Supporting information

New Oxime Phosphonates Participated Visible Photocatalysis: Synthesis of β-Aminophosphonates

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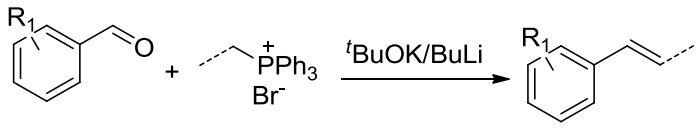
1. General information

^{1}H NMR (400 MHz) and ^{13}CNMR (100 MHz) spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. ^{31}P NMR (162 MHz) spectra and ^{19}F NMR(376 MHz) were recorded on the same instrument. Mass spectra were mearsured using Thermo Scientific DSQ II. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

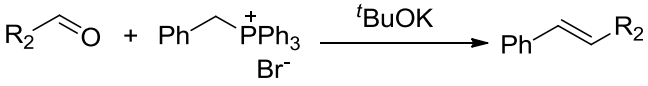
2. Synthesis of substrates

2.1 Synthesis of alkenes



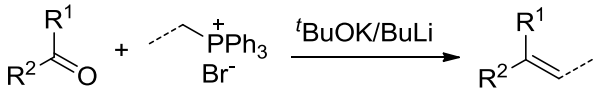
The Preparation of Alkenes (Method A)

Method A: To a suspension of Me/EtPPh$_3$Br (26.70/27.75 g, 75.0 mmol, 1.5 equiv.) in THF (120.00 mL), ^{t}BuOK (8.98 g, 80.0 mmol, 1.6 equiv.) was added portionwise. The reaction was allowed to stir at room temperature for 30 min. It was then cooled to 0 ℃ and a solution of corresponding aldehyde (50.0 mmol, 1.0 equiv.) in THF (50.00 mL) was added dropwise. The mixture was stirred at 0 ℃ for 30 min and then warmed to room temperature for 1.5 h. The reaction was quenched with water. The aqueous phase was extracted with Et_2O three times. The organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography to afford corresponding alkenes.



The Preparation of Alkenes (Method B)

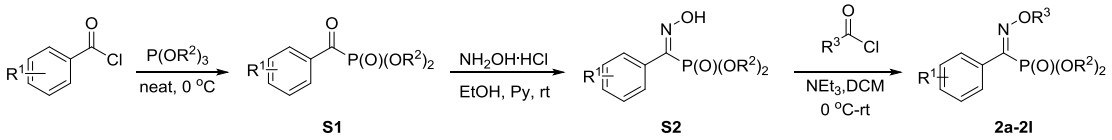
Method B: To a suspension of BnPPh$_3$Br (25.92 g, 60.0 mmol, 1.5 equiv.) in THF (120.00 mL), ^{t}BuOK (7.30 g, 80.0 mmol, 1.3 equiv.) was added portionwise. The reaction was allowed to stir at room temperature for 30 min. It was then cooled to 0 ℃ and a solution of corresponding aldehyde (50.0 mmol, 1.0 equiv.) in THF (50.00 mL) was added dropwise. The mixture was stirred at 0 ℃ for 30 min and then warmed to room temperature for 1.5 h. The reaction was quenched with water. The aqueous phase was extracted with Et_2O three times. The organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography to afford corresponding alkenes.



The Preparation of Alkenes (Method C)

Method C: To a suspension of Me/EtPPh$_3$Br (32.40 g, 75.0 mmol, 1.5 equiv.) in THF (120.00 mL), ^{t}-BuOK (8.98 g, 80.0 mmol, 1.5 equiv.) was added portionwise. The reaction was allowed to stir at room temperature for 30 min. It was then cooled to 0 ℃ and a solution of corresponding ketone (50.0 mmol, 1.0 equiv.) in THF (50.00 mL) was added dropwise. The mixture was warmed to 70 ^{o}C for 1 h. The reaction was quenched with water. The aqueous phase was extracted with Et_2O three times. The organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography to afford corresponding alkenes.

2.2. Synthesis of phosphoryl oxime ethers



2a-2l were synthesized according to the preference[1].

Synthesis of **S1**

To a 100 mL round bottom flask equipped with a magnetic stir bar was charged with benzoyl chloride (1.05 equiv) was added the triethyl phosphate (1.0 equiv) at 0 ^{o}C, then the mixture was stirred for 2 h to give the **S1**, which could be used for the next step without further purification.

Synthesis of **S2**

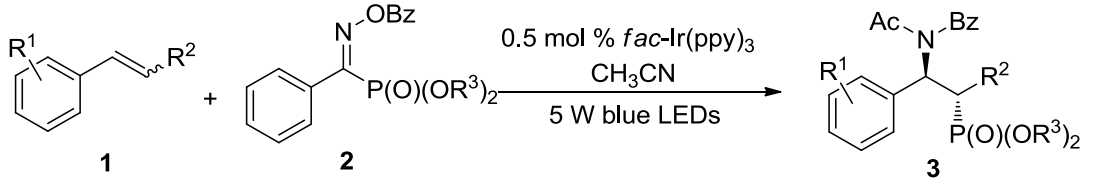
The above afforded **S1** was solved with EtOH (40 mL), and to the mixture was added hydroxylamine hydrochloride (1.1 euqiv) and pyridine (1.2 equiv). Then the mixture was stirred overnight at rt. Quenched the reaction with 1N HCl (aq), and extracted with EA, washed by water and brine. The organic phase was collected and the solvent was removed under vacuum to give the crude product **S2**, which could be used for the next step without further purification.

Synthesis of **2a**-**2l**

The aboved afforded **S2** was solved with DCM (40 mL), and to the mixture was added triethylamine (1.2 equiv) and benzoyl chloride (1.05 equiv) at 0 ^{o}C. Then the mixture was allowed to rt and stirred overnight to give the final product after purification by chromatography (the product was storability and stability toward moisture and oxygen.)

3. General Procedures.

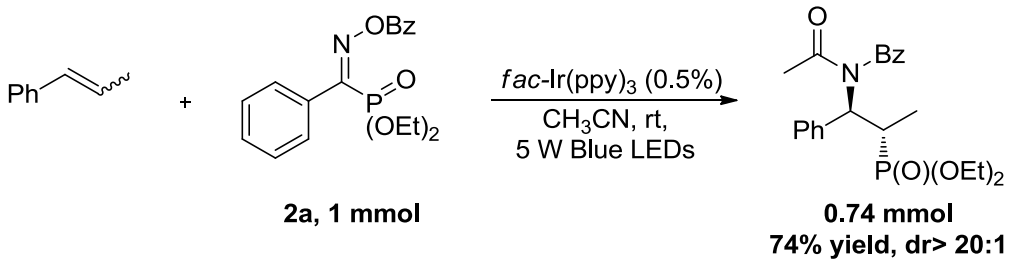
3.1. General procedure for Phosphoryl radical onto alkenes



A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with alkenes (0.6 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %), phosphorus reagents (0.4 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. CH_3CN (2.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue

LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (petroleum: isopropanol = 20:1), to give the product.

3.2. Procedure for Phosphoryl radical onto alkenes of 2a



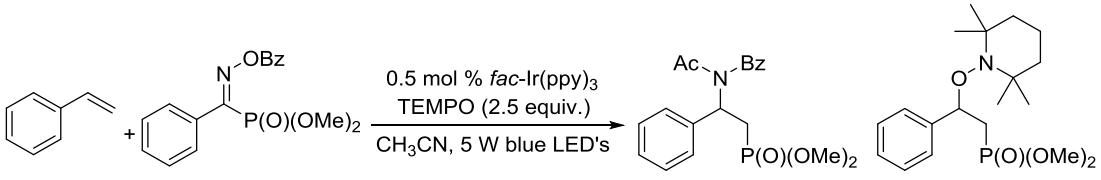
2a, 1 mmol **0.74 mmol**
74% yield, dr> 20:1

A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with alkenes (1.5 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.005 mmol, 0.5 mol %), phosphorus reagents (1.0 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. CH_3CN (5.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (petroleum: isopropanol = 20:1), to give the product **3a** in 78% yield (dr > 20:1).

diethyl (1-(N-acetylbenzamido)-1-phenylpropan-2-yl)phosphonate (**3a**): yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.0 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.42-7.34 (m, 4H), 7.29-7.21 (m, 3H), 5.95 (t, *J* = 7.3 Hz, 1H), 3.96-3.74 (m, 3H), 3.74-3.62 (m, 1H), 3.62-3.46 (m, 1H), 1.79 (s, 3H), 1.41 (dd, *J* = 17.2, 7.2 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.52, 172.89, 138.17, 136.57, 132.94, 129.28, 128.84, 128.59, 128.00, 127.95, 125.67, 61.43 (t, *J* = 7.7 Hz), 33.89 (d, *J* = 138.5 Hz), 27.35, 16.15, 16.09, 15.97, 15.90 (dd, *J* = 18.1, 12.1 Hz), 12.74 (d, *J* = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.35, 30.51. HRMS calcd for $C_{22}H_{28}NNaO_5P^+$: $[M+Na]^+$ 440.1597, found 440.1597.

4. Mechanism studies.

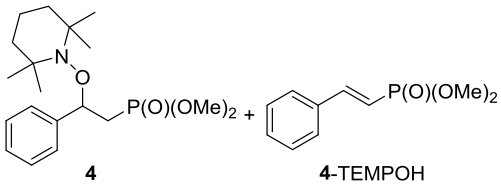
4.1. Radical trapping experiment



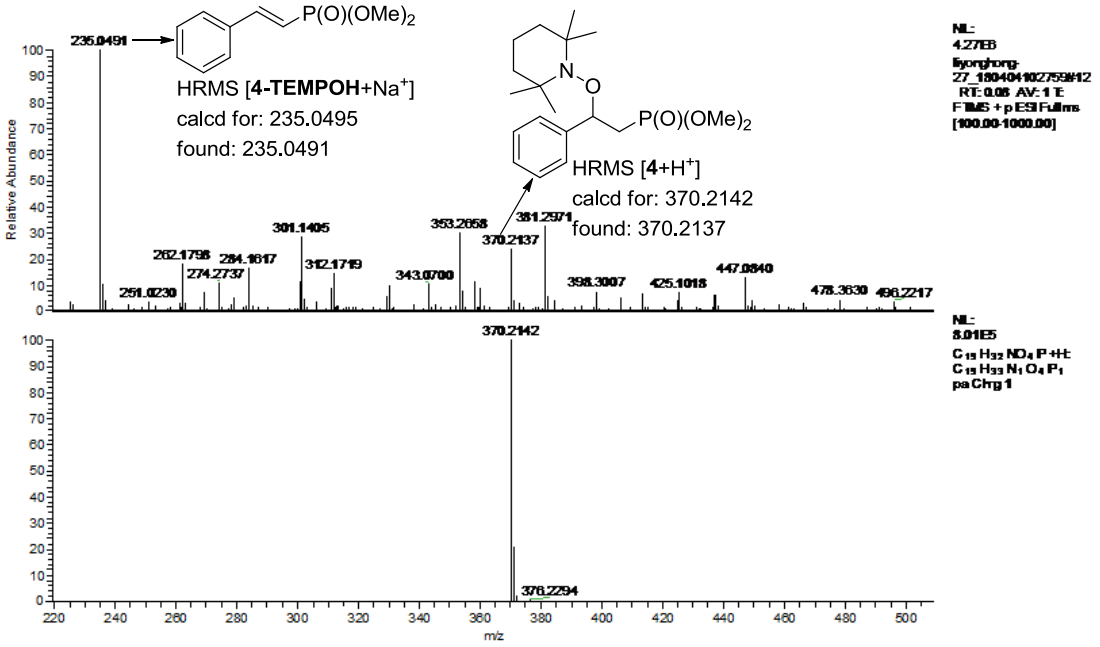
not detected **4** calcd for: 370.2142
found: 370.2137

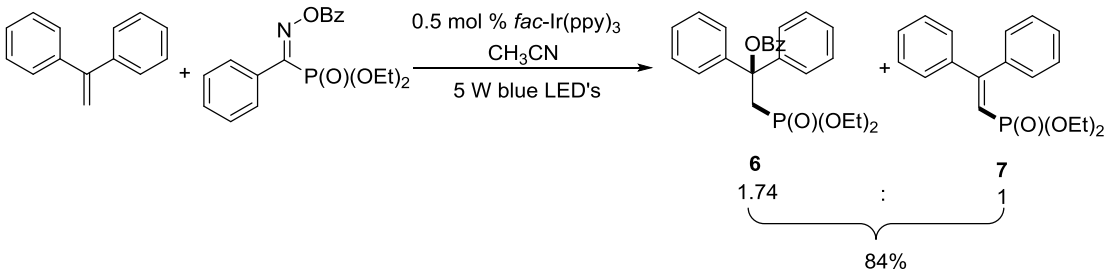
A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with alkenes (0.6 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %) TEMPO (1 mmol, 2.5 equiv.) and phosphorus reagents (0.4 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. CH_3CN (2.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed, the reaction was completely inhibited by TEMPO and no **3a** was formed. The compound **4** and [**4**-TEMPOH] were

detected by HRMS.

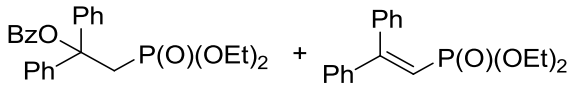


dimethyl (2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phosphonate (**4**): HRMS **4** calcd for $C_{19}H_{33}NO_4P^+$: $[M+H]^+$ 370.2142, found 370.2137; [**4**-TEMPOH] calcd for $C_{10}H_{13}NaO_3P^+$: $[M+Na]^+$ 370.2142, found 370.2137

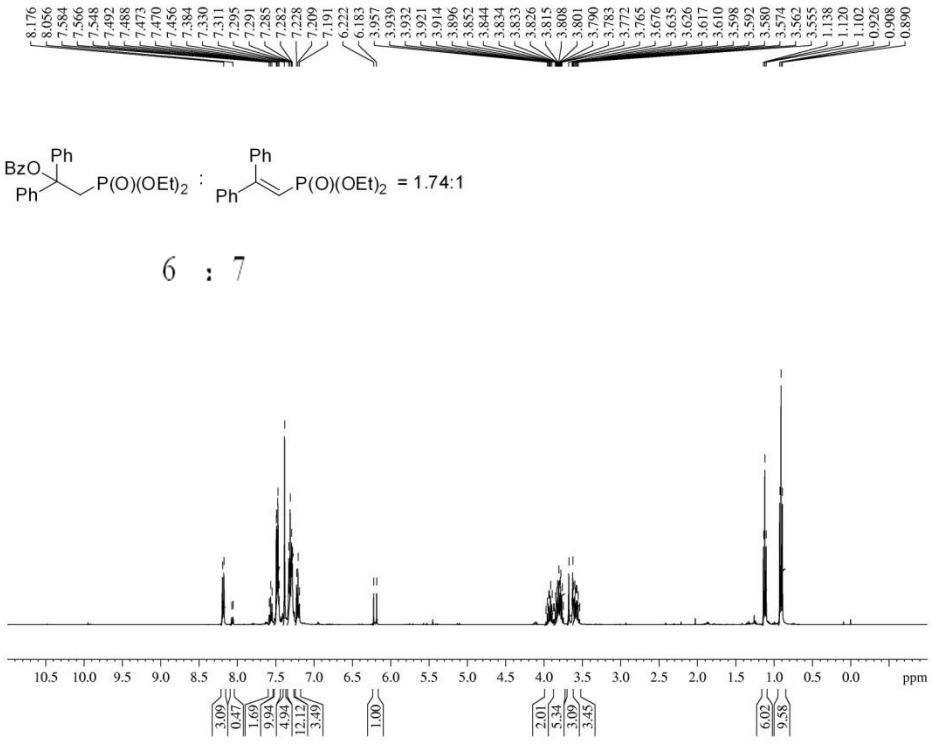


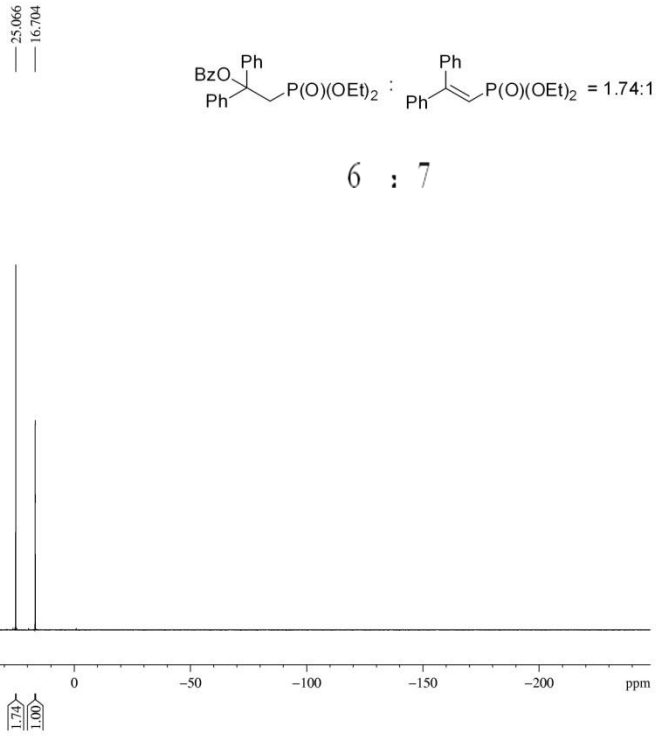


A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with ethene-1,1-diyldibenzene (0.6 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %) and phosphorus reagents (0.4 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. CH_3CN (2.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (petroleum: isopropanol = 20:1), to give the product.



2-(diethoxyphosphoryl)-1,1-diphenylethyl benzoate (**6**)*/diethyl (2,2-diphenylvinyl)phosphonate*(**7**)：131 mg, white solid, total yield: 84%, 1.74:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49-7.36 (m, 6H), 7.38 (s, 3H), 7.36-7.26 (m, 8H), 7.21 (t, *J* = 7.3 Hz, 2H), 6.20 (d, *J* = 15.6 Hz, 0.6H), 3.99-3.74 (m, 4H), 3.65 (d, *J* = 20.2 Hz, 2H), 3.63-3.52 (m, 1H), 1.12 (t, *J* = 7.1 Hz, 4H), 0.91 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.55, 159.96, 159.90, 144.77, 144.69, 141.36, 141.14, 138.72, 138.64, 132.74, 131.21, 129.63, 129.55, 129.53, 129.49, 129.22, 128.49, 128.23, 128.14, 128.12, 128.02, 127.96, 127.65, 127.01, 125.17, 115.41, 113.49, 82.32 (d, *J* = 6.2 Hz), 61.31(dd, *J* = 12.2 Hz, 6.0 Hz), 34.13 (d, *J* = 142.5 Hz), 15.97 (d, *J* = 6.8 Hz), 15.75 (d, *J* = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.07, 16.70.

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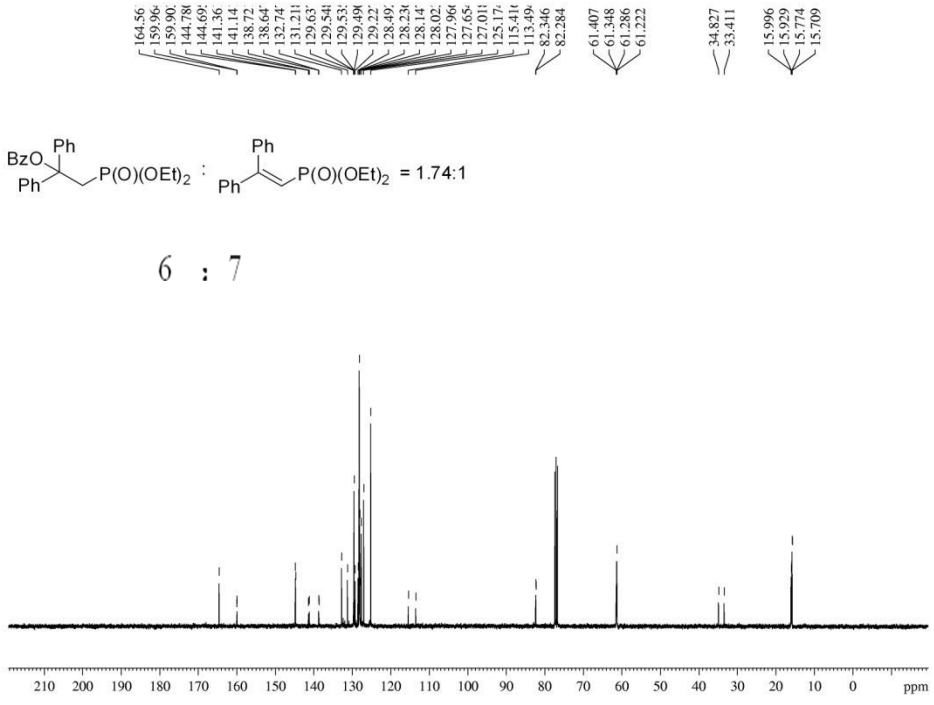
16.704
BzO
Ph
Ph
P(O)(OEt)2
:
Ph
Ph
P(O)(OEt)2
= 1.74:1
6 : 7
100
50
0
−50
−100
−150
−200
ppm
1.74
1.00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159.90
144.78
144.69
141.36
141.14
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138.64
132.74
131.21
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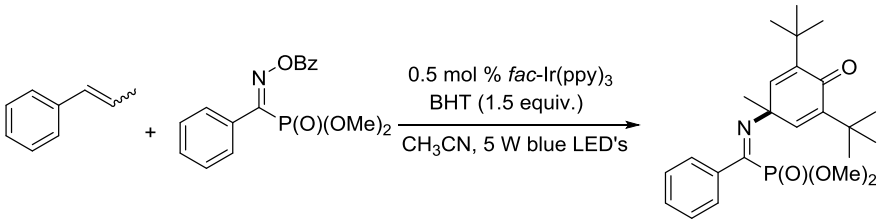
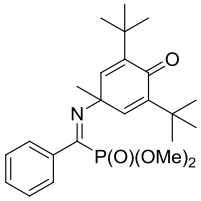
129.54
129.53
129.49
129.22
128.49
128.23
128.14
128.02
127.96
127.65
127.01
125.17
115.41
113.49
82.346
82.284
61.407
61.348
61.286
61.222
34.827
33.411
15.996
15.929
15.774
15.709
BzO
Ph
Ph
P(O)(OEt)2
:
Ph
Ph
P(O)(OEt)2
= 1.74:1
6 : 7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4.2. Iminyl radical trapping experiment

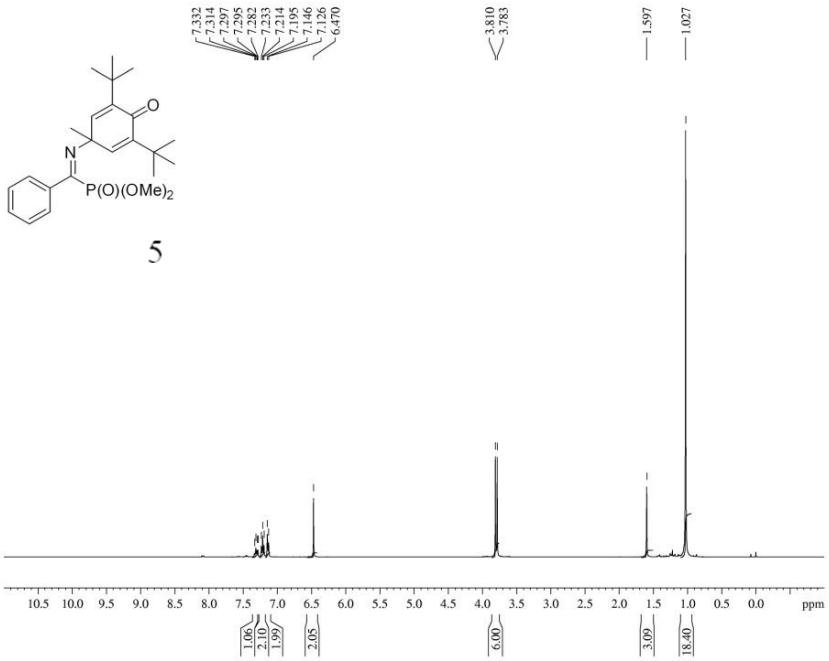


5 54%

A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with ethene-1,1-diyldibenzene (0.6 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %), BHT (0.6 mmol, 1.5 equiv.) and phosphorus reagents (0.4 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. CH_3CN (2.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (petroleum: isopropanol = 20:1), to give the product.



dimethyl (((2,6-di-tert-butyl-4-methylphenoxy)imino)(phenyl)methyl)phosphonate (**5**): 93 mg, yellow liquid，yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 2H), 3.80 (d, *J* = 10.7 Hz, 6H), 1.60 (s, 3H), 1.03 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.56, 171.20 (d, *J* = 217.5 Hz), 143.79, 142.82 (d, *J* = 2.2 Hz), 135.10 (d, *J* = 30.5 Hz), 129.97, 128.06 (d, *J* = 1.8 Hz), 126.82 (d, *J* = 3.9 Hz), 62.84 (d, *J* = 31.6 Hz), 54.23 (d, *J* = 217.5 Hz), 34.33, 32.49, 28.98; ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.44. HRMS calcd for $C_{24}H_{34}NNaO_4P^+$: $[M+Na]^+$ 454.2118, found 454.2114.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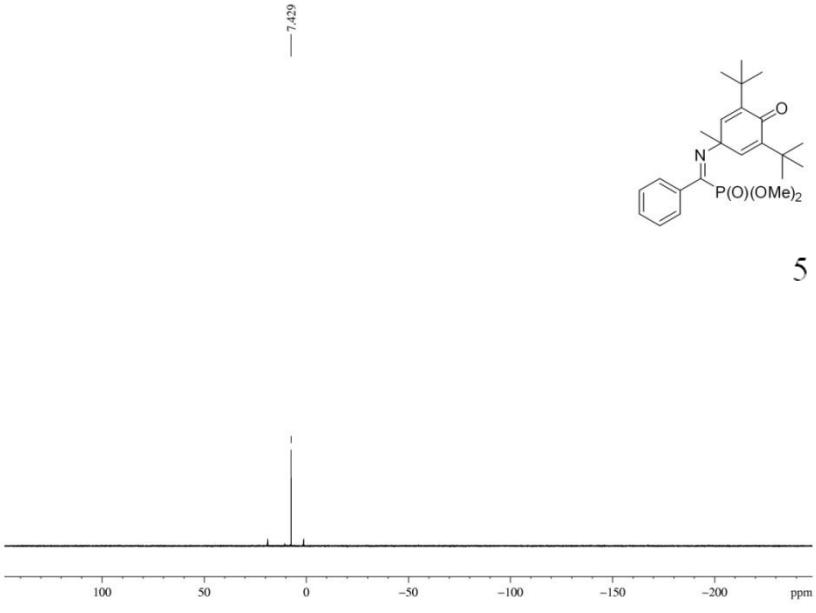
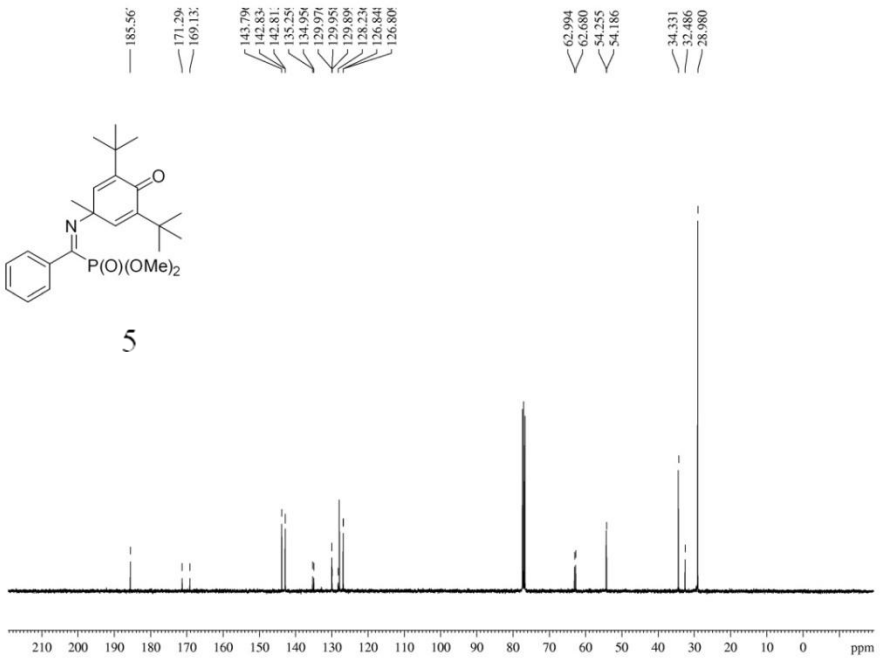
7.295
7.282
7.233
7.214
7.195
7.146
7.126
6.470
3.810
3.783
1.597
1.027
O
N
P(O)(OMe)2
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.06
2.10
1.99
2.05
6.00
3.09
18.40

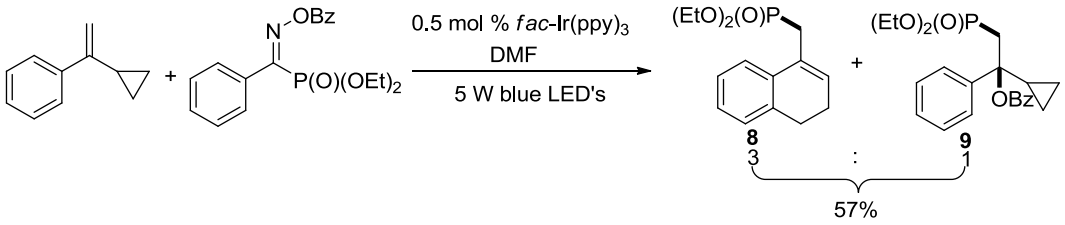
5


7.429
O
N
P(O)(OMe)2
100 50 0 −50 −100 −150 −200 ppm

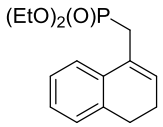
5



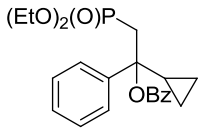
4.3. Clock experiment



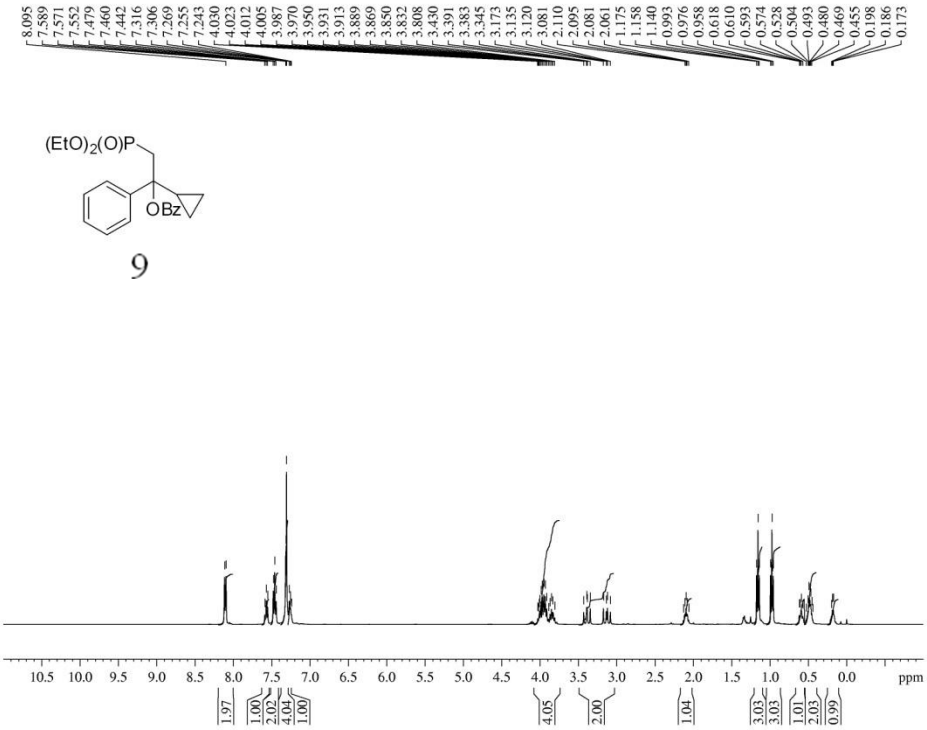
A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with (1-cyclopropylvinyl)benzene (0.6 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %) and phosphorus reagents (0.4 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. DMF (2.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (petroleum: isopropanol = 20:1), to give the product.

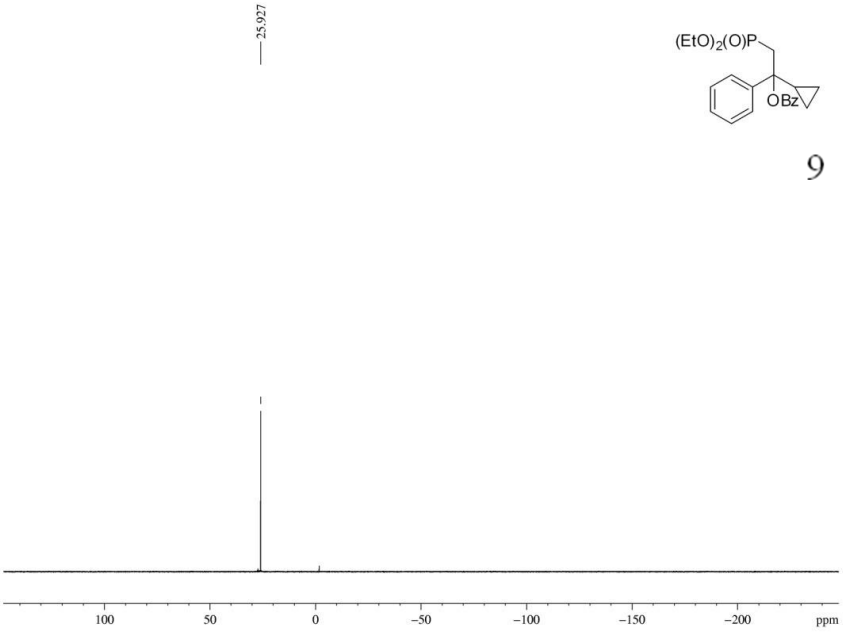


Diethyl ((3,4-dihydronaphthalen-1-yl)methyl)phosphonate (**8**)**:** 50.4 mg, yellow liquid, yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 5.92 (q, *J* = 6.9 Hz, 1H), 4.05-3.83 (m, 4H), 3.67 (t, *J* = 6.8 Hz, 3H), 3.12 (d, *J* = 22.5 Hz, 2H), 2.78 (qd, *J* = 6.9, 4.7 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 6H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 27.03. HRMS calcd for $C_{24}H_{34}NNaO_4P^+$: $[M+H]^+$ 281.1307, found 281.1303.

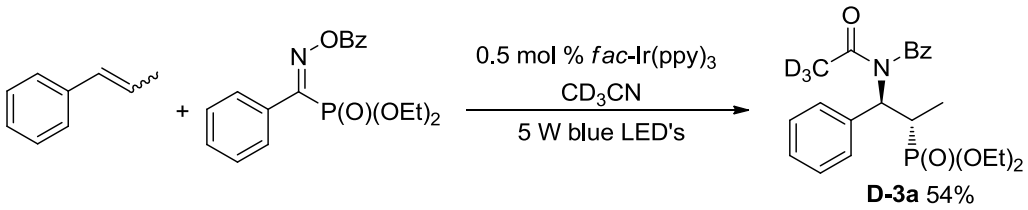


1-cyclopropyl-2-(diethoxyphosphoryl)-1-phenylethyl benzoate (**9**): 24 mg, yellow liquid, yield: 15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38-7.21 (m, 5H), 4.07-3.76 (m, 4H), 3.39 (dd, *J* = 18.7, 15.4 Hz, 1H), 3.13 (dd, *J* = 21.4, 15.3 Hz, 1H), 2.18-1.99 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.60 (dd, *J* = 12.2, 5.3 Hz, 1H), 0.48 (dt, *J* = 9.8, 5.1 Hz, 2H), 0.23-0.13 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.94. HRMS calcd for $C_{24}H_{34}NNaO_4P^+$: $[M+Na]^+$ 454.2118, found 454.2114.



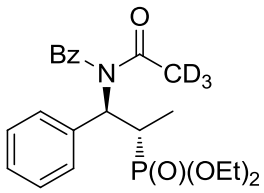


4.4. Deuterium-labled experiment

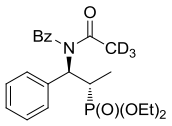


D-3a 54%

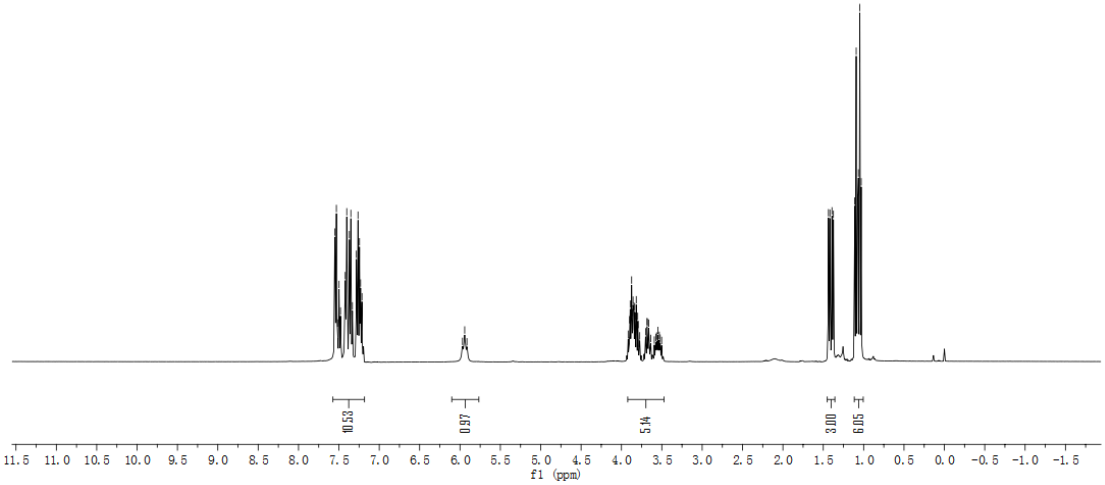
A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with prop-1-en-1-ylbenzene (0.6 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %) and phosphorus reagents (0.4 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. CD_3CN (2.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (petroleum: isopropanol = 20:1), to give the product.

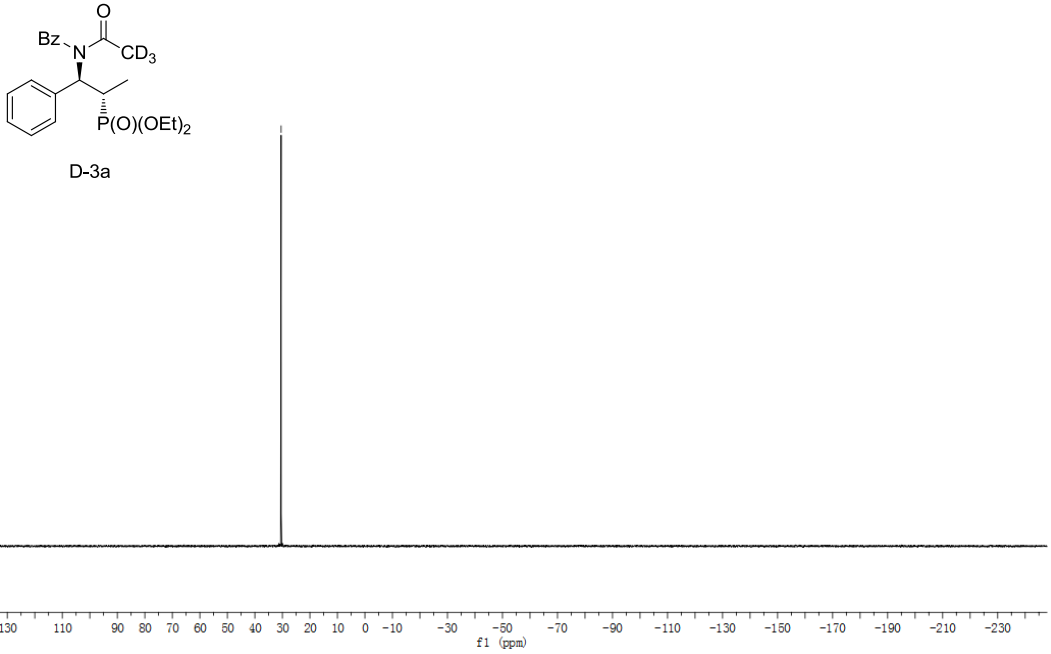


diethyl (1-(N-(acetyl-d3)benzamido)-1-phenylpropan-2-yl)phosphonate (**D-3a**): 90.7 mg, yellow liquid, yield: 54%, dr = 24:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.21 (m, 10H), 5.97-5.91 (t, J = 24 Hz, 1H), 3.92-3.50 (m, 5H), 1.41-1.37 (dd, J = 8 Hz, 3H), 1.11-1.03 (td, J = 16.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.55, 172.96, 138.30, 136.67, 132.93, 129.36, 128.86, 128.65, 127.97, 61.54 (t, $J_{C\text{-}P}$ = 7.1 Hz), 34.69, 33.31, 16.17 (dd, $J_{C\text{-}P}$ = 16.2 Hz), 12.81 (d, $J_{C\text{-}P}$ = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.46. HRMS calcd for $C_{22}H_{25}D_3NO_5P$: $[M+H]^+$ 421.1893, found 421.2439.


O
Bz
N
CD3
P(O)(OEt)2

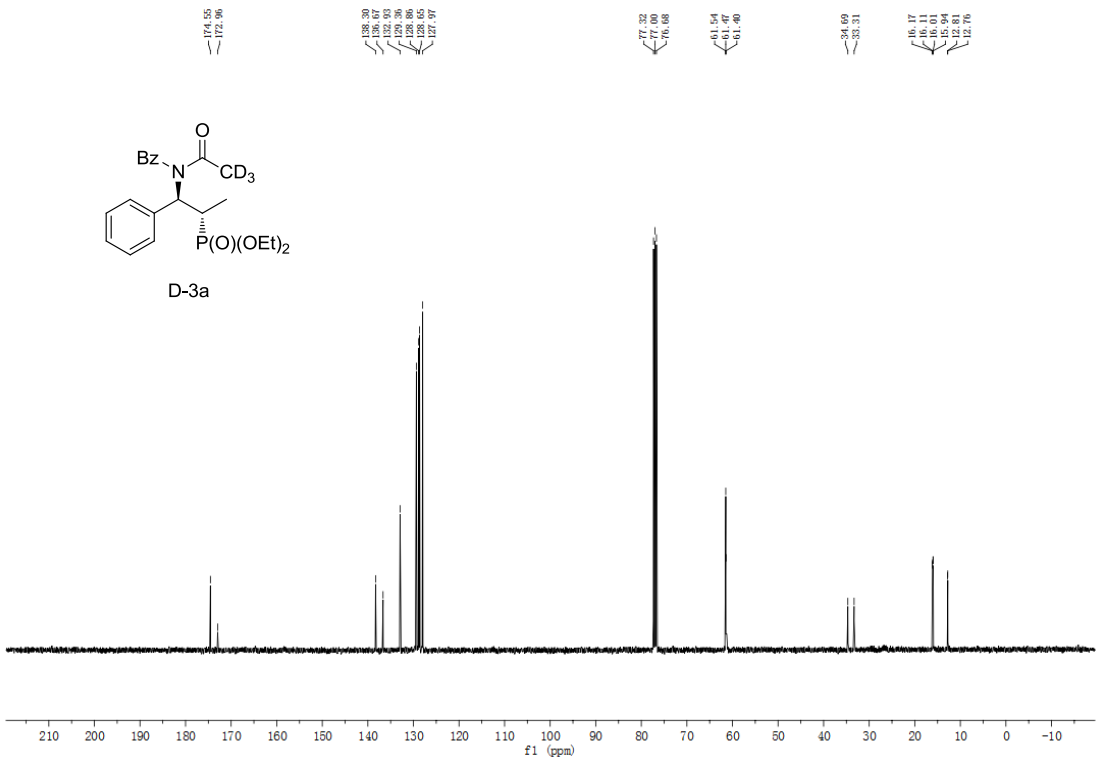
D-3a


10.53
0.97
5.14
3.00
6.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


30.46
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

O
Bz
N
CD3
P(O)(OEt)2

D-3a



4.6. Luminescence quenching experiments

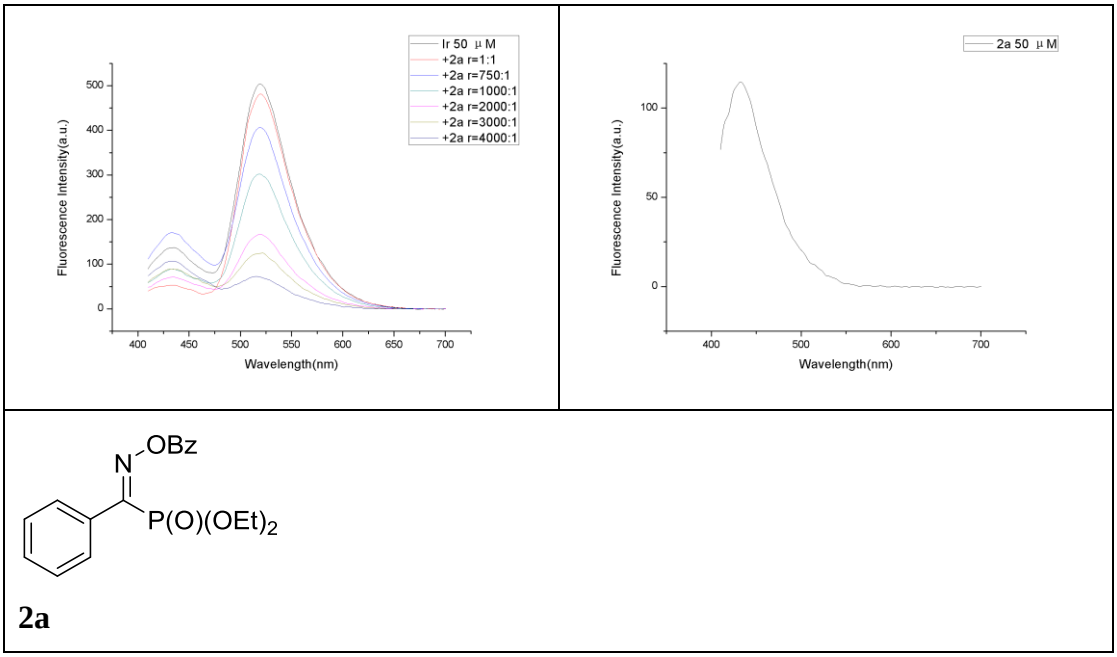
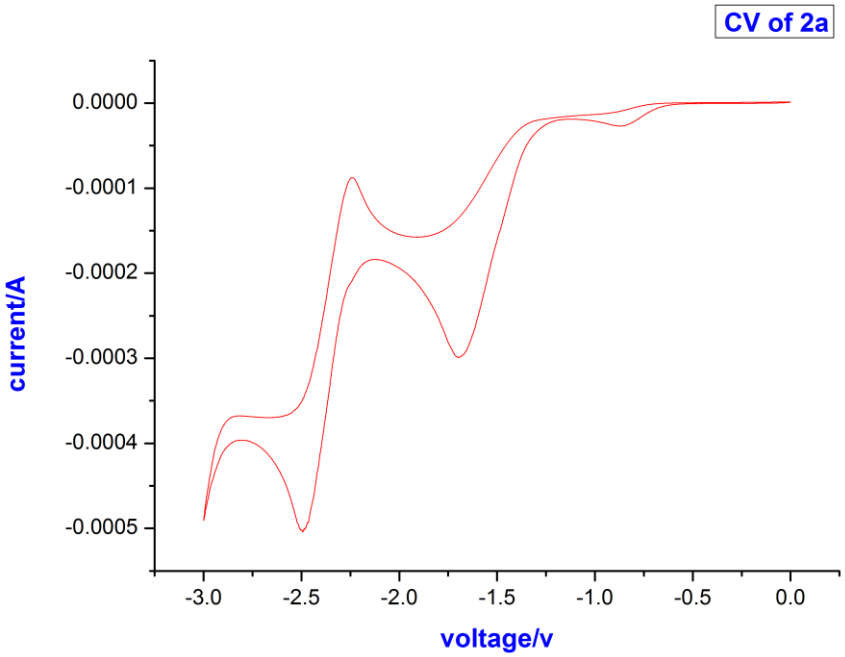


Figure *S1*

Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. All *fac*-Ir(ppy)$_3$ solutions were excited at 382 nm and the emission intensity at 522 nm was observed. In a typical experiment, the emission spectrum of a 1×10^{-5} M solution of *fac*-Ir(ppy)$_3$ in CH_3CN was collected. A significant decrease of *fac*-Ir(ppy)$_3$ luminescence was successfully observed in the presence of **2a** (Figure *S1*). This result suggested that it was the substrate **2a** that quenched the excited photocatalyst * *fac*-Ir(ppy)$_3$.

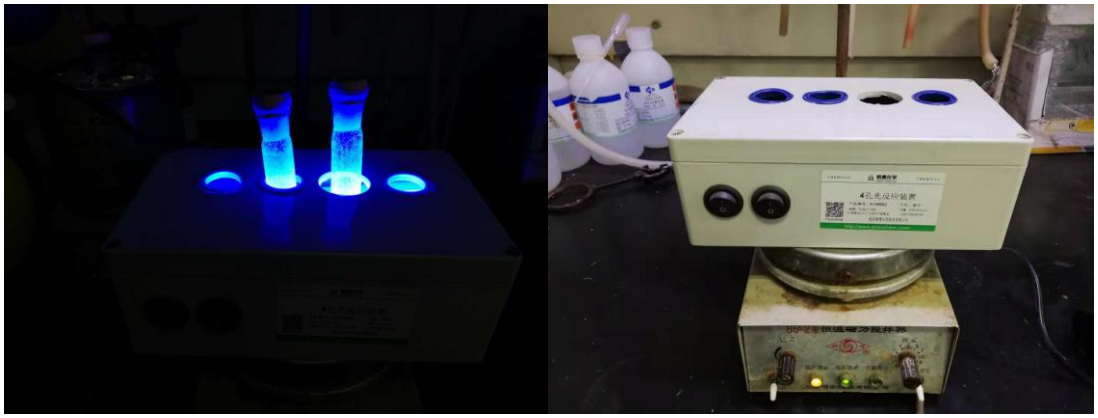
4.6 Cyclic voltammetry for compound 2a



E_{2a}= -1.69 and -2.48 versus SCE

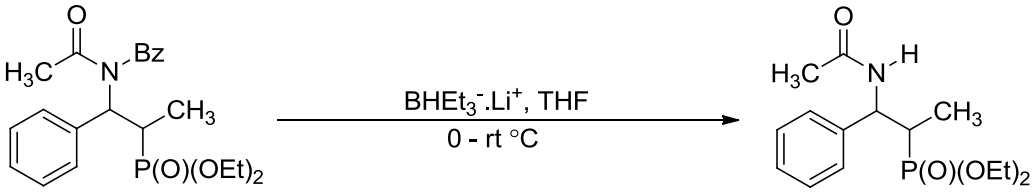
Cyclic voltammerty(CV) was taken using a CHI66OD potentiostation.CV measurement of **2a** was carried out in 0.1 M of Bu_4NPF_6/MeCN at a scan rate of 100 mV/s. The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference is SCE. Hence, E_{2a}= -1.69 and -2.48 versus SCE. $E_{1/2}(fac\text{-}Ir(ppy)_3^{+}/fac\text{-}Ir(ppy)_3^{*})$= − 1.73 versus SCE. These results suggested the excited photocatalyst $Ir(ppy)_3$* reduces the o-benzoyl oxime substrate **2a**.

