

# Palladium-Catalyzed *N*-Alkenylation of *N*-Aryl Phosphoramidates with Alkenes

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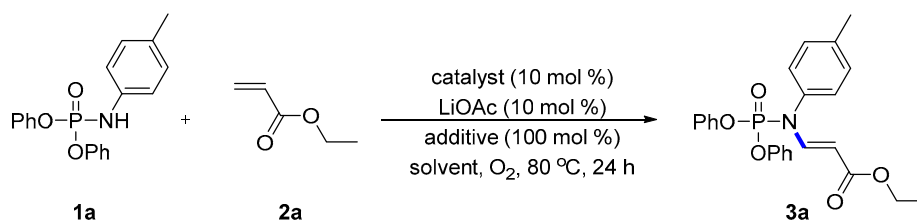
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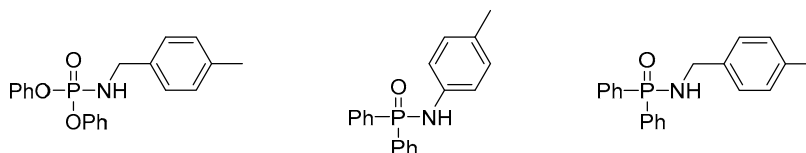
## Reaction Optimization<sup>a</sup>



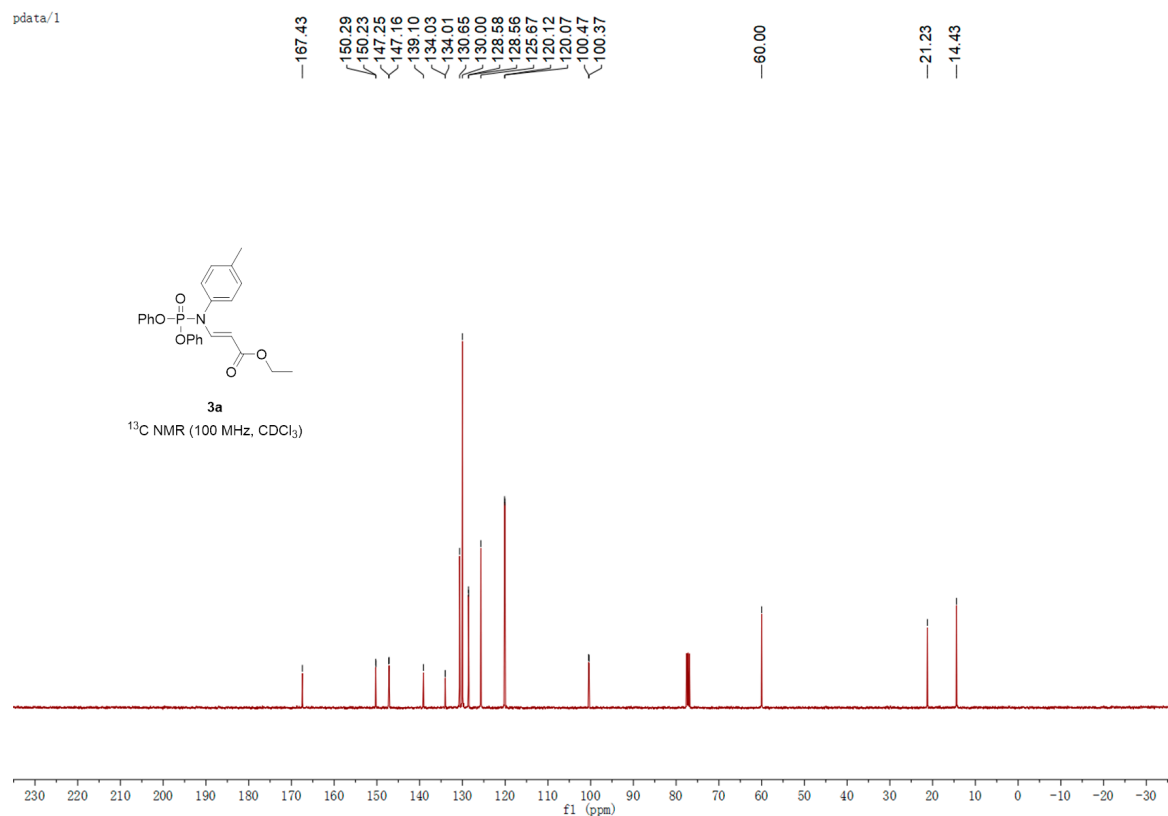
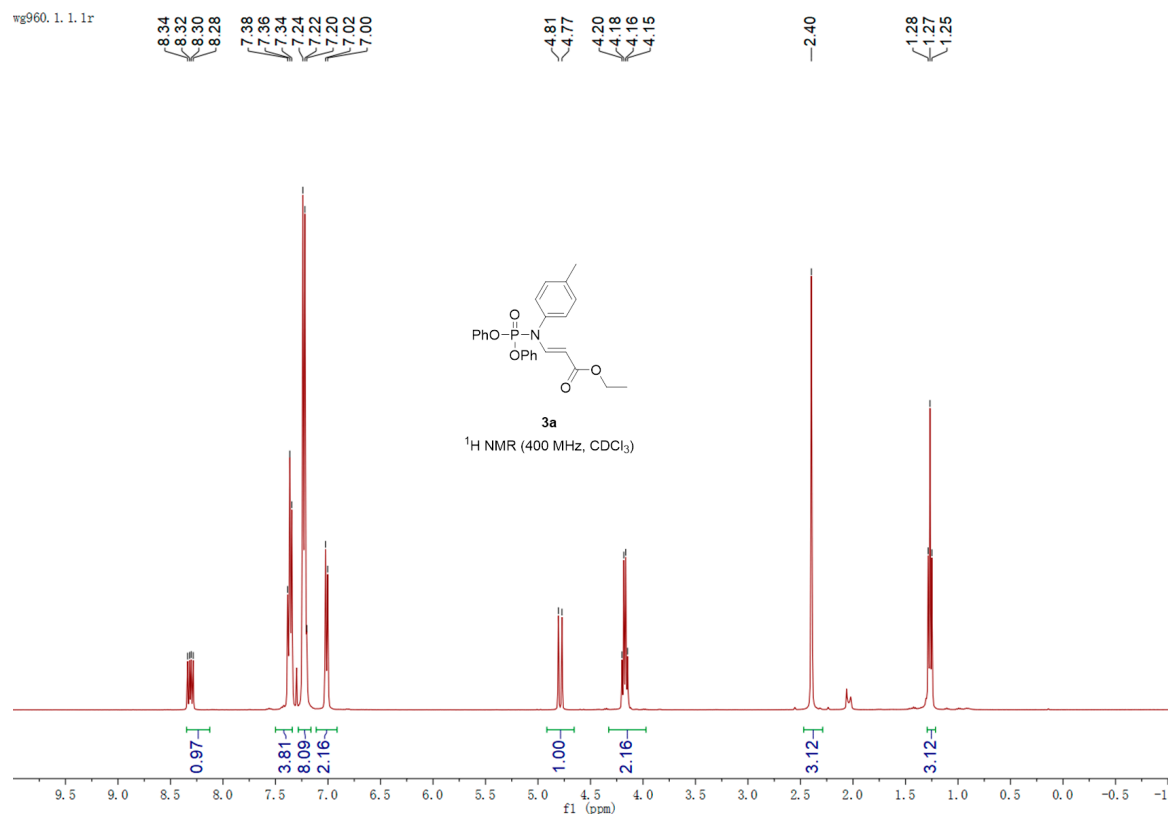
entry	catalyst	additive	solvent	yield (%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub>	Cu(OAc) <sub>2</sub>	DME	0
2	Pd(OAc) <sub>2</sub>	CuCl <sub>2</sub>	DME	0
3	Pd(OAc) <sub>2</sub>	BQ	DME	0
4	Pd(OAc) <sub>2</sub>	pyridine	DME	0
5	Pd(OAc) <sub>2</sub>	LiBr	DME	0
6	Pd(OAc) <sub>2</sub>	TBAF	DME	0
7	Pd(OAc) <sub>2</sub>	TBAC	DME	0
8	Pd(OAc) <sub>2</sub>	TBAB	DME	65
9	Pd(OAc) <sub>2</sub>	TBAI	DME	0
10	PdCl <sub>2</sub>	TBAB	DME	0
11	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	TBAB	DME	0
12	Pd(PhCN) <sub>2</sub> Cl <sub>2</sub>	TBAB	DME	0
13	Pd(acac) <sub>2</sub>	TBAB	DME	0
14	Pd(OAc) <sub>2</sub>	TBAB	THF	45
15	Pd(OAc) <sub>2</sub>	TBAB	Dioxane	33
16	Pd(OAc) <sub>2</sub>	TBAB	toluene	21
17	Pd(OAc) <sub>2</sub>	TBAB	DMSO	0
18	Pd(OAc) <sub>2</sub>	TBAB	DMF	0
19	Pd(OAc) <sub>2</sub>	TBAB	TMBE	80
20	Pd(TFA) <sub>2</sub>	TBAB	TMBE	89
21 <sup>c</sup>	Pd(TFA) <sub>2</sub>	TBAB	TMBE	7
22 <sup>d</sup>	Pd(TFA) <sub>2</sub>	TBAB	TMBE	29
23 <sup>e</sup>	Pd(TFA) <sub>2</sub>	TBAB	TMBE	77
24 <sup>f</sup>	Pd(TFA) <sub>2</sub>	TBAB	TMBE	72
25 <sup>g</sup>	Pd(TFA) <sub>2</sub>	TBAB	TMBE	71
26		TBAB	TMBE	0

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (0.02 mmol), LiOAc (0.02 mmol), additive (0.2 mmol), solvent (2 ml), under O<sub>2</sub>, heated at 80 °C for 24 h. <sup>b</sup> Isolated yield. <sup>c</sup> Under N<sub>2</sub> atmosphere. <sup>d</sup> Under air atmosphere. <sup>e</sup> at 70 °C. <sup>f</sup> at 90 °C. <sup>g</sup> 80% TBAB.

### Invalid substrate

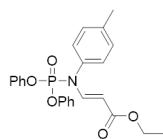


# $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ and $^{19}\text{F}$ NMR spectra of products



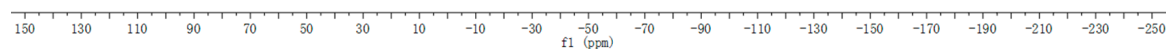
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9.54



**3a**

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )

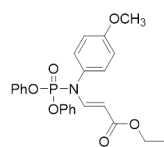


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8.19  
8.17  
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6.86  
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6.86  
6.84

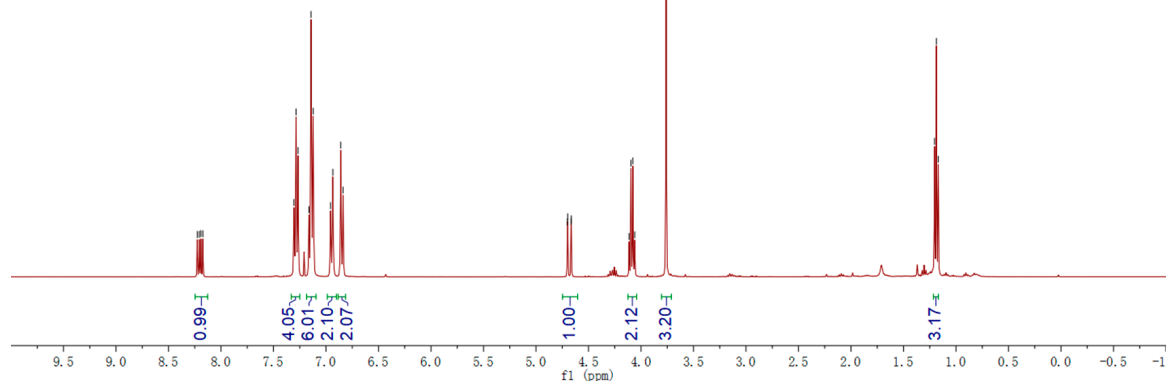
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4.08  
4.06  
3.76

1.20  
1.19  
1.17



**3b**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



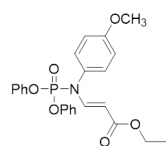


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147.38  
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120.10  
120.05  
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100.32

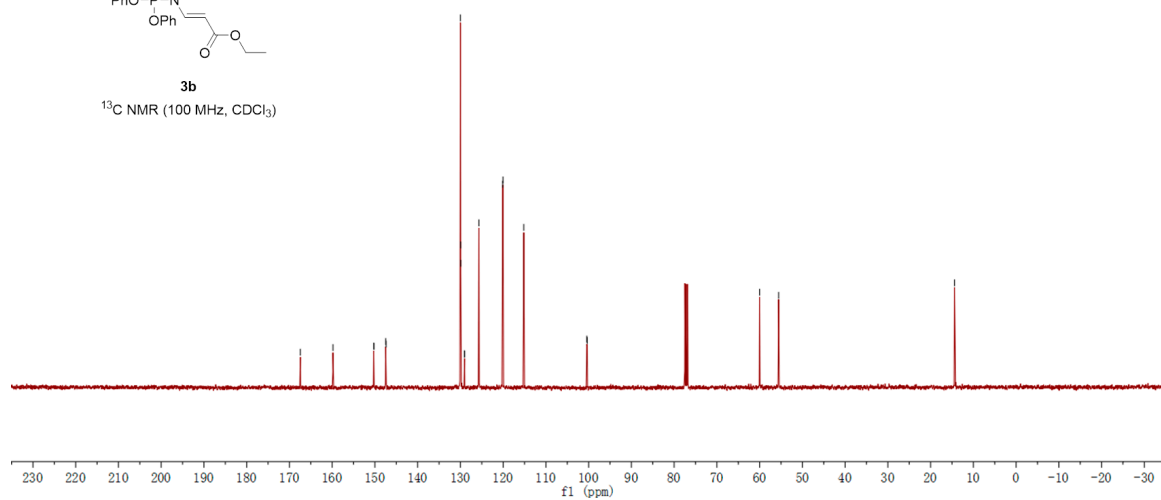
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—14.42



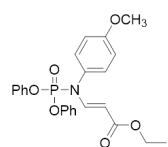
**3b**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



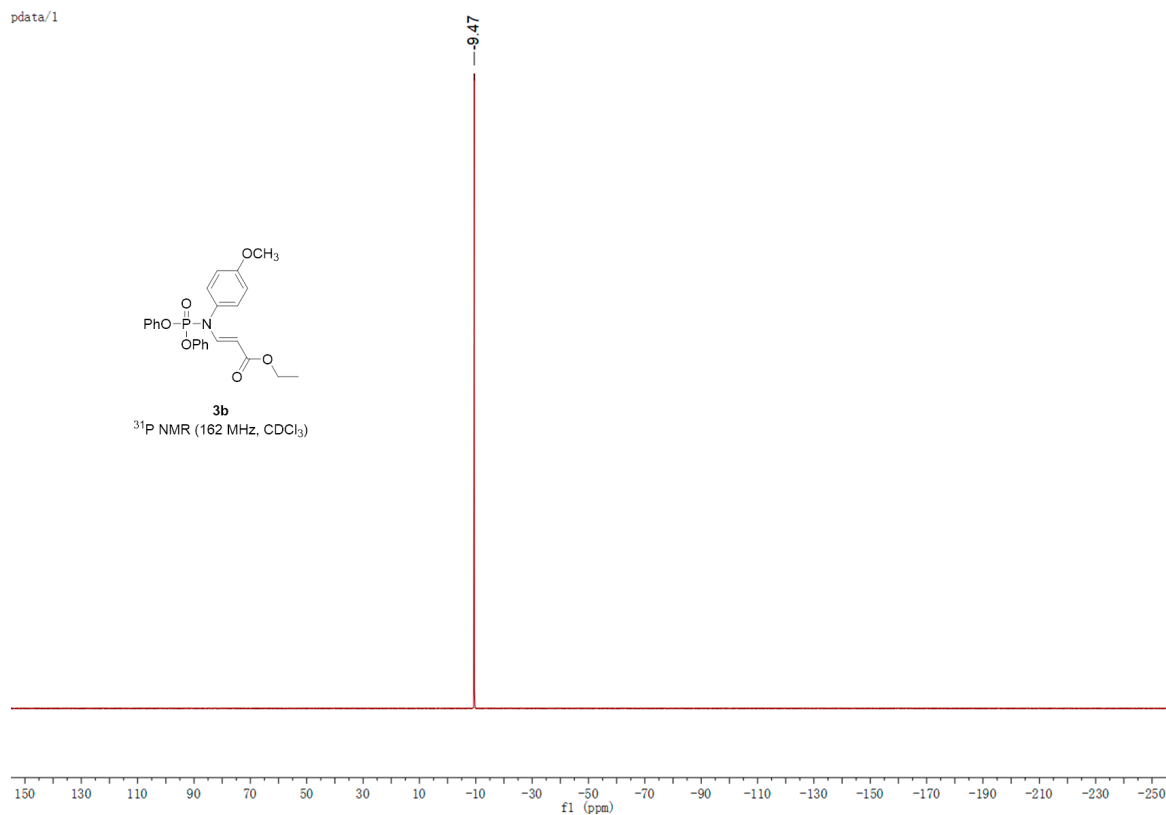
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—9.47



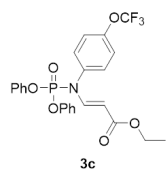
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<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)

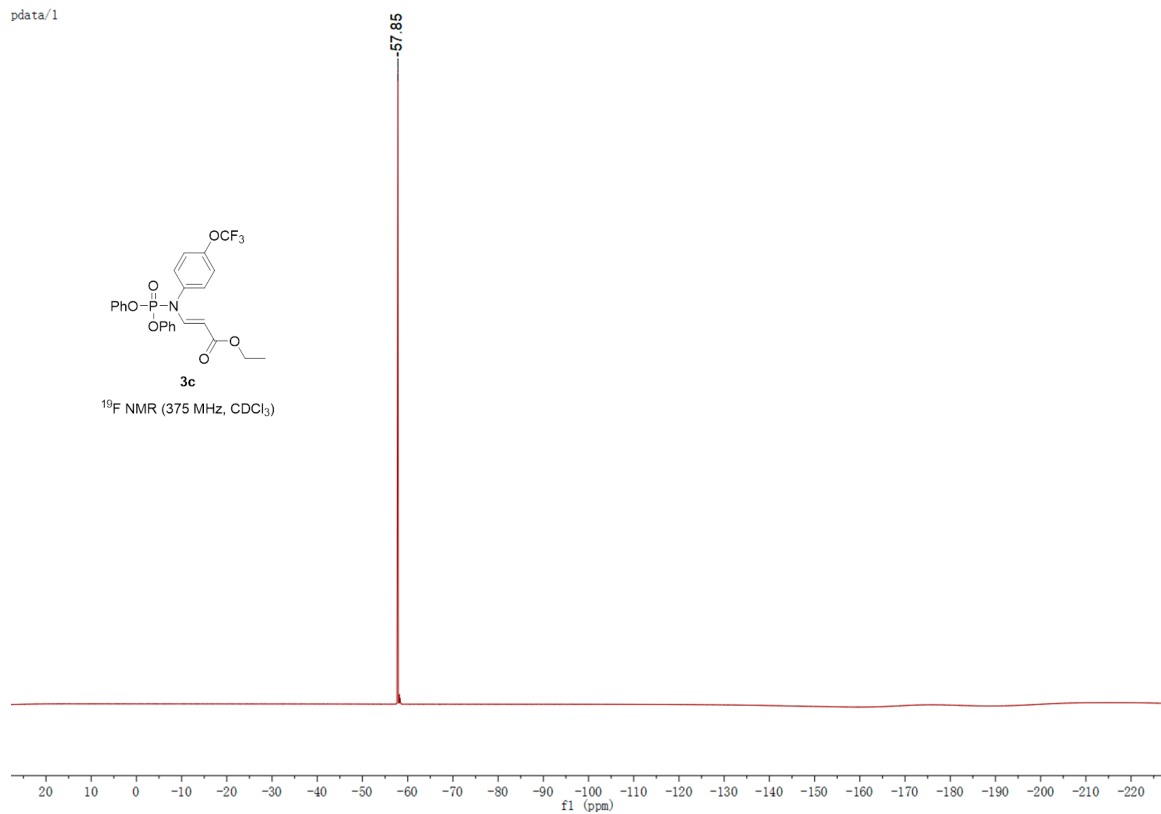




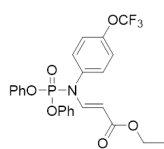
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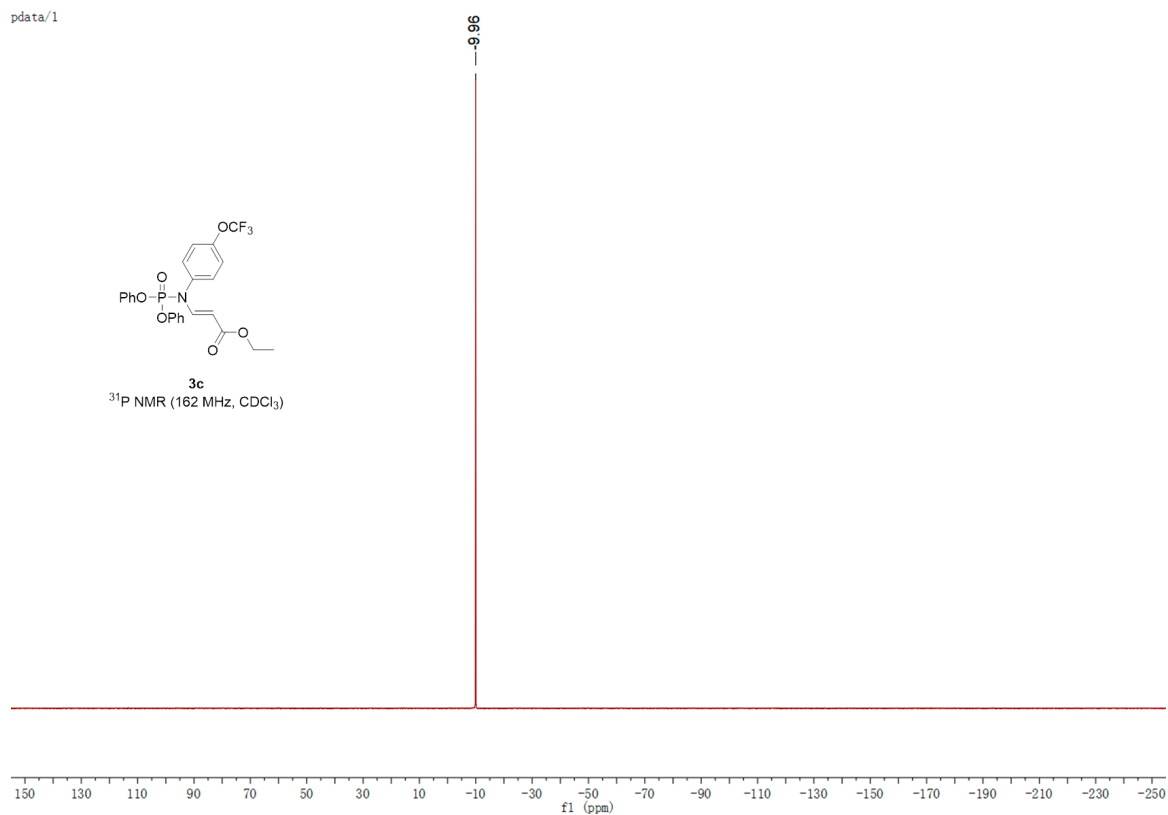
**3c**  
<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>)

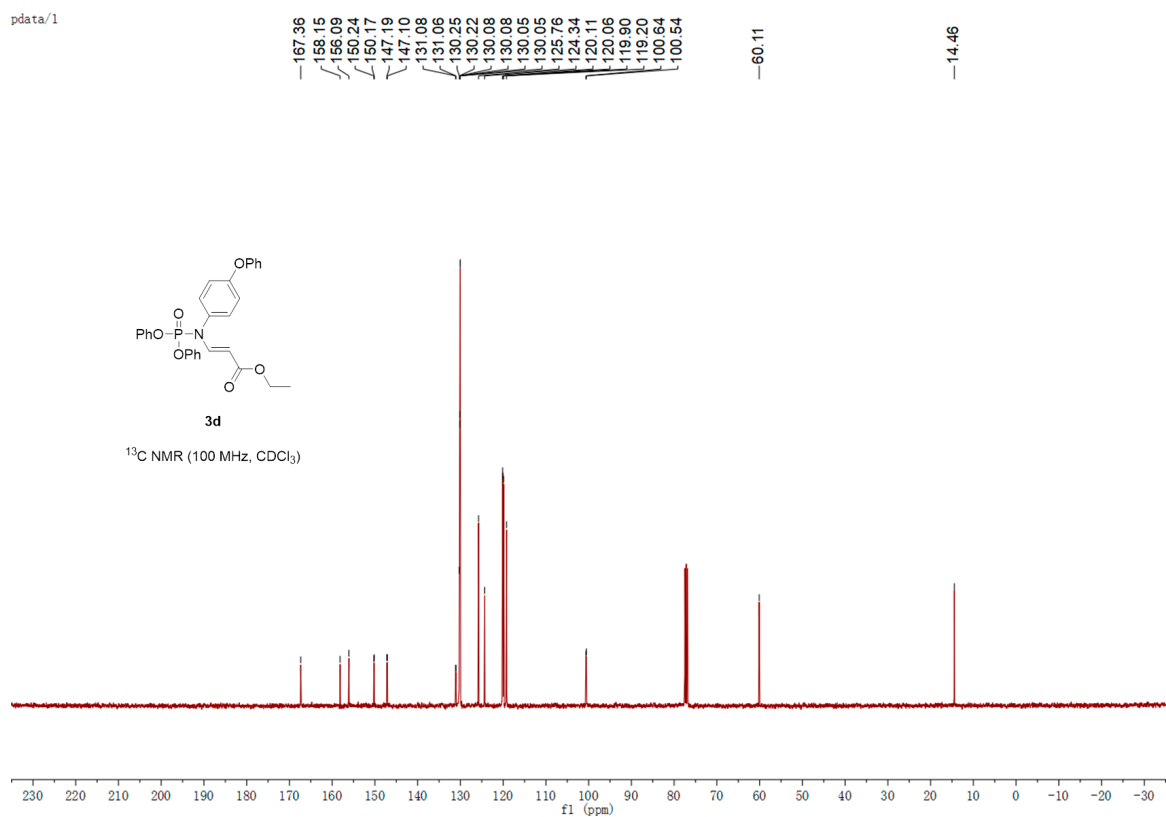
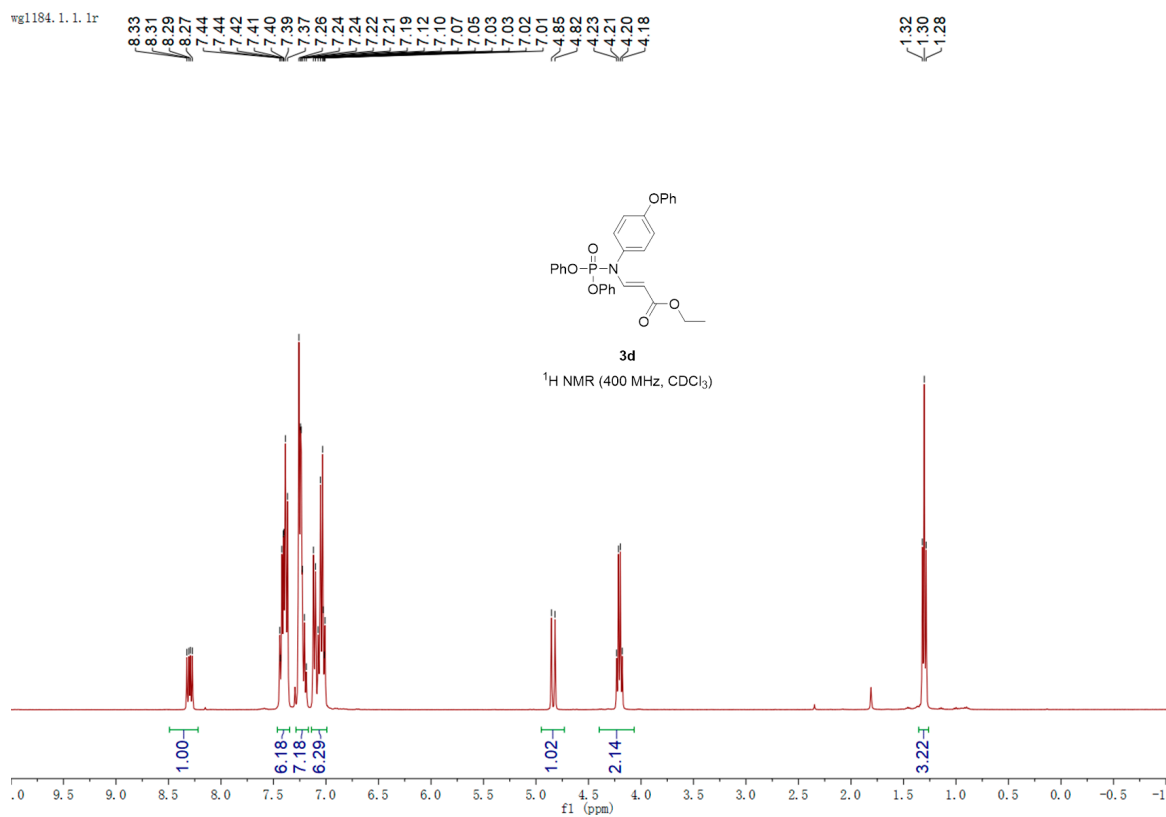


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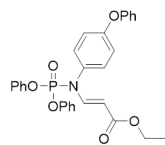


**3c**  
<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)

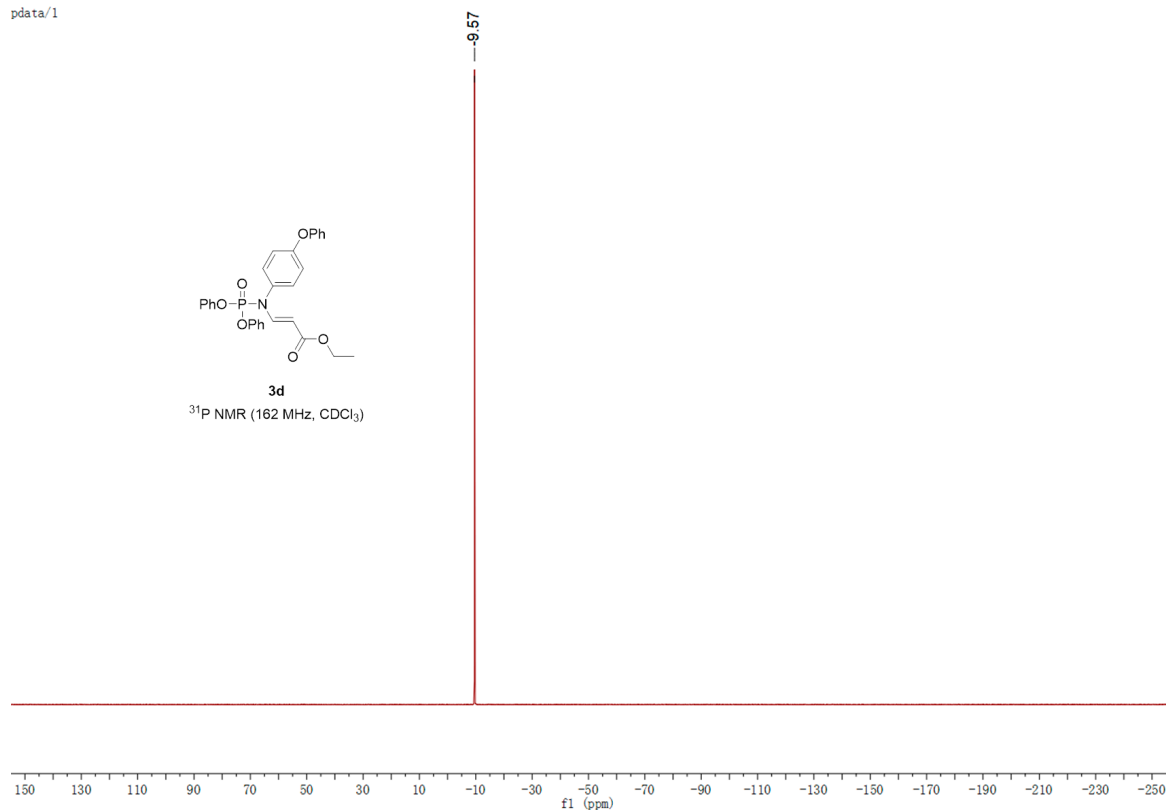




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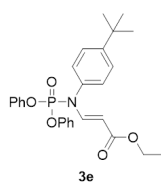


**3d**  
 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )

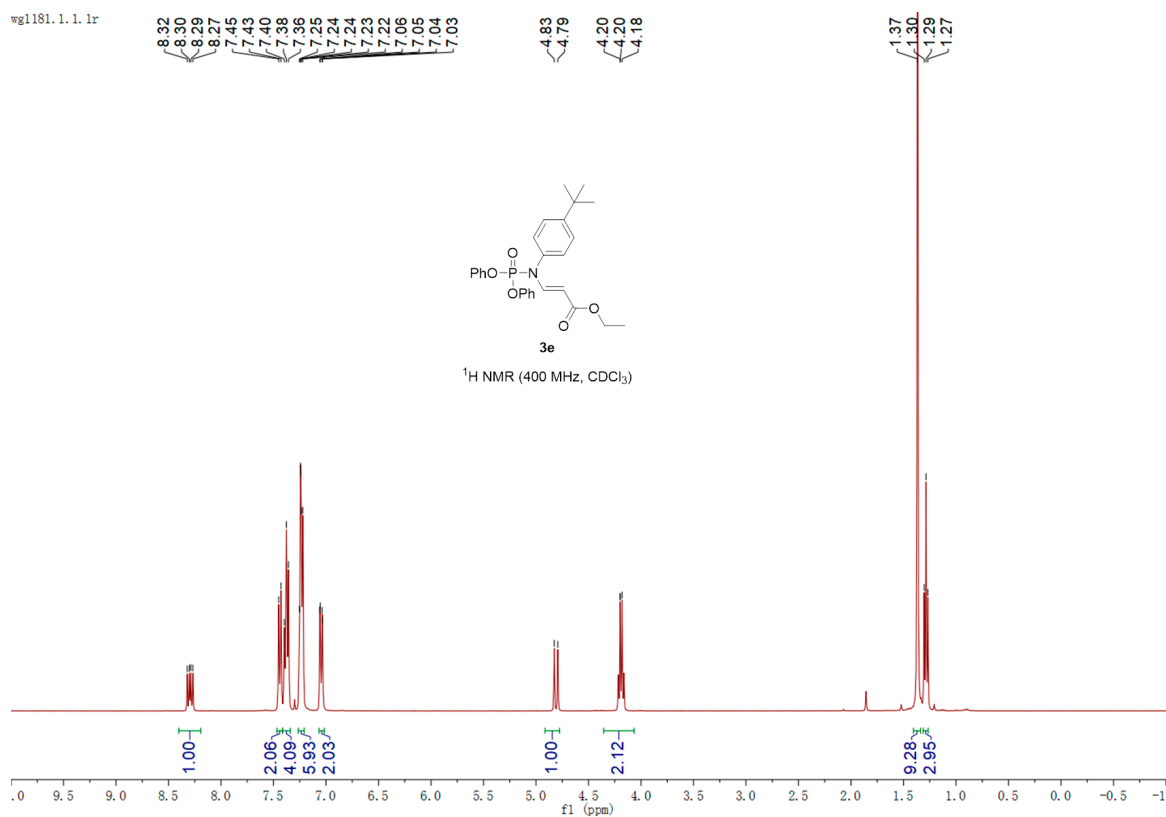


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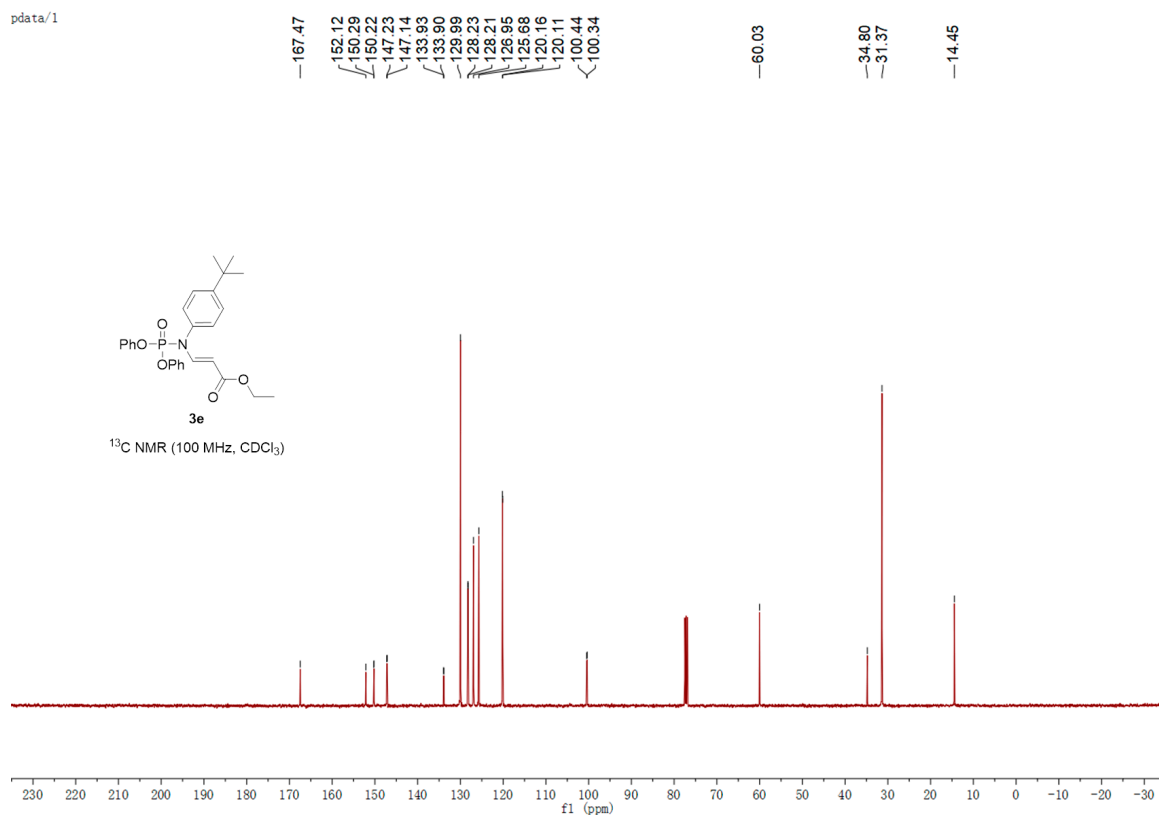
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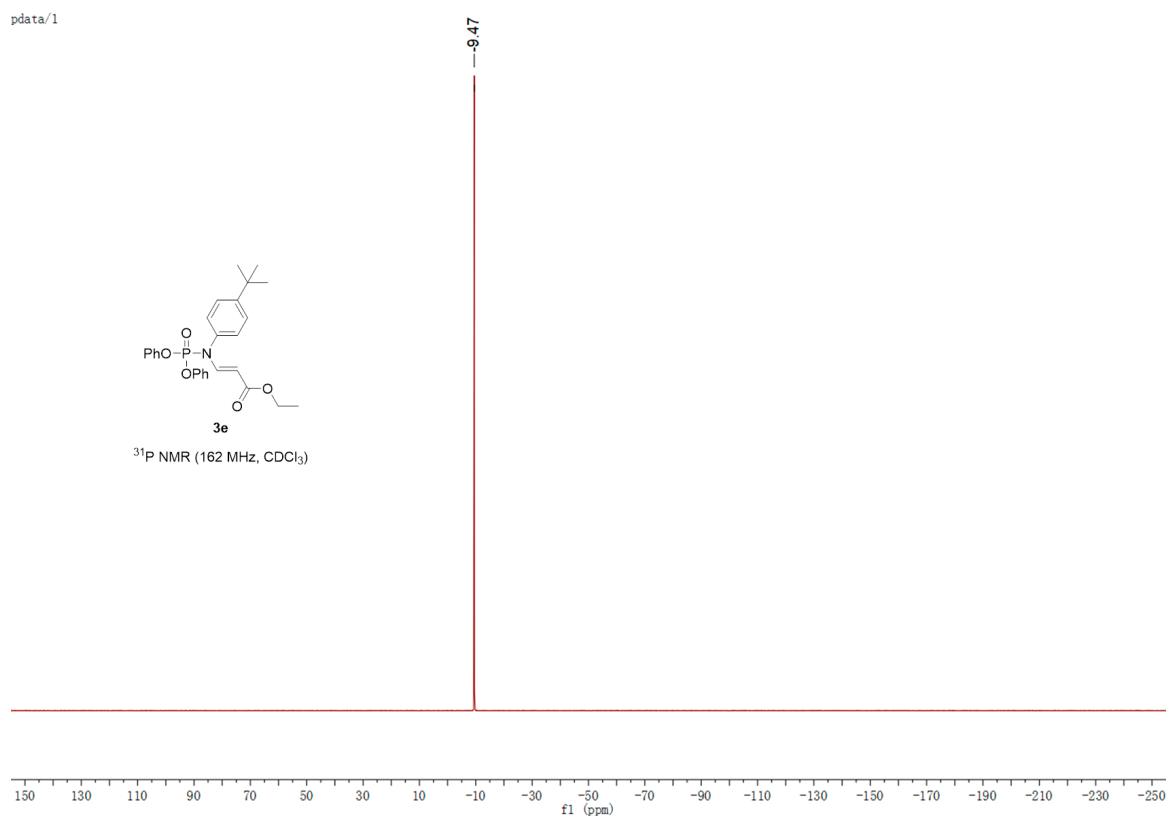
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 $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

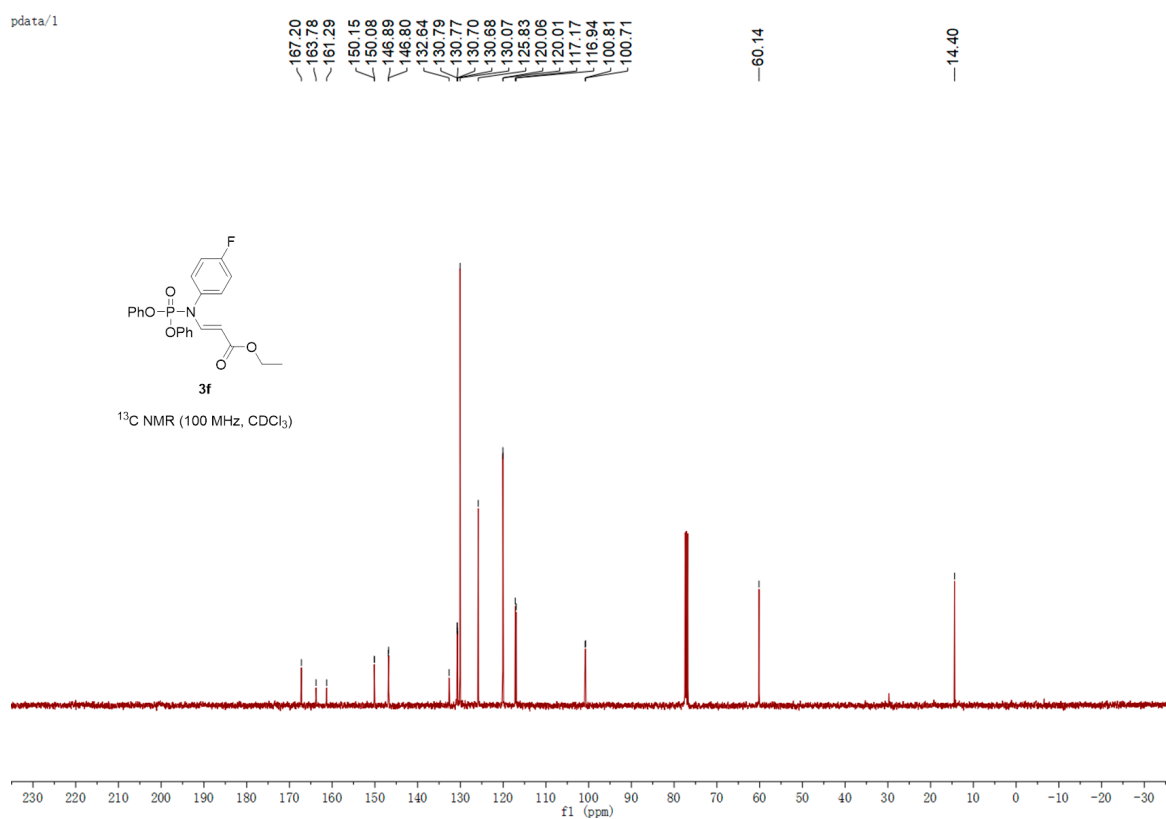
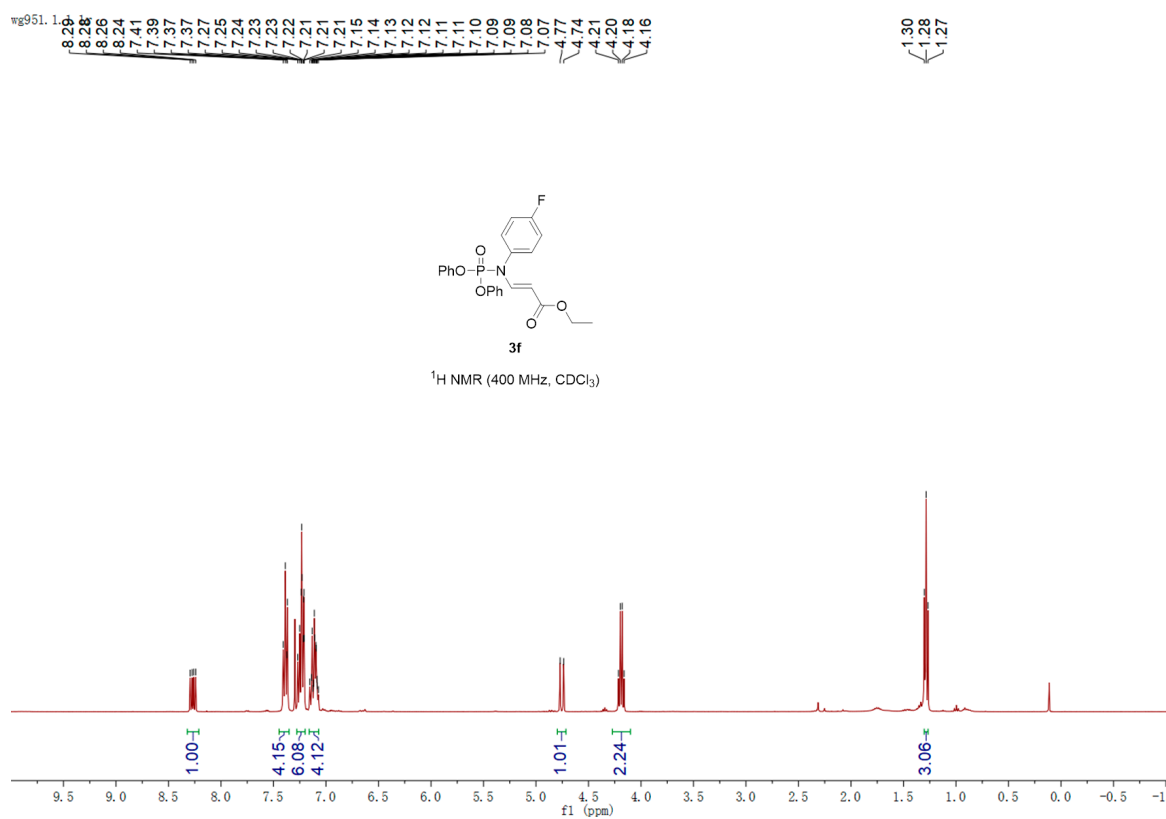


