Supporting Information

for

β-Ketophosphonates Formation via Deesterification or Deamidation of Cinnamyl/Alkynyl Carboxylates or Amides with H-phosphonates

Yao Zhou,[a] Mingxin Zhou,[a] Ming Chen,[b] Jihu Su,[b] Jiangfeng Du,[b] and Qiuling Song *[a, c]

[a] Institute of Next Generation Matter Transformation, College of Chemical Engineering, College of Materials Science & Engineering at Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, P. R. China

[b] Hefei National Laboratory for Physical Sciences at Microscale, Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

[c] Beijing National Laboratory for Molecular Sciences, Beijing, 100190, P. R. China

fax:86-592-6162990; email: qsong@hqu.edu.cn

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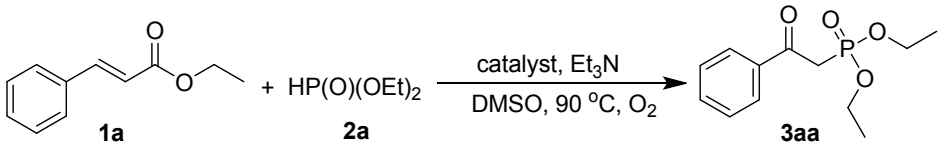
1. General information

All chemicals were purchased from Adamas Reagent, Ltd, energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. All reagents and solvents were purchased from commercial suppliers and used without further purification. Unless otherwise stated, all experiments were conducted in a sealed tube under O_2 atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR , δ = 77.00 for ^{13}C-NMR) as an internal reference. ^{31}P-NMR spectra were recorded at 200 MHz and chemical shifts were reported in ppm relative to external 85% phosphoric acid (d = 0.0 ppm). Coupling constants (*J*) were reported in Hertz (Hz).

2. Optimization of reaction conditions

Table S1. The reaction performed with different catalysts with 1a and 2a.

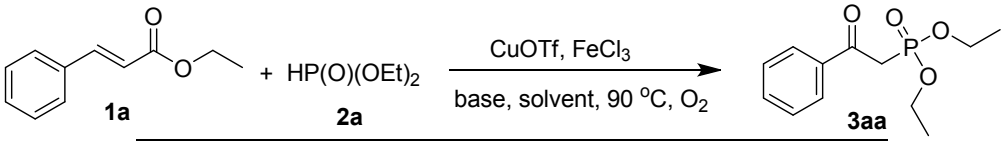


1a **2a** **3aa**

Entry	Catalyst	Cocatalyst	Yield [a]
1	$FeCl_3$	$Cu(TFA)_2$	56%
2	$FeCl_3$	CuBr	50%
3	$FeCl_3$	CuCl	65%
4	$FeCl_3$	$CuBr_2$	41%
5	$FeCl_3$	$Cu(MeCN)_4PF_6$	67%[b]
6	$FeCl_3$	$Cu(acac)_2$	63%
7	$FeCl_3$	$Cu(OAc)_2$	66%
8	$FeCl_3$	$Cu(OTf)_2$	42%
9	$FeCl_3$	CuOTf	69%[b]
10	$Fe(ClO)_3$	CuOTf	Trace
11	$FeCl_2$	CuOTf	67%
12	$Fe(acac)_2$	CuOTf	N.D.
13	$FeBr_2$	CuOTf	54%

Reaction conditions:**1a** (0.5 mmol), **2a** (1.5 mmol), 10 mol% of the iron salt, 5 mol% of the copper salt and Et_3N (0.5 mmol) in DMSO (1.0 mL), 90 °C, 17 h. [a] GC yields. [b] Isolated yield.

Table S2. The reaction performed in different solvents and bases with 1a and 2a

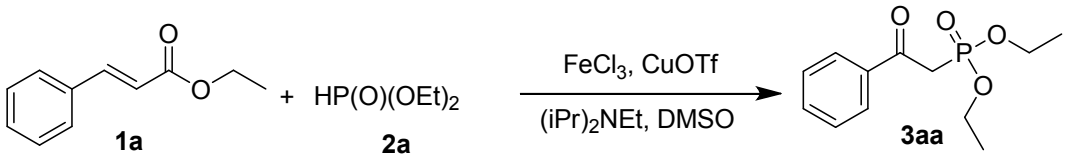


1a **2a** **3aa**

Entry	Base	Solvent	Yield [a]
1	-	DMSO	N.D.
2	Et_3N	DMSO	69%[b]
3	DBU	DMSO	45%
4	$(nBu)_3N$	DMSO	68%
5	TMG	DMSO	56%
6	$(iPr)_2NEt$	DMSO	70%[b]
7	Na_2CO_3	DMSO	30%
8	K_2CO_3	DMSO	36%
9	tBuOK	DMSO	Trace
10	$(iPr)_2NEt$	DMF	64%
11	$(iPr)_2NEt$	CH_3CN	43%
12	$(iPr)_2NEt$	H_2O	N.D.
13	$(iPr)_2NEt$	Toluene	35%

Reaction conditions: 1a (0.5 mmol), 2a (1.5 mmol), 10 mol% of $FeCl_3$, 5 mol% of CuOTf and bsae (0.5 mmol) in solvent (1.0 mL) , 90 °C,17h. [a] GC yields. [b] Isolated yields.

Table S3. Optimization of reaction conditions



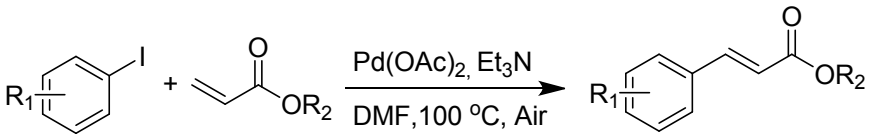
Entry	Catalyst (mol%)	Cocatalyst(mol%)	Atmosphere	Temp(^{o}C)	Time(h)	Yeild [a]
1	$FeCl_3$(10)	CuOTf(5)	N_2	90	17	N.D.
2	$FeCl_3$(10)	CuOTf(5)	Air	90	17	47%
3	$FeCl_3$(10)	CuOTf(5)	O_2	90	17	70%[b]
4	$FeCl_3$(10)	CuOTf(5)	O_2	80	17	65%
5	$FeCl_3$(10)	CuOTf(5)	O_2	100	17	53%
6	$FeCl_3$(5)	CuOTf(5)	O_2	90	17	58%
7	$FeCl_3$(15)	CuOTf(5)	O_2	90	17	61%
8	$FeCl_3$(10)	CuOTf(2.5)	O_2	90	17	50%
9	$FeCl_3$(10)	CuOTf(10)	O_2	90	17	65%
10	$FeCl_3$(10)	CuOTf(5)	O_2	90	20	73%[b]
11	**$FeCl_3$(10)**	**CuOTf(5)**	**O_2**	**90**	**24**	**79%[b]**
12[c]	**$FeCl_3$(10)**	**CuOTf(5)**	**O_2**	**90**	**24**	**74%[b]**
13	-	CuOTf(5)	O_2	90	24	N.D.
14	$FeCl_3$(10)	-	O_2	90	24	7%

Reaction conditions:1a (0.5 mmol), 2a (1.5mmol), 10 mol% $FeCl_3$, 5 mol% CuOTf and $(iPr)_2NEt$ (0.5 mmol) in DMSO (1.0 mL). [a] GC yields. [b] Isolated yields.[c] 2a 1.3 mmol.

3. General procedure for starting materials

3.1 General procedure for the synthesis of α,β-unsaturated esters

The starting materials of **3ba**, **3ca, 3ea**, **3ga**, **3ha**, **3ja**, **3ka**, **3la**, **3ma** in the Scheme 2 and the cinnamate ester **1d** in the Scheme 3 were synthesized following a modified form of the procedures.[1] Other cinnamates of the Scheme 2 in the paper were purchased from the commercial suppliers.

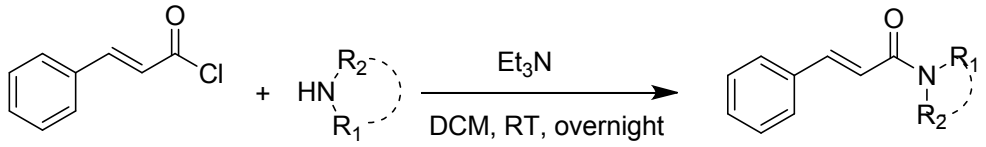


A mixture of iodobenzene (5 mmol), acrylate, $Pd(OAc)_2$ (0.3 mol%), Et_3N (6 mmol) and DMF (6 mL) was placed in a screw caped reaction

vial. The resulting reaction mixture was stirred at 100 °C for 24 h. Upon completion of the reaction, the resulting solution was extracted with EtOAc and saturated brine three times. The combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed via rotary evaporator and the crude product was purified with flash chromatography (silica gel, petroleum ether/Ethyl acetate = 30:1) to afford the corresponding cinnamic acid esters.

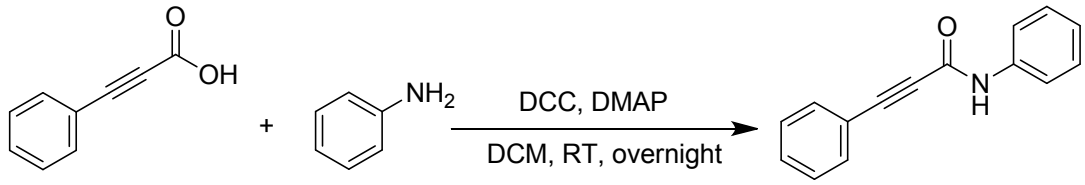
3.2 General procedure for the synthesis of α,β-unsaturated amides

Method A:



5.5 mmol (1.1 equiv) of corresponding amine and 6 mmol (1.2 equiv) of triethylamine were dissolved in 20 mL CH_2Cl_2 in 100 mL round-bottom flask. Then the Flask was cooled down to 0 °C via an ice bath, 5 mmol (1.0 equiv) of cinnamoyl chloride was added to the Flask. The resulting mixture was stirred overnight at room temperature. Upon completion of the reaction, the resulting solution was extracted with CH_2Cl_2 and saturated brine three times. The combined organic layers were dried over Na_2SO_4 and the solvent was removed via rotary evaporation. In case of need, the residue was additionally purified by column chromatography (silica gel, petroleum ether/Ethyl acetate = 10:1) to afford the corresponding α,β-unsaturated amides.

Method B:

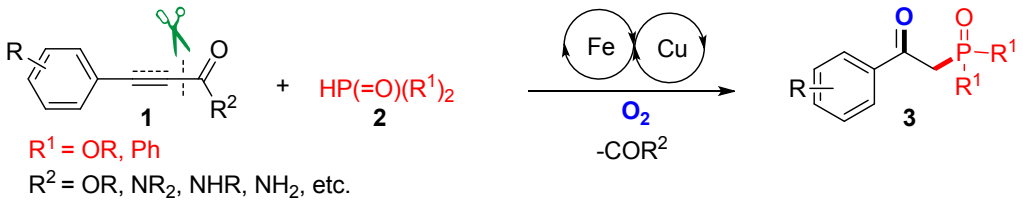


To a solution of 5 mmol (1 equiv) of phenylpropiolic acid, 5.5 mmol (1.1 equiv) of phenylamine in 20 mL CH_2Cl_2 5.5 mmol (1.1 equiv) of DCC and 0.5 mmol (10 mol %) of DMAP were added. The resulting

mixture was stirred overnight at room temperature. Upon completion of the reaction, the resulting solution was extracted with CH_2Cl_2 and saturated brine three times. The combined organic layers were dried over Na_2SO_4 and the solvent was removed via rotary evaporation. The residue was purified by column chromatography (silica gel, petroleum ether/Ethyl acetate = 10:1) to afford the corresponding α,β-unsaturated amides.

The synthesis of N,N-dimethyl-3-phenylacrylamide (**1f**) was employed the Heck reaction as the preparation method of cinnamic acid esters. The synthesis of α,β-unsaturated amides **1h** ~ **1m** was employed the method A. The synthesis of N,3-diphenylpropiolamide (**1p**) was employed the method B. N,N-dimethyl-3-phenylpropiolamide (**1q**) was synthesized following the method of the previous procedure.[2] Other substrates of the Scheme 3 in the paper were purchased from the commercial suppliers.

4. General process for the synthesis of β-Ketophosphonates



H-phosphonates **2** (1.3 mmol) was added to a mixture of CuOTf (5 mol%), $FeCl_3$ (10 mol%) and **1** (0.5 mmol) in DMSO (1 mL). Then $(iPr)_2NEt$ (0.5 mmol) was added to the mixture in a sealed tube. After that, the reaction mixture was heated at 90 °C under O_2 atmosphere for 24 h. Upon completion of the reaction, ethyl acetate (20 mL) was added to the mixture, and then washed with saturated brine (15 mL × 3). The combined water layers were extracted with ethyl acetate (15 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed via rotary evaporator and the crude product was purified by flash column chromatography on silica gel (petroleum

ether/Ethyl acetate = 5:3, then petroleum ether/Ethyl acetate = 1:1) to obtain the desired product **3**.

5. The procedure for gram scale experiment

Diethyl phosphonate (2.9 g, 20.8 mmol) was added to a mixture of CuOTf (84.8 mg, 5 mol%), $FeCl_3$ (129.6 mg, 10 mol%) and ethyl cinnamate (1.41 g, 8 mmol) in DMSO (10 mL). Then $(iPr)_2NEt$ (1.04 g, 8 mmol) was added to the mixture in a Schlenk tube with an O_2 balloon covered on. After that, the reaction mixture was stirred at 90 °C for 24 h. Upon completion of the reaction, ethyl acetate (30 mL) was added, and then washed with saturated brine (25 mL × 3). The combined water layers were extracted with ethyl acetate (25 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed via rotary evaporator and the crude product was purified with flash chromatography (silica gel, petroleum ether/Ethyl acetate = 2:1) to give 1.39 g (68 %) of diethyl (2-oxo-2-phenylethyl)-phosphonate as a yellow oil.

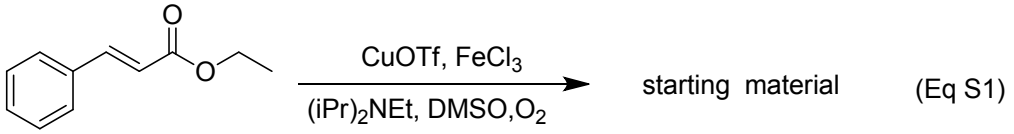
6. Preliminary mechanistic studies

6.1 Control experiments

When the reactions were performed in the absence of either iron salt (entry 13 in Table S3) or copper salt (entry 14 in Table S3), only trace amount of desired product **3aa** were obtained; when O_2 was replaced by N_2 or air, trace or much lower amount of the desired product **3aa** were respectively formed (entry 1 and 2 in Table S3), implying that O_2 is also an essential prerequisite for this reaction. These control experiments suggested that molecular dioxygen, CuOTf and $FeCl_3$ were all indispensable to this reaction.

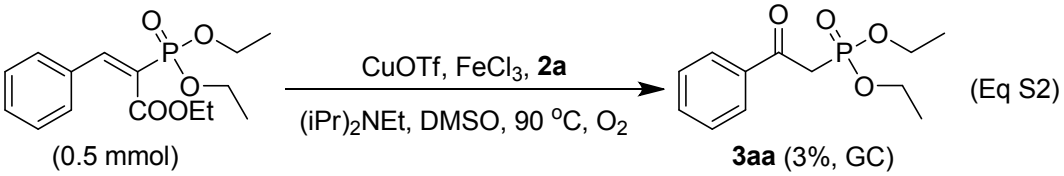
In order to understand the reaction intermediates, ethyl cinnamate (**1a**) was conducted in the standard conditions without diethyl phosphonate (**2a**), it turned out that the ethyl cinnamate (**1a**) still stayed intact and no styrene, acetophenone or other substances were detected by GC-MS (Eq

S1), indicating that cleavage of ethyl cinnamate (**1a**) couldn't be the first step under this conditions. This might also suggest that addition of phosphorous radical generated from H-phosphonates to C=C bond should occur prior to the cleavege of ester group, instead of verse vide



(Eq S1)

When (E)-ethyl 2-(diethoxyphosphoryl)-3-phenylacrylate, which was synthesized following the method of the previous procedure,[3] was conducted in the standard conditions with the excessive equivalent of diethyl phosphonate (**2a**), (E)-ethyl-2-(diethoxyphosphoryl)-3-phenylacrylate also remained a lot and **3aa** only 3% detected by GC (Eq S2), implying that the (E)-ethyl-2-(diethoxyphosphoryl)-3-phenylacrylate was not a key intermediate of this oxyphosphorylation reaction.



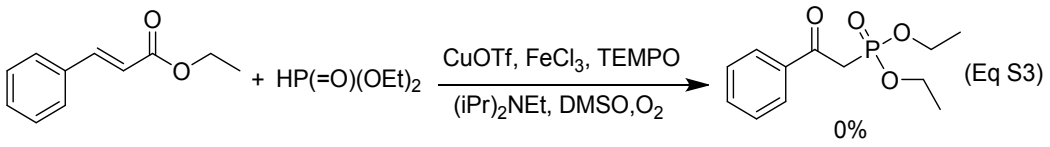
(0.5 mmol) **3aa** (3%, GC) (Eq S2)

6.2 Radical trapping experiments

The oxyphosphorylation reaction with H-phosphonates under dioxygen or air is well known to proceed via a radical process in previous reports,[4,5,6] therefore a radical pathway was also supposed to be involved in this oxyphosphorylation reaction of cinnamate.

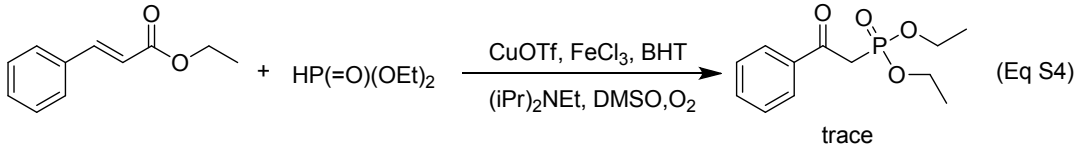
(1) The procedure for radical capture experiments with TEMPO:

Diethyl phosphonate (**2a**) (180 mg, 1.3 mmol) was added to a mixture of CuOTf (5.3 mg, 5 mol%), $FeCl_3$ (8.1 mg, 10 mol%), TEMPO (233 mg, 1.5 mmol) and ethyl cinnamate (**1a**) (88.1 mg, 0.5 mmol) in DMSO (1 mL). Then $(iPr)_2NEt$ (64.8 mg, 0.5 mmol) was added to the mixture in a sealed tube. After that, the reaction mixture was stirred at 90 °C under O_2 atmosphere for 24 h. The result that **3aa** was not detected and a lot of ethyl cinnamate was detected by GC-MS (Eq S3).



(2) The procedure for radical capture experiments with BHT:

Diethyl phosphonate (**2a**) (180 mg, 1.3 mmol), was added to a mixture of CuOTf (5.3 mg, 5 mol%), $FeCl_3$ (8.1 mg, 10 mol%), BHT (197.9 mg, 1.5 mmol) and ethyl cinnamate (**1a**) (88 mg, 0.5 mmol) in DMSO (1 mL). Then $(iPr)_2NEt$ (64.8 mg, 0.5 mmol) was added to the mixture in a sealed tube. After that, the reaction mixture was stirred at 90 °C under O_2 atmosphere for 24 h. And **3aa** was detected only 4% by GC (Eq S4).

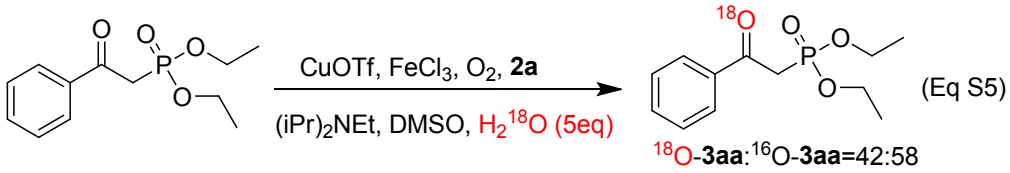


Based on the radical trapping experiments, this transformations were totally inhibited by TEMPO and BHT (Eqs S3 and S4), suggesting that a radical process might be involved in the oxyphosphorylation reaction.

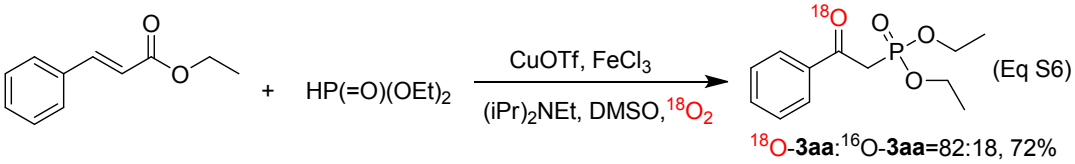
6.3 Isotope labeling experiments

To elucidate the origination of the carbonyl oxygen atom of β-ketophosphonates, labeling experiments were performed. The results demonstrated that the carbonyl oxygen atom of β-ketophosphonates should originate exclusively from dioxygen.

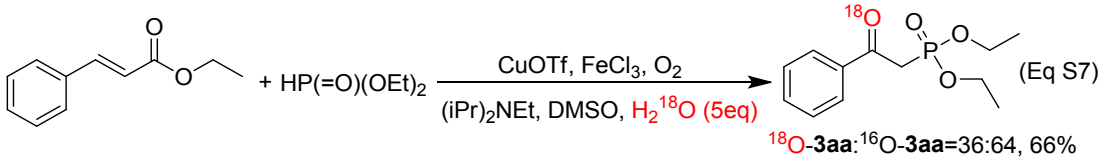
Firstly, water scrambling experiment was conducted with the product ^{16}O-**3aa** in the standard conditions. ^{16}O-**3aa** (128 mg, 0.5 mmol) was added to a mixture of $(EtO)_2P(O)H$ (180 mg, 1.3 mmol), CuOTf (5.3 mg, 5 mol%), $FeCl_3$ (8.1 mg, 10 mol%), $H_2{}^{18}O$ (27 mg, 5 equiv) in DMSO (1 mL) at room temperature. Then $(iPr)_2NEt$ (64.6 mg, 0.5 mmol) was added to the mixture in a sealed tube. After that, the reaction mixture was stirred at 90 °C under O_2 for 24 h. The result was that 42% of product was incorporated by ^{18}O (Eq S5), indicating that oxygenexchange with water occurred under the standard conditions.



Subsequently, substrates **1a** and **2a** were performed under $^{18}O_2$ in the standard conditions. Diethyl-phosphonate (**2a**) (180 mg, 1.3 mmol) was added to a mixture of CuOTf (5.3 mg, 5 mol%), $FeCl_3$ (8.1 mg, 10 mol%) and ethyl cinnamate (**1a**) (88.1 mg, 0.5 mmol) in DMSO (1 mL). Then $(iPr)_2NEt$ (64.8 mg, 0.5 mmol) was added to the mixture in a Schlenk tube. After that, the tube was evacuated with N_2 thrice and with $^{18}O_2$ twice. The reaction mixture was stirred at 90 °C for 24 h. ^{18}O-**3aa** : ^{16}O-**3aa** = 82 : 18, 72% (Eq S6).

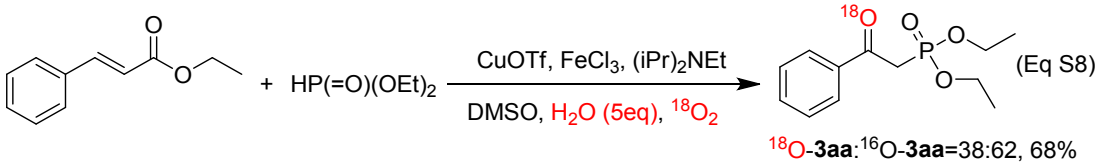


And then, the reaction was conducted in the presence of 5.0 equiv of $H_2{}^{18}O$ under O_2. Diethyl phosphonate (180 mg, 1.3 mmol) was added to a mixture of CuOTf (5.3 mg, 5 mol%), $FeCl_3$ (8.1 mg, 10 mol%), ethyl cinnamate (88.1 mg, 0.5 mmol) and $H_2{}^{18}O$ (27 mg, 5 equiv) in DMSO (1 mL). Then $(iPr)_2NEt$ (0.5 mmol) was added to the mixture in a Schlenk tube. After that, the reaction mixture was stirred at 90 °C under O_2 atmosphere for 24 h. ^{18}O-**3aa**:^{16}O-**3aa** = 36 : 64, 66% (Eq S7).



Finally, the reaction of **1a** and **2a** was conducted in the presence of H_2O (5 equiv) under $^{18}O_2$. Diethyl phosphonate (183.7 mg, 1.3 mmol) was added to a mixture of CuOTf (5.3 mg, 5 mol%), $FeCl_3$ (8.4 mg, 10 mol%), ethyl cinnamate (88.1 mg, 0.5 mmol) and H_2O (27.6 mg, 5 equiv) in DMSO (1 mL). Then $(iPr)_2NEt$ (0.5 mmol) was added to the mixture in a Schlenk tube. After that the tube was evacuated with N_2

thrice and with $^{18}O_2$ twice. The reaction mixture was stirred at 90 °C for 24 h. ^{18}O-**3aa**:^{16}O-**3aa** = 38 : 62, 68% (Eq S8).



^{18}O-**3aa**:^{16}O-**3aa**=38:62, 68%

On the basis of all above ^{18}O labeled experiments (Eqs S5-S8), we can determine that the oxygen in carbonyl group should be exclusively from dioxygen. According to this reaction (Eq S7), If the oxygen was from water, the ratio of ^{18}O-**3aa**:^{16}O-**3aa** should be 5:1, that is ca. 82% ^{18}O-**3aa** should be detected since one equivalent of water was from the reaction, yet there was only 36% of ^{18}O-**3aa** was detected in the real system. Moreover, 38% ^{18}O-labeled and 62% unlabeled products were detected when the reaction of **1a** and **2a** was conducted in the presence of H_2O (5 equiv) under $^{18}O_2$ (Eq S8), the low level of ^{18}O in desired product **3aa** in Eq S8 comes from the water scrambling reaction. Combination of analyse the results and the ^{18}O labeled experiments, we could tell that carbonyl oxygen atom of the β-ketophosphonates originated from molecular oxygen.