4.7 Irradiation setup picture



5. Removing the protecting groups

5.1 removing the Bz group[2]

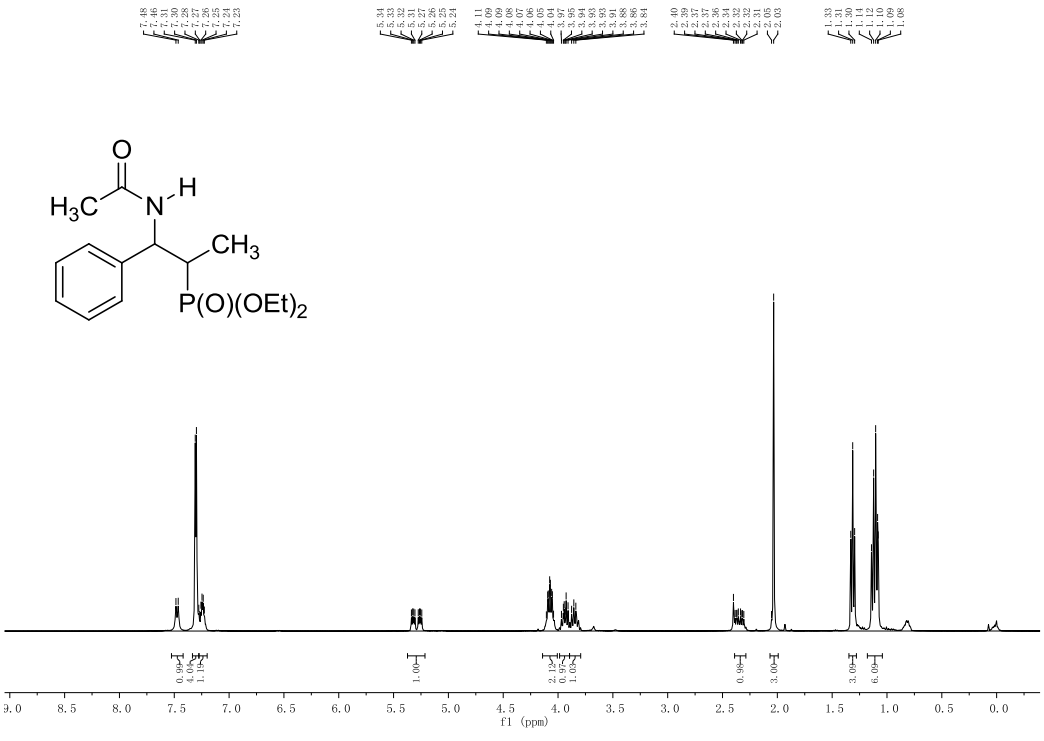


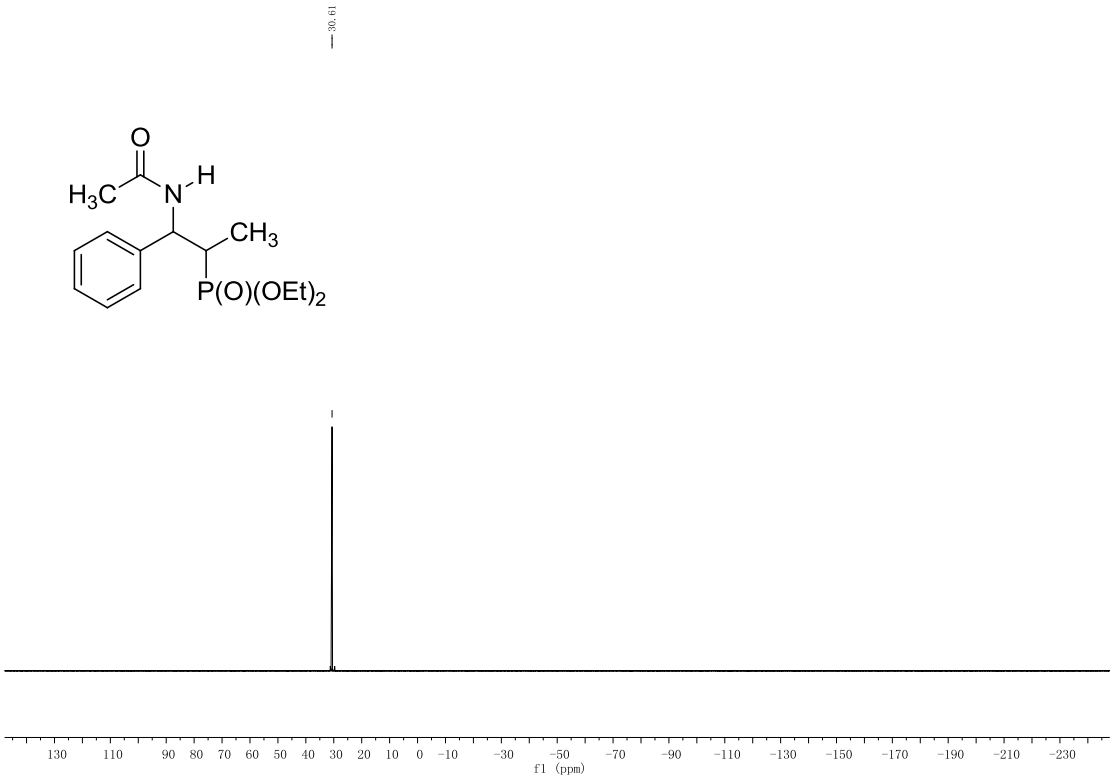
3a **5a**, 86%

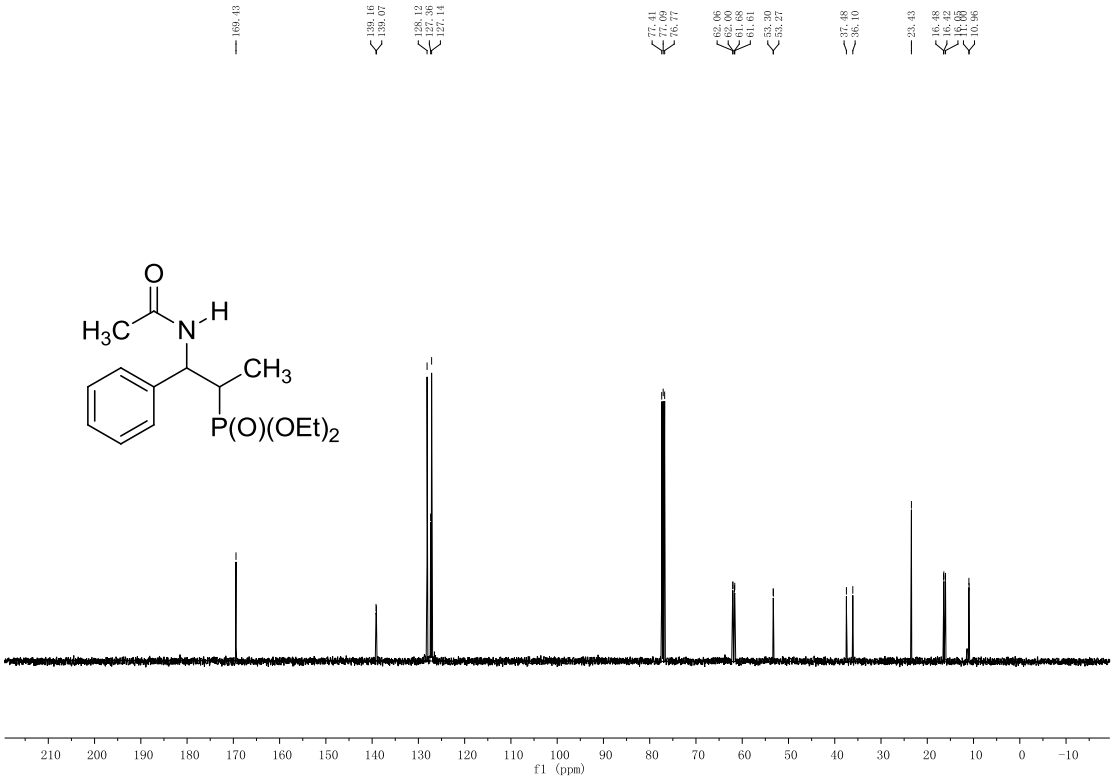
A 5.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with diethyl (1-(*N*-acetylbenzamido)-1-phenylpropan-2-yl)phosphonate **3a** (0.3 mmol, 1.0 equiv.), 1.5ml $LiEt_3BH$ (1M in THF) were dropwise added with syringe under Ar at 0 ^oC.Then stir at room temperature for 3h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (ethyl acetate: MeOH = 20:1) to give the product **5a** (colorless oil, 86 % yield).

Diethyl (1-acetamido-1-phenylpropan-2-yl)phosphonate (5a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 4.3 Hz, 4H), 7.29 – 7.18 (m, 1H), 5.29 (ddd, *J* = 25.0, 8.4, 4.4 Hz, 1H), 4.13 – 4.02 (m, 2H), 3.98 – 3.89 (m, 1H), 3.89 – 3.80 (m, 1H), 2.39 – 2.27 (m, 1H), 2.03 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.15 – 1.04 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43 (s), 139.12 (d, *J* = 8.4 Hz), 128.12 (s), 127.36 (s), 127.14 (s), 61.84 (dd, *J* = 38.7, 7.0 Hz), 53.29 (d, *J* = 3.6 Hz), 36.79 (d, *J* = 138.9 Hz), 23.43 (s), 16.27 (dd, *J* = 36.6, 6.0 Hz), 10.98 (d, *J* = 4.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43 (s), 139.12 (d, *J* = 8.4 Hz), 128.12 (s), 127.36 (s), 127.14 (s), 61.84 (dd, *J* = 38.7, 7.0 Hz), 53.29 (d, *J* = 3.6 Hz), 36.79 (d, *J* = 138.9 Hz), 23.43 (s), 16.27 (dd, *J* = 36.6, 6.0 Hz), 10.98 (d, *J* = 4.5 Hz). IRMS calcd for $C_{15}H_{24}NNaO_4P^+$: $[M+Na]^+$: 336.1341,found 336.2203.

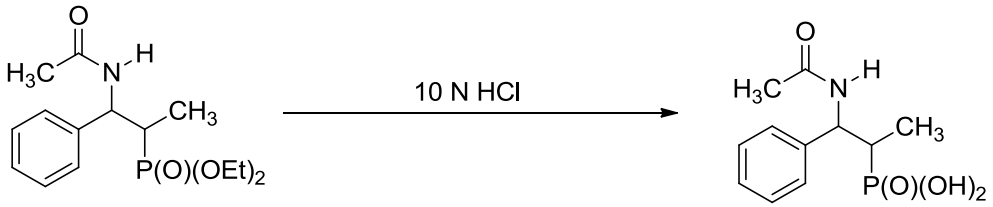



30.61
O
H3C
N
H
CH3
P(O)(OEt)2
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


169.43
139.16
139.07
128.12
127.36
127.14
77.41
77.09
76.77
62.06
62.00
61.88
61.61
53.30
53.27
37.48
36.10
23.43
16.48
16.42
16.05
15.99
10.96
O
H3C
N
H
CH3
P(O)(OEt)2
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)

5.2 hydrolysis of phosphonate

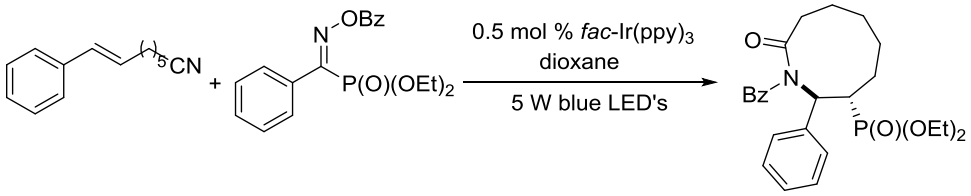
The procedure is same as our former report for published in *Chem. Eur. J.* **2018**, *24*, 14363.



5a **6a**

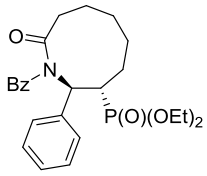
6. Applications

6.1. Intramolecular cyclization reaction

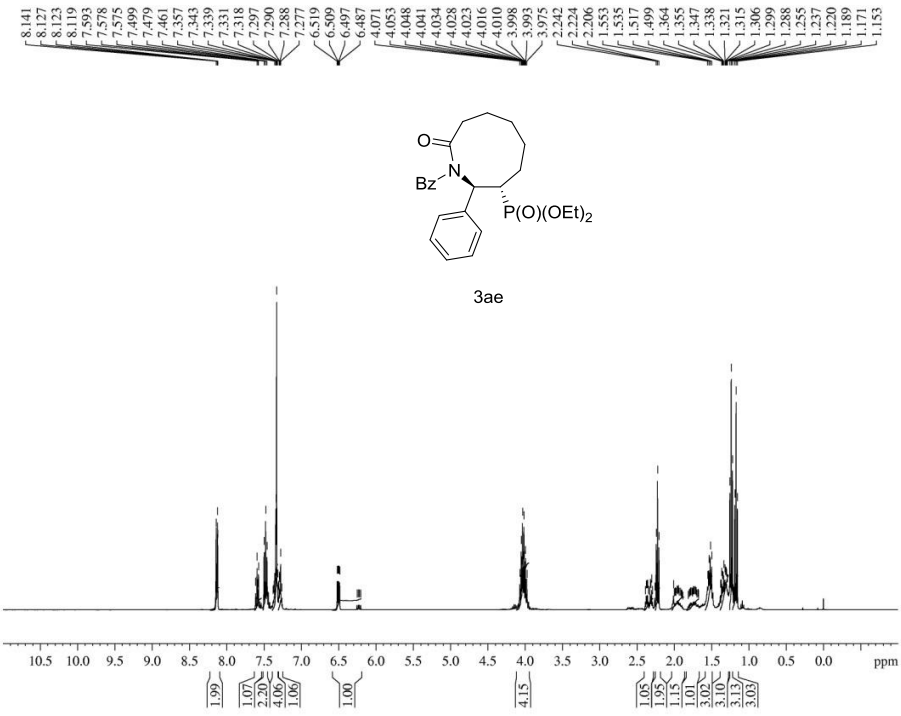


3ae 57%

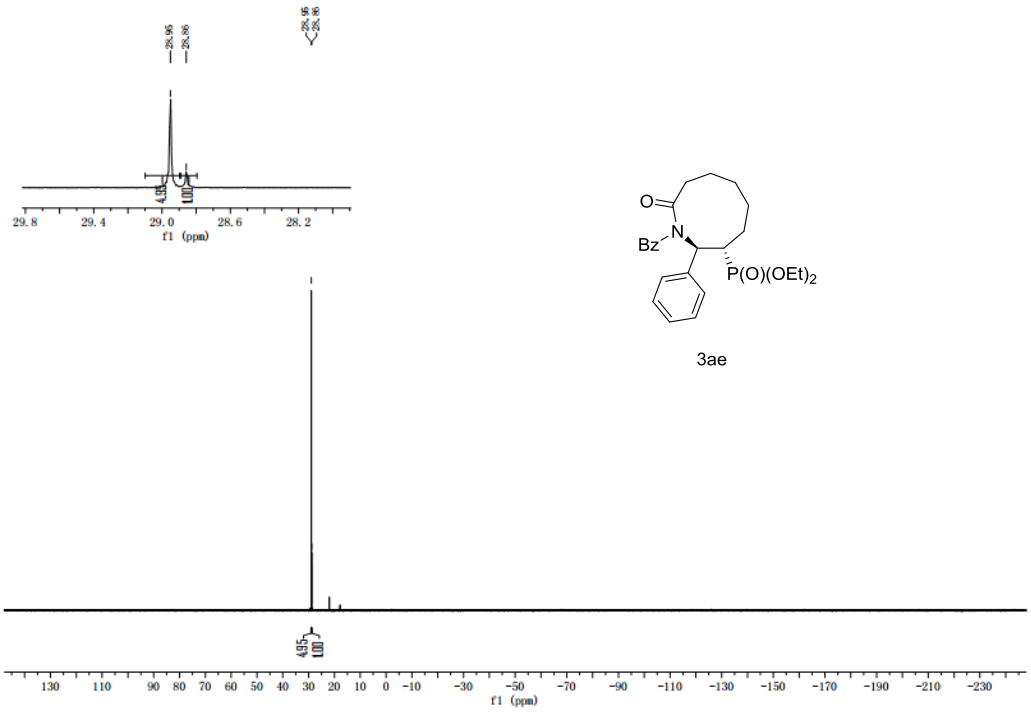
A 10.00 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with 4-phenylbut-3-enenitrile (0.6 mmol, 1.5 equiv.), *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %) and phosphorus reagents (0.4 mmol, 1.0 equiv.). The flask was evacuated and backfilled with Ar for 3 times. dioxane (2.00 mL, 0.2 M) were added with syringe under Ar. The mixture was then irradiated by a 5 W blue LED lamp (away from tube 5-10 cm) at room temperature for 8 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography (petroleum: isopropanol = 20:1), to give the product.



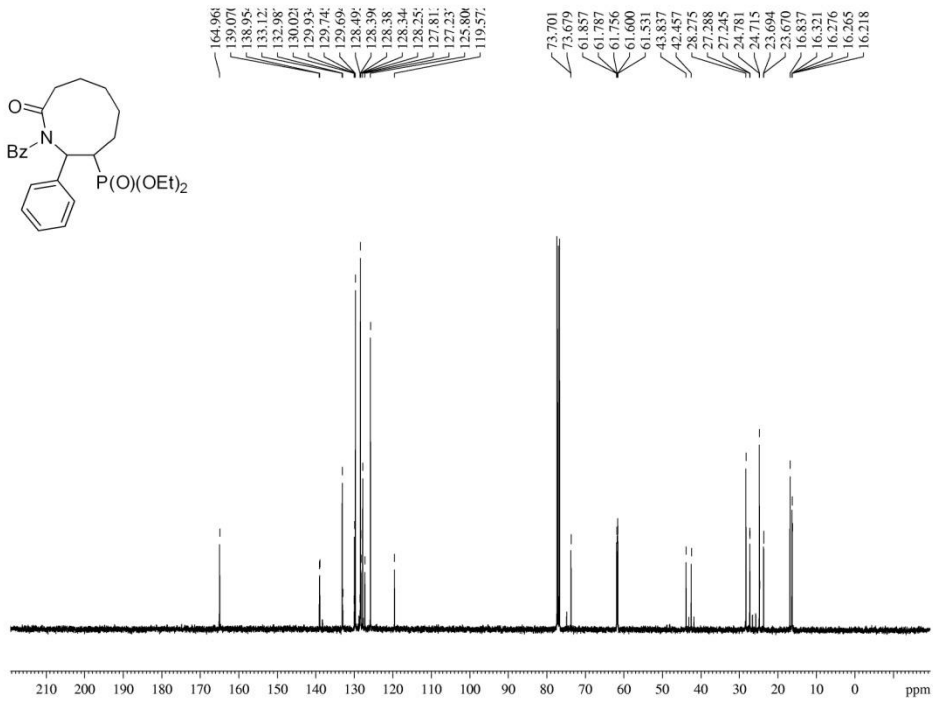
diethyl (1-benzoyl-9-oxo-2-phenylazonan-3-yl)phosphonate (**3ae**): eluent (petroleum: isopropanol = 20:1), 98 mg, yellow liquid, yield: 57%, dr = 5:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.14 (m, 2H), 7.53-7.62 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.38-7.32 (m, 4H), 7.30-7.26 (m, 1H), 6.50 (dd, *J* = 8.9, 4.0 Hz, 1H), 4.11-3.95 (m, 1H), 2.34 (ddt, *J* = 21.6, 7.6, 4.2 Hz, 1H), 2.22 (t, *J* = 7.1 Hz, 2H), 2.01-1.88 (m, 1H), 1.82-1.67 (m, 1H), 1.58-1.49 (m, 3H), 1.38-1.28 (m, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.97, 139.01 (d, *J* = 11.7 Hz), 133.12, 130.02, 129.93, 129.74, 129.69, 128.39, 128.38, 127.81, 127.24, 125.81, 119.57, 73.69 (d, *J* = 2.2 Hz), 61.94 (d, *J* = 25.8, 7.0 Hz), 43.84, 42.46, 28.27, 27.27 (d, *J* = 4.4 Hz), 24.78, 23.68 (d, *J* = 2.3 Hz), 16.84, 16.30 (d, *J* = 4.5 Hz), 16.24 (d, *J* = 4.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.94. HRMS calcd for $C_{23}H_{30}NNaO_5P^+$: $[M+Na]^+$ 454.1754, found 454.1750.


8.141
8.127
8.123
8.119
7.593
7.578
7.575
7.499
7.479
7.461
7.357
7.343
7.339
7.331
7.318
7.297
7.290
7.288
7.277
6.519
6.509
6.497
6.487
4.071
4.053
4.048
4.041
4.034
4.028
4.023
4.016
4.010
3.998
3.993
3.975
2.242
2.224
2.206
1.553
1.535
1.517
1.499
1.364
1.355
1.347
1.338
1.321
1.315
1.306
1.299
1.288
1.255
1.237
1.220
1.189
1.171
1.153
O
N
Bz
P(O)(OEt)2
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.99
1.07
2.20
4.06
1.06
1.00
4.15
1.05
1.95
1.15
1.01
3.02
3.10
3.13
3.03

3ae


29.06
29.06
28.96
28.86
4.35
1.00
29.8 29.4 29.0 28.6 28.2
f1 (ppm)
O
N
Bz
P(O)(OEt)2
4.35
1.00
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

3ae

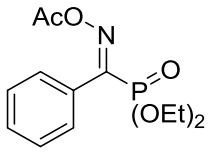


7. Refference

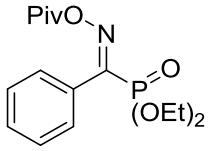
1.T.-I. Chudakova; Y.-V. Rassuakanaya; A.-A. Sinitsa; P.-P. Onyśko, *Russian Journal of General Chemistry*. **2009**, *79*, 195.

2. H. Tanaka, K. Ogasawara, *Tetrahedron Letters*, **2002**, *43*, 4417.

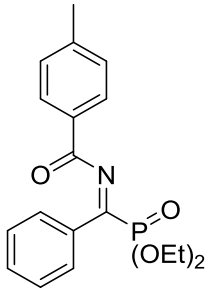
8. Characterization data



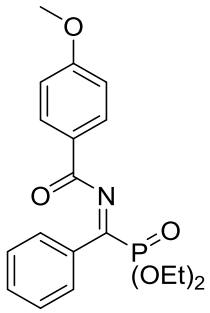
diethyl((acetoxyimino)(phenyl)methyl)phosphonate (**2c**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.45-7.39 (m, 3H), 4.28-4.13 (m, 4H), 2.12 (s, 2H), 1.33-1.25 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 167.8, 159.9, 158.1, 152.1, 150.6, 130.2, 129.8, 129.7, 129.2, 129.0, 128.9, 128.6, 128.3, 128.0, 64.3, 63.2, 19.3, 16.1. Eluent (petroleum: isopropanol = 20:1).



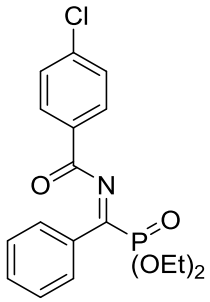
diethyl (phenyl((pivaloyloxy)imino)methyl)phosphonate (**2d**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70-7.53 (m, 2H), 7.45-7.44 (m, 3H), 4.29-4.09 (m, 4H), 1.37-1.30 (m, 6H), 1.12 (s, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 174.3, 160.9, 160.3, 159.6, 159.3, 132.4, 130.5, 130.2, 129.3, 129.1, 128.3, 128.1, 64.4, 63.1, 38.5, 26.9, 16.1. Eluent (petroleum: isopropanol = 20:1).



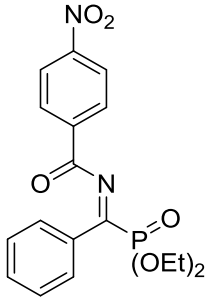
diethyl (((4-methylbenzoyl)imino)(phenyl)methyl)phosphonate (**2e**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19-7.97 (m, 1H), 7.72-7.65 (m, 3H), 7.49-7.48 (m, 2H), 7.47-7.42 (m, 1H), 7.32-7.31 (m, 1H), 7.19-7.18 (m, 1H), 4.34-4.12 (m, 4H), 2.44-2.37 (m, 3H), 1.38-1.23 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 169.4, 163.1, 160.7, 144.7, 144.5, 143.8, 132.3, 130.5, 130.3, 130.2, 130.0, 129.7, 129.4, 129.3, 129.2, 129.1, 128.9, 128.4, 128.3, 127.1, 125.2, 125.1, 64.5, 21.7, 16.1. Eluent (petroleum: isopropanol = 20:1).



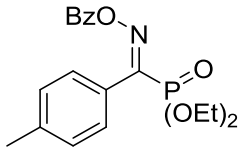
diethyl (((4-methoxybenzoyl)imino)(phenyl)methyl)phosphonate (**2f**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27-8.25 (m, 1H), 7.79-7.72 (m, 3H), 7.50-7.42 (m, 3H), 7.01-6.99 (m, 1H), 6.87-6.85 (m, 1H), 4.33-4.10 (m, 4H), 3.88-3.82 (m, 3H), 1.38-1.26 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 164.0, 163.8, 162.7, 160.4, 159.4, 159.1, 132.3, 132.0, 131.8, 130.5, 130.3, 129.3, 129.1, 128.4, 128.3, 120.0, 113.9, 113.5, 64.4, 63.4, 55.4, 16.1. Eluent (petroleum: isopropanol = 20:1).



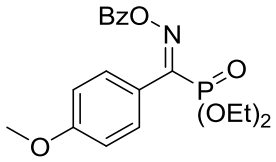
diethyl (((4-chlorobenzoyl)imino)(phenyl)methyl)phosphonate (**2g**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75-7.74 (m, 2H), 7.64-7.63 (m, 2H), 7.57-7.50 (m, 3H), 7.37-7.36 (m, 2H), 4.33-4.30 (m, 4H), 1.38-1.36 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ162.2, 161.4, 160.1, 140.2, 131.4, 131.0, 129.3, 129.2, 128.9, 128.6, 128.4, 128.3, 126.5, 64.6, 16.2. Eluent (petroleum: isopropanol = 20:1).



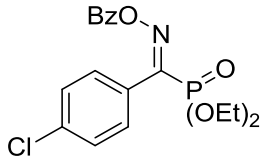
diethyl (((4-nitrobenzoyl)imino)(phenyl)methyl)phosphonate (**2h**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50-8.49 (m, 1H), 8.37-8.36 (m, 1H), 8.25-8.24 (m, 1H), 7.58-7.57 (m, 1H), 7.73-7.72 (m, 1H), 7.64-7.41 (m, 4H), 4.33-4.12 (m, 4H), 1.38-1.27 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 162.4, 162.3, 161.3, 161.2, 161.1, 150.9, 150.8, 133.5, 131.4, 130.9, 130.8, 130.7, 129.2, 129.1, 128.7, 128.6, 128.5, 128.2, 123.8, 64.6, 63.7, 63.3, 16.2. Eluent (petroleum: isopropanol = 20:1).



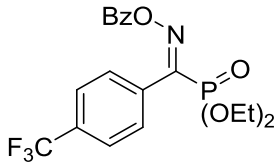
Diethyl (((benzoyloxy)imino)(p-tolyl)methyl)phosphonate (**2i**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31-8.29 (m, 1H), 7.88-7.86 (m, 1H), 7.67-7.60 (m, 2H), 7.54-7.50 (m, 1H), 7.43-7.39 (m, 1H), 7.31-7.24 (m, 2H), 4.34-4.13 (m, 4H), 2.42-2.39 (m, 3H), 1.38-1.26 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ168.6, 163.0, 162.9, 160.8, 159.8, 159.4, 140.9, 140.8, 133.6, 133.5, 132.8, 130.1, 129.8, 129.6, 129.1, 129.0, 128.5, 128.1, 128.0, 127.9, 126.1, 64.4, 63.3, 21.4, 16.1. Eluent (petroleum: isopropanol = 20:1).



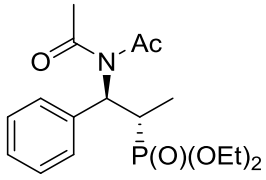
diethyl(((benzoyloxy)imino)(4-methoxyphenyl)methyl)phosphonate (**2j**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30-7.89 (m, 2H), 7.78-7.73 (m, 2H), 7.63-7.50 (m, 2H), 7.44-7.41 (m, 1H), 7.01-6.94 (m, 2H), 4.34-4.13 (m, 4H), 3.88-3.85 (m, 3H), 1.39-1.27 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 163.2, 163.1, 161.8, 161.2, 160.3, 160.1, 159.3, 158.7, 133.7, 133.6, 132.9, 131.0, 130.9, 130.8, 130.1, 129.7, 128.6, 128.2, 124.6, 124.4, 121.3, 121.2, 113.8, 64.4, 63.3, 55.3, 16.2. Eluent (petroleum: isopropanol = 20:1).



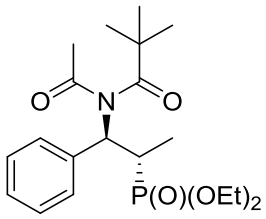
diethyl(((benzoyloxy)imino)(4-chlorophenyl)methyl)phosphonate (**2k**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29-8.09 (m, 1H), 7.84-7.83 (m, 1H), 7.74-7.73 (m, 1H), 7.65-7.63 (m, 1H), 7.59-7.57 (m, 1H), 7.54-7.41 (m, 4H), 4.35-4.15 (m, 4H), 1.39-1.28 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 169.8, 162.9, 162.8, 159.8, 158.9, 158.5, 137.2, 136.7, 133.9, 133.8, 133.3, 131.0, 130.8, 130.6, 130.3, 130.2, 130.0, 129.9, 129.1, 128.8, 128.7, 128.5, 128.3, 127.8, 127.6, 127.5, 64.7, 63.6, 16.2. Eluent (petroleum: isopropanol = 20:1).



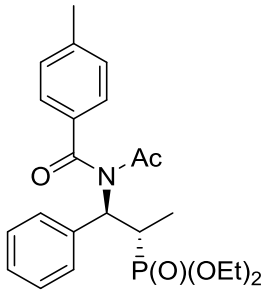
diethyl (((benzoyloxy)imino)(4-(trifluoromethyl)phenyl)methyl)phosphonate (**2l**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30-7.40 (m, 9H), 4.36-4.17 (m, 4H), 1.40-1.29 (m, 6H); ^{13}C NMR (152 MHz, $CDCl_3$) δ 17.0, 162.9, 162.7, 159.9, 158.9, 158.5, 134.0, 133.9, 133.4, 132.9, 132.5, 132.3, 132.1, 130.3, 130.1, 129.7, 129.6, 129.2, 128.9, 128.8, 128.4, 127.7, 125.5, 125.3, 125.2, 124.6, 122.8, 64.8, 64.6, 16.2. Eluent (petroleum: isopropanol = 20:1).



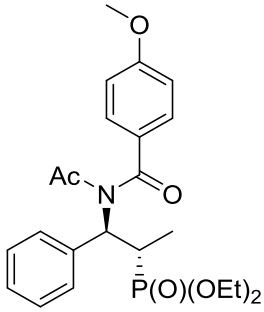
diethyl (1-(N-acetylacetamido)-1-phenylpropan-2-yl)phosphonate (**2ac**): eluent (petroleum: isopropanol = 20:1), 95.2 mg, yellow liquid, yield: 67%, dr > 50:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.33-7.27 (m, 3H), 5.32-5.26 (q, *J* = 12.0 Hz, 1H), 3.98-3.91 (m, 2H), 3.78-3.74 (m, 1H), 3.55-3.48 (m, 2H), 2.41 (s, 6H), 1.28-1.23 (dd, *J* = 20.0 Hz, 3H), 1.16-1.13 (dd, *J* = 4.0 Hz, 3H), 1.01-0.98 (t, *J* = 8.0 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.20, 138.10, 129.34, 127.96 (*J* = 2.02 Hz), 61.75 (*J* = 7.07 Hz), 61.50 (*J* = 7.07 Hz), 33.71, 33.23, 26.95, 16.11 (q, *J* = 12.1 Hz), 12.43 (d, *J* = 5.05 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.30. HRMS calcd for $C_{17}H_{26}NO_5P$: $[M+H]^+$ 356.1549, found 356.1581.



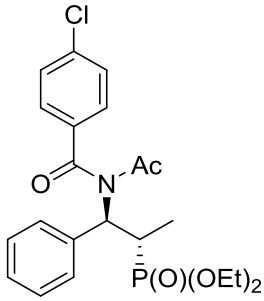
N-acetyl-N-(2-((diethylperoxy)(oxo)-l4-phosphanyl)-1-phenylpropyl)pivalamide (**2ad**): eluent (petroleum: isopropanol = 20:1), 102.0 mg, yellow liquid, yield: 64%, dr = 8.7:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 5H), 5.16-5.11 (t, *J* = 12.0 Hz, 1H), 3.98-3.84 (m, 2H), 3.79-3.73 (m, 1H), 3.55-3.37 (m, 2H), 2.42 (s, 3H), 1.41-1.35 (t, *J* = 16.0 Hz, 3H), 1.14-1.17 (dd, *J* = 4.0 Hz, 3H), 0.98-0.95 (t, *J* = 8.0 Hz, 3H), 0.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.87, 173.04, 137.41, 129.48, 128.46, 128.22, 128.04, 127.20, 62.36, 61.73, 61.46, 43.99, 35.70, 34.34, 27.50, 23.61, 16.13 (t, *J* = 14Hz), 12.41 (d, *J* = 6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.05, 30.62. HRMS calcd for $C_{20}H_{32}NO_5P$: $[M+H]^+$ 398.2018, found 398.2064.



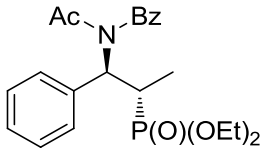
diethyl (1-(N-acetyl-4-methylbenzamido)-1-phenylpropan-2-yl)phosphonate (**2ae**): eluent (petroleum: isopropanol = 20:1), 51.7 mg, yellow liquid, yield: 30%, dr = 14:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (d, *J* = 6.0 Hz, 2H), 7.32-7.20 (m, 5H), 7.15-7.13 (d, *J* = 6.0 Hz, 2H), 5.95 (m, 1H), 3.90-3.66 (m, 5H), 2.35 (s, 3H), 1.79 (s, 3H), 1.43-1.37 (dd, *J* = 12.0 Hz, 3H), 1.11-1.03 (td, *J* = 12.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.51, 172.73, 144.02, 138.27, 133.84, 129.53, 129.53, 129.31, 128.87, 127.92, 127.89, 61.53 (td, *J* = 17.2 Hz), 34.74 (d, *J* = 139.4 Hz), 27.20, 21.53, 16.15 (dd, *J* = 17.2 Hz), 12.76 (d, *J* = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.60. HRMS calcd for $C_{23}H_{30}NO_5P$: $[M+H]^+$ 432.1832, found 432.1834.



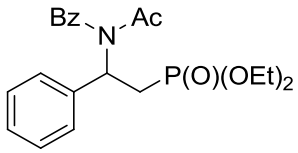
diethyl (1-(N-acetyl-4-methoxybenzamido)-1-phenylpropan-2-yl)phosphonate (**2af**): eluent (petroleum: isopropanol = 20:1), 80.5 mg, yellow liquid, yield: 45%, dr = 14:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (d, *J* = 6.0 Hz, 2H), 7.39-7.37 (d, *J* = 6.0 Hz, 2H), 7.24-7.19 (m, 3H), 6.82-6.80 (d, *J* = 6.0 Hz, 2H), 5.95 (m, 1H), 3.92-3.48 (m, 8H), 1.81 (s, 3H), 1.44-1.38 (dd, *J* = 12.0 Hz, 3H), 1.11-1.03 (td, *J* = 12.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.93, 172.21, 163.49, 138.18, 131.14, 129.19, 128.72, 127.87, 127.83, 114.04, 61.46 (dd, *J* = 9.1 Hz), 55.36, 34.81 (d, *J* = 38.4 Hz), 16.08 (dd, *J* = 16.2Hz), 12.67 (d, *J* = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.64. HRMS calcd for $C_{23}H_{30}NO_6P$: $[M+H]^+$ 448.1811, found 448.1814.



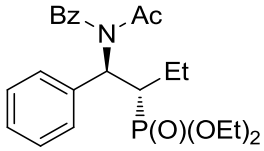
diethyl (1-(N-acetyl-4-chlorobenzamido)-1-phenylpropan-2-yl)phosphonate (**2ag**): eluent (petroleum: isopropanol = 20:1), 117.3 mg, yellow liquid, yield: 68%, dr > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.36-7.22 (m, 7H), 5.93-5.88 (t, *J* = 12.0 Hz, 1H), 3.91-3.80 (m, 3H), 3.69-3.63 (m, 1H), 3.56-3.47 (m, 1H), 1.85 (s, 1H), 1.43-1.37 (dd, *J* = 16.0 Hz, 3H), 1.10-1.04 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.51, 172.39, 139.42, 138.02, 134.84, 129.92, 129.15, 128.04 (t, *J* = 4.1Hz), 61.52, 34.91, 33.07, 27.10, 16.10 (t, *J* = 13.1 Hz), 12.73 (d, *J* = 8.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.28. HRMS calcd for $C_{22}H_{27}ClNO_5P$: $[M+H]^+$ 452.1315, found 432.1429.



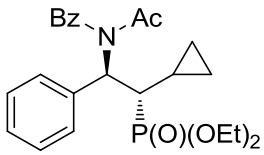
diethyl (1-(N-acetylbenzamido)-1-phenylpropan-2-yl)phosphonate (**3a**): eluent (petroleum: isopropanol = 20:1), 105 mg, yellow liquid, yield: 74%, dr > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.0 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.42-7.34 (m, 4H), 7.29-7.21 (m, 3H), 5.95 (t, *J* = 7.3 Hz, 1H), 3.96-3.74 (m, 3H), 3.74-3.62 (m, 1H), 3.62-3.46 (m, 1H), 1.79 (s, 3H), 1.41 (dd, *J* = 17.2, 7.2 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.52, 172.89, 138.17, 136.57, 132.94, 129.28, 128.84, 128.59, 128.00, 127.95, 125.67, 61.43 (t, *J* = 7.7 Hz), 33.89 (d, *J* = 138.5 Hz), 27.35, 16.15, 16.09, 15.97, 15.90 (dd, *J* = 18.1, 12.1 Hz), 12.74 (d, *J* = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.35, 30.51. HRMS calcd for $C_{22}H_{28}NNaO_5P^+$: $[M+Na]^+$ 440.1597, found 440.1597.



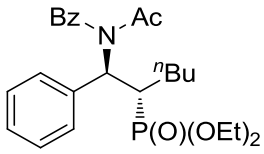
diethyl (2-(N-acetylbenzamido)-2-phenylethyl)phosphonate (**3b**): eluent (petroleum: isopropanol = 20:1), 108 mg, yellow liquid, yield: 67%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 6.14 (td, *J* = 10.4, 4.6 Hz, 1H), 4.15-3.99 (m, 4H), 3.40 (td, *J* = 16.0, 10.7 Hz, 1H), 2.66-2.46 (m, 1H), 1.84 (s, 3H), 1.27 (dd, *J* = 12.5, 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.51, 173.47, 139.08, 138.93, 136.54, 132.22, 128.38, 128.36, 127.97, 127.38, 61.43 (dd, *J* = 37.2 Hz, 6.5 Hz), 54.24 (d, *J* = 3.1 Hz), 28.76, 27.80, 27.35, 15.96 (dd, *J* = 5.8 Hz, 4.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.74. HRMS calcd for $C_{21}H_{26}NNaO_5P^+$: $[M+Na]^+$ 426.1441, found 426.1443.



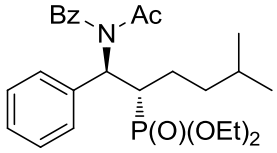
diethyl (1-(N-acetylbenzamido)-1-phenylbutan-2-yl)phosphonate (**3c**): eluent (petroleum: isopropanol = 20:1), 98 mg, yellow liquid, yield: 62%, dr = 12:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.8 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 16.0 Hz, 2H), 7.38 (dt, *J* = 16.2 Hz, 2H), 7.31-7.22 (m, 3H), 6.07-5.94 (m, 1H), 3.96-3.72 (m, 3H), 3.66-3.41 (m, 2H), 2.08-1.72 (m, 2H), 1.75 (s, 3H), 1.18 (t, *J* = 7.5 Hz, 3H), 1.08 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.40, 173.35, 138.48, 136.80, 132.90, 129.47, 128.86, 128.53, 127.92, 127.90, 61.15 (t, *J* = 7.7 Hz), 59.92, 40.16 (t, *J* = 136.4 Hz), 27.83, 20.76 (d, *J* = 4.6 Hz), 16.02 (dd, *J* = 12.9 Hz, 6.0 Hz), 11.10 (d, *J* = 2.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.12, 29.82. HRMS calcd for $C_{23}H_{30}NNaO_5P^+$: $[M+Na]^+$ 454.1754, found 454.1750.



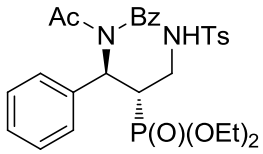
diethyl (1-(N-acetylbenzamido)-1-phenylbutan-2-yl)phosphonate (**3d**): eluent (petroleum: isopropanol = 20:1), 110 mg, yellow liquid, yield: 70%, dr >20:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 6.9 Hz, 1H), 6.23 (t, *J* = 10.9 Hz, 1H), 4.00-3.84 (m, 2H), 3.84-3.75 (m, 1H), 3.69 (ddd, *J* = 16.8, 9.3, 7.5 Hz, 1H), 2.81 (dt, *J* = 17.1, 11.3 Hz, 1H), 1.80 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H), 1.00-0.88 (m, 1H), 0.74-0.63 (m, 3H), 0.54-0.50 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.47, 172.79, 137.71, 136.94, 132.66, 129.70, 128.68, 128.42, 127.62, 127.49, 61.32 (t, *J* = 6.4 Hz), 60.61 (t, *J* = 8.9 Hz), 43.46 (d, *J* = 137.3 Hz), 27.48, 16.00 (dd, *J* = 12.1 Hz, 6.3 Hz), 9.74 (d, *J* = 5.6 Hz), 4.97 (d, *J* = 14.6 Hz), 4.07; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.94, 28.19. HRMS calcd for $C_{24}H_{30}NNaO_5P^+$: $[M+Na]^+$ 466.1754, found 466.1753.



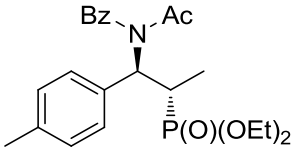
diethyl (1-(N-acetylbenzamido)-1-phenylhexan-2-yl)phosphonate (**3e**): eluent (petroleum: isopropanol = 20:1), 129 mg, yellow liquid, yield: 51%, dr = 12:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.30-7.21 (m, 3H), 5.98 (t, *J* = 10.9 Hz, 1H), 3.94-3.83 (m, 1H), 3.83-3.72 (m, 2H), 3.63-3.45 (m, 2H), 1.91-1.67 (m, 2H), 1.76 (s, 3H), 1.60 (dt, *J* = 14.7, 7.4 Hz, 2H), 1.39-1.26 (m, 2H), 1.07 (td, *J* = 7.0, 1.5 Hz, 6H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.36, 173.29, 138.47, 136.69, 132.91, 129.44, 128.80, 128.53, 127.88, 127.85, 61.07 (t, *J* = 6.8 Hz), 60.22, 38.85 (d, *J* = 136.6 Hz), 28.60 (d, *J* = 1.8 Hz), 27.76, 27.47(d, *J* = 4.4 Hz), 23.17, 16.00 (dd, *J* = 10.5 Hz, 6.5 Hz), 13.79; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.20, 29.92. HRMS calcd for $C_{25}H_{34}NNaO_5P^+$: $[M+Na]^+$ 482.2067, found 482.2066.



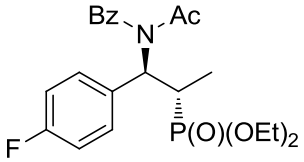
diethyl (1-(N-acetylbenzamido)-4-methyl-1-phenylpentan-2-yl)phosphonate (**3f**): eluent (petroleum: isopropanol = 20:1), 94 mg, yellow liquid, yield: 57%, dr = 12:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 5.96 (t, *J* = 11.1 Hz, 1H), 3.94-3.78 (m, 2H), 3.78-3.60 (m, 2H), 3.60-3.44 (m, 1H), 2.19-2.03 (m, 1H), 1.95-1.78 (m, 1H), 1.77 (s, 3H), 1.45-1.27 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H), 0.98 (dd, *J* = 13.9, 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.30, 172.91, 138.33, 136.69, 132.86, 129.45, 128.79, 128.54, 127.79, 127.75, 61.26 (dd, *J* = 11.6 Hz, 7.0 Hz), 60.89 (d, *J* = 7.0 Hz), 37.59, 36.70 (d, *J* = 4.2 Hz), 36.23, 27.52, 26.13 (d, *J* = 2.6 Hz), 23.87, 21.52, 16.02 (dd, *J* = 21.5, 6.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.55, 30.05. HRMS calcd for $C_{25}H_{34}NNaO_5P^+$: $[M+Na]^+$ 482.2067, found 482.2070.



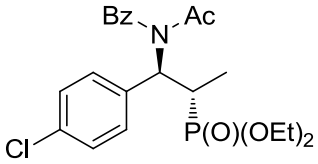
Diethyl (1-(N-acetylbenzamido)-3-(4-methylphenylsulfonamido)-1-phenylpropan-2-yl)phosphon -ate (**3g**): eluent (petroleum: isopropanol = 20:1), 105.5 mg, yellow liquid, yield: 45%, dr = 17:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 6.7 Hz, 2H), 7.48 (t, *J* = 4.4 Hz, 1H), 7.36-7.31 (m, 6H), 7.28-7.24 (m, 3H), 6.13 (s, 1H), 5.93 (q, *J* = 6.7 Hz, 1H), 3.81-3.62 (m, 4H), 3.54-3.45 (m, 2H), 3.36-3.28 (m, 1H), 2.42 (s, 3H), 1.81 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.85, 173.62, 143.22, 137.21, 136.66, 136.26, 132.98, 129.55, 129.07, 128.83, 128.50, 128.30, 128.14, 127.20, 62.09 (dd, *J* = 32.0, 7.0 Hz), 41.78 (d, *J* = 6.7 Hz), 39.06, 37.70, 27.71, 21.43, 15.85 (dd, *J* = 5.5, 5.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.98, 26.32. HRMS calcd for $C_{29}H_{35}N_2NaO_7PS^+$: $[M+H]^+$ 609.1795, found 609.1791.



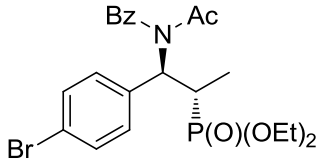
diethyl (1-(N-acetylbenzamido)-1-(p-tolyl)propan-2-yl)phosphonate (**3h**): eluent (petroleum: isopropanol = 20:1), 122 mg, yellow liquid, yield: 71%, dr = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.90 (t, *J* = 11.3 Hz, 1H), 4.00-3.77 (m, 3H), 3.77 -3.63 (m, 1H), 3.63-3.46 (m, 1H), 2.26 (s, 3H), 1.79 (s, 3H), 1.41 (dd, *J* = 17.3, 7.2 Hz, 1H), 1.11 (t, *J* = 7.0 Hz,3H), 1.07 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.47, 172.95, 137.50, 136.66, 135.20, 132.79, 132.69, 129.82, 129.20, 128.77, 128.64, 128.61, 128.54, 128.10, 125.58, 61.62 (d, *J* = 6.2Hz), 39.42, 38.06, 33.57 (d, *J* = 136.4Hz), 27.24, 20.94, 16.37, 16.32, 16.10 (dd, *J* = 13.2Hz, 6.4Hz), 15.86, 12.74, 12.71(d, *J* = 5.6Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.47, 30.66. HRMS calcd for $C_{23}H_{30}NNaO_5P^+$: $[M+Na]^+$ 454.1754, found 454.1750.



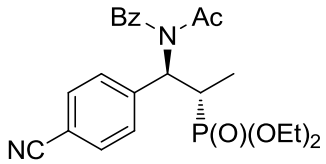
diethyl (1-(N-acetylbenzamido)-1-(4-fluorophenyl)propan-2-yl)phosphonate (**3i**): eluent (petroleum: isopropanol = 20:1),123.5 mg, yellow liquid, yield: 71%, dr = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 3H), 7.37 (m, 4H), 6.96 (t, *J* = 8.7 Hz, 2H), 5.92 (t, *J* = 10.9 Hz, 1H), 3.98-3.79 (m, 3H), 3.78-3.68 (m, 1H), 3.59-3.38 (m, 1H), 1.78 (s, 3H), 1.38 (dd, *J* = 17.2, 7.2 Hz, 3H), 1.11 (q, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.34, 172.98, 163.46, 161.01, 136.49, 134.29, 134.25, 133.06, 131.25, 131.17, 128.93, 128.60, 127.37, 127.29, 114.92, 114.81, 114.70, 114.60, 61.55 (d, *J* = 6.9 Hz), 38.58 (d, *J* = 136.5 Hz), 34.16 (d, *J* = 136.5 Hz), 27.39, 16.37 (t, *J* = 5.4 Hz), 16.08 (dd, *J* = 16.4 Hz, 6.4 Hz), 12.71 (t, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.00, 30.24; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.97, -115.74. HRMS calcd for $C_{22}H_{27}FNNaO_5P^+$: $[M+Na]^+$ 458.1503, found 458.1502.



