Supporting Information

Iron-catalyzed alkoxyl radical-mediated C-C bond cleavage/phosphorothiolation: A new approach to functionalized *S*-alkyl phosphorothioates

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Table of Contents

1. General Information

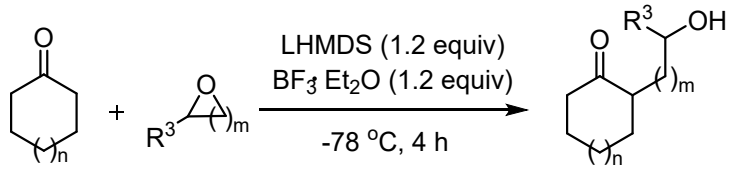
Unless otherwise noted, reagents and solvents were obtained from commercial suppliers and were used without further purification. All catalytic reactions were carried out under nitrogen in Schlenk-tube. Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60F-254. Column chromatography purifications were carried out using silica gel. Melting points were measured using open glass capillaries in a SGW® X-4A apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer at ambient temperature. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were recorded on a Bruker V 70 and only major peaks were reported in cm^{-1}. HRMS were obtained on a WATERS I-Class VION IMS Q-Tof with an ESI source.

2. Starting Materials

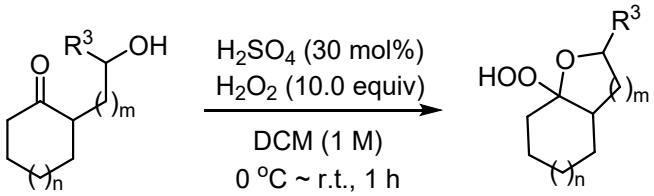
2.1 The Synthesis of Cycloalkyl Hydroperoxides 1

The cycloalkyl hydroperoxides **1a-r** were prepared according to the literature.[1] The NMR spectra of the known compounds were in full accordance with the data in the literature.

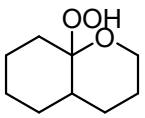
2.2 General Procedure for the Synthesis of Hemiketal Hydroperoxides 4



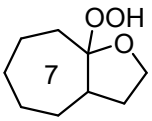
To a stirred solution of LHMDS (1.0 M in THF, 1.2 equiv.) in THF at -78 °C was added cyclic ketone (10 mmol, 1.0 equiv.) over 5 mins. After 1 h, epoxide (2.0 equiv.) was added to the reaction solution. After 1 h, the $BF_3{\cdot}Et_2O$ (1.2 equiv.) was added very slowly. The reaction mixture was stirred for 2 h at -78 °C and the reaction was quenched by the addition of saturated aqueous NH_4Cl solution at -78 °C. Layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Finally, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to obtain the α-hydroxyalkyl ketone.



To a reaction flask was added a solution of H_2O_2 (30% wt in H_2O, 10.0 equiv.), and conc. H_2SO_4 (30 mol%), then a solution of α-hydroxyalkyl ketone (1.0 equiv) in DCM (1.0 M) at 0 °C was added. The reaction mixture was stirred for 1 h at room temperature. The aqueous layer was extracted with DCM, and the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Finally, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1~10:1) to obtain the hemiketal hydroperoxide **4a**-**4g**.



4a



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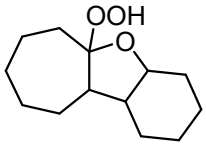

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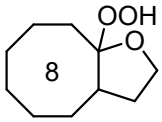

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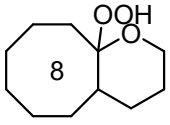
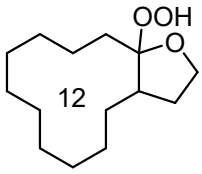
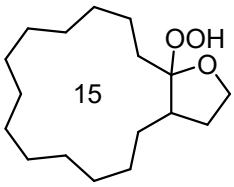


4e

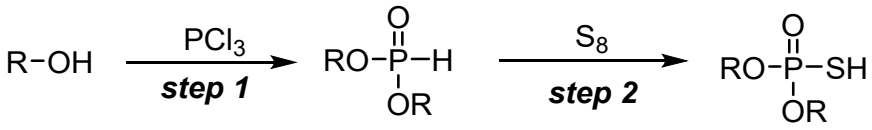


4f



4g

2.3 General Procedure for the Synthesis of *S*-Hydrogen Phosphorothioates[2] 2a-d, 2f.



Step 1

To a solution of the appropriate alcohol (3.0 equiv.) and pyridine (2.0 equiv.) in Et_2O (0.3 M) at 0 °C was added PCl_3 (1.0 equiv.) over the course of 1 h. After complete addition, the reaction mixture was allowed to slowly warm to ambient temperature, and stirred for 16 h. The white suspension was then filtered under suction, and the residual pyridinium chloride was washed twice with Et_2O. The combined filtrates were concentrated in vacuo to yield the desired phosphonates as colorless liquids.

Step 2

To a two-necked round-bottom flask equipped with a reflux condenser and a rubber septum a suspension of the above phosphonate (1.0 equiv.) and solid S_8 (1.1 equiv.) in Et_2O was added under argon. Then, NEt_3 (1.1 equiv.) was added slowly. After full conversion of the phosphonate, as monitored by ^{31}P NMR spectra, the suspension was diluted with Et_2O to 100 mL and then washed with aqueous HCl (100 mL, 1M), dried over $MgSO_4$, and concentrated in vacuo. The resulting suspension was filtered over a small cotton plug to obtain the *S*-hydrogen phosphorothioates **2a-2d** and **2f**.

2.4 General Procedure for the Synthesis of *S*-Hydrogen Phosphorothioate 2e.

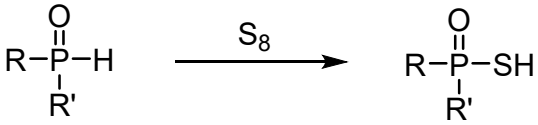
Step 1

To a solution of 4-Chloro-1-butanol (3 equiv.) in DCM (1.5 mL) was added PCl_3 (1.0 equiv.) in DCM (0.5 M) over the course of 1h. Liberated HCl was removed by a constant nitrogen stream. After complete addition, the dropping funnel was washed with additional DCM (20 mL) and the reaction mixture was stirred for 16 h while purging nitrogen to remove all dissolved HCl. The solution was then concentrated in vacuo to yield the desired phosphonate.

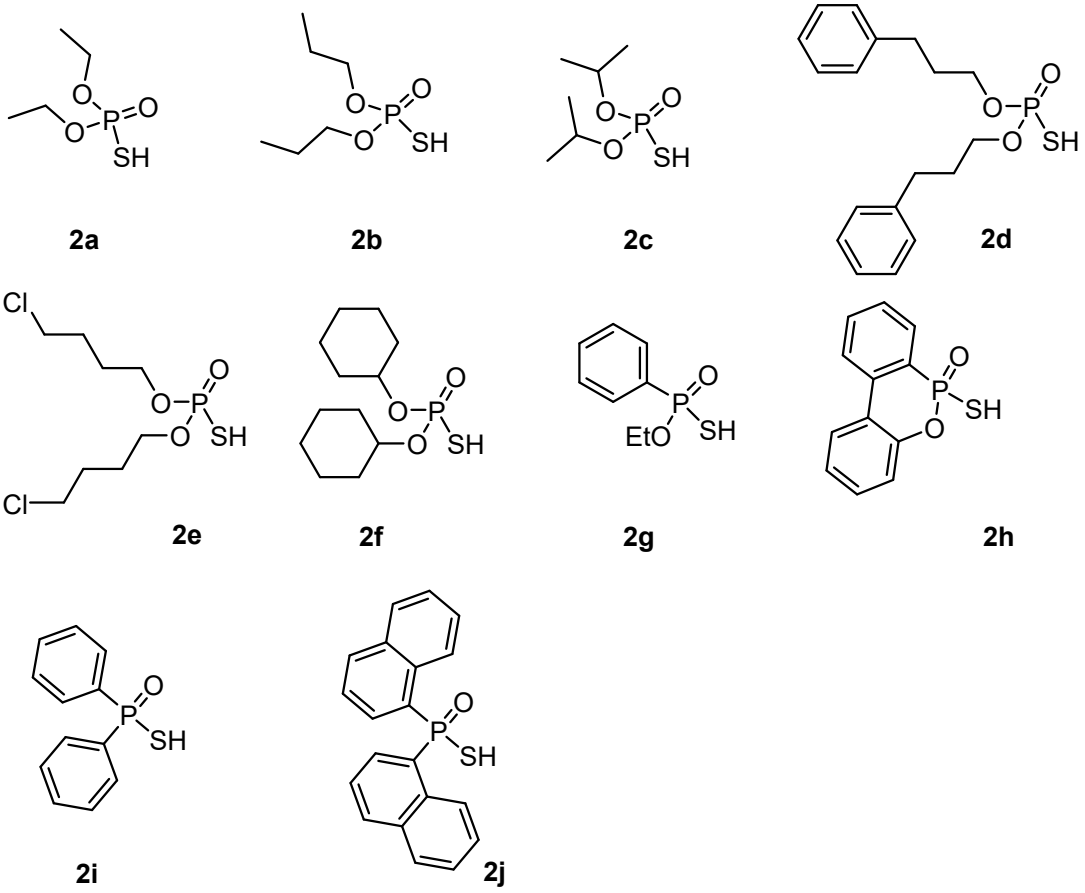
Step 2

To a two-necked round-bottom flask equipped with a reflux condenser and a rubber septum a suspension of the above phosphonate (1.0 equiv.) and solid S_8 (1.1 equiv.) in Et_2O was added under argon. Then, NEt_3 (1.1 equiv.) was added slowly. After full conversion of the phosphonate, as monitored by ^{31}P NMR spectroscopy, the suspension was diluted with Et_2O to 100 mL and then washed with aqueous HCl (100 mL, 1M), dried over $MgSO_4$, and concentrated in vacuo. The resulting suspension was filtered over a small cotton plug to obtain the *S*-hydrogen phosphorothioate **2e**.

2.5 General Procedure for the Synthesis of P(O)SH Compounds 2g-j.



The precursors of P(O)SH compounds **2g-2j** were obtained from commercial suppliers. To a two-necked round-bottom flask equipped with a reflux condenser and a rubber septum a suspension of the above phosphonate (1.0 equiv.) and solid S_8 (1.1 equiv.) in Et_2O was added under argon. Then, NEt_3 (1.1 equiv.) was added slowly. After full conversion of the phosphonate precursors, as monitored by ^{31}P NMR spectra, the suspension was diluted with Et_2O to 100 mL and then washed with aqueous HCl(100 mL, 1 M), dried over $MgSO_4$, concentrated under reduced pressure, and finally dried under vacuum. The resulting suspension was filtered over a small cotton plug to obtain the corresponding P(O)SH compounds **2g-2j**.

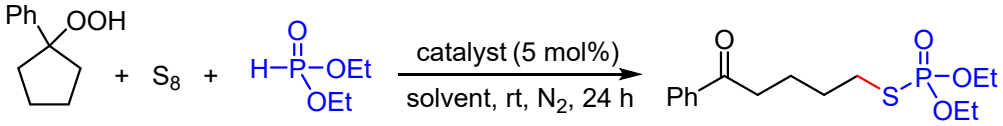


3. Detailed Optimization of Reaction Conditions

3.1 General Procedure for Three-Component Coupling of $HP(O)(OEt)_2$ with S_8 and Cyclopentyl Hydroperoxide 1a

To 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added catalyst and S_8 (0.4 mmol, 2.0 equiv.). Then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl hydroperoxide **1a** (0.2 mmol, 1.0 equiv.) and $HP(O)(OEt)_2$ (0.4 mmol, 2.0 equiv.) in solvent (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at room temperature for schedule time. After the reaction completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the desired product **3aa**.

3.2 Optimization of catalyst and solvent



1a **3aa**

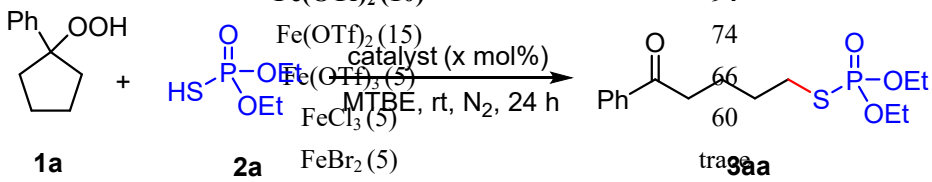
Entry	Catalyst (mol%)	Solvent	Yield[a] (%)
1	CuI (10)	MTBE	27
2	$Cu(OAc)_2$(10)	MTBE	35
3	$Fe(OTf)_3$ (10)	MTBE	10
4	$FeCl_3 \cdot 6H_2O$ (10)	MTBE	20
5	$FeCl_2$ (10)	MTBE	trace
6	$Fe(OTf)_2$ (10)	MTBE	27
7	$Fe(OTf)_2$ (10)	EA	8
8	$Fe(OTf)_2$ (10)	DME	trace
9	$Fe(OTf)_2$ (10)	DCM	13
10	$Fe(OTf)_2$ (10)	toluene	n.r.
11	$Fe(OTf)_2$(10)	MeOH	n.r.

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), $HPO(OEt)_2$ (0.4 mmol, 2.0 equiv.), S_8 (0.4 mmol, 2.0 equiv.), catalyst (10 mol%), and solvent (2.0 mL), rt 24 h, under N_2. Isolated yields.

3.3 General Procedure for Phosphorothiolation of Cyclopentyl Hydroperoxide 1a

A 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added catalyst, then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl hydroperoxide **1a** (0.2 mmol, 1.0 equiv.) and $HSP(O)(OEt)_2$ **2a** (0.4 mmol, 2.0 equiv.) in solvent (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at room temperature for schedule time. After the reaction completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the target product **3aa**.

Entry	Catalyst (mol%)	Yield (%)
1	CuI (5)	64
2	$Cu(OAc)_2$ (5)	60
3	CuOTf (5)	64
4	$Co(acac)_2$(5)	trace
5	$NiCl_2$(5)	n.r.
6	$Fe(OTf)_2$ (5)	71
7	**$Fe(OTf)_2$ (10)**	**94**
8	$Fe(OTf)_2$ (15)	74
9	$Fe(OTf)_3$ (5)	66
10	$FeCl_3$ (5)	60
11	$FeBr_2$ (5)	trace
12	$Fe(OAc)_2$ (5)	57



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

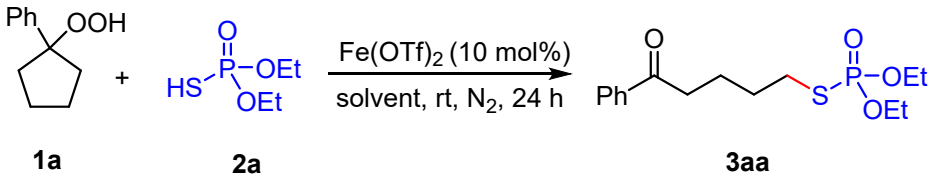
3.4 Optimization of Phosphorothiolation of Cyclopentyl Hydroperoxide 1a

Catalyst and Amount

13	$Fe(acac)_2$ (5)	54

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), catalyst (x mol%), and MTBE (2 mL), rt 24 h, under N_2. Isolated yields.

Solvent

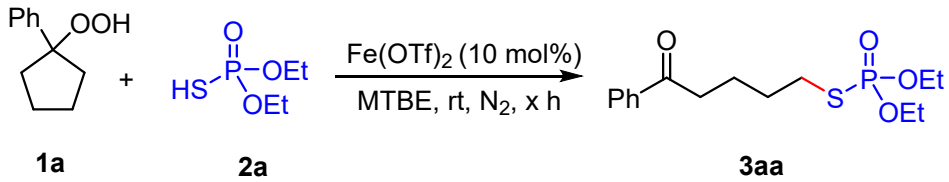


1a **2a** **3aa**

Entry	Solvent	Yield (%)
1	MeCN	44
2	THF	50
3	MTBE	94
4	1,4-dioxane	42
5	EtOH	38
6	EtOAc	85
7	toluene	62
8	DMSO	trace
9	DMF	trace

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Fe(OTf)_2$ (10 mol%), and solvent (2 mL), rt 24 h, under N_2. Isolated yields.

Time and Amount of 2a

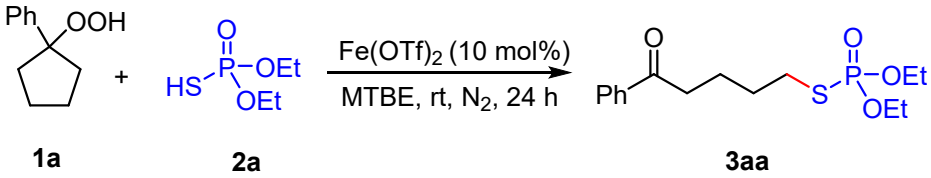


1a **2a** **3aa**

Entry	Time (h)	Yield (%)
1	24	94
2	**12**	**94**
3	6	86
4	12	80[b]

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Fe(OTf)_2$ (10 mol%), and MTBE (2 mL), rt x h, under N_2. Isolated yields. [b]**1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.)

Control Experiments



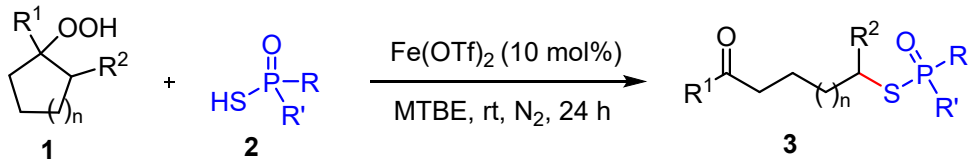
1a **2a** **3aa**

Entry	Variation from standard Conditions	Yield (%)
1	-	94
2	Without $Fe(OTf)_2$, rt	trace
3	Without $Fe(OTf)_2$, 60 °C	17
4	Under air	25

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Fe(OTf)_2$ (10 mol%), and MTBE (2 mL), rt 24 h, under N_2. Isolated yields.

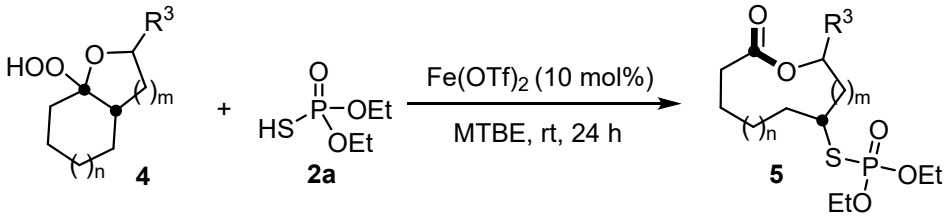
4. Representative Procedures for C-C Bond Cleavage/Phosphorothiolation

4.1 Representative Procedure for Phosphorothiolation of Cycloalkyl Hydroperoxi -des 1 with 2



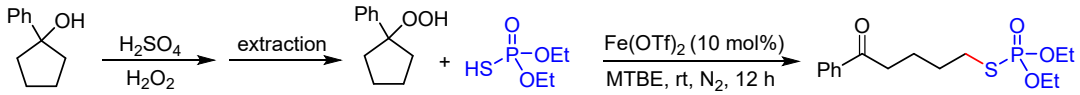
To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added $Fe(OTf)_2$ (0.02 mmol, 10 mol%). Then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cycloalkyl hydroperoxide **1** (0.2 mmol, 1.0 equiv.), and *S*-hydrogen phosphorothioate **2** (0.4 mmol, 2.0 equiv.) in MTBE (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at room temperature for 24 h. After the reaction completed, the organic layer was concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the target products **3**.

4.2 Representative Procedure for Phosphorothiolation of Hemiketal Hydroperox -ides 4 with 2a



To a 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added $Fe(OTf)_2$ (0.02 mmol, 10 mol%). Then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of hemiketal hydroperoxide **4** (0.2 mmol, 1.0 equiv.), and diethyl thiophosphate **2a** (0.4 mmol, 2.0 equiv.) in MTBE (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at room temperature for 24 h. After the reaction completed, the organic layer was concentrated in vacuo, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target products **5**.

4.3 Representative Telescoped Procedure for Phosphorothiolation of Cycloalkanol



1a' *step 1* **1a** **2a** *step 2* **3aa**, 90% total yield

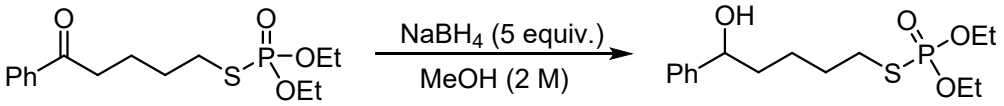
Step 1:

To a 10 mL reaction tube equipped with a magnetic stirrer was added a solution of H_2O_2 (30% wt in H_2O, 10.0 equiv.), and conc. H_2SO_4 (30 mol%). Then a solution of the alcohol **1a'** (0.2 mmol, 1.0 equiv.) in DCM (1.0 M) at 0 °C was added. Then, the reaction mixture was stirred for 1 h from 0 °C to 25 °C. After the reaction completed, it was diluted with DCM (5.0 mL) and H_2O (5.0 mL). The organic layer was separated and the water layer was extracted with DCM (3 × 5 mL). The combined organic layer was washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product **1a** was used in the next step without further purification

Step 2:

The second step procedure was followed the above-mentioned procedure 4.1, using the crude **1a** instead of the purified **1a**. The total yield of **3aa** based on the alcohol **1a'** was given in Scheme 3.

5. Procedures for Derivatizations of 3aa

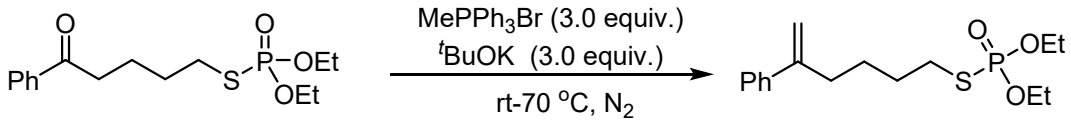


3aa **6aa**, 80%

5.1 Reduction of 3aa

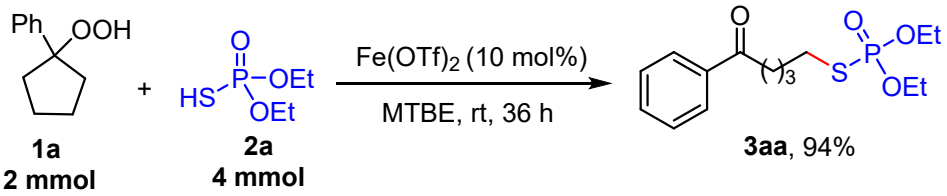
To a 10 mL oven-dried reaction tube equipped with a magnetic stirrer was added a solution of **3aa** (0.2 mmol, 1.0 equiv.) in MeOH (4 mL). Then, $NaBH_4$ (1.0 mmol, 5.0 equiv.) was added slowly at 0 °C. The reaction mixture was stirred until **3aa** completely converted. After that, 20 mL of H_2O was added, and the water layer was extracted with DCM (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Finally, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the target product **6aa** (80%, 51.5 mg).

5.2 Wittig Reaction of 3aa



3aa **7aa**, 82%

To the mixture of ^{t}BuOK (0.3 mmol, 1.5 equiv.) and $MePPh_3Br$ (0.3 mmol, 1.5 equiv.) was added anhydrous THF (1 mL) under nitrogen atmosphere. The suspension was stirred at room temperature for 1 h, and then the **3aa** (0.2 mmol, 1.0 equiv.) was added. The resulting mixture was stirred at 70 °C for 24 h. During the reaction, when the yellow reaction solution fades midway, another amount of ylide solution (prepared with ^{t}BuOK (0.3 mmol, 1.5 equiv.) and $MePPh_3Br$ (0.3 mmol, 1.5 equiv.) in advance) needs to be added under nitrogen atmosphere. Then the mixture was filtered. After evaporation of the organic solvent, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the target product **7aa** (82%, 53.4 mg).

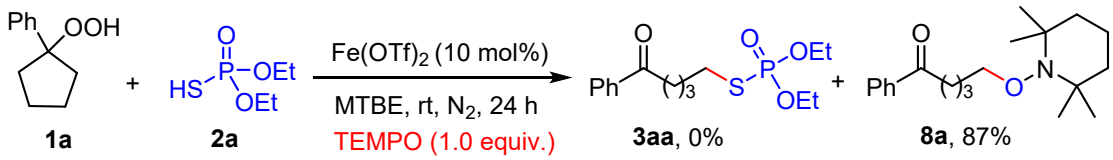


6. Large-Scale Synthesis of 3aa

To 100 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added $Fe(OTf)_2$ (0.2 mmol, 10 mol%), then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of **1a** (2 mmol, 1.0 equiv.) and **2a** (4 mmol, 2.0 equiv.) in MTBE (20.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at room temperature for 36 h. After the reaction completed. The combined organic layer was concentrated in vacuo and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the target product **3aa** in 94% yield (617.8 mg).

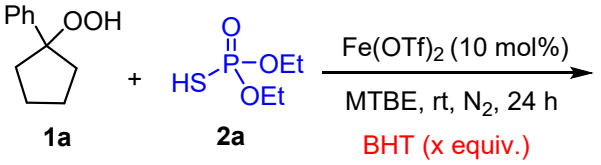
7. Mechanistic Investigation

7.1 Radical Trapping Experiment



To 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added $Fe(OTf)_2$ (0.02 mmol, 10 mol%), and TEMPO (0.2 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl hydroperoxide **1a** (0.2 mmol, 1.0 equiv.) and **2a** (0.4 mmol, 2.0 equiv.) in MTBE (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at room temperature for 24 h. It was found that no **3aa** was detected, along with TEMPO-adduct **8a** isolated in 87% yield. These results indicate that a radical intermediate might be involved in this transformation.

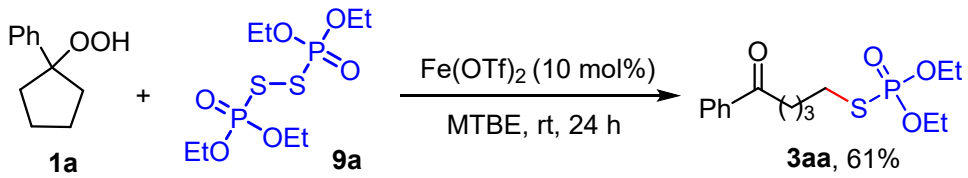
7.2 Radical Inhibiting Experiment



x	Yield of **3aa**
1	88%
2	83%
3	85%

To 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added $Fe(OTf)_2$ (0.02mmol, 10 mol%) and BHT (0.2 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl hydroperoxide **1a** (0.2 mmol, 1.0 equiv.) and **2a** (0.4 mmol, 2.0 equiv.) in MTBE (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and mixture was stirred at room temperature for 24 h. In this case, the product **3a** could be isolated in 88% yield, which is comparable with that in the absence of BHT. Moreover, 2.0 equiv and 3.0 equiv of BHT were added to the reaction of **1a** and **2a**, respectively. It was found that the addition of BHT did not affect the yield of **3aa** obviously.

7.3 Key Intermediate Examination Experiment



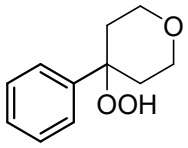
Step 1

To a solution of $HSP(O)(OEt)_2$ **2a** (1.0 equiv.) in MeCN (1 M) was added TBHP (1.0 equiv., 70% aq.) by syringe. Then, the mixture was stirred for 8 h at 60 °C. After the reaction completed, the organic layer was concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the phosphoryl persulfide **9a**.

Step 2

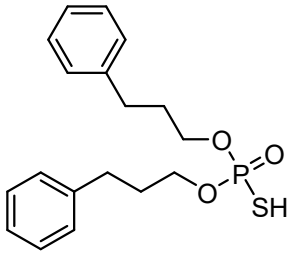
To 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was added $Fe(OTf)_2$ (0.02mmol, 10 mol%). Then the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cycloalkyl hydroperoxide **1a** (0.2 mmol, 1.0 equiv.) and phosphoryl persulfide **9a** (0.4 mmol, 2.0 equiv.) in MTBE (2.0 mL) was added by syringe under nitrogen atmosphere. The tube was then sealed and the mixture was stirred at room temperature for 24 h. After the reaction completed, the organic layer was concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product **3aa** in 61% yield.

8. Characterization of Starting Material 2d



1s

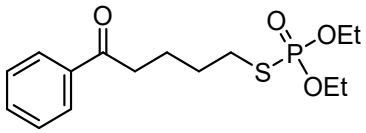
4-Hydroperoxy-4-phenyltetrahydro-2H-pyran (1s) White solid (727.5 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.33 (tt, *J* = 6.4, 1.2 Hz, 2H), 3.91 – 3.78 (m, 4H), 2.15 – 2.10 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 128.9, 81.7, 63.7, 34.0. IR (neat): υ_{max} (cm^{-1}) 3300, 2956, 1603, 1359, 1128, 834, 783. HRMS (ESI) calcd for $C_{18}H_{28}O_3NPS$ $[M+NH_4]^+$ 212.1281, found 212.1275.



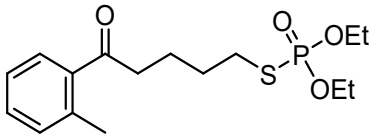
2d

***O,O*-Bis(3-phenylpropyl) *S*-hydrogen phosphorothioate (2d)** Yellow oil (61.8 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 7.22 – 7.17 (m, 6H), 5.16 – 5.13 (m, 1H), 4.14 – 4.11 (t, *J* = 8.0 Hz, 4H), 2.76 – 2.72 (t, *J* = 7.6 Hz, 4H), 2.06 – 2.00 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 128.6, 128.6, 126.2, 67.5 (d, *J* = 5.3 Hz), 31.8 (d, *J* = 3.9 Hz), 31.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 67.0. IR (neat): υ_{max} (cm^{-1}) 3027, 2954, 1603, 1015, 745. HRMS (ESI) calcd for $C_{18}H_{24}O_3PS$ $[M+H]^+$ 351.1178,
found 357.1181.

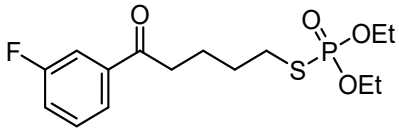
9. Characterizations of Products 3



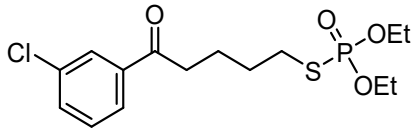
***O,O*-Diethyl *S*-(5-oxo-5-phenylpentyl) phosphorothioate (3aa)** Colorless oil (61.8 mg, 94%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 4.21 – 4.10 (m, 4H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.92 – 2.85 (m, 2H), 1.88 – 1.79 (m, 4H), 1.35 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 137.0, 133.2, 128.7, 128.1, 63.7 (d, *J* = 6.0 Hz), 37.8, 30.8 (d, *J* = 3.9 Hz), 30.5 (d, *J* = 5.4 Hz), 23.1, 16.2 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. IR (neat): υ_{max} (cm^{-1}) 2932, 1721, 1015, 789, 572. HRMS (ESI) calcd for $C_{15}H_{24}O_4PS$ $[M+H]^+$ 331.1127, found 331.1133.



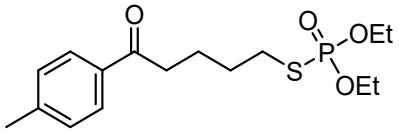
***O,O*-Diethyl *S*-(5-oxo-5-(o-tolyl)pentyl) phosphorothioate (3ba)** Colorless oil (55.2 mg, 80%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$), 7.61 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 6.4 Hz, 1H), 7.25 (t, *J* = 6.8 Hz, 2H), 4.22 – 4.11 (m, 4H), 2.94 – 2.84 (m, 4H), 2.48 (s, 3H), 1.82 – 1.79 (m, 4H), 1.36 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 138.1, 138.0, 132.1, 131.4, 128.5, 125.8, 63.7 (d, *J* = 6.0 Hz), 40.8, 30.8 (d, *J* = 3.9 Hz), 30.5 (d, *J* = 5.4 Hz), 23.3, 21.4, 16.2 (d, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. IR (neat): υmax (cm^{-1}) 2929, 1685, 1455, 1016, 759, 572. HRMS (ESI) calcd for $C_{16}H_{26}O_4PS$ $[M+H]^+$ 345.1284 found 345.1286.



***O,O*-Diethyl *S*-(5-(3-fluorophenyl)-5-oxopentyl) phosphorothioate (3ca)** Colorless oil (62.6 mg, 90%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 9.6 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.25 – 7.22 (m, 1H), 4.20 – 4.01 (m, 4H), 2.97 (t, *J* = 6.4 Hz, 2H), 2.90 – 2.83 (m, 2H), 1.86– 1.75 (m, 4H), 1.36 – 1.32 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4 (d, J_F = 1.9 Hz), 163.0 (d, J_F = 246.4 Hz), 139.0 (d, J_F = 6.0 Hz), 130.4 (d, J_F = 7.6 Hz), 123.8 (d, J_F = 3.0 Hz), 120.2 (d, J_F = 21.4 Hz), 114.8 (d, J_F = 22.0 Hz), 63.6 (d, J_p = 6.0 Hz), 38.0, 30.7 (d, J_p = 3.9 Hz), 30.4 (d, J_p = 5.0 Hz), 22.9, 16.2 (d, J_p = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. IR (neat): υ_{max} (cm^{-1}) 2936, 1687, 1443, 1019, 790, 573. HRMS (ESI) calcd for $C_{15}H_{23}O_4FPS$ $[M+H]^+$ 349.1033, found 349.1037

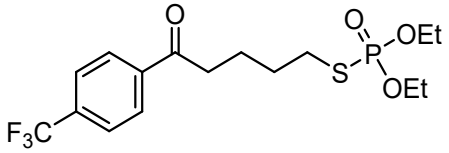


***O,O*-Diethyl *S*-(5-(3-chlorophenyl)-5-oxopentyl) phosphorothioate (3da)** Colorless oil (56.2 mg, 77%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 1.6 Hz, 1H), 7.83 – 7.81 (m 1H), 7.83 – 7.81 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 4.23 – 4.10 (m, 4H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.92 – 2.84 (m, 2H), 1.89 – 1.74 (m, 4H), 1.88 – 1.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 138.4, 135.1, 133.1 130.1, 128.2, 126.2, 63.7 (d, *J* = 5.9 Hz), 38.0, 30.7 (d, *J* = 3.8 Hz), 30.4 (d, *J* = 5.2 Hz), 22.9, 16.2 (d, *J* = 7.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6. IR (neat): υ_{max} (cm^{-1}) 2936, 1687, 1443, 1019, 790, 573. HRMS (ESI) calcd for $C_{15}H_{22}O_4ClPSK$ $[M+K]^+$ 403.0311, found 403.0297.

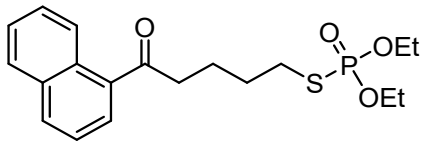


***O,O*-Diethyl *S*-(5-oxo-5-(p-tolyl)pentyl) phosphorothioate (3ea)** Colorless oil (51.1 mg, 74%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 2H), 7.38 – 7.32 (m, 2H), 4.22 – 4.10 (m, 4H), 2.99 (t, *J* = 6.8 Hz, 2H), 2.92 – 2.85 (m, 2H), 2.41(s, 3H), 1.89 – 1.77 (m, 4H), 1.37 – 1.34 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 138.5, 137.0, 134.0, 128.65, 128.62,

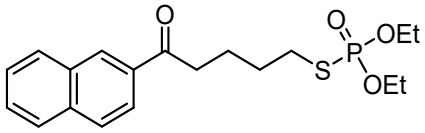
125.4, 63.7 (d, J = 5.8 Hz), 37.9, 30.8 (d, J = 3.8 Hz), 30.5 (d, J = 5.5 Hz), 23.2, 21.5, 16.2 (d, J = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.7. IR (neat): υ_{max} (cm^{-1}) 2927, 1682, 1448, 1019, 967, 787, 574. HRMS (ESI) calcd for $C_{16}H_{26}O_4PS$ $[M+H]^+$ 345.1284, found 345.1291.



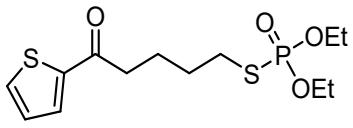
***O,O*-Diethyl *S*-(5-oxo-5-(4-(trifluoromethyl)phenyl)pentyl) phosphorothioate (3fa)** Colorless oil (61.2 mg, 77%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$), 8.04 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 4.20 – 4.09 (m, 4H), 3.02 (t, J = 6.7 Hz, 2H), 2.91 – 2.84 (m, 2H), 1.89 – 1.75 (m, 4H), 1.34 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 139.6, 134.5 (q, J_F = 32.6 Hz), 128.4, 125.8 (q, J_F = 3.7 Hz), 123.7 (q, J_F = 271.1 Hz), 63.7 (d, J_p = 6.1 Hz), 38.1, 30.6 (d, J_p = 3.8 Hz), 30.4 (d, J_p = 5.3 Hz), 22.8, 16.1 (d, J_p = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. IR (neat): υ_{max} (cm^{-1}) 2937, 1692, 1251, 1016, 793, 573. HRMS (ESI) calcd for $C_{16}H_{23}F_3O_4PS$ $[M+H]^+$ 399.1001, found 399.1003.



***O,O*-Diethyl *S*-(5-(naphthalen-1-yl)-5-oxopentyl) phosphorothioate (3ga)** Colorless oil (59.3 mg, 78%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 9.2 Hz, 2H), 7.60 – 7.47 (m, 3H), 4.23 – 4.10 (m, 4H), 3.09 (t, J = 6.8 Hz, 2H), 2.93 – 2.86 (m, 2H), 1.95 – 1.79 (m, 4H), 1.35 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 136.1, 134.1, 132.7, 130.2, 128.6, 128.0, 127.5, 126.6, 125.8, 124.5, 63.7 (d, J = 5.9 Hz), 41.4, 30.8 (d, J =3.8 Hz), 30.5 (d, J = 5.4 Hz), 23.6, 16.2 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1. IR (neat): υ_{max} (cm^{-1}) 2982, 1681, 1245, 1169, 1019, 786, 574. HRMS (ESI) calcd for $C_{19}H_{26}O_4PS$ $[M+H]^+$ 381.1284, found 381.1288.

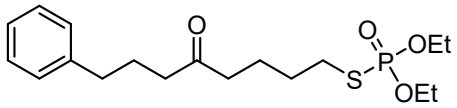


***O,O*-Diethyl *S*-(5-(naphthalen-2-yl)-5-oxopentyl) phosphorothioate (3ha)** Colorless oil (55.5 mg, 73%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.02 – 7.94 (m, 2H), 7.87 (t, J = 8.4 Hz, 2H), 7.61 – 7.52 (m, 2H), 4.21 – 4.10 (m, 4H), 3.13 (t, J = 6.8 Hz, 2H), 2.94 – 2.87 (m, 2H), 1.93 – 1.81 (m, 4H), 1.35 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 135.7, 134.2, 132.6, 129.7,129.6, 128.57, 128.55, 127.9, 126.9, 123.9, 63.7 (d, J = 6.0 Hz), 37.9, 30.8 (d, J = 3.9 Hz), 30.5 (d, J = 5.5 Hz), 23.3, 16.2 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1. IR (neat): υmax (cm^{-1}) 2982, 1679, 1248, 1019, 757, 573. HRMS (ESI) calcd for $C_{19}H_{26}O_4PS$ $[M+H]^+$ 381.1284, found 381.1288.

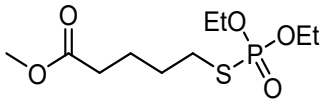


***O,O*-Diethyl *S*-(5-oxo-5-(thiophen-2-yl)pentyl) phosphorothioate (3ia)** Colorless oil (48.4 mg, 72%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 3.2 Hz, 1H),

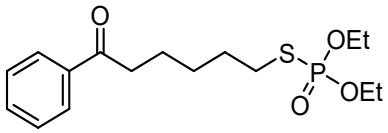
7.63 (d, *J* = 4.8 Hz, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 4.23 – 4.10 (m, 4H), 2.95 – 2.84 (m, 4H), 1.90 – 1.77 (m, 4H), 1.35 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 144.3, 133.7, 132.0, 128.3, 63.7 (d, *J* = 6.0 Hz), 38.6, 30.7 (d, *J* = 3.8 Hz), 30.5 (d, *J* = 5.1 Hz), 23.5, 16.2 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. IR (neat): υmax (cm^{-1}) 2929, 1660, 1162, 1015, 734, 574. HRMS (ESI) calcd for $C_{13}H_{22}O_4PS$ $[M+H]^+$ 337.0692, found 337.0697.



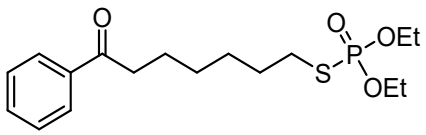
***O,O*-Diethyl *S*-(5-oxo-8-phenyloctyl) phosphorothioate (3ja)** Colorless oil (66.2 mg, 89%). R_f = 0.5 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 3H), 7.29 – 7.24 (m, 2H), 4.30 – 4.19 (m, 4H), 2.92 – 2.89 (m, 2H), 2.72 – 2.68 (m, 2H), 2.51 – 2.47 (m, 4H), 2.02 – 1.90 (m, 2H), 1.76 – 1.75 (m, 4H), 1.46 – 1.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.3, 141.7, 128.6, 128.5, 126.1, 63.7 (d, *J* = 6.1 Hz), 42.1, 42.0, 35.2, 30.7, 30.5, 30.4, 25.3, 22.7, 16.2 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. IR (neat): υmax (cm^{-1}) 2933, 1711, 1163, 1019, 754, 573. HRMS (ESI) calcd for $C_{18}H_{30}O_4PS$ $[M+H]^+$ 373.1597, found 373.1606.



Methyl 5-((diethoxyphosphoryl)thio)pentanoate (3ka) Colorless oil (51.7 mg, 57%). R_f = 0.5 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 – 4.09 (m, 4H), 3.66 (s, 3H), 2.86 – 2.80 (m, 2H), 2.34 – 2.31 (m, 2H), 1.74 – 1.70 (m, 4H), 1.35 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 63.7 (d, *J* = 6.0 Hz), 51.8, 33.5, 30.6 (d, *J* = 3.6 Hz), 30.3 (d, *J* = 5.5 Hz), 23.9, 16.2 (d, *J* = 7.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. IR (neat): υ_{max} (cm^{-1}) 2984, 1737, 1012, 750, 550. HRMS (ESI) calcd for $C_{10}H_{22}O_5PS$ $[M+H]^+$ 285.0920, found 285.0930.

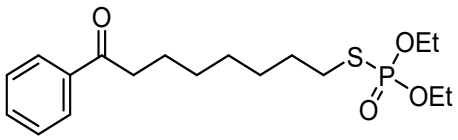


***O,O*-Diethyl *S*-(6-oxo-6-phenylhexyl) phosphorothioate (3la)** Colorless oil (39.3 mg, 57%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.21 – 4.09 (m, 4H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.88 – 2.80 (m, 2H), 1.80 – 1.71 (m, 4H), 1.53 – 1.47 (m, 2H), 1.35 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 137.1, 133.1, 128.7, 128.1, 77.4, 63.6 (d, *J* = 5.9 Hz), 38.4, 30.8 (d, *J* = 5.2 Hz), 28.3, 23.7, 16.2 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2. IR (neat): υ_{max} (cm^{-1}) 2933, 1683, 1019, 966, 759, 573. HRMS (ESI) calcd for $C_{16}H_{26}O_4PS$ $[M+H]^+$ 345.1284 found 345.1289.

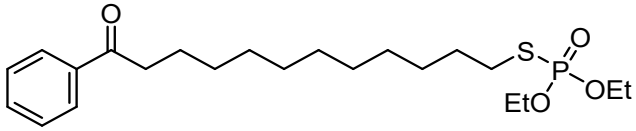


***O,O*-Diethyl *S*-(7-oxo-7-phenylheptyl) phosphorothioate (3ma)** Colorless oil (52.7 mg, 74%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.19 – 4.08 (m, 4H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.85 – 2.77 (m, 2H). 1.76 – 1.65 (m, 4H), 1.43 – 1.38 (m, 4H), 1.33 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 137.0 133.0, 128.7, 128.1, 63.5 (d, *J* = 5.9 Hz), 38.4, 30.9 (d, *J* = 3.9 Hz), 30.7 (d, *J* = 5.7 Hz), 28.8, 28.5, 24.1,

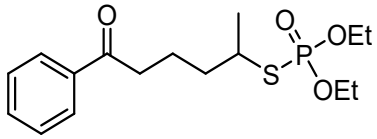
16.2 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2. IR (neat): υ_{max} (cm^{-1}) 2933, 1683, 1019, 966, 756, 572. HRMS (ESI) calcd for $C_{17}H_{28}O_4PS$ $[M+H]^+$ 359.1440, found 359.1444.



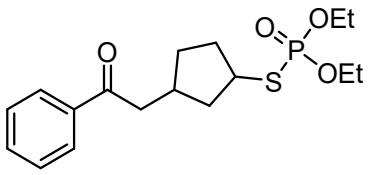
***O,O*-Diethyl *S*-(8-oxo-8-phenyloctyl) phosphorothioate (3na)** Colorless oil (56.5 mg, 76%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 4.18 – 4.12 (m, 4H), 2.96 (t, J = 7.6 Hz, 2H), 2.85 – 2.78 (m, 2H), 1.75 – 1.67 (m, 4H), 1.44 – 1.38 (m, 3H), 1.35 (t, J = 7.6 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 137.1, 133.0, 128.7, 128.1, 63.6 (d, J = 5.8 Hz), 38.6, 31.0 (d, J = 3.7 Hz), 30.8 (d, J = 5.7 Hz), 29.3, 29.0, 28.5, 24.3, 16.2 (d, J = 7.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.3. IR (neat): υ_{max} (cm^{-1}) 2924, 1685, 1249, 1019, 760, 573. HRMS (ESI) calcd for $C_{18}H_{30}O_4PS$ $[M+H]^+$ 373.1597, found 373.1617.



