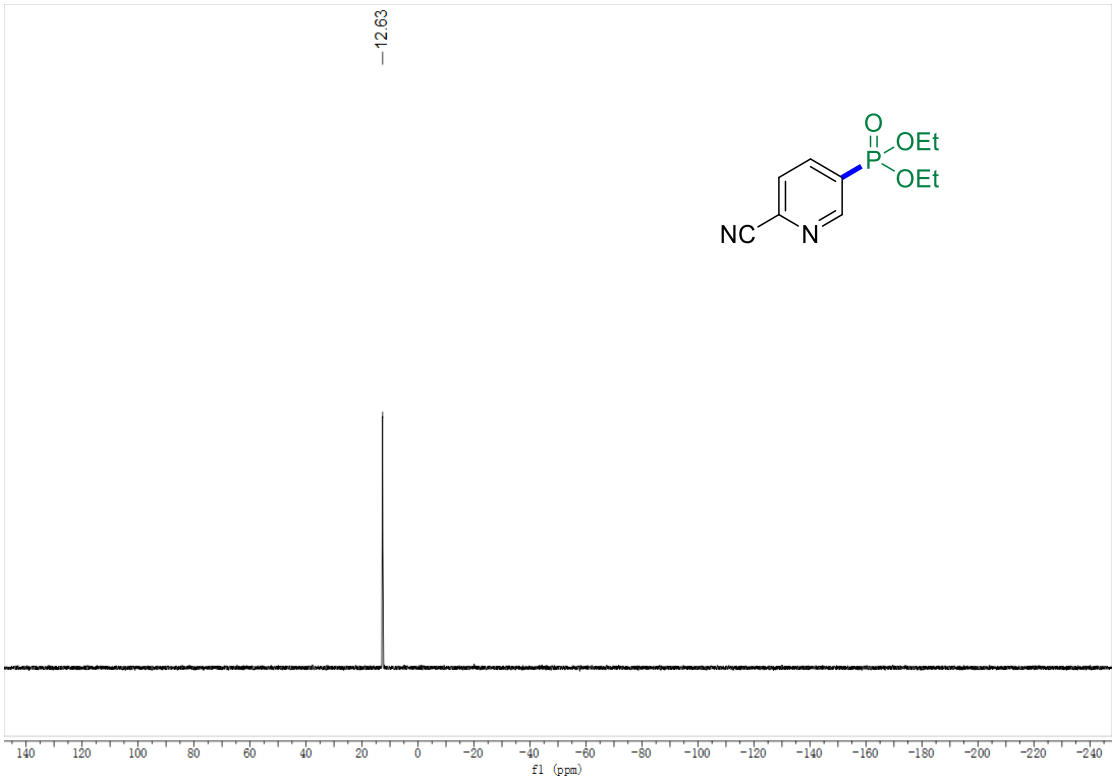
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ac**



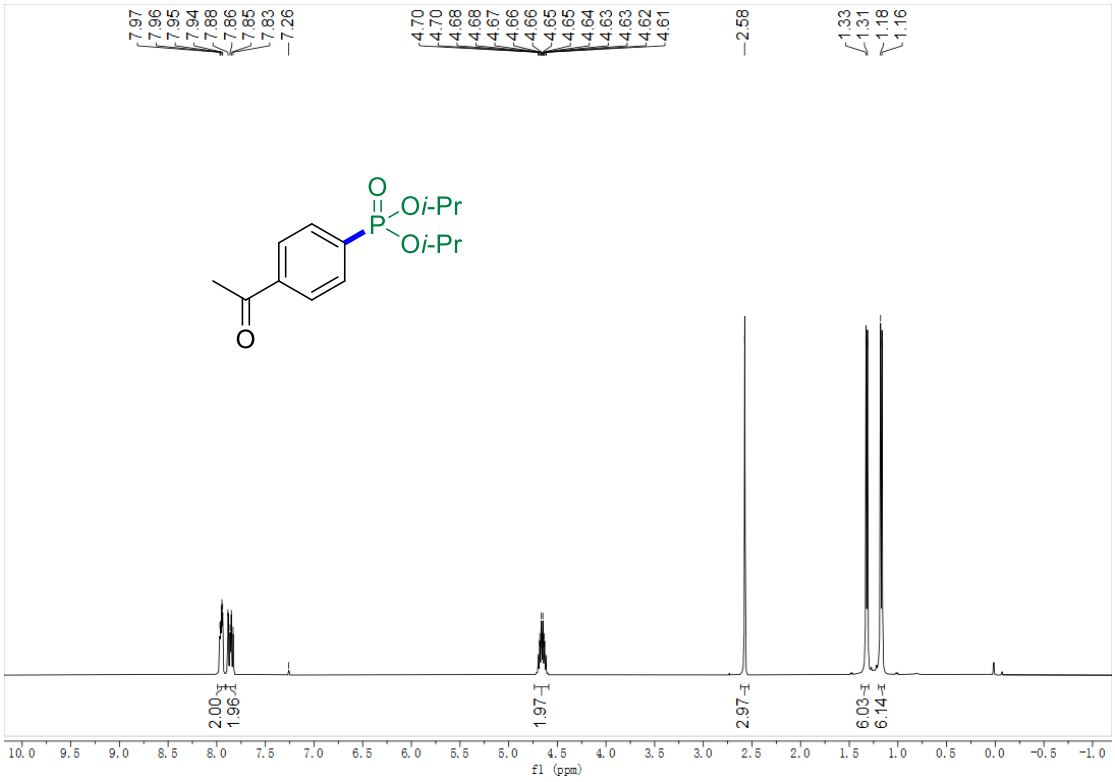
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ac**



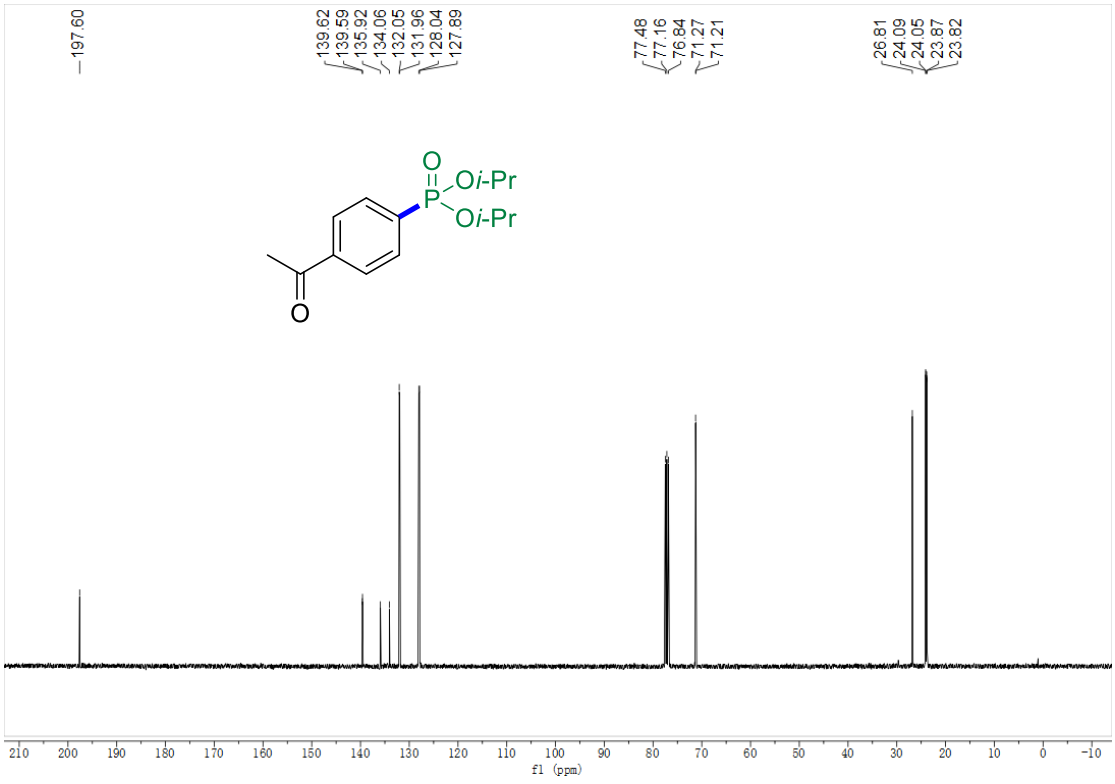
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ac**



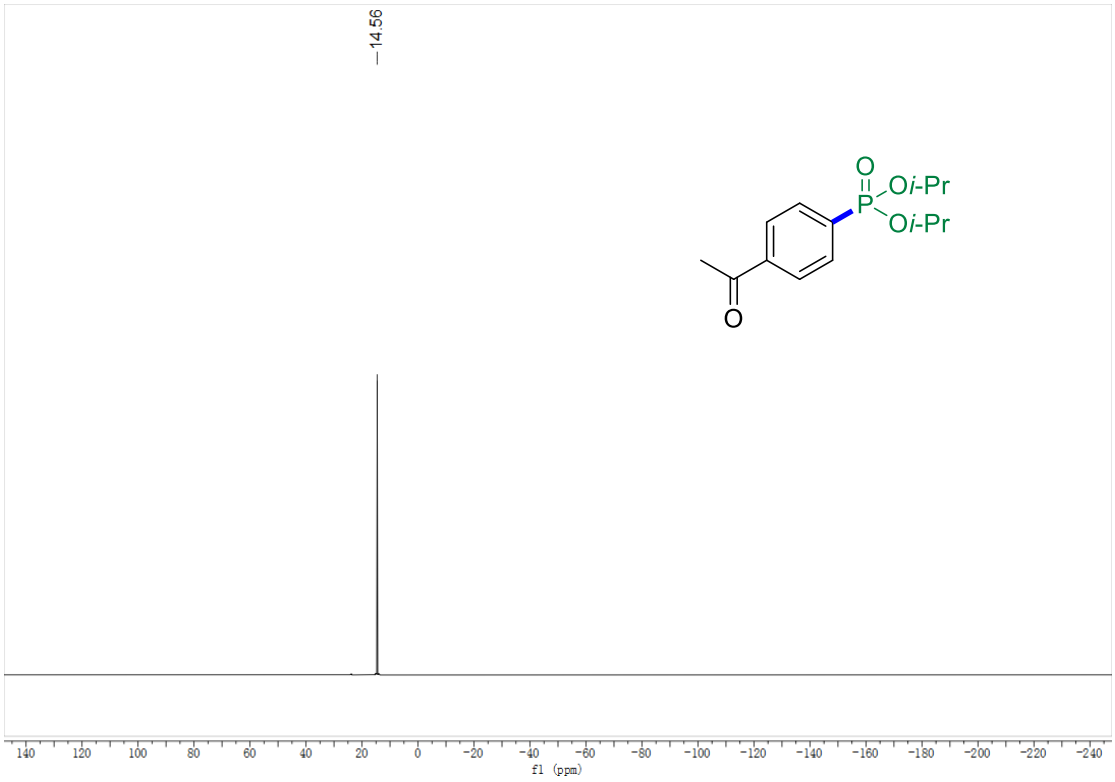
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4af**



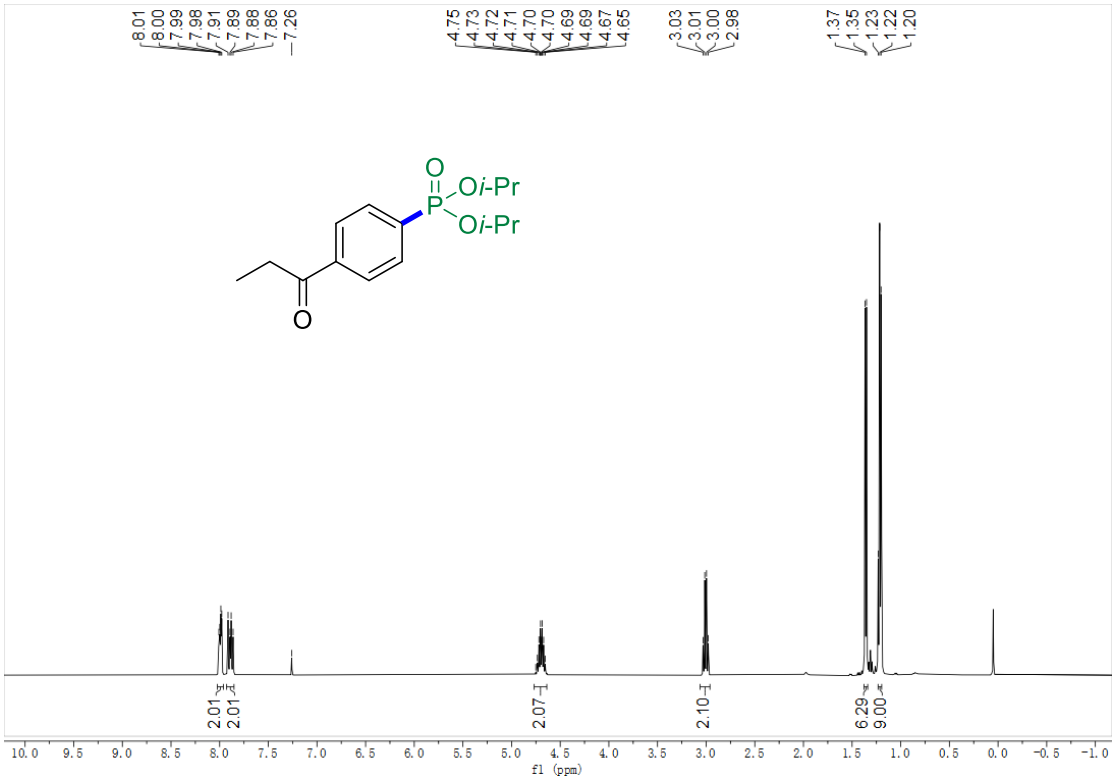
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4af**



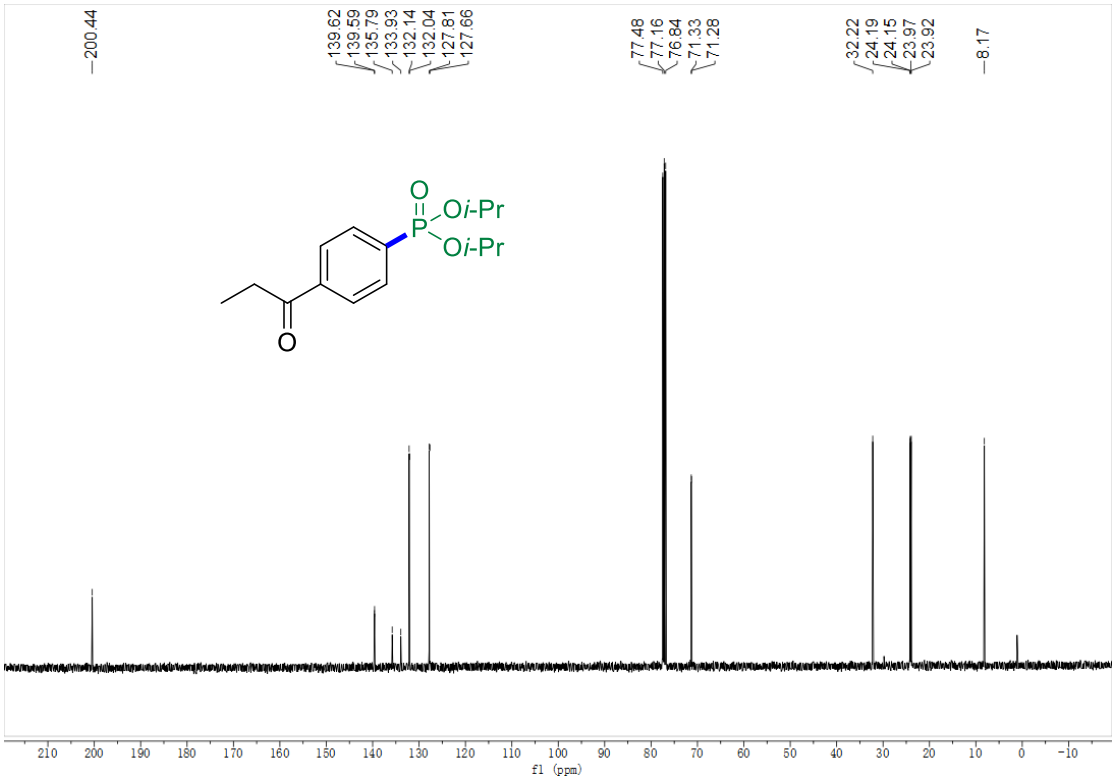
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4af**



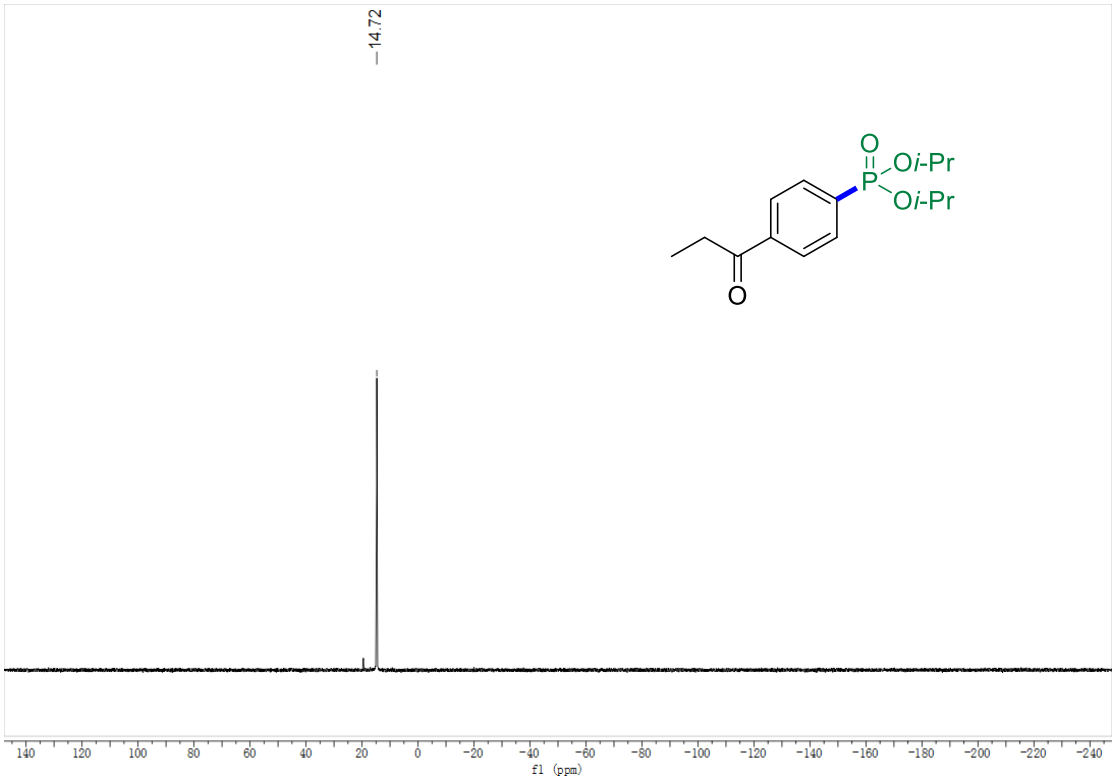
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ag**