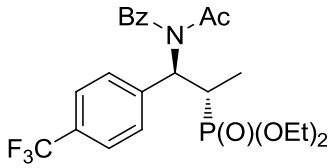
diethyl (1-(N-acetylbenzamido)-1-(4-chlorophenyl)propan-2-yl)phosphonate (**3j**): eluent (petroleum: isopropanol = 20:1), 148 mg, yellow liquid, yield: 82%, dr = 7:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 3H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.31 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.90 (t, *J* = 10.9 Hz, 1H), 3.96-3.81 (m, 3H), 3.81-3.67 (m, 1H), 3.58-3.40 (m, 1H), 1.78 (s, 3H), 1.38 (dd, *J* = 17.7, 7.0 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.10, 172.92, 136.84, 136.35, 133.59, 132.99, 130.79, 128.87, 128.52, 128.01, 127.93, 127.12, 61.48 (dd, *J* = 7.0 Hz, 2.7 Hz), 38.44 (d, *J* = 136.8 Hz), 33.85 (d, *J* = 139.0 Hz), 27.35, 16.27 (d, *J* = 4.6 Hz), 15.95 (dd, *J* = 9.9 Hz, 6.2 Hz), 12.58 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.80, 30.00. HRMS calcd for $C_{22}H_{27}ClNNaO_5P^+$: $[M+Na]^+$ 474.1208, found 474.1208.



diethyl (1-(N-acetylbenzamido)-1-(4-bromophenyl)propan-2-yl)phosphonate (**3k**): eluent (petroleum: isopropanol = 20:1), 142.5 mg, yellow liquid, yield: 72%, dr = 7:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.46-7.37 (m, 8H), 5.87 (t, *J* = 11.1 Hz, 1H), 3.96-3.82 (m, 3H), 3.82-3.70 (m, 1H), 3.56-3.40 (m, 1H), 1.77 (s, 3H), 1.37 (dd, *J* = 17.2, 7.2 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.17, 173.05, 137.39, 136.41, 133.08, 131.21, 131.00, 129.81, 128.95, 128.62, 128.10, 127.54, 121.94, 68.71 (d, *J* = 5.5 Hz), 33.88 (d, *J* = 139.0 Hz), 27.44, 16.34 (d, *J* = 4.9 Hz), 16.02 (dd, *J* = 11.0 Hz, 6.3 Hz), 12.63 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.86, 30.06. HRMS calcd for $C_{22}H_{27}BrNNaO_5P^+$: $[M+Na]^+$ 518.0702, found 518.0702.

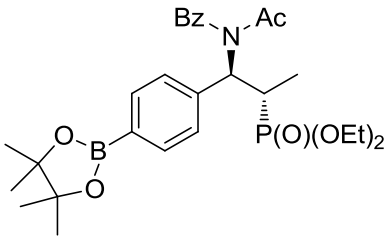


diethyl (1-(N-acetylbenzamido)-1-(4-cyanophenyl)propan-2-yl)phosphonate (**3l**): eluent (petroleum: isopropanol = 20:1), 83 mg, yellow liquid, yield: 47%, dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.62-7.50 (m, 2 H), 7.45-7.36 (m, 4H), 5.98 (d, *J* = 10.9 Hz, 1H), 3.98-3.72 (m, 4H), 3.65-3.42 (m, 1H), 1.77 (s, 3H), 1.38 (dd, *J* = 17.2, 7.3 Hz, 3H), 1.22-1.03 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.38, 174.19, 173.95, 173.10, 143.52, 143.16, 136.35, 136.18, 136.12, 133.39, 133.18, 131.72, 130.30, 129.63, 129.11, 129.00, 128.61, 127.63, 118.58, 111.64, 61.73 (dd, *J* = 6.9 Hz, 4.5 Hz), 61.62 (dd, *J* = 7.6 Hz, 2.2 Hz), 33.62 (d, *J* = 139.1 Hz), 32.92 (d, *J* = 139.1 Hz), 31.72, 27.65, 27.52, 16.12 (dd, *J* = 11.0 Hz, 5.8 Hz), 16.11 (dd, *J* = 15.3 Hz, 5.8 Hz), 12.59 (d, *J* = 5.8 Hz), 8.07; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.68, 32.43, 29.91, 29.50. HRMS calcd for $C_{23}H_{27}N_2NaO_5P^+$: $[M+Na]^+$ 465.1550, found 465.1560.

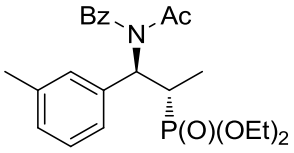


diethyl(1-(N-acetylbenzamido)-1-(4-(trifluoromethyl)phenyl)propan-2-yl)phosphonate(**3m**):
eluent (petroleum: isopropanol = 20:1), 56 mg, yellow liquid, yield: 29%, dr = 8:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.55-7.50 (m, 3H), 7.46-7.37 (m, 4H), 5.96 (t, *J* = 11.1 Hz, 1H), 3.97-3.82 (m, 3H), 3.82-3.70 (m, 1H), 3.62-3.45 (m, 1H), 1.78 (s, 3H), 1.39 (dd, *J* = 17.3, 7.2 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.14, 173.21, 142.38, 136.38, 133.24, 130.53, 130.21, 129.95, 129.89, 129.57, 129.07, 128.69, 128.15, 127.27, 126.17, 125.33, 125.02, 124.91, 124.87, 124.83, 122.62, 61.70 (dd, *J* = 7.0 Hz, 4.5 Hz), 33.77 (d, *J* = 139.2 Hz), 27.63, 16.01 (dd, *J* = 13.4 Hz, 7.0 Hz), 12.66 (d, *J* = 5.7 Hz); ^{31}P

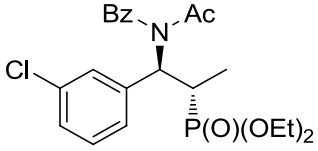
NMR (162 MHz, $CDCl_3$) δ 32.74, 29.79; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43, -62.69. HRMS calcd for $C_{23}H_{27}F_3NNaO_5P^+$: $[M+Na]^+$ 508.1471, found 508.1469.



diethyl(1-(N-acetylbenzamido)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-2-yl)phosphonate (**3n**): eluent (petroleum: isopropanol = 20:1), 87 mg, yellow liquid, yield: 40%, dr = 13:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, *J* = 3.7, 1.4 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 5.95 (t, *J* = 11.1 Hz, 1H), 3.94-3.81 (m, 2H), 3.81-3.65 (m, 2H), 3.64-3.46 (m, 1H), 1.77 (s, 3H), 1.40 (dd, *J* = 17.3, 7.2 Hz, 3H), 1.31 (s, 12H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32, 173.00, 141.17, 136.61, 134.41, 132.88, 132.04, 131.94, 128.87, 128.64, 128.47, 128.35, 83.65, 61.50 (dd, *J* = 7.1 Hz, 3.3 Hz), 33.76 (d, *J* = 138.7 Hz), 27.37, 24.74 (d, *J* = 6.1 Hz), 16.04(dd, *J* = 15.7 Hz, 6.4 Hz), 12.70 (d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.25, 30.31. HRMS calcd for $C_{28}H_{39}BNNaO_5P^+$: $[M+Na]^+$ 566.2449, found 566.2441.

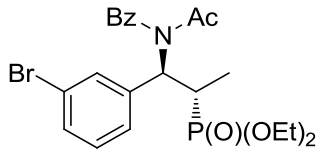


diethyl (1-(N-acetylbenzamido)-1-(m-tolyl)propan-2-yl)phosphonate (**3o**): eluent (petroleum: isopropanol = 20:1), 108.6 mg, yellow liquid, yield: 63%, dr = 16:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 3H), 7.33 (d, *J* = 6.6 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.89 (t, *J* = 11.2 Hz, 1H), 3.95-3.74 (m, 3H), 3.73-3.59 (m, 1H), 3.59-3.45 (m, 1H), 2.29 (s, 3H), 1.79 (s, 3H), 1.40 (dd, *J* = 17.2, 7.2 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.50, 172.88, 138.13, 137.30, 136.70, 132.83, 130.06, 128.79, 128.64, 128.61, 127.79, 126.34, 61.40 (t, *J* = 6.5Hz), 34.01 (d, *J* = 138.7Hz), 27.27, 21.31, 15.99 (dd, *J* = 14.7Hz, 5.4Hz), 12.76 (d, *J* = 5.7Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.38, 30.55. HRMS calcd for $C_{23}H_{30}NNaO_5P^+$: $[M+Na]^+$ 454.1754, found 454.1752.

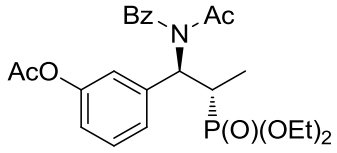


diethyl (1-(N-acetylbenzamido)-1-(3-chlorophenyl)propan-2-yl)phosphonate (**3p**): eluent (petroleum: isopropanol = 20:1), 127 mg, yellow liquid, yield: 67%, dr = 20:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.44 (m, *J* =11.0, 4.4 Hz, 3H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.21 (m, 2H), 5.88 (t, *J* = 11.1 Hz, 1H), 3.97-3.81 (m, 3H), 3.82-3.70 (m, 1H), 3.49 (m, 1H), 1.78 (s, 1H), 1.38 (dd, *J* = 17.3, 7.2 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.08, 172.97, 140.31, 136.39, 133.62, 133.06, 129.66, 129.12, 128.93, 128.63, 128.03, 127.67, 61.55 (dd, *J* = 7.1 Hz, 3.4 Hz), 60.88, 34.27 (d, *J* = 139.1

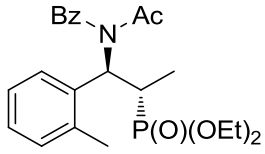
Hz), 27.45, 16.00 (dd, *J* = 13.0 Hz, 6.4 Hz), 12.61 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.74, 29.89. HRMS calcd for $C_{22}H_{27}ClNNaO_5P^+$: $[M+Na]^+$ 474.1208, found 474.1208.



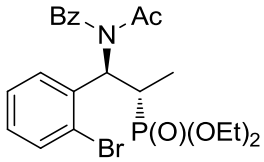
diethyl (1-(N-acetylbenzamido)-1-(3-bromophenyl)propan-2-yl)phosphonate (**3q**): eluent (petroleum: isopropanol = 20:1), 142 mg, yellow liquid, yield: 72%, dr >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.48 (dd, *J* = 12.8, 7.6 Hz, 3H), 7.43-7.35 (m, 3H), 7.14 (t, *J* = 7.9 Hz, 1H), 5.87 (t, *J* = 11.0 Hz, 1H), 3.98-3.82 (m, 3H), 3.83-3.69 (m, 1H), 3.58-3.40 (m, 1H), 1.79 (s, 3H), 1.38 (dd, *J* = 17.3, 7.2 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.96, 172.86, 140.49, 136.27, 133.00, 132.46, 131.91, 131.82, 130.88, 129.35, 128.86, 128.55, 128.36, 128.24, 128.05, 121.70, 61.48 (dd, *J* = 6.9 Hz, 4.6 Hz), 33.66 (d, *J* = 139.1Hz), 27.36, 15.93 (dd, *J* = 11.6 Hz, 7.0 Hz), 12.51 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.66, 29.88. HRMS calcd for $C_{22}H_{27}BrNNaO_5P^+$: $[M+Na]^+$ 518.0702, found 518.0702.



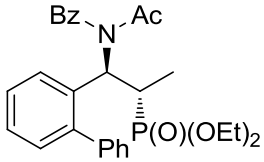
3-(1-(N-acetylbenzamido)-2-(diethoxyphosphoryl)propyl)phenyl acetate (**3r**): eluent (petroleum: isopropanol = 20:1), 125.5 mg, yellow liquid, yield: 63%, dr = 16:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.42-7.34 (m, 3H), 7.34-7.31 (m, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.02-6.94 (m, 1H), 5.99-5.83 (m, 1H), 3.96-3.79 (m, 3H), 3.79-3.66 (m, 1H), 3.57-3.42 (m, 1H), 2.26 (s, 3H), 1.78 (s, 3H), 1.39 (dd, *J* = 17.2, 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.36, 172.92, 169.05, 150.33, 139.96, 136.45, 132.97, 128.89, 128.67, 128.65, 126.71, 122.71, 121.23, 61.57 (dd, *J* = 6.5 Hz, 6.0 Hz), 33.39 (d, *J* = 139.0 Hz), 27.34, 20.97, 16.00 (dd, *J* = 16.4 Hz, 6.4 Hz), 12.61 (d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.00, 30.16. HRMS calcd for $C_{24}H_{30}NNaO_7P^+$: $[M+Na]^+$ 498.1652, found 498.1651.



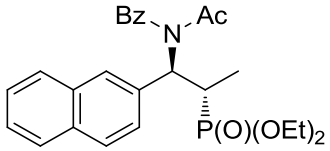
diethyl (1-(N-acetylbenzamido)-1-(o-tolyl)propan-2-yl)phosphonate (**3s**): eluent (petroleum: isopropanol = 20:1), 108.6 mg, yellow liquid, yield: 63%, dr = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.49-7.43 (m, 1H), 7.32 (dt, *J* = 15.3, 7.6 Hz, 4H), 7.13 (d, *J* = 6.9 Hz, 1H), 7.06 (td, *J* = 7.4, 1.0 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.37 (t, *J* = 11.1 Hz, 1H), 3.91-3.79 (m, 3H), 3.79-3.61 (m, 1H), 3.60-3.40 (m, 1H), 2.55 (s, 3H), 1.77 (s, 3H), 1.44 (dd, *J* = 17.2, 7.2 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.19, 171.43, 136.97, 136.63, 135.96, 133.24, 133.13, 130.20, 130.16, 129.03, 128.76, 128.66, 127.70, 126.87, 126.25, 125.45, 125.23, 67.26 (*J* = 3.6 Hz), 61.99 (dd, *J* = 46.1 Hz, 7.2Hz), 61.30 (dd, *J* = 13.5 Hz, 6.9 Hz), 35.85 (d, *J* = 35.9 Hz), 30.90 (d, *J* = 138.0 Hz), 26.57, 20.01, 16.31 (dd, *J* = 8.7 Hz, 5.7 Hz), 15.94 (dd, *J* = 23.1 Hz, 5.8 Hz), 12.48 (d, *J* = 5.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.69, 30.72. HRMS calcd for $C_{23}H_{30}NNaO_5P^+$: $[M+Na]^+$ 454.1754, found 454.1751.



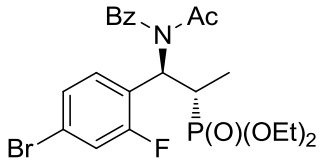
diethyl (1-(N-acetylbenzamido)-1-(2-bromophenyl)propan-2-yl)phosphonate (**3t**): eluent (petroleum: isopropanol = 20:1), 116 mg, yellow liquid, yield: 56%, dr >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 5.8 Hz, 0.47H), 7.97 (d, *J* = 5.8 Hz, 0.13H), 7.94 (d, *J* = 5.8 Hz, 0.33H), 7.59-7.42 (m, 4H), 7.42-7.03 (m, 4H), 6.42 (t, *J* = 11.2 Hz, 0.53H), 5.86-5.73 (m, 0.14H), 5.74-5.63 (m, 0.27H), 4.29-3.76 (m, 4H), 3.62-3.43 (m, 0.55H), 2.82-2.56 (m, 0.41H), 2.06 (s, 0.47H), 2.06 (s, 0.80H), 2.06 (s, 1.60H), 1.44 (dd, *J* = 17.3, 7.3 Hz, 1.59H), 1.39 (t, *J* = 7.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 1.72H), 1.25 (t, *J* = 7.1 Hz, 1.80H), 1.14 (dd, *J* = 17.7, 7.5 Hz, 0.54H), 1.07 (dd, *J* = 18.1, 7.6 Hz, 0.84H), 1.02 (t, *J* = 7.1 Hz, 1.71H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.85, 170.58, 136.43, 136.20, 133.15, 132.60, 131.96, 129.23, 128.85, 128.71, 126.32, 125.19, 61.48 (dd, *J* = 33.1 Hz, 6.9 Hz), 58.87, 34.10 (d, *J* = 137.6 Hz), 26.19, 15.98 (dd, *J* = 34.0 Hz, 5.8 Hz), 12.11(d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.56, 29.66. HRMS calcd for $C_{22}H_{27}BrNNaO_5P^+$: $[M+Na]^+$ 518.0702, found 518.0702.



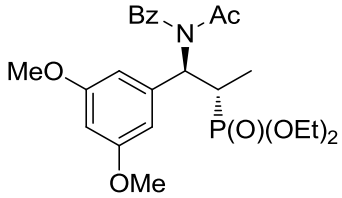
diethyl(1-([1,1'-biphenyl]-2-yl)-1-(N-acetylbenzamido)propan-2-yl)phosphonate (**3u**): eluent (petroleum: isopropanol = 20:1), 134 mg, yellow liquid, yield: 65%, dr>21:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.1 Hz, 1H), 7.66-7.39 (m, 6H), 7.36-7.27 (m, 4H), 7.24-7.15 (m, 3H), 6.10 (t, *J* = 11.5 Hz, 1H), 4.09-3.89 (m, 2H), 3.89-3.71 (m, 2H), 3.71-3.53 (m, 1H), 1.44 (s, 3H), 1.37 (dd, *J* = 17.2, 7.2 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.05, 171.79, 142.60, 141.03, 136.22, 134.53, 132.62, 130.28, 129.58, 129.43, 128.45, 128.34, 127.70, 127.33, 126.63, 61.46 (dd, *J* = 15.2 Hz, 7.0 Hz), 56.51(d, *J* = 6.7 Hz), 34.47, (d, *J* = 136.1 Hz), 24.25, 16.00 (dd, *J* = 17.3 Hz, 6.1 Hz), 12.18 (d, *J* = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.28, 30.98. HRMS calcd for $C_{28}H_{32}NNaO_5P^+$: $[M+Na]^+$ 516.1907, found 516.1910.



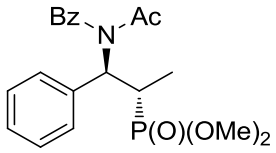
diethyl (1-(N-acetylbenzamido)-1-(naphthalen-2-yl)propan-2-yl)phosphonate (**3v**): eluent (petroleum: isopropanol = 20:1), 97 mg, yellow liquid, yield: 47%, dr = 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.81 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.79-7.68 (m, 3H), 7.44 (ddd, *J* = 6.6, 5.0, 2.8 Hz, 6H), 7.31 (t, *J* = 7.7 Hz, 2H), 6.11 (t, *J* = 11.2 Hz, 1H), 3.89-3.74 (m, 3H), 3.74-3.53 (m, 2H), 1.78 (s, 3H), 1.45 (dd, *J* = 17.3, 7.2 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 6H), 0.94 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.42, 173.18, 136.63, 135.73, 132.92, 132.90, 132.86, 128.86, 128.76, 128.66, 128.24, 127.52, 127.32, 127.24, 126.00, 125.80, 61.50 (d, *J* = 6.9Hz), 33.88 (d, *J* = 139.0Hz), 27.47, 15.94 (d, *J* = 11.5Hz, 6.9Hz), 12.82 (d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.34, 30.44. HRMS calcd for $C_{26}H_{30}NNaO_5P^+$: $[M+Na]^+$ 490.1754, found 490.1752.



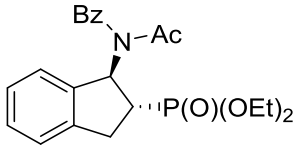
diethyl(1-(N-acetylbenzamido)-1-(4-bromo-2-fluorophenyl)propan-2-yl)phosphonate (**3w**): eluent (petroleum: isopropanol = 20:1), 122 mg, yellow liquid, yield: 57%, dr = 15:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.21 (dd, *J* = 13.6, 5.0 Hz, 1H), 6.17 (t, *J* = 11.3 Hz, 1H), 4.10-3.85 (m, 1H), 3.58-3.38 (m, 1H), 1.87 (s, 1H), 1.38 (dd, *J* = 17.1, 7.2 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.20, 172.08, 161.50, 159.00, 136.07, 133.12, 132.56, 132.52, 128.90, 128.56, 126.61, 126.58, 124.38, 124.25, 122.06, 121.97, 118.59, 118.33, 61.74 (dd, *J* = 11.2Hz, 7.1Hz), 52.87, 32.93 (d, *J* = 140.0Hz), 26.66, 16.05 (dd, *J* = 20.0Hz, 6.2Hz), 12.25 (d, *J* = 5.8Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.38, 29.40; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.59, -113.30. HRMS calcd for $C_{22}H_{26}BrFNNaO_5P^+$: $[M+Na]^+$ 536.0608, found 536.0607.



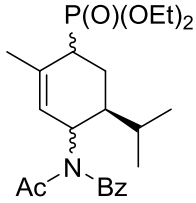
diethyl(1-(N-acetylbenzamido)-1-(3,5-dimethoxyphenyl)propan-2-yl)phosphonate (**3x**): eluent (petroleum: isopropanol = 20:1), 146 mg, yellow liquid, yield: 73%, dr > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 6.70 (d, *J* = 2.2 Hz, 2H), 6.33 (t, *J* = 2.2 Hz, 1H), 5.83 (t, *J* = 11.1 Hz, 1H), 3.94-3.82 (m, 3H), 3.82-3.75 (m, 1H), 3.73 (s, 6H), 3.55-3.39 (m, 1H), 1.80 (s, 3H), 1.39 (dd, *J* = 17.2, 7.2 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.54, 172.83, 160.25, 140.48, 136.69, 132.92, 128.85, 128.74, 107.53, 100.19, 61.50 (dd, *J* = 7.1 Hz, 3.4 Hz), 55.25, 34.21 (d, *J* = 138.8 Hz), 27.27, 16.06 (dd, *J* = 15.4 Hz, 6.5 Hz), 12.78 (d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.23, 30.34. HRMS calcd for $C_{24}H_{32}NNaO_7P^+$: $[M+Na]^+$ 500.1809, found 500.1805.



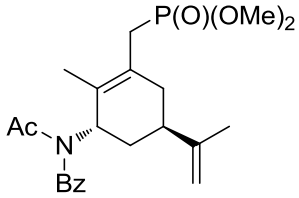
dimethyl (1-(N-acetylbenzamido)-1-phenylpropan-2-yl)phosphonate (**3y**): eluent (petroleum: isopropanol = 20:1), 128.5 mg, yellow liquid, yield: 78%, dr > 20:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.1 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.94 (dd, *J* = 14.2, 8.1 Hz, 1H), 5.94 (dd, *J* = 14.2, 8.1 Hz, 1H), 3.68-3.51 (m, 1H), 3.68-3.51 (m, 1H), 3.47 (d, *J* = 10.7 Hz, 3H), 3.47 (d, *J* = 10.7 Hz, 3H), 3.35 (d, *J* = 10.7 Hz, 3H), 3.35 (d, *J* = 10.7 Hz, 3H), 1.77 (d, *J* = 8.0 Hz, 3H), 1.46-1.37 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.45, 172.80, 137.96, 136.48, 132.96, 129.19, 128.82, 128.57, 128.04, 128.00, 52.14 (t, *J* = 7.2Hz), 33.76 (d, *J* = 138.7 Hz), 27.29, 12.71 (d, *J* = 5.8Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.94, 33.15. HRMS calcd for $C_{20}H_{24}NNaO_5P^+$: $[M+Na]^+$ 412.1284, found 412.1281.



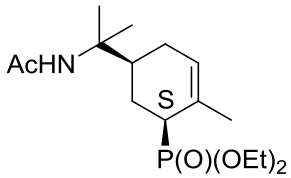
diethyl (1-(N-acetylbenzamido)-2,3-dihydro-1H-inden-2-yl)phosphonate (**3z**): eluent (petroleum: isopropanol = 20:1), 95 mg, yellow liquid, yield: 57%, dr > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.1 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 10.9 Hz, 4H), 6.21 (dd, *J* = 17.1, 8.3 Hz, 1H), 4.16-4.00 (m, 4H), 3.55 (td, *J* = 17.7, 9.0 Hz, 1H), 3.42 (ddd, *J* = 15.9, 9.5, 6.1 Hz, 1H), 3.17 (td, *J* = 16.7, 8.6 Hz, 1H), 2.05 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.15, 173.53, 140.58, 140.47, 140.36, 140.23, 136.18, 132.62, 128.79, 127.94, 126.95, 124.78, 121.94, 63.29, 61.94 (dd, *J* = 30.2 Hz, 6.6 Hz), 39.66 (d, *J* = 148.7 Hz), 32.00, 27.52, 16.31 (t, *J* = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.86, 27.39. HRMS calcd for $C_{22}H_{26}NNaO_5P^+$: $[M+Na]^+$ 438.1441, found 438.1441.



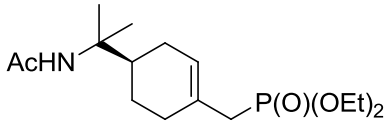
Diethyl ((4S,5S)-4-(N-acetylbenzamido)-5-isopropyl-2-methylcyclohex-2-en-1-yl)phosphonate (**3aa**): eluent (petroleum: isopropanol = 20:1), 88.7 mg, yellow liquid, yield: 51%, dr = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 5.49 (s, 1H), 5.38 (s, 1H), 4.14-4.07 (m, 4H), 2.64 (dd, *J* = 27.1, 6.1 Hz, 1H), 2.38-2.17 (m, 1H), 2.11-1.97 (m, 2H), 1.87 (s, 6H), 1.68 (td, *J* = 13.3, 6.7 Hz, 1H), 1.32 (td, *J* = 7.1, 3.3 Hz, 6H), 0.94 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.84, 173.95, 136.91, 133.85 (d, *J* = 9.1 Hz), 133.02, 129.01, 128.94, 124.13 (d, *J* = 12.9 Hz), 62.12 (d, *J* = 7.0 Hz), 61.29 (d, *J* = 7.2 Hz), 40.63, 39.28 (d, *J* = 134.1 Hz), 28.29, 27.97, 23.89, 22.75, 21.02, 19.75, 16.49 (dd, *J* = 9.8, 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.64, 28.60. HRMS calcd for $C_{23}H_{34}NNaO_5P^+$: $[M+Na]^+$ 458.2067, found 458.2061.



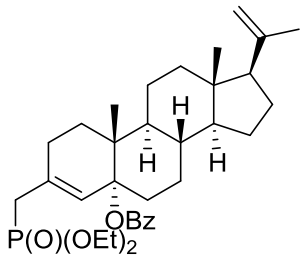
Dimethyl (((3S,5R)-3-(N-acetylbenzamido)-2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)meth yl)phosphonate (**3ab**): eluent (petroleum: isopropanol = 20:1), 92 mg, yellow liquid, yield: 55%, dr > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.00 (s, 1H), 4.72 (d, *J* = 20.9 Hz, 2H), 3.74 (dd, *J* = 10.8, 4.9 Hz, 6H), 2.81-2.52 (m, 3H), 2.39 (d, *J* = 17.7 Hz, 1H), 2.23-2.07 (m, 2H), 1.93 (s, 3H), 1.91-1.83 (m, 1H), 1.72 (s, 3H), 1.69-1.64 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.69, 172.82, 147.42, 136.42, 132.85, 128.89, 128.84, 128.52 (d, *J* = 12.9 Hz), 124.50 (d, *J* = 11.8 Hz), 109.50, 57.24 (d, *J* = 2.7 Hz), 52.46 (dd, *J* = 6.7, 4.7 Hz), 37.04, 35.33, 32.44, 31.21 (d, *J* = 138.3 Hz), 27.22, 21.24, 16.56 (d, *J* = 3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.91. HRMS calcd for $C_{22}H_{30}NNaO_5P^+$: $[M+Na]^+$ 442.1754, found 442.1757.



diethyl ((5S)-5-(2-acetamidopropan-2-yl)-2-methylcyclohex-2-en-1-yl)phosphonate (**3ac**): eluent (petroleum: isopropanol = 20:1), 106 mg, yellow liquid, yield: 51%.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (s, 1H), 5.60 (s, 1H), 4.12 (p, *J* = 7.2 Hz, 4H), 2.70-2.50 (m, 1H), 2.24 (ddd, *J* = 24.2, 11.2, 6.7 Hz, 2H), 2.09 (d, *J* = 4.0 Hz, 1H), 1.94 (s, 3H), 1.84 (s, 3H), 1.36 (s, 1H), 1.36-1.27 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.78, 128.69, 128.60, 125.53, 125.41, 63.80, 61.95, 61.88, 61.75, 61.68, 55.85, 40.38, 39.04, 38.59, 26.20, 26.17, 25.41, 25.37, 24.42, 23.93, 23.34, 21.94, 16.42, 16.36, 16.32. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.12. HRMS calcd for $C_{16}H_{30}NNaO_4P^+$: $[M+Na]^+$ 354.1805, found 354.1807.

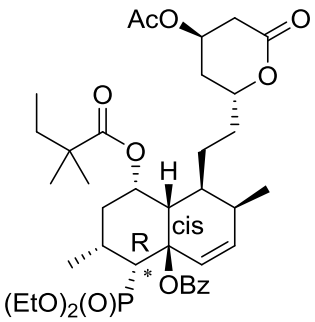


(R)-diethyl ((4-(2-acetamidopropan-2-yl)cyclohex-1-en-1-yl)methyl)phosphonate (**3ad**): eluent (petroleum: isopropanol = 20:1), 106 mg, yellow liquid, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H), 5.51 (s, 1H), 4.09 (dq, *J* = 14.2, 7.1 Hz, 4H), 2.50 (dd, *J* = 21.5, 2.7 Hz, 2H), 2.27-2.12 (m, 3H), 2.12-1.99 (m, 1H), 1.93 (s, 3H), 1.89-1.72 (m, 2H), 1.38-1.18 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.40, 128.18, 128.07, 125.84, 125.72, 63.80, 61.74, 61.67, 61.60, 56.03, 40.09, 35.17, 33.80, 30.32, 30.29, 26.71, 26.68, 24.38, 24.02, 23.93, 23.71, 16.37, 16.31. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.91. HRMS calcd for $C_{16}H_{30}NNaO_4P^+$: $[M+Na]^+$ 354.1805, found 354.1803.



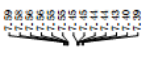
(5R,8S,9S,10R,13S,14S,17R)-3-((diethoxyphosphoryl)methyl)-10,13-dimethyl-17-(prop-1-en-2-yl)-2,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-5-yl benzoate (**3af**): eluent (petroleum: isopropanol = 20:1), 106 mg, yellow liquid, yield: 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.46 (d, *J* = 5.1 Hz, 1H), 4.84 (s, 1H), 4.69 (s, 1H), 4.11-4.19 (m, 4H), 2.58 (dd, *J* = 22.1, 4.7 Hz, 2H), 2.14-1.94 (m, 3H), 1.85-1.80 (m, 1H), 1.77-1.73 (m, 2H), 1.73 (s, 3H), 1.69-1.47 (m, 6H), 1.45-1.40 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 6H), 1.29 (dd, *J* = 11.0, 3.0 Hz, 1H), 1.21-1.13 (m, 2H), 1.09-1.00 (m, 2H), 0.96 (s, 3H), 0.89-0.78 (m, 1H), 0.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.59, 145.50, 133.15 (d, *J* = 12.3 Hz), 132.97, 132.19 (d, *J* = 11.0 Hz), 130.20, 129.92, 128.22, 110.64, 72.32 (d, *J* = 2.1 Hz), 62.07 (dd, *J* = 8.5, 6.9 Hz), 56.63 (d, *J* = 123.3 Hz), 43.29, 43.16, 38.79, 38.49, 35.22, 35.20, 35.08, 33.83, 28.68, 28.04, 26.67 (d, *J* = 2.6 Hz), 25.32, 24.51, 24.06, 22.47, 16.43 (d, *J* = 6.0 Hz), 16.07, 12.67; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.69. HRMS calcd for

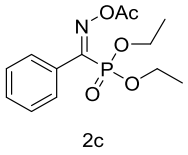
$C_{34}H_{49}NaO_5P^+$: $[M+Na]^+$ 591.3210, found 591.3213.

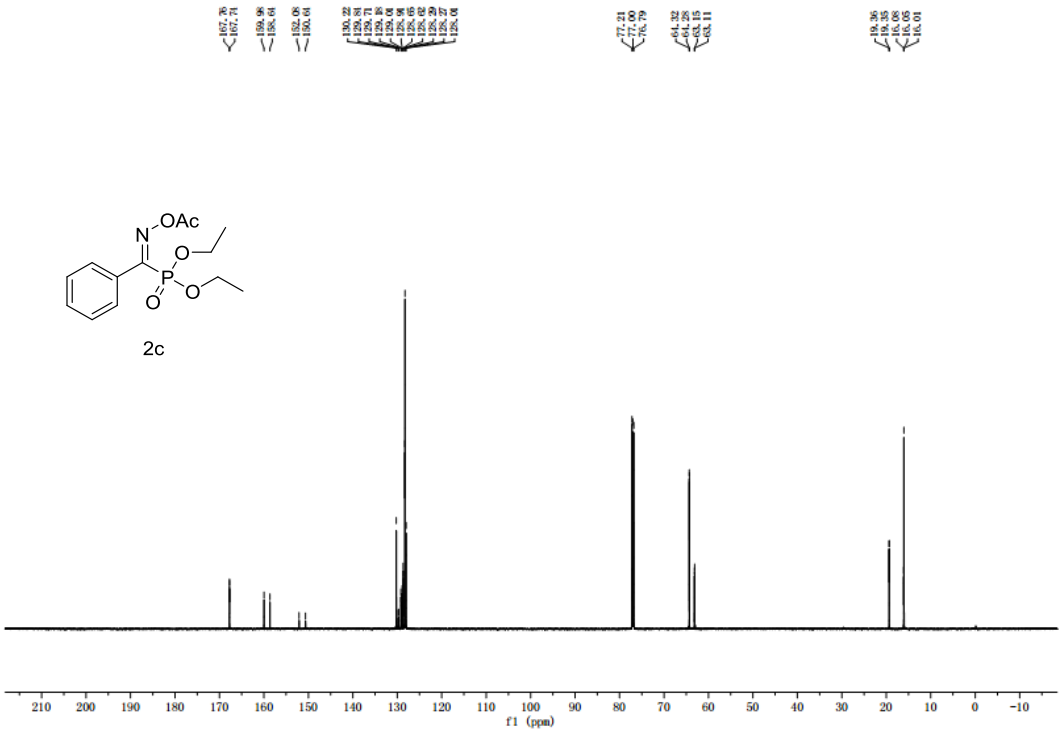


(1S,2S,3R,4R,4aR,5S,7R)-4-(2-((2R,4R)-4-acetoxy-6-oxotetrahydro-2H-pyran-2-yl)ethyl)-2-(diethoxyphosphoryl)-5-((2,2-dimethylbutanoyl)oxy)-3,7-dimethyl-1,2,3,4,4a,5,6,7-octahydronaphthalen-1-yl benzoate (**3ag**): eluent (petroleum: isopropanol = 20:1), 146 mg, yellow liquid, yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 5.67 (s, 1H), 5.24 (s, 1H), 5.15 (s, 1H), 4.49 (s, 1H), 4.14-4.02 (m, 4H), 3.71 (s, 2H), 2.80-2.66 (m, 4H), 2.50 (d, *J* = 23.4 Hz, 1H), 2.37-2.33 (m, 4H), 2.12-2.03 (m, 1H), 2.08 (s, 3H), 1.96 (s, 2H), 1.77-1.65 (m, 4H), 1.59-1.53 (m, 3H), 1.31 (dd, *J* = 14.6, 7.2 Hz, 6H), 1.16-1.13 (m, 8H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.93, 169.95, 168.85, 132.95, 129.86, 128.95, 128.27, 78.34, 77.32, 77.21, 77.01, 76.69, 76.38, 66.12, 65.51, 64.95, 62.50, 62.43, 61.73, 61.66, 60.47, 49.20, 47.86, 42.78, 41.37, 40.10, 35.30, 32.94, 32.88, 31.36, 30.25, 29.61, 29.39, 27.76, 24.68, 24.29, 22.92, 22.49, 22.32, 21.18, 20.98, 16.61, 16.55, 16.44, 16.38, 9.38, 0.94. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.19. HRMS calcd for $C_{38}H_{55}NaO_{11}P^+$: $[M+Na]^+$ 741.3374, found 741.3377.

9. Spectra



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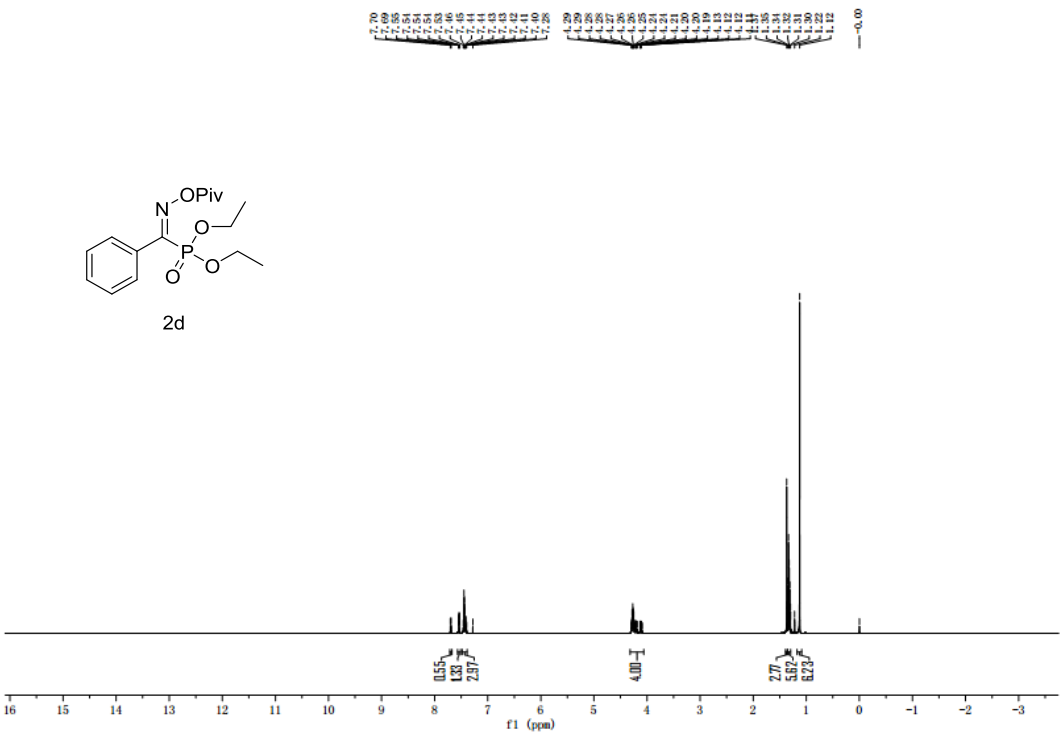
P
O
O
2c
f1 (ppm)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P
O
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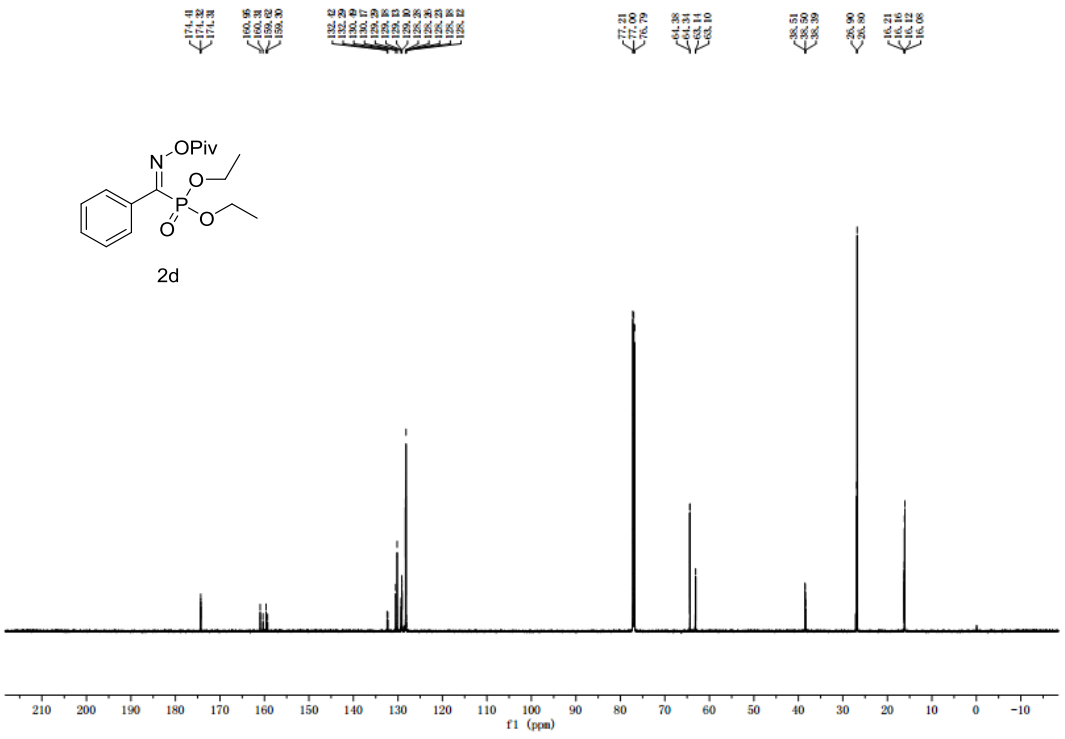
2d
f1 (ppm)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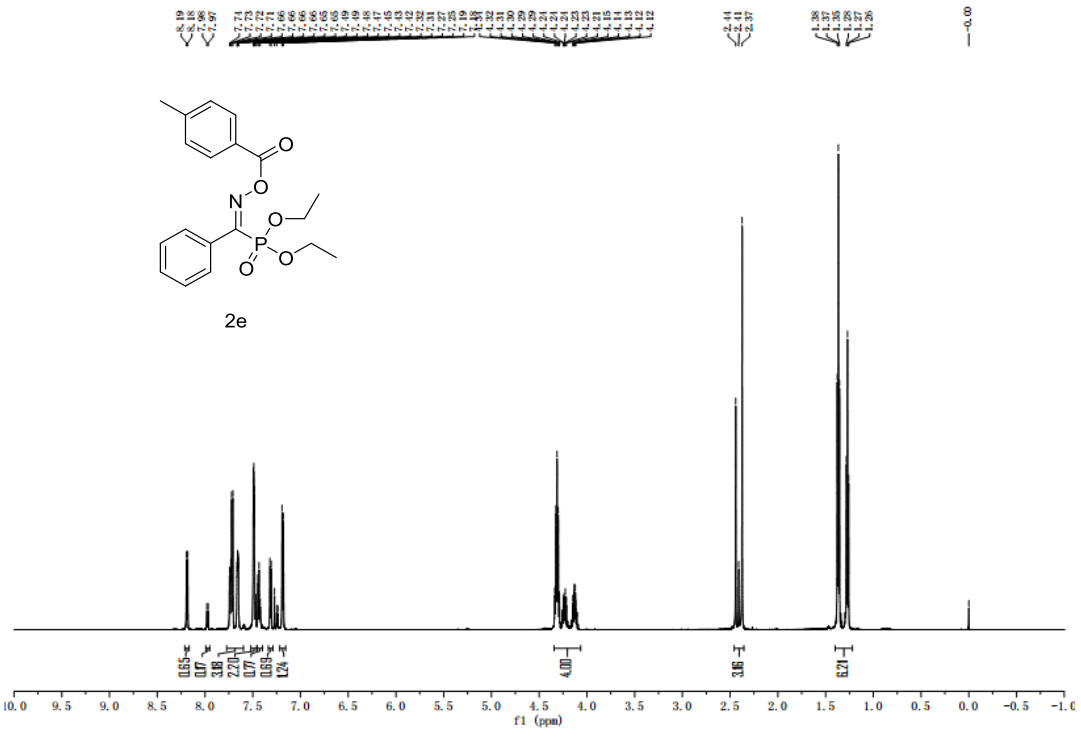
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P
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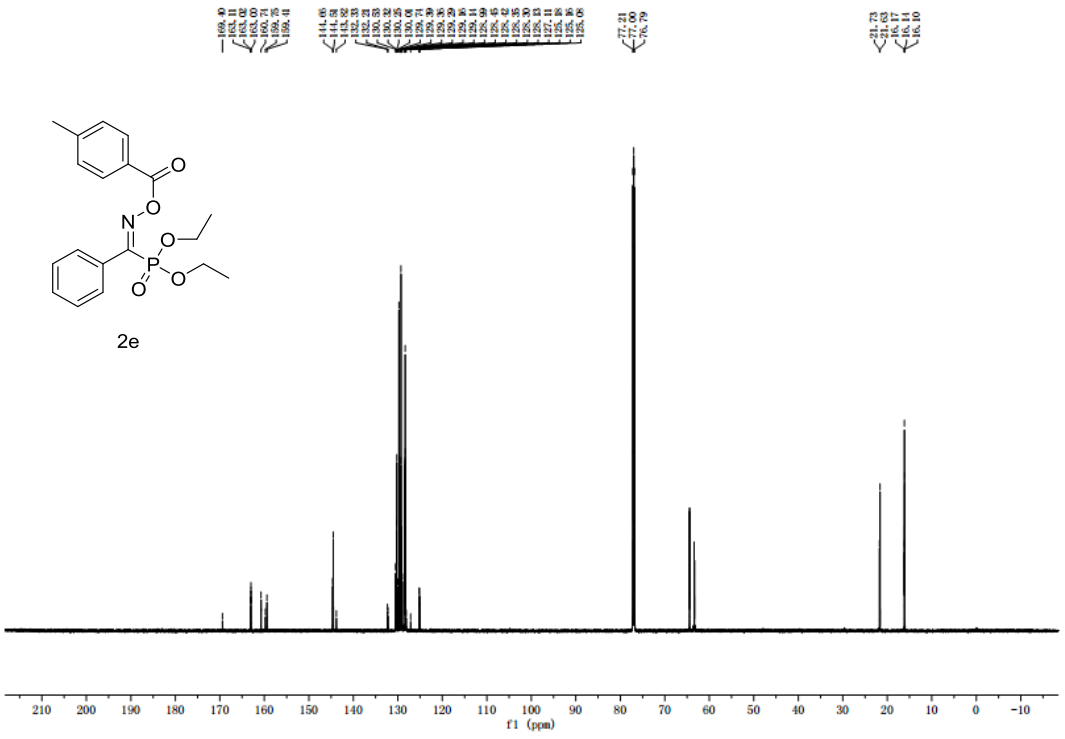
2e
f1 (ppm)



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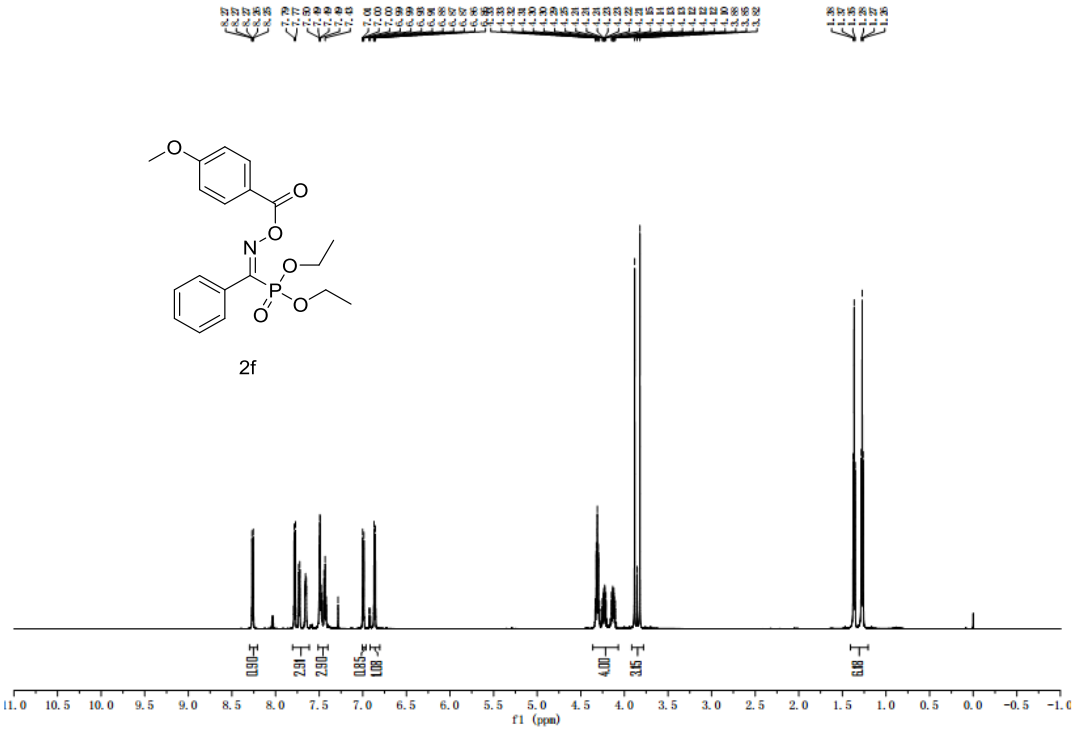

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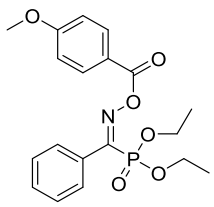

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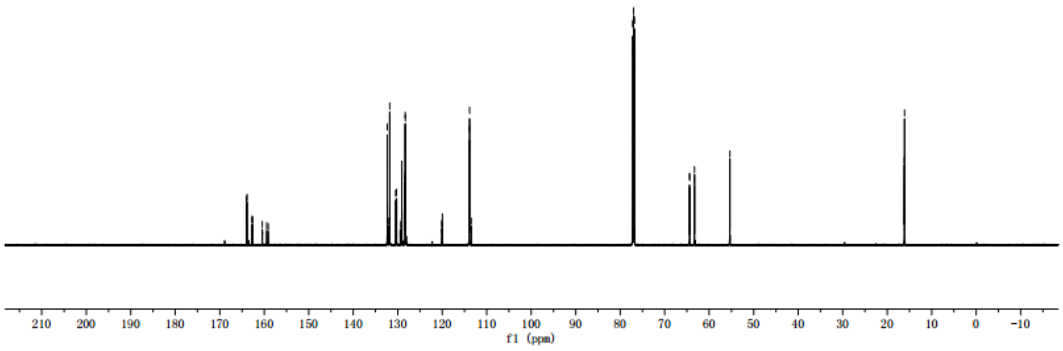

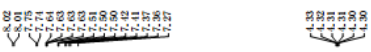

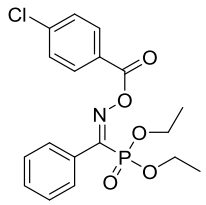

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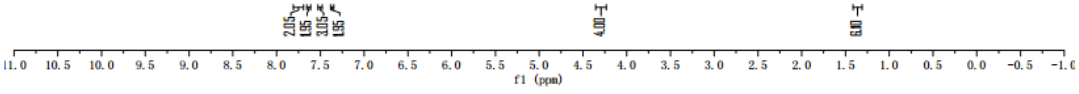