***O,O*-Diethyl *S*-(12-oxo-12-phenyldodecyl) phosphorothioate (3oa)** Colorless oil (70.2 mg, 82%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.57 – 7.52 (m, 1H), 7.48 – 7.44 (m, 2H), 4.23 – 4.08 (m, 4H), 2.96 (t, J = 7.2 Hz, 2H), 2.86 – 2.78 (m, 2H), 1.76 – 1.64 (m, 6H), 1.39 – 1.33 (td, J = 7.2, 0.8 Hz, 12H), 1.27 – 1.26 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 137.1, 133.0, 128.6, 128.1, 68.1, 63.5 (d, J = 5.9 Hz), 38.7, 31.0 (d, J = 3.8 Hz), 30.9 (d, J = 5.7 Hz), 29.55, 29.52, 29.4, 29.1, 28.6, 25.7, 24.4, 16.2 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1. IR (neat): υ_{max} (cm^{-1}) 2926, 1684, 1019, 755, 572. HRMS (ESI) calcd for $C_{22}H_{38}O_4PS$ $[M+H]^+$ 429.2223, found 429.2234.

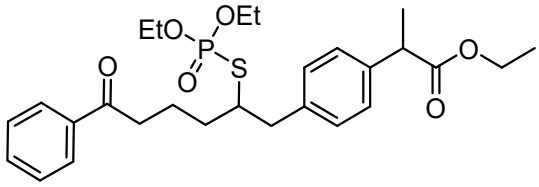


***O,O*-Diethyl *S*-(6-oxo-6-phenylhexan-2-yl) phosphorothioate (3pa)** Colorless oil (64.0 mg, 93%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.94 (m, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.2 Hz, 2H), 4.22 – 4.07 (m, 4H), 3.43 – 3.35 (m, 1H), 3.00 (td, J = 7.2, 2.4 Hz, 2H), 1.92 – 1.86 (m, 2H), 1.80 – 1.71 (m, 2H), 1.46 (d, J = 6.8 Hz, 3H), 1.34 (td, J = 6.8, 2.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 137.0, 133.2, 128.7, 128.1, 63.6 (d, J = 3.4 Hz), 42.9 (d, J = 3.6 Hz), 38.04, 37.97, 23.6 (d, J = 4.6 Hz), 21.6, 16.2 (d, J = 7.3 Hz). δ ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.4. IR (neat): υmax (cm^{-1}) 2928, 1684, 1019, 752, 575. HRMS (ESI) calcd for $C_{16}H_{26}O_4PS$ $[M+H]^+$ 345.1284, found 345.1291.

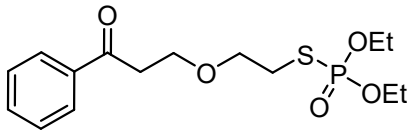


***O,O*-Diethyl *S*-(3-(2-oxo-2-phenylethyl)cyclopentyl) phosphorothioate (3qa)** Colorless oil (57.0 mg,

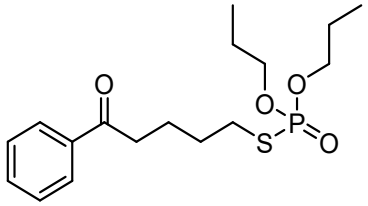
80%, 1:1 dr). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 6.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.20 – 4.09 (m, 4H), 3.67 – 3.58 (m, 0.5 H), 3.54 – 3.44 (m, 0.5 H), 3.06 (d, *J* = 6.0 Hz, 1H), 3.01 (d, *J* = 6.8 Hz, 1H), 2.75 – 2.68 (m, 0.5H), 2.54 – 2.46 (m, 1H), 2.23 – 1.58 (m, 5.5H), 1.35 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 137.11, 137.08, 133.20, 133.19, 128.7, 128.2, 128.1, 63.62 (d, *J* = 2.5 Hz), 63.57 (d, *J* = 2.9 Hz), 44.9, 44.6, 44.0 (d, *J* = 3.4 Hz), 43.7 (d, *J* = 3.5 Hz), 42.3 (d, *J* = 7.0 Hz), 41.5 (d, 6.3 Hz), 35.5 (d, *J* = 7.1 Hz), 35.1, 34.7 (d, *J* = 6.3 Hz), 34.1, 32.0, 31.2, 16.2 (d, *J* = 7.2 Hz). δ ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.2, 27.0. IR (neat): υmax (cm^{-1}) 2979, 1683, 1016, 754, 574. HRMS (ESI) calcd for $C_{27}H_{26}O_4PS$ $[M+H]^+$ 357.1284, found 357.1289.



Ethyl 2-(4-(2-((diethoxyphosphoryl)thio)-6-oxo-6-phenylhexyl)phenyl)propanoate (3ra) Colorless oil (72.8 mg, 70%, 1:1 dr). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.55 (tt, *J* = 7.6, 0.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.20 (q, *J* = 9.6 Hz, 4H), 4.16 – 4.05 (m, 3H), 4.01 – 3.91 (m, 3H), 3.71 (q, *J* = 7.2 Hz, 1H), 3.54 – 3.64 (m, 1H), 3.05 – 2.91 (m, 4H), 2.07 – 1.97 (m, 1H), 1.87 – 1.72 (m, 3H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.28 (dt, *J* = 11.2, 6.8 Hz, 6H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 174.7, 139.1, 137.5, 137.0, 133.1, 129.8, 128.7, 128.1, 127.6, 63.6 (d, *J* = 6.4 Hz), 63.5 (d, *J* = 2.6 Hz), 60.8, 49.5 (d, *J* = 3.5 Hz), 45.3, 42.7 (d, *J* = 1.4 Hz), 38.2, 35.2 (d, *J* = 3.4 Hz), 21.3, 18.8 (d, *J* = 2.9 Hz), 16.2 (d, *J* = 4.1 Hz), 16.1 (d, *J* = 3.7 Hz),14.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. IR (neat): υmax (cm^{-1}) 2935, 1730, 1685, 1164, 1017, 792, 571. HRMS (ESI) calcd for $C_{27}H_{38}O_6PS$ $[M+H]^+$ 521.2121, found 521.2127.

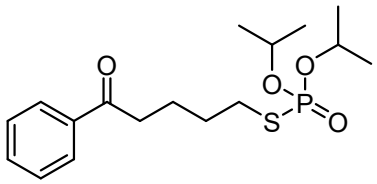


***O,O*-Diethyl *S*-(2-(3-oxo-3-phenylpropoxy)ethyl) phosphorothioate (3sa)** Colorless oil (38.8 mg, 56%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.22 – 4.07 (m, 4H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 3.23 (t, *J* = 6.4 Hz, 2H), 3.01 – 2.94 (m, 2H), 1.33 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 136.9, 133.3, 128.7, 128.2, 70.4 (d, *J* = 4.7 Hz), 66.3, 63.7(d, *J* = 5.9 Hz), 38.7, 30.3 (d, *J* = 3.7 Hz), 16.1 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2. IR (neat): υmax (cm^{-1}) 2983, 1683, 1249, 1110, 964, 789, 570. HRMS (ESI) calcd for $C_5H_{23}O_5PSNa$ $[M+Na]^+$ 369.0896, found 369.0907.

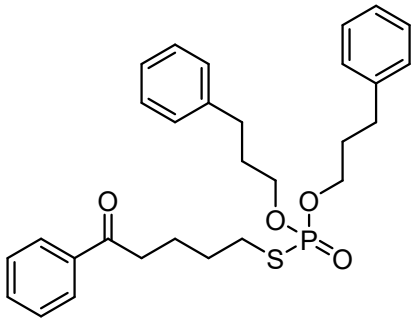


***S*-(5-Oxo-5-phenylpentyl) *O,O*-dipropyl phosphorothioate (3ab)** Colorless oil (58.0 mg, 81%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.56 (tt, *J* = 6.4, 1.2 Hz, 1H), 7.46 (tt, *J* = 7.6, 1.6 Hz, 2H), 4.11 – 3.98 (m, 4H), 3.01 (t, *J* = 6.8 Hz, 2H),

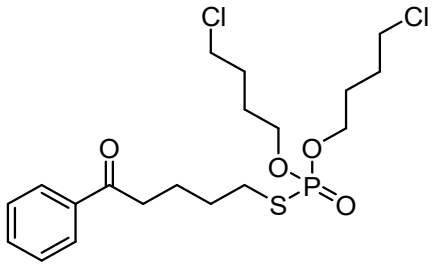
2.92 – 2.85 (m, 2H), 1.85 – 1.80 (m, 2H), 1.75 – 1.70 (m, 4H), 1.28 – 1.22 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 137.0, 133.2, 128.8, 128.2, 69.2 (d, *J* = 6.4 Hz), 37.9, 30.7 (d, *J* = 3.9 Hz), 30.6 (d, *J* = 5.4 Hz), 23.7 (d, *J* = 7.2 Hz), 23.2, 10.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2. IR (neat): υmax (cm^{-1}) 2925, 1685, 1247, 733, 574. HRMS (ESI) calcd for $C_{17}H_{27}O_4PSNa$ $[M+Na]^+$ 381.1260, found 381.1265.



***O,O*-Diisopropyl *S*-(5-oxo-5-phenylpentyl) phosphorothioate (3ac)** Colorless oil (54.4 mg, 76%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.77 – 4.79 (m, 2H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.92 – 2.85 (m, 2H), 1.88 – 1.78 (m, 4H), 1.37-1.33 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 136.9, 133.2, 128.8, 128.1, 72.7 (d, *J* = 6.3 Hz), 37.9, 30.9 (d, *J* = 3.9 Hz), 30.4 (d, *J* = 6.0 Hz), 24.0 (d, *J* = 4.0 Hz), 23.8 (d, *J* = 5.4 Hz), 23.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.5. IR (neat): υ_{max} (cm^{-1}) 2929, 1685, 1104, 769, 609. HRMS (ESI) calcd for $C_{17}H_{28}O_4PS$ $[M+H]^+$ 359.1440, found 359.1450.

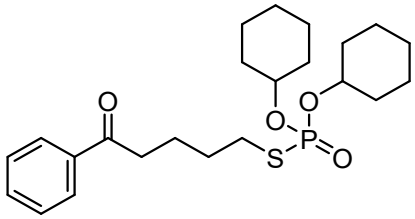


***S*-(5-Oxo-5-phenylpentyl) *O,O*-bis(3-phenylpropyl) phosphorothioate (3ad)** Colorless oil (85.7 mg, 84%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.56 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.30 – 7.26 (m, 4H), 7.20 – 7.17 (m, 6H), 4.18 – 4.04 (m, 4H), 2.99 (t, *J* = 6.4 Hz, 2H), 2.94 – 2.87 (m, 2H), 2.73 (t, *J* = 7.2 Hz, 4H), 2.07 – 1.99 (m, 4H), 1.90 – 1.77 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 141.0, 136.9, 133.2, 128.7, 128.56, 128.55, 128.1, 126.2, 66.9 (d, *J* = 6.4 Hz), 53.6, 37.8, 31.8, 30.8 (d, *J* = 3.7 Hz), 30.6 (d, *J* = 5.2 Hz), 23.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. IR (neat): υ_{max} (cm^{-1}) 2949, 1684, 1006, 796, 748, 573. HRMS (ESI) calcd for $C_{29}H_{35}O_4PSNa$ $[M+Na]^+$ 511.2066, found 511.2074.

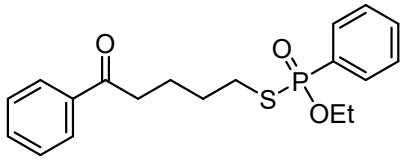


***O,O*-Bis(4-chlorobutyl) *S*-(5-oxo-5-phenylpentyl) phosphorothioate (3ae)** Colorless oil (57.2 mg, 63%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 4.18 – 4.05 (m, 4H), 3.57 (t, *J* =6.0 Hz, 4H), 3.0 (d, *J* = 6.8 Hz, 2H), 2.92 – 2.85 (m, 2H), 1.97 – 1.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 136.9,

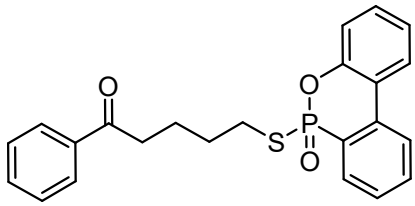
133.2, 128.8, 128.1, 77.4, 66.7 (d, J = 6.1 Hz), 44.5, 37.8, 30.9 (d, J = 3.8 Hz), 30.6 (d, J = 5.2 Hz), 28.8, 27.6 (d, J = 7.2 Hz), 23.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0. IR (neat): υ_{max} (cm^{-1}) 2956, 1683, 1180, 846, 736, 574. HRMS (ESI) calcd for $C_{19}H_{30}Cl_2O_4PS$ $[M+H]^+$ 455.0974, found 455.0982.



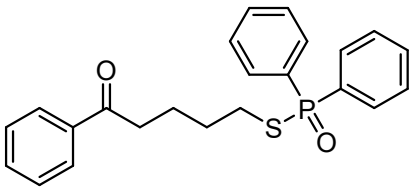
***O,O*-Dicyclohexyl *S*-(5-oxo-5-phenylpentyl) phosphorothioate (3af)** Colorless oil (67.4 mg, 77%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.0, 0.8 Hz, 2H), 7.56 (tt, J = 6.8, 1.2 Hz, 1H), 7.46 (tt, J =8.0, 1.2 Hz, 2H), 4.49 – 4.40 (m, 2H), 3.00 (t, J = 6.4 Hz, 2H), 2.92 – 2.85 (m, 2H), 1.98 – 1.92 (m, 4H), 1.86 – 1.80 (m, 3H), 1.75 – 1.73 (m, 4H), 1.61 – 1.47 (m, 6H), 1.39 – 1.19 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 137.0, 133.2, 128.7, 128.1, 37.9, 33.7 (d, J = 3.6 Hz), 33.5 (d, J = 4.7 Hz), 30.9 (d, J = 3.8 Hz), 30.4 (d, J = 6.0 Hz), 25.3, 23.7, 23.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.5. IR (neat): υ_{max} (cm^{-1}) 2933, 1686, 1250, 790, 609. HRMS (ESI) calcd for $C_{23}H_{35}O_4PSNa$ $[M+Na]^+$ 461.1886, found 461.1894.



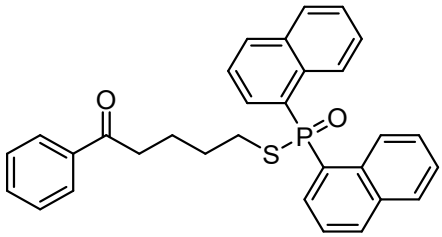
***O*-Ethyl *S*-(5-oxo-5-phenylpentyl) phenylphosphonothioate (3ag)** Colorless oil (55.0 mg, 76%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H), 7.57 – 7.43 (m, 6H), 4.28 – 4.21 (m, 2H), 2.91 (t, J = 1.6 Hz, 2H), 2.82 – 2.75 (m, 2H), 1.80 – 1.64 (m, 4H), 1.39 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 136.9, 133.2, 132.6 (d, J = 2.1 Hz), 131.3, 131.2, 128.7, 128.6, 128.1, 62.3 (d, J = 6.6 Hz), 37.8, 30.3 (d, J = 3.2 Hz), 30.2 (d, J = 1.7 Hz), 23.0, 16.5 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.2. IR (neat): υ_{max} (cm^{-1}) 2932, 1683, 1022, 749, 597. HRMS (ESI) calcd for $C_{19}H_{23}O_3PSNa$ $[M+Na]^+$ 385.0998, found 385.1007.



5-((6-Oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)thio)-1-phenylpentan-1-one (3ah) Colorless oil (35.1 mg, 43%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.90 (m, 5H), 7.70 (tt, J = 7.6, 1.2 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 7.29 – 7.28 (m, 1H), 7.25 – 7.21 (m, 1H), 2.97 – 2.87 (m, 4H), 1.79 – 1.76 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 149.6 (d, J = 9.3 Hz), 136.9, 136.2 (d, J = 7.5 Hz), 133.9 (d, J = 1.8 Hz), 133.2, 130.9, 130.6 (d, J = 10.8 Hz), 128.8, 128.7, 128.1, 126.6, 125.3, 125.1, 124.0 (d, J = 11.0 Hz), 122.4 (d, J = 12.1 Hz), 120.6 (d, J = 6.6 Hz), 37.7, 30.5 (d, J = 4.6 Hz), 29.9 (d, J = 3.2 Hz), 23.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.9. IR (neat): υ_{max} (cm^{-1}) 2925, 1682, 1234, 1116, 755, 578. HRMS (ESI) calcd for $C_{23}H_{21}O_3PSNa$ $[M+Na]^+$ 431.0841, found 431.0849.

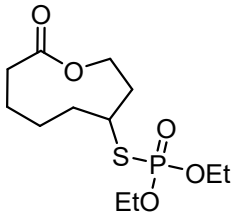


***S*-(5-Oxo-5-phenylpentyl) diphenylphosphinothioate (3ai)** Colorless oil (35.5 mg, 45%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 6H), 7.56 – 7.42 (m, 9H), 2.91 – 2.81 (m, 4H), 1.80 – 1.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 136.9, 133.1, 132.4 (d, *J* = 2.9 Hz), 131.6, 131.5, 128.9, 128.7 (d, *J* = 5.1 Hz), 128.1, 37.7, 30.2 (d, *J* = 4.6 Hz), 29.2 (d, *J* = 1.7 Hz), 23.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.5. IR (neat): υ_{max} (cm^{-1}) 2927, 1683, 1288, 1114, 723, 568. HRMS (ESI) calcd for $C_{23}H_{23}O_2PSNa$ $[M+Na]^+$ 417.1049, found 417.1057.

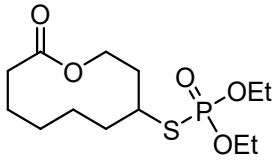


***S*-(5-Oxo-5-phenylpentyl) di(naphthalen-1-yl)phosphinothioate (3aj)** Colorless oil (41.5 mg, 42%). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 – 8.83 (m, 2H), 8.11 – 8.01 (m, 4H), 7.92 – 7.87 (m, 4H), 7.54 – 7.44 (m, 9H), 3.11 – 3.04 (m, 2H), 2.93 – 2.89 (m, 2H), 1.84 – 1.80 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 136.9, 134.1 (d, *J* = 9.9 Hz), 133.9, 133.3 (d, *J* = 12.3 Hz), 133.2, 133.1, 130.1, 129.0, 128.7, 128.1, 127.5, 127.1 (d, *J* = 4.6 Hz), 126.7, 124.6 (d, *J* = 5.2 Hz), 37.8, 30.3 (d, *J* = 4.3 Hz), 29.9 (d, *J* = 1.2 Hz), 23.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.2. IR (neat): υ_{max} (cm^{-1}) 2928, 1682, 1268, 1025, 735, 573. HRMS (ESI) calcd for $C_{31}H_{28}O_2PS$ $[M+H]^+$ 495.1542, found 495.1548.

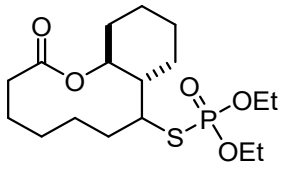
10. Characterizations of Products 5



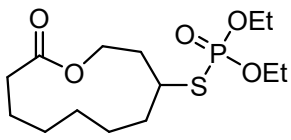
***O,O*-Diethyl *S*-(9-oxooxonan-4-yl) phosphorothioate (5aa)** Colorless oil (25.4 mg, 41%). R_f = 0.3 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 – 4.27 (m, 2H), 4.20 – 4.07 (m, 4H), 3.52 – 3.46 (m, 1H), 2.34 – 2.23 (m, 3H), 2.19 – 2.11 (m, 1H), 1.82 – 1.77 (m, 3H), 1.72 – 1.60 (m, 3H), 1.34 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 63.8 (d, *J* = 3.6 Hz), 63.7 (d, *J* = 3.7 Hz), 62.6, 43.9 (d, *J* = 3.8 Hz), 35.2 (d, *J* = 5.7 Hz), 34.1, 24.4, 21.7, 16.2 (d, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.0. IR (neat): υ_{max} (cm^{-1}) 2928, 1731, 1444, 1013, 793. HRMS (ESI) calcd for $C_{12}H_{23}O_5PSNa$ $[M+Na]^+$ 333.0896, found 333.0908.



***O,O*-Diethyl *S*-(10-oxooxecan-4-yl) phosphorothioate (5ba)** Colorless oil (44.7 mg, 69%). R_f = 0.3 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 – 4.40 (m, 1H), 4.30 – 4.26 (m, 1H), 4.19 – 4.06 (m, 4H), 3.63 – 3.56 (m, 1H), 2.36 – 2.28 (m, 3H), 2.12 – 1.98 (m, 2H), 1.89 – 1.77 (m, 4H), 1.57 – 1.45 (m, 3H), 1.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 63.8 (d, *J* = 3.7 Hz), 63.7 (d, *J* = 3.7 Hz), 62.6, 45.7 (d, *J* = 3.4 Hz), 34.8, 32.2 (d, *J* = 7.5 Hz), 31.0 (d, *J* = 3.8 Hz), 27.3, 20.8, 20.5, 16.2 (d, *J* = 7.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.2. IR (neat): υmax (cm^{-1}) 3454, 2958, 1445, 1016, 970, 790. HRMS (ESI) calcd for $C_{13}H_{26}O_5PS$ $[M+H]^+$ 325.1233, found 325.1241.

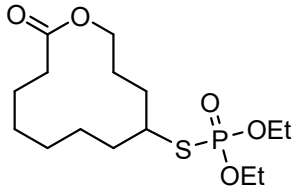


***O,O*-Diethyl *S*-((8aS,12aS)-2-oxododecahydro-2H-benzo[b]oxecin-8-yl) phosphorothioate (5ca)** Colorless oil (44.7 mg, 69%, 37:4:1 dr). R_f = 0.3 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 – 4.49 (m, 1H), 4.20 – 4.02 (m, 4H), 3.06 – 2.78 (m, 1H), 2.50 – 2.44 (m, 1H), 2.40 – 2.44 (m, 1H), 2.28 – 2.21 (m, 1H), 2.04 – 1.98 (m, 2H), 1.92 – 1.85 (m, 1H), 1.75 – 1.60 (m, 7H), 1.51 – 1.47 (m, 1H), 1.32 (td, *J* = 7.2, 0.4 Hz, 6H), 1.30 – 1.08 (m, 4H), 1.06 – 0.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 63.6 (d, *J* = 6.5 Hz), 63.5 (d, *J* = 6.6 Hz), 53.5 (d, *J* = 2.9 Hz), 45.8 (d, *J* = 5.8 Hz), 35.0, 34.5, 33.0, 32.1, 26.6, 25.5, 24.7, 23.3, 21.9, 16.2 (d, *J* =7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3, 28.8, 28.5. IR (neat): υ_{max} (cm^{-1}) 2933, 2860, 1449, 1154, 1017, 754. HRMS (ESI) calcd for $C_{17}H_{32}O_5PS$ $[M+H]^+$ 379.1703, found 379.1708.

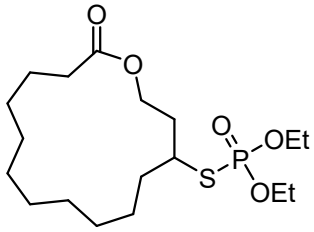


***O,O*-Diethyl *S*-(11-oxooxacycloundecan-4-yl) phosphorothioate (5da)** Colorless oil (37.9 mg, 56%).

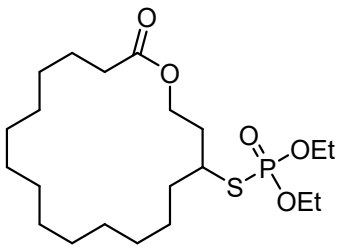
R_f = 0.3 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 – 4.06 (m, 6H), 3.55 – 3.45 (m, 1H), 2.35 – 2.27 (m, 3H), 2.20 – 2.11 (m, 2H), 1.77 – 1.57 (m, 4H), 1.53 – 1.47 (m, 2H), 1.42 – 1.31 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 63.8, 63.7 (d, *J* = 5.4 Hz), 62.1, 45.1 (d, *J* = 3.4 Hz), 35.3, 33.2 (d, *J* = 4.1 Hz), 32.4 (d, *J* = 7.5 Hz), 25.7, 24.6, 21.4, 20.6, 16.1 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.1. IR (neat): υ_{max} (cm^{-1}) 2935, 1730, 1443, 1156, 1016, 760. HRMS (ESI) calcd for $C_{14}H_{27}O_5PSNa$ $[M+Na]^+$ 361.1209, found 361.1214.



***O,O*-Diethyl *S*-(12-oxooxacyclododecan-4-yl) phosphorothioate(5ea)** Colorless oil (19.4 mg, 27%). R_f = 0.3 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 – 4.48 (m, 1H), 4.22 – 4.11 (m, 4H), 4.01 – 3.95 (m, 1H), 3.57 – 3.49 (m, 1H), 2.46 – 2.31(m, 2H), 2.04 – 1.94 (m, 2H), 1.82 – 1.71 (m, 5H), 1.64 – 1.53 (m, 3H), 1.47 – 1.43 (m, 2H), 1.36 (t, *J* =6.8 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 64.2, 63.6 (d, *J* = 5.7 Hz), 44.7 (d, *J* = 3.5 Hz), 34.1, 33.3 (d, *J* = 3.7 Hz), 31.0 (d, *J* = 6.9 Hz), 25.3, 24.7, 24.0, 23.6, 22.7,16.2 (d, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5. IR (neat): υ_{max} (cm^{-1}) 2939, 1732, 1447, 1145, 1017, 791. HRMS (ESI) calcd for $C_{15}H_{29}O_5PSLi$ $[M+Li]^+$ 359.1628, found 359.1629.



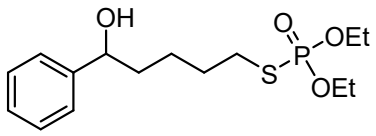
***O,O*-Diethyl *S*-(15-oxooxacyclopentadecan-4-yl) phosphorothioate (5fa)** Colorless oil (37.8 mg, 48%). R_f = 0.3 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 – 4.27 (m, 1H), 4.20 – 4.08 (m, 5H), 3.37 – 3.29 (m, 1H), 2.35 – 2.31 (m, 2H), 2.15 – 2.04 (m, 3H), 1.83 – 1.76 (m, 1H), 1.68 – 1.61 (m, 3H), 1.59 – 1.42 (m, 3H), 1.34 (td, *J* = 7.2, 0.8 Hz, 6H), 1.33 – 1.29 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 63.7 (d, *J* = 2.6 Hz), 63.6 (d, *J* = 3.0 Hz), 61.9, 44.6 (d, *J* = 3.7 Hz), 35.9 (d, *J* = 3.9 Hz), 34.4 (d, *J* = 5.9 Hz), 34.0, 27.6, 26.6, 26.42, 26.36, 26.2, 25.9, 25.2, 24.6, 16.2 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9. IR (neat): υ_{max} (cm^{-1}) 2928, 2856, 1734, 1444, 1165, 1016, 793. HRMS (ESI) calcd for $C_{18}H_{36}O_5PS$ $[M+H]^+$ 395.2016, found 395.2024.



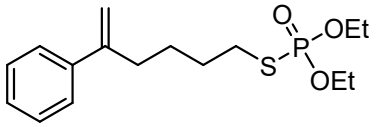
***O,O*-Diethyl *S*-(18-oxooxacyclooctadecan-4-yl) phosphorothioate (5ga)** Colorless oil (35.8 mg, 41%). R_f = 0.3 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 – 4.29 (m, 1H), 4.22 – 4.08 (m, 5H), 3.38 – 3.29 (m, 1H), 2.30 (td, *J* = 7.6, 1.2 Hz, 2H), 2.09 – 1.97 (m, 3H), 1.79 – 1.58 (m, 5H), 1.53 – 1.40 (m, 4H), 1.34 (t, *J* = 7.2 Hz, 6H), 1.28 – 1.23 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

173.8, 63.7 (d, J = 6.4 Hz), 61.6, 44.8 (d, J = 3.6 Hz), 36.2 (d, J = 4.8 Hz), 34.8 (d, J = 5.0 Hz), 34.5, 27.9, 27.8, 27.7, 27.4, 27.1, 27.0, 26.84, 26.80, 26.6, 25.8, 24.6, 16.2 (d, J = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.0. IR (neat): υ_{max} (cm^{-1}) 2926, 2855, 1735, 1460, 1247, 1017, 794. HRMS (ESI) calcd for $C_{21}H_{42}O_5PS$ $[M+H]^+$ 437.2485, found 437.2496.

11. Characterizations of Products 6aa and 7aa.



***O,O*-Diethyl *S*-(5-hydroxy-5-phenylpentyl) phosphorothioate (6aa)** Colorless oil (53.1 mg, 80%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 4H), 7.29 – 7.26 (m,1H), 4.68 – 4.65 (m, 1H), 4.19 – 4.06 (m, 4H), 2.84 – 2.77 (m, 2H), 2.25 – 2.02 (m, 1H), 1.86 – 1.68 (m, 4H), 1.59 – 1.38 (m, 2H), 1.34 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 128.5, 127.6, 125.9, 74.2, 63.6 (d, *J* = 5.8 Hz), 38.5, 30.7 (d, *J* = 3.2 Hz), 30.6 (d, *J* = 1.7 Hz), 24.8, 16.1 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. IR (neat): υ_{max} (cm^{-1}) 3410, 2984, 1239, 1016, 792. HRMS (ESI) calcd for $C_{15}H_{26}O_4PS$ $[M+H]^+$ 333.1284, found 333.1286.



***O,O*-Diethyl *S*-(5-phenylhex-5-en-1-yl) phosphorothioate (7aa)** Colorless oil (53.8 mg, 82%). R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 5.20 (d, *J* = 0.9 Hz, 1H), 4.99 (d, *J* = 0.9 Hz, 1H), 4.15 – 3.99 (m, 4H), 2.78 – 2.71 (m, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.52 – 1.48 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ148.0, 141.0, 128.4, 127.5, 126.2, 112.8, 63.6 (d, *J* = 5.8 Hz), 34.8, 30.8 (d, *J* = 3.8 Hz), 30.5 (d, *J* = 5.5 Hz), 27.1, 16.2 (d, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8. IR (neat): υ_{max} (cm^{-1}) 2983, 1258, 1018, 968, 753. HRMS (ESI) calcd for $C_{16}H_{26}O_3PS$ $[M+H]^+$ 329.1335, found 329.1334.

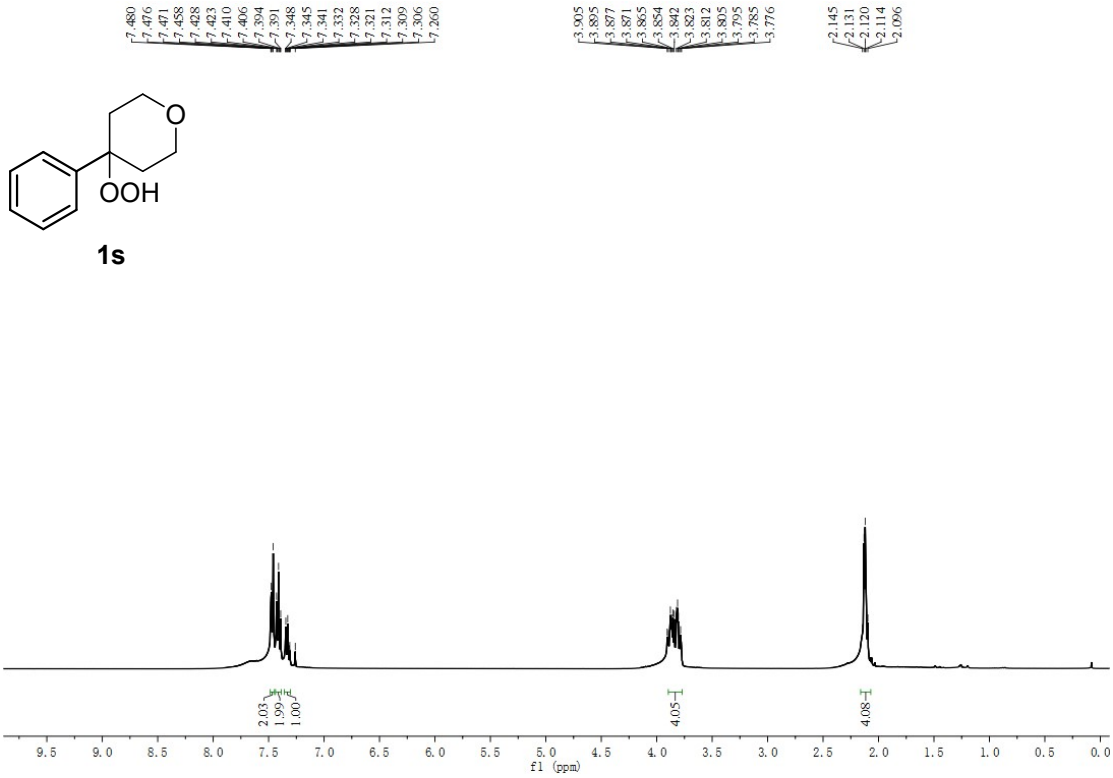
12. References

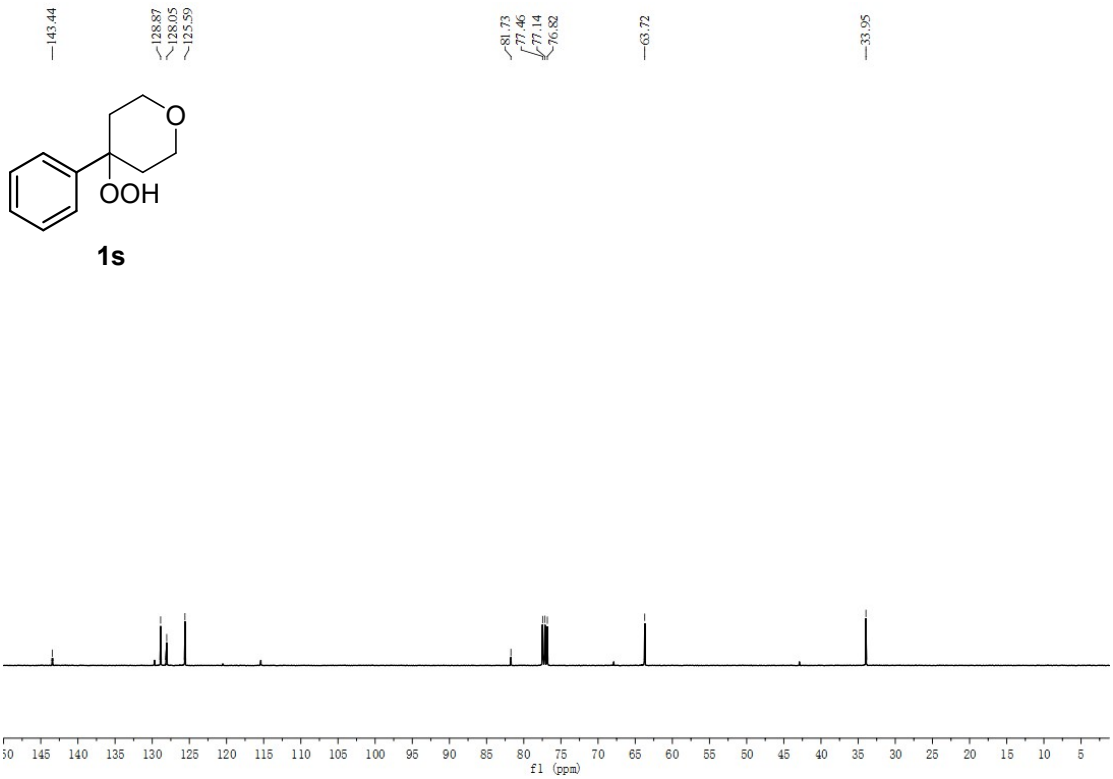
1 (a) S. Liu, M. Bai, P. F. Xu, Q. X. Sun, X. H. Duan, et al., Copper-catalyzed radical ring-opening halogenation with HX, *Chem Commun*, 2021, **57**, 8652-8655. (b) S. Liu, P. Ma, L. Zhang, S. Shen, H.-J. Miao, L. Liu, K. N. Houk, X.-H. Duan, L.-N. Guo, Cheap metal catalyzed ring expansion/cross-coupling cascade: A new route to functionalized medium-sized and macrolactones, *Chem. Sci.*, 2023, DOl: 10.1039/D2SC06157K

2 (a) N. Santschi and A. Togni, Electrophilic trifluoromethylation of S-hydrogen phosphorothioates, *J. Org. Chem*, 2011, **76**, 4189-4193. (b) M. J. Bodner, R. M. Phelan, M. F. Freeman, R. Li and C. A. Townsend, Non-heme iron oxygenases generate natural structural diversity in carbapenem antibiotics, *J. Am. Chem. Soc*, 2010, **132**, 12-13.

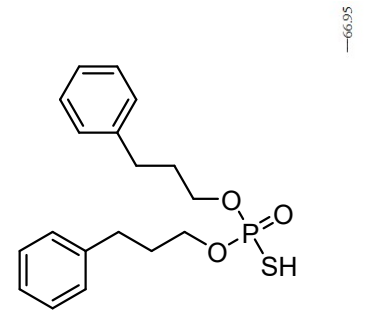
13. ^{31}P NMR, ^{1}H NMR and ^{13}C NMR Spectra of Starting Materials

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **1s**

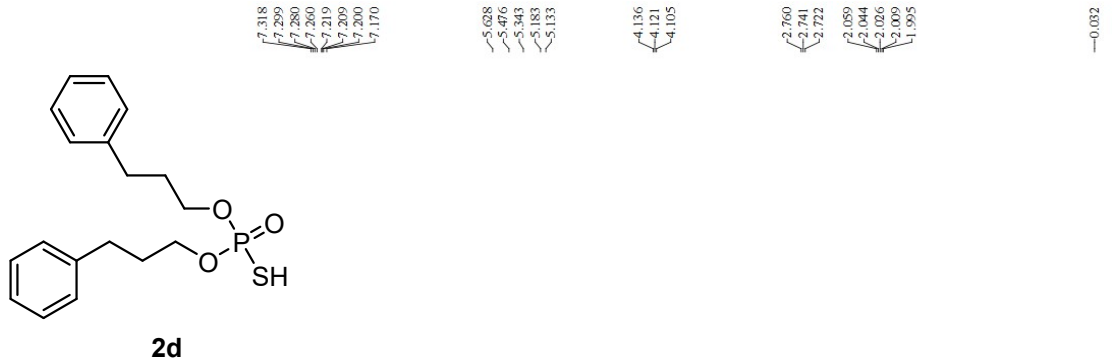




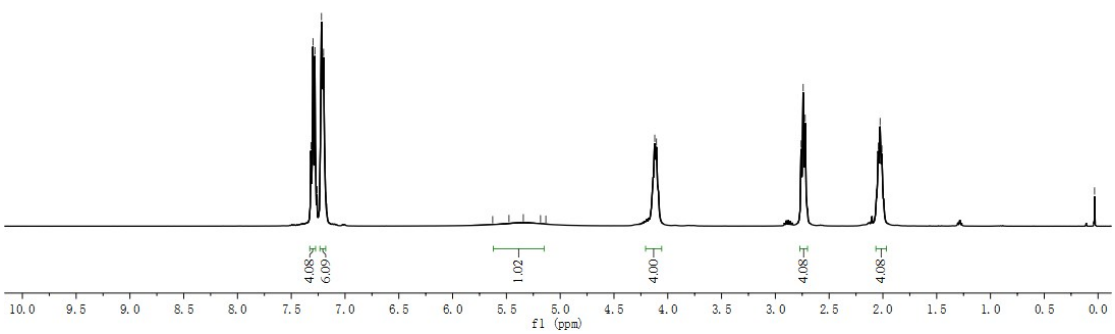
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **2d**

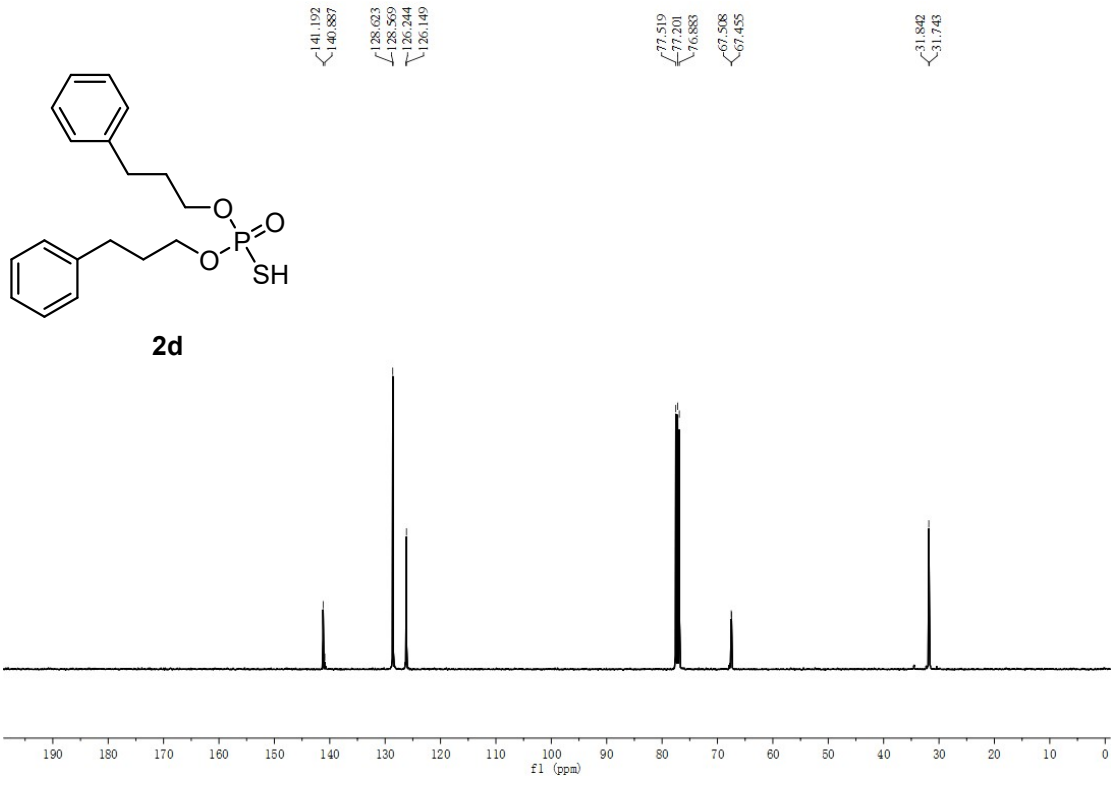


2d



2d

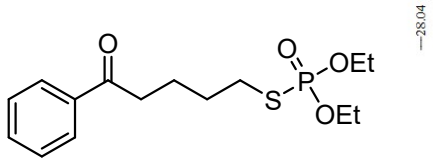



141.192
140.887
128.623
128.569
126.244
126.149
77.519
77.201
76.883
67.508
67.455
31.842
31.743
O
O
P
O
SH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

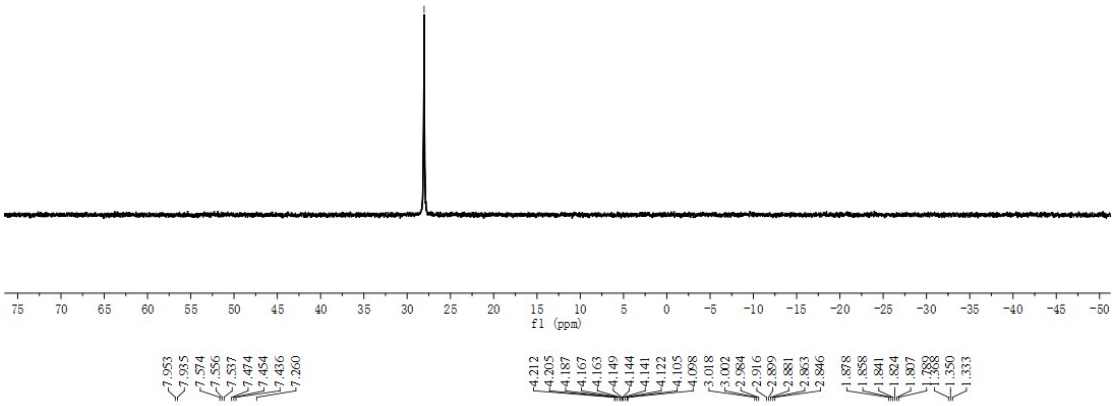
2d

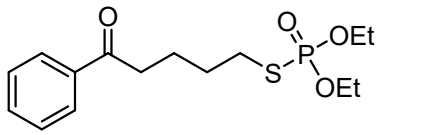
15. ^{31}P NMR, ^{1}H NMR and ^{13}C NMR Spectra of Products 3 and 5

