Efficient Access to α-Substituted β-Keto Phosphonates via NHC-Catalyzed Dehaloacylation of α-Bromo Phosphonates

Supporting Information

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1. General information

All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Brüker ASCEND 400 (400 MHz) spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 377 MHz, ^{31}P: 162 MHz), and deuterated $CDCl_3$ was used as solvent. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H, ^{13}C, and ^{31}P NMR spectra, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.0 ppm; DMSO: δH = 2.50 ppm, δC = 40.0 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). High-resolution mass spectrometer analysis (HRMS) was performed on a Thermo Fisher Q Exactive mass spectrometer. Analytical thin-layer chromatography (TLC) was carried out on a pre-coated silica gel plate (0.2 mm thickness). All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

2. Optimization of the reaction conditions[a]

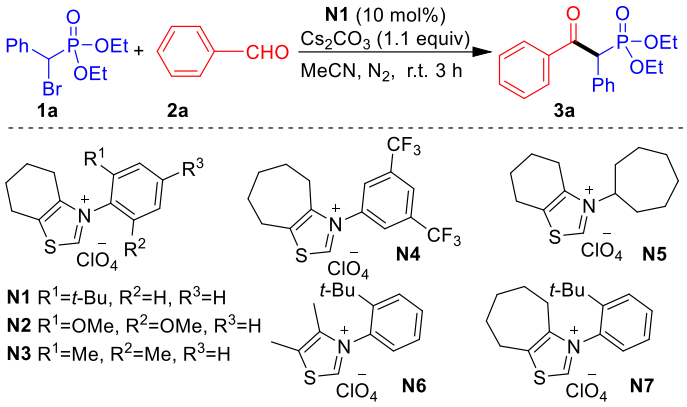


Table S1.

Entry	Variation from the initial conditions	**3a**[%][b]
1	none	13
2	60 °C instead of room temperature	59
3	80 °C instead of room temperature	74
4	As entry 3, **N2** instead of **N1**	45
5	As entry 3, **N3** instead of **N1**	39
6	As entry 3, **N4** instead of **N1**	26
7	As entry 3, **N5** instead of **N1**	27
8	As entry 3, **N6** instead of **N1**	19
9	As entry 3, **N7** instead of **N1**	55
10	As entry 3, DMSO, EtOAc instead of MeCN	16, 63
11	As entry 3, THF or 1,4-dioxane instead of MeCN	45, 62
12	As entry 3, DCM instead of MeCN	90
13	As entry 3, DCE instead of MeCN	22
14	As entry 12, K_3PO_4 instead of Cs_2CO_3	98(90)[c]
15	As entry 12, DBU instead of Cs_2CO_3	24
16	As entry 12, Na_2CO_3, K_2CO_3 instead of Cs_2CO_3	0, 12
17	As entry 14, without NHC or base	0

[a] Reaction conditions: **1a** (1.0 equiv), **2a** (1.2 equiv), NHC (10 mol%), K_3PO_4 (1.1 equiv), DCM (1.0 mL), N_2 atmosphere, 80 °C, 3 h . [b] The yield is determined by ^1H NMR of the reaction mixture with 1,3,5-trimethoxybenzene being used as internal standard. [c] Isolated yields.

3. Mechanistic study and proposed reaction pathway.

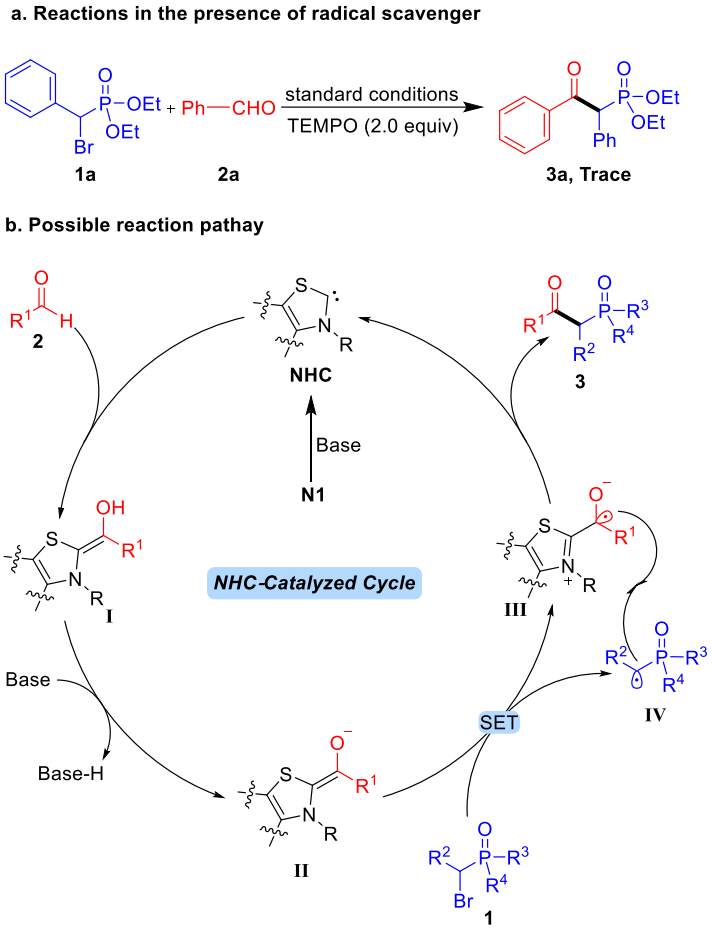
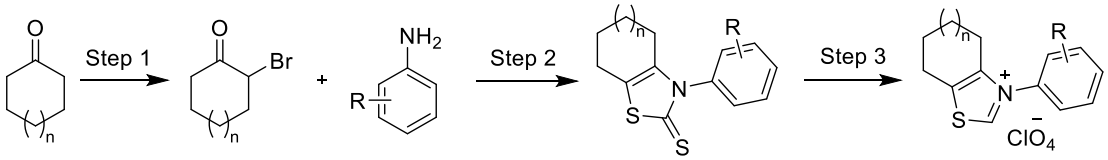


Figure S1

Radical trapping experiment: In an oven dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1a** (0.1 mmol), **2a** (0.12 mmol), **N1**(10 mol%), Tempo (0.2 mmol, 2 equiv) and 0.11 mmol K_3PO_4 were added to degassed DCM (1 mL) under the nitrogen atmosphere. Then, the reaction mixture was stirred under 80 ℃ for 3 h.

4. Supplementary Methods

4.1 Preparation and characterization of carbene catalysts



Scheme S1.

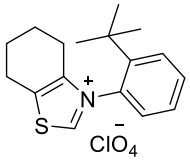
Step 1: A round-bottom flask was charged with the ketone (1.0 equiv) in CH_2Cl_2 (0.25 mL/mmol). At room temperature, *p*-toluenesulfonic acid monohydrate (0.1 equiv) was added in one portion, followed by portionwise addition of *N*-bromosuccinimide (1.0 equiv). The reaction was cooled as necessary. After complete conversion, *n*-pentane was added, and stirring was continued for an additional 5-10 min. The solid was collected by suction filtration and washed with *n*-pentane. The organic phase was then washed successively with saturated aqueous $Na_2S_2O_5$ solution,

half-saturated aqueous $NaHCO_3$ solution, and brine. The organic phase was dried over anhydrous $MgSO_4$, and the volatiles were removed under reduced pressure. The crude product obtained was used directly in the next step without further purification.

Step 2: A solution of the aniline (1.0 equiv) in DMSO (0.50 mL/mmol) was treated with 20 N aq. NaOH solution (1.0 equiv). At 0 °C CS_2 (1.0 equiv) was added dropwise and stirred for 1 h at room temperature. The ketone (1.0 equiv) was added 0 °C and the mixture was stirred for 1-3 h at room temperature. H_2O (1 mL/mmol) was added, the mixture was stirred for 10 min at 0 °C and the supernatant solution was decanted three times. The resulting slurry was suspended in EtOH (1 mL/mmol), concd. HCl (0.05 mL/mmol) was added and the mixture was heated to reflux for 1 h. After cooling, a precipitate formed. The precipitate was collected by filtration, washed with H_2O, and the resulting solid was used directly in the next step without further purification.

Step 3: A solution of the thione (1.0 equiv) in glacial acetic acid (4.12 mL/mmol) was treated under water bath cooling dropwise with H_2O_2 (3.3 equiv) and was stirred for 30 min at that temperature. The volatile components were removed under reduced pressure. The residue was dissolved in MeOH (0.69 mL/mmol). At 0 °C a mixture of sodium perchlorate monohydrate (4.12 equiv) in a mixture of MeOH/H_2O = 2/1 (3.45 mL/mmol) was added. The reaction mixture was extracted with CH_2Cl_2 and H_2O. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting solid was recrystallized from methanol.[1]

3-(2-(tert-butyl)phenyl)-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium perchlorate(N1)



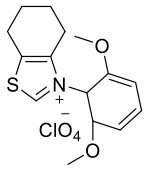
According to Method in Section 4.1: According to Step 1, 19.63 g of cyclohexanone (200 mmol), 35.60 g of NBS (200 mmol), and 3.80 g of *p*-toluenesulfonic acid monohydrate (20 mmol) were used to obtain 31.16 g of 2-bromocyclohexan-1-one (88% yield). According to Step 2, 7.46 g of 2-(tert-butyl)aniline (50 mmol) and 3.81 g of CS_2 (50 mmol) were taken, followed by the addition of 8.85 g of 2-bromocyclohexan-1-one (50 mmol). After the reaction, 3.12 g of crude 3-(2-(tert-butyl)phenyl)-4,5,6,7-tetrahydrobenzo[d]thiazole-2(3H)-thione (21% yield) was obtained, which was used directly in the next step without purification. According to Step 3, 3.12 g of the above thione (10.3 mmol) was treated with H_2O_2 and glacial acetic acid, then reacted with 5.96 g of sodium perchlorate monohydrate. After recrystallization from methanol, 2.64 g of pure **N1** solid (69% yield) was obtained. The overall yield for the three steps is 14%. The characterization data for **N1** are as follows.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.70 – 7.68(m, 1H), 7.59 – 7.55 (m, 1H), 7.42 – 7.38 (m, 1H), 7.35 – 7.32 (m, 1H), 3.16 – 3.09 (m, 1H), 2.98 – 2.92 (m, 1H), 2.59 – 2.51 (m, 1H), 2.34 – 2.27 (m, 1H), 2.07 – 1.90 (m, 3H), 1.85 – 1.76 (m, 1H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.31, 145.66, 145.20, 136.48, 131.92, 130.01, 129.05, 128.21, 36.15, 31.74, 24.22, 23.81, 21.52, 20.75.

HRMS (ESI-TOF, m/z): Found: *m/z* 272.1476. Calcd for $C_{17}H_{21}NS^+$ $(M+H)^+$ 272.1467

3-(2,6-dimethoxycyclohexa-2,4-dien-1-yl)-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium perchlorate (N2)



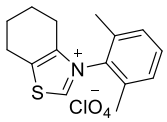
According to Method in Section 4.1： According to Step 1, 19.63 g of cyclohexanone (200 mmol), 35.60 g of NBS (200 mmol), and 3.80 g of *p*-toluenesulfonic acid monohydrate (20 mmol) were used to obtain 31.16 g of 2-bromocyclohexan-1-one (88% yield). According to Step 2, 22.98 g of 2,6-dimethoxyaniline (150 mmol) and 11.42 g of CS_2 (150 mmol) were taken, followed by the addition of 26.55 g of 2-bromocyclohexan-1-one (150 mmol) to obtain 16.33 g of crude product 3-(2,6-dimethoxyphenyl)-4,5,6,7-tetrahydrobenzo[d]thiazole-2(3H)-thione (35%), which was used directly in the next step without purification. According to Step 3, 16.33 g of the thione (53.1 mmol) was treated with H_2O_2 and glacial acetic acid, then reacted with 30.73 g of sodium perchlorate monohydrate, and after recrystallization from methanol, 10.38 g of pure **N2** solid (52%) was obtained. The overall yield for the three steps is 19%.The following are the characterization data for **N2**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.51 (t, J = 8.6 Hz, 1H), 6.73 (d, J = 8.6 Hz, 2H), 3.81 (s, 6H), 2.99 – 2.96 (m, 2H), 2.41 - 2.37(m, 2H), 1.99 – 1.93 (m, 2H), 1.92 – 1.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.45, 154.52, 144.94, 134.77, 133.56, 112.53, 104.60, 56.51, 23.66, 22.42, 21.61, 20.63.

HRMS (ESI-TOF, m/z): Found: *m/z* 276.1063. Calcd for $C_{15}H_{17}NO_2S^+$ $(M+H)^+$ 276.1052

3-(2,6-dimethylcyclohexa-2,4-dien-1-yl)-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium perchlorate (N3)



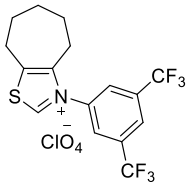
According to Method in Section 4.1： According to Step 1, 19.63 g of cyclohexanone (200 mmol), 35.60 g of NBS (200 mmol), and 3.80 g of *p*-toluenesulfonic acid monohydrate (20 mmol) were used to obtain 31.16 g of 2-bromocyclohexan-1-one (88% yield). According to Step 2, 6.06 g of 2,6-dimethylaniline (50 mmol) and 3.81 g of CS_2 (50 mmol) were taken, followed by the addition of 8.85 g of 2-bromocyclohexan-1-one (50 mmol) to obtain 10.18 g of crude product 3-(2,6-dimethylphenyl)-4,5,6,7-tetrahydrobenzo[d]thiazole-2(3H)-thione (74%), which was used directly in the next step without purification. According to Step 3, 10.18 g of the thione (37.0 mmol) was treated with H_2O_2 and glacial acetic acid, then reacted with 21.41 g of sodium perchlorate monohydrate, and after recrystallization from methanol, 5.32 g of pure **N3** solid (42%) was obtained. The overall yield for the three steps is 31%. The following are the characterization data for **N3**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.67 (s, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.27 (s, 2H), 3.02 (t, J = 6.0 Hz, 2H), 2.31 (t, J = 6.0, 2H), 2.04 (s, 6H), 2.04 – 1.97 (m, 2H), 1.94 – 191 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$):δ 160.7, 144.3, 142.9, 136.9, 134.0, 131.6, 129.6, 23.8, 22.9, 21.7, 20.9, 17.5.

HRMS (ESI-TOF, m/z): Found: *m/z* 244.1161. Calcd for $C_{15}H_{17}NS^+$ $(M+Na)^+$ 244.1154

3-(3,5-bis(trifluoromethyl)phenyl)-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium perchlorate (N4)



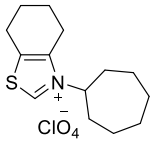
According to Method in Section 4.1： According to Step 1, 22.43 g of cycloheptanone (200 mmol), 35.60 g of NBS (200 mmol), and 3.80 g of *p*-toluenesulfonic acid monohydrate (20 mmol) were used to obtain 32.86 g of 2-bromocycloheptanone (86% yield). According to Step 2, 11.46 g of 3,5-bis(trifluoromethyl)aniline (50 mmol) and 3.81 g of CS_2 (50 mmol) were taken, followed by the addition of 9.55 g of 2-bromocycloheptanone (50 mmol) to obtain 10.56 g of crude product 3-(3,5-bis(trifluoromethyl)phenyl)-3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione (53%), which was used directly in the next step without purification. According to Step 3, 10.56 g of the thione (26.6 mmol) was treated with H_2O_2 and glacial acetic acid, then reacted with 15.39 g of sodium perchlorate monohydrate, and after recrystallization from methanol, 4.57 g of pure **N4** solid (37%) was obtained. The overall yield for the three steps is 20%. The following are the characterization data for **N4**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (s, 1H), 8.14 – 8.12 (m, 3H), 3.06 – 3.04 (m, 2H), 2.71 – 2.68 (m, 2H), 1.93 – 1.88 (m, 4H), 1.76 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, DMSO):δ 157.8, 148.6, 139.1, 138.7, 132.1 (q, J = 34.1 Hz), 129.1 (d, J = 4.0 Hz), 126.5 – 125.4 (m), 123.0 (q, J = 273.2 Hz), 30.2, 27.5, 27.0, 26.4, 24.6.

HRMS (ESI-TOF, m/z): Found: *m/z* 366.0746. Calcd for $C_{16}H_{13}F_6NS^+$ $(M+H)^+$ 366.0745

3-cycloheptyl-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium perchlorate (N5)



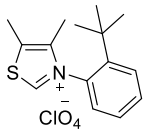
According to Method in Section 4.1: According to Step 1, 19.63 g of cyclohexanone (200 mmol), 35.60 g of NBS (200 mmol), and 3.80 g of *p*-toluenesulfonic acid monohydrate (20 mmol) were used to obtain 31.16 g of 2-bromocyclohexan-1-one (88% yield). According to Step 2, 5.66 g of cycloheptylamine (50 mmol) and 3.81 g of CS_2 (50 mmol) were taken, followed by the addition of 8.85 g of 2-bromocyclohexan-1-one (50 mmol) to obtain 11.62 g of crude product 3-cycloheptyl-4,5,6,7-tetrahydrobenzo[d]thiazole-2(3H)-thione (87%), which was used directly in the next step without purification. According to Step 3, 11.62 g of the thione (43.5 mmol) was treated with H_2O_2 and glacial acetic acid, then reacted with 25.17 g of sodium perchlorate monohydrate, and after recrystallization from methanol, 10.34 g of pure **N5** solid (71%) was obtained. The overall yield for the three steps is 62%. The following are the characterization data for **N5**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 4.51 – 4.43 (m, 1H), 2.92 – 2.84 (m, 4H), 2.21 - 2.15 (m, 2H), 2.10 – 2.07 (m, 1H), 2.05 – 2.04 (m, 1H), 2.02 – 1.98 (m,2H), 1.96 – 1.92 (m, 2H), 1.91 – 1.85 (m, 2H), 1.69 – 1.64 (m, 4H), 1.62 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.69, 143.07, 136.16, 65.00, 35.29, 26.69, 24.30, 23.86, 23.28, 21.61, 20.91.

HRMS (ESI-TOF, m/z): Found: *m/z* 236.1458. Calcd for $C_{14}H_{21}NS^+$ $(M+H)^+$ 236.1467

3-(2-(tert-butyl)phenyl)-4,5-dimethylthiazol-3-ium perchlorate (N6)



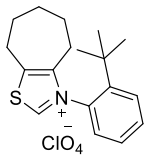
According to Method in Section 4.1： According to Step 2, 8.95 g of 2-(tert-butyl)aniline (60 mmol) and 4.58 g of CS_2 (60 mmol) were taken, followed by the addition of 6.39 g of 3-chloro-2-butanone (60 mmol) to obtain 8.53 g of crude product 3-(2-(tert-butyl)phenyl)-4,5-dimethylthiazole-2(3H)-thione (51%), which was used directly in the next step without purification. According to Step 3, 8.53 g of the thione (30.6 mmol) was treated with H_2O_2 and glacial acetic acid, then reacted with 17.71 g of sodium perchlorate monohydrate, and after recrystallization from methanol, 6.89 g of pure **N6** solid (65%) was obtained. The overall yield for the three steps is 33%. The following are the characterization data for **N6**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.72 – 7.69 (m, 1H), 7.61 – 7.57 (m, 1H), 7.44 – 7.39 (m, 1H), 7.31 – 7.29 (m, 1H), 2.78 – 2.49 (m, 3H), 2.36 – 2.02 (m, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.98, 145.19, 143.74, 134.29, 134.16, 132.04, 130.10, 129.12, 128.34, 36.17, 31.72, 12.84, 12.66.

HRMS (ESI-TOF, m/z): Found: *m/z* 246.1319. Calcd for C15H19NS$^+$ $(M+H)^+$ 246.1310

3-(2-(tert-butyl)phenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[d]thiazol-3-ium perchlorate (N7)



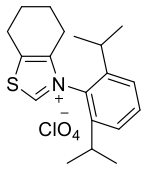
According to Method in Section 4.1： According to Step 1, 22.43 g of cycloheptanone (200 mmol), 35.60 g of NBS (200 mmol), and 3.80 g of *p*-toluenesulfonic acid monohydrate (20 mmol) were used to obtain 32.86 g of 2-bromocycloheptanone (86% yield). According to Step 2, 22.38 g of 2-(tert-butyl)aniline (150 mmol) and 11.43 g of CS_2 (150 mmol) were taken, followed by the addition of 28.65 g of 2-bromocycloheptanone (150 mmol) to obtain 18.41 g of crude product 3-(2-(tert-butyl)phenyl)-3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione (39%), which was used directly in the next step without purification. According to Step 3, 18.41 g of the thione (58.0 mmol) was treated with H_2O_2 and glacial acetic acid, then reacted with 33.56 g of sodium perchlorate monohydrate, and after recrystallization from methanol, 12.98 g of pure **N7** solid (65%) was obtained. The overall yield for the three steps is 22%. The following are the characterization data for **N7**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (s, 1H), 7.72 – 7.69 (m, 1H), 7.61 – 7.56 (m, 1H), 7.41 – 7.37 (m, 1H), 7.29 – 7.27 (m, 1H), 3.19 – 3.04 (m, 2H), 2.72 – 2.65 (m, 1H), 2.60 – 2.53 (m, 1H), 1.98 – 1.91 (m, 3H), 1.84 – 1.73 (m, 2H), 1.64 – 1.62 (m, 1H), 1.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.62, 149.52, 145.25, 139.90, 134.33, 131.88, 129.88, 129.15, 128.11, 36.07, 31.63, 30.44, 28.23, 28.00, 26.42, 24.85.

HRMS (ESI-TOF, m/z): Found: *m/z* 286.1629 Calcd for C18H23NS$^+$ $(M+H)^+$ 286.1623

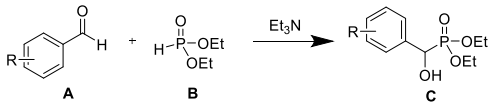
3-(2,6-diisopropylphenyl)-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium perchlorate (N8)



According to Method in Section 4.1

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 – 9.85 (m, 1H), 7.60 – 7.56 (m, 1H), 7.37 – 7.34 (m, 2H), 3.12 (s, 2H), 2.27 (s, 2H), 2.10 – 2.06 (m, 2H), 2.05 – 1.97 (m, 2H), 1.90 (d, J = 6.3 Hz, 2H), 1.20 – 1.13 (m, 12H). This compound has already been reported in the literature.[1]

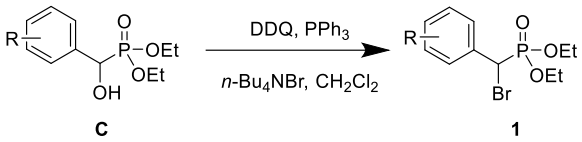
4.2 Preparation of Starting Materials



Scheme S2.

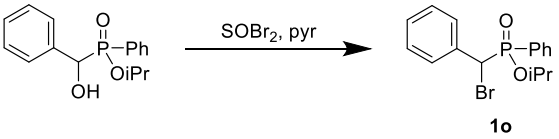
General Procedure for the Synthesis of α-Hydroxy-Phosphonates: A mixture of aldehyde (1.01 equiv), diethylphosphite (1.00 equiv), and triethylamine (0.50 equiv) was stirred at room temperature or 50 °C for the indicated time. The reaction mixture was then diluted with chloroform and concentrated under reduced pressure to remove Et_3N.[2]

4.3 Typical procedure for the preparation of diethyl α-bromobenzylphosphonate



Scheme S3.

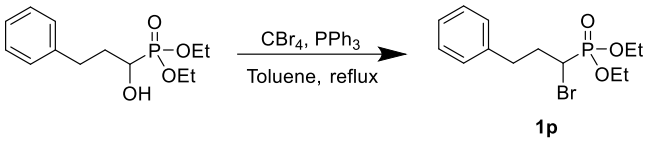
Method A: n-Bu_4NBr (2 mmol, 0.644 g) was added to a stirring mixture of DDQ (2 mmol, 0.454 g) and PPh_3 (2 mmol, 0.524 g) in dry CH_2Cl_2 (10 mL) at room temperature. Then **C** (1 mmol, 0.244 g) was added to the reaction mixture, and the progress of the reaction was monitored by TLC. After 5 h, the reaction mixture was washed with H_2O (3 × 20 mL). The organic layer was separated and dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent afforded a crude product that was purified by preparative plate chromatography (silica gel) eluted with PE/EtOAc (3 : 1) to afford diethyl α-bromobenzylphosphonate in 98% yield (0.3 g) as a yellow oily compound.[3]



Scheme S4

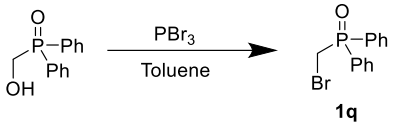
Method B: In a round bottom flask, α-hydroxy benzylic phosphonates (4 mmol) was dissolved in dry DCM (10 mL), and dry pyridine (5 mmol) was added. Thionyl bromide or thionyl chloride (5 mmol) was then added to the round bottom flask under inert atmosphere. The round bottom flask was sealed with a septum, cooled in an ice bath, and slowly allowed to come to room temperature overnight. The solvent was then evaporated, and the crude product was dissolved in ethyl acetate. The organic layer was washed with 1 M HCl, saturated $NaHCO_3$, water, brine, then dried over Na_2SO_4 and filtered. Evaporation of the solvent afforded a crude product that was purified by

preparative plate chromatography (silica gel) eluted with Hexane/EtOAc (3 : 1) to afford α-halobenzylphosphonates as yellow oily compounds.[4]



Scheme S5

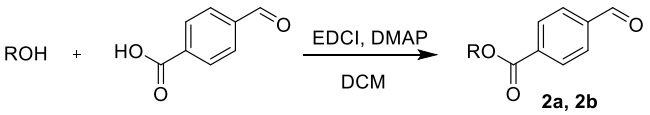
Method C: Carbon tetrabromide(7.63 g, 0.023 mol) is added in one portion to a stirred solution of diethyl 1-hydroxyalkylphosphonate (0.02 mol) and triphenylphosphine (6.56 g, 0.025 mol) in dry toluene (25 mL) at room temperature(ice-water bath). Stirring is continued for 15 min at room temperature, and the mixture is then refluxed for 8 h. The solvent is removed in vacuo, and the brown, semisolid residue is extracted with hexane (3 × 50 ml). The combined extracts are filtered, and the solvent is evaporated under reduced pressure. The oily residue is distilled in vacuo to give analytically pure **1p**.[5]



Scheme S6

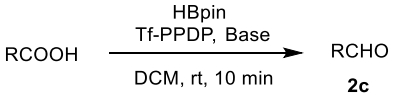
Method D: A mixture of diaryl(hydroxymethyl)phosphine oxide (3.48 g, 15.0 mmol) and PBr_3 (1.62 g, 6.0 mmol) in 10 mL of anhydrous toluene was stirred in a 100 °C heating mantle for 1-3 h. Then the reaction mixture was diluted with an equal volume of chloroform. The organic solution was washed with water, $NaHCO_3$ saturated solution, water, and dried over Na_2SO_4. The solvent was removed in a vacuum, and the products were crystallized on standing as a white solid.[6]

4.4 Typical procedure for the preparation of aldehydes derived from drug molecules



Scheme S7

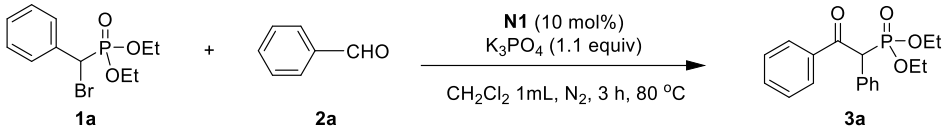
Method A: To a solution of the 4-carboxybenzaldehyde (6 mmol, 1.2 equiv) in DCM (0.02 mmol/mL) was added EDCI (13 mmol, 2.6 equiv) at rt under an Ar atmosphere. Then, the resulting mixture was stirred for 5 min. Then the DMAP (2.5 mmol, 0.5 equiv) and the corresponding alcohol (5 mmol, 1.0 equiv) were added. After stirring overnight at rt, the mixture was washed with Na_2CO_3, H_2O, and brine. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in a vacuum, and the crude residue was then purified by column chromatography on silica gel.[7]



Scheme S8

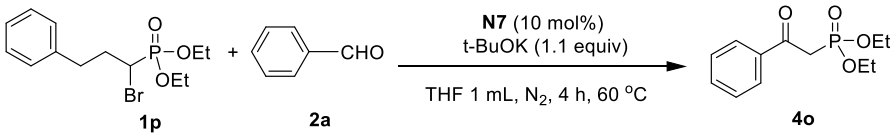
Method B: To a 25 mL Schlenk tube equipped with a magnetic stirring bar, carboxylic acid (0.3 or 1.0 mmol, 1.0 equiv), base (1.6 or 1.8 equiv), and DCM (2.0 ~ 5.0 mL) were added under a dry nitrogen atmosphere. Then the Tf-PPDP (1.7 equiv) and HBpin (1.1 ~ 1.8 equiv) were added to the reaction mixture. After the reaction was stirred for 10 min, the crude mixture was quenched by H_2O and extracted by DCM (3 × 3.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford the desired aldehydes.[8]

4.5 General procedure for substrate scope



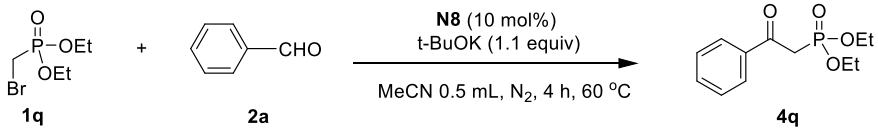
Scheme S9

The model reaction A: In an oven dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1a** (0.1 mmol), **2a** (0.12 mmol), **N1**(10 mol%), and 0.11 mmol K_3PO_4 were added to degassed DCM (1 mL) under the nitrogen atmosphere. Then, the reaction mixture was stirred under 80 ℃ for 3 h. After completion of the reaction, the mixture removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate from 2/1) to afford **3a** (90%).



Scheme S10

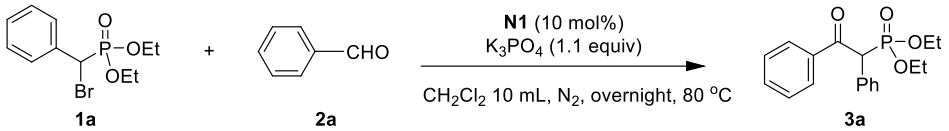
The model reaction B: In an oven dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1p** (0.1 mmol), **2a** (0.12 mmol), **N7**(10 mol%), and 0.11 mmol t-BuOK were added to degassed THF (1 mL) under the nitrogen atmosphere. Then, the reaction mixture was stirred under 60 ℃ for 4 h. After completion of the reaction, the mixture removed under vacuum. The residue was purified by column chromatography on silica gel to afford **4o** (51%).



Scheme S11

The model reaction C: In an oven dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1q** (0.05 mmol), **2a** (0.06 mmol), **N8**(10 mol%), and 0.055 mmol t-BuOK were added to degassed MeCN (0.5 mL) under the nitrogen atmosphere. Then, the reaction mixture was stirred under 60 ℃ for 4 h. After completion of the reaction, the mixture removed under vacuum. The residue was purified by column chromatography on silica gel to afford **4q** (60%).

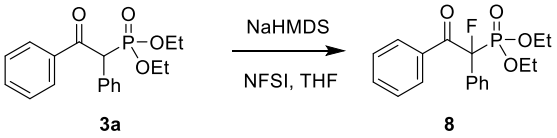
4.6 Gram-scale synthesis and chemical transformation of products



Scheme S12

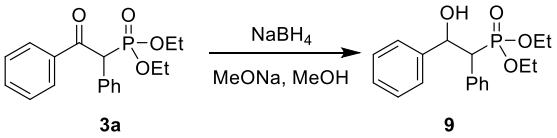
In an oven dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1** (1.53 g), **2a** (0.64 g), **N2**(0.19 g), and K_3PO_4(1.16 g) were added to degassed DCM (10 mL) under the nitrogen atmosphere. Then, the reaction mixture was stirred under 80 ℃ for overnight. After completion of the reaction, the mixture removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate from 2/1) to afford **3a** (79%).

4.7 Further methods for product transformation



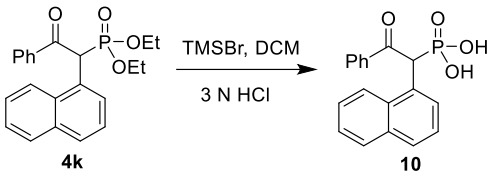
Scheme S13

Method A: To a solution of **3a** (0.097 g, 0.29 mmol) in dry THF (3 mL) at -78℃ was added a solution of NaHMDS (0.22 mL, 2.0 M in THF, 0.44 mmol) over a period of 10 min under an atmosphere of dry argon. The resulting solution was stirred for 1 h at -78 ℃. A solution of NFSI (0.12 g, 0.38 mmol) in dry THF (2 mL) was added over a period of 10 min, and the resulting solution stirred at -78 ℃ for 2 h. The solution was allowed to warm to -30 ℃, and a precipitate formed, and quenched with 0.01 M hydrochloric acid. Volatiles were removed under reduced pressure, and the residue extracted with CH_2Cl_2. The organic layers were combined and concentrated by rotary evaporation. The crude material was purified via flash column chromatography of silica gel to yield **8** (0.093 g, 91% yield).[9]



Scheme S14

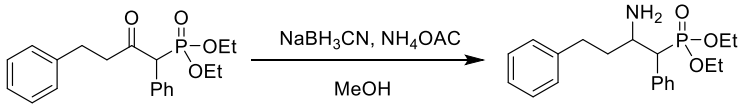
Method B: A 100 mL two-necked round-bottom flask, equipped with a magnetic stir bar and fitted with a rubber septum, was charged with **3a** (0.15 mmol), methanol (5 mL), and NaOMe (0.0075 mmol) at 25 °C. Powdered $NaBH_4$ (0.3 mmol) was added in one portion to the reaction mixture with constant stirring. The progress of the reaction was followed by TLC. The mixture was stirred for 3 h at 25 °C. The reaction was quenched by the addition of excess methanol. The resultant solution was evaporated on a rotary evaporator at reduced pressure, and the residue was extracted with CH_2Cl_2(5 × 10 mL). The organic layers were combined and concentrated by rotary evaporation. The crude material was purified via flash column chromatography of silica gel to yield **9** (0.0390 g, 78% yield).[10]



4k 10

Scheme S15

Method C: To a stirred solution of 0.0704 g of **3a** in 3 mL of CH_2Cl_2 was added a solution of 0.162 g of bromotrimethylsilane in 3 mL of CH_2Cl_2, and the mixture was stirred for 18 h, then concentrated under reduced pressure. The residue was treated with 3 N HCl (aq) and stirred for 3 h. The precipitate was collected, rinsed with ether, and dissolved in boiling methanol. The product precipitates upon addition of ethyl acetate to the boiling methanol solution. The precipitate was collected and rinsed with ethyl acetate to afford 0.0470 g (80%) of **10** as a solid.[11]



3af 11

Scheme S16

Method D: β-Keto phosphonate **3af** (0.072 g) was dissolved in dried MeOH (5 mL). NH_4OAc (0.611 g) was added and the reaction was heated to 25 °C for 10 min followed by addition of $NaBH_3CN$ (0.0664 g) and reflux at 60 °C for 16 h. Solvent removal was performed using reduced pressure and the remaining was dissolved in 0.5 M aq NaOH (5 mL) followed by extraction with EtOAc (3 × 10 mL). The organic layers were combined and concentrated by rotary evaporation. The crude material was purified via flash column chromatography of silica gel to yield **11** (0.055 g, 76%).[12]

5. Antibacterial studies of the products

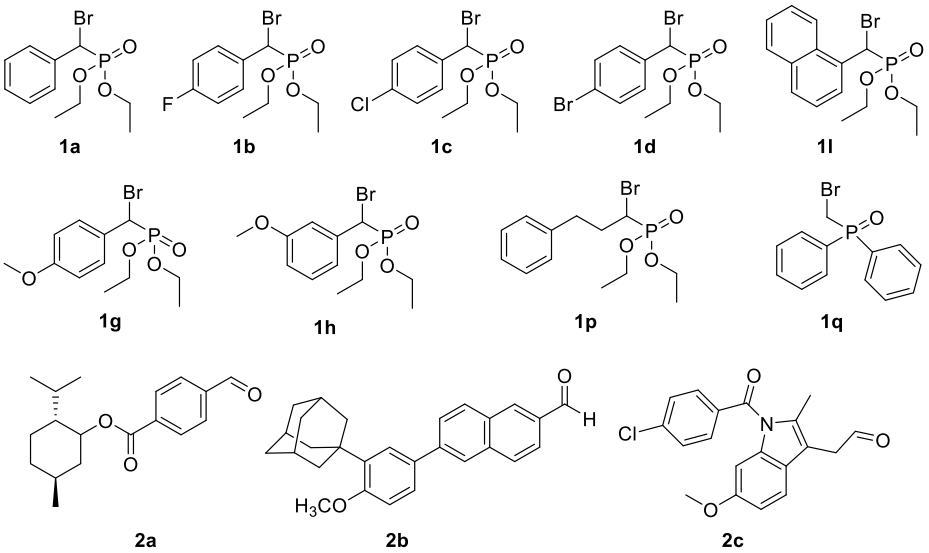
Table S2. In vitro antibacterial activity of the new compounds. (50 μg/mL)

Compd	Inhibition rate (%)							
	Rs	*Ps*	*Fo*	*Ss*	*Af*	*Pc*	*Fg*	*Ab*
3c	35.77±3.55	53.6±2.04	35.97±1.01	59.15±0.99	57.28±1.42	52.31±3.12	45.39±2.06	55.76±1.51
3r	46.02±1.66	31.65±2.25	24.82±1.47	33.45±3.14	18.27±1.07	48.74±1.90	66.05±1.03	23.05±1.68
3h	42.68±1.19	4.32±2.93	22.30±1.23	37.68±3.14	77.71±1.39	42.76±3.02	68.63±0.81	24.91±2.43
3g	15.16±1.57	3.24±3.12	26.26±1.47	23.94±4.52	24.46±0.88	51.02±2.42	71.08±0.89	24.16±2.20
3q	22.36±3.48	21.94±1.47	25.54±1.07	32.75±1.26	20.74±1.76	49.22±2.18	45.88±2.90	29.00±2.95
3ac	52.44±3.01	75.18±1.07	47.12±1.07	78.52±1.44	59.13±1.07	44.22±3.94	67.45±1.58	69.14±0.82
3n	35.37±1.06	39.57±3.26	28.06±1.59	53.17±3.29	38.70±1.52	42.50±1.34	63.53±2.21	47.21±3.95
3z	58.94±3.99	11.08±4.16	23.74±1.01	27.11±2.00	5.57±1.28	51.41±4.19	44.58±2.11	21.56±2.95
3ad	39.84±2.97	30.94±2.46	35.25±1.23	65.85±2.23	32.51±1.39	45.61±2.36	49.80±2.51	35.69±4.65
3d	38.62±2.54	49.28±2.04	32.37±1.01	65.14±1.60	46.75±1.39	45.24±2.12	71.08±0.88	59.85±1.27
3k	21.32±1.62	10.79±2.93	25.54±1.07	27.11±3.14	17.03±3.16	48.32±2.13	49.08±2.52	21.56±0.82
3s	42.28±2.97	6.47±2.93	22.30±2.46	30.28±1.21	16.10±1.28	52.82±1.56	66.67±3.56	39.41±2.27
3e	38.62±4.84	10.79±3.41	21.58±1.59	33.10±3.95	15.48±0.93	52.13±2.11	57.20±1.63	18.59±2.10
3b	28.46±2.97	5.40±2.28	32.37±4.02	53.52±4.36	49.85±1.42	43.36±1.81	65.86±1.62	32.34±1.77
3i	13.28±1.41	10.79±1.59	25.90±1.59	36.41±2.50	19.50±1.76	40.34±2.87	70.85±0.81	27.88±2.74
3f	43.5±1.67	52.16±1.92	29.50±2.01	69.01±2.31	47.68±1.28	39.18±2.53	44.31±1.34	53.16±1.27
3t	65.45±3.2	11.51±3.48	22.66±1.47	26.06±4.68	19.20±1.42	47.39±2.32	73.43±1.03	45.72±3.74
3j	48.02±2.36	12.52±2.95	21.94±1.47	35.21±1.25	14.24±2.26	44.59±2.19	55.35±0.81	9.29±1.64
3x	34.96±4.05	15.83±2.46	28.06±3.03	42.25±3.22	32.51±1.39	53.06±2.12	55.69±0.86	39.78±2.84
3o	32.36±2.22	39.57±1.74	34.53±1.59	35.56±4.64	41.80±1.39	31.62±1.68	52.61±2.60	53.16±2.20
Mancozeb	70.73±3.64	66.19±2.93	87.77±2.01	42.25±2.61	42.72±0.69	64.31±3.01	87.9±1.56	31.97±1.10
Azoxystrobin	67.07±3.57	56.12±3.41	56.12±1.01	57.75±2.42	52.01±2.26	54.23±2.04	61.62±1.63	59.13±2.04

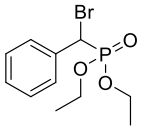
All data were obtained as the average of three replicates; the commercial bactericides Mancozeb and Azoxystrobin were selected as the positive control; The antifungal activities of the compounds against *Rhizoctonia solani (Rs), Phomopsis sp. (Ps), Fusarium oxysporum f. sp. capsicum (Fo), Sclerotinia sclerotiorum (Ss), Phytophthora capsici (Pc), Fusarium graminearum (Fg)*, and *Alternaria brassicicola (Ab)* were evaluated using the mycelial growth rate method.[13]

6. Analytical data of products

The following substrates have all been previously reported.



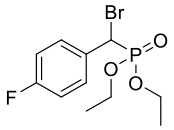
diethyl (bromo(phenyl)methyl)phosphonate (1a)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.52 (m, 2H), 7.37 – 7.31 (m, 3H), 4.85 (d, $^1J_{P\text{-}H}$ = 13.0 Hz, 1H), 4.26 – 4.16 (m, 2H), 4.09 – 3.99 (m, 1H), 3.91 – 3.81 (m, 1H), 1.33 (t, J = 7.0 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H). This compound has already been reported in the literature.[14]

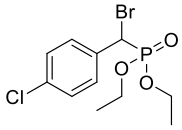
diethyl (bromo(4-fluorophenyl)methyl)phosphonate (1b)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.52 (m, 2H), 7.02 (t, J = 8.5 Hz, 2H), 4.83 (d, $^1J_{P\text{-}H}$ = 13.2 Hz, 1H), 4.25 – 4.16 (m, 2H), 4.09 – 3.99 (m, 1H), 3.94 – 3.83(m, 1H), 1.32 (t, J = 7.0 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). This compound has already been reported in the literature.[15]

diethyl (bromo(4-chlorophenyl)methyl)phosphonate (1c)

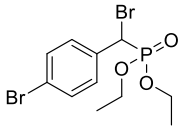


According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.47(m, 2H), 7.32– 7.29 (m, 2H), 4.81 (d, $^1J_{P\text{-}H}$ = 13.2 Hz, 1H), 4.25 – 4.17 (m, 2H), 4.10 – 4.01 (m, 1H), 3.95 – 3.88 (m, 1H), 1.32 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.0

Hz, 3H). This compound has already been reported in the literature.[14]

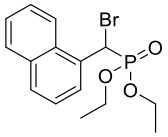
diethyl (bromo(4-bromophenyl)methyl)phosphonate (1d)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.38 (m, 4H), 4.78 (d, $^1J_{P\text{-}H}$ = 13.3 Hz, 1H), 4.22 – 4.14 (m, 2H), 4.10 – 3.99 (m, 1H), 3.93 – 3.82 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). This compound has already been reported in the literature. [15]

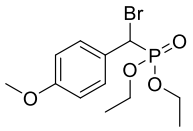
diethyl (bromo(naphthalen-1-yl)methyl)phosphonate (1l)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 8.10 – 7.97 (m, 1H), 7.89 – 7.83 (m, 2H), 7.61 – 7.57 (m, 1H), 7.53 – 7.49 (m, 2H), 5.80 (d, $^1J_{P\text{-}H}$ = 11.5 Hz, 1H), 4.35 – 4.21 (m, 2H), 4.09 – 3.95 (m, 1H), 3.80 – 3.71 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H). This compound has already been reported in the literature.[3]

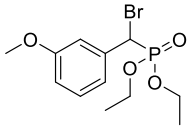
diethyl (bromo(4-methoxyphenyl)methyl)phosphonate (1g)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.47 (m, 2H), 6.86 – 6.84 (m, 2H), 4.84 (d, $^1J_{P\text{-}H}$ = 12.8 Hz, 1H), 4.27 – 4.16 (m, 2H), 4.08 – 3.98 (m, 1H), 3.90 – 3.82 (m, 1H), 3.79 (s, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). This compound has already been reported in the literature.[3]

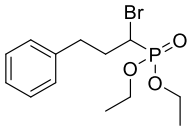
diethyl (bromo(3-methoxyphenyl)methyl)phosphonate (1h)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.18 (m, 1H), 7.12 – 7.06 (m, 3H), 6.85 – 6.81 (m, 1H), 4.80 (d, $^1J_{P\text{-}H}$ = 13.0 Hz, 1H), 4.24 – 4.14 (m, 2H), 4.11 – 3.99 (m, 1H), 3.91 – 3.81 (m, 1H), 3.78 (s, 3H), 1.33 – 1.28 (m, 3H), 1.15 – 1.10 (m, 3H). This compound has already been reported in the literature.[15]

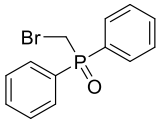
diethyl (1-bromo-3-phenylpropyl)phosphonate (1p)



According to Method C in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 2H), 7.23 – 7.19 (m, 3H), 4.24 – 4.10 (m, 4H), 3.75 – 3.69 (m, 1H), 3.05 – 2.98 (m, 1H), 2.80 – 2.72 (m, 1H), 2.45 – 2.35 (m, 1H), 2.24 – 2.15 (m, 1H), 1.35 – 1.30 (m, 6H). This compound has already been reported in the literature.[16]

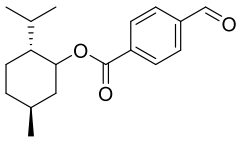
diethyl (bromomethyl)phosphonate (1q)



According to Method D in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.77(m, 4H), 7.60 – 7.48 (m, 6H), 3.80 (d, $^1J_{P\text{-}H}$ = 5.7 Hz, 2H). This compound has already been reported in the literature.[6]

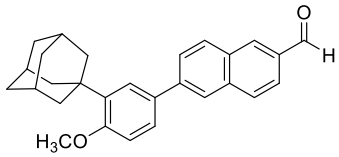
(2R,5S)-2-isopropyl-5-methylcyclohexyl 4-formylbenzoate (2a)



According to Method A in Section 4.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 8.45 – 8.32 (m, 2H), 8.09 – 7.99 (m, 2H), 7.26 (d, *J* = 7.7, 1H), 7.14 – 7.05 (m, 1H), 6.95 (d, *J* = 1.8, 1H), 3.09 – 2.99 (m, 1H), 2.35 (s, 3H), 1.22 (d, *J* = 6.8, 6H). This compound has already been reported in the literature.[7]

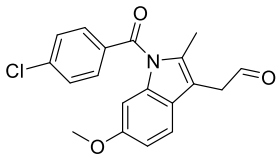
6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthaldehyde (2b)



According to Method A in Section 4.4

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (s, 1H), 8.34 (d, J = 1.2, 1H), 8.04 (dd, J = 5.1, 3.3, 2H), 7.97 (d, J = 1.1, 2H), 7.84 (dd, J = 8.6, 1.8, 1H), 7.61 (d, J = 2.4, 1H), 7.56 (dd, J = 8.4, 2.3, 1H), 7.01 (d, J = 8.5, 1H), 3.91 (s, 3H), 2.19 (d, J = 3.0, 6H), 2.14 – 2.08 (m, 3H), 1.81 (t, J = 3.1, 6H). This compound has already been reported in the literature.[7]

2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)acetaldehyde (2c)

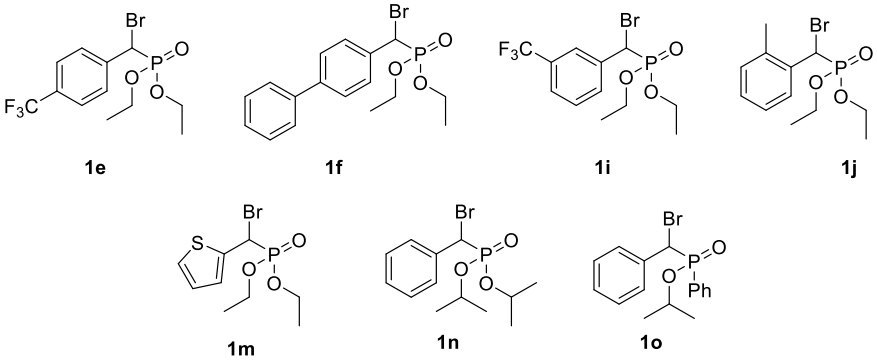


According to Method B in Section 4.4

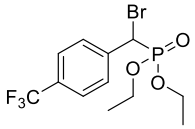
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (t, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.5 Hz,

2H), 6.88 – 6.84 (m, 2H), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.82 (s, 3H), 3.72 (d, *J* = 2.4 Hz, 2H), 2.37 (s, 3H). This compound has already been reported in the literature.[8]

The following substrates have not been previously reported.



diethyl (bromo(4-(trifluoromethyl)phenyl)methyl)phosphonate (1e)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.68 – 7.58 (m, 4H), 4.87 (d, $^{1}J_{P\text{-}H}$ = 13.5 Hz, 1H), 4.26 – 4.18 (m, 2H), 4.13 – 4.02 (m, 1H), 3.99 – 3.90 (m, 1H), 1.35 – 1.30 (m, 3H), 1.20 – 1.15 (m, 3H).

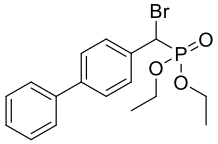
^{13}C NMR (101 MHz, CDCl$_3$): δ 138.7 (d, *J* = 3.1 Hz), 130.9 (qd, *J* = 32.7, 2.5 Hz), 129.9 (d, *J* = 6.3 Hz), 125.6 – 125.5 (m), 123.7 (q, *J* = 272.4 Hz), 64.4 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 64.1 (d, $^{2}J_{P\text{-}C}$ = 6.9 Hz), 40.3 (d, $^{1}J_{P\text{-}C}$ = 158.0 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz).

^{31}P NMR (**162 MHz**, **CDCl$_3$**): δ 16.36.

^{19}F NMR (377 MHz, CDCl$_3$): δ -62.84 (d, *J* = 3.5 Hz).

HRMS (ESI-TOF, m/z): Found: m/z374.9969. Calcd for $C_{12}H_{15}BrF_3O_3P$ $(M+H)^+$ 374.9967

diethyl ([1,1'-biphenyl]-4-ylbromomethyl)phosphonate (1f)



According to Method A in Section 4.3

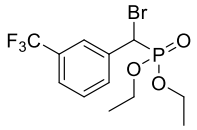
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 – 7.63 (m, 2H), 7.60 – 7.56 (m, 4H), 7.46 – 7.42 (m, 2H), 7.38 – 7.33 (m, 1H), 4.92 (d, $^{1}J_{P\text{-}H}$ = 13.0 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.14 – 4.04 (m, 1H), 3.98 – 3.88 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 141.7 (d, $J_{P\text{-}C}$ = 2.4 Hz), 140.1, 133.5 (d, $J_{P\text{-}C}$ = 3.3 Hz), 129.8 (d, $J_{P\text{-}C}$ = 6.6 Hz), 128.7, 127.6, 127.2 (d, $J_{P\text{-}C}$ = 1.7 Hz), 127.0, 64.1 (d, $^{2}J_{P\text{-}C}$ = 7.0 Hz), 64.0 (d, $^{2}J_{P\text{-}C}$ = 6.9 Hz), 41.2 (d, $^{1}J_{P\text{-}C}$ = 159.6 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 5.9 Hz), 16.1 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz)

^{31}P NMR (**162 MHz**, **CDCl$_3$**): δ 17.04.

HRMS (ESI-TOF, m/z): Found: m/z383.0406. Calcd for $C_{17}H_{20}BrO_3P$ $(M+H)^+$ 383.0406

diethyl (bromo(3-(trifluoromethyl)phenyl)methyl)phosphonate (1i)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.77 (m, 2H), 7.59 – 7.57 (m, 1H), 7.50 – 7.47 (m, 1H), 4.88 (d, $^{1}J_{P\text{-}H}$ = 13.6 Hz, 1H), 4.29 – 4.17 (m, 2H), 4.13 – 4.03 (m, 1H), 4.01 – 3.91 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H).

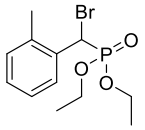
^{13}C NMR (101 MHz, $CDCl_3$): δ 135.8 (d, J= 3.6 Hz), 132.9 (d, J= 6.0 Hz), 130.9 (qd, J = 32.5, 1.4 Hz), 129.2 (d, $J_{P\text{-}C}$ = 1.8 Hz), 126.3 - 126.2 (m), 125.8 – 125.5 (m), 123.7 (q, J = 272.5 Hz), 64.4 (d, $^{2}J_{P\text{-}C}$ = 7.2 Hz), 64.1 (d, $^{2}J_{P\text{-}C}$ = 6.9 Hz), 40.4 (d, $^{1}J_{P\text{-}C}$ = 158.5 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 5.9 Hz), 16.1 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$):δ 16.29.

^{19}F NMR (377 MHz, $CDCl_3$):δ -62.77.

HRMS (ESI-TOF, m/z): Found: m/z374.9965. Calcd for $C_{12}H_{15}BrF_3O_3P$ $(M+H)^+$ 374.9967

diethyl (bromo(o-tolyl)methyl)phosphonate (1j)



According to Method A in Section 4.3

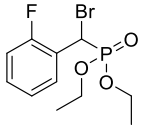
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.85 (m, 1H), 7.25 – 7.17 (m, 2H), 7.14 – 7.12 (m, 1H), 5.15 (d, $^{1}J_{P\text{-}H}$ = 13.9 Hz, 1H), 4.29 – 4.14 (m, 2H), 4.09 – 4.00 (m, 1H), 3.92 – 3.81 (m, 1H), 2.38 (s, 3H), 1.34 (t, J = 7.0 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$):δ 136.0 (d, $J_{P\text{-}C}$ = 9.1 Hz), 132.9 (d, $J_{P\text{-}C}$ = 2.5 Hz), 130.5 (d, $J_{P\text{-}C}$ = 3.9 Hz), 130.2, 128.8 (d, $J_{P\text{-}C}$ = 2.2 Hz), 126.7 (d, $J_{P\text{-}C}$ = 2.2 Hz), 64.0 (d, $^{2}J_{P\text{-}C}$ = 7.0 Hz), 63.9 (d, $^{2}J_{P\text{-}C}$ = 6.9 Hz), 37.4 (d, $^{1}J_{P\text{-}C}$ = 161.1 Hz), 19.4, 16.3 (d, $^{3}J_{P\text{-}C}$ = 5.9 Hz), 16.1 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 17.95.

HRMS (ESI-TOF, m/z): Found: m/z321.0250. Calcd for $C_{12}H_{18}BrO_3P$ $(M+H)^+$ 321.0249

diethyl (bromo(2-fluorophenyl)methyl)phosphonate (1k)



According to Method A in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.84 (m, 1H), 7.36 – 7.29 (m, 1H), 7.23 – 7.17 (m, 1H), 7.09 – 7.02 (m, 1H), 5.35 – 5.29 (m, 1H), 4.32 – 4.22 (m, 2H), 4.14 – 4.06 (m, 1H), 4.04 – 3.94 (m, 1H), 1.39 – 1.34 (m, 3H), 1.32 – 1.16 (m, 3H).

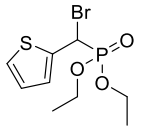
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4 (dd, J = 248.9, 8.5 Hz), 131.8 (dd, J = 3.9, 1.8 Hz), 130.6 (dd, J = 8.6, 2.2 Hz), 124.7 (dd, J = 4.0, 2.2 Hz), 122.3 (dd, J = 13.4, 2.5 Hz), 115.2 (dd, J = 22.1, 1.5 Hz), 64.3 (d, $^{2}J_{P\text{-}C}$ = 7.0 Hz), 64.0 (d, $^{2}J_{P\text{-}C}$ = 7.0 Hz), 32.1 (dd, $^{1}J_{P\text{-}C}$ = 163.0, 4.0 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 6.0 Hz), 16.1 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$):δ 16.68 (d, J = 4.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -117.37 (t, J = 5.1 Hz).

HRMS (ESI-TOF, m/z): Found: m/z 324.9996. Calcd for $C_{11}H_{15}BrFO_3P$ $(M+H)^+$ 324.9998

diethyl (bromo(thiophen-2-yl)methyl)phosphonate (1m)



According to Method A in Section 4.3

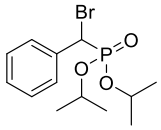
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 2H), 7.00 – 6.96 (m, 1H), 5.22 (d, $^{1}J_{P-H}$ = 13.9， 1H), 4.28 – 4.21 (m, 2H), 4.19 – 4.11 (m, 1H), 4.08 – 3.98 (m, 1H), 1.36 – 1.32 (m, 3H), 1.26 – 1.21 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 129.4 (d, J_{P-C} = 7.7 Hz), 128.9 (d, J_{P-C} = 7.5 Hz), 127.4 (dd, J = 65.6, J_{P-C} =2.0 Hz), 127.2 (dd, J = 61.6, J_{P-C} =2.0 Hz), 64.44 (d, $^{2}J_{P-C}$ = 3.5 Hz), 64.37 (d, $^{2}J_{P-C}$ = 3.3 Hz), 35.97 (d, $^{1}J_{P-C}$ = 166.2 Hz), 16.39 (d, $^{3}J_{P-C}$ = 5.9 Hz), 16.25 (d, $^{3}J_{P-C}$ = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 15.50 (d, J = 30.9 Hz).

HRMS (ESI-TOF, m/z): Found: m/z334.9479. Calcd for $C_9H_{14}BrO_3PS$ $(M+H)^+$ 334.9476

diisopropyl (bromo(phenyl)methyl)phosphonate (1n)



According to Method A in Section 4.3

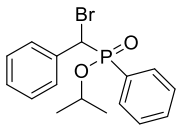
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.50 (m, 2H), 7.38 – 7.24 (m, 3H), 4.96 – 4.68 (m, 2H), 4.61 – 4.37 (m, 1H), 1.34 (d, J = 6.2 Hz, 3H), 1.31 (d, J = 6.2 Hz, 3H), 1.25 (d, J = 6.2 Hz, 3H), 0.94 (d, J = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 134.9 (d, J_{P-C} = 3.0 Hz), 129.5 (d, J_{P-C} = 6.6 Hz), 128.8 (d, J_{P-C} = 2.1 Hz), 128.5 (d, J_{P-C} = 1.6 Hz), 72.7 (d, $^{2}J_{P-C}$ = 7.1 Hz), 72.6 (d, $^{2}J_{P-C}$ = 7.2 Hz), 42.1 (d, $^{1}J_{P-C}$ = 160.9 Hz), 24.2 (d, $^{3}J_{P-C}$ = 2.8 Hz), 24.1 (d, $^{3}J_{P-C}$ = 3.2 Hz), 23.68(d, $^{3}J_{P-C}$ = 5.9 Hz), 23.0 (d, $^{3}J_{P-C}$ = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 15.52.

HRMS (ESI-TOF, m/z): Found: m/z 357.0225. Calcd for $C_{13}H_{20}BrO_3P$ $(M+Na)^+$ 357.0223

isopropyl (bromo(phenyl)methyl)(phenyl)phosphinate (1o, dr: 1: 1.1)



According to Method B in Section 4.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 2H), 7.57 – 7.52 (m, 3H), 7.47 – 7.39 (m, 5H), 7.34 – 7.27 (m, 7H), 7.21 – 7.17 (m, 3H), 4.8 – 4.81 (m, 3H), 4.69 – 4.60 (m, 1H), 1.47 (d, J = 6.1 Hz, 3H), 1.27 (d, J = 6.2 Hz, 3H), 1.19 (d, J = 2.0 Hz, 3H), 1.18 (d, J = 2.0 Hz, 3H).

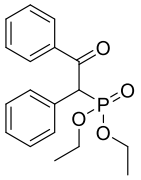
^{13}C NMR (101 MHz, $CDCl_3$): δ 134.3, 134.2, 134.1, 134.0, 132.7 (d, J_{P-C} = 9.4 Hz), 132.6, 132.5 (d, J_{P-C} = 9.4 Hz), 132.4, 129.8 (d, J_{P-C} = 5.3 Hz), 129.7 (d, J_{P-C} = 5.6 Hz), 128.7 (d, J_{P-C} = 2.3 Hz), 128.6 (d, J_{P-C} = 2.5 Hz), 128.3 (d, J_{P-C} = 1.7 Hz), 128.2 (d, J_{P-C} = 2.2 Hz), 128.1 (d, J_{P-C} = 7.1 Hz), 128.0 (d, J

$J_{P\text{-}C}$ = 6.9 Hz), 71.7 (t, $^{2}J_{P\text{-}C}$ = 6.4 Hz), 46.4, 46.2 (d, $^{1}J_{P\text{-}C}$ = 101.7 Hz), 24.2 (d, $^{3}J_{P\text{-}C}$ = 4.3 Hz), 24.1 (d, $^{3}J_{P\text{-}C}$ = 4.3 Hz), 24.0 (d, $^{3}J_{P\text{-}C}$ = 4.0 Hz), 23.8 (d, $^{3}J_{P\text{-}C}$ = 4.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 31.41, 31.35.

HRMS (ESI-TOF, m/z): Found: m/z 375.0120. Calcd for C16H18BrO2P $(M+Na)^+$ 375.0122

diethyl (2-(4-nitrophenyl)-2-oxo-1-phenylethyl)phosphonate(3a)



According to Method A in Section 4.5

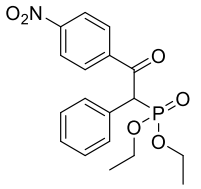
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.94 (m, 2H), 7.55-7.49 (m, 3H), 7.43-7.39 (m, 2H), 7.36 – 7.27(m, 3H), 5.34 (d, $^{1}J_{P\text{-}H}$ = 22.3 Hz, 1H), 4.16 – 4.00 (m, 4H), 1.23-1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.6 (d, $^{2}J_{P\text{-}C}$ = 5.2 Hz), 136.5 (d, $J_{P\text{-}C}$ = 5.6 Hz), 133.3, 131.4 (d, $J_{P\text{-}C}$ = 9.1 Hz), 129.6 (d, $J_{P\text{-}C}$ = 6.4 Hz), 128.9, 128.8 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.6, 127.8 (d, $J_{P\text{-}C}$ = 3.3 Hz), 63.2 (d, $^{2}J_{P\text{-}C}$ = 6.8 Hz), 62.9 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.3 (d, $^{1}J_{P\text{-}C}$ = 138.2 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 3.4 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 3.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.69.

HRMS (ESI-TOF, m/z): Found: *m/z* 333.1250. Calcd for $C_{18}H_{21}O_4P$ $(M+H)^+$ 333.1250

diethyl (2-(4-nitrophenyl)-2-oxo-1-phenylethyl)phosphonate(3b)



According to Method A in Section 4.5

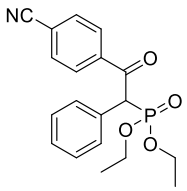
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.24 (m, 2H), 8.11 – 8.08 (m, 2H), 7.51 – 7.49 (m, 2H), 7.38 – 7.30 (m, 3H), 5.28 (d, $^{1}J_{P\text{-}H}$ = 22.7 Hz, 1H), 4.17 – 4.01 (m, 4H), 1.23 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.3 (d, $^{2}J_{P\text{-}C}$ = 5.2 Hz), 150.2, 141.0 (d, $J_{P\text{-}C}$ = 5.4 Hz), 130.5 (d, $J_{P\text{-}C}$ = 9.0 Hz), 129.9, 129.6 (d, $J_{P\text{-}C}$ = 6.1 Hz), 128.5 (d, $J_{P\text{-}C}$ = 3.0 Hz), 128.3 (d, $J_{P\text{-}C}$ = 3.2 Hz), 123.8, 63.6 (d, $^{2}J_{P\text{-}C}$ = 6.8 Hz), 63.2 (d, $^{2}J_{P\text{-}C}$ = 7.3 Hz), 55.0 (d, $^{1}J_{P\text{-}C}$ = 137.7 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 3.4 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 3.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$):δ 18.35.

HRMS (ESI-TOF, m/z): Found: *m/z* 400.0905. Calcd for $C_{18}H_{20}NO_6P$ $(M+Na)^+$ 400.0920

diethyl (2-(4-cyanophenyl)-2-oxo-1-phenylethyl)phosphonate(3c)



According to Method A in Section 4.5

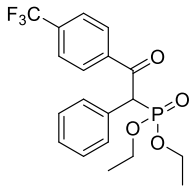
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03Z (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.38 – 7.29 (m, 3H), 5.26 (d, $^{1}J_{P\text{-}H}$ = 22.6 Hz, 1H), 4.11 – 4.00 (m, 4H), 1.22-1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.4 (d, $^{2}J_{P-C}$ = 5.1 Hz), 139.5(d, J_{P-C} = 5.5 Hz), 132.4, 130.6 (d, J_{P-C} = 9.0 Hz), 129.6 (d, J_{P-C} = 6.2 Hz), 129.2, 129.0 (d, J_{P-C} = 2.6 Hz), 128.2 (d, J_{P-C} = 3.2 Hz), 117.7, 116.5, 63.5 (d, $^{2}J_{P-C}$ = 6.7 Hz), 63.1 (d, $^{2}J_{P-C}$ = 7.2 Hz), 54.7 (d, $^{1}J_{P-C}$ = 137.7 Hz), 16.3 (d, $^{3}J_{P-C}$ = 3.7 Hz), 16.2 (d, $^{3}J_{P-C}$ = 3.8 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 18.53.

HRMS (ESI-TOF, m/z): Found: *m/z* 358.1199. Calcd for C19H20NO4P $(M+H)^+$ 358.1202

diethyl (2-oxo-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)phosphonate(3d)



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.37-7.28(m, 3H), 5.31 (d, $^{1}J_{P-H}$ = 22.5 Hz, 1H), 4.16-4.01 (m, 4H), 1.23-1.18 (m, 6H).

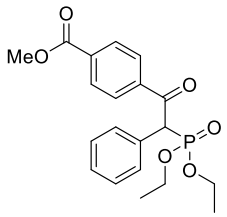
^{13}C NMR (101 MHz, $CDCl_3$): δ 192.7 (d, *J* = 5.2 Hz), 139.2 (d, *J* = 5.5 Hz), 134.5(q, *J* = 32.6 Hz), 130.8 (d, *J* = 9.0 Hz), 129.6 (d, *J* = 6.2 Hz), 128.9 (d, *J* = 2.5 Hz), 128.1 (d, *J* = 3.1 Hz), 126.1(q, *J*= 273.7Hz）, 125.6 (d, *J* = 3.7 Hz), 63.4 (d, $^{2}J_{P-C}$ = 6.7 Hz), 63.1 (d, $^{2}J_{P-C}$ = 7.1 Hz), 54.6 (d, $^{1}J_{P-C}$ = 138.1 Hz), 16.3 (d, $^{3}J_{P-C}$ = 4.0 Hz), 16.2 (d, $^{3}J_{P-C}$ = 4.1 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): 18.85.

^{19}F NMR (377 MHz, $CDCl_3$): δ -63.24.

HRMS (ESI-TOF, m/z): Found: *m/z* 423.0945. Calcd for $C_{19}H_{20}F_3O_4P$ $(M+Na)^+$ 423.0943

methyl 4-(2-(diethoxyphosphoryl)-2-phenylacetyl)benzoate(3e)



According to Method A in Section 4.5

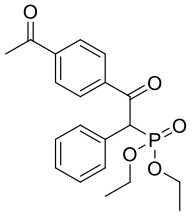
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.51 (m, 2H), 7.36 – 7.28 (m, 3H), 5.32 (d, $^{1}J_{P-H}$ = 22.4 Hz, 1H), 4.15-4.00 (m, 4H), 3.91 (s, 3H), 1.21-1.17 (m,6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.2 (d, $^{2}J_{P-C}$ = 5.2 Hz), 165.9, 139.7 (d, J_{P-C} = 5.4 Hz), 133.9, 130.9 (d, J_{P-C} = 8.9 Hz), 129.7 (d, J_{P-C} = 3.6 Hz), 129.6, 128.8 (d, J_{P-C} = 2.5 Hz), 128.7, 128.0 (d, J_{P-C} = 3.0 Hz), 63.3 (d, $^{2}J_{P-C}$ = 6.7 Hz), 63.0 (d, $^{2}J_{P-C}$ = 7.1 Hz), 54.6 (d, $^{1}J_{P-C}$ = 137.9 Hz), 52.4, 16.2 (d, $^{3}J_{P-C}$ = 2.7 Hz), 16.1 (d, $^{3}J_{P-C}$ = 2.7 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 19.07.

HRMS (ESI-TOF, m/z): Found: m/z 413.1129. Calcd for $C_{20}H_{23}O_6P$ $(M+Na)^+$ 413.1124

diethyl (2-(4-acetylphenyl)-2-oxo-1-phenylethyl)phosphonate(3f)



According to Method A in Section 4.5

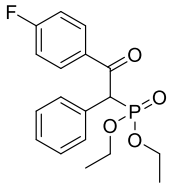
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.37 – 7.29 (m, 3H), 5.32 (d, $^{1}J_{P\text{-}H}$ = 22.4 Hz, 1H), 4.16 – 4.00 (m, 4H), 2.60 (s, 3H), 1.23 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.2, 193.1 (d, $^{2}J_{P\text{-}C}$ = 5.4 Hz), 140.1, 139.7 (d, $J_{P\text{-}C}$ = 5.5 Hz), 131.0 (d, $J_{P\text{-}C}$ = 8.9 Hz), 129.6 (d, $J_{P\text{-}C}$ = 6.2 Hz), 129.1, 128.9 (d, $J_{P\text{-}C}$ = 2.8 Hz), 128.4, 128.0 (d, $J_{P\text{-}C}$ = 3.2 Hz), 63.3 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 63.0 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.7 (d, $^{1}J_{P\text{-}C}$ = 138.0 Hz), 26.8, 16.2 (d, $^{2}J_{P\text{-}C}$ = 3.4 Hz), 16.2 (d, $^{2}J_{P\text{-}C}$ = 3.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.02.

HRMS (ESI-TOF, m/z): Found: *m/z* 397.1184. Calcd for $C_{20}H_{23}O_5P$ $(M+Na)^+$ 397.1175

diethyl (2-(4-fluorophenyl)-2-oxo-1-phenylethyl)phosphonate(3g).



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01– 7.97 (m, 2H), 7.54 – 7.51 (m, 2H), 7.37 – 7.25 (m, 3H), 7.10 – 7.06 (m, 2H), 5.29 (d, $^{1}J_{P\text{-}H}$ = 22.3 Hz, 1H), 4.19 – 3.99 (m, 5H), 1.23-1.18 (m, 6H).

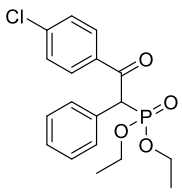
^{13}C NMR (101 MHz, $CDCl_3$): δ 192.0 (d, *J* = 5.1 Hz), 165.7 (d, *J* = 255.9 Hz), 132.7 (dd, *J* = 5.6, 3.0 Hz), 131.6 (d, *J* = 9.5 Hz), 131.2 (d, *J* = 9.1 Hz), 129.5 (d, *J* = 6.2 Hz), 128.7 (d, *J* = 2.8 Hz), 127.9 (d, *J* = 3.2 Hz), 115.6 (d, *J* = 22.0 Hz), 63.2 (d, $^{2}J_{P\text{-}C}$ = 6.6 Hz), 62.8 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.3 (d, $^{1}J_{P\text{-}C}$ = 138.2 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 4.0 Hz), 16.1 (d, $^{3}J_{P\text{-}C}$ = 4.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.35.

^{19}F NMR (377 MHz, $CDCl_3$): δ -104.34.

HRMS (ESI-TOF, m/z): Found: *m/z* 351.1157. Calcd for $C_{18}H_{20}FO_4P$ $(M+H)^+$ 351.1156

diethyl (2-(4-chlorophenyl)-2-oxo-1-phenylethyl)phosphonate(3h)



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.87 (m, 2H), 7.51 – 7.49 (m, 2H), 7.38 – 7.28 (m, 5H), 5.26 (d, $^{1}J_{P\text{-}H}$ = 22.4 Hz, 1H), 4.15 – 3.99 (m, 4H), 1.22 – 1.17 (m, 6H).

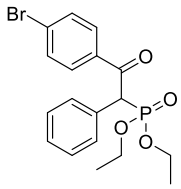
^{13}C NMR (101 MHz, $CDCl_3$): δ 192.4 (d, $^{2}J_{P\text{-}C}$ = 5.1 Hz), 139.9, 134.8 (d, $J_{P\text{-}C}$ = 5.7 Hz), 131.2 (d, $J_{P\text{-}C}$ = 9.0 Hz), 130.3, 129.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 128.9, 128.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.0 (d, $J_{P\text{-}C}$ = 3.3

Hz).·63.2 (d, $^{2}J_{P\text{-}C}$ = 6.8 Hz), 62.9 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.3 (d, $^{1}J_{P\text{-}C}$ = 138.2 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 4.0 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 4.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.25.

HRMS (ESI-TOF, m/z): Found: *m/z* 389.0682. Calcd for $C_{18}H_{20}ClO_4P$ $(M+Na)^+$ 389.0679

diethyl (2-(4-bromophenyl)-2-oxo-1-phenylethyl)phosphonate(3i)



According to Method A in Section 4.5

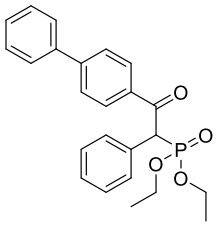
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.49 (m, 2H), 7.36– 7.28 (m, 3H), 5.25 (d, $^{2}J_{P\text{-}H}$ = 22.4 Hz, 1H), 4.17 – 3.99 (m, 4H), 1.22-1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.6(d, $^{1}J_{P\text{-}C}$ = 5.1 Hz), 135.1 (d, $J_{P\text{-}C}$ = 5.6 Hz), 131.9, 131.1 (d, $J_{P\text{-}C}$ = 9.0 Hz), 130.4, 129.6 (d, $J_{P\text{-}C}$ = 6.2 Hz), 128.8(d, $J_{P\text{-}C}$ = 2.6 Hz), 128.6, 128.0 (d, $J_{P\text{-}C}$ = 3.2 Hz), 63.3 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 62.9 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.3 (d, $^{1}J_{P\text{-}C}$ = 138.3 Hz), 16.3(d, $^{1}J_{P\text{-}C}$ = 3.6 Hz), 16.2 (d, $^{1}J_{P\text{-}C}$ = 3.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.24.

HRMS (ESI-TOF, m/z): Found: *m/z* 433.0166. Calcd for $C_{18}H_{20}BrO_4P$ $(M+Na)^+$ 433.0174

diethyl (2-([1,1'-biphenyl]-4-yl)-2-oxo-1-phenylethyl)phosphonate（3j）



According to Method A in Section 4.5

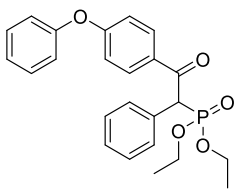
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.55 (m, 4H), 7.46-7.43 (m, 2H), 7.40– 7.34 (m, 3H), 7.31 – 7.27 (m,1H), 5.37 (d, $^{1}J_{P\text{-}H}$ = 22.2 Hz, 1H), 4.21 – 4.02 (m, 4H), 1.25-1.19 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.0 (d, $^{2}J_{P\text{-}C}$ = 5.2 Hz), 146.0, 139.5, 135.0 (d, $J_{P\text{-}C}$ = 5.7 Hz), 131.4(d, $J_{P\text{-}C}$ = 9.1 Hz), 129.6, 129.6, 129.5, 128.8, 128.7 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.2, 127.8 (d, $J_{P\text{-}C}$ = 3.2 Hz), 127.1 (d, $J_{P\text{-}C}$ = 1.7 Hz), 63.2 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 62.9 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.3(d, $^{1}J_{P\text{-}C}$ = 138.4 Hz), 16.3 (d, $^{2}J_{P\text{-}C}$ = 3.6 Hz), 16.2 (d, $^{2}J_{P\text{-}C}$ = 3.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.75.

HRMS (ESI-TOF, m/z): Found: *m/z* 409.1564. Calcd for $C_{24}H_{25}O_4P$ $(M+H)^+$ 409.1563

diethyl (2-oxo-2-(4-phenoxyphenyl)-1-phenylethyl)phosphonate(3k)



According to Method A in Section 4.5

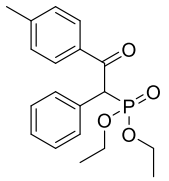
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.52 – 7.50 (m, 2H), 7.40 – 7.27 (m, 5H), 7.21-7.17 (m, 1H), 7.04 – 7.02 (m, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.28 (d, $^1J_{P\text{-}H}$ = 22.1 Hz, 1H), 4.20 – 4.00 (m, 4H), 1.24-1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.0 (d, $^2J_{P\text{-}C}$ = 5.2 Hz), 162.3, 155.1, 131.6 (d, $J_{P\text{-}C}$ = 9.1 Hz), 131.3, 130.8 (d, $J_{P\text{-}C}$ = 5.8 Hz), 130.0, 129.6 (d, $J_{P\text{-}C}$ = 6.2 Hz), 128.7 (d, $J_{P\text{-}C}$ = 2.7 Hz), 127.8 (d, $J_{P\text{-}C}$ = 3.2 Hz), 124.7, 120.3, 117.1, 63.2 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 62.8 (d, $^2J_{P\text{-}C}$ = 7.1 Hz), 54.2 (d, $^1J_{P\text{-}C}$ = 138.7 Hz), 16.3(d, $^2J_{P\text{-}C}$ = 4.9 Hz), 16.2 (d, $^2J_{P\text{-}C}$ = 5.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.83.

HRMS (ESI-TOF, m/z): Found: *m/z* 425.1521. Calcd for $C_{24}H_{25}O_5P$ $(M+H)^+$ 425.1512

diethyl (2-oxo-1-phenyl-2-(p-tolyl)ethyl)phosphonate(3l)



According to Method A in Section 4.5

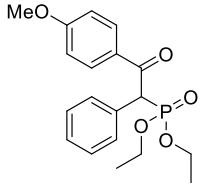
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.34 – 7.27 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.31 (d, $^1J_{P\text{-}H}$ = 22.1 Hz, 1H), 4.18 – 3.96 (m, 4H), 2.36 (s, 3H), 1.23-1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.1 (d, $^2J_{P\text{-}C}$= 5.2 Hz), 144.3, 133.9 (d, $J_{P\text{-}C}$ = 5.7 Hz), 131.6 (d, $J_{P\text{-}C}$ = 9.0 Hz), 129.6 (d, $J_{P\text{-}C}$ = 6.2 Hz), 129.2, 129.0, 128.7 (d, $J_{P\text{-}C}$ = 2.8 Hz), 127.7 (d, $J_{P\text{-}C}$ = 3.3 Hz), 63.1 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 62.9 (d, $^2J_{P\text{-}C}$ = 7.0 Hz), 54.2 (d, $^1J_{P\text{-}C}$ = 138.5 Hz), 21.5, 16.3 (d, $^3J_{P\text{-}C}$ = 3.8 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 3.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.97.

HRMS (ESI-TOF, m/z): Found: *m/z* 347.1405. Calcd for $C_{19}H_{23}O_4P$ $(M+H)^+$ 347.1406

diethyl (2-(4-methoxyphenyl)-2-oxo-1-phenylethyl)phosphonate（3m）



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.52 (m, 2H), 7.36 – 7.27 (m, 3H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.30 (d, $^1J_{P\text{-}H}$ = 22.1 Hz, 1H), 4.18 – 4.01 (m, 4H), 3.83 (s, 3H), 1.26 – 1.18 (m, 6H).

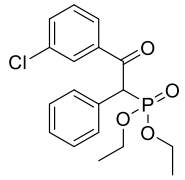
^{13}C NMR (101 MHz, $CDCl_3$): δ 192.0 (d, $^2J_{P\text{-}C}$ = 5.2 Hz), 163.7, 131.8 (d, $J_{P\text{-}C}$ = 9.1 Hz), 131.3, 129.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 129.3 (d, $J_{P\text{-}C}$ = 5.7 Hz), 128.7 (d, $J_{P\text{-}C}$ = 2.7 Hz), 127.7 (d, $J J_{P\text{-}C}$ = 3.2 Hz),

113.78, 63.1 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 62.8 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 55.4, 54.0 (d, $^{1}J_{P\text{-}C}$ = 138.6 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 4.7 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 4.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.08.

HRMS (ESI-TOF, m/z): Found: *m/z* 385.1175. Calcd for $C_{19}H_{23}O_5P$ $(M+Na)^+$ 385.1175

diethyl (2-(3-chlorophenyl)-2-oxo-1-phenylethyl)phosphonate（3n）



According to Method A in Section 4.5

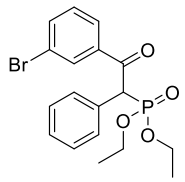
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.37 – 7.29 (m, 4H), 5.27 (d, $^{1}J_{P\text{-}H}$ = 22.4 Hz, 1H), 4.15 – 4.00 (m, 4H), 1.23 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.4 (d, $^{2}J_{P\text{-}C}$ = 5.3 Hz), 138.0 (d, $J_{P\text{-}C}$ = 5.6 Hz), 134.9, 133.2, 130.9 (d, $J_{P\text{-}C}$ = 9.0 Hz), 129.8, 129.6 (d, $J_{P\text{-}C}$ = 6.2 Hz), 128.9, 128.8 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.0 (d, $J_{P\text{-}C}$ = 3.3 Hz), 126.9, 63.3 (d, $^{2}J_{P\text{-}C}$ = 6.8 Hz), 63.0 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.4 (d, $^{1}J_{P\text{-}C}$ = 137.9 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 3.2 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 3.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.08.

HRMS (ESI-TOF, m/z): Found: *m/z* 389.0679. Calcd for $C_{18}H_{20}ClO_4P$ $(M+Na)^+$ 389.0679

diethyl (2-(3-bromophenyl)-2-oxo-1-phenylethyl)phosphonate（3o）



According to Method A in Section 4.5

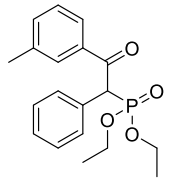
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (t, *J* = 1.9 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.9, 1H), 7.53 – 7.50 (m, 2H), 7.37 – 7.27 (m, 4H), 5.26 (d, $^{1}J_{P\text{-}H}$ = 22.5 Hz, 1H), 4.15 – 4.00 (m, 4H), 1.22 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.3 (d, $^{2}J_{P\text{-}C}$ = 5.2 Hz), 138.2 (d, $J_{P\text{-}C}$ = 5.5 Hz), 136.1, 131.8, 130.9 (d, $J_{P\text{-}C}$ = 9.0 Hz), 130.1, 129.6 (d, $J_{P\text{-}C}$ = 6.2 Hz), 128.8 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.0 (d, $J_{P\text{-}C}$ = 3.3 Hz), 127.4, 122.9, 63.3 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 63.0 (d, $^{2}J_{P\text{-}C}$ = 7.0 Hz), 54.4 (d, $^{1}J_{P\text{-}C}$ = 137.8 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 2.9 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 3.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.98.

HRMS (ESI-TOF, m/z): Found: *m/z* 433.0174. Calcd for $C_{18}H_{20}BrO_4P$ $(M+Na)^+$ 433.0174

diethyl (2-oxo-1-phenyl-2-(m-tolyl)ethyl)phosphonate（3p）



According to Method A in Section 4.5

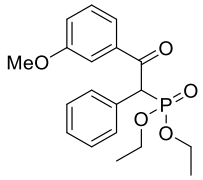
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.73 (m, 2H), 7.55 – 7.53 (m, 2H), 7.36 – 7.27 (m, 5H), 5.34 (d, $^{1}J_{P\text{-}H}$ = 22.2 Hz, 1H), 4.19 – 4.00 (m, 4H), 2.37 (s, 3H), 1.24 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.8 (d, $^{2}J_{P\text{-}C}$ = 5.2 Hz), 137.4, 135.5 (d, $J_{P\text{-}C}$ = 5.5 Hz), 133.1, 130.5(d, $J_{P\text{-}C}$ = 9.1 Hz), 128.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 128.3, 127.7(d, $J_{P\text{-}C}$ = 2.7 Hz), 127.4, 126.8 (d, $J_{P\text{-}C}$ = 3.2 Hz), 125.1, 62.1 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 61.9 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 53.3 (d, $^{1}J_{P\text{-}C}$ = 138.1 Hz), 20.3, 15.3 (d, $^{3}J_{P\text{-}C}$ = 3.4 Hz), 15.2 (d, $^{3}J_{P\text{-}C}$ = 3.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.82.

HRMS (ESI-TOF, m/z): Found: *m/z* 369.1226. Calcd for $C_{19}H_{23}O_4P$ $(M+Na)^+$ 369.1226

diethyl (2-(3-methoxyphenyl)-2-oxo-1-phenylethyl)phosphonate（3q）



According to Method A in Section 4.5

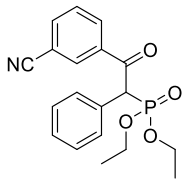
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.48 (m, 4H), 7.36 – 7.27 (m, 4H), 7.07 – 7.05 (m, 1H), 5.31 (d, $^{1}J_{P\text{-}H}$ = 22.1 Hz, 1H), 4.15 – 4.00 (m, 3H), 3.81 (s, 3H), 1.25 – 1.18 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.4 (d, $^{2}J_{P\text{-}C}$ = 5.1 Hz), 159.7, 137.8 (d, $J_{P\text{-}C}$ = 5.7 Hz), 131.4 (d, $J_{P\text{-}C}$ = 9.1 Hz), 129.6 (d, $J_{P\text{-}C}$ = 6.2 Hz), 129.5, 128.8 (d, $J_{P\text{-}C}$ = 2.8 Hz), 127.8 (d, $J_{P\text{-}C}$ = 3.2 Hz), 121.5, 120.0, 113.0, 63.2 (d, $^{2}J_{P\text{-}C}$ = 6.6 Hz), 62.9 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 55.3, 54.4 (d, $^{1}J_{P\text{-}C}$ = 138.4 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 3.9 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 3.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.70.

HRMS (ESI-TOF, m/z): Found: *m/z* 385.1190. Calcd for $C_{19}H_{23}O_5P$ $(M+Na)^+$ 385.1175

diethyl (2-(3-cyanophenyl)-2-oxo-1-phenylethyl)phosphonate(3r)



According to Method A in Section 4.5

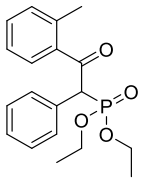
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23– 8.16 (m, 2H), 7.81 – 7.78 (m, 1H), 7.58 – 7.49 (m, 3H), 7.39 – 7.31(m, 3H), 5.26 (d, $^{1}J_{P\text{-}H}$ = 22.7 Hz, 1H), 4.16 – 4.01 (m, 4H), 1.23 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7 (d, $^{2}J_{P\text{-}C}$ = 5.2 Hz), 137.3 (d, $J_{P\text{-}C}$ = 5.5 Hz), 136.1, 132.8, 132.5, 130.5 (d, $J_{P\text{-}C}$ = 9.0 Hz), 129.6, 129.6 (d, $J_{P\text{-}C}$ = 3.2 Hz), 129.0 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.3 (d, $J_{P\text{-}C}$ = 3.2 Hz), 117.7, 113.2, 63.5 (d, $^{2}J_{P\text{-}C}$ = 6.8 Hz), 63.1 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 54.5 (d, $^{1}J_{P\text{-}C}$ = 137.8 Hz), 16.3 (d, $^{3}J_{P\text{-}C}$ = 3.9 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 4.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.51.

HRMS (ESI-TOF, m/z): Found: *m/z* 380.1009. Calcd for $C_{19}H_{20}NO_4P$ $(M+Na)^+$ 380.1022

diethyl (2-oxo-1-phenyl-2-(o-tolyl)ethyl)phosphonate（3s）



According to Method A in Section 4.5

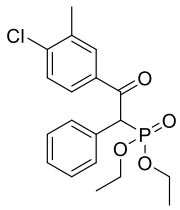
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.53 (m, 3H), 7.37 – 7.29 (m, 4H), 7.21-7.18 (m, 2H), 5.18 (d, $^1J_{P-H}$ = 22.8 Hz, 1H), 4.17 – 3.95 (m, 4H), 2.45 (s, 3H), 1.22-1.16 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.0 (d, $^2J_{P-C}$ = 4.9 Hz), 138.5, 138.3 (d, J_{P-C} = 4.6 Hz), 131.7, 131.4, 131.2 (d, J_{P-C} = 8.8 Hz), 129.6 (d, J_{P-C} = 6.4 Hz), 128.7 (d, J_{P-C} = 2.6 Hz), 128.3, 127.9 (d, J_{P-C} = 3.2 Hz), 125.5, 63.1 (d, $^2J_{P-C}$ = 6.7 Hz), 62.9 (d, $^2J_{P-C}$ = 7.2 Hz), 57.3 (d, $^1J_{P-C}$ = 135.1 Hz), 20.9, 16.3 (d, $^3J_{P-C}$ = 3.1 Hz), 16.2 (d, $^3J_{P-C}$ = 3.2 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 19.57.

HRMS (ESI-TOF, m/z): Found: *m/z* 369.1208. Calcd for $C_{19}H_{23}O_4P$ $(M+Na)^+$ 369.1226

diethyl (2-(4-chloro-3-methylphenyl)-2-oxo-1-phenylethyl)phosphonate（3t）



According to Method A in Section 4.5

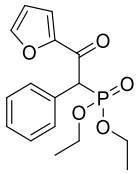
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.70– 7.68 (m, 1H), 7.51 – 7.50(m, 2H), 7.37 – 7.28 (m, 4H), 5.26 (d, $^1J_{P-H}$ = 22.3 Hz, 1H), 4.17 – 3.99 (m, 4H), 2.38 (s, 3H), 1.23-1.17(m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.7 (d, $^2J_{P-C}$ = 5.1 Hz), 140.0, 136.6, 134.8 (d, J_{P-C} = 5.6 Hz), 131.2, 131.2, 129.6(d, J_{P-C} = 6.2 Hz), 129.2, 128.8 (d, J_{P-C} = 2.6 Hz), 127.9 (d, J_{P-C} = 3.3 Hz), 127.6, 63.2 (d, $^2J_{P-C}$ = 6.7 Hz), 62.9 (d, $^2J_{P-C}$ = 7.1 Hz), 54.2 (d, $^1J_{P-C}$ = 138.3 Hz), 20.0, 16.3 (d, $^3J_{P-C}$ = 3.8 Hz), 16.2 (d, $^3J_{P-C}$ = 4.0 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 19.44.

HRMS (ESI-TOF, m/z): Found: *m/z* 381.1013. Calcd for $C_{19}H_{22}ClO_4P$ $(M+Na)^+$ 381.1017

diethyl (2-(furan-2-yl)-2-oxo-1-phenylethyl)phosphonate(3u)



According to Method A in Section 4.5

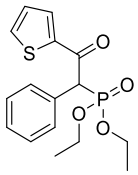
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.05 – 8.04 (m, 1H), 7.85 (d, J = 3.6 Hz, 1H), 7.61 – 7.59 (m, 3H), 7.37 – 7.27 (m, 3H), 6.74 (dd, J = 3.6, 1.7 Hz, 1H), 5.47 (d, $^1J_{P-H}$ = 22.7 Hz, 1H), 4.02 – 3.87 (m, 4H), 1.13-1.07 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 181.5 (d, $^2J_{P-C}$ = 5.4 Hz), 151.4 (d, J_{P-C} = 7.0 Hz), 149.7, 132.2 (d, J_{P-C} = 8.4 Hz), 130.2 (d, J_{P-C} = 6.6 Hz), 128.8 (d, J_{P-C} = 2.1 Hz), 128.1 (d, J_{P-C} = 2.7 Hz), 121.8, 113.3, 63.0 (d, $^2J_{P-C}$ = 6.6 Hz), 62.7 (d, $^2J_{P-C}$ = 6.9 Hz), 52.9 (d, $^1J_{P-C}$ = 134.1 Hz), 16.5 (d, $^3J_{P-C}$ = 5.4 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 18.98.

HRMS (ESI-TOF, m/z): Found: *m/z* 345.0858. Calcd for $C_{16}H_{19}O_5P$ $(M+Na)^+$ 345.0862

diethyl (2-oxo-1-phenyl-2-(thiophen-2-yl)ethyl)phosphonate(3v)



According to Method A in Section 4.5

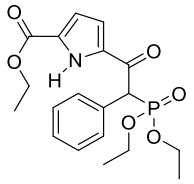
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 (dd, J = 3.9, 1.0 Hz, 1H), 8.06 (dd, J = 4.9, 0.9 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.37 – 7.24 (m, 4H), 5.71 (d, $^1J_{P\text{-}H}$ = 22.3 Hz, 1H), 4.01 – 3.90(m, 4H), 1.12-1.07 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 186.9 (d, $^2J_{P\text{-}C}$ = 5.2 Hz), 143.8 (d, $J_{P\text{-}C}$ = 6.4 Hz), 137.2, 135.9, 132.5 (d, $J_{P\text{-}C}$ = 8.6 Hz), 130.2, 129.4, 128.8 (d, $J_{P\text{-}C}$ = 2.2 Hz), 128.1 (d, $J_{P\text{-}C}$ = 2.8 Hz), 62.9 (d, $^2J_{P\text{-}C}$ = 6.6 Hz), 62.6 (d, $^2J_{P\text{-}C}$ = 6.9 Hz), 53.5(d,$^1J_{P\text{-}C}$ = 134.2 Hz), 16.5 (d, $^3J_{P\text{-}C}$ = 5.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.85.

