Cetyltrimethyl Ammonium Bromide Catalysed Oxidative Cross Dehydrogenative Coupling of Benzylic C(sp^3)–H Bonds in Methylarenes with P(O)–OH Compounds

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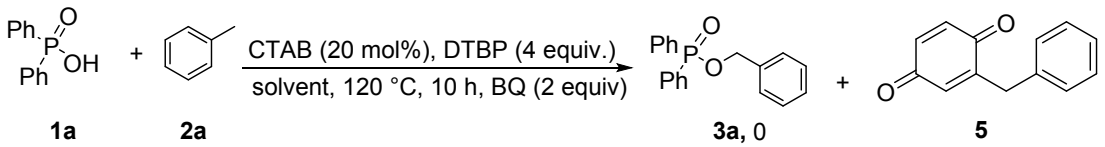
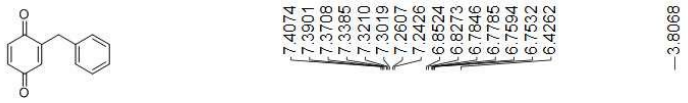
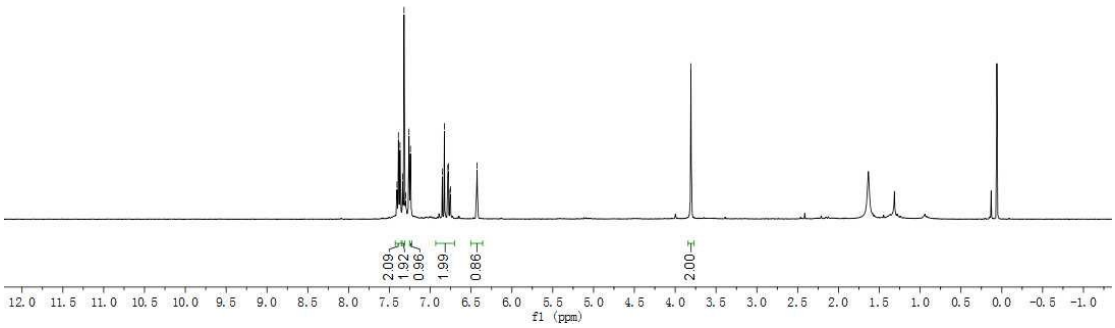
Control experiments



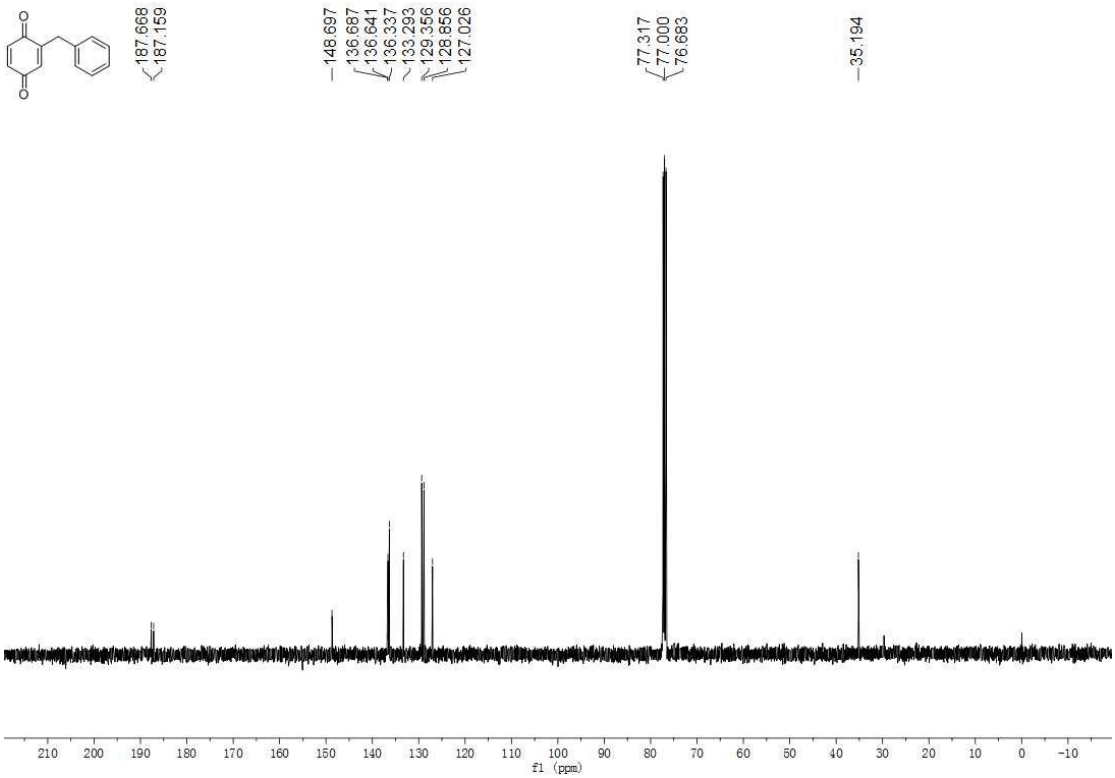
1a **2a** **3a,** 0 **5**

$Ph_2P(O)OH$ (**1a**) (0.1 mmol), CTAB (20 mol%), DTBP (0.4 mmol) BQ (0.2 mmol) and toluene (**2a**) (0.5 ml) were added in a 25-mL Schlenk tube with magnetic stirring at room temperature. With constant stirring the resulting mixture was heated to 120 °C and kept at this temperature for 10 h. Then the reaction solution was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel (4.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dry-loaded onto a silica gel column and purified by flash chromatography using petroleum ether/ethyl acetate = 10 / 1, (v/v) as eluent to give **5**.



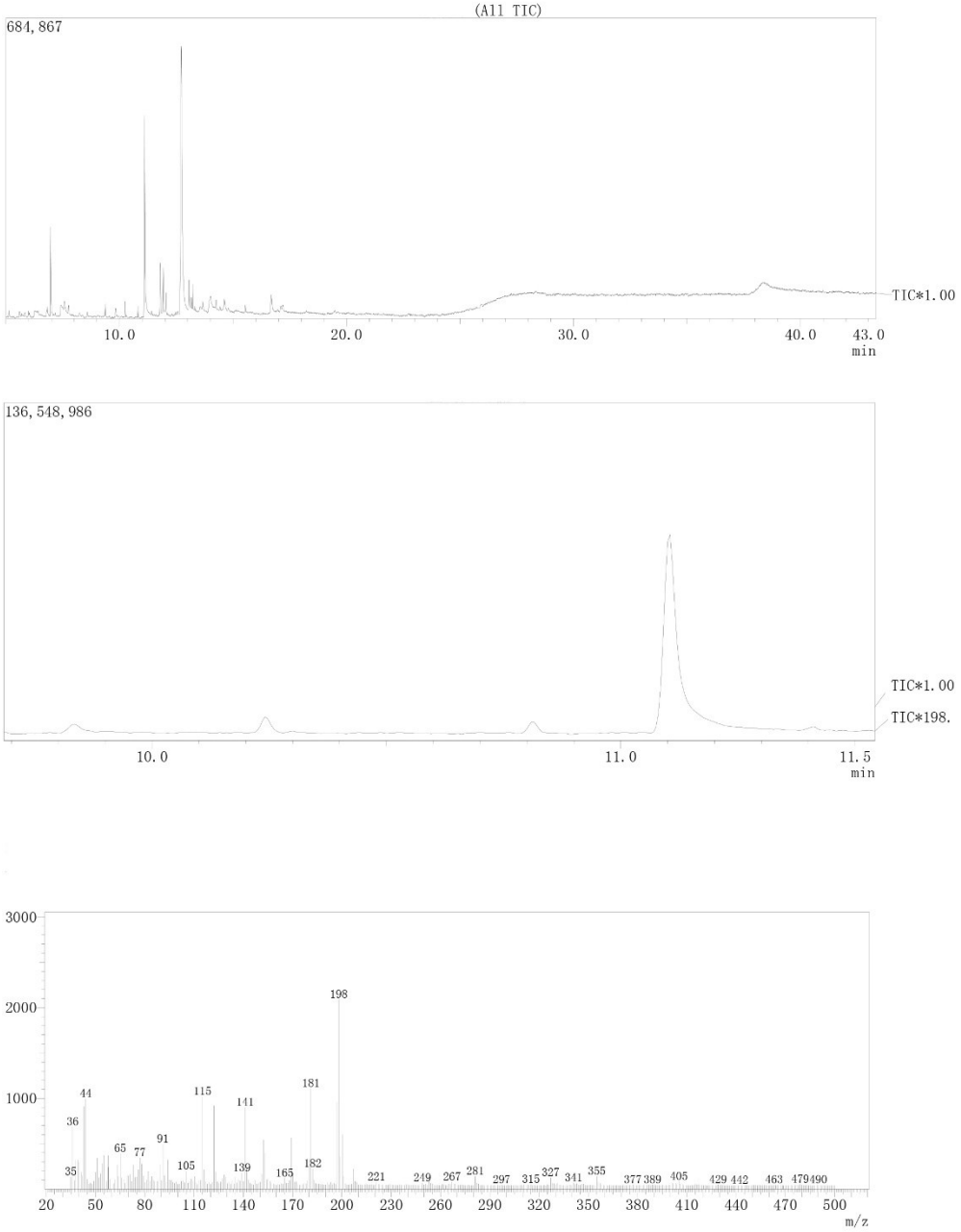


^1H NMR (400MHz, $CDCl_3$) spectrum of compound **5**



^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **5**

Yellow oil [1] R_f = 0.40 (petroleum ether/ethyl acetate = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 2H), 7.34–7.30 (m, 2H), 7.24 (s, 1H), 6.85–6.75 (m, 2H), 6.43 (s, 1H), 3.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7 (s), 187.2 (s), 148.7 (s), 136.7 (s), 136.6 (s), 136.3 (s), 133.3 (s), 129.4 (s), 128.9 (s), 127.0 (s), 35.2 (s).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30.0
40.0
43.0
min
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TIC*1.00
TIC*198.
10.0
11.0
11.5
min
3000
2000
1000
198
181
115
141
44
36
91
65
77
105
139
165
182
35
221
249
267
281
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315
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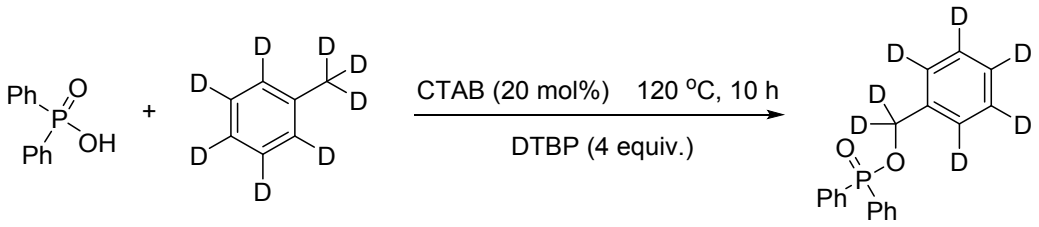
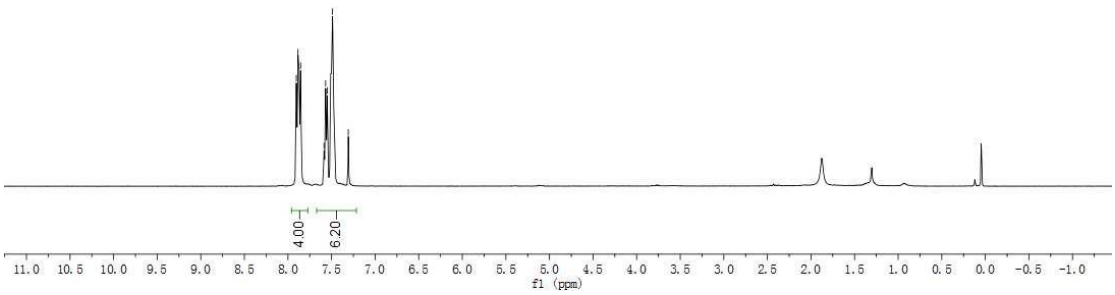
m/z



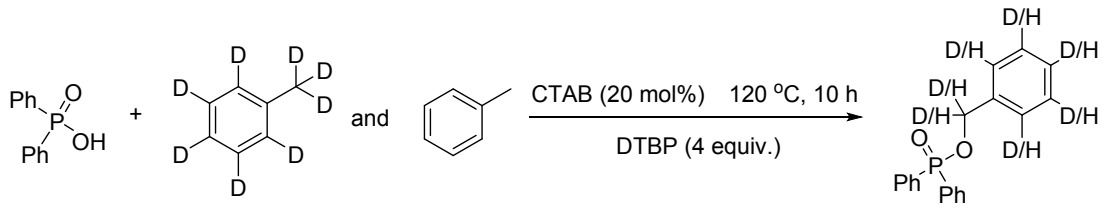
[D_7-3a], 57%

$Ph_2P(O)OH$ (0.1 mmol), CTAB (20 mol%), DTBP (0.4 mmol) and toluene-d_8 (0.5 ml) were added in a 25-mL Schlenk tube with magnetic stirring at room temperature. With constant stirring the resulting mixture was heated to 120 °C and kept at this temperature for 10 h. Then the reaction solution was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel (4.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dry-loaded onto a silica gel column and purified by flash chromatography using petroleum ether/ethyl acetate = 5 / 1 (v/v) as eluent to give **[D_7-3a]**.



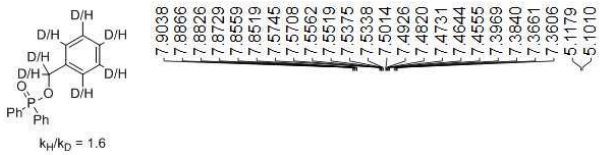
^1H NMR (400MHz, $CDCl_3$) spectrum of compound **[D_7-3a]**

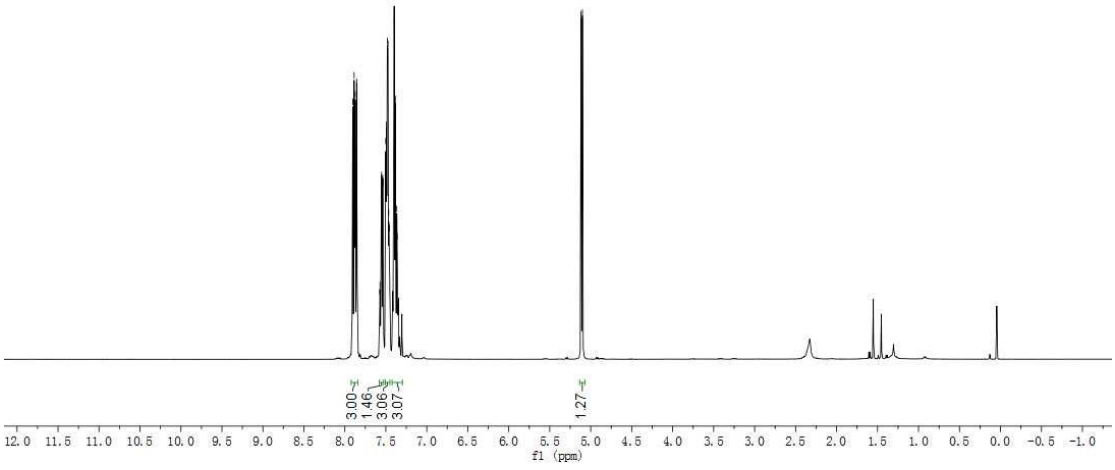
Colorless oil R_f = 0.20 (petroleum ether/ethyl acetate = 2:1) ^1H NMR (400 MHz, $CDCl_3$) δ 7.90–7.85 (m, 4H), 7.59–7.30 (m, 6H).



toluene/toluene-d_8=1/1 **$[H_7/D_7]$-3a**

$Ph_2P(O)OH$ (0.1 mmol), CTAB (20 mol%), DTBP (0.4 mmol) and solvent (1.0 ml, toluene/toluene-d_8, 1:1, v/v) were added in a 25-mL Schlenk tube with magnetic stirring at room temperature. With constant stirring the resulting mixture was heated to 120 °C and kept at this temperature for 10 h. Then the reaction solution was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel (4.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dry-loaded onto a silica gel column and purified by flash chromatography using petroleum ether/ethyl acetate = 5 / 1 (v/v) as eluent to give **$[H_7/D_7]$-3a**.

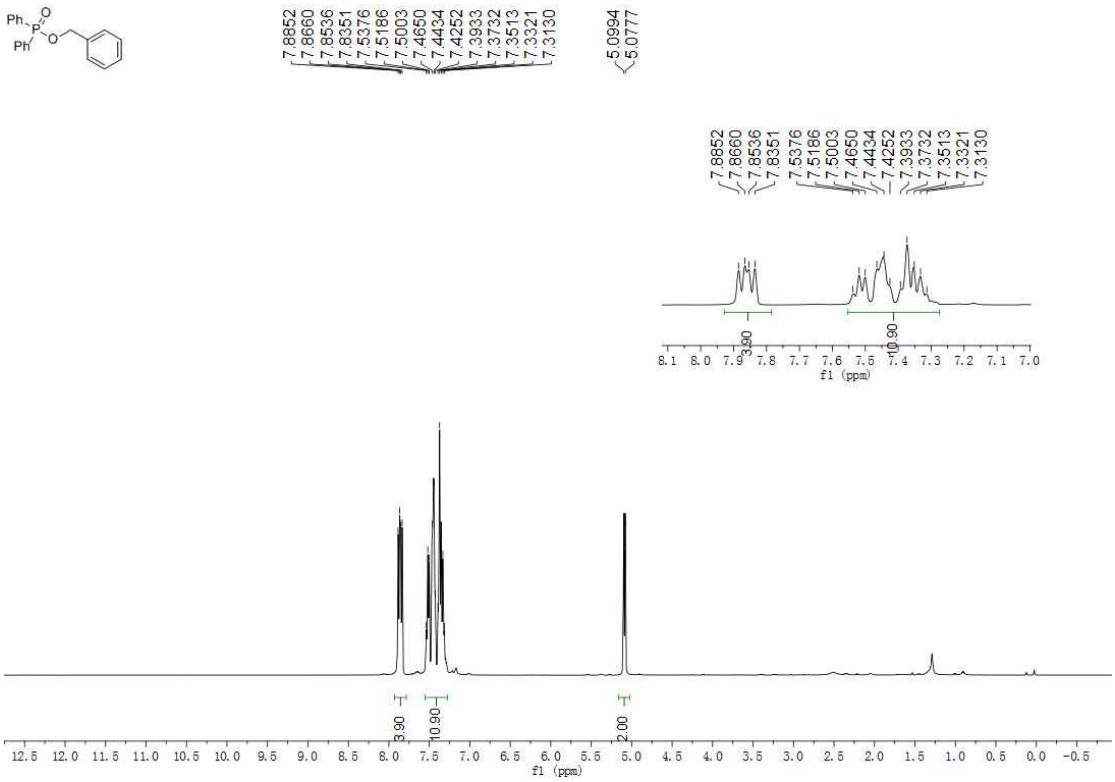




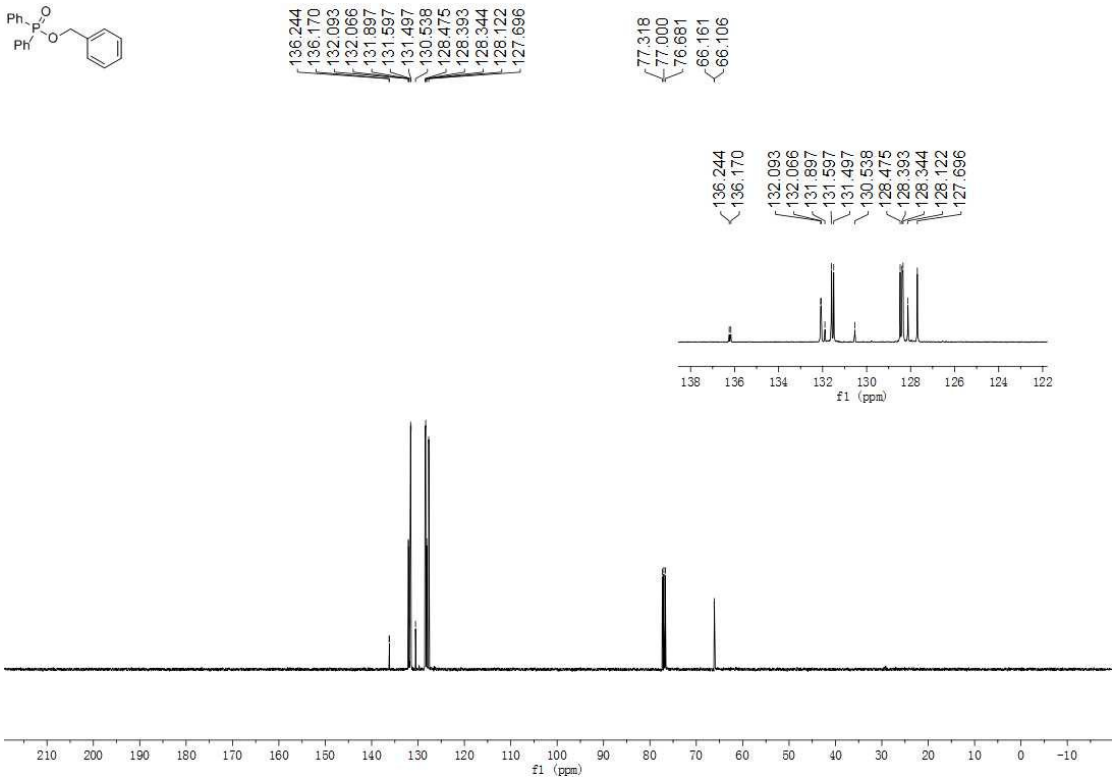
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **$[H_7/D_7]$-3a**

Colorless oil R_f = 0.20 (petroleum ether/ethyl acetate = 2:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.85 (m, 3H), 7.57–7.53 (m, 1H), 7.50–7.46 (m, 3H), 7.40–7.36 (m, 3H), 5.11 (d, J = 6.8 Hz, 1H).

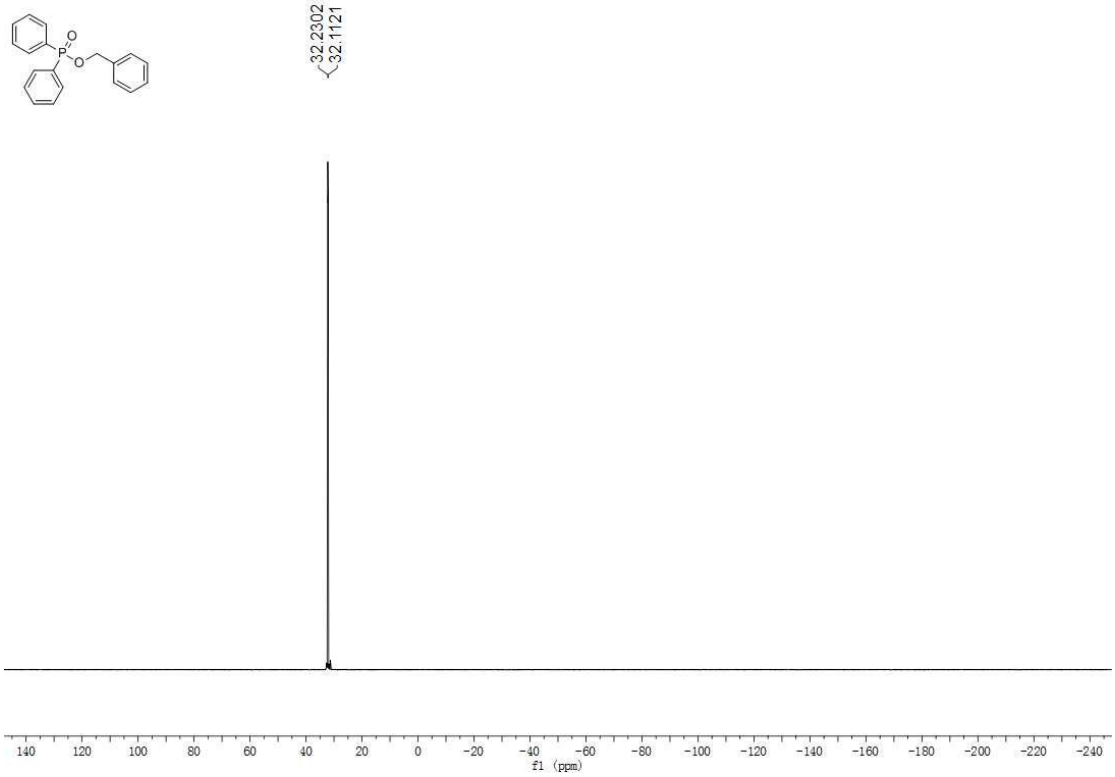
Copies of ^{1}H, ^{13}C, ^{31}P NMR charts of the Compounds



