Supporting Information

High-throughput experimentation and machine learning-promoted Synthesis of α-phosphoryloxy ketones via Ru-catalyzed P(O)O–H insertion reactions of sulfoxonium ylides

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1. General Information

Materials. Reactions were carried out under a nitrogen atmosphere in oven-dried Schlenk tubes unless otherwise specified. The heat source is IKA magnetic stirrer with RCT Basic. Reagents were purchased from commercial suppliers (Energy, Bidepharm, Macklin, Alfa Aesar, Sigma-Aldrich, and J&K Scientific) and used with no further purification. Catalysts and ligands were stored in glovebox. Anhydrous solvents in sure-seal bottle were purchased from Energy and used with no further purification. All reactions were set up inside Vigor glovebox with constant N_2 purge (oxygen typically < 5 ppm). Organic solutions were concentrated under reduced pressure on a Heidolph rotary evaporator using a water bath.

Instruments. ^{1}H and ^{13}C NMR spectra were recorded at 600 MHz (^{13}C at 150 MHz) on Bruker Avance III 600 MHz spectrometer as indicated. NMR spectra run in solutions of deuterated chloroform ($CDCl_3$) with residual chloroform as internal standard (7.26 ppm for ^{1}H and 77.00 ppm for ^{13}C) or in solutions of deuterated dimethyl sulfoxide (DMSO-d_6) with residual dimethyl sulfoxide as internal standard (2.50 ppm for ^{1}H, and 39.50 ppm for ^{13}C), and chemical shifts were reported in parts per million (ppm). ^{31}P NMR spectra were recorded on a Bruker Avance III 600 MHz (^{31}P at 243 MHz), and were reported unreferenced. ^{19}F NMR spectra were recorded on a Bruker Avance III 600 MHz (^{19}F at 564 MHz), and were reported unreferenced. Abbreviations for signal multiplicity are as follow: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra. Flash column chromatography was performed on silica gel (300–400 mesh) with the solvents given in the procedures. Thin layer chromatographic (TLC) analysis was performed with glass-backed silica gel plates, visualizing with UV light (254 nm). The high resolution mass spectra (HRMS) were measured on a Waters Xevo G2-XS using electrospray ionization time-of-flight (ESI-TOF).

Standard Workflow

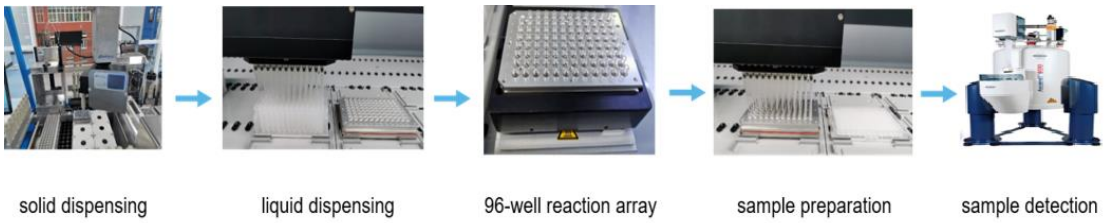


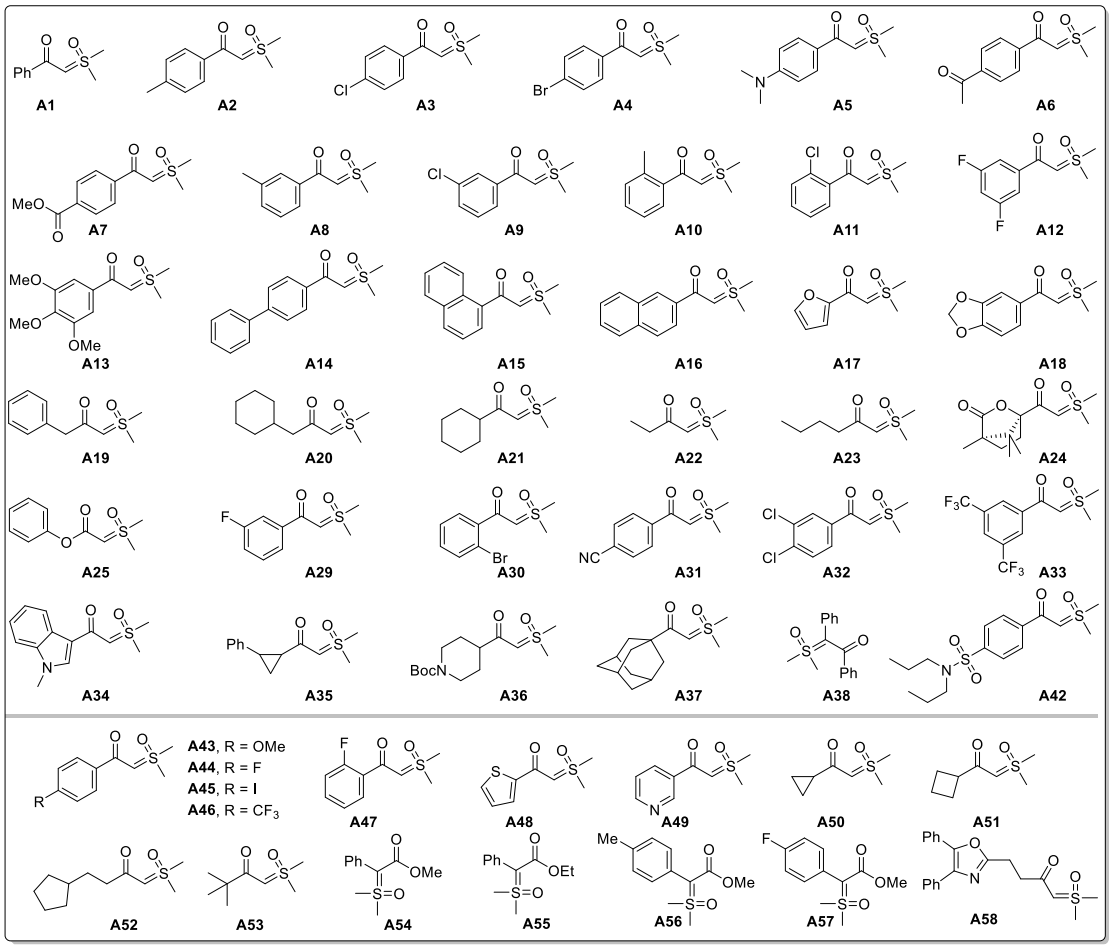
Figure S1. A 900 μL-glass tube equipped with a magnetic stir bar (C3*5 mm) was charged with catalyst (5 mol%), sulfoxonium ylide (0.0075 mmol, 1.5 equiv), and phosphinic acid (0.005 mmol, 1.0 equiv); then CH_3CN (100 μL)

was added. The plate was sealed and stirred (820 r/min in IKA RCT basic) at 100 ºC for 12 h under N_2 atmosphere. After completion of the reaction, the reaction mixture was cooled to room temperature, the plate was opened and add internal standard to each well (100 μL of 1.0 M triphenylphosphine solution in MeOH). The Opentrons 8-channels pipetting device was used to add 200 μL MeOH to each well, mixed dissolution. Then, the Opentrons 8-channels pipetting device was used to transfer 200 μL of reaction liquor to a deep well plate (each well, 2 mL). At that point, organic solutions for 2 mL deep well plate were concentrated under reduced pressure on a miniVac at 37 ºC for 4 h under 10 mbar. Finally, pipette was used to add 300 μL $CDCl_3$ to each well, mixed dissolution, were sampled into 3 mm NMR tube and analyzed by ^{31}P NMR.

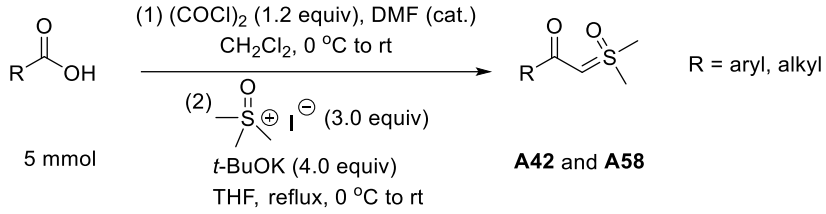
2. General Procedure for the Preparation of Sulfoxonium Ylides

A) Synthesis of Sulfoxonium Ylides

The following sulfoxonium ylides were used in this study and were prepared according to the previous literature.[1–3] Compounds **A1–A25**, **A29–A35**, **A37**, **A38**, **A43–A52**, and **A54–A57** have been our previous reported,[4,5] and their spectroscopic data matched those reported in the literature. The remaining compounds are new compounds. All new compounds have been characterized by ^{1}H NMR and ^{13}C NMR.



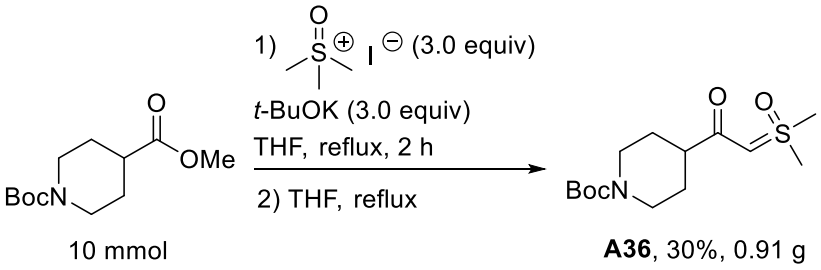
a) Synthesis of sulfoxonium ylides from carboxylic acids[1,6]



A 100 mL oven-dried round bottom flask, equipped with a magnetic stir bar, was purged with nitrogen gas and charged with carboxylic acid (5 mmol) in anhydrous dichloromethane (15 mL), which was added DMF (3 drops) at 0 °C and $(COCl)_2$ (1.2 equiv) was subsequently added dropwise by syringe. After 15 min, the reaction mixture was allowed to warm to room temperature overnight. After removal of the volatiles under vacuum, the crude product was used directly without any further purification.

The *t*-BuOK (4.0 equiv) was suspended in THF (1.0 M solution) and trimethylsulfoxonium iodide (3.0 equiv) at once in a three-necked flask fitted with a condenser. The mixture was refluxed for 2 h resulting in a yellow cloudy suspension. The reaction was cooled down to 0 °C and acyl chloride was added dropwise as a solution in THF (1.0 equiv, 1.0 M). After warming up to room temperature the mixture was stirred for 3 h. Afterwards volatiles were removed under reduced pressure and the residue was dissolved in equal amounts of ethyl acetate and H_2O. The crude product was extracted with ethyl acetate (3 × the volume of the aqueous phase), and the organic layer was then dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired sulfoxonium ylides.

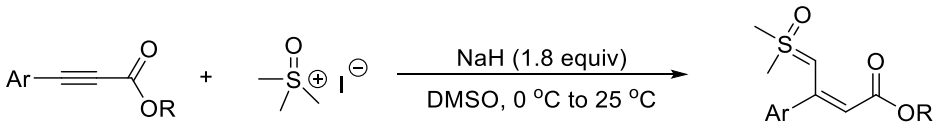
b) Synthesis of sulfoxonium ylide from carboxylate ester



The preparation of this compound was performed according to a literature reference.[7] Under N_2 atmosphere, trimethylsulfoxonium iodide (3.0 equiv) was suspended in dry THF (20 mL) in a flame-dried 100 mL round bottom flask, that was protected from light with aluminium foil. The *t*-BuOK (3 equiv) was added and the mixture was stirred at reflux for 2 hours. After cooling to room temperature, 1-(*tert*-butyl) 4-methyl piperidine-1,4-dicarboxylate (12.3 mmol, 1.0 equiv) in THF (10 mL) was added and the mixture was stirred at reflux overnight. The mixture was filtered through a plug of celite and all volatiles were removed under vacuum. Purification by flash chromatography

(DCM/MeOH = 98:2) followed by recrystallization using EtOAc/petroleum ether afforded **A36** as white solid.

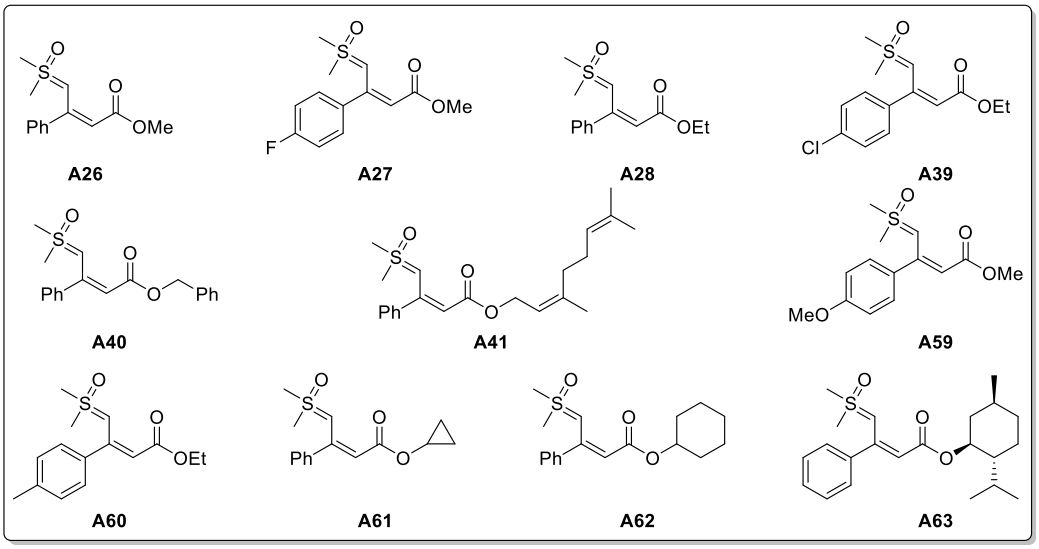
B) Synthesis of Vinyl Sulfoxonium Ylides



2 mmol (1.5 equiv) **A26-A28, A39-A41**, and **A59-A63**

The preparation of this compound was performed according to a literature reference.[8,9] To an oven-dried, N_2-purged 100 mL round-bottomed flask equipped with a magnetic stir bar, trimethylsulfoxonium iodide (1.5 equiv, 3.0 mmol) (recrystallized from water and dried at 70 ºC under vacuum overnight) is added and suspended in DMSO (15 mL). To the resulting suspension sodium hydride (1.8 equiv, 3.6 mmol) is added and stirred for 20 min at room temperature, after which it becomes a clear, homogeneous solution of dimethylsulfoxonium methylide. To a separate, oven dried, N_2-purged 100 mL round-bottom flask equipped with a magnetic stir bar, added the phenyl propiolate (1.0 equiv, 2.0 mmol) in DMSO (20 mL) and the resulting solution is cooled to 0 ºC (ice/water bath). The pre-made methylide solution is added via cannula or syringe dropwise over 5 min. The resulting mixture is stirred for 2 hours at room temperature and then poured into crushed ice (75 mL by volume) with vigorous stirring. The precipitate was collected, washed with *n*-hexane and used directly without further purification.

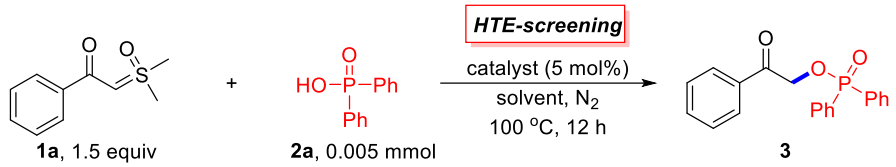
The following vinyl sulfoxonium ylides were used in this study.



3. General Experimental Procedure

A) Reaction Optimization

Table S1. HTE screening of catalyst and solvent for P(O)O–H insertion reaction of 1a and 2a[a]

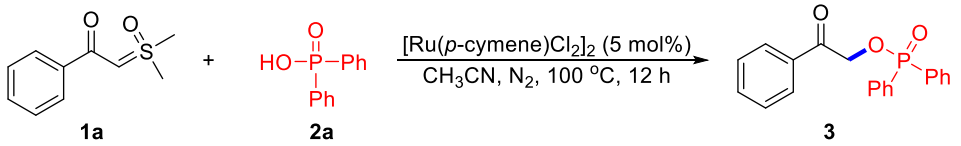


	[Ru(*p*-cymene)Cl$_2$]$_2$	Ru(acac)$_3$	RuCl$_3$	[Rh(COD)Cl]$_2$	[Rh(Cp*)Cl$_2$]$_2$	[Ir(COD)Cl]$_2$	Pd(OAc)$_2$	CF$_3$COOAg	Cu(acac)$_2$	CuI	FeCl$_3$	Co(acac)$_3$
DCE	**89**	**25**	**33**	**22**	**13**	**10**	**10**	**0**	**3**	**0**	**25**	**0**
THF	**70**	**0**	**0**	**24**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
1,4-dioxane	**60**	**21**	**0**	**58**	**14**	**20**	**18**	**10**	**6**	**0**	**8**	**0**
toluene	**76**	**14**	**18**	**52**	**21**	**16**	**4**	**6**	**0**	**0**	**0**	**0**
CH$_3$CN	**93**	**28**	**27**	**33**	**34**	**42**	**18**	**0**	**12**	**20**	**56**	**7**
DMF	**47**	**21**	**13**	**43**	**36**	**0**	**11**	**0**	**10**	**0**	**0**	**0**
DMSO	**3**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
MeOH	**4**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

numbers indicated yield (%) of **3**

[a]Reaction conditions: **1a** (0.0075 mmol), **2a** (0.005 mmol), catalyst (5 mol%) in solvent (100 μL) at 100 °C for 12 h under N_2 atmosphere. Yields were determined by ^{31}P NMR using triphenylphosphine as internal standard.

Table S2. Screening of temperature for P(O)O–H insertion reaction of 1a and 2a[a]

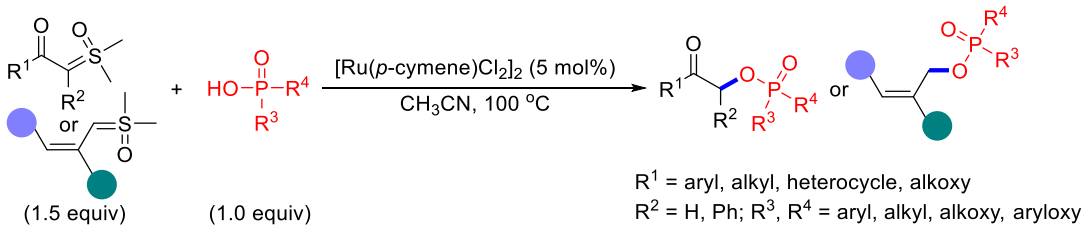


entry	catalyst	temp (°C)	**3a** (%)[b]
1	[Ru(*p*-cymene)Cl$_2$]$_2$	100	95
2	[Ru(*p*-cymene)Cl$_2$]$_2$	120	88
3	[Ru(*p*-cymene)Cl$_2$]$_2$	80	42
4	-	100	12
5[c]	[Ru(*p*-cymene)Cl$_2$]$_2$	100	81

[a]Reaction conditions: **1a** (0.15 mmol), **2a** (0.10 mmol), and [Ru(*p*-cymene)Cl$_2$]$_2$ (5 mol%) in CH$_3$CN (1.0 mL) at 100 °C for 12 h under N_2 atmosphere. [b]Yields were determined by ^{31}P NMR using triphenylphosphine as internal standard. [c][Ru(*p*-cymene)Cl$_2$]$_2$ (2.5 mol%), 24 h.

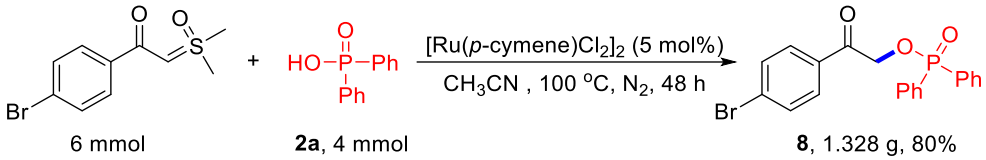
We tested different reaction temperatures and observed that 100 °C was the most efficient (Table S2, entries 1−3). Interestingly, a 12% yield of **3** was achieved in the absence of the catalyst (Table S2, entry 4). Although the reaction could proceed without it, the ruthenium catalyst was essential for enhancing the reaction efficiency. In addition, an 81% yield was obtained when the catalyst loading was reduced to 2.5 mol% (Table S2, entry 5).

B) General Experimental Procedure for Ru-Catalyzed P(O)O–H Insertion Reactions of Sulfoxonium Ylides



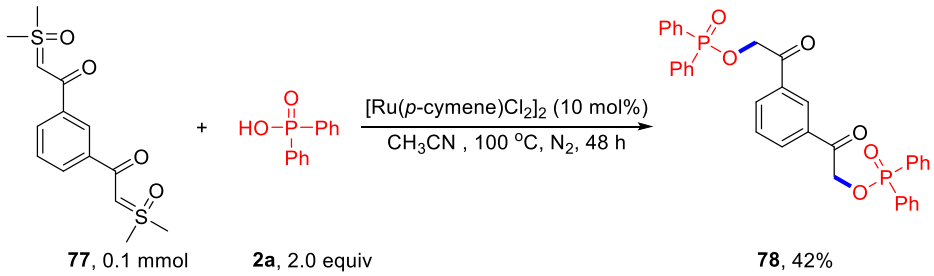
An oven dried Schlenk tube of 25 mL equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (3. 0 mg, 0.005 mmol, 5 mol%), sulfoxonium ylide (0.15 mmol, 1.5 equiv), and phosphinic acid (0.1 mmol, 1.0 equiv); then CH_3CN (1.0 mL) was added. The reaction mixture was stirred (820 r/min in IKA RCT basic) at 100 °C for 12 h under N_2 atmosphere. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude product was extracted with ethyl acetate (3 × 3.0 mL), and the solution was washed with saturated solution of NH_4Cl (3.0 mL), and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired products.

C) Gram-Scale Synthesis of 8



An oven dried Schlenk tube of 100 mL equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (120 mg, 0.2 mmol, 5 mol%), sulfoxonium ylide (6 mmol, 1.5 equiv), and diphenylphosphinic acid (**2a**, 4 mmol, 1.0 equiv); then CH_3CN (40 mL) was added. The reaction mixture was stirred (820 r/min in IKA RCT basic) at 100 °C for 48 h under N_2 atmosphere. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude product was extracted with ethyl acetate (3 × 15 mL), and the solution was washed with saturated solution of NH_4Cl (25 mL), and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to afford α-phosphoryloxy ketone **8** in 80% yield (1.328 g).

D) Synthesis of Bis-α-Phosphoryloxy Ketone 75

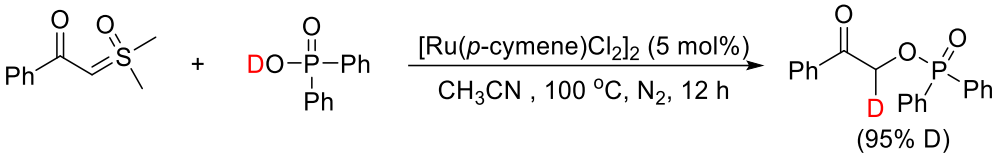


77, 0.1 mmol **2a**, 2.0 equiv **78**, 42%

An oven dried Schlenk tube of 25 mL equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (6 mg, 0.01 mmol, 10 mol%), sulfoxonium ylide (**77**, 0.1 mmol, 1.0 equiv), and diphenylphosphinic acid (**2a**, 0.2 mmol, 2.0 equiv); then CH_3CN (1.0 mL) was added. The reaction mixture was stirred (820 r/min in IKA RCT basic) at 100 °C for 48 h under N_2 atmosphere. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude product was extracted with dichloromethane (3 × 3.0 mL), and the solution was washed with saturated solution of NH_4Cl (3.0 mL), and dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to afford bis-α-phosphoryloxy ketone **78** in 42% yield (24.9 mg).

4. Reaction Mechanism

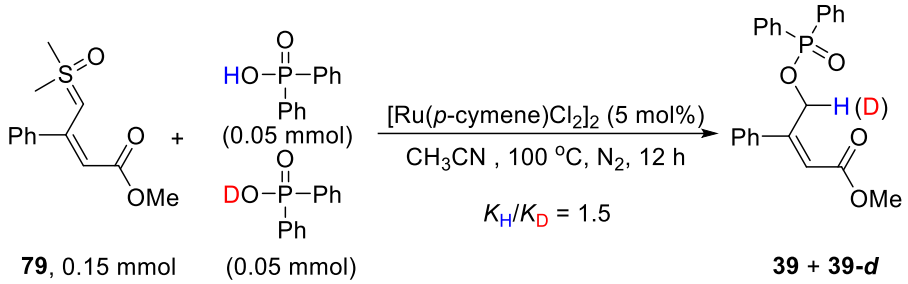
A) Deuterium Labeling Experiment



1a, 1.5 equiv **2a-*d***, 0.1 mmol **3-*d***, 77%

An oven dried Schlenk tube of 25 mL equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (3 mg, 0.005 mmol, 5 mol%), sulfoxonium ylide **1a** (0.15 mmol, 1.5 equiv), and deuterated diphenylphosphinic acid (**2a-*d***, 0.2 mmol, 2.0 equiv); then CH_3CN (1.0 mL) was added. The reaction mixture was stirred (820 r/min in IKA RCT basic) at 100 ºC for 12 h under N_2 atmosphere. After completion, the reaction mixture was returned to room temperature. The crude product was extracted with ethyl acetate (3 × 3.0 mL), and the solution was washed with saturated solution of NH_4Cl (3.0 mL), and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to afford the product **3-*d*** in 77% yield (26.0 mg).

B) Competitive Kinetic Isotopic Experiment



79, 0.15 mmol (0.05 mmol) **39** + **39-*d***

An oven dried Schlenk tube of 25 mL equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (3.0 mg, 0.005 mmol, 5 mol%), vinyl sulfoxonium ylide (**79**, 0.15 mmol, 1.5 equiv), and CH_3CN (1.0 mL); then diphenylphosphinic acid (**2a**, 0.05 mmol, 0.5 equiv) and deuterated diphenylphosphinic acid (**2a-*d***, 0.05 mmol, 0.5 equiv) were added. The reaction mixture was stirred (820 r/min in IKA RCT basic) at 100 ºC for 12 h under N_2 atmosphere. After completion, the reaction mixture was returned to room temperature. The crude product was extracted with ethyl acetate (3 × 3.0 mL), and the solution was washed with saturated solution of NH_4Cl (3.0 mL), and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the mixture of **39** and **39-*d*** in 63% yield (K_H/K_D = 1.5, 24.7 mg). KIE was determined by ^{1}H NMR analysis (Figure S2).

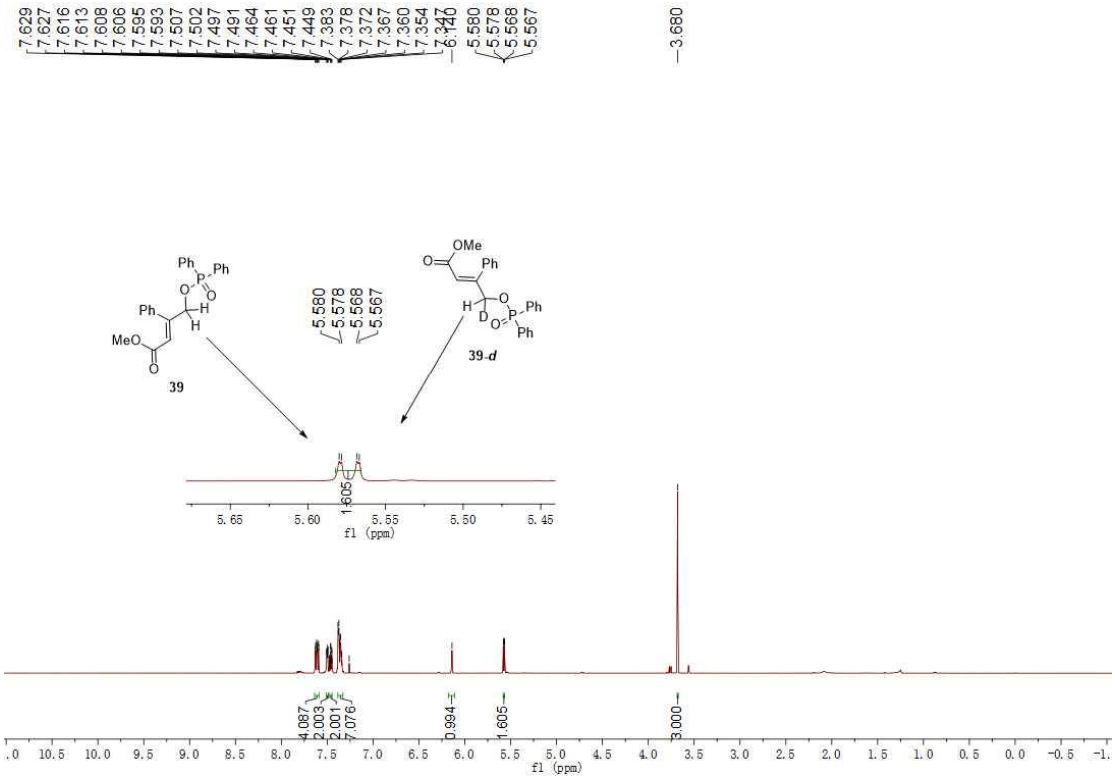
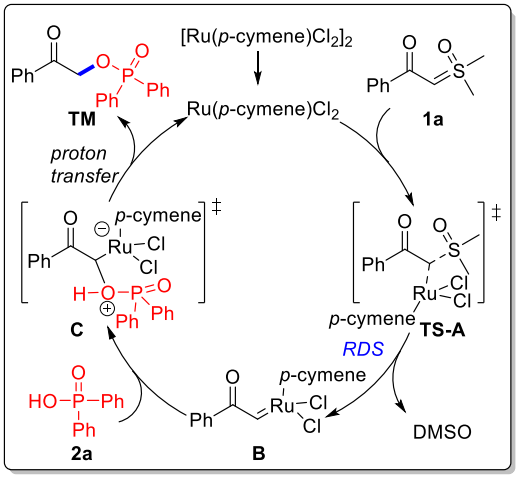


Figure S2. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of kinetic isotope experiment.

The above results suggested that the metal carbene formation, rather than the proton transfer, was most probably the rate-determining step (RDS)..

Scheme S1. Proposed Reaction Mechanism



Initially, the ruthenium catalyst coordinates to the sulfoxonium ylide **1a** to form transition state **TS-A**, subsequently, which releases a molecule of DMSO to produce highly active Ru-carbene species intermediate **B**. Then, Ru-carbene reacts with diphenylphosphinic acid **2a** to form an oxonium ylide intermediate **C**. Finally, intermediate **C** undergoes an intramolecular proton transfer, giving the desired O–H insertion product (TM) and regenerating the ruthenium catalyst.

5. HTE for Substrate Scope

a) Reaction Setup

A 900 μL-glass tube equipped with a magnetic stir bar (C3*5 mm) was charged with catalyst (5 mol%), sulfoxonium ylide (0.0075 mmol, 1.5 equiv), and phosphinic acid (0.005 mmol, 1.0 equiv); then CH_3CN (100 μL) was added. The plate was sealed and stirred (820 r/min in IKA RCT basic) at 100 ºC for 12 h under N_2 atmosphere. After completion of the reaction, the reaction mixture was cooled to room temperature, the plate was opened and add internal standard to each well (100 μL of 1.0 M triphenylphosphine solution in MeOH). The Opentrons 8-channels pipetting device was used to add 200 μL MeOH to each well, mixed dissolution. Then, the Opentrons 8-channels pipetting device was used to transfer 200 μL of reaction liquor to a deep well plate (each well, 2 mL). At that point, organic solutions for 2 mL deep well plate were concentrated under reduced pressure on a miniVac at 37 ºC for 4 h under 10 mbar. Finally, pipette was used to add 300 μL $CDCl_3$ to each well, mixed dissolution, were sampled into 3 mm NMR tube and analyzed by ^{31}P NMR.

b) Plate Layout

Under optimal conditions, below is a summary **(Figure S3)** of other 28 sulfoxonium ylides and 15 phosphinic acids used in this work, furnishing 420 scattered of micromolar reactions via HTE.

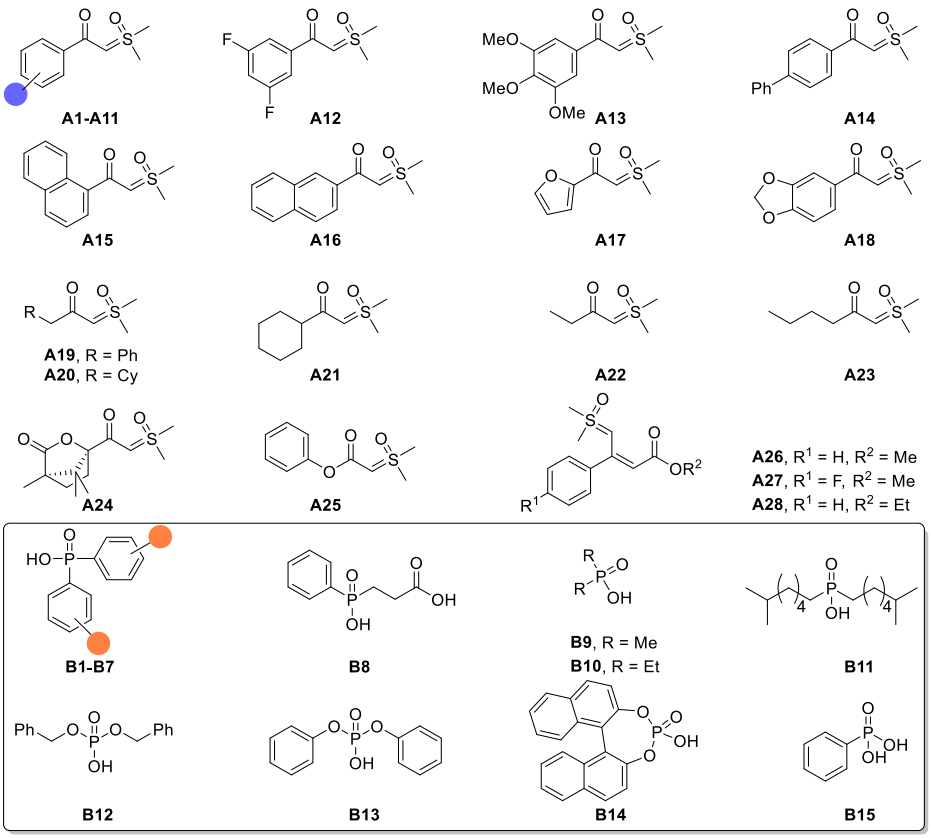


Figure S3. All reaction components for 420 scattered of micromolar reactions.

Table S3−S7 describe the components of each well for each plate.

Table S3. Layout of plate 1.

	1	2	3	4	5	6	7	8	9	10	11
A	A1/B1	A9/B1	A17/B1	A25/B1	A5/B2	A13/B2	A21/B2	A1/B3	A9/B3	A17/B3	A25/B3
B	A2/B1	A10/B1	A18/B1	A26/B1	A6/B2	A14/B2	A22/B2	A2/B3	A10/B3	A18/B3	A26/B3
C	A3/B1	A11/B1	A19/B1	A27/B1	A7/B2	A15/B2	A23/B2	A3/B3	A11/B3	A19/B3	A27/B3
D	A4/B1	A12/B1	A20/B1	A28/B1	A8/B2	A16/B2	A24/B2	A4/B3	A12/B3	A20/B3	A28/B3
E	A5/B1	A13/B1	A21/B1	A1/B2	A9/B2	A17/B2	A25/B2	A5/B3	A13/B3	A21/B3	
F	A6/B1	A14/B1	A22/B1	A2/B2	A10/B2	A18/B2	A26/B2	A6/B3	A14/B3	A22/B3	
G	A7/B1	A15/B1	A23/B1	A3/B2	A11/B2	A19/B2	A27/B2	A7/B3	A15/B3	A23/B3	
H	A8/B1	A16/B1	A24/B1	A4/B2	A12/B2	A20/B2	A28/B2	A8/B3	A16/B3	A24/B3	

Table S4. Layout of plate 2.

	1	2	3	4	5	6	7	8	9	10	11
A	A1/B4	A9/B4	A17/B4	A25/B4	A5/B5	A13/B5	A21/B5	A1/B6	A9/B6	A17/B6	A25/B6
B	A2/B4	A10/B4	A18/B4	A26/B4	A6/B5	A14/B5	A22/B5	A2/B6	A10/B6	A18/B6	A26/B6
C	A3/B4	A11/B4	A19/B4	A27/B4	A7/B5	A15/B5	A23/B5	A3/B6	A11/B6	A19/B6	A27/B6
D	A4/B4	A12/B4	A20/B4	A28/B4	A8/B5	A16/B5	A24/B5	A4/B6	A12/B6	A20/B6	A28/B6
E	A5/B4	A13/B4	A21/B4	A1/B5	A9/B5	A17/B5	A25/B5	A5/B6	A13/B6	A21/B6	
F	A6/B4	A14/B4	A22/B4	A2/B5	A10/B5	A18/B5	A26/B5	A6/B6	A14/B6	A22/B6	
G	A7/B4	A15/B4	A23/B4	A3/B5	A11/B5	A19/B5	A27/B5	A7/B6	A15/B6	A23/B6	
H	A8/B4	A16/B4	A24/B4	A4/B5	A12/B5	A20/B5	A28/B5	A8/B6	A16/B6	A24/B6	

Table S5. Layout of plate 3.

	1	2	3	4	5	6	7	8	9	10	11
A	A1/B7	A9/B7	A17/B7	A25/B7	A5/B8	A13/B8	A21/B8	A1/B9	A9/B9	A17/B9	A25/B9
B	A2/B7	A10/B7	A18/B7	A26/B7	A6/B8	A14/B8	A22/B8	A2/B9	A10/B9	A18/B9	A26/B9
C	A3/B7	A11/B7	A19/B7	A27/B7	A7/B8	A15/B8	A23/B8	A3/B9	A11/B9	A19/B9	A27/B9
D	A4/B7	A12/B7	A20/B7	A28/B7	A8/B8	A16/B8	A24/B8	A4/B9	A12/B9	A20/B9	A28/B9
E	A5/B7	A13/B7	A21/B7	A1/B8	A9/B8	A17/B8	A25/B8	A5/B9	A13/B9	A21/B9	
F	A6/B7	A14/B7	A22/B7	A2/B8	A10/B8	A18/B8	A26/B8	A6/B9	A14/B9	A22/B9	
G	A7/B7	A15/B7	A23/B7	A3/B8	A11/B8	A19/B8	A27/B8	A7/B9	A15/B9	A23/B9	
H	A8/B7	A16/B7	A24/B7	A4/B8	A12/B8	A20/B8	A28/B8	A8/B9	A16/B9	A24/B9	

Table S6. Layout of plate 4.

	1	2	3	4	5	6	7	8	9	10	11
A	A1/B10	A9/B10	A17/B10	A25/B10	A5/B11	A13/B11	A21/B11	A1/B12	A9/B12	A17/B12	A25/B12
B	A2/B10	A10/B10	A18/B10	A26/B10	A6/B11	A14/B11	A22/B11	A2/B12	A10/B12	A18/B12	A26/B12
C	A3/B10	A11/B10	A19/B10	A27/B10	A7/B11	A15/B11	A23/B11	A3/B12	A11/B12	A19/B12	A27/B12
D	A4/B10	A12/B10	A20/B10	A28/B10	A8/B11	A16/B11	A24/B11	A4/B12	A12/B12	A20/B12	A28/B12
E	A5/B10	A13/B10	A21/B10	A1/B11	A9/B11	A17/B11	A25/B11	A5/B12	A13/B12	A21/B12	
F	A6/B10	A14/B10	A22/B10	A2/B11	A10/B11	A18/B11	A26/B11	A6/B12	A14/B12	A22/B12	
G	A7/B10	A15/B10	A23/B10	A3/B11	A11/B11	A19/B11	A27/B11	A7/B12	A15/B12	A23/B12	
H	A8/B10	A16/B10	A24/B10	A4/B11	A12/B11	A20/B11	A28/B11	A8/B12	A16/B12	A24/B12	

Table S7. Layout of plate 5.

	1	2	3	4	5	6	7	8	9	10	11
A	A1/B13	A9/B13	A17/B13	A25/B13	A5/B14	A13/B14	A21/B14	A1/B15	A9/B15	A17/B15	A25/B15
B	A2/B13	A10/B13	A18/B13	A26/B13	A6/B14	A14/B14	A22/B14	A2/B15	A10/B15	A18/B15	A26/B15
C	A3/B13	A11/B13	A19/B13	A27/B13	A7/B14	A15/B14	A23/B14	A3/B15	A11/B15	A19/B15	A27/B15
D	A4/B13	A12/B13	A20/B13	A28/B13	A8/B14	A16/B14	A24/B14	A4/B15	A12/B15	A20/B15	A28/B15
E	A5/B13	A13/B13	A21/B13	A1/B14	A9/B14	A17/B14	A25/B14	A5/B15	A13/B15	A21/B15	
F	A6/B13	A14/B13	A22/B13	A2/B14	A10/B14	A18/B14	A26/B14	A6/B15	A14/B15	A22/B15	
G	A7/B13	A15/B13	A23/B13	A3/B14	A11/B14	A19/B14	A27/B14	A7/B15	A15/B15	A23/B15	
H	A8/B13	A16/B13	A24/B13	A4/B14	A12/B14	A20/B14	A28/B14	A8/B15	A16/B15	A24/B15	

c) Yield Determination

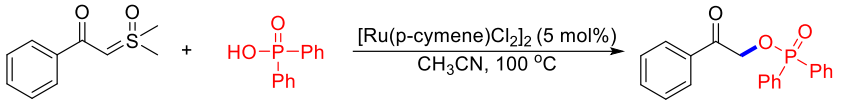


Figure S4. Reaction summary for plate 1, row 1, column 1.

In light of the unique ^{31}P NMR shift of the α-phosphoryloxy ketones, we were able to identify the reaction yield by ^{31}P NMR analysis. The reaction above (**Figure S4**) was set up in 96-well plate 1 (84 reactions) following the HTE protocol described in the general section. After 12 h, the reaction was analyzed by ^{31}P NMR ($CDCl_3$) and the yield determined using triphenylphosphine as an internal standard (**Figure S5**).

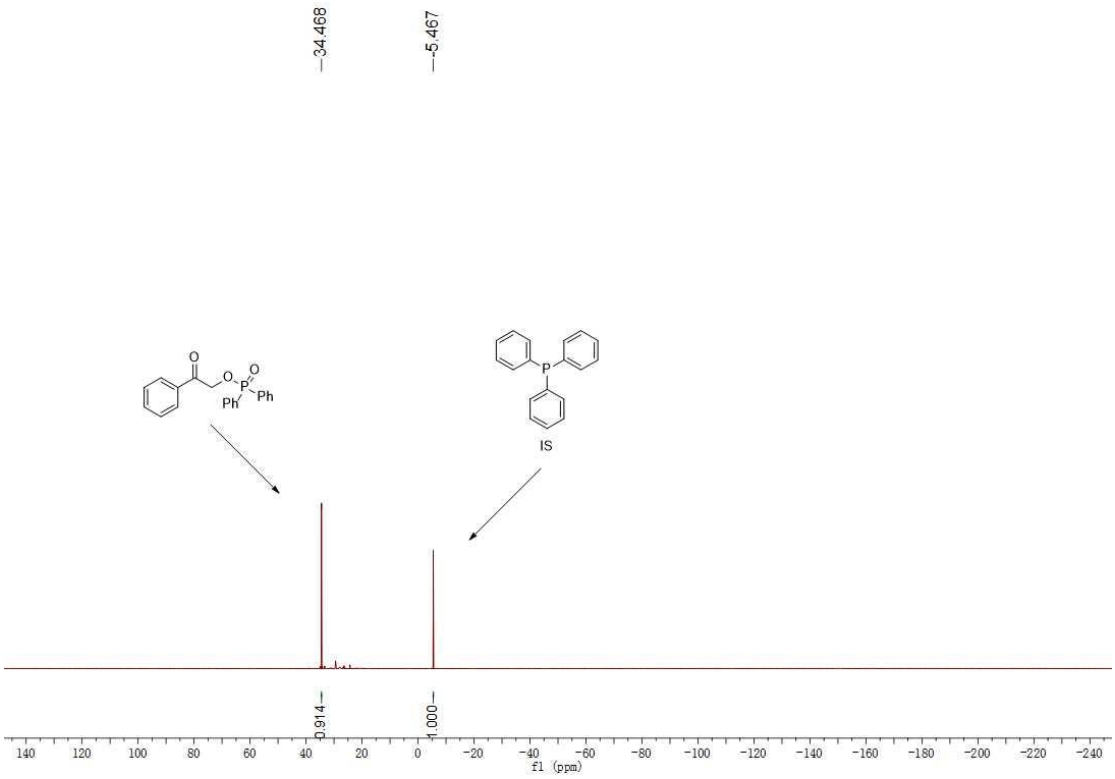


Figure S5. Crude ^{31}P NMR spectra for plate 1, row 1, column 1.

Table S8. Chemical shifts of ^{31}P NMR of product and internal standard.

entry	characteristic peak	chemical shift	results
product	P compound (s)	34.47 ppm	0.91, 91% yield
internal standard	PPh_3 (s)	-5.47 ppm	1

d) Reaction Yield Presented as Heatmap

	1	2	3	4	5	6	7	8	9	10	11
A	91	88	81	0	45	75	60	55	53	43	0
B	81	74	75	70	52	70	47	57	42	39	47
C	95	79	70	68	35	69	55	62	48	30	42
D	93	63	65	82	64	72	48	67	30	33	53
E	80	80	79	75	61	67	0	41	56	34	
F	61	58	61	74	43	59	87	34	65	22	
G	46	90	60	78	65	84	72	32	24	31	
H	77	95	58	75	36	58	77	55	45	39	

Figure S6. Plate 1 yields (%).

	1	2	3	4	5	6	7	8	9	10	11
A	79	47	52	0	64	80	60	56	56	49	0
B	78	65	51	50	58	88	50	65	65	52	50
C	83	57	63	50	45	73	51	72	72	49	57
D	72	48	49	37	80	80	60	66	66	42	51
E	52	39	48	96	85	73	0	49	49	40	
F	47	75	49	93	76	0	73	45	45	22	
G	44	78	57	90	76	60	64	36	36	23	
H	65	82	47	91	68	76	66	54	54	43	

Figure S7. Plate 2 yields (%).

	1	2	3	4	5	6	7	8	9	10	11
A	67	55	53	0	1	0	3	80	65	65	0
B	62	55	58	60	6	3	4	80	62	40	25
C	70	48	52	64	0	0	3	74	45	40	20
D	72	41	46	63	6	0	6	73	70	30	26
E	60	36	48	6	2	5	0	42	29	32	
F	35	69	31	6	0	4	0	42	82	30	
G	31	67	20	3	4	0	0	31	72	20	
H	60	71	48	0	0	0	0	69	76	10	

Figure S8. Plate 3 yields (%).

	1	2	3	4	5	6	7	8	9	10	11
A	78	62	71	0	41	35	0	41	58	20	0
B	87	65	67	4	30	58	0	36	44	41	69
C	85	66	45	0	26	38	0	30	48	36	62
D	78	62	25	9	39	41	2	46	51	48	60
E	53	74	20	43	38	17	0	57	57	52	
F	58	86	18	44	32	27	0	37	71	23	
G	30	81	11	46	36	10	0	44	58	46	
H	80	73	20	40	35	0	0	35	60	30	

Figure S9. Plate 4 yields (%).

	1	2	3	4	5	6	7	8	9	10	11
A	21	12	10	0	0	0	0	30	30	16	0
B	23	6	2	21	0	0	0	33	33	15	51
C	21	8	13	21	0	0	0	29	29	16	62
D	18	8	4	35	0	0	0	37	37	18	59
E	4	15	4	0	0	0	0	8	8	12	
F	6	13	15	0	0	0	0	0	0	10	
G	5	12	6	0	0	0	0	16	16	14	
H	10	15	13	0	0	0	0	36	36	5	

Figure S10. Plate 5 yields (%).

6. HTE for 336 Unknown Reactions

a) Plate Layout

Under optimal conditions, we performed the 336 reactions for external dataset prediction via THE, which were randomly designed by experimenters. As shown in **Figure S11**, those new reactions included some unseen substrates, such as sulfoxonium ylides (**A29−A42**) and phosphinic acids (**B16−B18**).

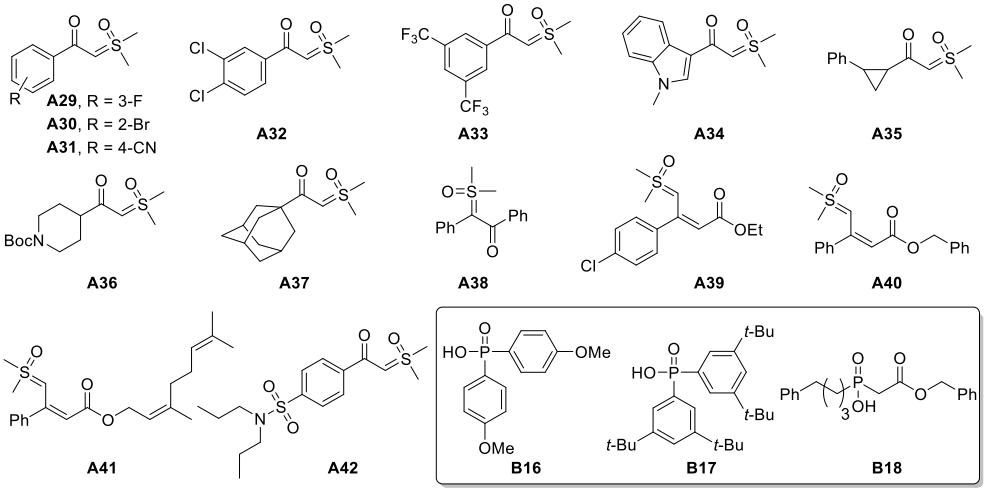


Figure S11. Unseen substrates.

Table S9−S13 describe the components of each well for each plate (42 sulfoxonium ylides and 18 phosphinic acids).

Table S9. Layout of plate 6.

	1	2	3	4	5	6	7	8	9	10	11
A	A29/B1	A37/B1	A31/B2	A39/B2	A33/B3	A41/B3	A35/B4	A29/B5	A37/B5	A31/B6	A39/B6
B	A30/B1	A38/B1	A32/B2	A40/B2	A34/B3	A42/B3	A36/B4	A30/B5	A38/B5	A32/B6	A40/B6
C	A31/B1	A39/B1	A33/B2	A41/B2	A35/B3	A29/B4	A37/B4	A31/B5	A39/B5	A33/B6	A41/B6
D	A32/B1	A40/B1	A34/B2	A42/B2	A36/B3	A30/B4	A38/B4	A32/B5	A40/B5	A34/B6	A42/B6
E	A33/B1	A41/B1	A35/B2	A29/B3	A37/B3	A31/B4	A39/B4	A33/B5	A41/B5	A35/B6	
F	A34/B1	A42/B1	A36/B2	A30/B3	A38/B3	A32/B4	A40/B4	A34/B5	A42/B5	A36/B6	
G	A35/B1	A29/B2	A37/B2	A31/B3	A39/B3	A33/B4	A41/B4	A35/B5	A29/B6	A37/B6	
H	A36/B1	A30/B2	A38/B2	A32/B3	A40/B3	A34/B4	A42/B4	A36/B5	A30/B6	A38/B6	

Table S10. Layout of plate 7.

	1	2	3	4	5	6	7	8	9	10	11
A	A29/B7	A37/B7	A31/B8	A39/B8	A33/B9	A41/B9	A35/B10	A29/B11	A37/B11	A31/B12	A39/B12
B	A30/B7	A38/B7	A32/B8	A40/B8	A34/B9	A42/B9	A36/B10	A30/B11	A38/B11	A32/B12	A40/B12
C	A31/B7	A39/B7	A33/B8	A41/B8	A35/B9	A29/B10	A37/B10	A31/B11	A39/B11	A33/B12	A41/B12
D	A32/B7	A40/B7	A34/B8	A42/B8	A36/B9	A30/B10	A38/B10	A32/B11	A40/B11	A34/B12	A42/B12
E	A33/B7	A41/B7	A35/B8	A29/B9	A37/B9	A31/B10	A39/B10	A33/B11	A41/B11	A35/B12	
F	A34/B7	A42/B7	A36/B8	A30/B9	A38/B9	A32/B10	A40/B10	A34/B11	A42/B11	A36/B12	
G	A35/B7	A29/B8	A37/B8	A31/B9	A39/B9	A33/B10	A41/B10	A35/B11	A29/B12	A37/B12	
H	A36/B7	A30/B8	A38/B8	A32/B9	A40/B9	A34/B10	A42/B10	A36/B11	A30/B12	A38/B12	

Table S11. Layout of plate 8.

	1	2	3	4	5	6
A	A29/B13	A37/B13	A31/B14	A39/B14	A33/B15	A41/B15
B	A30/B13	A38/B13	A32/B14	A40/B14	A34/B15	A42/B15
C	A31/B13	A39/B13	A33/B14	A41/B14	A35/B15	
D	A32/B13	A40/B13	A34/B14	A42/B14	A36/B15	
E	A33/B13	A41/B13	A35/B14	A29/B15	A37/B15	
F	A34/B13	A42/B13	A36/B14	A30/B15	A38/B15	
G	A35/B13	A29/B14	A37/B14	A31/B15	A39/B15	
H	A36/B13	A30/B14	A38/B14	A32/B15	A40/B15	

Table S12. Layout of plate 9.

	1	2	3	4	5	6	7	8	9	10	11
A	A1/B16	A9/B16	A17/B16	A25/B16	A33/B16	A41/B16	A7/B17	A15/B17	A23/B17	A31/B17	A39/B7
B	A2/B16	A10/B16	A18/B16	A26/B16	A34/B16	A42/B16	A8/B17	A16/B17	A24/B17	A32/B17	A40/B17
C	A3/B16	A11/B16	A19/B16	A27/B16	A35/B16	A1/B17	A9/B17	A17/B17	A25/B17	A33/B17	A41/B17
D	A4/B16	A12/B16	A20/B16	A28/B16	A36/B16	A2/B17	A10/B17	A18/B17	A26/B17	A34/B17	A42/B17
E	A5/B16	A13/B16	A21/B16	A29/B16	A37/B16	A3/B17	A11/B17	A19/B17	A27/B17	A35/B17	
F	A6/B16	A14/B16	A22/B16	A30/B16	A38/B16	A4/B17	A12/B17	A20/B17	A28/B17	A36/B17	
G	A7/B16	A15/B16	A23/B16	A31/B16	A39/B16	A5/B17	A13/B17	A21/B17	A29/B17	A37/B17	
H	A8/B16	A16/B16	A24/B16	A32/B16	A40/B16	A6/B17	A14/B17	A22/B17	A30/B17	A38/B17	

Table S13. Layout of plate 10.

	1	2	3	4	5	6
A	A1/B18	A9/B18	A17/B18	A25/B18	A33/B18	A41/B18
B	A2/B18	A10/B18	A18/B18	A26/B18	A34/B18	A42/B18
C	A3/B18	A11/B18	A19/B18	A27/B18	A35/B18	
D	A4/B18	A12/B18	A20/B18	A28/B18	A36/B18	
E	A5/B18	A13/B18	A21/B18	A29/B18	A37/B18	
F	A6/B18	A14/B18	A22/B18	A30/B18	A38/B18	
G	A7/B18	A15/B18	A23/B18	A31/B18	A39/B18	
H	A8/B18	A16/B18	A24/B18	A32/B18	A40/B18	

b) Reaction Yield Presented as Heatmap

	1	2	3	4	5	6	7	8	9	10	11
A	81	73	65	60	42	48	58	75	72	57	61
B	83	80	71	56	36	49	45	77	77	56	55
C	85	80	50	53	38	63	58	90	65	50	48
D	92	70	48	45	45	67	70	71	70	40	50
E	60	69	55	41	42	72	45	62	62	52	
F	58	72	49	48	50	66	54	54	58	41	
G	70	62	55	50	60	46	52	65	50	45	
H	69	72	69	54	45	45	44	70	50	65	

Figure S12. Plate 6 yields (%).

	1	2	3	4	5	6	7	8	9	10	11
A	46	55	7	0	20	28	52	29	20	33	72
B	55	57	0	7	45	36	20	34	41	46	66
C	58	60	0	11	55	68	46	37	0	48	65
D	54	62	12	6	30	70	70	36	10	40	48
E	48	59	5	70	30	73	7	18	3	50	
F	42	50	0	62	69	67	12	20	30	54	
G	57	5	0	71	24	20	23	26	43	34	
H	40	0	5	50	24	42	34	0	43	64	

Figure S13. Plate 7 yields (%).

	1	2	3	4	5	6
A	8	12	0	0	30	34
B	16	9	0	0	23	36
C	14	27	0	3	20	
D	10	30	0	0	31	
E	11	41	0	23	10	
F	10	23	0	36	39	
G	16	0	0	25	69	
H	16	0	0	40	50	

Figure S14. Plate 8 yields (%).

	1	2	3	4	5	6	7	8	9	10	11
A	48	40	39	0	31	51	37	53	34	65	45
B	45	37	36	38	16	38	65	72	45	60	49
C	46	57	32	36	33	71	59	56	0	58	46
D	46	33	36	35	42	65	46	40	44	45	56
E	38	39	39	36	33	66	56	46	50	46	
F	37	43	30	64	40	73	45	46	49	38	
G	23	36	32	40	39	70	51	29	46	49	
H	44	43	40	44	35	41	71	31	54	63	

Figure S15. Plate 9 yields (%).

	1	2	3	4	5	6
A	53	28	40	5	31	35
B	37	35	22	35	30	40
C	33	27	25	35	32	
D	36	35	23	40	29	
E	35	30	30	30	33	
F	21	42	22	29	32	
G	23	34	25	27	40	
H	30	35	21	34	35	

Figure S16. Plate 10 yields (%).

7. Development of Machine Learning Model

a) Preparation

All codes were executed in KNIME (the Konstanz Information Miner), which is a free and open-source data analytics platform and can be easily used by chemists without programming background. All workflows for modelling were provided in https://hub.knime.com/theliaogroup/spaces/P(O)O–H_insertion/latest.

b) Date Set

In our study, two datasets were used, one dataset for modelling and one dataset for external validation. The SMILES of sulfoxonium ylides, phosphinic acids, and products, as well as the corresponding yields were included in datasets.

(1) Data set A (420 reactions data) was split as 80/20, 336 reactions data were used as training set, 84 reactions data were used as test set for modeling.

(2) Data set B (336 unknown reactions data) included 14 unseen sulfoxonium ylides and 3 unseen phosphinic acids, which were used as an external validation set for the model built from dataset. We used dataset A to build model, and then used dataset B as an external validation for the model built from dataset A.

(3) As shown in the **Figure S17**, dataset A was split as 80/20 at the work unit (named Partitioning), 420 reactions data were inputted the work unit [named XGBoost Tree Ensemble Learner (Regression)] as training set and the training set will be divided into two parts, training set and validation set, automatically by this work unit. But we cannot know how this unit divides the dataset. At the same time, remaining dataset A (evaluate set, including 84 reactions data) will be input to the work unit [named XGBoost Predictor (Regression)]. This unit is used to confirm if the hyper-parameters are best for models by the results (R^2, MAE, and RMSE).

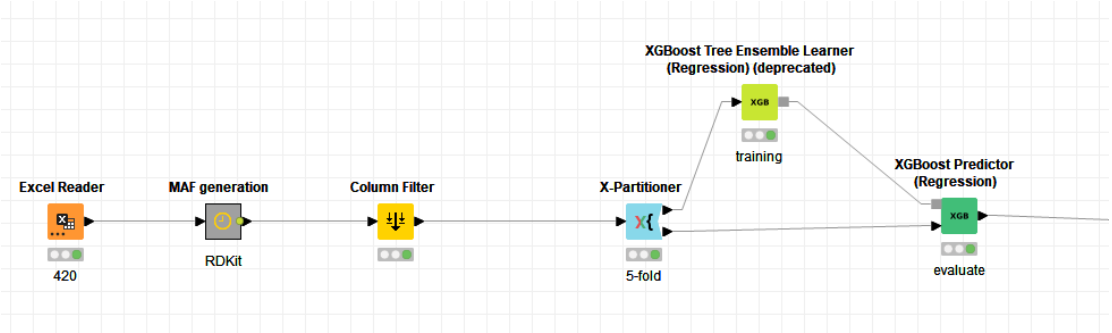


Figure S17. Part of the workflow of KNIME (one of the workflows).

c) Molecular additive fingerprints (MAF)

We provided a representation, molecular additive fingerprints (MAF) as inputs, that show the capacity of reaction prediction in good practices. The example for MAF development in this reaction were shown in **Figure S18**.

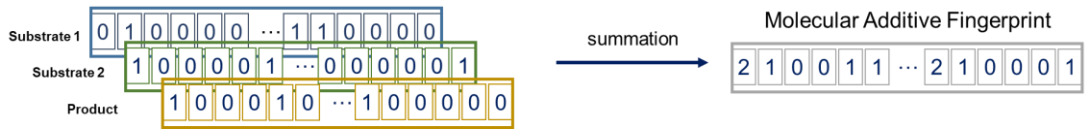


Figure S18. Example of the generation of MAF fingerprints in this reaction.

d) RDKit descriptors

RDKit descriptor generation was conducted in a KNIME workflow. In total, 119 descriptors were calculated for each reaction component using "RDKit Descriptors Calculation" node. The descriptors we used are as following: *SlogP, SMR, LabuteASA, TPSA, AMW, ExactMW, NumLipinskiHBA, NumLipinskiHBD, NumRotatableBonds, NumHBD, NumHBA, NumAmideBonds, NumHeteroAtoms, NumHeavyAtoms, NumAtoms, NumStereocenters, NumUnspecifiedStereocenters, NumRings, NumAromaticRings, NumSaturatedRings, NumAliphaticRings, NumAromaticHeterocycles, NumSaturatedHeterocycles, NumAliphaticHeterocycles, NumAromaticCarbocycles, NumSaturatedCarbocycles, NumAliphaticCarbocycles, FractionCSP3, Chi0v, Chi1v, Chi2v, Chi3v, Chi4v, Chi1n, Chi2n, Chi3n, Chi4n, HallKierAlpha, kappa1, kappa2, kappa3, slogp_VSA1, slogp_VSA2, slogp_VSA3, slogp_VSA4, slogp_VSA5, slogp_VSA6, slogp_VSA7, slogp_VSA8, slogp_VSA9, slogp_VSA10, slogp_VSA11, slogp_VSA12, smr_VSA1, smr_VSA2, smr_VSA3, smr_VSA4, smr_VSA5, smr_VSA6, smr_VSA7, smr_VSA8, smr_VSA9, smr_VSA10, peoe_VSA1, peoe_VSA2, peoe_VSA3, peoe_VSA4, peoe_VSA5, peoe_VSA6, peoe_VSA7, peoe_VSA8, peoe_VSA9, peoe_VSA10, peoe_VSA11, peoe_VSA12, peoe_VSA13, peoe_VSA14, MQN1, MQN2, MQN3, MQN4, MQN5, MQN6, MQN7, MQN8, MQN9, MQN10, MQN11, MQN12, MQN13, MQN14, MQN15, MQN16, MQN17, MQN18, MQN19, MQN20, MQN21, MQN22, MQN23, MQN24, MQN25, MQN26, MQN27, MQN28, MQN29, MQN30, MQN31, MQN32, MQN33, MQN34, MQN35, MQN36, MQN37, MQN38, MQN39, MQN40, MQN41, MQN42.*

e) One-hot encoding

A one-hot encoding based on all available reaction substrates was generated. The bit value '0' or '1' corresponds to the absence or presence for specific reaction component. The creation of one-hot descriptor was done via a KNIME workflow and an array of one-hot encodings of substrates and products was calculated in "One to Many" node. As shown in **Figure S19**, the generation of one-hot encoding in substrate exploration, respectively.

One-hot encoding (total length m = 89)	Substrate1	Substrate2
	$A_1\ A_2\ A_3 \ldots A_{80}$	$B_1\ B_2\ B_3 \ldots B_9$
	[0 1 0 … 0	1 0 0 … 0]

Figure S19. The generation of one-hot encoding in substrate exploration.

f) Multiple fingerprint feature (MFF)

The MFF Software Tool is based on RDKit, a widely established open-source chemoinformatics package, as a

chemical Python library. The calculation of MFF was conducted in a KNIME workflow. As Sandfort et al. reported[13], multiple fingerprint feature (MFF), an array of 2D structural fingerprints (71,375 bits), were generated based on RDKit. The MFF of each substrate was then concatenated in the order of ketones, alkynes, and urea derivatives. The final size of MFF in substrate exploration is 142,750 bits.

g) Differential reaction fingerprint (DRFP)

The DRFP algorithm takes a reaction SMILES as an input and creates a binary fingerprint based on the symmetric difference of two sets containing the circular molecular n-grams generated from the molecules listed left and right from the reaction arrow, respectively, without the need for distinguishing between reactants and reagents. The fingerprint creation algorithm available as a pypi package (drfp). The source code, data, and documentation are available on GitHub (https://github.com/reymond-group/drfp)[14].

h) Machine Learning Methods

Four commonly used ML methods were proceeded for modelling, including eXtreme Gradient Boosting (XGB), Gradient Boosted Trees (GBT), Random Forest Regression (RF), and Support Vector Regression (SVR). 80% of the dataset (336 reactions) were used to train our regression model and the remaining 20% were used as test set (84 reactions). The model performance was then evaluated by coefficient of determination (R^2), mean absolute error (MAE), and root mean squared error (RMSE).

Table S14. The hyper-parameters of 4 models.

Model	Hyper-parameters
Random Forest	Enable Hilighting (#patterns to store) = 2000, tree depth = 10, Minimum node size = 5, number of models = 100, Use static random seed = 68909
Gradient Tree Boosting	Limit number of levels = 4, number of models (n_estimators) = 100, learning rate = 0.1, alpha = 0.95
XGBoost	Boosting rounds = 100, Use static random seed = 68909, Manual numbers of threads = 4, Objective = 'squarederror', Booster = 'tree', Eta = 0.1, Gamma = 0, Maximum depth = 10, Minimum child weight = 5. Maximum delta step = 0, Subsampling rate = 0.8
SVR	Type of SVR = 'nu-SVM', Kernal = 'linear', Cost = 1.5, nu = 0.5, Cachesize = 3163, Epsilon = 0.001

Table S15. The hyper-parameters of XGB model for grid search.

Hyper-parameters	Considered values
booster	tree
eta	{0.05, **0.1**, 0.15, 0.2}
min child weight	{**5**, 6, 7}

max depth	{6, 8, **10**}
boosting rounds	{50, **100**, 150}

As shown in **Figure S20**, we can get the following page by open the work unit of model, and where we can change all kinds of hype-parameters of four models.

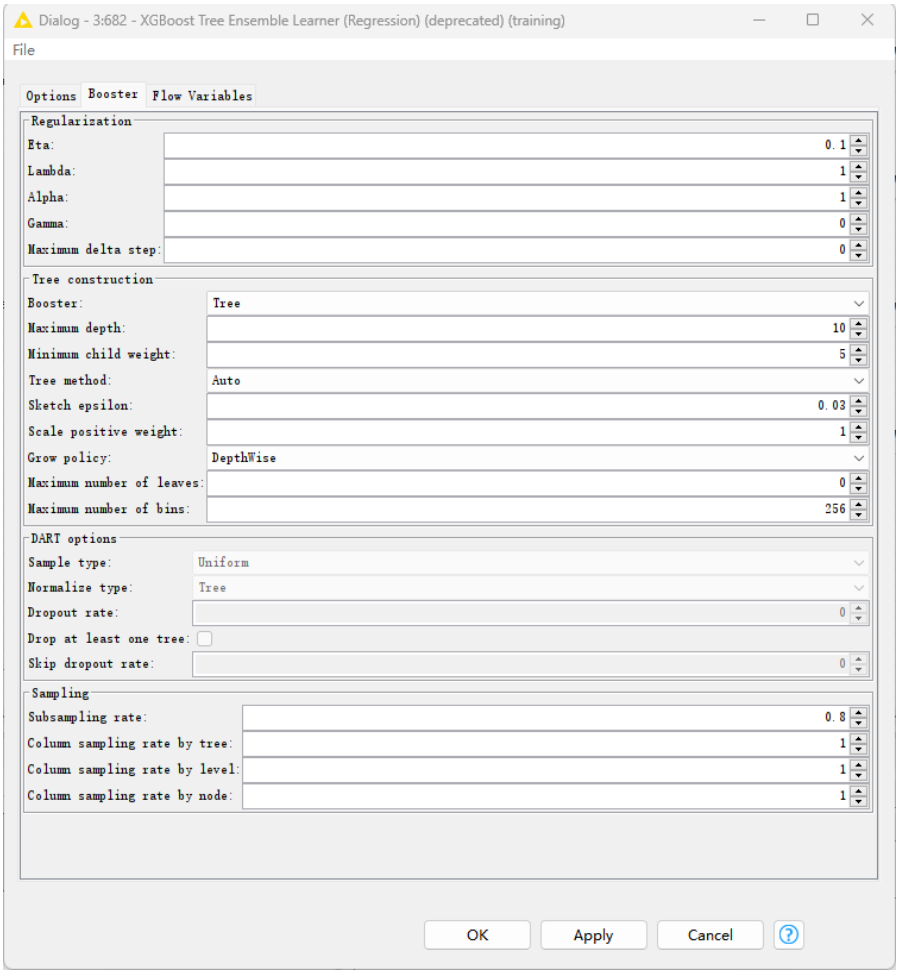


Figure S20. The page of changing hype-parameters.

i) The Development of ML-Based Models using MAF, RDKit, One-hot, MFF and DRFP

As shown in Table S16, five types of descriptors were applied for model building and 20 models were obtained in total.

Table S16. The development of ML-based models using MAF, RDKit and One-hot.

entry	model	R^2	MAE (%)	RMSE (%)
1	SVR-MAF	0.77	9.6	13.2
2	GBT-MAF	0.88	7.0	9.6
3	RF-MAF	0.84	8.3	10.9
4	XGB-MAF	0.86	7.4	10.2

5	SVR-RDKit	0.73	10.3	14.4
6	GBT-RDKit	0.88	6.7	9.4
7	RF-RDKit	0.86	7.7	10.5
8	XGB-RDkit	**0.89**	**6.6**	**9.3**
9	SVR-one hot	0.58	15.2	18.0
10	GBT-one hot	0.75	10.3	13.7
11	RF-one hot	0.70	12.1	15.3
12	XGB-one hot	0.79	9.0	12.6
13	SVR-MFF	0.87	8.1	10.0
14	GBT-MFF	0.86	8.4	10.6
15	RF-MFF	0.88	7.1	9.6
16	XGB-MFF	0.89	7.0	9.5
17	SVR-DRFP	0.82	8.9	11.9
18	GBT-DRFP	0.84	7.8	11.1
19	RF-DRFP	0.77	10.5	13.3
20	XGB-DRFP	0.83	8.0	11.3

j) Performance of XGB-RDKit Model

As shown in **Figure S21**, XGB-RDKit model deliver the best performance overall, with a result of R^2 value of 0.89, MAE of 6.6%, and RMSE of 9.3%.

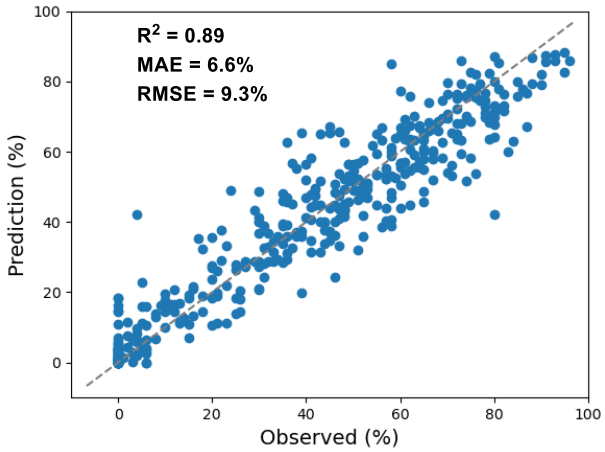


Figure S21. Prediction results on validation set for XGB-RDKit model.

Under the obtained best model (XGB-RDKit), we also evaluated 10 random splits of the entire data set (420 reaction data). These results are shown in Table S17, with a best result of R^2 value of 0.89, MAE of 6.56%, and RMSE of 9.26%.

Table S17. Results for 10 random splits of 420 reaction data.

splits	R^2	MAE	RMSE
splits 01	0.88	6.59	9.47
splits 02	0.86	7.08	10.10
splits 03	0.87	6.99	9.96
splits 04	0.87	6.96	10.13
splits 05	0.88	6.66	9.55
splits 06	0.88	6.62	9.70
splits 07	0.87	6.99	10.05
splits 08	**0.89**	**6.56**	**9.26**
splits 09	0.87	7.03	10.05
splits 10	0.86	7.29	10.40
average	0.87	6.88	9.87

k) Performance of External Dataset

Our best model in yield prediction (XGB-RDKit model, as shown in **Figure S21**) was then evaluated on external dataset. The performance of external test is shown in **Figure S22**, with a result of R^2 value of 0.77, MAE of 8.0%, and RMSE of 10%.

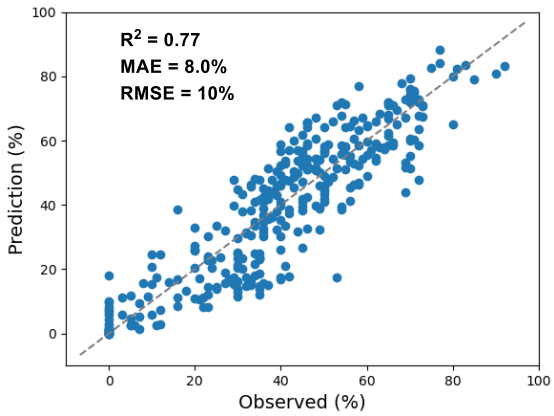
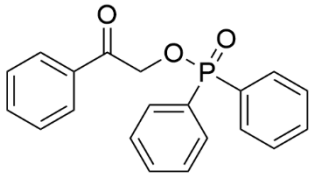


Figure S22. Regression plot for external dataset (336 scattered reactions).

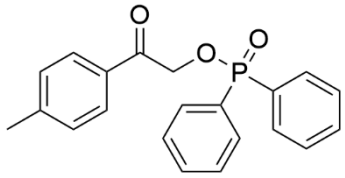
8. Characterization Data for the Products

2-Oxo-2-phenylethyl diphenylphosphinate (3)[10]



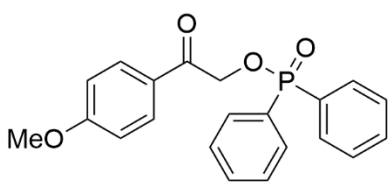
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 91% yield (30.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93–7.88 (m, 4H), 7.86–7.83 (m, 2H), 7.56–7.48 (m, 3H), 7.467.40 (m, 6H), 5.29 (d, J = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.2 (d, $J_{C\text{-}P}$ = 6.8 Hz), 133.9, 133.8, 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 137.4 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 127.6, 65.7 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.4.

2-oxo-2-(*p*-tolyl)ethyl diphenylphosphinate (4)[10]



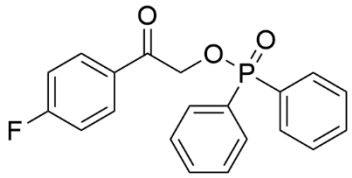
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 83% yield (27.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94–7.88 (m, 4H), 7.78–7.71 (m, 2H), 7.54–7.50 (m, 2H), 7.47–7.43 (m, 4H), 7.23 (d, J = 8.4 Hz, 2H), 5.27 (d, J = 7.5 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.8 (d, $J_{C\text{-}P}$ = 6.8 Hz), 144.8, 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 131.5, 130.7 (d, $J_{C\text{-}P}$ = 137.4 Hz), 129.5, 128.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 127.8, 65.6 (d, $J_{C\text{-}P}$ = 5.6 Hz), 21.7. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.3.

2-(4-methoxyphenyl)-2-oxoethyl diphenylphosphinate (5)[10]



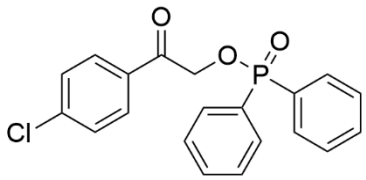
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 73% yield (26.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93–7.87 (m, 4H), 7.83 (d, J = 9.0 Hz, 2H), 7.52–7.48 (m, 2H), 7.45–7.40 (m, 4H), 6.89 (d, J = 9.0 Hz, 2H), 5.23 (d, J = 7.5 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.7 (d, $J_{C\text{-}P}$ = 6.9 Hz), 163.9, 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.6 (d, $J_{C\text{-}P}$ = 137.4 Hz), 129.9, 128.5 (d, $J_{C\text{-}P}$ = 13.4 Hz), 126.9, 113.9, 65.4 (d, $J_{C\text{-}P}$ = 5.6 Hz), 55.4. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.2.

2-(4-fluorophenyl)-2-oxoethyl diphenylphosphinate (6)[10]



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 82% yield (29.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.86 (m, 6H), 7.54–7.49 (m, 2H), 7.47–7.42 (m, 4H), 7.10 (t, J = 8.6 Hz, 2H), 5.25 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.8 (d, $J_{C\text{-}P}$ = 6.8 Hz), 166.0 (d, $J_{C\text{-}F}$ = 256.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.49 (d, $J_{C\text{-}P}$ = 137.3 Hz), 130.47 (d, $J_{C\text{-}F}$ = 9.5 Hz), 130.42, 128.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.0 Hz), 65.6 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.6. ^{19}F NMR (564 MHz, $CDCl_3$): δ -103.2.

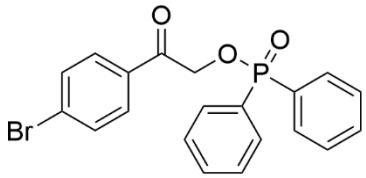
2-(4-chlorophenyl)-2-oxoethyl diphenylphosphinate (7)[10]



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 98% yield (36.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.86 (m, 4H), 7.82–7.77 (m, 2H), 7.55–7.50 (m, 2H), 7.48–7.42 (m, 4H), 7.42–7.37 (m, 2H), 5.24 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.3 (d, $J_{C\text{-}P}$ = 6.8 Hz), 140.3, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.3, 131.7, 131.6, 130.5 (d, $J_{C\text{-}P}$ = 137.2 Hz), 129.1 (d, $J_{C\text{-}P}$ = 4.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.3 Hz), 65.6 (d, $J_{C\text{-}P}$

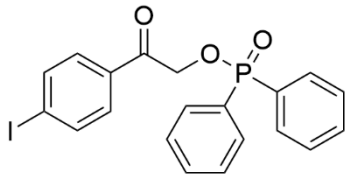
= 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.6.

2-(4-bromophenyl)-2-oxoethyl diphenylphosphinate (8)[10]



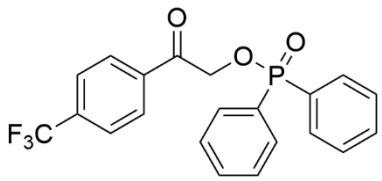
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 93% yield (38.5mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.86 (m, 4H), 7.76–7.71 (m, 2H), 7.61–7.57 (m, 2H), 7.56–7.51 (m, 2H), 7.49–7.43 (m, 4H), 5.24 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.5 (d, $J_{C\text{-}P}$ = 6.7 Hz), 132.7, 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.2, 131.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.3 Hz), 129.3, 129.2, 128.7 (d, $J_{C\text{-}P}$ = 13.4 Hz), 65.6 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.7.

2-(4-iodophenyl)-2-oxoethyl diphenylphosphinate (9)



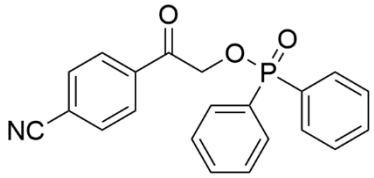
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 86% yield (39.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.86 (m, 4H), 7.81–7.79 (m, 2H), 7.58–7.55 (m, 2H), 7.54–7.51 (m, 2H), 7.48–7.43 (m, 4H), 5.23 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.82 (d, $J_{C\text{-}P}$ = 6.8 Hz), 138.1, 133.2, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.3 Hz), 129.0, 128.6 (d, $J_{C\text{-}P}$ = 13.5 Hz), 102.0, 65.5 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.6. HRMS (ESI-TOF) *m/z* calcd. for $C_{20}H_{16}INaO_3P[M+Na]^+$, 484.9774, found 484.9778.

2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl diphenylphosphinate (10)[10]



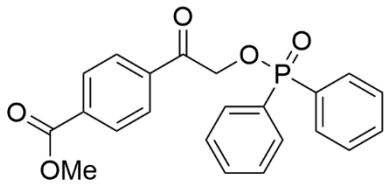
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 95% yield (38.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, J = 7.7 Hz, 2H), 7.88 (dd, J = 12.5, 7.3 Hz, 4H), 7.69 (d, J = 6.8 Hz, 2H), 7.52 (d, J = 6.3 Hz, 2H), 7.48–7.42 (m, 4H), 5.30 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.7 (d, $J_{C\text{-}P}$ = 6.7 Hz), 136.7, 134.9 (q, $J_{C\text{-}F}$ = 33.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.4 (d, $J_{C\text{-}P}$ = 137.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 128.2, 125.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.3 (d, $J_{C\text{-}F}$ = 272.8 Hz), 65.8 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.9. ^{19}F NMR (564 MHz, $CDCl_3$): δ -63.3.

2-(4-cyanophenyl)-2-oxoethyl diphenylphosphinate (11)



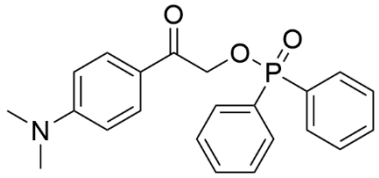
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a yellow oil in 96% yield (34.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98–7.95 (m, 2H), 7.89–7.84 (m, 4H), 7.76–7.73 (m, 2H), 7.56–7.53 (m, 2H), 7.49–7.45 (m, 4H), 5.27 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.5 (d, $J_{C\text{-}P}$ = 6.6 Hz), 136.9, 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.6, 131.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 137.1 Hz), 128.7, 128.6, 128.3, 117.6, 117.1, 65.8 (d, $J_{C\text{-}P}$ = 5.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 35.0. HRMS (ESI-TOF) *m/z* calcd. for $C_{21}H_{16}NNaO_3P[M+Na]^+$, 384.0760, found 384.0762.

methyl 4-(2-((diphenylphosphoryl)oxy)acetyl)benzoate (12)[10]



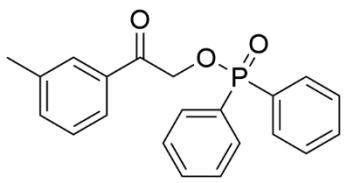
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a white solid in 48% yield (18.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, J = 8.4 Hz, 2H), 7.95–7.85 (m, 6H), 7.55 (t, J = 7.1 Hz, 2H), 7.50–7.44 (m, 4H), 5.31 (d, J = 7.6 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.1 (d, $J_{C\text{-}P}$ = 6.7 Hz), 165.9, 137.2, 134.6, 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.6 Hz), 130.0, 128.7 (d, $J_{C\text{-}P}$ = 13.5 Hz), 127.7, 65.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 52.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.8.

2-(4-(dimethylamino)phenyl)-2-oxoethyl diphenylphosphinate (13)



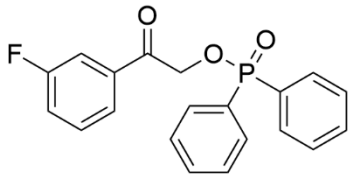
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a yellow solid in 90% yield (34.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96–7.89 (m, 4H), 7.77 (d, J = 8.9 Hz, 2H), 7.51 (t, J = 7.4 Hz, 2H), 7.47–7.42 (m, 4H), 6.60 (d, J = 8.9 Hz, 2H), 5.21 (d, J = 7.2 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 189.9 (d, $J_{C\text{-}P}$ = 7.1 Hz), 153.7, 132.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.9 (d, $J_{C\text{-}P}$ = 137.6 Hz), 129.9, 128.5 (d, $J_{C\text{-}P}$ = 13.2 Hz), 121.8, 110.7, 65.3 (d, $J_{C\text{-}P}$ = 5.6 Hz), 39.9. ^{31}P NMR (243 MHz, $CDCl_3$): δ 33.9. HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{22}NNaO_3P[M+Na]^+$, 402.1230, found 402.1233.

2-oxo-2-(*m*-tolyl)ethyl diphenylphosphinate (14)[10]



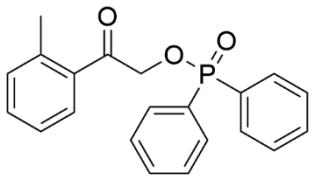
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 75% yield (26.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94–7.87 (m, 4H), 7.69–7.61 (m, 2H), 7.52 (t, J = 7.4 Hz, 2H), 7.47–7.42 (m, 4H), 7.39–7.28 (m, 2H), 5.29 (d, J = 7.4 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.4 (d, $J_{C\text{-}P}$ = 6.9 Hz), 138.7, 134.6, 133.9, 132.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.6 (d, $J_{C\text{-}P}$ = 137.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 5.5 Hz), 128.5, 128.2, 124.8, 65.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 21.2. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.4.

2-(3-fluorophenyl)-2-oxoethyl diphenylphosphinate (15)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 81% yield (28.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.84 (m, 4H), 7.60 (d, J = 8.5 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.48–7.37 (m, 5H), 7.24 (d, J = 7.3 Hz, 1H), 5.26 (d, J = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.2 (dd, $J_{C\text{-}P}$ = 6.8, 2.2 Hz), 162.7 (d, $J_{C\text{-}F}$ = 249.0 Hz), 135.9 (d, $J_{C\text{-}P}$ = 6.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 7.6 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.3 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 123.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 120.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 114.5 (d, $J_{C\text{-}F}$ = 22.6 Hz), 65.7 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.7. ^{19}F NMR (564 MHz, $CDCl_3$): δ -110.8. HRMS (ESI-TOF) *m/z* calcd. for $C_{20}H_{16}FNaO_3P[M+Na]^+$, 377.0713, found 377.0716.

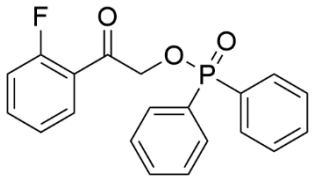
2-oxo-2-(*o*-tolyl)ethyl diphenylphosphinate (16)[10]



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 70% yield (24.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.83 (m, 4H), 7.51 (t, J = 7.5 Hz, 2H), 7.48–7.41 (m, 5H), 7.37 (t, J = 7.5 Hz, 1H), 7.25–7.18 (m, 2H), 5.13 (d, J = 7.9 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.8 (d, $J_{C\text{-}P}$ = 6.5 Hz), 138.9,

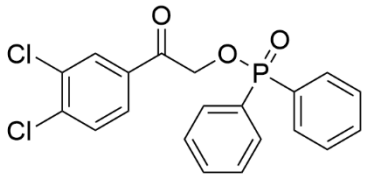
134.1, 132.4 (d, J_{C-P} = 2.9 Hz), 132.13, 132.11, , 131.7 (d, J_{C-P} = 10.4 Hz), 130.6 (d, J_{C-P} = 137.3 Hz), 128.5 (d, J_{C-P} = 13.2 Hz), 128.0, 125.7, 66.7 (d, J_{C-P} = 5.6 Hz), 21.1. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1.

2-(2-fluorophenyl)-2-oxoethyl diphenylphosphinate (17)



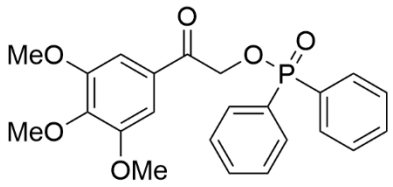
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a white solid in 76% yield (26.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97–7.88 (m, 5H), 7.56–7.50 (m, 3H), 7.47–7.42 (m, 4H), 7.25–7.22 (m, 1H), 7.15–7.04 (m, 1H), 5.20 (dd, *J* = 8.2, 3.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.7 (dd, J_{C-P} = 6.3, 5.1 Hz), 162.1 (d, J_{C-F} = 254.5 Hz), 135.6 (d, J_{C-F} = 9.1 Hz), 132.4 (d, J_{C-P} = 2.8 Hz), 131.7 (d, J_{C-P} = 10.4 Hz), 130.8 (d, J_{C-P} = 137.4 Hz), 130.6 (d, J_{C-F} = 3.2 Hz), 128.5 (d, J_{C-P} = 13.4 Hz), 124.8 (d, J_{C-F} = 3.1 Hz), 122.3 (d, J_{C-F} = 14.6 Hz), 116.5 (d, J_{C-F} = 23.4 Hz), 68.8 (dd, J_{C-P} = 13.9, 5.3 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.0. ^{19}F NMR (565 MHz, $CDCl_3$): δ -107.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{20}H_{16}FNaO_3P[M+Na]^+$, 377.0713, found 377.0715.

2-(3,4-dichlorophenyl)-2-oxoethyl diphenylphosphinate (18)



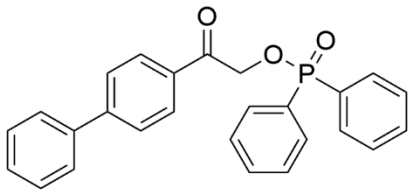
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 92% yield (37.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 2.0 Hz, 1H), 7.90–7.85 (m, 4H), 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55–7.49 (m, 3H), 7.48–7.41 (m, 4H), 5.22 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.5 (d, J_{C-P} = 6.7 Hz), 138.5, 133.5, 133.4, 132.6 (d, J_{C-P} = 2.8 Hz), 131.7 (d, J_{C-P} = 10.5 Hz), 130.9, 130.4 (d, J_{C-P} = 137.1 Hz), 129.8, 128.6 (d, J_{C-P} = 13.3 Hz), 126.8, 65.6 (d, J_{C-P} = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.9. HRMS (ESI-TOF) *m/z* calcd. for $C_{20}H_{15}Cl_2NaO_3P[M+Na]^+$, 427.0028, found 427.0031.

2-oxo-2-(3,4,5-trimethoxyphenyl)ethyl diphenylphosphinate (19)



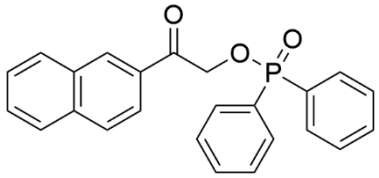
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 84% yield (35.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93–7.86 (m, 4H), 7.56–7.50 (m, 2H), 7.48–7.43 (m, 4H), 7.14 (s, 2H), 5.26 (d, J = 7.5 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.3 (d, $J_{C\text{-}P}$ = 7.1 Hz), 153.2, 143.1, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.6 (d, $J_{C\text{-}P}$ = 137.3 Hz), 129.1, 128.6 (d, $J_{C\text{-}P}$ = 13.5 Hz), 105.2, 65.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 60.9, 56.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.6. HRMS (ESI-TOF) *m/z* calcd. for $C_{23}H_{23}NaO_6P[M+Na]^+$, 449.1124, found 449.1123.

2-([1,1'-biphenyl]-4-yl)-2-oxoethyl diphenylphosphinate (20)



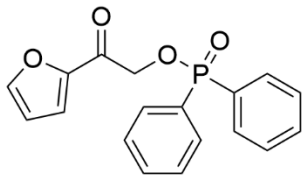
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 66% yield (27.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98–7.89 (m, 6H), 7.67 (d, J = 8.6 Hz, 2H), 7.60 (dd, J = 8.3, 1.2 Hz, 2H), 7.56–7.52 (m, 2H), 7.51–7.44 (m, 6H), 7.40 (t, J = 7.4 Hz, 1H), 5.34 (d, J = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.9 (d, $J_{C\text{-}P}$ = 7.0 Hz), 146.6, 139.5, 132.7, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 137.4 Hz), 128.9, 128.6 (d, $J_{C\text{-}P}$ = 13.5 Hz), 128.4, 128.3, 127.4, 127.2, 65.8 (d, $J_{C\text{-}P}$ = 5.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.5. HRMS (ESI-TOF) *m/z* calcd. for $C_{26}H_{21}NaO_3P[M+Na]^+$, 435.1121, found 435.1125.

2-(naphthalen-2-yl)-2-oxoethyl diphenylphosphinate (21)



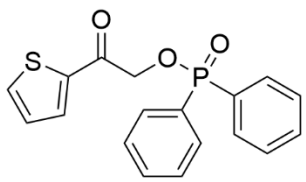
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 98% yield (37.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.97–7.91 (m, 5H), 7.90–7.81 (m, 3H), 7.61–7.56 (m, 1H), 7.55–7.50 (m, 3H), 7.48–7.43 (m, 4H), 5.44 (d, J = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.2 (d, $J_{C\text{-}P}$ = 6.8 Hz), 135.8, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.2, 131.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.2, 130.6 (d, $J_{C\text{-}P}$ = 137.3 Hz), 129.53, 129.46, 128.8, 128.7, 128.6 (d, $J_{C\text{-}P}$ = 13.3 Hz), 127.7, 126.9, 123.1, 65.8 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.6. HRMS (ESI-TOF) *m/z* calcd. for $C_{24}H_{20}O_3P[M+H]^+$, 387.1145, found 387.1136.

2-(furan-2-yl)-2-oxoethyl diphenylphosphinate (22)



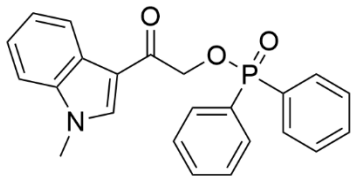
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a yellow oil in 84% yield (27.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.80 (m, 4H), 7.55–7.46 (m, 3H), 7.44–7.37 (m, 4H), 7.22 (d, J = 3.6 Hz, 1H), 6.48 (dd, J = 3.6, 1.7 Hz, 1H), 5.09 (d, J = 7.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 181.6 (d, $J_{C\text{-}P}$ = 7.1 Hz), 150.1, 146.8, 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.4 (d, $J_{C\text{-}P}$ = 137.3 Hz), 128.5 (d, $J_{C\text{-}P}$ = 13.3 Hz), 118.1, 112.4, 65.0 (d, $J_{C\text{-}P}$ = 5.5 Hz). HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{15}NaO_4P[M+Na]^+$, 349.0600, found 349.0603.

2-oxo-2-(thiophen-2-yl)ethyl diphenylphosphinate (23)



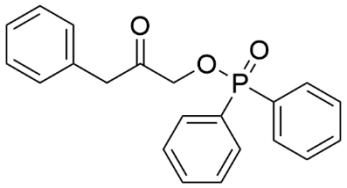
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a yellow oil in 80% yield (27.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94–7.85 (m, 4H), 7.71 (d, J = 3.8 Hz, 1H), 7.67 (d, J = 4.9 Hz, 1H), 7.55–7.51 (m, 2H), 7.48–7.43 (m, 4H), 7.10 (t, J = 4.4 Hz, 1H), 5.15 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 185.6 (d, $J_{C\text{-}P}$ = 7.3 Hz), 140.2, 134.5, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.3, 131.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.3 Hz), 128.3, 65.6 (d, $J_{C\text{-}P}$ = 5.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.5. HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{15}NaO_3PS[M+Na]^+$, 365.0372, found 365.0371.

2-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl diphenylphosphinate (25)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a brown oil in 62% yield (24.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38–8.32 (m, 1H), 7.93 (dd, J = 12.4, 7.7 Hz, 4H), 7.81 (s, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.49–7.44 (m, 4H), 7.33–7.29 (m, 3H), 5.03 (d, J = 7.0 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 187.4 (d, $J_{C\text{-}P}$ = 7.7 Hz), 137.1, 135.7, 132.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 137.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.3 Hz), 126.3, 123.7, 122.9, 122.4, 113.2, 109.7, 66.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 33.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 33.9. HRMS (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}NNaO_3P[M+Na]^+$, 412.1073, found 412.1075.

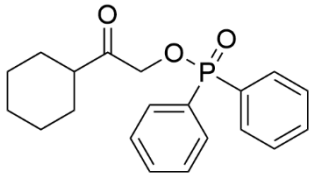
2-oxo-3-phenylpropyl diphenylphosphinate (26)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 73% yield (25.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85–7.78 (m, 4H), 7.56–7.51 (m, 2H), 7.48–7.41 (m, 4H), 7.28 (dd, J = 7.9, 6.3 Hz, 2H), 7.26–7.22 (m, 1H), 7.15–7.11 (m, 2H), 4.63 (d, J = 8.0 Hz, 2H), 3.79 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ

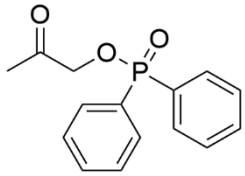
202.1 (d, $J_{C\text{-}P}$ = 6.5 Hz), 132.6, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.3 (d, $J_{C\text{-}P}$ = 137.1 Hz), 129.3, 128.7, 128.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 127.2, 67.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 46.1. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.2. HRMS (ESI-TOF) *m/z* calcd. for $C_{21}H_{19}NaO_3P[M+Na]^+$, 373.0964, found 373.0962.

2-cyclohexyl-2-oxoethyl diphenylphosphinate (27)[10]



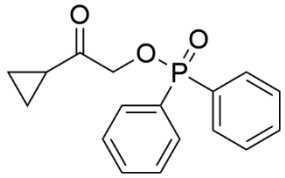
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with dichloromethane/ethyl acetate (2/1) to afford a yellow solid in 81% yield (27.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88–7.80 (m, 4H), 7.54–7.49 (m, 2H), 7.47–7.39 (m, 4H), 4.63 (d, *J* = 7.8 Hz, 2H), 2.47–2.39 (m, 1H), 1.78–1.69 (m, 4H), 1.61 (dd, *J* = 10.7, 3.2 Hz, 1H), 1.35–1.26 (m, 2H), 1.25–1.12 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.9 (d, $J_{C\text{-}P}$ = 6.4 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.3 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.2 Hz), 66.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 46.9, 27.9, 25.5, 25.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 33.8.

2-oxopropyl diphenylphosphinate (28)



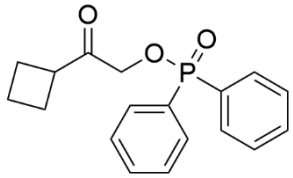
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 51% yield (14.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 12.4, 7.8 Hz, 4H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47–7.43 (m, 4H), 4.53 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.7 (d, $J_{C\text{-}P}$ = 6.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.4 (d, $J_{C\text{-}P}$ = 137.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.3 Hz), 67.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 26.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.0. HRMS (ESI-TOF) *m/z* calcd. for $C_{15}H_{15}NaO_3P[M+Na]^+$, 297.0651, found 297.0653.

2-cyclopropyl-2-oxoethyl diphenylphosphinate (29)



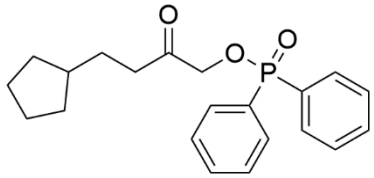
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 37% yield (11.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90–7.84 (m, 4H), 7.57–7.52 (m, 2H), 7.50–7.44 (m, 4H), 4.72 (d, J = 7.8 Hz, 2H), 2.09–2.01 (m, 1H), 1.14–1.08 (m, 2H), 1.00–0.92 (m, 2H). ^{13}C NMR (150MHz, $CDCl_3$): δ 204.4 (d, $J_{C\text{-}P}$ = 6.6 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.6 (d, $J_{C\text{-}P}$ = 137.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.3 Hz), 68.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 17.1, 11.7. ^{31}P NMR (243 MHz, $CDCl_3$): δ 33.8. HRMS (ESI-TOF) *m/z* calcd. for $C_{17}H_{17}NaO_3P[M+Na]^+$, 323.0808, found 323.0811.

2-cyclobutyl-2-oxoethyl diphenylphosphinate (30)



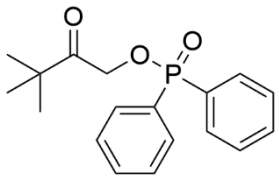
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 78% yield (24.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (dd, J = 12.4, 8.0 Hz, 4H), 7.54 (t, J = 7.4 Hz, 2H), 7.49–7.43 (m, 4H), 4.56 (d, J = 7.7 Hz, 2H), 3.54–3.28 (m, 1H), 2.28–2.19 (m, 2H), 2.16–2.09 (m, 2H), 2.03–1.91 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.5 (d, $J_{C\text{-}P}$ = 6.5 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.6 (d, $J_{C\text{-}P}$ = 137.3 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.2 Hz), 66.2 (d, $J_{C\text{-}P}$ = 6.1 Hz), 41.9, 24.0, 18.0. ^{31}P NMR (243 MHz, $CDCl_3$): δ 33.8. HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{19}NaO_3P[M+Na]^+$, 337.0964, found 337.0966.

4-cyclopentyl-2-oxobutyl diphenylphosphinate (31)[10]



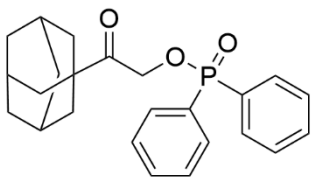
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 60% yield (21.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.77 (m, 4H), 7.56–7.52 (m, 2H), 7.49–7.44 (m, 4H), 4.56 (d, J = 7.9 Hz, 2H), 2.60–2.35 (m, 2H), 1.73–1.65 (m, 3H), 1.60–1.54 (m, 4H), 1.50–1.42 (m, 2H) , 1.07 – 0.97 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.1 (d, $J_{C\text{-}P}$ = 6.2 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.4 Hz), 67.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 39.5, 38.1, 32.4, 29.3, 25.0. ^{31}P NMR (243 MHz, $CDCl_3$): δ 33.9.

3, 3 -dimethyl-2-oxobutyl diphenylphosphinate (32)[10]



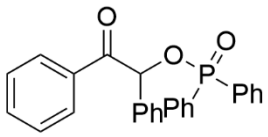
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 66% yield (20.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (dd, J = 12.4, 7.7 Hz, 4H), 7.51 (t, J = 7.4 Hz, 2H), 7.47–7.41 (m, 4H), 4.84 (d, J = 8.0 Hz, 2H), 1.08 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 208.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.6 (d, $J_{C\text{-}P}$ = 137.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 13.2 Hz), 63.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 42.8, 26.0. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1.

2-(adamantan-1-yl)-2-oxoethyl diphenylphosphinate (33)



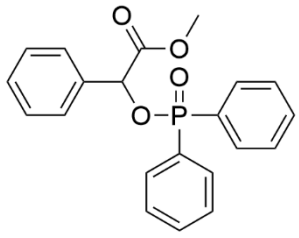
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 70% yield (27.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89–7.82 (m, 4H), 7.54–7.47 (m, 2H), 7.45–7.40 (m, 4H), 4.81 (d, J = 7.9 Hz, 2H), 1.97 (s, 3H), 1.75–1.66 (m, 9H), 1.62 (d, J = 11.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.5 (d, $J_{C\text{-}P}$ = 5.7 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 137.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 13.5 Hz), 64.0 (d, $J_{C\text{-}P}$ = 5.6 Hz), 45.2, 37.7, 36.2, 27.5. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.0. HRMS (ESI-TOF) *m/z* calcd. for $C_{24}H_{27}NaO_3P[M+Na]^+$, 417.1590, found 417.1595.

2-oxo-1,2-diphenylethyl diphenylphosphinate (34)[11]



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 84% yield (34.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88–7.81 (m, 4H), 7.72 (dd, J = 12.4, 7.5 Hz, 2H), 7.48–7.41 (m, 5H), 7.40–7.36 (m, 2H), 7.35–7.30 (m, 4H), 7.27–7.19 (m, 3H), 6.74 (d, J = 9.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 193.8 (d, $J_{C\text{-}P}$ = 3.9 Hz), 134.9 (d, $J_{C\text{-}P}$ = 4.3 Hz), 134.3, 133.3, 132.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 4.2 Hz), 131.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 14.0 Hz), 128.9, 128.8 (d, $J_{C\text{-}P}$ = 6.5 Hz), 128.4, 128.4, 128.3 (d, $J_{C\text{-}P}$ = 6.3 Hz), 128.2, 128.1, 77.2 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1.