HRMS (ESI-TOF, m/z): Found: *m/z* 361.0626. Calcd for $C_{16}H_{19}O_4PS$ $(M+Na)^+$ 361.0633

ethyl 5-(2-(diethoxyphosphoryl)-2-phenylacetyl)-1H-pyrrole-2-carboxylate(3w)



According to Method A in Section 4.5

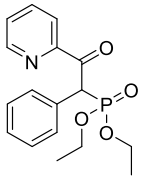
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.55 – 7.52 (m, 2H), 7.35 – 7.28 (m, 3H), 6.88 (dd, J = 4.1, 2.5 Hz, 1H), 6.83 (dd, J = 4.1, 2.5 Hz, 1H), 5.01 (d, $^1J_{P\text{-}H}$ = 22.7 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 4.14– 3.96 (m, 4H), 1.34 (t, J = 7.1 Hz, 3H), 1.21-1.16(m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.3 (d, $^2J_{P\text{-}C}$ = 5.1 Hz), 150.3, 141.1 (d, $J_{P\text{-}C}$ = 5.5 Hz), 130.9, 130.5 (d, $J_{P\text{-}C}$ = 9.0 Hz), 129.9, 129.7 (d, $J_{P\text{-}C}$ = 6.1 Hz), 129.0 (d, $J_{P\text{-}C}$ = 2.8 Hz), 128.3 (d, $J_{P\text{-}C}$ = 3.2 Hz), 123.8, 63.5 (d, $^2J_{P\text{-}C}$ = 6.9 Hz), 63.2 (d, $^2J_{P\text{-}C}$ = 7.0 Hz), 54.9 (d, $^1J_{P\text{-}C}$ = 137.8 Hz), 29.6, 22.6, 16.3 (d, $^3J_{P\text{-}C}$ = 3.2 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 3.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.00.

HRMS (ESI-TOF, m/z): Found: *m/z* 384.1368. Calcd for $C_{21}H_{22}NO_4P$ $(M+H)^+$ 384.1359

diethyl (2-oxo-1-phenyl-2-(pyridin-2-yl)ethyl)phosphonate(3x)



According to Method A in Section 4.5

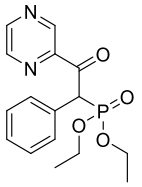
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.78 (dt, J = 4.7, 1.4 Hz, 1H), 8.04 – 8.01 (m, 2H), 7.73-7.69 (m, 1H), 7.59 – 7.56 (m, 2H), 7.37 – 7.27 (m, 3H), 6.46 (d, $^1J_{P\text{-}H}$ = 22.5 Hz, 1H), 3.99-3.84 (m, 4H), 1.07-1.02(m, 6H)

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.7 (d, $^2J_{P\text{-}C}$ = 4.5 Hz), 152.0 (d, $J_{P\text{-}C}$ = 3.5 Hz), 149.7, 138.5, 131.8 (d, $J_{P\text{-}C}$ = 8.5 Hz), 130.5 (d, $J_{P\text{-}C}$ = 6.6 Hz), 128.9, 128.8, 128.1 (d, $J_{P\text{-}C}$ = 2.8 Hz), 122.9, 63.0 (d, $^2J_{P\text{-}C}$ = 6.6 Hz), 62.7 (d, $^2J_{P\text{-}C}$ = 7.0 Hz), 49.9 (d, $^1J_{P\text{-}C}$ = 133.0 Hz), 16.4 (d, $^3J_{P\text{-}C}$ = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.08.

HRMS (ESI-TOF, m/z): Found: *m/z* 356.1024. Calcd for $C_{17}H_{20}NO_4P$ $(M+Na)^+$ 356.1022

diethyl (2-oxo-1-phenyl-2-(pyrazin-2-yl)ethyl)phosphonate(3y)



According to Method A in Section 4.5

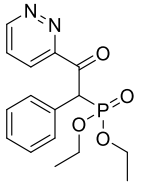
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (d, J = 1.4 Hz, 1H), 8.73 (d, J = 2.5 Hz, 1H), 8.65 – 8.64(m, 1H), 7.64 – 7.61 (m, 2H), 7.35 – 7.27 (m, 3H), 6.31 (d, $^1J_{P\text{-}H}$ = 22.6 Hz, 1H), 4.14– 3.99 (m, 4H), 1.20-1.15 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.9 (d, $^2J_{P\text{-}C}$ = 4.7 Hz), 147.9, 146.7 (d, $J_{P\text{-}C}$ = 4.3 Hz), 144.5, 143.3, 130.6 (d, $J_{P\text{-}C}$ = 8.8 Hz), 130.1 (d, $J_{P\text{-}C}$ = 6.4 Hz), 128.6 (d, $J_{P\text{-}C}$ = 2.5 Hz), 127.9 (d, $J_{P\text{-}C}$ = 3.0 Hz), 63.3 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 62.9 (d, $^2J_{P\text{-}C}$ = 7.1 Hz), 50.6 (d, $^1J_{P\text{-}C}$ = 135.4 Hz), 16.2(d, $^3J_{P\text{-}C}$ = 1.0 Hz), 16.1 (d, $^3J_{P\text{-}C}$ = 1.0Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.13.

HRMS (ESI-TOF, m/z): Found: *m/z* 357.0983. Calcd for $C_{16}H_{19}N_2O_4P$ $(M+Na)^+$ 357.0974

diethyl (2-oxo-1-phenyl-2-(pyridazin-3-yl)ethyl)phosphonate(3z)



According to Method A in Section 4.5

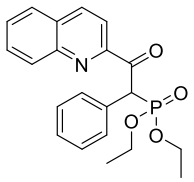
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (dd, J = 5.0, 1.8 Hz, 1H), 8.18 (dd, J = 8.5, 1.8 Hz, 1H), 7.70 – 7.62 (m, 3H), 7.36 – 7.28(m, 3H), 6.64 (d, $^1J_{P\text{-}H}$ = 22.6 Hz, 1H), 4.13 – 3.96 (m, 4H), 1.20 – 1.13 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.3 (d, $^2J_{P\text{-}C}$ = 4.9 Hz), 154.9 (d, $J_{P\text{-}C}$ = 3.9 Hz), 153.3, 130.6 (d, $J_{P\text{-}C}$ = 8.7 Hz), 130.3 (d, $J_{P\text{-}C}$ = 6.4 Hz), 128.6 (d, $J_{P\text{-}C}$ = 2.5 Hz), 127.9(d, $J_{P\text{-}C}$ = 3.0 Hz), 127.3, 125.7, 63.5(d, $^2J_{P\text{-}C}$ = 6.8 Hz), 63.1 (d, $^2J_{P\text{-}C}$ = 7.3 Hz), 54.9 (d, $^1J_{P\text{-}C}$ = 137.7 Hz), 16.3 (d, $^3J_{P\text{-}C}$ = 3.4 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 3.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.00.

HRMS (ESI-TOF, m/z): Found: *m/z* 335.1149. Calcd for $C_{16}H_{19}N_2O_4P$ $(M+H)^+$ 335.1155

diethyl (2-(isoquinolin-3-yl)-2-oxo-1-phenylethyl)phosphonate（3aa）



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.21 (m, 2H), 8.16 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.81-7.75 (m, 3H), 7.63 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.28 – 7.24(m, 1H), 6.85 (d, $^1J_{P\text{-}H}$ = 22.0 Hz, 1H), 4.16-4.01(m, 4H), 1.21-1.11 (m, 6H).

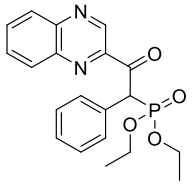
^{13}C NMR (101 MHz, $CDCl_3$): δ 194.7 (d, $^2J_{P\text{-}C}$ = 4.5 Hz), 151.6 (d, $J_{P\text{-}C}$ = 4.2 Hz), 146.8, 137.1, 131.4 (d, $J_{P\text{-}C}$ = 8.7 Hz), 130.6, 130.2 (d, $J_{P\text{-}C}$ = 6.6 Hz), 130.0, 129.6, 128.8, 128.4 (d, $J_{P\text{-}C}$ = 2.4

Hz), 127.6 (d, J_{P-C} = 3.0 Hz), 127.5, 118.5, 63.0 (d, $^{2}J_{P-C}$ = 6.6 Hz), 62.8 (d, $^{2}J_{P-C}$ = 7.1 Hz), 49.9 (d, $^{1}J_{P-C}$ = 135.6 Hz), 16.1 (t, $^{3}J_{P-C}$ = 5.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.43.

HRMS (ESI-TOF, m/z): Found: *m/z* 406.1184. Calcd for $C_{21}H_{22}NO_4P$ $(M+Na)^+$ 406.1178

diethyl (2-oxo-1-phenyl-2-(quinoxalin-2-yl)ethyl)phosphonate（3ab）



According to Method A in Section 4.5

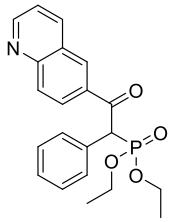
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 8.23-8.21 (m, 1H), 8.16 – 8.14(m, 1H), 7.91-7.83 (m,2H), 7.73– 7.71 (m, 2H), 7.37 – 7.27 (m, 3H), 6.59 (d, $^{1}J_{P-H}$ = 22.5 Hz, 1H), 4.16– 4.01 (m, 4H), 1.21-1.12(m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.1 (d, $^{2}J_{P-C}$ = 4.7 Hz), 145.3 (d, J_{P-C} = 4.4 Hz), 143.9, 143.5, 140.6, 132.5, 130.8, 130.7 (d, J_{P-C} = 8.8 Hz), 130.5, 130.1 (d, J_{P-C} = 6.4 Hz), 129.3, 128.6 (d, J_{P-C} = 2.4 Hz), 127.9 (d, J_{P-C} = 3.0 Hz), 63.2 (d, $^{2}J_{P-C}$ = 6.7 Hz), 62.9 (d, $^{2}J_{P-C}$ = 7.2 Hz), 50.4 (d, $^{1}J_{P-C}$ = 135.5 Hz), 16.2 (d, $^{3}J_{P-C}$ = 2.4 Hz), 16.1 (d, $^{3}J_{P-C}$ = 2.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.42.

HRMS (ESI-TOF, m/z): Found: *m/z* 407.1120. Calcd for $C_{20}H_{21}N_2O_4P$ $(M+Na)^+$ 407.1131

diethyl (2-(isoquinolin-6-yl)-2-oxo-1-phenylethyl)phosphonate(3ac)



According to Method A in Section 4.5

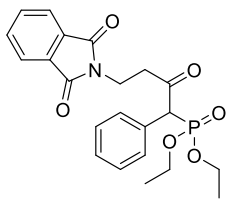
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 8.24-8.22 (m，2H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.60-7.57(m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.37 – 7.28 (m, 3H), 5.48 (d, $^{1}J_{P-H}$ = 22.5 Hz, 1H), 4.19– 4.01 (m, 4H), 1.23-1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.0 (d, $^{2}J_{P-C}$ = 5.2 Hz), 152.8, 149.9, 137.6, 134.3 (d, J_{P-C} = 5.4 Hz), 131.2 (d, J_{P-C} = 8.9 Hz), 130.6, 130.0, 129.6 (d, J_{P-C} = 6.2 Hz), 128.8 (d, J_{P-C} = 2.9 Hz), 128.0, 128.0 (d, J_{P-C} = 2.9 Hz), 127.3, 121.9, 63.3 (d, $^{2}J_{P-C}$ = 6.7 Hz), 63.0 (d, $^{2}J_{P-C}$ = 7.1 Hz), 54.5 (d, $^{1}J_{P-C}$ = 137.8 Hz), 16.2 (d, $^{3}J_{P-C}$ = 3.6 Hz), 16.2 (d, $^{3}J_{P-C}$ = 3.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.27.

HRMS (ESI-TOF, m/z): Found: *m/z* 378.1103. Calcd for $C_{18}H_{20}NO_6P$ $(M+H)^+$ 378.1101

diethyl (4-(1,3-dioxoisoindolin-2-yl)-2-oxo-1-phenylbutyl)phosphonate(3ad)



According to Method A in Section 4.5

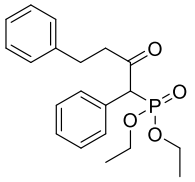
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.78 (m, 2H), 7.72 – 7.67 (m, 2H), 7.44 – 7.41 (m, 2H), 7.33 – 7.26 (m, 3H), 4.42 (d, $^1J_{P-H}$ = 24.0 Hz, 1H), 4.12 – 3.85 (m, 6H), 3.18 – 2.98 (m, 2H), 1.26 – 1.16 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4 (d, $^2J_{P-C}$ = 4.4 Hz), 167.8, 133.8, 131.9, 130.3 (d, J_{P-C} = 7.9 Hz), 129.7(d, J_{P-C} = 6.9 Hz), 128.6 (d, J_{P-C} = 2.1 Hz), 128.0 (d, J_{P-C} = 2.8 Hz), 123.1, 63.2 (d, $^2J_{P-C}$ = 6.9 Hz), 62.9 (d, $^2J_{P-C}$ = 7.0 Hz), 59.3 (d, $^1J_{P-C}$ = 132.3 Hz), 40.9(d, $^3J_{P-C}$ = 3.2 Hz), 32.8, 16.2 (d, $^3J_{P-C}$ = 5.0 Hz), 16.1 (d, $^3J_{P-C}$ = 5.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.51.

HRMS (ESI-TOF, m/z): Found: *m/z* 452.236. Calcd for $C_{22}H_{24}NO_6P$ $(M+Na)^+$ 452.1233

diethyl (2-oxo-1,4-diphenylbutyl)phosphonate (3ae)



According to Method A in Section 4.5

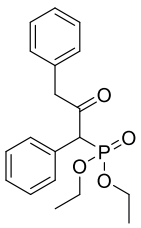
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.41 (m, 2H), 7.35 – 7.29 (m, 3H), 7.26 – 7.22(m, 2H), 7.18 – 7.11(m, 3H), 4.41 (d, $^1J_{P-H}$ = 23.6 Hz, 1H), 4.08– 3.90 (m, 4H), 3.06 – 2.80 (m, 4H), 1.23– 1.16 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.2 (d, $^2J_{P-C}$ = 4.7 Hz), 140.5, 130.7 (d, J_{P-C} = 8.2 Hz), 129.6 (d, J_{P-C} = 6.9 Hz), 128.6(d, J_{P-C} = 2.2 Hz), 128.3, 128.3, 127.9 (d, J_{P-C} = 2.8 Hz), 126.0, 63.2 (d, $^2J_{P-C}$ = 6.9 Hz), 62.8 (d, $^2J_{P-C}$ = 7.0 Hz), 59.2 (d, $^1J_{P-C}$ = 132.5 Hz), 44.8 (d, $^3J_{P-C}$ = 3.1 Hz), 29.5, 16.2 (d, $^3J_{P-C}$ = 2.3 Hz), 16.1 (d, $^3J_{P-C}$ = 2.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.91.

HRMS (ESI-TOF, m/z): Found: *m/z* 383.1368. Calcd for $C_{20}H_{25}O_4P$ $(M+Na)^+$ 383.1382

diethyl (2-oxo-1,3-diphenylpropyl)phosphonate (3af)



According to Method A in Section 4.5

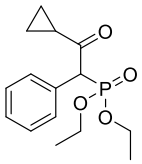
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 8H), 7.13 – 7.11 (m, 2H), 4.55 (d, $^1J_{P-H}$ = 23.4 Hz, 1H), 4.13 – 4.00 (m, 4H), 3.90 (s, 2H), 1.27 – 1.19 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.72 (d, $^2J_{P-C}$ = 4.7 Hz), 133.37, 130.84 (d, J_{P-C} = 8.3 Hz), 129.77 (d, J_{P-C} = 6.8 Hz), 129.66, 128.67, 128.65, 127.94 (d, J_{P-C} = 2.9 Hz), 127.18, 63.31 (d, $^2J_{P-C}$ = 6.8 Hz), 62.91 (d, $^2J_{P-C}$ = 7.2 Hz), 57.86 (d, $^1J_{P-C}$ = 133.2 Hz), 50.18 (d, $^3J_{P-C}$ = 3.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.74.

HRMS (ESI-TOF, m/z): Found: *m/z* 347.1403. Calcd for $C_{19}H_{23}O_4P$ $(M+Na)^+$ 347.1406

diethyl (2-cyclopropyl-2-oxo-1-phenylethyl)phosphonate (3ag)



According to Method A in Section 4.5

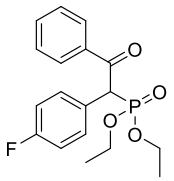
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.47 – 7.44 (m, 2H), 7.36 – 7.28(m, 3H), 4.55 (d, $^1J_{P\text{-}H}$ = 23.7 Hz, 1H), 4.10 – 3.92 (m, 4H), 2.20 – 2.14 (m, 1H), 1.21 (dt, J = 23.5, 7.0 Hz, 6H), 1.12 – 1.04 (m, 2H), 0.95 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 203.2 (d, $^2J_{P\text{-}C}$ = 4.1 Hz), 131.2 (d, $J_{P\text{-}C}$ = 7.8 Hz), 129.9 (d, $J_{P\text{-}C}$ = 6.9 Hz), 128.6 (d, $J_{P\text{-}C}$ = 2.2 Hz), 127.8 (d, $J_{P\text{-}C}$ = 2.9 Hz), 63.1 (d, $^2J_{P\text{-}C}$ = 6.8 Hz), 62.7 (d, $^2J_{P\text{-}C}$ = 7.0 Hz), 60.1 (d, $^1J_{P\text{-}C}$ = 133.4 Hz), 21.3 (d, $J_{P\text{-}C}$ = 4.1 Hz), 16.2 (d, $J_{P\text{-}C}$ = 4.6 Hz), 16.2 (d, $J_{P\text{-}C}$ = 4.6 Hz), 12.3 (d, $J_{P\text{-}C}$ = 3.4 Hz).

^{31}P NMR (**162 MHz**, **CDCl$_3$**): δ 19.37.

HRMS (ESI-TOF, m/z): Found: *m/z* 319.1056. Calcd for $C_{18}H_{20}FO_4P$ $(M+Na)^+$ 319.1069

diethyl (1-(4-fluorophenyl)-2-oxo-2-phenylethyl)phosphonate(4a)



According to Method A in Section 4.5

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.97 – 7.91 (m, 2H), 7.59 – 7.48 (m, 3H), 7.42 (m, 2H), 7.03 (t, J = 8.6 Hz, 2H), 5.33 (d, $^1J_{P\text{-}H}$ = 22.5 Hz, 1H), 4.19 – 3.95 (m, 4H), 1.19 (m，6H).

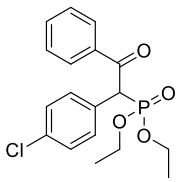
^{13}C NMR (101 MHz, CDCl$_3$): δ 193.4 (d, $^2J_{P\text{-}C}$ = 5.1 Hz), 162.4 (dd, J = 247.1, $J_{P\text{-}C}$ = 3.6 Hz), 136.3 (d, $J_{P\text{-}C}$ = 5.1 Hz), 133.5, 131.3 (dd, J = 8.1, $J_{P\text{-}C}$ = 6.4 Hz), 128.8, 128.6, 127.2 (dd, J = 9.1, $J_{P\text{-}C}$ = 3.3 Hz), 115.7 (dd, J = 21.6, $J_{P\text{-}C}$ = 2.7 Hz), 63.2 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 63.0 (d, $^2J_{P\text{-}C}$ = 7.1 Hz), 53.2 (d, $^1J_{P\text{-}C}$ = 138.0 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 3.7 Hz), 16.1 (d, $^3J_{P\text{-}C}$ = 4.0 Hz).

^{31}P NMR (**162 MHz**, **CDCl$_3$**): δ 19.34.

^{19}F NMR (377 MHz, CDCl$_3$): δ -114.22 (d, J = 4.9 Hz).

HRMS (ESI-TOF, m/z): Found: *m/z* 351.1151. Calcd for $C_{18}H_{20}FO_4P$ $(M+Na)^+$ 319.1069

diethyl (1-(4-chlorophenyl)-2-oxo-2-phenylethyl)phosphonate(4b)



According to Method A in Section 4.5

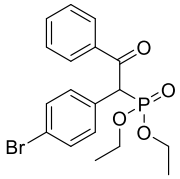
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94– 7.92 (m, 2H), 7.56 – 7.40 (m, 5H), 7.31 (d, J = 8.4 Hz, 2H), 5.32 (d, $^1J_{P\text{-}H}$ = 22.5 Hz, 1H), 4.16 –4.00 (m, 4H), 1.23-1.17 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 193.3 (d, $^2J_{P\text{-}C}$ = 5.2 Hz), 136.2 (d, $J_{P\text{-}C}$ = 5.1 Hz), 134.0 (d, $J_{P\text{-}C}$ = 4.0 Hz), 133.5, 130.9 (d, $J_{P\text{-}C}$ = 6.3 Hz), 130.0 (d, $J_{P\text{-}C}$ = 9.1 Hz), 128.9 (d, $J_{P\text{-}C}$ = 2.8 Hz), 128.8, 128.6, 63.3 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 63.0 (d, $^2J_{P\text{-}C}$ = 7.2 Hz), 53.4 (d, $^1J_{P\text{-}C}$ = 137.5 Hz), 16.3 (d, $^3J_{P\text{-}C}$ = 4.4 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 4.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.02.

HRMS (ESI-TOF, m/z): Found: *m/z* 367.0870. Calcd for $C_{18}H_{20}ClO_4P$ $(M+H)^+$ 367.0860

diethyl (1-(4-bromophenyl)-2-oxo-2-phenylethyl)phosphonate(4c)



According to Method A in Section 4.5

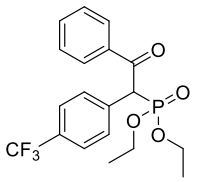
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.92 (m, 2H), 7.56 – 7.52 (m, 1H), 7.48 – 7.40 (m, 6H), 5.30 (d, $^1J_{P-H}$ = 22.4 Hz, 1H), 4.17 – 3.98 (m, 4H), 1.23-1.17 （m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.2 (d, $^2J_{P-C}$ = 5.2 Hz), 136.2 (d, J_{P-C} = 5.0 Hz), 133.6, 131.9 (d, J_{P-C} = 2.8 Hz), 131.3 (d, J_{P-C} = 6.3 Hz), 130.5 (d, J_{P-C} = 9.2 Hz), 128.8, 128.6, 122.2 (d, J_{P-C} = 4.1 Hz), 63.3 (d, $^2J_{P-C}$ = 6.8 Hz), 63.1 (d, $^2J_{P-C}$ = 7.0 Hz), 53.5 (d, $^1J_{P-C}$ = 137.6 Hz), 16.3 (d, $^3J_{P-C}$ = 4.4 Hz), 16.2 (d, $^3J_{P-C}$ = 4.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.87.

HRMS (ESI-TOF, m/z): Found: *m/z* 411.0365. Calcd for $C_{18}H_{20}BrO_4P$ $(M+H)^+$ 411.0355

diethyl (2-oxo-2-phenyl-1-(4-(trifluoromethyl)phenyl)ethyl)phosphonate(4d)



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.94 (m, 2H), 7.70-7.67 m, 2H), 7.61-7.54 m, 3H), 7.46-7.42 (m, 2H), 5.43 (d, $^1J_{P-H}$ = 22.7 Hz, 1H), 4.15 – 4.02 (m, 4H), 1.23-1.17 (m, 6H).

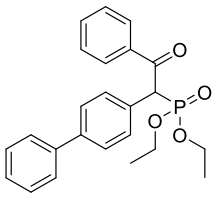
^{13}C NMR (101 MHz, $CDCl_3$): δ 193.0 (d, J = 5.4 Hz), 136.3 (d, J = 4.6 Hz), 135.6 (d, J = 9.1 Hz), 133.7, 130.1(d, J = 32.3 Hz), 130.2 (d, J = 6.2 Hz), 128.9, 128.7, 125.7-125.7 (m), 123.99 (q, J = 271.8 Hz), 63.45 (d, $^2J_{P-C}$ = 6.7 Hz), 63.21 (d, $^2J_{P-C}$ = 7.1 Hz), 53.98 (d, $^1J_{P-C}$ = 136.3 Hz), 16.30 (d, $^3J_{P-C}$ = 4.4 Hz), 16.23 (d, $^3J_{P-C}$ = 4.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.51

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.68 (d, J = 2.6 Hz).

HRMS (ESI-TOF, m/z): Found: *m/z* 401.1127. Calcd for $C_{19}H_{20}F3O_4P$ $(M+H)^+$ 401.1124

diethyl (1-([1,1'-biphenyl]-4-yl)-2-oxo-2-phenylethyl)phosphonate(4e)



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.97 (m, 2H), 7.62 – 7.51 (m, 7H), 7.45-7.40（ m, 5H), 7.35 – 7.31 (m, 1H), 5.40 (d, $^1J_{P-H}$ = 22.2 Hz, 1H), 4.20 – 4.03 (m, 4H), 1.26-1.21 (m, 6H).

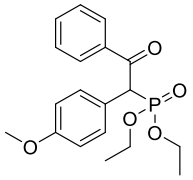
^{13}C NMR (101 MHz, $CDCl_3$): δ 193.5 (d, $^2J_{P-C}$ = 5.3 Hz), 140.7 (d, J_{P-C} = 3.4 Hz), 140.3 (d, J_{P-C} = 1.4 Hz), 136.4 (d, J_{P-C} = 5.4 Hz), 133.4, 130.3 (d, J_{P-C} = 9.3 Hz), 130.0 (d, J_{P-C} = 6.4 Hz), 128.9,

128.7, 128.6, 127.4 (d, J_{P-C} = 2.9 Hz), 127.4, 127.0, 63.2 (d, $^{2}J_{P-C}$ = 6.7 Hz), 63.0 (d, $^{2}J_{P-C}$ = 7.0 Hz), 53.9 (d, $^{1}J_{P-C}$ = 138.1 Hz), 16.3 (d, $^{3}J_{P-C}$ = 2.9 Hz), 16.2 (d, $^{3}J_{P-C}$ = 3.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.73.

HRMS (ESI-TOF, m/z): Found: *m/z* 409.1567. Calcd for $C_{24}H_{25}O_4P$ $(M+H)^+$ 409.1563

diethyl (1-(4-methoxyphenyl)-2-oxo-2-phenylethyl)phosphonate(4f)



According to Method A in Section 4.5

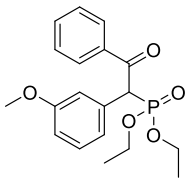
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.38 (m, 5H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.27 (d, $^{1}J_{P-H}$ = 22.0 Hz, 1H), 4.15 – 3.76 (m, 4H), 3.76 (s, 3H), 1.223-1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.8 (d, $^{2}J_{P-C}$ = 4.8 Hz), 159.2 (d, J_{P-C} = 3.2 Hz), 136.4 (d, J_{P-C} = 5.7 Hz), 133.2, 130.7 (d, J_{P-C} = 6.2 Hz), 128.8, 128.5, 123.2 (d, J_{P-C} = 9.2 Hz), 114.2 (d, J_{P-C} = 2.6 Hz), δ 63.0 (d, $^{2}J_{P-C}$ = 6.7 Hz), 62.8 (d, $^{2}J_{P-C}$ = 7.2 Hz), 55.1, 53.3 (d, $^{1}J_{P-C}$ = 139.4 Hz), 16.3 (d, $^{3}J_{P-C}$ = 3.3 Hz), 16.2 (d, $^{3}J_{P-C}$ = 3.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.21.

HRMS (ESI-TOF, m/z): Found: *m/z* 385.1179. Calcd for $C_{19}H_{23}O_5P$ $(M+Na)^+$ 385.1175

diethyl (1-(3-methoxyphenyl)-2-oxo-2-phenylethyl)phosphonate(4g)



According to Method A in Section 4.5

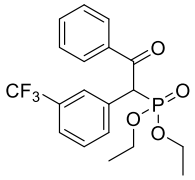
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.93 (m, 2H), 7.23 – 7.49 (m, 1H), 7.42-7.38 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.85 – 6.80 (m, 1H), 5.30 (d, $^{1}J_{P-H}$ = 22.0 Hz, 1H), 4.17 – 3.79 (m, 4H), 3.79 (s, 3H), 1.24-1.19(m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.5 (d, $^{2}J_{P-C}$ = 5.3 Hz), 159.7 (d, J_{P-C} = 2.9 Hz), 136.4 (d, J_{P-C} = 5.7 Hz), 133.3, 132.6 (d, J_{P-C} = 9.0 Hz), 129.6 (d, J_{P-C} = 2.9 Hz), 128.8, 128.5, 122.0 (d, J_{P-C} = 6.5 Hz), 115.0 (d, J_{P-C} = 6.0 Hz), 113.6 (d, J_{P-C} = 3.3 Hz), 63.2 (d, $^{2}J_{P-C}$ = 6.7 Hz), 62.9 (d, $^{2}J_{P-C}$ = 6.9 Hz), 55.2, 54.2 (d, $^{1}J_{P-C}$ = 138.7 Hz), 16.3 (d, $^{3}J_{P-C}$ = 3.2 Hz), 16.2 (d, $^{3}J_{P-C}$ = 3.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.72.

HRMS (ESI-TOF, m/z): Found: *m/z* 363.1353. Calcd for $C_{19}H_{23}O_5P$ $(M+H)^+$ 363.1355

diethyl (2-oxo-2-phenyl-1-(3-(trifluoromethyl)phenyl)ethyl)phosphonate(4h)



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.96 (m, 2H), 7.82 – 7.77 (m, 2H), 7.58 – 7.54 (m, 2H), 7.49 – 7.43 (m, 3H), 5.43 (d, $^{1}J_{P-H}$ = 22.9 Hz, 1H), 4.15 – 3.99 (m, 4H), 1.22-1.16 m, 6H).

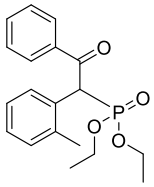
^{13}C NMR (101 MHz, $CDCl_3$): δ 193.0 (d, *J* = 5.4 Hz), 136.31 (d, *J* = 4.4 Hz), 133.7, 133.1 (d, *J* = 6.3 Hz), 132.6 (d, *J* = 9.2 Hz), 131.47 – 130.4 (m), 128.9,128.7, 126.58 – 126.47 (m), 124.8 – 124.6 (m),123.8(q, *J* = 273.7Hz), 63.4(d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 63.1 (d, $^{2}J_{P\text{-}C}$ = 7.1 Hz), 53.7 (d, $^{1}J_{P\text{-}C}$ = 135.8 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 1.9 Hz), 16.1 (d, $^{3}J_{P\text{-}C}$ = 1.8 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 18.30.

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.62.

HRMS (ESI-TOF, m/z): Found: *m/z* 401.1127. Calcd for $C_{19}H_{20}F_3O_4P$ $(M+H)^+$ 401.1124

diethyl (2-oxo-2-phenyl-1-(o-tolyl)ethyl)phosphonate(4i)



According to Method A in Section 4.5

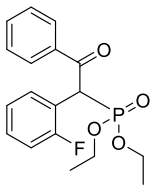
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.82 (m, 2H), 7.56 – 7.47 (m, 2H), 7.40-7.36 (m,, 2H), 7.22 – 7.12 (m, 3H), 5.50 (d, $^{1}J_{P\text{-}H}$ = 21.9 Hz, 1H), 4.21 – 3.96 (m, 4H), 2.57 (s, 3H), 1.24 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2 (d, $^{2}J_{P\text{-}C}$ = 5.1 Hz), 136.4 (d, $J_{P\text{-}C}$ = 6.6 Hz), 136.1 (d, $J_{P\text{-}C}$ = 7.0 Hz), 133.2, 130.9 (d, $J_{P\text{-}C}$ = 2.7 Hz), 129.8, 129.8, 129.4 (d, $J_{P\text{-}C}$ = 4.9 Hz), 128.6, 127.9 (d, $J_{P\text{-}C}$ = 3.4 Hz), 126.4 (d, $J_{P\text{-}C}$ = 3.3 Hz), 63.0 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 62.7 (d, $^{2}J_{P\text{-}C}$ = 7.2 Hz), 50.4 (d, $^{1}J_{P\text{-}C}$ = 141.4 Hz), 20.1, 16.3 (d, $^{3}J_{P\text{-}C}$ = 3.6 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 3.7 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 20.99.

HRMS (ESI-TOF, m/z): Found: *m/z* 347.1401. Calcd for $C_{19}H_{23}O_4P$ $(M+H)^+$ 347.1406

diethyl (1-(2-fluorophenyl)-2-oxo-2-phenylethyl)phosphonate(4j)



According to Method A in Section 4.5

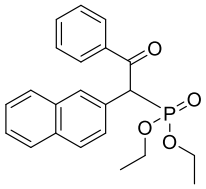
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.95 (m, 2H), 7.77 – 7.72 (m, 1H), 7.55 – 7.51 (m, 1H), 7.44 – 7.40 (m, 2H), 7.29 – 7.23 (m, 1H), 7.14 – 7.06(m, 2H), 5.76 (d, $^{1}J_{P\text{-}H}$ = 22.5 Hz, 1H), 4.17 – 4.06 (m, 4H), 1.23-1.18(m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.1(d, *J* = 5.1 Hz), 159.8 (dd, *J* = 246.3, 7.7 Hz), 136.0 (d, *J* = 5.4 Hz), 133.6, 131.1 (dd, *J* = 4.7, 2.2 Hz), 129.6 (dd, *J* = 8.4, 3.1 Hz), 128.8, 128.6, 124.4 (t, *J* = 3.3 Hz), 118.8 (dd, *J* = 14.4, 8.5 Hz), 115.3 (dd, *J* = 22.6, 2.4 Hz), 63.3 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 62.9 (d, $^{2}J_{P\text{-}C}$ = 6.8 Hz), 44.9 (dd, *J* = 140.9, 2.3 Hz), 16.1 (t, $^{3}J_{P\text{-}C}$ = 5.7 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 19.20 (d, *J* = 5.0 Hz).

HRMS (ESI-TOF, m/z): Found: *m/z* 351.1165. Calcd for $C_{18}H_{20}FO_4P$ $(M+H)^+$ 351.1156

diethyl (1-(naphthalen-2-yl)-2-oxo-2-phenylethyl)phosphonate (4k)



According to Method A in Section 4.5

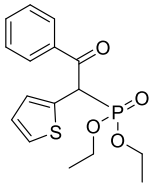
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.6 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.80 – 7.77 (m, 1H), 7.74 – 7.71 (m, 1H), 7.68 – 7.64 (m, 1H), 7.56 – 7.52 (m, 1H), 7.45 – 7.40 (m, 2H), 7.30 – 7.26 (m, 2H), 6.11 (d, $^1J_{P\text{-}H}$ = 21.7 Hz, 1H), 4.15 – 3.96 (m, 4H), 1.14 – 1.08 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.9 (d, $^2J_{P\text{-}C}$ = 5.1 Hz), 136.1 (d, $J_{P\text{-}C}$ = 6.7 Hz), 134.3 (d, $J_{P\text{-}C}$ = 2.4 Hz), 133.2, 131.0 (d, $J_{P\text{-}C}$ = 5.8 Hz), 129.2, 128.6 (d, $J_{P\text{-}C}$ = 3.7 Hz), 128.6, 128.5, 127.9 (d, $J_{P\text{-}C}$ = 6.3 Hz), 127.3(d, $J_{P\text{-}C}$ = 9.1 Hz), 126.8, 125.7, 125.5 (d, $J_{P\text{-}C}$ = 4.0 Hz), 122.9 (d, $J_{P\text{-}C}$ = 1.6 Hz), 63.0 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 62.4 (d, $^2J_{P\text{-}C}$ = 7.2 Hz), 49.3 (d, $^1J_{P\text{-}C}$ = 143.4 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 6.1 Hz)

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.53.

HRMS (ESI-TOF, m/z): Found: m/z 383.1409. Calcd for $C_{22}H_{23}O_4P$ $(M+H)^+$ 383.1406

diethyl (2-oxo-2-phenyl-1-(thiophen-2-yl)ethyl)phosphonate(4l)



According to Method A in Section 4.5

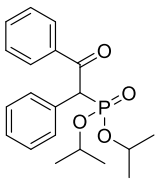
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 8.01 (m, 2H), 7.59 – 7.57 (m, 1H), 7.56 – 7.45 (m, 2H), 7.28 – 7.26 (m, 1H), 7.20 – 7.18(m, 1H), 6.99 – 6.97 (m, 1H), 5.72 (d, $^1J_{P\text{-}H}$ = 23.8 Hz, 1H), 4.15 – 3.98 (m, 4H), 1.22 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.8 (d, $^2J_{P\text{-}C}$ = 4.7 Hz), 136.2 (d, $J_{P\text{-}C}$ = 3.5 Hz), 133.6, 132.1 (d, $J_{P\text{-}C}$ = 11.1 Hz), 129.0, 128.6, 128.0 (d, $J_{P\text{-}C}$ = 7.8 Hz), 126.7(d, $J_{P\text{-}C}$ = 3.5 Hz), 126.1 (d, $J_{P\text{-}C}$ = 3.9 Hz), 63.6 (d, $^2J_{P\text{-}C}$ = 6.8 Hz), 63.5 (d, $^2J_{P\text{-}C}$ = 7.3 Hz), 49.0 (d, $^1J_{P\text{-}C}$ = 136.1 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 3.0 Hz), 16.1 (d, $^3J_{P\text{-}C}$ = 3.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 17.21.

HRMS (ESI-TOF, m/z): Found: *m/z* 339.0809. Calcd for $C_{16}H_{19}O_4PS$ $(M+H)^+$ 339.0814

diisopropyl (2-oxo-1,2-diphenylethyl)phosphonate(4m)



According to Method A in Section 4.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.7 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.44 – 7.40 (m, 2H), 7.36 – 7.27 (m, 3H), 5.31 (d, $^1J_{P\text{-}H}$ = 22.6 Hz, 1H), 4.72 – 4.62 (m, 2H), 1.28 (d, J = 6.2 Hz, 3H), 1.23 (d, J = 6.2 Hz, 3H), 1.15 (d, J = 6.2 Hz, 3H), 1.08 (d, J = 6.2 Hz, 3H).

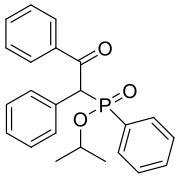
^{13}C NMR (101 MHz, $CDCl_3$): δ 193.6 (d, $^2J_{P\text{-}C}$ = 5.2 Hz), 136.7 (d, $J_{P\text{-}C}$ = 5.1 Hz), 133.1, 131.5 (d, $J_{P\text{-}C}$ = 8.9 Hz), 129.8 (d, $J_{P\text{-}C}$ = 6.5 Hz), 128.8, 128.5 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.4, 127.6 (d, $J_{P\text{-}C}$ = 3.2 Hz), 71.7 (d, $^2J_{P\text{-}C}$ = 7.0 Hz), 71.4 (d, $^2J_{P\text{-}C}$ = 7.3 Hz), 54.6 (d, $^1J_{P\text{-}C}$ = 138.5 Hz), 24.2 (d, $^3J_{P\text{-}C}$ = 2.9

Hz), 23.9 (d, $^{3}J_{P\text{-}C}$ = 3.5 Hz), 23.5 (d, $^{3}J_{P\text{-}C}$ = 5.7 Hz), 23.2 (d, $^{3}J_{P\text{-}C}$ = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 17.70.

HRMS (ESI-TOF, m/z): Found: m/z 383.1382. Calcd for $C_{20}H_{25}O_4P$ $(M+Na)^+$ 383.1382

isopropyl (2-oxo-1,2-diphenylethyl)(phenyl)phosphinate (4n，dr: 6: 1)



According to Method A in Section 4.5

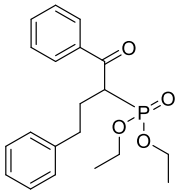
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.7 Hz, 2H), 7.65 – 7.44 (m, 4H), 7.40 – 7.28 (m, 6H), 7.22 – 7.21 (m, 3H), 5.42 (dd, $^{1}J_{P\text{-}H}$ = 18.8, 11.8 Hz, 1H), 4.71 – 4.59 (m, 1H), 1.27 – 1.25 (m, 3H), 1.16 (d, J = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2 (d, $^{2}J_{P\text{-}C}$ = 3.9 Hz), 193.9 (d, $^{2}J_{P\text{-}C}$ = 4.4 Hz), 137.2 (d, $J_{P\text{-}C}$ = 3.9 Hz), 137.1 (d, $J_{P\text{-}C}$ = 3.8 Hz), 133.13, 133.13, 132.8 (d, $J_{P\text{-}C}$ = 9.6, Hz), 132.7 (d, $J_{P\text{-}C}$ = 9.9, Hz) 132.2 (d, $J_{P\text{-}C}$ = 3.0 Hz), 132.1 (d, $J_{P\text{-}C}$ = 3.0 Hz), 131.2 (d, $J_{P\text{-}C}$ = 6.6 Hz), 131.1 (d, $J_{P\text{-}C}$ = 7.0 Hz), 130.7, 130.7, 129.9 (d, $J_{P\text{-}C}$ = 5.3 Hz), 129.8 (d, $J_{P\text{-}C}$ = 6.06 Hz), 129.4, 129.3, 128.8, 128.7, 128.8 (d, $J_{P\text{-}C}$ = 7.07 Hz), 128.4 (d, $J_{P\text{-}C}$ = 8.1 Hz), 127.8 (d, $J_{P\text{-}C}$ = 13.1 Hz), 127.7 (d, $J_{P\text{-}C}$ = 13.1 Hz), 127.6 (d, $J_{P\text{-}C}$ = 3.0 Hz), 127.6 (d, $J_{P\text{-}C}$ = 3.0 Hz), 71.0 (d, $^{2}J_{P\text{-}C}$ = 7.0 Hz), 70.8 (d, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 57.9 (d, $^{1}J_{P\text{-}C}$ = 93.6Hz), 57.8 (d, $^{1}J_{P\text{-}C}$ = 95.6Hz), 24.2 (d, $^{3}J_{P\text{-}C}$ = 3.03 Hz), 24.1 (d, $^{3}J_{P\text{-}C}$ = 4.04 Hz), 24.0 (d, $^{3}J_{P\text{-}C}$ = 4.04 Hz), 23.9 (d, $^{3}J_{P\text{-}C}$ = 5.05 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 34.89.

HRMS (ESI-TOF, m/z): Found: m/z 379.1450. Calcd for $C_{23}H_{23}O_3P$ $(M+H)^+$ 379.1457

diethyl (1-oxo-1,4-diphenylbutan-2-yl)phosphonate (4o)



According to Method B in Section 4.5

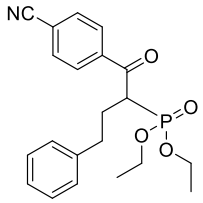
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.15 (m, 3H), 7.08 (d, *J* = 7.3 Hz, 2H), 4.14 – 3.95 (m, 5H), 2.75 – 2.48 (m, 3H), 2.33 – 2.24 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.1 Hz,3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.9 (d, $^{2}J_{P\text{-}C}$ = 5.4 Hz), 140.4, 137.5 (d, $J_{P\text{-}C}$ = 1.4 Hz), 133.2, 128.6, 128.5, 128.4, 128.3, 126.1, 62.7 (d, $^{2}J_{P\text{-}C}$ = 6.9 Hz), 62.5(d, $^{2}J_{P\text{-}C}$ = 6.9 Hz), 46.2 (d, $^{1}J_{P\text{-}C}$ = 127.7 Hz), 34.0 (d, $^{2}J_{P\text{-}C}$ = 15.1 Hz), 28.9 (d, $^{3}J_{P\text{-}C}$ = 4.4 Hz), 16.2 (d, $^{3}J_{P\text{-}C}$ = 5.9 Hz), 16.0 (d, $^{3}J_{P\text{-}C}$ = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.19.

HRMS (ESI-TOF, m/z): Found: m/z 361.1562. Calcd for $C_{20}H_{26}O_4P$ $(M+H)^+$ 361.1563

diethyl (1-(4-cyanophenyl)-1-oxo-4-phenylbutan-2-yl)phosphonate (4p)



According to Method B in Section 4.5

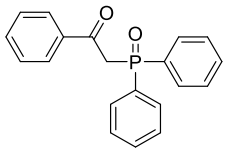
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.23– 7.17 (m, 3H), 7.05 – 7.03 (m, 2H), 4.11 – 3.95 (m, 5H), 2.74 – 2.49 (m, 3H), 2.35 – 2.25 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.8 (d, $^2J_{P\text{-}C}$ = 5.6 Hz), 140.4, 139.9, 132.1, 128.9, 128.5 (d, $J_{P\text{-}C}$ = 5.9 Hz), 127.2 (d, $J_{P\text{-}C}$ = 29.9 Hz), 126.4, 117.8, 116.3, 62.9 (d, $^2J_{P\text{-}C}$ = 6.9 Hz), 62.8 (d, $^2J_{P\text{-}C}$ = 6.9 Hz), 46.7 (d, $^1J_{P\text{-}C}$ = 127.0 Hz), 33.9 (d, $^2J_{P\text{-}C}$ = 14.6 Hz), 28.5 (d, $^3J_{P\text{-}C}$ = 4.4 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 5.9 Hz), 16.1 (d, $^3J_{P\text{-}C}$ = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 21.09.

HRMS (ESI-TOF, m/z): Found: m/z 386.1517. Calcd for $C_{21}H_{25}NO_4P$ $(M+H)^+$ 386.1516

2-(diphenylphosphoryl)-1-phenylethan-1-one (4q)



According to Method C in Section 4.5

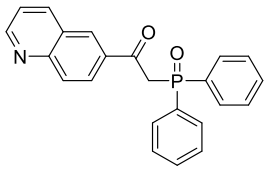
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.97 (m, 2H), 7.83 – 7.78 (m, 4H), 7.56 – 7.50 (m, 3H), 7.48 – 7.42 (m, 6H), 4.14 (d, $^1J_{P\text{-}H}$ = 15.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.8 (d, $^2J_{P\text{-}C}$ = 5.6 Hz), 136.9, 133.5, 132.1 (d, $J_{P\text{-}C}$ = 2.8 Hz), 131.9 (d, $J_{P\text{-}C}$ = 103.4 Hz), 131.1 (d, $J_{P\text{-}C}$ = 9.8 Hz), 129.2, 128.6 (d, $J_{P\text{-}C}$ = 12.3 Hz), 128.5, 43.3 (d, $^1J_{P\text{-}C}$ = 57.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 17.70.

HRMS (ESI-TOF, m/z): Found: m/z 321.1033. Calcd for $C_{20}H_{17}O_2P$ $(M+H)^+$ 321.1038

2-(diphenylphosphoryl)-1-(quinolin-6-yl)ethan-1-one (4r)



According to Method C in Section 4.5

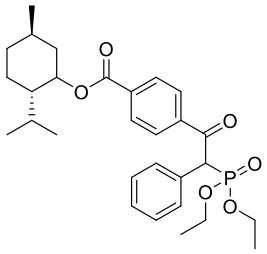
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.63 (d, *J* = 2.1 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.23 – 8.20 (m, 1H), 8.0 – 8.08 (m, 1H), 7.85 – 7.80 (m, 4H), 7.55 – 7.45 (m, 7H), 4.27 (d, $^1J_{P\text{-}H}$ = 15.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.1 (d, $^2J_{P\text{-}C}$ = 5.5 Hz), 152.9, 137.9, 134.7, 132.4, 132.3, 131.7(d, $J_{P\text{-}C}$ = 104.0 Hz), 131.9, 131.1 (d, $J_{P\text{-}C}$ = 10.1 Hz), 129.9, 128.7 (d, $J_{P\text{-}C}$ = 12.3 Hz), 127.9, 127.3, 121.9, 43.8 (d, $^1J_{P\text{-}C}$ = 56.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 26.91.

HRMS (ESI-TOF, m/z): Found: m/z 372.1153. Calcd for $C_{23}H_{18}NO_2P$ $(M+H)^+$ 372.1147

2-isopropyl-5-methylcyclohexyl 4-(2-(diethoxyphosphoryl)-2-phenylacetyl)benzoate(5， dr: > 20: 1)



According to Method A in Section 4.5

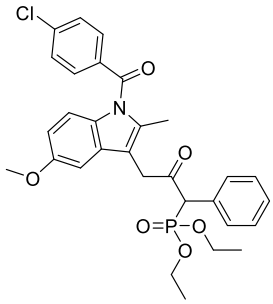
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.52-7.49 (m, 2H), 7.36– 7.27 (m, 3H), 5.32 (dd, $^{1}J_{P-H}$ = 22.4, 1.8 Hz, 1H), 4.95-4.88(m, 1H), 4.18 – 4.01 (m, 4H), 2.12-2.07 (m, 1H), 1.93-1.86 (m, 1H), 1.75-1.69 (m, 2H), 1.58-1.50 (m, 2H), 1.23-1.18 (m, 6H), 1.15 – 1.03 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 7H), 0.76 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.2 (d, $^{2}J_{P-C}$ = 5.2 Hz), 165.0, 139.5 (dd, *J* = 5.6, 2.4 Hz), 134.7 (d, J_{P-C} = 1.1 Hz), 131.0 (dd, *J* = 9.0, 2.5 Hz), 129.7 (d, J_{P-C} = 2.7 Hz), 129.6, 128.9 (d, J_{P-C} = 2.8 Hz), 128.7 (d, J_{P-C} = 2.1 Hz), 128.0 (d, J_{P-C} = 3.2 Hz), δ 75.5, 63.3 (d, $^{2}J_{P-C}$ = 6.7 Hz), 63.0 (d, $^{2}J_{P-C}$ = 7.0 Hz), 54.7 (d, $^{1}J_{P-C}$ = 138.4 Hz), 47.1, 40.8, 34.2, 31.4, 26.4 (d, J_{P-C} = 5.3 Hz), 23.5 (d, J_{P-C} = 5.4 Hz), 21.9, 20.7 (d, J_{P-C} = 2.8 Hz), 16.4 (d, J_{P-C} = 5.1 Hz), 16.3 (d, $^{3}J_{P-C}$ = 3.1 Hz), 16.2 (d, $^{3}J_{P-C}$ = 3.2 Hz).

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 19.20.

HRMS (ESI-TOF, m/z): Found: *m/z* 515.2560. Calcd for $C_{29}H_{39}O_6P$ $(M+H)^+$ 515.2557

diethyl(3-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-2-oxo-1-phenylpropyl)phosphonate（6）



According to Method A in Section 4.5

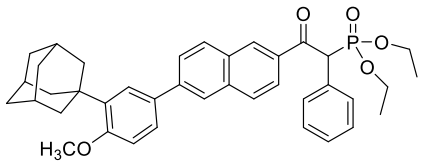
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.59 (m, 2H), 7.46 – 7.44 (m, 2H), 7.34 – 7.29 (m, 5H), 6.90-6.87 (m, 1H), 6.76-6.75 (m, 1H), 6.67 – 6.64 (m, 1H), 4.56 (d, $^{1}J_{P-H}$ = 22.7 Hz, 1H), 4.12 – 3.96 (m, 4H), 3.95 – 3.85 (m, 2H), 3.74 (s, 3H), 2.16 (s, 3H), 1.23 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1 (d, $^{2}J_{P-C}$ = 4.5 Hz), 168.1, 156.1, 139.2, 136.3, 133.7, 131.1, 130.8 (d, J_{P-C} = 8.5 Hz), 130.6 (d, J_{P-C} = 27.4 Hz), 129.5 (d, J_{P-C} = 6.6 Hz), 129.0, 128.6 (d, J_{P-C} = 2.4 Hz), 128.0 (d, J_{P-C} = 3.0 Hz), 115.0, 112.0, 111.7, 100.8, 63.3 (d, $^{2}J_{P-C}$ = 6.9 Hz), 62.9 (d, $^{2}J_{P-C}$ = 7.2 Hz), 57.5 (d, $^{1}J_{P-C}$ = 133.9 Hz), 55.6, 39.3 (d, $^{3}J_{P-C}$ = 3.8 Hz), 16.2 (d, $^{3}J_{P-C}$ = 6.0 Hz), 13.2.

^{31}P NMR (**162 MHz**, **$CDCl_3$**): δ 18.69.

HRMS (ESI-TOF, m/z): Found: *m/z* 568.1653. Calcd for $C_{30}H_{31}ClNO_6P$ $(M+H)^+$ 568.1650

diethyl(2-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-2-oxo-1-phenylethyl)phosphonate（7）



According to Method A in Section 4.5

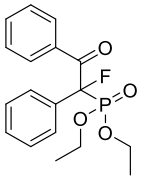
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 1.8 Hz, 1H), 8.03 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.97 – 7.95 (m, 2H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 5.53 (d, $^1J_{P\text{-}H}$ = 22.3 Hz, 1H), 4.20 – 4.04 (m, 4H), 3.90 (s, 3H), 2.18 (d, *J* = 3.1 Hz, 6H), 2.10 (d, *J* = 3.3 Hz, 2H), 1.81 (d, *J* = 3.1 Hz, 6H), 1.22 (q, *J* = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.3 (d, $^2J_{P\text{-}C}$ = 5.2 Hz), 158.9, 141.9, 138.9, 136.0, 133.3 (d, $J_{P\text{-}C}$ = 5.5 Hz), 132.2, 131.6 (d, $J_{P\text{-}C}$ = 9.0 Hz), 131.0, 130.7, 130.0, 129.7 (d, $J_{P\text{-}C}$ = 6.3 Hz), 128.7 (d, J = 2.6 Hz), 128.5, 127.8 (d, $J_{P\text{-}C}$ = 3.2 Hz), 126.5, 125.8, 125.7, 124.6, 124.5, 112.0, 63.2 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 62.9 (d, $^2J_{P\text{-}C}$ = 7.1 Hz), 55.1, 54.2 (d, $^1J_{P\text{-}C}$ = 137.8 Hz), 40.5, 37.1, 37.0, 29.0, 16.3 (d, $^3J_{P\text{-}C}$ = 2.9 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 3.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 19.88.

HRMS (ESI-TOF, m/z): Found: *m/z* 623.2927. Calcd for $C_{39}H_{43}O_5P$ $(M+H)^+$ 623.2920

diethyl (1-fluoro-2-oxo-1,2-diphenylethyl)phosphonate (8)



According to Method A in Section 4.7

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.854– 7.81 (m, 2H), 7.67 – 7.64 (m, 2H), 7.51 – 7.33 (m, 6H), 4.27 – 4.08 (m, 4H), 1.30 – 1.23(m, 6H).

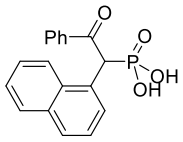
^{13}C NMR (101 MHz, $CDCl_3$): δ 194.4 (dd, *J* = 24.0, *J* =1.9 Hz), 134.47 – 133.98 (m), 133.4, 132.5 (dd, J = 20.2, 2.8 Hz), 129.9 (d, *J* = 6.1 Hz), 129.0 (d, *J* = 3.0 Hz), 128.6 (t, J = 2.3 Hz), 128.2, 124.8 (dd, J = 9.0, 4.2 Hz), 100.9 (dd, *J* = 201.0, 171.5 Hz), 64.4 (d, $^2J_{P\text{-}C}$ = 3.8 Hz), 64.3 (d, $^2J_{P\text{-}C}$ = 4.1 Hz), 16.3 (d, $^3J_{P\text{-}C}$ = 3.9 Hz), 16.2 (d, $^3J_{P\text{-}C}$ = 3.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 11.52 (d, *J* = 85.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -169.80 (d, *J* = 86.0 Hz).

HRMS (ESI-TOF, m/z): Found: *m/z* 351.1166. Calcd for $C_{18}H_{20}FO_4P$ $(M+H)^+$ 351.1156

(1-(naphthalen-1-yl)-2-oxo-2-phenylethyl)phosphonic acid (9)



According to Method C in Section 4.7

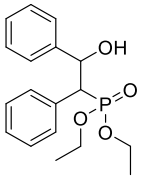
^{1}H NMR (400 MHz, DMSO): δ 8.42 (d, J = 8.5 Hz, 1H), 8.00 – 7.82 (m, 5H), 7.62 – 7.42 (m, 6H), 6.22 (d, $^1J_{P\text{-}H}$ = 22.8 Hz, 1H).

^{13}C NMR (101 MHz, DMSO): δ 194.8 (d, $^2J_{P\text{-}C}$ = 5.5 Hz), 136.7 (d, $J_{P\text{-}C}$ = 4.4 Hz), 133.6, 133.2, 131.2 (d, $J_{P\text{-}C}$ = 6.7 Hz), 129.6 (d, $J_{P\text{-}C}$ = 7.8 Hz), 128.7, 128.6, 128.4, 128.0 (d, $J_{P\text{-}C}$ = 6.0 Hz), 127.5 (d, $J_{P\text{-}C}$ = 2.8 Hz), 126.5, 125.55, 125.2 (d, $J_{P\text{-}C}$ = 2.9 Hz), 123.6, 49.1 (d, $^1J_{P\text{-}C}$ = 131.2 Hz).

^{31}P NMR (162 MHz, DMSO): δ 14.89.

HRMS (ESI-TOF, m/z): Found: m/z 349.0594. Calcd for $C_{18}H_{15}O_4P$ $(M+Na)^+$ 349.0600

diethyl (2-hydroxy-1,2-diphenylethyl)phosphonate(10, dr: > 20: 1)



According to Method B in Section 4.7

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 – 7.10 (m, 10H), 5.29 – 5.23 (m, 1H), 4.63 (d, J = 3.2 Hz, 1H), 4.11 – 3.40 (m, 4H), 3.44 (dd, $^1J_{P-H}$ = 19.7, 9.2 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H).

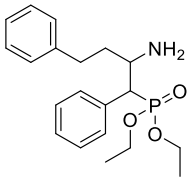
^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5 (d, J_{P-C} = 14.2 Hz), 134.1 (d, J_{P-C} = 6.8 Hz), 129.7 (d, J_{P-C} = 6.7 Hz), 128.2 (d, J_{P-C} = 2.1 Hz), 127.8, 127.4, 127.1 (d, J_{P-C} = 2.7 Hz), 126.6, 75.0 (d, $^2J_{P-C}$ = 3.8 Hz), 62.9 (d, $^2J_{P-C}$ = 7.1 Hz), 62.3 (d, $^2J_{P-C}$ = 7.0 Hz), 53.3 (d, $^1J_{P-C}$ = 132.9 Hz), 16.2 (t, $^3J_{P-C}$ = 5.8 Hz).

13C NMR (101 MHz, Chloroform-d) δ 75.01 (d, J = 3.8 Hz), 62.99 (d, J = 7.1 Hz), 62.36 (d, J = 7.0 Hz), 53.34 (d, J = 132.9 Hz), 16.20 (t, J = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.18.

HRMS (ESI-TOF, m/z): Found: *m/z* 357.1225. Calcd for $C_{18}H_{23}O_4P$ $(M+H)^+$ 357.1226

diethyl (2-amino-1,4-diphenylbutyl)phosphonate (11, dr: 9 : 1)



According to Method D in Section 4.7

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.41 (m, 2H), 7.36 – 7.31 (m, 3H), 7.30 – 7.24 (m, 2H), 7.18 – 7.16 (m, 3H), 4.15 – 4.03 (m, 2H), 3.93 – 3.83 (m, 1H), 3.71 – 3.62 (m, 1H), 3.56 – 3.49 (m, 1H), 3.12 (dd, $^1J_{P-H}$ = 23.4, 4.0 Hz, 1H), 2.82 – 2.64 (m, 2H), 1.94 – 1.89 (m, 1H), 1.80 – 1.72 (m, 1H), 1.57 – 1.47 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.7, 132.9 (d, J_{P-C} = 4.3 Hz), 130.5 (d, J_{P-C} = 8.3 Hz), 128.4 (d, J_{P-C} = 1.3 Hz), 128.3, 128.3, 127.5 (d, J_{P-C} = 2.1 Hz), 125.8, 62.8 (d, $^2J_{P-C}$ = 7.1 Hz), 61.6 (d, $^2J_{P-C}$ = 7.2 Hz), 50.9 (d, $^3J_{P-C}$ = 2.0 Hz), 50.0 (d, $^1J_{P-C}$ = 137.9 Hz), 37.6 (d, $^2J_{P-C}$ = 12.1 Hz), 32.6, 16.3(d, $^3J_{P-C}$ = 5.9 Hz), 16.0 (d, $^3J_{P-C}$ = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.46.

HRMS (ESI-TOF, m/z): Found: m/z 362.1875. Calcd for $C_{20}H_{28}NO_3P$ $(M+H)^+$ 362.1879