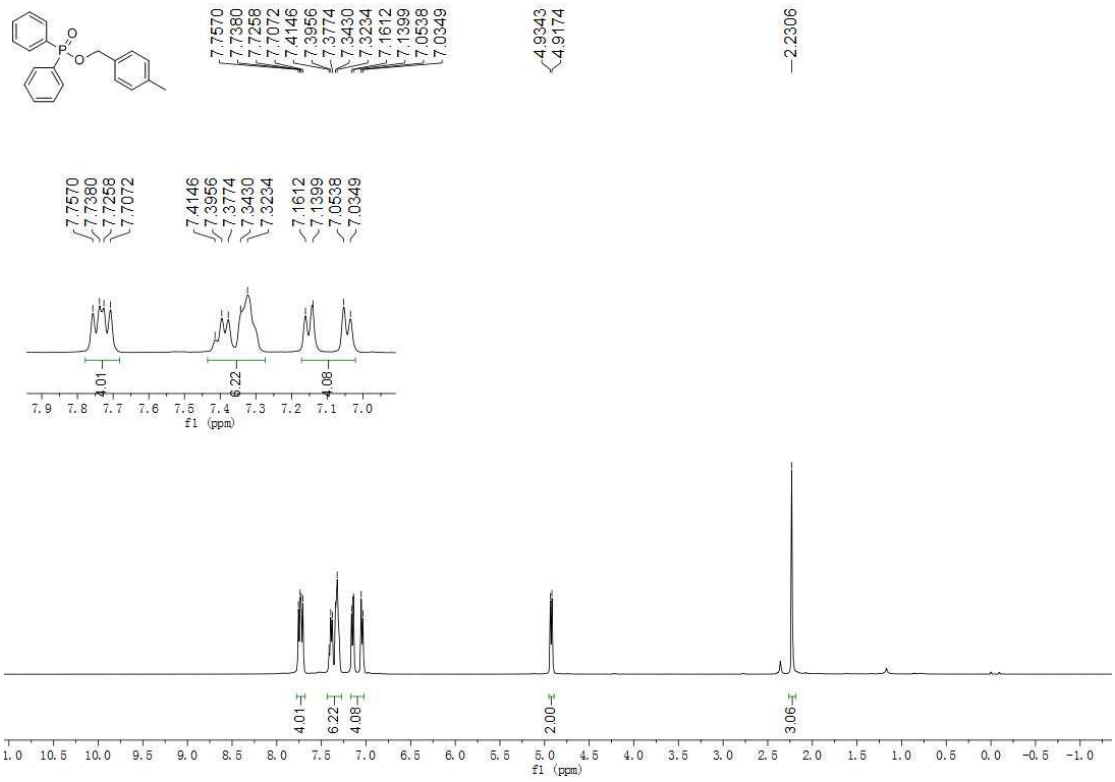
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3a** [2, 3]



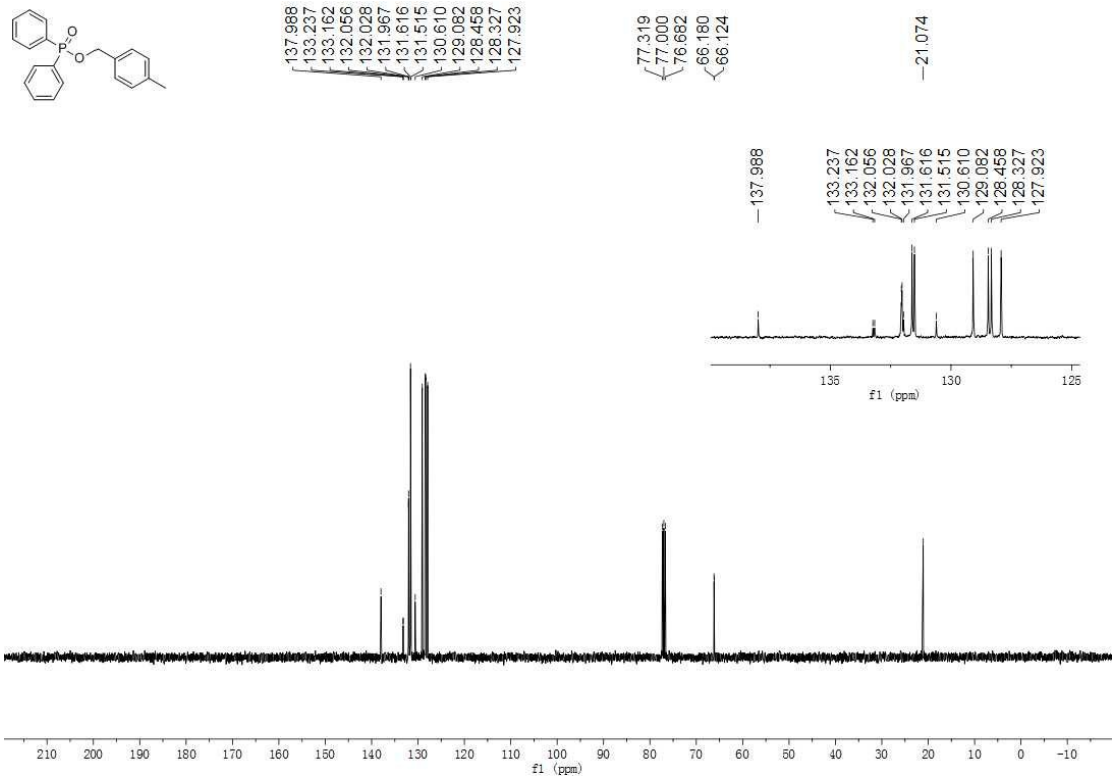
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3a** [2, 3]



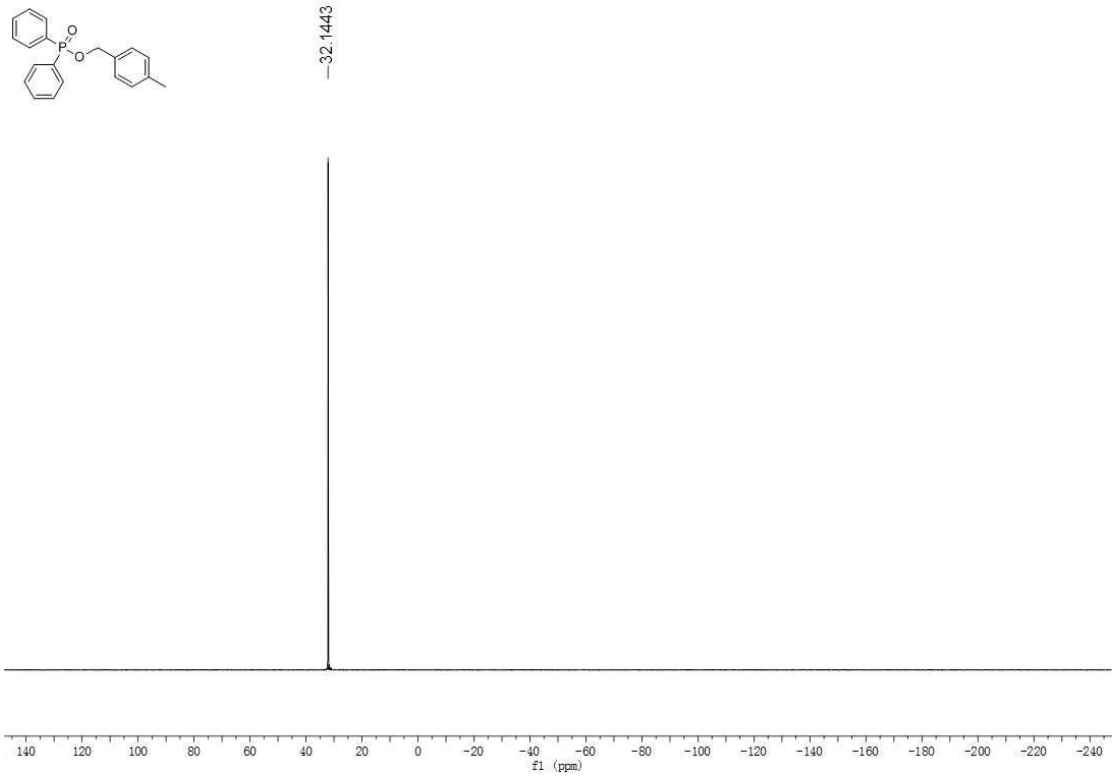
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3a** [2, 3]



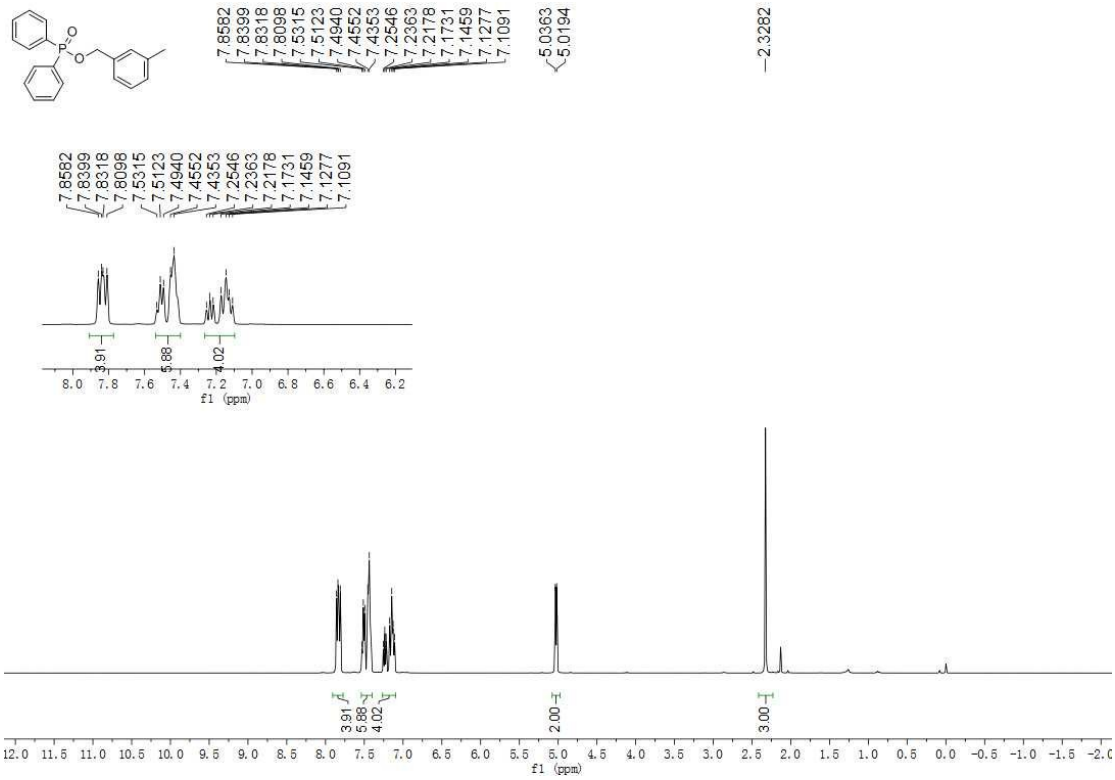
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3b**



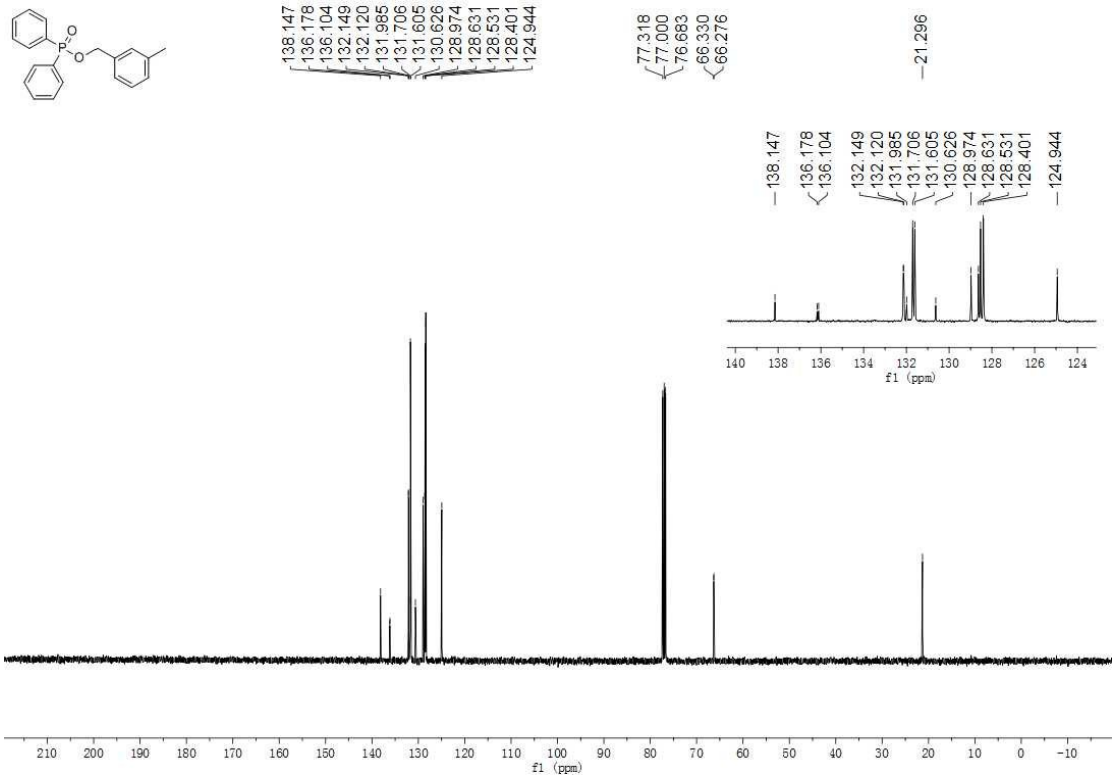
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3b**



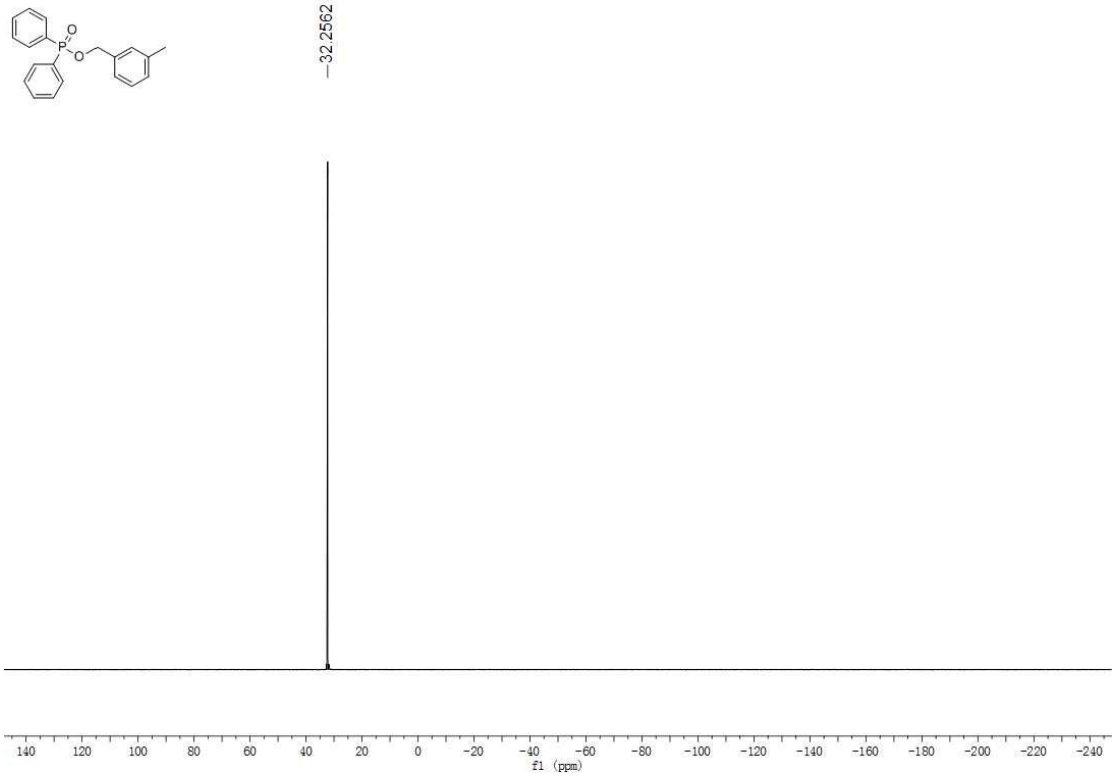
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3b**



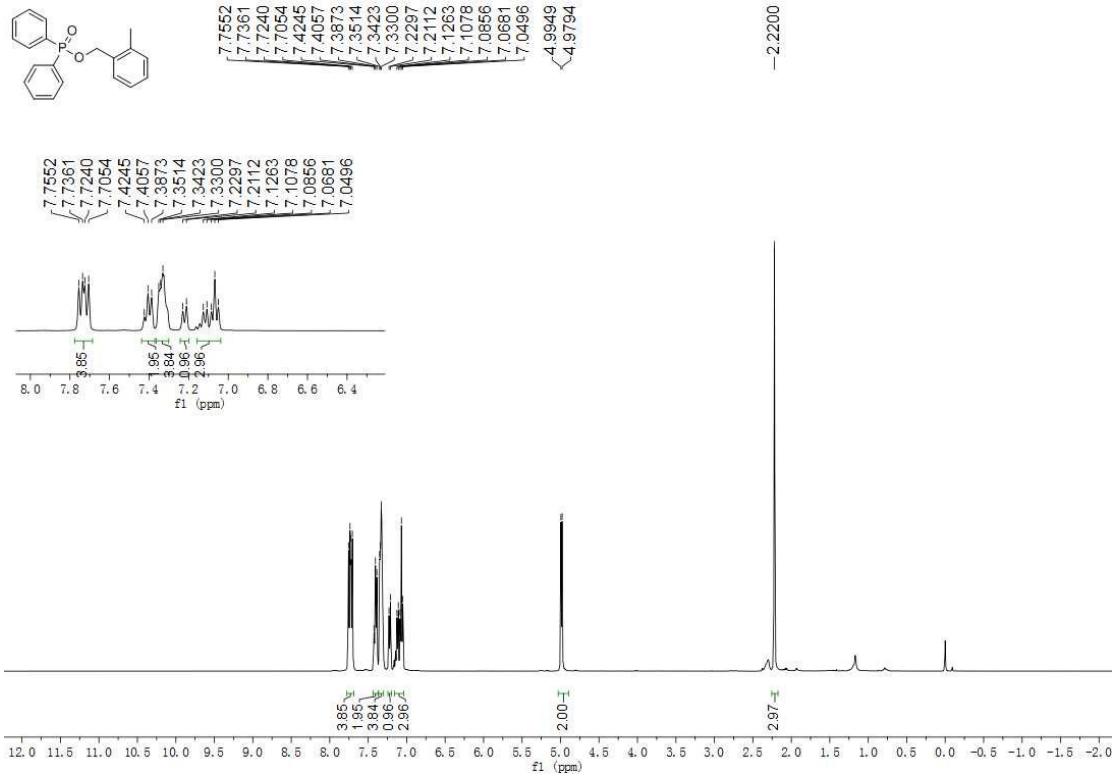
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3c**



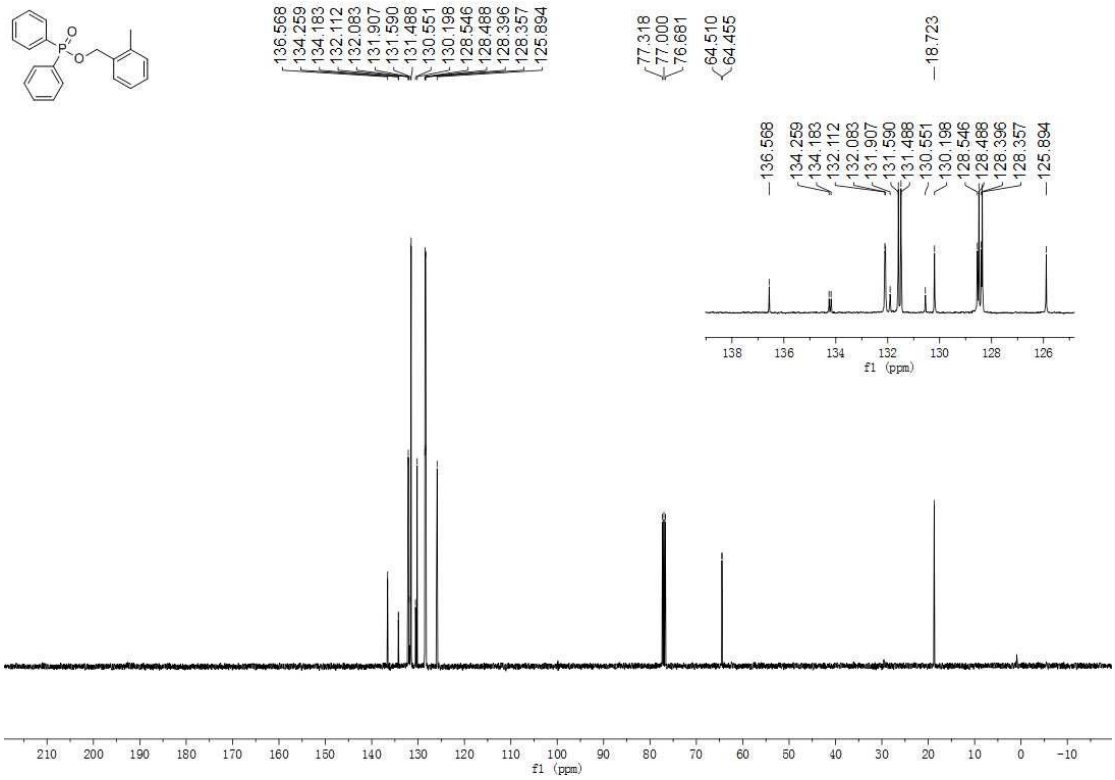
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3c**



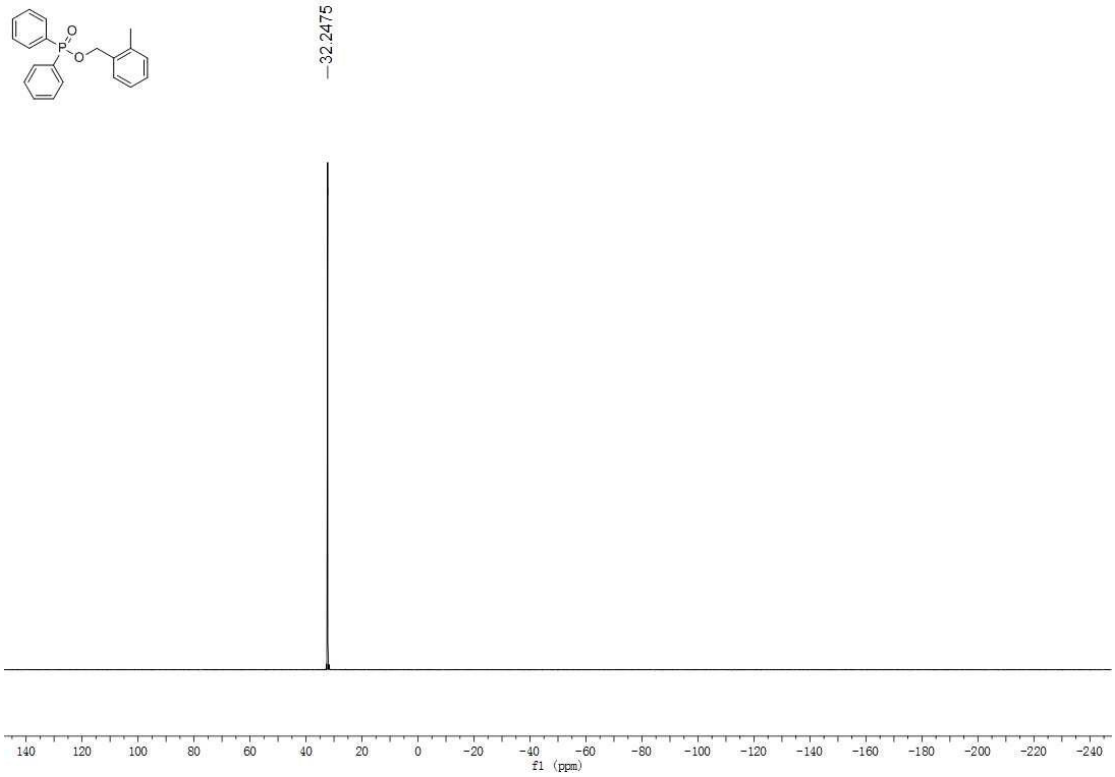
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3c**



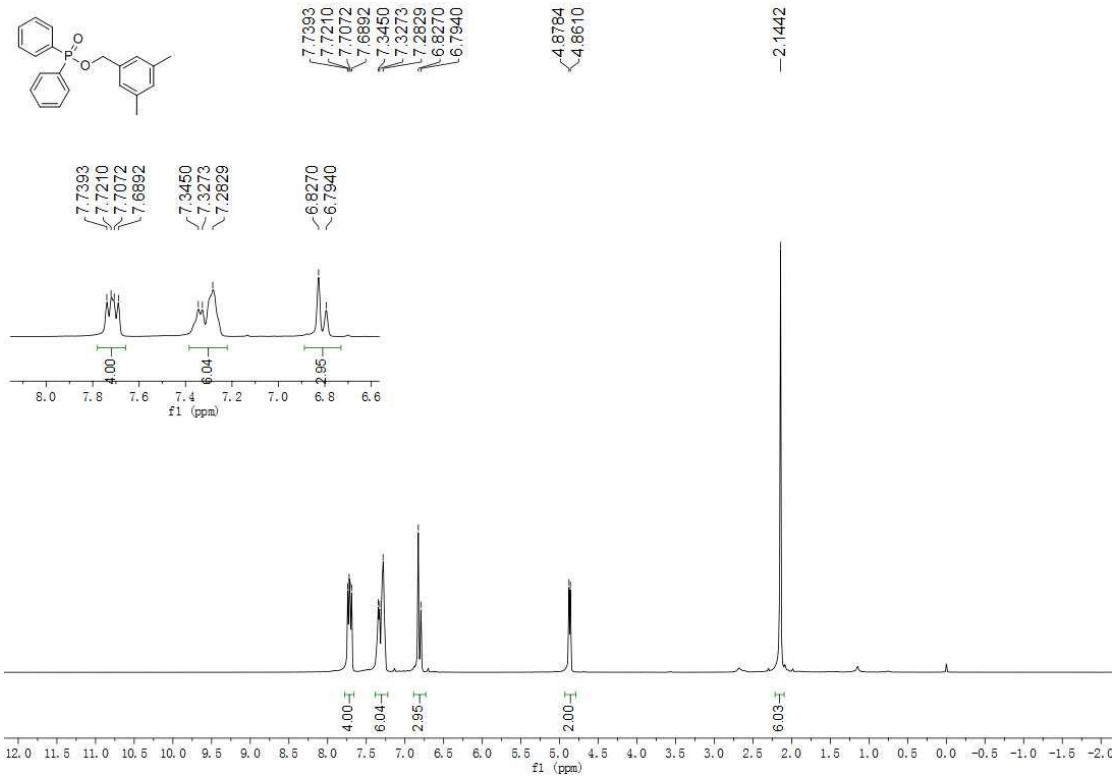
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3d**