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3aa**

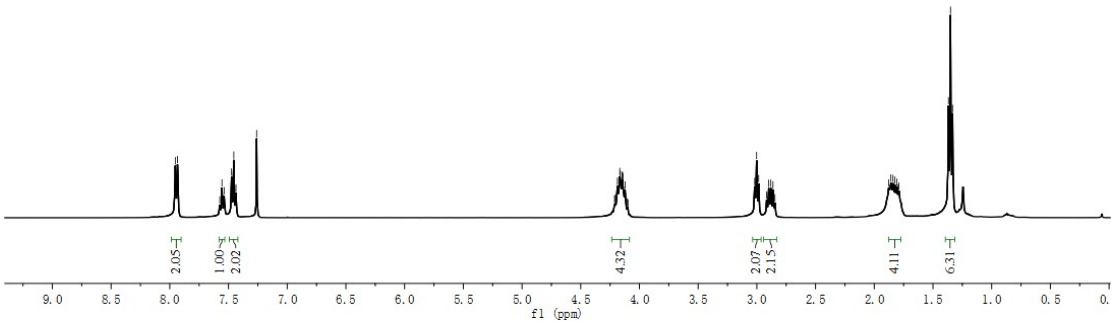


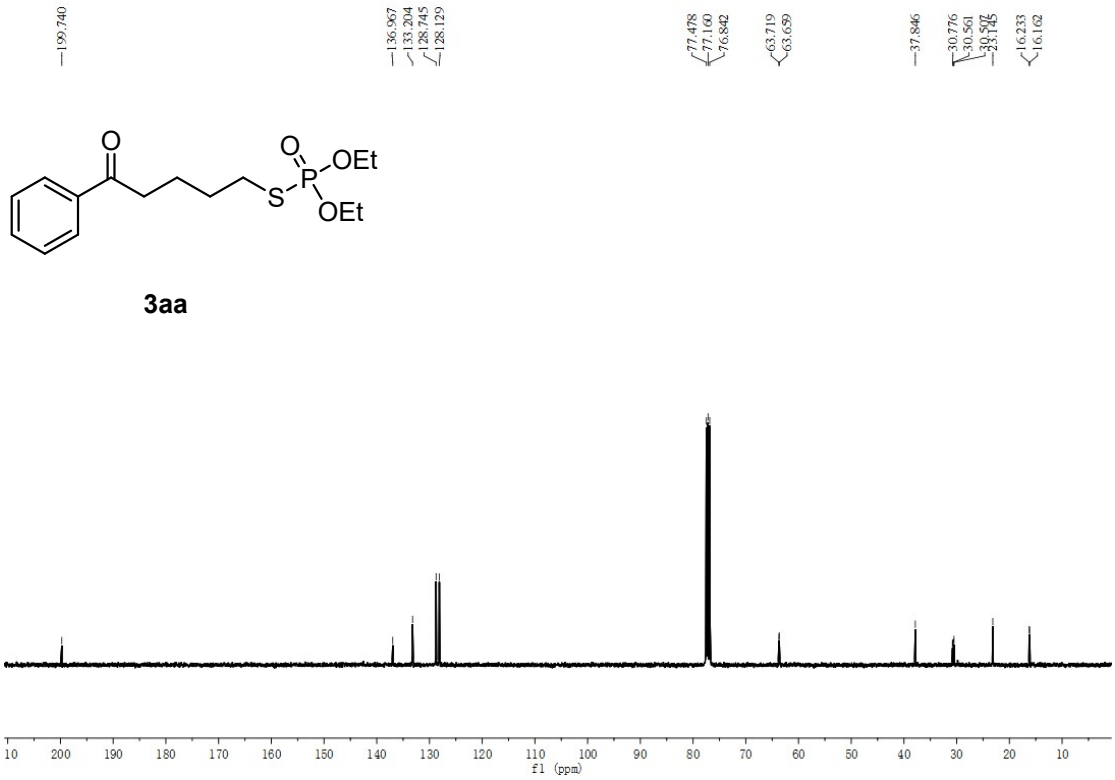
3aa



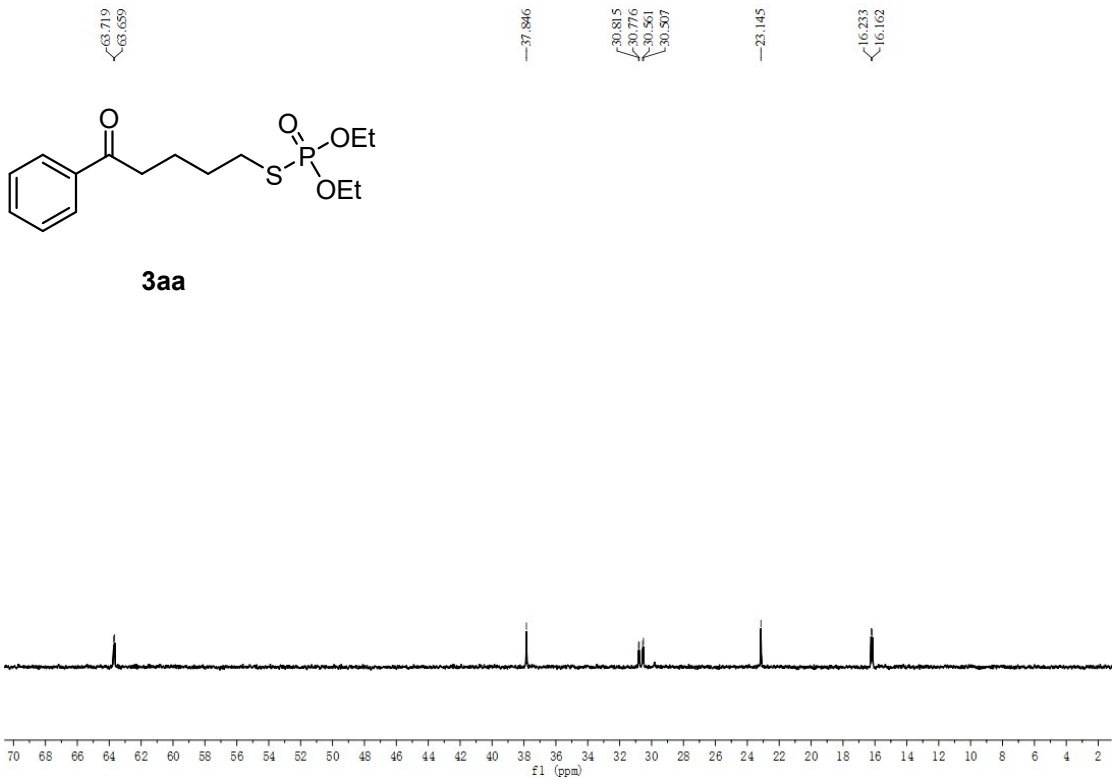


3aa



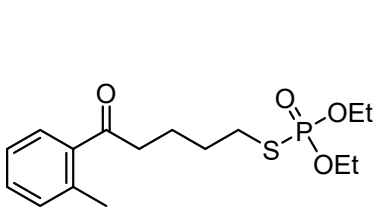

199.740
136.967
133.294
128.745
128.129
77.478
77.160
76.842
63.719
63.659
37.846
30.776
30.561
23.145
16.233
16.162
O
O
OEt
S
P
OEt
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3aa

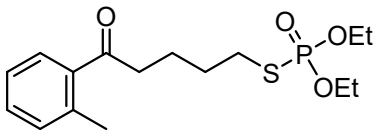

63.719
63.659
37.846
30.815
30.776
30.561
30.507
23.145
16.233
16.162
O
O
OEt
S
P
OEt
70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

3aa

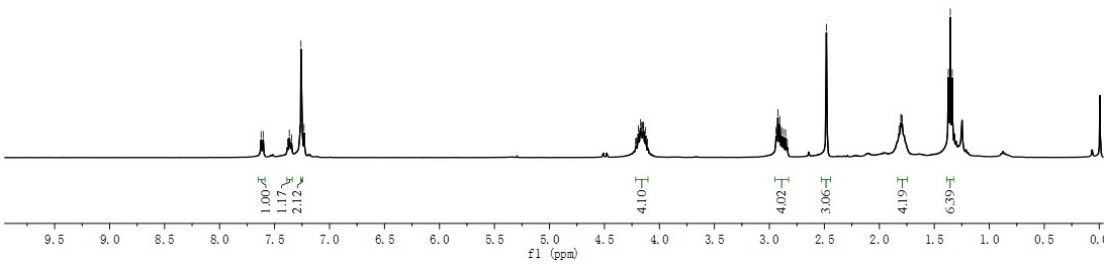
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ba**

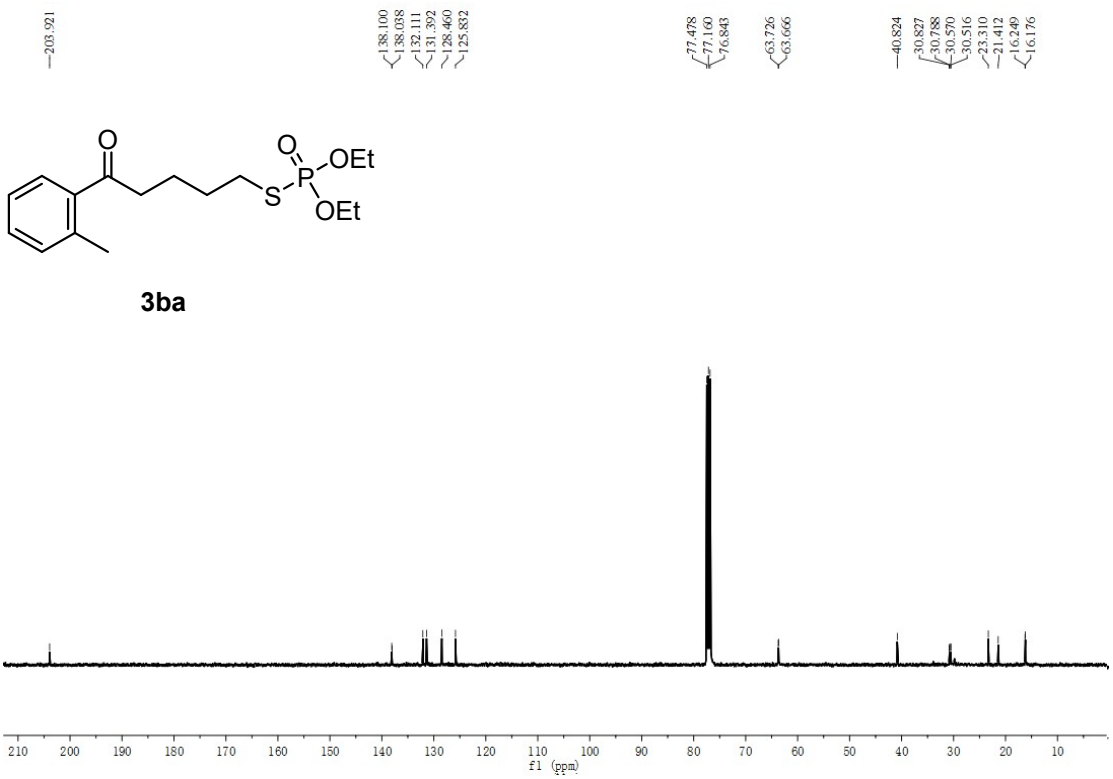


3ba

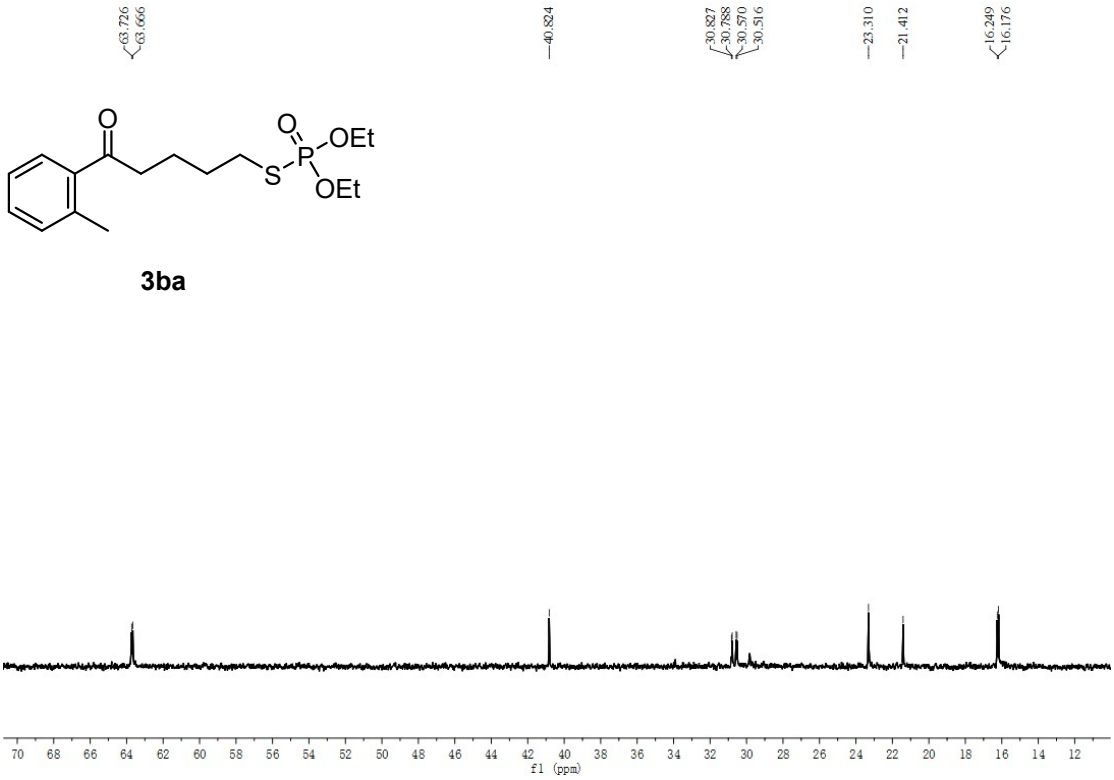


3ba



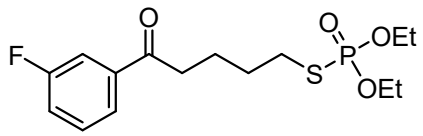

203.921
138.100
138.038
132.111
131.392
128.460
125.832
77.478
77.160
76.843
63.726
63.666
40.824
30.827
30.788
30.570
30.516
23.310
21.412
16.249
16.176
O
O
OEt
P
S
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3ba

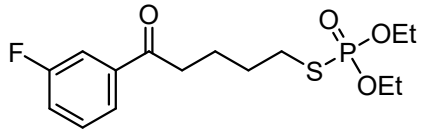

63.726
63.666
40.824
30.827
30.788
30.570
30.516
23.310
21.412
16.249
16.176
O
O
OEt
P
S
OEt
70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12
f1 (ppm)

3ba

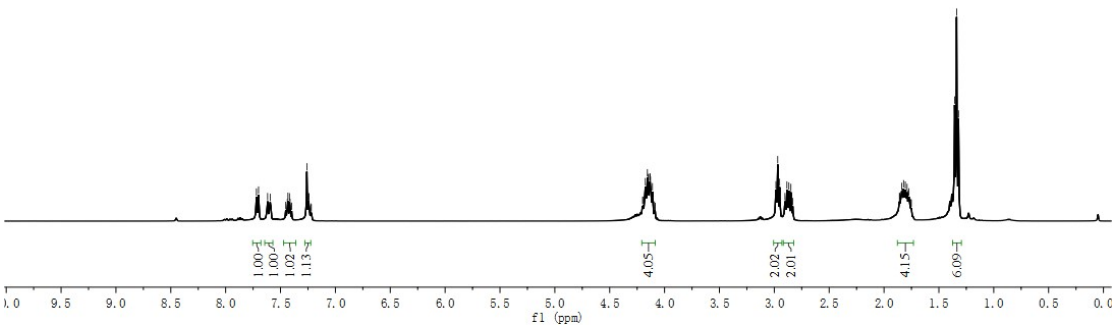
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ca**

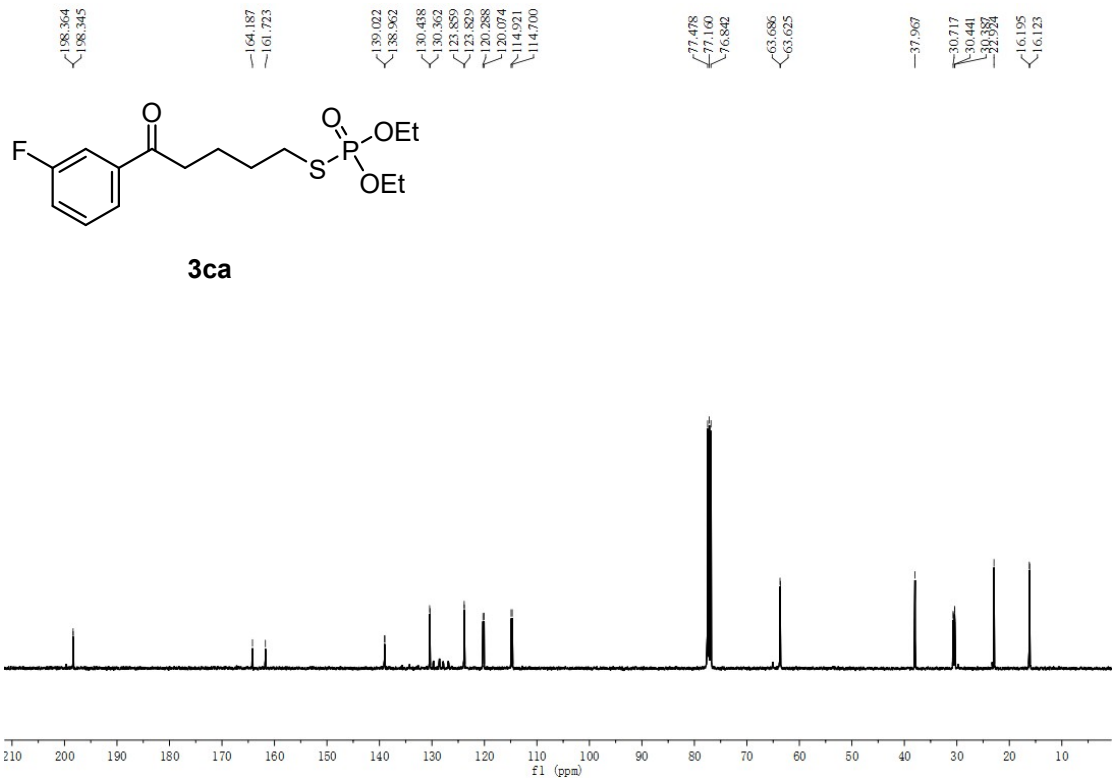


3ca

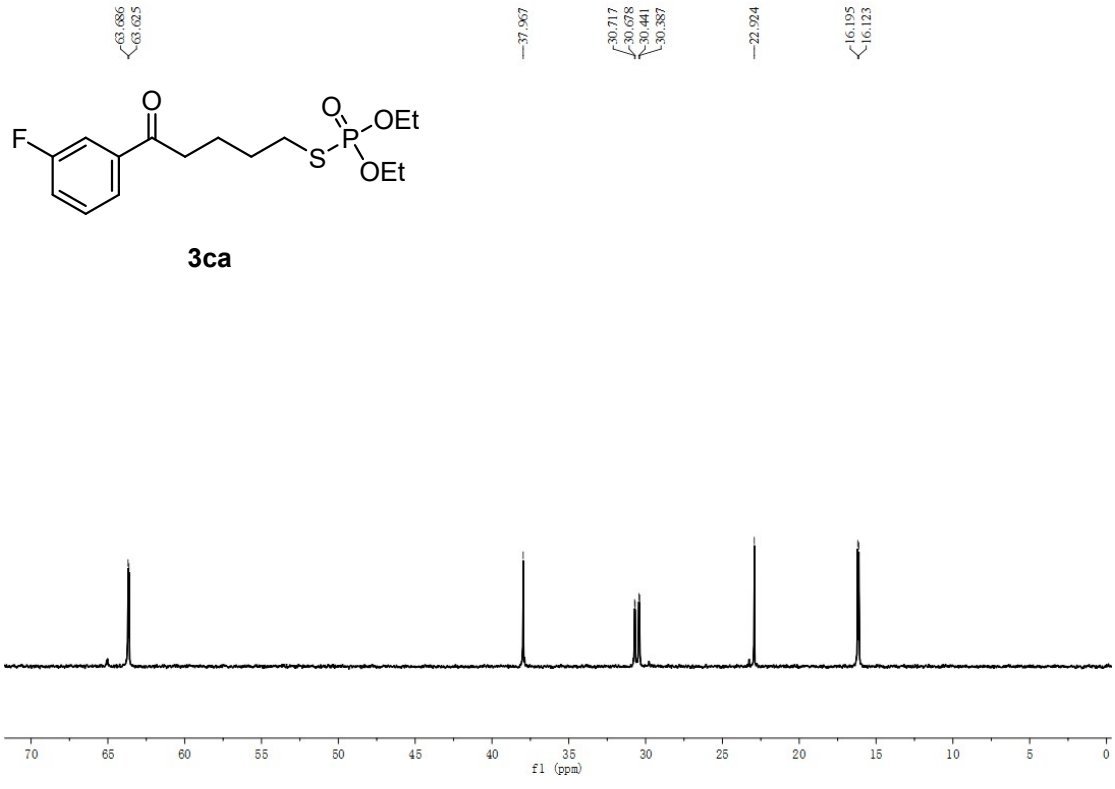


3ca



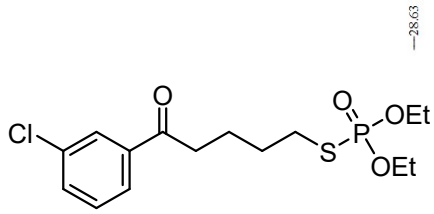

198.364
198.345
164.187
161.723
139.022
138.962
130.438
130.362
123.859
123.829
120.288
120.074
114.921
114.700
77.478
77.160
76.842
63.686
63.625
37.967
30.717
30.441
22.924
16.195
16.123
O
F
O
OEt
S
P
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3ca

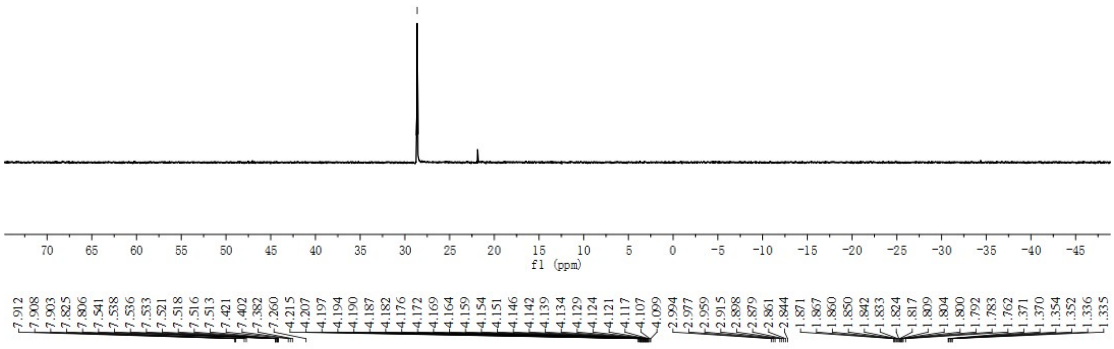

63.686
63.625
37.967
30.717
30.678
30.441
30.387
22.924
16.195
16.123
O
F
O
OEt
S
P
OEt
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

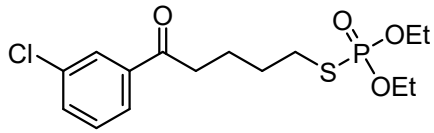
3ca

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3da**

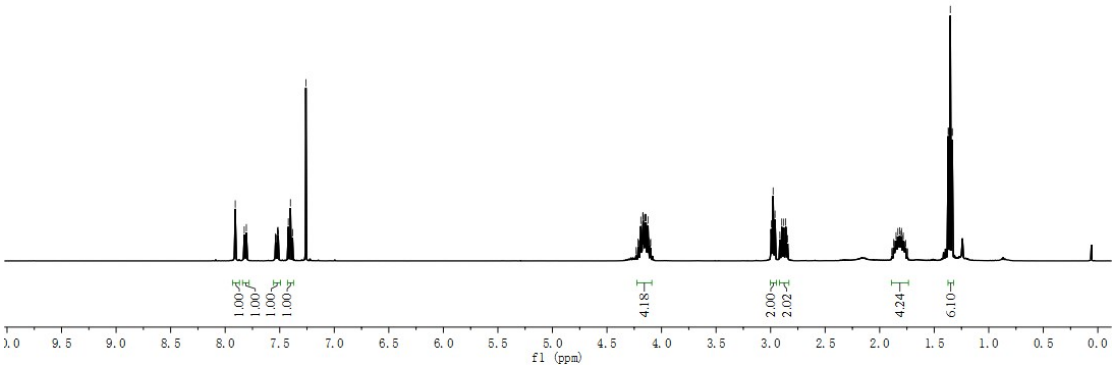


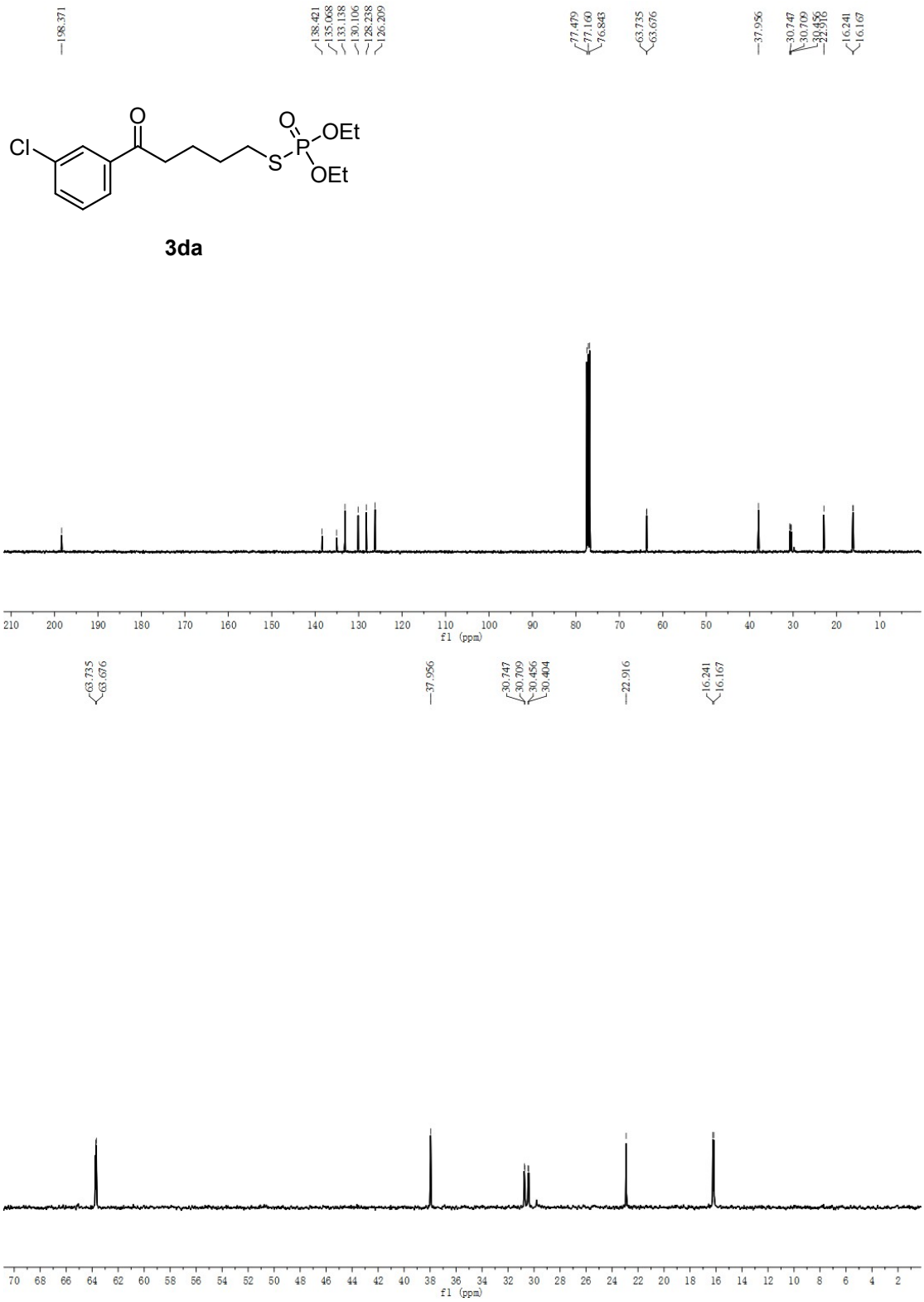
3da





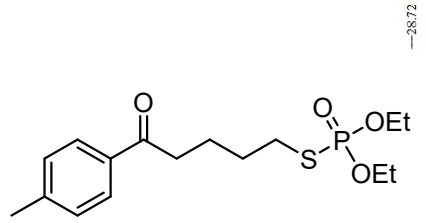
3da



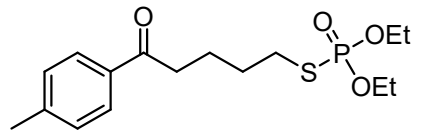

198.371
138.421
135.068
133.138
130.106
128.238
126.209
77.479
77.160
76.843
63.735
63.676
37.956
30.747
30.709
30.456
30.404
22.916
16.241
16.167
Cl
O
O
P
OEt
OEt
S
f1 (ppm)

3da

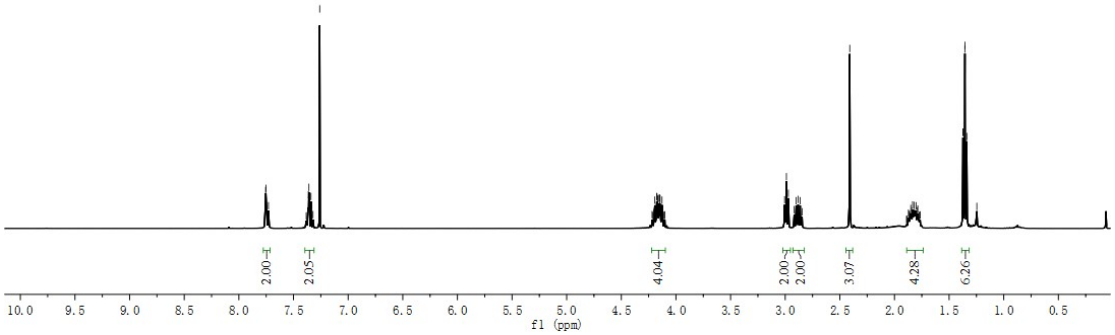
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ea**

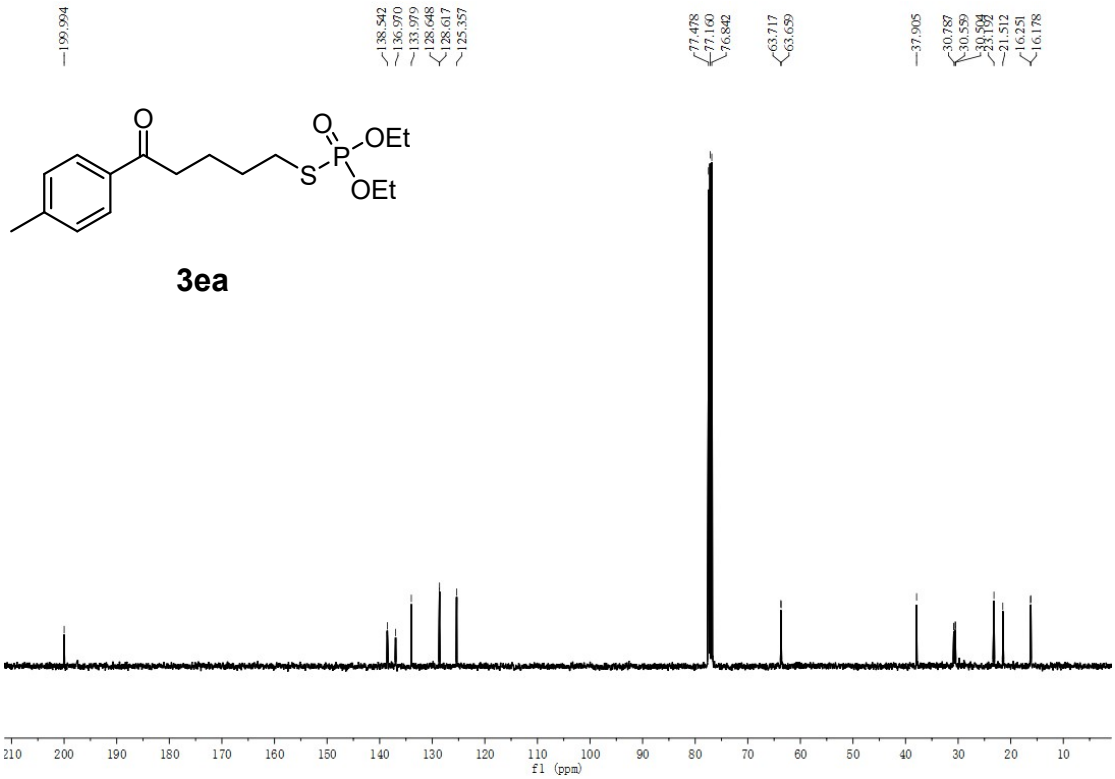


3ea

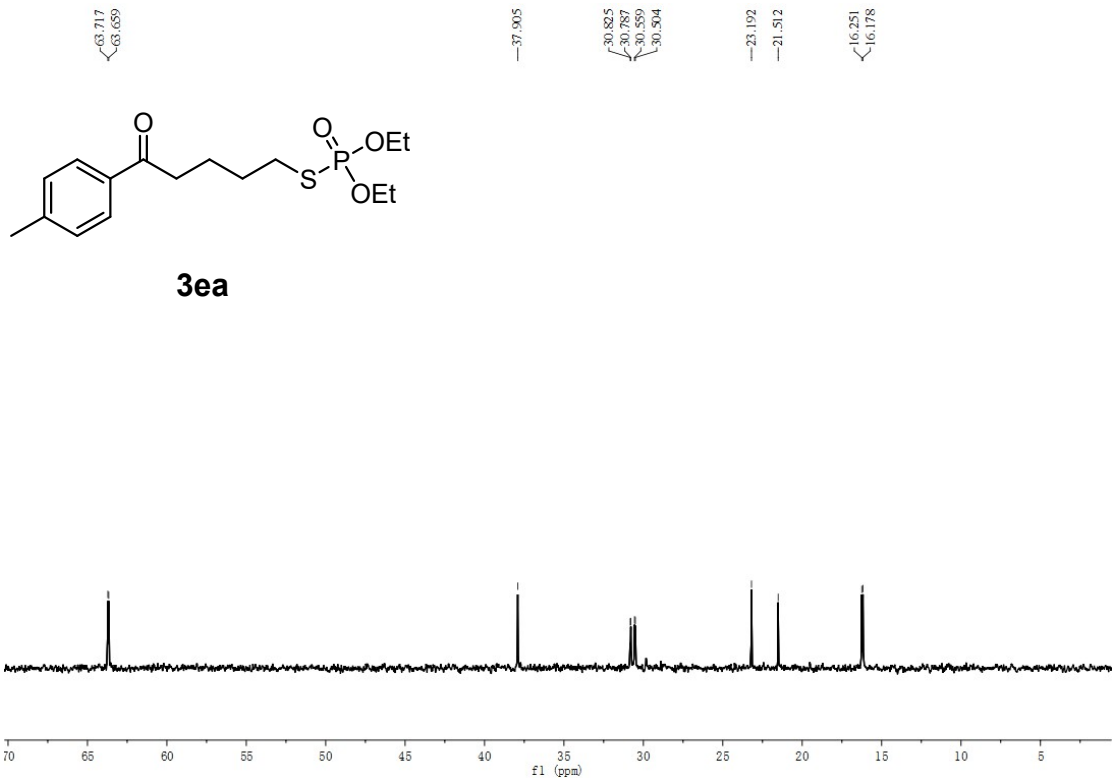


3ea



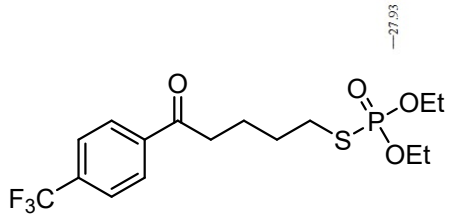

199.994
138.542
136.970
133.979
128.648
128.617
125.357
77.478
77.160
76.842
63.717
63.659
37.905
30.787
30.559
30.504
23.192
21.512
16.251
16.178
O
O
OEt
P
S
OEt
f1 (ppm)

3ea

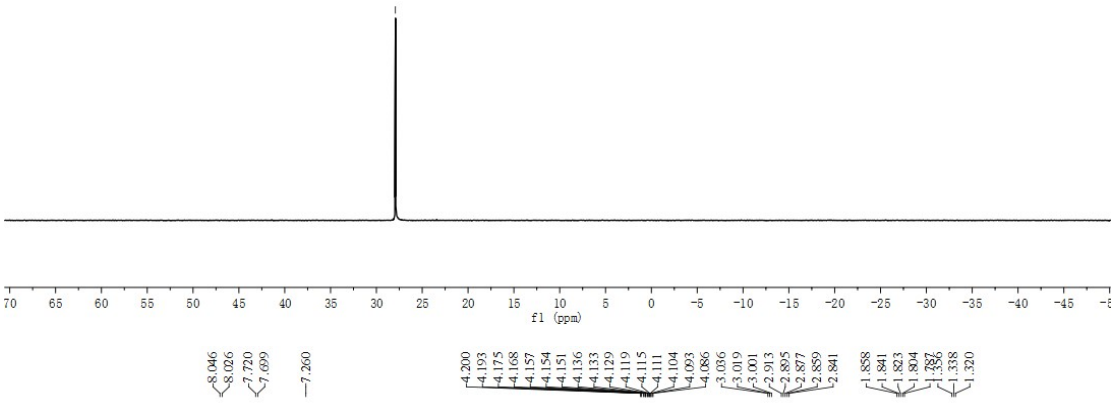

63.717
63.659
37.905
30.825
30.787
30.559
30.504
23.192
21.512
16.251
16.178
O
O
OEt
P
S
OEt
f1 (ppm)

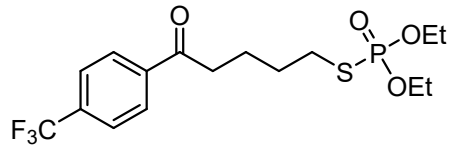
3ea

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3fa**

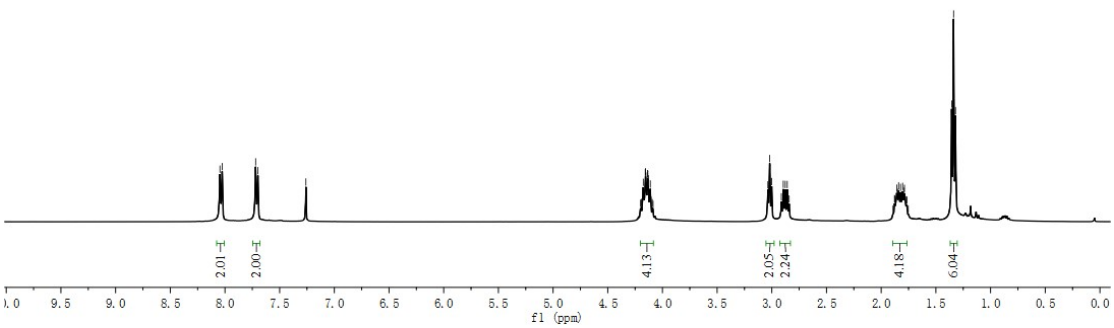


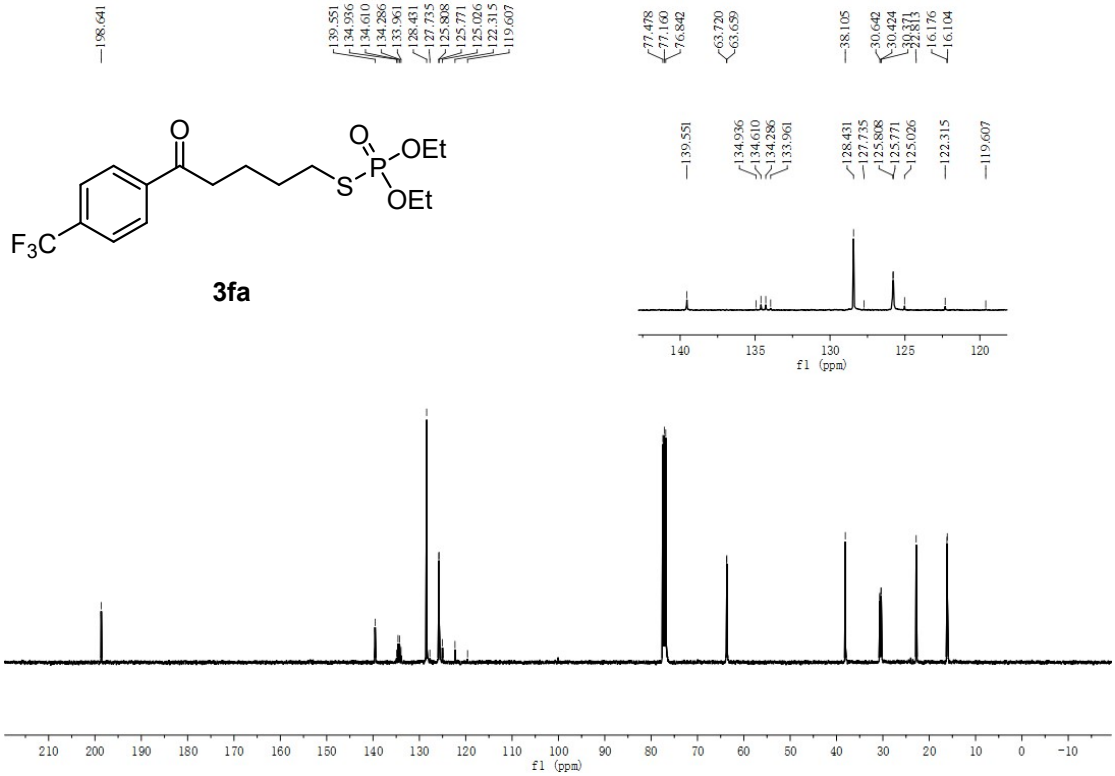
3fa

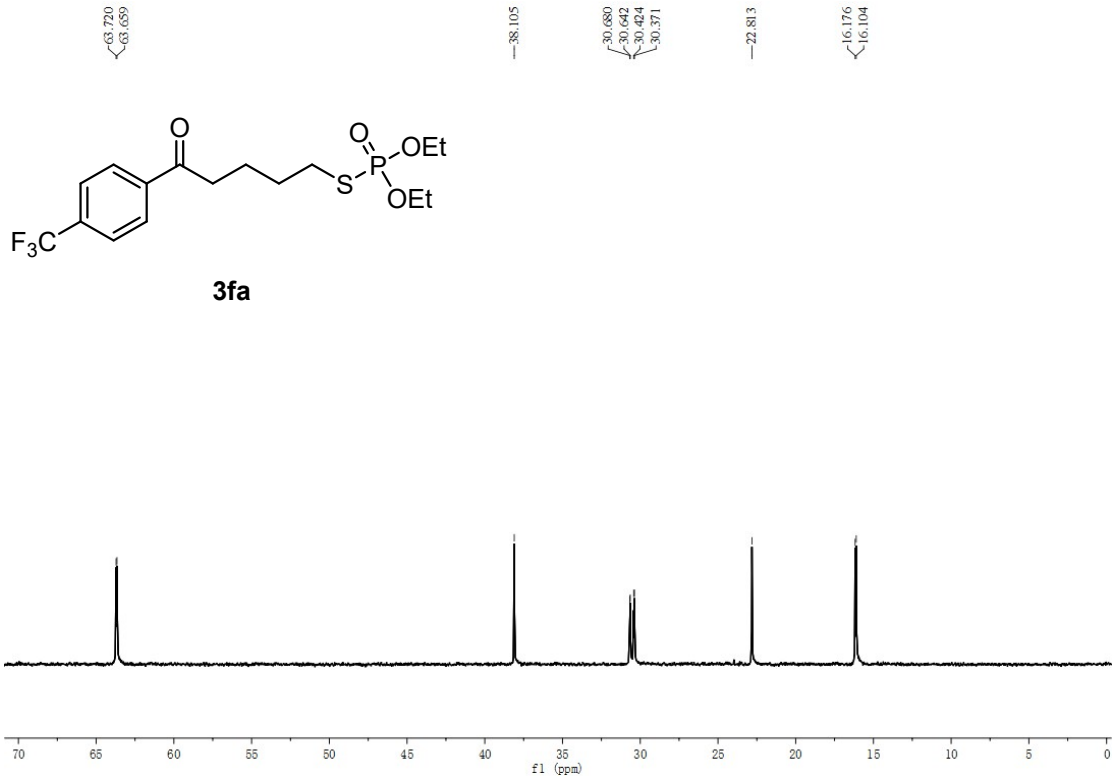




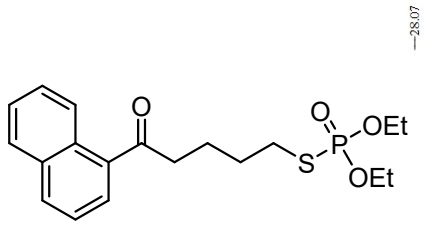
3fa



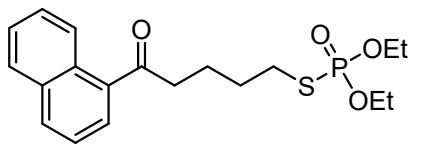

198.641
139.551
134.936
134.610
134.286
133.961
128.431
127.735
125.808
125.771
125.026
122.315
119.607
77.478
77.160
76.842
63.720
63.659
38.105
30.642
30.424
30.371
22.813
16.176
16.104
O
O
OEt
S
P
OEt
F3C
3fa
f1 (ppm)


63.720
63.659
38.105
30.680
30.642
30.424
30.371
22.813
16.176
16.104
O
O
OEt
S
P
OEt
F3C
3fa
f1 (ppm)

