

## Supporting information

### Organoselenium-Catalyzed Vicinal Dichlorination of Unsaturated Phosphonates

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**Table S1** Screening of reaction conditions

<p><b>1a</b></p>			
C4	C5	C6	
C7	C8	C9	
Entry <sup>a</sup>	Cat. (mol %)	Yield (%)	d.r.(anti/syn) <sup>b</sup>
1	C4(5)	89	4 : 1
2	C5(5)	91	3 : 1
3	C6(5)	87	3 : 1
4	C7(5)	92	4 : 1
5	C8(5)	90	4 : 1
6	C9(5)	92	2 : 1

<sup>a</sup> **1a** (0.20 mmol),  $\text{SO}_2\text{Cl}_2$  (0.22 mol), catalyst (5 mol%),  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (1.5 mL), -20 °C, 5 min, isolated yield. <sup>b</sup> Determined by  $^1\text{H}$  NMR spectroscopy analysis of the integral area of  $\alpha$ -H.

**Table S2** Studying the reaction mechanism

Entry <sup>a</sup>	T(°C)	Catalyst	Yield (%)	d.r.(anti/syn) <sup>b</sup>
1	25	-	95	1 :1
2	-20	-	trace	-
3	-20	PhSeSePh(C1)	89	6 :1
4	-20	<sup>n</sup> Bu <sub>4</sub> NCl	trace	-
5	-20	<sup>n</sup> Bu <sub>4</sub> NCl	trace	-

<sup>a</sup> Alkene (0.20 mmol), SO<sub>2</sub>Cl<sub>2</sub> (0.22 mol), catalyst (5 mol%), ClCH<sub>2</sub>CH<sub>2</sub>Cl (1.5 mL), 5 min, isolated yield. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy analysis of the integral area of  $\alpha$ -H.

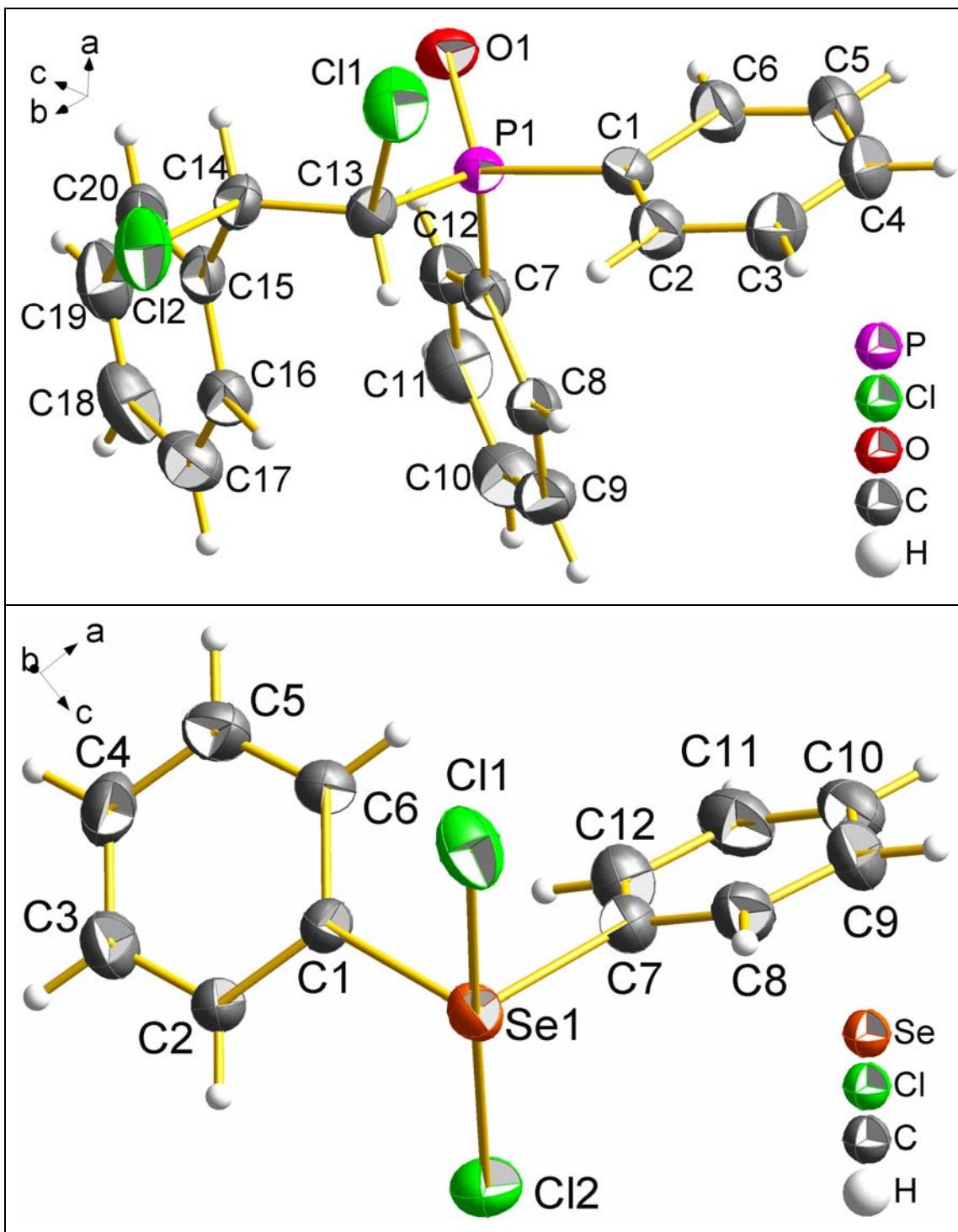
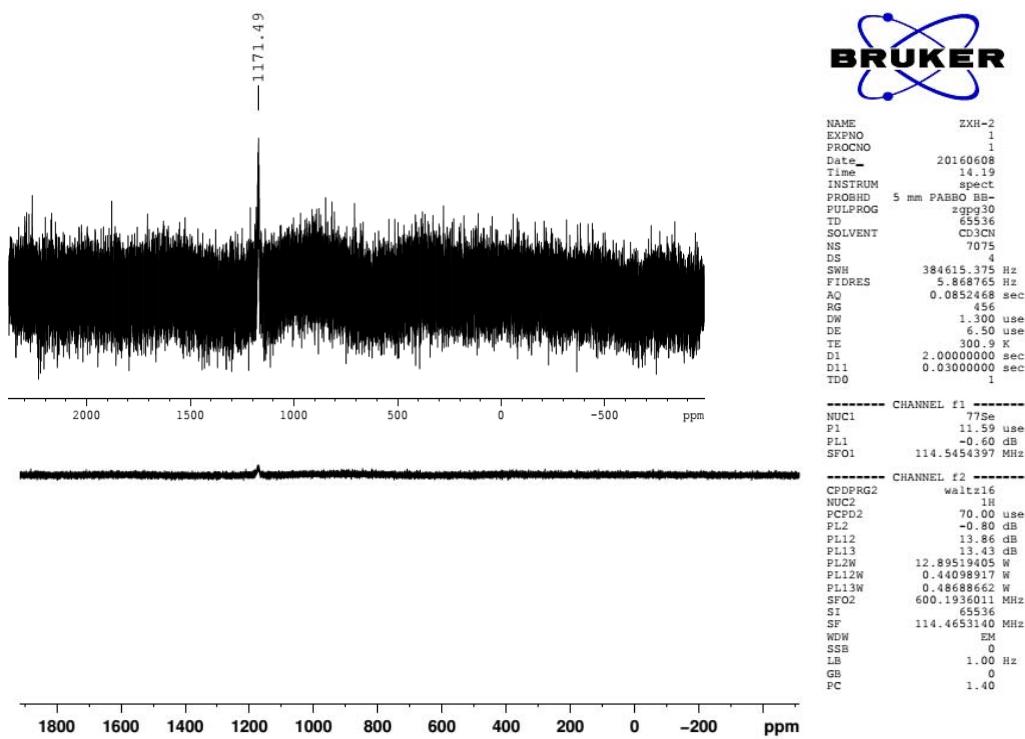
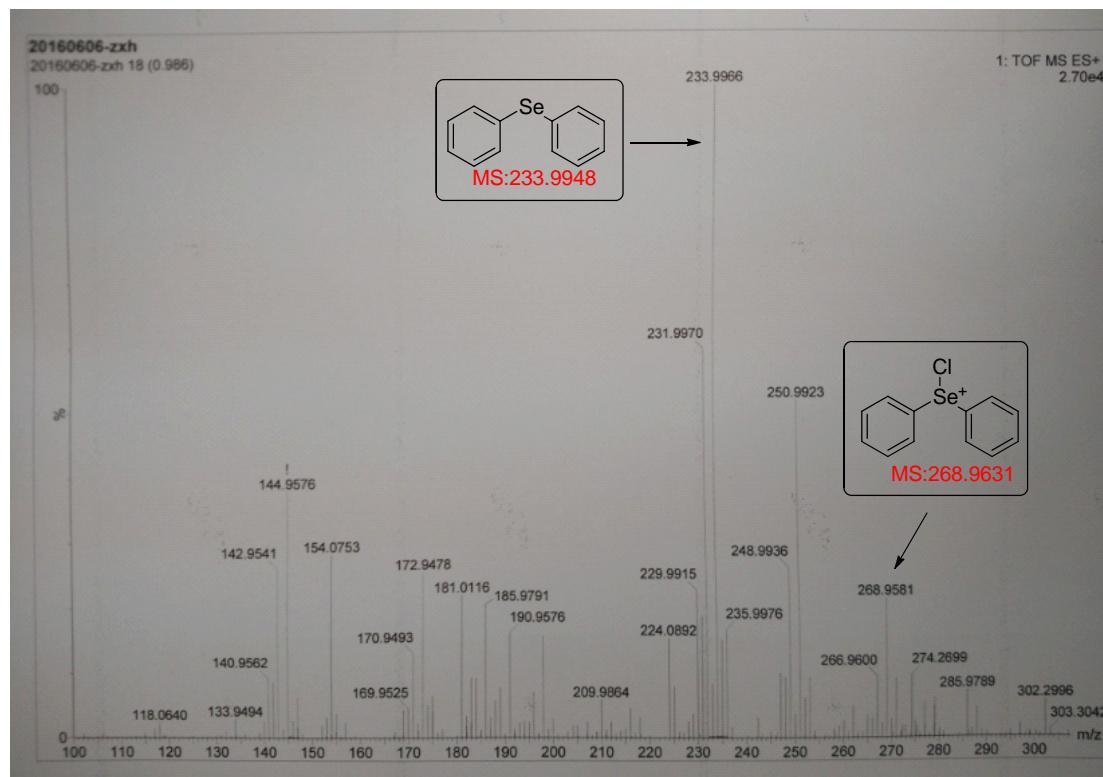


Fig. S1 The X-ray structures of **2s** (up) and **5** (bottom)

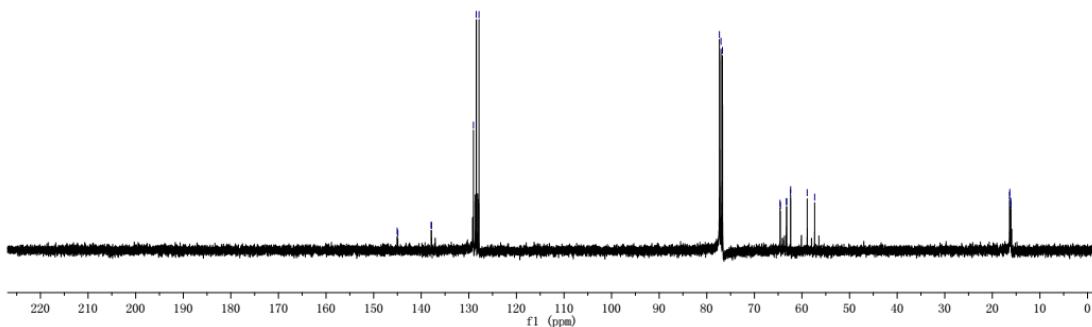
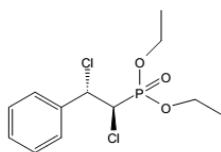
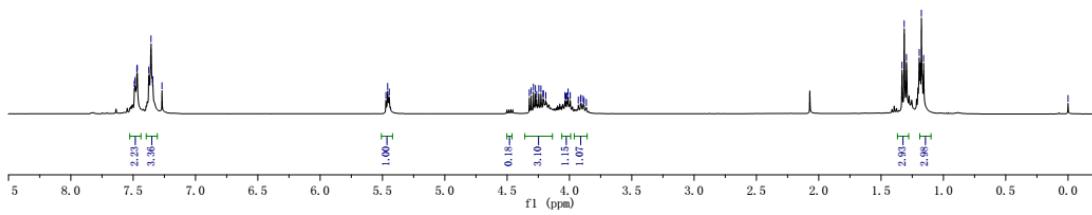
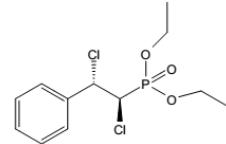


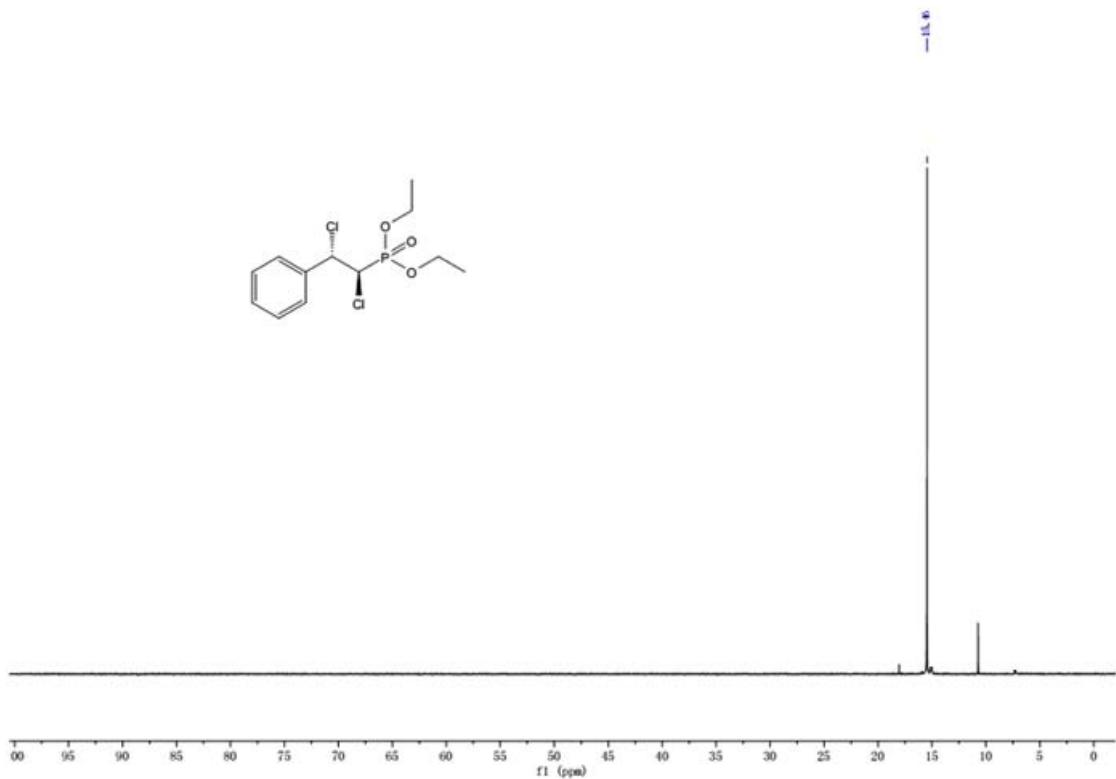
**Fig. S2** The  $^{77}\text{Se}$  NMR spectrum of reaction mixtures (**1a**/SO<sub>2</sub>Cl<sub>2</sub>/PhSeSePh=1:1.1/0.05) at -20 °C for 5 min.