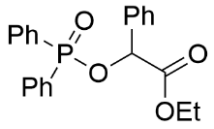
methyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (35)[11]



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 53% yield (19.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.86 (m, 2H), 7.75–7.68 (m, 2H), 7.56–7.52 (m, 1H), 7.50–7.45 (m, 3H), 7.42 (dd, J = 6.5, 3.0 Hz, 2H), 7.38–7.33 (m, 2H), 7.33–7.29 (m, 3H), 5.83 (d, J = 9.9 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (150

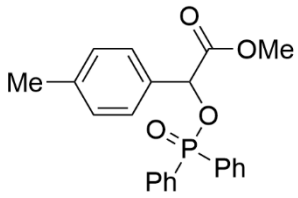
MHz, $CDCl_3$): δ 169.5 (d, J_{C-P} = 4.3 Hz), 135.2 (d, J_{C-P} = 4.7 Hz), 132.4 (d, J_{C-P} = 2.8 Hz), 132.3 (d, J_{C-P} = 3.0 Hz), 131.8 (d, J_{C-P} = 4.6 Hz), 131.7 (d, J_{C-P} = 4.9 Hz), 130.5 (d, J_{C-P} = 39.5 Hz), 129.1, 128.7, 128.5, 128.4, 128.3, 127.3, 74.1 (d, J_{C-P} = 5.0 Hz), 52.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.3.

ethyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (36)[12]



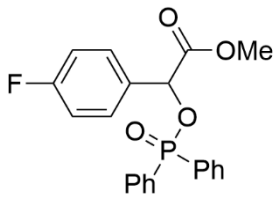
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a colorless oil in 66% yield (25.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.85 (m, 2H), 7.76–7.69 (m, 2H), 7.57–7.51 (m, 1H), 7.50–7.44 (m, 3H), 7.44–7.41 (m, 2H), 7.36 (td, J = 7.7, 3.6 Hz, 2H), 7.33–7.29 (m, 3H), 5.81 (d, J = 10.0 Hz, 1H), 4.40–3.86 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1 (d, J_{C-P} = 4.3 Hz), 135.3 (d, J_{C-P} = 4.8 Hz), 132.4 (d, J_{C-P} = 2.8 Hz), 132.3 (d, J_{C-P} = 3.0 Hz), 131.8 (d, J_{C-P} = 2.9 Hz), 131.7 (d, J_{C-P} = 2.8 Hz), 131.5 (d, J_{C-P} = 35.9 Hz), 130.6 (d, J_{C-P} = 35.4 Hz), 129.0, 128.6, 128.4 (d, J_{C-P} = 25.0 Hz), 128.4 (d, J_{C-P} = 2.0 Hz), 127.2, 74.2 (d, J_{C-P} = 5.2 Hz), 61.7, 13.9. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1.

methyl 2-((diphenylphosphoryl)oxy)-2-(*p*-tolyl)acetate (37)[12]



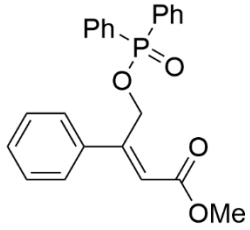
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a colorless solid in 55% yield (20.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90–7.83 (m, 2H), 7.75–7.68 (m, 2H), 7.56–7.51 (m, 1H), 7.49–7.43 (m, 3H), 7.38–7.34 (m, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.78 (d, J = 9.9 Hz, 1H), 3.65 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.7 (d, J_{C-P} = 4.6 Hz), 139.1, 132.34, 132.35, 132.3 (d, J_{C-P} = 5.0 Hz), 132.26, 132.2, 131.8, 131.78 (d, J_{C-P} = 2.5 Hz), 131.7, 129.4, 128.4 (t, J_{C-P} = 13.1 Hz), 127.3, 74.1 (d, J_{C-P} = 5.0 Hz), 52.6, 21.2. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.1.

methyl 2-((diphenylphosphoryl)oxy)-2-(4-fluorophenyl)acetate (38)[12]



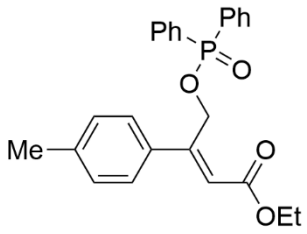
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a colorless oil in 70% yield (26.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90–7.84 (m, 2H), 7.75–7.66 (m, 2H), 7.59–7.52 (m, 1H), 7.51–7.45 (m, 3H), 7.42–7.34 (m, 4H), 7.03–6.96 (m, 2H), 5.81 (d, J = 10.0 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.4 (d, $J_{C\text{-}P}$ = 5.0 Hz), 163.1 (d, $J_{C\text{-}F}$ = 248.4 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 1.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 0.8 Hz), 131.4, 131.3 (d, $J_{C\text{-}P}$ = 18.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 4.4 Hz), 130.4 (d, $J_{C\text{-}P}$ = 23.5 Hz), 129.3 (d, $J_{C\text{-}P}$ = 8.6 Hz), 128.5 (t, $J_{C\text{-}P}$ = 13.6 Hz), 115.7 (d, $J_{C\text{-}P}$ = 21.9 Hz), 73.4 (d, $J_{C\text{-}F}$ = 5.0 Hz), 52.7. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.4. ^{19}F NMR (564 MHz, CDCl3): δ -112.1.

methyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-phenylbut-2-enoate (39)



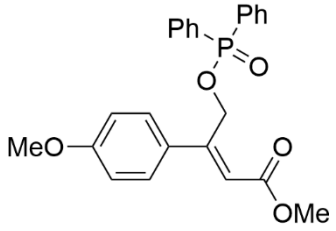
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 71% yield (27.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64–7.58 (m, 4H), 7.51–7.49 (m, 2H), 7.48–7.45 (m, 2H), 7.39–7.33 (m, 7H), 6.14 (s, 1H), 5.57 (dd, J = 6.9, 0.9 Hz, 2H), 3.68 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 152.9 (d, $J_{C\text{-}P}$ = 7.8 Hz), 137.9, 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.3 Hz), 131.1 (d, $J_{C\text{-}P}$ = 136.9 Hz), 129.2, 128.5, 128.4, 128.3, 127.4, 119.9, 60.3 (d, $J_{C\text{-}P}$ = 4.9 Hz), 51.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{23}H_{21}NaO_4P[M+Na]^+$, 415.1070, found 415.1084.

ethyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-(*p*-tolyl)but-2-enoate (40)



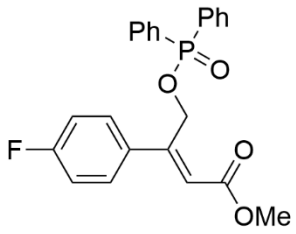
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 66% yield (27.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67–7.60 (m, 4H), 7.49–7.43 (m, 2H), 7.44–7.39 (m, 2H), 7.39–7.33 (m, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.13 (d, *J* = 0.9 Hz, 1H), 5.57 (dd, *J* = 6.9, 0.8 Hz, 2H), 4.15–4.11 (m, 2H), 2.37 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.5, 152.4 (d, $J_{C\text{-}P}$ = 7.5 Hz), 139.4, 134.9, 132.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 131.1 (d, $J_{C\text{-}P}$ = 125.4 Hz), 129.2, 128.3 (d, $J_{C\text{-}P}$ = 13.4 Hz), 127.2, 119.7, 60.4, 60.2 (d, $J_{C\text{-}P}$ = 4.9 Hz), 21.2, 14.2. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.3. HRMS (ESI-TOF) *m/z* calcd. for $C_{25}H_{25}NaO_4P[M+Na]^+$, 443.1383, found 443.1385.

methyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-(4-methoxyphenyl)but-2-enoate (41)



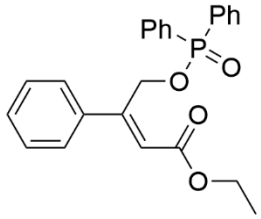
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 55% yield (23.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72–7.63 (m, 4H), 7.53–7.44 (m, 4H), 7.40–7.35 (m, 4H), 6.93–6.88 (m, 2H), 6.12 (s, 1H), 5.57 (d, *J* = 7.5 Hz, 2H), 3.83 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 160.7, 152.0 (d, $J_{C\text{-}P}$ = 7.7 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), δ 130.3 (d, $J_{C\text{-}P}$ = 110.7 Hz), 128.8, 128.4 (d, $J_{C\text{-}P}$ = 13.2 Hz), 118.2, 113.9, 59.9 (d, $J_{C\text{-}P}$ = 4.9 Hz), 55.3, 51.5. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.5. HRMS (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}NaO_5P[M+Na]^+$, 445.1175, found 445.1177.

methyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-(4-fluorophenyl)but-2-enoate (42)



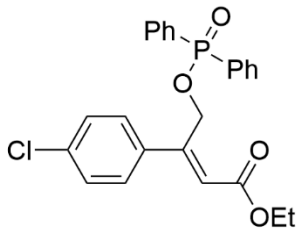
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 70% yield (28.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67–7.60 (m, 4H), 7.52–7.46 (m, 4H), 7.40–7.32 (m, 4H), 7.09–7.00 (m, 2H), 6.11 (s, 1H), 5.56 (d, J = 8.0 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.7, 164.2, 162.5, 151.9 (d, $J_{C\text{-}P}$ = 7.6 Hz), 133.9 (d, $J_{C\text{-}F}$ = 3.4 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.3 Hz), δ 131.0 (d, $J_{C\text{-}P}$ = 137.0 Hz), 129.3 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 13.5 Hz), 119.9, 115.5 (d, $J_{C\text{-}F}$ = 21.7 Hz), 60.2 (d, $J_{C\text{-}P}$ = 4.9 Hz), 51.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.7. ^{19}F NMR (564 MHz, $CDCl_3$): δ -111.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}FNaO_4P[M+Na]^+$, 433.0975, found 433.0977.

ethyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-phenylbut-2-enoate (43)



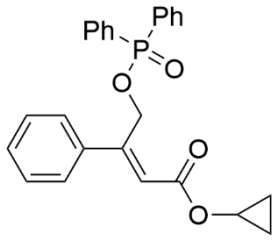
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 82% yield (33.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65–7.59 (m, 4H), 7.52–7.44 (m, 4H), 7.40–7.33 (m, 7H), 6.13 (s, 1H), 5.58 (d, J = 7.8 Hz, 2H), 4.49–3.81 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.4, 152.7 (d, $J_{C\text{-}P}$ = 7.7 Hz), 137.9, 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.3 Hz), δ 131.1 (d, $J_{C\text{-}P}$ = 136.8 Hz), 129.2, 128.5, 128.4, 128.3, 127.4, 120.5, 60.5, 60.3 (d, $J_{C\text{-}P}$ = 4.9 Hz), 14.2. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{24}H_{23}NaO_4P[M+Na]^+$, 429.1226, found 429.1227.

ethyl (*Z*)-3-(4-chlorophenyl)-4-((diphenylphosphoryl)oxy)but-2-enoate (44)



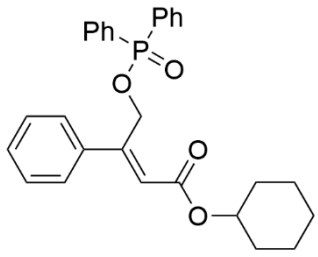
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 82% yield (36.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65–7.59 (m, 4H), 7.49–7.41 (m, 4H), 7.39–7.34 (m, 4H), 7.34–7.30 (m, 2H), 6.14–5.99 (m, 1H), 5.56 (dd, J = 7.1, 1.0 Hz, 2H), 4.40–3.86 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 151.4 (d, $J_{C\text{-}P}$ = 7.6 Hz), 136.3, 135.2, 132.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 10.3 Hz), δ 130.9 (d, $J_{C\text{-}P}$ = 136.8 Hz), 128.7 (d, $J_{C\text{-}P}$ = 7.6 Hz), 128.4 (d, $J_{C\text{-}P}$ = 13.2 Hz), 120.8, 60.6, 60.1 (d, $J_{C\text{-}P}$ = 4.9 Hz), 14.1. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{24}H_{22}ClNaO_4P[M+Na]^+$, 463.0836, found 463.0843.

cyclohexyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-phenylbut-2-enoate (45)



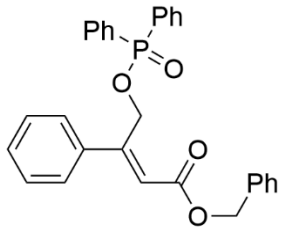
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 61% yield (25.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.51–7.44 (m, 4H), 7.39–7.33 (m, 7H), 6.07 (d, J = 0.8 Hz, 1H), 5.58 (dd, J = 6.9, 1.0 Hz, 2H), 4.19–3.96 (m, 1H), 0.75–0.71 (m, 2H), 0.71–0.67 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2, 153.4 (d, $J_{C\text{-}P}$ = 7.7 Hz), 137.8, 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.3 Hz), δ 131.0 (d, $J_{C\text{-}P}$ = 136.8 Hz), 129.3, 128.5, 128.4, 128.3, 127.4, 119.8, 60.3 (d, $J_{C\text{-}P}$ = 4.9 Hz), 48.9, 5.2. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.5. HRMS (ESI-TOF) *m/z* calcd. for $C_{25}H_{23}NaO_4P[M+Na]^+$, 441.1226, found 441.1221.

cyclohexyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-phenylbut-2-enoate (46)



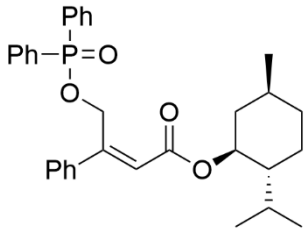
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a yellow oil in 46% yield (21.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63–7.58 (m, 4H), 7.52–7.49 (m, 2H), 7.48–7.44 (m, 2H), 7.39–7.33 (m, 7H), 6.12 (s, 1H), 5.59 (dd, J = 6.8, 0.9 Hz, 2H), 4.83–4.62 (m, 1H), 1.88–1.80 (m, 2H), 1.74–1.67 (m, 2H), 1.57–1.50 (m, 1H), 1.43–1.31 (m, 4H), 1.25 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.9, 152.4 (d, J_{C-P} = 7.9 Hz), 137.9, 132.1 (d, J_{C-P} = 3.0 Hz), 131.6 (d, J_{C-P} = 10.4 Hz), δ 131.1 (d, J_{C-P} = 136.9 Hz), 129.1, 128.4 (d, J_{C-P} = 2.8 Hz), 128.3, 127.4, 121.0, 72.9, 60.4 (d, J_{C-P} = 4.9 Hz), 31.6, 25.3, 23.7. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.3. HRMS (ESI-TOF) *m/z* calcd. for $C_{28}H_{29}NaO_4P[M+Na]^+$, 483.1696, found 483.1691.

benzyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-phenylbut-2-enoate (47)



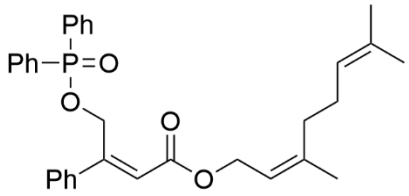
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 74% yield (34.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65–7.57 (m, 4H), 7.51 (dd, J = 6.7, 3.0 Hz, 2H), 7.48–7.44 (m, 2H), 7.40–7.32 (m, 12H), 6.19 (d, J = 0.8 Hz, 1H), 5.61 (d, J = 7.9 Hz, 2H), 5.14 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 153.5 (d, J_{C-P} = 7.6 Hz), 137.8, 135.7, 132.1 (d, J_{C-P} = 2.8 Hz), 131.6 (d, J_{C-P} = 10.3 Hz), δ 131.0 (d, J_{C-P} = 137.0 Hz), 129.3, 128.5, 128.5, 128.4, 128.3 (d, J_{C-P} = 2.2 Hz), 128.3, 127.4, 119.9, 66.3, 60.3 (d, J_{C-P} = 4.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.5. HRMS (ESI-TOF) *m/z* calcd. for $C_{29}H_{25}NaO_4P[M+Na]^+$, 491.1383, found 491.1390.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*Z*)-4-((diphenylphosphoryl)oxy)-3-phenylbut-2-enoate (48)



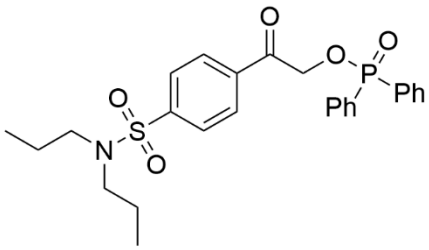
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a colorless oil in 61% yield (31.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63–7.58 (m, 4H), 7.52–7.50 (m, 2H), 7.48–7.44 (m, 2H), 7.39–7.33 (m, 7H), 6.12 (d, J = 0.8 Hz, 1H), 5.70–5.49 (m, 2H), 4.81–4.59 (m, 1H), 2.00–1.93 (m, 2H), 1.88–1.81 (m, 1H), 1.71–1.64 (m, 2H), 1.51–1.44 (m, 1H), 1.39–1.33 (m, 1H), 1.10–1.01 (m, 1H), 0.99–0.93 (m, 1H), 0.89 (dd, J = 21.1, 6.8 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.9, 152.8 (d, $J_{C\text{-}P}$ = 7.8 Hz), 137.9, 132.1 (t, $J_{C\text{-}P}$ = 2.6 Hz), 131.6 (dd, $J_{C\text{-}P}$ = 10.4, 5.9 Hz), δ 131.1 (d, $J_{C\text{-}P}$ = 126.6 Hz), 130.6, 129.1, 128.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.3 (d, $J_{C\text{-}P}$ = 1.9 Hz), 127.4, 120.8, 74.3, 60.4 (d, $J_{C\text{-}P}$ = 4.9 Hz), 46.9, 40.9, 34.2, 31.4, 26.2, 23.4, 22.0, 20.7, 16.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.3. HRMS (ESI-TOF) *m/z* calcd. for $C_{32}H_{37}NaO_4P[M+Na]^+$, 539.2322, found 539.2328.

(*Z*)-3,7-dimethylocta-2,6-dien-1-yl (*Z*)-4-((diphenylphosphoryl)oxy)-3-phenylbut-2-enoate (49)



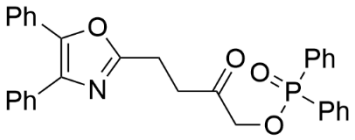
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a colorless oil in 74% yield (38.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64–7.58 (m, 4H), 7.51–7.44 (m, 4H), 7.38–7.32 (m, 7H), 6.14 (s, 1H), 5.59 (dd, J = 6.8, 0.9 Hz, 2H), 5.34 (t, J = 7.6 Hz, 1H), 5.13–5.02 (m, 1H), 4.72–4.49 (m, 2H), 2.21–1.97 (m, 4H), 1.76 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3, 152.9 (d, $J_{C\text{-}P}$ = 7.9 Hz), 142.8, 137.9, 132.1, 132.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.3 Hz), δ 131.0 (d, $J_{C\text{-}P}$ = 137.0 Hz), 129.1, 128.4 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.3, 127.34, 123.5, 120.3, 118.9, 61.1, 60.3 (d, $J_{C\text{-}P}$ = 4.8 Hz), 33.9, 32.1, 26.6, 25.6, 24.9, 23.5, 17.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{32}H_{35}NaO_4P[M+Na]^+$, 537.2165, found 537.2167.

2-(4-(*N,N*-dipropylsulfamoyl)phenyl)-2-oxoethyl diphenylphosphinate (50)



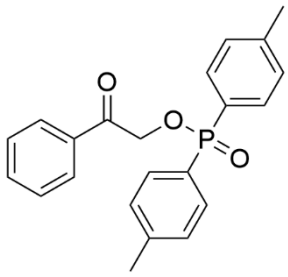
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a colorless oil in 82% yield (40.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99–7.96 (m, 2H), 7.90–7.85 (m, 6H), 7.57–7.51 (m, 2H), 7.48–7.44 (m, 4H), 5.29 (d, J = 7.8 Hz, 2H), 3.21–2.88 (m, 4H), 1.63–1.41 (m, 4H), 0.84 (t, J = 7.4 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.6 (d, $J_{C\text{-}P}$ = 6.7 Hz), 144.9, 136.6, 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.4 (d, $J_{C\text{-}P}$ = 137.3 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.5 Hz), 128.4, 127.3, 65.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 49.8, 21.8, 11.1. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.9. HRMS (ESI-TOF) *m/z* calcd. for $C_{26}H_{30}NNaO_5P[M+Na]^+$, 522.1475, found 522.1472.

4-(4,5-diphenyloxazol-2-yl)-2-oxobutyl diphenylphosphinate (51)



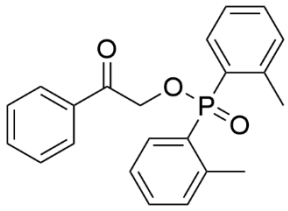
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 22% yield (11.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89–7.83 (m, 4H), 7.59 (dd, J = 8.1, 1.4 Hz, 2H), 7.56–7.51 (m, 4H), 7.49–7.43 (m, 5H), 7.37–7.30 (m, 5H), 4.68 (d, J = 8.0 Hz, 2H), 3.30–2.97 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.7, 145.5, 135.0, 132.6 (d, $J_{C\text{-}P}$ = 3.1 Hz), 132.1, 132.1, 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.4 (d, $J_{C\text{-}P}$ = 137.0 Hz), 128.9, 128.8, 128.6 (d, $J_{C\text{-}P}$ = 5.9 Hz), 128.5, 128.5, 128.0, 127.9, 126.5, 67.9, 35.3, 21.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.2. HRMS (ESI-TOF) *m/z* calcd. for $C_{31}H_{26}NNaO_4P[M+Na]^+$, 530.1492, found 530.1496.

2-oxo-2-phenylethyl di-*p*-tolylphosphinate (52)[10]



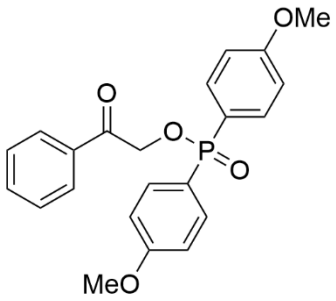
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a colorless oil in 75% yield (27.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (dd, J = 8.4, 1.2 Hz, 2H), 7.78 (dd, J = 12.3, 8.1 Hz, 4H), 7.61–7.52 (m, 1H), 7.48–7.41 (m, 2H), 7.27–7.26 (m, 2H), 7.25 (t, J = 0.7 Hz, 2H), 5.27 (d, J = 7.4 Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.6, 142.9, 134.2, 133.9, 131.8 (d, $J_{C\text{-}P}$ = 10.8 Hz), 129.4 (d, $J_{C\text{-}P}$ = 13.7 Hz), 128.8, 127.8, 127.6 (d, $J_{C\text{-}P}$ = 139.9 Hz), 65.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 21.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 35.4.

2-oxo-2-phenylethyl di-*o*-tolylphosphinate (53)



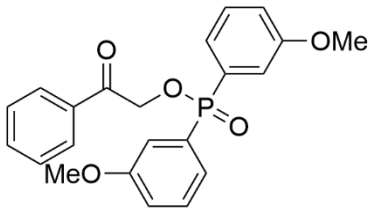
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 69% yield (25.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (dd, J = 13.5, 7.7 Hz, 2H), 7.88 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.47–7.39 (m, 4H), 7.34–7.27 (m, 2H), 7.22–7.17 (m, 2H), 5.30 (d, J = 6.6 Hz, 2H), 2.39 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.4 (d, $J_{C\text{-}P}$ = 7.6 Hz), 141.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 134.1, 133.8, 133.6, 133.55, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 12.7 Hz), 129.6 (d, $J_{C\text{-}P}$ = 2.1 Hz), 128.2 (d, $J_{C\text{-}P}$ = 158.7 Hz), 125.6 (d, $J_{C\text{-}P}$ = 12.7 Hz), 65.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 21.1 (d, $J_{C\text{-}P}$ = 4.3 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 35.3. HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{21}NaO_3P[M+Na]^+$, 387.1121, found 387.1115.

2-oxo-2-phenylethyl bis(4-methoxyphenyl)phosphinate (54)[10]



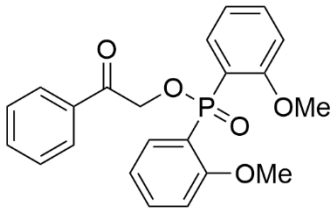
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a yellow oil in 93% yield (36.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (dd, J = 8.4, 1.2 Hz, 2H), 7.84–7.80 (m, 4H), 7.59–7.55 (m, 1H), 7.47–7.42 (m, 2H), 6.95 (dd, J = 8.8, 2.8 Hz, 4H), 5.26 (d, J = 7.5 Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.6 (d, $J_{C\text{-}P}$ = 7.0 Hz), 162.8 (d, $J_{C\text{-}P}$ = 3.2 Hz), 134.1, 133.9, 133.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.8, 127.8, 122.2 (d, $J_{C\text{-}P}$ = 145.3 Hz), 114.1 (d, $J_{C\text{-}P}$ = 14.5 Hz), 65.6 (d, $J_{C\text{-}P}$ = 5.3 Hz), 55.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 35.3.

2-oxo-2-phenylethyl bis(3-methoxyphenyl)phosphinate (55)



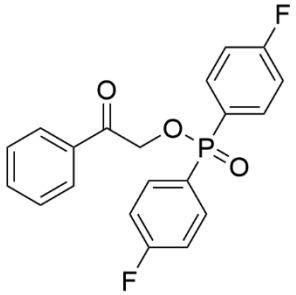
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 68% yield (26.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.48–7.42 (m, 6H), 7.39–7.32 (m, 2H), 7.06 (dd, J = 7.9, 2.2 Hz, 2H), 5.30 (d, J = 7.5 Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.3 (d, $J_{C\text{-}P}$ = 6.9 Hz), 159.5 (d, $J_{C\text{-}P}$ = 16.8 Hz), 134.1, 133.9, 131.8 (d, $J_{C\text{-}P}$ = 137.0 Hz), 129.9 (d, $J_{C\text{-}P}$ = 15.8 Hz), 128.8, 127.7, 124.0 (d, $J_{C\text{-}P}$ = 10.3 Hz), 119.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 116.1 (d, $J_{C\text{-}P}$ = 11.7 Hz), 65.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 55.4. ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{21}NaO_5P[M+Na]^+$, 419.1019, found 419.1017.

2-oxo-2-phenylethyl bis(2-methoxyphenyl)phosphinate (56)



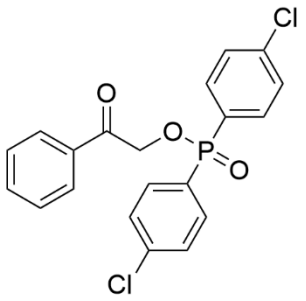
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a yellow solid in 63% yield (25.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05–7.95 (m, 2H), 7.91 (dd, J = 8.4, 1.2 Hz, 2H), 7.57–7.52 (m, 1H), 7.50–7.37 (m, 4H), 7.09–6.98 (m, 2H), 6.83 (dd, J = 8.1, 6.4 Hz, 2H), 5.27 (d, J = 7.4 Hz, 2H), 3.60 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 193.3 (d, $J_{C\text{-}P}$ = 7.5 Hz), 161.1 (d, $J_{C\text{-}P}$ = 4.2 Hz), 134.7 (d, $J_{C\text{-}P}$ = 6.8 Hz), 134.5, 133.9 (d, $J_{C\text{-}P}$ = 2.3 Hz), 133.5, 128.6, 127.9, 120.4 (d, $J_{C\text{-}P}$ = 13.0 Hz), 119.7 (d, $J_{C\text{-}P}$ = 141.4 Hz), 111.1 (d, $J_{C\text{-}P}$ = 8.1 Hz), 65.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 55.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 30.8. HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{21}NaO_5P[M+Na]^+$, 419.1019, found 419.1016.

2-oxo-2-phenylethyl bis(4-fluorophenyl)phosphinate (57)[10]



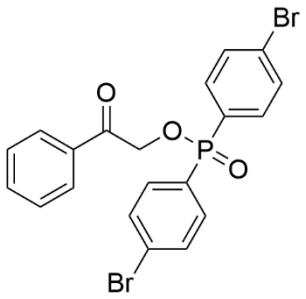
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a faint yellow oil in 58% yield (21.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95–7.89 (m, 4H), 7.86 (dd, J = 8.4, 1.2 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.20–7.12 (m, 4H), 5.31 (d, J = 8.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.2 (d, $J_{C\text{-}P}$ = 6.4 Hz), 165.5 (d, $J_{C\text{-}P}$ = 254.3, 3.6 Hz) , 134.5 (d, $J_{C\text{-}P}$ = 11.9, $J_{C\text{-}F}$ =8.9 Hz), 134.1, 133.9, 128.9, 127.7, 127.1 (d, $J_{C\text{-}P}$ = 142.3, $J_{C\text{-}F}$ =3.2 Hz), 116.2 (d, $J_{C\text{-}P}$ = 21.4, $J_{C\text{-}F}$ =14.7 Hz), 65.9 (d, $J_{C\text{-}P}$ = 5.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.7. ^{19}F NMR (564 MHz, $CDCl_3$): δ -105.2.

2-oxo-2-phenylethyl bis(4-chlorophenyl)phosphinate (58)[10]



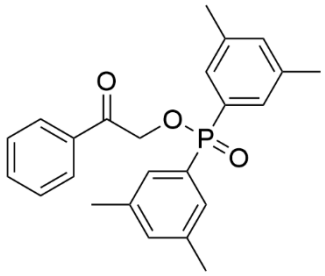
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow oil in 69% yield (27.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89–7.78 (m, 6H), 7.66–7.55 (m, 1H), 7.517.41 (m, 6H), 5.31 (d, J = 8.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.9, 139.4 (d, $J_{C\text{-}P}$ = 3.8 Hz), 134.1, 133.8, 133.2 (d, $J_{C\text{-}P}$ = 11.4 Hz), 129.1 (d, $J_{C\text{-}P}$ = 14.1 Hz), 128.9, 128.9 (d, $J_{C\text{-}P}$ = 140.6 Hz), 127.7, 65.9 (d, $J_{C\text{-}P}$ = 5.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.5.

2-oxo-2-phenylethyl bis(4-bromophenyl)phosphinate (59)



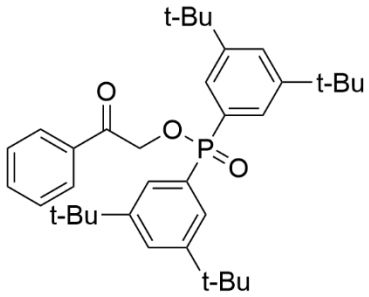
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 77% yield (37.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.4, 1.3 Hz, 2H), 7.79–7.71 (m, 4H), 7.64–7.55 (m, 5H), 7.49–7.40 (m, 2H), 5.31 (d, J = 8.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.9 (d, $J_{C\text{-}P}$ = 6.1 Hz), 134.1, 133.8, 133.2 (d, $J_{C\text{-}P}$ = 11.4 Hz), 132.1 (d, $J_{C\text{-}P}$ = 14.1 Hz), 129.3 (d, $J_{C\text{-}P}$ = 140.4 Hz), 128.9, 128.0 (d, $J_{C\text{-}P}$ = 3.5 Hz), 127.6, 65.9 (d, $J_{C\text{-}P}$ = 5.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 32.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{20}H_{15}Br_2NaO_3P[M+Na]^+$, 514.9018, found 514.9023.

2-oxo-2-phenylethyl bis(3,5-dimethylphenyl)phosphinate (60)



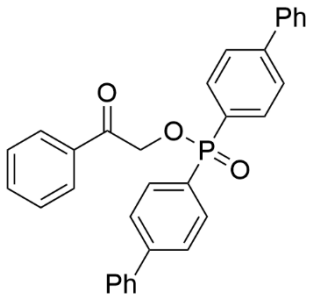
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 85% yield (33.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.50 (d, J = 12.7 Hz, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.13 (s, 2H), 5.25 (d, J = 7.1 Hz, 2H), 2.31 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 138.3, 133.2, 134.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 133.7, 130.4 (d, $J_{C\text{-}P}$ = 135.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 10.4 Hz), 128.7, 127.7, 65.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 21.2. ^{31}P NMR (243 MHz, $CDCl_3$): δ 35.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{24}H_{25}NaO_3P[M+Na]^+$, 415.1434, found 415.1435.

2-oxo-2-phenylethyl bis(3,5-di-*tert*-butylphenyl)phosphinate (61)



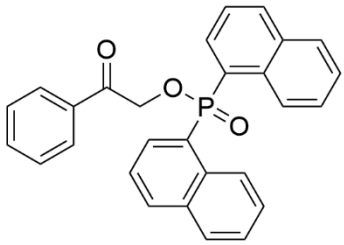
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 81% yield (45.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (dd, J = 8.3, 1.2 Hz, 2H), 7.77 (dd, J = 13.1, 1.9 Hz, 4H), 7.60–7.54 (m, 3H), 7.47–7.40 (m, 2H), 5.27 (d, J = 7.8 Hz, 2H), 1.31 (s, 36H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.8 (d, $J_{C\text{-}P}$ = 6.6 Hz), 151.1 (d, $J_{C\text{-}P}$ = 13.1 Hz), 134.4, 133.7, 129.8 (d, $J_{C\text{-}P}$ = 135.4 Hz), 128.8, 127.8, 126.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 126.1 (d, $J_{C\text{-}P}$ = 10.9 Hz), 65.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 35.0, 31.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 37.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{36}H_{49}NaO_3P[M+Na]^+$, 583.3312, found 583.3315.

2-oxo-2-phenylethyl di([1,1'-biphenyl]-4-yl)phosphinate (62)



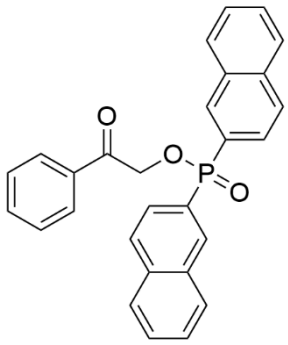
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a colorless oil in 97% yield (47.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (dd, J = 12.2, 8.4 Hz, 4H), 7.91 (dd, J = 8.4, 1.2 Hz, 2H), 7.75–7.64 (m, 4H), 7.61–7.54 (m, 5H), 7.50–7.43 (m, 6H), 7.41–7.34 (m, 2H), 5.38 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.3 (d, $J_{C\text{-}P}$ = 6.6 Hz), 145.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 139.8, 133.9, 133.9, 132.3 (d, $J_{C\text{-}P}$ = 10.6 Hz), 129.7, 128.9, 128.2 (d, $J_{C\text{-}P}$ = 166.1 Hz), 128.1, 127.4, 127.3, 127.2, 65.8 (d, $J_{C\text{-}P}$ = 5.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.5. HRMS (ESI-TOF) *m/z* calcd. for $C_{32}H_{25}NaO_3P[M+Na]^+$, 511.1434, found 511.1434.

2-oxo-2-phenylethyl di(naphthalen-1-yl)phosphinate (63)



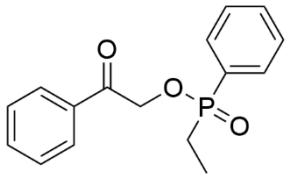
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 59% yield (25.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.71–8.67 (m, 2H), 8.34–8.27 (m, 2H), 8.05 (d, J = 8.2 Hz, 2H), 7.91–7.83 (m, 4H), 7.59–7.47 (m, 7H), 7.45–7.40 (m, 2H), 5.41 (d, J = 7.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.3 (d, $J_{C\text{-}P}$ = 7.4 Hz), 134.3 (d, $J_{C\text{-}P}$ = 10.3 Hz), 134.1, 133.9 (d, $J_{C\text{-}P}$ = 3.1 Hz), 133.8, 133.7, 133.6, 132.9 (d, $J_{C\text{-}P}$ = 10.9 Hz), 128.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.8, 127.8, 127.7, 127.1 (d, $J_{C\text{-}P}$ = 133.8 Hz), 126.5 (d, $J_{C\text{-}P}$ = 4.6 Hz), 124.7 (d, $J_{C\text{-}P}$ = 15.2 Hz), 66.1 (d, $J_{C\text{-}P}$ = 5.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 36.9. HRMS (ESI-TOF) *m/z* calcd. for $C_{28}H_{21}NaO_3P[M+Na]^+$, 459.1121, found 459.1125.

2-oxo-2-phenylethyl di(naphthalen-2-yl)phosphinate (64)



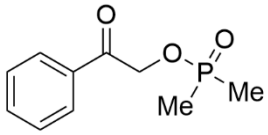
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with dichloromethane/methanol (80/1) to afford a yellow oil in 66% yield (28.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.60 (d, J = 14.4 Hz, 2H), 7.97–7.81 (m, 10H), 7.62–7.51 (m, 5H), 7.44 (t, J = 7.7 Hz, 2H), 5.40 (d, J = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.4 (d, $J_{C\text{-}P}$ = 6.9 Hz), 135.0 (d, $J_{C\text{-}P}$ = 2.4 Hz), 134.1, 134.0, 133.9, 132.4 (d, $J_{C\text{-}P}$ = 14.7 Hz), 129.1, 128.8, 128.7, 128.6, 128.4, 127.8 (d, $J_{C\text{-}P}$ = 10.9 Hz), 127.8 (d, $J_{C\text{-}P}$ = 138.0 Hz), 126.9, 126.4 (d, $J_{C\text{-}P}$ = 11.2 Hz), 65.9 (d, $J_{C\text{-}P}$ = 5.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{28}H_{21}NaO_3P[M+Na]^+$, 459.1121, found 459.1123.

2-oxo-2-phenylethyl ethyl(phenyl)phosphinate (65)



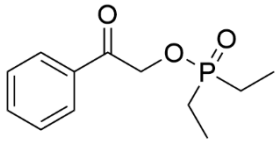
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a colorless oil in 54% yield (15.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.77 (m, 4H), 7.59–7.55 (m, 2H), 7.52–7.47 (m, 2H), 7.46–7.42 (m, 2H), 5.39 (dd, J = 16.6, 7.2 Hz, 1H), 5.01 (dd, J = 16.6, 8.3 Hz, 1H), 2.14–1.95 (m, 2H), 1.22–1.14 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.7 (d, $J_{C\text{-}P}$ = 6.4 Hz), 134.0, 133.9, 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.8, 128.7, 128.6, 128.5, 127.7, 65.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), δ 22.6 (d, $J_{C\text{-}P}$ = 9.8 Hz), 22.9 (d, $J_{C\text{-}P}$ = 100.6 Hz), 5.7 (d, $J_{C\text{-}P}$ = 5.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 50.0. HRMS (ESI-TOF) *m/z* calcd. for $C_{16}H_{17}NaO_3P[M+Na]^+$, 311.0808, found 311.0811.

2-oxo-2-phenylethyl dimethylphosphinate (66)



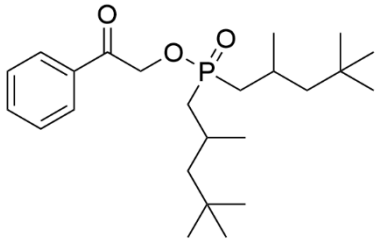
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with DCM/MeOH (10/1) to afford a yellow solid in 94% yield (19.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (dd, J = 8.4, 1.2 Hz, 2H), 7.61–7.54 (m, 1H), 7.45 (t, J = 7.8 Hz, 2H), 5.30 (d, J = 10.7 Hz, 2H), 1.61 (d, J = 14.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 193.3 (d, $J_{C\text{-}P}$ = 3.8 Hz), 133.9, 133.8, 128.8, 127.6, 65.6 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.4 (d, $J_{C\text{-}P}$ = 94.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 57.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{10}H_{13}NaO_3P[M+Na]^+$, 235.0495, found 235.0496.

2-oxo-2-phenylethyl diethylphosphinate (67)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 83% yield (19.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, J = 8.3 Hz, 2H), 7.56 (t, J = 7.8 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 5.29 (d, J = 9.7 Hz, 2H), 1.97–1.66 (m, 4H), 1.41–0.95 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 193.5 (d, $J_{C\text{-}P}$ = 3.8 Hz), 133.9, 133.8, 128.8, 127.6, 65.7 (d, $J_{C\text{-}P}$ = 6.3 Hz), 20.9 (d, $J_{C\text{-}P}$ = 90.1 Hz), 5.7 (d, $J_{C\text{-}P}$ = 5.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 64.8. HRMS (ESI-TOF) *m/z* calcd. for $C_{12}H_{17}NaO_3P[M+Na]^+$, 263.0808, found 263.0812.

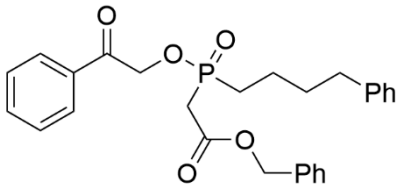
2-oxo-2-phenylethyl bis(2,4,4-trimethylpentyl)phosphinate (68)



The title compound was prepared according to the general procedure and purified by column chromatography on

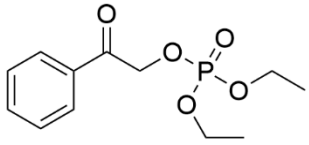
silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a colorless oil in 51% yield (20.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 5.3, 2.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.28 (d, *J* = 8.9 Hz, 2H), 2.10–2.01 (m, 2H), 1.92–1.82 (m, 2H), 1.76–1.62 (m, 2H), 1.40–1.30 (m, 2H), 1.21–1.15 (m, 2H), 1.12 (t, *J* = 6.9 Hz, 6H), 0.90 (d, *J* = 3.7 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 193.4 (d, $J_{C\text{-}P}$ = 4.8 Hz), 134.2 (t, $J_{C\text{-}P}$ = 4.6 Hz), 133.8 (t, $J_{C\text{-}P}$ = 3.8 Hz), 128.8 (t, $J_{C\text{-}P}$ = 1.9 Hz), 127.7 (t, $J_{C\text{-}P}$ = 6.0 Hz), 66.3–64.9 (m), 52.8 (dd, $J_{C\text{-}P}$ = 12.0, 7.6 Hz), 40.1–38.4 (m), 31.1 (d, $J_{C\text{-}P}$ = 4.1 Hz), 29.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 24.6 (d, $J_{C\text{-}P}$ = 4.4 Hz), 24.6–24.0 (m). ^{31}P NMR (243 MHz, $CDCl_3$): δ 60.6. HRMS (ESI-TOF) *m/z* calcd. for $C_{24}H_{41}NaO_3P[M+Na]^+$, 431.2686, found 431.2682.

benzyl 2-((2-oxo-2-phenylethoxy)(4-phenylbutyl)phosphoryl)acetate (69)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with dichloromethane/methanol (2/1) to afford a white solid in 53% yield (24.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38–7.26 (m, 7H), 7.17 (dd, *J* = 15.7, 7.5 Hz, 3H), 5.34–5.24 (m, 2H), 5.20–5.14 (m, 2H), 3.14 (d, *J* = 16.3 Hz, 2H), 2.61 (t, *J* = 7.0 Hz, 2H),1.83–1.62 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.8 (d, $J_{C\text{-}P}$ = 3.8 Hz), 166.1 (d, $J_{C\text{-}P}$ = 4.2 Hz), 141.8, 135.1, 133.9, 133.8, 128.9, 128.6, 128.5 (d, $J_{C\text{-}P}$ = 4.8 Hz), 128.3 (d, $J_{C\text{-}P}$ = 3.5 Hz), 127.7, 125.8, 67.5, 66.4 (d, $J_{C\text{-}P}$ = 7.0 Hz), 37.2 (d, $J_{C\text{-}P}$ = 76.8 Hz) , 35.3, 32.3 (d, $J_{C\text{-}P}$ = 16.4 Hz), 29.2 (d, $J_{C\text{-}P}$ = 96.9 Hz) , 21.0 (d, $J_{C\text{-}P}$ = 4.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 51.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{27}H_{29}NaO_5P[M+Na]^+$, 487.1645, found 487.1646.

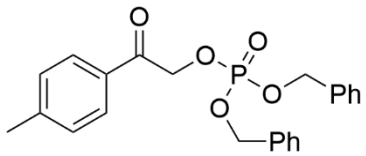
diethyl (2-oxo-2-phenylethyl) phosphate (70)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 34% yield (9.3 mg). ^{1}H NMR

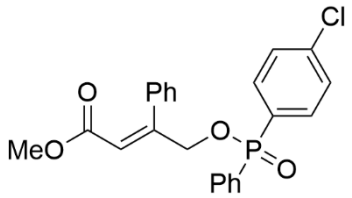
(600 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 5.30 (d, J = 9.9 Hz, 2H), 4.35–4.10 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.2 (d, $J_{C\text{-}P}$ = 5.4 Hz), 133.9 (d, $J_{C\text{-}P}$ = 3.4 Hz), 128.9, 127.7, 68.7 (d, $J_{C\text{-}P}$ = 5.1 Hz), 64.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 16.1 (d, $J_{C\text{-}P}$ = 6.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ -0.9. HRMS (ESI-TOF) *m/z* calcd. for $C_{12}H_{17}NaO_5P[M+Na]^+$, 295.0706, found 295.0709.

dibenzyl (2-oxo-2-(*p*-tolyl)ethyl) phosphate (71)



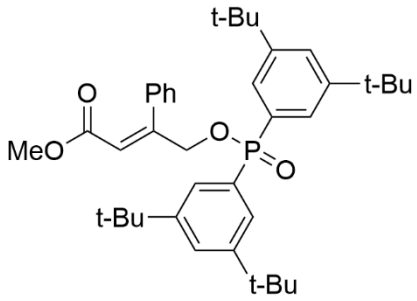
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 31% yield (12.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78–7.64 (m, 2H), 7.39–7.31 (m, 10H), 7.27–7.27 (m, 1H), 7.26–7.25 (m, 1H), 5.33–5.01 (m, 6H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 144.9, 135.7 (d, $J_{C\text{-}P}$ = 7.1 Hz), 131.4, 129.5, 128.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 128.1, 127.9, 127.8, 69.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 68.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 21.7. ^{31}P NMR (243 MHz, $CDCl_3$): δ -0.9. HRMS (ESI-TOF) *m/z* calcd. for $C_{23}H_{23}NaO_5P[M+Na]^+$, 433.1175, found 433.1177.

methyl (*E*)-4-(((4-chlorophenyl)(phenyl)phosphoryl)oxy)-3-phenylbut-2-enoate (72)



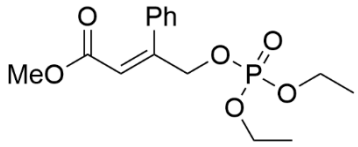
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 55% yield (23.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62–7.57 (m, 2H), 7.54–7.50 (m, 2H), 7.50–7.46 (m, 3H), 7.40–7.35 (m, 5H), 7.34–7.31 (m, 2H), 6.14 (d, J = 0.8 Hz, 1H), 5.66–5.49 (m, 2H), 3.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.7, 152.8 (d, $J_{C\text{-}P}$ = 7.6 Hz), 138.7 (d, $J_{C\text{-}P}$ = 3.7 Hz), 137.7, 133.0 (d, $J_{C\text{-}P}$ = 11.3 Hz), 132.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 10.4 Hz), 131.2, 130.1 (d, $J_{C\text{-}P}$ = 283.8 Hz), 129.3, 129.2, 128.7, 128.7, 128.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 128.4, 127.3, 120.1, 60.4 (d, $J_{C\text{-}P}$ = 4.8 Hz), 51.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ 31.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{23}H_{20}ClNaO_4P[M+Na]^+$, 449.0680, found 449.0678.

methyl (*E*)-4-((bis(3,5-di-*tert*-butylphenyl)phosphoryl)oxy)-3-phenylbut-2-enoate (73)



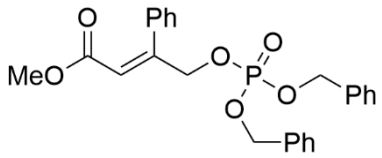
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a yellow solid in 50% yield (30.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57–7.54 (m, 2H), 7.53–7.50 (m, 6H), 7.41–7.37 (m, 3H), 6.14 (d, J = 0.9 Hz, 1H), 5.57 (dd, J = 6.2, 1.0 Hz, 2H), 3.65 (s, 3H), 1.25 (s, 36H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.7, 153.3 (d, $J_{C\text{-}P}$ = 8.2 Hz), 150.8 (d, $J_{C\text{-}P}$ = 12.7 Hz), 138.0, 130.3 (d, $J_{C\text{-}P}$ = 135.1 Hz), 129.3, 128.5, 127.4, 126.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 125.8 (d, $J_{C\text{-}P}$ = 10.9 Hz), 119.7, 59.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 51.4, 34.9, 31.3. ^{31}P NMR (243 MHz, $CDCl_3$): δ 35.1. HRMS (ESI-TOF) *m/z* calcd. for $C_{39}H_{53}NaO_4P[M+Na]^+$, 639.3574, found 639.3576.

methyl (*E*)-4-((diethoxyphosphoryl)oxy)-3-phenylbut-2-enoate (74)



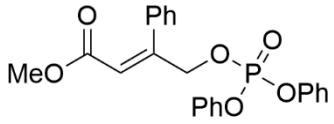
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow solid in 46% yield (15.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52–7.44 (m, 2H), 7.41–7.32 (m, 3H), 6.18 (d, J = 0.8 Hz, 1H), 5.59 (dd, J = 7.0, 1.0 Hz, 2H), 4.03–3.82 (m, 4H), 3.77 (s, 3H), 1.30–1.10 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 152.8 (d, $J_{C\text{-}P}$ = 8.1 Hz), 137.7, 129.3, 128.5, 127.3, 120.1, 63.8 (d, $J_{C\text{-}P}$ = 5.8 Hz), 62.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 51.7, 15.9 (d, $J_{C\text{-}P}$ = 6.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ -1.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{15}H_{21}NaO_6P[M+Na]^+$, 351.0968, found 351.0971.

methyl (*E*)-4-((bis(benzyloxy)phosphoryl)oxy)-3-phenylbut-2-enoate (75)



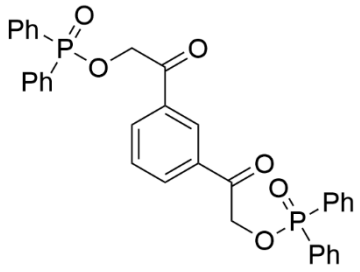
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a yellow oil in 86% yield (38.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47–7.44 (m, 2H), 7.36 (dd, *J* = 4.9, 1.6 Hz, 3H), 7.31 (dd, *J* = 5.1, 1.9 Hz, 6H), 7.24 (dd, *J* = 6.9, 2.7 Hz, 4H), 6.17 (d, *J* = 1.0 Hz, 1H), 5.63 (dd, *J* = 7.2, 1.0 Hz, 2H), 4.96–4.68 (m, 4H), 3.75 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 152.4 (d, $J_{C\text{-}P}$ = 8.1 Hz), 137.5, 135.7 (d, $J_{C\text{-}P}$ = 7.1 Hz), 129.3, 128.5, 128.4, 128.3, 127.8, 127.3, 120.2, 69.1 (d, $J_{C\text{-}P}$ = 5.6 Hz), 62.9 (d, $J_{C\text{-}P}$ = 4.8 Hz), 51.6. ^{31}P NMR (243 MHz, $CDCl_3$): δ -1.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{25}H_{25}NaO_6P[M+Na]^+$, 475.1281, found 475.1280.

methyl (*E*)-4-((diphenoxyphosphoryl)oxy)-3-phenylbut-2-enoate (76)



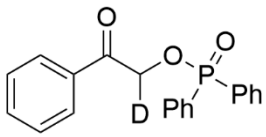
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a yellow solid in 48% yield (20.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.38–7.32 (m, 3H), 7.27 (s, 1H), 7.25 (s, 3H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 4H), 6.19 (s, 1H), 5.83 (d, *J* = 7.3 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 151.8 (d, $J_{C\text{-}P}$ = 8.2 Hz), 150.4 (d, $J_{C\text{-}P}$ = 7.2 Hz), 137.3, 129.6, 129.5, 128.6, 127.2, 125.2, 120.6, 120.0 (d, $J_{C\text{-}P}$ = 4.9 Hz), 64.1 (d, $J_{C\text{-}P}$ = 5.2 Hz), 51.7. ^{31}P NMR (243 MHz, $CDCl_3$): δ -12.4. HRMS (ESI-TOF) *m/z* calcd. for $C_{23}H_{21}NaO_6P[M+Na]^+$, 447.0968, found 447.0969.

1,3-phenylenebis(2-oxoethane-2,1-diyl) bis(diphenylphosphinate) (78)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 42% yield (24.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (t, J = 1.5 Hz, 1H), 8.08 (dd, J = 7.8, 1.7 Hz, 2H), 7.92–7.85 (m, 8H), 7.59–7.51 (m, 5H), 7.49–7.44 (m, 8H), 5.29 (d, J = 7.9 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.7 (d, $J_{C\text{-}P}$ = 6.5 Hz), 134.6, 132.7, 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 137.2 Hz), 129.6, 128.7 (d, $J_{C\text{-}P}$ = 13.4 Hz), 127.1, 65.9 (d, $J_{C\text{-}P}$ = 5.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$): δ 34.8. HRMS (ESI-TOF) *m/z* calcd. for $C_{34}H_{28}NaO_6P_2[M+Na]^+$, 617.1253, found 617.1255.

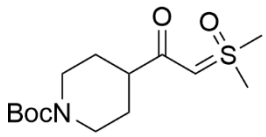
2-oxo-2-phenylethyl-1-*d* diphenylphosphinate (3-*d*)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a yellow oil in 77% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96–7.90 (m, 4H), 7.89–7.84 (m, 2H), 7.60–7.56 (m, 1H), 7.55–7.52 (m, 2H), 7.49–7.43 (m, 6H), 5.31 (d, J = 7.5 Hz, 1H).

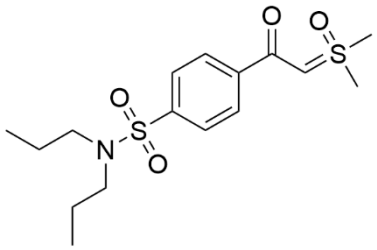
9. Characterization Data for Sulfoxonium Ylides

***tert*-butyl 4-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)piperidine-1-carboxylate (A36)**[6]



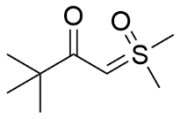
The title compound was prepared according to the general procedure to afford a white solid in 75 % yield (2.27 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.35 (s, 1H), 4.04 (s, 2H), 3.33 (s, 6H), 2.73–2.60 (m, 2H), 2.12 (t, *J* = 11.7 Hz, 1H), 1.71 (d, *J* = 12.7 Hz, 2H), 1.49–1.40 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.3, 154.6, 79.2, 68.5, 46.5, 43.9, 43.1, 42.0, 40.8, 28.8, 28.3.

4-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-*N,N*-dipropylbenzenesulfonamide (A42)[5]



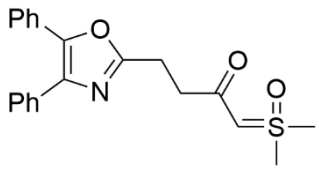
The title compound was prepared according to the general procedure to afford a white solid in 85 % yield (1.79 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55–7.49 (m, 2H), 7.38 (dd, *J* = 4.3, 2.3 Hz, 3H), 6.28 (s, 1H), 4.77 (s, 1H), 3.66 (s, 3H), 2.96 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 158.2, 140.9, 129.1, 128.8, 128.2, 95.5, 70.3, 50.2, 44.3.

1-(dimethyl(oxo)- λ^6-sulfaneylidene)-3,3-dimethylbutan-2-one(A53)



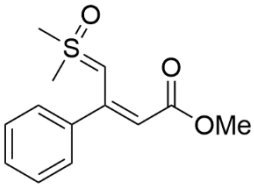
The title compound was prepared according to the general procedure to afford a white solid in 70 % yield (0.71 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.43 (s, 1H), 3.36 (s, 6H), 1.10 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.8, 66.3, 42.3, 40.8, 27.8. HRMS (ESI-TOF) *m/z* calcd. for $C_8H_{16}NaO_2S[M+Na]^+$, 199.0763, found 199.0766.

1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(4,5-diphenyloxazol-2-yl)butan-2-one (A58)



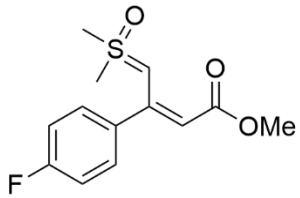
The title compound was prepared according to the general procedure to afford a yellow solid in 50 % yield (0.920 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64–7.61 (m, 2H), 7.59–7.56 (m, 2H), 7.37–7.29 (m, 6H), 4.45 (s, 1H), 3.37 (s, 6H), 3.15 (dd, *J* = 8.4, 7.1 Hz, 2H), 2.75 (dd, *J* = 8.4, 7.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 187.9, 163.0, 145.1, 135.0, 132.6, 129.1, 128.6, 128.5, 128.3, 127.9, 127.8, 126.4, 69.1, 42.3, 37.2, 24.3. HRMS (ESI-TOF) *m/z* calcd. for $C_{21}H_{21}NNaO_3S[M+Na]^+$, 390.1134, found 390.1136.

methyl (*Z*)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-phenylbut-2-enoate (A26)[8]



The title compound was prepared according to the general procedure to afford a white solid in 92 % yield (0.460 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55–7.49 (m, 2H), 7.38 (dd, *J* = 4.3, 2.3 Hz, 3H), 6.28 (s, 1H), 4.77 (s, 1H), 3.66 (s, 3H), 2.96 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 158.2, 140.9, 129.1, 128.8, 128.2, 95.5, 70.3, 50.2, 44.3.

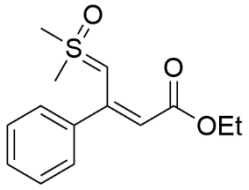
methyl (*Z*)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-(4-fluorophenyl)but-2-enoate (A27)[8]



The title compound was prepared according to the general procedure to afford a yellow solid in 85 % yield (0.46 g). ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.44–7.38 (m, 2H), 7.26–7.20 (m, 2H), 6.17 (s, 1H), 4.32 (s, 1H), 3.47 (s, 3H), 3.10 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.1, 162.9, 161.3, 157.2, 137.4 (d, *J* = 3.2 Hz), 130.7 (d, *J* = 8.3

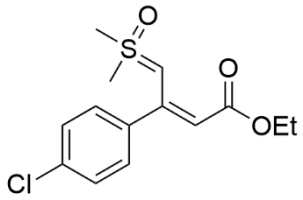
Hz), 114.9 (d, J = 21.3 Hz), 91.6, 73.4, 49.3, 43.3. ^{19}F NMR (564 MHz, DMSO-d_6): δ -113.4.

ethyl (*Z*)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-phenylbut-2-enoate (A28)



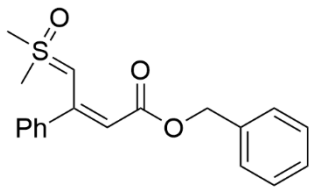
The title compound was prepared according to the general procedure to afford a yellow solid in 90 % yield (0.48 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (dd, J = 6.5, 3.0 Hz, 2H), 7.42–7.35 (m, 3H), 6.28 (s, 1H), 4.78 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.96 (s, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.6, 158.0, 141.0, 129.1, 128.7, 128.2, 96.1, 70.1, 58.6, 44.3, 14.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{14}H_{18}NaO_3S[M+Na]^+$, 289.0869, found 289.0871.

ethyl (*Z*)-3-(4-chlorophenyl)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)but-2-enoate (A39)



The title compound was prepared according to the general procedure to afford a white solid in 90 % yield (0.54 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 6.24 (s, 1H), 4.74 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.01 (s, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.4, 156.6, 139.4, 134.8, 130.5, 128.5, 96.5, 69.7, 58.7, 44.5, 14.6. HRMS (ESI-TOF) *m/z* calcd. for $C_{14}H_{17}ClNaO_3S[M+Na]^+$, 323.0479, found 323.0482.

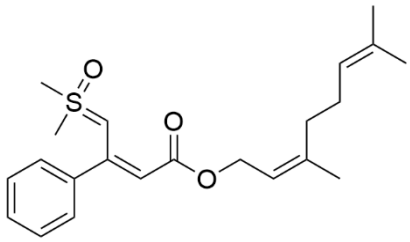
benzyl (*Z*)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-phenylbut-2-enoate (A40)[8]



The title compound was prepared according to the general procedure to afford a yellow solid in 85 % yield (0.56 g).

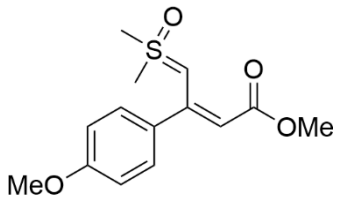
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55–7.51 (m, 2H), 7.38 (d, *J* = 6.7 Hz, 5H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.29 (s, 1H), 5.14 (s, 2H), 4.85 (s, 1H), 2.96 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.2, 158.5, 140.9, 137.5, 129.1, 128.8, 128.4, 128.2, 127.9, 127.6, 95.6, 70.7, 64.5, 44.3.

(*Z*)-3,7-dimethylocta-2,6-dien-1-yl (Z)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-phenylbut-2-enoate (A41)



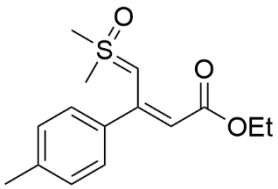
The title compound was prepared according to the general procedure to afford a yellow solid in 65 % yield (0.49 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54–7.50 (m, 2H), 7.37 (d, *J* = 4.3 Hz, 3H), 6.28 (s, 1H), 5.41 (t, *J* = 7.0 Hz, 1H), 5.10 (t, *J* = 6.5 Hz, 1H), 4.79 (s, 1H), 4.57 (d, *J* = 7.1 Hz, 2H), 2.96 (s, 6H), 2.14–2.10 (m, 2H), 2.10–2.06 (m, 2H), 1.75 (s, 3H), 1.67 (s, 3H), 1.59 (d, *J* = 4.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.6, 158.0, 141.2 (d, *J* = 31.2 Hz), 131.9, 129.1, 128.7, 128.2, 123.8, 120.4, 96.0, 70.2, 59.4, 44.3, 32.2, 26.7, 25.7, 23.5, 17.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{30}NaO_3S[M+Na]^+$, 397.1808, found 397.1812.

methyl (*Z*)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-(4-methoxyphenyl)but-2-enoate (A59)[8]



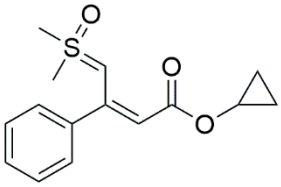
The title compound was prepared according to the general procedure to afford a yellow solid in 71 % yield (0.40 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54–7.43 (m, 2H), 6.94–6.85 (m, 2H), 6.26 (s, 1H), 4.77 (s, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 2.99 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 160.1, 158.1, 133.4, 130.4, 113.6, 95.3, 70.4, 55.3, 50.2, 44.3.

ethyl (*Z*)-4-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-(*p*-tolyl)but-2-enoate (A60)



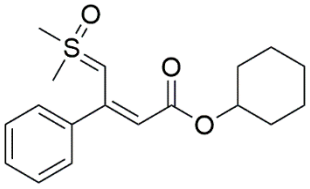
The title compound was prepared according to the general procedure to afford a yellow solid in 80 % yield (0.45 g). ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.26 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 6.16 (s, 1H), 4.30 (s, 1H), 3.94 (q, J = 7.1 Hz, 2H), 3.05 (s, 6H), 2.33 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H).. ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.8, 158.3, 138.4, 137.8, 128.6, 128.4, 91.6, 73.2, 57.2, 43.1, 38.9, 20.8, 14.7. HRMS (ESI-TOF) *m/z* calcd. for $C_{15}H_{20}NaO_3S[M+Na]^+$, 303.1025, found 303.1023.

cyclopropyl (*Z*)-4-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-phenylbut-2-enoate (A61)



The title compound was prepared according to the general procedure to afford a white solid in 70 % yield (0.39 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52–7.47 (m, 2H), 7.38–7.34 (m, 3H), 6.33 (s, 1H), 4.70 (s, 1H), 4.07–3.97 (m, 1H), 2.96 (s, 6H), 0.70–0.62 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.4, 158.6, 140.9, 129.0, 128.8, 128.2, 128.1, 95.2, 70.9, 58.4, 47.2, 44.2, 40.9, 18.4, 5.1. HRMS (ESI-TOF) *m/z* calcd. for $C_{15}H_{18}NaO_3S[M+Na]^+$, 301.0869, found 301.0870.

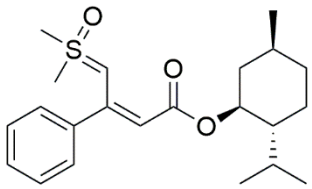
cyclohexyl (*Z*)-4-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-phenylbut-2-enoate (A62)[9]



The title compound was prepared according to the general procedure to afford a yellow solid in 63 % yield (0.40 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57–7.50 (m, 2H), 7.37 (dd, J = 3.7, 2.7 Hz, 3H), 6.29 (s, 1H), 4.78 (s, 1H), 2.96 (s, 6H), 1.89 (dd, J = 8.3, 4.0 Hz, 2H), 1.77–1.68 (m, 2H), 1.43–1.35 (m, 4H), 1.34–1.30 (m, 1H), 1.28–1.19 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.2, 157.7, 141.1, 129.1, 128.7, 128.2, 96.8, 70.7, 69.9, 44.4, 32.2, 25.6, 24.1.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl(*Z*)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-phenylbut-2-enoate (A63)



The title compound was prepared according to the general procedure to afford a white solid in 70 % yield (0.53 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55–7.51 (m, 2H), 7.39–7.34 (m, 3H), 6.27 (s, 1H), 4.75 (s, 1H), 4.69–4.60 (m, 1H), 2.99 (s, 3H), 2.93 (s, 3H), 1.68 (s, 6H), 1.23 (t, *J* = 7.0 Hz, 1H), 1.11–1.03 (m, 1H), 0.97–0.92 (m, 1H), 0.88 (dd, *J* = 12.7, 6.8 Hz, 6H), 0.77 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.3, 157.6, 141.1, 129.1, 128.6, 128.2, 96.7, 72.0, 69.9, 47.2, 44.3 (d, *J* = 5.9 Hz), 41.6, 34.4, 31.5, 26.1, 23.7, 22.1, 20.8, 16.6. HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{32}NaO_3S[M+Na]^+$, 399.1964, found 399.1967.

10. References

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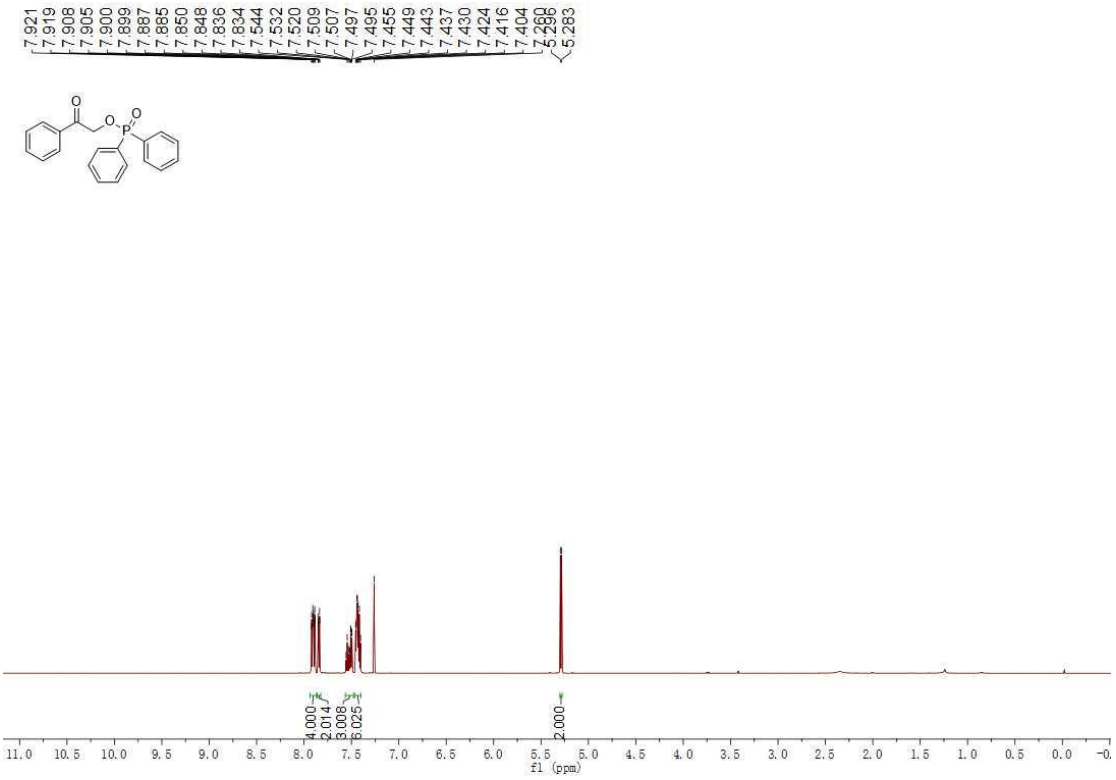
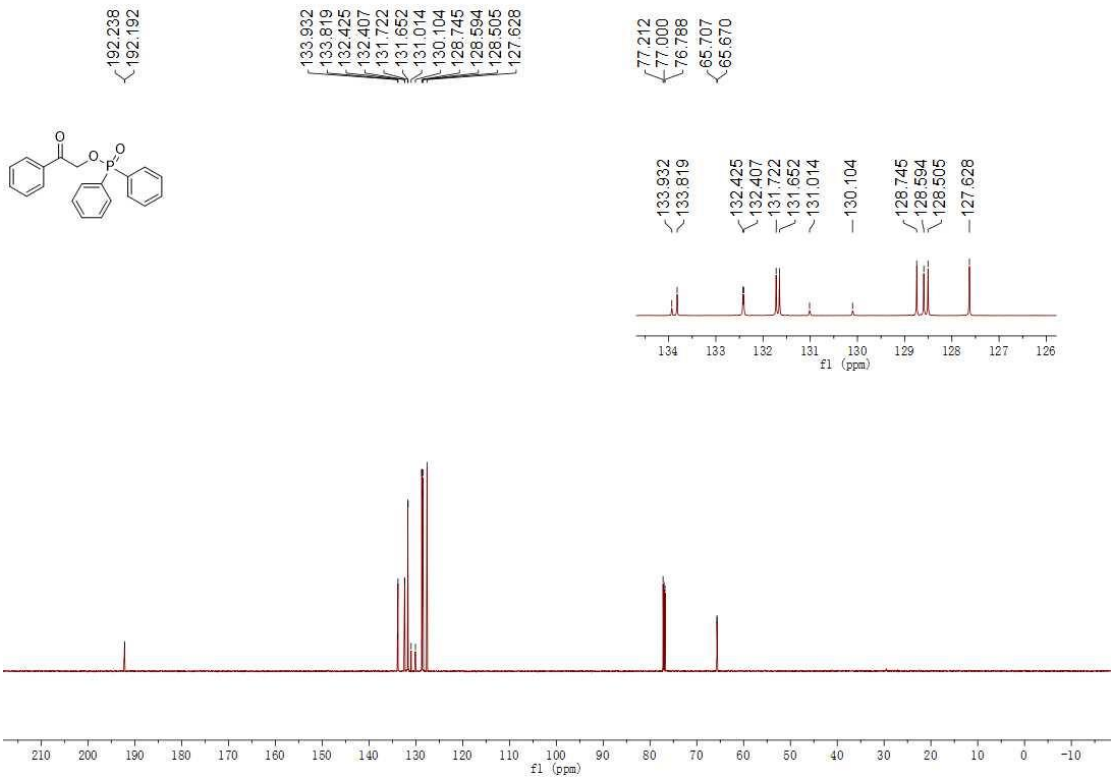
11. NMR Spectral Data for Isolated Products and Sulfoxonium Ylides

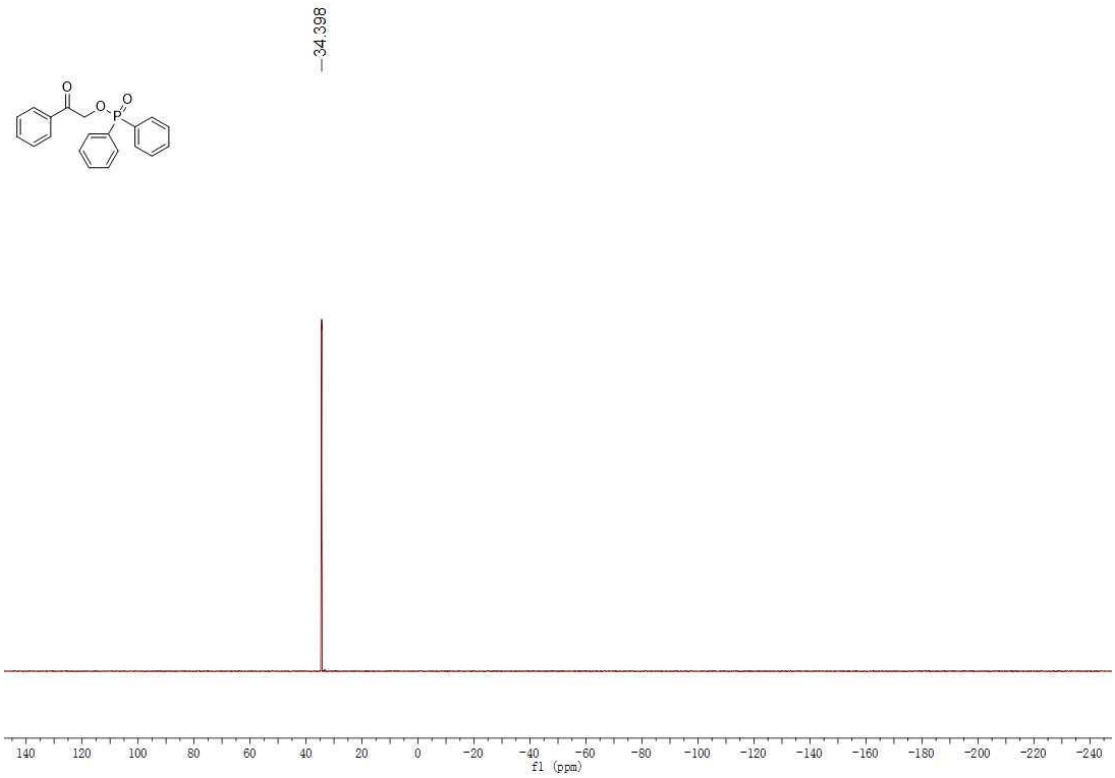
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **3**



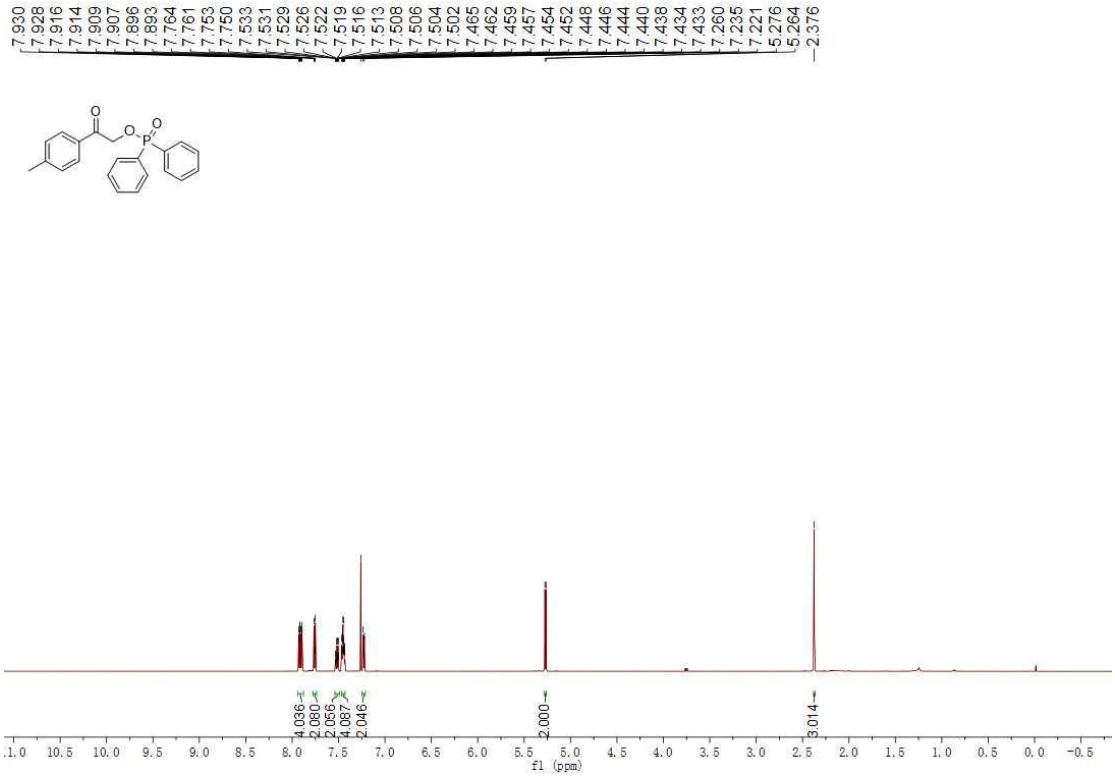
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **3**



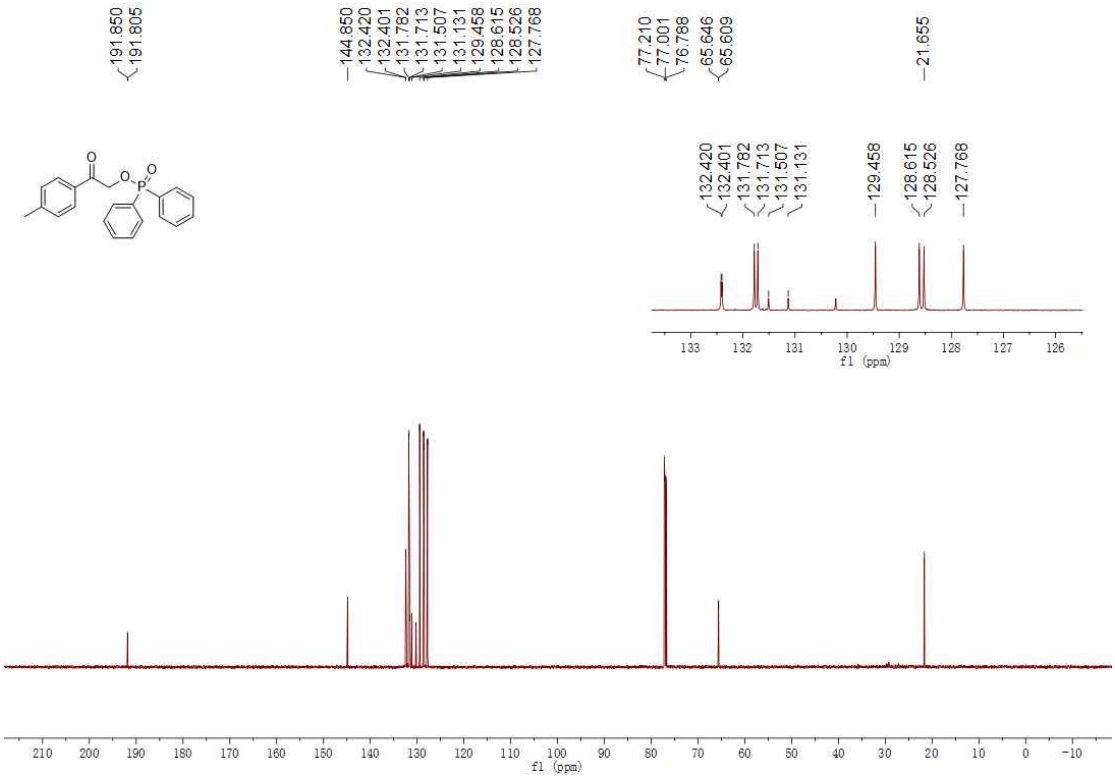
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **3**



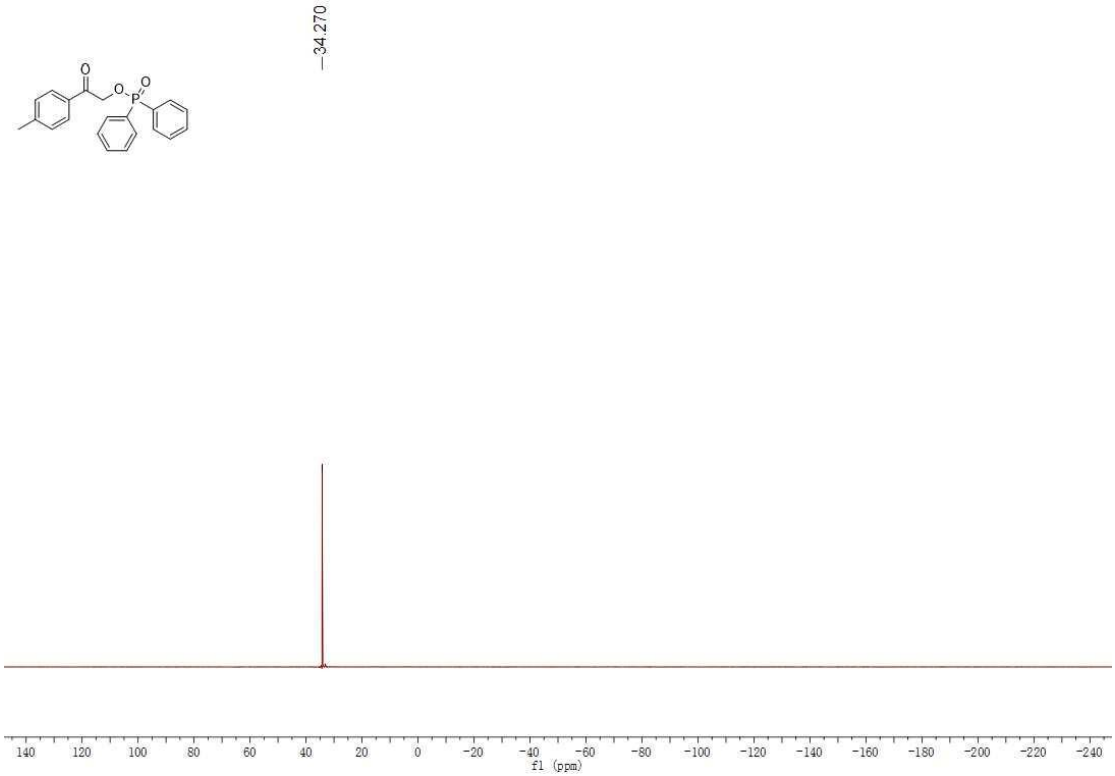
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **4**



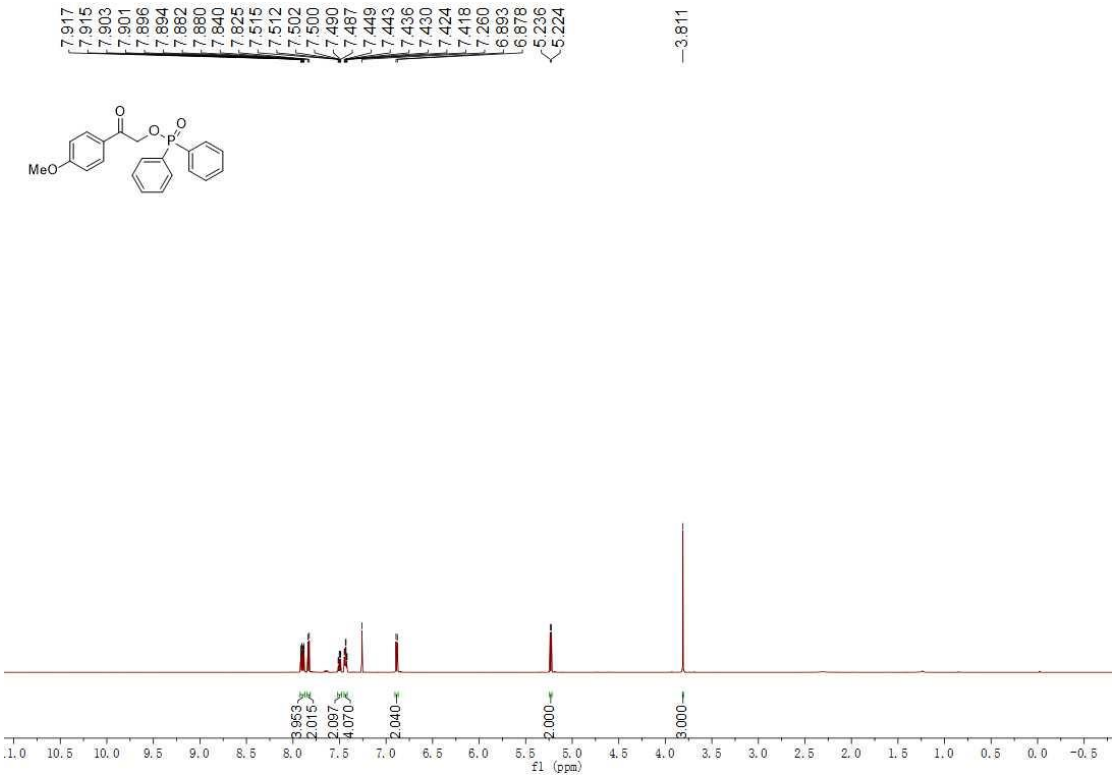
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **4**



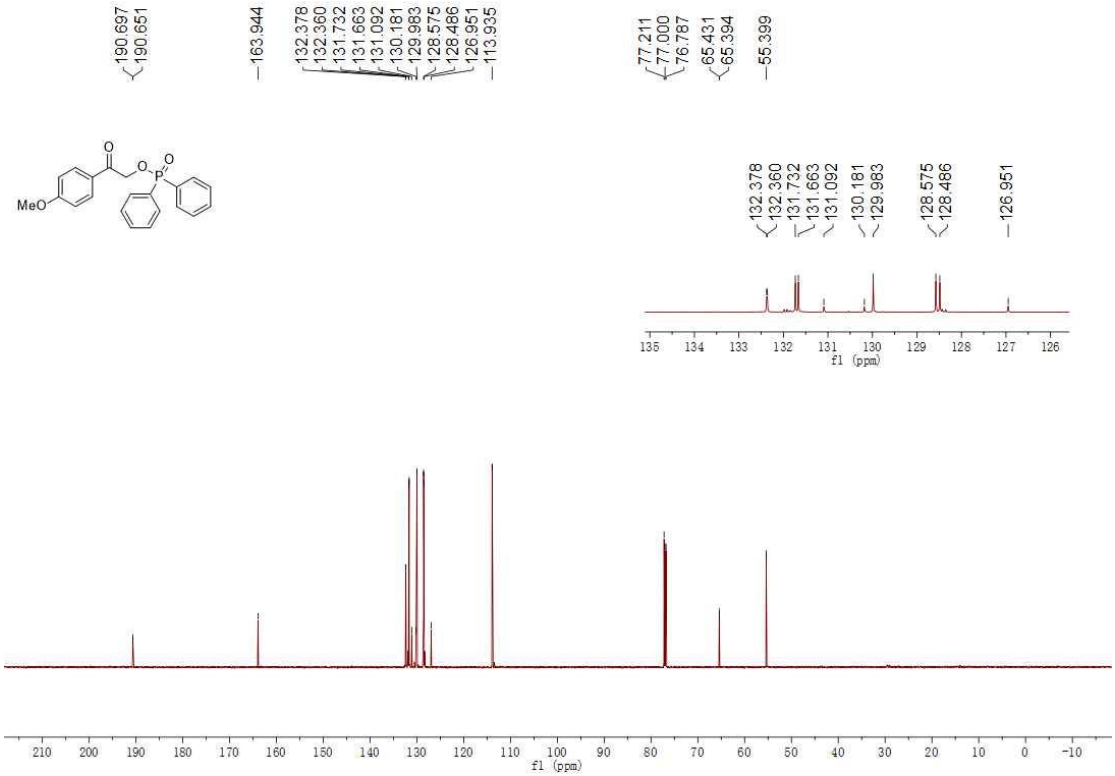
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **4**



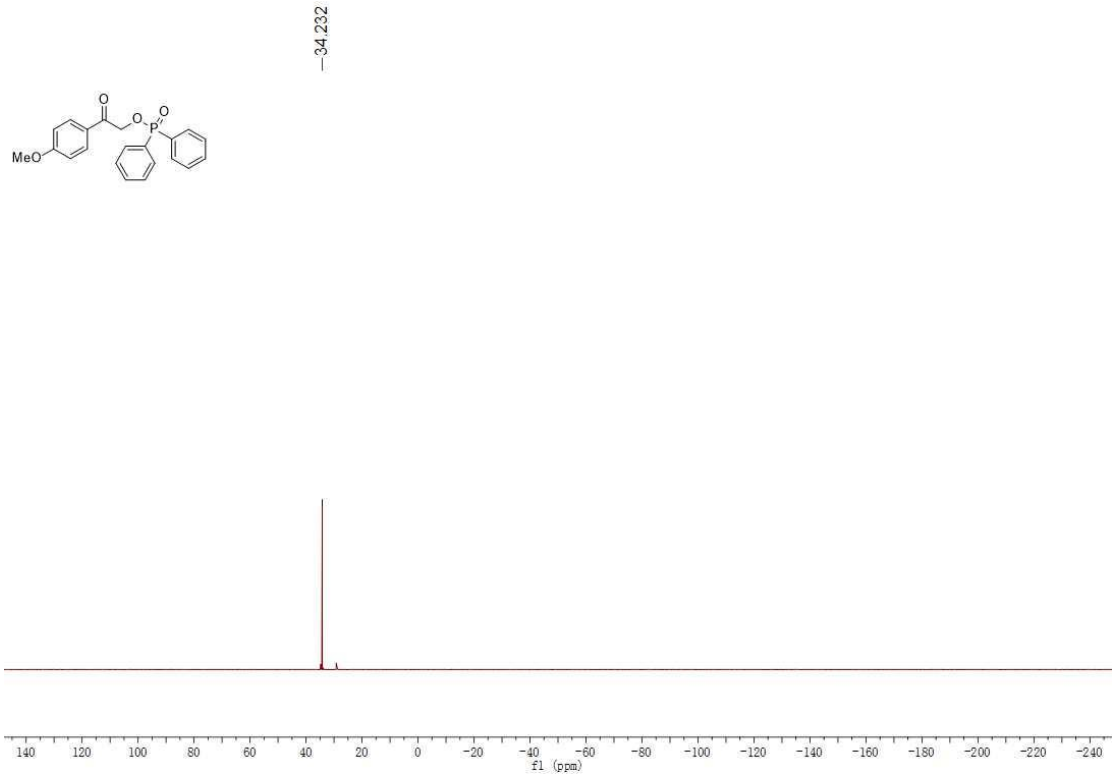
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **5**



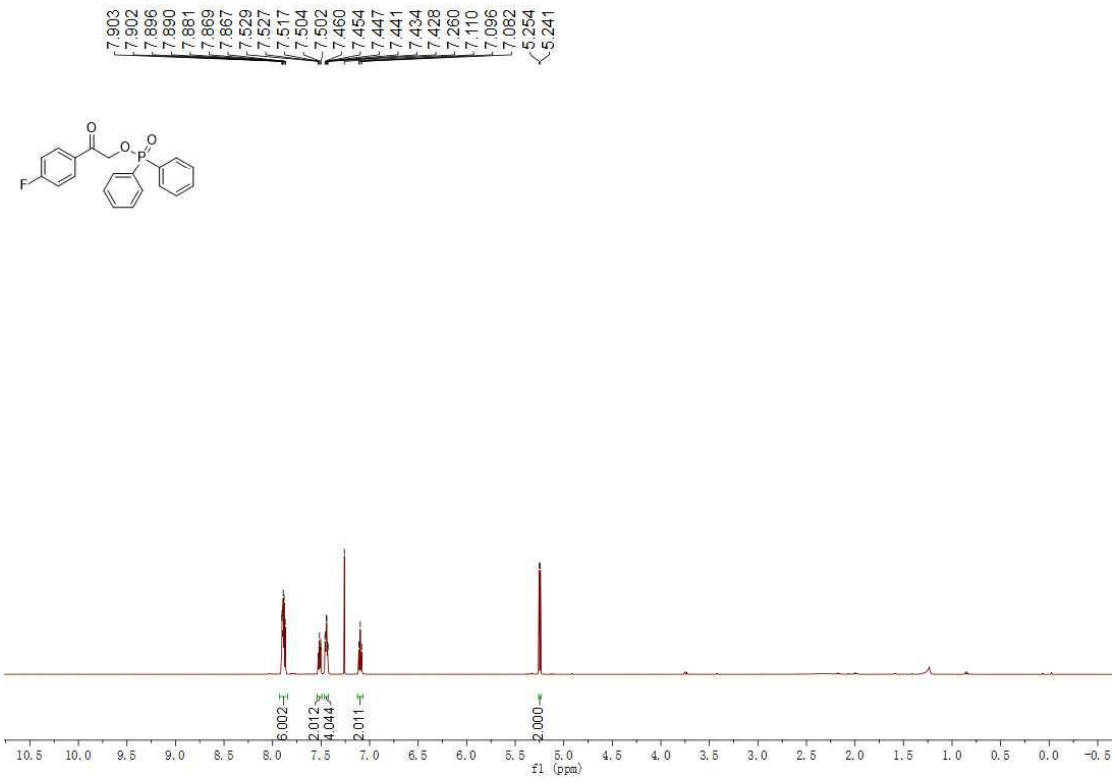
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **5**



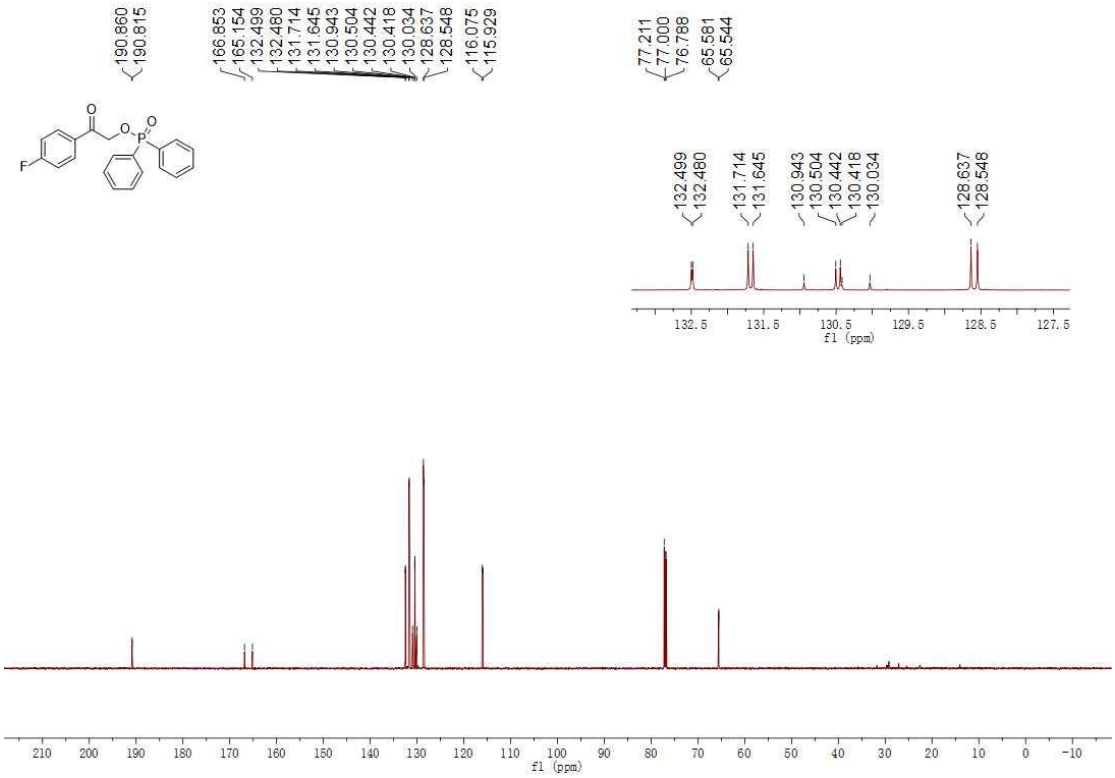
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **5**



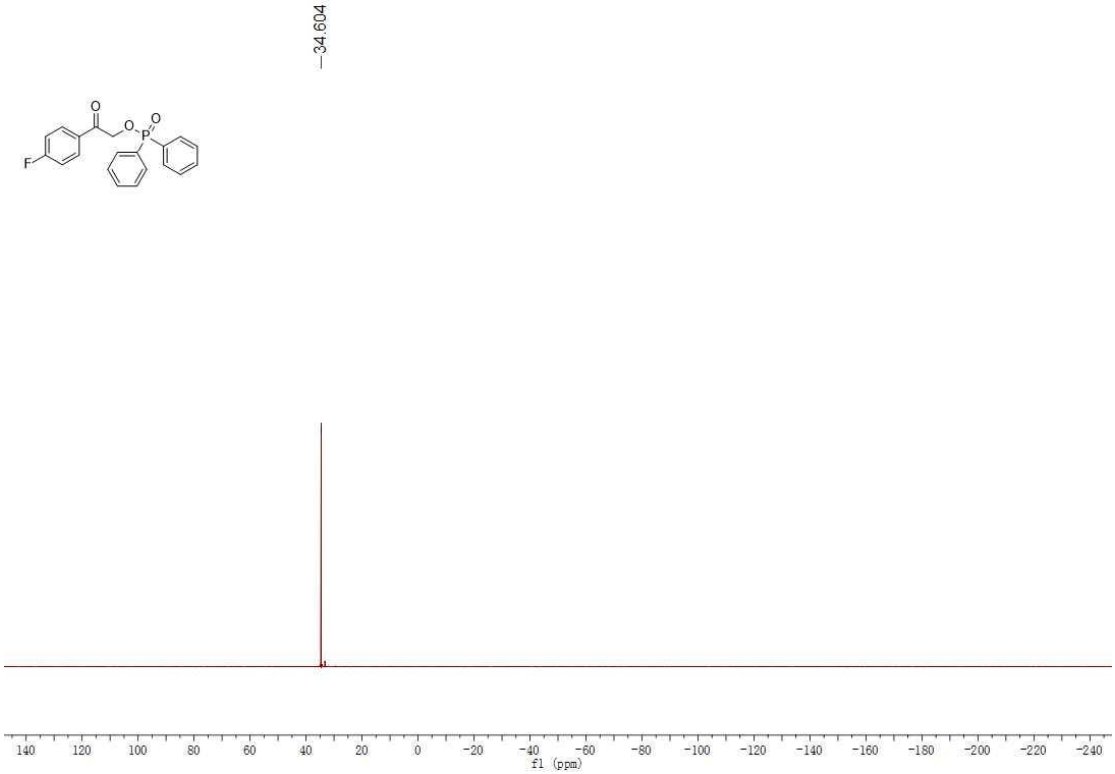
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **6**



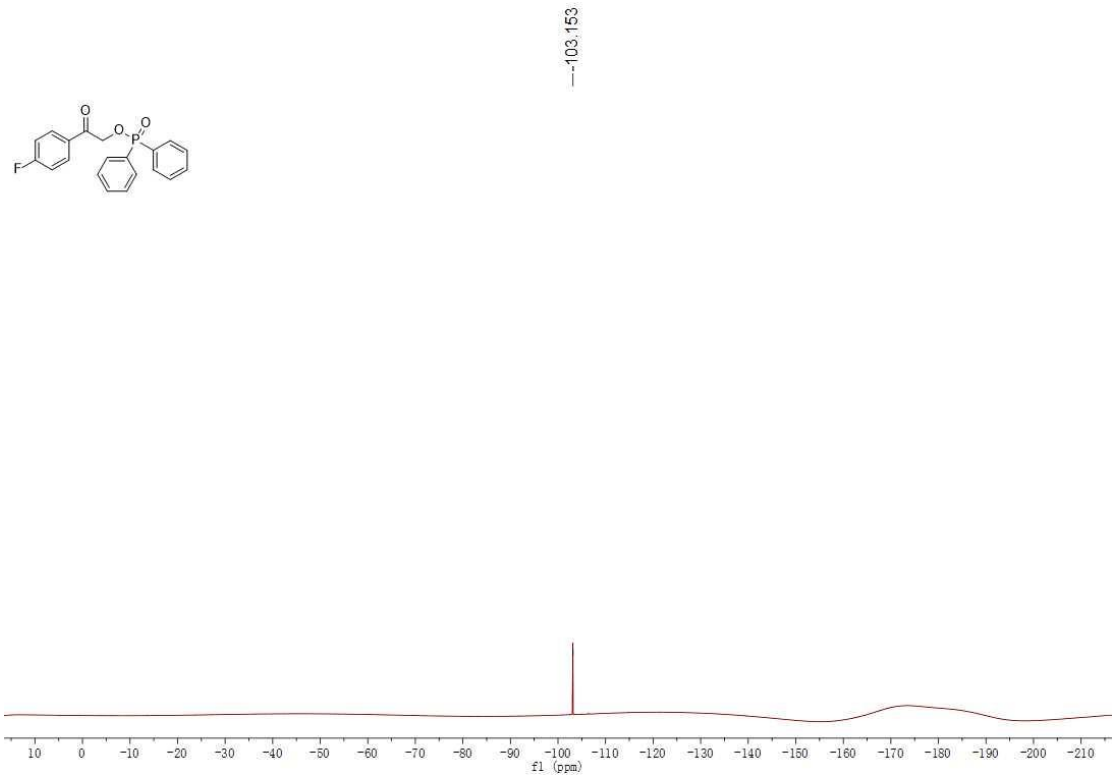
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **6**



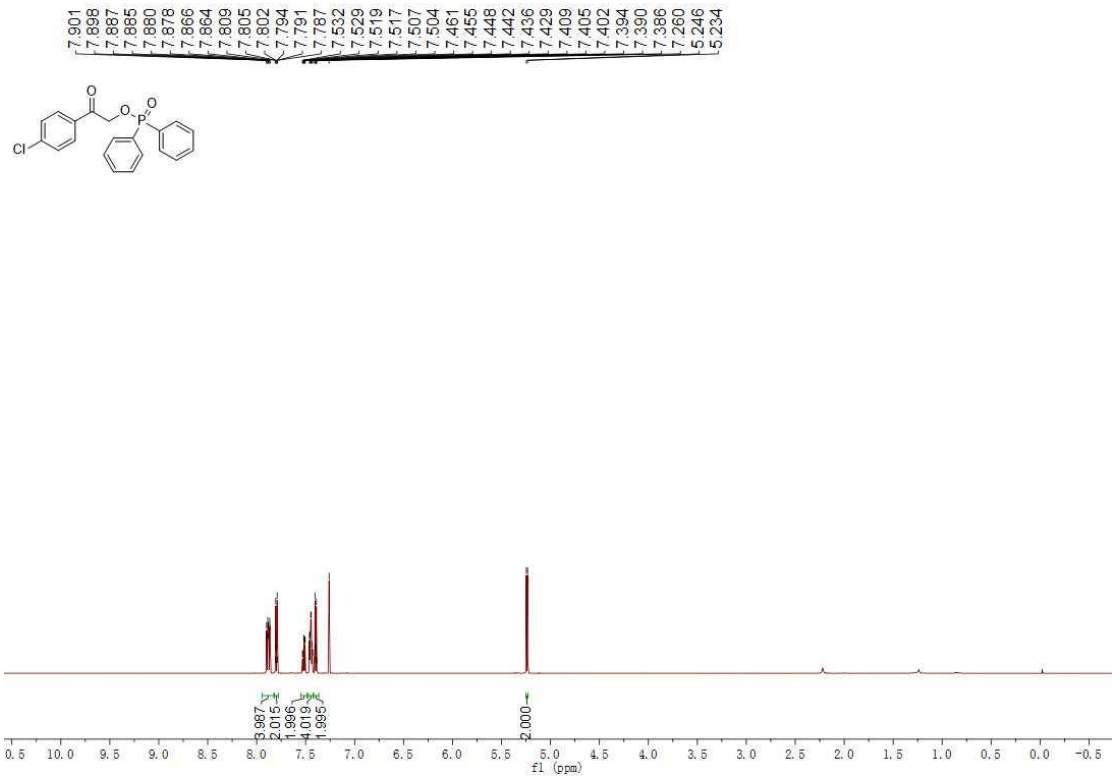
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **6**



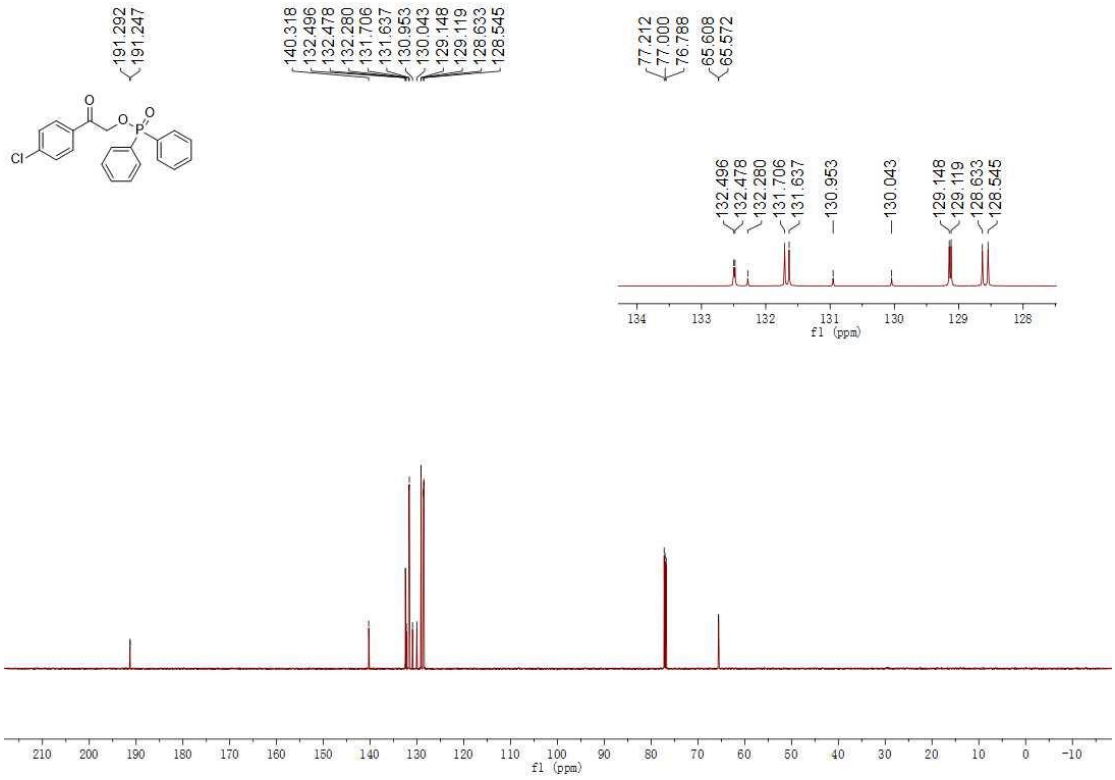
^{19}F NMR (564 MHz, $CDCl_3$) Spectrum of **6**