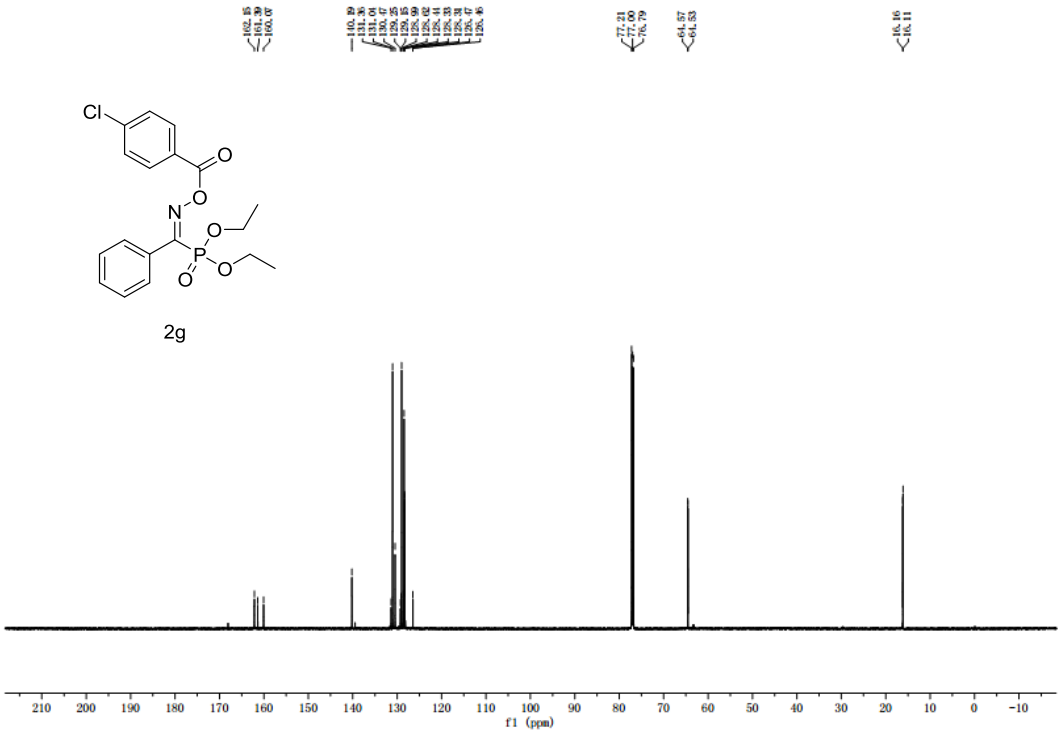
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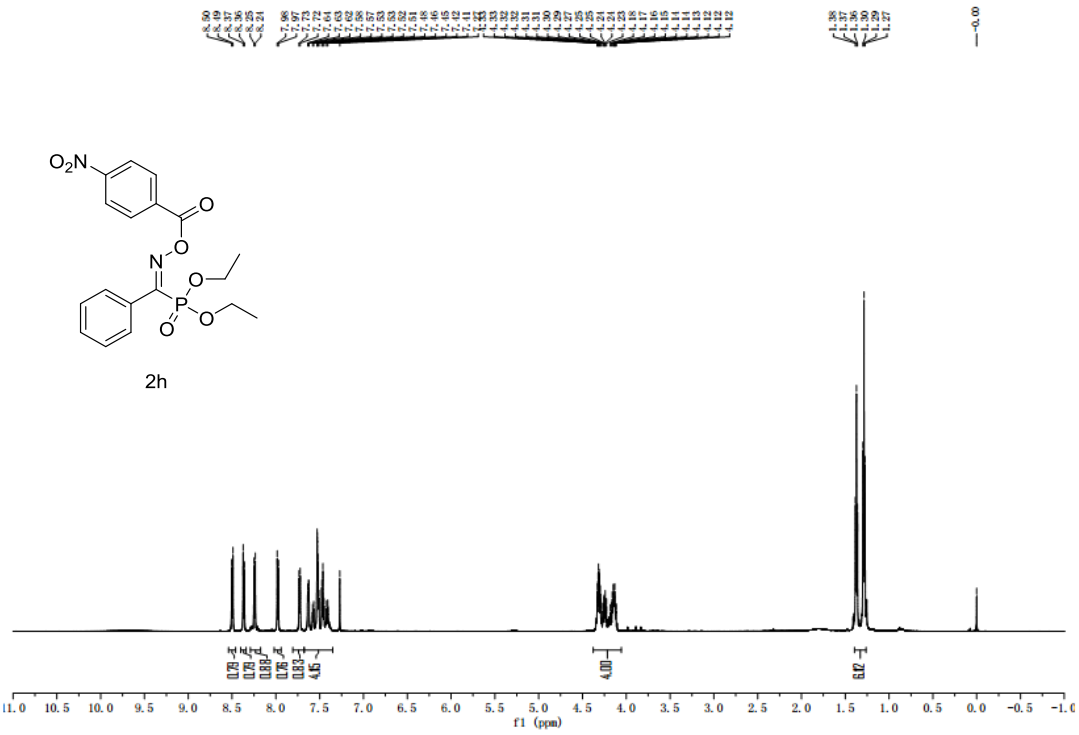
O
O
2g
f1 (ppm)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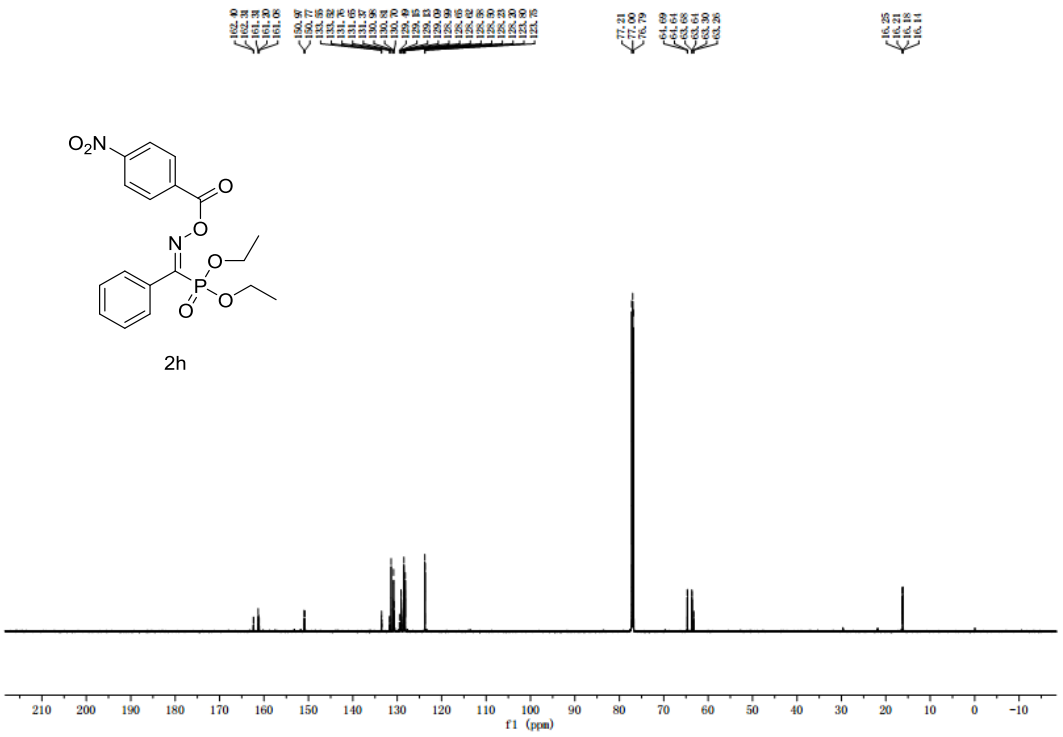
2h
f1 (ppm)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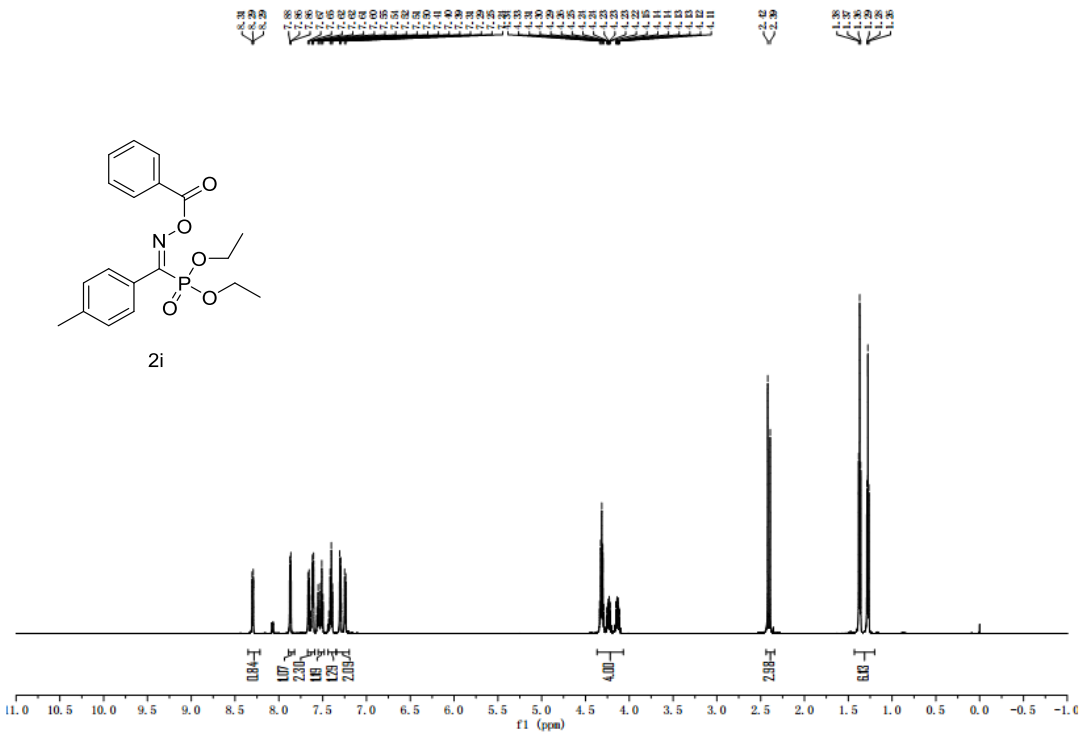
2h
f1 (ppm)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2i
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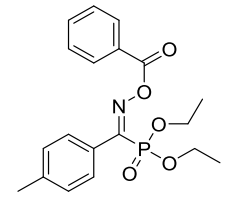

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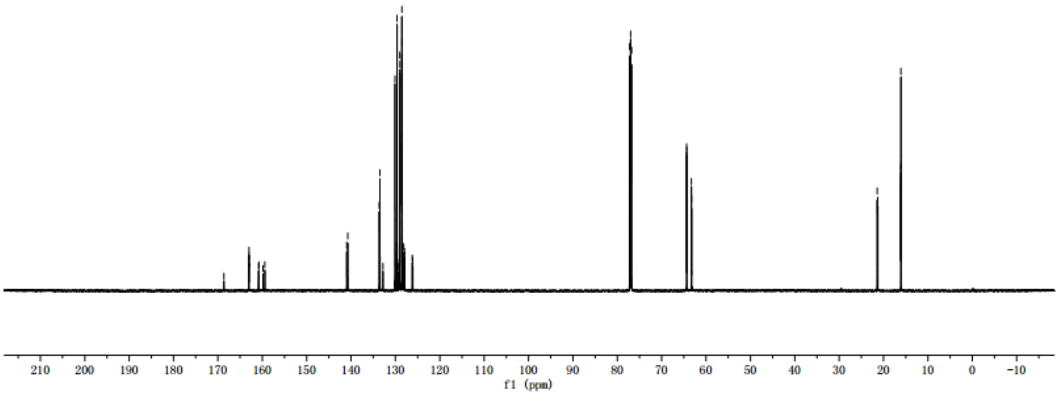

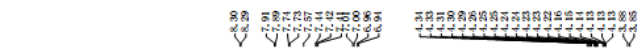

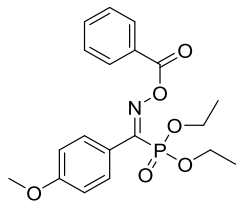

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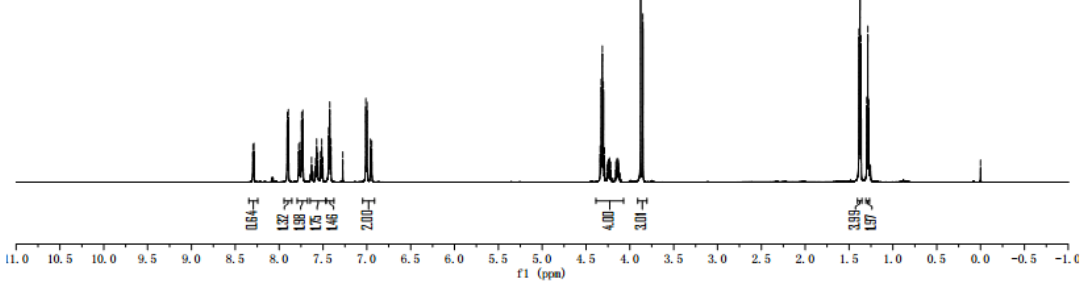

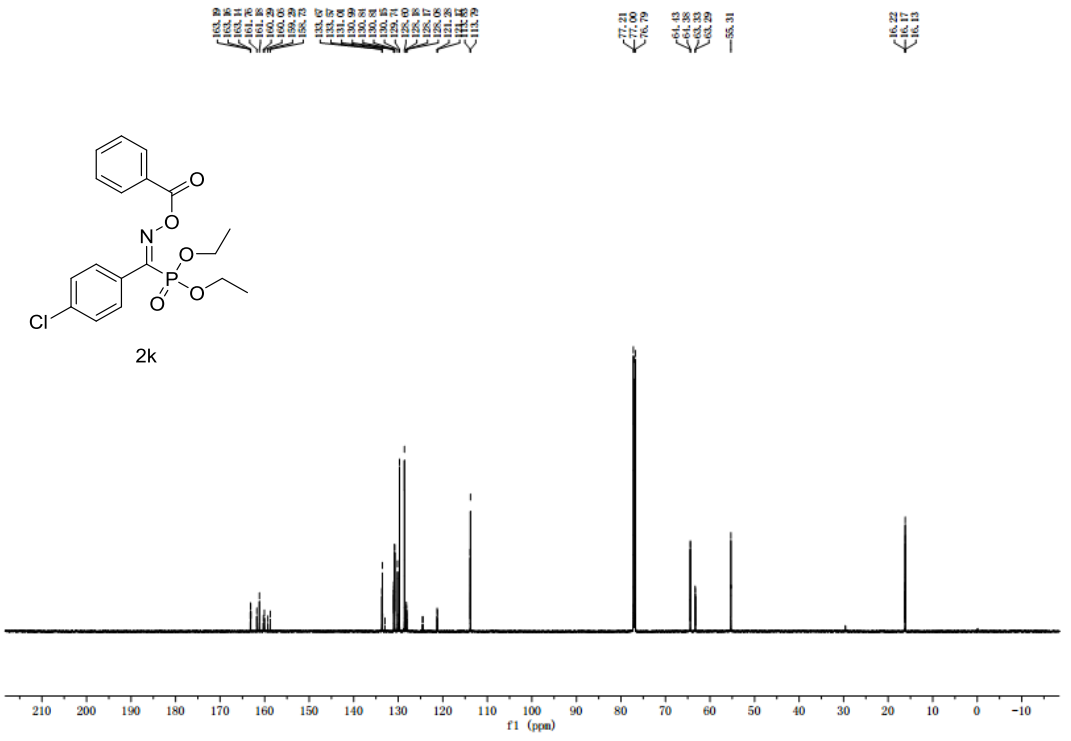
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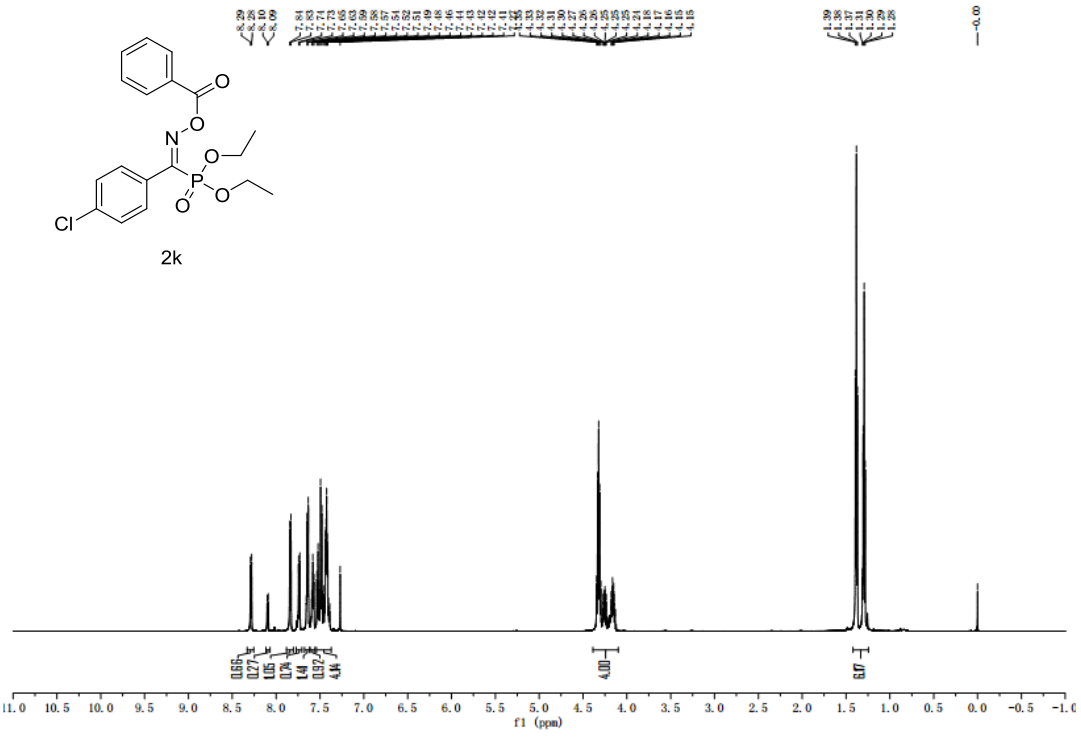
f1 (ppm)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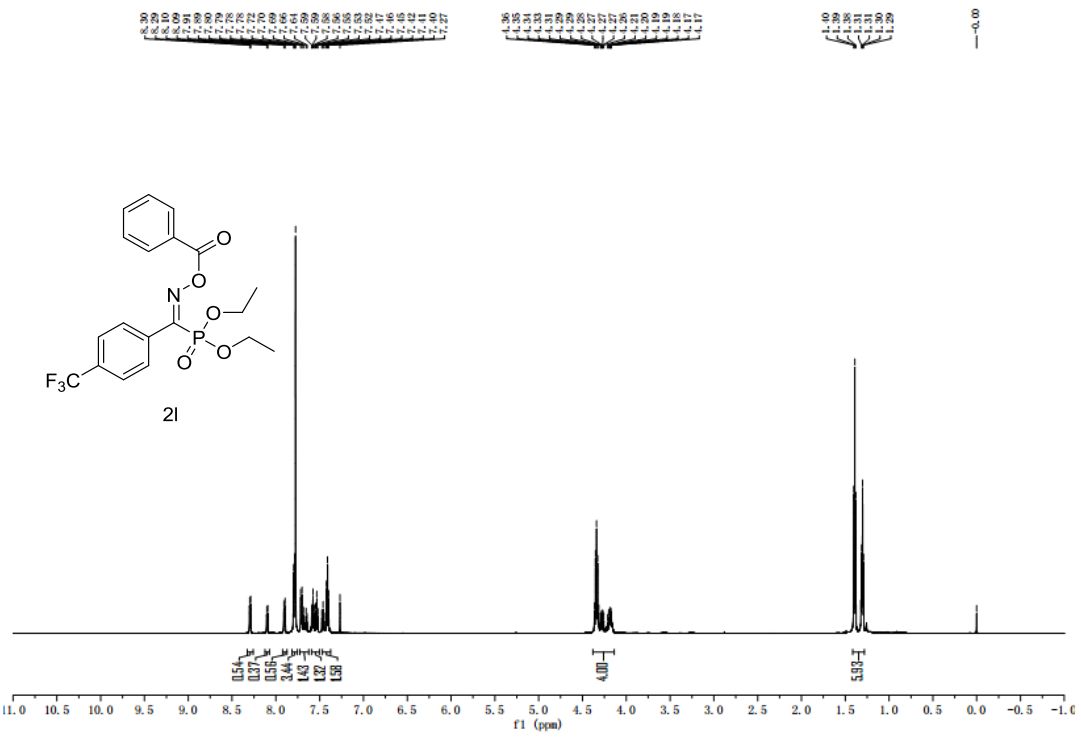
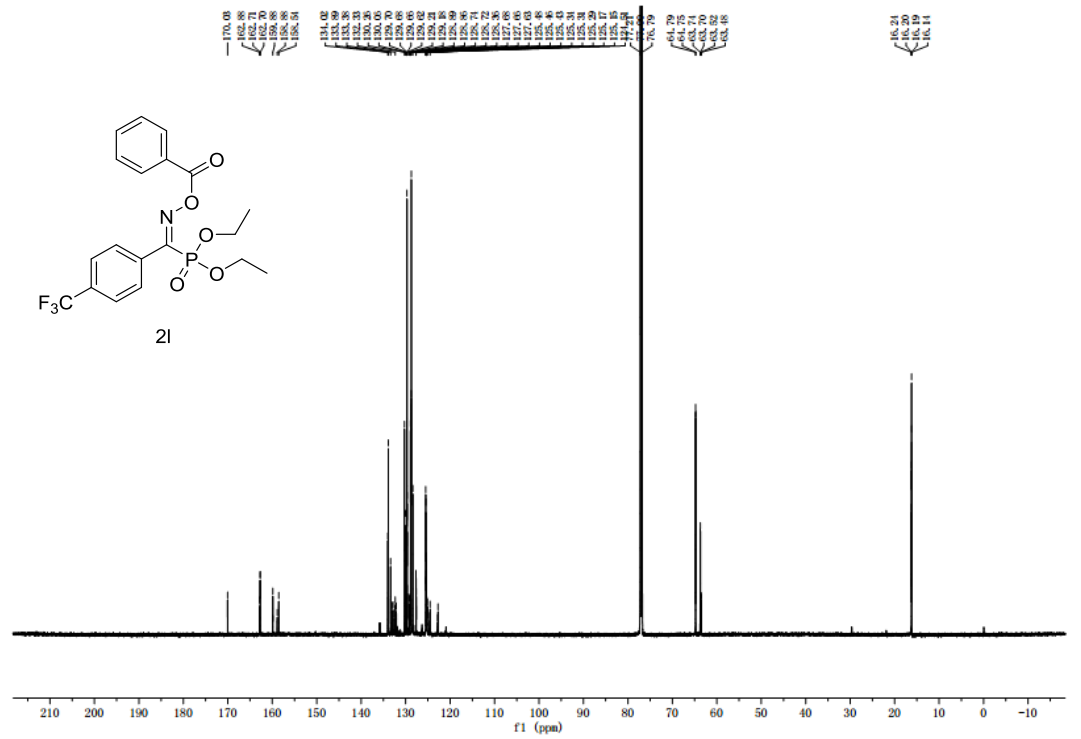
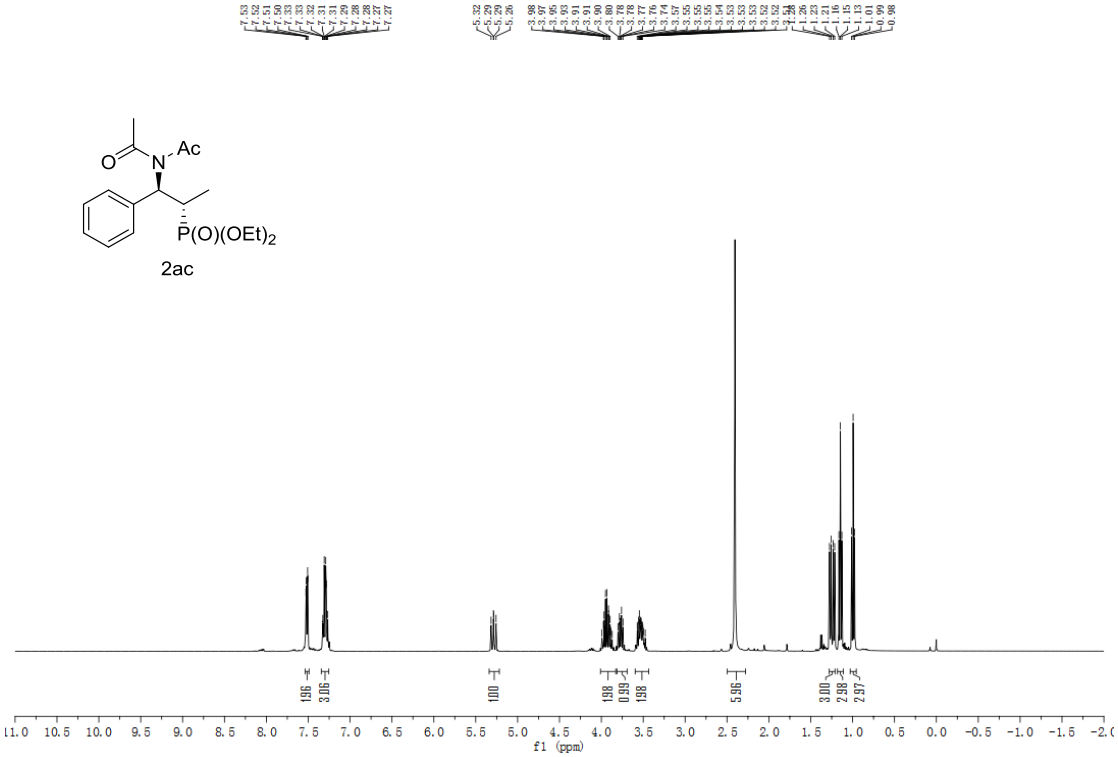
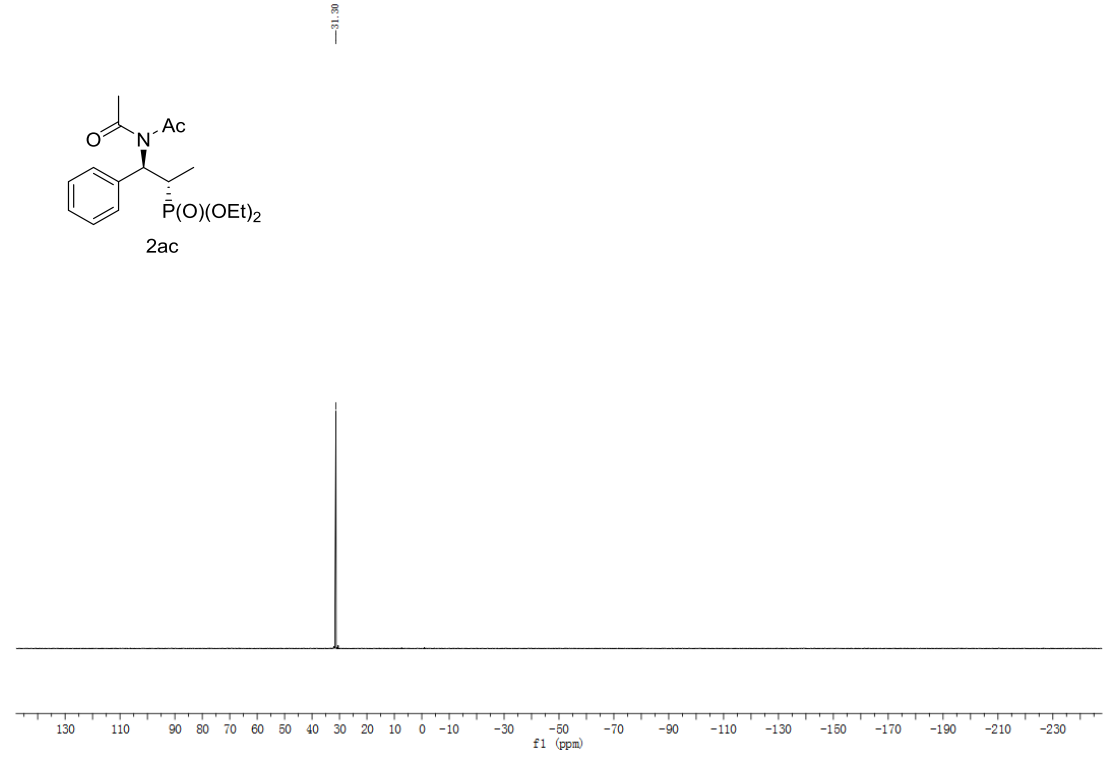
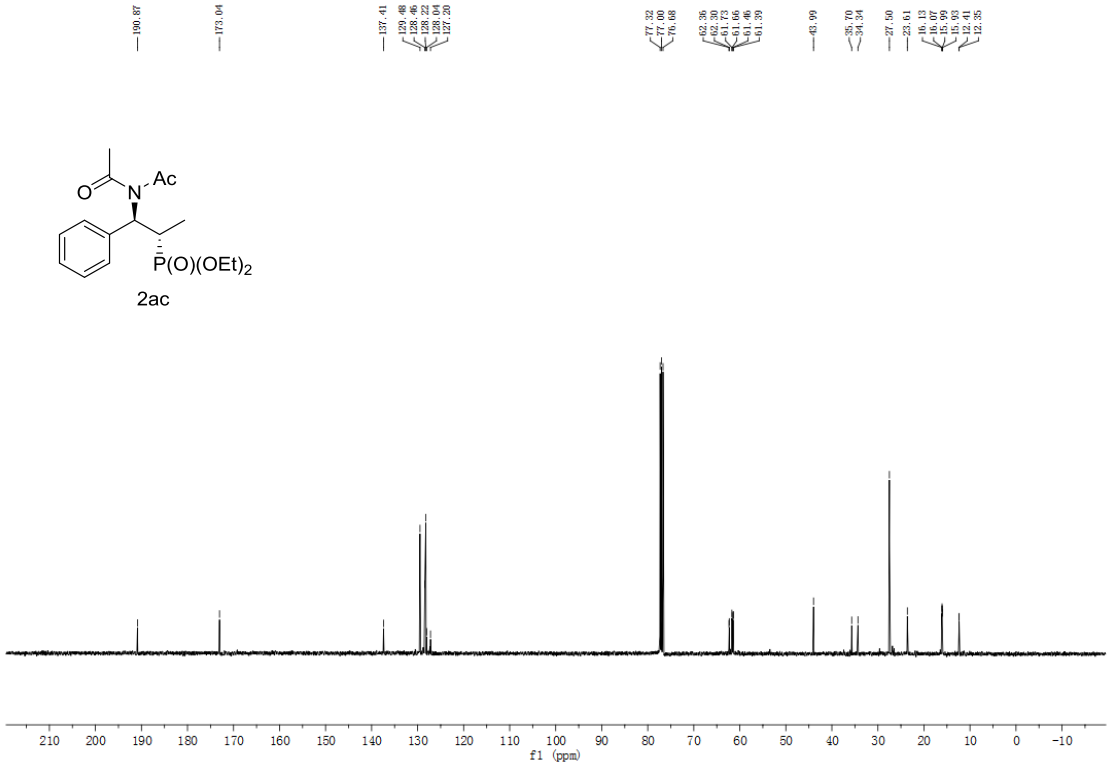
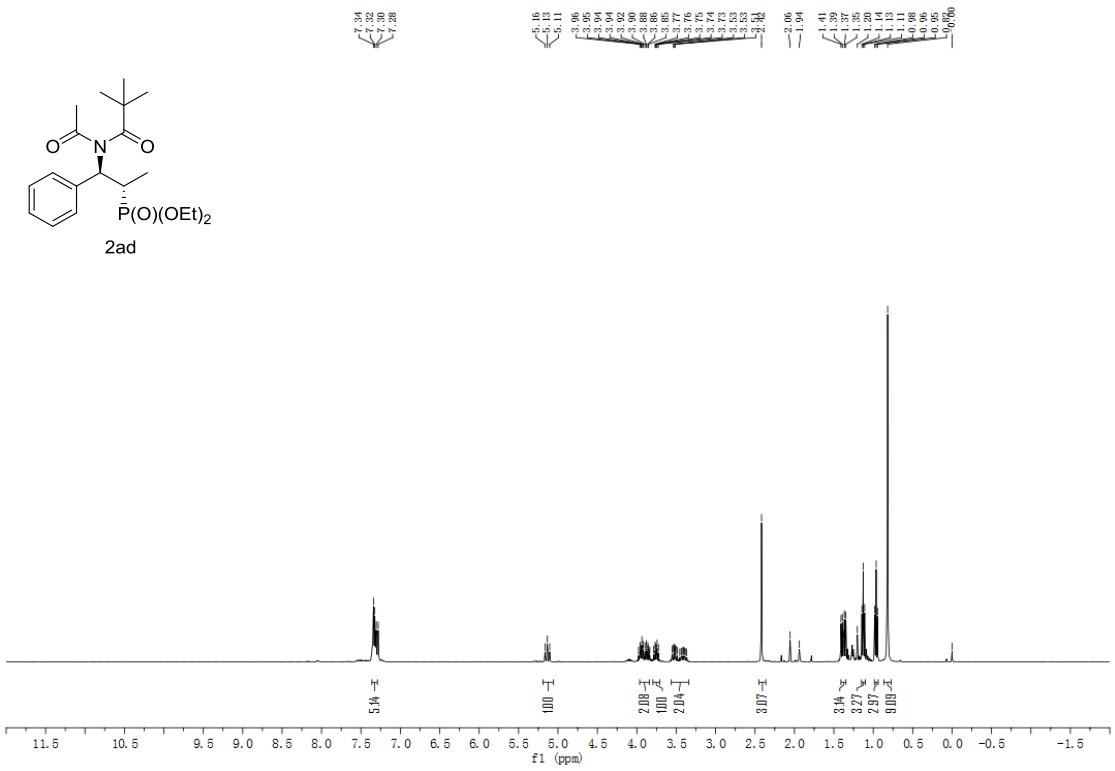

2l
f1 (ppm)

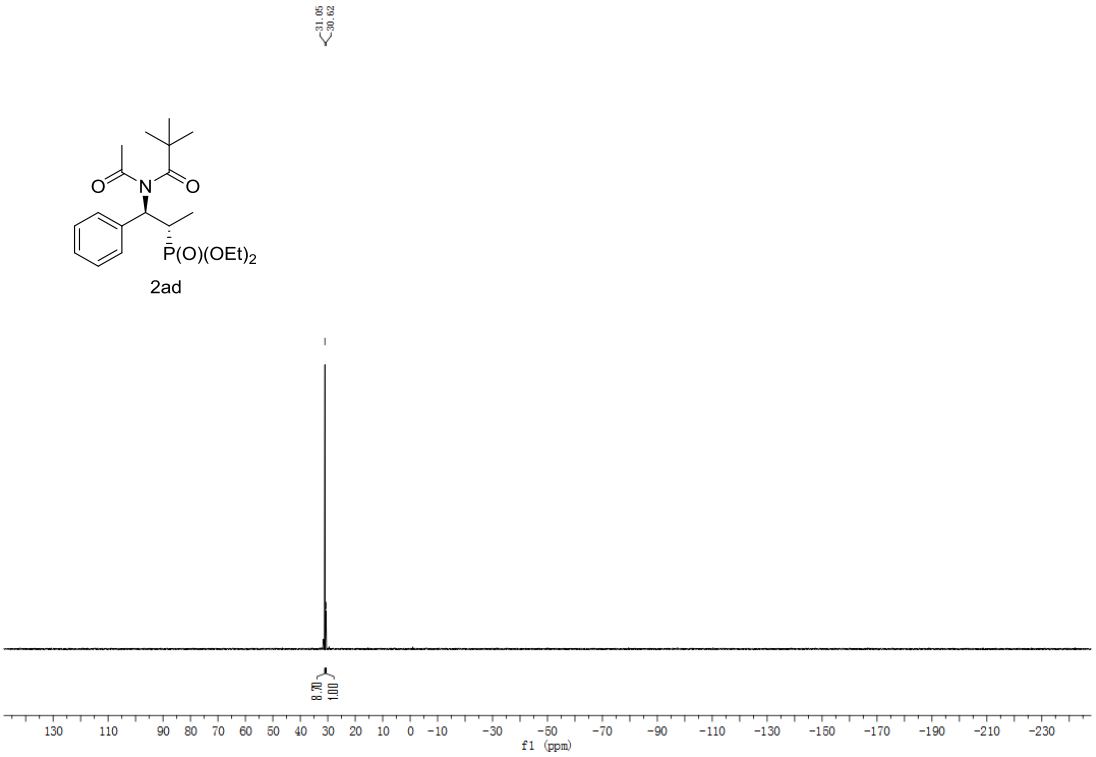

2l
f1 (ppm)


Ac
P(O)(OEt)2
2ac
1.96
3.06
1.00
1.98
0.99
1.98
5.96
3.00
2.98
2.97
f1 (ppm)

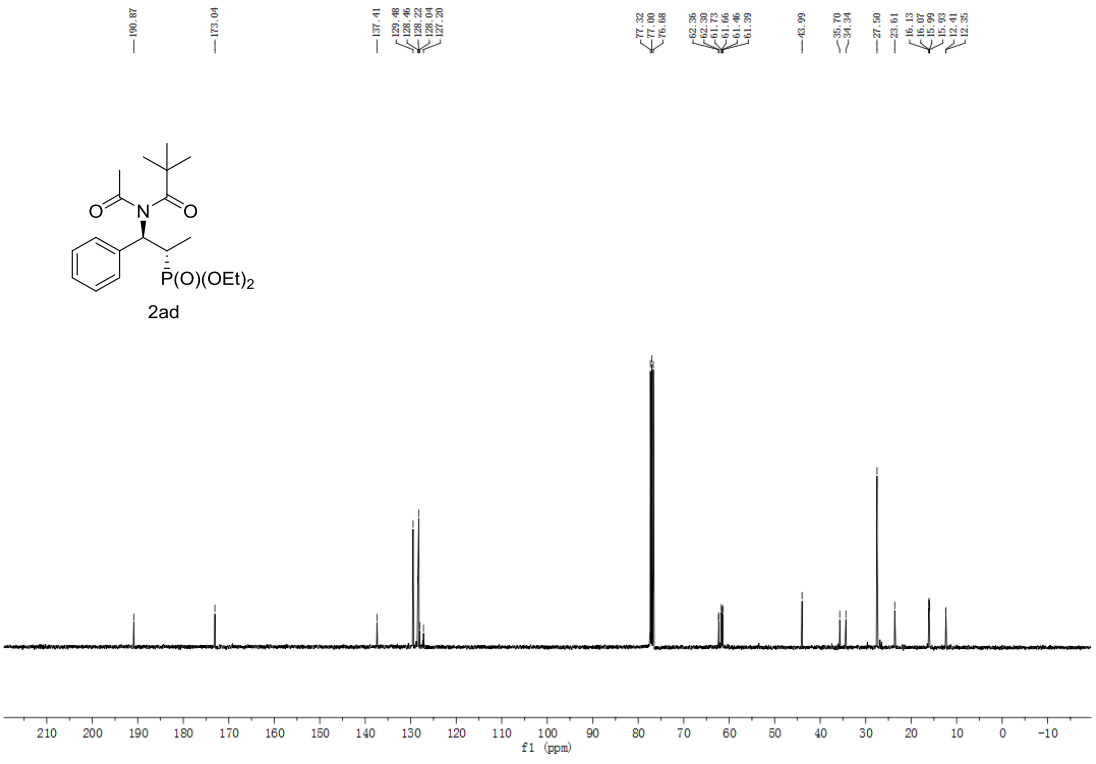

31.30
Ac
P(O)(OEt)2
2ac
f1 (ppm)


190.87
173.04
137.41
129.48
128.46
128.22
128.04
127.20
77.32
77.00
76.68
62.36
62.30
61.73
61.56
61.46
61.39
43.99
35.70
34.94
27.50
23.61
16.13
16.07
15.99
15.93
12.41
12.35
O
N
Ac
P(O)(OEt)2
2ac
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)

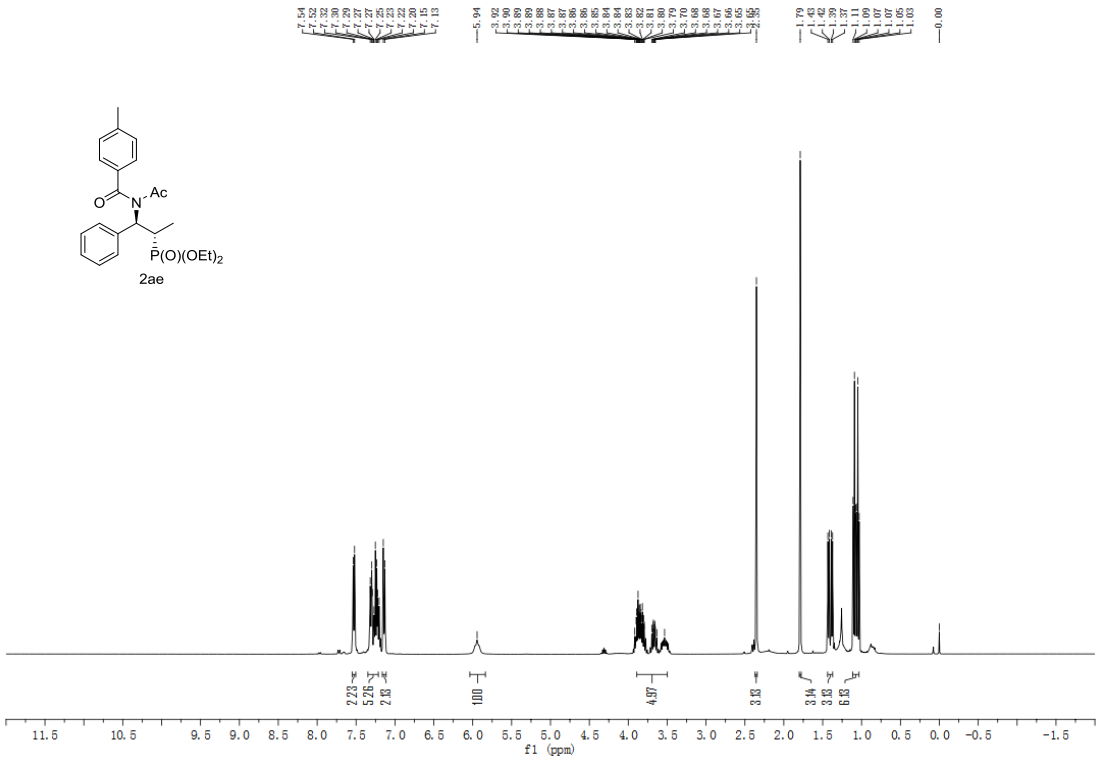

7.34
7.32
7.30
7.28
5.16
5.13
5.11
3.96
3.95
3.94
3.94
3.92
3.90
3.88
3.86
3.85
3.77
3.76
3.75
3.74
3.73
3.53
3.53
2.42
2.06
1.94
1.41
1.39
1.37
1.35
1.20
1.14
1.13
1.11
1.11
0.98
0.96
0.95
0.93
0.00
O
N
O
P(O)(OEt)2
2ad
5.14
1.00
2.08
1.00
2.04
3.07
3.14
3.27
2.97
9.09
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)

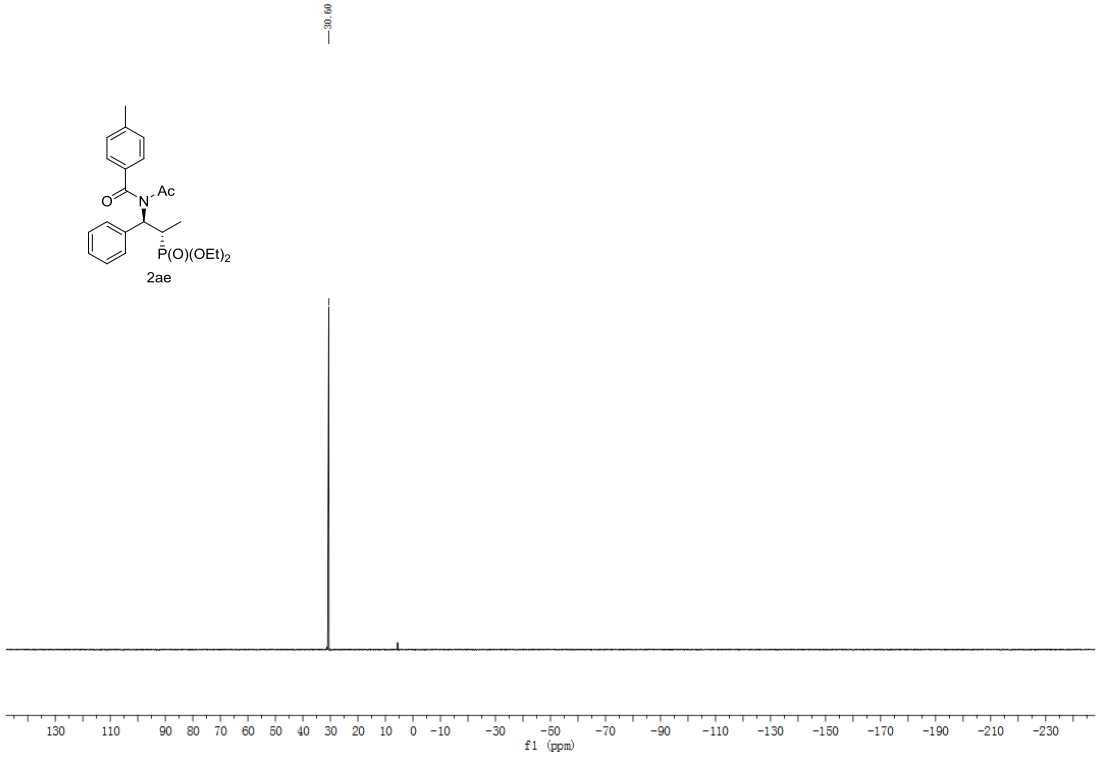

31.05
30.62
O
N
O
P(O)(OEt)2
8.70
1.00
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

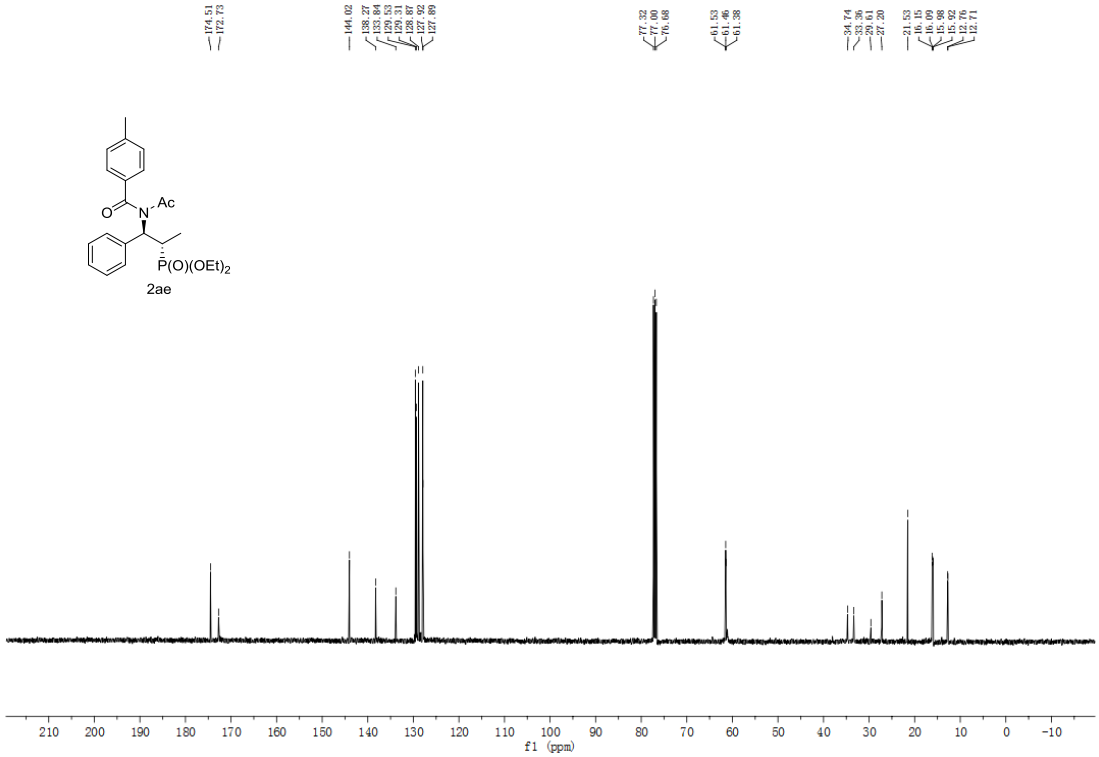
2ad

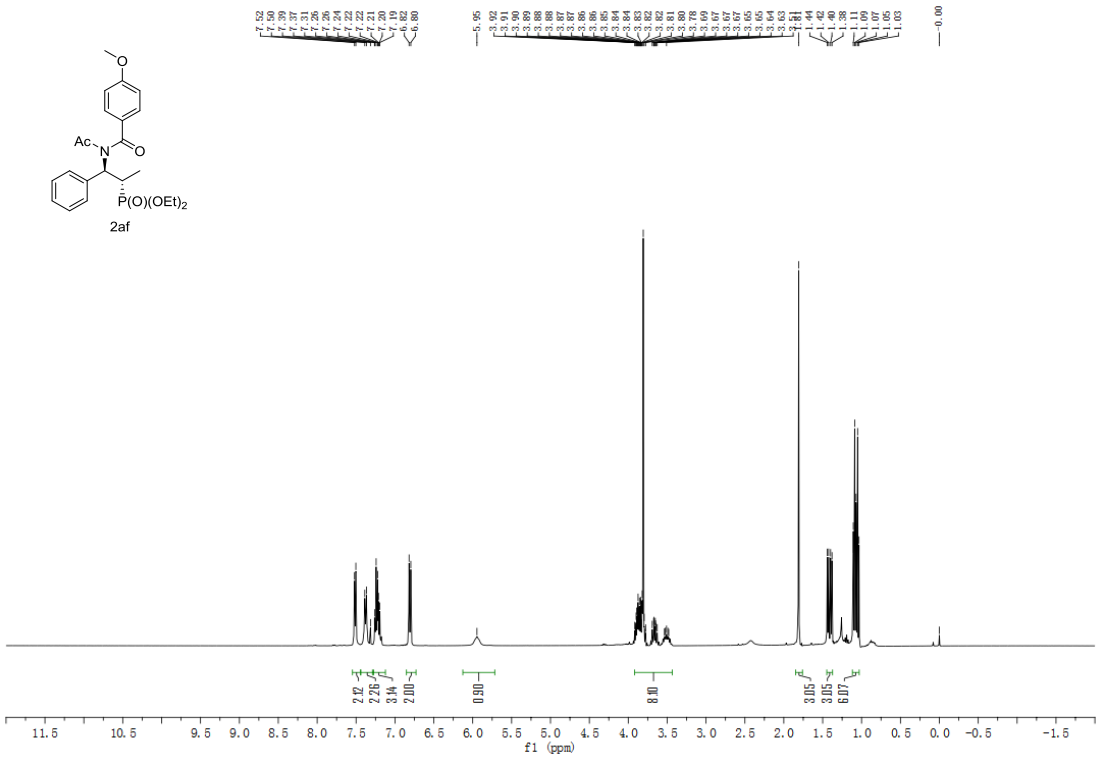

190.87
173.04
137.41
129.48
128.46
128.22
128.04
127.20
77.32
77.00
76.68
62.36
62.30
61.73
61.66
61.46
61.39
43.99
35.70
34.34
27.50
23.61
16.13
16.07
15.99
15.93
12.41
12.35
O
N
O
P(O)(OEt)2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2ad