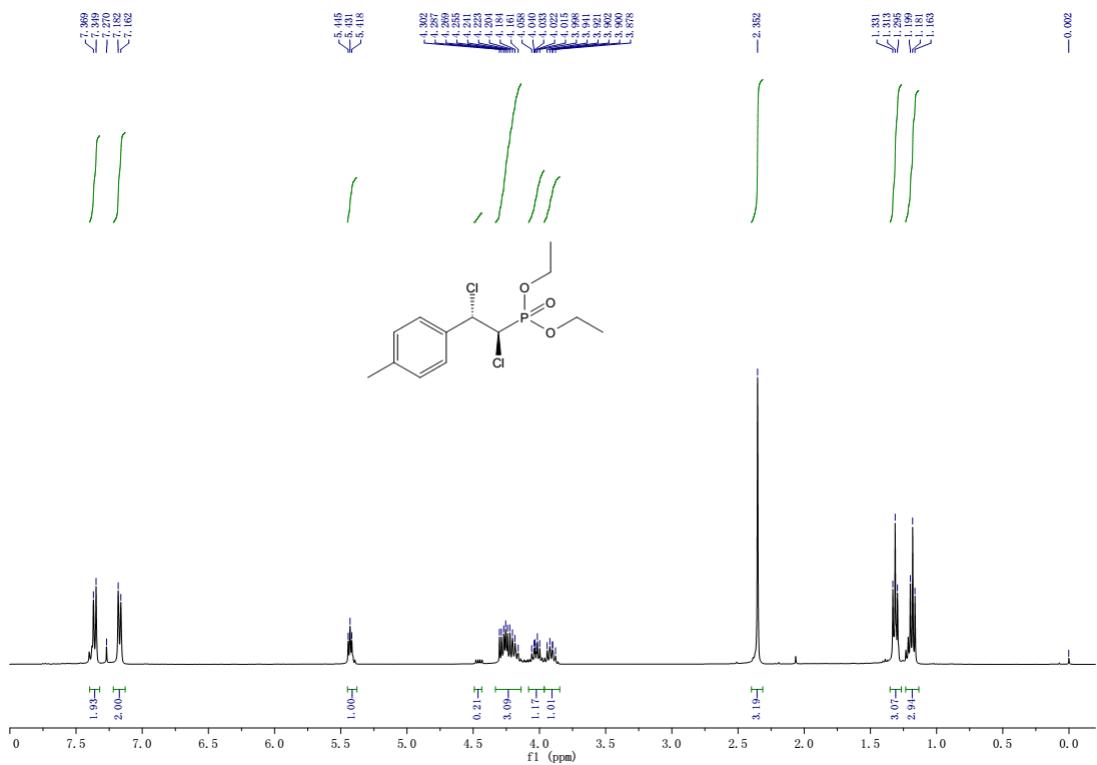
**Fig. S3** The HRMS spectrum of reaction mixture (**1a**/SO<sub>2</sub>Cl<sub>2</sub>/PhSeSePh=1:1.1/0.05) at -20 °C for 5 min.

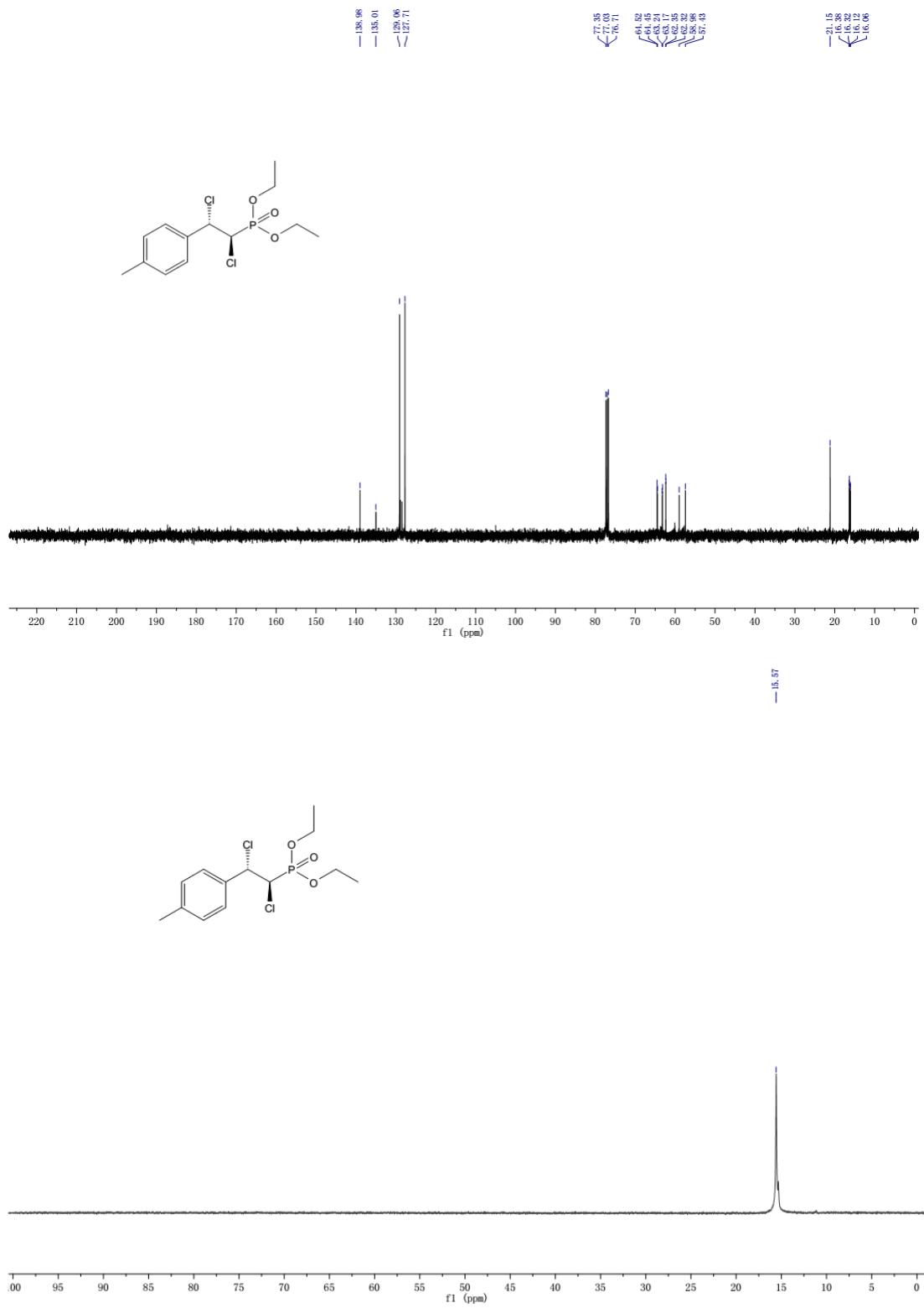
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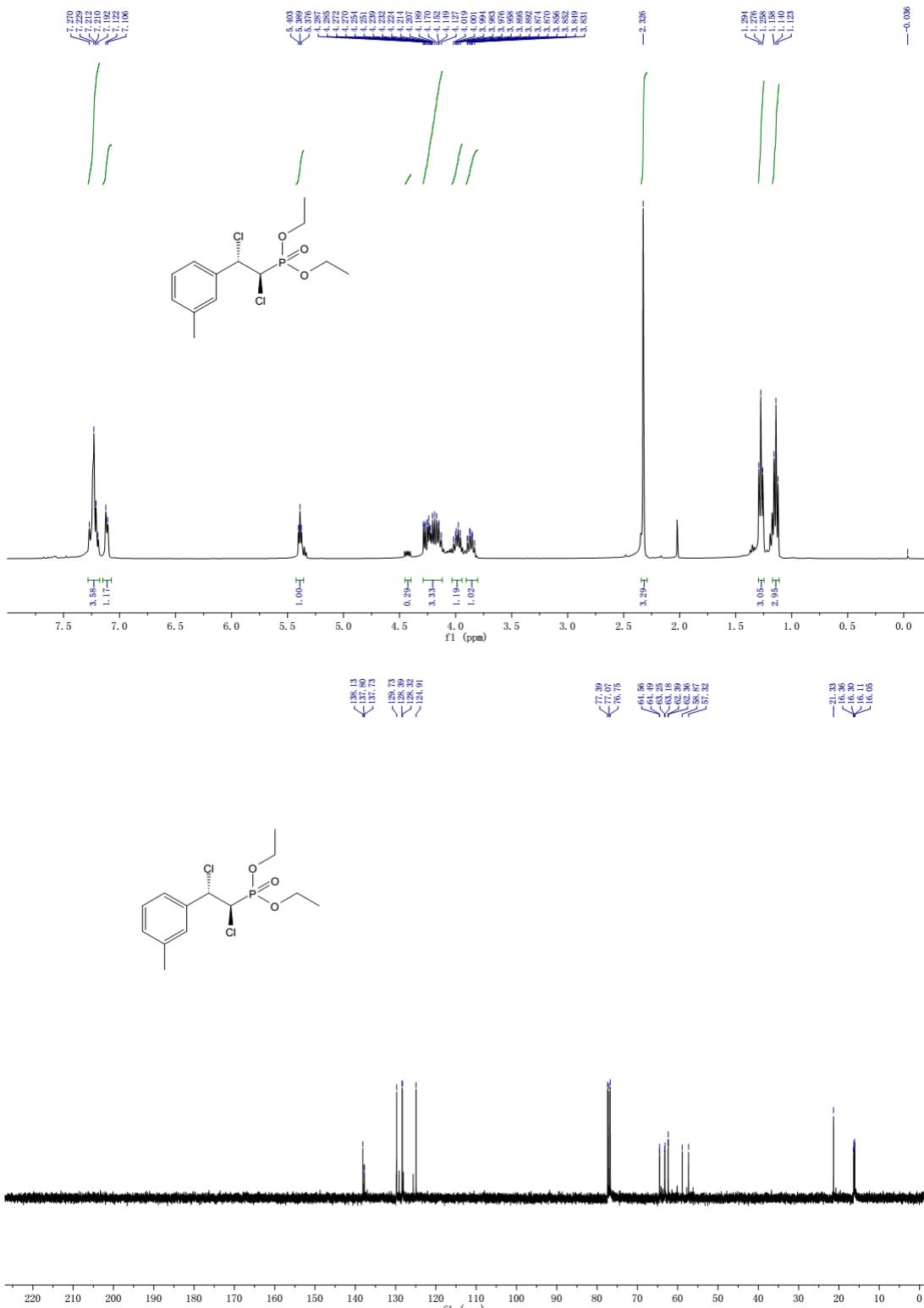


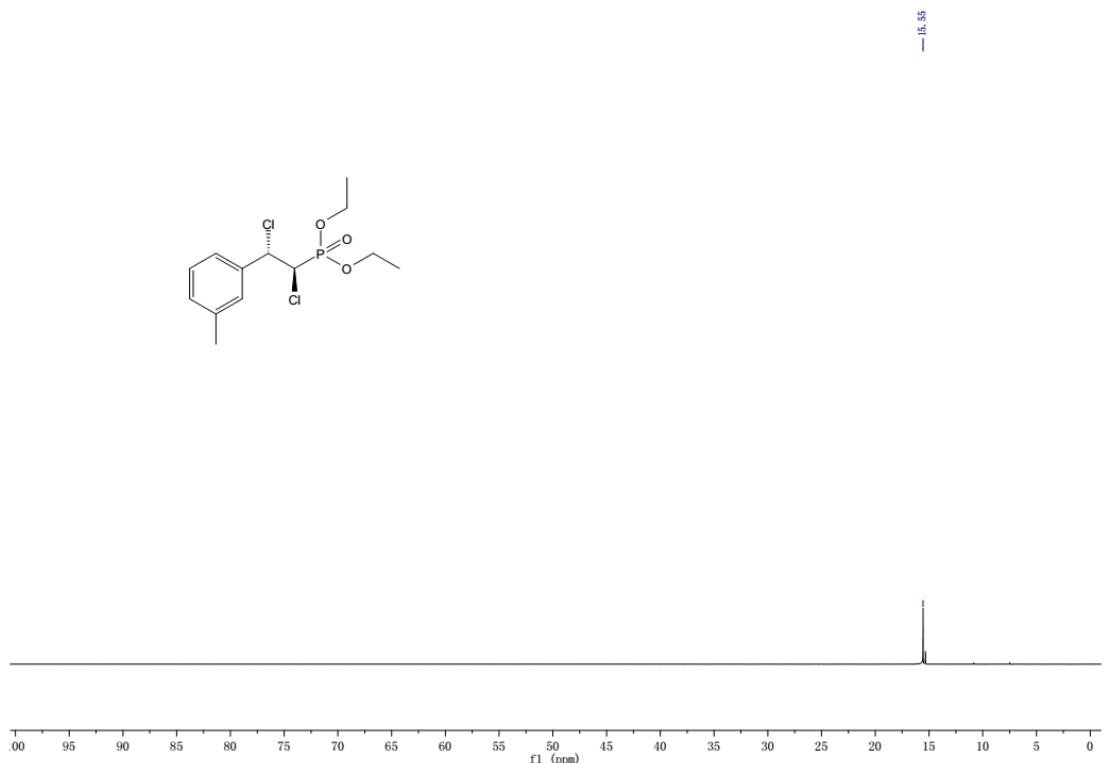
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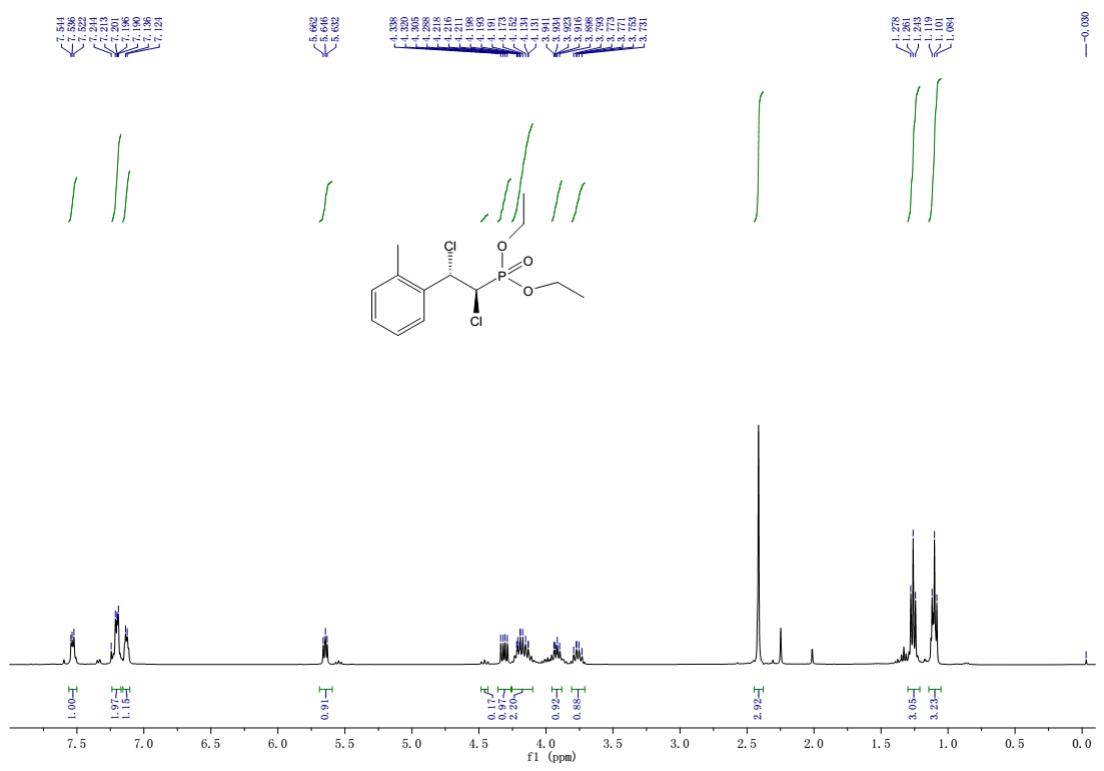