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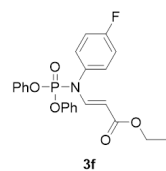
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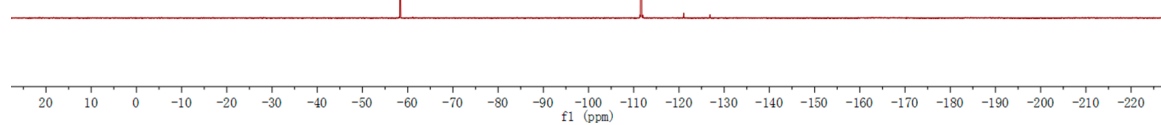


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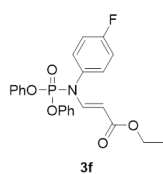


$^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ )

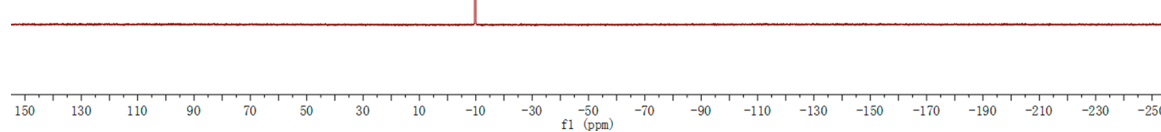


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---9.82



$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )

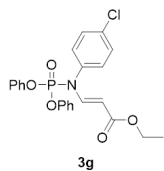




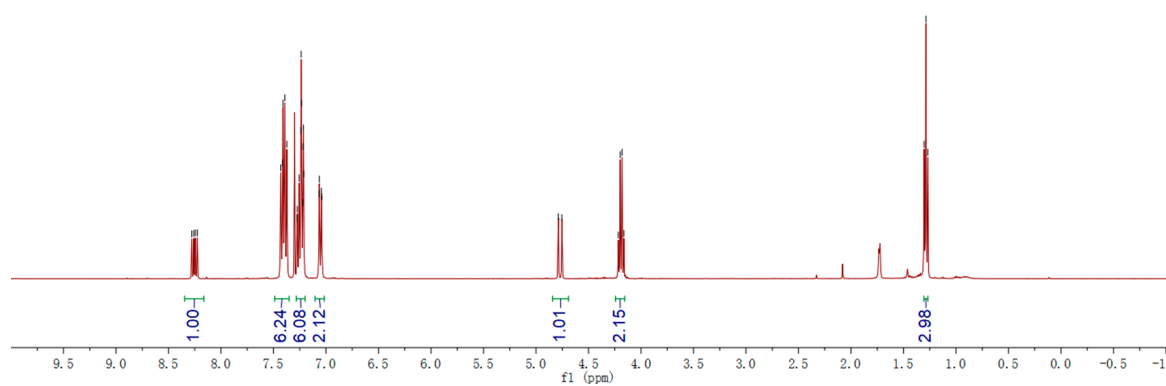
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8.26  
8.24  
8.23  
7.43  
7.41  
7.39  
7.37  
7.28  
7.27  
7.26  
7.24  
7.24  
7.23  
7.22  
7.21  
7.07  
7.06  
7.04  
7.04  
4.79  
4.75  
4.22  
4.20  
4.18  
4.16

1.30  
1.29  
1.27



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

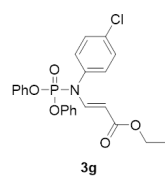


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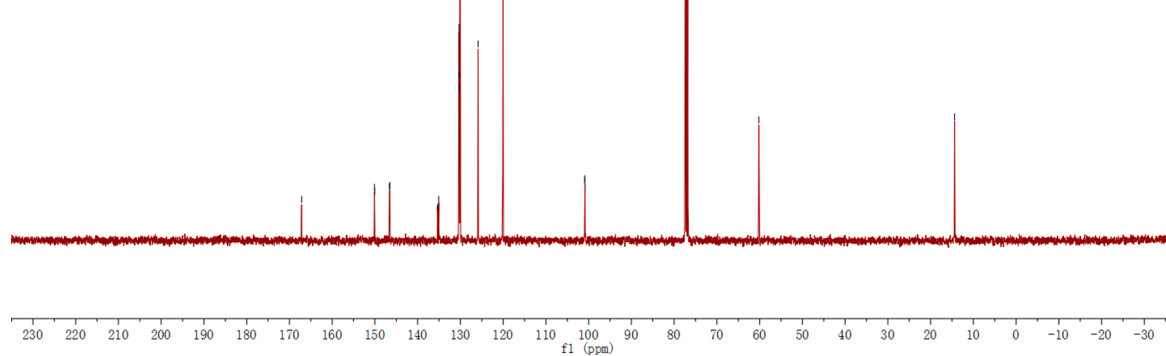
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150.11  
150.04  
146.59  
146.50  
135.36  
135.07  
130.32  
130.27  
130.25  
130.09  
125.87  
120.08  
120.03  
100.94  
100.85

60.17

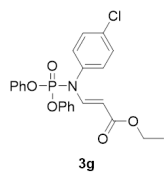
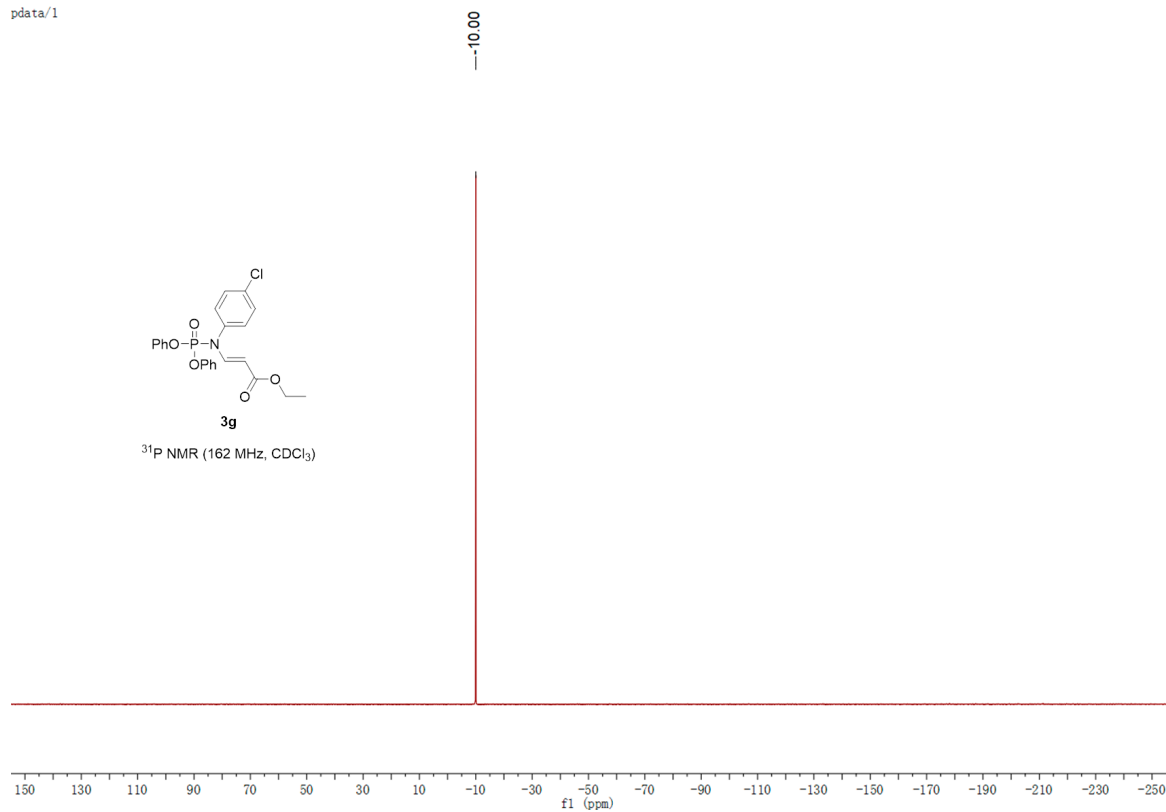
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<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

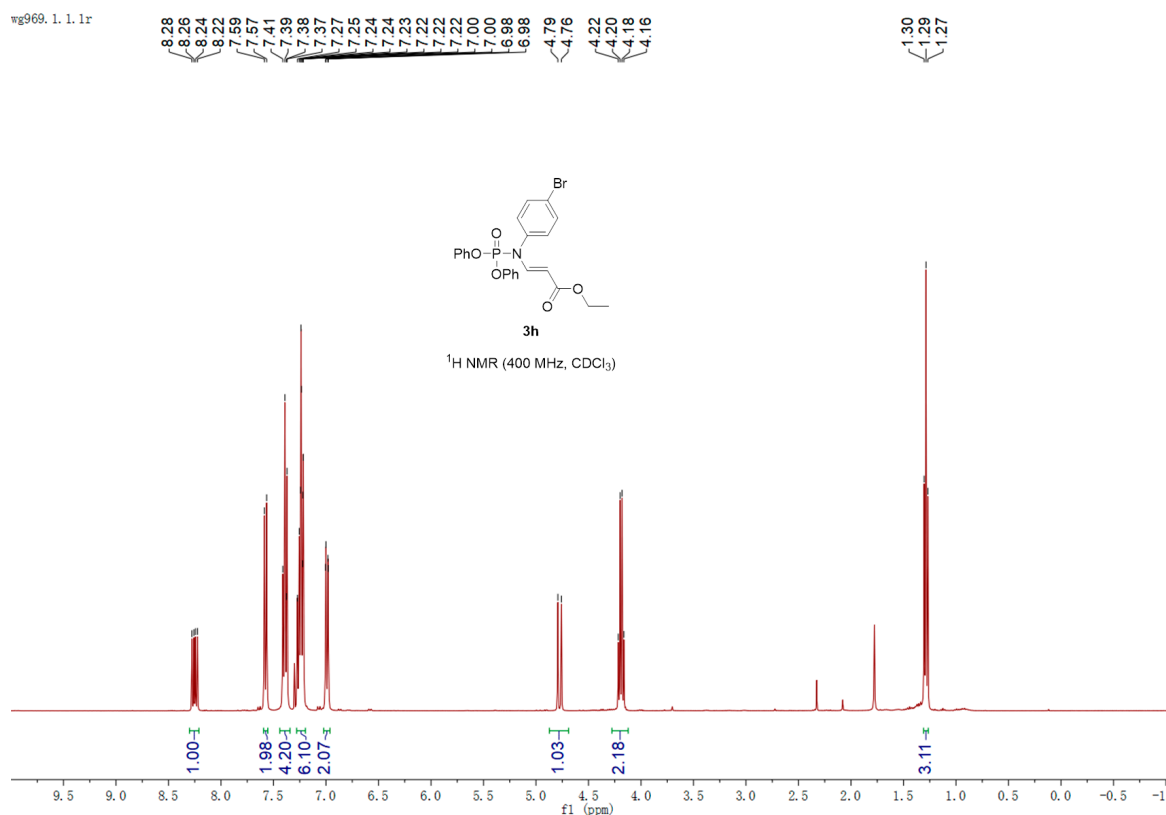


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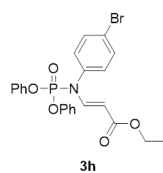


<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)

mg969, 1. 1. 1r



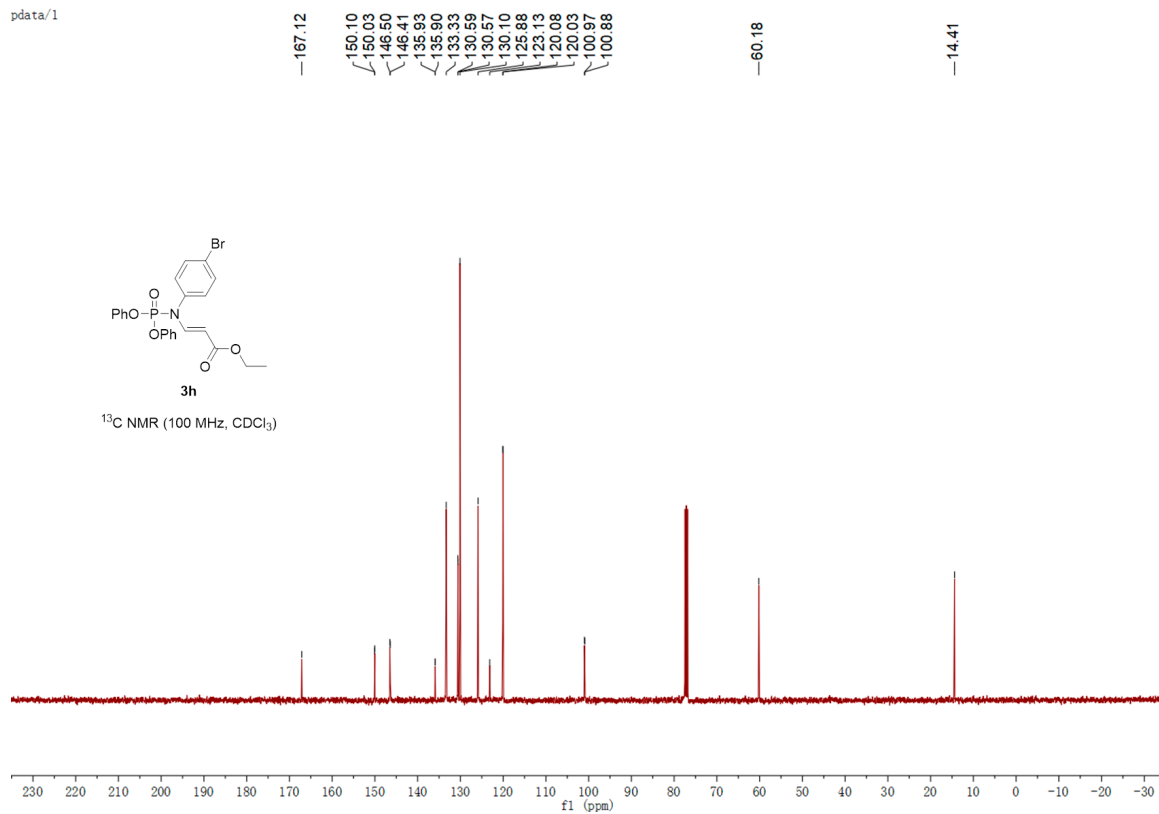
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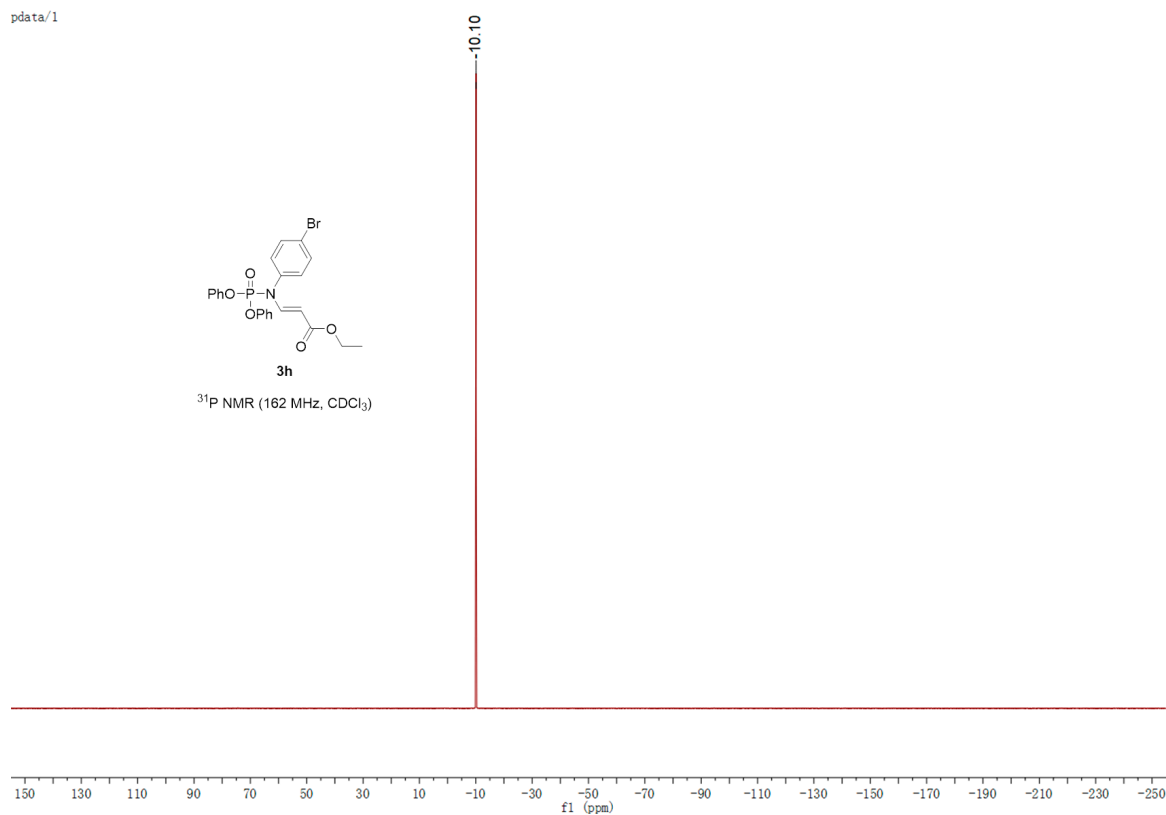
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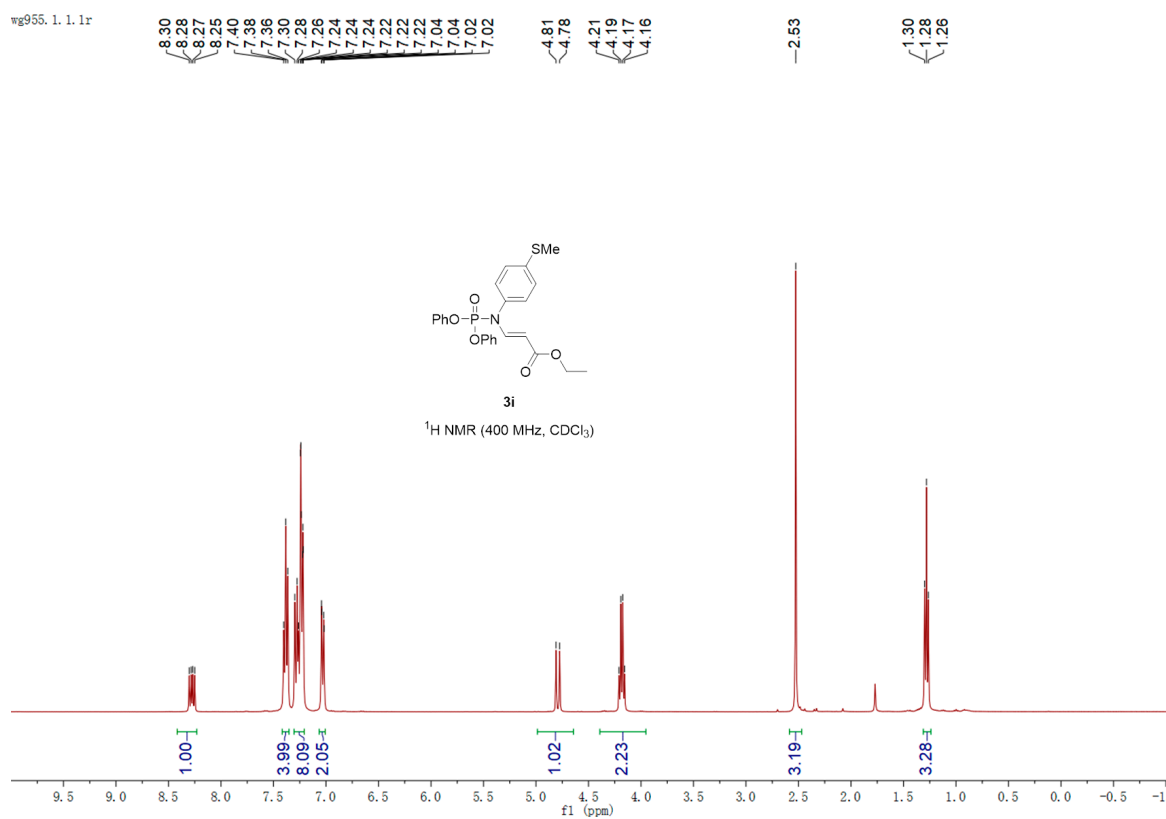
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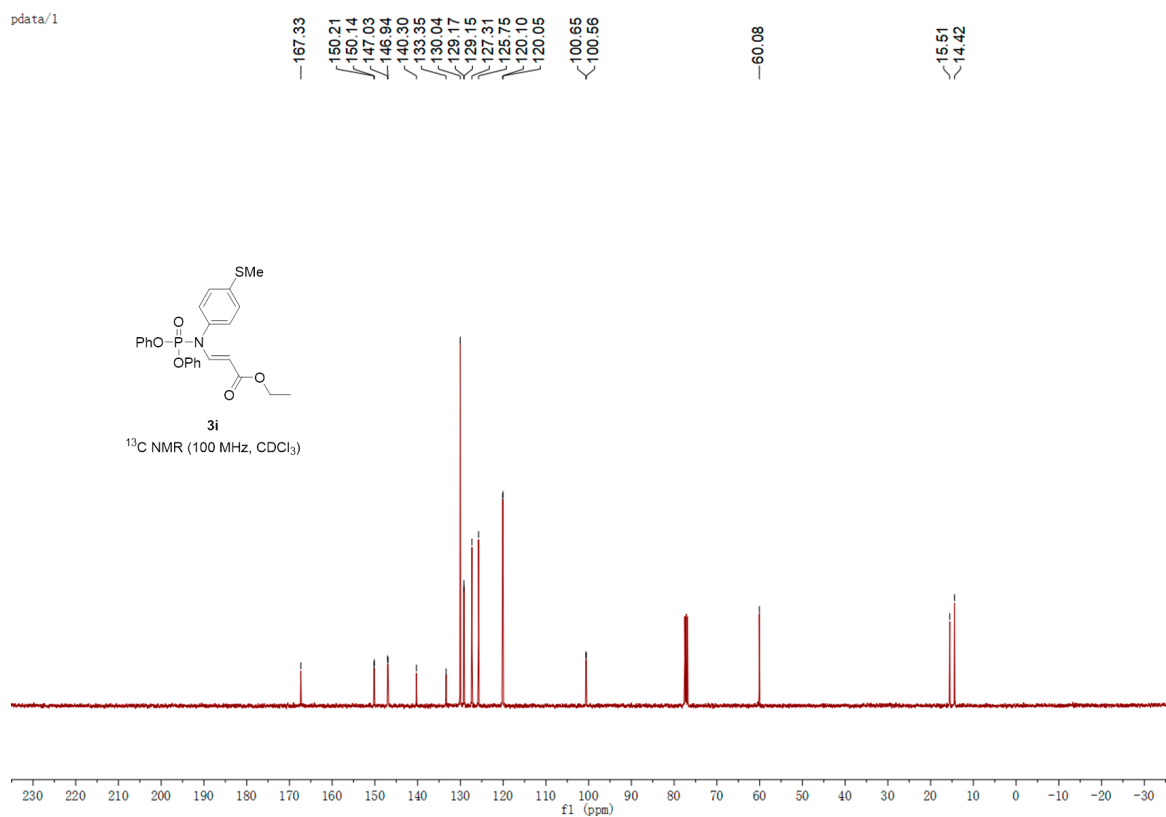
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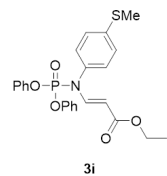
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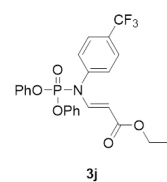
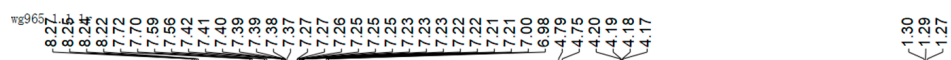
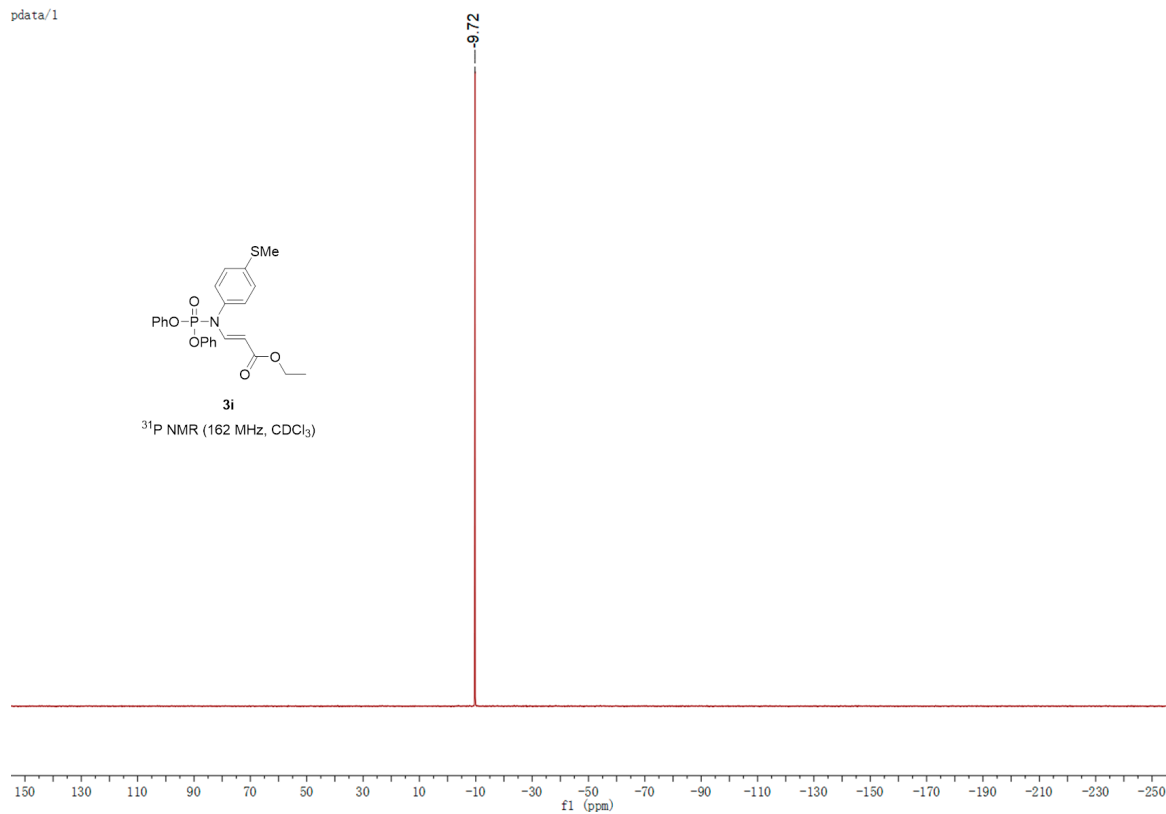
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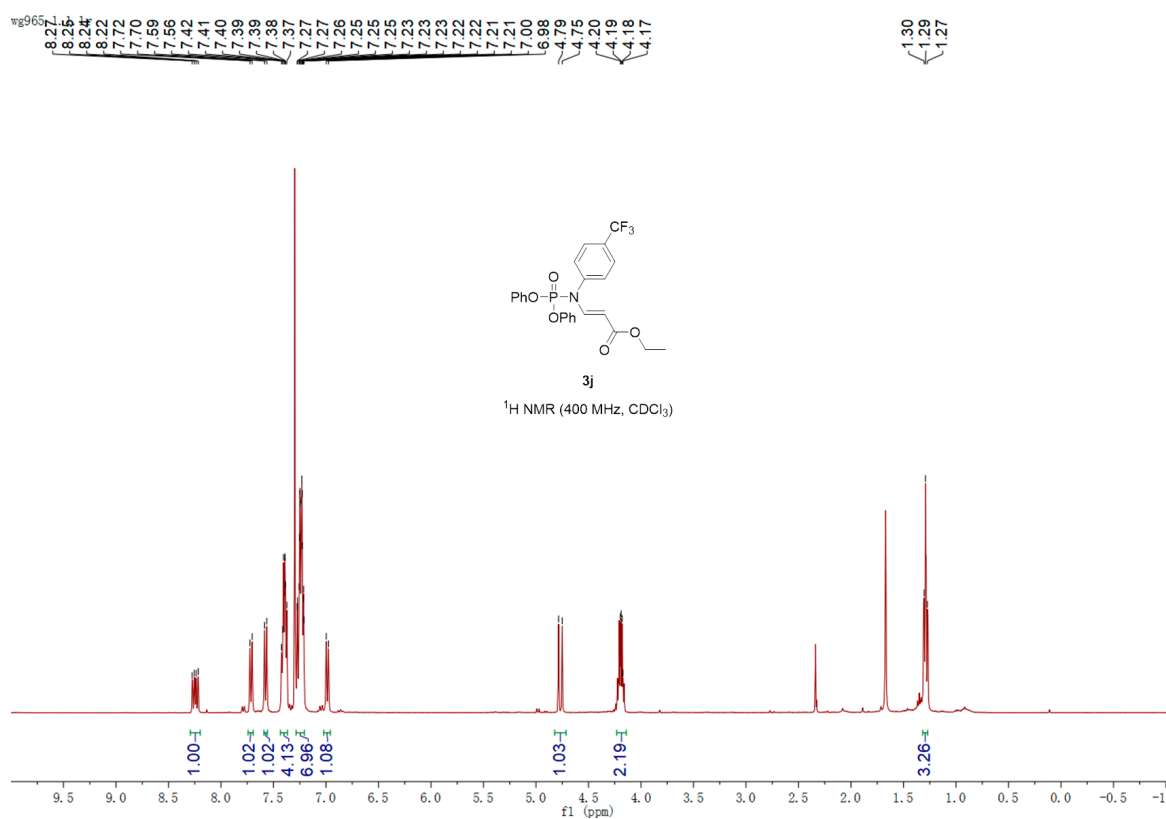
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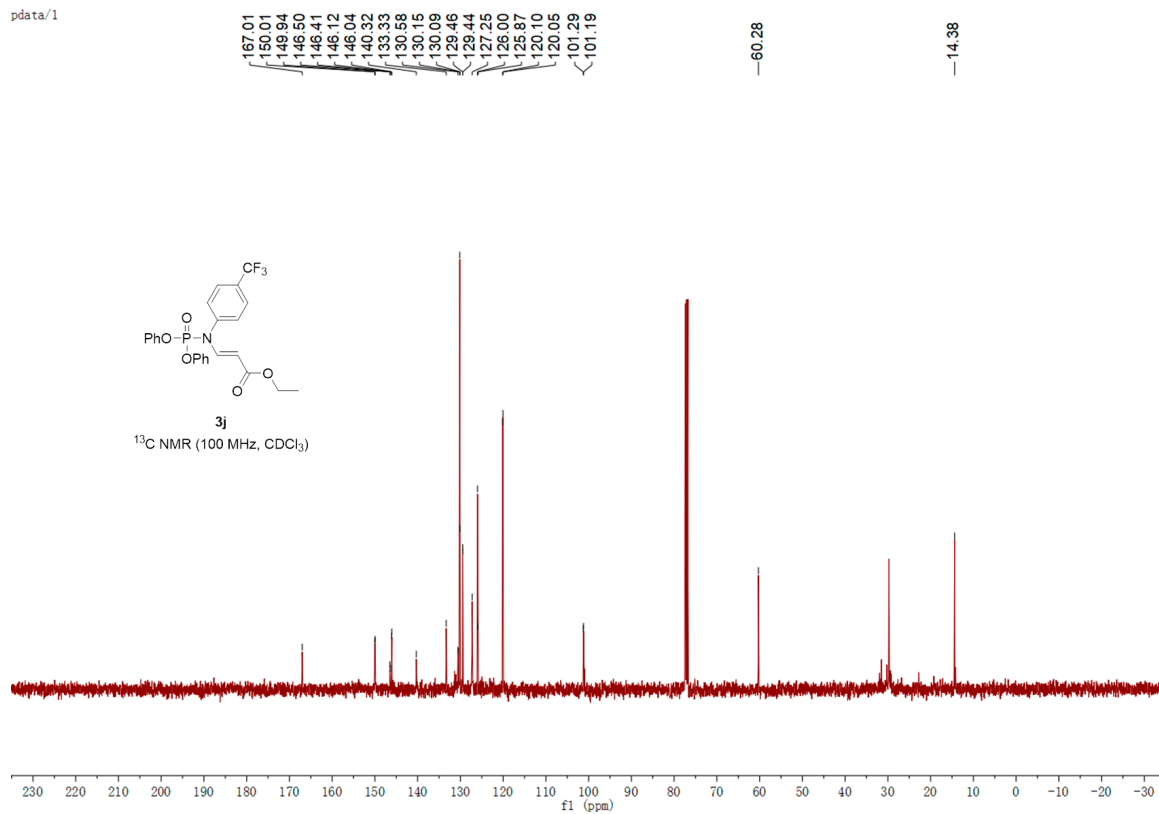
$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )



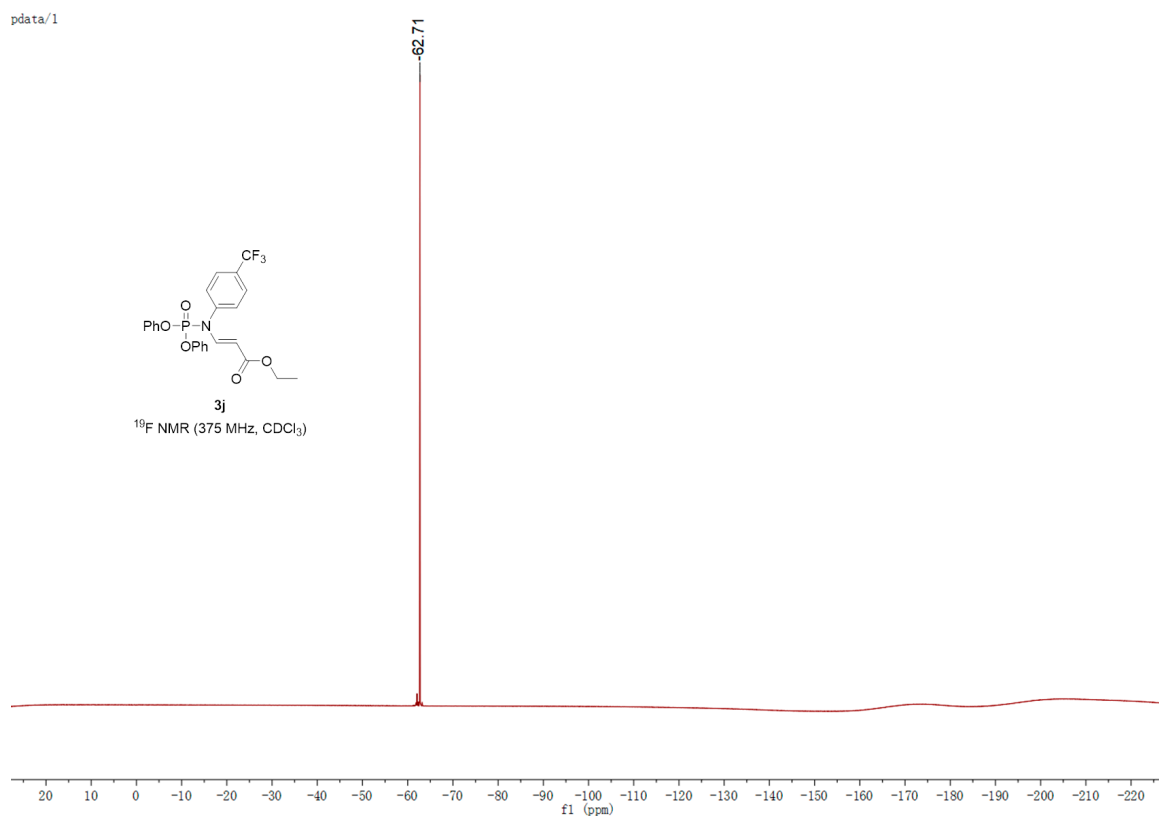
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



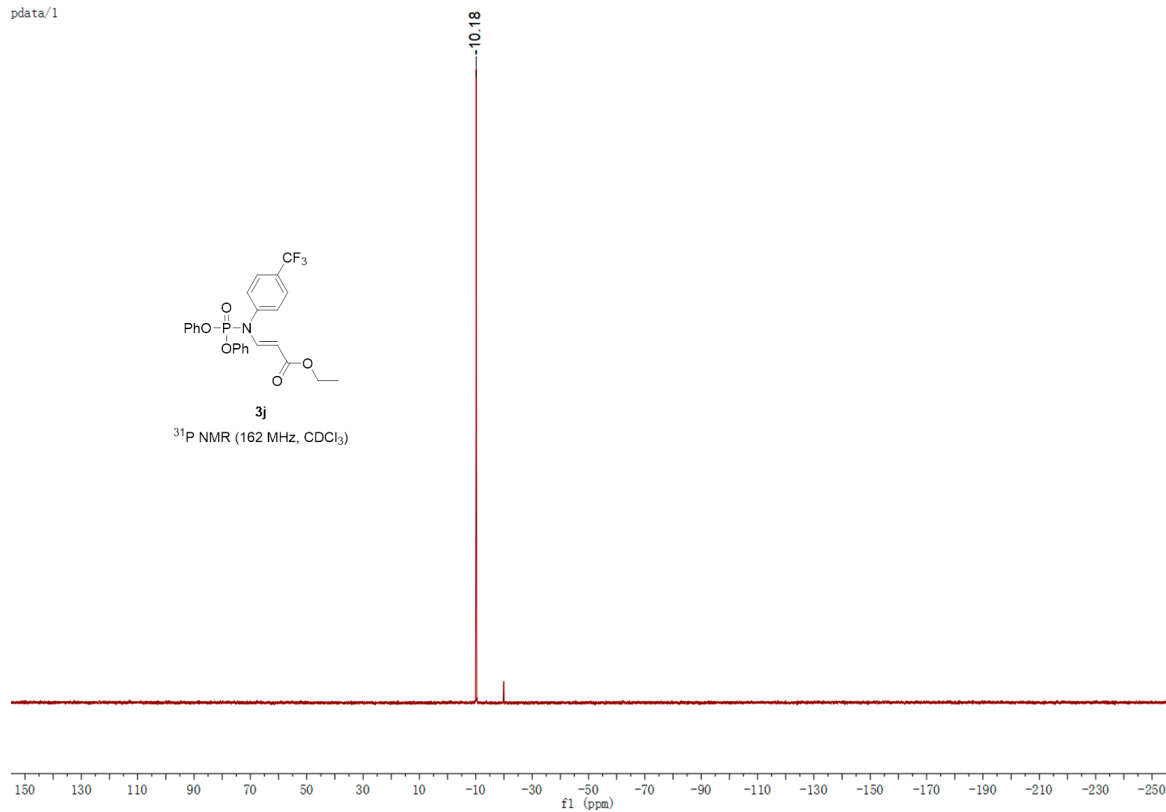
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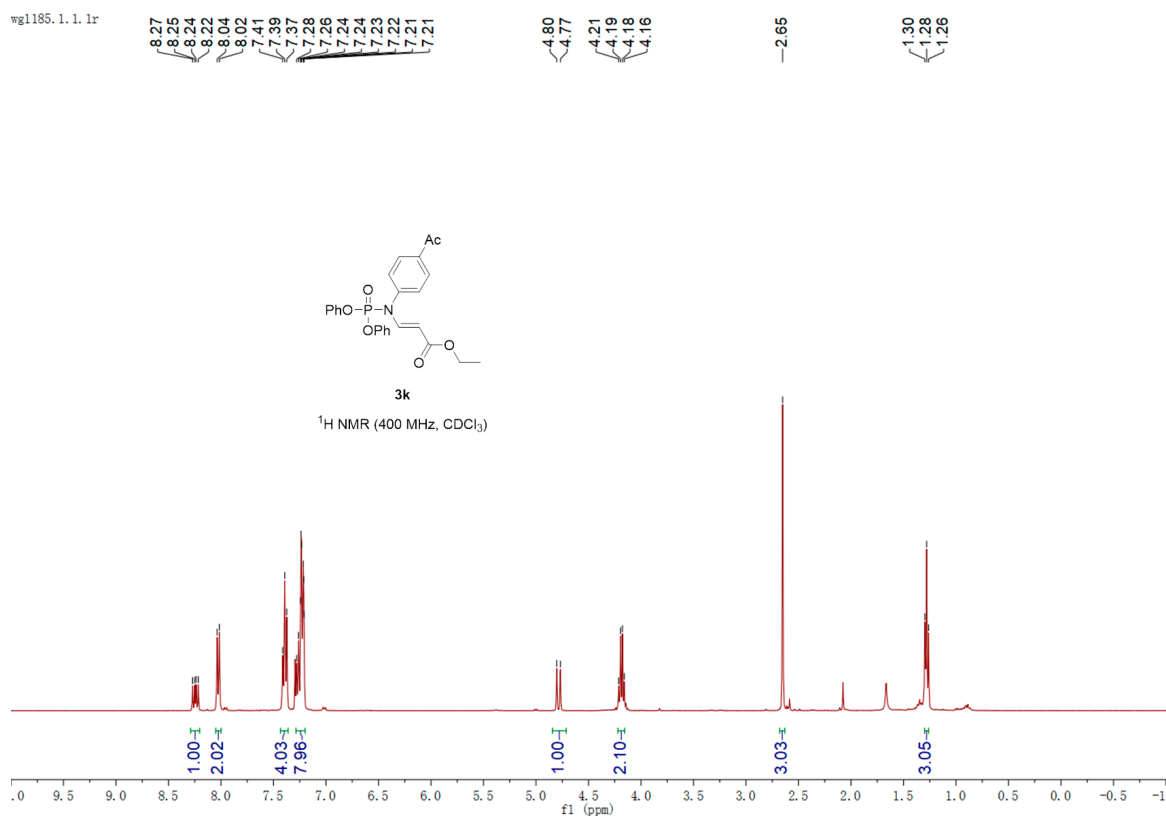
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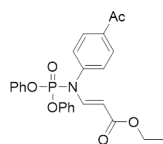