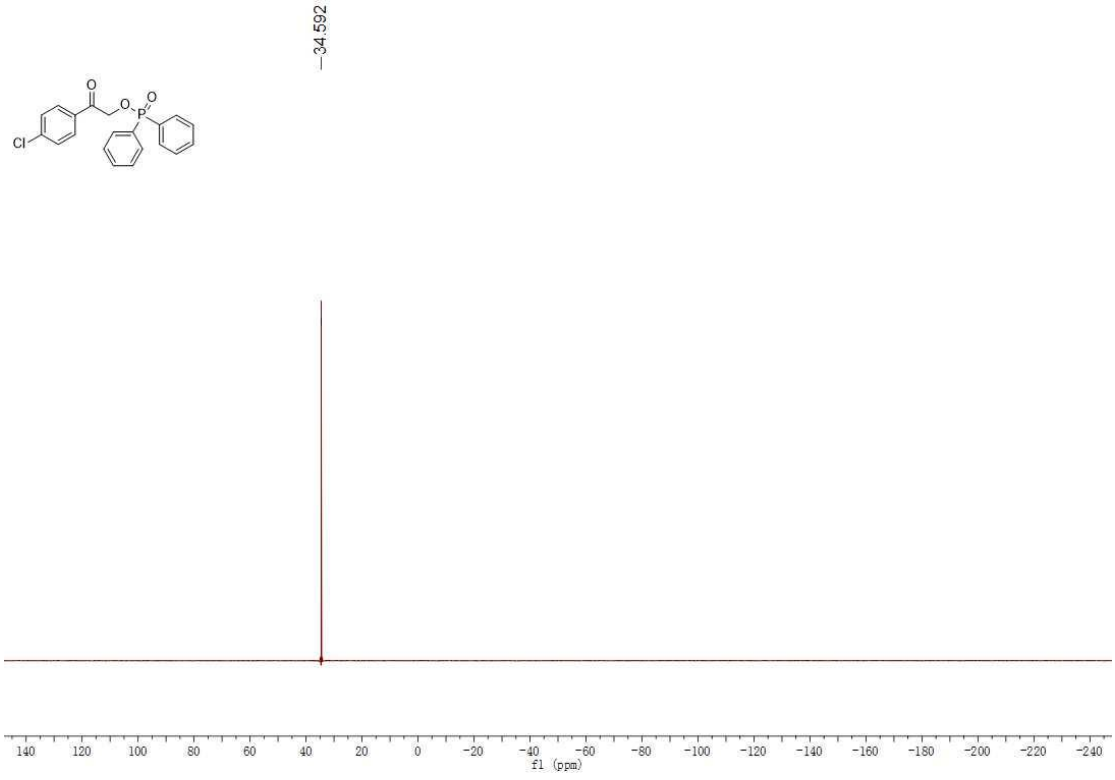
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **7**



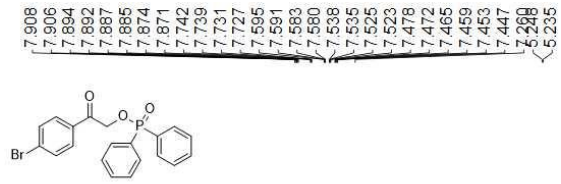
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **7**

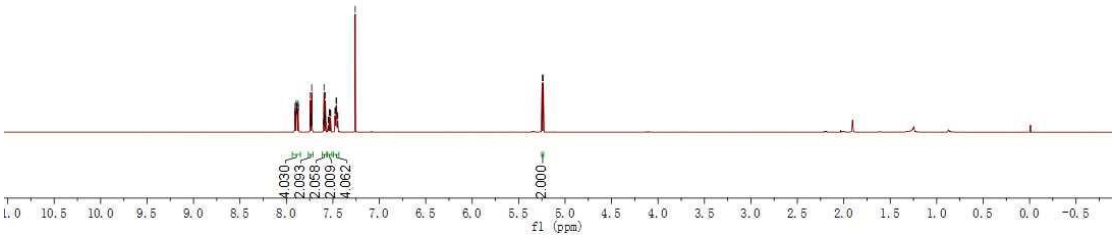


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **7**

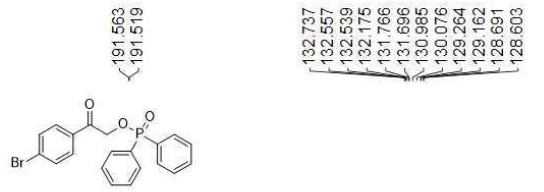


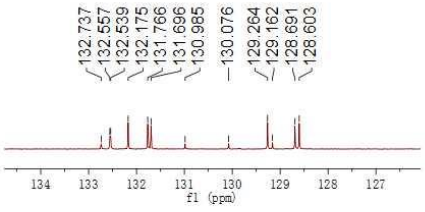
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **8**

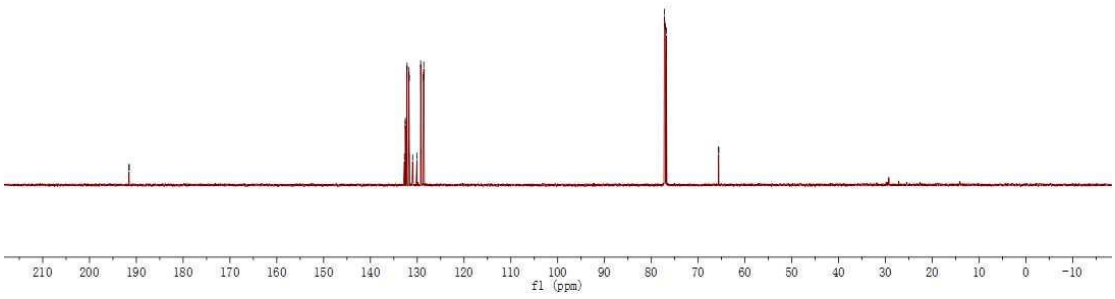




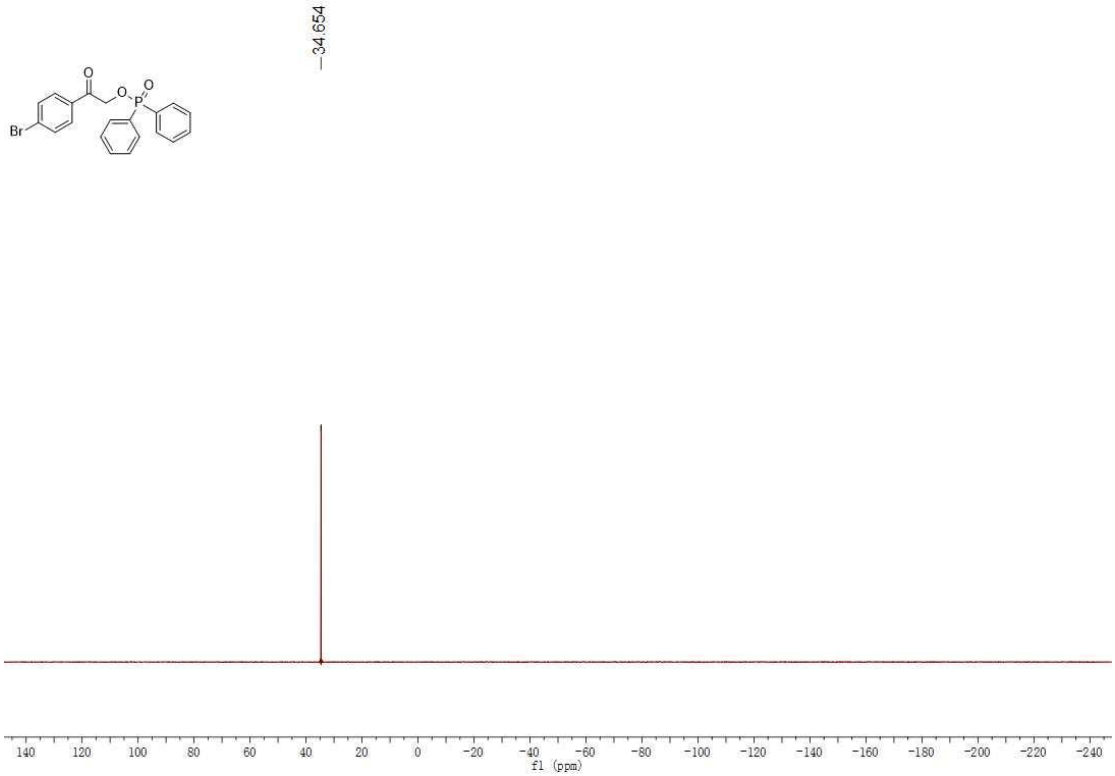
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **8**



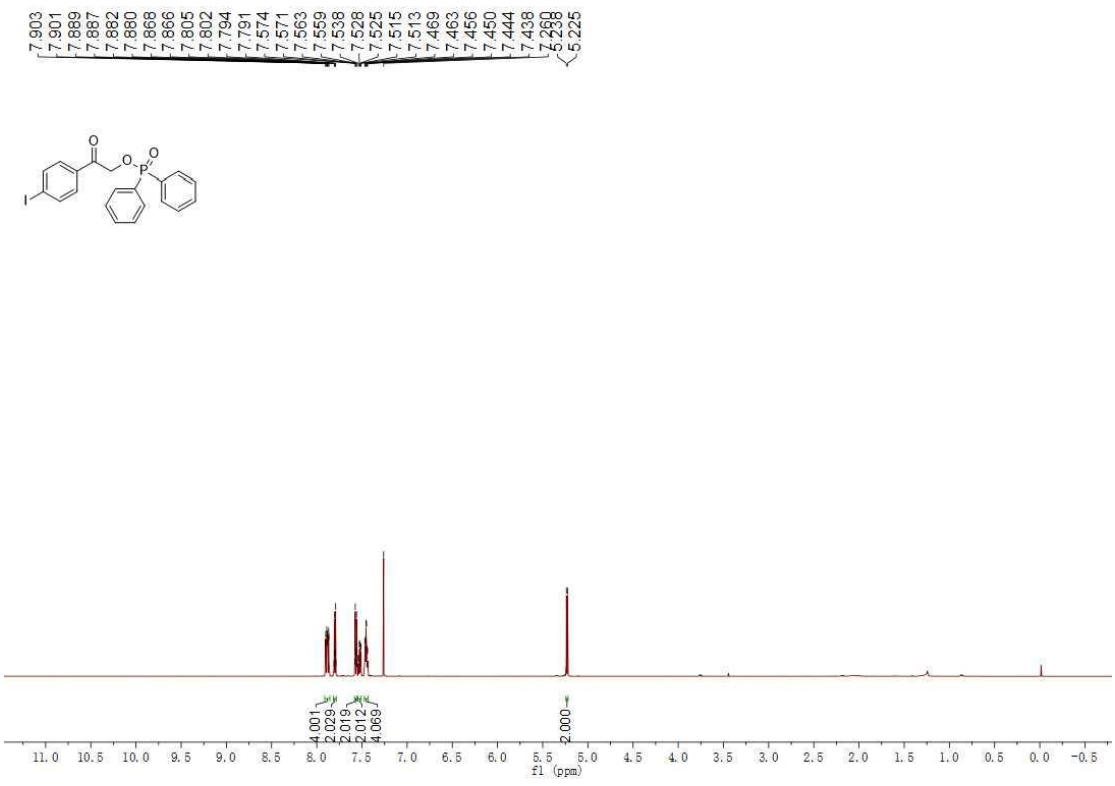




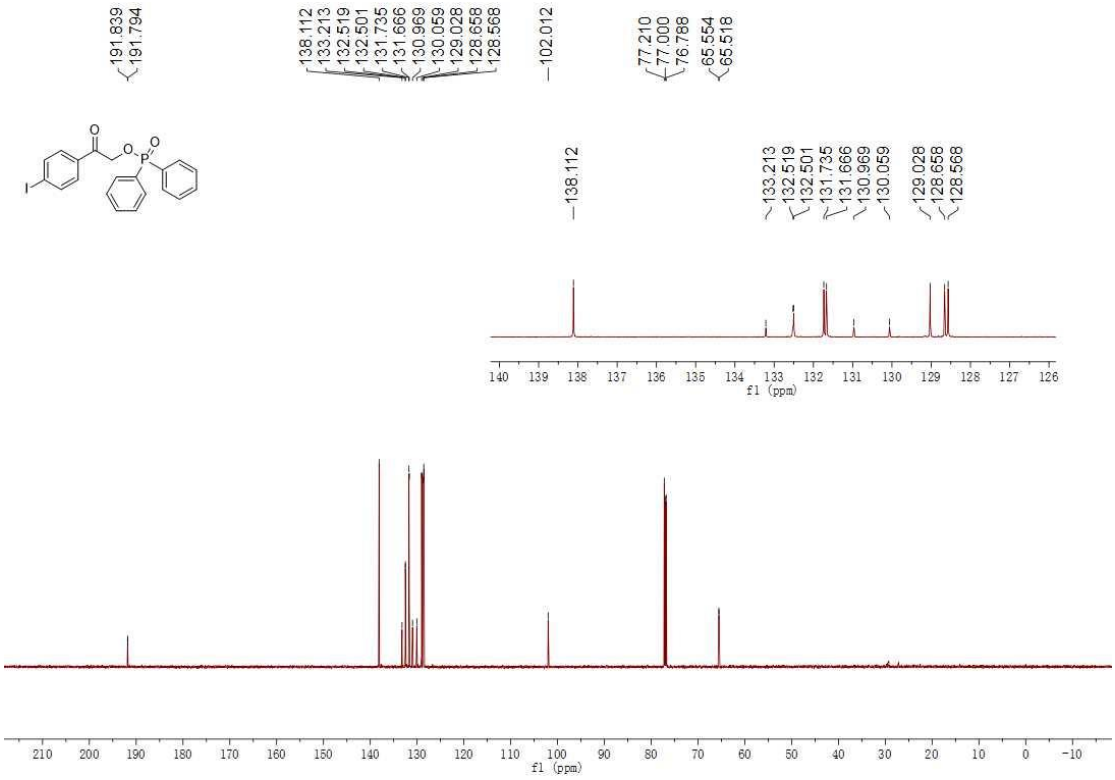
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **8**



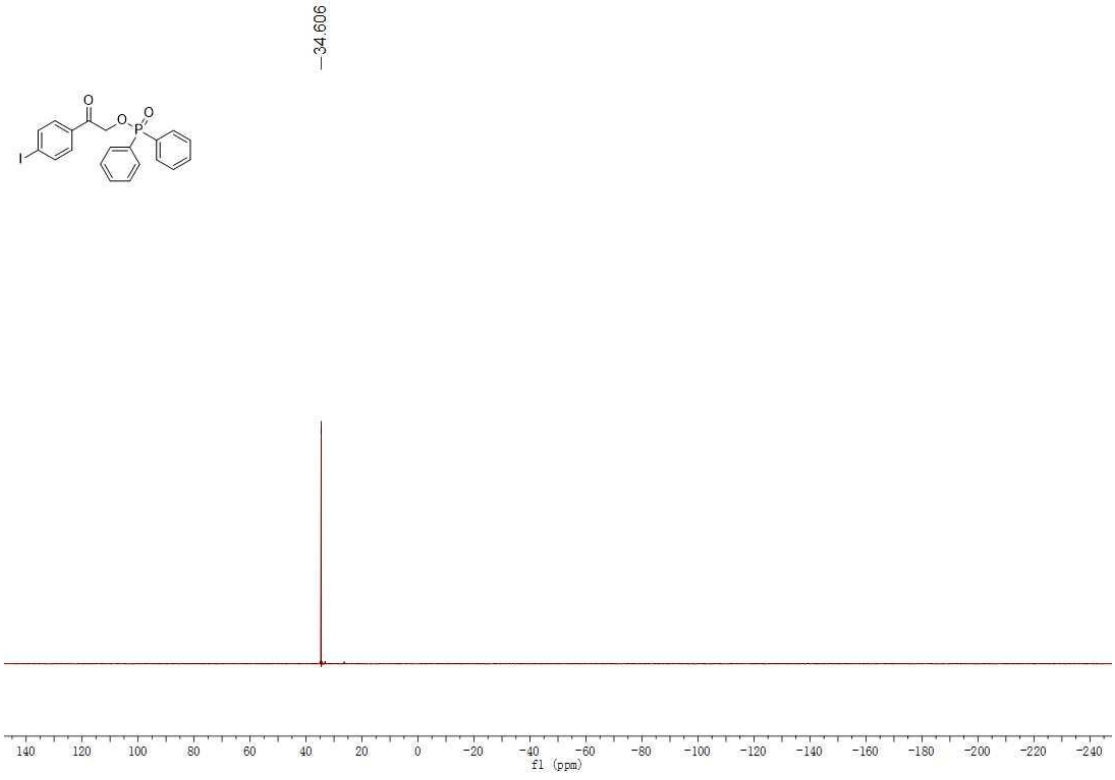
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **9**



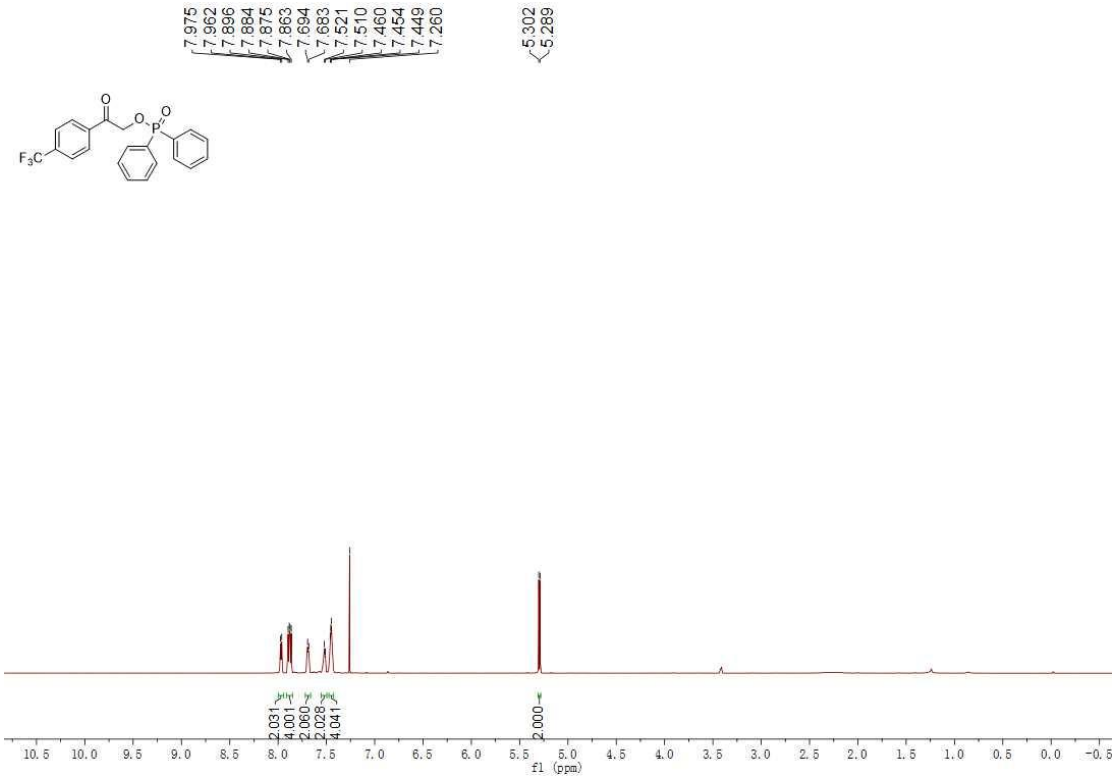
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **9**



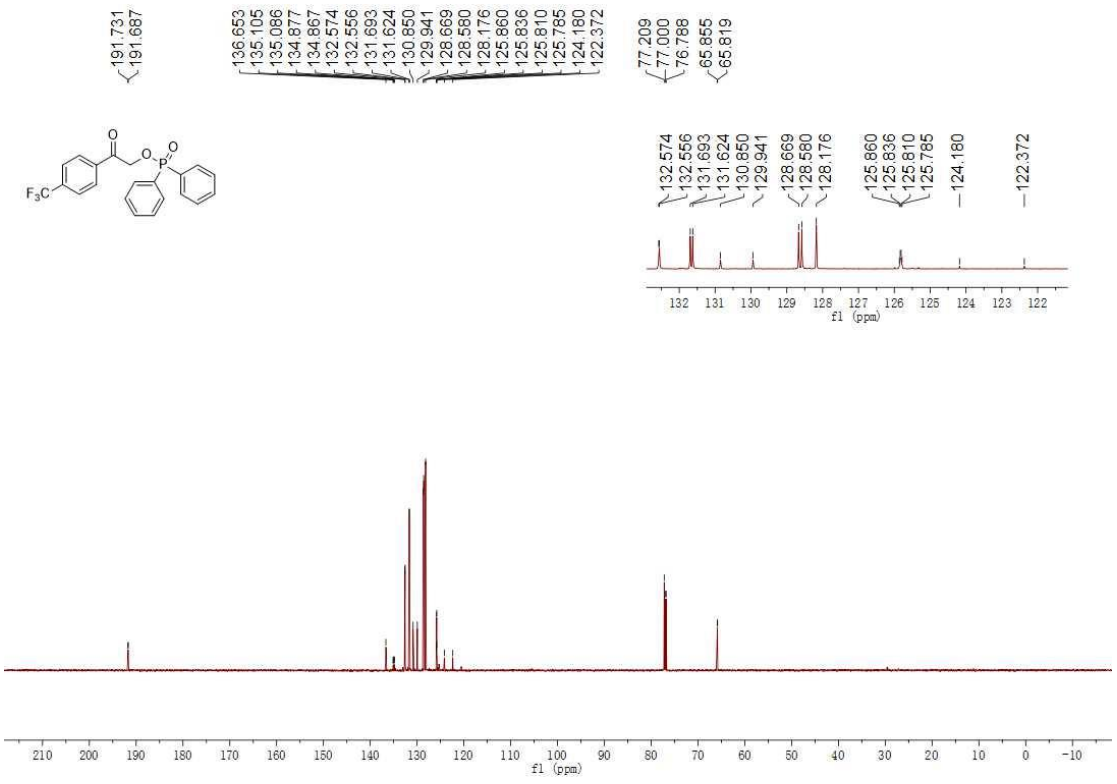
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **9**



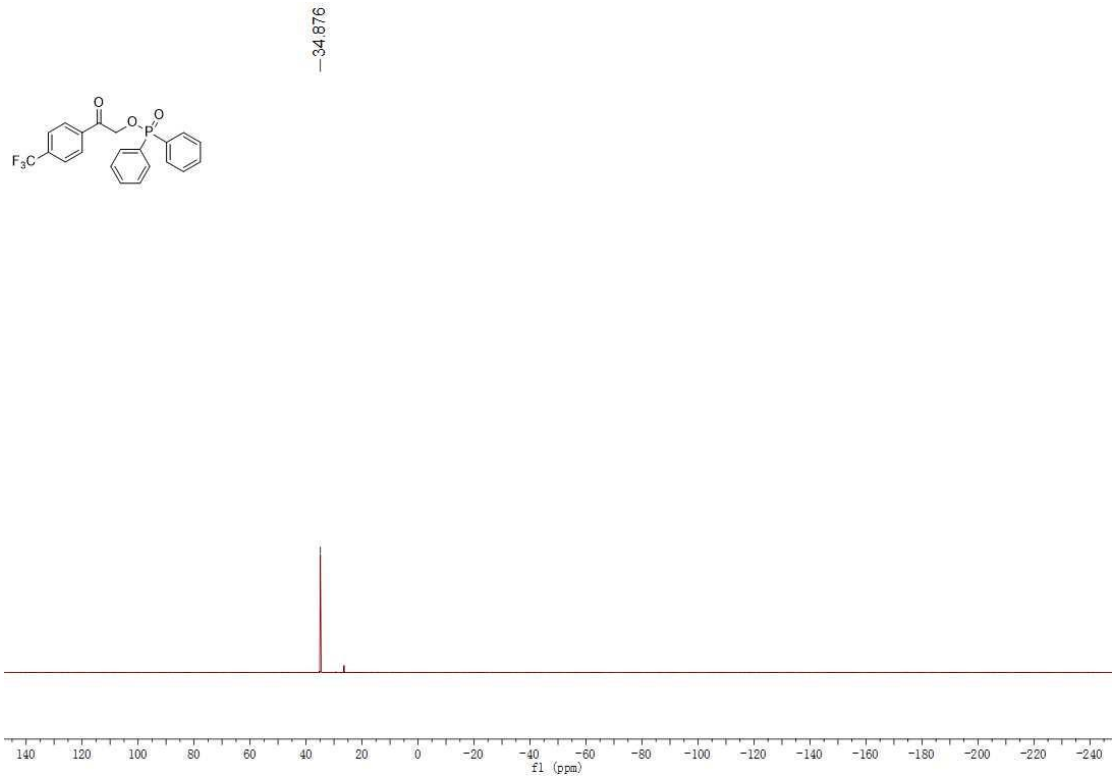
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **10**



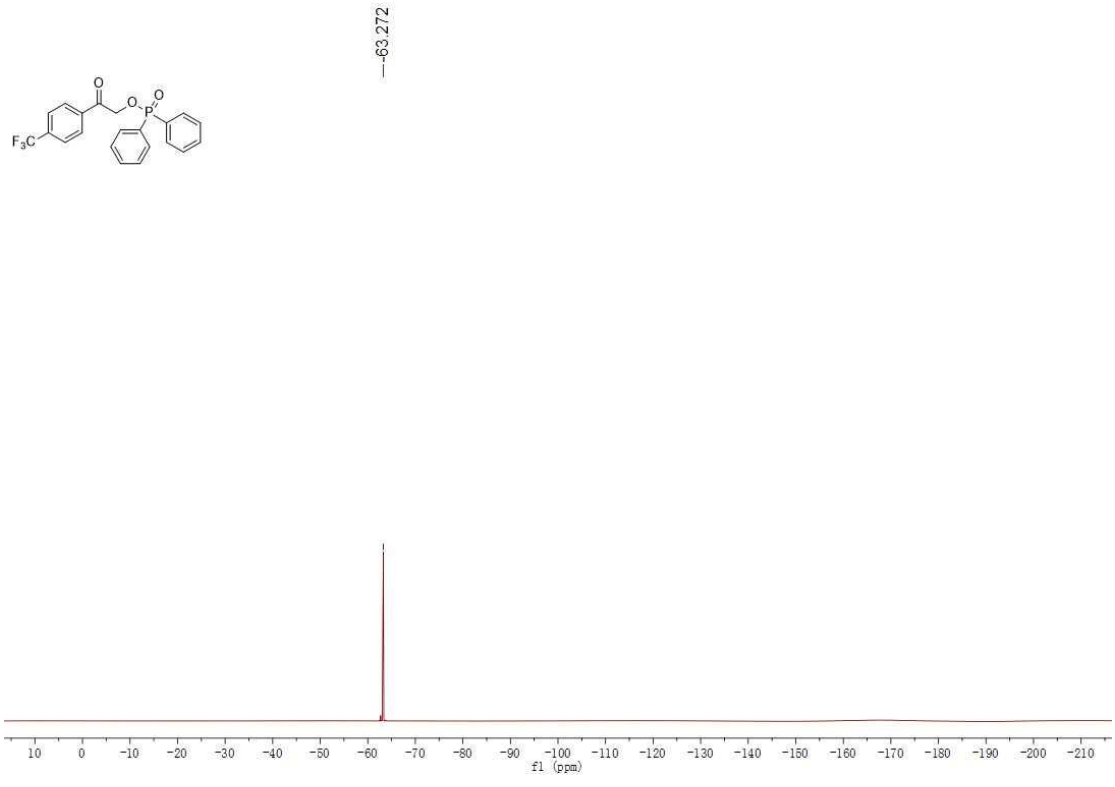
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **10**



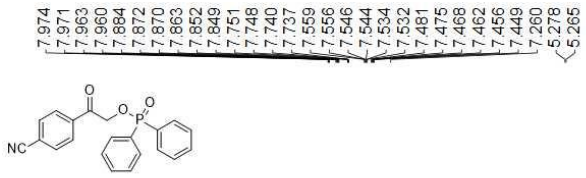
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **10**

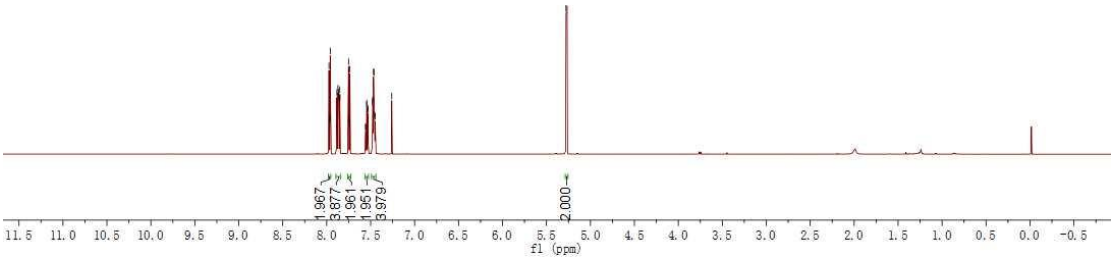


^{19}F NMR (564 MHz, $CDCl_3$) Spectrum of **10**

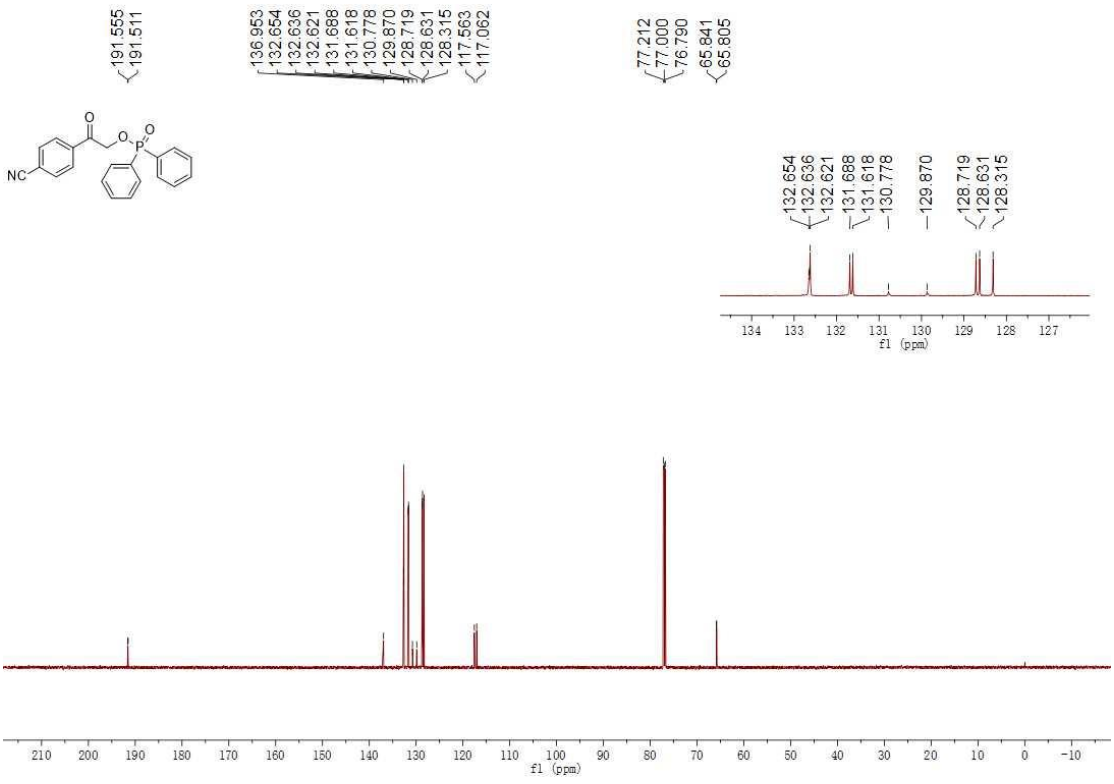


^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **11**

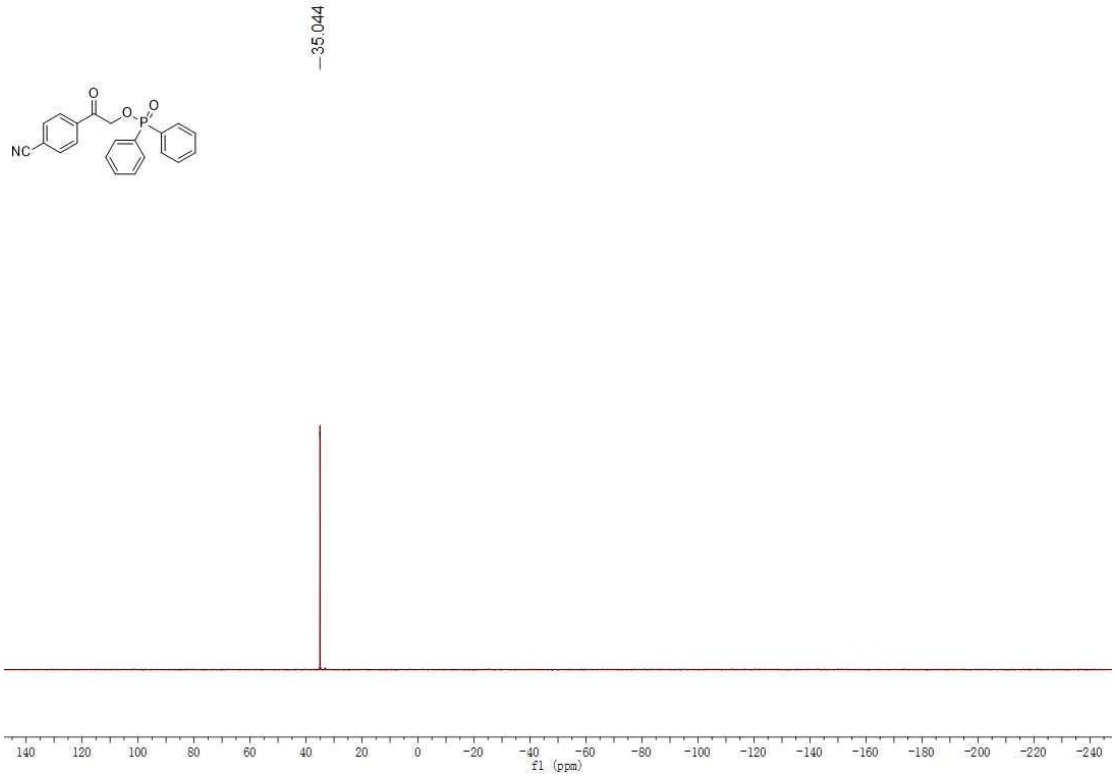




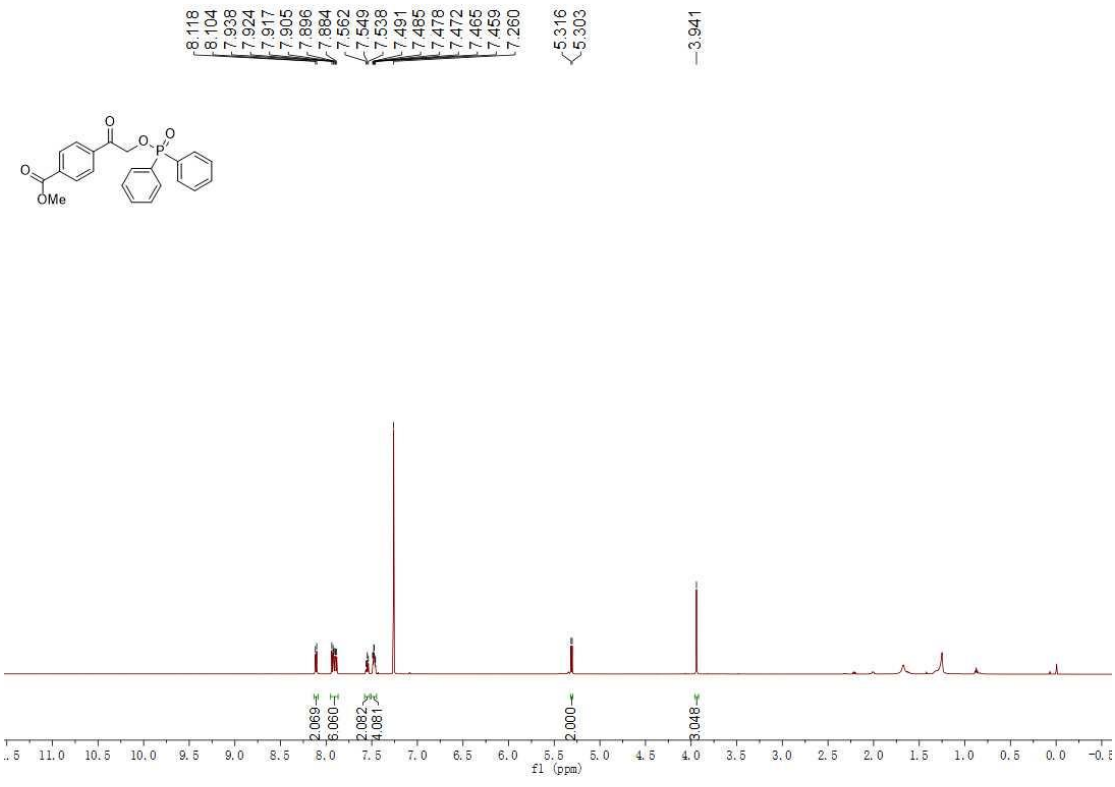
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **11**



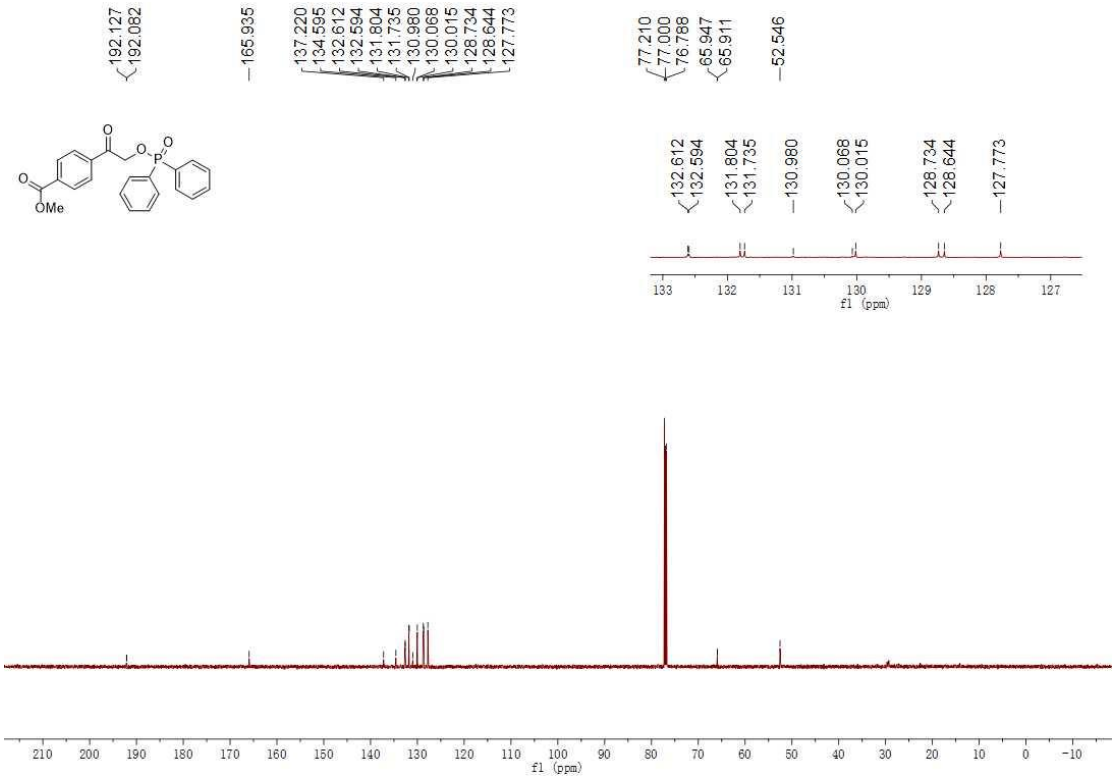
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **11**



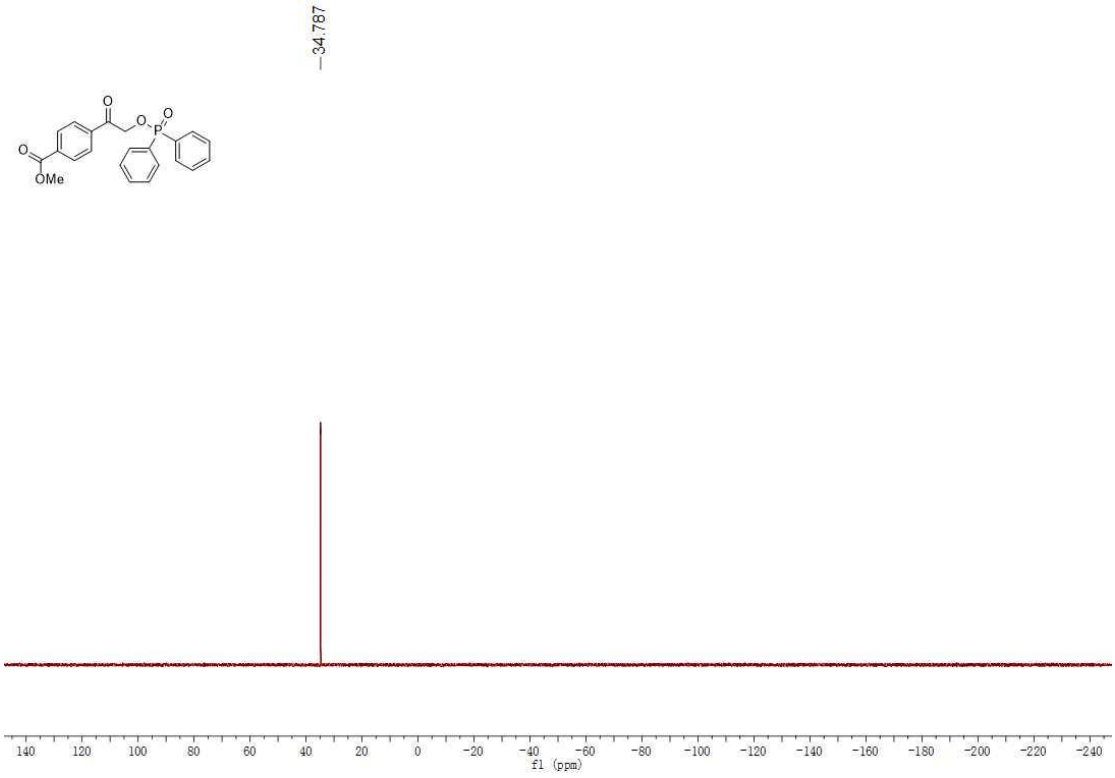
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **12**



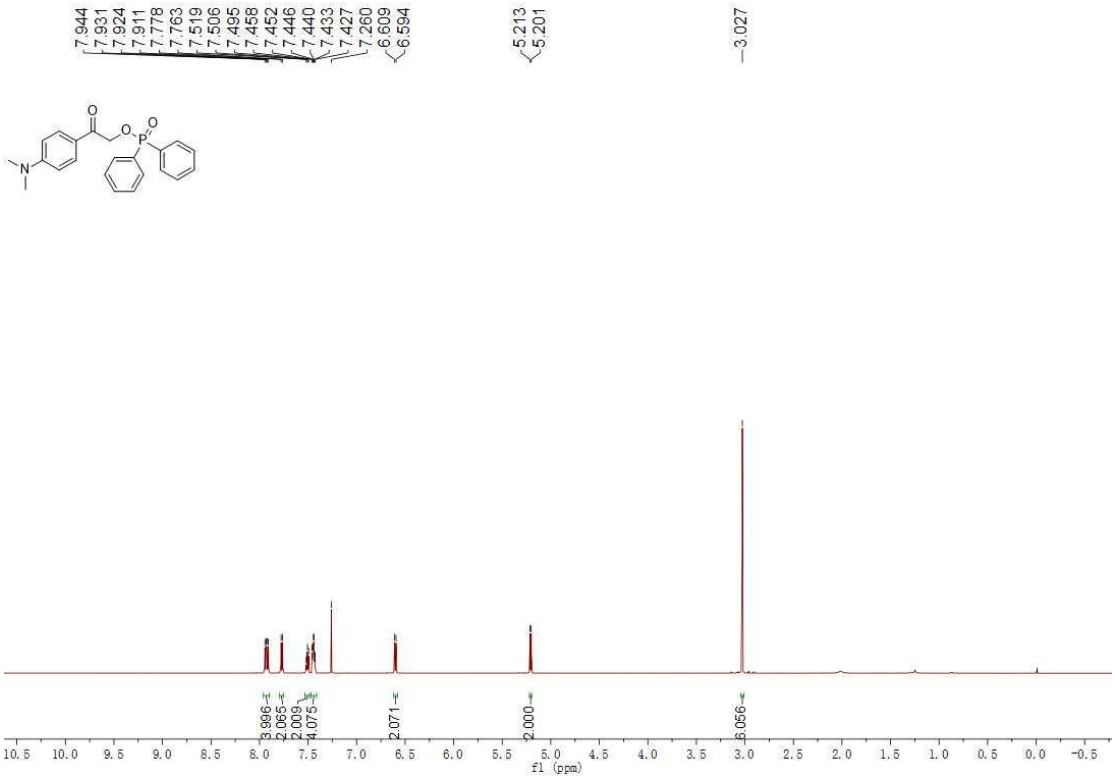
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **12**



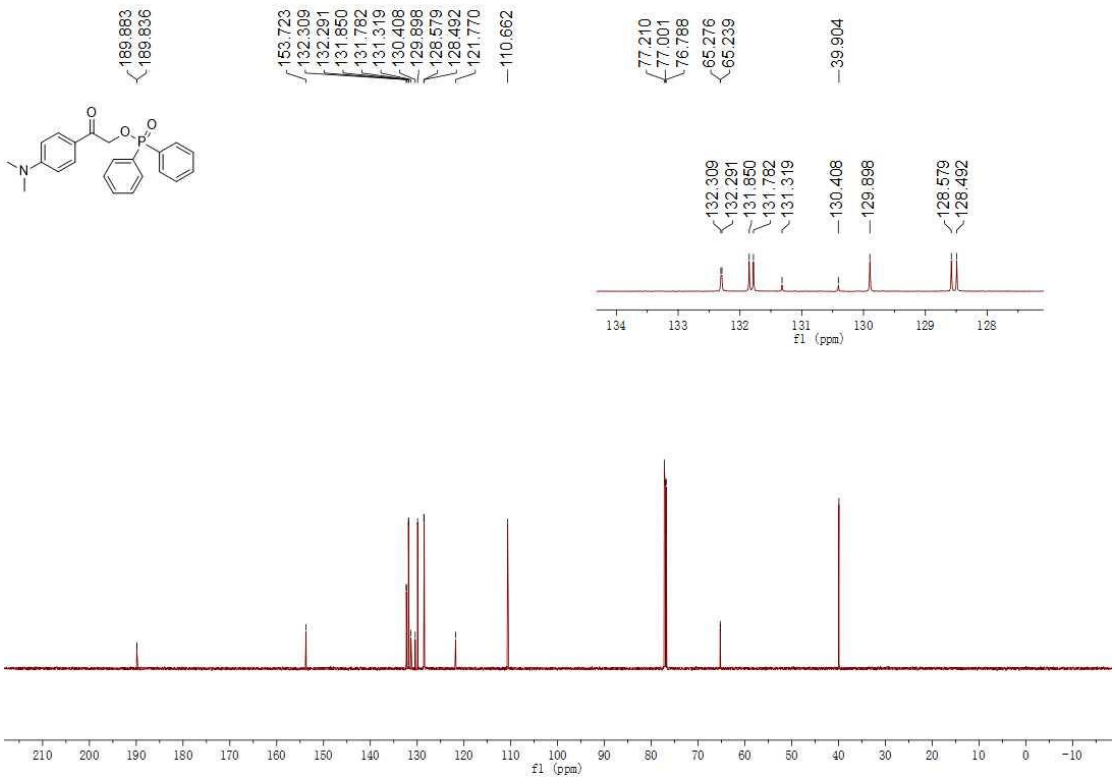
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **12**



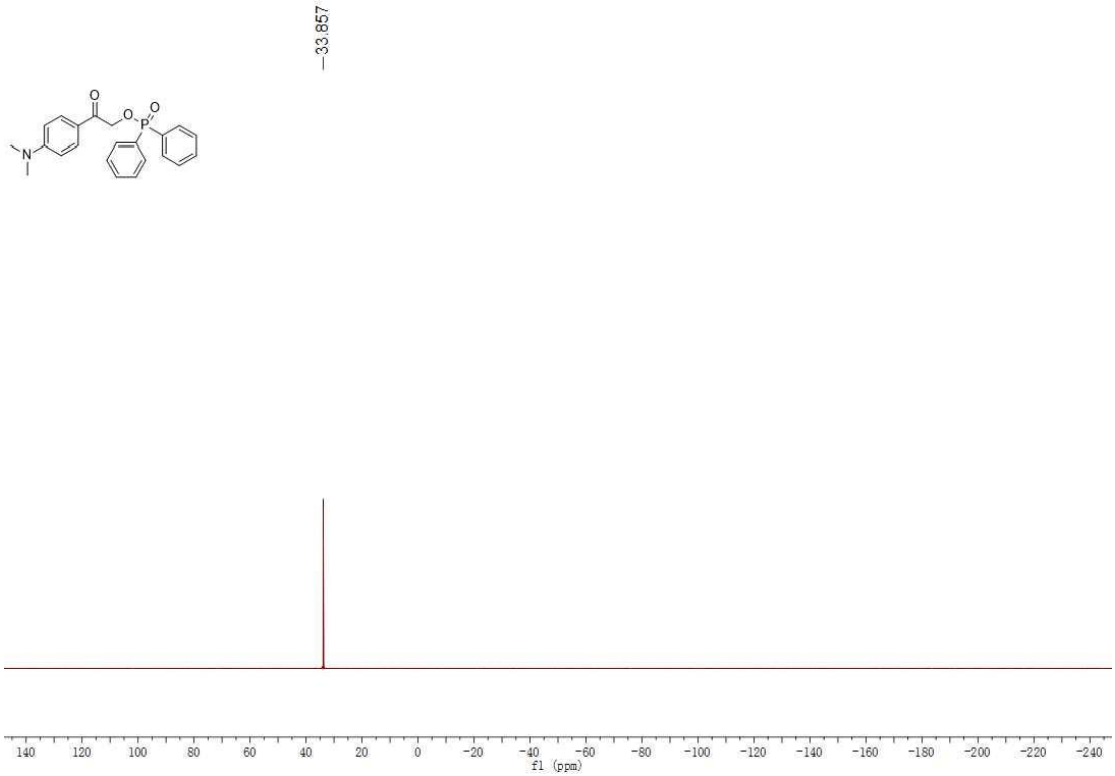
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **13**



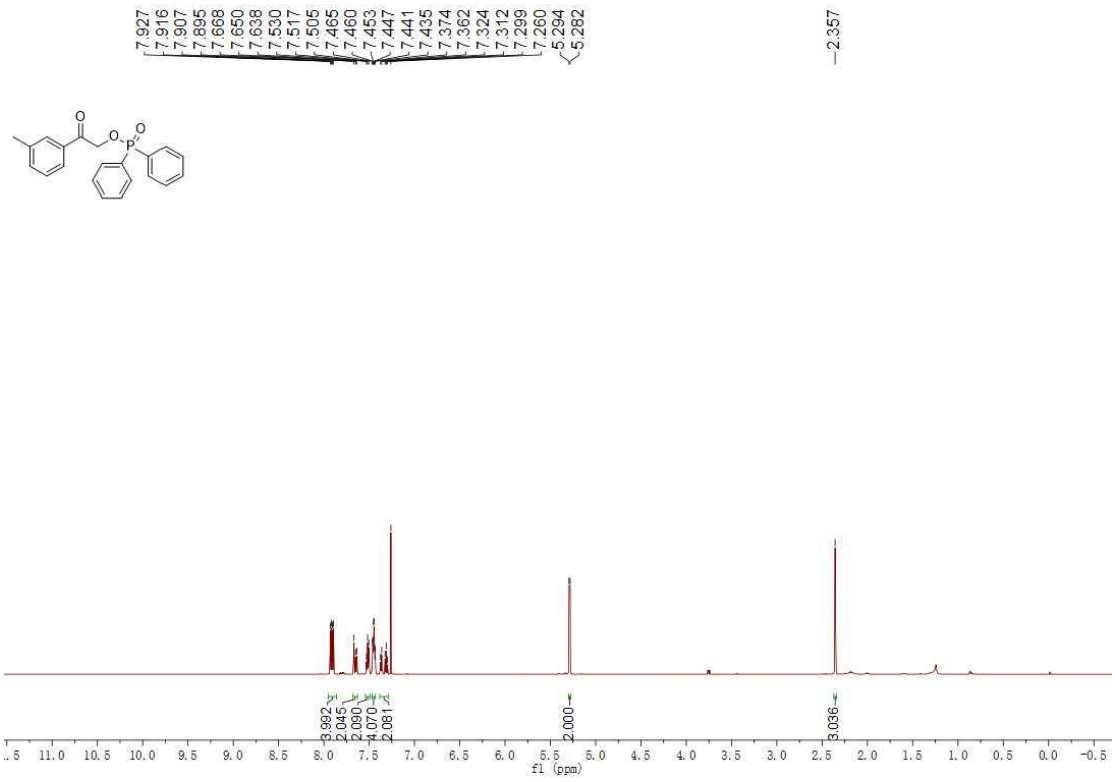
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **13**



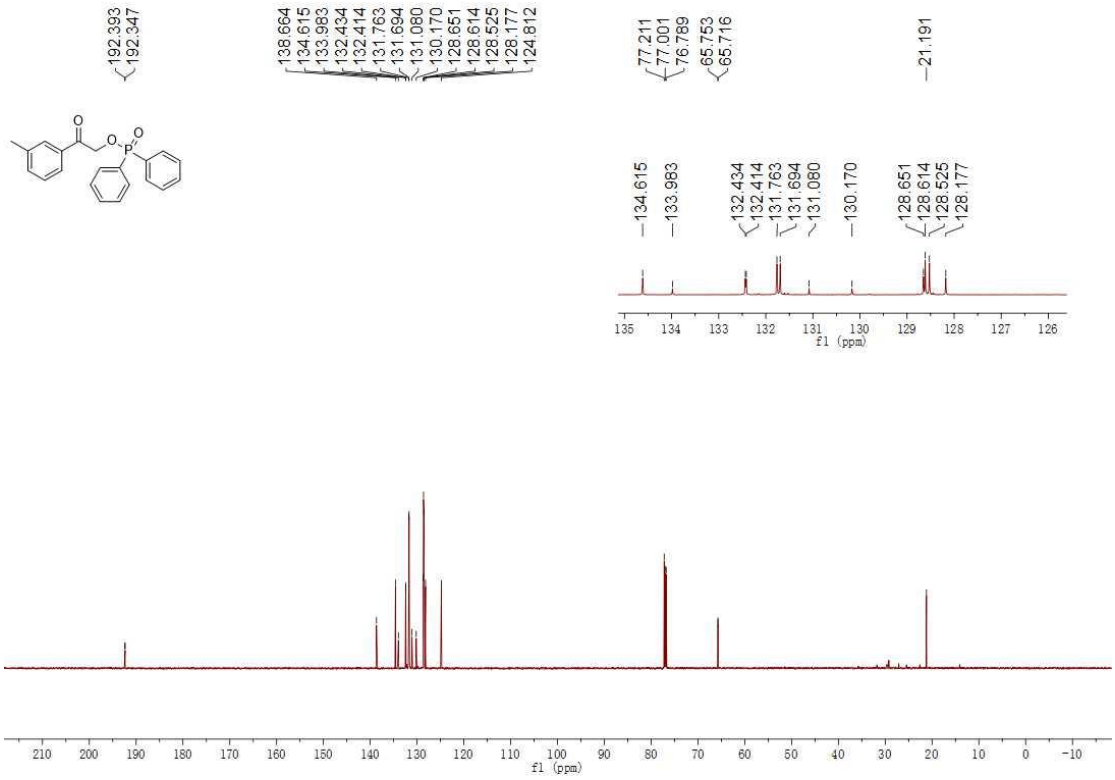
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **13**



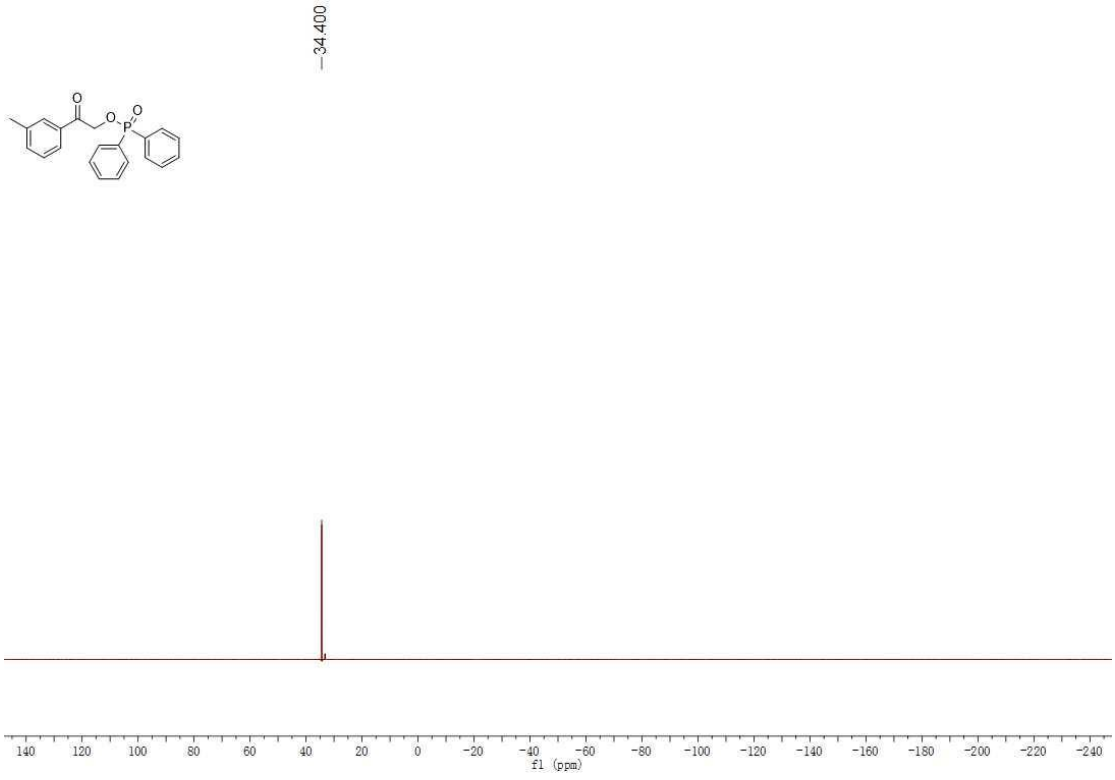
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **14**



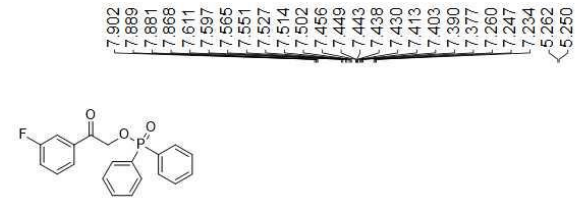
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **14**

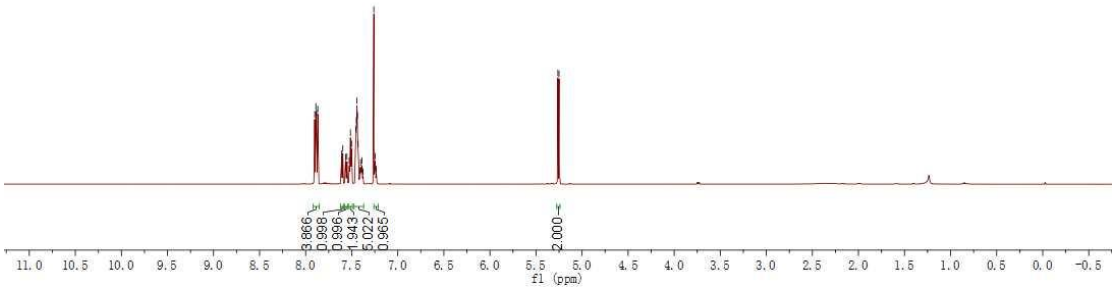


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **14**

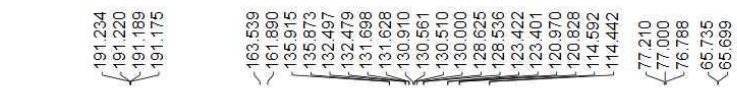


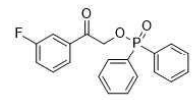
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **15**

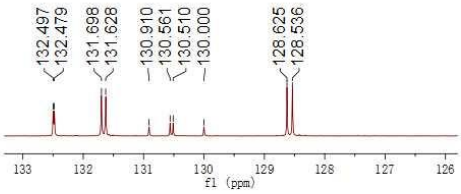


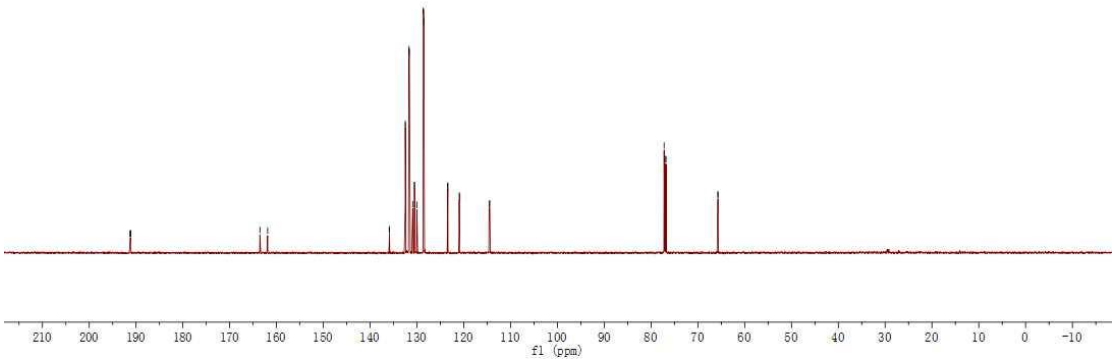


^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **15**

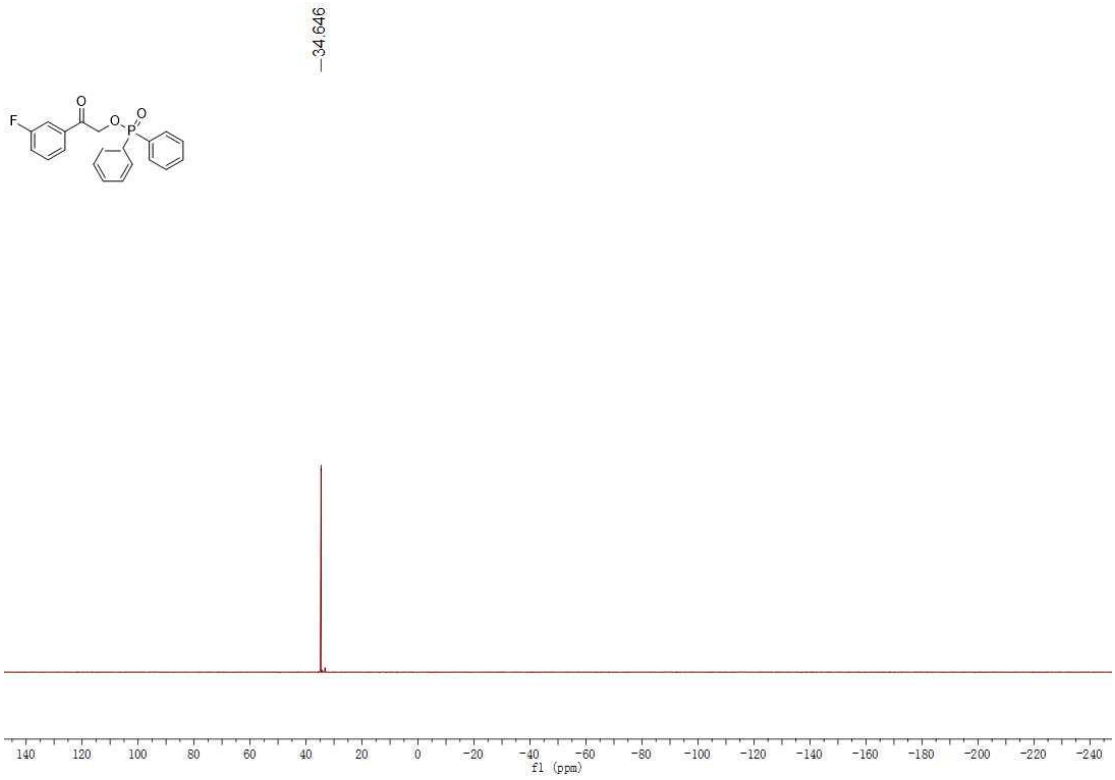




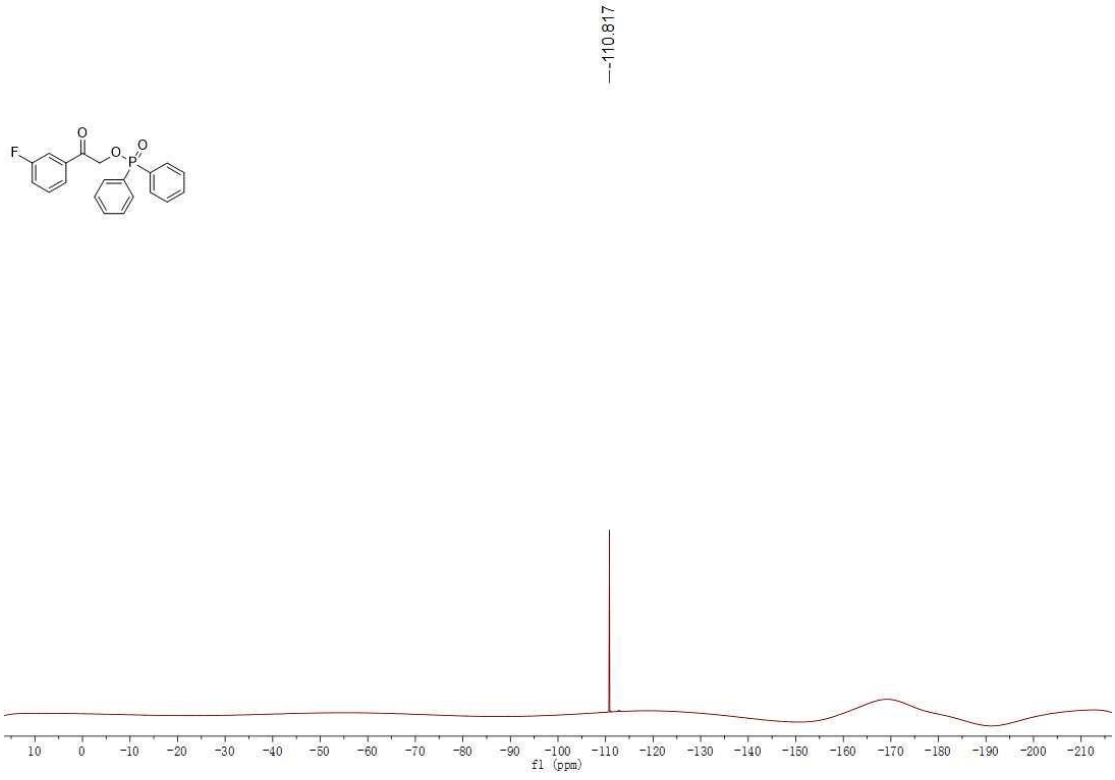




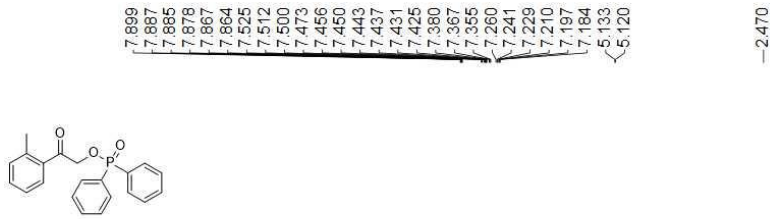
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **15**

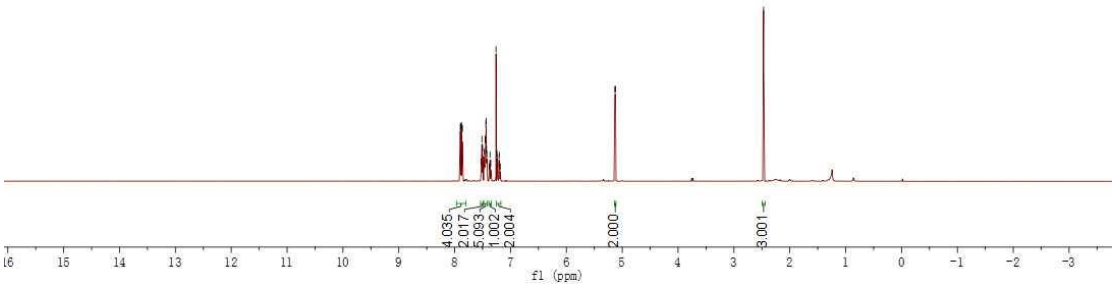


^{19}F NMR (564 MHz, $CDCl_3$) Spectrum of **15**

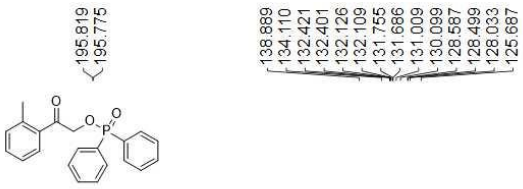


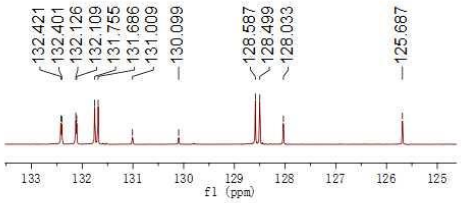
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **16**

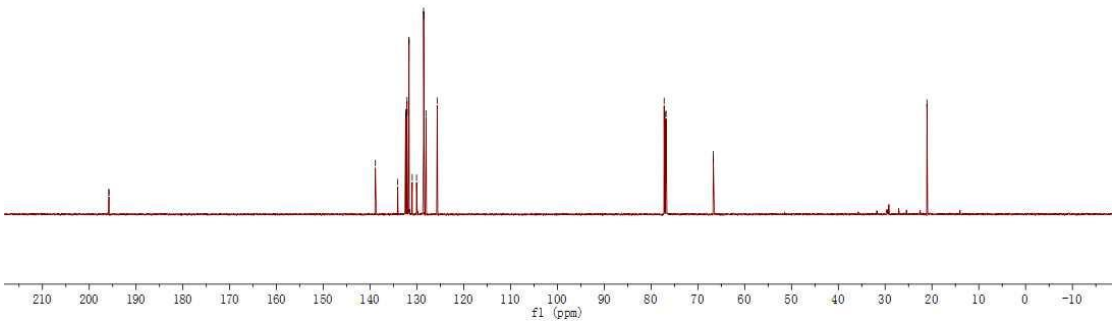




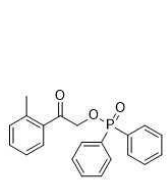
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **16**



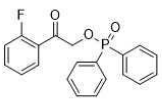


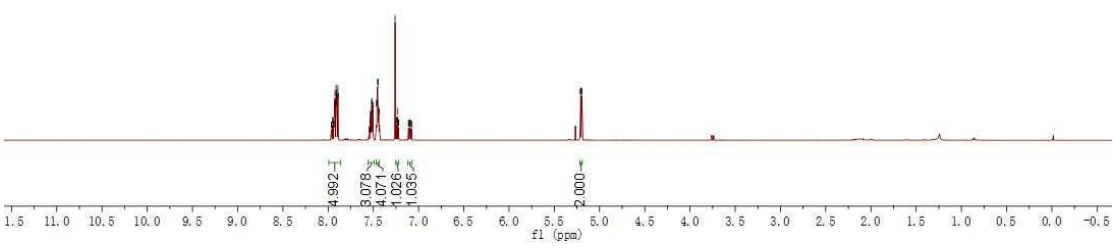


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **16**

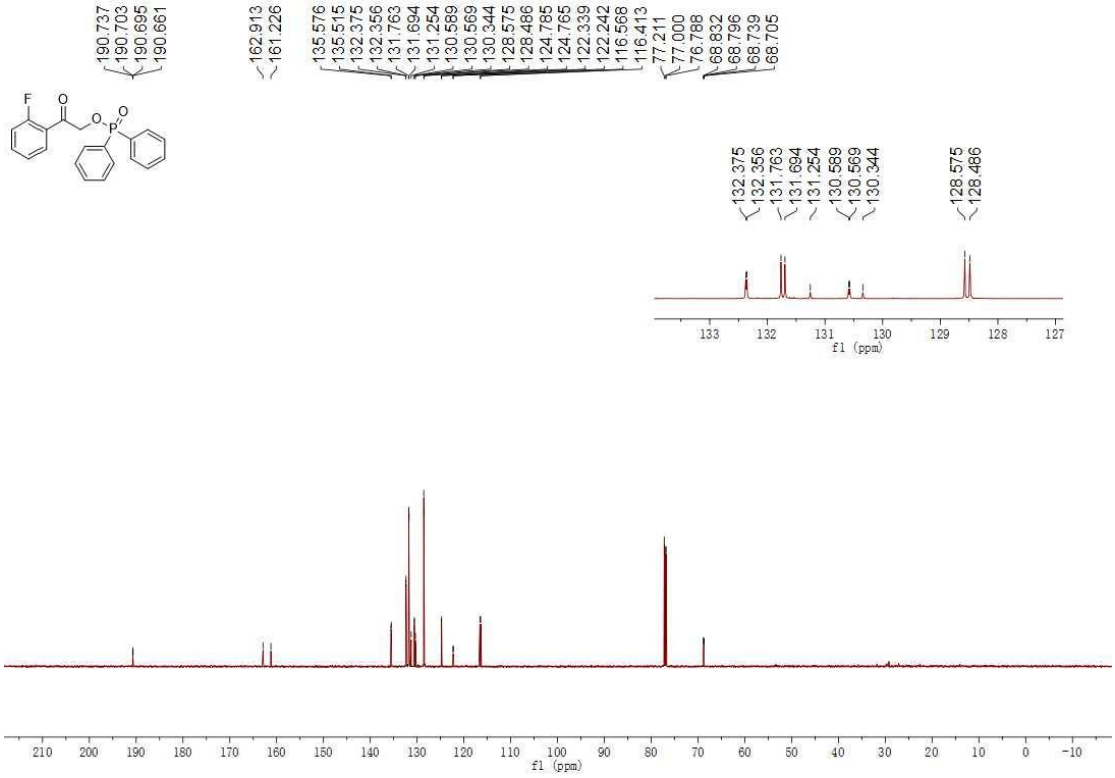


^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **17**

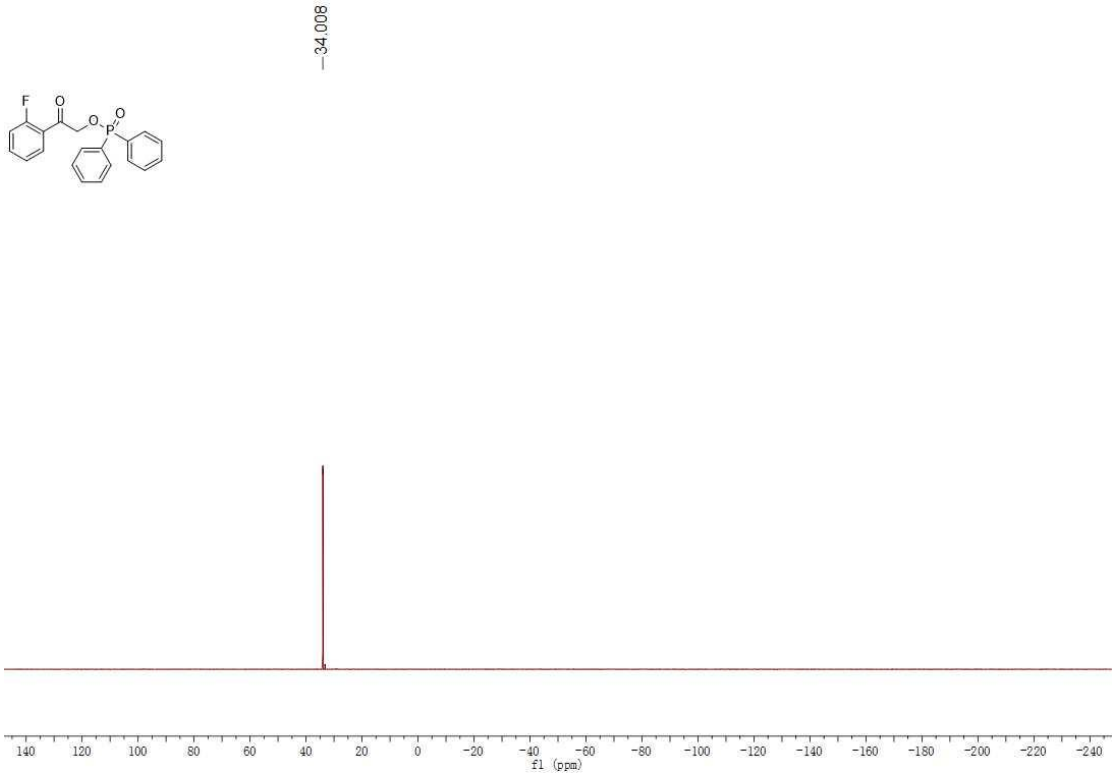




^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **17**

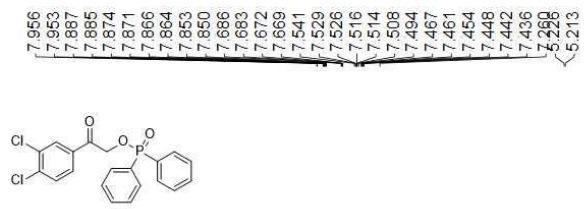


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **17**

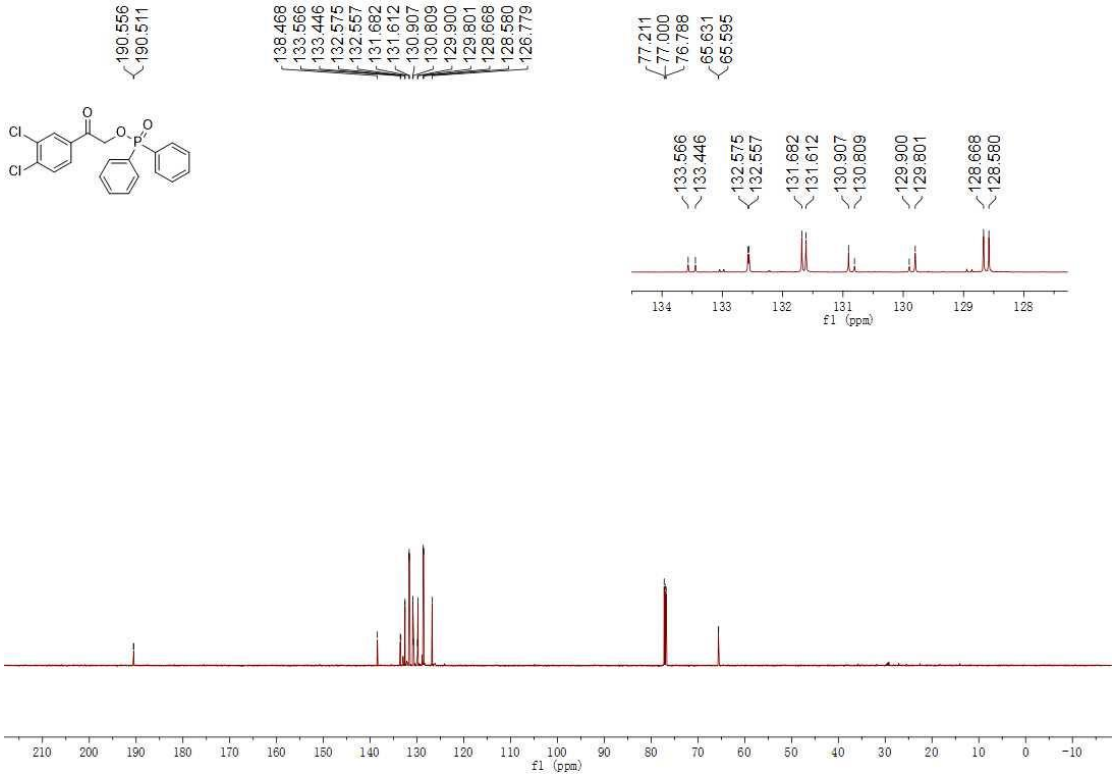


^{19}F NMR (564 MHz, $CDCl_3$) Spectrum of **17**

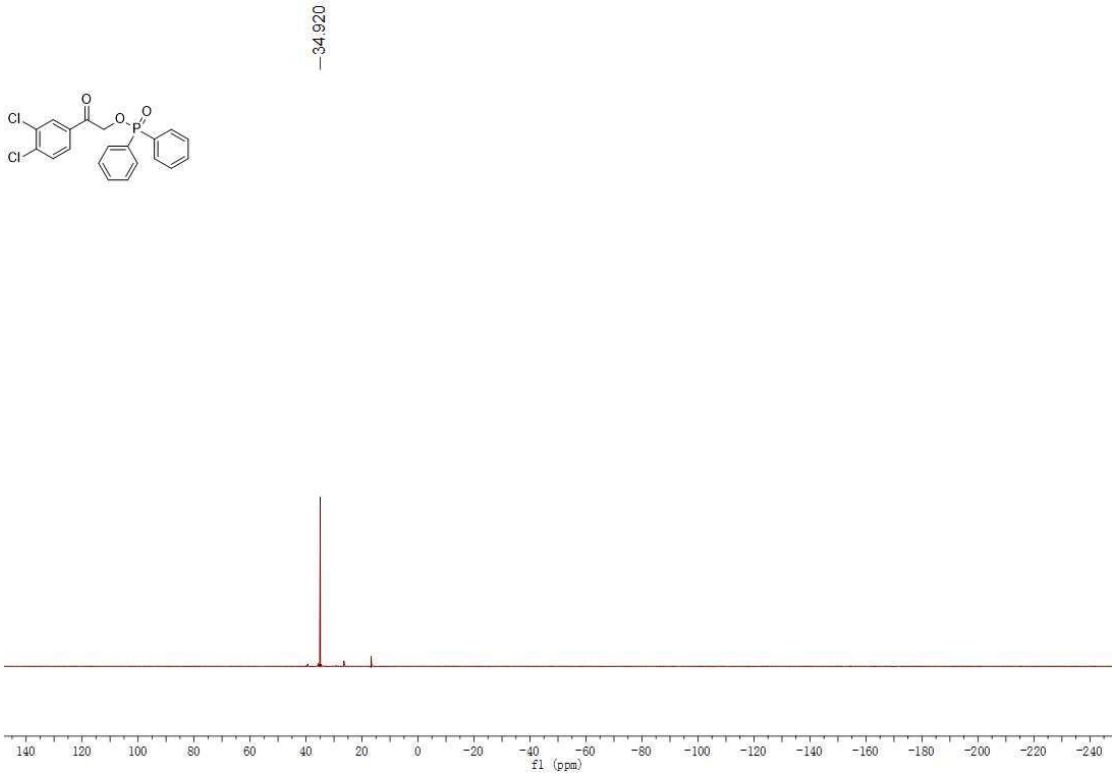
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **18**



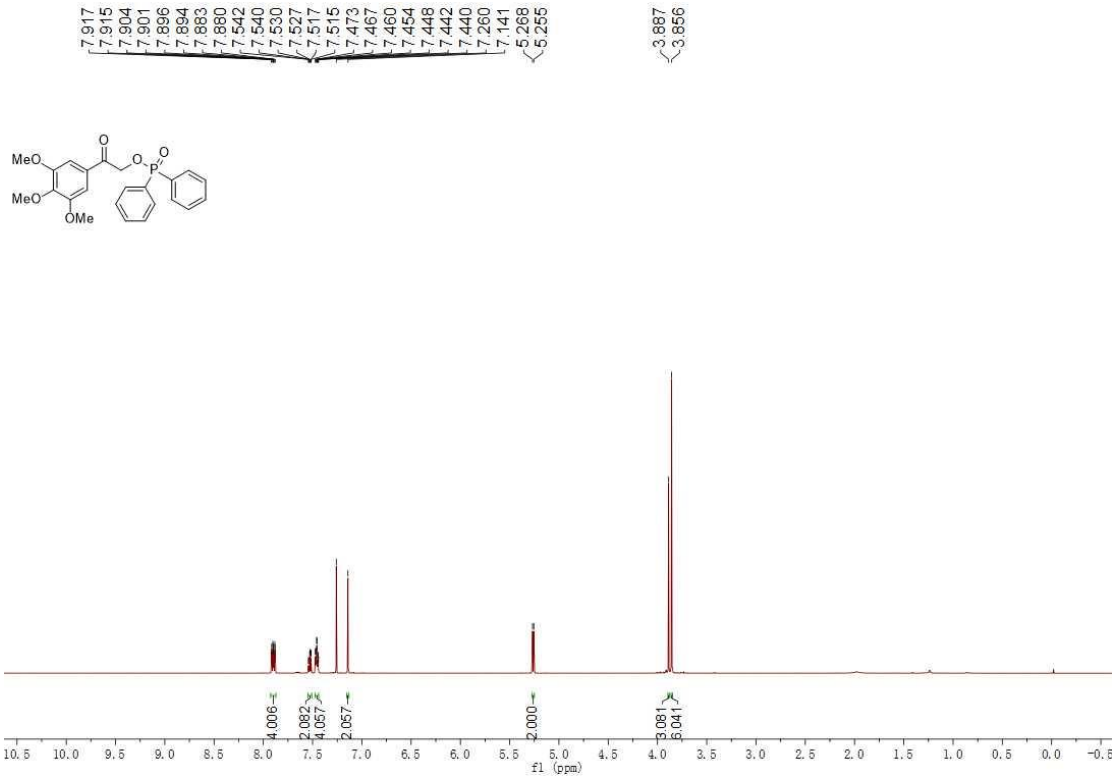
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **18**



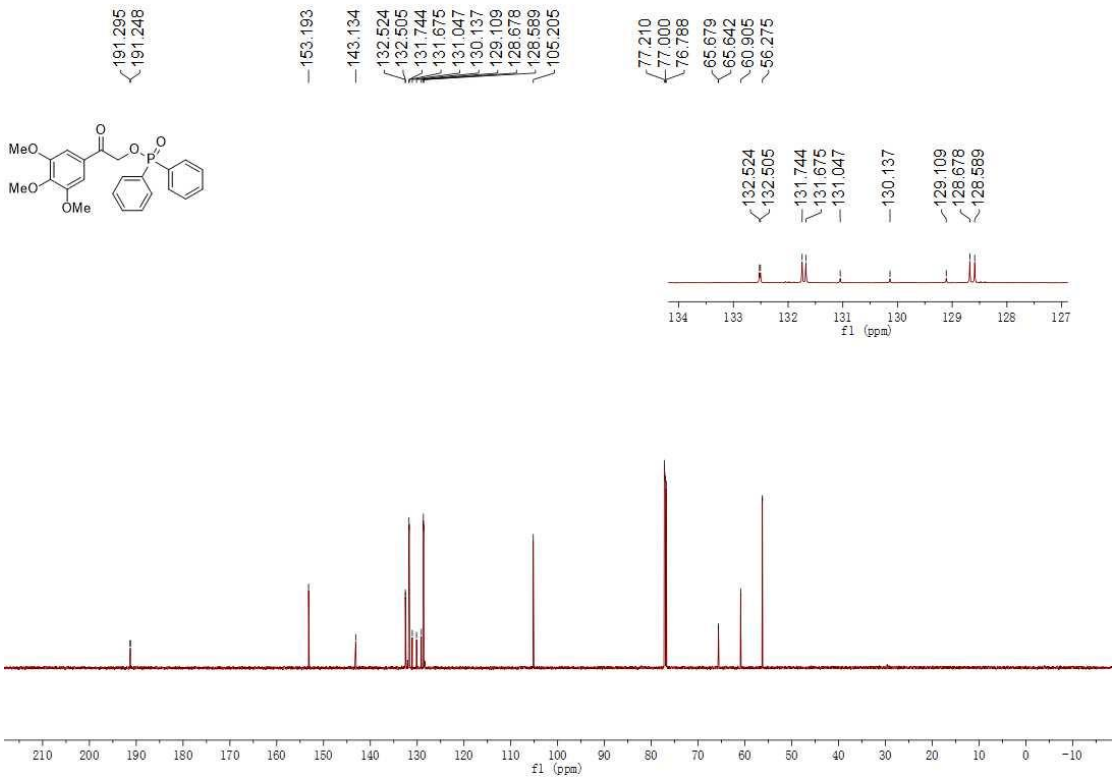
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **18**



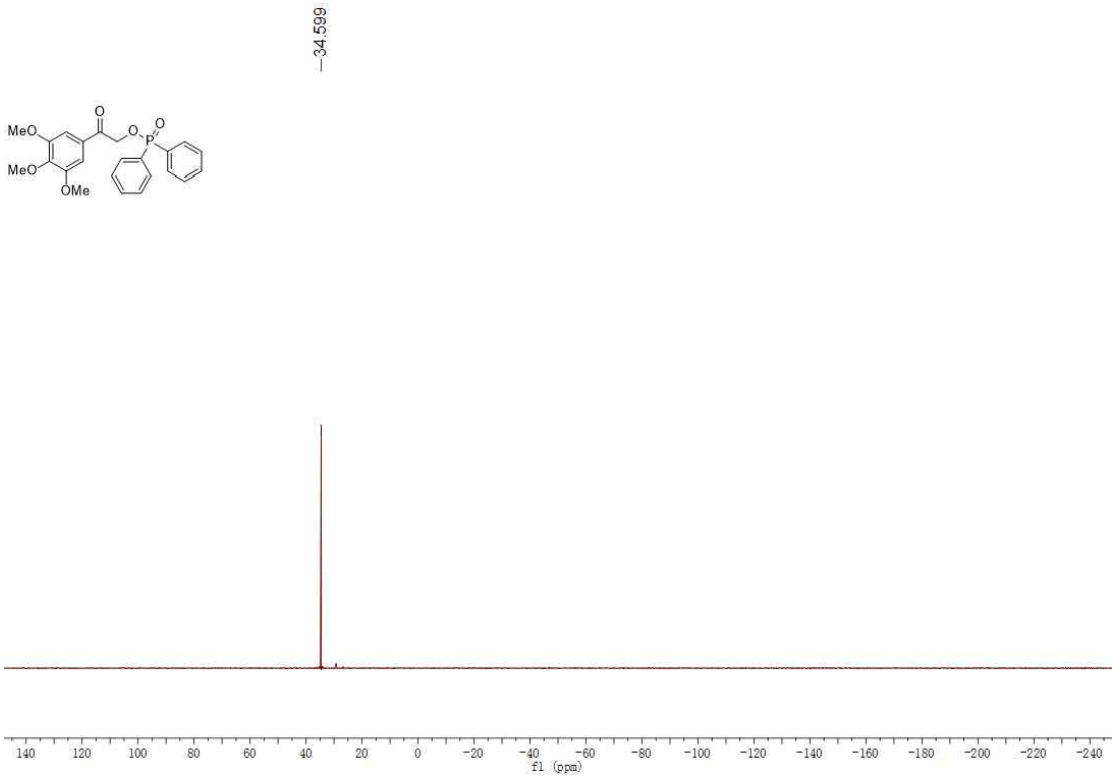
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **19**



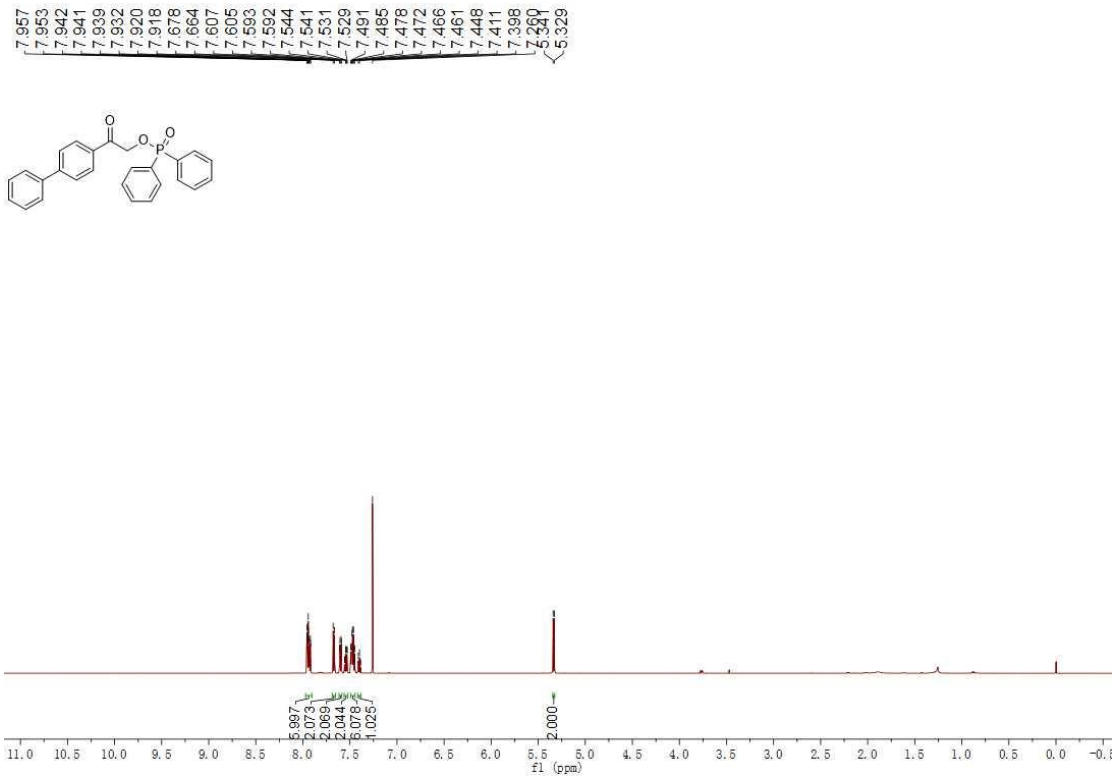
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **19**



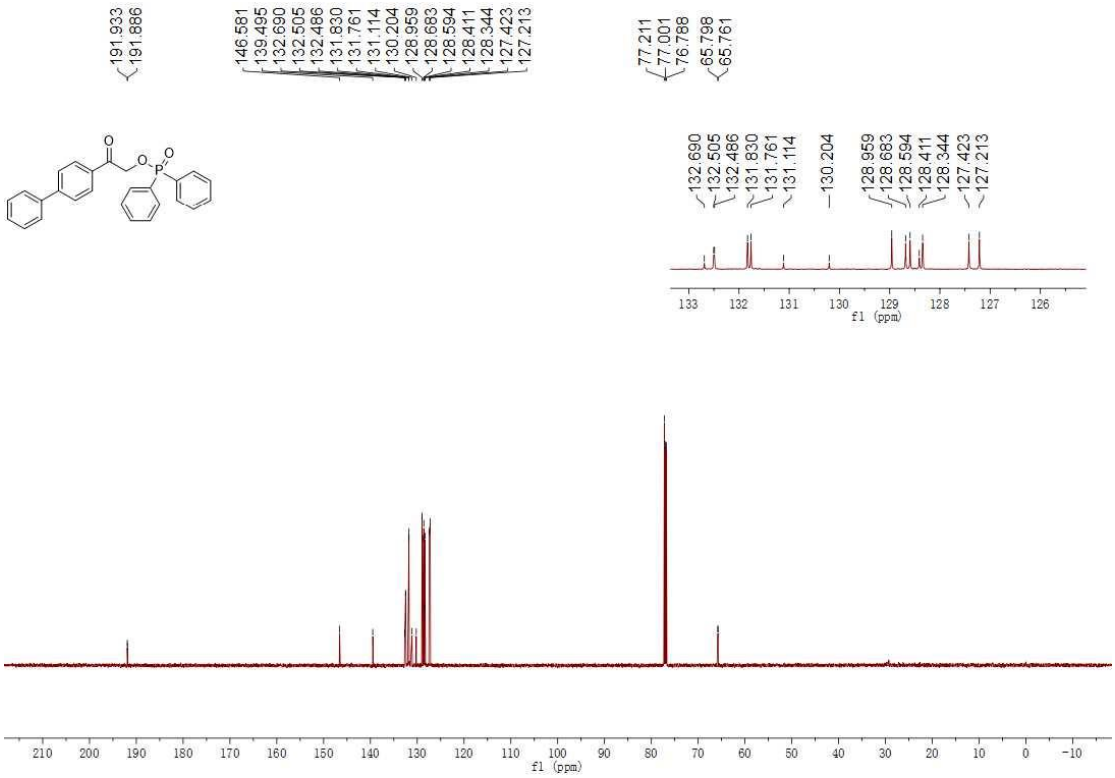
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **19**



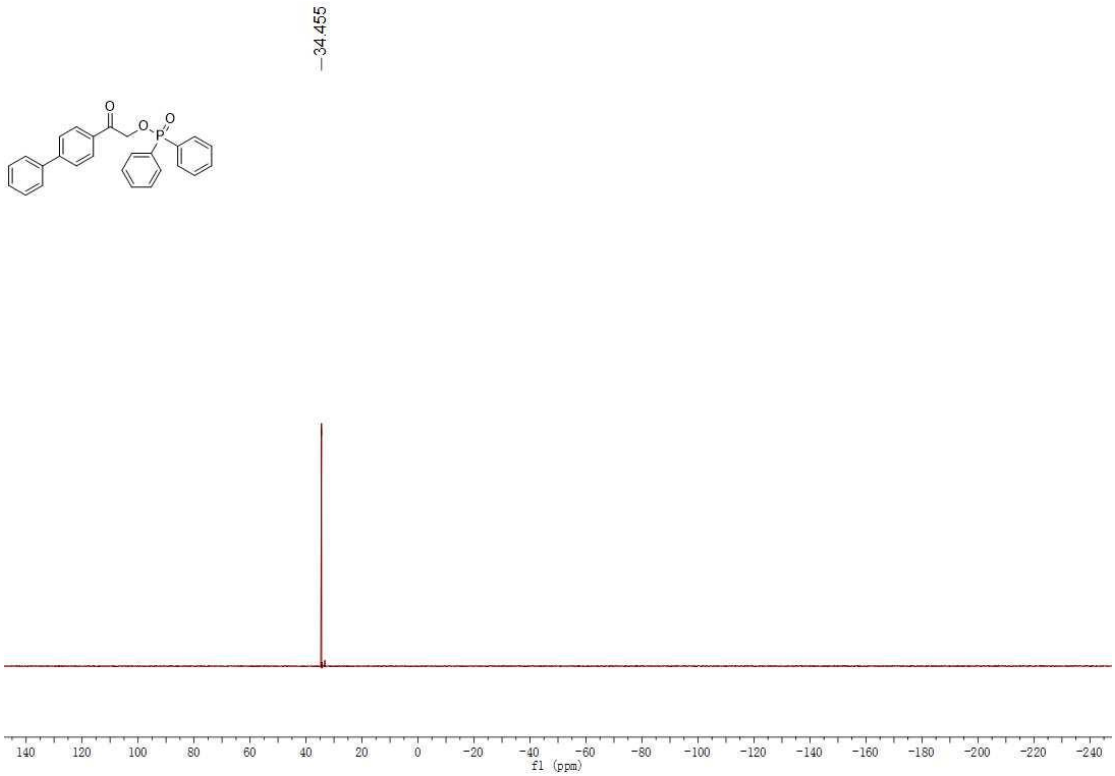
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **20**



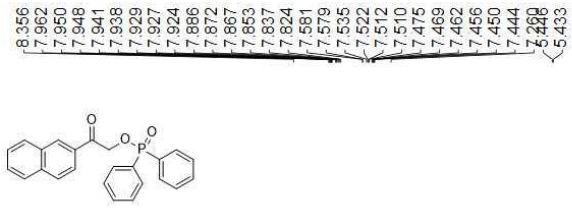
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **20**

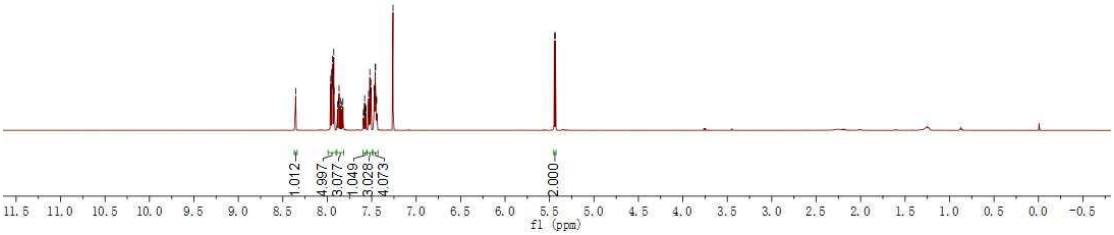


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **20**

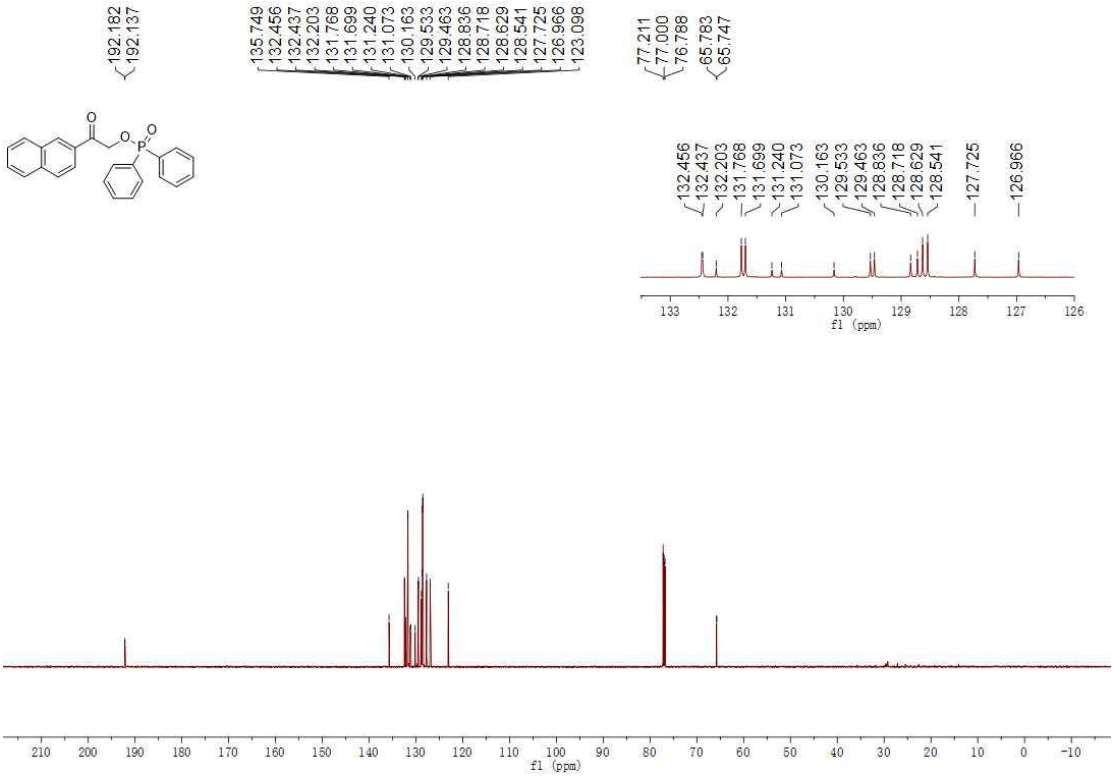


^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **21**

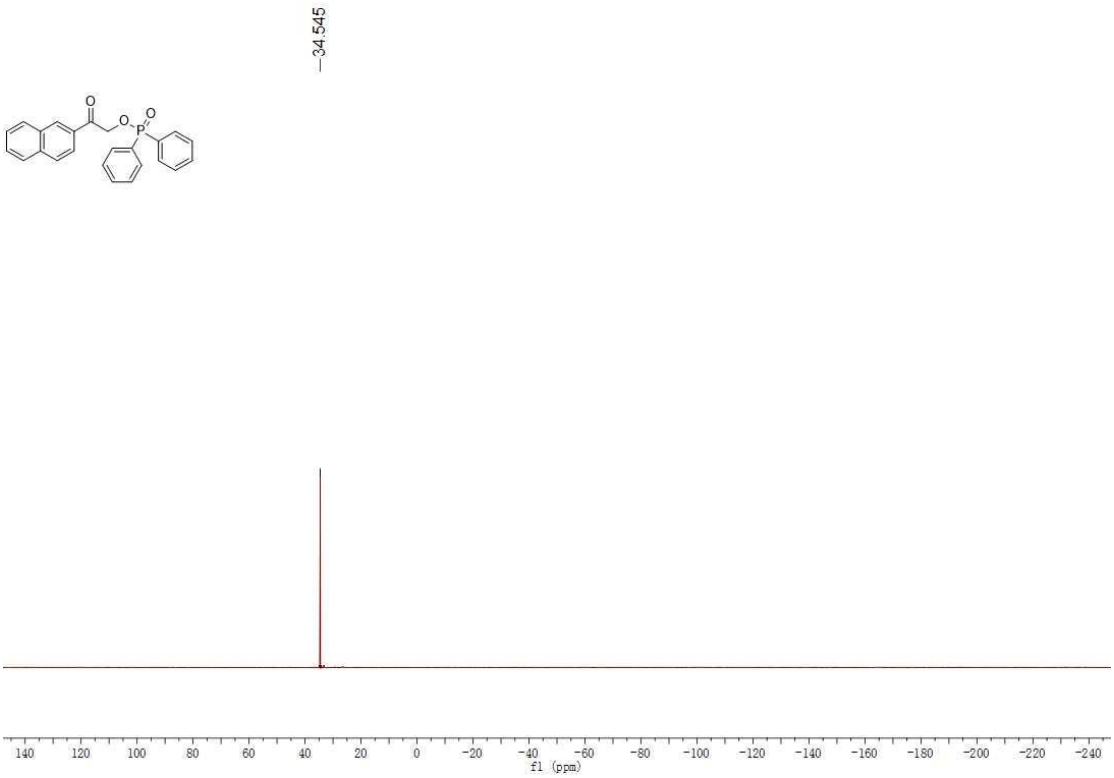




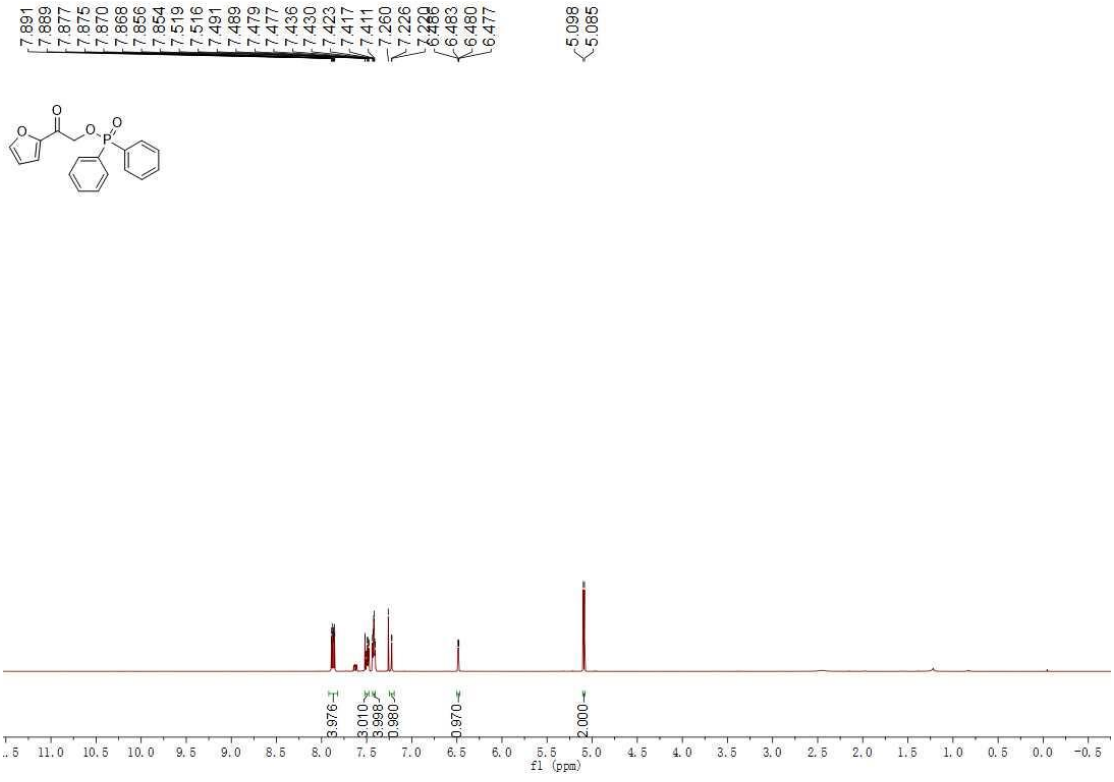
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **21**