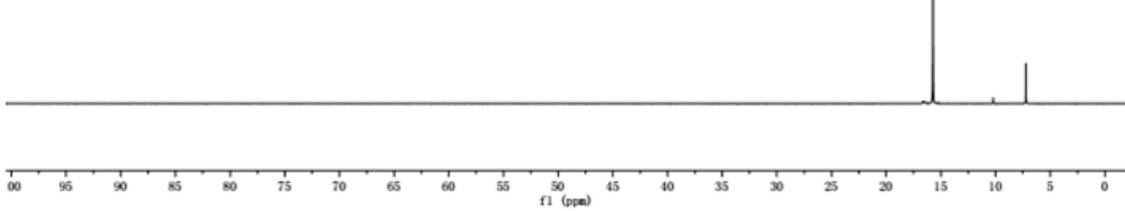
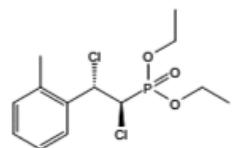
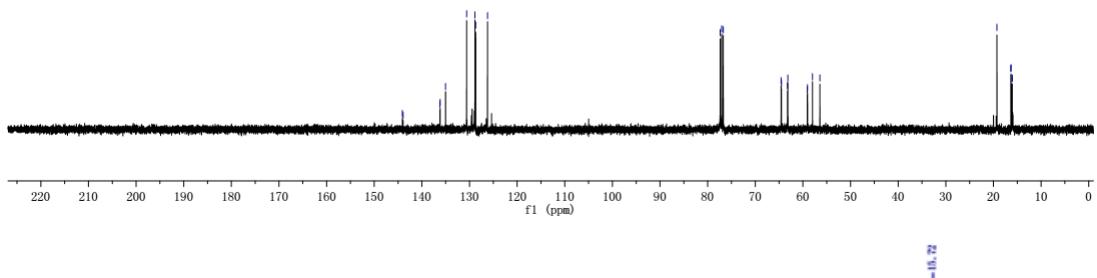
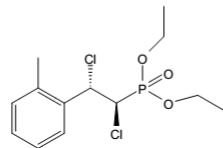
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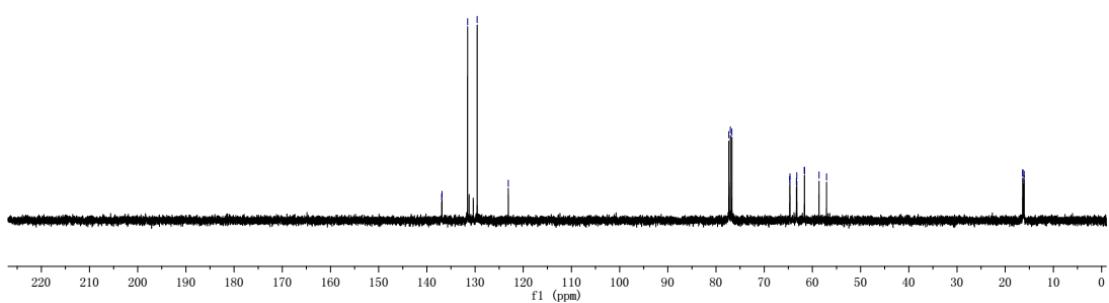
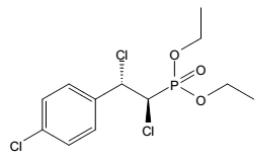
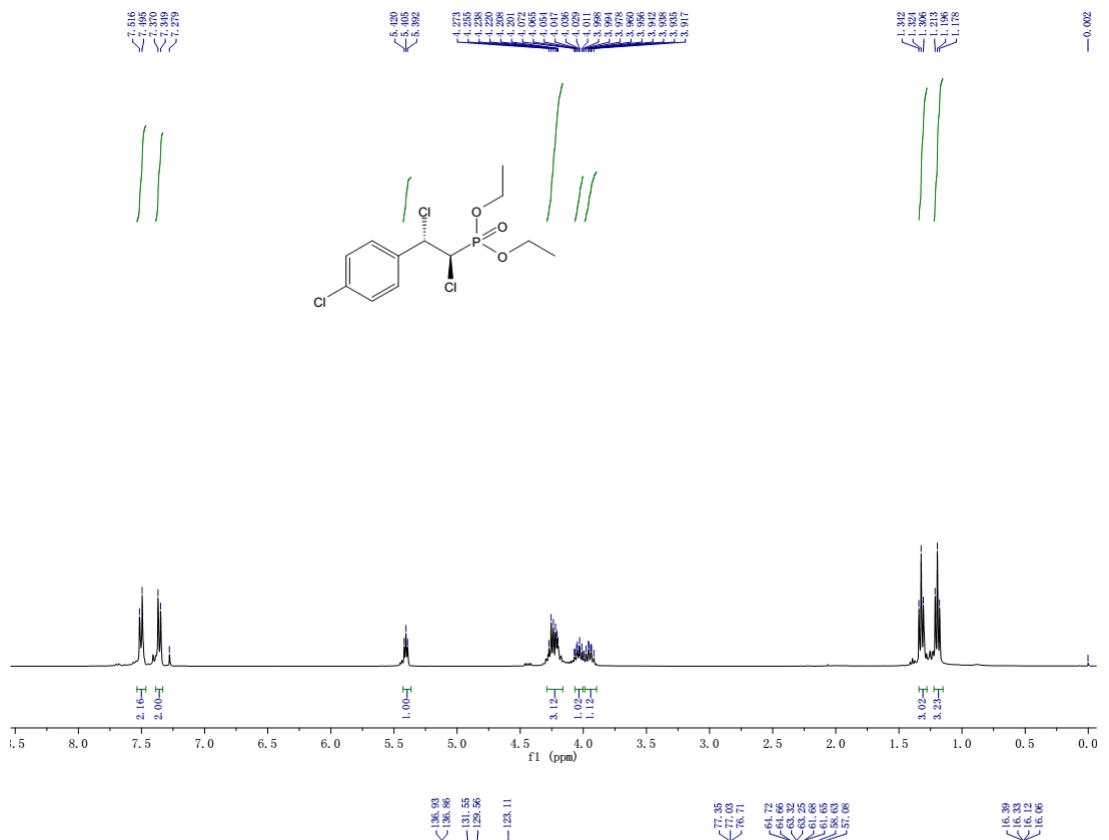


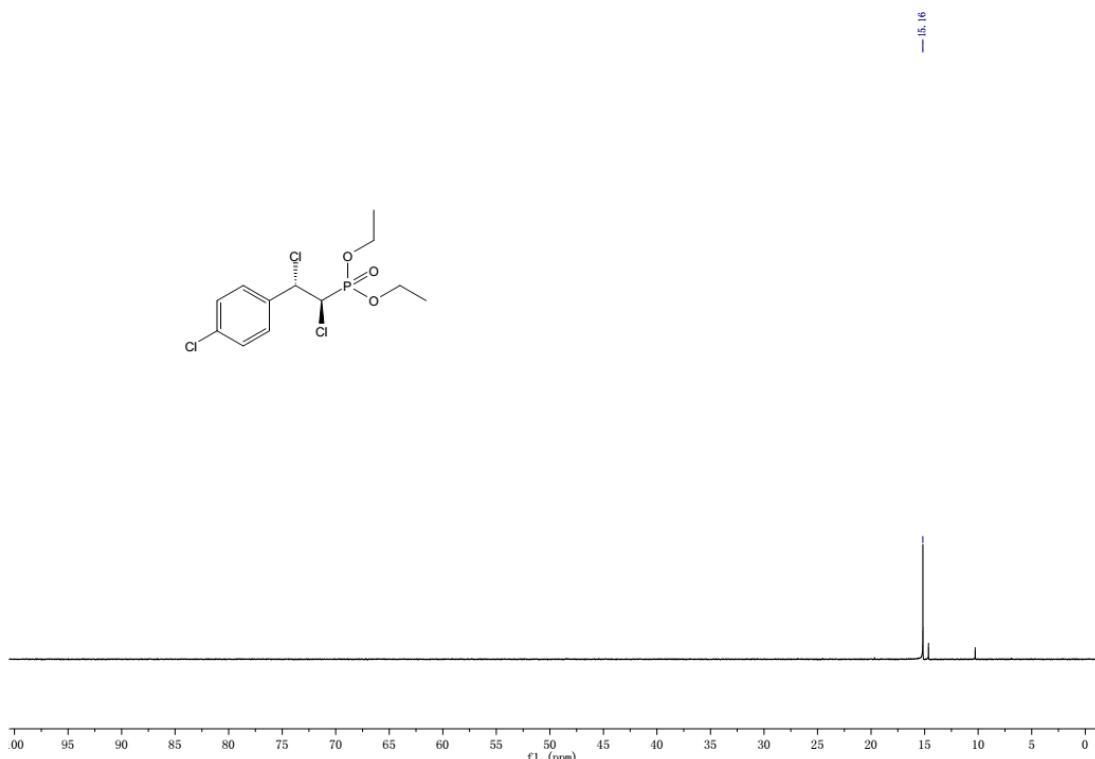
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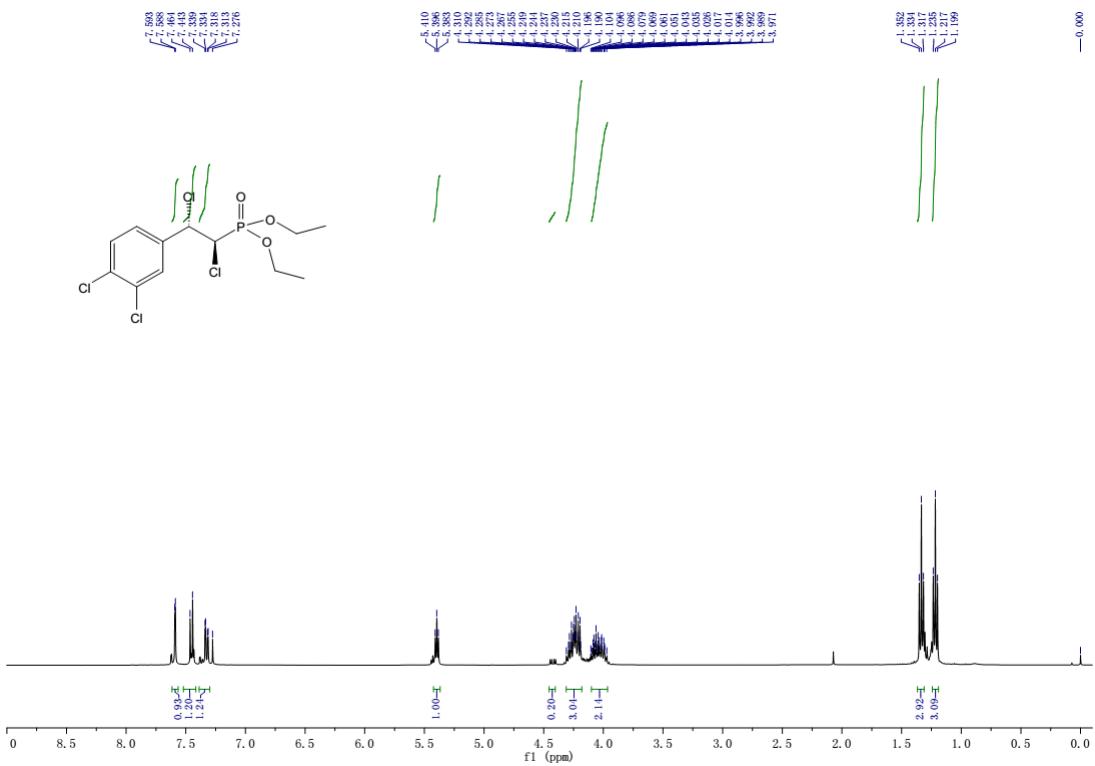