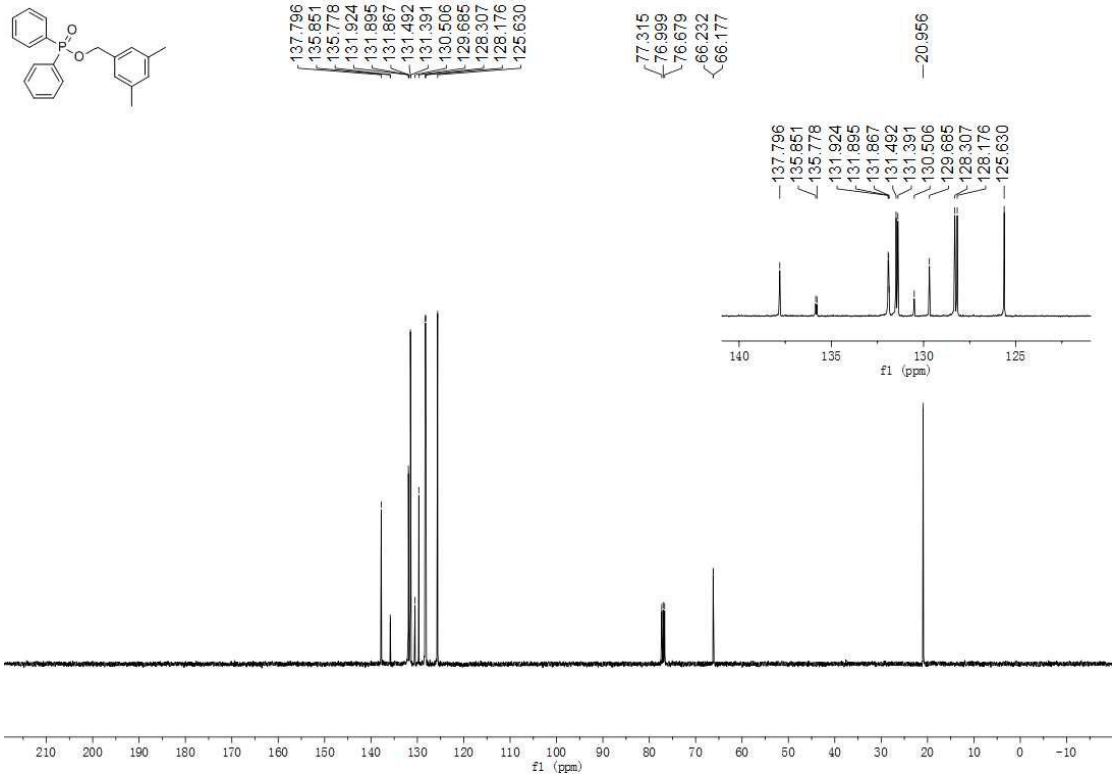
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3d**



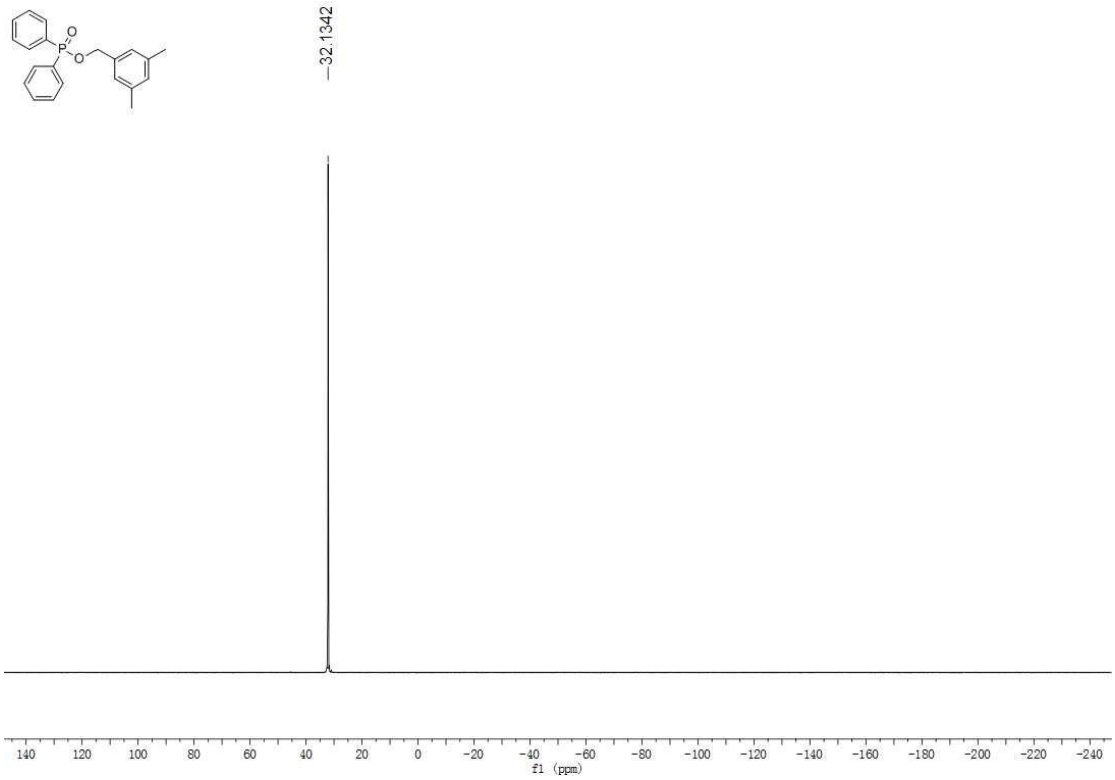
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3d**



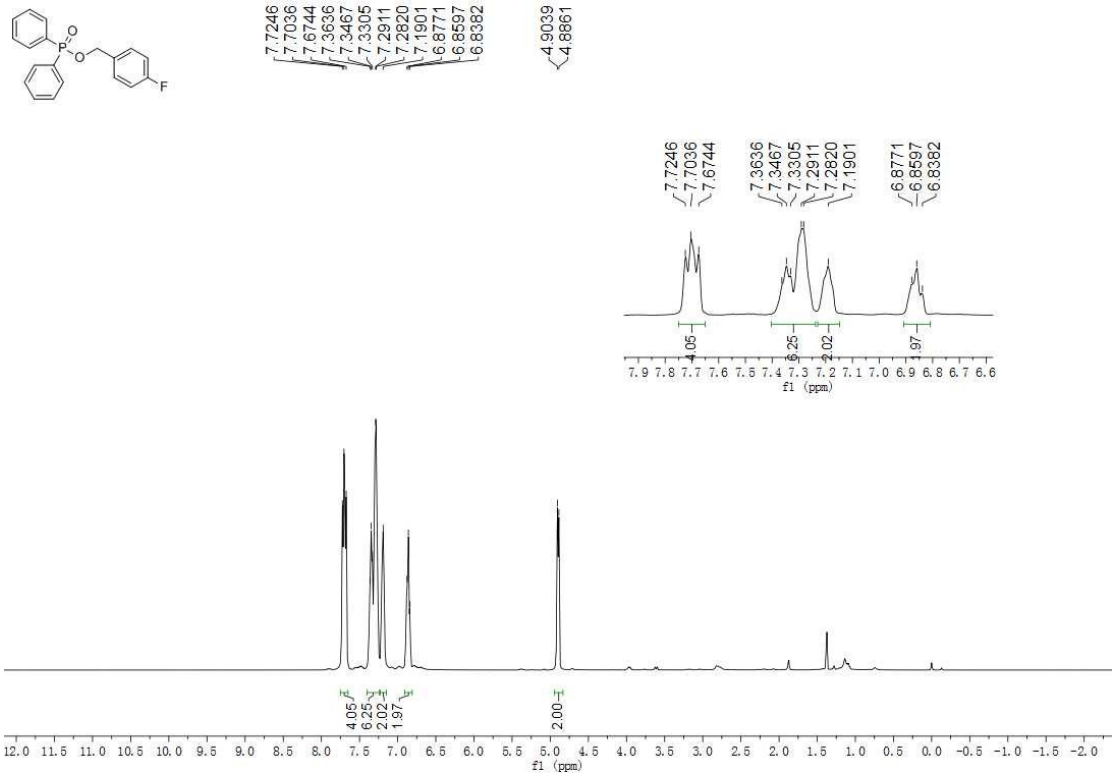
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3e**



^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3e**



^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3e**



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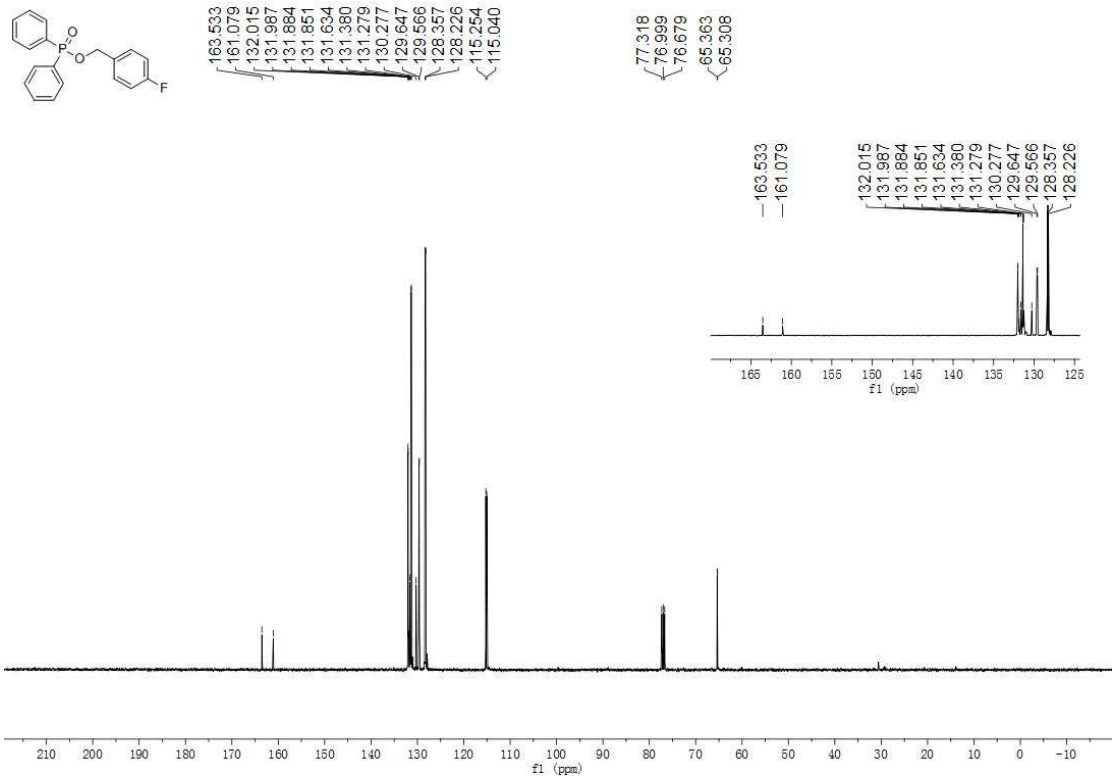
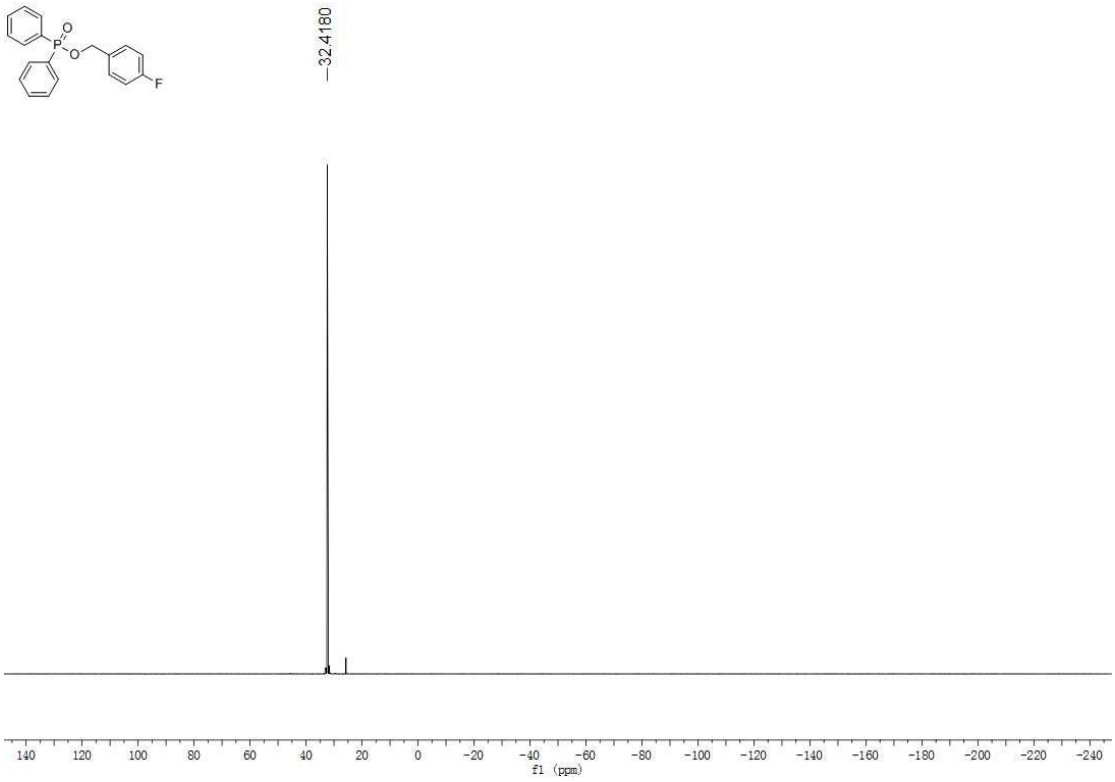
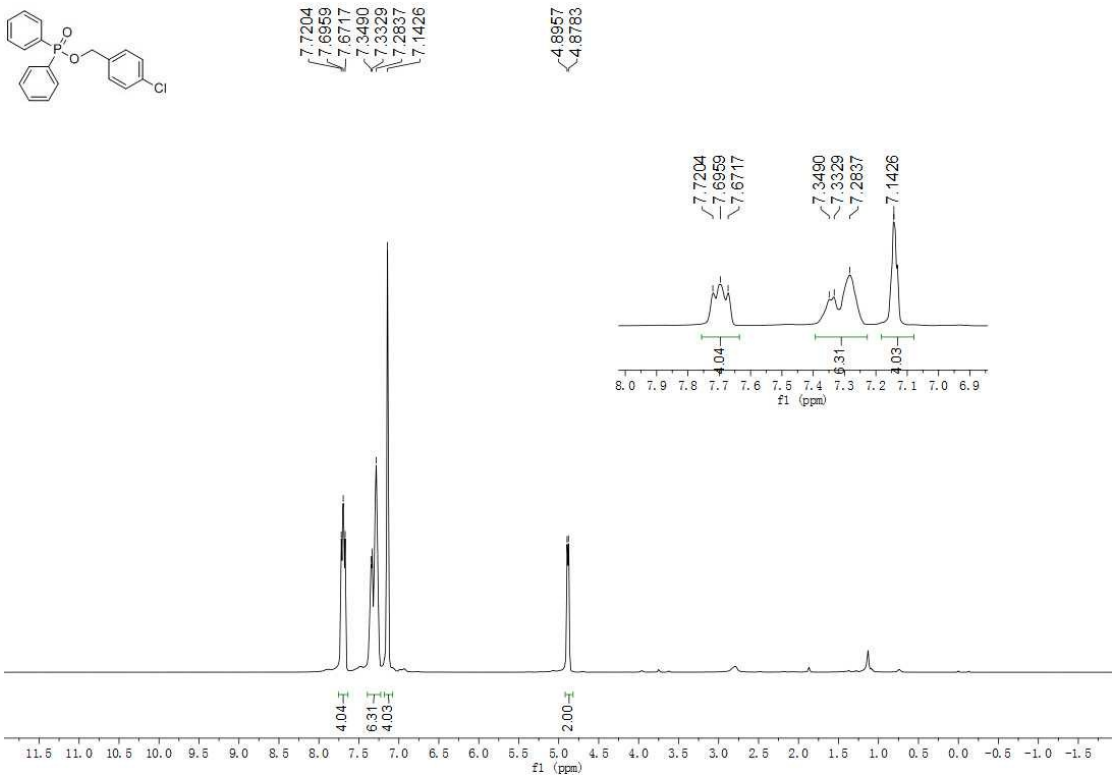


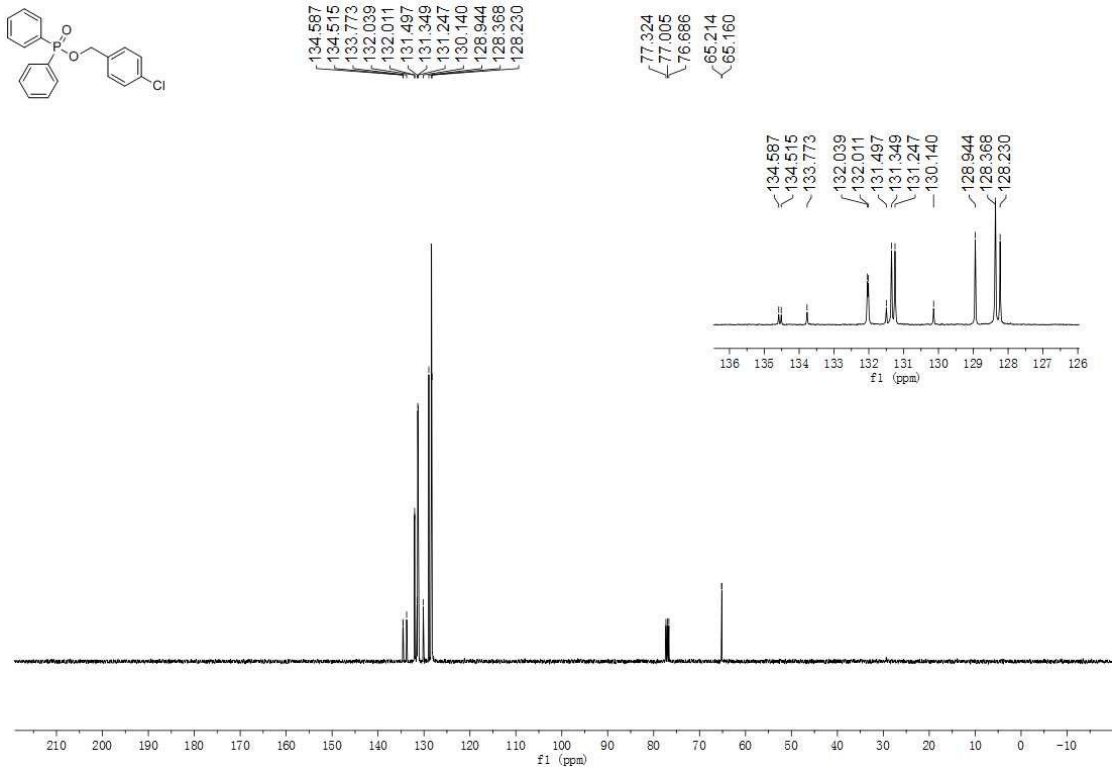
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3f**



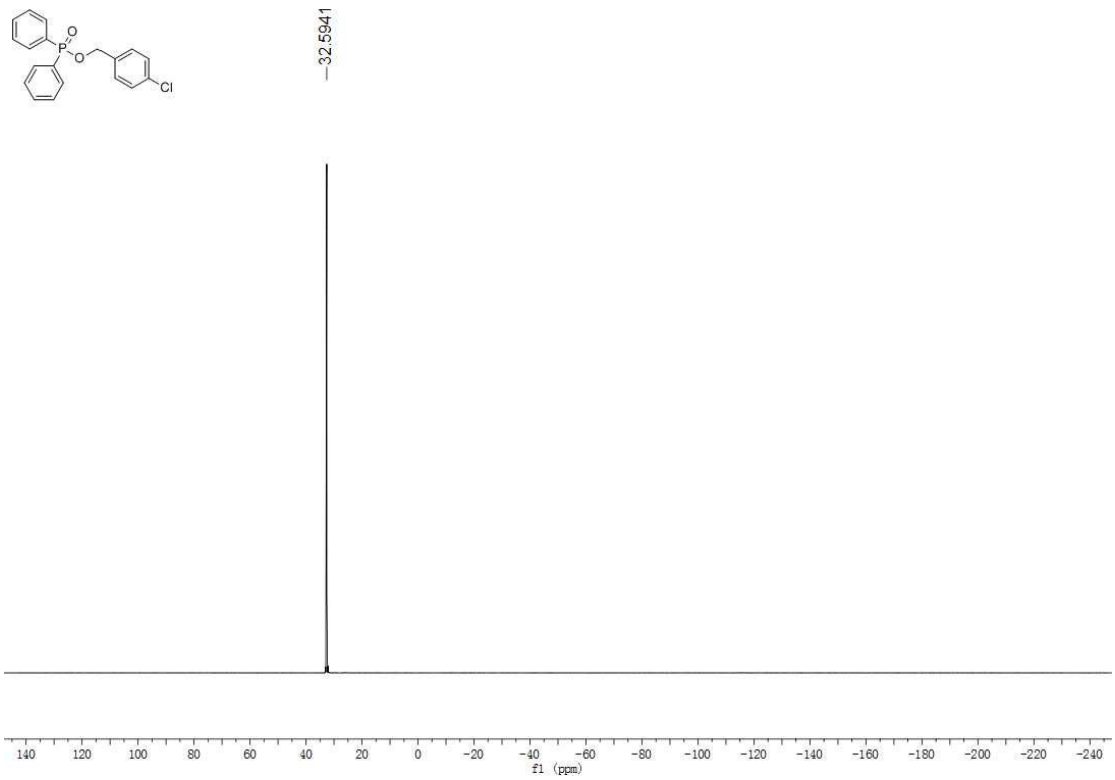
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3f**



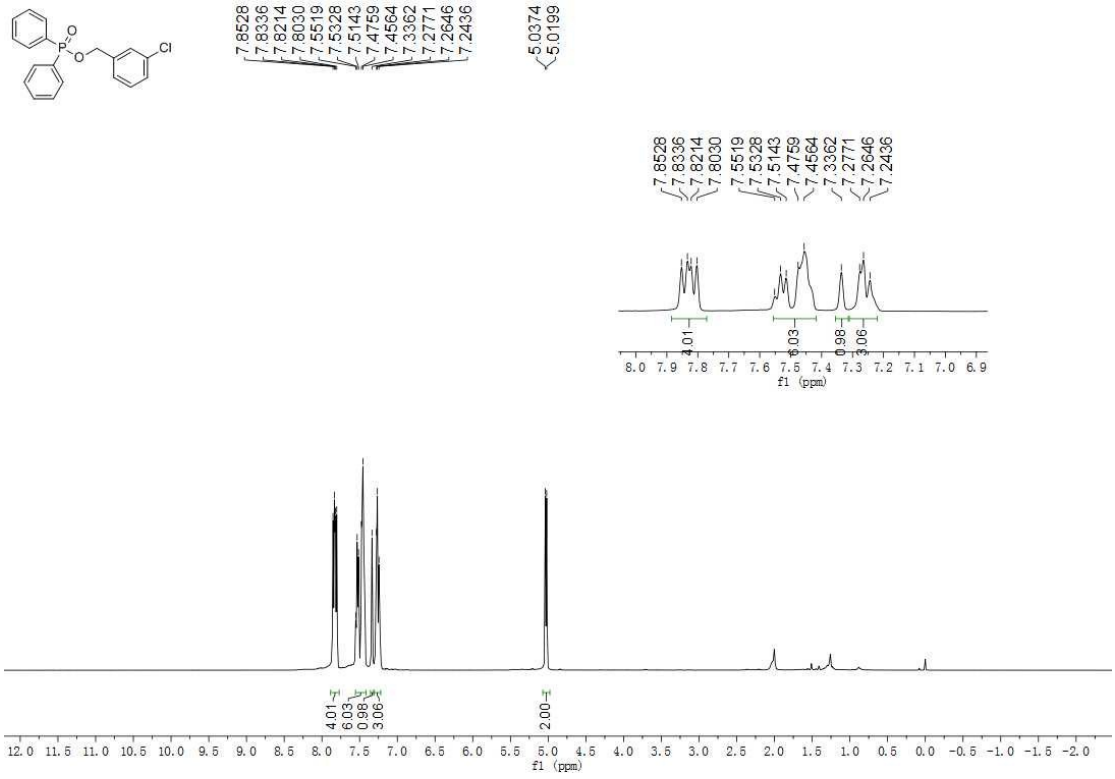
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3g**



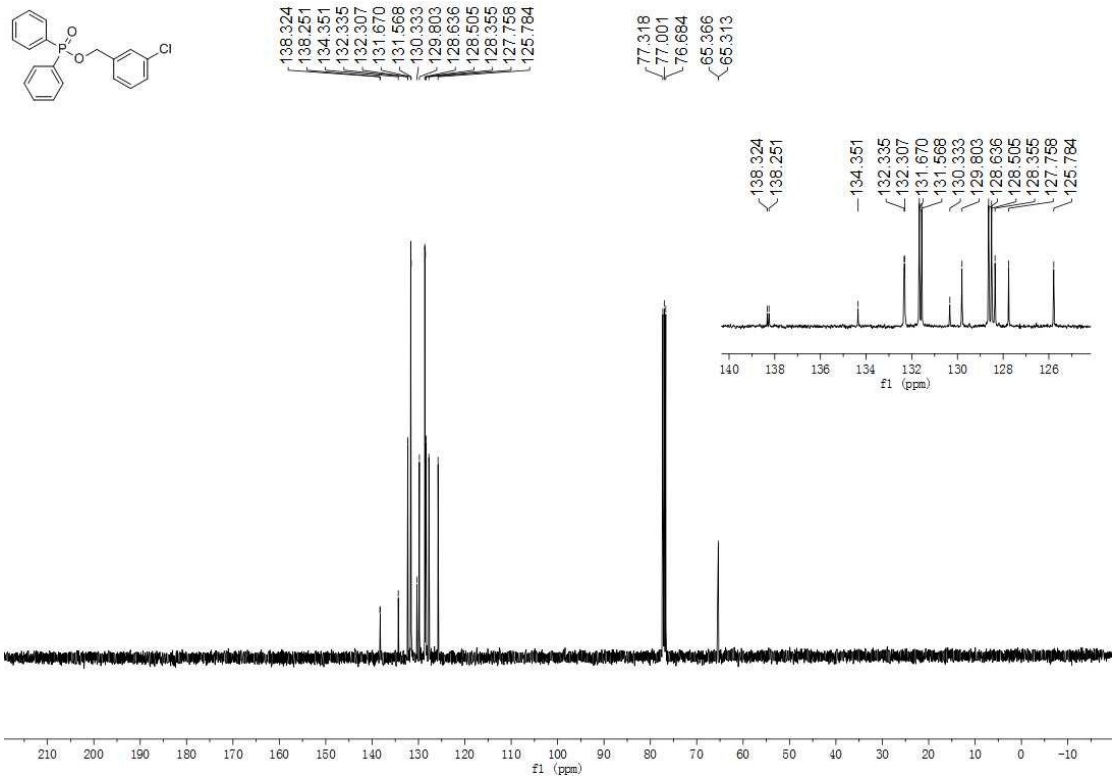
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3g**