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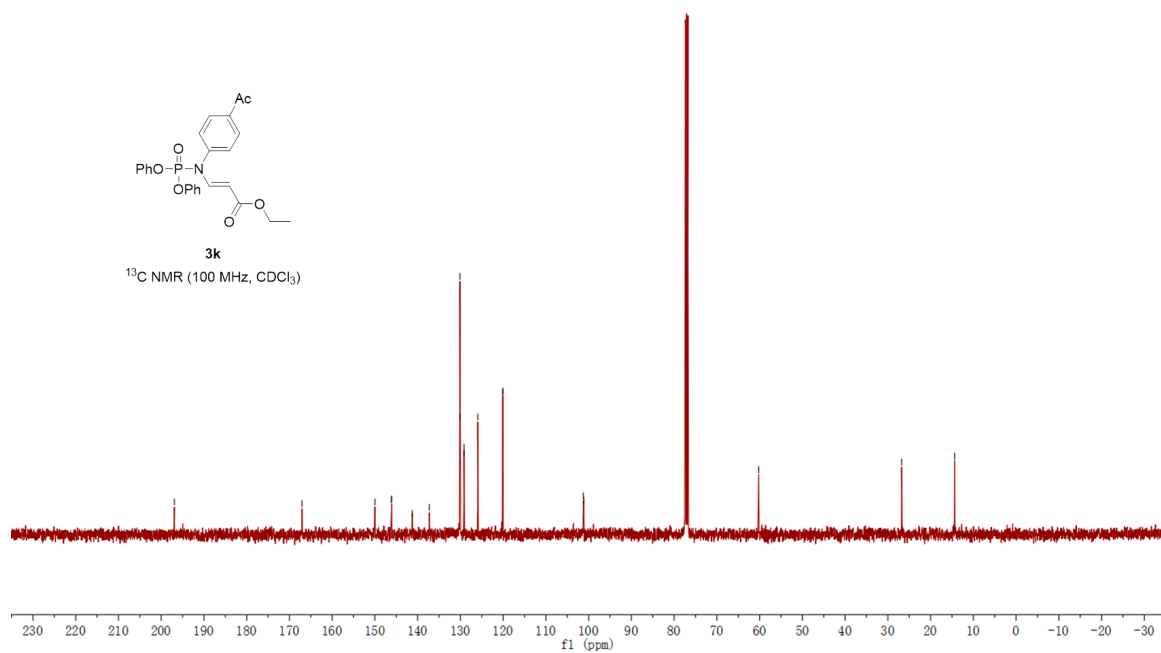
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<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  
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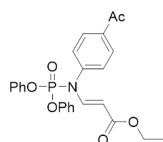


**3k**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

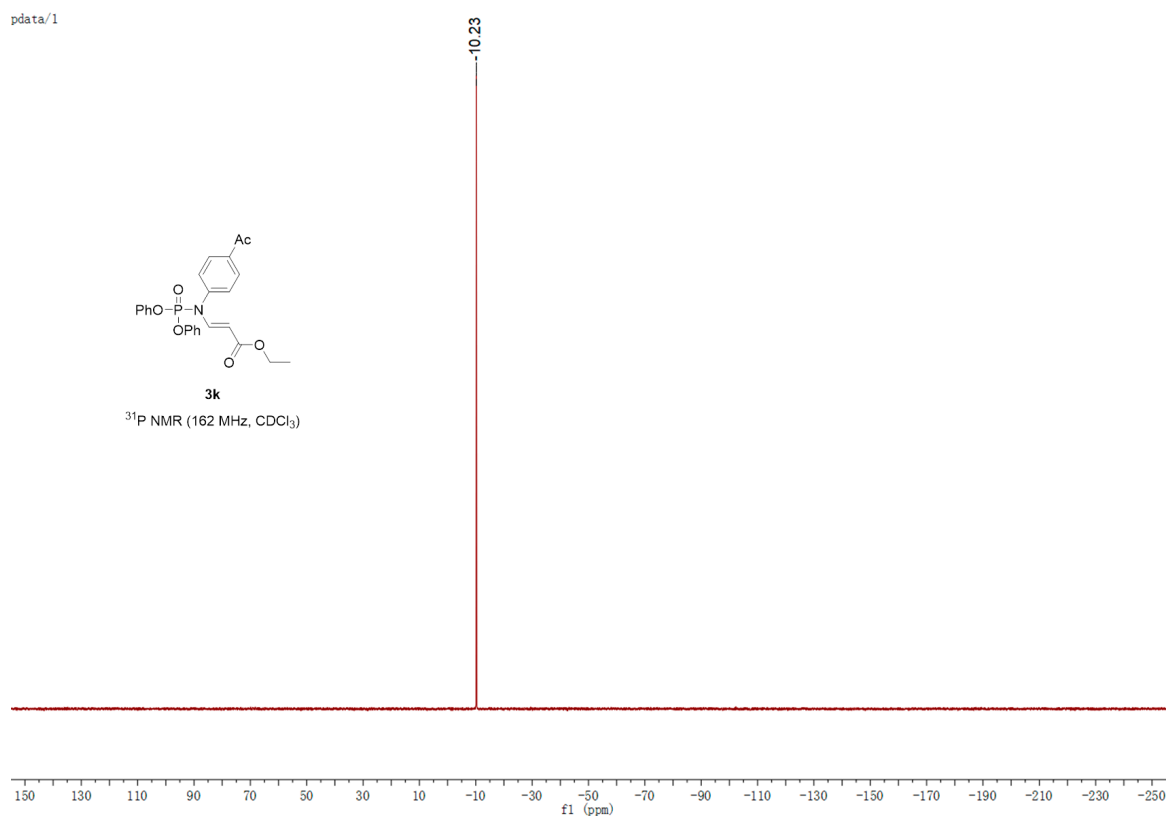


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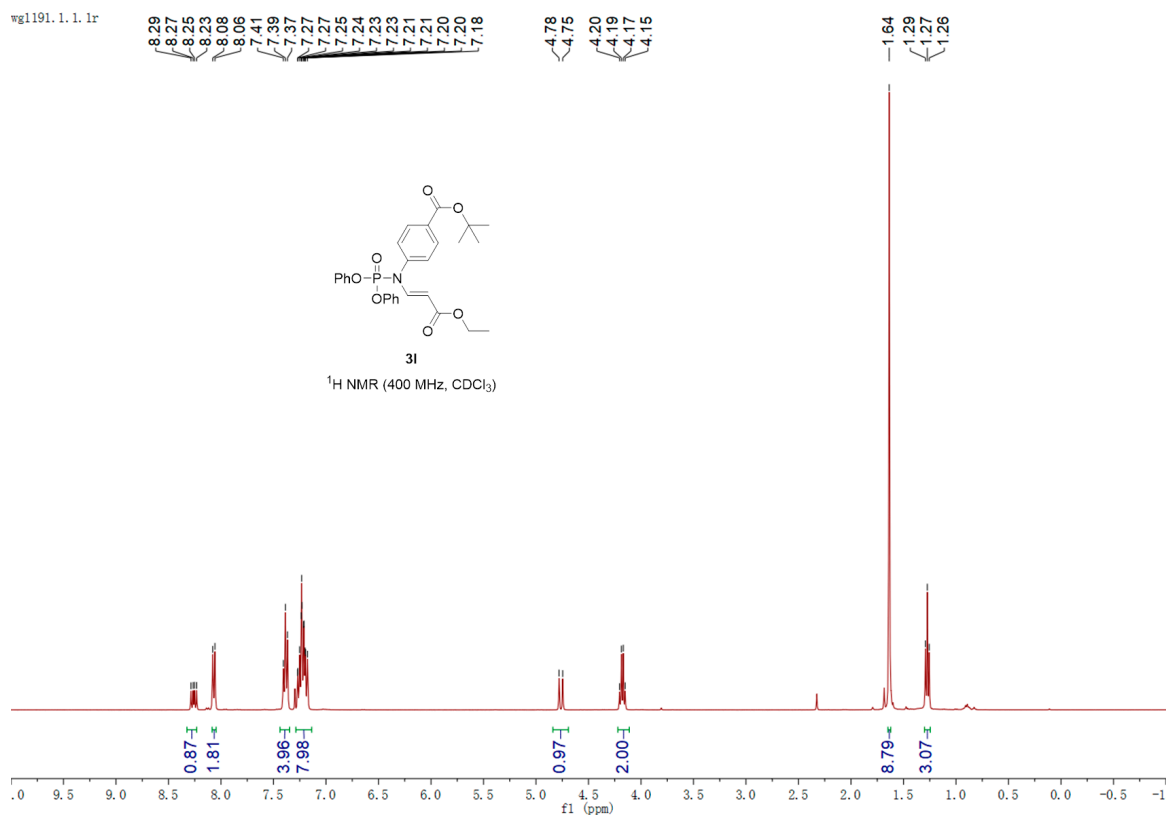
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<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)

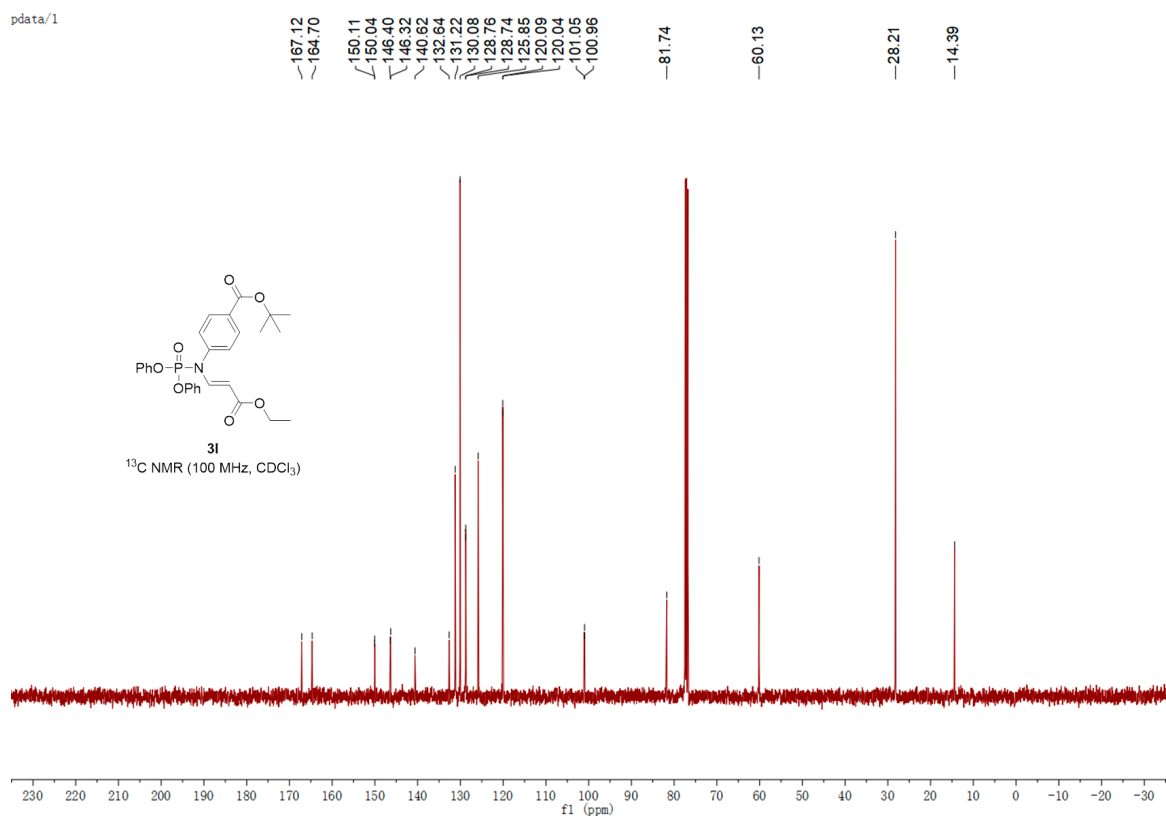




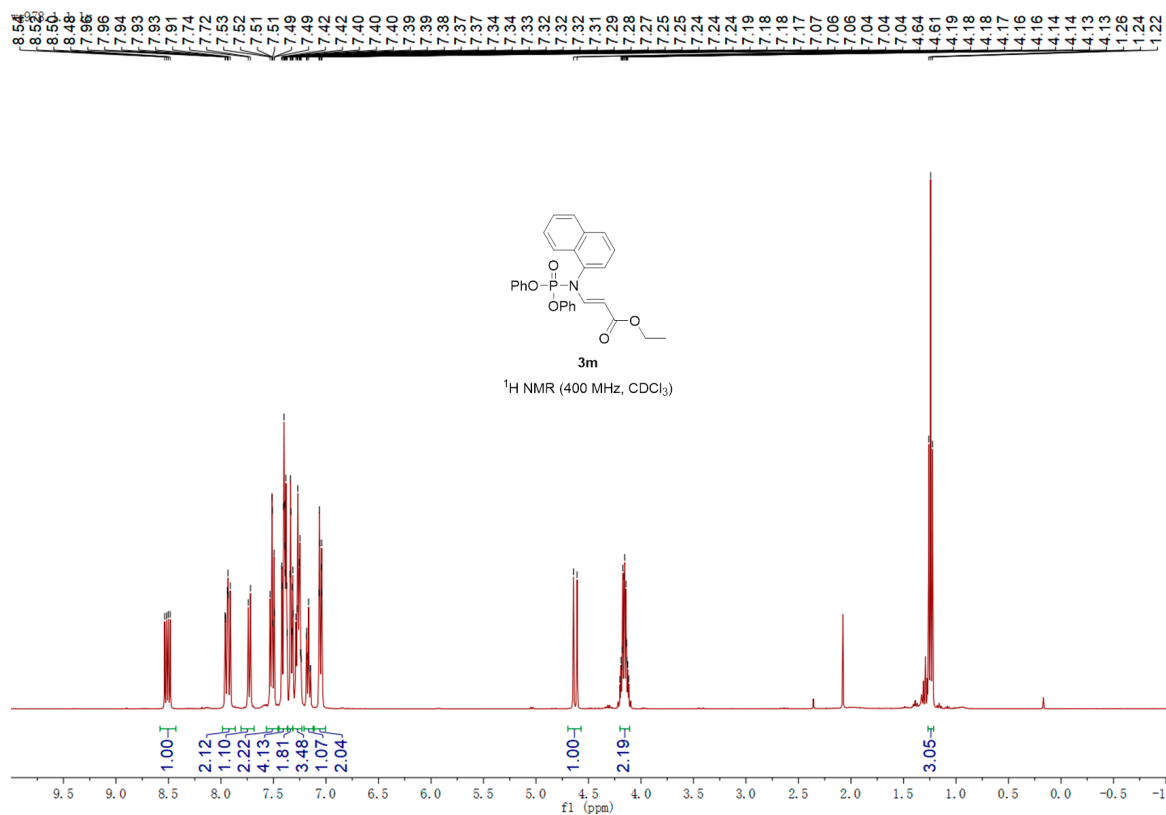
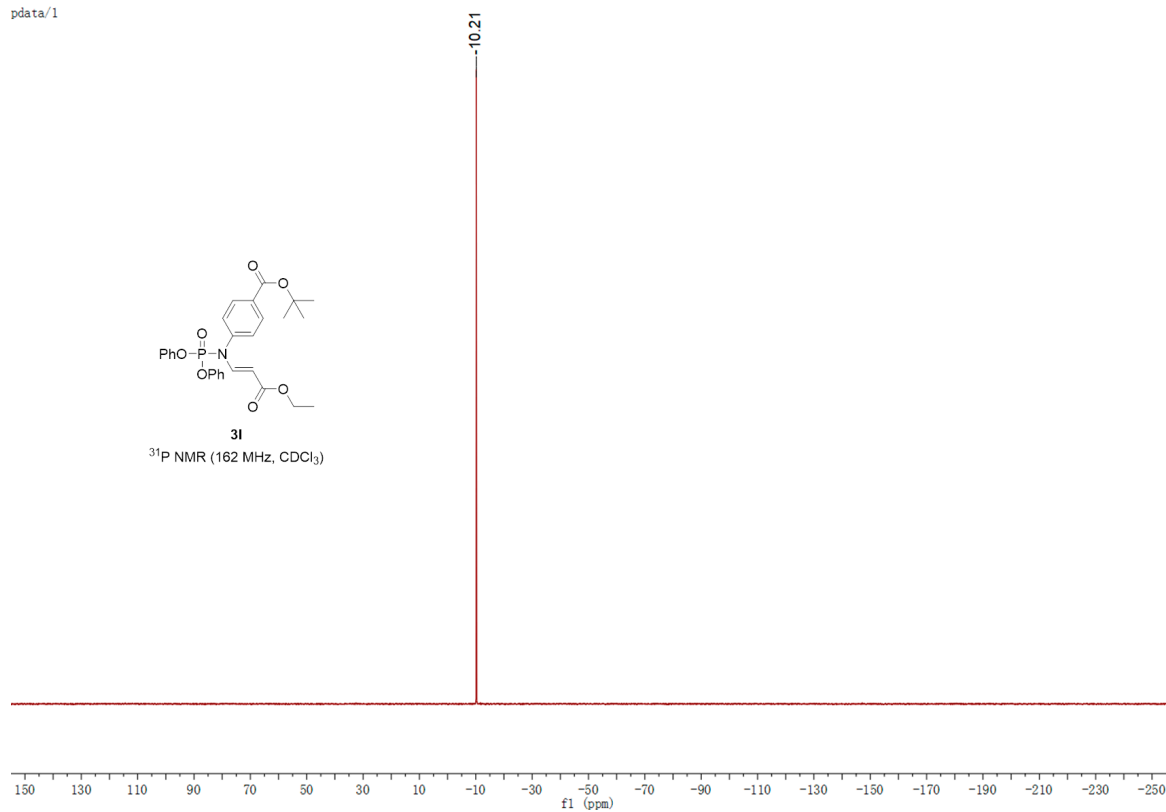
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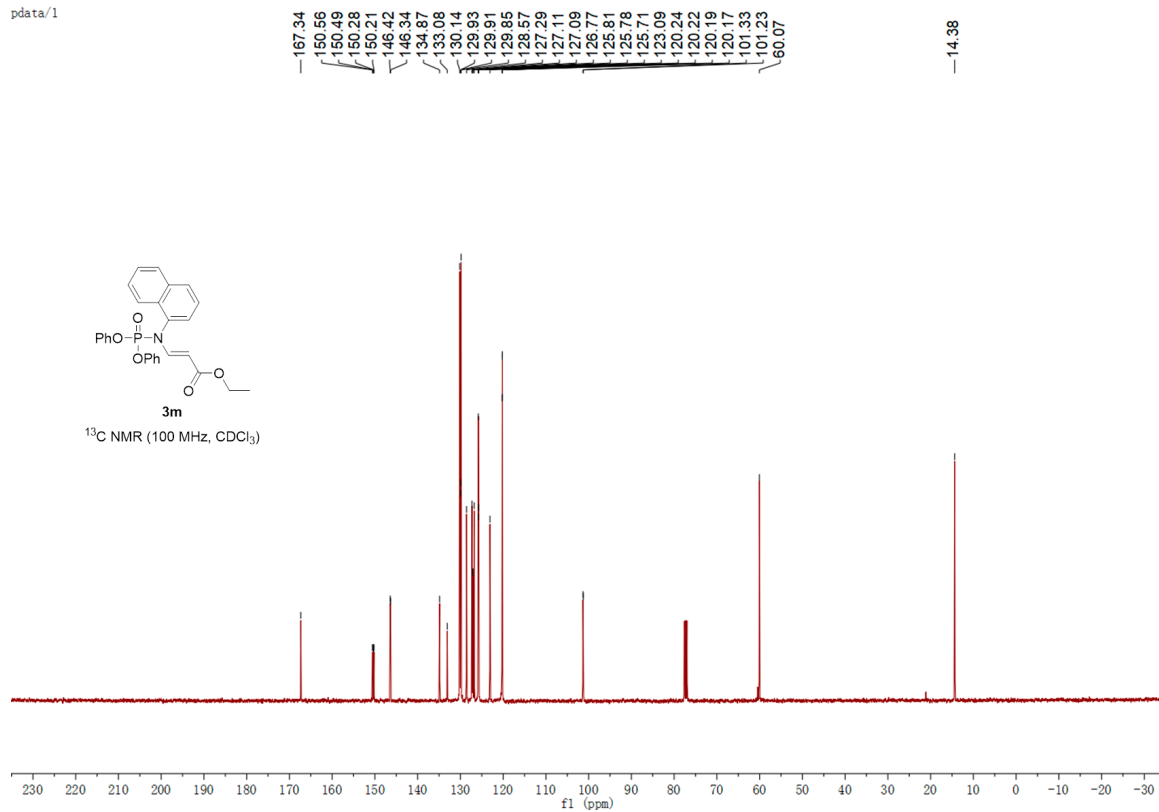
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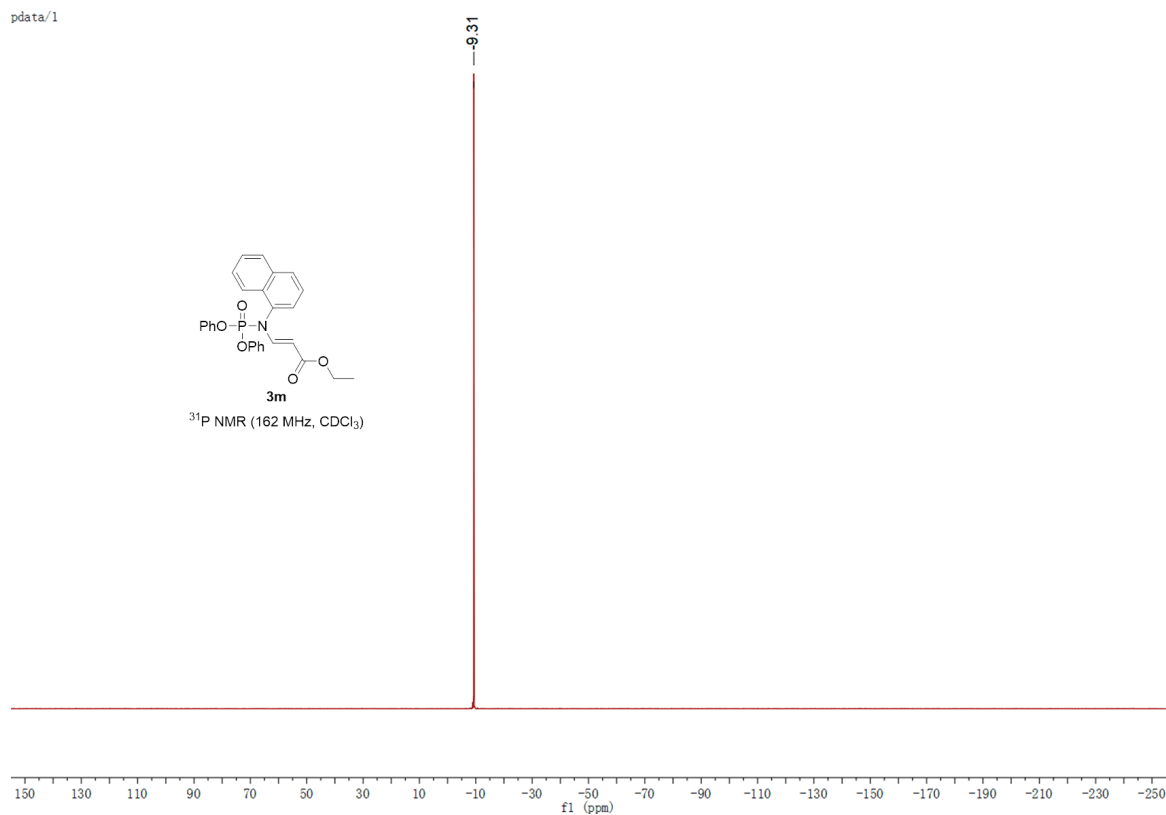
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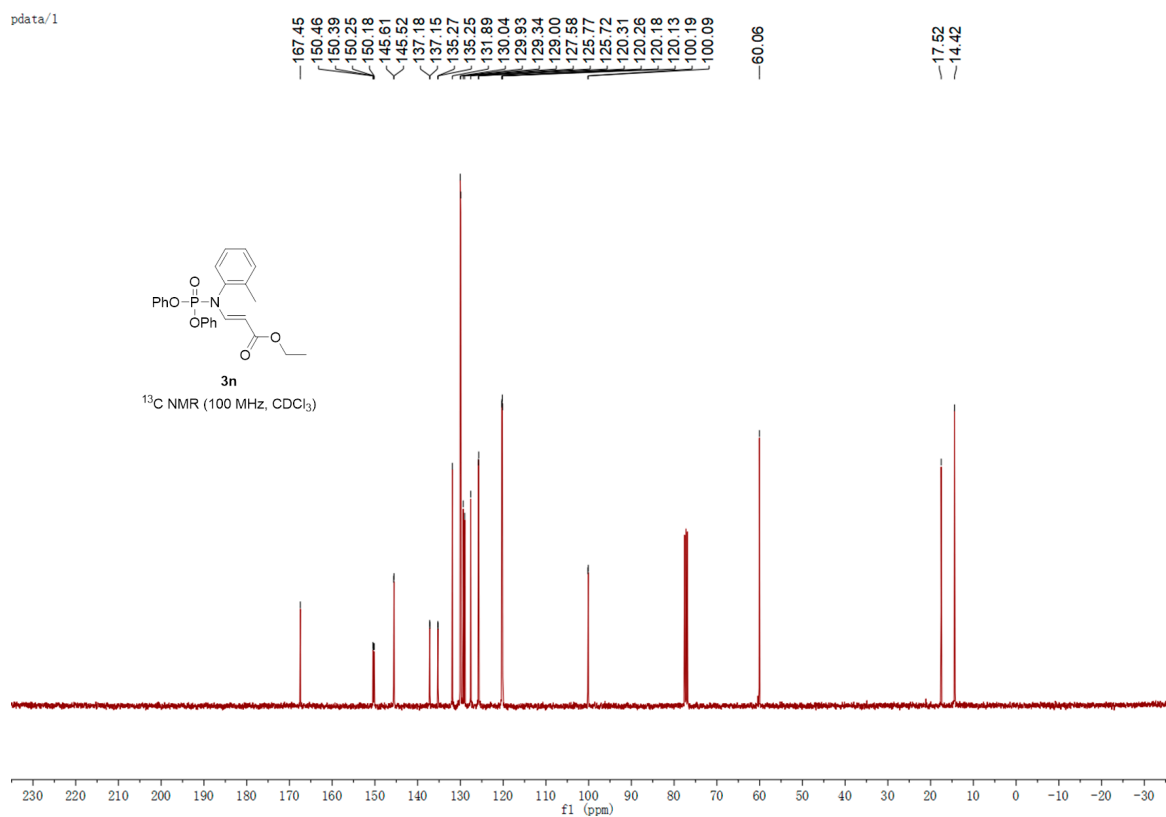
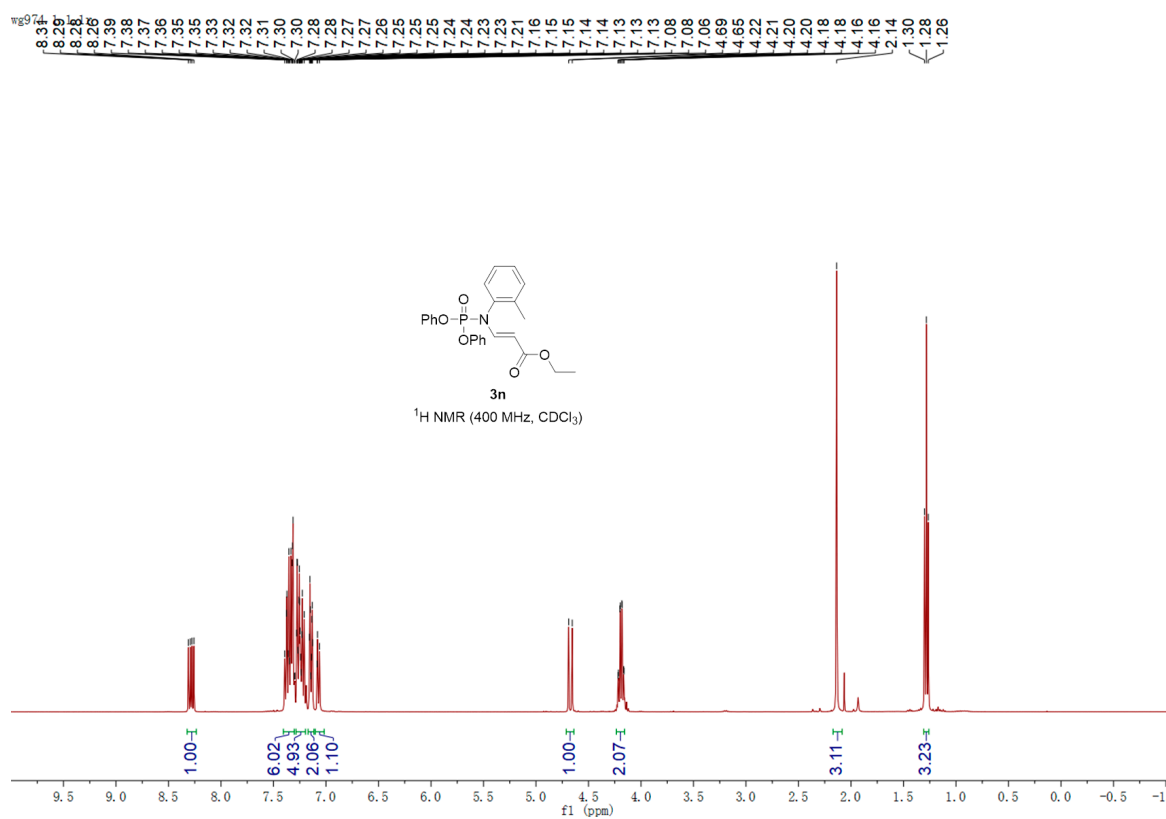


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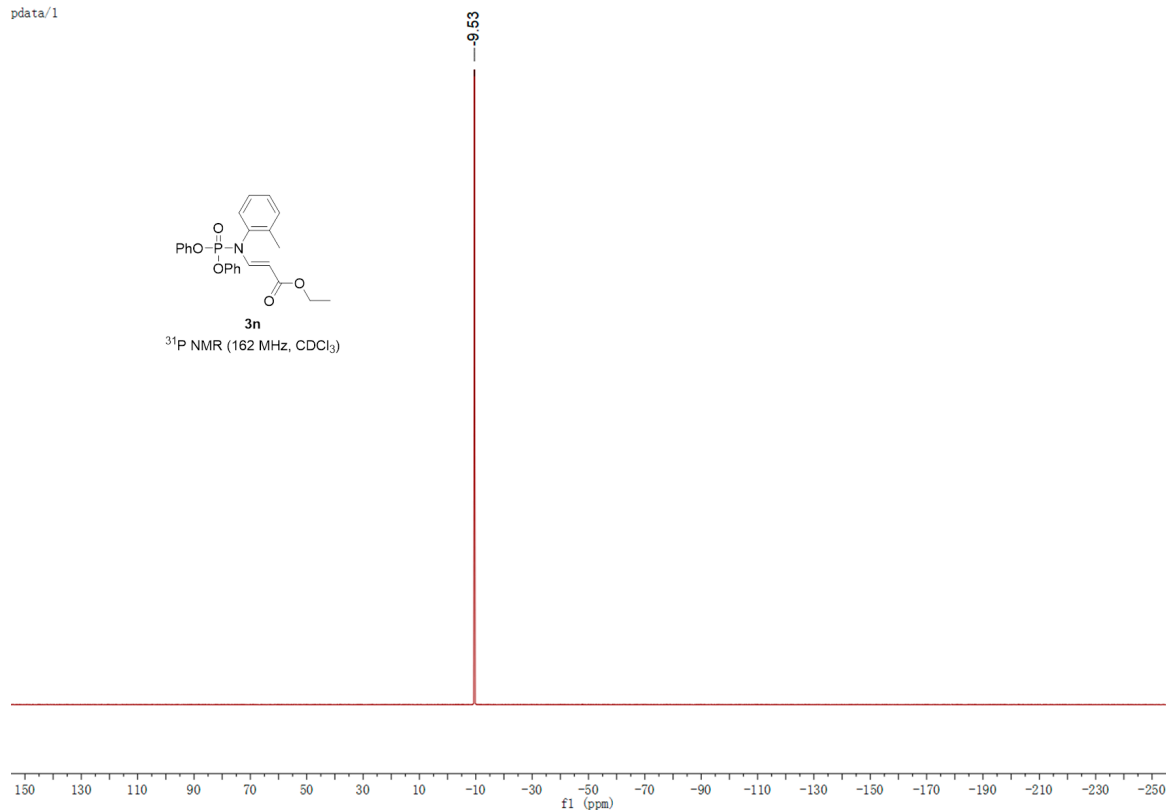
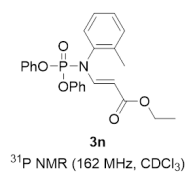


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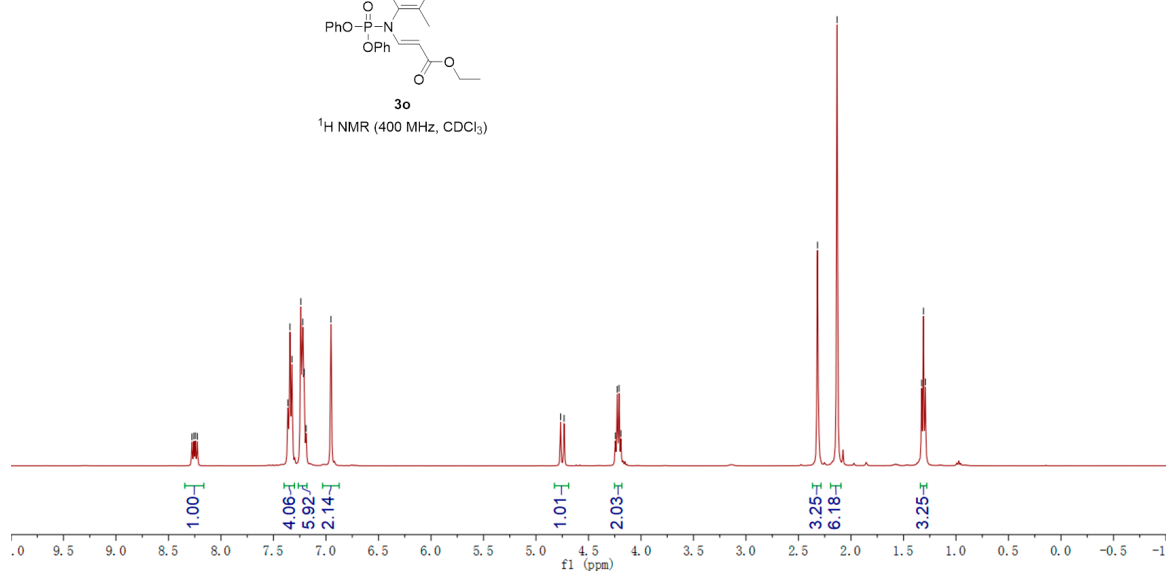
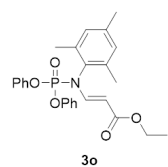


pdata/1

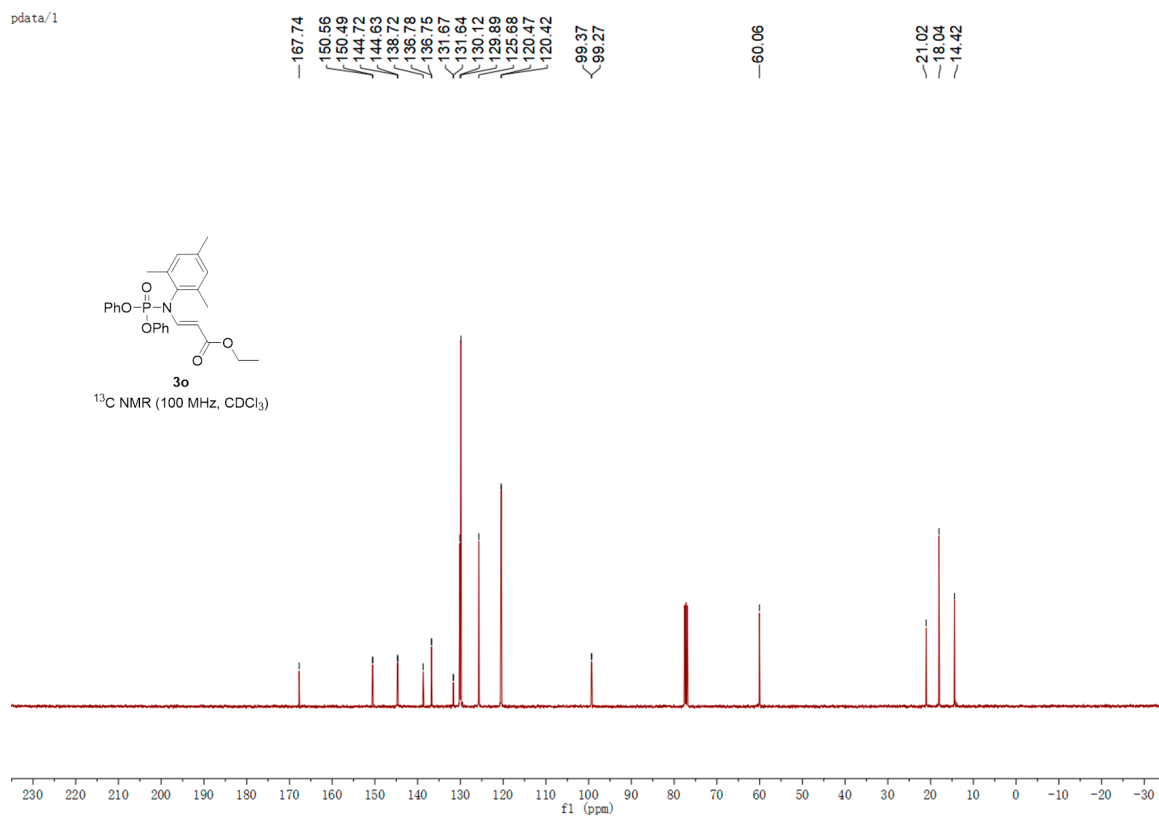


wg1192.1.1.1r

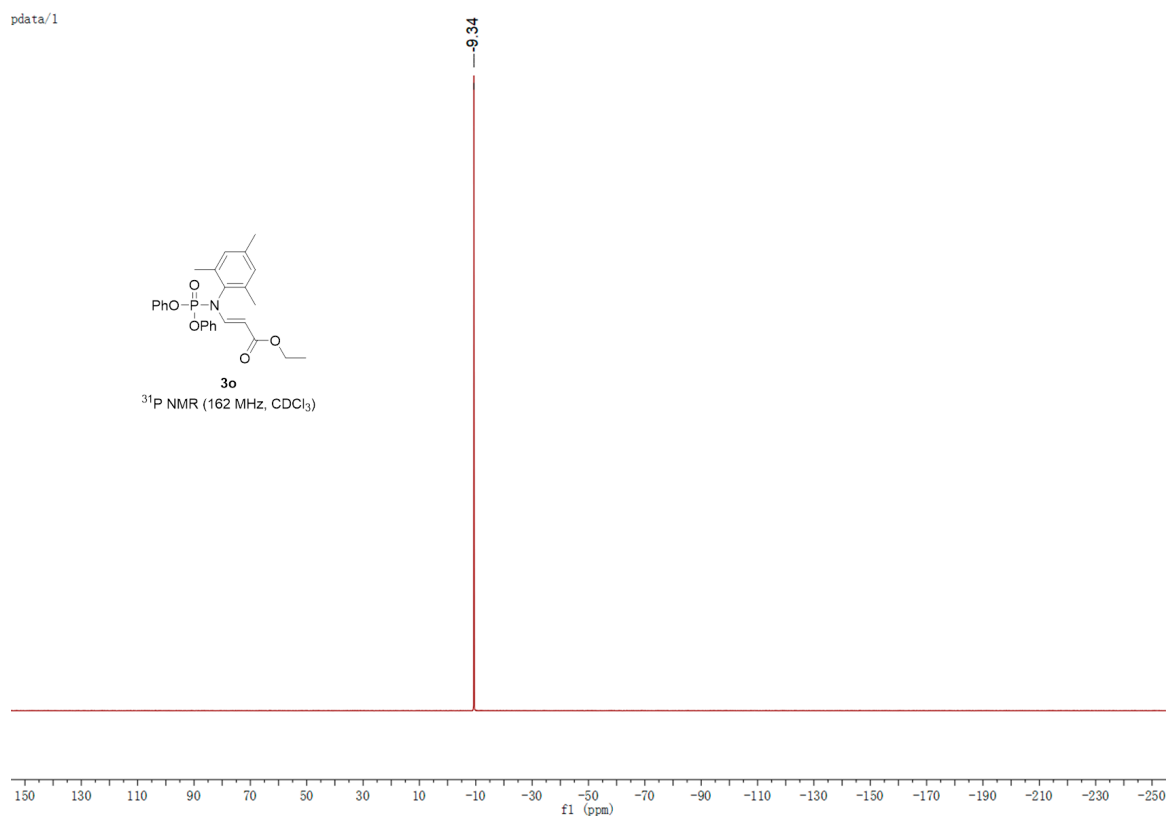
8.28  
8.26  
8.24  
8.23  
7.96  
7.94  
7.92  
7.92  
7.24  
7.22  
7.21  
7.19  
6.95  
4.77  
4.73  
4.24  
4.23  
4.21  
4.19  
-2.32  
-2.13  
1.33  
1.31  
1.29



pdata/1



pdata/1



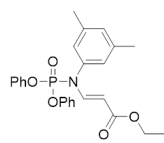
wg957.1.1.1r

8.42  
8.40  
8.39  
8.37  
7.52  
7.50  
7.48  
7.37  
7.35  
7.34  
7.15  
6.79

4.92  
4.89  
4.33  
4.31  
4.29  
4.27

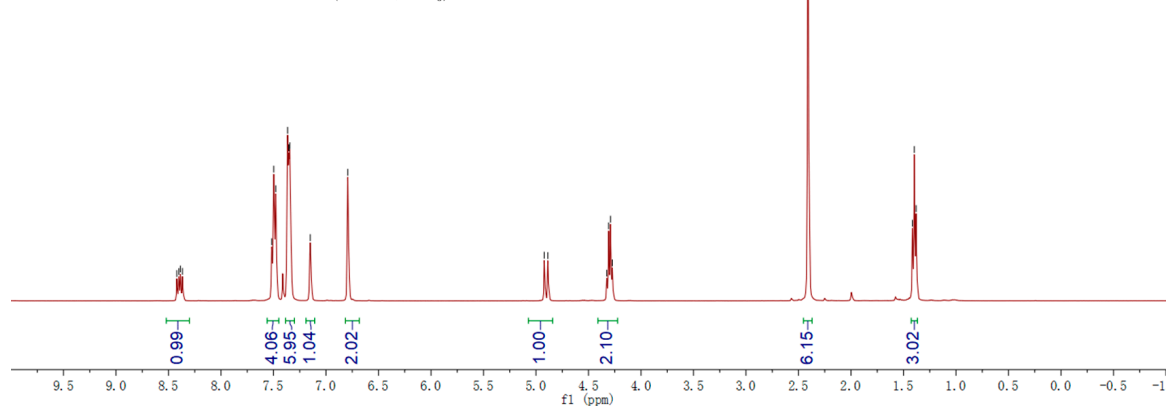
2.41

1.41  
1.40  
1.38



**3p**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

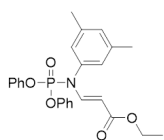


pdata/1

167.49  
150.35  
150.28  
147.19  
147.10  
139.71  
136.41  
136.38  
130.68  
129.96  
126.34  
126.31  
125.66  
120.17  
120.12  
100.46  
100.37