6. Supplementary Reference

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7. Supplementary Figures

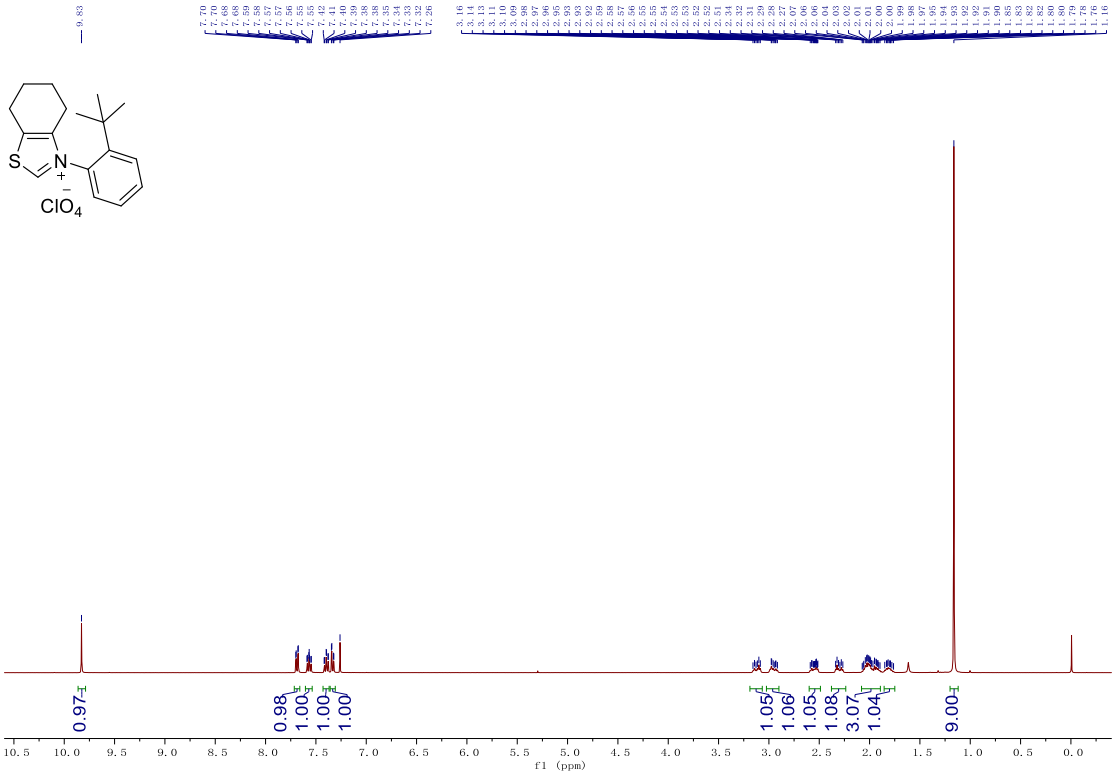

Figure S1. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **N1**

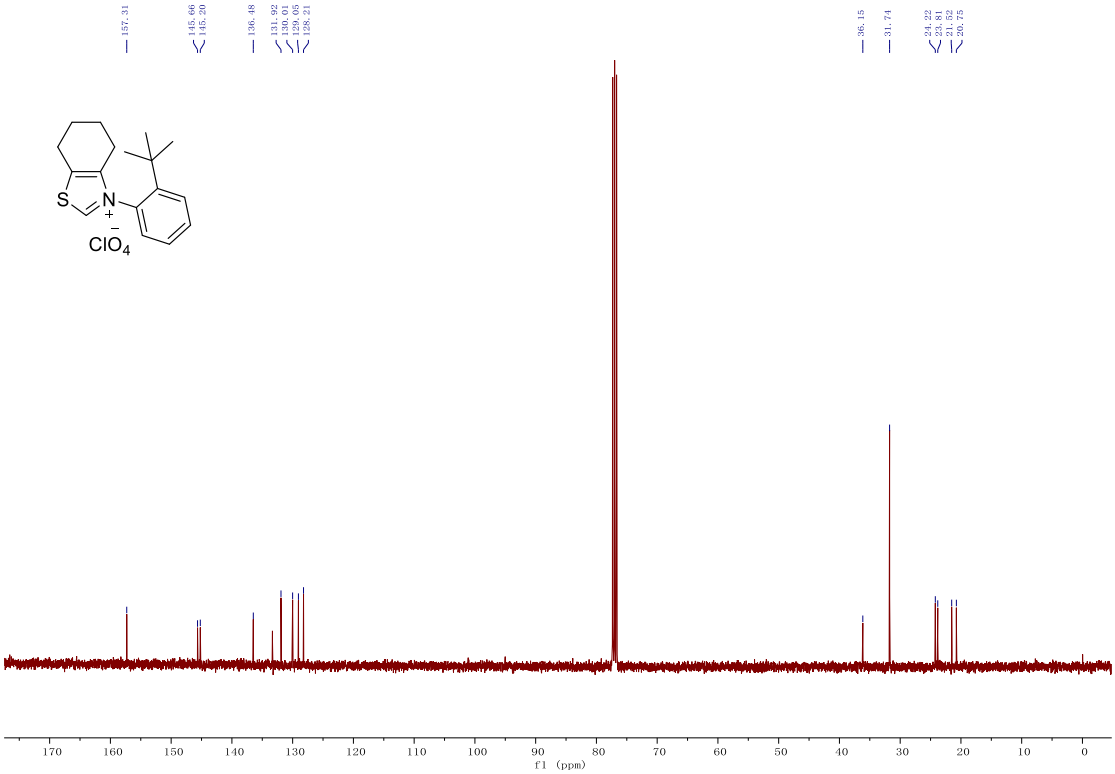

Figure S2. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **N1**

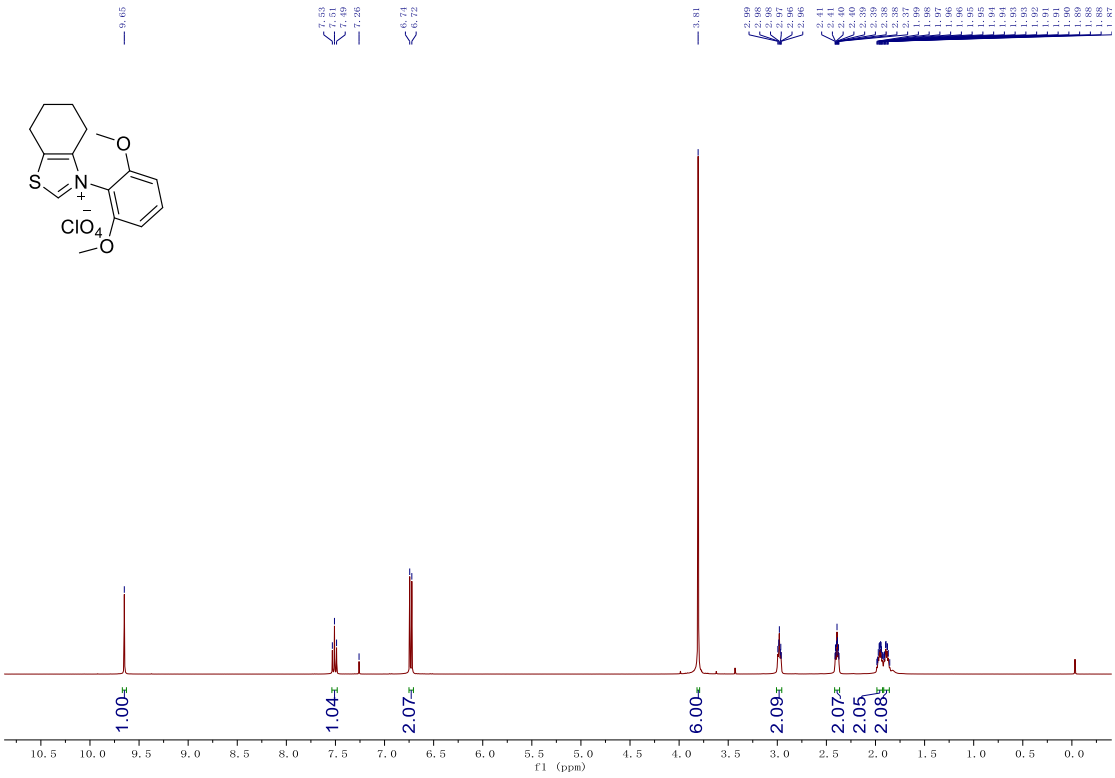

Figure S3. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **N2**

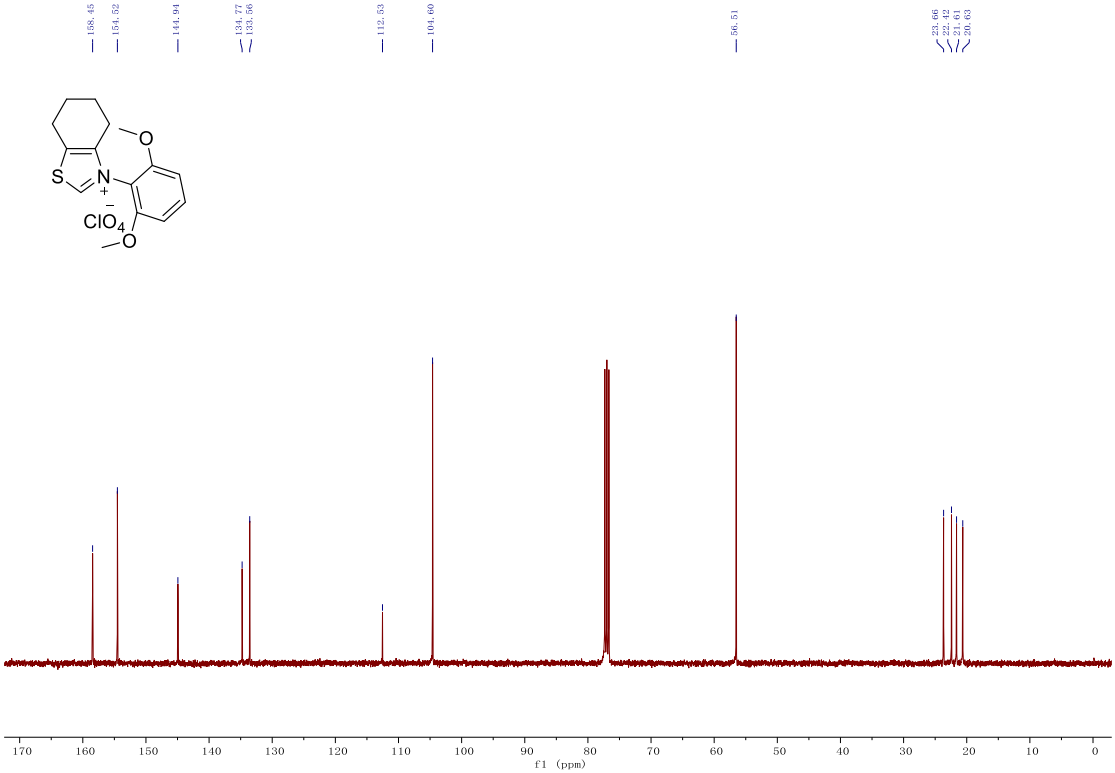

Figure S4. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **N2**

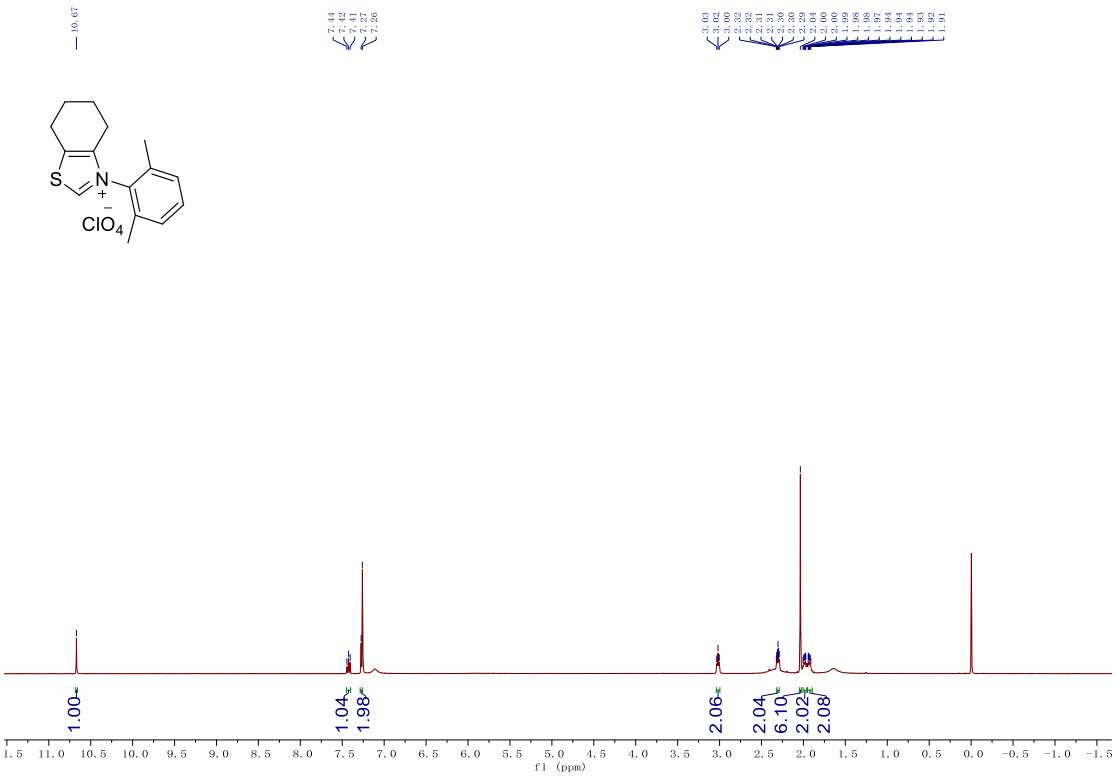

Figure S5. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **N3**

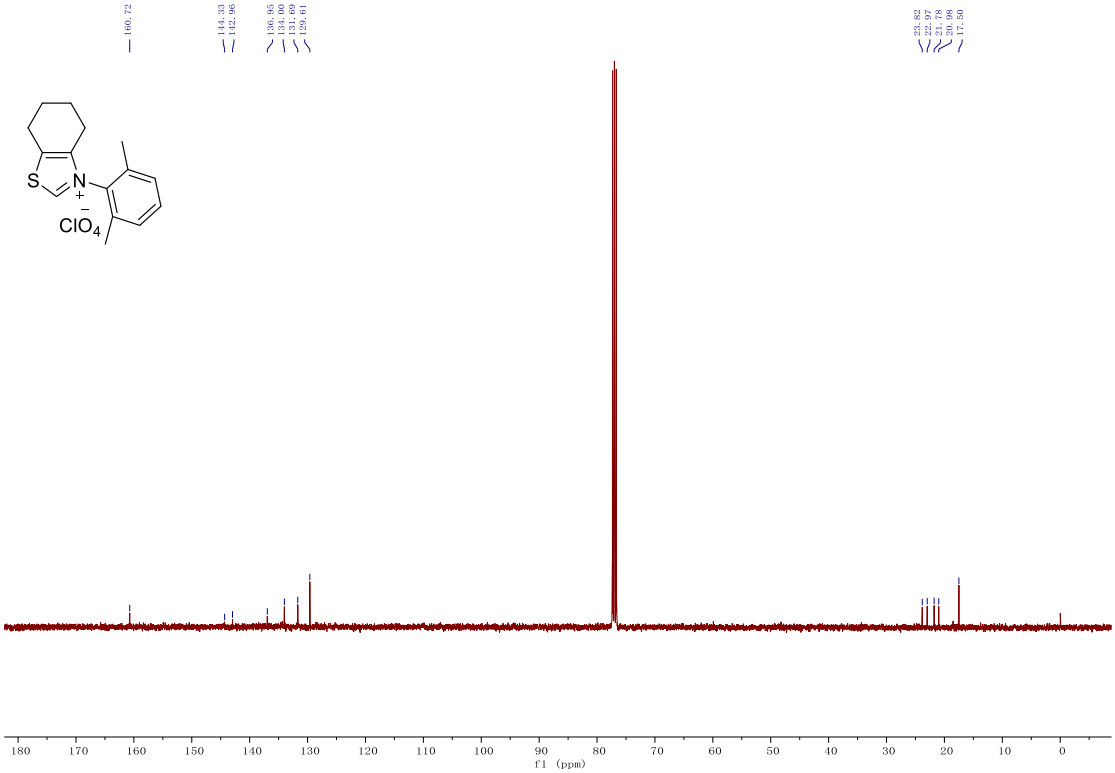

Figure S6. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **N3**

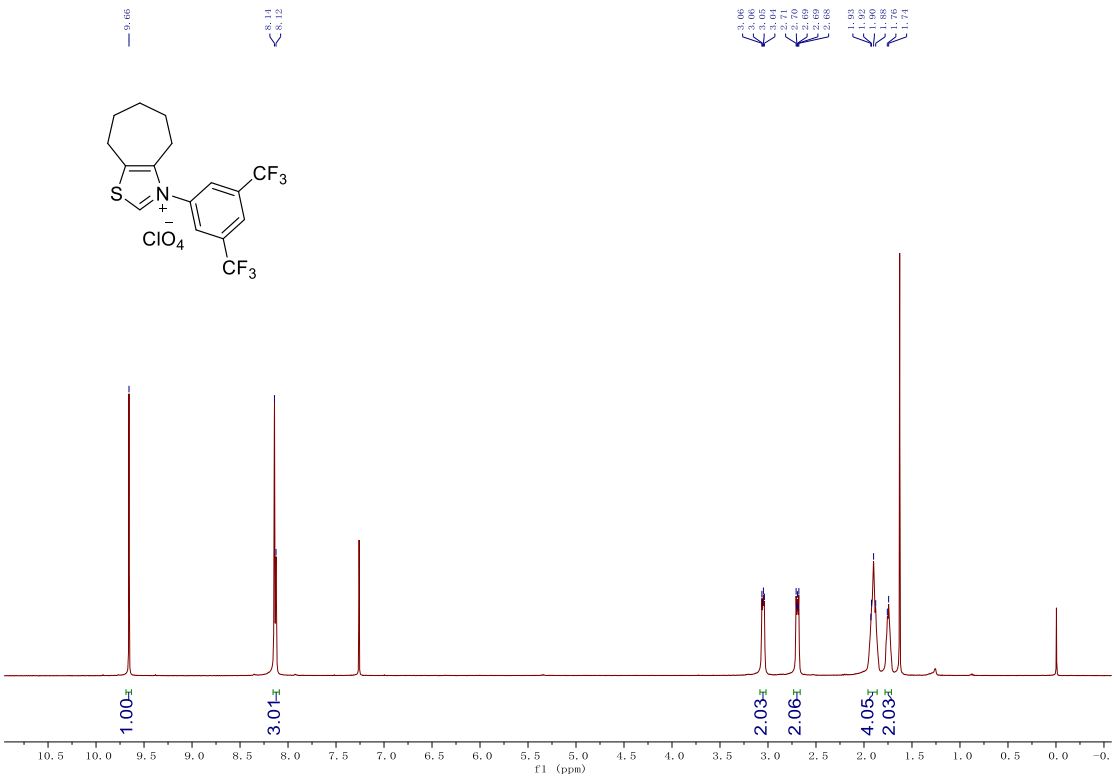

Figure S7. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **N4**

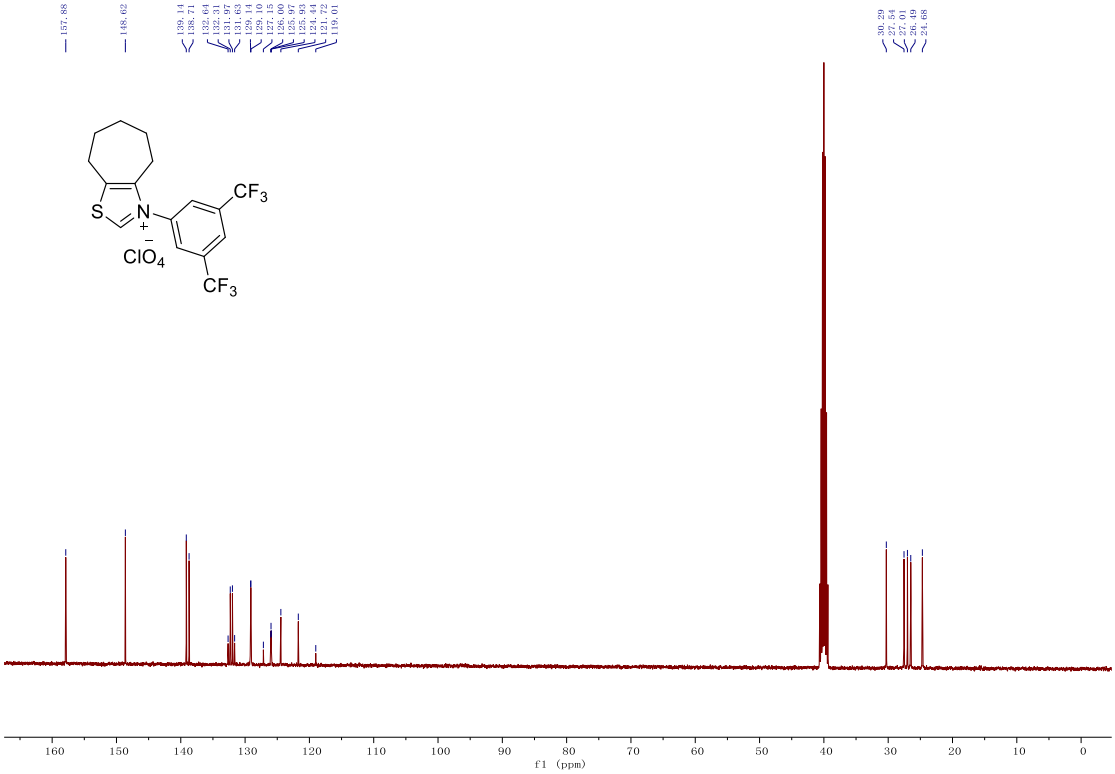

Figure S8. ^{13}**C NMR** (101 MHz, DMSO) spectrum of **N4**

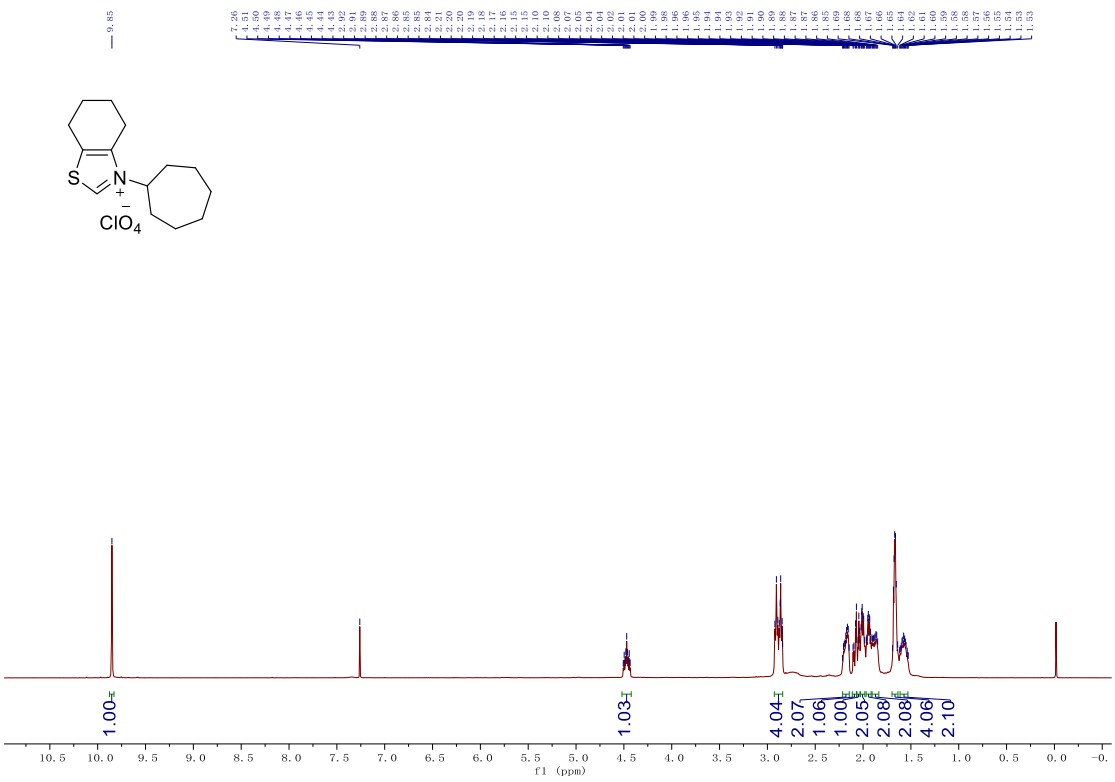

Figure S9. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **N5**

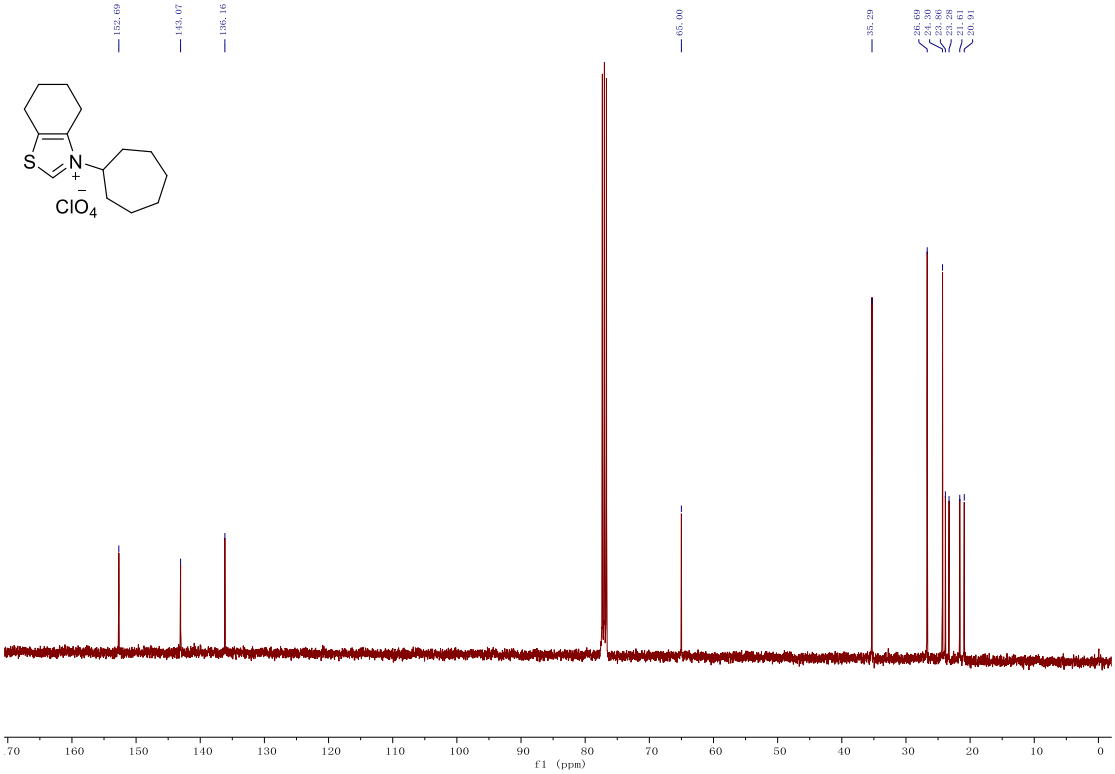

Figure S10. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **N5**

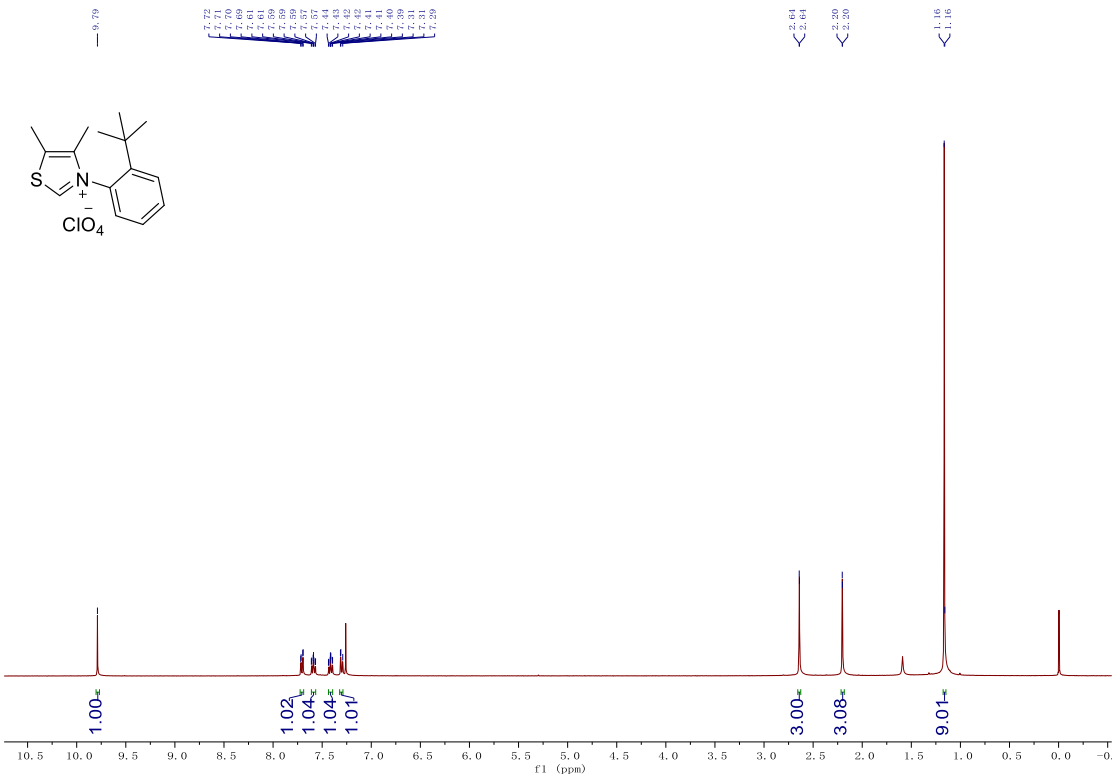

Figure S11. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **N6**

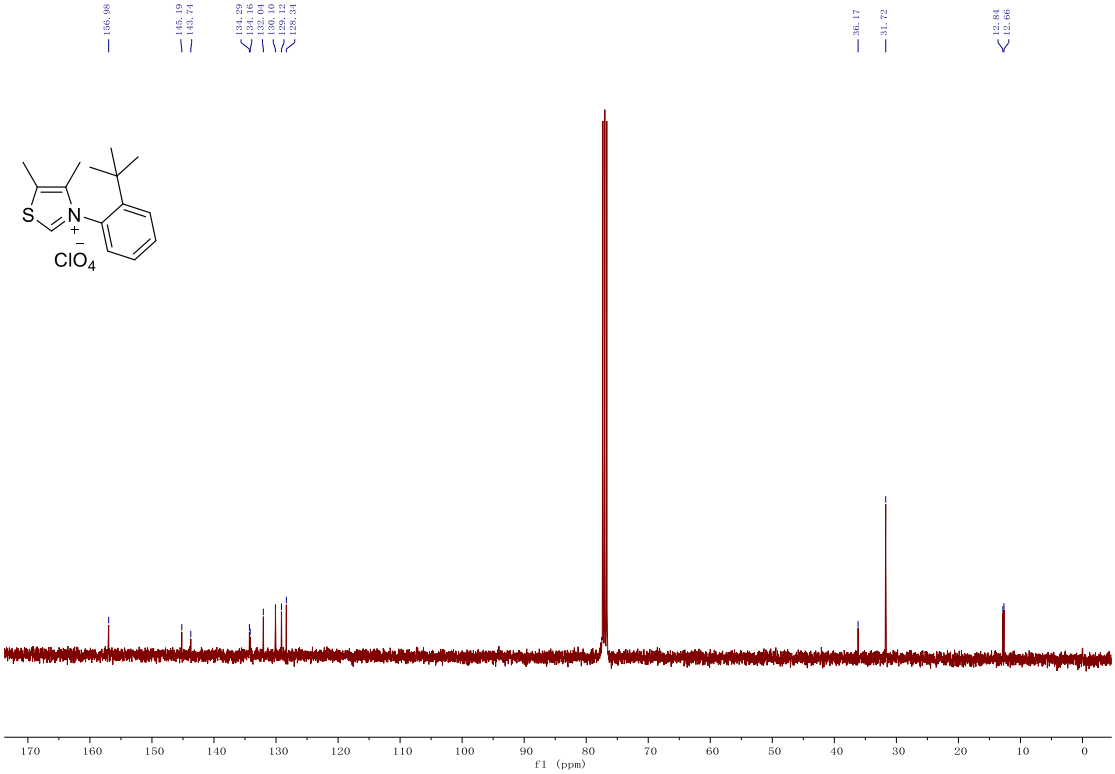

Figure S12. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **N6**

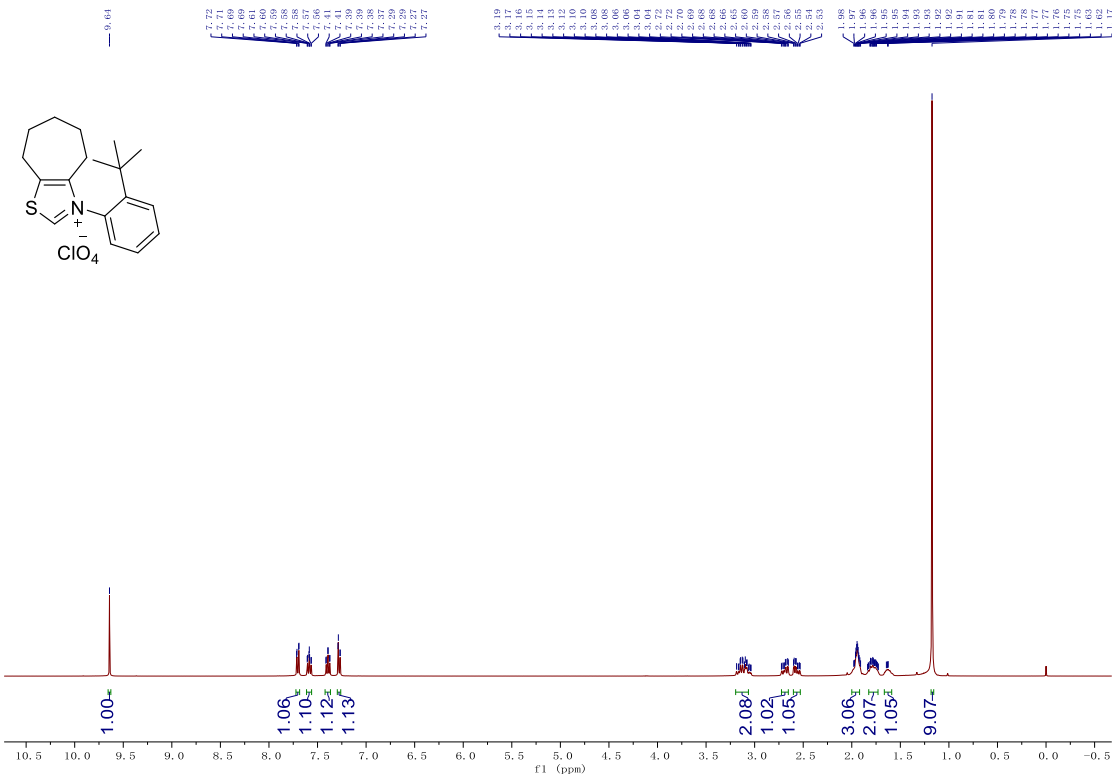

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **N7**

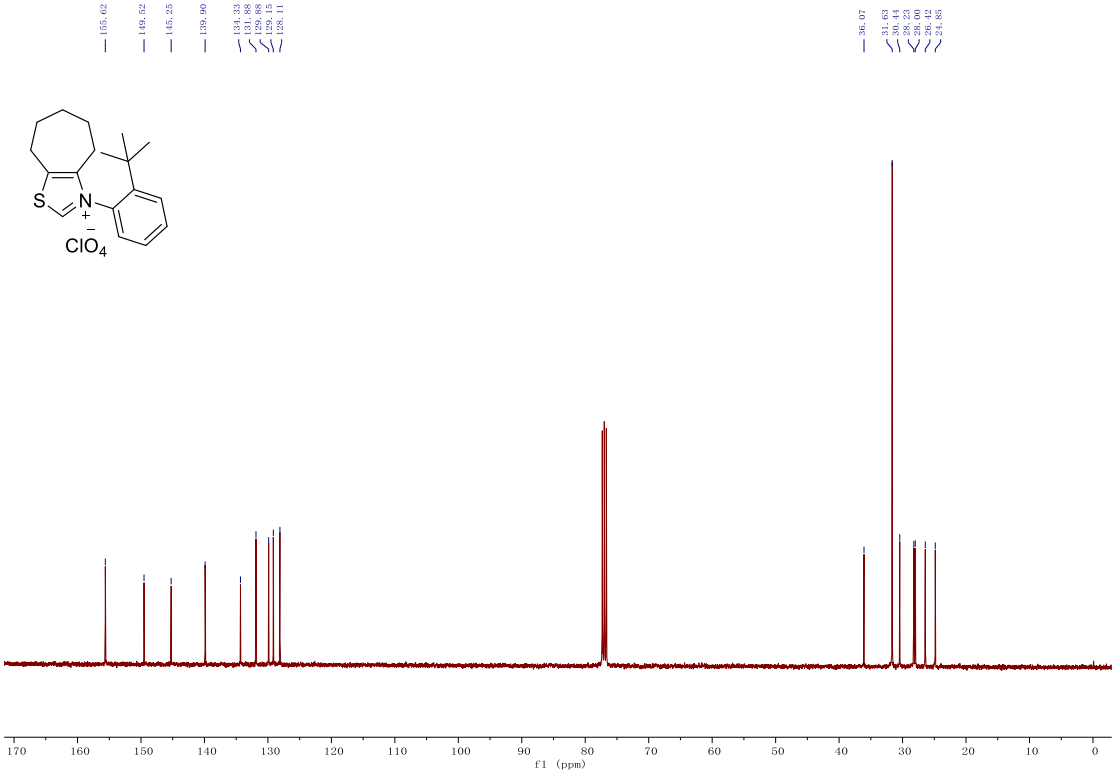

Figure S14. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **N7**

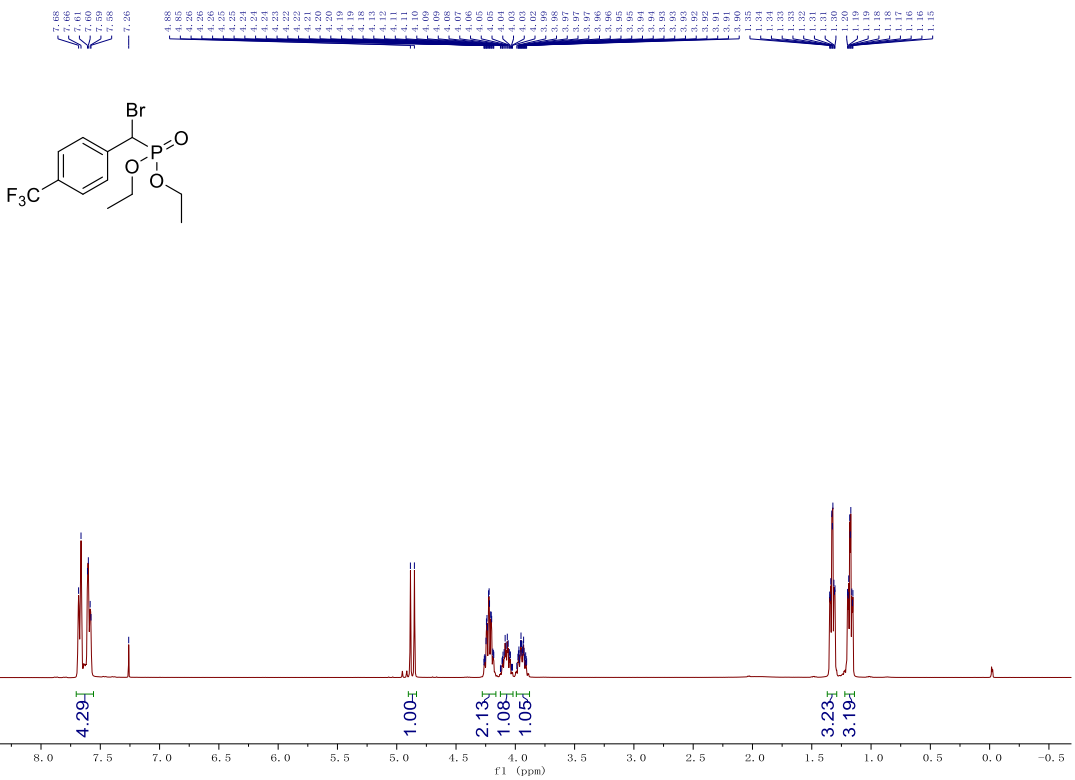

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1e**

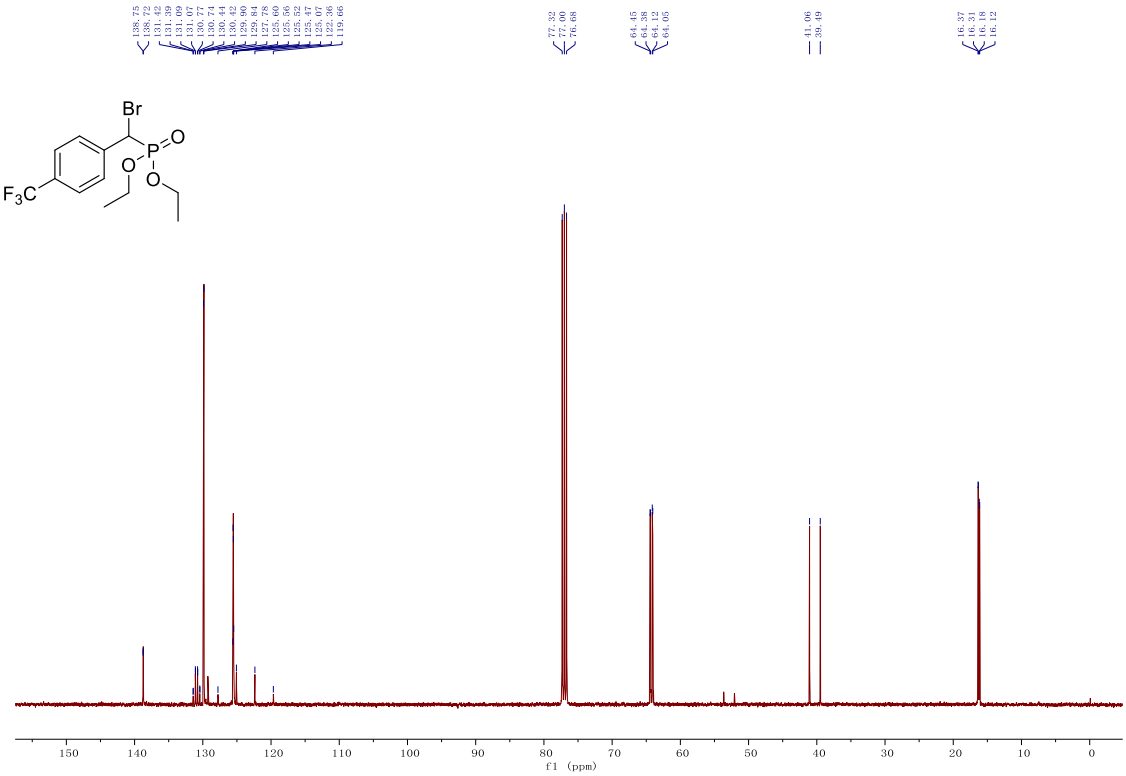

Figure S16. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1e**

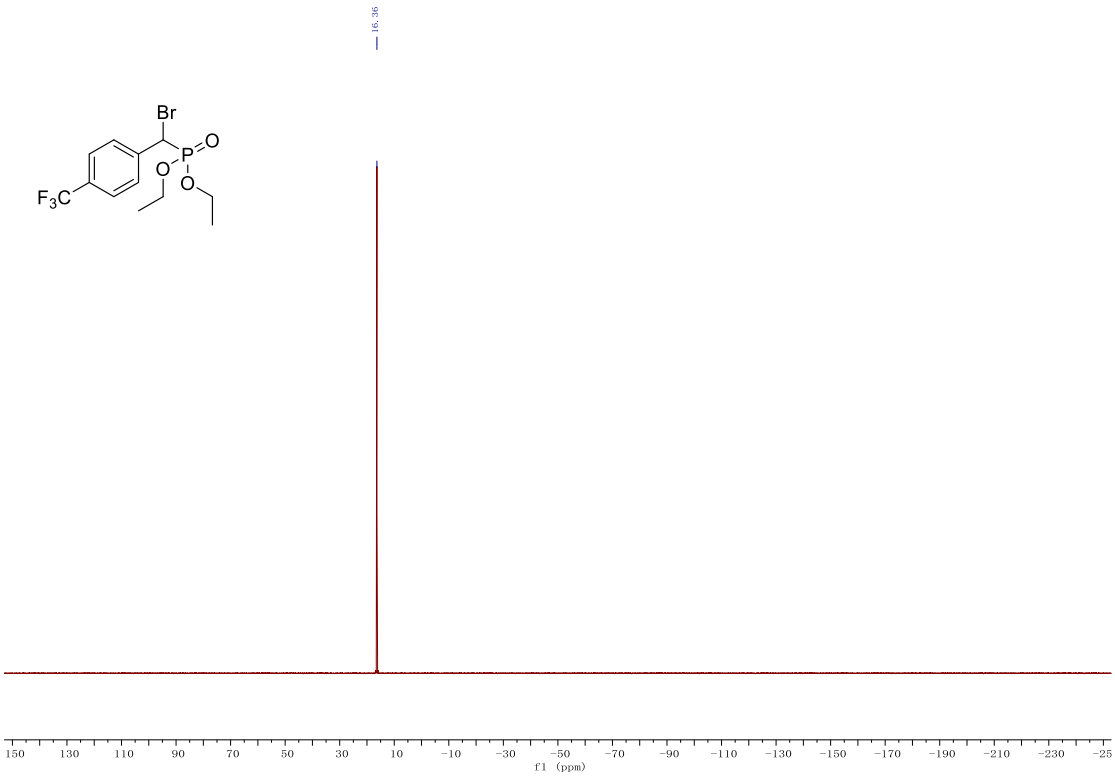

Figure S17. ^{31}**P NMR (162 MHz, CDCl$_3$)**.spectrum of **1e**

Figure S18. ^{19}**F NMR** (377 MHz, $CDCl_3$) spectrum of **1e**

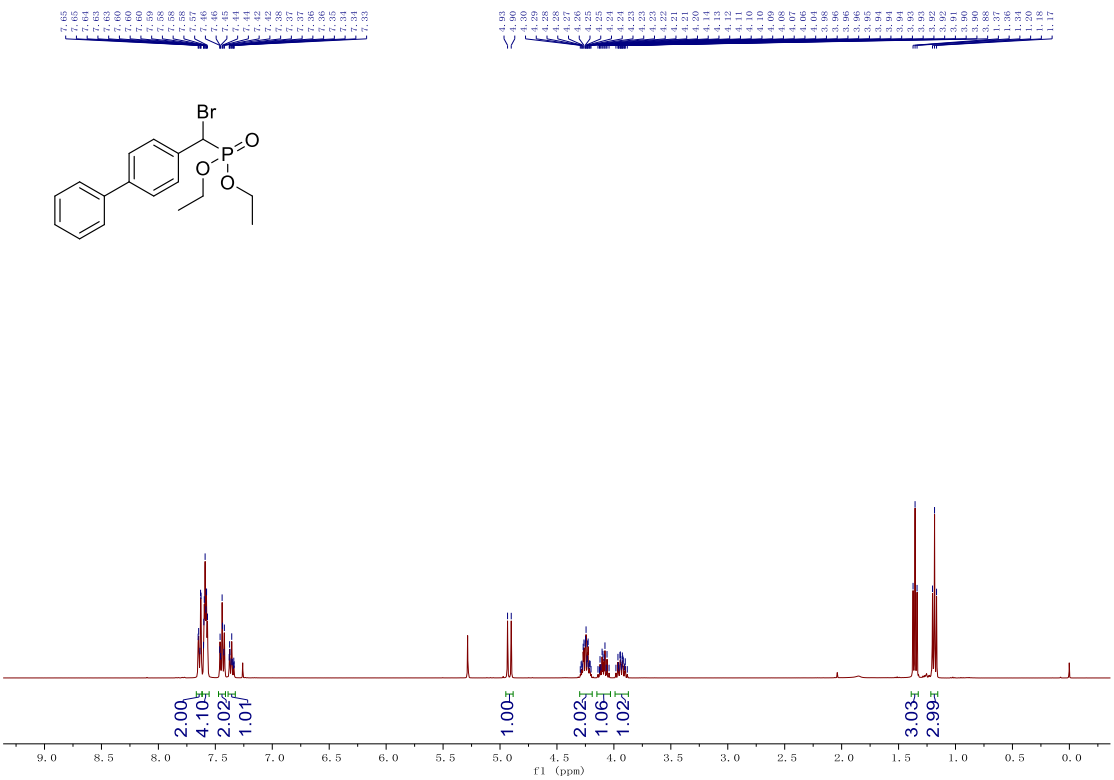

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f**

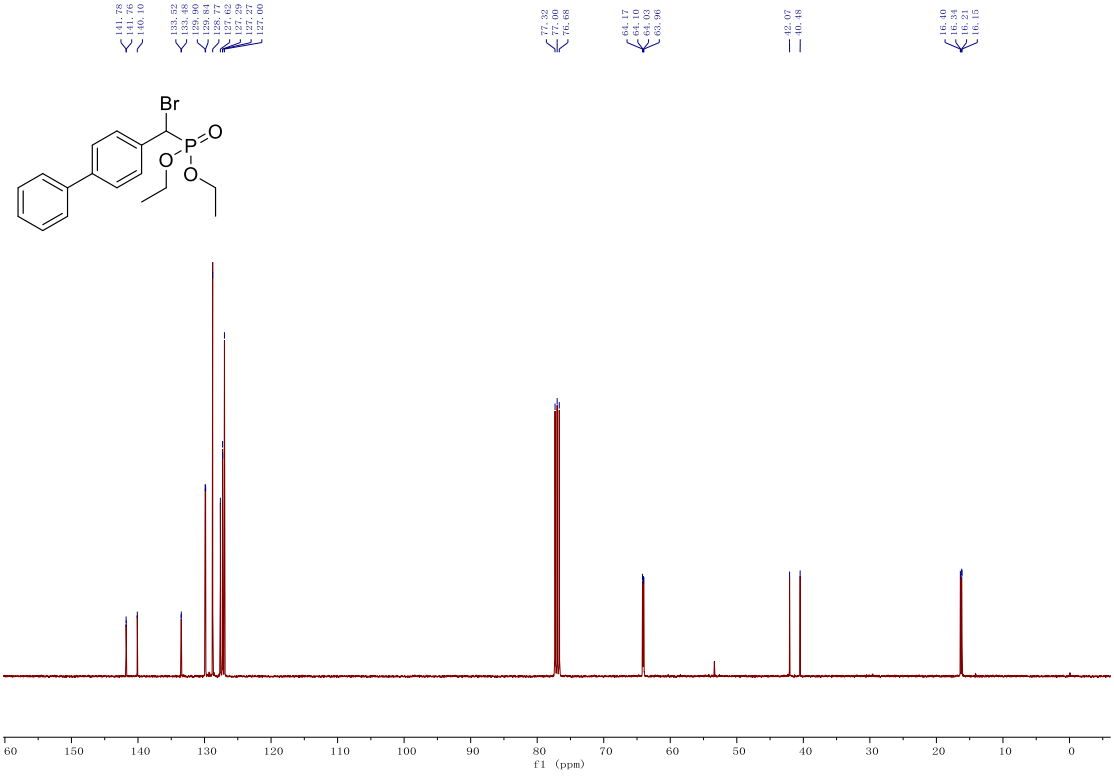

Figure S20. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1f**

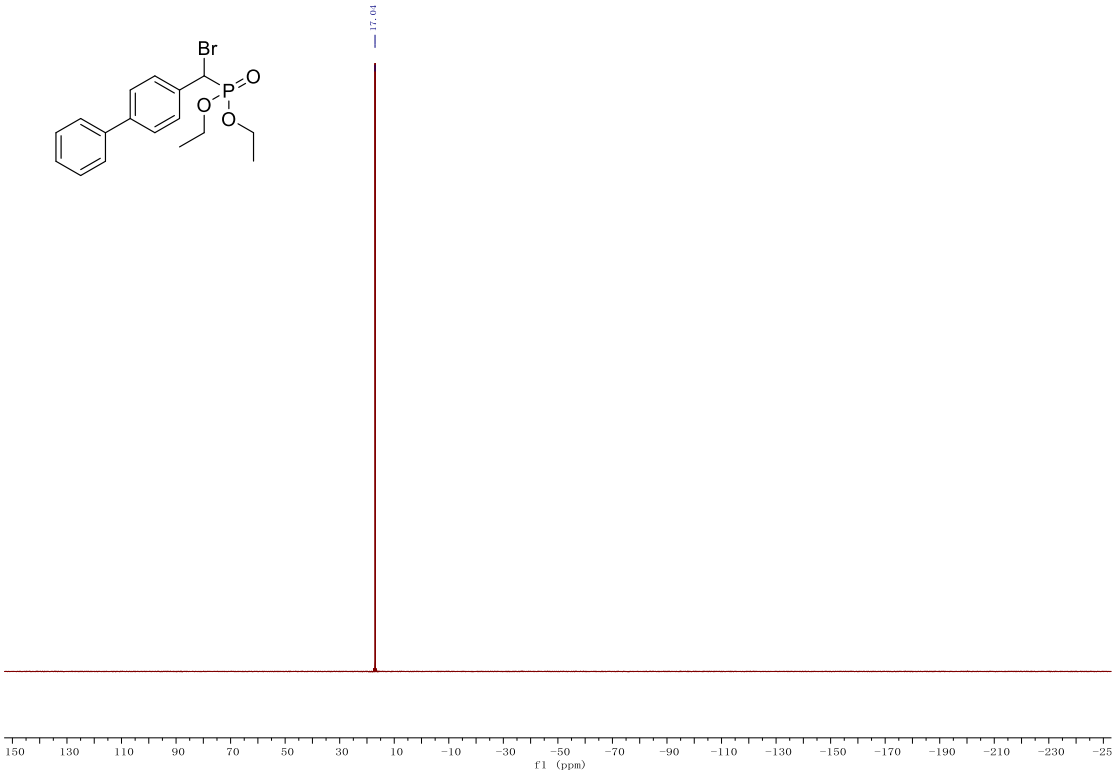

Figure S21. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **1f**

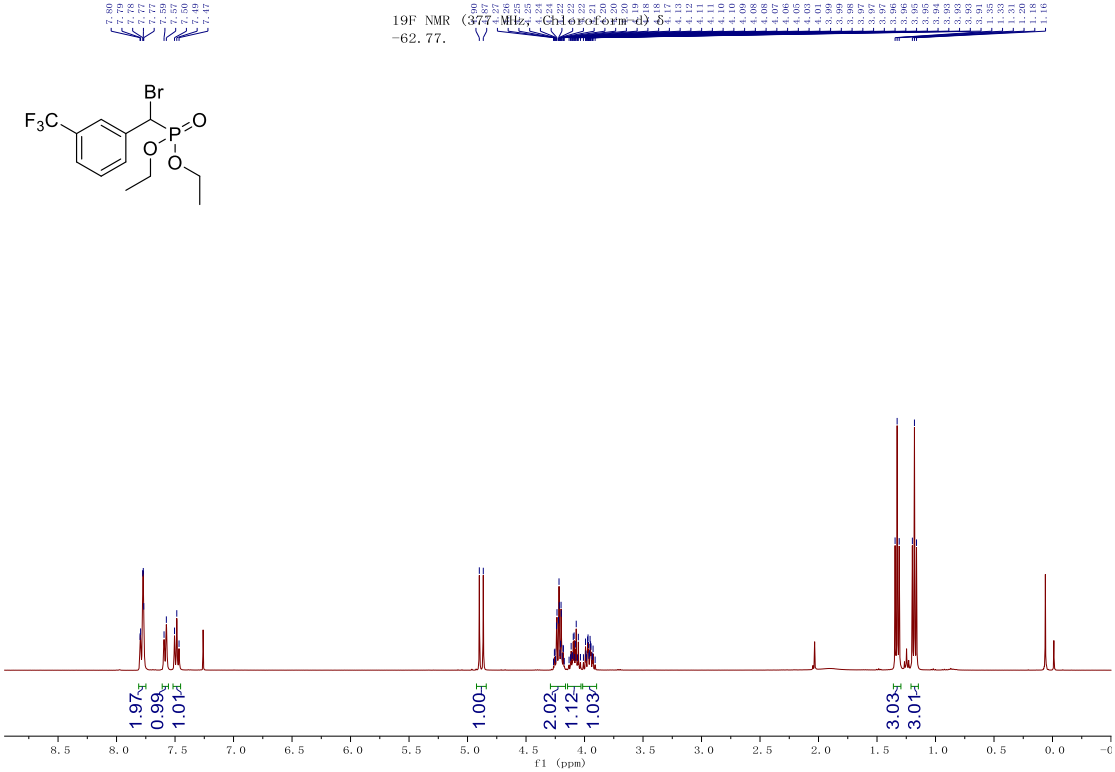

Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i**

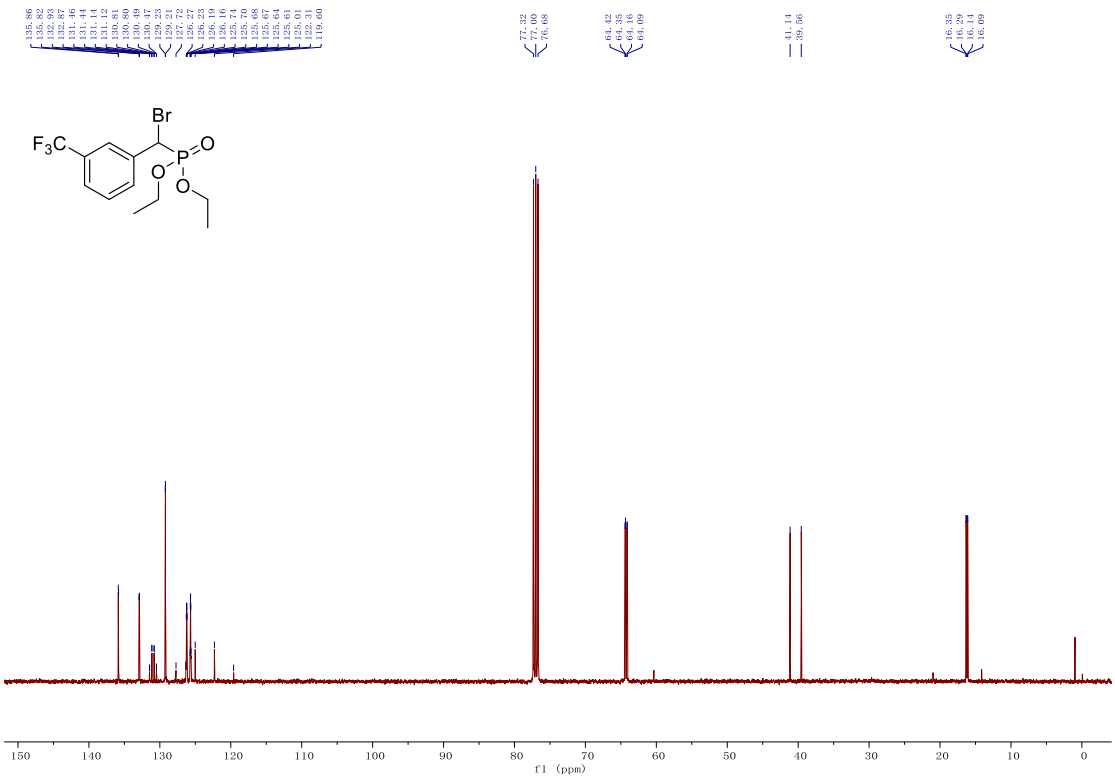

Figure S23. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1i**

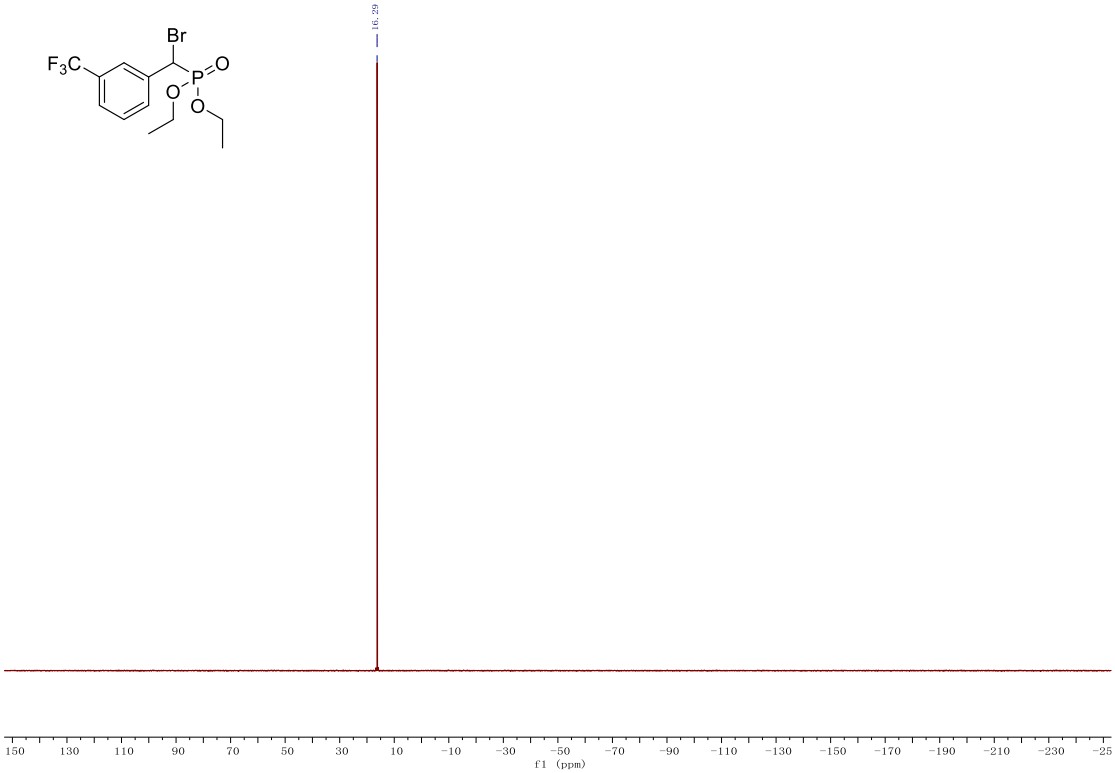

Figure S24. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **1i**

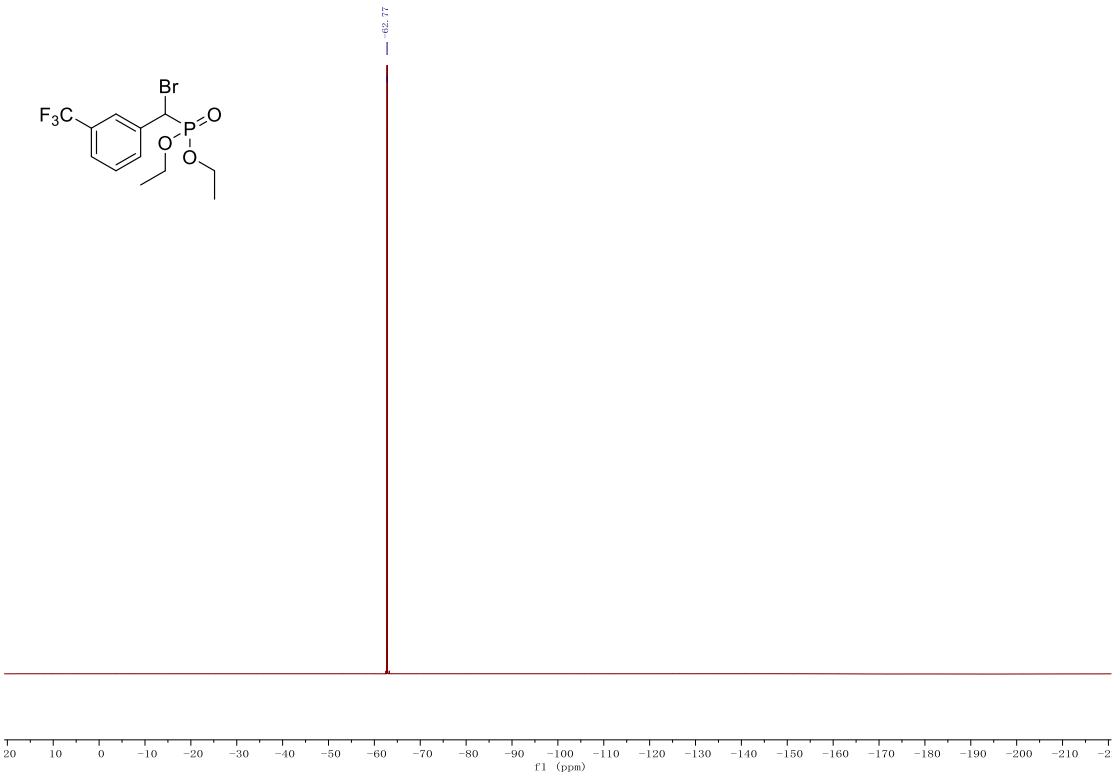

Figure S25. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **1i**

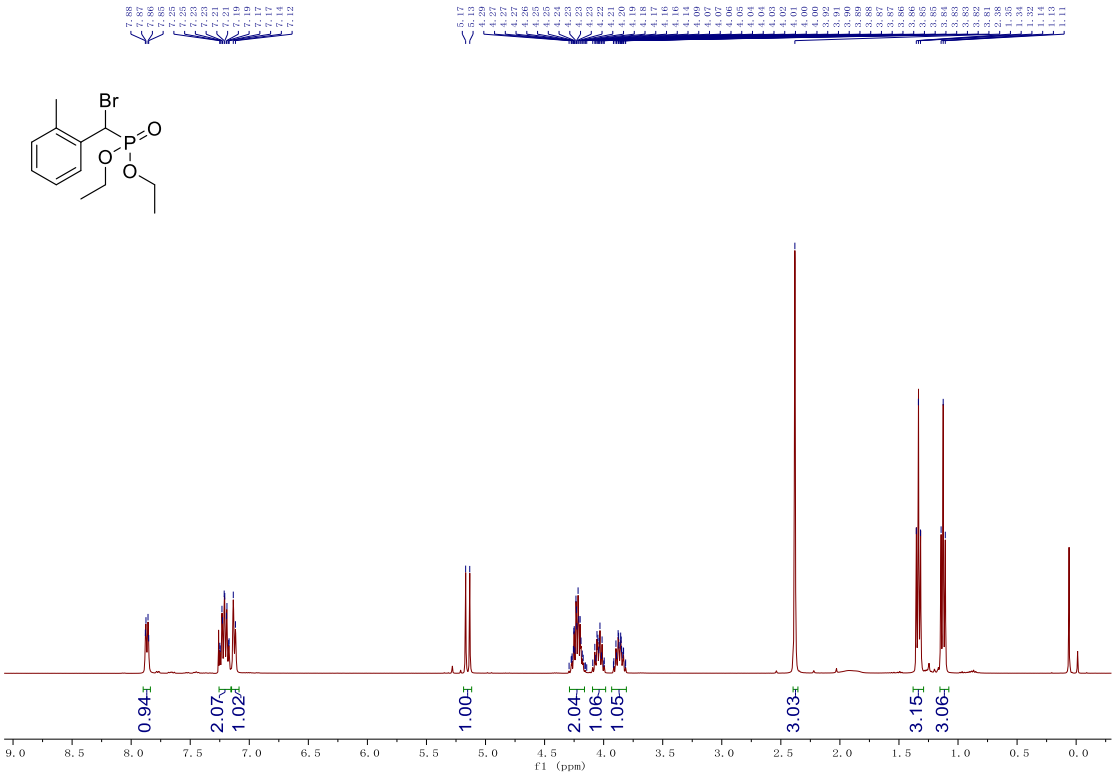

Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1j**

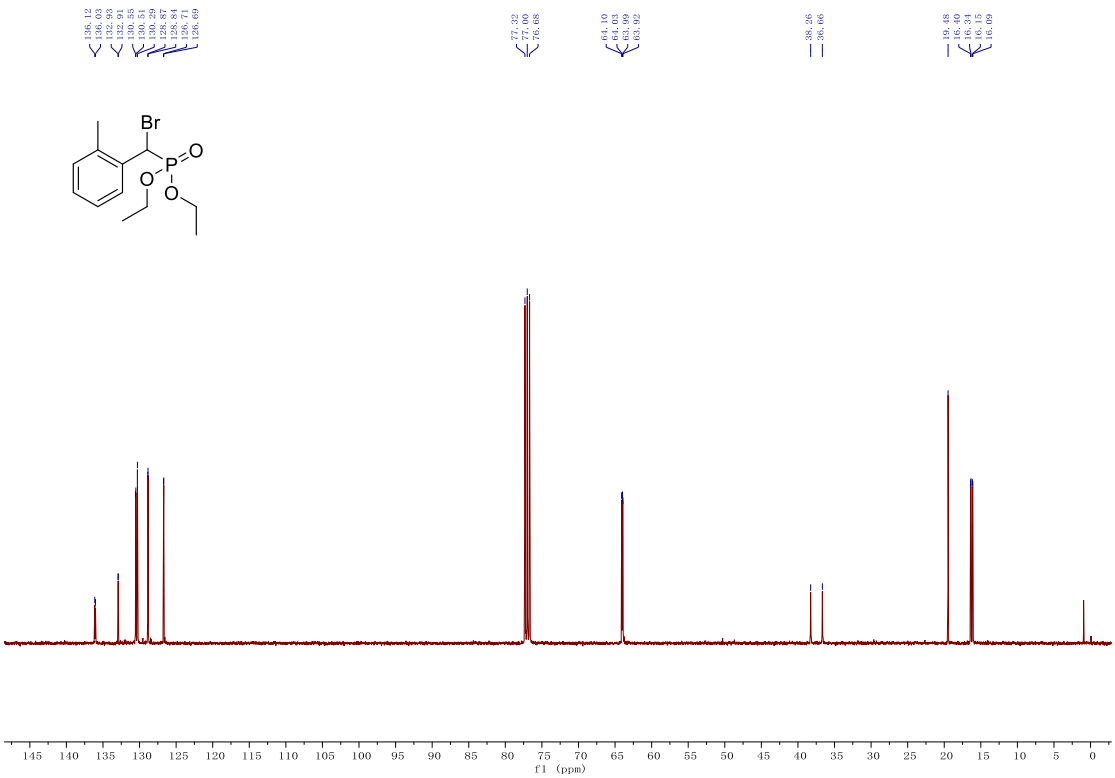

Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1j**

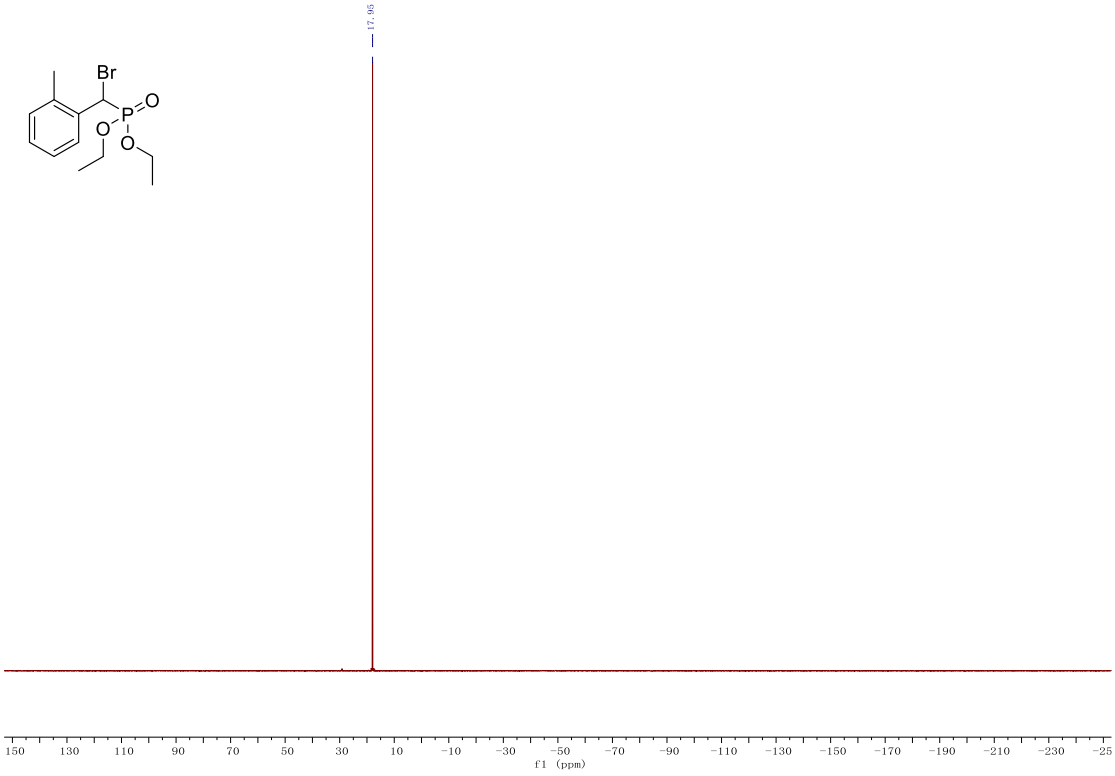

Figure S28. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **1j**

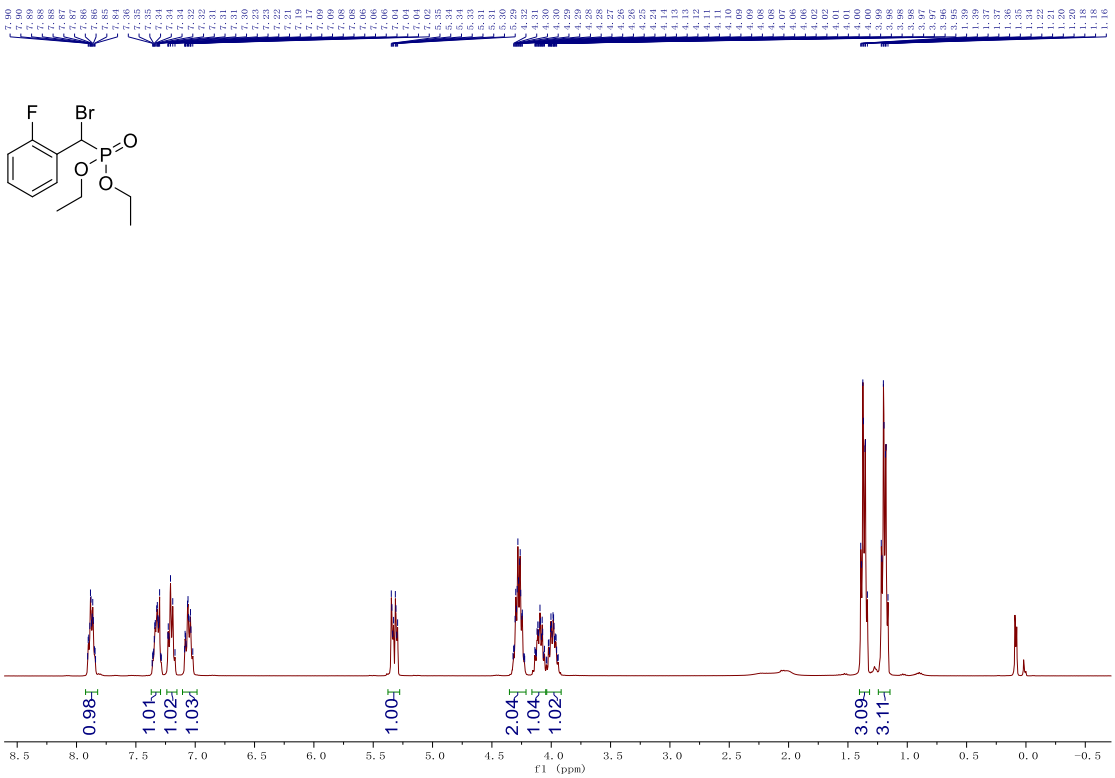

Figure S29. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **1k**

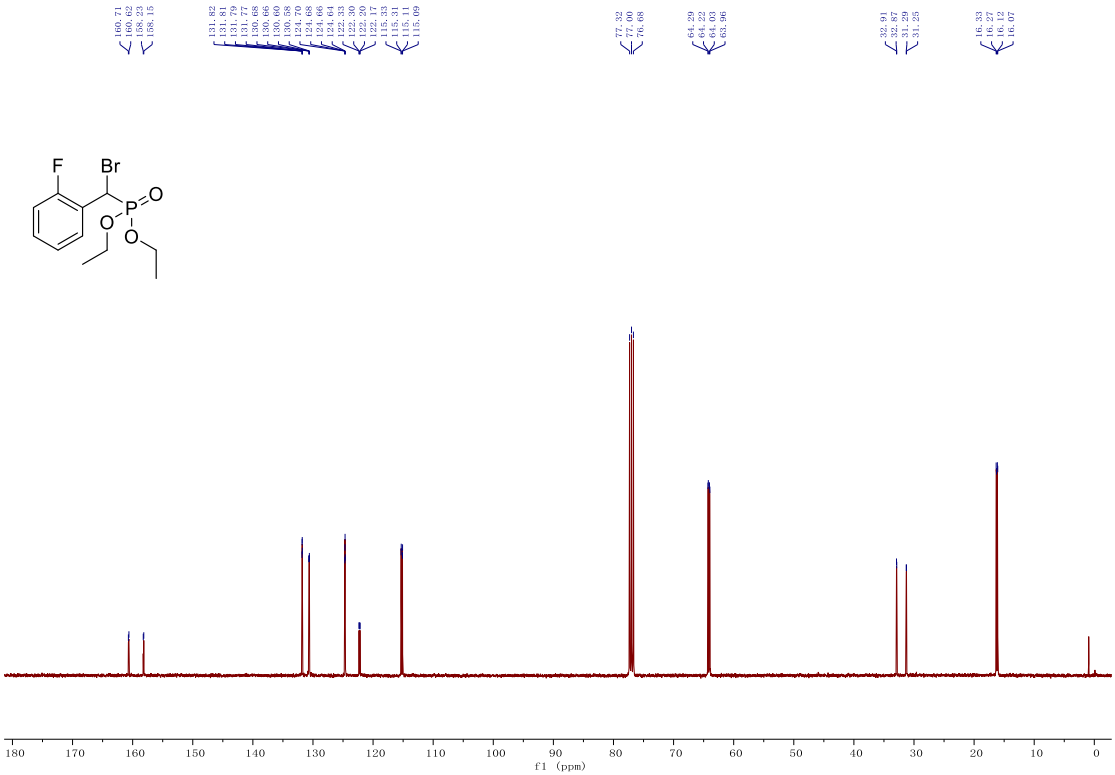

Figure S30. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **1k**

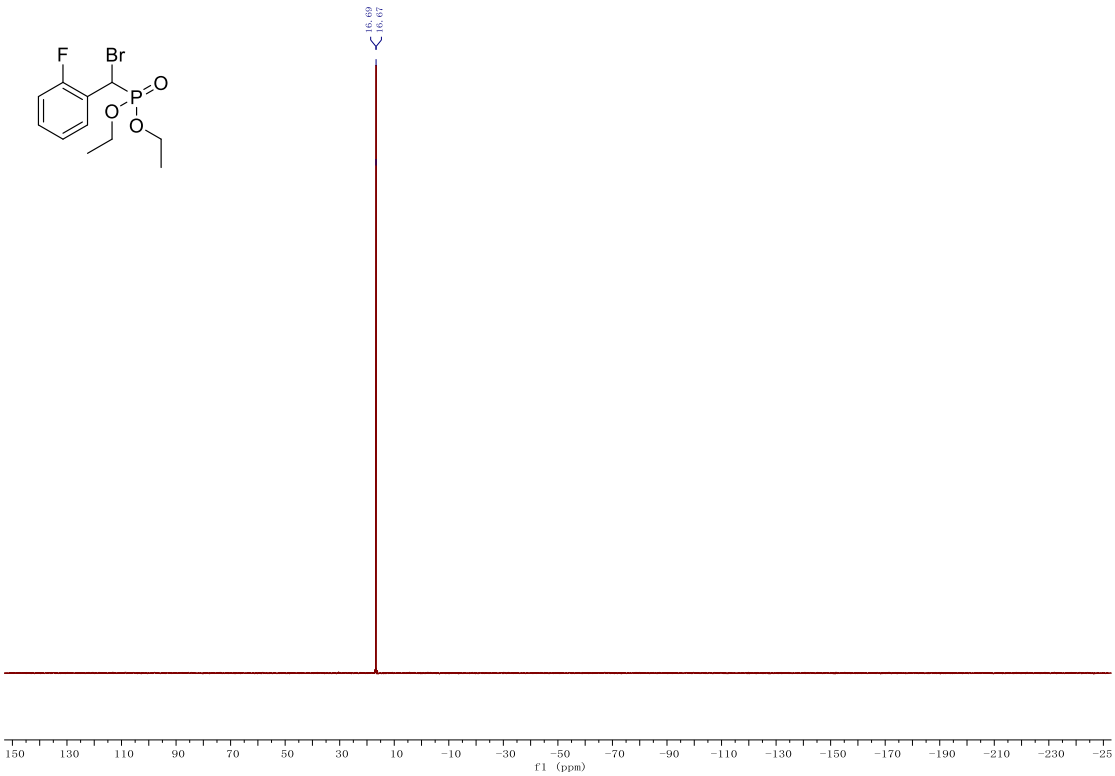

Figure S31. ^{31}**P NMR (162 MHz, CDCl$_3$)**.spectrum of **1k**

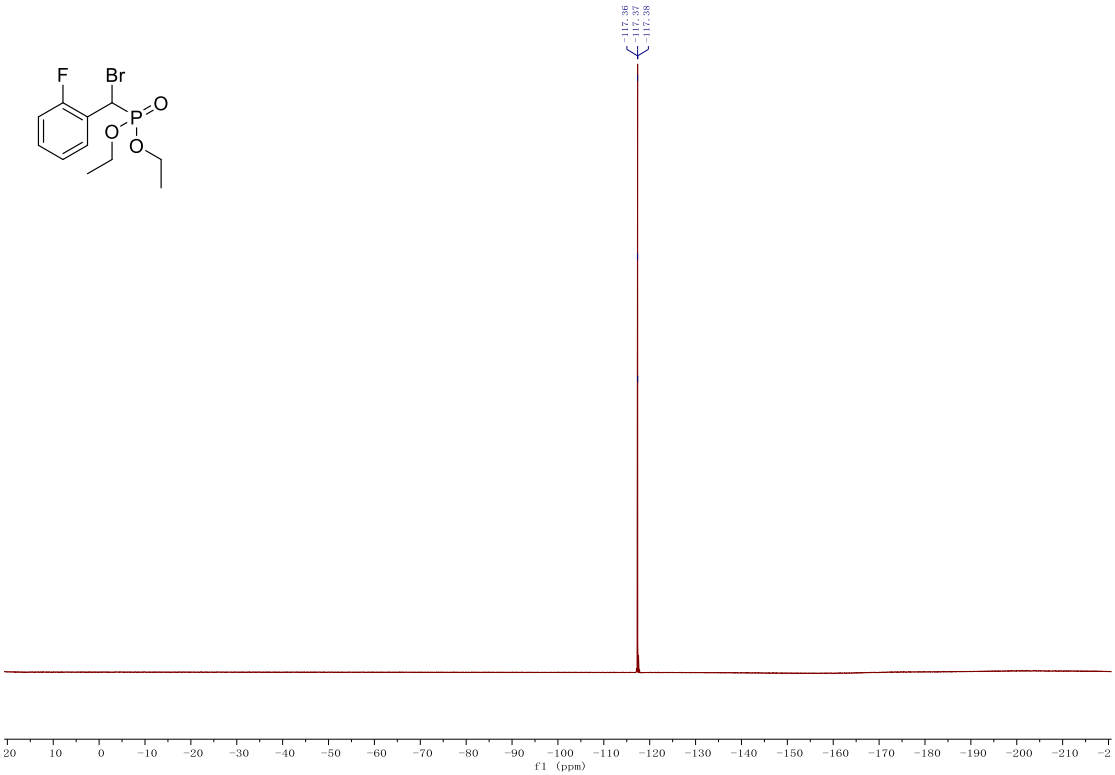

Figure S32. ^{19}**F NMR** (377 MHz, $CDCl_3$) spectrum of **1k**

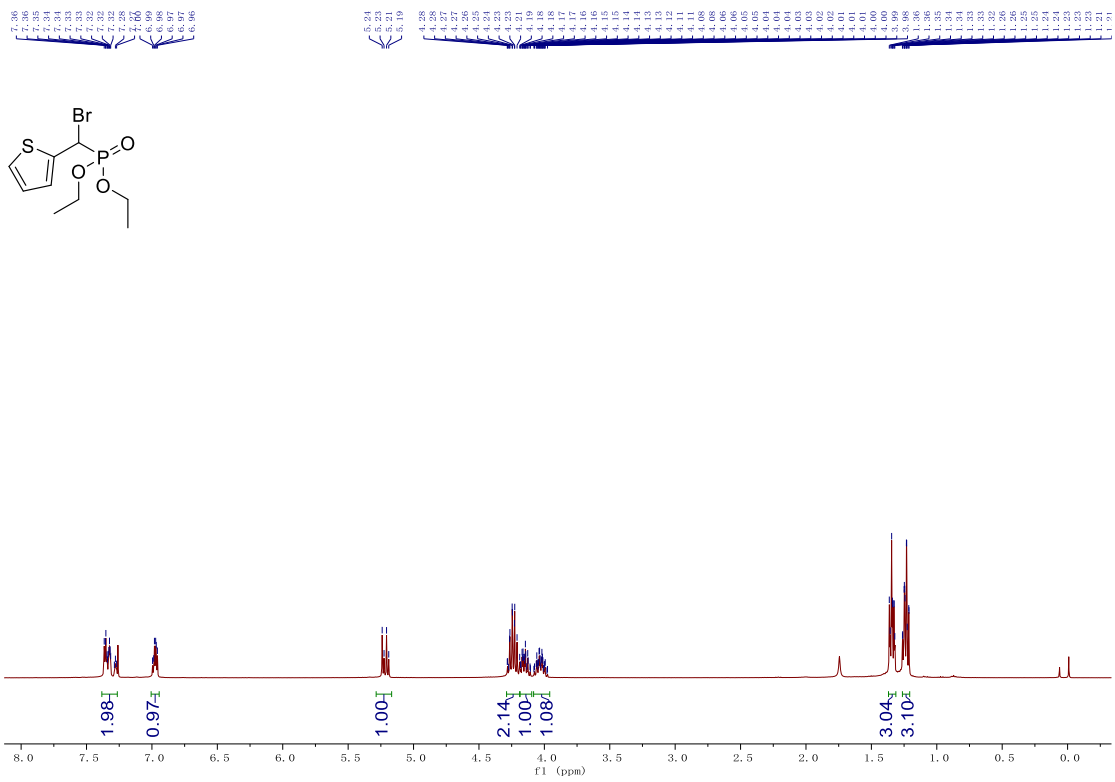

Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1m**

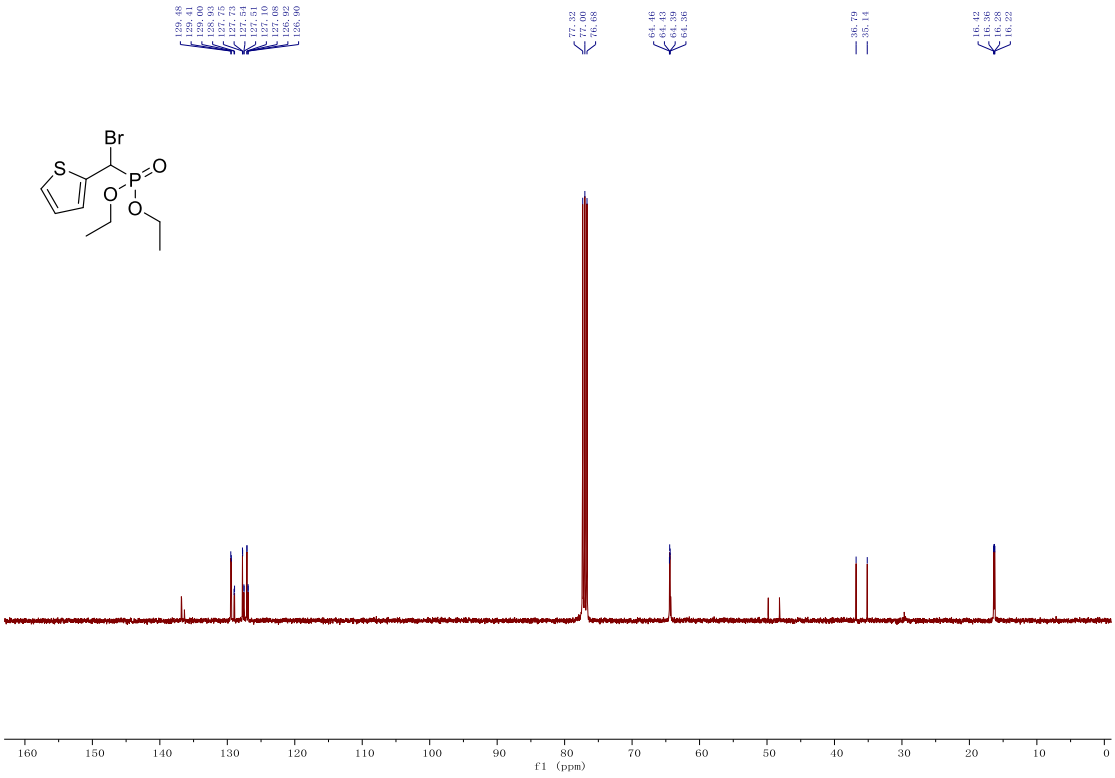

Figure S34 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1m**

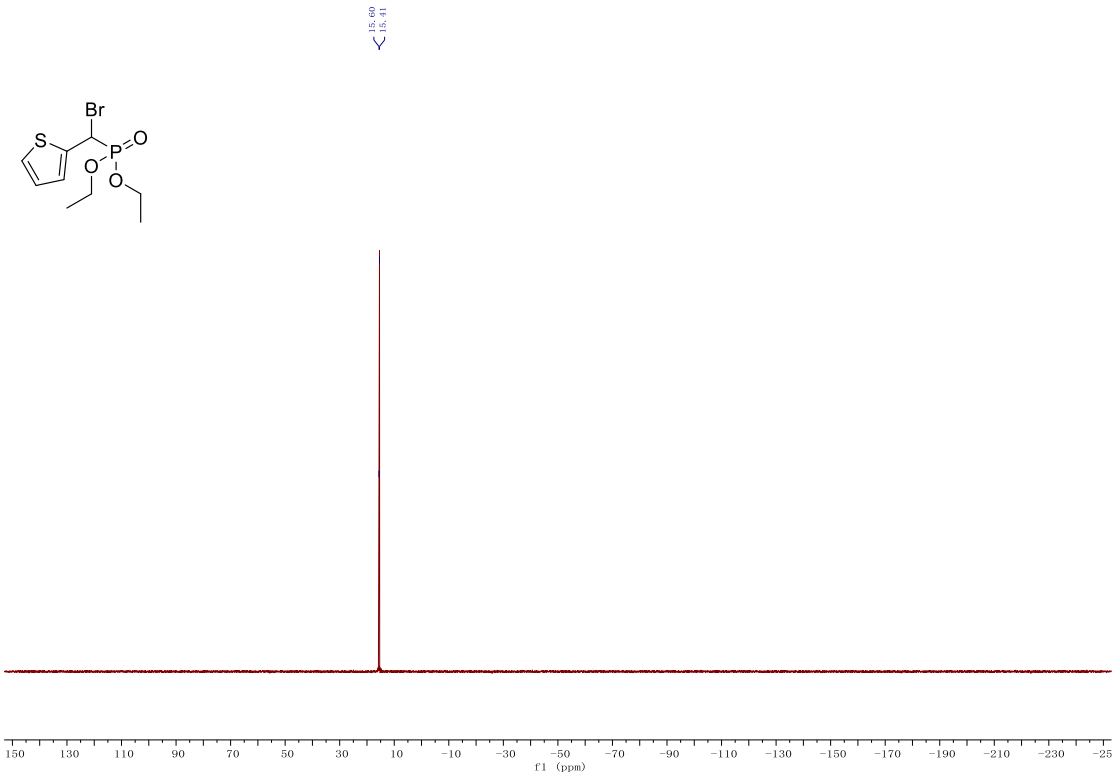

Figure S35. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **1m**

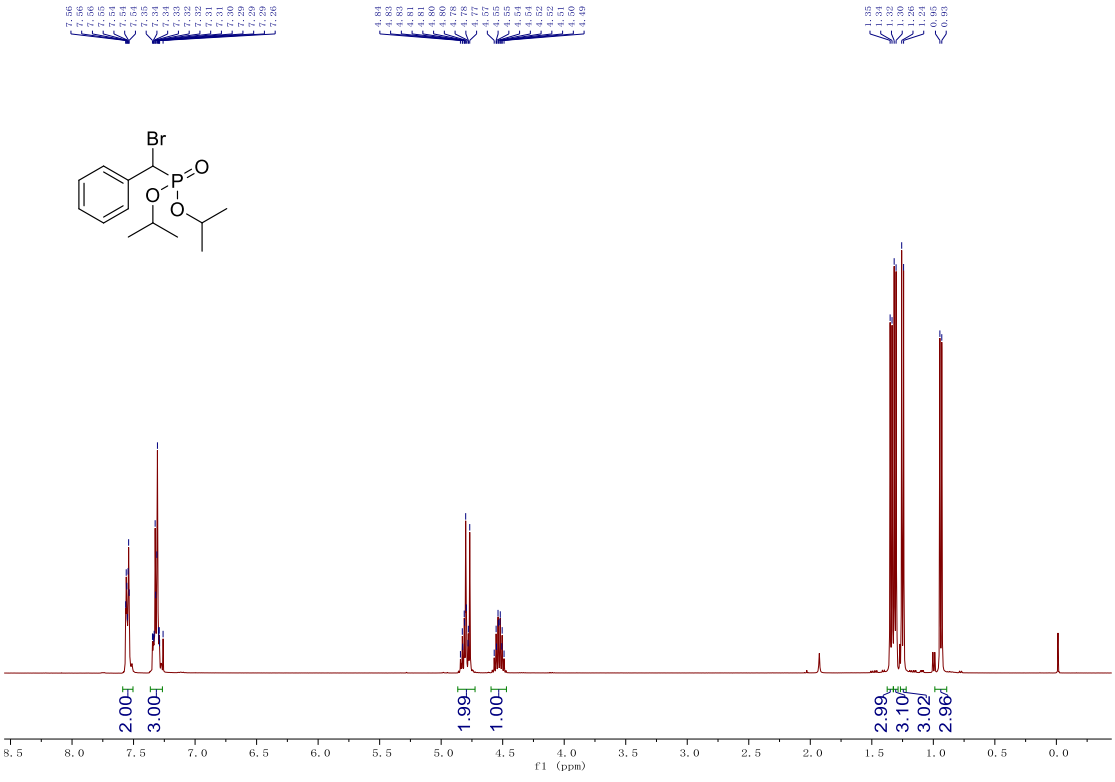

Figure S36. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **1n**

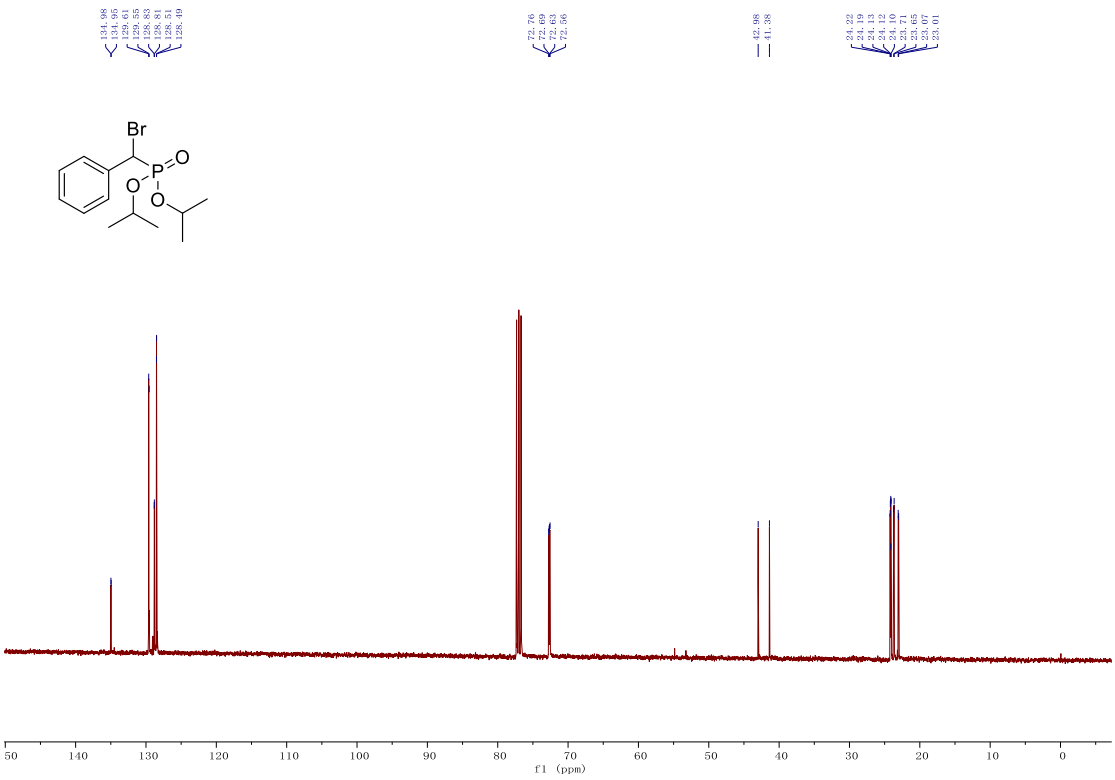