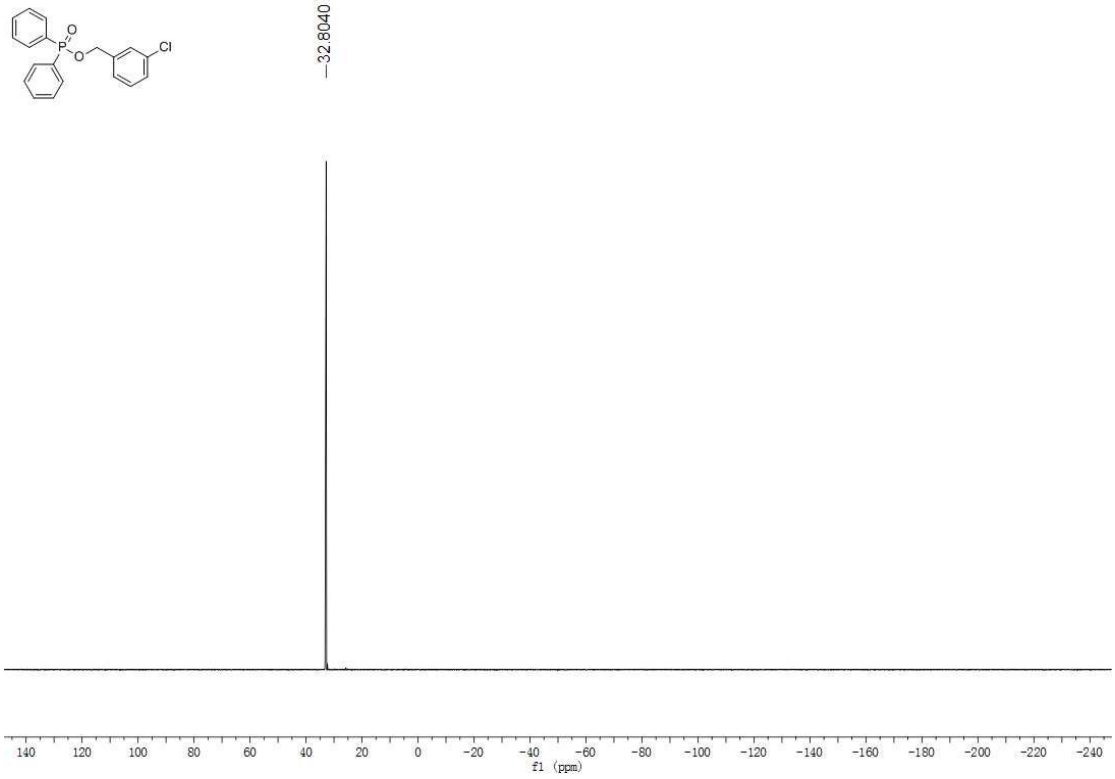
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3g**



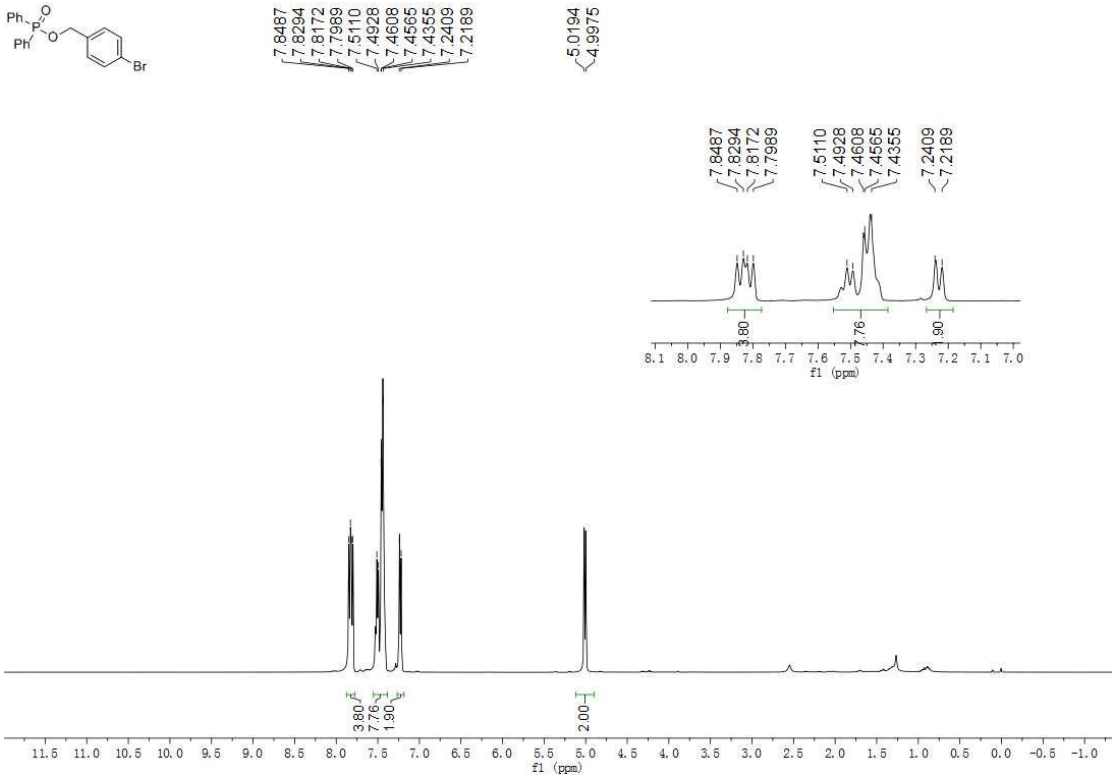
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3h**



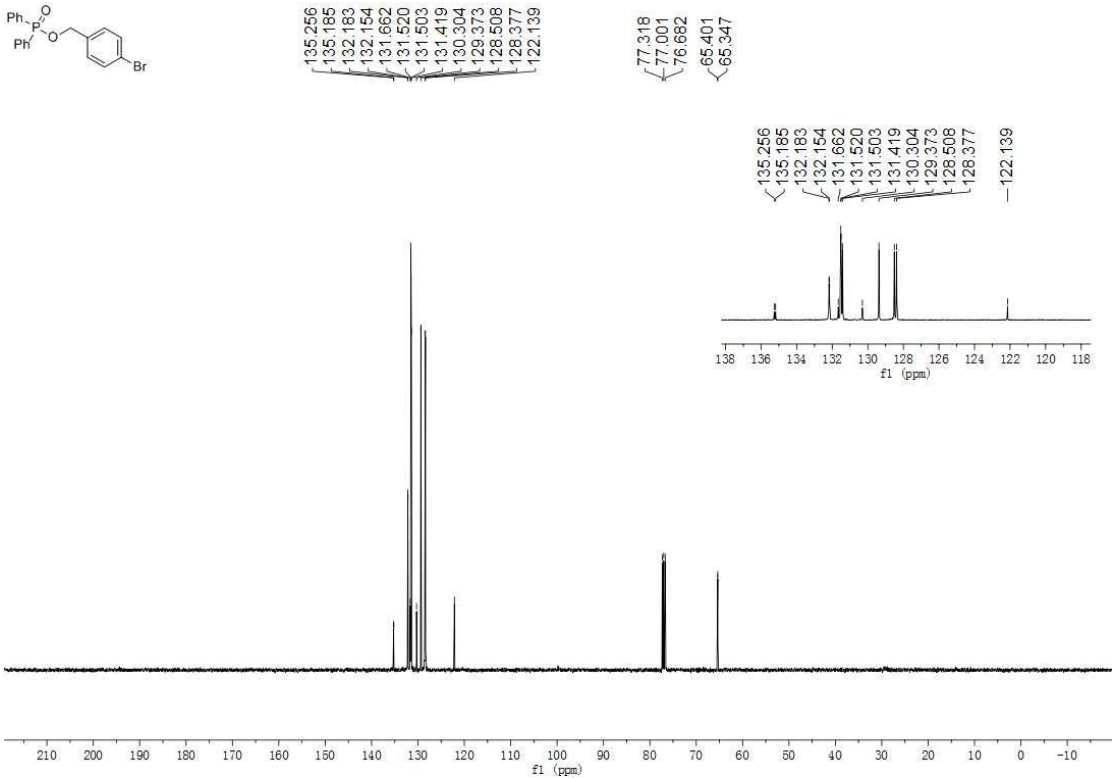
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3h**



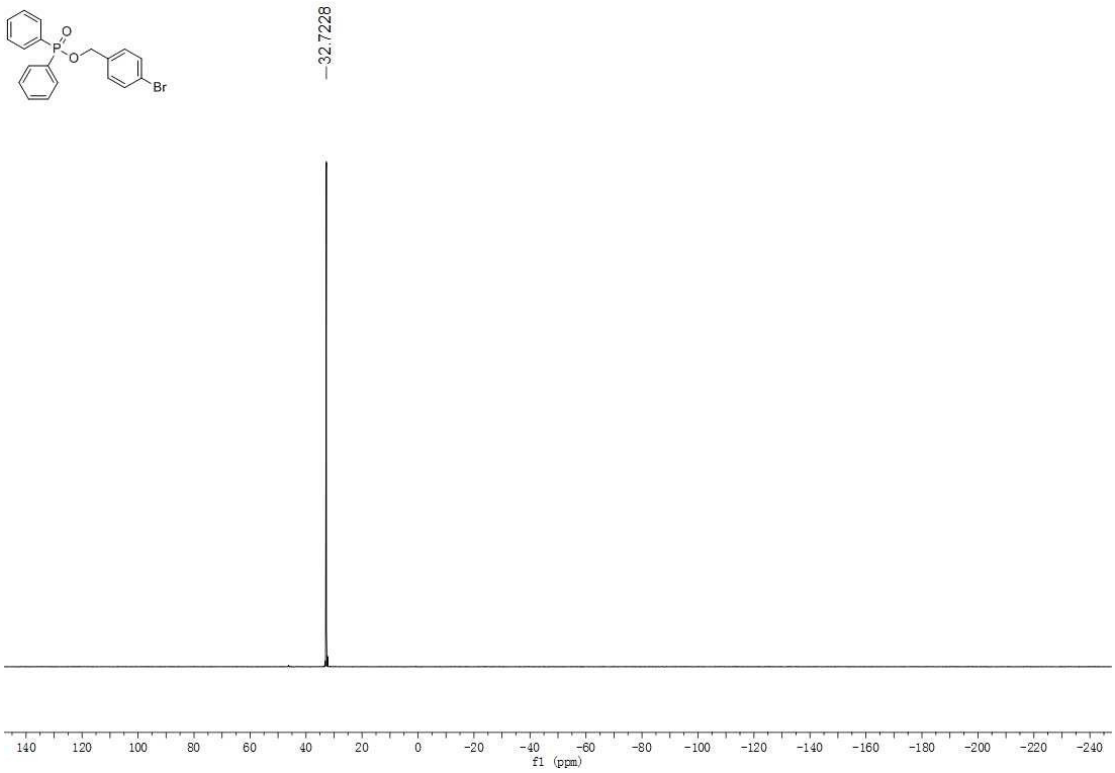
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3h**



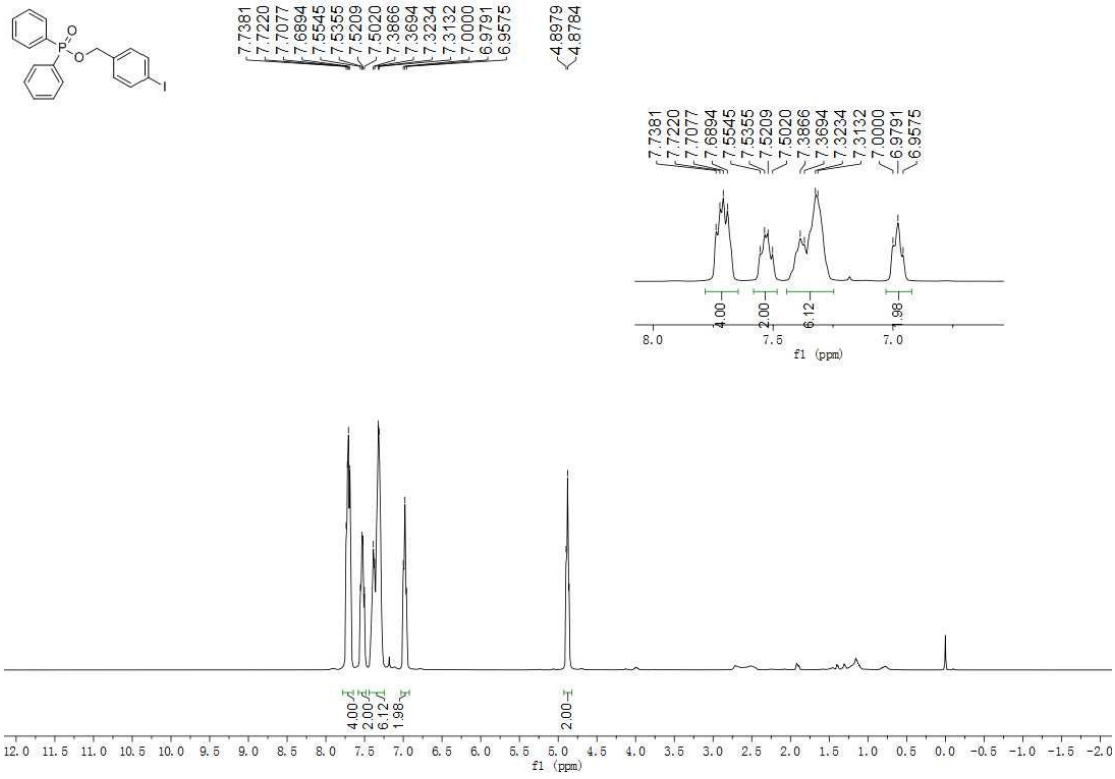
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3i**



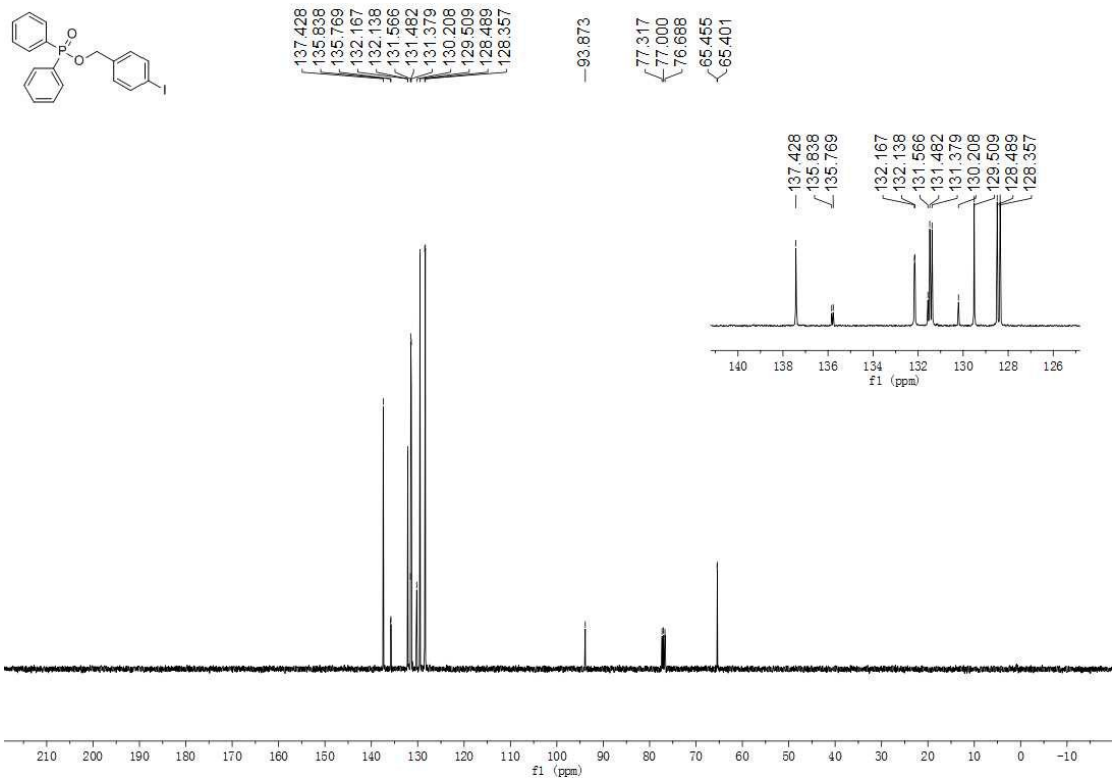
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3i**



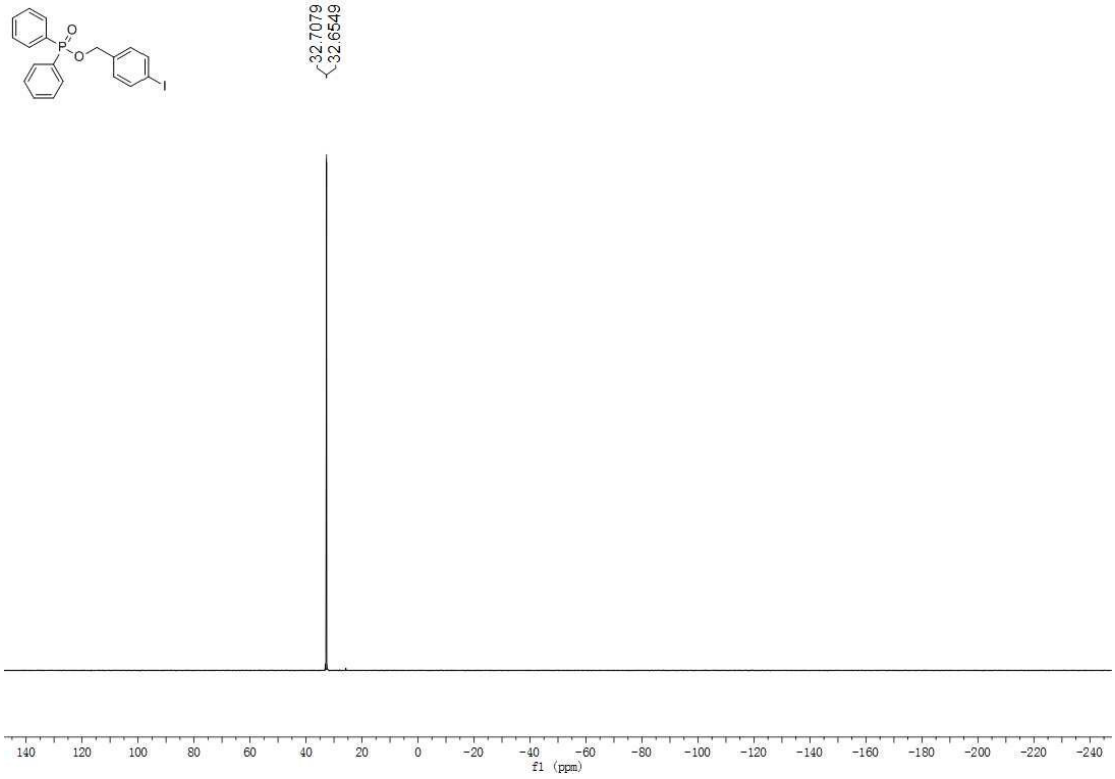
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3i**



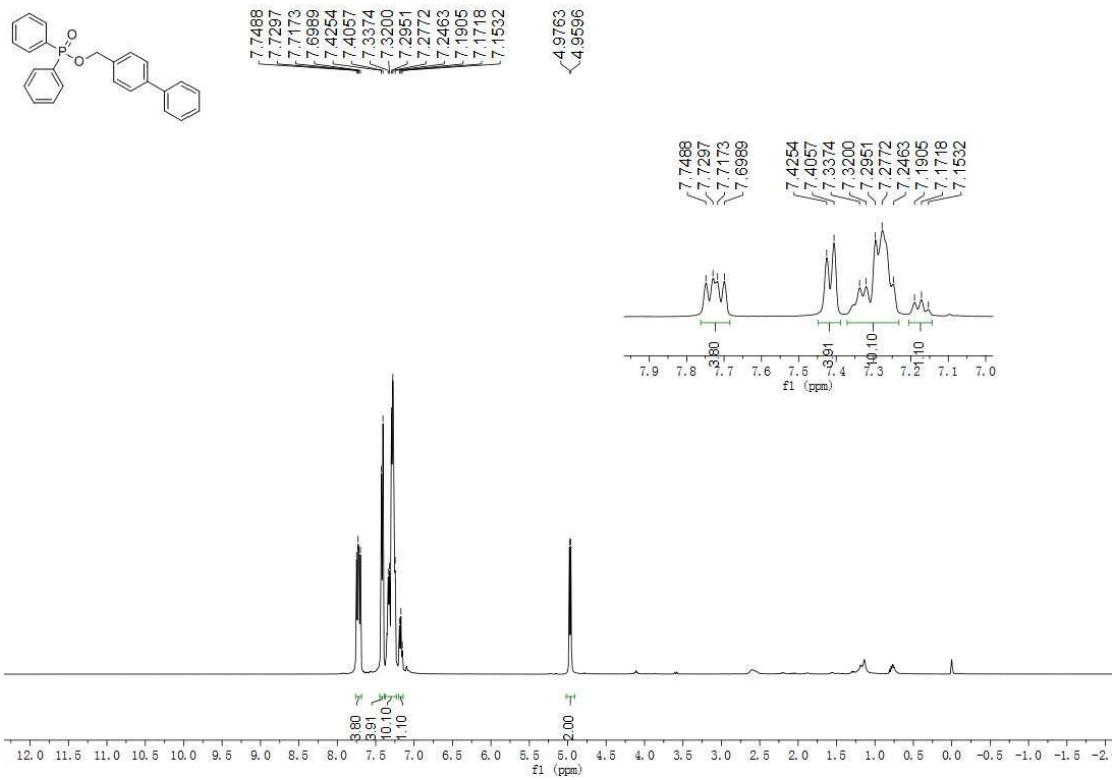
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3j**



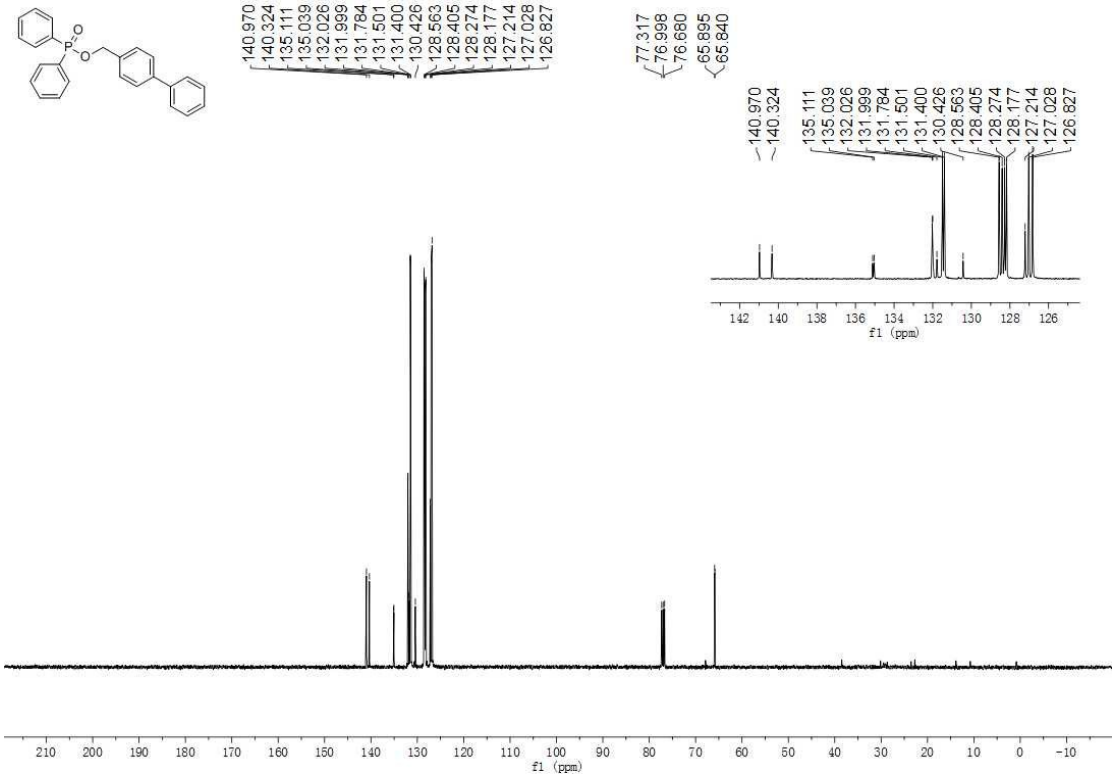
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3j**