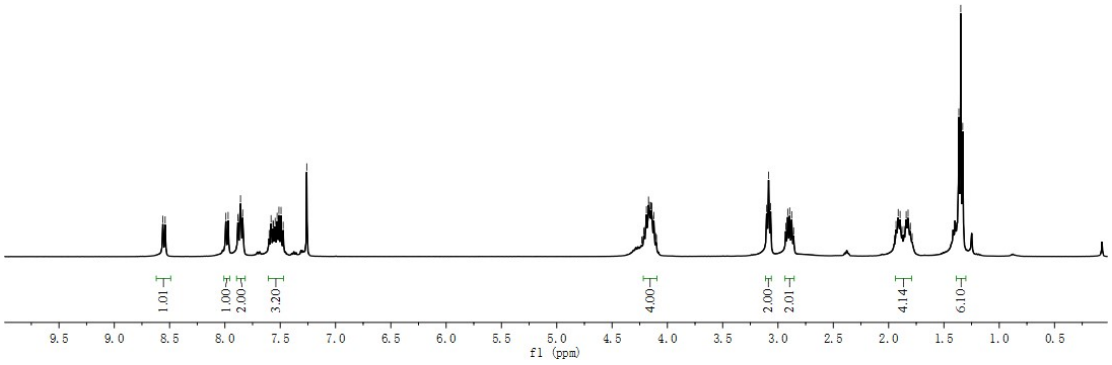
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ga**

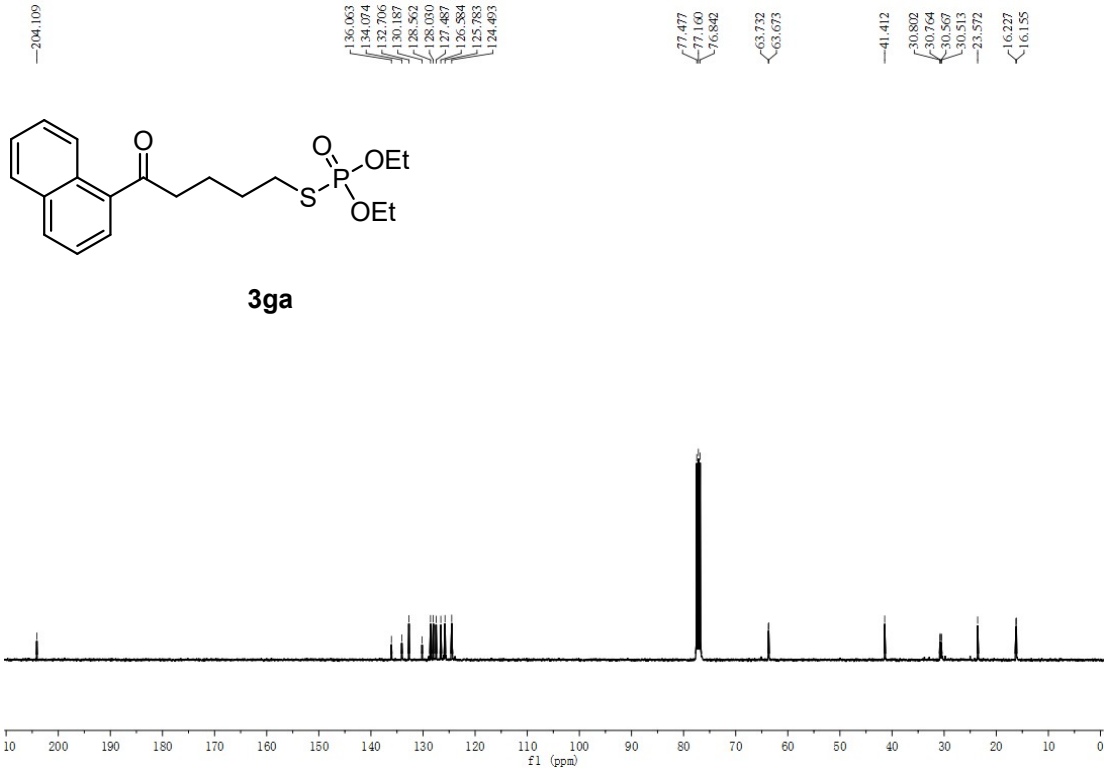


3ga

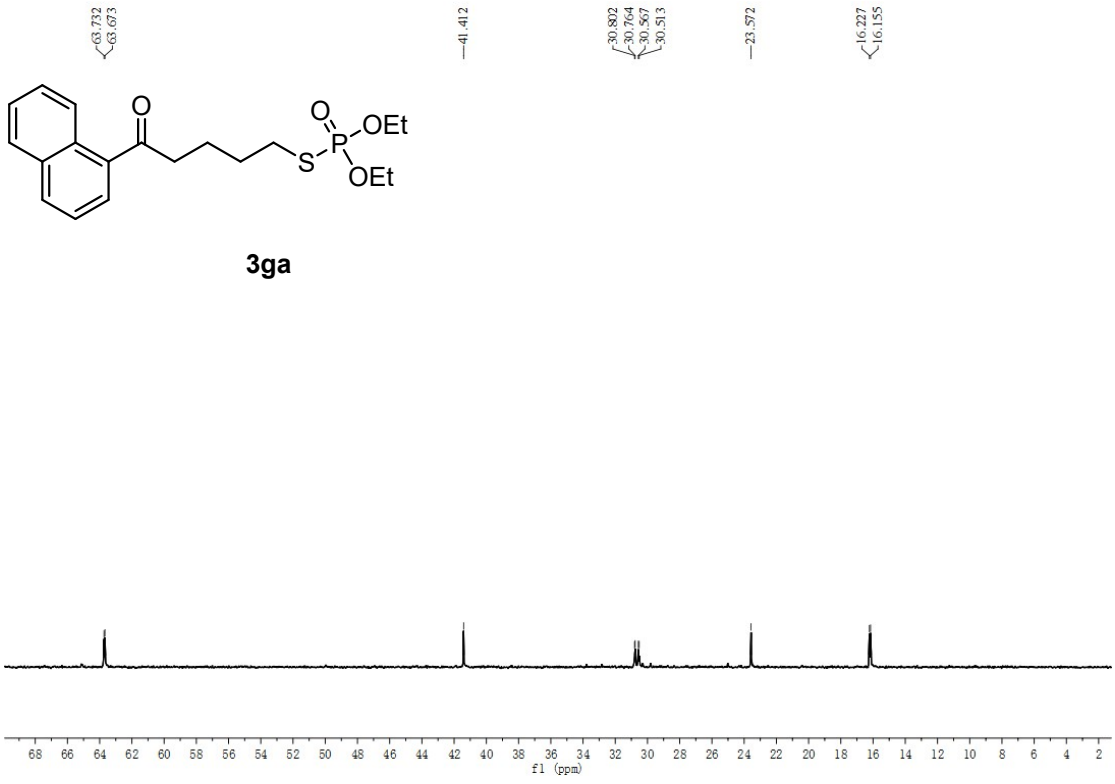


3ga



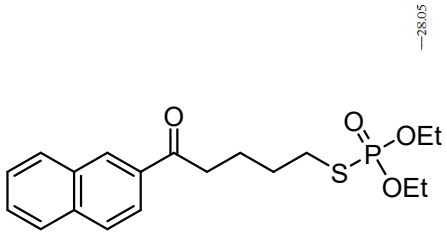

204.109
136.063
134.074
132.706
130.187
128.562
128.030
127.487
126.384
125.783
124.493
77.477
77.160
76.842
63.732
63.673
41.412
30.802
30.764
30.567
30.513
23.572
16.227
16.155
O
O
P
OEt
S
OEt
f1 (ppm)

3ga

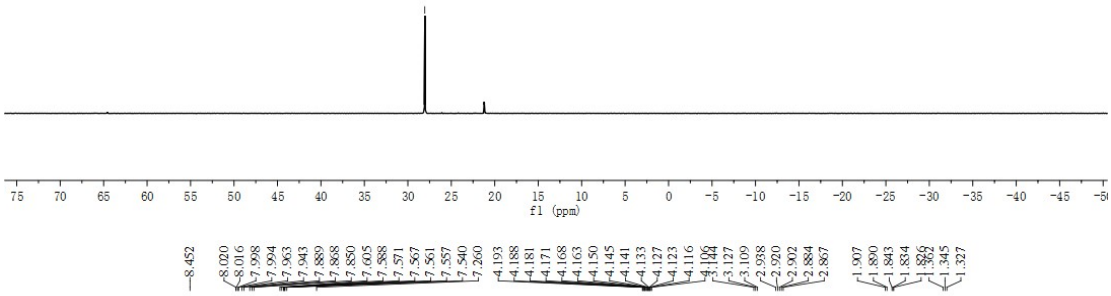

63.732
63.673
41.412
30.802
30.764
30.567
30.513
23.572
16.227
16.155
O
O
P
OEt
S
OEt
f1 (ppm)

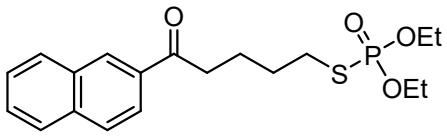
3ga

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ha**

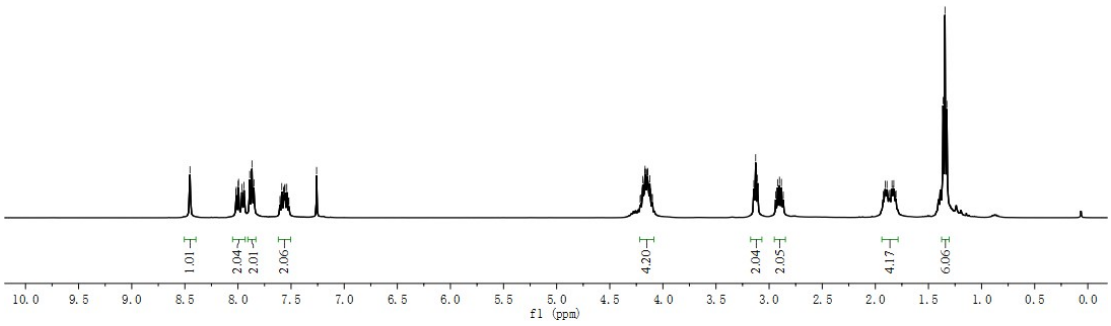


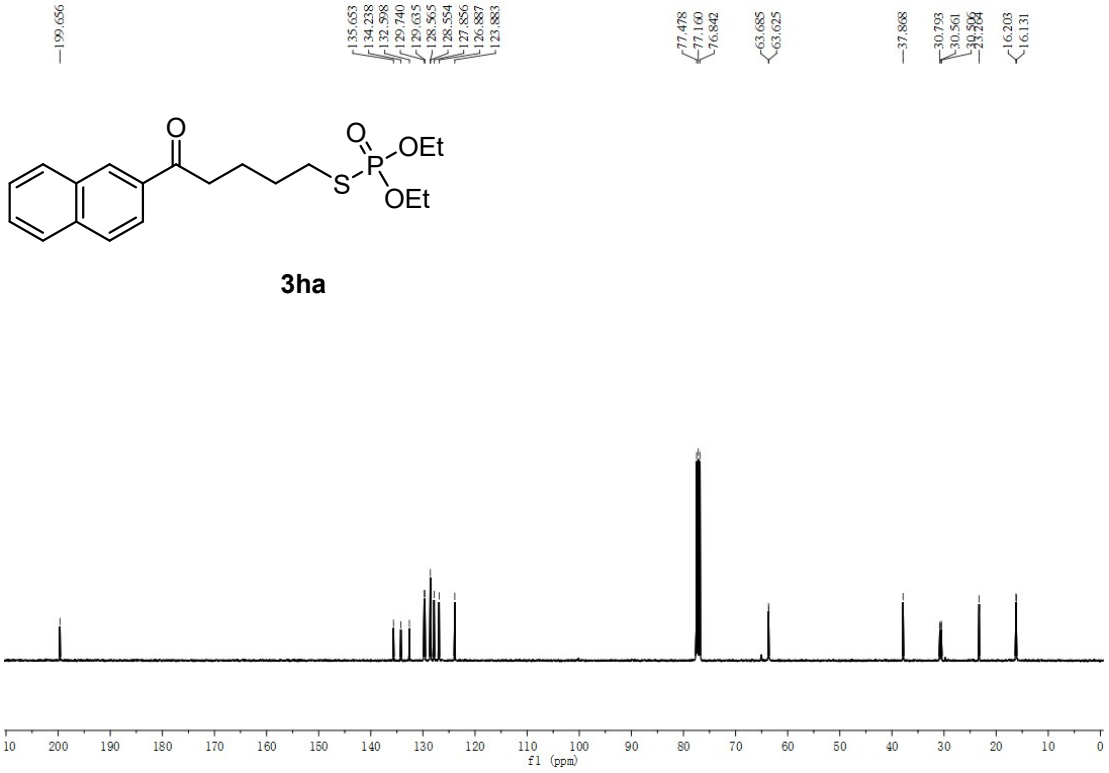
3ha



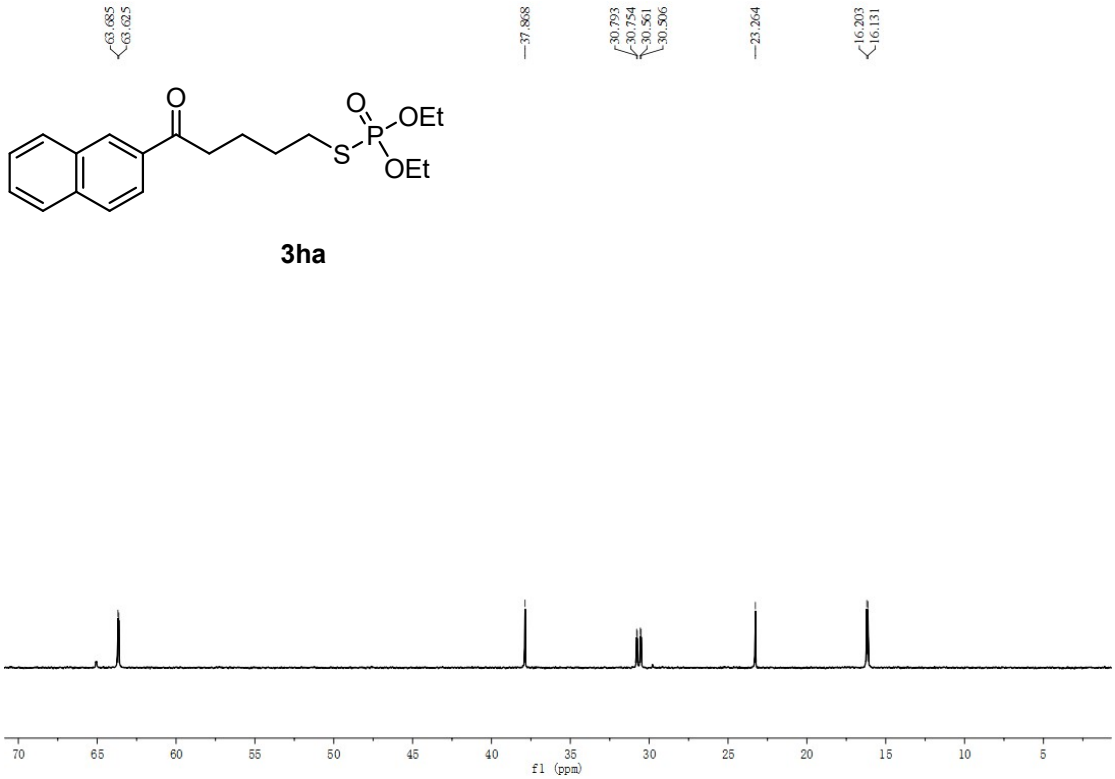


3ha



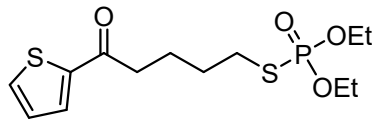

199.656
135.653
134.238
132.598
129.740
129.635
128.565
128.554
127.856
126.887
123.883
77.478
77.160
76.842
63.685
63.625
37.868
30.793
30.561
16.203
16.131
O
O
OEt
S
P
OEt
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ha

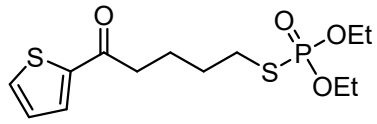

63.685
63.625
37.868
30.793
30.754
30.561
30.506
23.264
16.203
16.131
O
O
OEt
S
P
OEt
70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

3ha

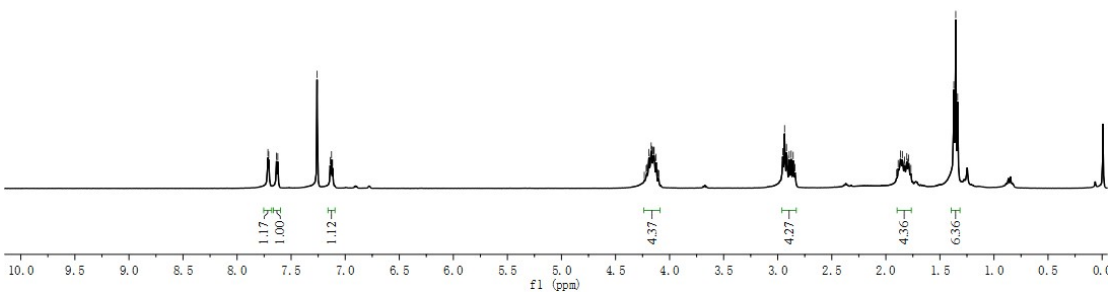
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ia**

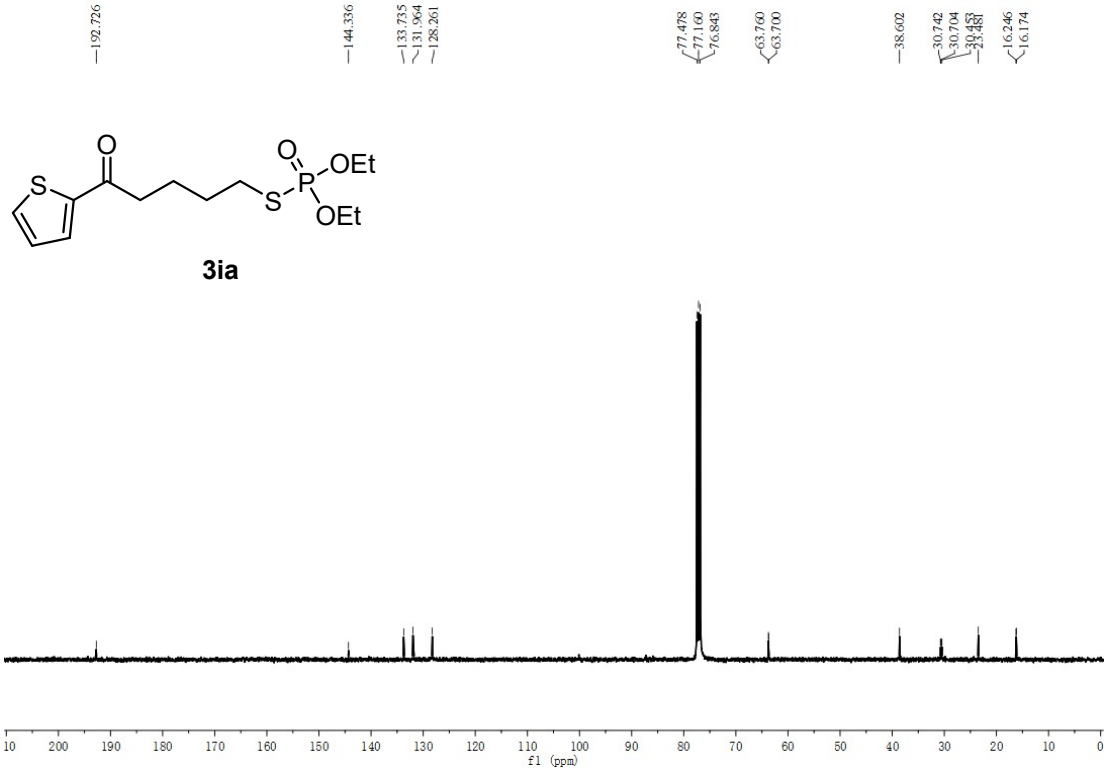


3ia

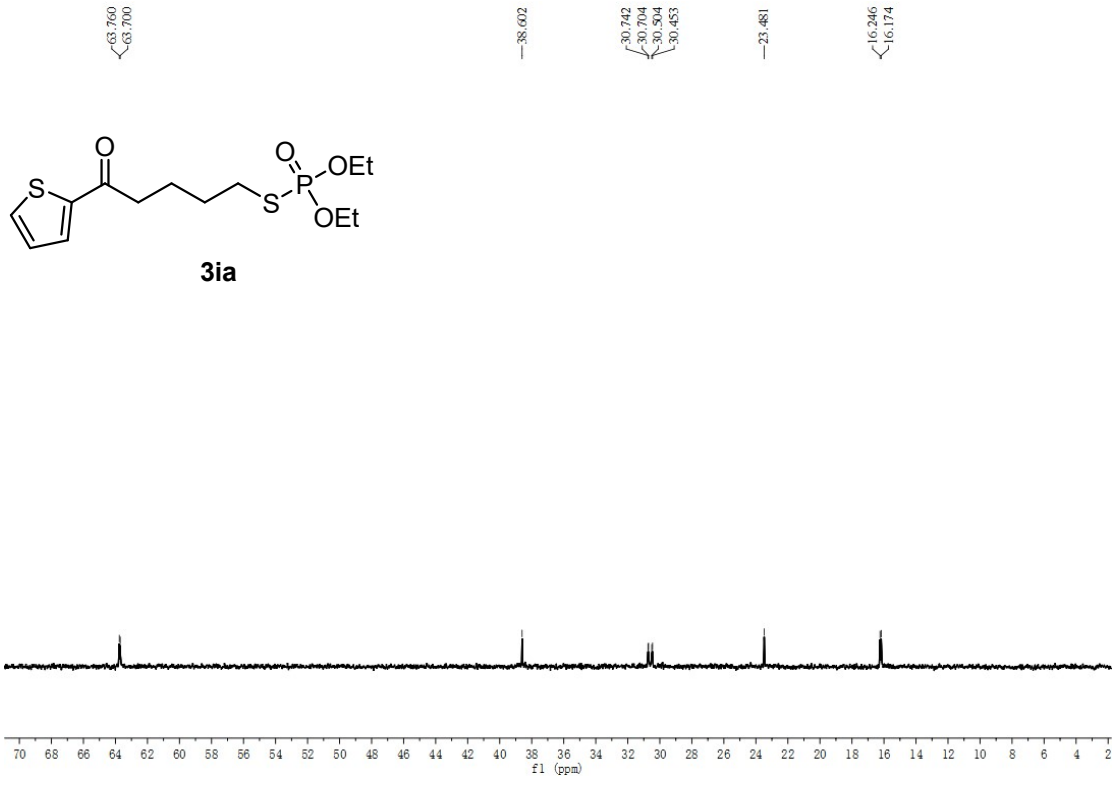


3ia



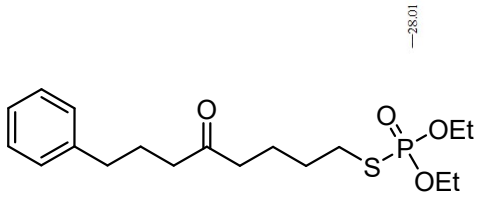

192.726
144.336
133.735
131.964
128.261
77.478
77.160
76.843
63.760
63.700
38.602
30.742
30.704
30.504
30.453
23.481
16.246
16.174
O
S
O
P
OEt
S
OEt
f1 (ppm)

3ia

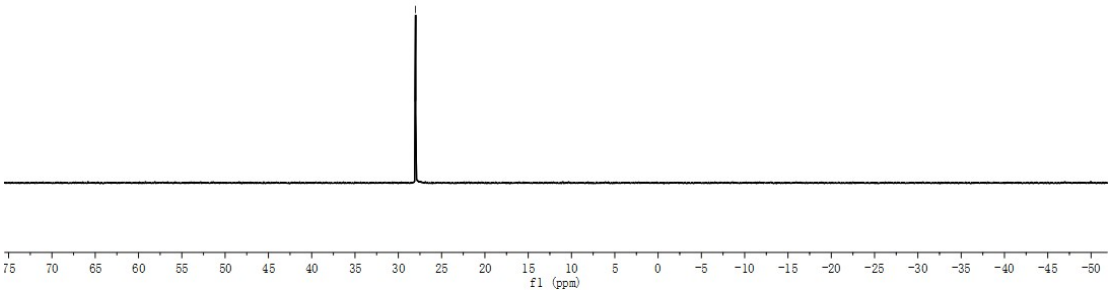

63.760
63.700
38.602
30.742
30.704
30.504
30.453
23.481
16.246
16.174
O
S
O
P
OEt
S
OEt
f1 (ppm)

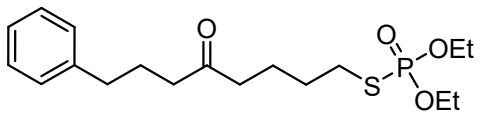
3ia

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ja**

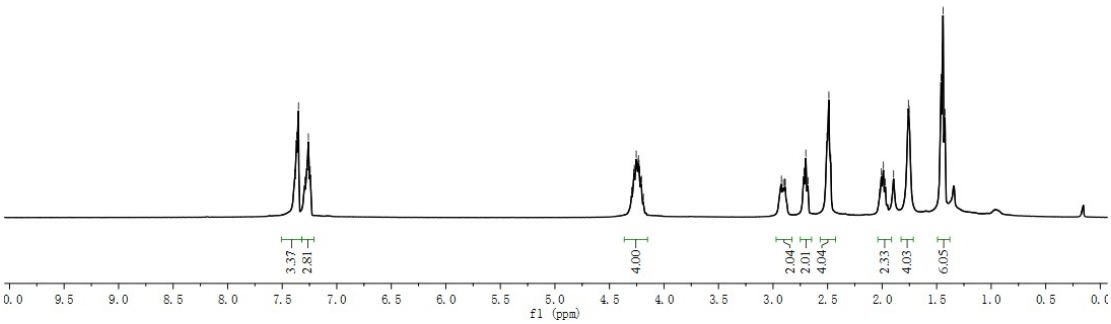


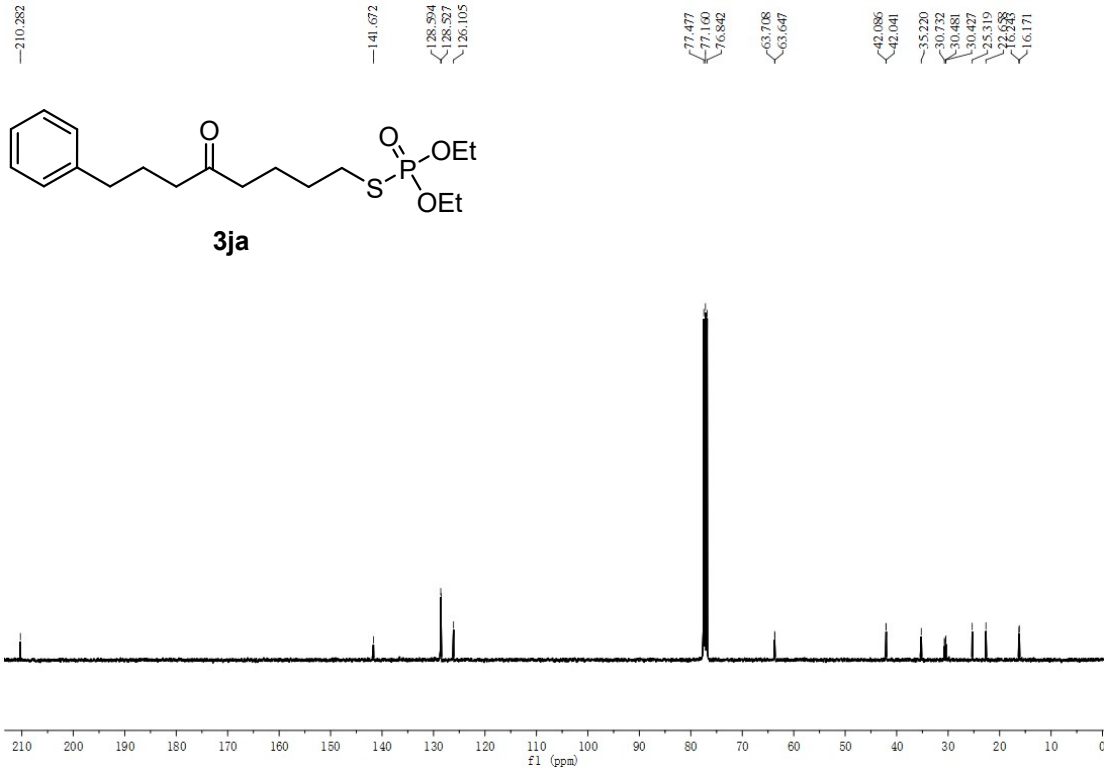
3ja



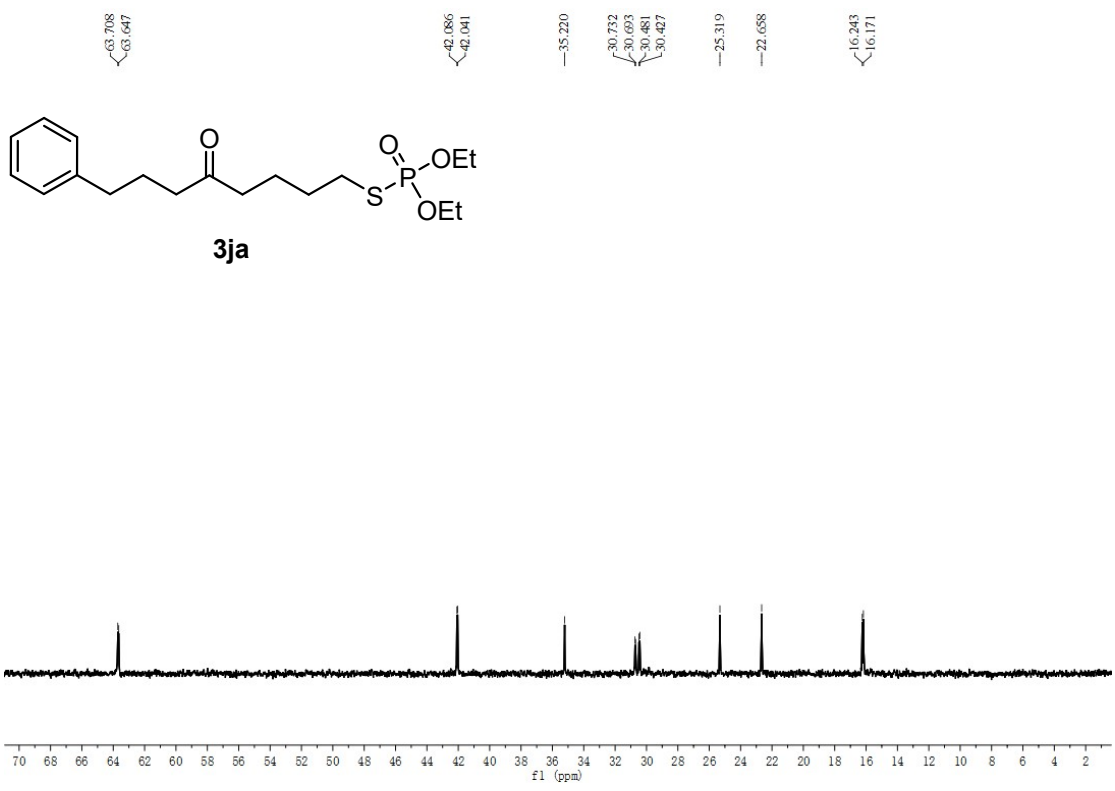


3ja



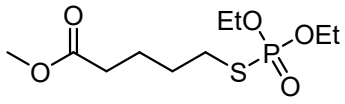

210.282
141.672
128.594
128.527
126.105
77.477
77.160
76.842
63.708
63.647
42.086
42.041
35.220
30.732
30.481
30.427
25.319
22.658
16.243
16.171
O
O
OEt
S
P
OEt
f1 (ppm)

3ja

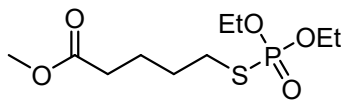

63.708
63.647
42.086
42.041
35.220
30.732
30.693
30.481
30.427
25.319
22.658
16.243
16.171
O
O
OEt
S
P
OEt
f1 (ppm)

3ja

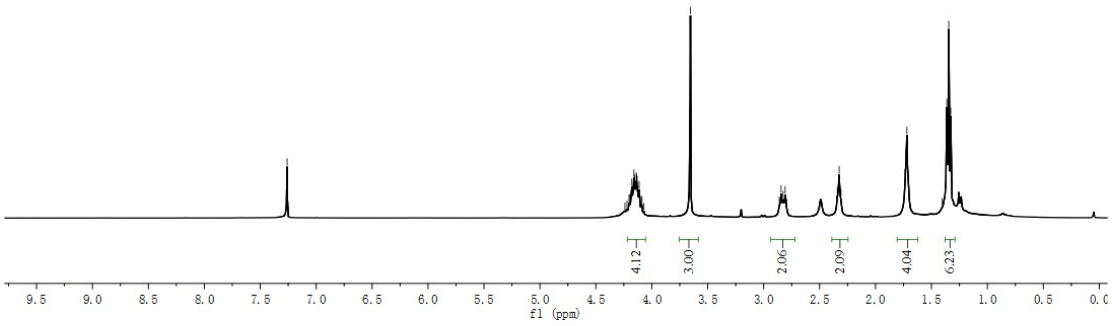
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ka**

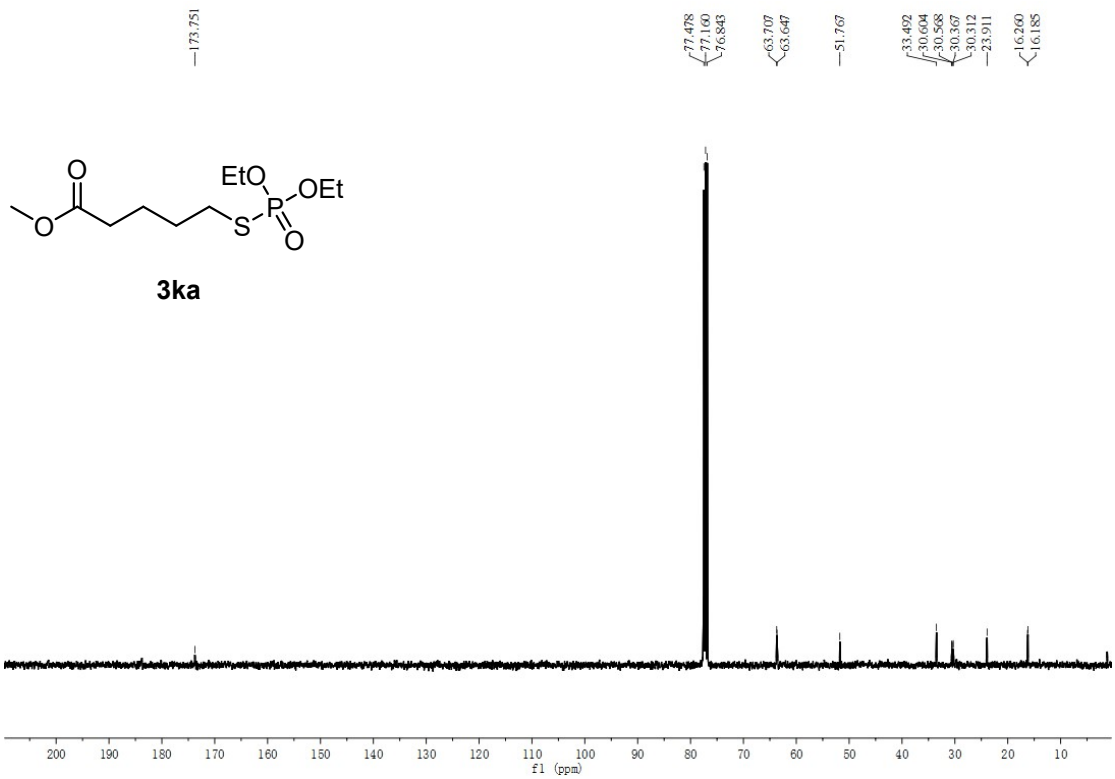


3ka

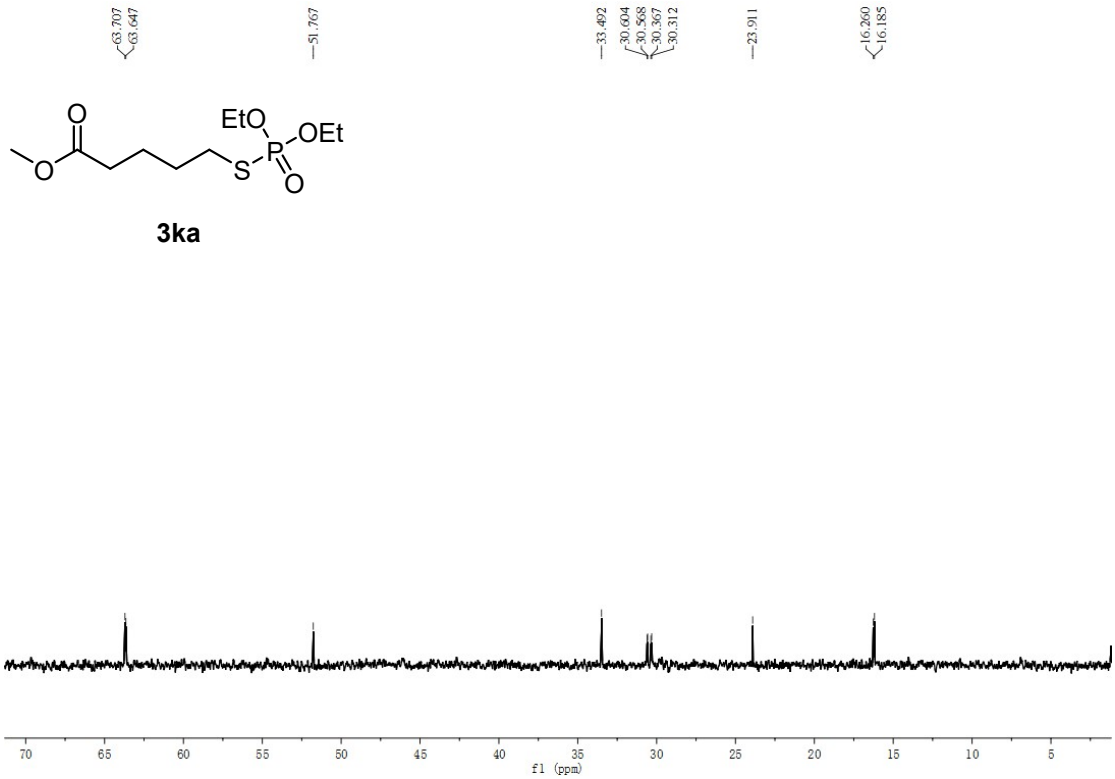


3ka



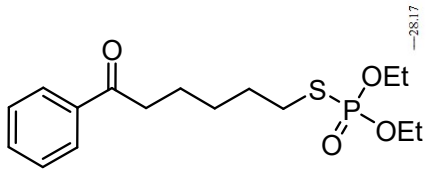

173.751
77.478
77.160
76.843
63.707
63.647
51.767
33.492
30.604
30.568
30.367
30.312
23.911
16.260
16.185
EtO
OEt
O
O
S
P
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3ka

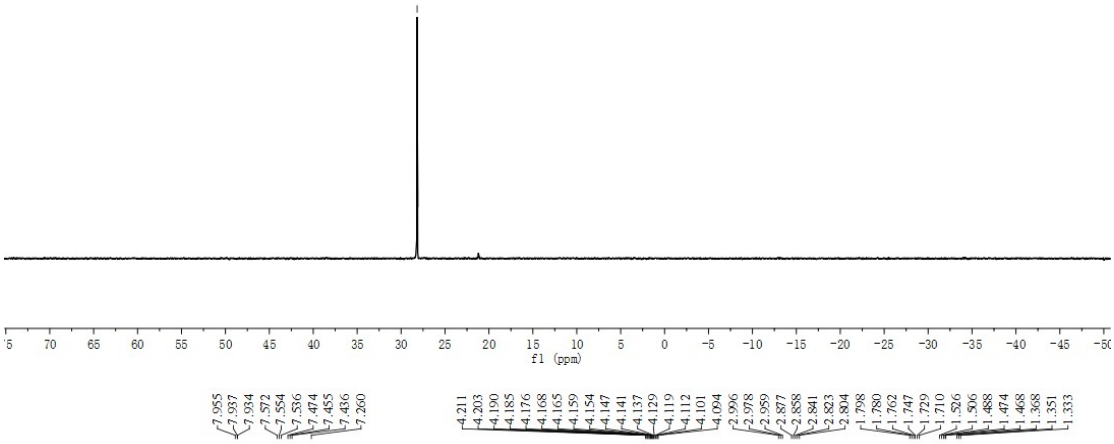

63.707
63.647
51.767
33.492
30.604
30.568
30.367
30.312
23.911
16.260
16.185
EtO
OEt
O
O
S
P
O
70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

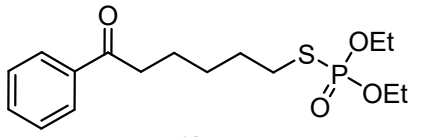
3ka

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3la**

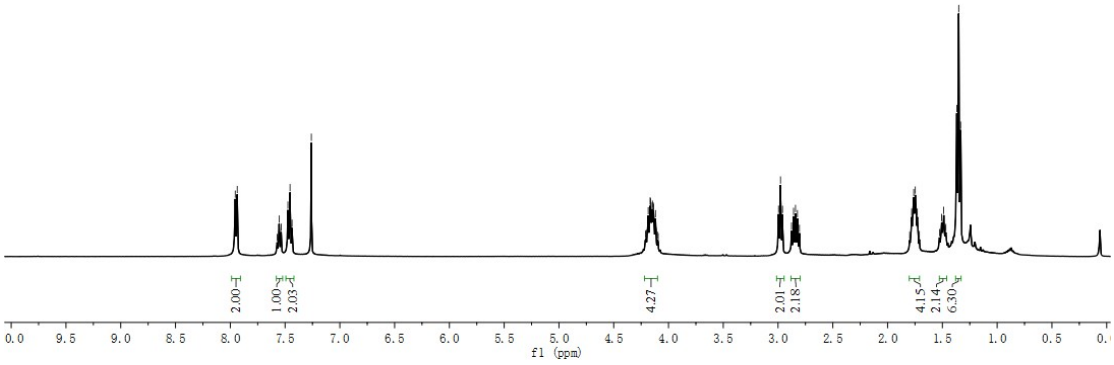


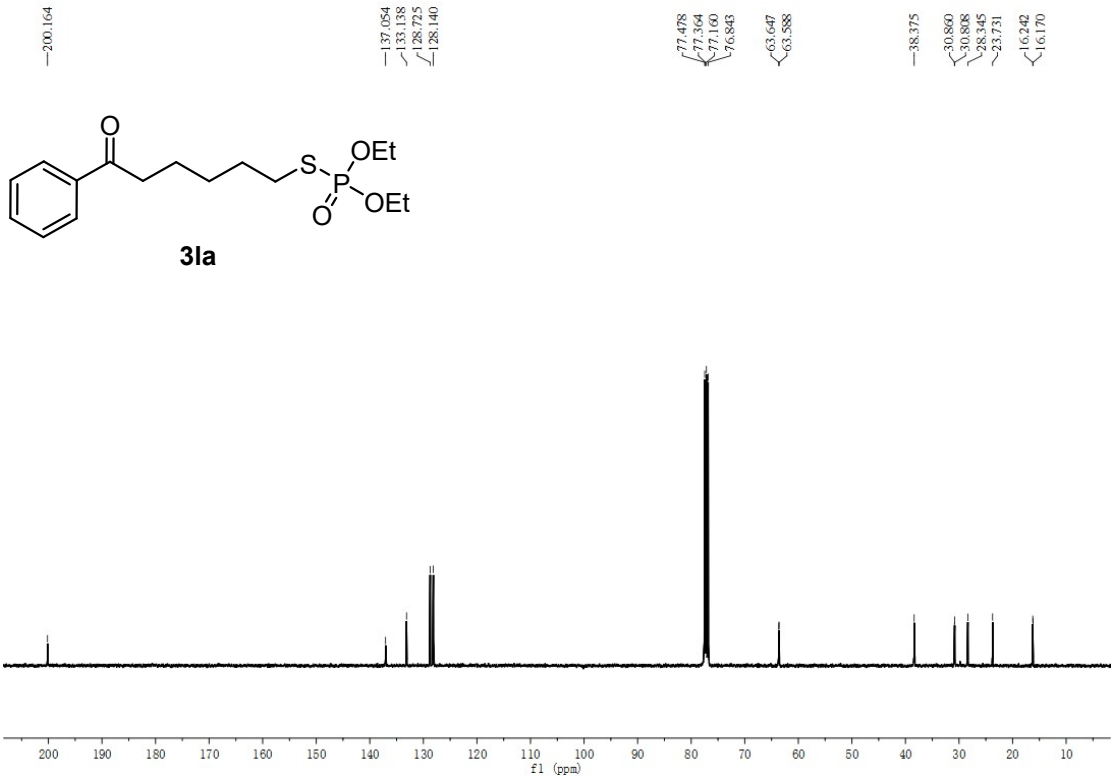
3la



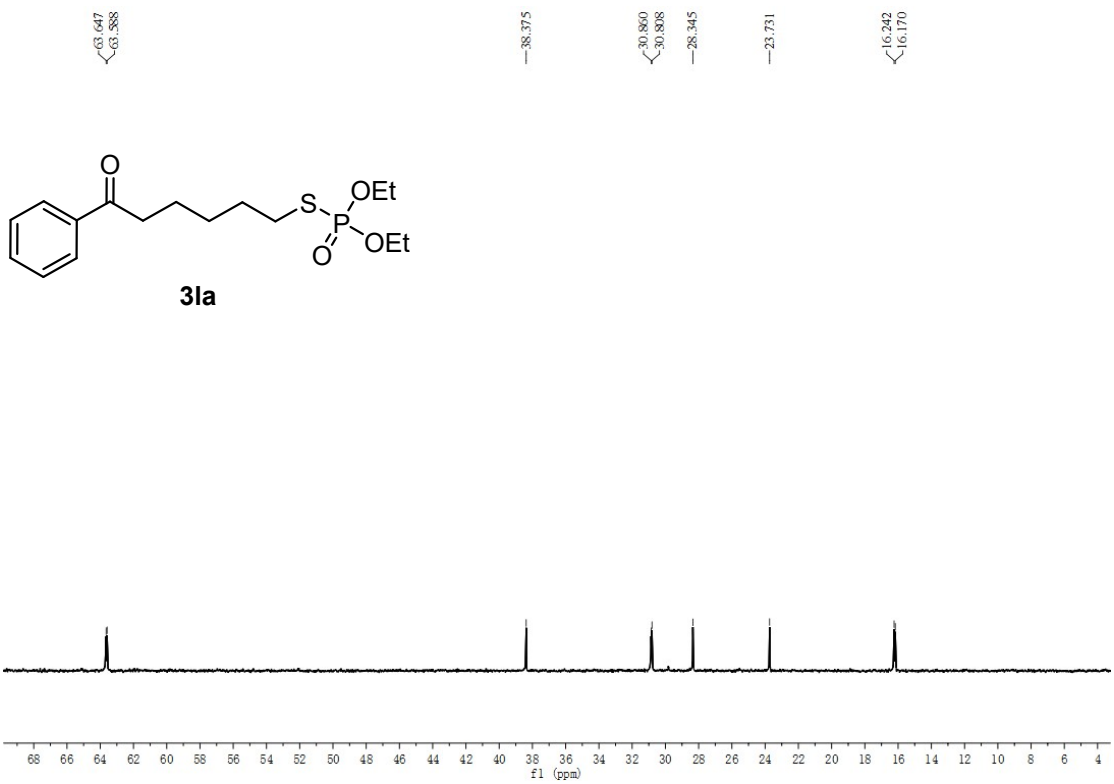


3la



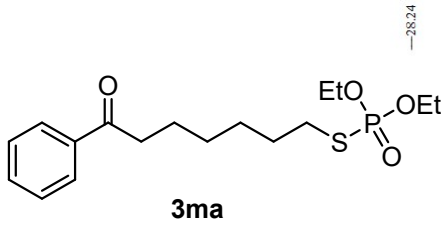

200.164
137.054
133.138
128.725
128.140
77.478
77.364
77.160
76.843
63.647
63.588
38.375
30.860
30.808
28.345
23.731
16.242
16.170
O
S
P
OEt
OEt
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3la