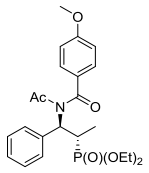

Ac
P(O)(OEt)2
2ae
f1 (ppm)


30.60
Ac
P(O)(OEt)2
2ae
f1 (ppm)

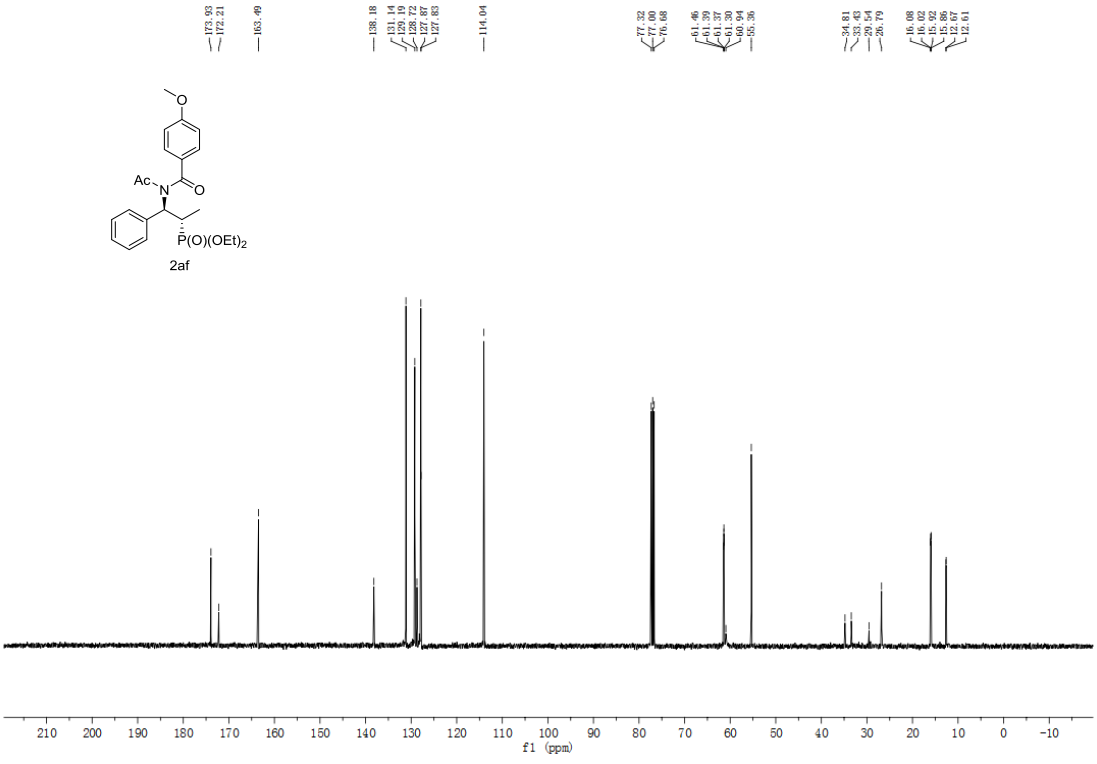

174.51
172.73
144.02
138.27
133.84
129.53
129.31
128.87
127.92
127.89
77.32
77.00
76.68
61.53
61.46
61.38
34.74
33.36
29.61
27.20
21.53
16.15
16.09
15.98
15.92
12.76
12.71
Ac
N
O
P(O)(OEt)2
2ae
f1 (ppm)


7.52
7.50
7.39
7.37
7.31
7.26
7.24
7.22
7.21
7.20
7.19
6.82
6.80
5.95
3.92
3.91
3.90
3.89
3.88
3.87
3.87
3.86
3.86
3.85
3.84
3.84
3.82
3.82
3.81
3.80
3.78
3.69
3.67
3.67
3.66
3.65
3.64
3.63
1.81
1.44
1.42
1.40
1.38
1.11
1.09
1.07
1.05
1.03
0.00
2.12
2.26
3.14
2.00
0.90
8.10
3.05
3.05
6.07
Ac
N
O
P(O)(OEt)2
2af
f1 (ppm)

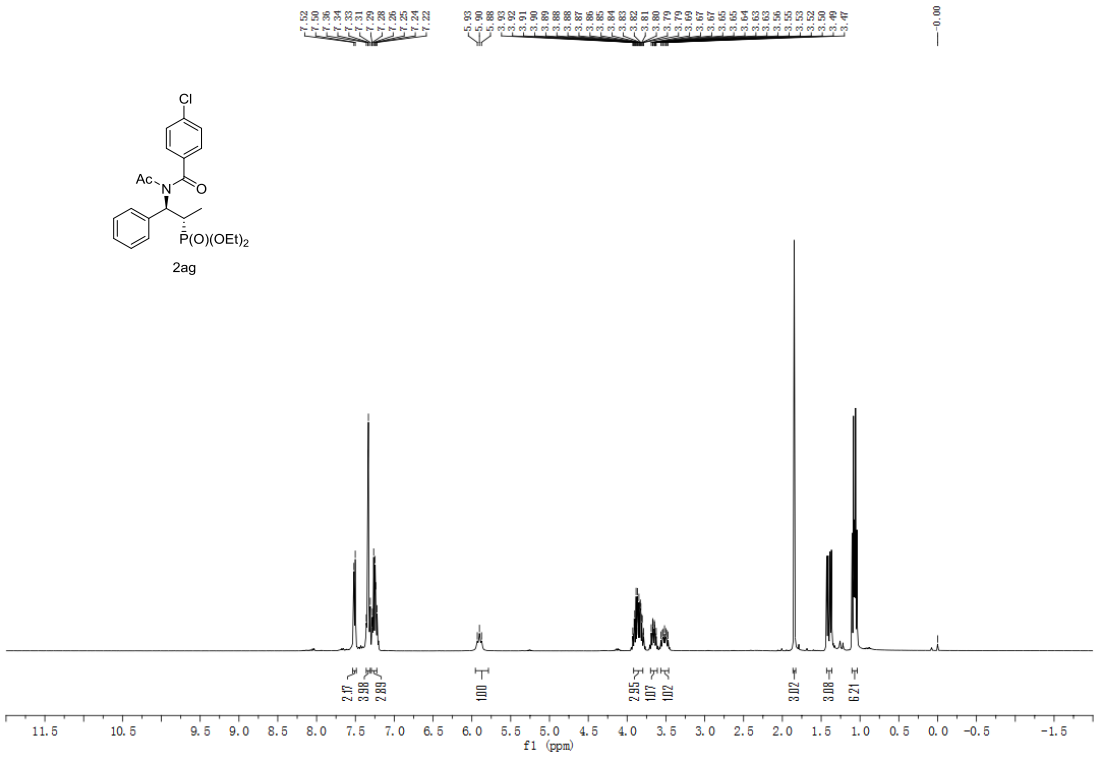
wch2295-2

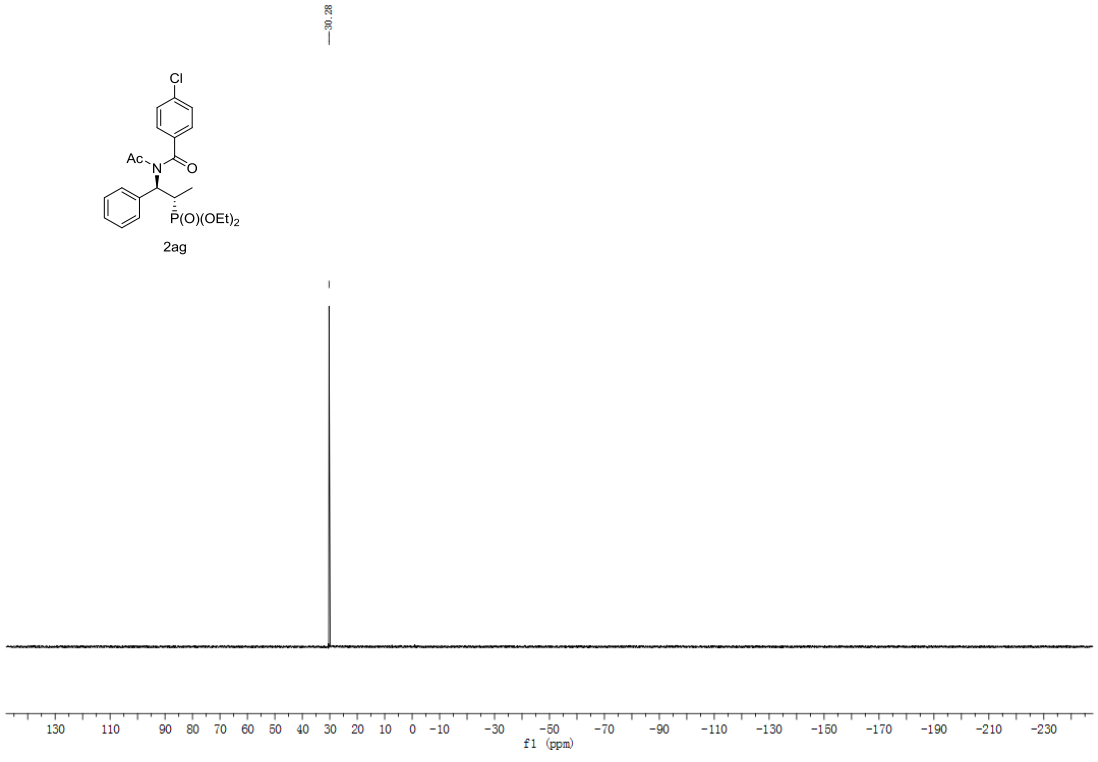


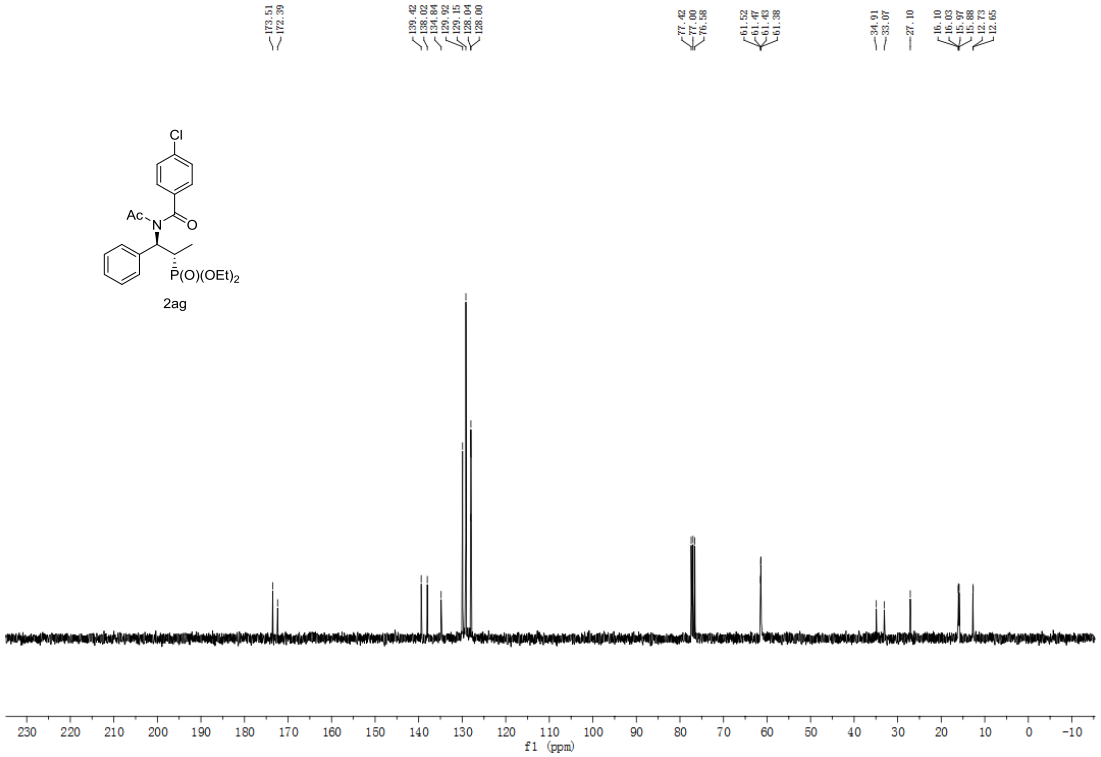
2af

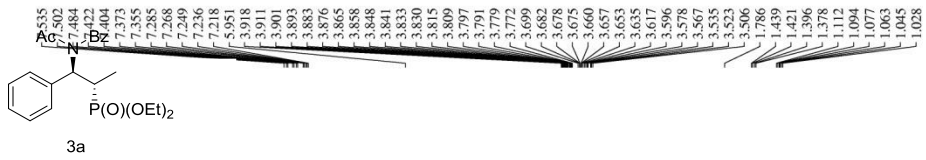


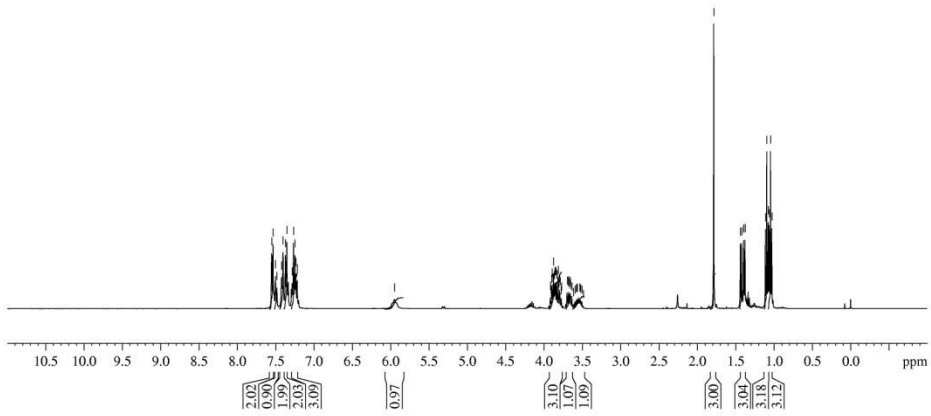
2af

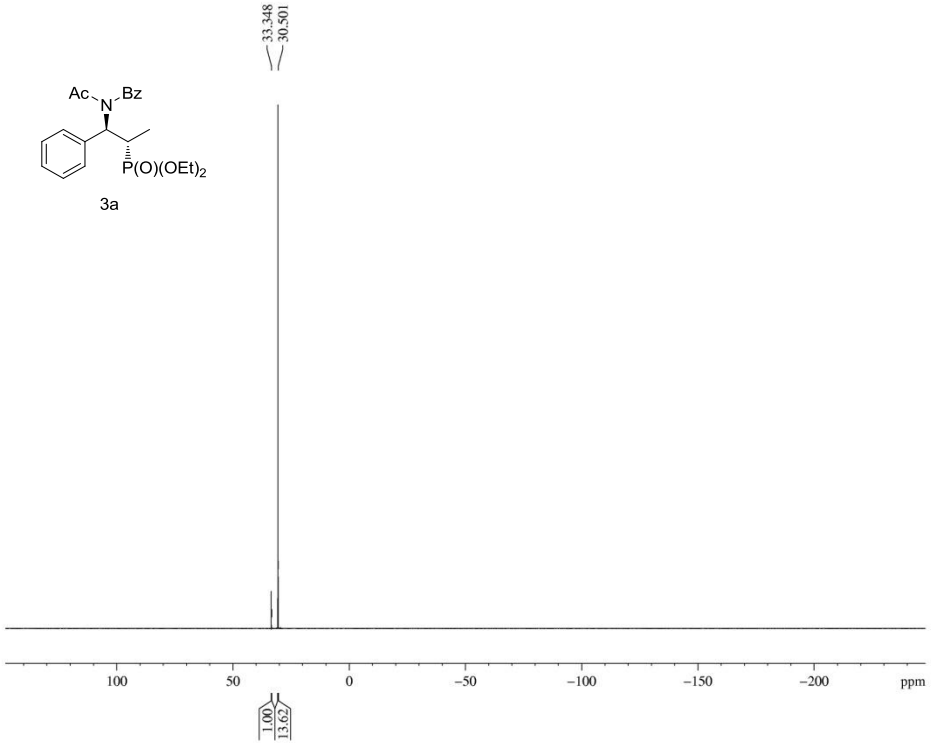

Cl
Ac
N
O
P(O)(OEt)2
2ag
f1 (ppm)

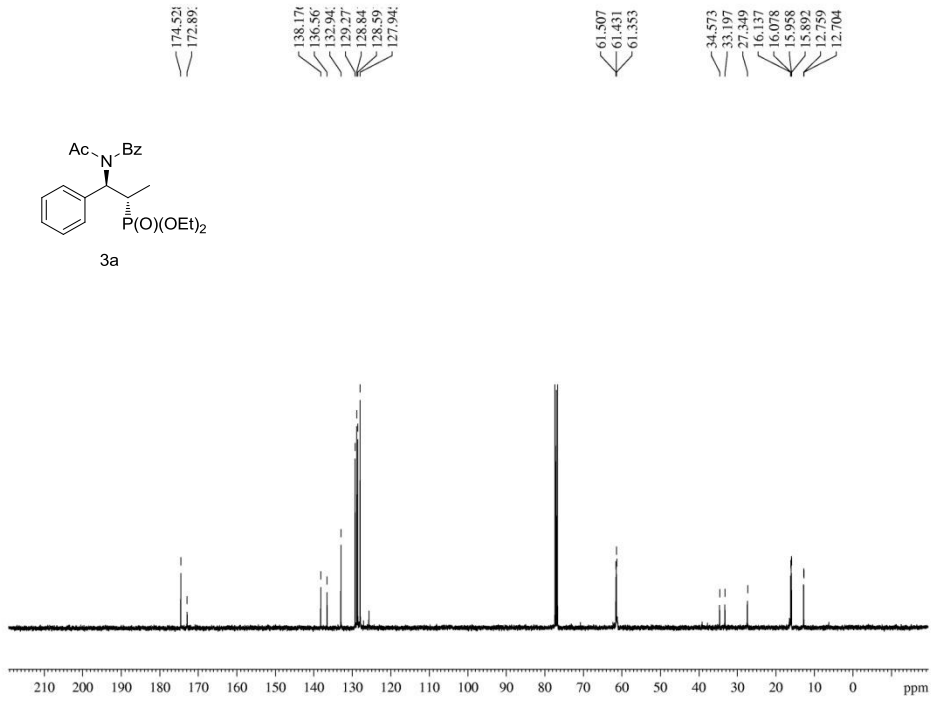

Cl
Ac
N
O
P(O)(OEt)2
2ag
f1 (ppm)

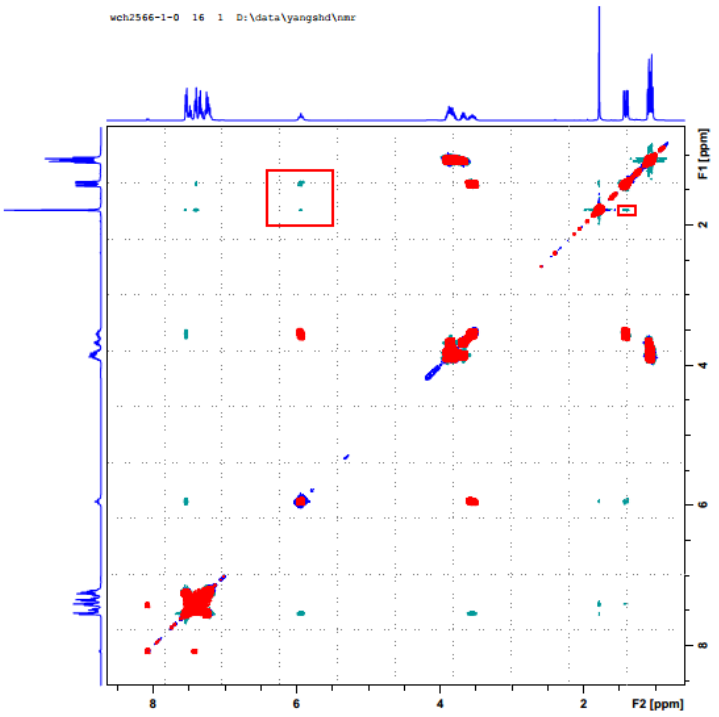

173.51
172.39
139.42
138.02
134.84
129.92
129.15
128.14
128.00
77.42
77.00
76.58
61.52
61.47
61.43
61.38
34.91
33.07
27.10
16.10
16.03
15.97
15.88
12.73
12.65
Cl
Ac
N
O
P(O)(OEt)2
2ag
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.535
7.502
7.484
7.422
7.404
7.373
7.355
7.285
7.268
7.249
7.236
7.218
5.951
3.918
3.911
3.901
3.893
3.883
3.876
3.865
3.858
3.848
3.841
3.833
3.830
3.815
3.809
3.797
3.791
3.779
3.772
3.699
3.682
3.678
3.675
3.660
3.657
3.653
3.635
3.617
3.596
3.578
3.567
3.535
3.523
3.506
1.786
1.439
1.421
1.396
1.378
1.112
1.094
1.077
1.063
1.045
1.028
Ac
N
Bz
P(O)(OEt)2
3a

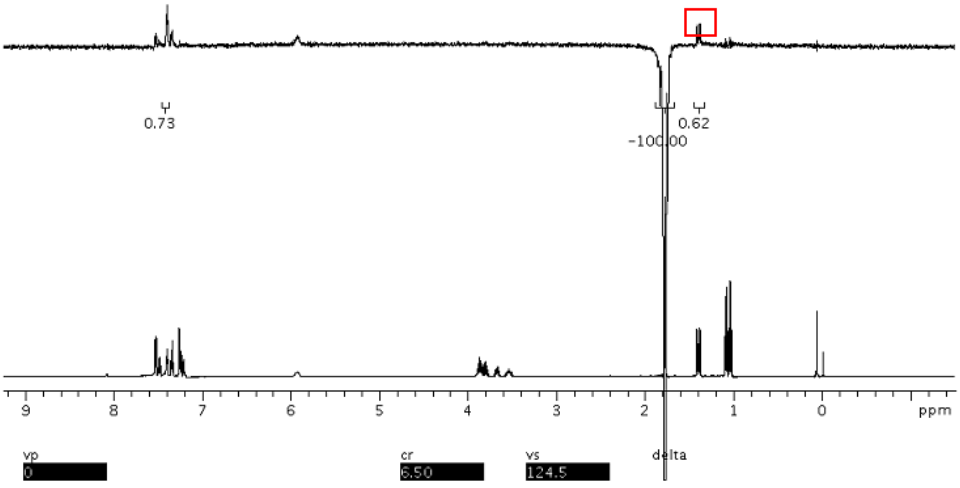

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
0.90
1.99
2.03
3.09
0.97
3.10
1.07
1.09
3.00
3.04
3.18
3.12


33.348
30.501
Ac
N
Bz
P(O)(OEt)2
3a
100
50
0
−50
−100
−150
−200
ppm
1.00
13.62

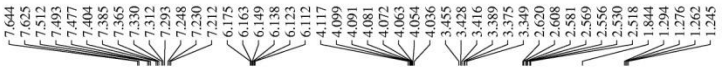

174.521
172.89
138.17
136.56
132.94
129.27
128.84
128.59
127.94
61.507
61.431
61.353
34.573
33.197
27.349
16.137
16.078
15.958
15.892
12.759
12.704
Ac
N
Bz
P(O)(OEt)2
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3a NOESY-COSY



3a 1D-NOESY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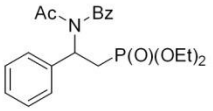
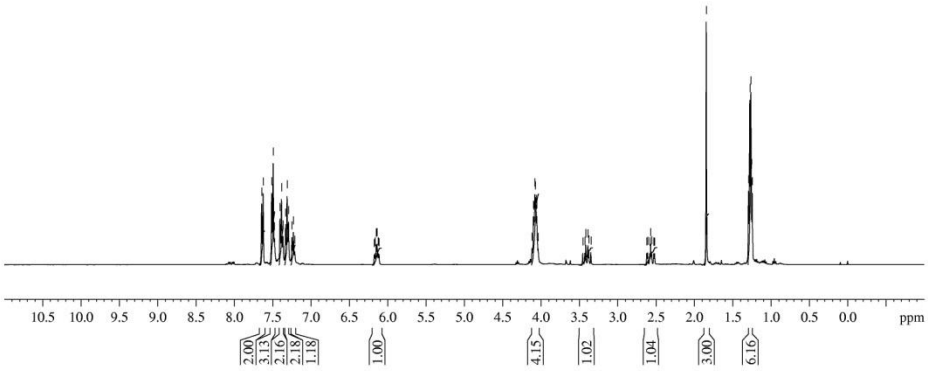
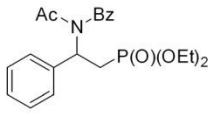
7.625
7.512
7.493
7.477
7.404
7.385
7.365
7.330
7.312
7.293
7.248
7.230
7.212
6.175
6.163
6.149
6.138
6.123
6.112
4.117
4.099
4.091
4.081
4.072
4.063
4.054
4.036
3.455
3.428
3.416
3.389
3.375
3.349
2.620
2.608
2.581
2.569
2.556
2.530
2.518
1.844
1.294
1.276
1.262
1.245


Ac
N
Bz
P(O)(OEt)2

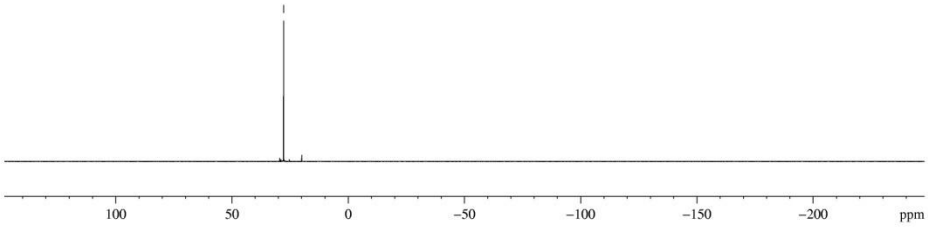
3b


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
3.13
2.16
2.18
1.18
1.00
4.15
1.02
1.04
3.00
6.16


27.733


Ac
N
Bz
P(O)(OEt)2

3b


100
50
0
−50
−100
−150
−200
ppm


173.5
173.4
139.0
138.9
136.5
132.2
128.3
128.3
127.9
127.3
61.64
61.58
61.27
61.21
54.25
54.22
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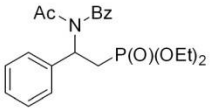
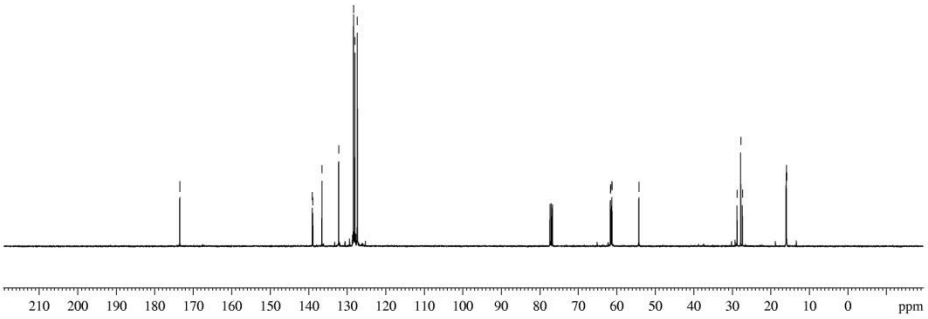
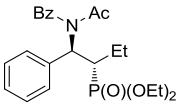
27.79
27.35
16.01
15.97
15.95
15.91

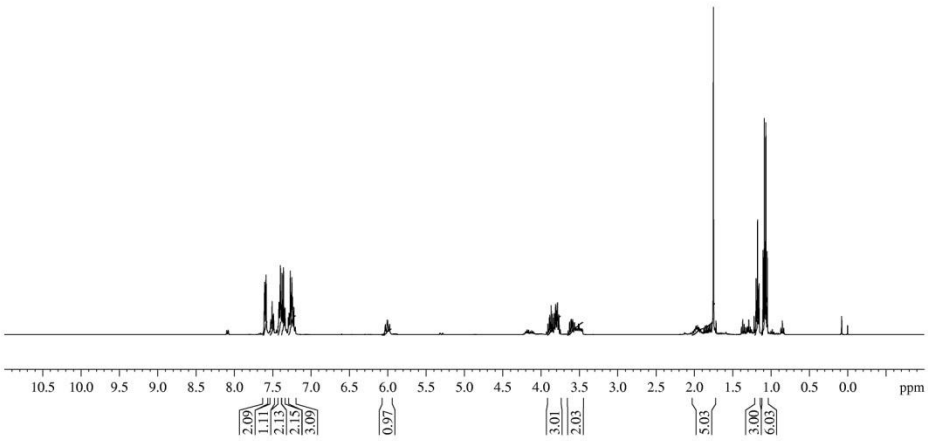

Ac
N
Bz
P(O)(OEt)2

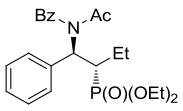
3b


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


Bz
N
Ac
Et
P(O)(OEt)2

3c

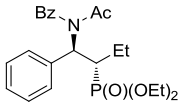

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.09
1.11
2.13
2.15
3.09
0.97
3.01
2.03
5.03
3.00
6.03


Bz
N
Ac
Et
P(O)(OEt)2

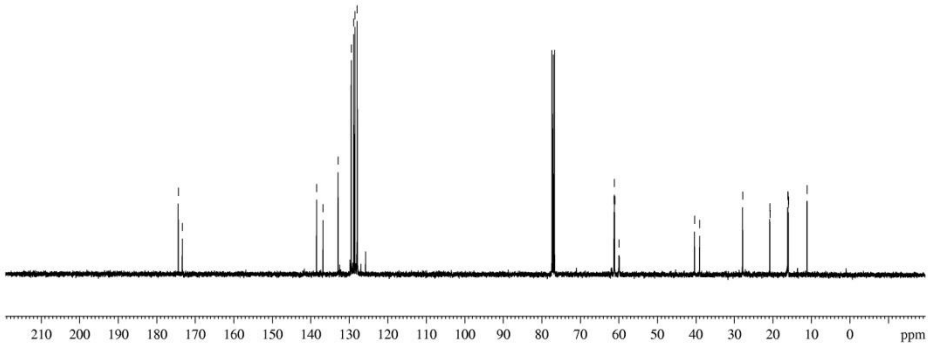
3c

33.114
29.813
100
50
0
−50
−100
−150
−200
ppm
1.00
12.34

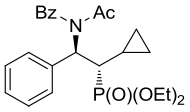
174.40
173.35
138.48
136.80
132.90
129.47
128.86
128.52
127.92
127.90
61.222
61.145
61.068
59.925
40.340
38.984
27.834
20.785
20.739
16.112
16.052
15.983
15.919
11.110
11.088


Bz
N
Ac
Et
P(O)(OEt)2

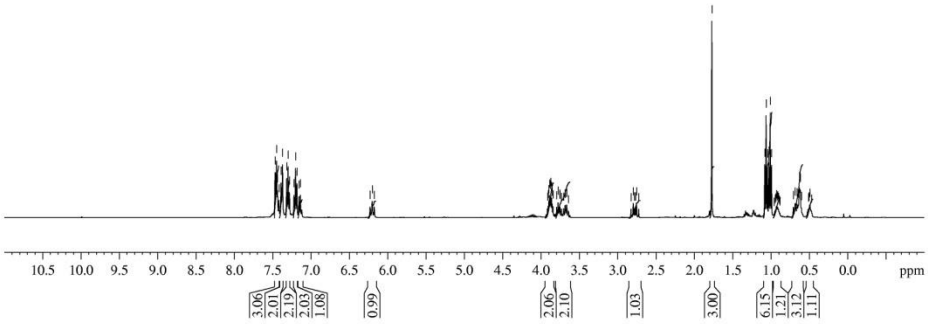
3c


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

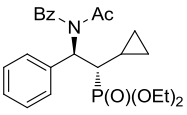

7.449
7.437
7.418
7.390
7.371
7.317
7.298
7.282
7.221
7.202
7.183
7.155
7.138
6.229
6.202
6.174
3.915
3.906
3.897
3.889
3.880
3.872
3.862
3.855
3.844
3.796
3.777
3.758
3.753
3.734
3.704
3.686
3.682
3.664
2.797
2.782
2.768
2.754
1.772
1.081
1.063
1.046
1.027
1.009
0.992
0.929
0.919
0.912
0.707
0.686
0.660
0.645
0.629
0.619
0.603
0.506
0.495


Bz
N
Ac
P(O)(OEt)2

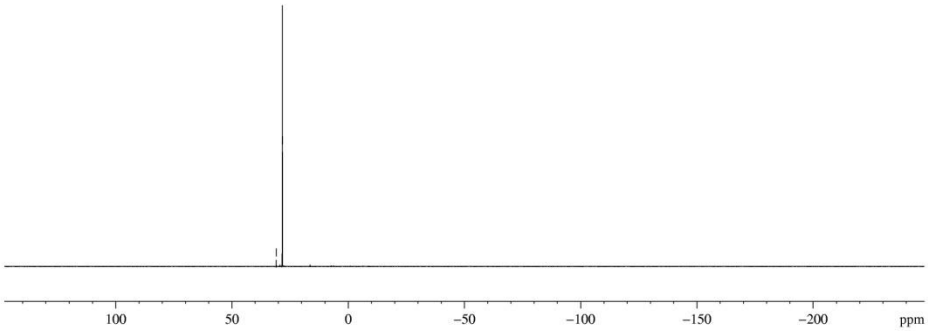
3d

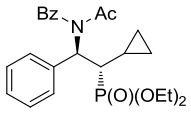

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.06
2.01
2.19
2.03
1.08
0.99
2.06
2.10
1.03
3.00
6.15
1.21
3.12
1.11


30.928
28.183

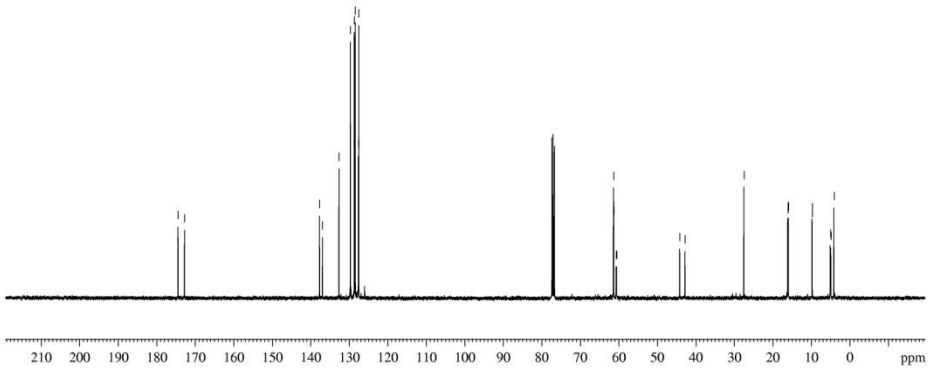

Bz
N
Ac
P(O)(OEt)2

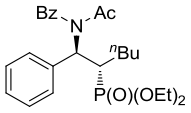
3d


100 50 0 −50 −100 −150 −200 ppm

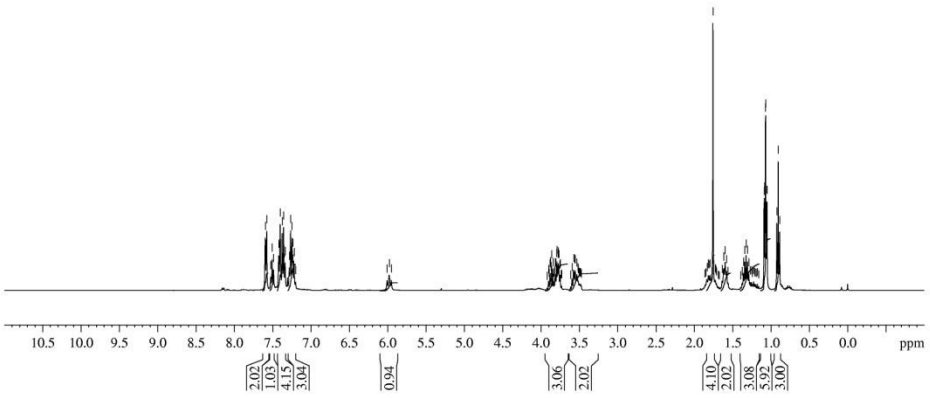


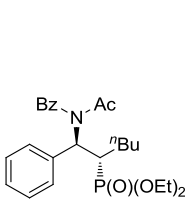
3d





3e

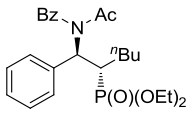



Bz
N
Ac
nBu
P(O)(OEt)2

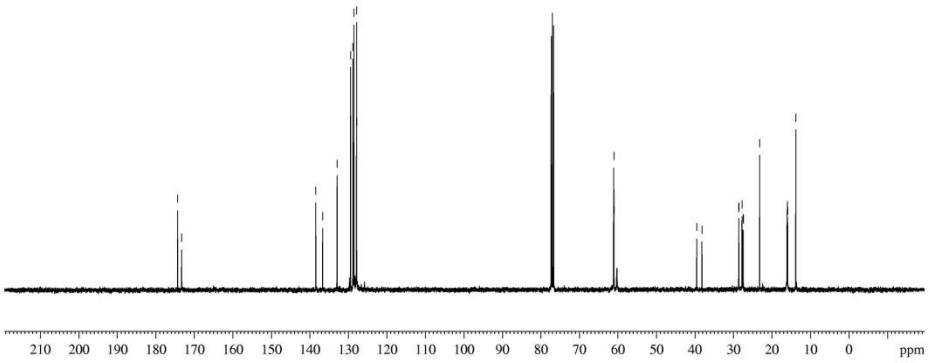
3e

33.196
29.911
100
50
0
−50
−100
−150
−200
ppm

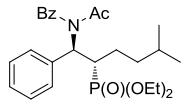

174.35
173.28
138.47
136.68
132.91
129.43
128.80
128.53
127.87
127.85
61.136
61.070
61.003
39.528
38.171
28.610
28.592
27.763
27.485
27.441
23.173
16.078
16.017
15.973
15.909
13.792


Bz
N
Ac
nBu
P(O)(OEt)2

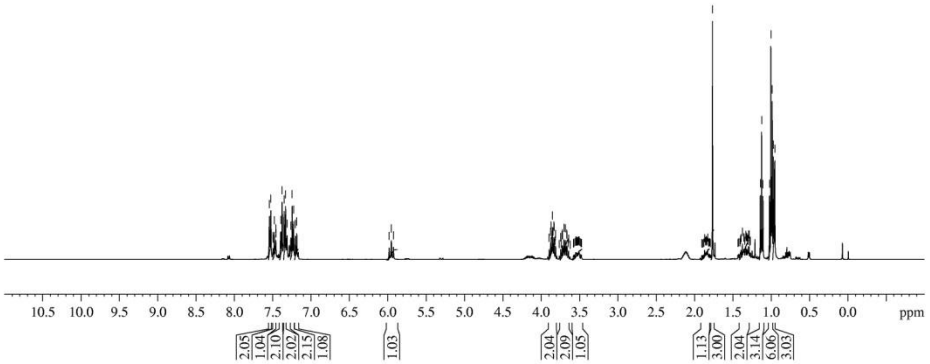
3e


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

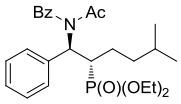

7.526
7.498
7.494
7.480
7.462
7.458
7.397
7.380
7.352
7.334
7.314
7.266
7.248
7.229
7.205
7.187
5.983
5.955
5.927
3.896
3.878
3.871
3.860
3.853
3.847
3.836
3.829
3.812
3.746
3.728
3.724
3.721
3.704
3.685
3.667
3.662
3.642
1.868
1.828
1.765
1.392
1.375
1.357
1.351
1.333
1.329
1.315
1.295
1.289
1.142
1.125
1.107
1.022
1.004
0.987
0.969
0.952


Bz
N
Ac
P(O)(OEt)2

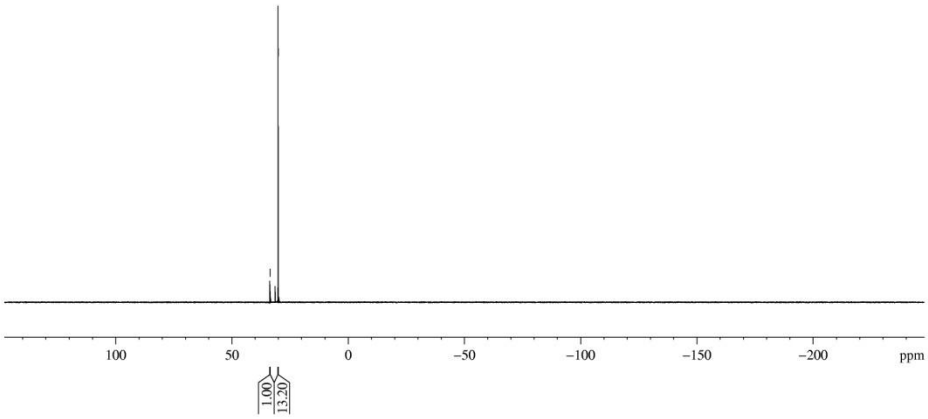
3f

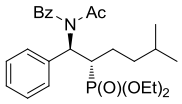

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05 1.04 2.10 2.02 2.15 1.08 1.03 2.04 2.09 1.05 1.13 3.00 2.04 3.14 6.06 3.03


33.546
30.043

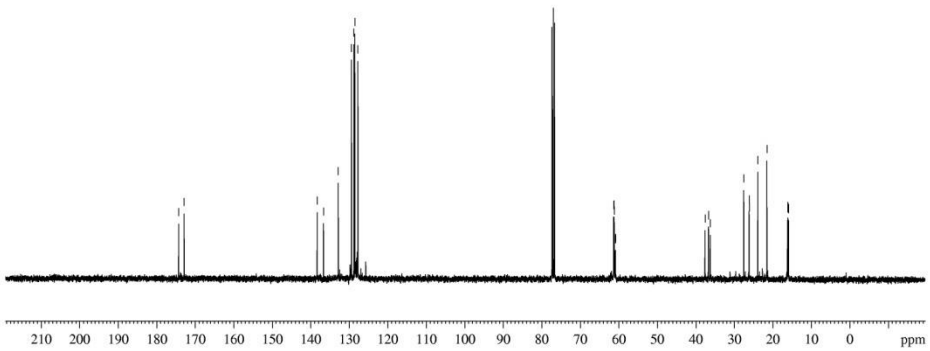

Bz
N
Ac
P(O)(OEt)2

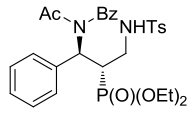
3f


100 50 0 −50 −100 −150 −200 ppm
1.00 13.20

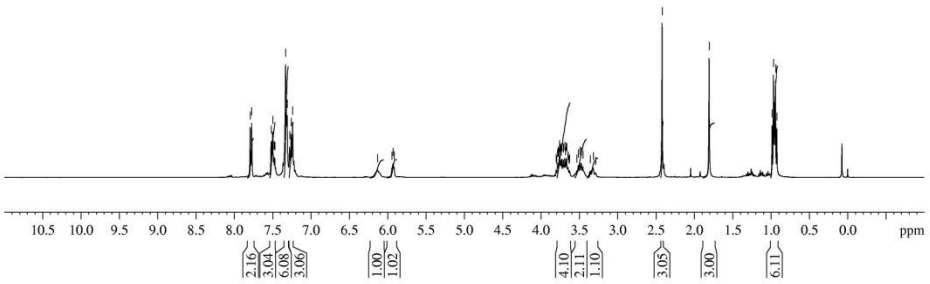

Bz
N
Ac
P(O)(OEt)2

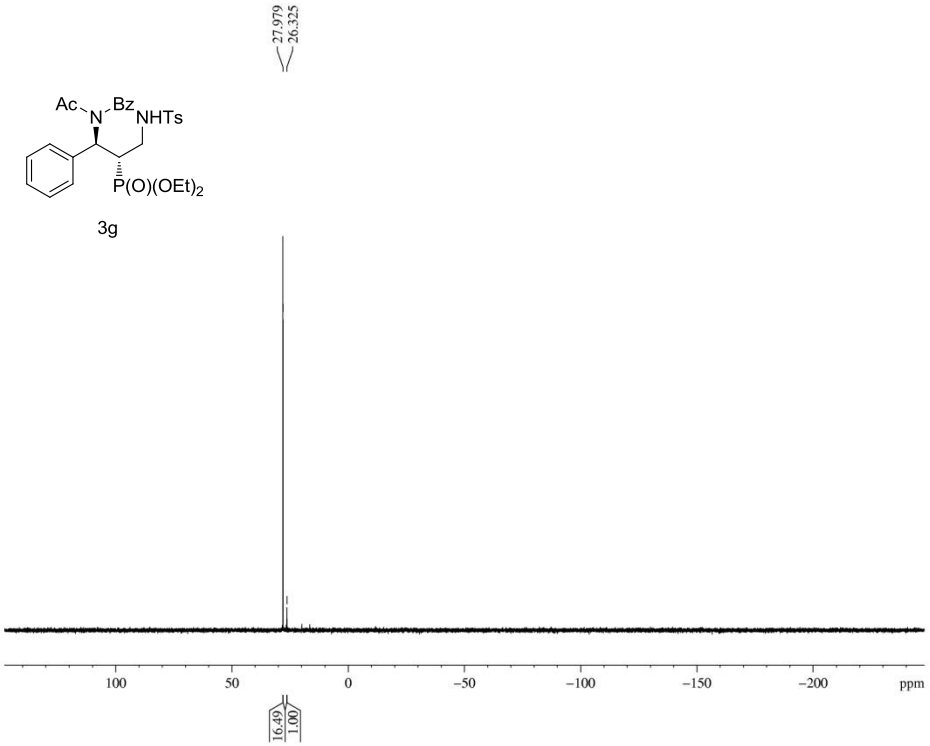
3f

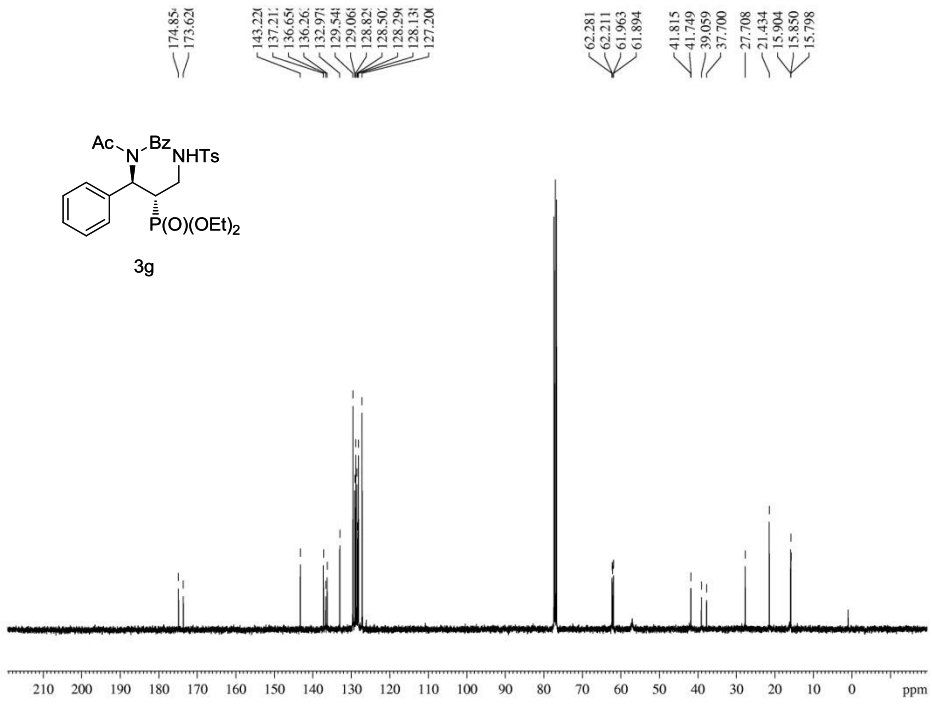

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Ac
N
Bz
NHTs
P(O)(OEt)2

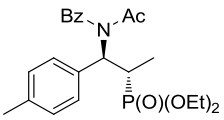
3g


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.16 3.04 6.08 3.06 1.00 1.02 4.10 2.11 1.10 3.05 3.00 6.11

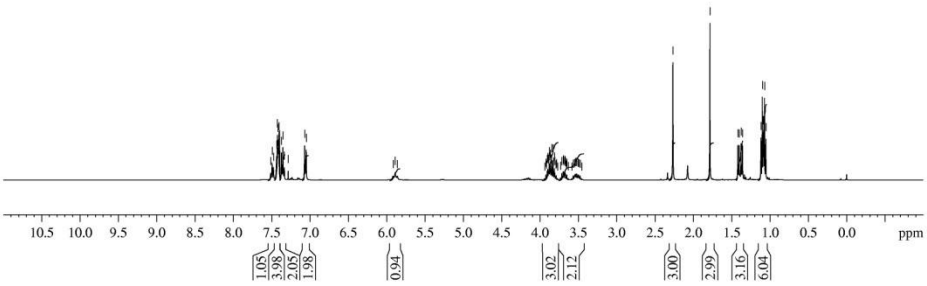

27.979
26.325
Ac
N
Bz
NHTs
P(O)(OEt)2
3g
100
50
0
−50
−100
−150
−200
ppm
16.49
1.00


174.85
173.62
143.22
137.21
136.65
136.26
132.97
129.54
129.06
128.82
128.50
128.29
128.13
127.20
62.281
62.211
61.963
61.894
41.815
41.749
39.059
37.700
27.708
21.434
15.904
15.850
15.798
Ac
N
Bz
NHTs
P(O)(OEt)2
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

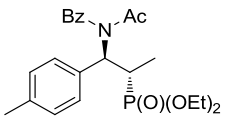

7.513
7.494
7.476
7.436
7.426
7.418
7.406
7.372
7.354
7.334
7.284
7.069
7.049
5.917
5.889
5.861
3.922
3.905
3.898
3.890
3.888
3.880
3.873
3.865
3.855
3.848
3.830
3.824
3.812
3.806
3.787
3.715
3.697
3.693
3.689
3.675
3.672
3.668
3.650
3.567
3.549
3.538
3.523
3.505
3.494
3.476
2.266
1.783
1.419
1.401
1.376
1.358
1.118
1.100
1.089
1.083
1.071
1.053