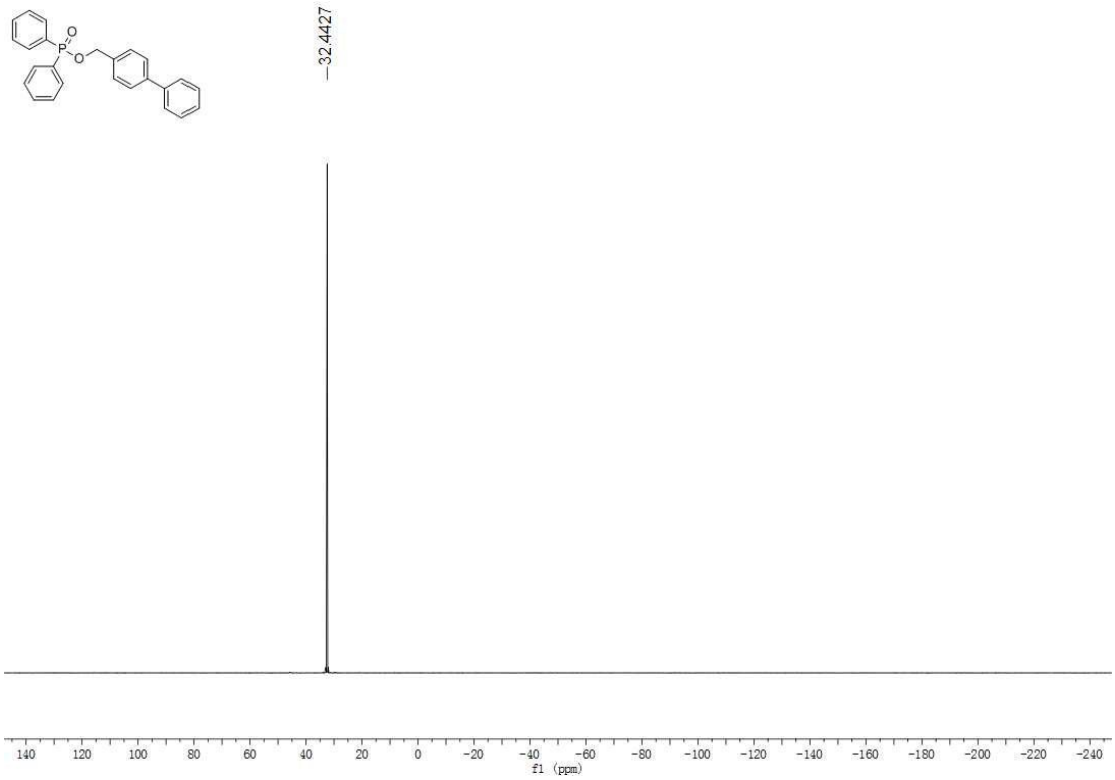
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3j**



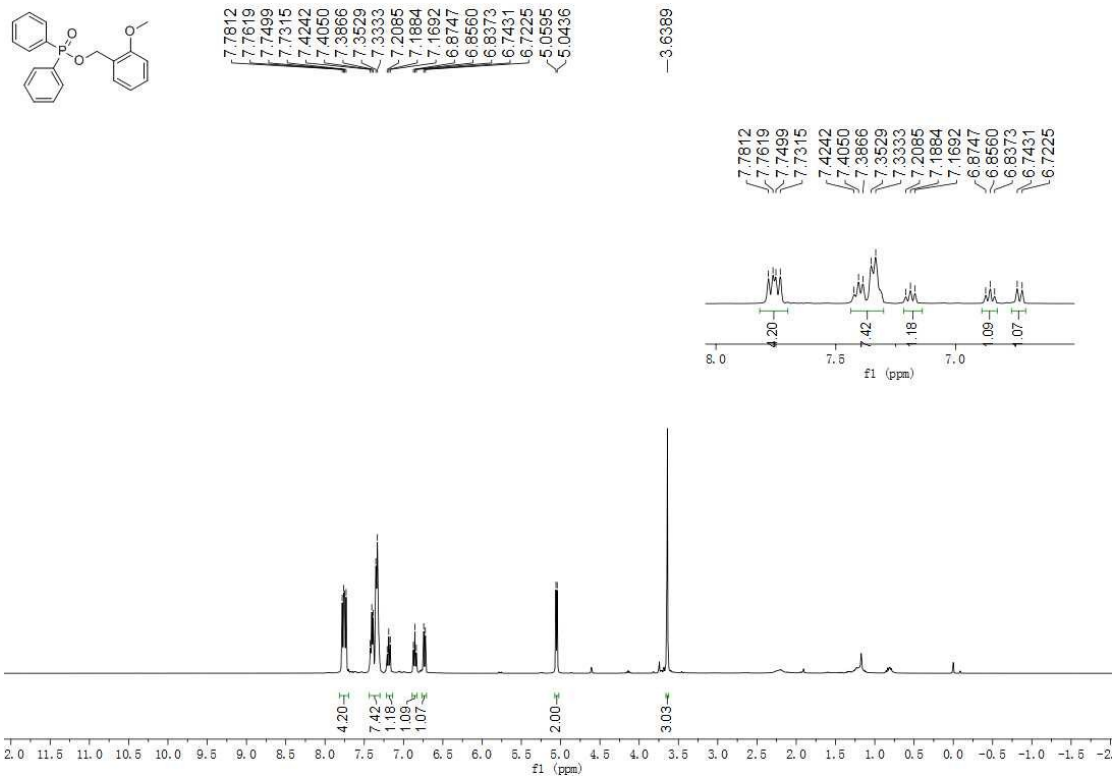
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3k**



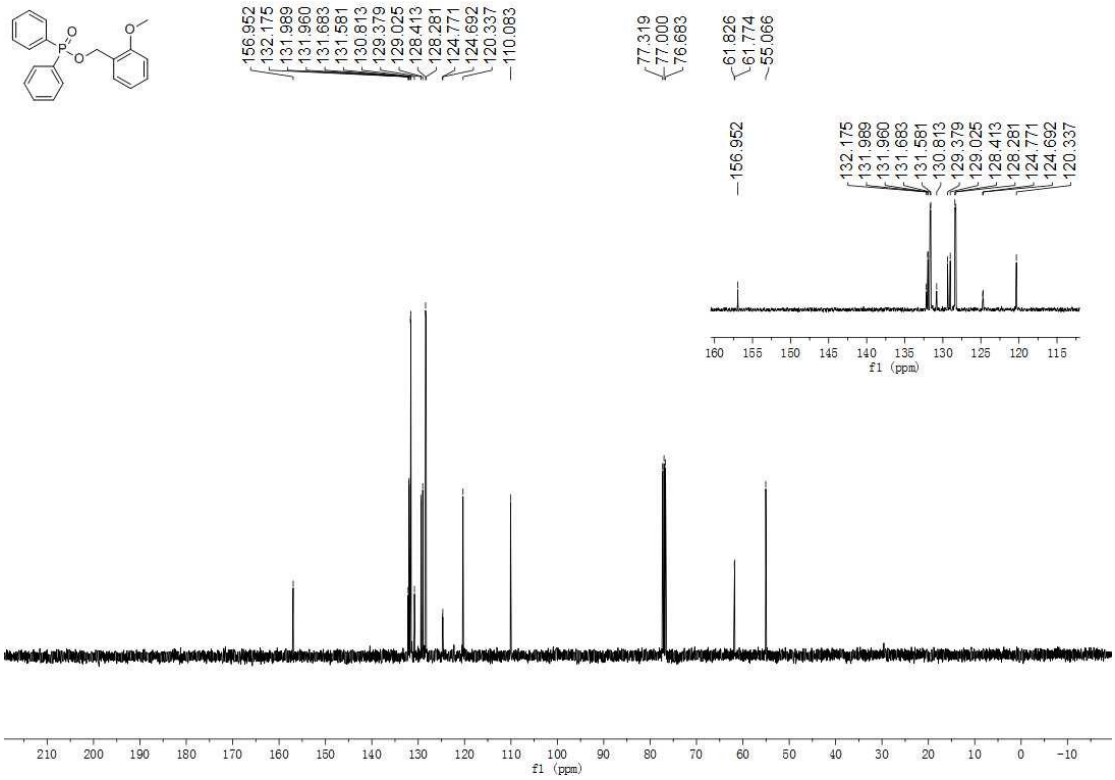
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3k**



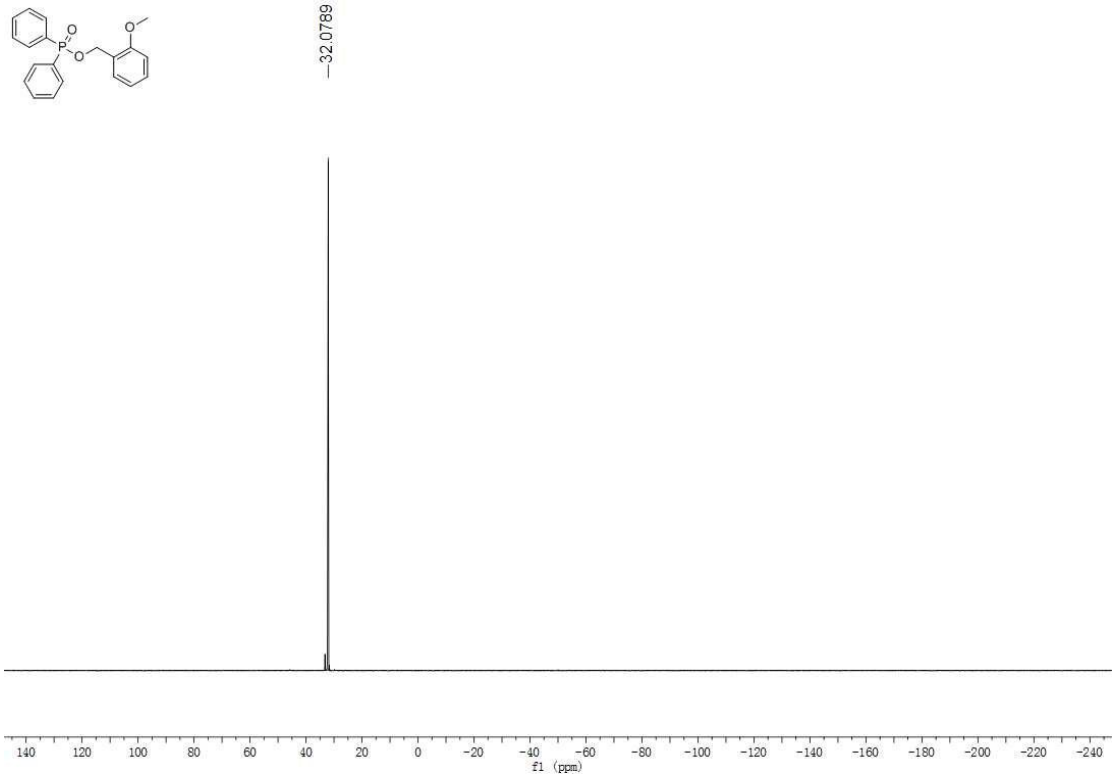
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3k**



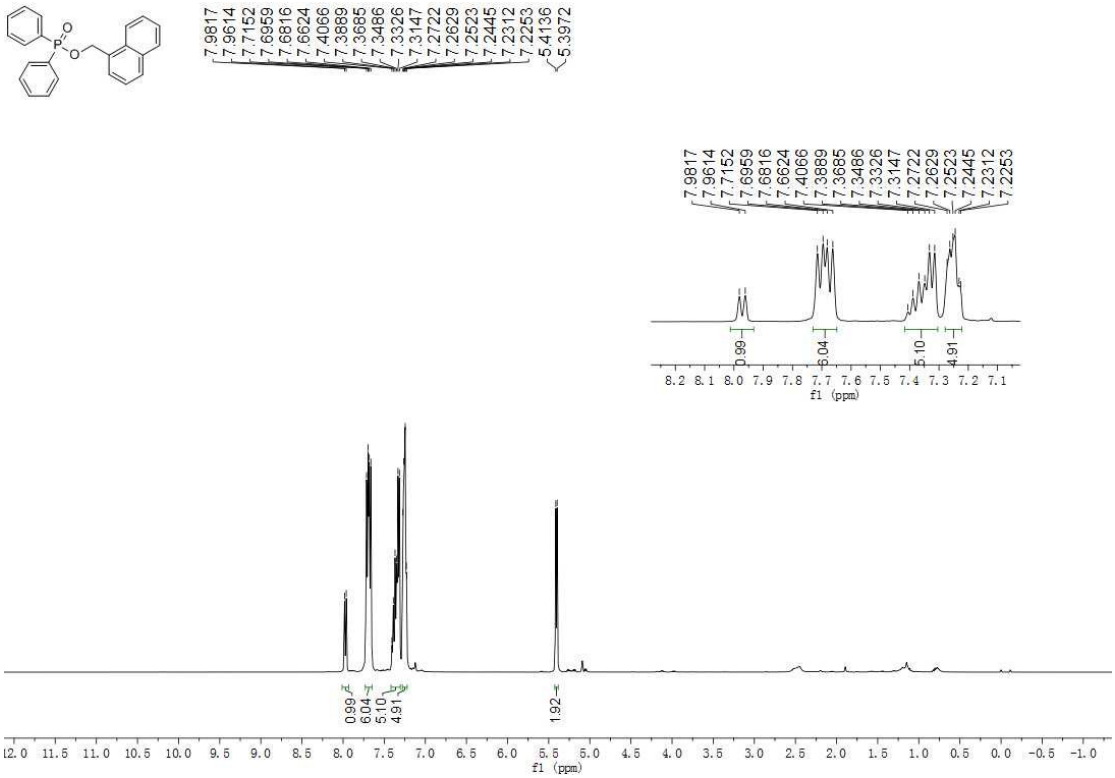
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3l**



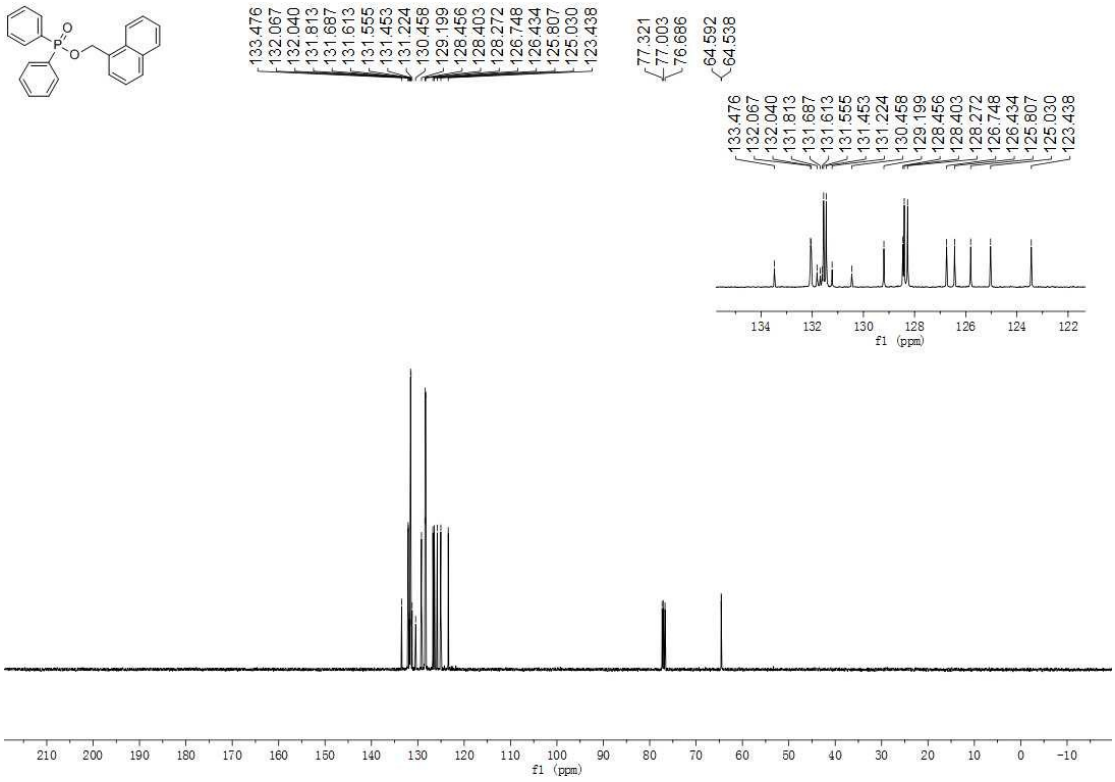
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3l**



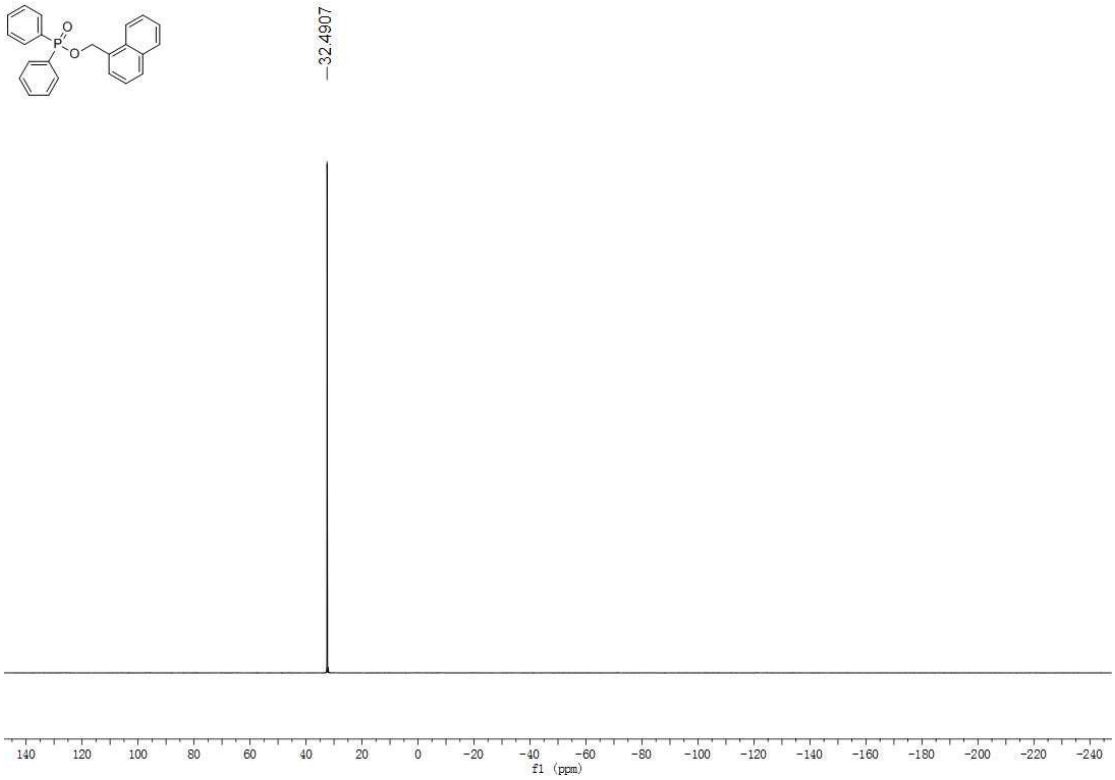
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3l**



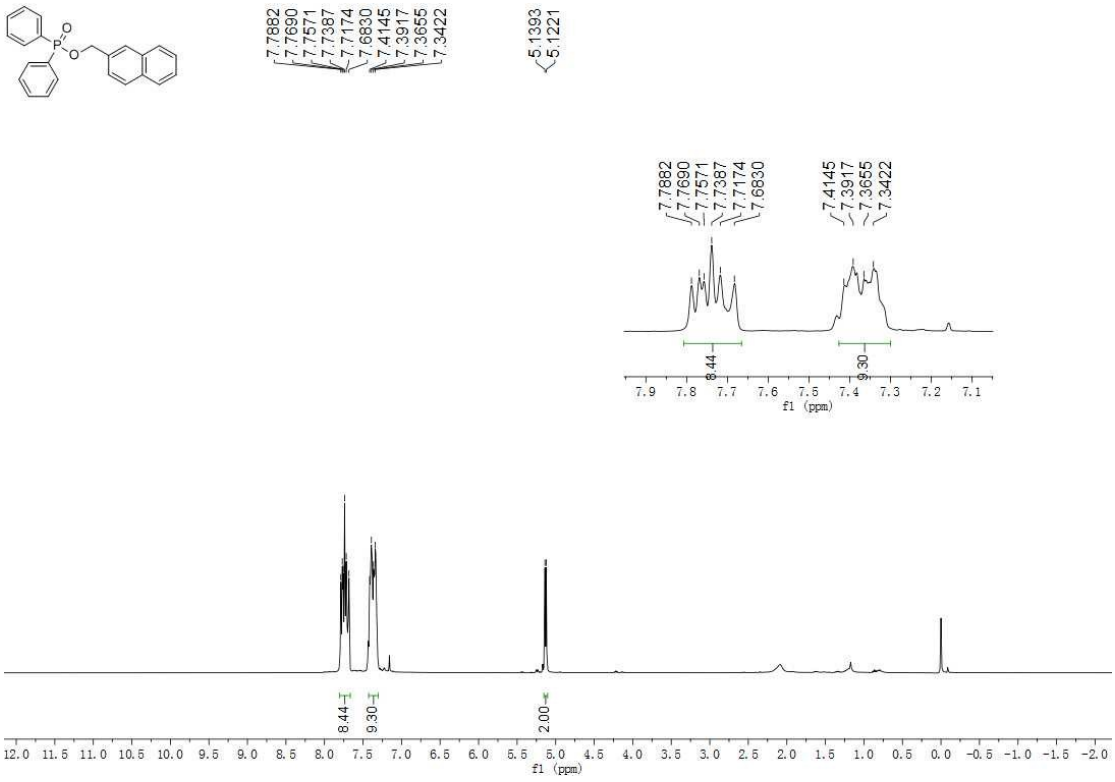
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3m**



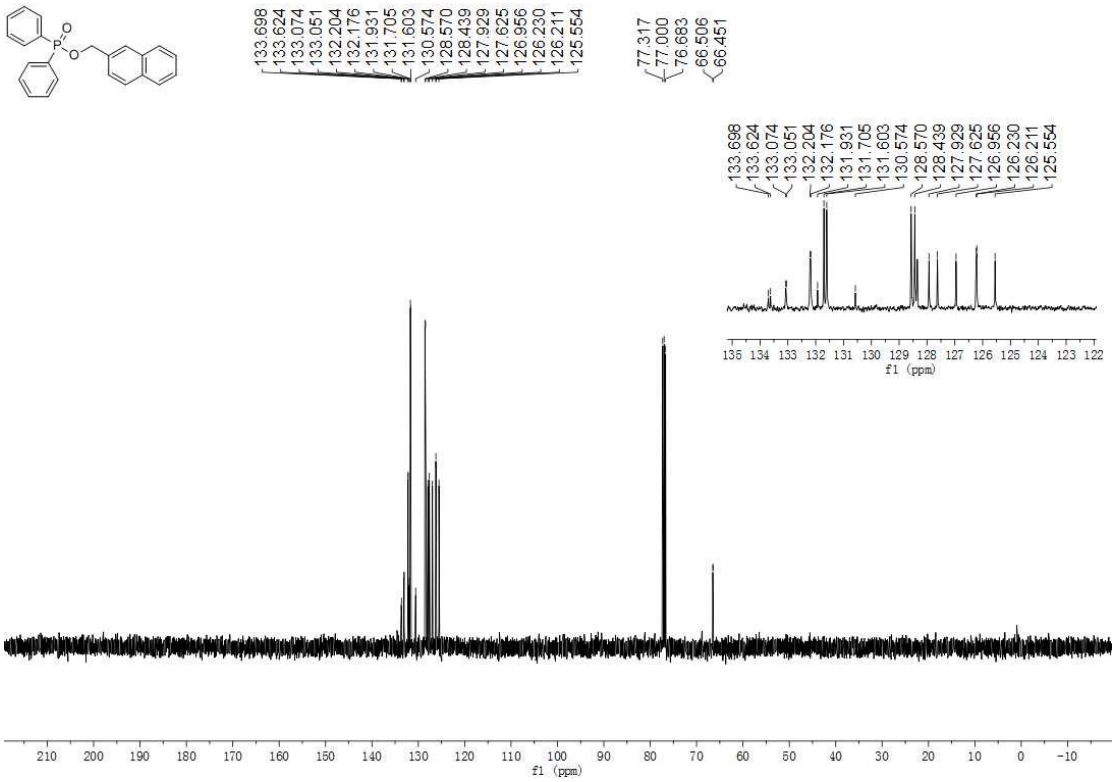
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3m**



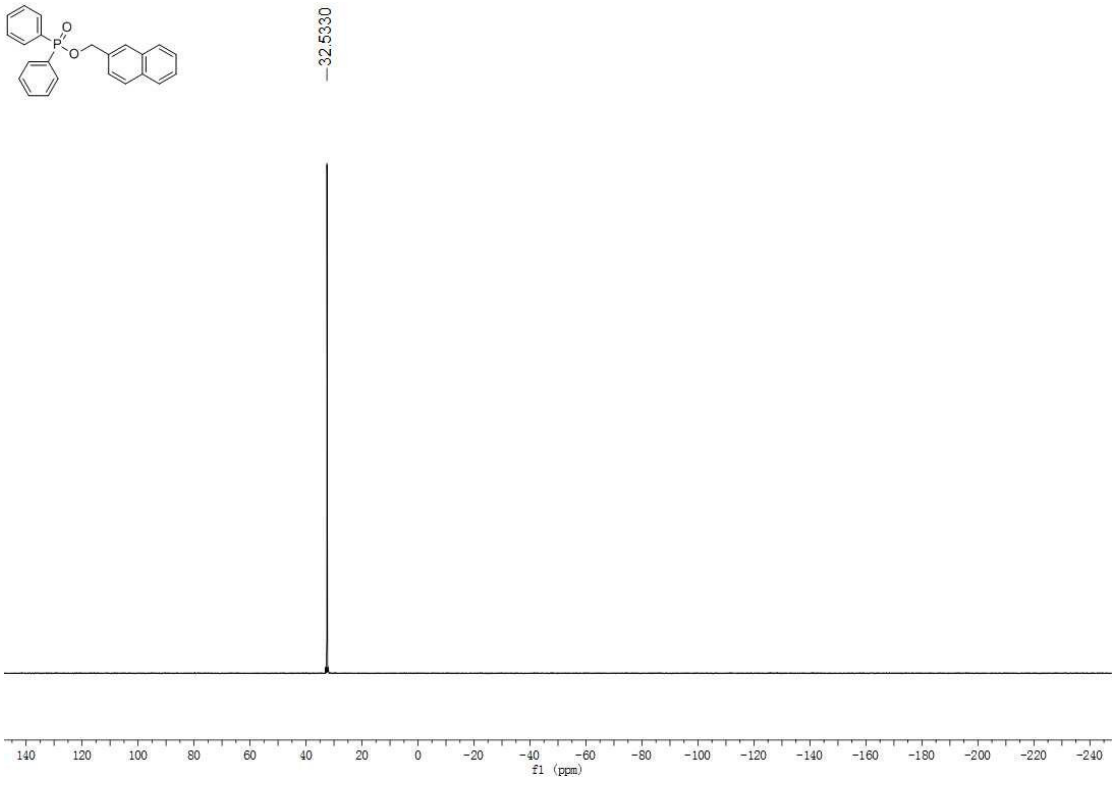
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3m**