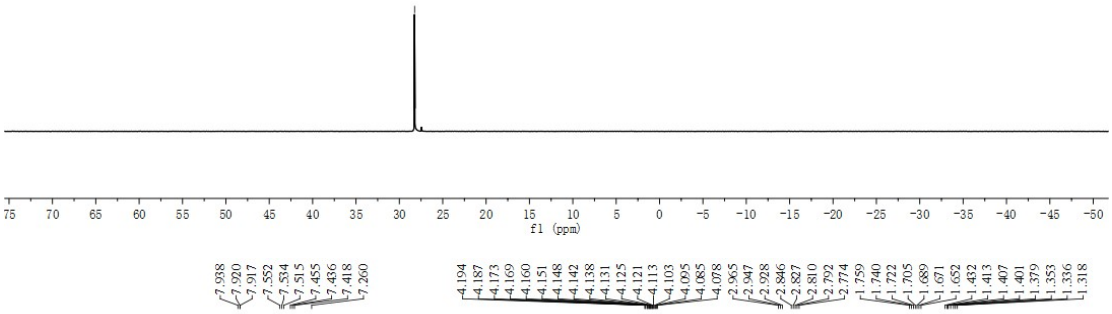

63.647
63.588
38.375
30.860
30.808
28.345
23.731
16.242
16.170
O
S
P
OEt
OEt
O
68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
f1 (ppm)

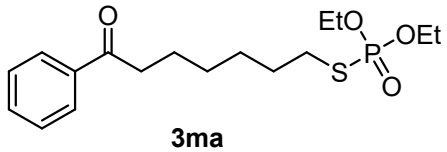
3la

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ma**

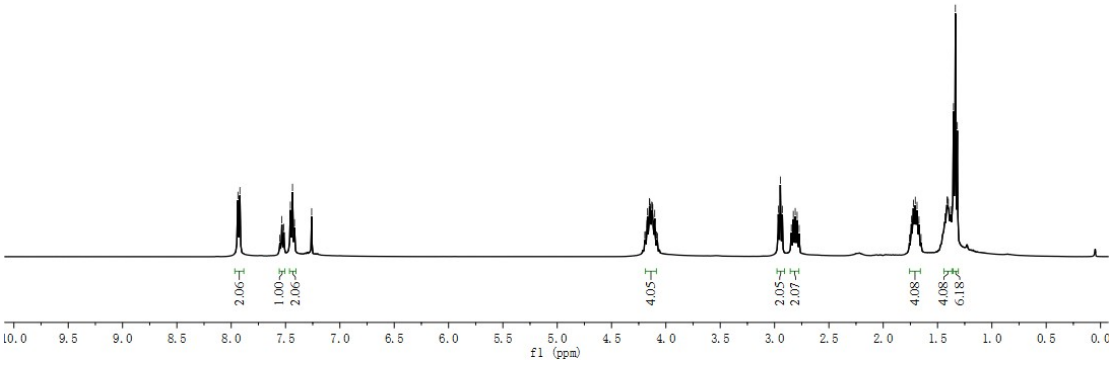


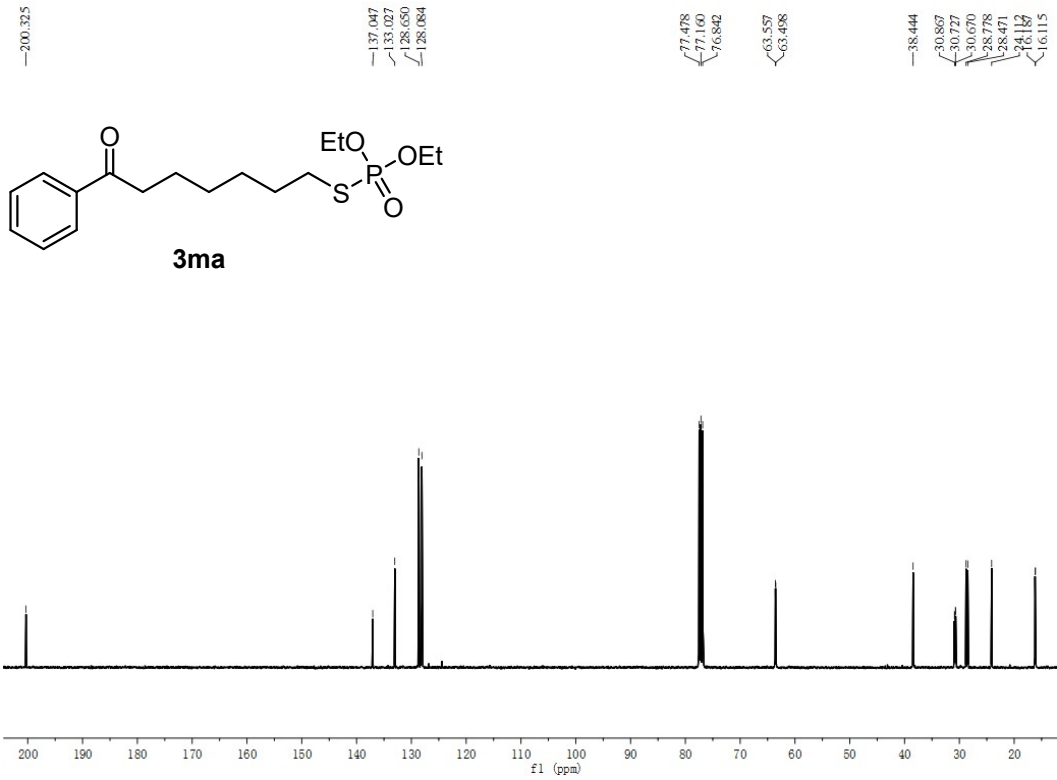
3ma

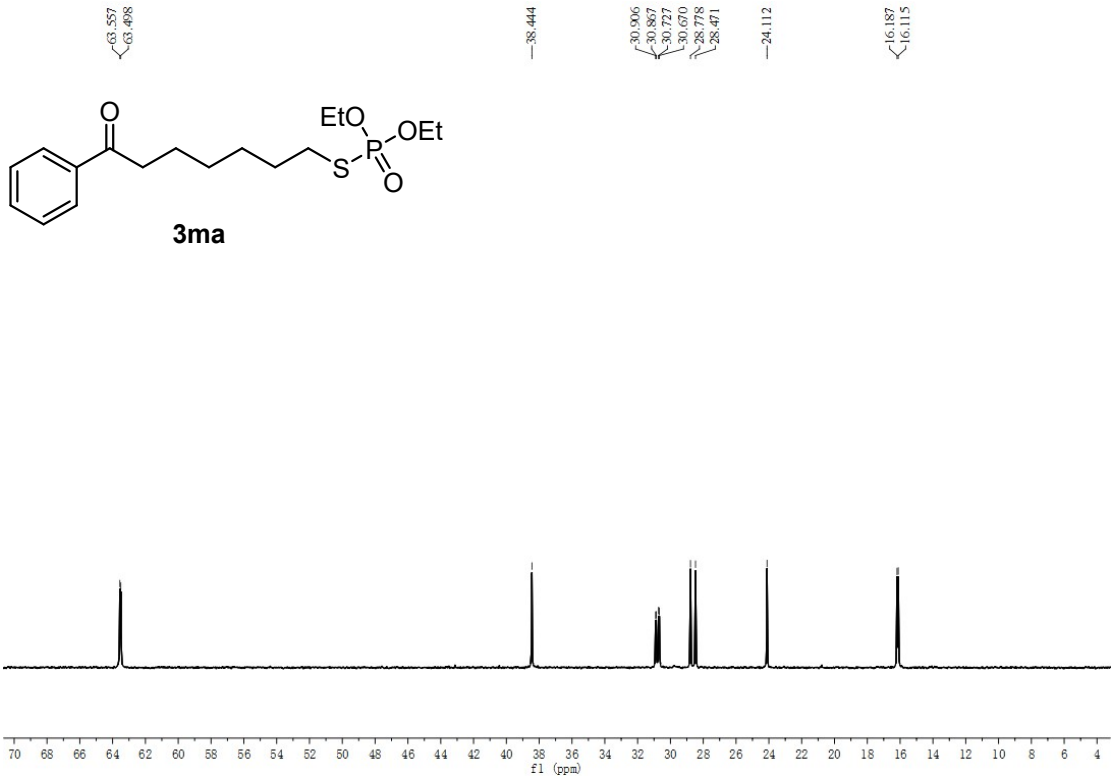




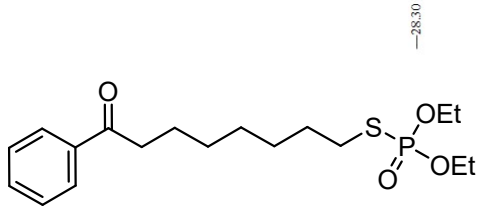
3ma



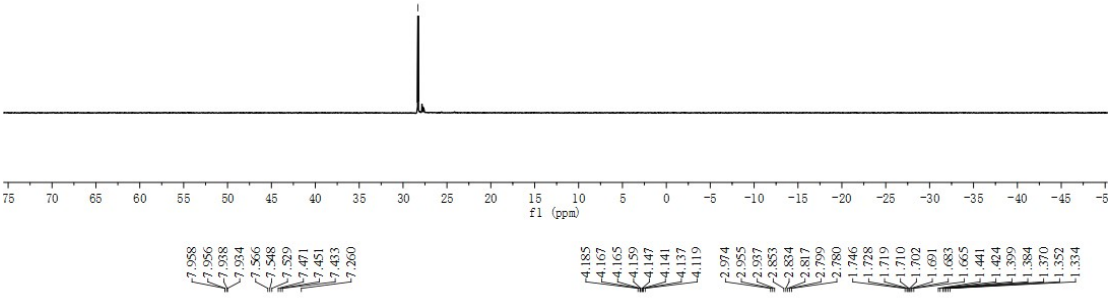

200.325
137.047
133.027
128.650
128.084
77.478
77.160
76.842
63.557
63.498
38.444
30.867
30.727
30.670
28.778
28.471
24.112
16.187
16.115
O
EtO
OEt
P
S
O
3ma
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

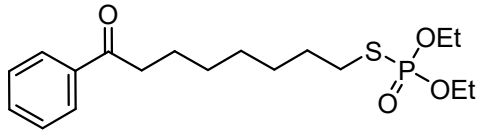

63.557
63.498
38.444
30.906
30.867
30.727
30.670
28.778
28.471
24.112
16.187
16.115
O
EtO
OEt
P
S
O
3ma
70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3na**

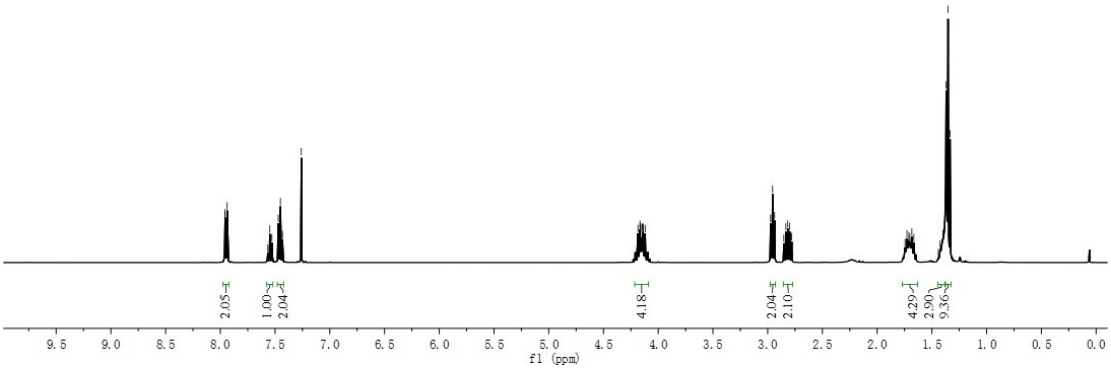


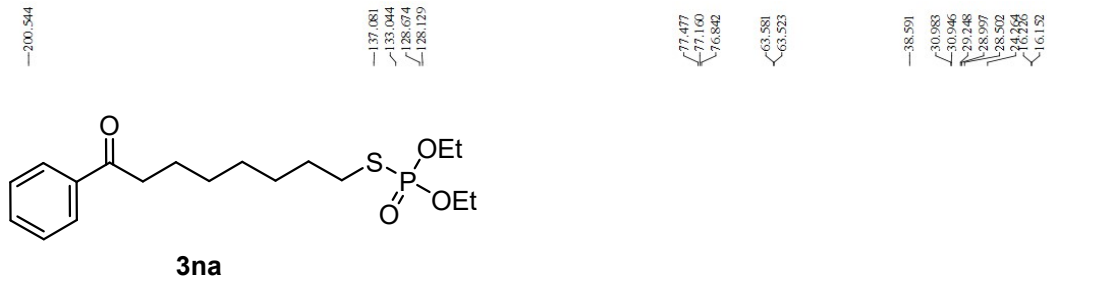
3na



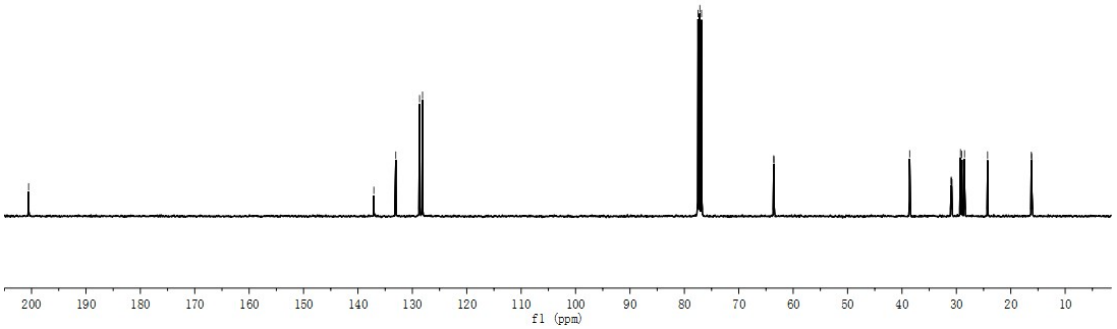


3na

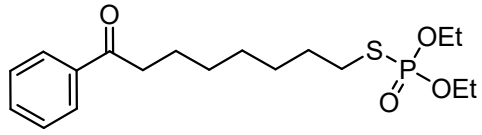



200.544
137.081
133.044
128.674
128.129
77.477
77.160
76.842
63.581
63.523
38.591
30.983
30.946
29.248
28.997
28.502
24.264
16.226
16.152
O
S
P
OEt
OEt
O

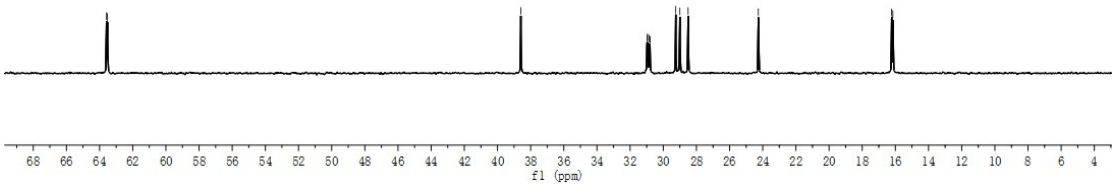
3na


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

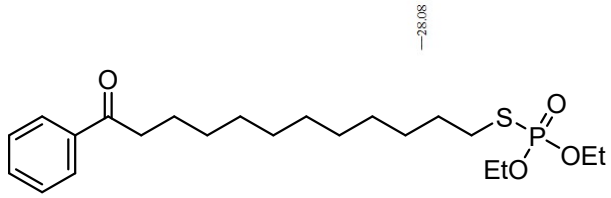

63.581
63.523
38.991
30.983
30.946
30.856
30.799
29.248
28.997
28.502
24.264
16.226
16.152


O
S
P
OEt
OEt
O

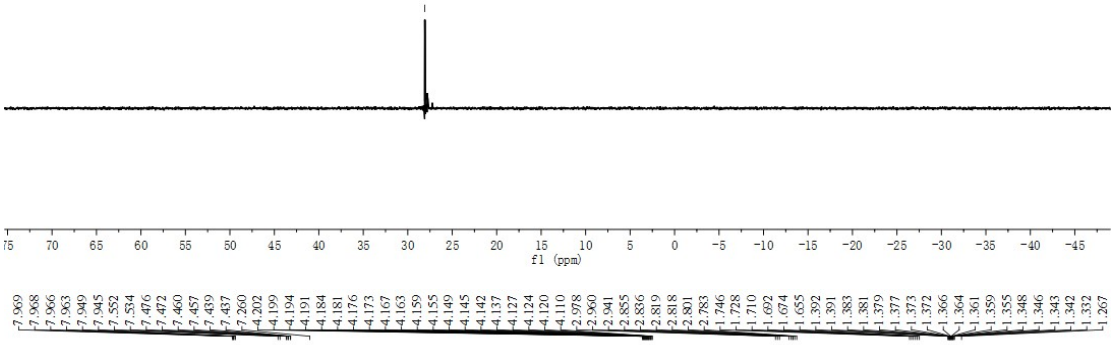
3na

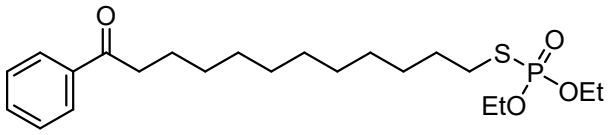

68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3oa**

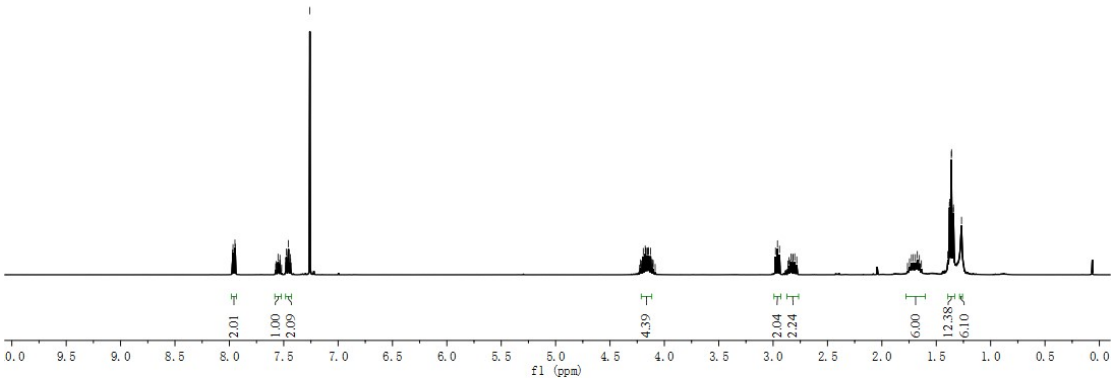


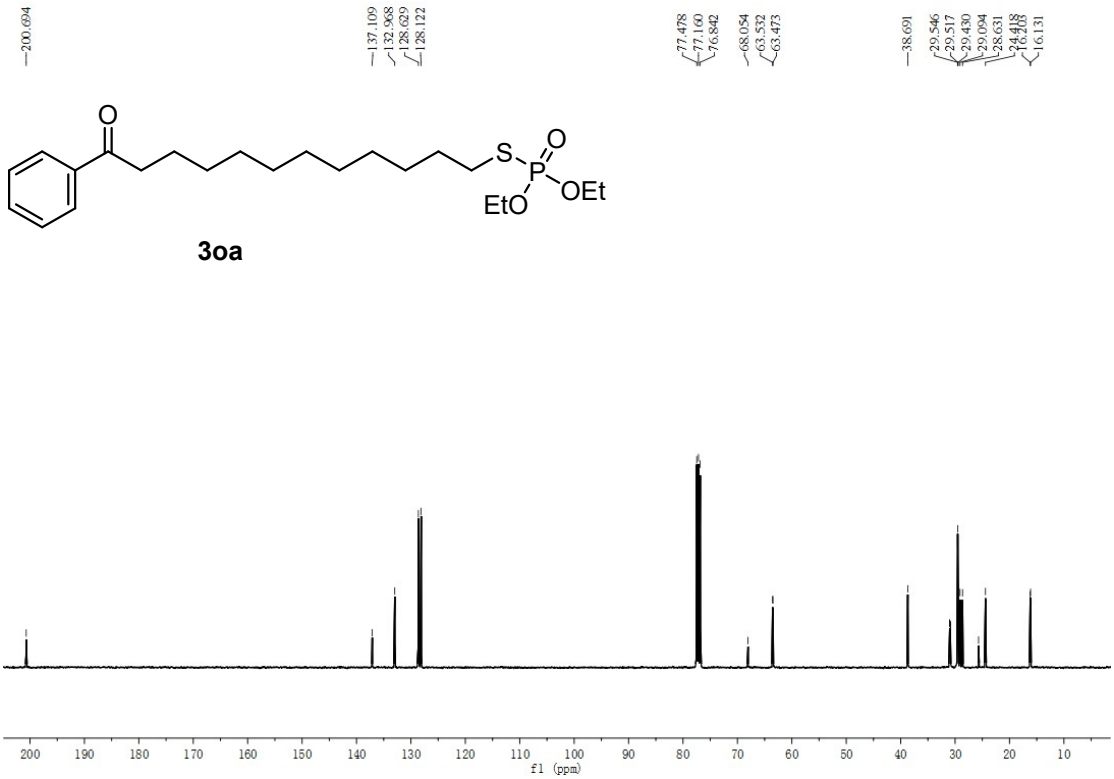
3oa



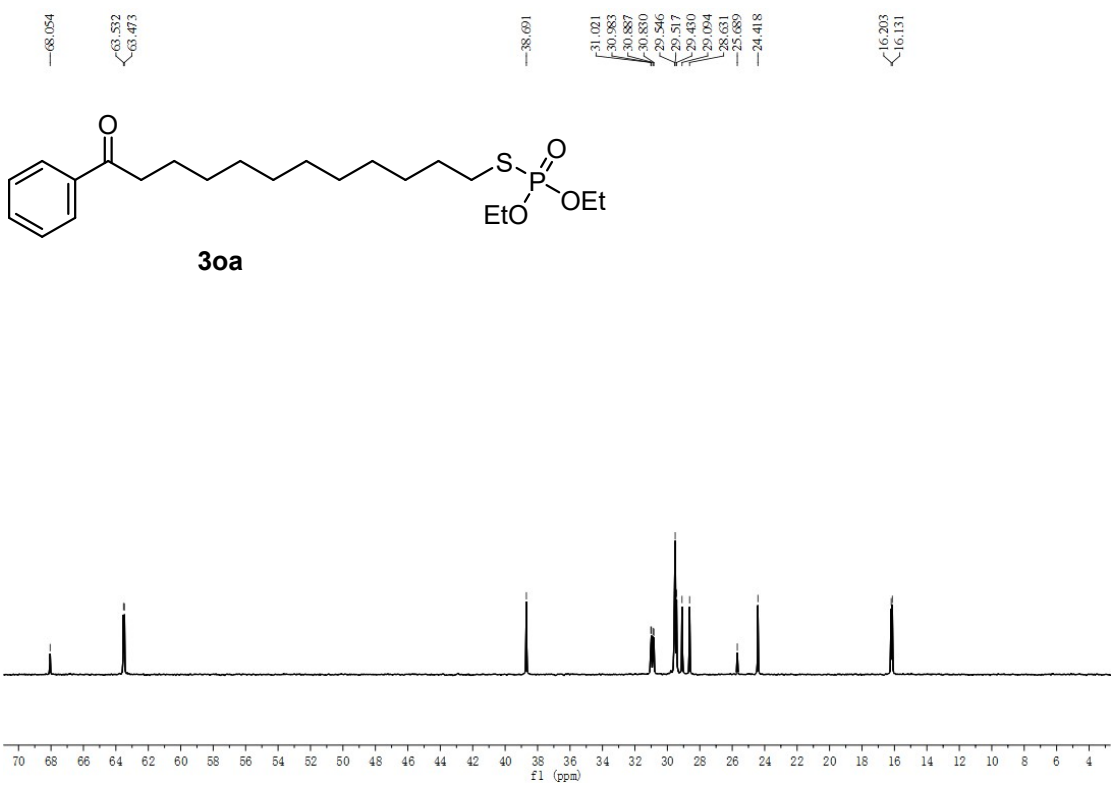


3oa



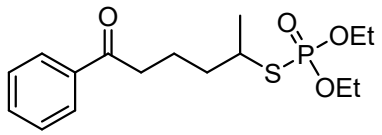

200.694
137.109
132.968
128.629
128.122
77.478
77.160
76.842
68.054
63.532
63.473
38.691
29.546
29.517
29.430
29.094
28.631
24.418
16.203
16.131
O
S
P
O
EtO
OEt
f1 (ppm)

3oa

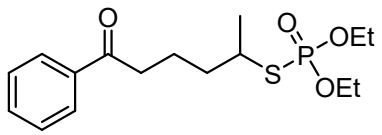

68.054
63.532
63.473
38.691
31.021
30.983
30.887
30.830
29.546
29.517
29.430
29.094
28.631
25.689
24.418
16.203
16.131
O
S
P
O
EtO
OEt
f1 (ppm)

3oa

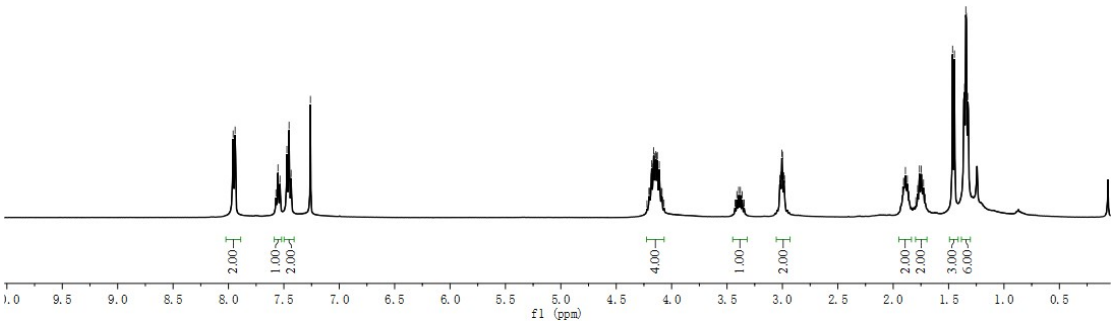
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3pa**

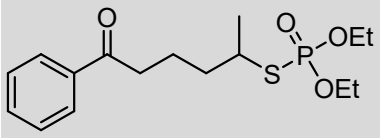


3pa

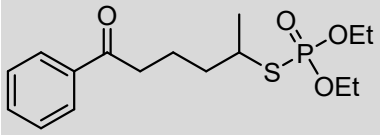


3pa



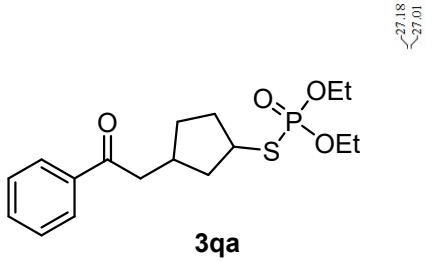


3pa

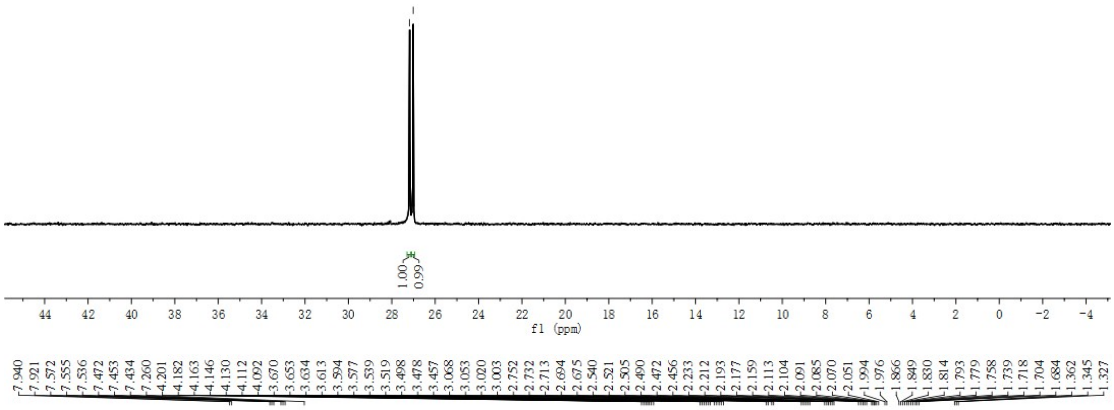


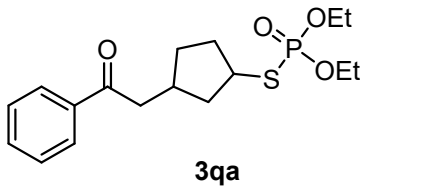
3pa

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3qa**

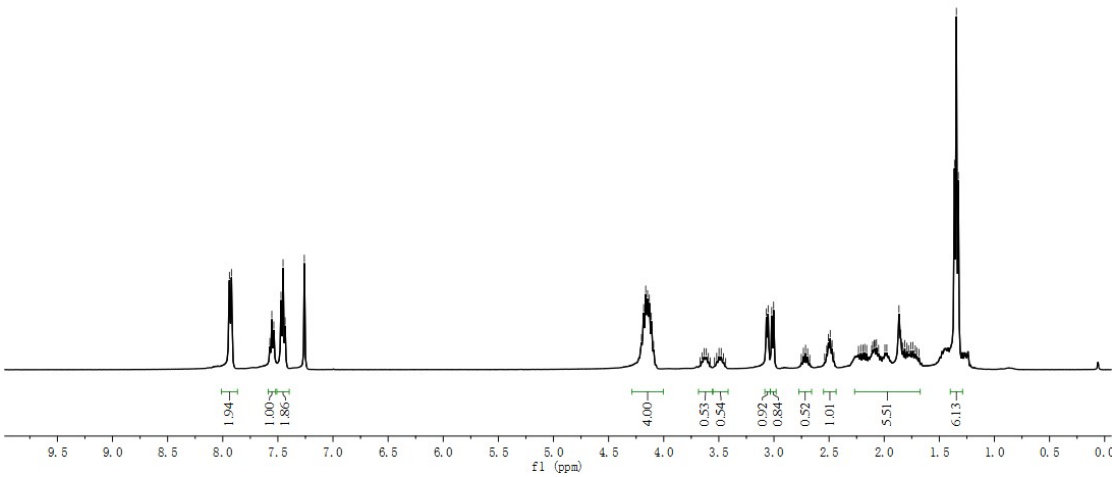


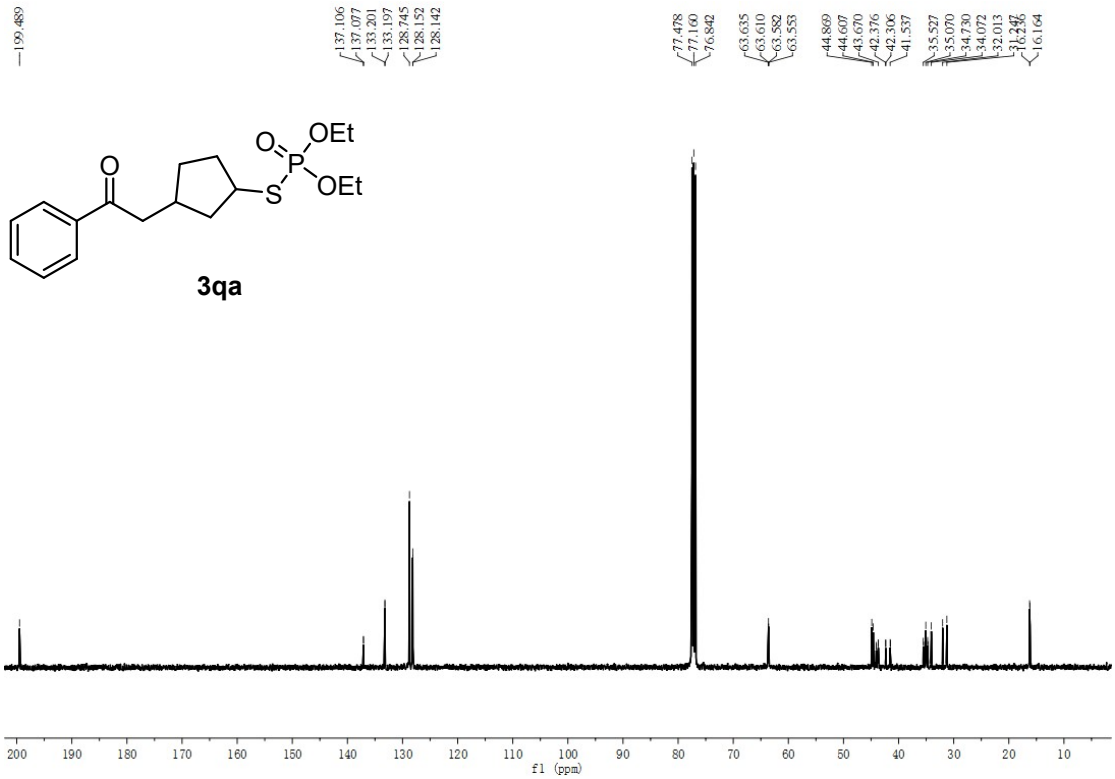
3qa

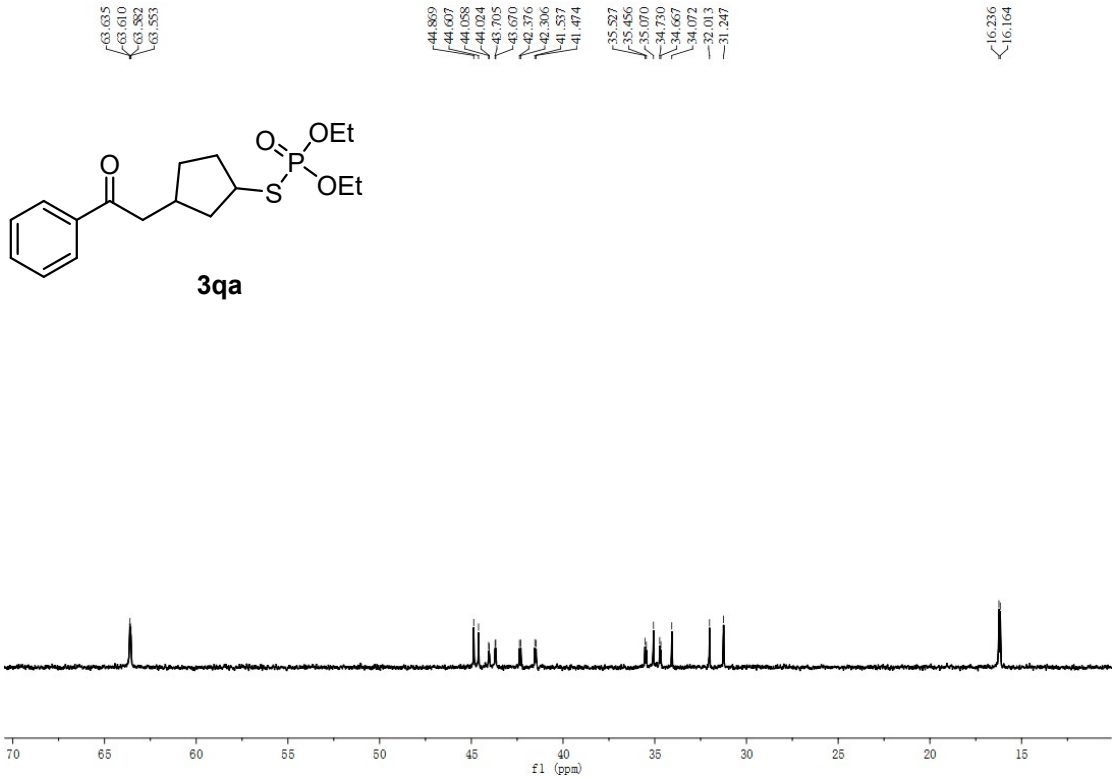




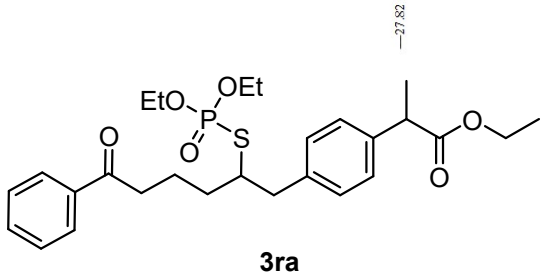
3qa



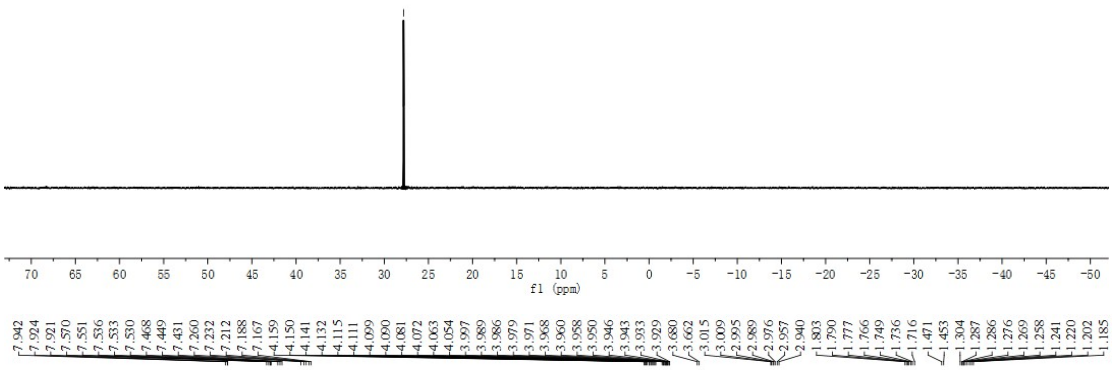

199.489
137.106
137.077
133.201
133.197
128.745
128.152
128.142
77.478
77.160
76.842
63.635
63.610
63.582
63.553
44.869
44.607
43.670
42.376
42.306
41.537
35.527
35.070
34.730
34.072
32.013
16.164
O
O
OEt
P
S
OEt
3qa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

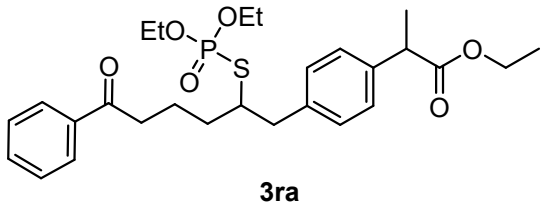

63.635
63.610
63.582
63.553
44.869
44.607
44.058
44.024
43.705
43.670
42.376
42.306
41.537
41.474
35.527
35.456
35.070
34.730
34.667
34.072
32.013
31.247
16.236
16.164
O
O
OEt
P
S
OEt
3qa
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ra**

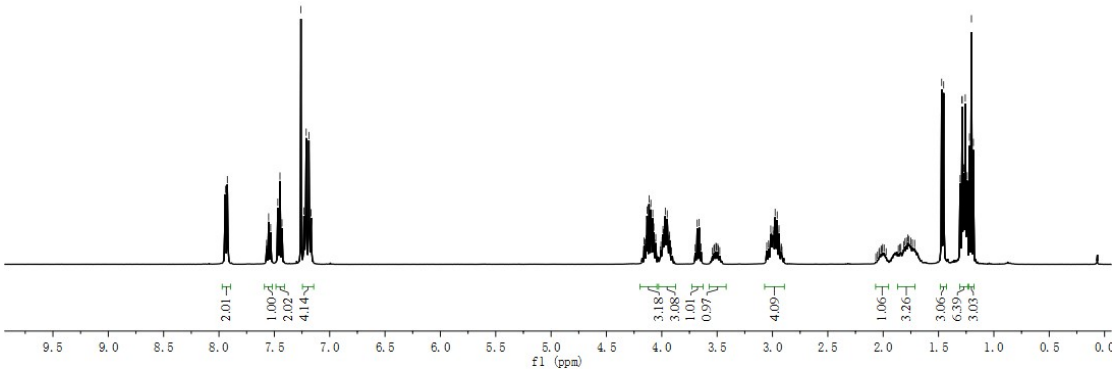


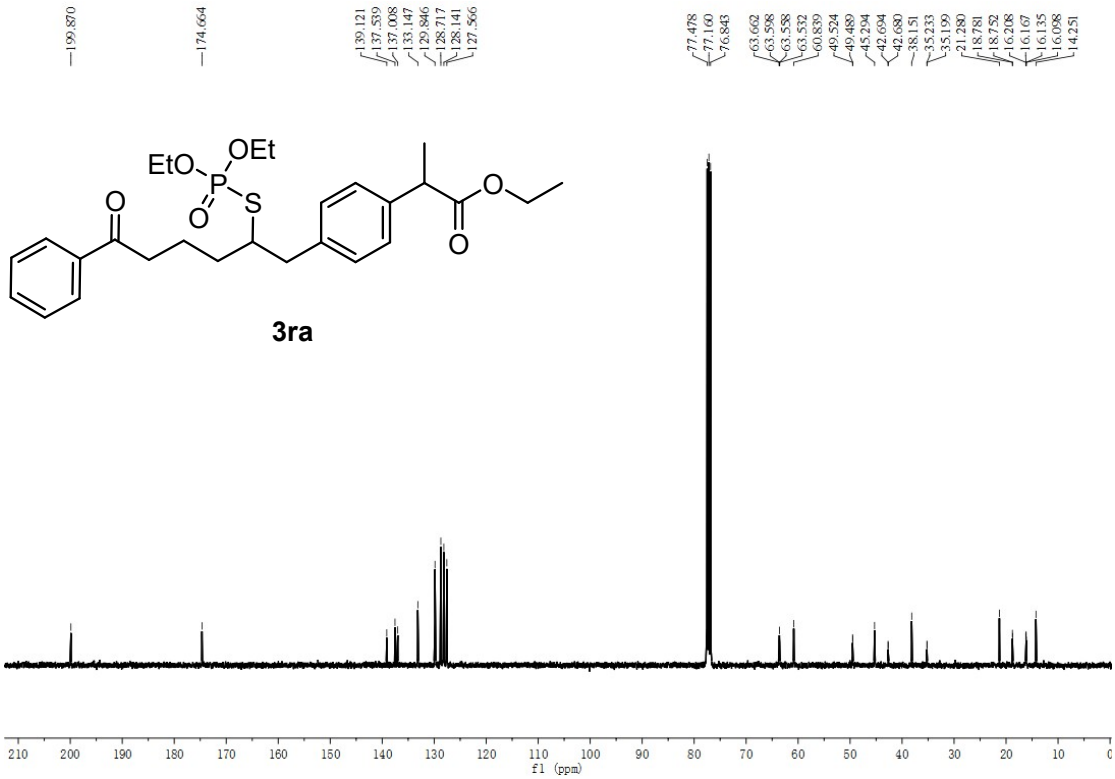
3ra



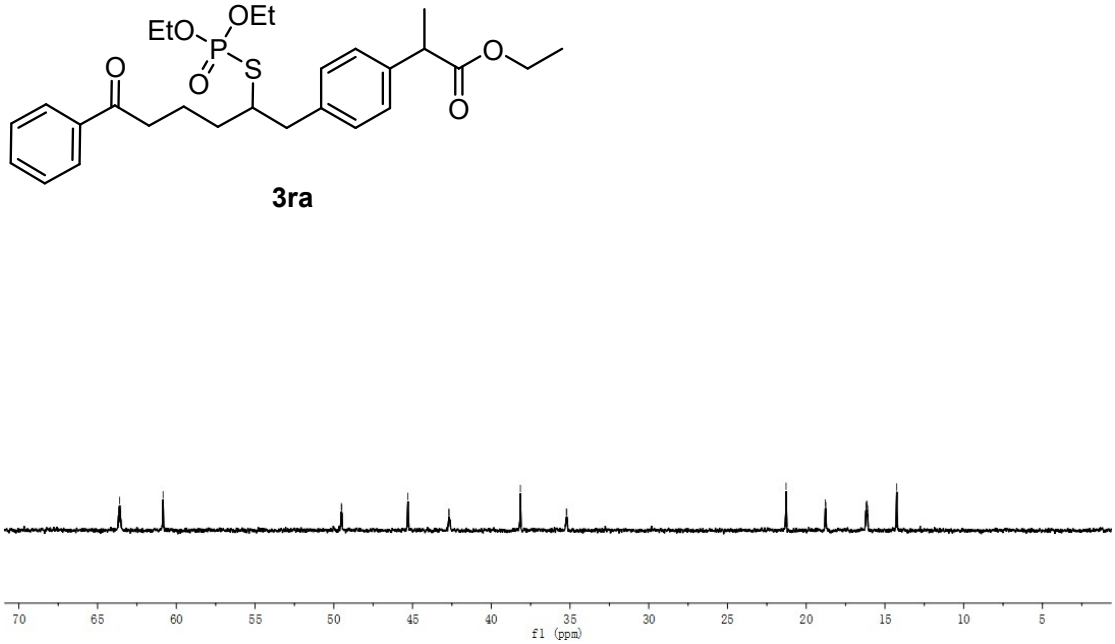


3ra



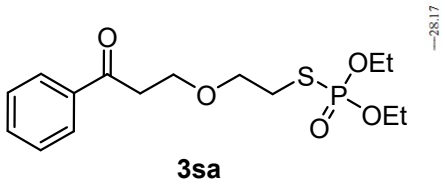

199.870
174.664
139.121
137.539
137.008
133.147
129.846
128.717
128.141
127.566
77.478
77.160
76.843
63.662
63.598
63.538
63.532
60.839
49.524
49.489
45.294
42.694
42.680
38.151
35.233
35.199
21.280
18.781
18.752
16.208
16.167
16.135
16.098
14.251
EtO
OEt
P
S
O
O
O
O
f1 (ppm)