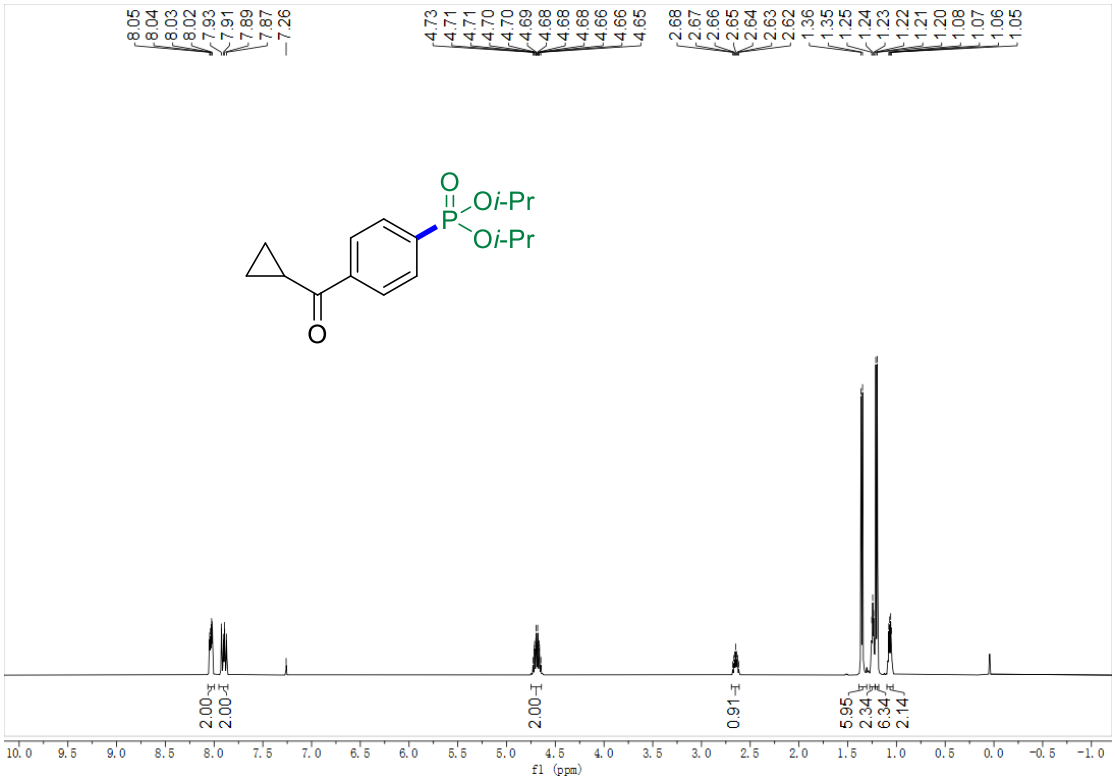
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ag**



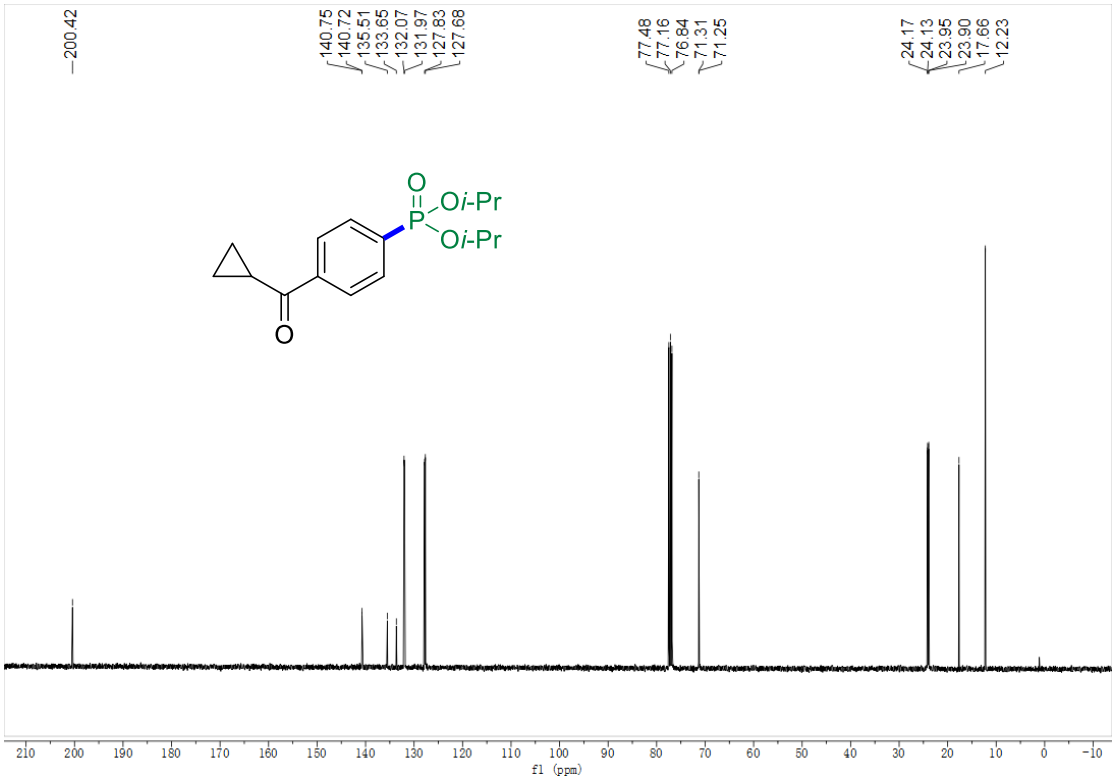
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ag**



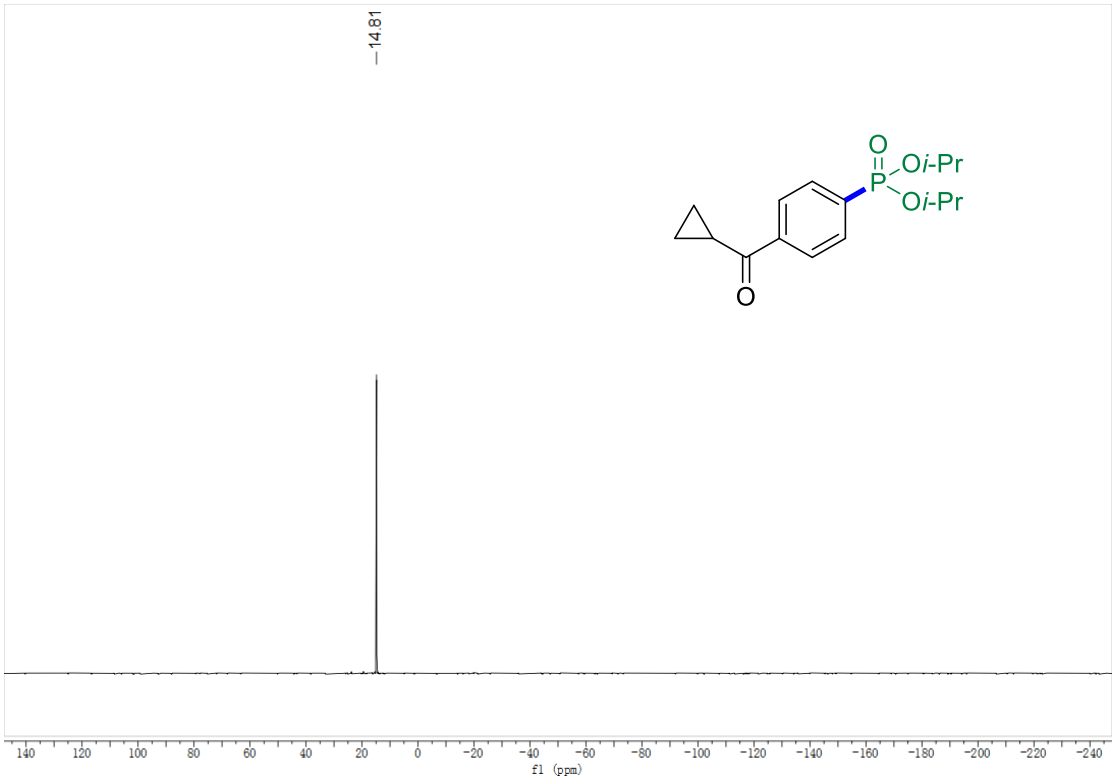
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ah**



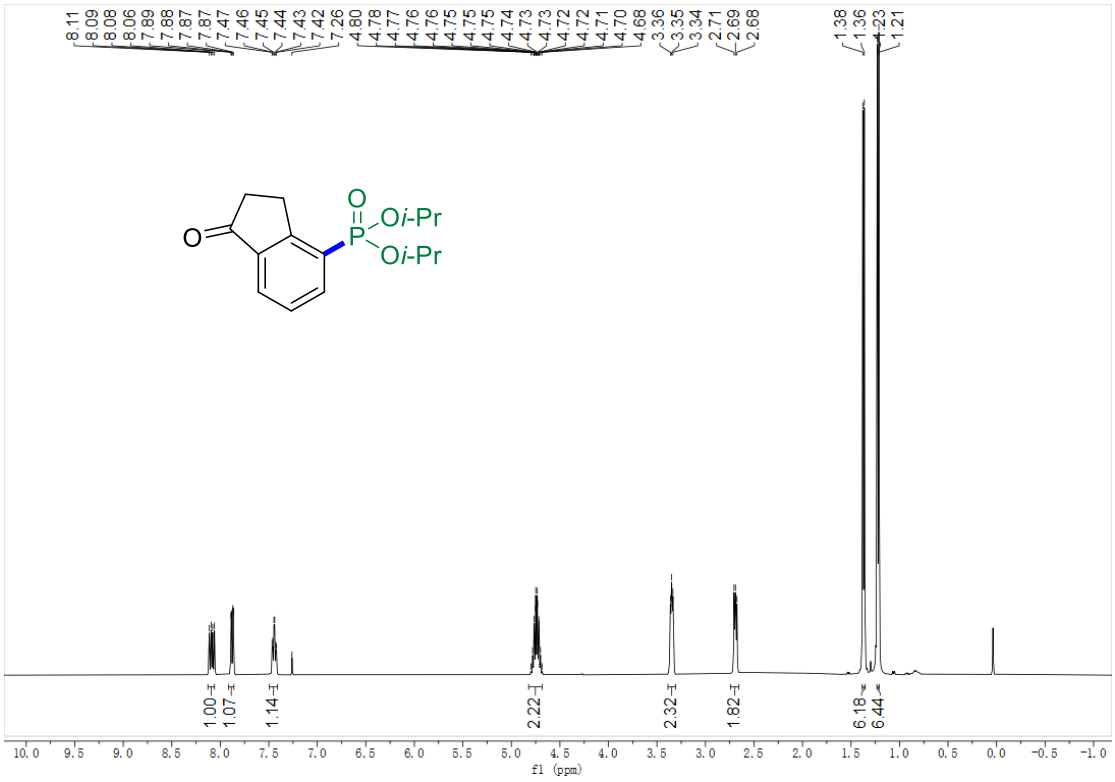
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ah**



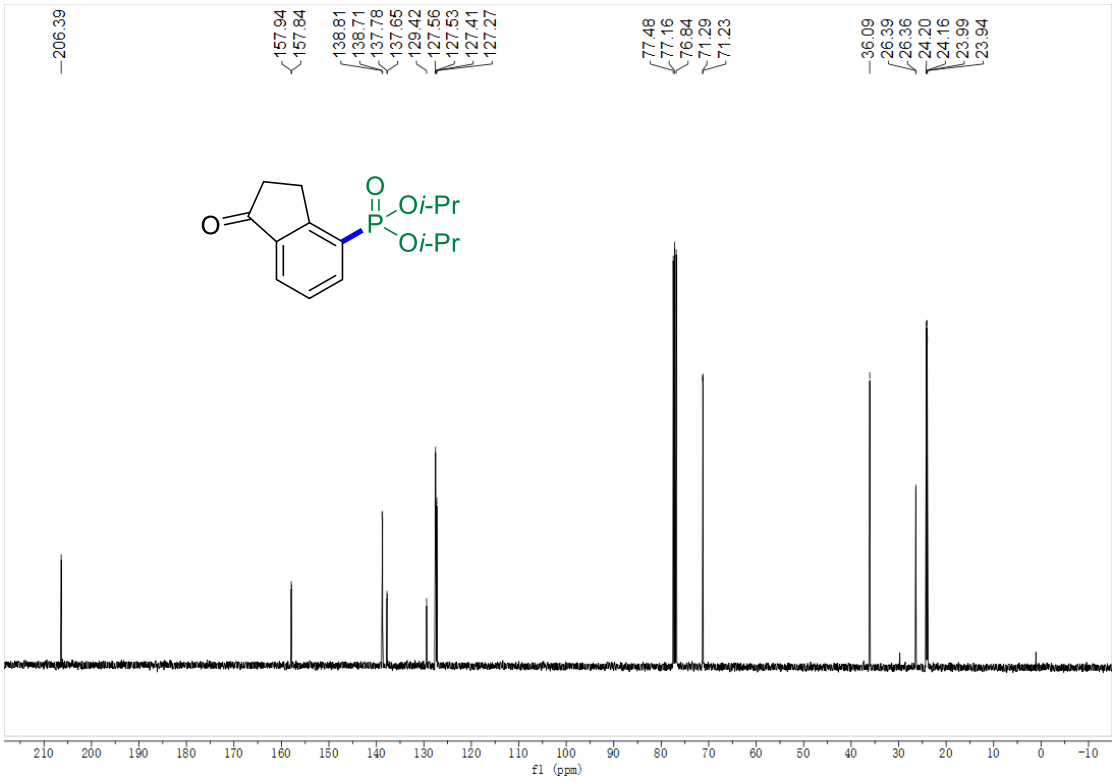
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ah**



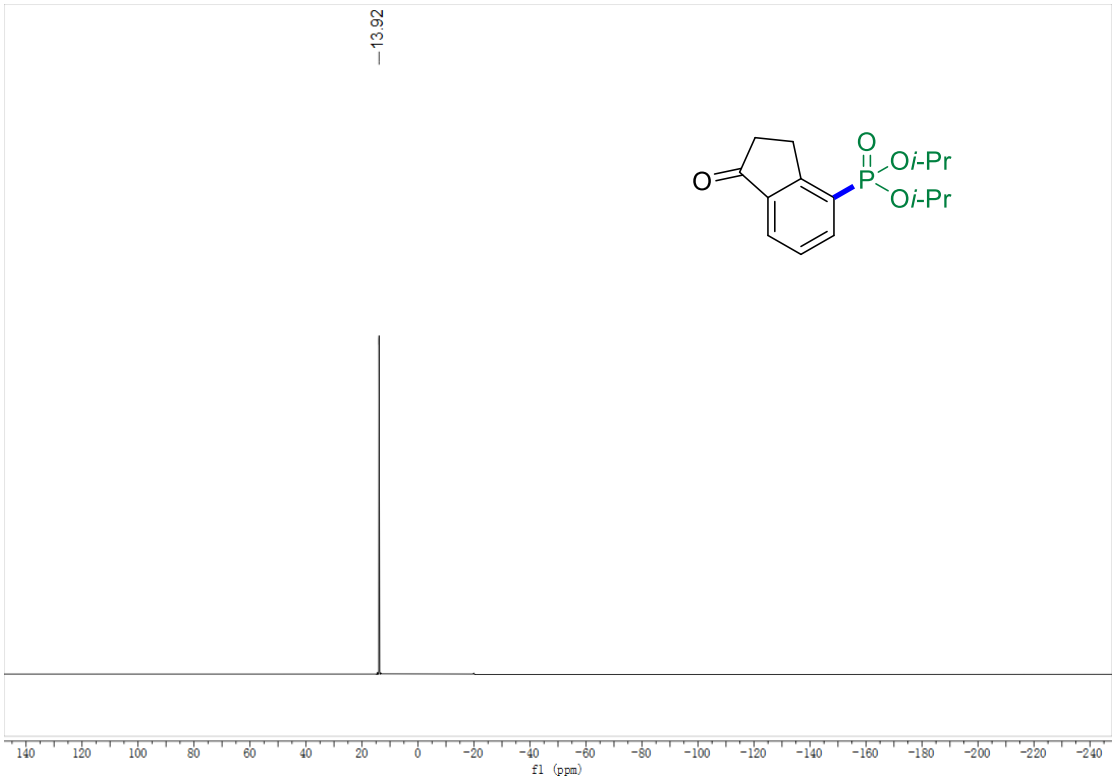
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ai**



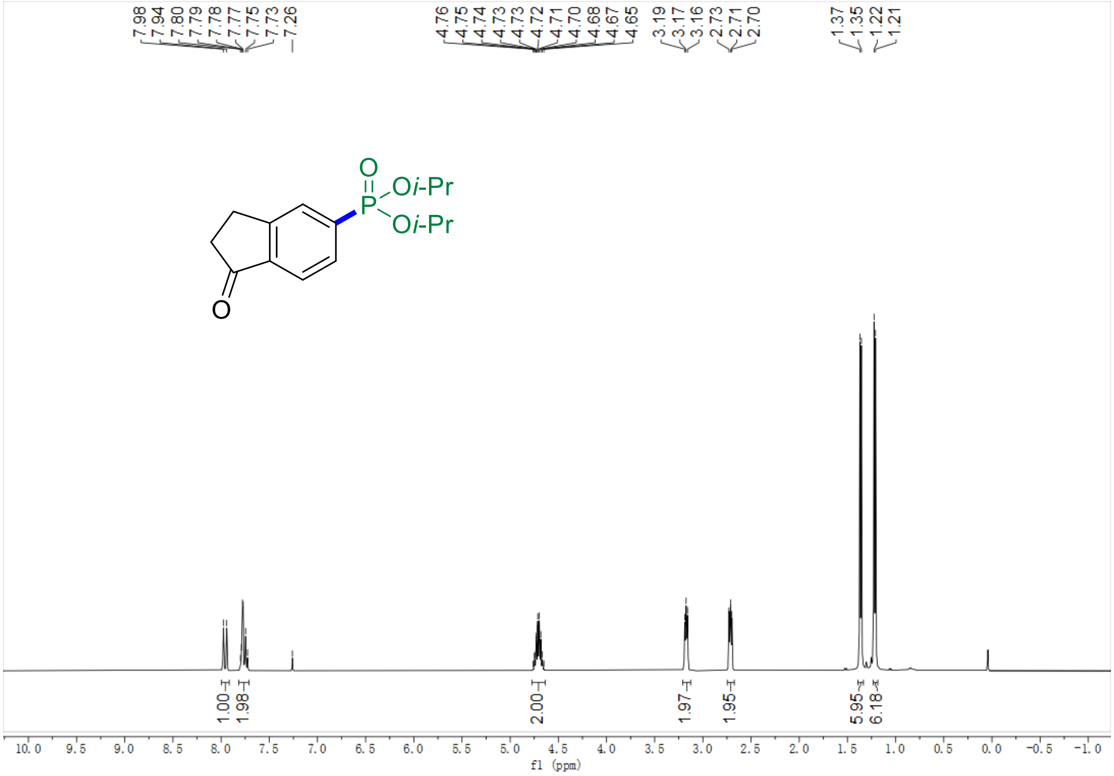
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ai**