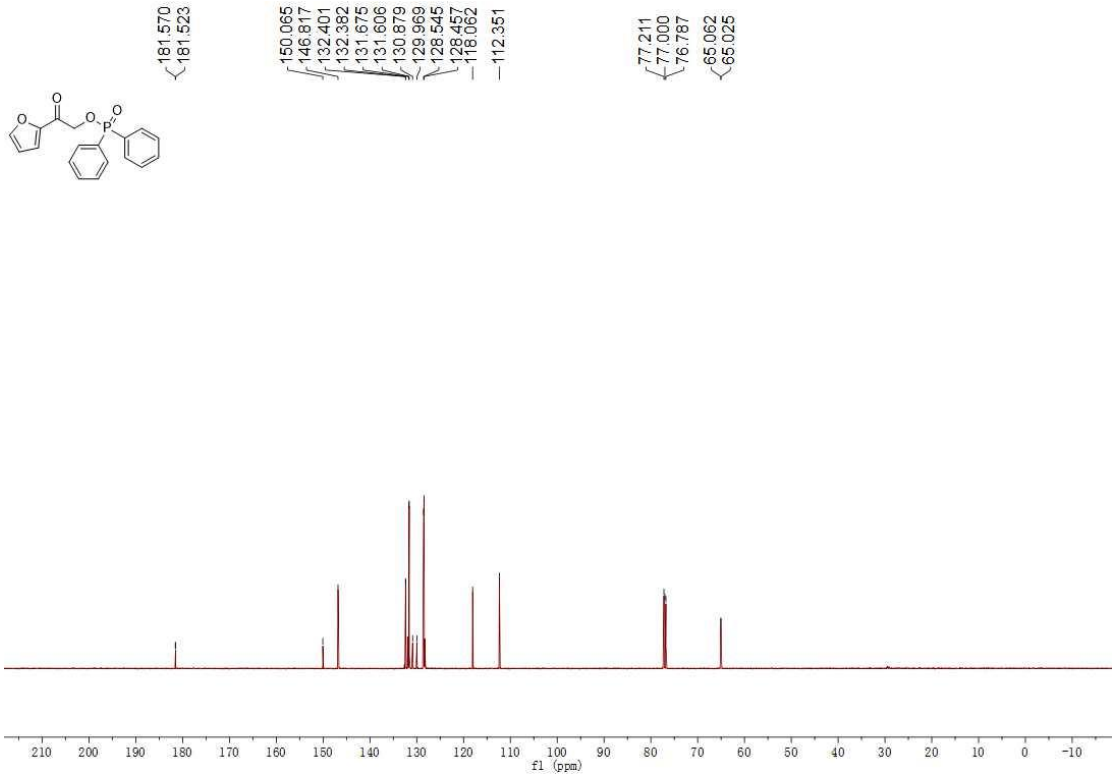
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **21**



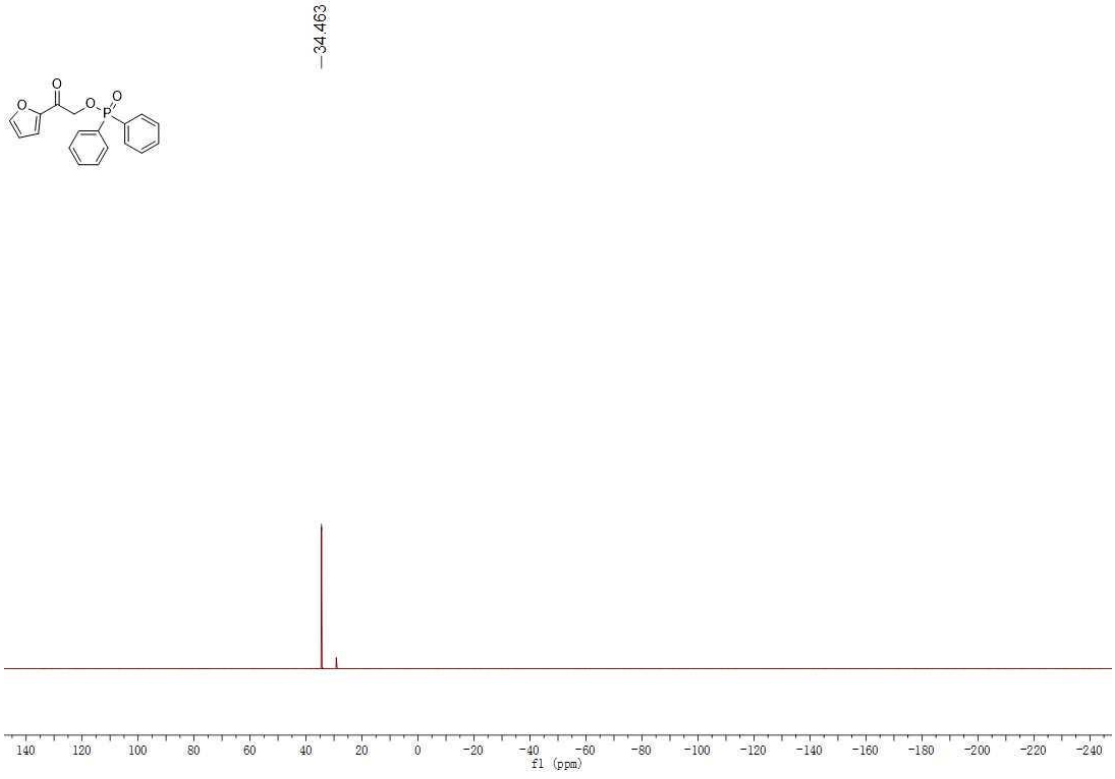
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **22**



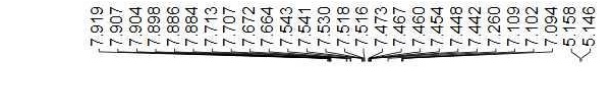
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **22**

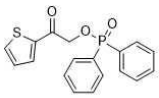


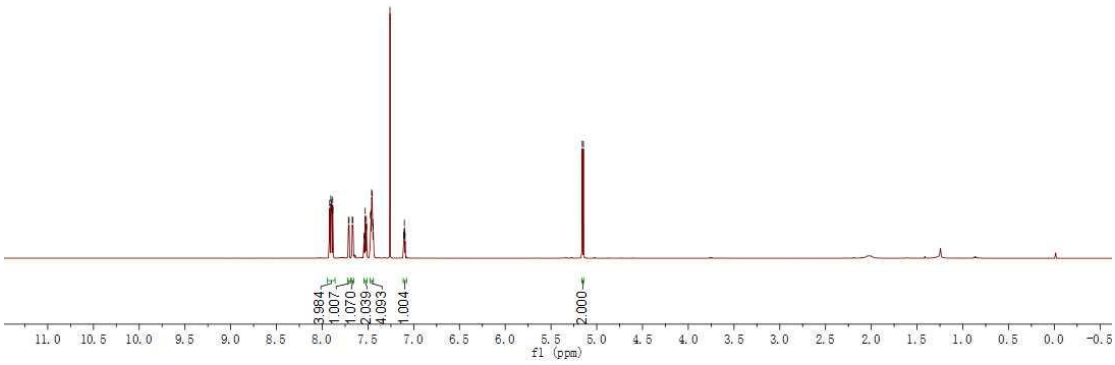
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **22**



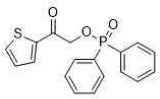
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **23**

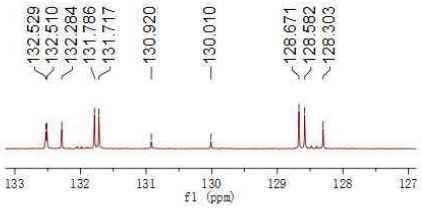


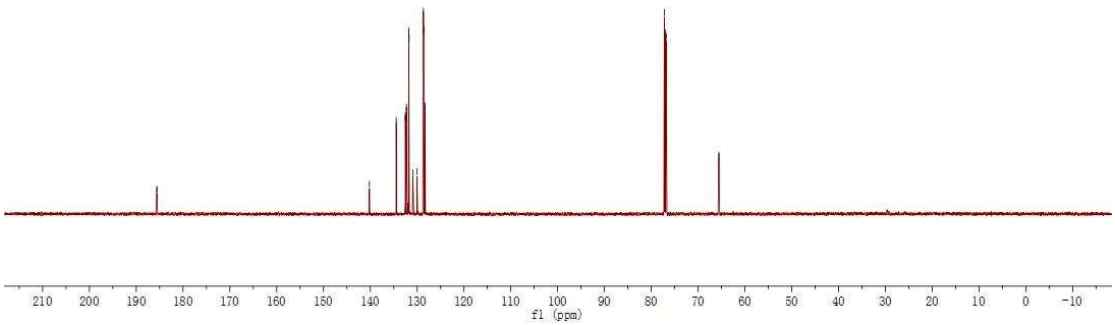




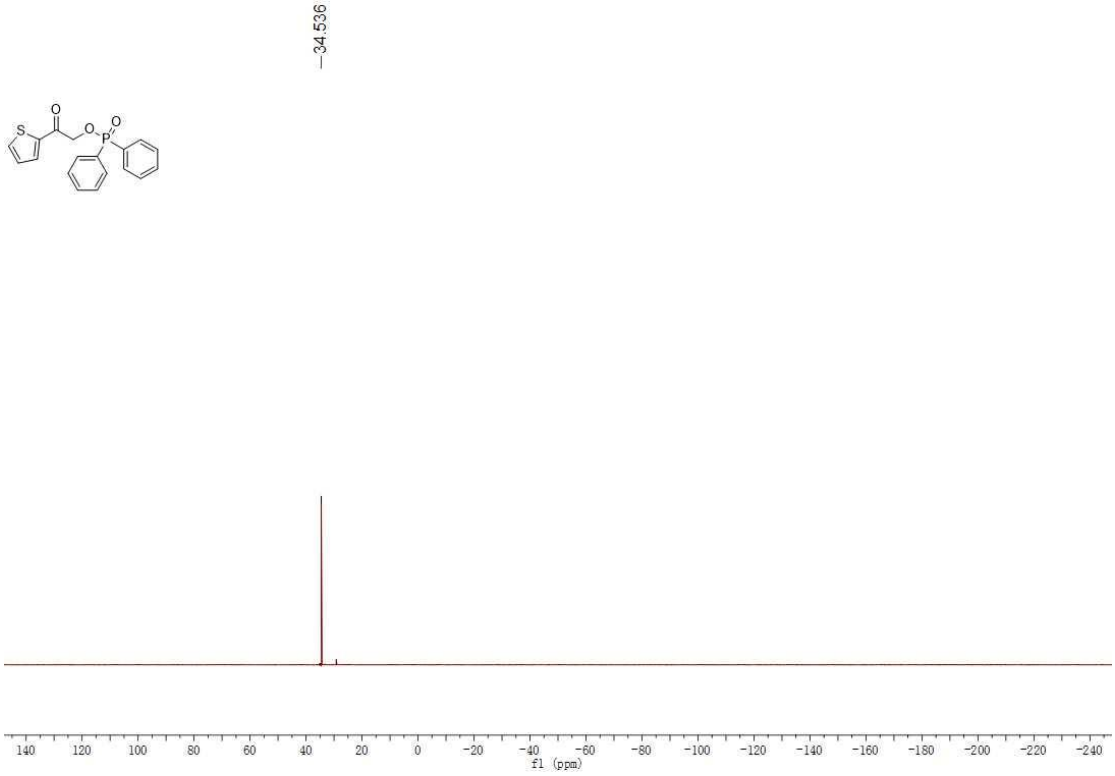
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **23**



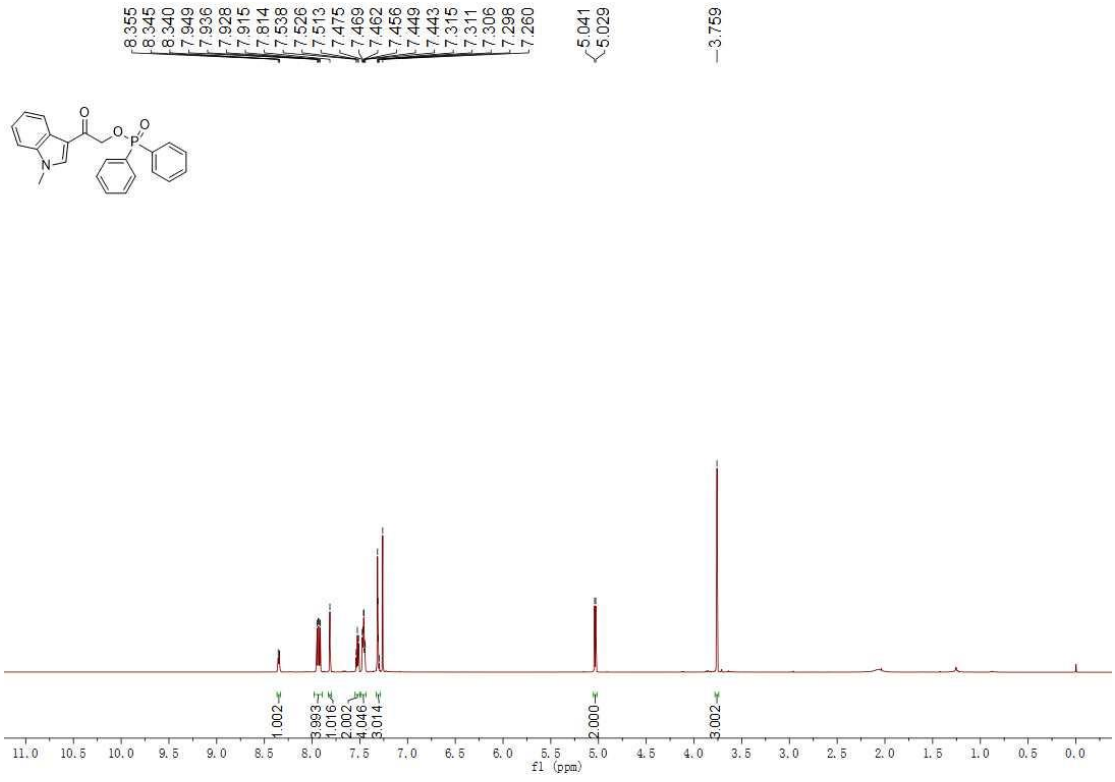




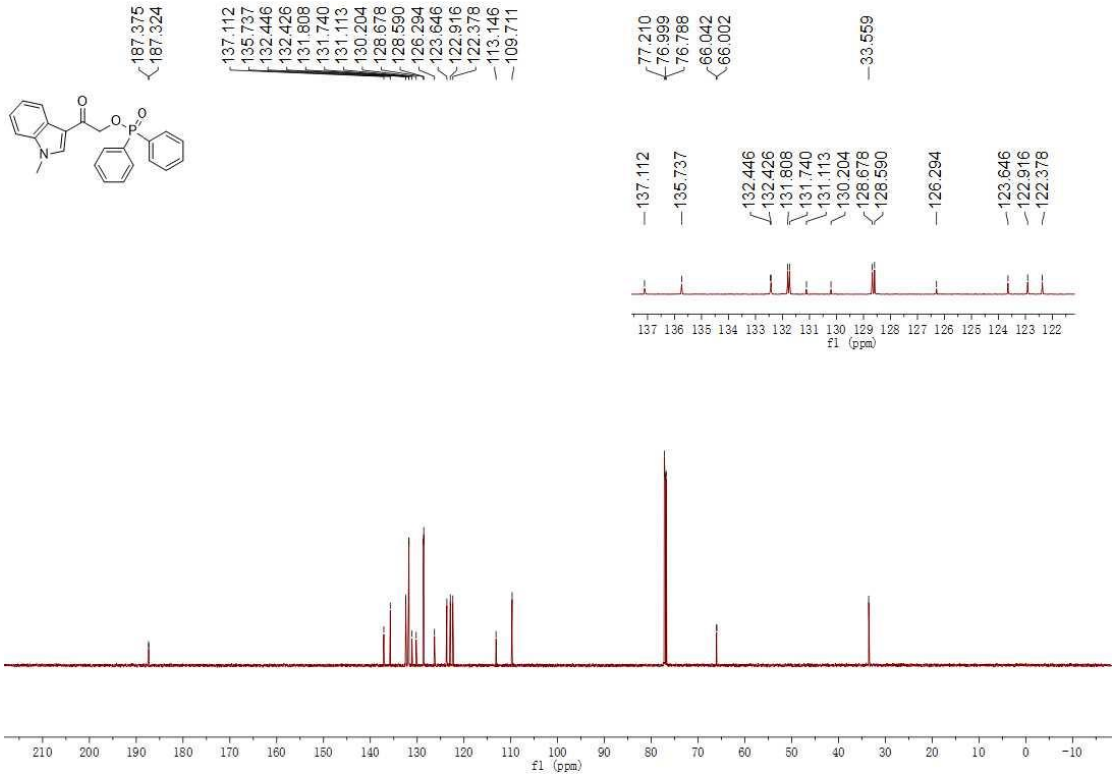
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **23**



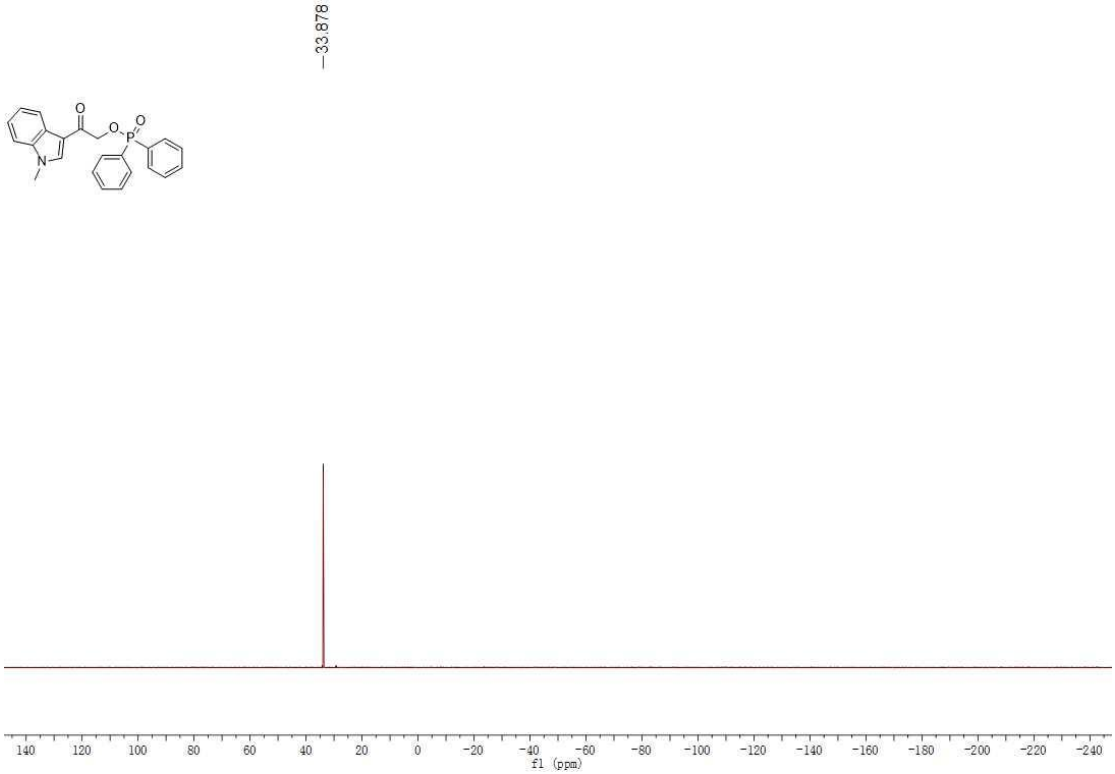
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **25**



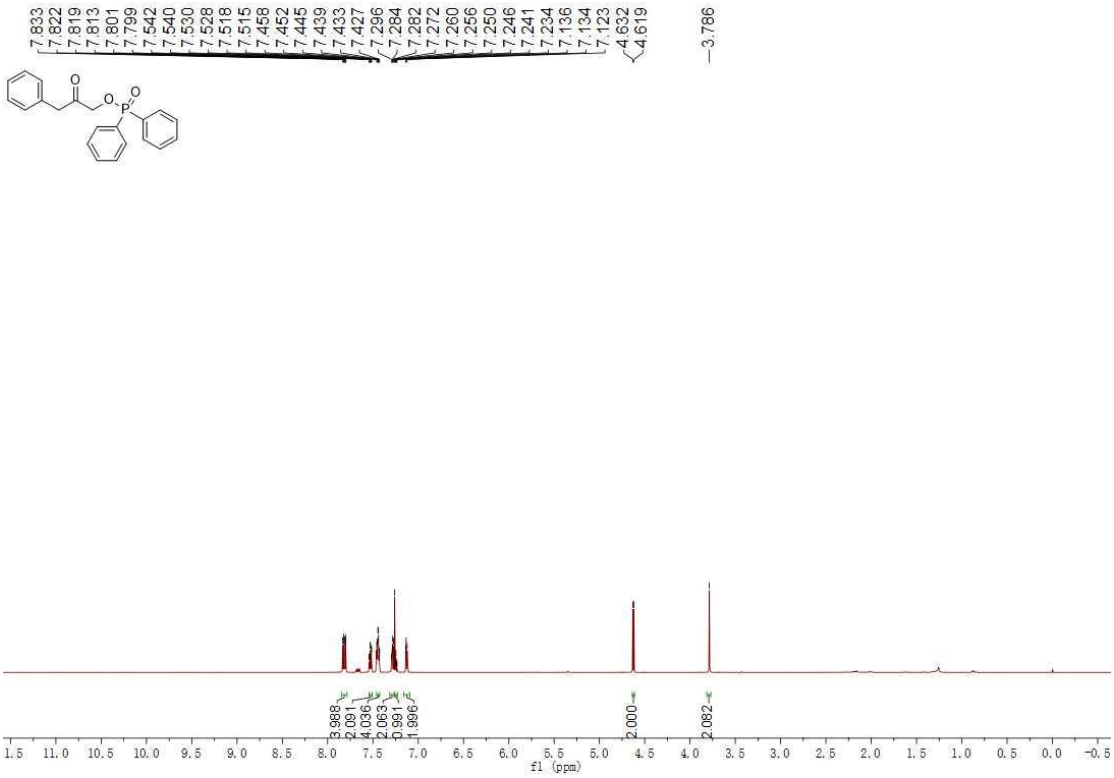
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **25**



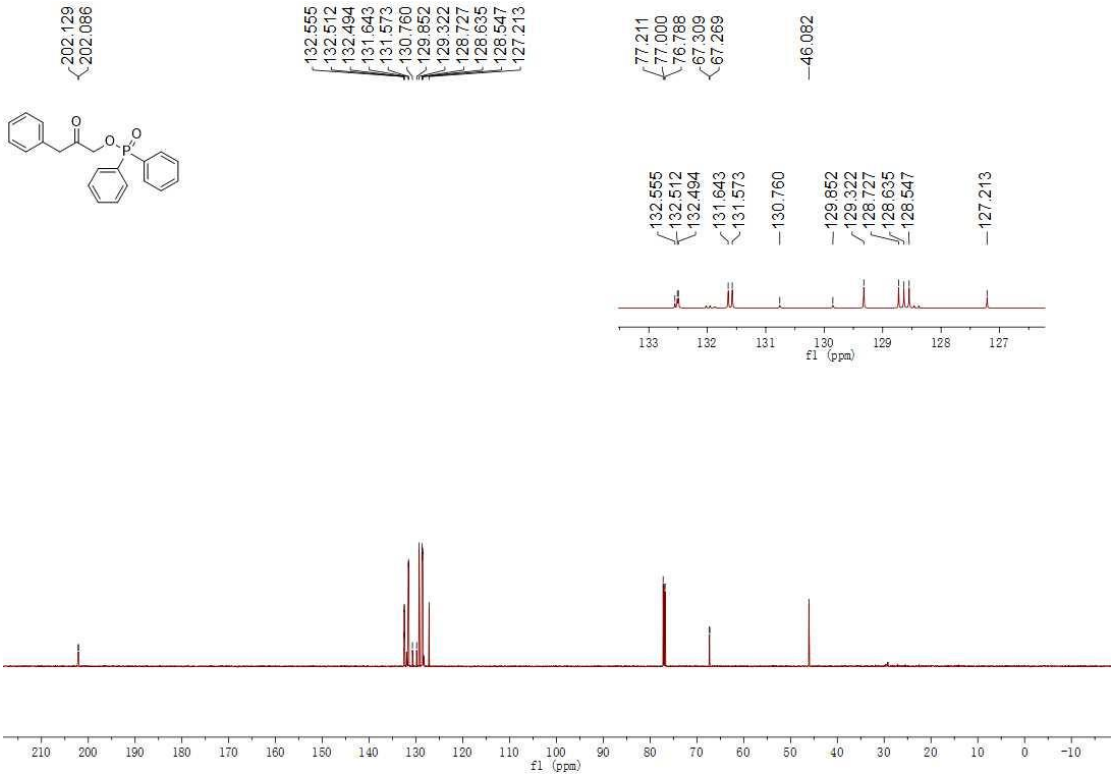
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **25**



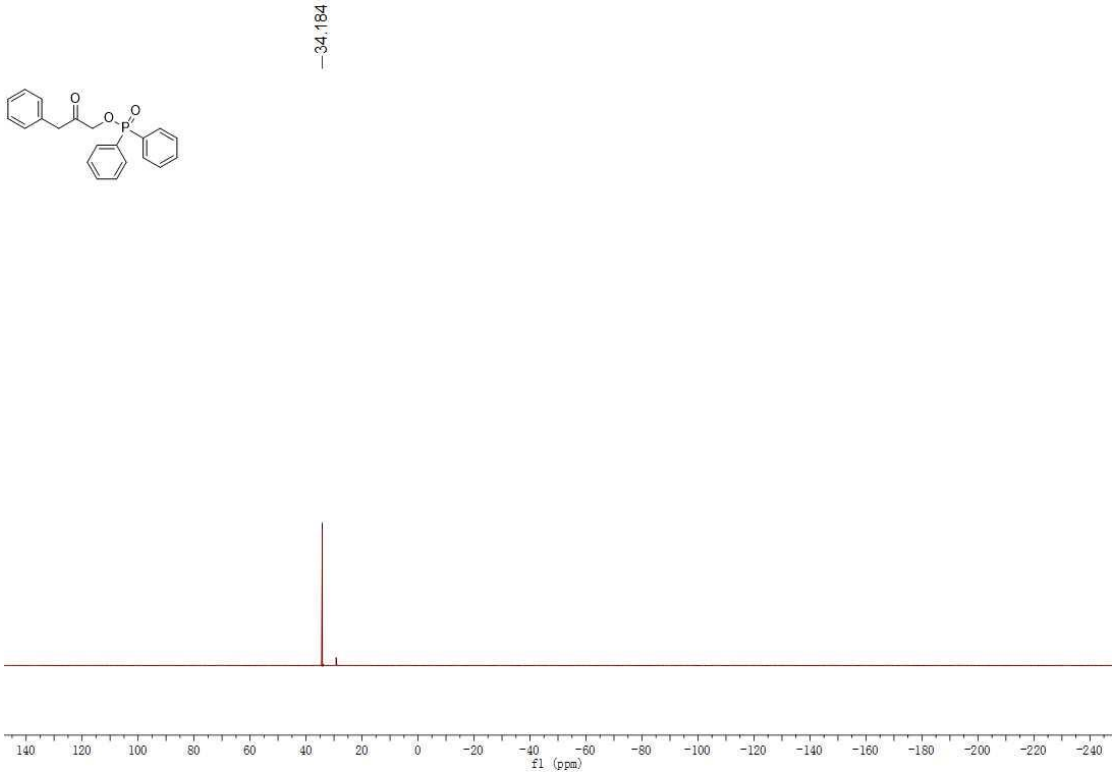
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **26**



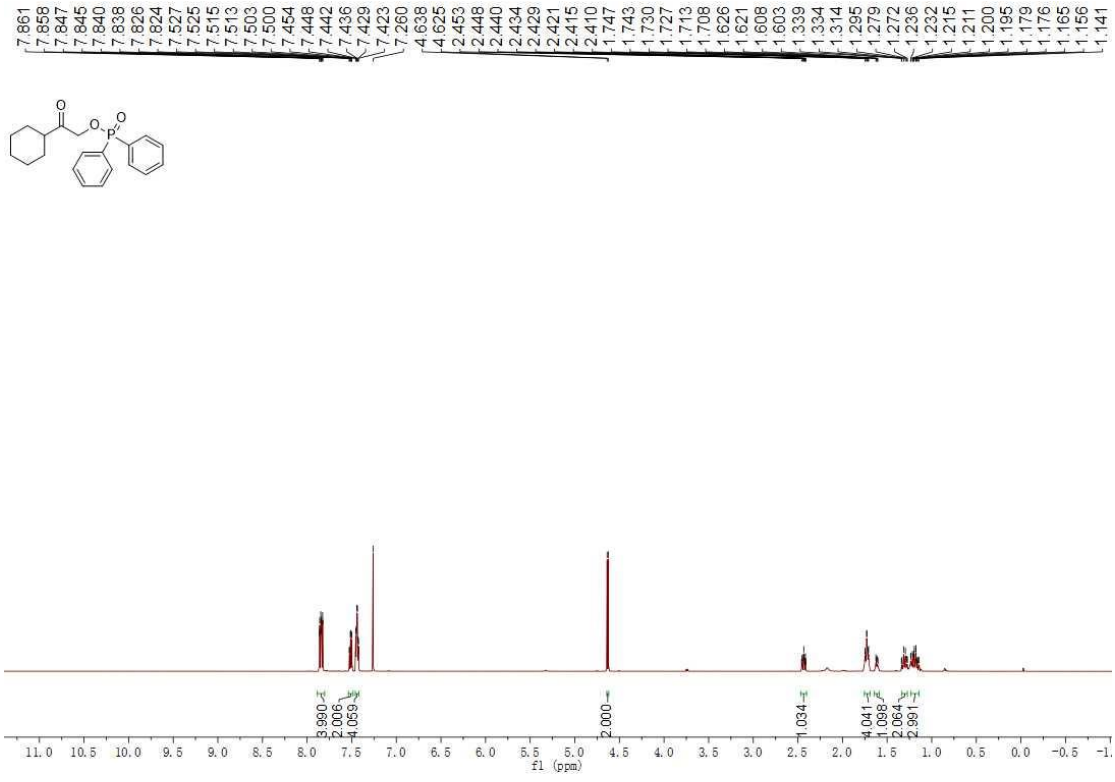
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **26**



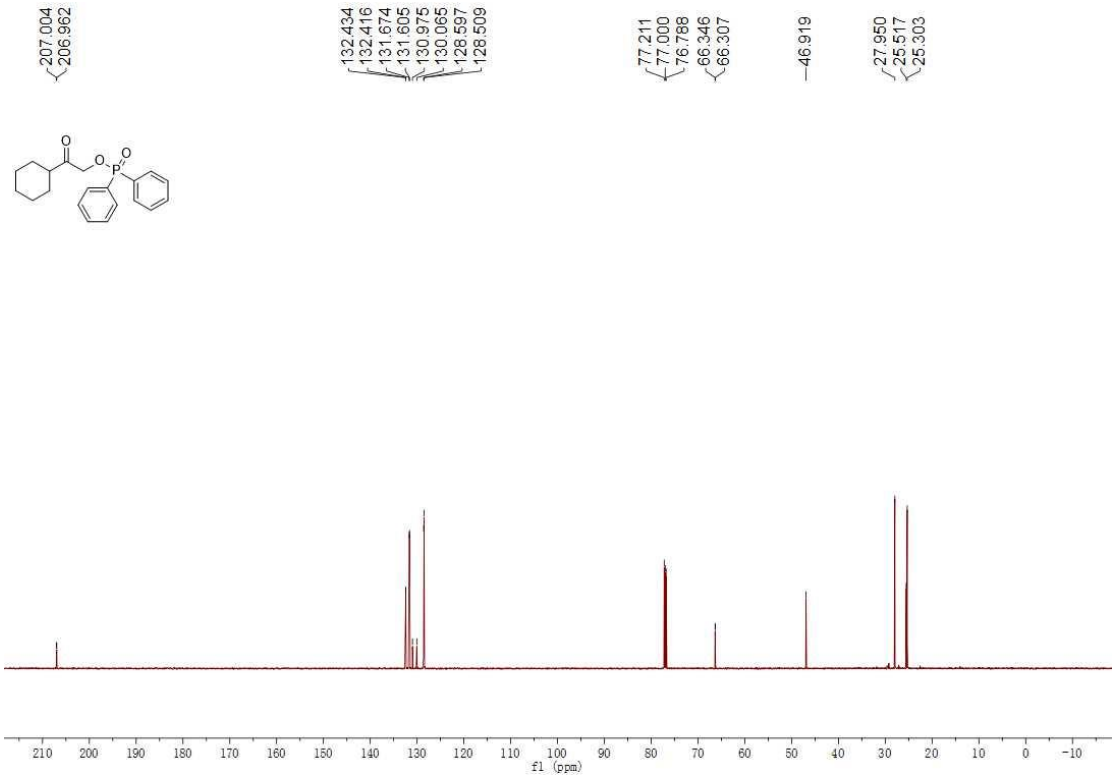
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **26**



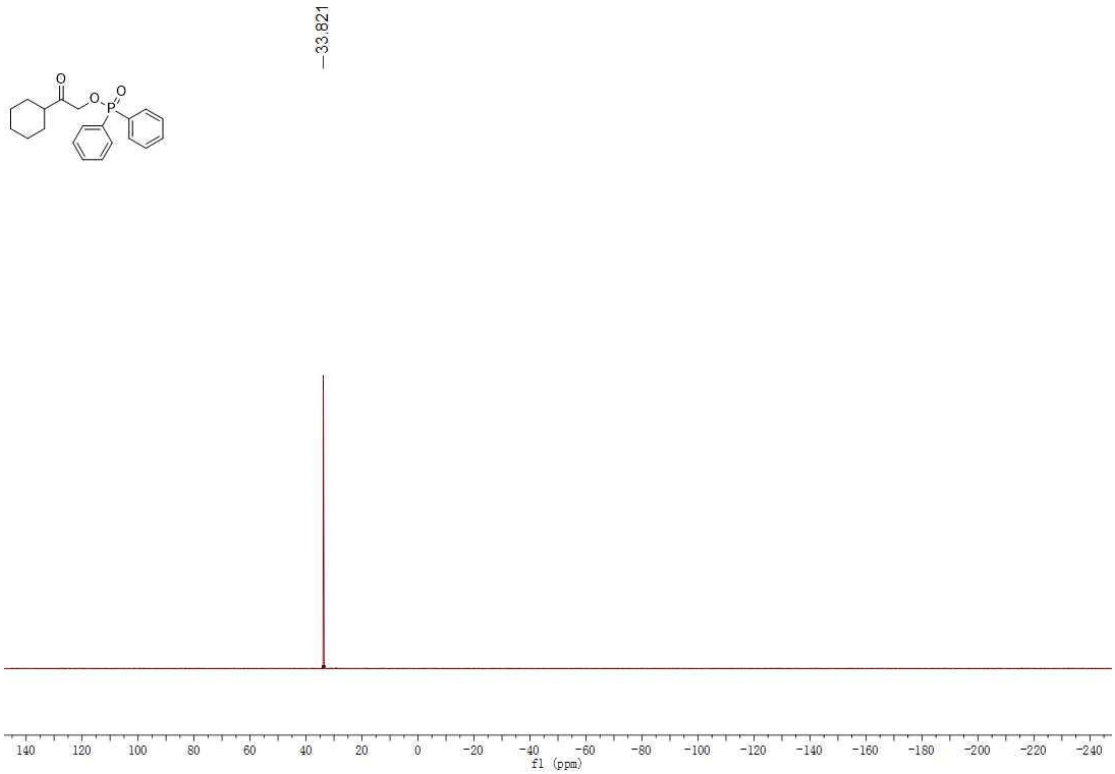
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **27**



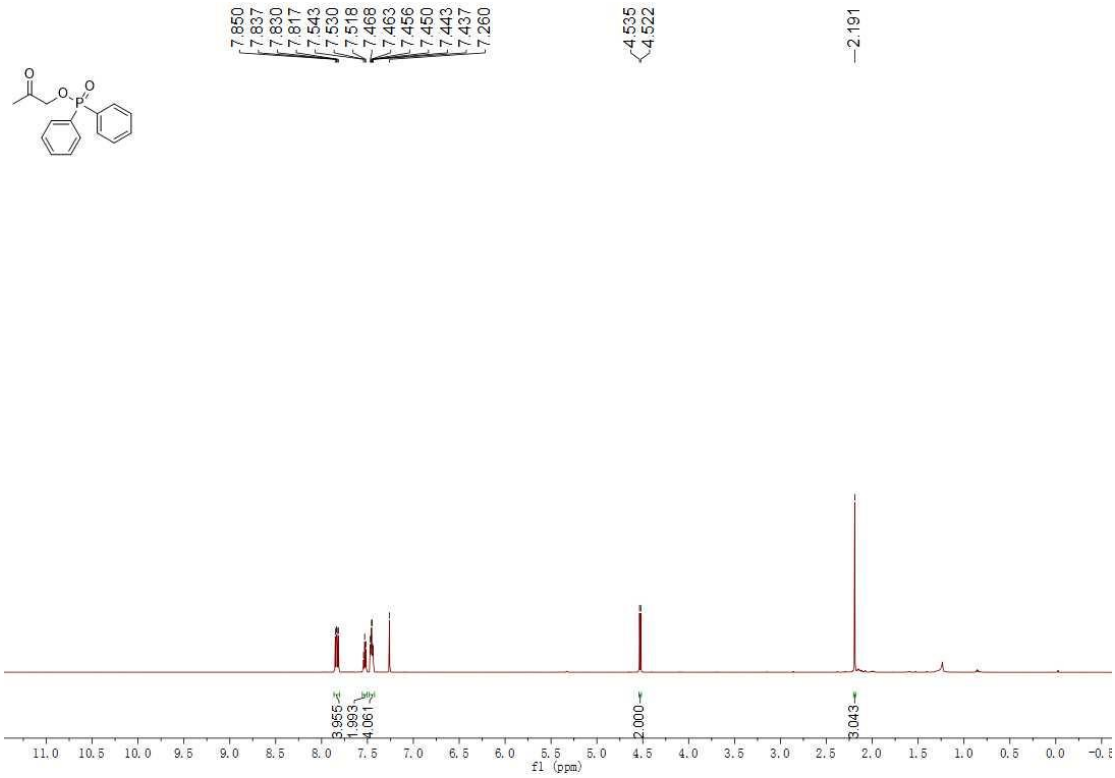
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **27**



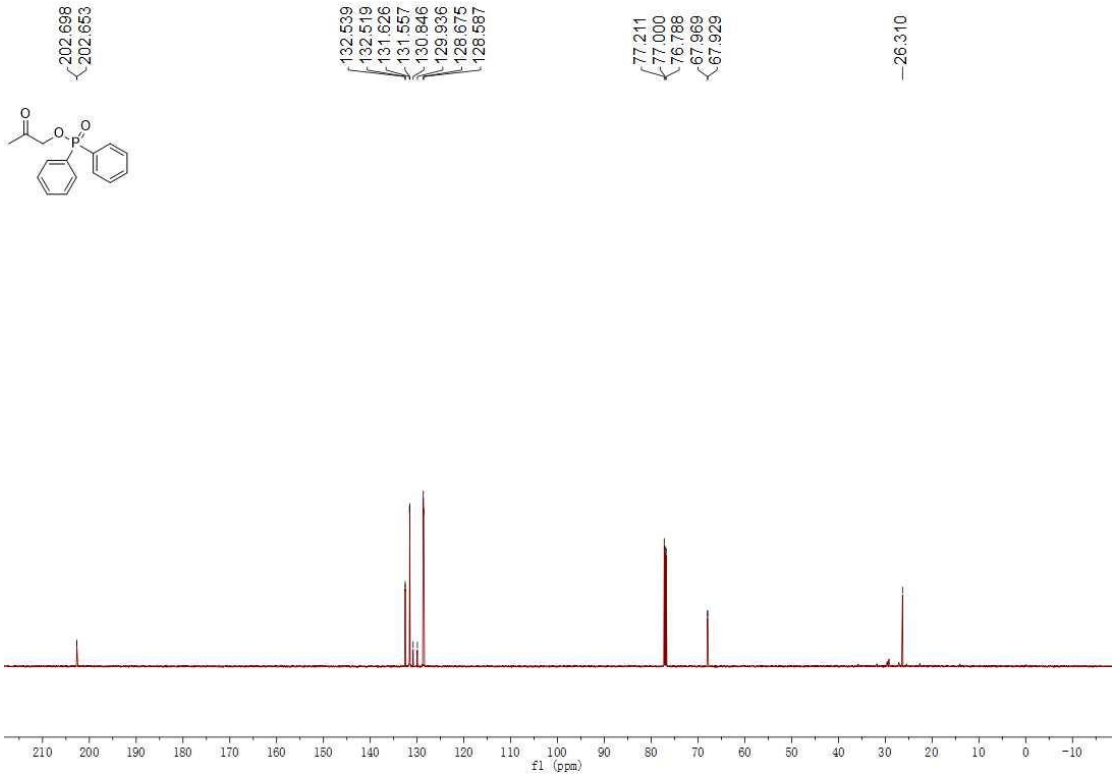
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **27**



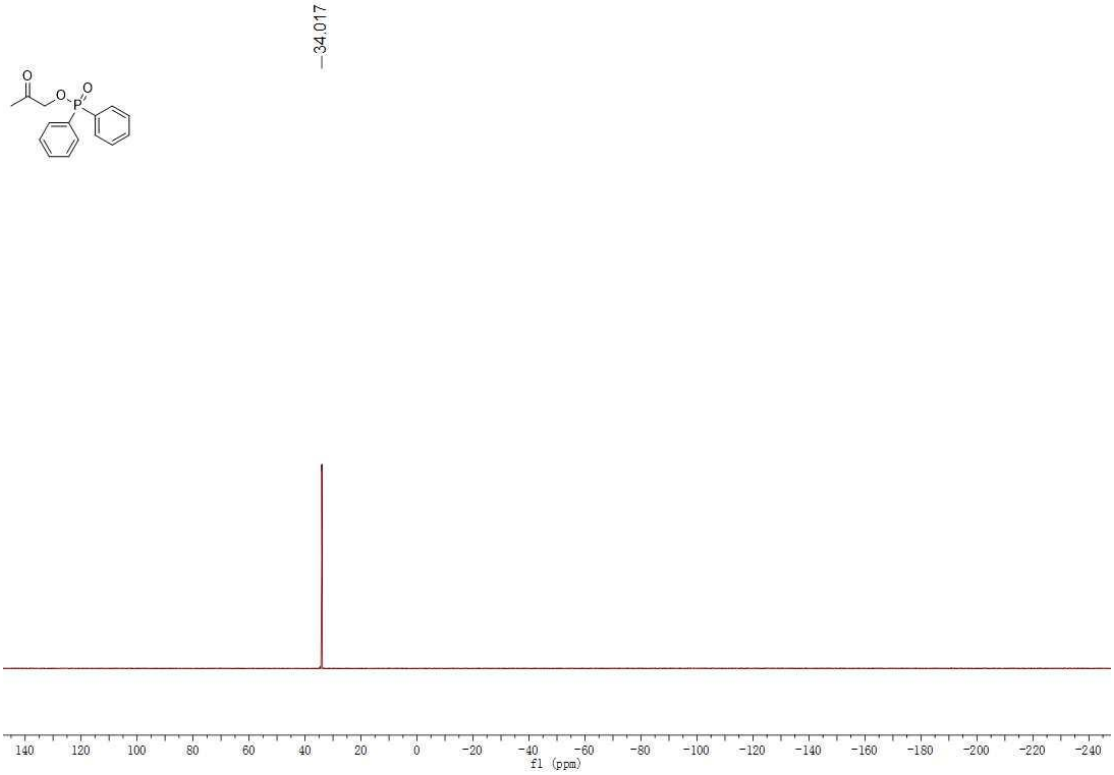
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **28**



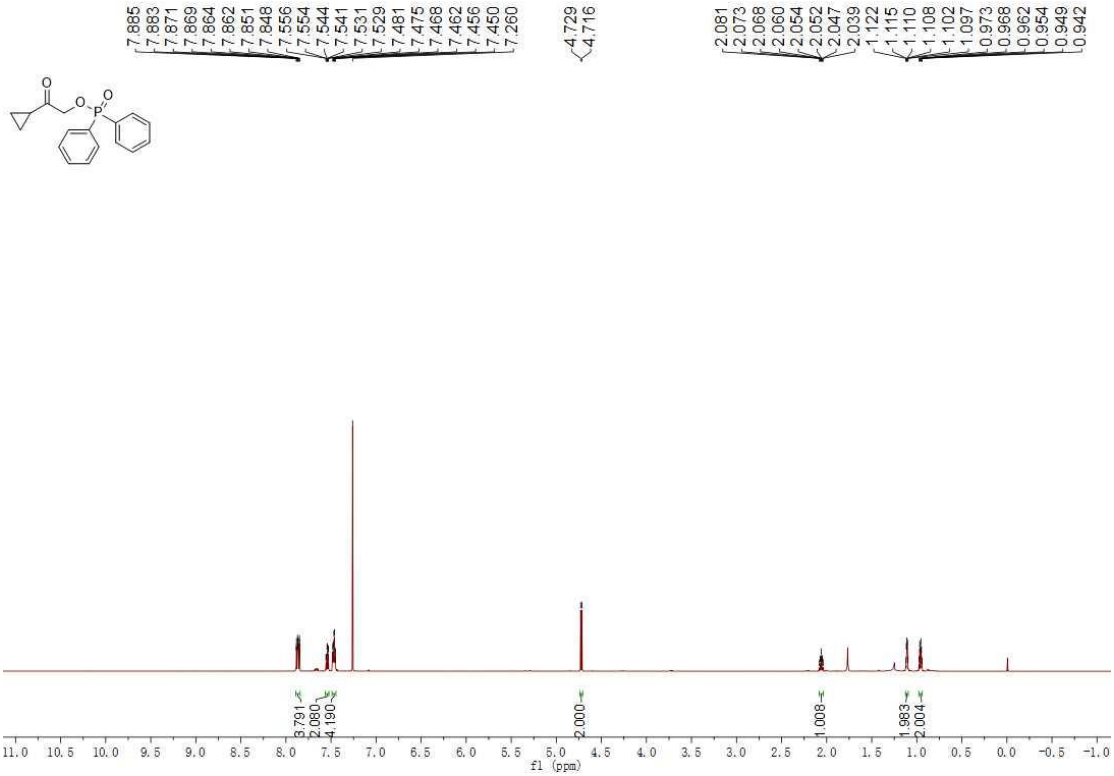
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **28**



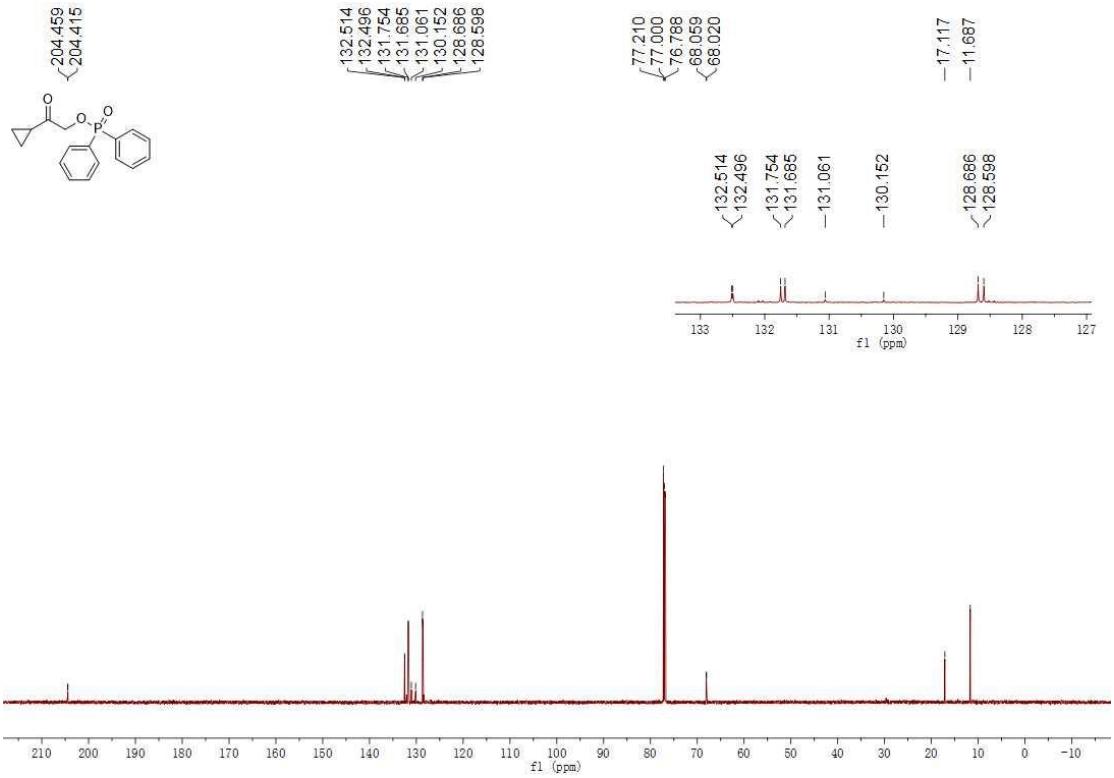
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **28**



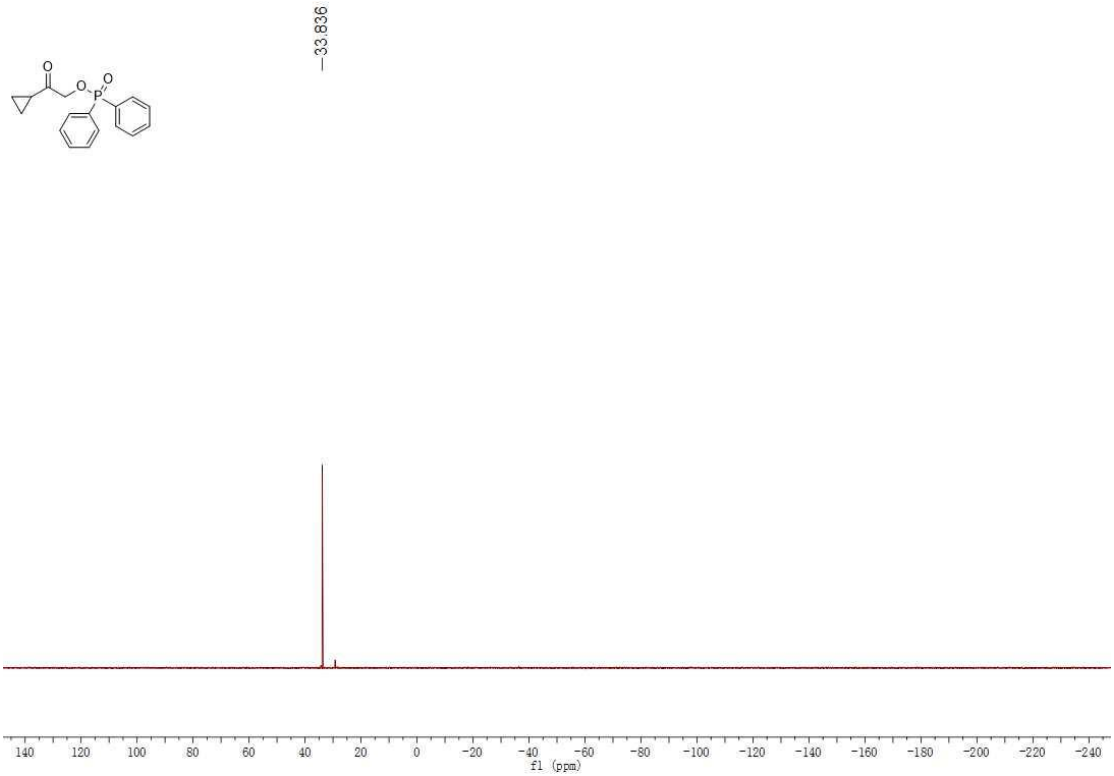
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **29**



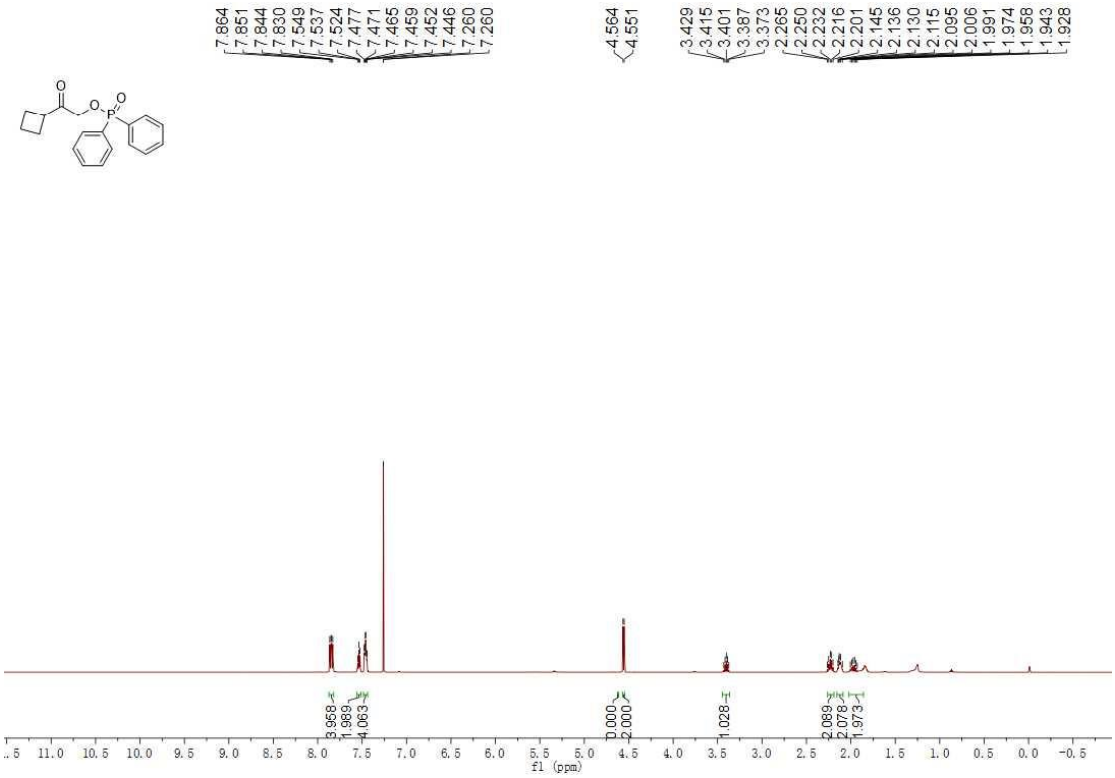
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **29**



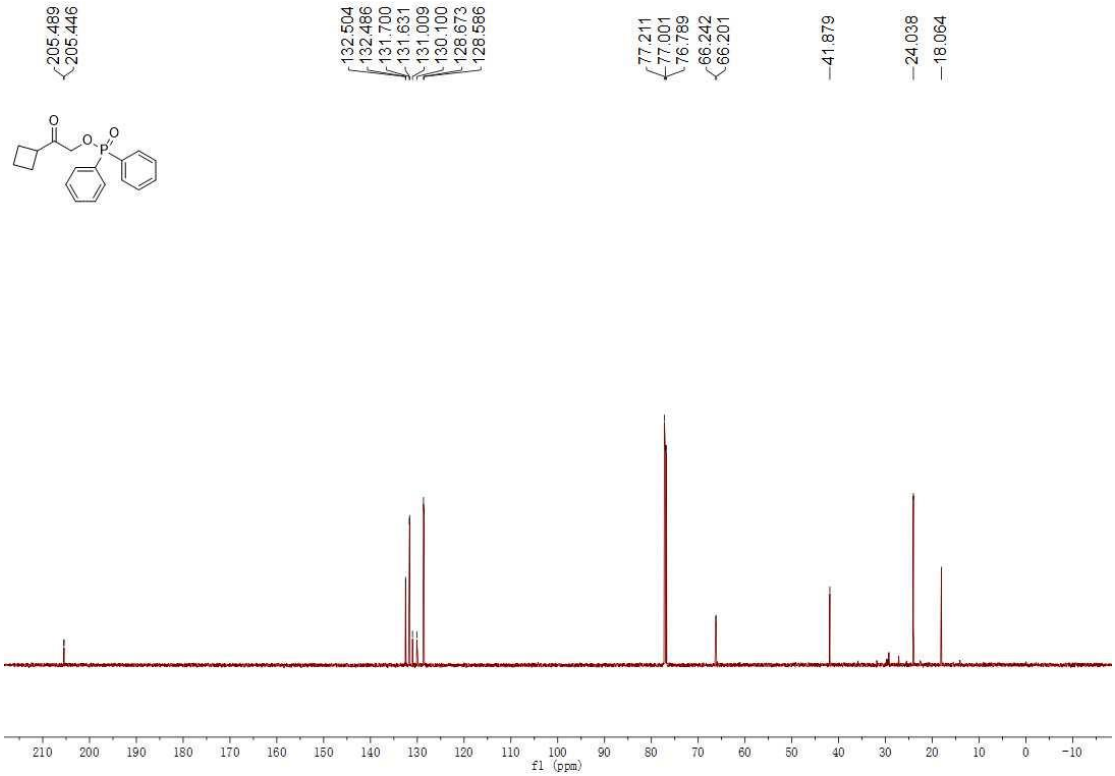
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **29**



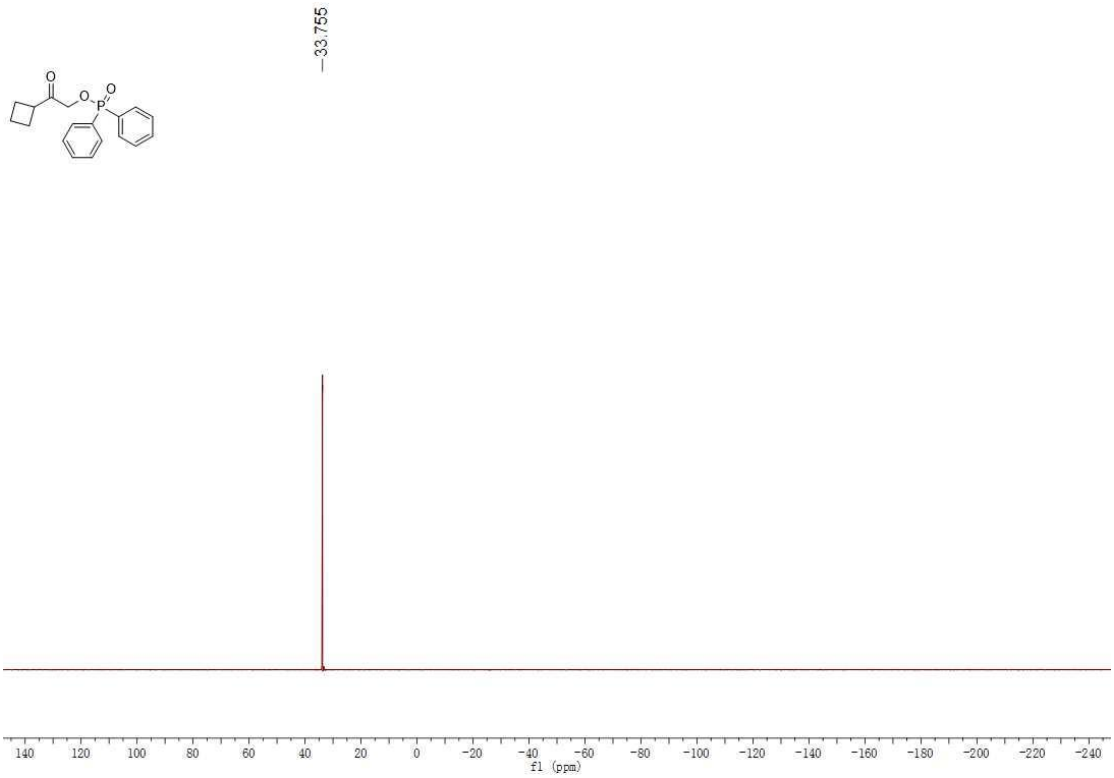
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **30**



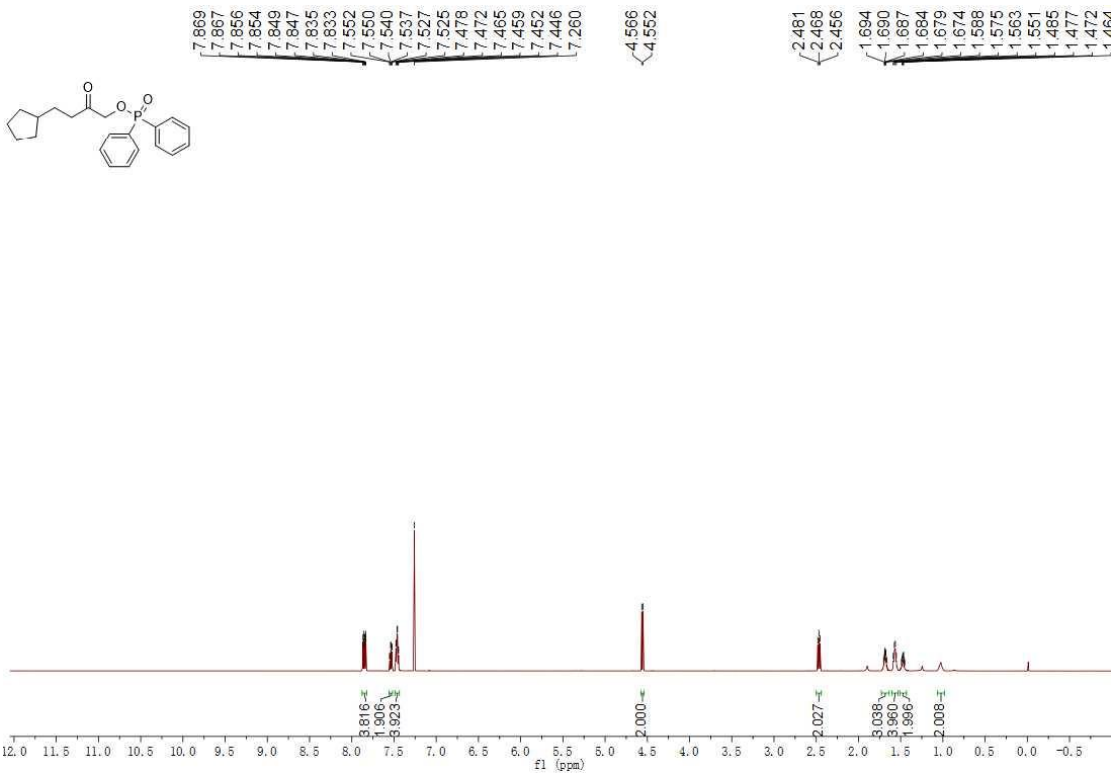
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **30**



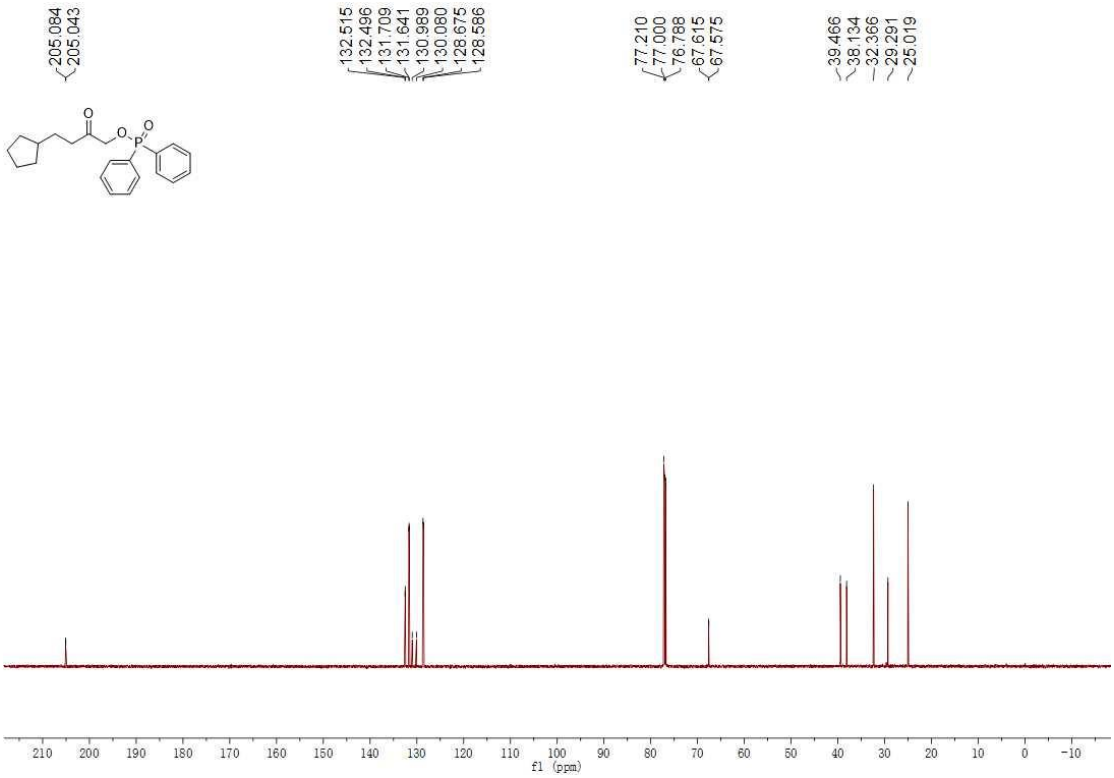
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **30**



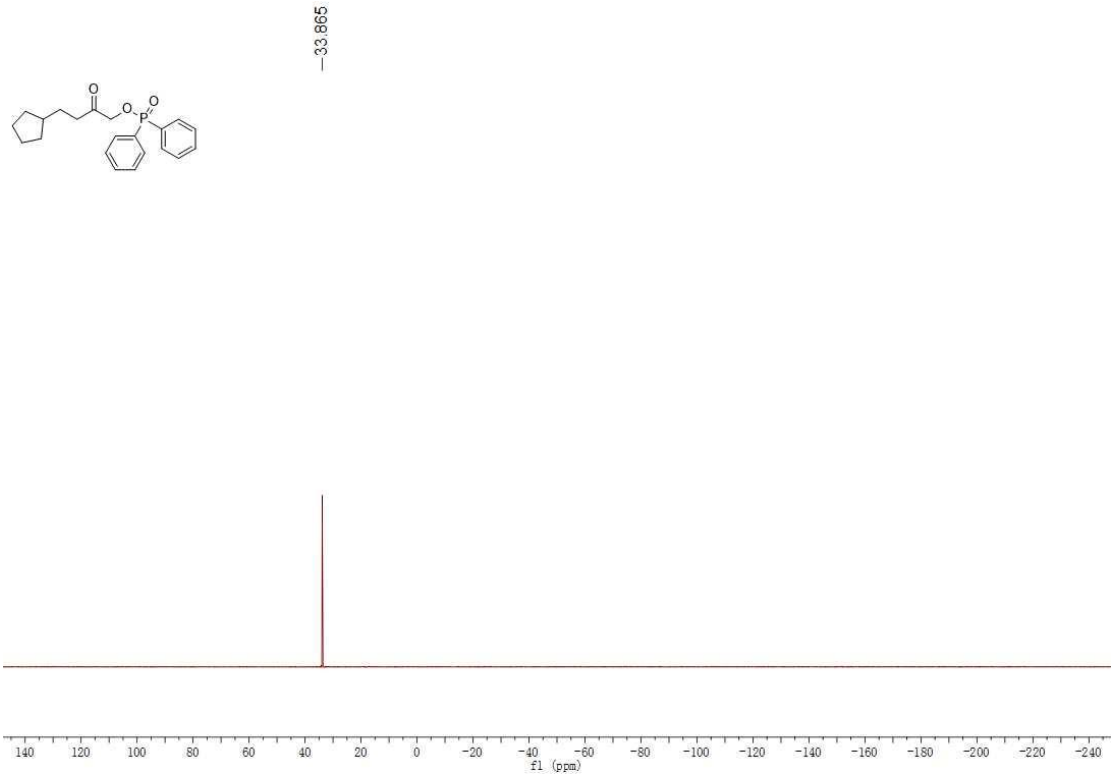
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **31**



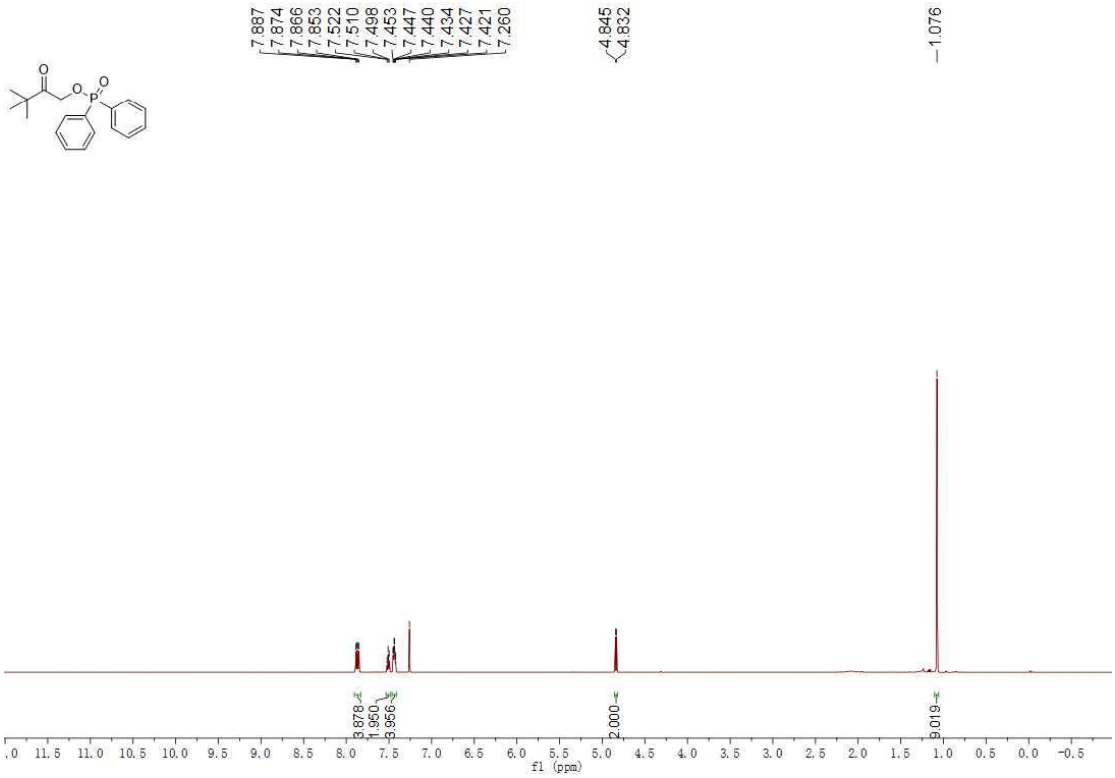
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **31**



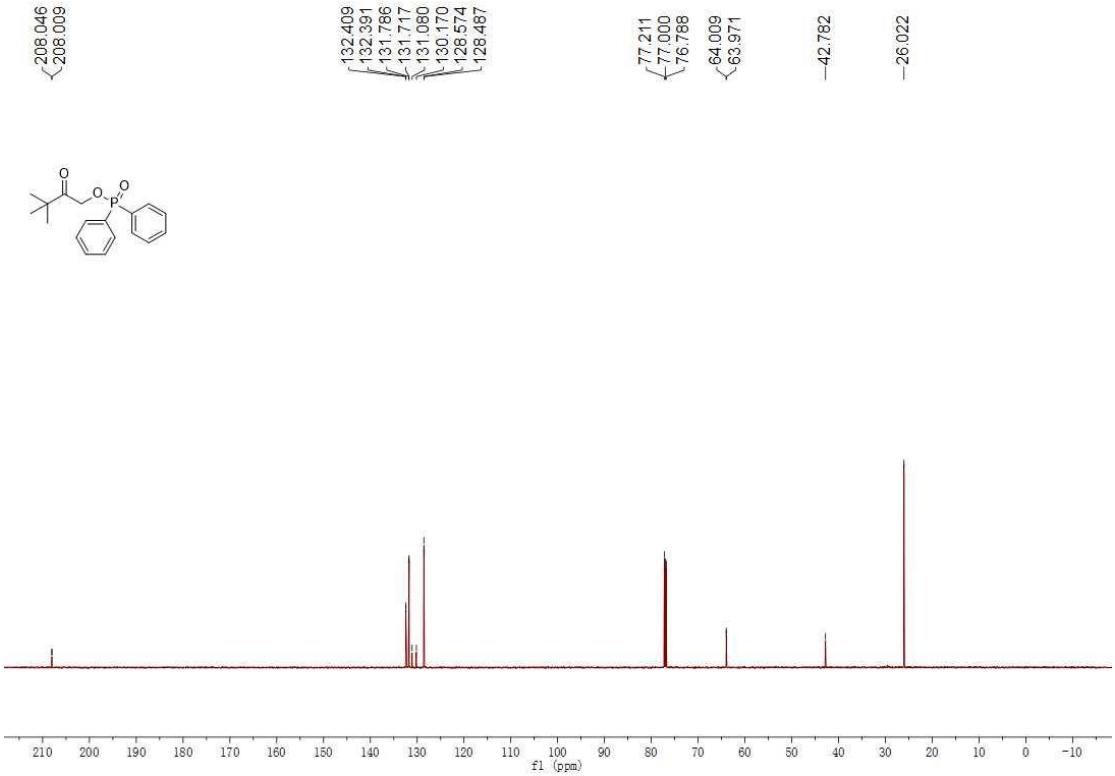
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **31**



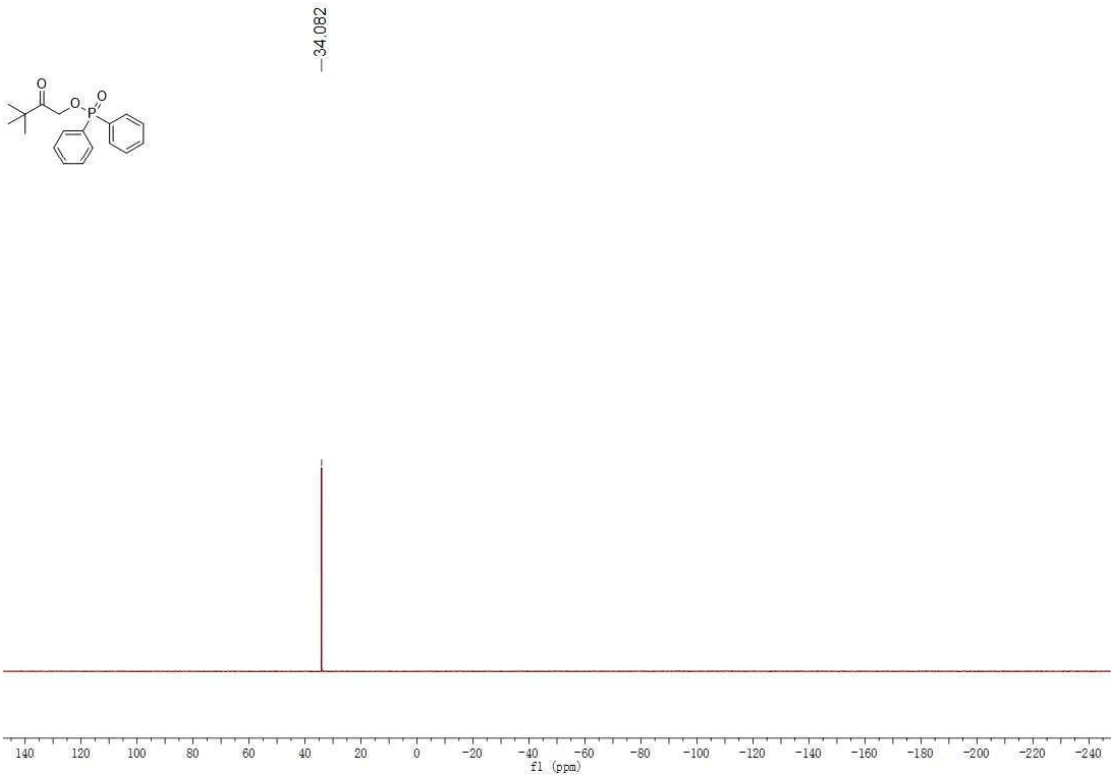
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **32**



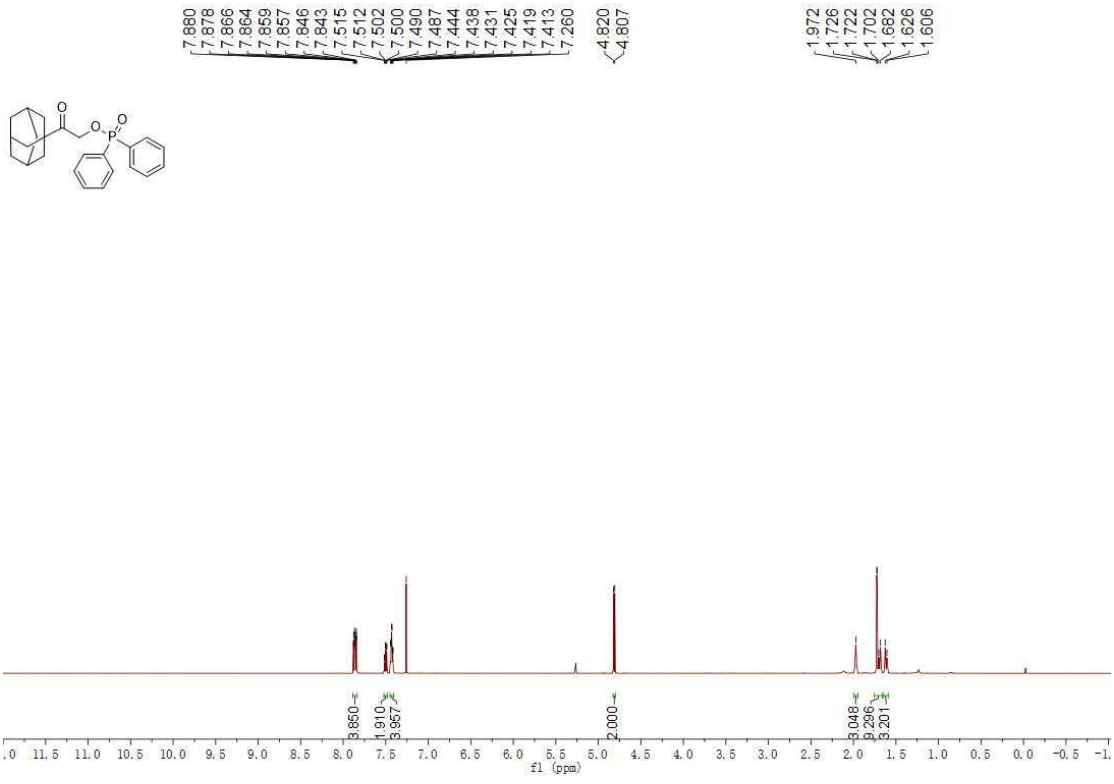
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **32**



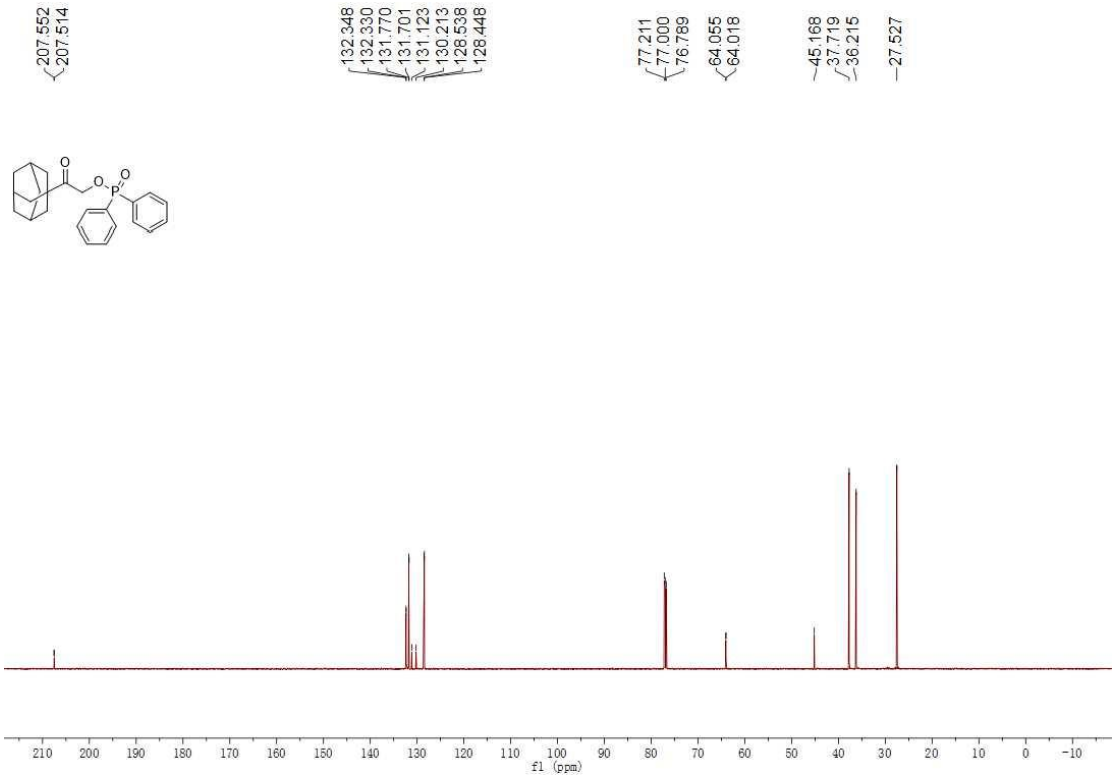
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **32**



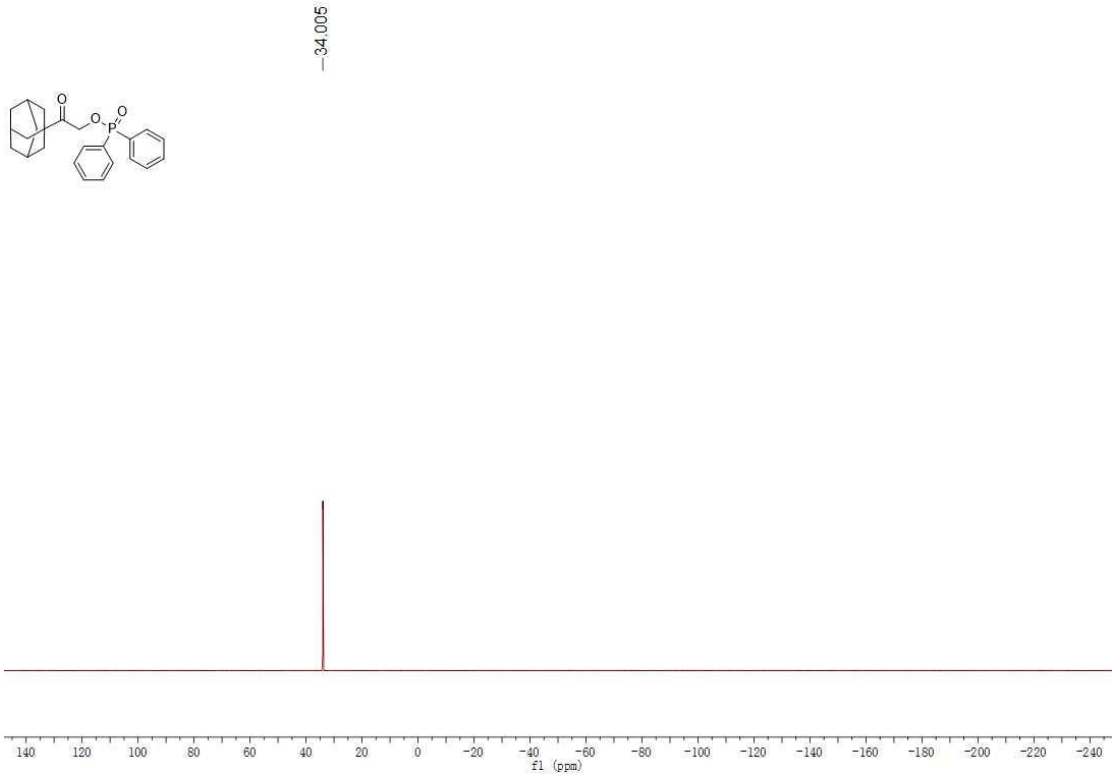
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **33**



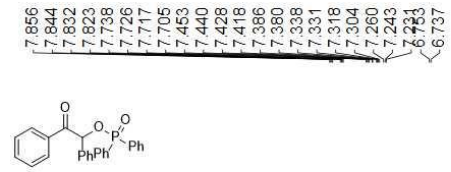
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **33**

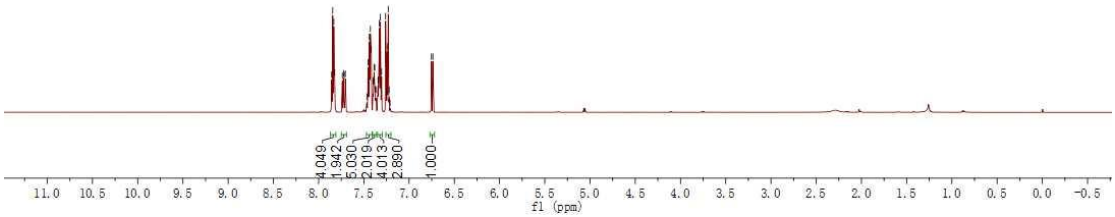


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **33**

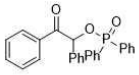


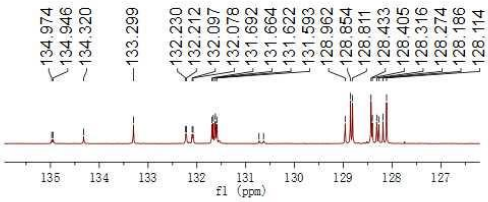
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **34**

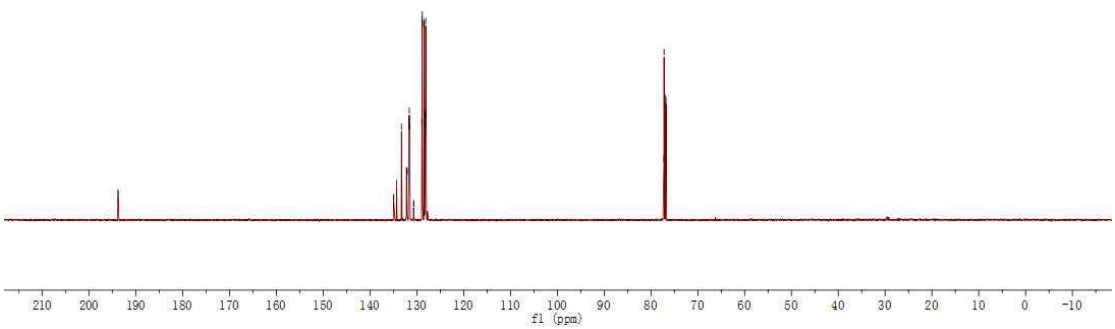




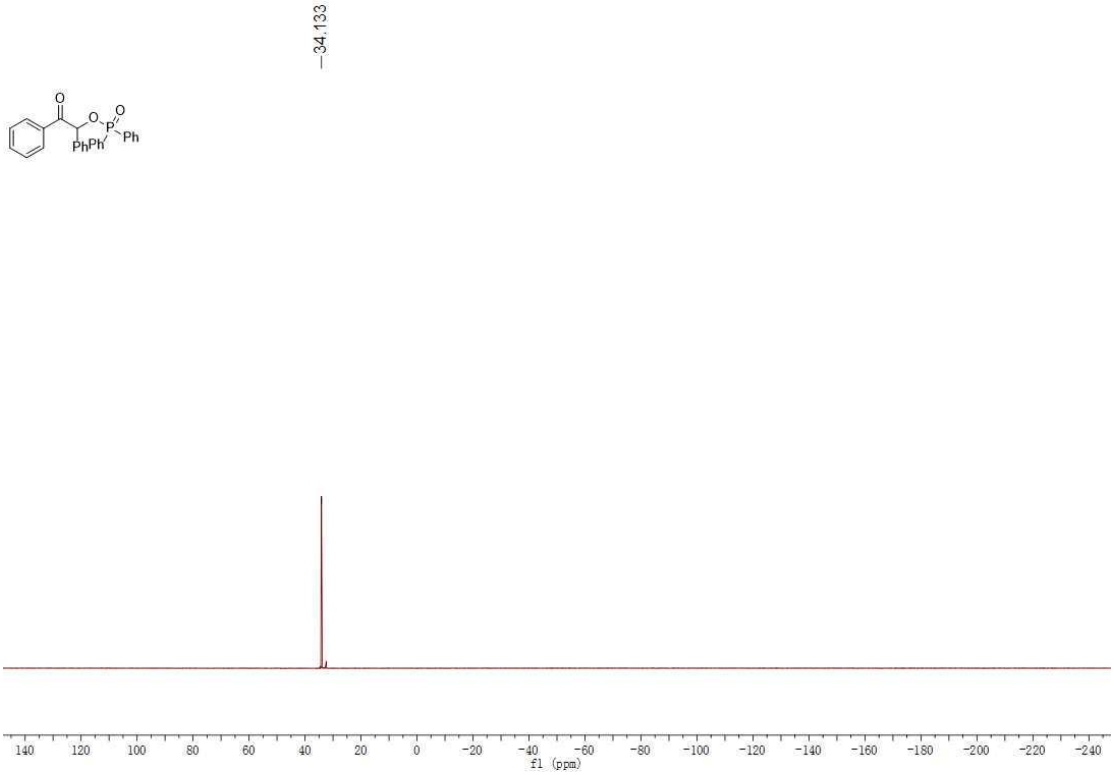
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **34**



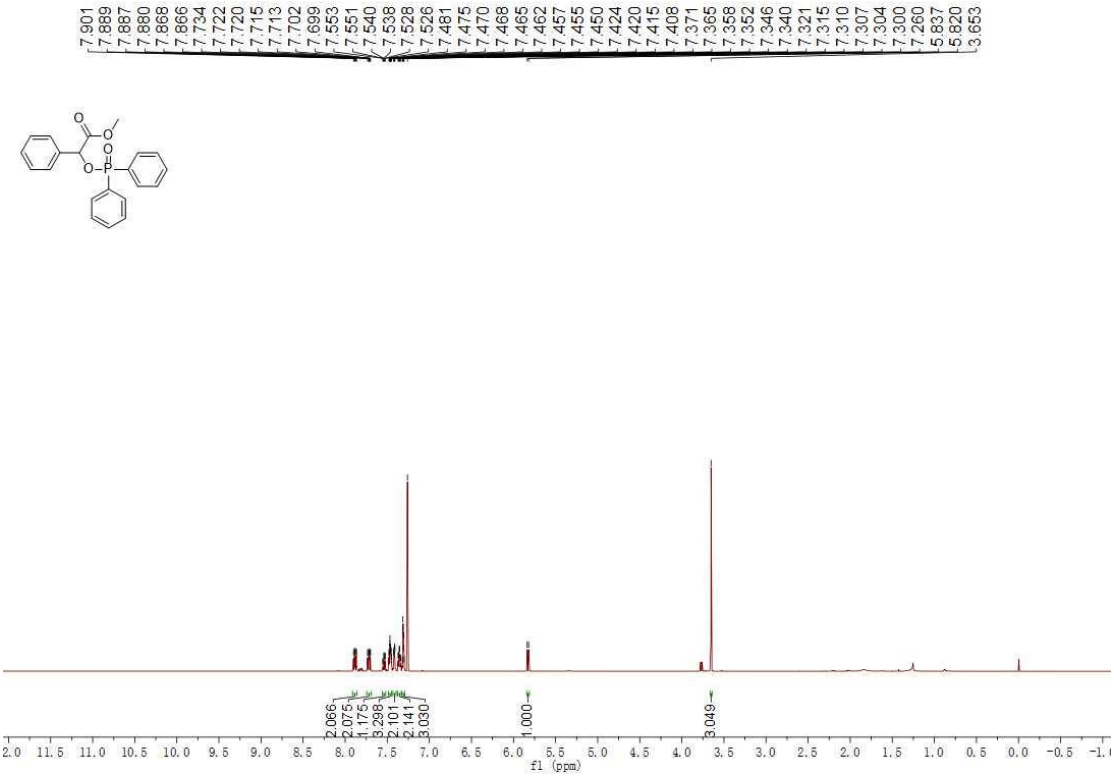




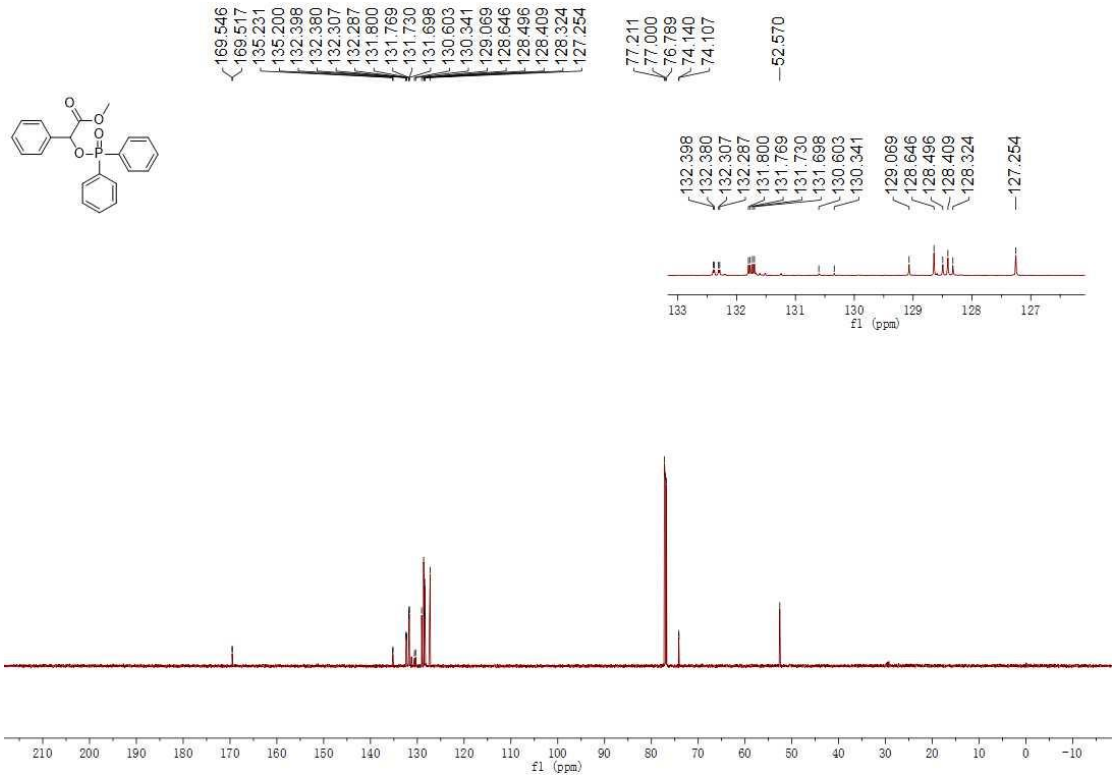
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **34**



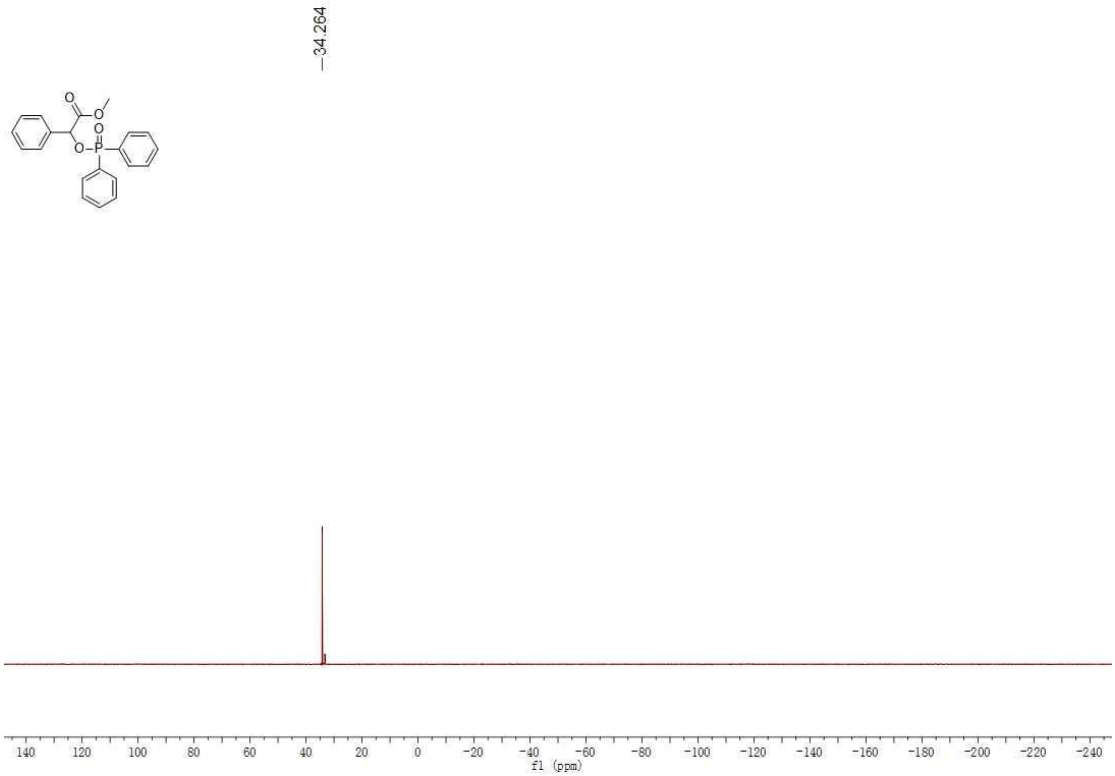
^{1}H NMR (600 MHz, $CDCl_3$) Spctrum of **35**



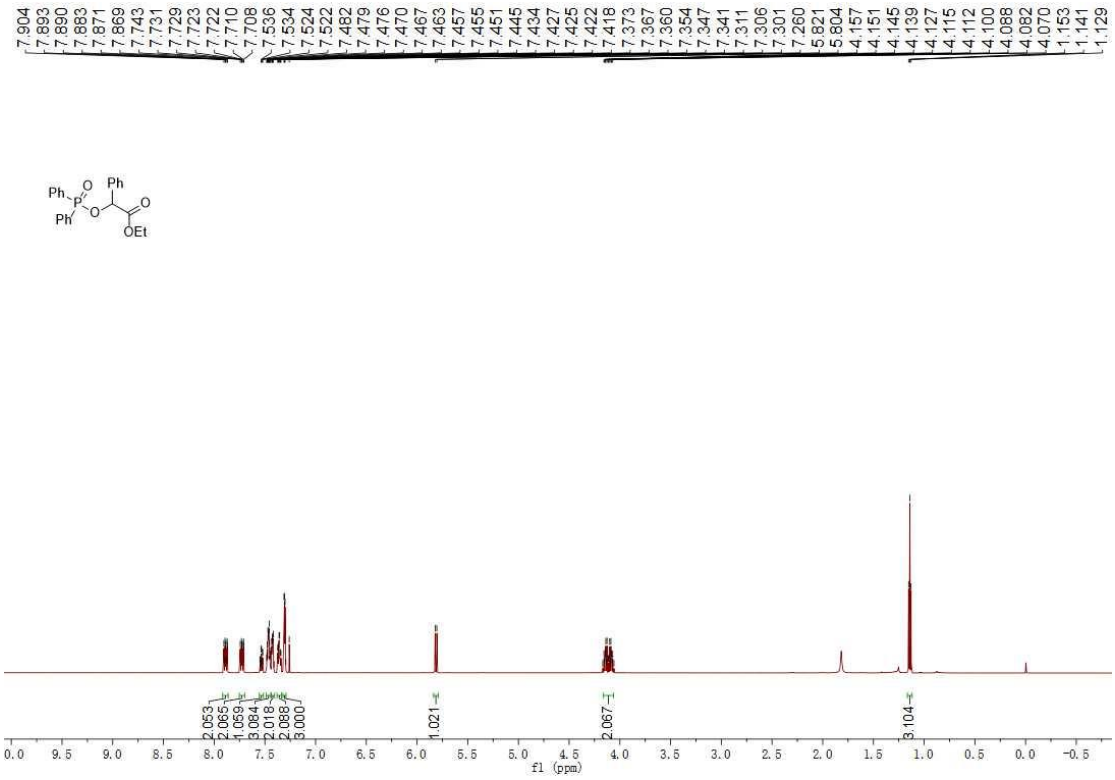
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **35**