3ra

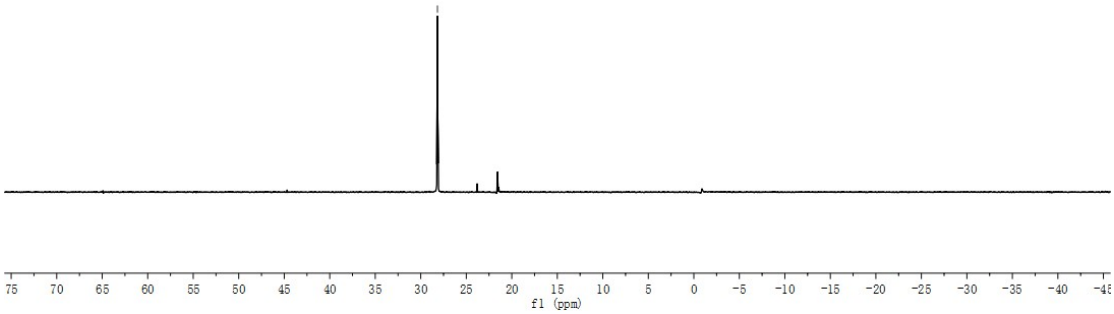

63.662
63.598
63.558
63.532
60.839
49.524
49.489
45.294
42.694
42.680
38.151
35.233
35.199
21.280
18.781
18.752
16.208
16.167
16.135
16.098
14.251
EtO
OEt
P
S
O
O
O
O
f1 (ppm)

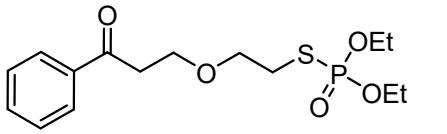
3ra

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3sa**

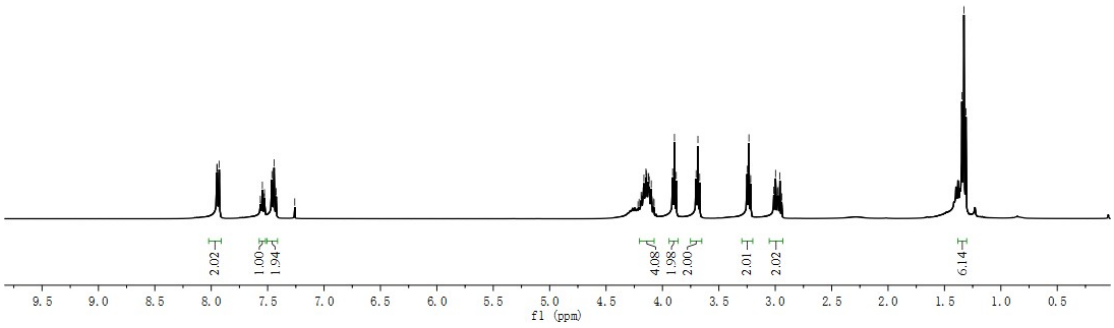


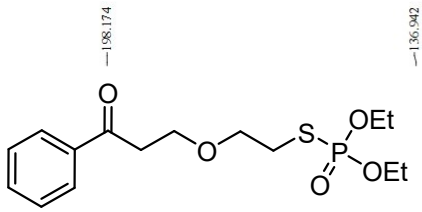
3sa



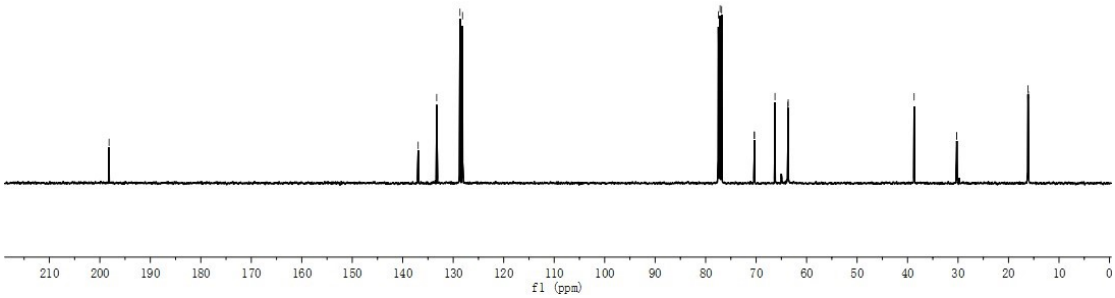


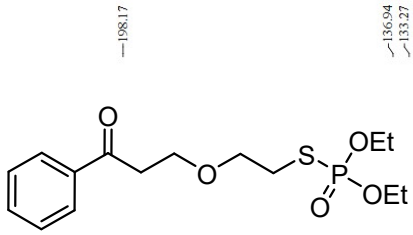
3sa



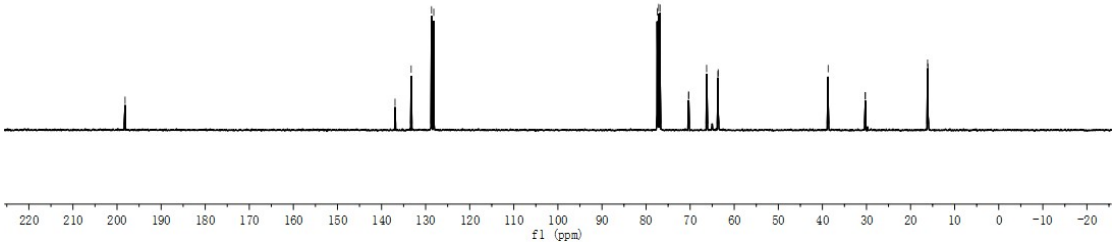

198.174
136.942
133.275
128.664
128.158
77.459
77.140
76.822
70.371
70.324
66.260
63.706
63.647
38.699
30.287
30.250
16.138
16.067
O
O
S
P
OEt
OEt
O

3sa

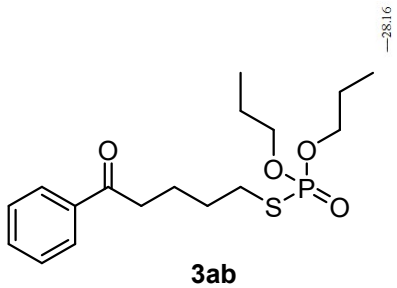

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


198.17
136.94
133.27
128.66
128.16
77.46
77.14
76.82
70.37
70.32
66.26
63.71
63.65
38.70
30.29
30.25
16.14
16.07
O
O
S
P
OEt
OEt
O

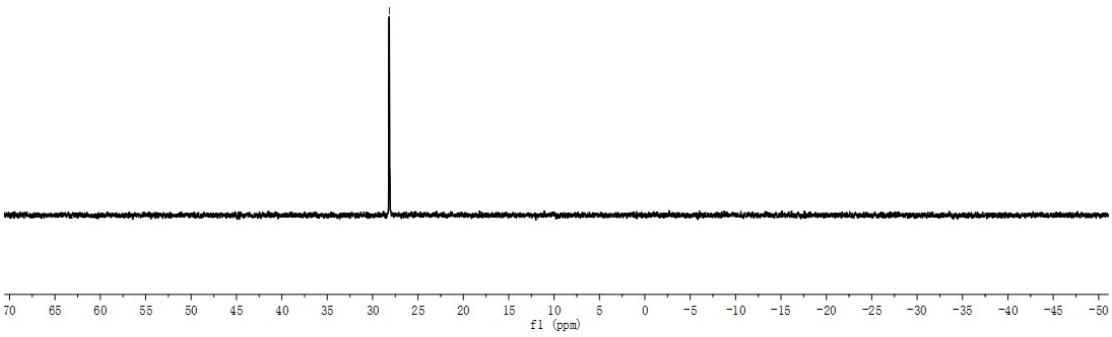
3sa

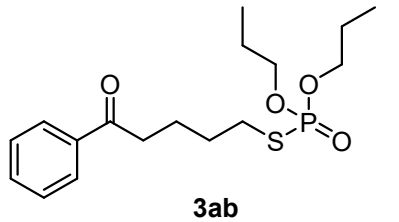

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ab**

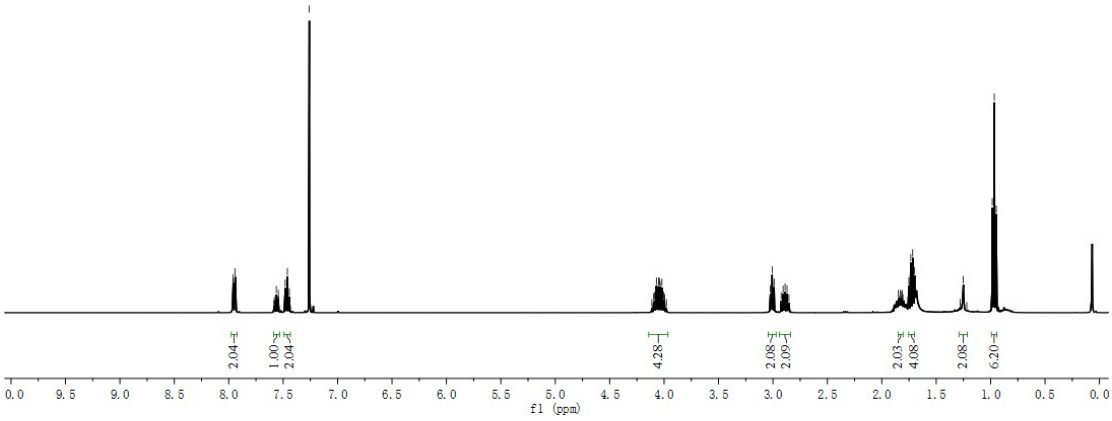


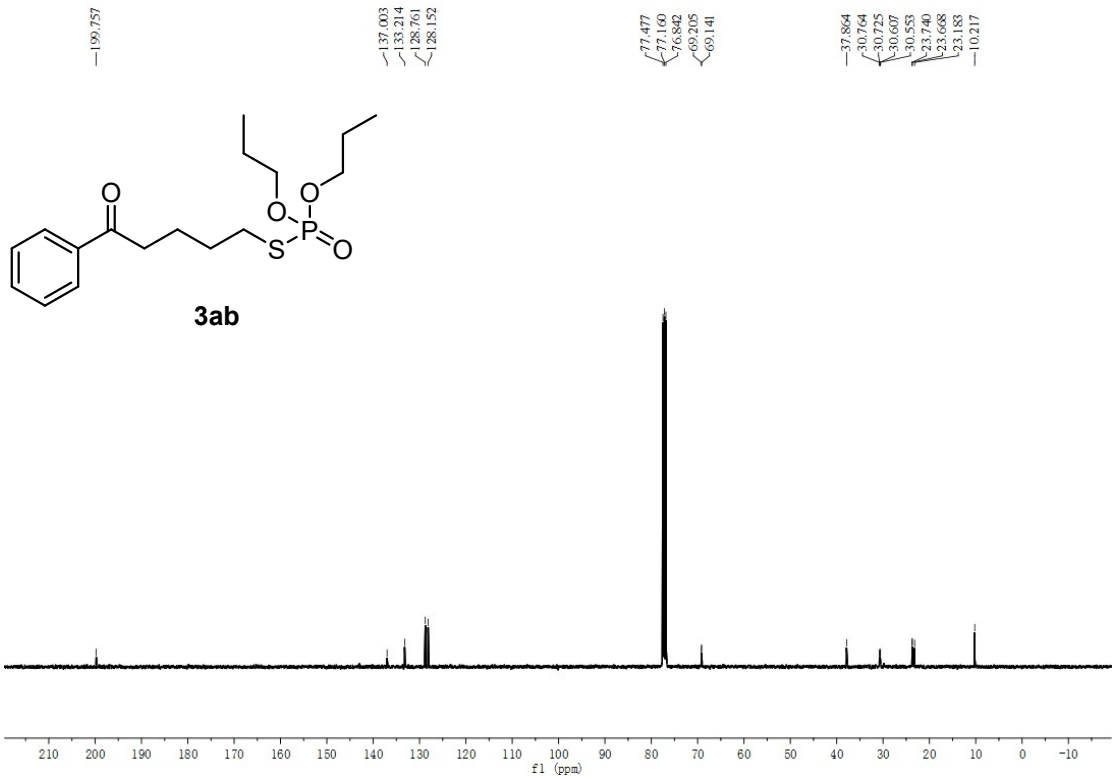
3ab

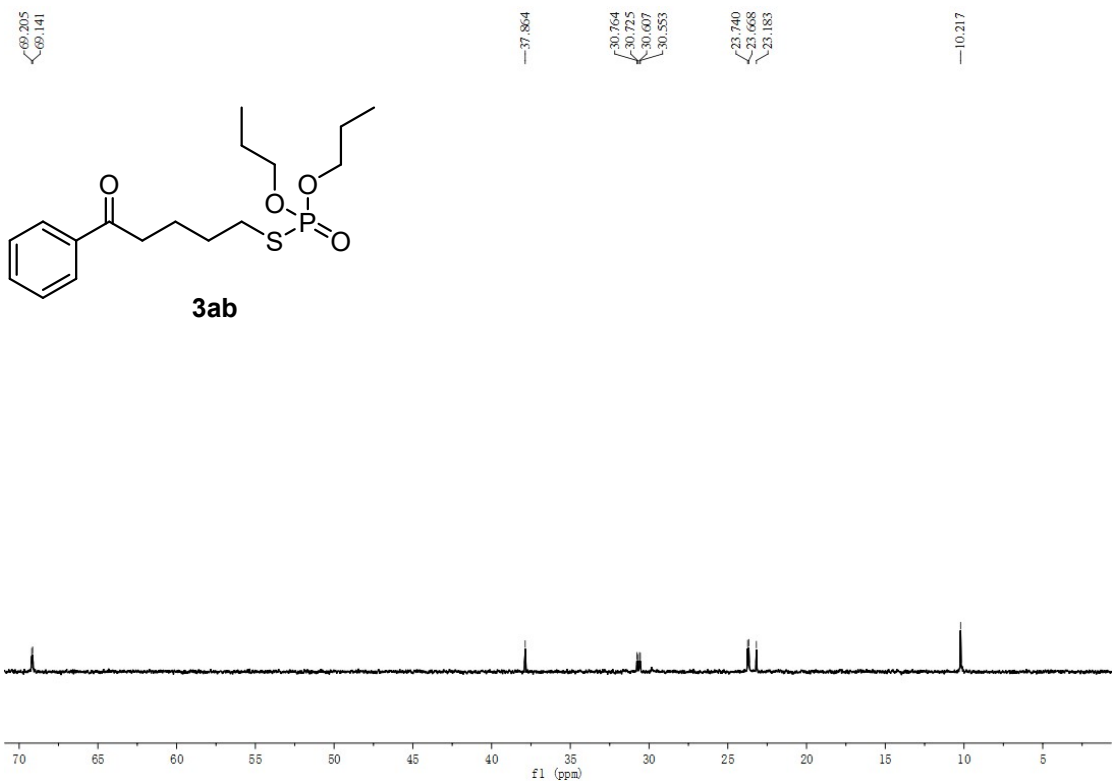




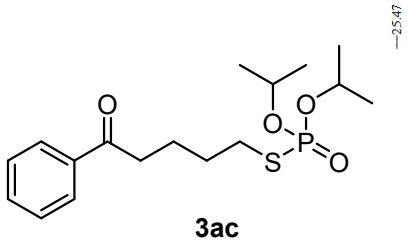
3ab



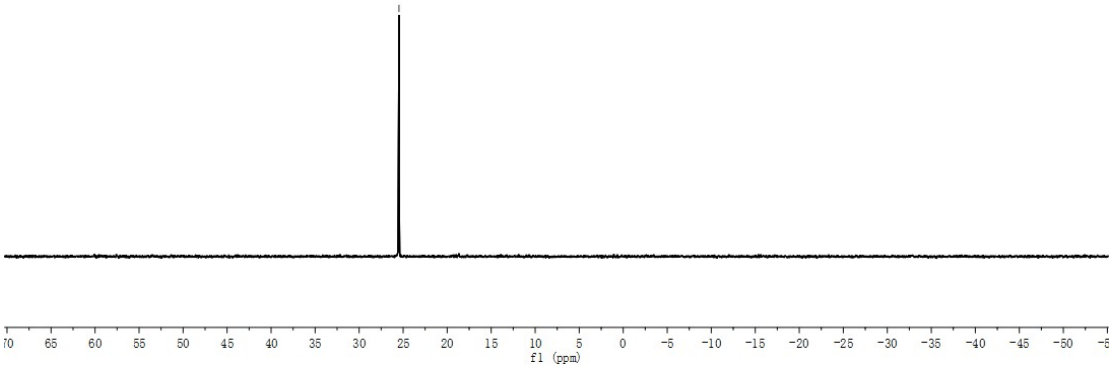

199.757
137.003
133.214
128.761
128.152
77.477
77.160
76.842
69.205
69.141
37.864
30.764
30.725
30.607
30.553
23.740
23.668
23.183
10.217
O
O
O
P
O
S
3ab
f1 (ppm)

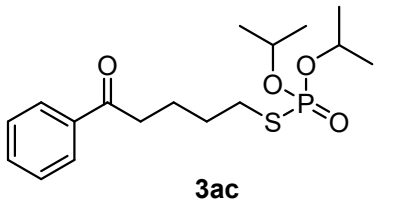

69.205
69.141
37.864
30.764
30.725
30.607
30.553
23.740
23.668
23.183
10.217
O
O
O
P
O
S
3ab
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ac**

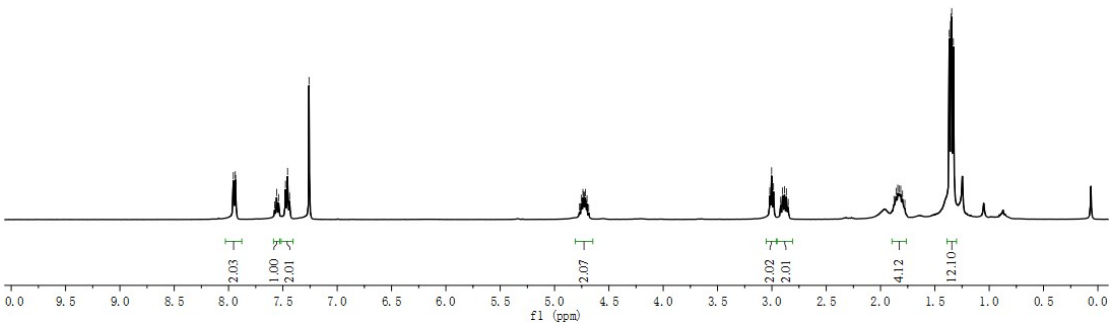


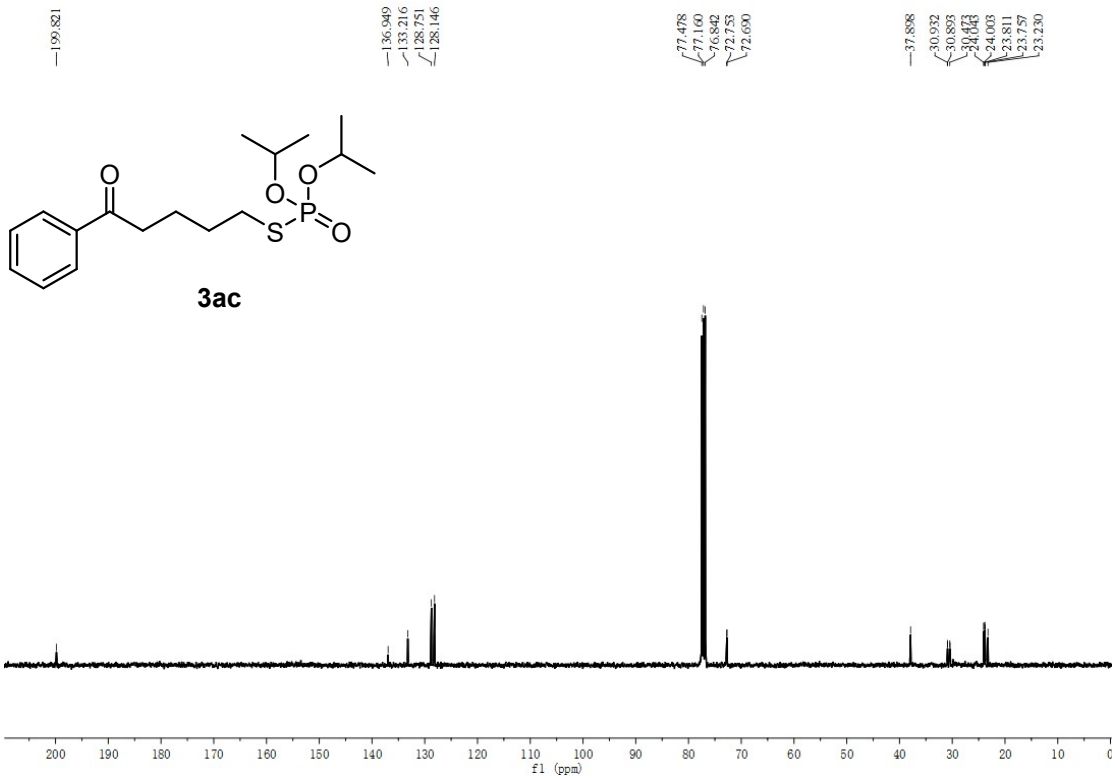
3ac

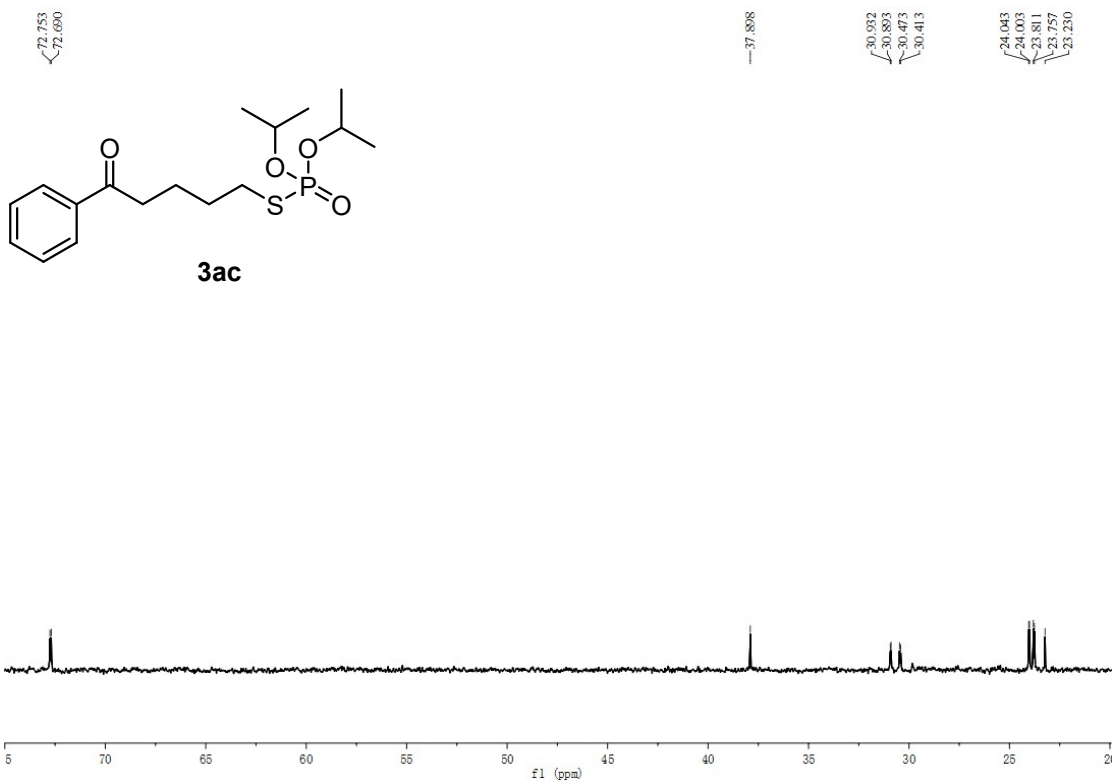




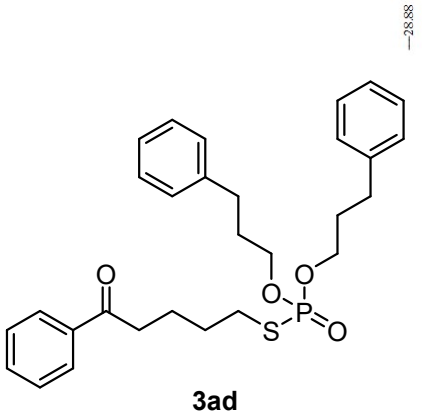
3ac



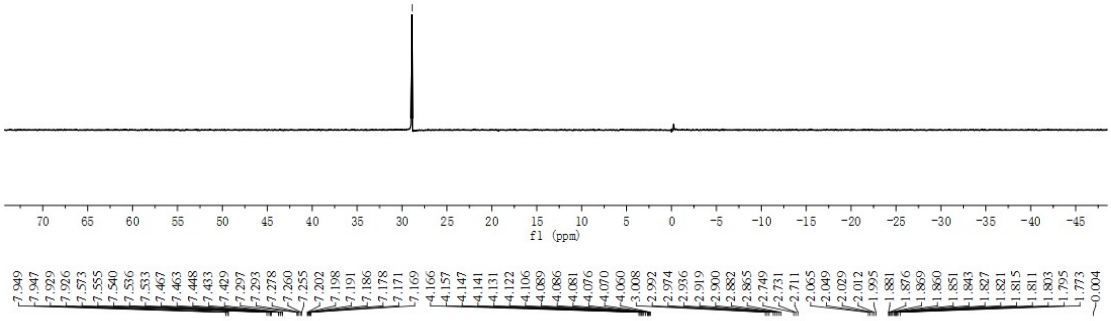

199.821
136.949
133.216
128.751
128.146
77.478
77.160
76.842
72.753
72.690
37.898
30.932
30.893
30.473
30.413
24.043
24.003
23.811
23.757
23.230
O
O
O
P
S
O
3ac
f1 (ppm)

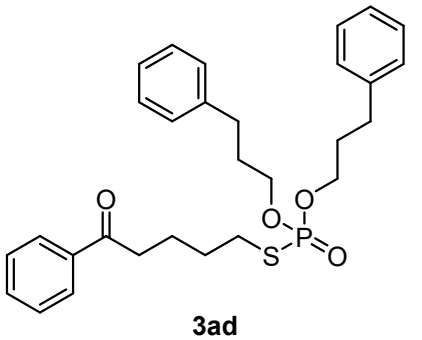

72.753
72.690
37.898
30.932
30.893
30.473
30.413
24.043
24.003
23.811
23.757
23.230
O
O
O
P
S
O
3ac
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ad**

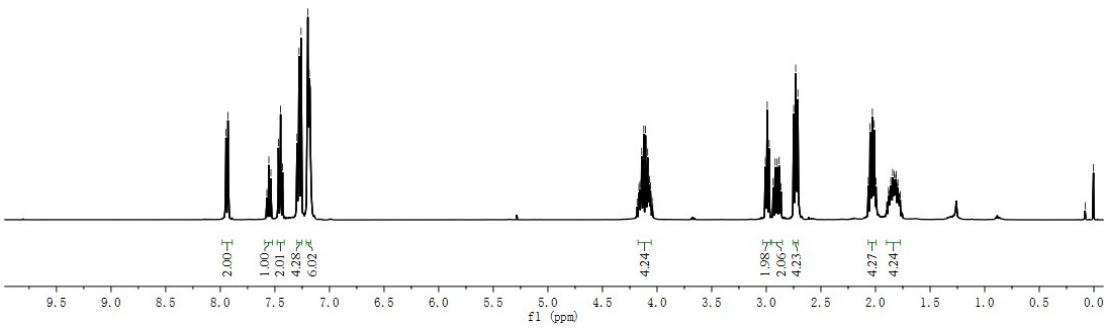


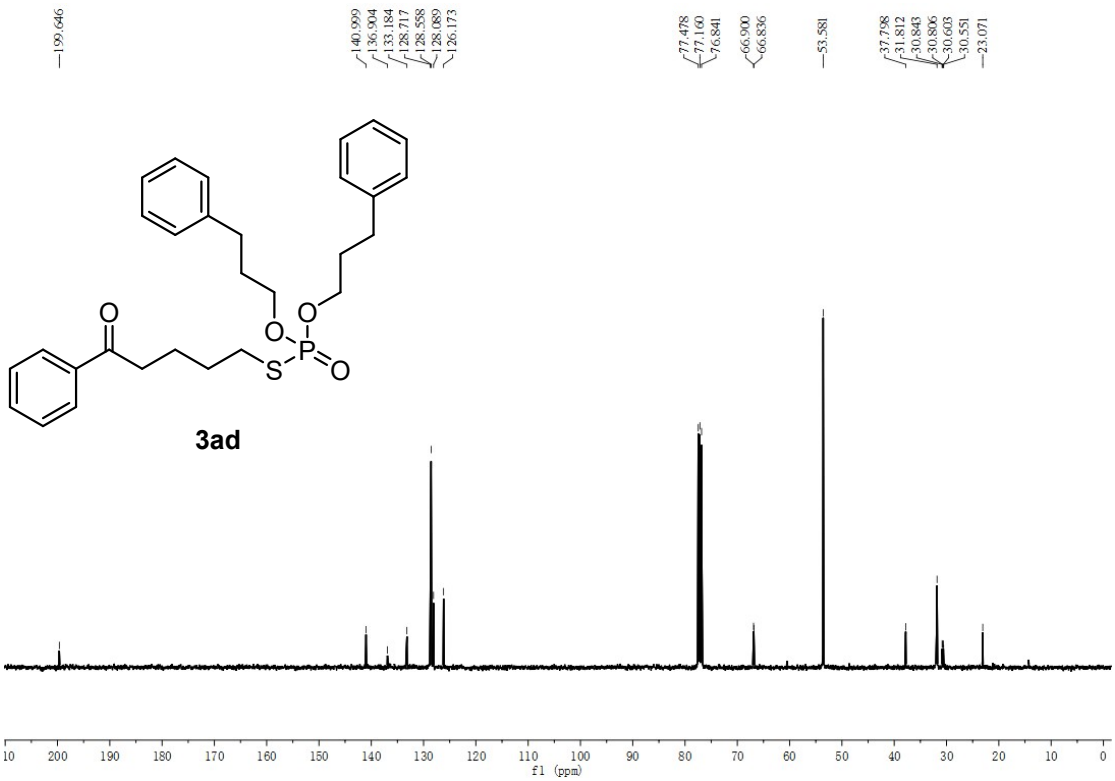
3ad

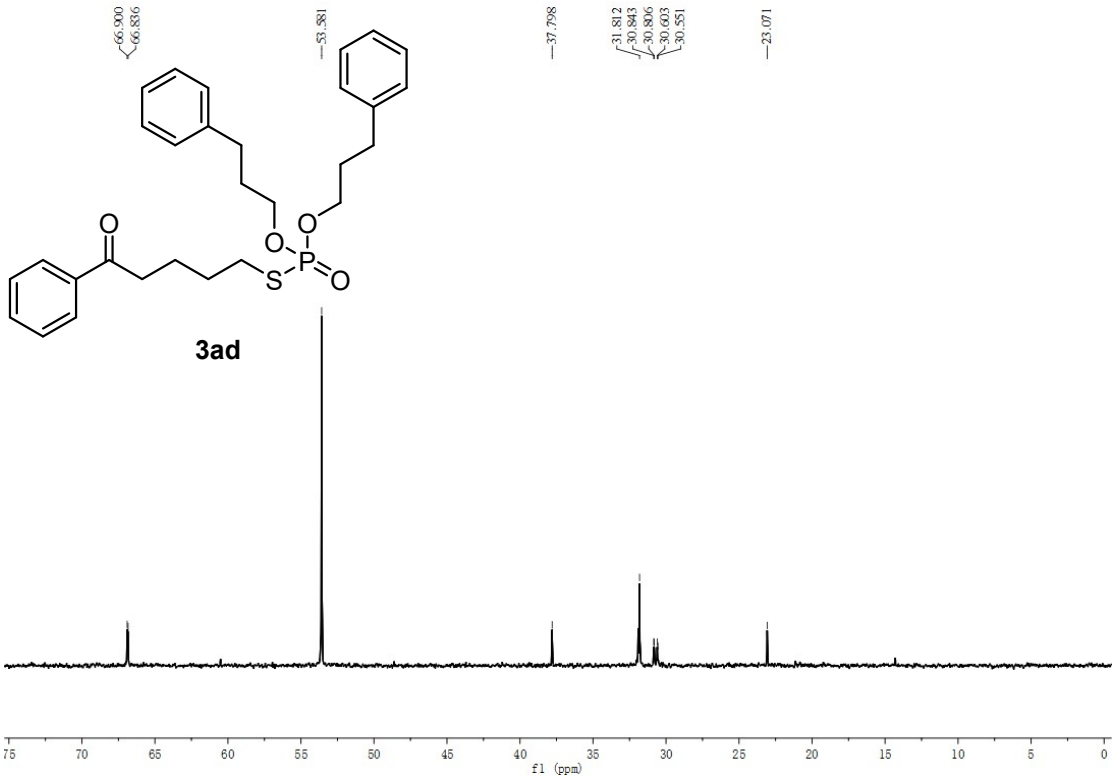




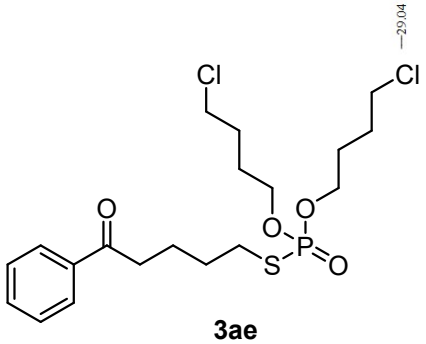
3ad



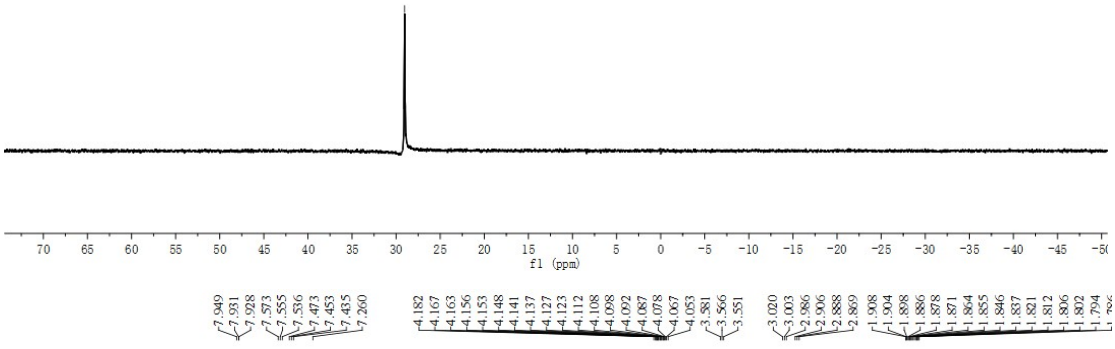

199.646
140.999
136.904
133.184
128.717
128.558
128.089
126.173
77.478
77.160
76.841
66.900
66.836
53.581
37.798
31.812
30.843
30.806
30.603
30.551
23.071
3ad
f1 (ppm)

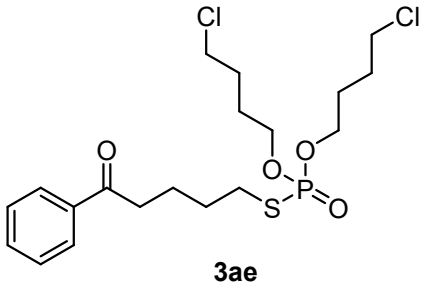

66.900
66.836
53.581
37.798
31.812
30.843
30.806
30.603
30.551
23.071
3ad
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ae**

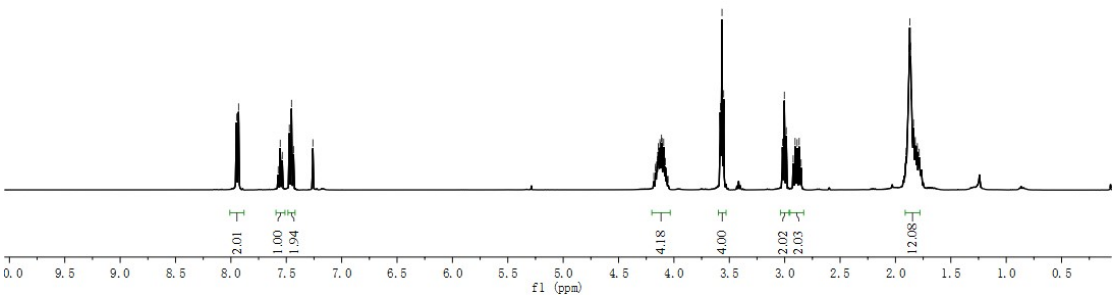


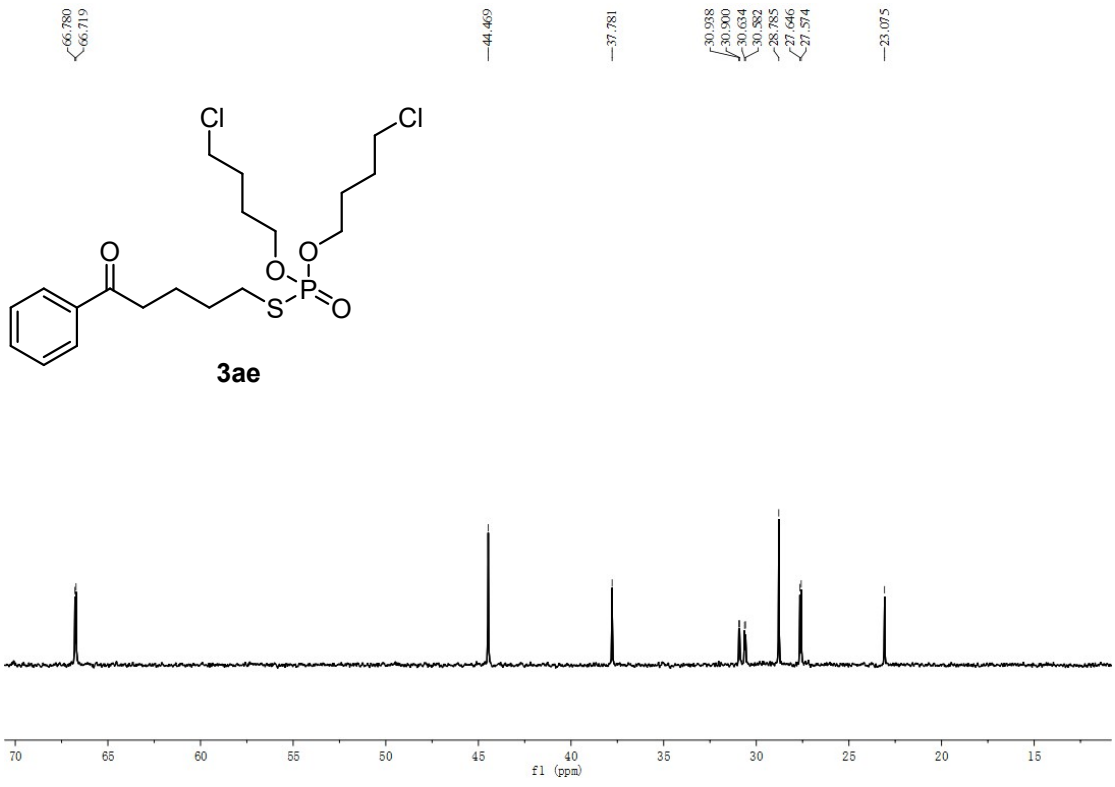
3ae



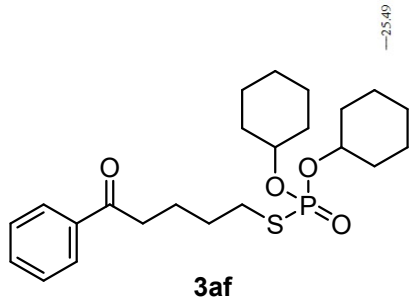


3ae

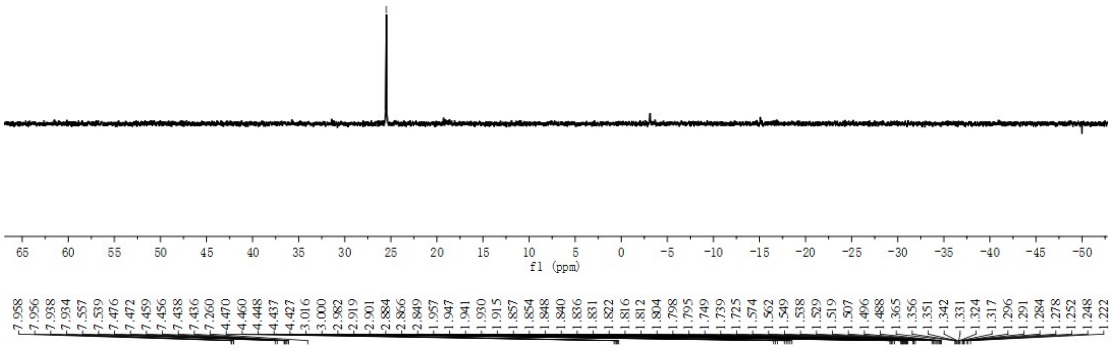


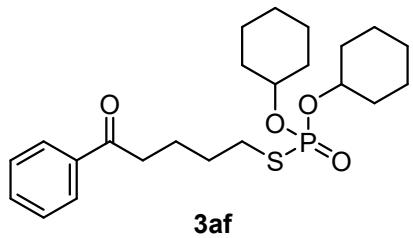

66.780
66.719
44.469
37.781
30.938
30.900
30.634
30.382
28.785
27.646
27.574
23.075
Cl
Cl
O
O
O
P
S
O
3ae
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3af**