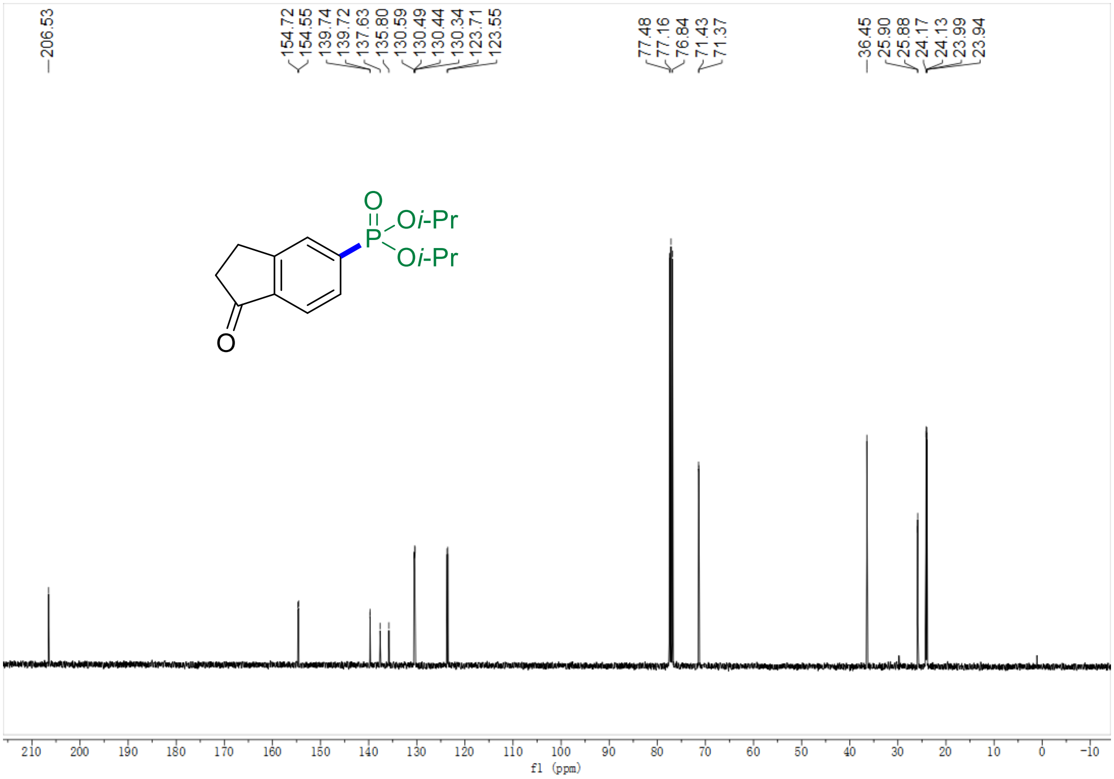
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ai**



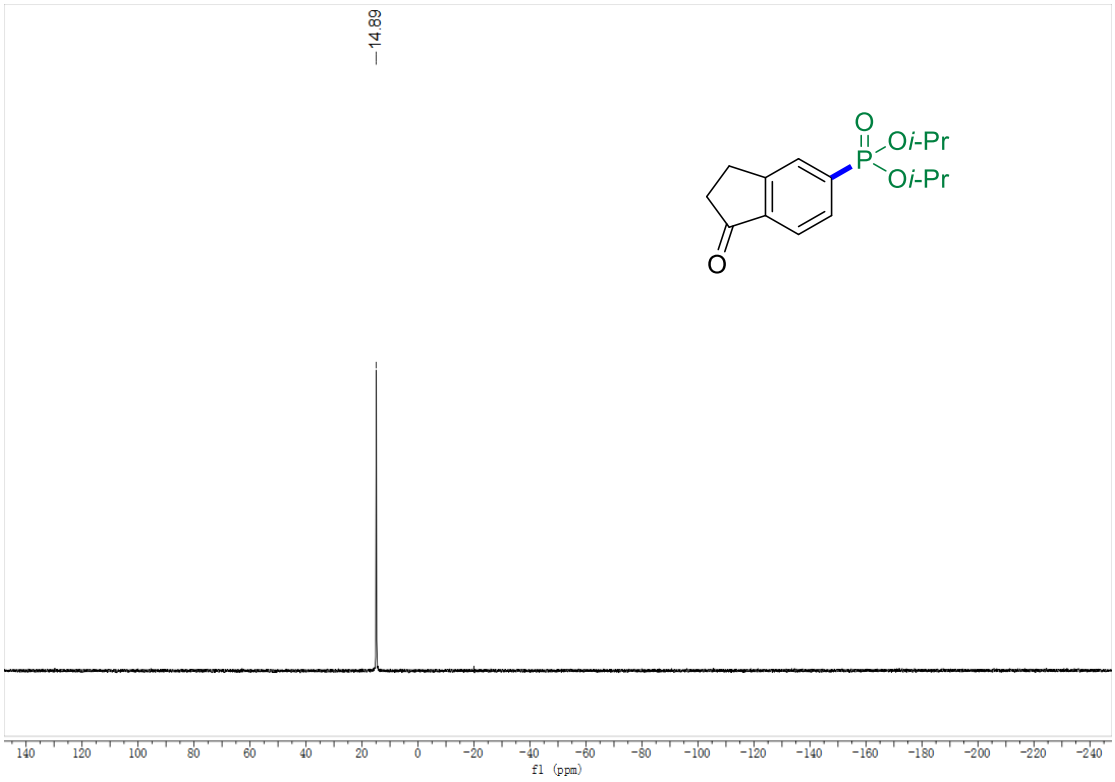
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aj**



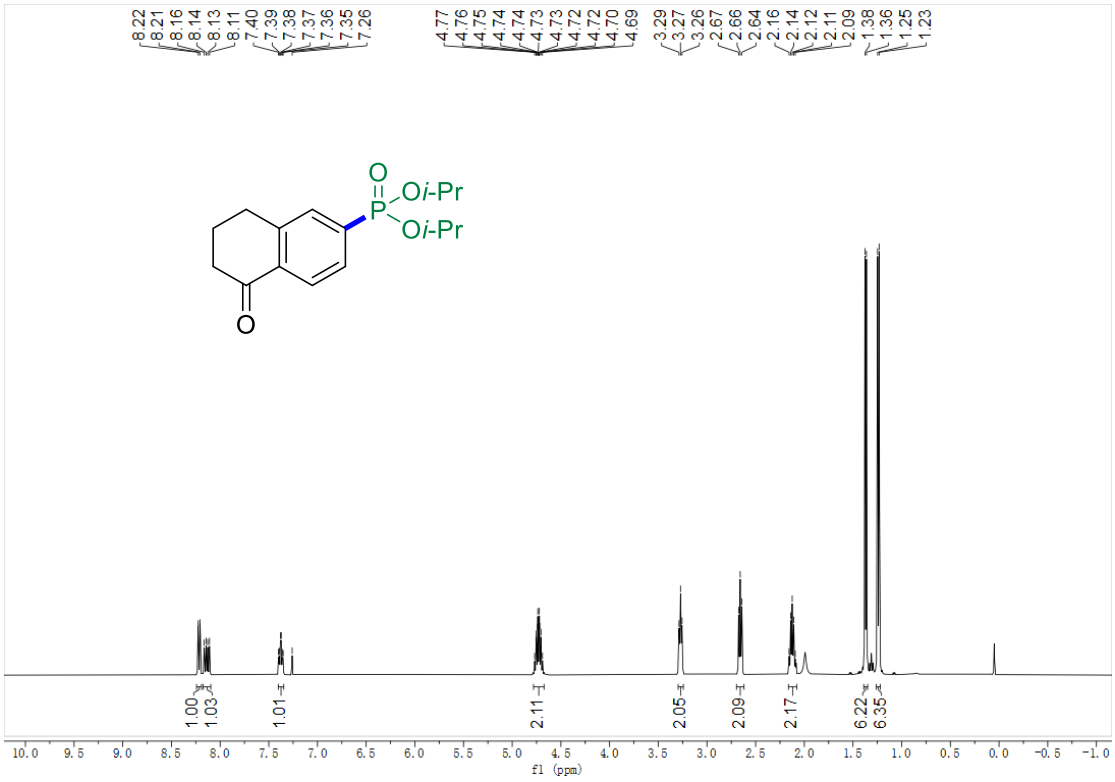
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4aj**



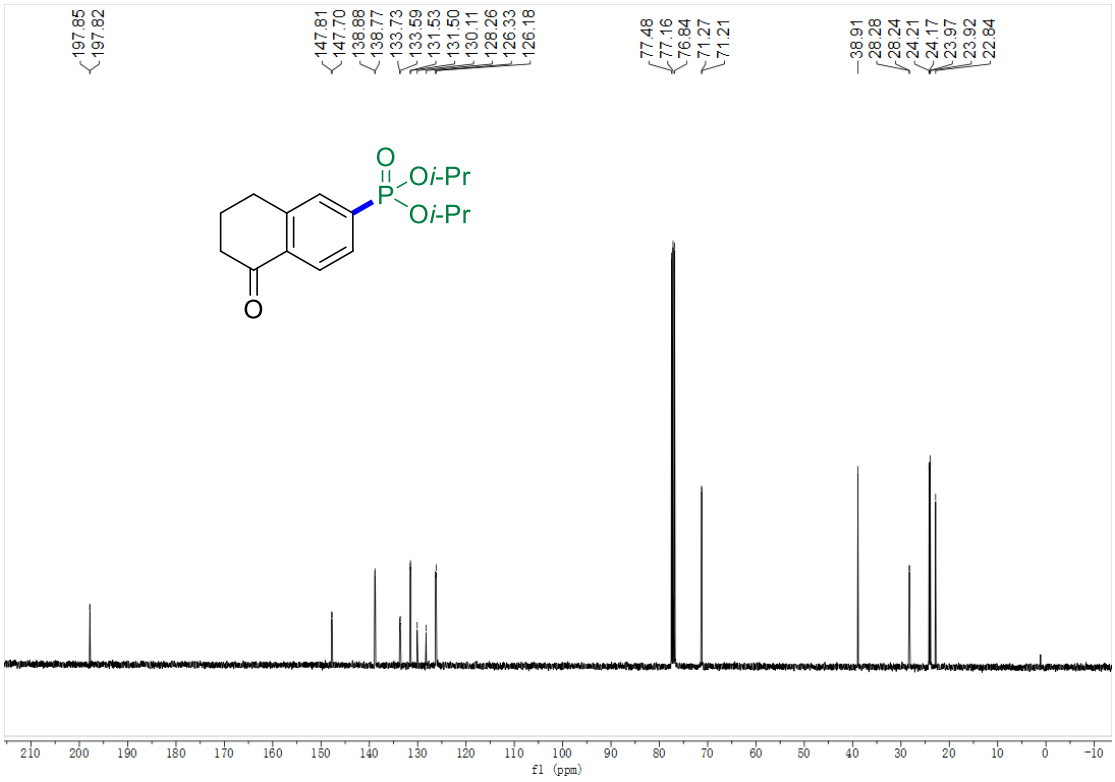
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4aj**



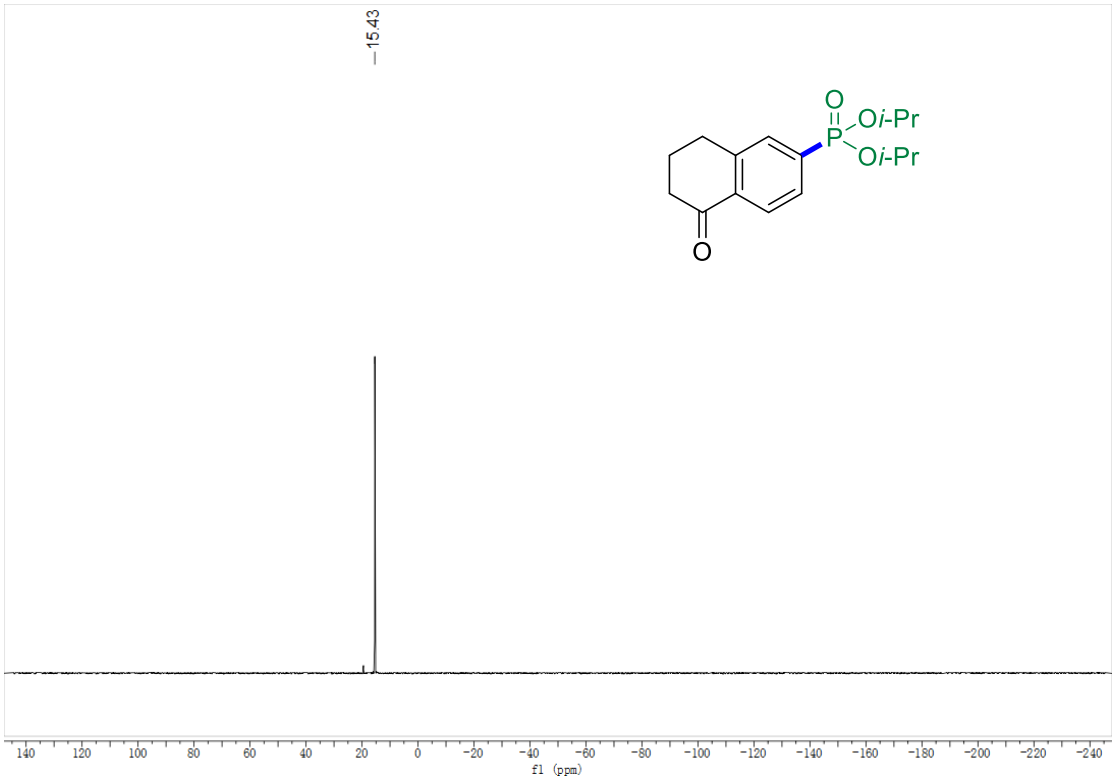
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ak**



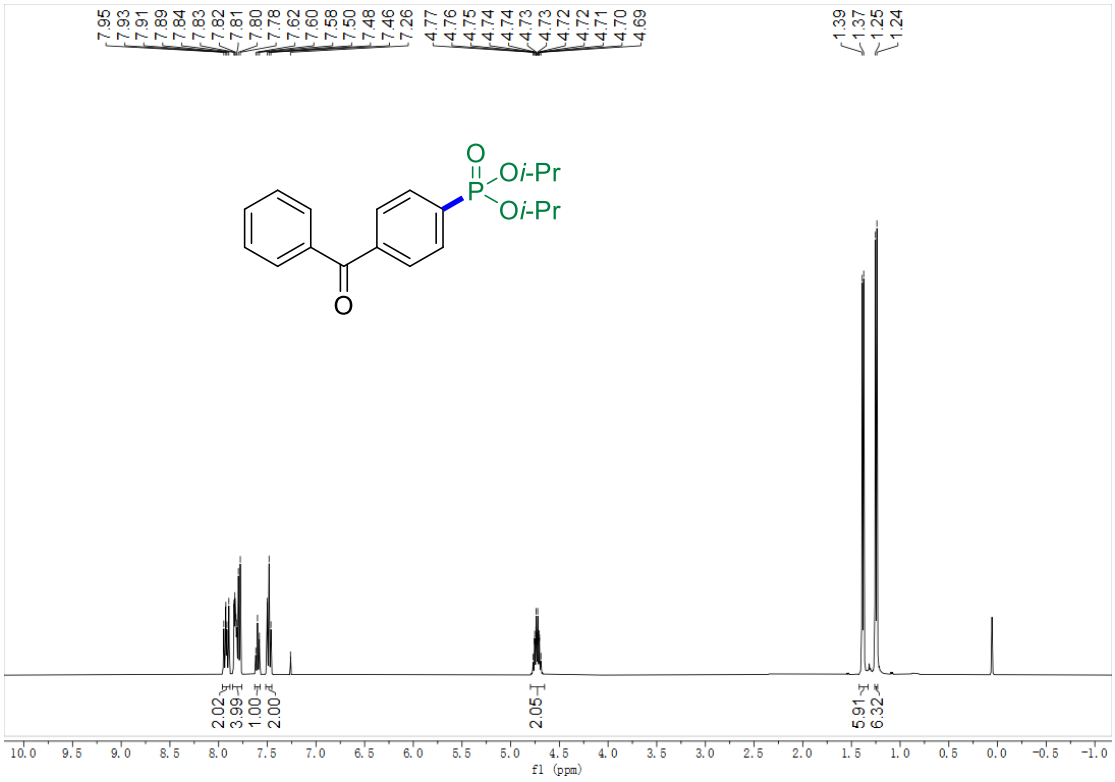
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ak**