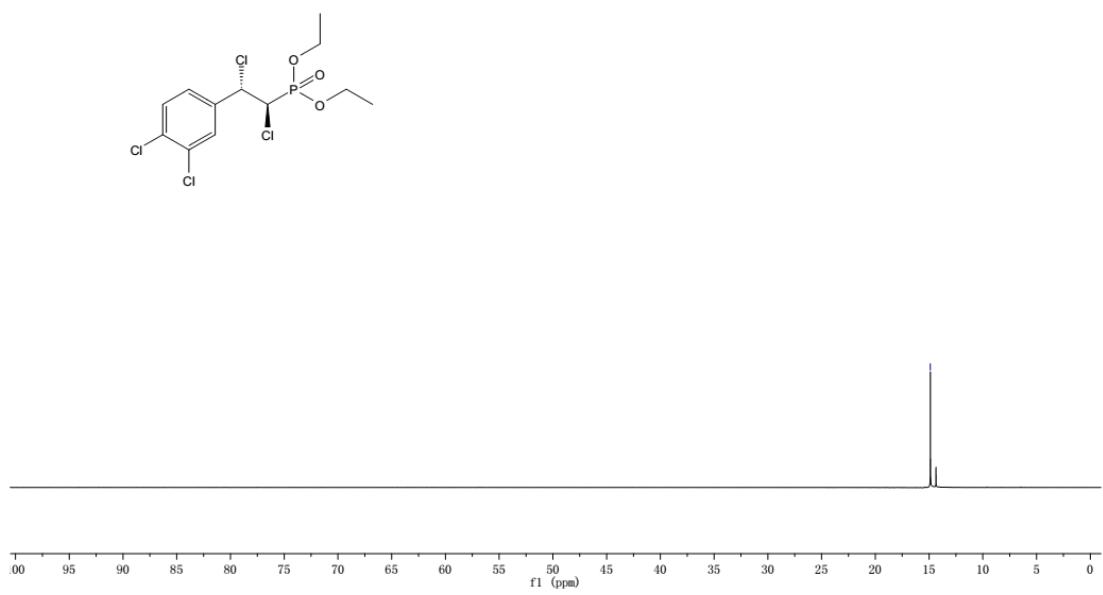
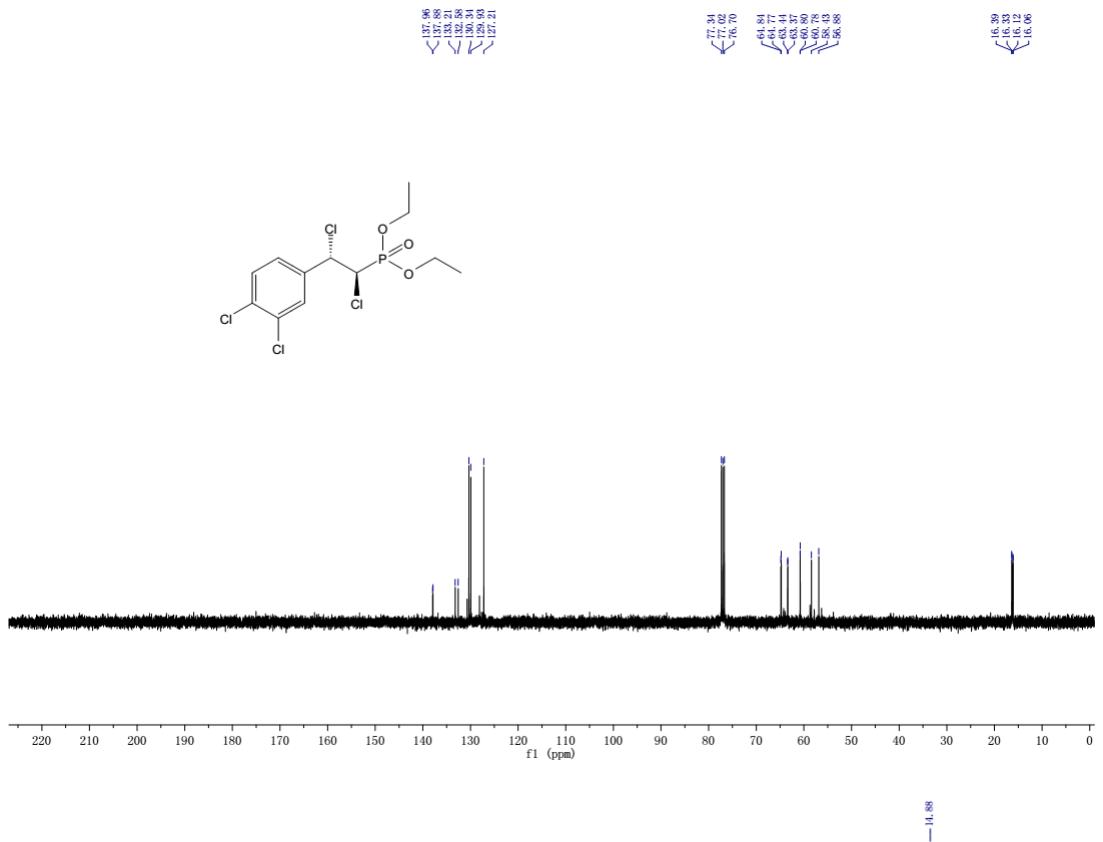
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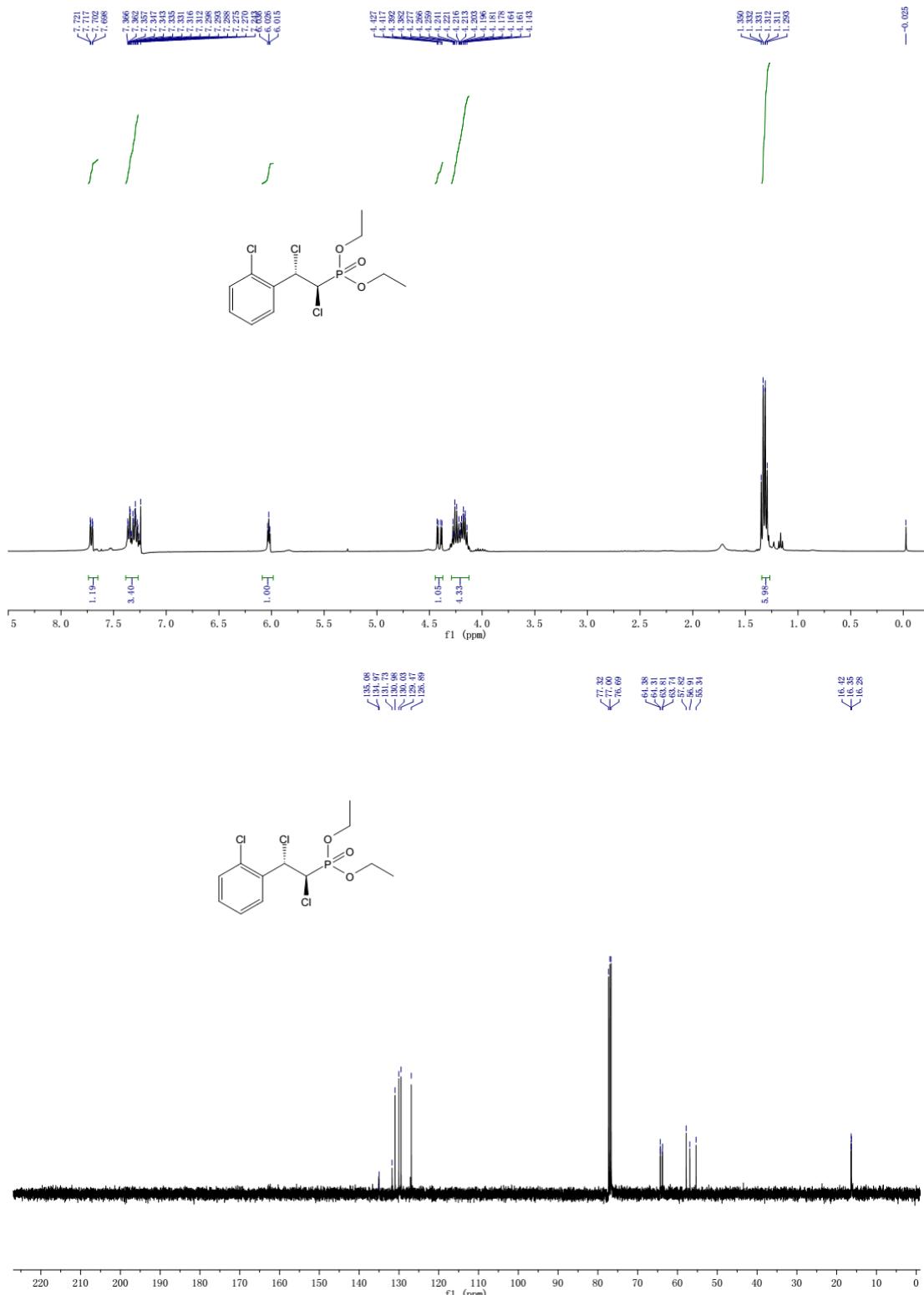


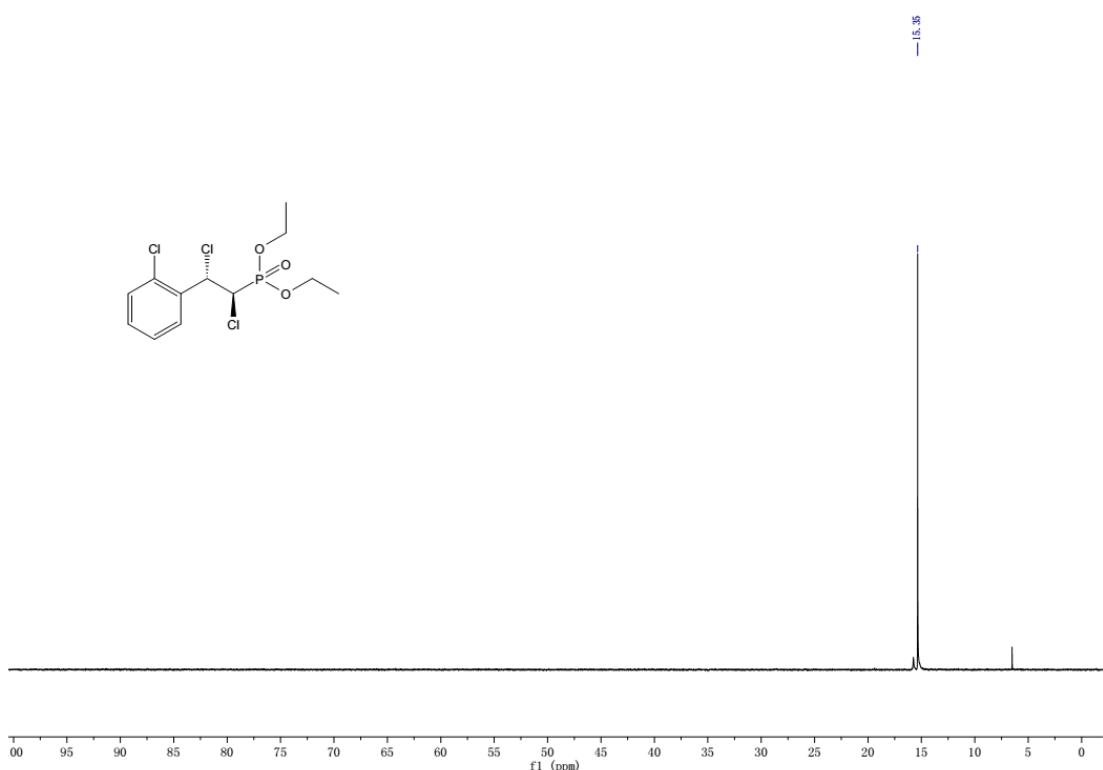
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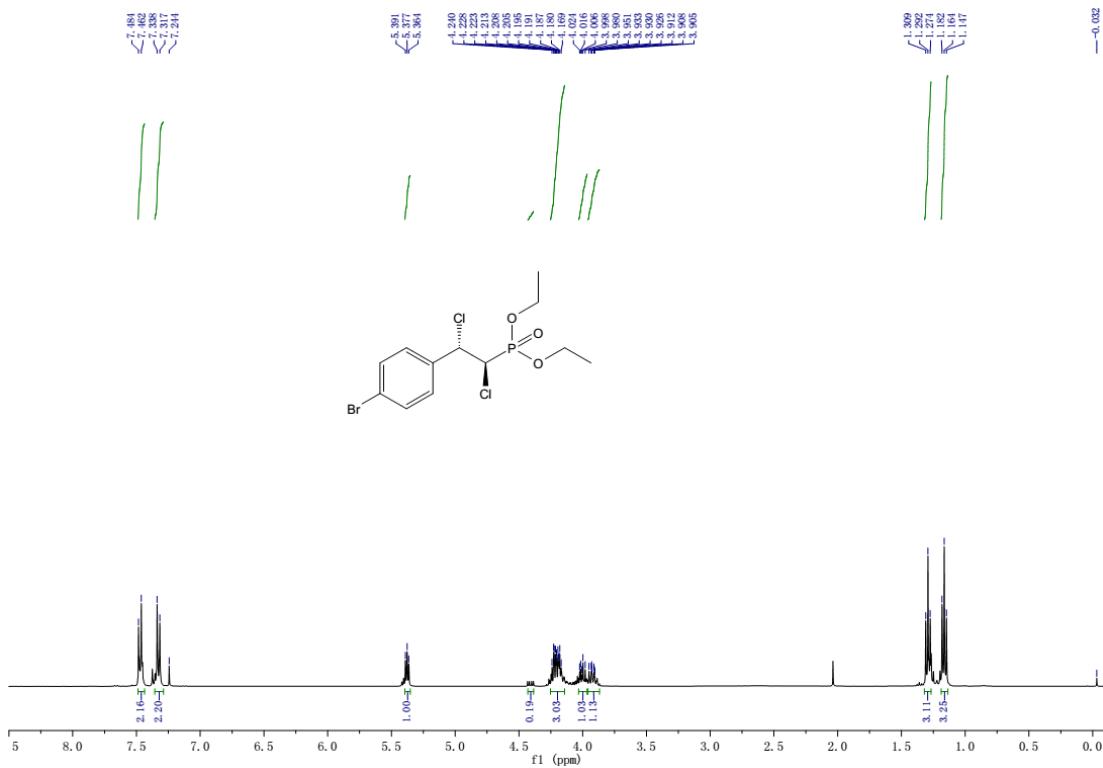


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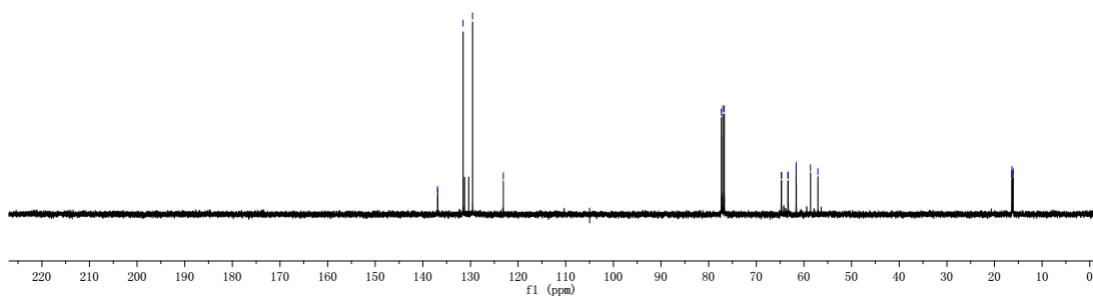
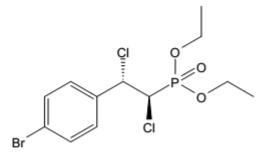
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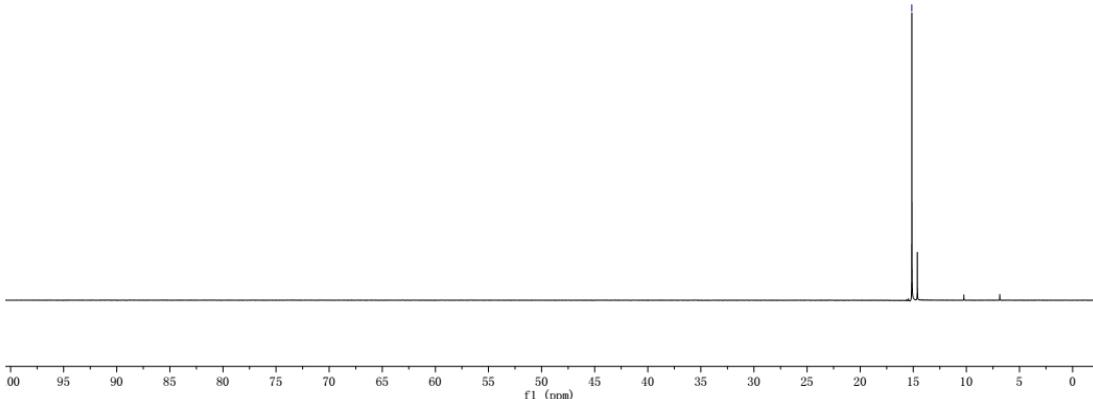
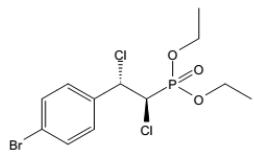
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—129.36  
—123.11