Figure S37. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1n**

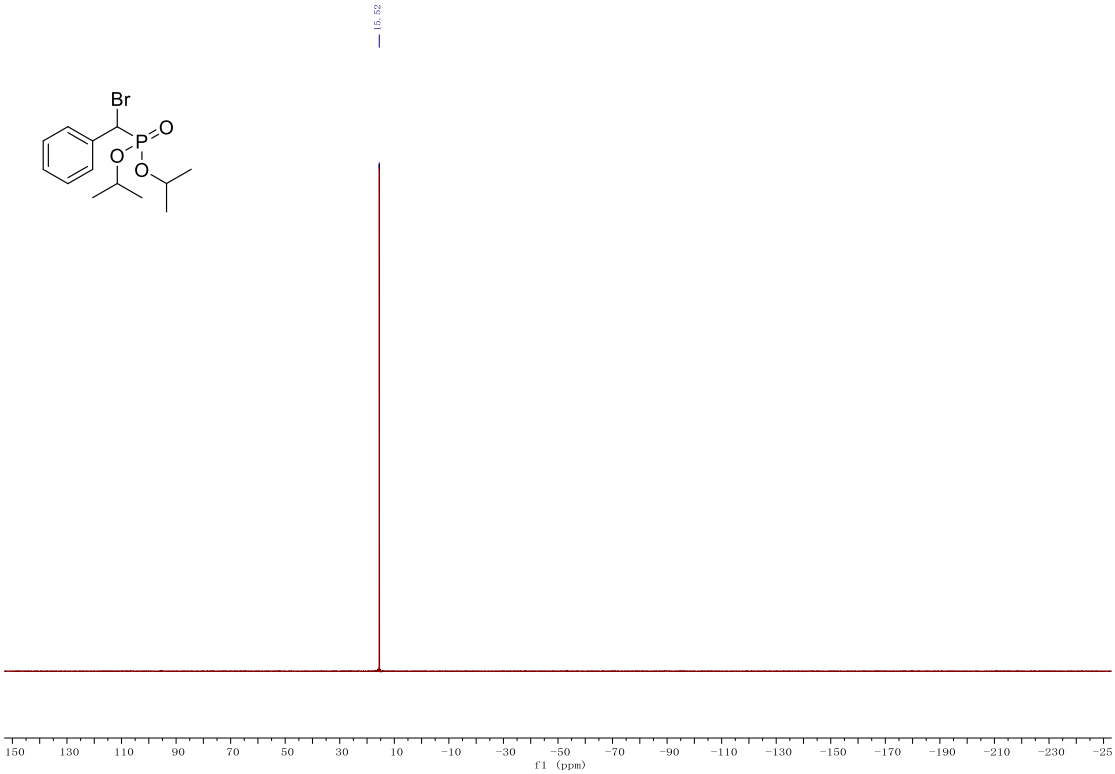

Figure S38. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **1n**

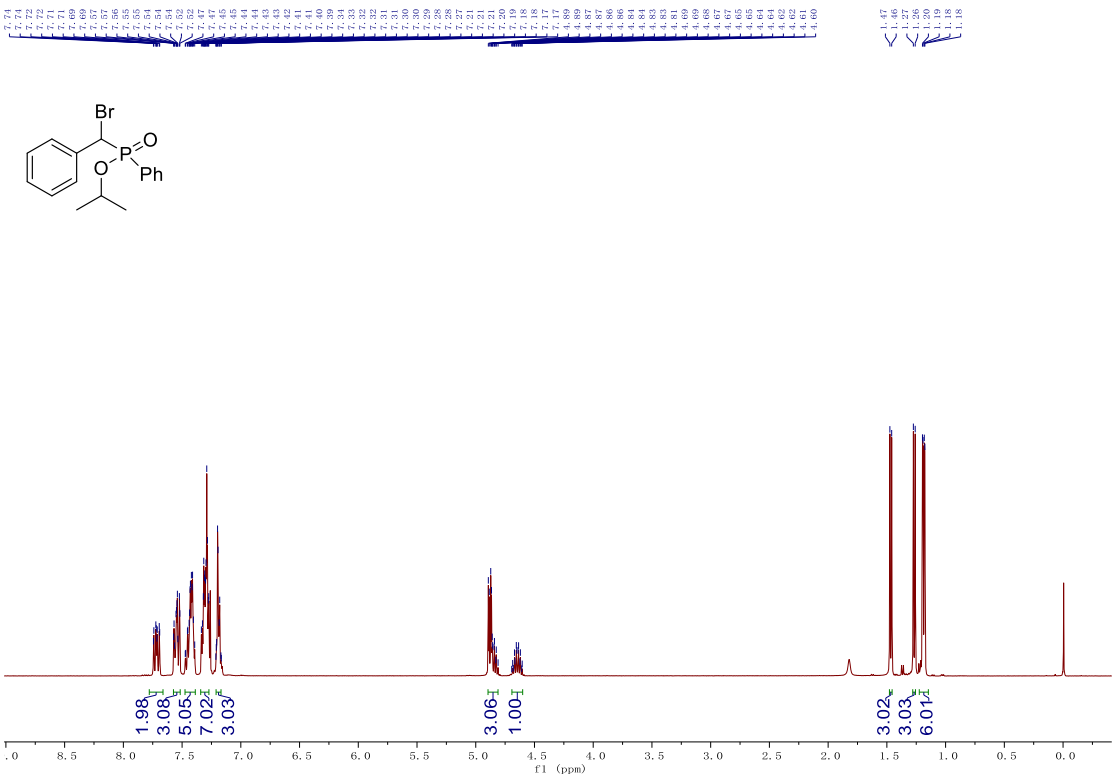

Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1o**

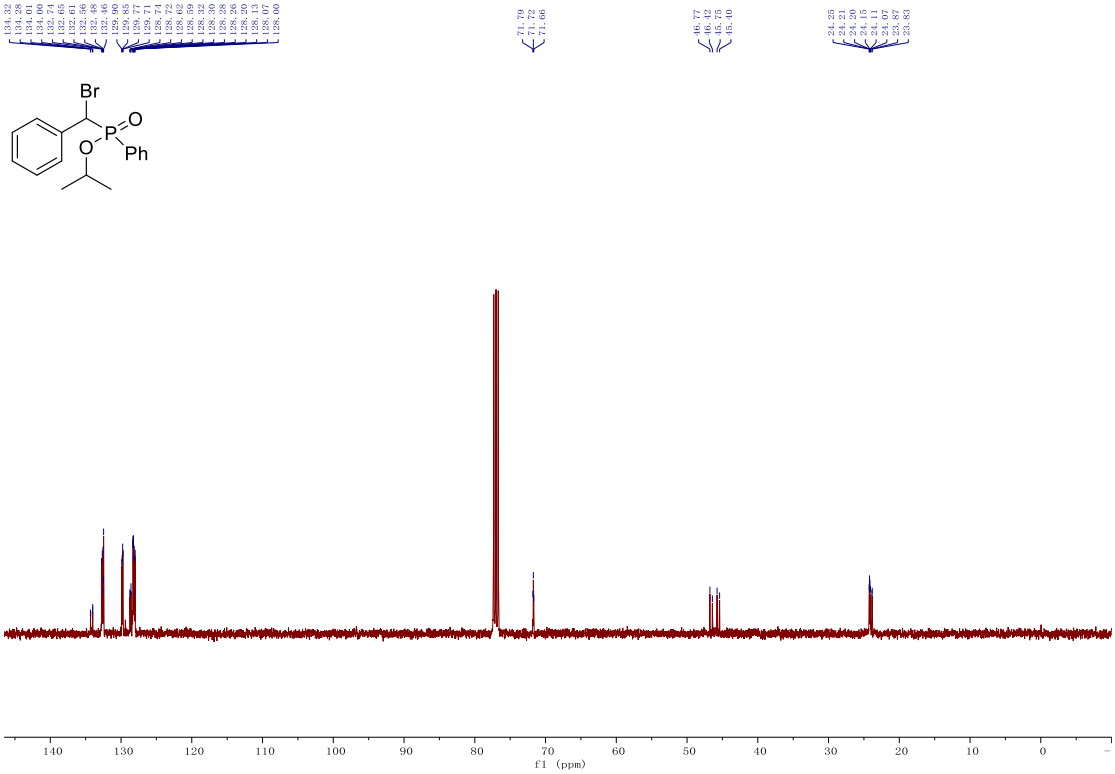

Figure S40. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1o**

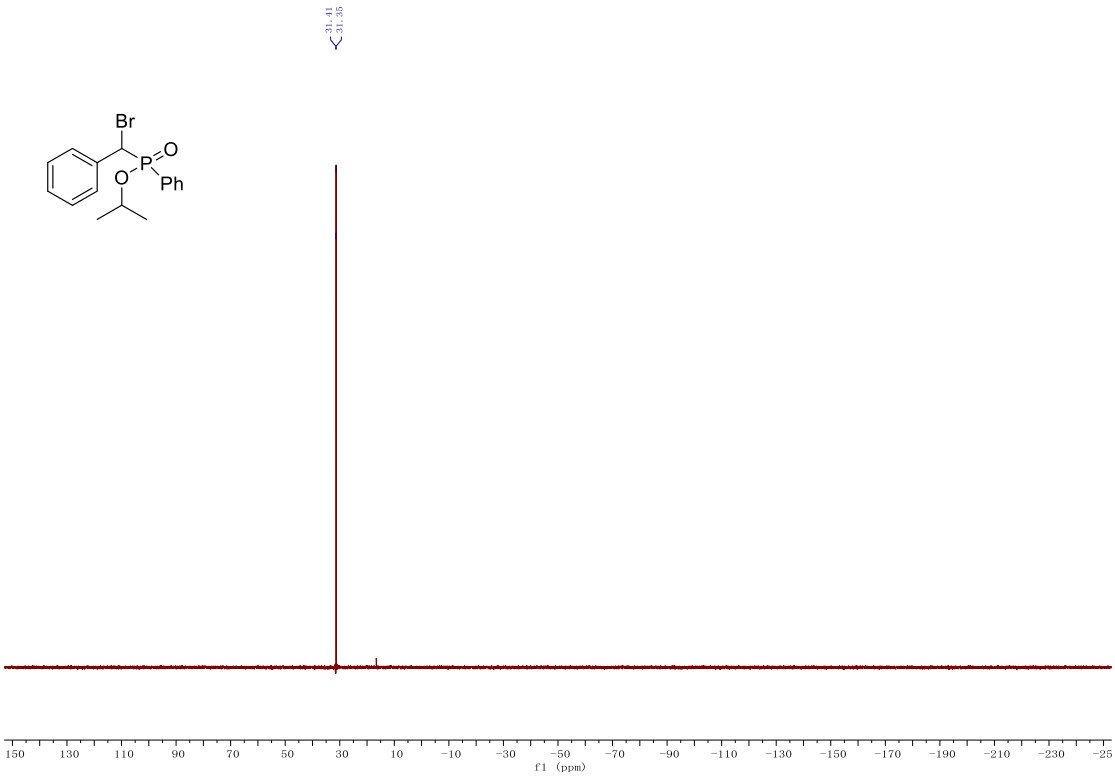

Figure S41. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **1o**

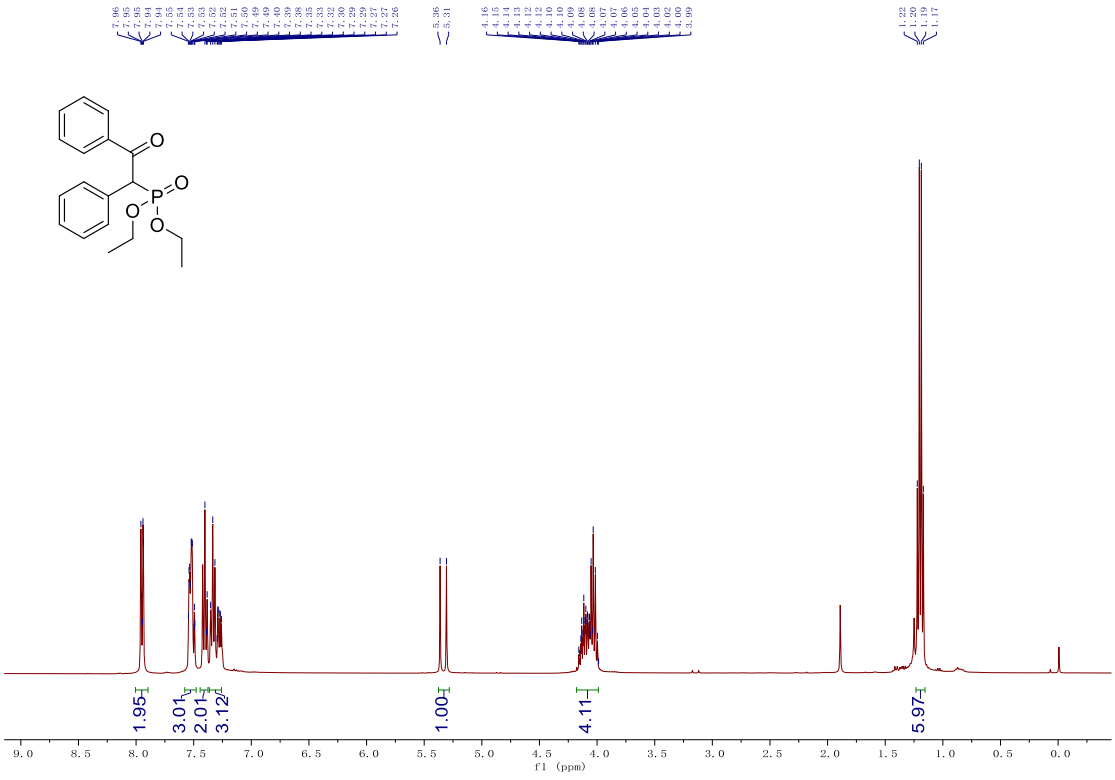

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**

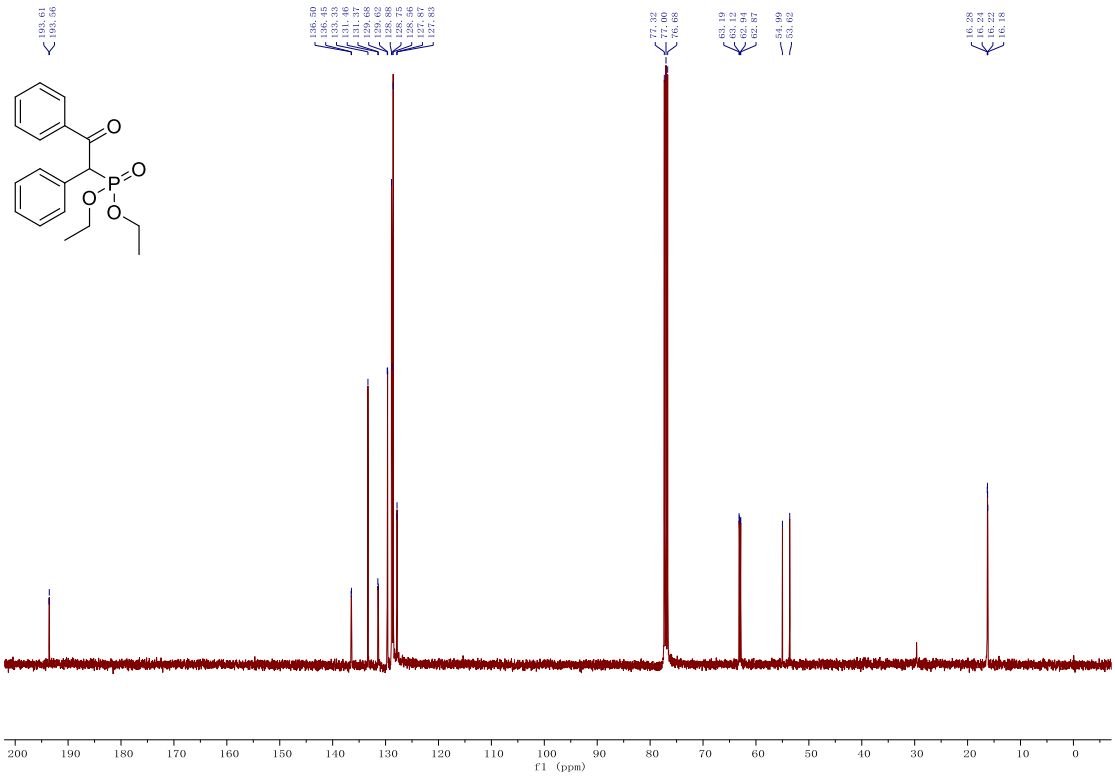

Figure S43. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3a**

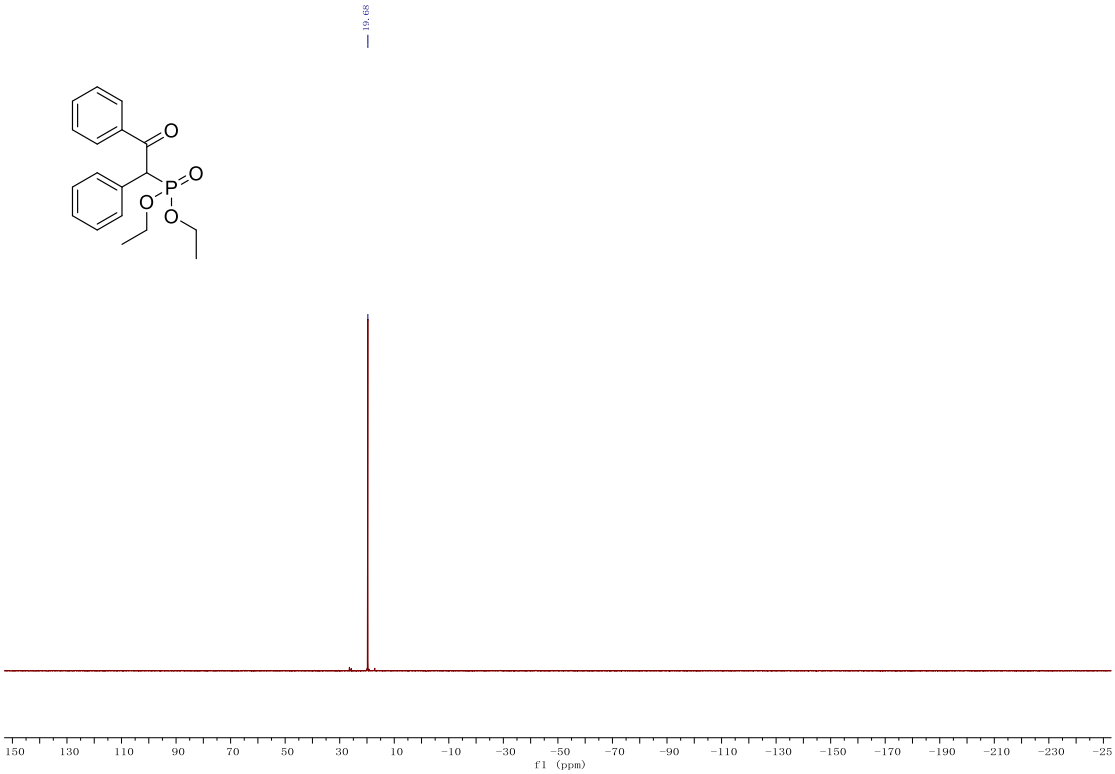

Figure S44. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3a**

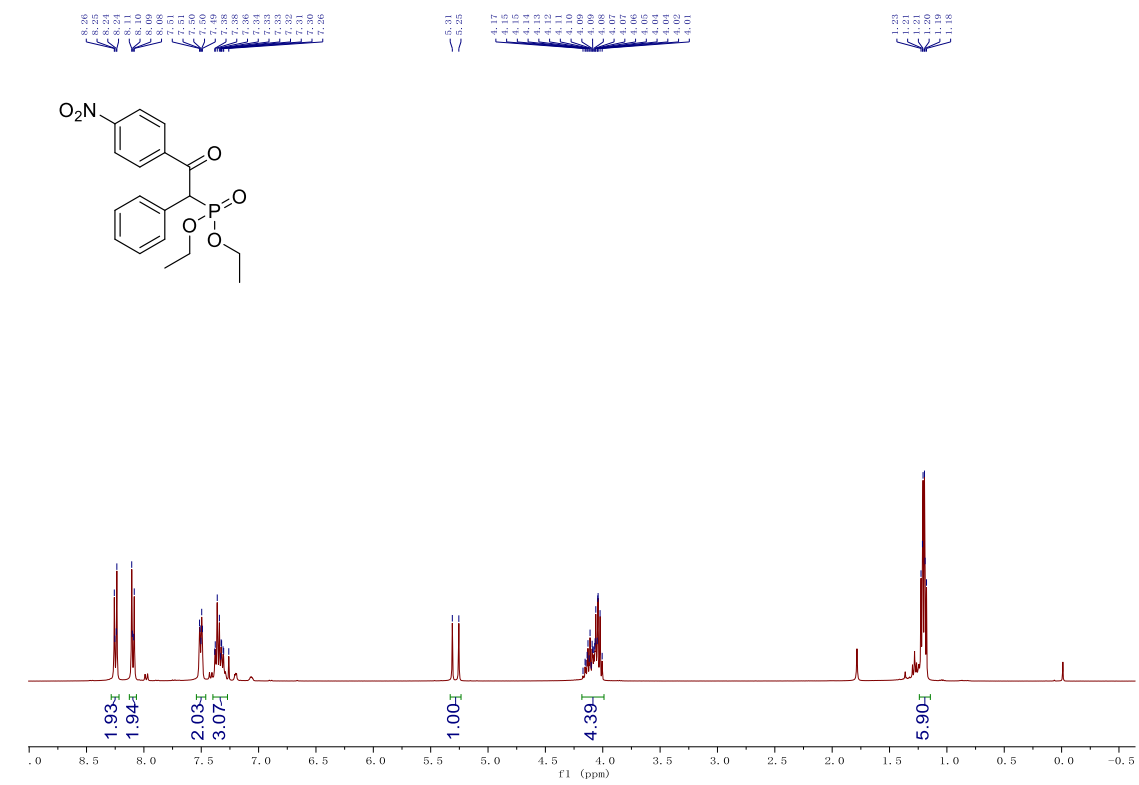

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**

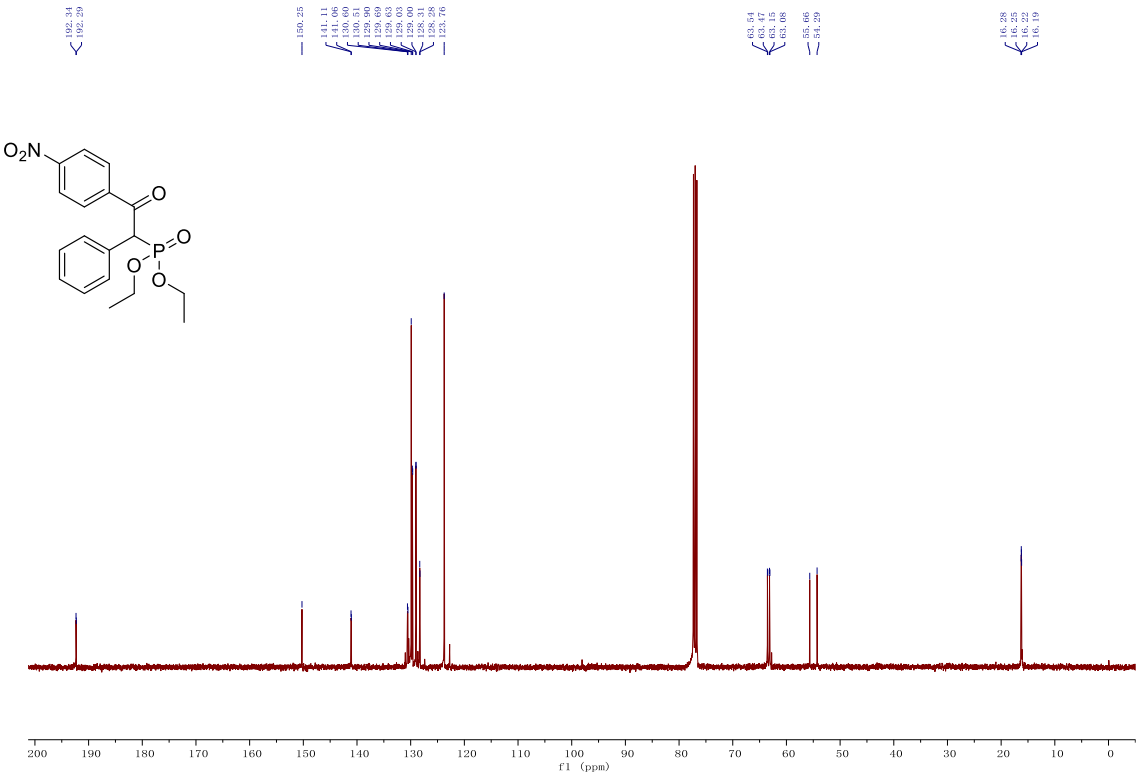

Figure S46. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3b**

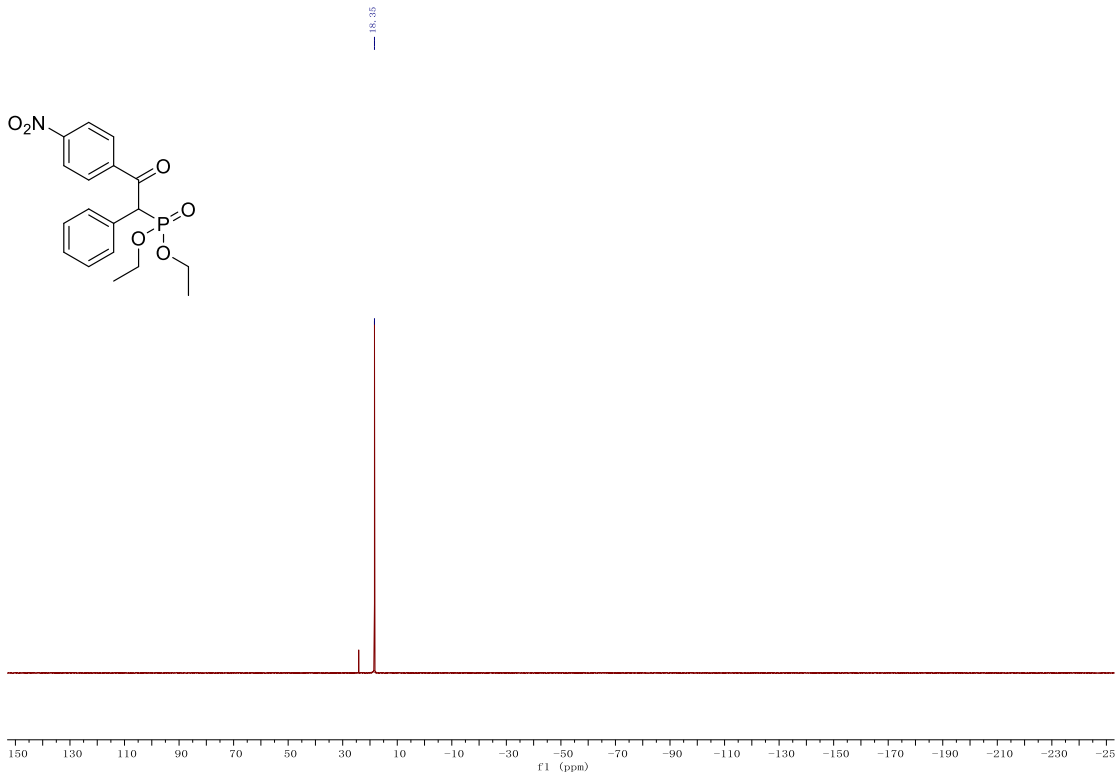

Figure S47. ^{31}**P NMR (162 MHz, CDCl$_3$)**.spectrum of **3b**

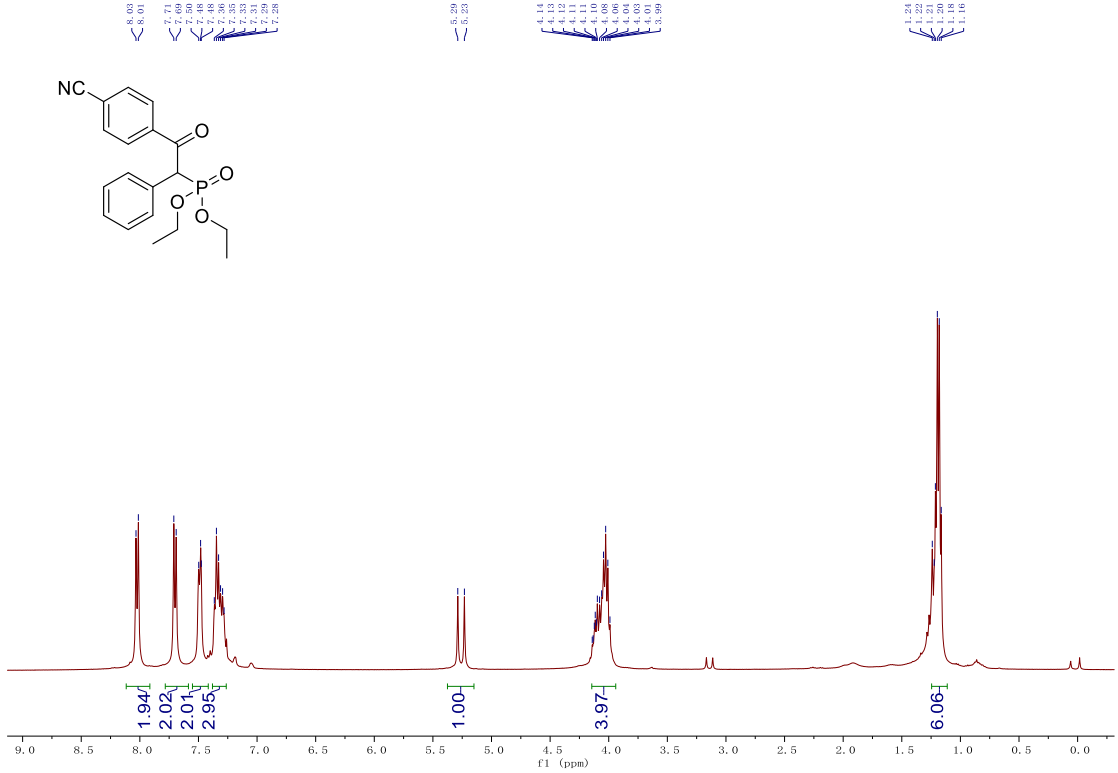

Figure S48. ^{1}**H NMR** (400 MHz, CDCl$_3$) spectrum of **3c**

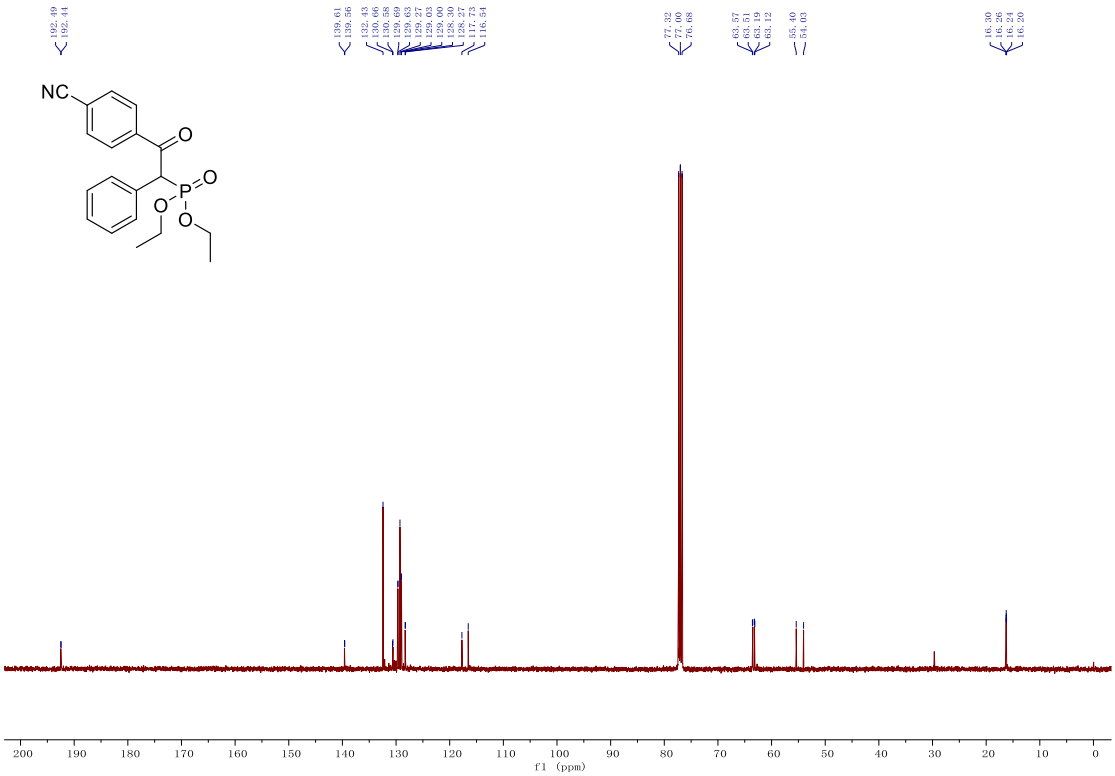

Figure S49. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3c**

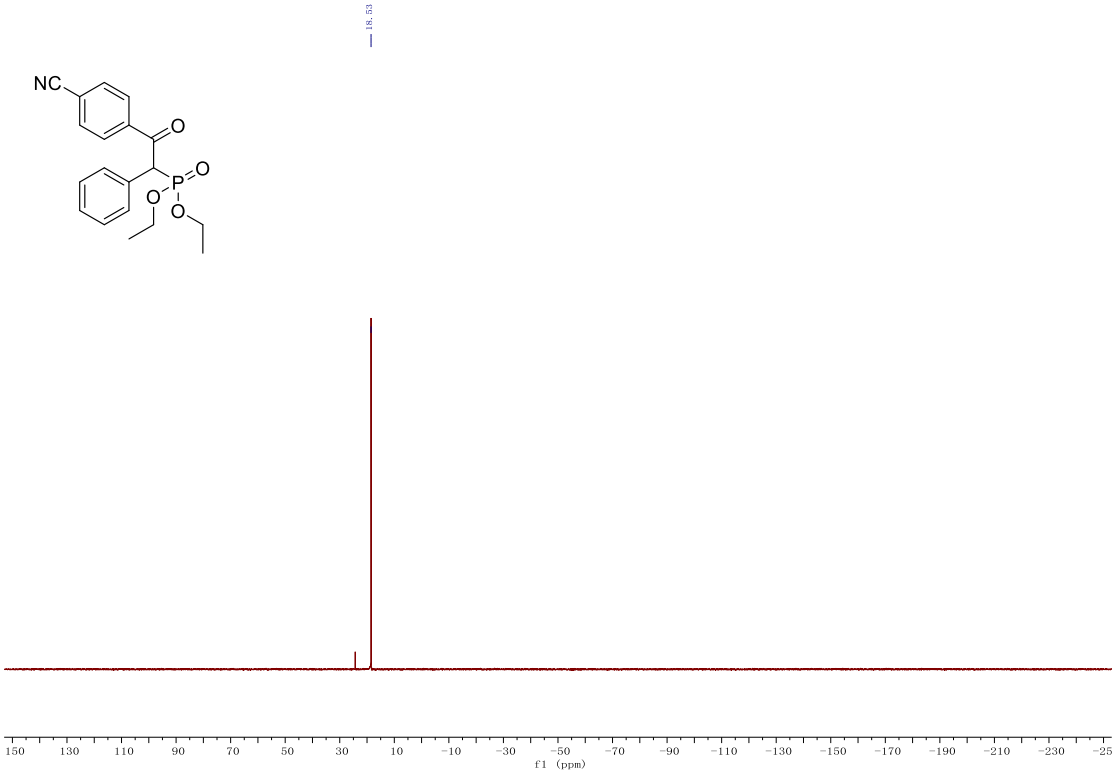

Figure S50. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **3c**

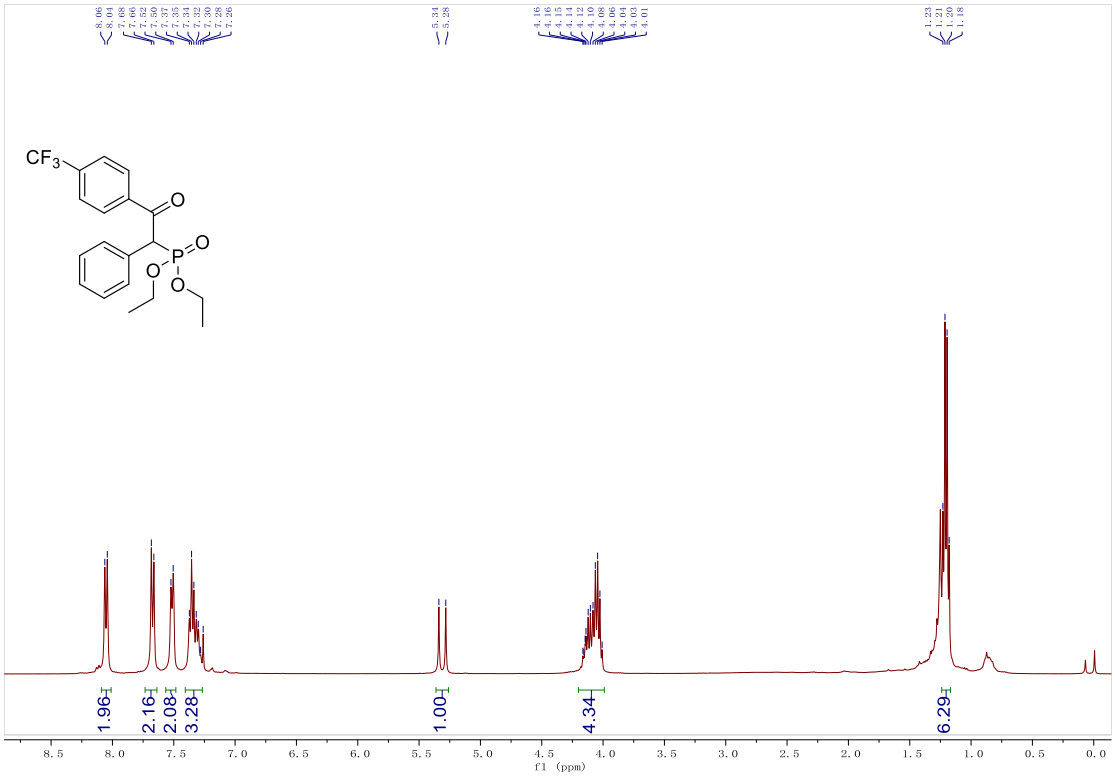

Figure S51. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3d**

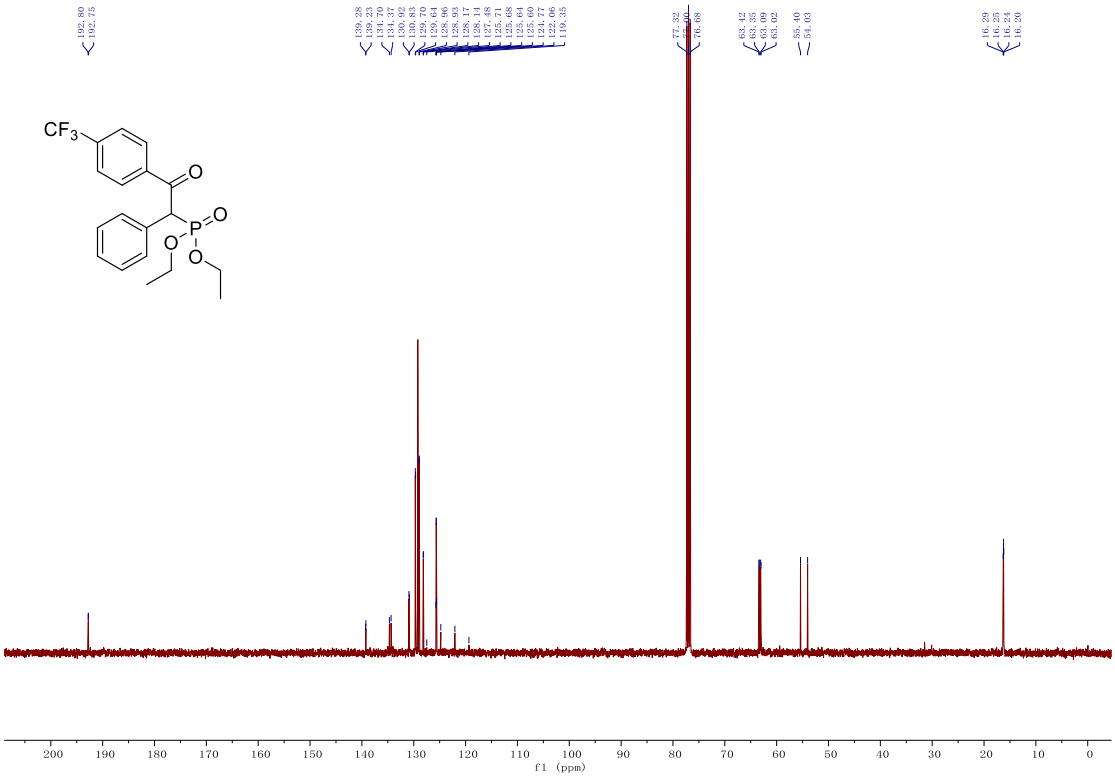

Figure S52. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3d**

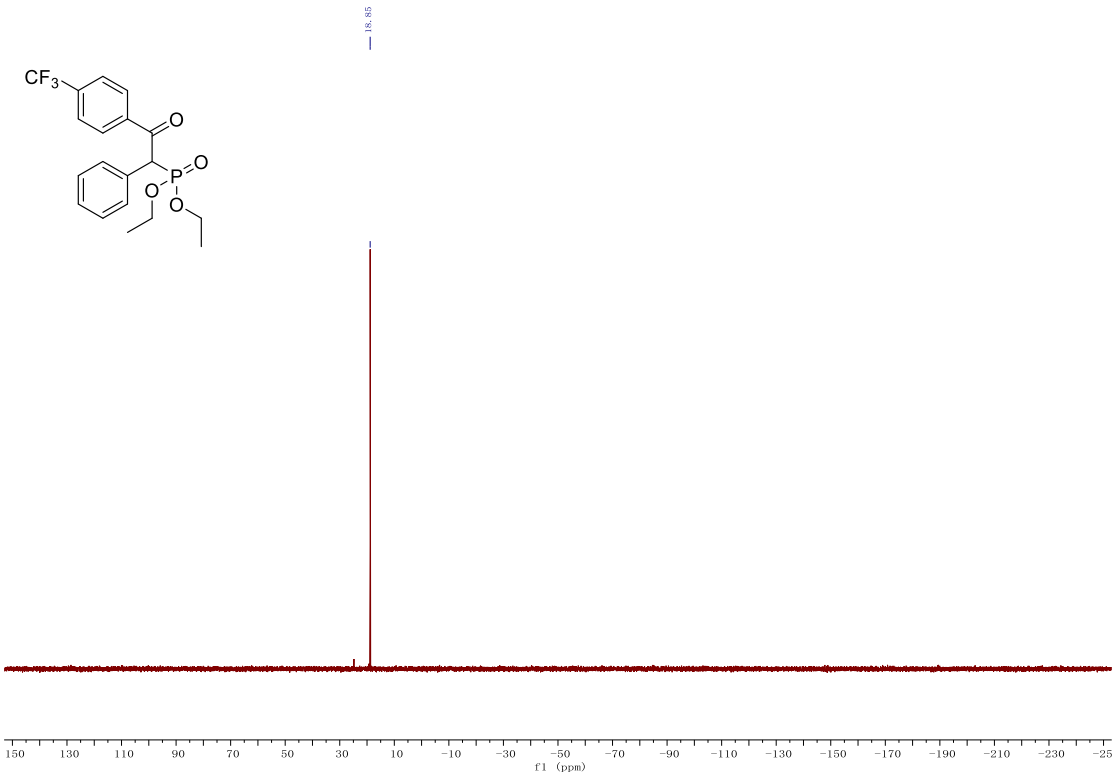

Figure S53. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3d**

Figure S54. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3d**

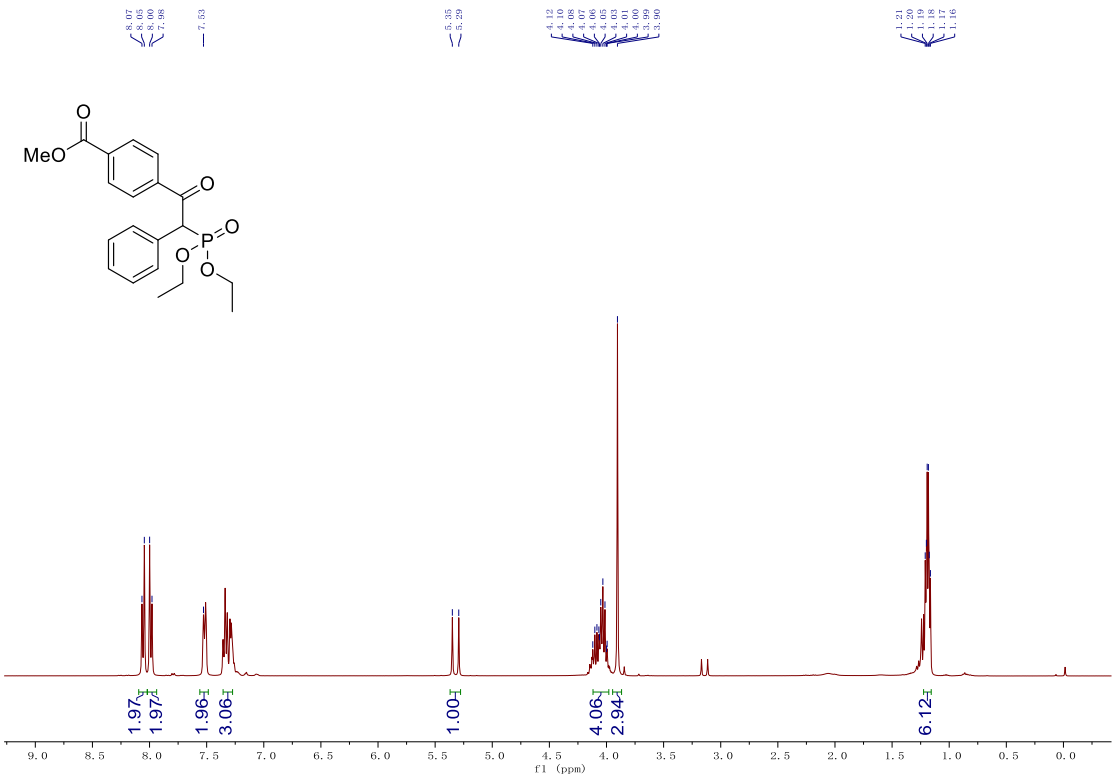

Figure S55. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3e**

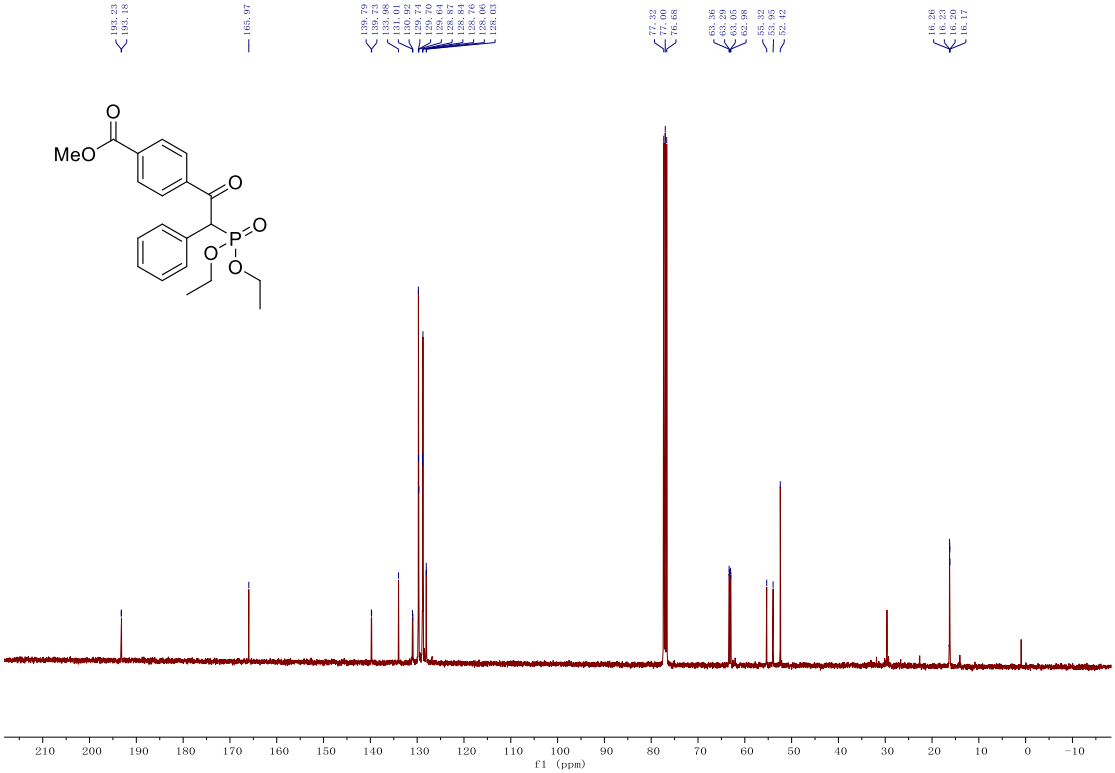

Figure S56. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3e**

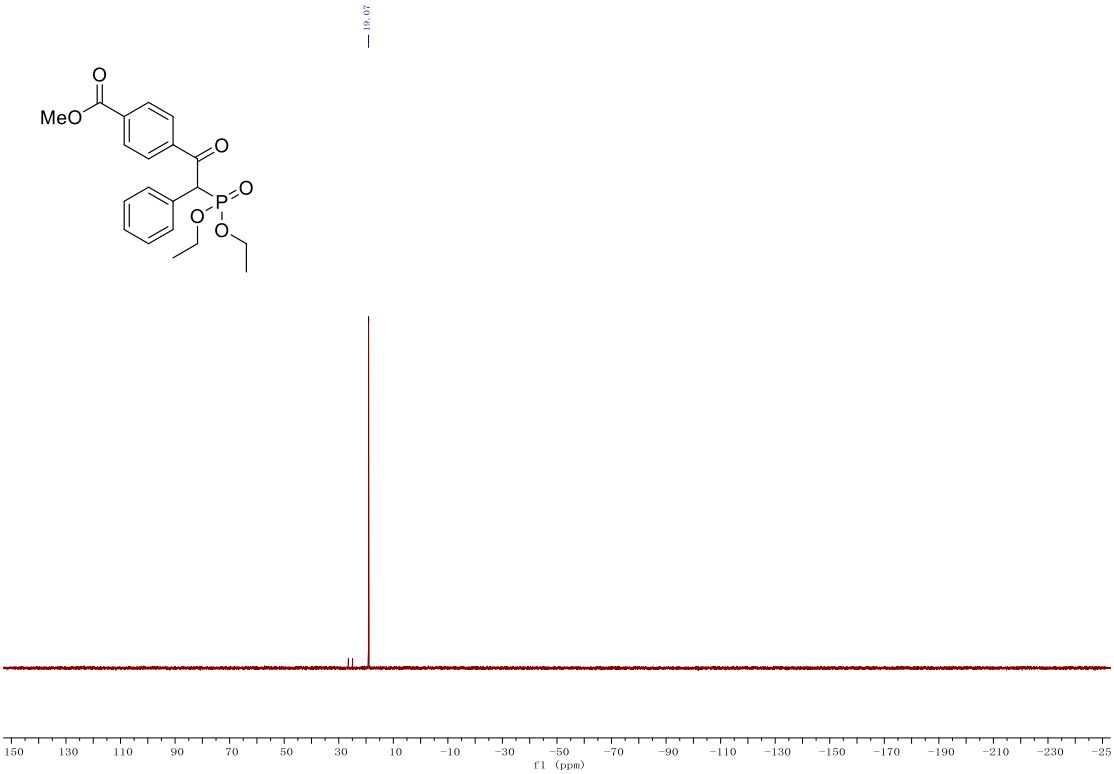

Figure S57. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3e**

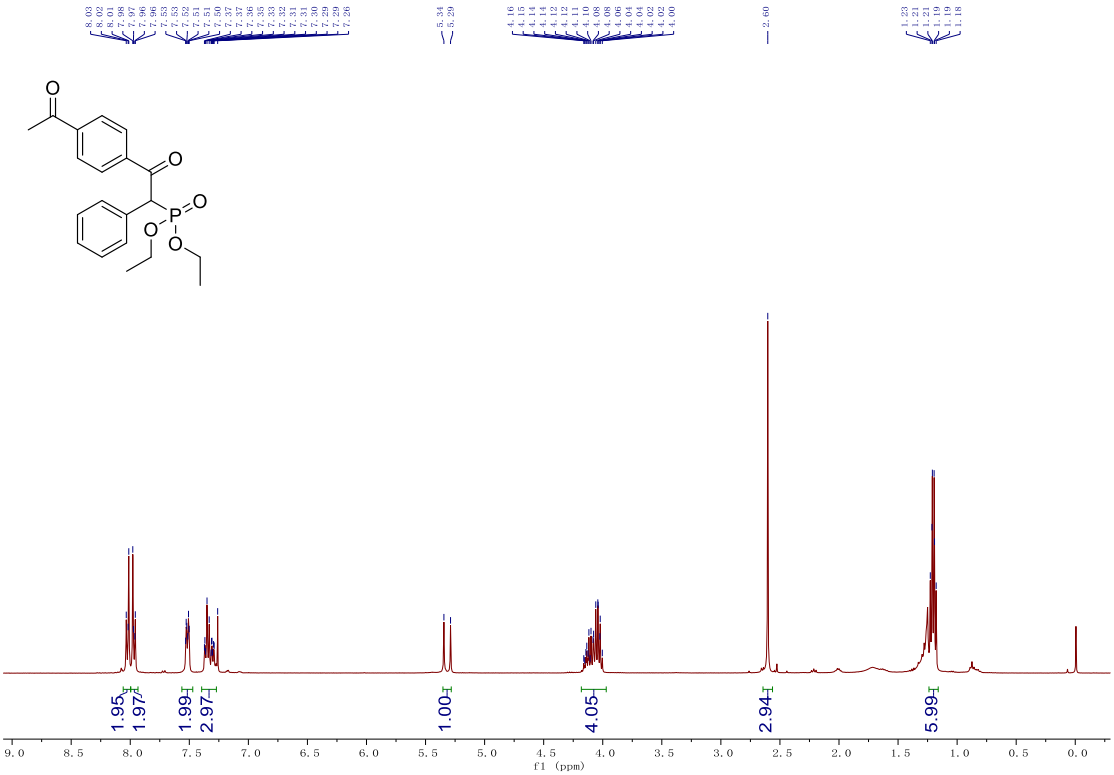

Figure S58. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3f**

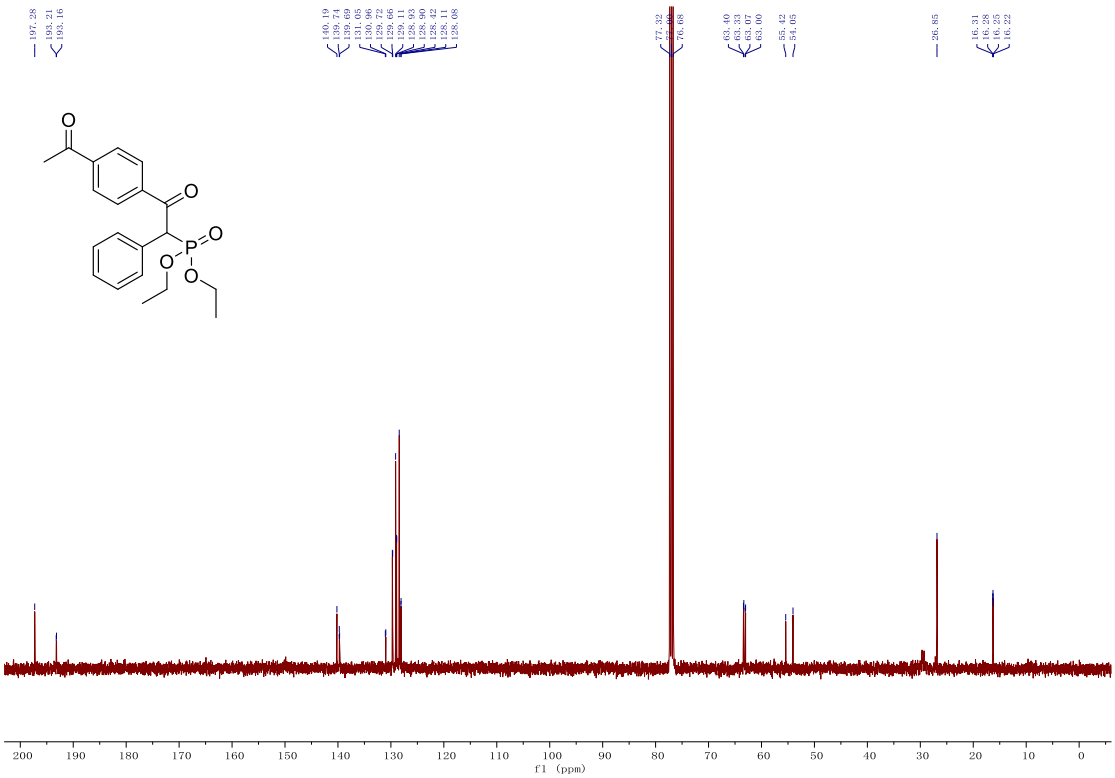

Figure S59. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3f**

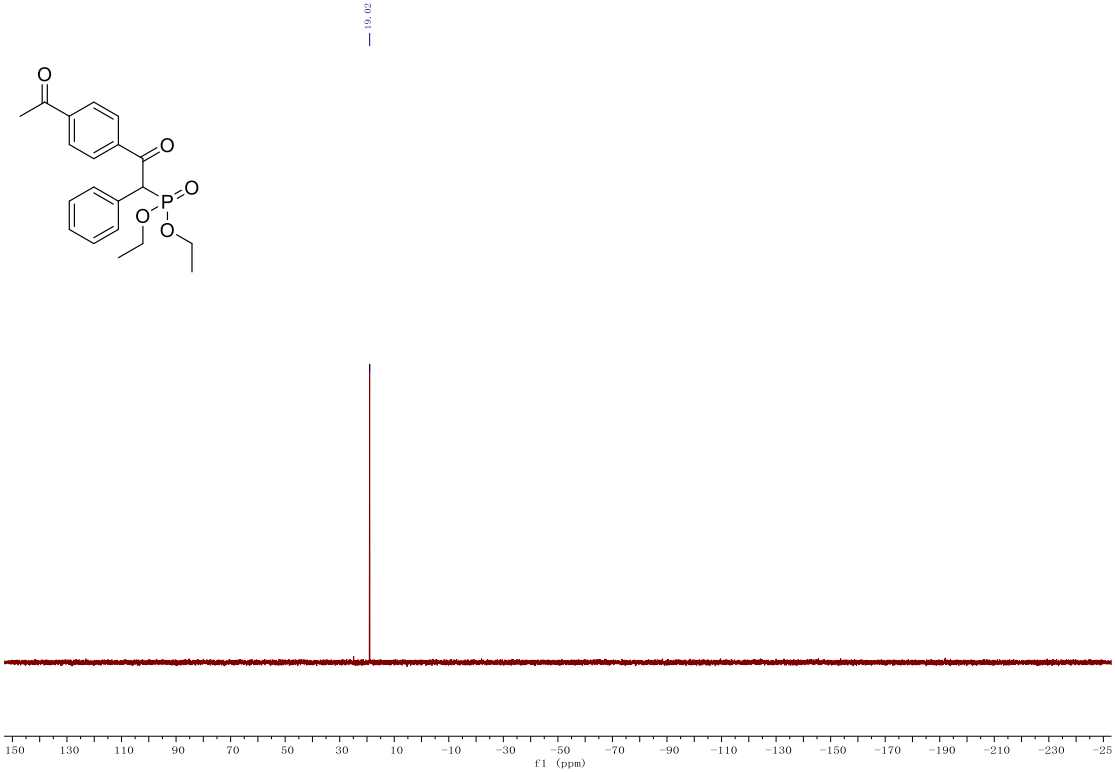

Figure S60. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **3f**

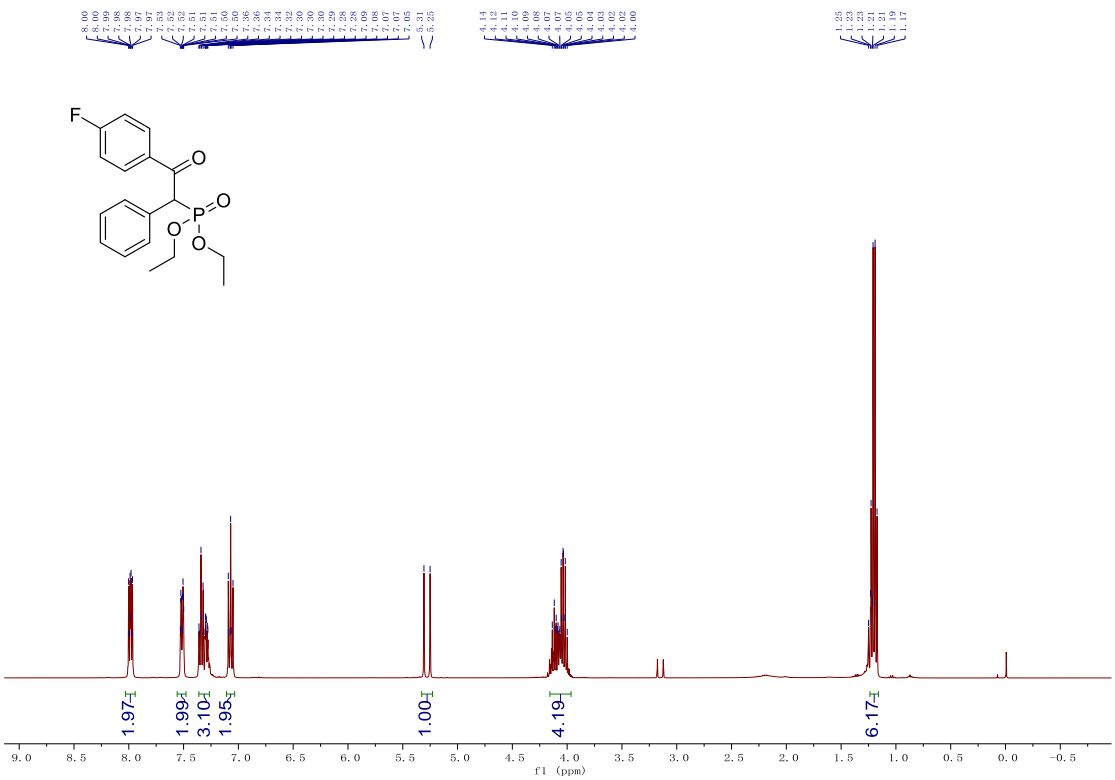

Figure S61. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3g**

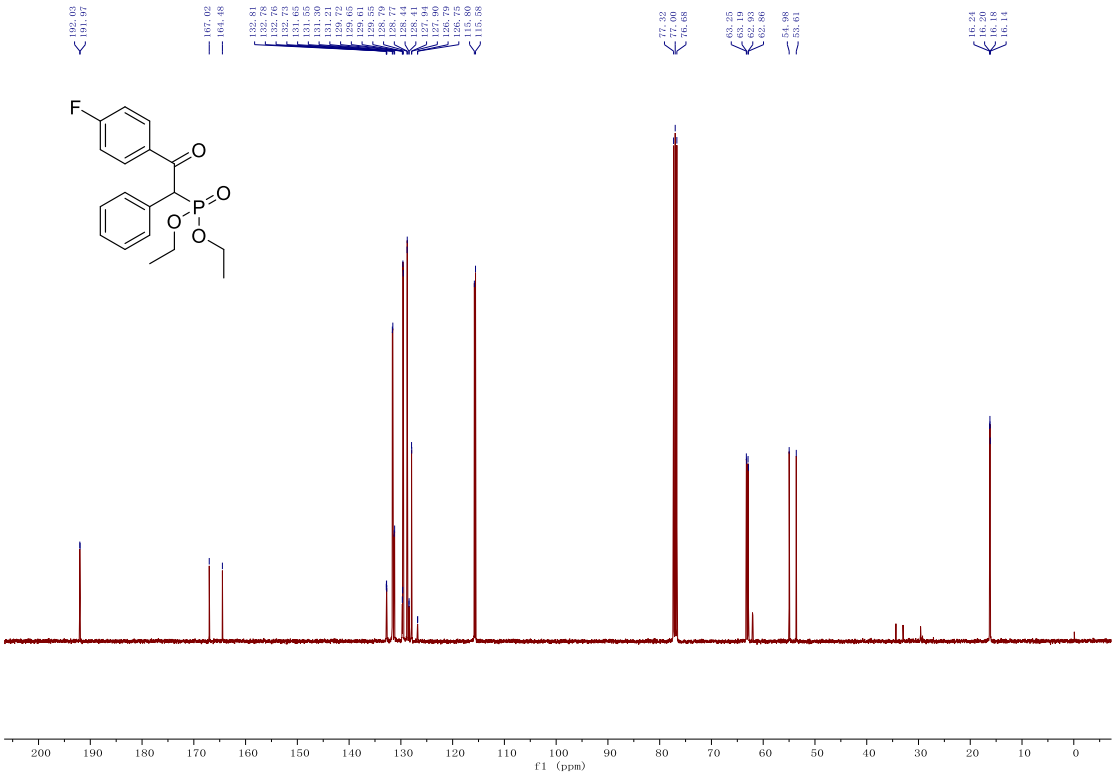

Figure S62. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3g**

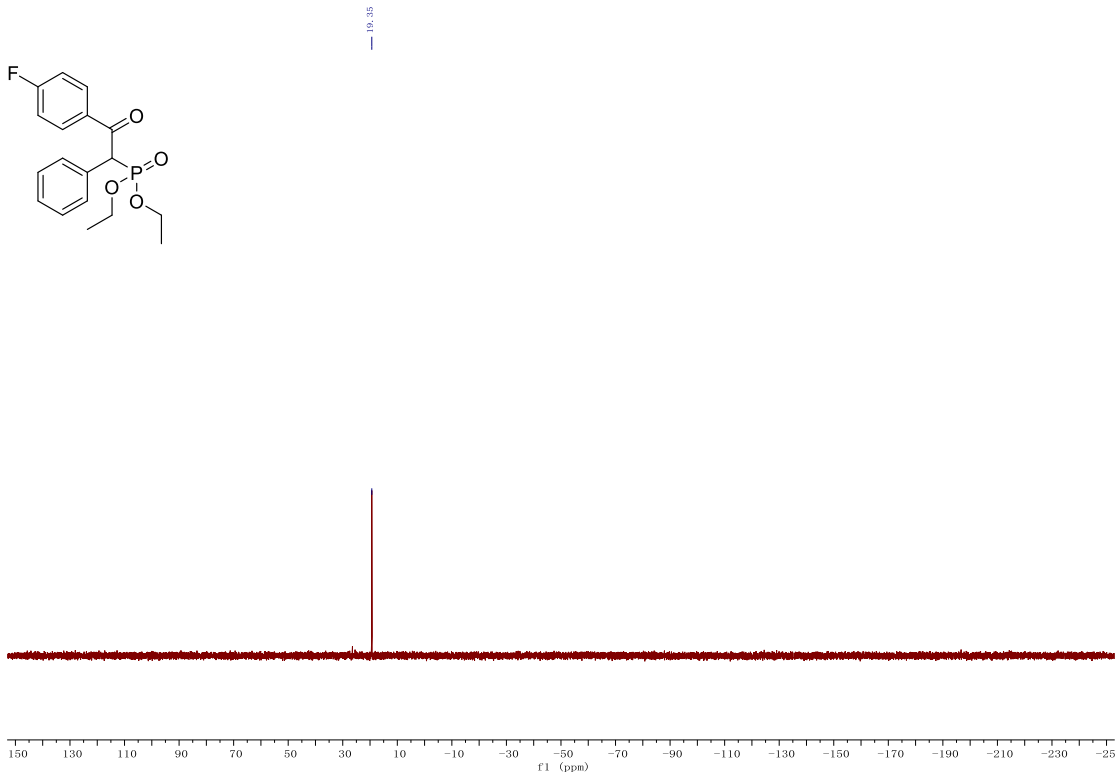

Figure S63. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3g**

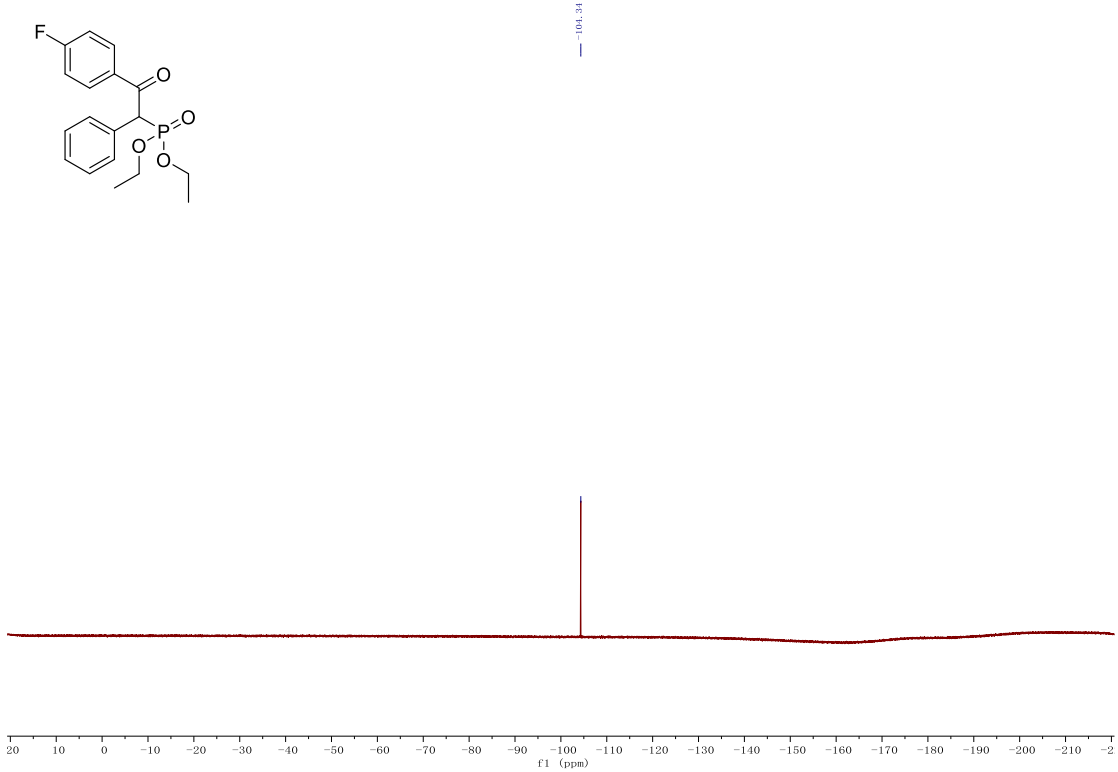

Figure S64. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3g**

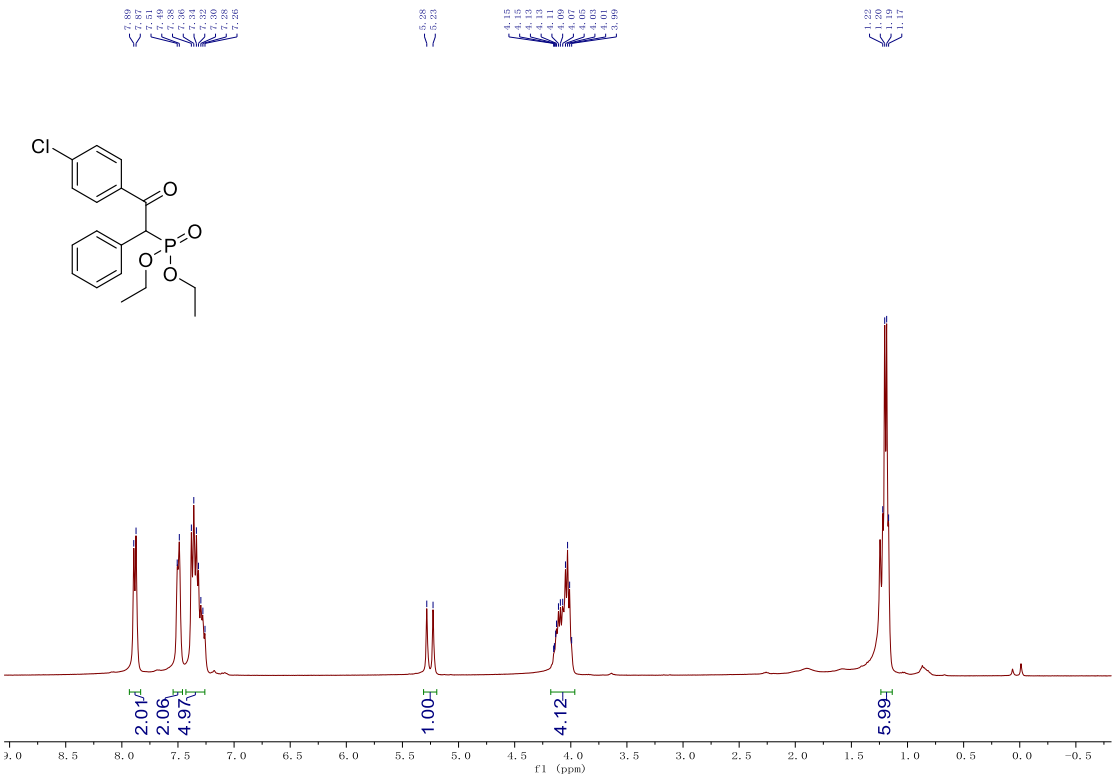

Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**

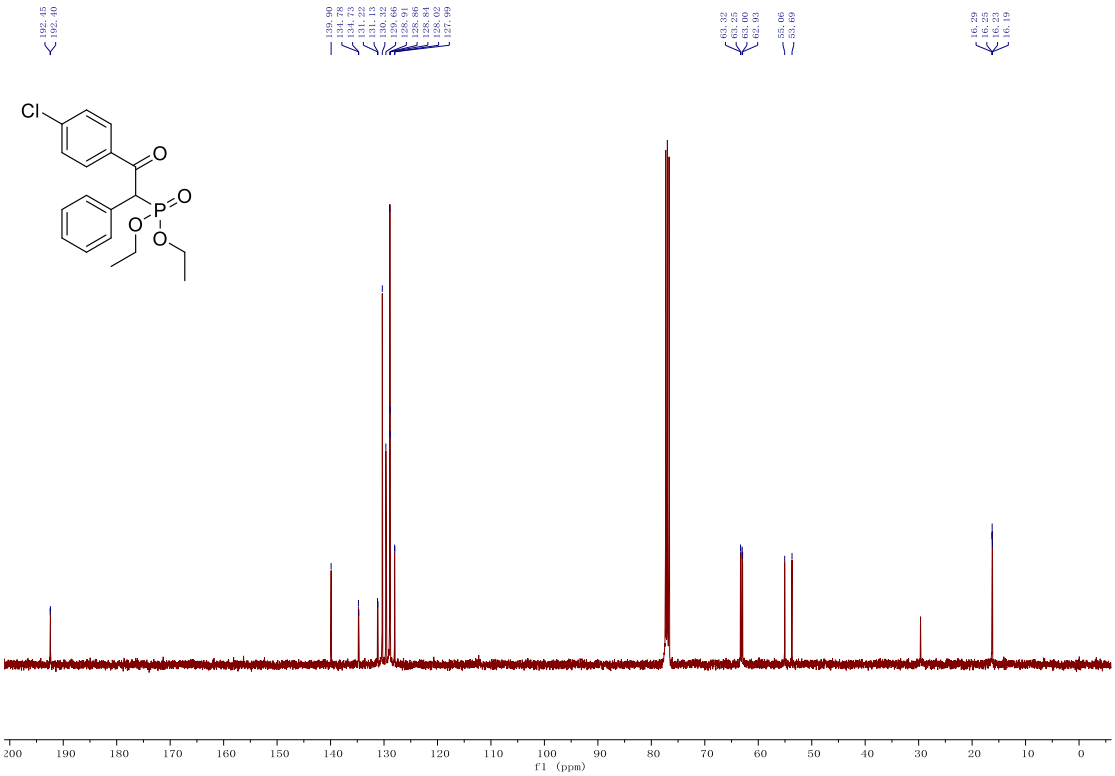

Figure S66. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3h**

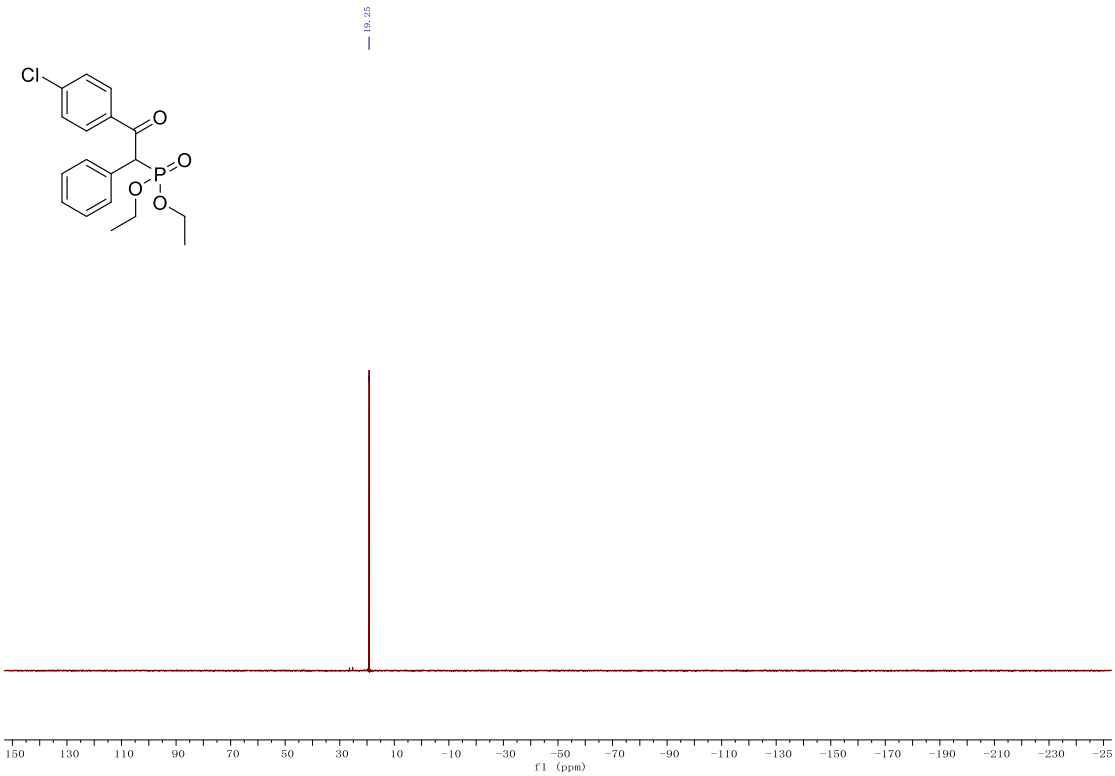

Figure S67. ^{31}**P NMR (162 MHz, CDCl$_3$)**.spectrum of **3h**

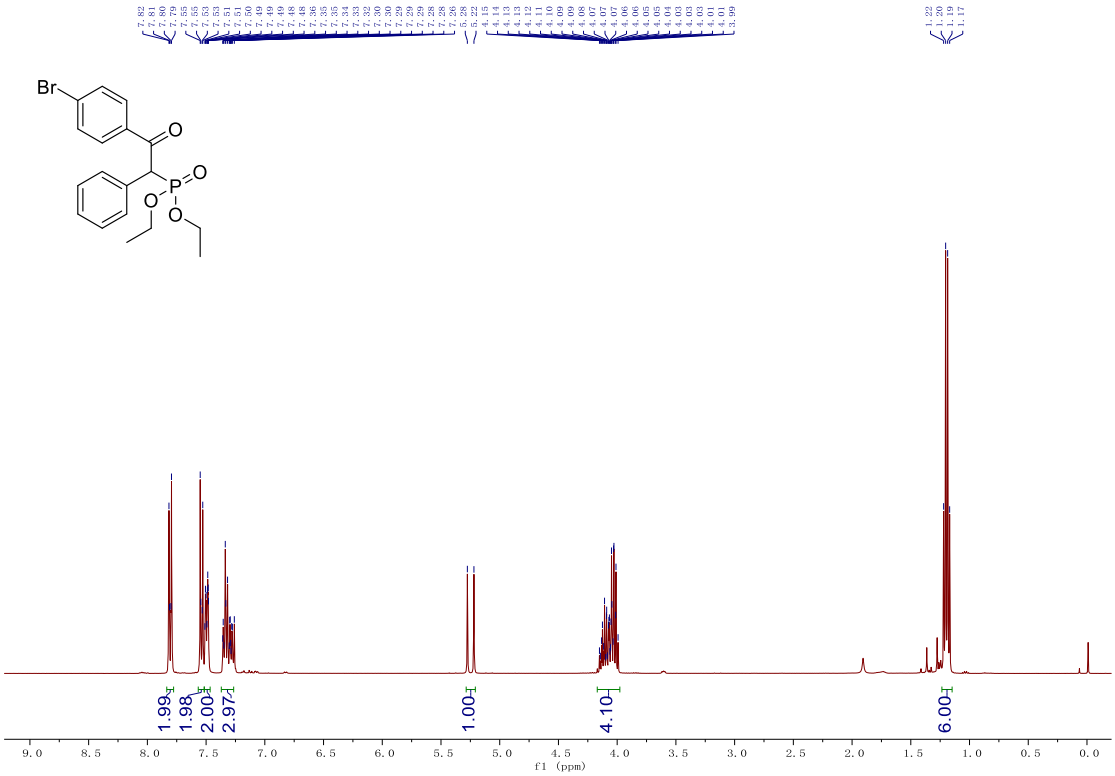

Figure S68. ^{1}**H NMR** (400 MHz, CDCl$_3$) spectrum of **3i**

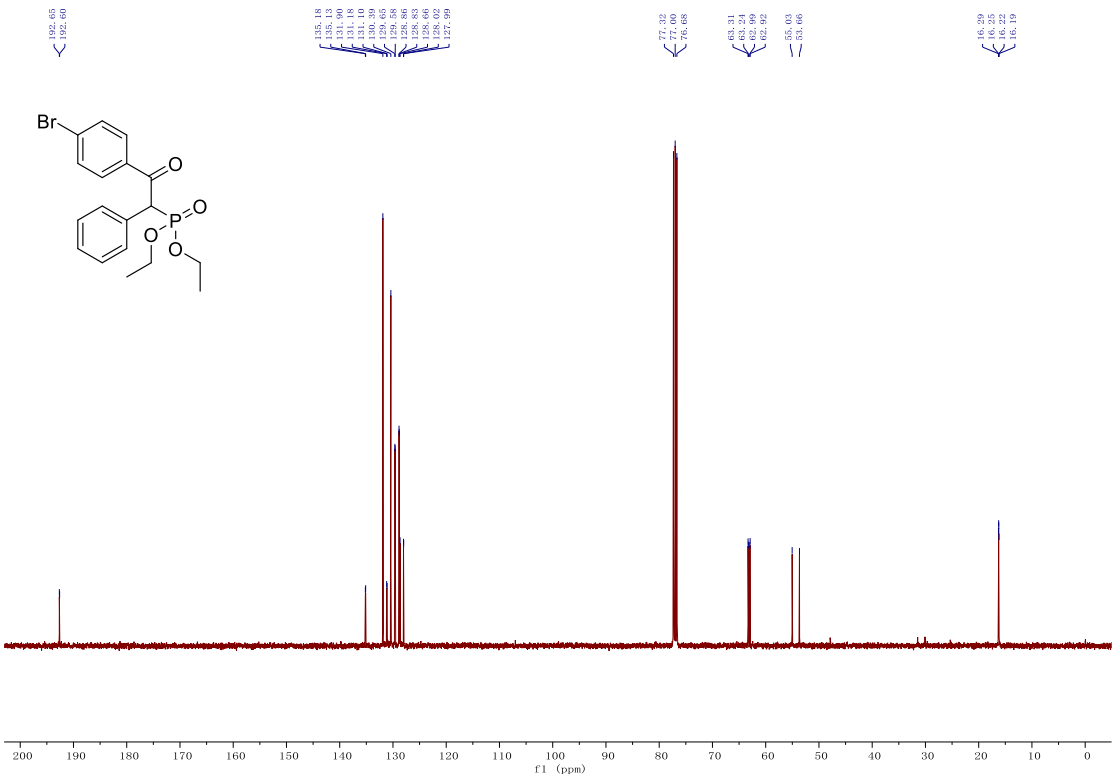

Figure S69. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3i**

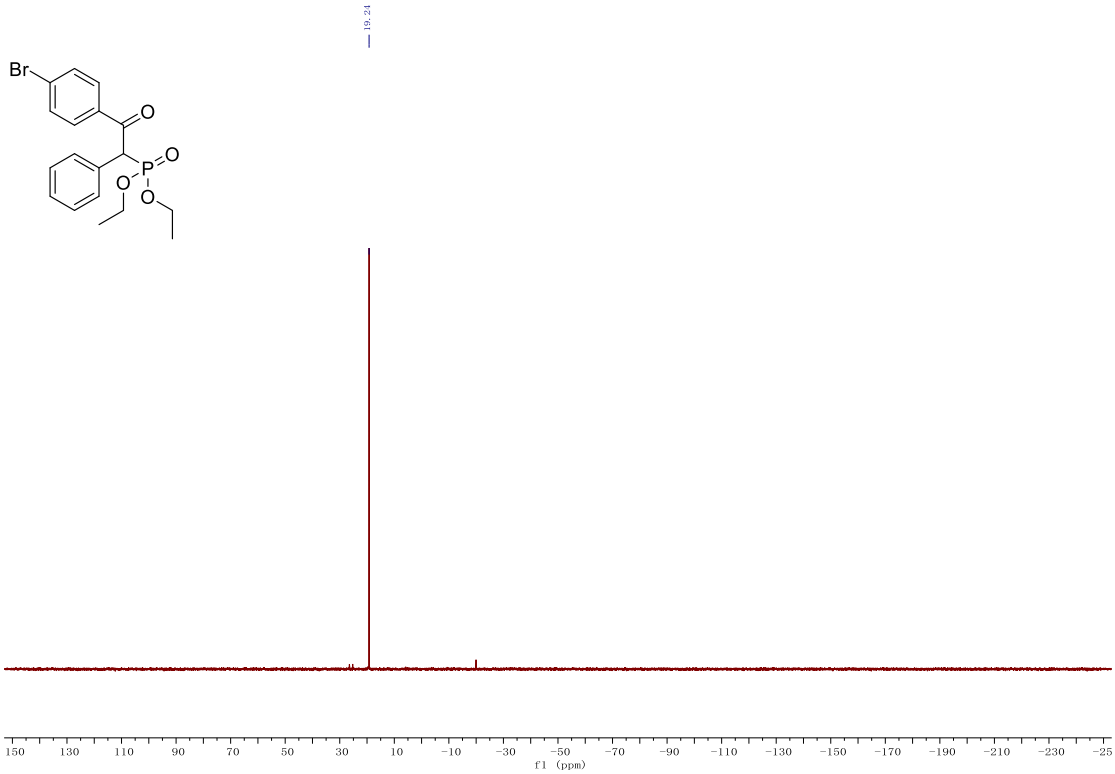

Figure S70. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **3i**

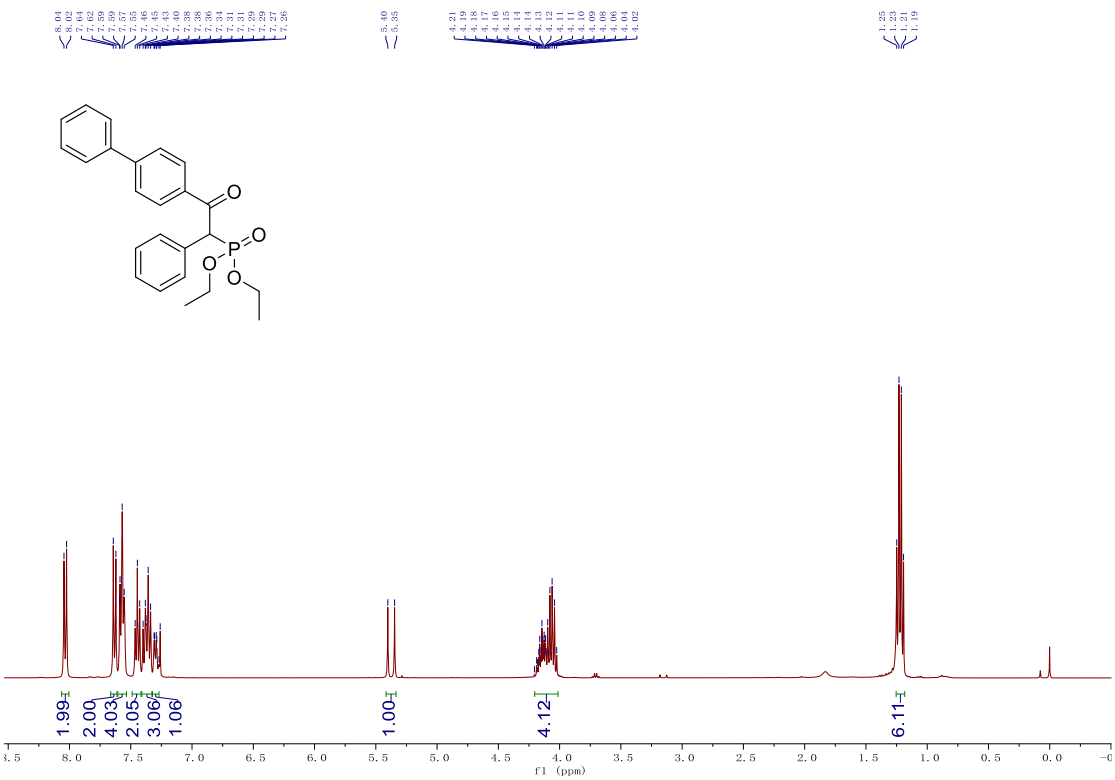

Figure S71. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3j**

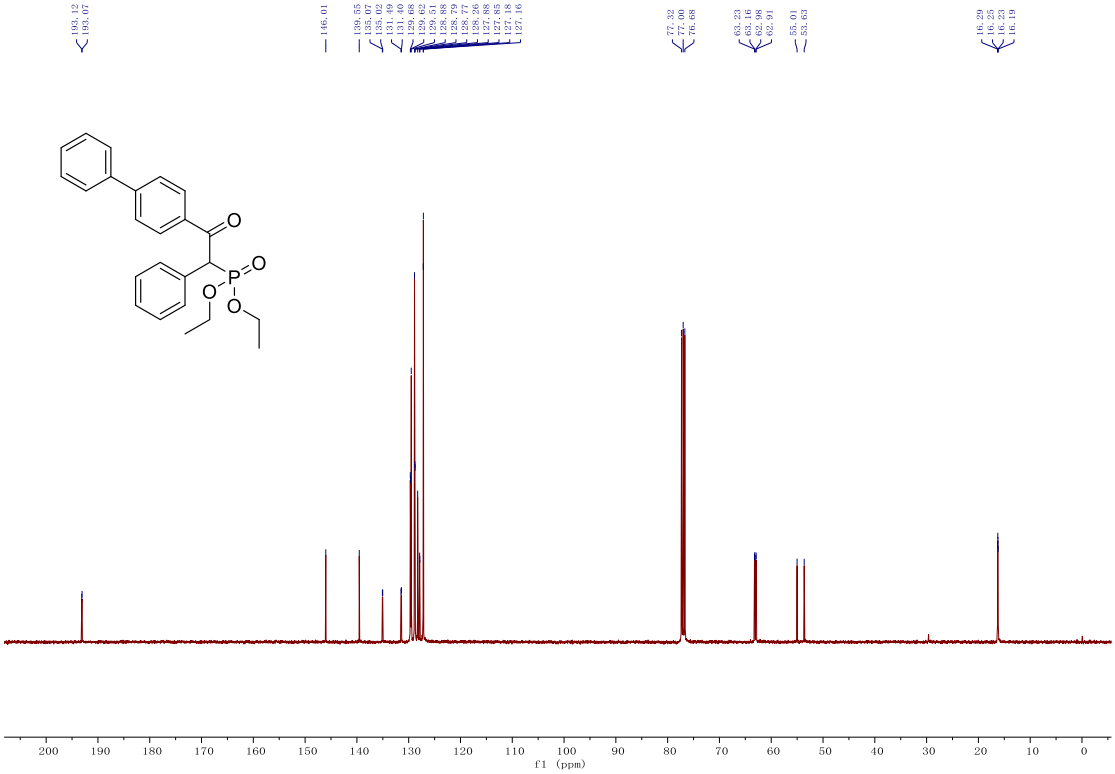

Figure S72. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3j**

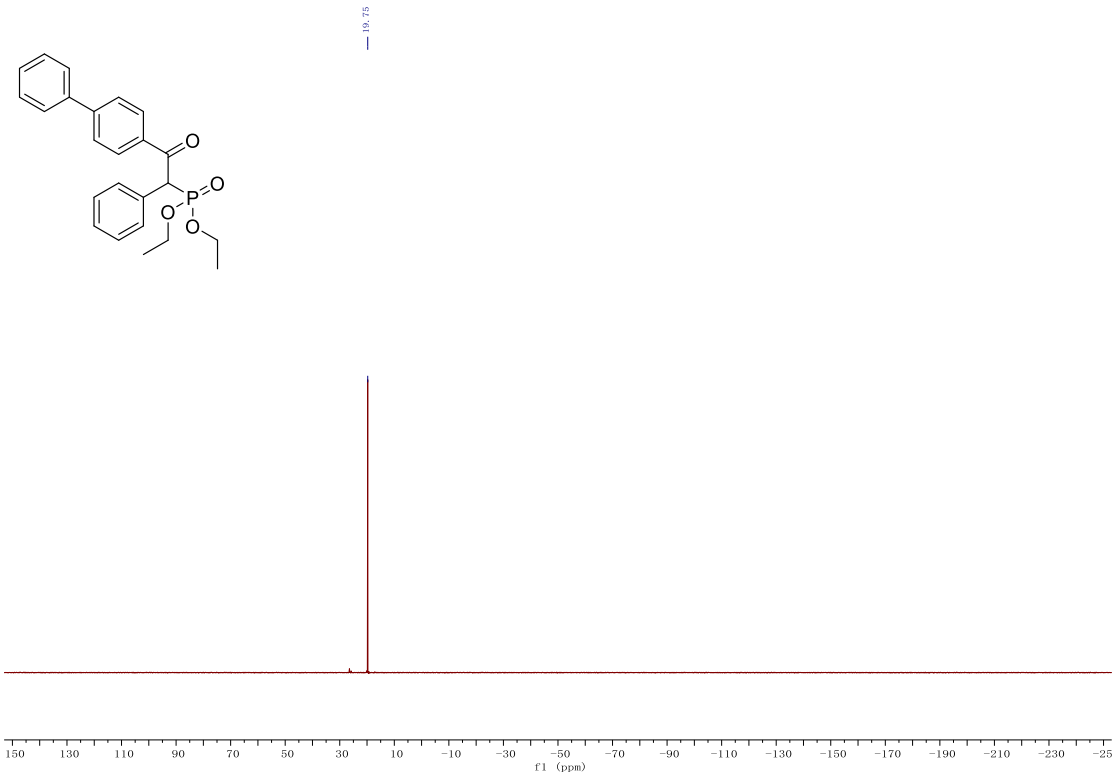

Figure S73. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3j**

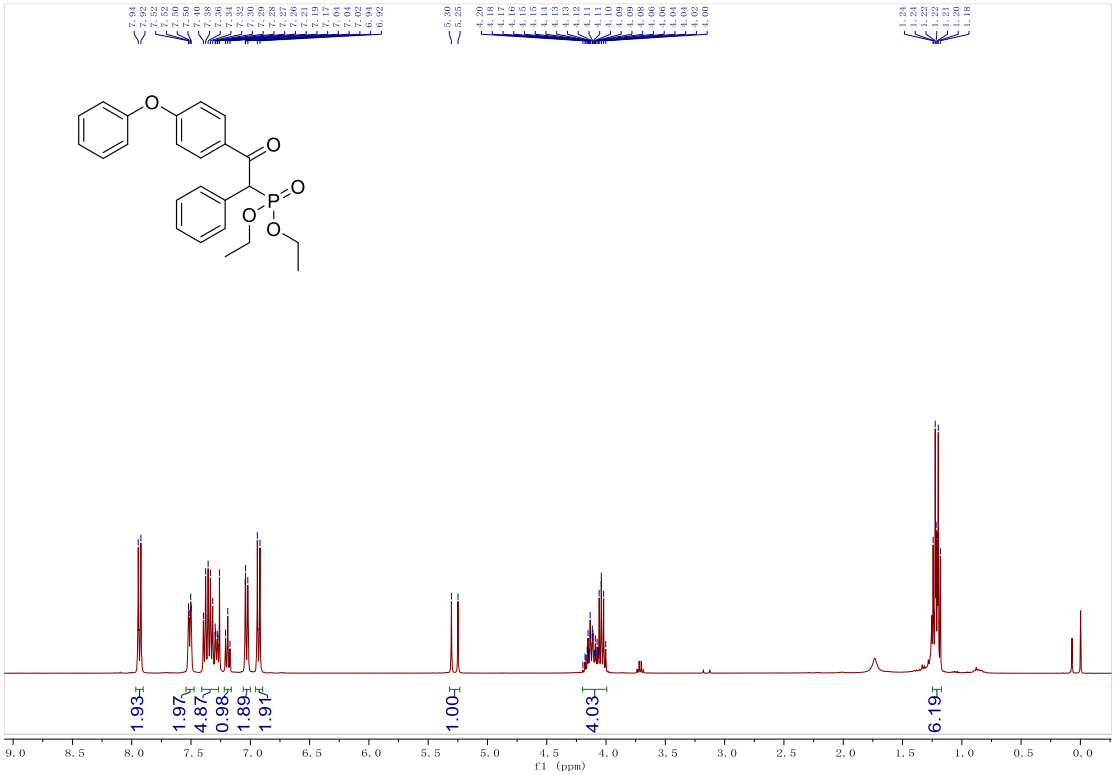

Figure S74. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3k**

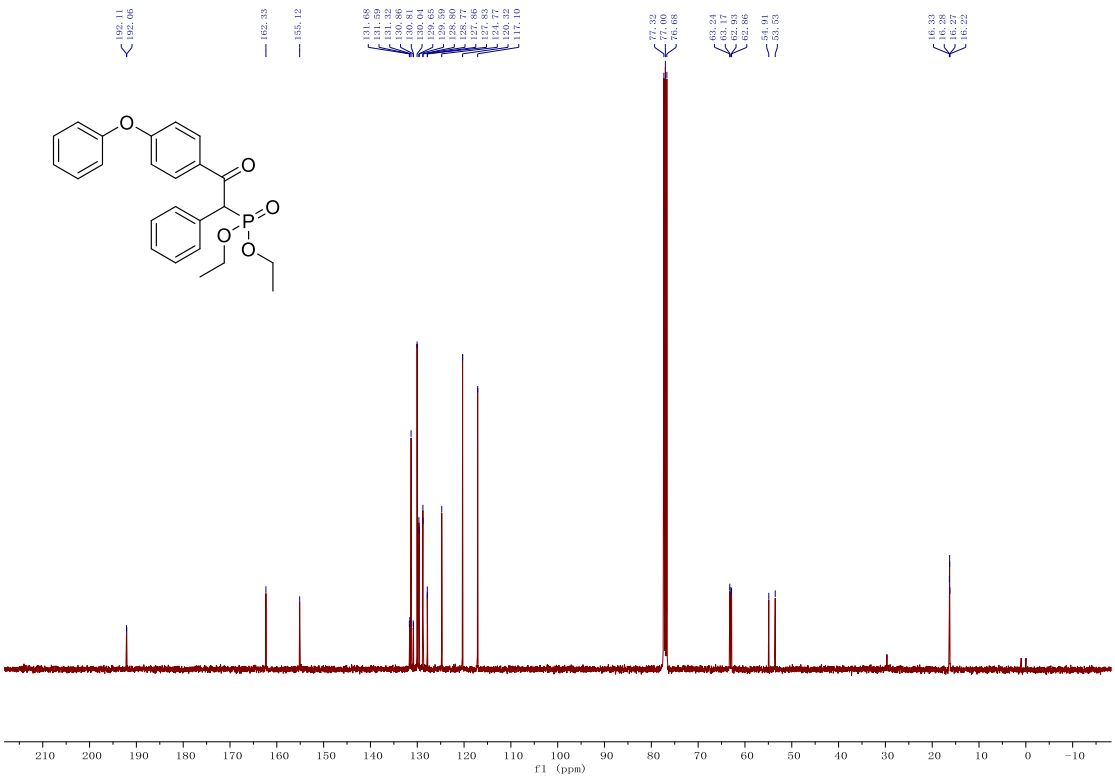