6.4 Analysis of EPR spectra

EPR measurements: EPR spectra were recorded at room temperature on a Bruker Elexsys E580 spectrometer: Mod. Amplitude=1 G; Time Constan=81.92 msec; Sweep time=81.92 sec; Power=5 mw. DMPO (5, 5-dimethyl-1-pyrroline N-oxide) was employed as the radical trap.

Firstly, the P-centered radical was determined by EPR. An EPR signal of phosphorous species was detected in the reaction of **2a**, $FeCl_3$ and $(iPr)_2NEt$ in DMSO (Figure S1). And when DMPO was added to the reaction, a signal of the trapped phosphorous radical was observed (A_P=46.7G, A_N=14.3G, $A_{H\beta}$=18.9G).

EPR spectrum of reaction system without 1a and CuOTf under O_2

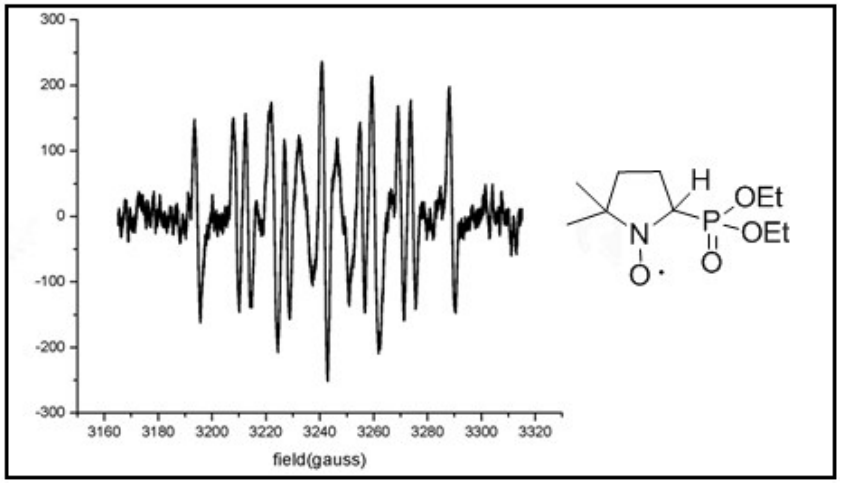


Figure S1. EPR spectra (X band, 9.7 GHz, RT) of conditions: A mixture of **2a** (1.3 mmol), $FeCl_3$ (0.050 mmol) and $(iPr)_2NEt$ (0.50 mmol) in DMSO (1 mL) was stirring at 90 ^oC under O_2 for 2 h. 0.02 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (2^*10^{-2} M). Then, this mixture was used for EPR measurement.

EPR spectrum of reaction system without 1a and $FeCl_3$ under O_2

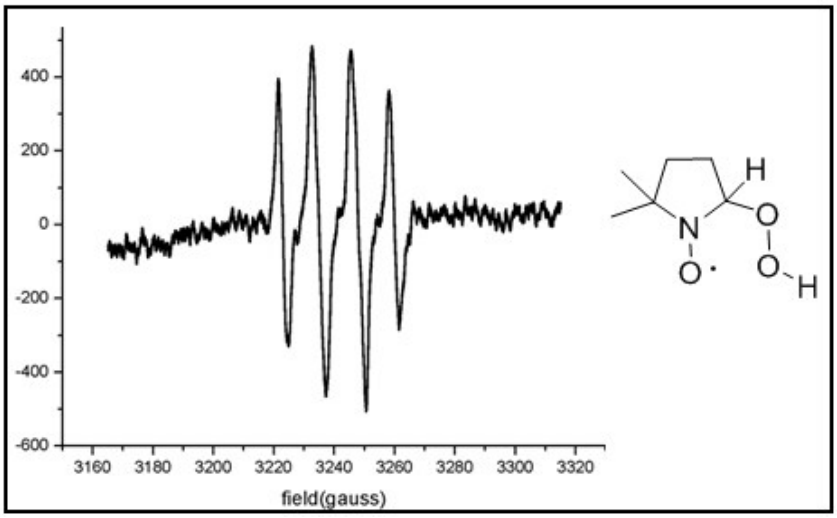


Figure S2. EPR spectra (X band, 9.7 GHz, RT) of conditions: A mixture of **2a** (1.3 mmol), CuOTf (0.025 mmol) and $(iPr)_2NEt$ (0.50 mmol) in DMSO (1 mL) was stirring at 90 ^oC under O_2 for 2 h. 0.02 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO (2*10-2 M). Then, this mixture was used for EPR measurement.

Subsequently, the reaction of **2a**, CuOTf and $(iPr)_2NEt$ in DMSO was used for EPR measurement (Figure S2). Interestingly, Figure S2

shows that no radical signal was observed above the noise level. It means that no radical was formed without Fe salts. Comparison the results with Figure S1, these results suggested that $FeCl_3$ could promote diethyl H-phosphonate (**2a**) to generate P-centered radical, while the formation of the P-centered radical has no relationship with CuOTf.

When DMPO was added to the reaction of **1a**, **2a**, CuOTf, $FeCl_3$ and $(iPr)_2NEt$ in DMSO, an EPR signal (A_N=13.9G, $A_{H\beta}$=11.9G) was observed (Figure S3). Compared this signal with the one from the reaction of **1a**, **2a**, CuOTf and $(iPr)_2NEt$ in DMSO (Figure S4), data analysis illustrated that they are two kinds of peroxide radicals. Comparison these results with Figure S2, the signal (A_N=12.9G, $A_{H\beta}$=10.3G，$A_{H\gamma}$=1.2G) in Figure S2 was identical to the one in Figure S2 and has some discrepancy to the one in Figure S3. Based on our hypothesis, we have reasons to believe that the peroxide signal in Figure S4 and S2 is hydrogen peroxide, yet the peroxide signal in Figure S3 should be •OOR.

EPR spectrum of standard reaction system

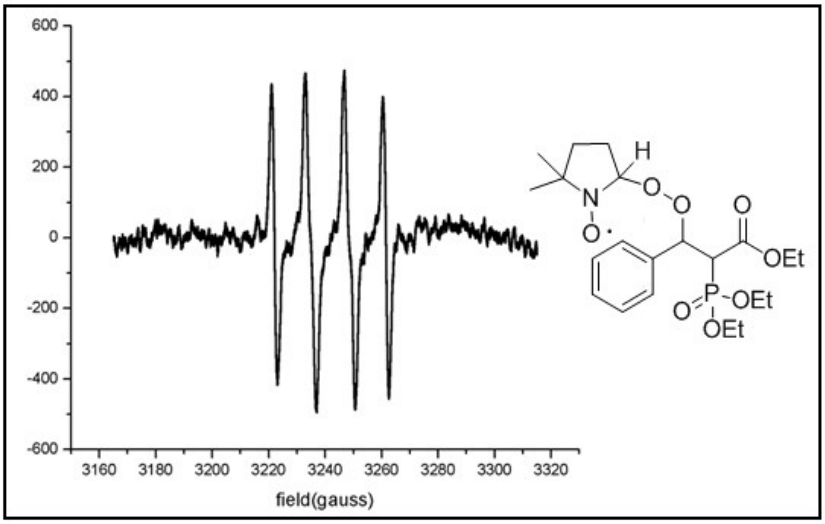


Figure S3. EPR spectra (X band, 9.7 GHz, RT) of conditions: A mixture of **1a** (0. 5 mmol), **2a** (1.3 mmol), CuOTf (0.025 mmol), $FeCl_3$ (0.050 mmol)and $(iPr)_2NEt$ (0.50 mmol) in DMSO (1 mL) was stirring at 90 ^oC under O_2 for 2 h. 0.02 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO ($2*10^{-2}$ M). Then, this mixture was used for EPR measurement

EPR spectrum of reaction system without $FeCl_3$ under O_2

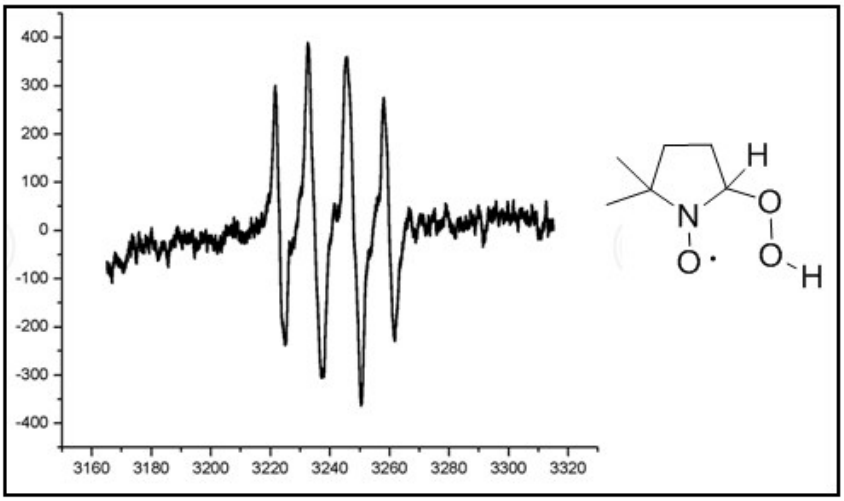


Figure S4. EPR spectra (X band, 9.7 GHz, RT) of conditions: A mixture of **1a** (0. 5 mmol), **2a** (1.3 mmol), CuOTf (0.025 mmol) and $(iPr)_2NEt$ (0.50 mmol) in DMSO (1 mL) was stirring at 90 °C under O_2 for 2 h. 0.02 mL of this reaction solution was taken out into a small tube, followed by the addition of 0.05 mL DMPO ($2*10^{-2}$ M). Then, this mixture was used for EPR measurement.

EPR spectra of DMPO radical adducts under various conditions

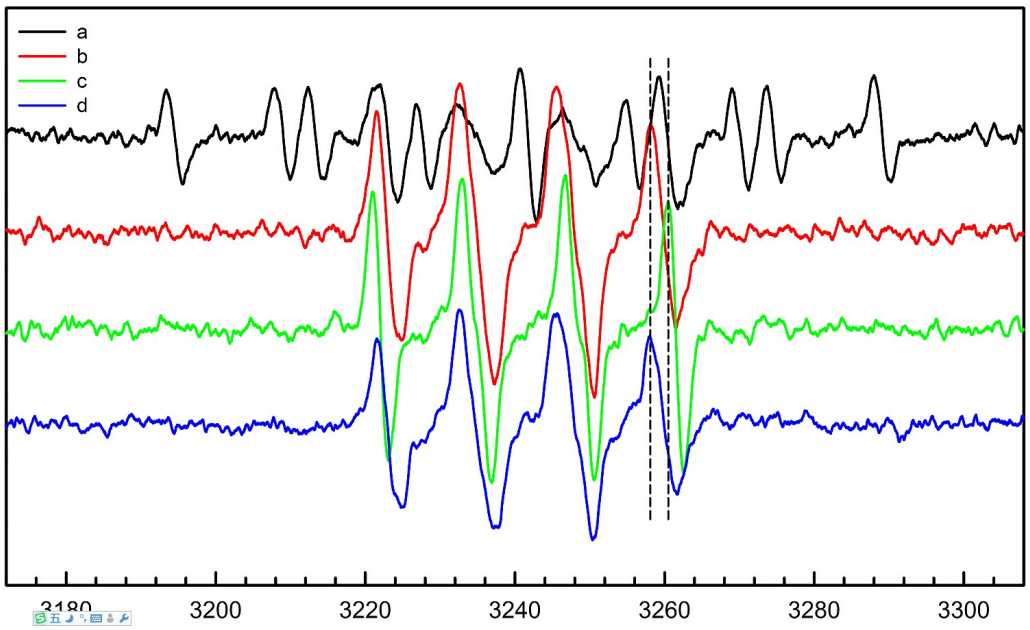
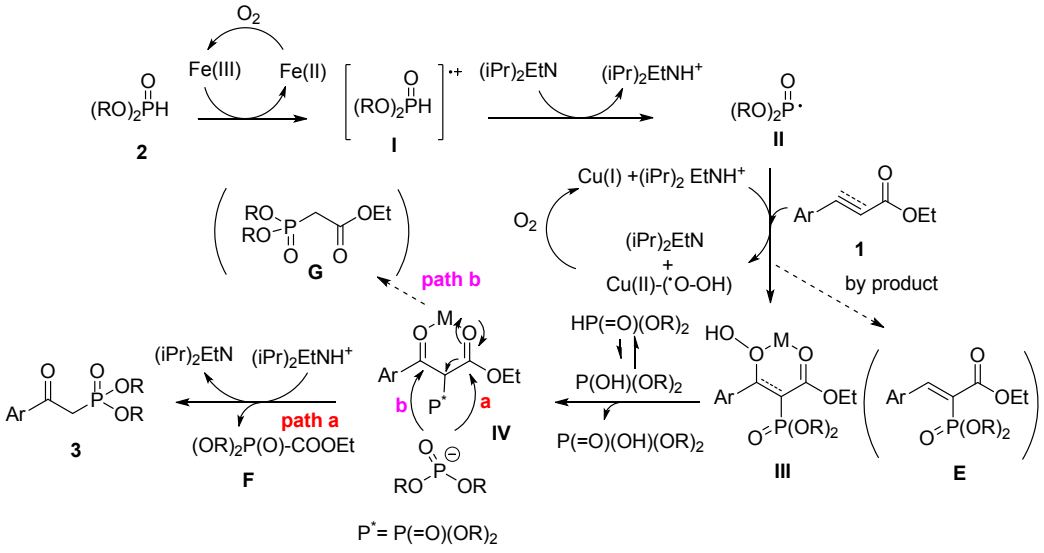


Figure S5. EPR spectra of DMPO radical adducts under various conditions with ethyl cinnamate (**1a**) and H-phosphonate **2a**: a) EPR spectrum of reaction system without **1a** and CuOTf under O_2; b) EPR spectrum of reaction system without **1a** and $FeCl_3$ under O_2; c) EPR spectrum of reaction system under standard conditions under O_2; d) EPR spectrum of reaction system without **1a** under O_2.

6.5 Conclusion and plausible reaction mechanism

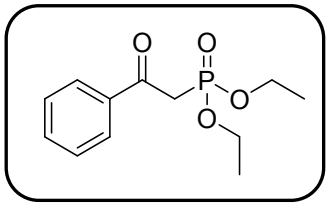
Based on all above results and previous reports,[4,5,6] a tentative mechanism for this tandem oxyphosphorylation is illustrated as shown in Scheme S1: single electron transfers from iron (**III**) species to $HP(=O)(OR)_2$ in the presence of molecular oxygen, forming dialkyl phosphonate cation radical **I**. The H^+ from the dialkyl phosphonate cation radical **I** is grabbed by the base leading to dialkyl phosphonyl radical **II**. This radical is trapped by cinnamate **1** to afford an in-situ generated C-centered radical, which further reacted with Cu(II)-(•O-OH) species under dioxygen atmosphere to form hydroperoxide species **III**, trace amount of byproduct **E** was detected on GCMS, which might come from the β-Hydrogen elimination. After reduction of the peroxide (one equivalent of H-phosphonate serves as reductant), α-ester-β-keto phosphonate **IV** was generated. Another one equivalent excess H-phosphonate acts as nucleophile to attack the carbonyl group in the ester, which also explains why ca. 3 equivalent of H-phosphonate was needed in order to get the optimized results (Table S3). Eventually the desired product **3** was afforded with the help of base.



Scheme S1 plausible reaction mechanism

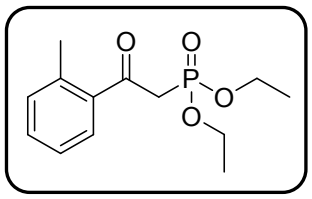
7. Characterization data for products

Diethyl (2-oxo-2-phenylethyl)phosphonate (3aa) (CAS :3453-00-7)[4,5,6,7]



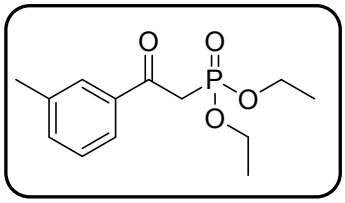
Yellow oil.^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 8.00 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 4.15-4.09 (m, 2H), 3.62 (d, J = 23.0 Hz, 2H), 1.27 (t, J = 7.0 Hz, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 191.9 (d, $J_{P\text{-}C}$ = 6.3 Hz), 136.5, 133.6, 129.0, 128.6, 62.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 38.5 (d, $J_{P\text{-}C}$ = 128.8 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 19.9.

Diethyl (2-oxo-2-(o-tolyl) ethyl) phosphonate (3ba) (CAS:67257-38-9)[5]



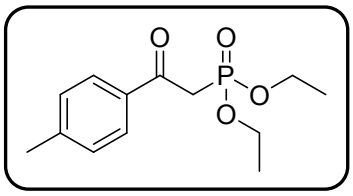
Yellow oil.^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.74 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.29-7.24 (m, 2H), 4.11-4.07 (m, 4H), 3.60 (d, J = 22.5 Hz, 2H), 2.51 (s, 3H), 1.26 (t, J = 7.5 Hz, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 195.0 (d, J = 6.3 Hz), 138.9, 137.2 (d, J = 2.5 Hz), 132.0, 131.9, 129.6, 125.7, 62.5 (d, J = 7.5 Hz), 41.0 (d, J = 128.8 Hz), 21.3, 16.2 (d, J = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 20.2.

Diethyl (2-oxo-2-(m-tolyl) ethyl) phosphonate (3ca) (CAS : 1613246-12-0)[5,6,8]



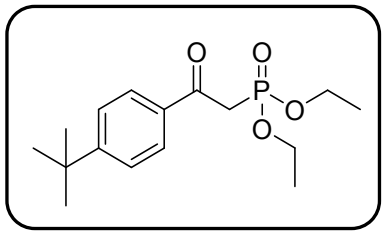
Yellow oil.^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ =7.78 (d, J = 8.5 Hz, 2H), 7.38-7.32 (m, 2H), 4.12-4.09 (m, 4H), 3.60 (d, J = 22.5 Hz, 2H), 2.39 (s, 3H), 1.26 (t, J = 7.0 Hz, 6H). ^{13}C-NMR (125 MHz, CDCl3) δ = 192.1 (d, $J_{P\text{-}C}$ = 6.7 Hz), 138.4, 136.6, 134.4, 129.4, 128.5, 62.6 (d, $J_{P\text{-}C}$ = 6.5 Hz), 38.5 (d, $J_{P\text{-}C}$ = 130.0 Hz), 21.3, 16.2 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 20.1.

Diethyl (2-oxo-2-(p-tolyl) ethyl) phosphonate (3da) (CAS :18276-81-8)[5,6,8]



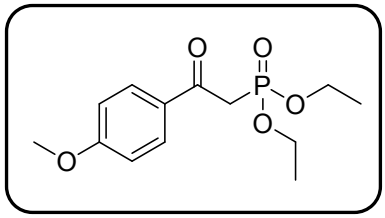
Yellow oil.^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.90 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H) 4.15-4.09 (m, 4H), 3.60 (d, J = 23.0 Hz, 2H), 2.40 (s, 3H), 1.28 (t, J = 7.0 Hz, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 191.4, 144.6, 134.1, 129.3, 129.2, 62.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 38.9 (d, $J_{P\text{-}C}$ = 130.0 Hz), 21.6, 16.2 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 20.2.

Diethyl (2-(4-(tert-butyl) phenyl) -2-oxoethyl) phosphonate (3ea) (CAS: 1613246-11-9)[5,6,8]



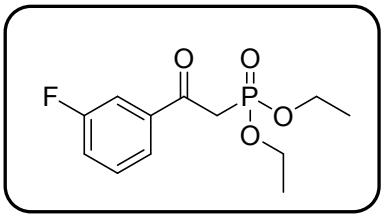
Yellow oil.^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.94 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 4.16-4.10 (m, 4H), 3.60 (d, J = 22.5 Hz, 2H), 1.33 (s, 9H), 1.28 (t, J = 7.0, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 191.5 (d, $J_{P\text{-}C}$ = 6.3 Hz), 157.5, 134.0, 129.0, 125.5, 62.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 38.9 (d, $J_{P\text{-}C}$ = 130.0 Hz), 35.2, 31.0, 16.2 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 20.2.

Diethyl (2-(4-methoxyphenyl)-2-oxoethyl) phosphonate (3fa) (CAS: 18276-85-2)[5,6,8]



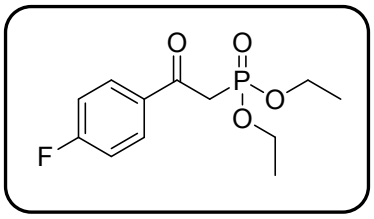
Yellow oil.^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.98 (d, J = 10.0 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 4.14-4.08 (m, 2H), 3.86 (s, 3H), 3.58 (d, J = 20.0 Hz, 2H), 1.29-1.25 (m, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 190.2 (d, $J_{P\text{-}C}$ = 6.3 Hz), 163.9, 131.4, 129.6, 113.7, 62.6 (d, $J_{P\text{-}C}$ = 7.5 Hz), 55.5, 38.7 (d, $J_{P\text{-}C}$ = 130.0 Hz), 16.3 (d, $J_{P\text{-}C}$ = 7.5 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 20.4.

Diethyl (2-(3-fluorophenyl)-2-oxoethyl) phosphonate (3ga) (CAS: 1682614-93-2)[6]



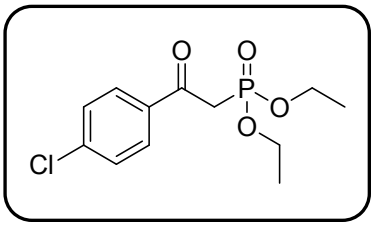
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.80 (dt, *J* = 1.0 Hz, *J* = 1.5 Hz, 1H), 7.69 (dt, *J* = 2.0 Hz, *J* = 2.5 Hz, 1H), 7.48-7.44 (m, 1H), 7.31 (td, *J* = 3.5 Hz,1H), 4.16-4.10 (m, 4H), 3.62 (d, *J* = 22.5 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 6H). ^{13}C-NMR (125 MHz, CDCl3) δ = 190.7 (dd, J_{P-C} = 6.3 Hz, J_{F-C} = 2.5 Hz), 163.7 (d, J_{F-C} = 247.5 Hz), 138.5 (d, J_{F-C} = 3.8 Hz), 130.3 (d, J_{F-C} = 7.6 Hz), 124.9 (d, J_{F-C} = 2.5 Hz), 120.7 (d, J_{F-C} = 21.3 Hz), 115.6 (d, J_{F-C} = 22.5 Hz), 62.8 (d, J_{P-C} = 6.3 Hz), 39.2 (d, J_{P-C}= 128.8 Hz), 16.2 (d, J_{P-C} = 6.3 Hz). ^{31}P-NMR (200 MHz, CDCl3) δ = 19.3.

Diethyl (2-(4-fluorophenyl)-2-oxoethyl) phosphonate (3ha) (CAS: 39758-40-2)[5,6,8]



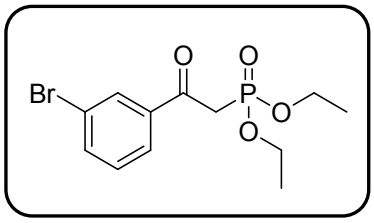
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) *δ* = 8.06-8.03 (m, 2H), 7.16-7.11 (m, 2H), 4.16-4.09 (m, 4H), 3.60 (d, *J* = 23.0 Hz, 2H), 1.28 (m, *J* = 7.0 Hz, 6H). **^{13}**C-NMR (125 MHz, $CDCl_3$) *δ* = 190.3 (d, J_{P-C} = 6.3 Hz), 167.0 (d, J_{F-C} = 198.8 Hz), 132.9, 131.8 (d, J_{F-C} = 8.8 Hz), 115.7 (d, J_{F-C} = 22.5 Hz), 62.8 (d, J_{P-C} = 6.3 Hz), 39.0 (d, J_{P-C} = 128.8 Hz), 16.2 (d, J_{P-C} = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) *δ* = 19.6.

Diethyl (2-(4-chlorophenyl)-2-oxoethyl) phosphonate (3ia) (CAS: 18276-82-9)[5,6]



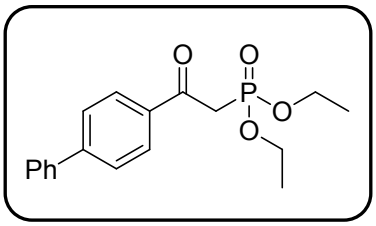
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) *δ* = 7.96 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 4.16-4.10 (m, 4H), 3.59 (d, *J* = 22.5 Hz, 2H), 1.28 (t, *J* = 8.0, 6H). **^{13}**C-NMR (125 MHz, $CDCl_3$) *δ* = 190.7 (d, J_{P-C} = 6.3 Hz), 140.3, 134.8, 130.5, 128.9, 62.7 (d, J_{P-C} = 7.5 Hz), 38.6 (d, J_{P-C} = 128.8 Hz), 16.2 (d, J_{P-C} = 6.3 Hz).^{31}P-NMR (200 MHz, $CDCl_3$) *δ* = 19.5.

Diethyl (2-(3-bromophenyl)-2-oxoethyl) phosphonate (3ja) (CAS: 155506-17-5)[8]



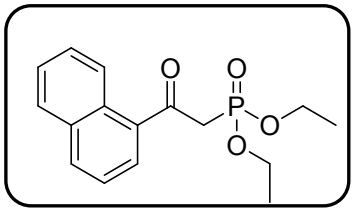
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.13 (t, J = 1.8 Hz, 1H), 7.94-7.92 (m, 1H), 7.71-7.69 (m, 1H), 7.34 (t, J = 7.5 Hz, 1H), 4.16-4.10 (m, 4H), 3.59 (d, J = 22.5 Hz, 2H), 1.27 (t, J = 7.0 Hz, 7H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 190.6 (d, J = 6.3 Hz), 138.2 (d, J = 1.3 Hz), 136.4, 132.0, 130.1, 127.6, 122.9, 62.8 (d, J = 6.3 Hz), 39.2 (d, J = 128.8 Hz), 16.2 (d, J = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 19.2.