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61.63  
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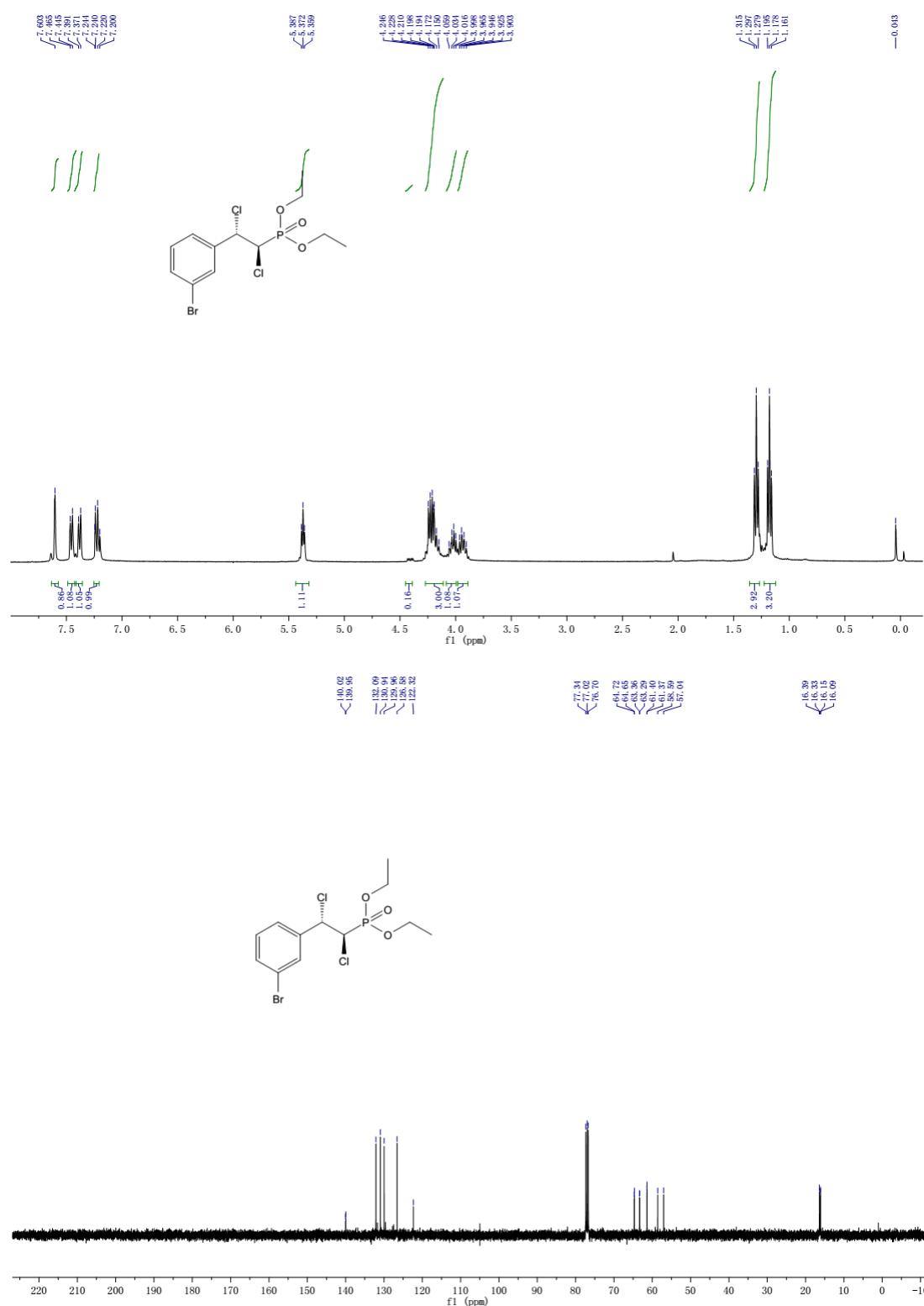
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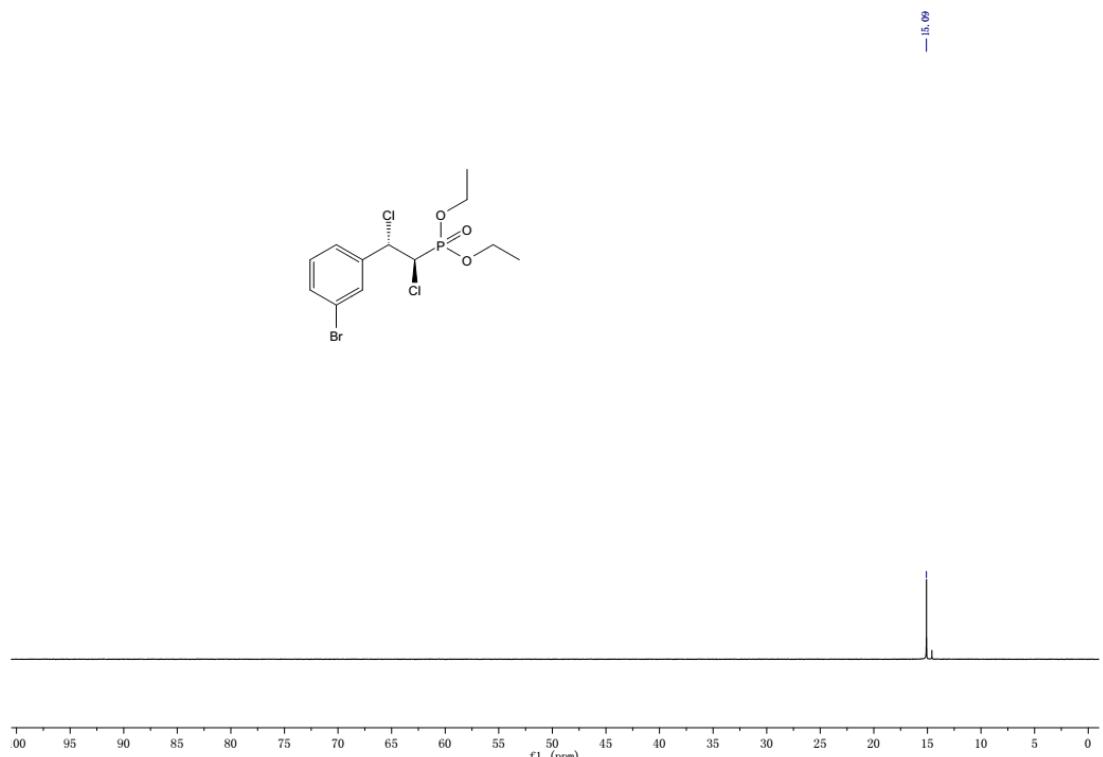


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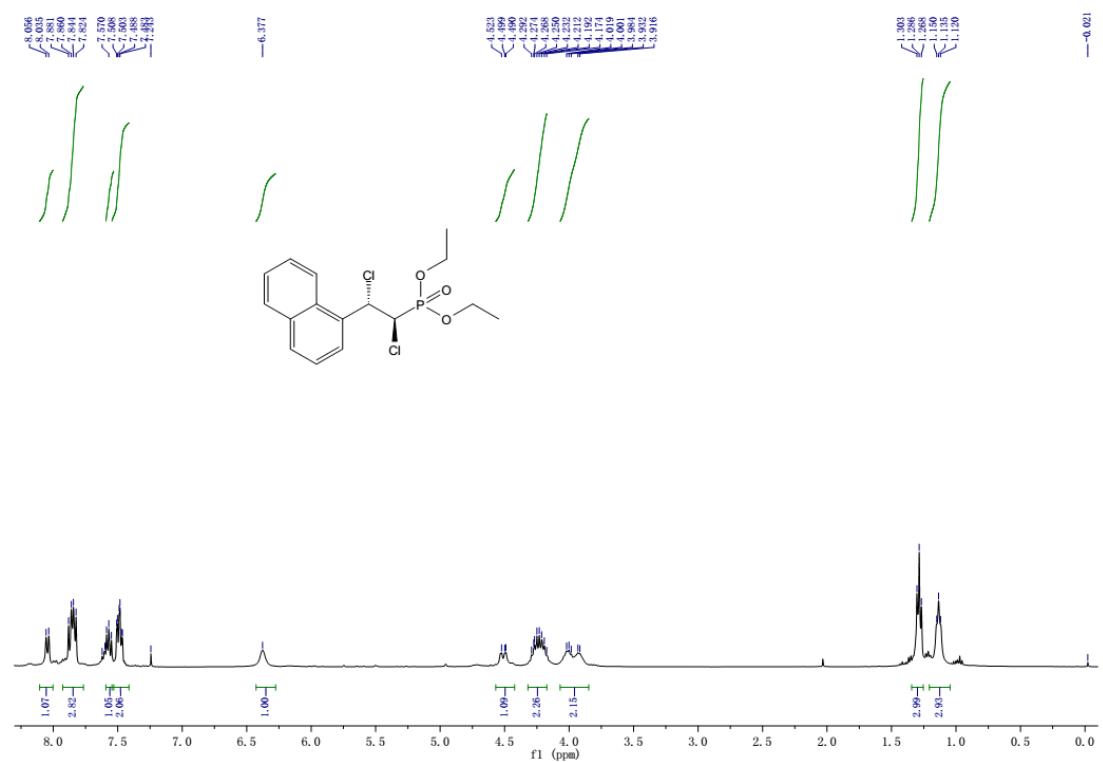


### Copies of $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR Spectra of **2i**





Copies of <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR Spectra of **2j**

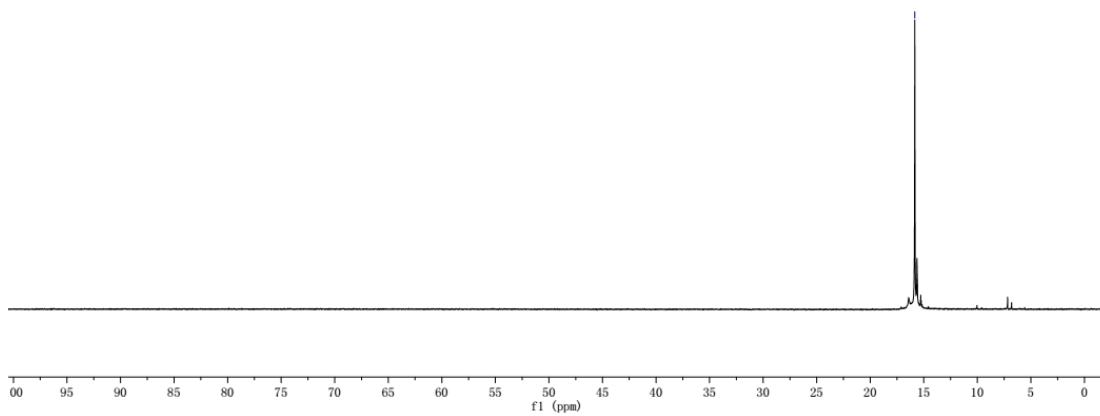
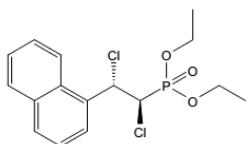
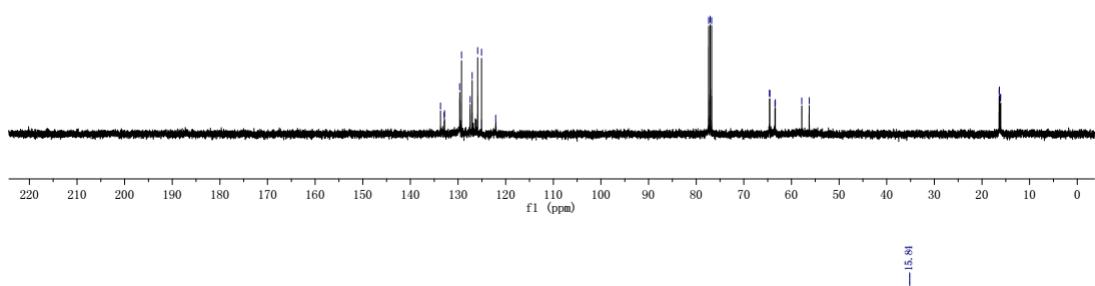
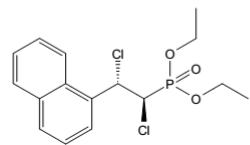


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127.17  
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125.07  
122.69

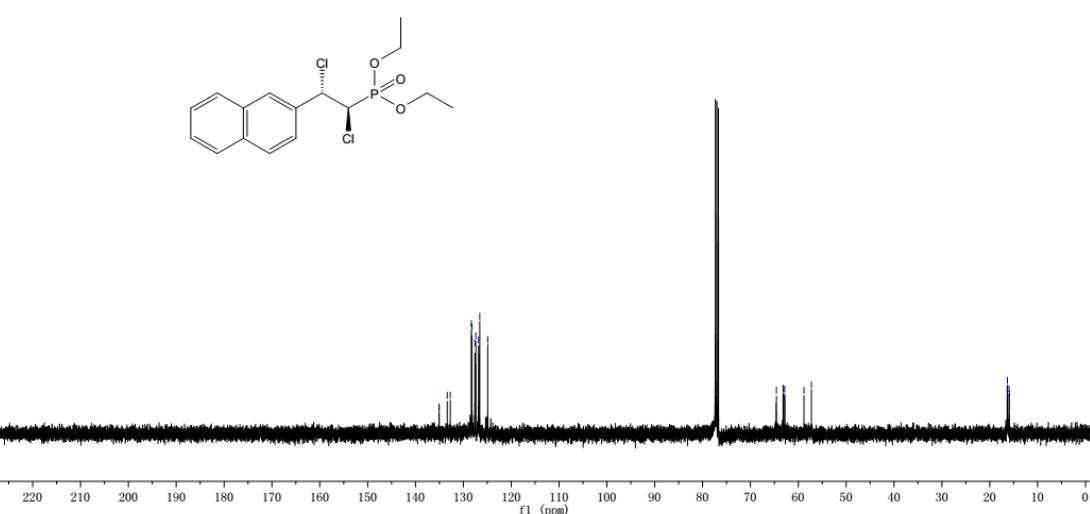
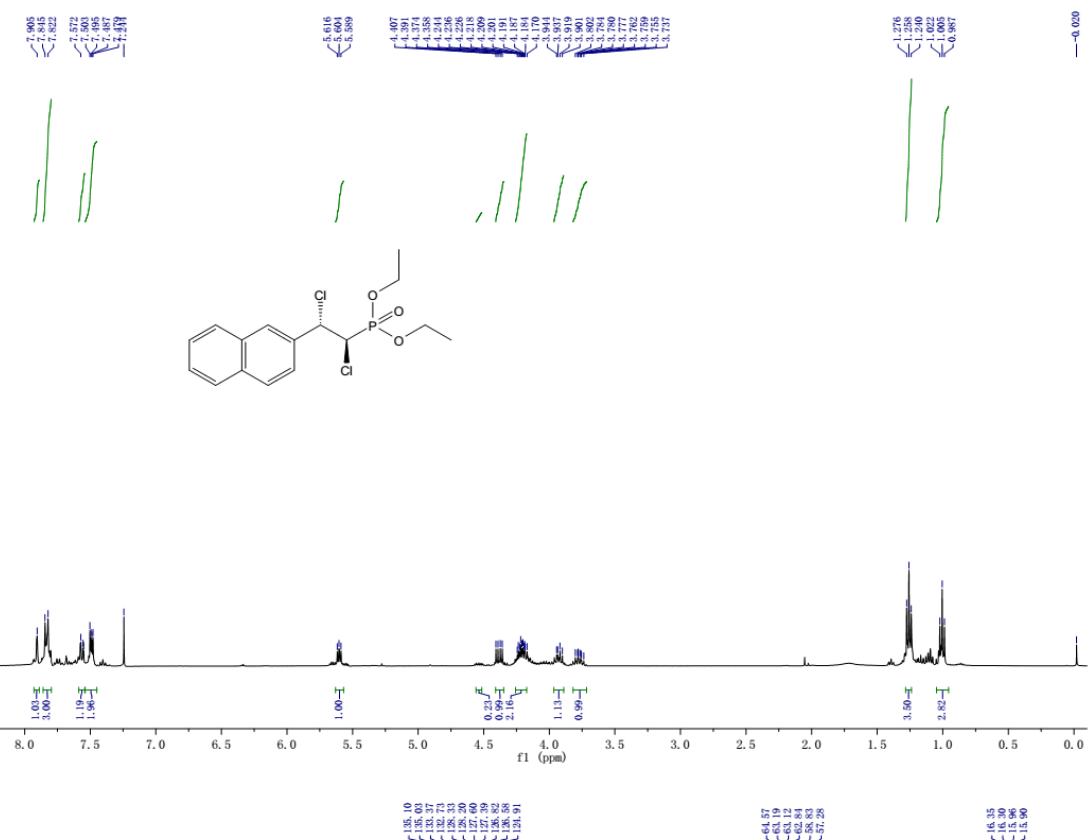
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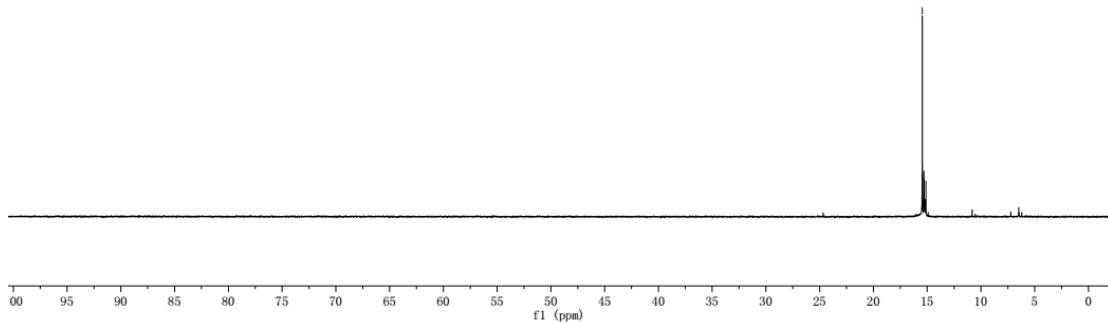
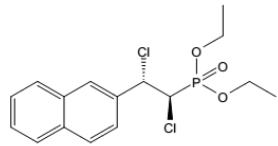
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16.40  
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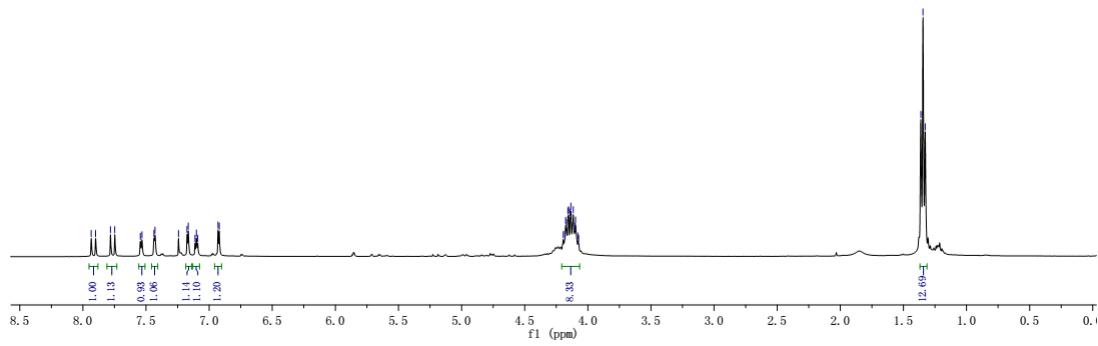
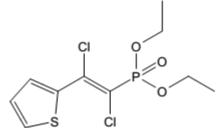
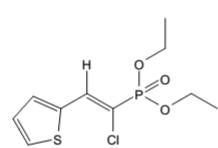