Bz
N
Ac
P(O)(OEt)2

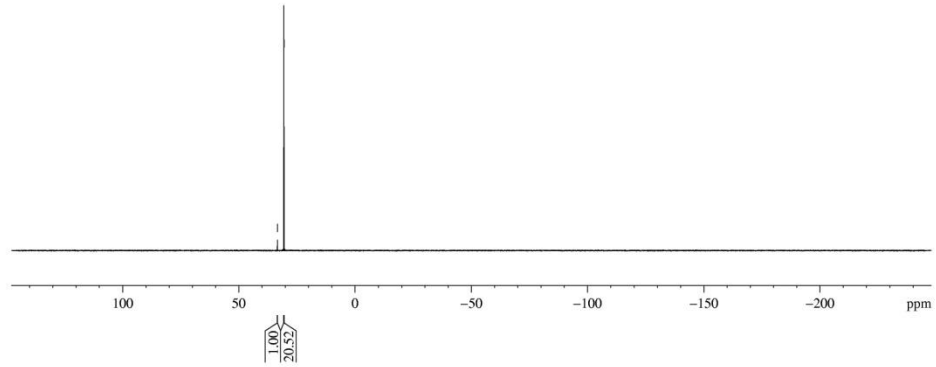
3h


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.05
3.98
2.05
1.98
0.94
3.02
2.12
3.00
2.99
3.16
6.04

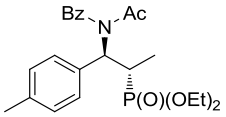

33
30


Bz
N
Ac
P(O)(OEt)2

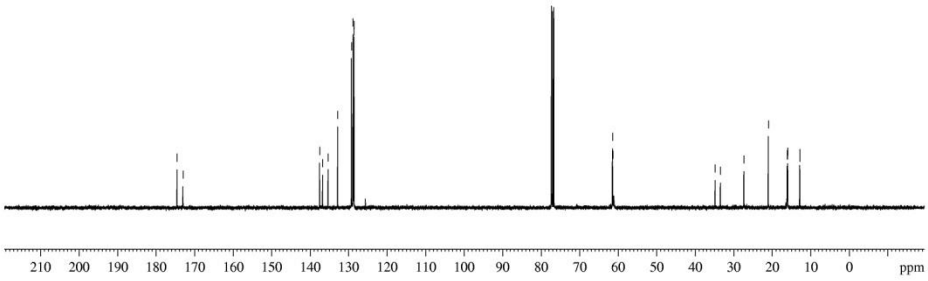
3h


100 50 0 −50 −100 −150 −200 ppm
1.00
20.52

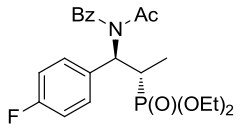

174.548
173.006
137.544
136.756
135.320
132.837
129.255
128.834
128.675
128.587
61.525
61.461
61.399
34.817
33.440
27.338
21.002
16.138
16.079
16.006
15.943
12.870
12.814


Bz
N
Ac
P(O)(OEt)2

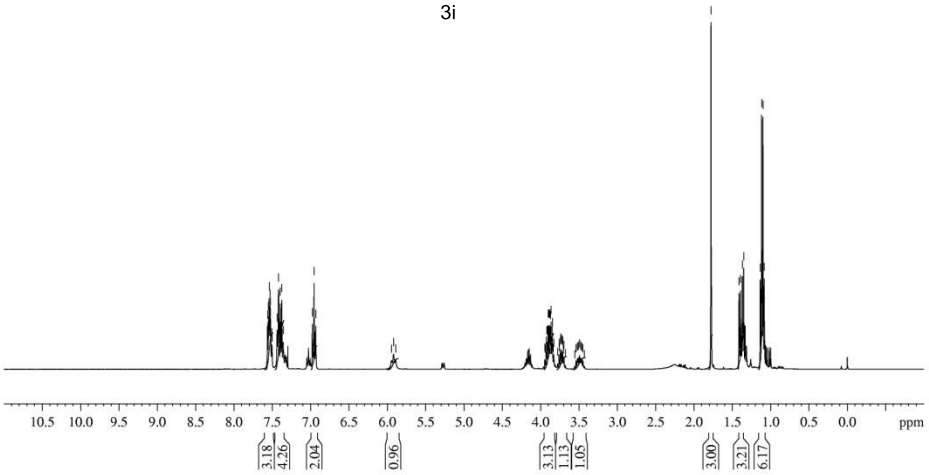
3h

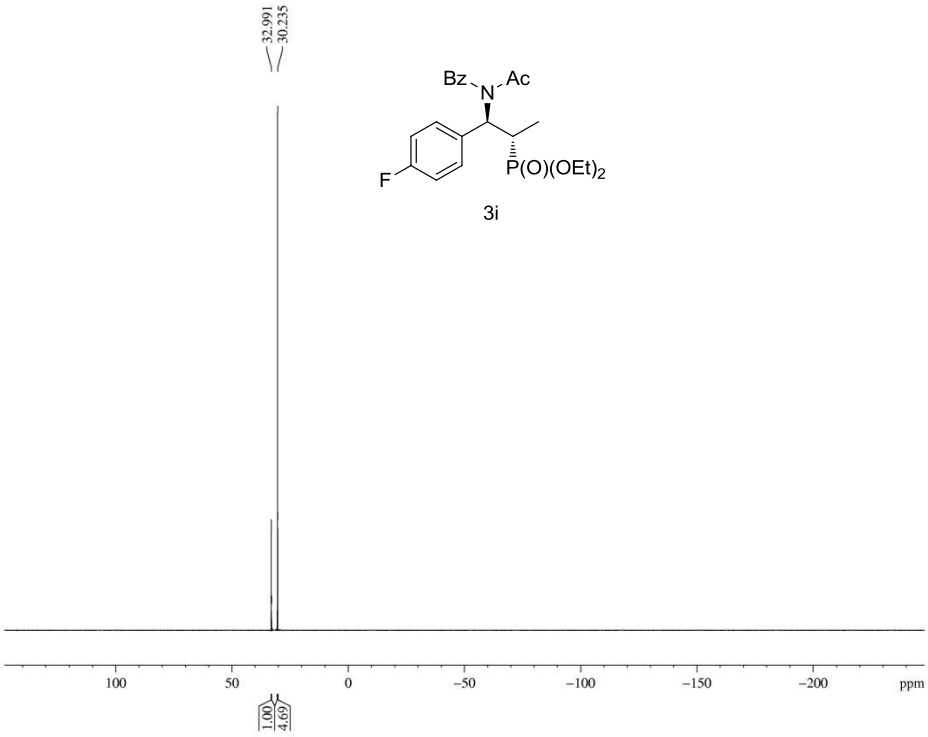

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.55
7.54
7.54
7.52
7.52
7.50
7.50
7.43
7.41
7.39
7.37
7.35
6.97
6.95
6.93
5.94
5.91
5.89
3.94
3.93
3.92
3.92
3.90
3.90
3.88
3.88
3.87
3.86
3.85
3.84
3.83
3.82
3.76
3.75
3.74
3.73
3.73
3.72
3.71
3.71
3.69
3.53
3.52
3.50
3.49
3.47
3.46
3.44
1.77
1.41
1.39
1.36
1.35
1.13
1.11
1.10
1.08

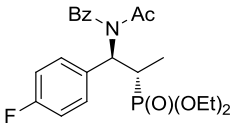

Bz
N
Ac
F
P(O)(OEt)2

3i

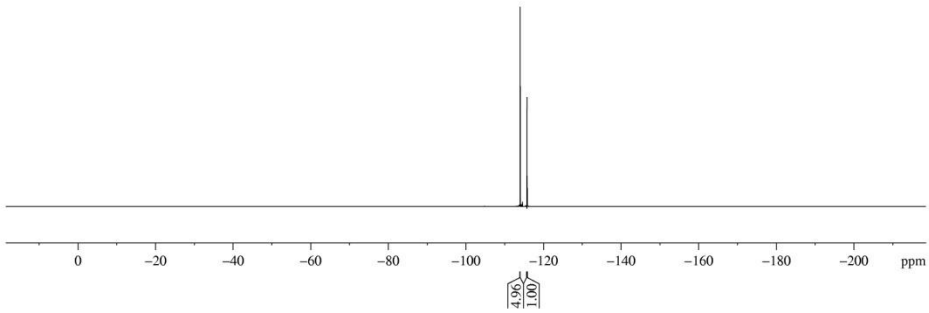

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.18
4.26
2.04
0.96
3.13
1.13
1.05
3.00
3.21
6.17

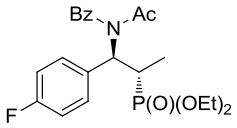

32.991
30.235
Bz
N
Ac
F
P(O)(OEt)2
100
50
0
−50
−100
−150
−200
ppm
1.00
4.69

3i

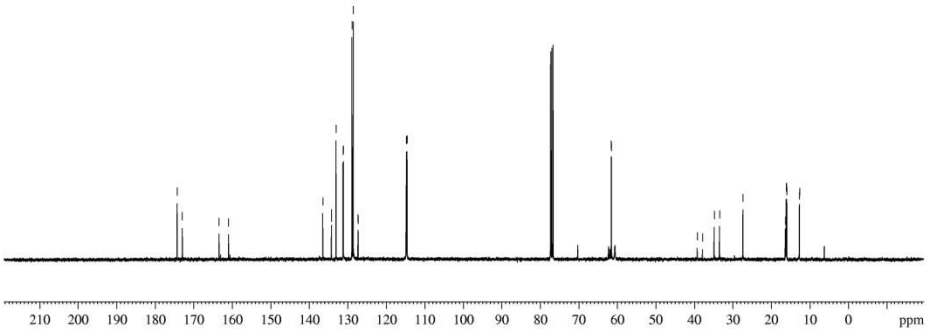

Bz
N
Ac
F
P(O)(OEt)2

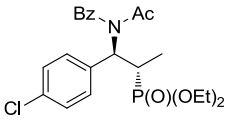
3i


0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm
4.96
1.00

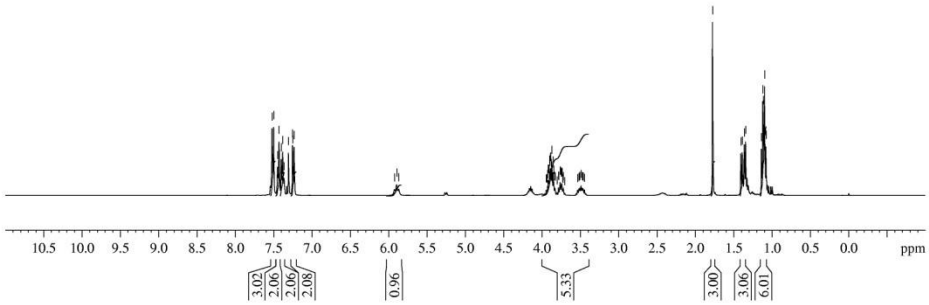

Bz
N
Ac
F
P(O)(OEt)2

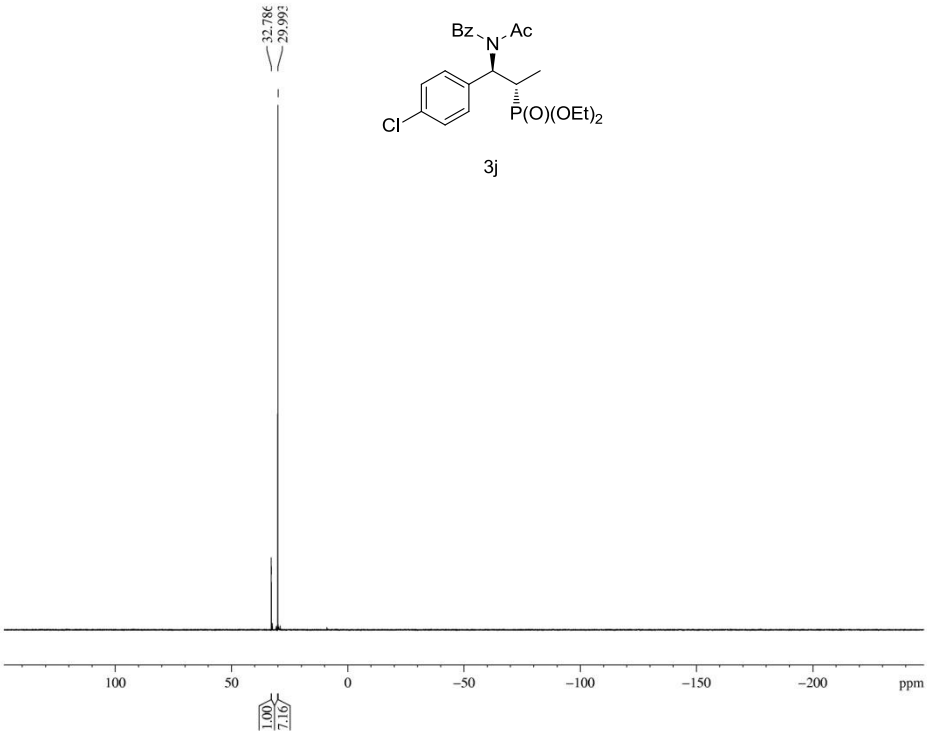
3i


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

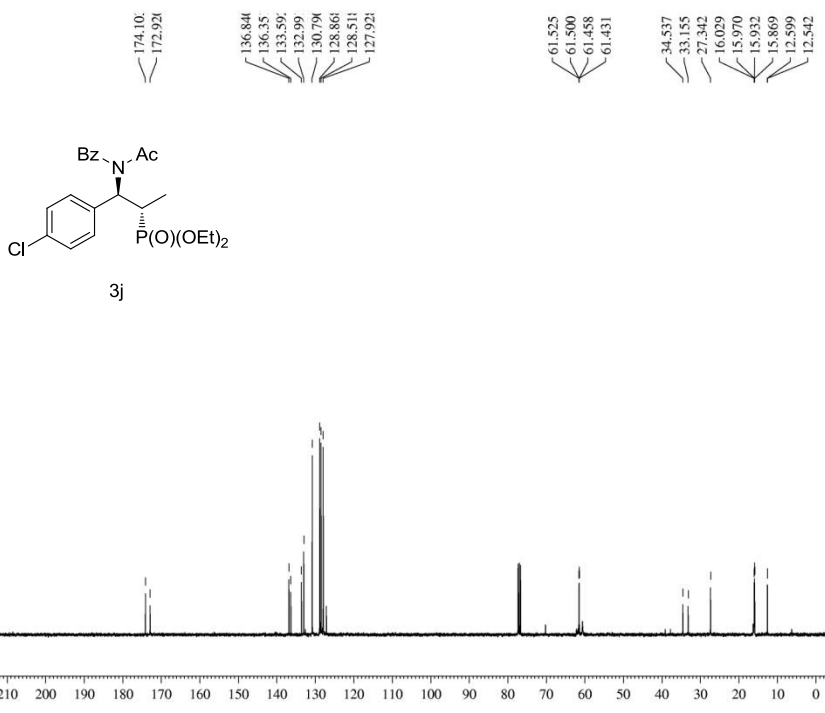

Bz
N
Ac
Cl
P(O)(OEt)2

3j


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.02
2.06
2.06
2.08
0.96
5.33
3.00
3.06
6.01

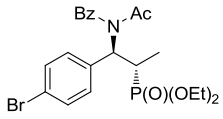

32.786
29.993
Bz
N
Ac
Cl
P(O)(OEt)2
100
50
0
−50
−100
−150
−200
ppm
1.00
7.16

3j

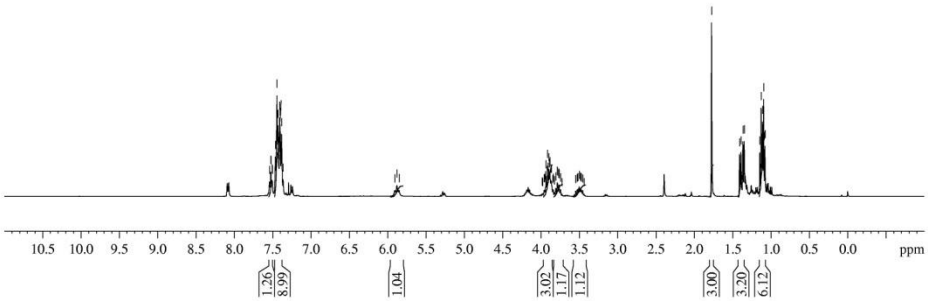

174.10
172.92
136.84
136.35
133.59
132.99
130.79
128.86
128.51
127.92
61.525
61.500
61.458
61.431
34.537
33.155
27.342
16.029
15.970
15.932
15.869
12.599
12.542
Bz
N
Ac
Cl
P(O)(OEt)2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3j

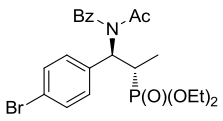

7.540
7.524
7.521
7.507
7.504
7.465
7.444
7.430
7.409
7.406
7.384
7.363
5.907
5.879
5.852
3.984
3.977
3.959
3.951
3.941
3.934
3.916
3.909
3.898
3.890
3.884
3.873
3.866
3.848
3.841
3.824
3.808
3.806
3.787
3.784
3.769
3.766
3.763
3.744
3.726
3.547
3.529
3.518
3.501
3.485
3.474
3.456
3.439
1.776
1.410
1.392
1.367
1.349
1.146


Bz
N
Ac
Br
P(O)(OEt)2

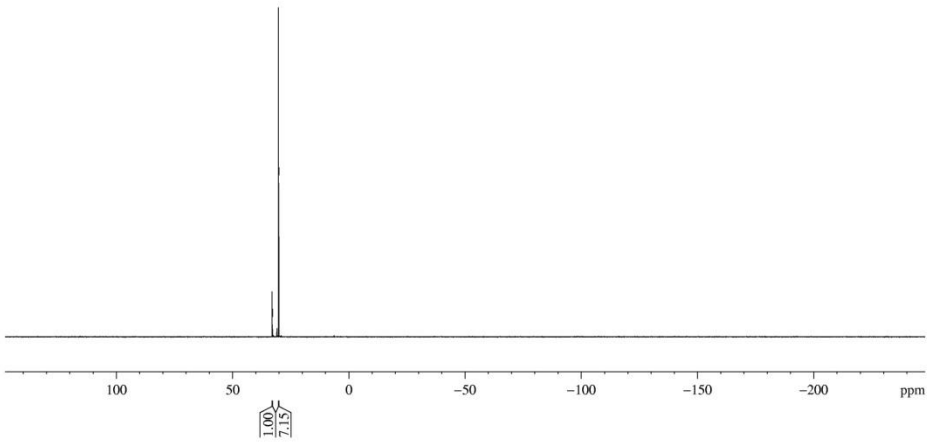
3k


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.26
8.99
1.04
3.02
1.17
1.12
3.00
3.20
6.12

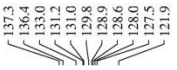

32.857
30.055


Bz
N
Ac
Br
P(O)(OEt)2

3k

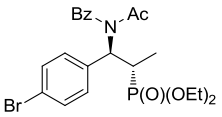

100 50 0 −50 −100 −150 −200 ppm
1.00
7.15


174.1
173.0

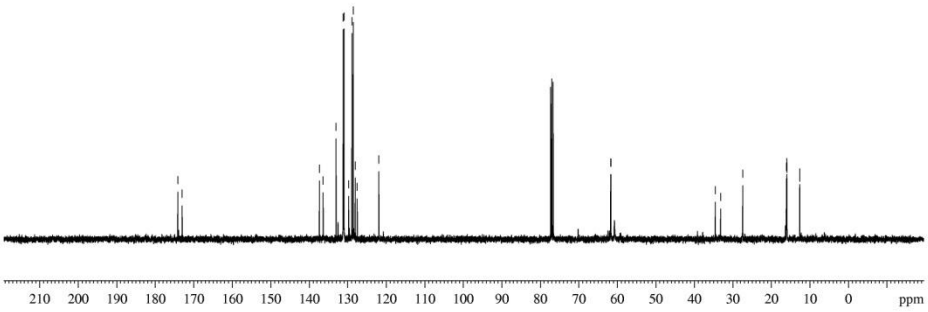

137.3
136.4
133.0
131.2
131.0
129.8
128.9
128.6
128.0
127.5
121.9

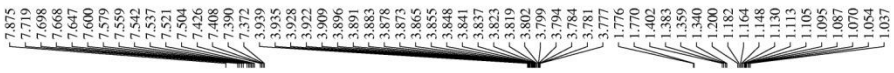

61.73
61.68

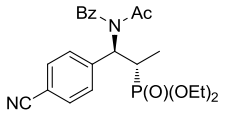

34.56
33.18
27.43
16.10
16.04
15.99
15.93
12.65
12.59


Bz
N
Ac
Br
P(O)(OEt)2

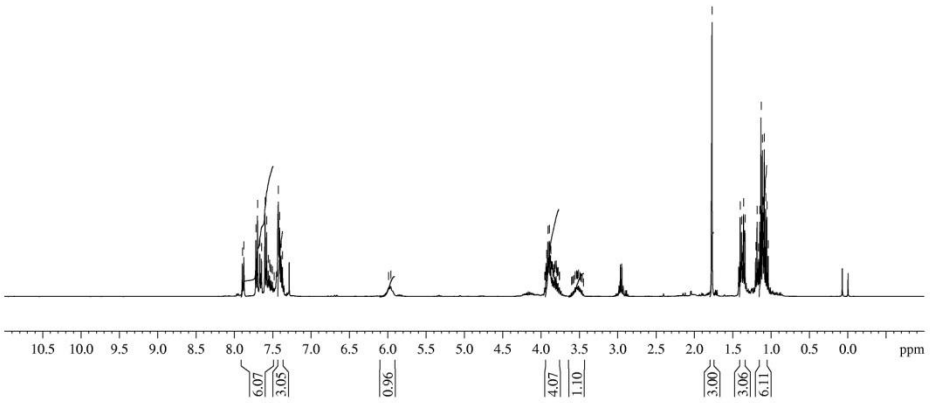
3k

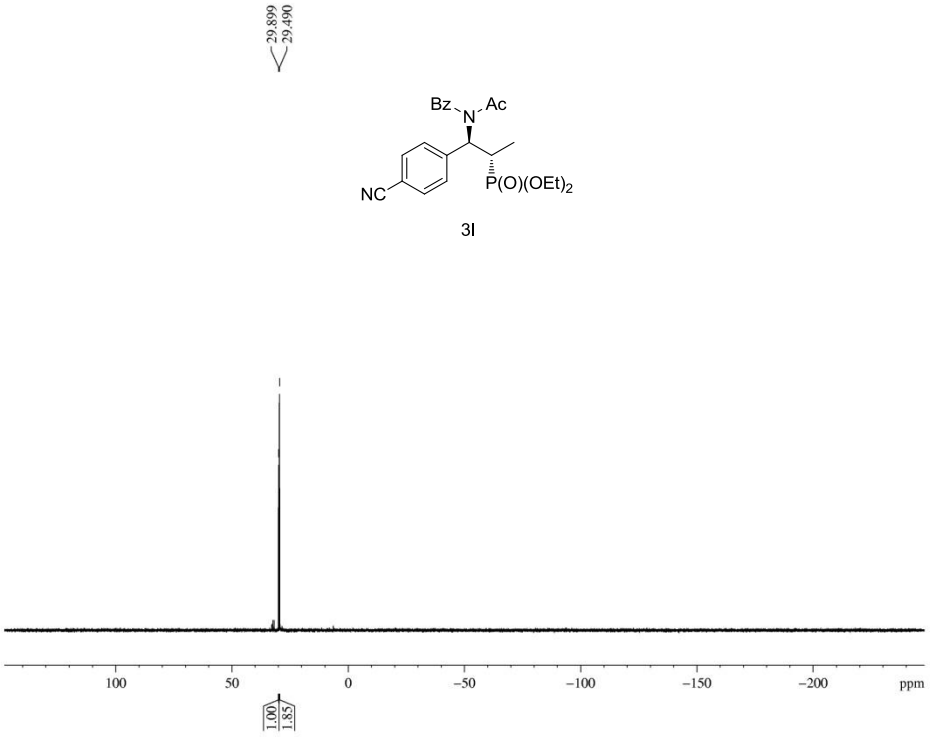

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

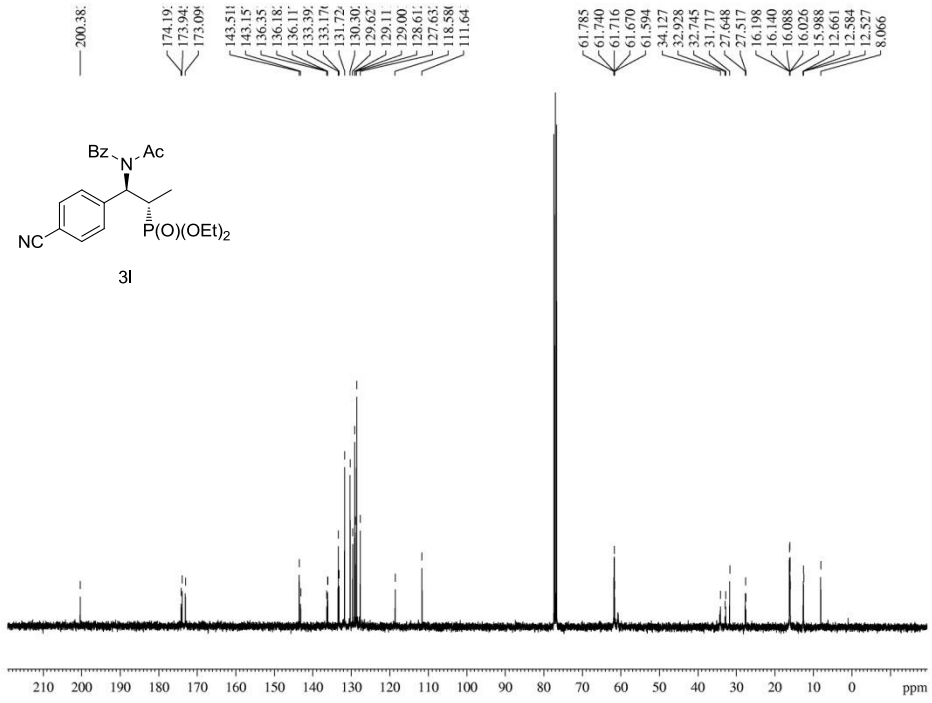

7.875
7.719
7.698
7.668
7.647
7.600
7.579
7.559
7.542
7.537
7.521
7.504
7.426
7.408
7.390
7.372
3.939
3.935
3.928
3.922
3.909
3.896
3.891
3.883
3.878
3.873
3.865
3.855
3.848
3.841
3.837
3.823
3.819
3.802
3.799
3.794
3.784
3.781
3.777
1.776
1.770
1.402
1.383
1.359
1.340
1.200
1.182
1.164
1.148
1.130
1.113
1.105
1.095
1.087
1.070
1.054
1.037


Bz
N
Ac
NC
P(O)(OEt)2

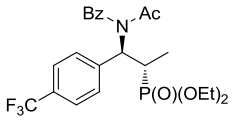
3l


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.07
3.05
0.96
4.07
1.10
3.00
3.06
6.11

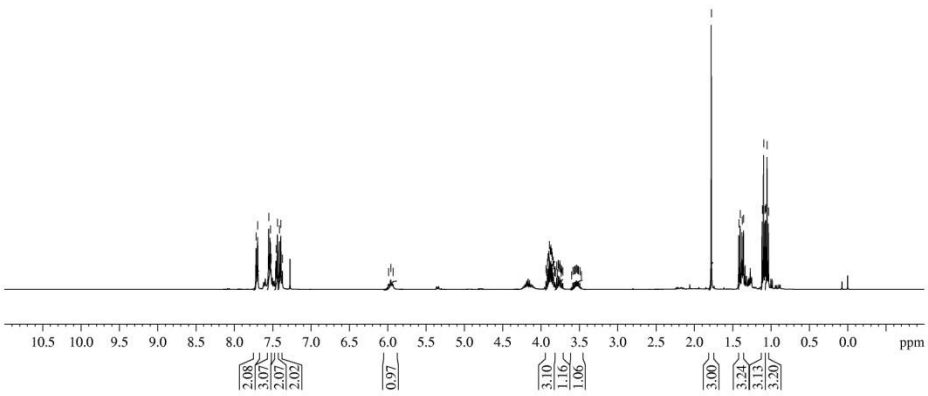

29.899
29.490
Bz
N
Ac
NC
P(O)(OEt)2
3l
100
50
0
−50
−100
−150
−200
ppm
1.00
1.85

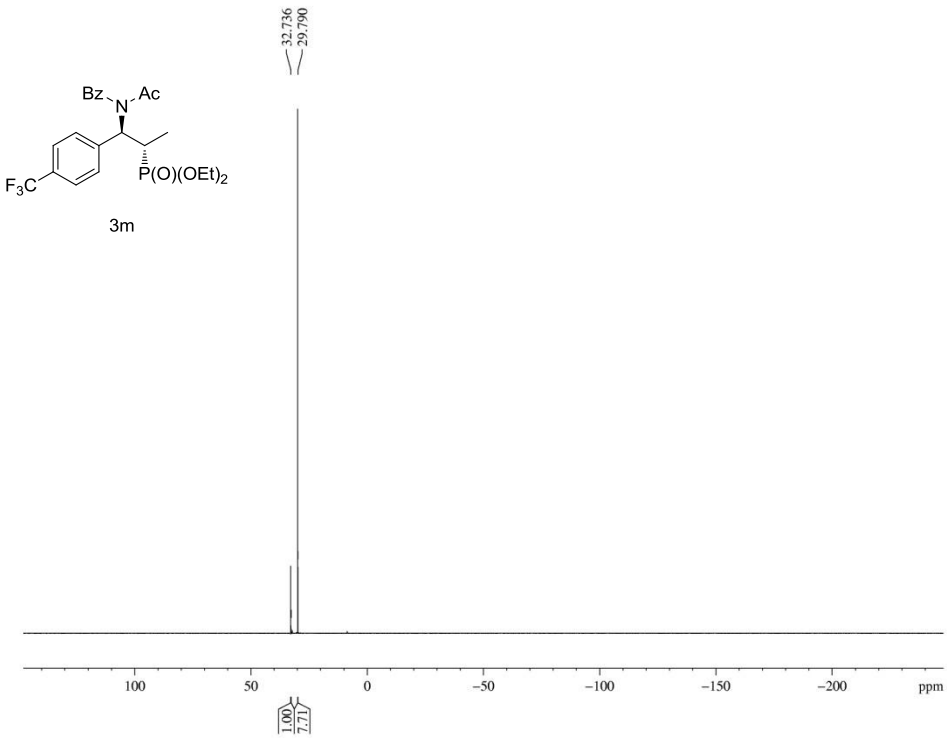

200.38
174.19
173.94
173.09
143.51
143.15
136.35
136.18
136.11
133.39
133.17
131.72
130.30
129.62
129.11
129.00
128.61
127.63
118.58
111.64
61.785
61.740
61.716
61.670
61.594
34.127
32.928
32.745
31.717
27.648
27.517
16.198
16.140
16.088
16.026
15.988
12.661
12.584
12.527
8.066
Bz
N
Ac
NC
P(O)(OEt)2
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.695
7.551
7.538
7.531
7.520
7.457
7.439
7.412
7.394
7.374
5.988
5.960
5.933
3.935
3.927
3.917
3.915
3.910
3.897
3.892
3.880
3.874
3.872
3.861
3.854
3.843
3.836
3.826
3.818
3.796
3.778
3.775
3.771
3.757
3.753
3.750
3.732
3.716
3.583
3.566
3.554
3.539
3.537
3.522
3.510
3.493
1.779
1.420
1.402
1.377
1.359
1.115
1.098
1.080
1.070
1.052
1.034

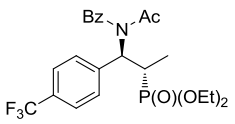

Bz
N
Ac
F3C
P(O)(OEt)2

3m


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.08
3.07
2.07
2.02
0.97
3.10
1.16
1.06
3.00
3.24
3.13
3.20


32.736
29.790
Bz
N
Ac
F3C
P(O)(OEt)2
100 50 0 −50 −100 −150 −200 ppm
1.00
7.71

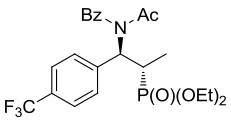
3m


Bz
N
Ac
F3C
P(O)(OEt)2

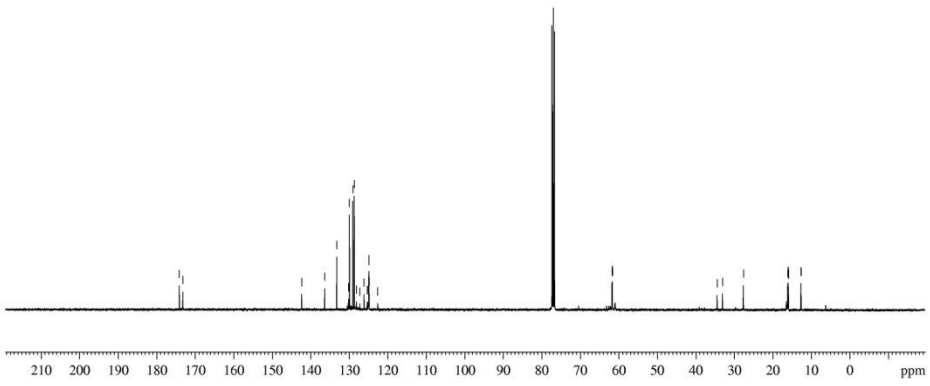
3m

-62.4
-62.6
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
7.60


174.14
173.21
142.37
136.37
133.24
130.21
129.95
129.06
128.68
128.14
127.26
126.17
125.32
125.05
125.01
124.94
124.90
124.86
124.83
122.62
61.760
61.715
61.690
61.645
34.459
33.076
27.627
16.106
16.047
15.973
15.910
12.684
12.627


Bz
N
Ac
F3C
P(O)(OEt)2

3m


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


7.696
7.545
7.525
7.489
7.487
7.471
7.468
7.422
7.404
7.366
7.348
7.328
5.950
3.910
3.903
3.893
3.885
3.877
3.867
3.859
3.850
3.841
3.822
3.804
3.802
3.797
3.785
3.779
3.777
3.773
3.767
3.760
3.747
3.743
3.730
3.725
3.722
3.708
3.704
3.700
3.683
3.577
3.562
3.559
3.545
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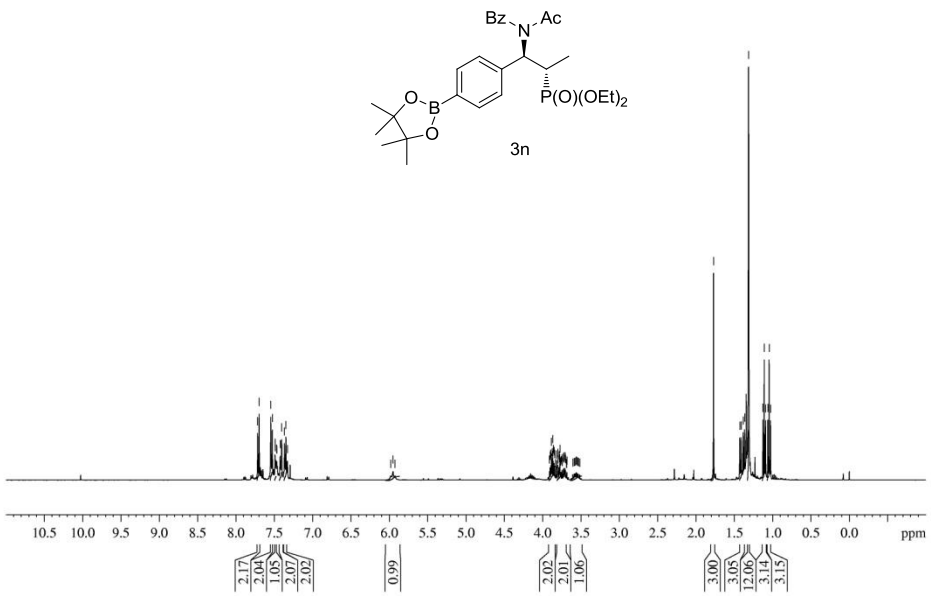
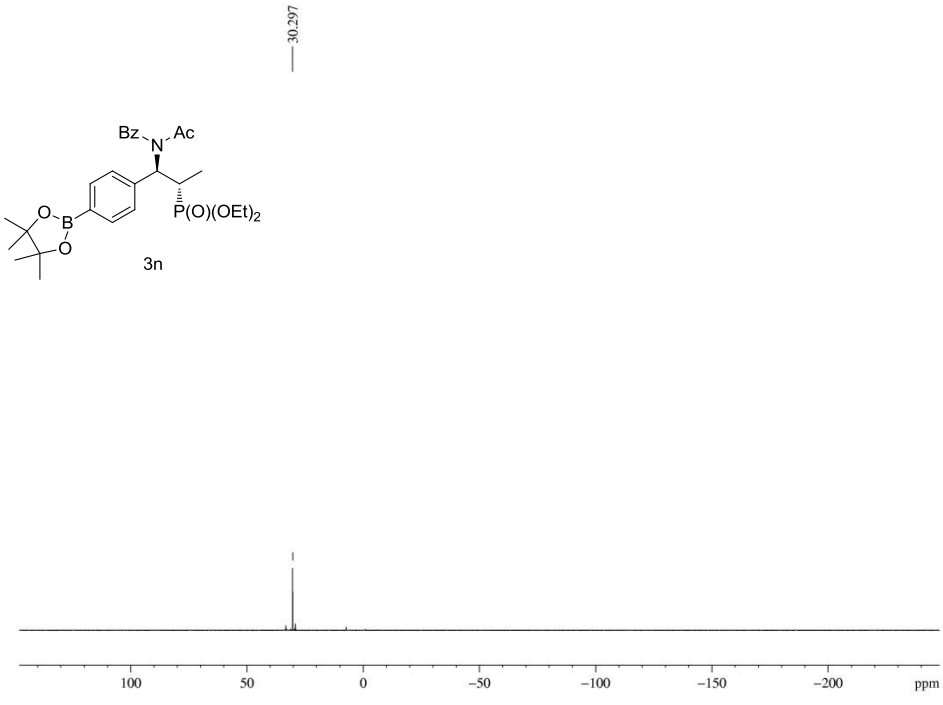
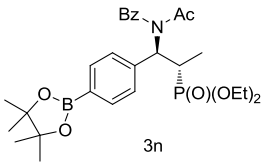
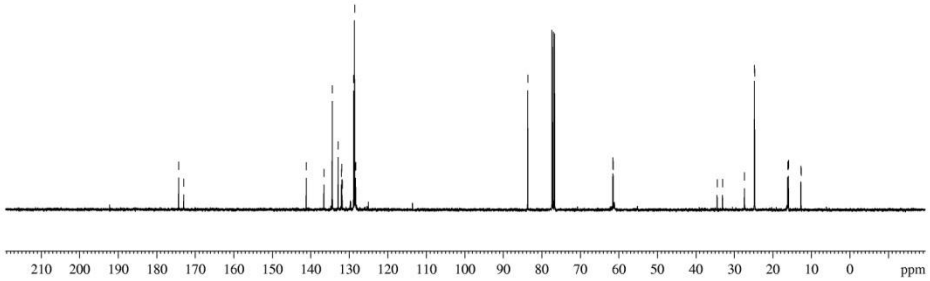
1.126
1.108
1.091
1.062
1.044
1.027

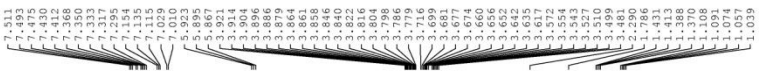

Bz
N
Ac
O
B
O
P(O)(OEt)2
3n
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.17
2.04
1.05
2.07
2.02
0.99
2.02
2.01
1.06
3.00
3.05
12.06
3.14
3.15

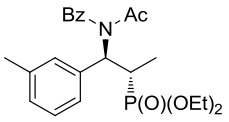

30.297
Bz
N
Ac
O
B
O
P(O)(OEt)2
3n
100 50 0 −50 −100 −150 −200 ppm



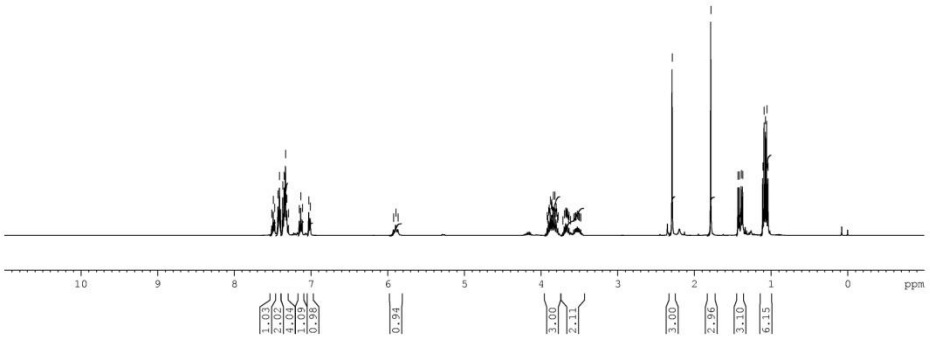
3n

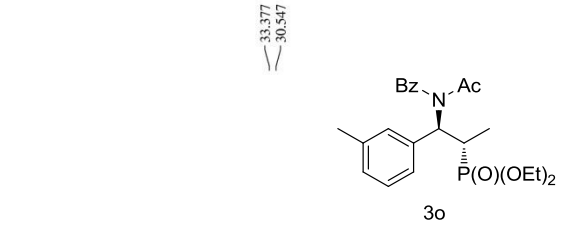




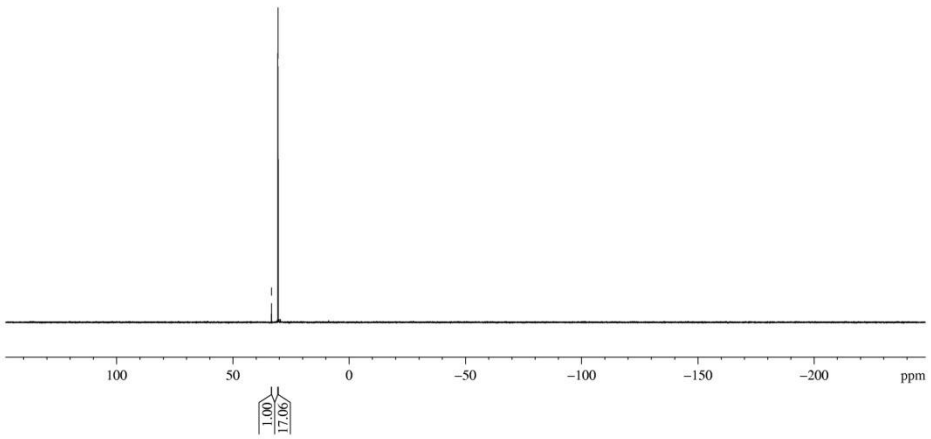


3o

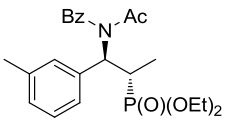



33.377
30.547
Bz
N
Ac
P(O)(OEt)2

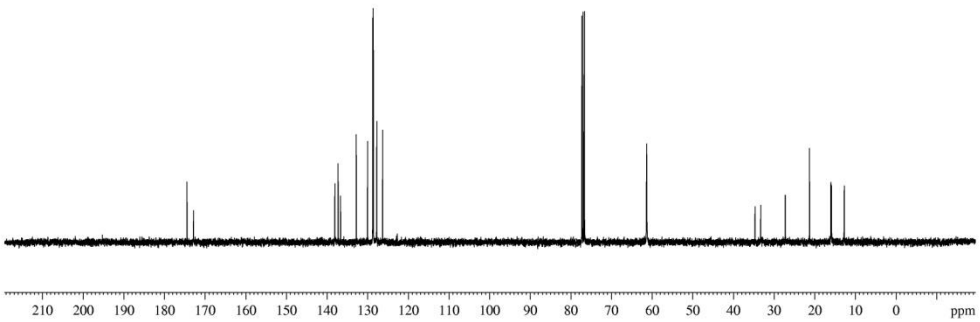
3o


100
50
0
−50
−100
−150
−200
ppm
1.00
17.06


174.49
172.88
138.12
137.30
136.70
132.83
130.06
128.79
128.64
128.61
127.79
126.34
61.46
61.40
61.33
34.69
33.31
27.27
21.31
16.08
16.02
15.94
15.87
12.78
12.73


Bz
N
Ac
P(O)(OEt)2

3o


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


7.549
7.531
7.513
7.467
7.449
7.433
7.429
7.410
7.391
7.371
7.304
7.229
7.224
7.215
7.213
7.205
7.199
5.883
3.946
3.928
3.921
3.904
3.899
3.889
3.886
3.881
3.872
3.864
3.854
3.847
3.829
3.803
3.785
3.782
3.778
3.764
3.760
3.757
3.739
3.536
3.519
3.507
3.492
3.475
3.463
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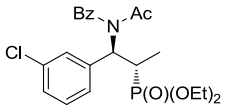
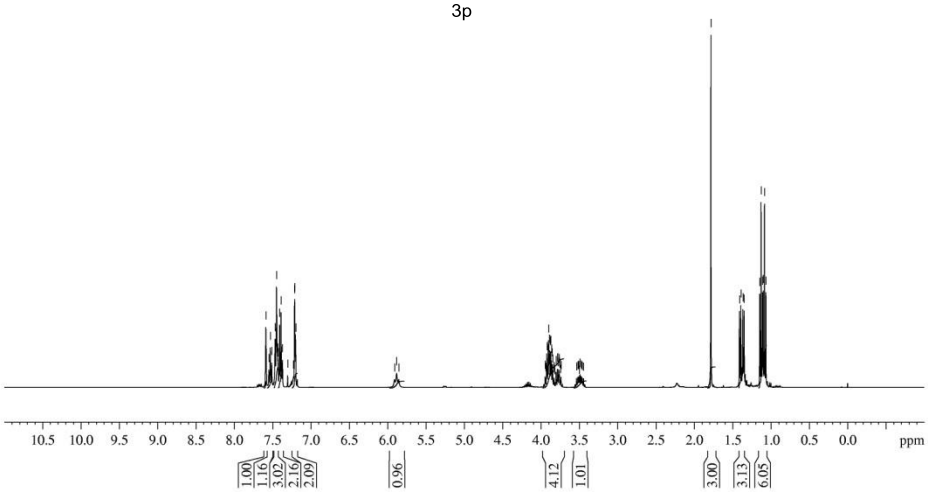
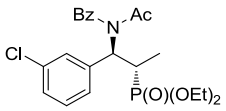
1.393
1.367
1.350
1.146
1.128
1.111
1.101
1.084
1.066


Bz
N
Ac
Cl
P(O)(OEt)2

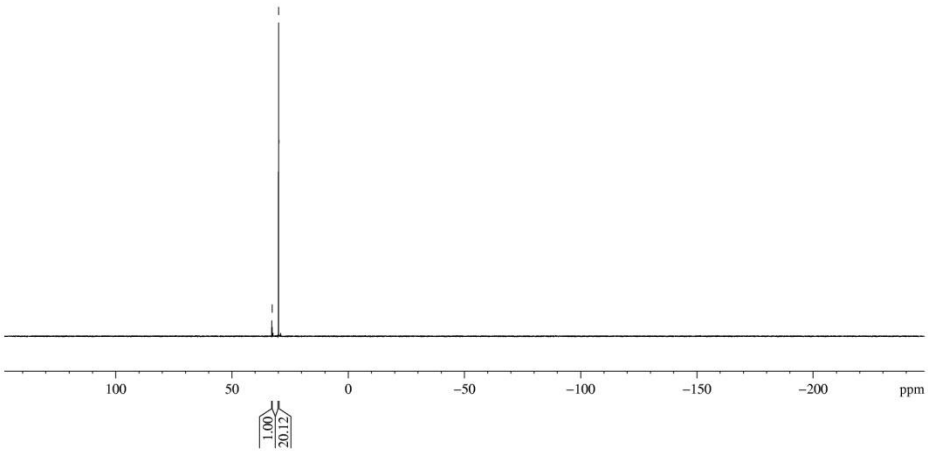
3p

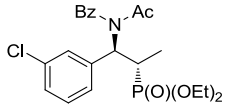

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.16
3.02
2.16
2.09
0.96
4.12
1.01
3.00
3.13
6.05


32.737
29.886

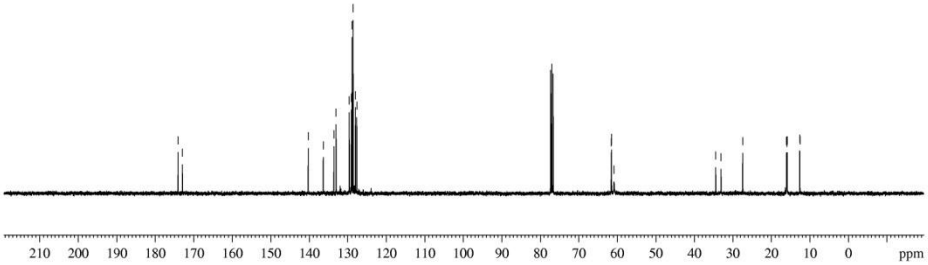

Bz
N
Ac
Cl
P(O)(OEt)2

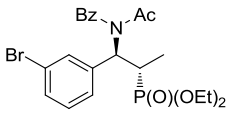
3p


100 50 0 −50 −100 −150 −200 ppm
1.00
20.12

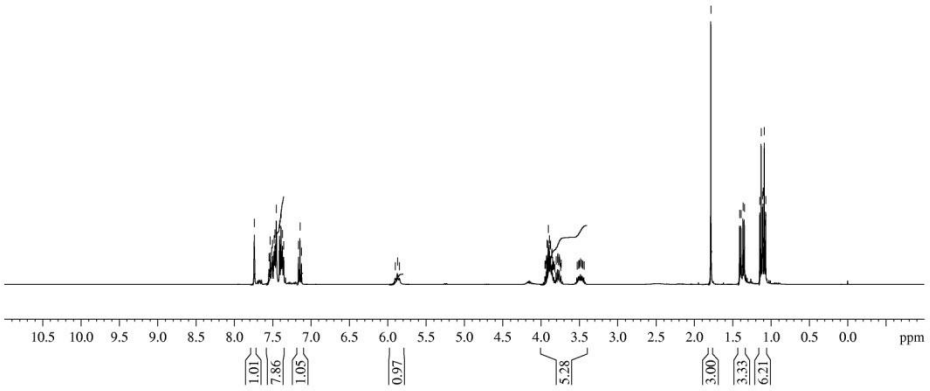

Bz
N
Ac
Cl
P(O)(OEt)2

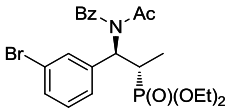
3p


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


Bz
N
Ac
Br
P(O)(OEt)2

3q


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
7.86
1.05
0.97
5.28
3.00
3.33
6.21