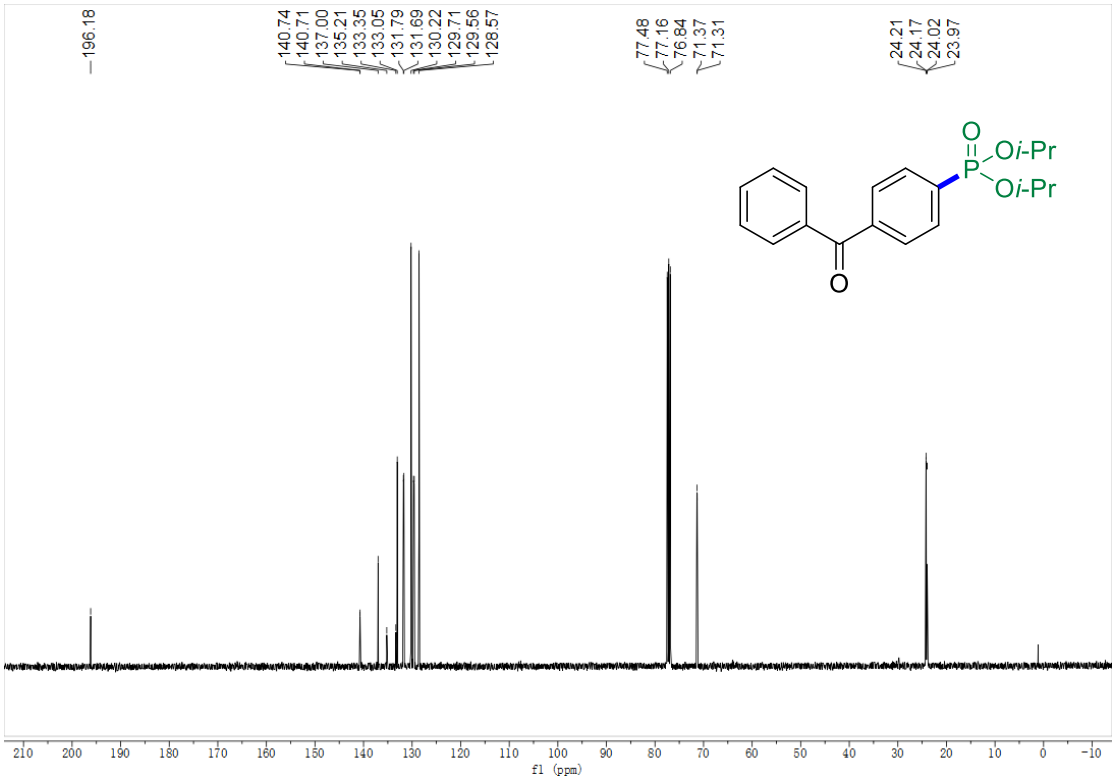
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ak**



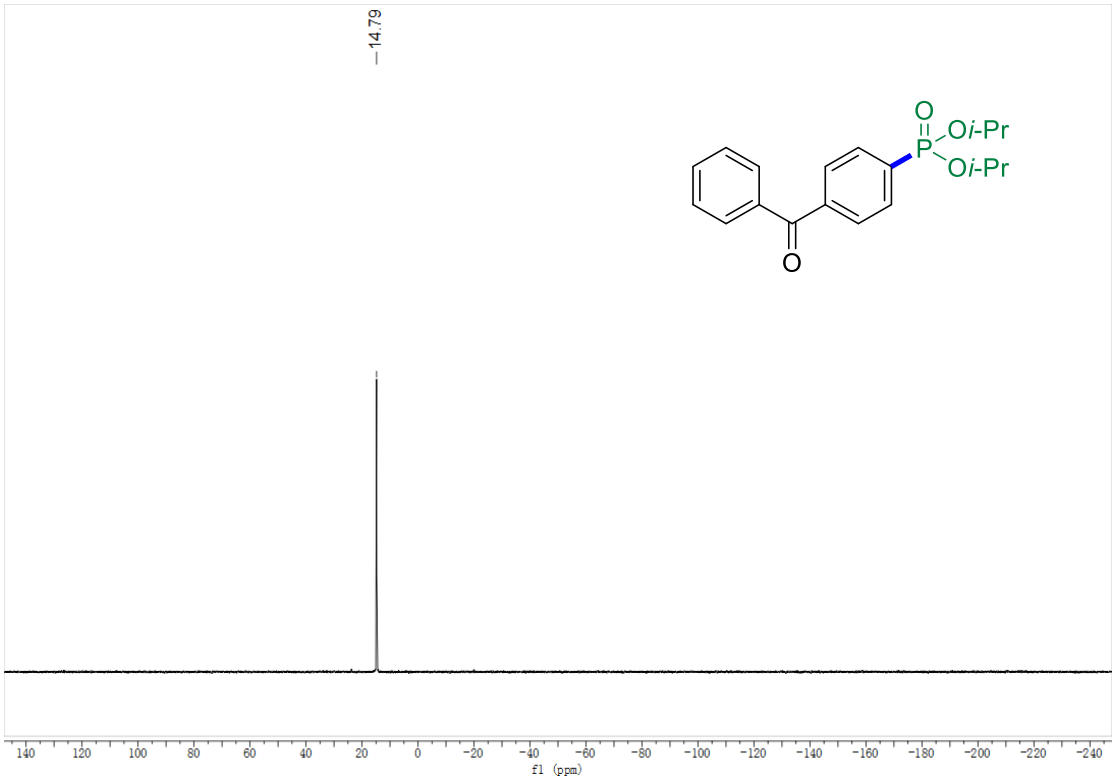
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4al**



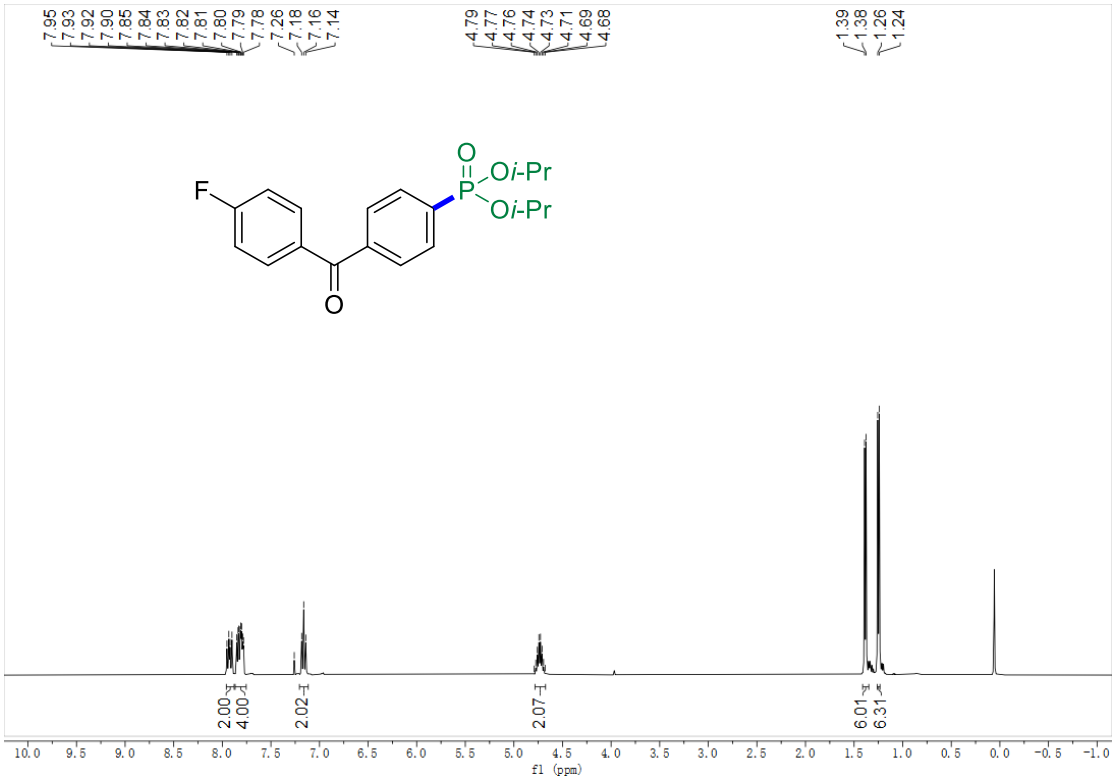
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4al**



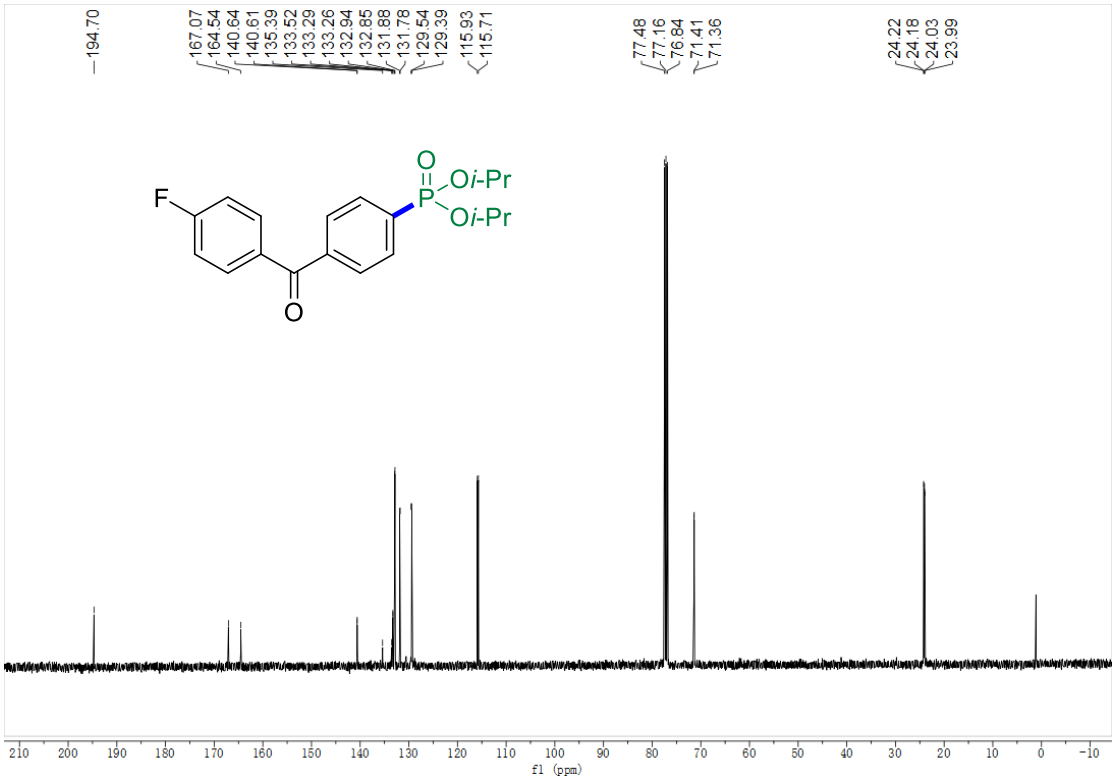
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4al**



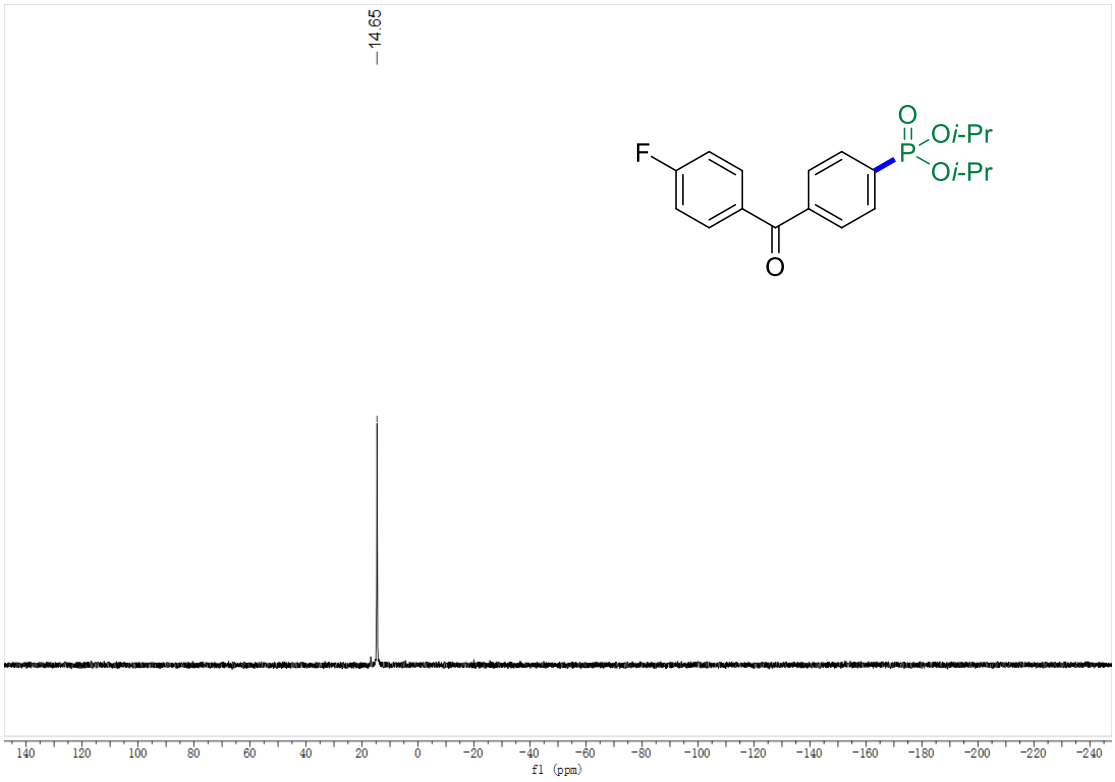
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4am**



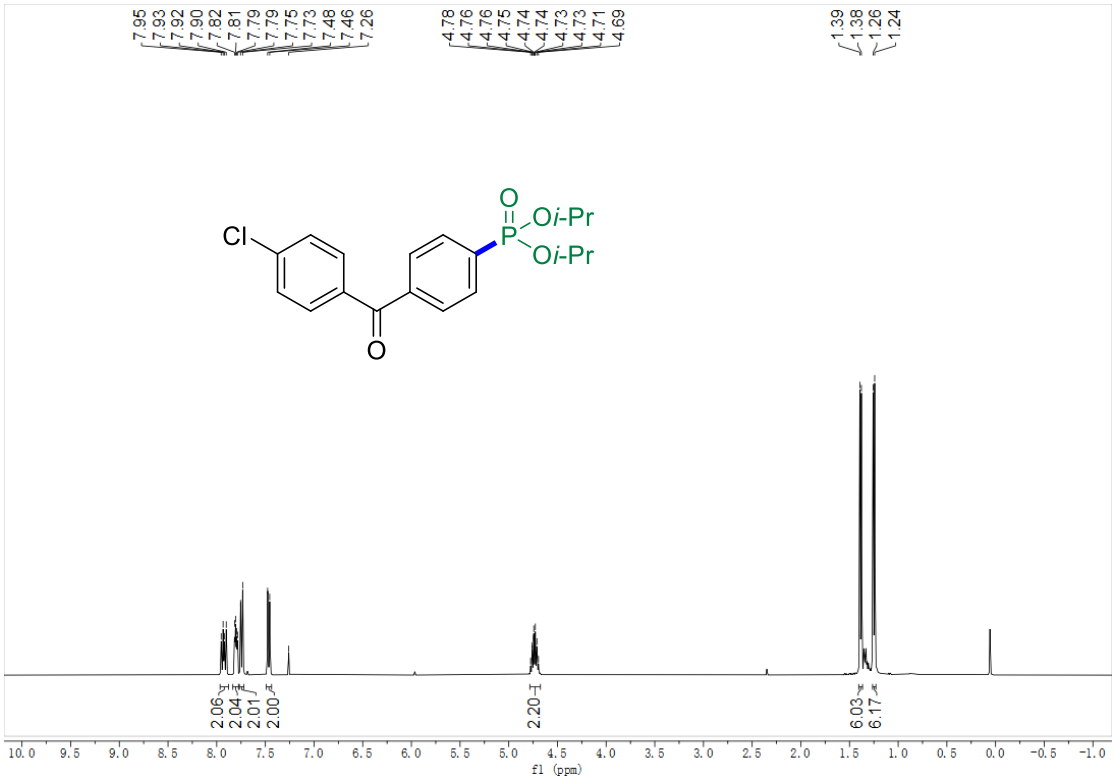
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4am**



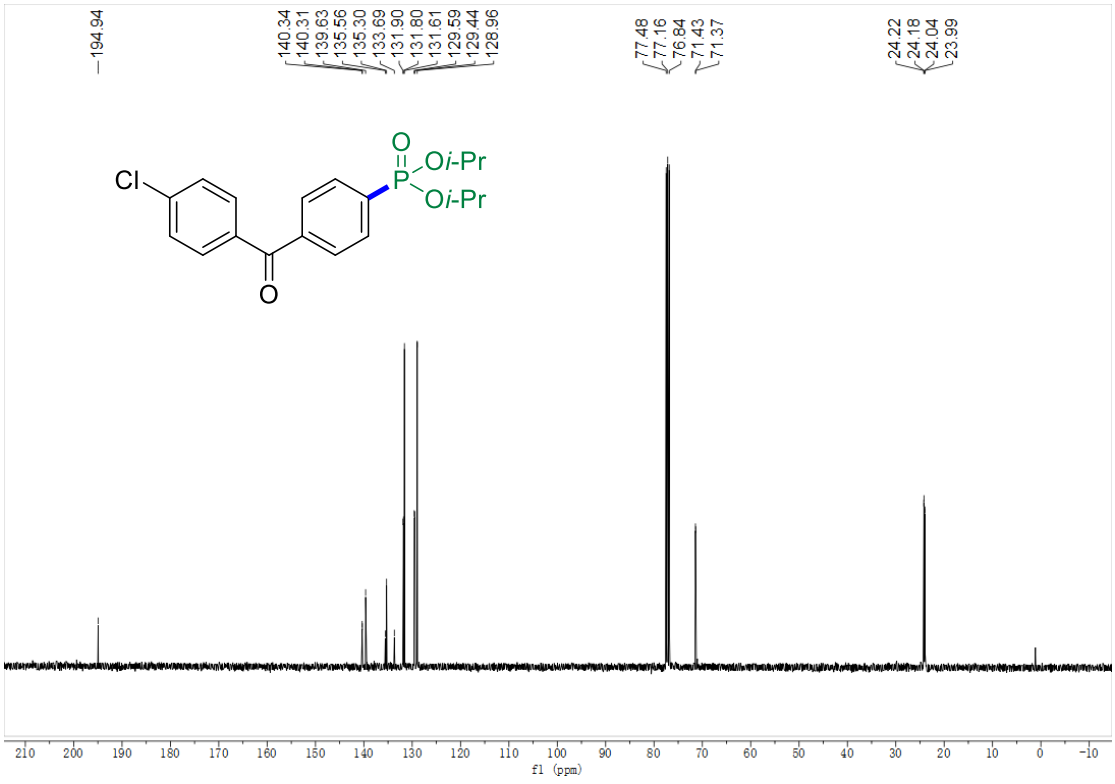
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4am**