Diethyl (2-([1,1'-biphenyl]-4-yl)-2-oxoethyl) phosphonate (3ka) (CAS: 42516-23-4)[5,6]



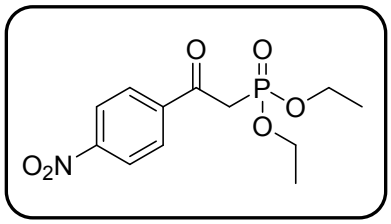
Light-yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 8.09 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.0 Hz, 4H), 7.63 (d, J = 7.0 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 4.19-4.12 (m, 4H), 3.66 (d, J = 22.5 Hz, 2H), 1.30 (t, J = 8.0 Hz, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 191.4 (d, $J_{P\text{-}C}$ = 6.3 Hz), 146.3, 139.7, 135.2 (d, $J_{P\text{-}C}$ = 2.5 Hz), 129.7, 129.0, 128.3, 127.3, 127.2, 62.7 (d, $J_{P\text{-}C}$ = 6.3 Hz), 38.6 (d, $J_{P\text{-}C}$ = 128.8 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 20.0.

Diethyl (2-(naphthalen-1-yl)-2-oxoethyl)phosphonate (3la) (CAS: 1682614-95-4)[6]



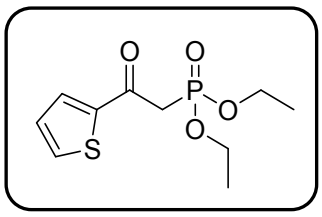
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 8.65 (d, J = 8.5 Hz, 1H), 8.01 (t, J = 7.5 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.62-7.58 (m, 1H), 7.55-7.50 (m, 2H), 4.14-4.08 (m, 4H), 3.75 (d, J = 22.5 Hz, 2H), 1.22 (t, J = 7.0 Hz, 6H). **^{13}**C-NMR (125 MHz, $CDCl_3$) δ = 195.0 (d, $J_{P\text{-}C}$ = 6.3 Hz), 135.0, 133.9, 133.5, 130.2, 129.2, 128.4, 128.2, 126.5, 125.8, 124.2, 62.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 42.2 (d, $J_{P\text{-}C}$ = 127.5 Hz), 16.1 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 20.1.

Diethyl (2-(4-nitrylphenyl)-2-oxoethyl) phosphonate (3ma) (CAS: 54109-18-1)[9]



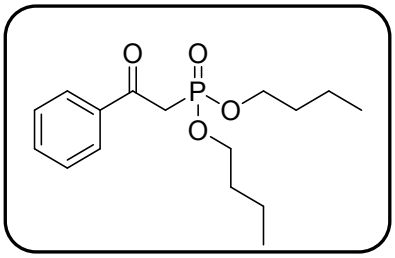
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 8.32(d, J = 8.5 Hz, 2H), 8.19 (d, J = 9.0 Hz, 2H), 4.17-4.11 (m, 4H), 3.66 (d, J = 23.0 Hz, 2H), 1.29 (t, J = 7.0, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 190.6 (d, $J_{P\text{-}C}$ = 6.3 Hz), 150.5, 140.8, 130.1, 123.8, 62.9 (d, $J_{P\text{-}C}$ = 6.3 Hz), 39.2 (d, $J_{P\text{-}C}$ = 128.8 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.3 Hz).^{31}P-NMR (200 MHz, $CDCl_3$) δ = 18.4.

Diethyl (2-oxo-2-(thiophen-2-yl) ethyl) phosphonate (3na) (CAS: 55984-14-0)[5,6]



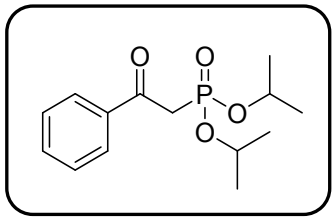
Yellowish-brown oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.80 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 22.5 Hz, 2H), 1.27 (t, J = 7.0, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 184.2 (d, $J_{P\text{-}C}$ = 6.3 Hz), 143.8, 135.0, 134.1, 128.3, 62.7. (d, $J_{P\text{-}C}$ = 6.3 Hz), 39.3 (d, $J_{P\text{-}C}$ = 130.0 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 19.4.

Dibutyl (2-oxo-2-phenylethyl) phosphonate (3ab) (CAS : 1034-94-2)[4,5,6]



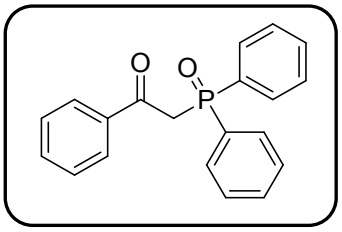
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 8.00-7.98 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 4.07-4.01 (m, 4H), 3.62 (d, J = 23.0 Hz, 1H), 1.60-1.55 (m, 4H), 1.33-1.27 (m, 4H), 0.87 (t, J = 8.5 Hz, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 191.8 (d, $J_{P\text{-}C}$ = 6.3 Hz), 136.5, 133.6, 129.0, 128.5, 66.3 (d, $J_{P\text{-}C}$ = 6.3 Hz), 38.3 (d, $J_{P\text{-}C}$ = 130.0 Hz), 32.3 (d, $J_{P\text{-}C}$ = 6.3 Hz), 18.6, 13.5. ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 19.9.

Diisopropyl (2-oxo-2-phenylethyl) phosphonate (3ac) (CAS : 57057-15-5)[4,5,6,7]



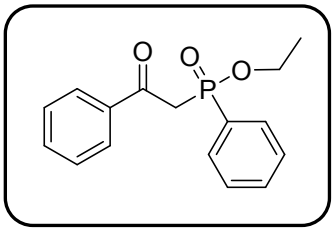
Light-yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 8.01 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.0 Hz, 2H), 4.75-4.68 (m, 2H), 3.59 (d, J = 23.0 Hz, 2H), 1.29 (dd, J = 4.0 Hz, 4.0 Hz, 12H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 192.1 (d, $J_{P\text{-}C}$ = 7.5 Hz), 136.7, 133.5, 129.1, 128.5, 71.5 (d, $J_{P\text{-}C}$ = 6.3 Hz), 39.7 (d, $J_{P\text{-}C}$ = 130.0 Hz), 23.9 (dd, $J_{P\text{-}C}$ = 3.8 Hz , 5.0 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 17.7.

2-(Diphenylphosphoryl)-1-phenylethanone (3ad) (CAS : 1733-58-0)[4,5,6,7]



Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.99-7.97 (m, 2H), 7.82-7.78 (m, 4H), 7.54-7.50 (m, 3H), 7.47-7.39 (m, 6H), 4.14 (d, J = 15.0 Hz, 2H). **^{13}**C-NMR (125 MHz, $CDCl_3$) δ = 192.8 (d, $J_{P\text{-}C}$ = 6.3 Hz), 136.9, 133.6, 132.3, 132.1 (d, $J_{P\text{-}C}$ = 2.5 Hz), 131.1 (d, $J_{P\text{-}C}$ = 46.3 Hz), 129.2, 128.6 (d, $J_{P\text{-}C}$ = 11.2 Hz), 128.5, 43.3 (d, $J_{P\text{-}C}$ = 57.5 Hz). ^{31}P-NMR (200 MHz, $CDCl_3$) δ = 27.0.

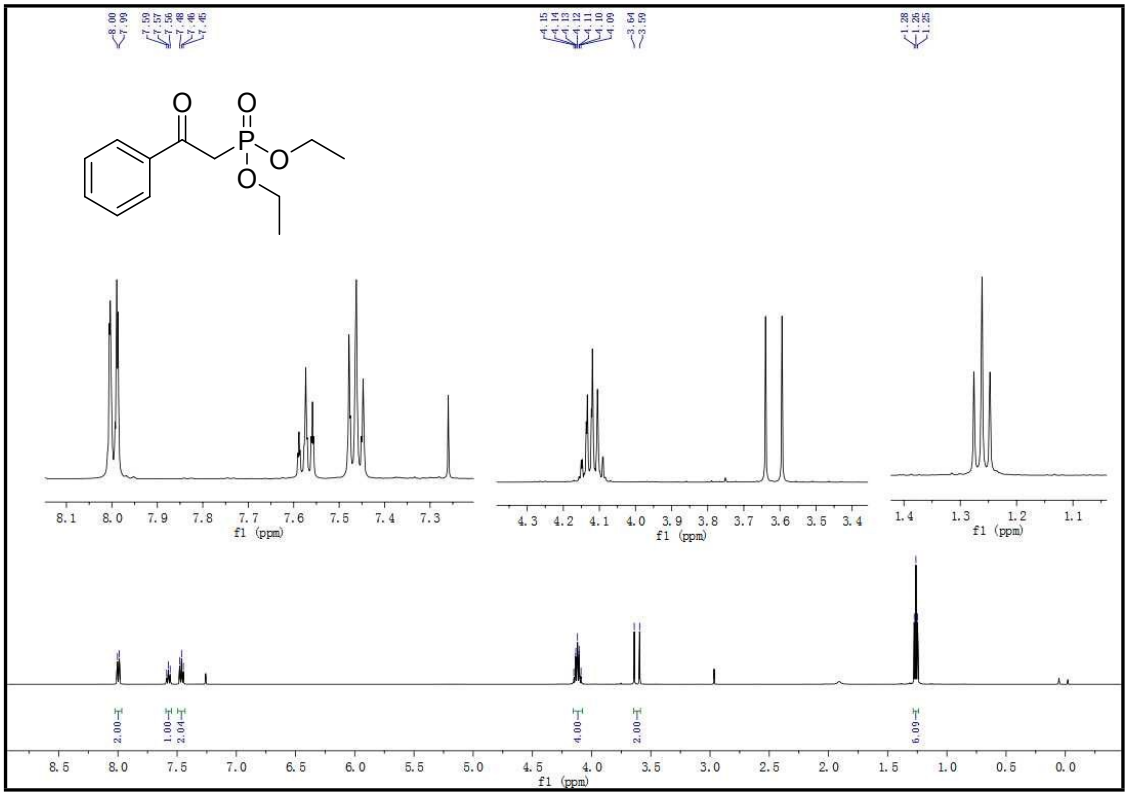
Ethyl (2-oxo-2-phenylethyl) (phenyl) phosphinate (3ae) (CAS : 51104-34-8)[4,6,7]

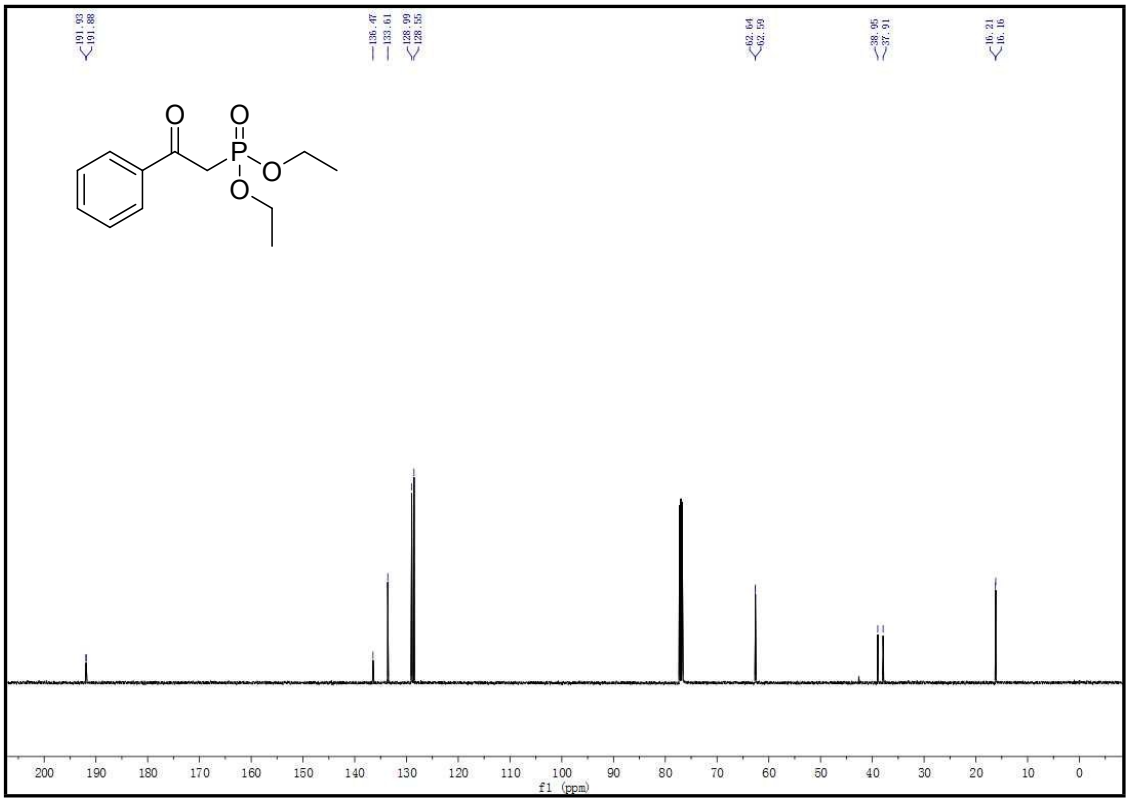


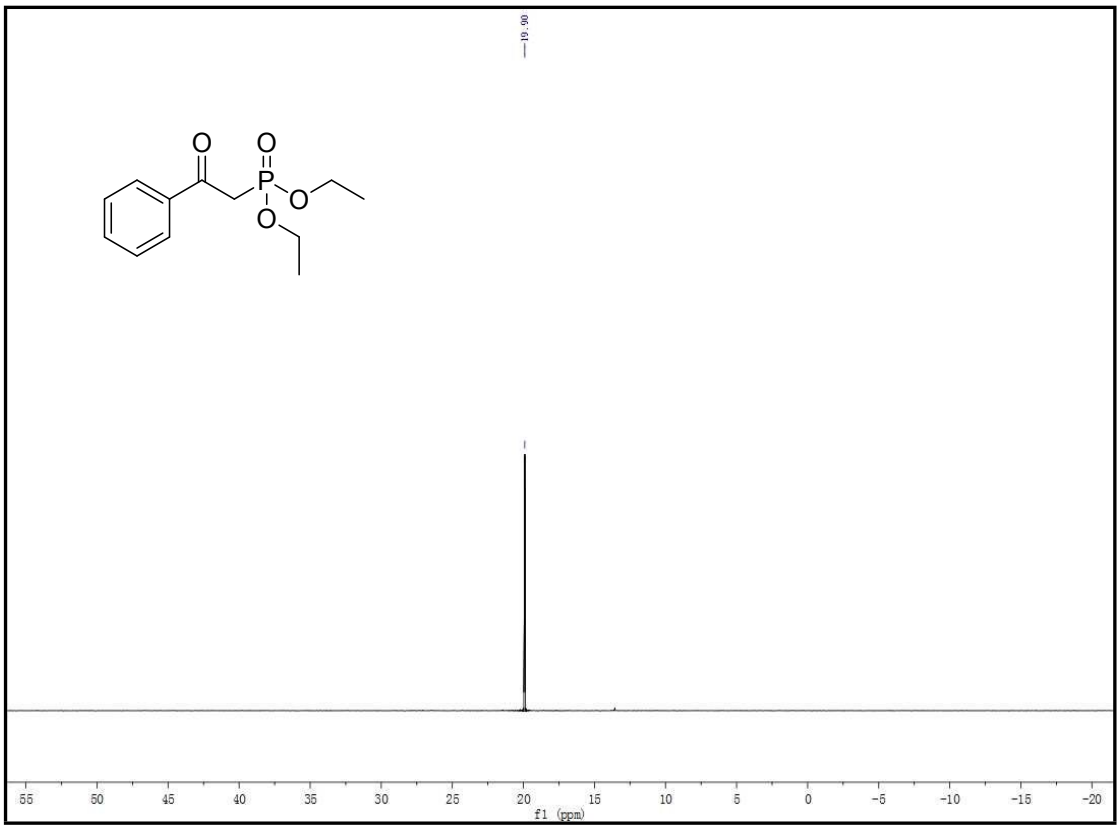
Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.95 (d, J = 7.2 Hz, 2H), 7.81-7.75 (m, 2H), 7.57-7.51 (m, 2H), 7.47-7.41 (m, 4H), 4.16-4.07 (m, 1H), 3.98-3.90 (m, 1H), 3.80 (dd, J = 18.5, 13.8 Hz, 2H), 1.25 (t, J = 7.0 Hz, 3H). **^{13}**C-NMR (125 MHz, $CDCl_3$) δ = 192.2 (d, $J_{P\text{-}C}$ = 5.5 Hz), 136.8, 133.5, 132.7 (d, $J_{P\text{-}C}$ = 2.9 Hz), 131.9 (d, $J_{P\text{-}C}$ = 10.1 Hz), 130.1 (d, $J_{P\text{-}C}$ = 131.3 Hz), 129.1, 128.6 (d, $J_{P\text{-}C}$ = 13.3 Hz), 128.5, 61.5 (d, $J_{P\text{-}C}$ = 6.3 Hz), 43.0 (d, $J_{P\text{-}C}$ = 85.8 Hz), 16.3 (d, $J_{P\text{-}C}$ = 6.3 Hz).^{31}P-NMR (200 MHz, $CDCl_3$) δ = 34.4.

8. NMR spectroscopic data

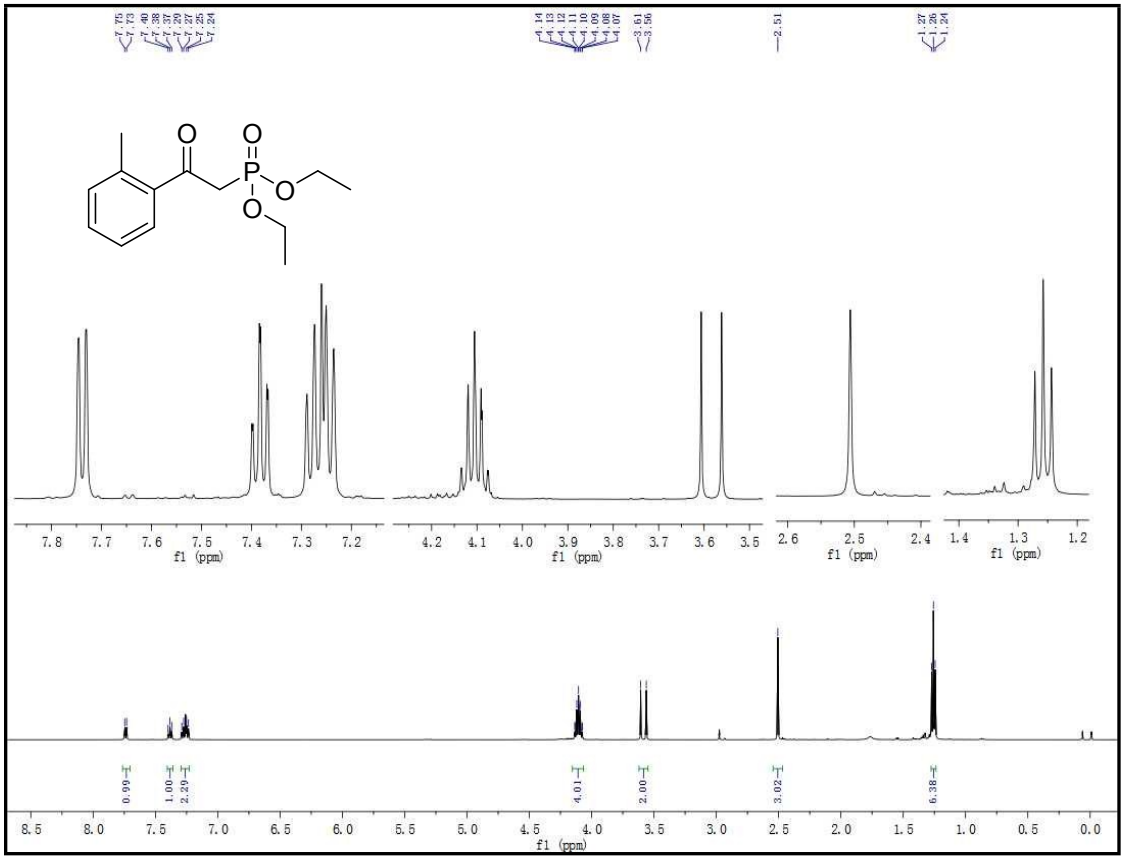
Diethyl (2-oxo-2-phenylethyl) phosphonate (3aa)

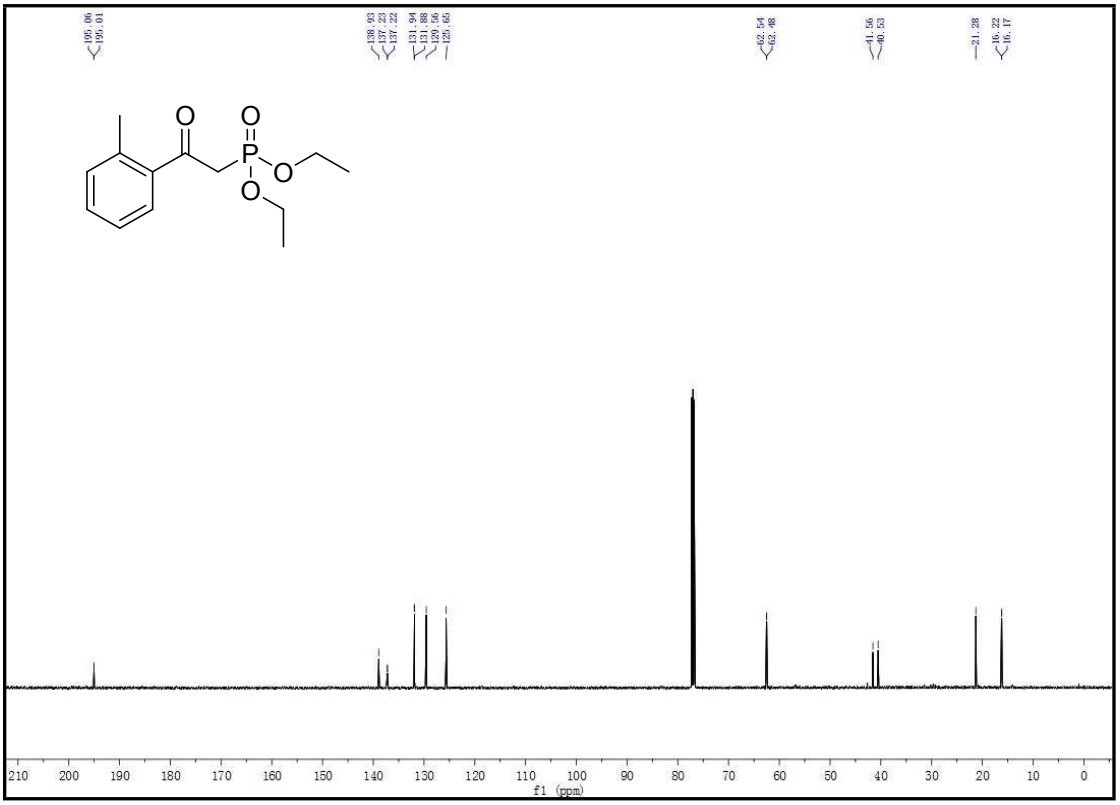


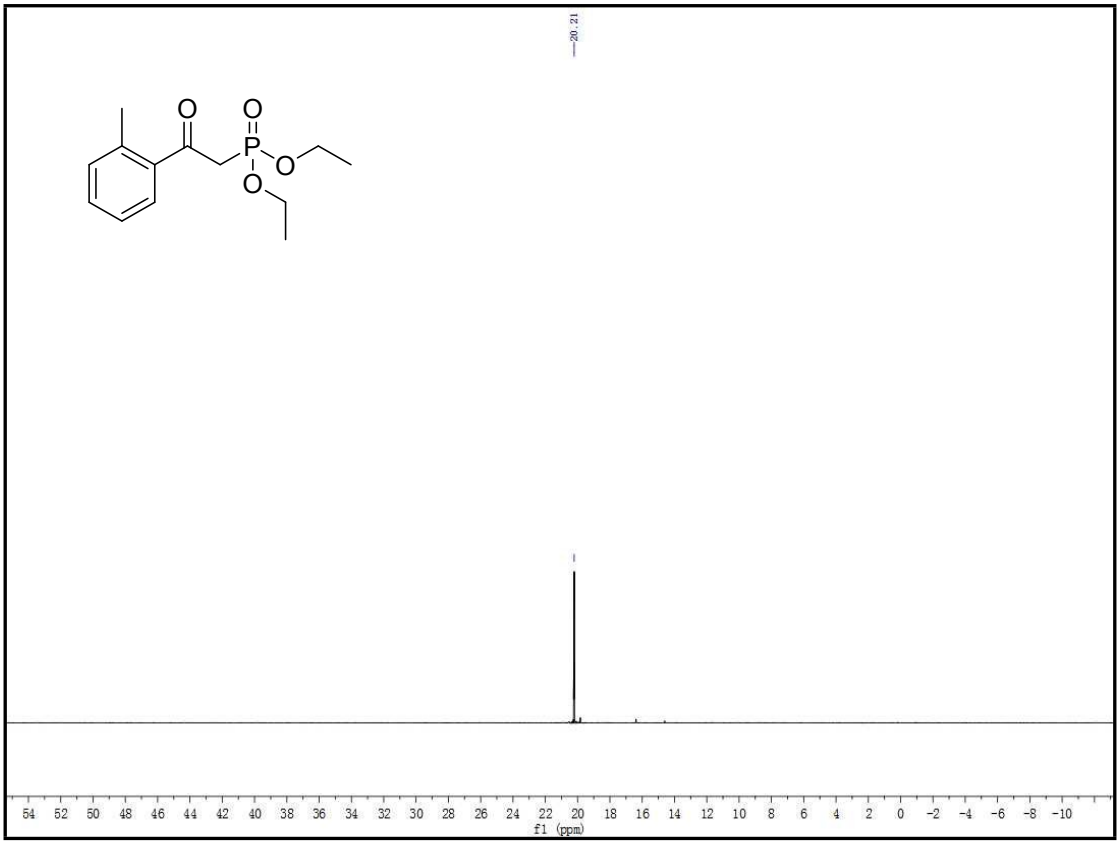




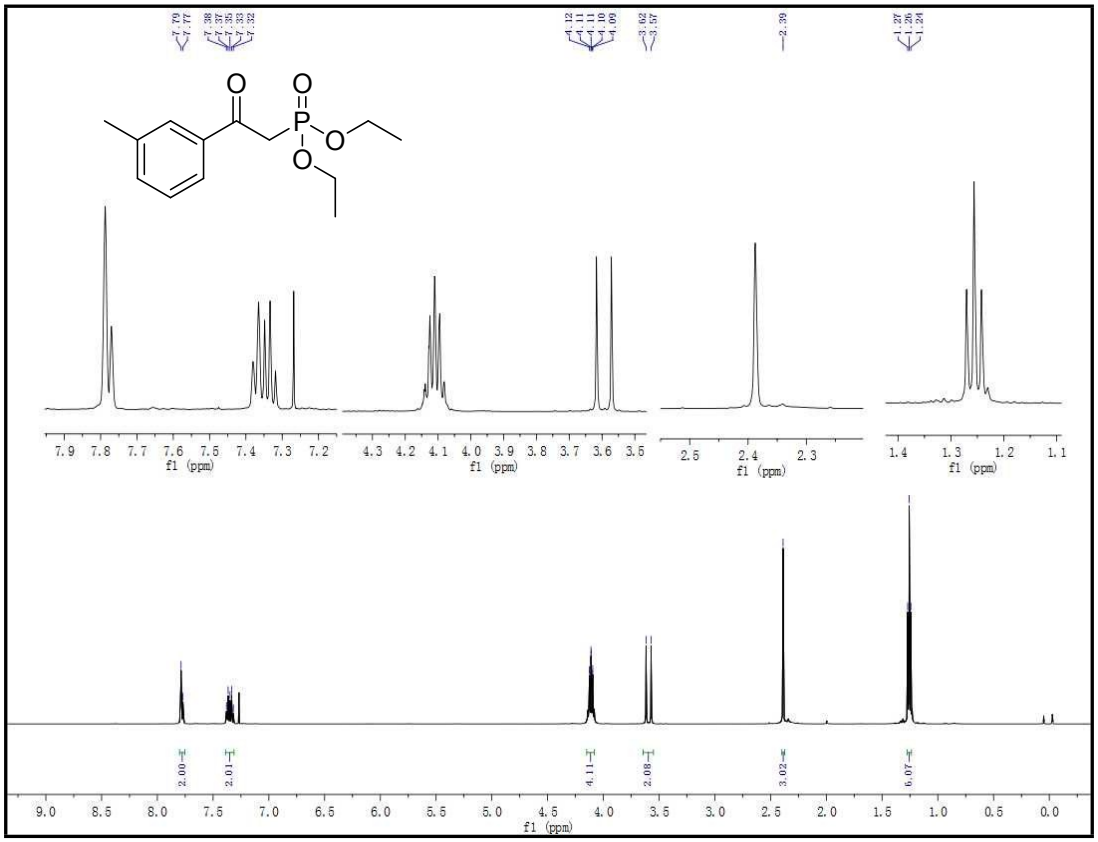
Diethyl (2-oxo-2-(o-tolyl)ethyl) phosphonate (3ba)