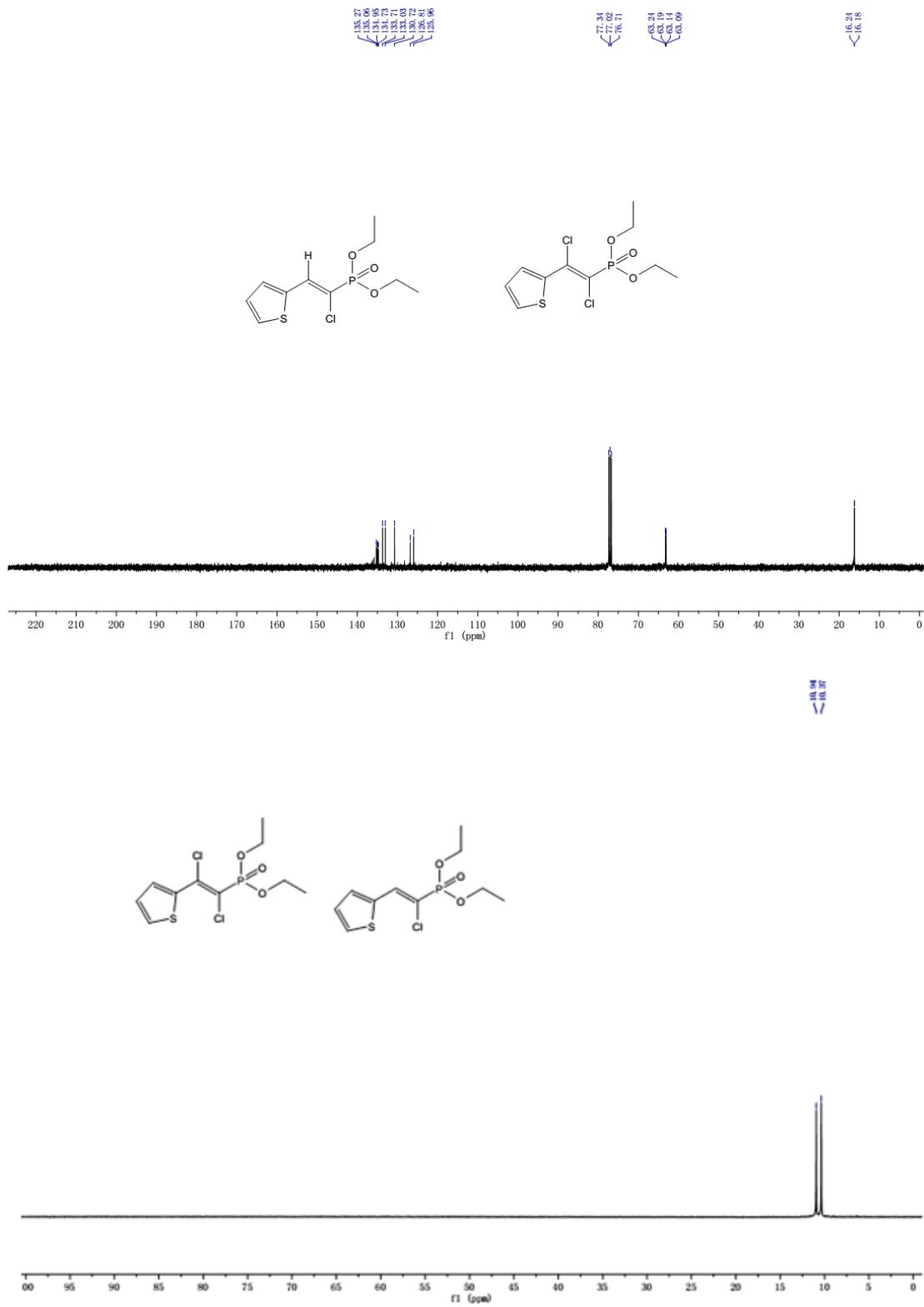
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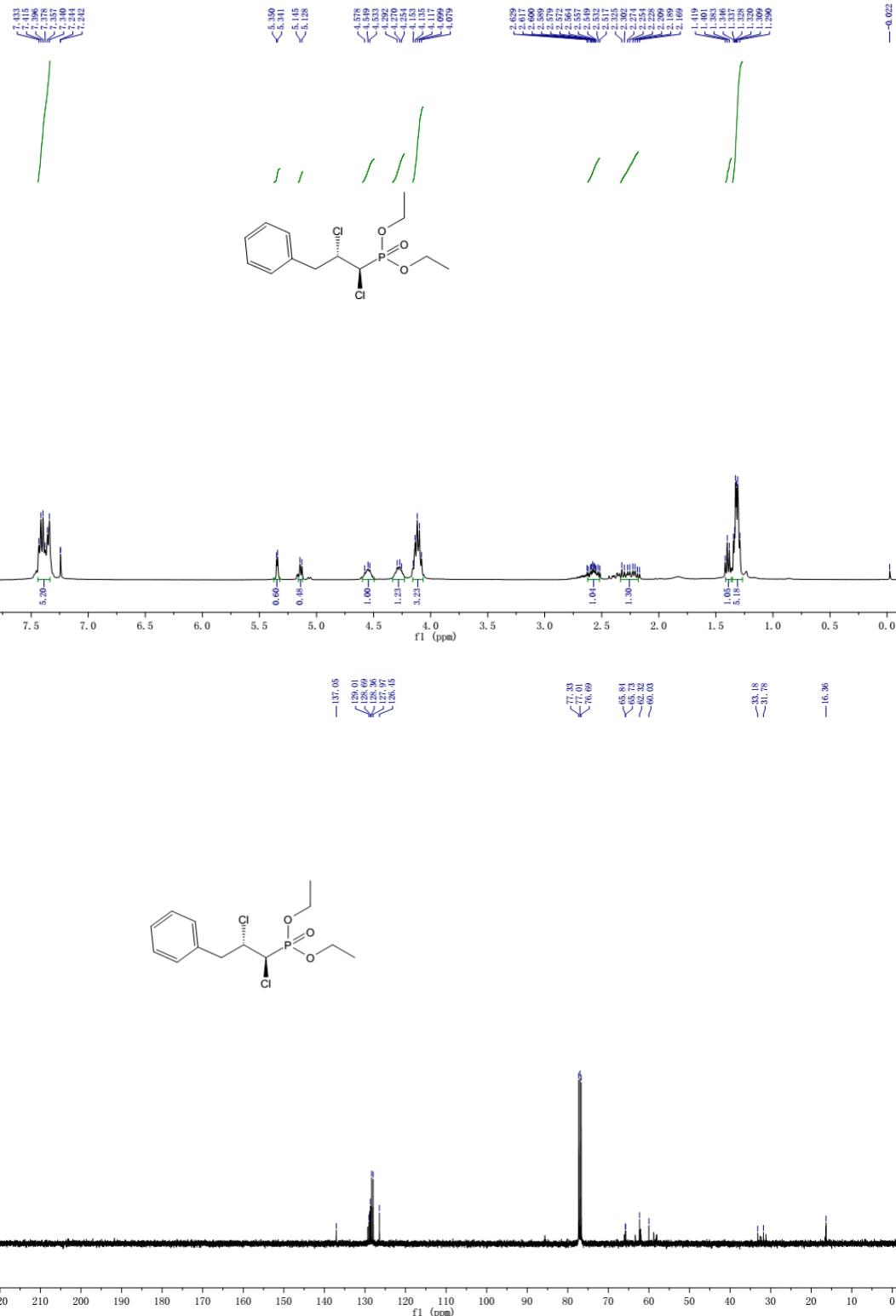


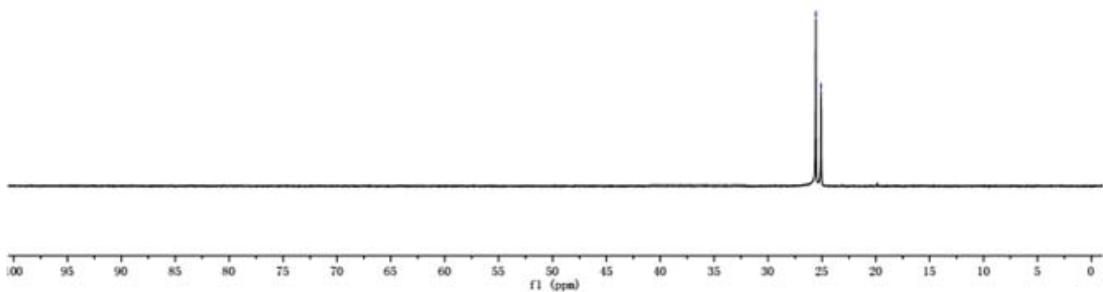
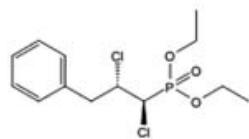
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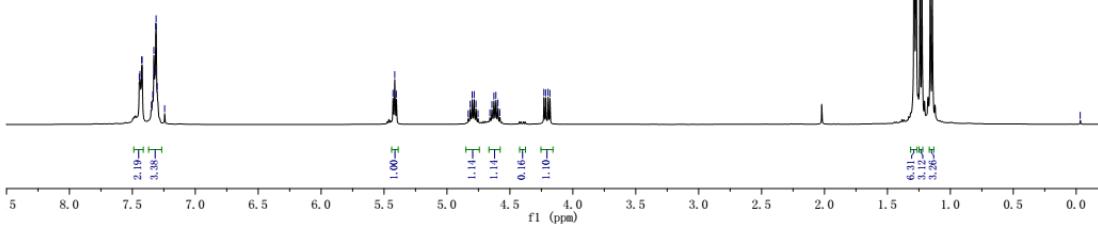
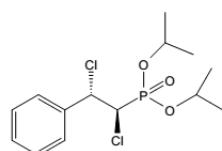