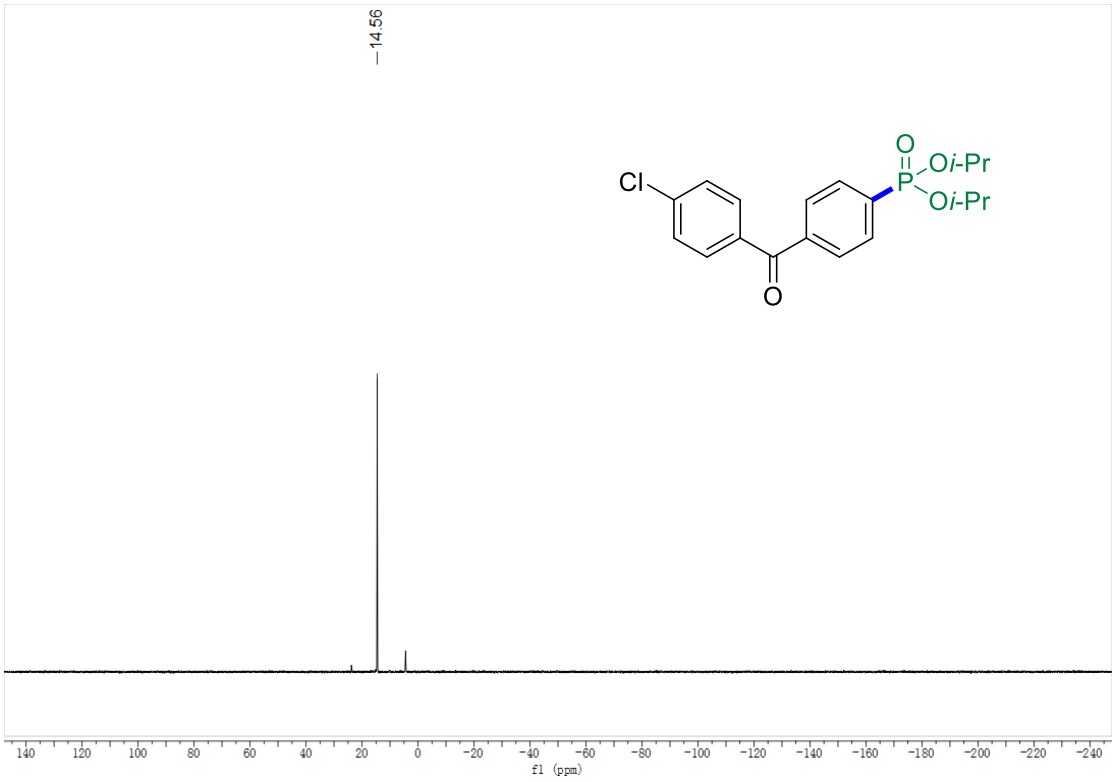
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4an**



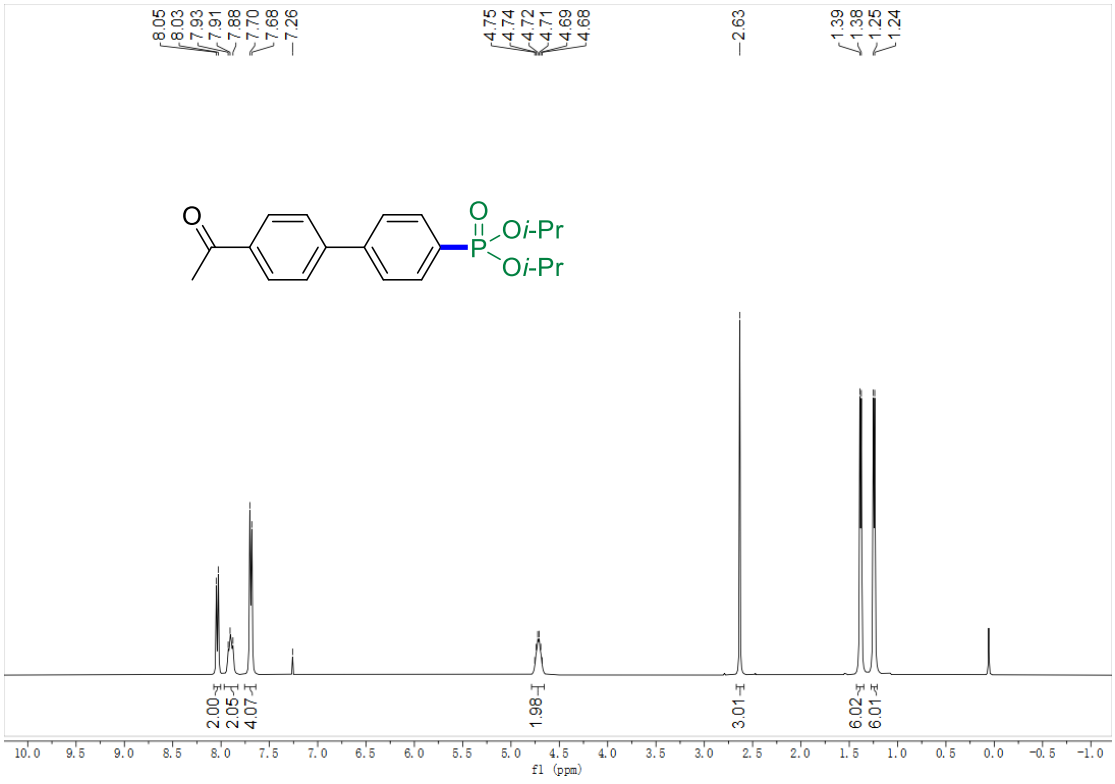
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4an**



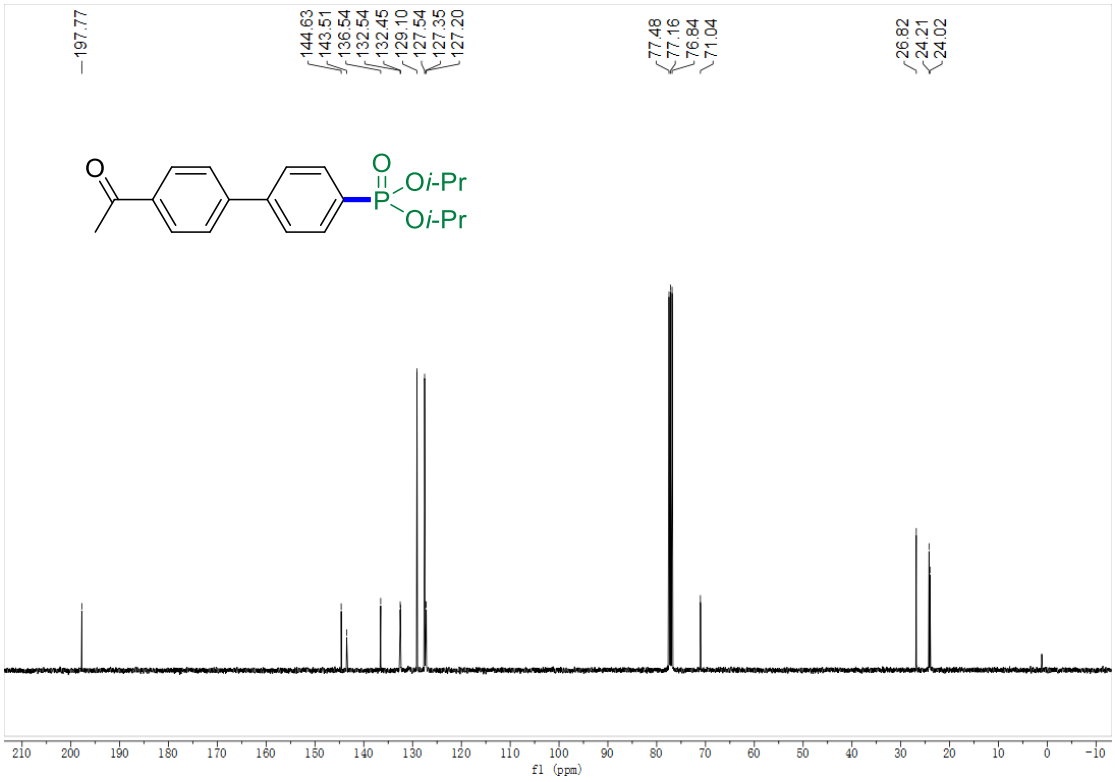
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4an**



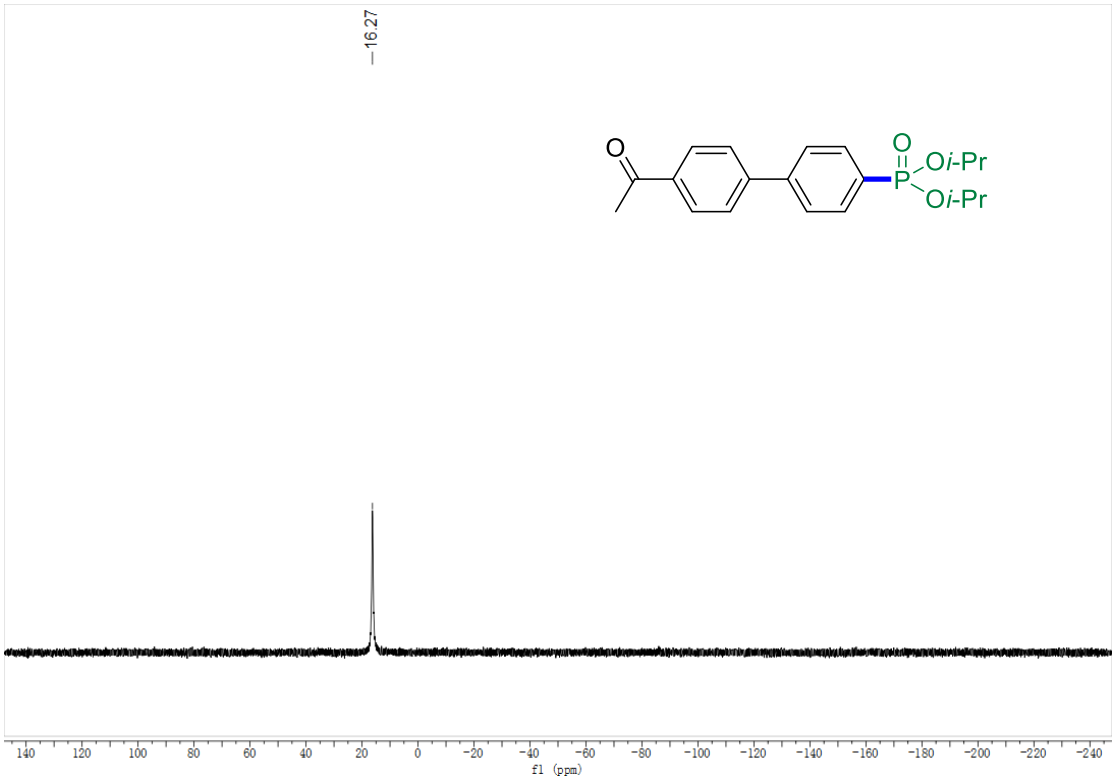
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ao**



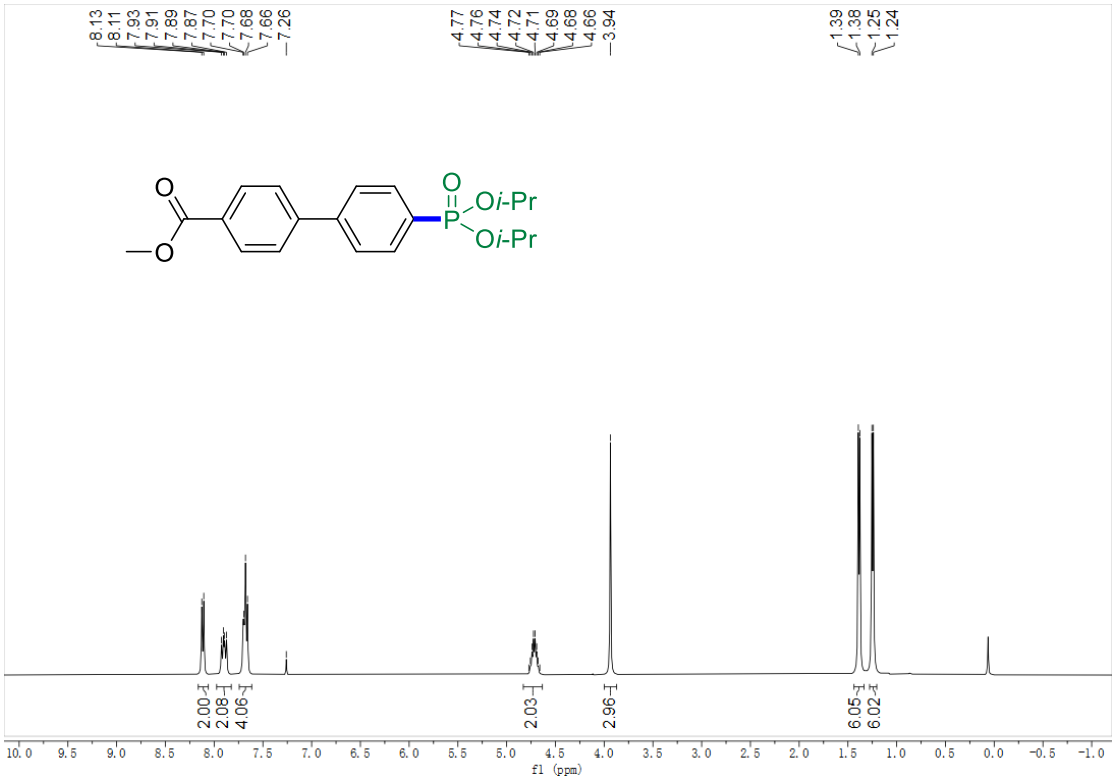
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ao**



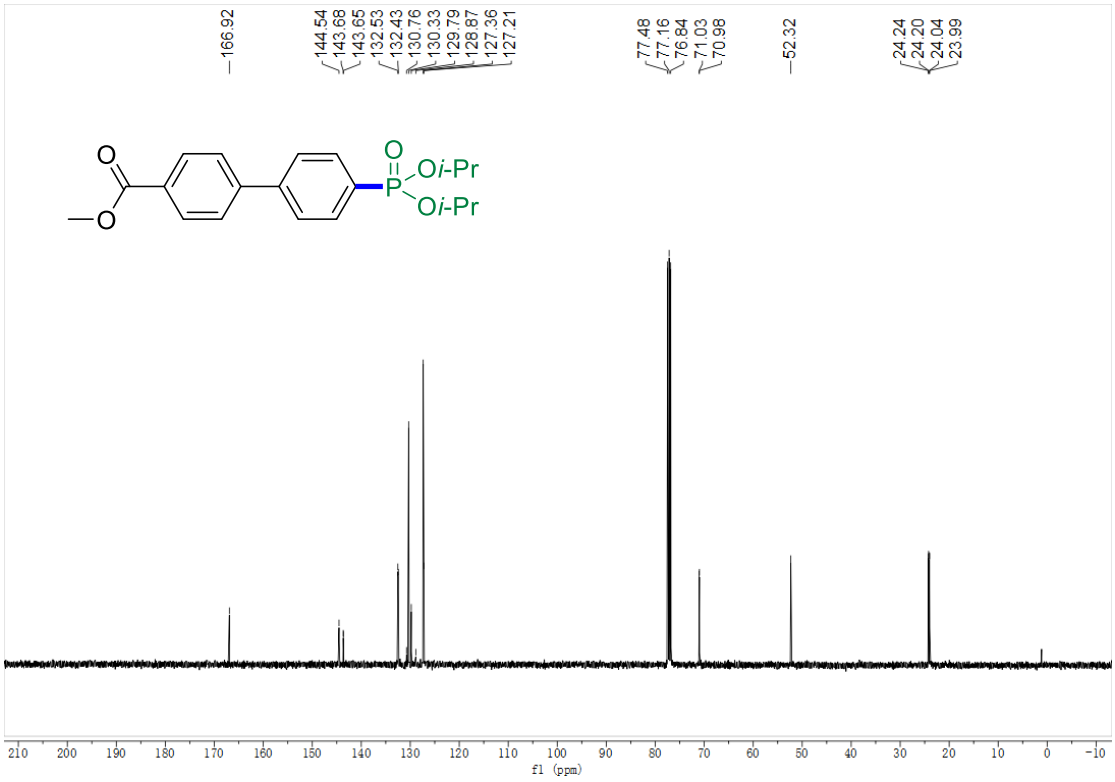
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ao**



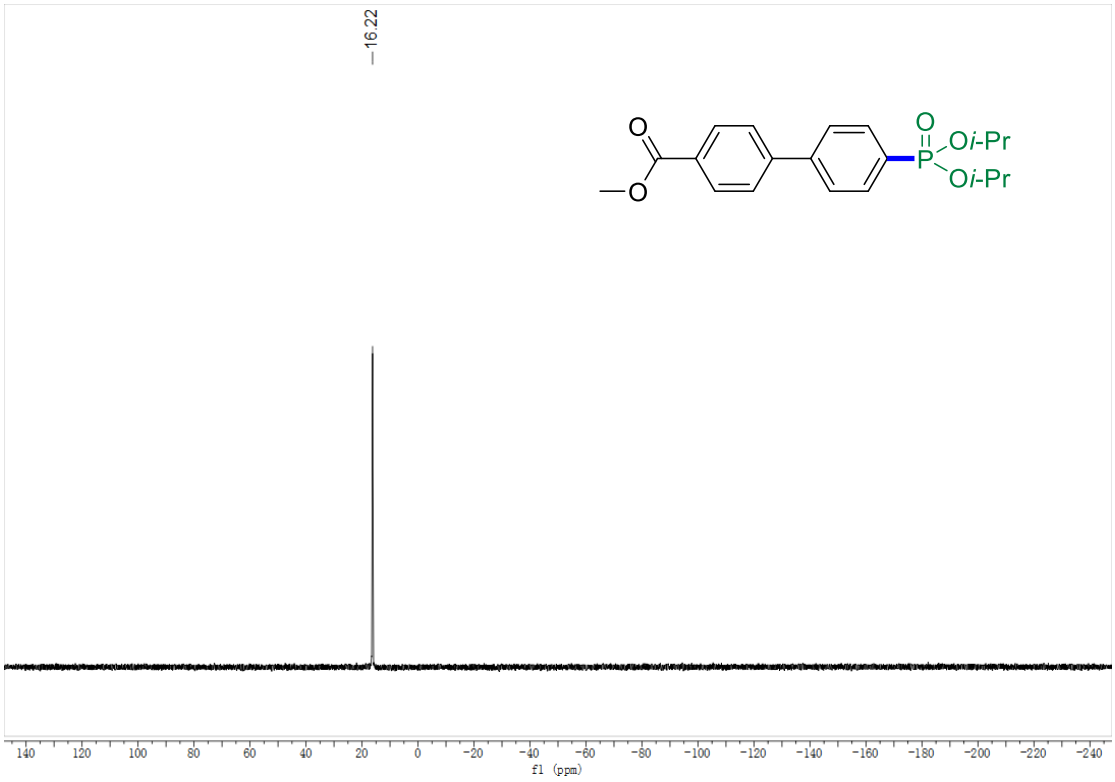
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ap**