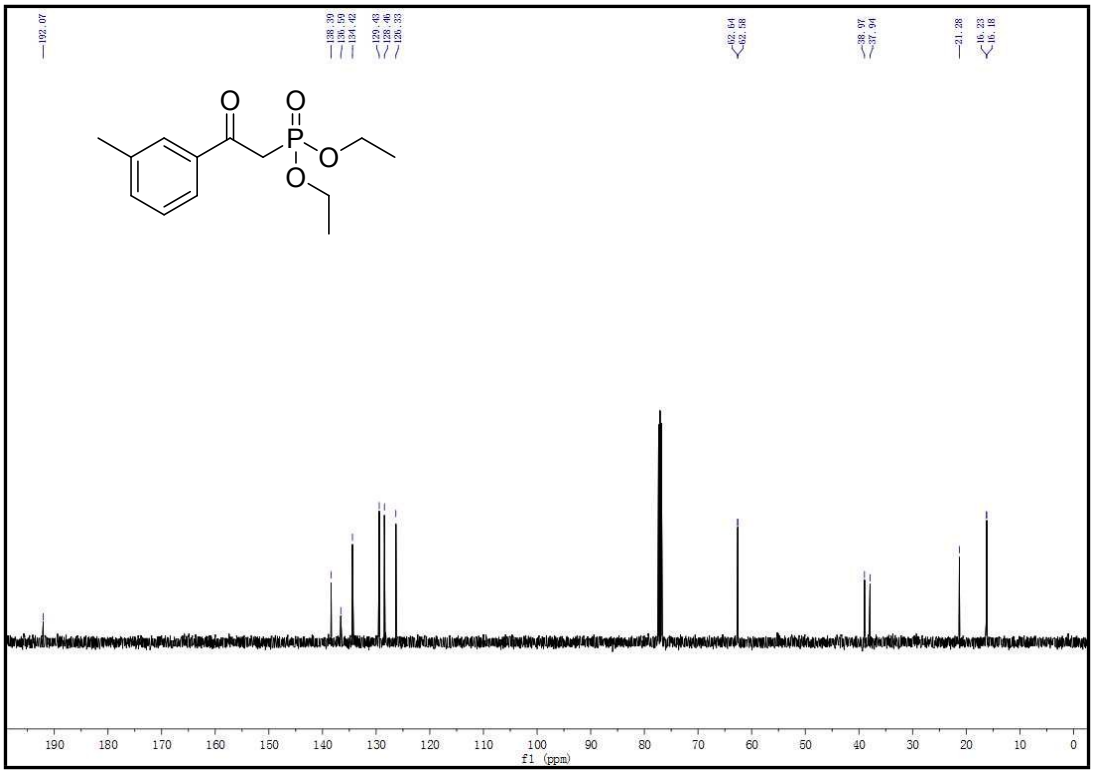


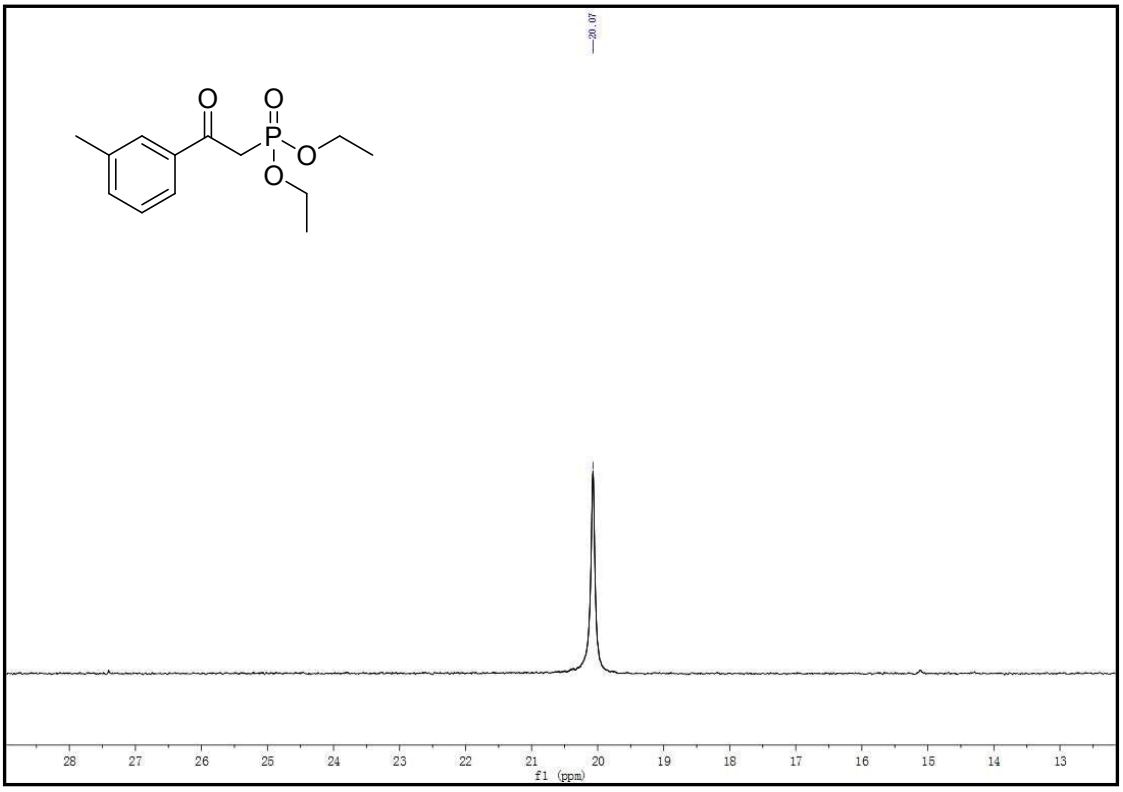

195.06
195.01
138.93
137.23
137.22
131.94
131.88
129.56
125.65
62.54
62.48
41.56
40.53
21.28
16.22
16.17
f1 (ppm)


20.21
f1 (ppm)

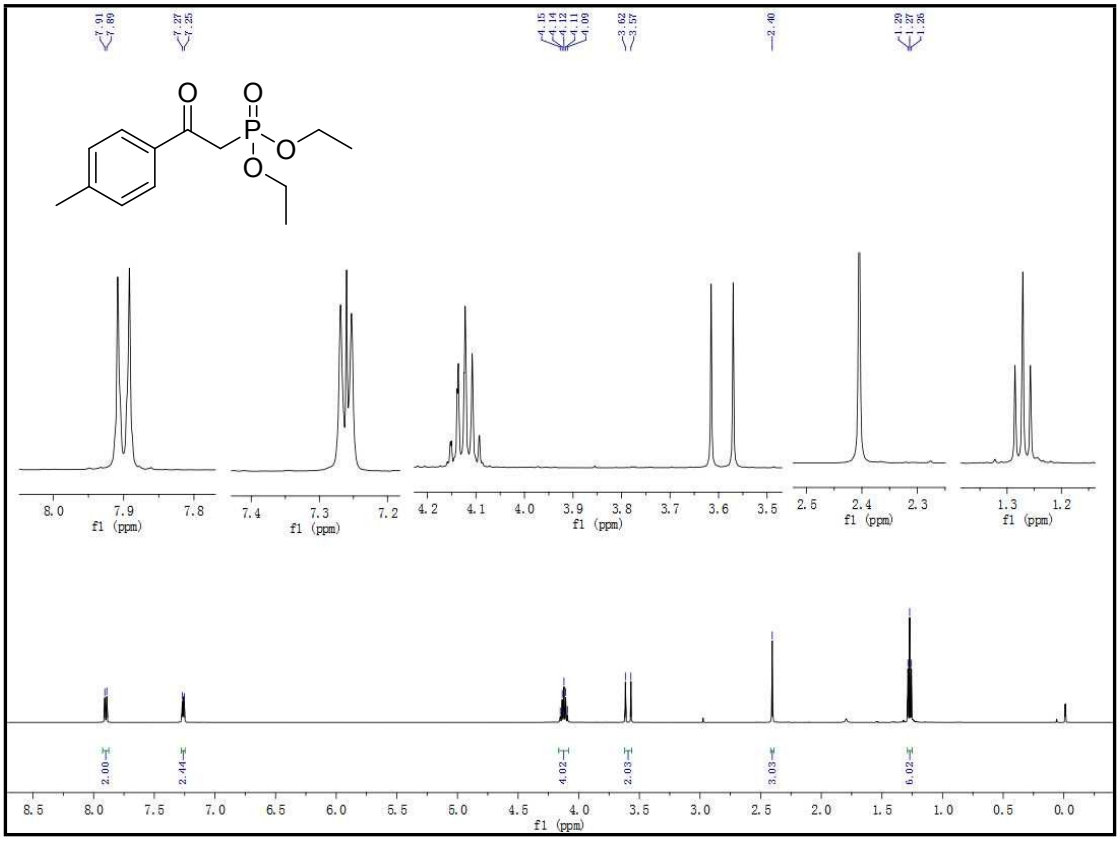
Diethyl (2-oxo-2-(m-tolyl) ethyl) phosphonate (3ca)

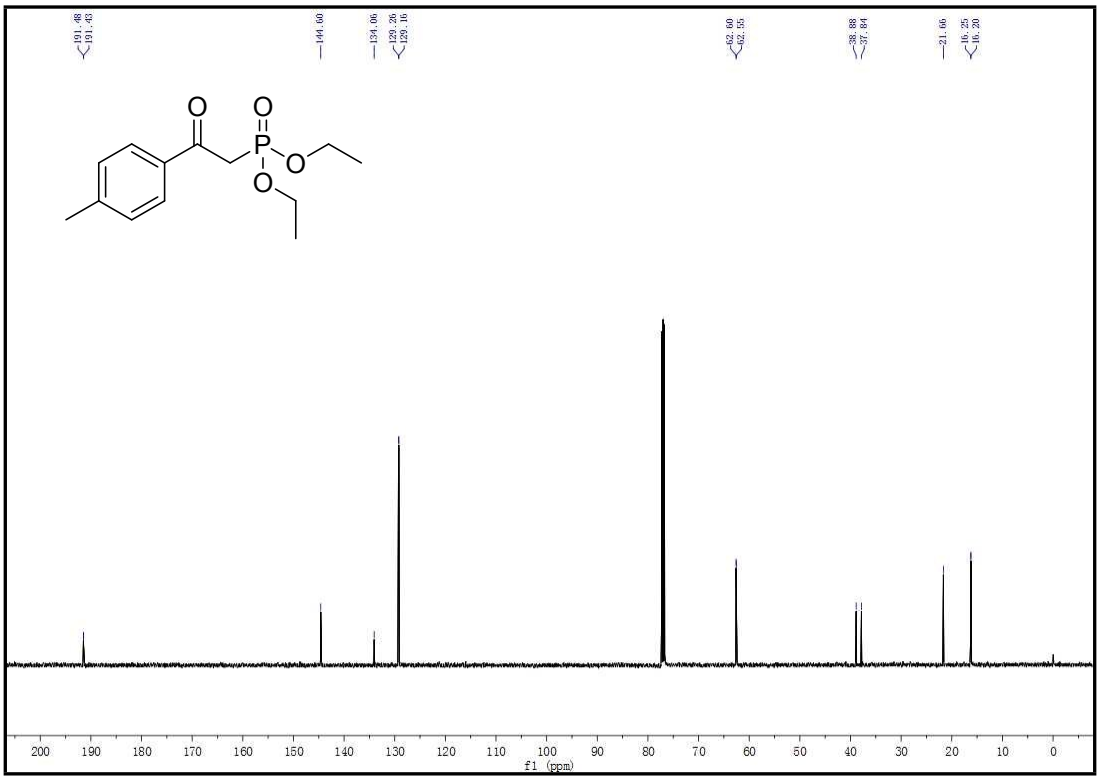


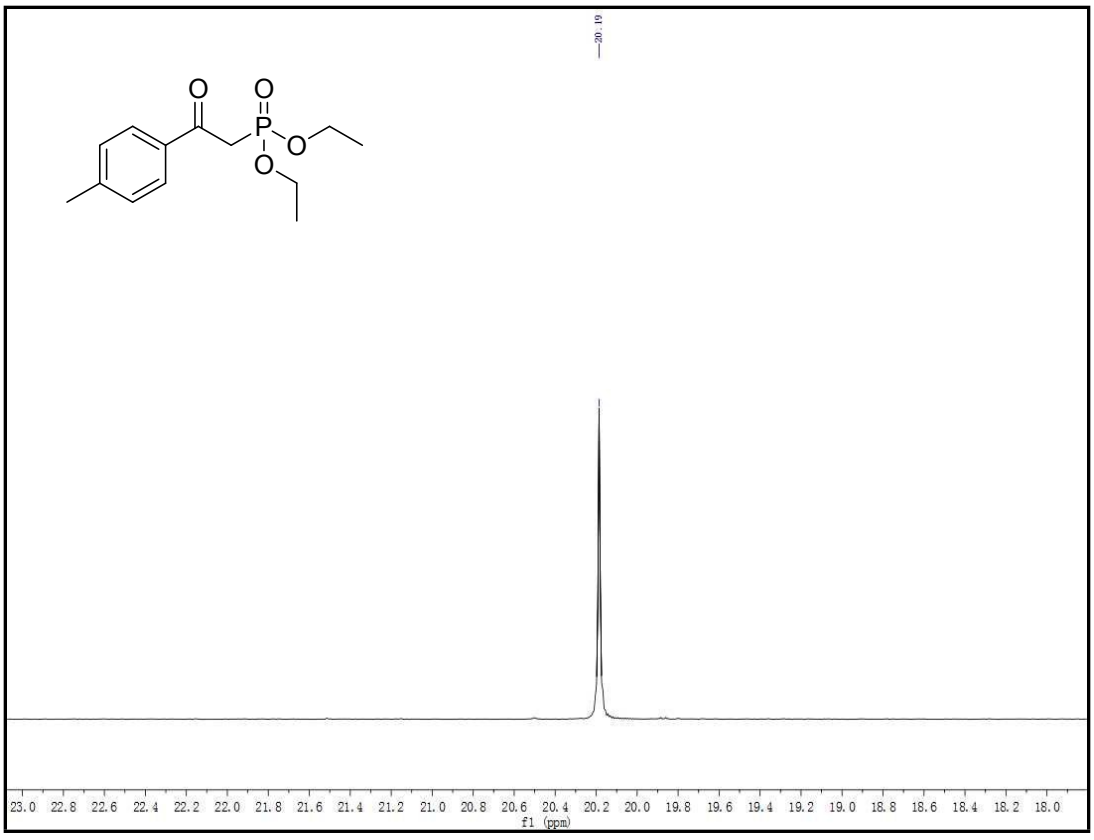




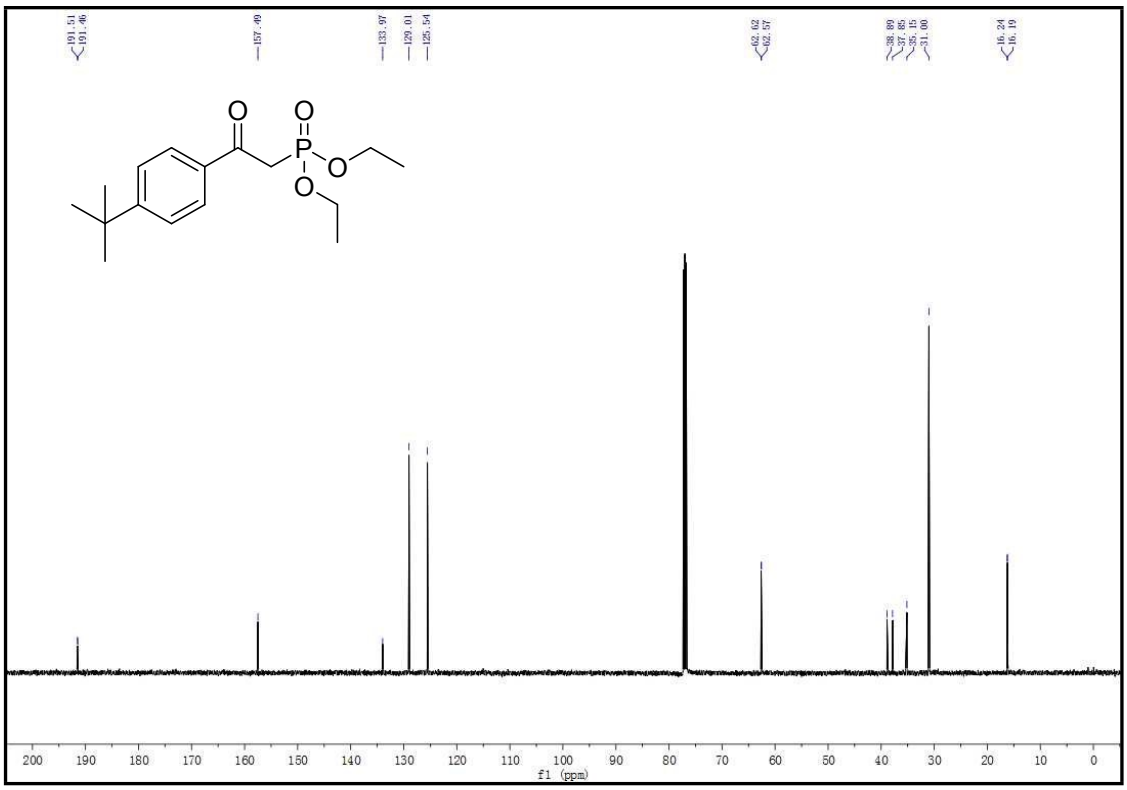
Diethyl (2-oxo-2-(p-tolyl) ethyl) phosphonate (3da)

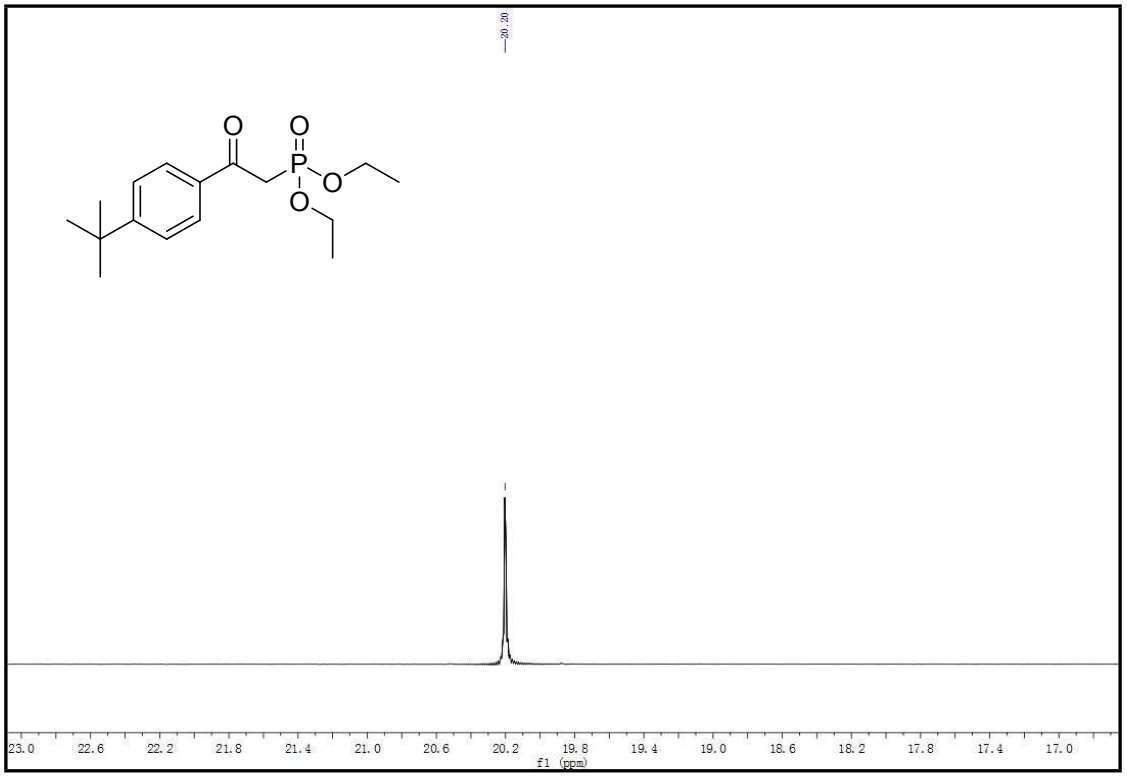



191.48
191.43
144.60
134.06
129.26
129.16
62.60
62.55
38.88
37.84
21.66
16.25
16.20
O
O
P
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

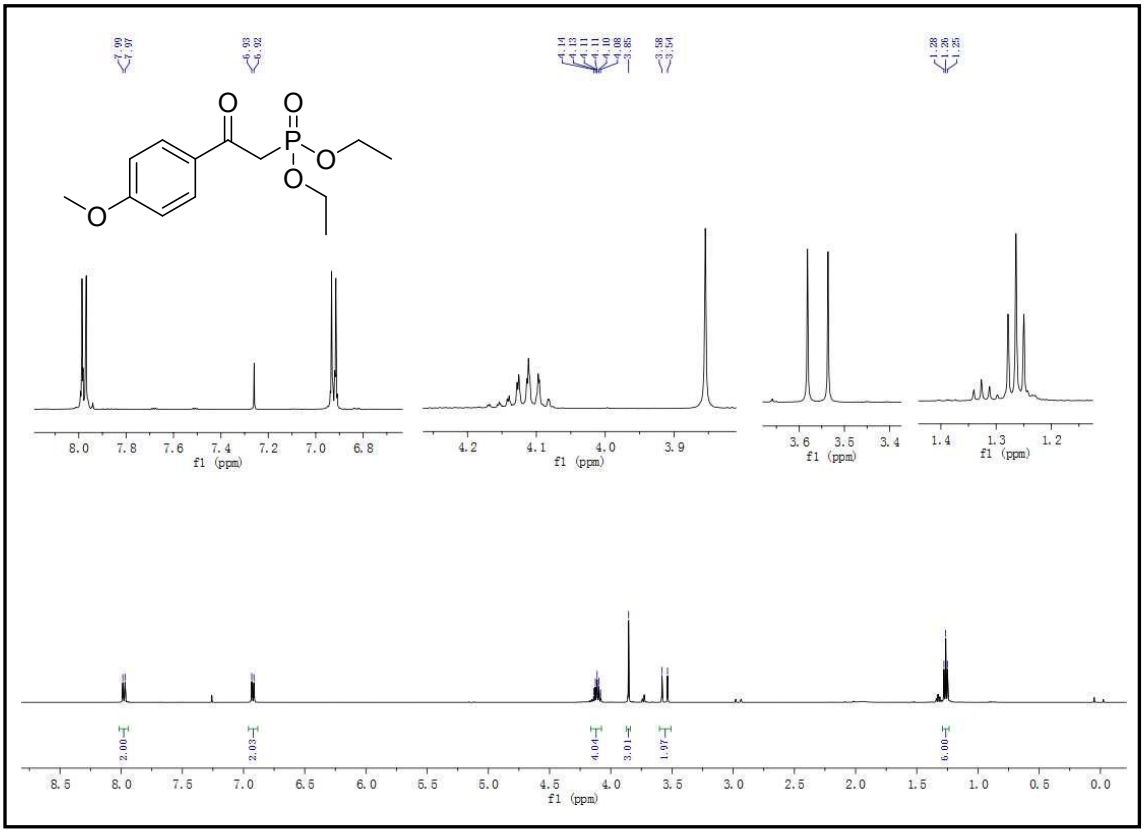

20.19
O
O
P
O
O
23.0 22.8 22.6 22.4 22.2 22.0 21.8 21.6 21.4 21.2 21.0 20.8 20.6 20.4 20.2 20.0 19.8 19.6 19.4 19.2 19.0 18.8 18.6 18.4 18.2 18.0
f1 (ppm)