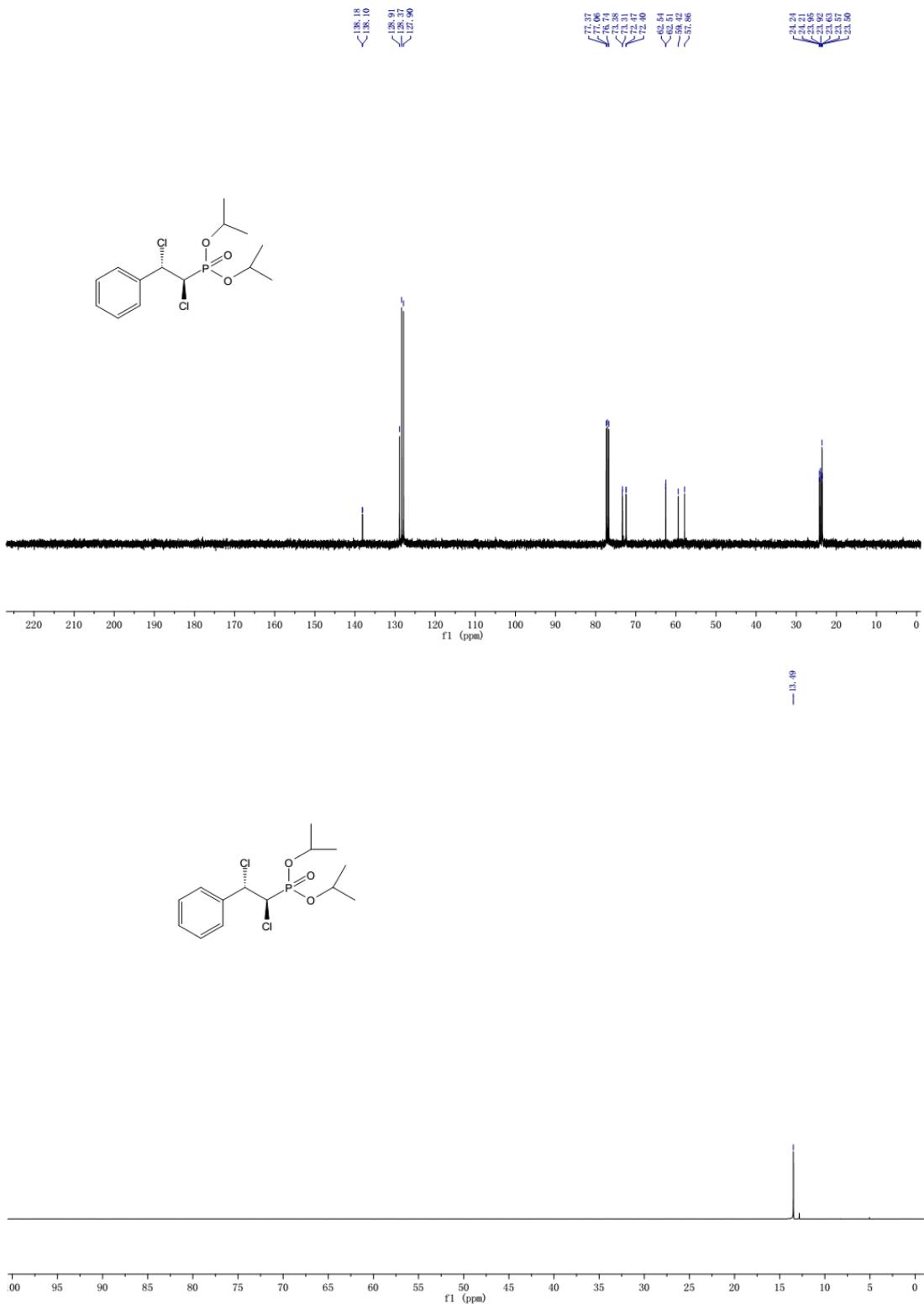


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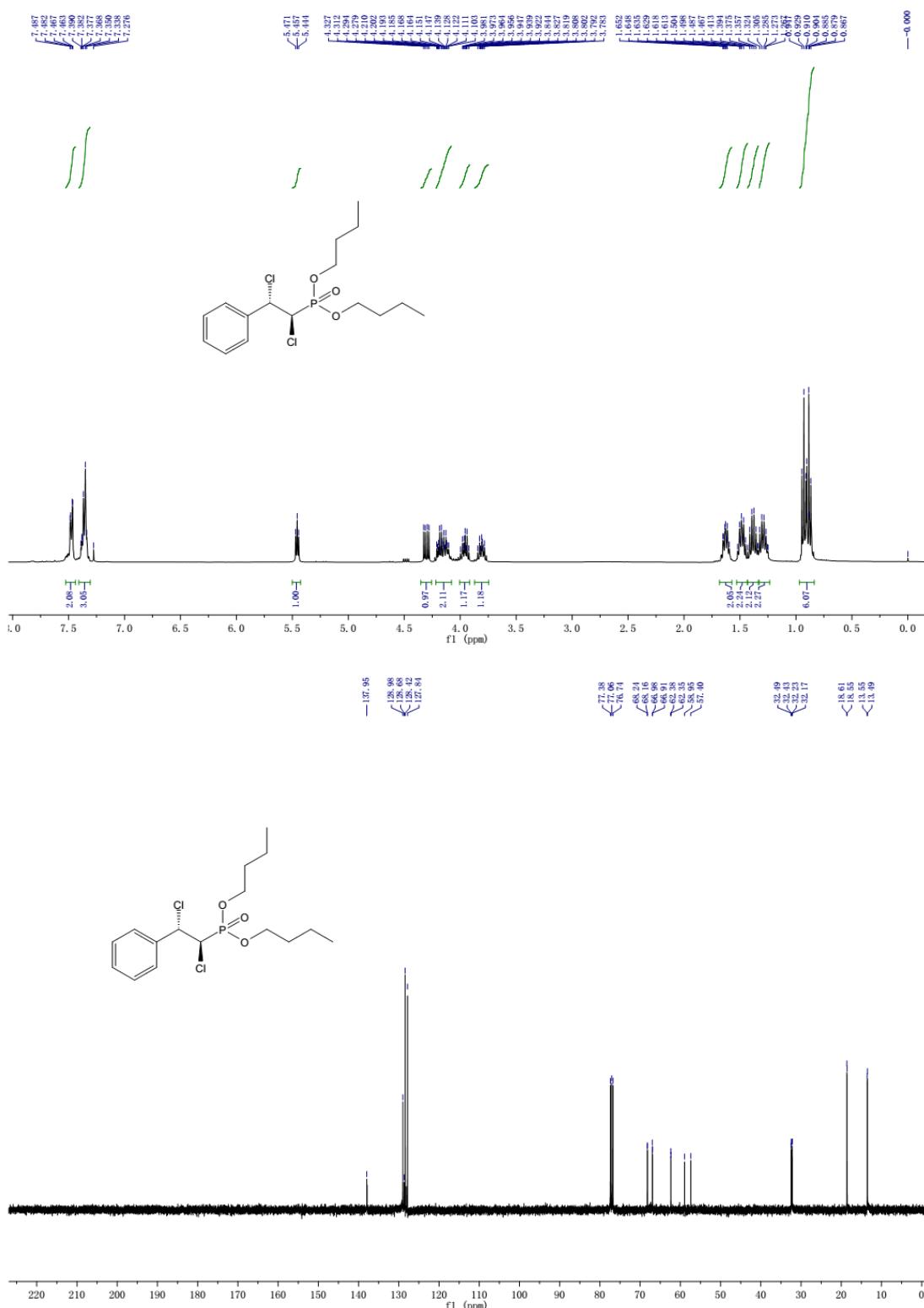


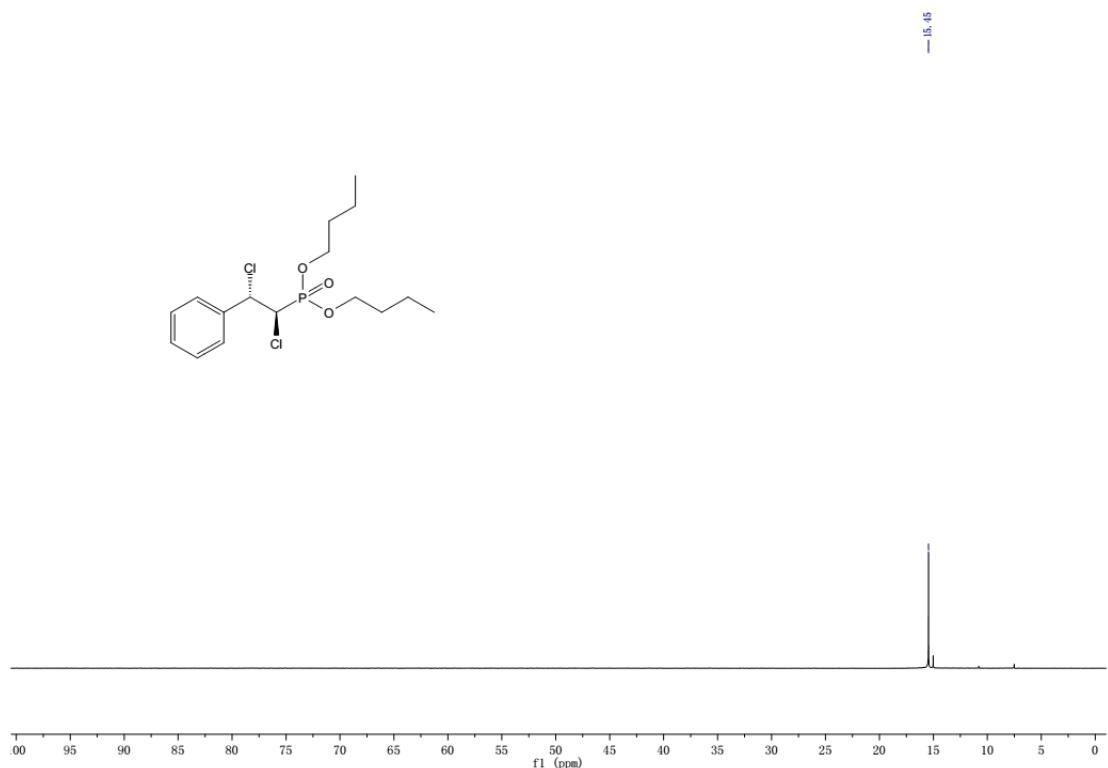
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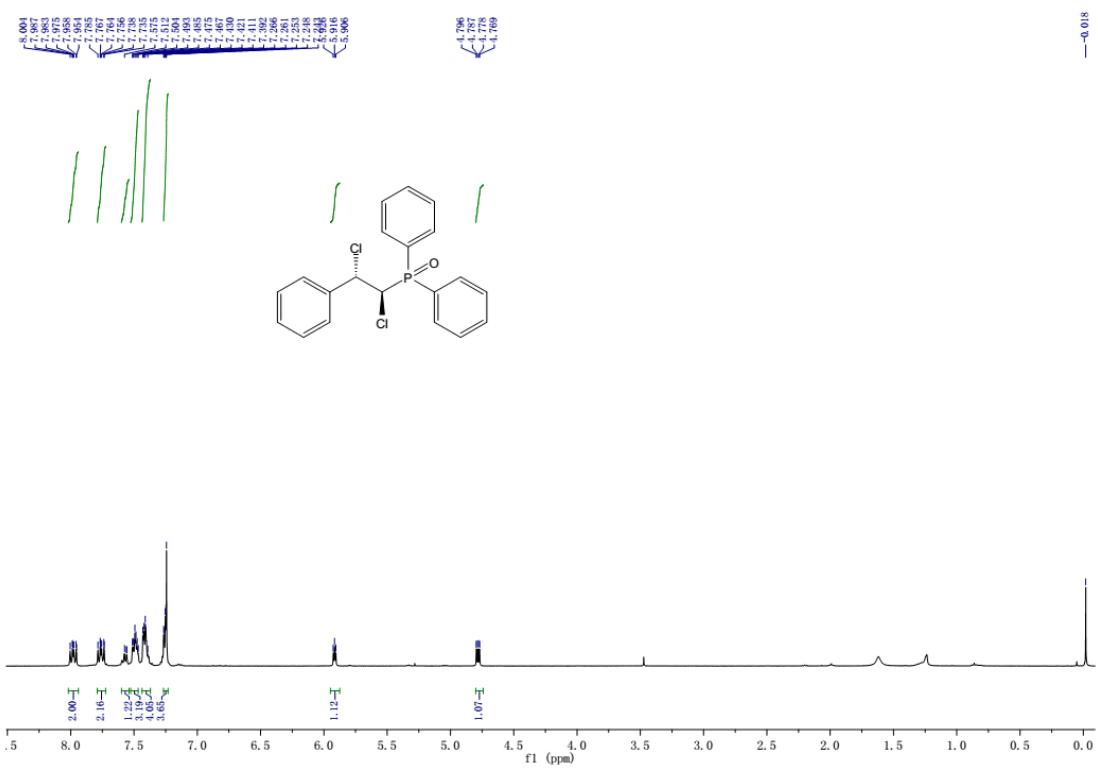


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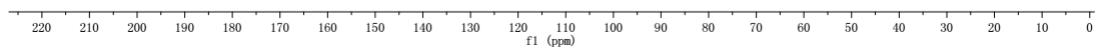
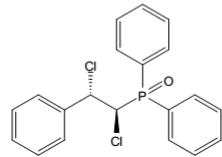




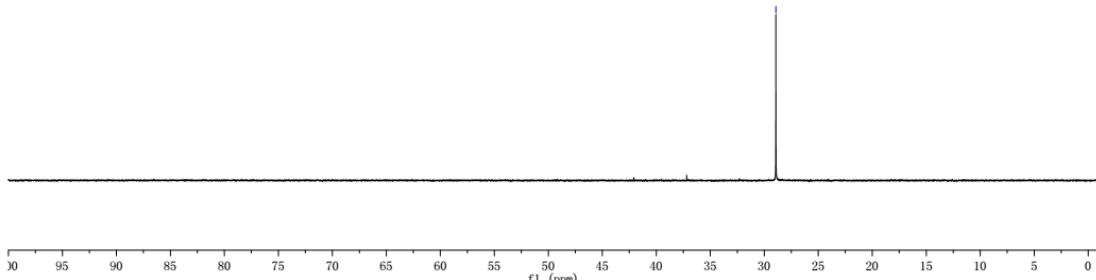
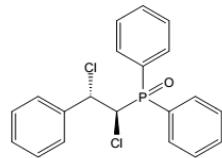
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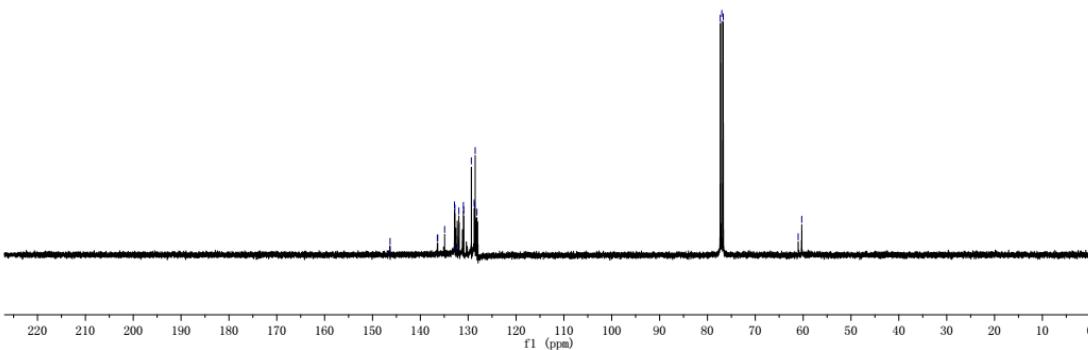
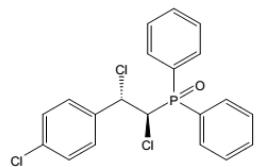
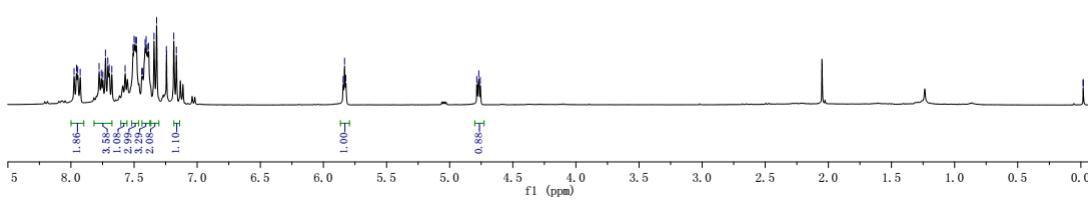
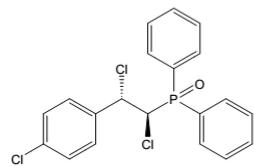
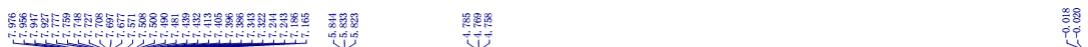
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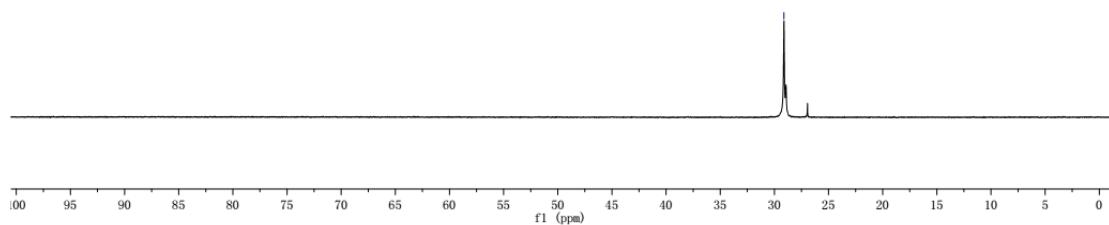
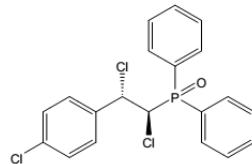


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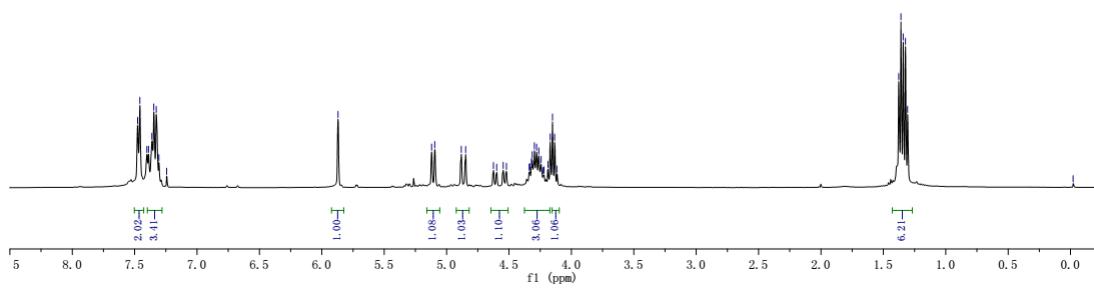
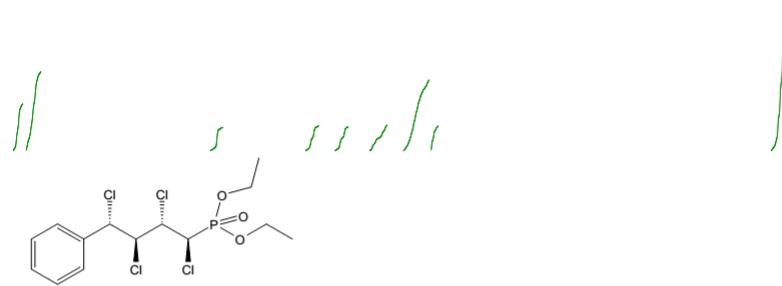