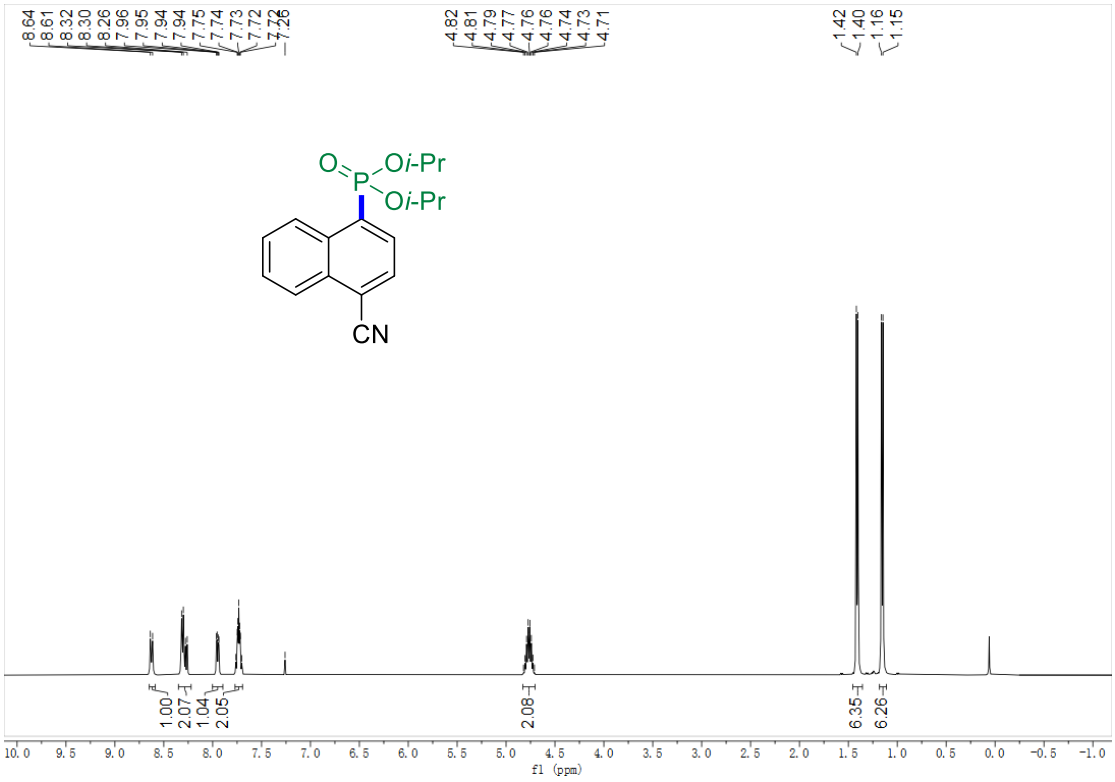
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ap**



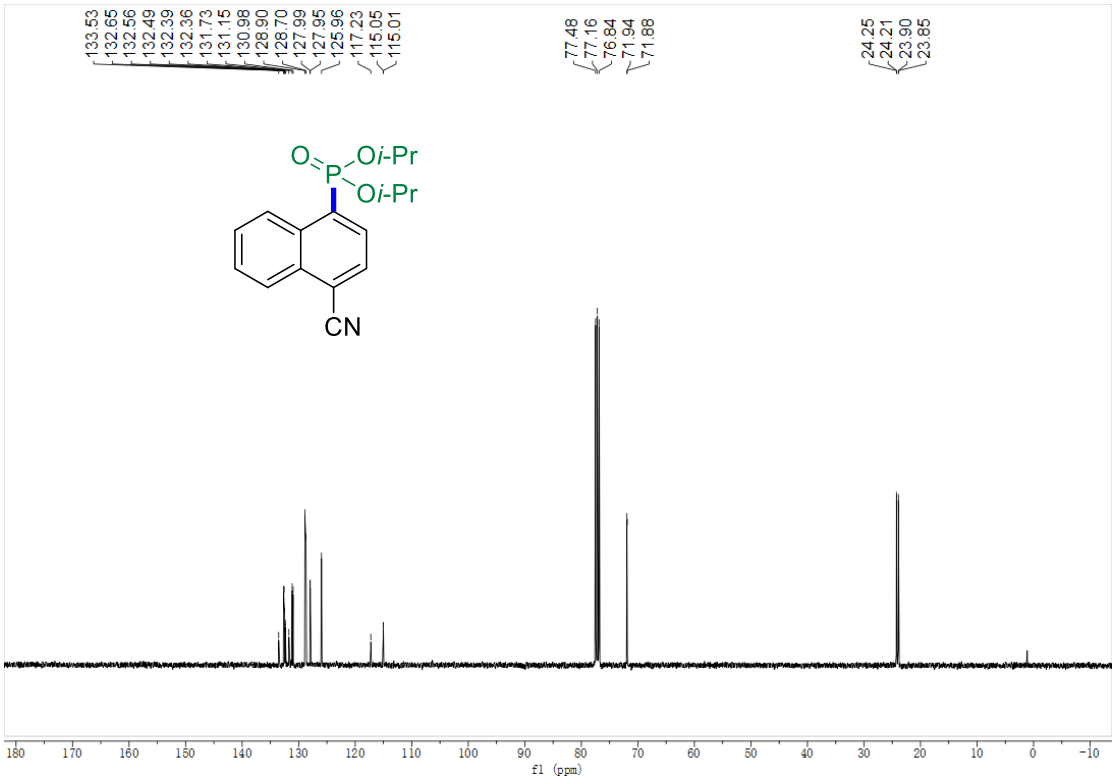
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ap**



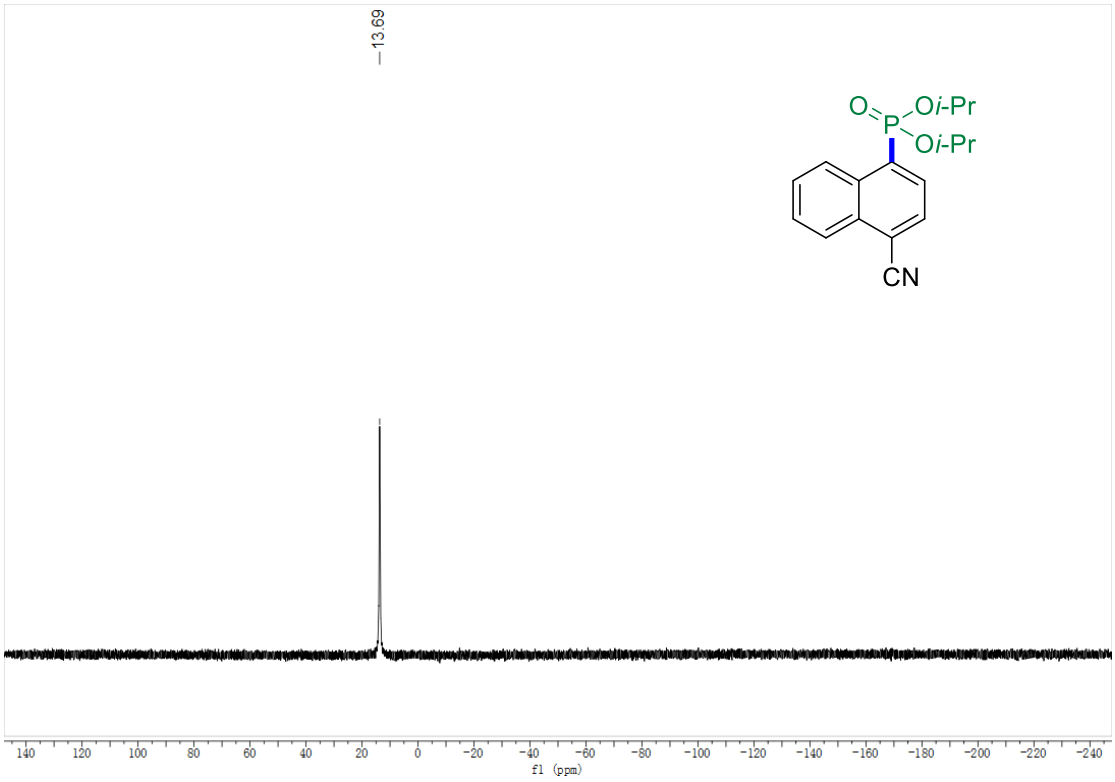
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aq**



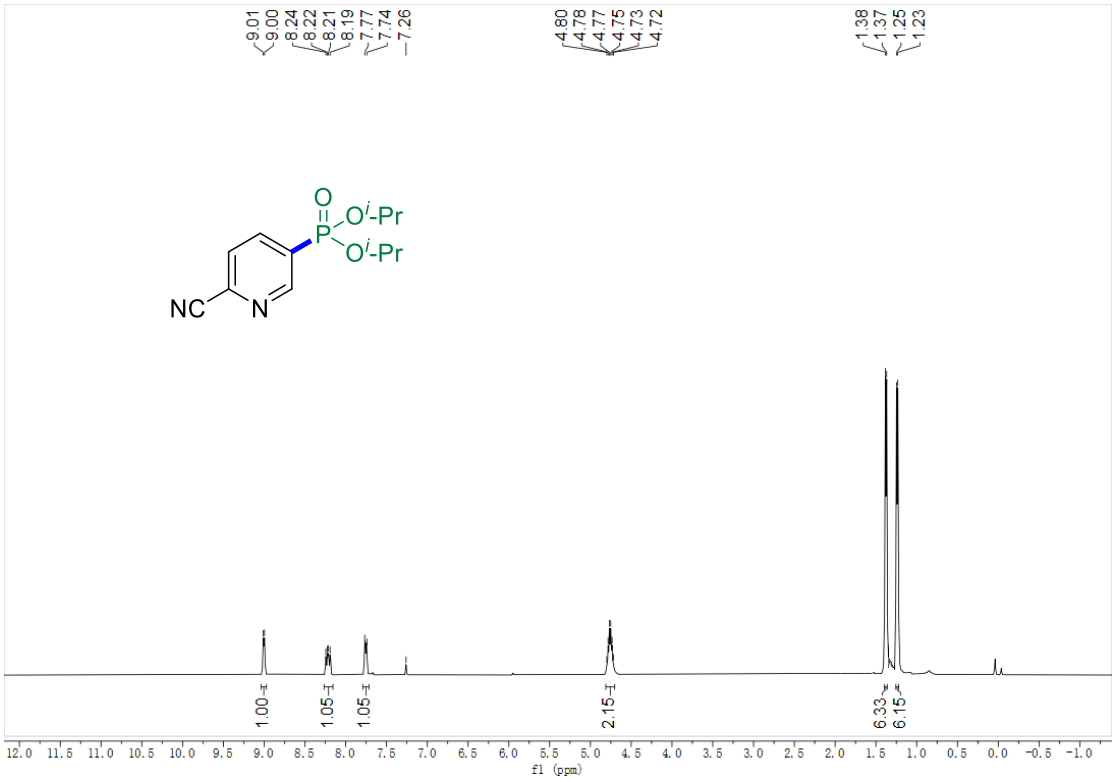
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4aq**



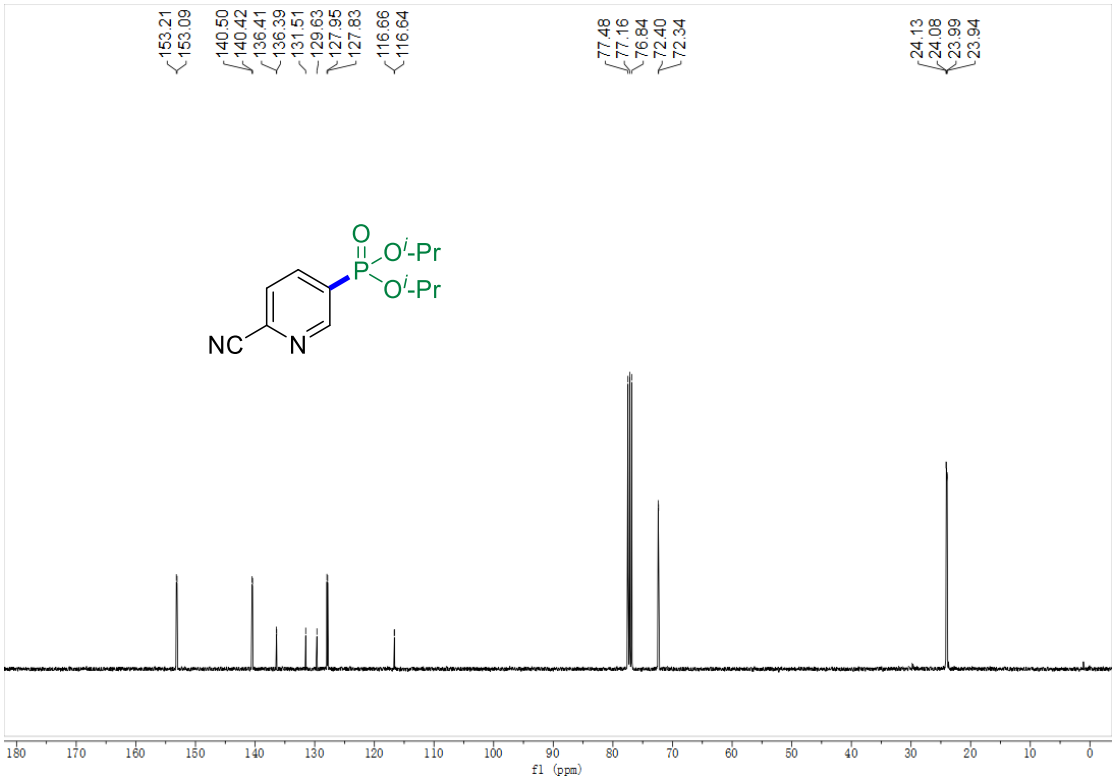
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4aq**



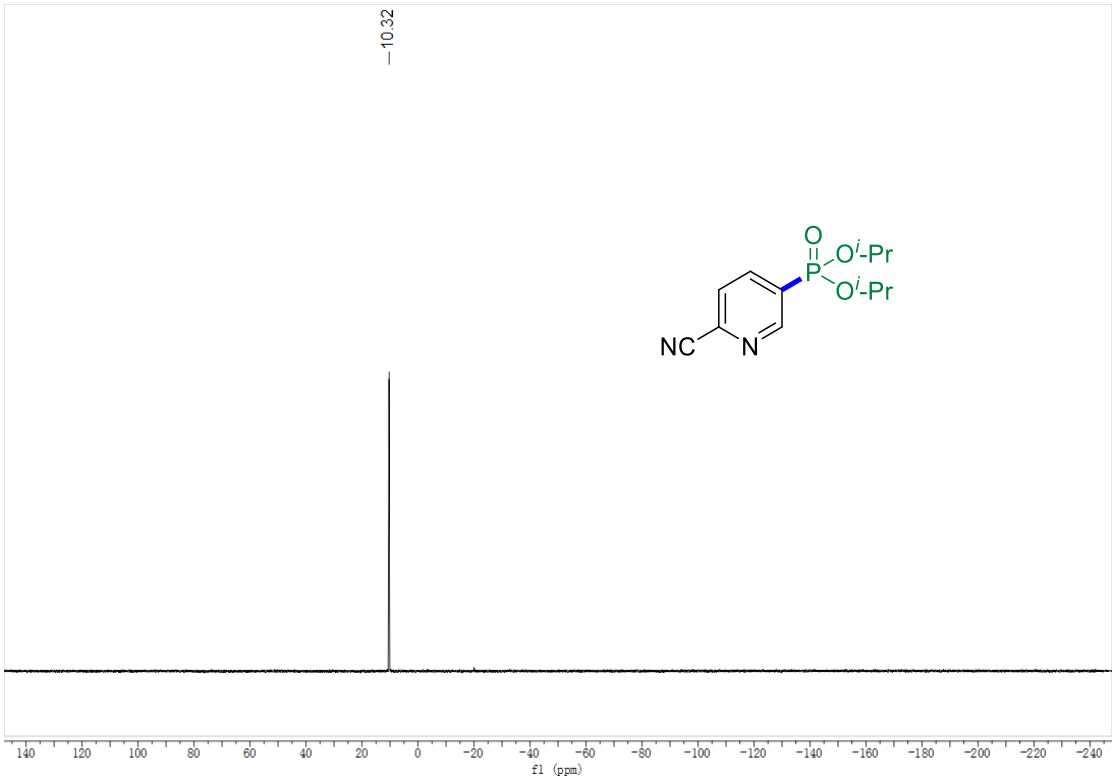
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ar**



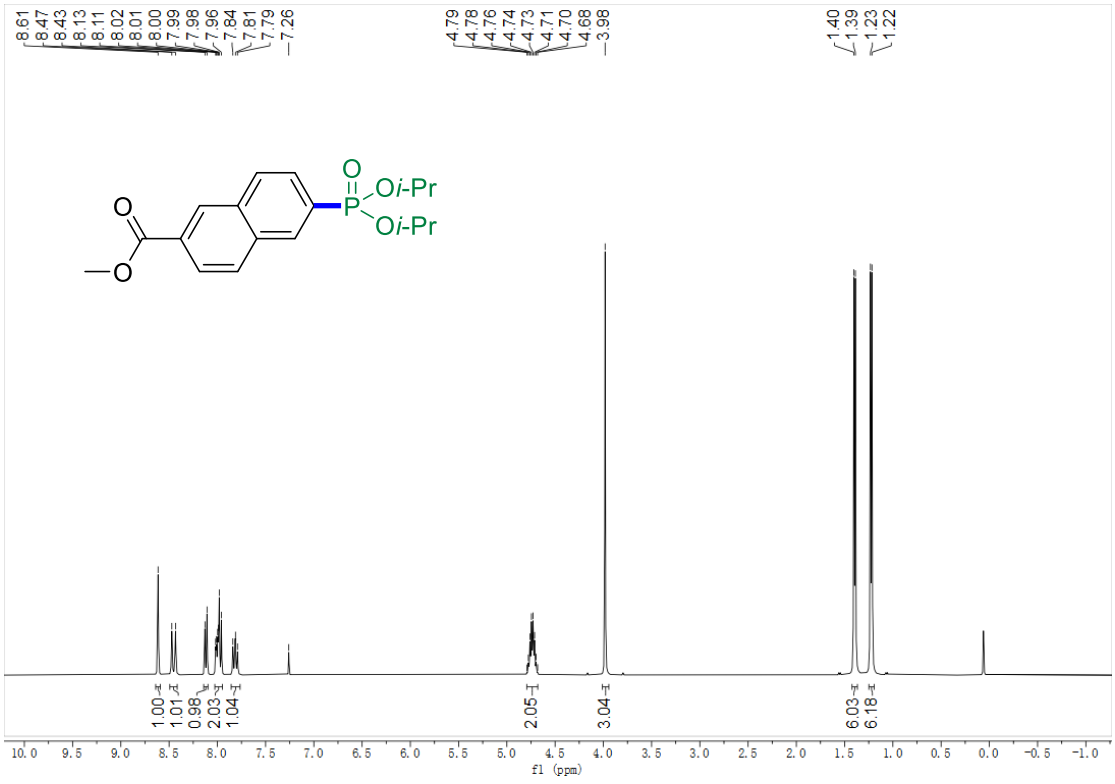
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4ar**