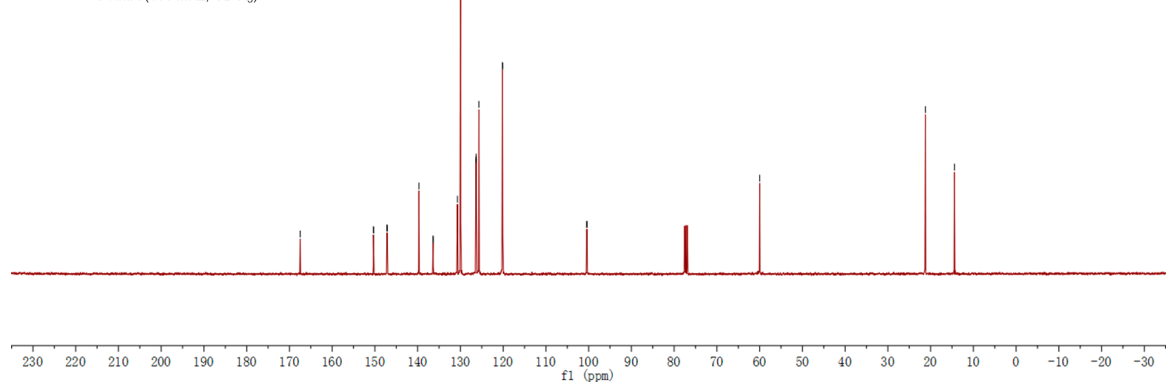
60.00

21.22  
14.44

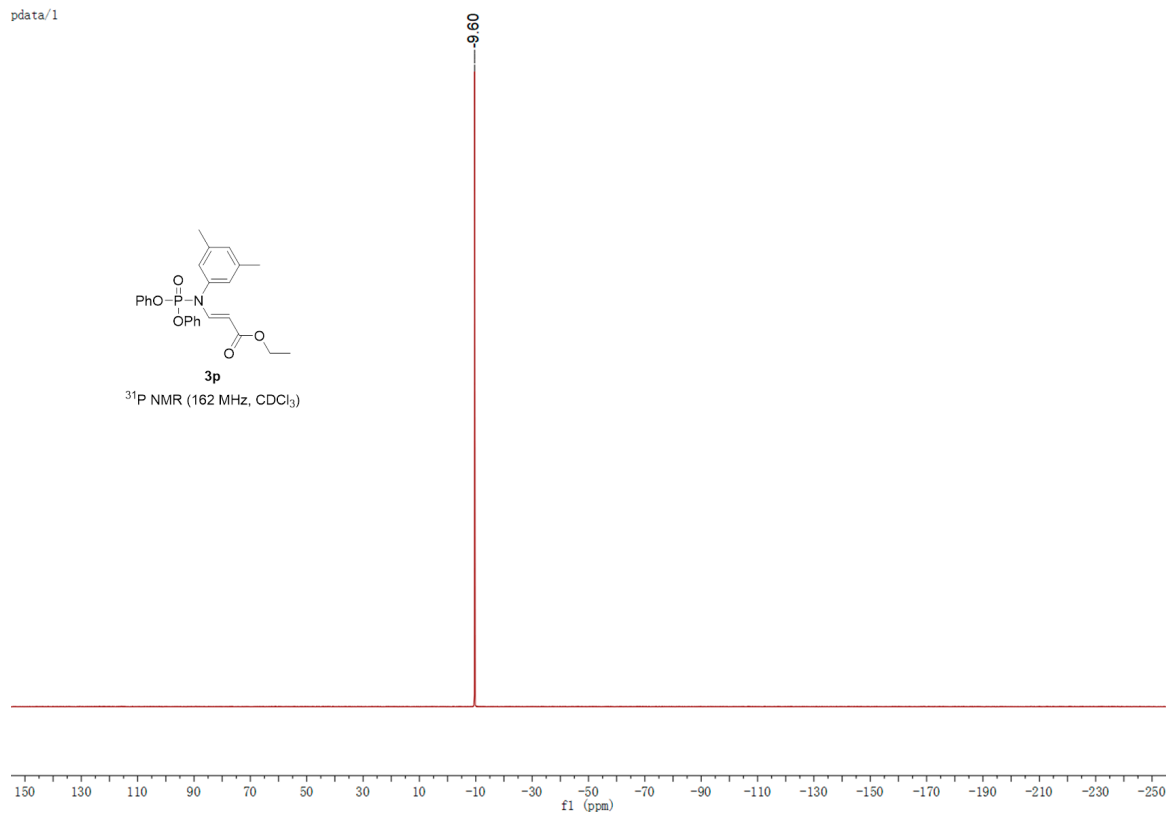


**3p**

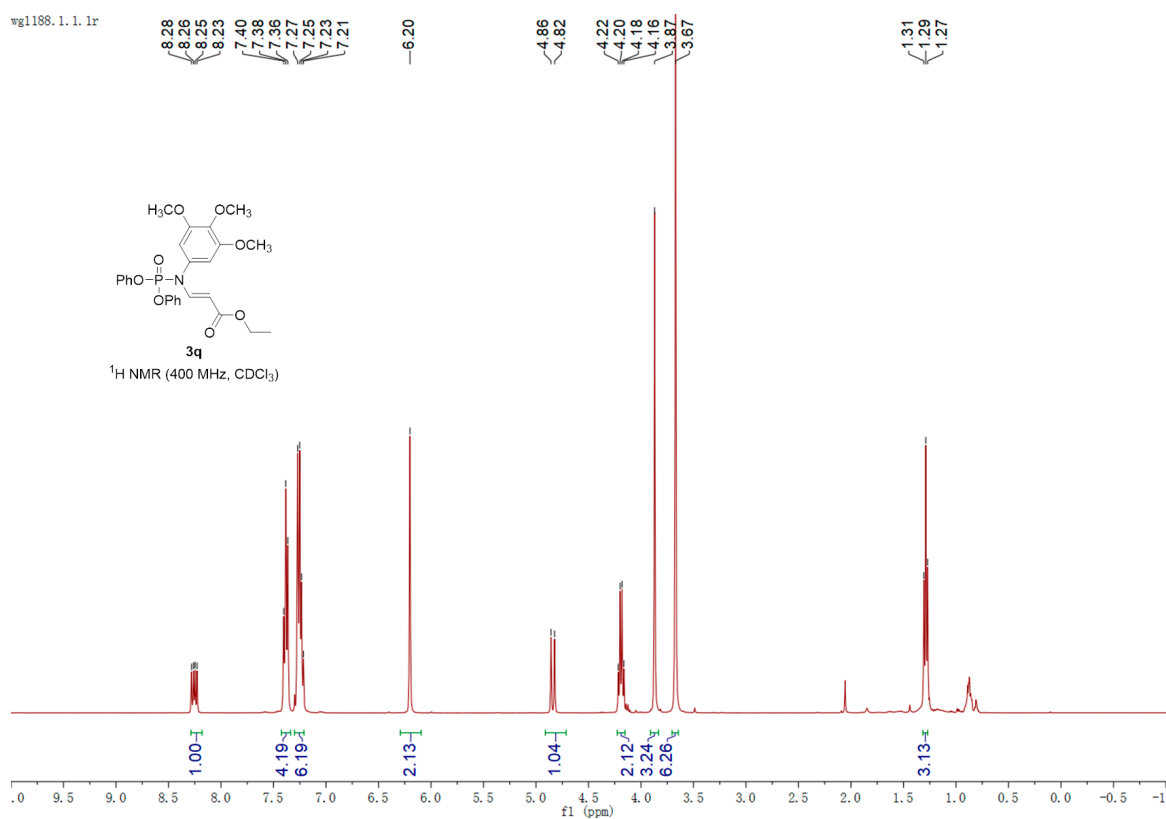
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



pdata/1

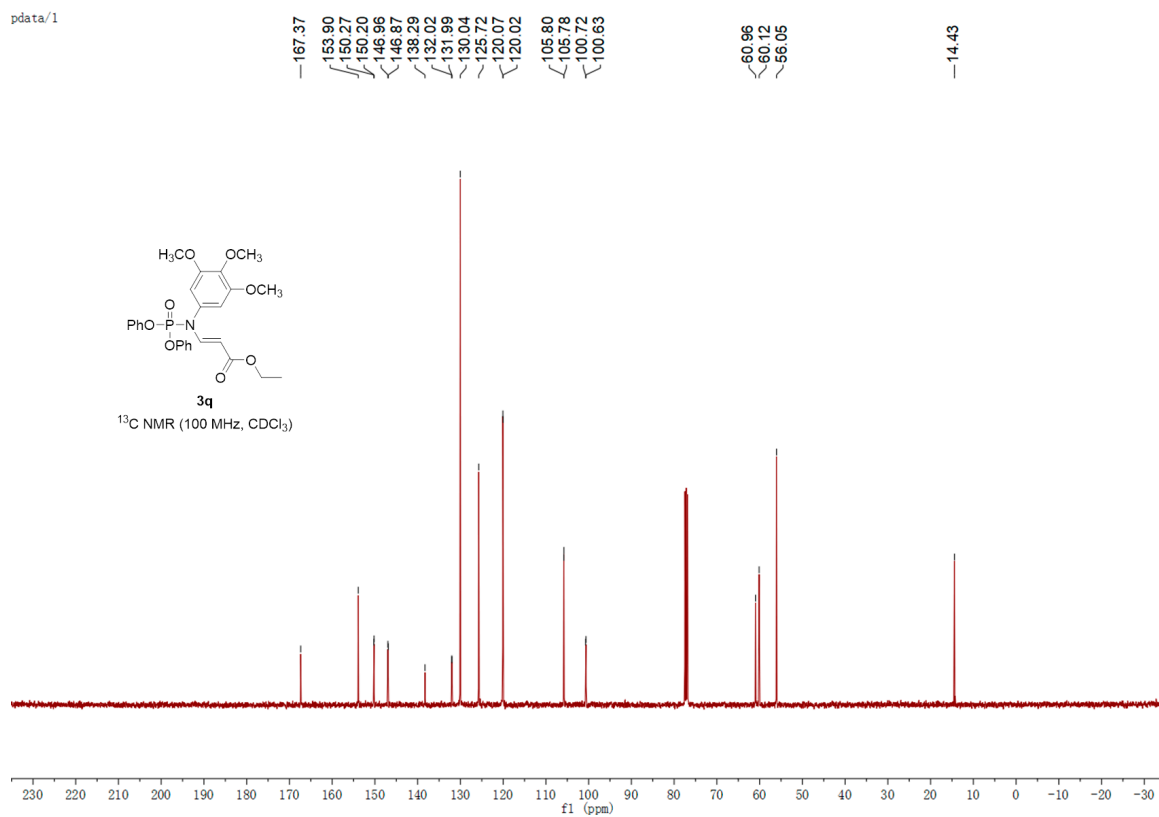


wg1188.1.1.1r

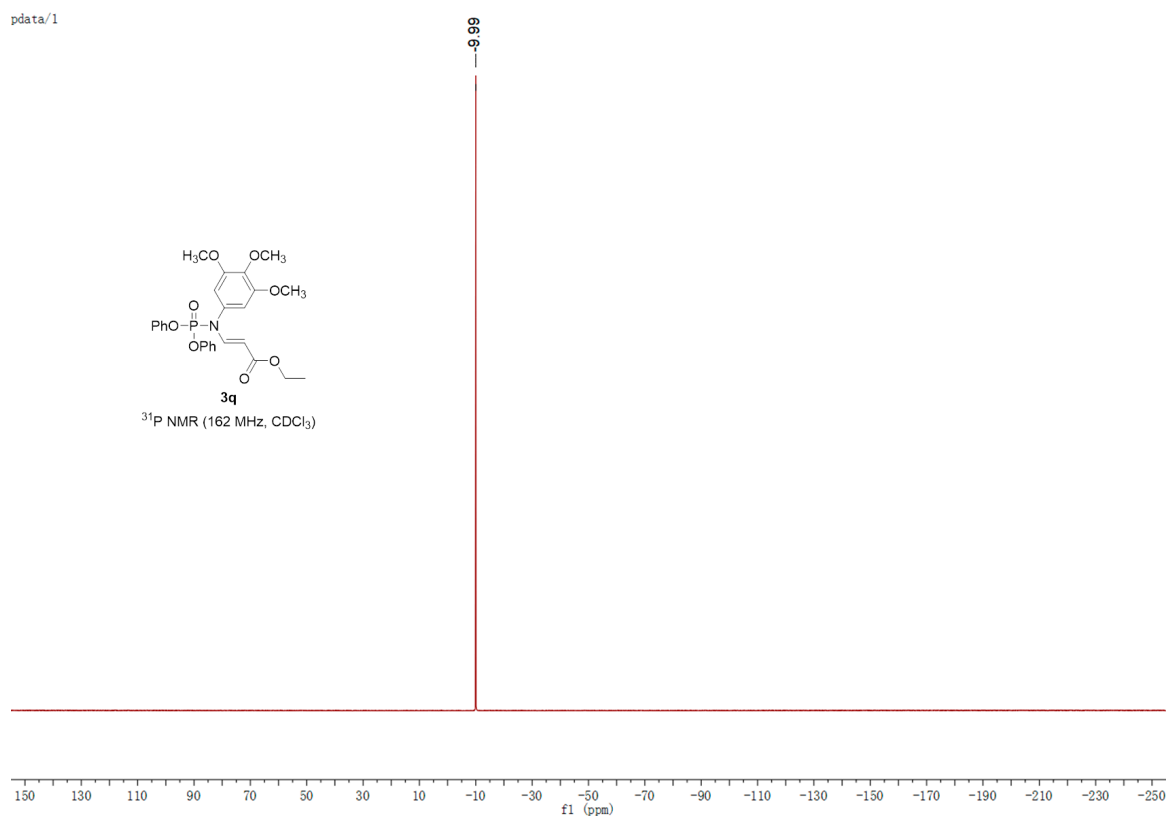




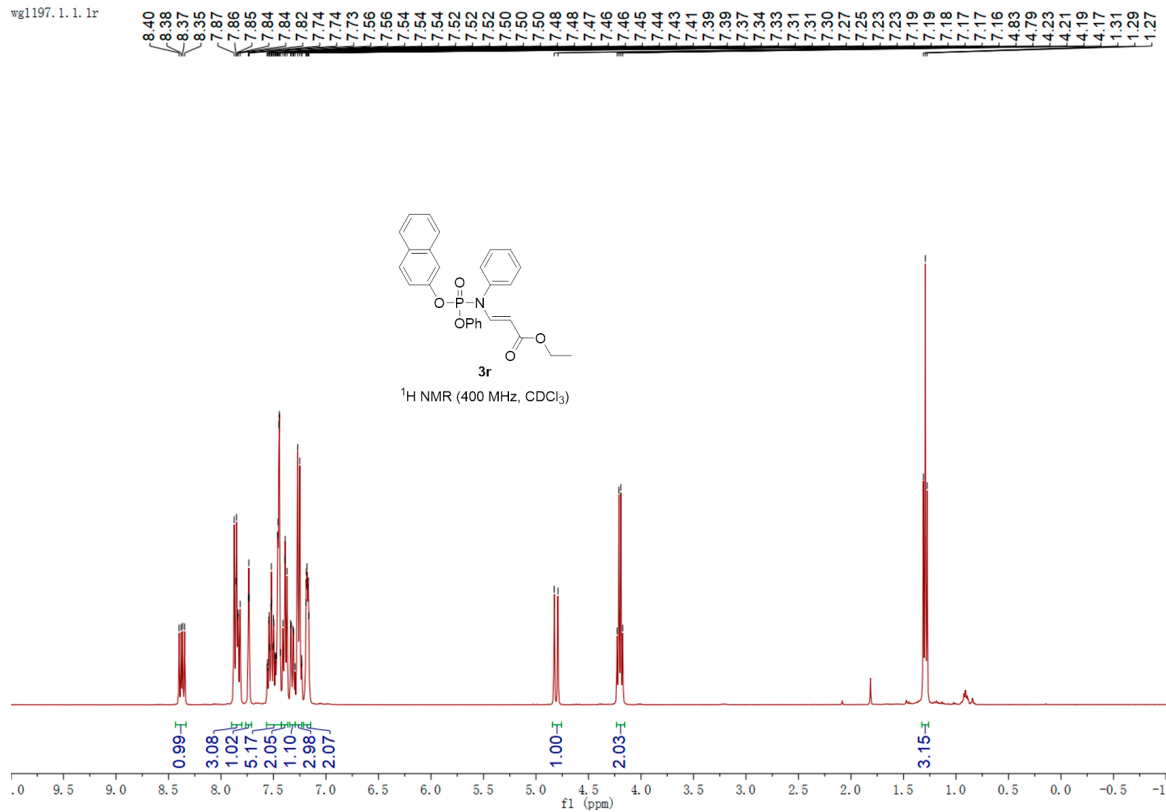
pdata/1



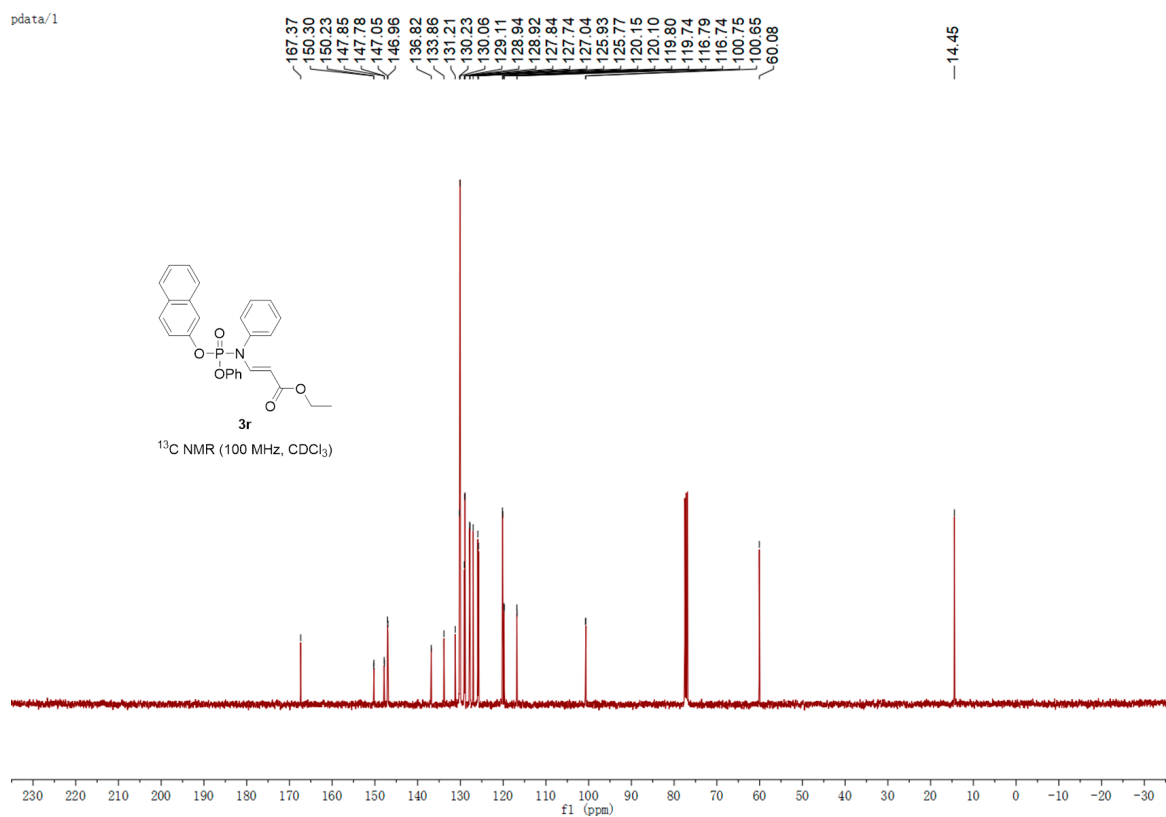
pdata/1



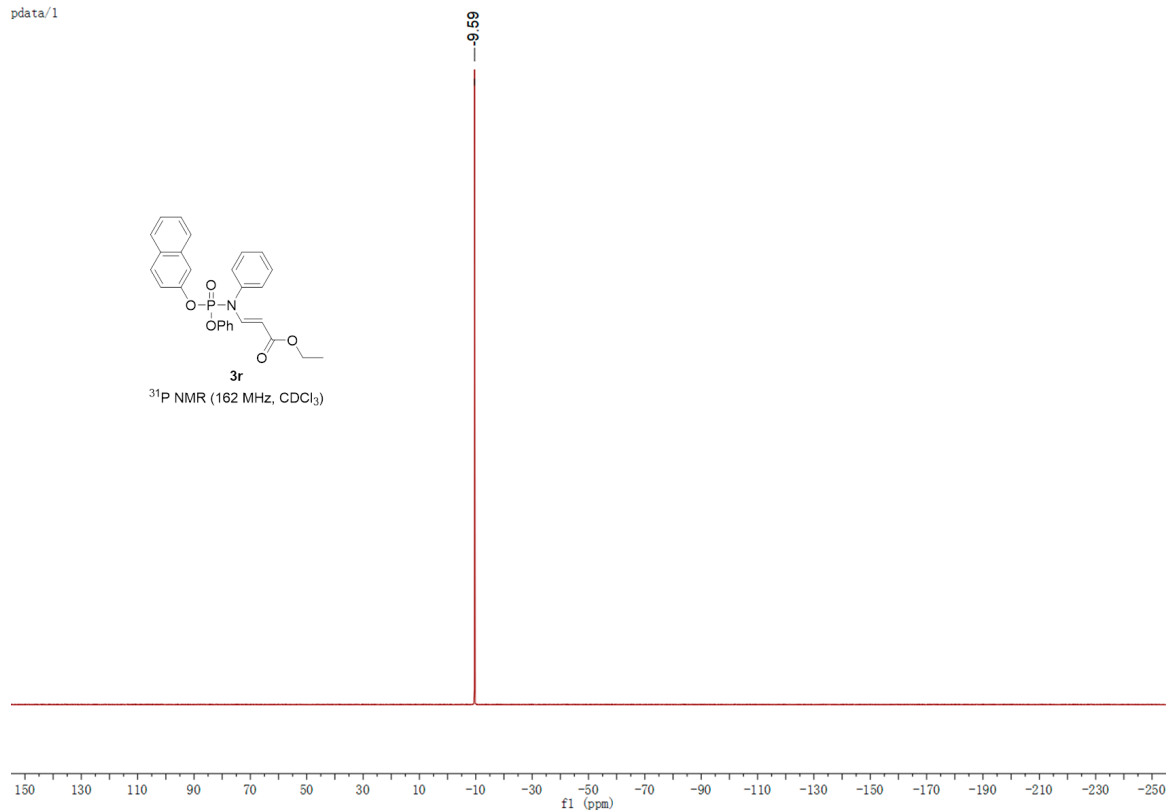
wg1197.1.1.1r



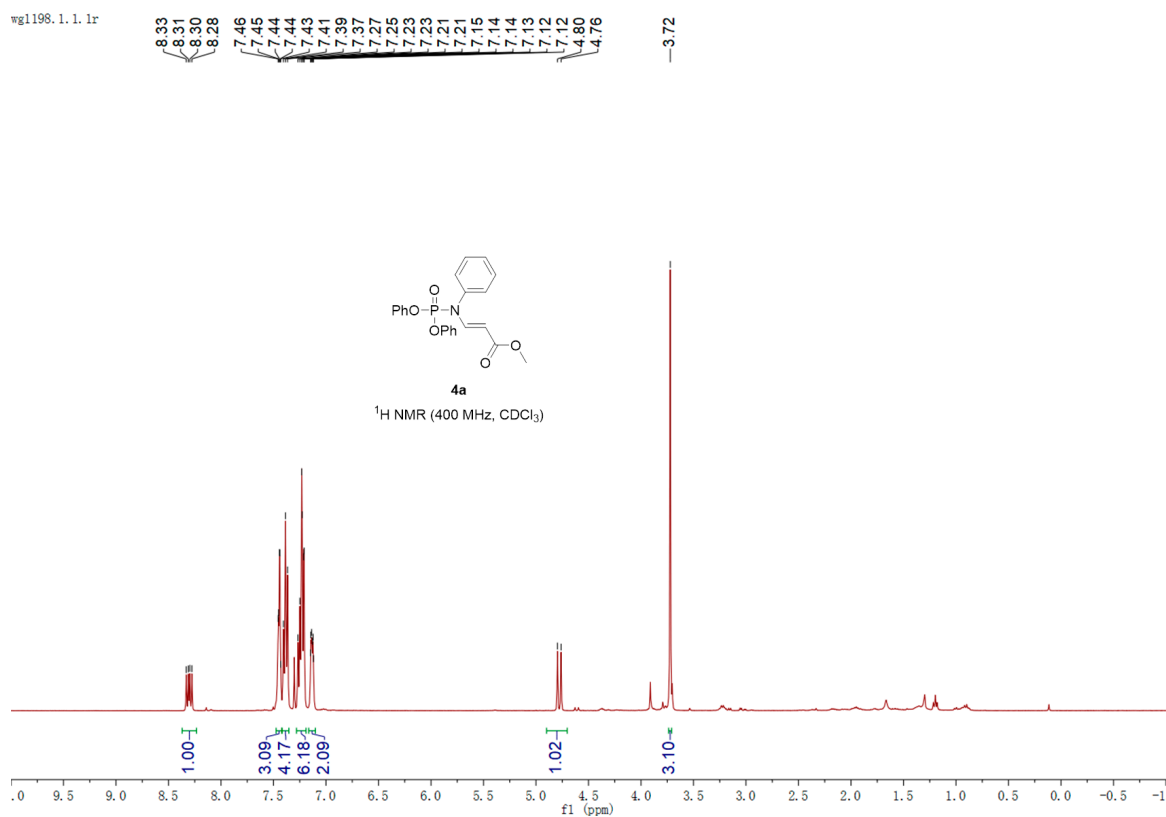
pdata/1



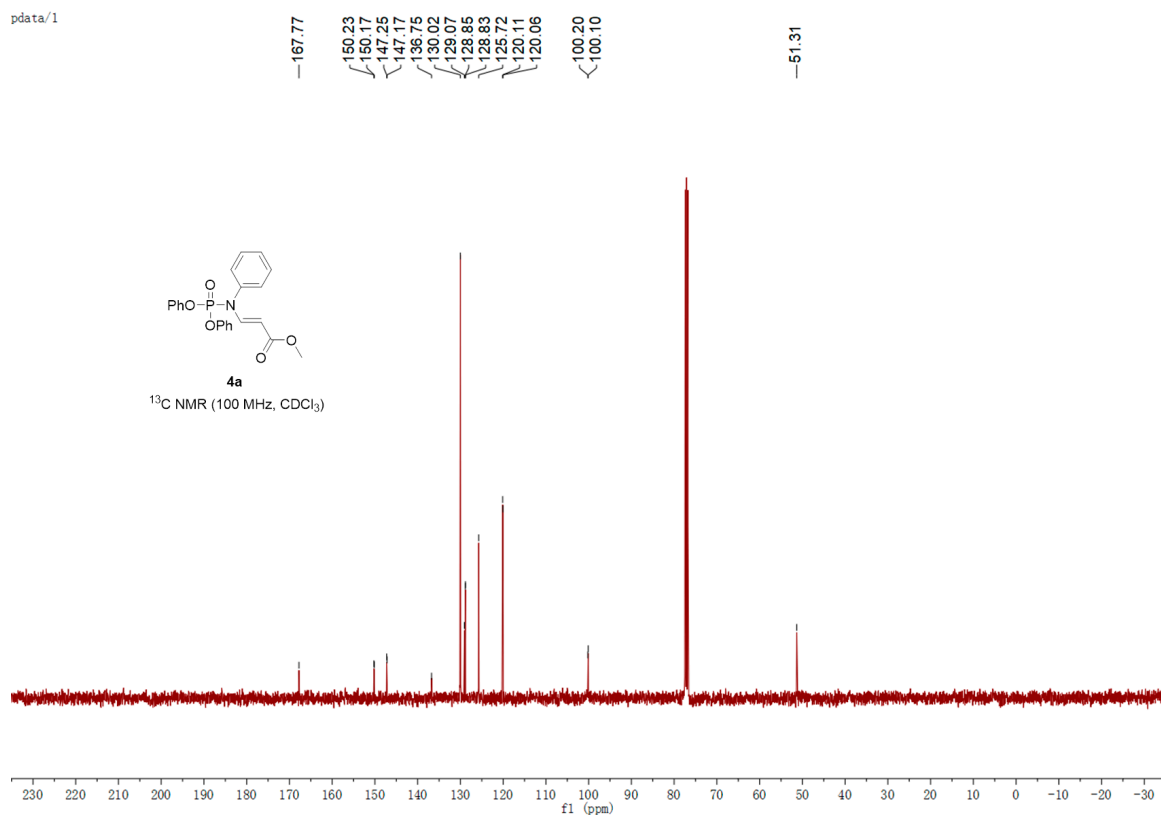
pdata/1



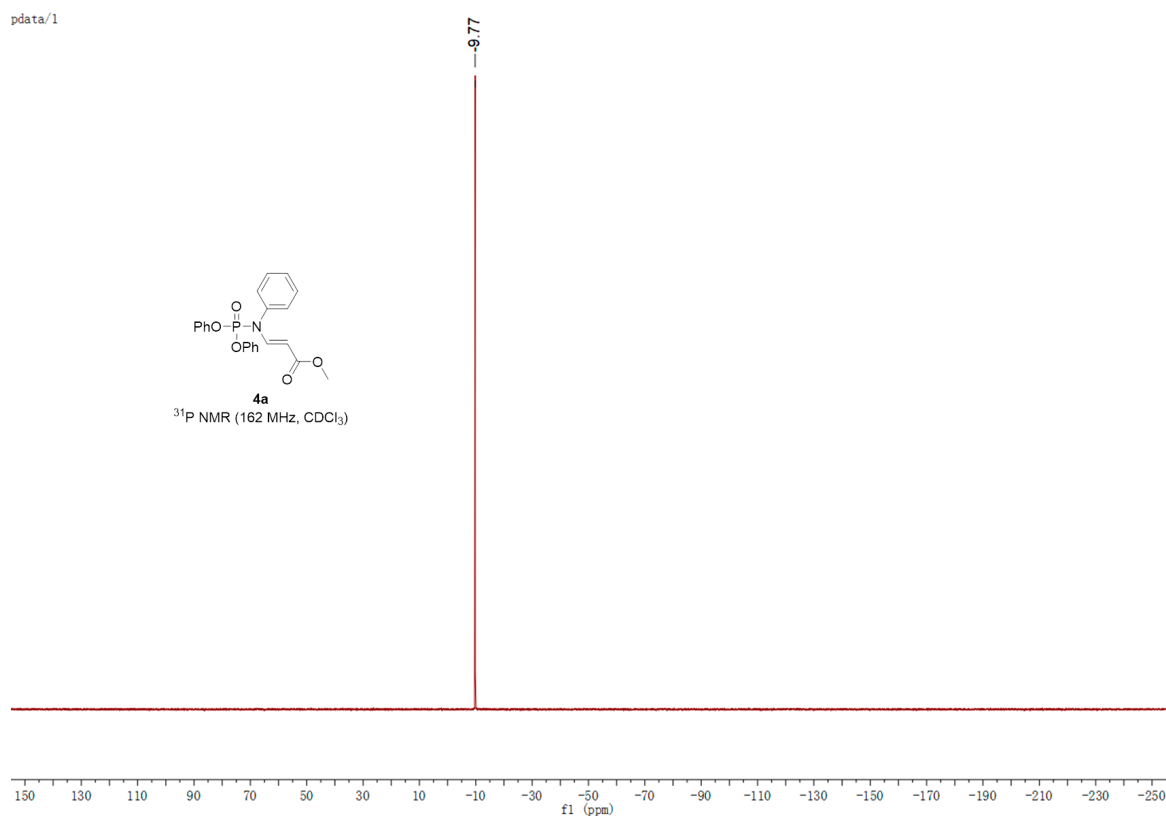
wg1198.1.1.1r



pdata/1

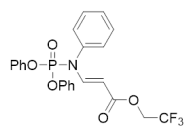


pdata/1



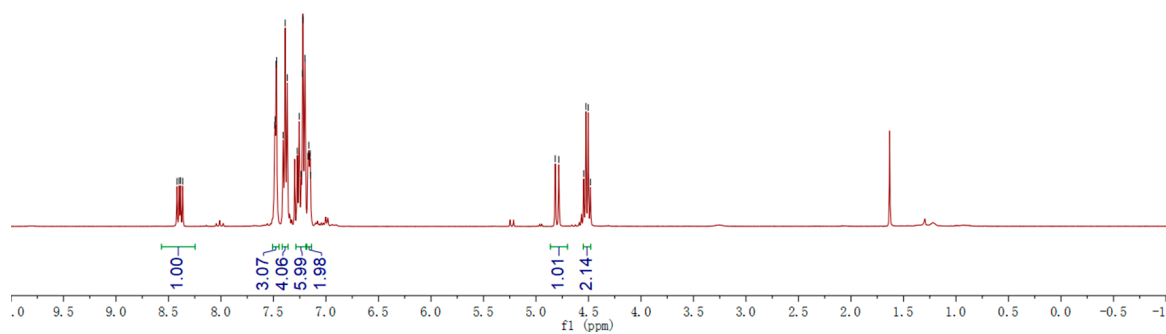
wg1200.1.1.1r

8.42  
8.40  
8.39  
8.36  
7.49  
7.48  
7.47  
7.41  
7.39  
7.37  
7.27  
7.26  
7.24  
7.22  
7.22  
7.20  
7.17  
7.16  
7.15  
7.15  
4.82  
4.78  
4.55  
4.52  
4.50  
4.48



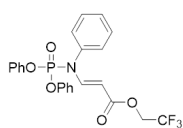
**4b**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



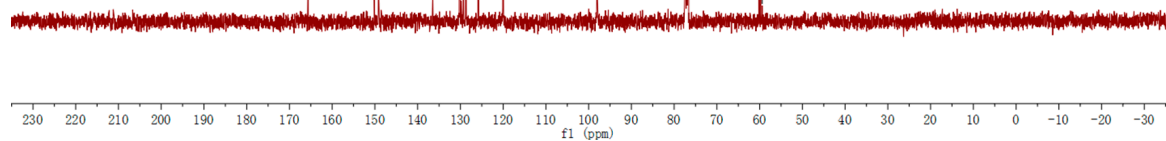
pdata/1

165.63  
150.16  
150.09  
149.20  
149.10  
136.46  
130.16  
130.06  
129.82  
129.33  
128.72  
125.83  
120.04  
119.99  
88.06  
87.96  
60.12  
59.76  
59.40

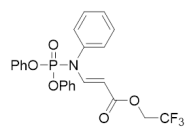


**4b**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

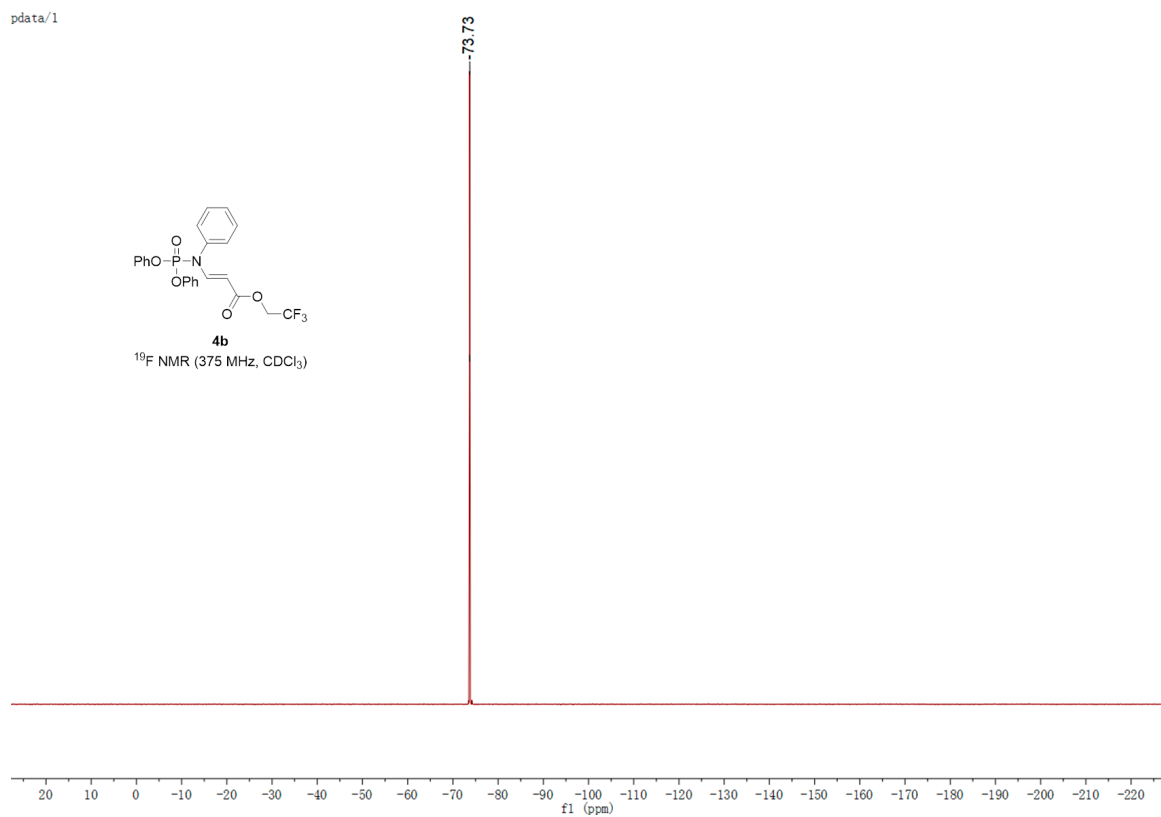


pdata/1

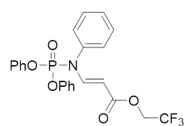


**4b**

$^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ )

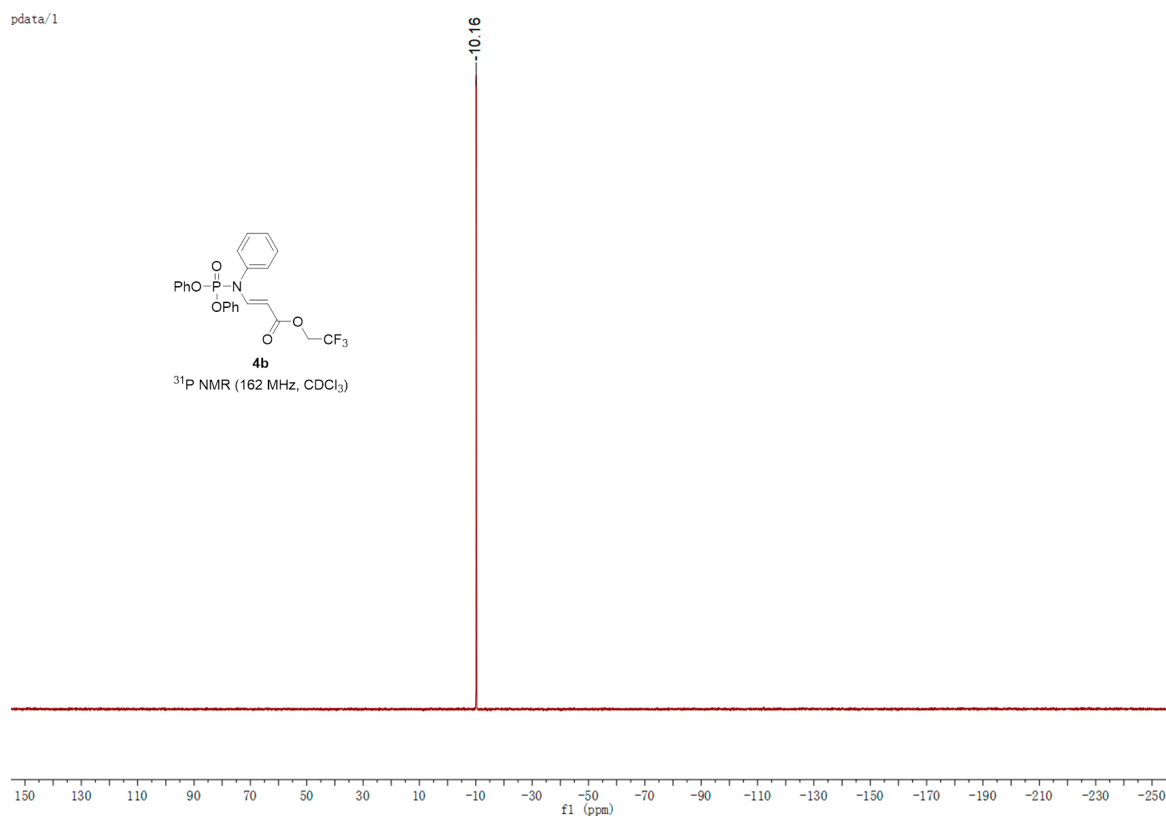


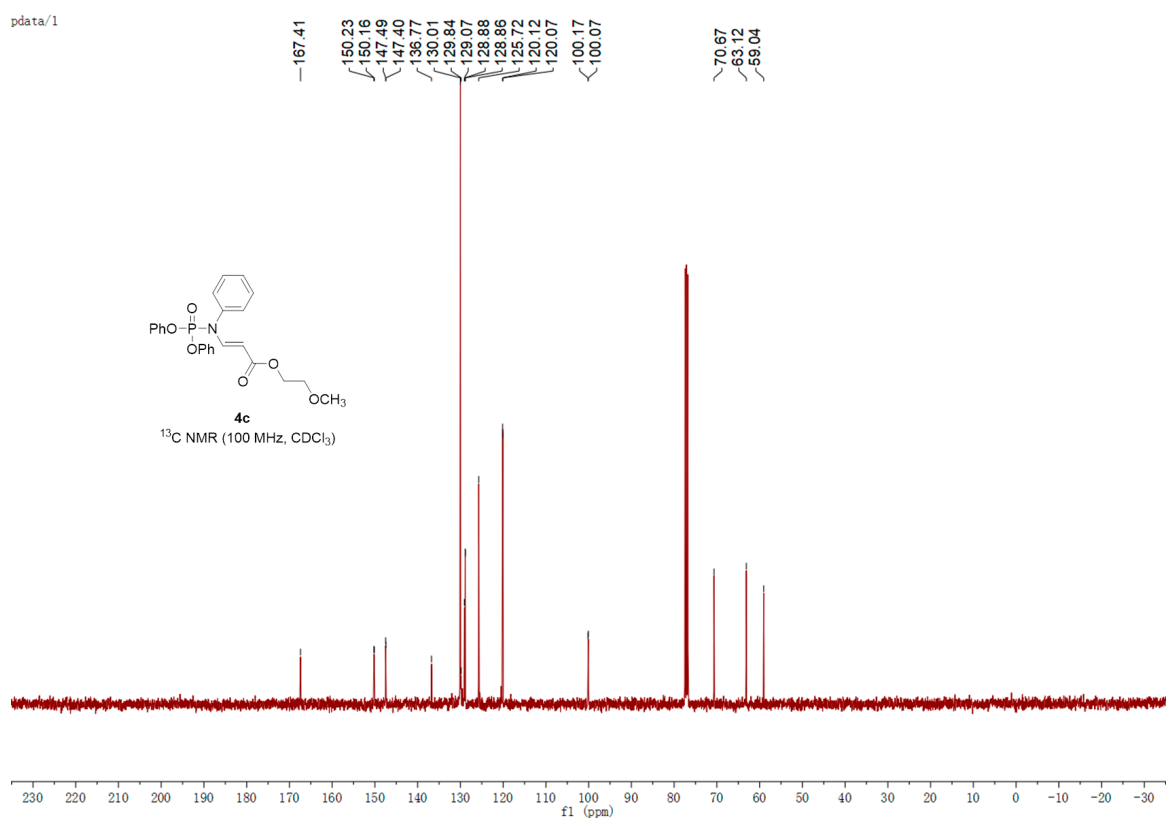
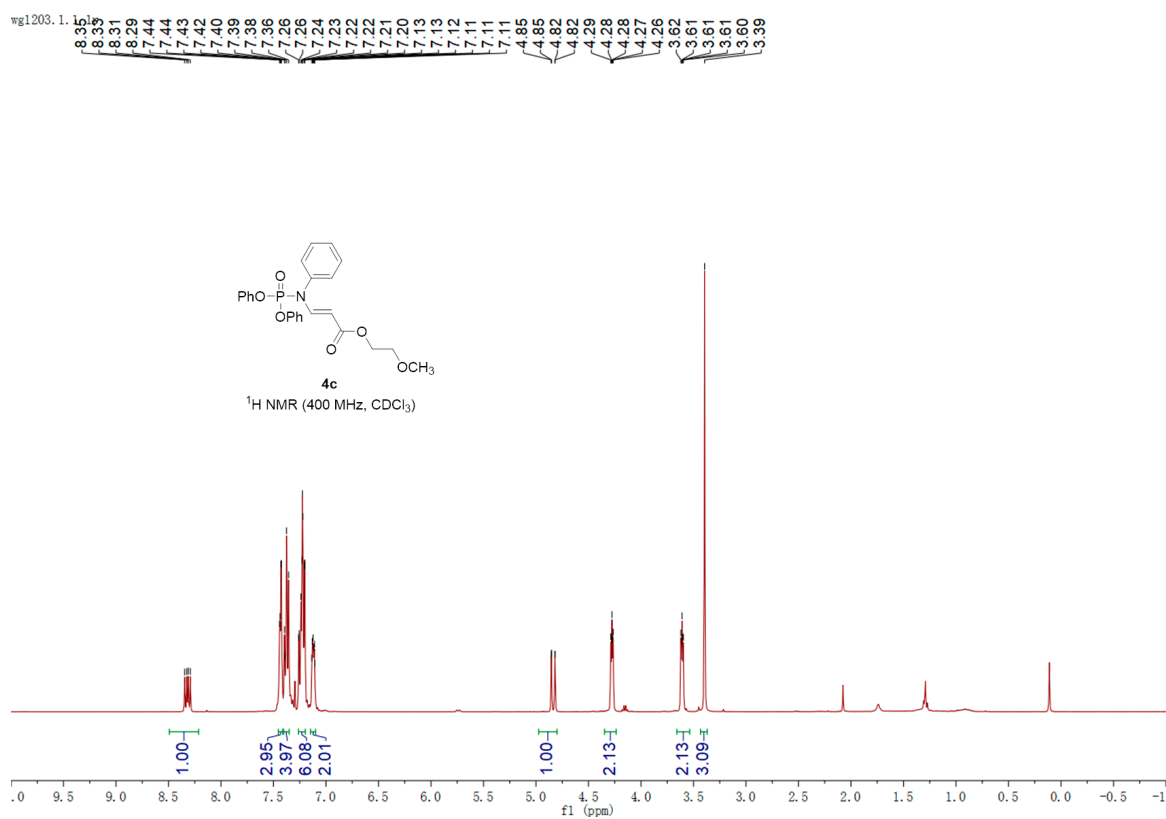
pdata/1