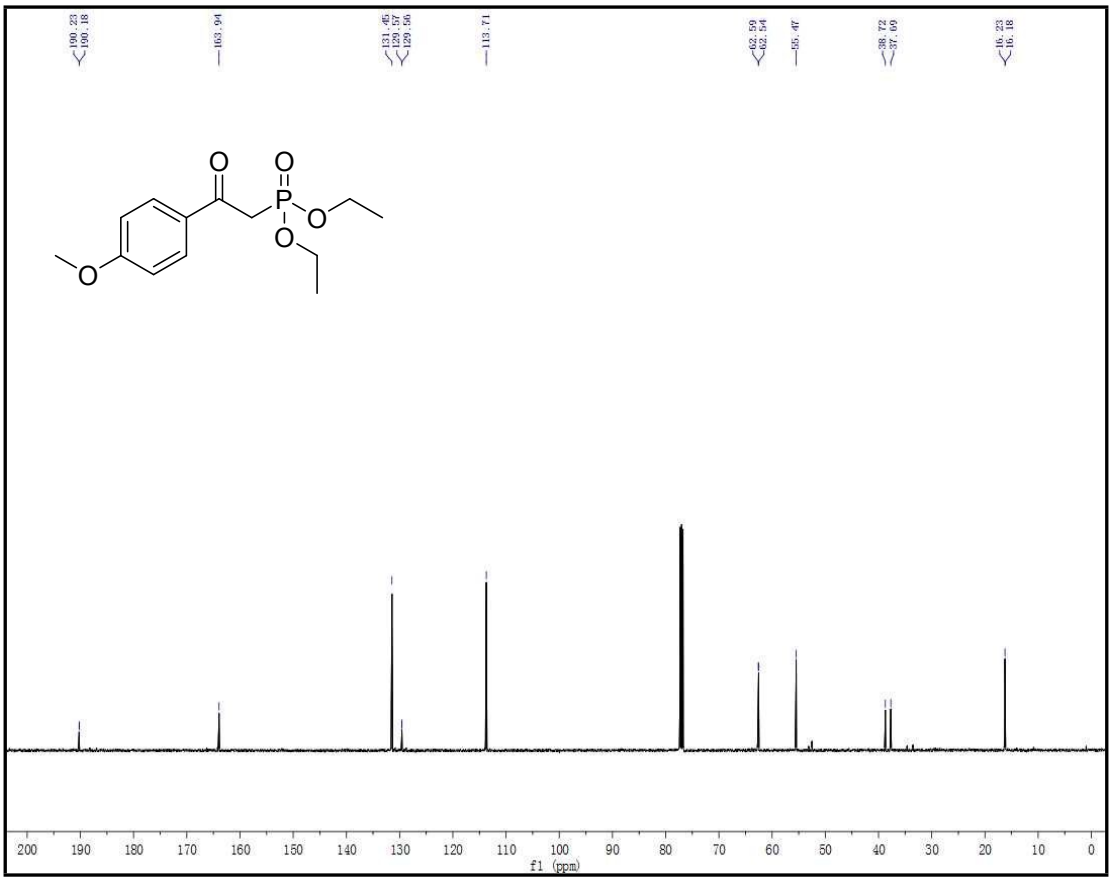
Diethyl (2-(4-(tert-butyl) phenyl)-2-oxoethyl) phosphonate (3ea)

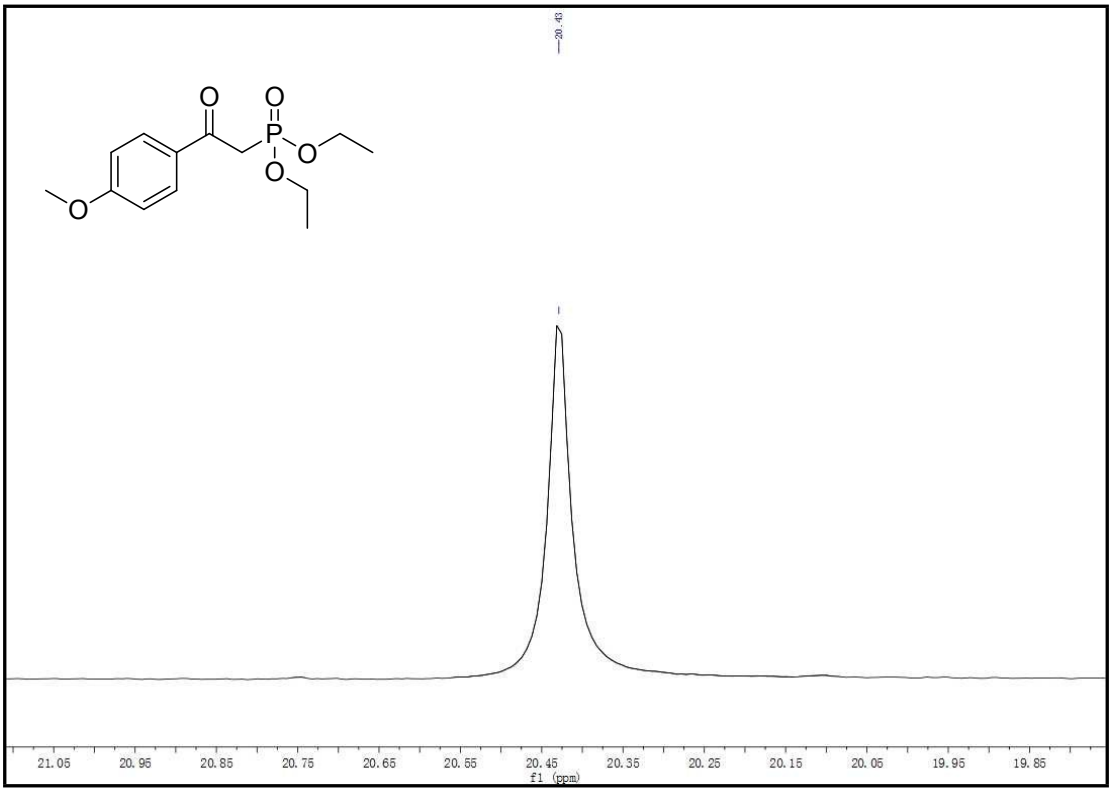




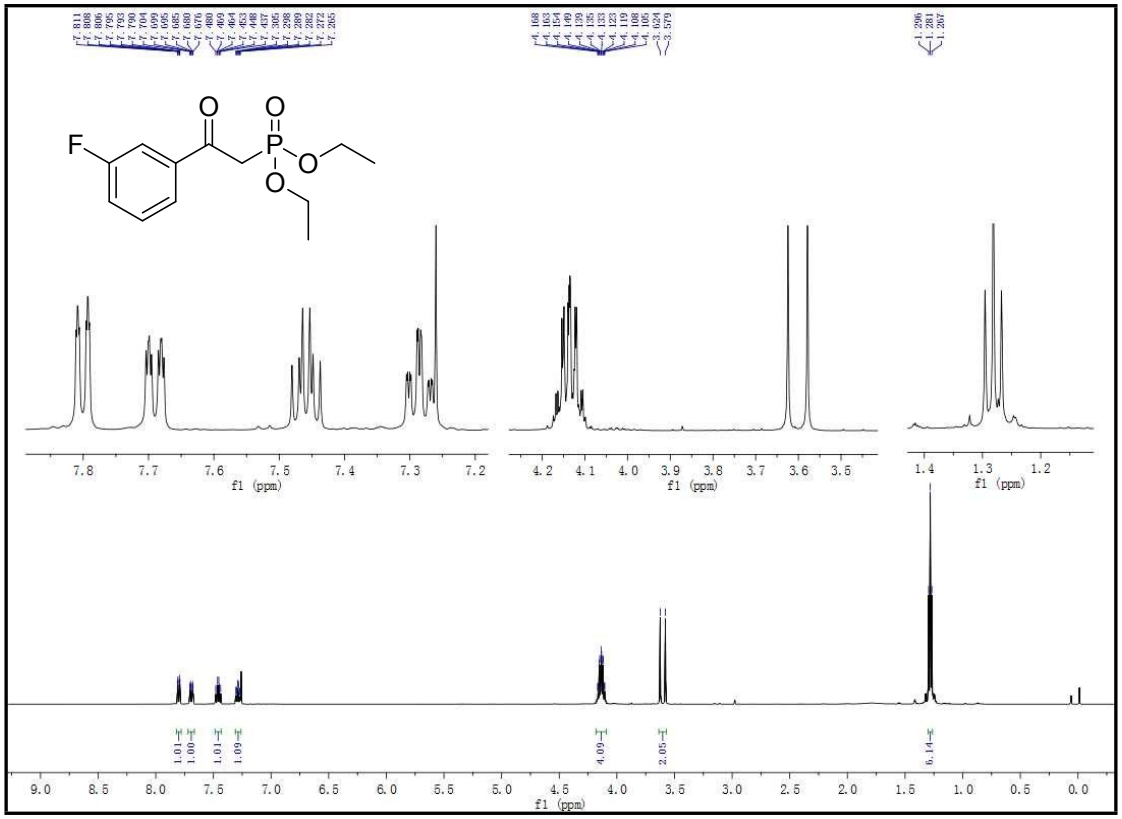
Diethyl (2-(4-methoxyphenyl)-2-oxoethyl) phosphonate (3fa)

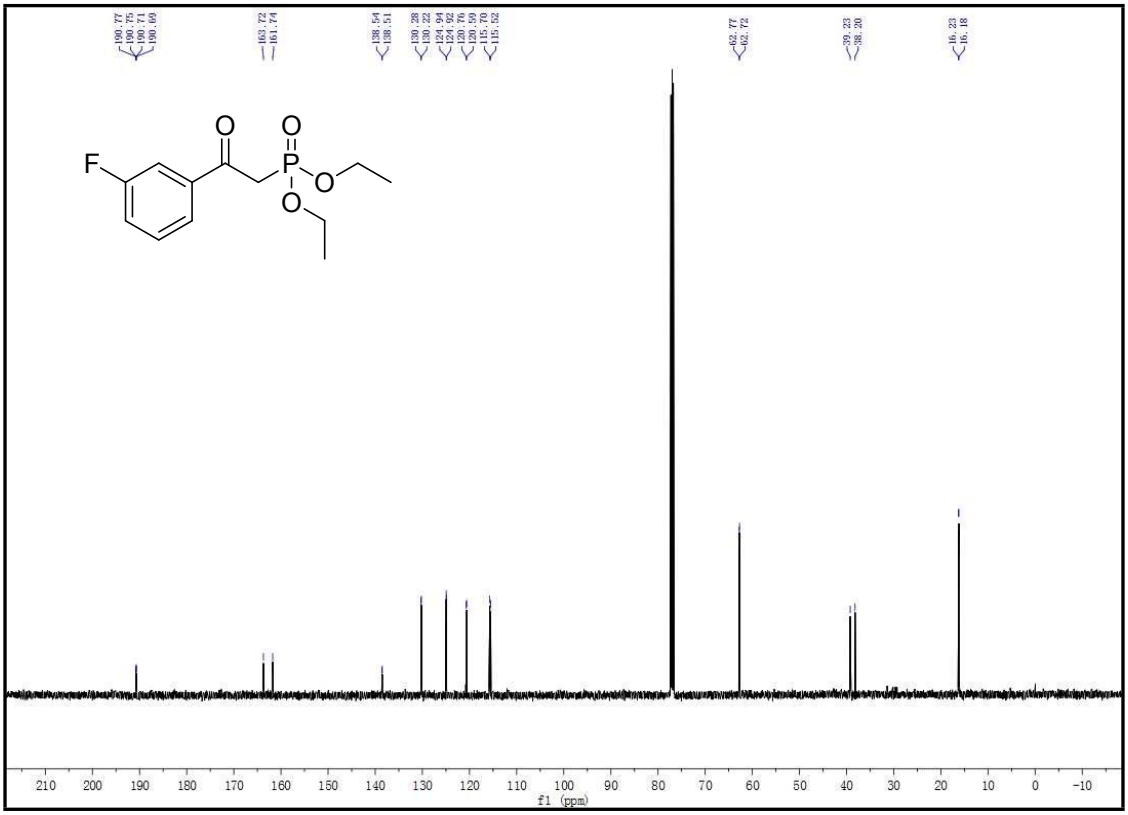


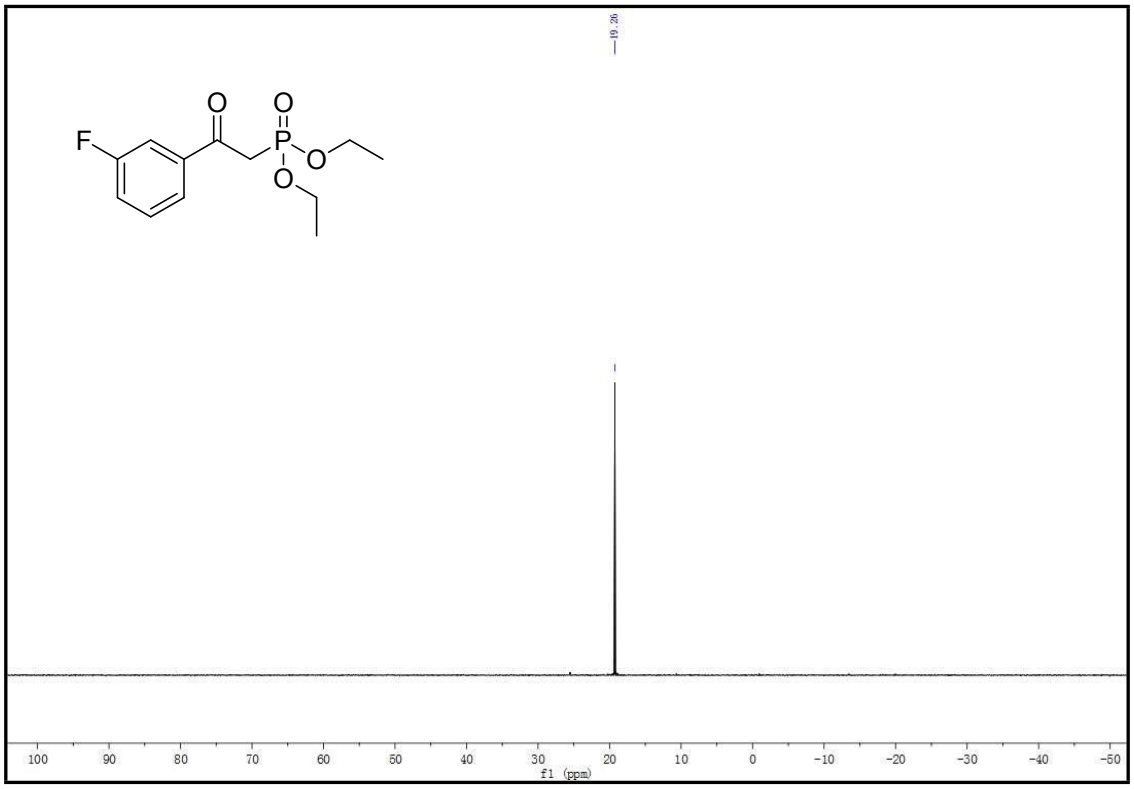

190.23
190.18
163.94
131.45
129.57
129.56
113.71
62.59
62.54
55.47
38.72
37.60
16.23
16.18
O
O
P
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


20.43
O
O
P
O
O
O
21.05 20.95 20.85 20.75 20.65 20.55 20.45 20.35 20.25 20.15 20.05 19.95 19.85
f1 (ppm)

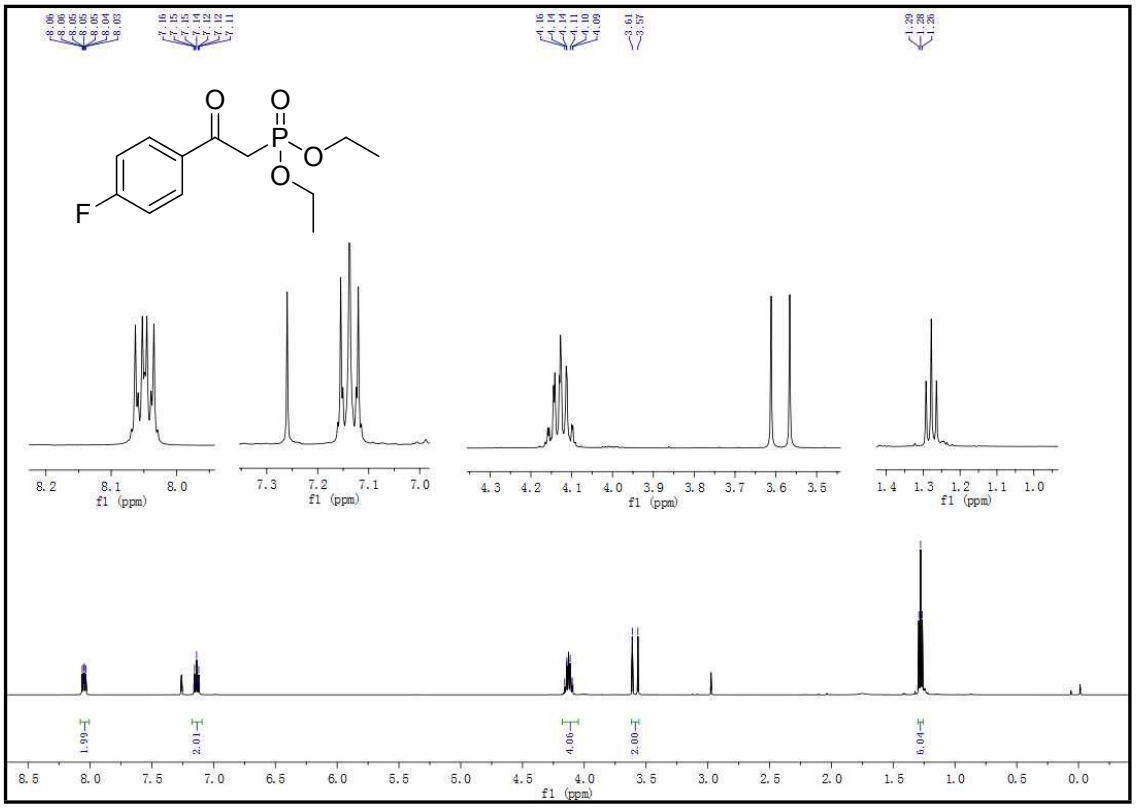
Diethyl (2-(3-fluorophenyl)-2-oxoethyl)phosphonate (3ga)

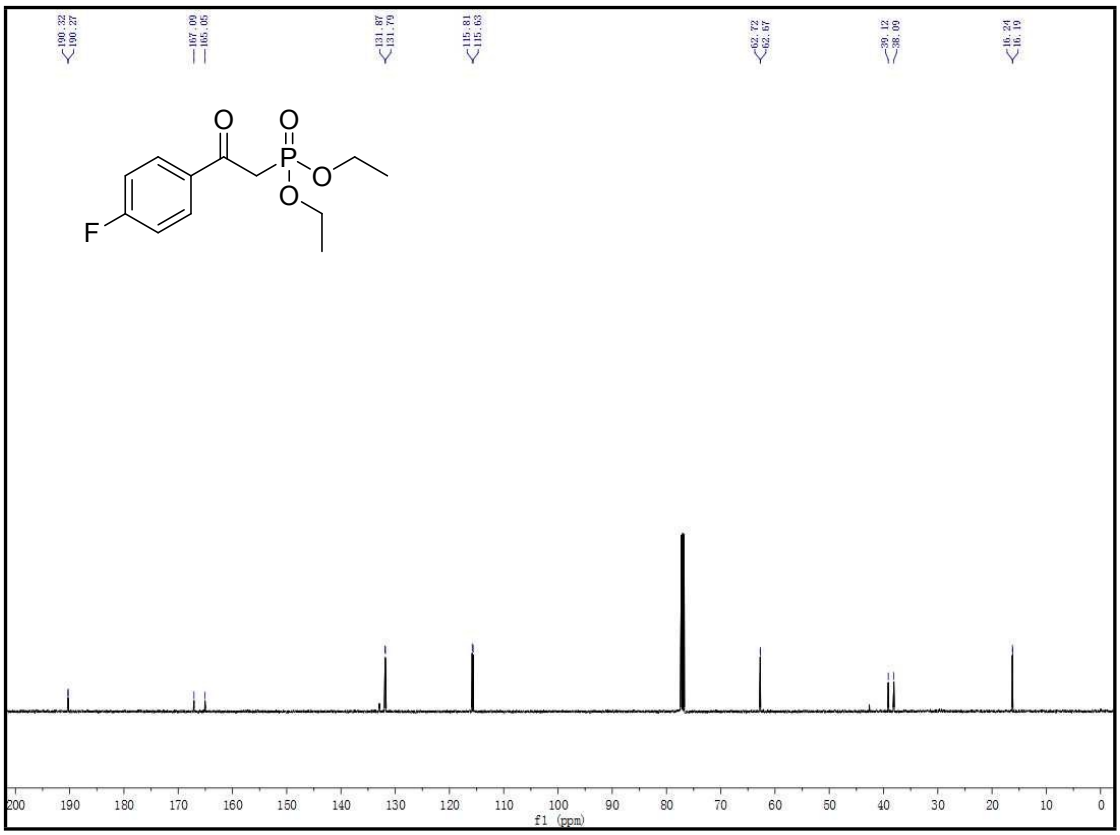


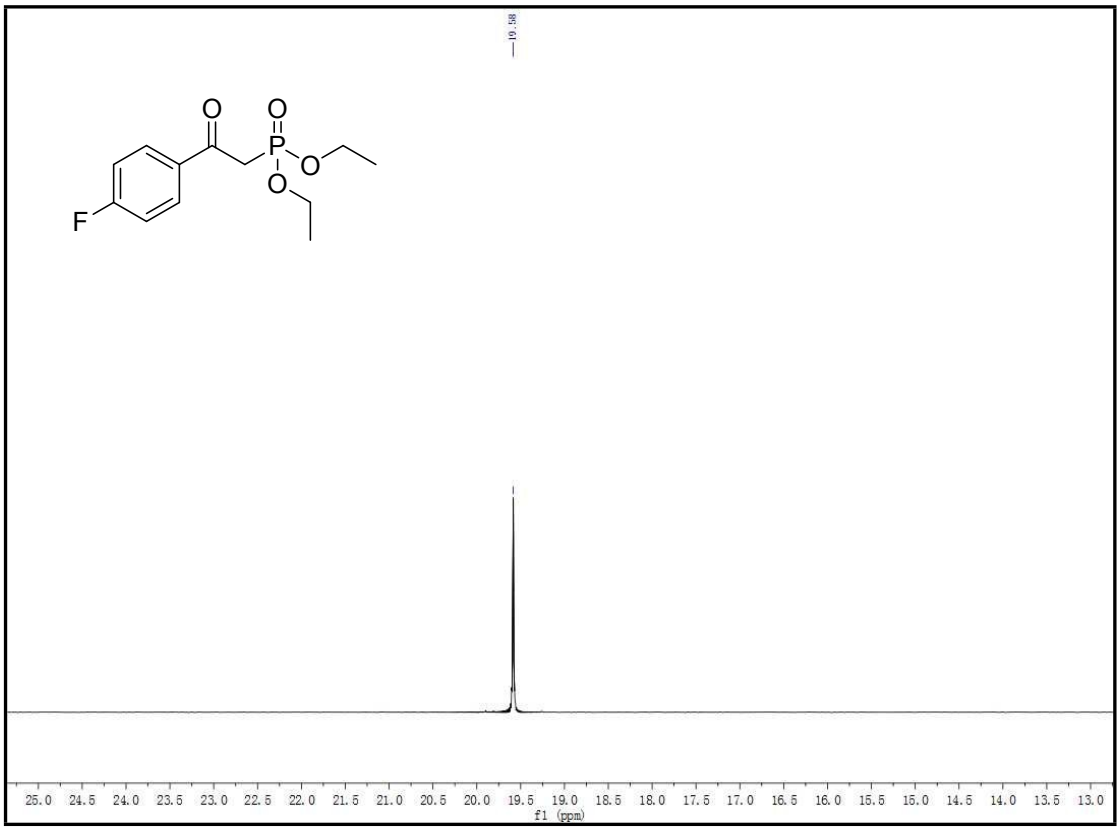




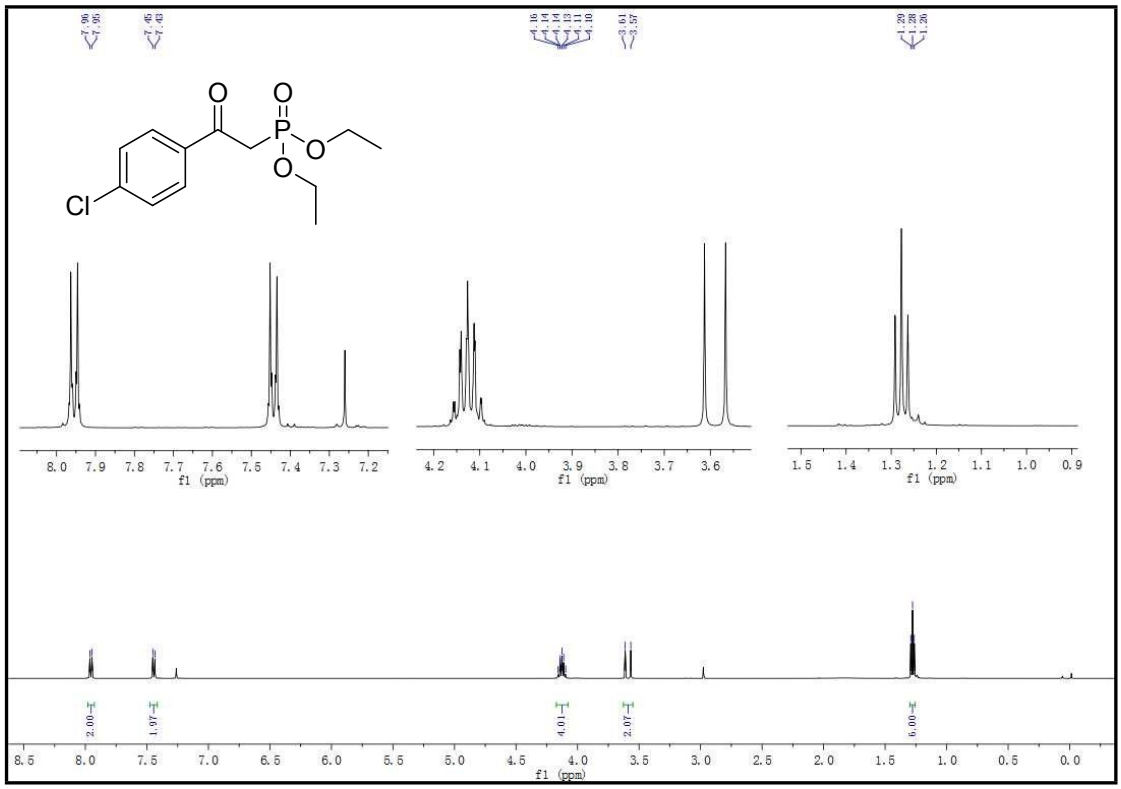
Diethyl (2-(4-fluorophenyl)-2-oxoethyl)phosphonate (3ha)