Figure S75. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3k**

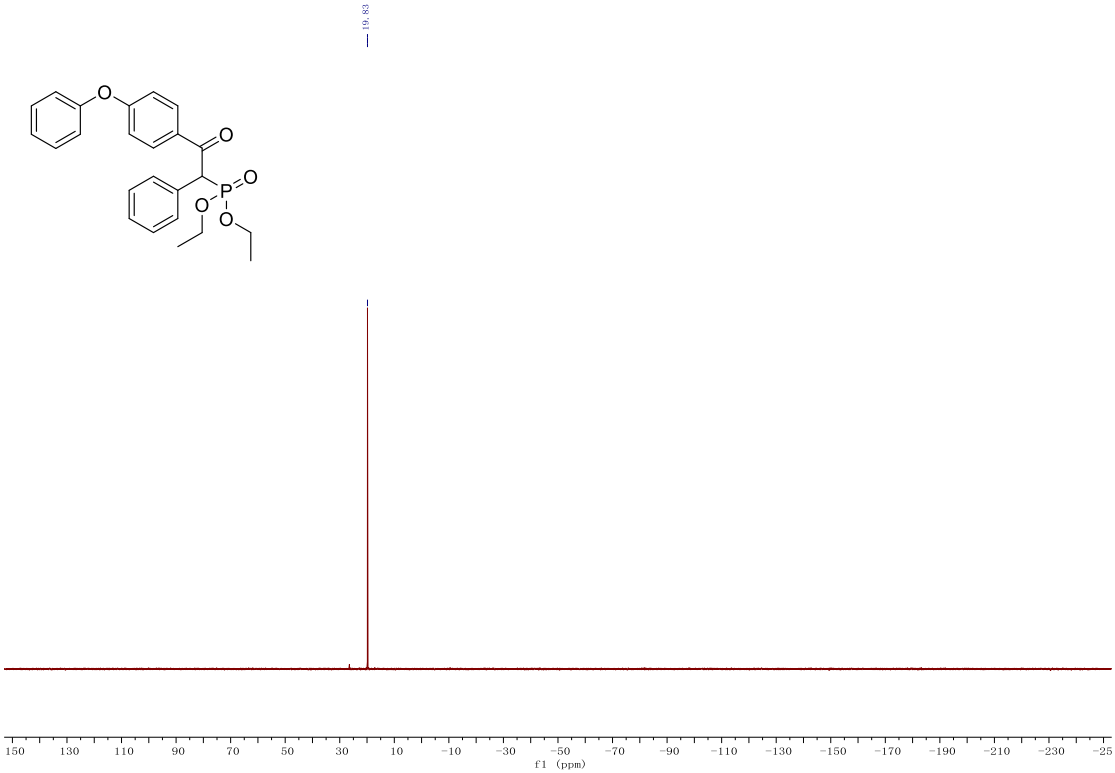

Figure S76. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3k**

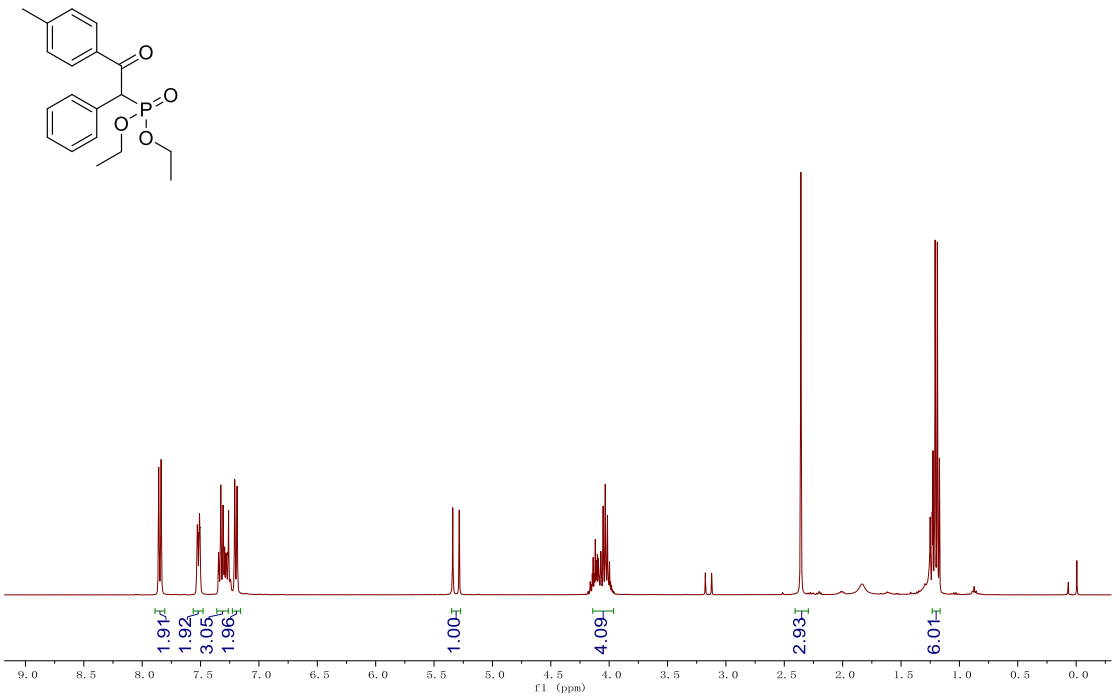

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**

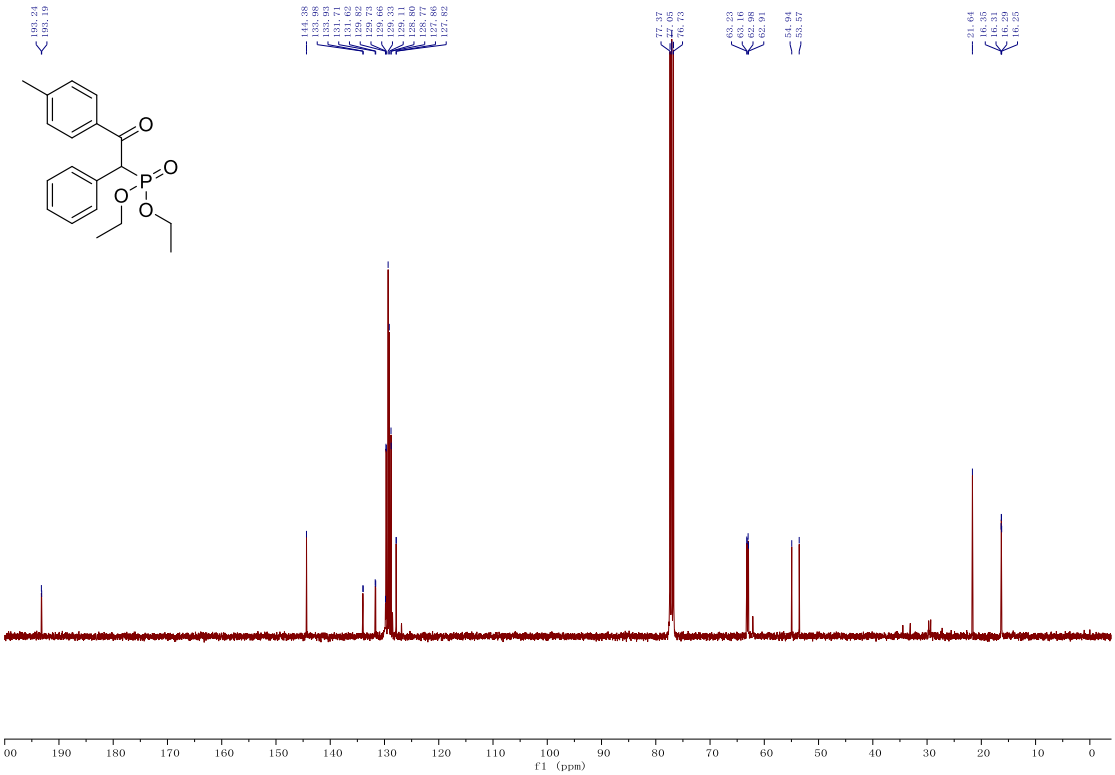

Figure S78. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3l**

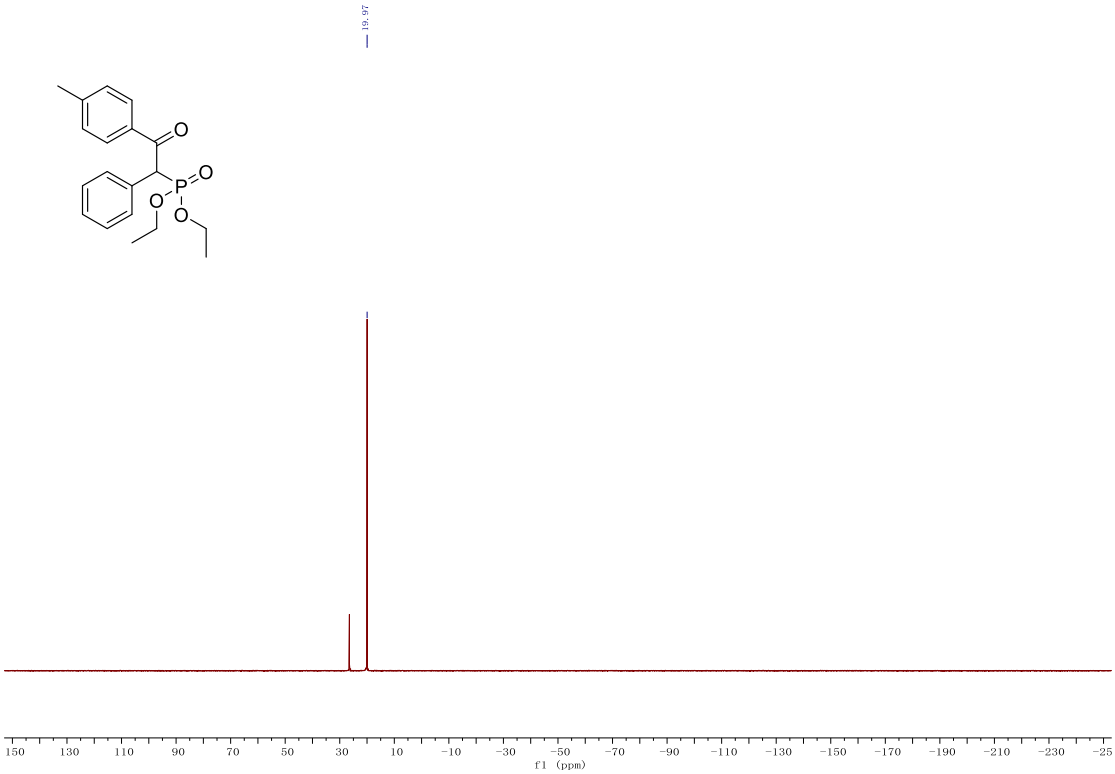

Figure S79. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3l**

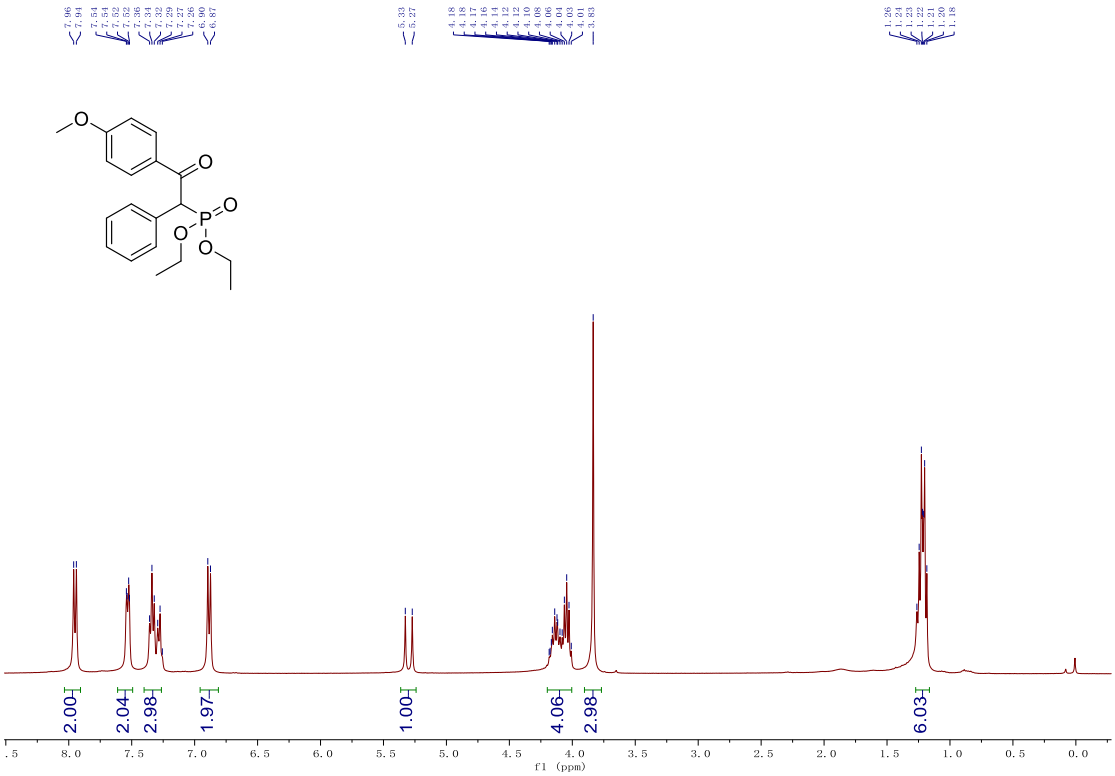

Figure S80. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3m**

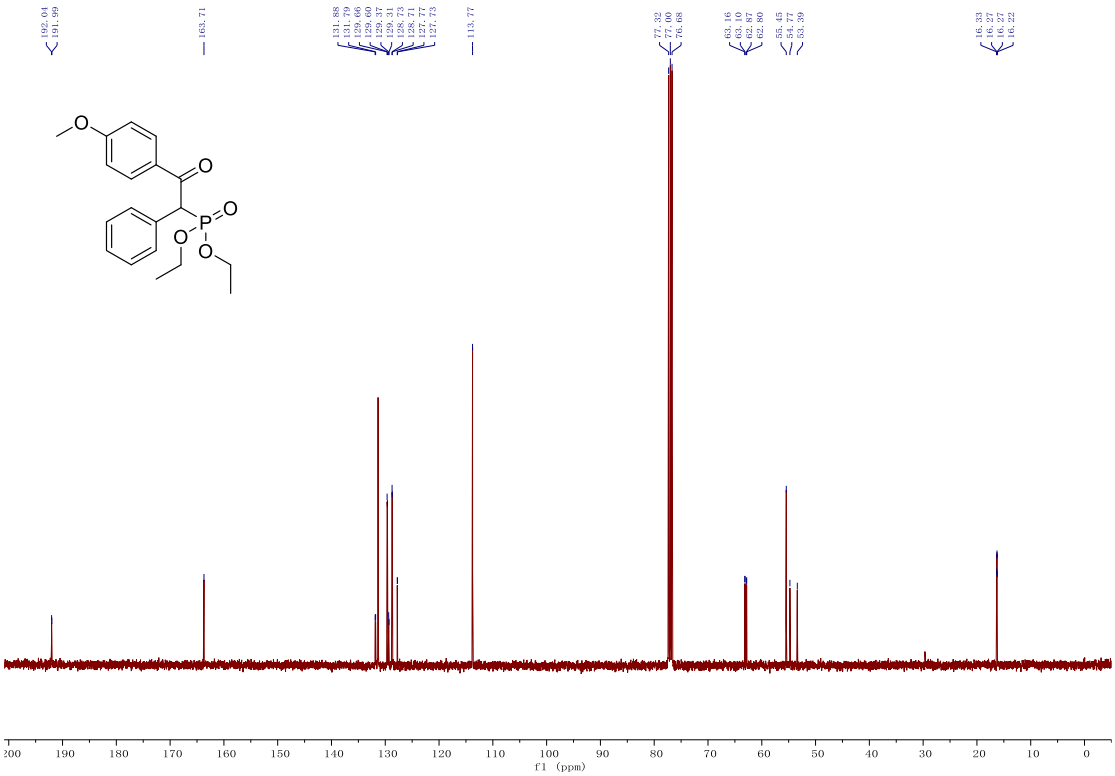

Figure S81. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3m**

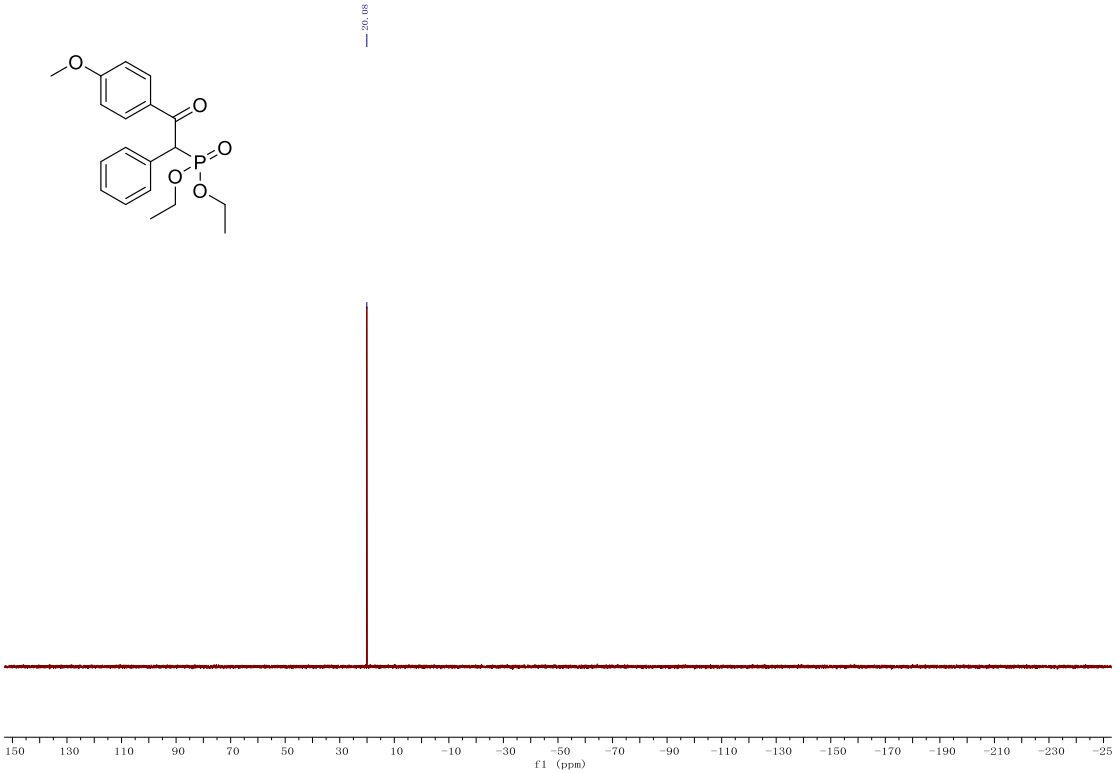

Figure S82. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3m**

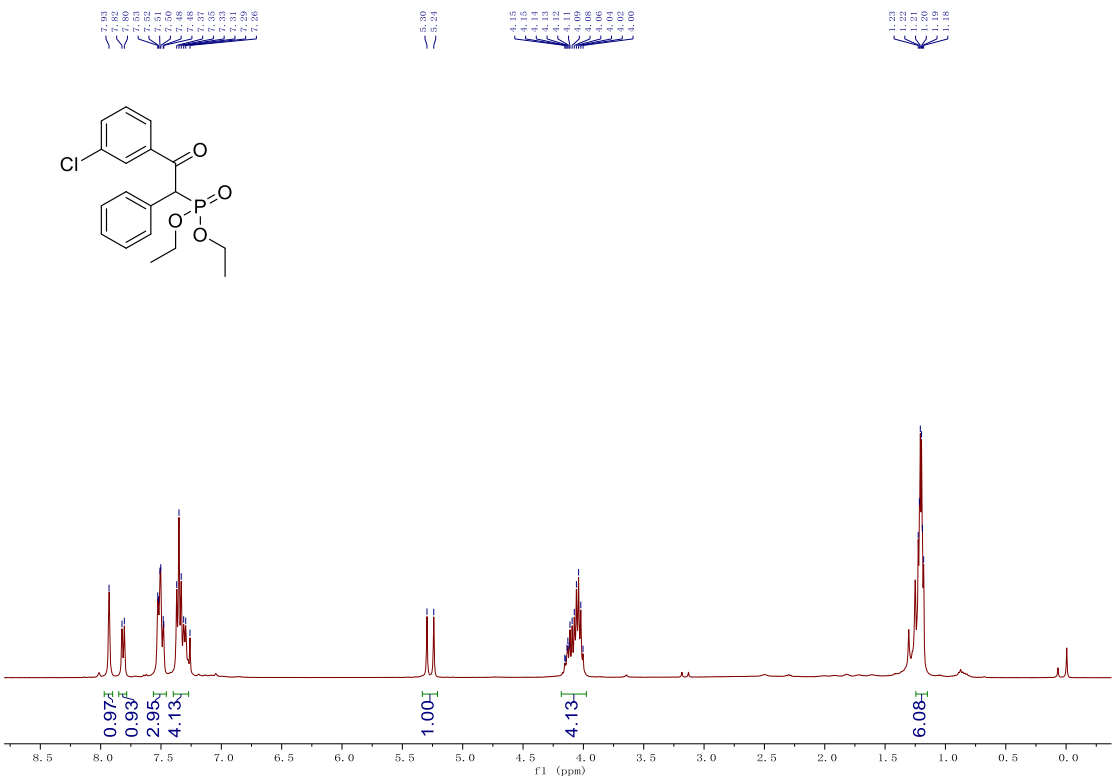

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**

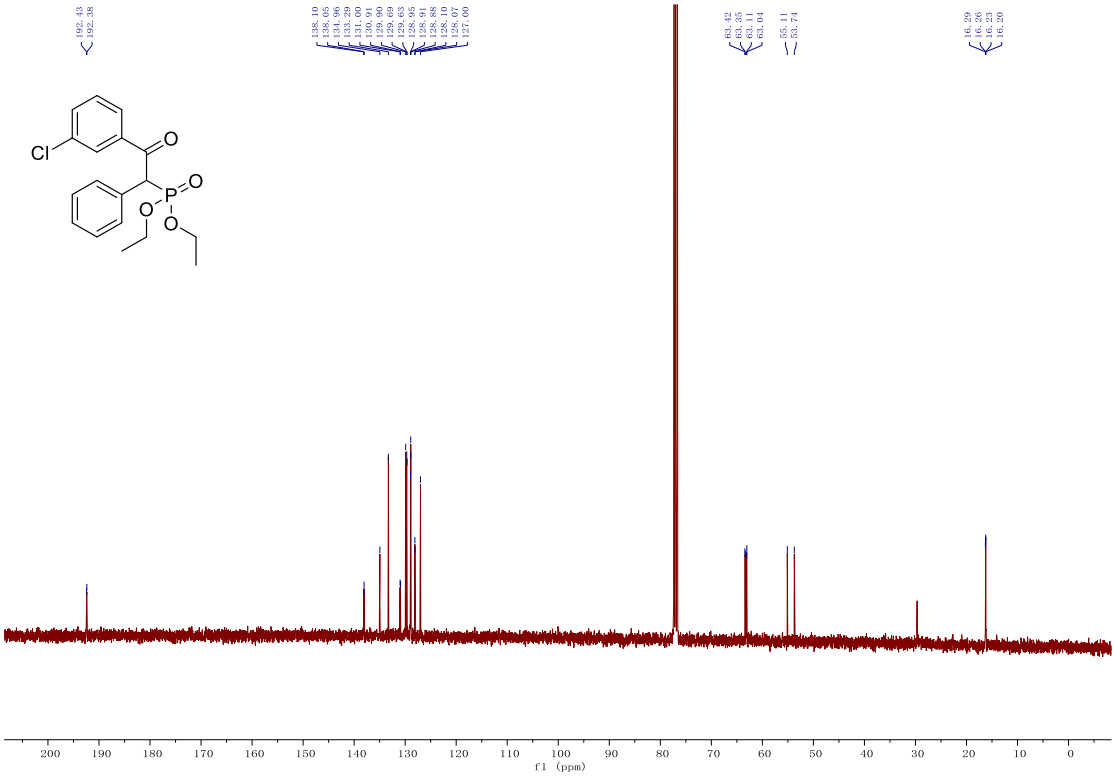

Figure S84. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3n**

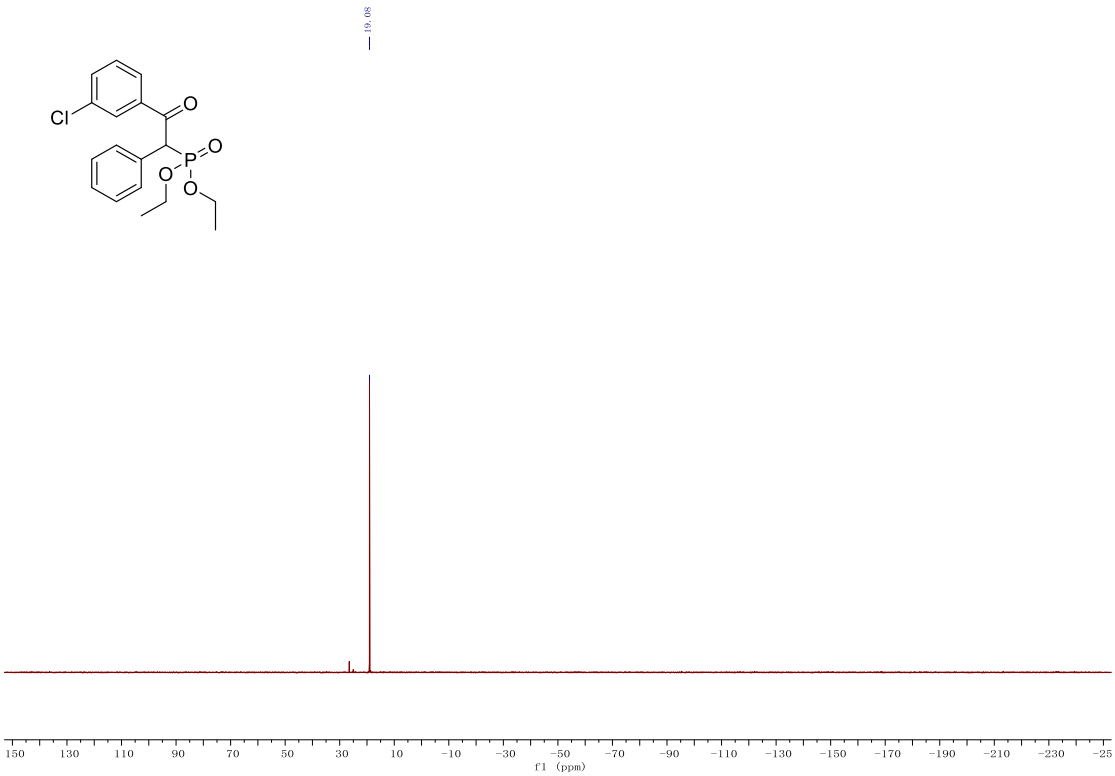

Figure S85. ^{31}**P NMR (162 MHz, CDCl$_3$)**.spectrum of **3n**

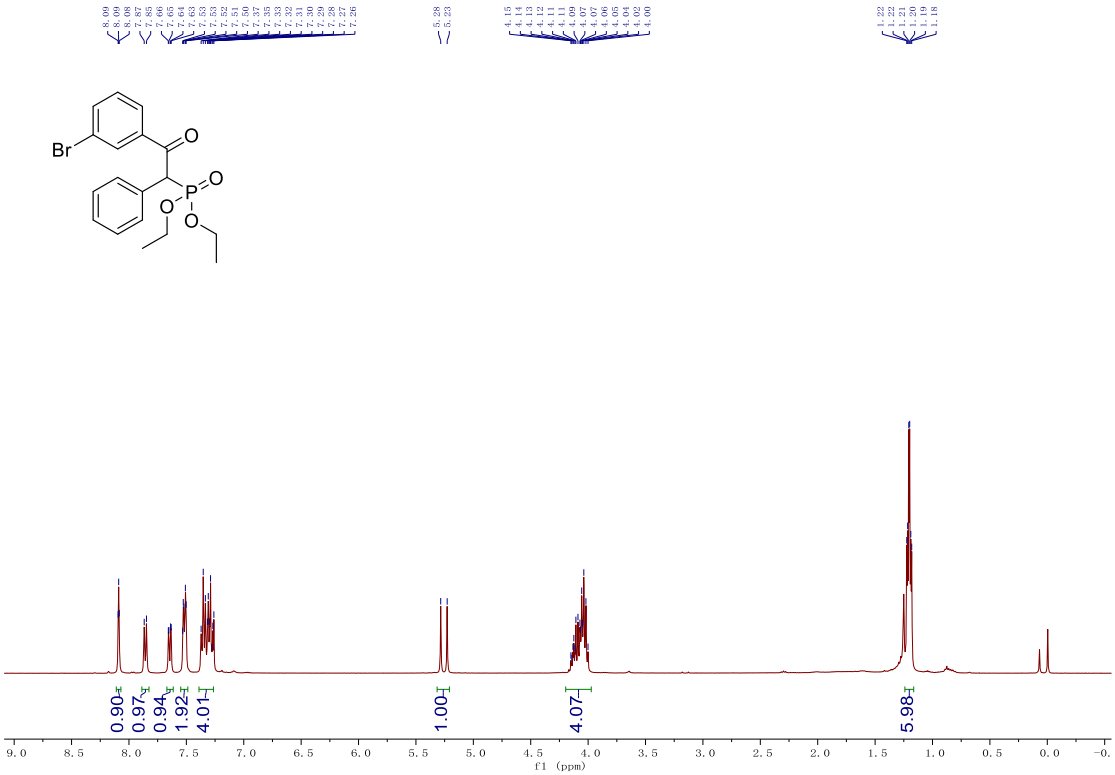

Figure S86. ^{1}**H NMR** (400 MHz, CDCl$_3$) spectrum of **3o**

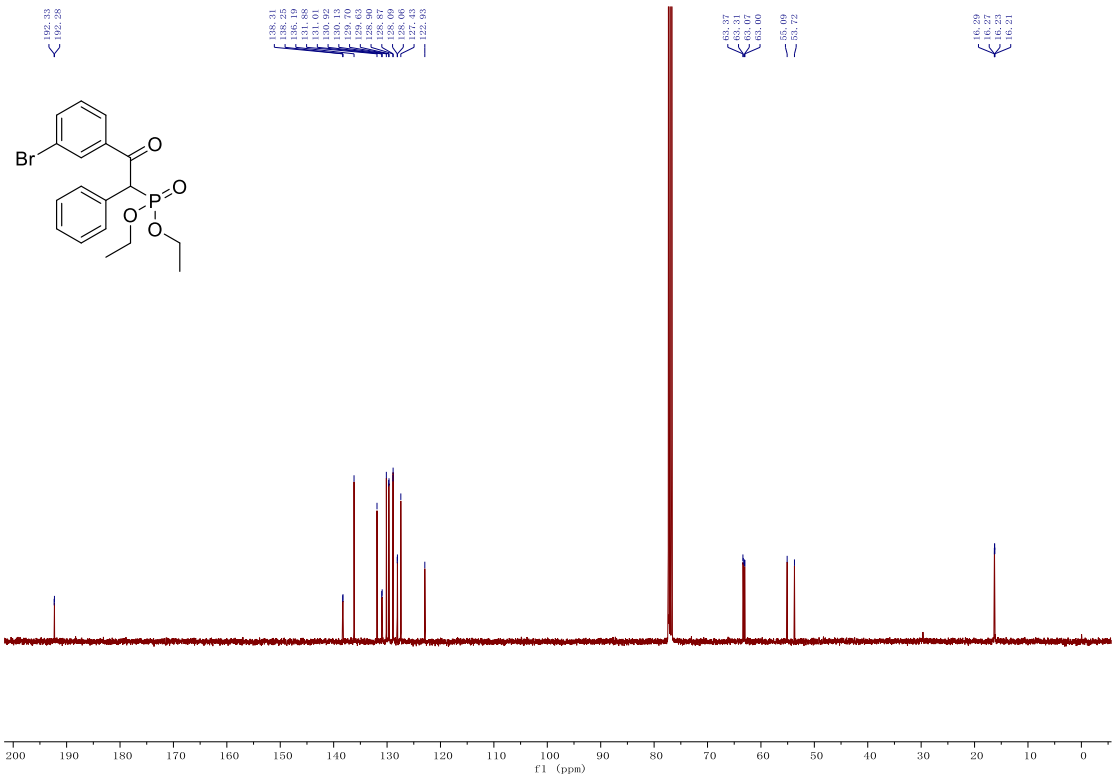

Figure S87. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3o**

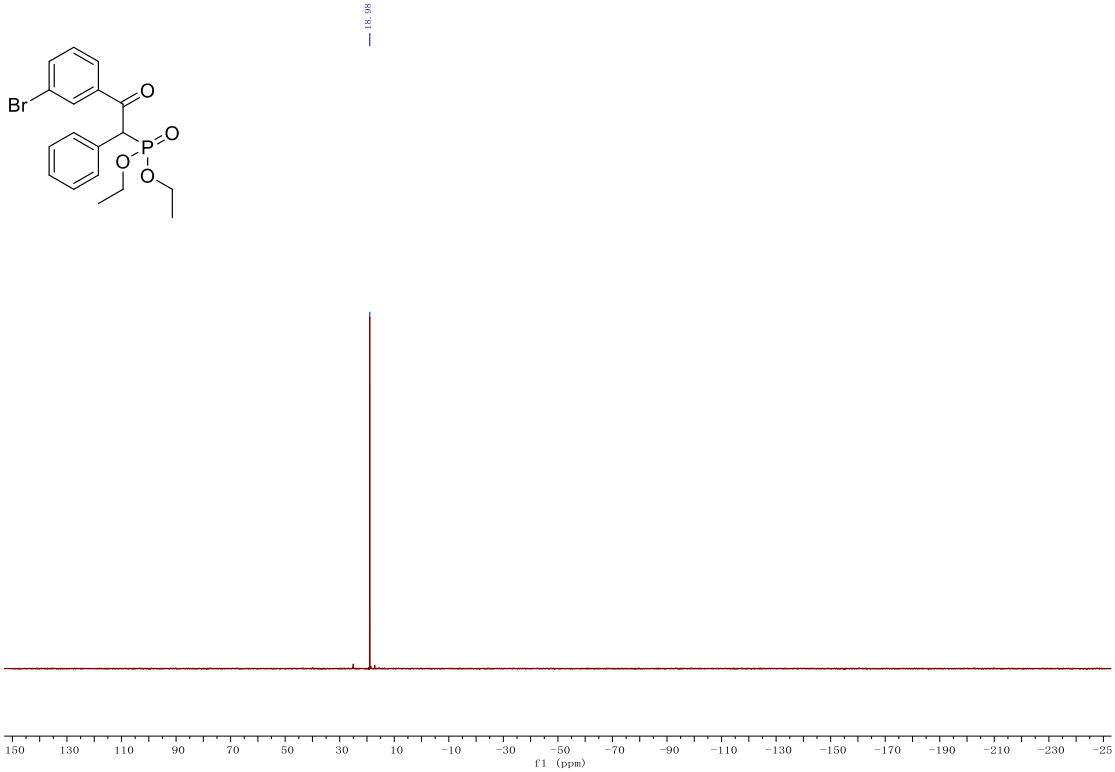

Figure S88. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3o**

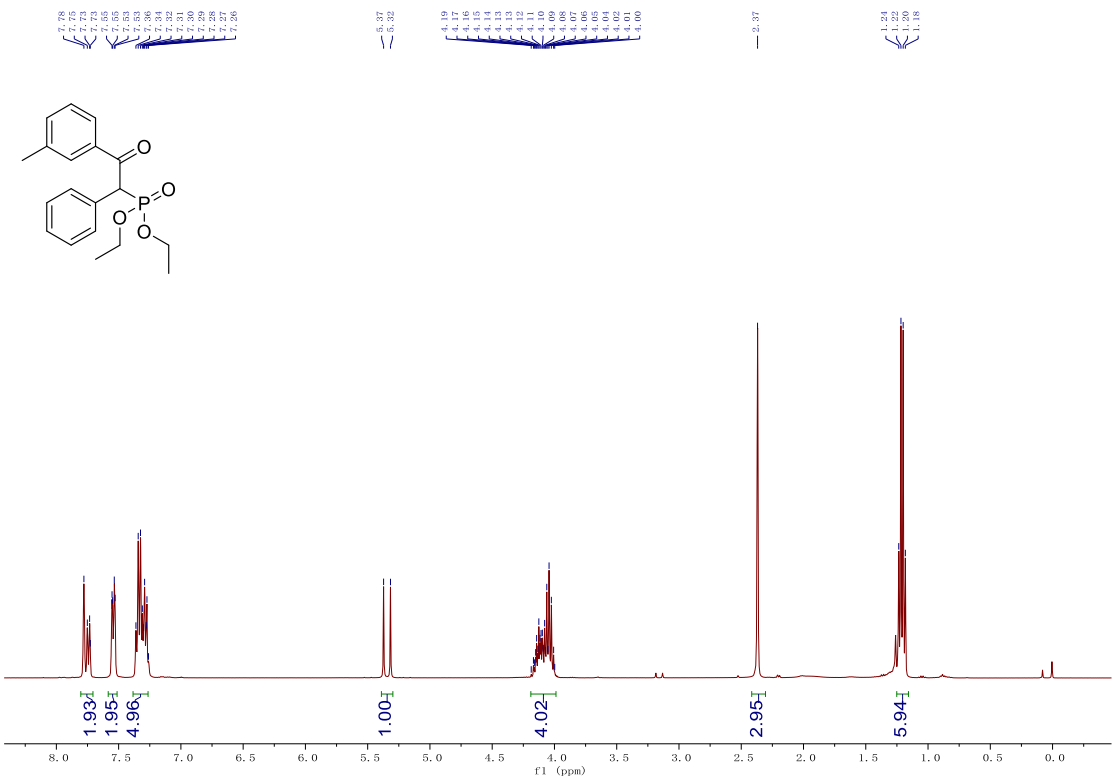

Figure S89. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3p**

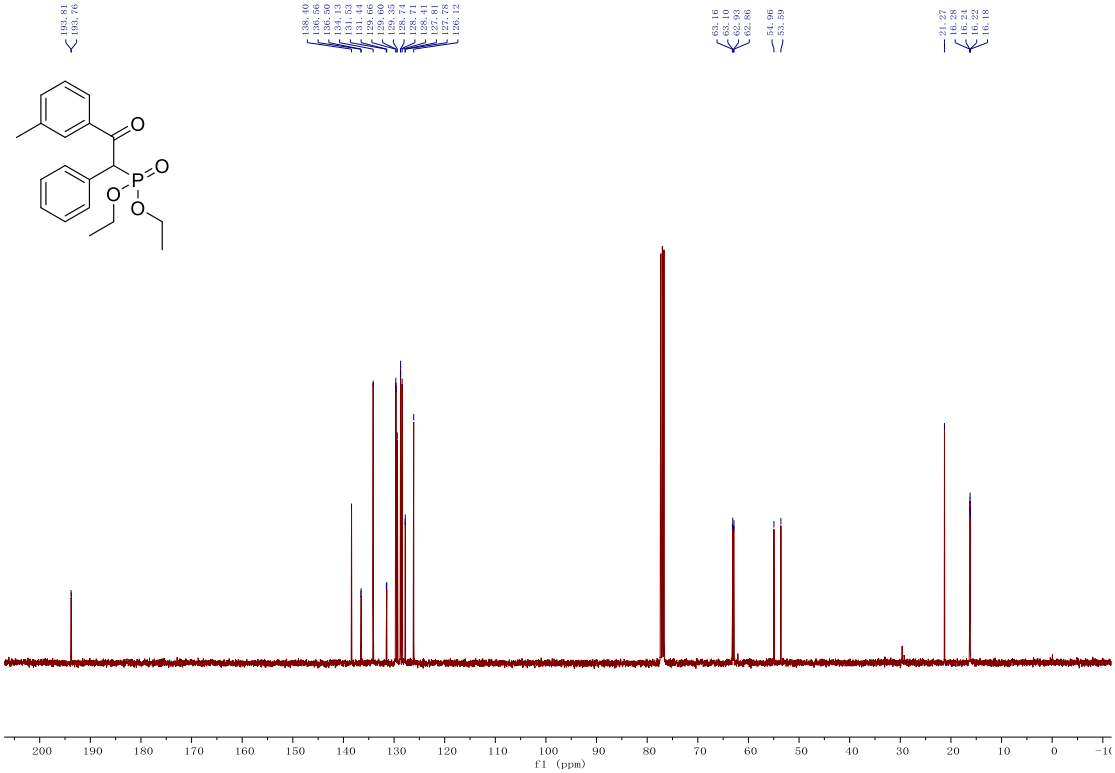

Figure S90. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3p**

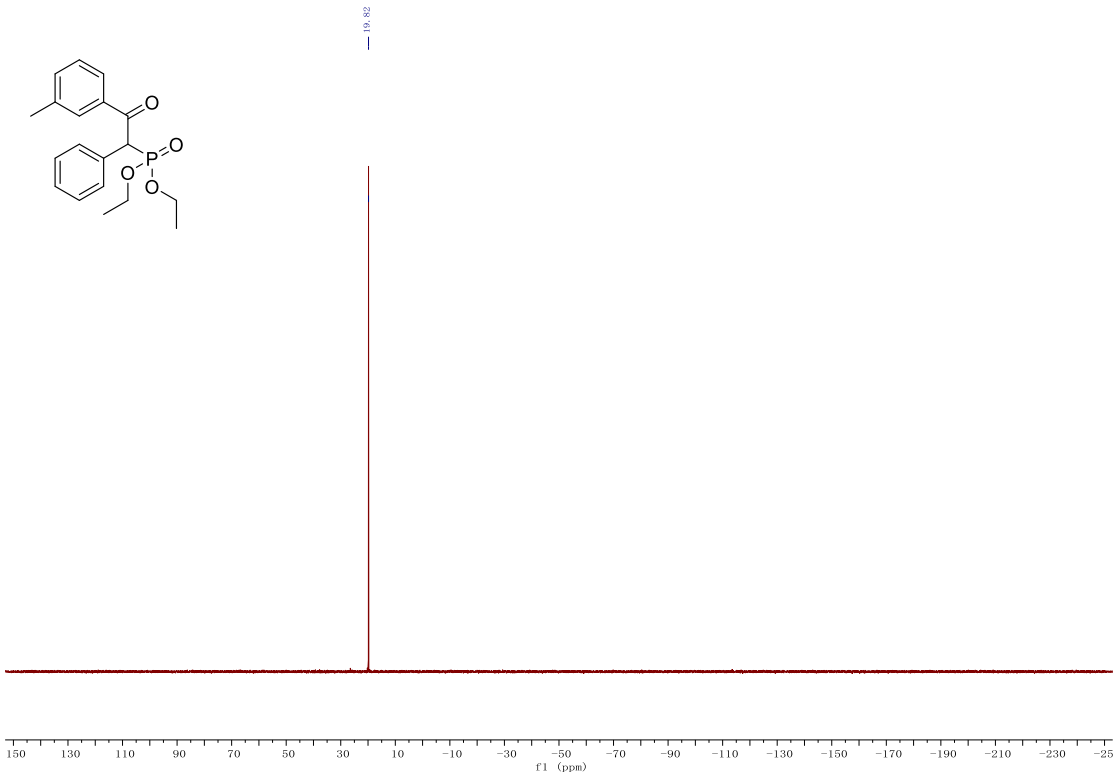

Figure S91. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3p**

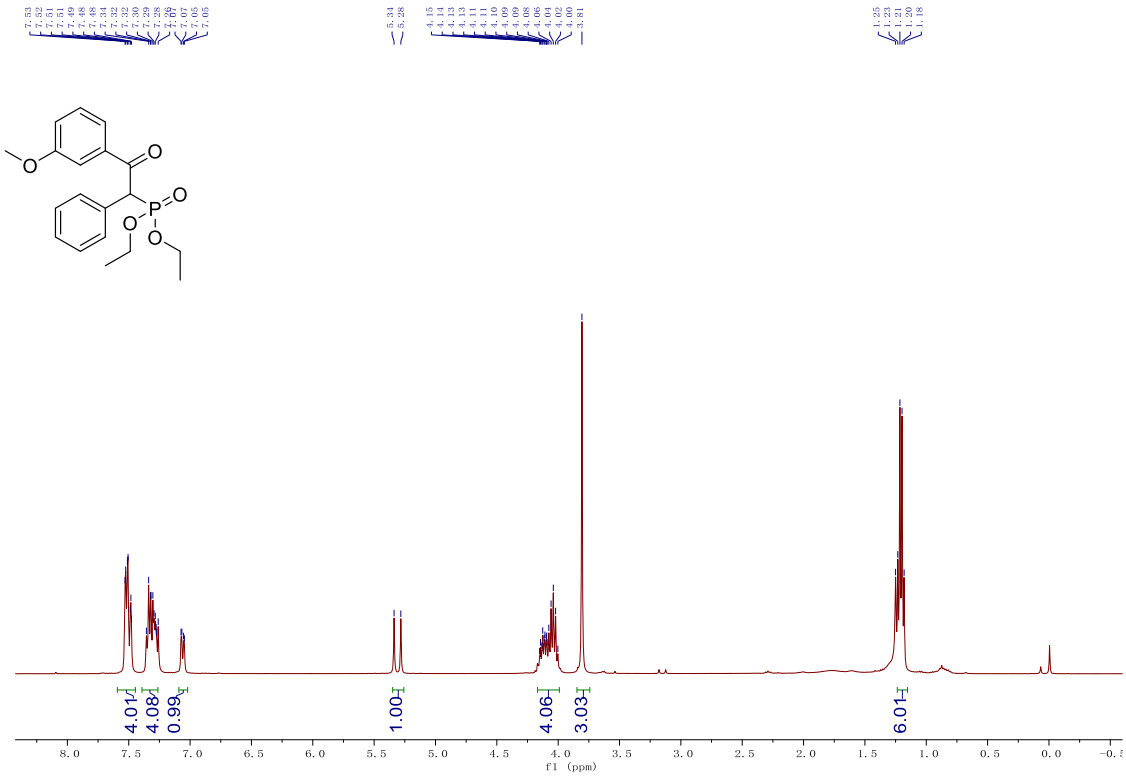

Figure S92. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**

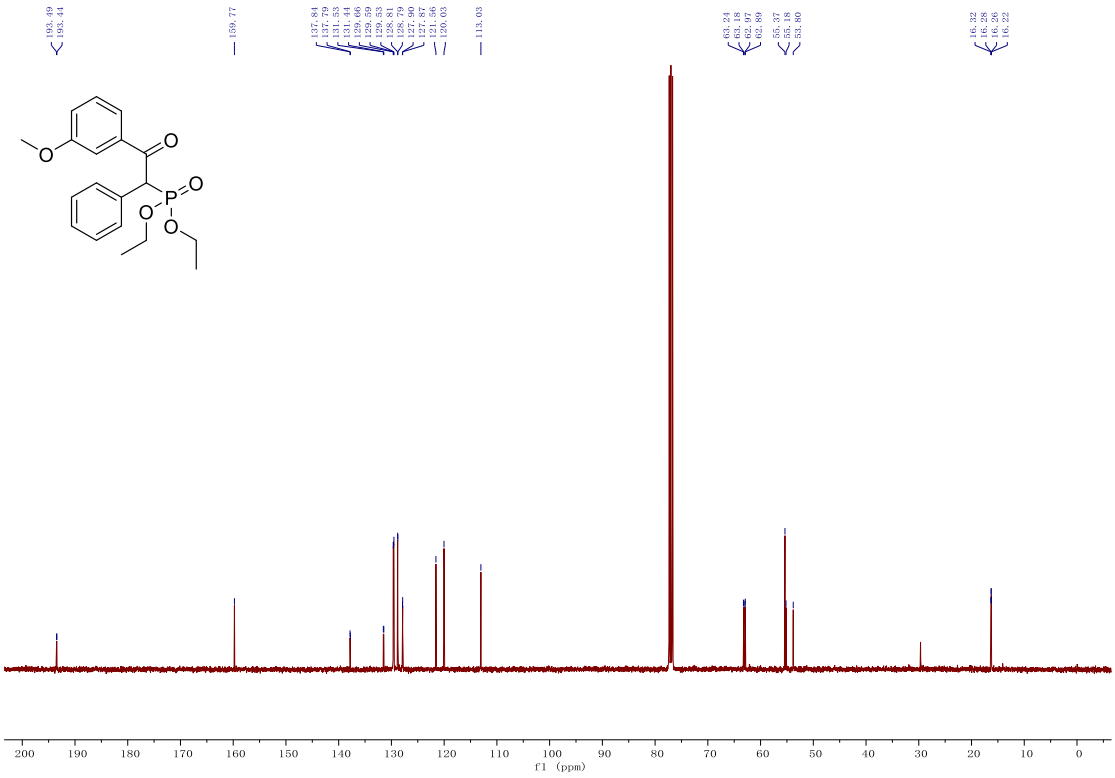

Figure S93. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3q**

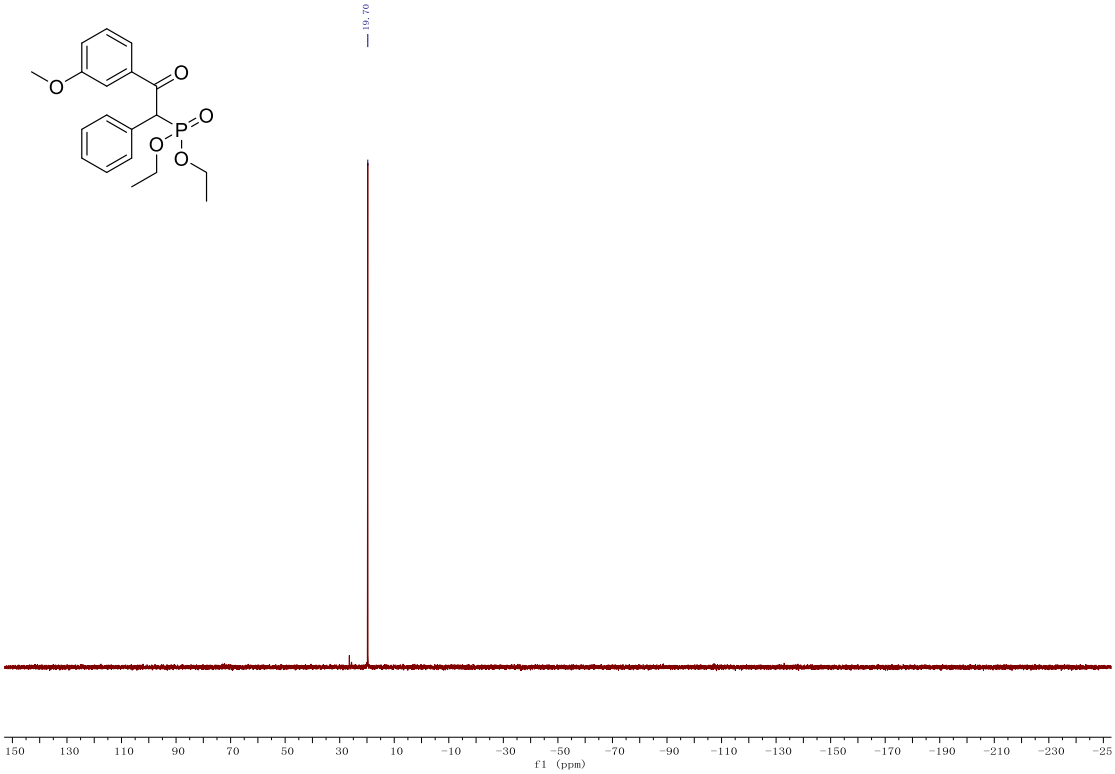

Figure S94. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3q**

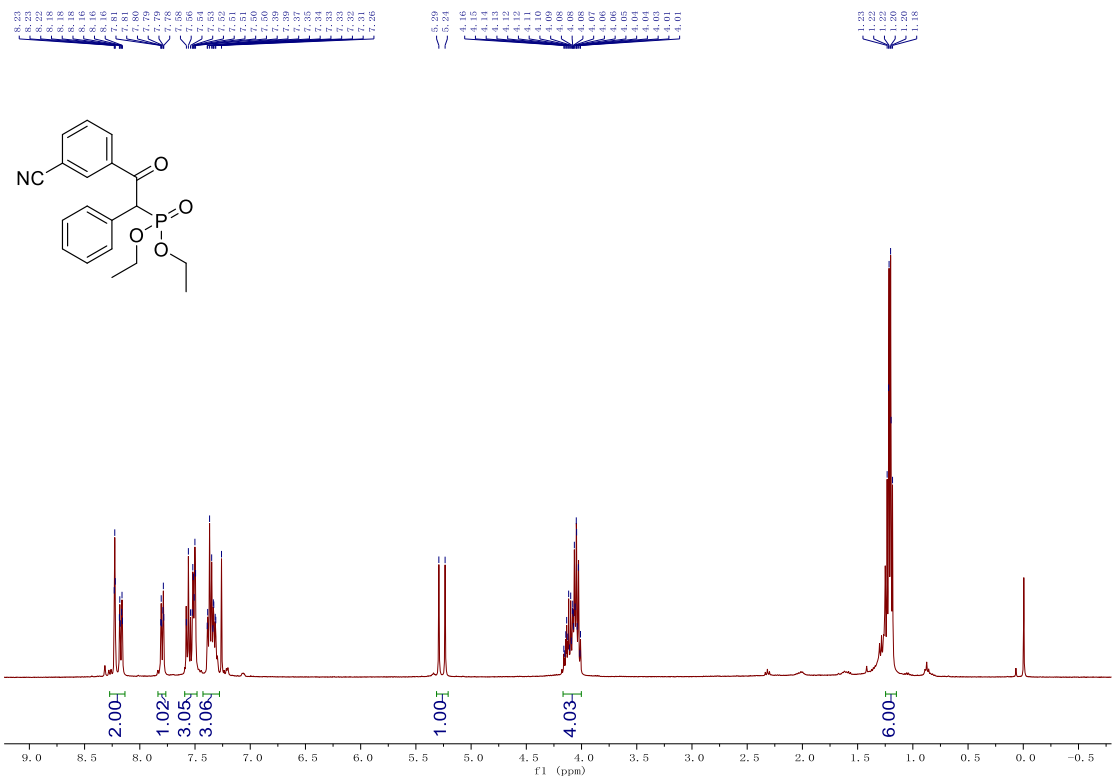

Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r**

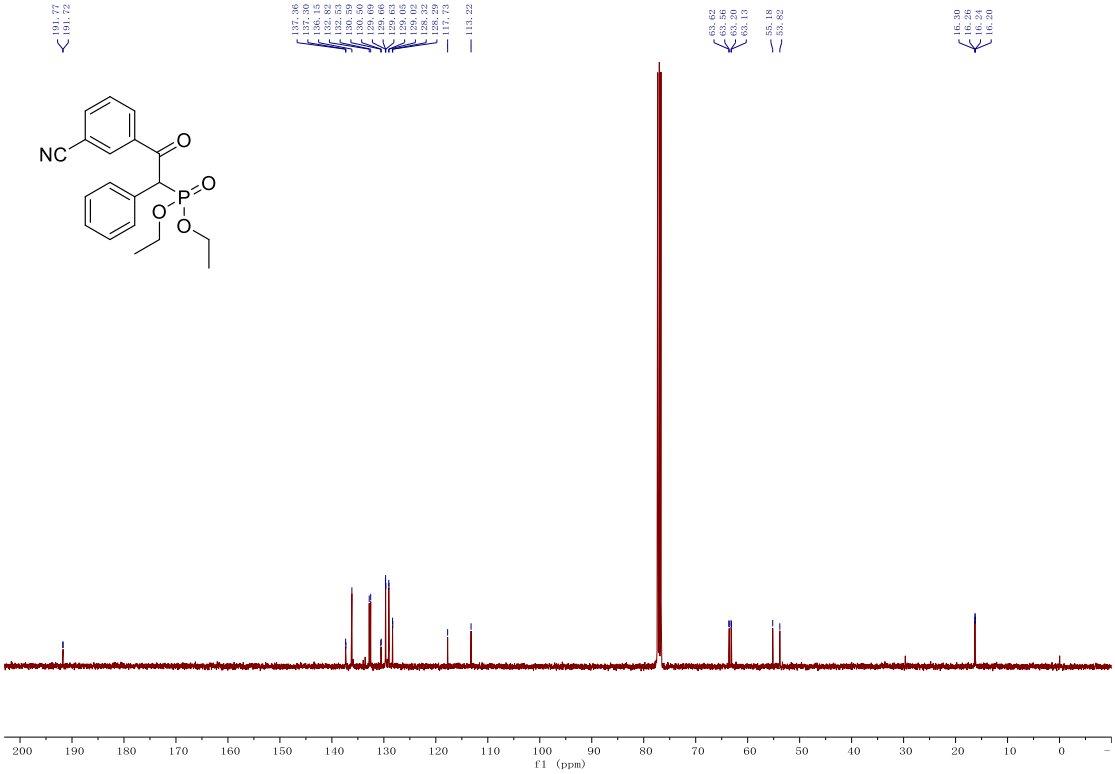

Figure S96. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3r**

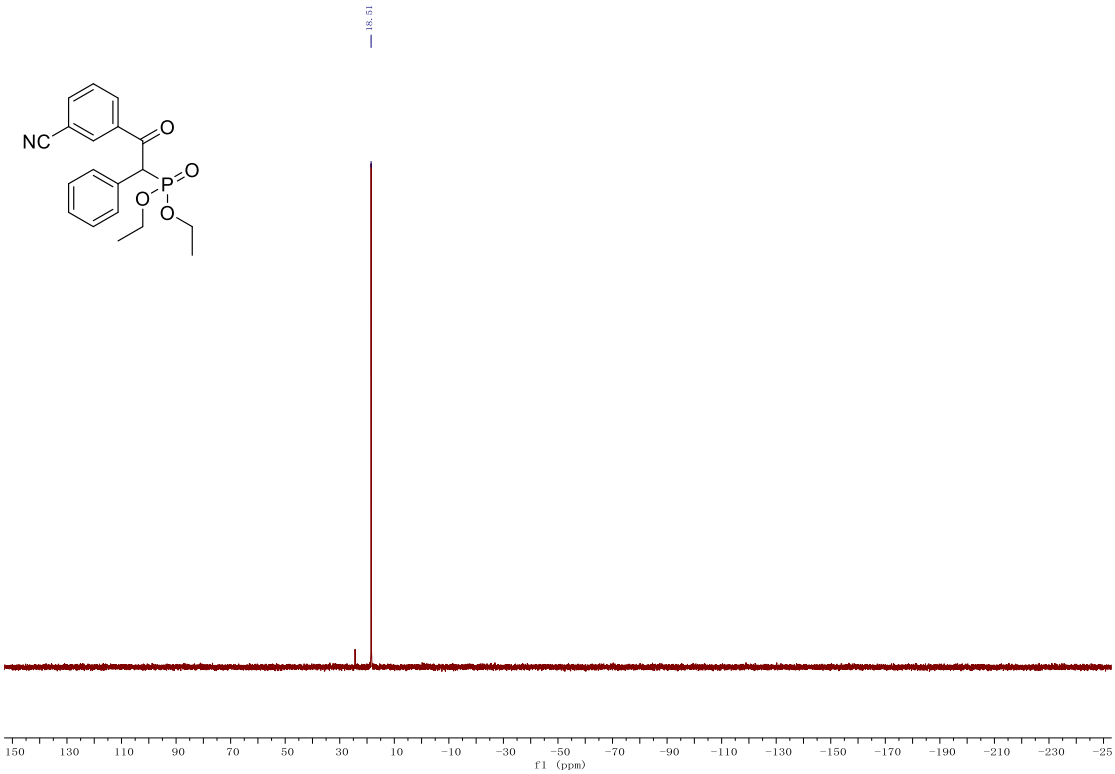

Figure S97. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3r**

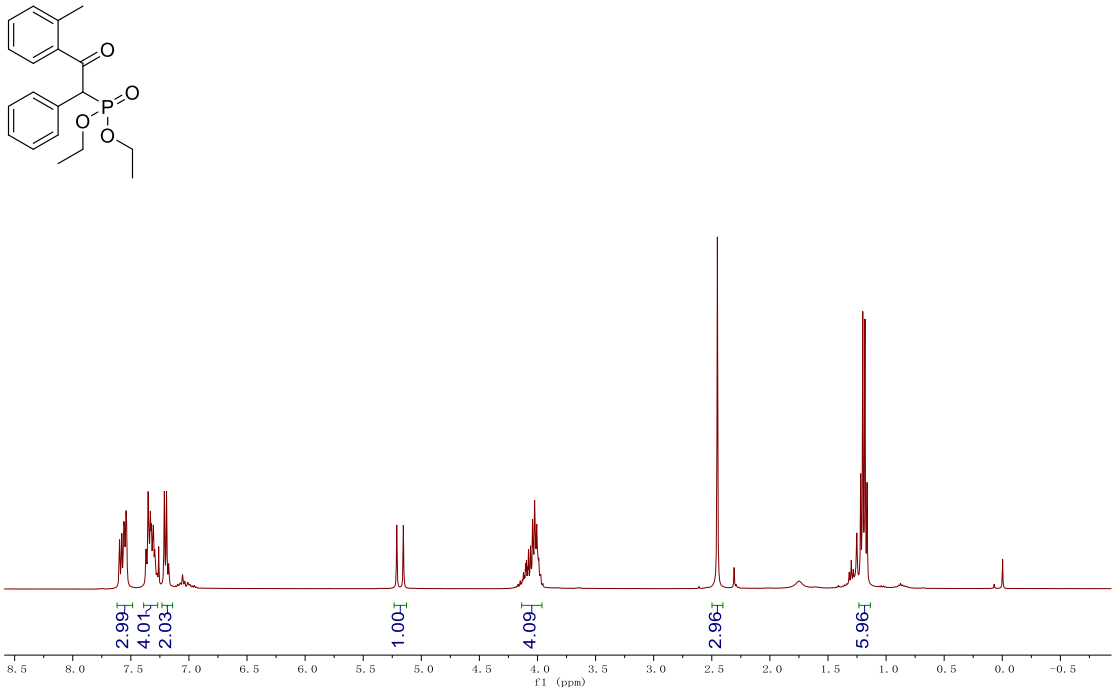

Figure S98. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3s**

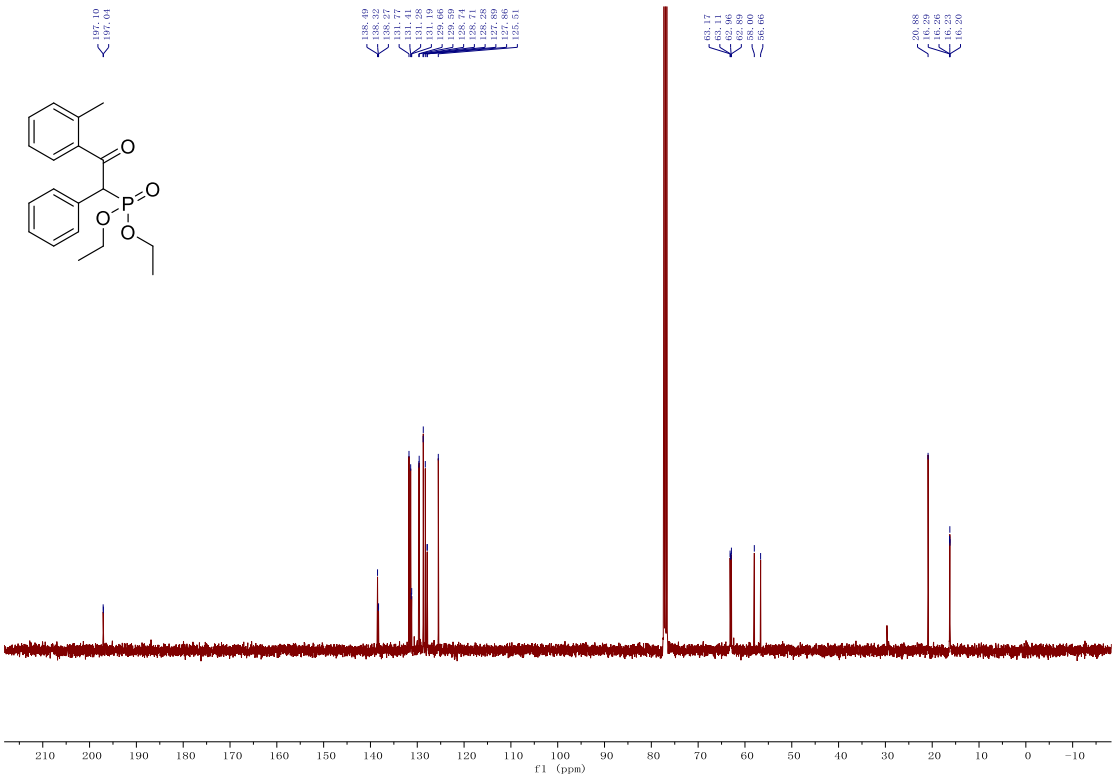

Figure S99. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3s**

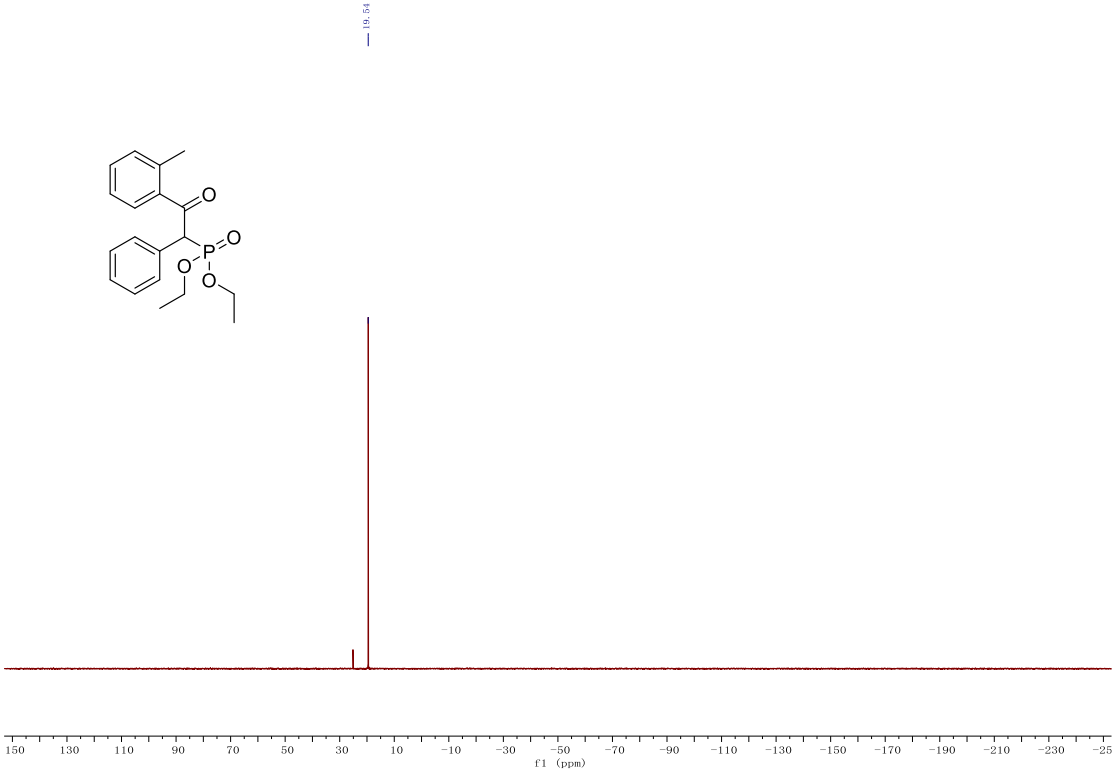

Figure S100. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3s**

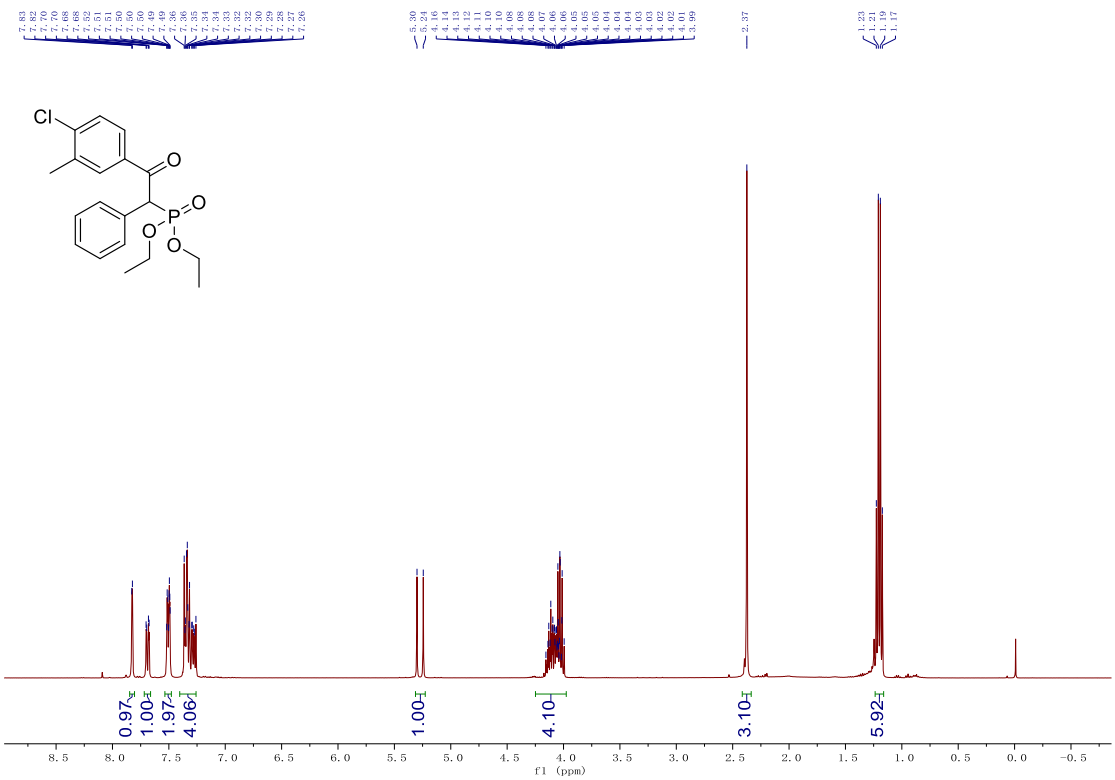

Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3t**

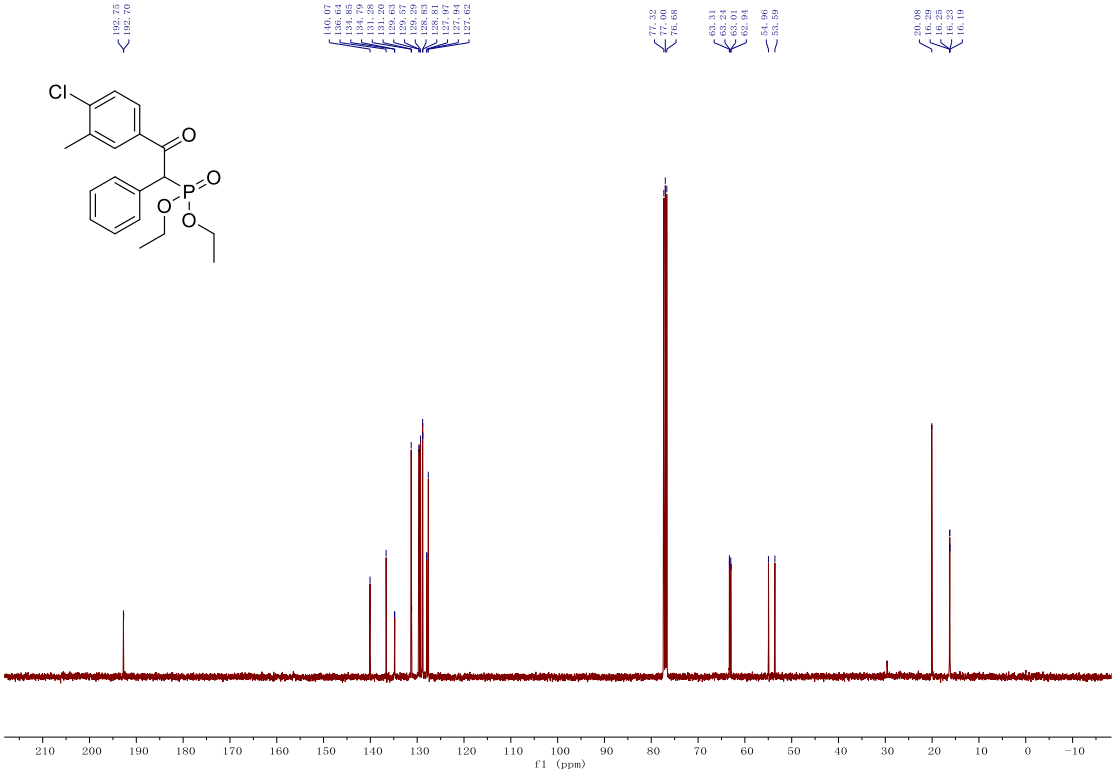

Figure S102. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3t**

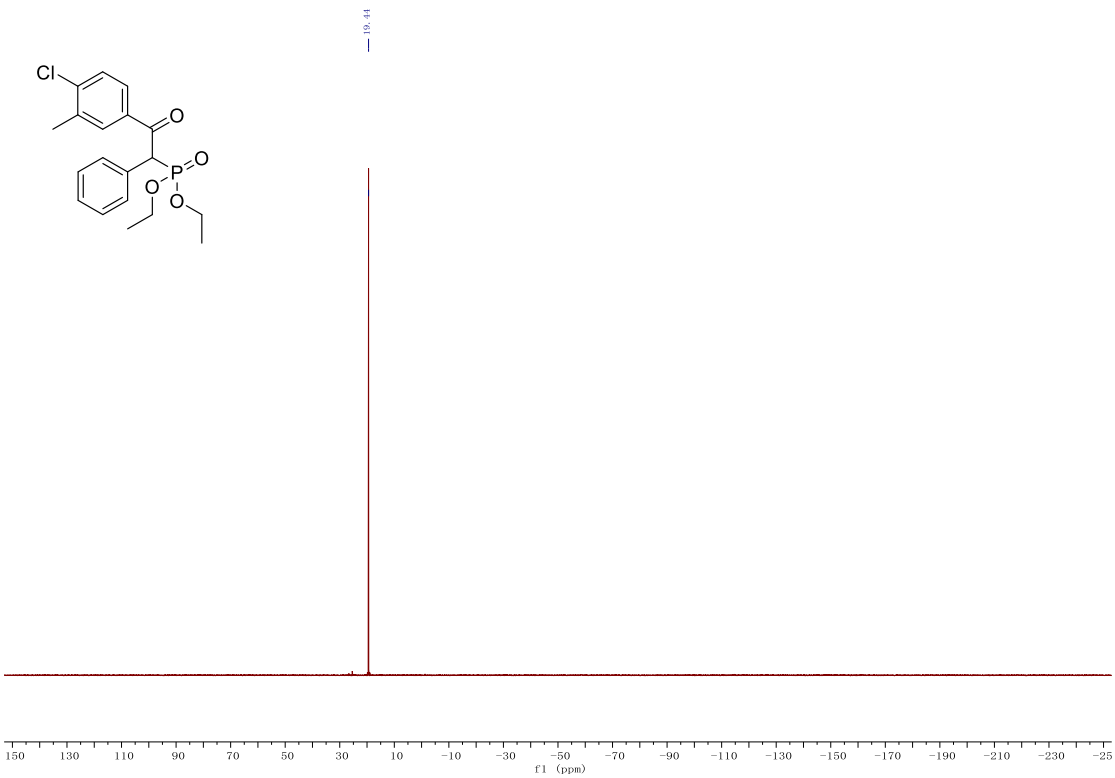

Figure S103. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3t**

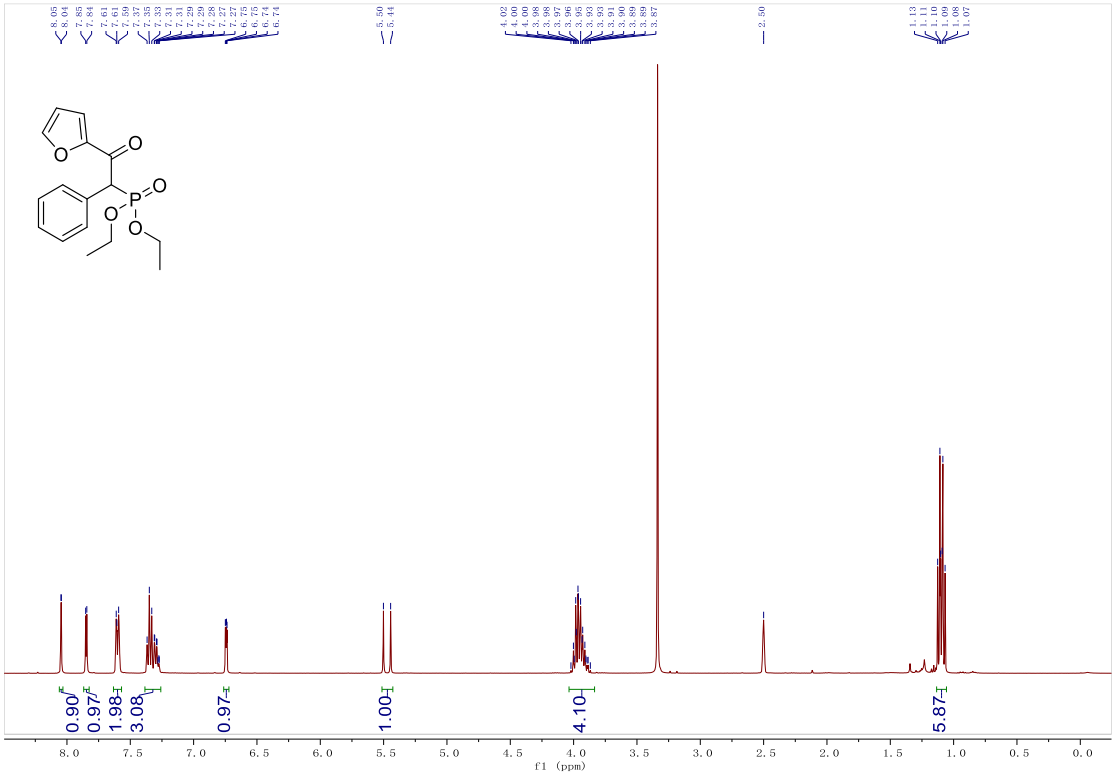

Figure S104. ^{1}**H NMR** (400 MHz, DMSO) spectrum of **3u**

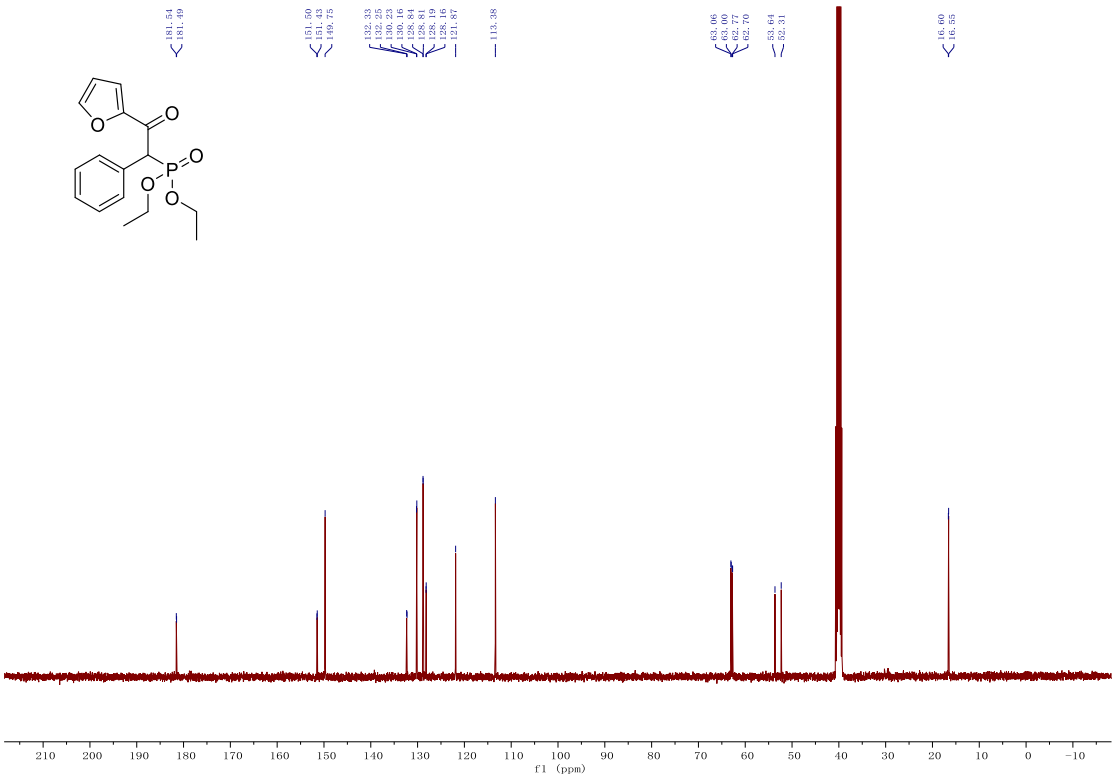

Figure S105. ^{13}**C NMR** (101 MHz, DMSO) spectrum of **3u**

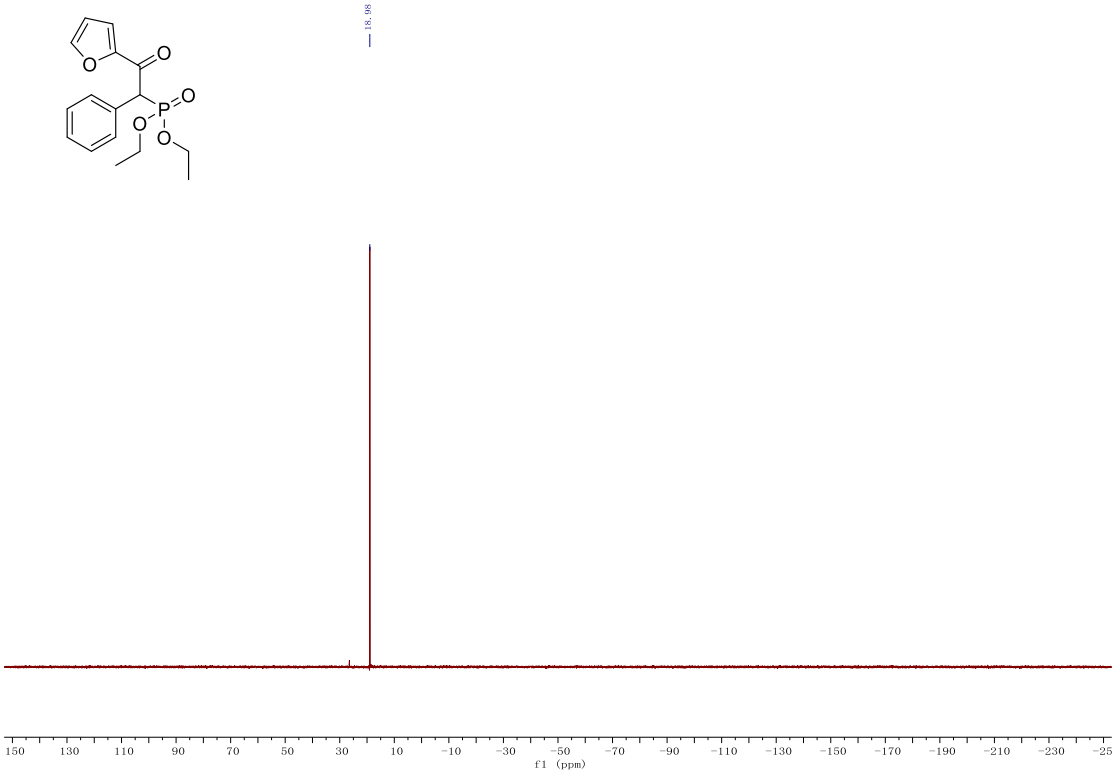

Figure S106. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **3u**

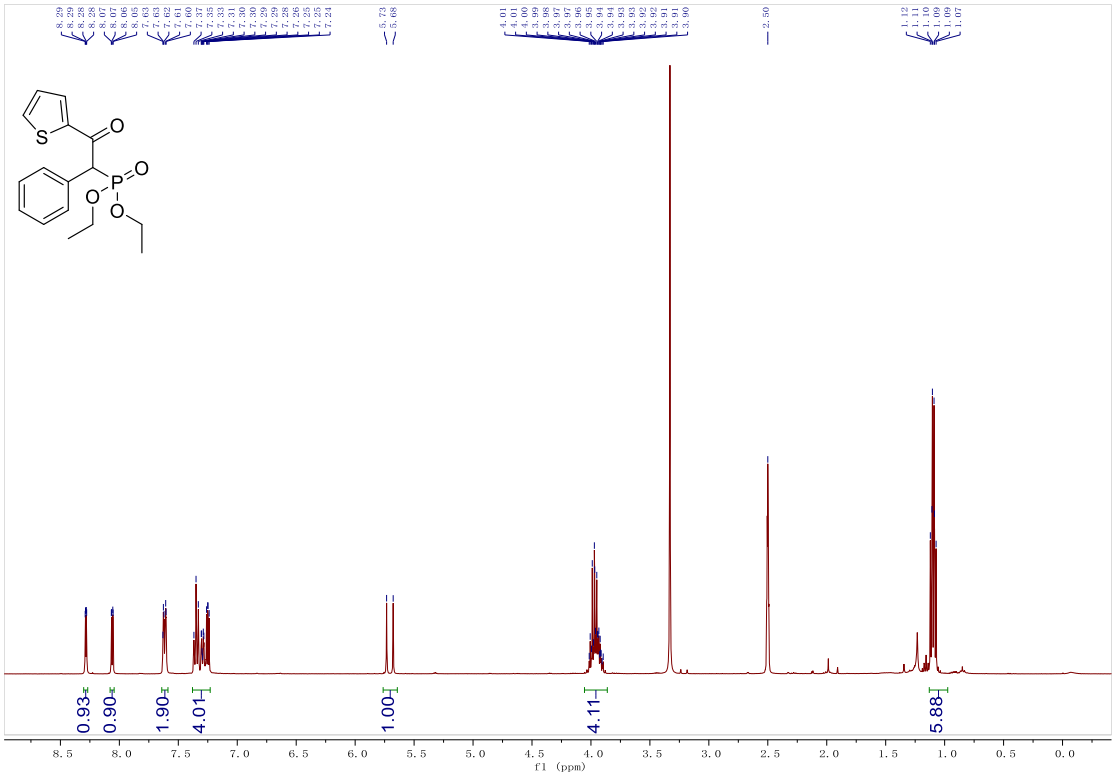

Figure S107. ^{1}**H NMR** (400 MHz, DMSO) spectrum of **3v**

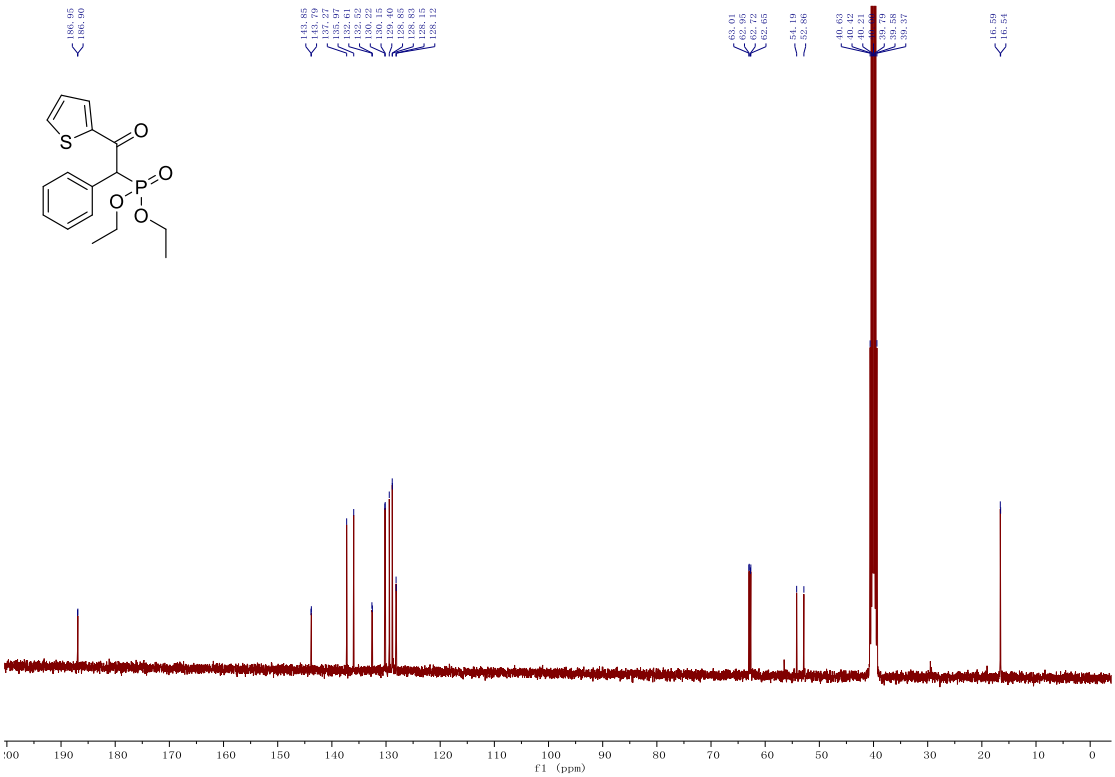

Figure S108. ^{13}**C NMR** (101 MHz, DMSO) spectrum of **3v**

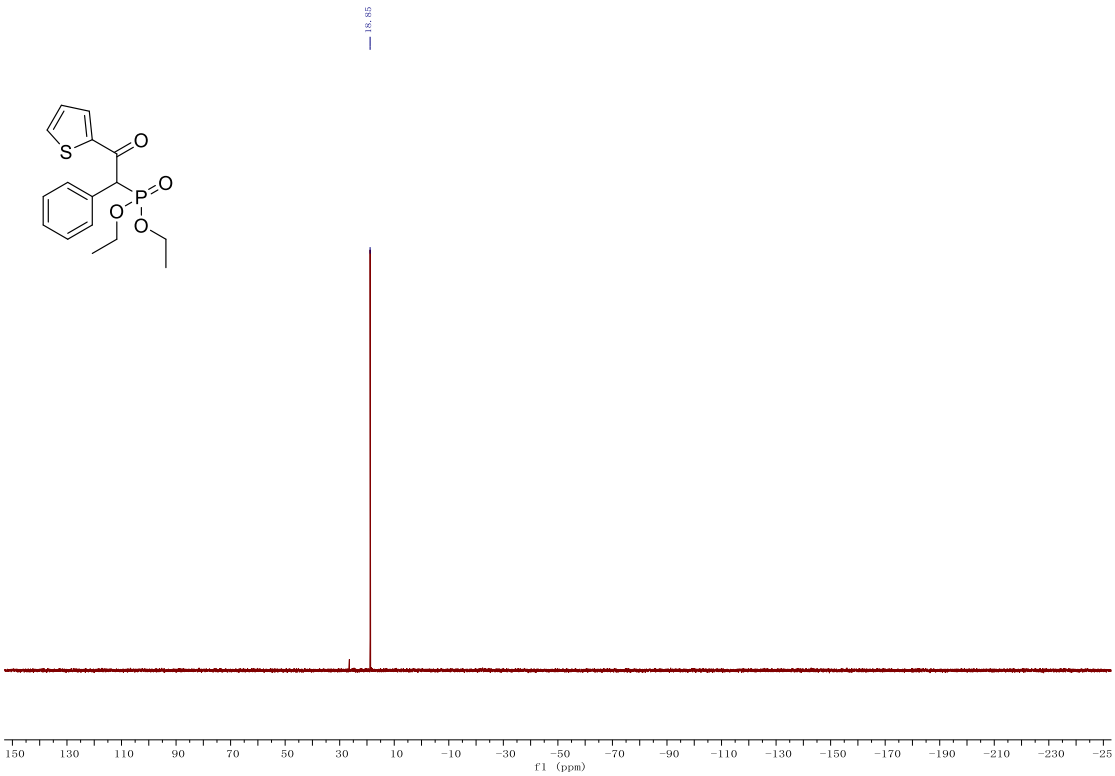

Figure S109. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3v**

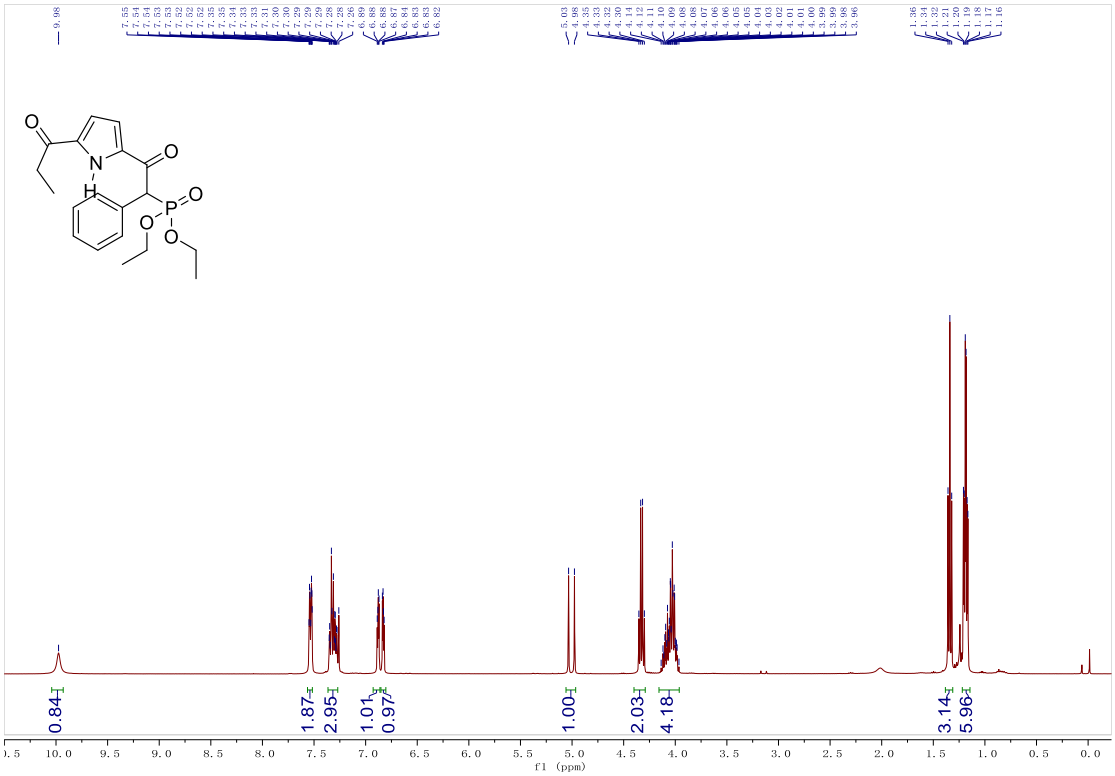

Figure S110. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3w**

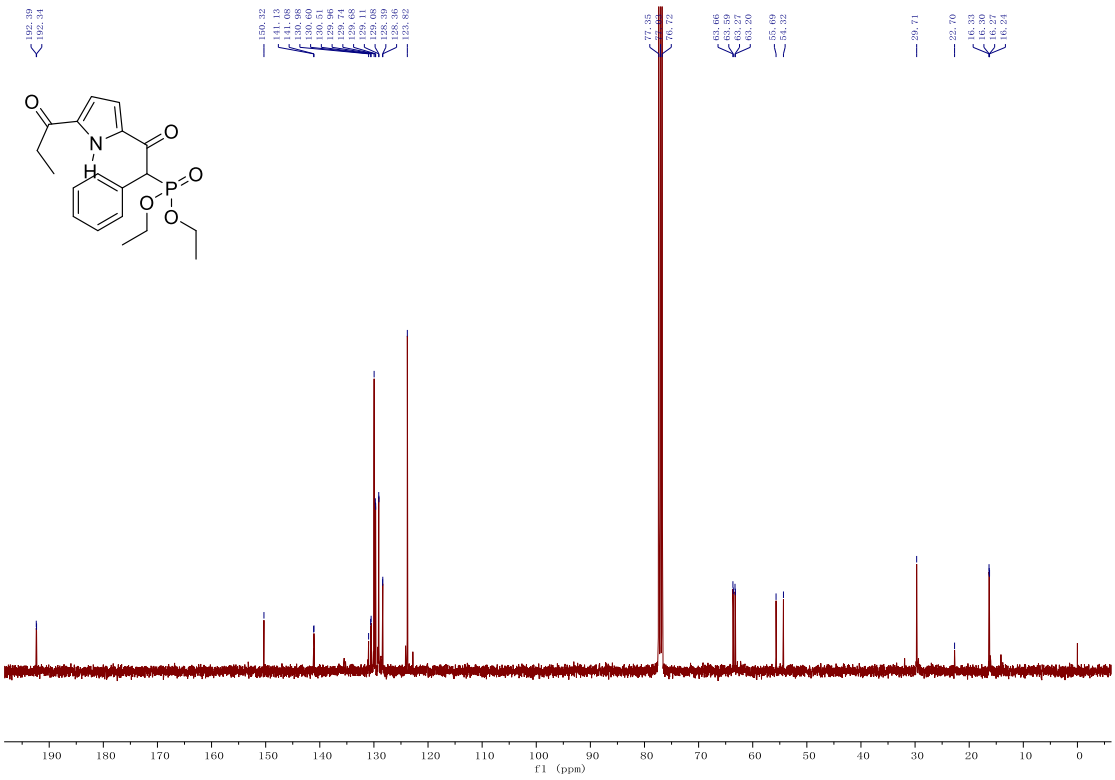

Figure S111. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3w**

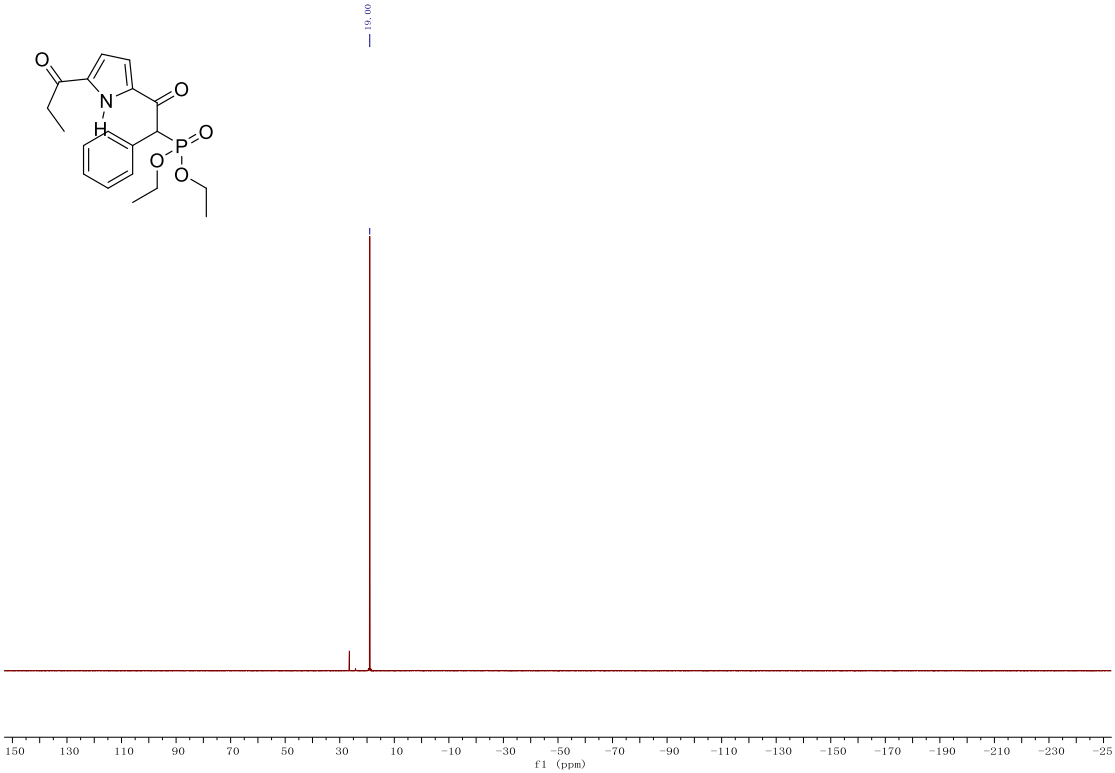