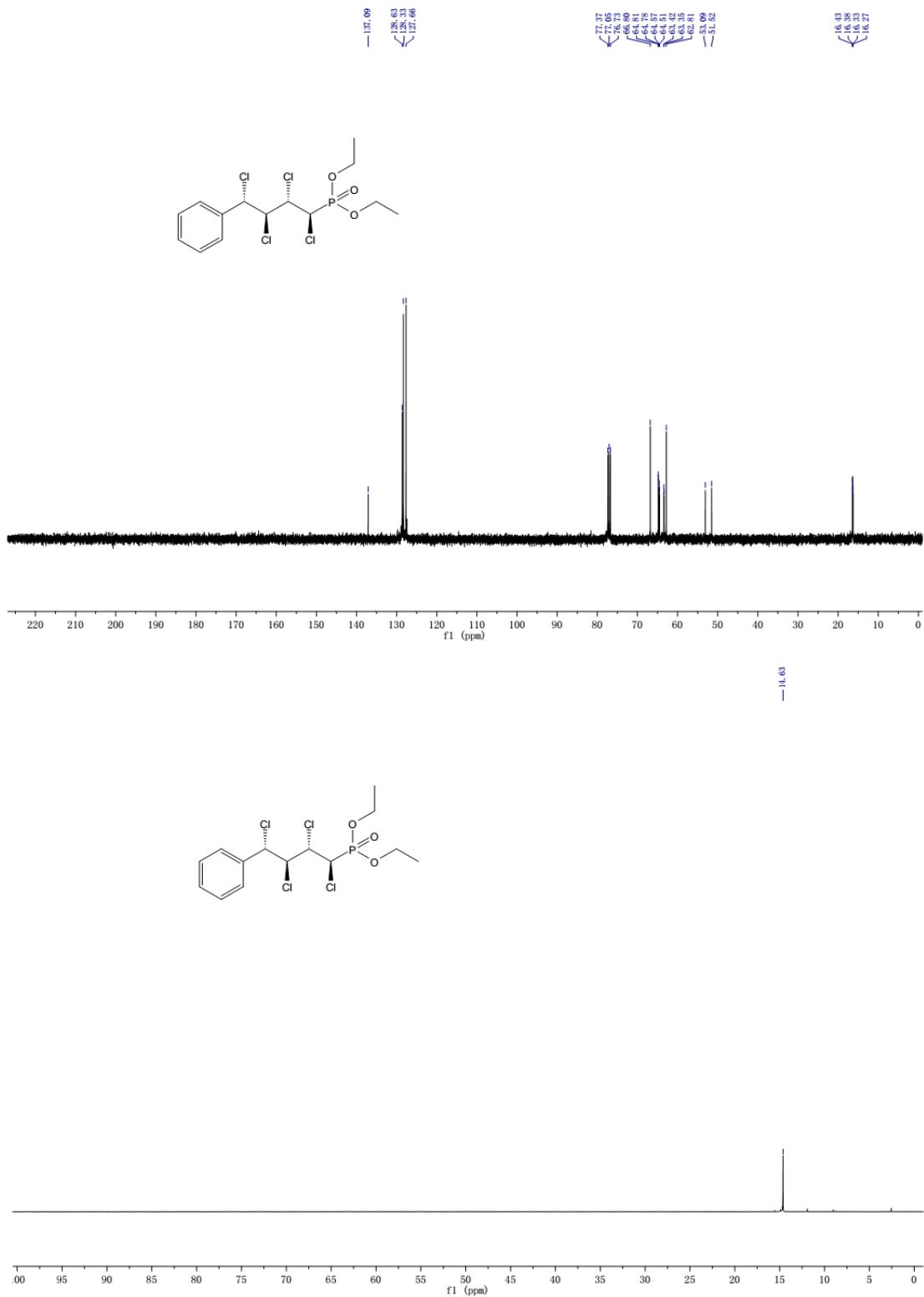
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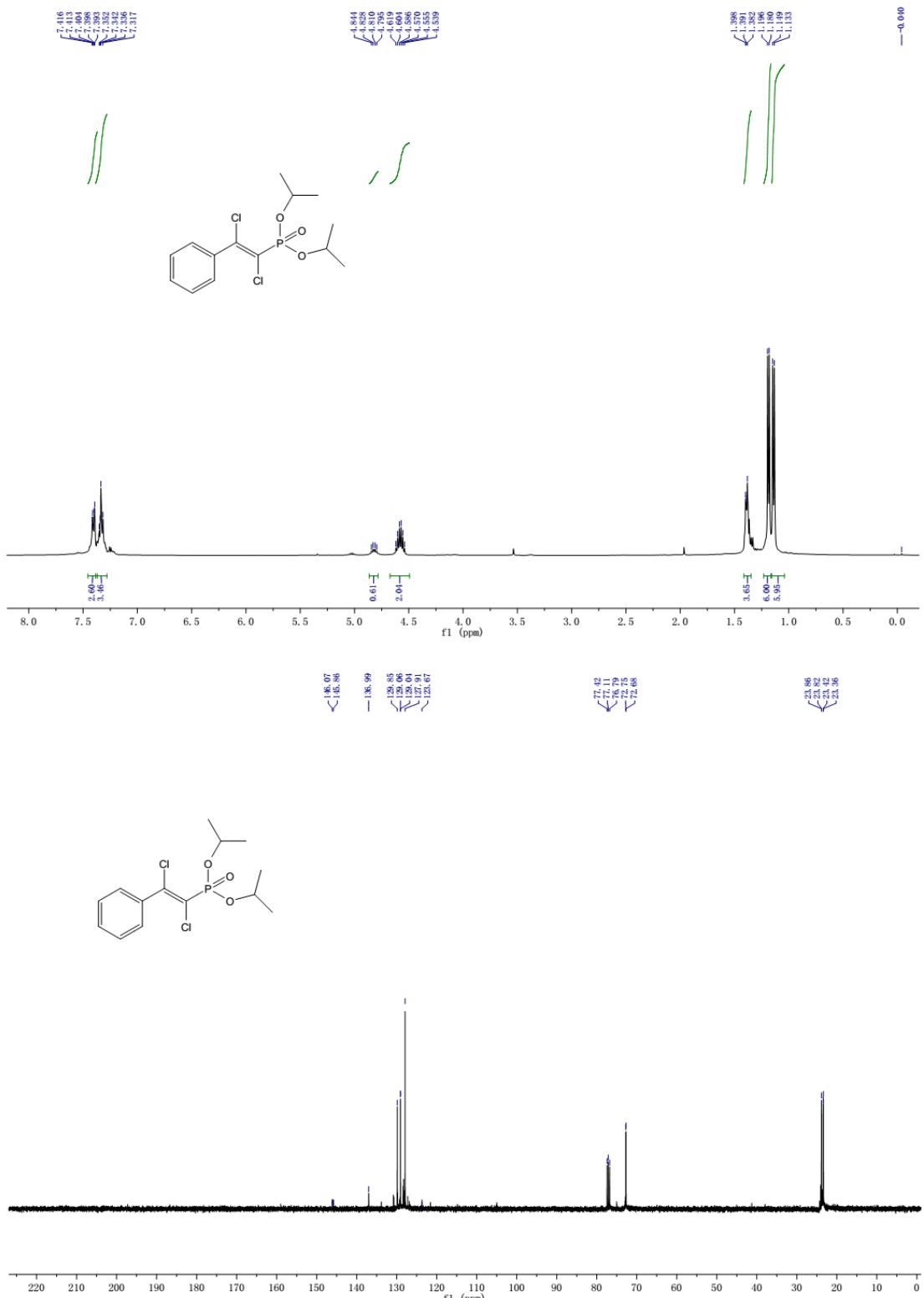


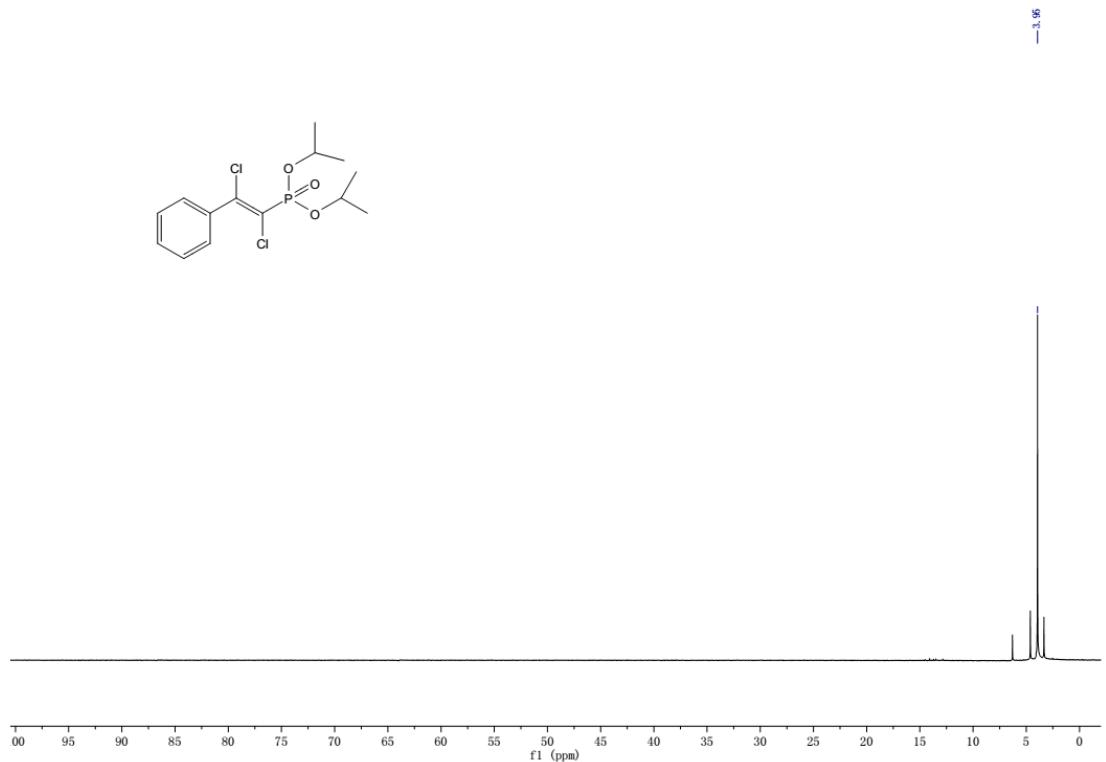
### Copies of $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR Spectra of **4a**



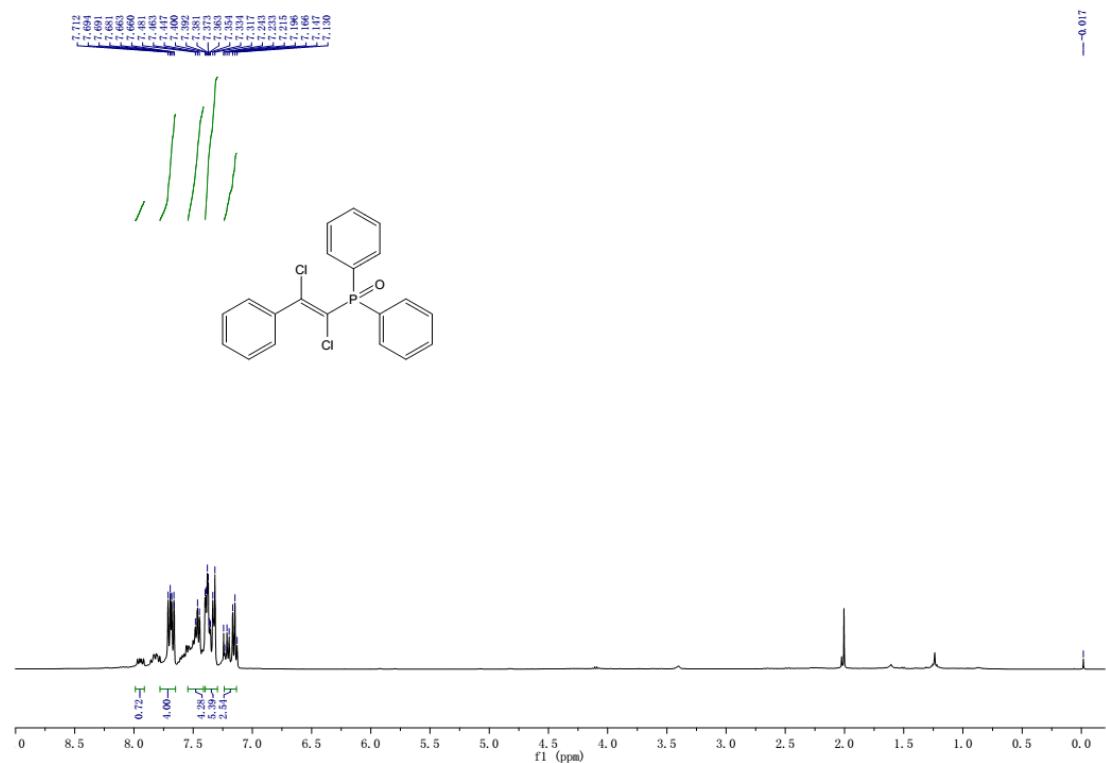


Copies of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR Spectra of **4b**

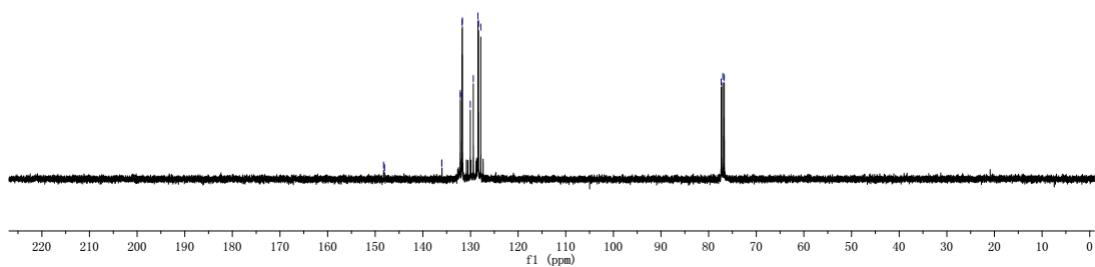
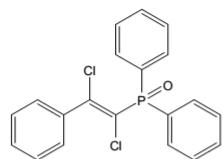




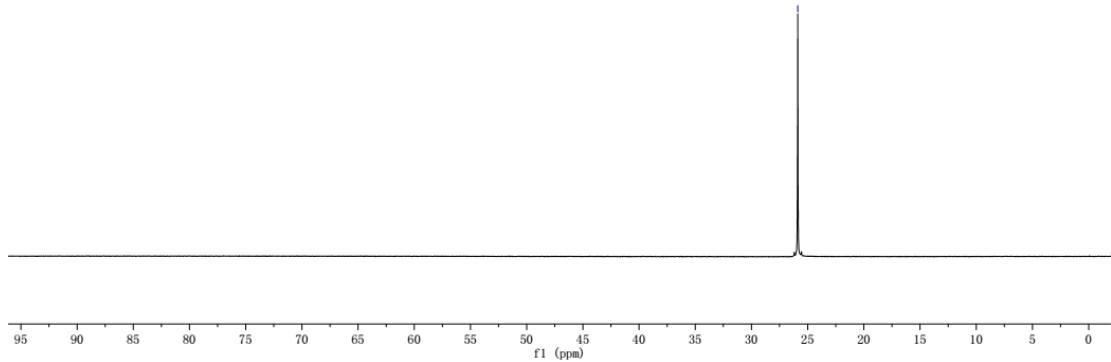
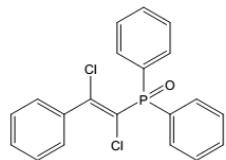
Copies of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR Spectra of **4c**



<sup>13</sup>C NMR chemical shifts (ppm): 198.25, 198.01, 196.02, 196.00, 192.11, 192.12, 132.12, 131.79, 131.69, 130.95, 129.92, 128.43, 128.30, 127.81, 77.46, 77.45, 76.73.



—25.88



Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of **5**