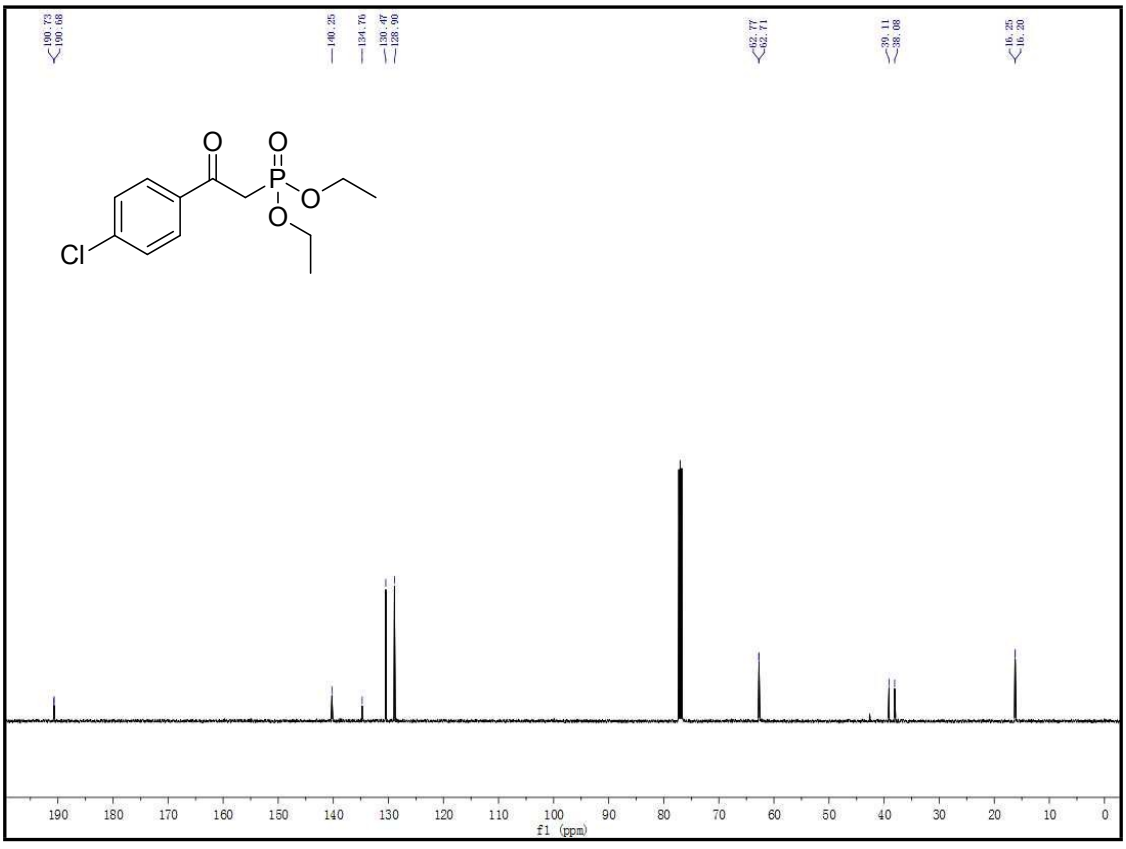


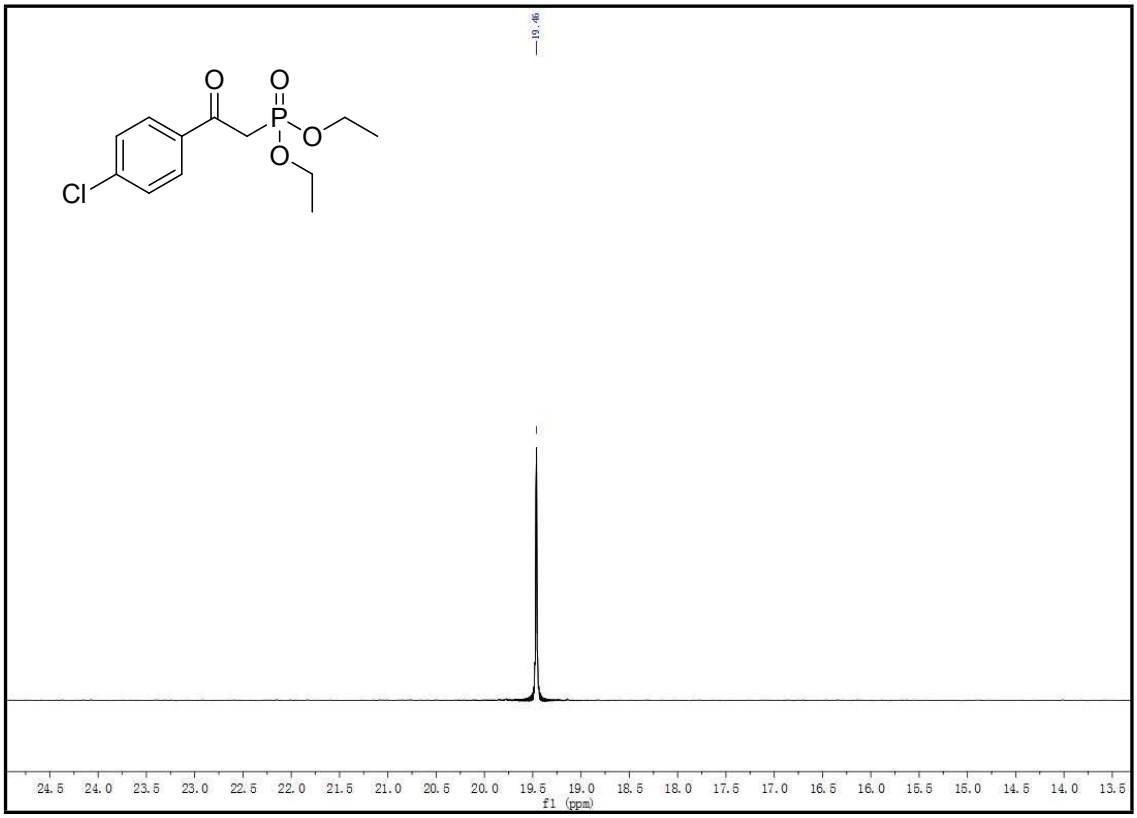

190.32
190.27
167.09
165.05
131.87
131.79
115.81
115.63
62.72
62.67
39.12
38.09
16.24
16.19
O
O
P
O
O
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


19.58
O
O
P
O
O
F
25.0 24.5 24.0 23.5 23.0 22.5 22.0 21.5 21.0 20.5 20.0 19.5 19.0 18.5 18.0 17.5 17.0 16.5 16.0 15.5 15.0 14.5 14.0 13.5 13.0
f1 (ppm)

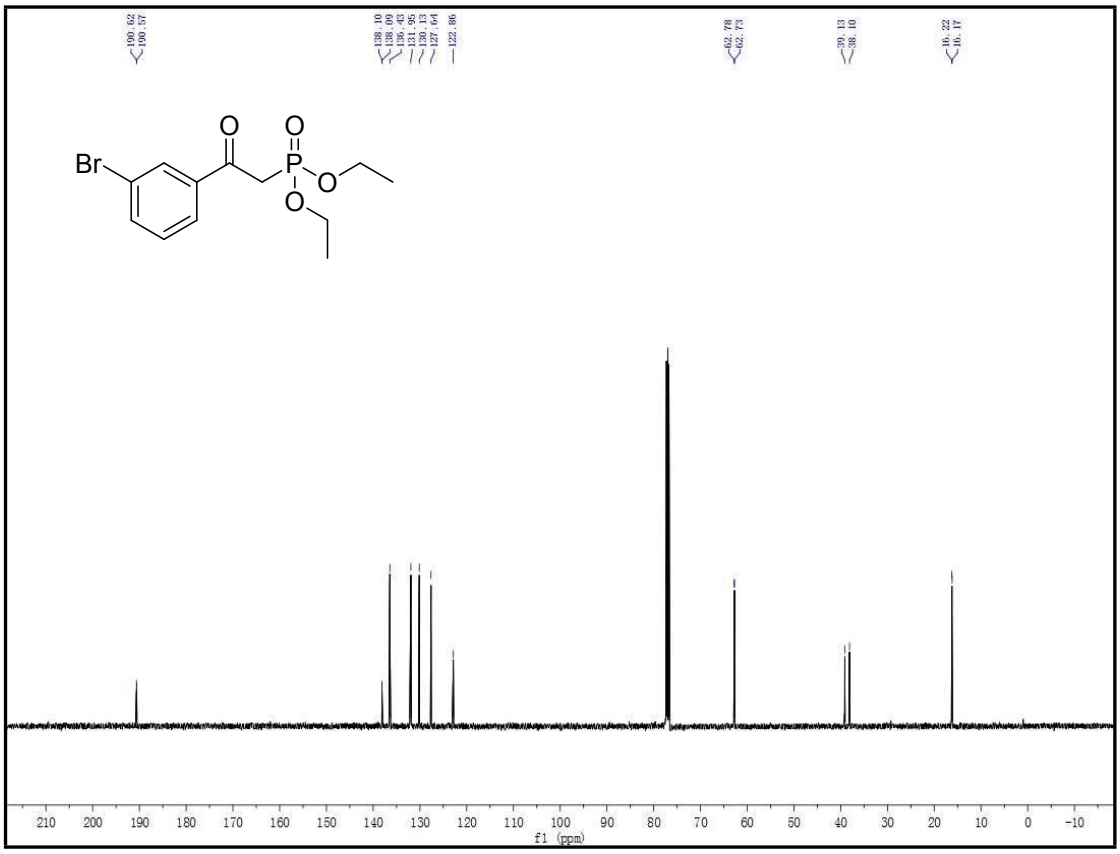
Diethyl(2-(4-chlorophenyl)-2-oxoethyl) phosphonate (3ia)

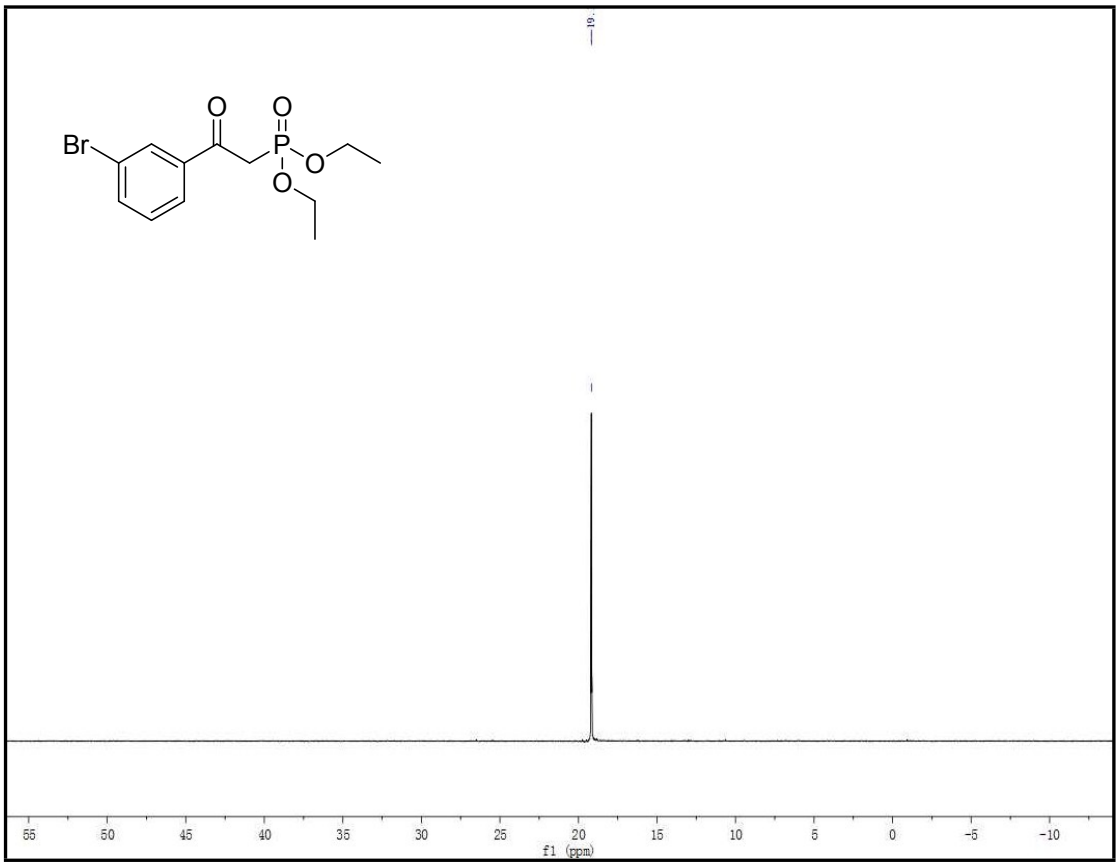




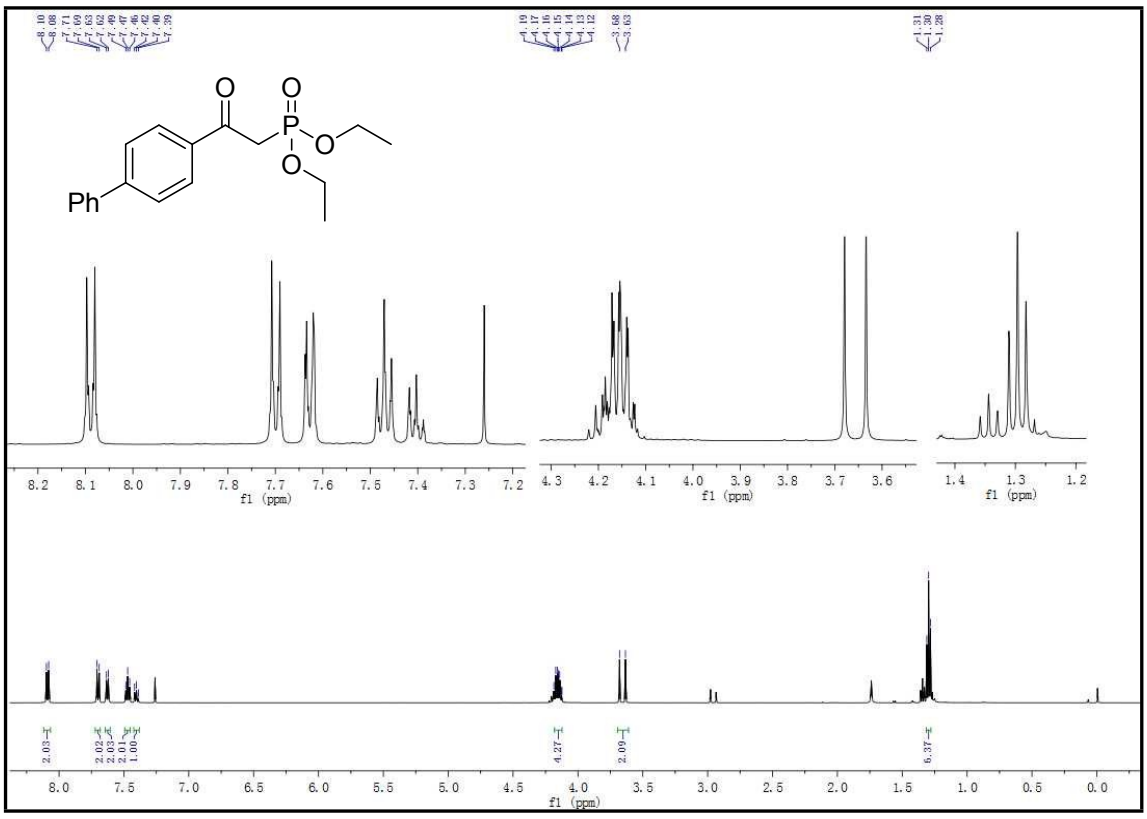


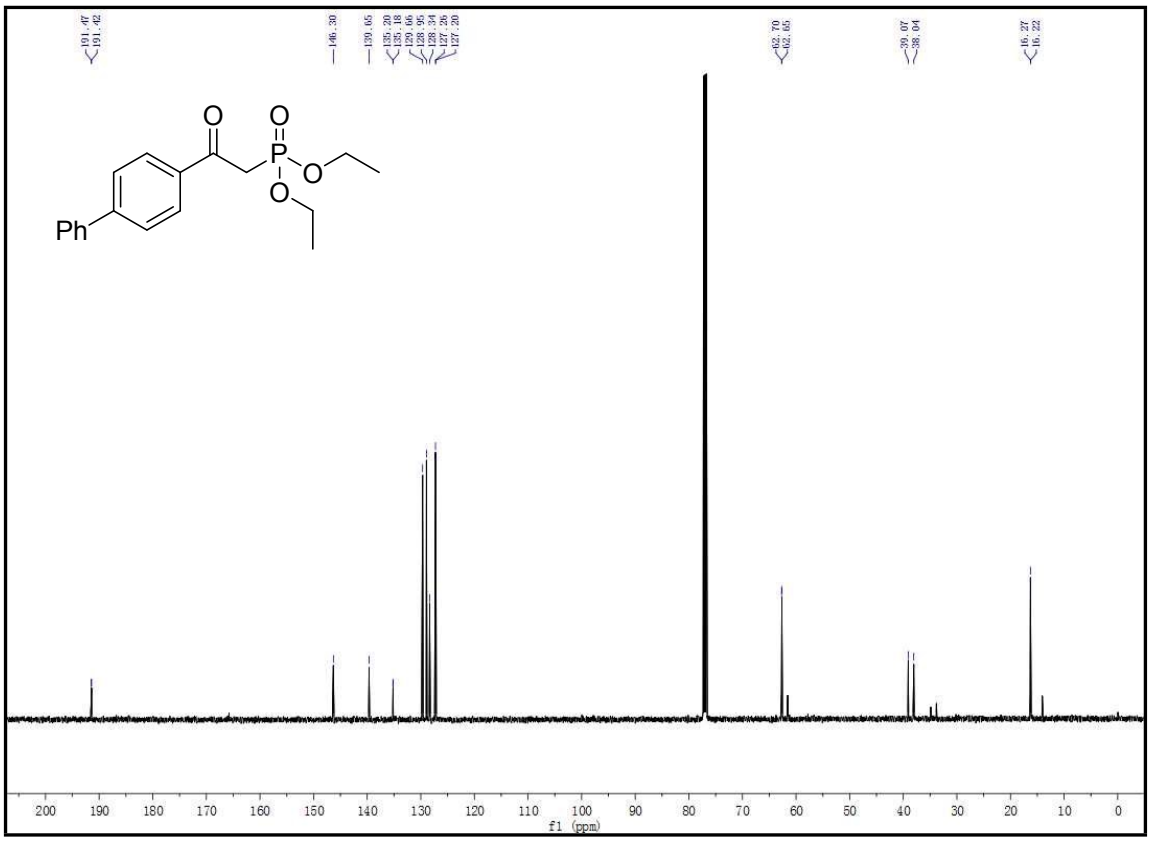
Diethyl (2-(3-bromophenyl)-2-oxoethyl) phosphonate (3ja)

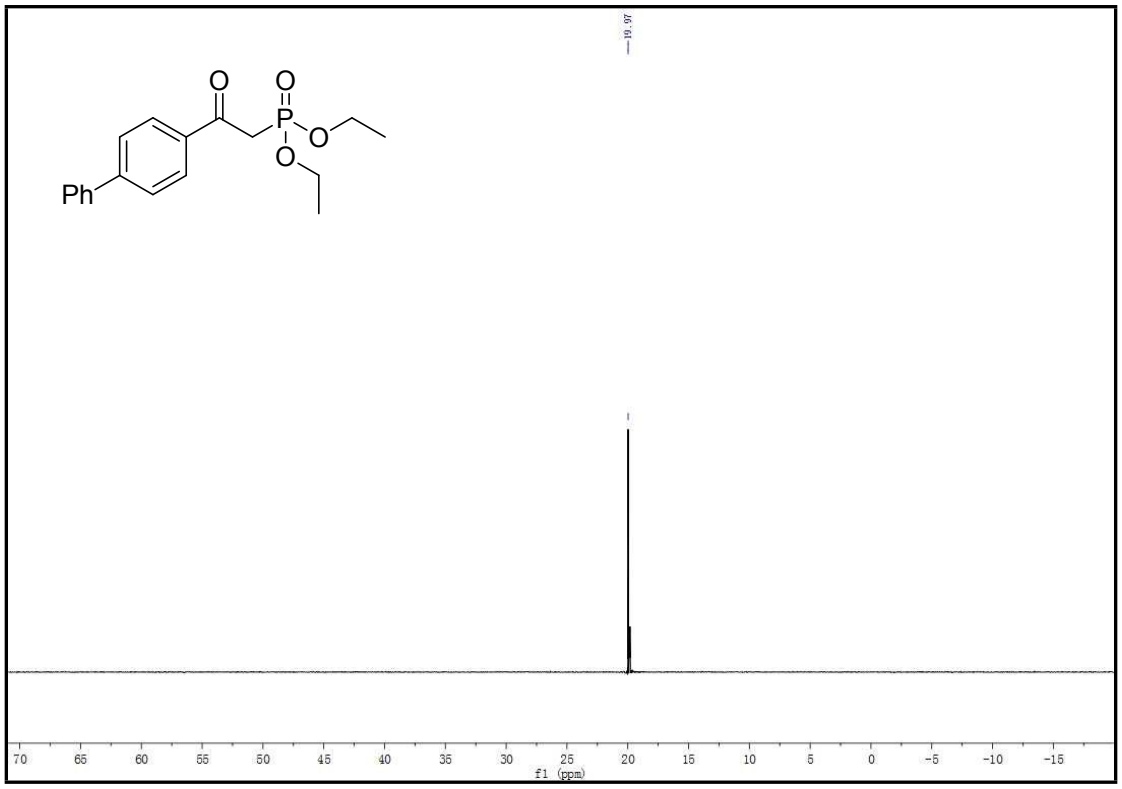

190.62
190.57
138.10
138.09
136.43
131.95
130.13
127.64
122.86
62.78
62.73
39.13
38.10
16.22
16.17
Br
O
O
P
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


19.
Br
O
O
P
O
O
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)

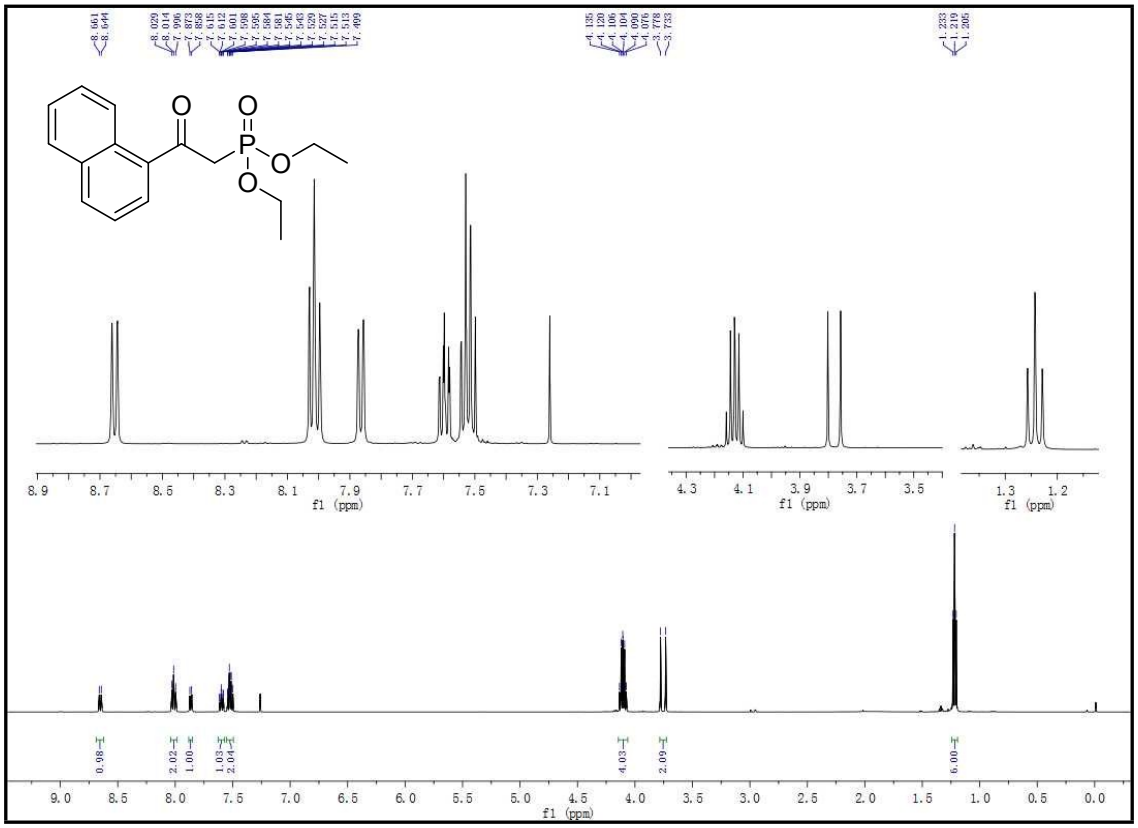
Diethyl (2-([1,1'-biphenyl]-4-yl)-2-oxoethyl) phosphonate (3ka)