Bz
N
Ac
Br
P(O)(OEt)2

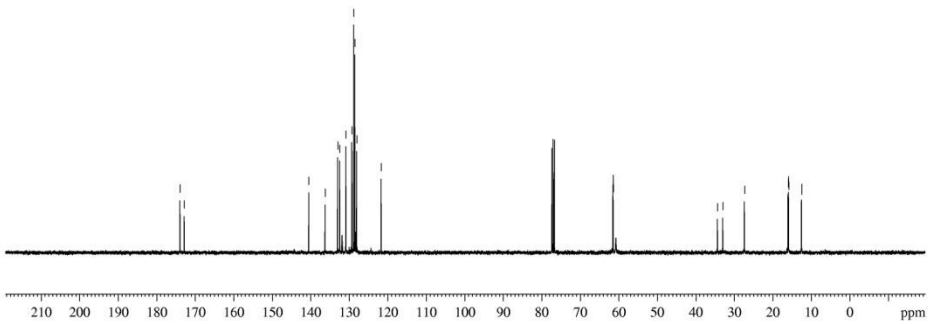
3q

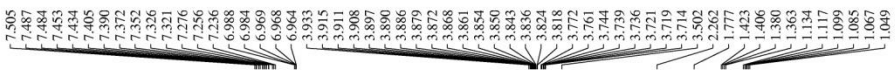
32.653
29.873
100
50
0
−50
−100
−150
−200
ppm

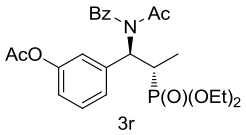

173.95
172.86
140.48
136.26
132.99
132.45
130.87
129.34
128.85
128.54
128.04
121.69
61.538
61.493
61.470
61.424
34.351
32.968
27.357
16.014
15.955
15.900
15.836
12.536
12.480

Bz
N
Ac
Br
P(O)(OEt)2

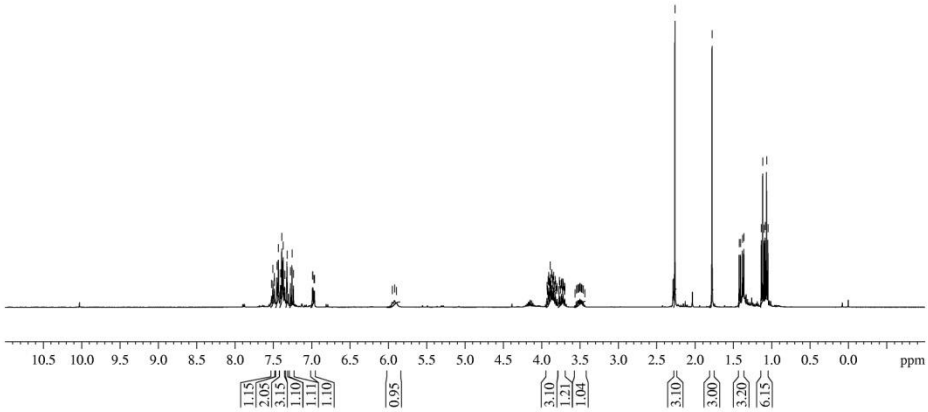
3q


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

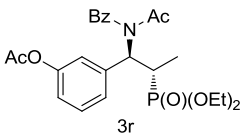

7.505
7.487
7.484
7.453
7.434
7.405
7.390
7.372
7.352
7.326
7.321
7.276
7.256
7.236
6.988
6.984
6.969
6.968
6.964
3.933
3.915
3.911
3.908
3.897
3.890
3.886
3.879
3.872
3.868
3.861
3.854
3.850
3.843
3.836
3.824
3.818
3.772
3.761
3.744
3.739
3.736
3.721
3.719
3.714
3.502
2.262
1.777
1.423
1.406
1.380
1.363
1.134
1.117
1.099
1.085
1.067
1.049


Bz
N
Ac
AcO
P(O)(OEt)2

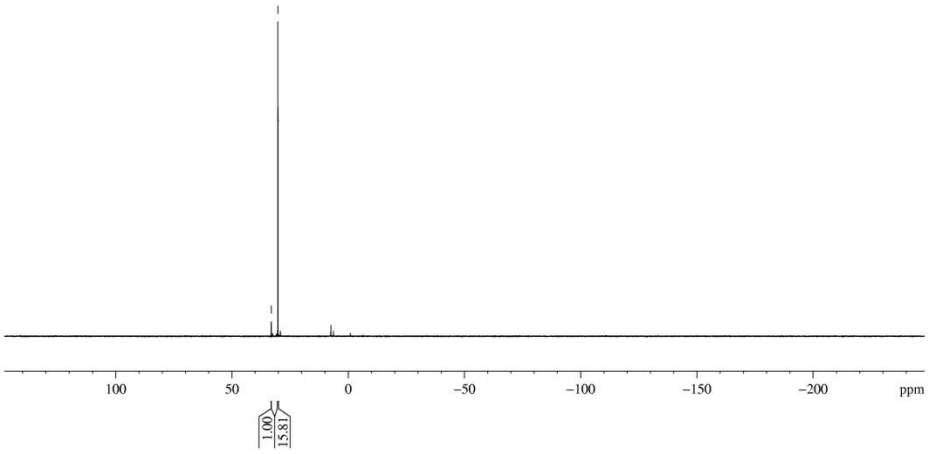
3r


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.15
2.05
3.15
1.10
1.11
1.10
0.95
3.10
1.21
1.04
3.10
3.00
3.20
6.15

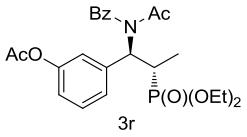

33.002
30.164


Bz
N
Ac
AcO
P(O)(OEt)2

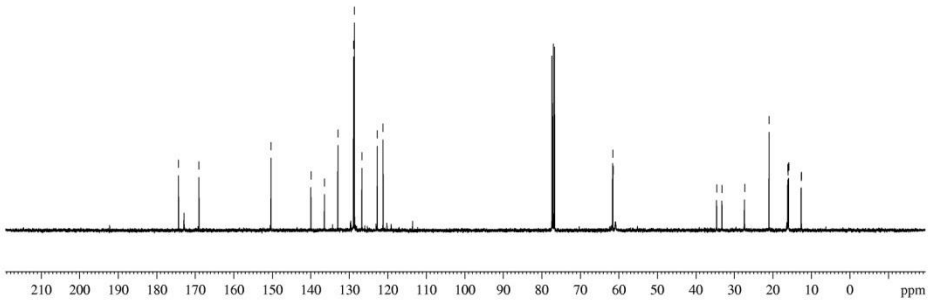
3r

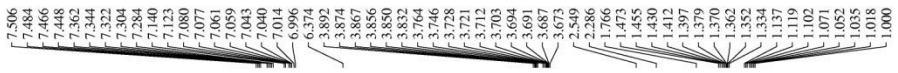

100 50 0 −50 −100 −150 −200 ppm
1.00
15.81

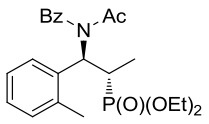

174.36
169.05
150.32
139.95
136.44
132.96
128.88
128.66
128.64
126.71
122.71
121.23
61.629
61.569
61.505
34.578
33.196
27.343
20.965
16.105
16.049
15.942
15.878
12.631
12.575


Bz
N
Ac
AcO
P(O)(OEt)2

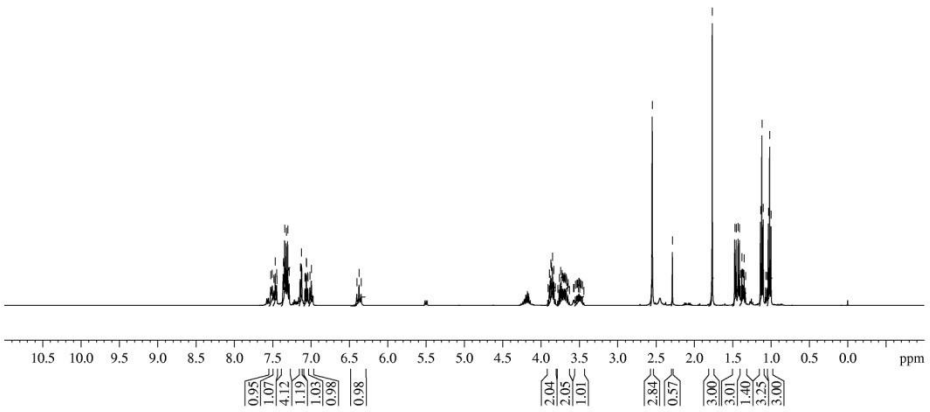
3r

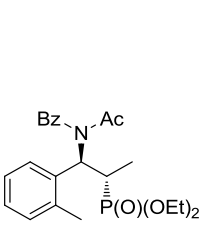

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.506
7.484
7.466
7.448
7.362
7.344
7.322
7.304
7.284
7.140
7.123
7.080
7.077
7.061
7.059
7.043
7.040
7.014
6.996
6.374
3.892
3.874
3.867
3.856
3.850
3.832
3.764
3.746
3.728
3.721
3.712
3.703
3.694
3.691
3.687
3.673
2.549
2.286
1.766
1.473
1.455
1.430
1.412
1.397
1.379
1.370
1.362
1.352
1.334
1.137
1.119
1.102
1.071
1.052
1.035
1.018
1.000


Bz
N
Ac
P(O)(OEt)2

3s

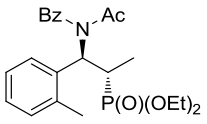

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
1.07
4.12
1.19
1.03
0.98
0.98
2.04
2.05
1.01
2.84
0.57
3.00
3.01
1.40
3.25
3.00


Bz
N
Ac
P(O)(OEt)2

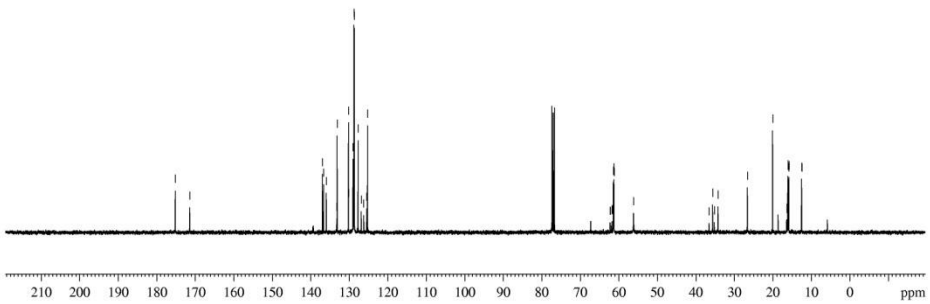
3s

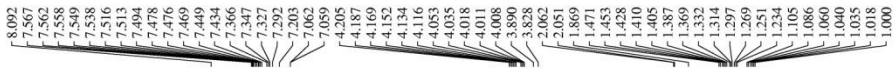
33.682
30.717
100
50
0
−50
−100
−150
−200
ppm
1.00
5.23

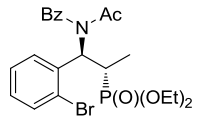

175.19
171.43
136.97
136.63
135.95
133.24
133.13
130.20
130.16
129.03
128.76
128.66
127.69
126.87
126.24
125.44
125.22
62.251
62.182
61.793
61.722
61.402
61.333
61.268
61.199
56.166
36.518
35.583
35.167
34.212
26.566
20.014
16.378
16.322
16.292
16.086
16.028
15.857
15.793
12.505
12.452


Bz
N
Ac
P(O)(OEt)2

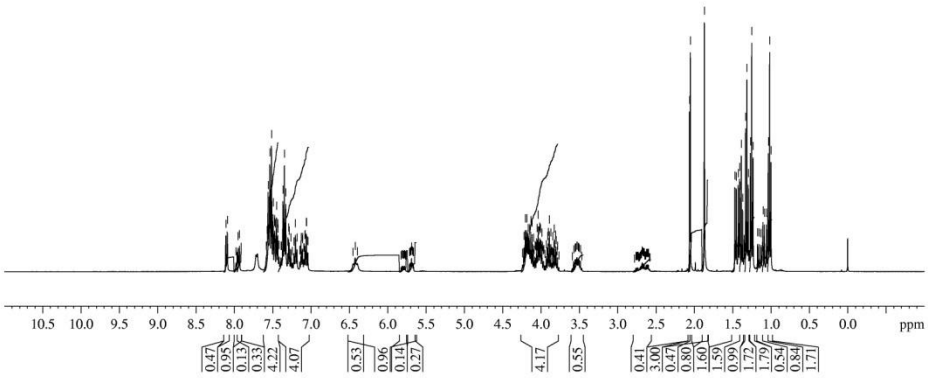
3s

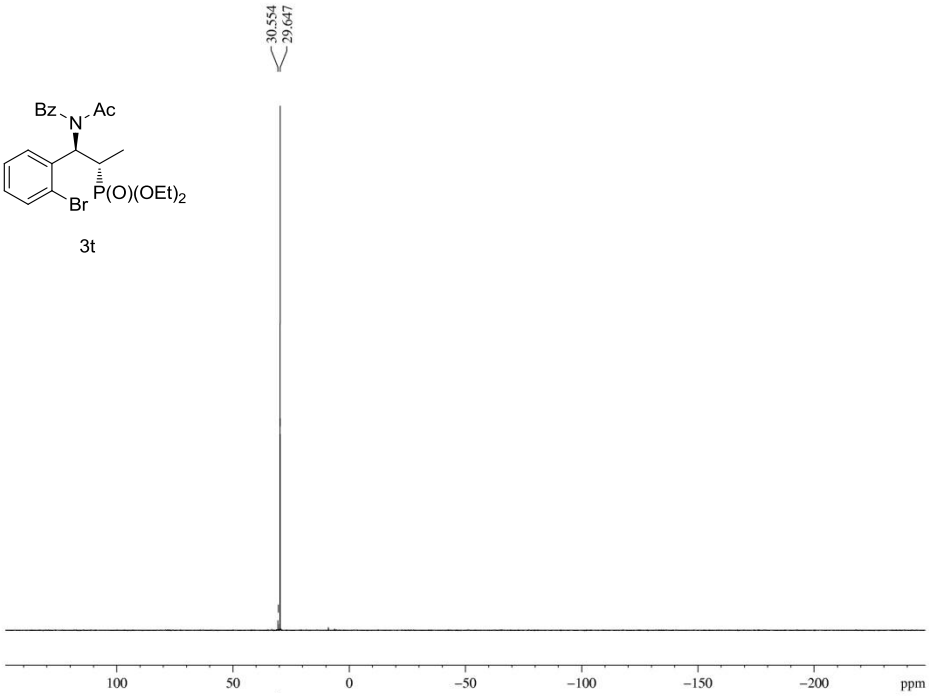

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.092
7.567
7.562
7.558
7.549
7.538
7.516
7.513
7.494
7.478
7.476
7.469
7.449
7.434
7.366
7.347
7.327
7.292
7.203
7.062
7.059
4.205
4.187
4.169
4.152
4.134
4.116
4.053
4.035
4.018
4.011
4.008
3.890
3.828
2.062
2.051
1.869
1.471
1.453
1.428
1.410
1.405
1.387
1.369
1.332
1.314
1.297
1.269
1.251
1.234
1.105
1.086
1.060
1.040
1.035
1.018
1.000

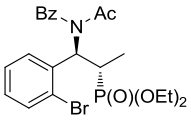

Bz
N
Ac
Br
P(O)(OEt)2

3t

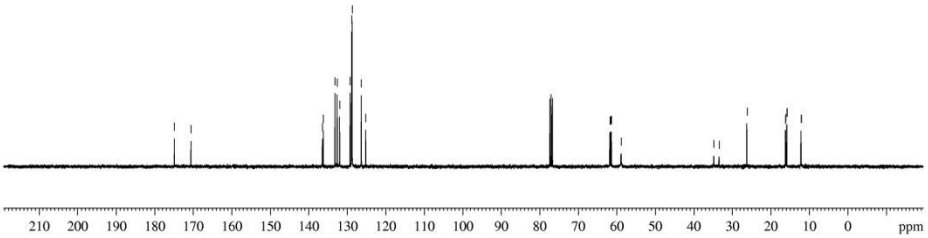

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.47
0.95
0.13
0.33
4.22
4.07
0.53
0.96
0.14
0.27
4.17
0.55
0.41
3.00
0.47
0.80
1.60
1.59
0.99
1.72
1.79
0.54
0.84
1.71

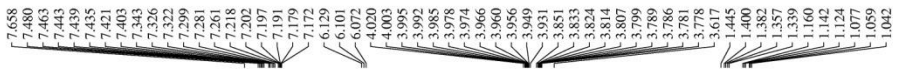

30.554
29.647
Bz
N
Ac
Br
P(O)(OEt)2
100 50 0 −50 −100 −150 −200 ppm

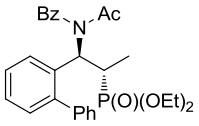
3t



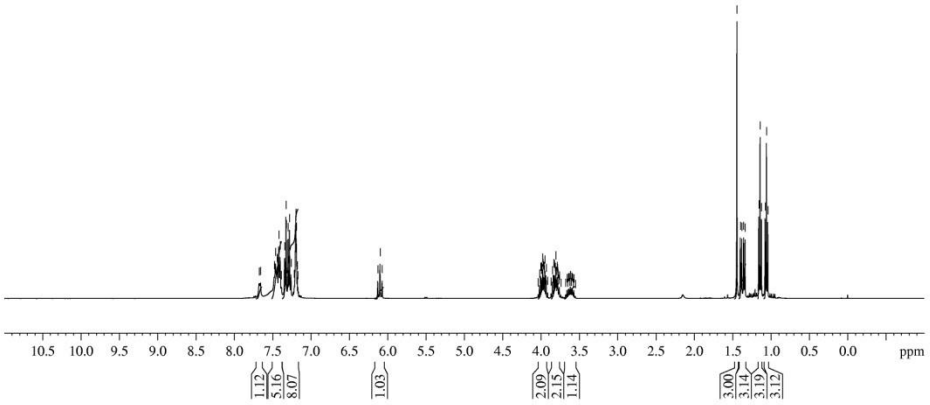
3t

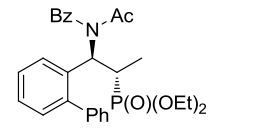






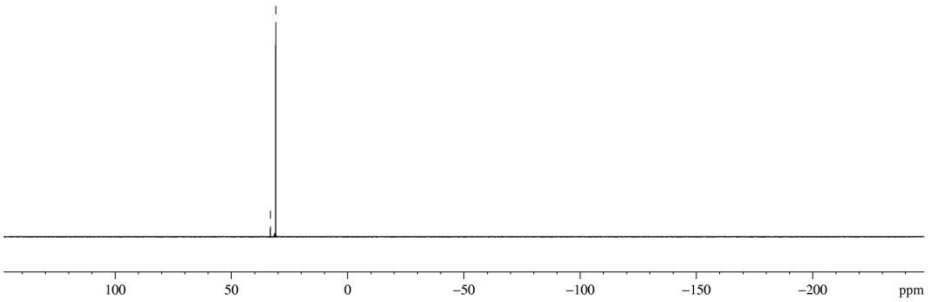
3u

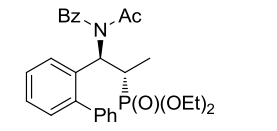



Bz
N
Ac
Ph
P(O)(OEt)2

3u


33.266
30.973


100
50
0
−50
−100
−150
−200
ppm

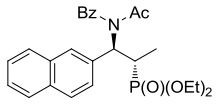

Bz
N
Ac
Ph
P(O)(OEt)2

3u

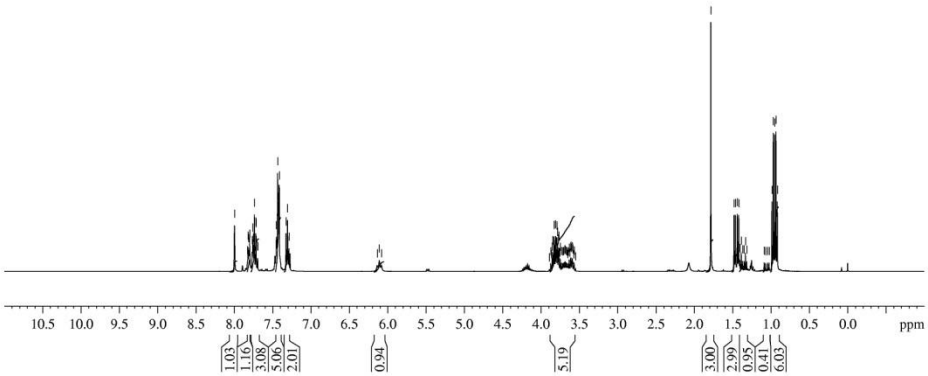

175.05
171.78
142.59
141.02
136.22
134.52
132.61
130.28
129.57
129.42
128.44
128.34
127.69
127.33
126.63
61.564
61.497
61.412
61.342
56.538
56.471
35.139
33.787
24.252
16.110
16.049
15.938
15.874
12.203
12.149

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

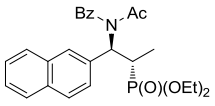

7.821
7.813
7.804
7.798
7.767
7.760
7.752
7.738
7.720
7.716
7.698
7.695
7.451
7.436
7.429
7.419
7.416
7.412
7.325
7.306
7.286
6.109
3.856
3.848
3.838
3.830
3.811
3.802
3.792
3.785
3.774
3.767
3.749
3.689
3.632
3.614
3.610
3.607
3.592
3.589
3.585
1.785
1.482
1.464
1.439
1.421
1.406
1.388
1.370
1.351
1.334
1.316
0.988
0.970
0.953
0.935
0.917


Bz
N
Ac
P(O)(OEt)2

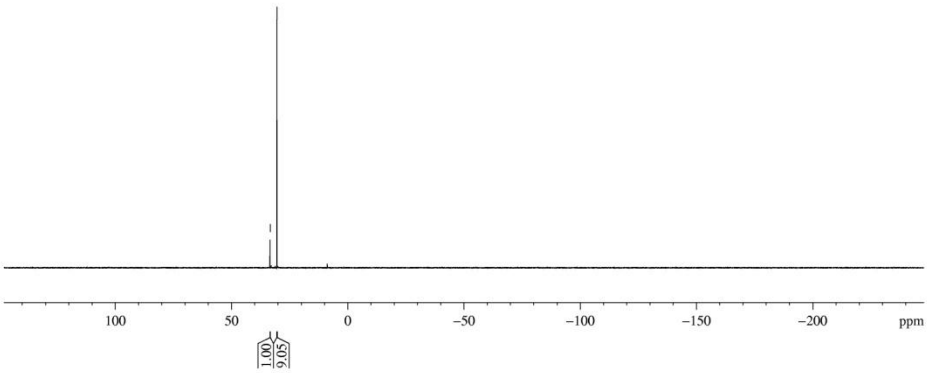
3v

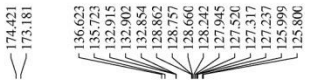

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.03
1.16
3.08
5.06
2.01
0.94
5.19
3.00
2.99
0.95
0.41
6.03

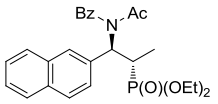

33.340
30.430


Bz
N
Ac
P(O)(OEt)2

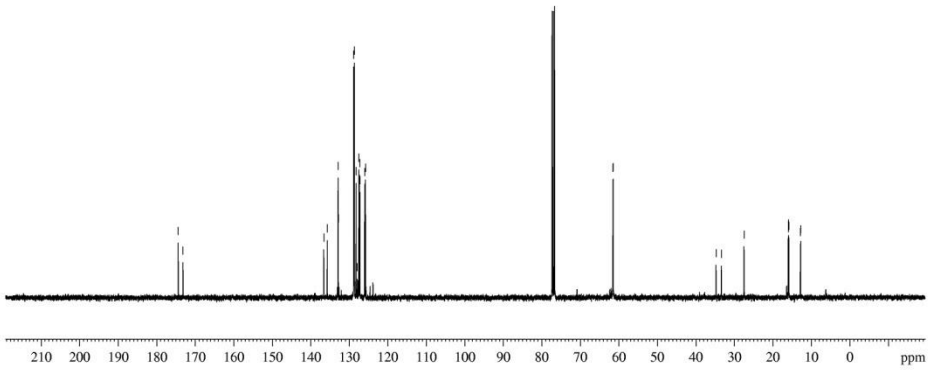
3v

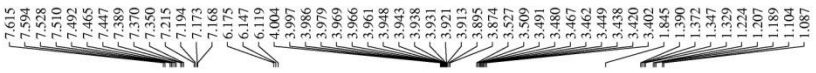

100 50 0 −50 −100 −150 −200 ppm
1.00
9.05

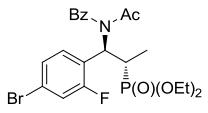

174.421
173.181
136.623
135.723
132.915
132.902
132.854
128.862
128.757
128.660
128.242
127.945
127.520
127.317
127.237
125.999
125.800
61.531
61.462
34.746
33.364
27.471
16.021
15.962
15.906
15.842
12.842
12.786


Bz
N
Ac
P(O)(OEt)2

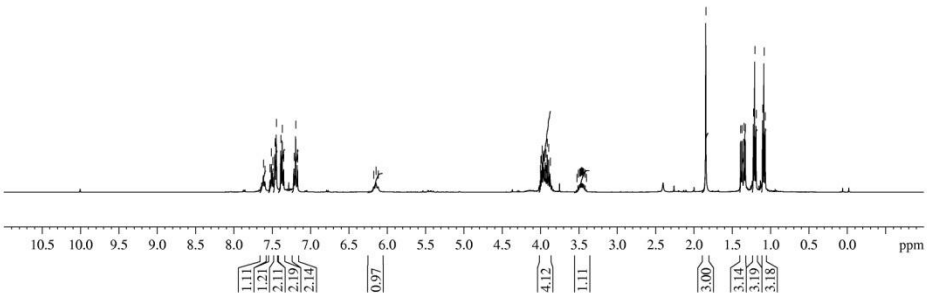
3v

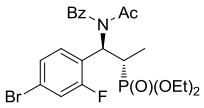

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.615
7.594
7.528
7.510
7.492
7.465
7.447
7.389
7.370
7.350
7.215
7.194
7.173
7.168
6.175
6.147
6.119
4.004
3.997
3.986
3.979
3.969
3.966
3.961
3.948
3.943
3.938
3.931
3.921
3.913
3.895
3.874
3.527
3.509
3.491
3.480
3.467
3.462
3.449
3.438
3.420
3.402
1.845
1.390
1.372
1.347
1.329
1.224
1.207
1.189
1.104
1.087


Bz
N
Ac
Br
F
P(O)(OEt)2

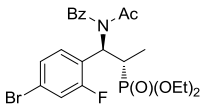
3w


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.11
1.21
2.11
2.19
2.14
0.97
4.12
1.11
3.00
3.14
3.19
3.18


Bz
N
Ac
Br
F
P(O)(OEt)2

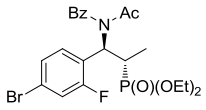
3w

30.381
29.391
100
50
0
−50
−100
−150
−200
ppm
1.00
15.00

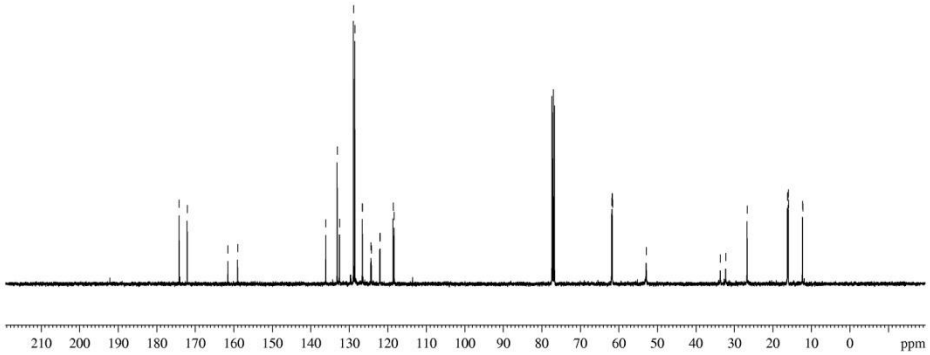

Bz
N
Ac
Br
F
P(O)(OEt)2

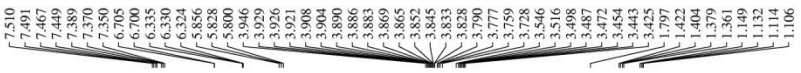
3w

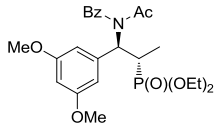
−112.5
−113.2
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm
15.18
1.00



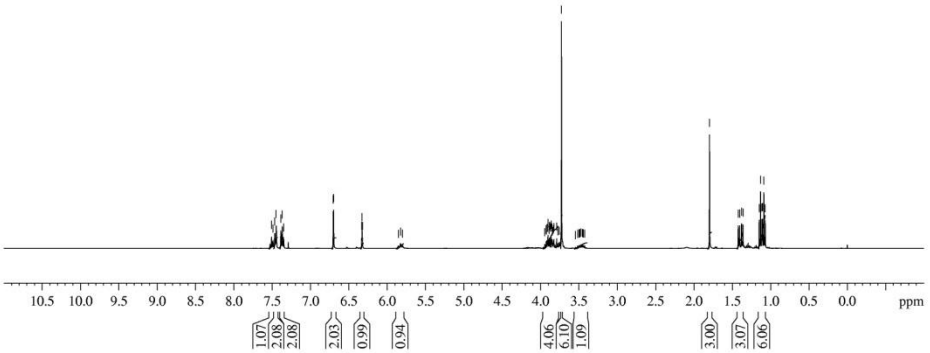
3w

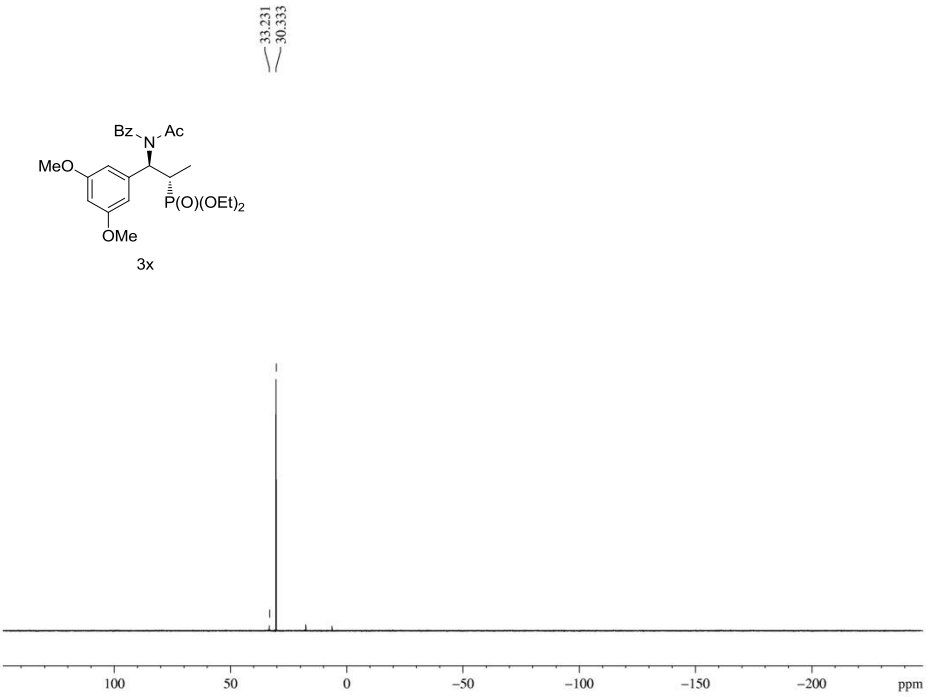


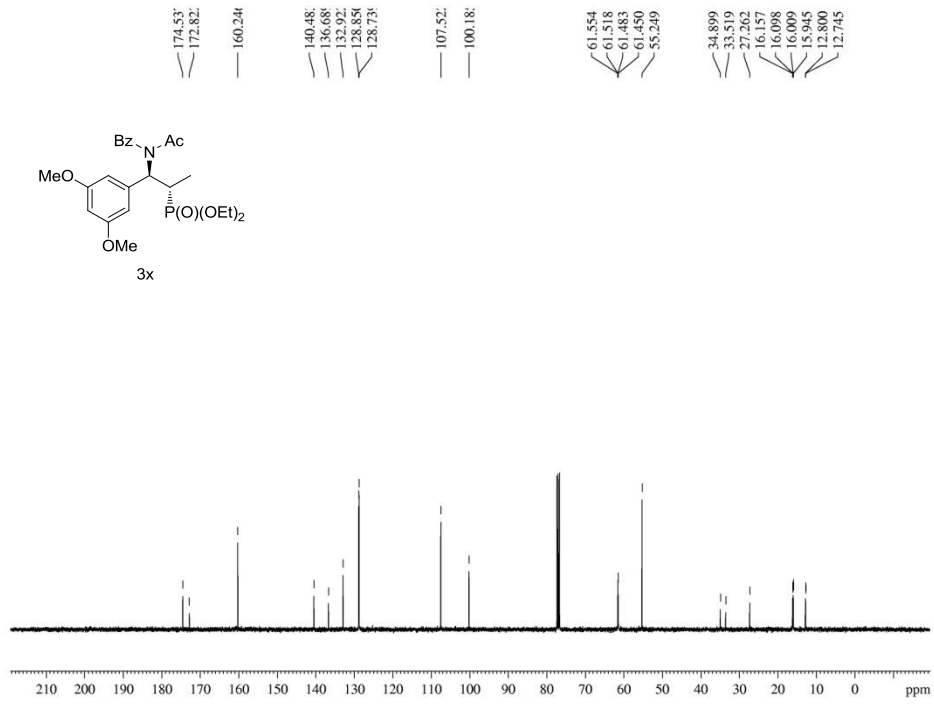




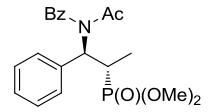
3x



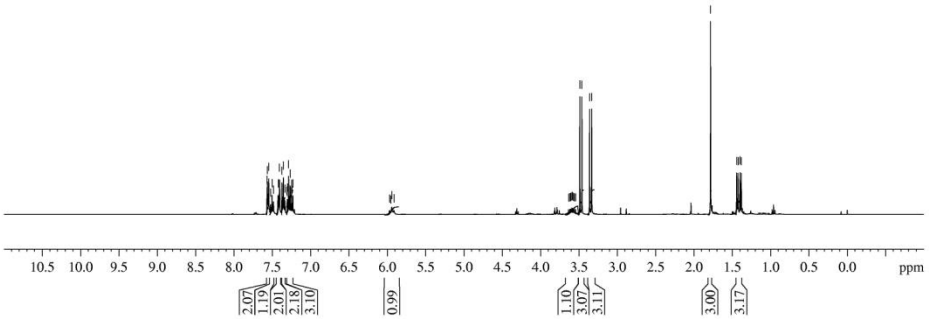

33.231
30.333
Bz
N
Ac
MeO
P(O)(OEt)2
OMe
3x
100
50
0
−50
−100
−150
−200
ppm


174.53
172.82
160.24
140.48
136.68
132.92
128.85
128.73
107.52
100.18
61.554
61.518
61.483
61.450
55.249
34.899
33.519
27.262
16.157
16.098
16.009
15.945
12.800
12.745
Bz
N
Ac
MeO
P(O)(OEt)2
OMe
3x
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

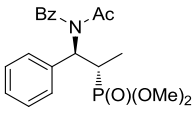

7.568
7.564
7.547
7.522
7.504
7.486
7.424
7.406
7.373
7.355
7.335
7.310
7.307
7.303
7.286
7.282
7.267
7.252
7.248
7.245
7.231
5.969
5.956
5.941
5.913
3.636
3.618
3.606
3.591
3.589
3.574
3.562
3.544
3.488
3.461
3.360
3.334
1.783
1.443
1.425
1.400
1.382


Bz
N
Ac
P(O)(OMe)2

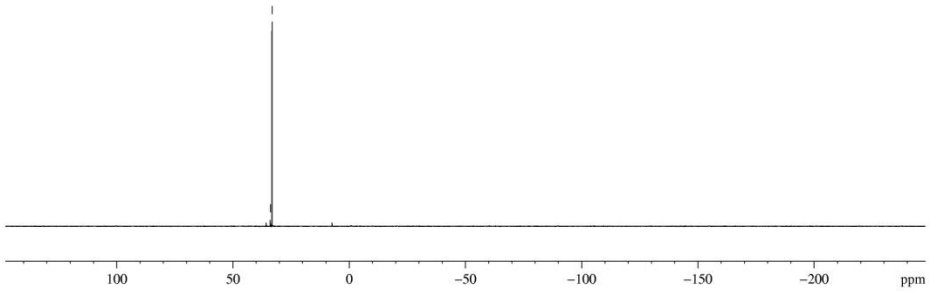
3y

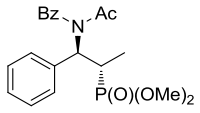

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.07
1.19
2.01
2.18
3.10
0.99
1.10
3.07
3.11
3.00
3.17


33.932
33.147

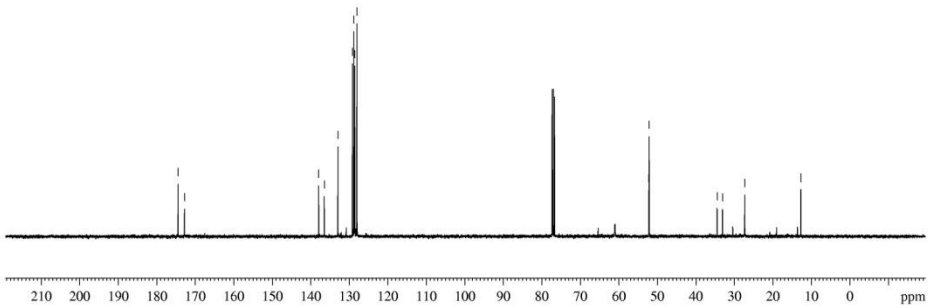

Bz
N
Ac
P(O)(OMe)2

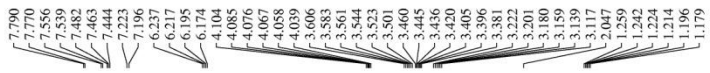
3y

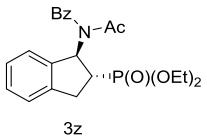

100 50 0 −50 −100 −150 −200 ppm



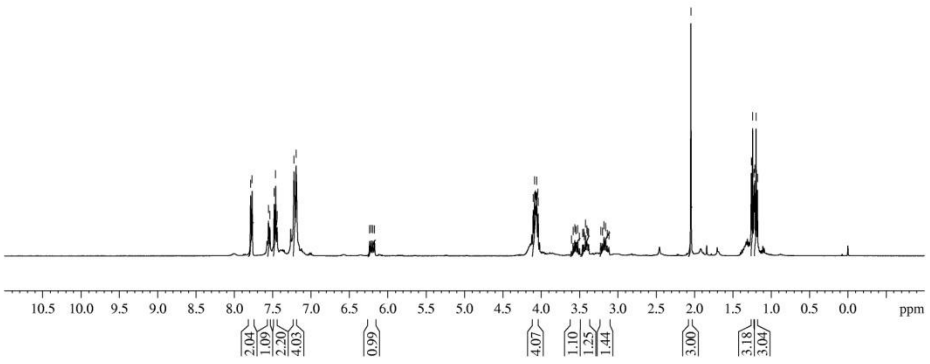
3y

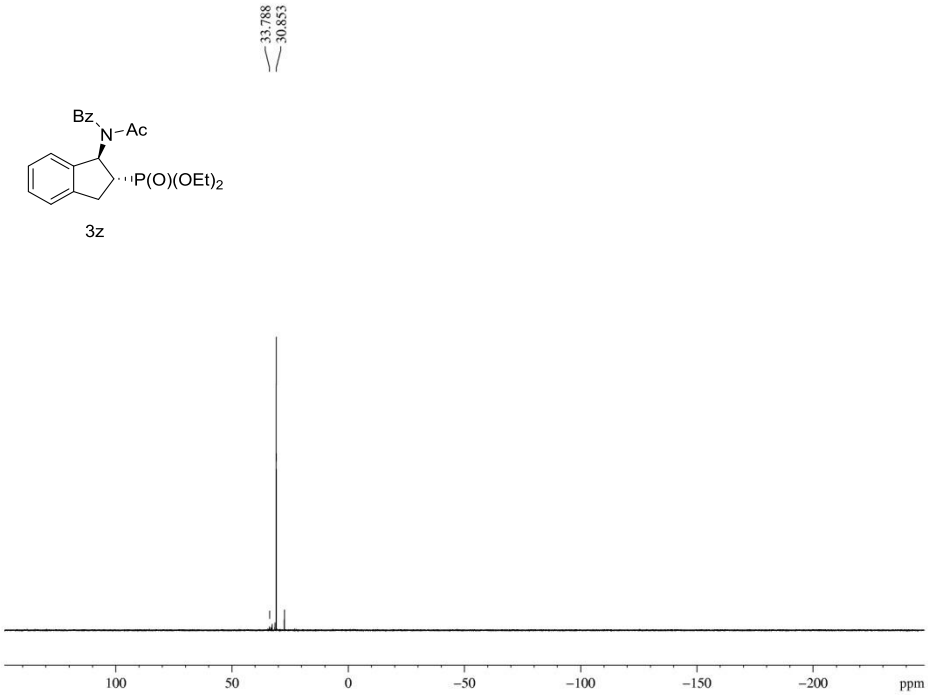


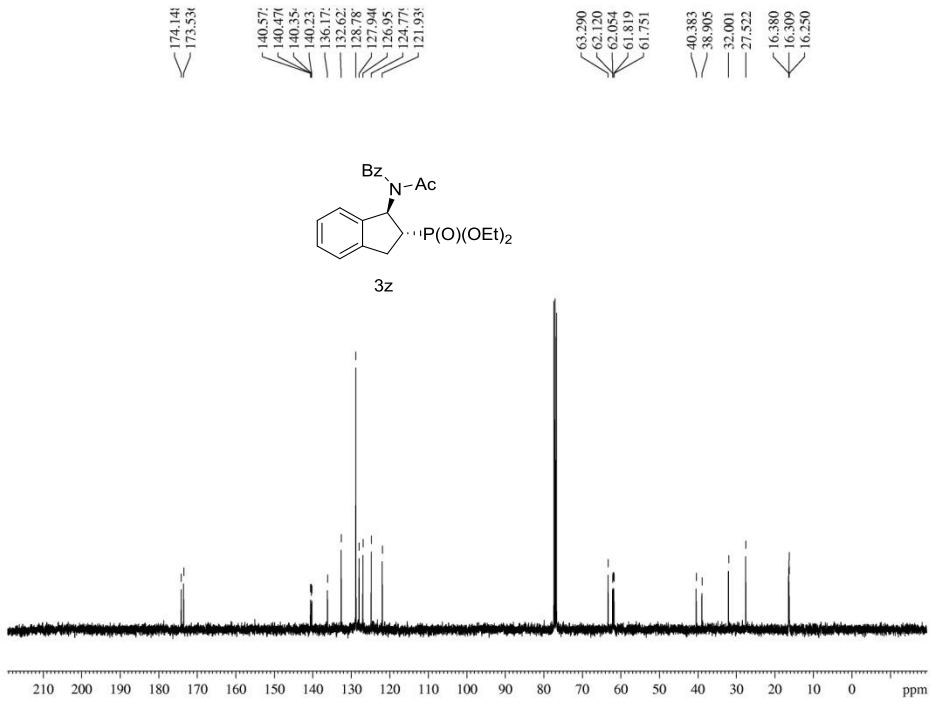


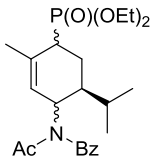


3z

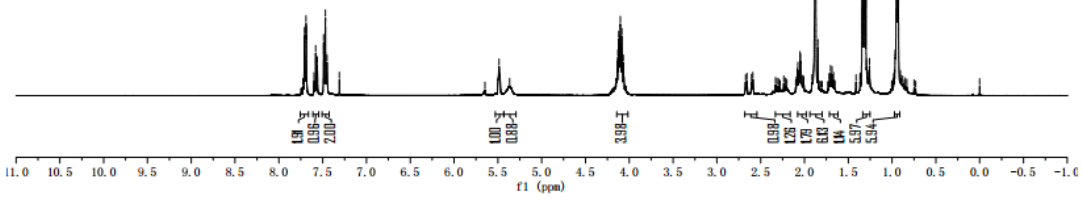


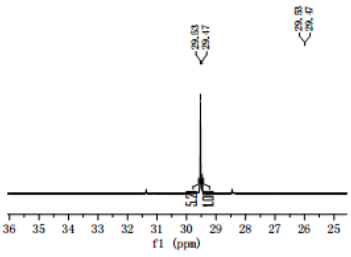

33.788
30.853
Bz
N–Ac
P(O)(OEt)2
3z
100
50
0
−50
−100
−150
−200
ppm

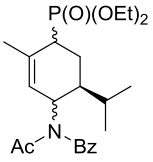

174.148
173.538
140.571
140.478
140.355
140.230
136.172
132.622
128.787
127.944
126.950
124.776
121.938
63.290
62.120
62.054
61.819
61.751
40.383
38.905
32.001
27.522
16.380
16.309
16.250
Bz
N–Ac
P(O)(OEt)2
3z
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