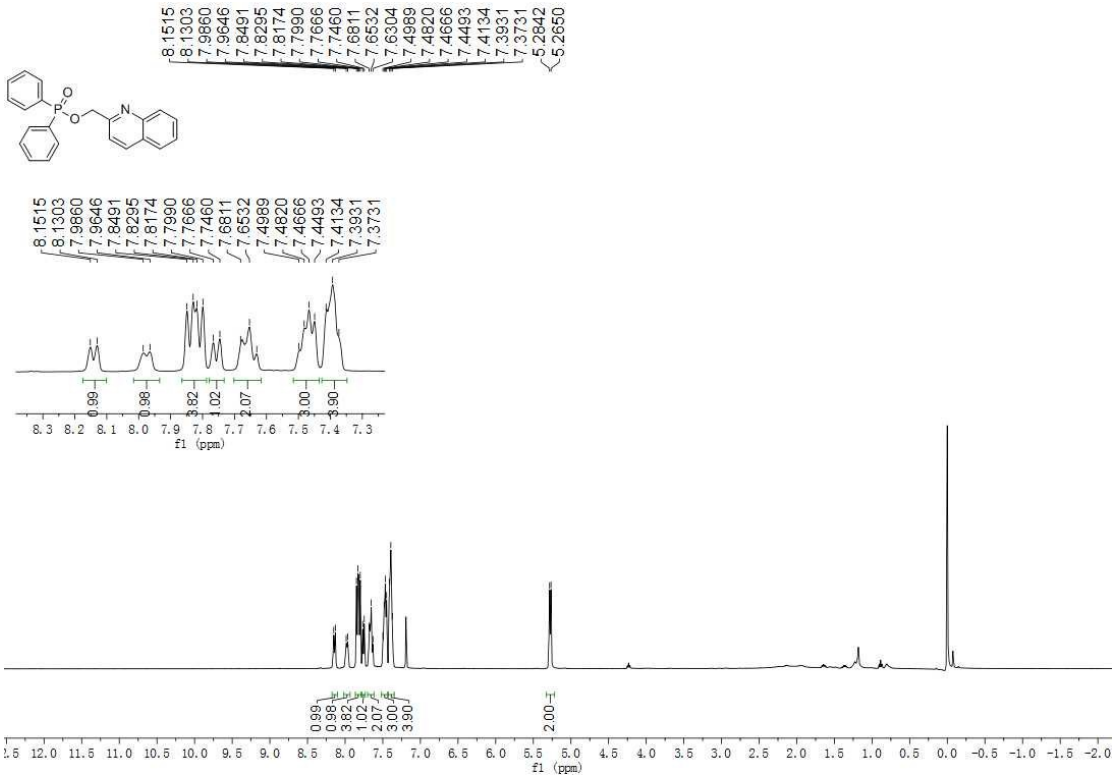
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3n**



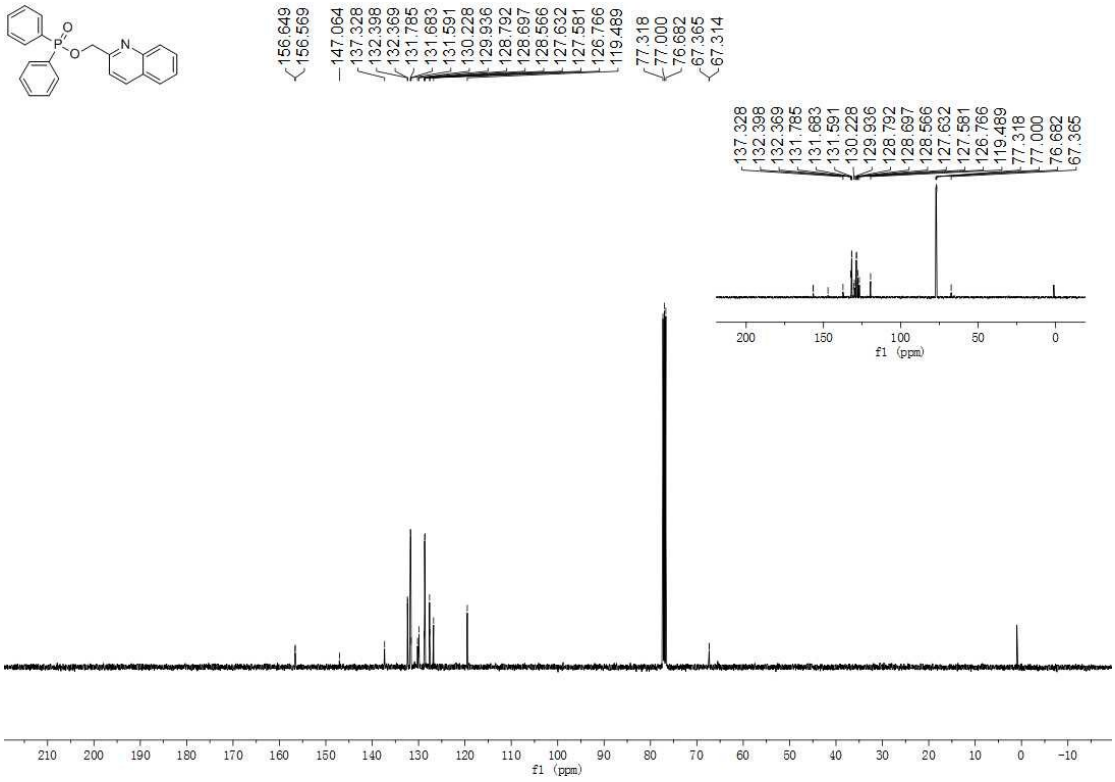
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3n**



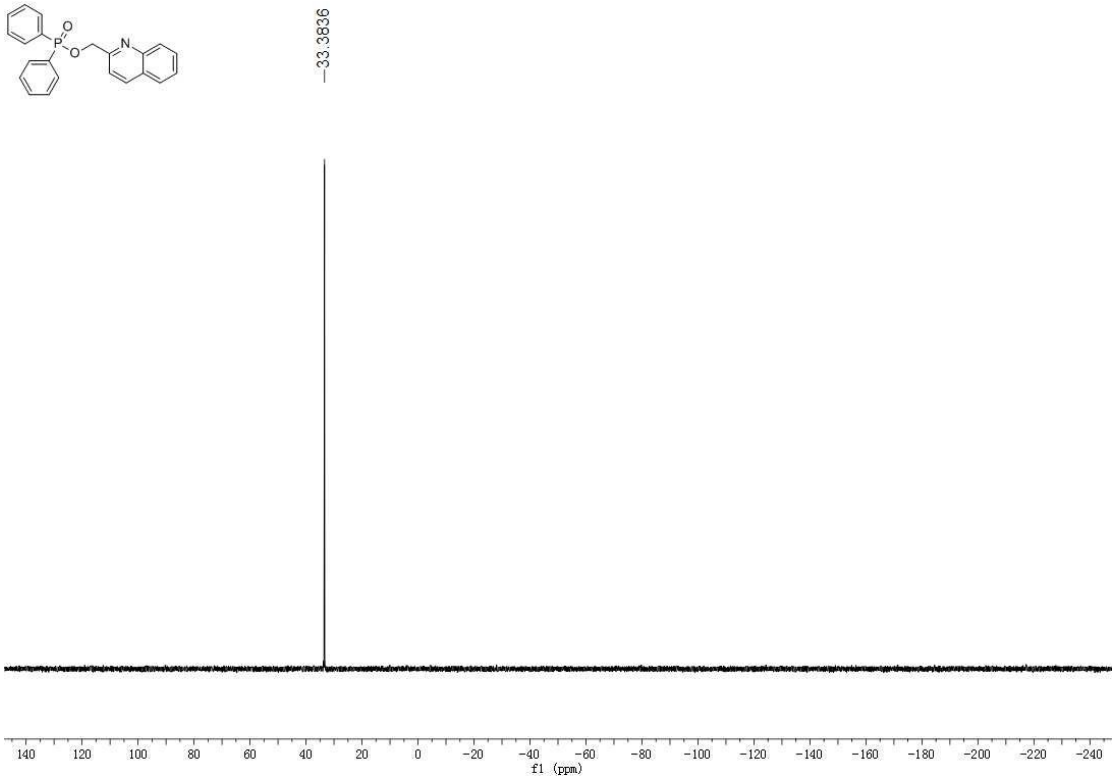
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3n**



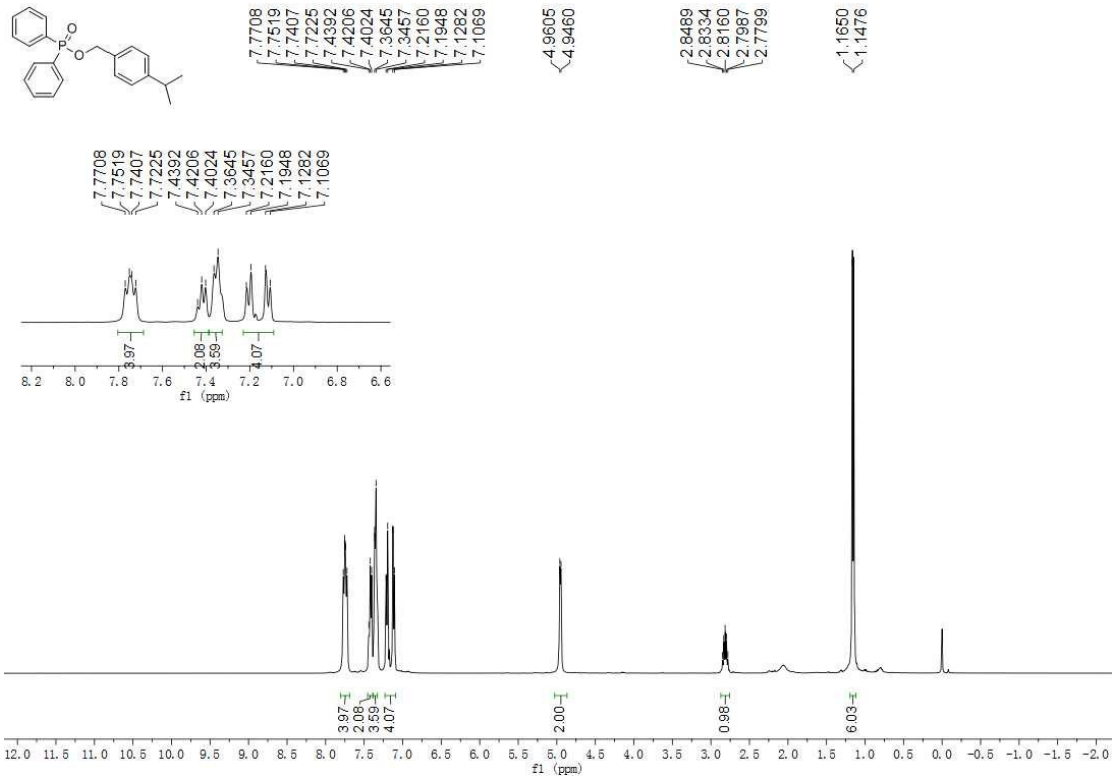
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3o**



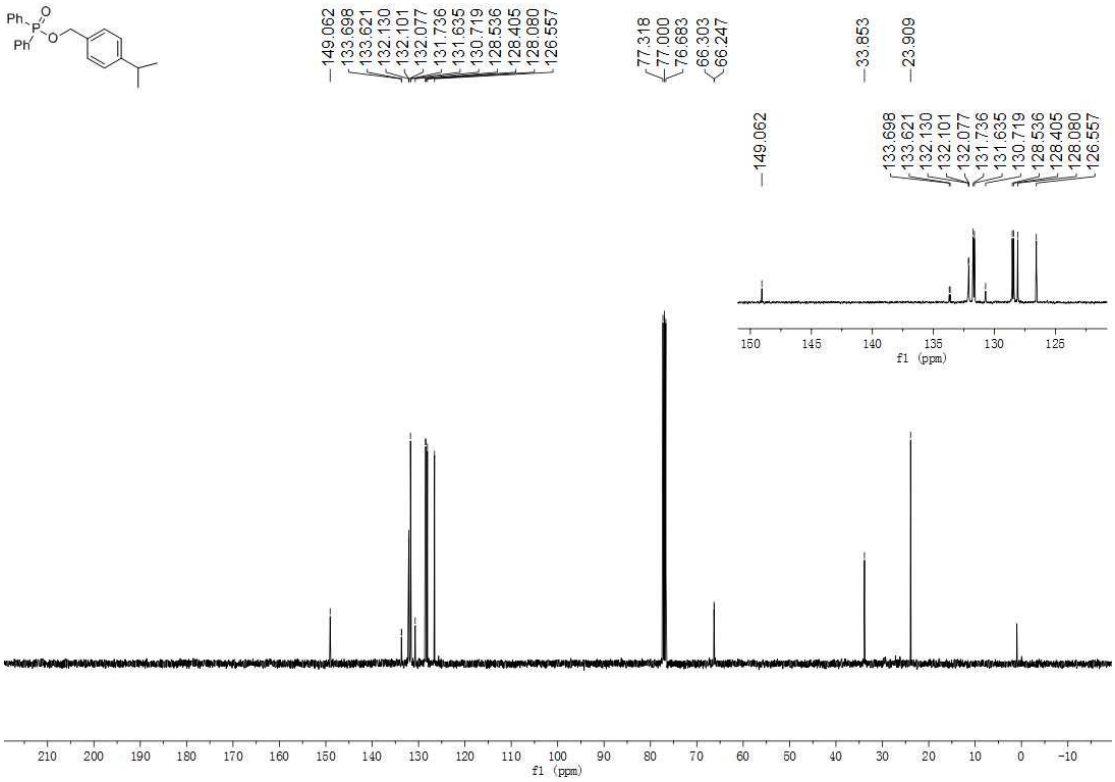
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3o** [3]



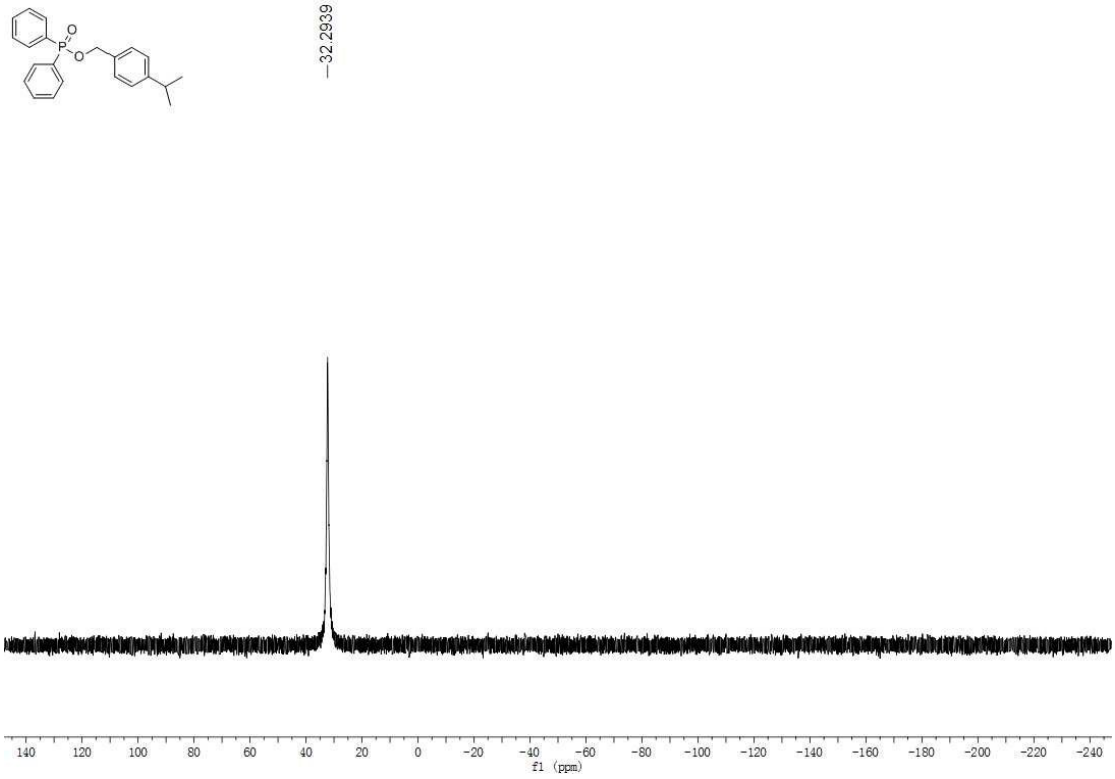
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3o**



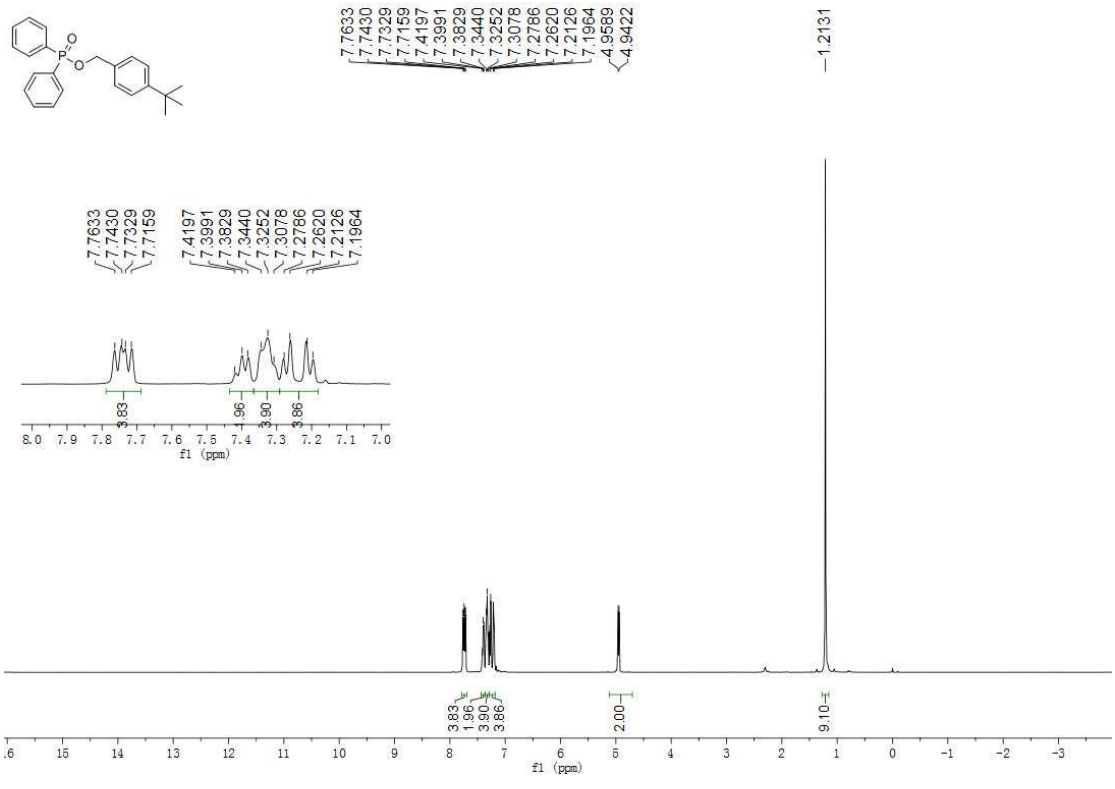
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3p**



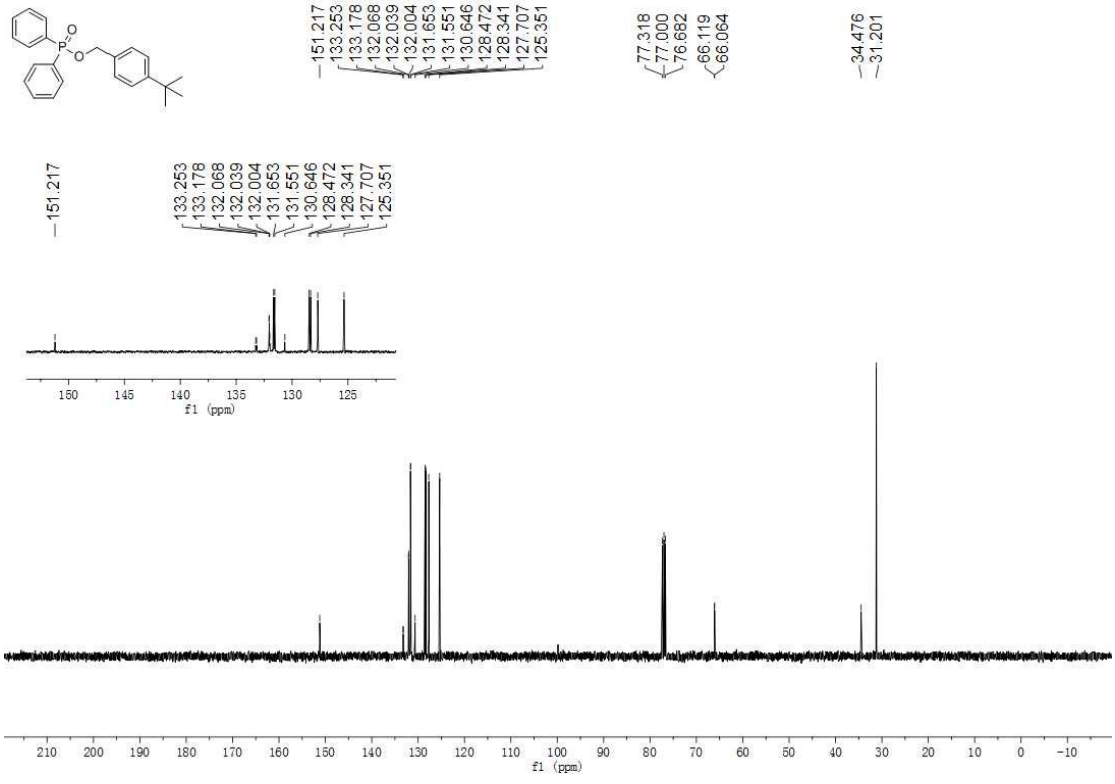
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3p**



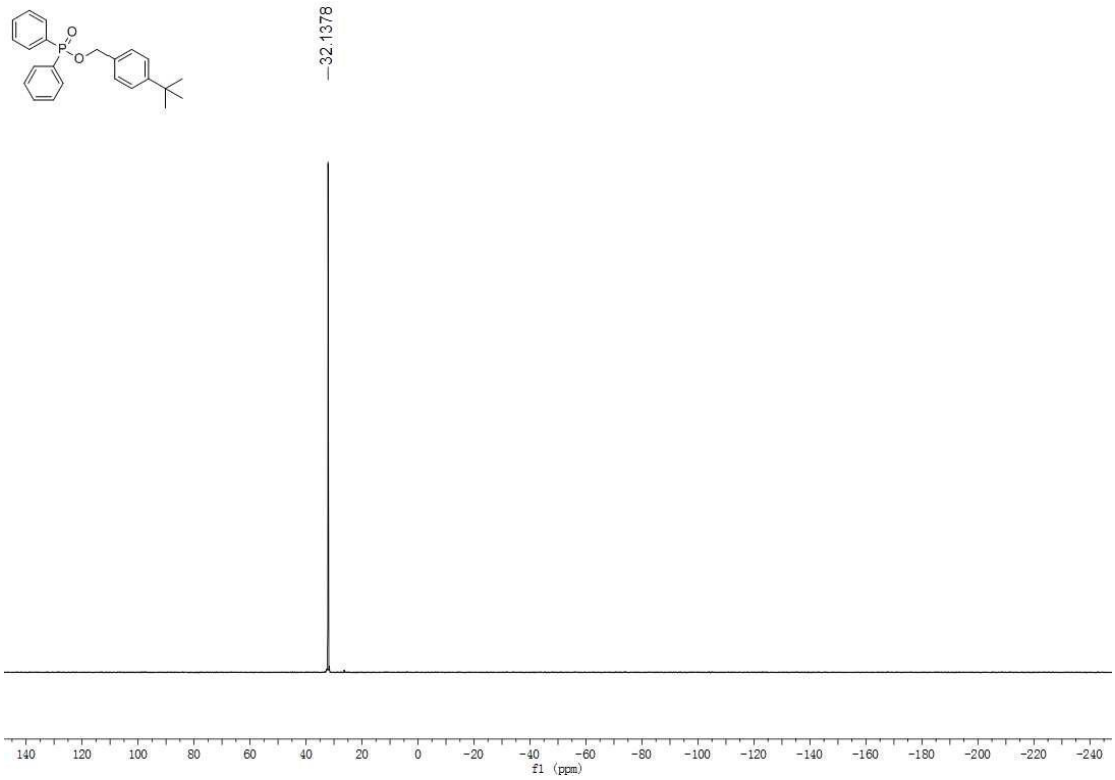
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3p**