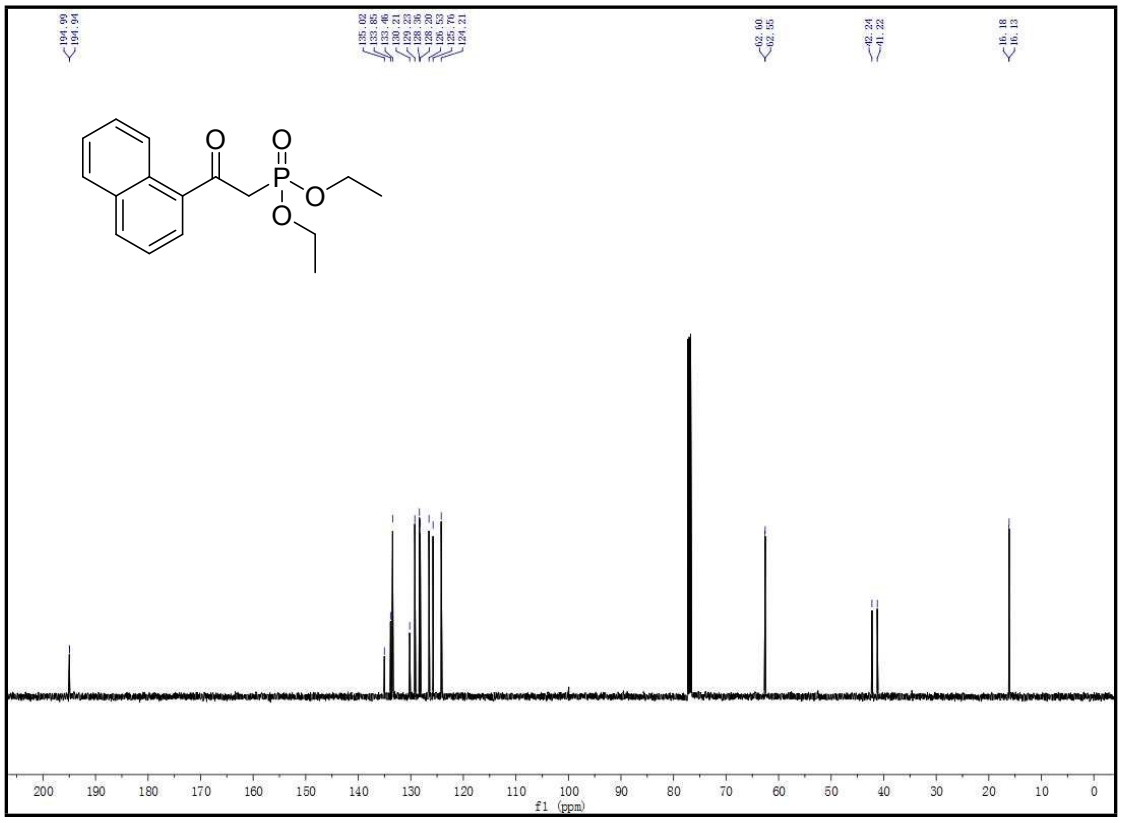


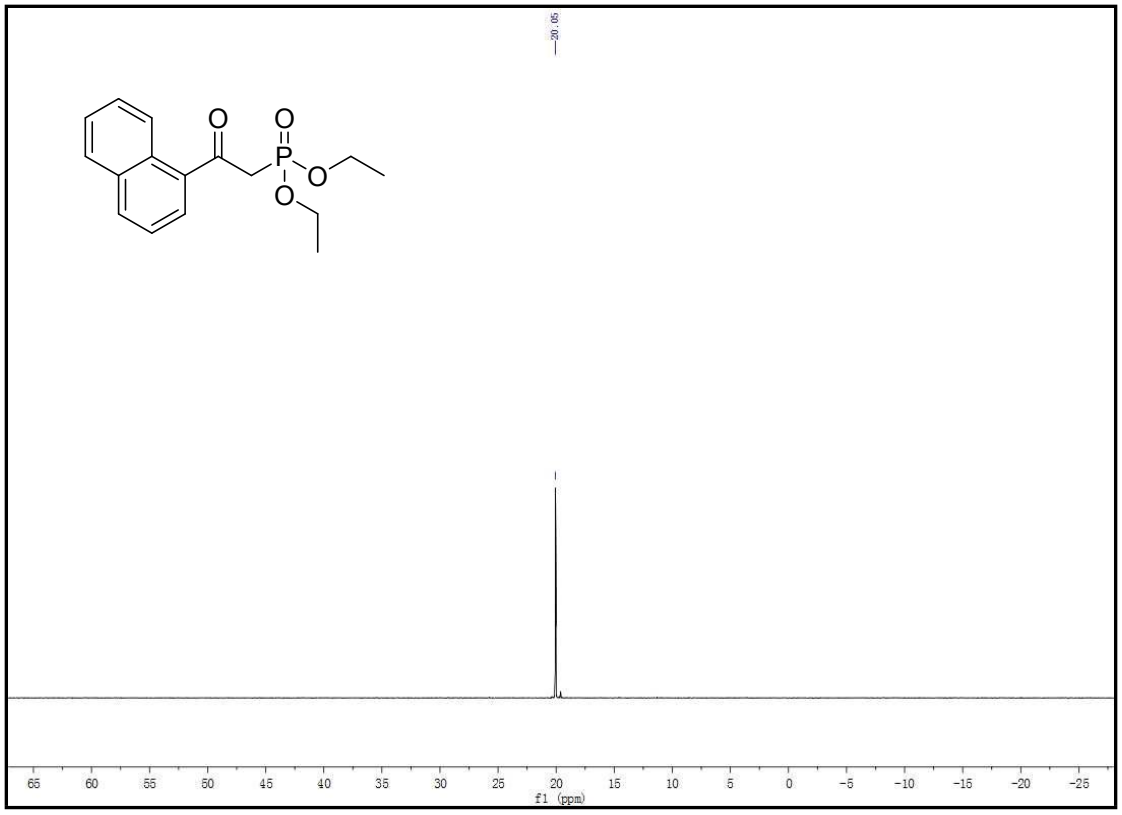




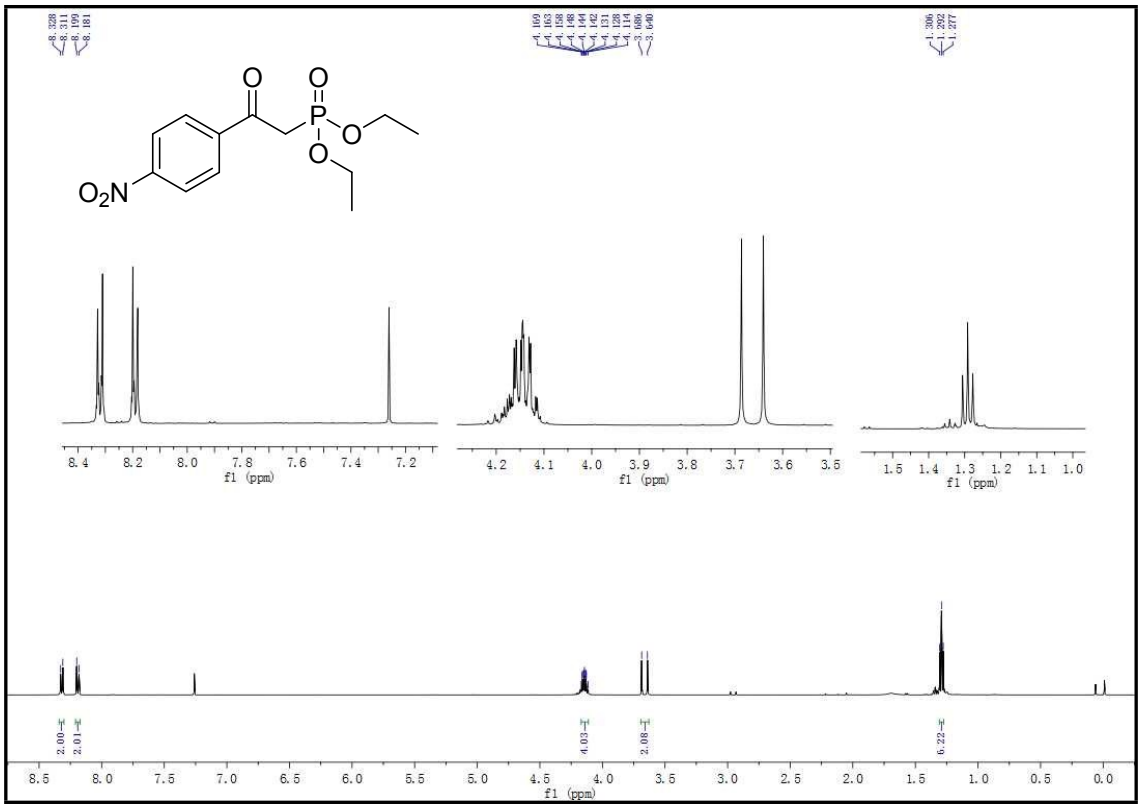
Diethyl(2-(naphthalen-1-yl)-2-oxoethyl)phosphonate (3la)

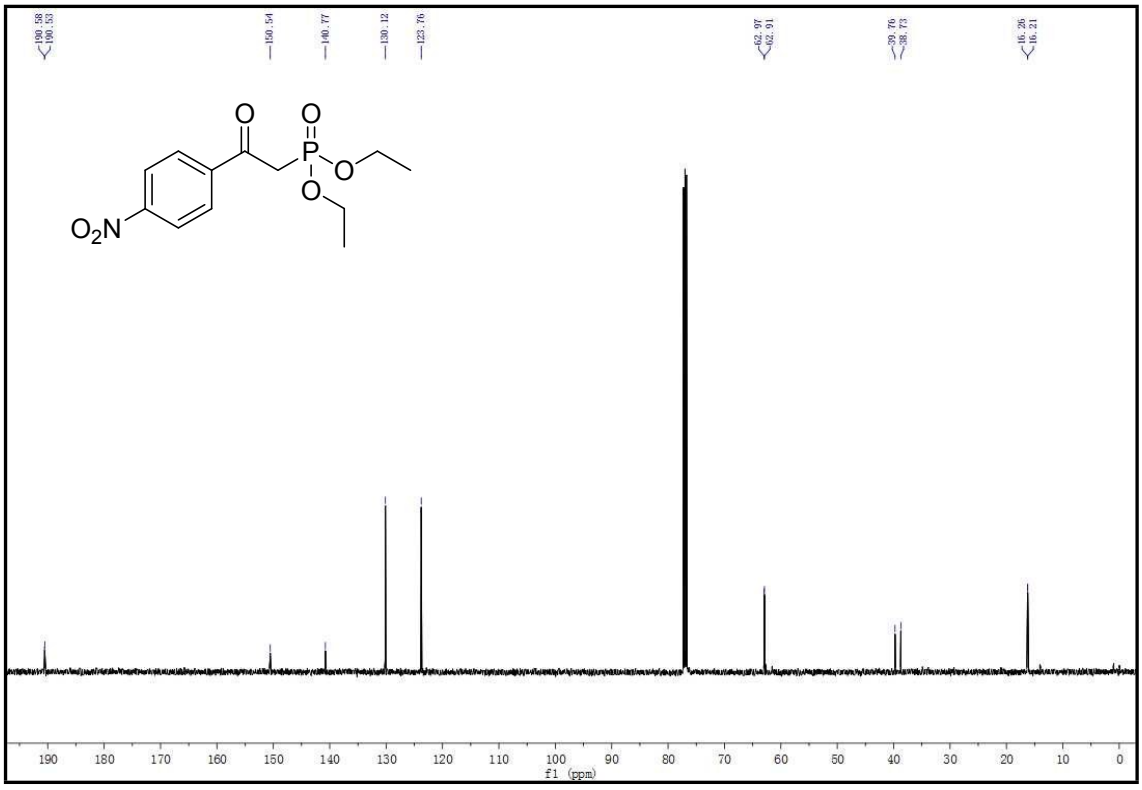


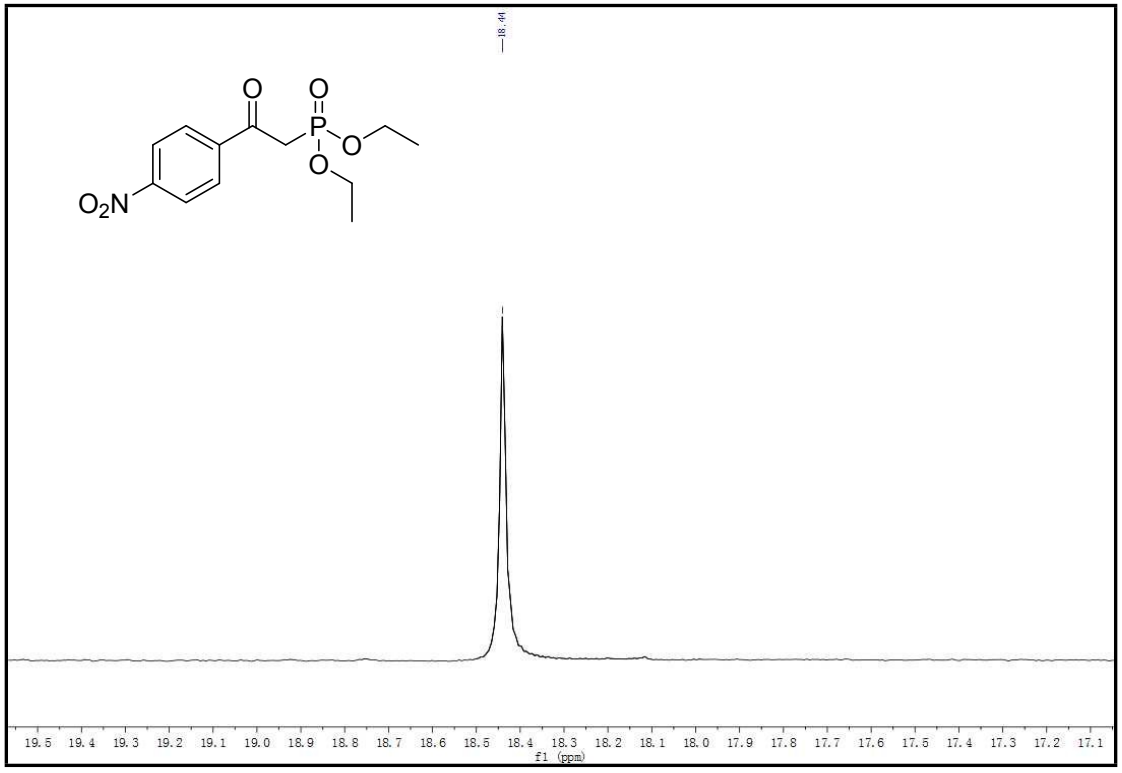

194.99
194.94
135.02
133.85
133.46
130.71
129.23
128.36
128.20
126.53
125.76
124.21
62.60
62.55
42.24
41.22
16.18
16.13
O
O
P
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


20.05
O
O
P
O
O
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

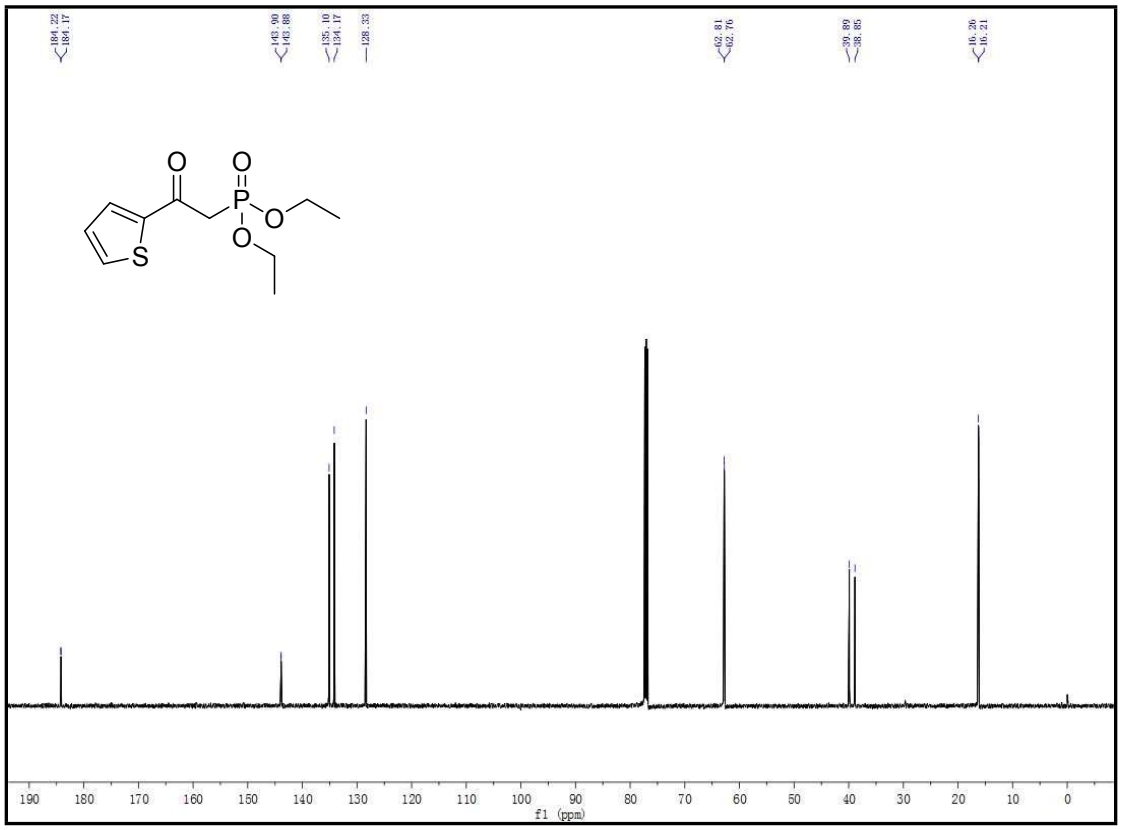
Diethyl (2-(4-nitrylphenyl)-2-oxoethyl) phosphonate (3ma)





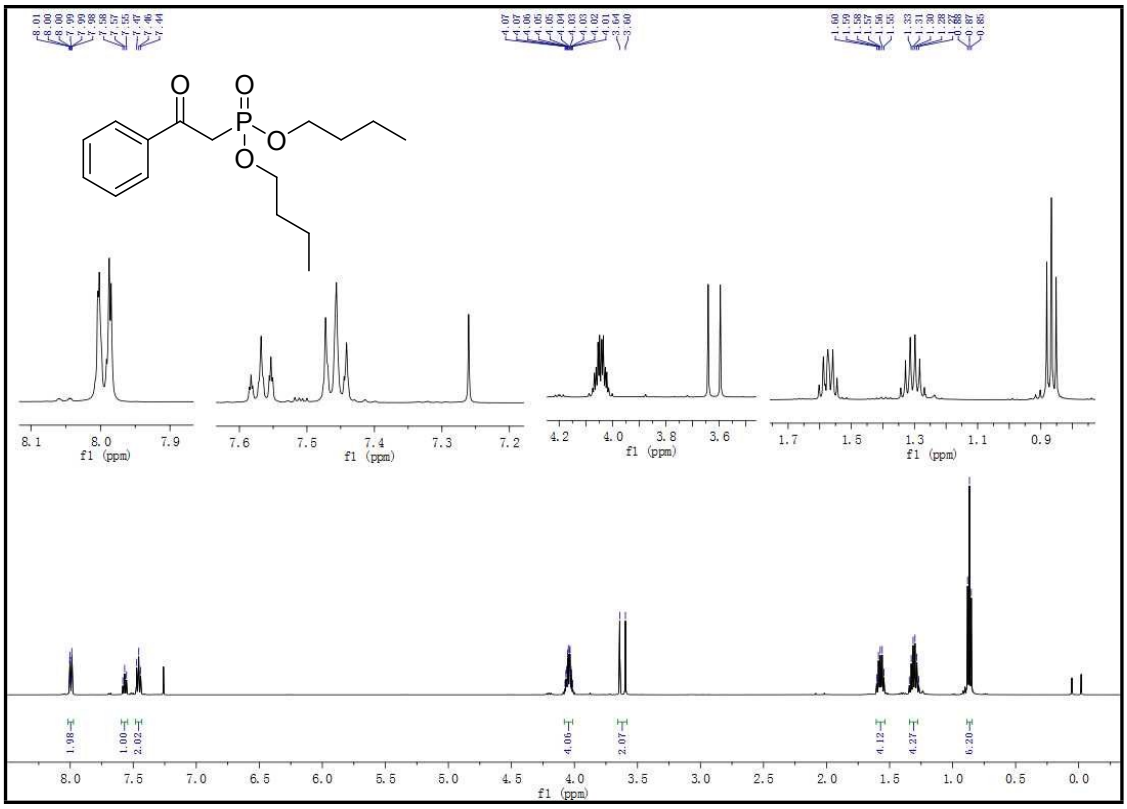


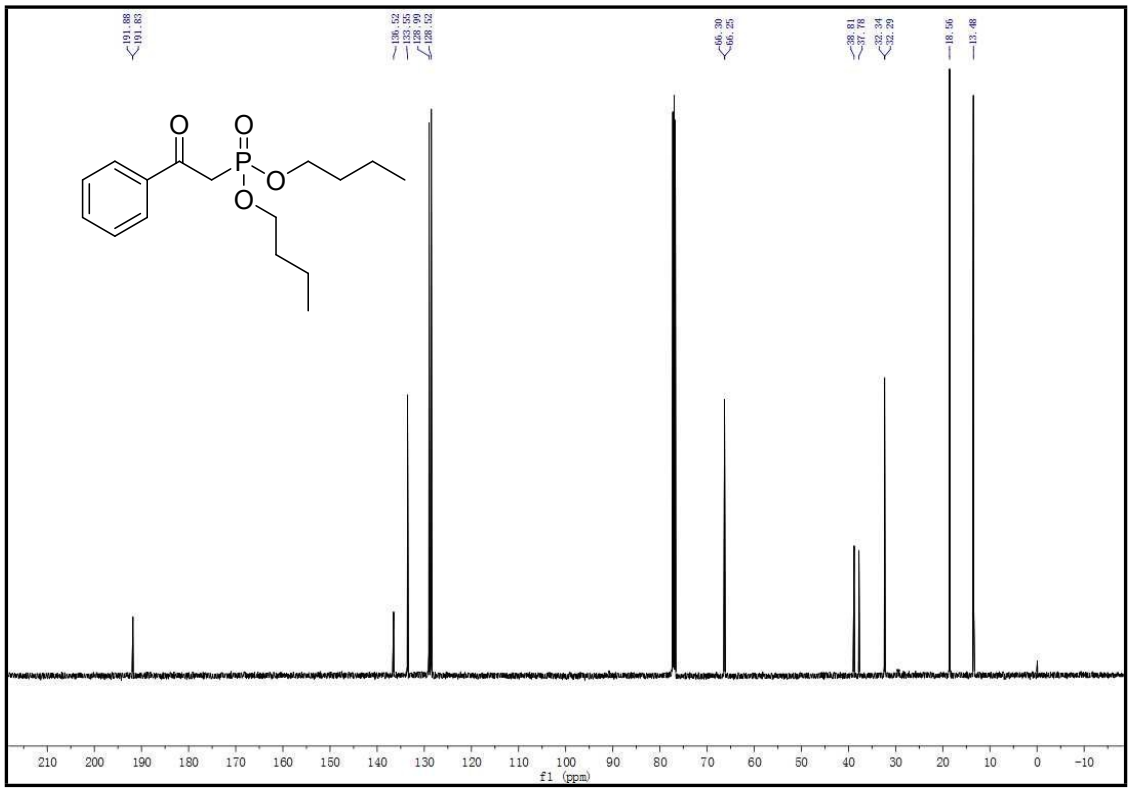
Diethyl (2-oxo-2-(thiophen-2-yl)ethyl) phosphonate (3na)

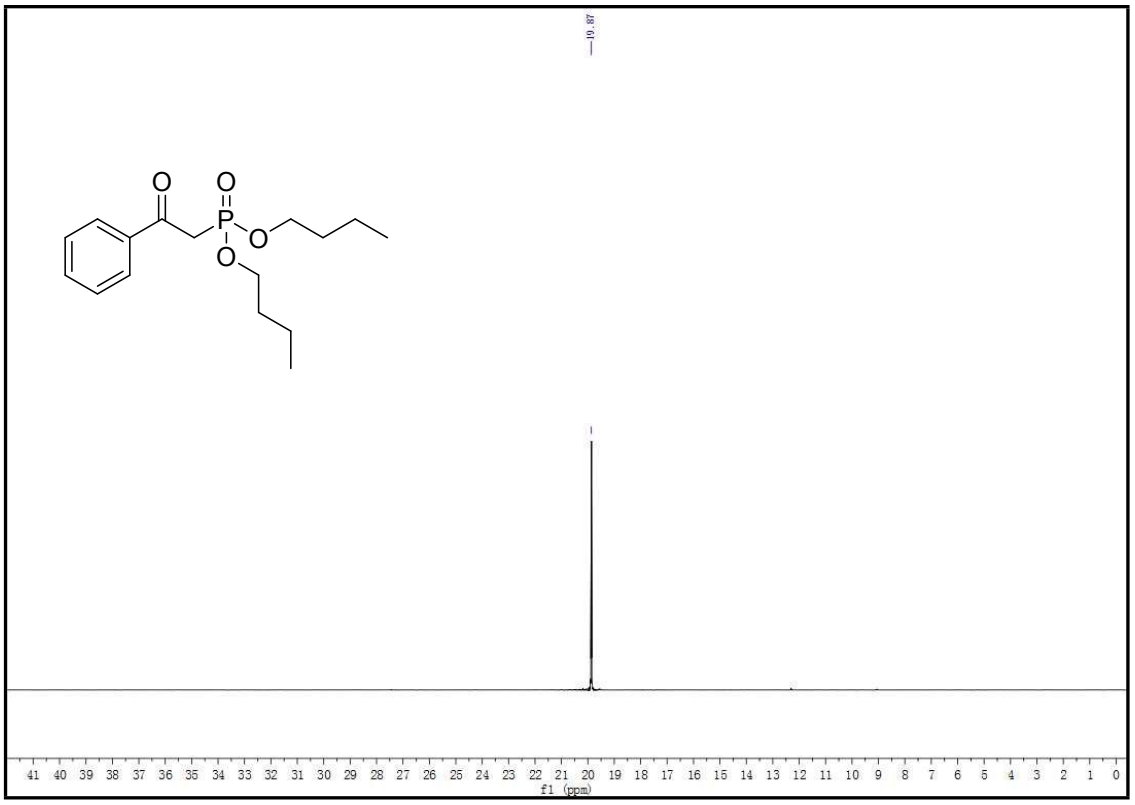

184.22
184.17
145.90
145.88
135.10
134.17
128.33
62.81
62.76
39.89
38.85
16.26
16.21
O
O
P
O
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