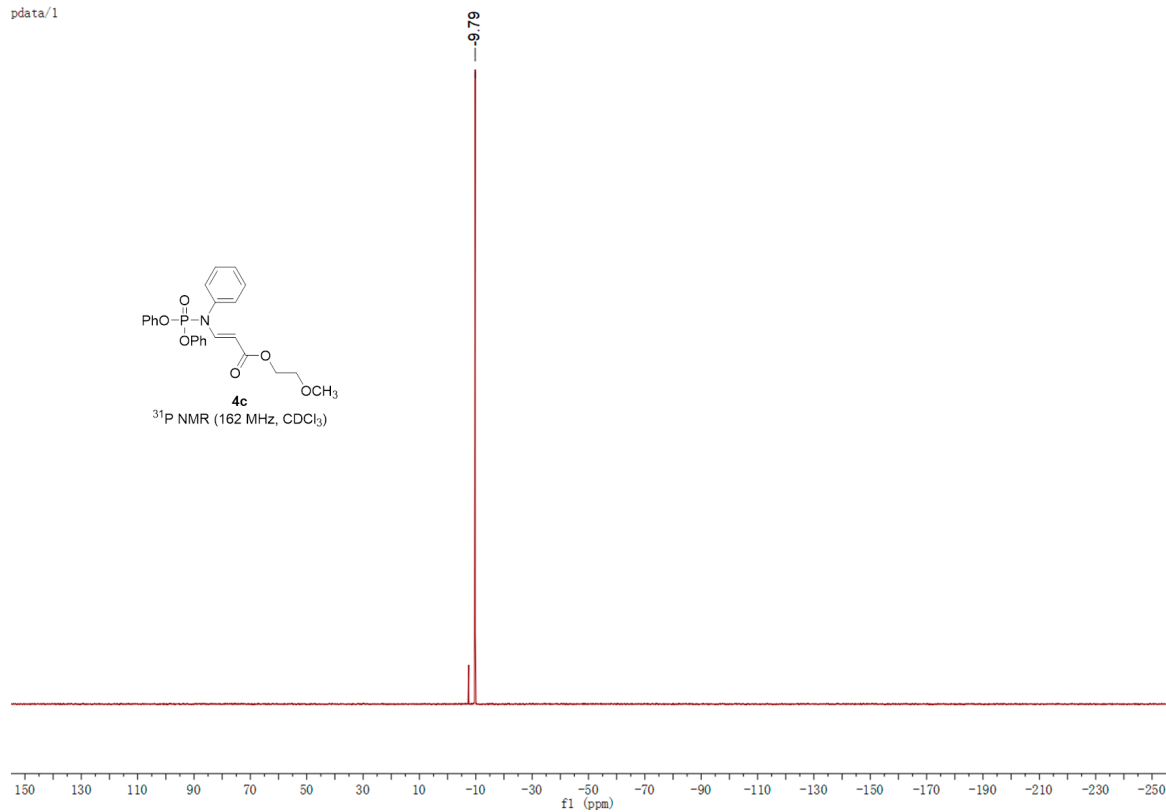
**4b**

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )

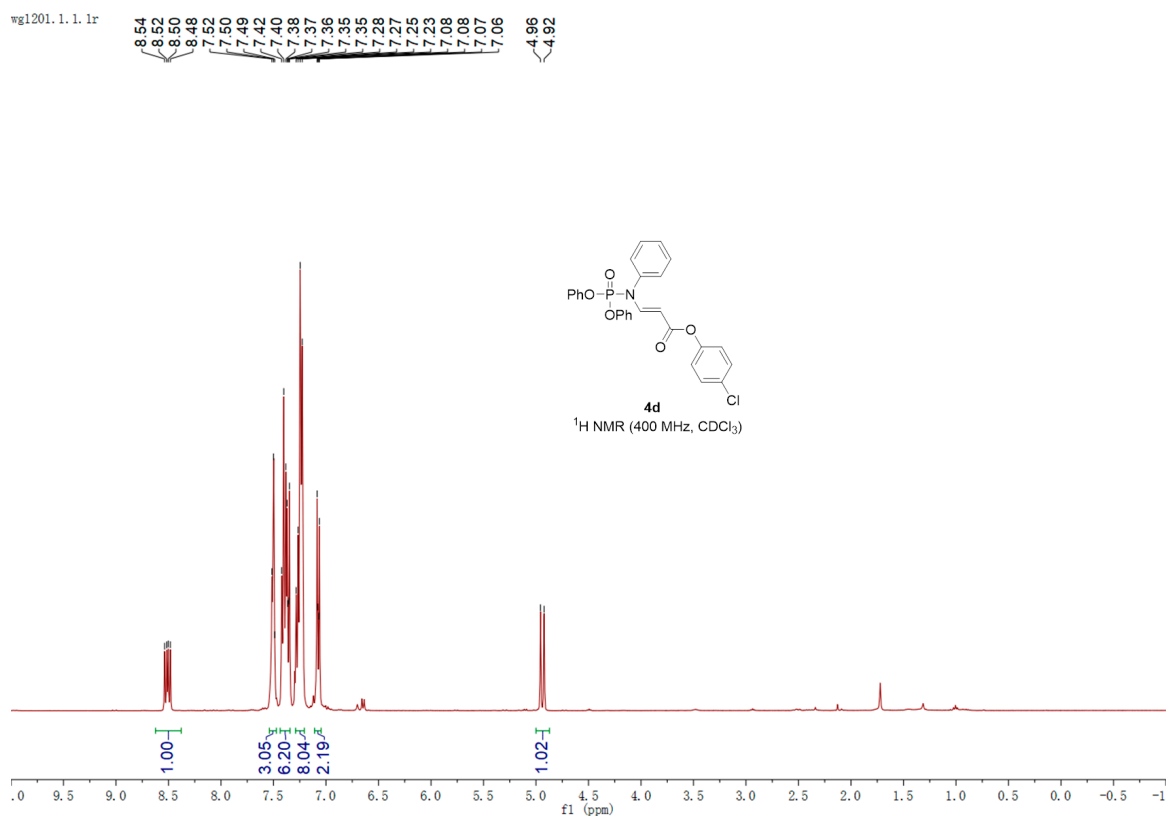




pdata/1

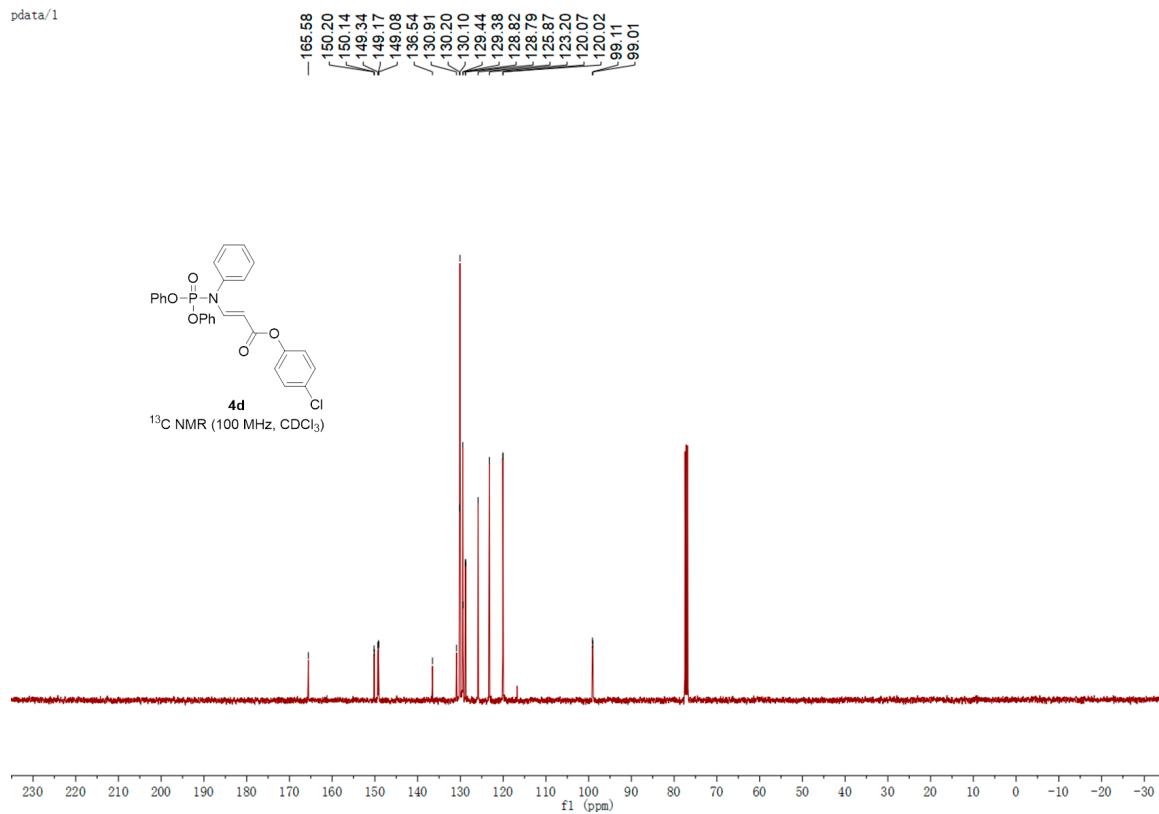


wg1201.1.1.1r

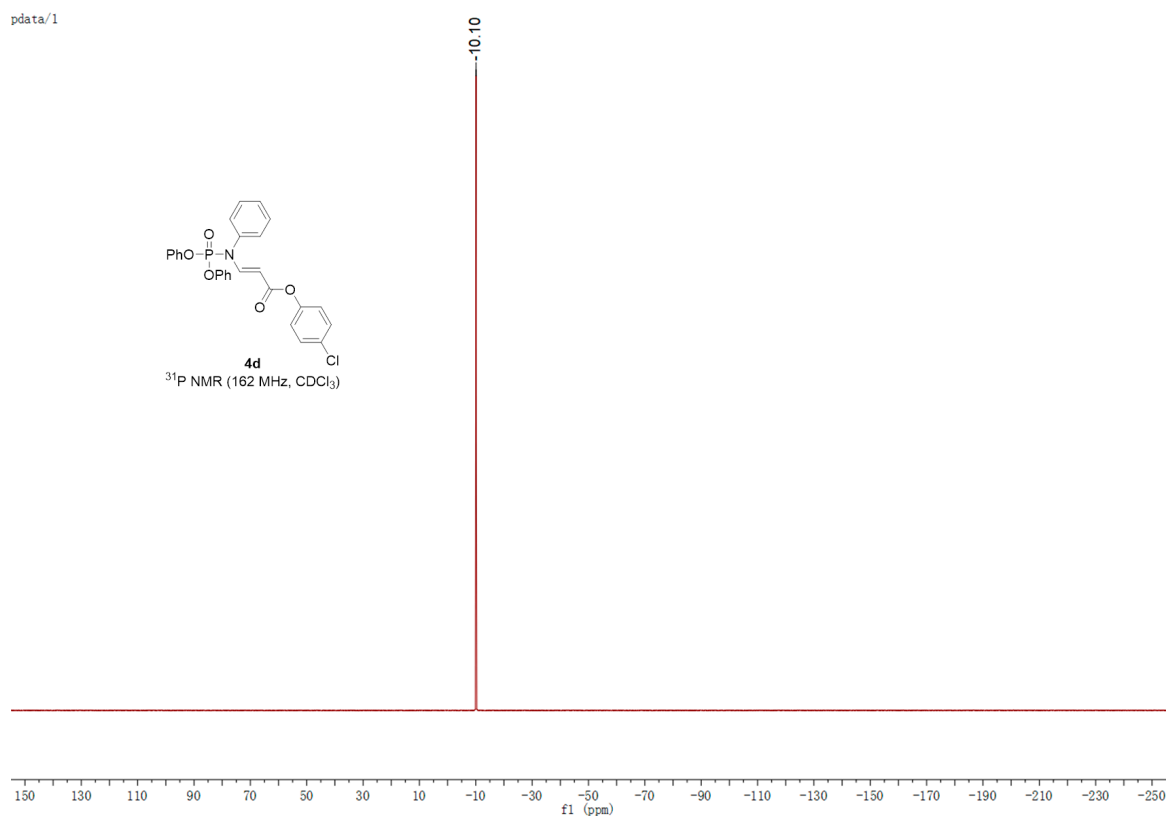


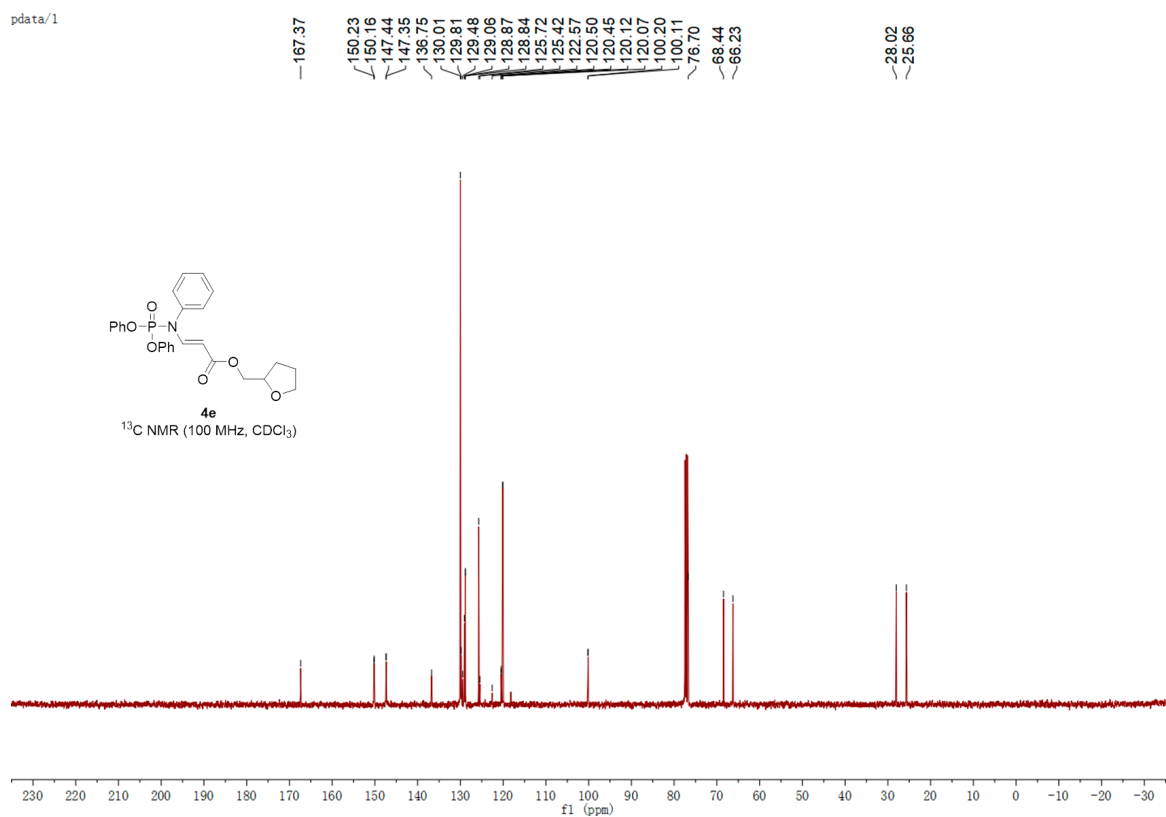
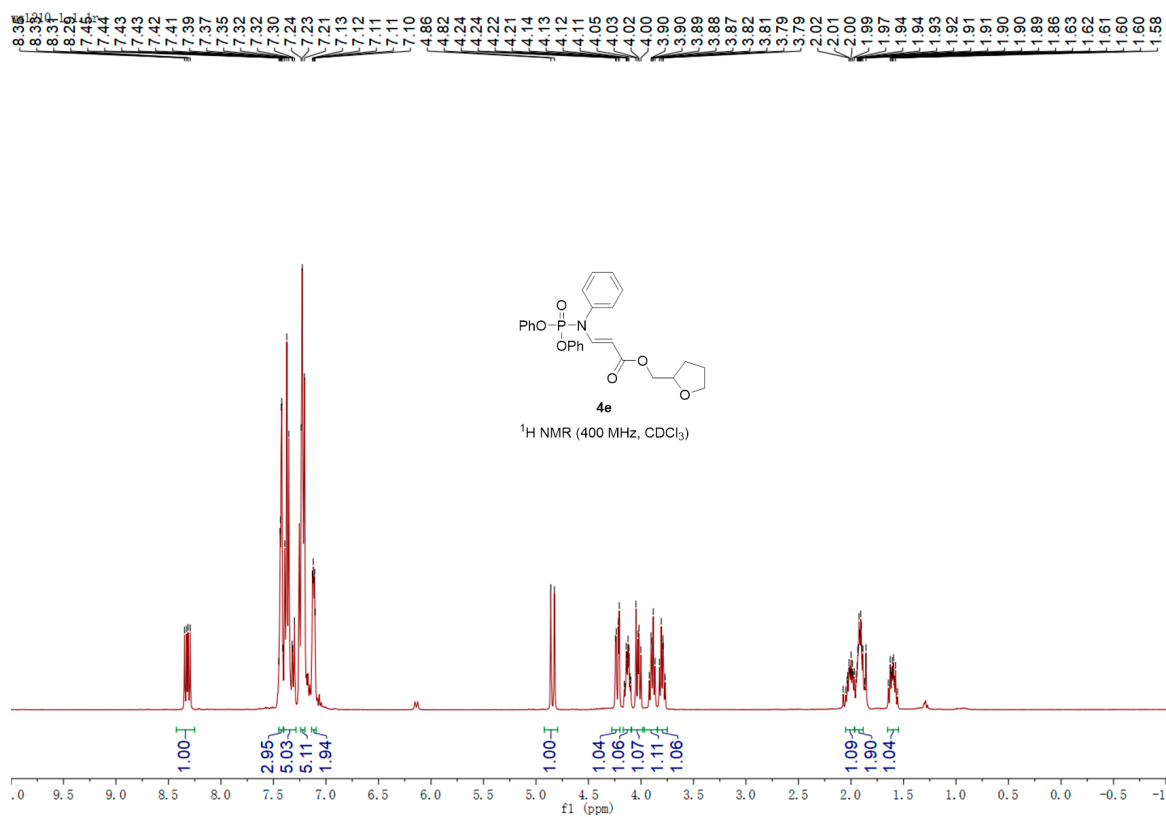


pdata/1



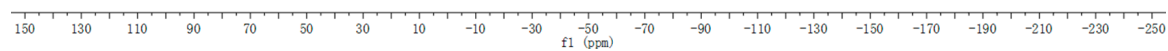
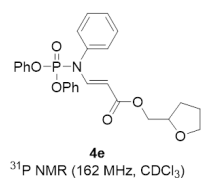
pdata/1





pdata/1

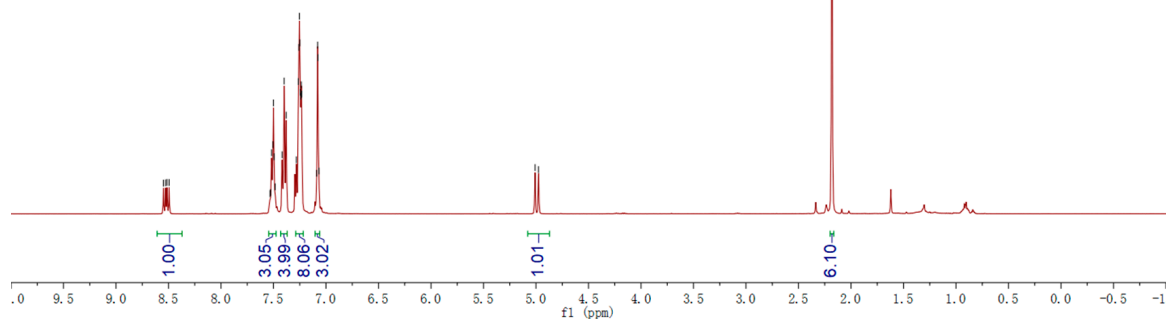
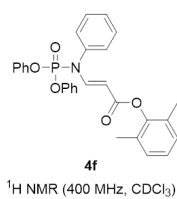
9.77



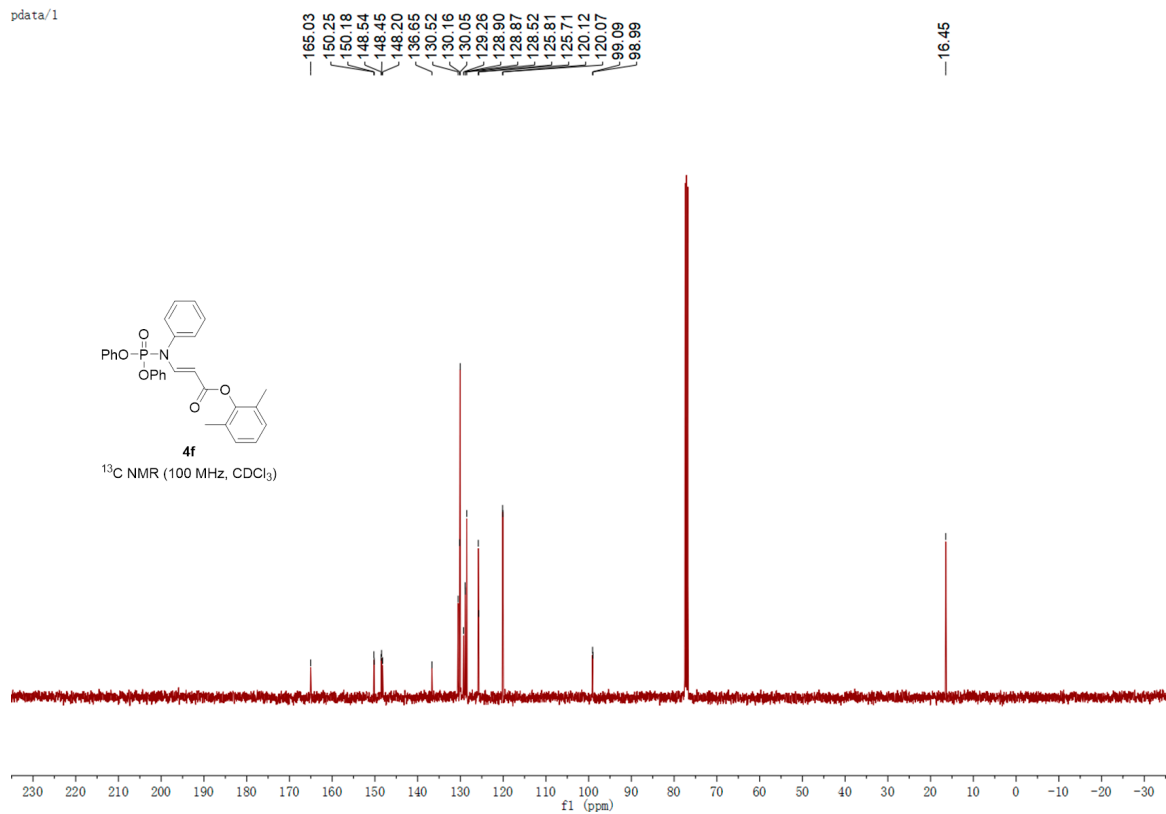
wg1207.1.1.1r

8.55  
8.53  
8.51  
8.49  
7.53  
7.53  
7.52  
7.50  
7.50  
7.49  
7.48  
7.42  
7.40  
7.38  
7.28  
7.26  
7.25  
7.25  
7.24  
7.24  
7.23  
7.09  
7.08  
7.07  
5.01  
4.98

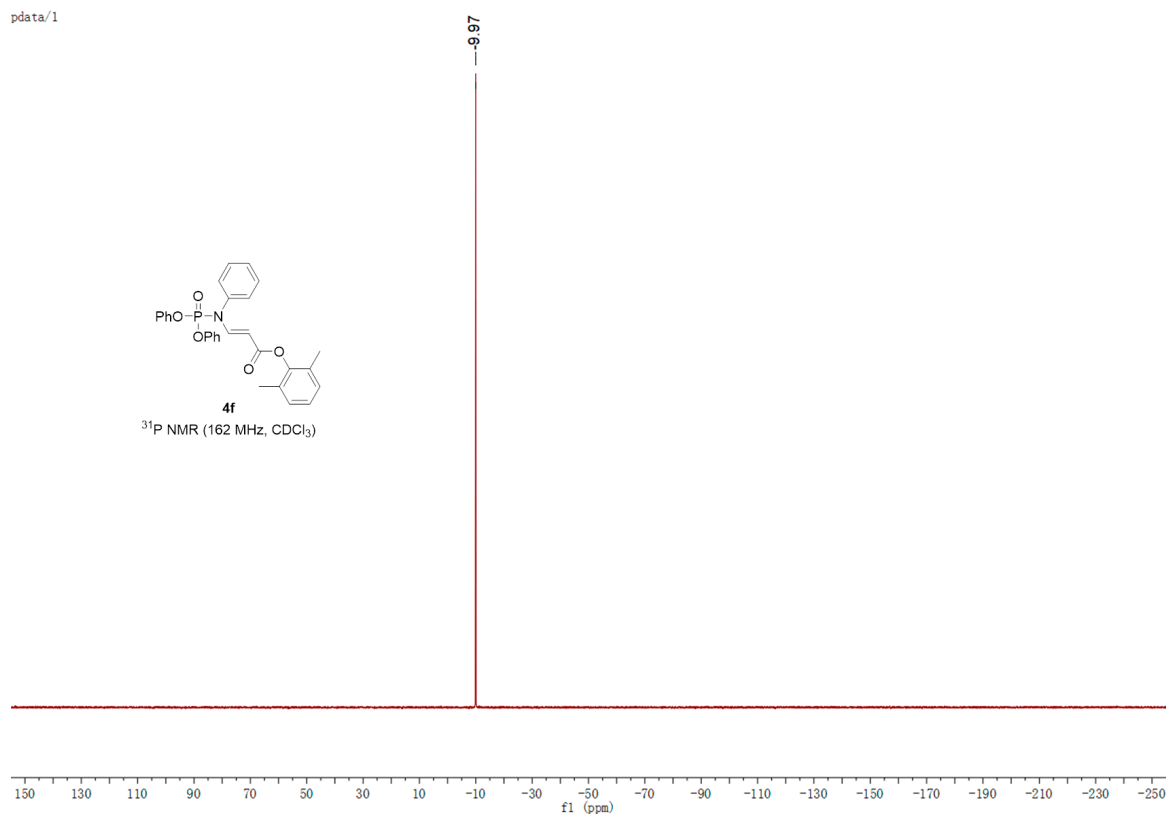
2.18

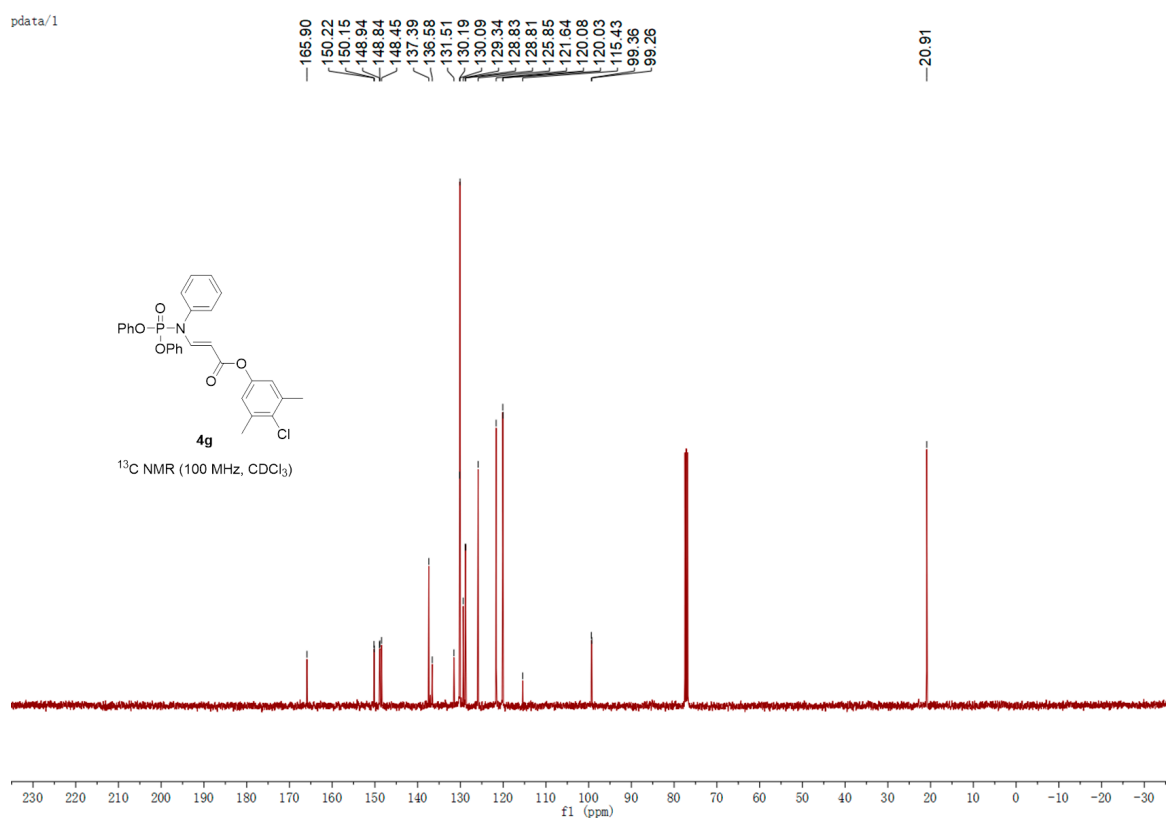
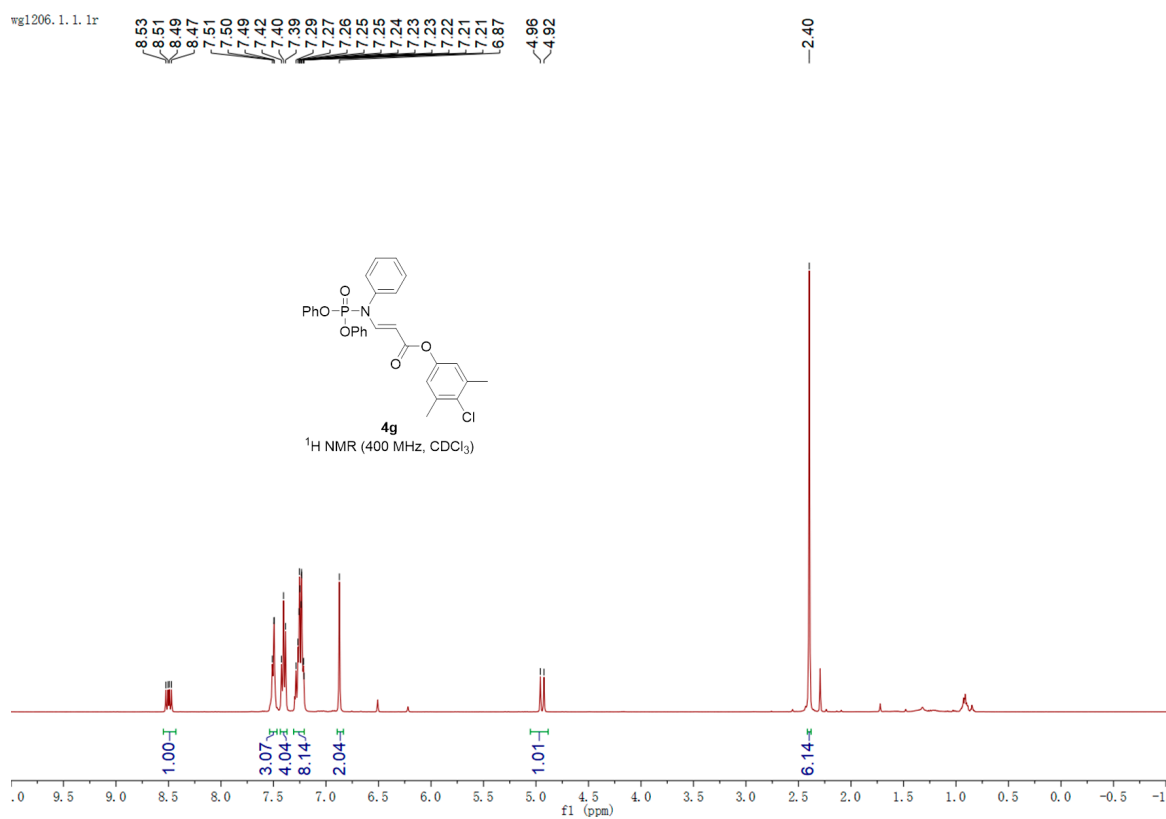