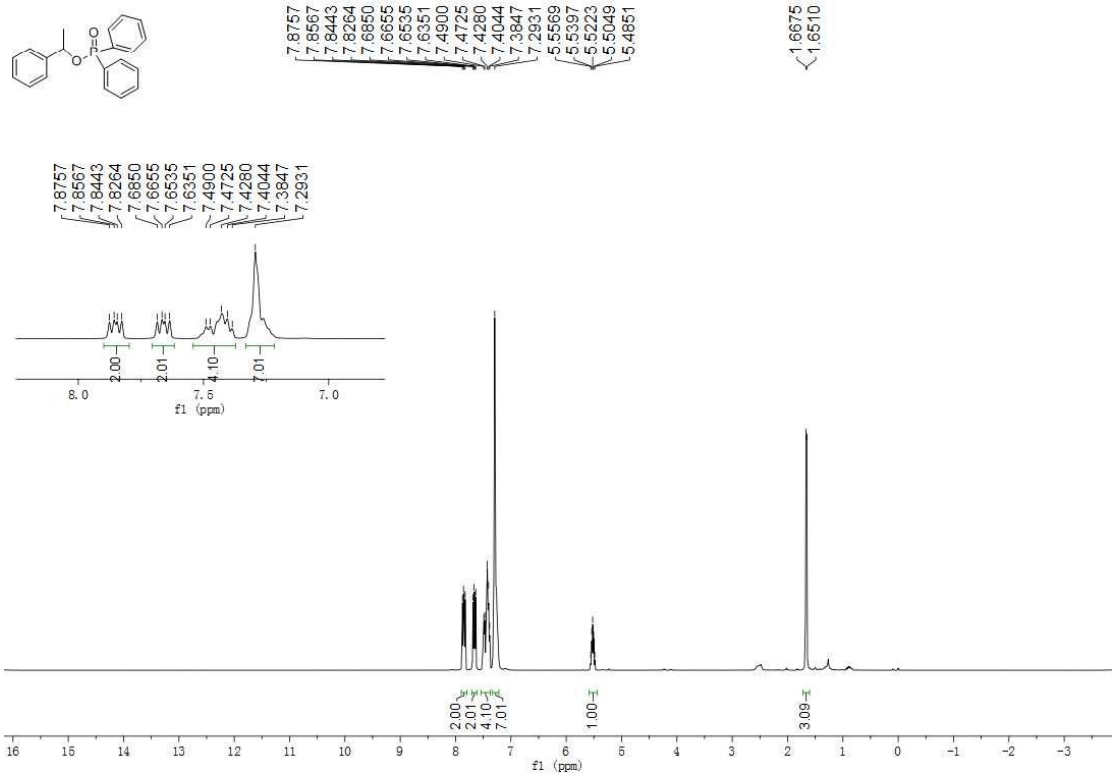
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3q**



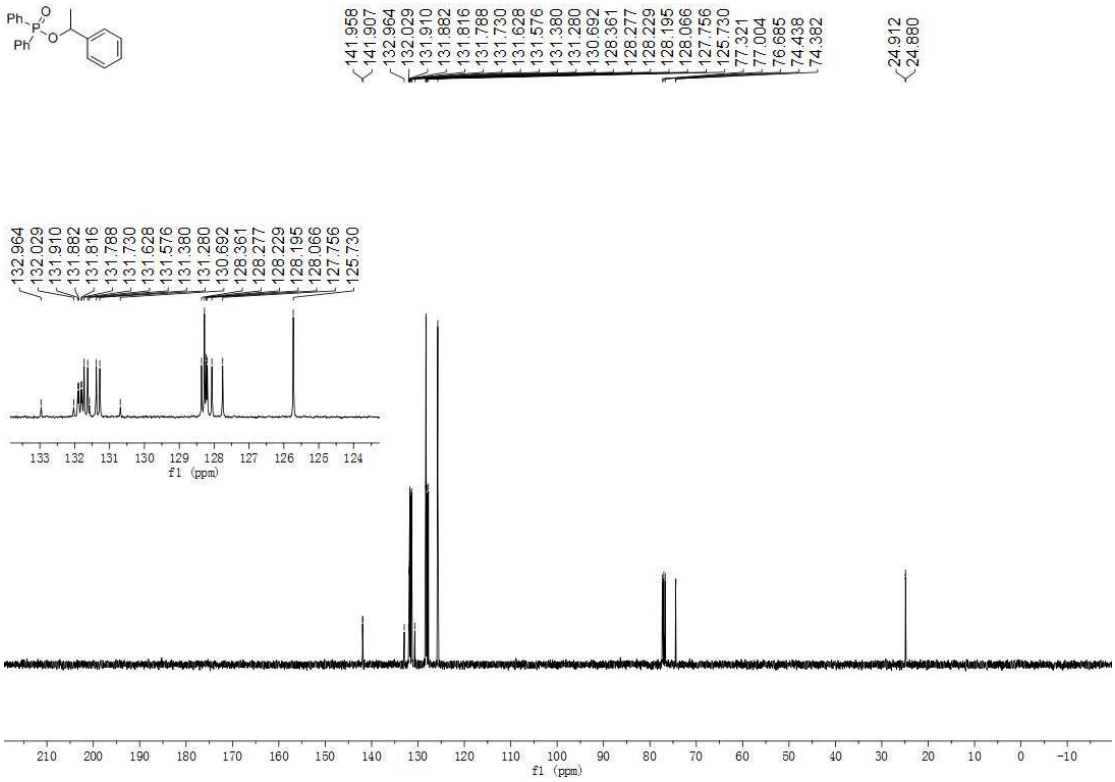
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3q**



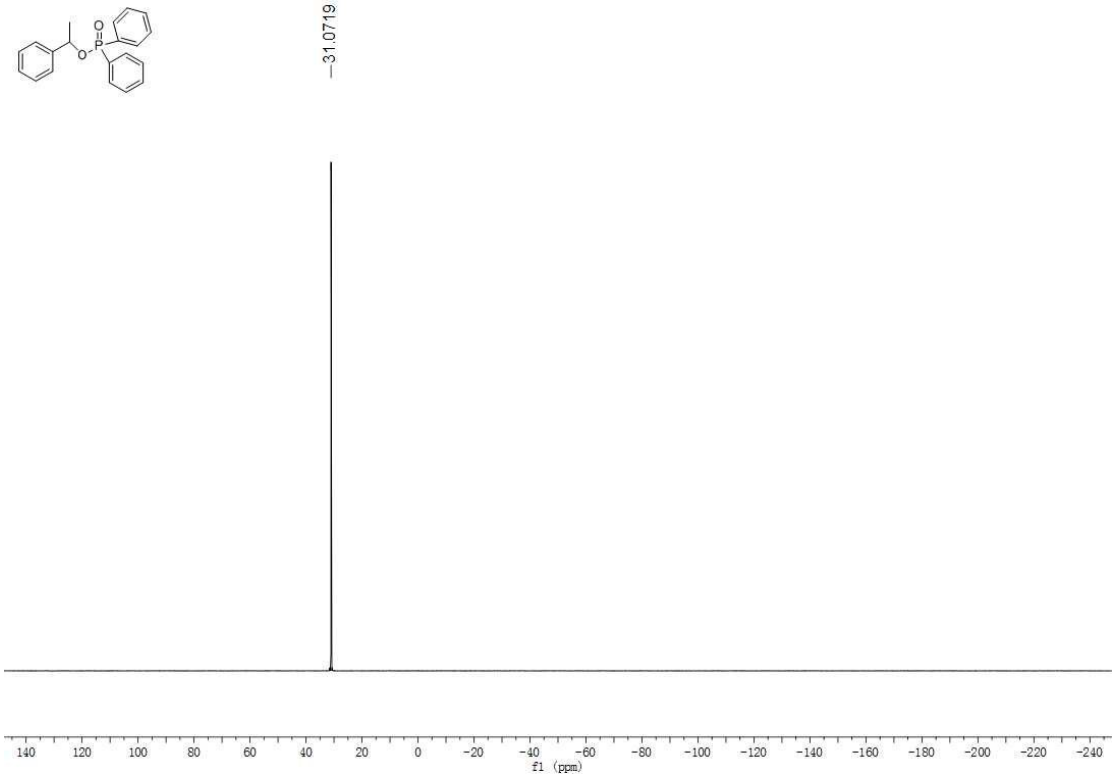
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3q**



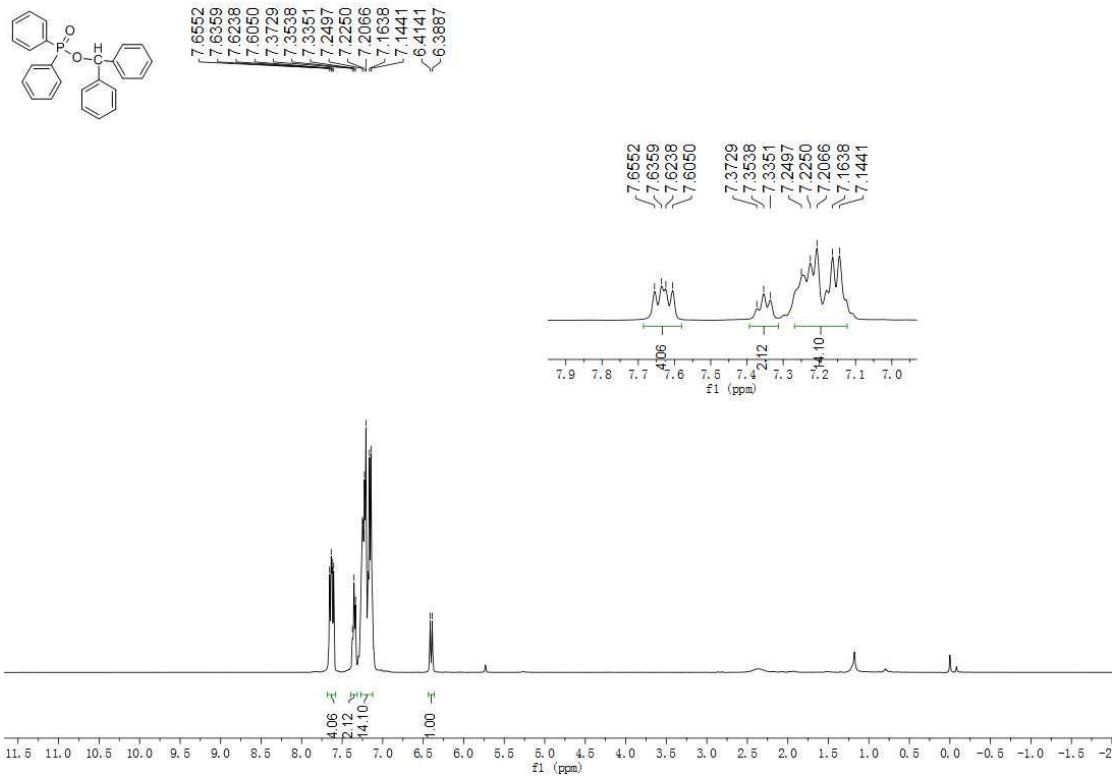
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3r**



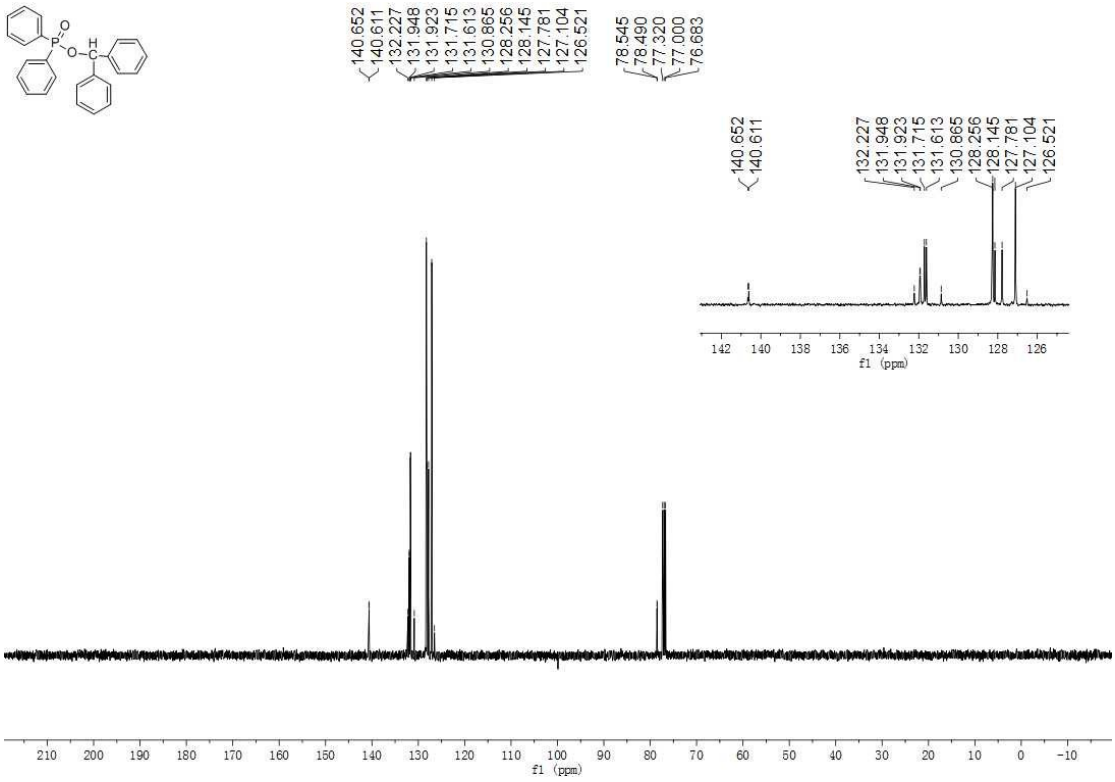
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3r** [3]



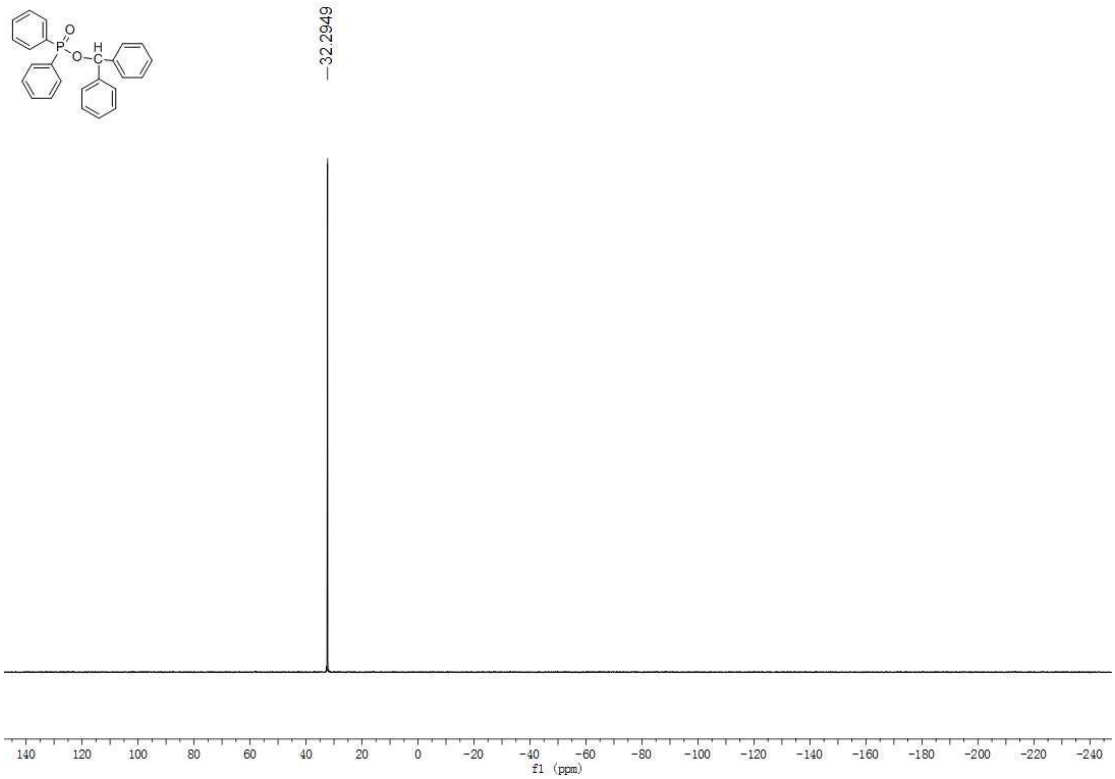
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3r**



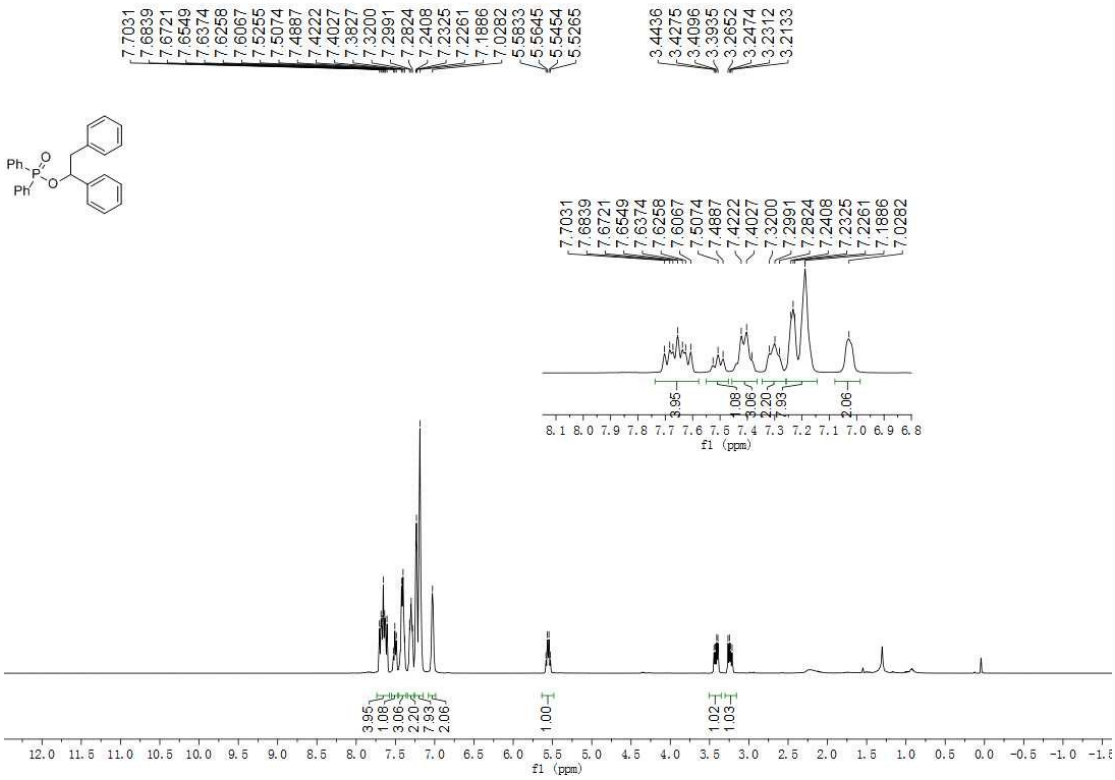
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3s**



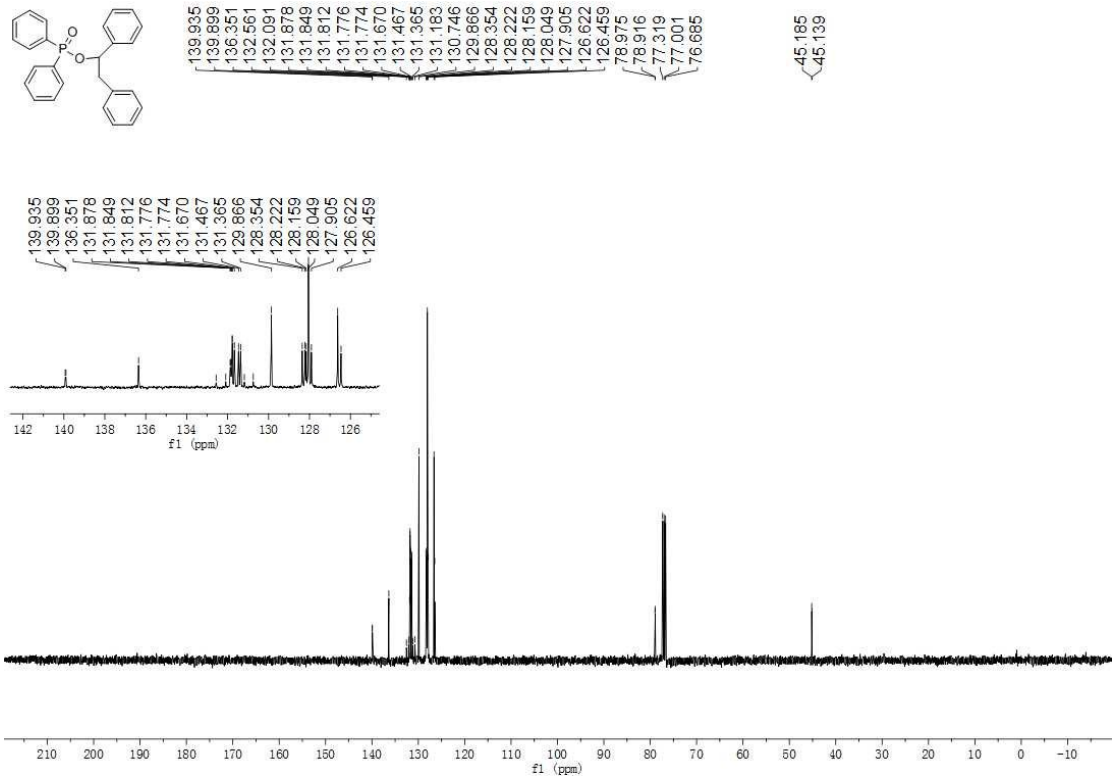
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3s**



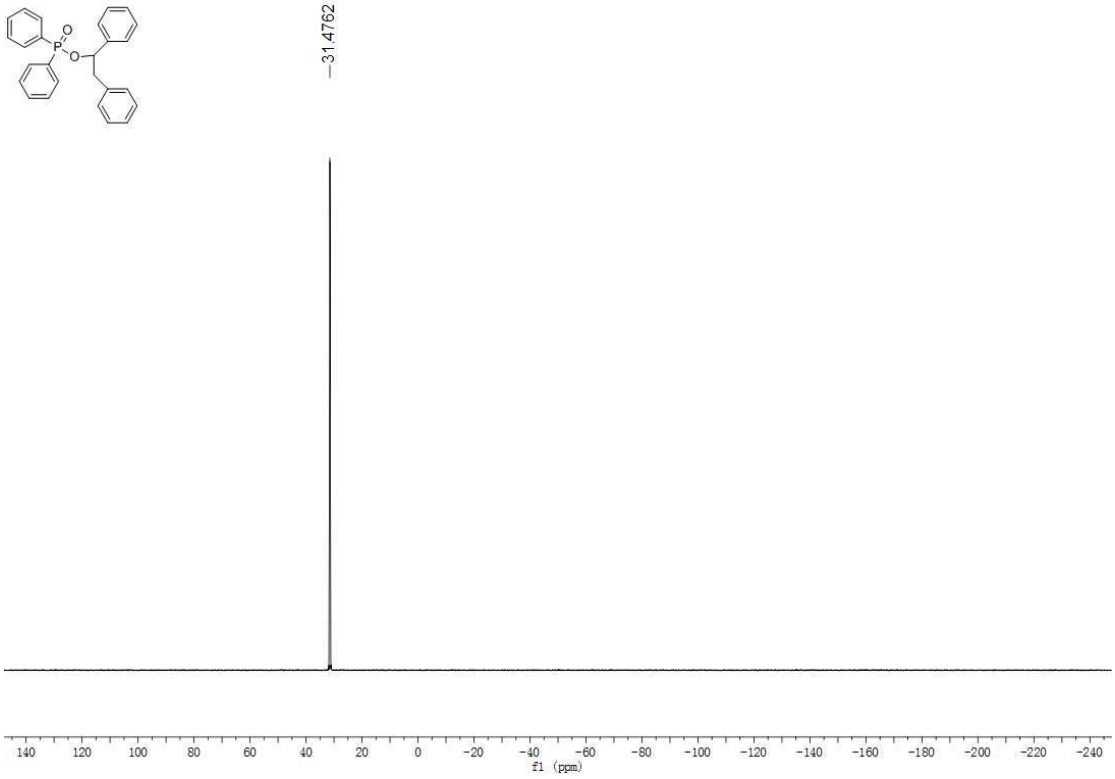
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3s**



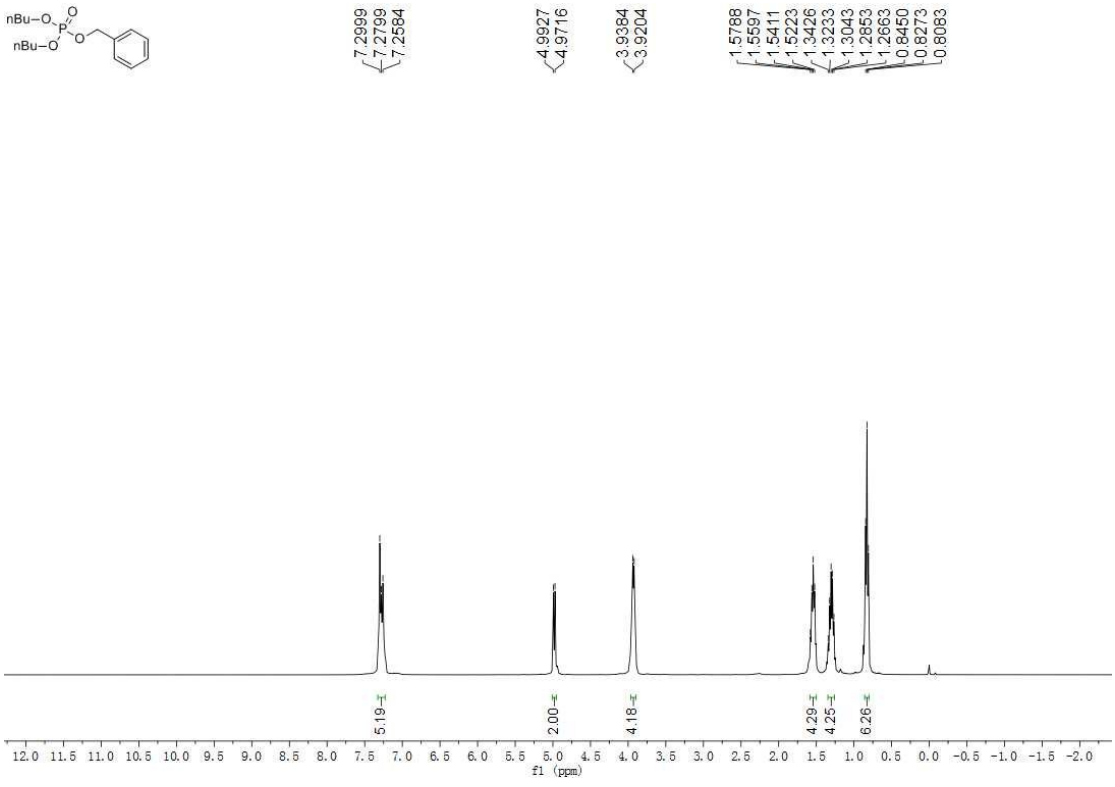
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3t**