19.41
O
O
P
O
O
S
46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)

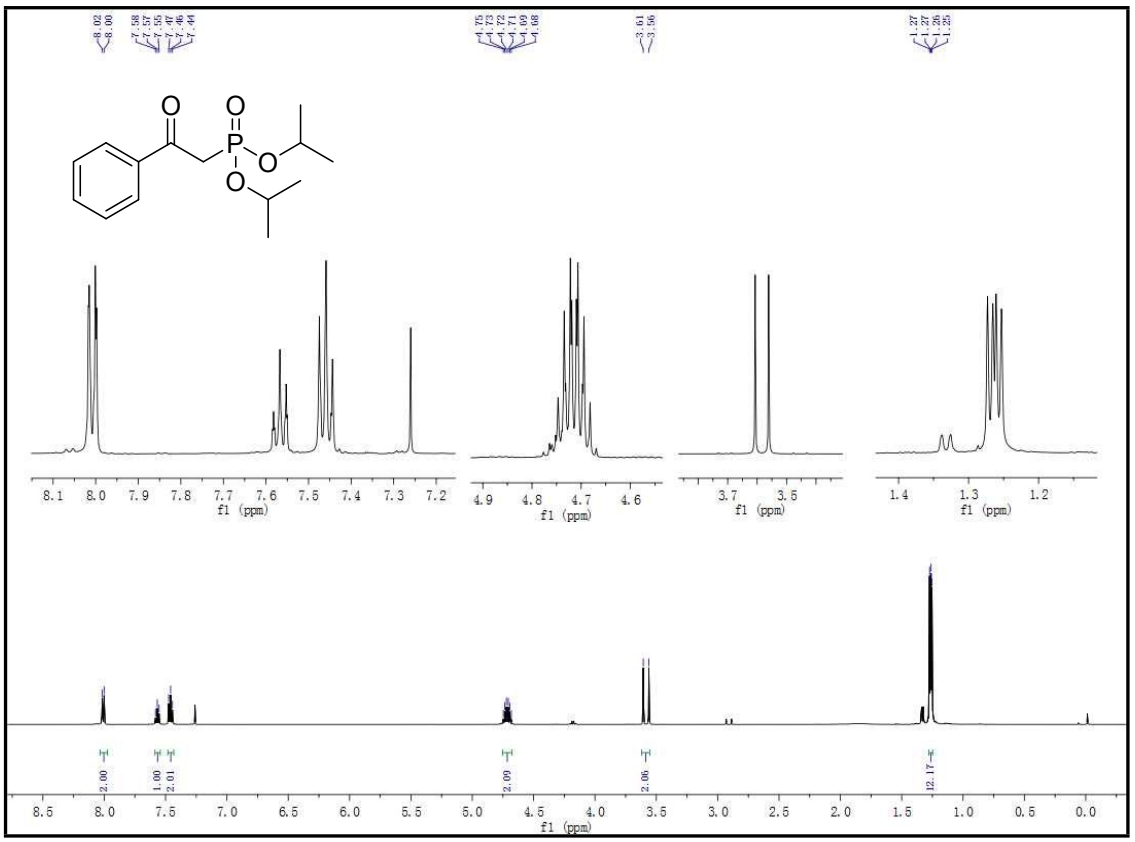
Dibutyl (2-oxo-2-phenylethyl) phosphonate (3ab)

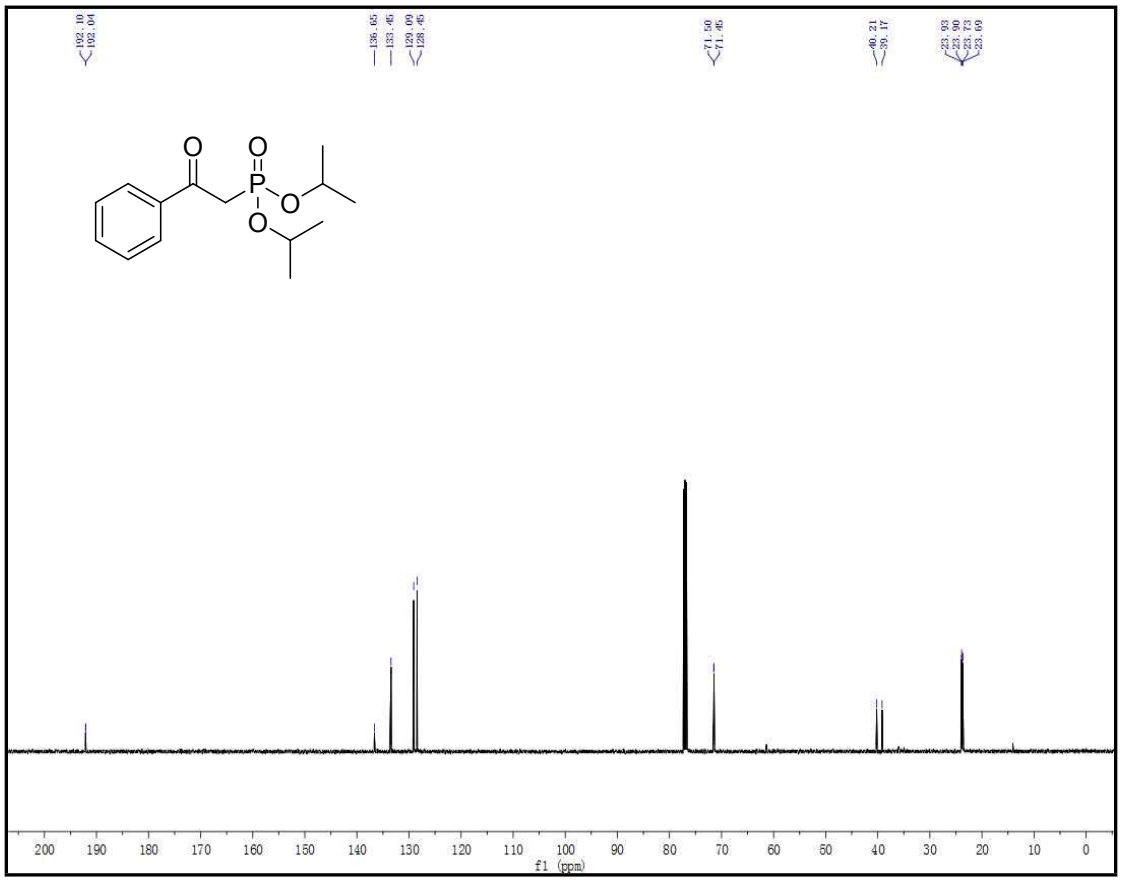


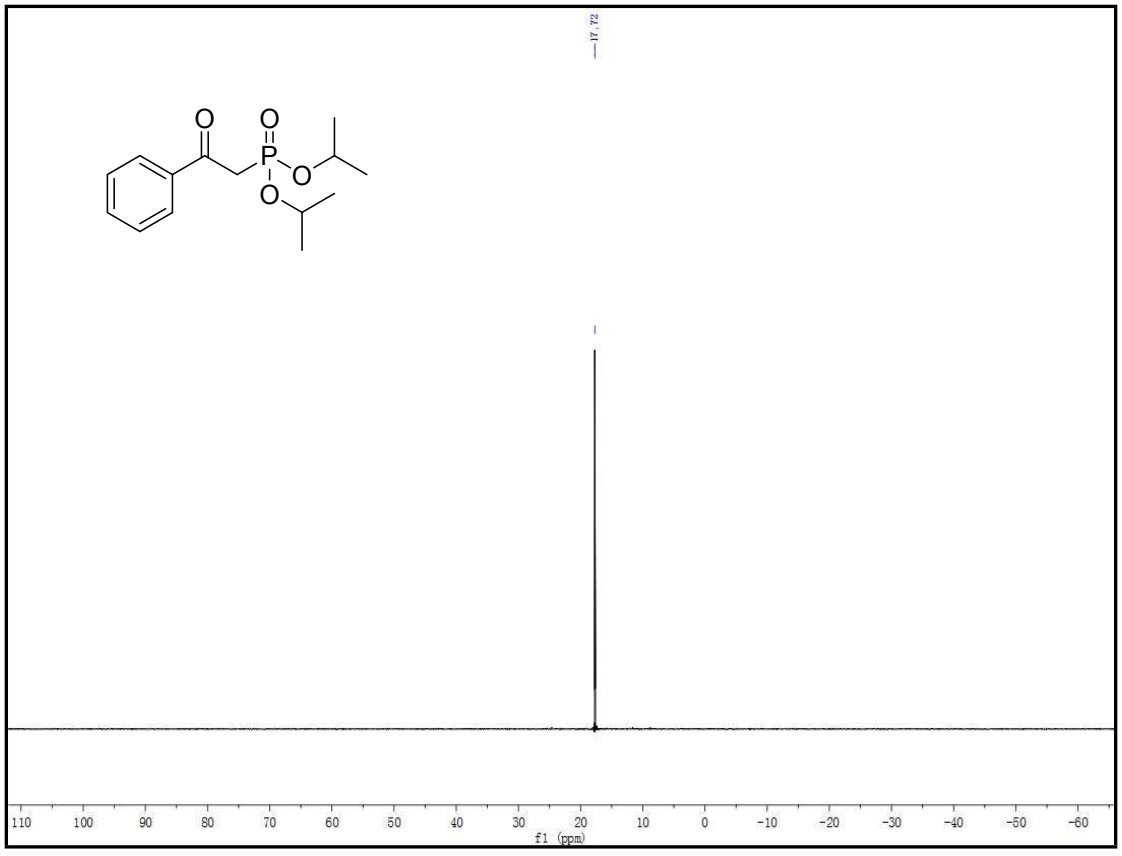




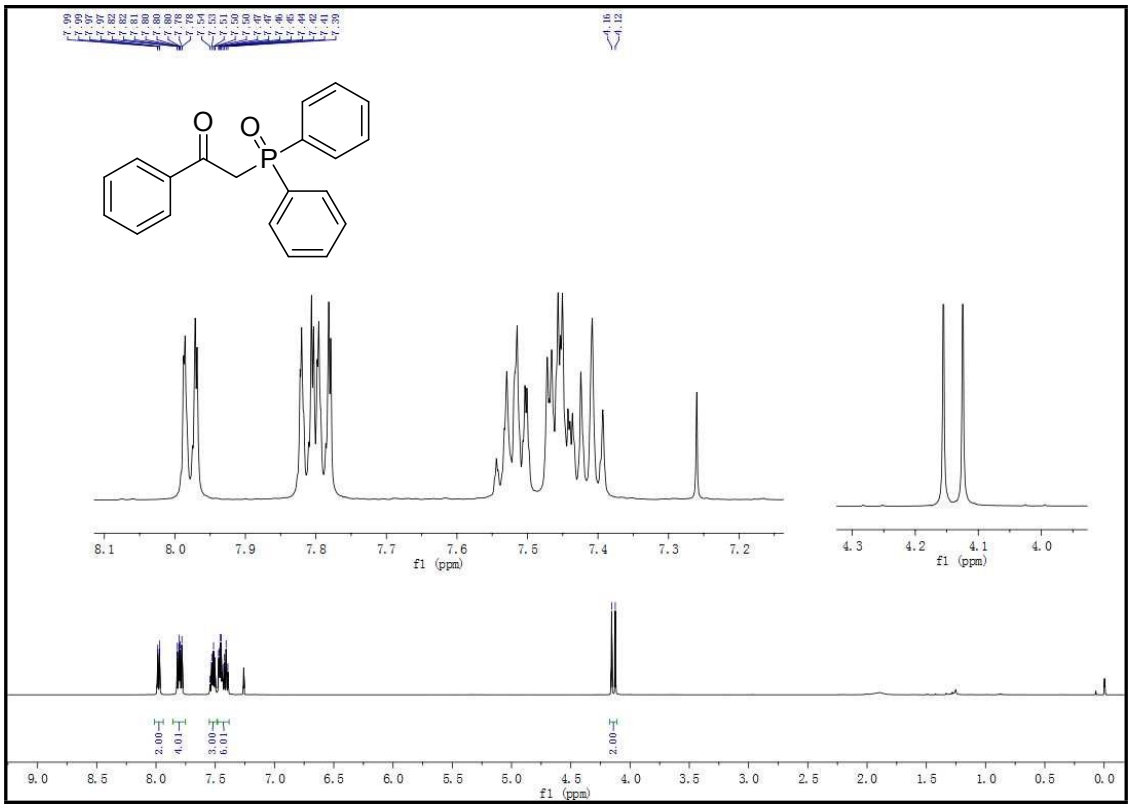
Diisopropyl (2-oxo-2-phenylethyl)phosphonate (3ac)

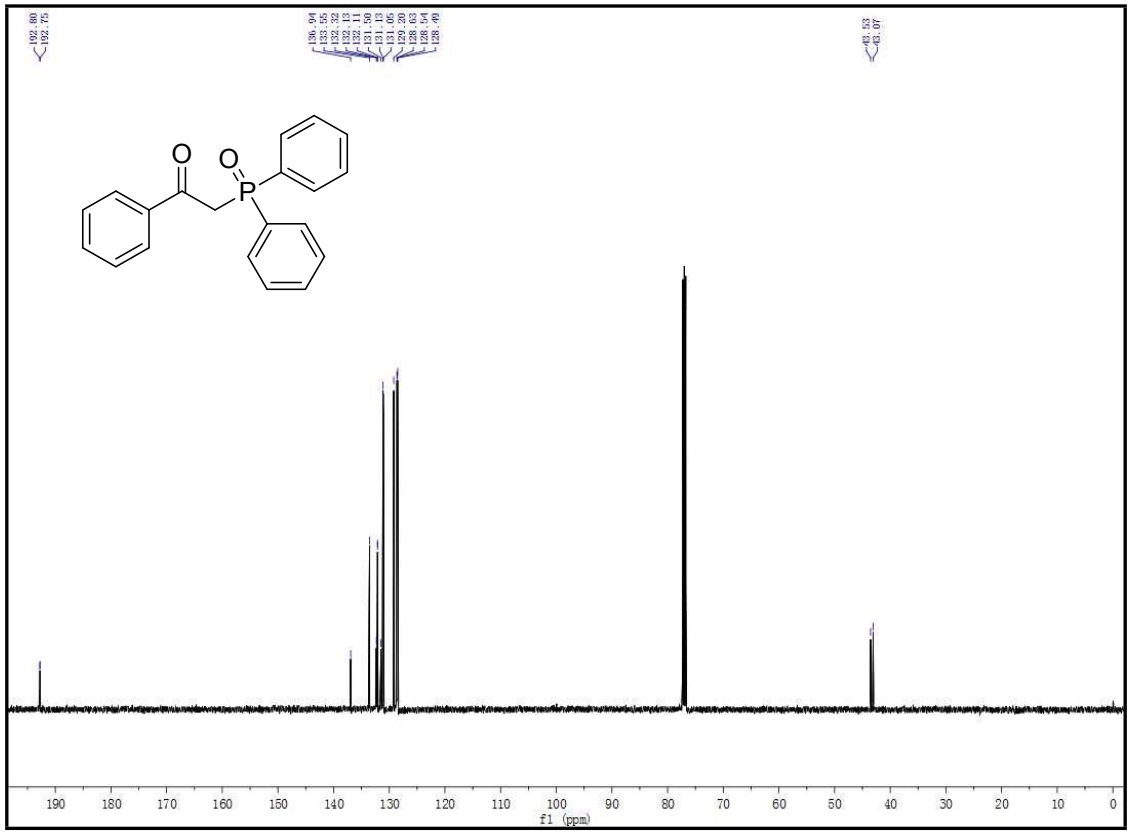



192.10
192.04
138.65
133.45
129.09
128.45
71.50
71.46
40.21
39.17
23.93
23.89
23.73
23.69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

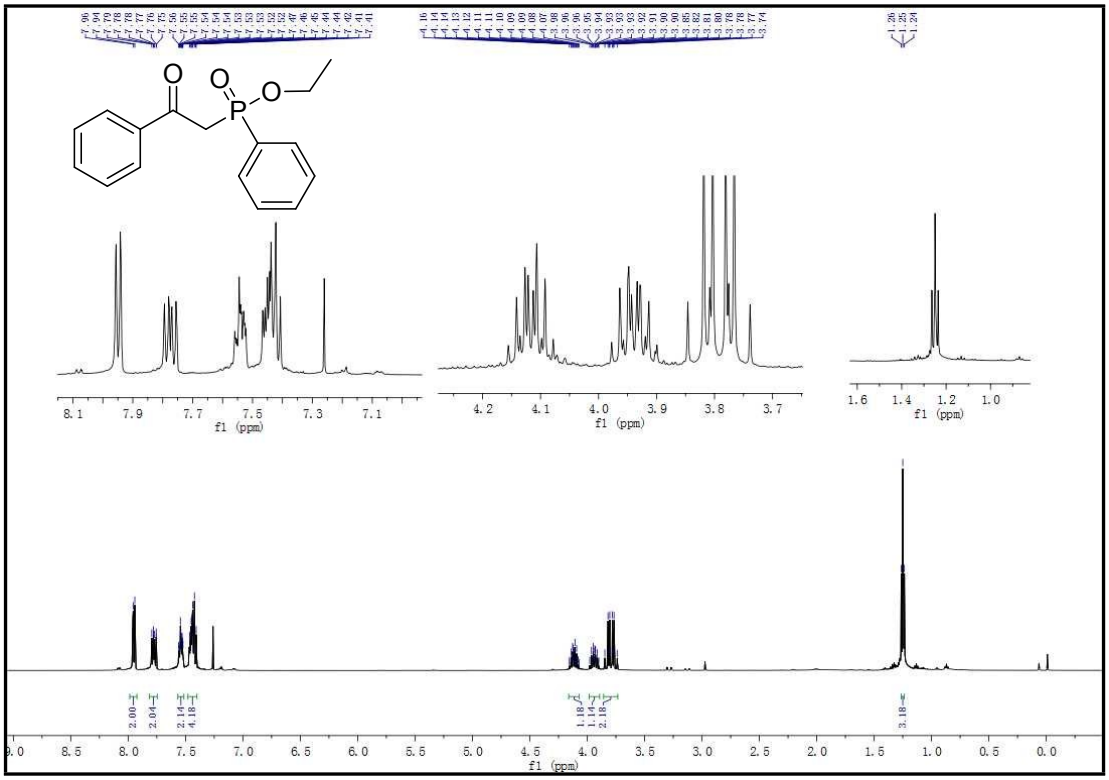

17.72
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

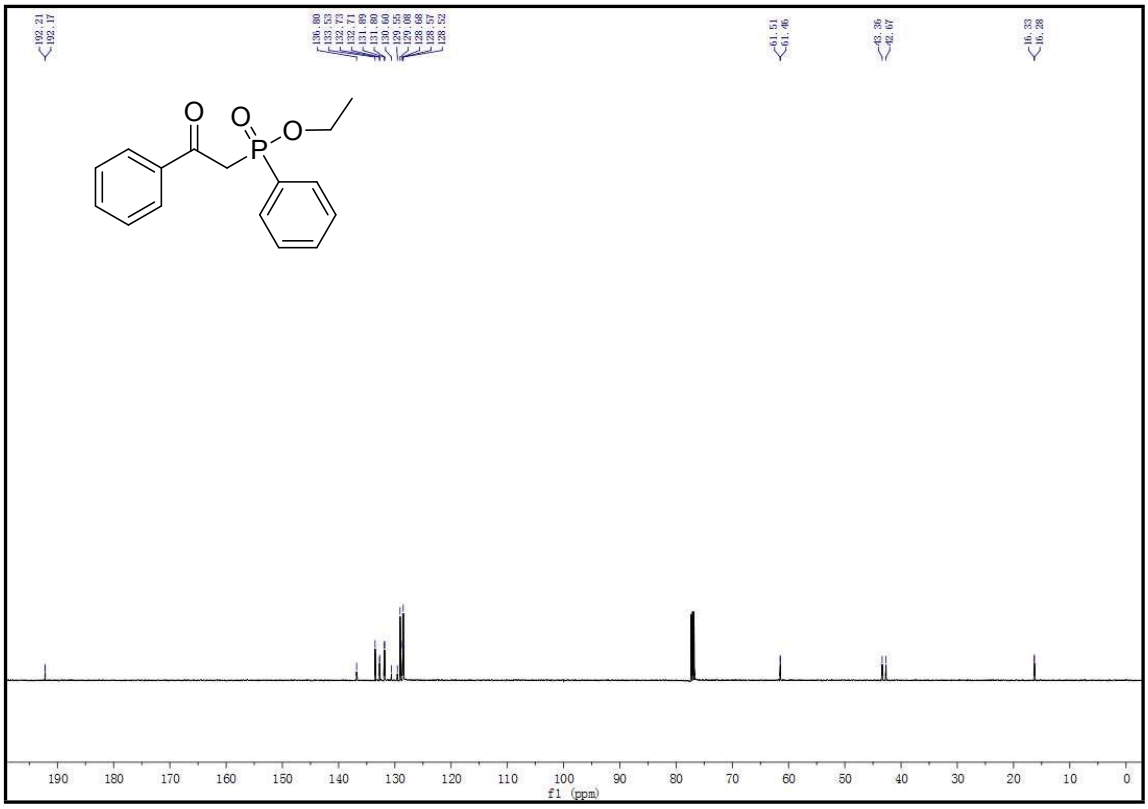
2-(Diphenylphosphoryl)-1-phenylethanone (3ad)

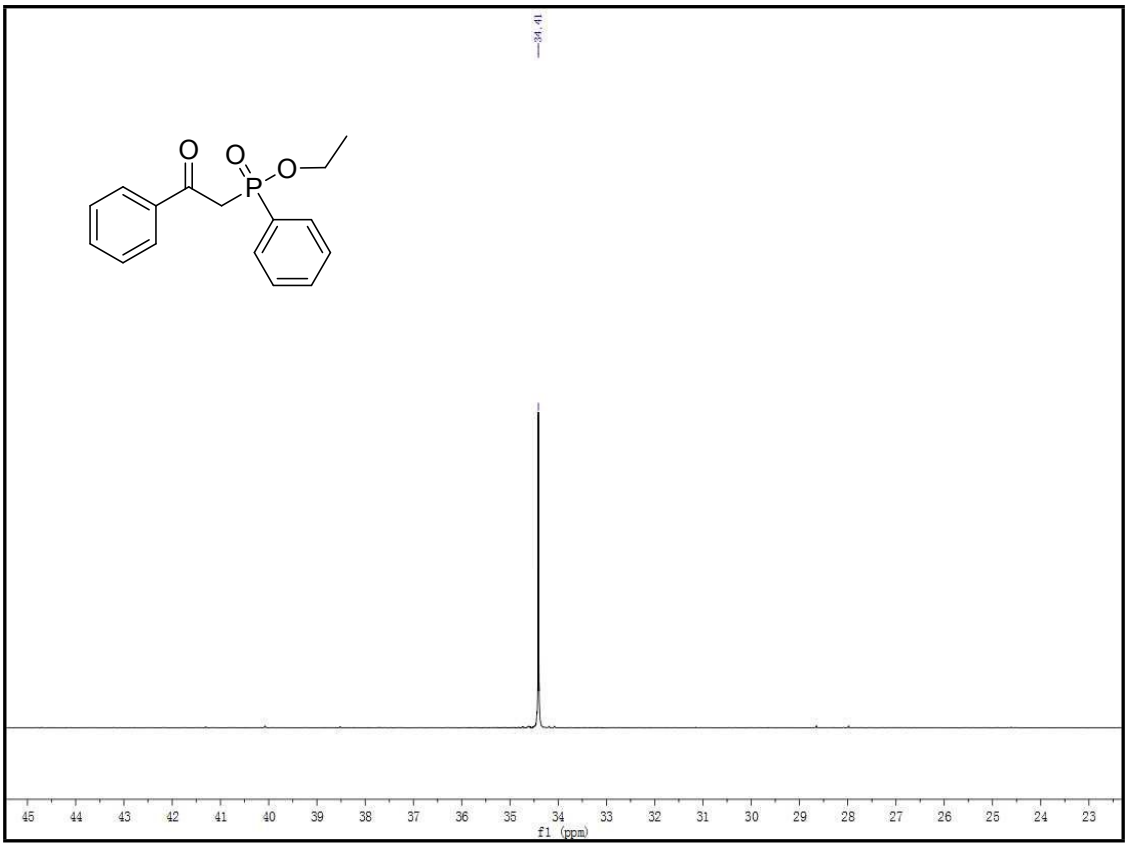




Ethyl (2-oxo-2-phenylethyl)(phenyl) phosphinate (3ae)




192.21
192.17
136.80
133.53
132.73
132.71
131.89
131.80
130.60
129.55
129.08
128.68
128.57
128.52
61.51
61.46
43.36
42.07
16.33
16.28
O
O
P
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


34.41
O
O
P
O
45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23
f1 (ppm)

9. References

1. (a) M. Filice, M. Marciello, M. P. Morales, J. M. Palomo, *Chem. Commun.,* 2013, **49**, 6876; (b) J. Masllorens, M. Moreno-Manas, A. Pia-Quintana A. Roglans, *Org. Lett.,* 2003, **5**, 155
2. Y. Xie, R. Song, X. Yang, J. Xiang, J. Li, *Eur. J. Org. Chem*., 2013, **25**, 5737.
3. X. Pan, J. Zou, G. Zhang, W. Zhang, *Chem. Commun.,* 2010, **46**, 1721.
4. W. Wei, J.-X. Ji, *Angew. Chem., Int. Ed.,* 2011, **50**, 9097.
5. N. Yi, R. Wang, H. Zou, W. He, W. Fu, W. He, *J. Org. Chem.,* 2015, **80**, 5023.
6. M. Zhou, M. Chen, Y. Zhou, K. Yang, J. Su, J. Du, Q. Song, *Org. Lett.,* 2015, **17**, 1786.
7. X. Chen, X. Li, X. Chen, L. Qu, J. Chen, K. Sun, Z. Liu, W. Bi, Y. Xia, H. Wu, Y. Zhao, *Chem. Commun.,* 2015, **51**, 3846..
8. L. Xie, R. Yuan, R. Wang, Z. Peng, J. Xiang, W. He, *Eur. J. Org. Chem*., 2014, **2014**, 2668.
9. W. Debrouwer, T.-S. A. Heugebaert, K.-V. Hecke, C.-V. Stevens, *J. Org. Chem.,* 2013, **78**, 8232