pdata/1

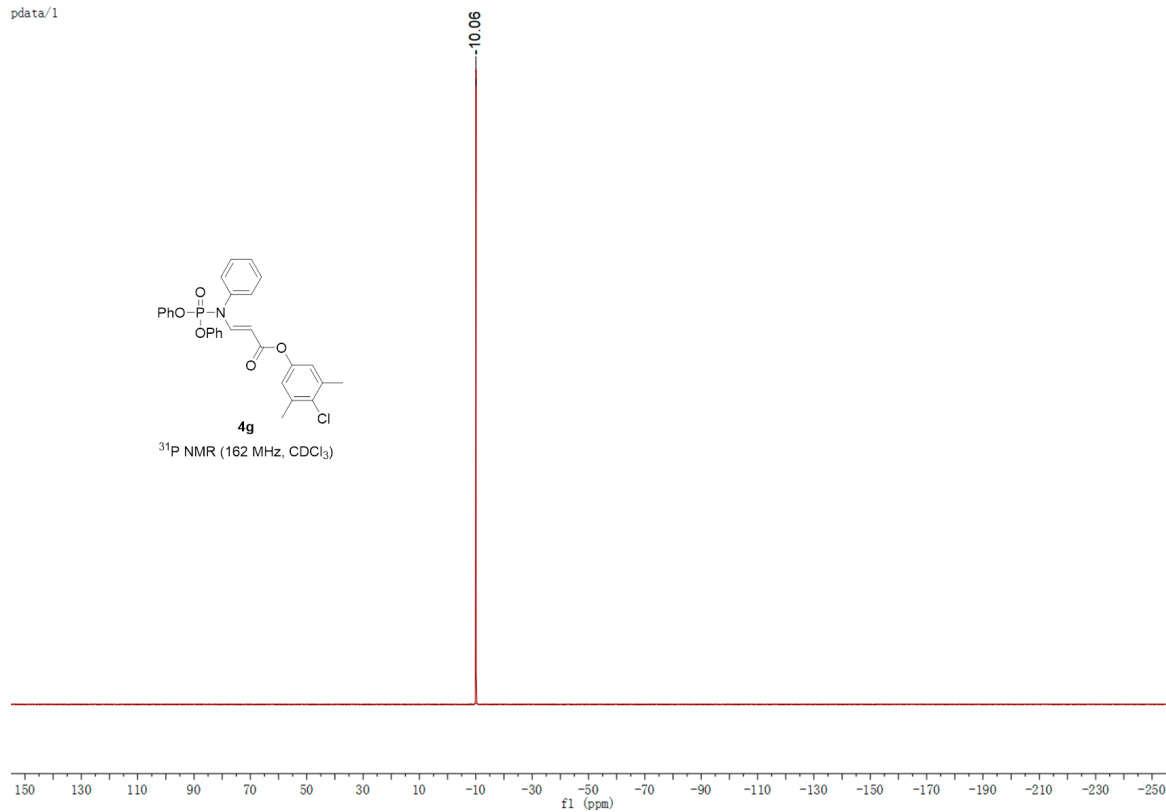


pdata/1

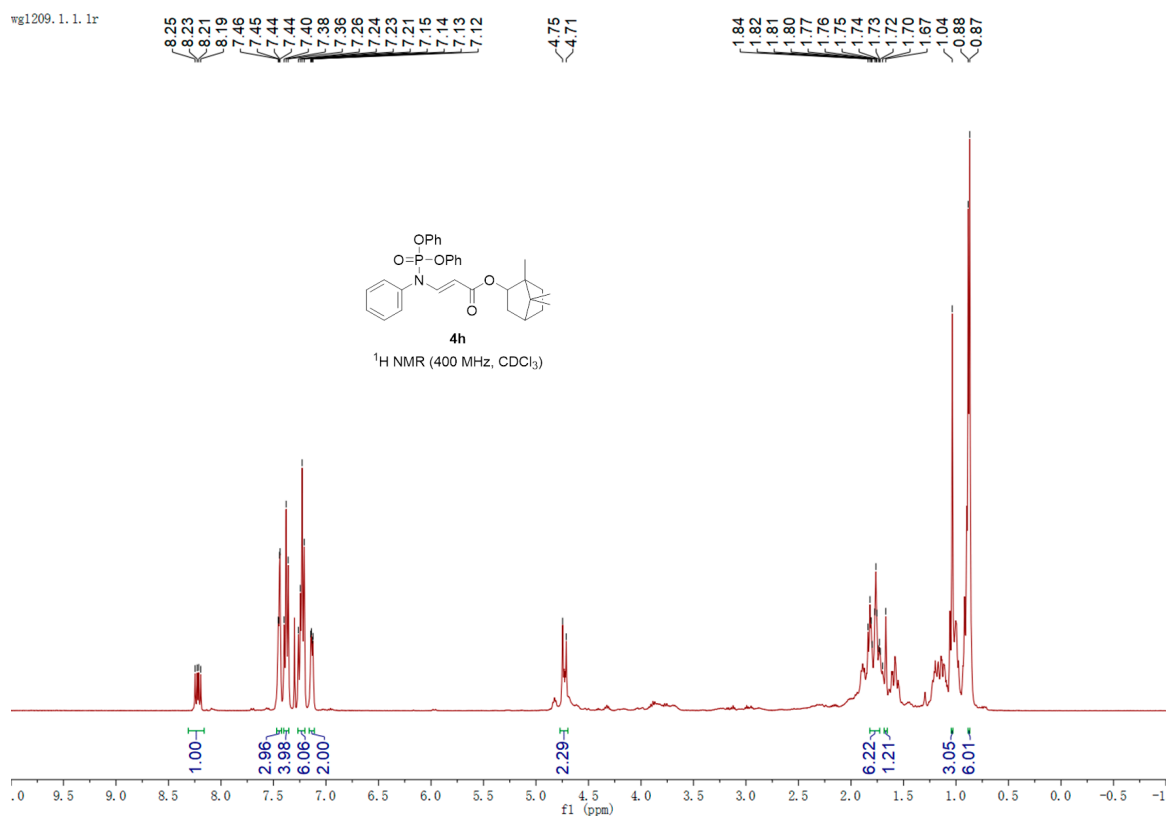




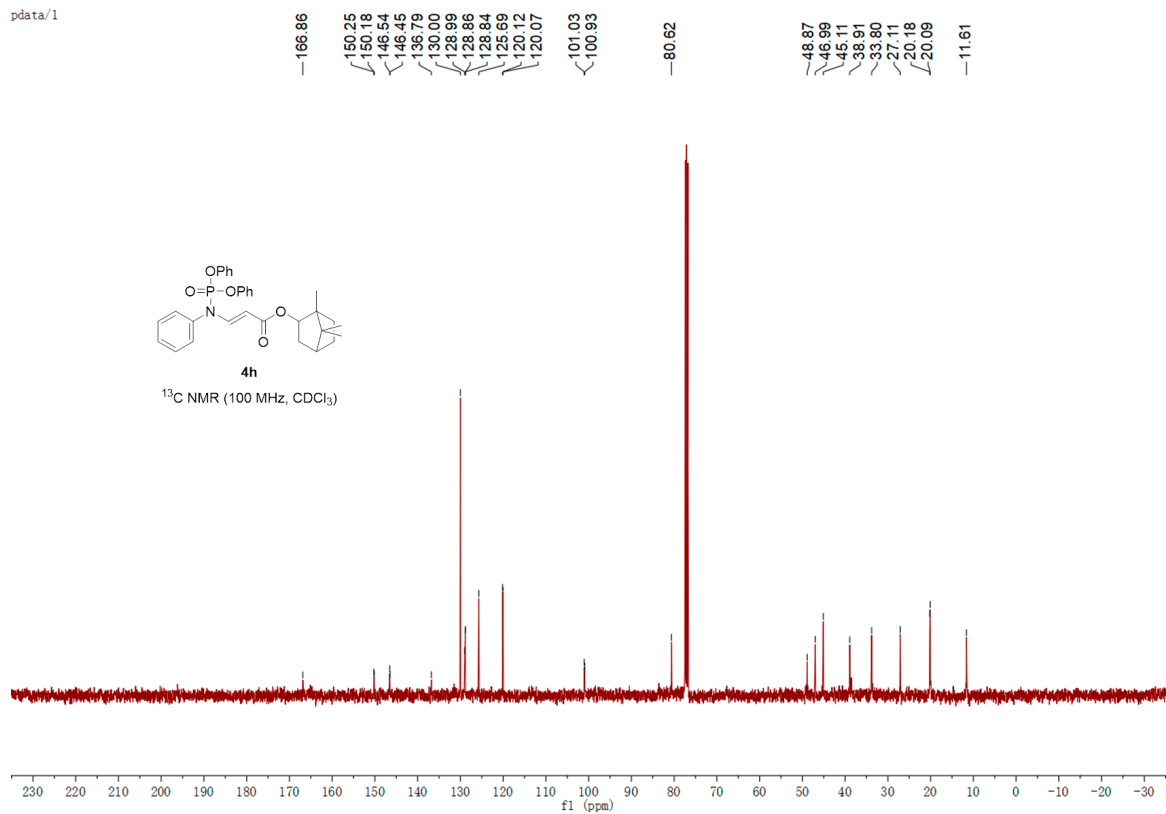
pdata/1



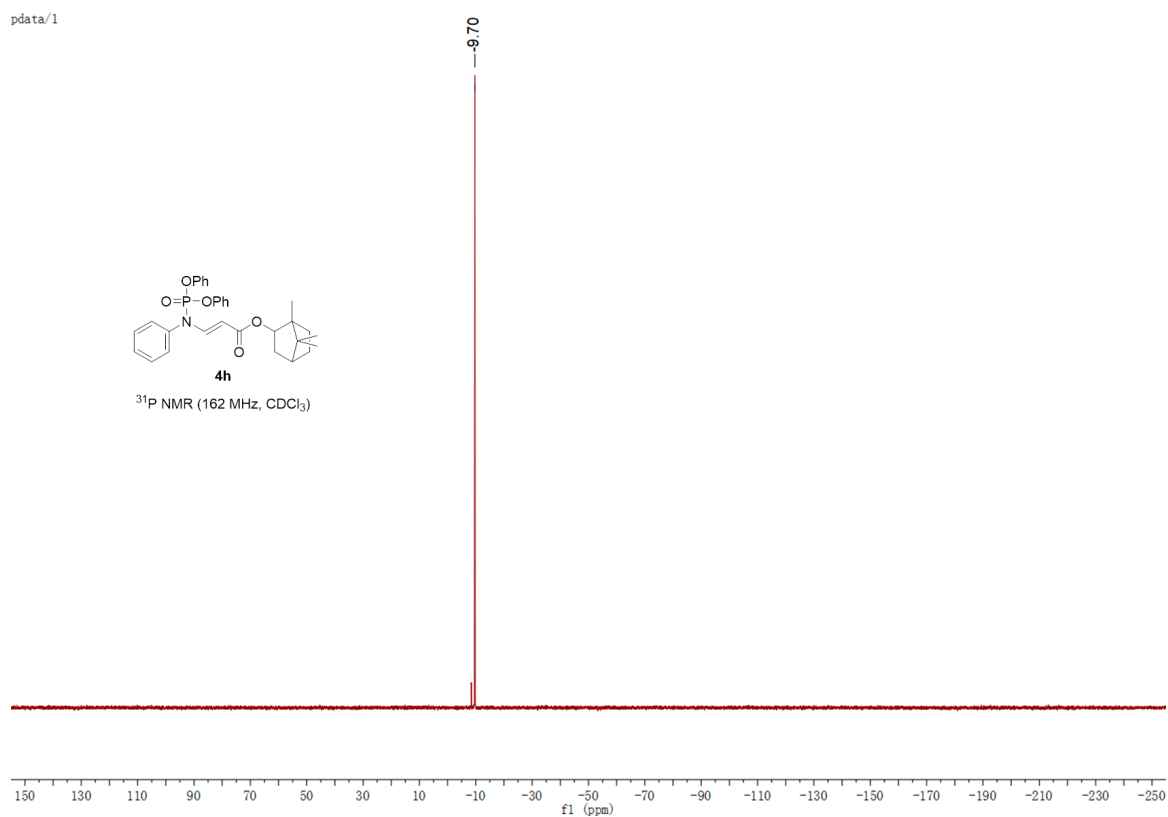
wg1209. 1. 1. 1r



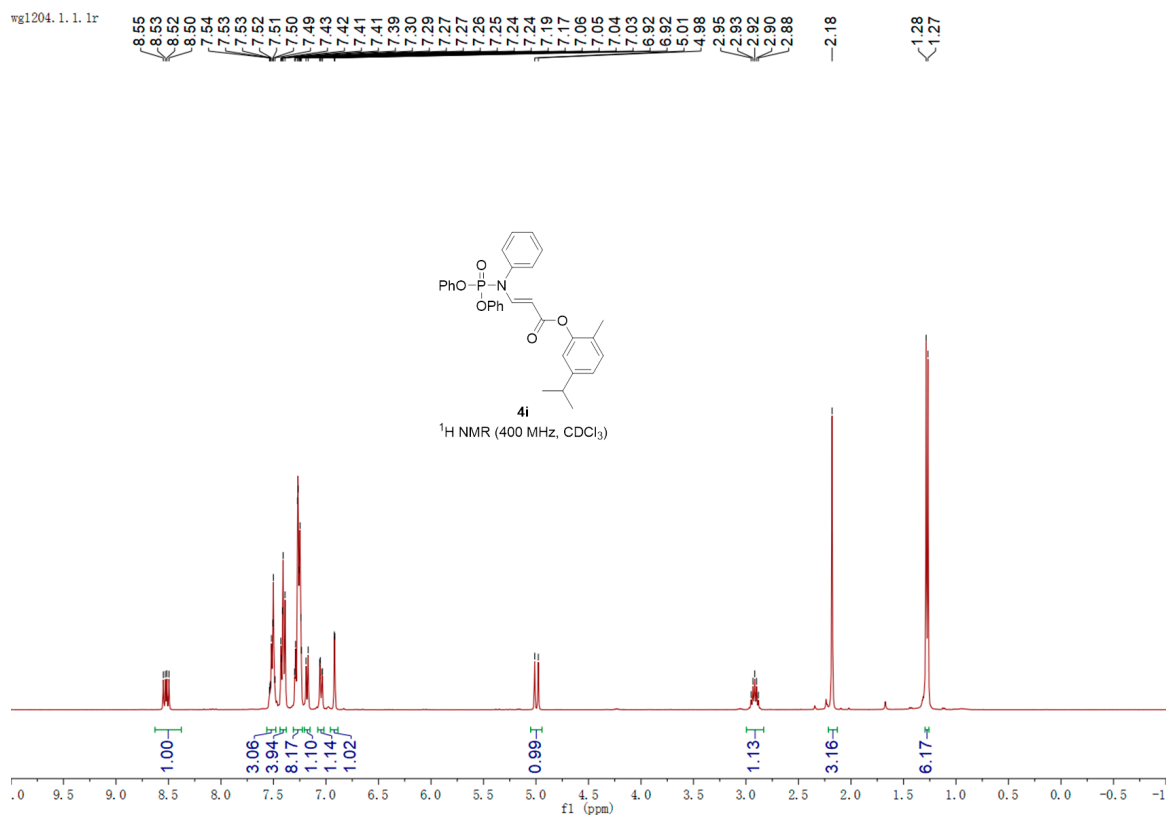
pdata/1



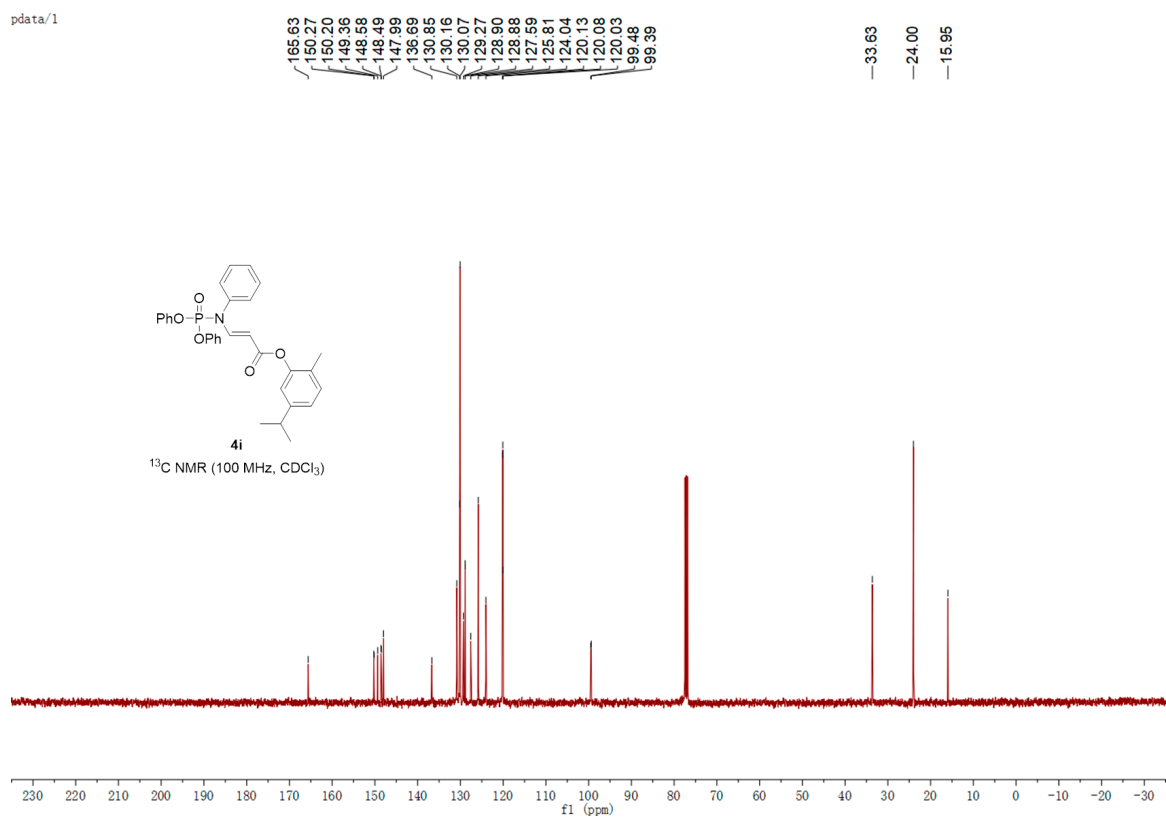
pdata/1



wg1204.1.1.1r

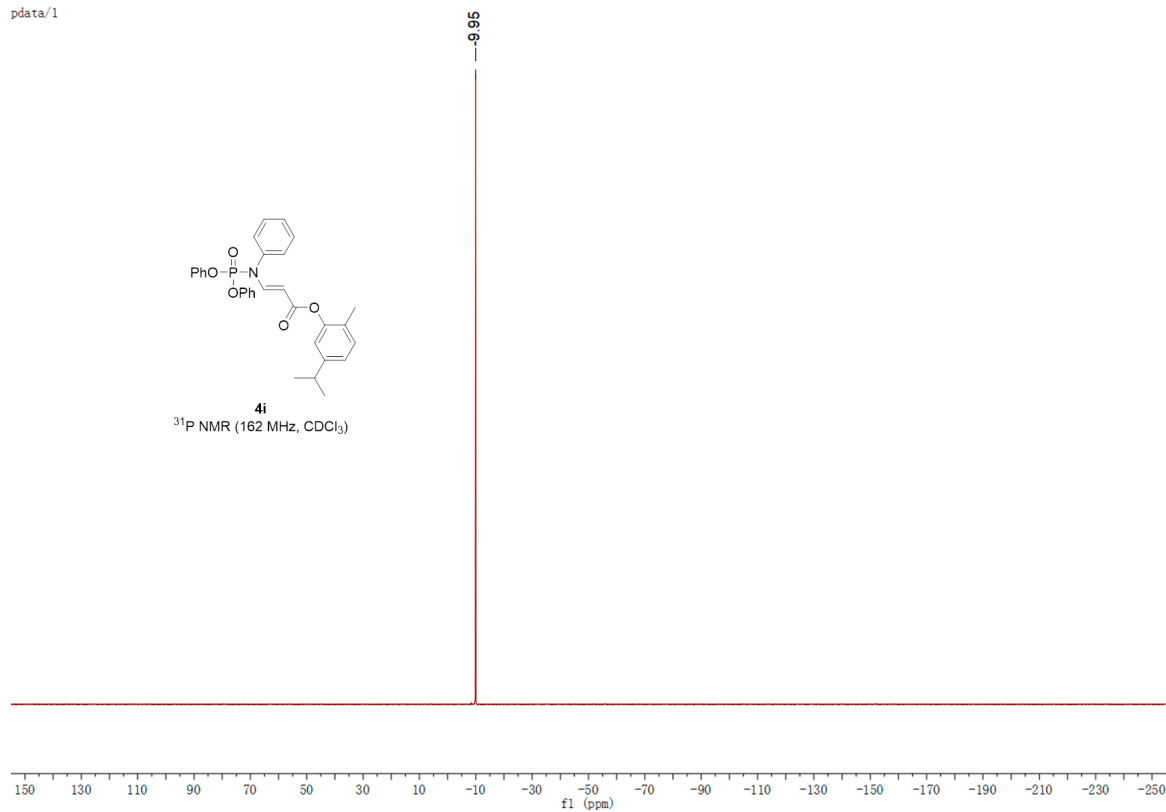


pdata/1

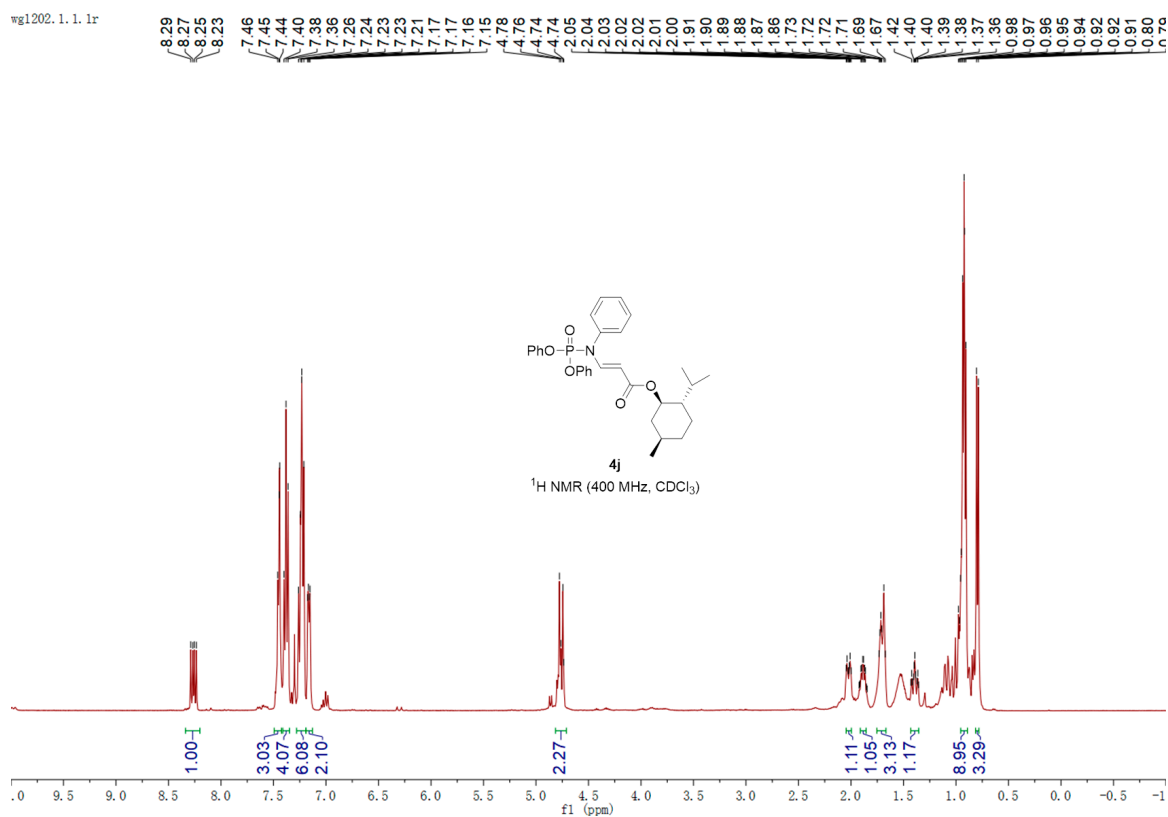




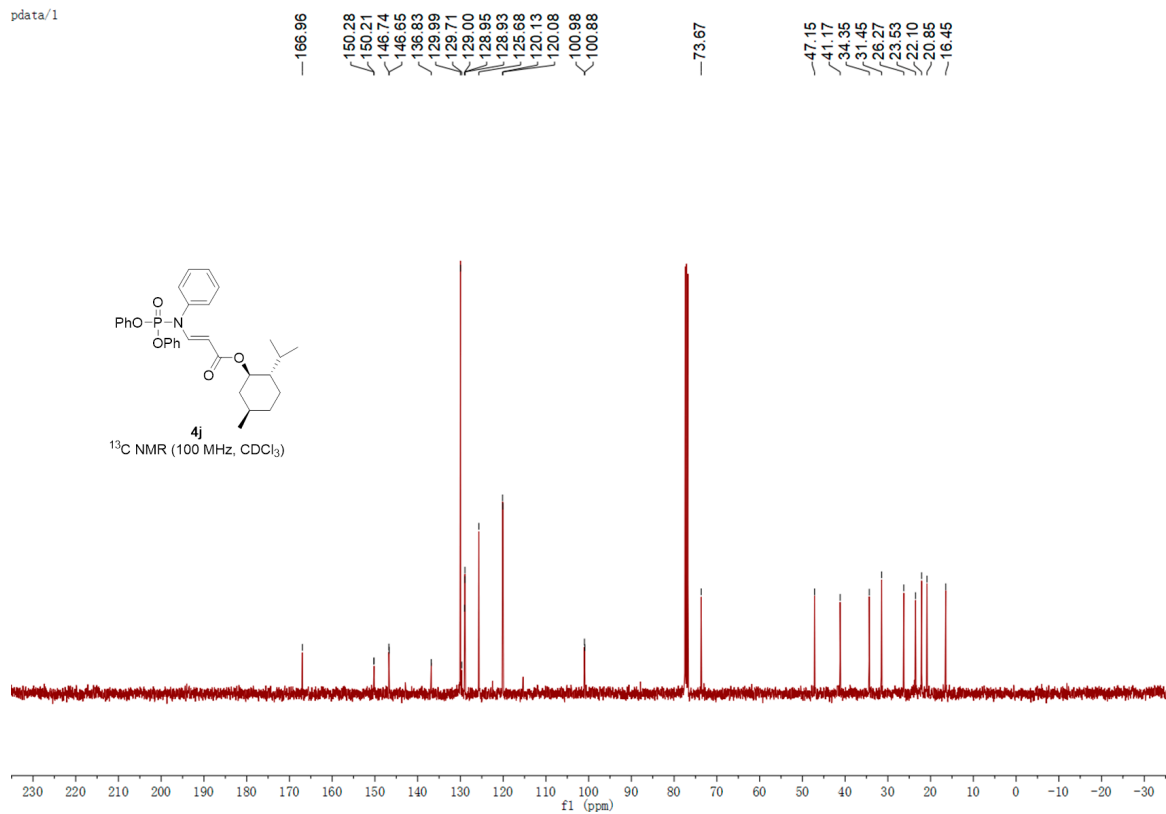
pdata/1



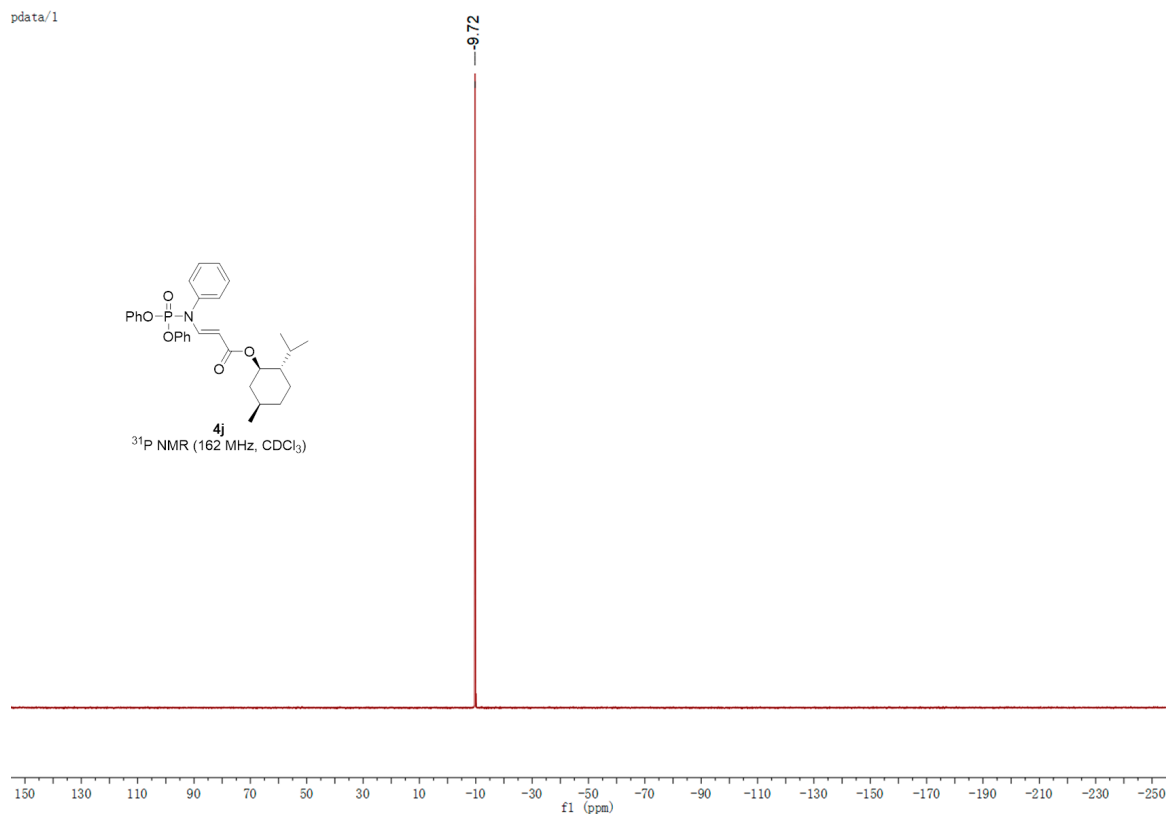
wg1202.1.1.1r



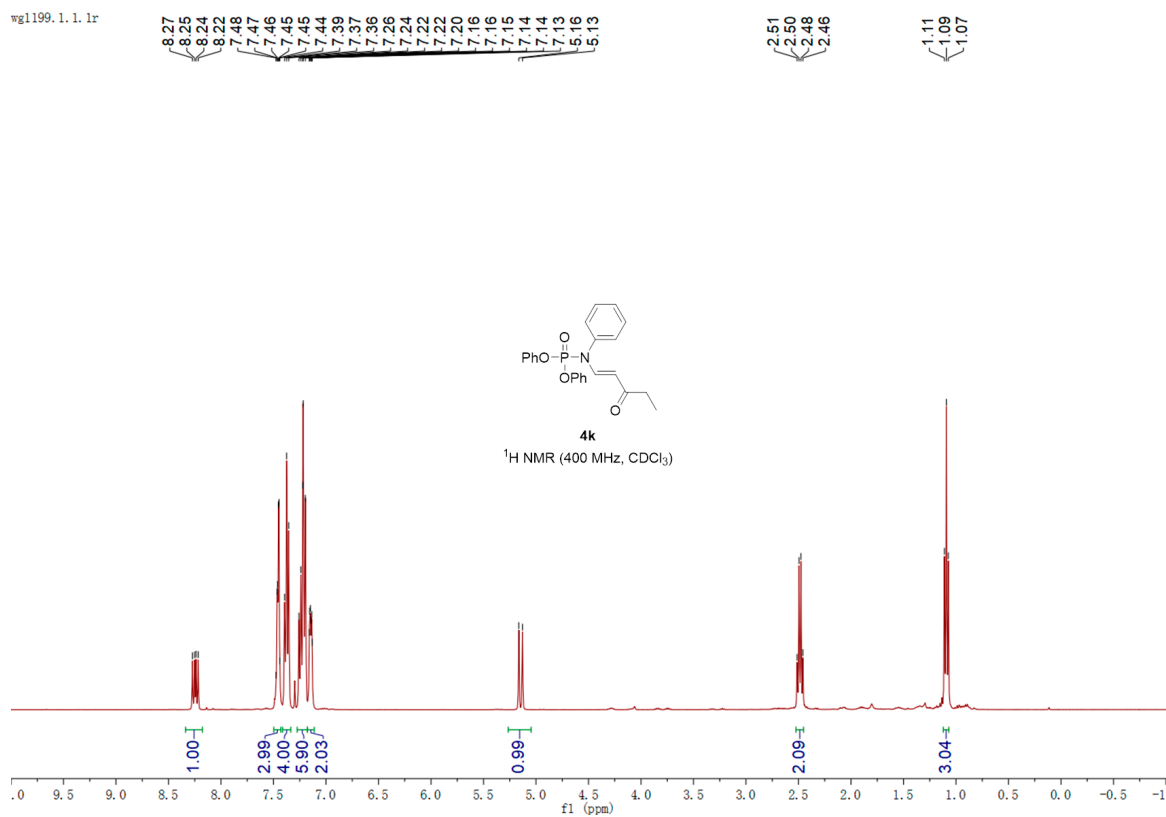
pdata/1



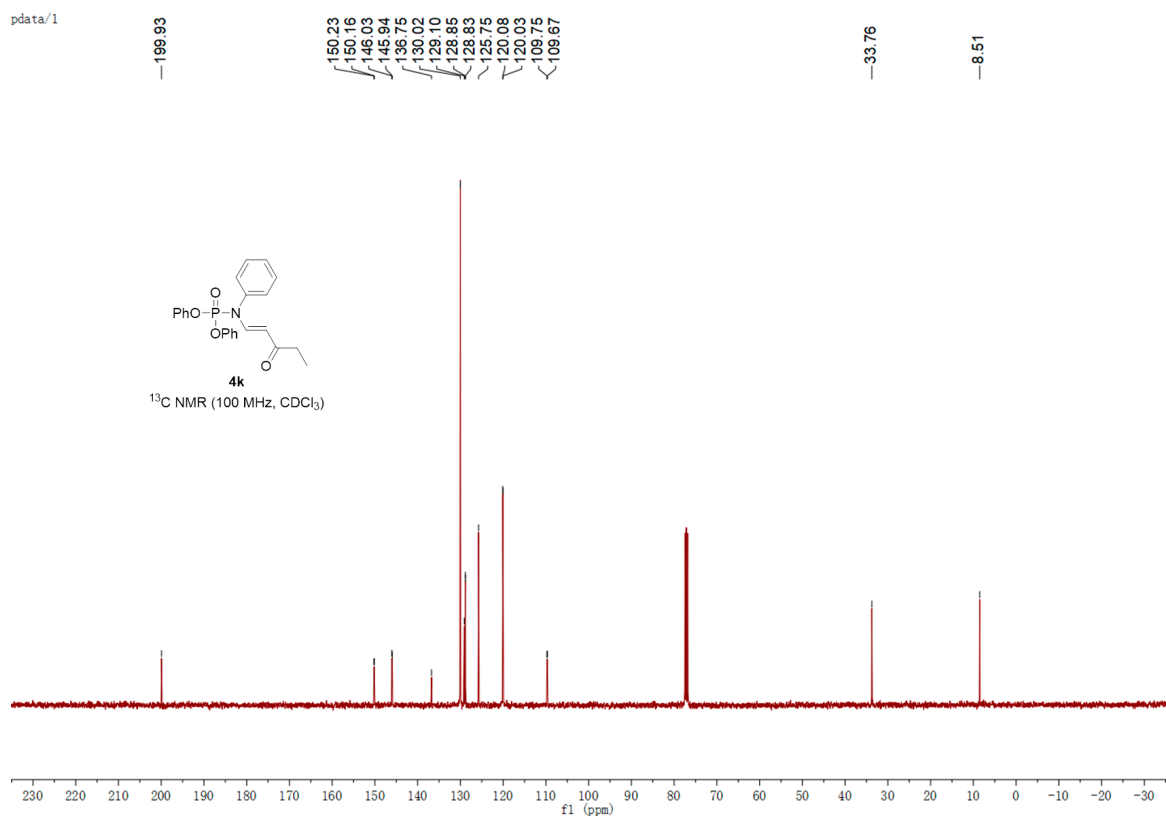
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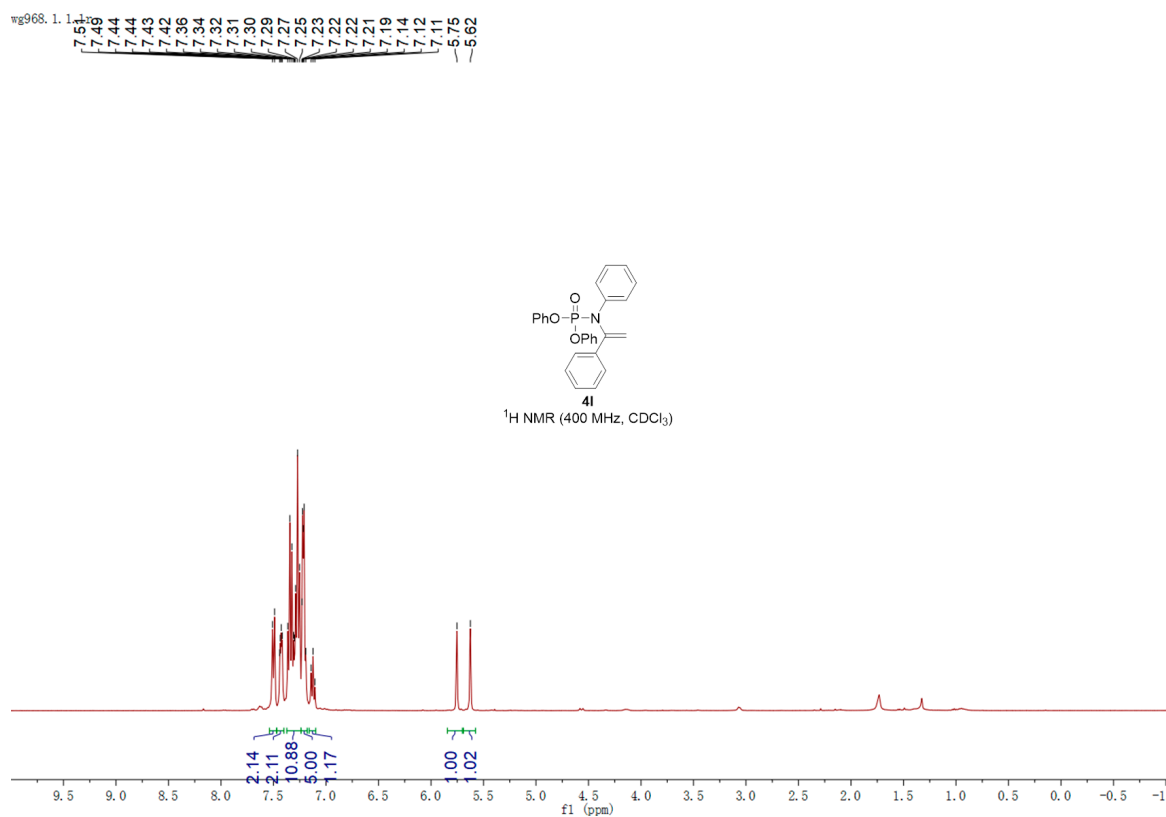
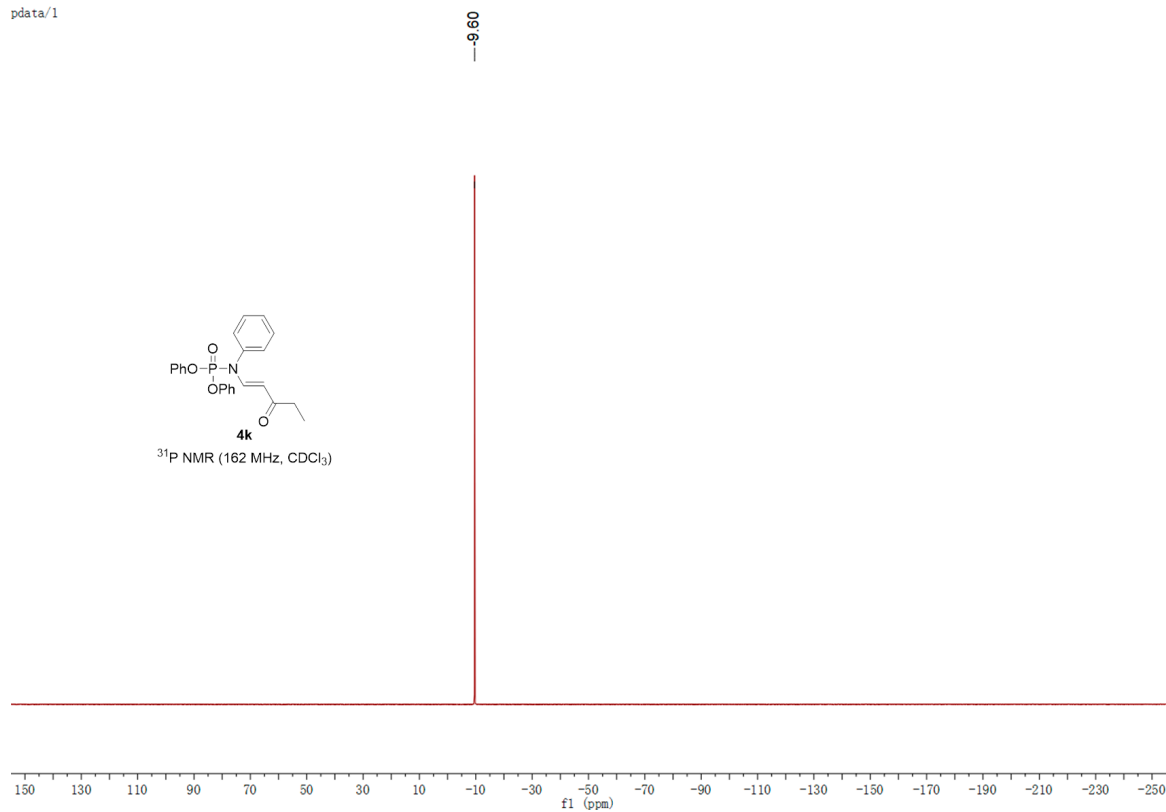
wg1199.1.1.1r



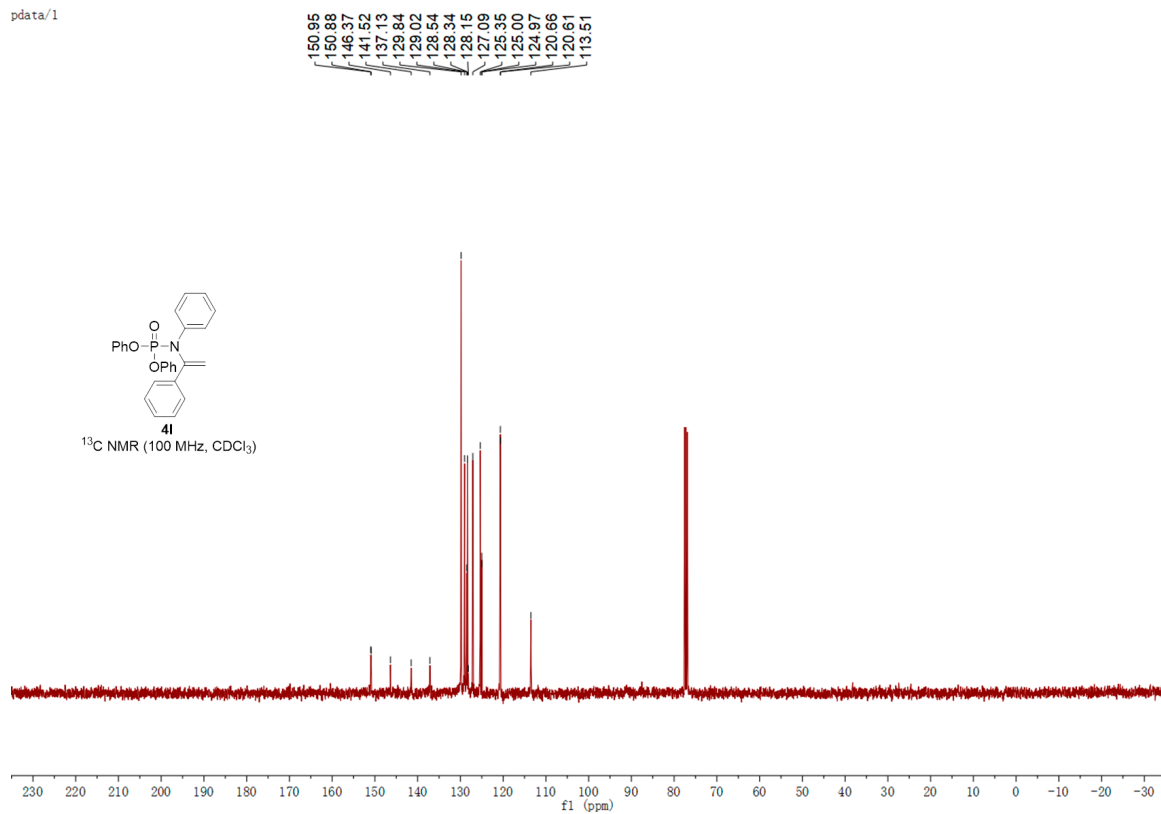
pdata/1



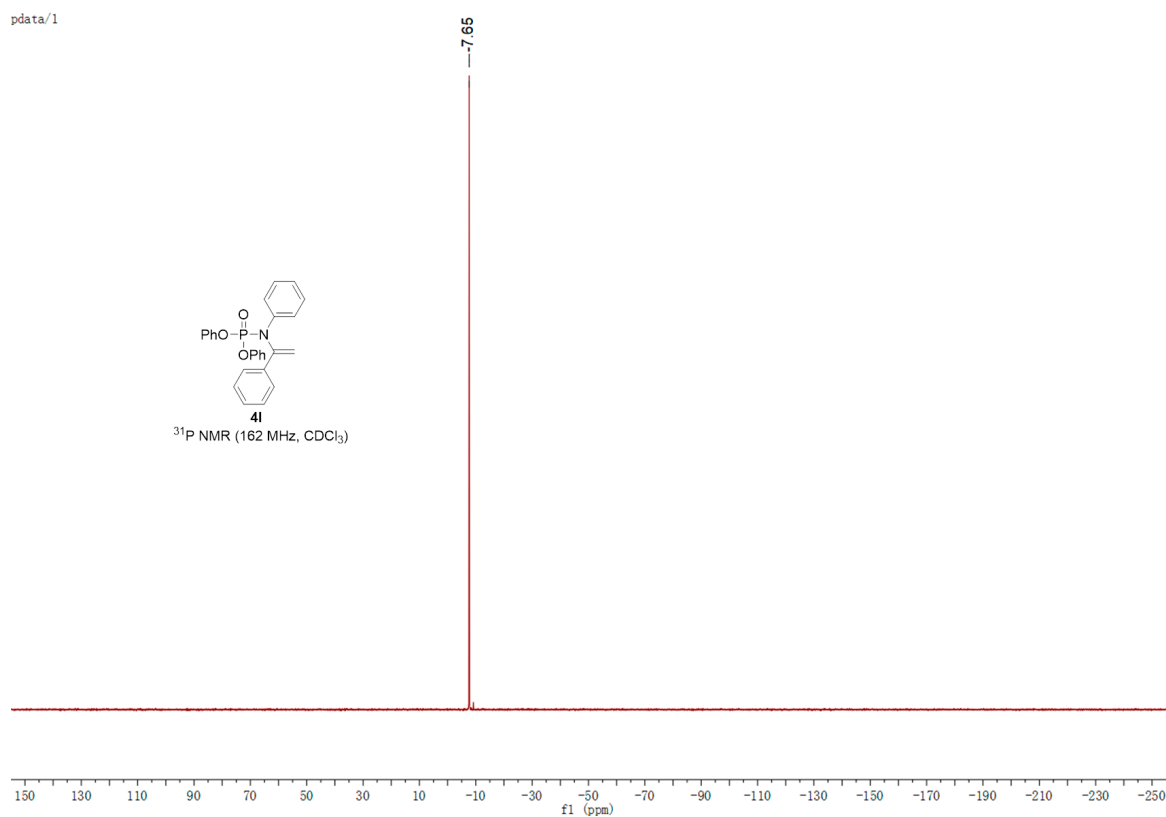
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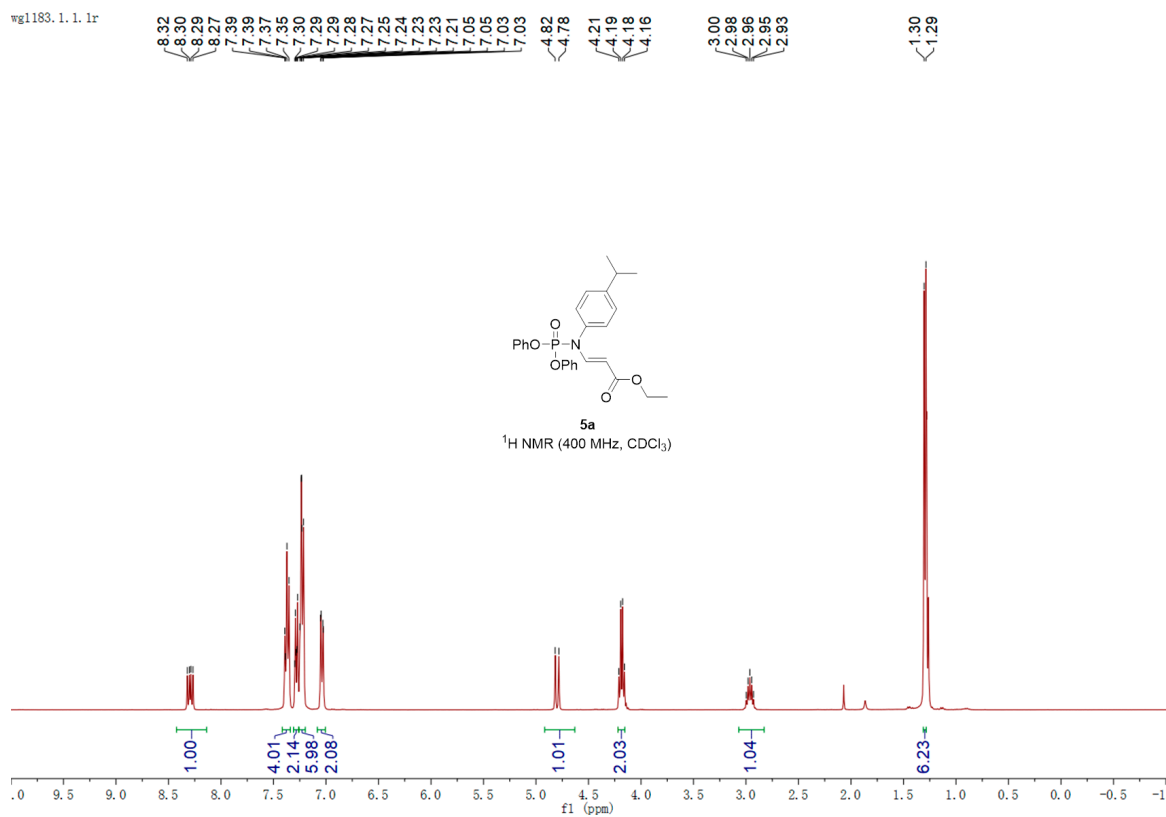
pdata/1



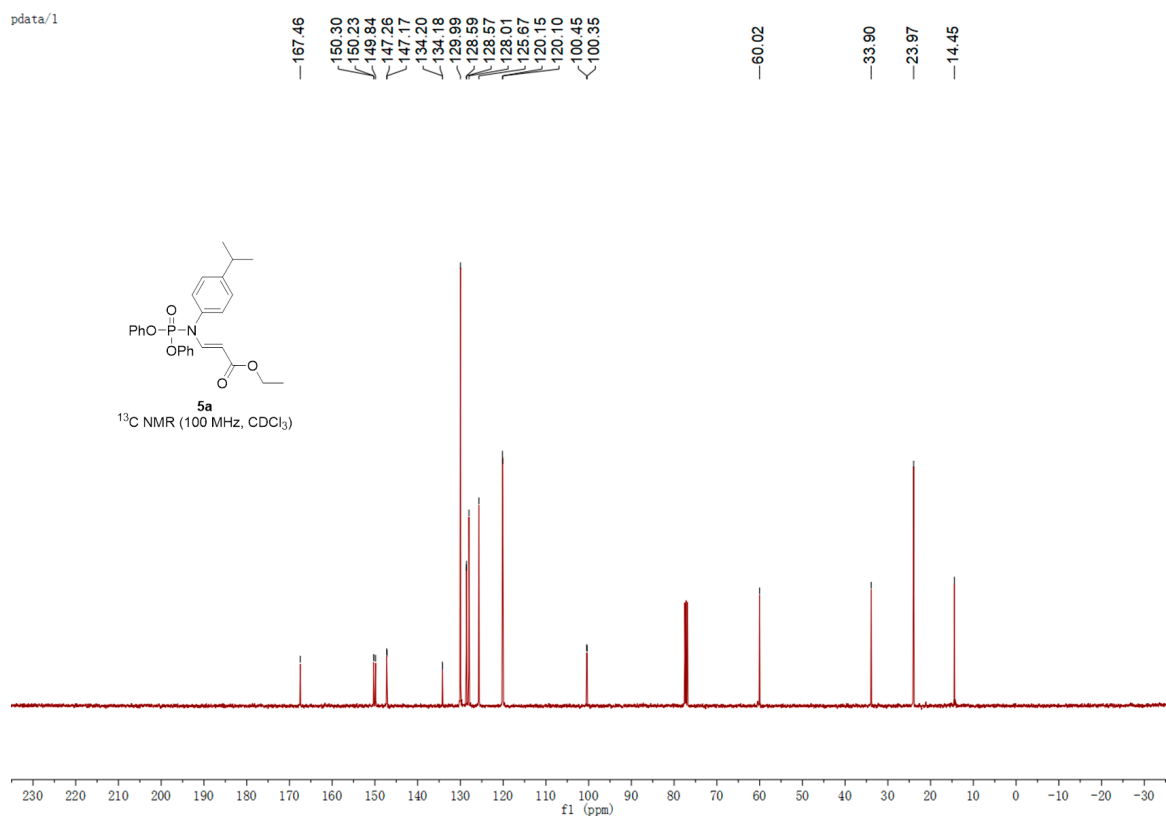
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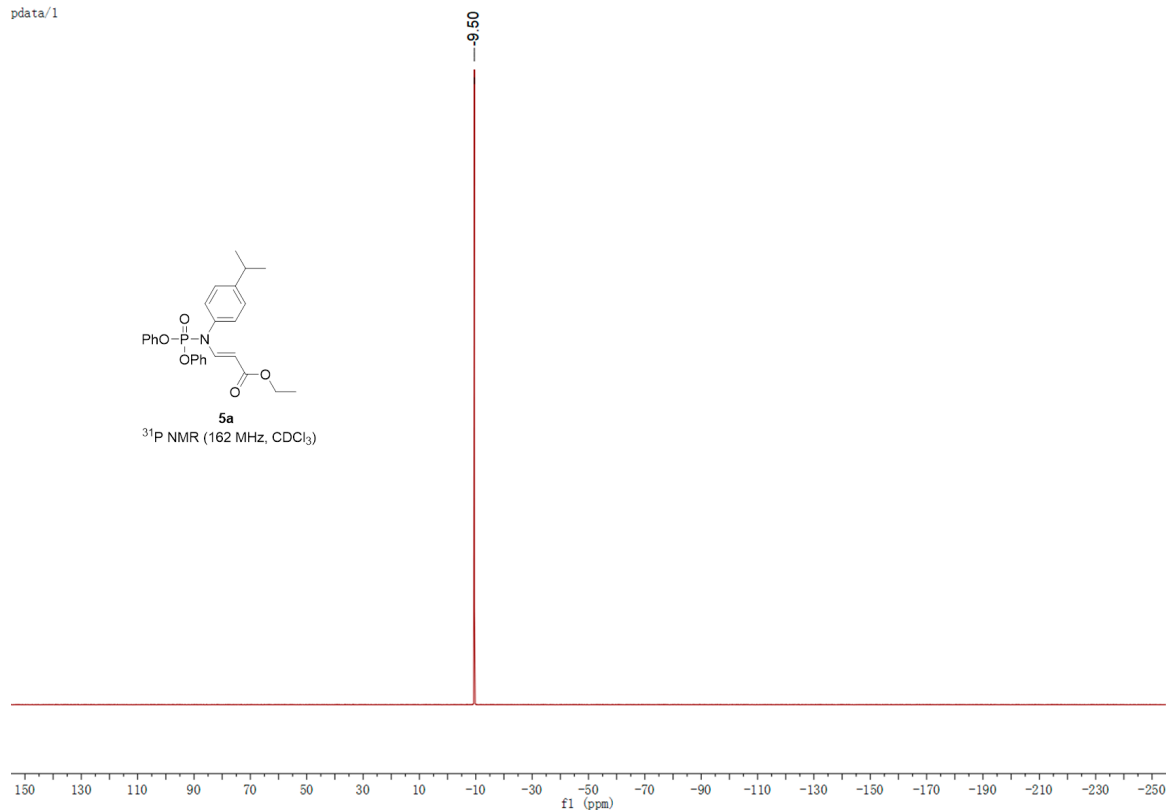
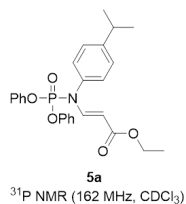
wg1183.1.1.1r



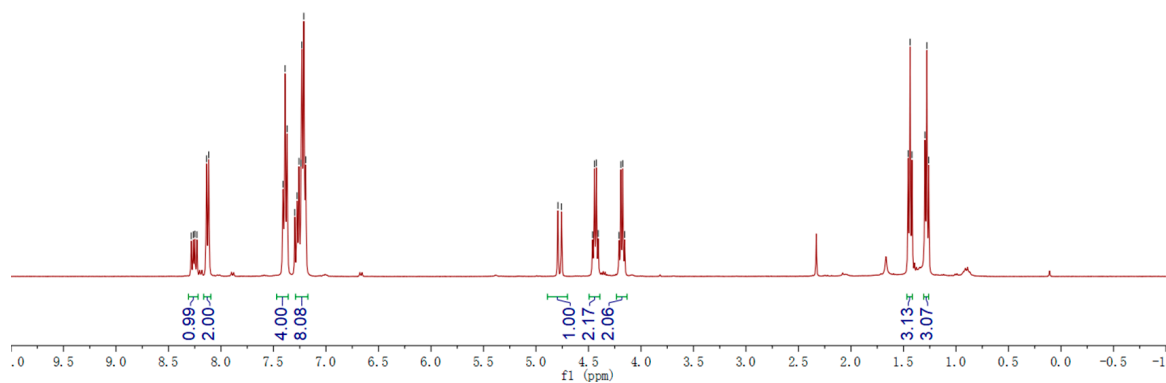
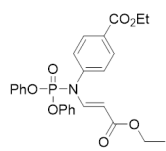
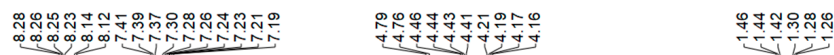
pdata/1