Figure S112. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3w**

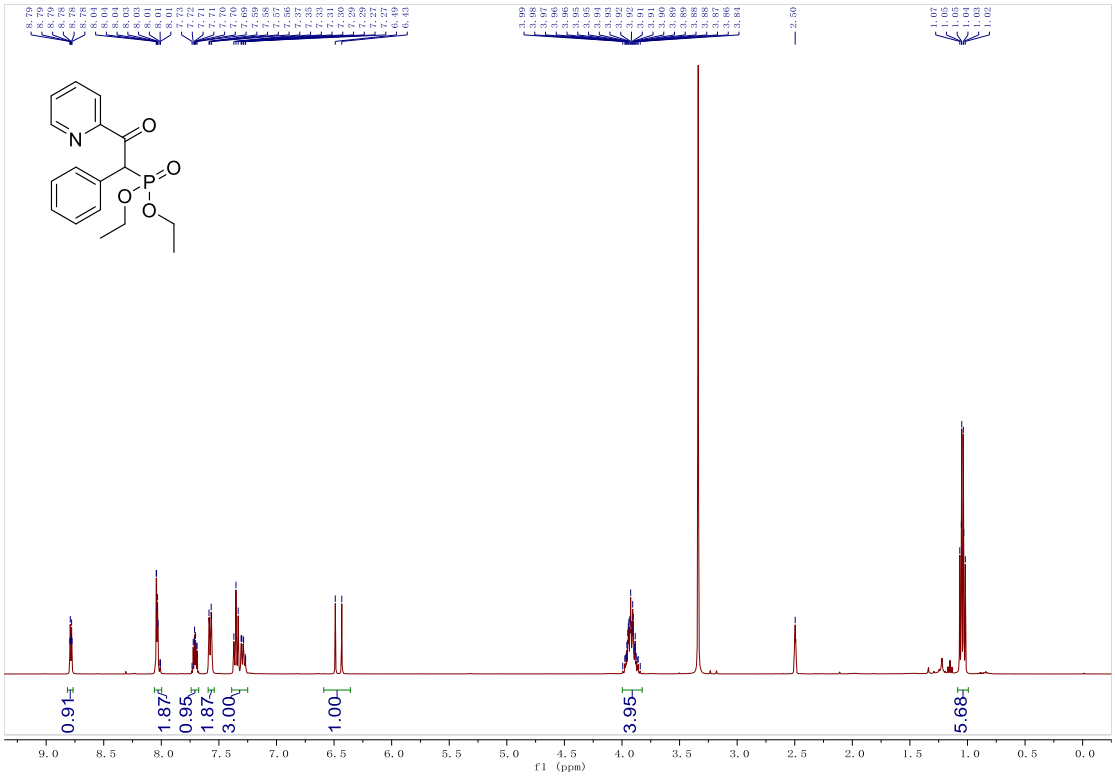

Figure S113. ^{1}H NMR (400 MHz, DMSO) spectrum of **3x**

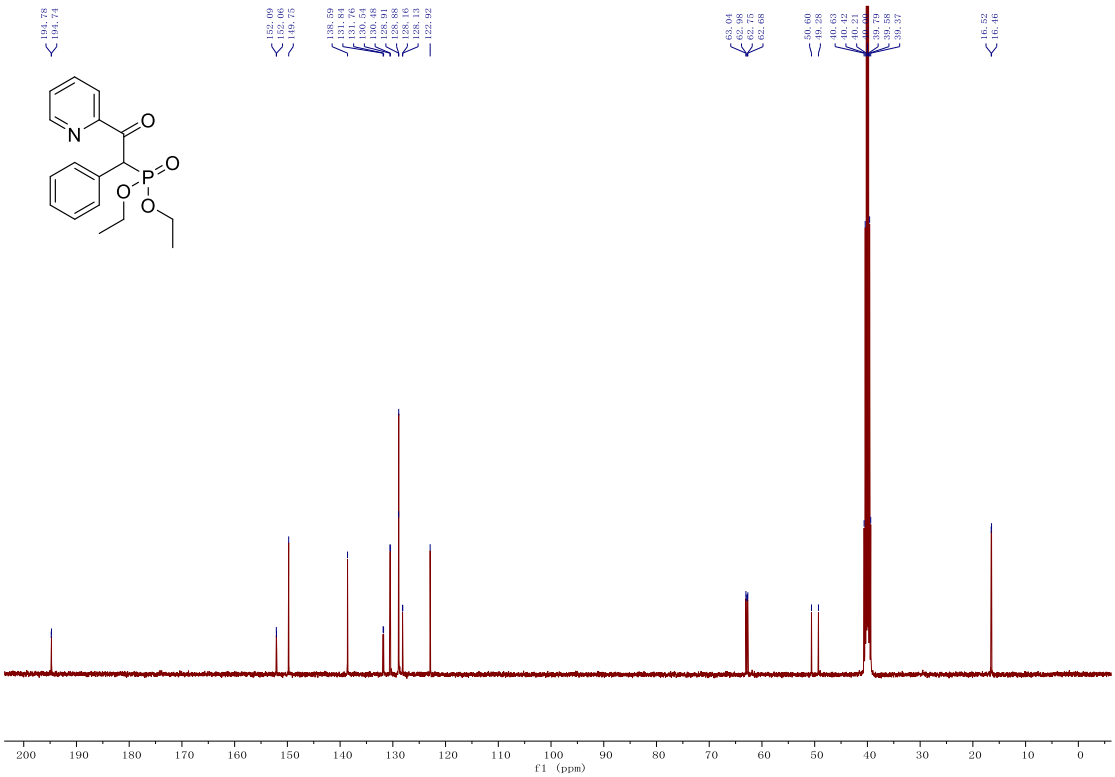

Figure S114. ^{13}C NMR (101 MHz, DMSO) spectrum of **3x**

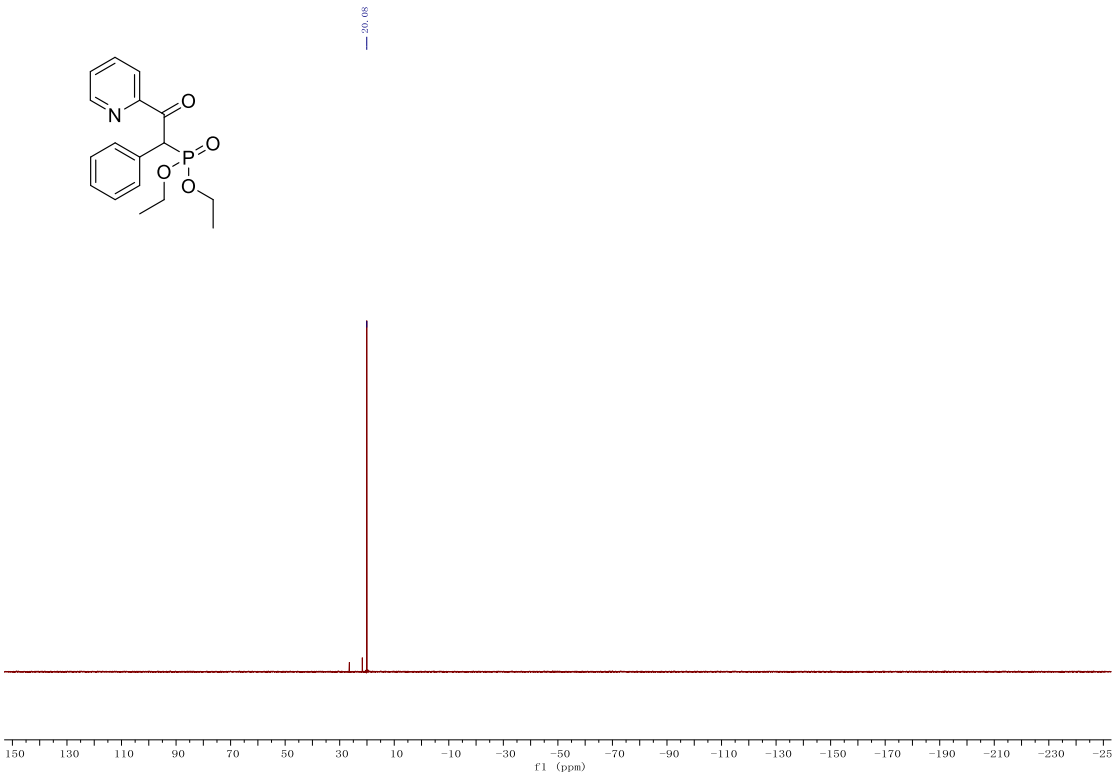

Figure S115. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3x**

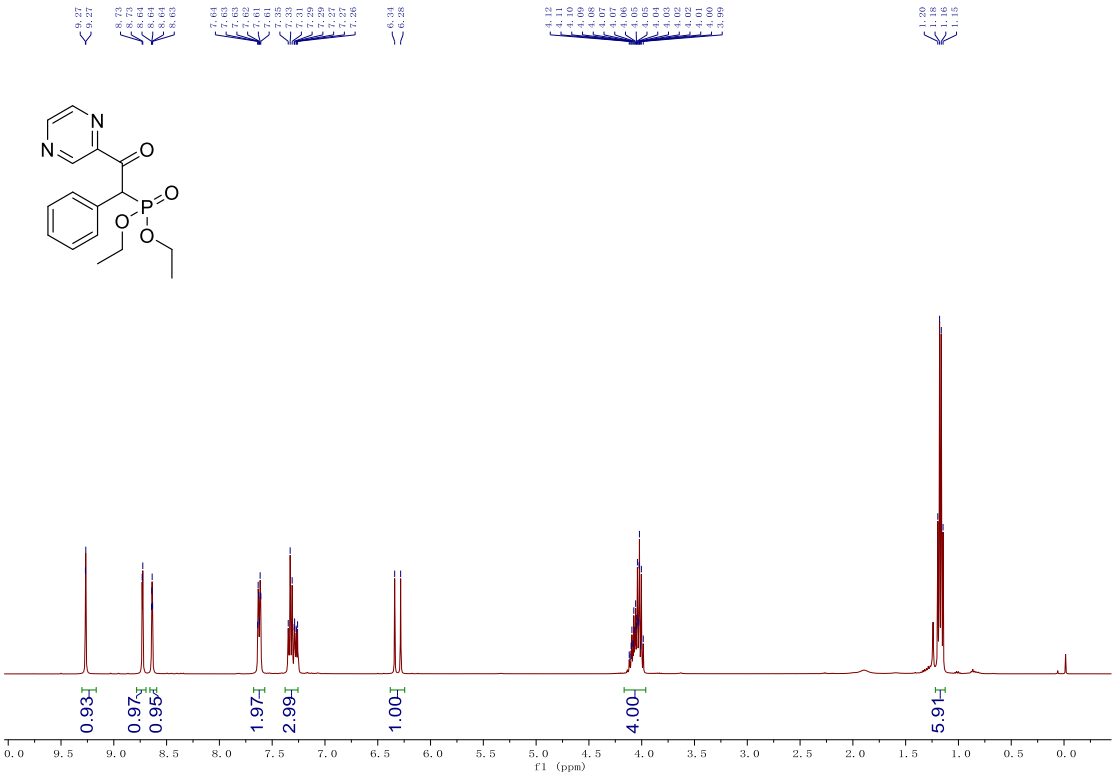

Figure S116. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3y**

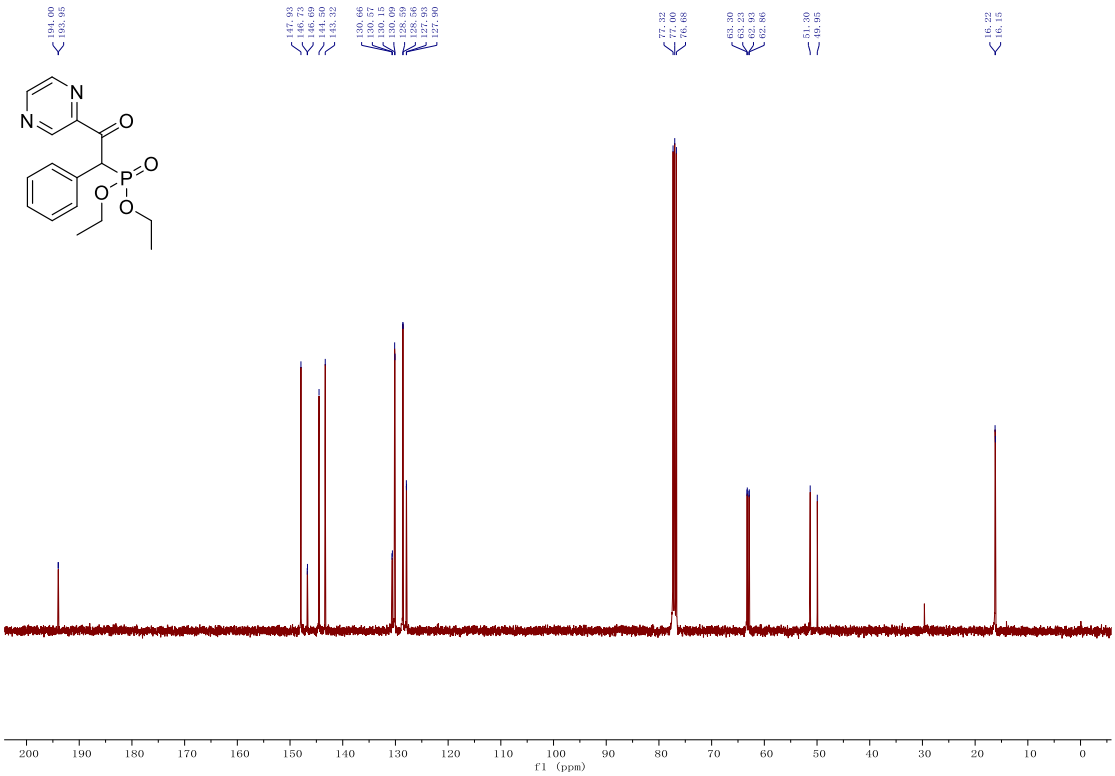

Figure S117. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3y**

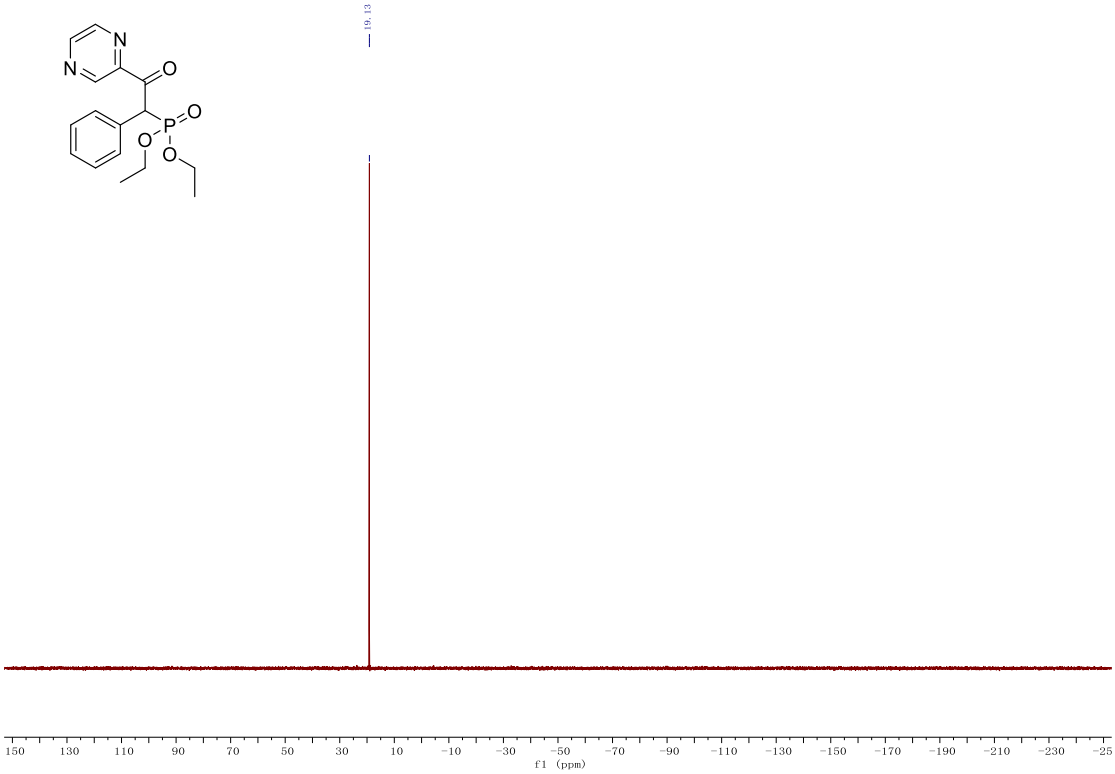

Figure S118. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **3y**

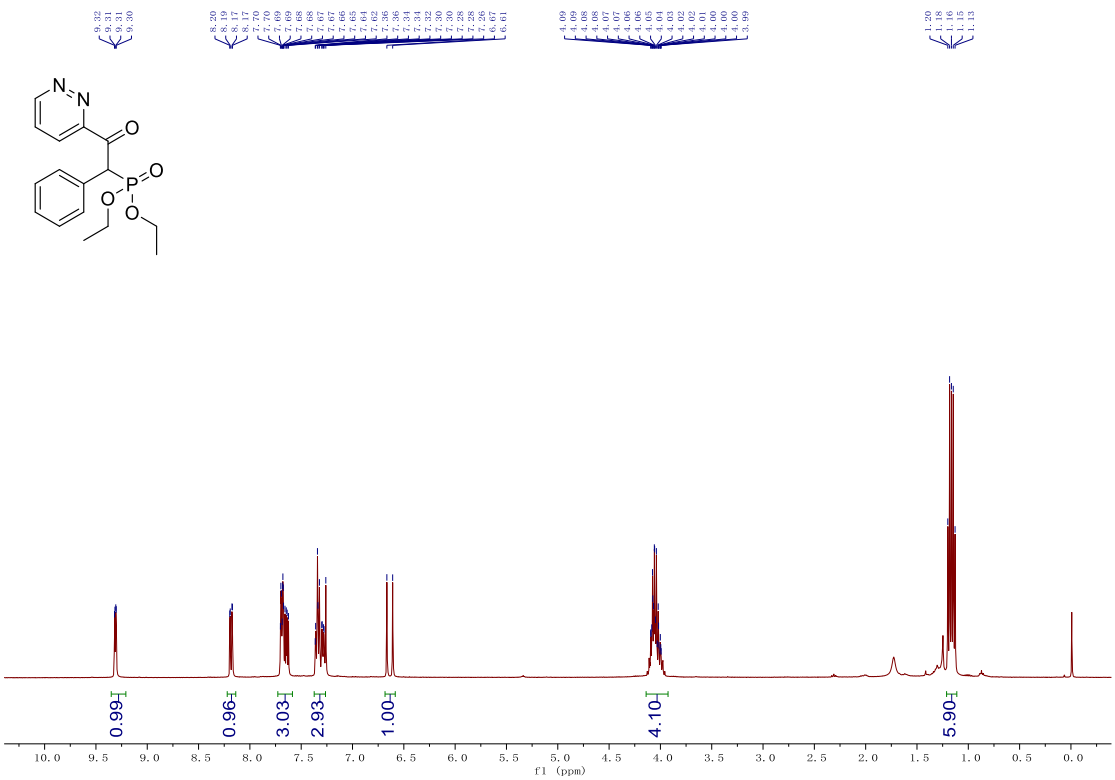

Figure S119. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3z**

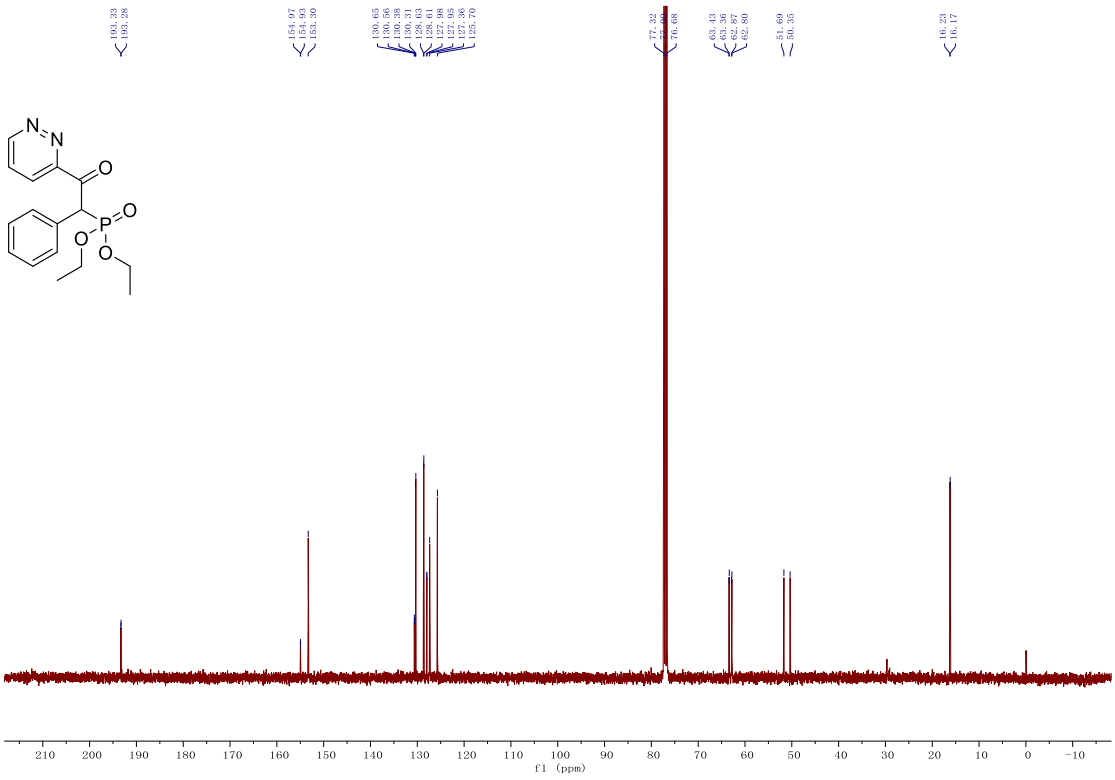

Figure S120. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3z**

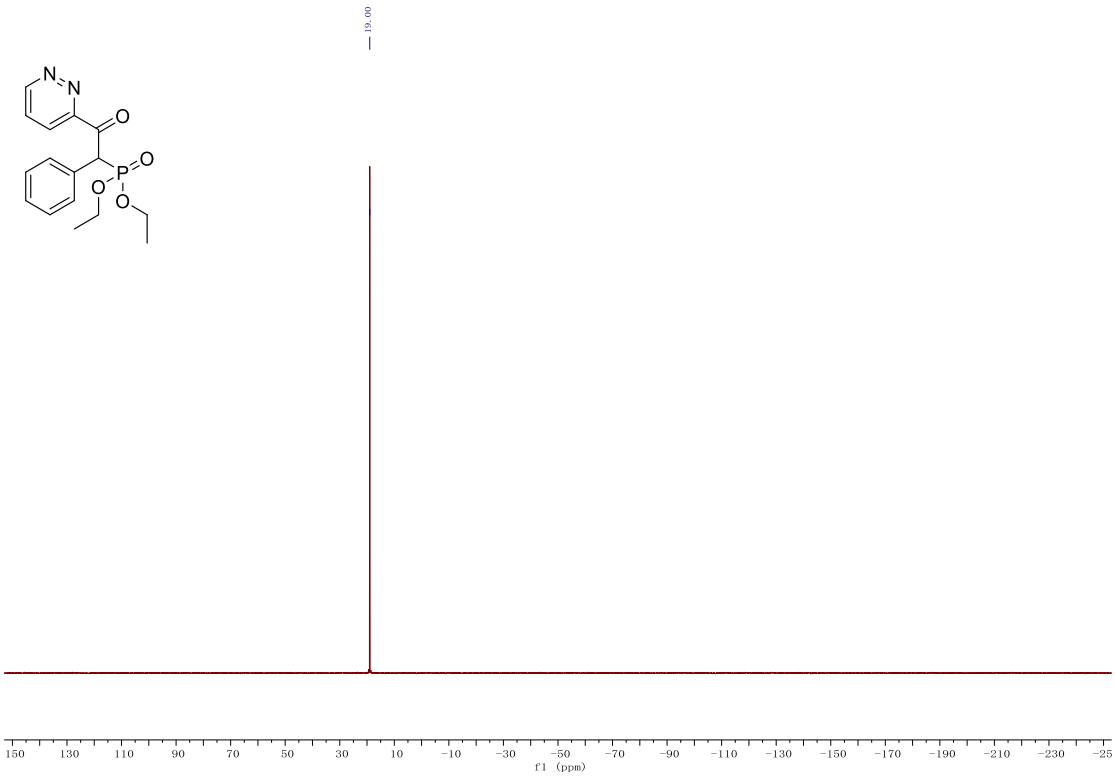

Figure S121. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3z**

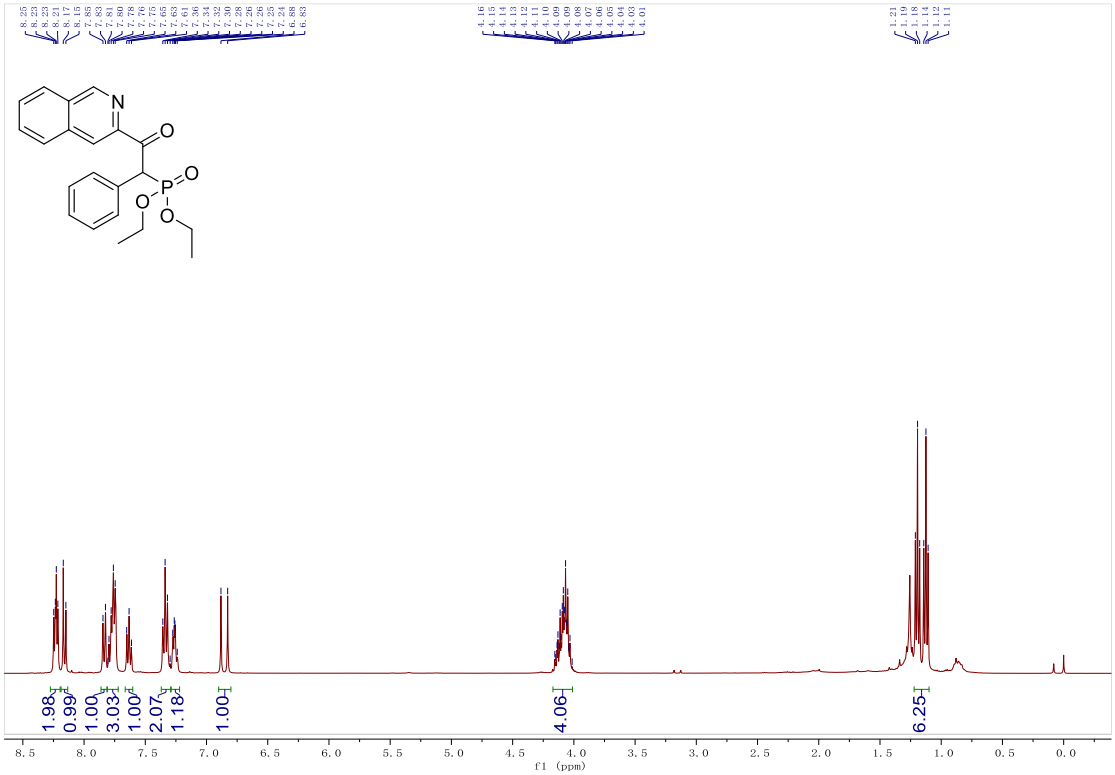

Figure S122. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**

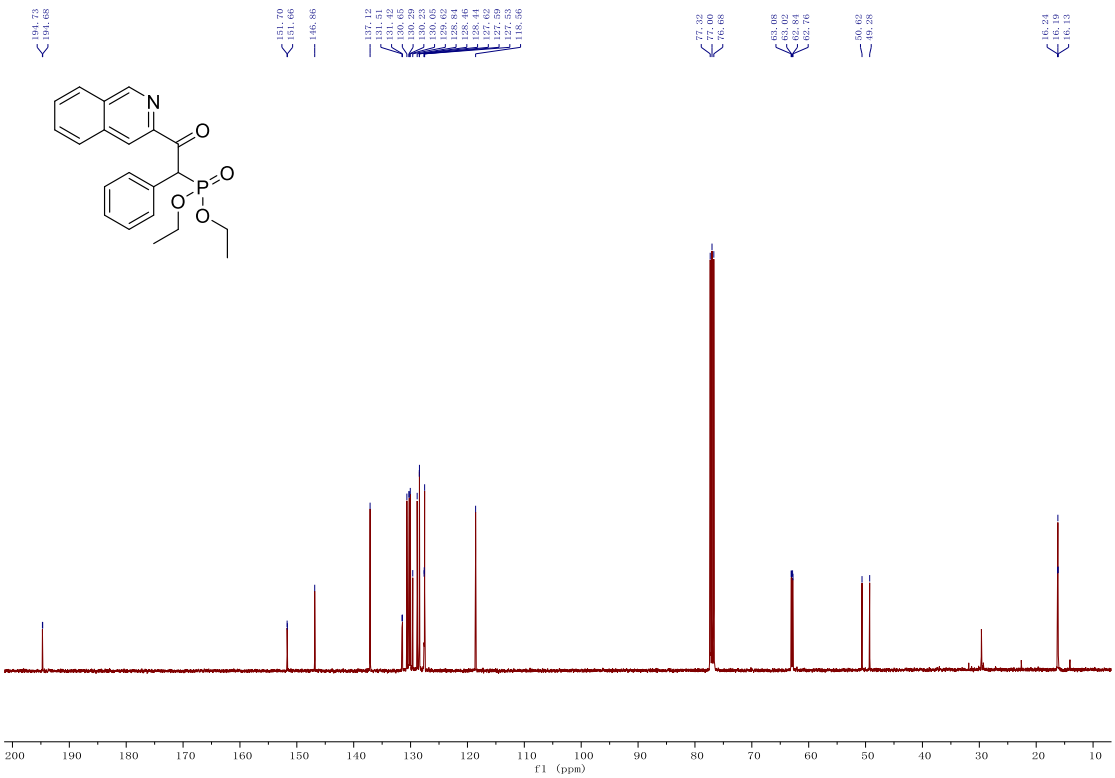

Figure S123. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3aa**

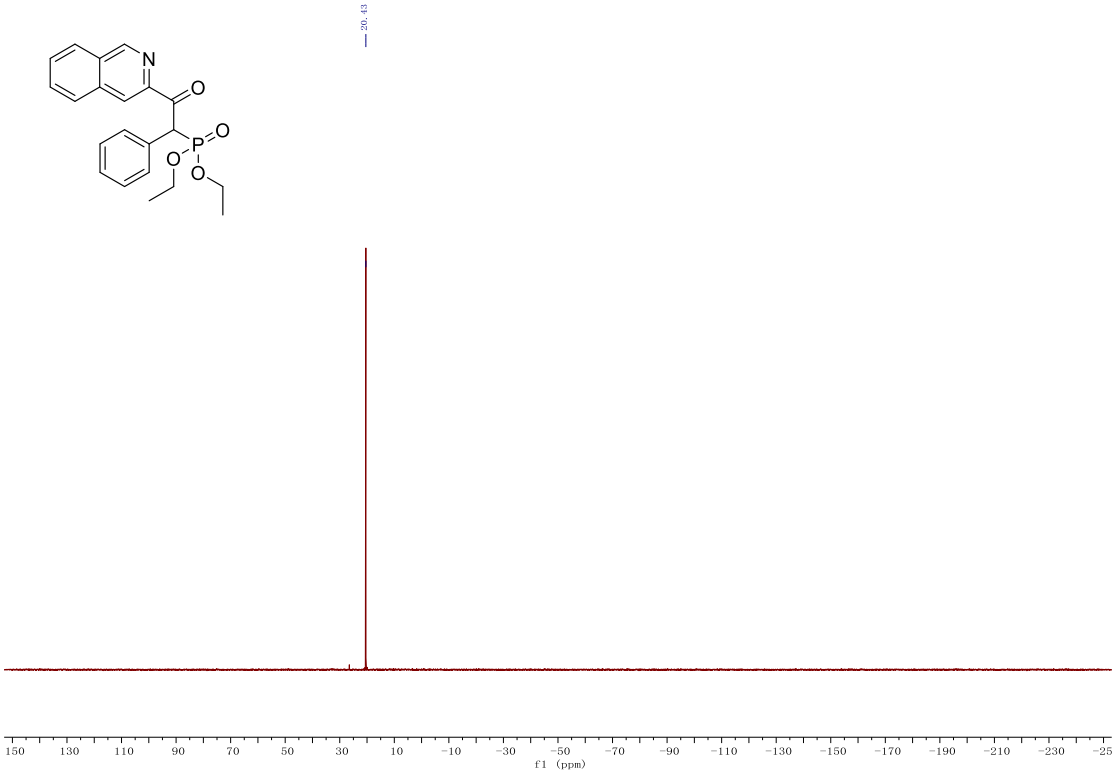

Figure S124. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3aa**

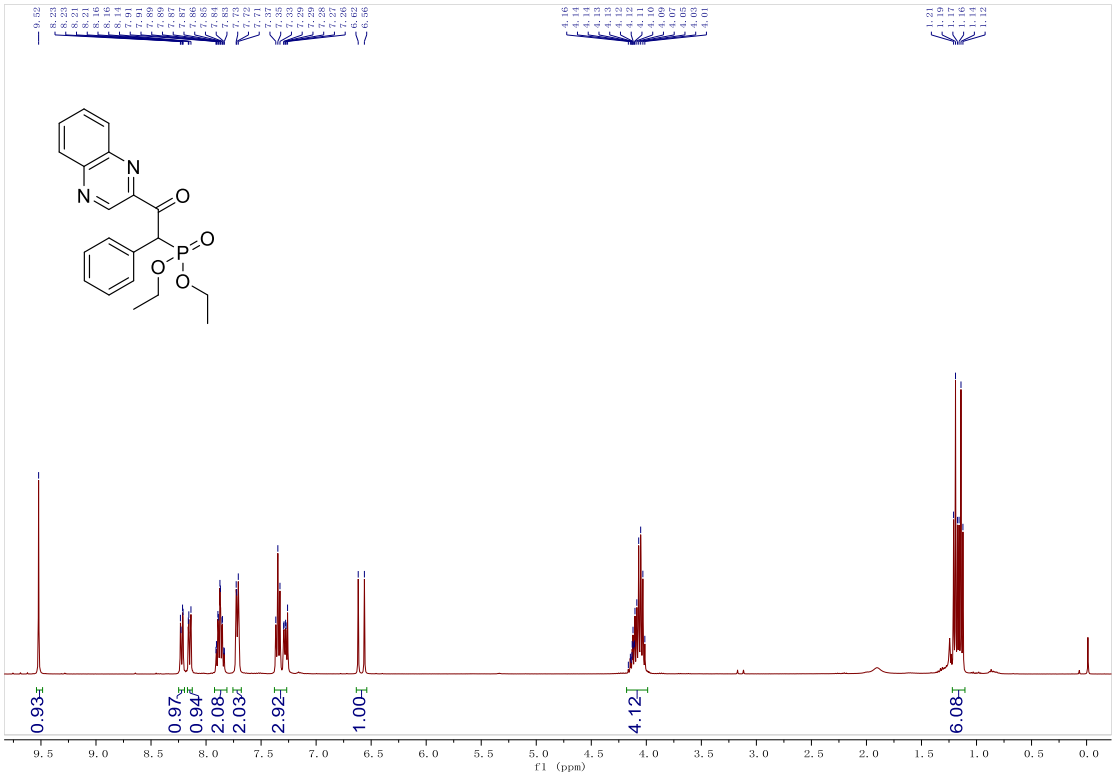

Figure S125. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**

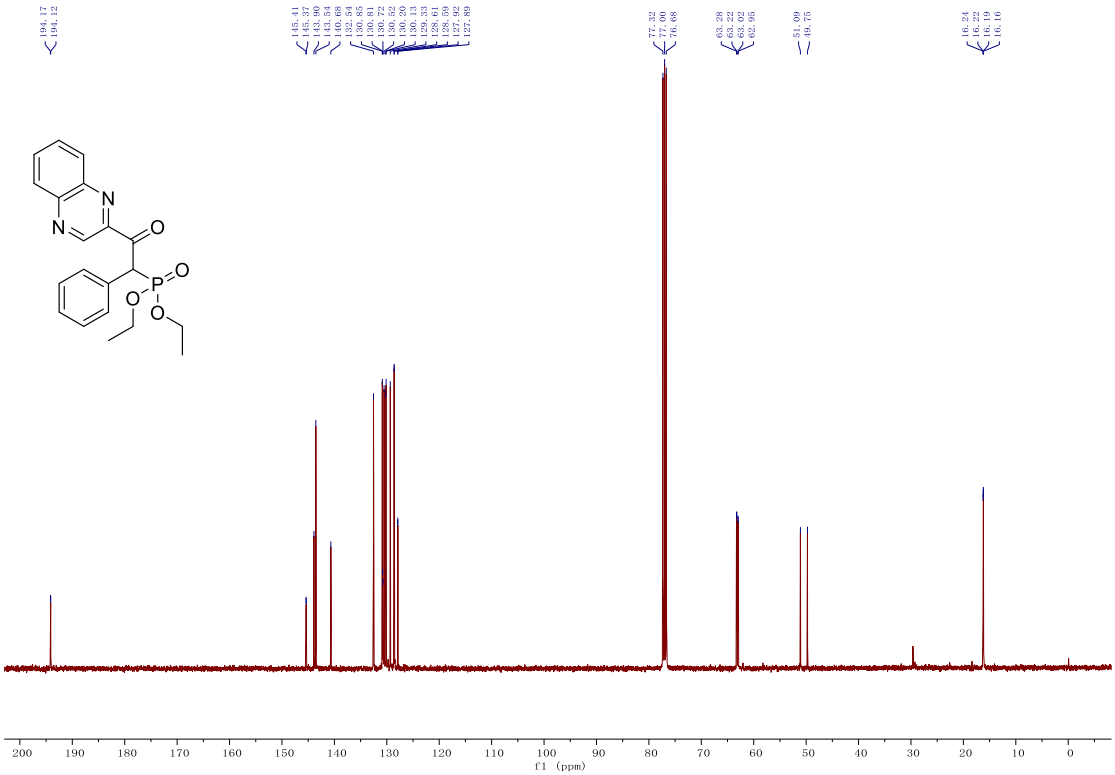

Figure S126. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ab**

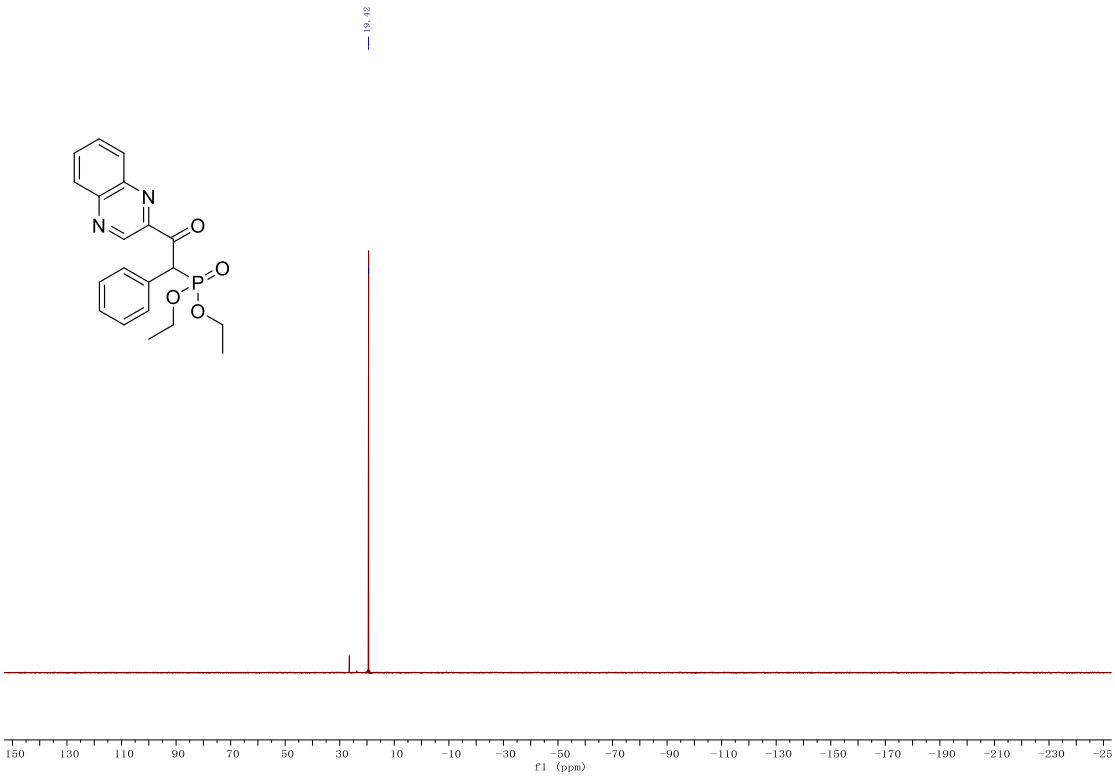

Figure S127. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3ab**

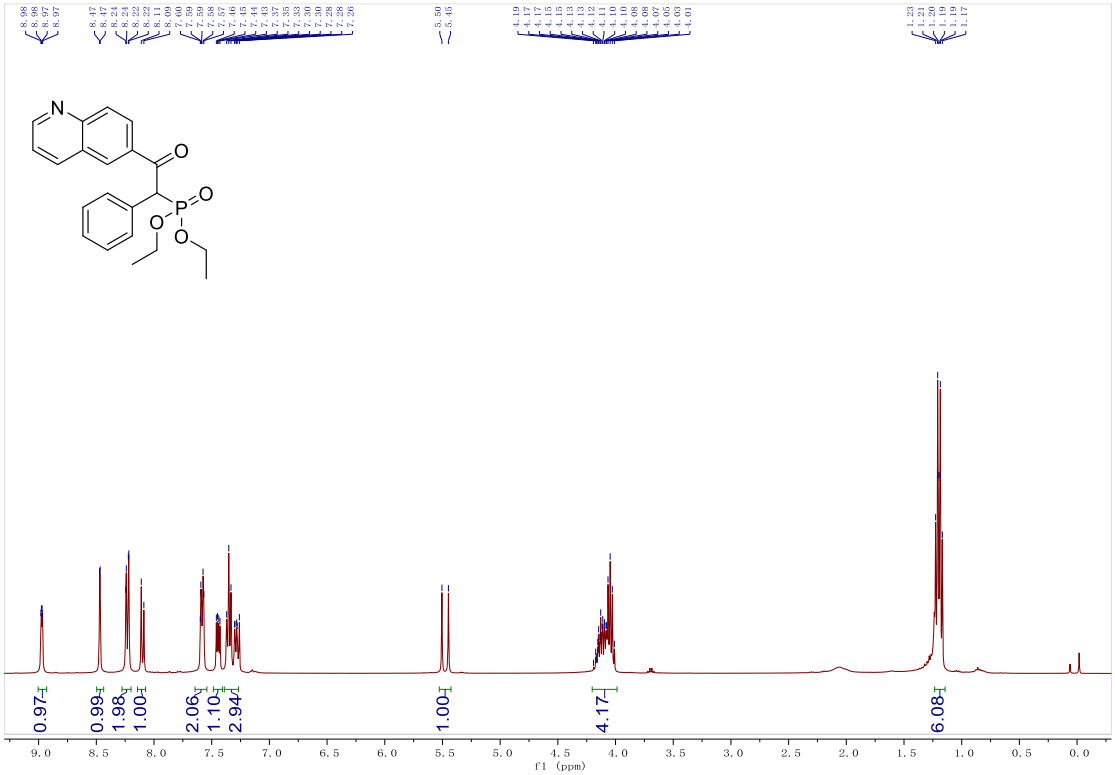

Figure S128. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ac**

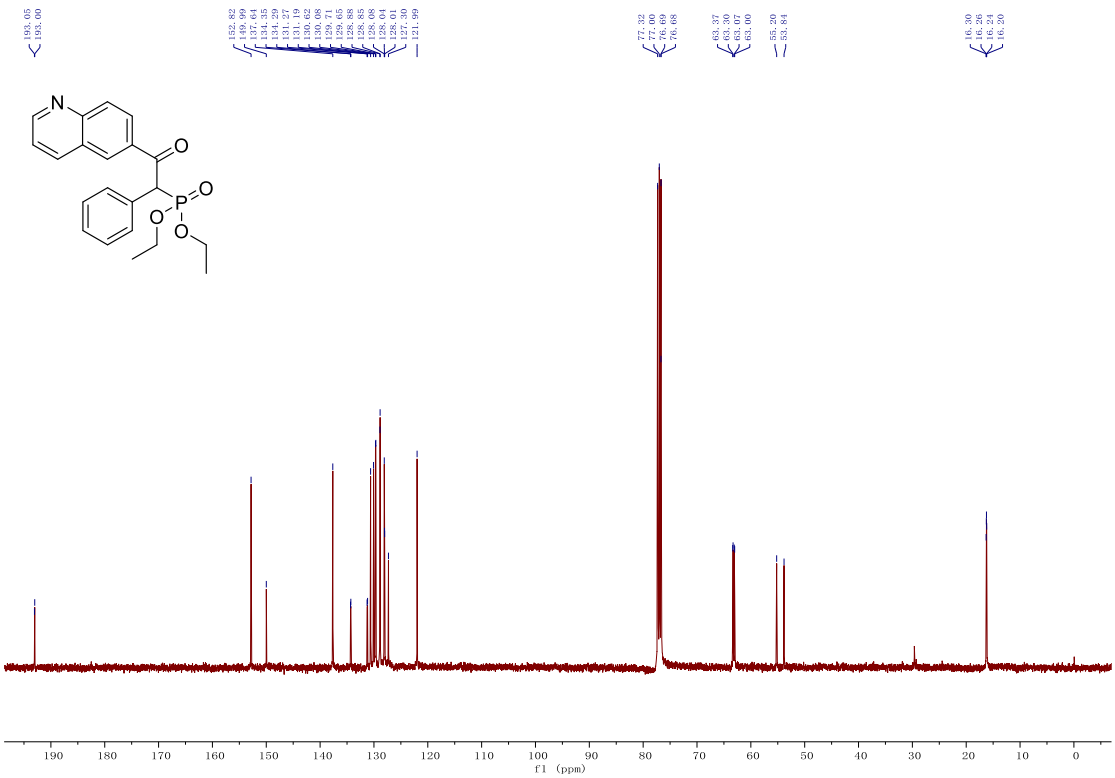

Figure S129. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ac**

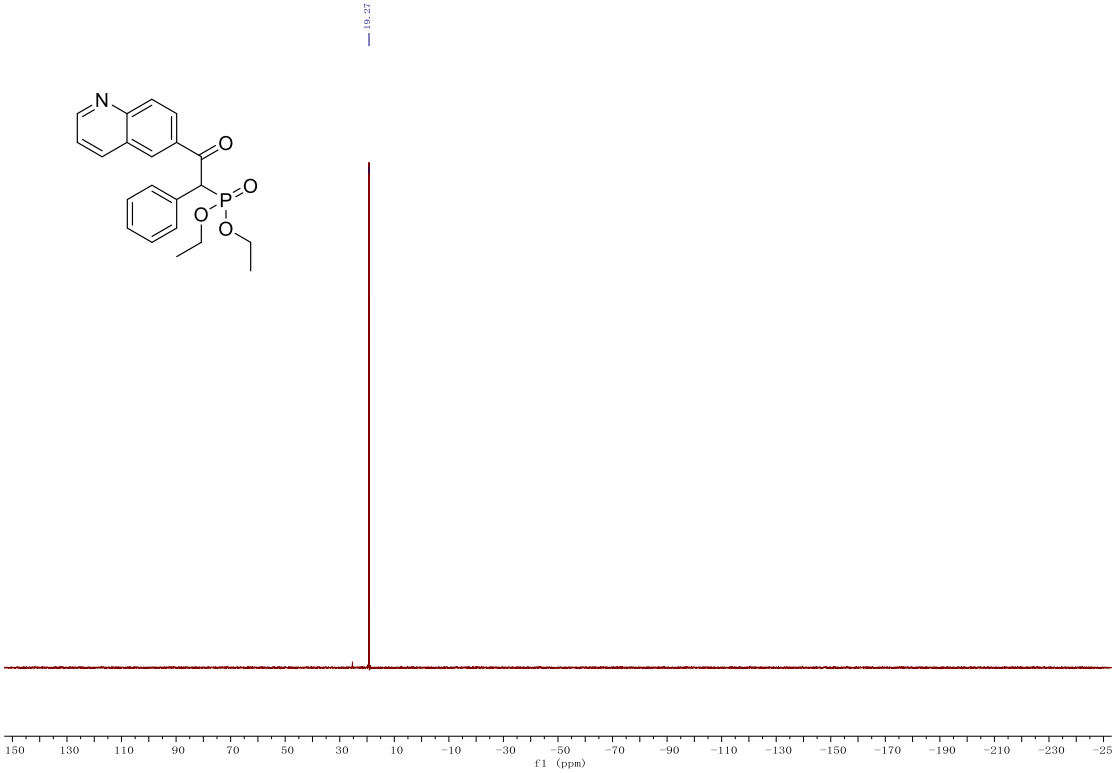

Figure S130. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3ac**

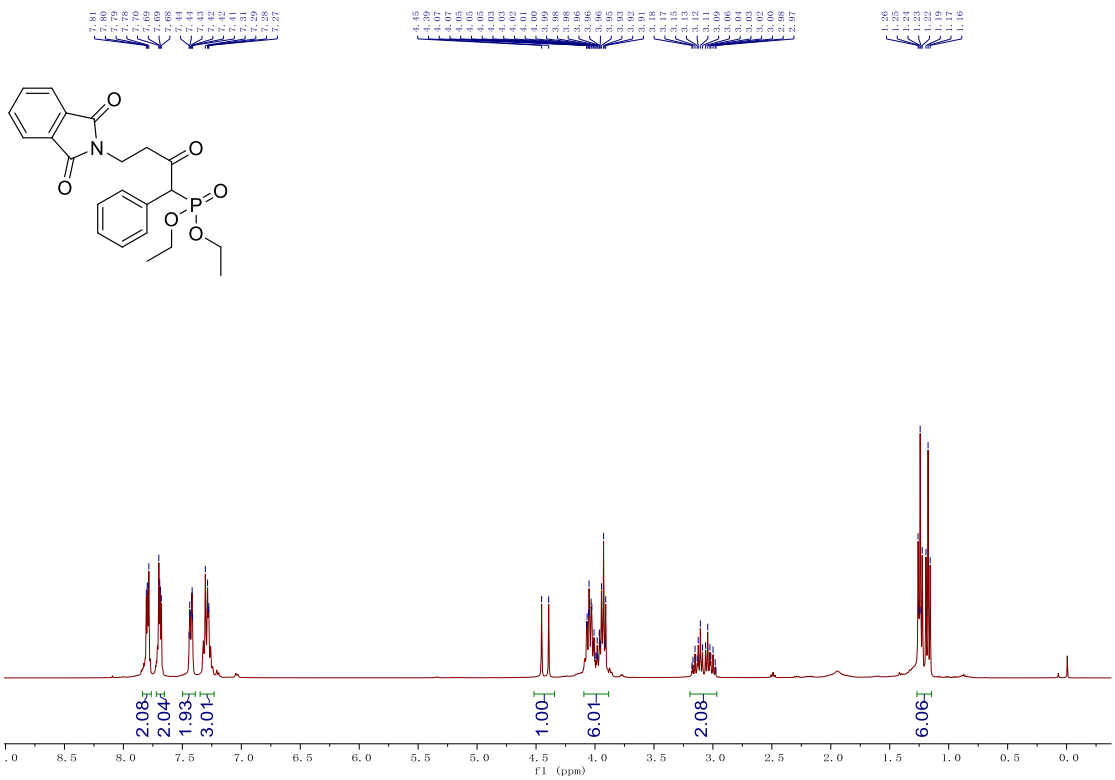

Figure S131. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**

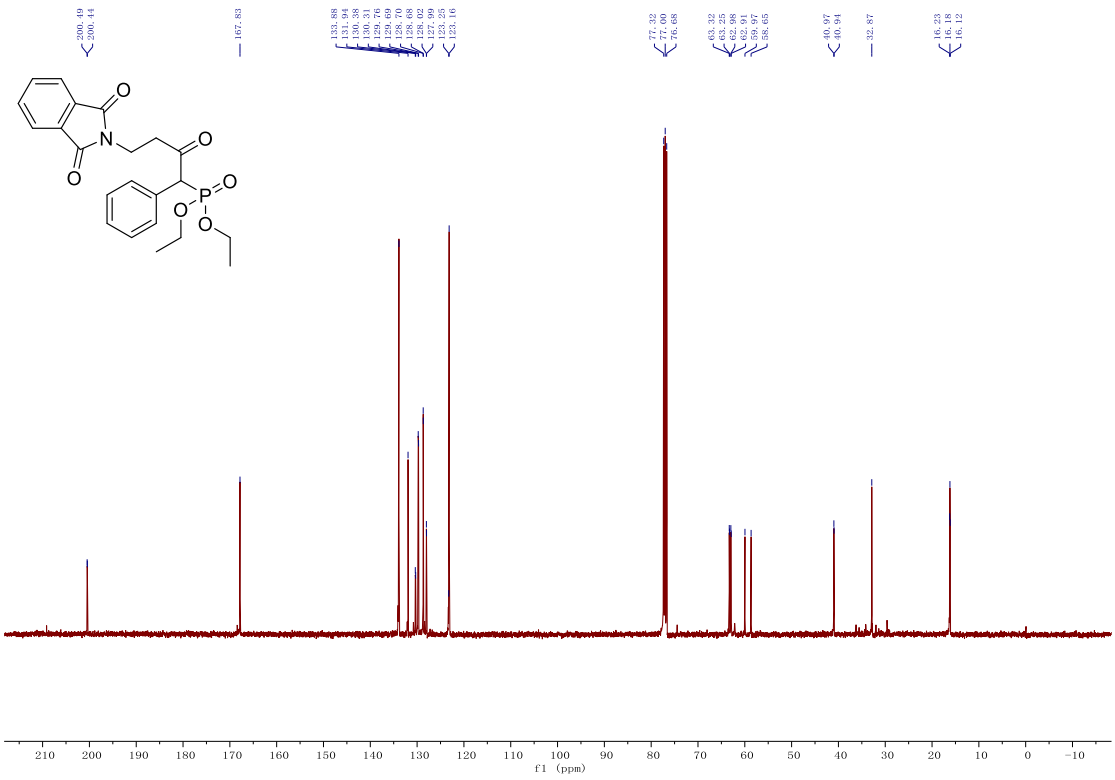

Figure S132. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ad**

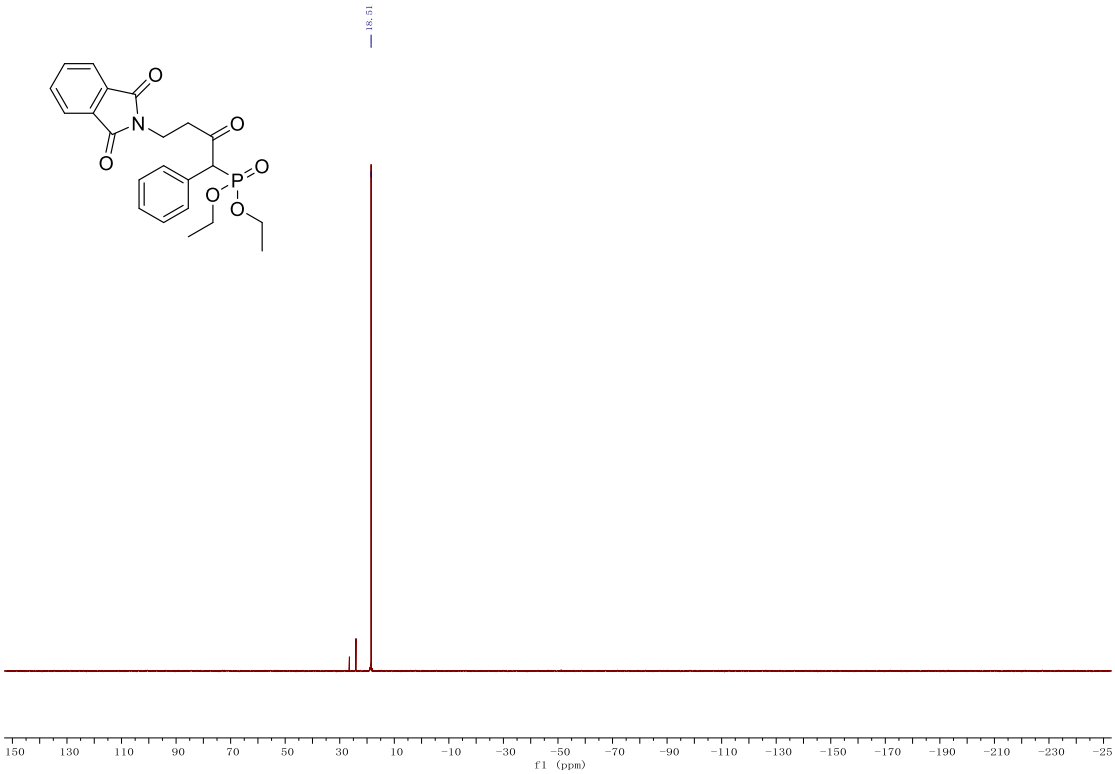

Figure S133. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3ad**

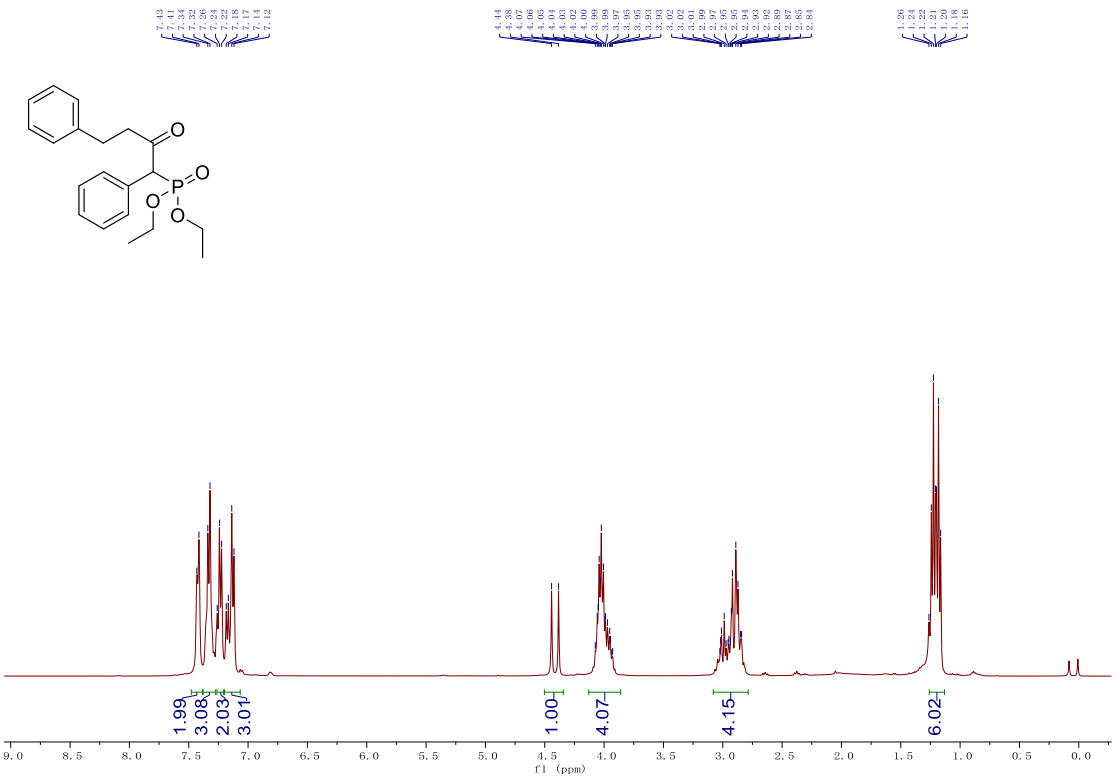

Figure S134. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**

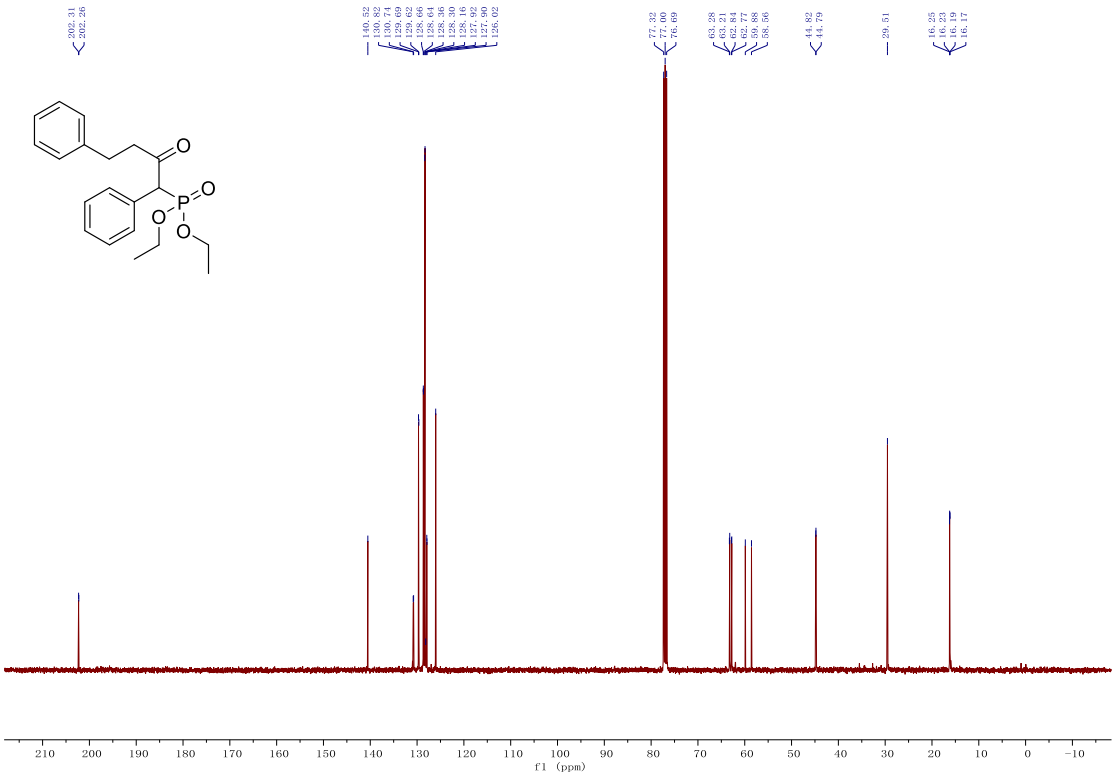

Figure S135. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ae**

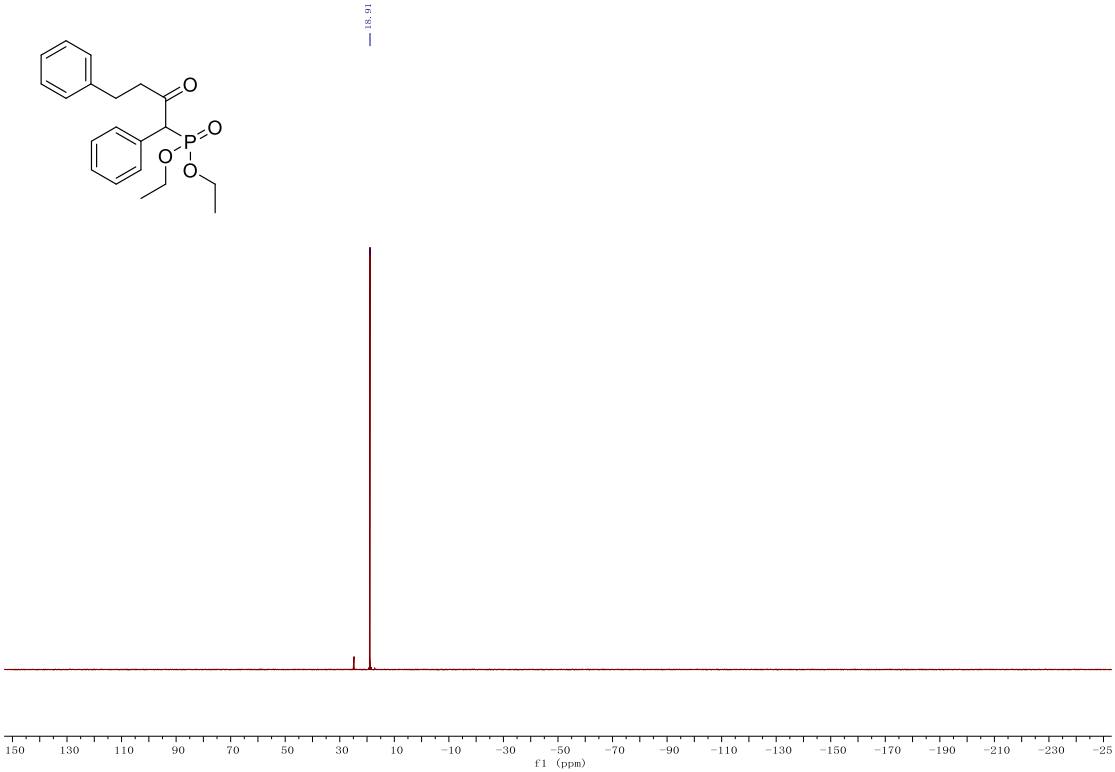

Figure S136. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **3ae**

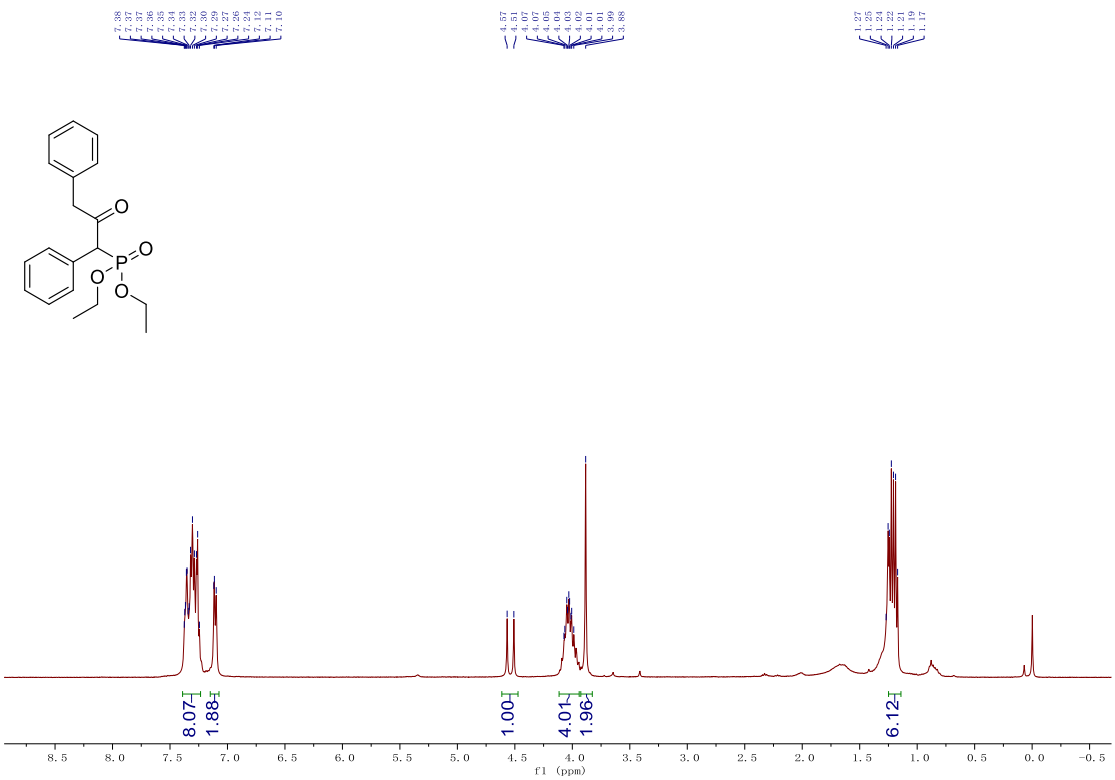

Figure S137. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **3af**

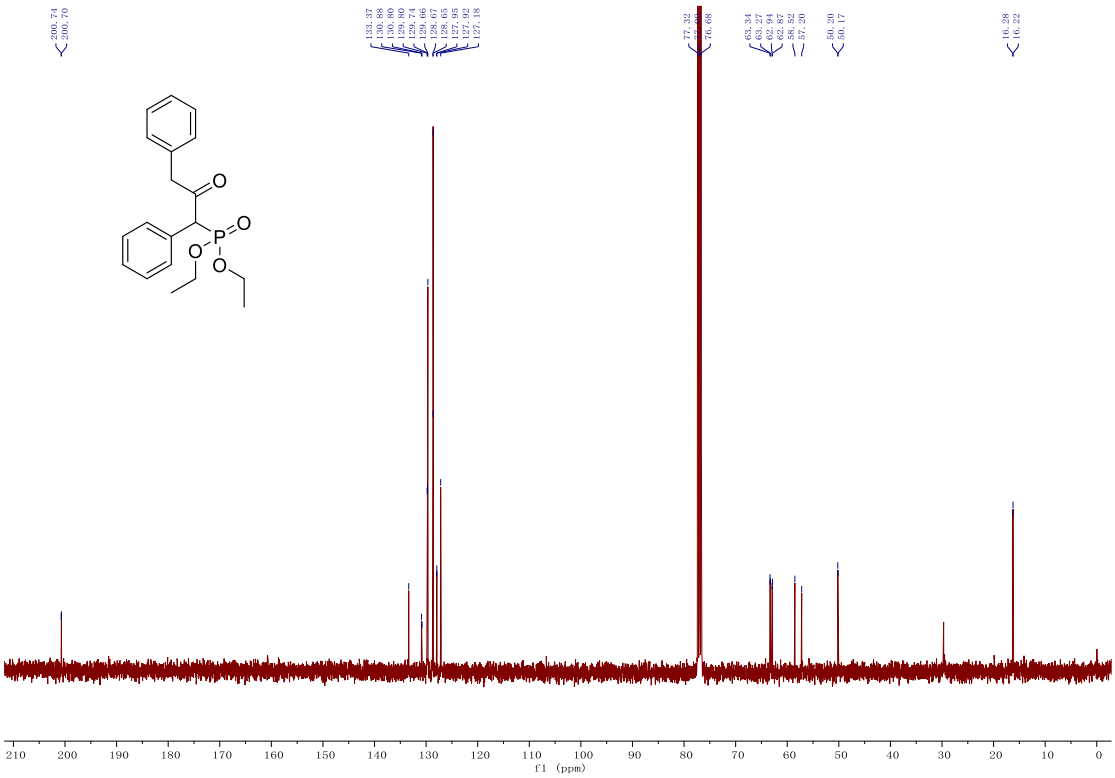

Figure S138. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **3af**

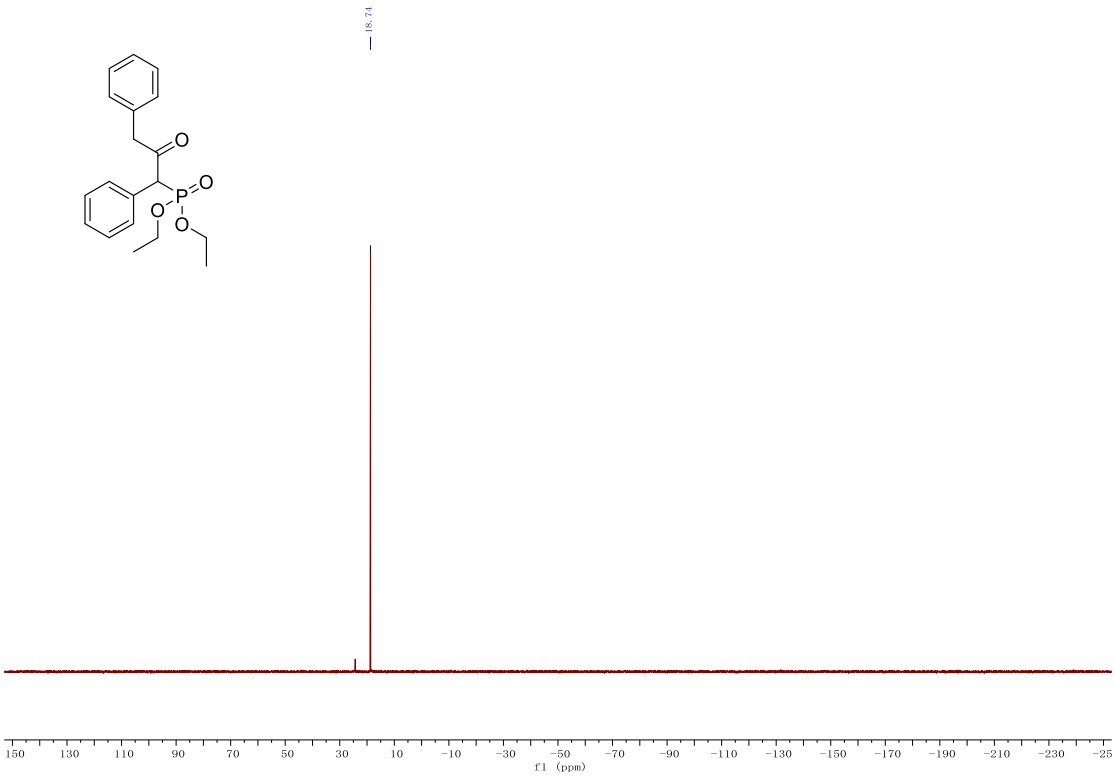

Figure S139. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3af**

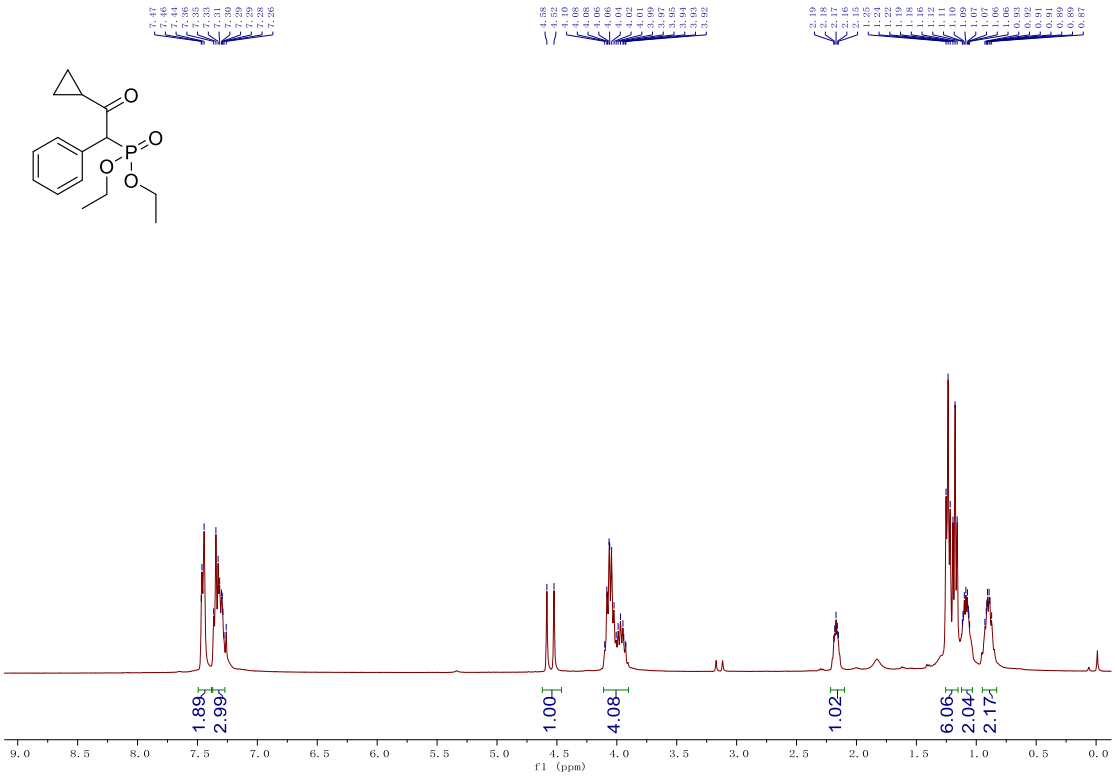

Figure S140. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ag**

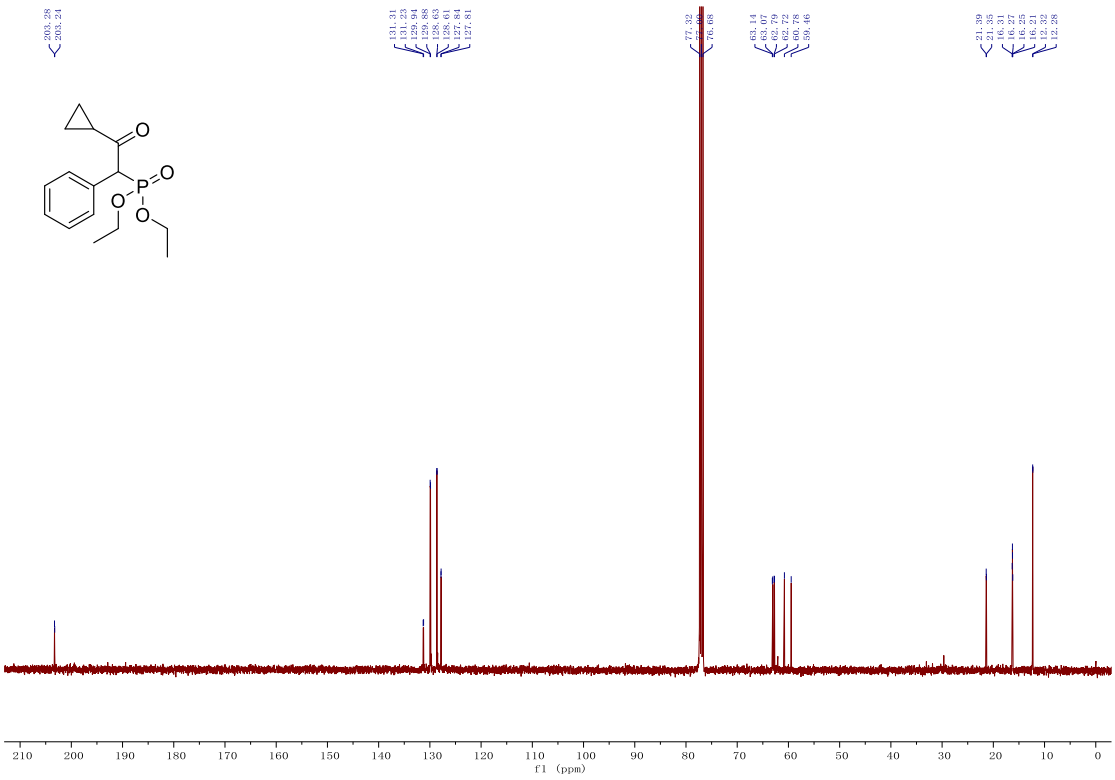

Figure S141.^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ag**

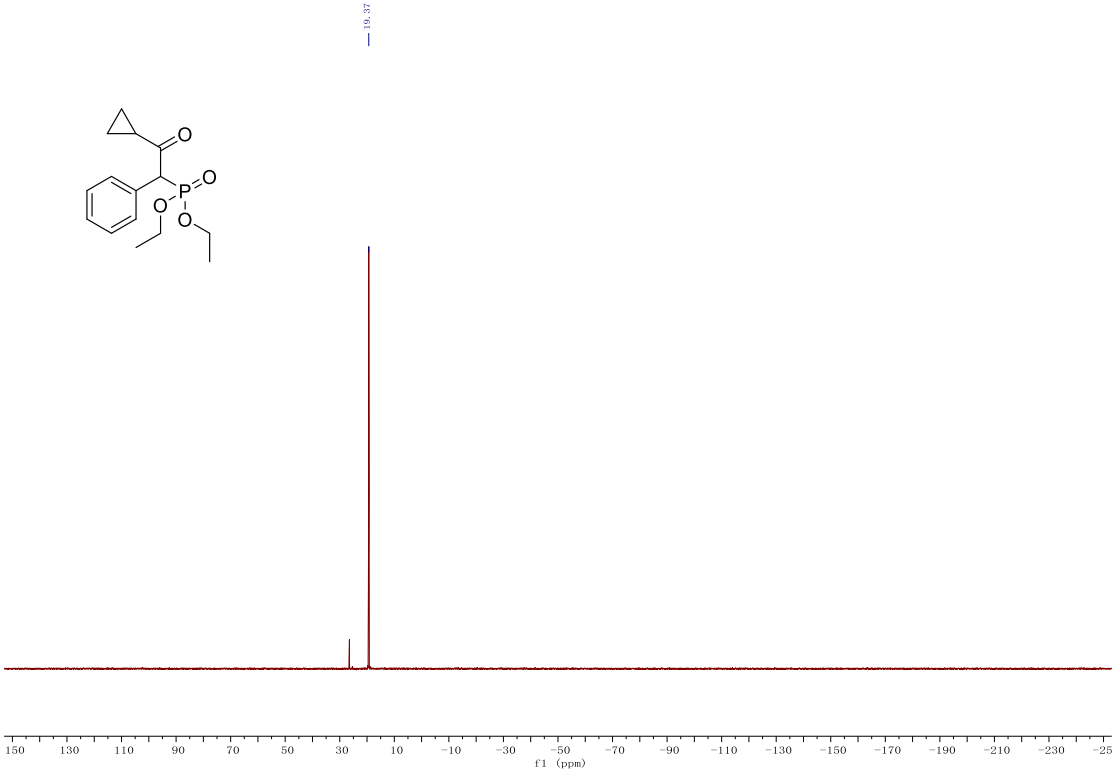

Figure S142. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **3ag**

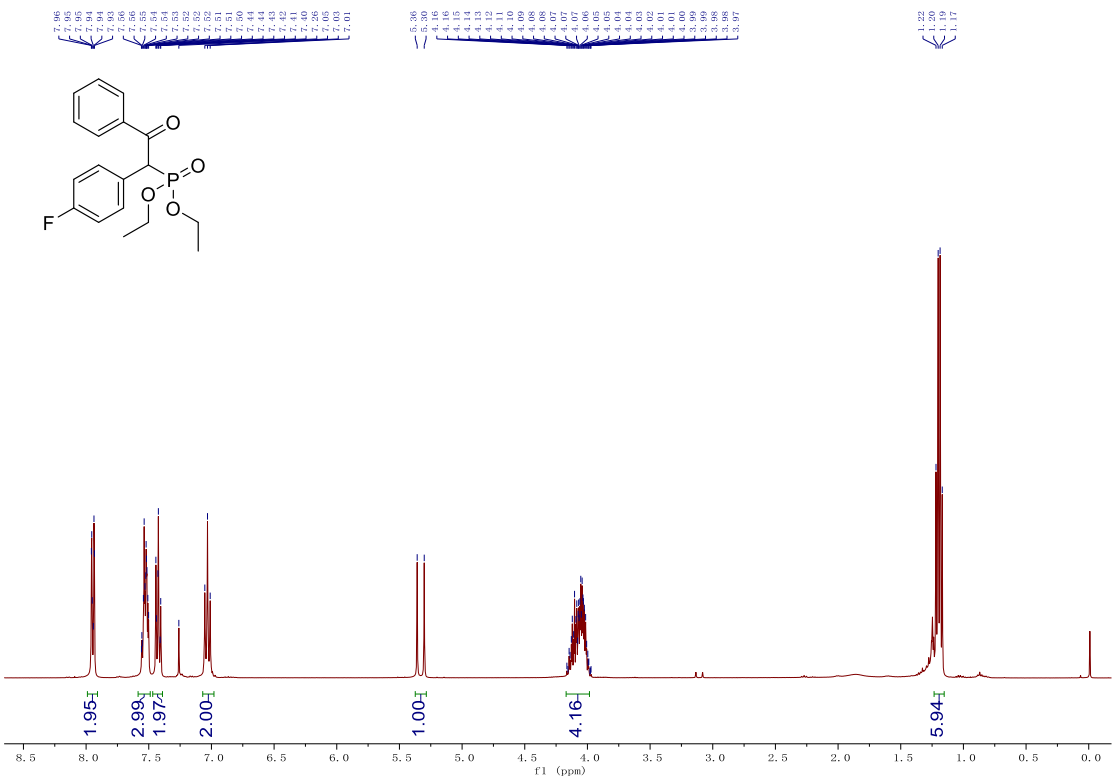

Figure S143. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**

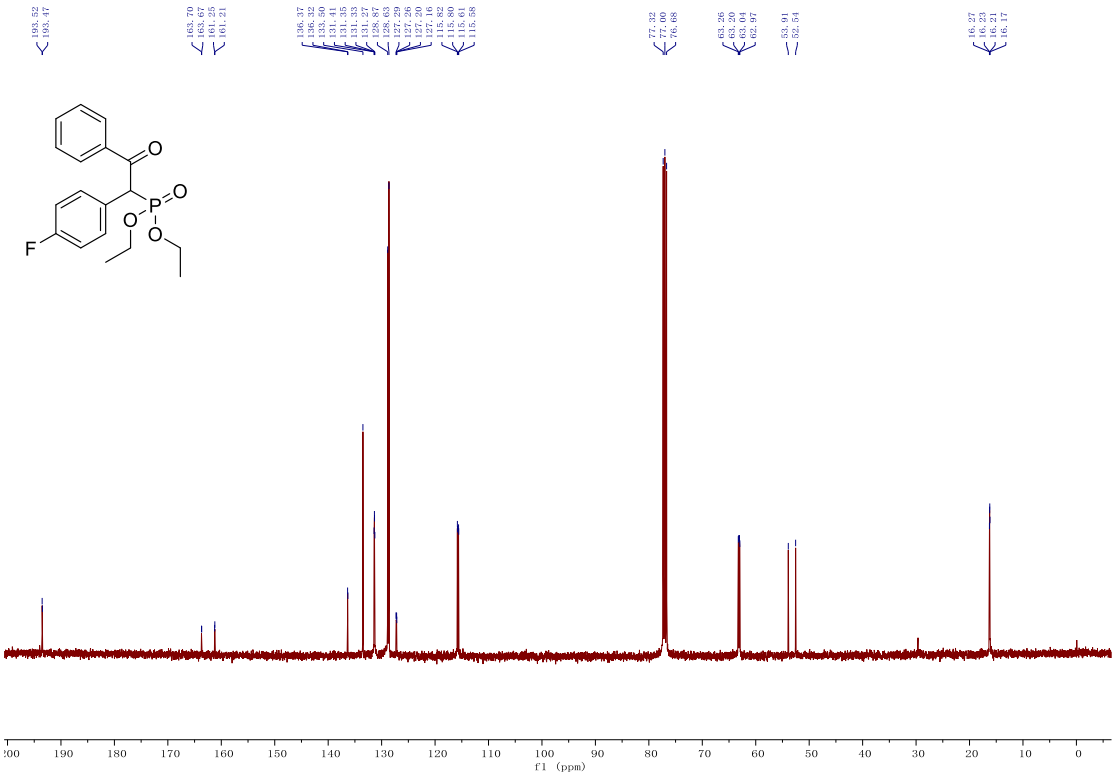

Figure S144. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4a**

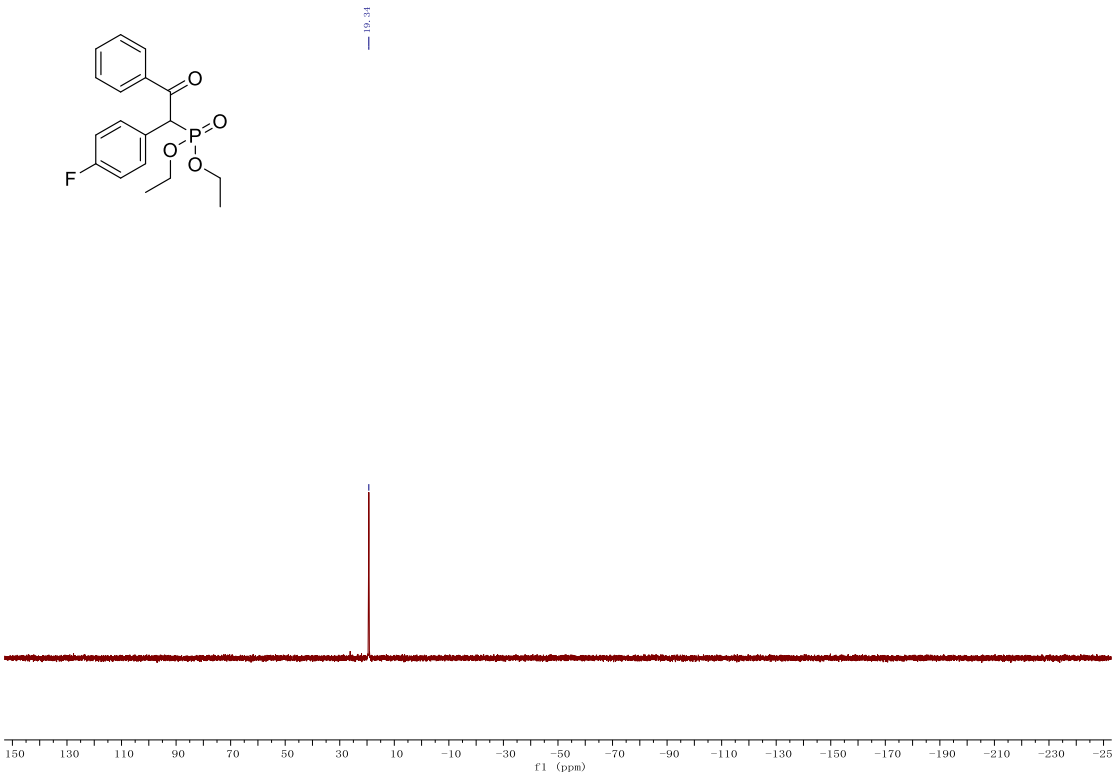

Figure S145. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **4a**

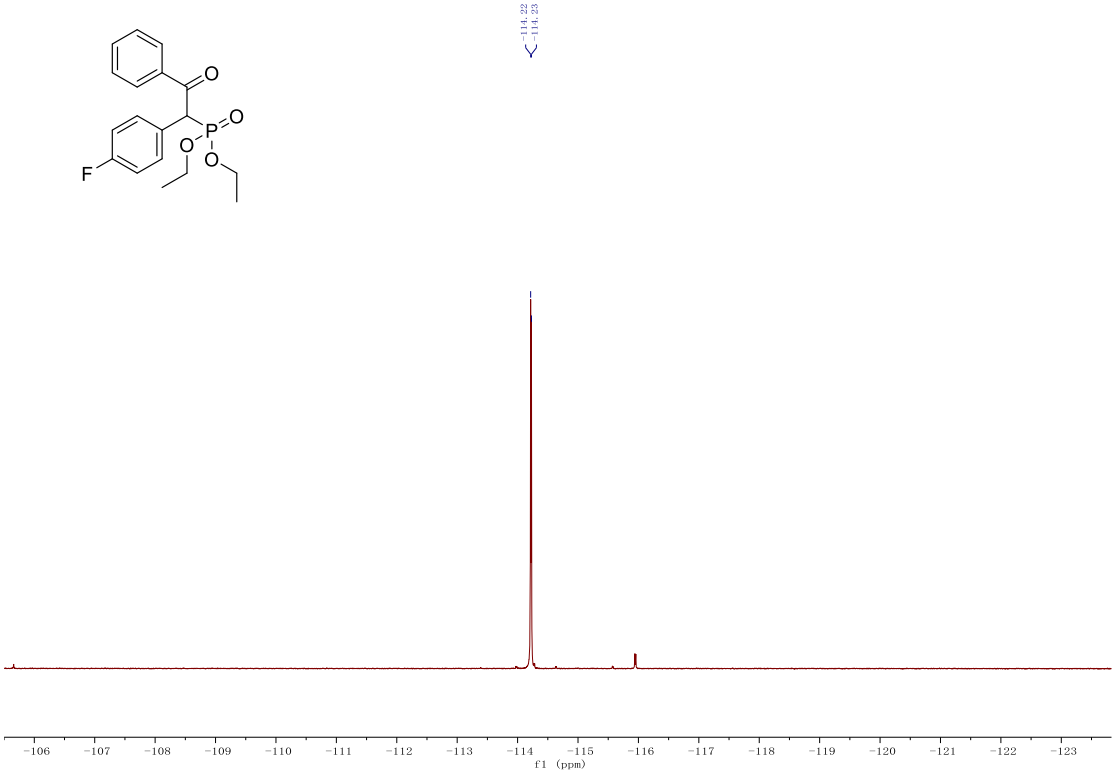

Figure S146. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **4a**

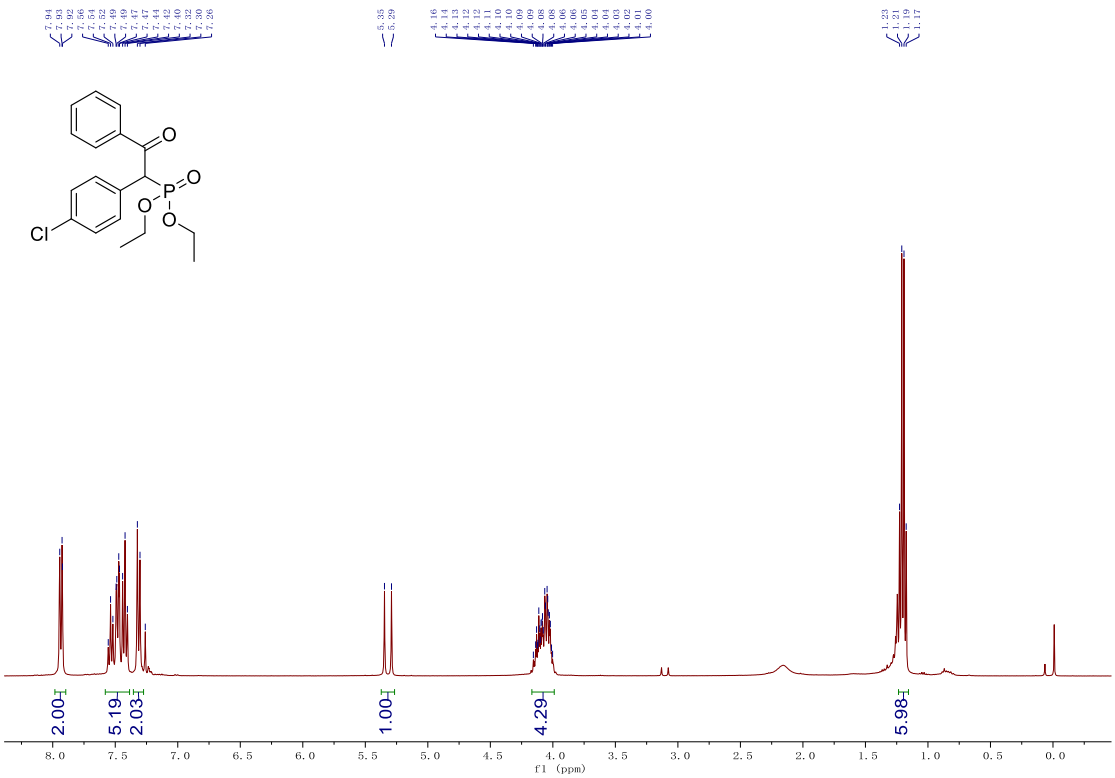

Figure S147. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4b**

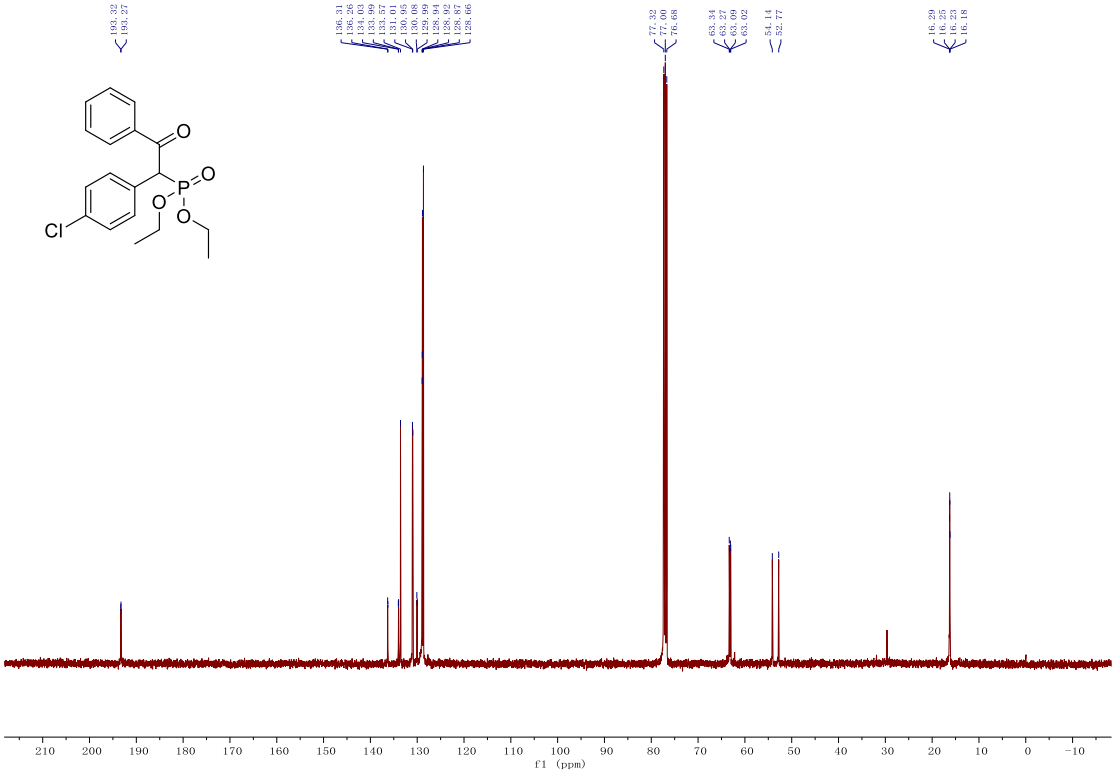

Figure S148. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4b**