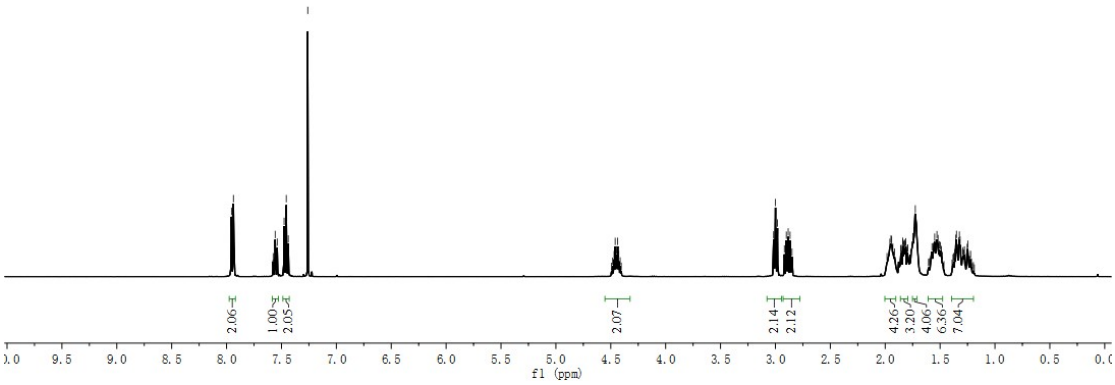


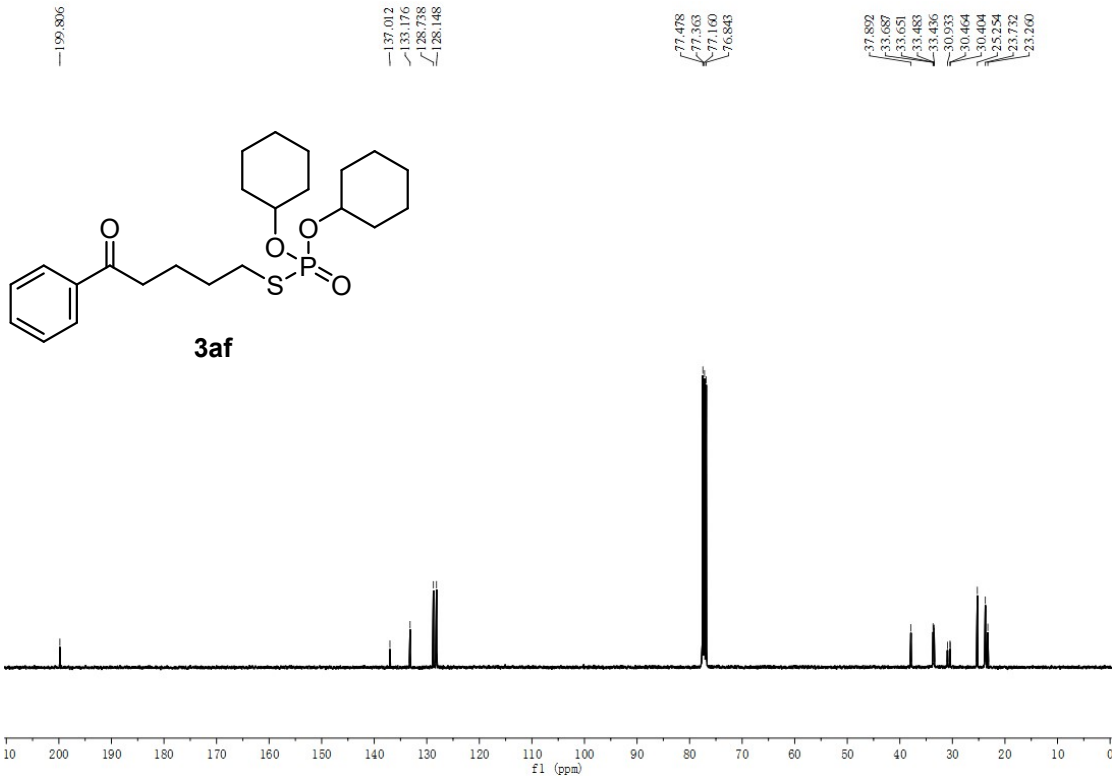
3af

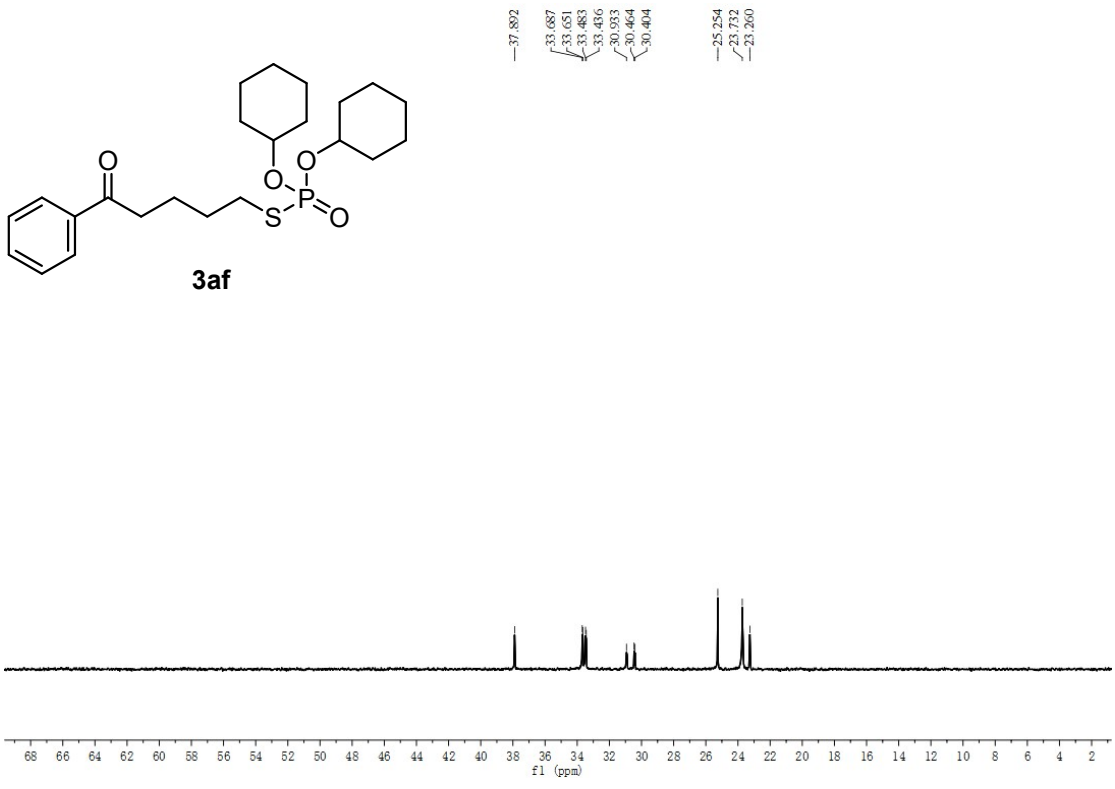




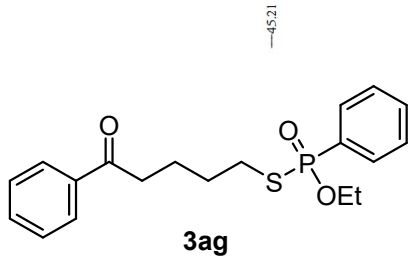
3af



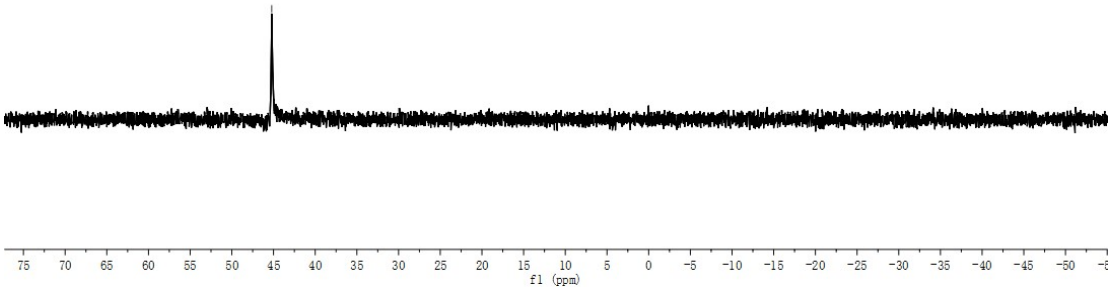

199.806
137.012
133.176
128.738
128.148
77.478
77.363
77.160
76.843
37.892
33.687
33.651
33.483
33.436
30.933
30.464
30.404
25.254
23.732
23.260
O
O
O
P
O
S
3af
f1 (ppm)

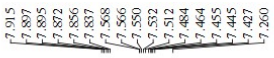

37.892
33.687
33.651
33.483
33.436
30.933
30.464
30.404
25.254
23.732
23.260
O
O
O
P
O
S
3af
f1 (ppm)

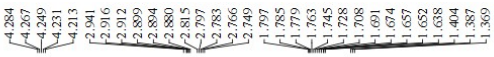
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ag**

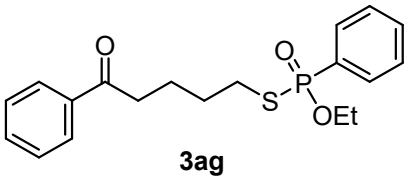


3ag

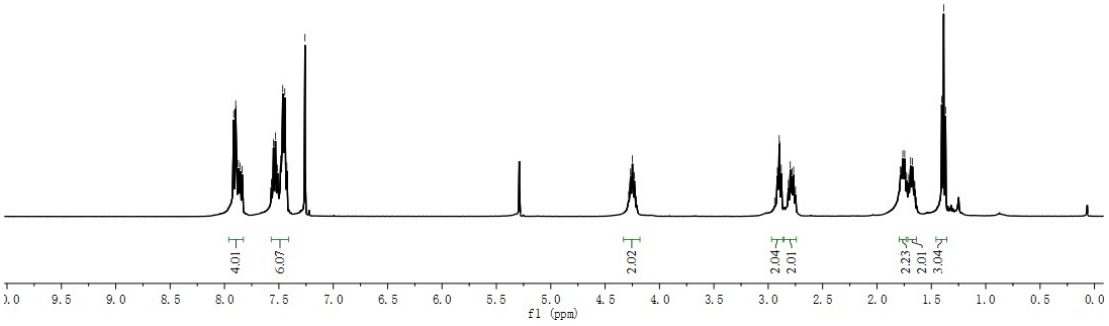


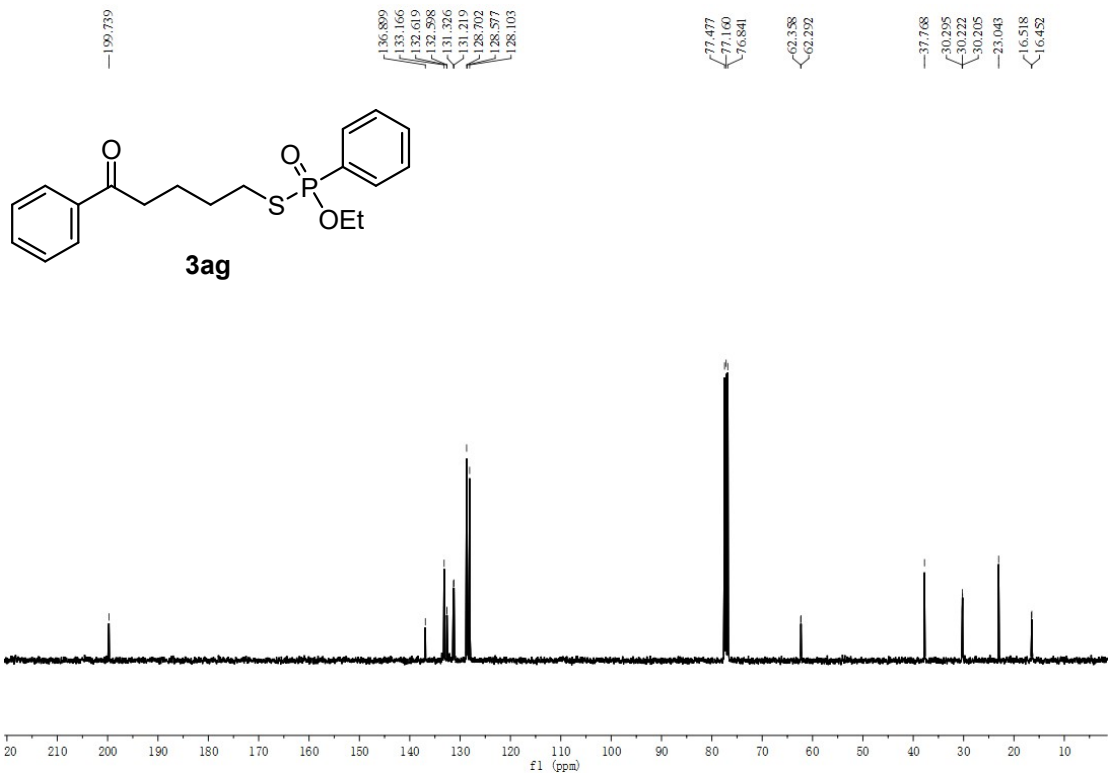




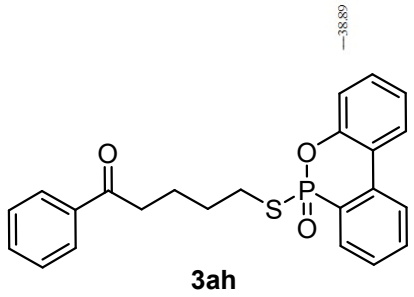


3ag

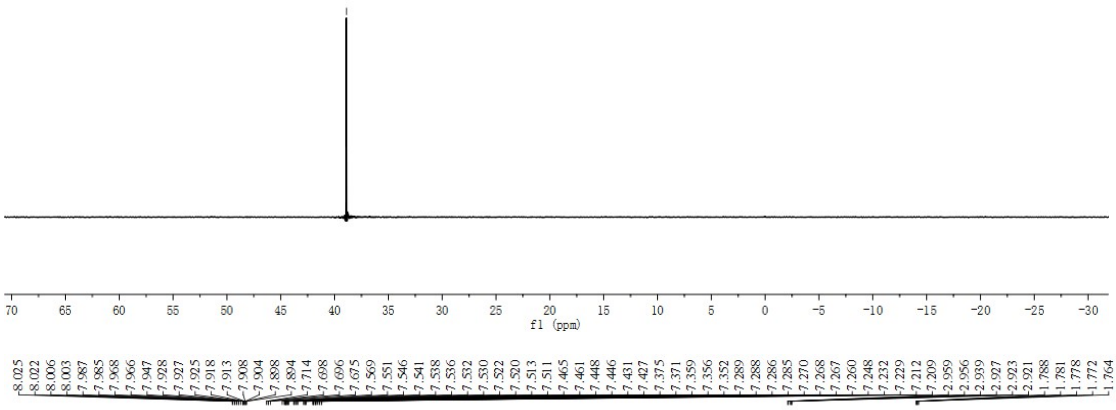


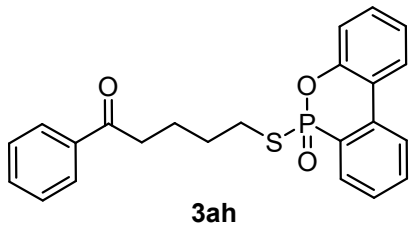

199.739
136.899
133.166
132.619
132.598
131.326
131.219
128.702
128.577
128.103
77.477
77.160
76.841
62.338
62.292
37.768
30.295
30.222
30.205
23.043
16.518
16.452
O
O
P
S
OEt
3ag
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ah**

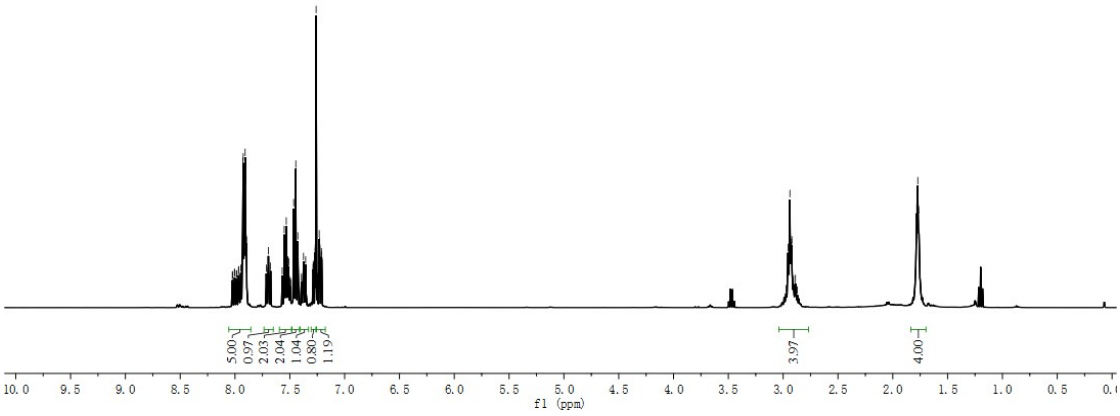


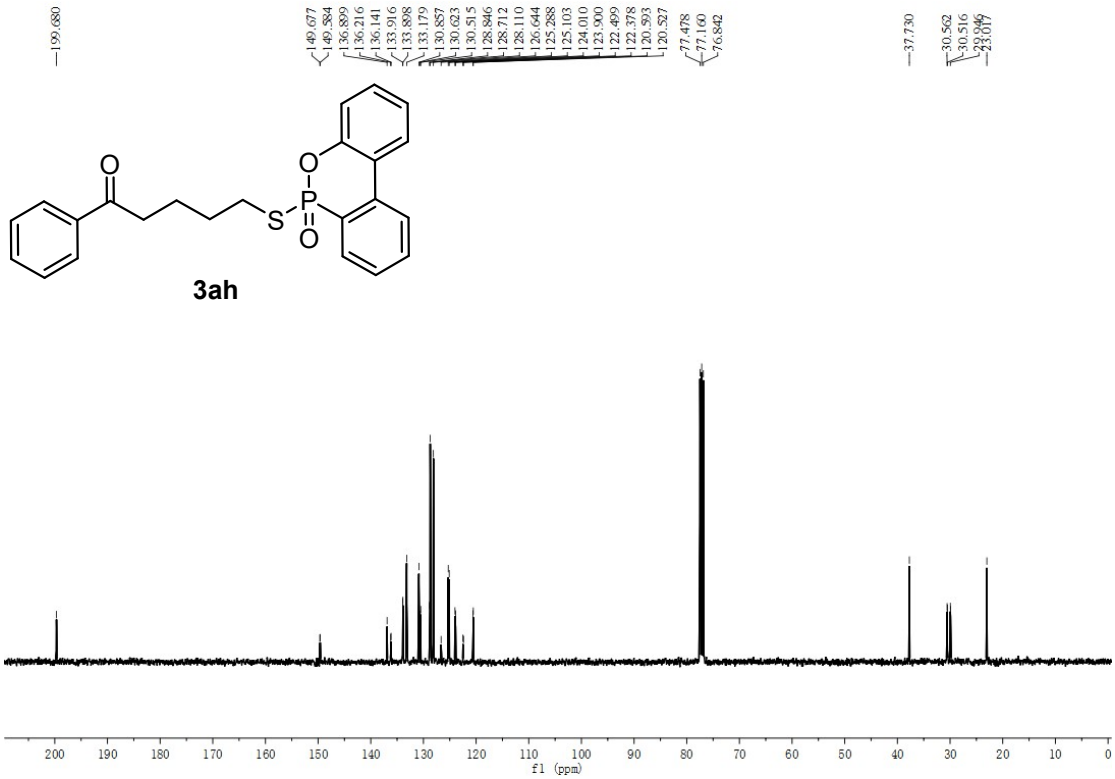
3ah

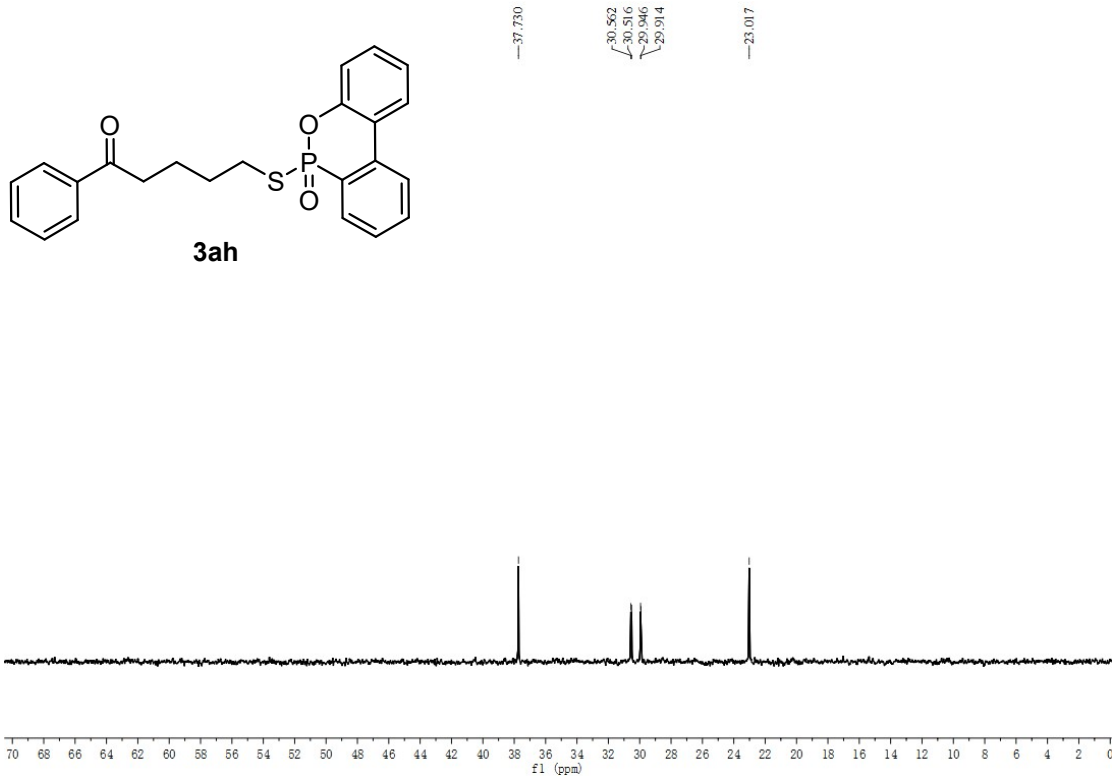




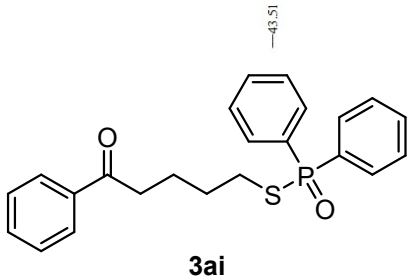
3ah



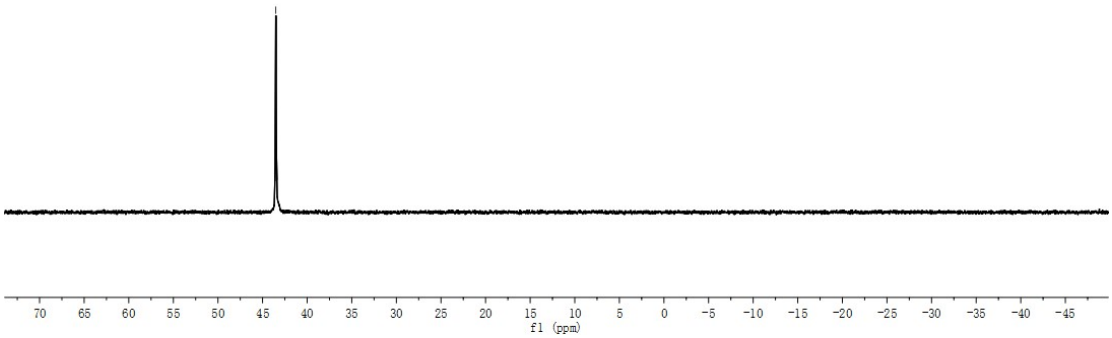

199.680
149.677
149.584
136.899
136.216
136.141
133.916
133.898
133.179
130.857
130.623
130.515
128.846
128.712
128.110
126.644
125.288
125.103
124.010
123.900
122.499
122.378
120.593
120.527
77.478
77.160
76.842
37.730
30.562
30.516
29.946
29.914
23.017
O
O
P
S
O
3ah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

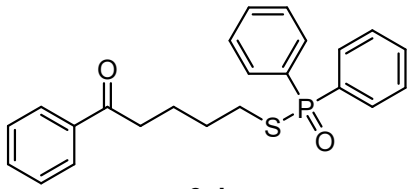

37.730
30.562
30.516
29.946
29.914
23.017
O
O
P
S
O
3ah
70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3ai**

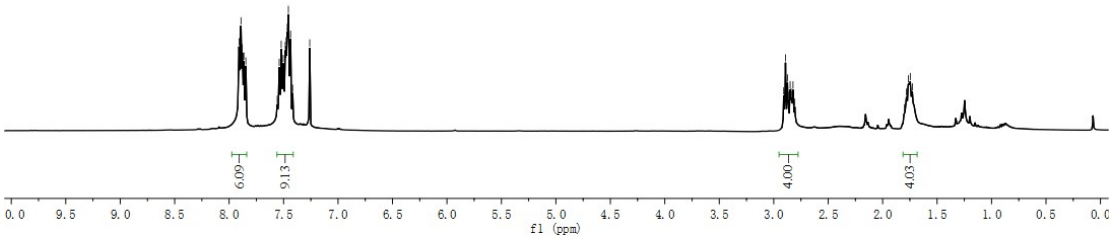


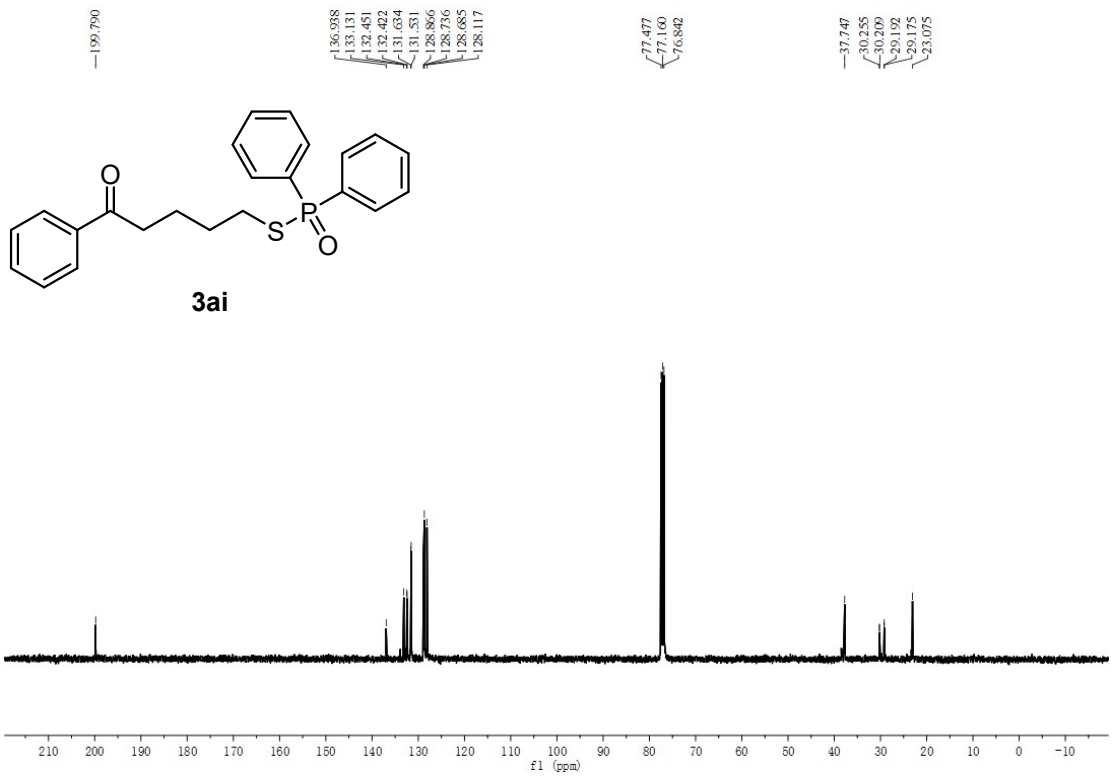
3ai



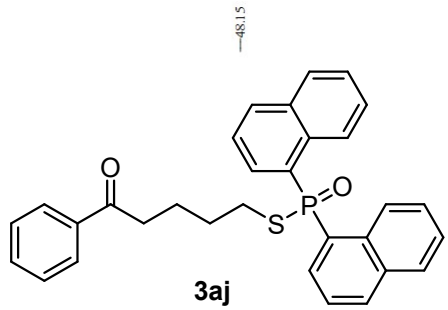


3ai

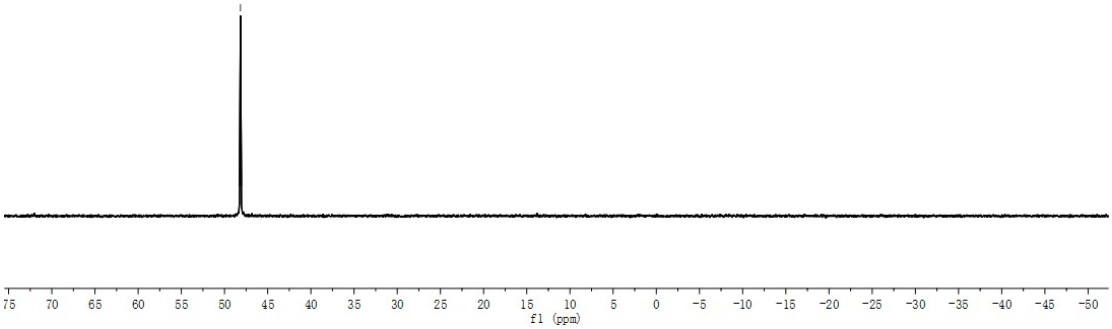


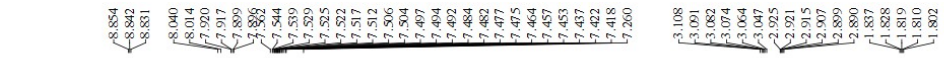

199.790
136.938
133.131
132.451
132.422
131.634
131.531
128.866
128.736
128.685
128.117
77.477
77.160
76.842
37.747
30.255
30.209
29.192
29.175
23.075
O
P
S
O
3ai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
37.747
30.255
30.209
29.192
29.175
23.075
O
P
S
O
3ai
65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

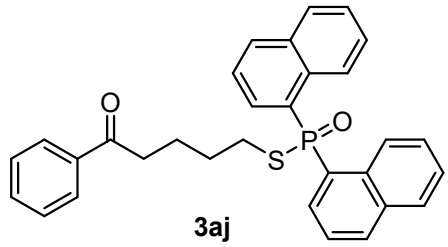
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3aj**



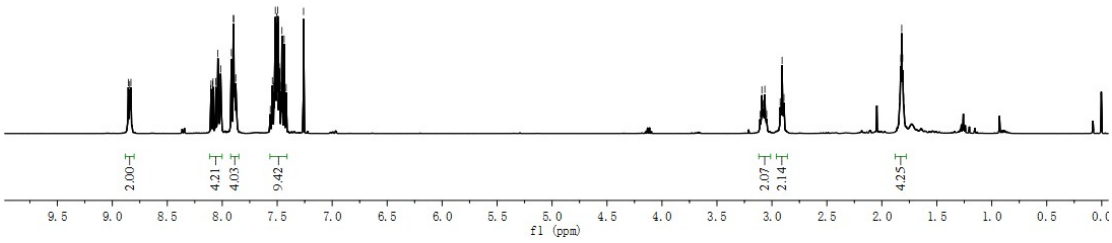
3aj

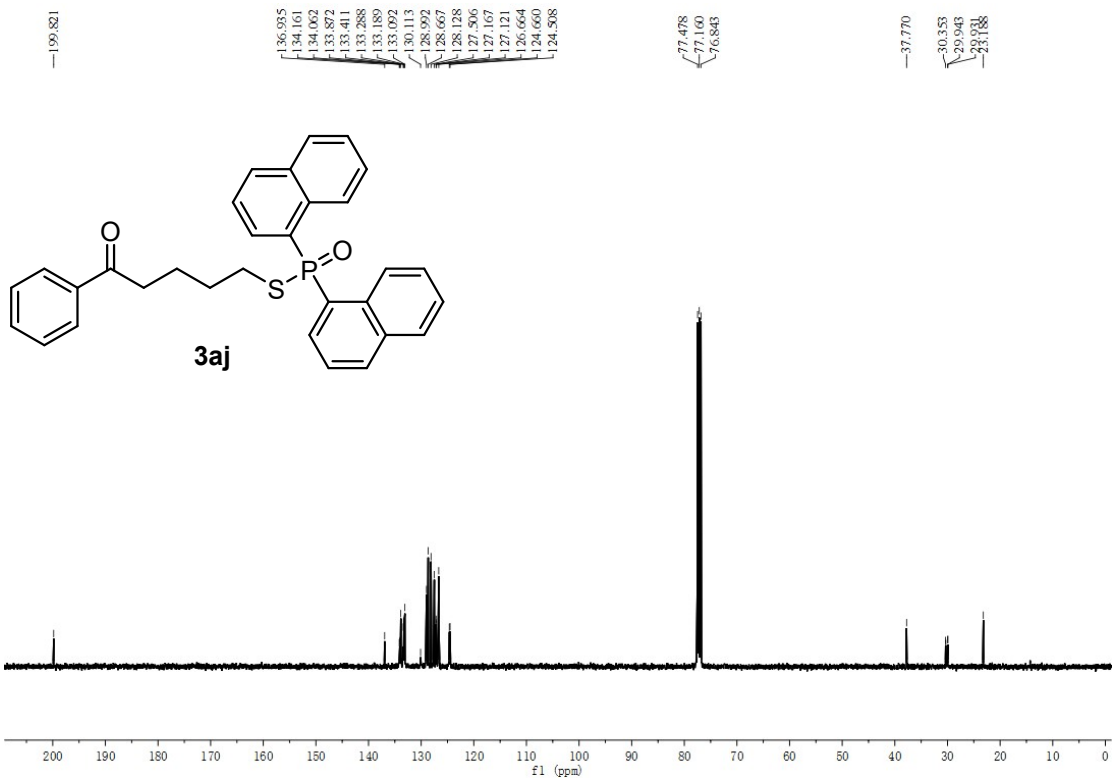


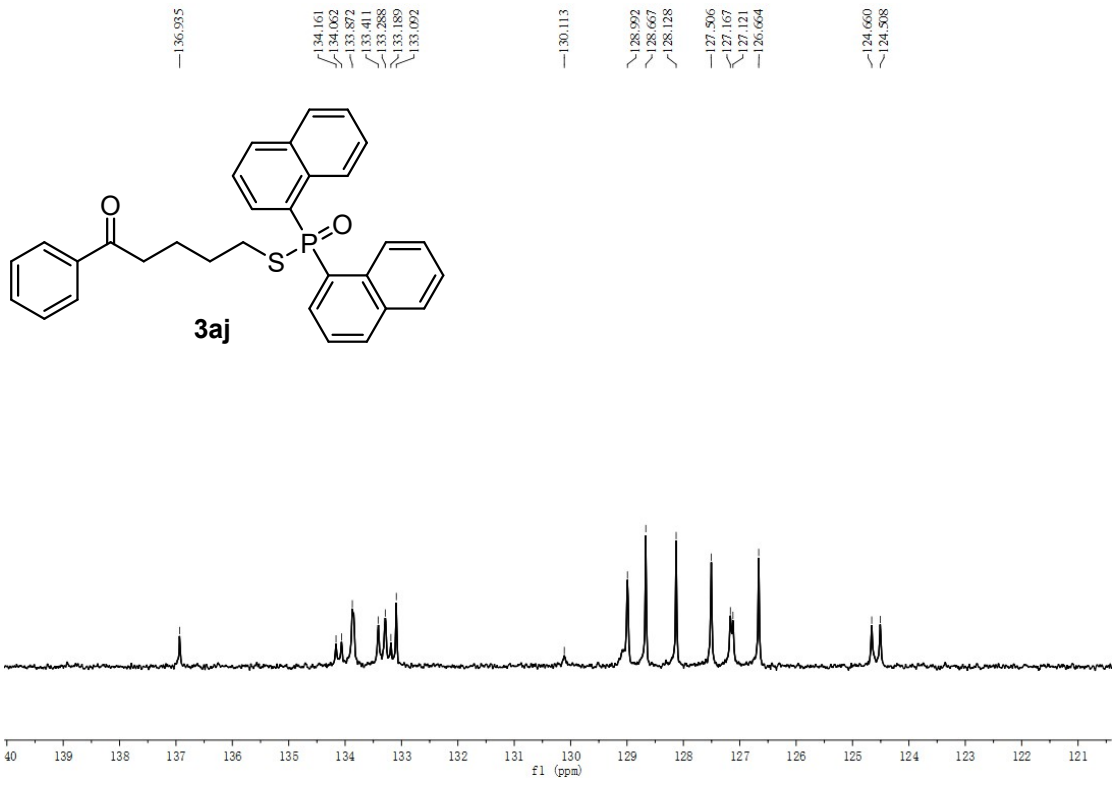




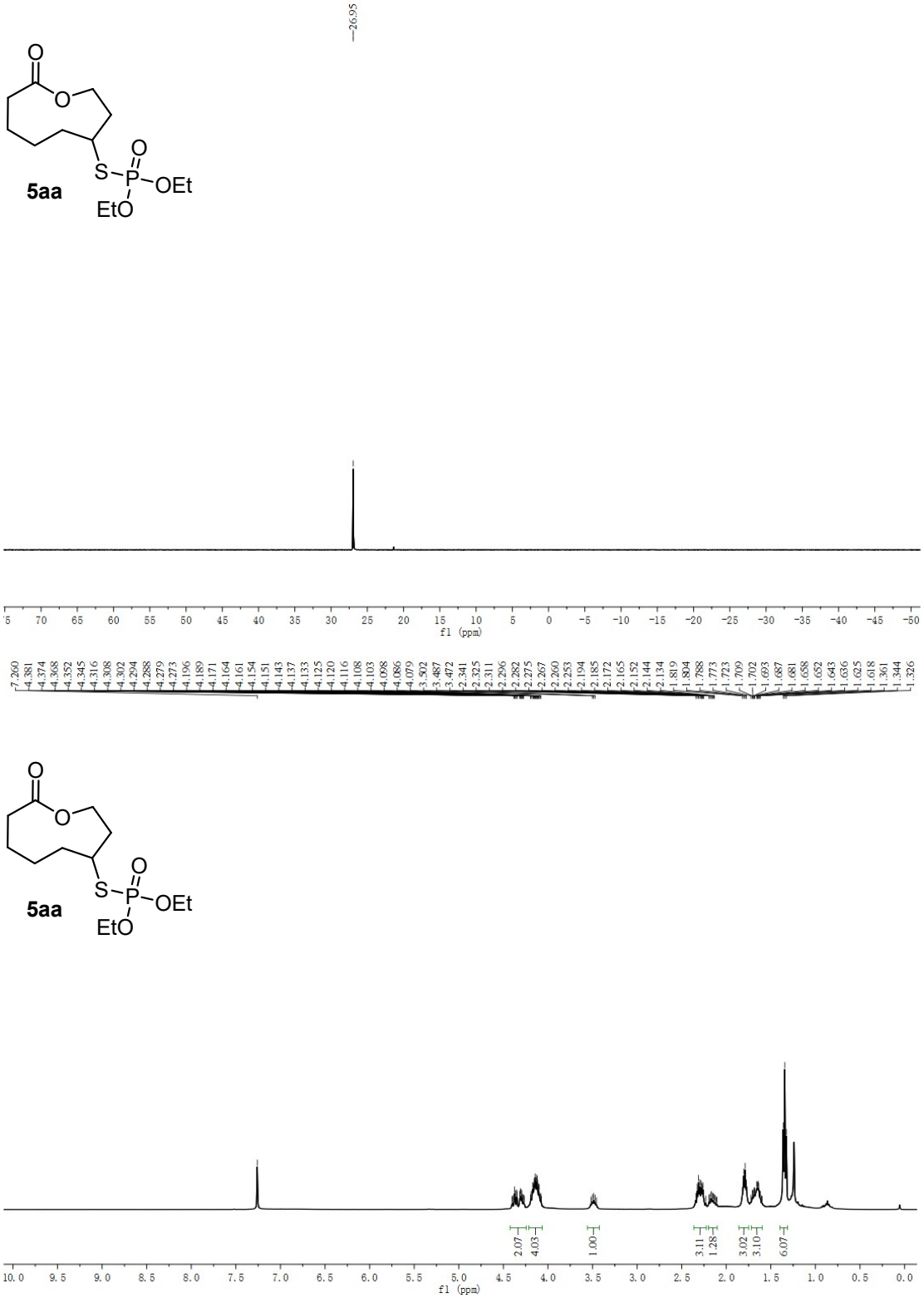
3aj

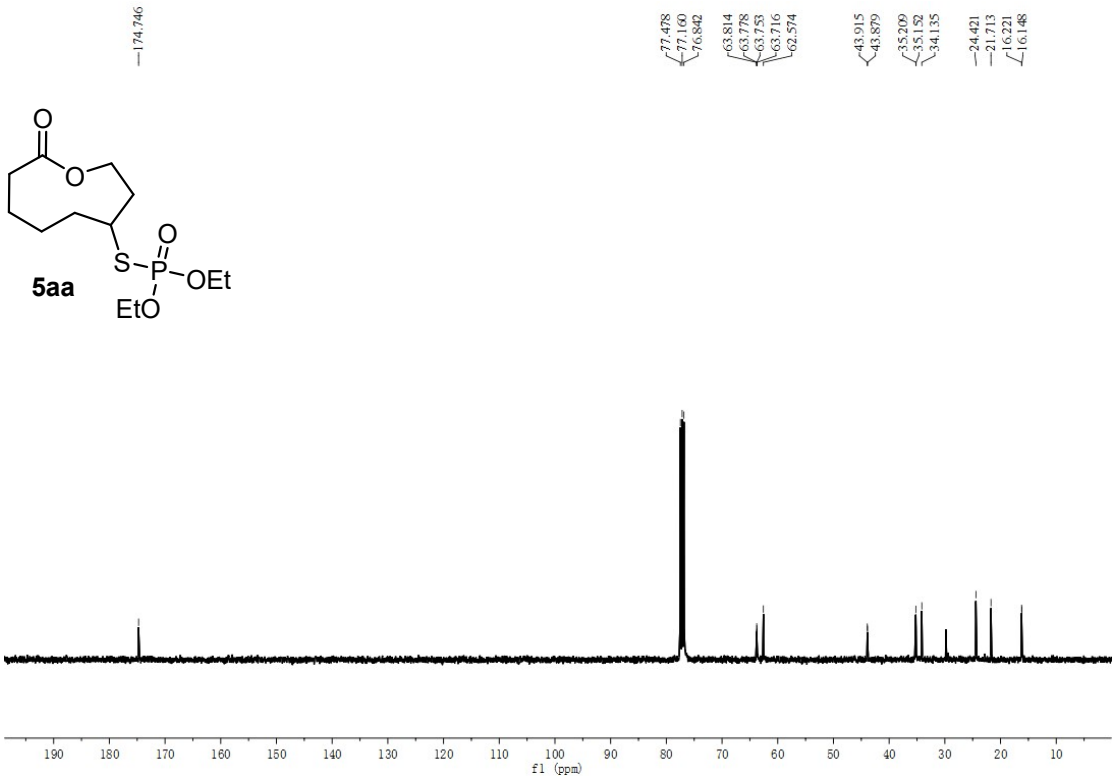


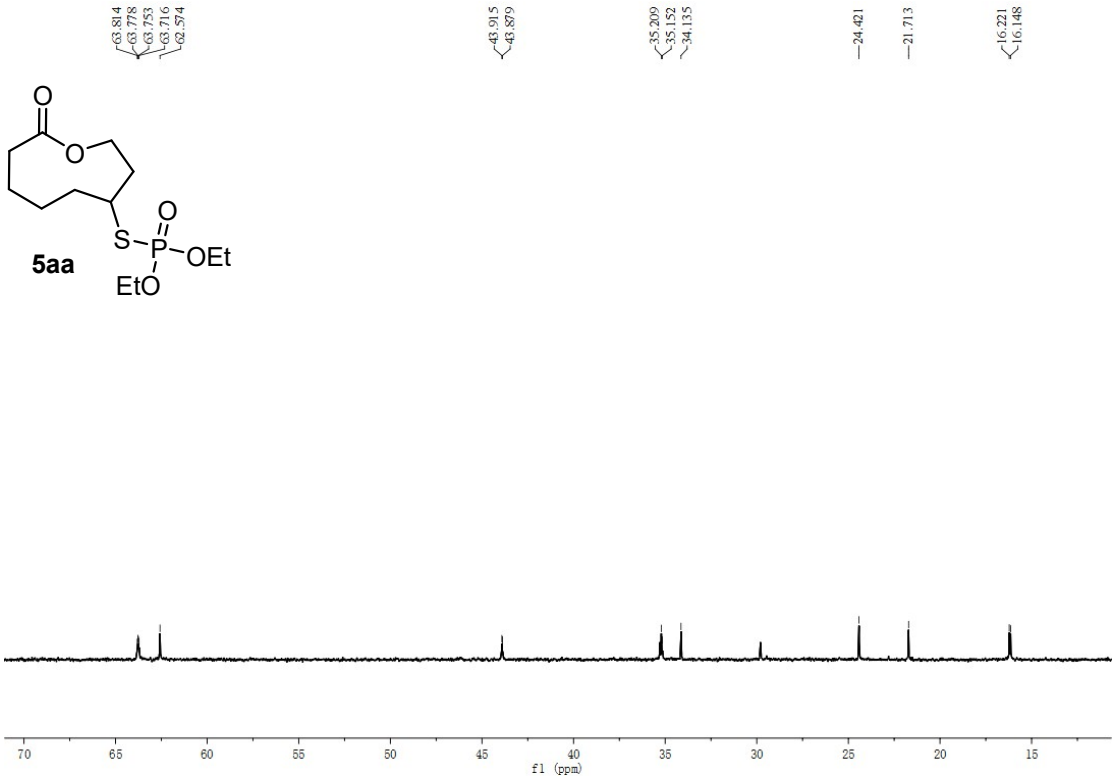

199.821
136.935
134.161
134.062
133.872
133.411
133.288
133.189
133.092
130.113
128.992
128.667
128.128
127.506
127.167
127.121
126.664
124.660
124.508
77.478
77.160
76.843
37.770
30.353
29.943
29.931
23.188
O
O
P
S
3aj
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


136.935
134.161
134.062
133.872
133.411
133.288
133.189
133.092
130.113
128.992
128.667
128.128
127.506
127.167
127.121
126.664
124.660
124.508
O
O
P
S
3aj
40
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
f1 (ppm)

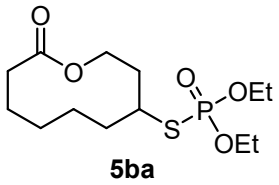
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **5aa**



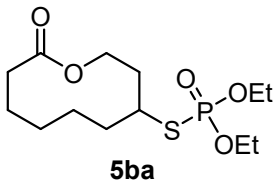

174.746
77.478
77.160
76.842
63.814
63.778
63.753
63.716
62.574
43.915
43.879
35.209
35.152
34.135
24.421
21.713
16.221
16.148
O
O
S
P
O
OEt
EtO
5aa
f1 (ppm)