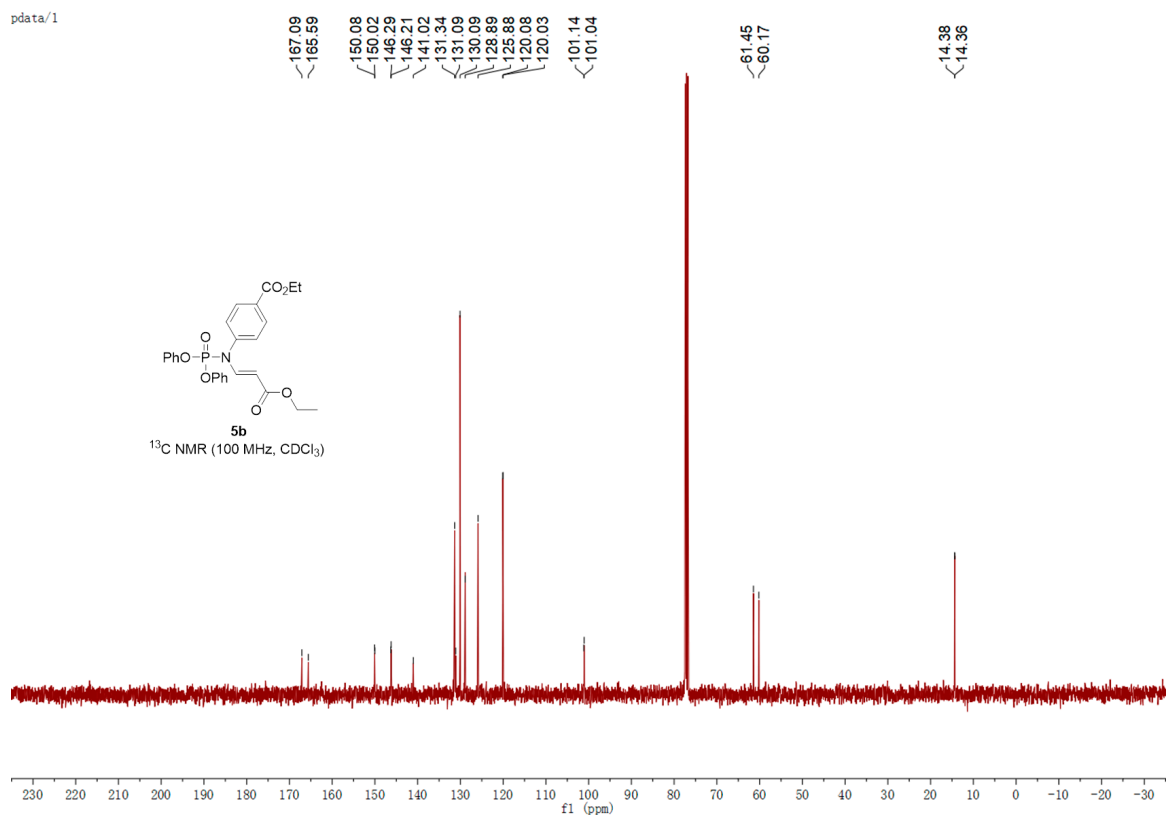
pdata/1



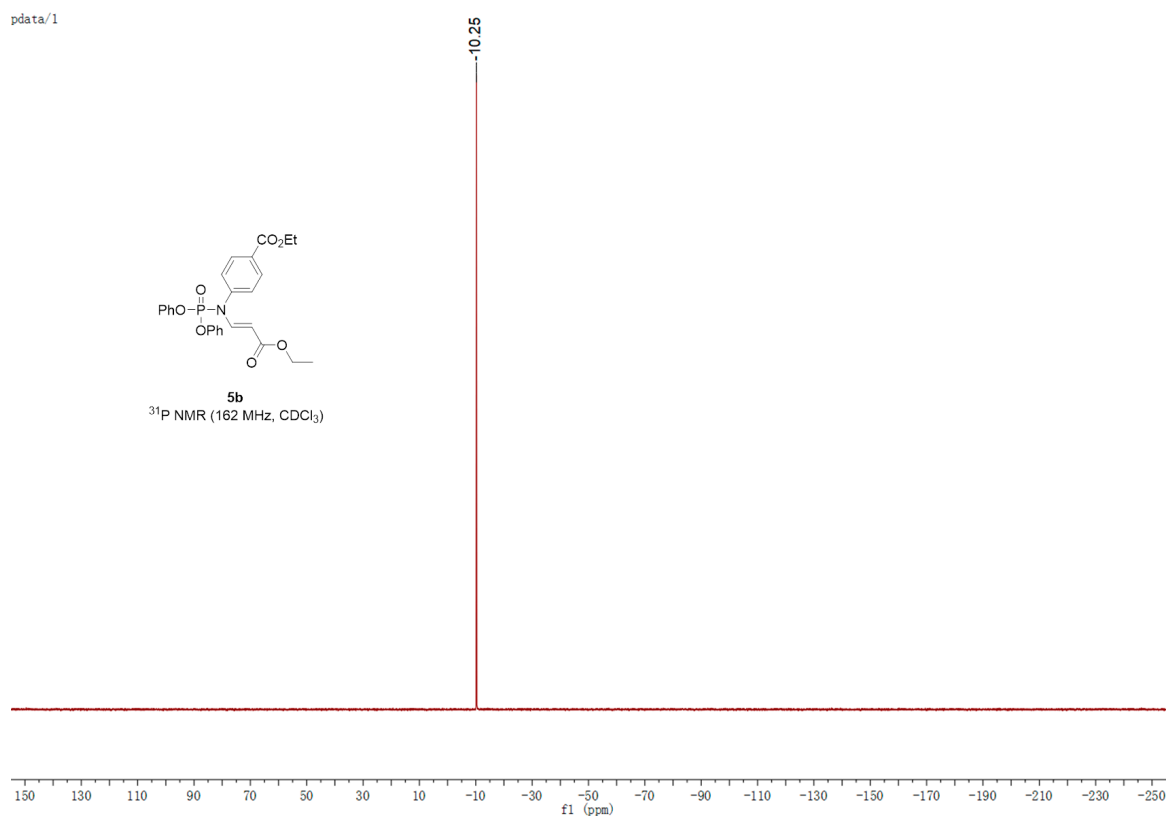
wg1187.1.1.1r



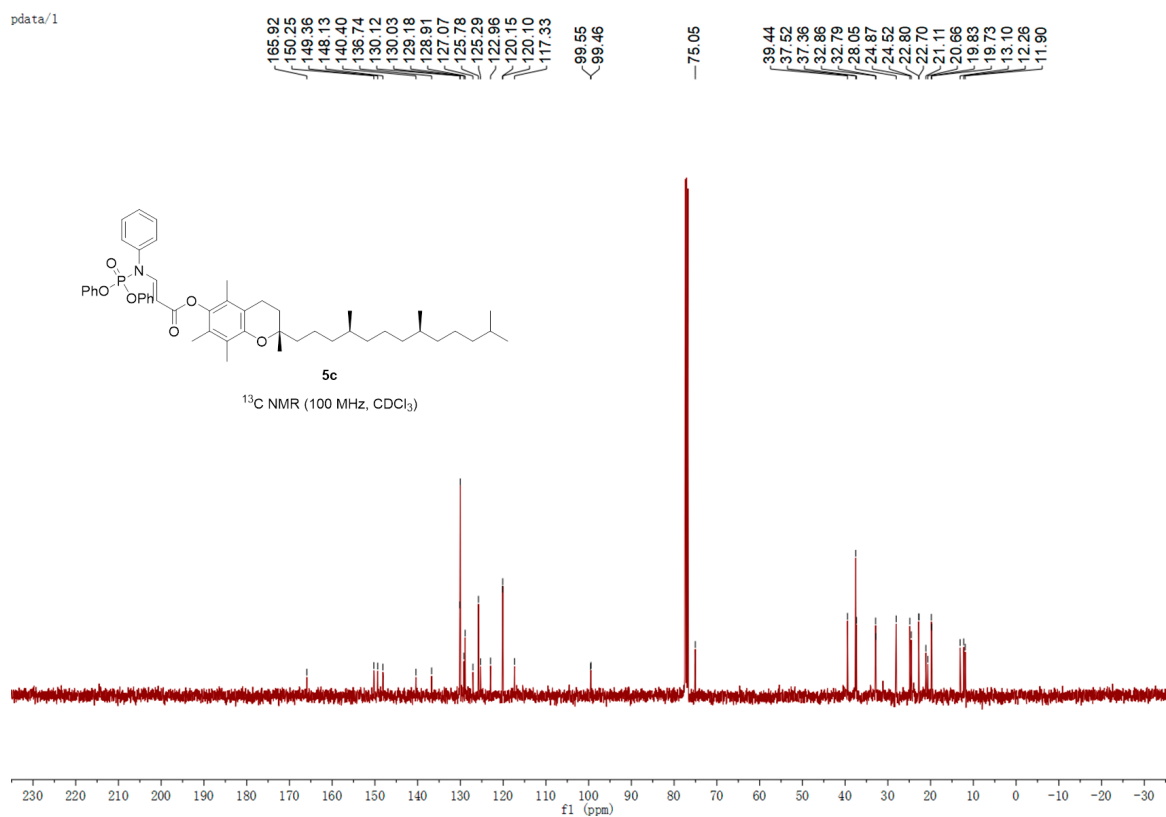
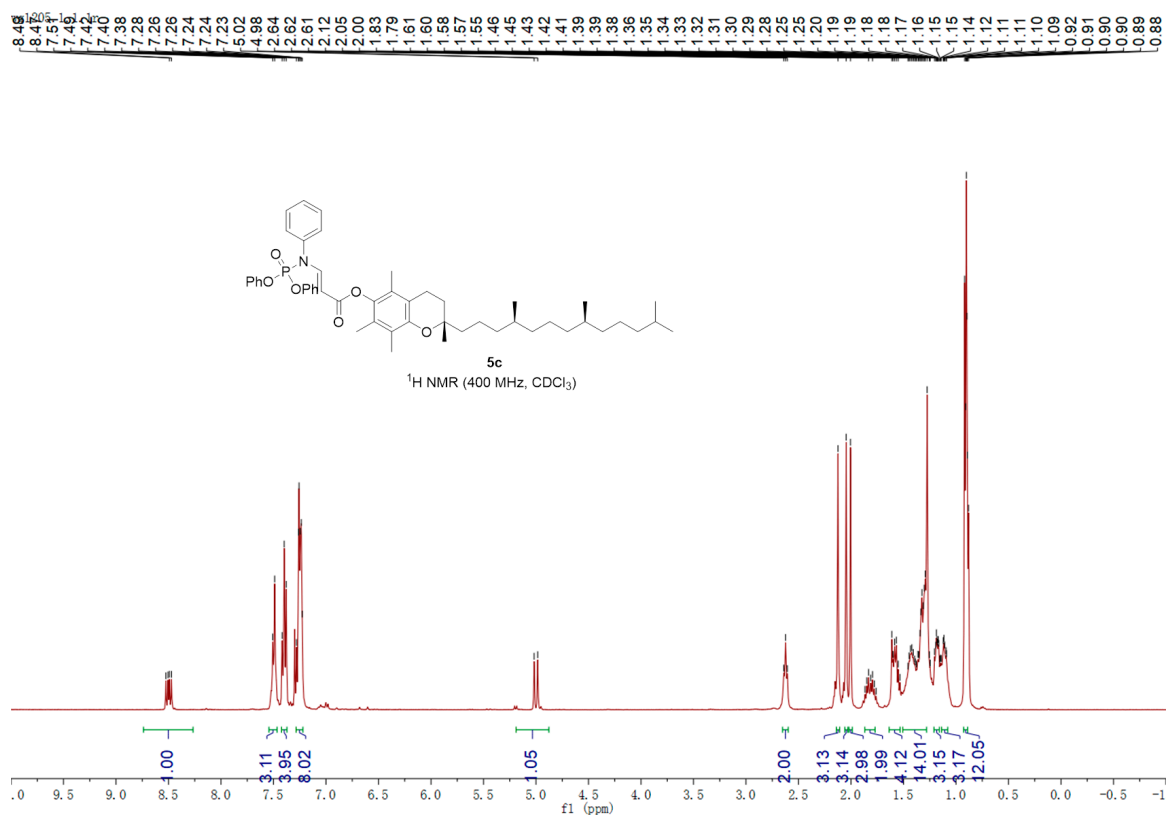
pdata/1



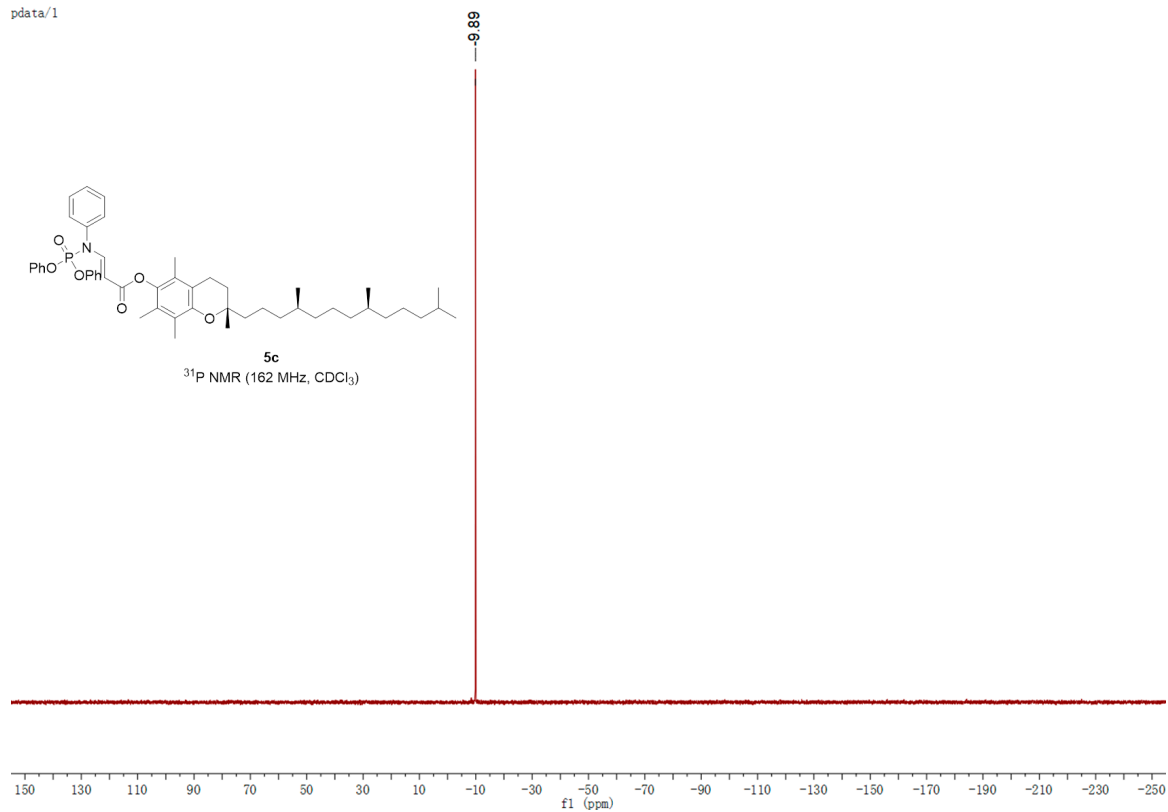
pdata/1





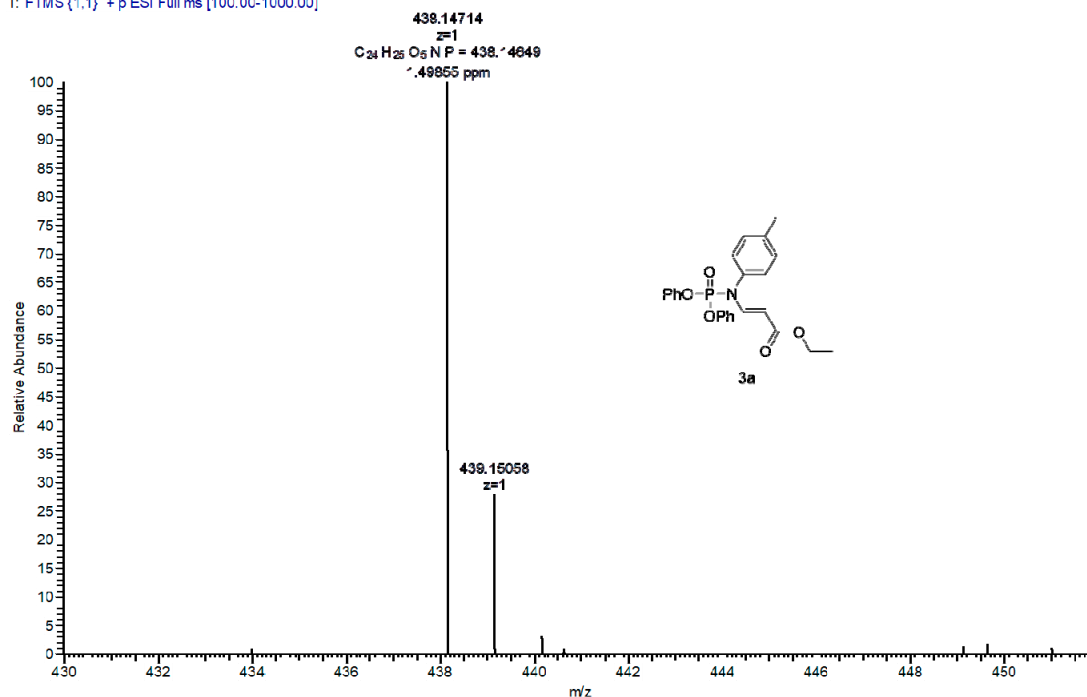


pdata/1

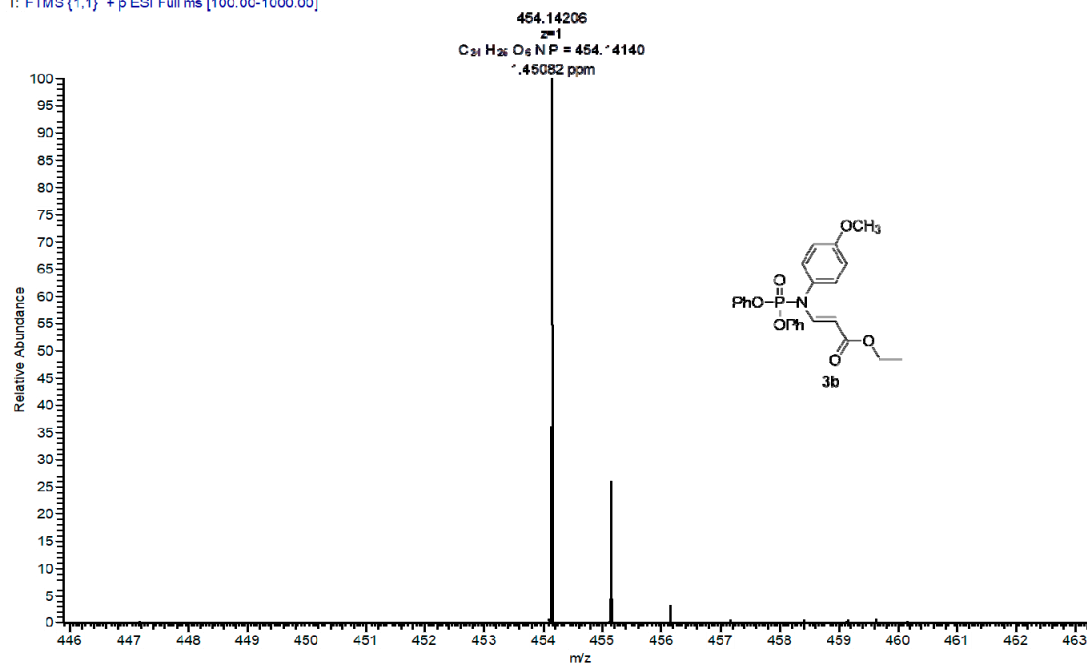


# HRMS spectra of products

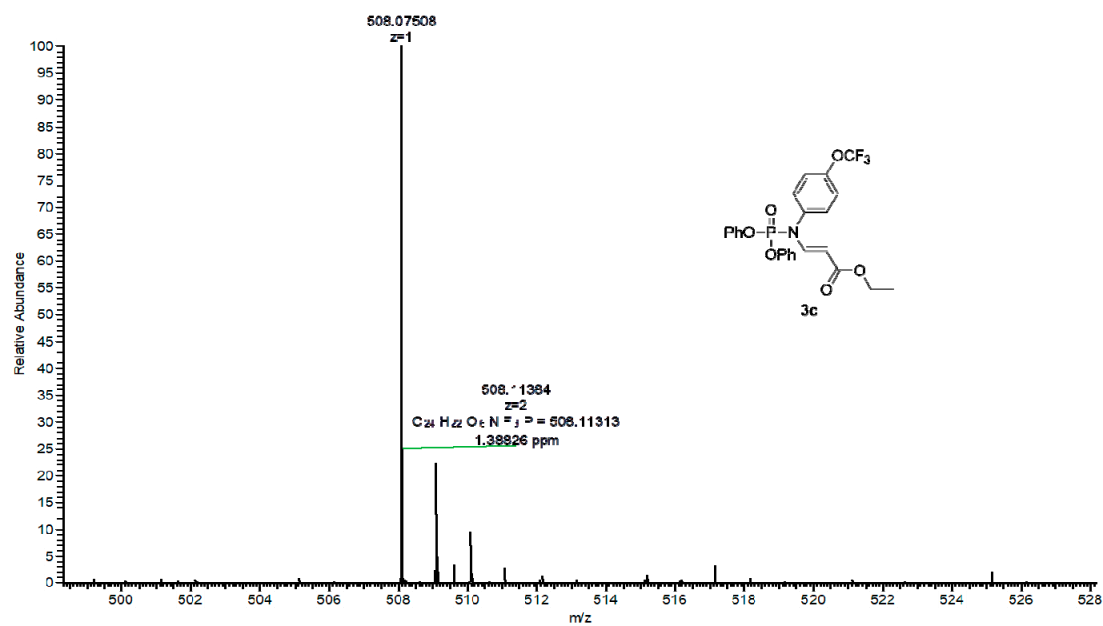
960 #51 RT: 0.74 AV: 1 SB: 24 0.01-0.09 0.77-1.02 NL: 2.07E5  
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



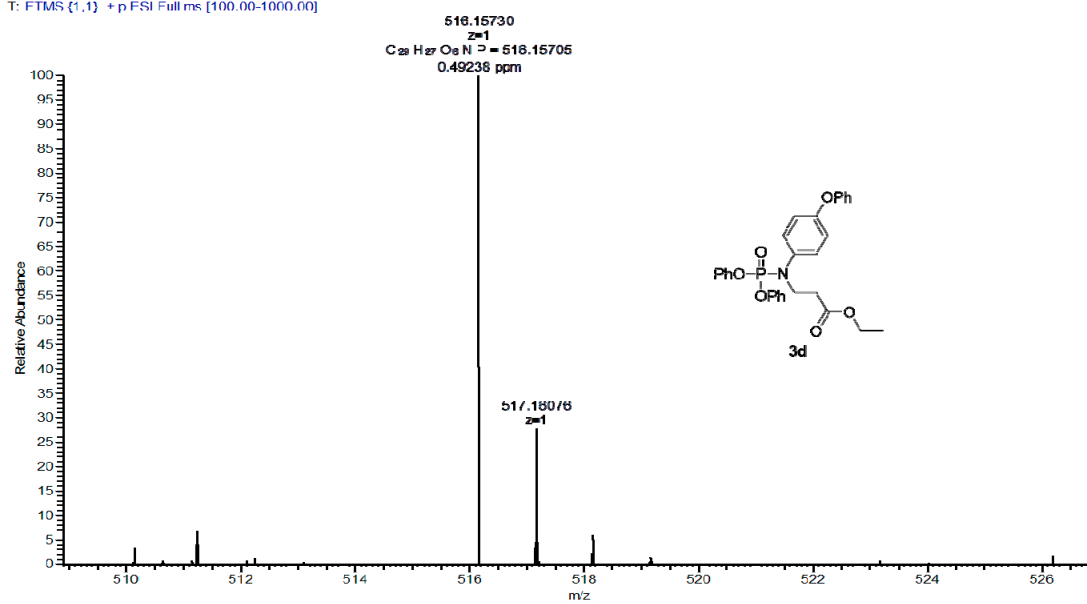
952 #31 RT: 0.45 AV: 1 NL: 1.21E6  
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



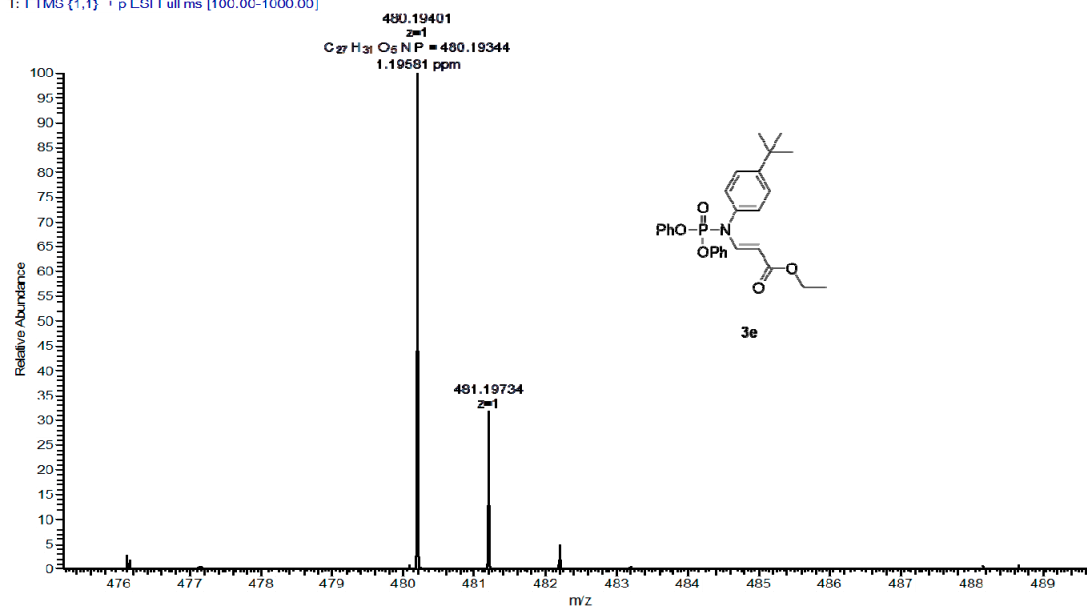
954 #33 RT: 0.48 AV: 1 SB: 24 0.01-0.09 0.78-1.03 NL: 7.24E5  
T: FTMS (1,1) +p ESI Full ms [100.00-1000.00]



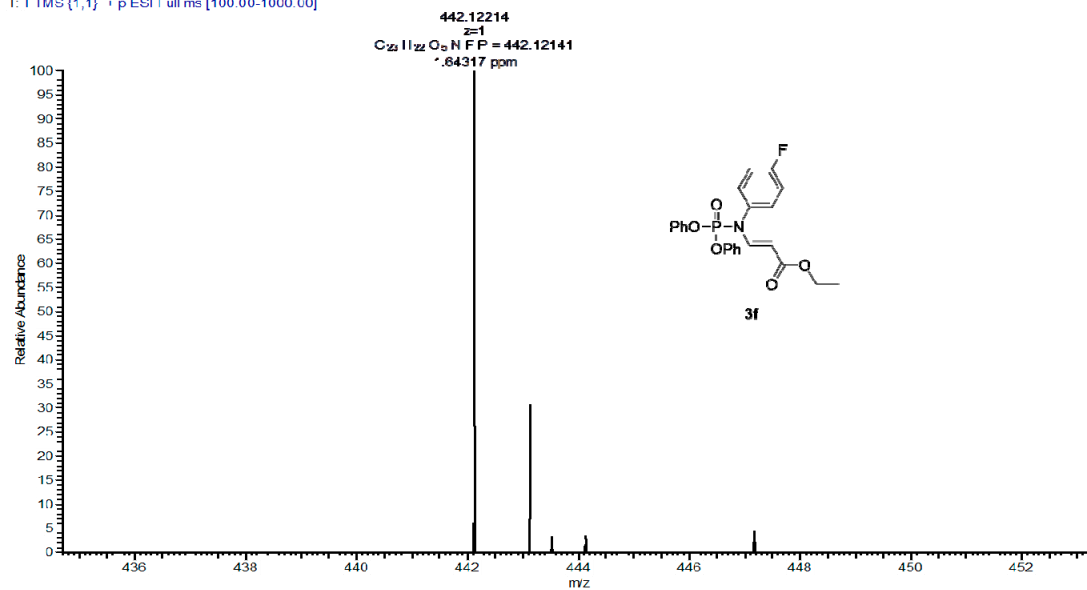
1184 #43 RT: 0.62 AV: 1 SB: 6 0.00-0.08 NL: 3.95E5  
T: FTMS (1,1) +p ESI Full ms [100.00-1000.00]



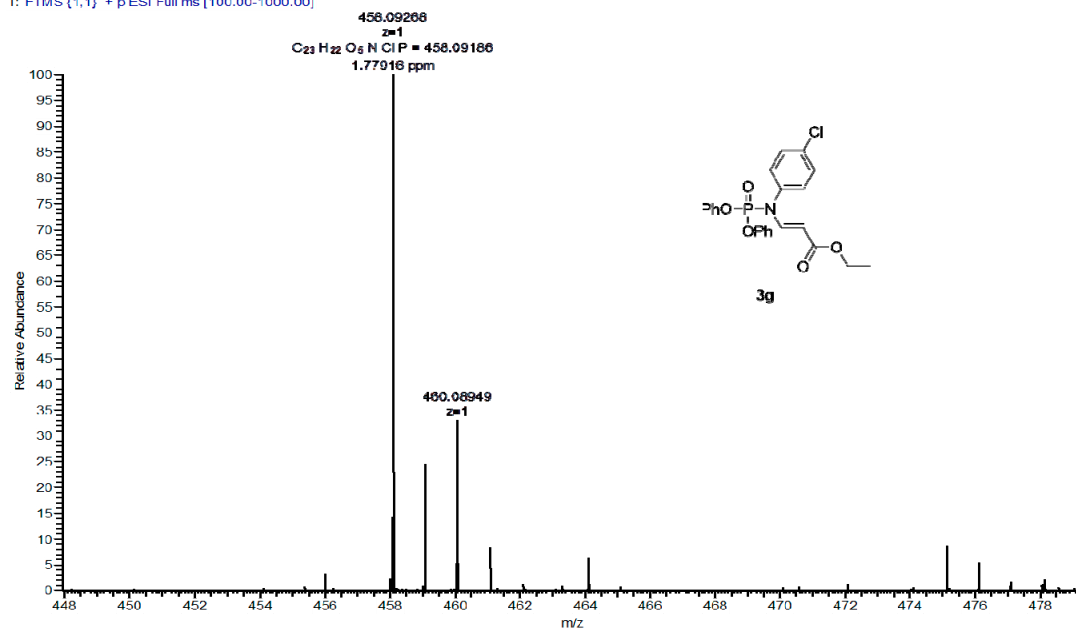
1181 #43 RT: 0.63 AV: 1 SB: 6 0.01-0.09 NL: 7.38E5  
T: LTMS (1,1) + p ESI Full ms [100.00-1000.00]



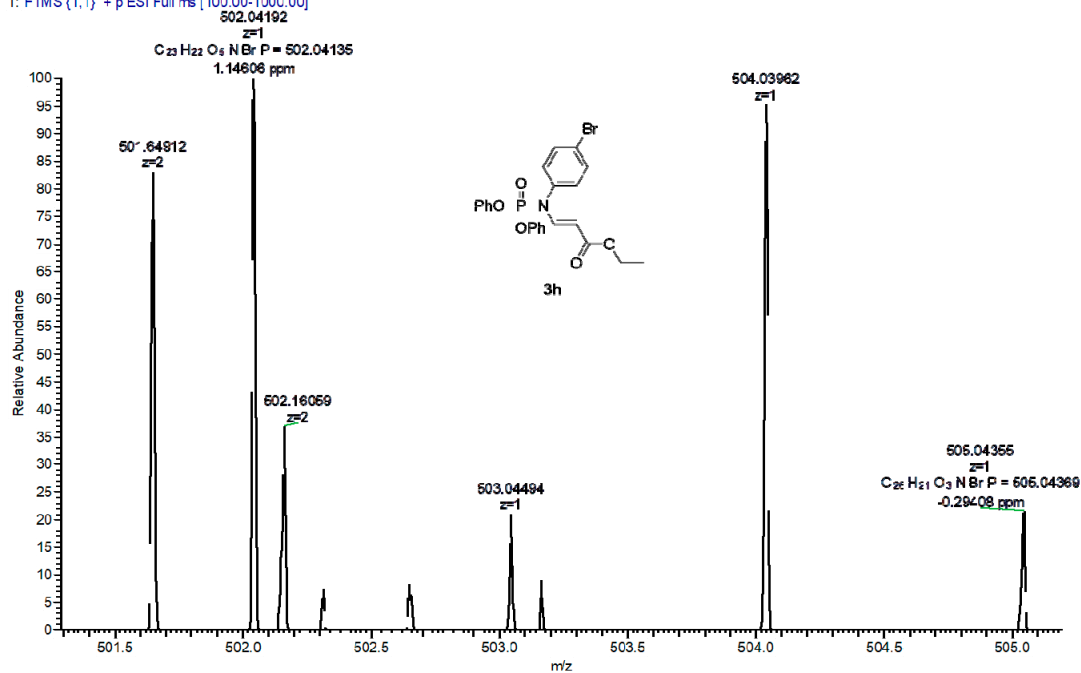
951 #85 RT: 0.95 AV: 1 SB: 24 0.01-0.09, 0.78-1.03 NL: 4.09E4  
T: LTMS (1,1) + p ESI Full ms [100.00-1000.00]



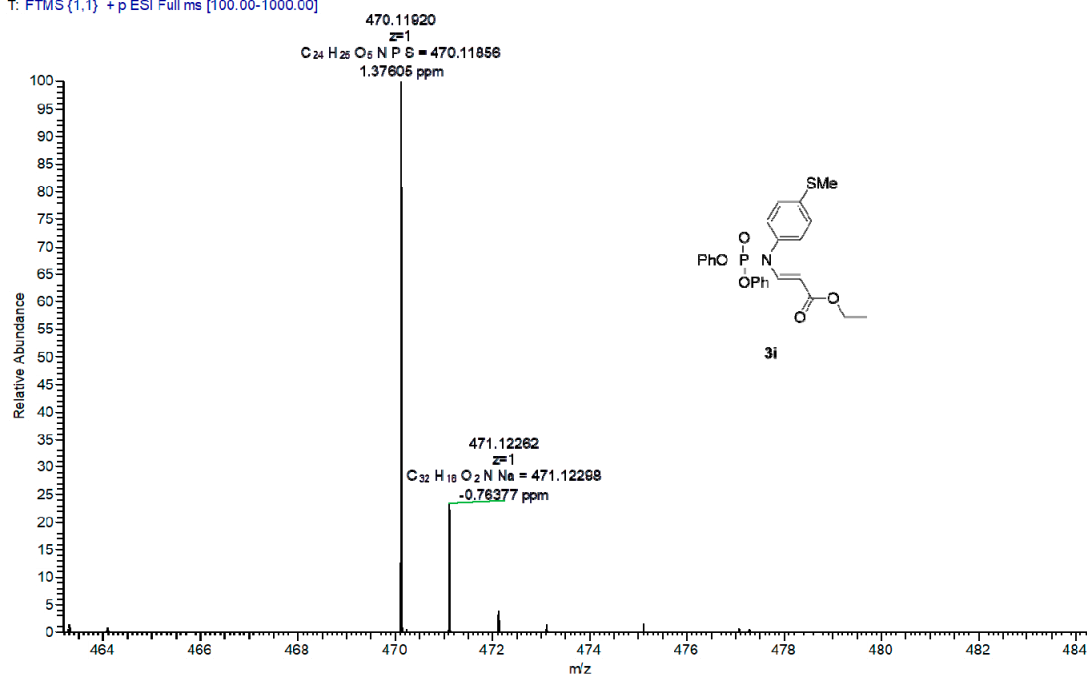
961 #13 RT: 0.20 AV: 1 SB: 24 0.01-0.09 0.78-1.03 NL: 7.03E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



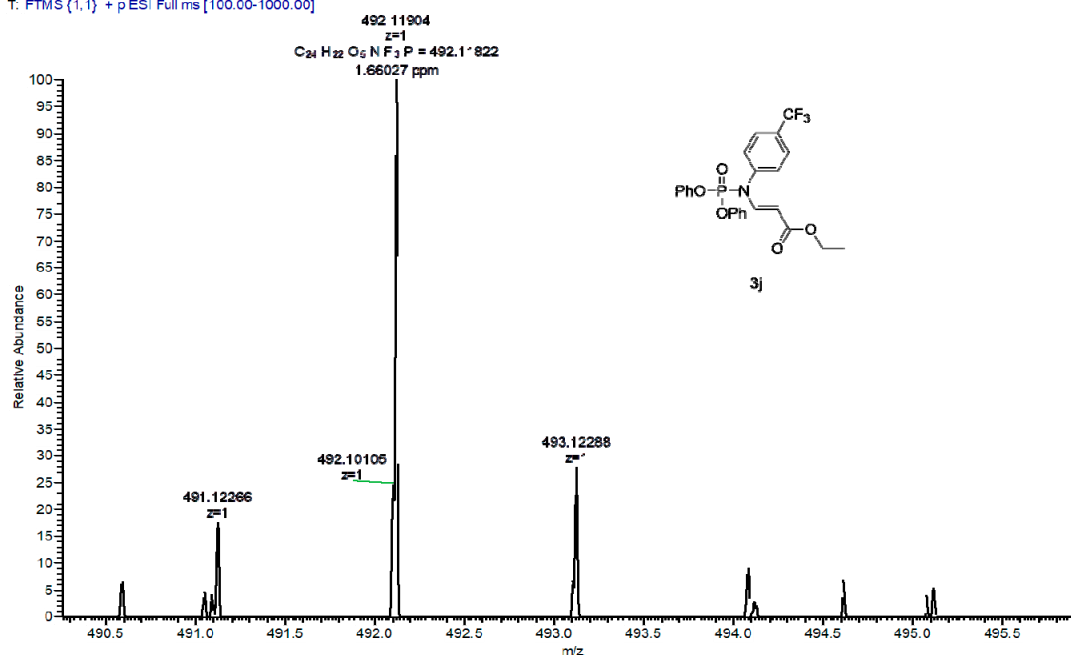
969 #11 RT: 0.17 AV: 1 SB: 6 0.01-0.09 NL: 5.64E4  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



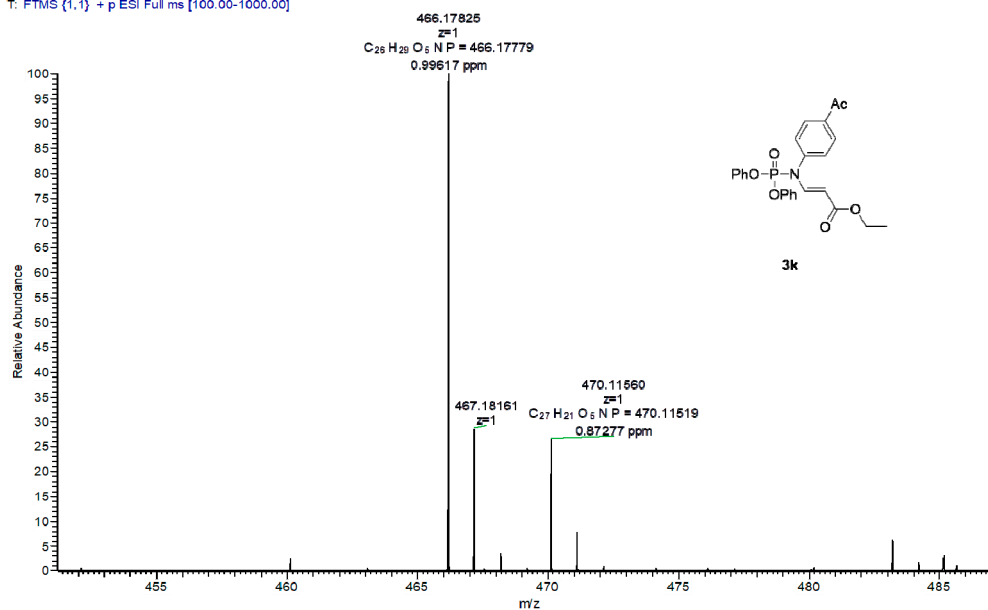
955 #13 RT: 0.20 AV: 1 SB: 24 0.01-0.09 0.78-1.03 NL: 5.41E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



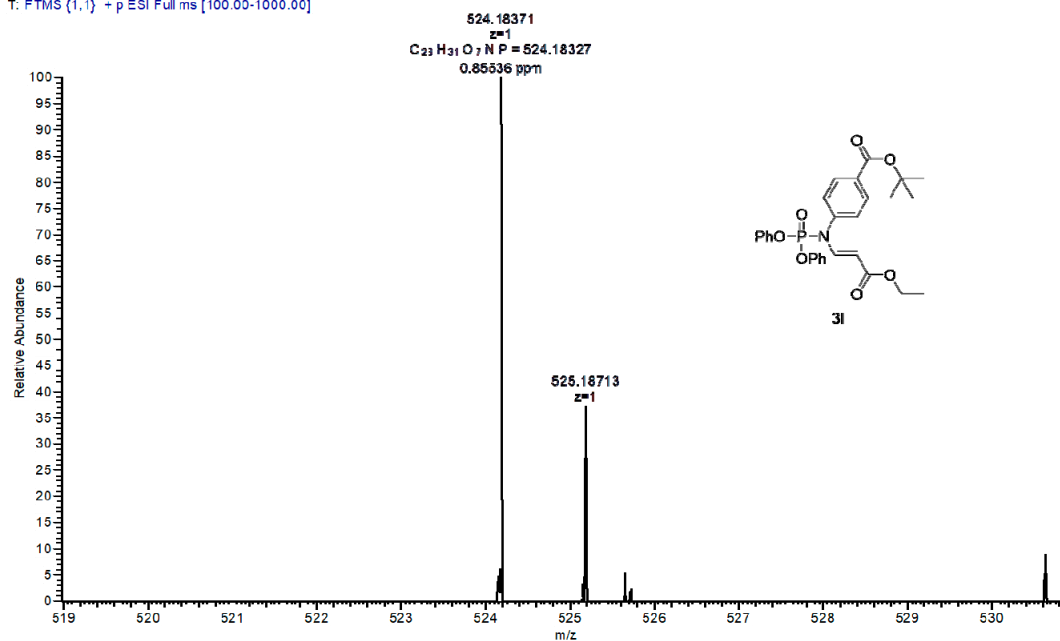
965 #47 RT: 0.71 AV: 1 SB: 6 0.01-0.09 NL: 1.63E4  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



1185 #47 RT: 0.68 AV: 1 SB: 6 0.01-0.09 NL: 3.69E5  
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

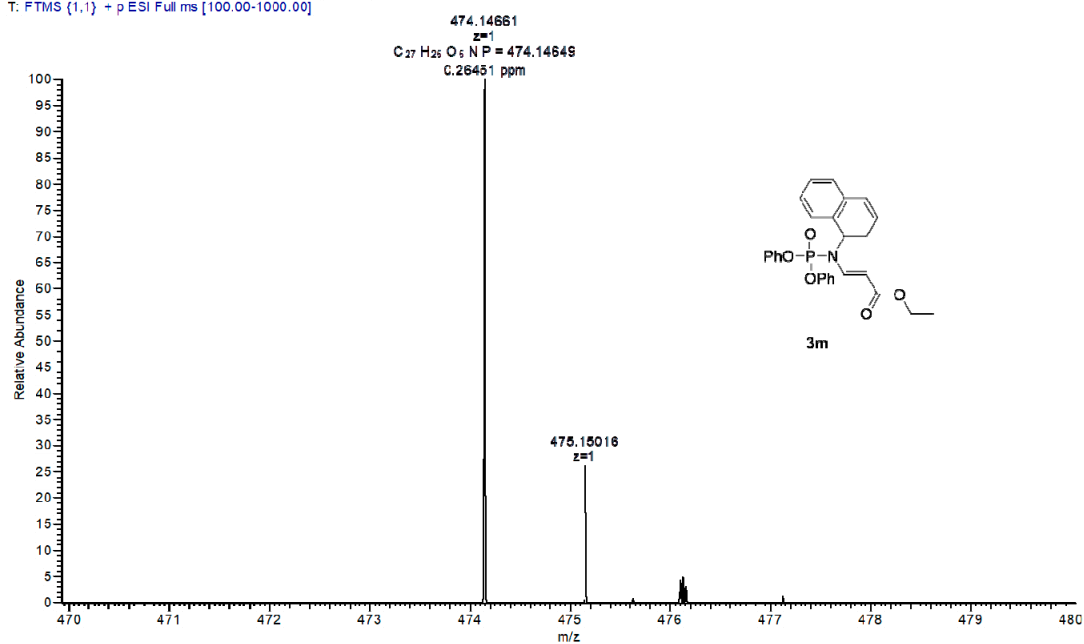


1191 #13 RT: 0.20 AV: 1 SB: 6 0.01-0.09 NL: 9.38E4  
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