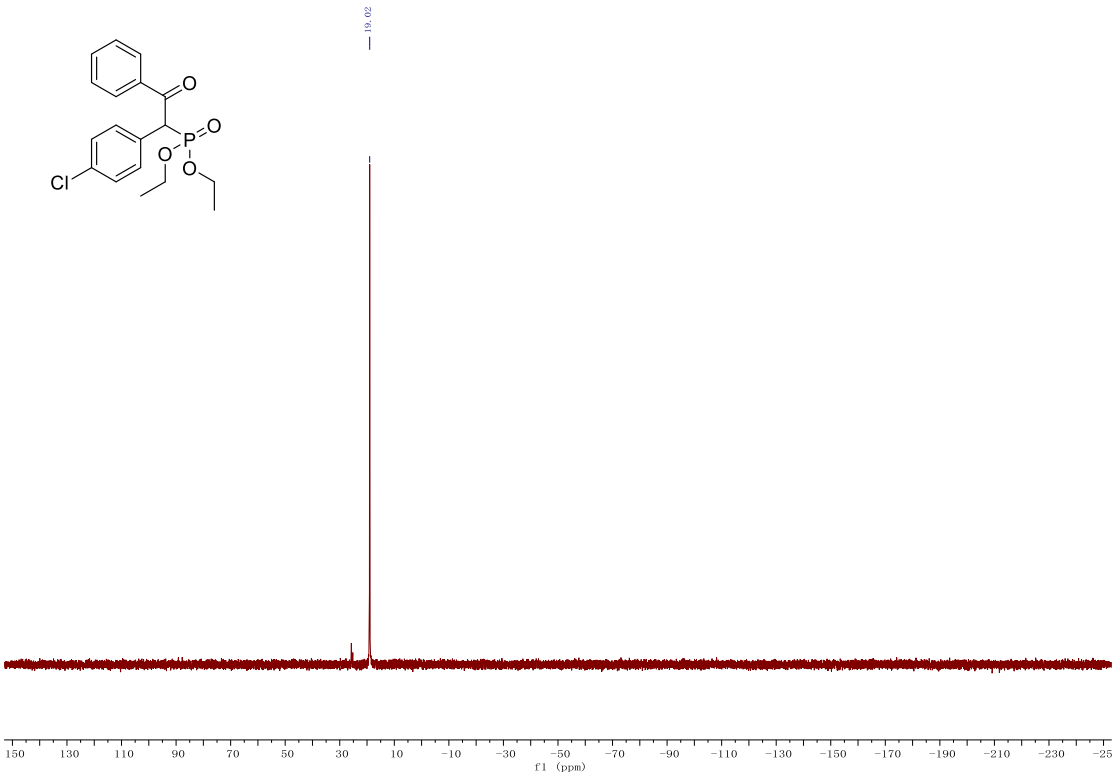

Figure S149. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4b**

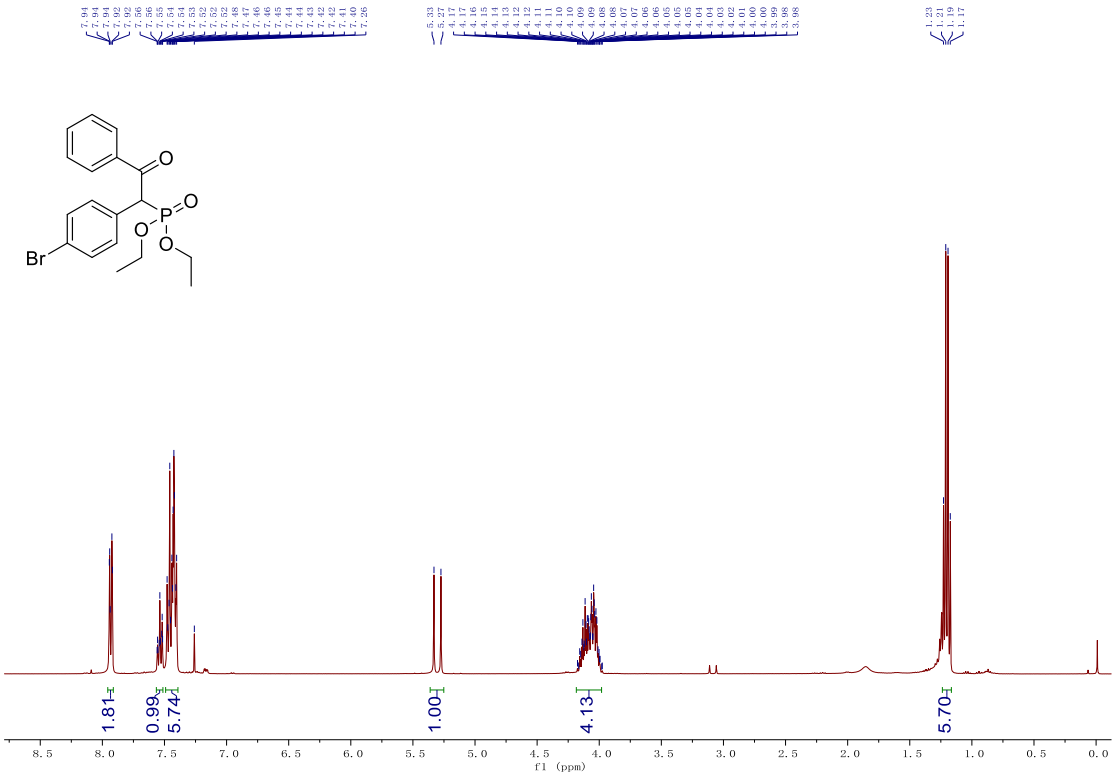

Figure S150. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4c**

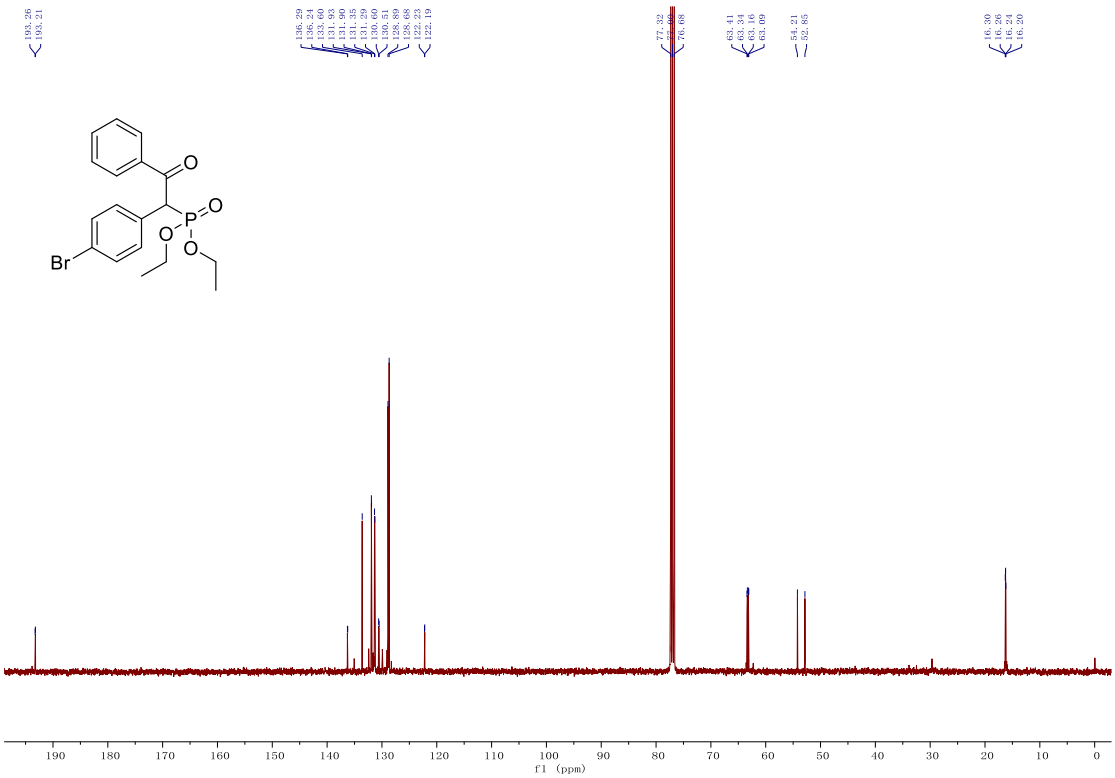

Figure S151 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4c**

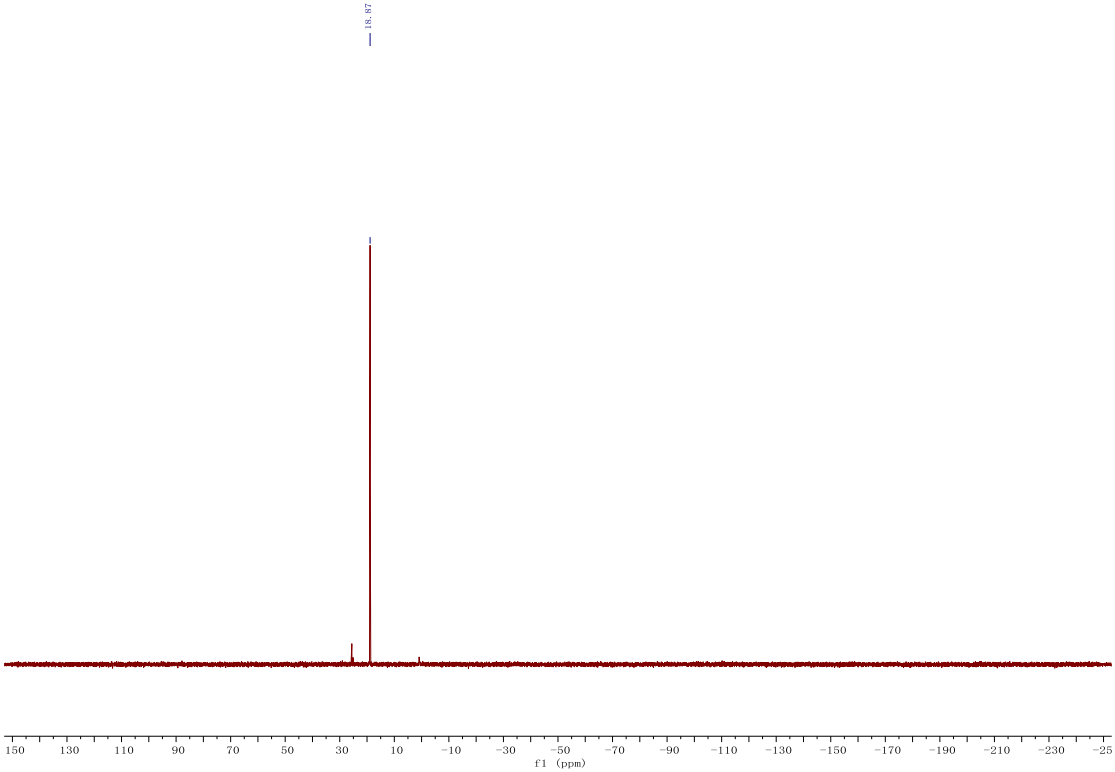

Figure S152. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **4c**

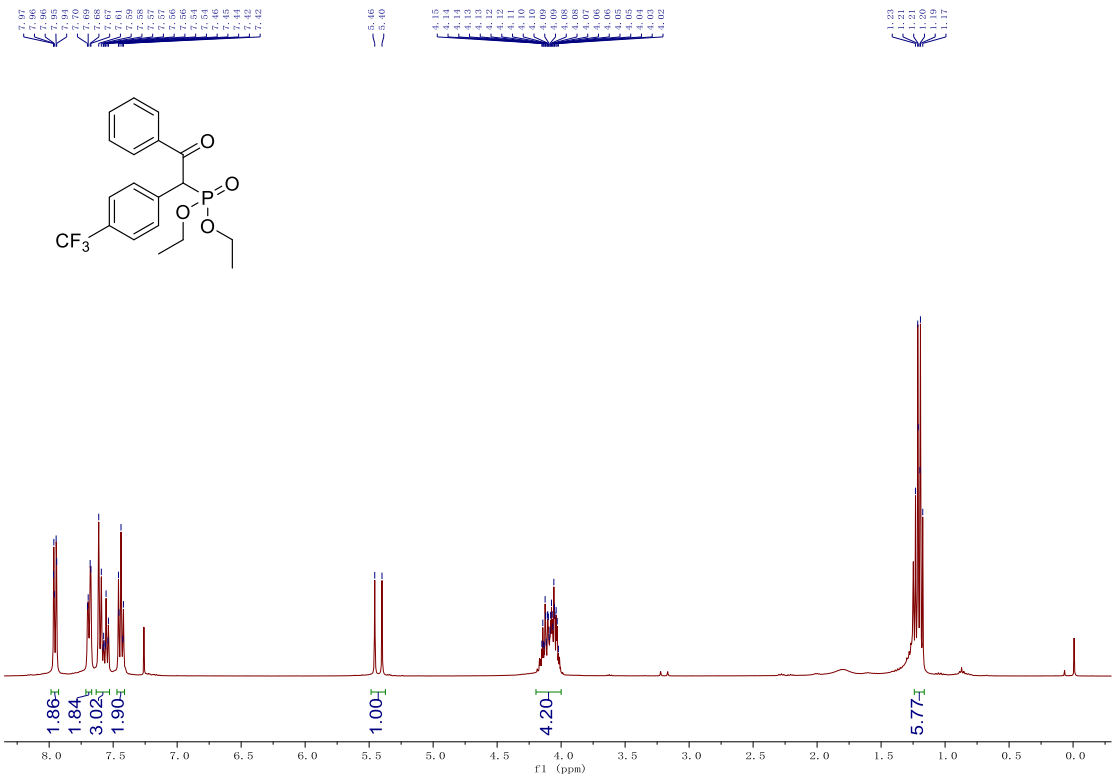

Figure S153. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**

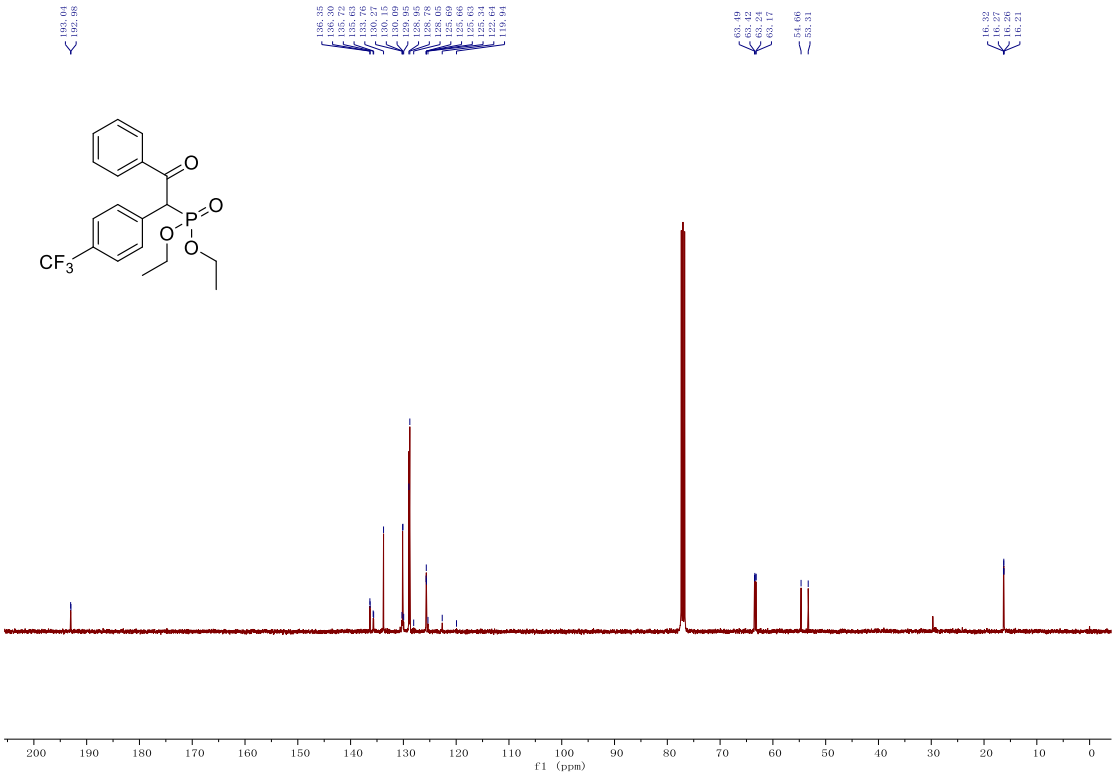

Figure S154. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4d**

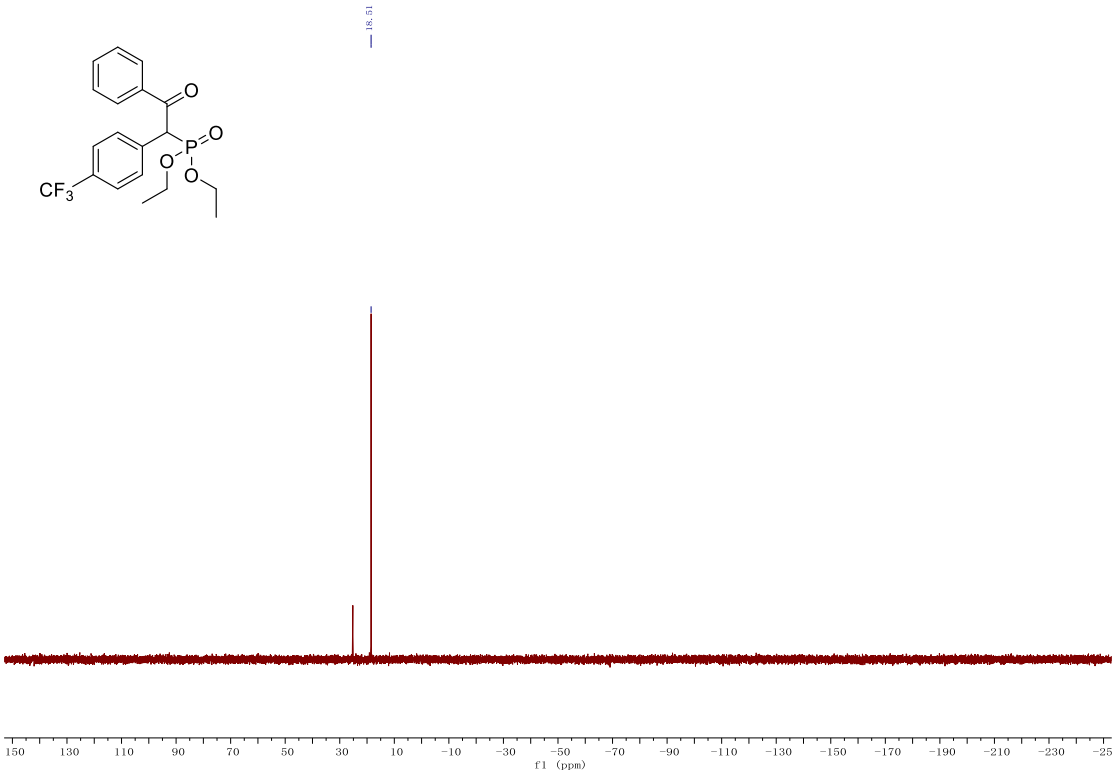

Figure S155. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4d**

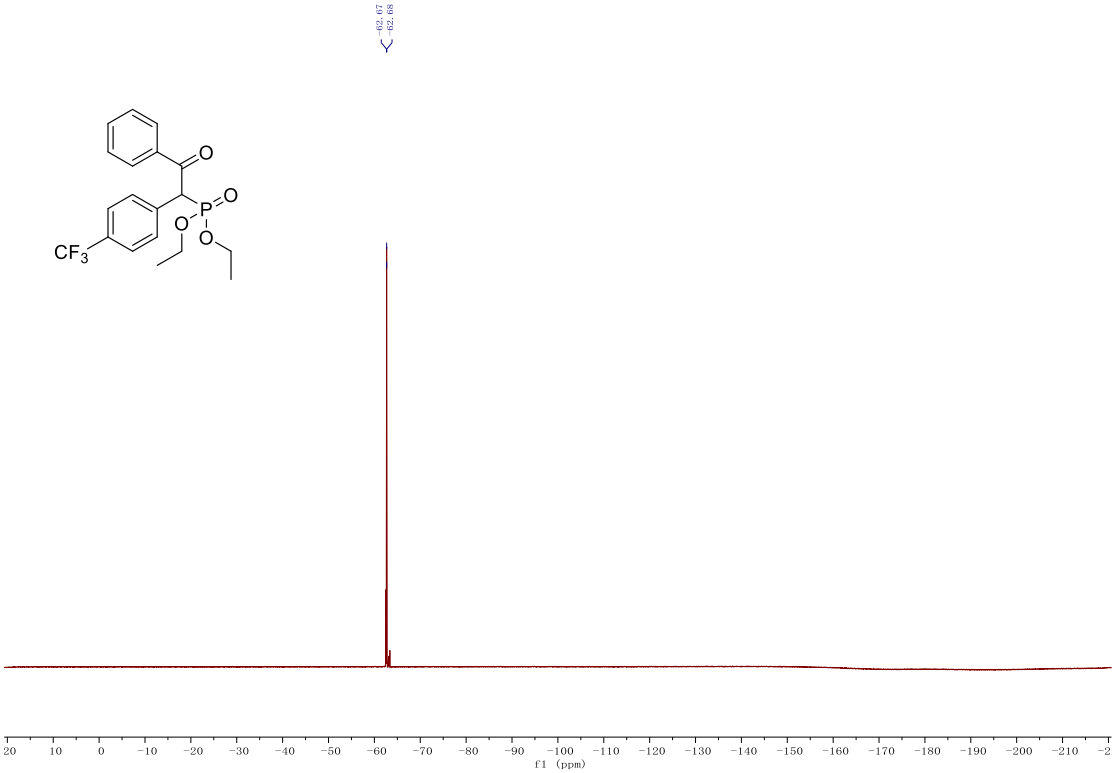

Figure S156. ^{19}**F NMR** (377 MHz, $CDCl_3$) spectrum of **4d**

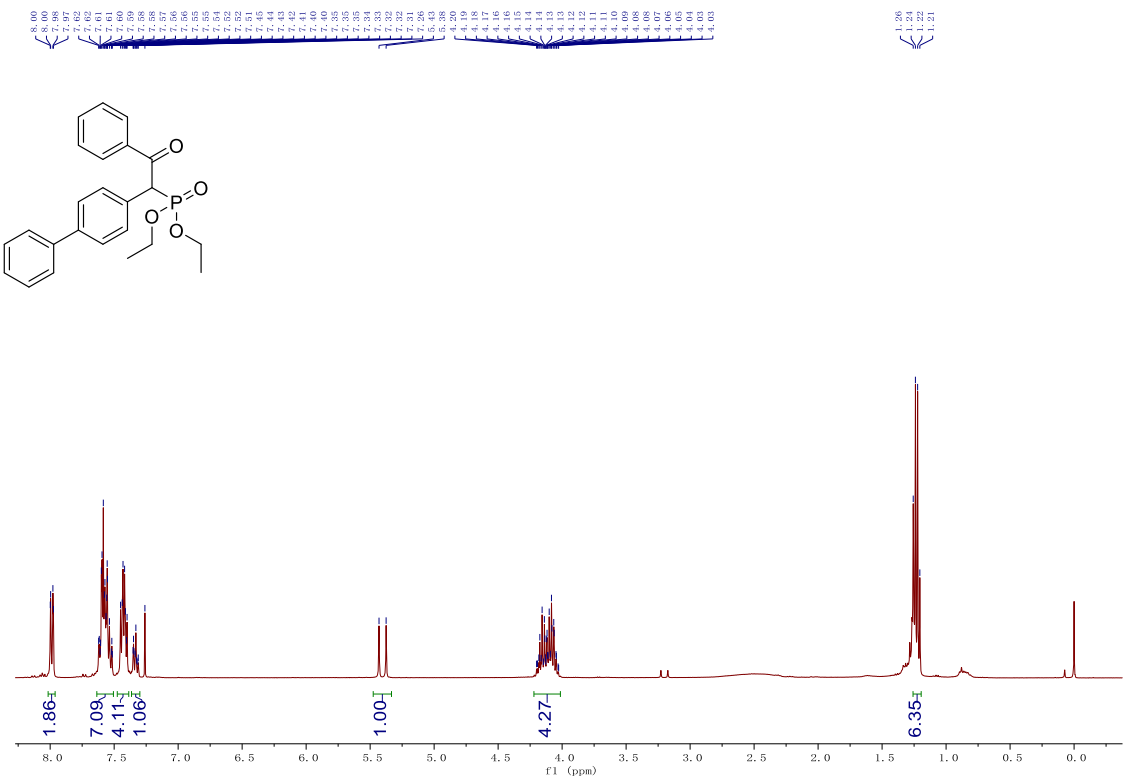

Figure S157. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4e**

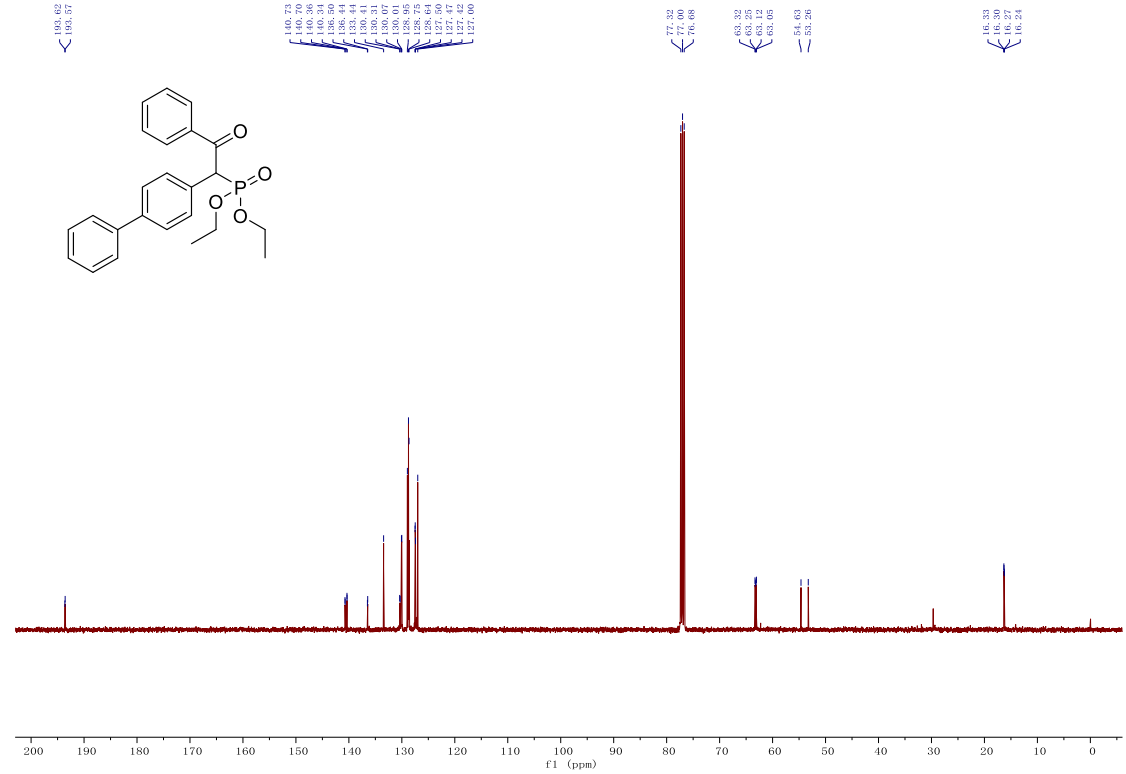

Figure S158. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4e**

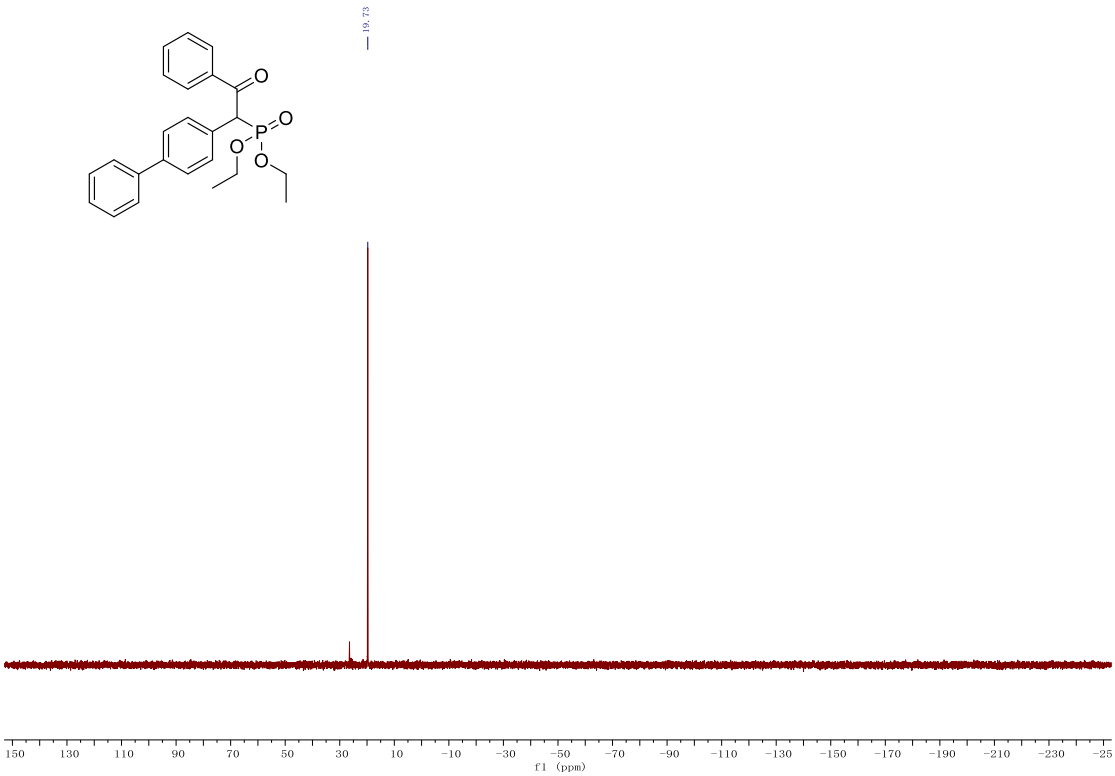

Figure S159. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4e**

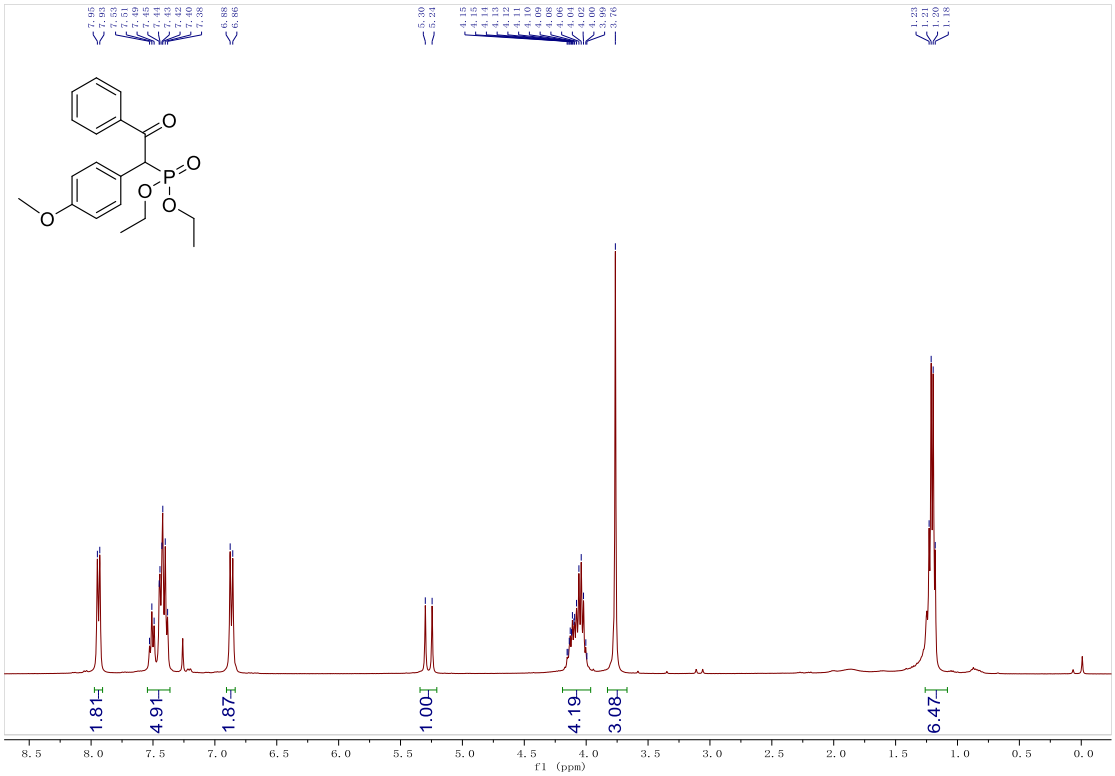

Figure S160. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4f**

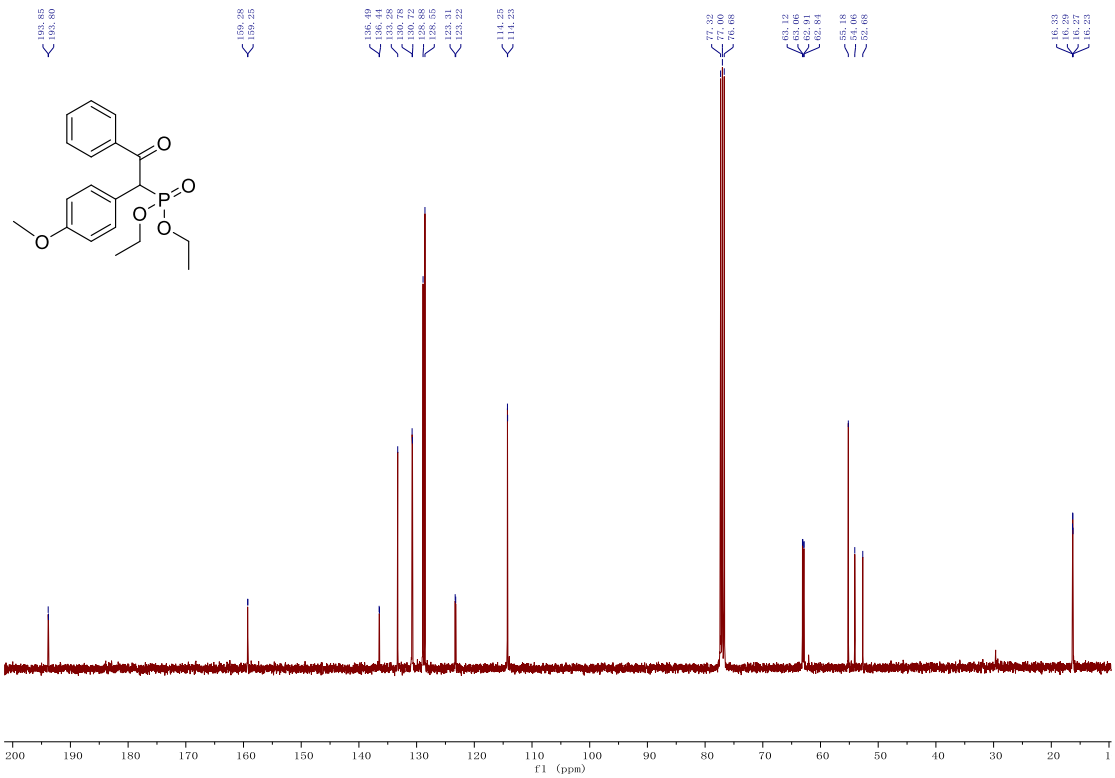

Figure S161. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4f**

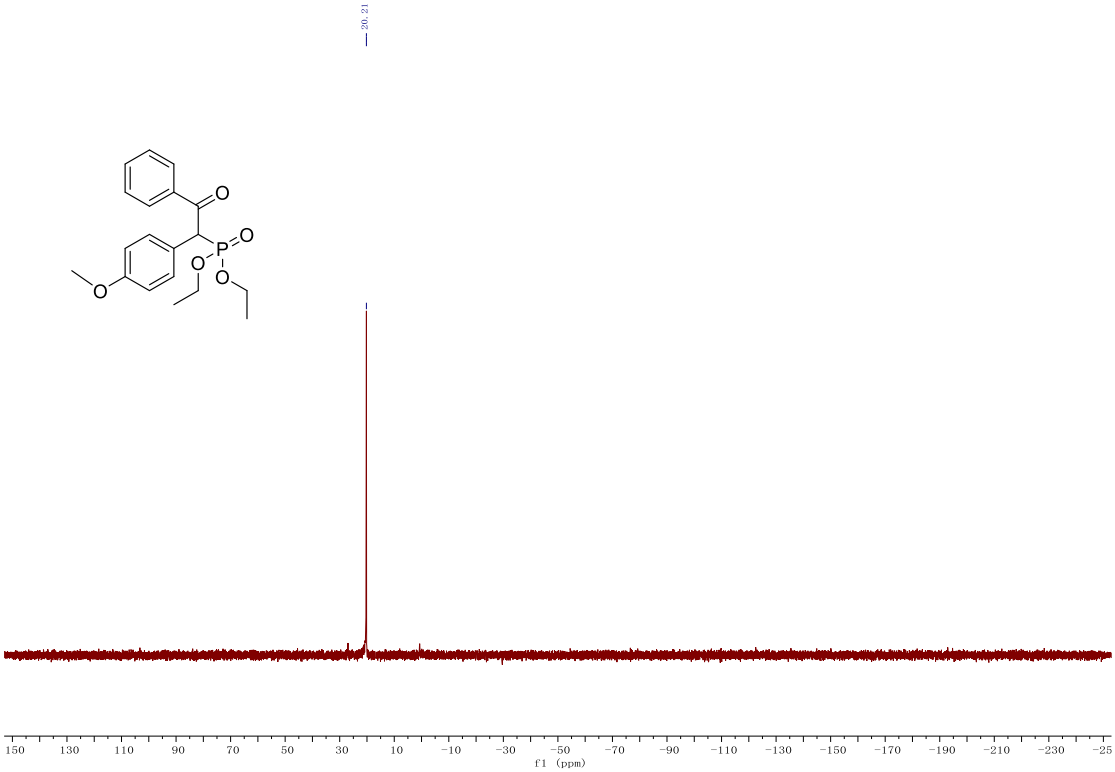

Figure S162. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4f**

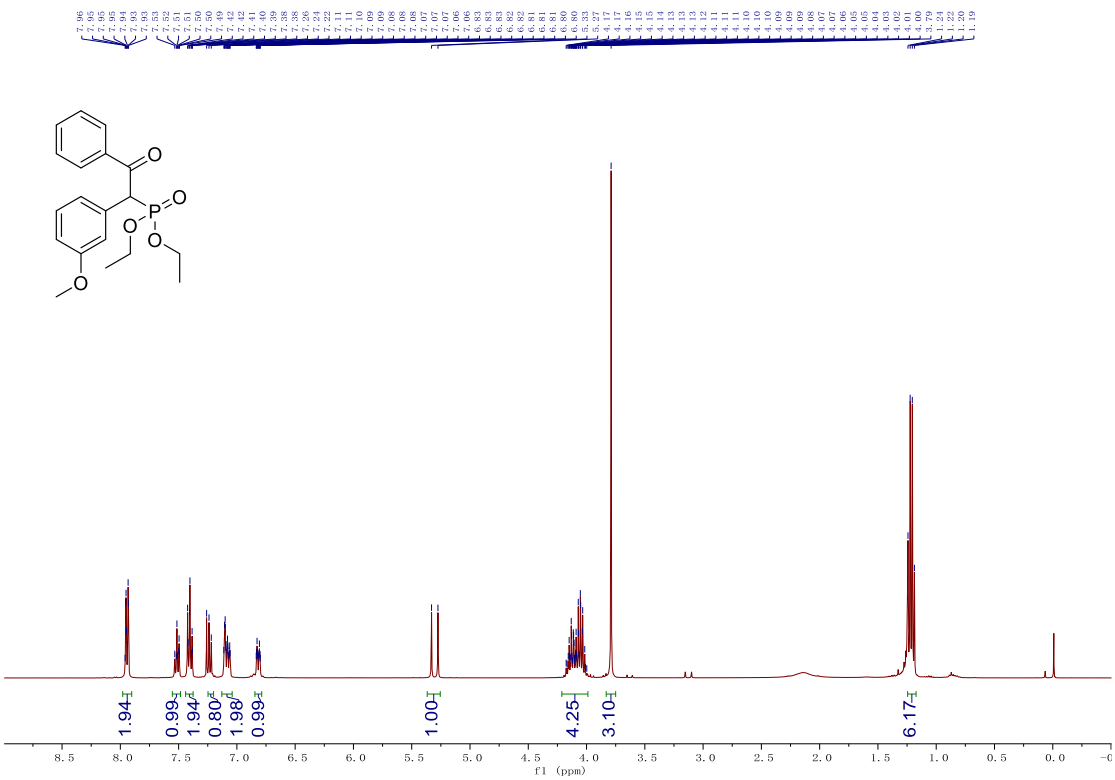

Figure S163. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum of **4g**

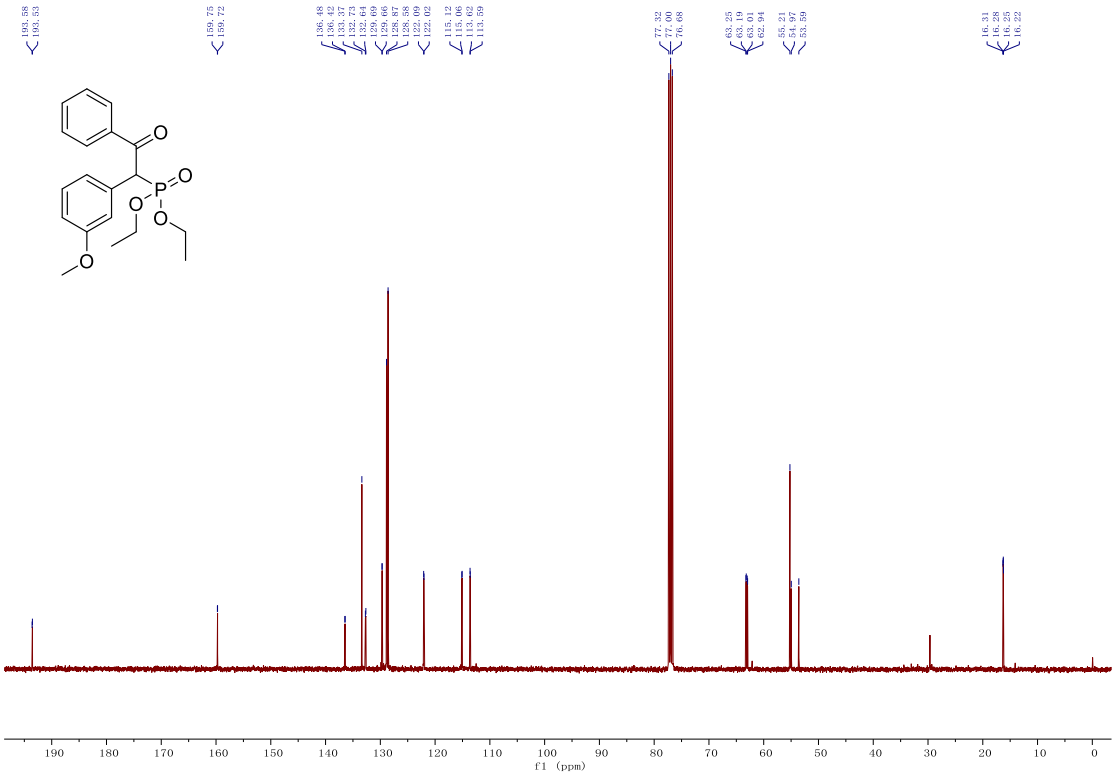

Figure S164. **^{13}C NMR** (101 MHz, $CDCl_3$) spectrum of **4g**

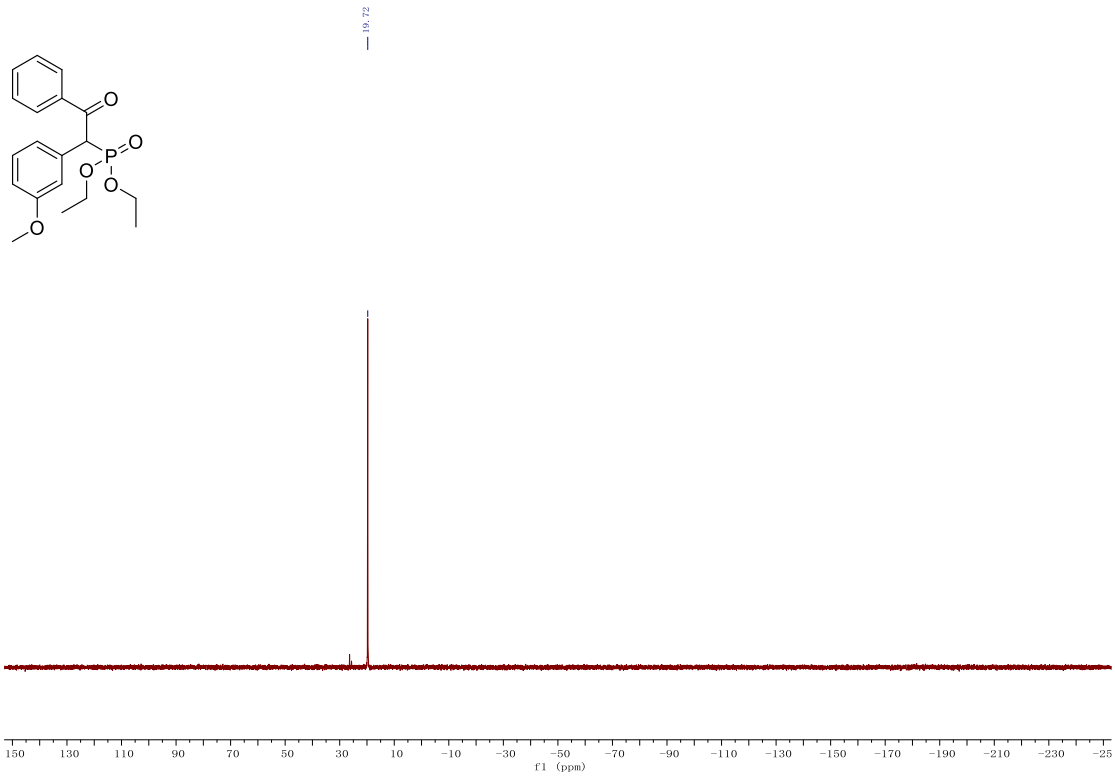

Figure S165. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4g**

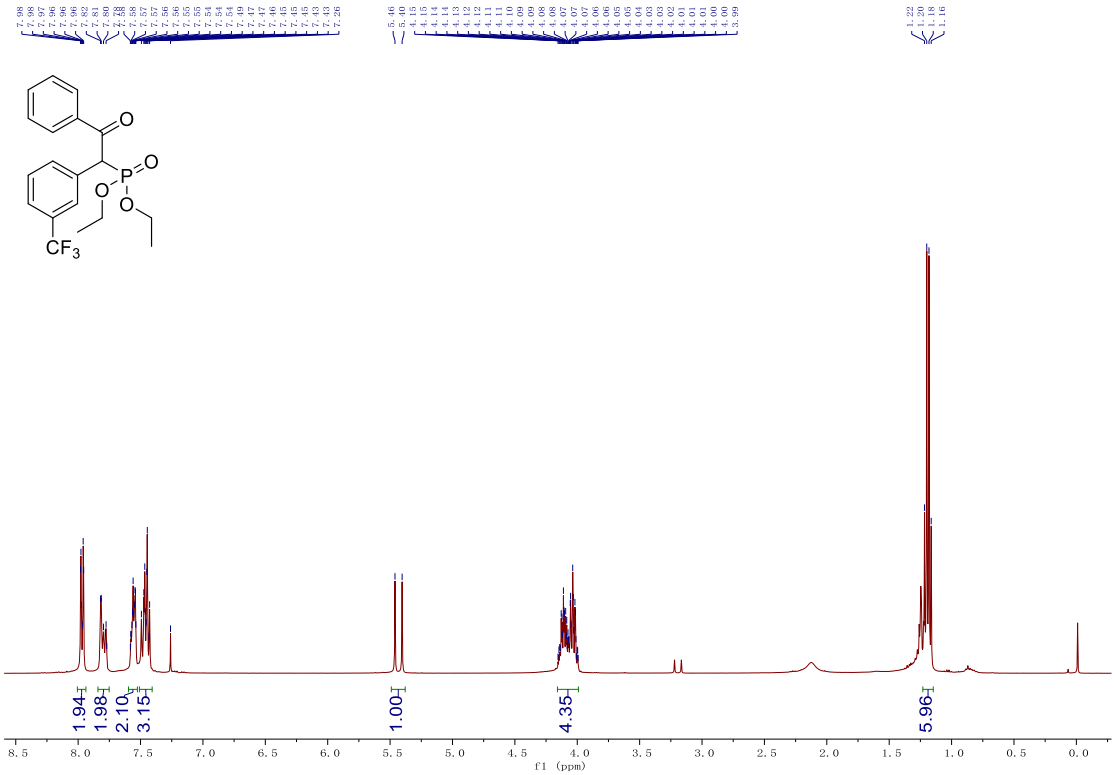

Figure S166. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4h**

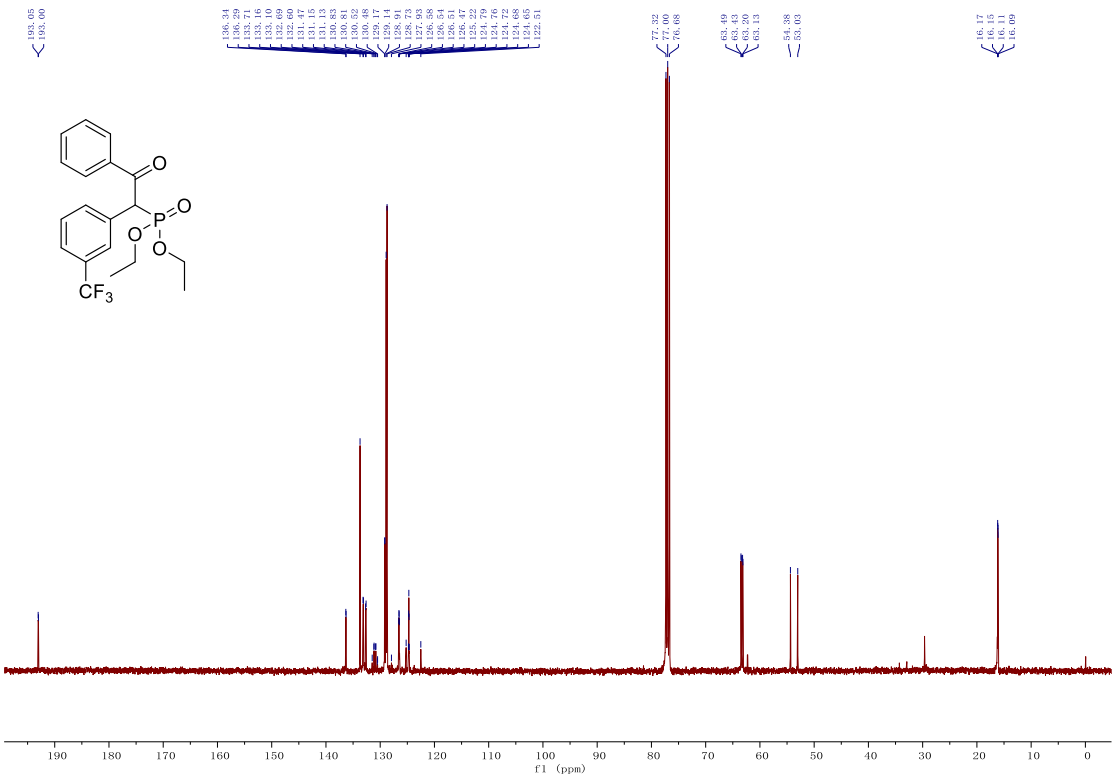

Figure S167. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4h**

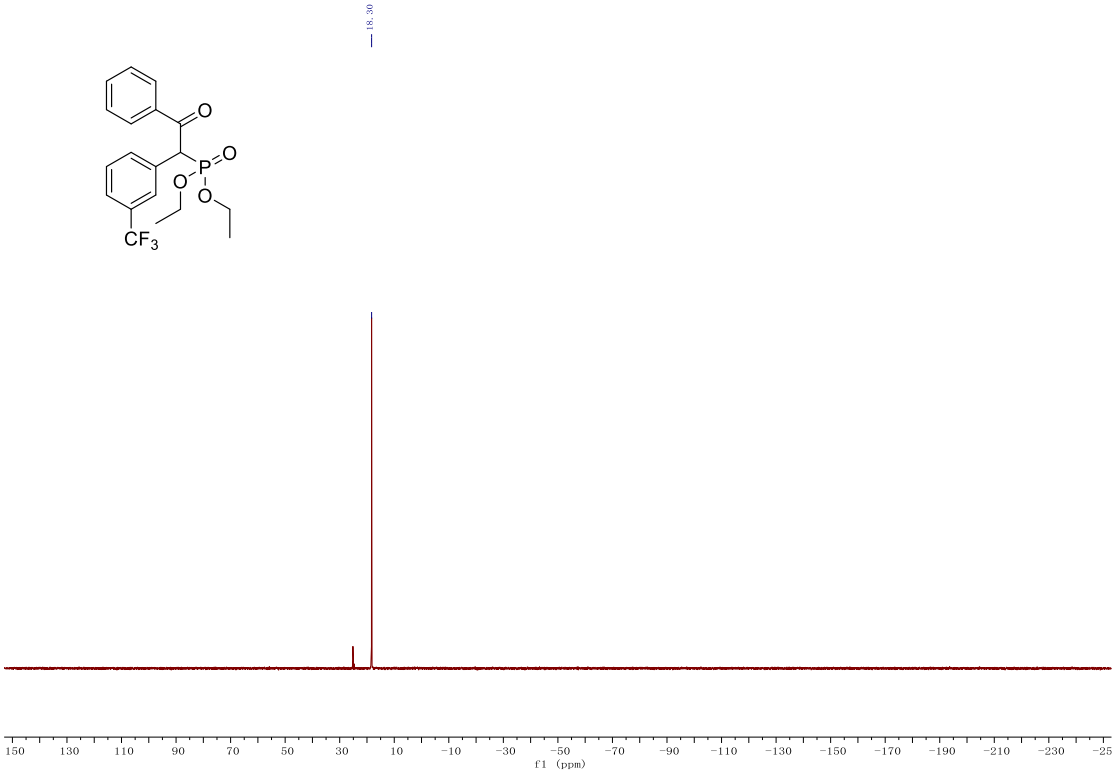

Figure S168. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4h**

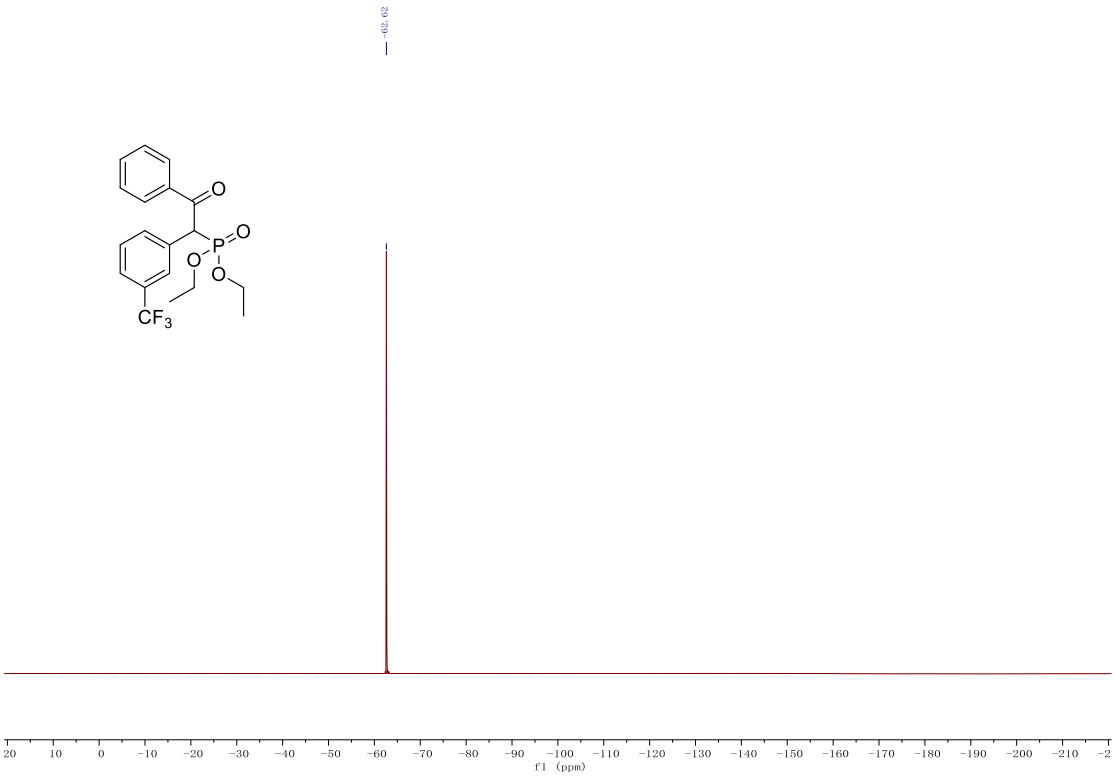

Figure S169. ^{19}**F NMR** (377 MHz, $CDCl_3$) spectrum of **4h**

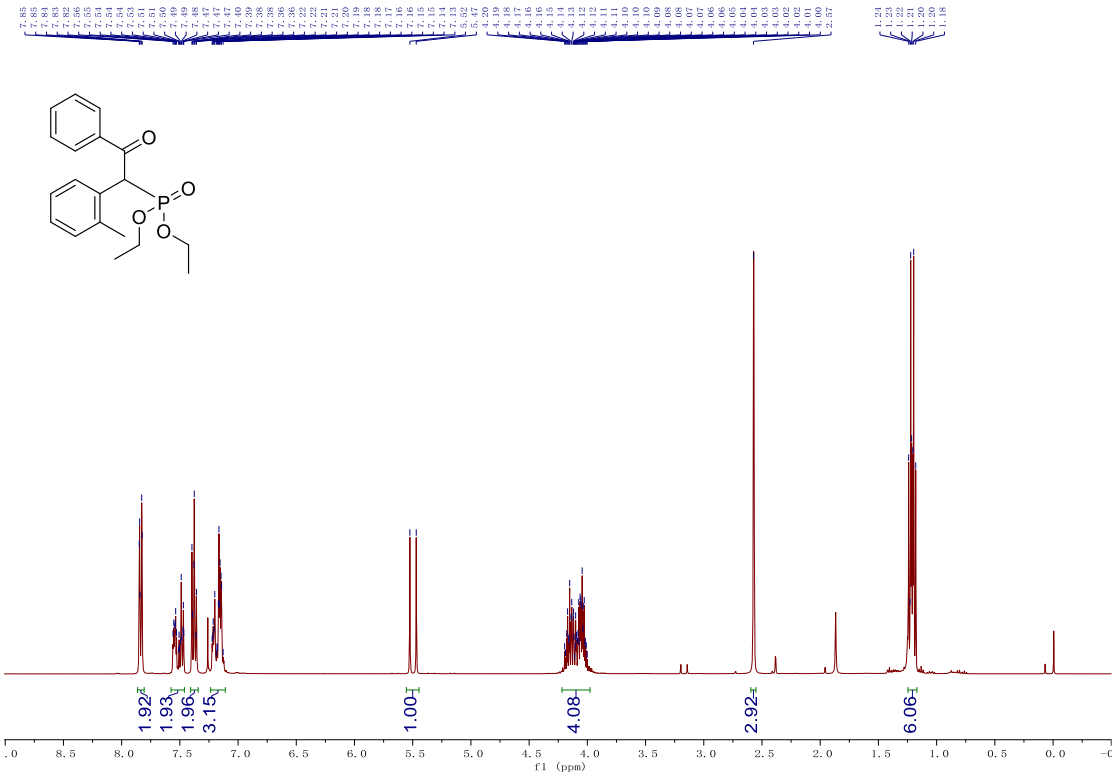

Figure S170. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4i**

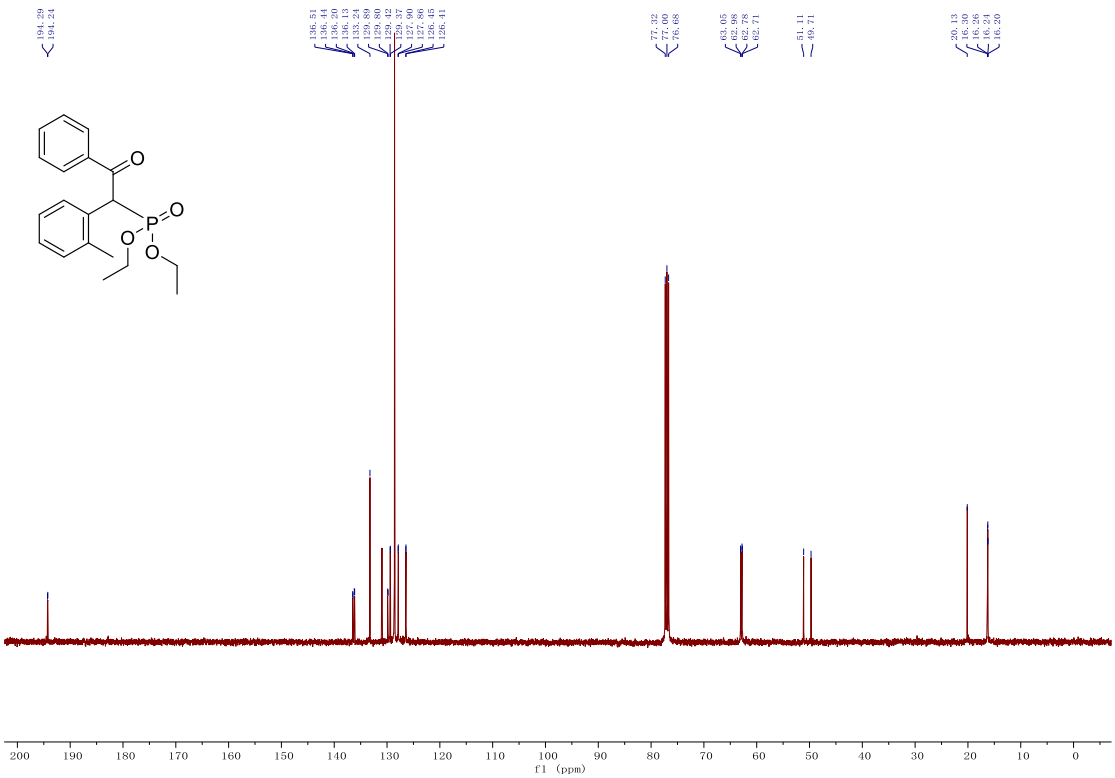

Figure S171. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4i**

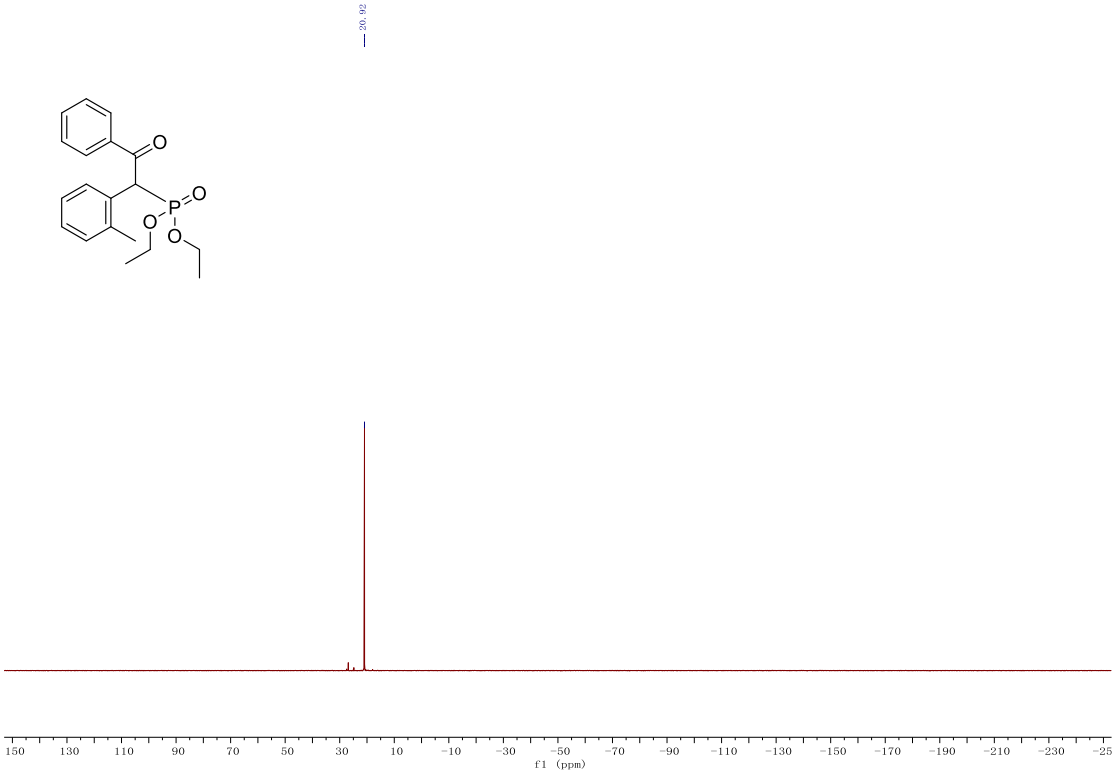

Figure S172. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4i**

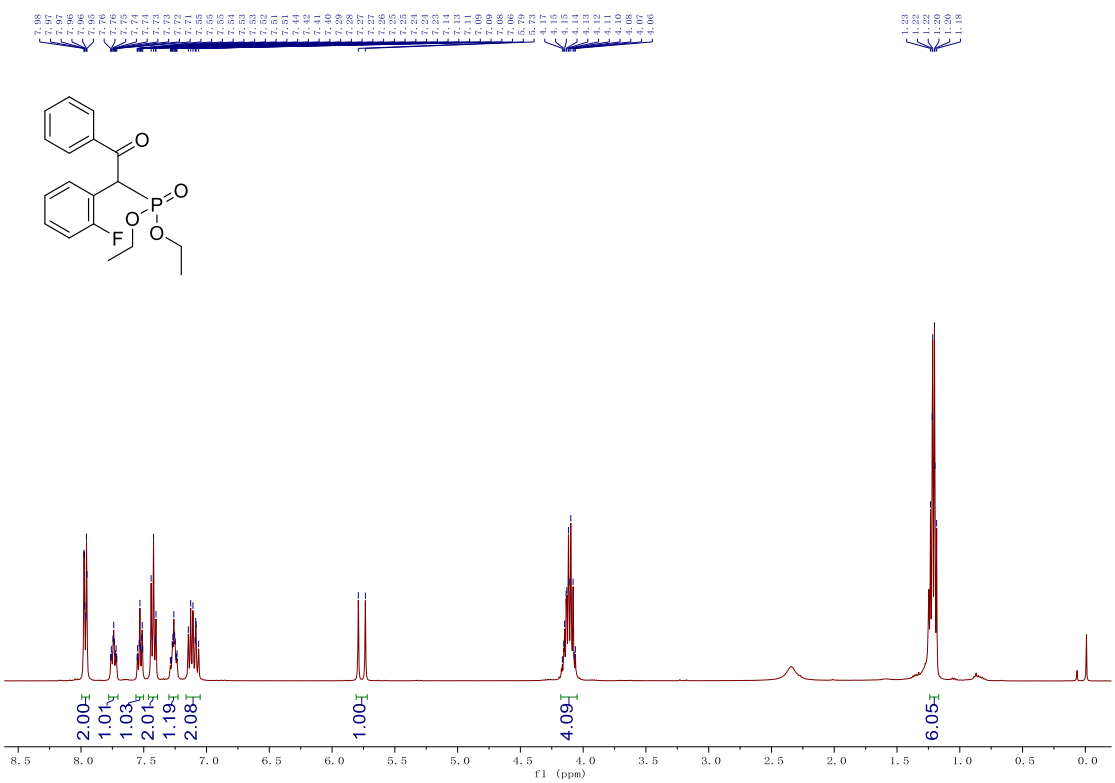

Figure S173. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j**

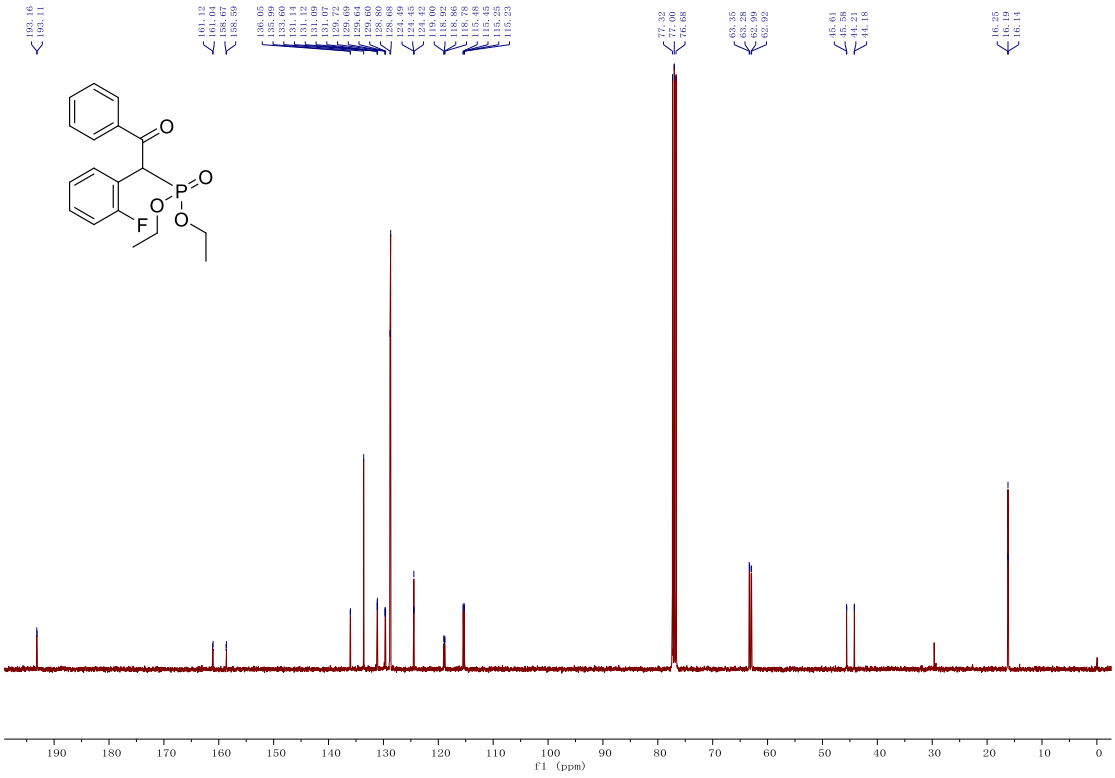

Figure S174. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4j**

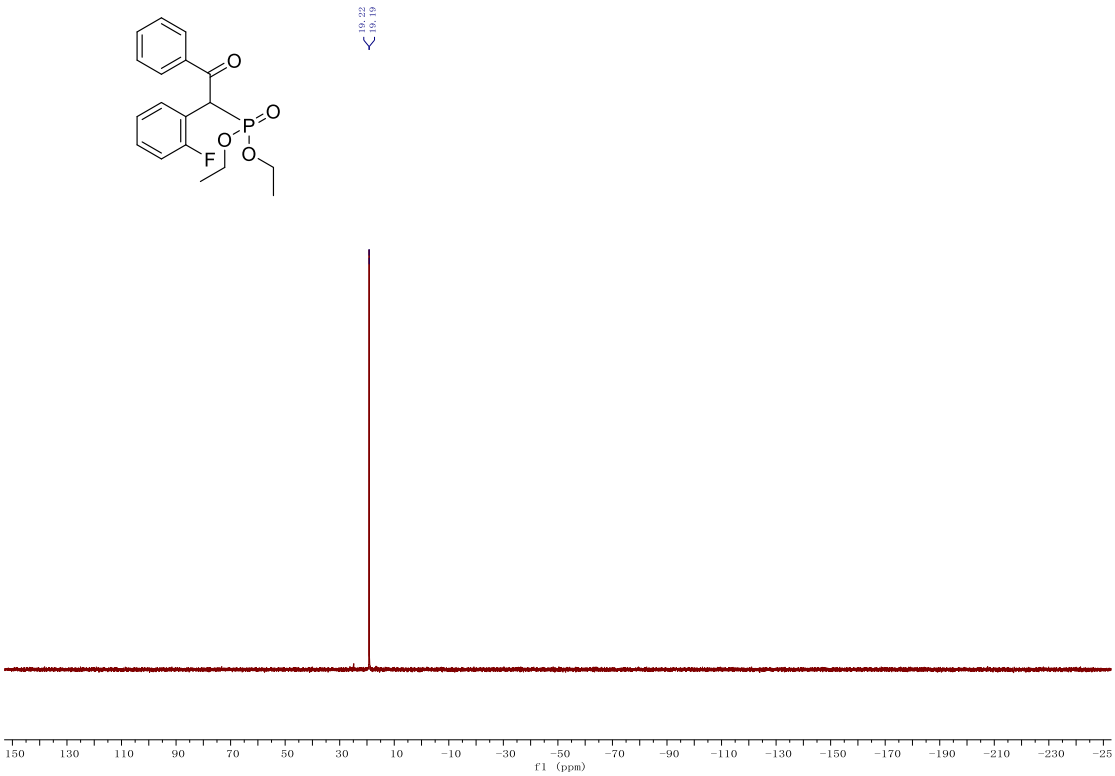

Figure S175. ^{31}**P NMR** (**162 MHz**, **CDCl$_3$**).spectrum of **4j**

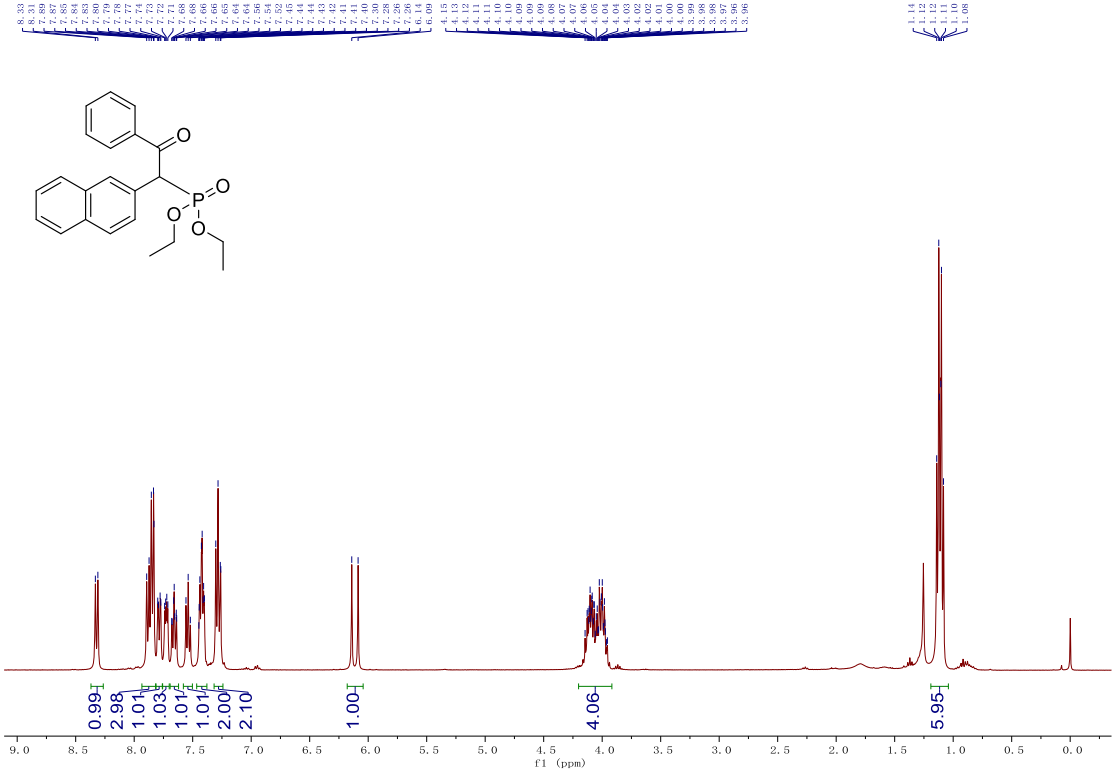

Figure S176. ^{1}**H NMR** (400 MHz, CDCl$_3$) spectrum of **4k**

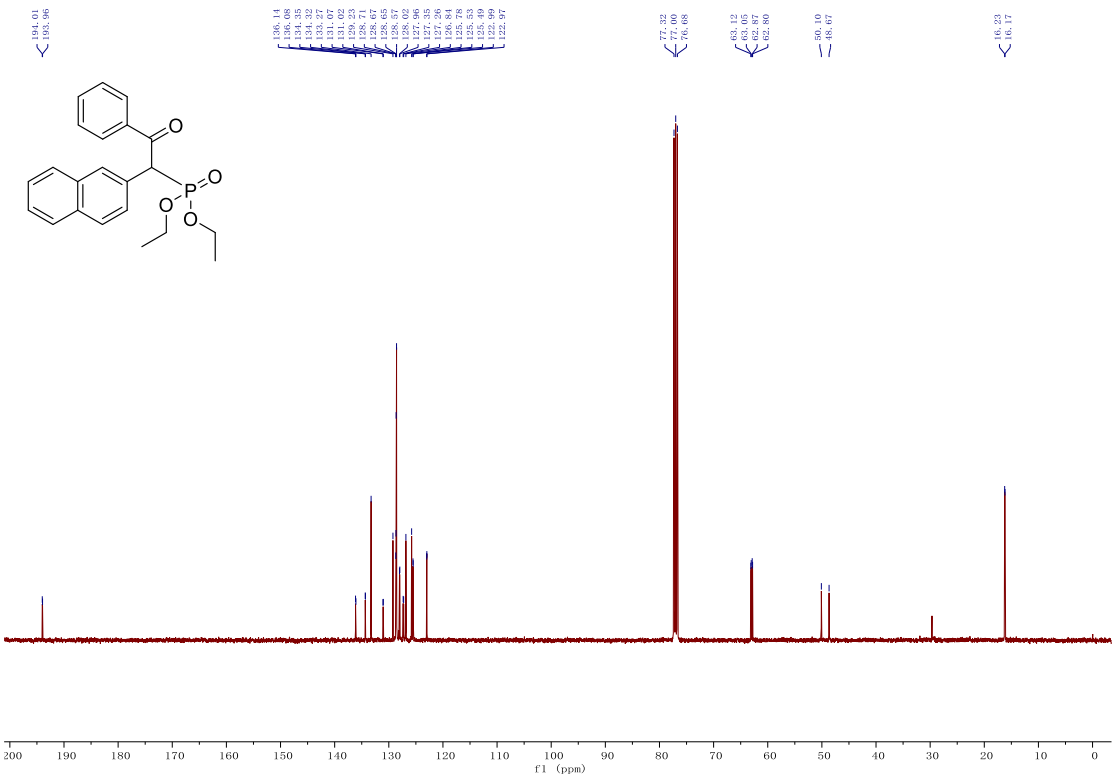

Figure S177. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4k**

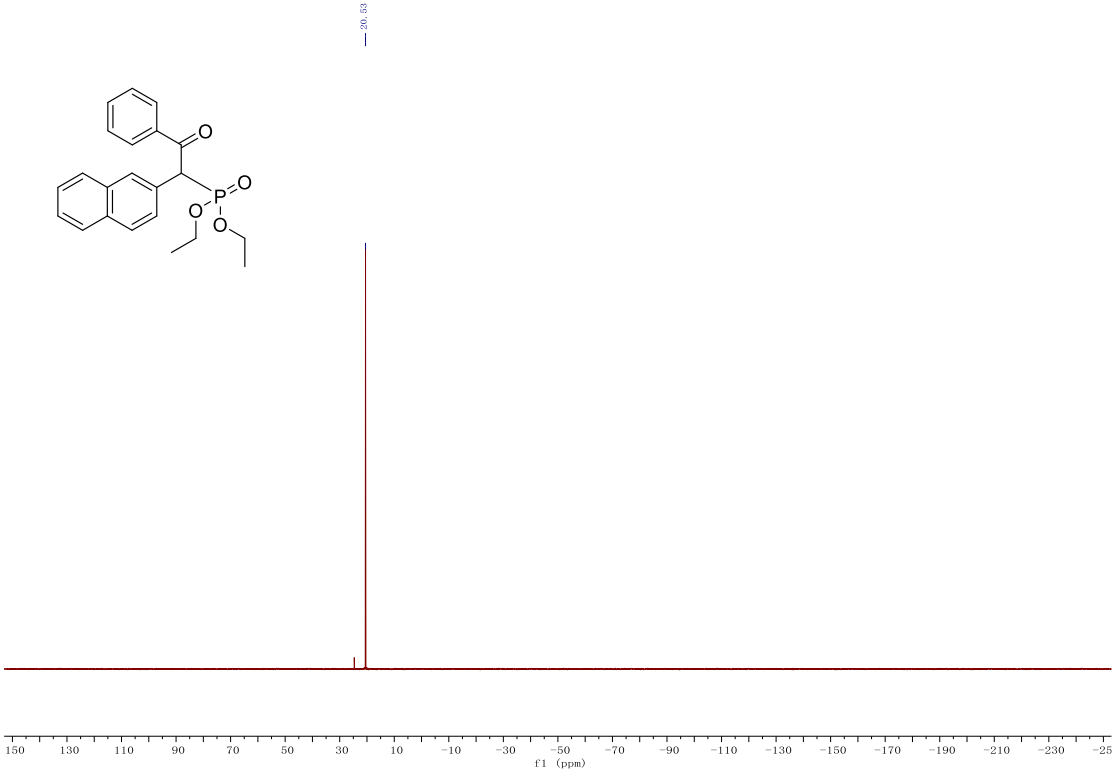

Figure S178. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4k**

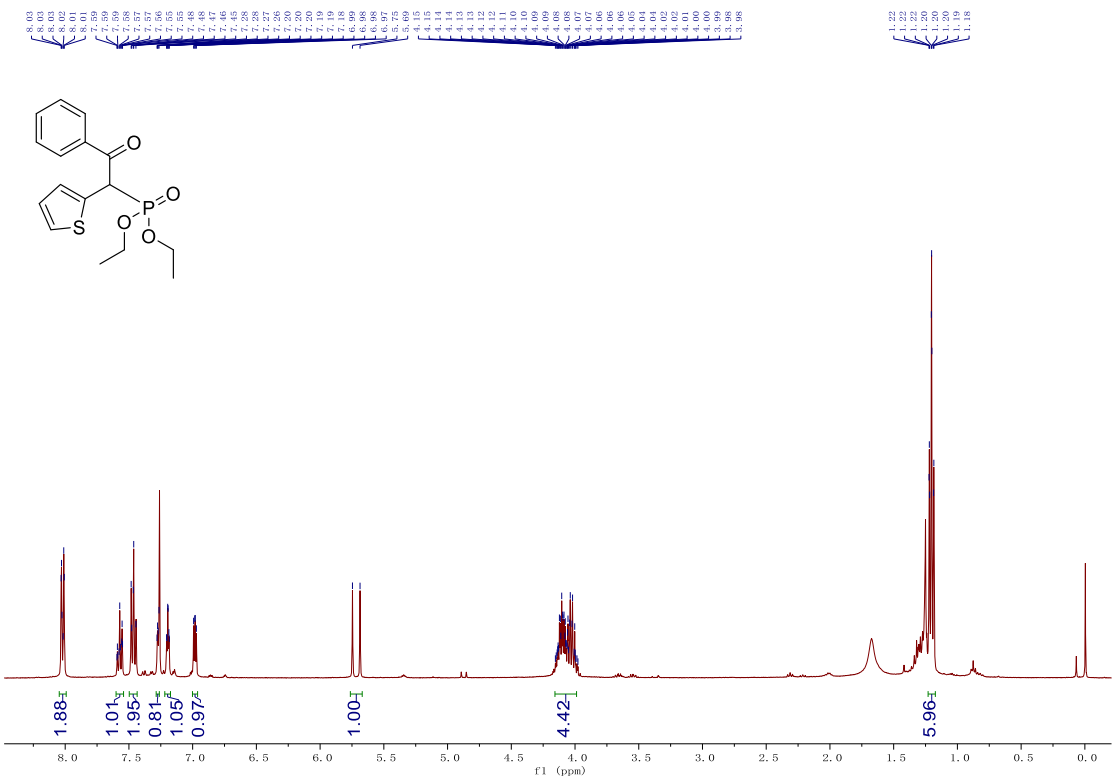

Figure S179. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4l**

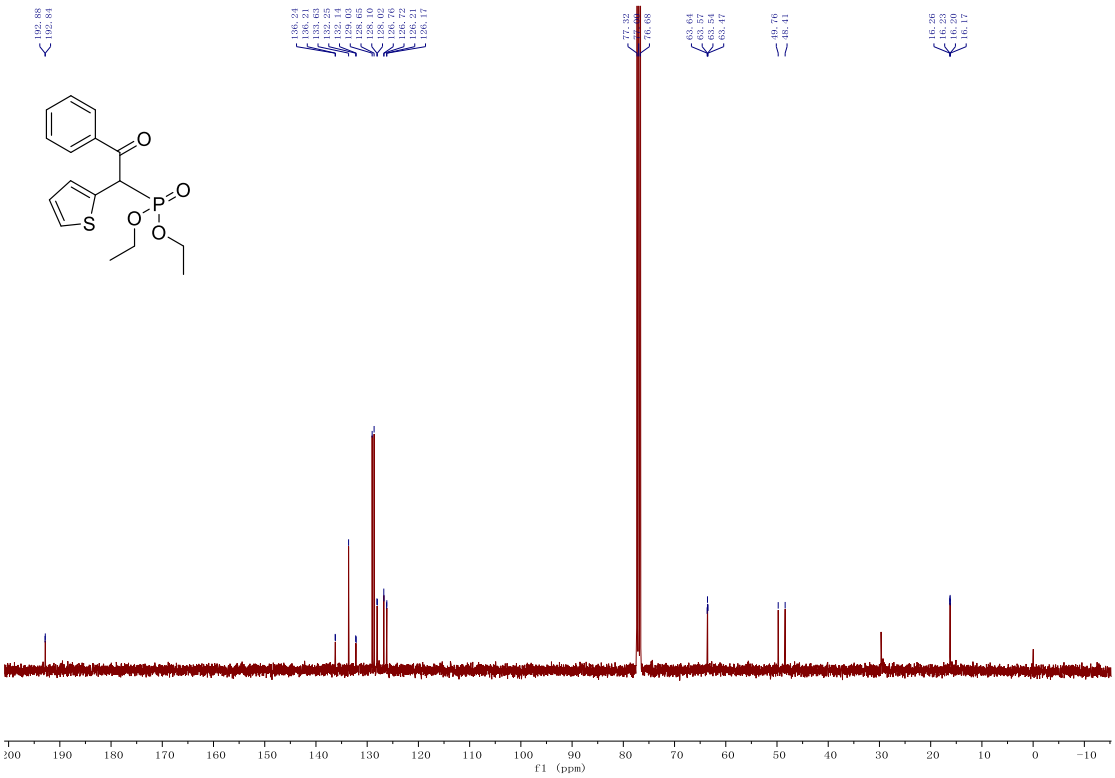

Figure S180. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4l**

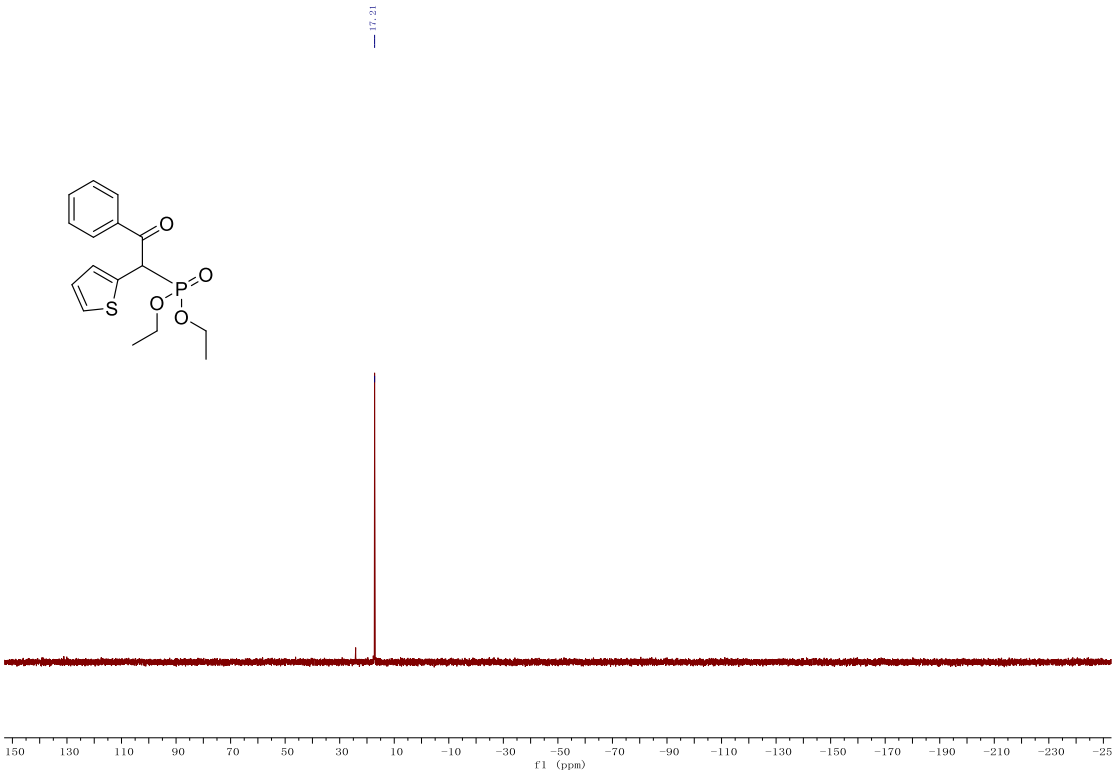

Figure S181. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4l**

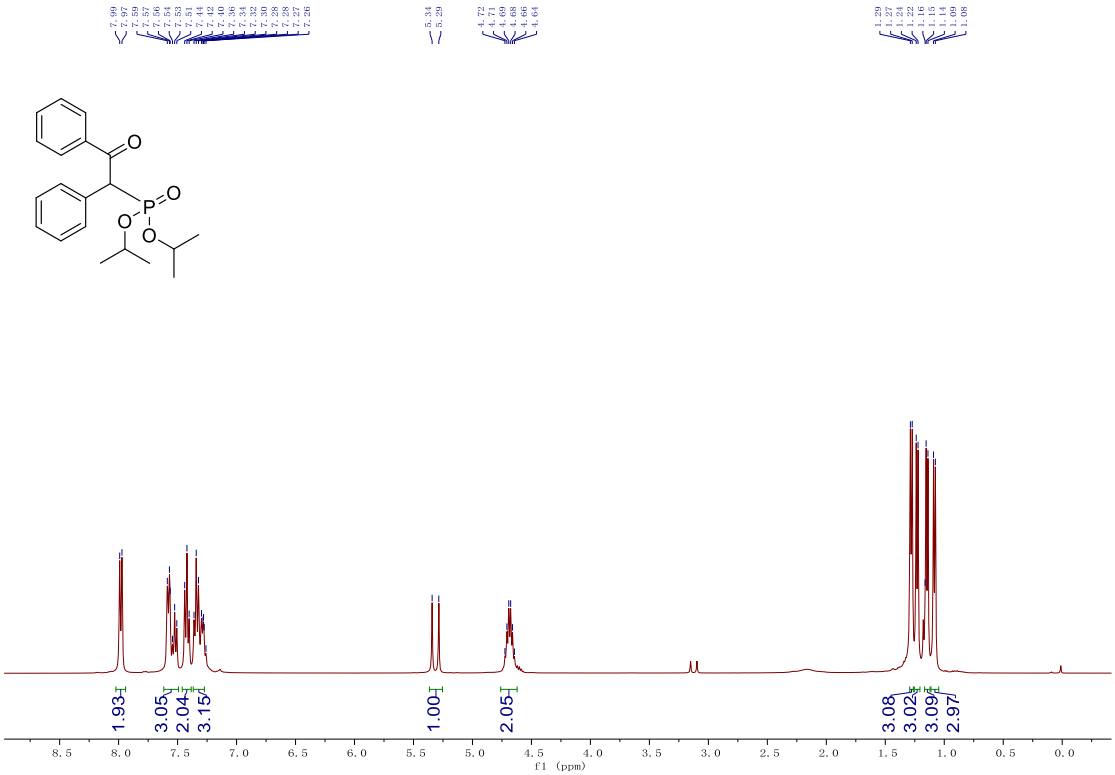

Figure S182. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4m**

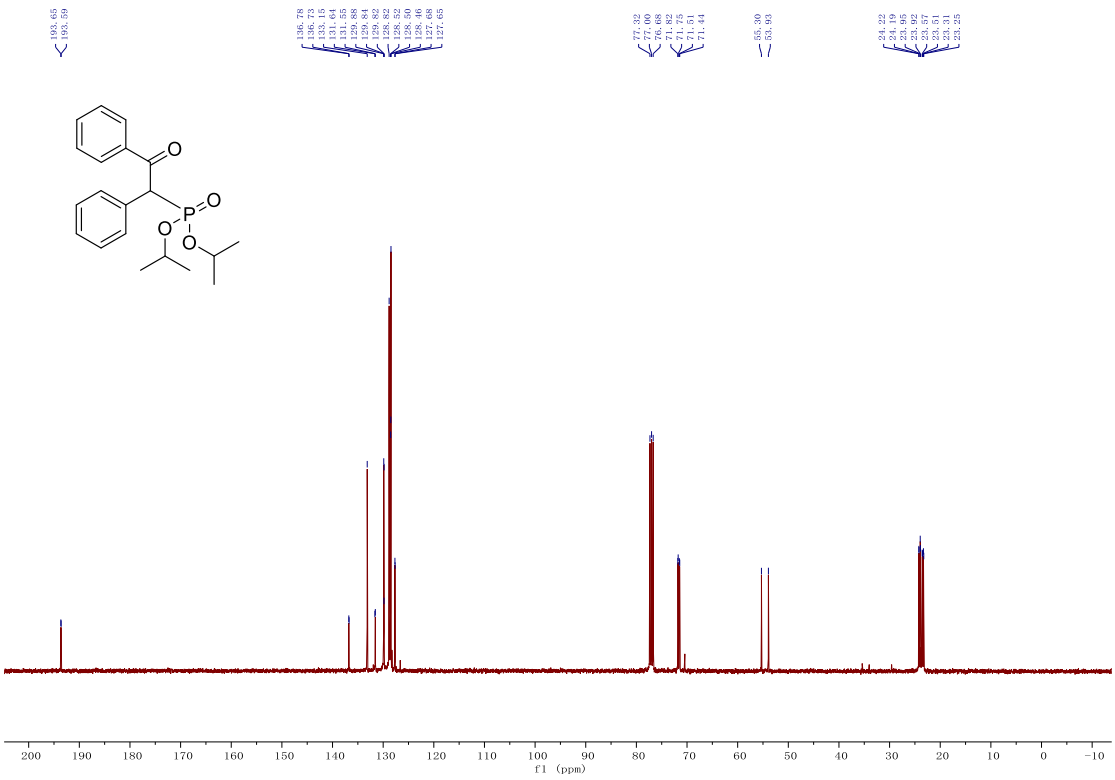

Figure S183. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4m**

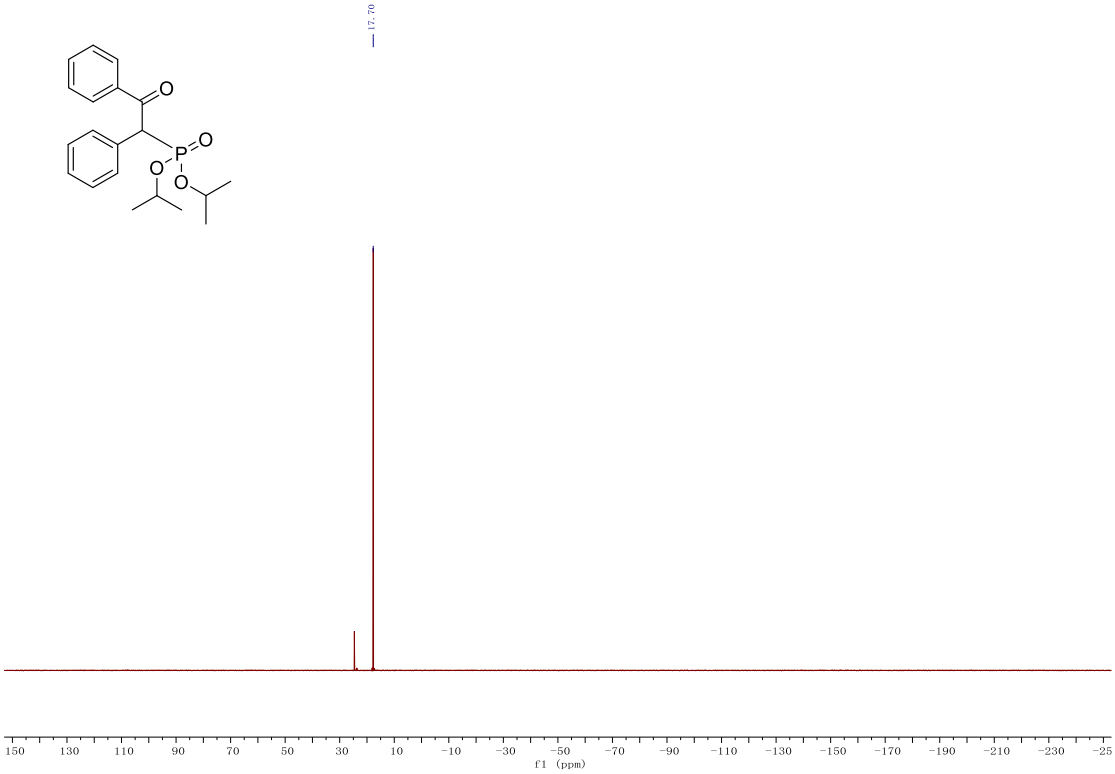

Figure S184. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **4m**

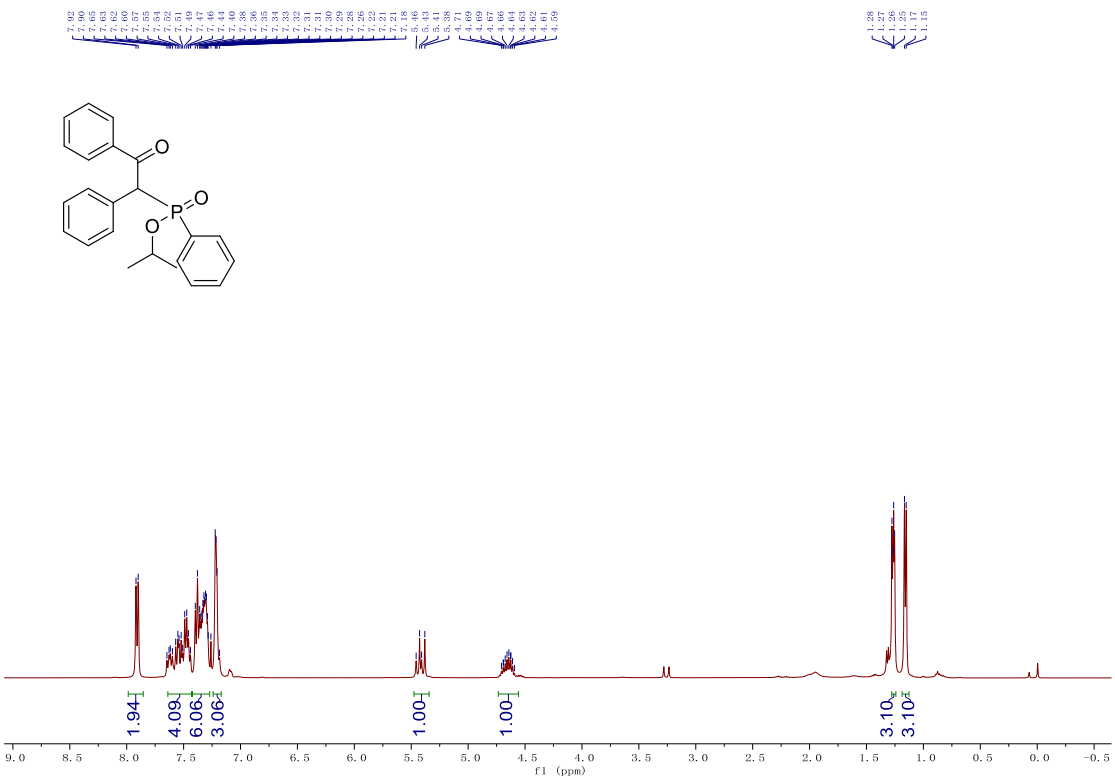