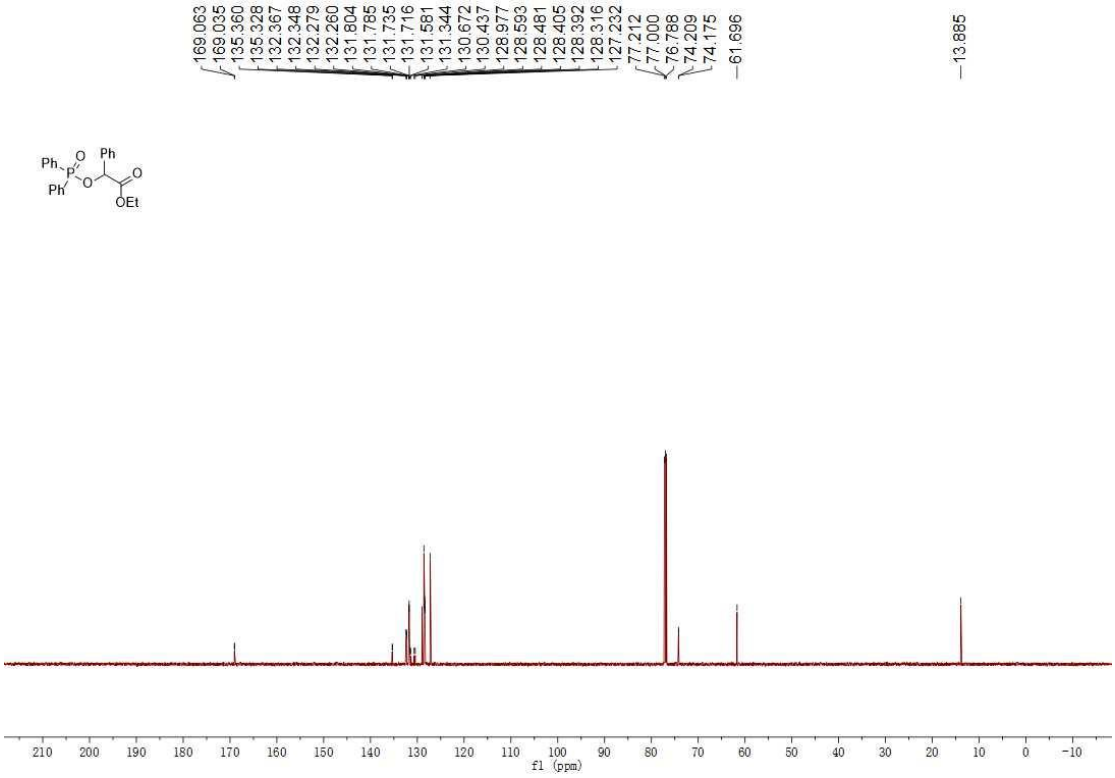
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **35**



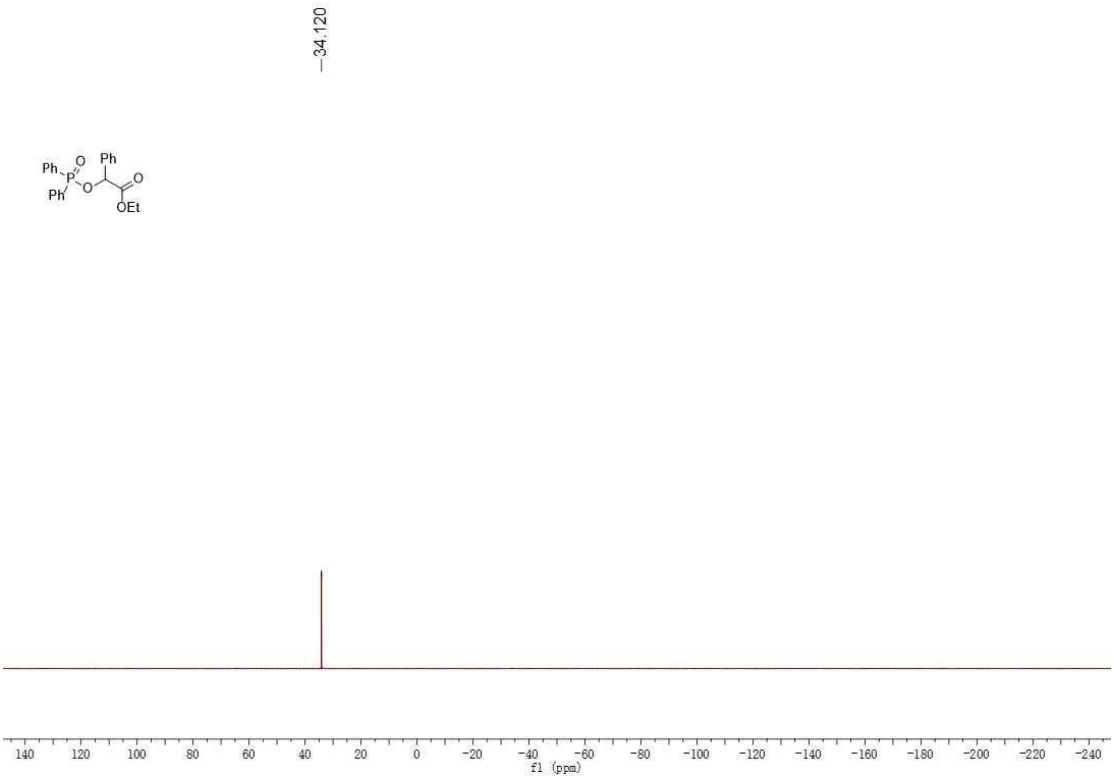
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **36**



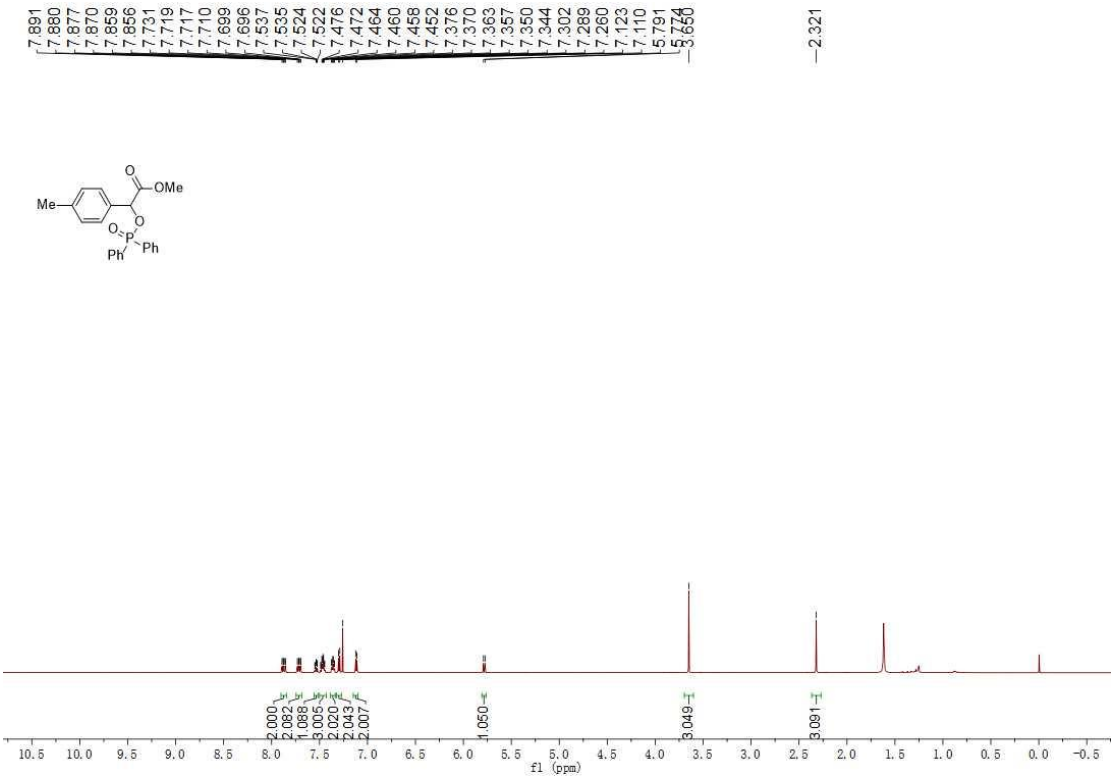
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **36**



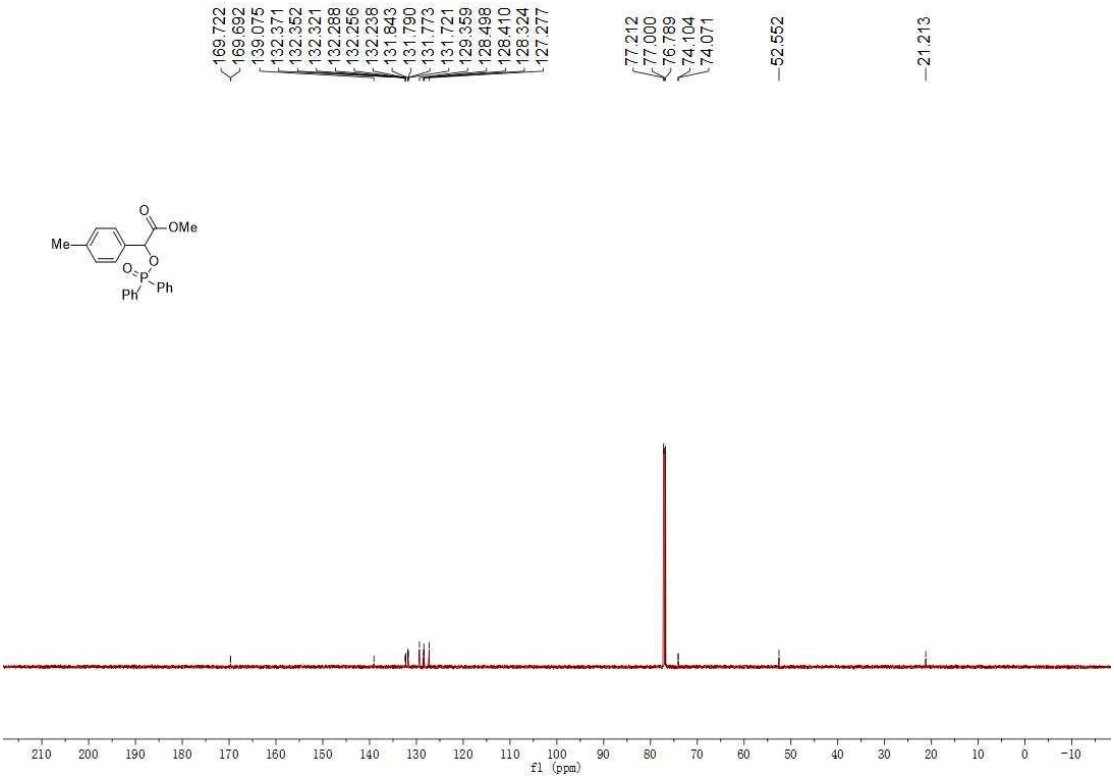
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **36**



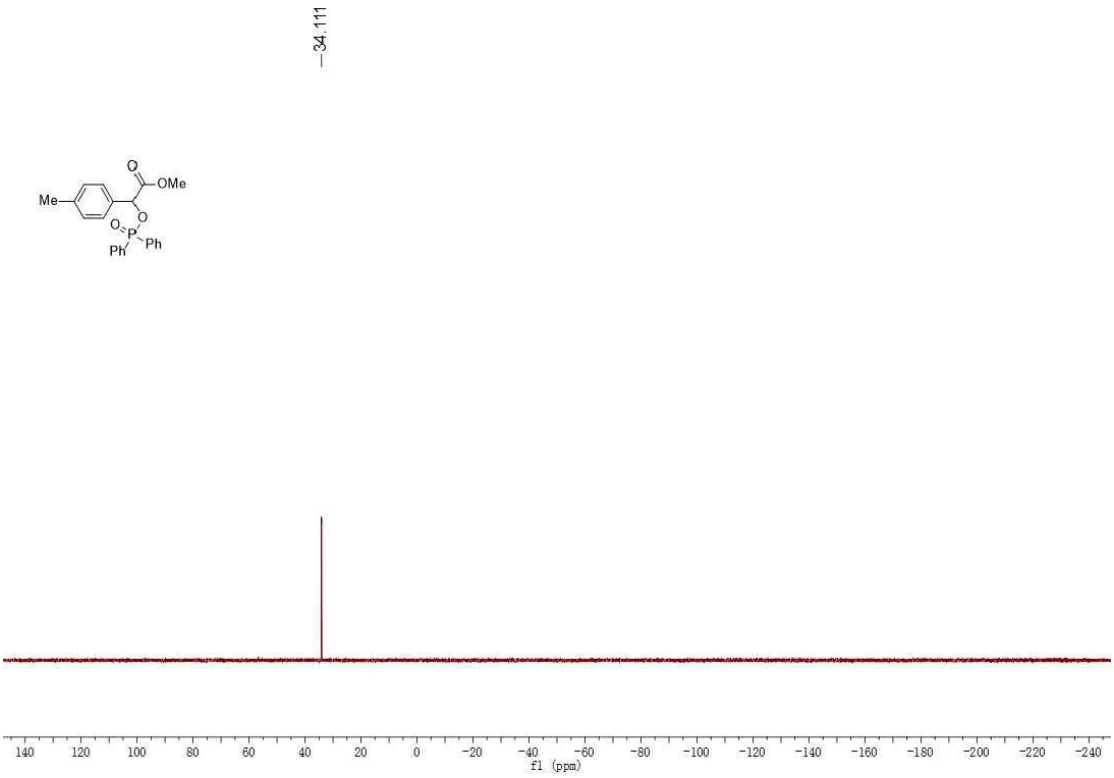
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **37**



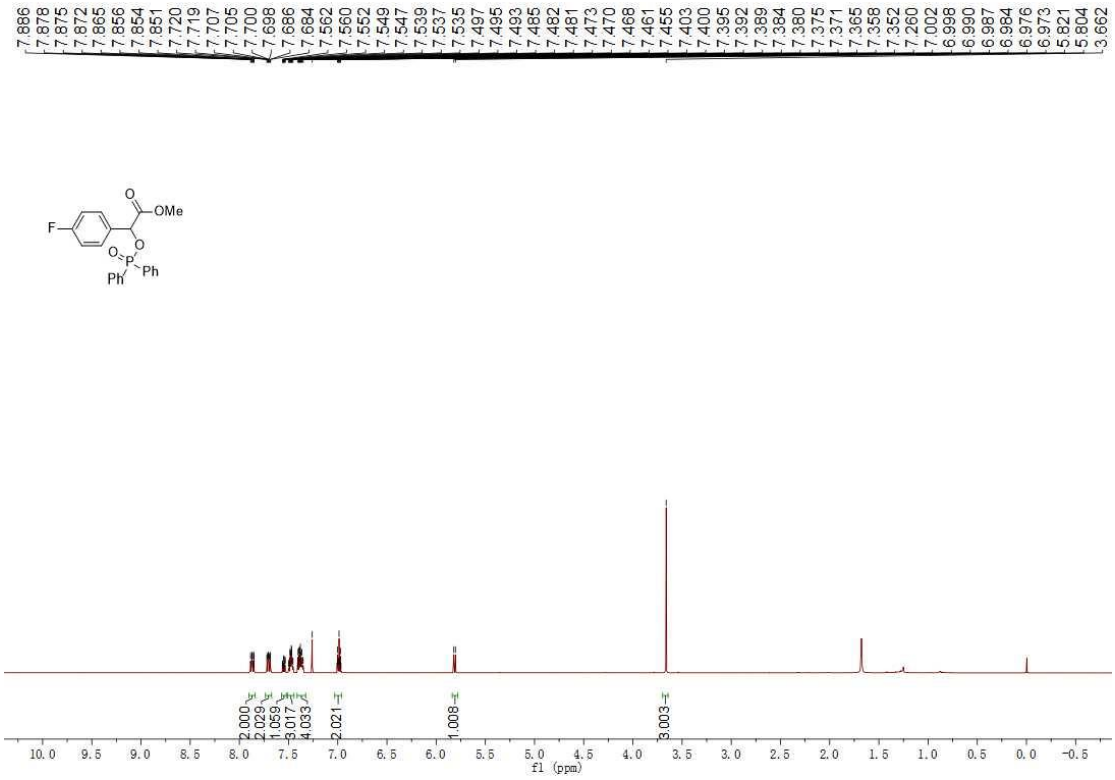
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **37**



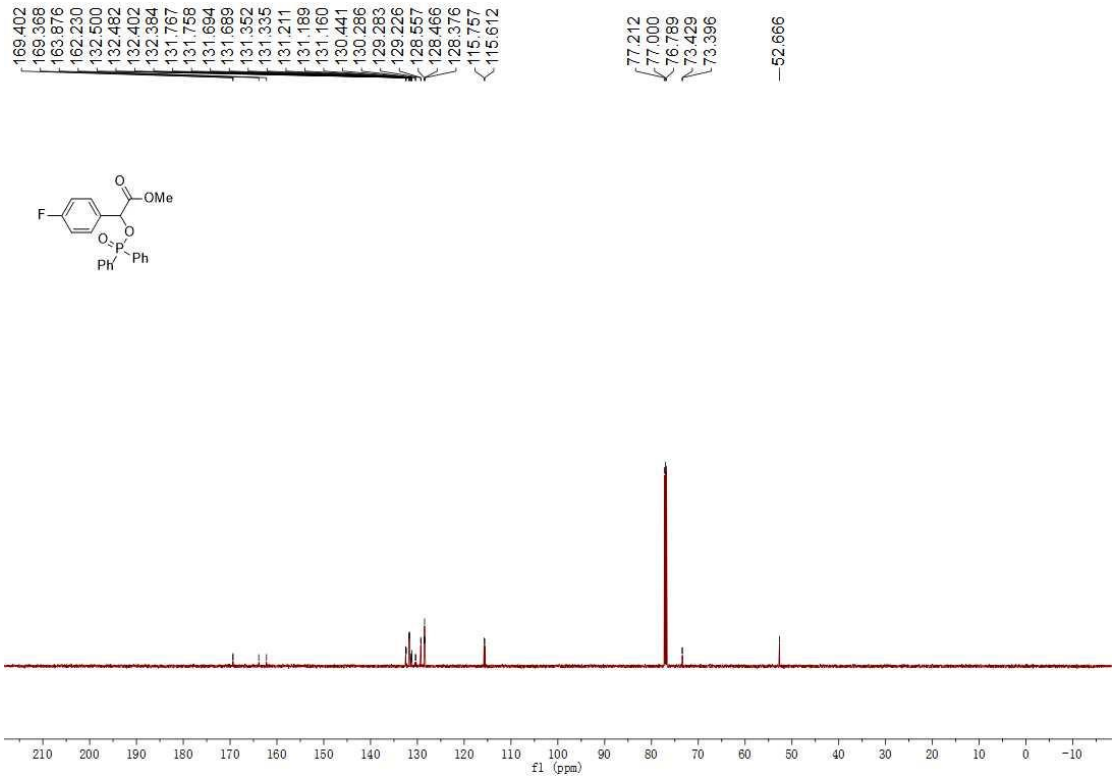
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **37**



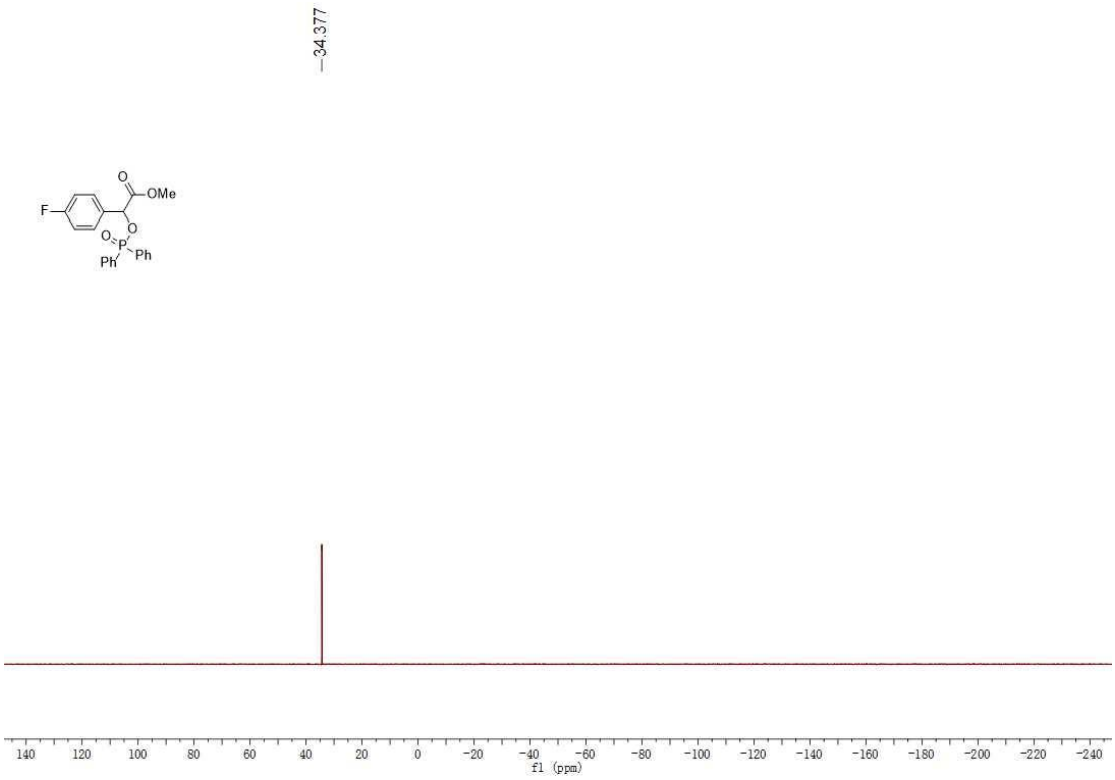
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **38**



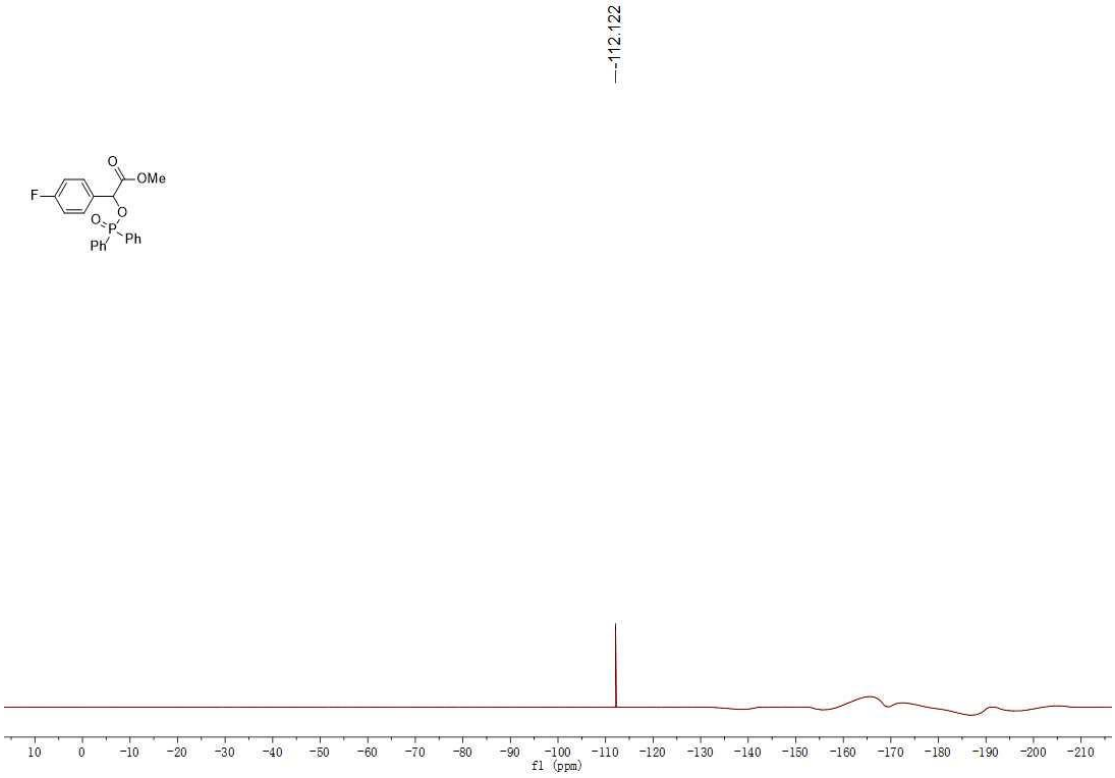
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **38**



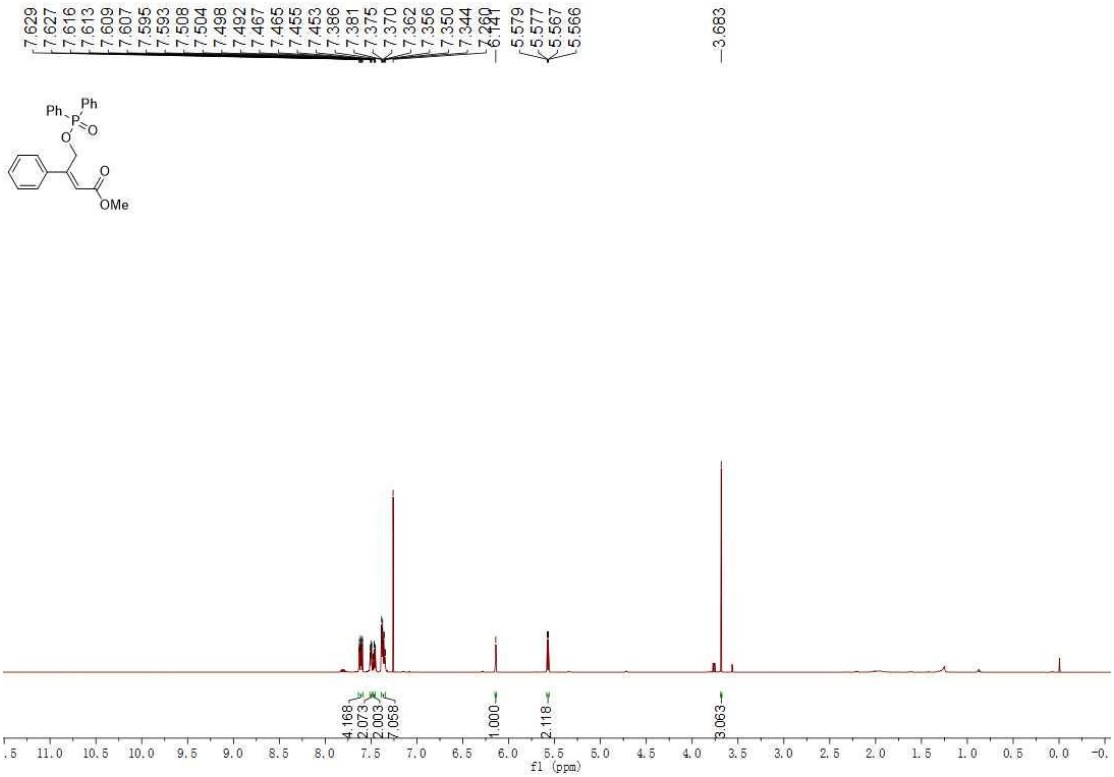
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **38**



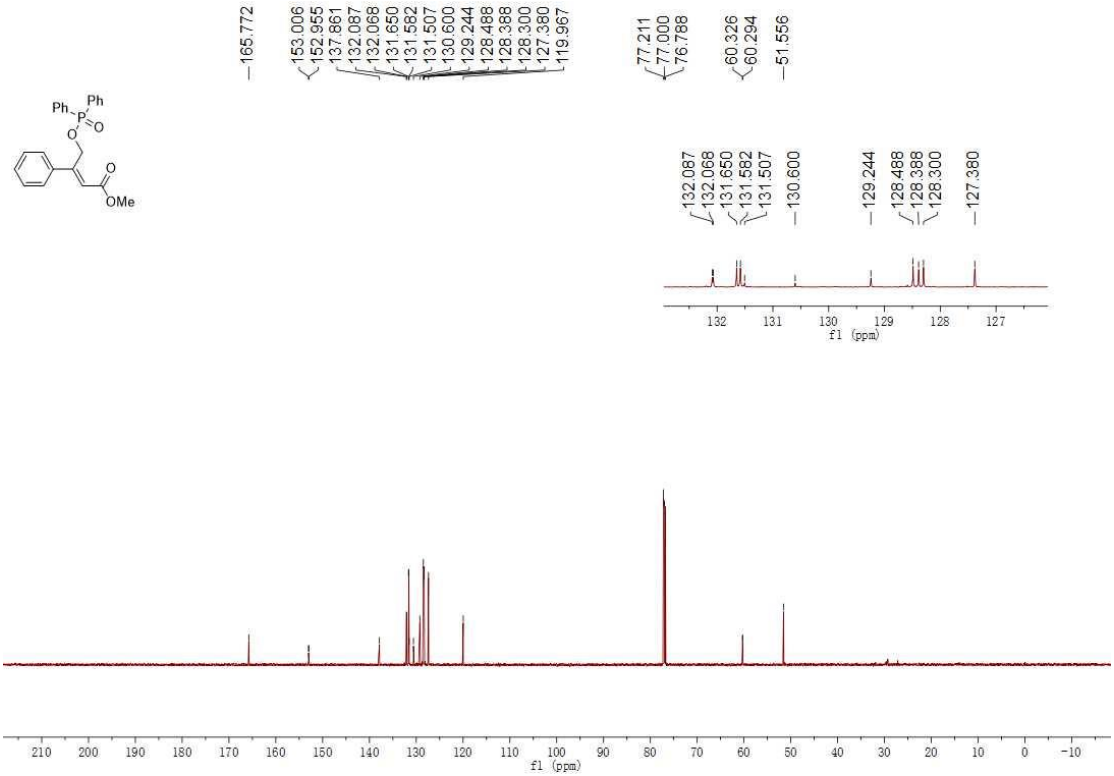
^{19}F NMR (564 MHz, $CDCl_3$) Spectrum of **38**



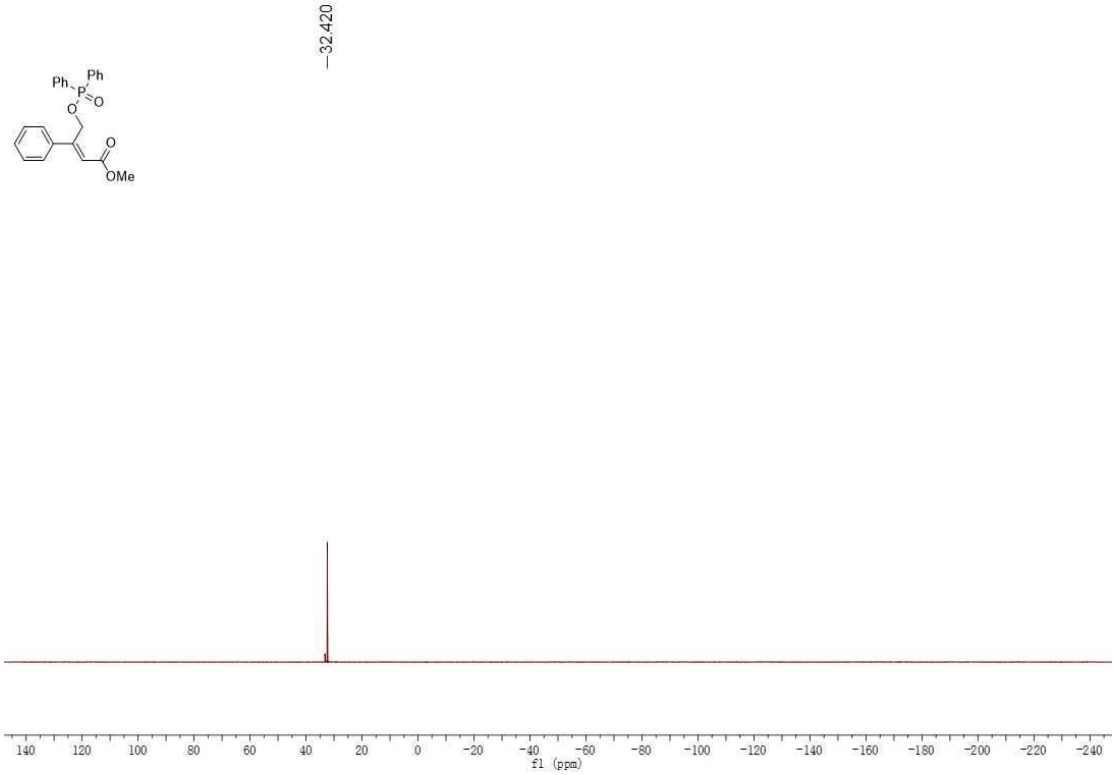
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **39**



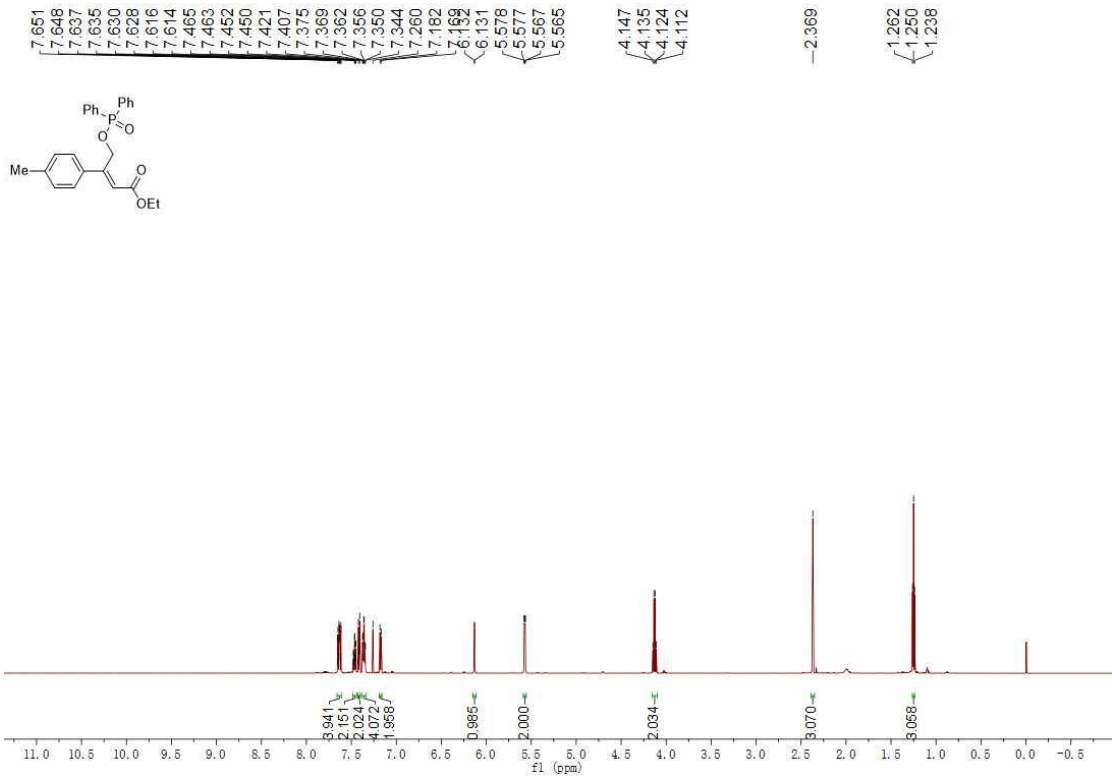
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **39**



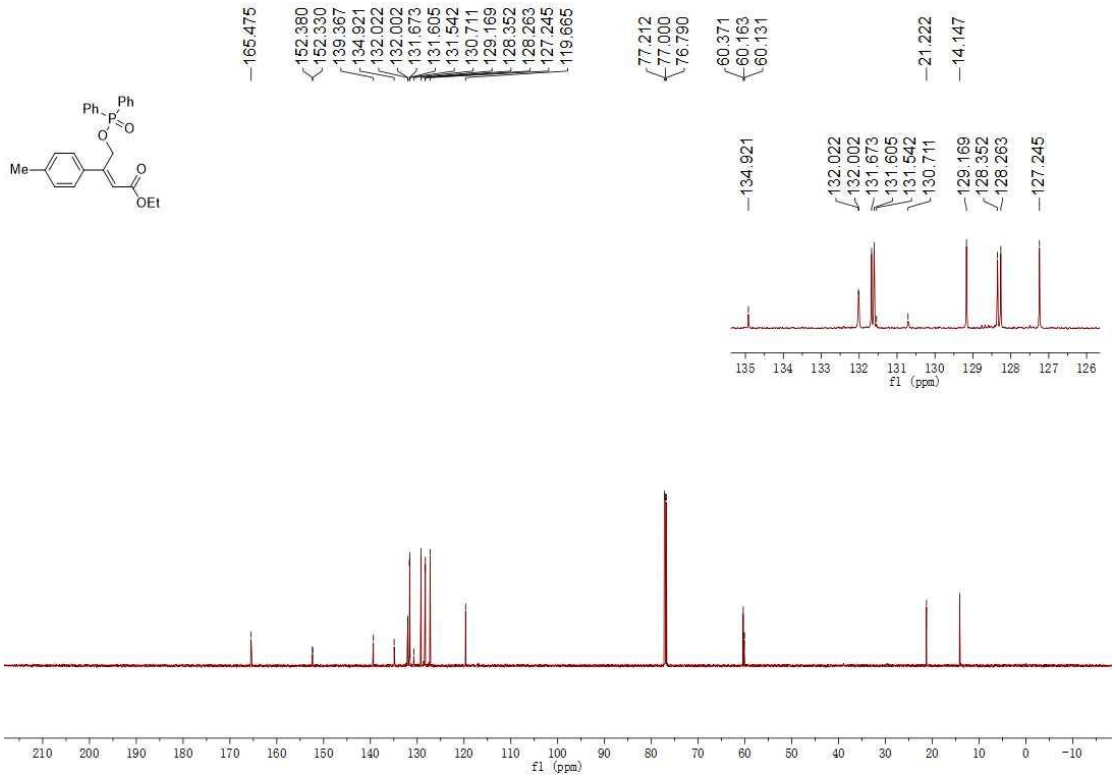
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **39**



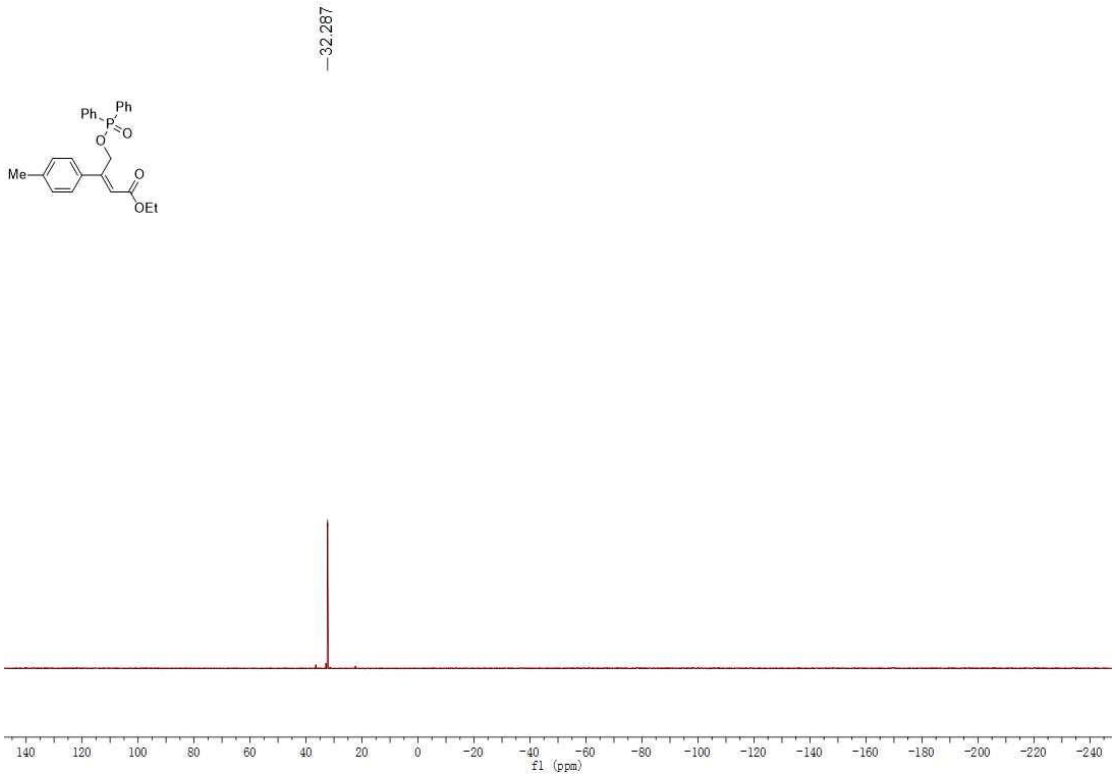
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **40**



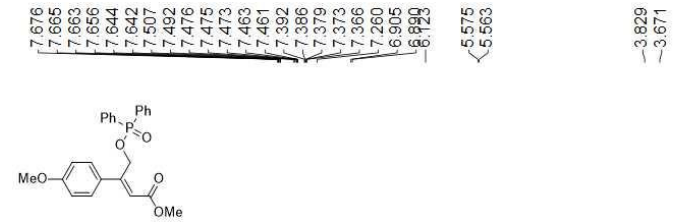
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **40**

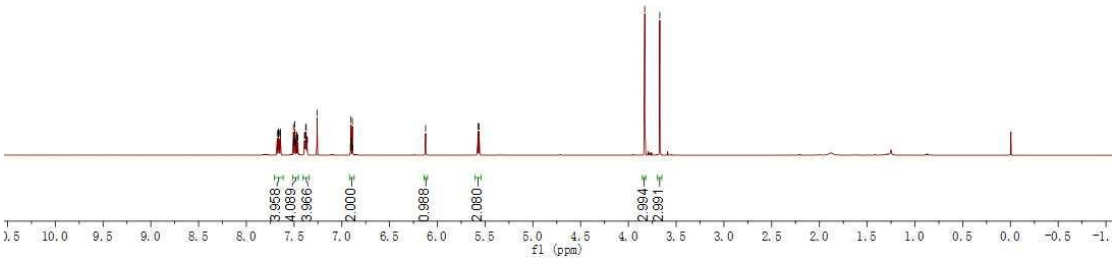


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **40**

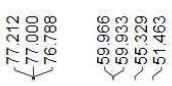


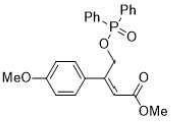
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **41**

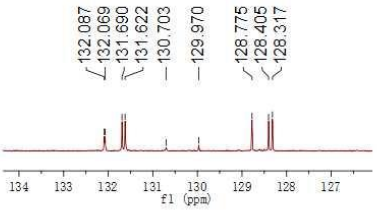


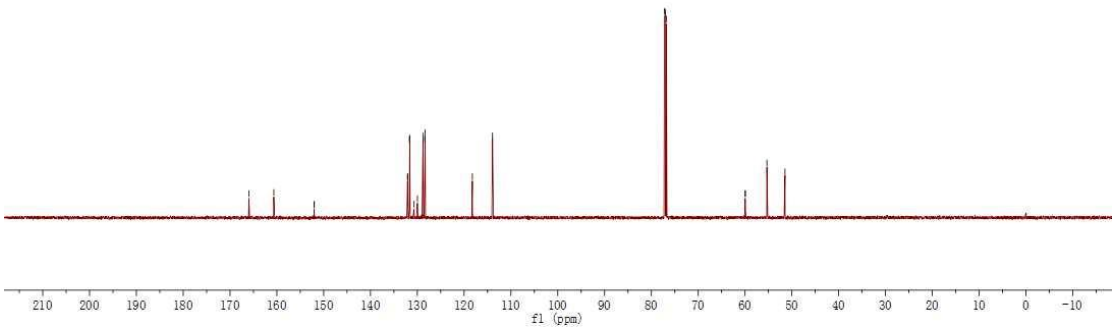


^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **41**

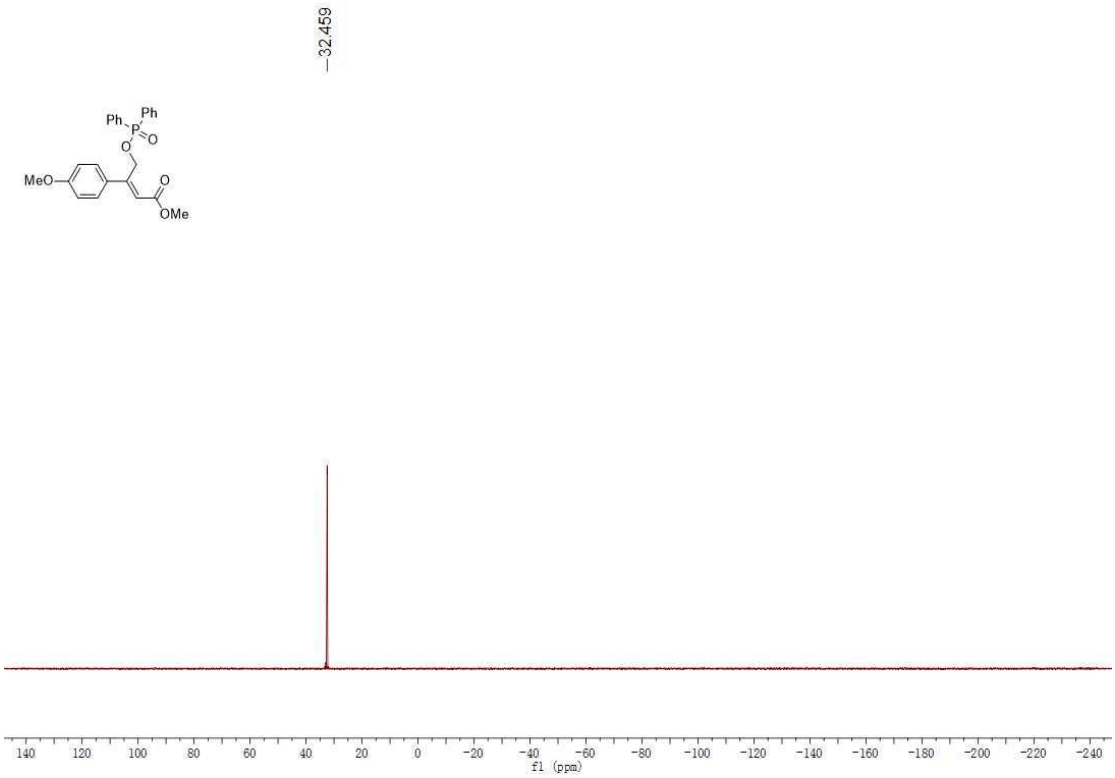




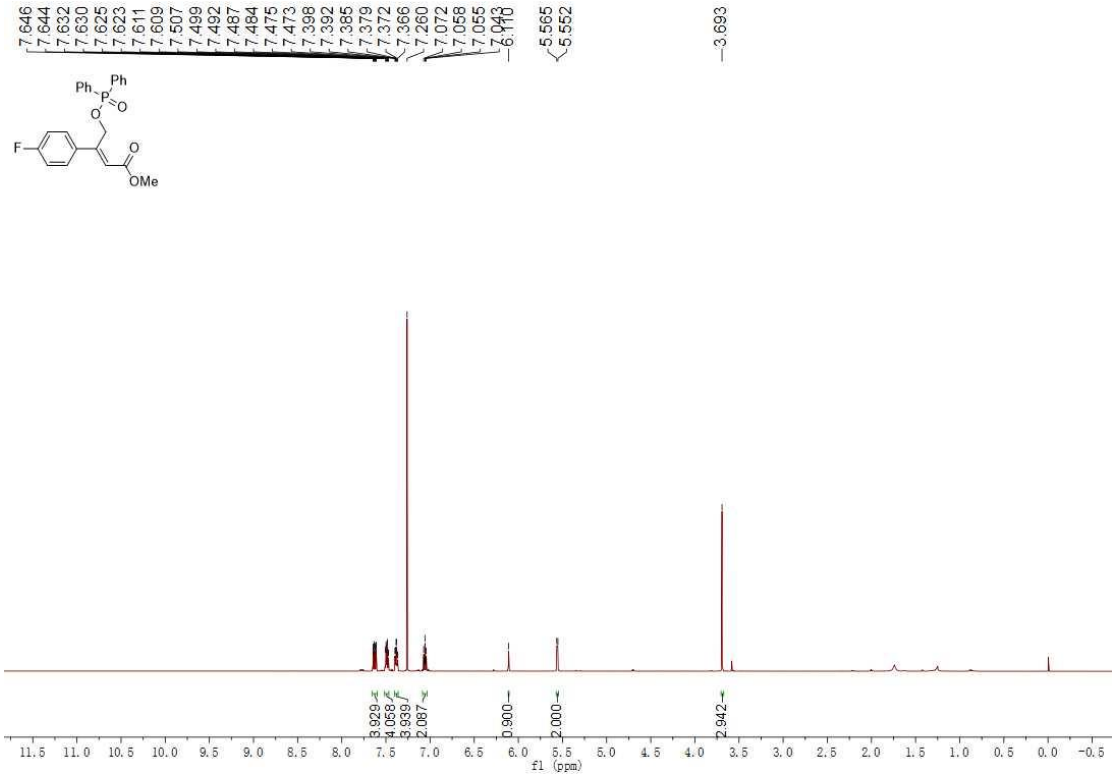




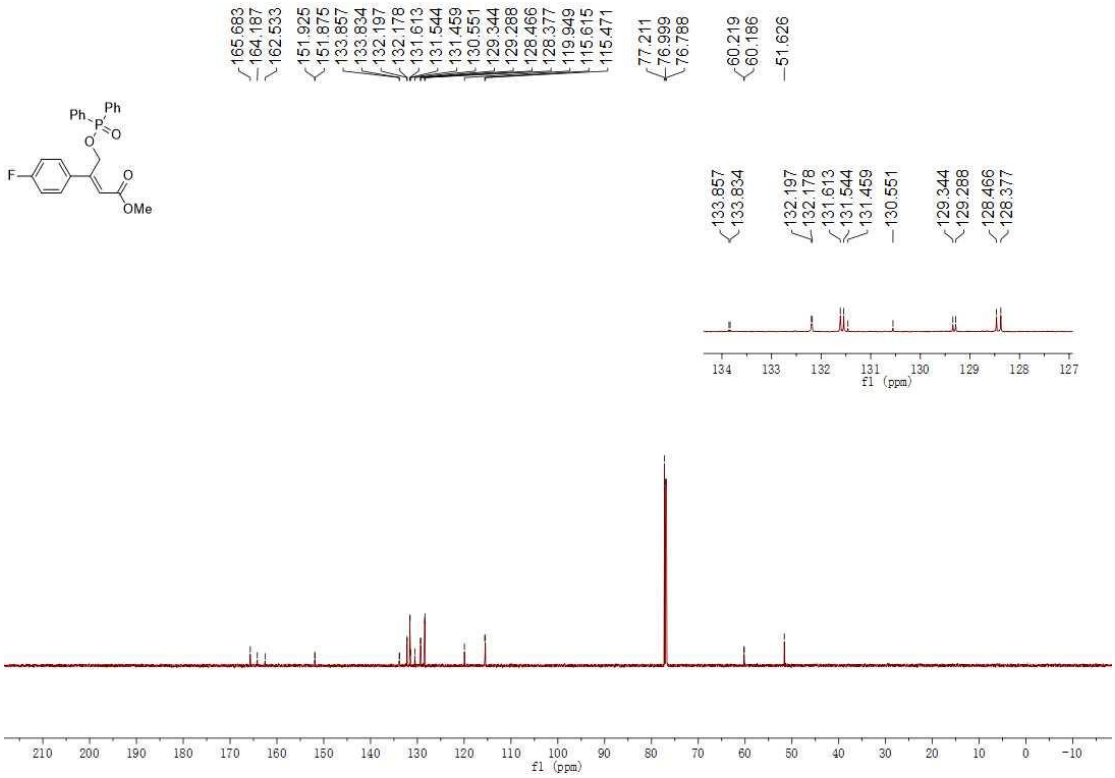
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **41**



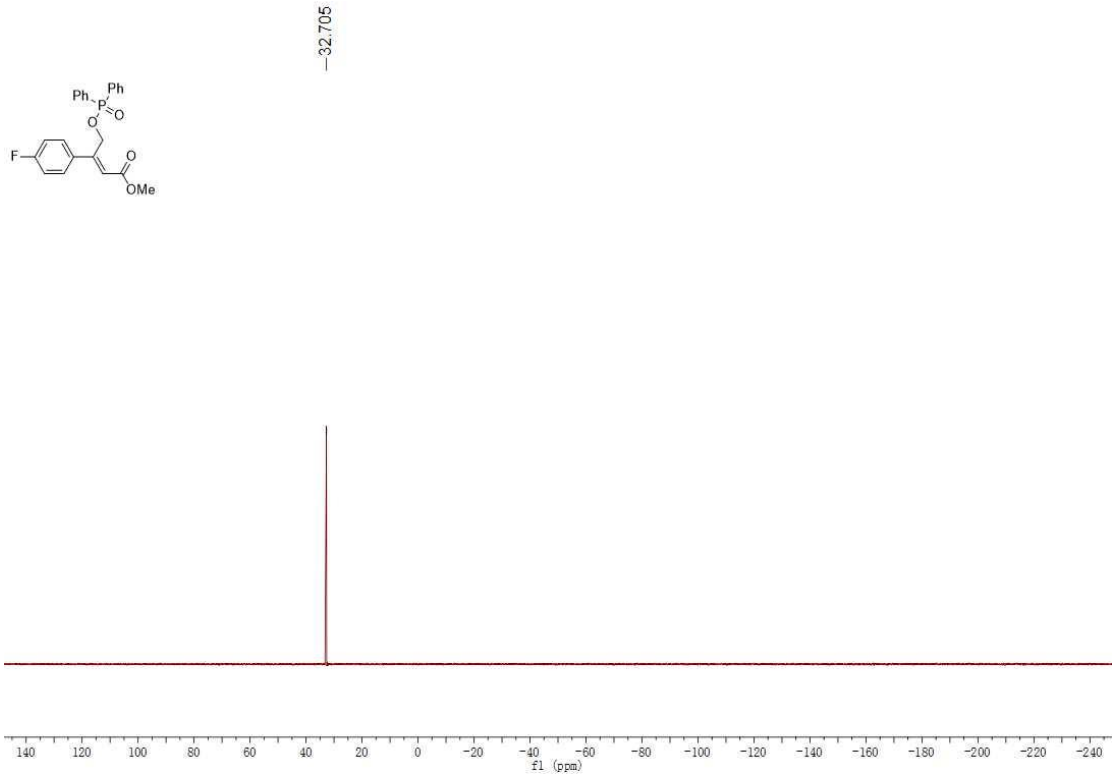
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **42**



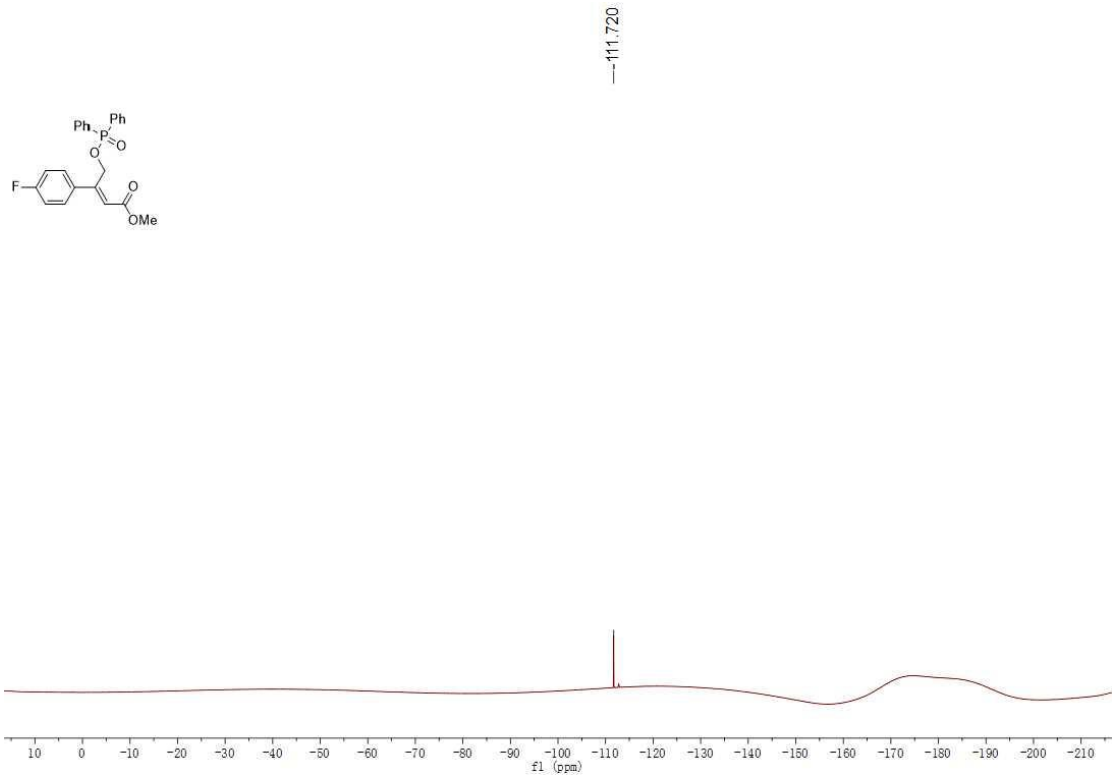
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **42**



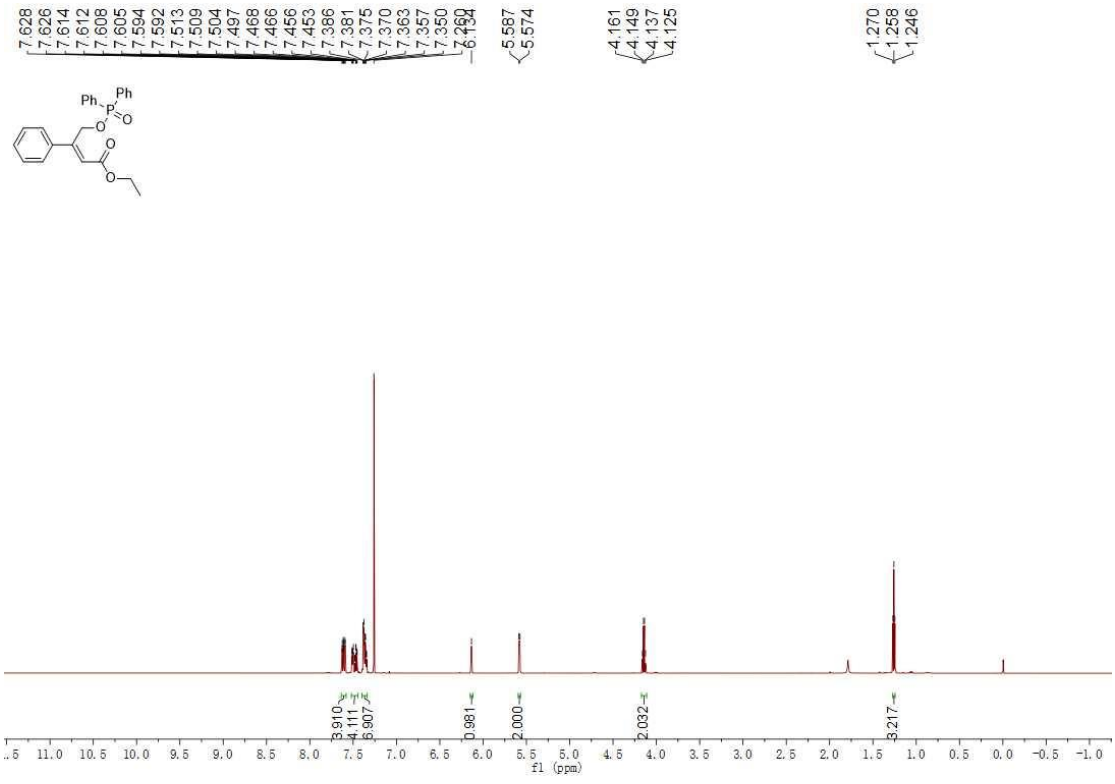
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **42**



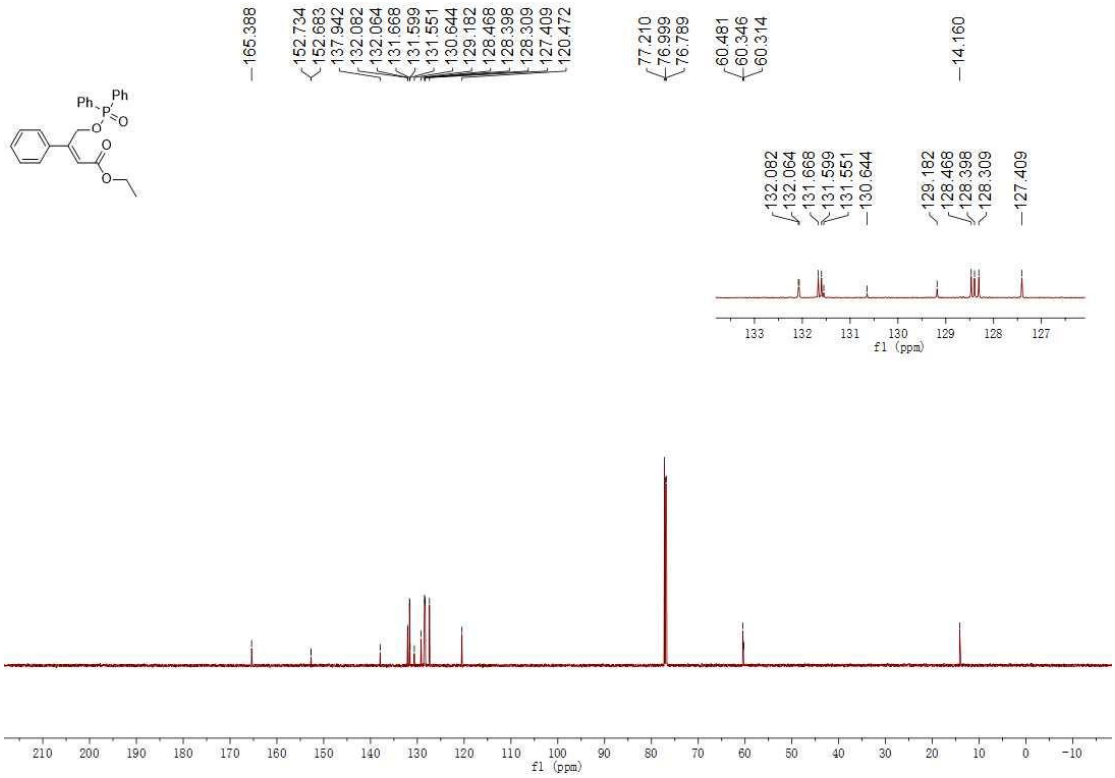
^{19}F NMR (564 MHz, $CDCl_3$) Spectrum of **42**



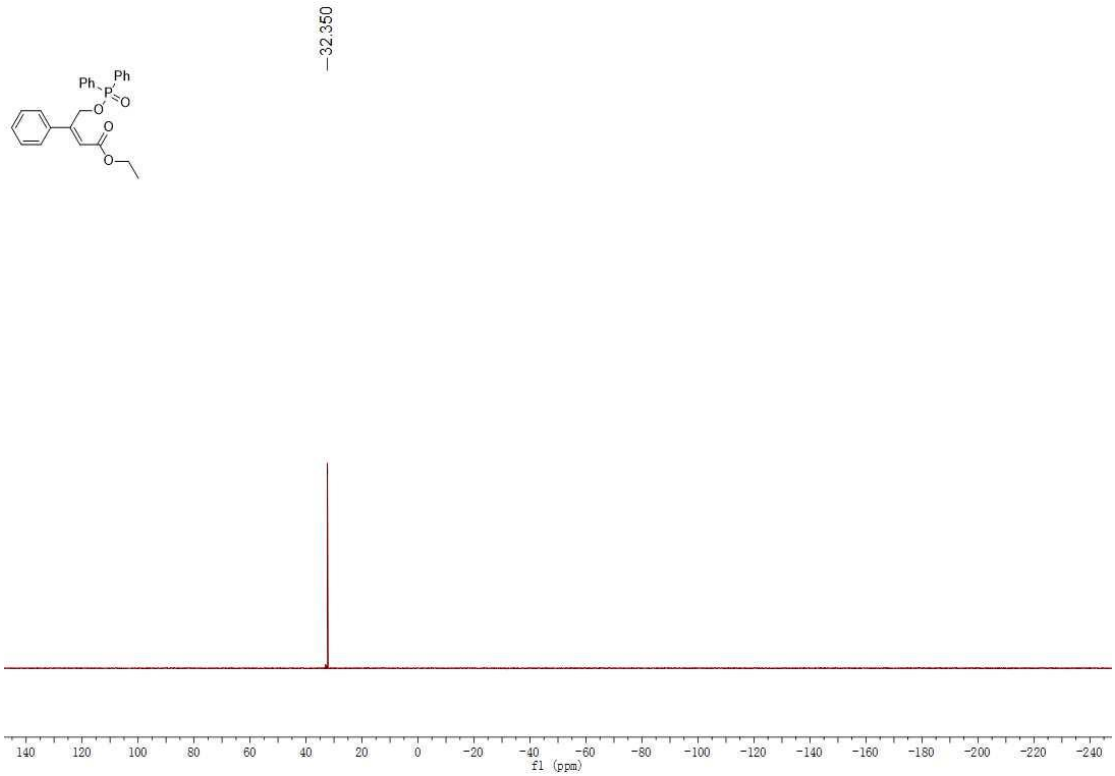
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **43**



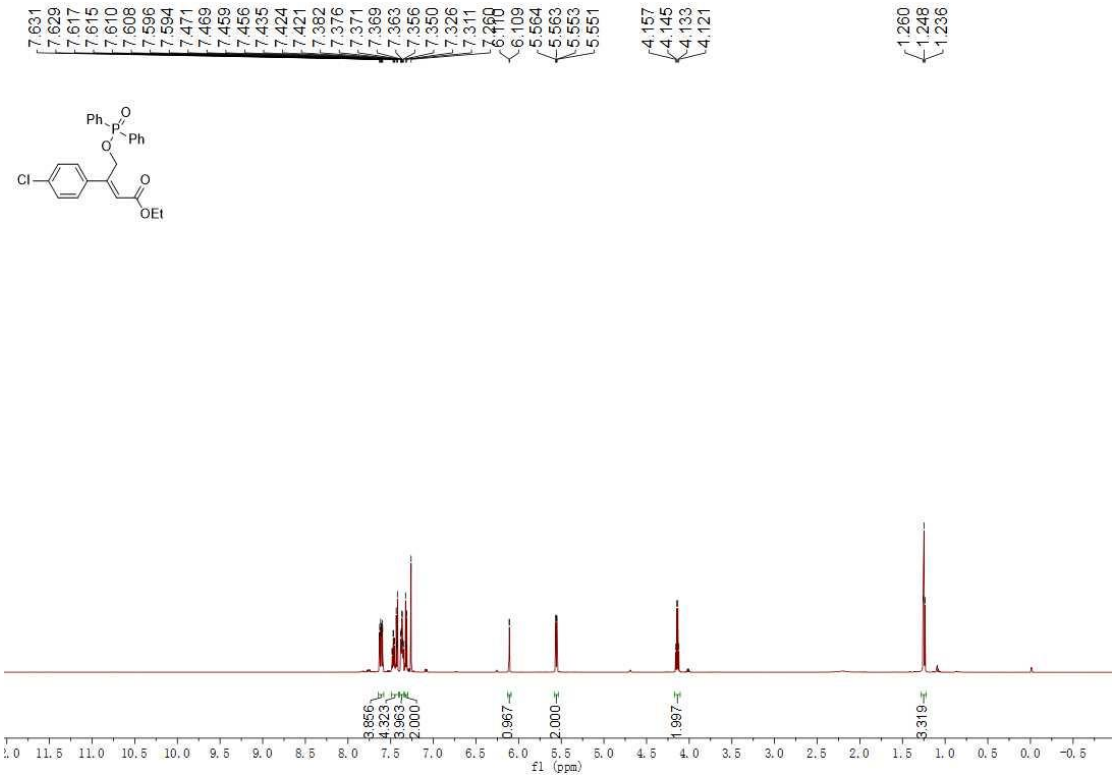
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **43**



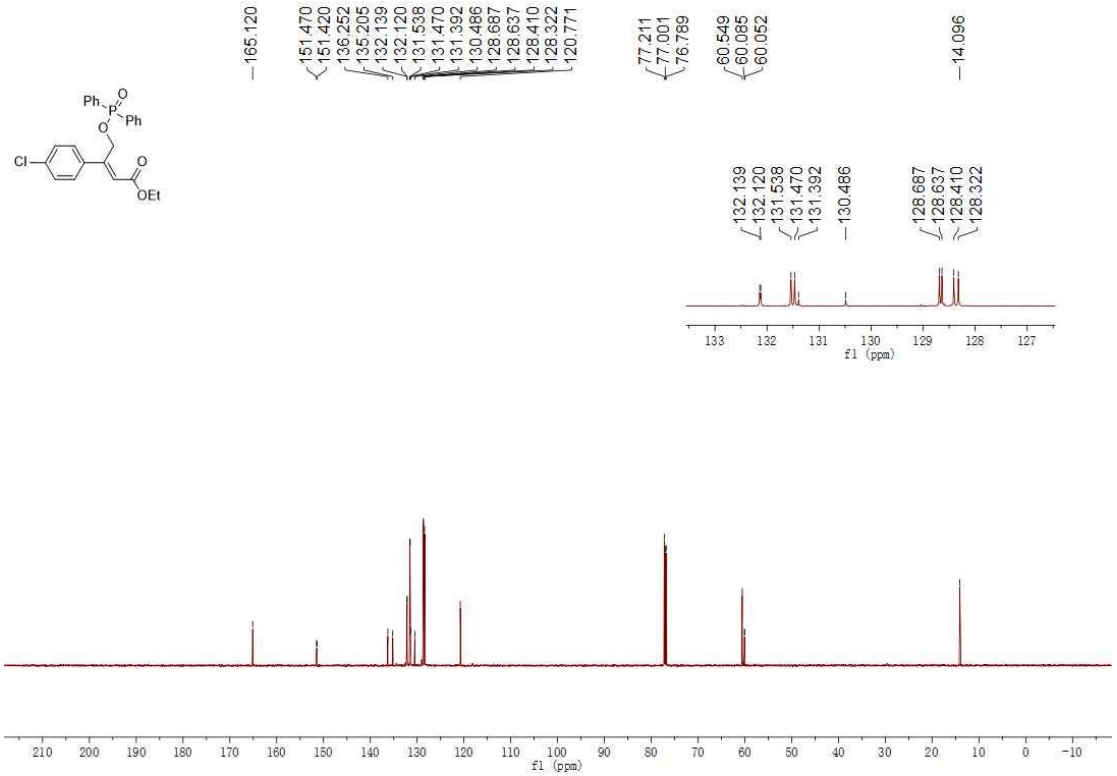
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **43**



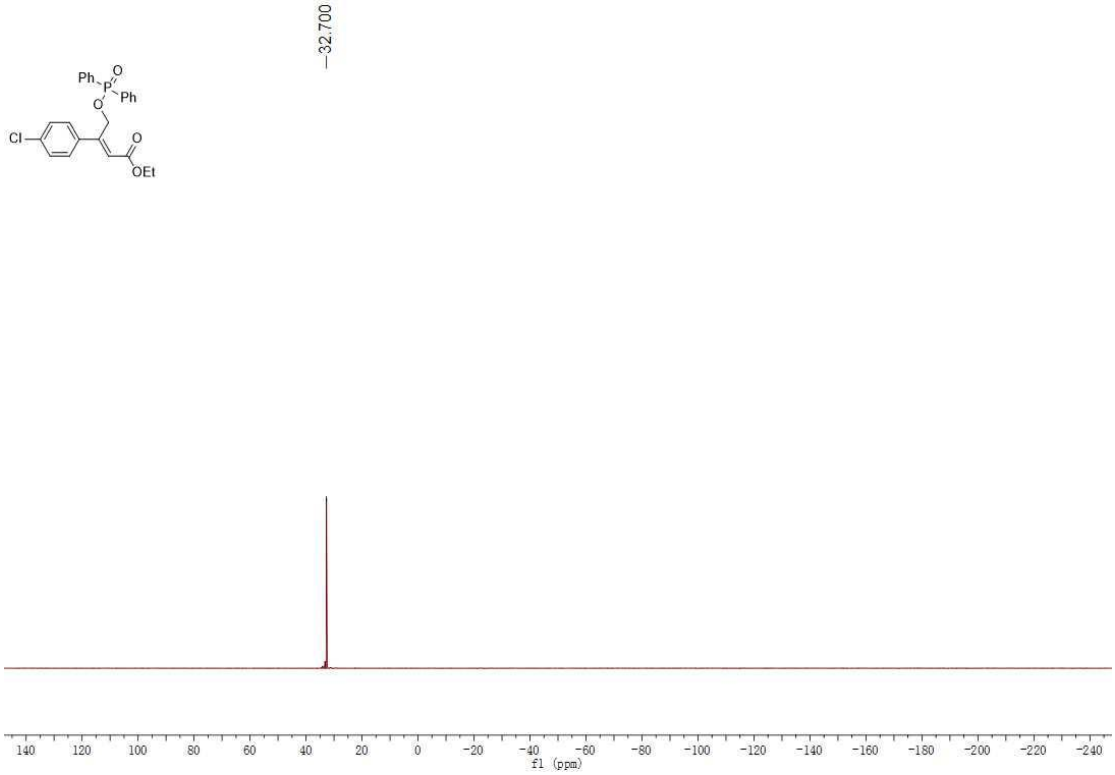
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **44**



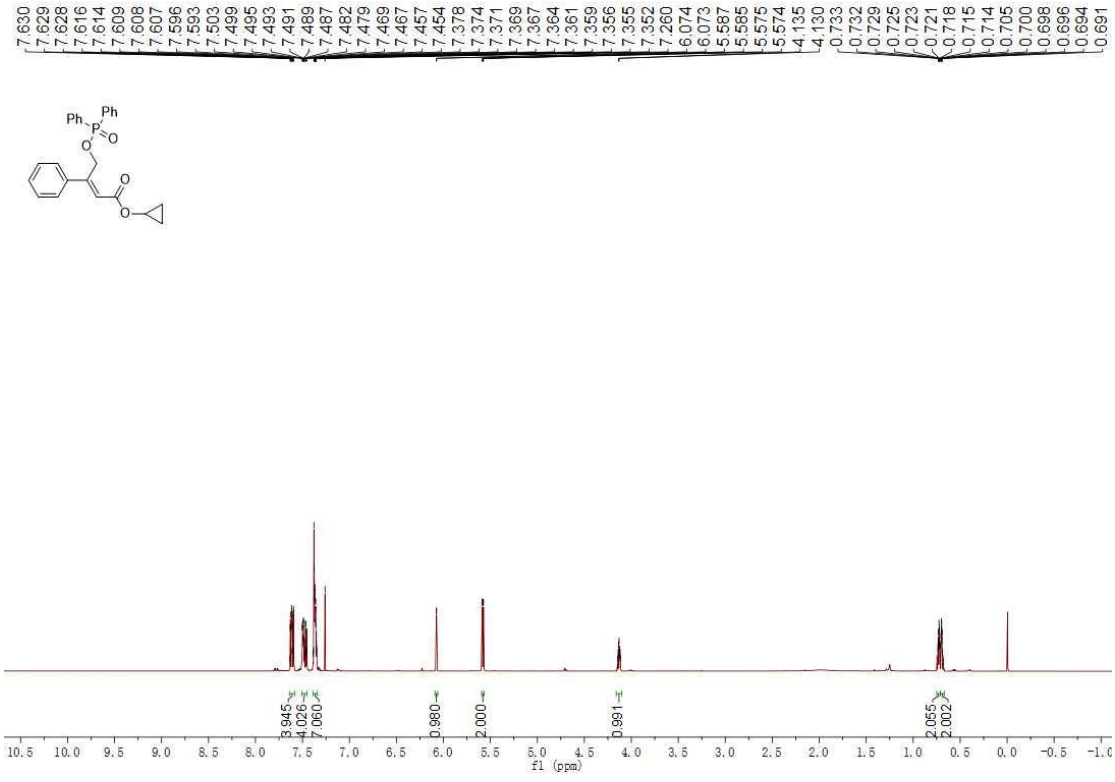
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **44**



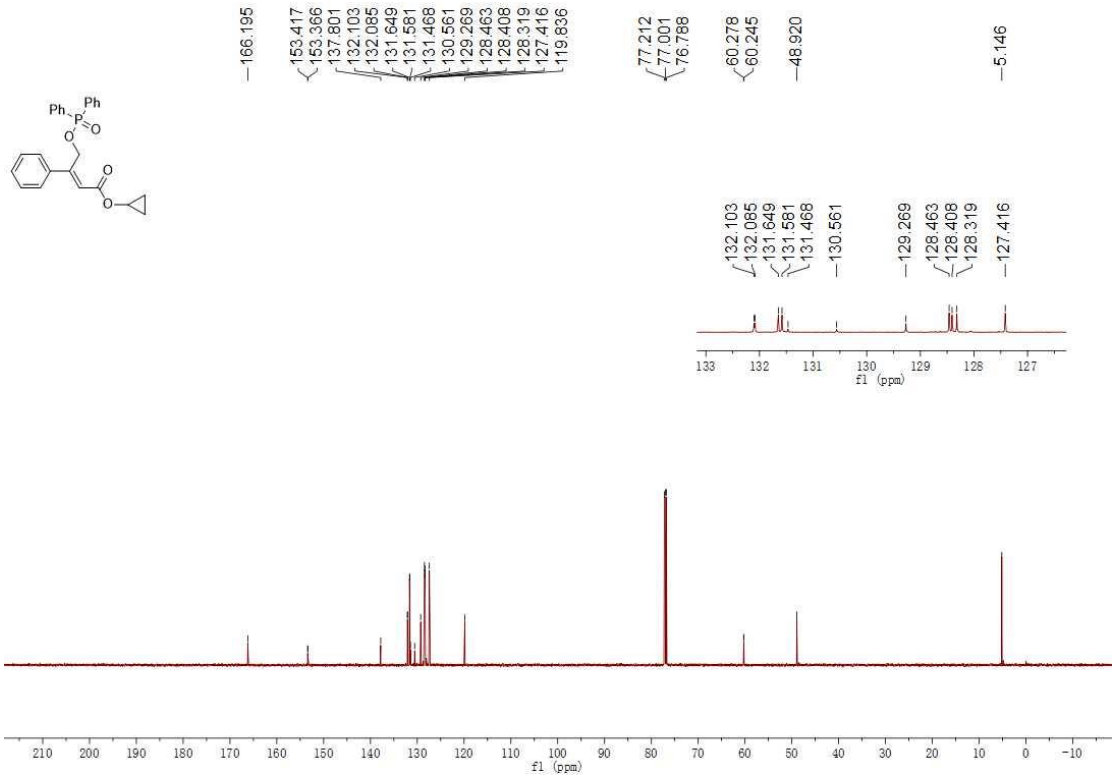
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **44**



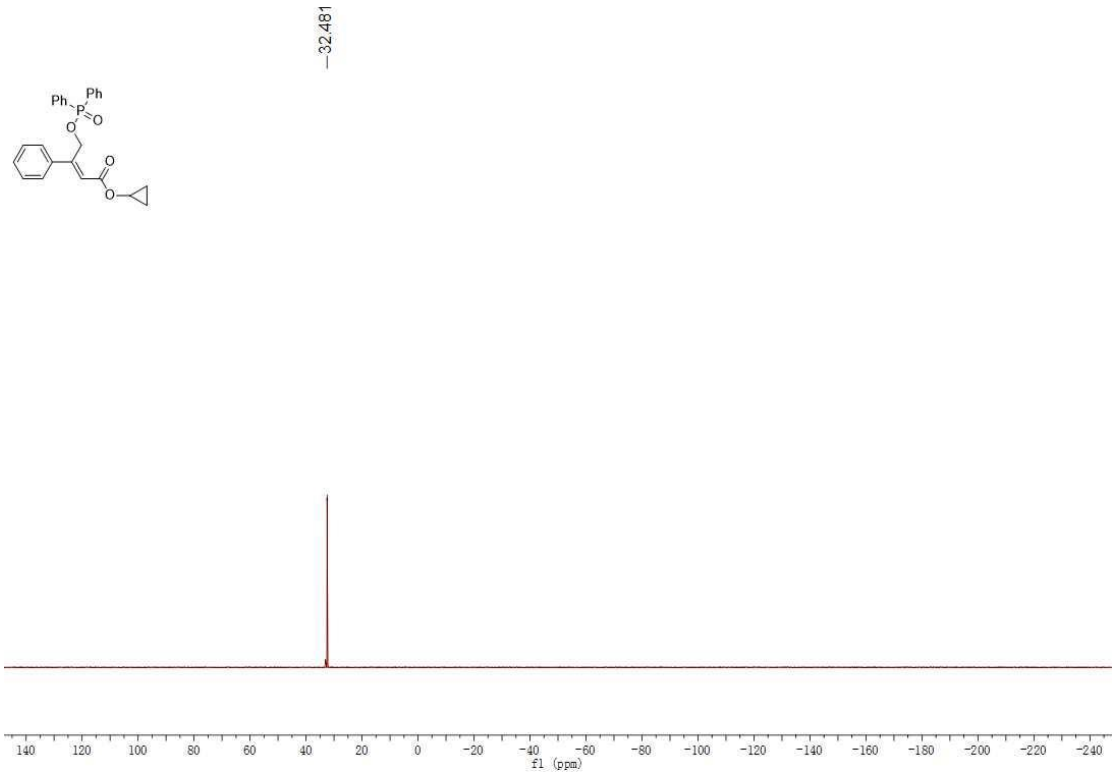
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **45**



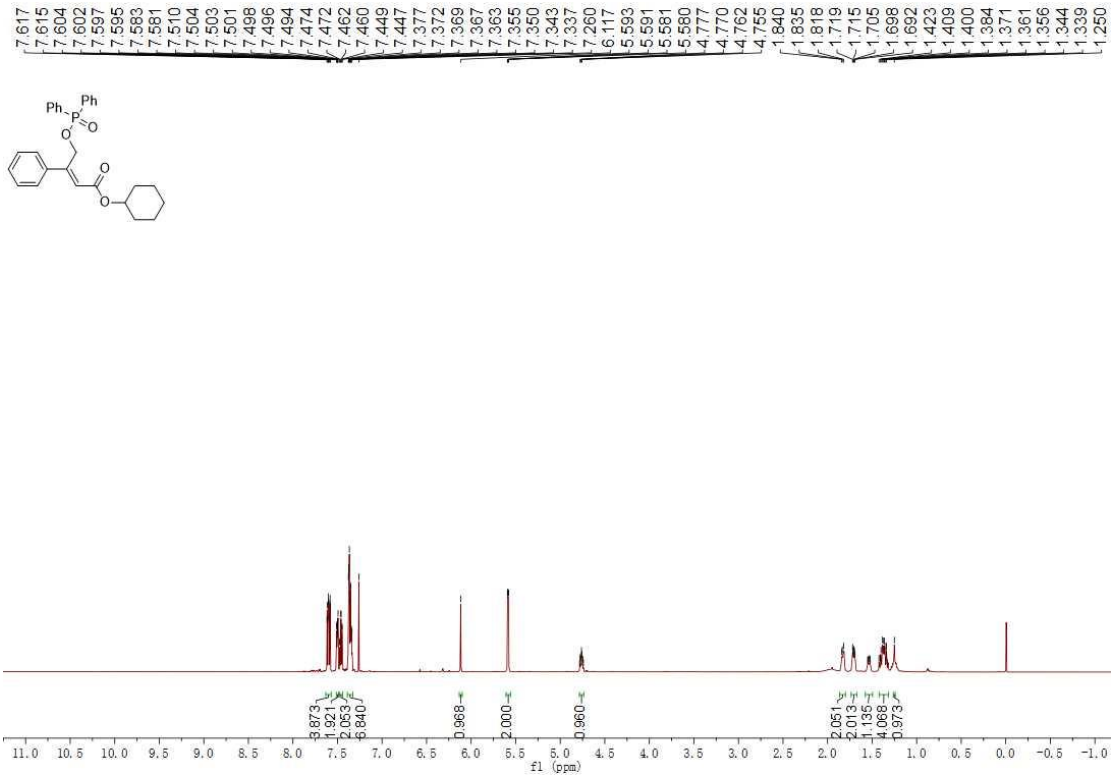
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **45**



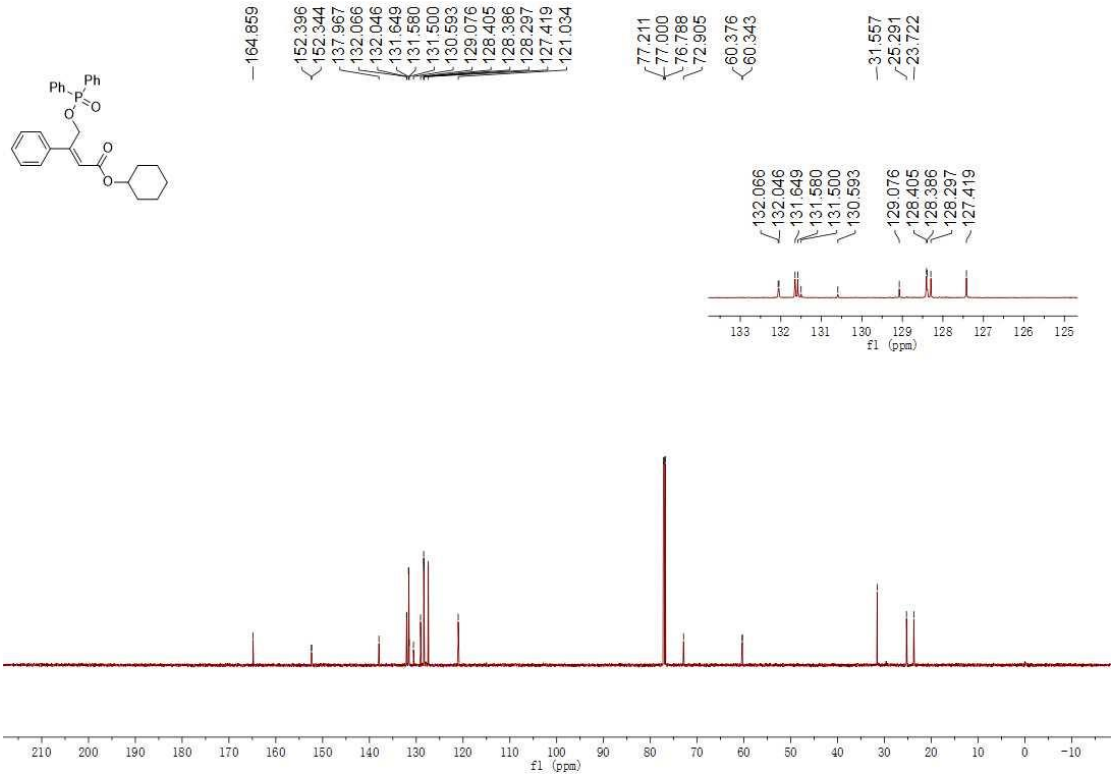
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **45**



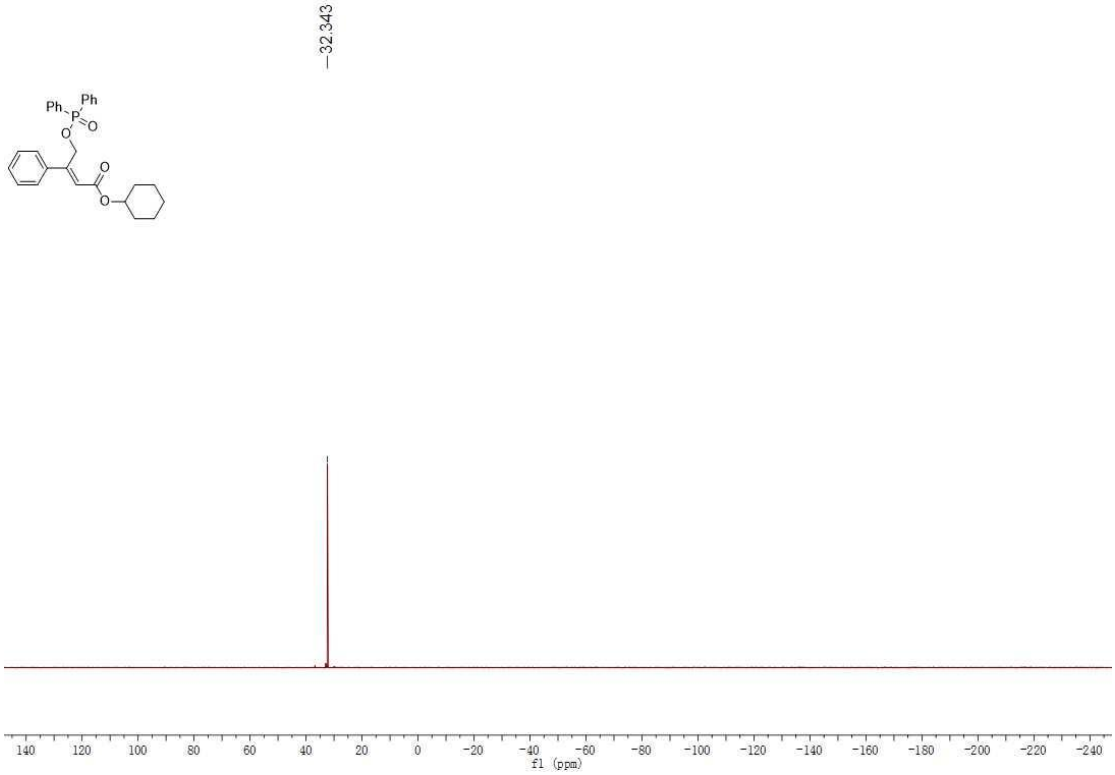
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **46**



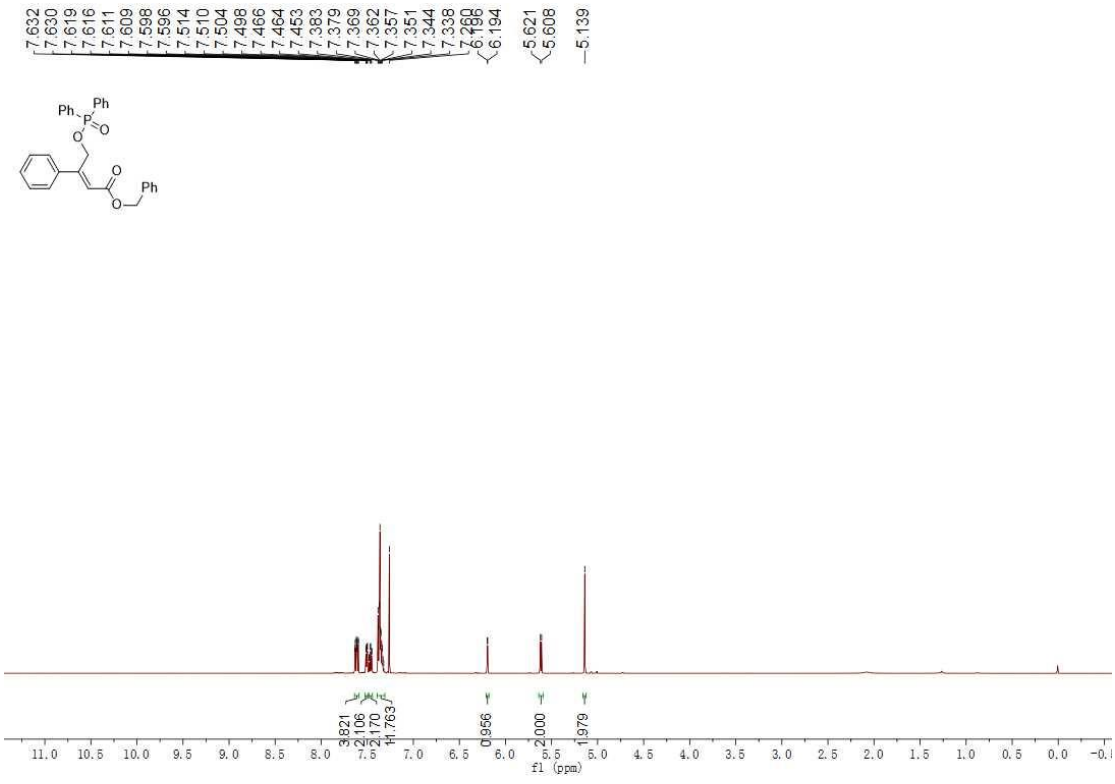
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **46**



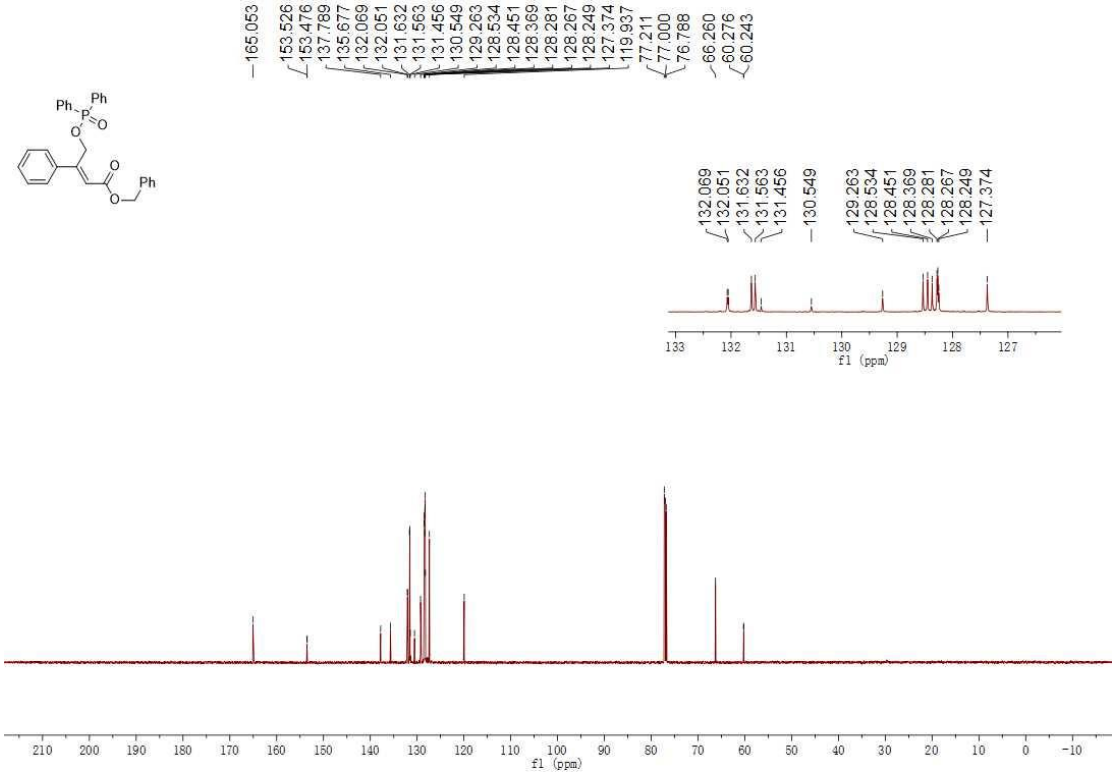
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **46**



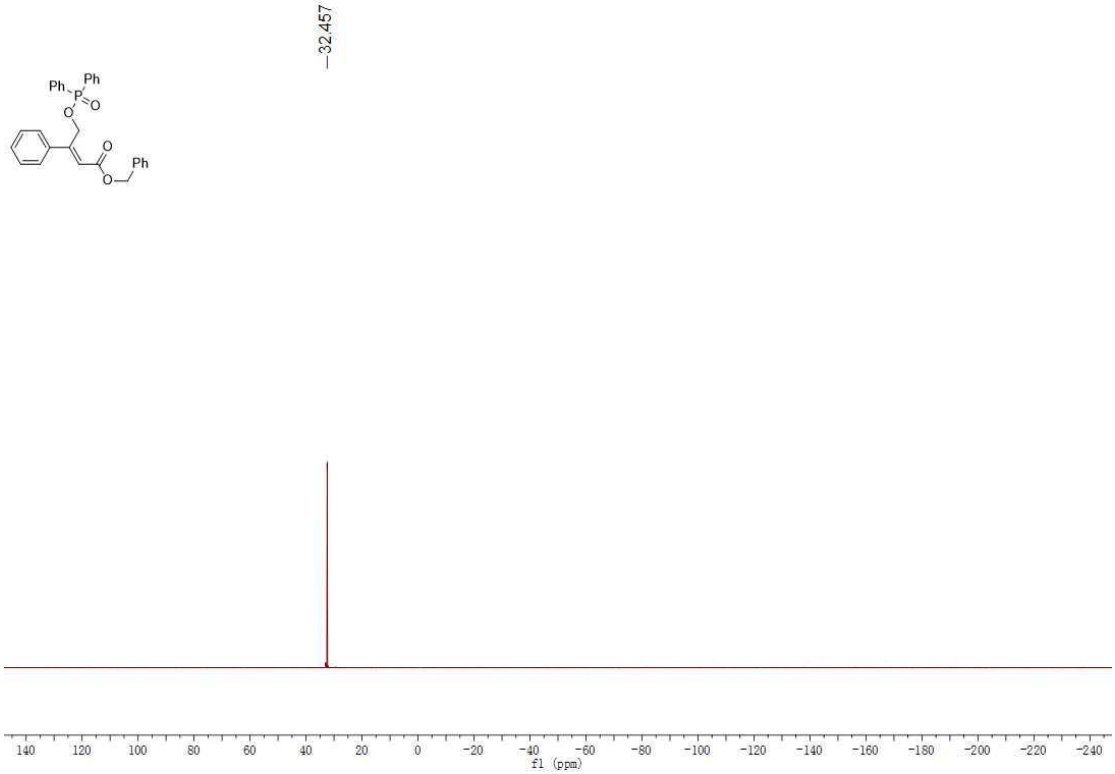
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **47**



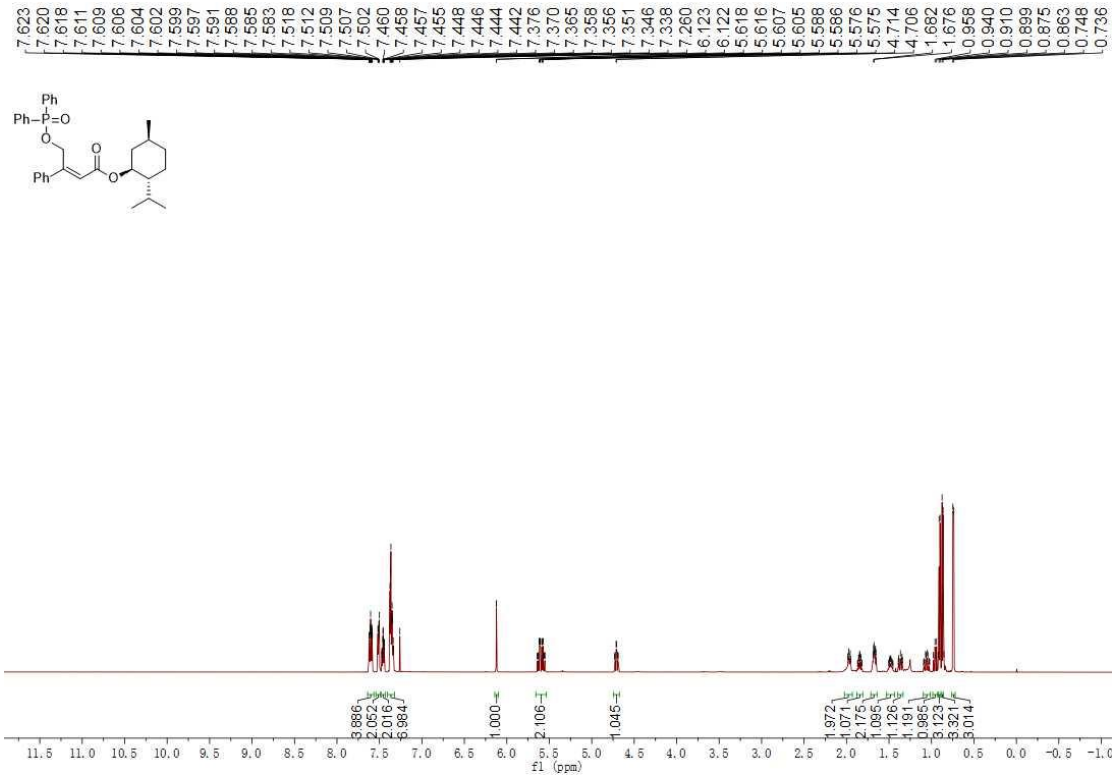
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **47**



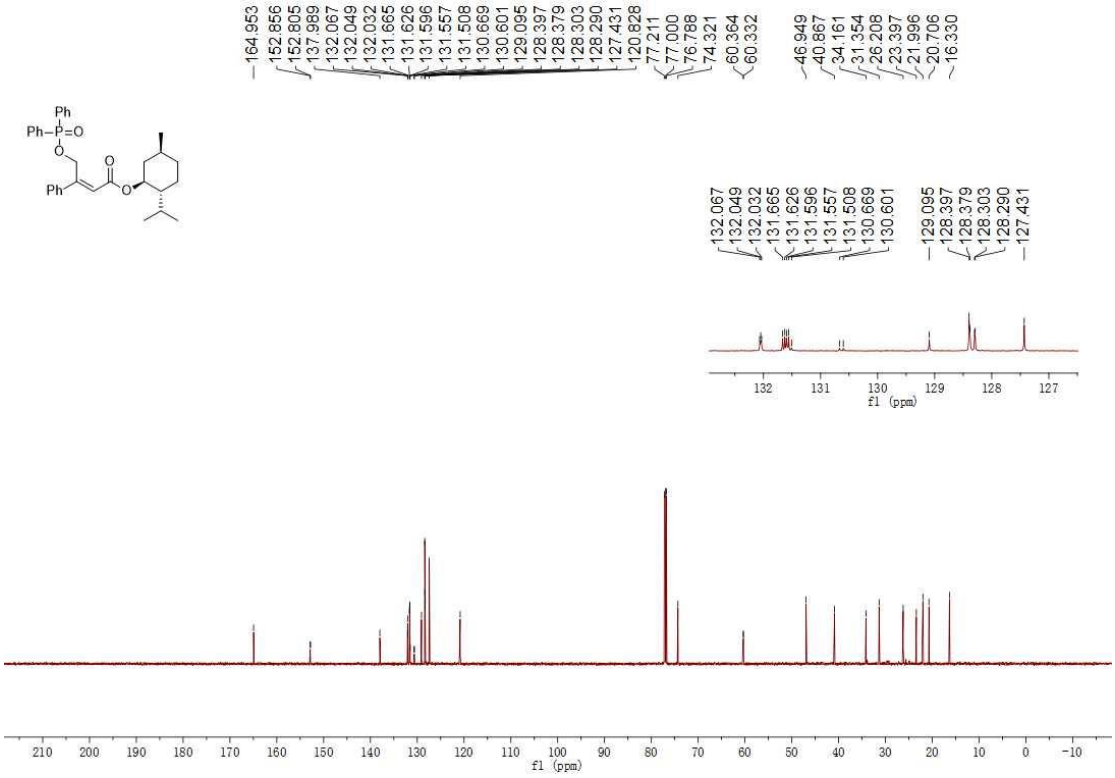
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **47**



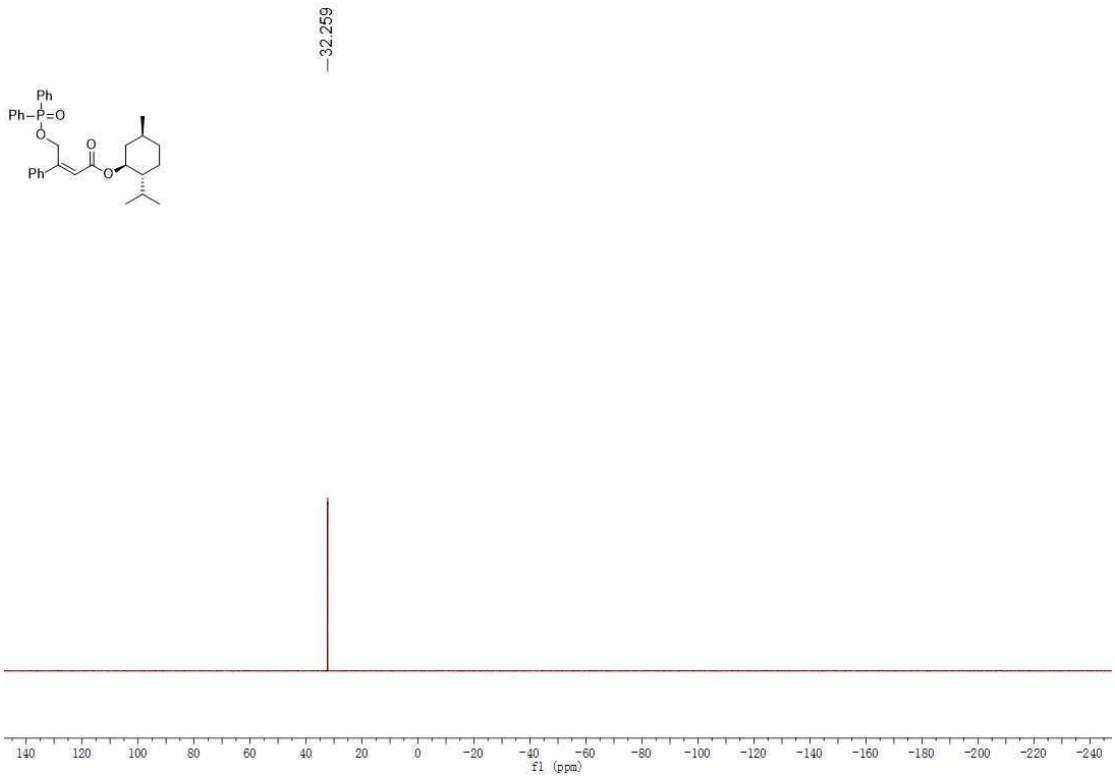
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **48**