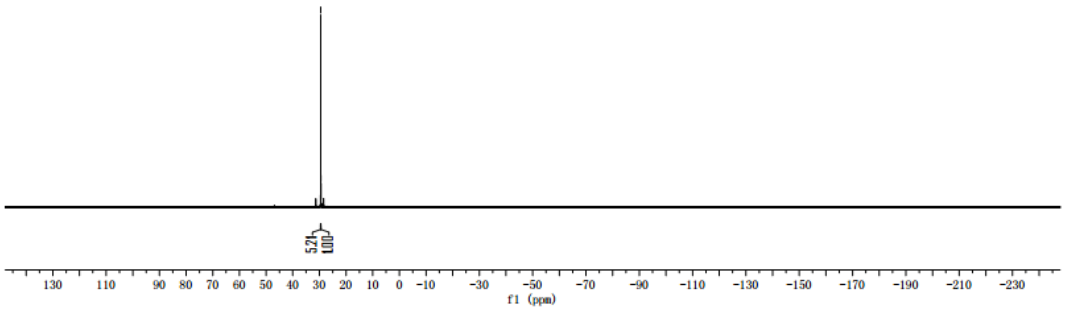
3aa

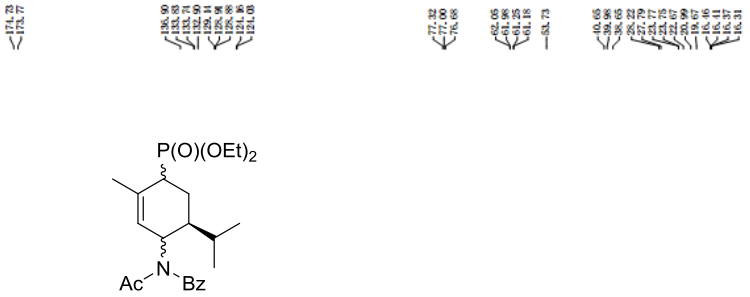




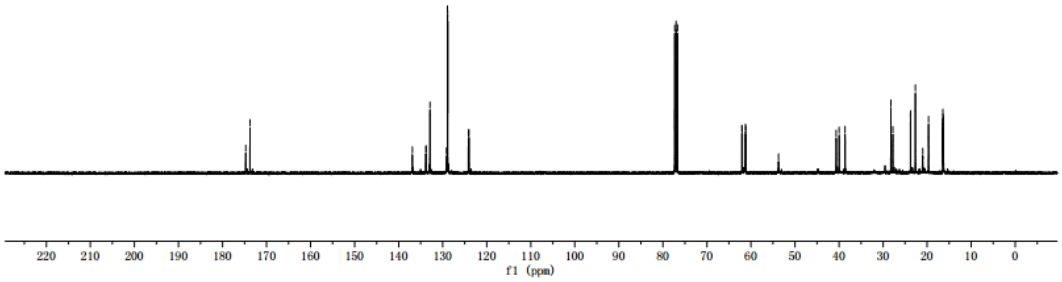


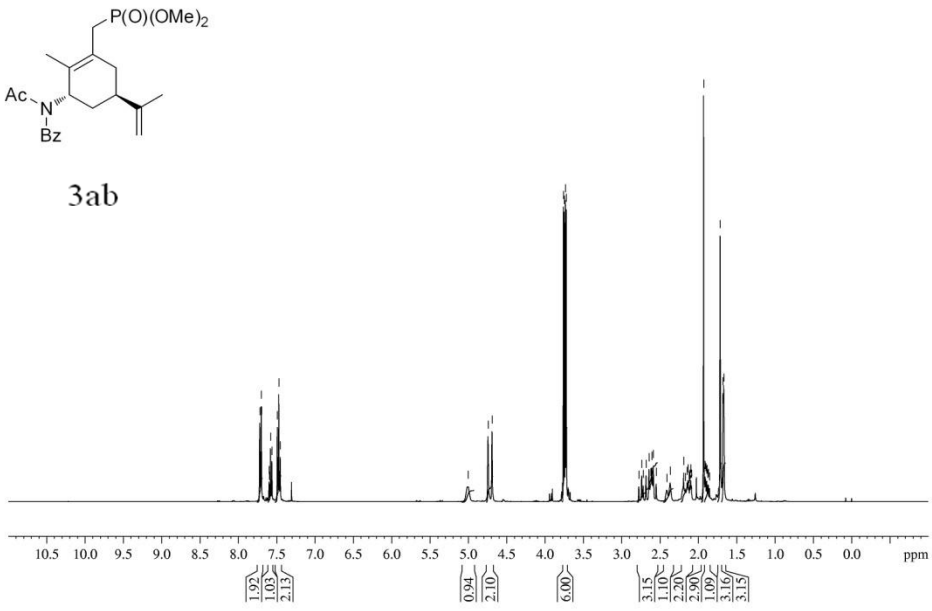
3aa



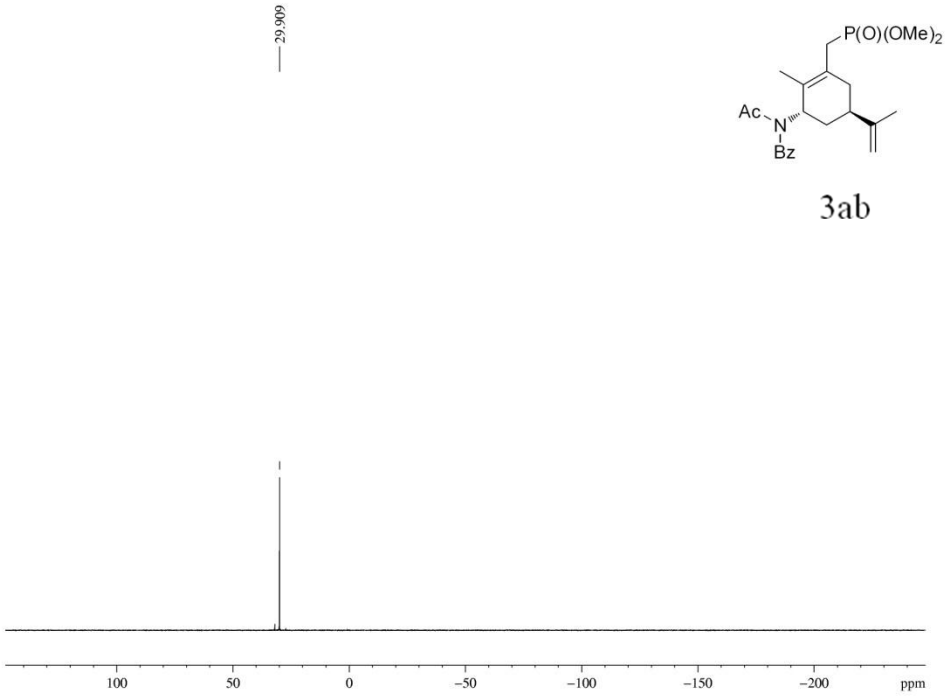


3aa

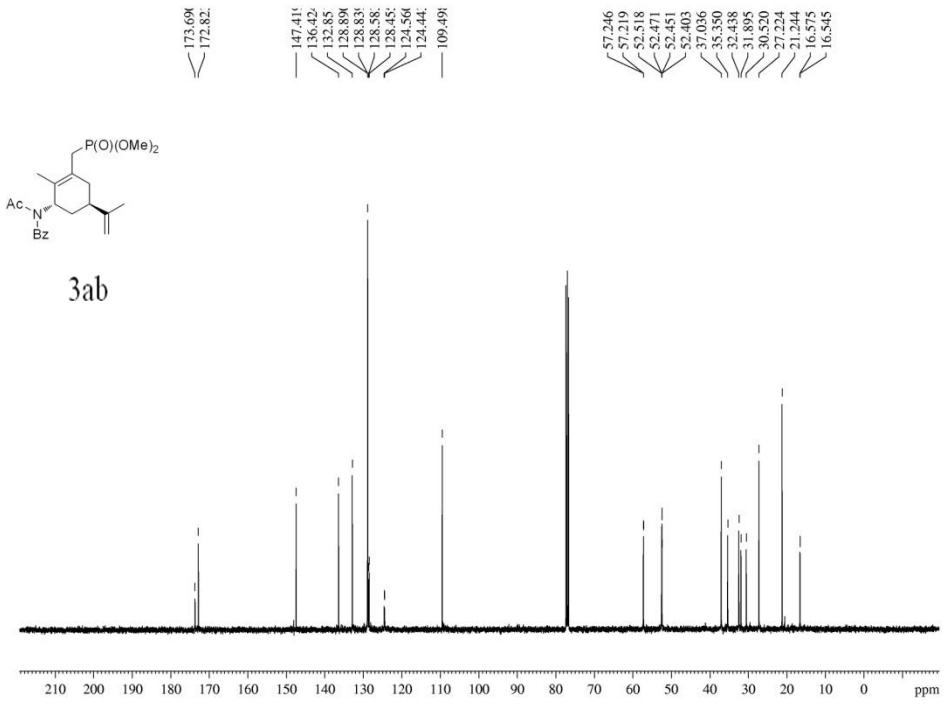




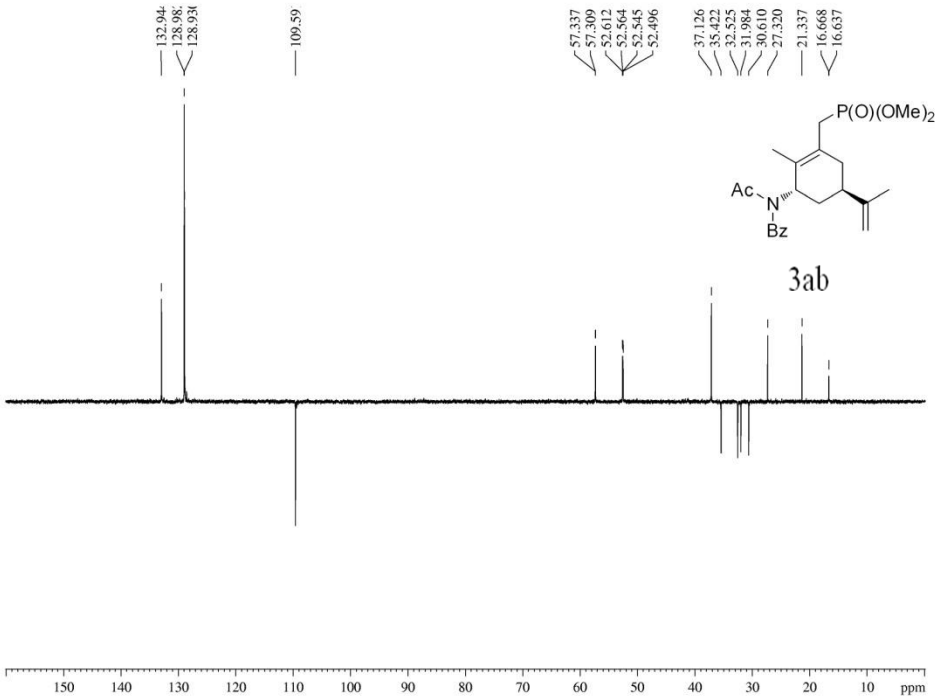
3ab

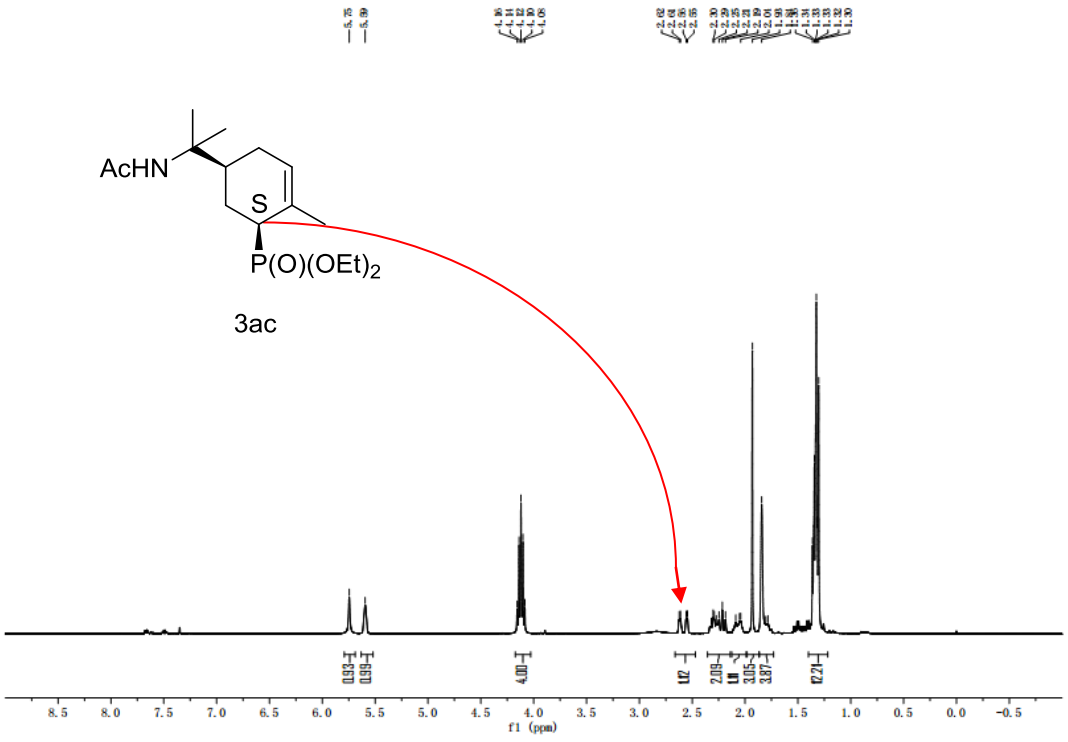

29.909
P(O)(OMe)2
Ac
N
Bz
100
50
0
−50
−100
−150
−200
ppm

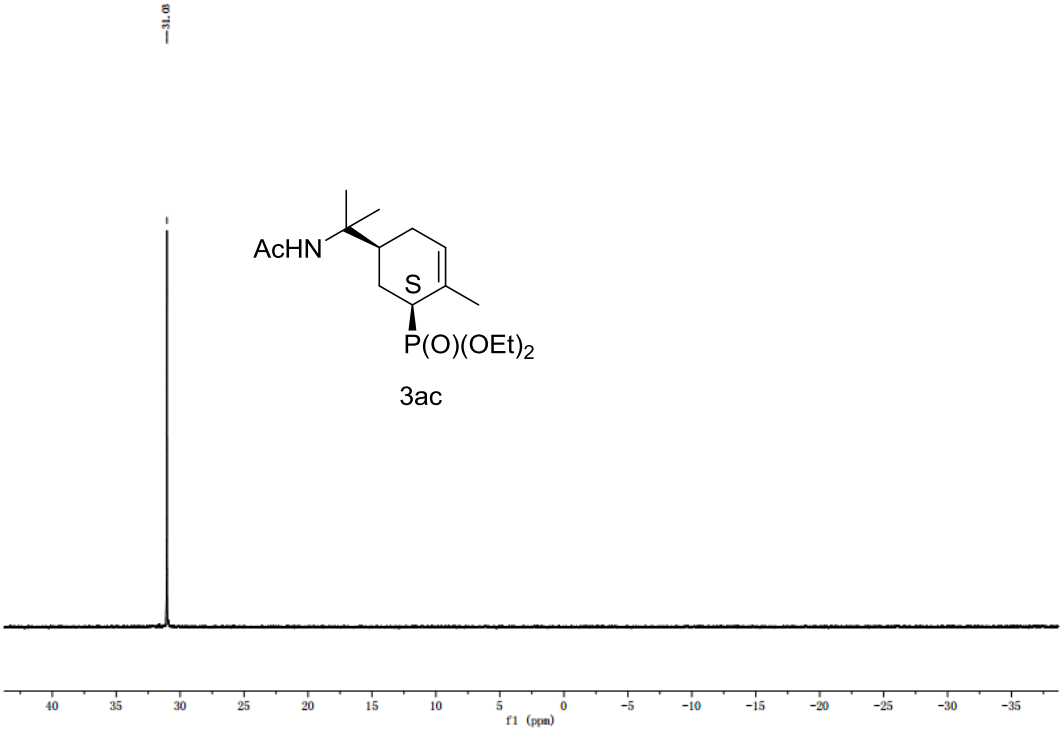
3ab

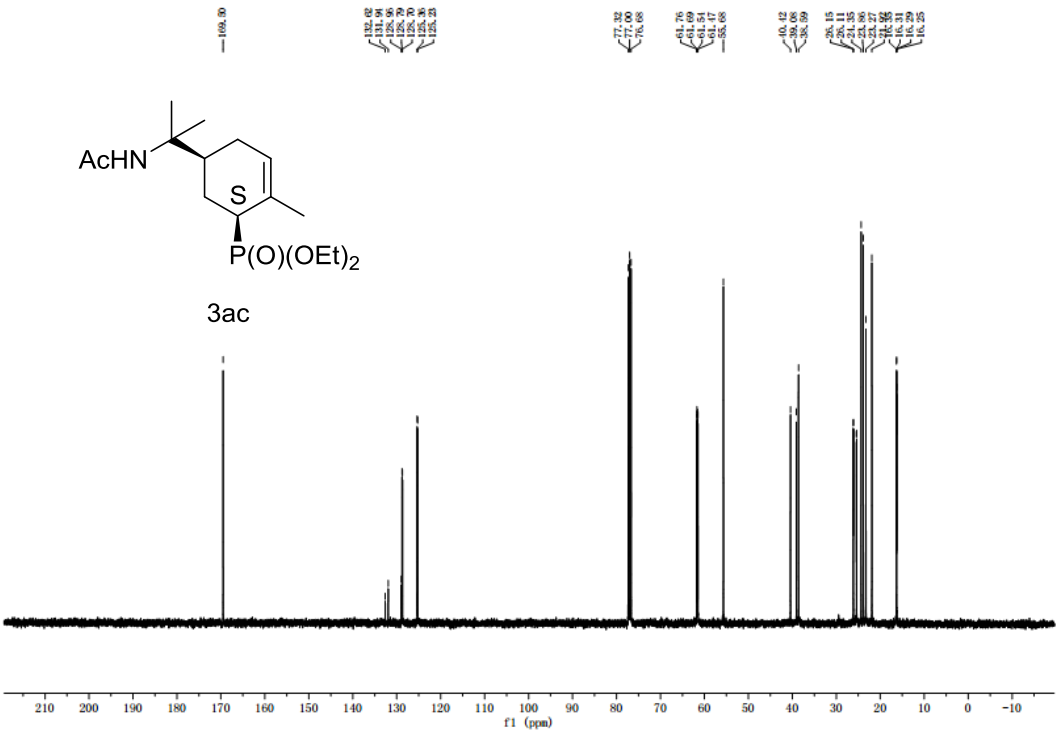

173.69
172.82
147.41
136.42
132.85
128.89
128.83
128.58
128.45
124.56
124.44
109.49
57.246
57.219
52.518
52.471
52.451
52.403
37.036
35.350
32.438
31.895
30.520
27.224
21.244
16.575
16.545
P(O)(OMe)2
Ac
N
Bz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

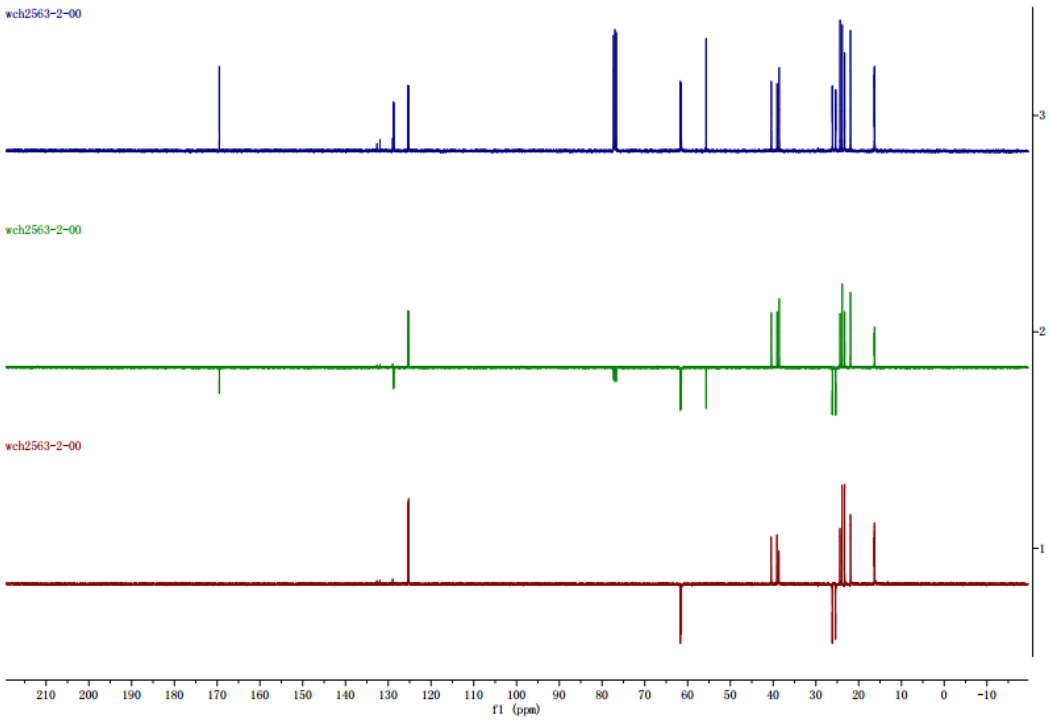
3ab


132.94
128.98
128.93
109.59
57.337
57.309
52.612
52.564
52.545
52.496
37.126
35.422
32.525
31.984
30.610
27.320
21.337
16.668
16.637
P(O)(OMe)2
Ac
N
Bz
3ab
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

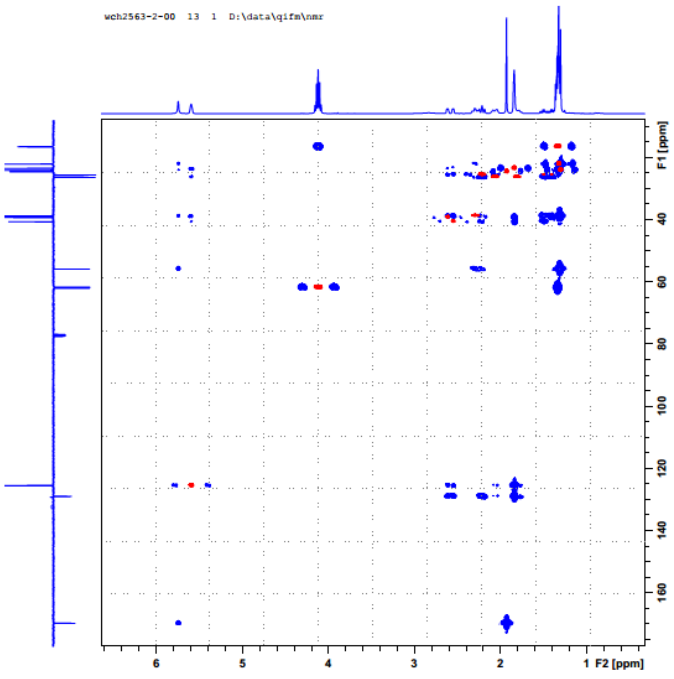

AcHN
S
P(O)(OEt)2
3ac
f1 (ppm)


31.08
AcHN
S
P(O)(OEt)2
3ac
f1 (ppm)

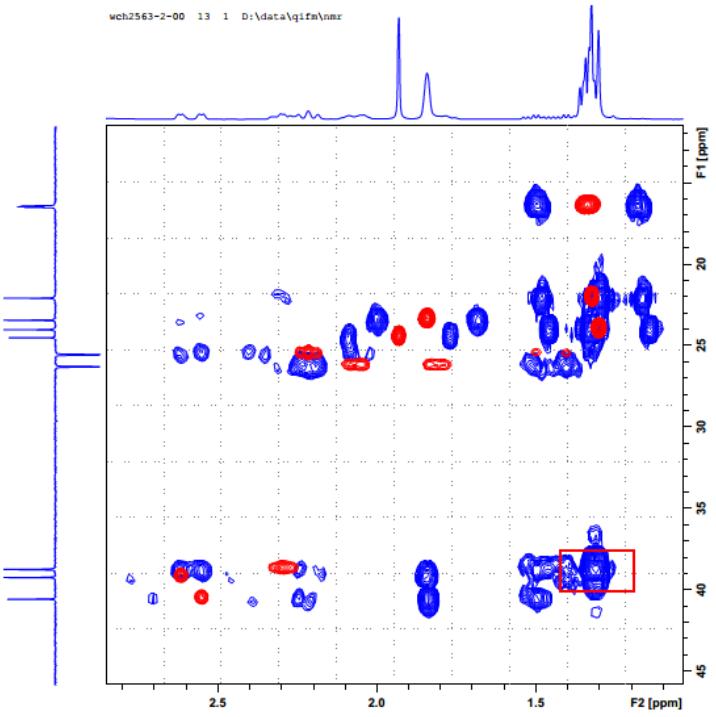

169.80
132.62
131.56
128.90
128.79
128.70
125.36
125.23
77.32
77.00
76.68
61.76
61.69
61.54
61.47
55.68
40.42
39.06
38.69
26.15
25.11
24.35
23.86
23.27
16.58
16.55
16.31
16.29
16.25
AcHN
S
P(O)(OEt)2
3ac
f1 (ppm)



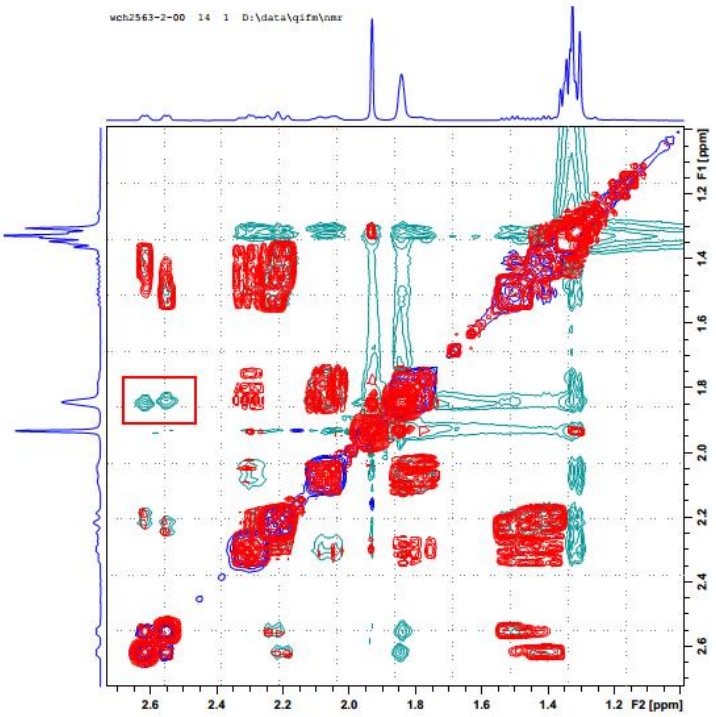
3ac ^{13}C-APT-DEPT 135



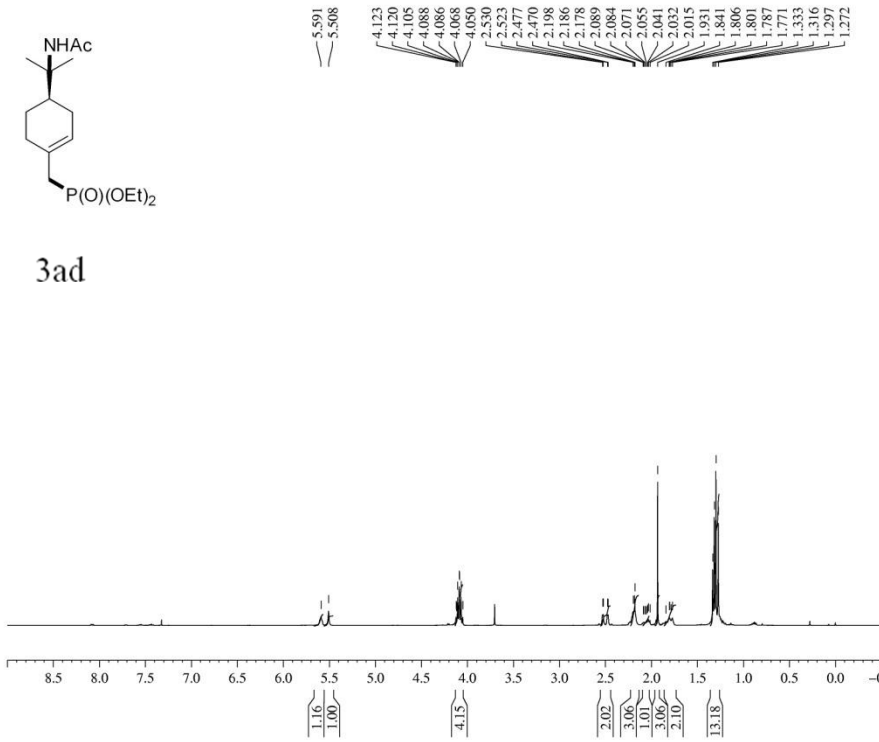
3ac HMBC-HMQC-APT



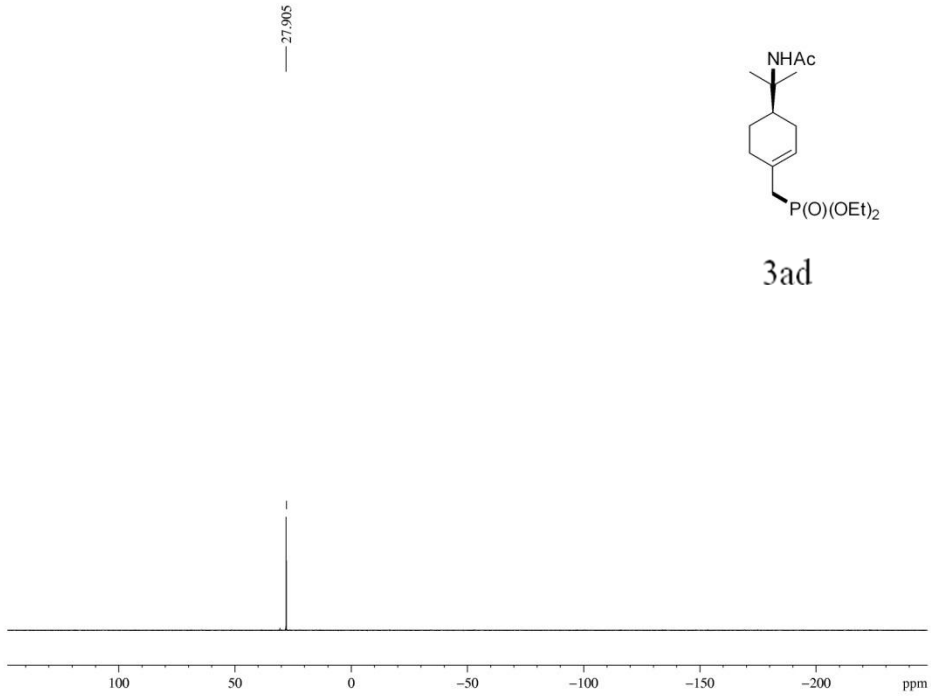
3ac HMBC-HMQC-APT



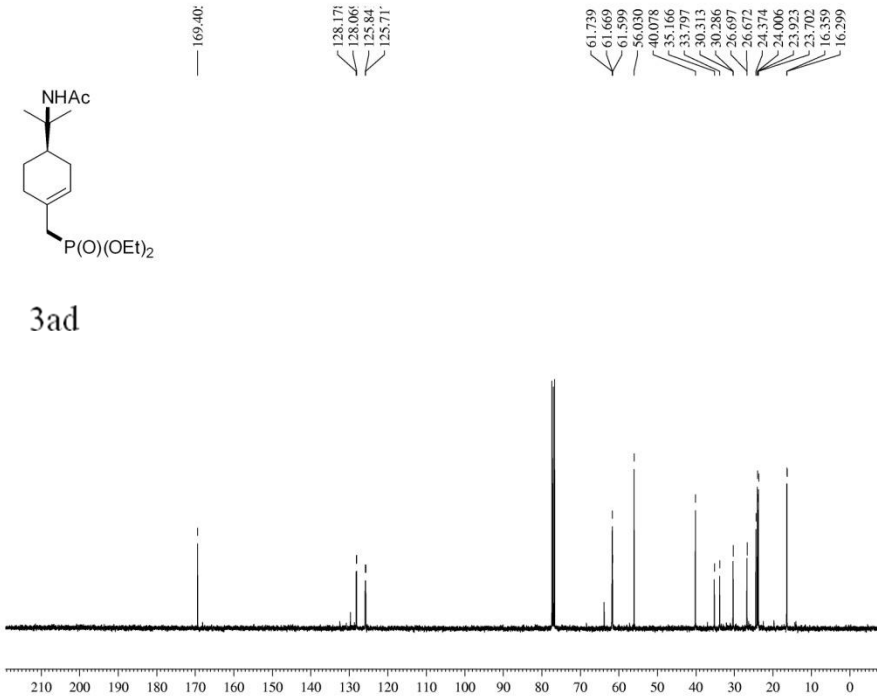
3ac NOESY-COSY


NHAc
P(O)(OEt)2
5.591
5.508
4.123
4.120
4.105
4.088
4.086
4.068
4.050
2.530
2.523
2.477
2.470
2.198
2.186
2.178
2.089
2.084
2.071
2.055
2.041
2.032
2.015
1.931
1.841
1.806
1.801
1.787
1.771
1.333
1.316
1.297
1.272
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.16
1.00
4.15
2.02
3.06
1.01
3.06
2.10
13.18

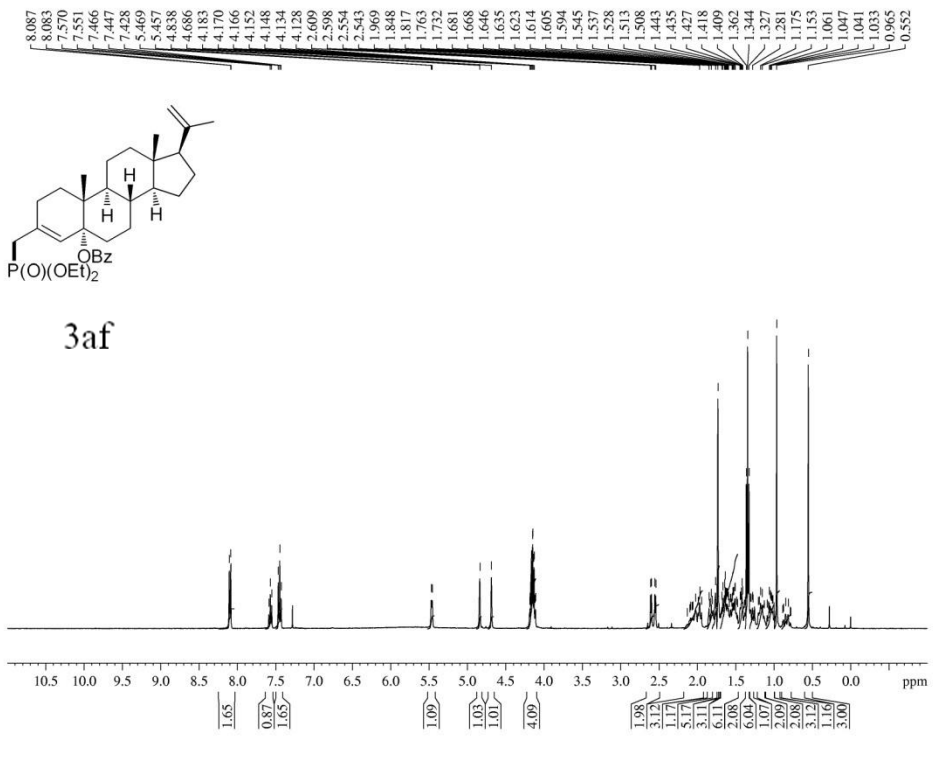
3ad


27.905
NHAc
P(O)(OEt)2
100 50 0 −50 −100 −150 −200 ppm

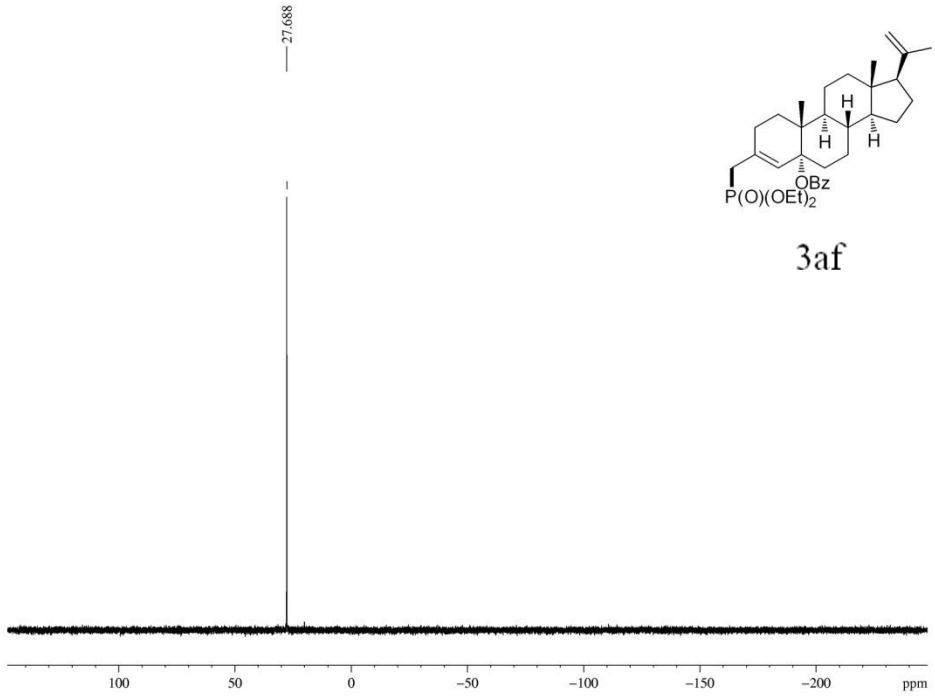
3ad


NHAc
P(O)(OEt)2
169.40
128.17
128.06
125.84
125.71
61.739
61.669
61.599
56.030
40.078
35.166
33.797
30.313
30.286
26.697
26.672
24.374
24.006
23.923
23.702
16.359
16.299
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

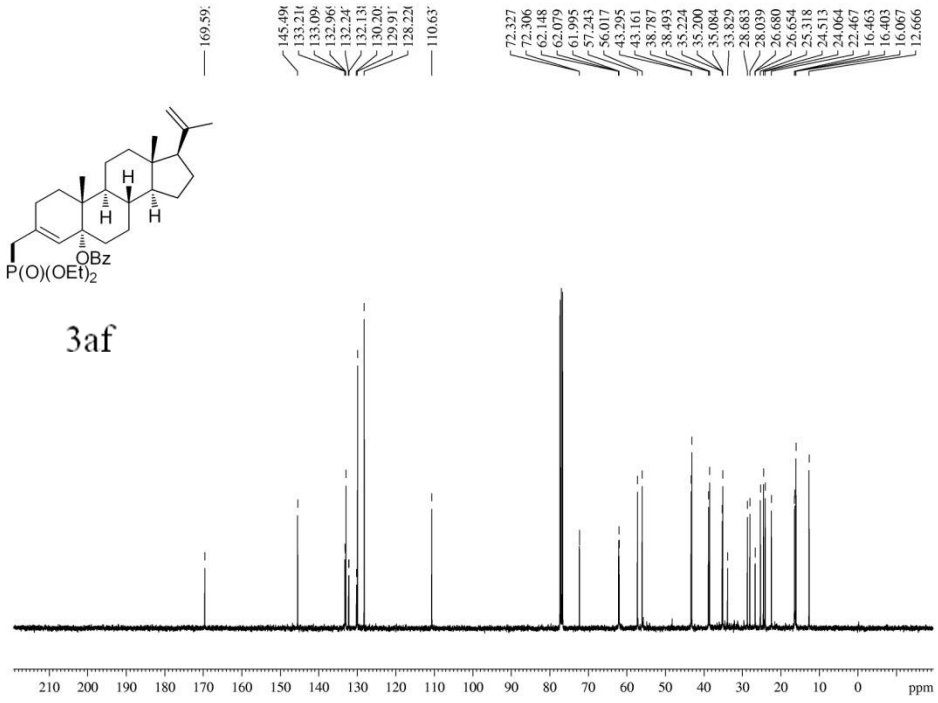
3ad


8.087
8.083
7.570
7.551
7.466
7.447
7.428
5.469
5.457
4.838
4.686
4.183
4.170
4.166
4.152
4.148
4.134
4.128
2.609
2.598
2.554
2.543
1.969
1.848
1.817
1.763
1.732
1.681
1.668
1.646
1.635
1.623
1.614
1.605
1.594
1.545
1.537
1.528
1.513
1.508
1.443
1.435
1.427
1.418
1.409
1.362
1.344
1.327
1.281
1.175
1.153
1.061
1.047
1.041
1.033
0.965
0.552
H
H
H
OBz
P(O)(OEt)2
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.65
0.87
1.65
1.09
1.03
1.01
4.09
1.98
3.12
1.17
5.17
3.11
6.11
2.08
6.04
1.07
2.09
2.08
3.12
1.16
3.00

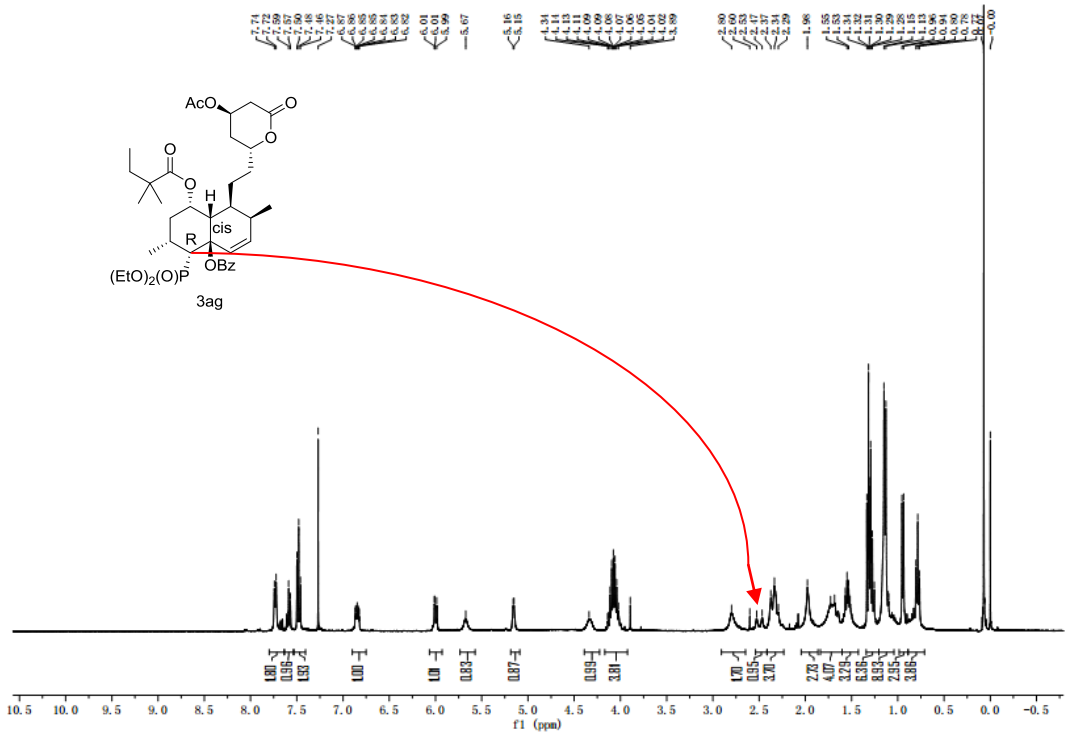
3af

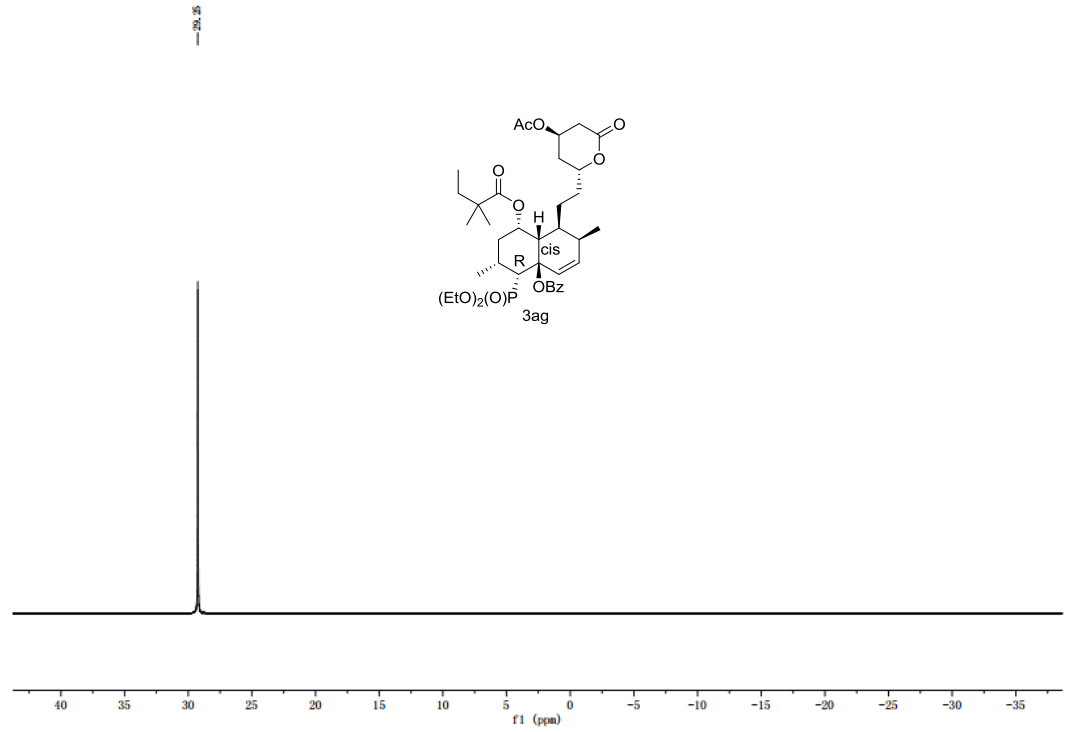

27.688
H
H
H
OBz
P(O)(OEt)2
100
50
0
−50
−100
−150
−200
ppm

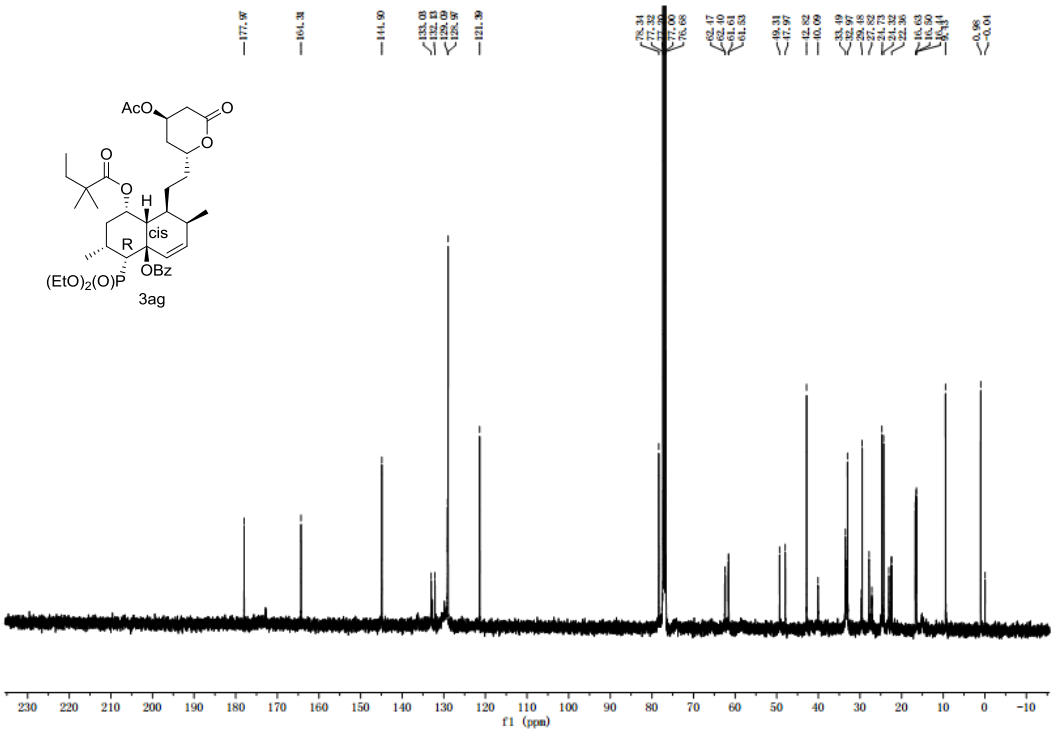
3af

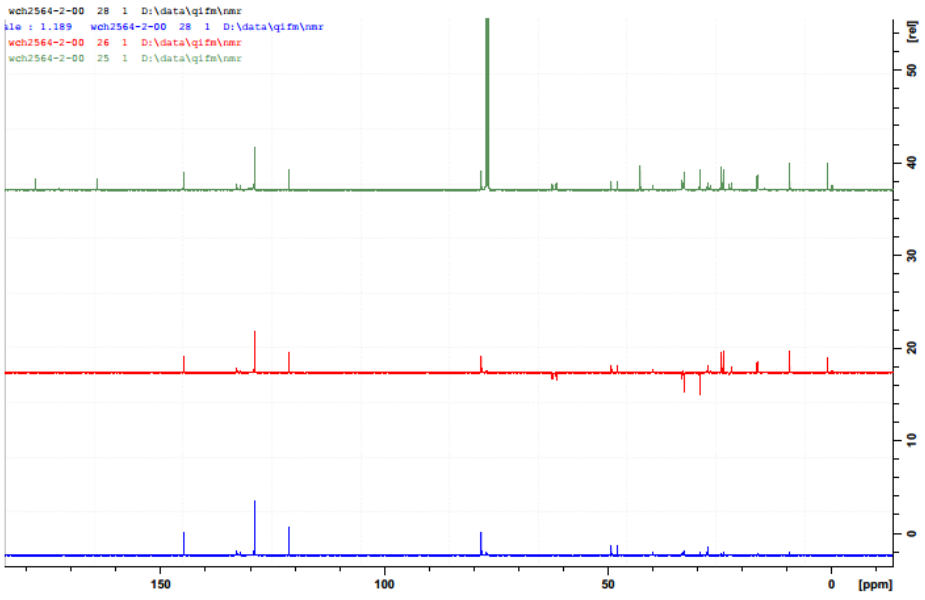

169.59
145.49
133.21
133.09
132.96
132.24
132.13
130.20
129.91
128.22
110.63
72.327
72.306
62.148
62.079
61.995
57.243
56.017
43.295
43.161
38.787
38.493
35.224
35.200
35.084
33.829
28.683
28.039
26.680
26.654
25.318
24.513
24.064
22.467
16.463
16.403
16.067
12.666
H
H
H
OBz
P(O)(OEt)2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3af

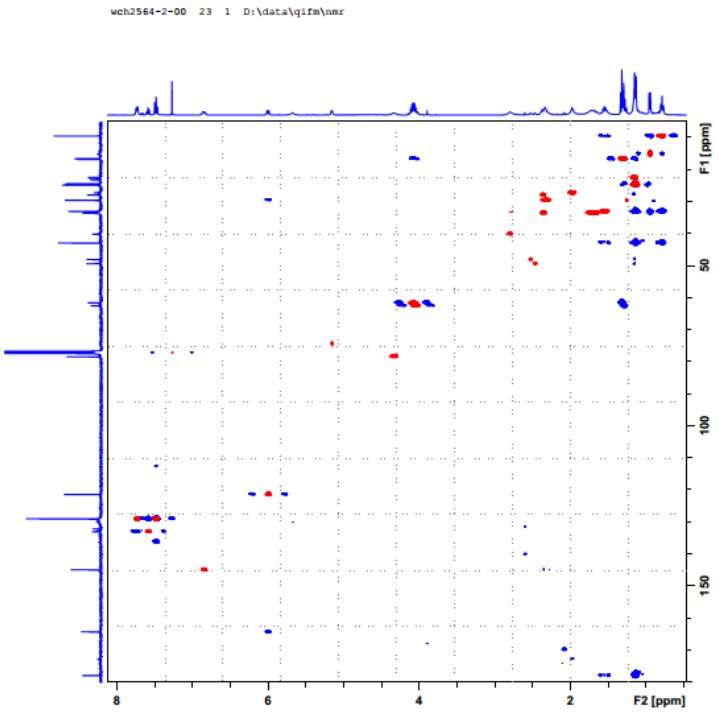

AcO
O
O
O
H
cis
R
OBz
(EtO)2(O)P
3ag
f1 (ppm)


AcO
O
O
O
H
cis
R
OBz
(EtO)2(O)P
3ag
f1 (ppm)

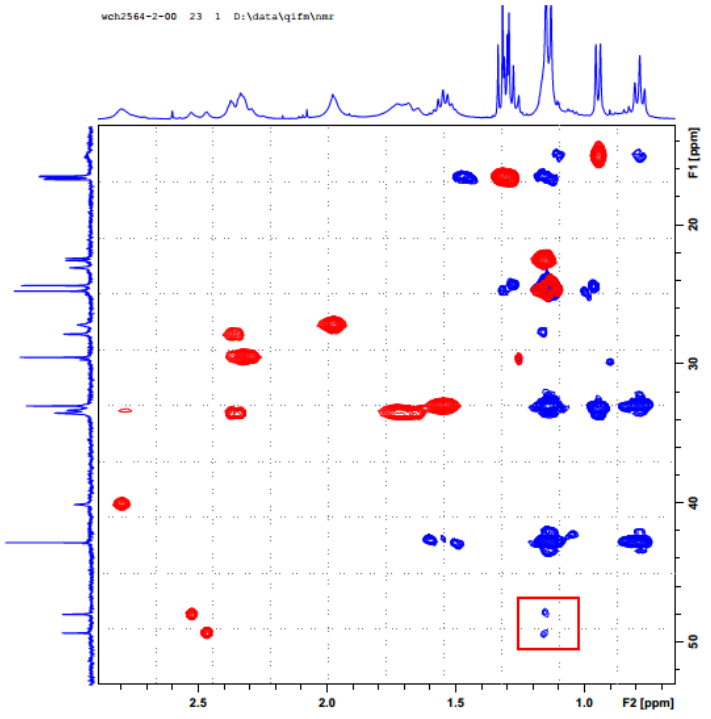




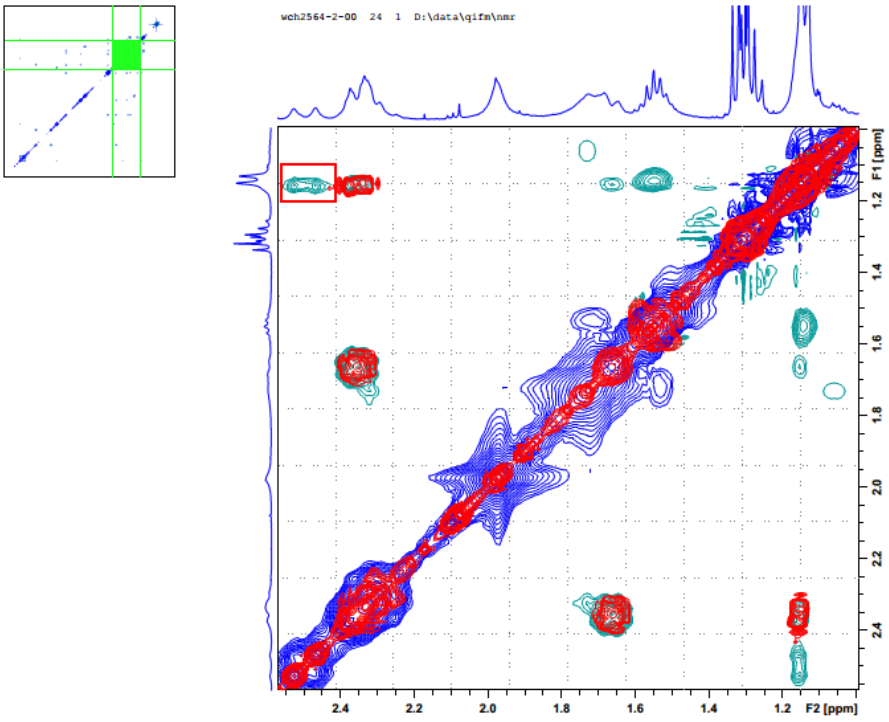
3ag ^{13}C- DEPT 135- DEPT 90



3ag HMBC-HMQC-^{13}C



3ag HMBC-HMQC-^{13}C



3ag NOESY-COSY