Figure S185. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4n**

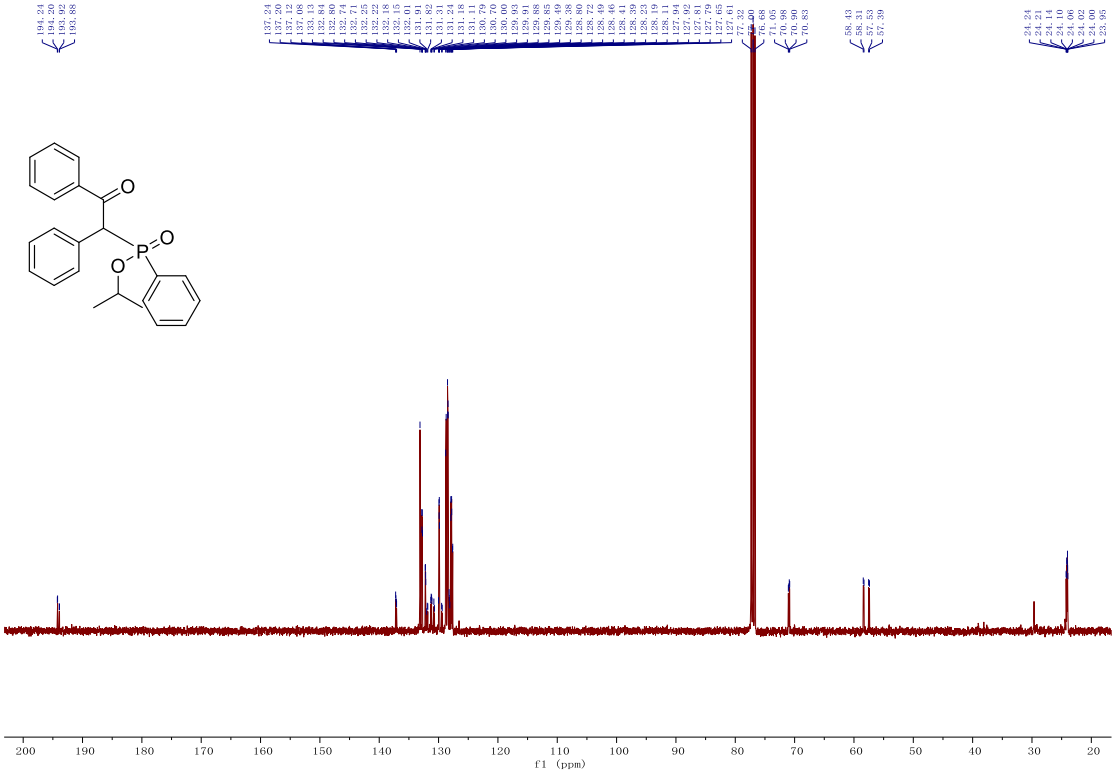

Figure S186. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4n**

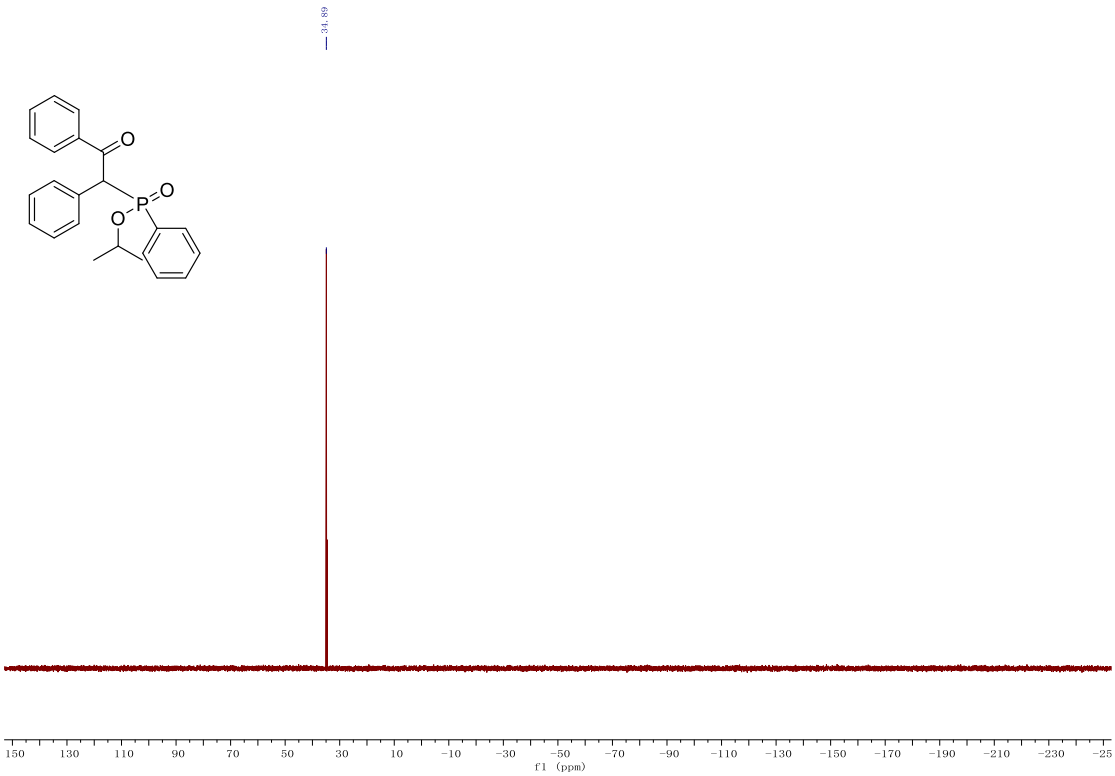

Figure S187. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **4n**

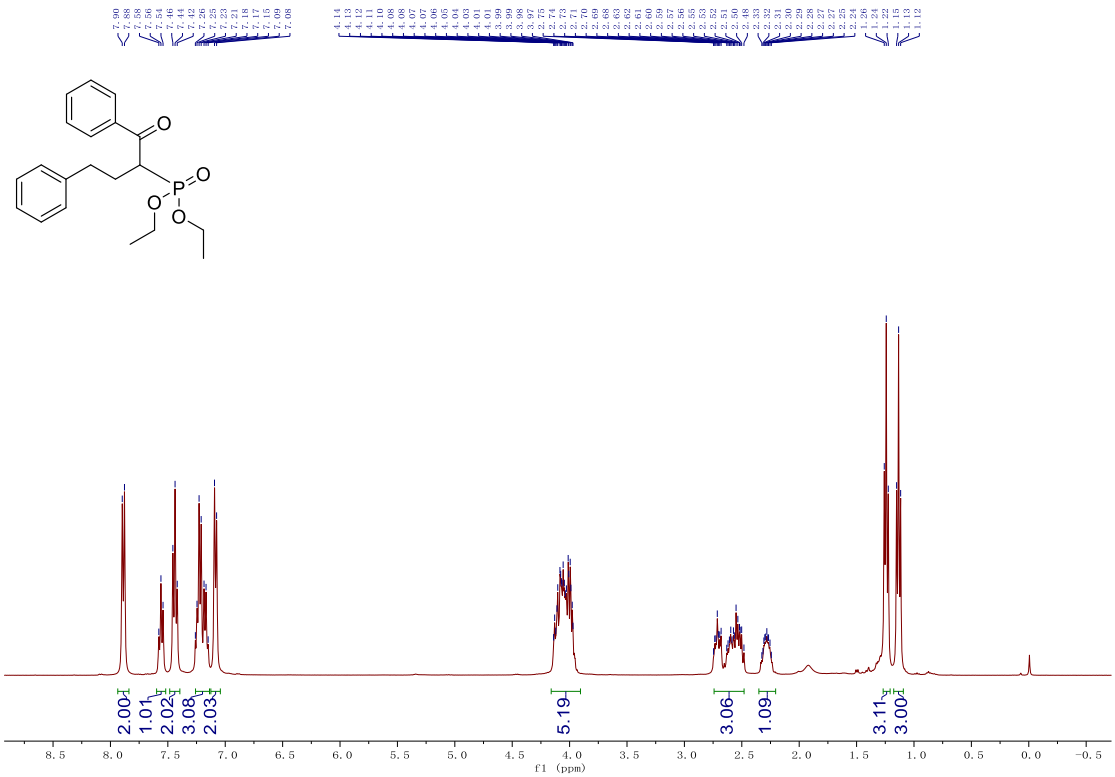

Figure S188. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4o**

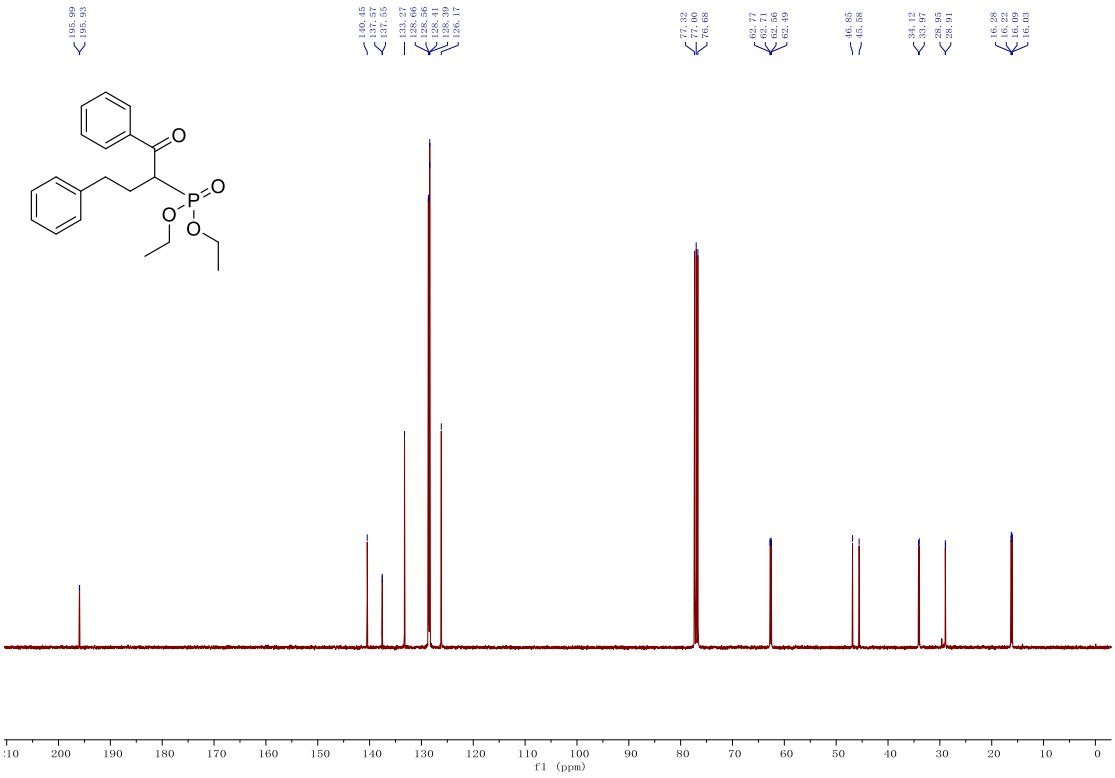

Figure S189. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4o**

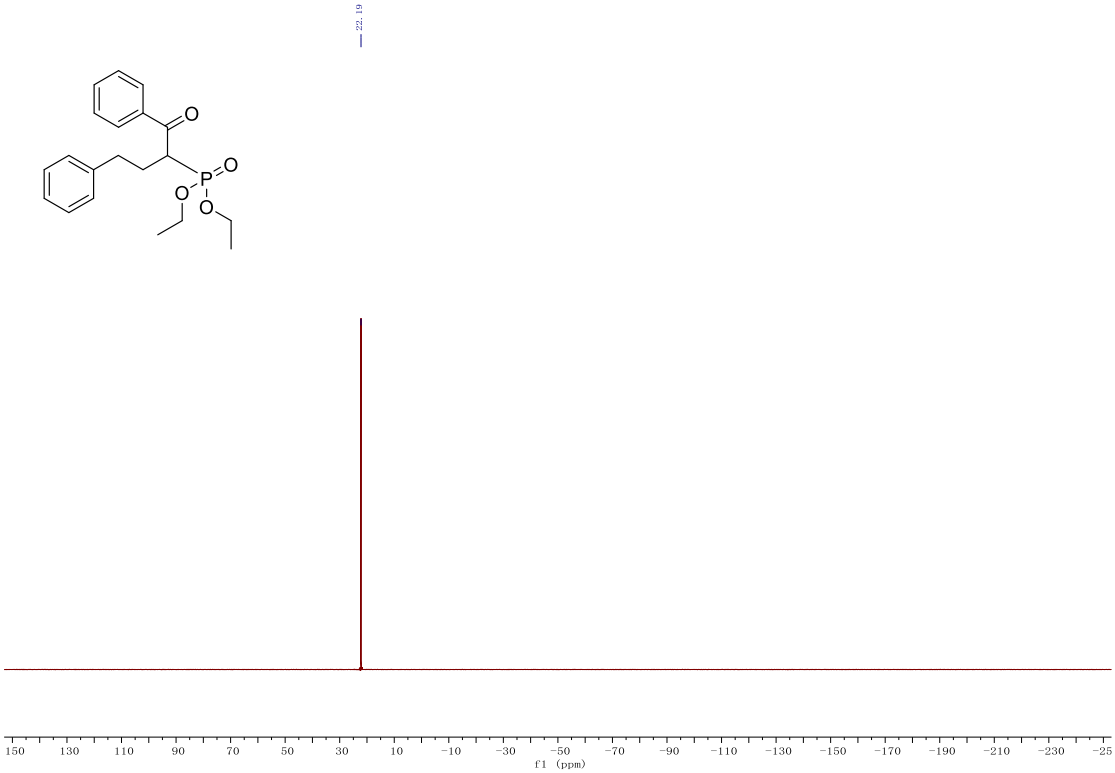

Figure S190. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **4o**

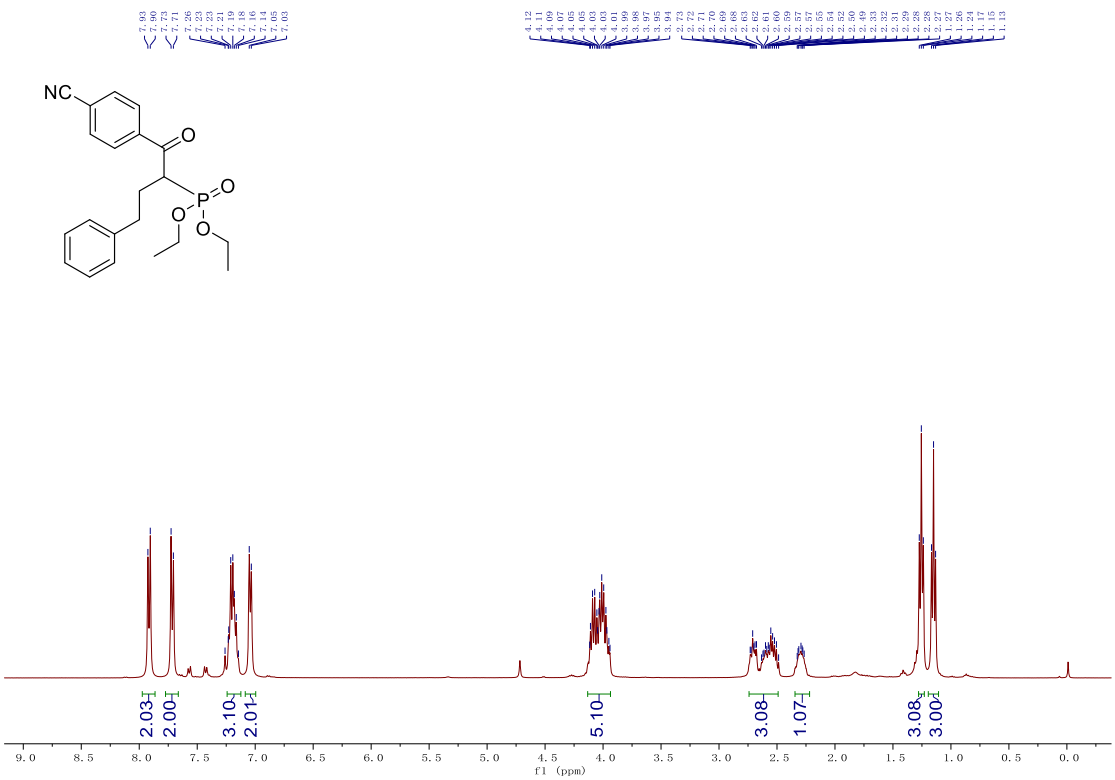

Figure S191. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **4p**

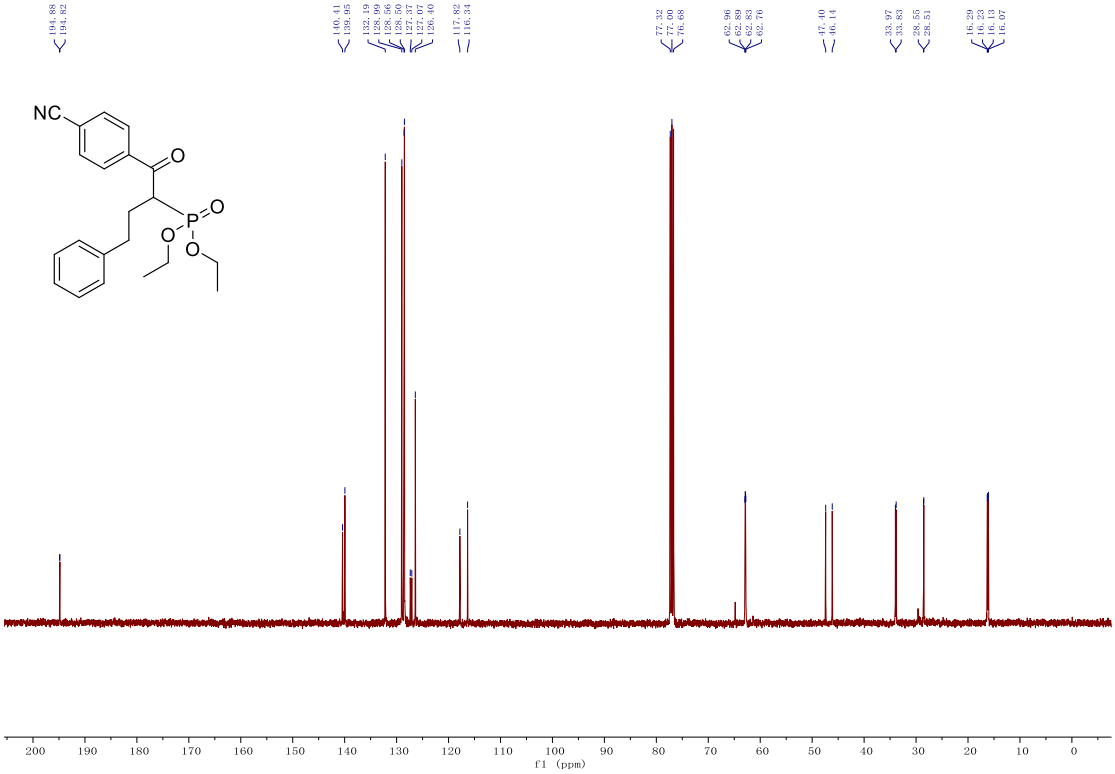

Figure S192. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4p**

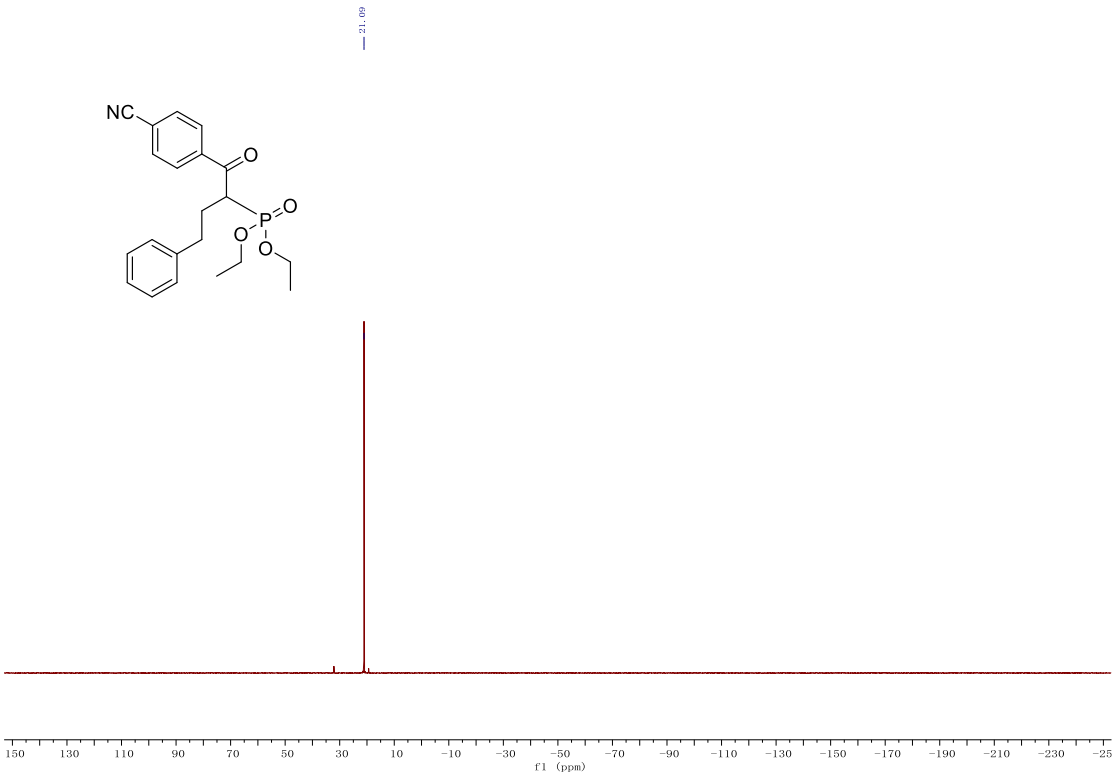

Figure S193. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **4p**

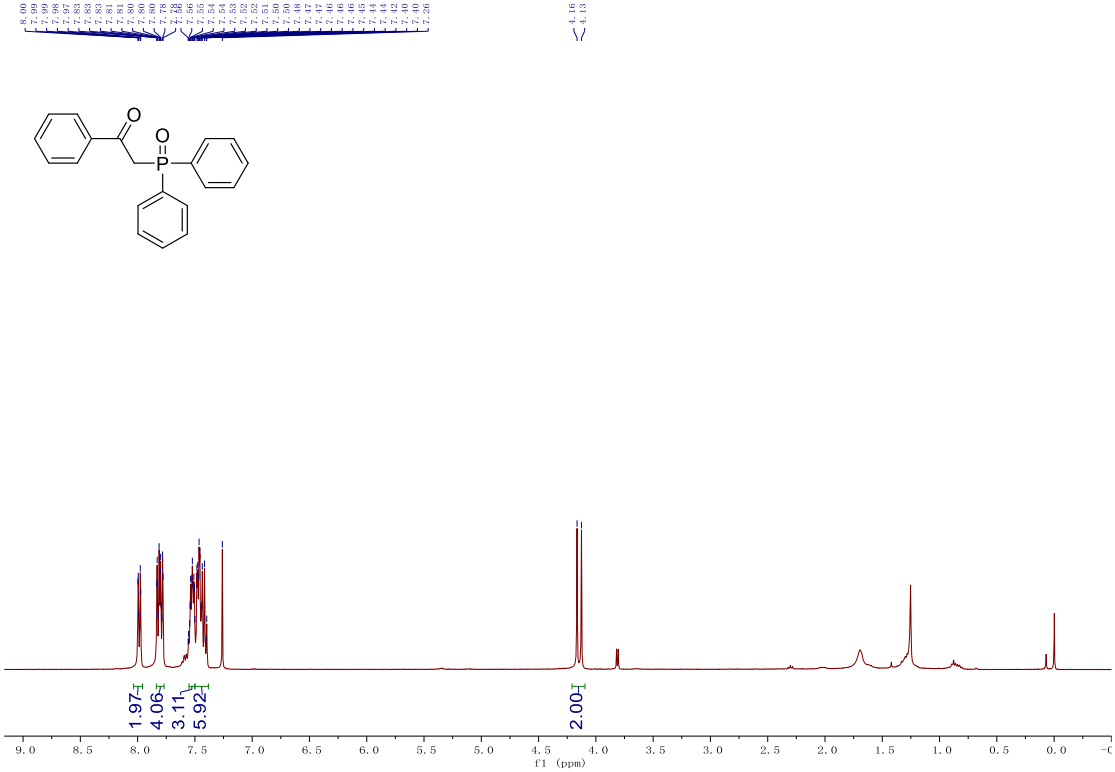

Figure S194. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4q**

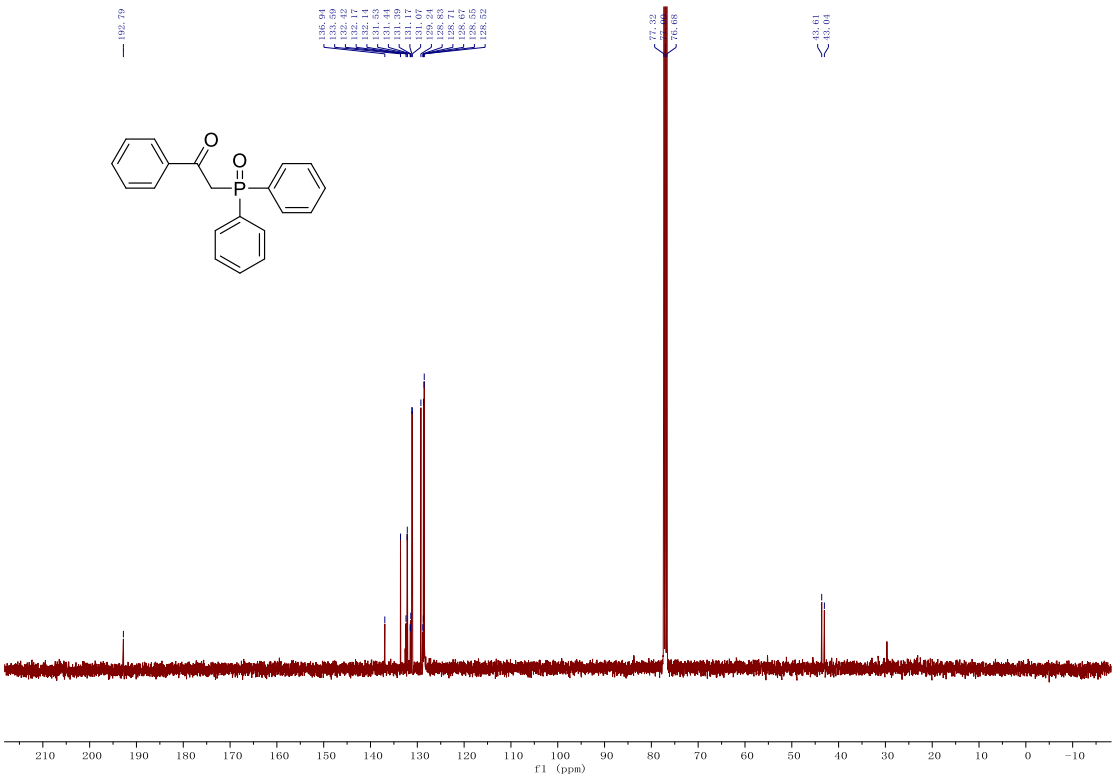

Figure S195. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **4q**

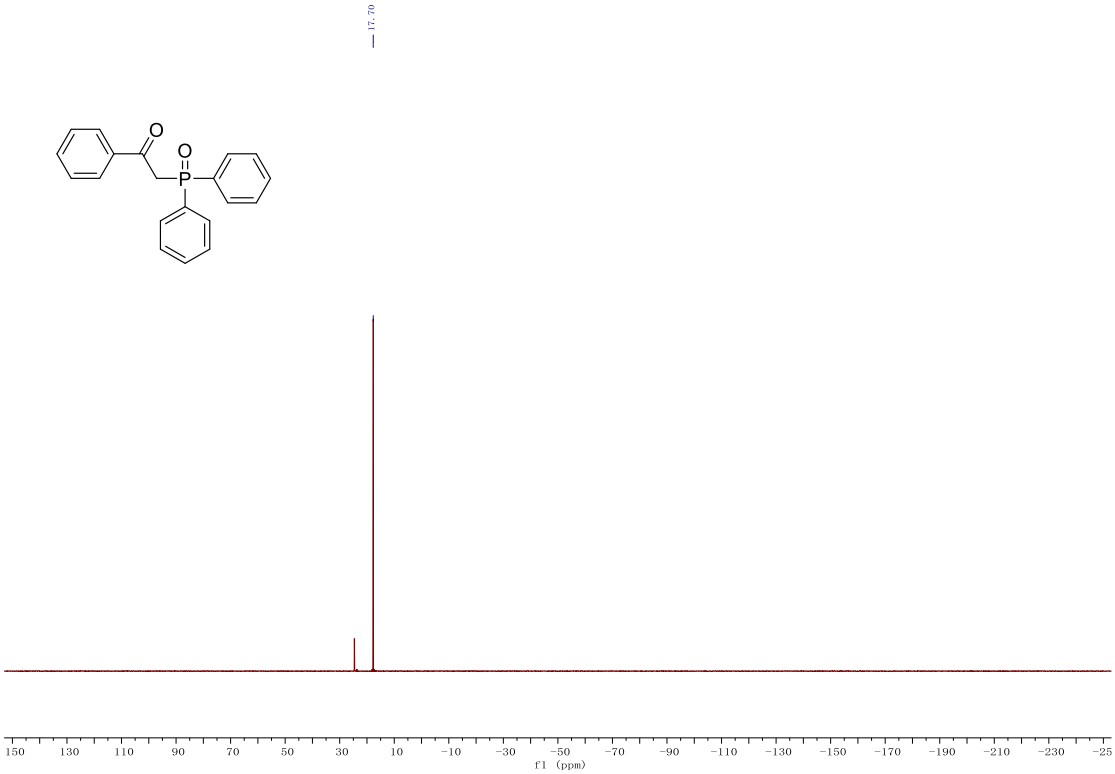

Figure S196 ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **4q**

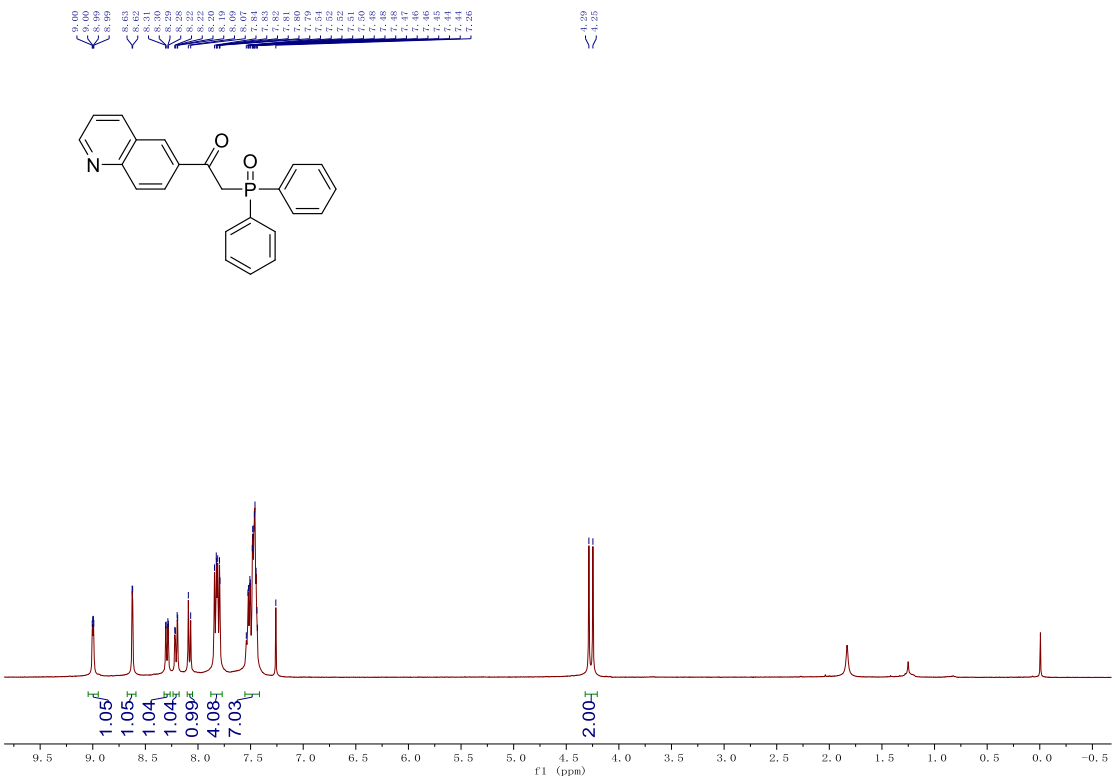

Figure S197. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**

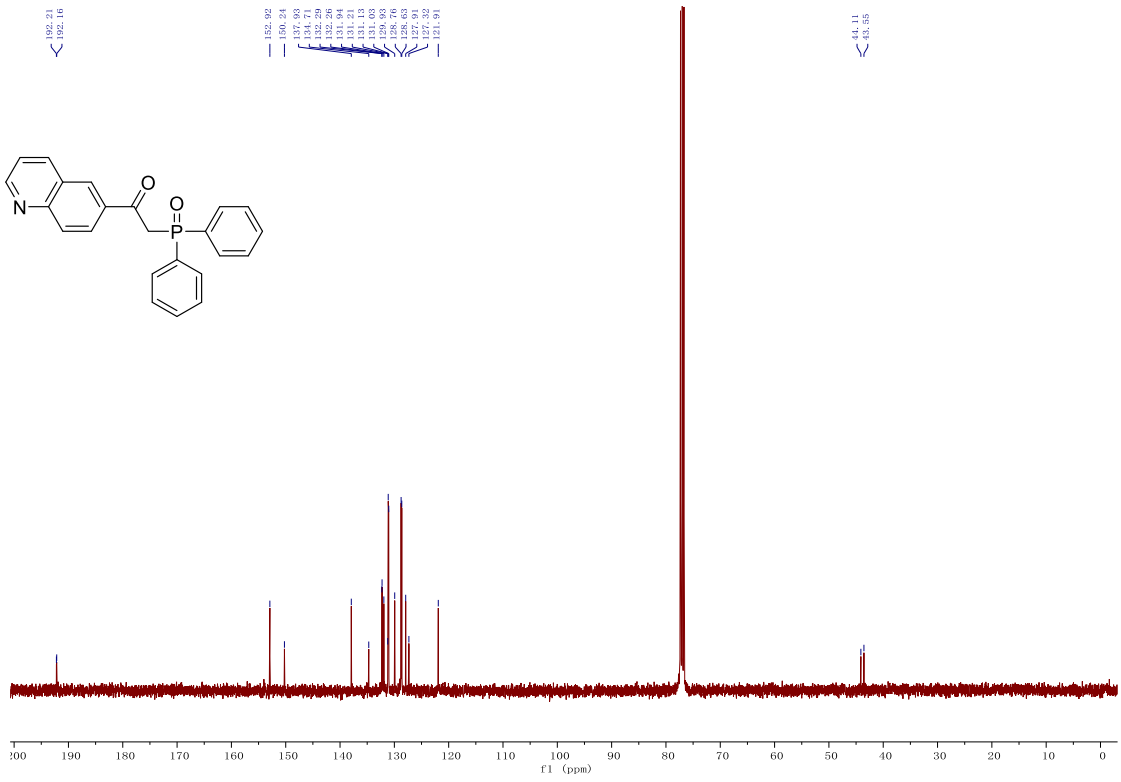

Figure S198. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4r**

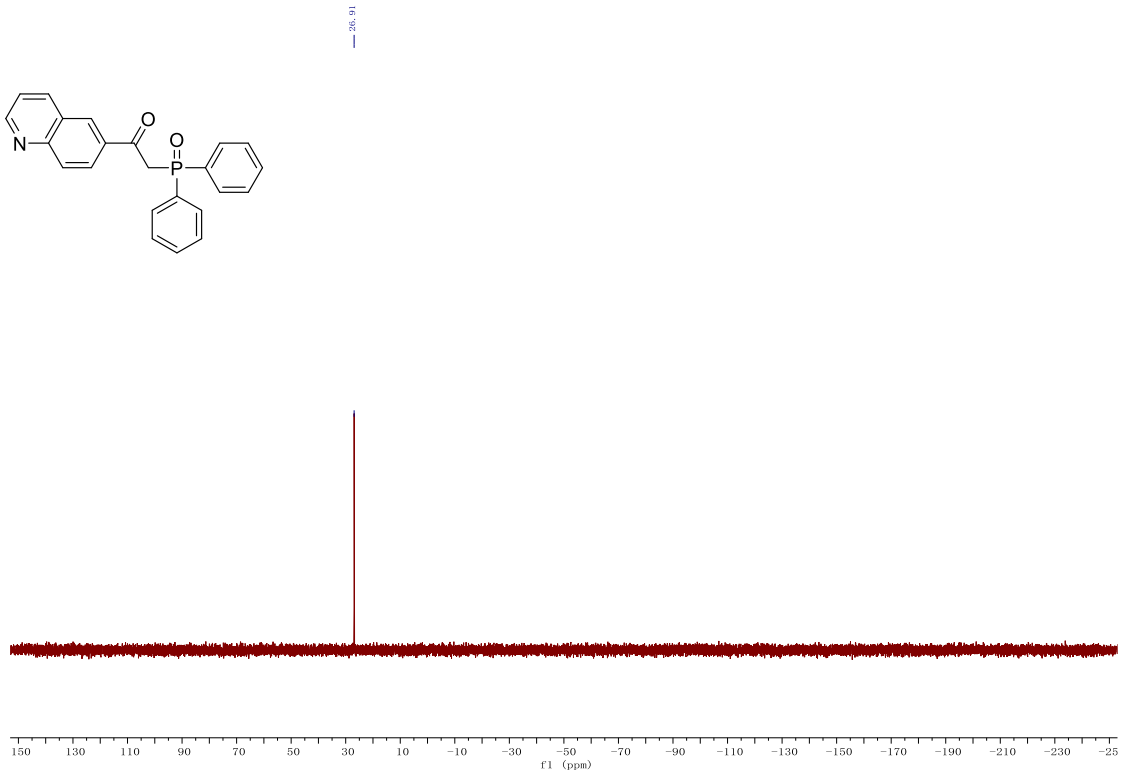

Figure S199. ^{31}**P NMR** (**162 MHz**, **$CDCl_3$**).spectrum of **4r**

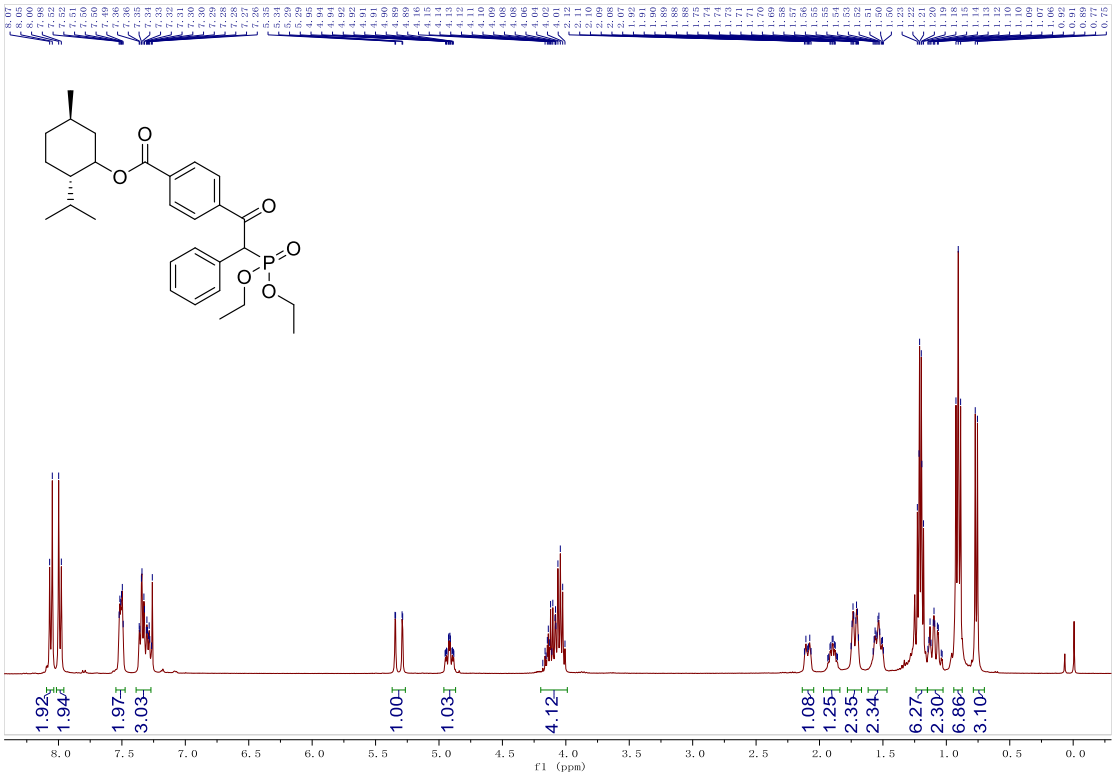

Figure S200. ^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of **5**

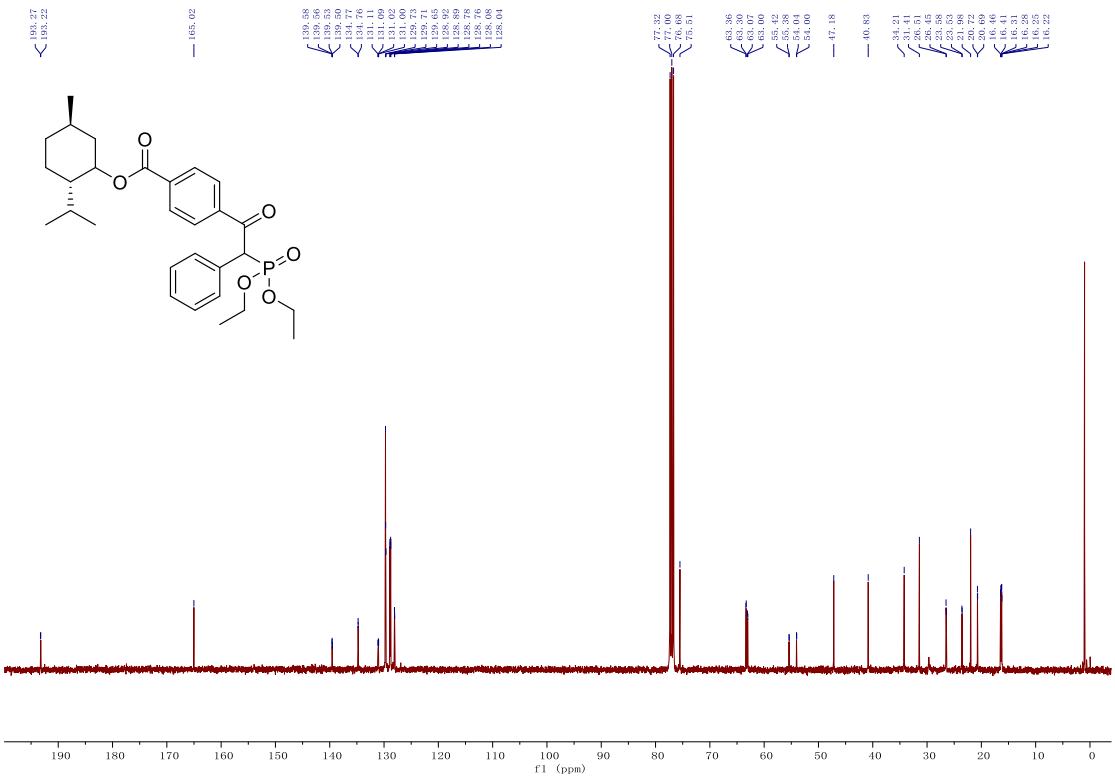

Figure S201. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **5**

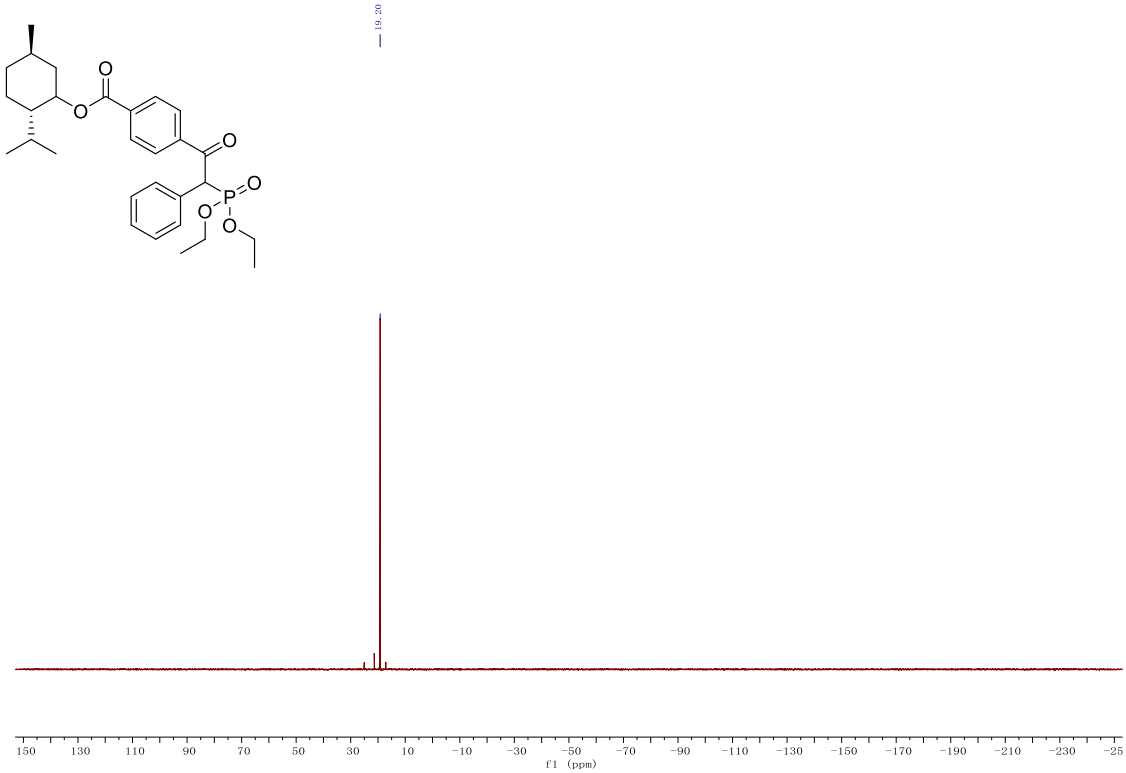

Figure S202. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **5**

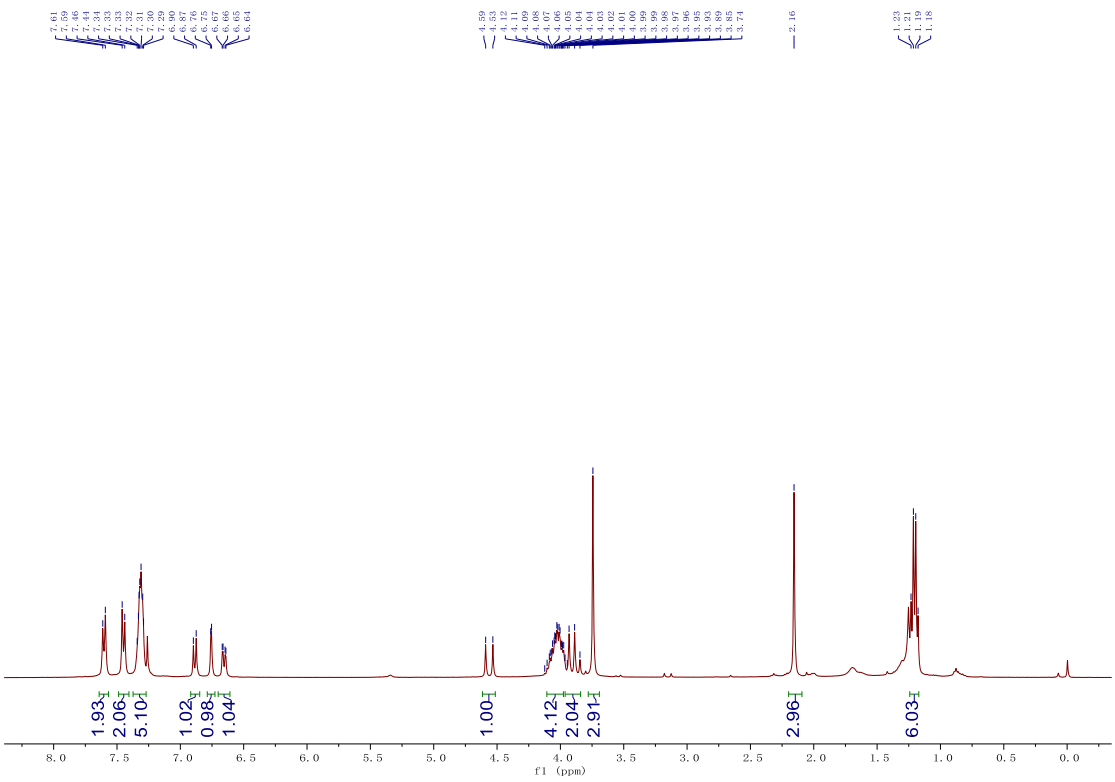

Figure S203. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**

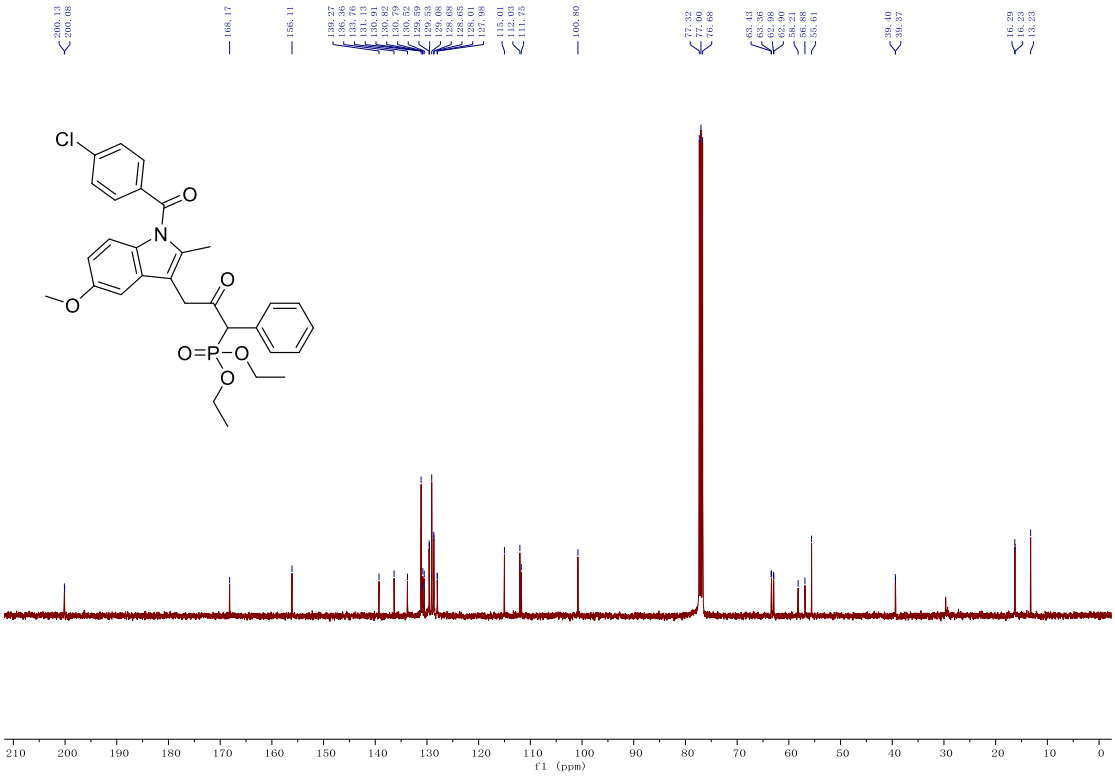

Figure S204. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6**

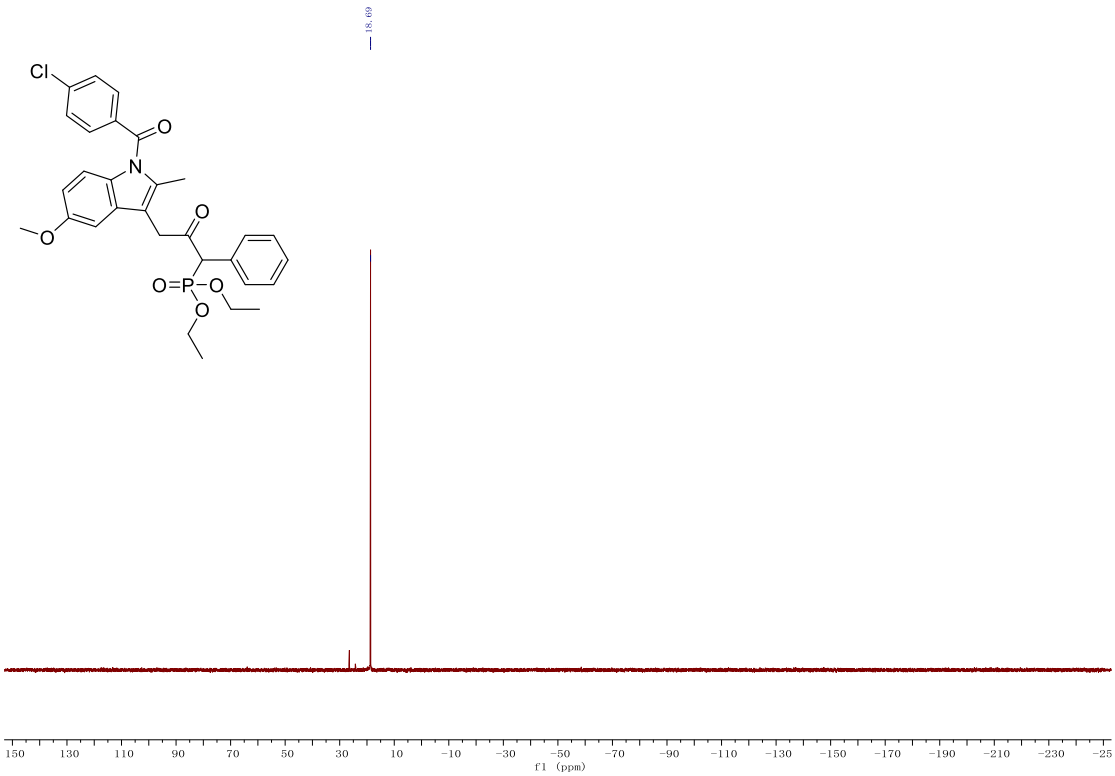

Figure S205. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **6**

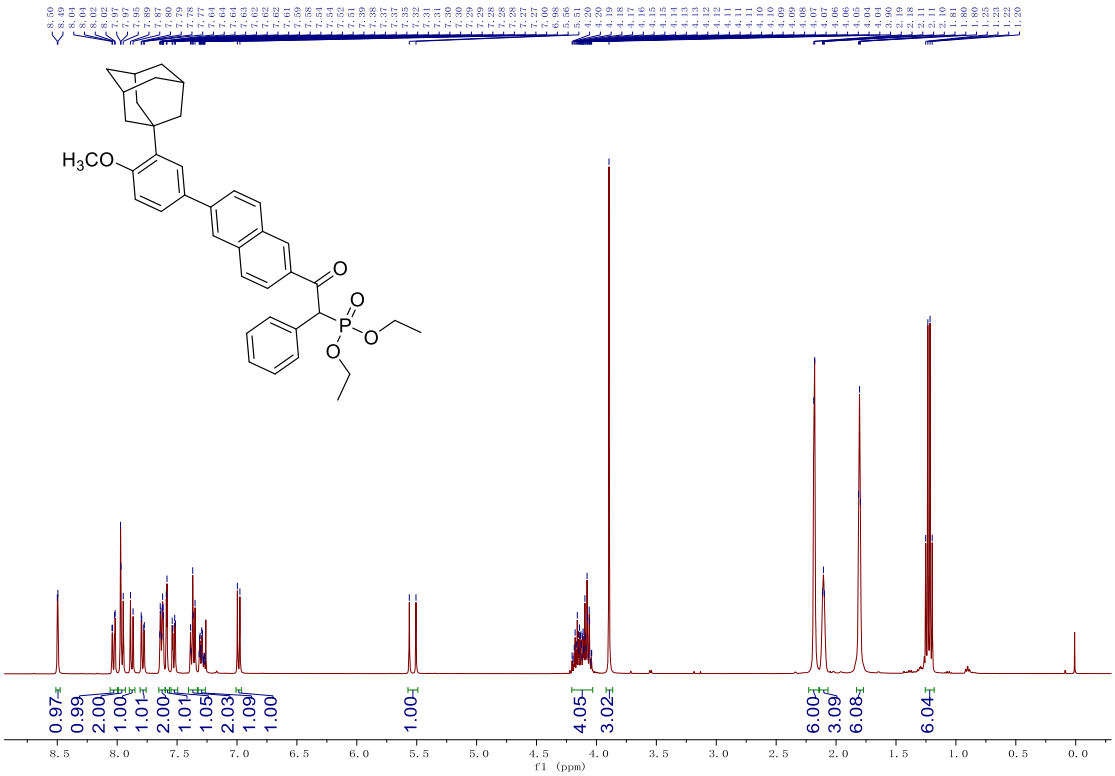

Figure S206. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

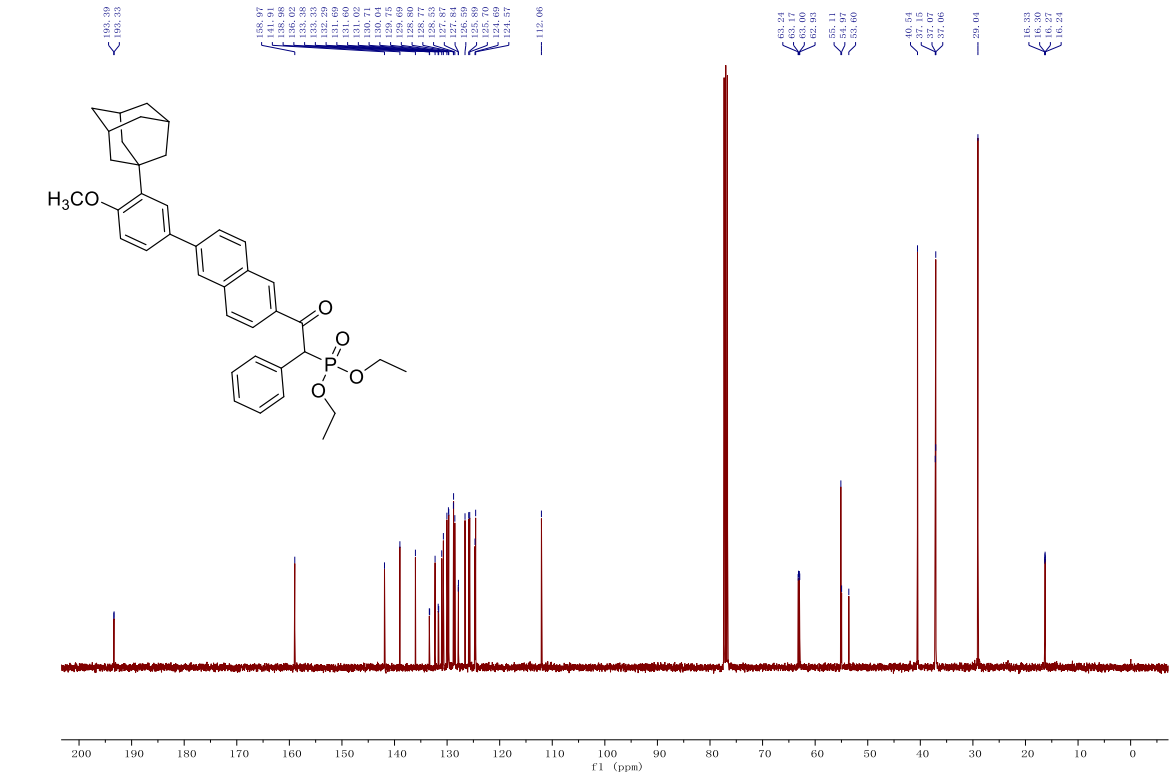

Figure S207. ^{13}**C NMR** (101 MHz, $CDCl_3$) spectrum of **7**

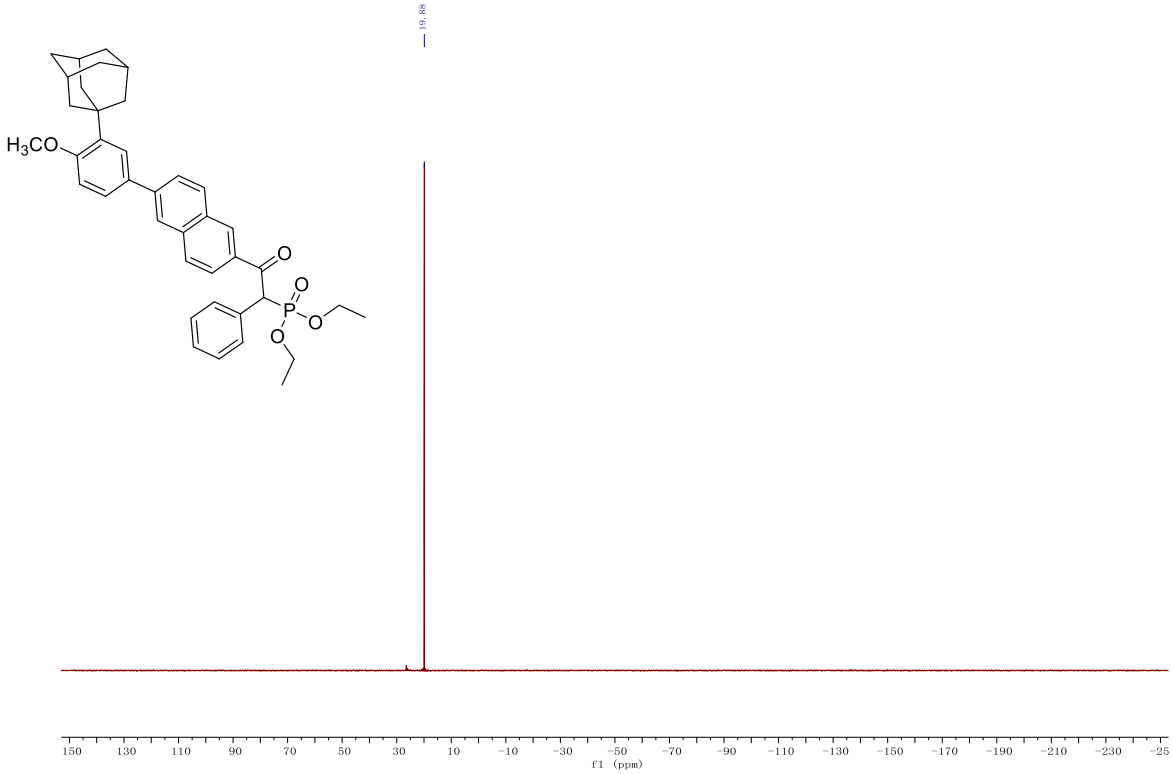

Figure S208. ^{31}**P NMR (162 MHz, $CDCl_3$)**.spectrum of **7**

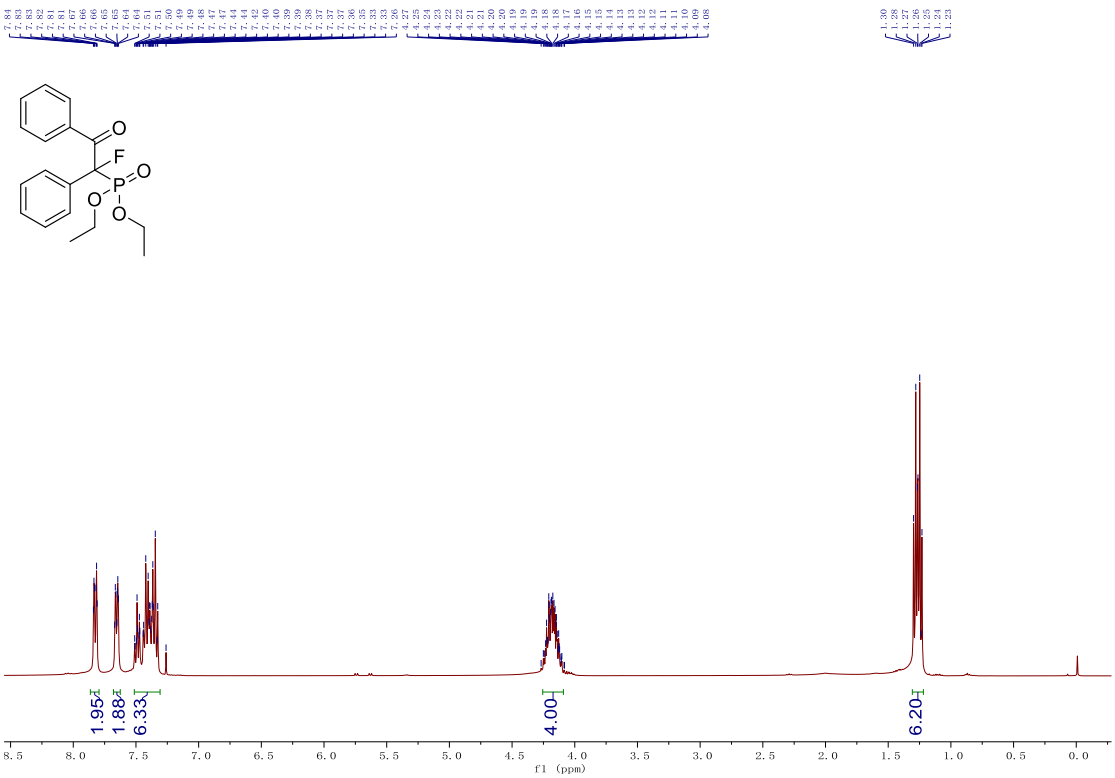

Figure S209. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**

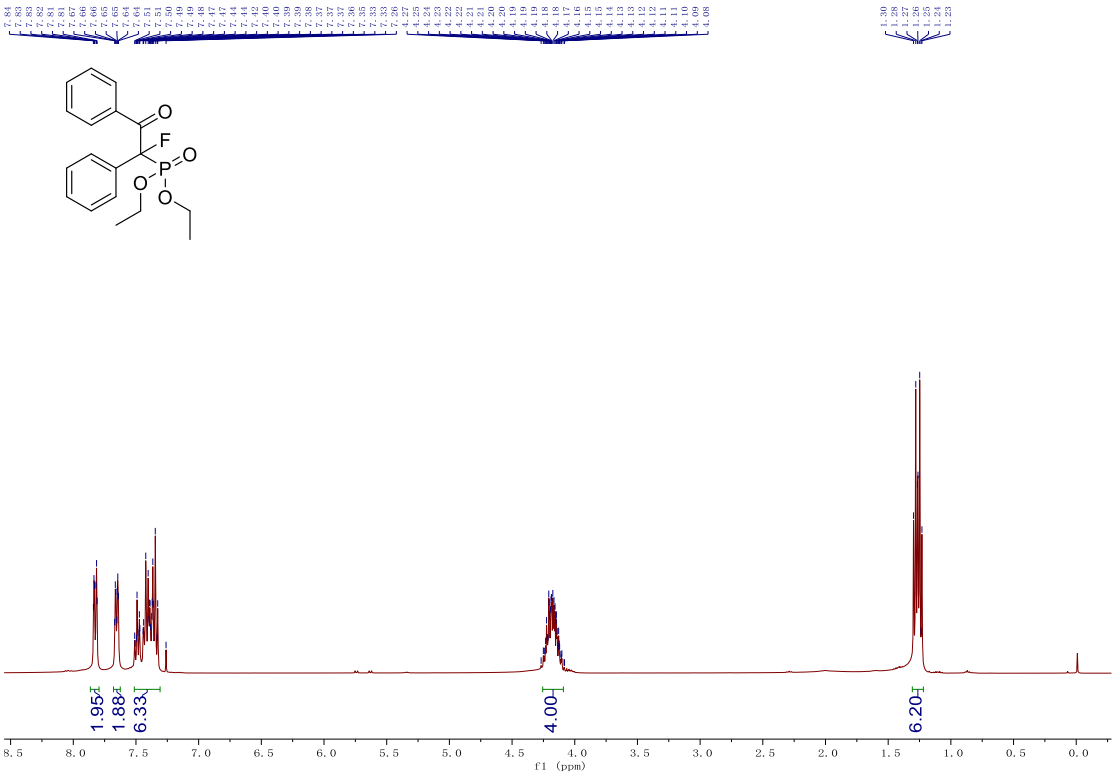

Figure S210. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **8**

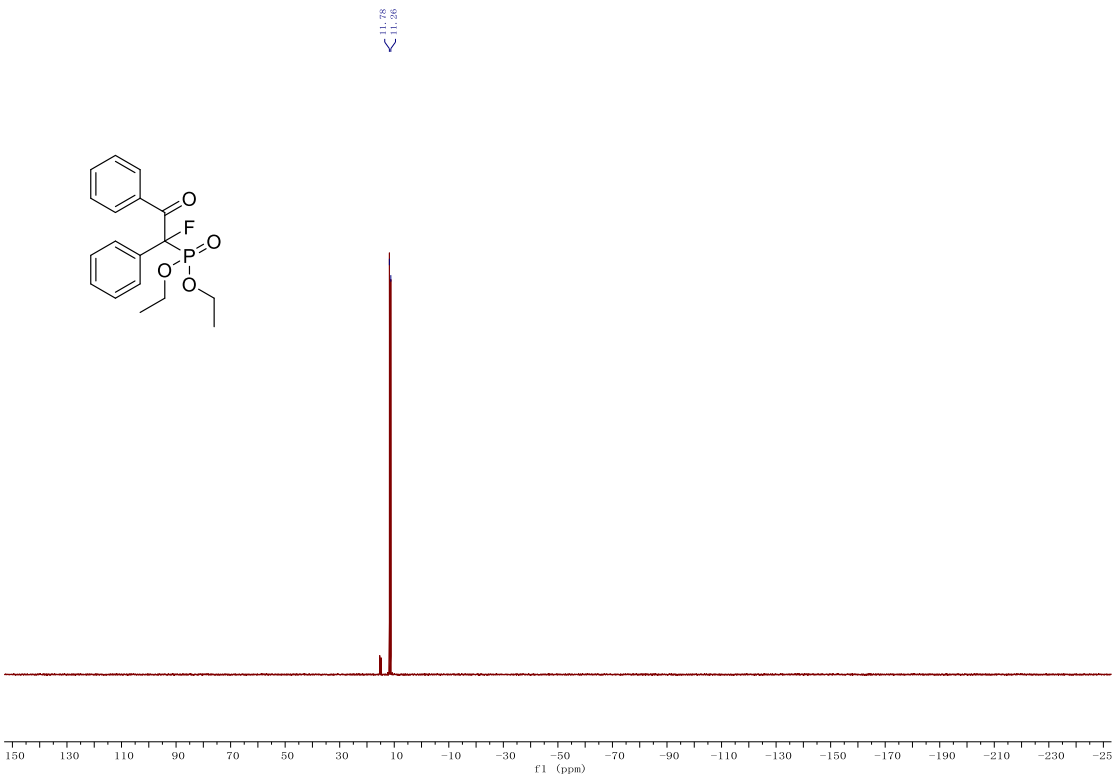

Figure S211. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **8**

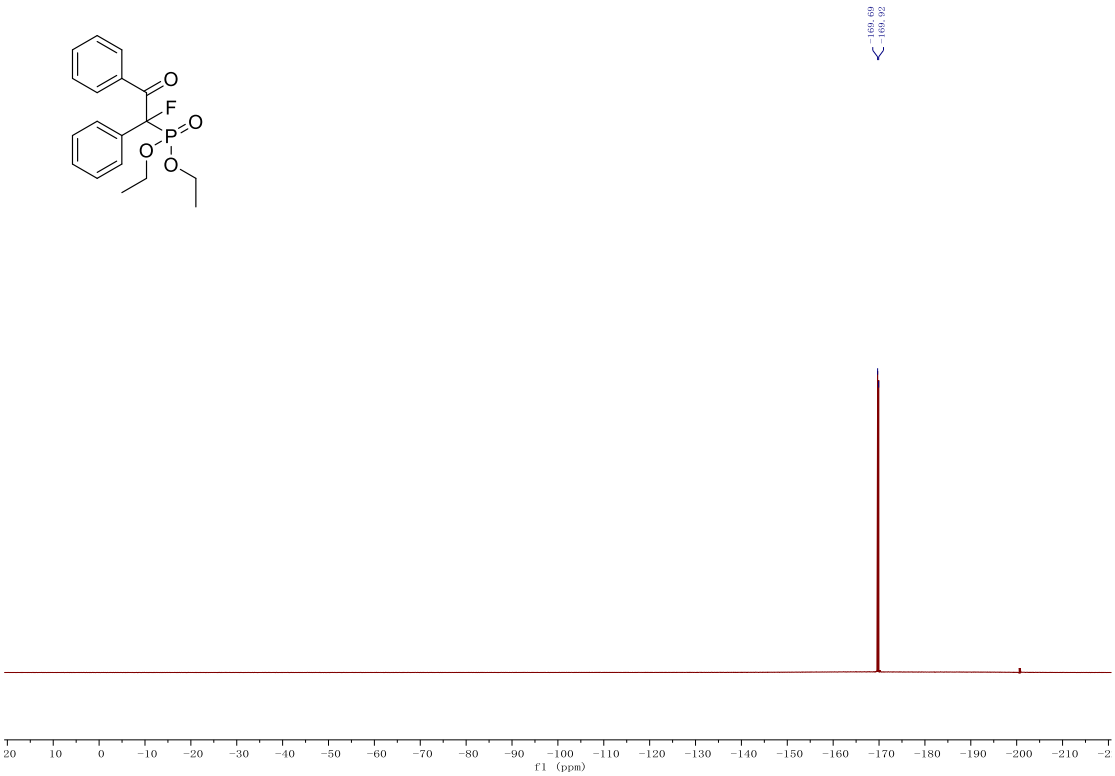

Figure S212. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **8**

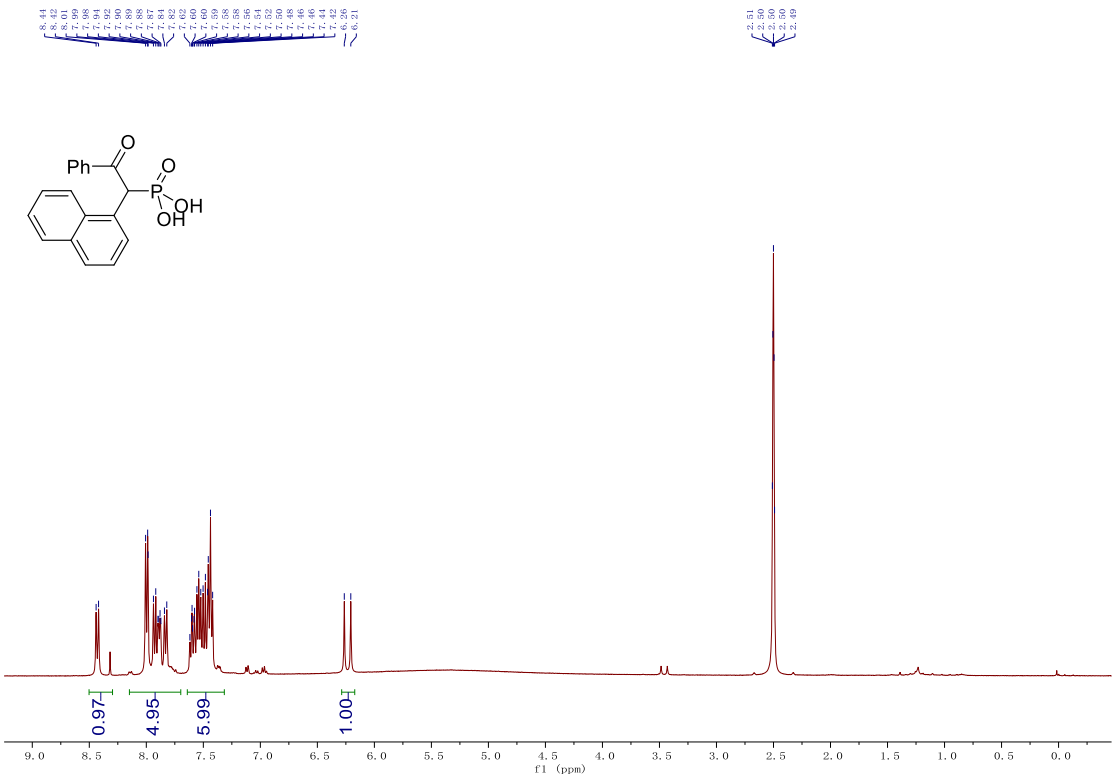

Figure S213. ^{1}H NMR (400 MHz, DMSO) spectrum of **9**

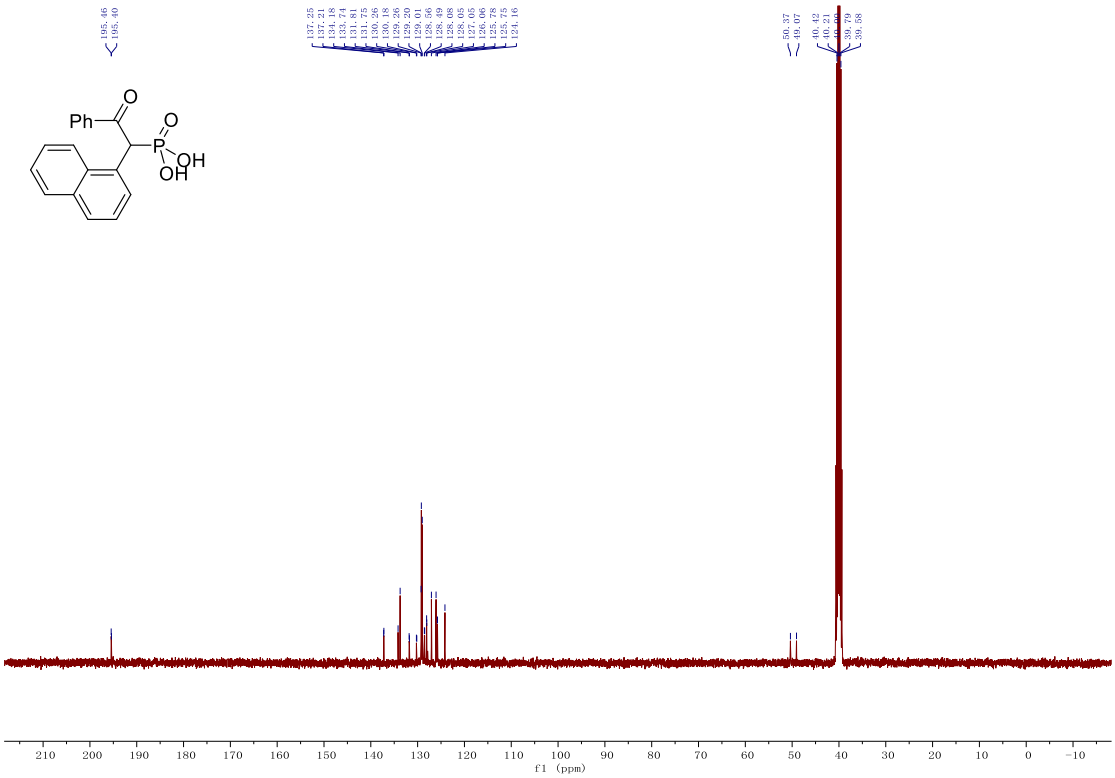

Figure S214. ^{13}C NMR (101 MHz, DMSO) spectrum of **9**

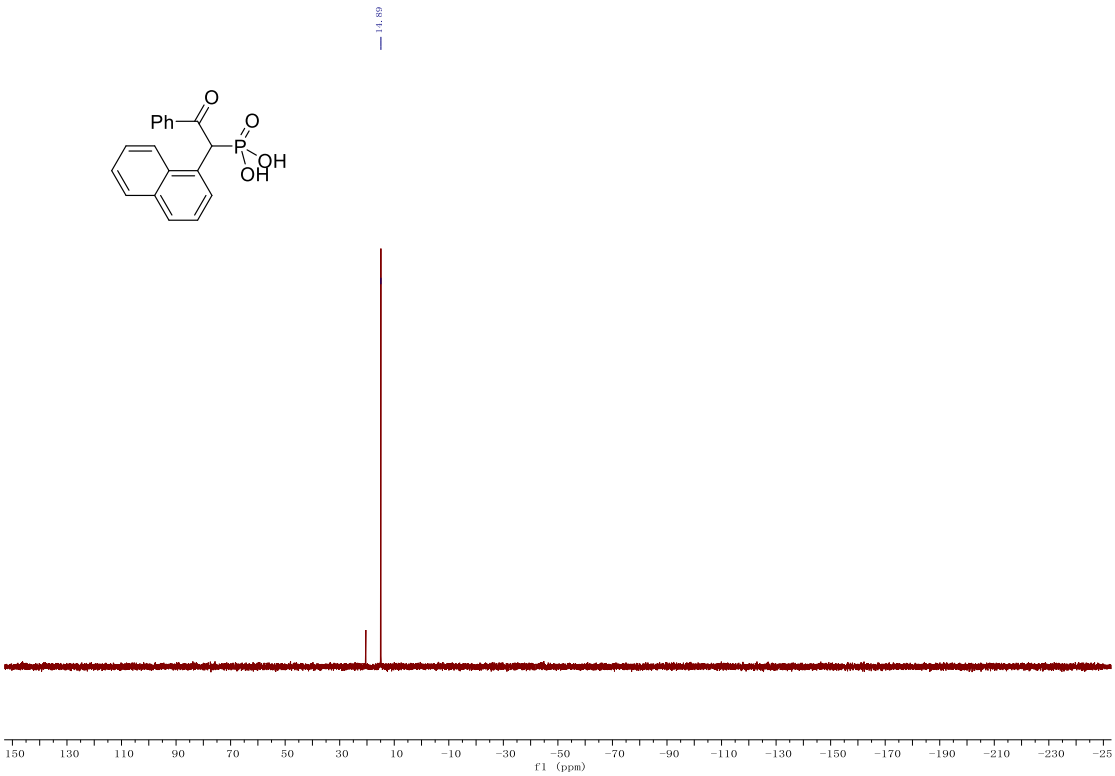

Figure S215. ^{31}P NMR (162 MHz, DMSO).spectrum of **9**

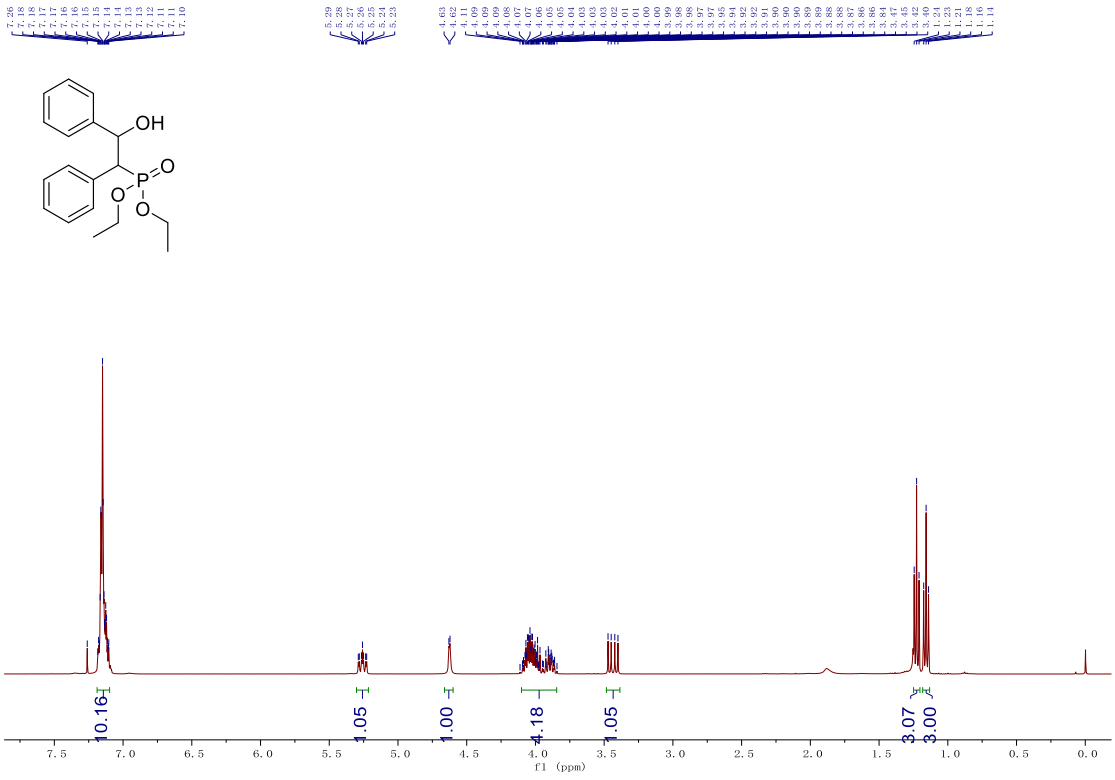

Figure S216. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

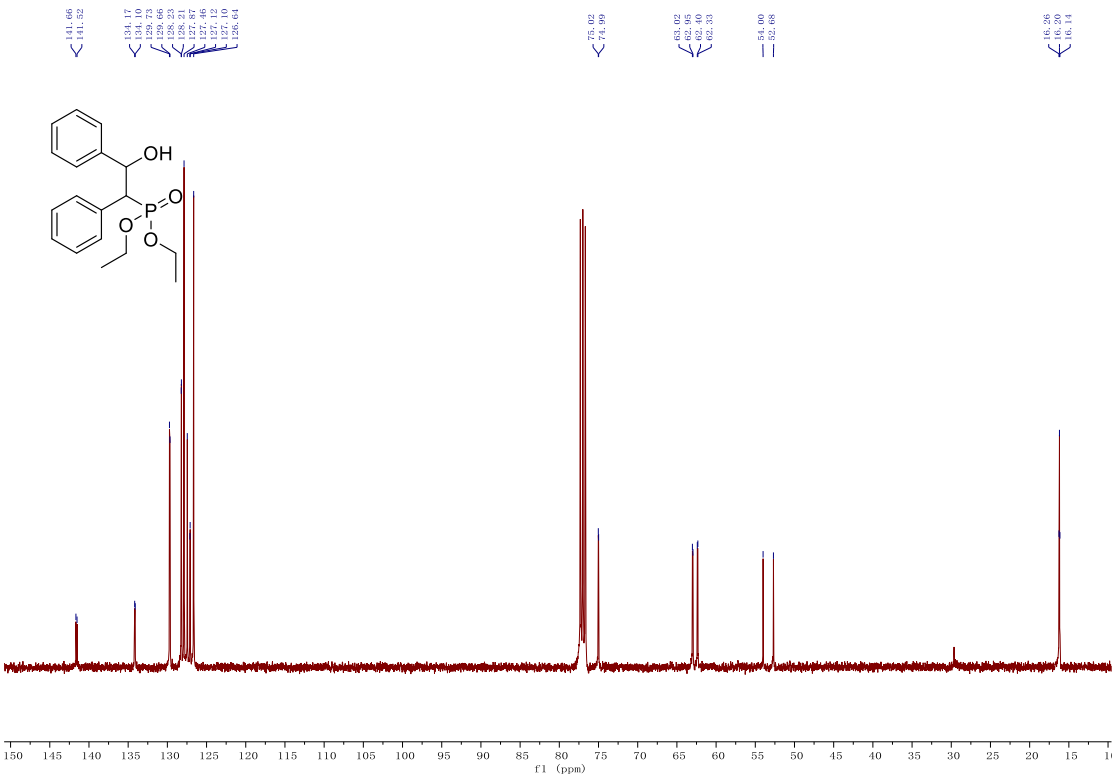

Figure S217. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **10**

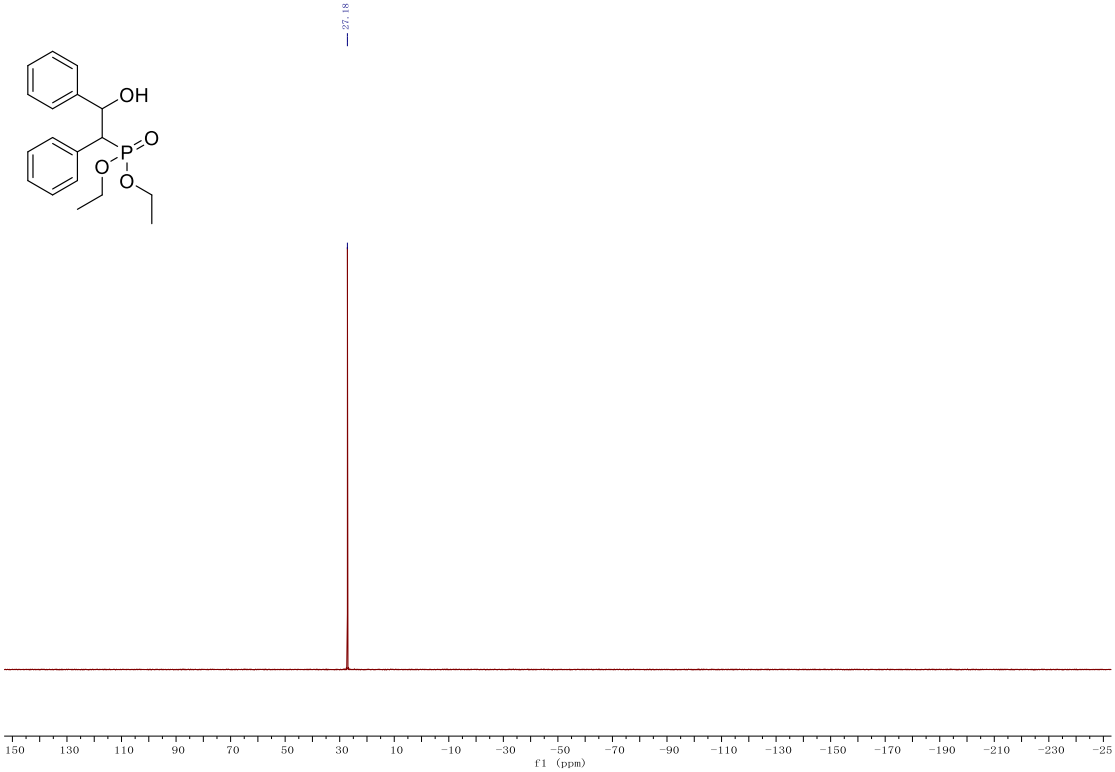

Figure S218. ^{31}P NMR (162 MHz, $CDCl_3$).spectrum of **10**

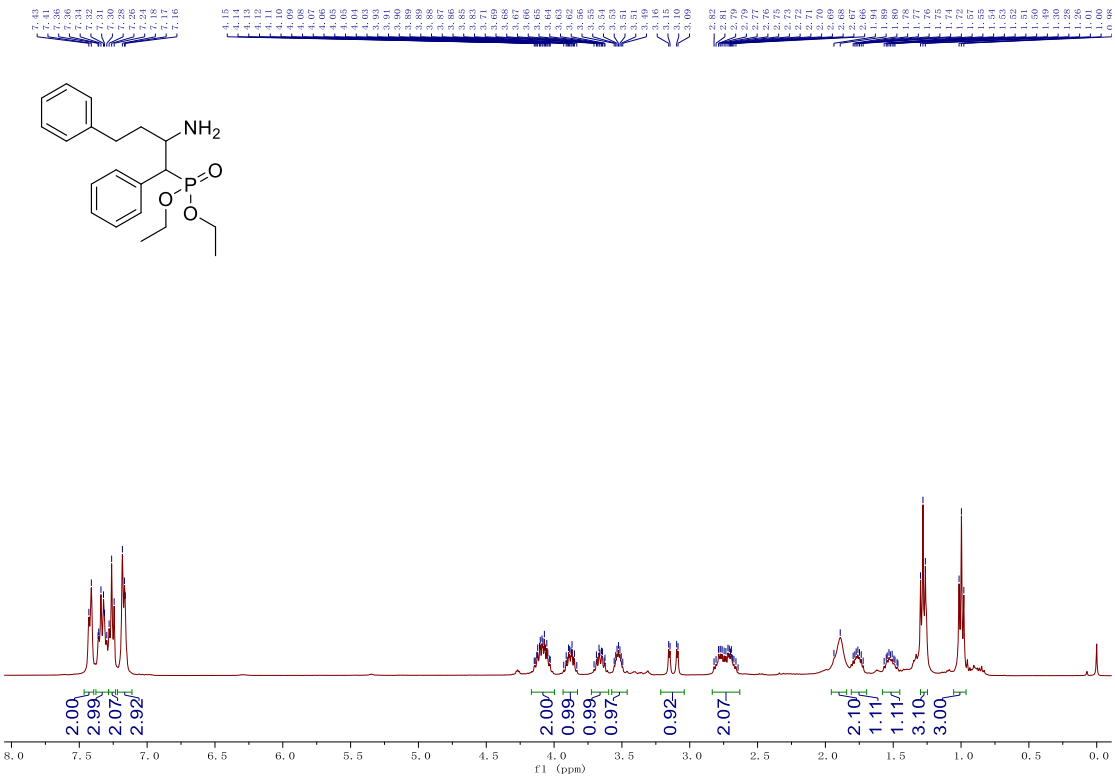

Figure S219. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

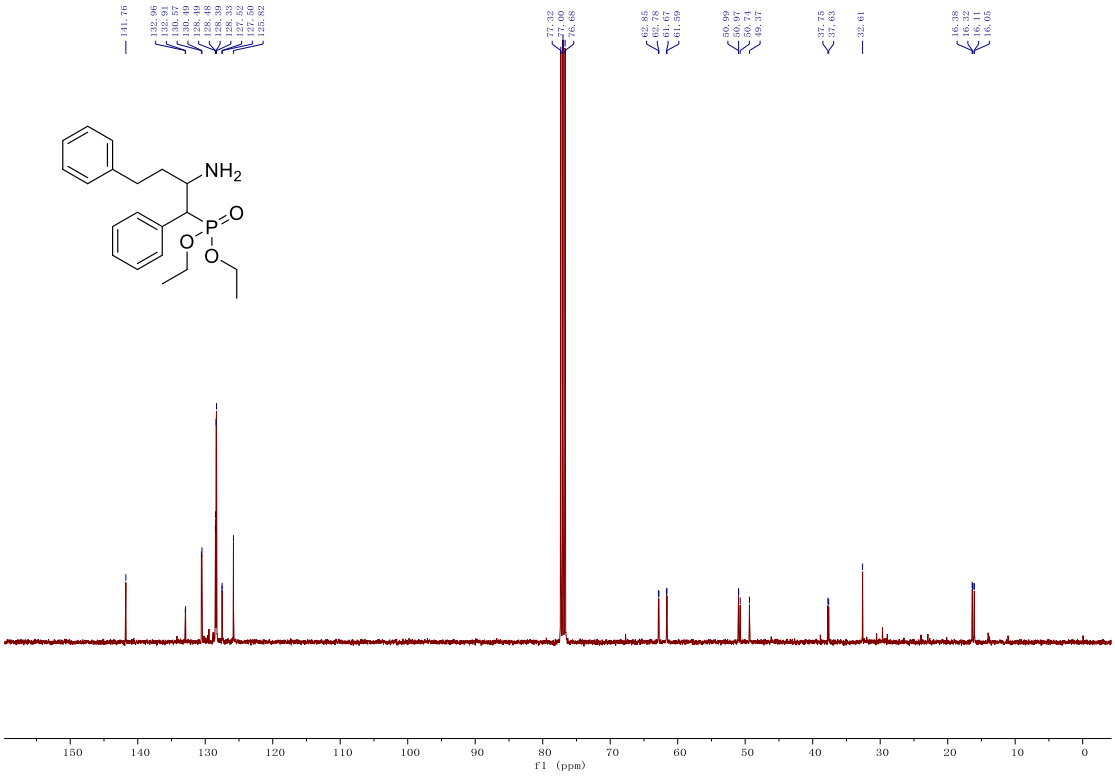

Figure S220. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **11**

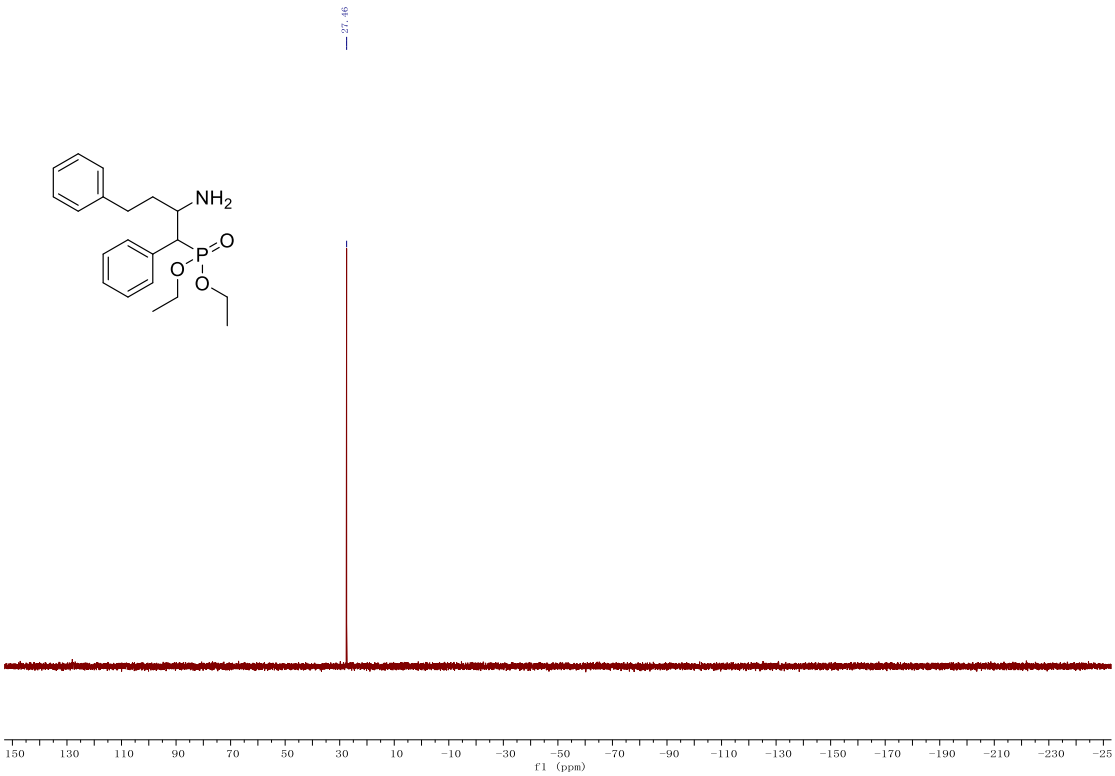

Figure S221. ^{31}**P NMR (162 MHz, CDCl$_3$)**.spectrum of **11**