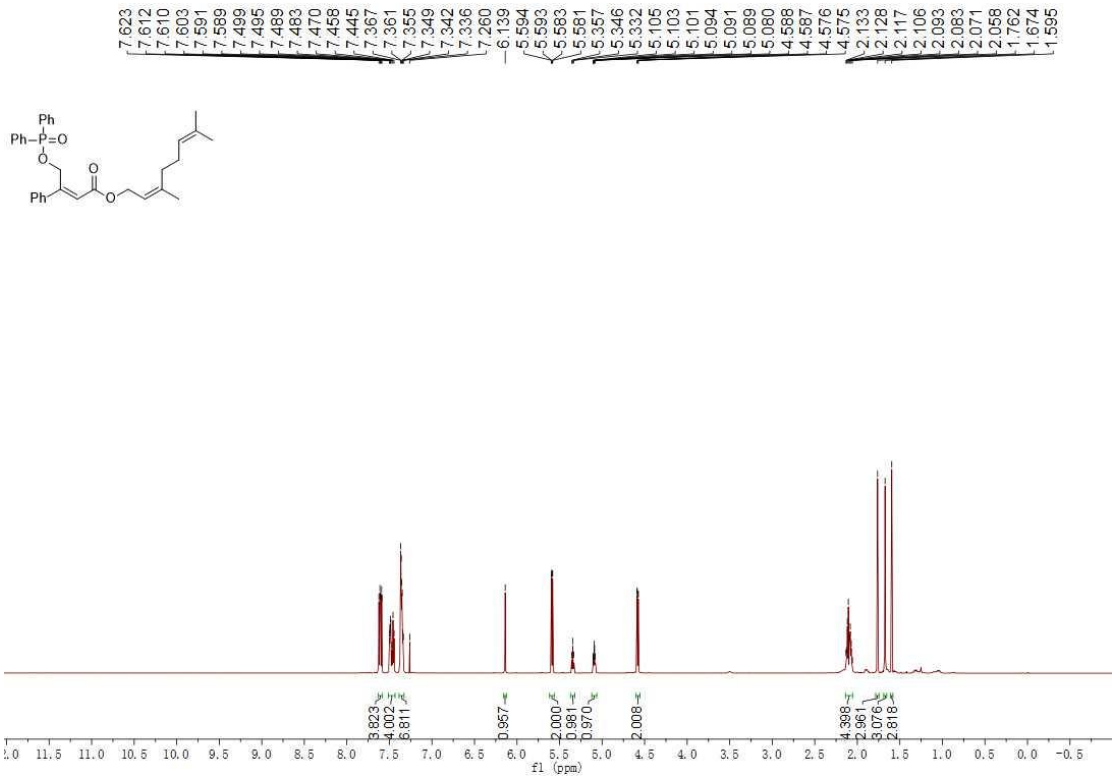
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **48**



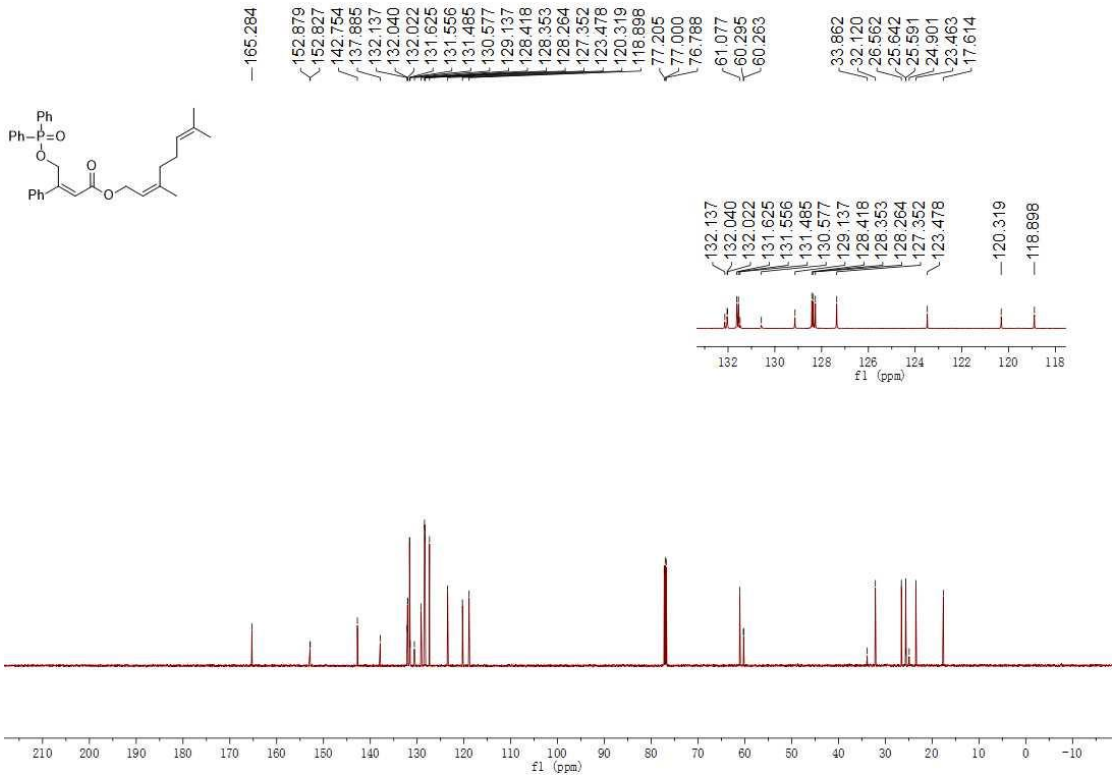
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **48**



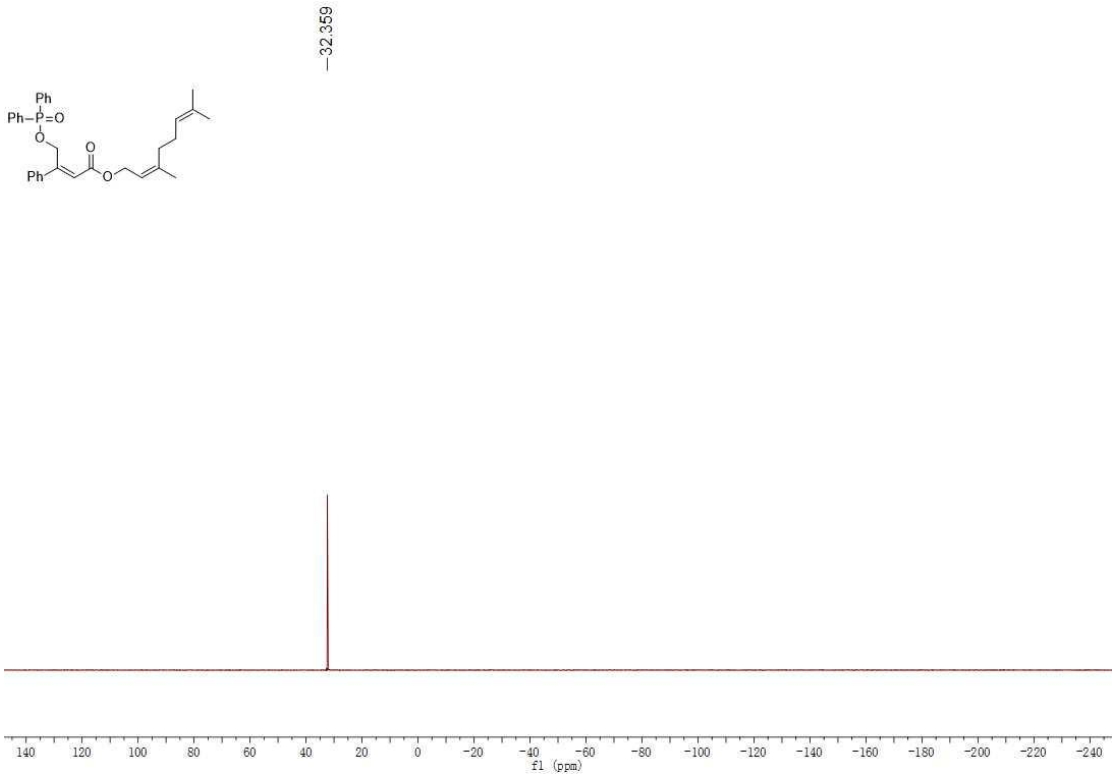
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **49**



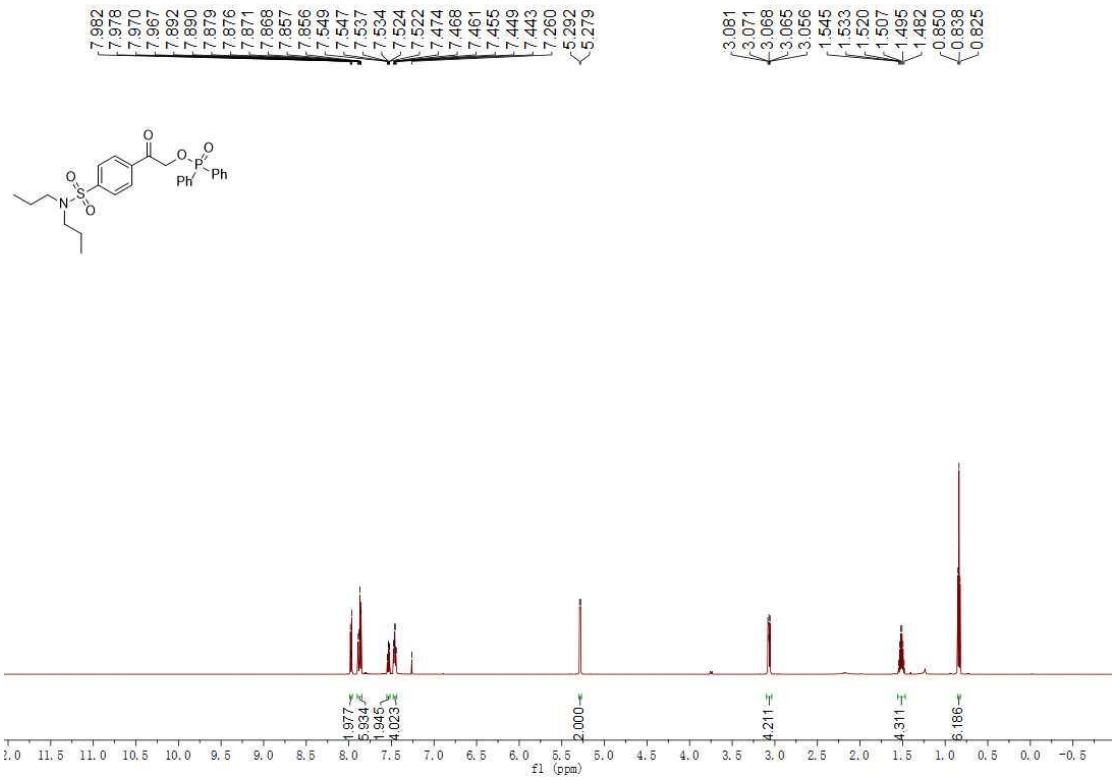
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **49**



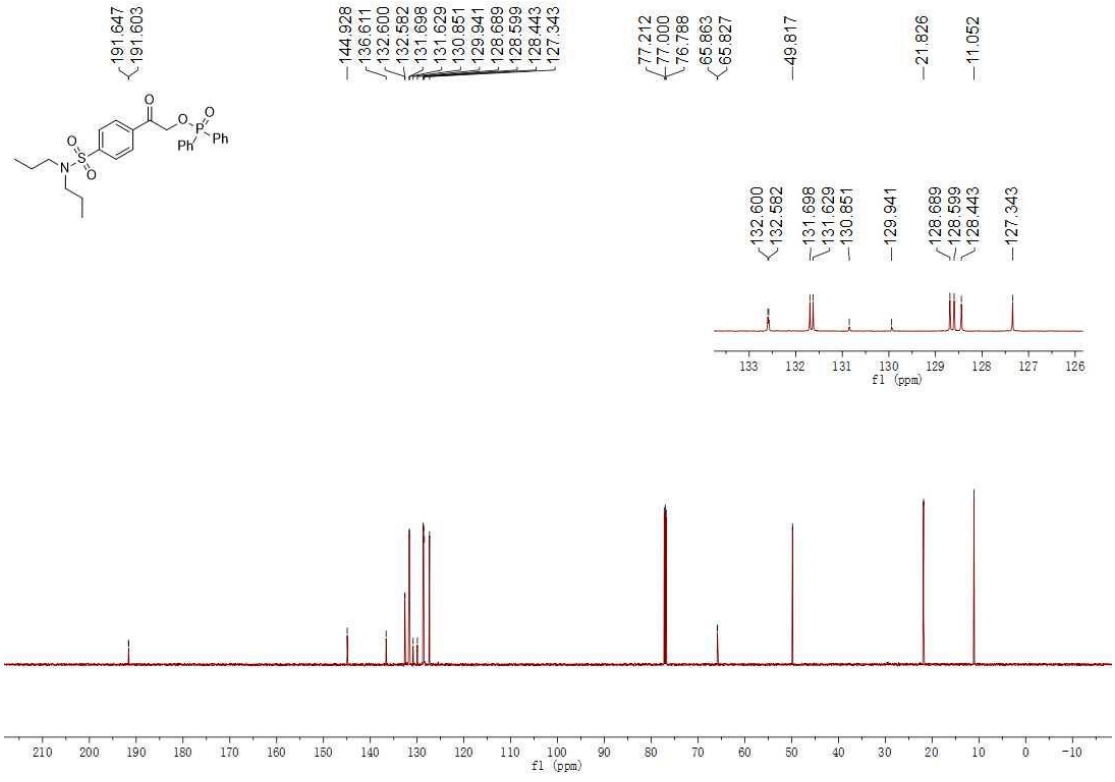
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **49**



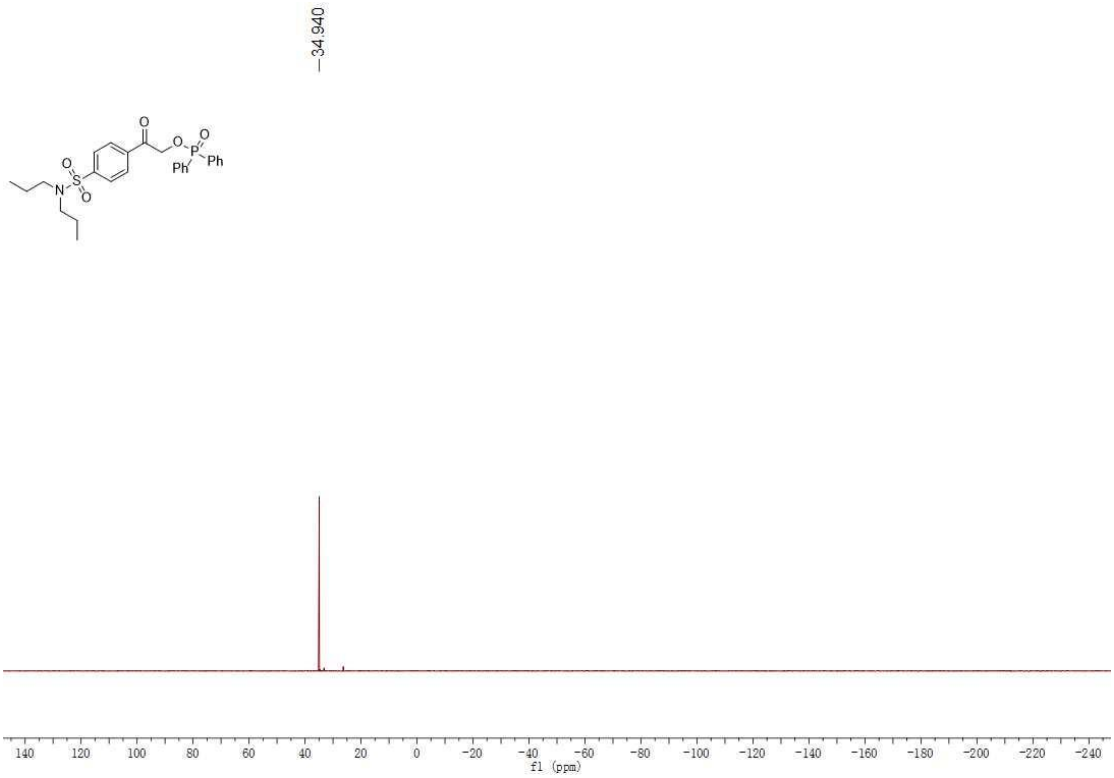
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **50**



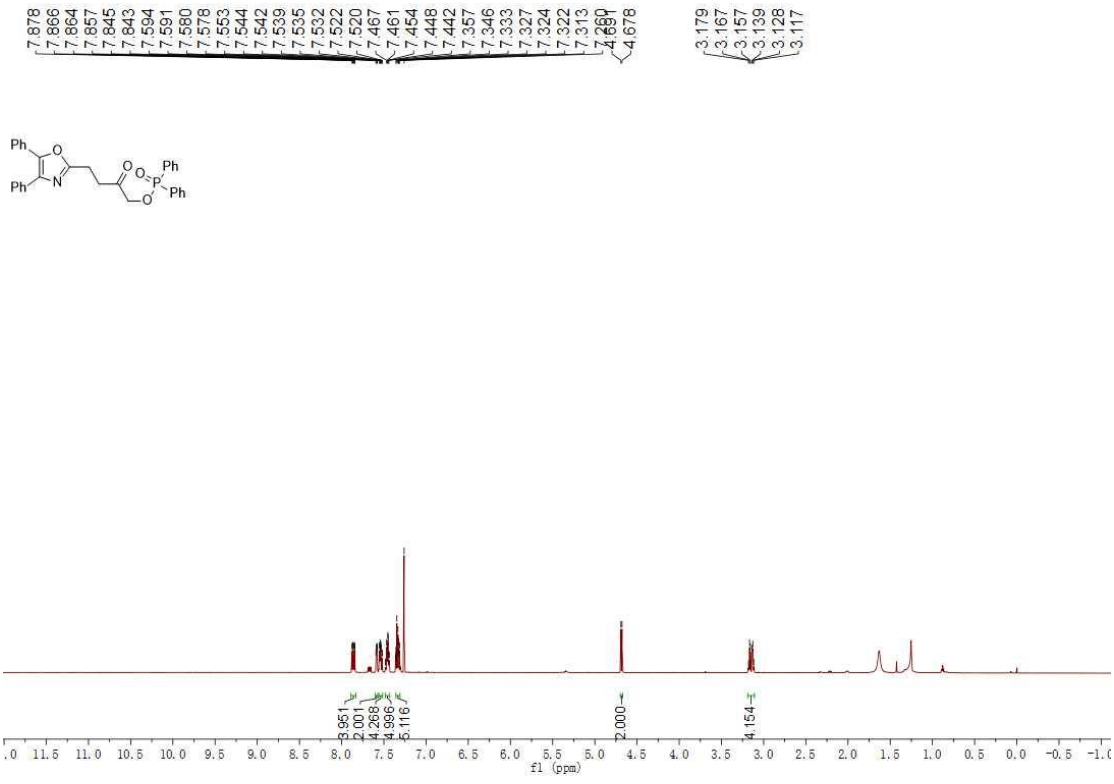
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **50**



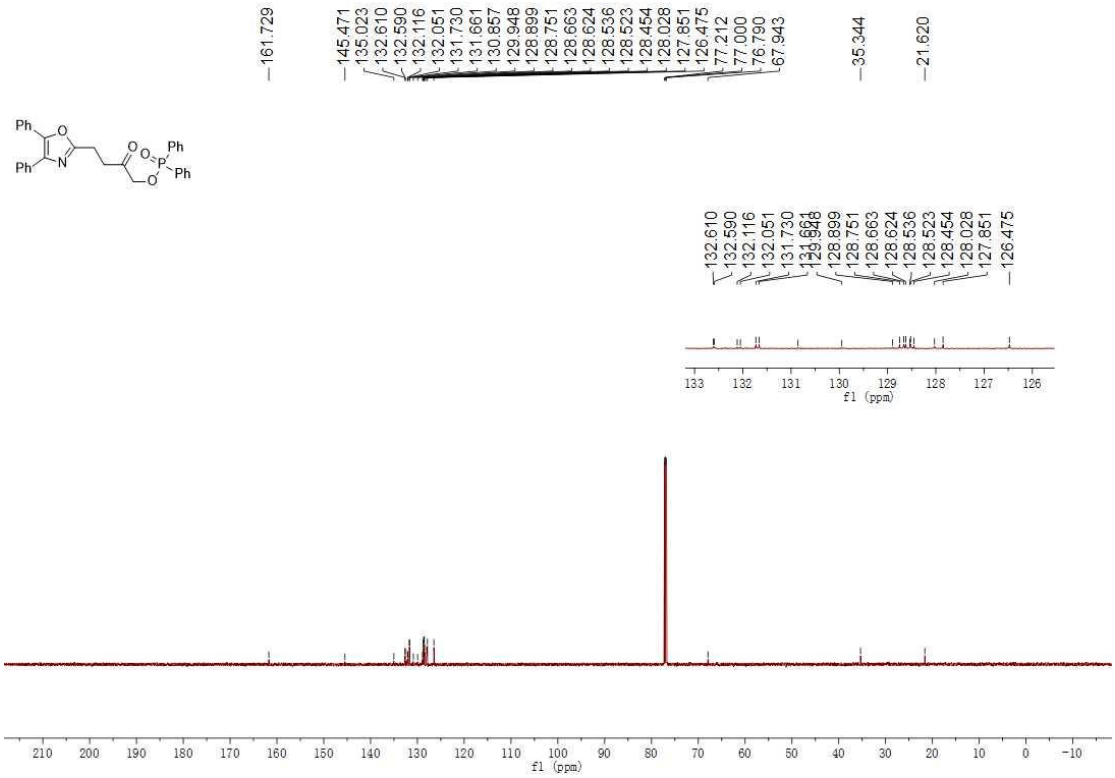
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **50**



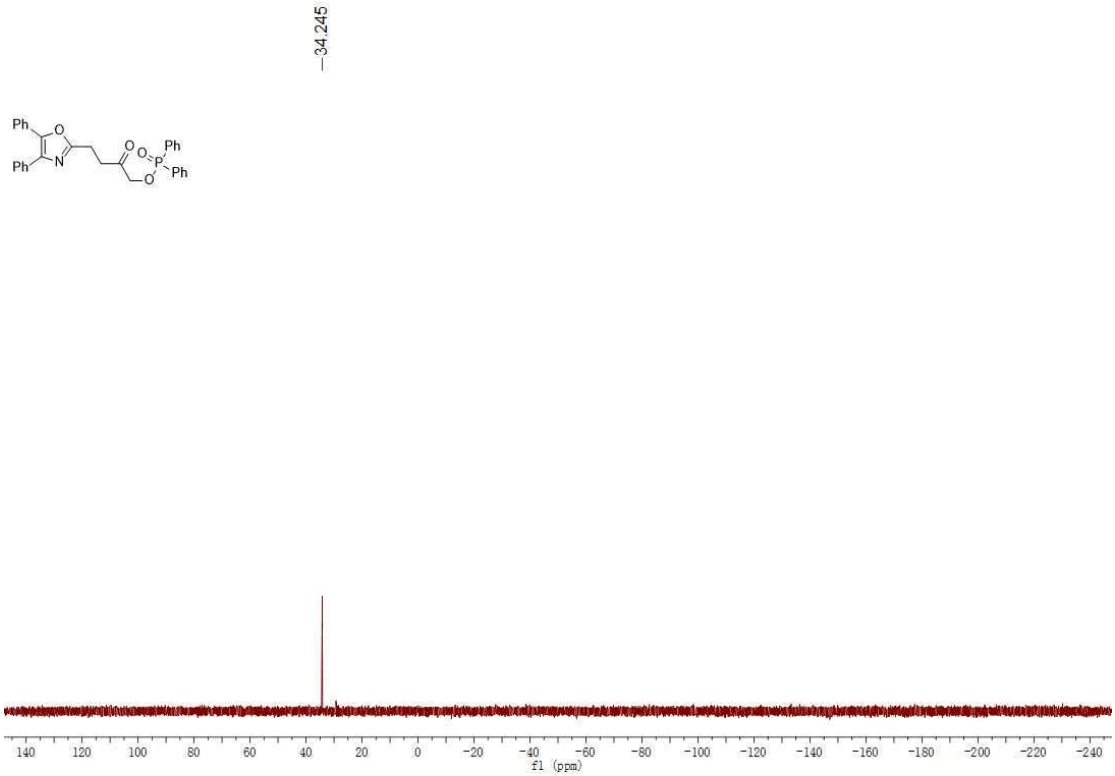
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **51**



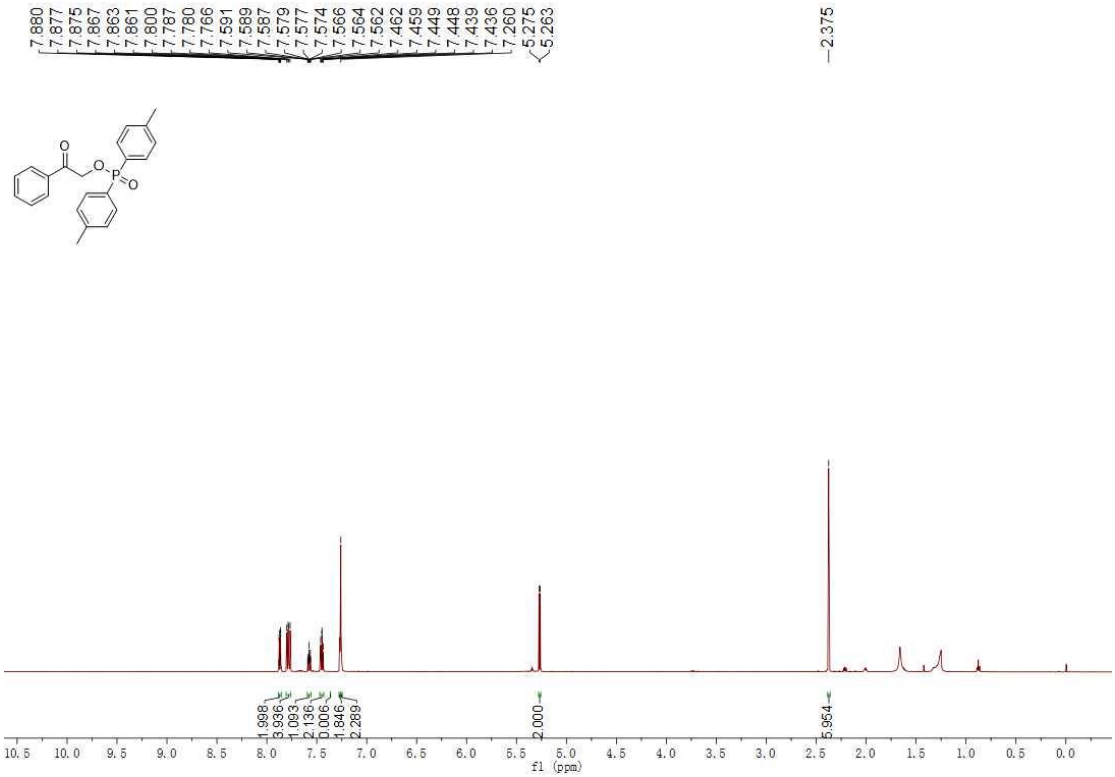
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **51**



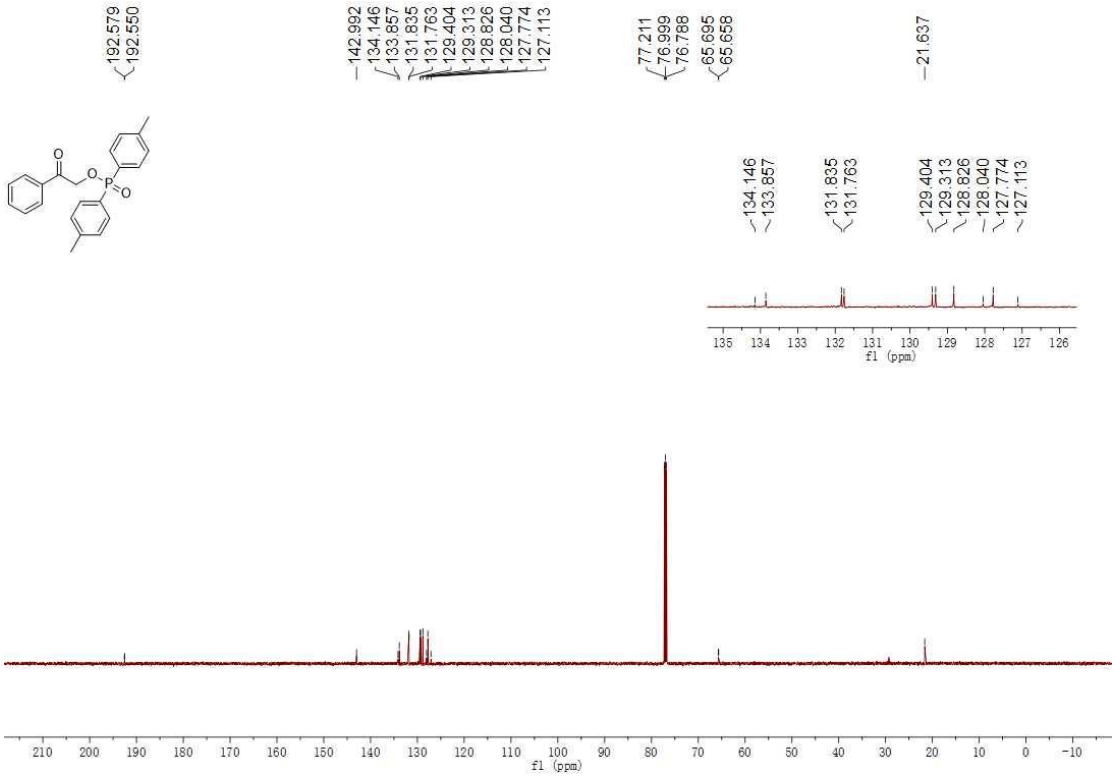
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **51**



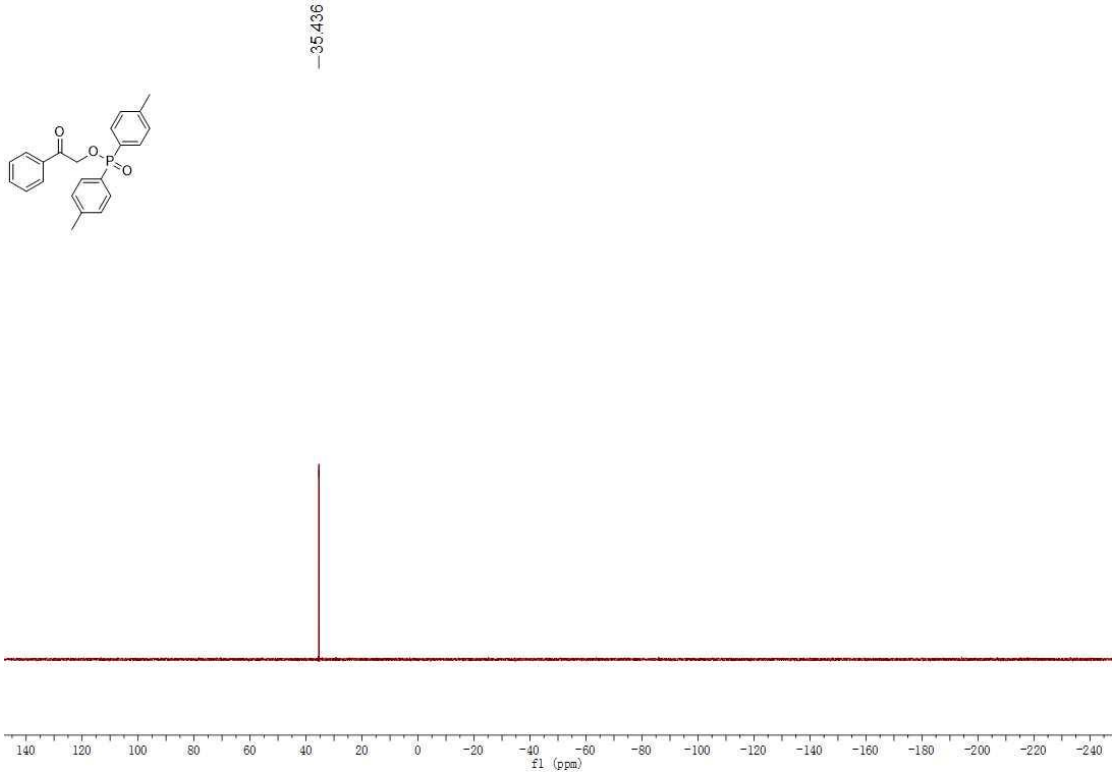
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **52**



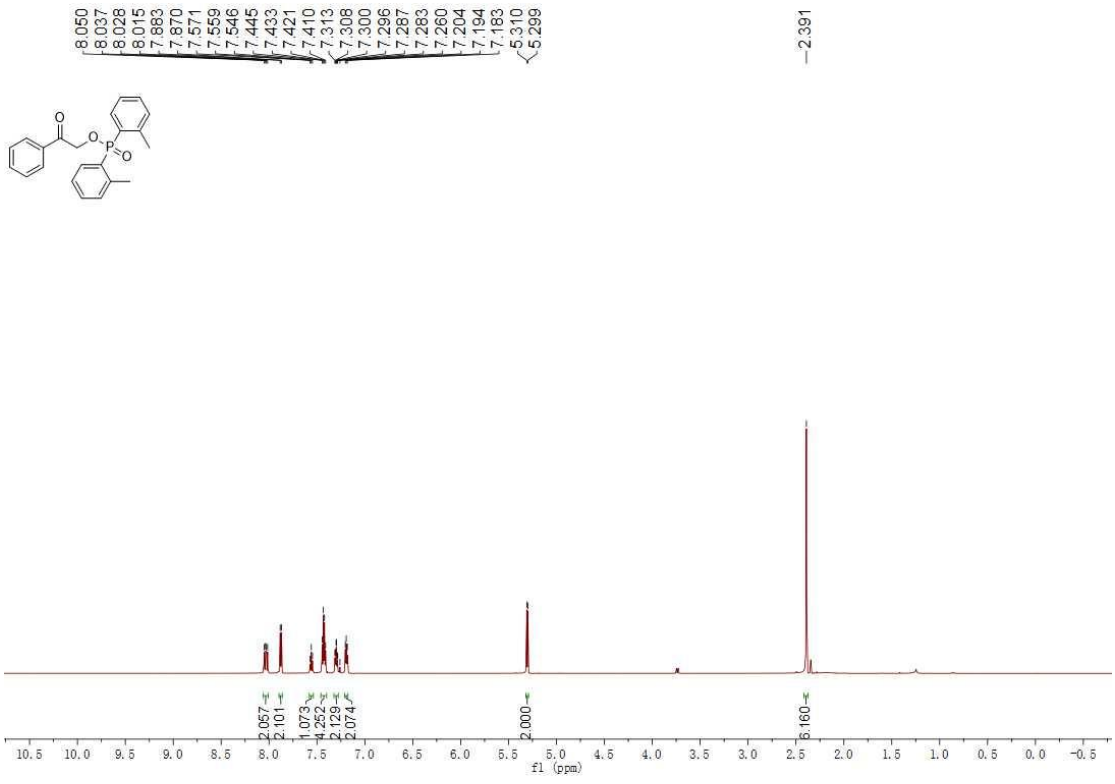
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **52**



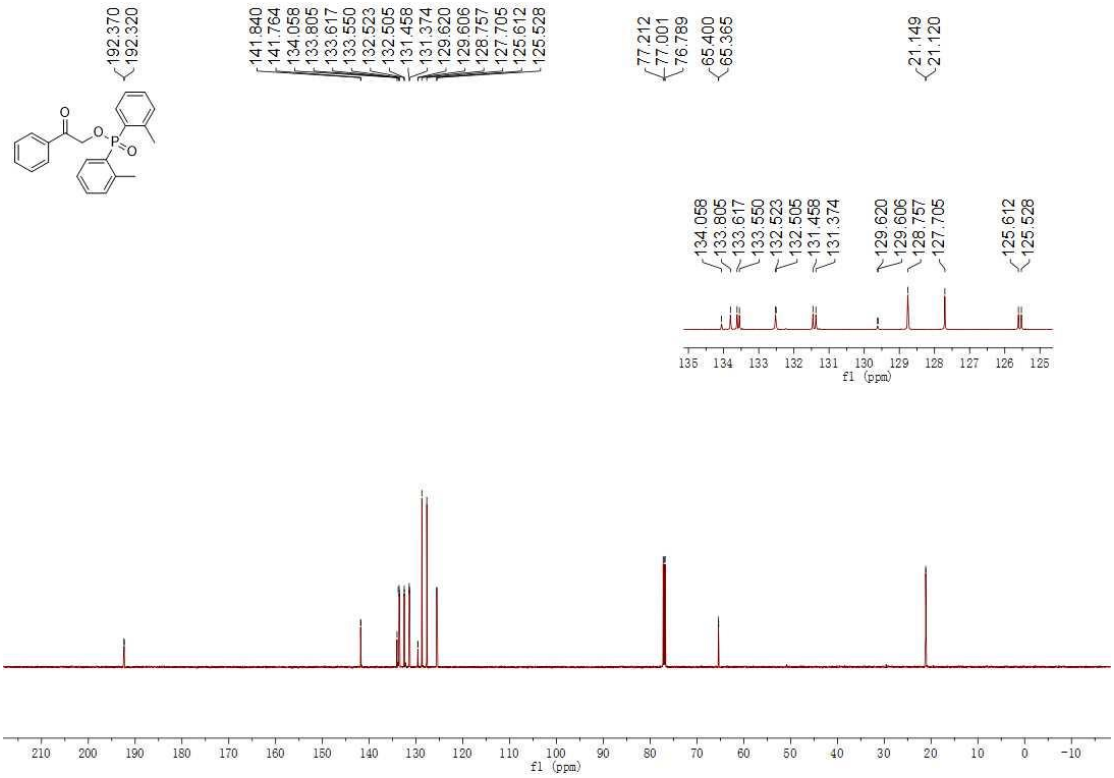
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **52**



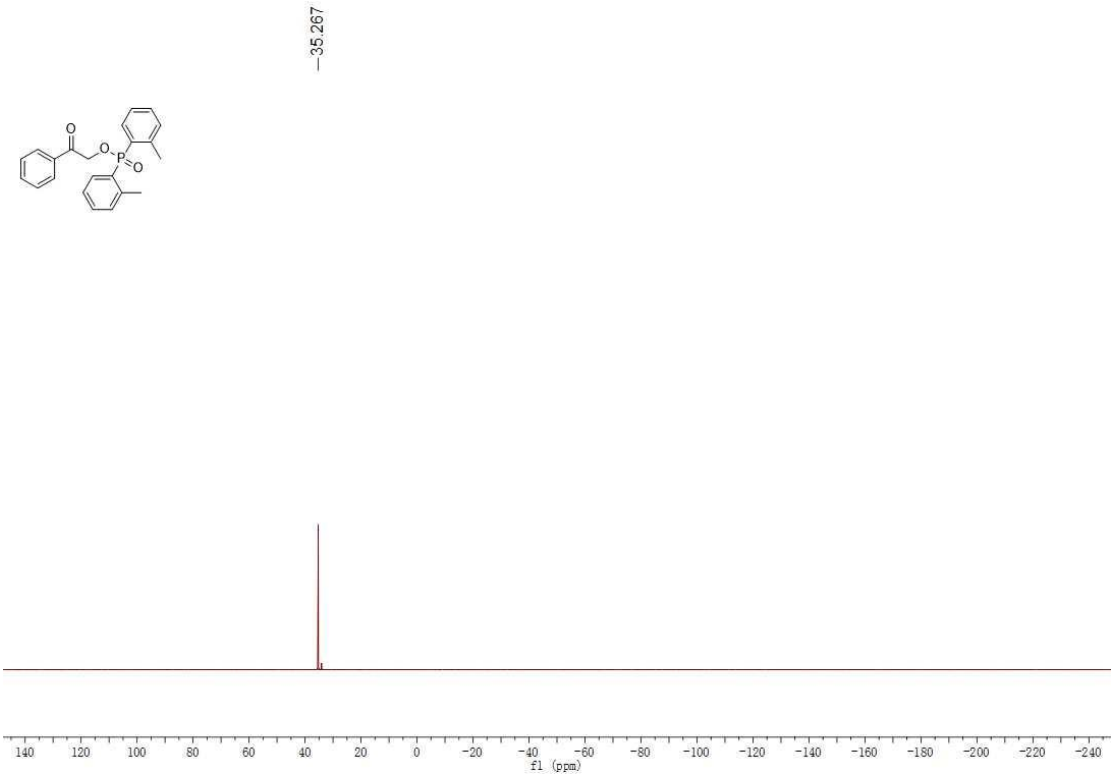
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **53**



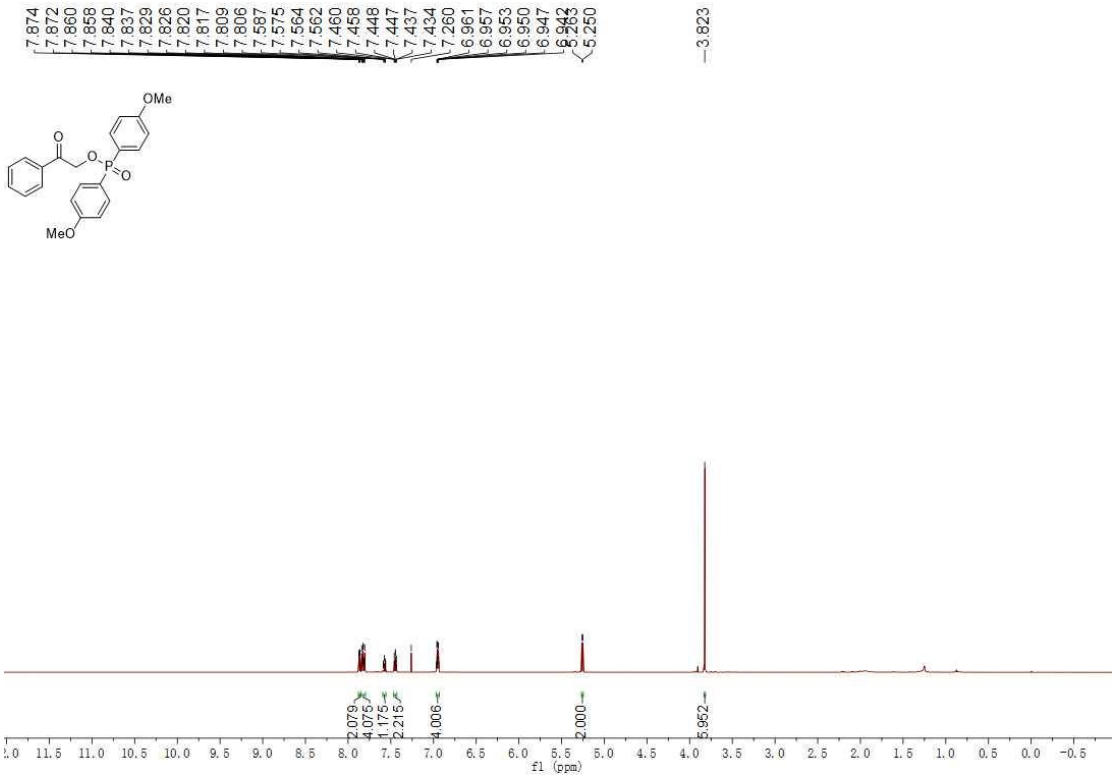
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **53**



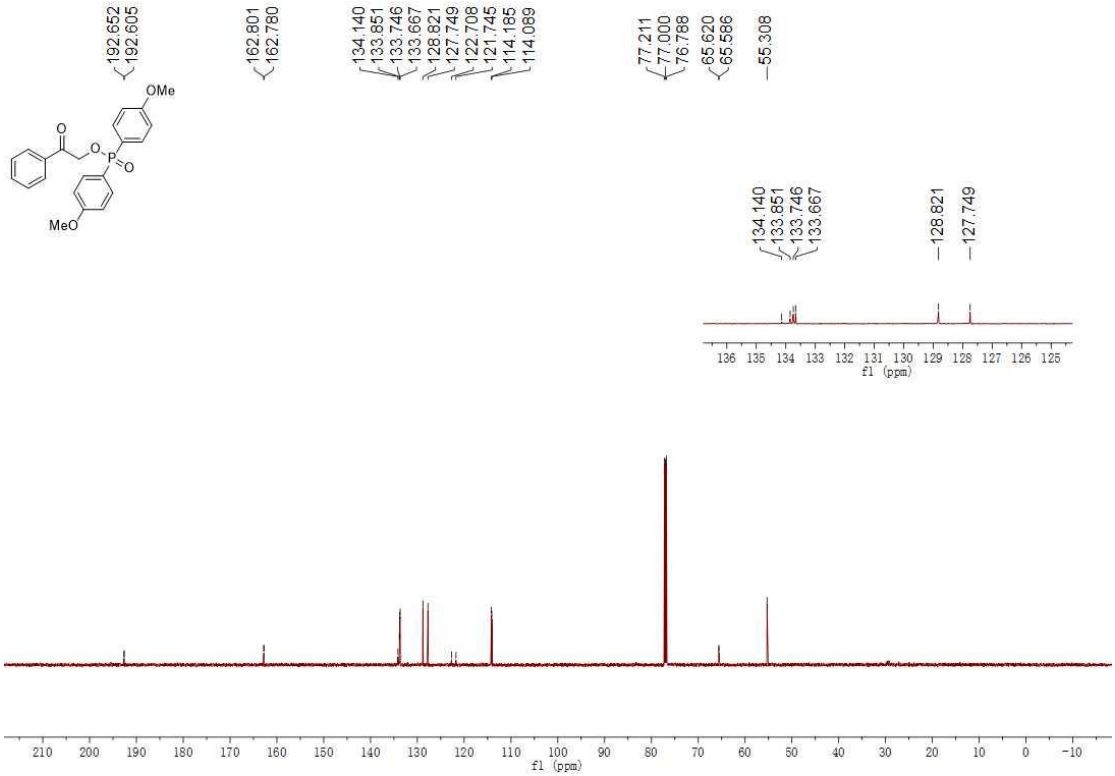
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **53**



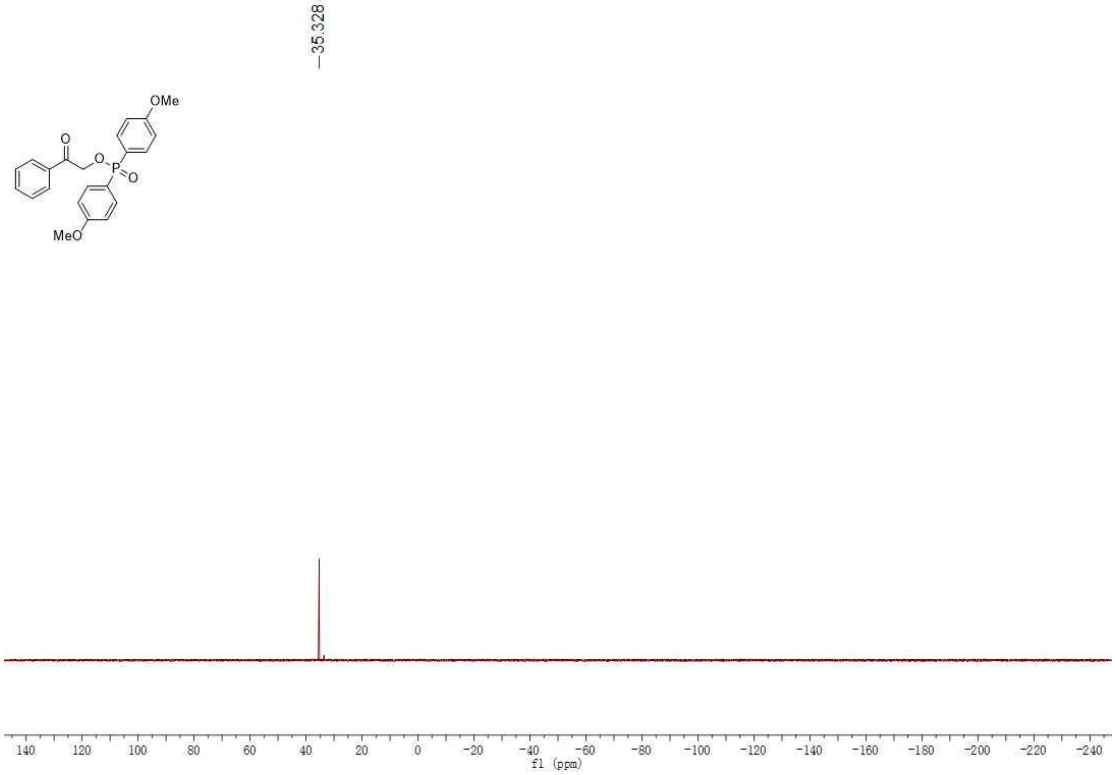
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **54**



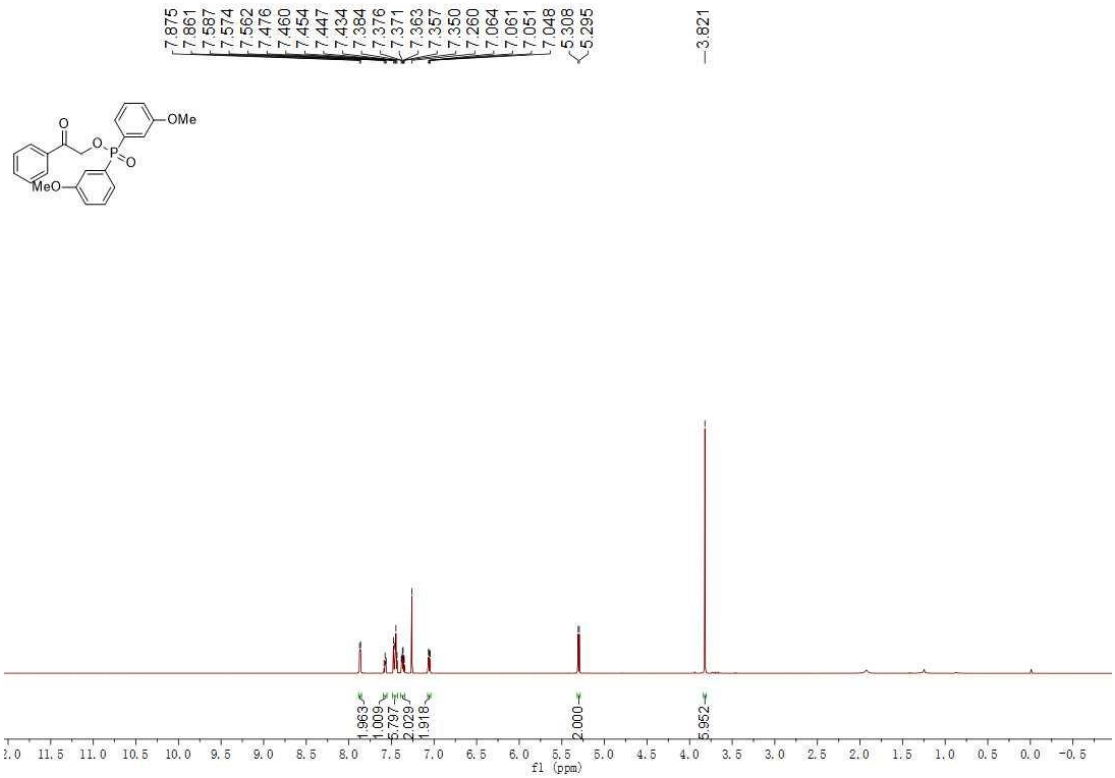
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **54**



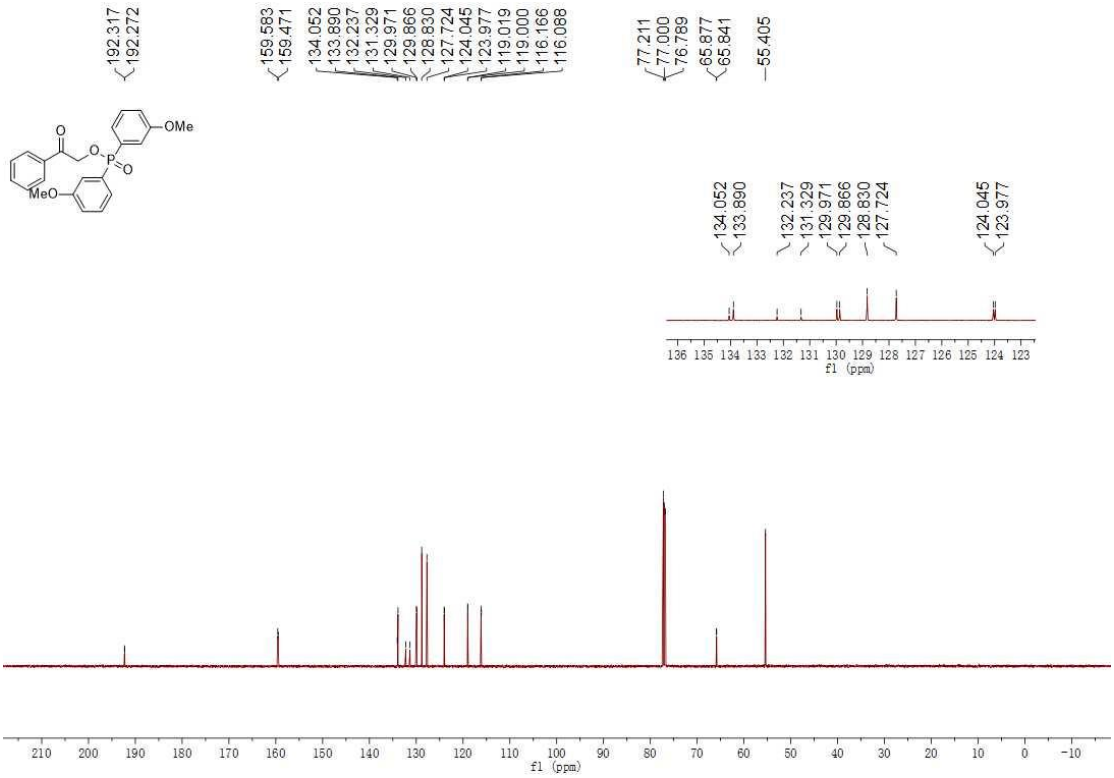
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **54**



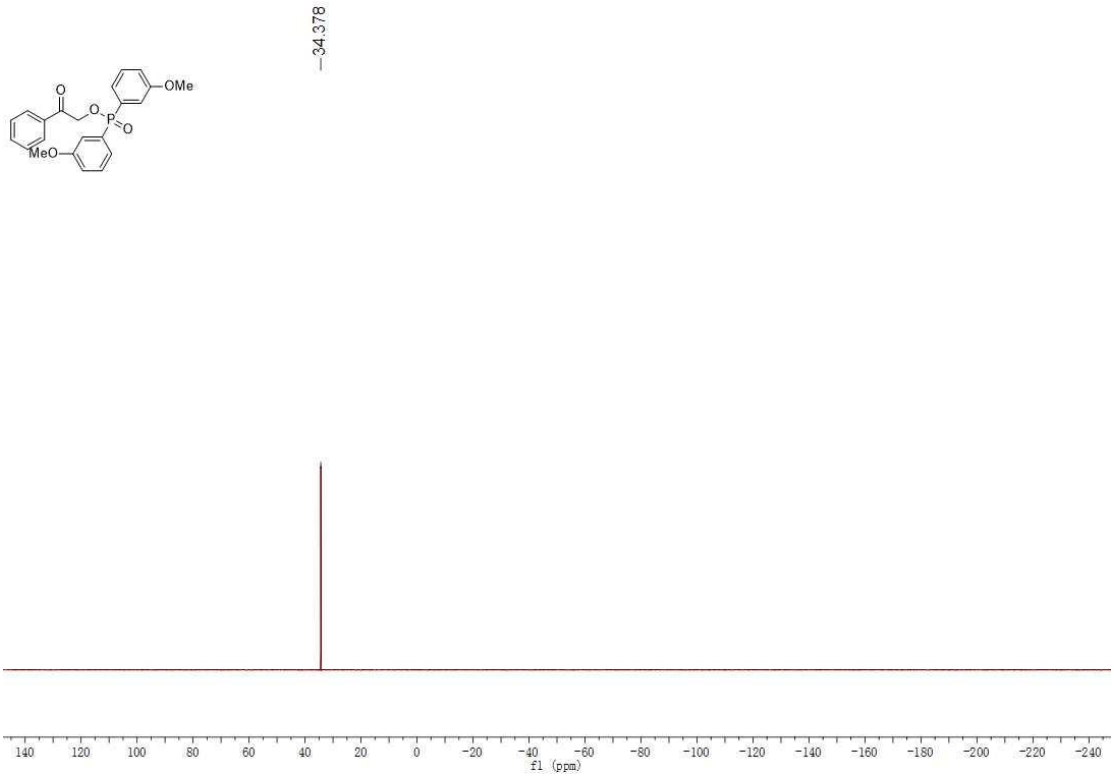
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **55**



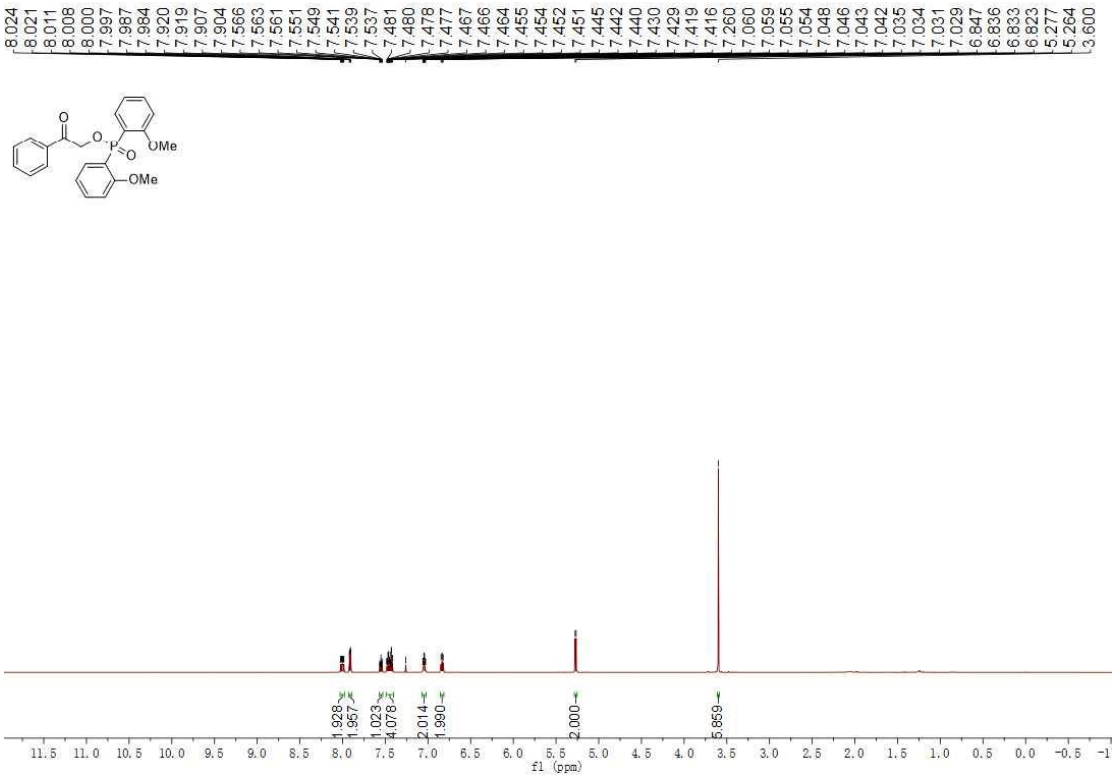
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **55**



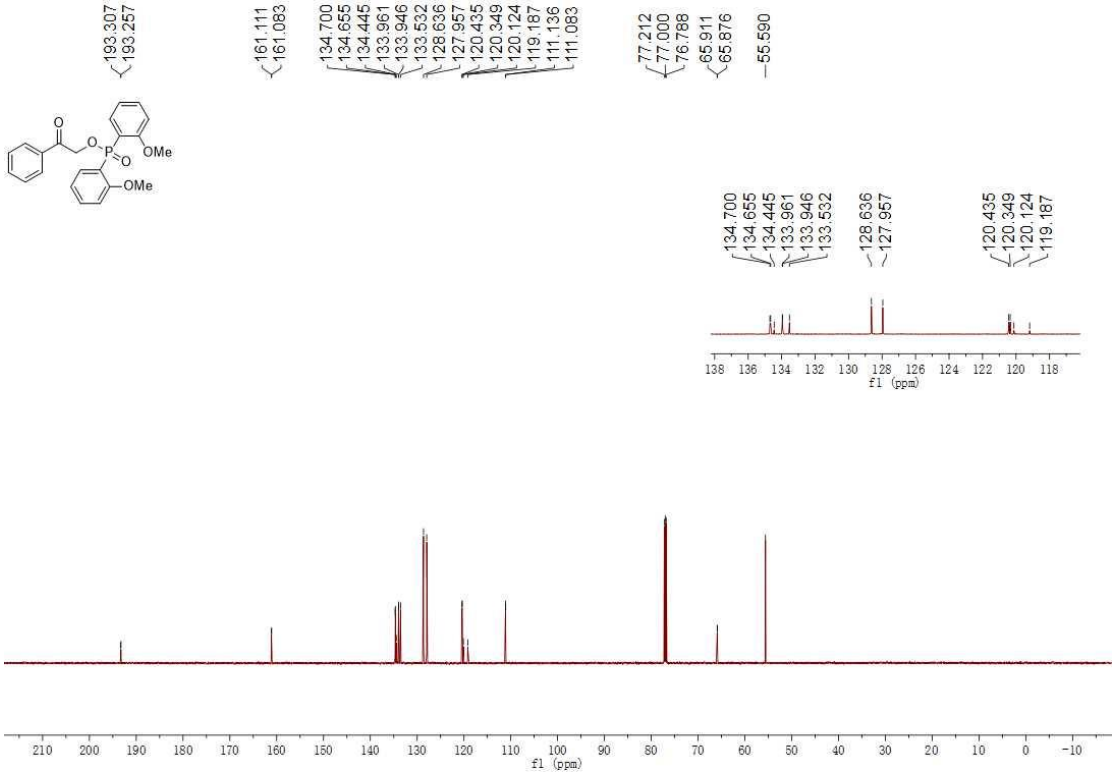
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **55**



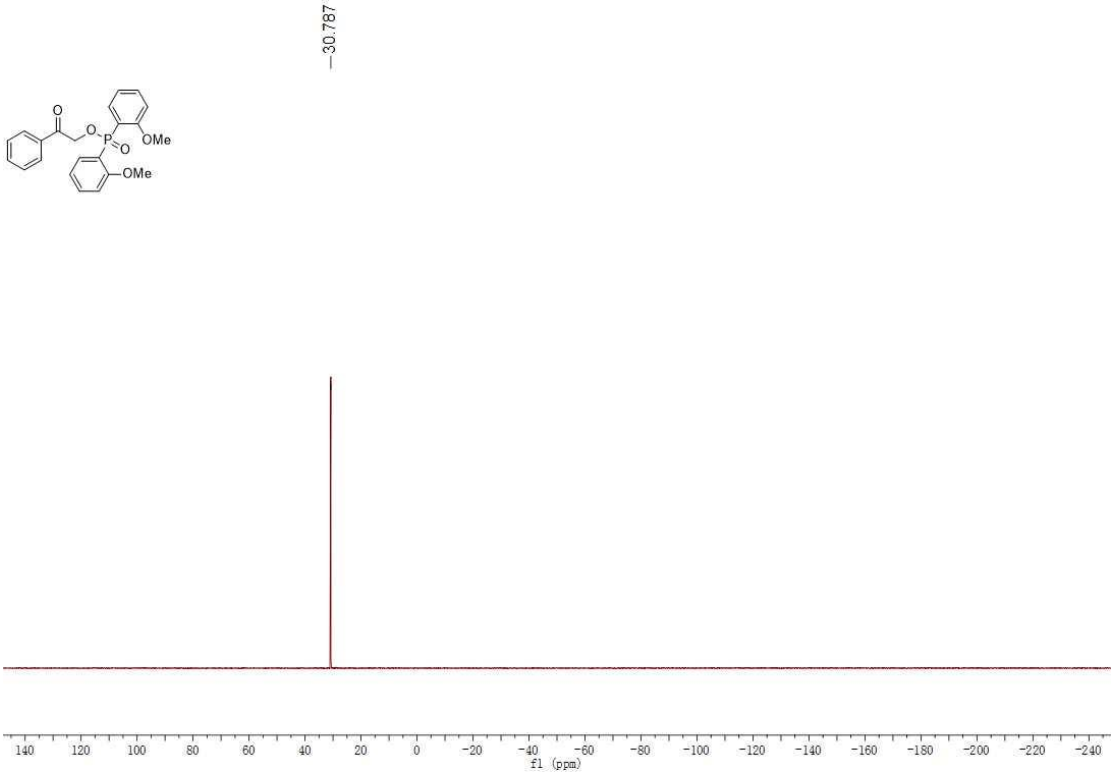
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **56**



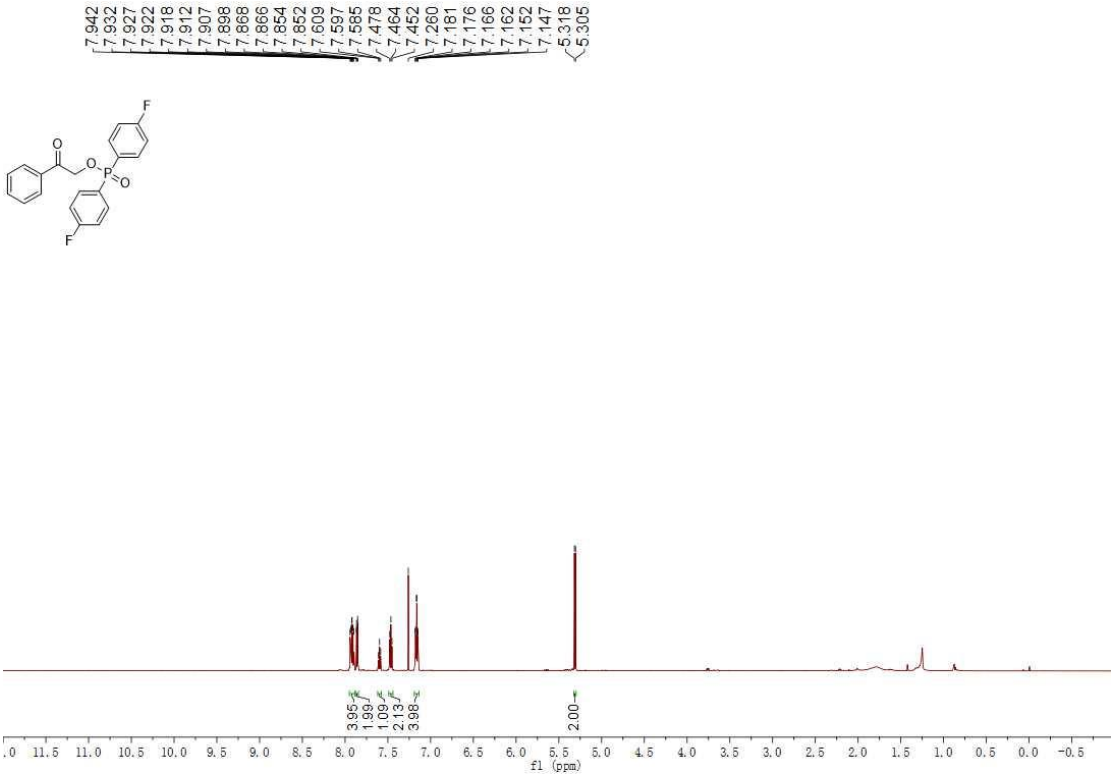
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **56**



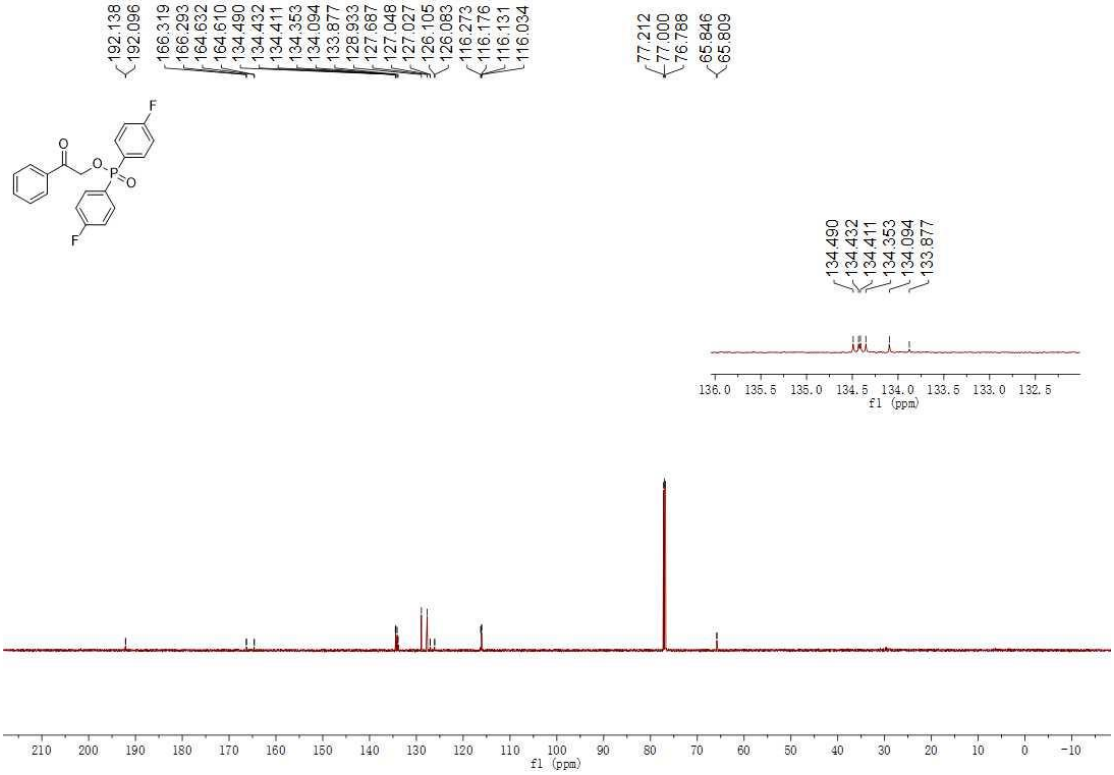
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **56**



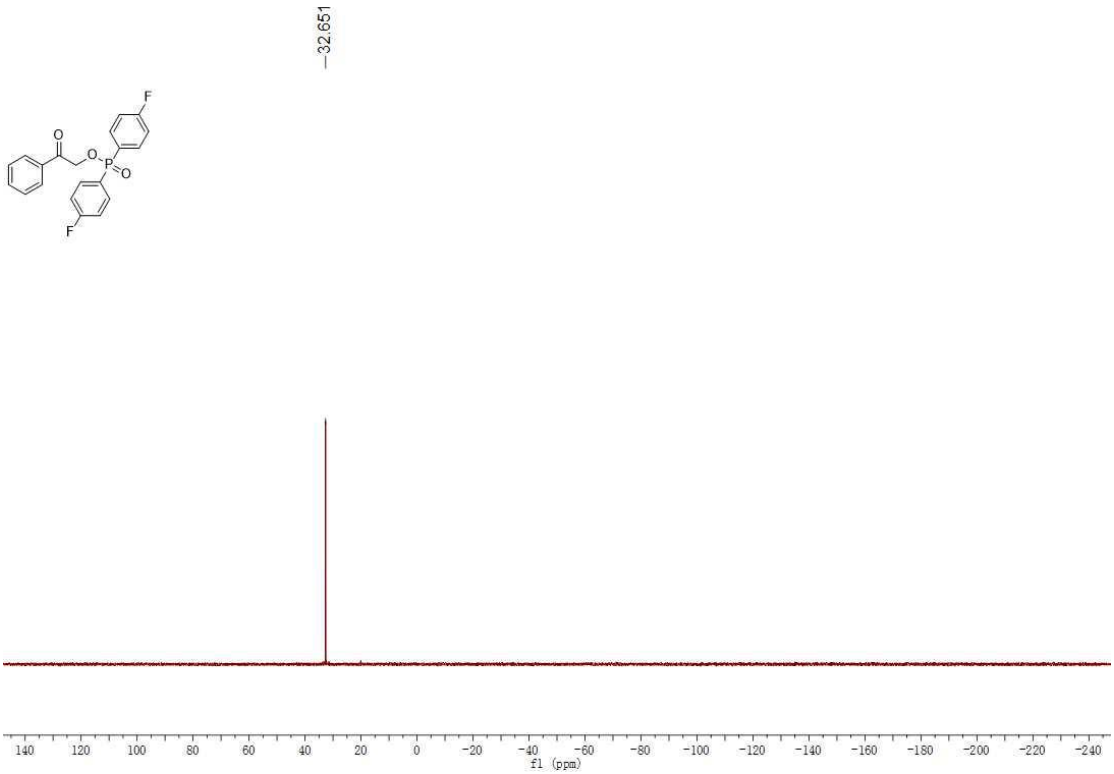
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **57**



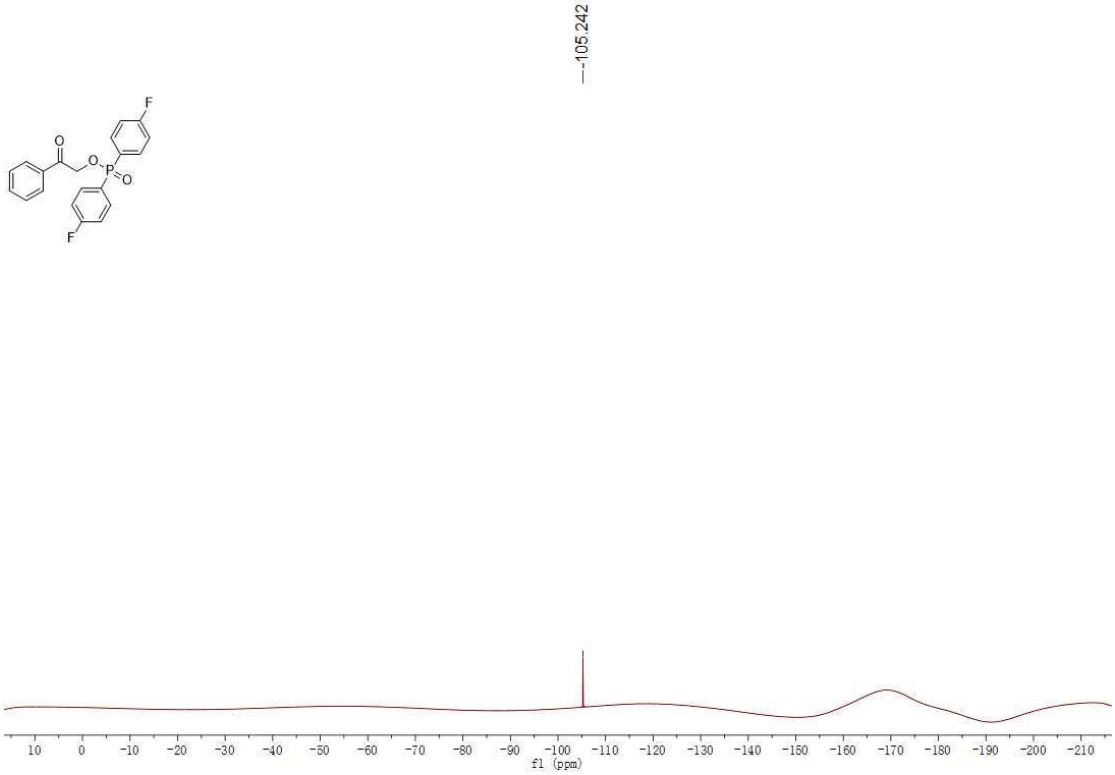
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **57**



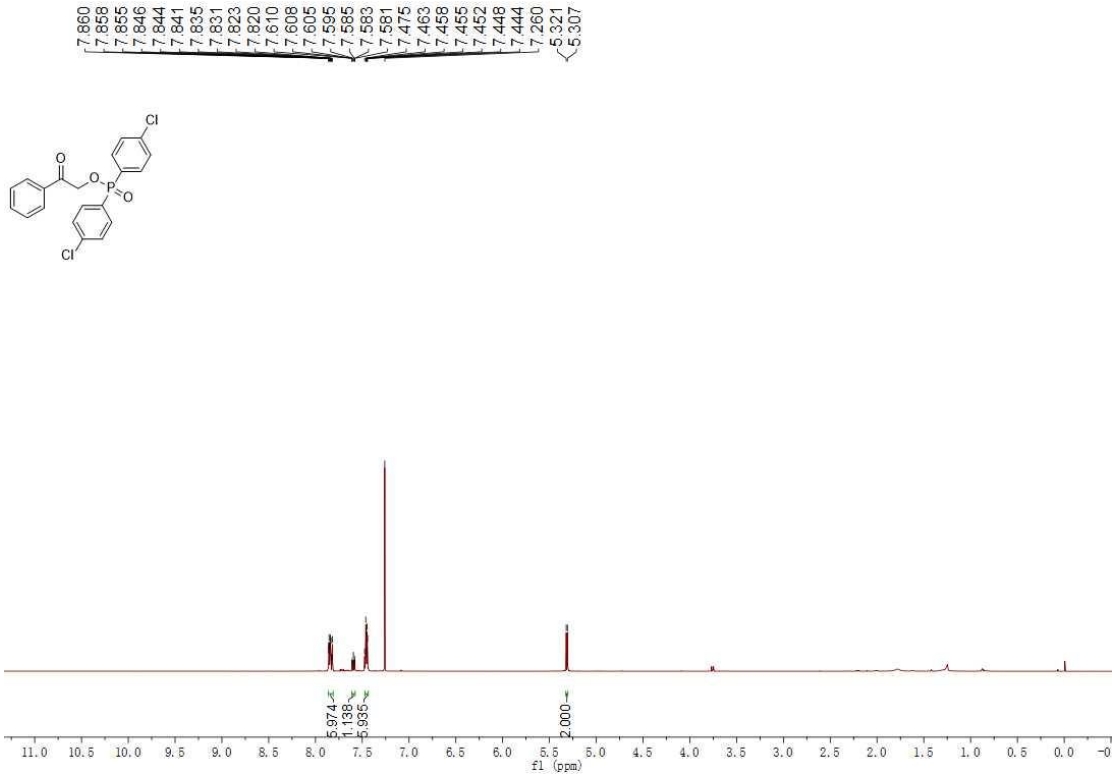
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **57**



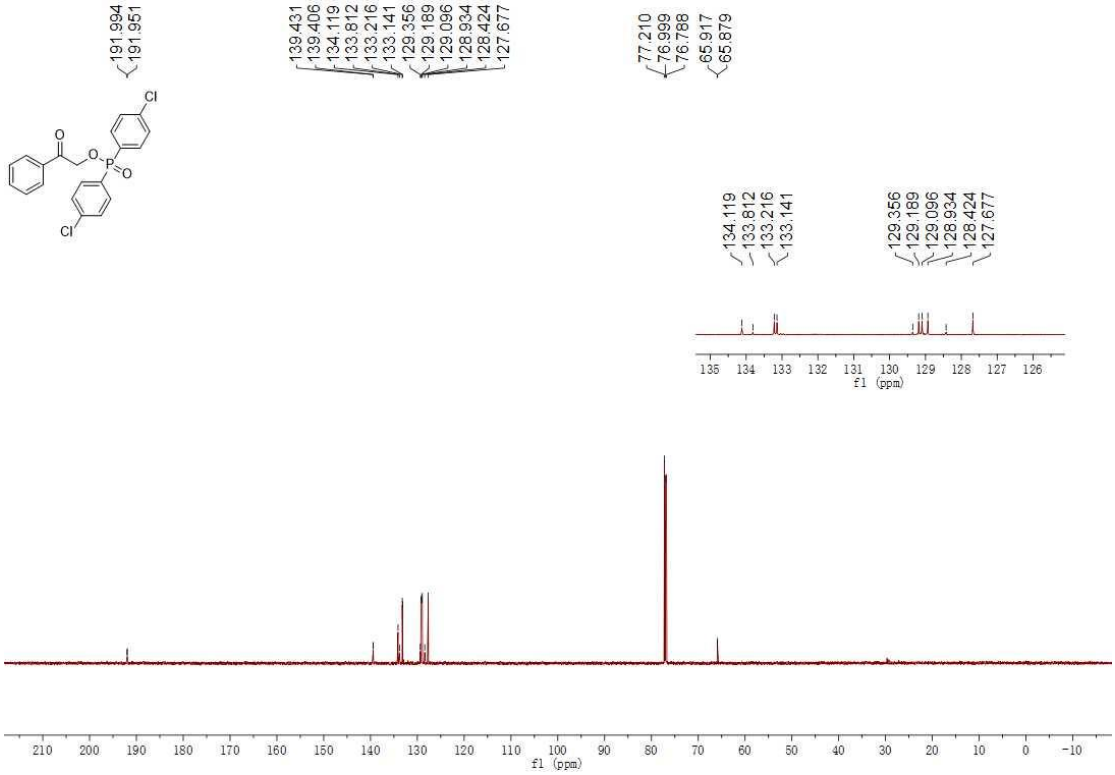
^{19}F NMR (564 MHz, $CDCl_3$) Spectrum of **57**



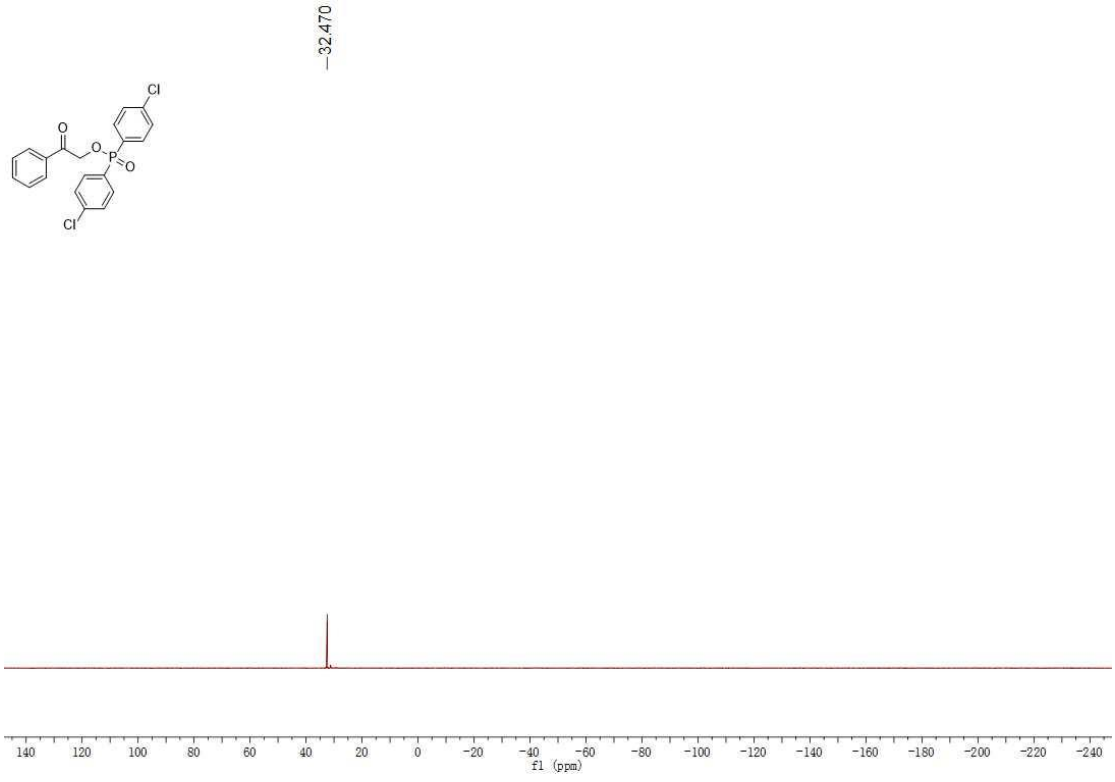
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **58**



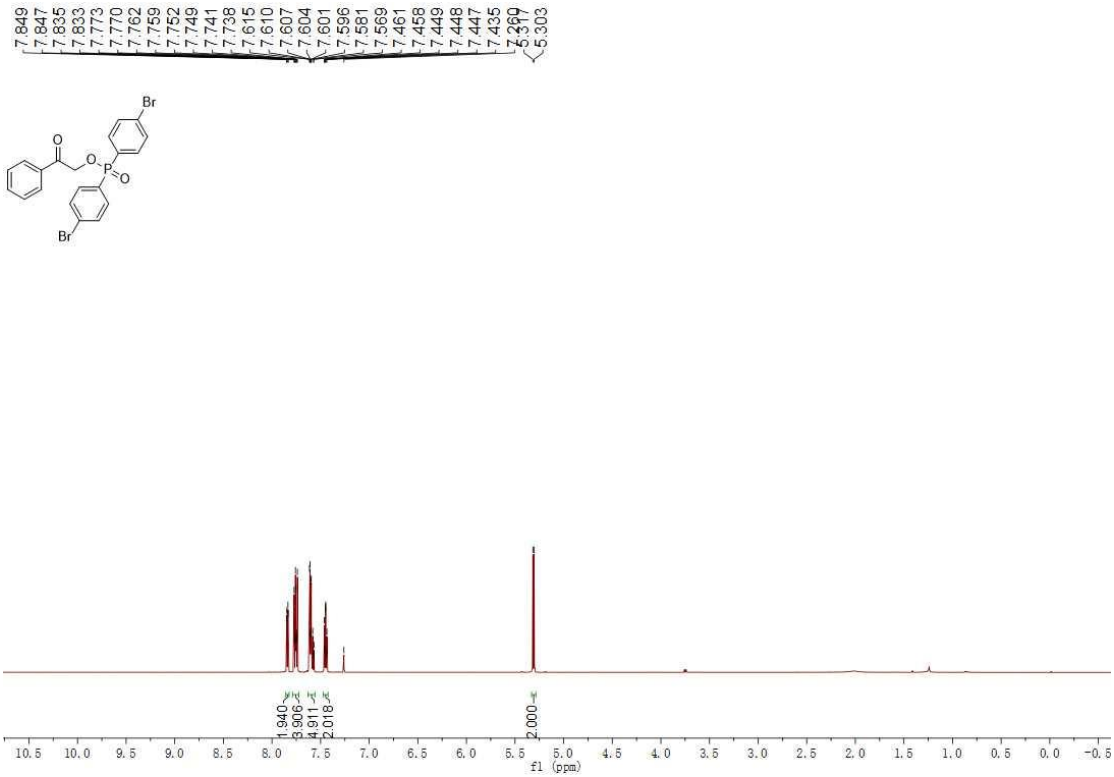
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **58**



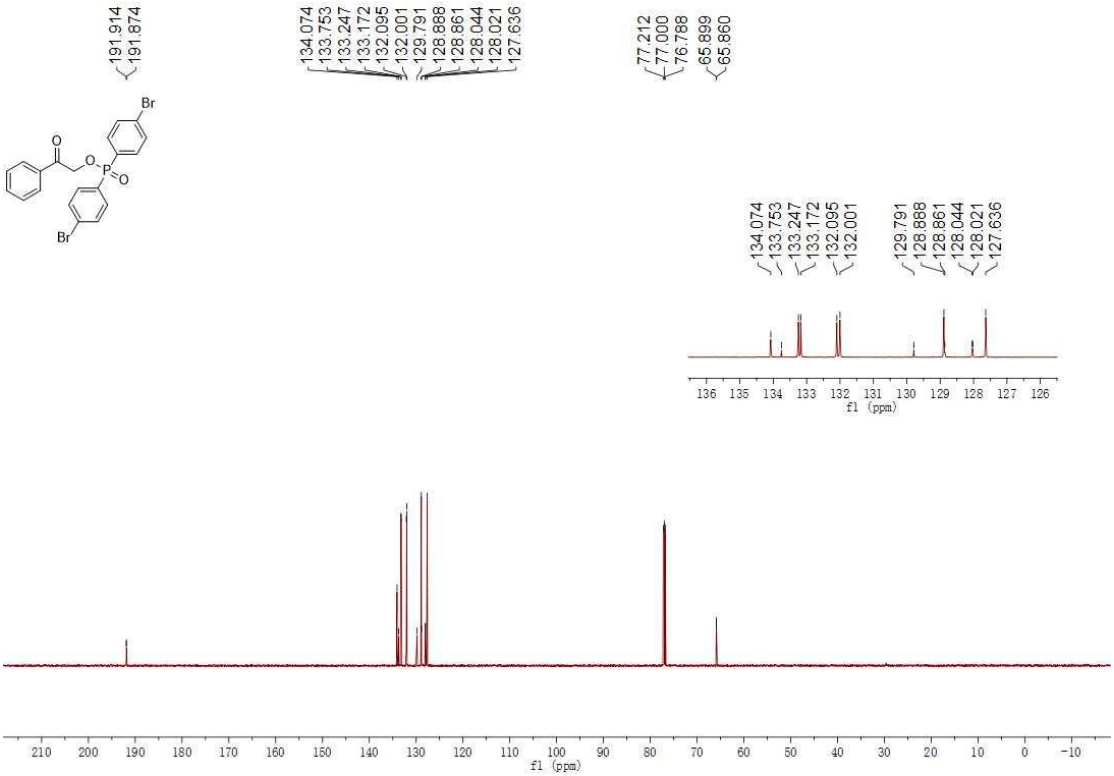
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **58**



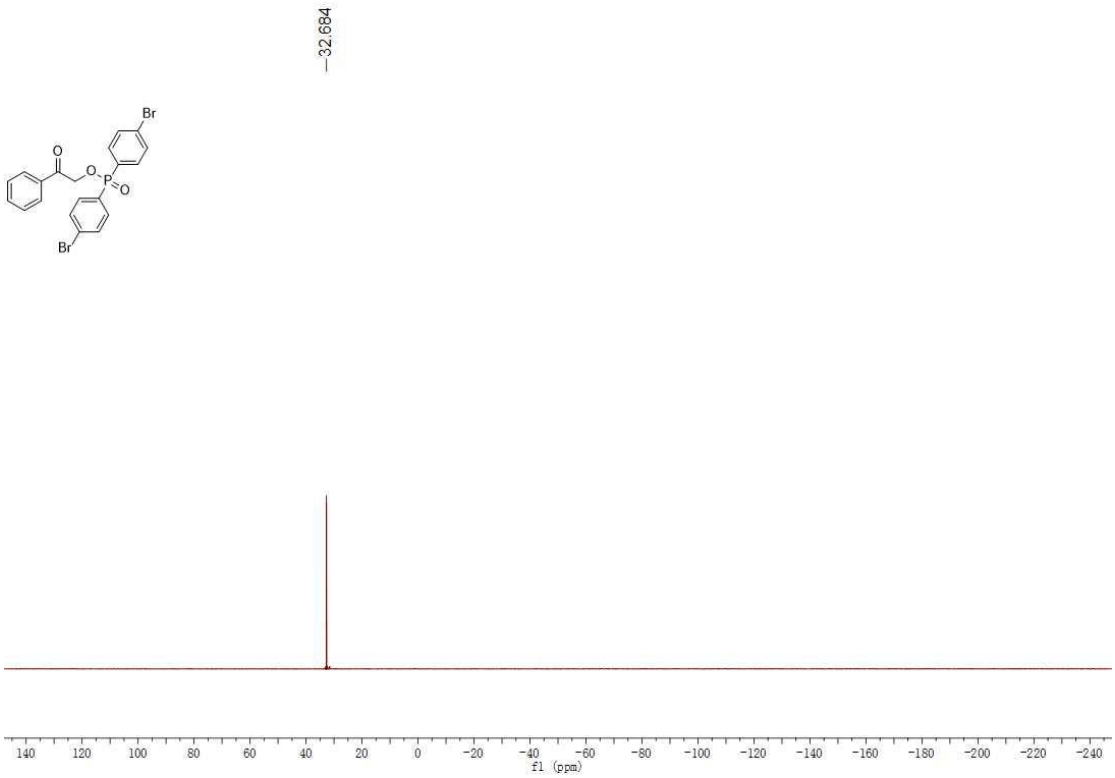
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **59**



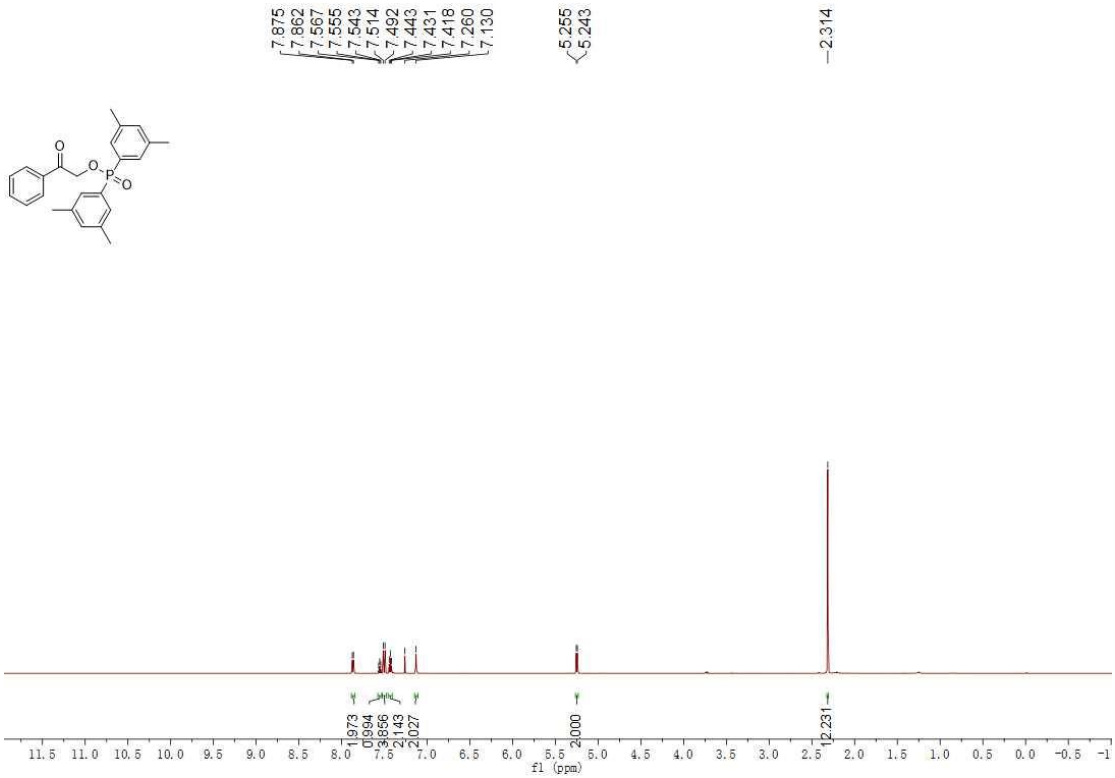
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **59**



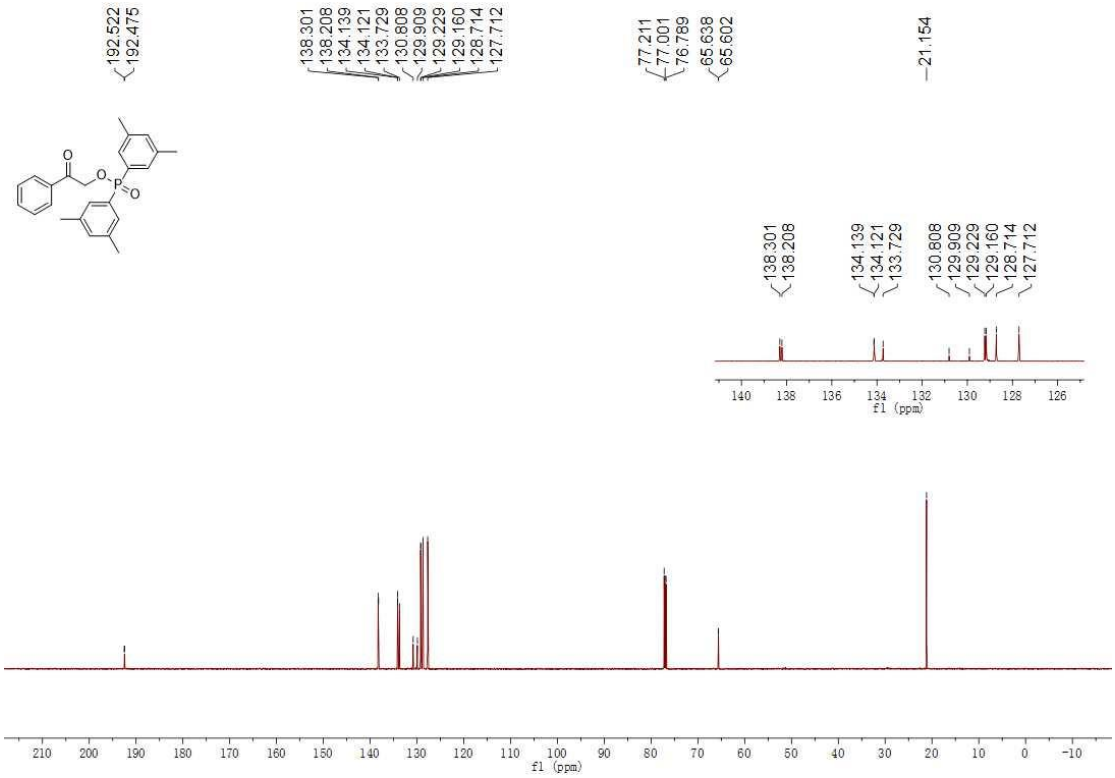
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **59**



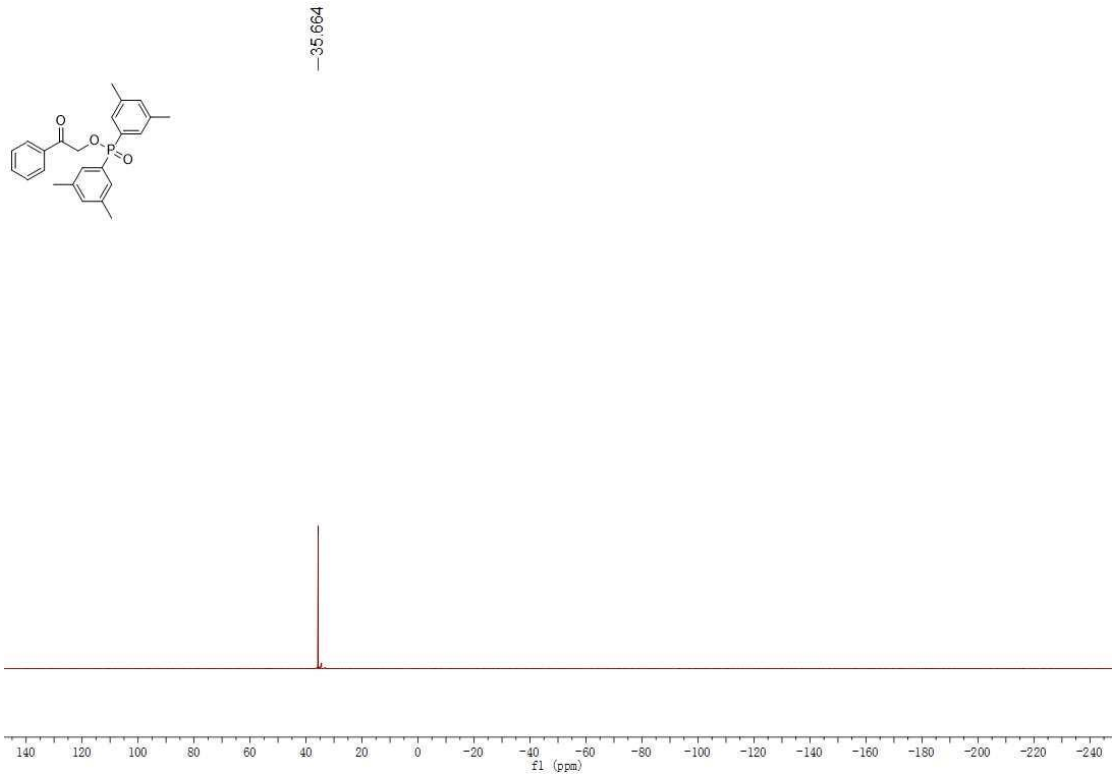
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **60**



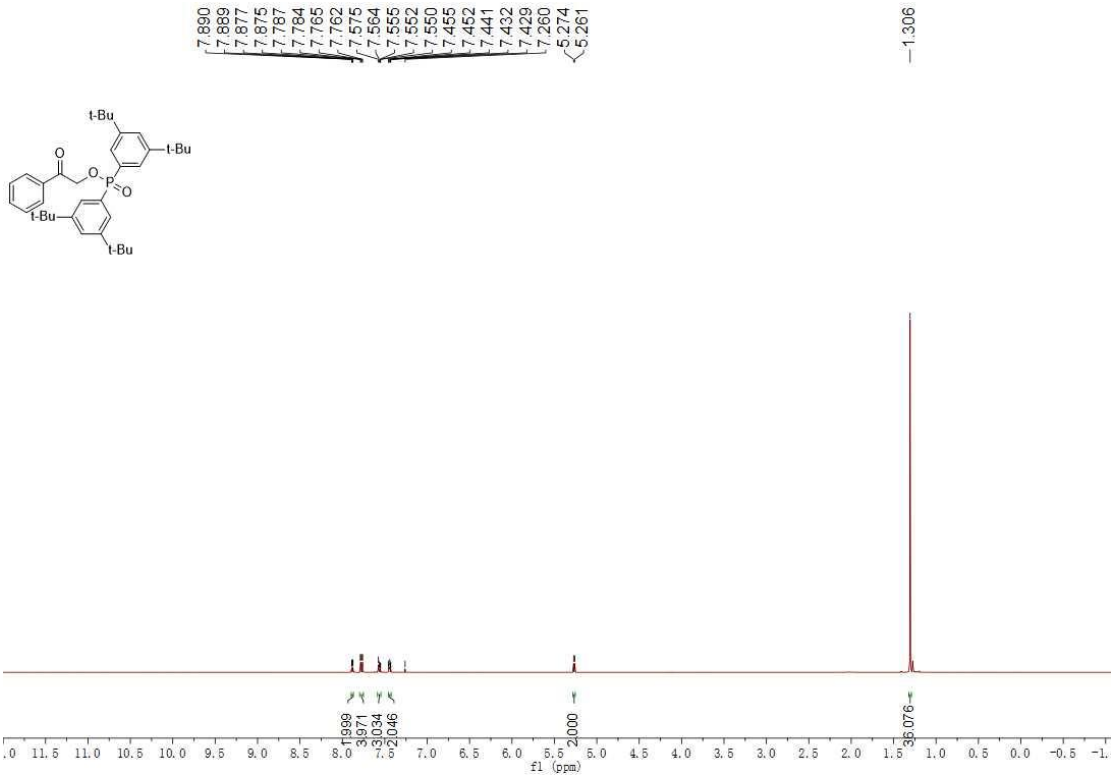
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **60**



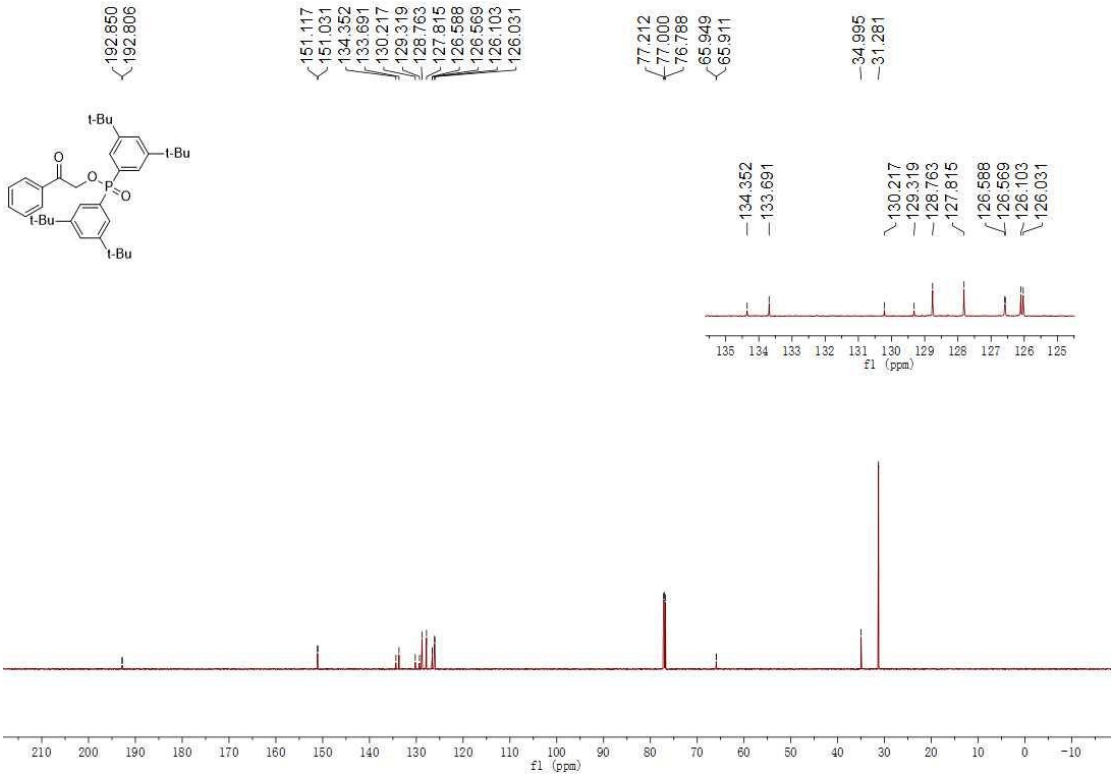
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **60**