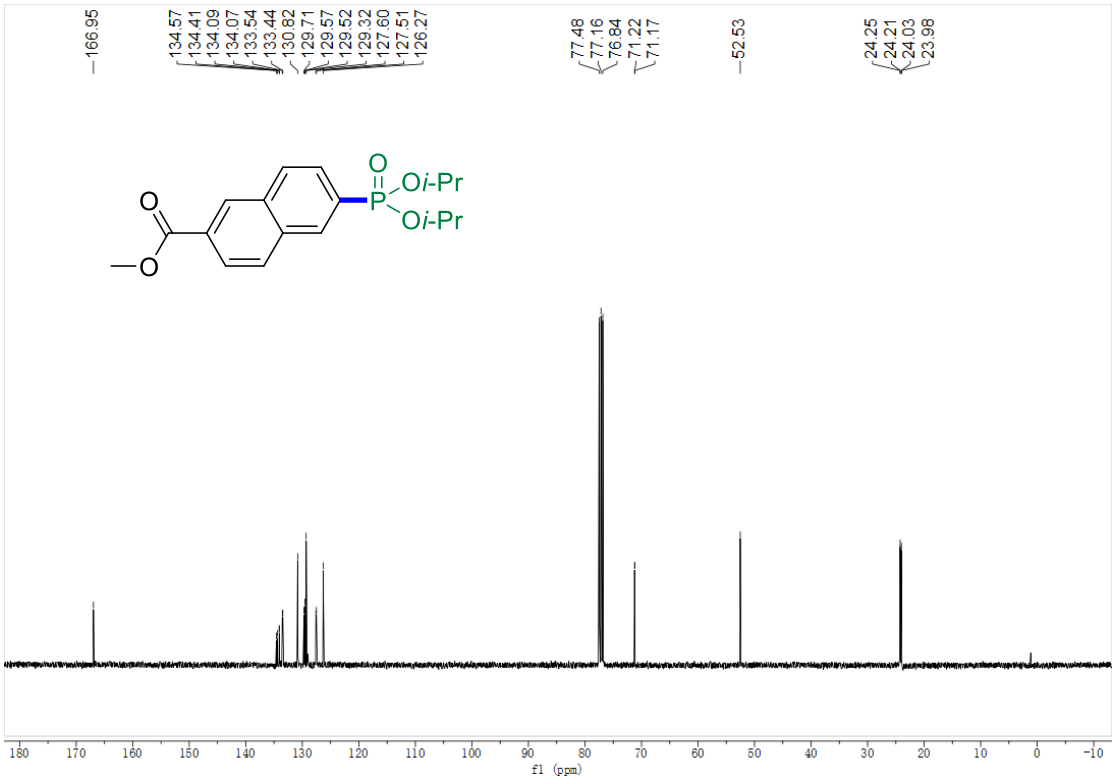
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4ar**



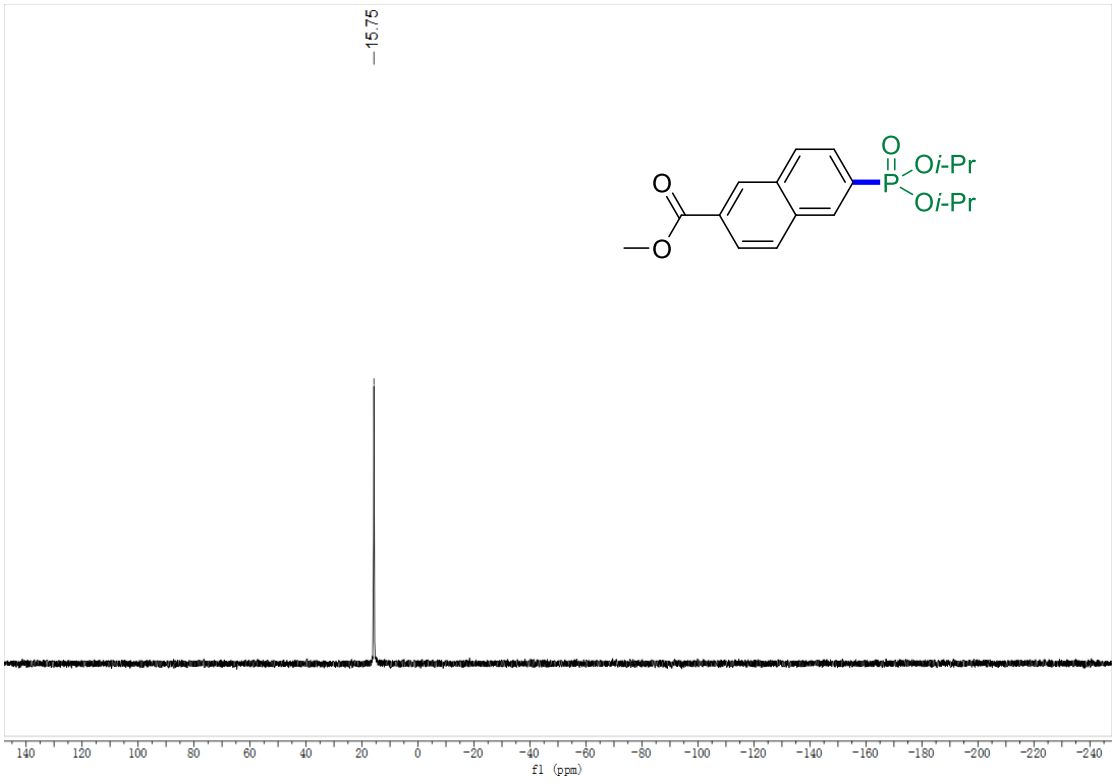
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4as**



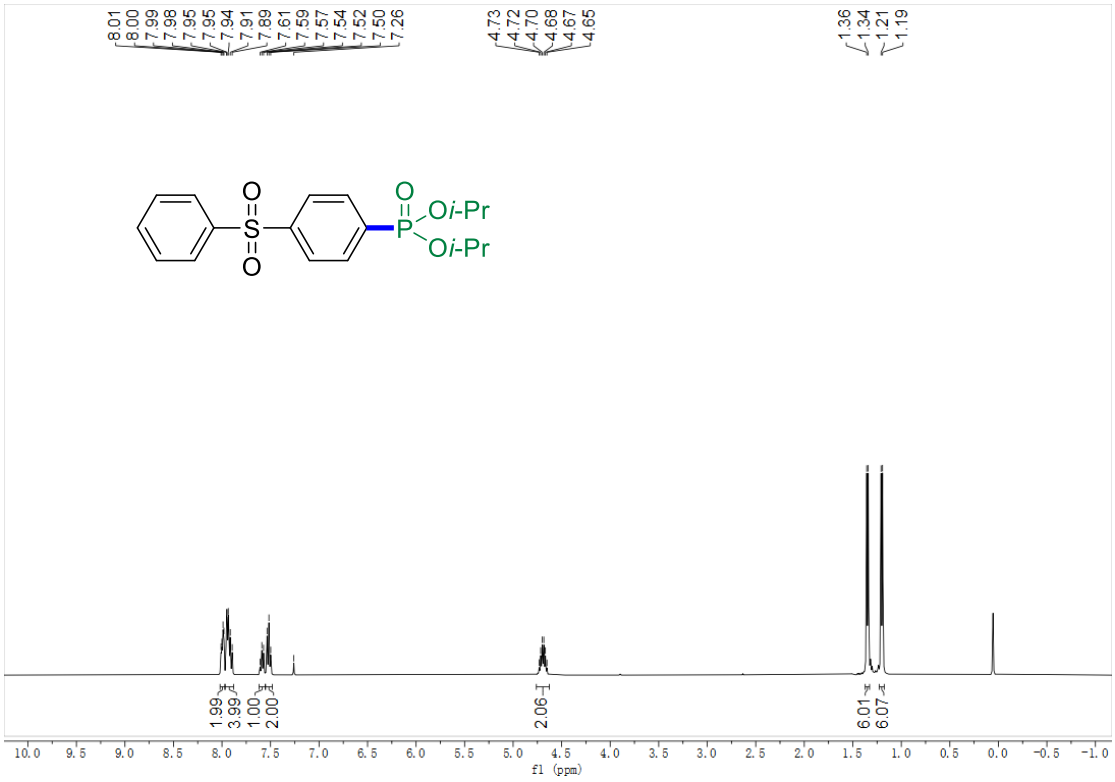
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4as**



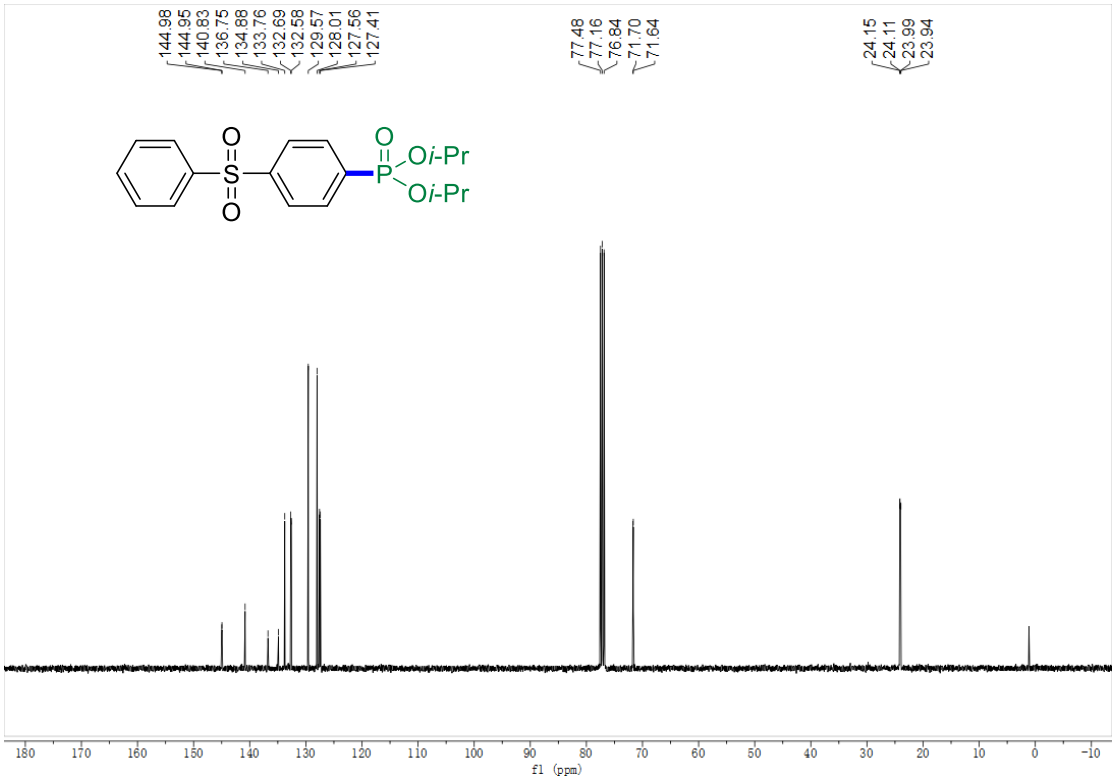
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4as**



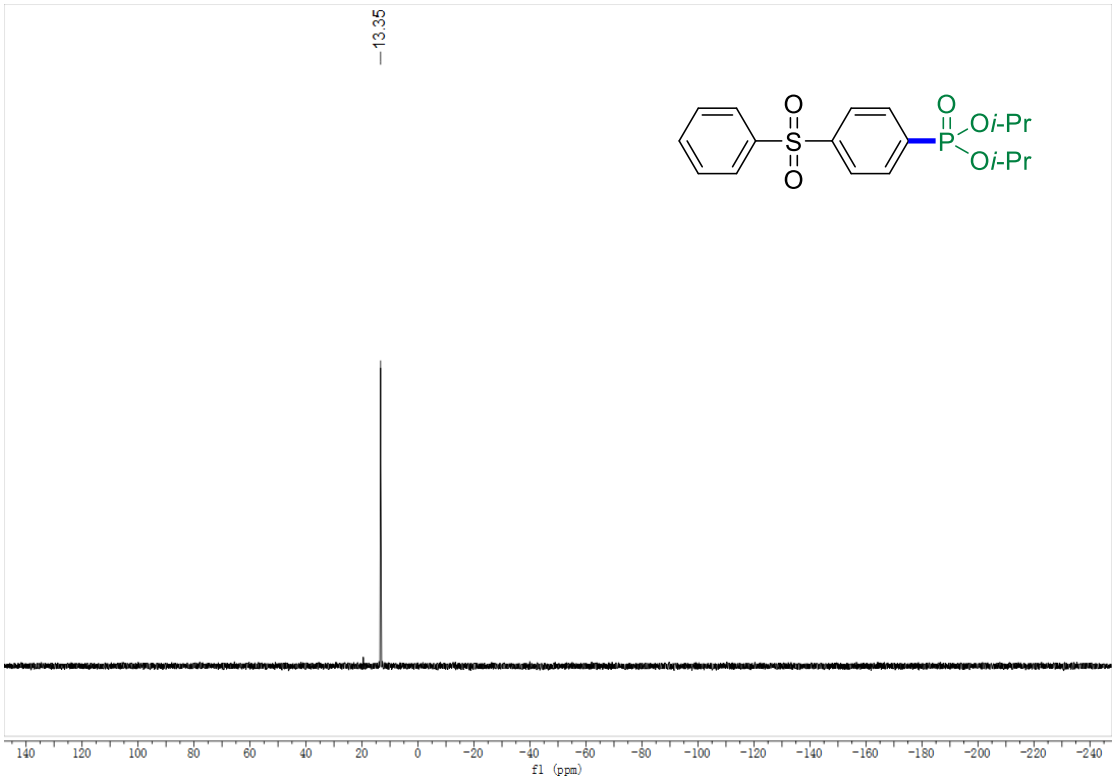
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4at**



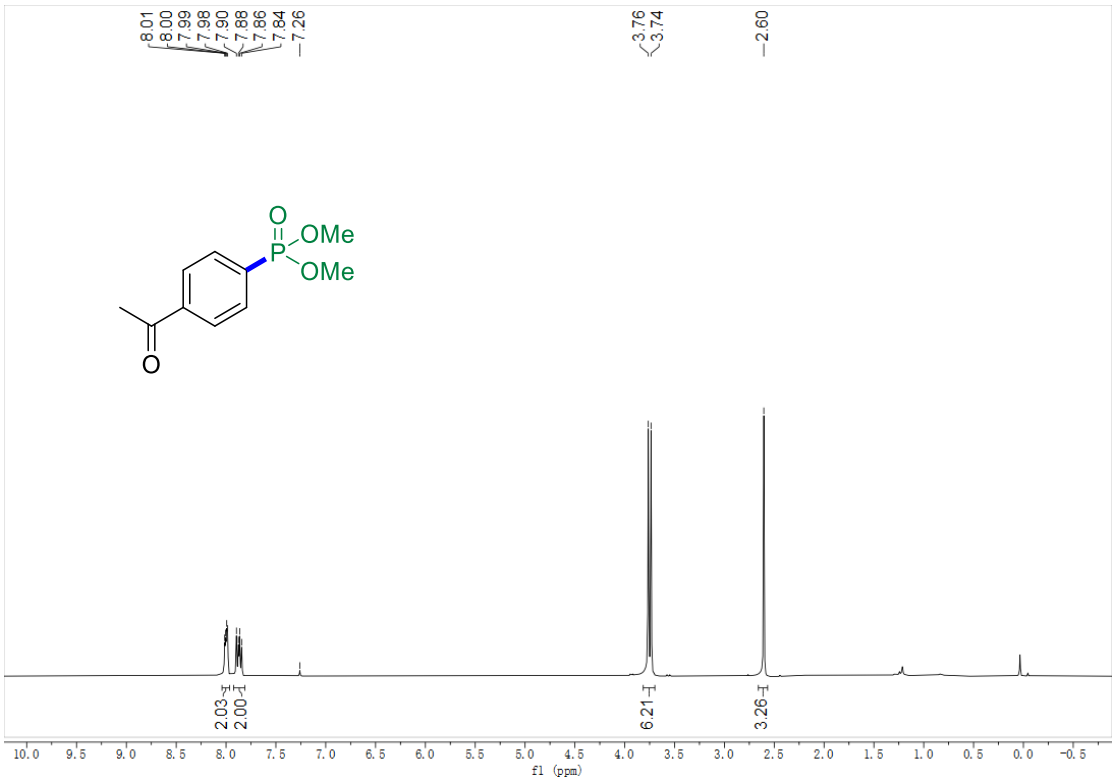
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4at**