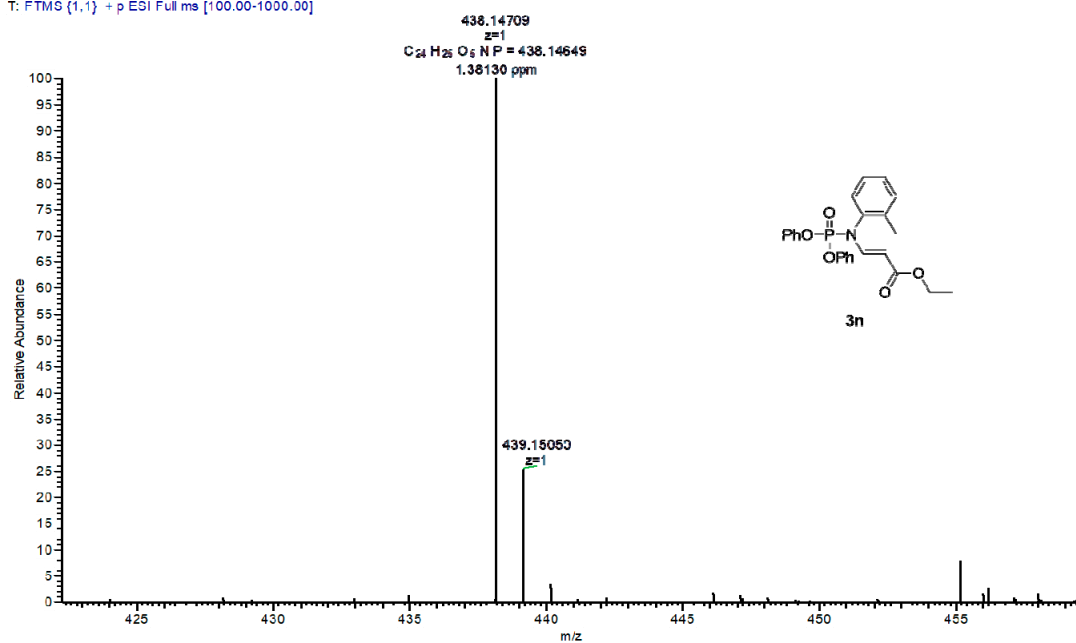




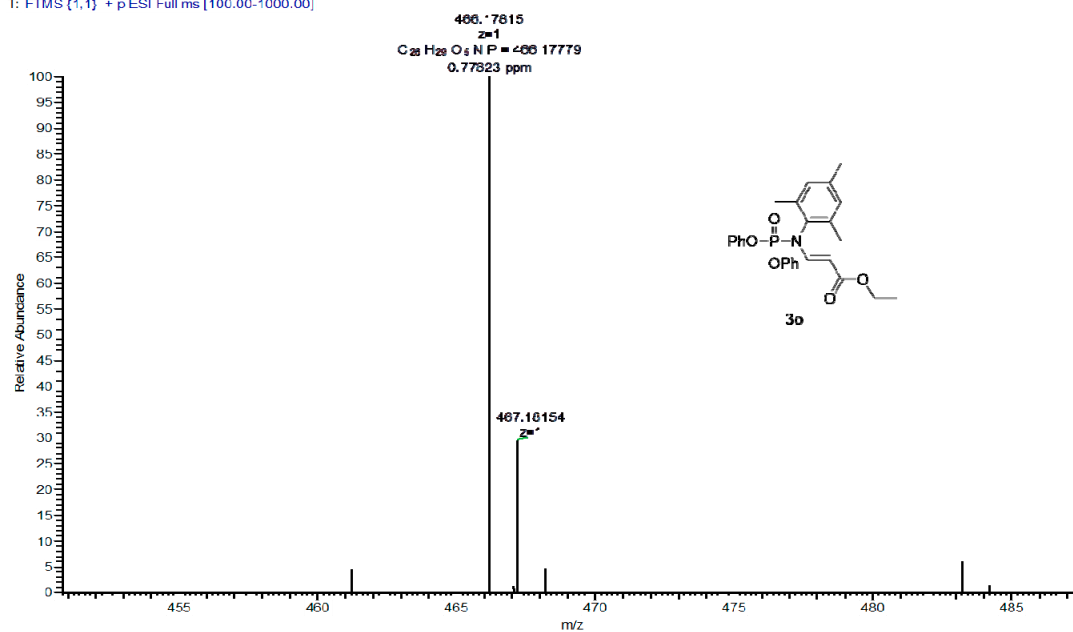
978 #43 RT: 0.63 AV: 1 SB: 6 0.01-0.09 NL: 4.44E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



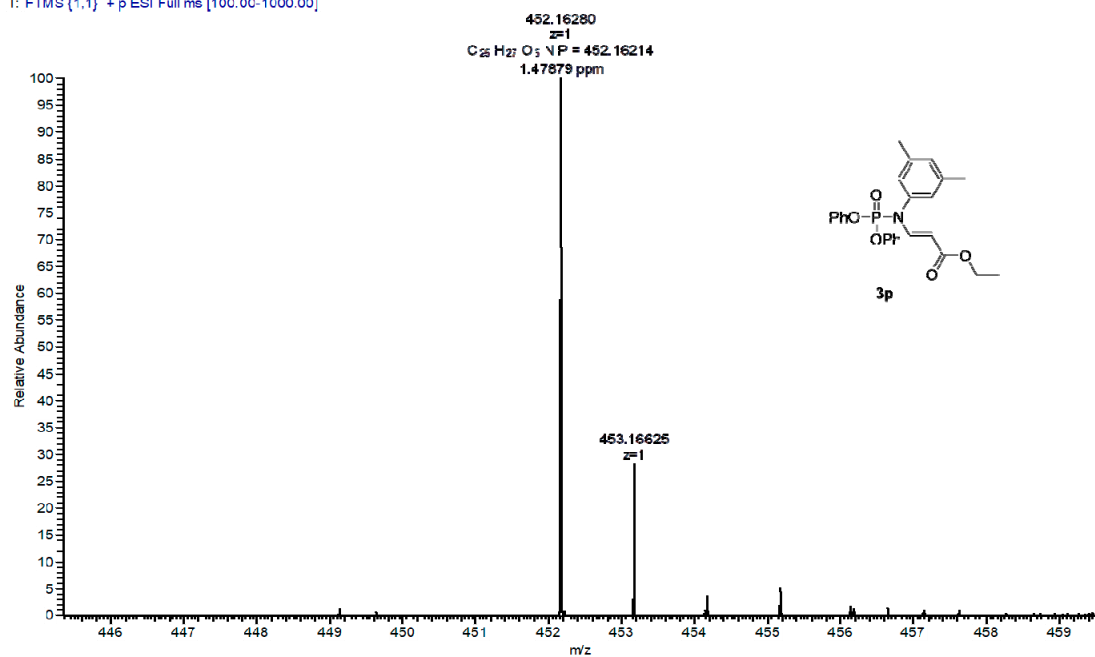
974 #21 RT: 0.31 AV: 1 SB: 6 0.01-0.09 NL: 1.22E6  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



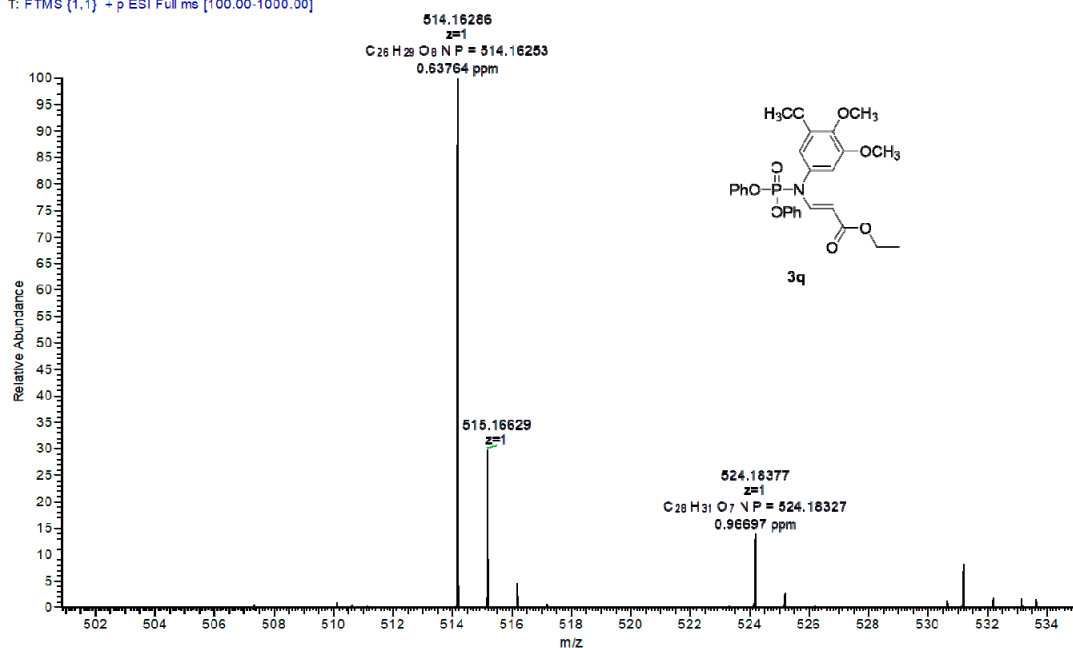
1192 #13 RT: 0.20 AV: 1 SB: 6 0.01-0.09 NL: 3.06E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



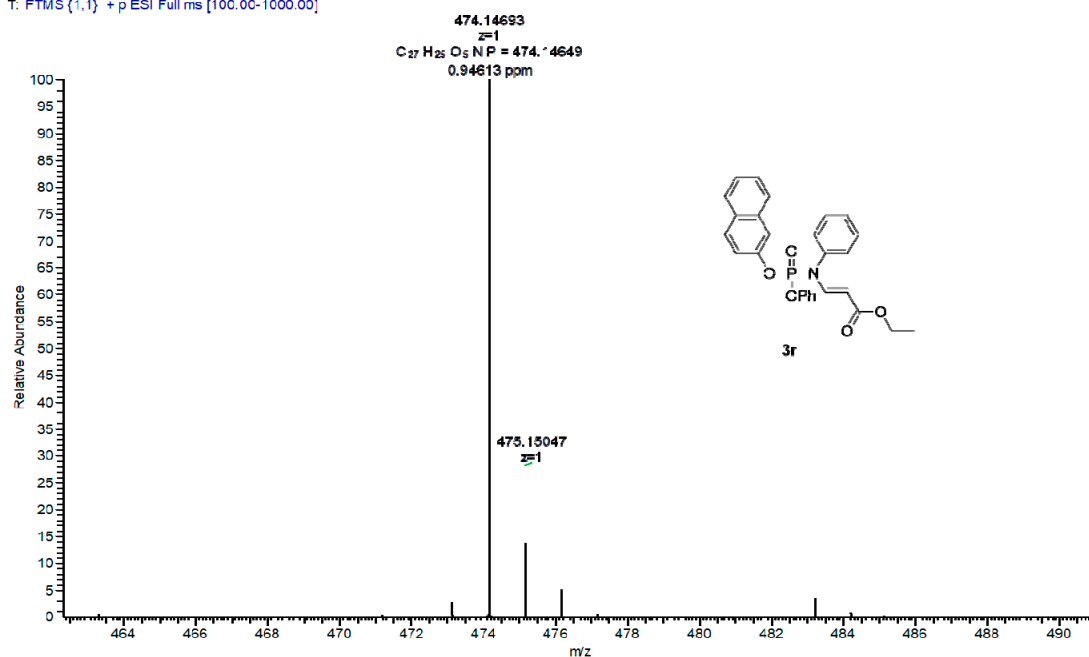
957 #51 RT: 0.75 AV: 1 SB: 24 0.01-0.09 0.78-1.03 NL: 3.78E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



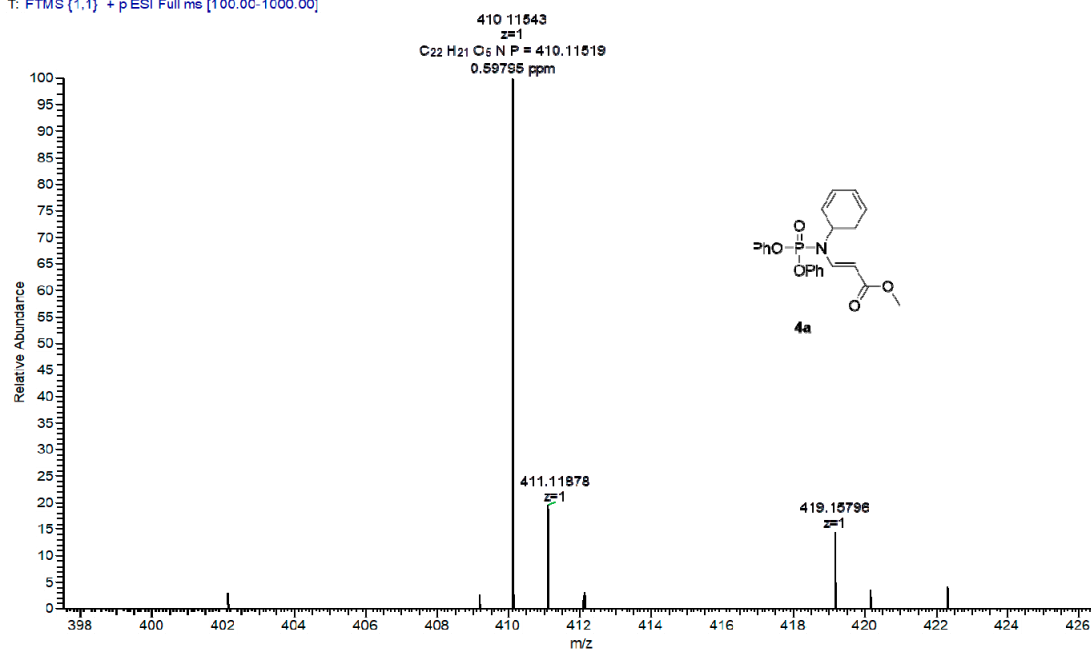
1188 #13 RT: 0.20 AV: 1 SB: 6 0.01-0.09 NL: 6.71E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



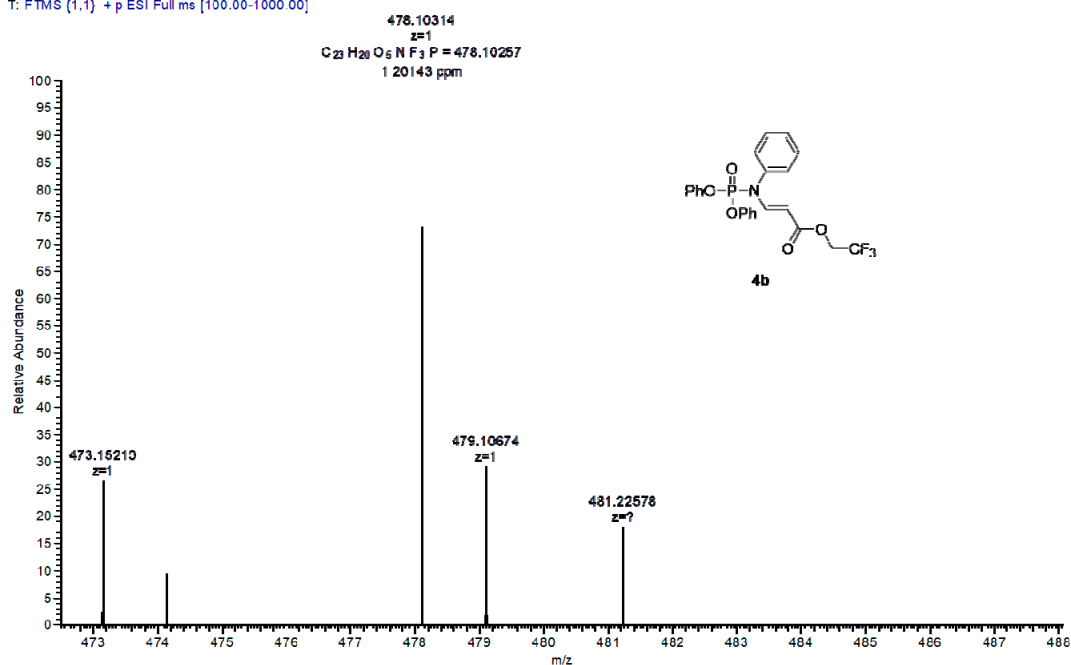
1197 #15 RT: 0.22 AV: 1 SB: 6 0.00-0.08 NL: 5.17E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



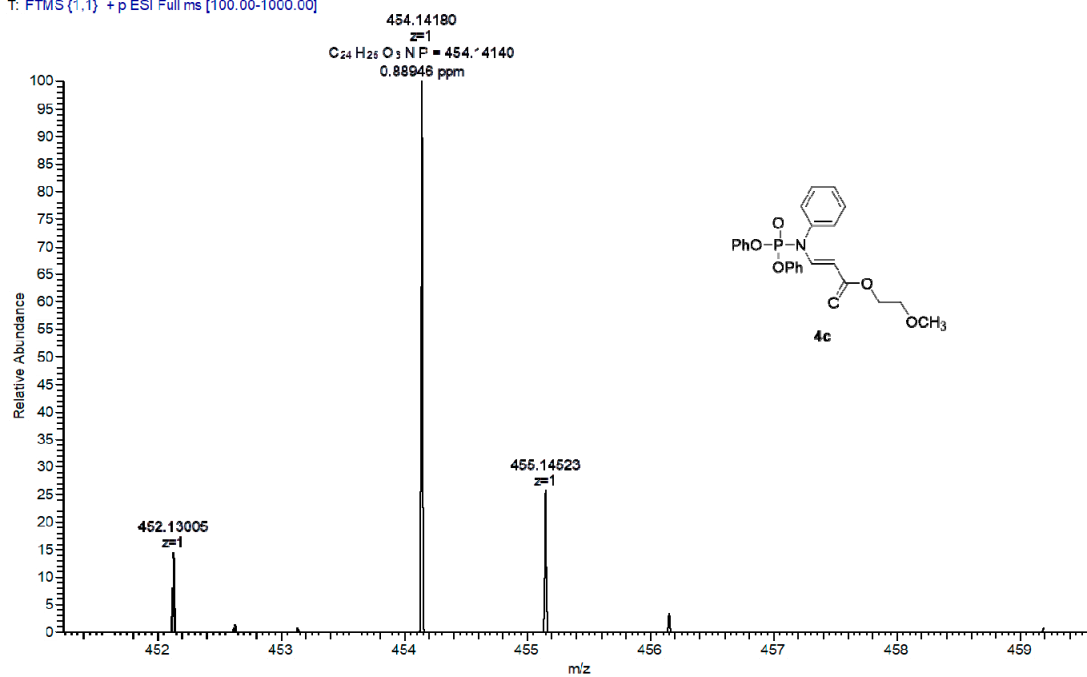
1198 #15 RT: 0.22 AV: 1 SB: 6 0.00-0.09 NL: 8.19E4  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



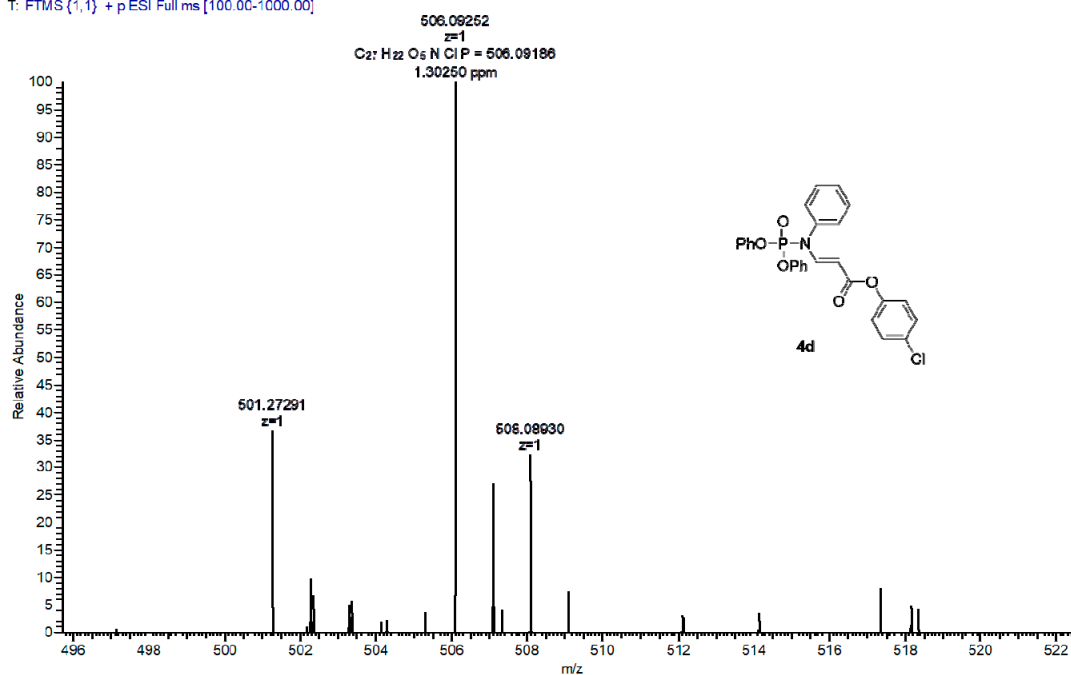
1200 #13 RT: 0.19 AV: 1 SB: 6 0.01-0.09 NL: 6.85E4  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



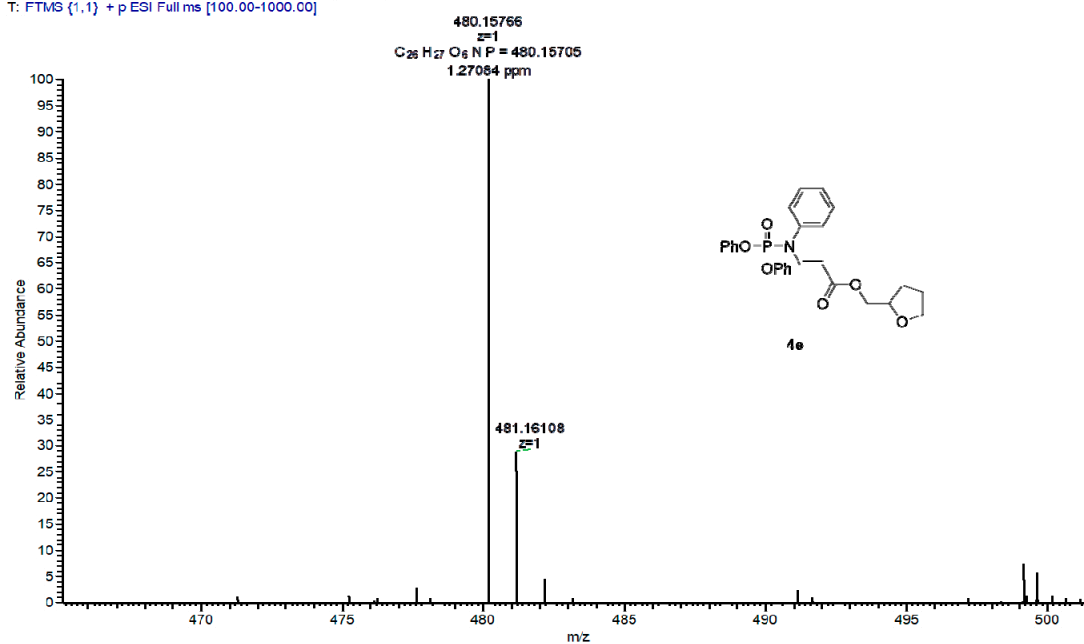
1203 #17 RT: 0.24 AV: 1 SB: 6 0.01-0.09 NL: 1.78E6  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



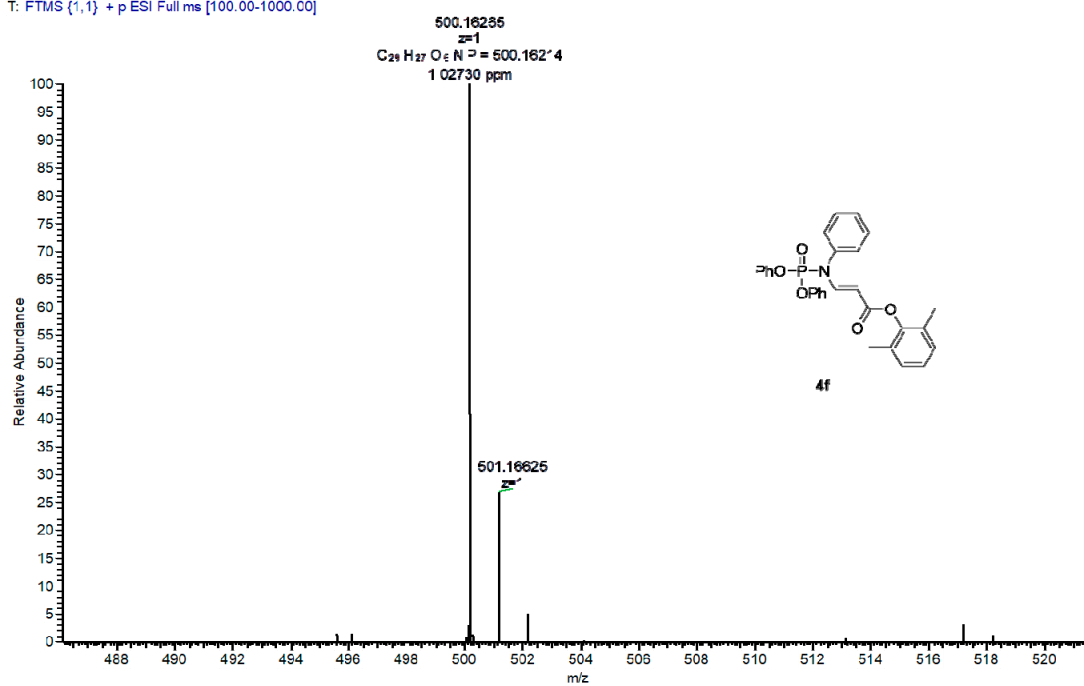
1201 #13 RT: 0.20 AV: 1 SB: 6 0.01-0.09 NL: 8.25E4  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



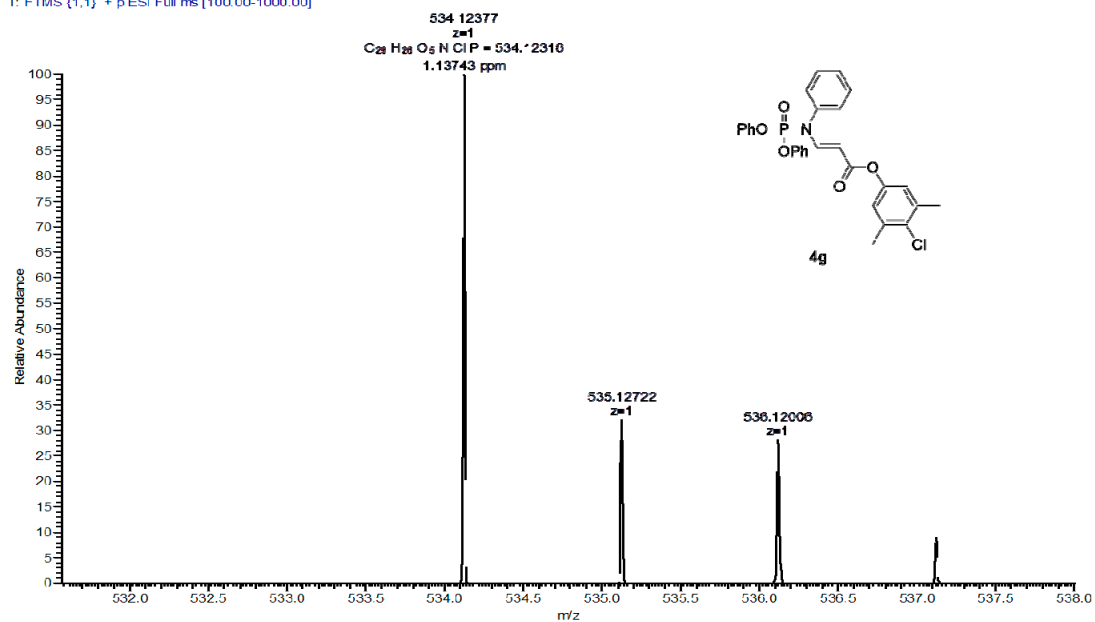
1210 #33 RT: 0.49 AV: 1 SB: 6 0.01-0.09 NL: 5.82E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



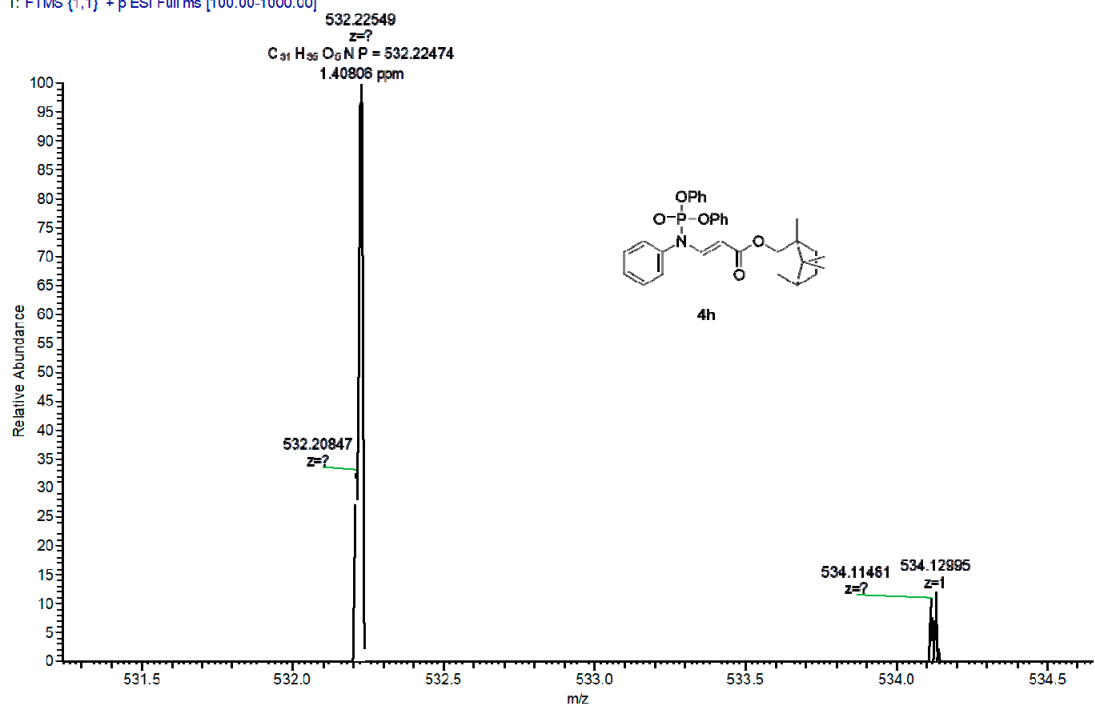
1207 #41 RT: 0.61 AV: 1 SB: 6 0.01-0.09 NL: 2.48E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



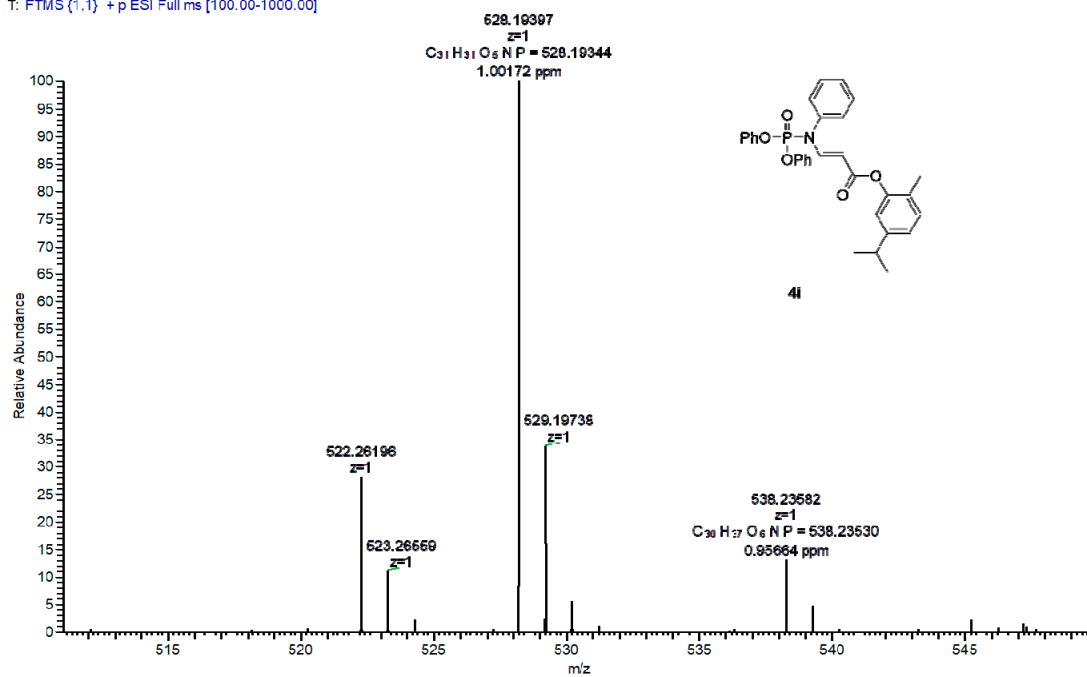
1206 #41 RT: 0.61 AV: 1 SB: 5 0.01-0.09 NL: 2.05E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



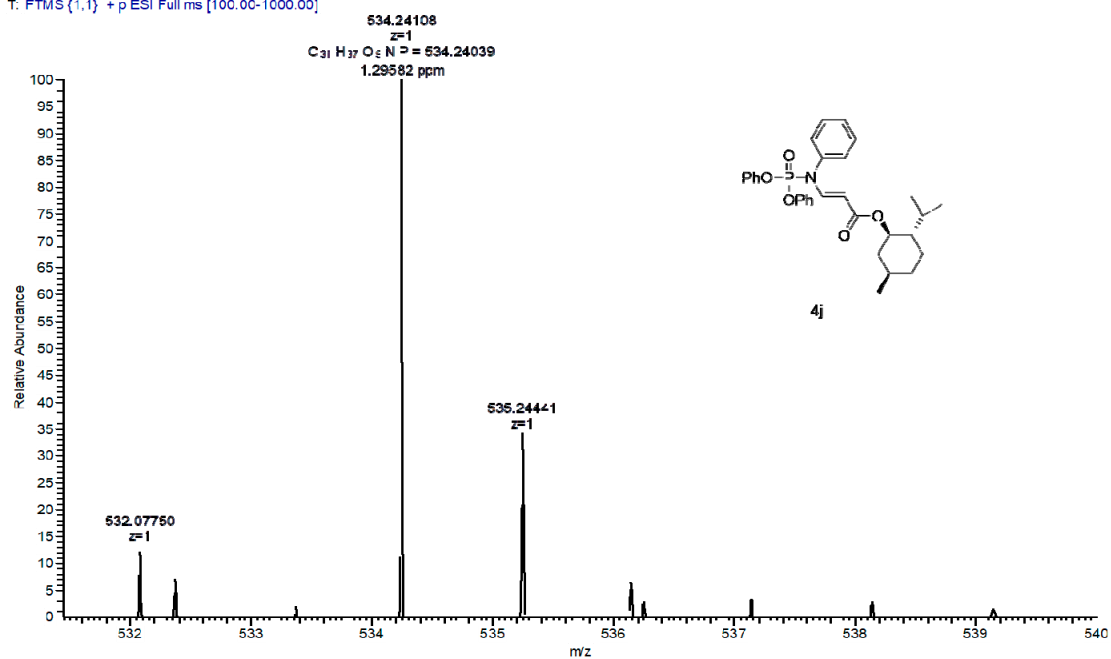
1209 #33 RT: 0.49 AV: 1 SB: 6 0.01-0.09 NL: 7.42E3  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



1204 #21 RT: 0.32 AV: 1 SB: 6 0.01-0.09 NL: 7.01E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]

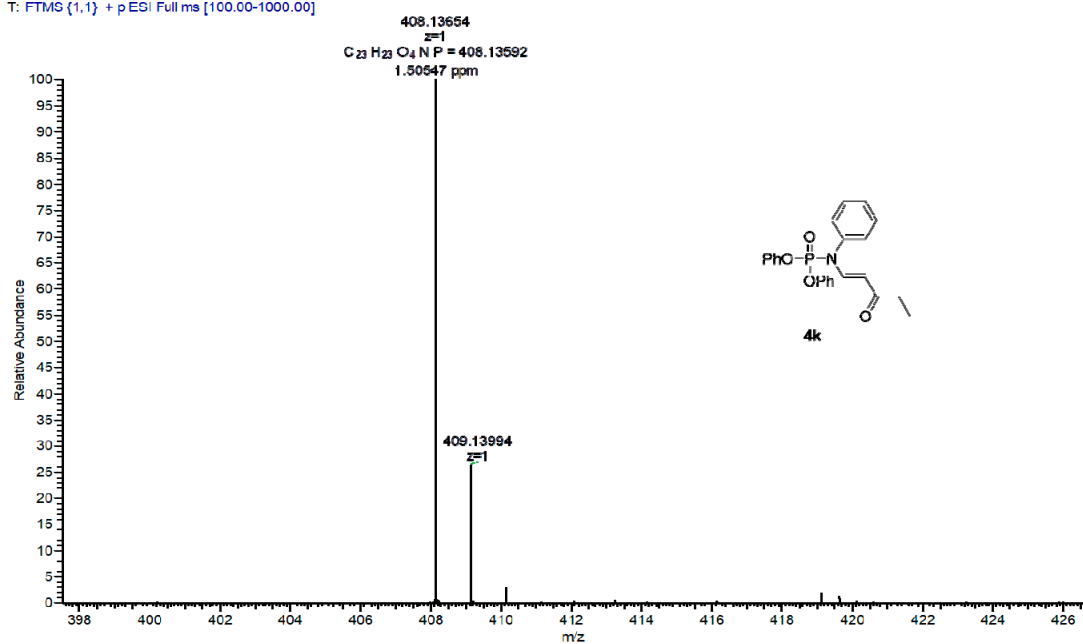


1202 #51 RT: 0.76 AV: 1 SB: 6 0.01-0.09 NL: 9.18E4  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]

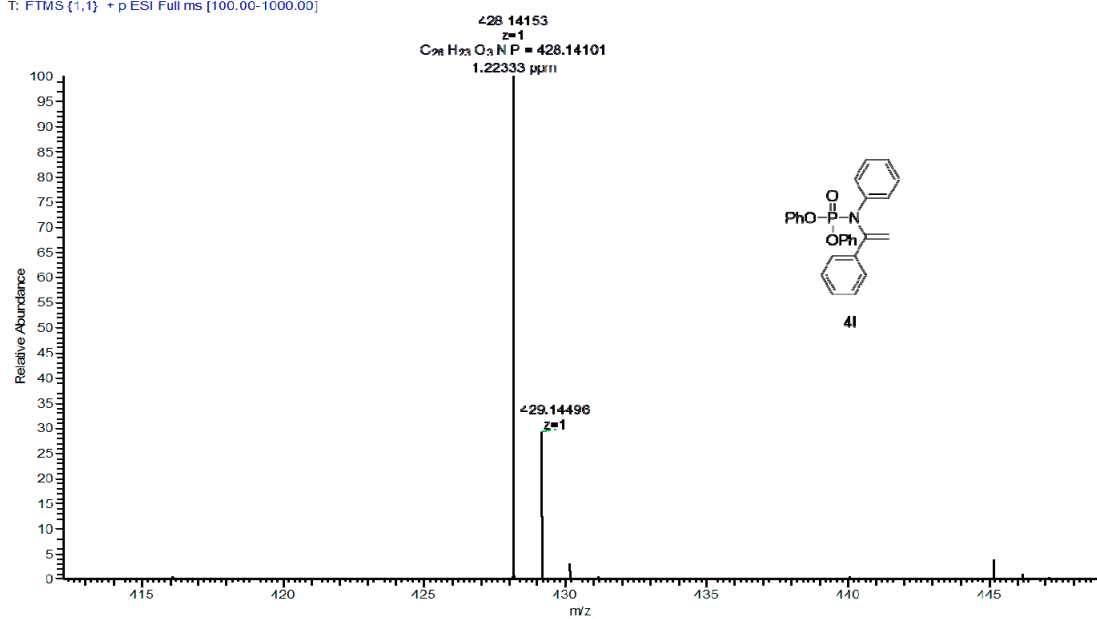




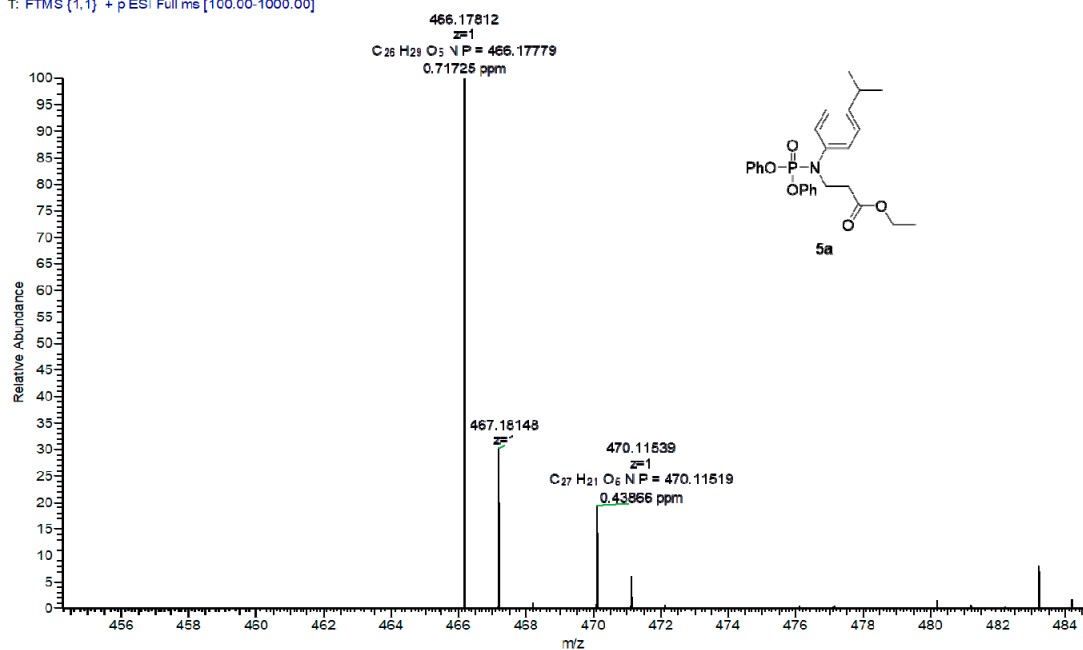
1199 #11 RT: 0.16 AV: 1 SB: 6 0.00-0.09 NL: 2.79E6  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



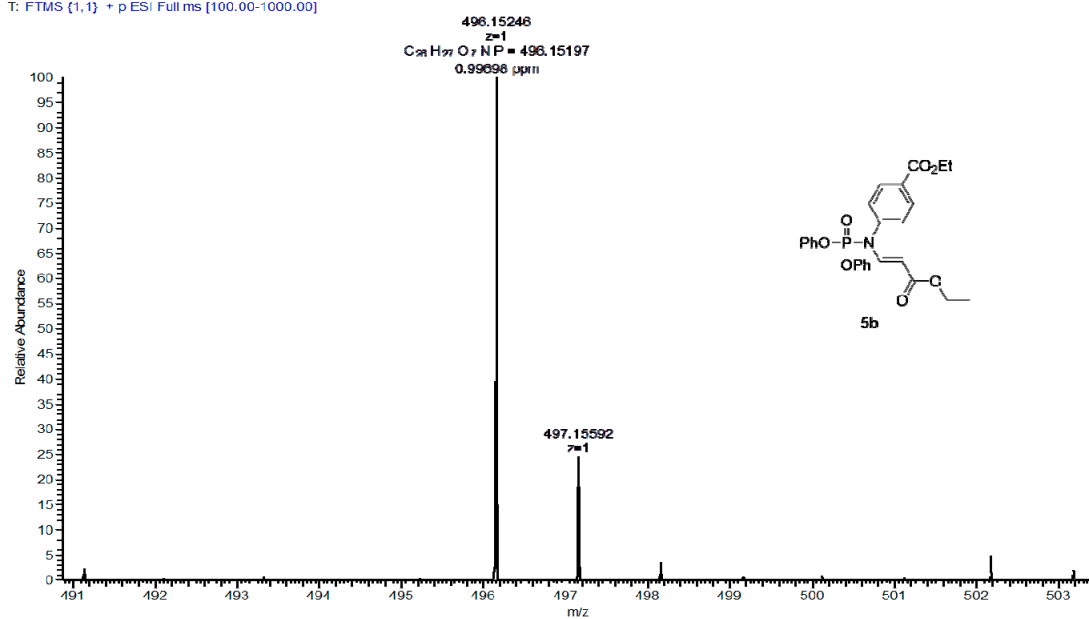
963 #21 RT: 0.29 AV: 1 SB: 6 0.01 0.09 NL: 1.21E6  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



1183 #43 RT: 0.63 AV: 1 SB: 6 0.00-0.08 NL: 1.06E6  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



1187 #13 RT: 0.20 AV: 1 SB: 6 0.01 0.09 NL: 6.76E5  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]



1205 #11 RT: 0.17 AV: 1 SB: 6 0.01-0.09 NL: 3.20E4  
T: FTMS (1,1) + p ESI Full ms [100.00-1000.00]