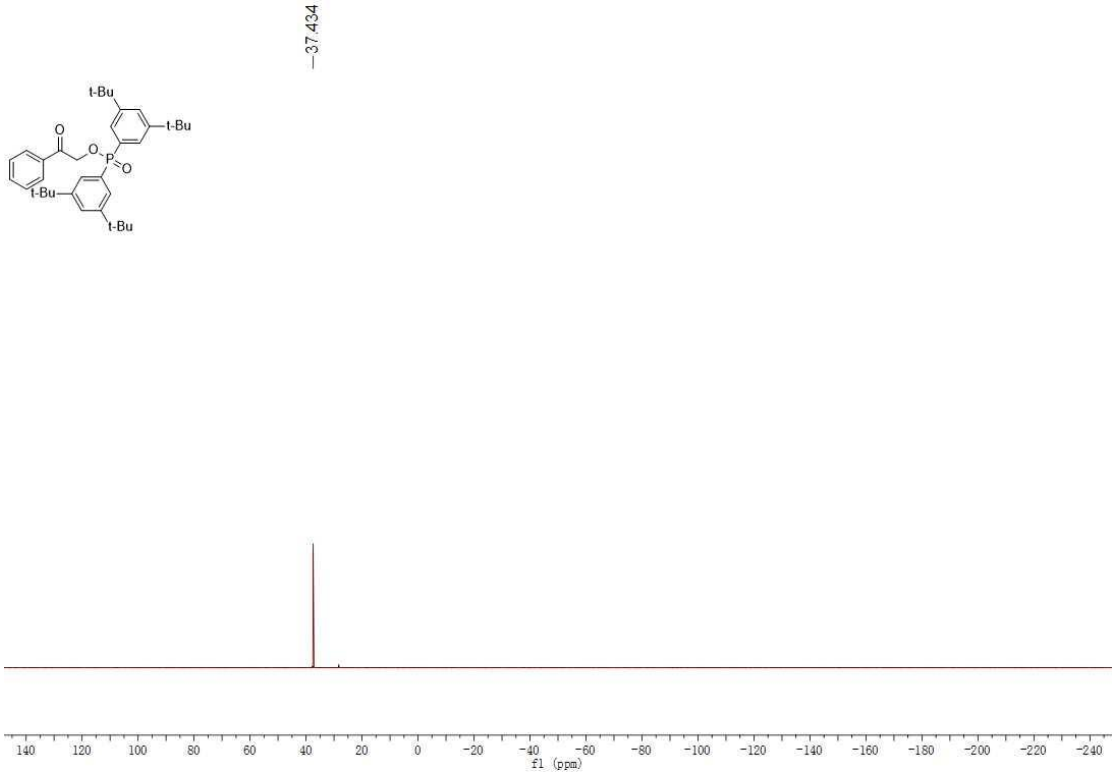
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **61**



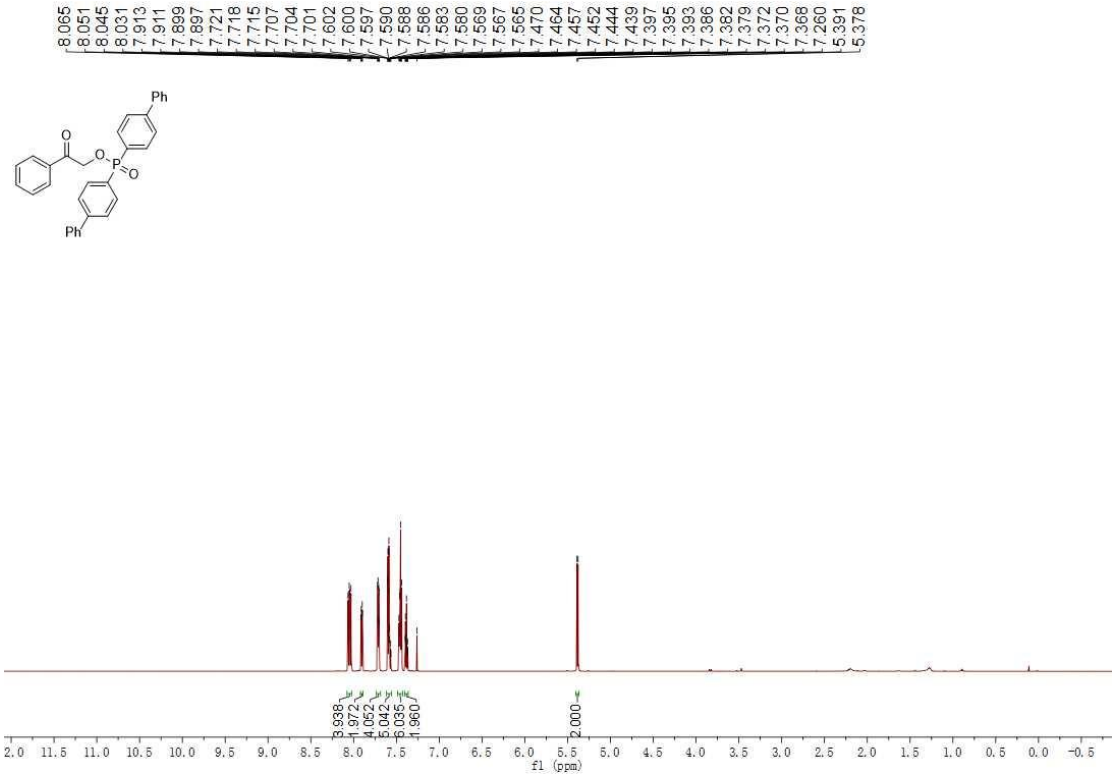
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **61**



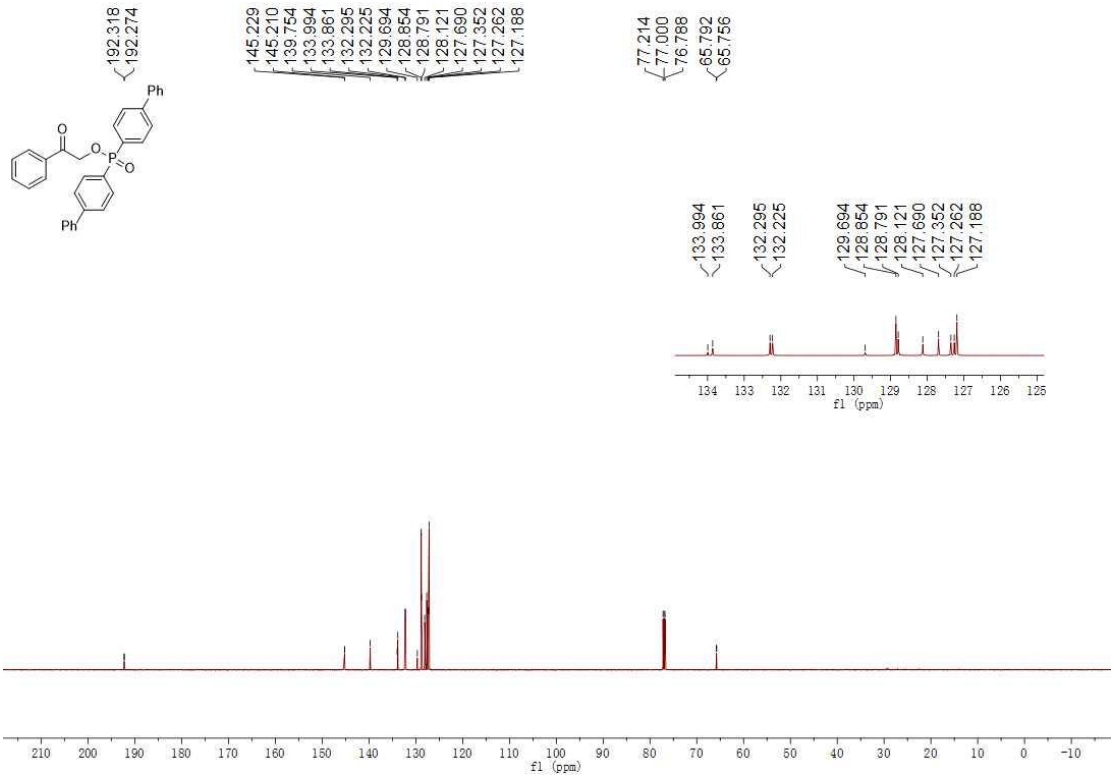
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **61**



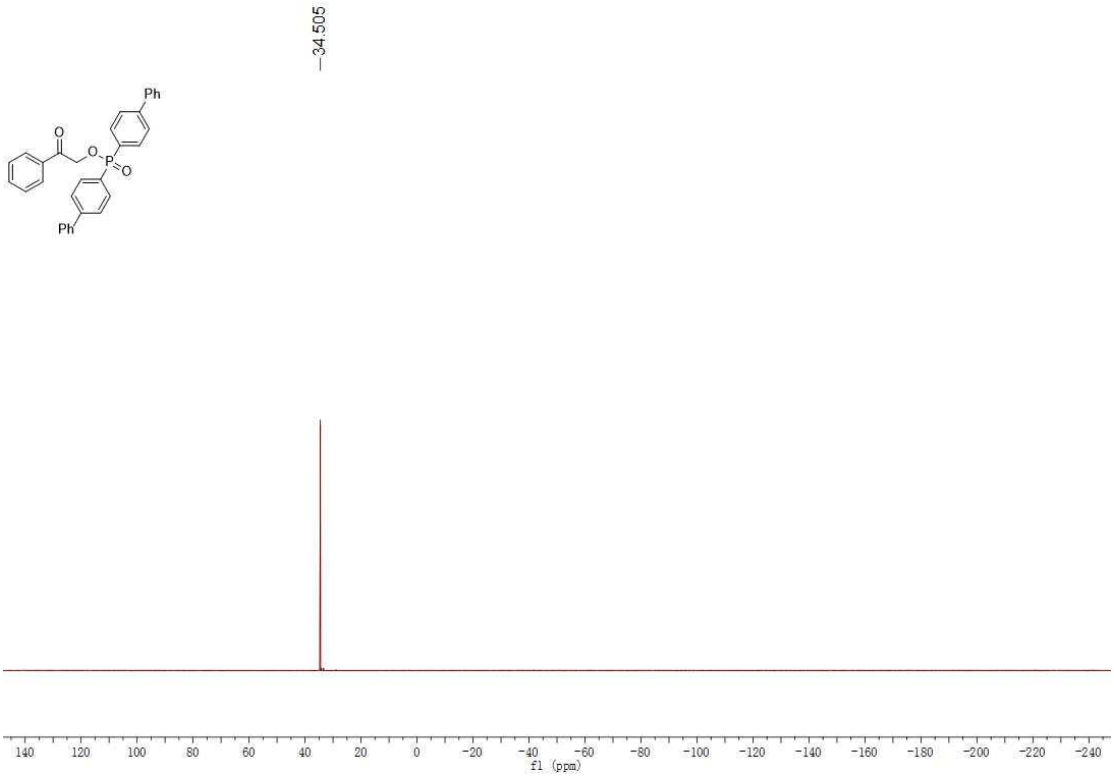
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **62**



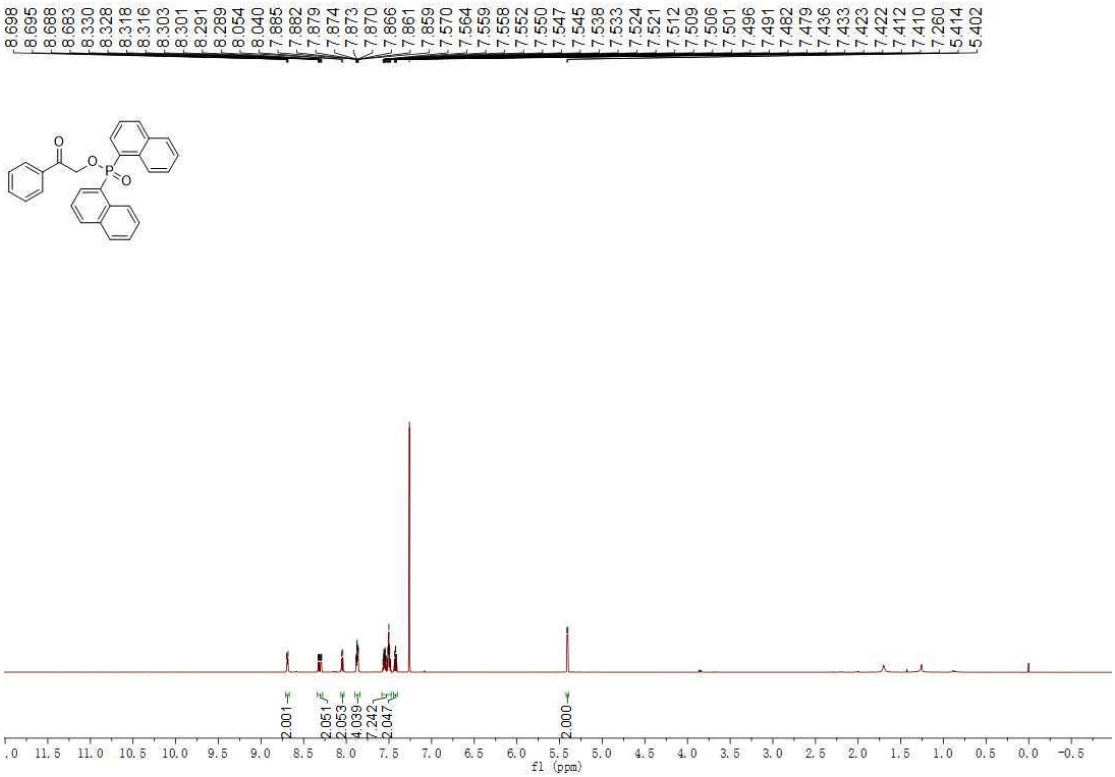
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **62**



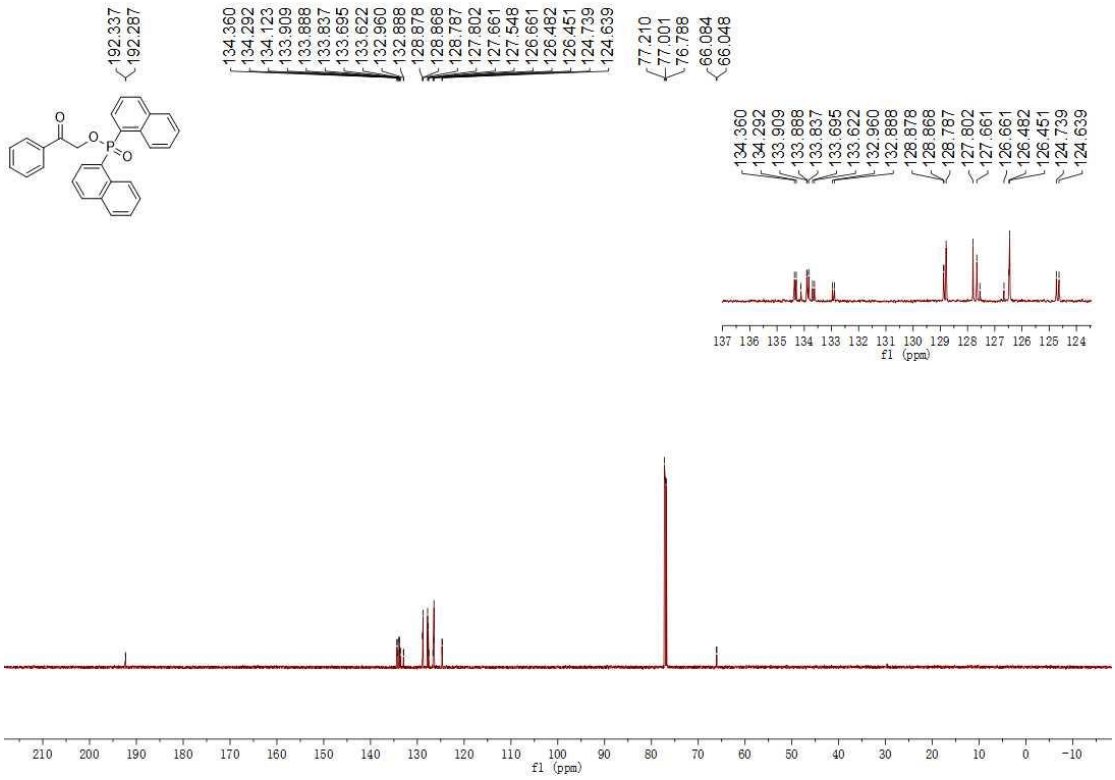
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **62**



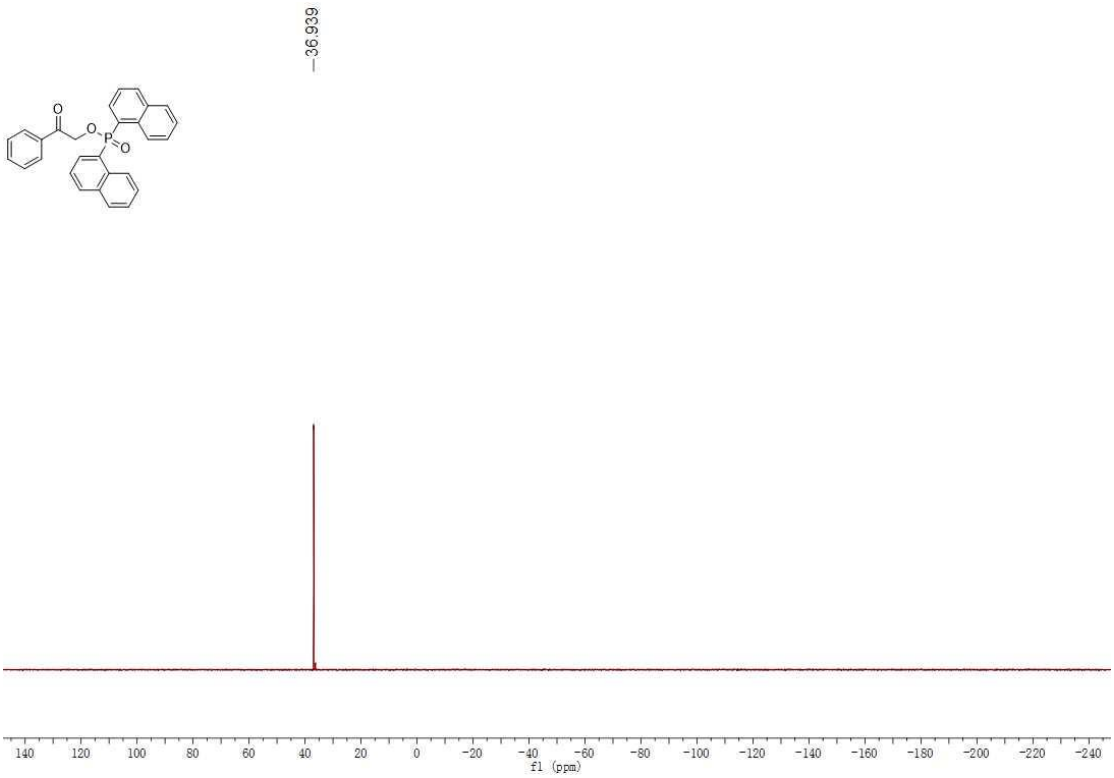
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **63**



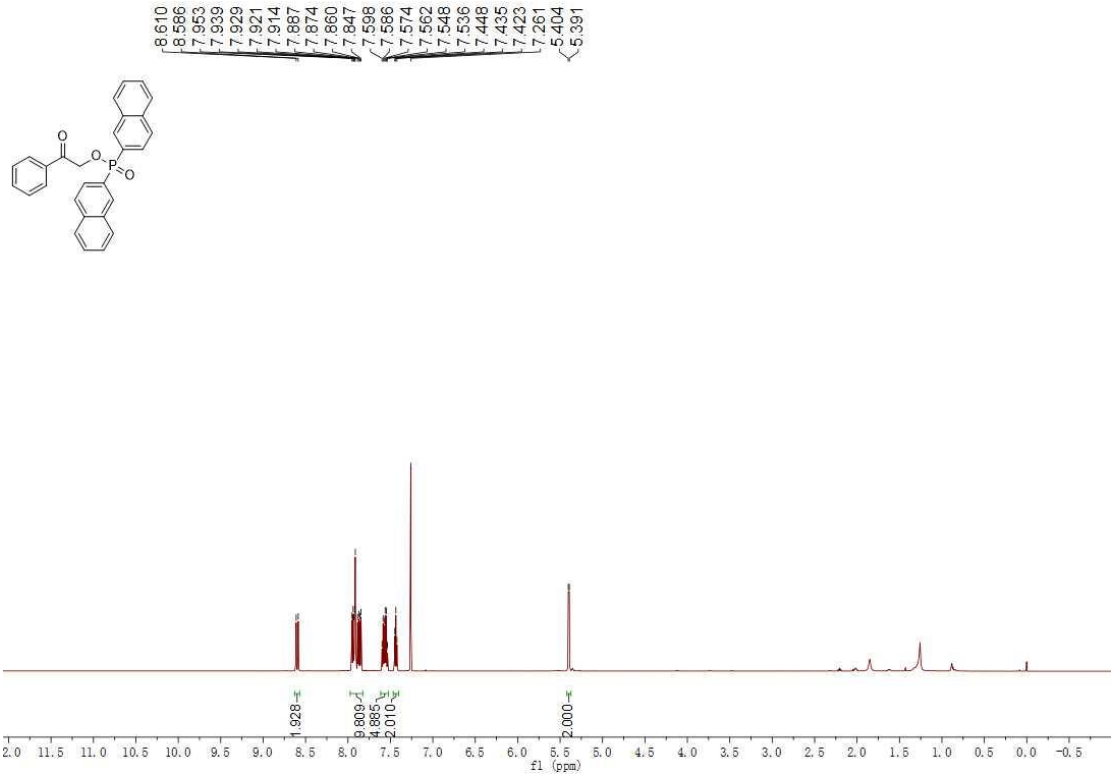
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **63**



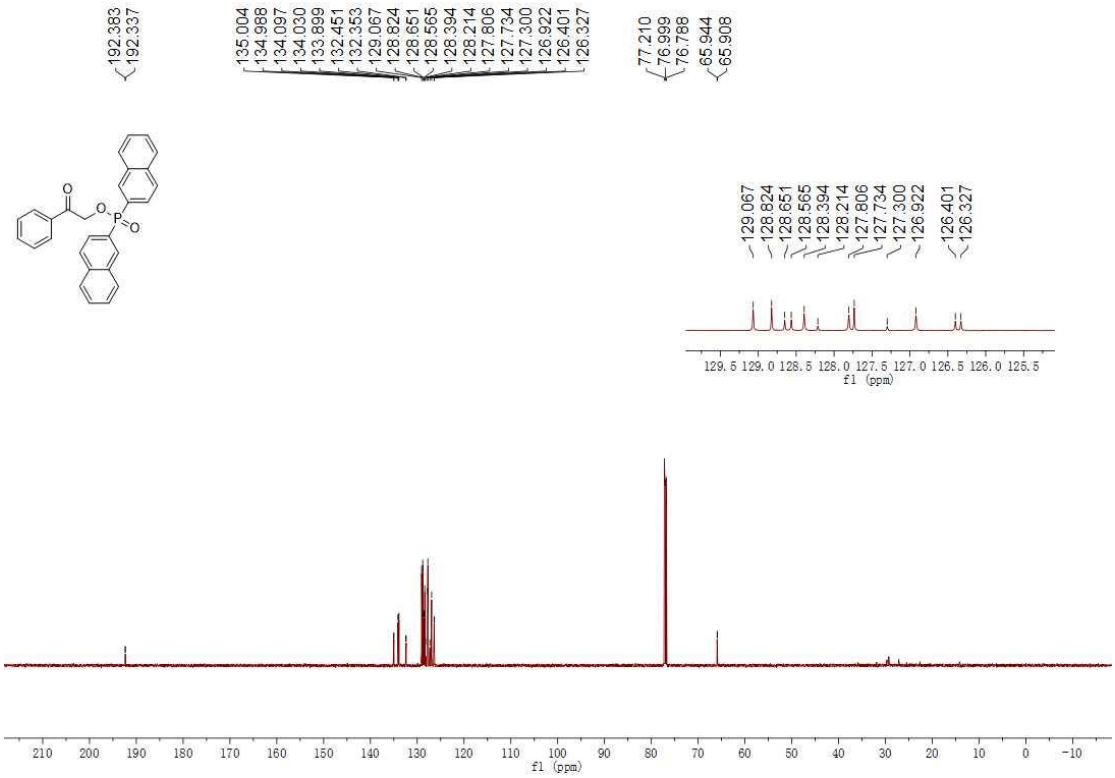
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **63**



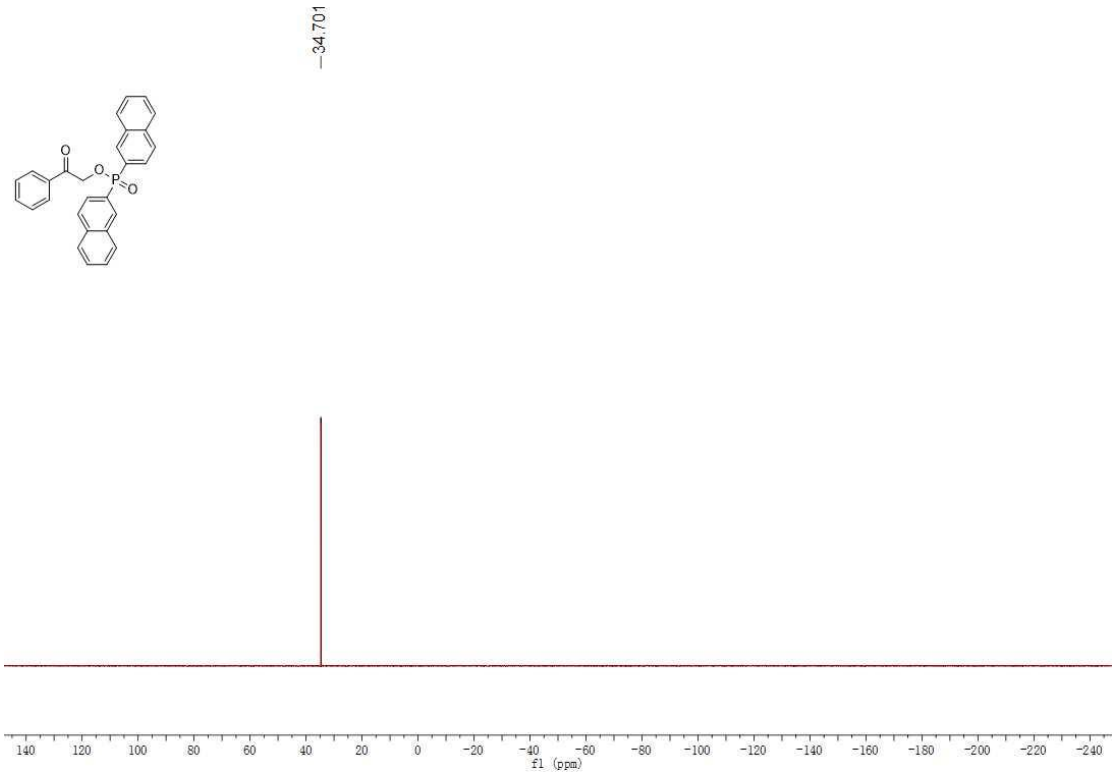
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **64**



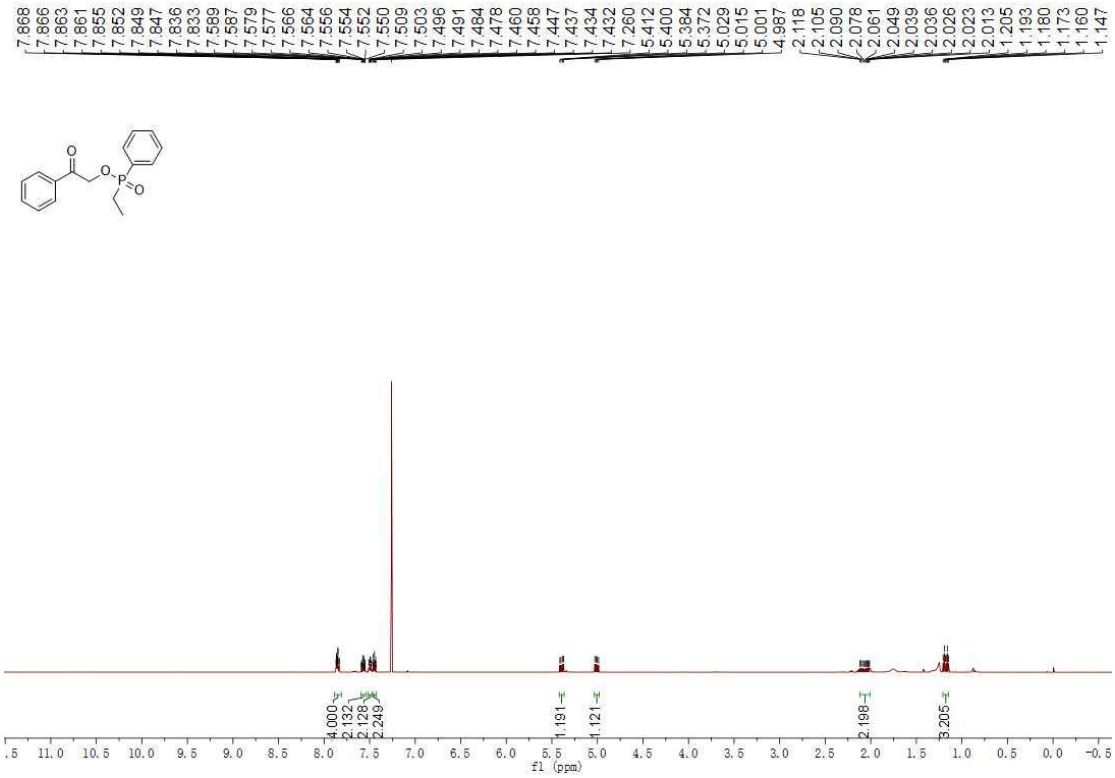
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **64**



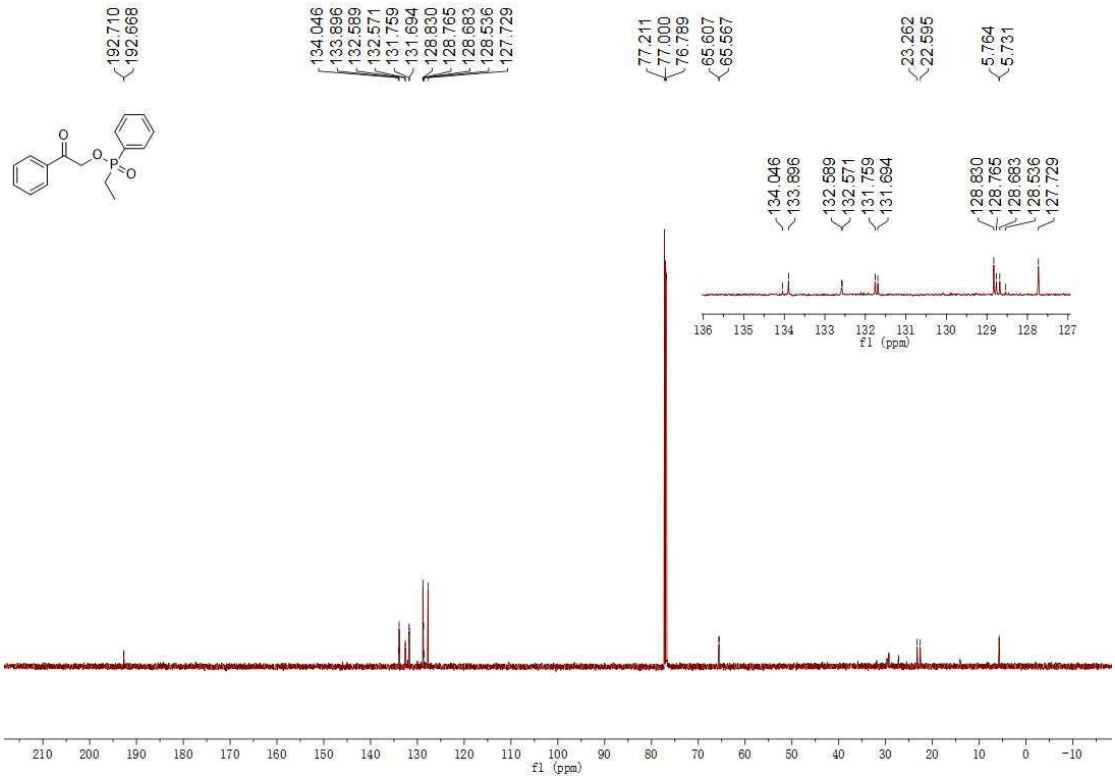
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **64**



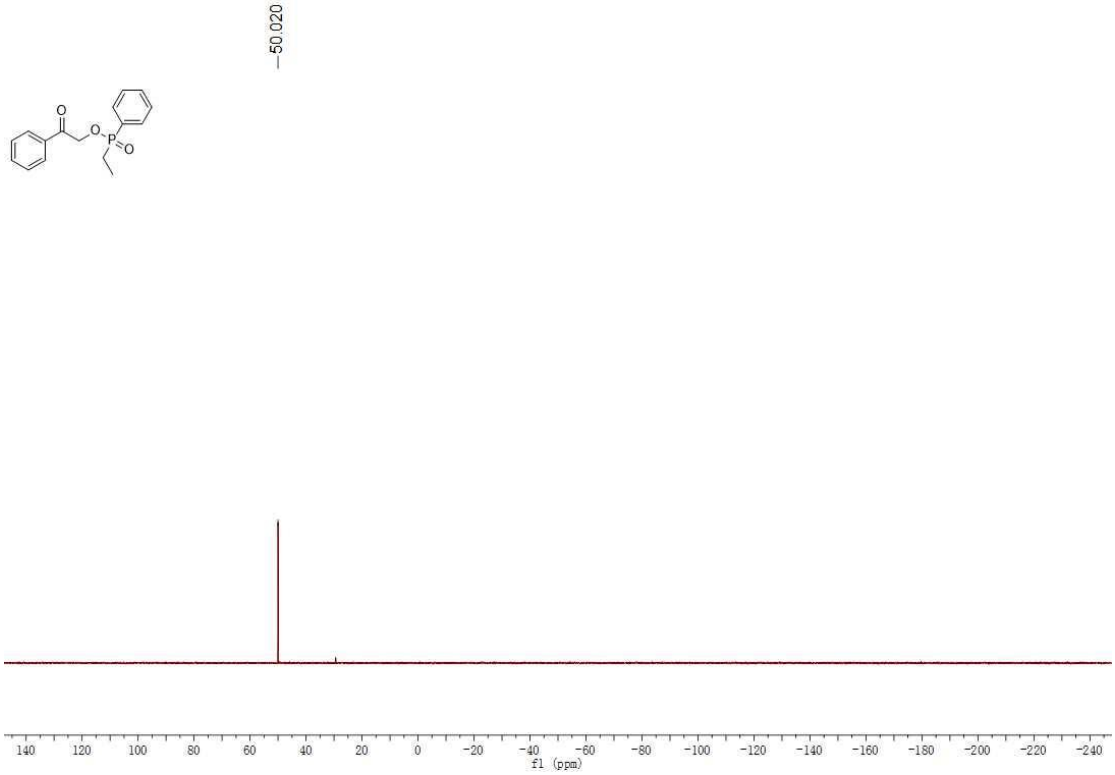
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **65**



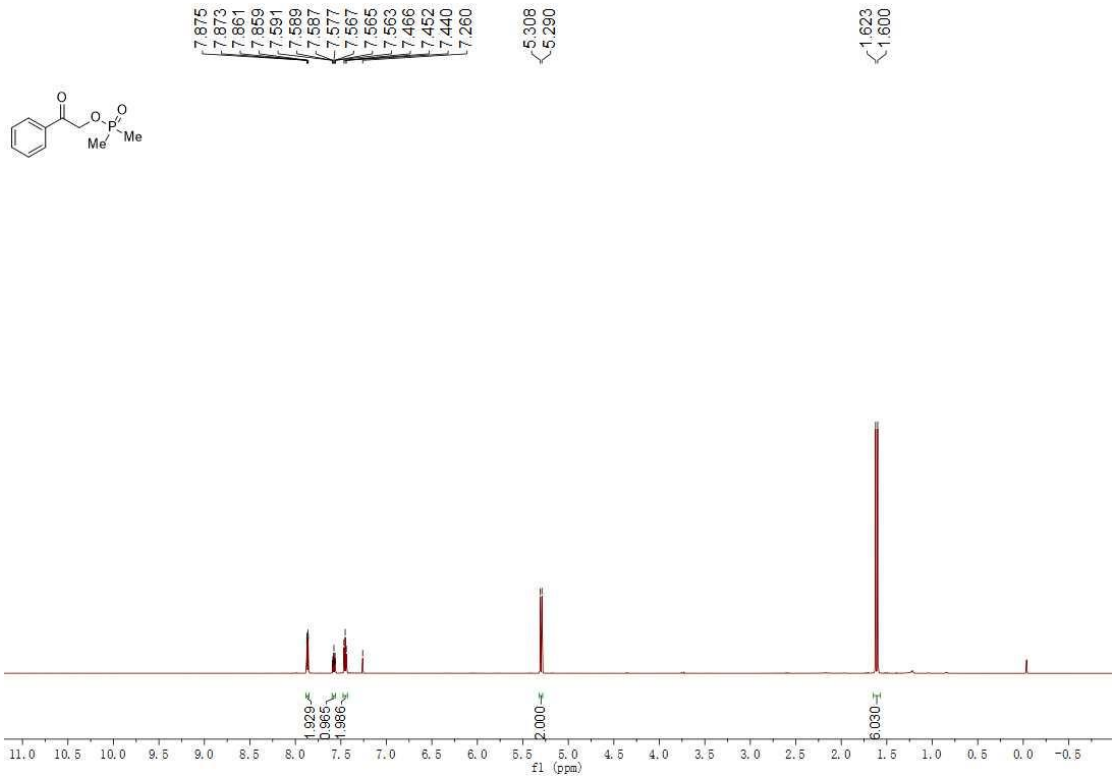
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **65**



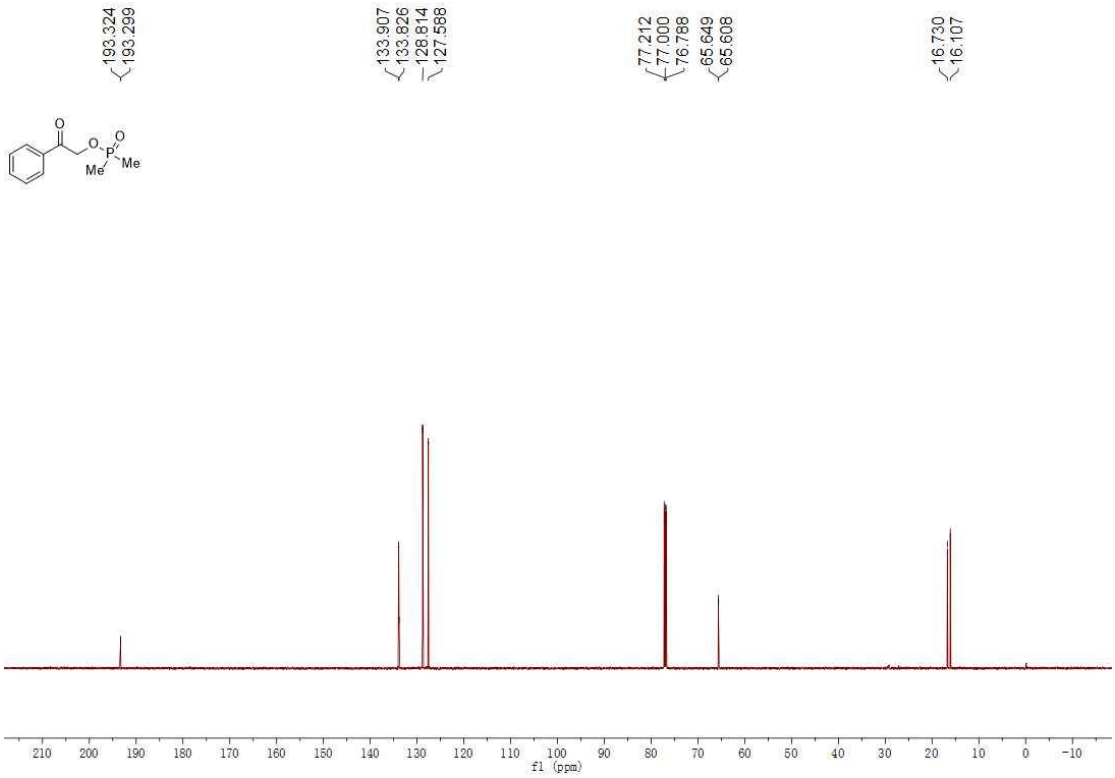
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **65**



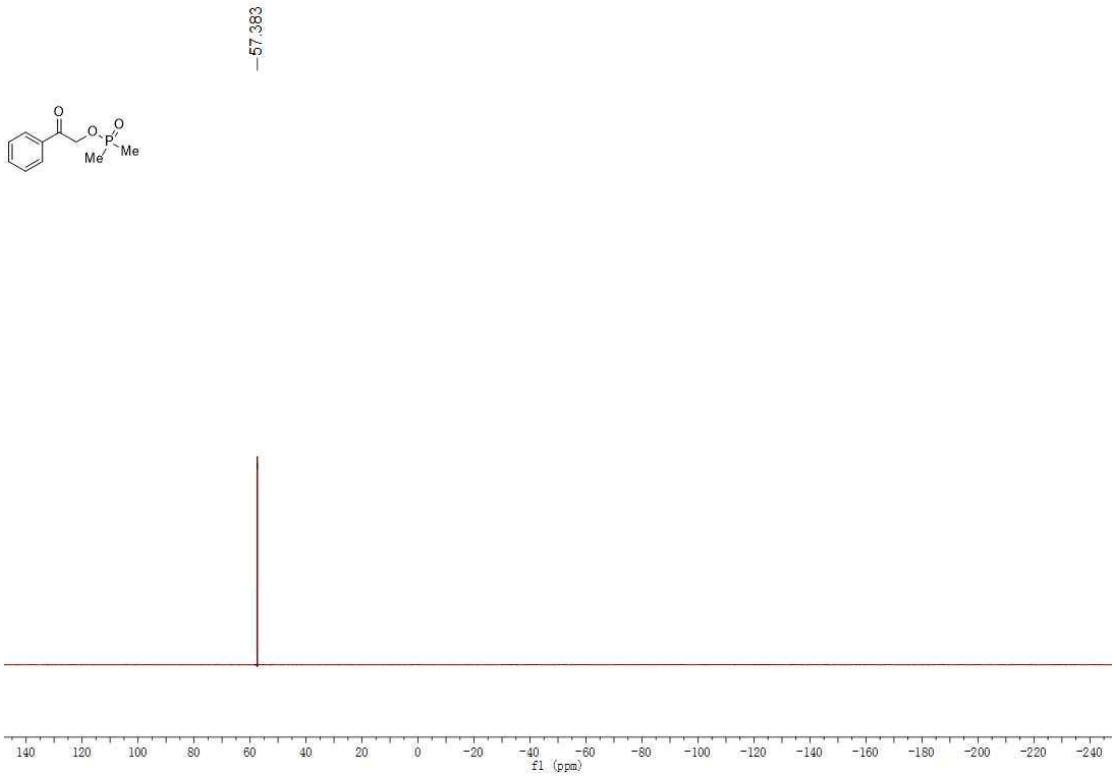
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **66**



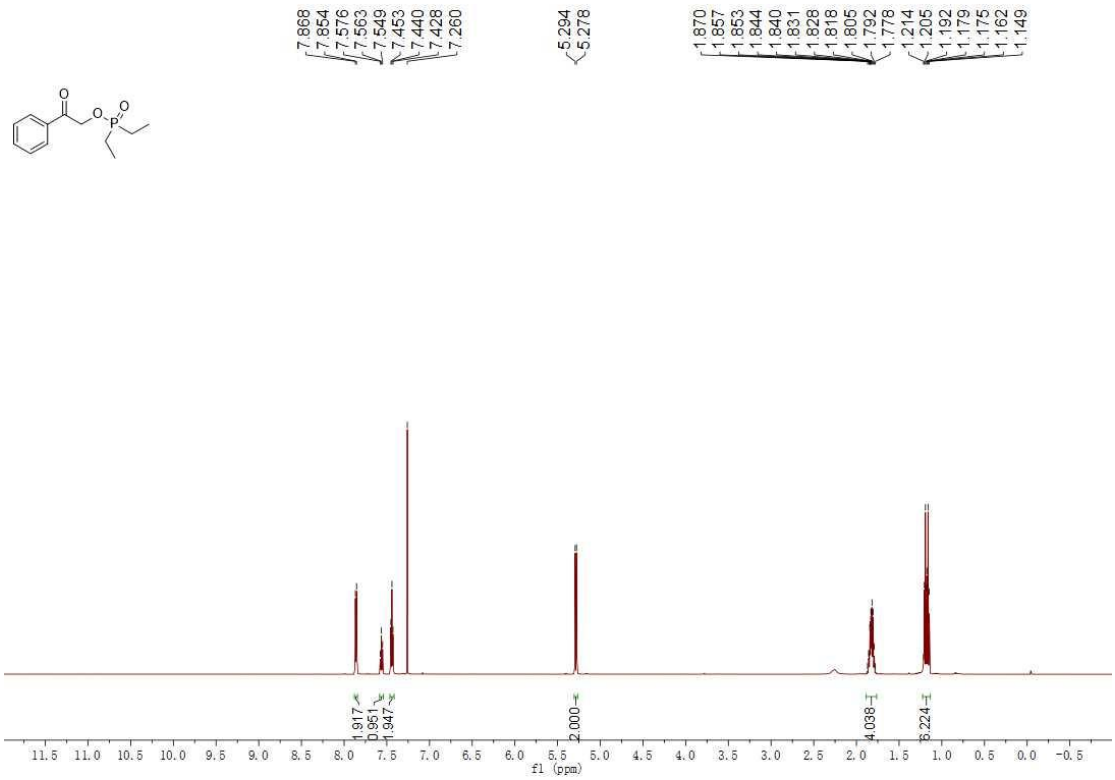
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **66**



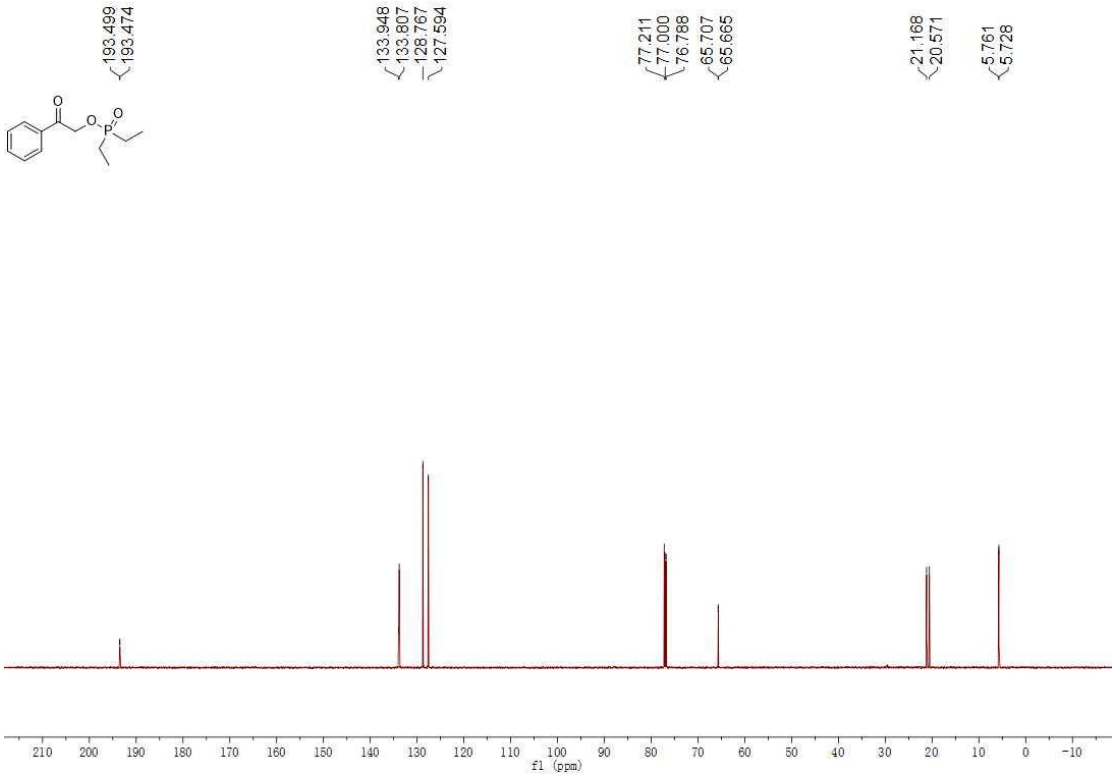
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **66**



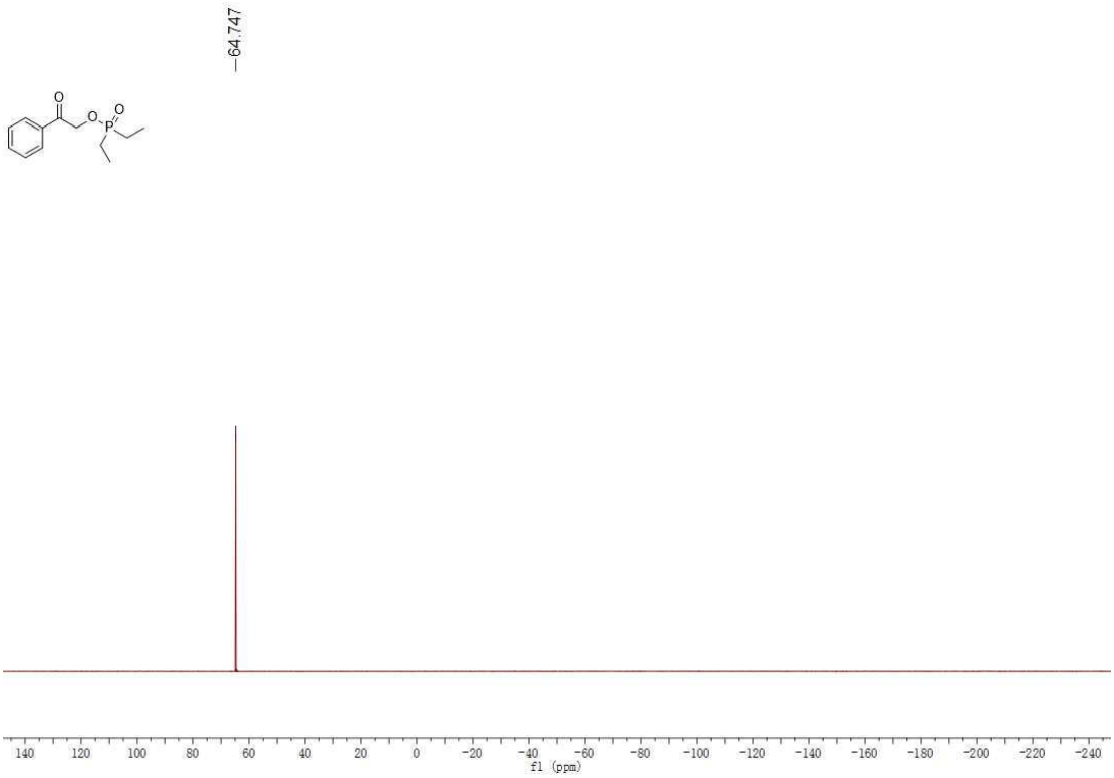
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **67**



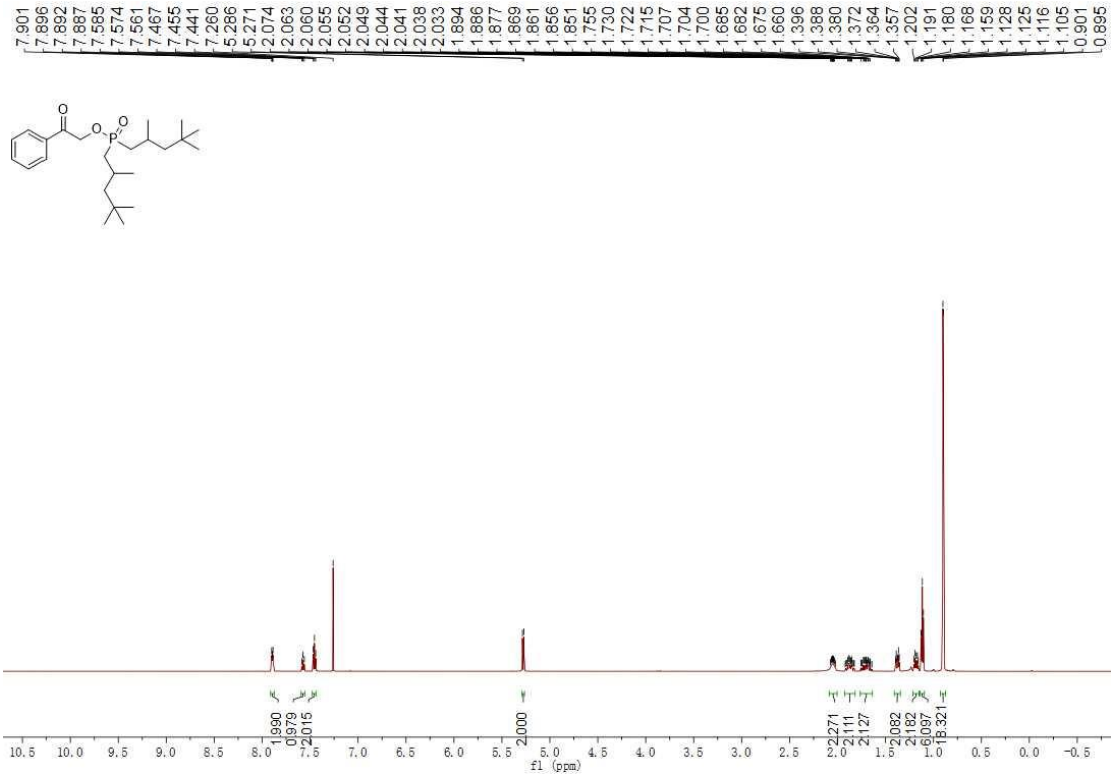
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **67**



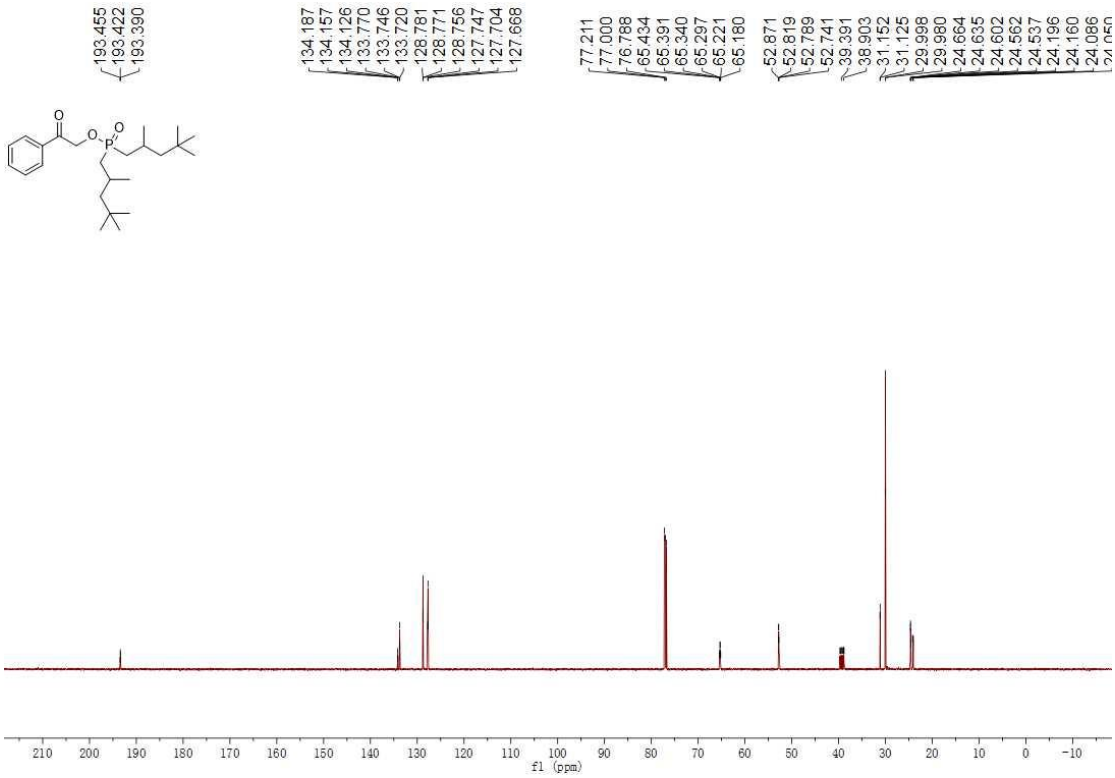
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **67**



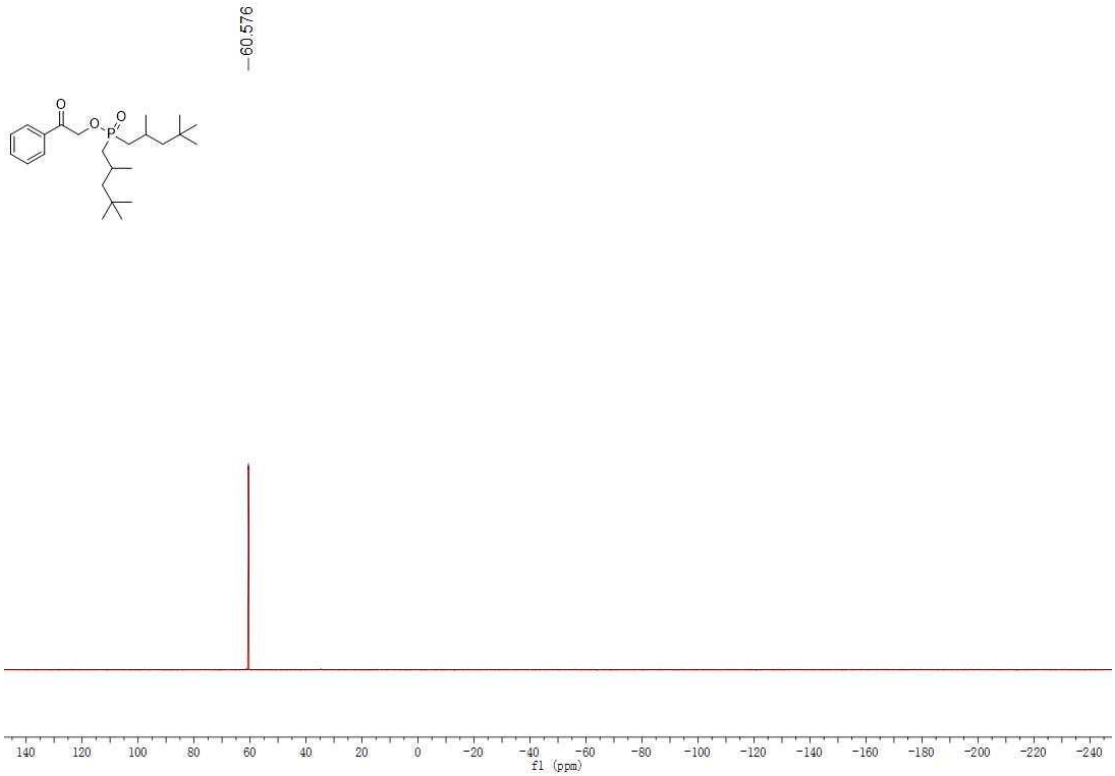
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **68**



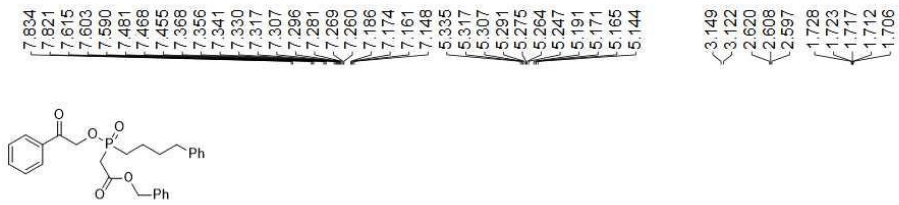
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **68**

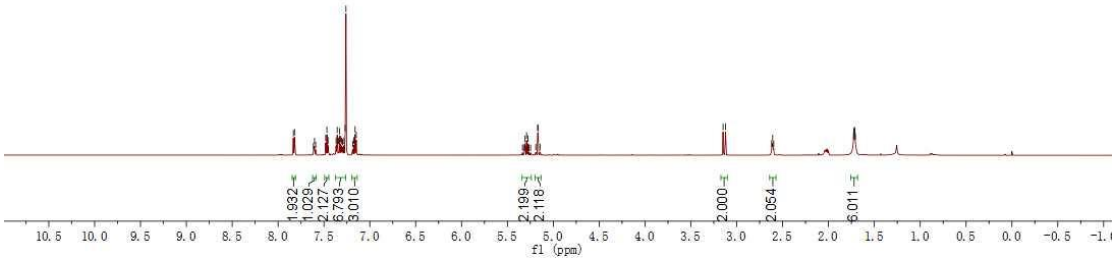


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **68**

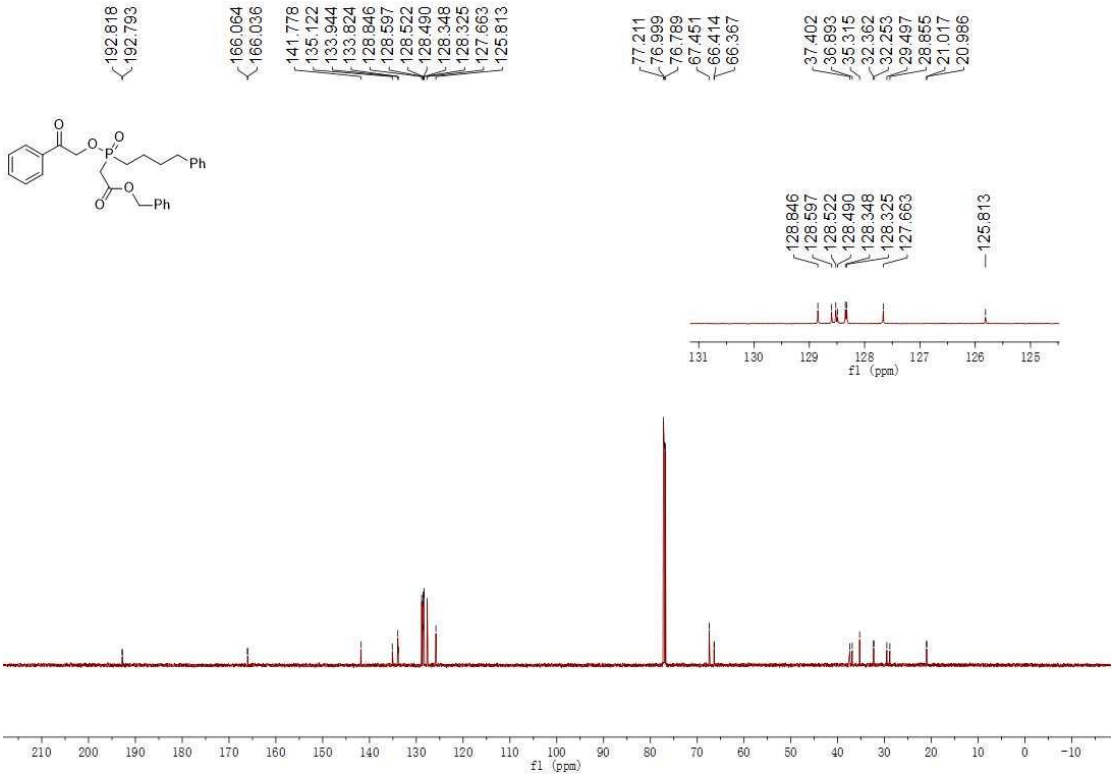


^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **69**

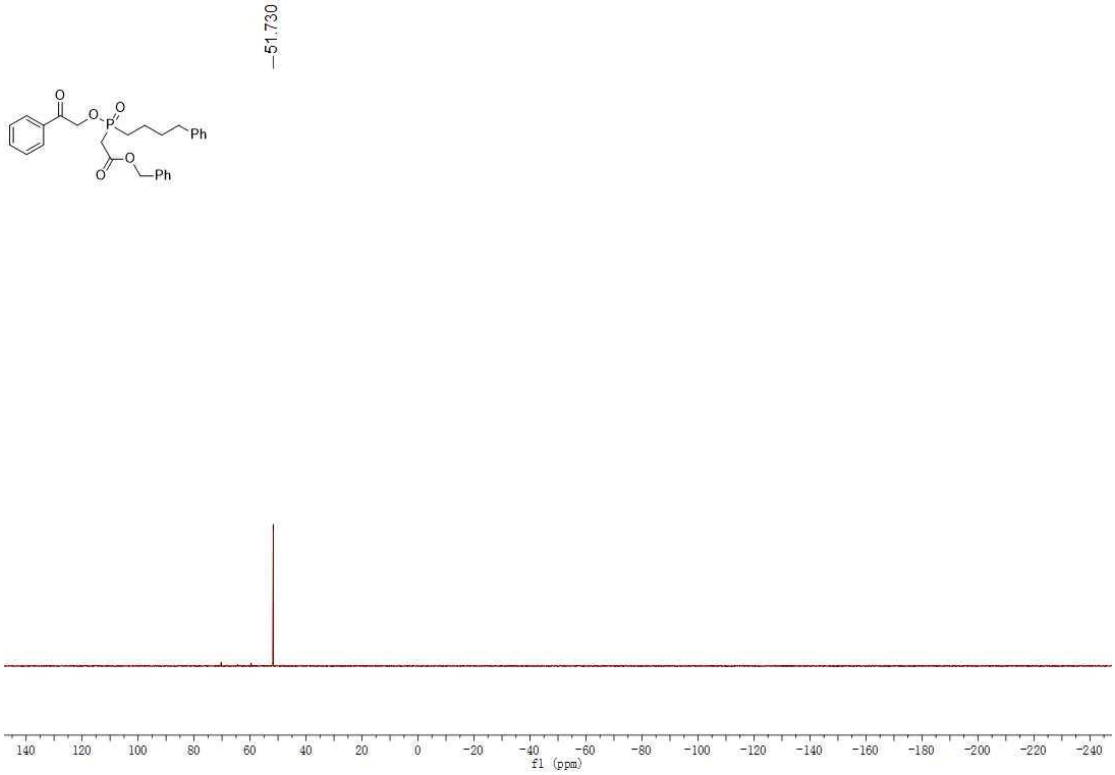




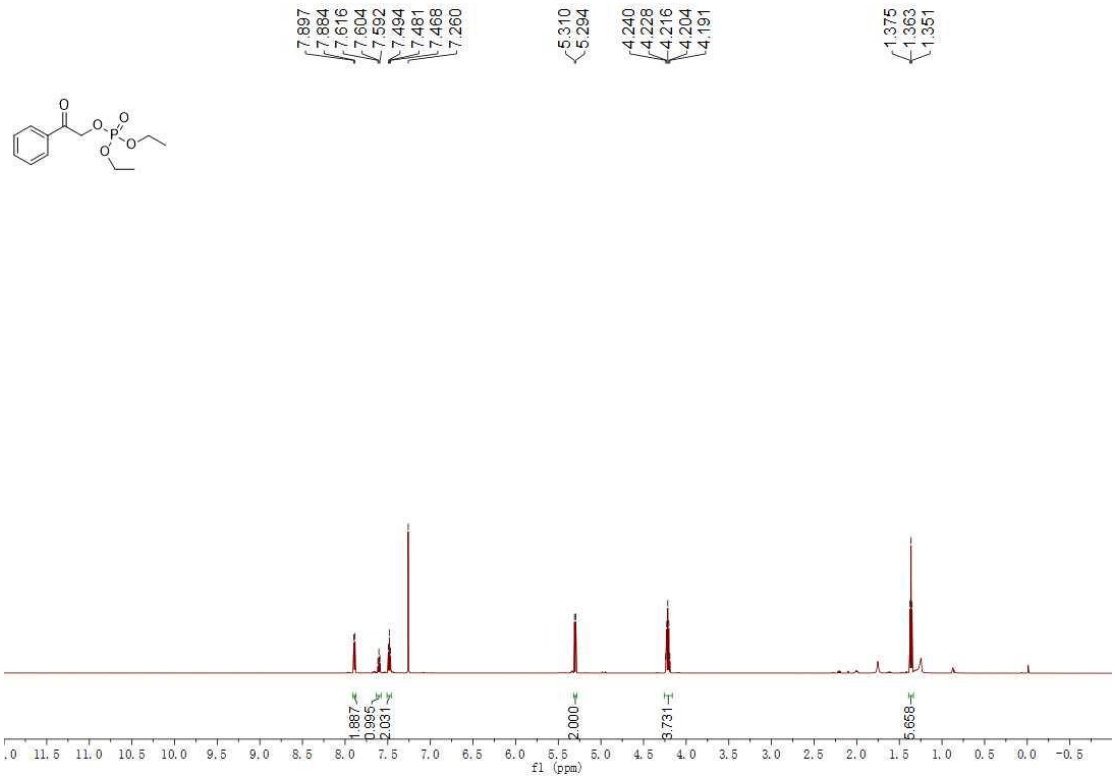
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **69**



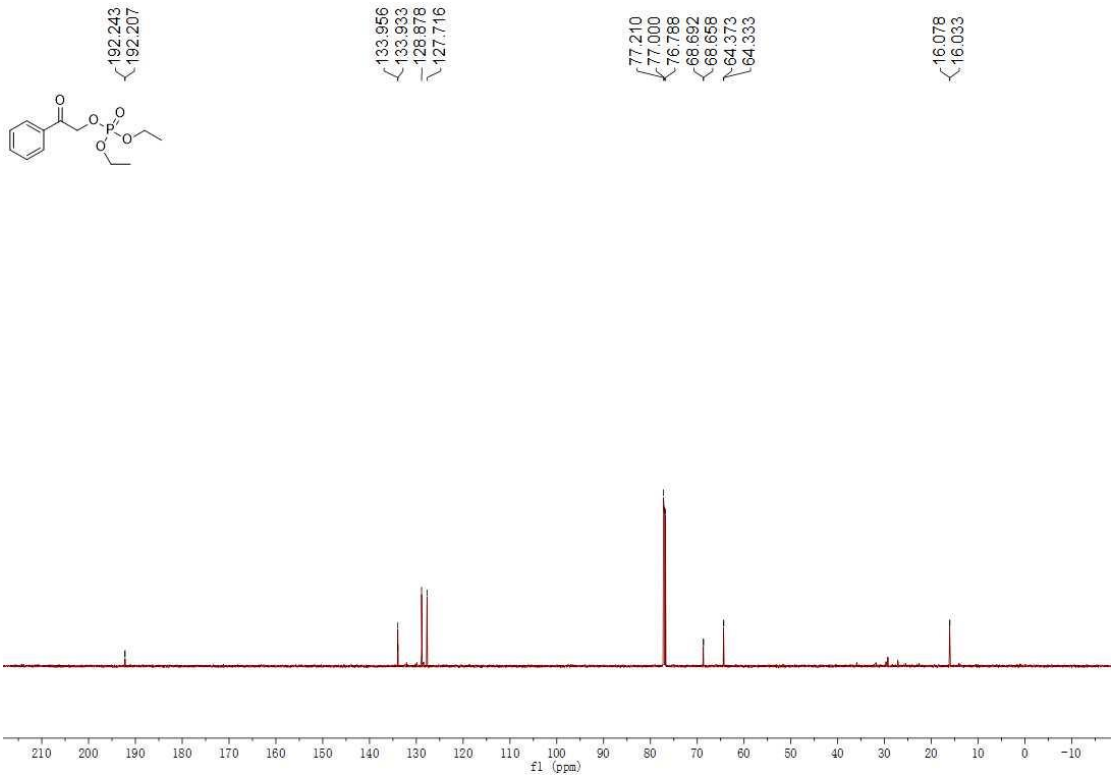
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **69**



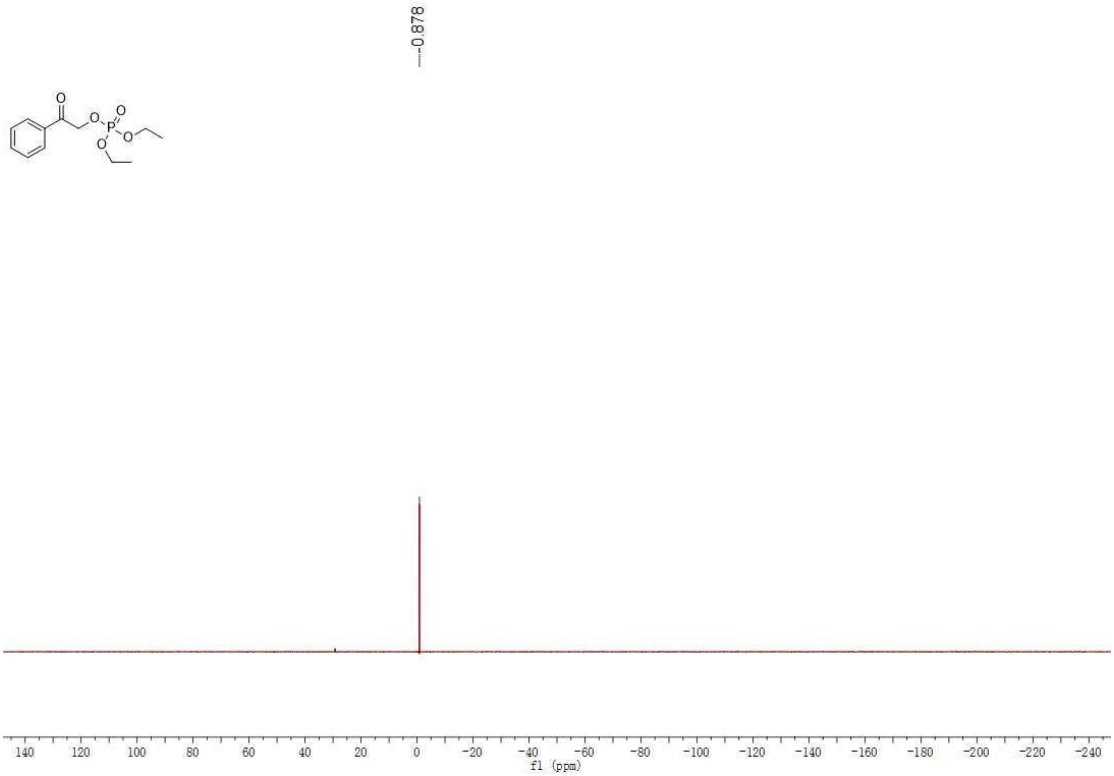
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **70**



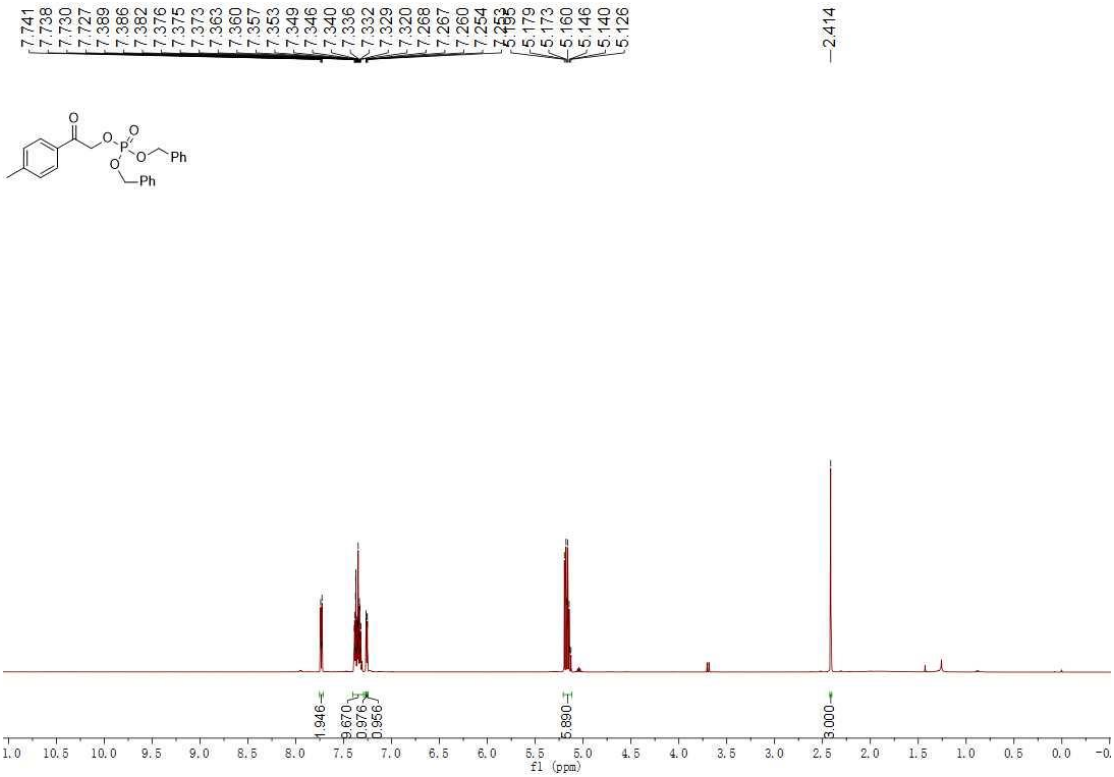
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **70**



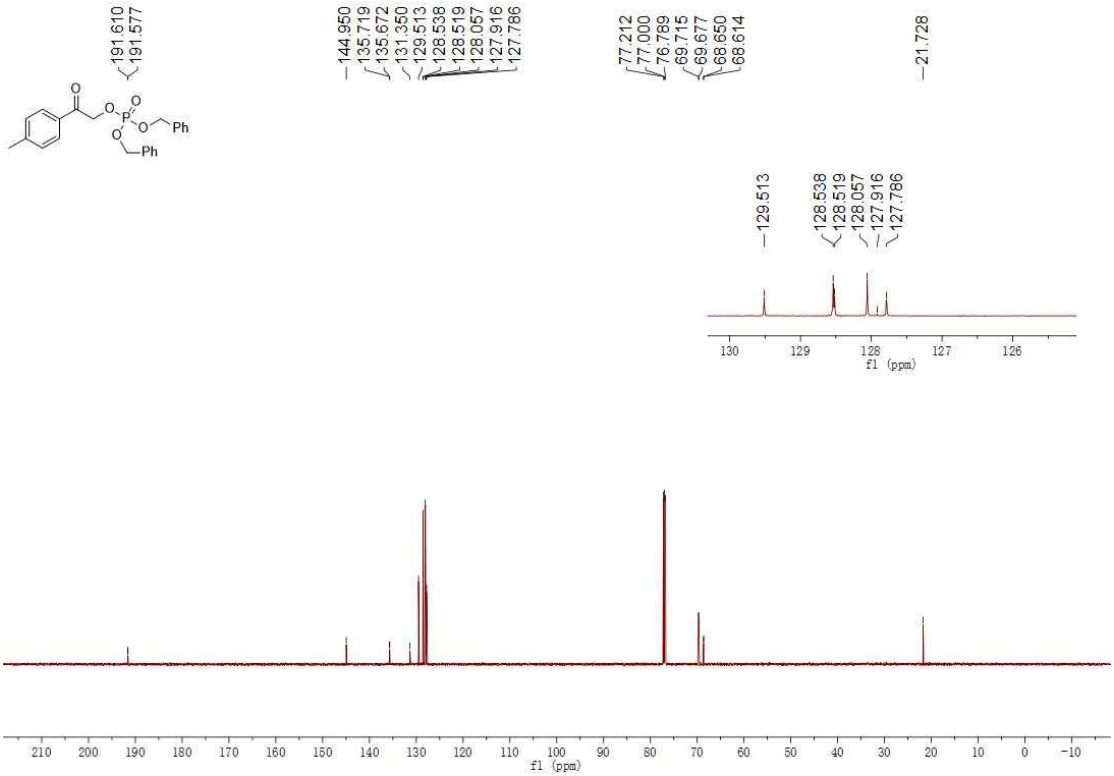
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **70**



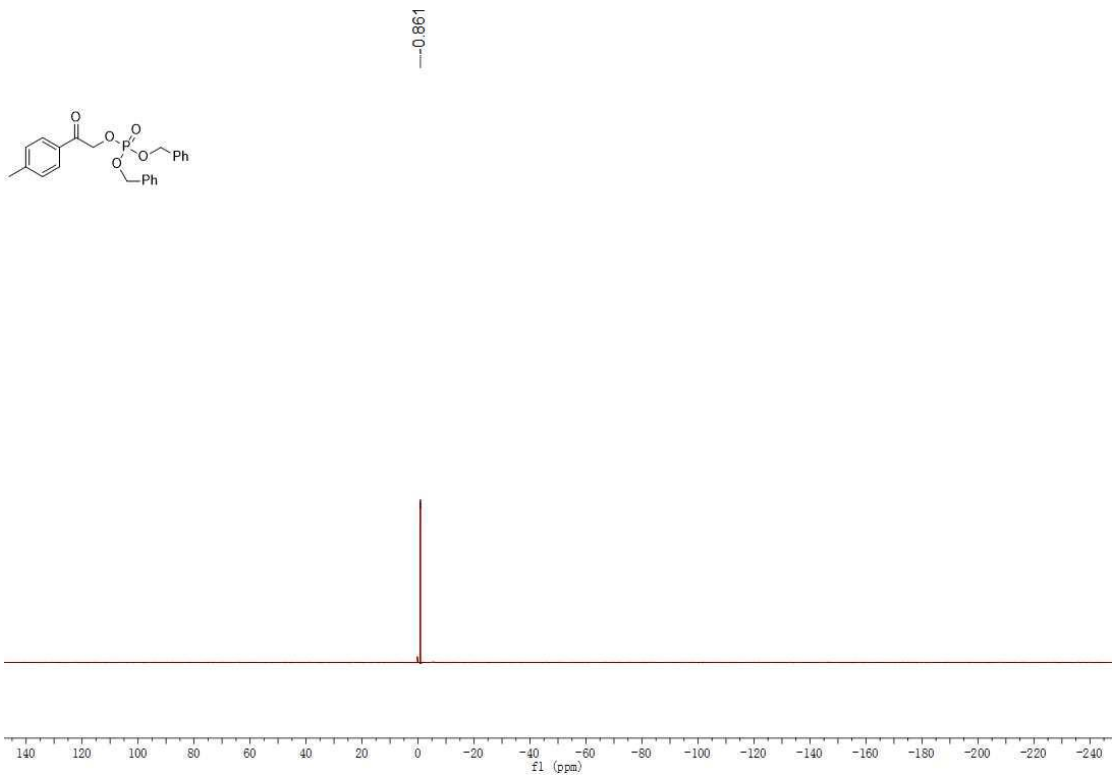
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **71**



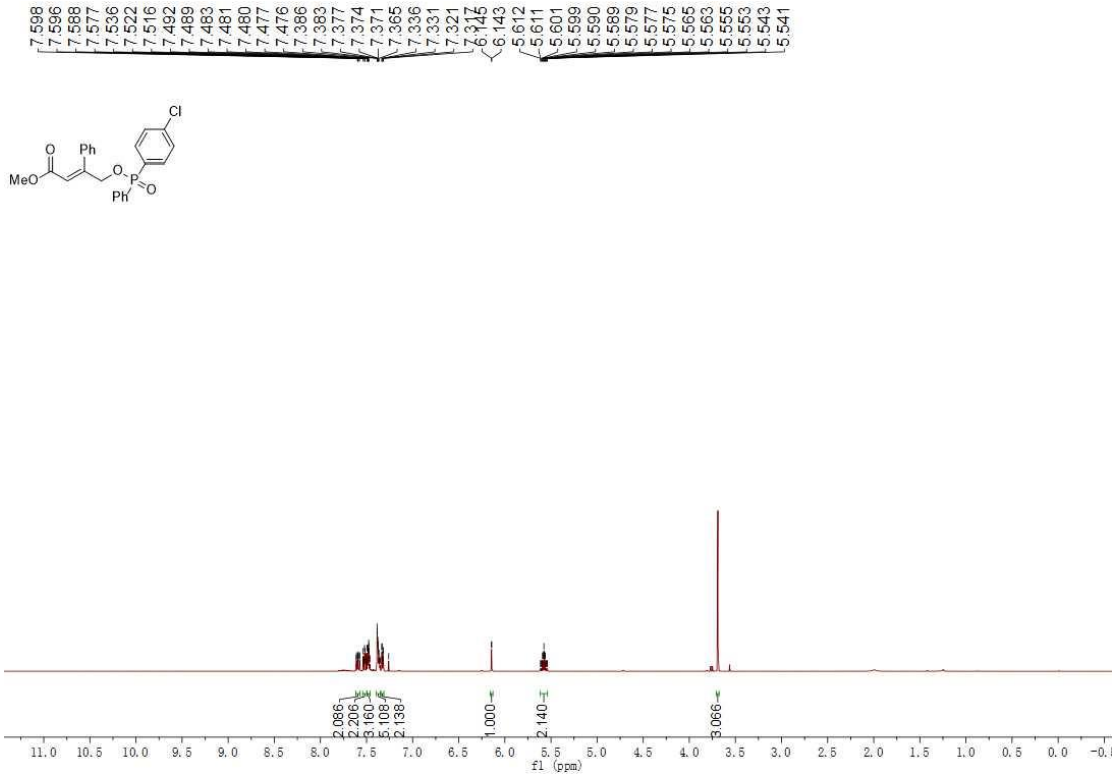
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **71**



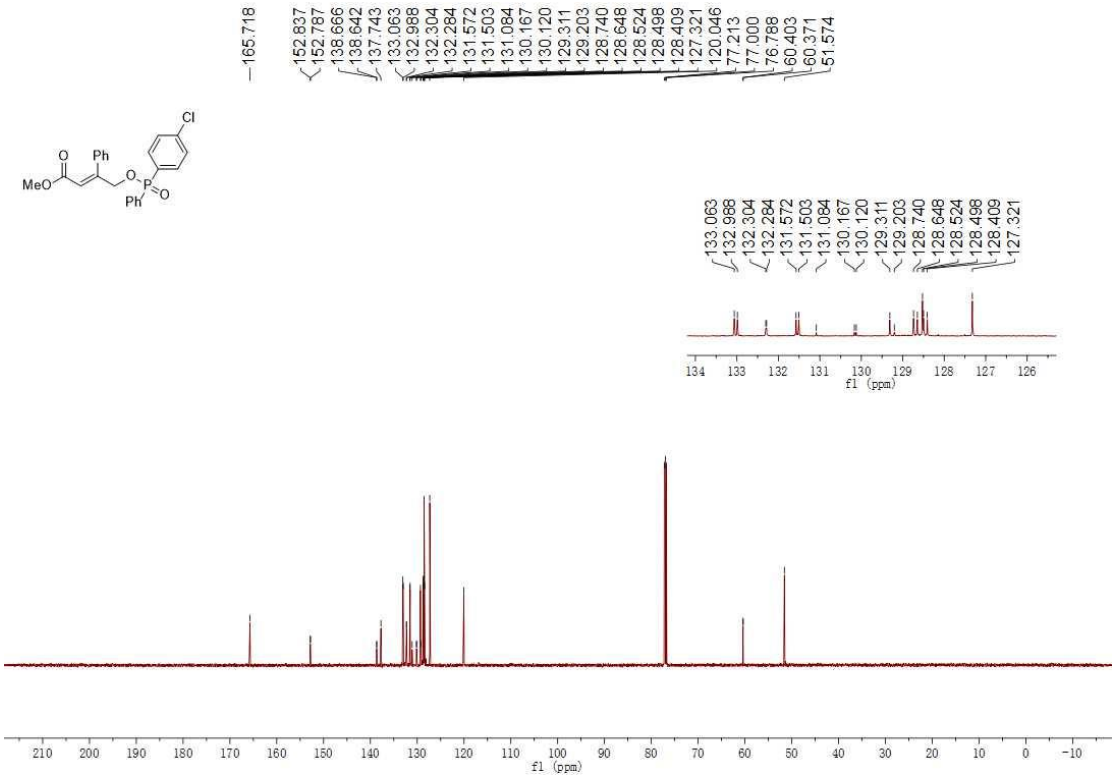
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **71**



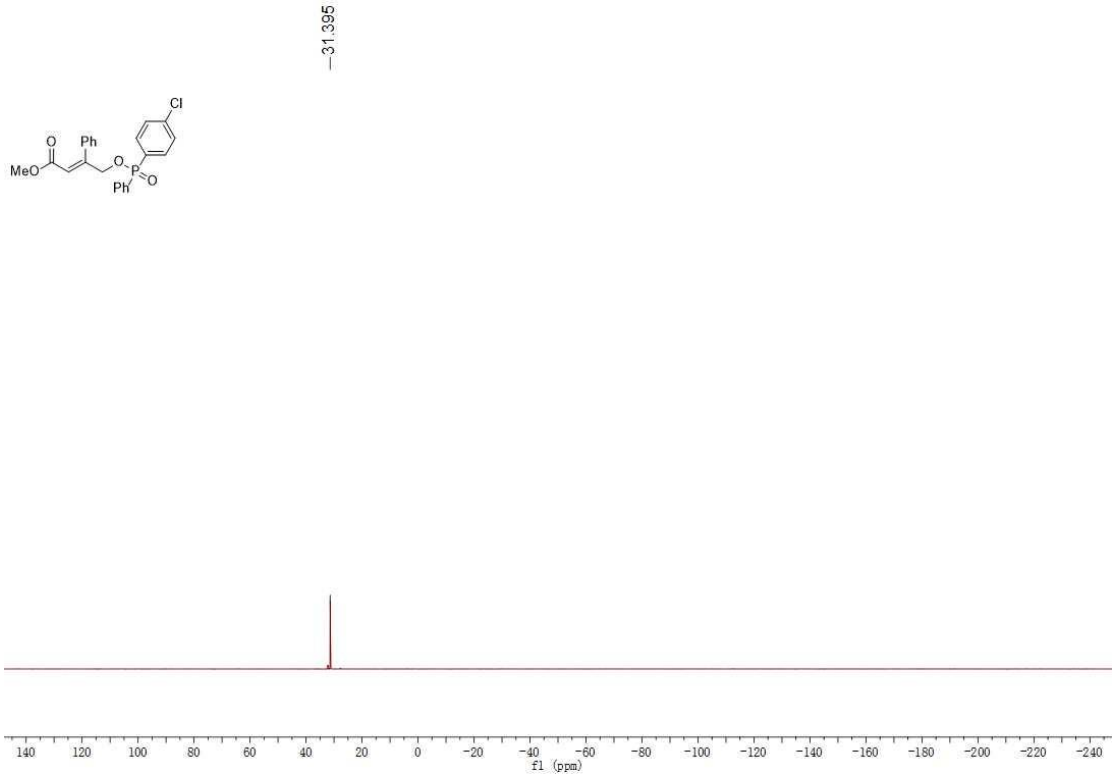
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **72**



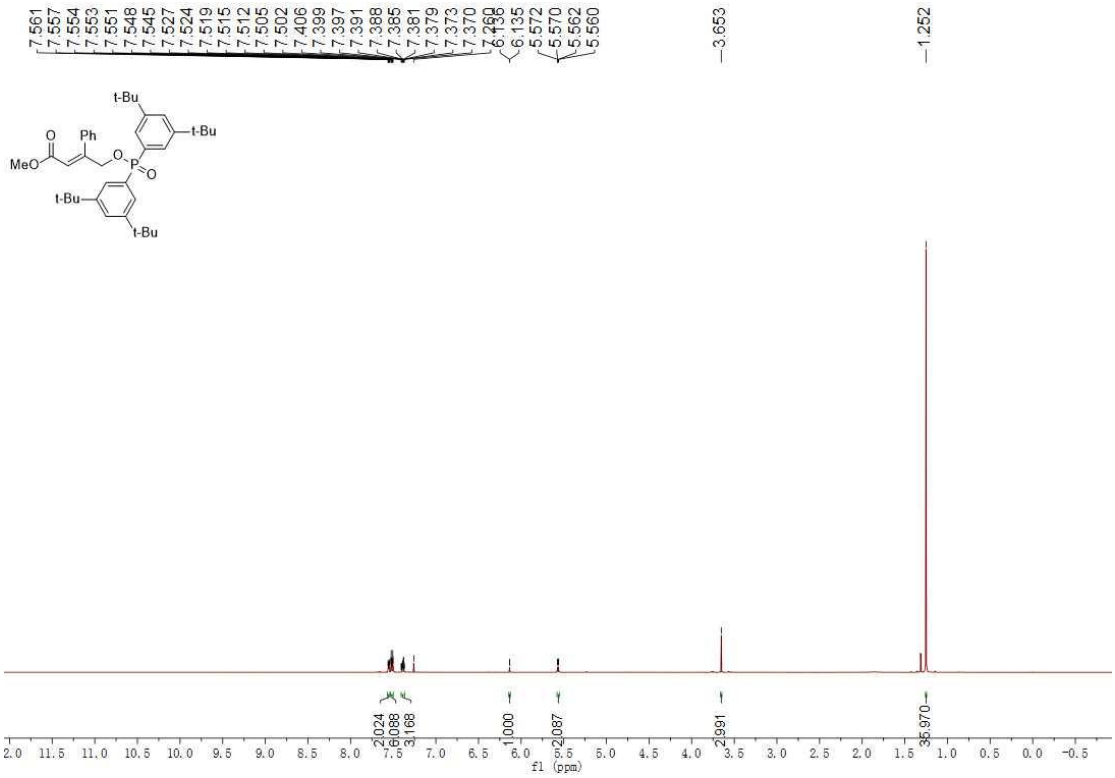
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **72**



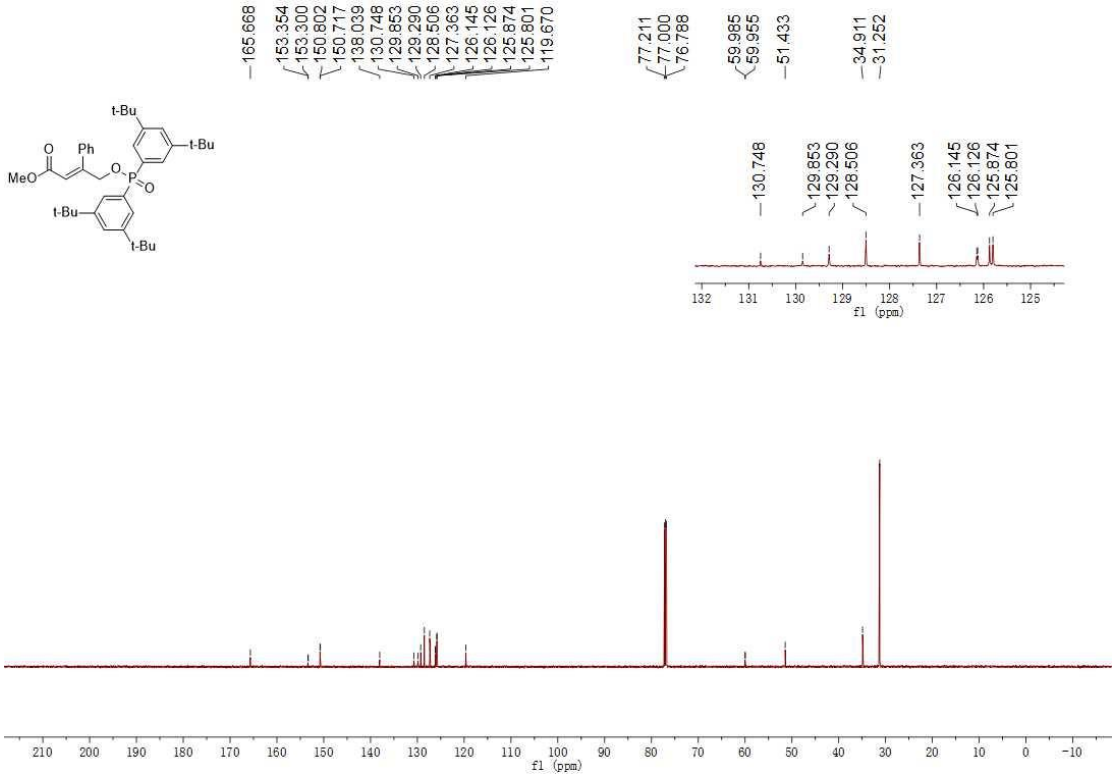
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **72**



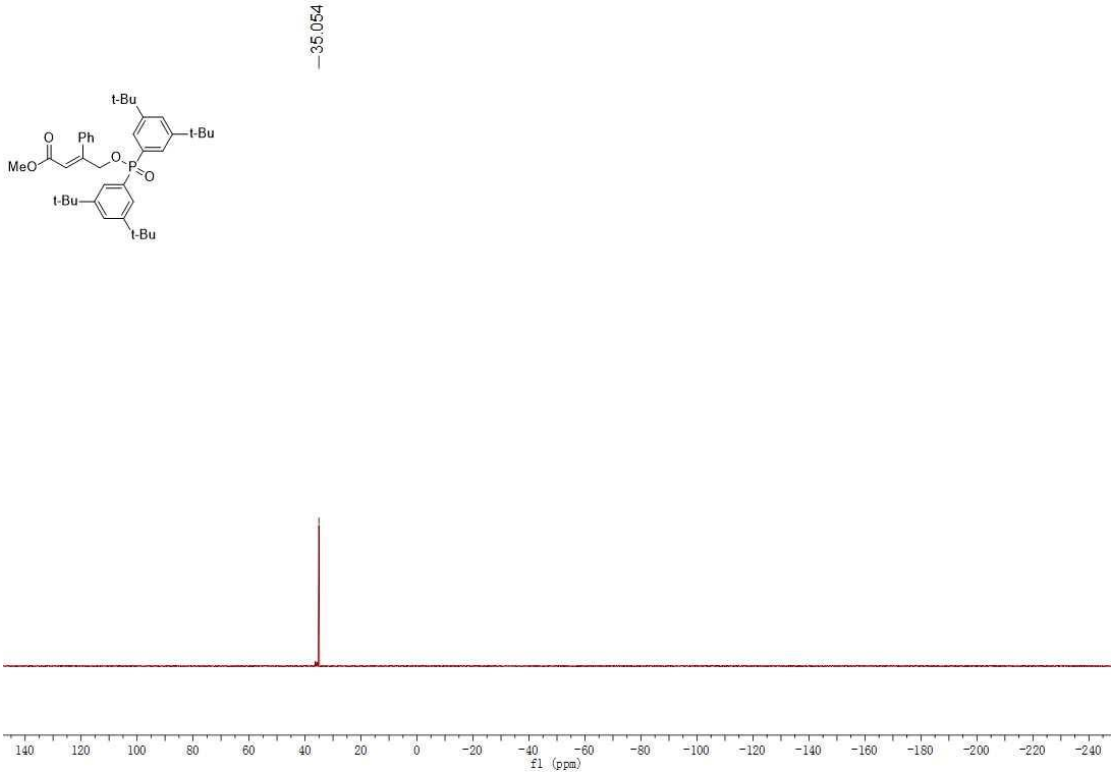
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **73**



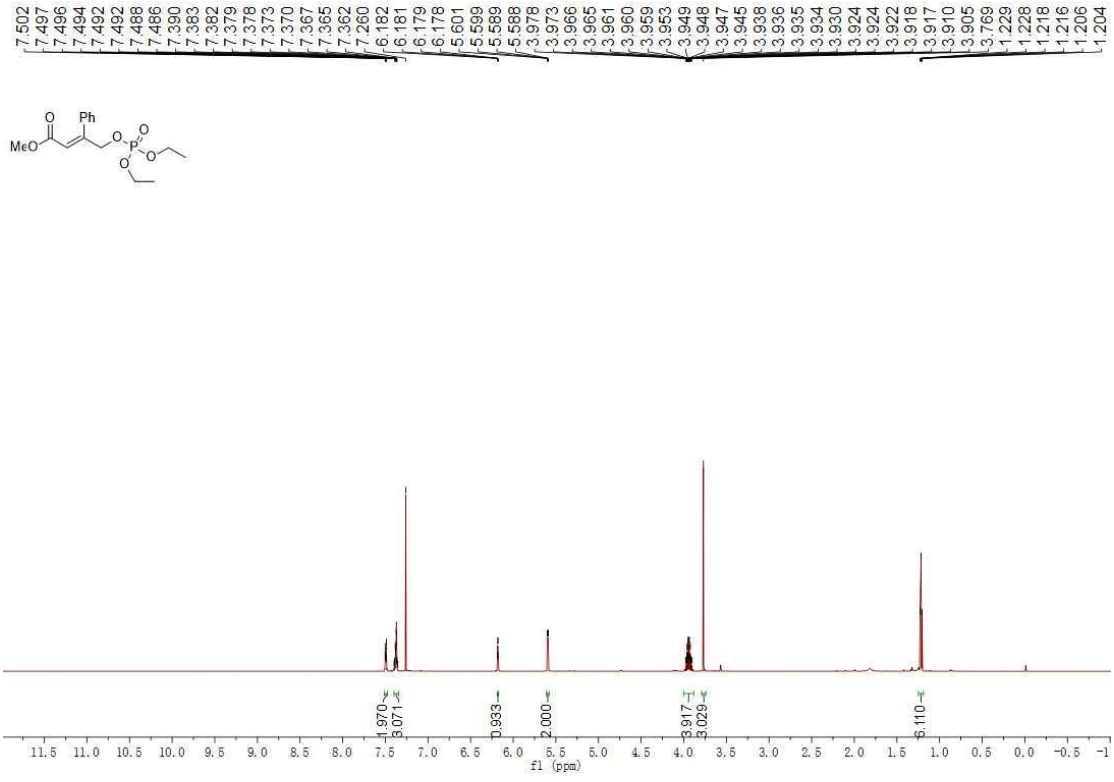
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **73**



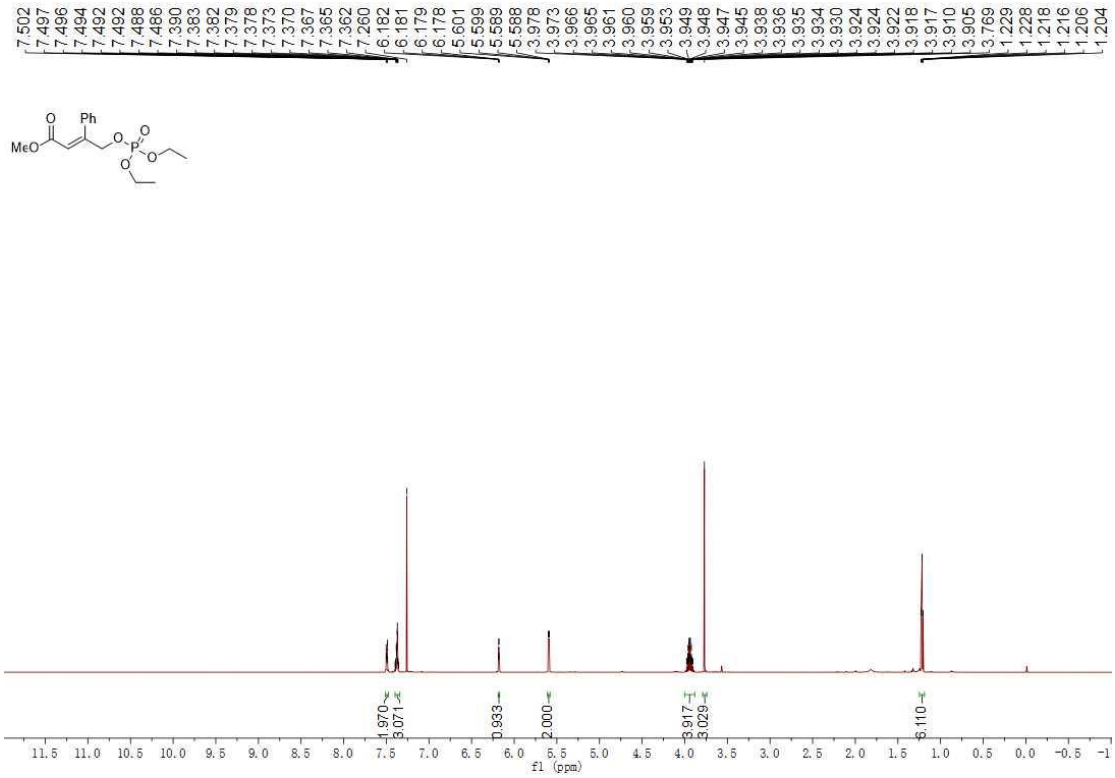
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **73**



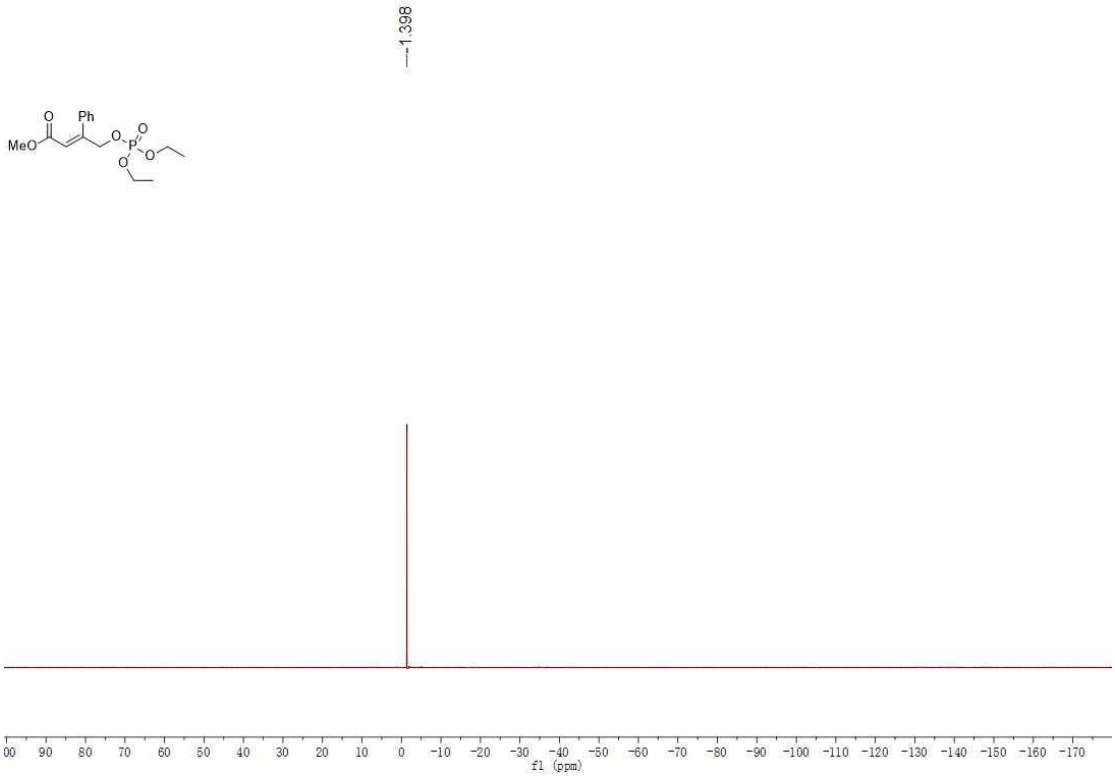
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **74**