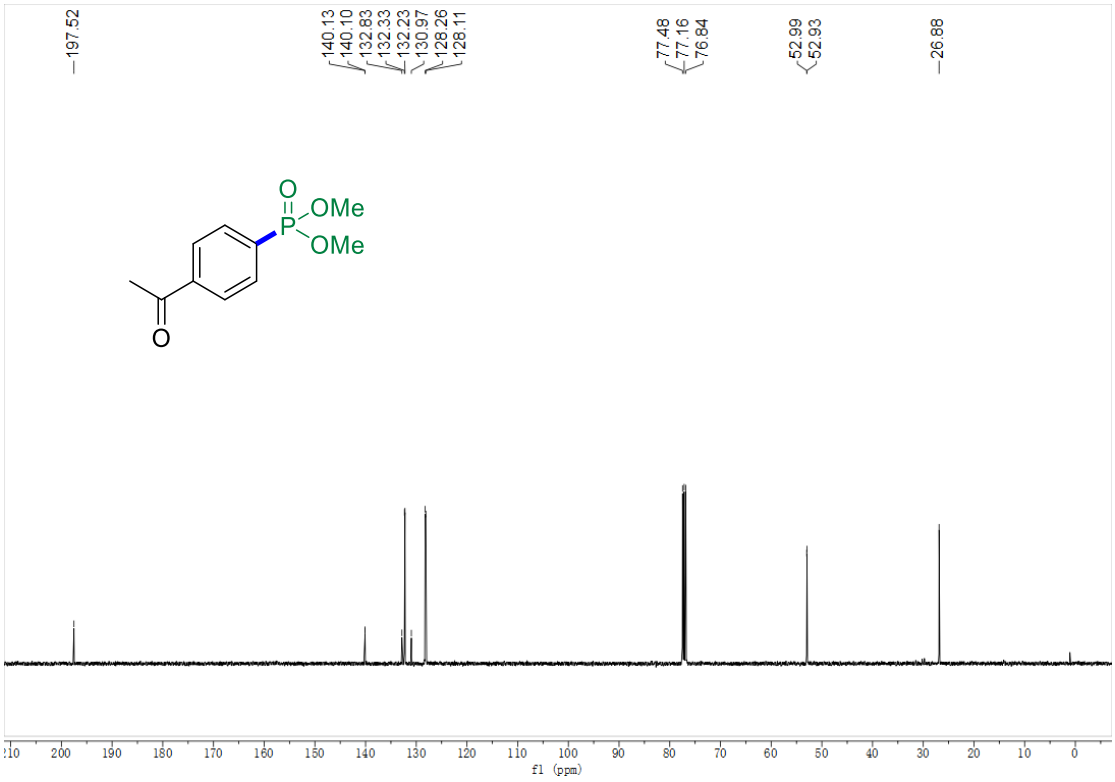
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4at**



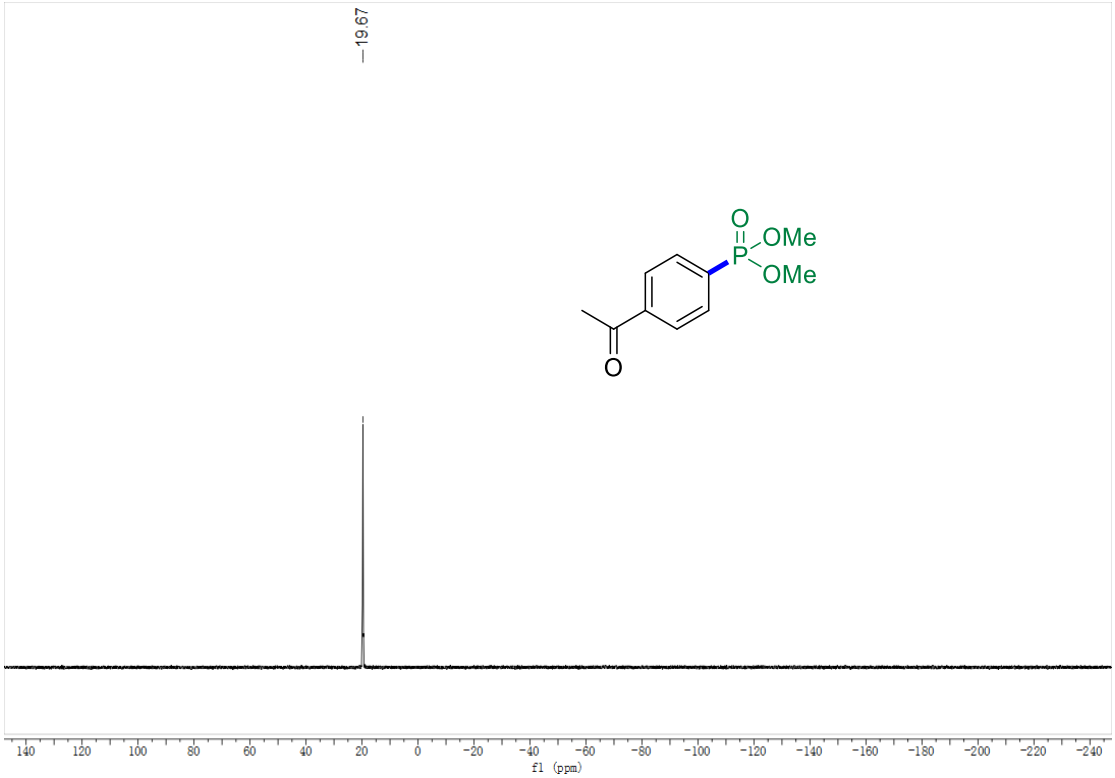
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4au**



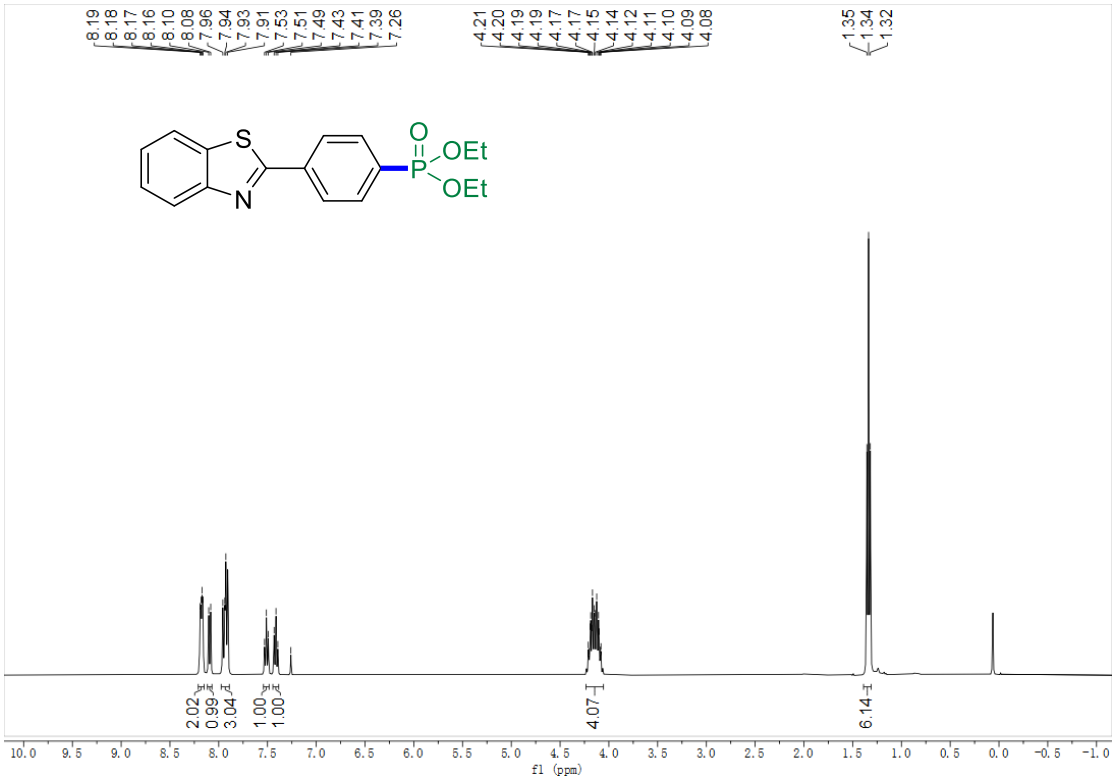
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4au**



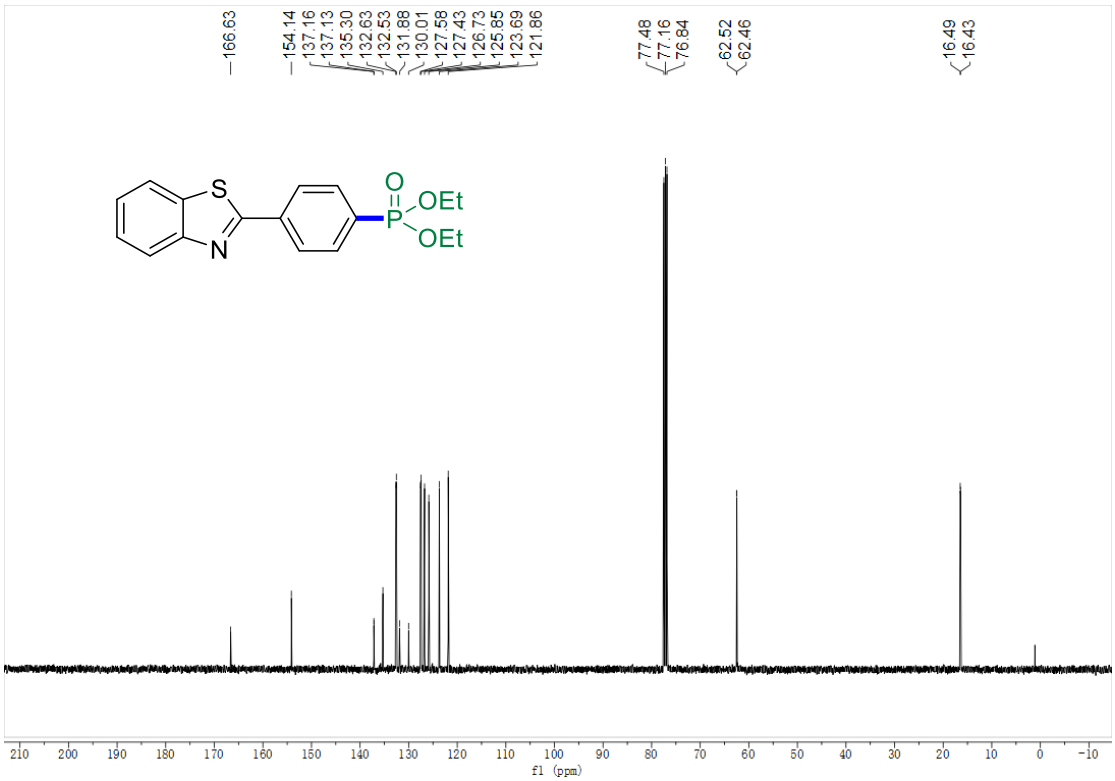
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4au**



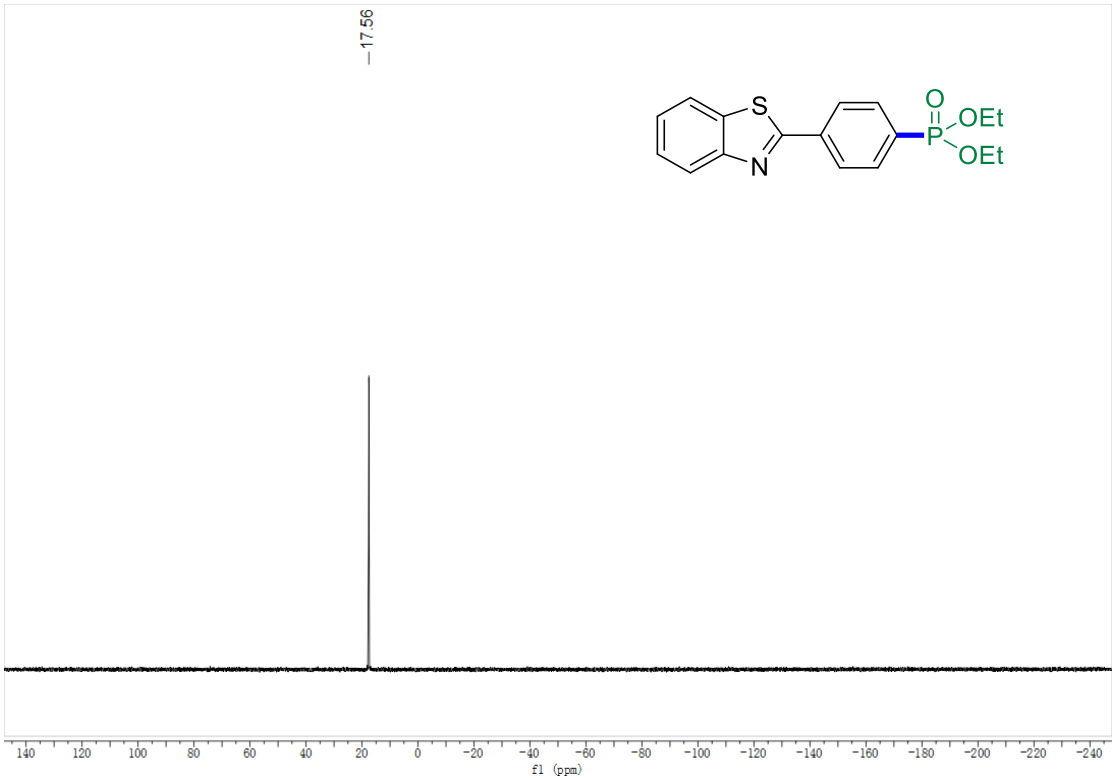
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4av**



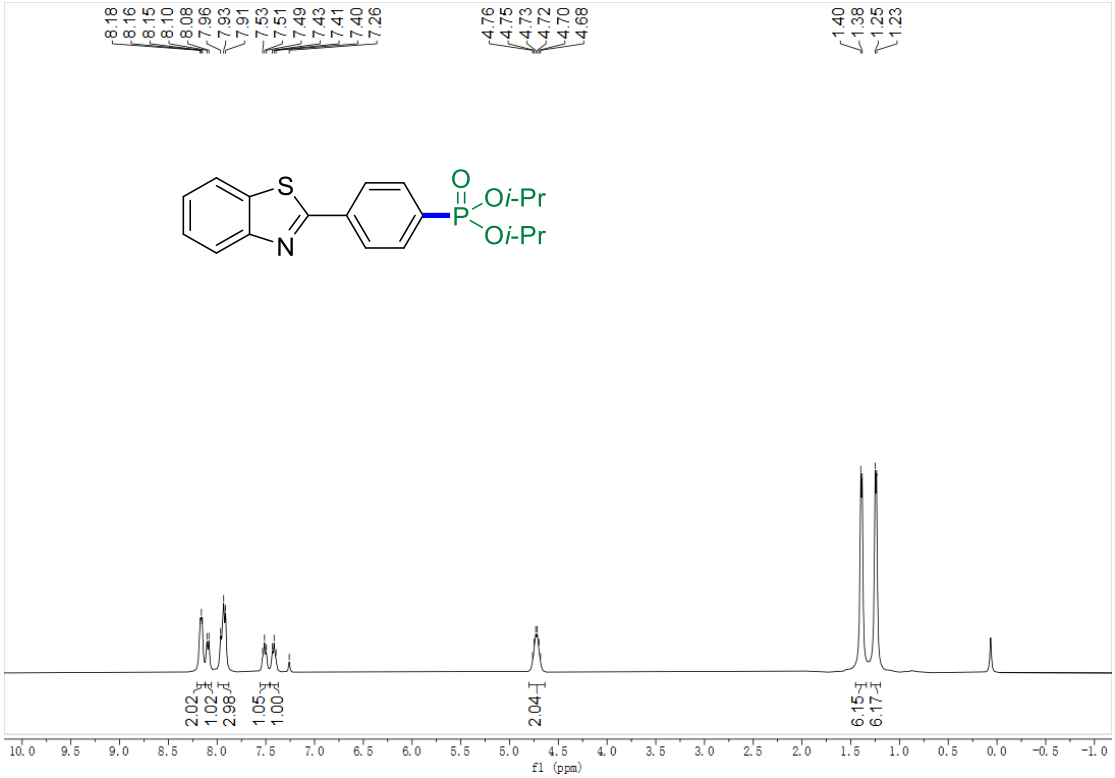
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4av**



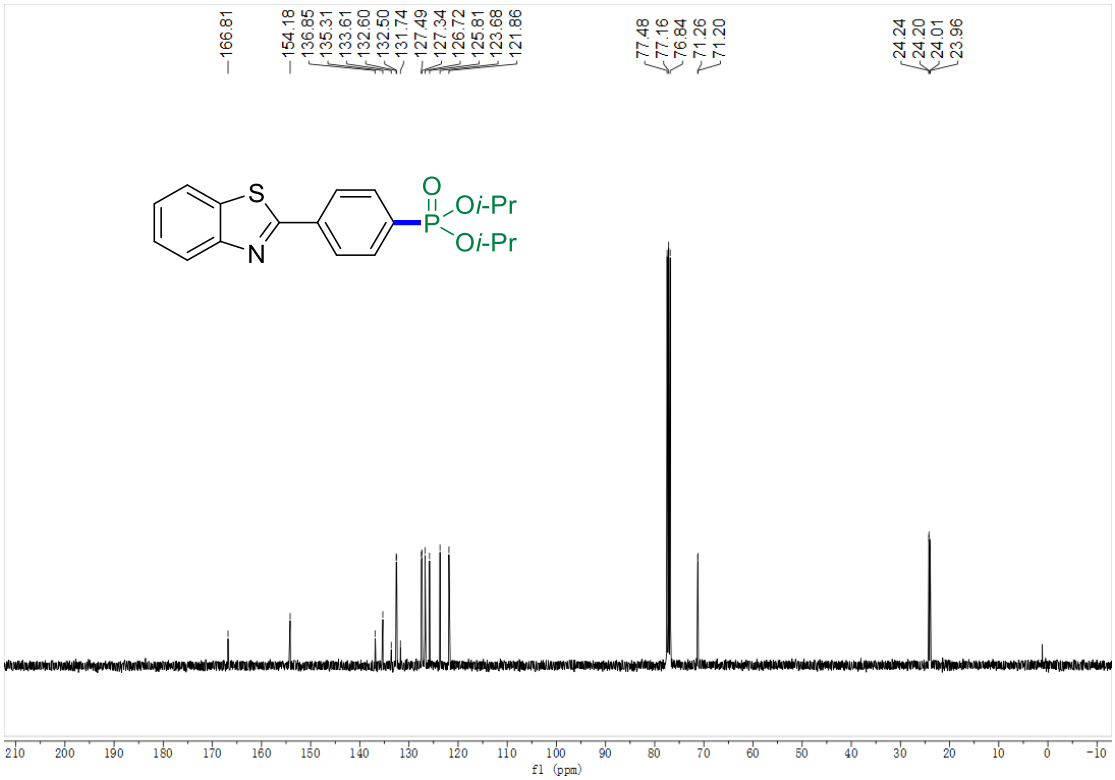
^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4av**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aw**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4aw**



^{31}P NMR (162 MHz, $CDCl_3$) Spectrum of **4aw**