63.814
63.778
63.753
63.716
62.574
43.915
43.879
35.209
35.152
34.135
24.421
21.713
16.221
16.148
O
O
S
P
O
OEt
EtO
5aa
f1 (ppm)

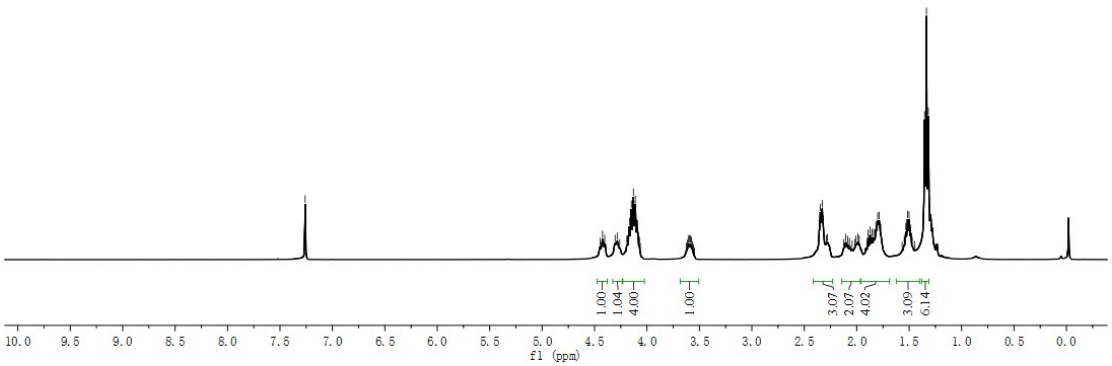
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **5ba**

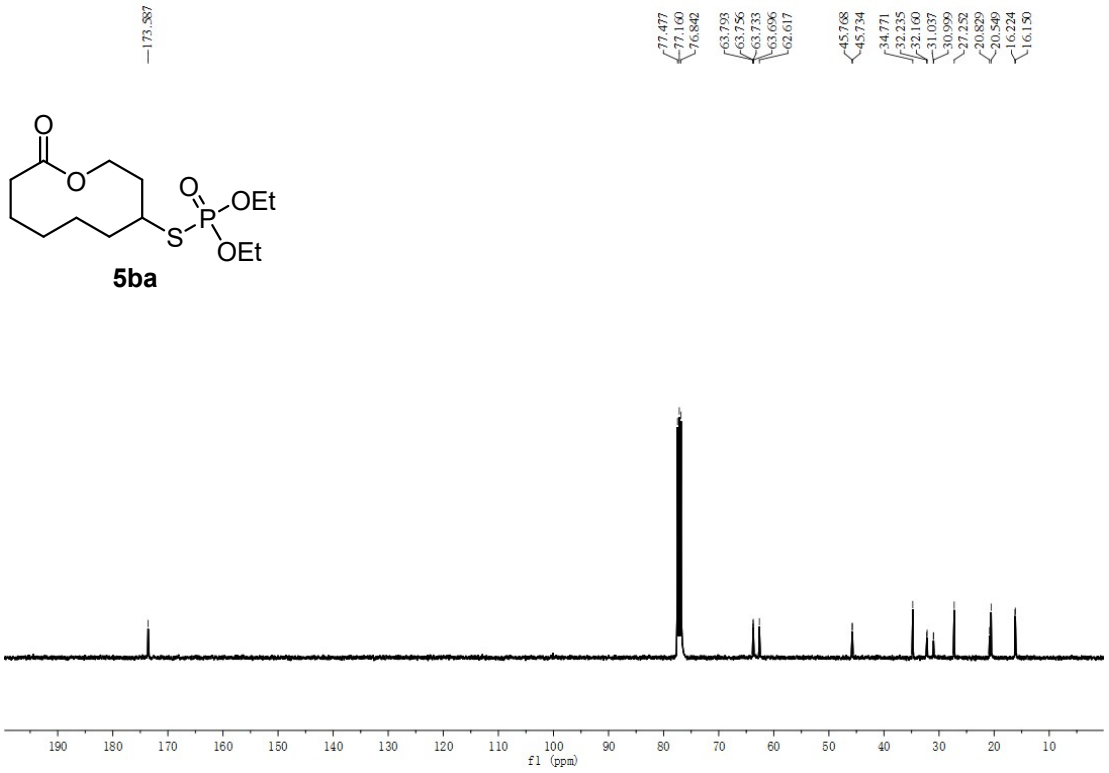


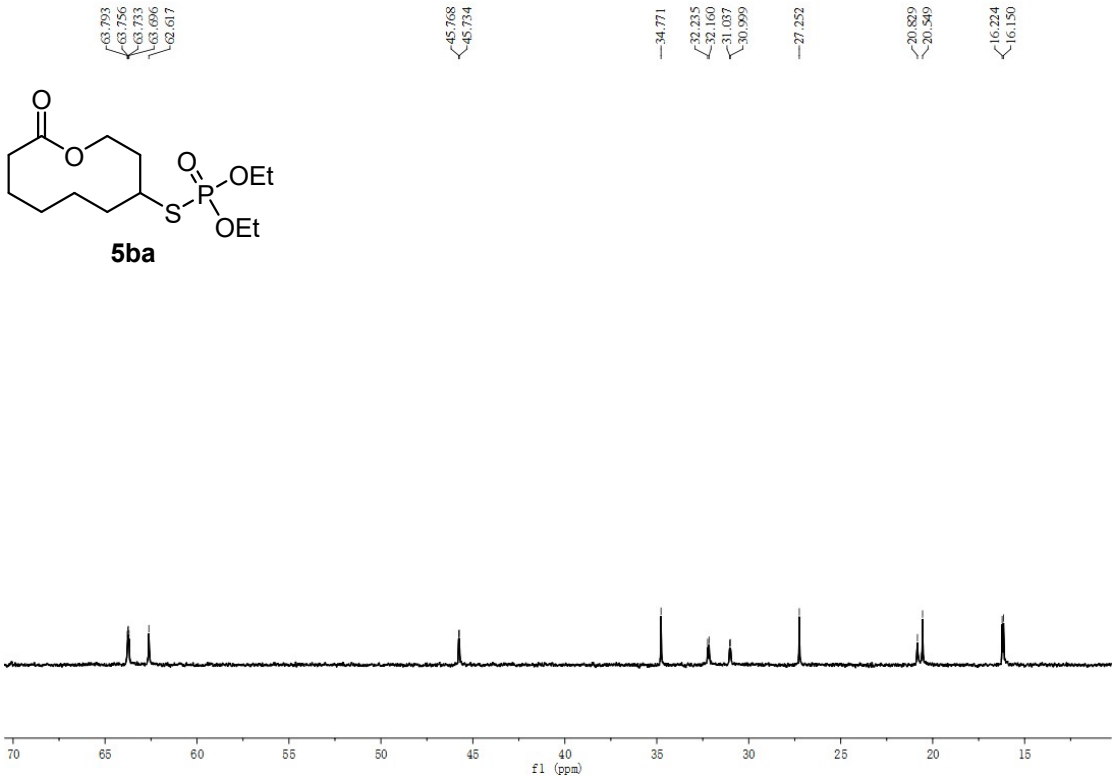
5ba



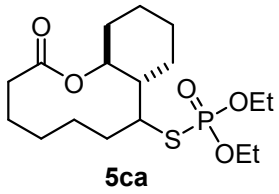
5ba



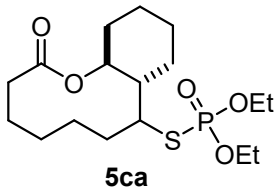

173.587
77.477
77.160
76.842
63.793
63.756
63.733
63.696
62.617
45.768
45.734
34.771
32.235
32.160
31.037
30.999
27.252
20.829
20.549
16.224
16.150
O
O
O
P
OEt
S
OEt
5ba
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


63.793
63.756
63.733
63.696
62.617
45.768
45.734
34.771
32.235
32.160
31.037
30.999
27.252
20.829
20.549
16.224
16.150
O
O
O
P
OEt
S
OEt
5ba
70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

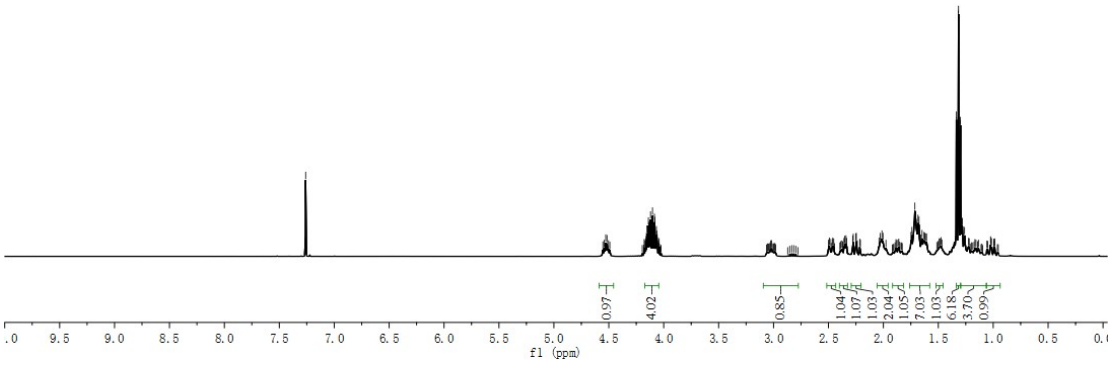
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **5ca**

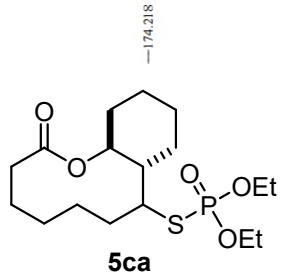


5ca



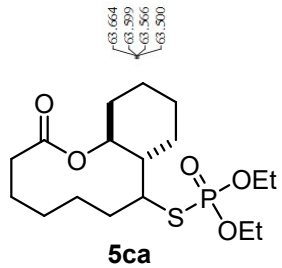
5ca




O
O
O
P
OEt
S
OEt

5ca

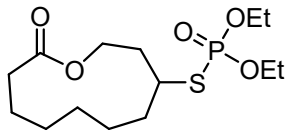
174.218
77.478
77.160
76.841
63.664
63.599
63.566
63.500
53.518
53.487
45.850
45.792
34.994
34.534
33.046
32.059
26.573
25.474
24.654
23.348
21.850
16.200
16.127
f1 (ppm)


O
O
O
P
OEt
S
OEt

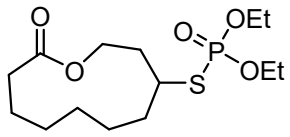
5ca

63.664
63.599
63.566
63.500
53.518
53.487
45.850
45.792
34.994
34.534
33.046
32.059
26.573
25.474
24.654
23.348
21.850
16.200
16.127
f1 (ppm)

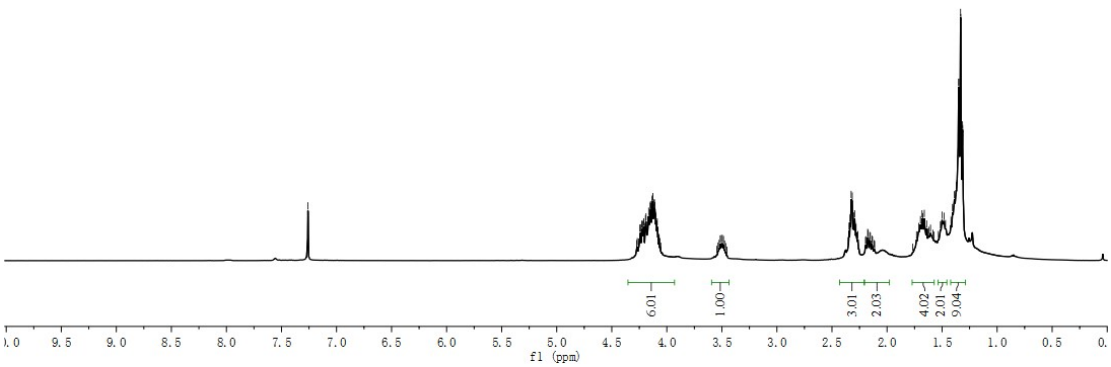
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **5da**

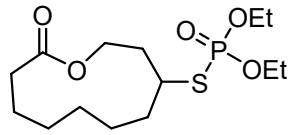


5da



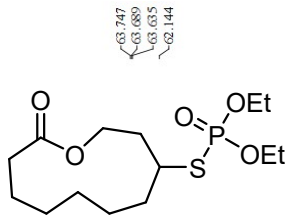
5da




O
O
OEt
O
P
OEt
S

5da

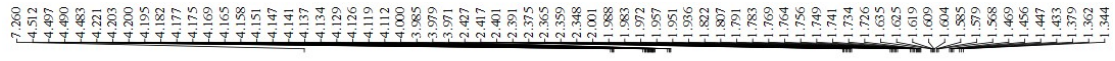
173.523
77.478
77.160
76.842
63.747
63.689
63.635
62.144
45.106
45.072
35.289
33.259
32.468
32.393
25.661
24.636
21.378
20.626
16.180
16.108
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

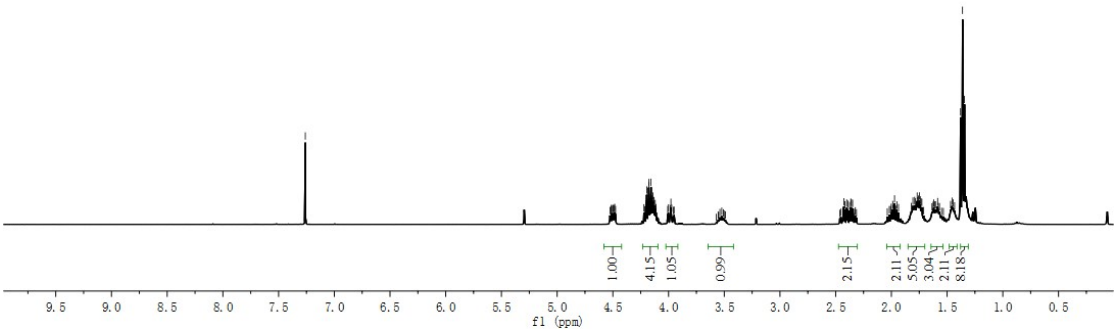

O
O
OEt
O
P
OEt
S

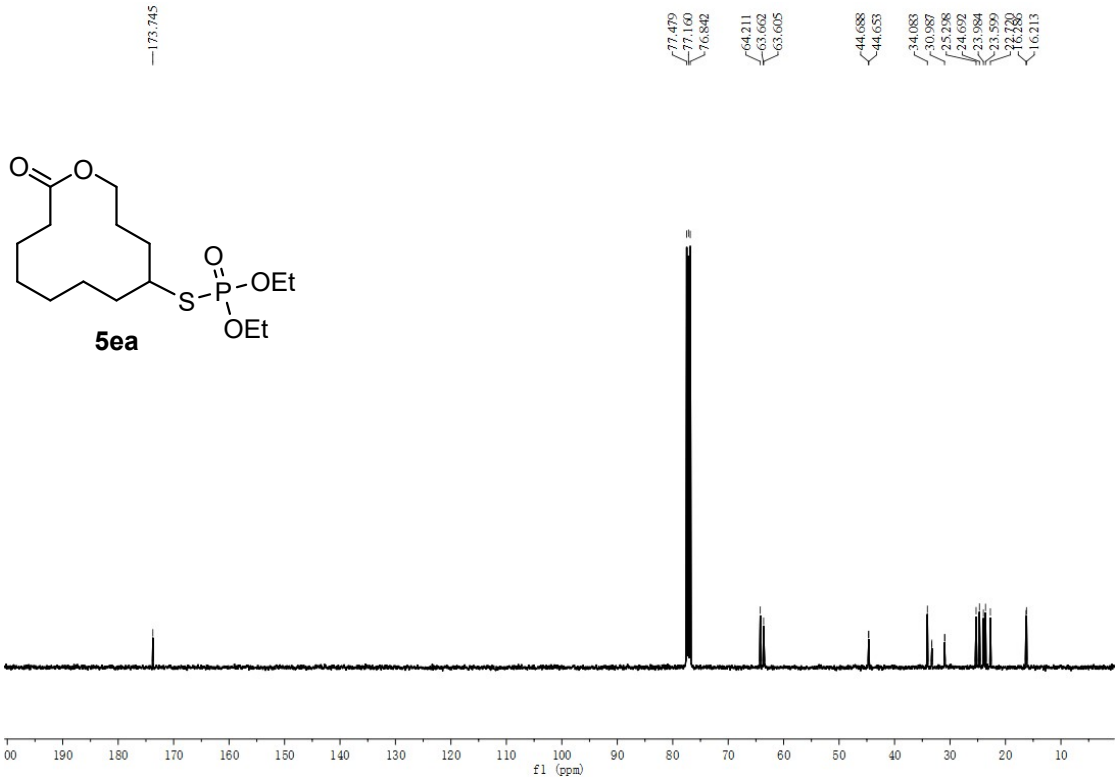
5da

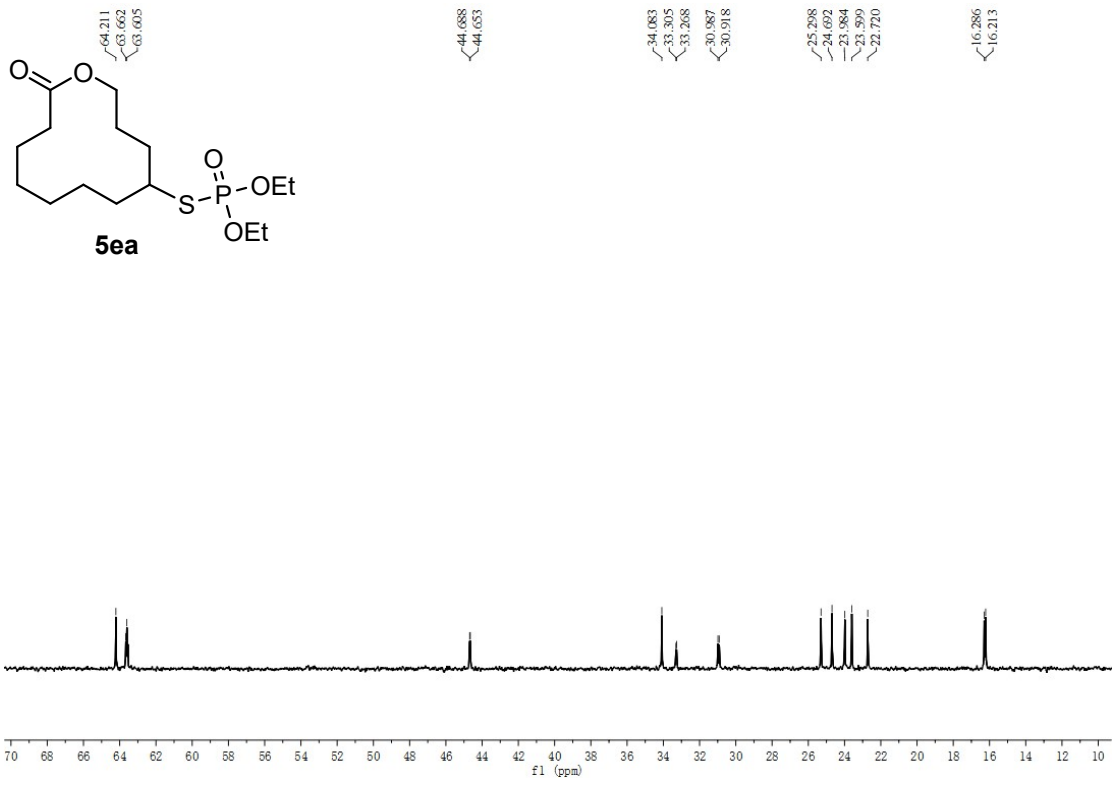
63.747
63.689
63.635
62.144
45.106
45.072
35.289
33.259
33.218
32.468
32.393
25.661
24.636
21.378
20.626
16.180
16.108
70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **5ea**

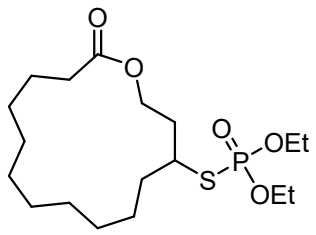




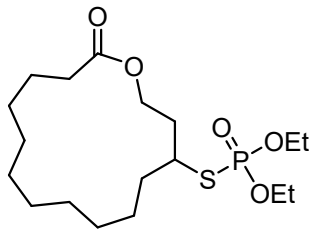

173.745
77.479
77.160
76.842
64.211
63.662
63.605
44.688
44.653
34.083
30.987
25.298
24.692
23.984
23.599
22.720
16.286
16.213
O
O
O
S
P
OEt
OEt
5ea
f1 (ppm)


64.211
63.662
63.605
44.688
44.653
34.083
33.305
33.268
30.987
30.918
25.298
24.692
23.984
23.599
22.720
16.286
16.213
O
O
O
S
P
OEt
OEt
5ea
f1 (ppm)

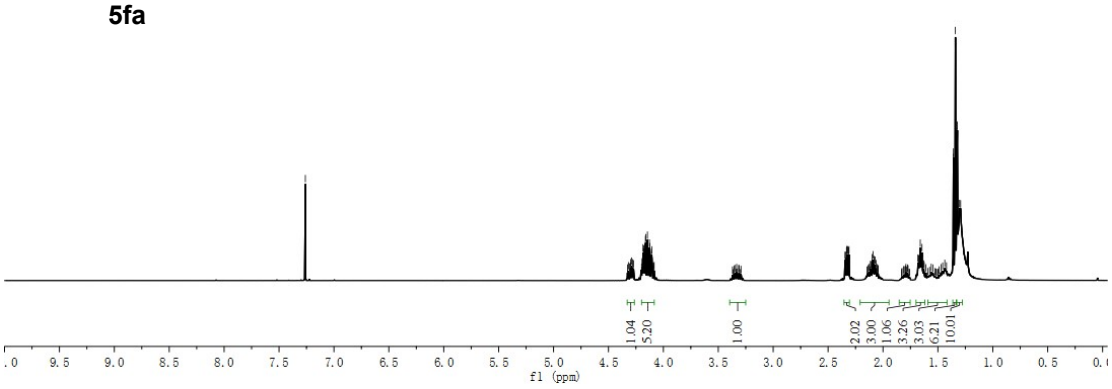
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **5fa**

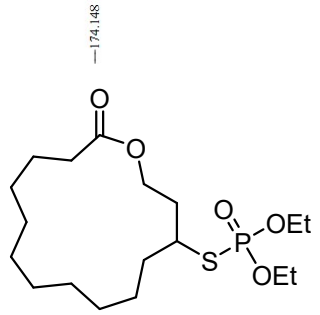


5fa

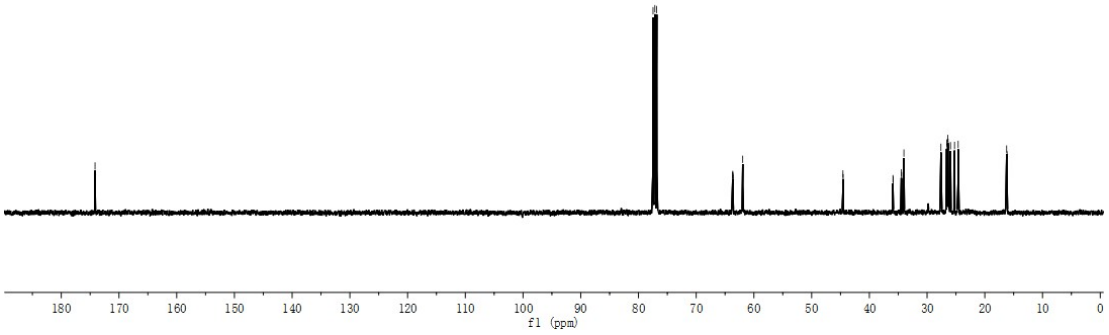


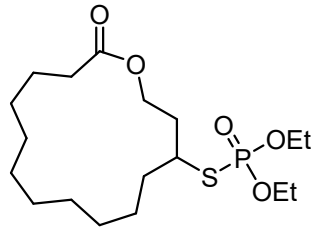
5fa



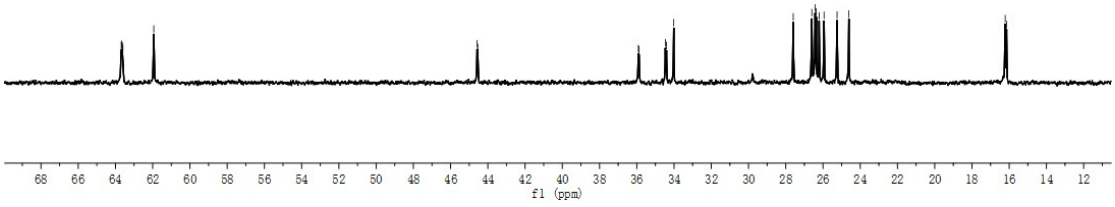

O
O
O
P
OEt
S
OEt

5fa

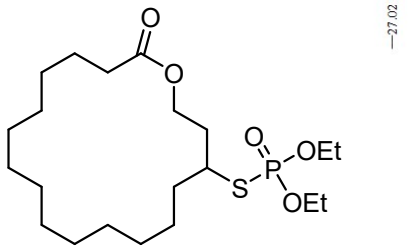

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
O
P
OEt
S
OEt

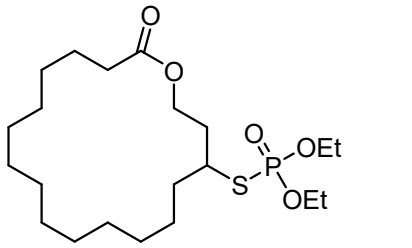
5fa


68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12
f1 (ppm)

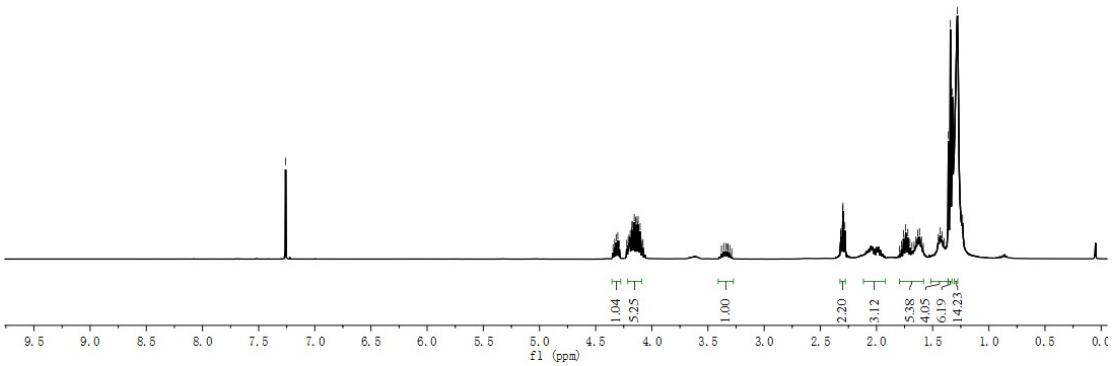
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **5ga**

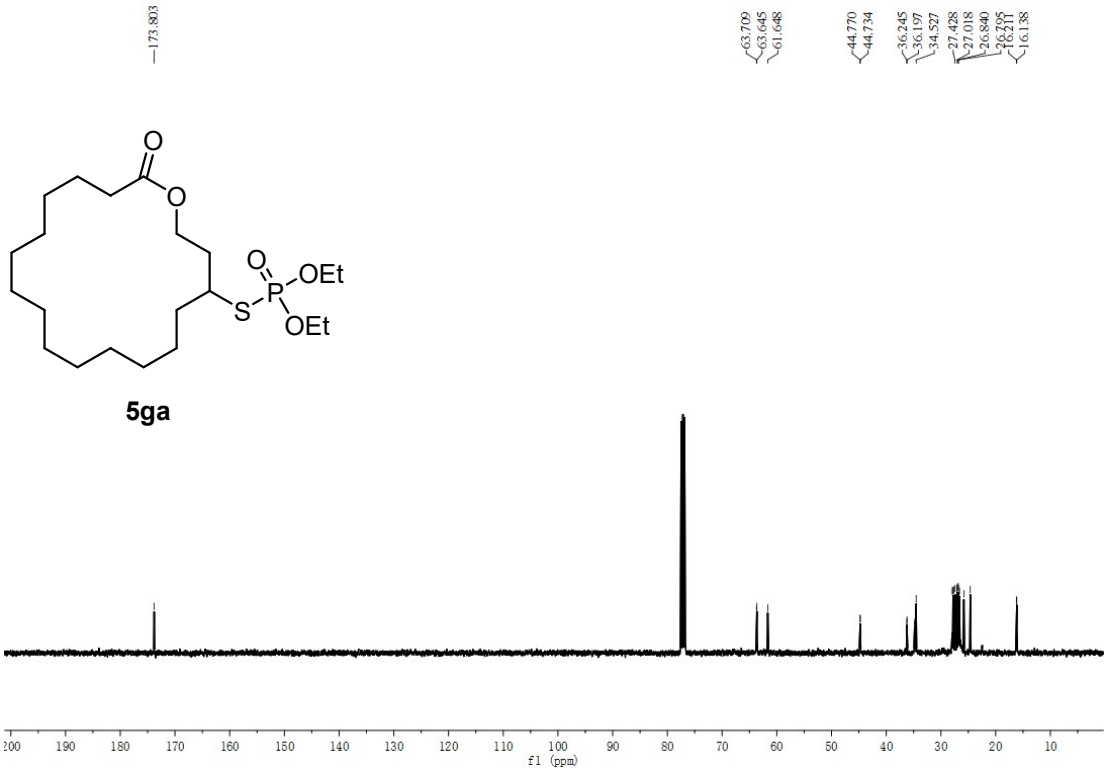


5ga

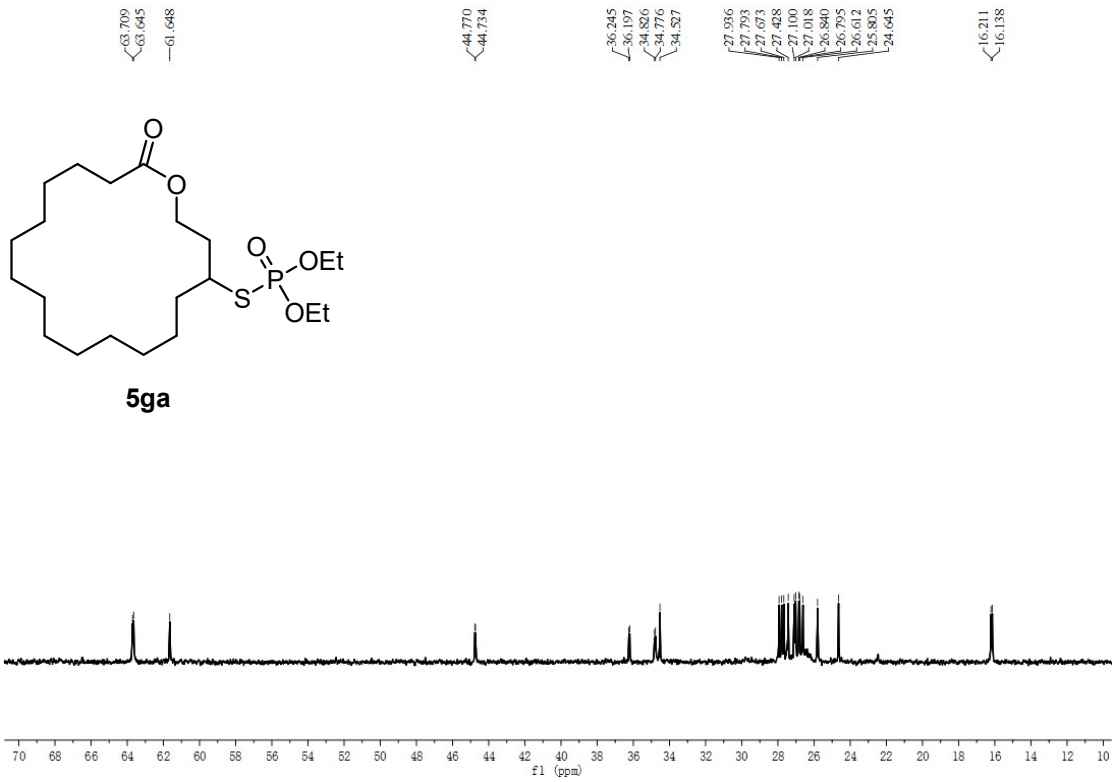


5ga




173.803
63.709
63.645
61.648
44.770
44.734
36.245
36.197
34.527
27.428
27.018
26.840
26.295
16.211
16.138
O
O
O
P
OEt
S
OEt
f1 (ppm)

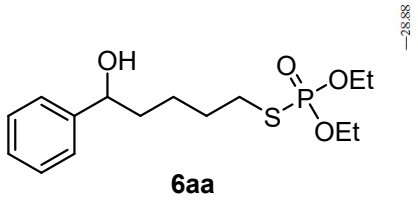
5ga


63.709
63.645
61.648
44.770
44.734
36.245
36.197
34.826
34.776
34.527
27.936
27.793
27.673
27.428
27.100
27.018
26.840
26.795
26.612
25.805
24.645
16.211
16.138
O
O
O
P
OEt
S
OEt
f1 (ppm)

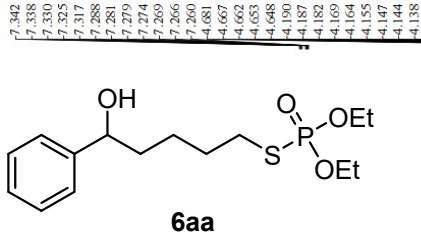
5ga

15. ^{31}P NMR, ^{1}H NMR and ^{13}C NMR Spectra of Products 6aa and 7aa

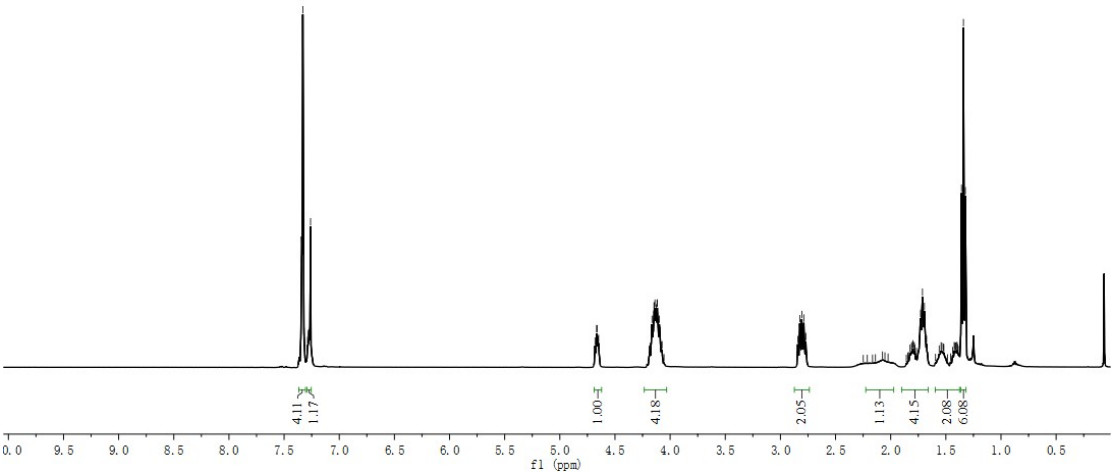
^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **6aa**

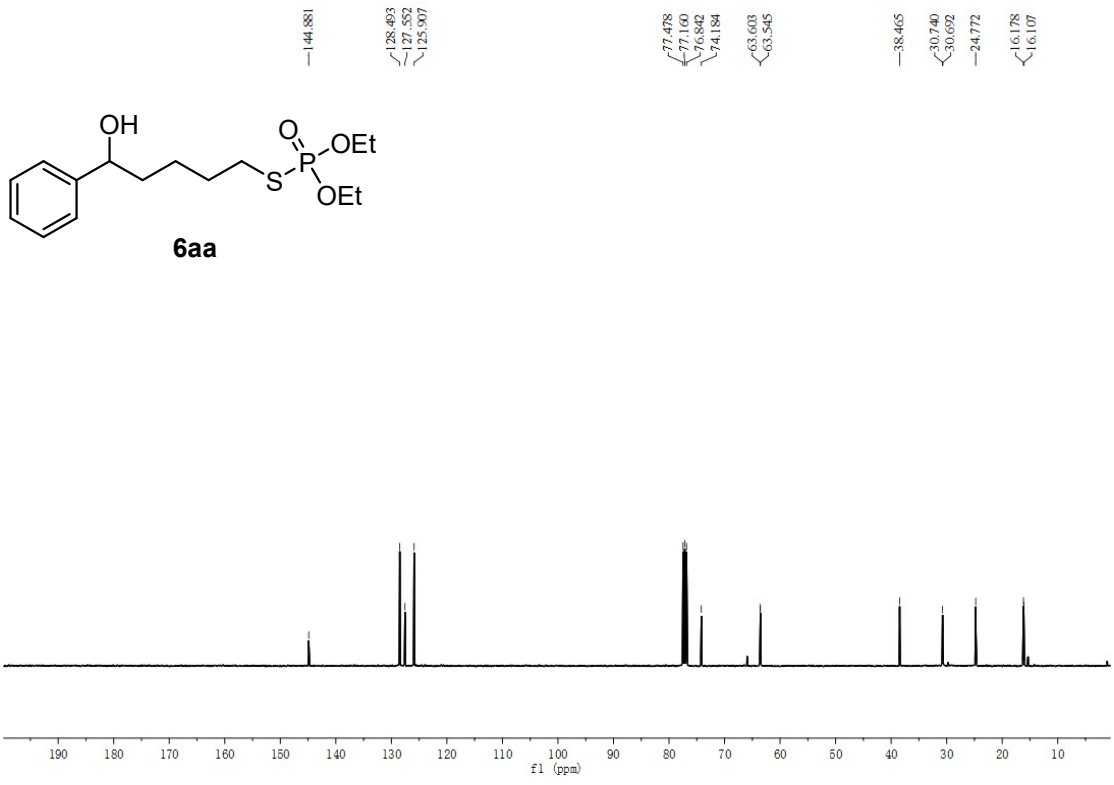


6aa

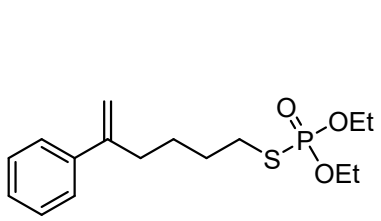


6aa

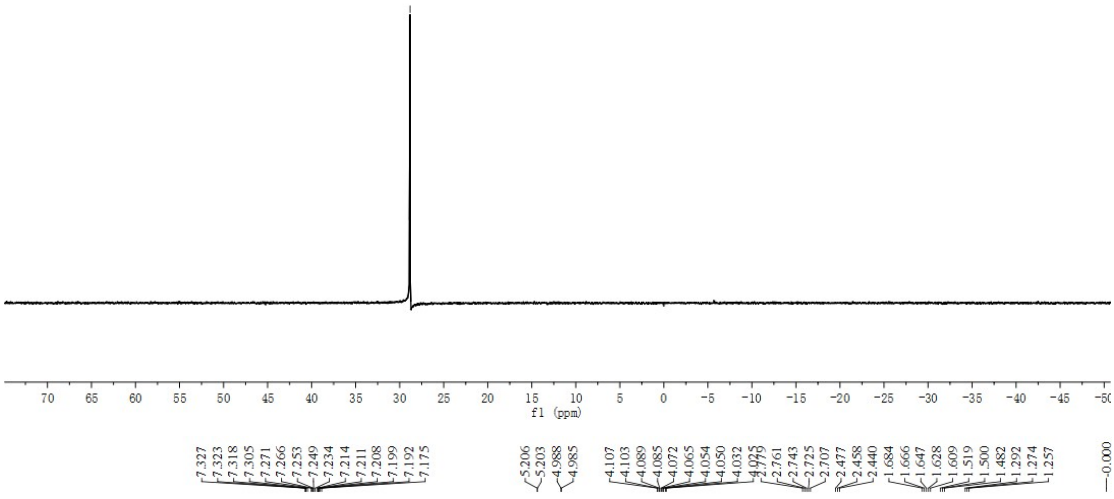


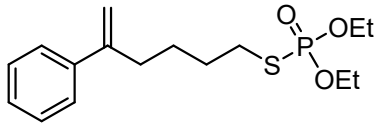

144.881
128.493
127.552
125.907
77.478
77.160
76.842
74.184
63.603
63.545
38.465
30.740
30.692
24.772
16.178
16.107
OH
O
OEt
P
S
OEt
6aa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{31}P NMR (162 MHz, $CDCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **7**

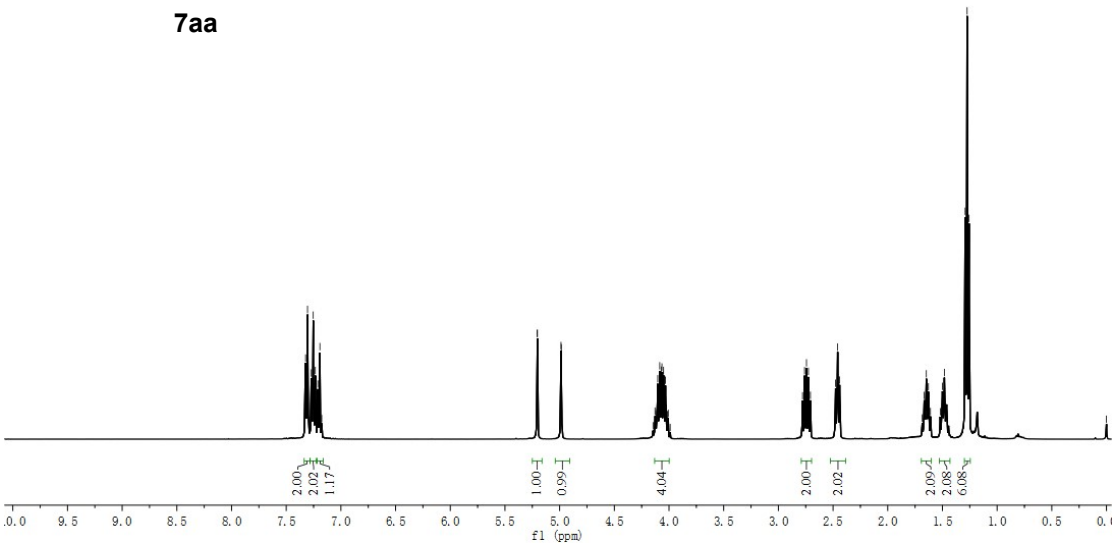


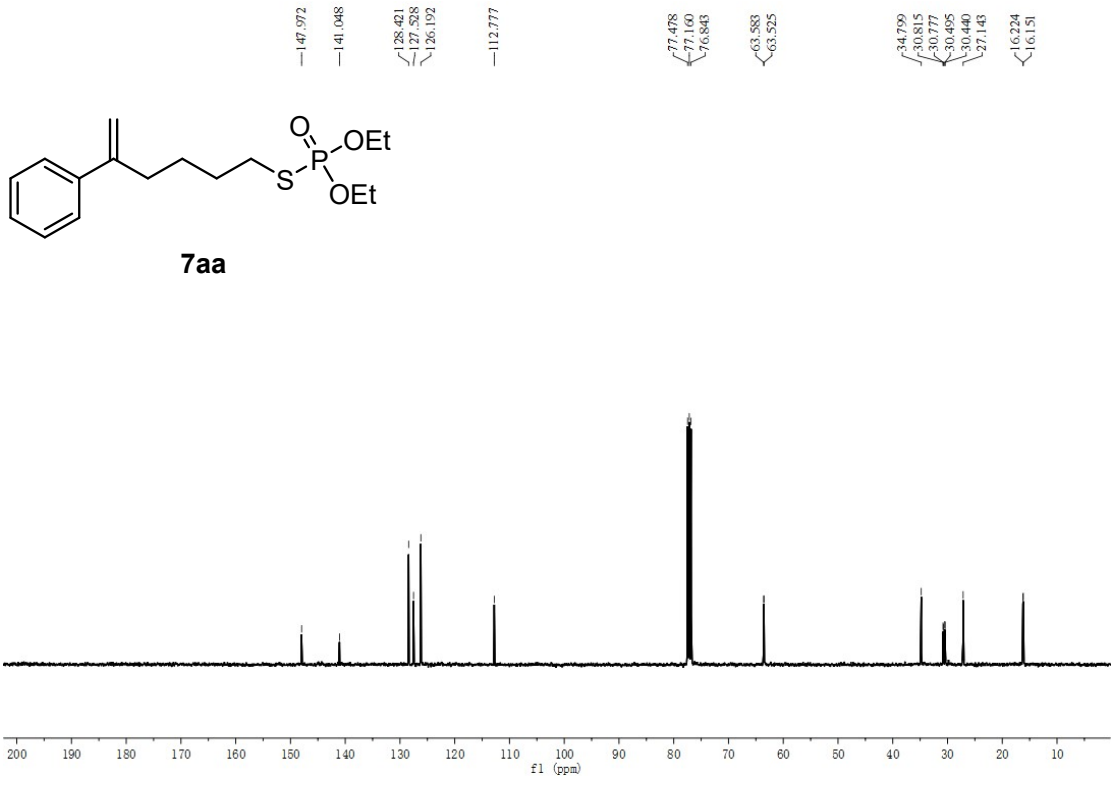
7aa





7aa




147.972
141.048
128.421
127.528
126.192
112.777
77.478
77.160
76.843
63.583
63.525
34.799
30.815
30.777
30.495
30.440
27.143
16.224
16.151
O
OEt
S
P
OEt
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

7aa