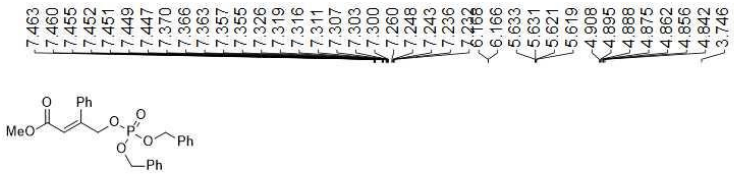
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **74**

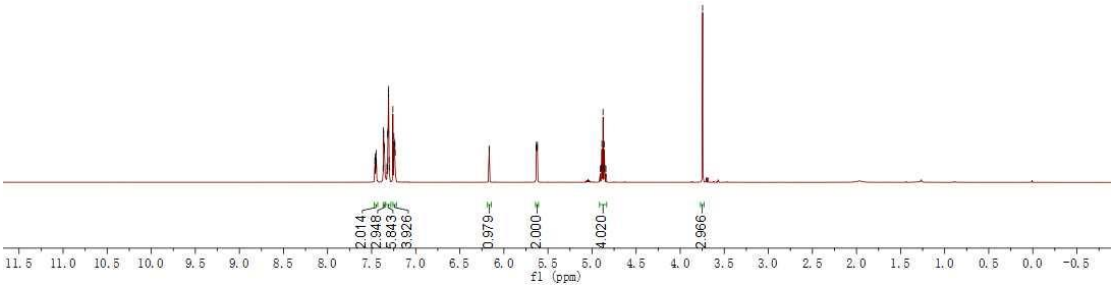


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **74**

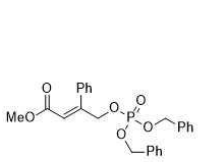


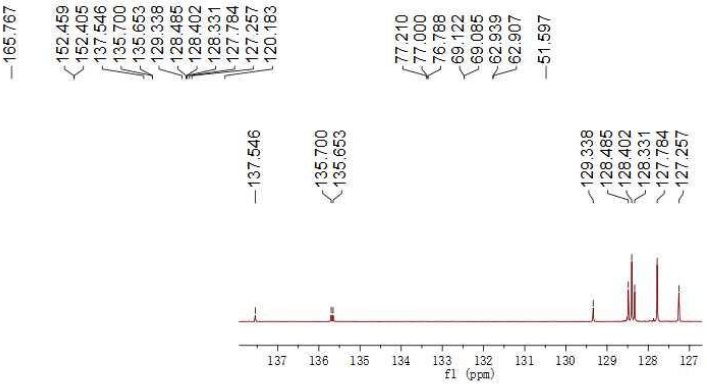
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **75**

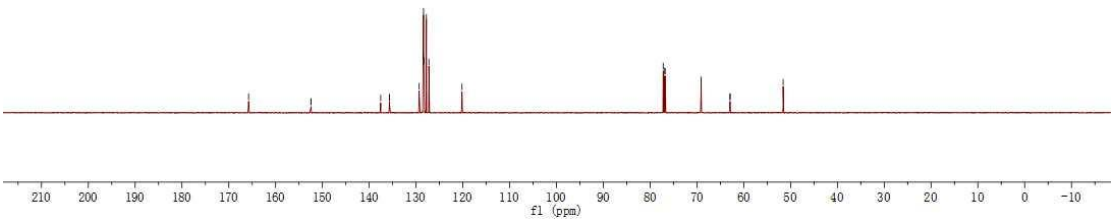




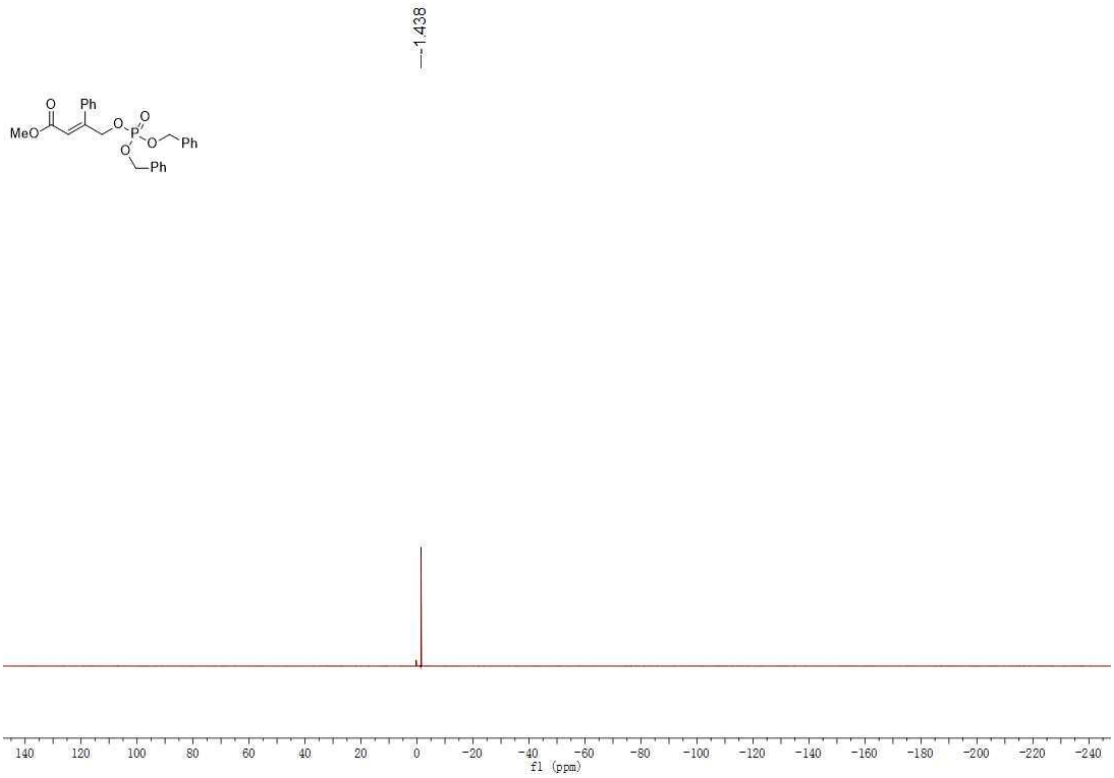
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **75**



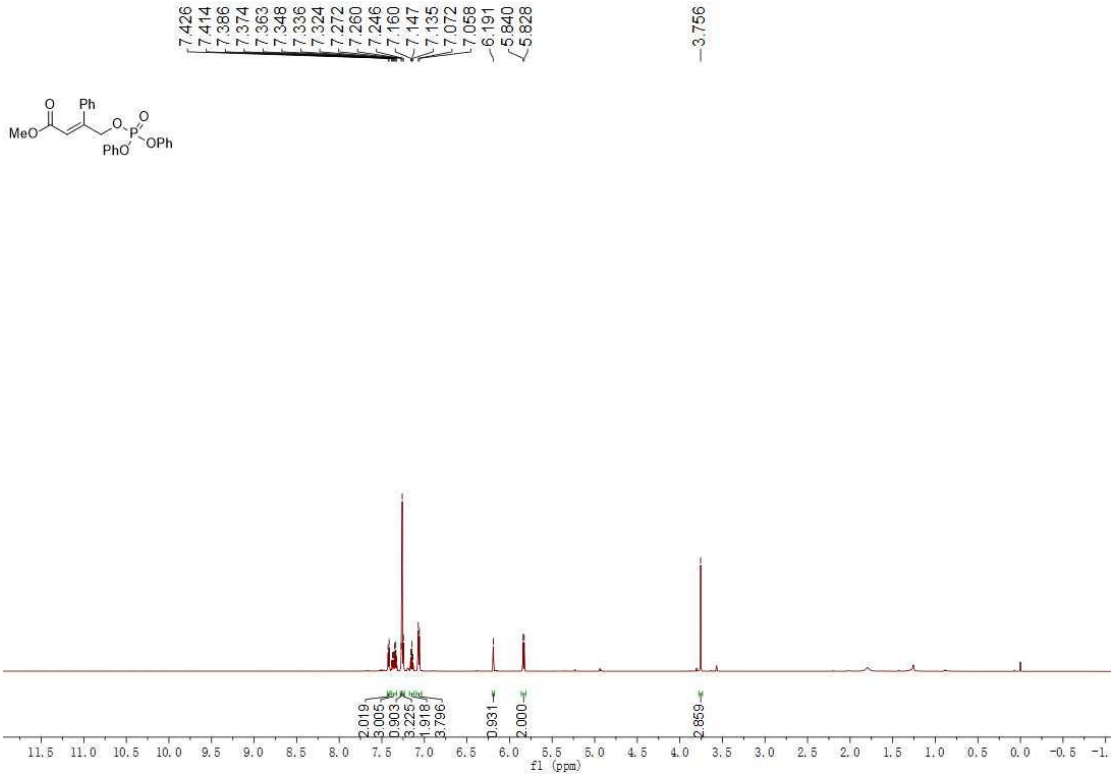




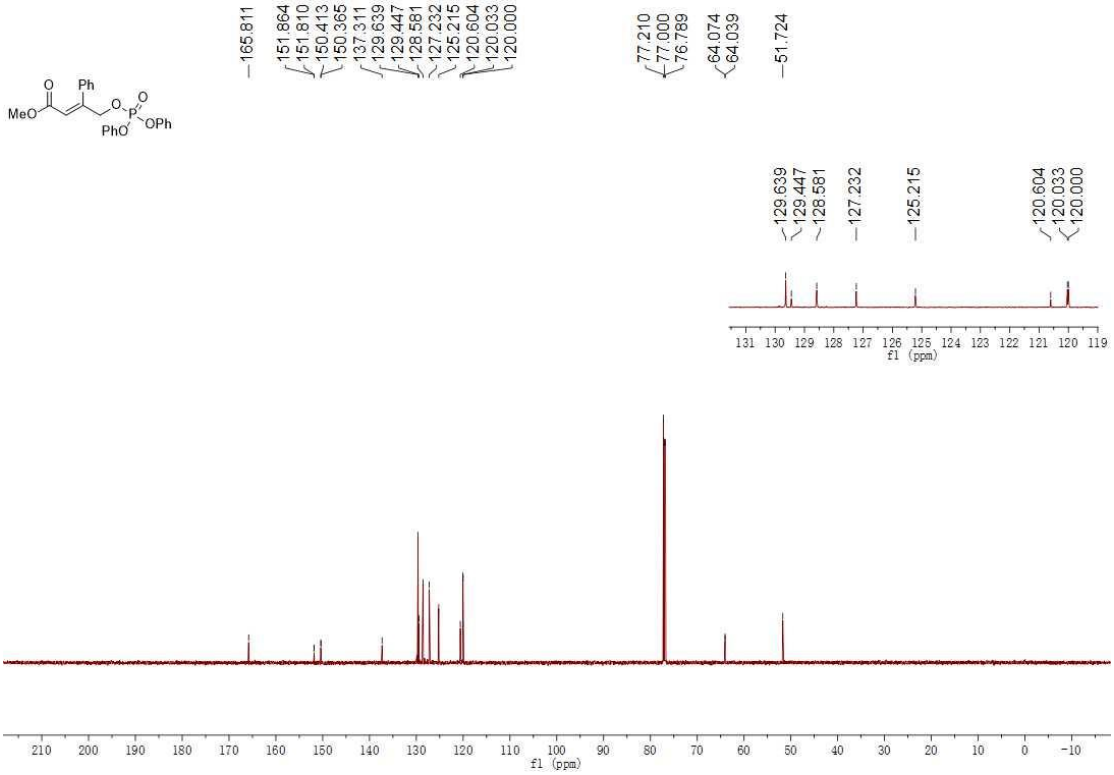
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **75**



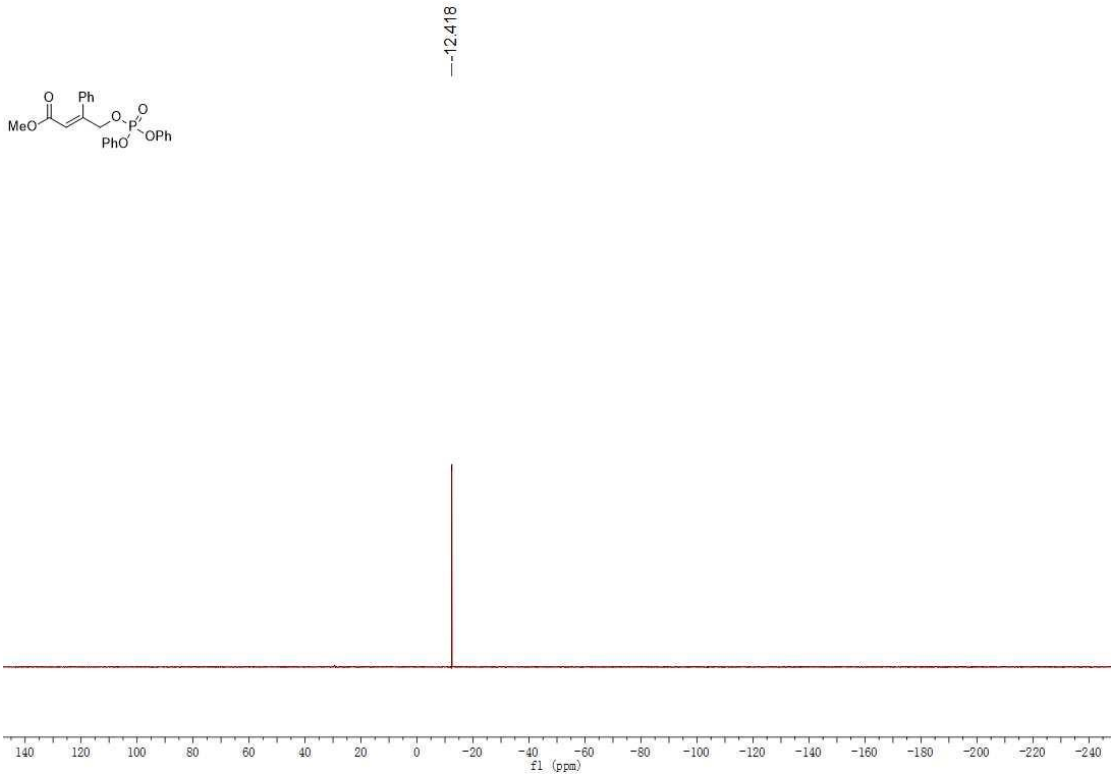
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **76**



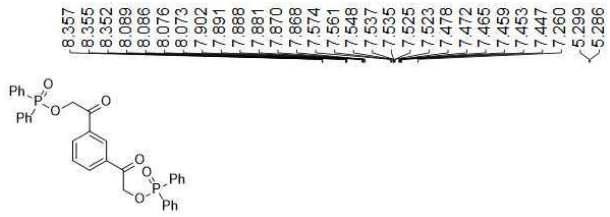
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **76**

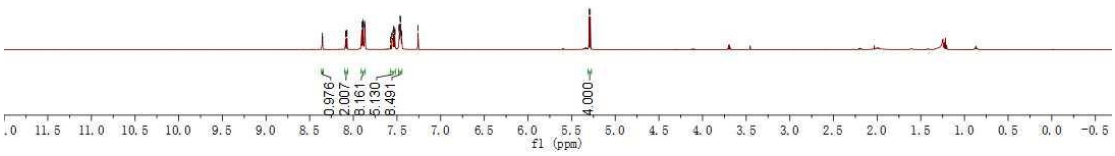


^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **76**

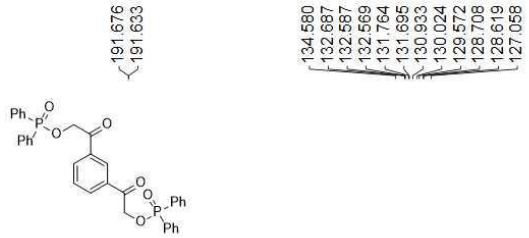


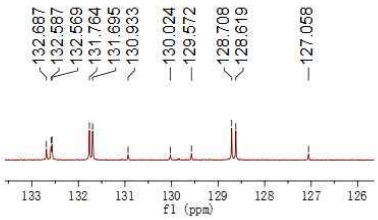
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **78**

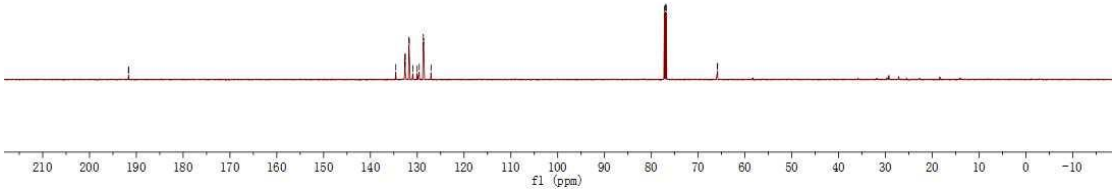




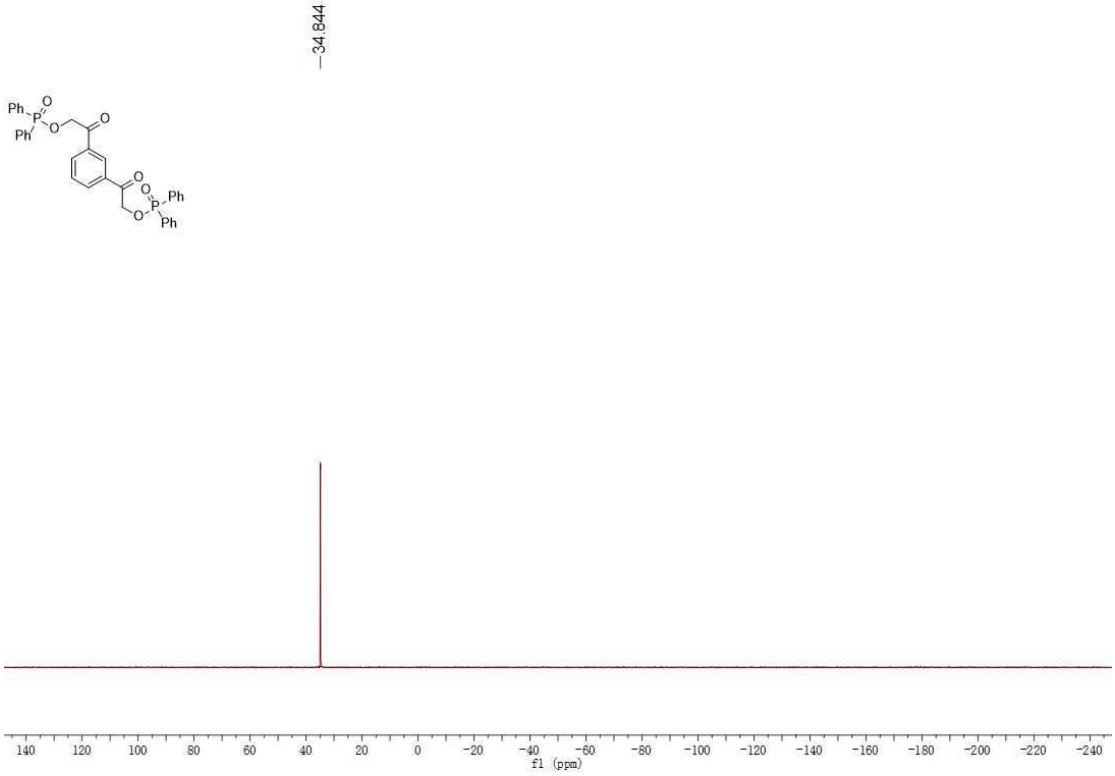
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **78**



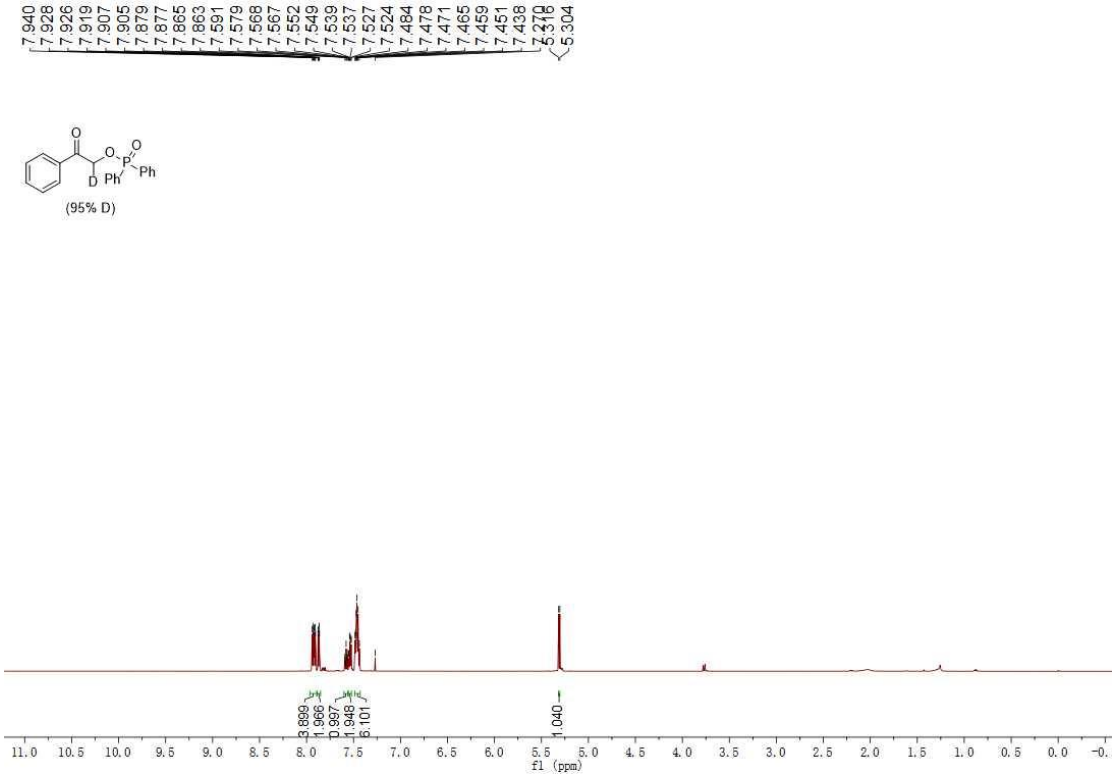




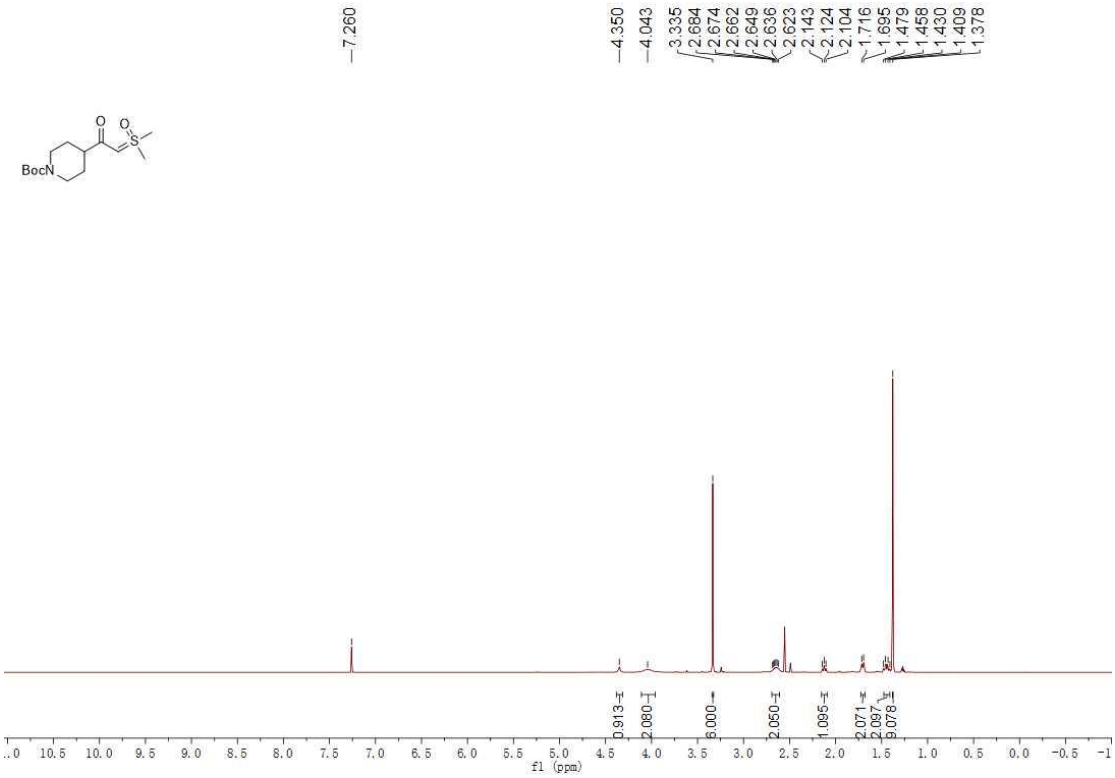
^{31}P NMR (243 MHz, $CDCl_3$) Spectrum of **78**



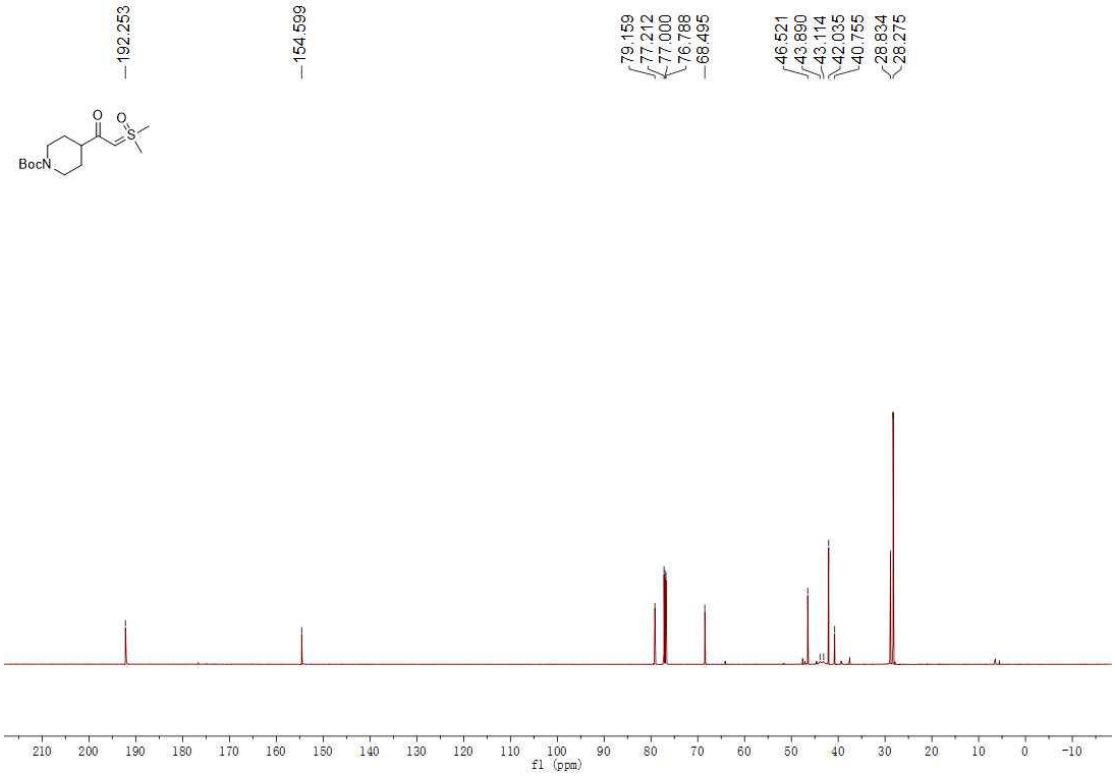
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **3-*d***



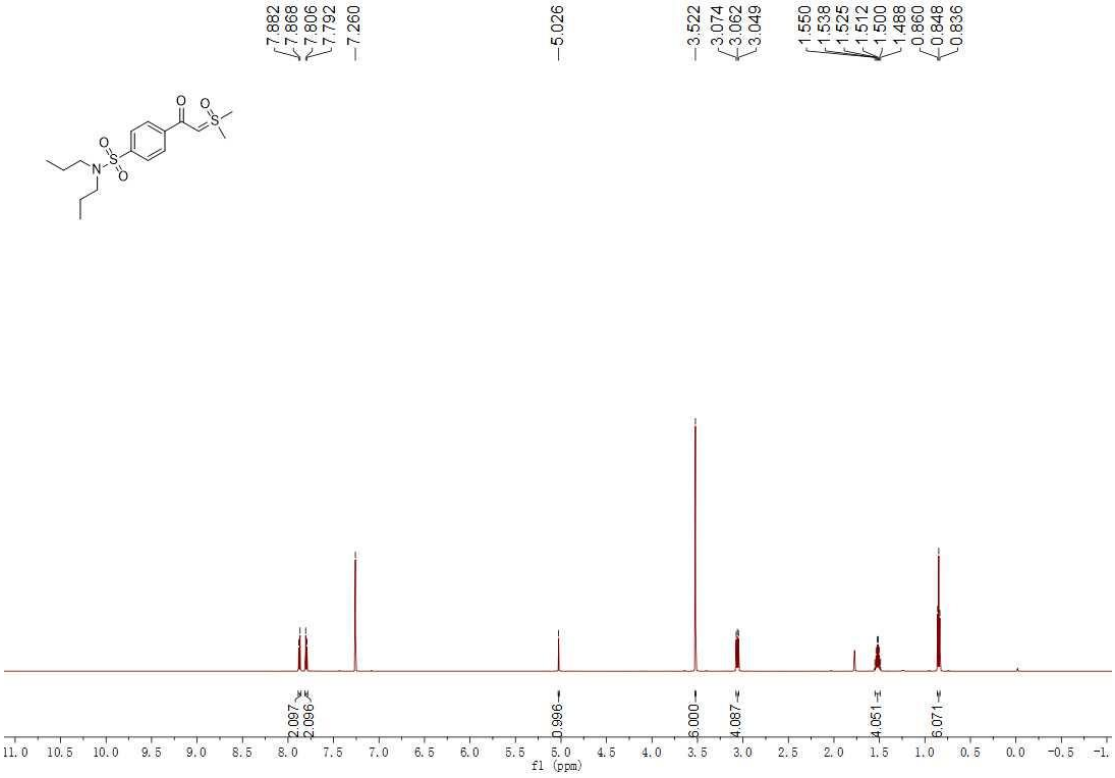
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A36**



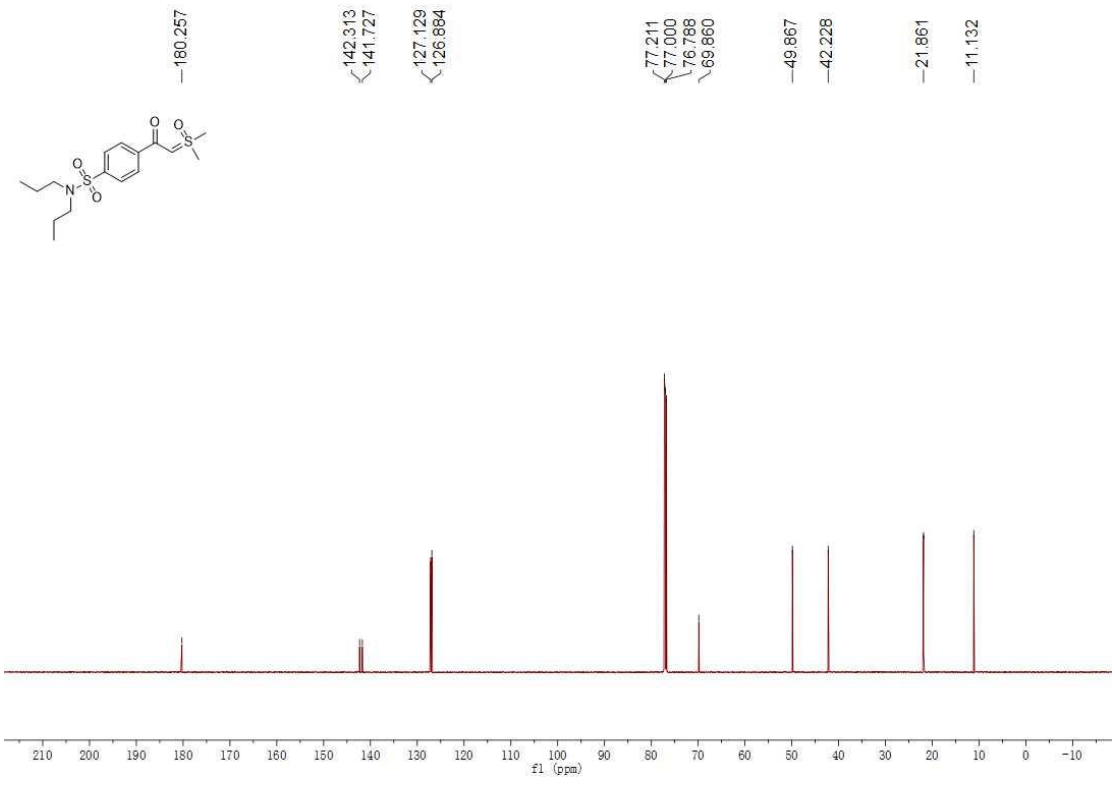
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A36**



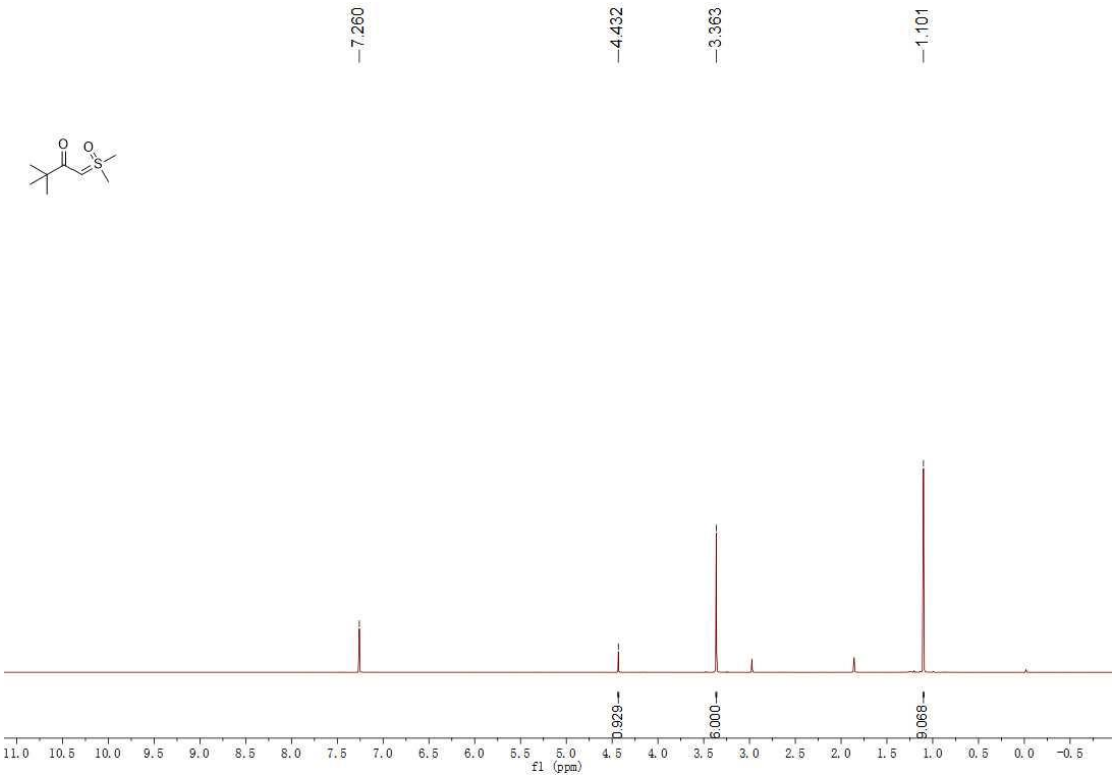
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A42**



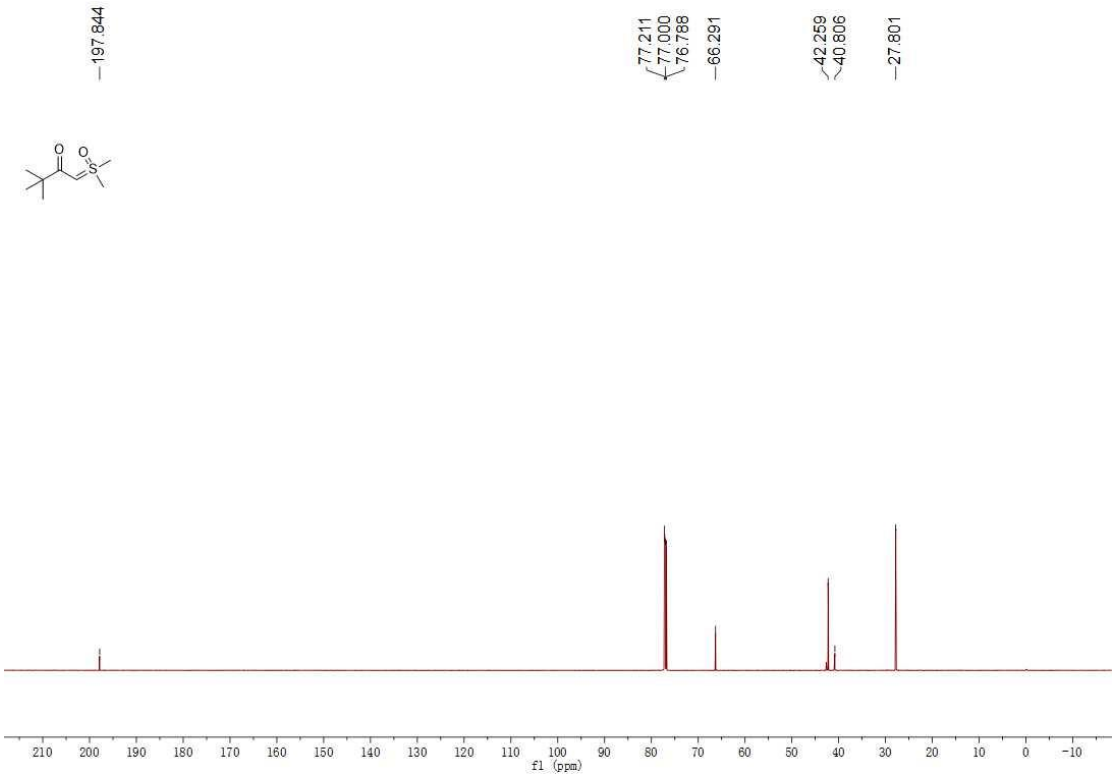
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A42**



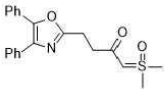
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A53**

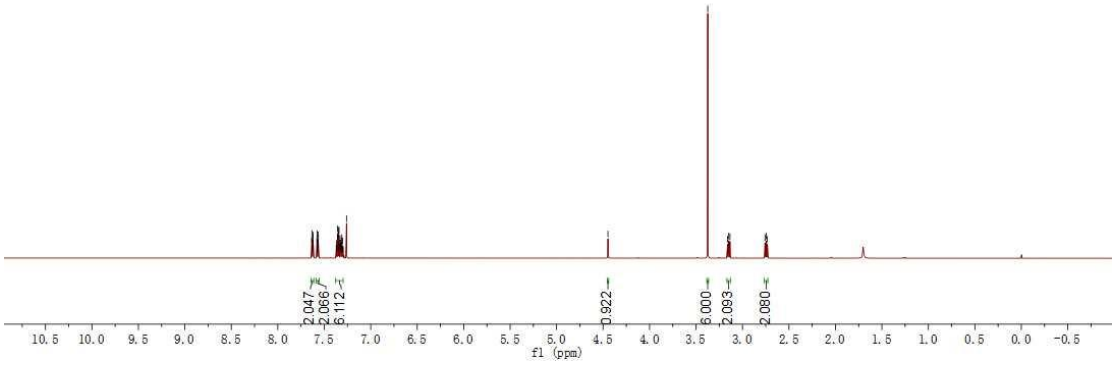


^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A53**

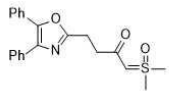


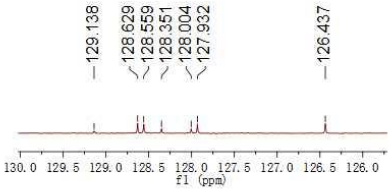
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A55**

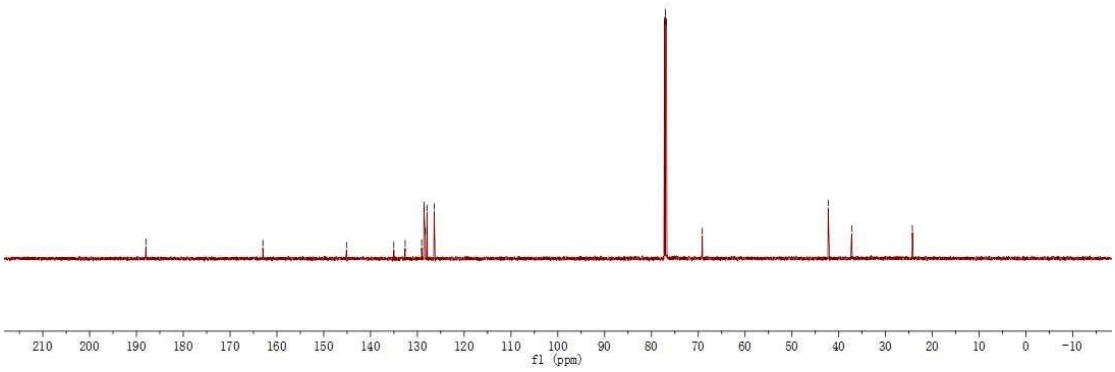




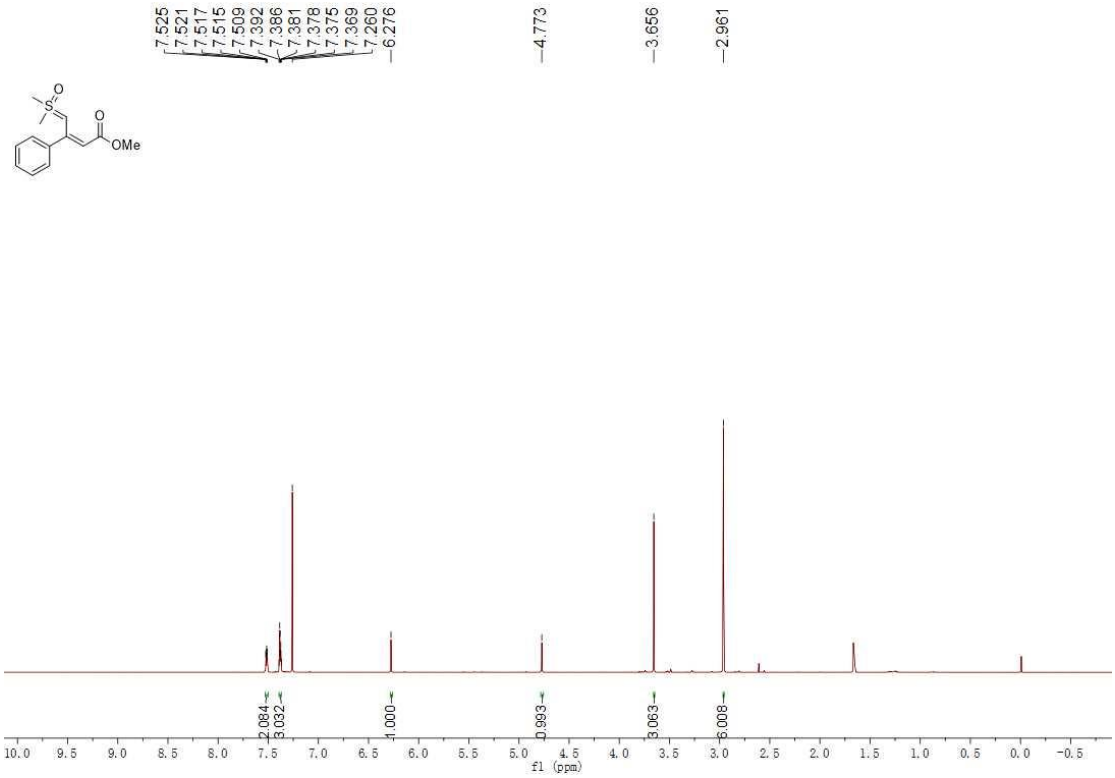
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A55**



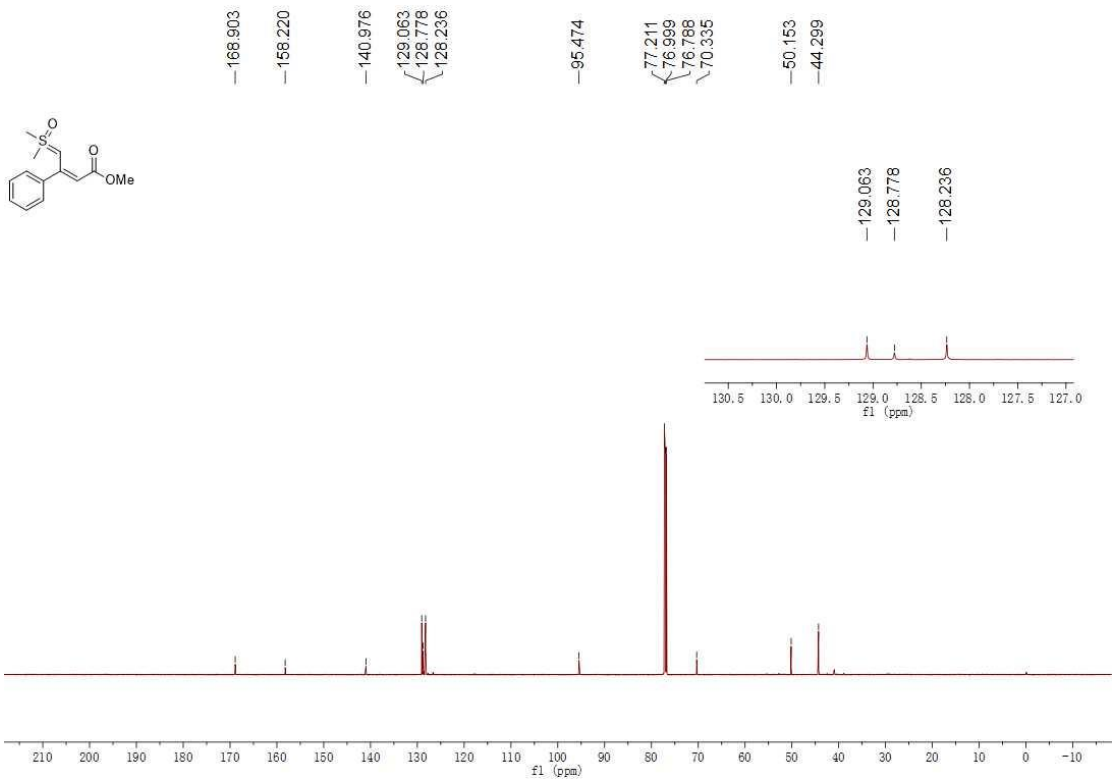




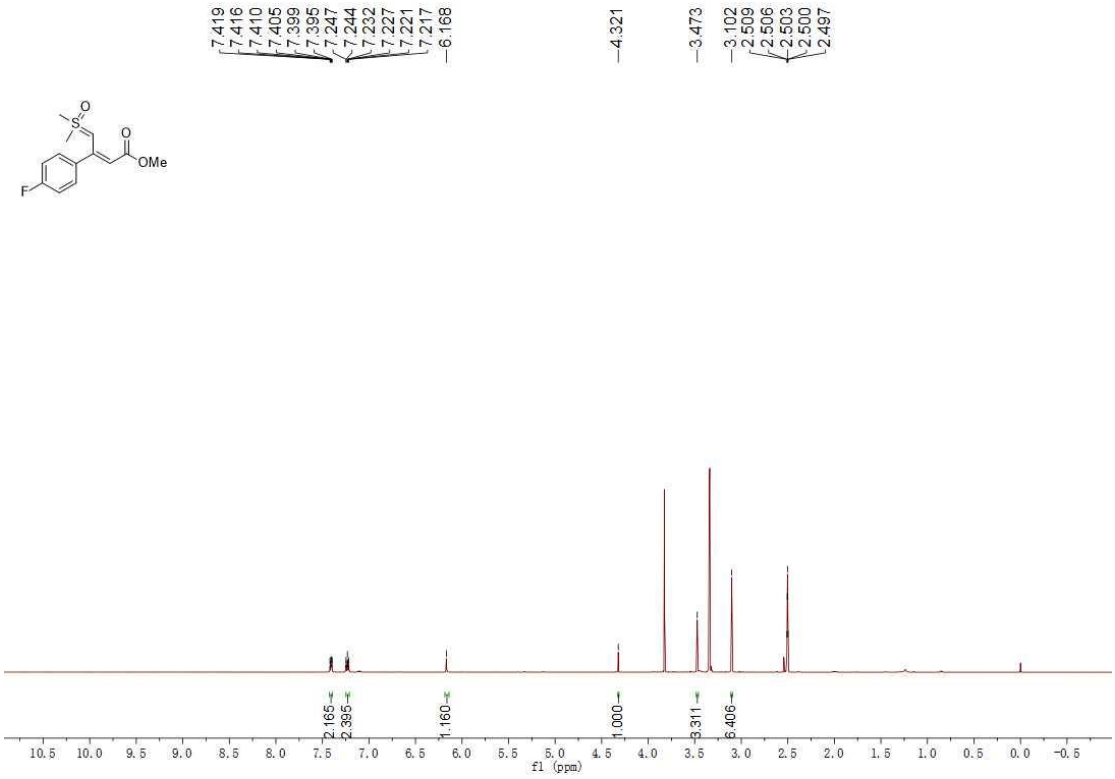
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A26**



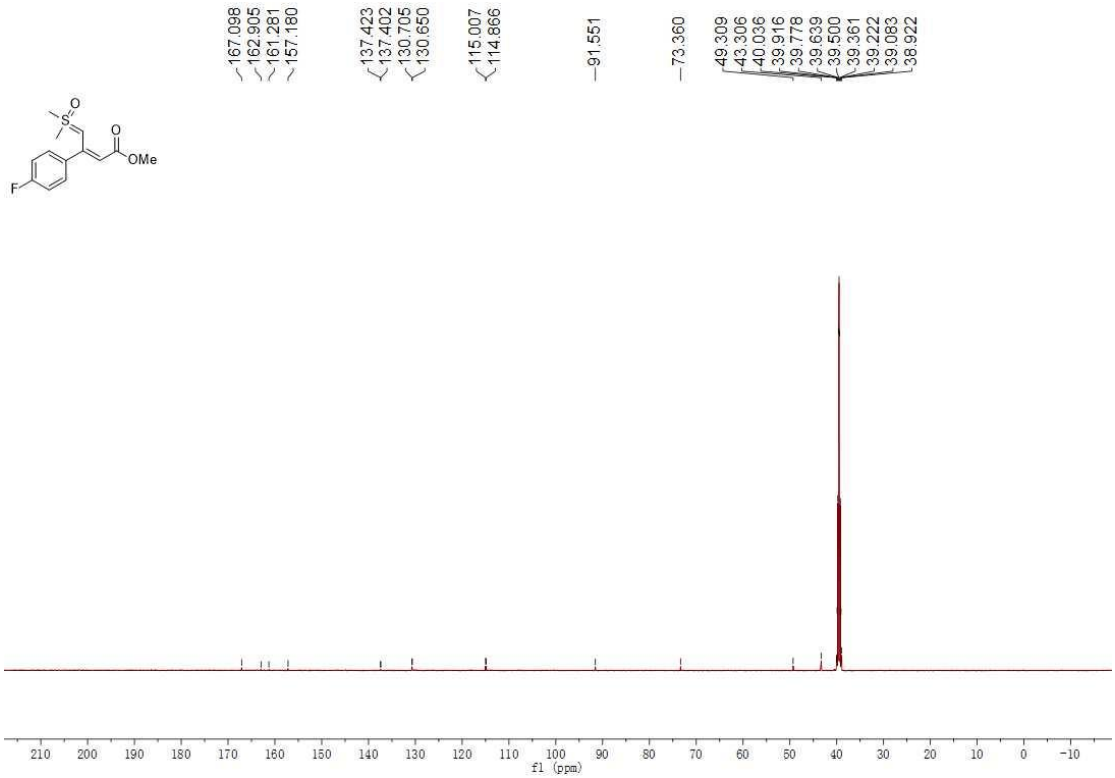
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A26**



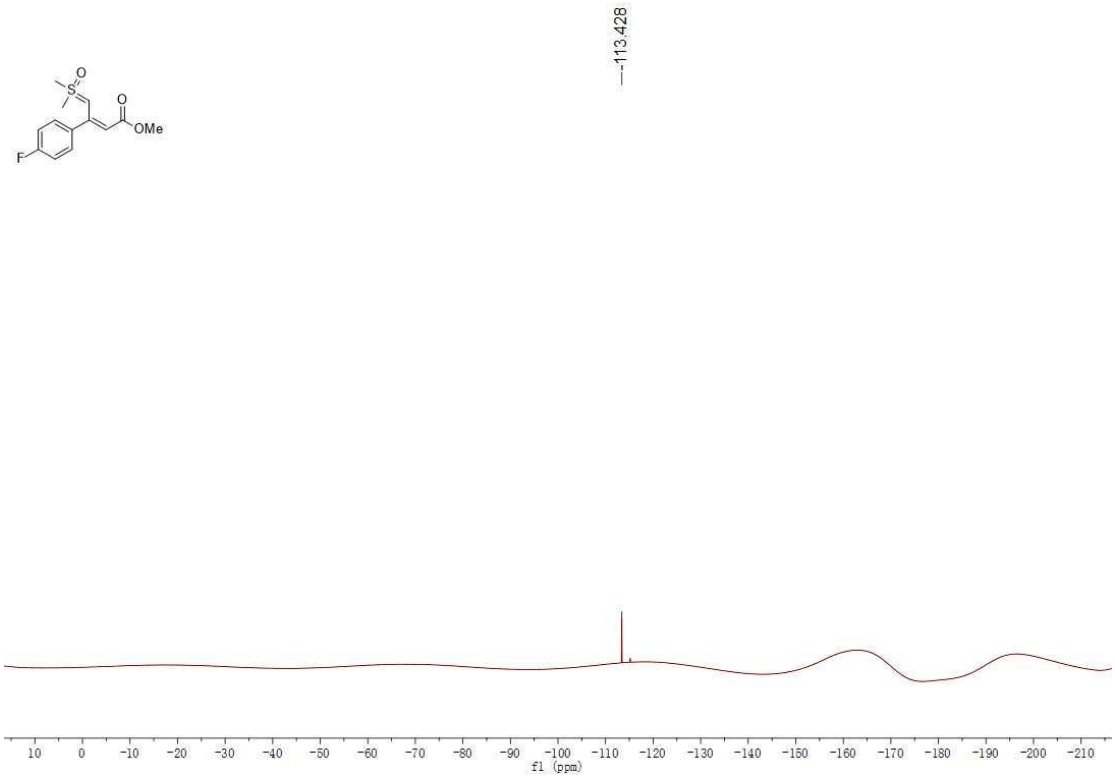
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **A27**



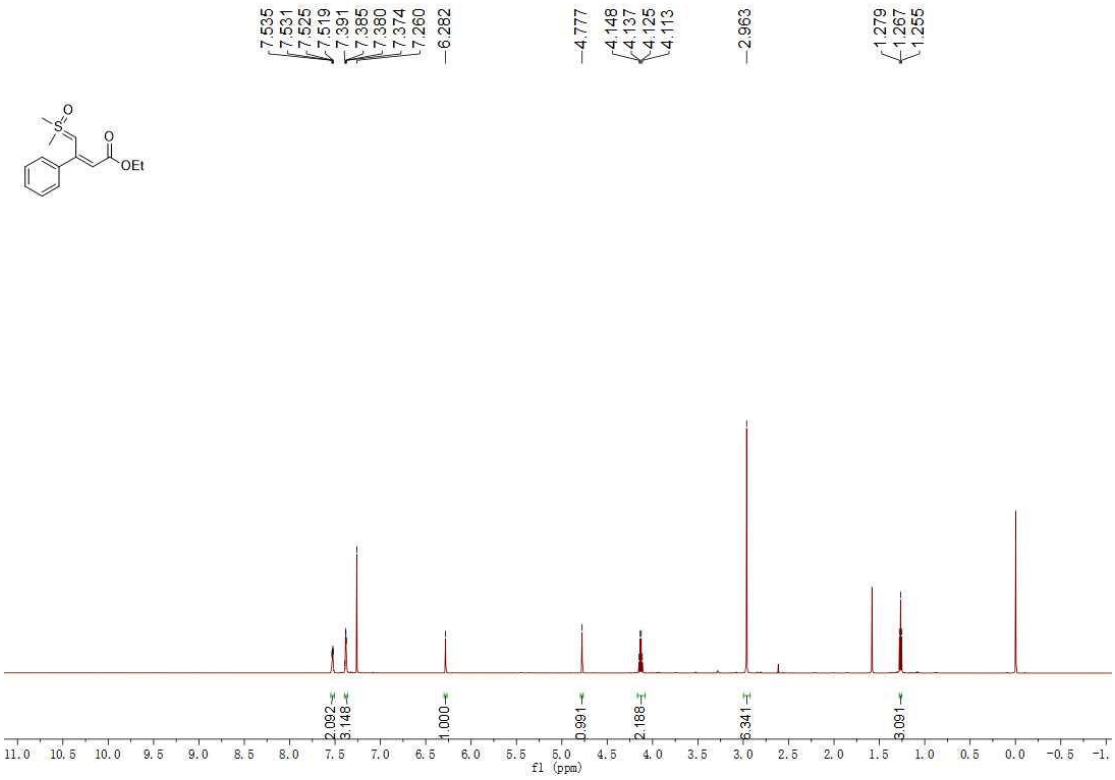
^{13}C NMR (150 MHz, DMSO-d_6) Spectrum of **A27**



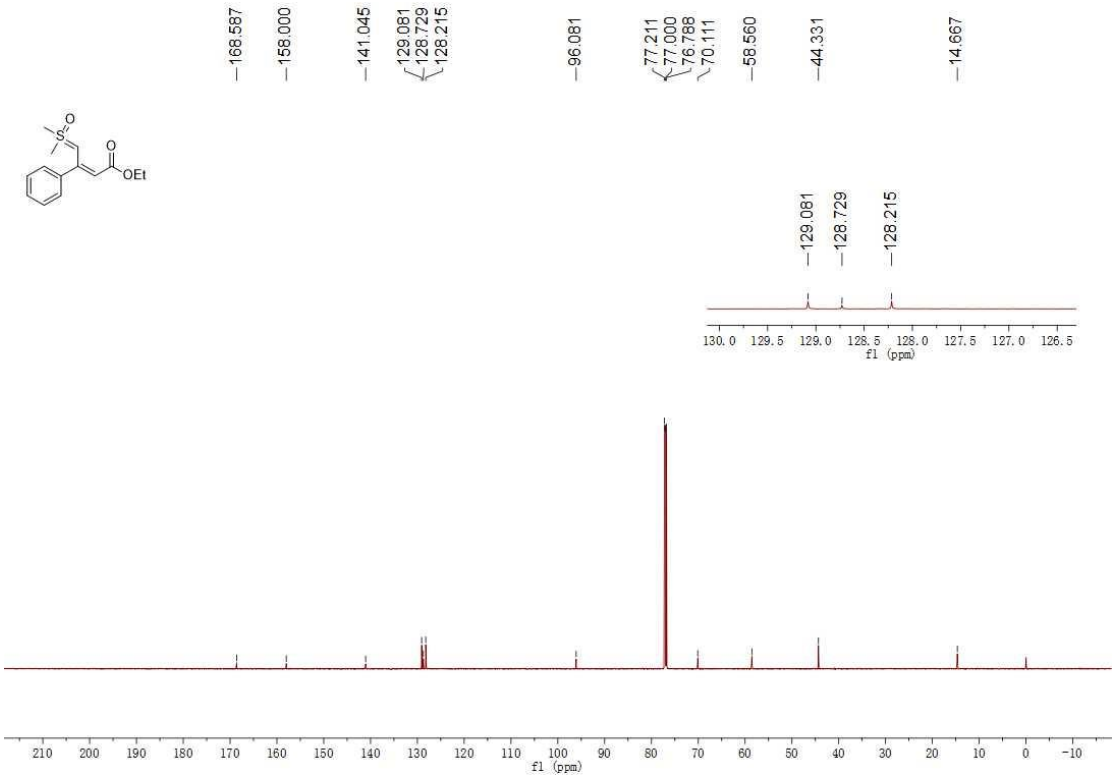
^{19}F NMR (564 MHz, DMSO-d_6) Spectrum of **A27**



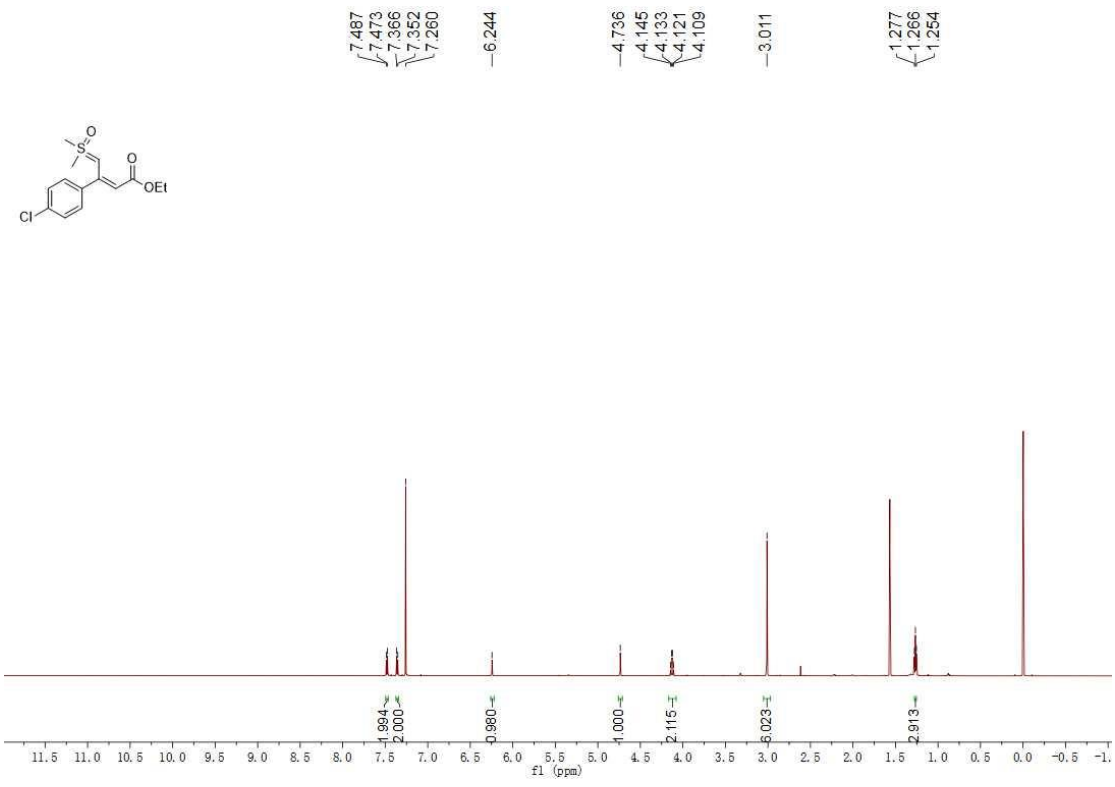
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A28**



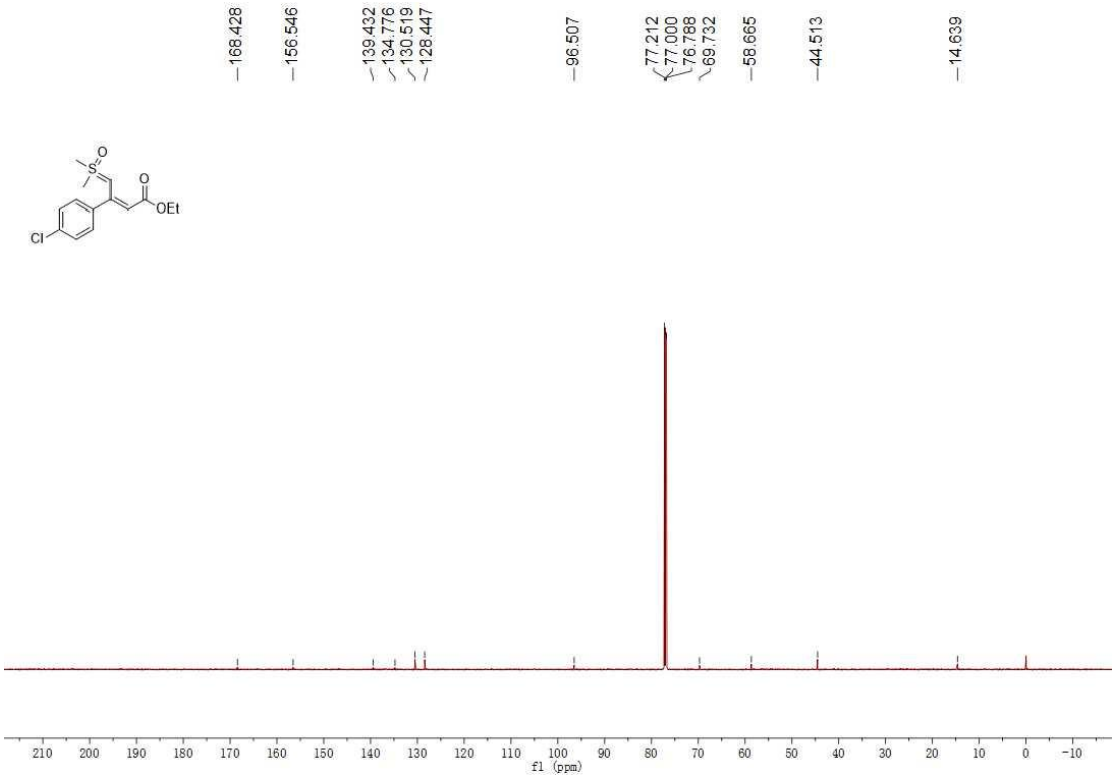
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A28**



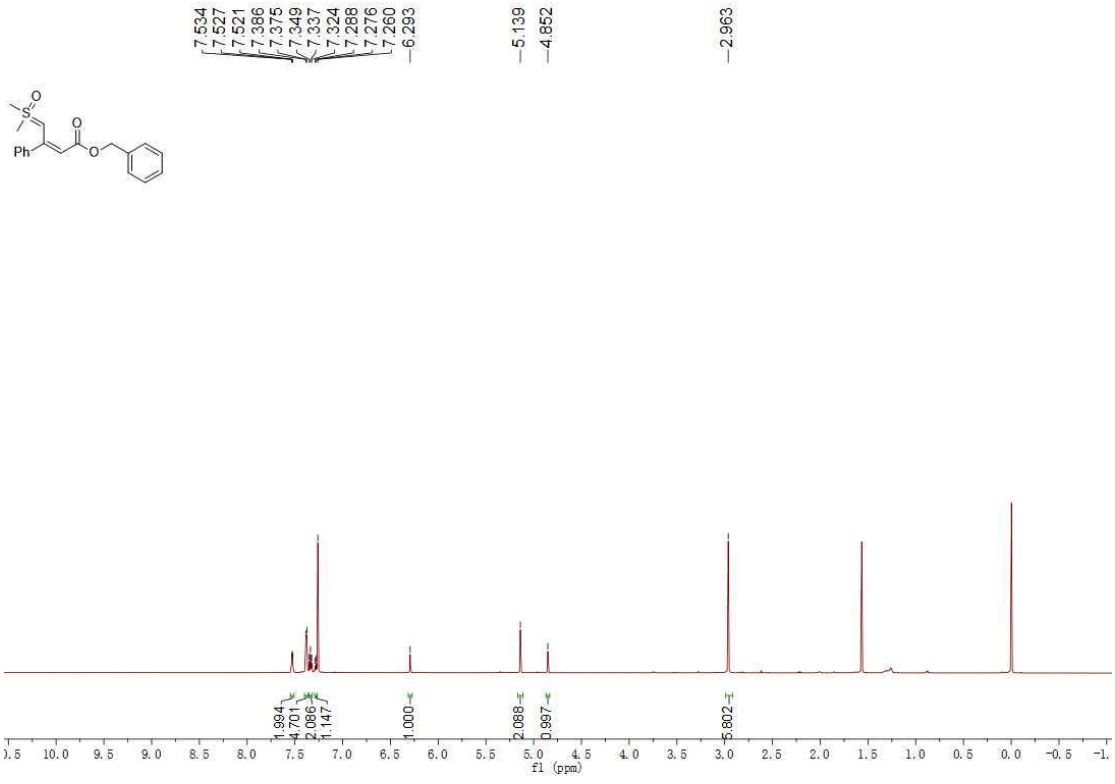
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A39**



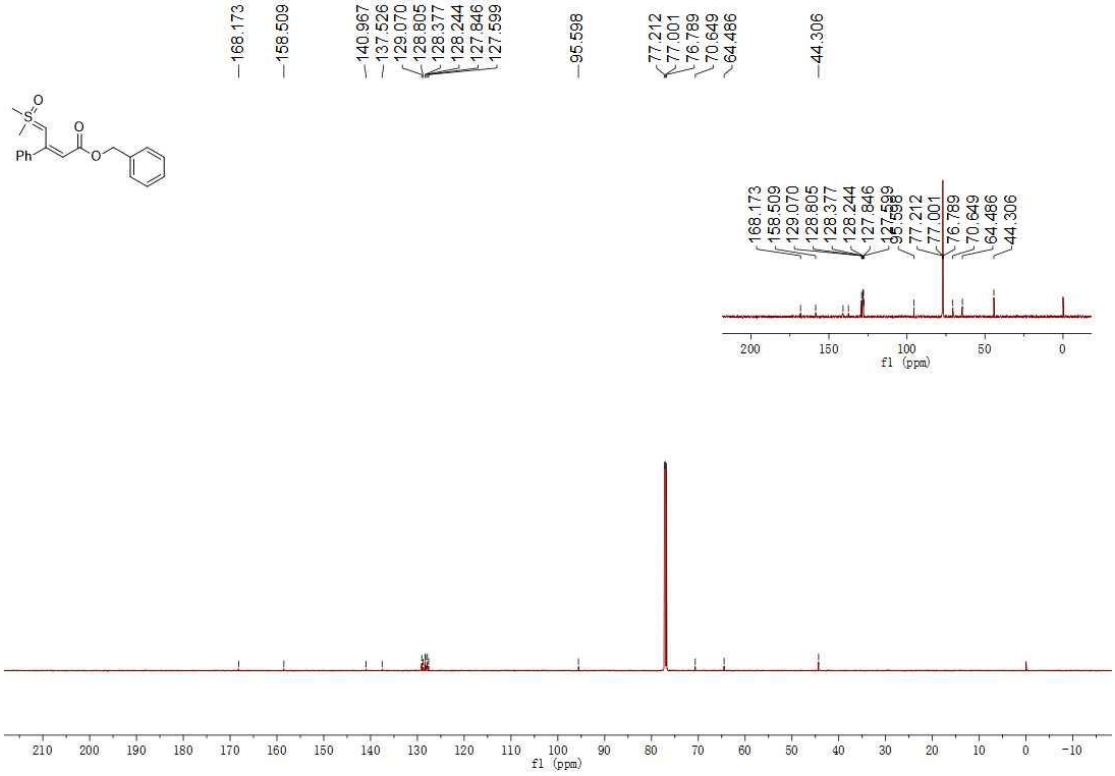
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A39**



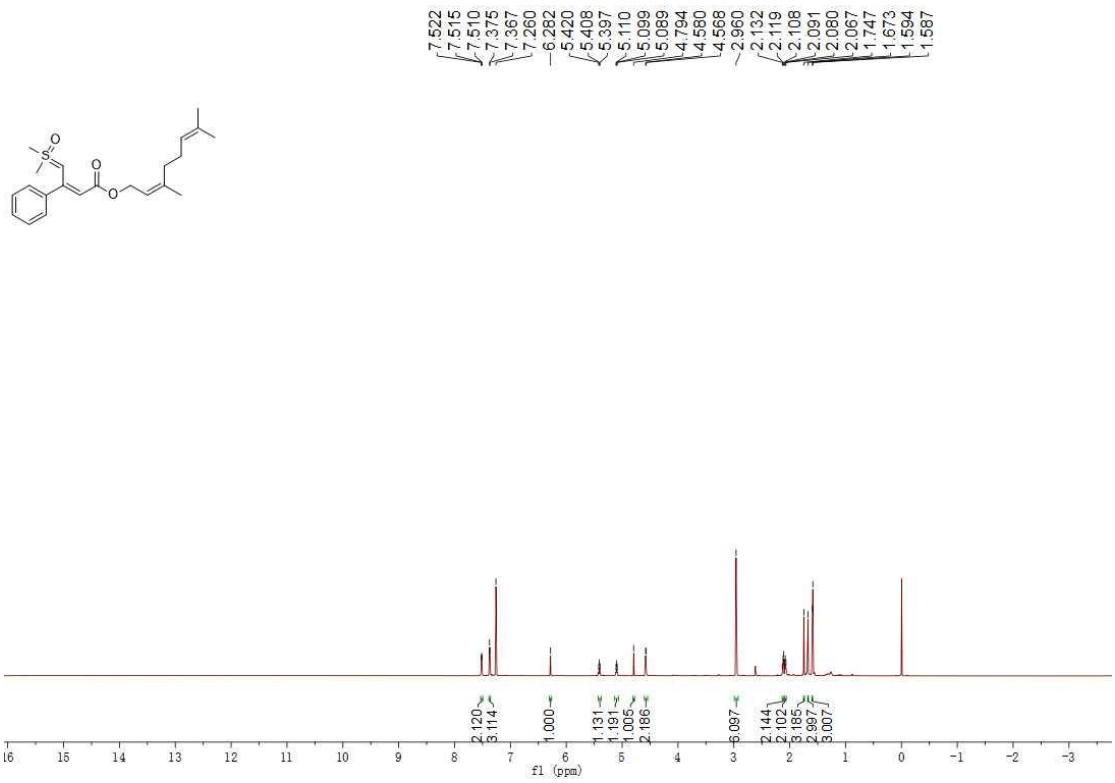
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A40**



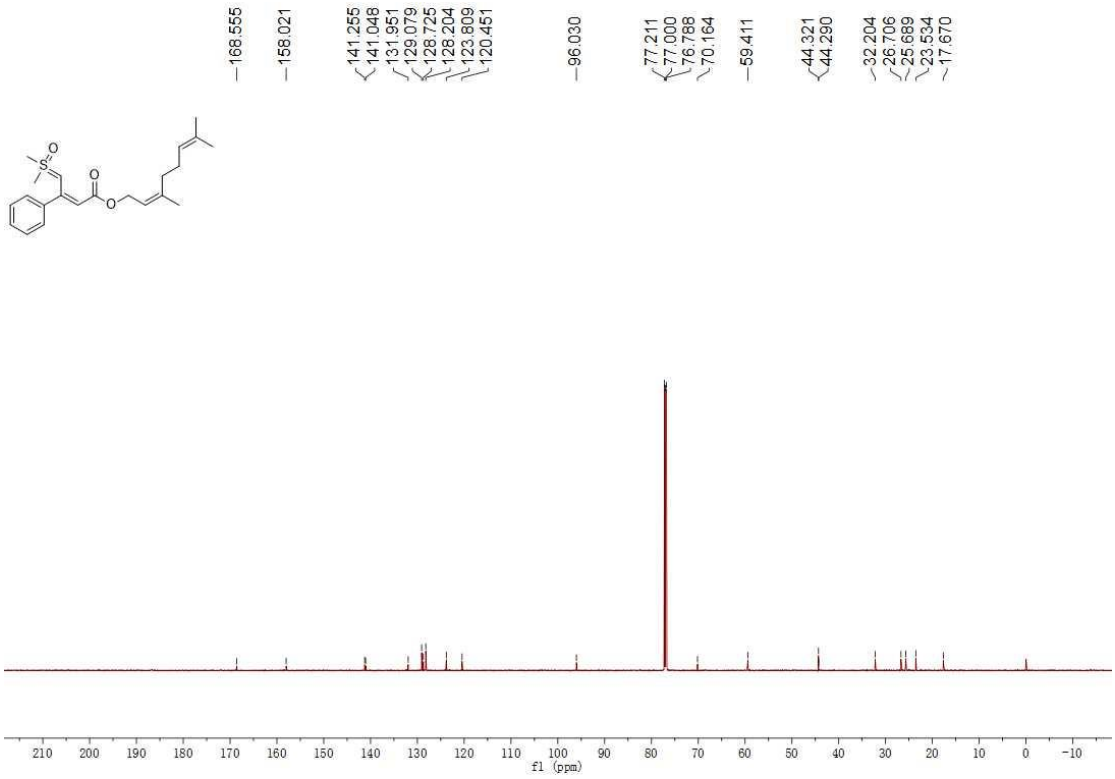
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A40**



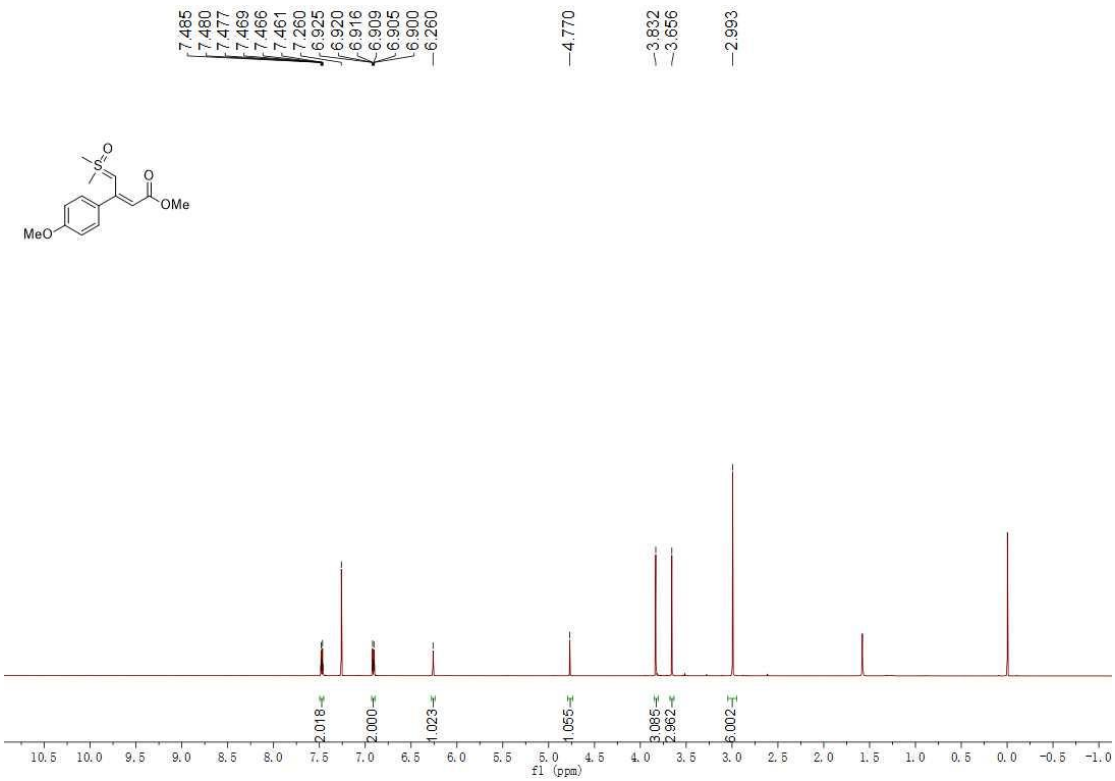
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A41**



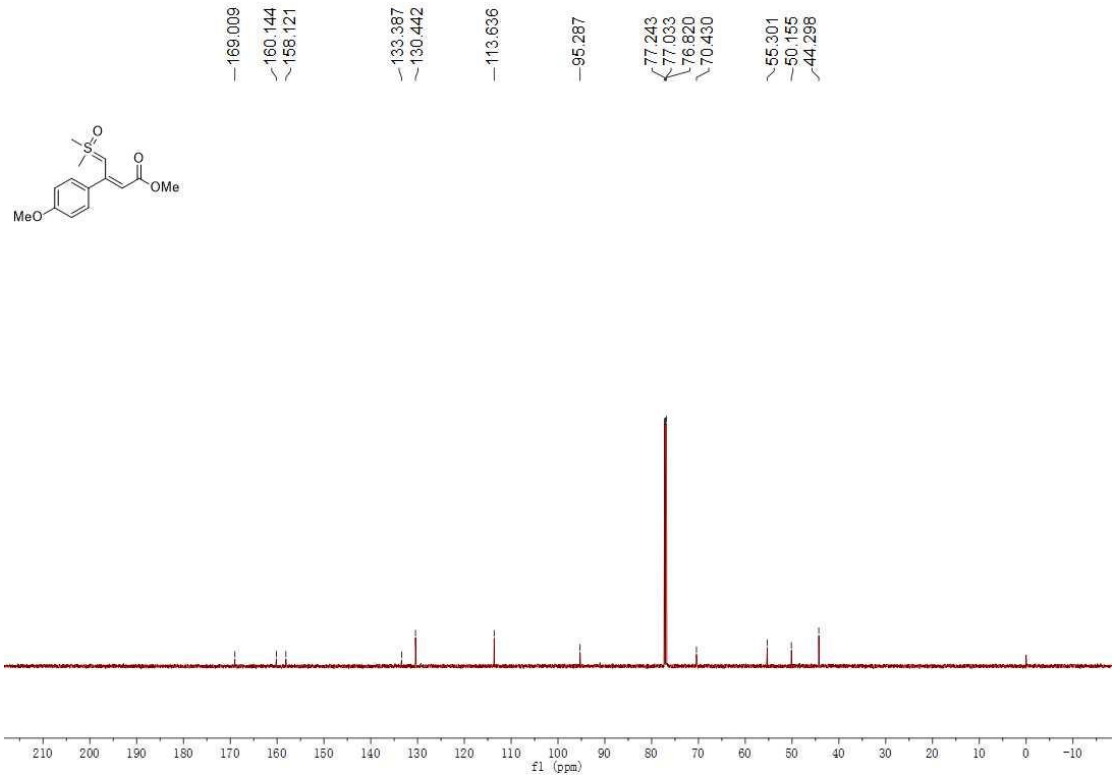
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A41**



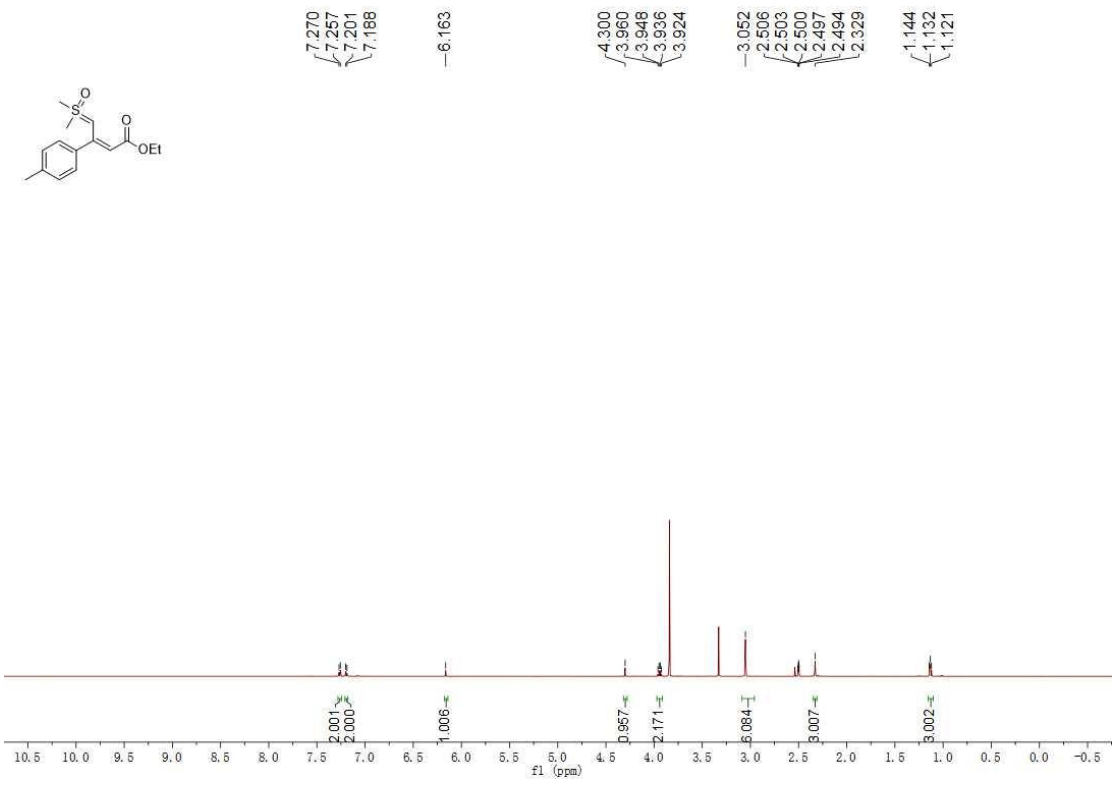
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A59**



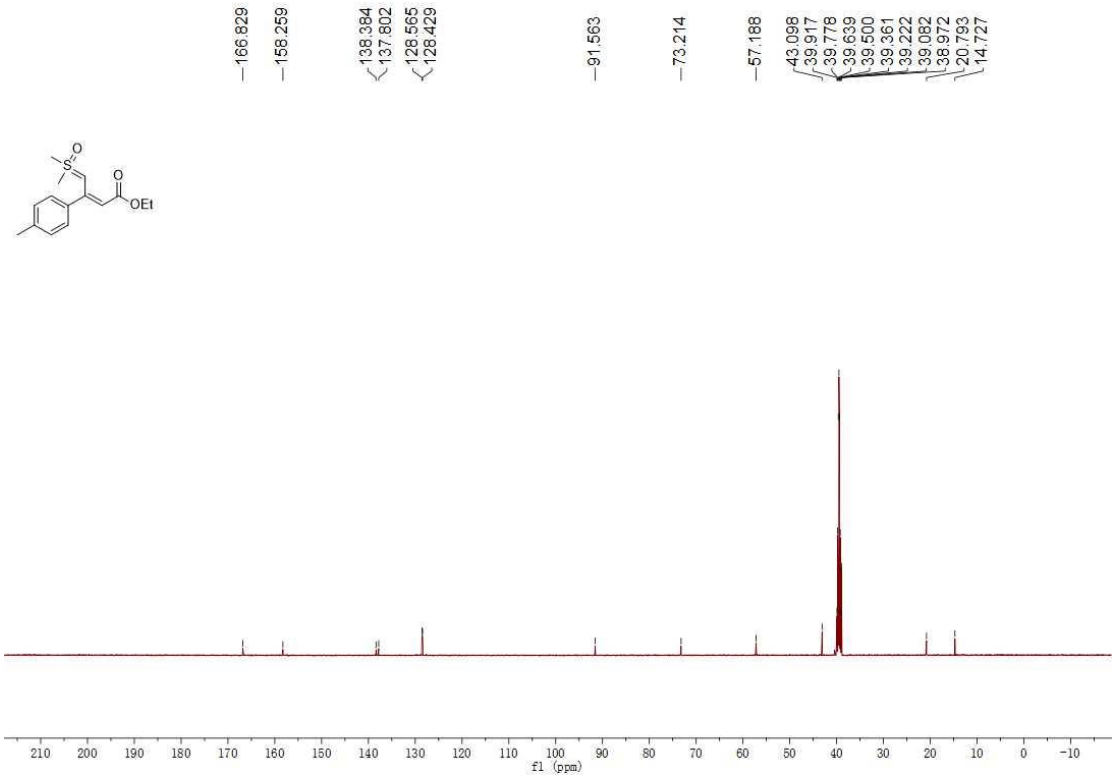
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A59**



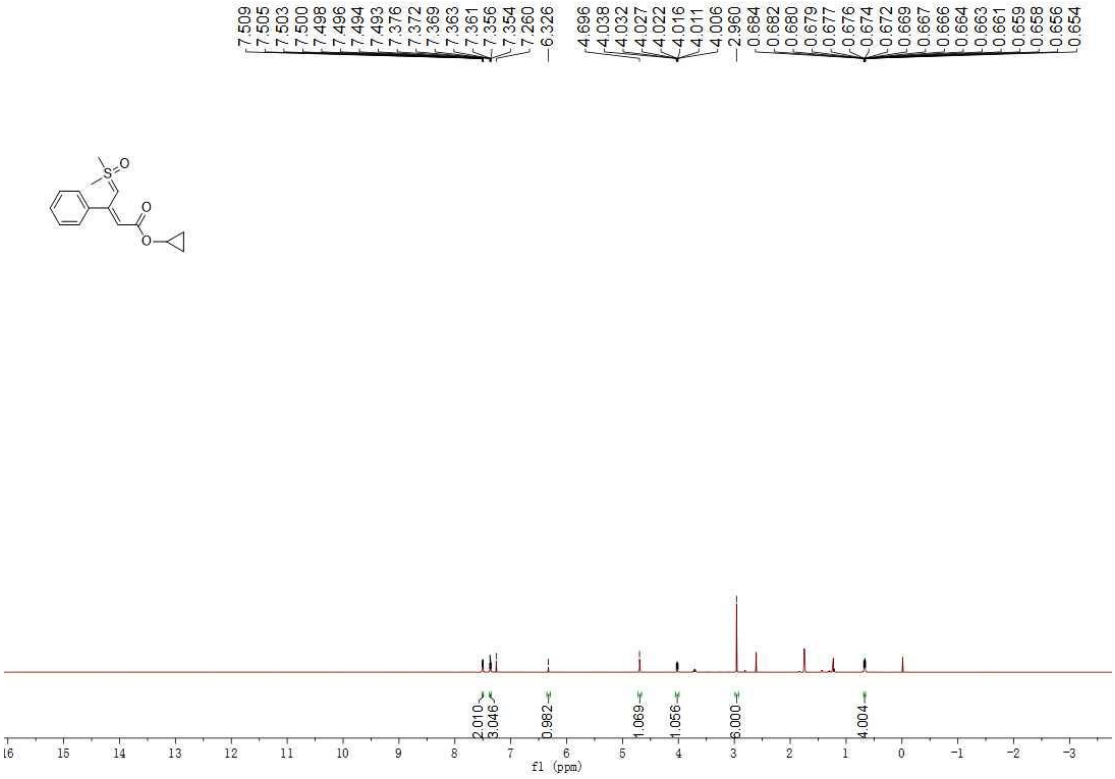
^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **A60**



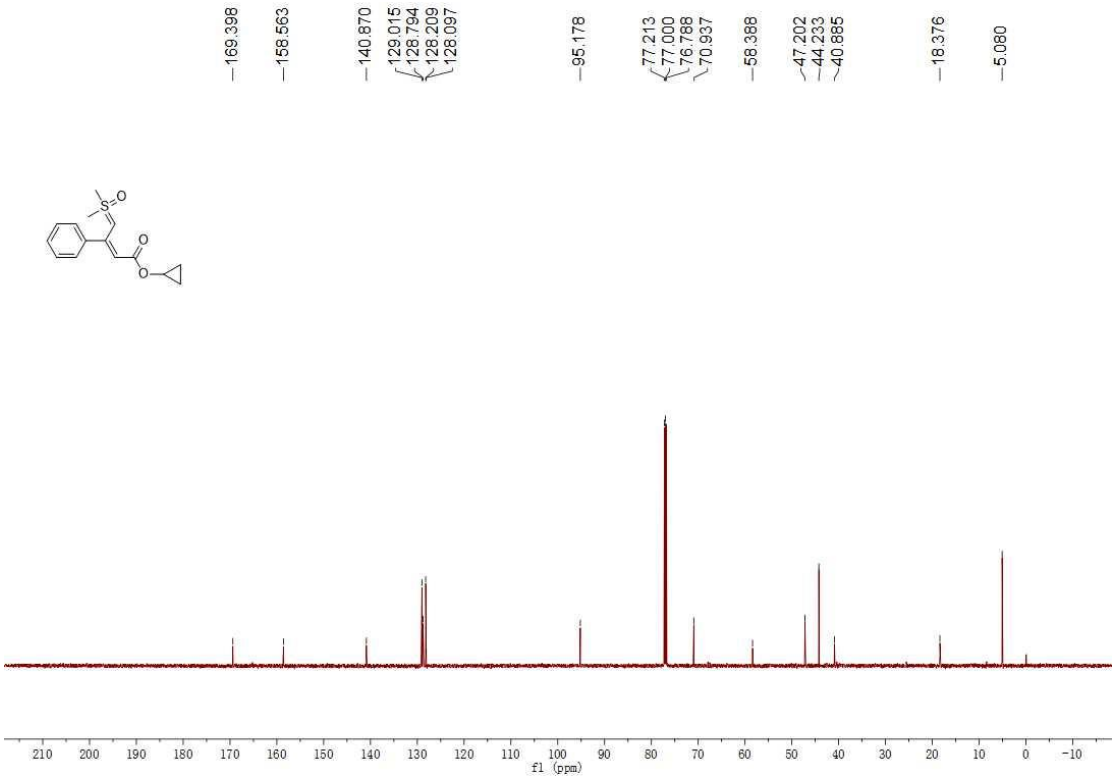
^{13}C NMR (150 MHz, DMSO-d_6) Spectrum of **A60**



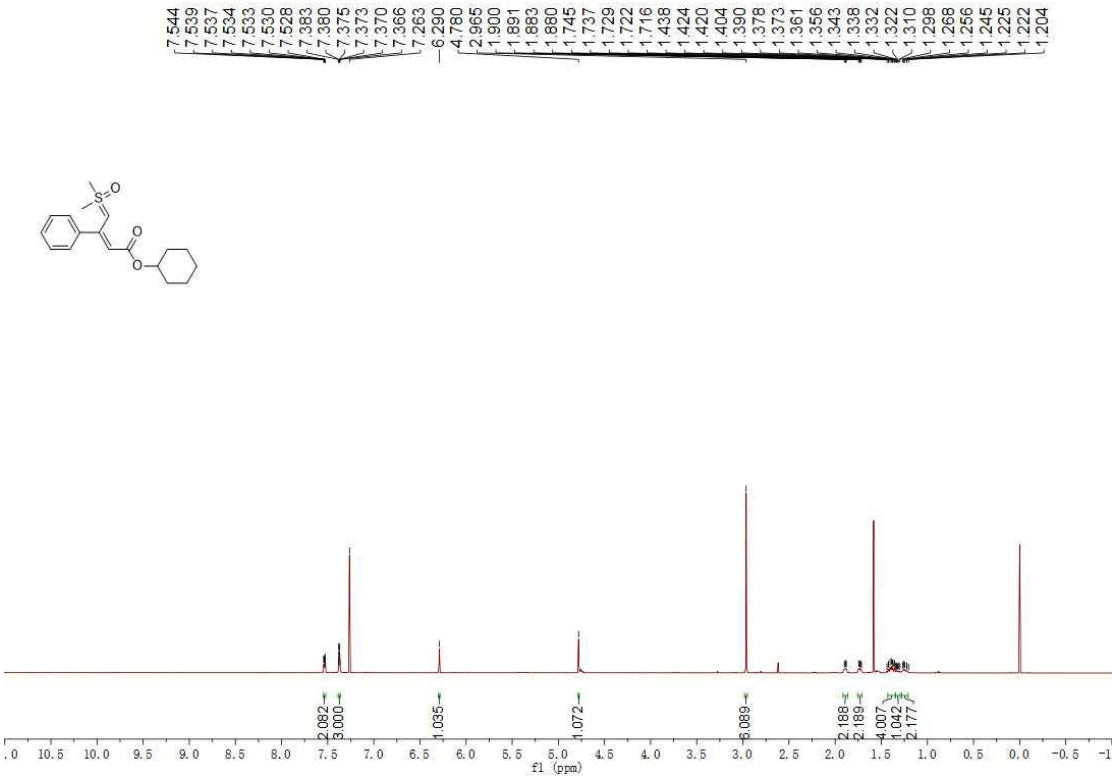
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A61**



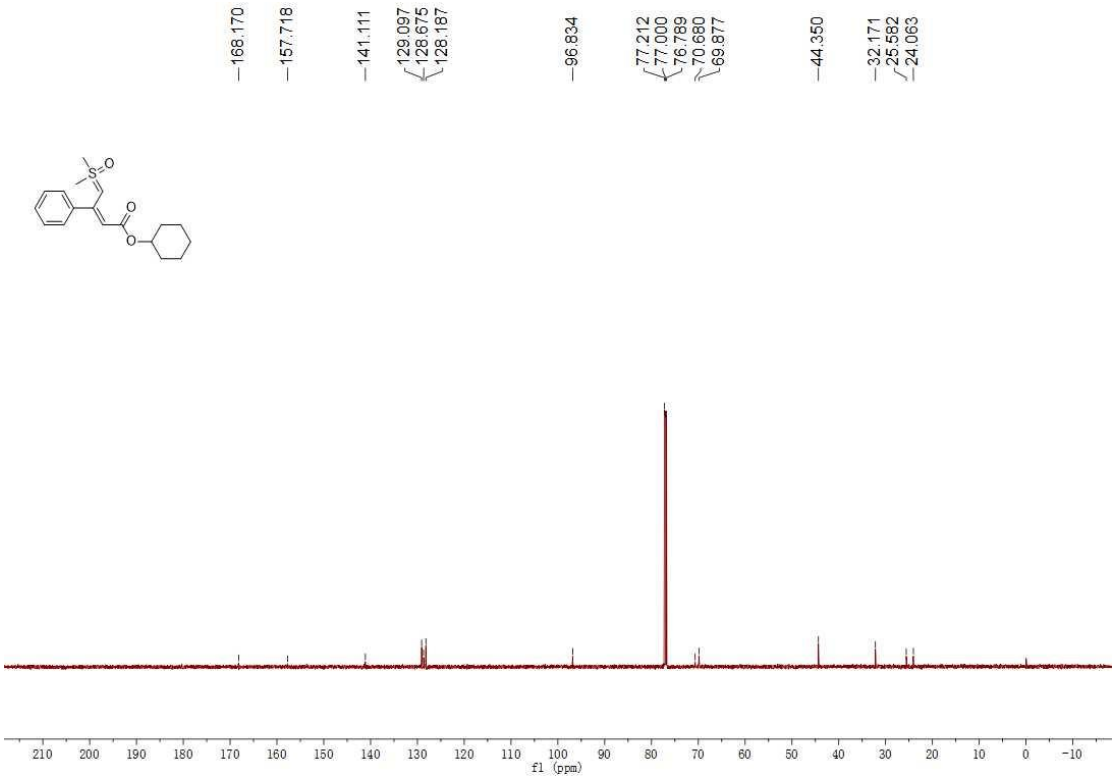
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A61**



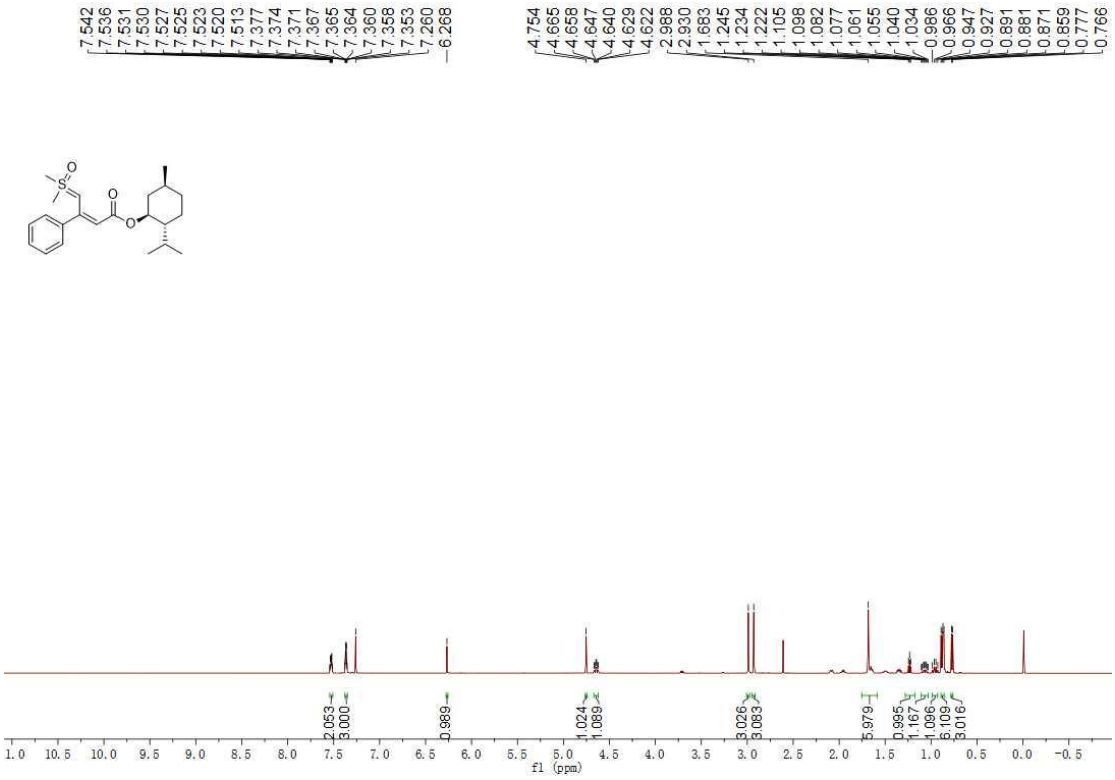
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A62**



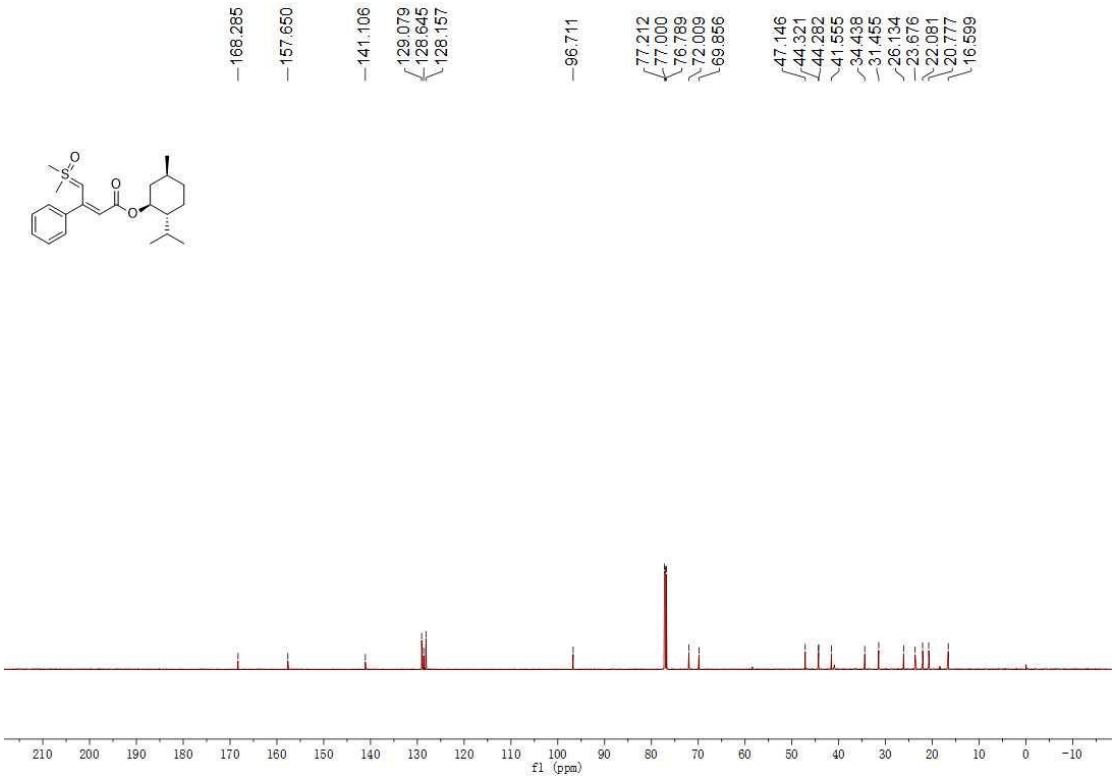
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A62**



^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **A63**



^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of **A63**



^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **2a-*d***