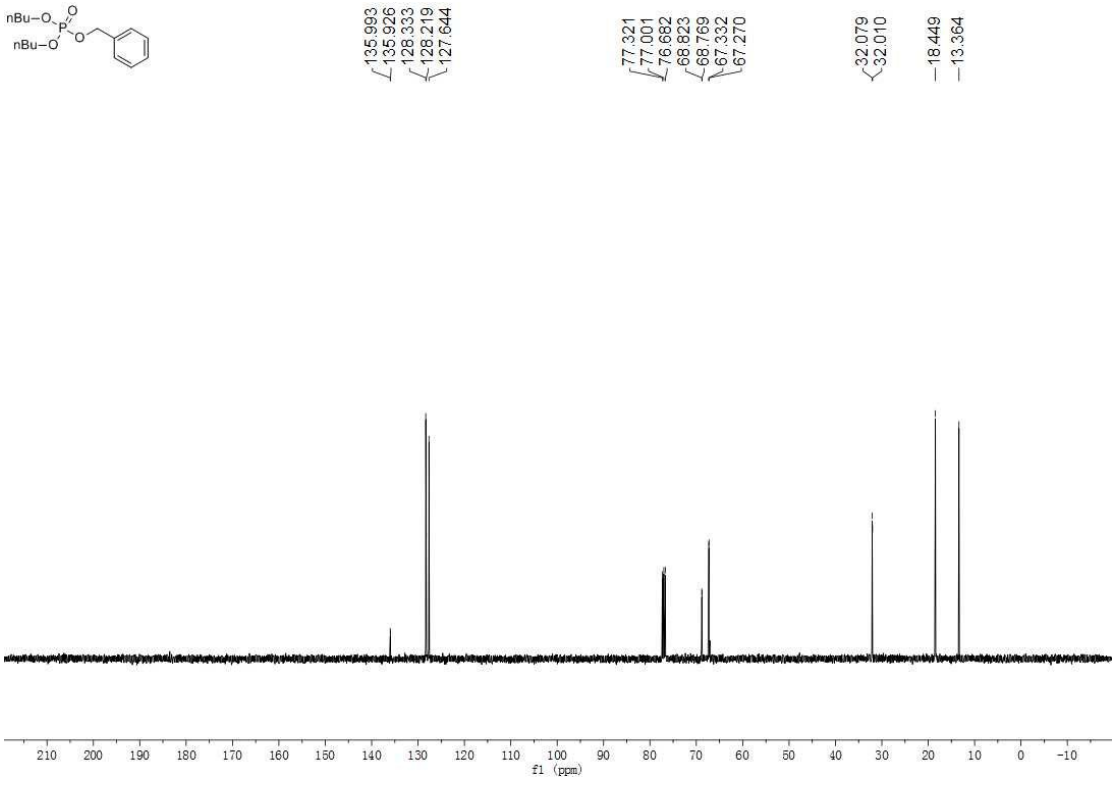
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **3t**



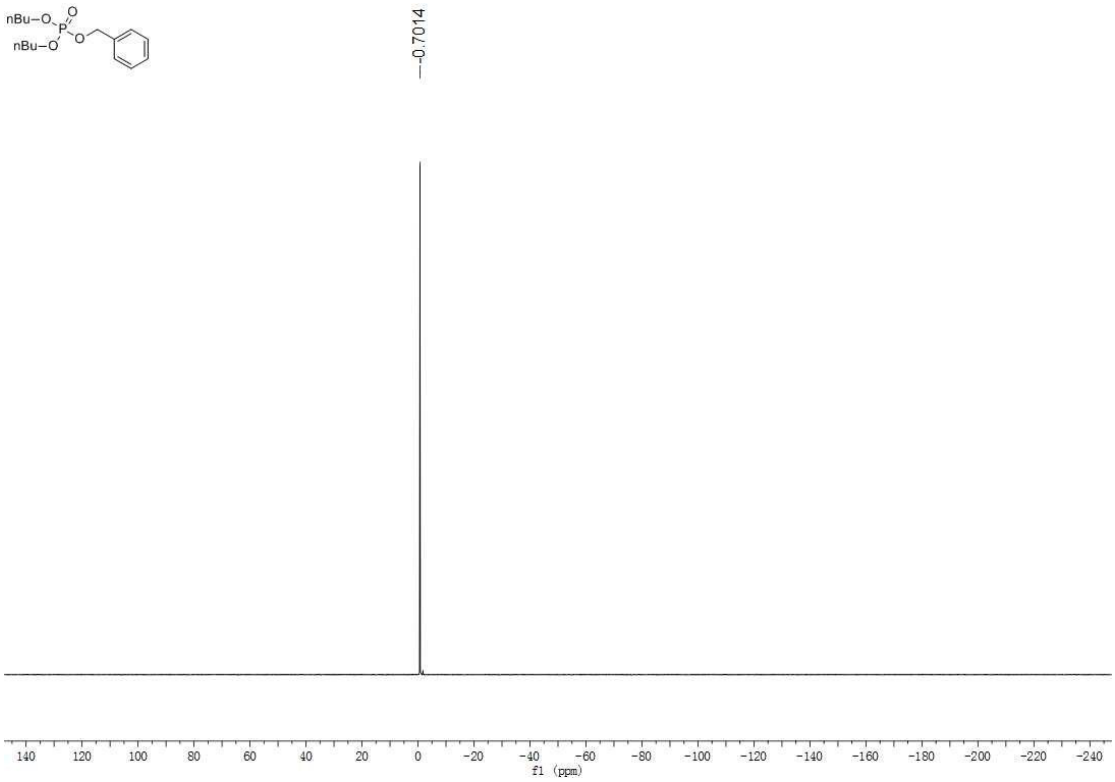
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **3t**



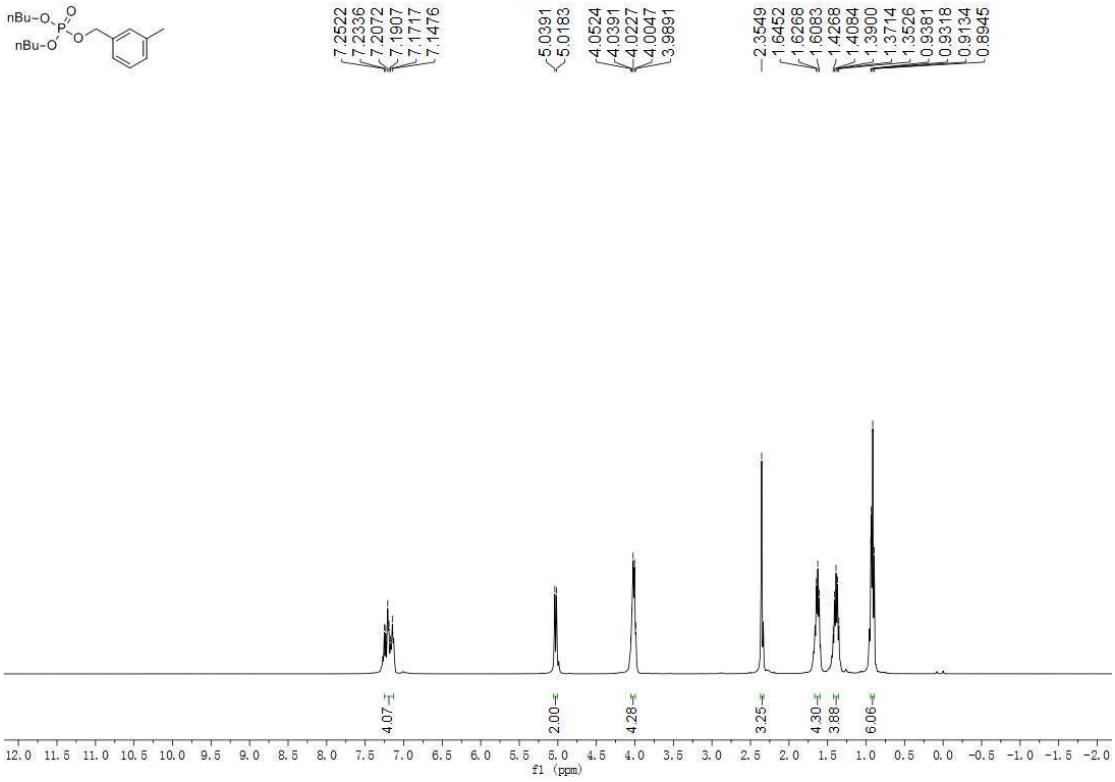
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4a** [3]



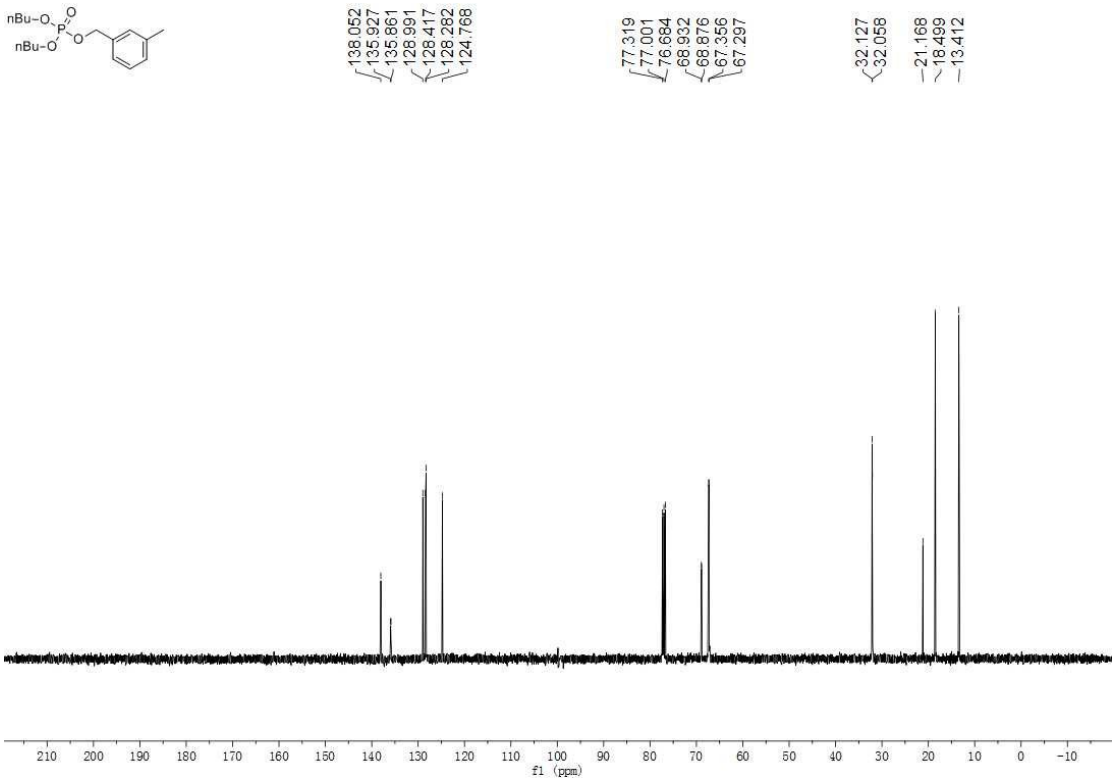
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4a** [3]



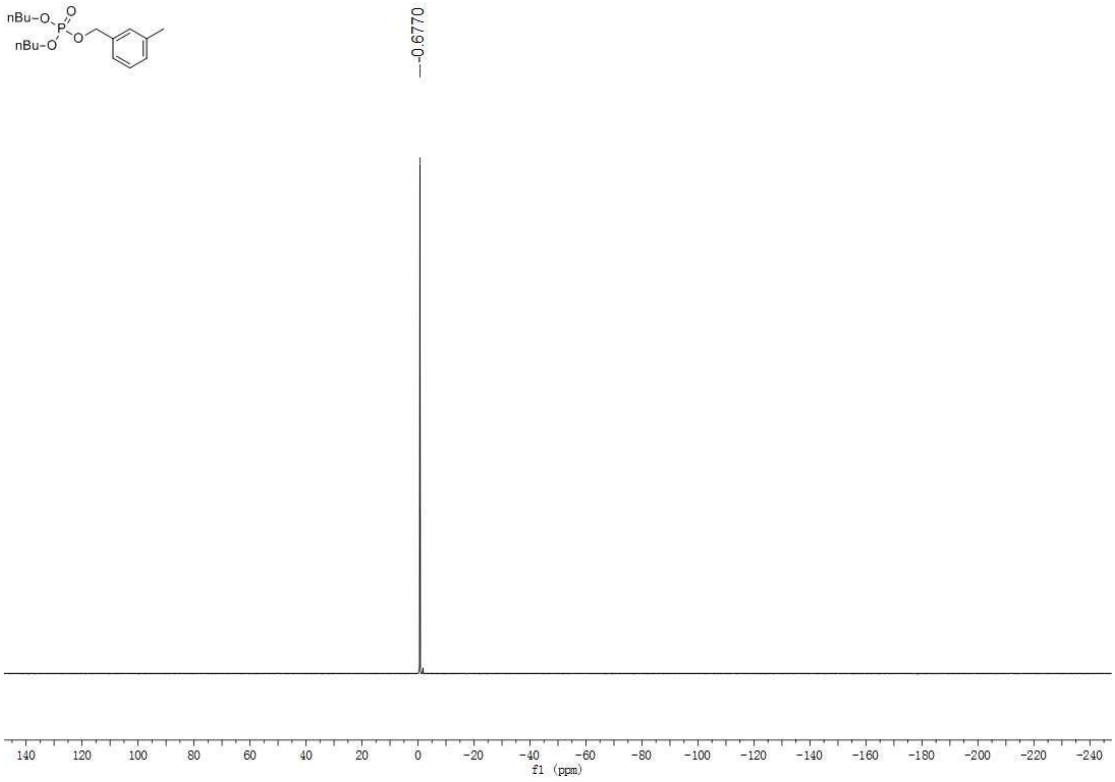
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4a**



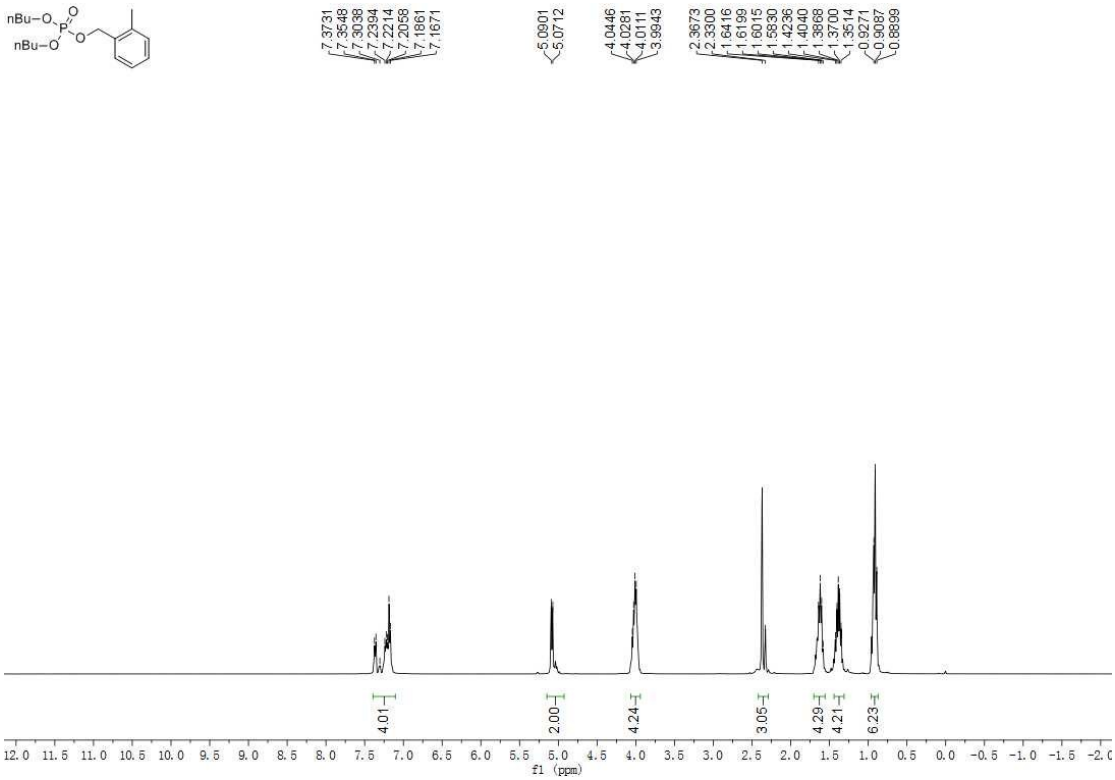
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4b**



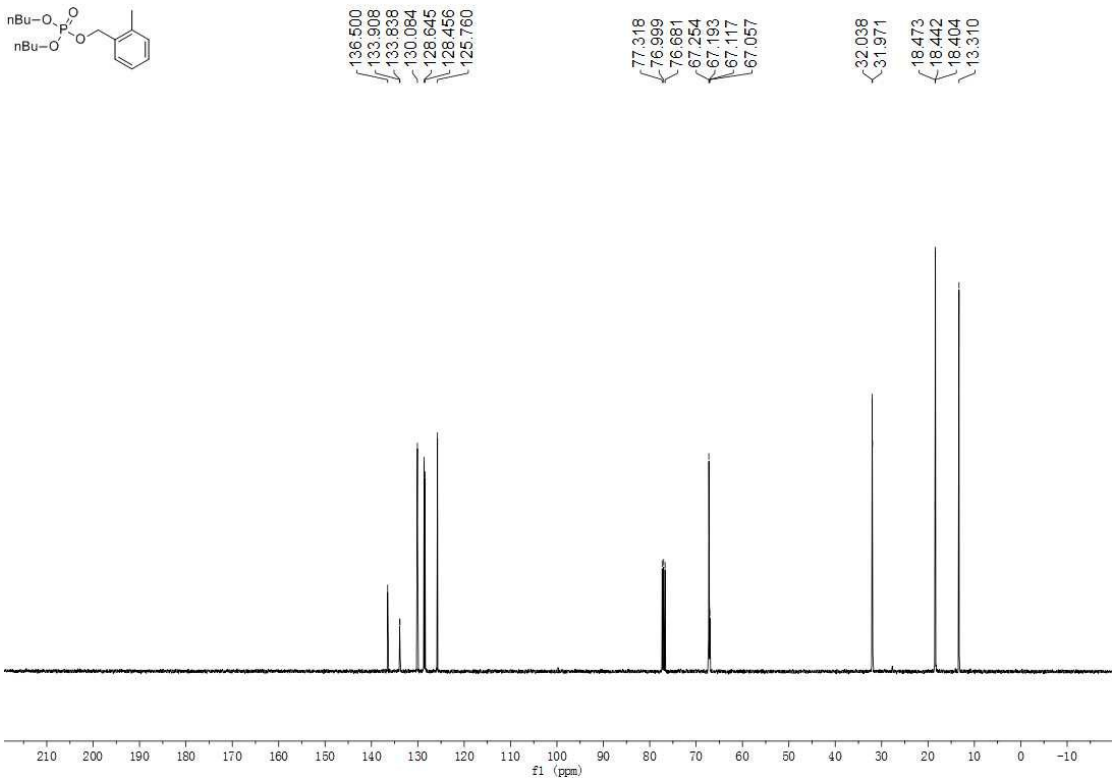
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4b**



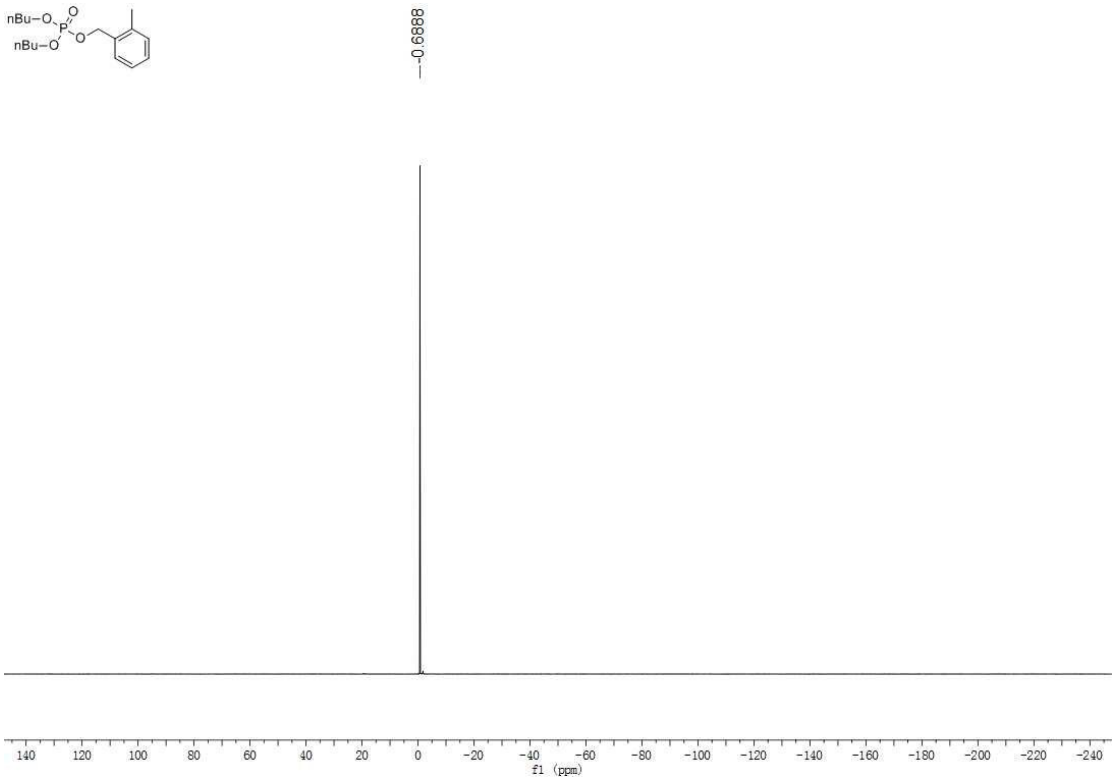
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4b**



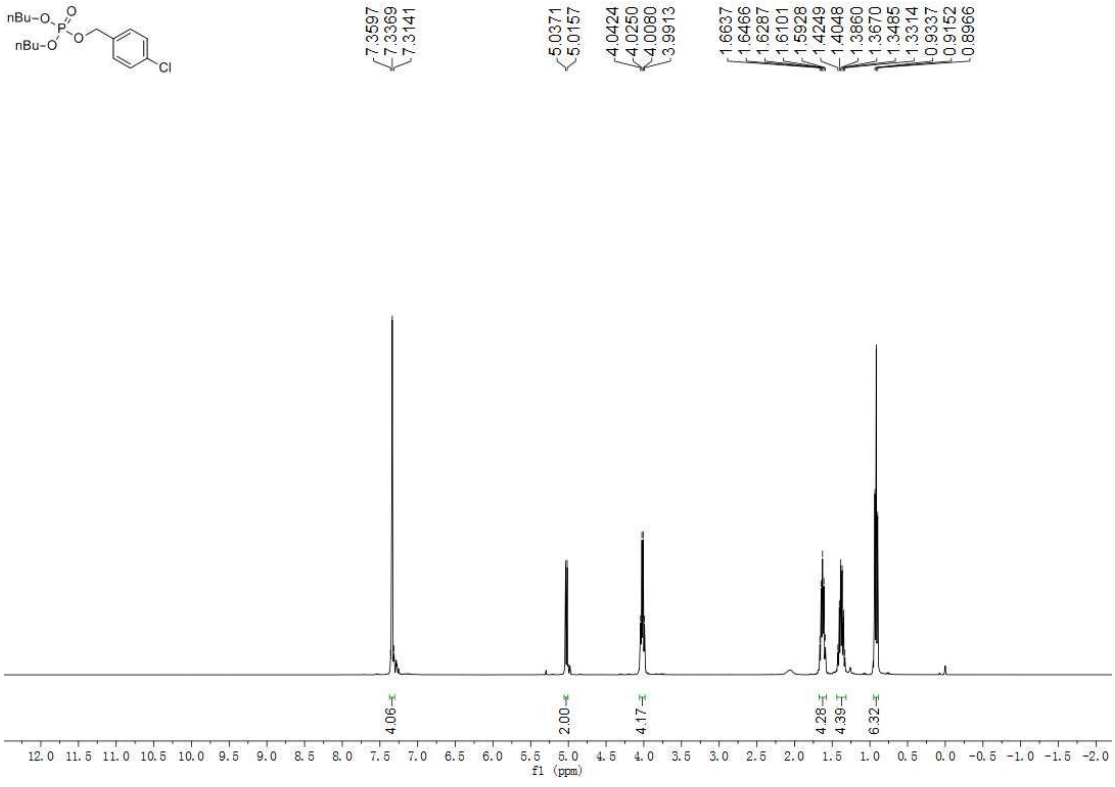
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4c**



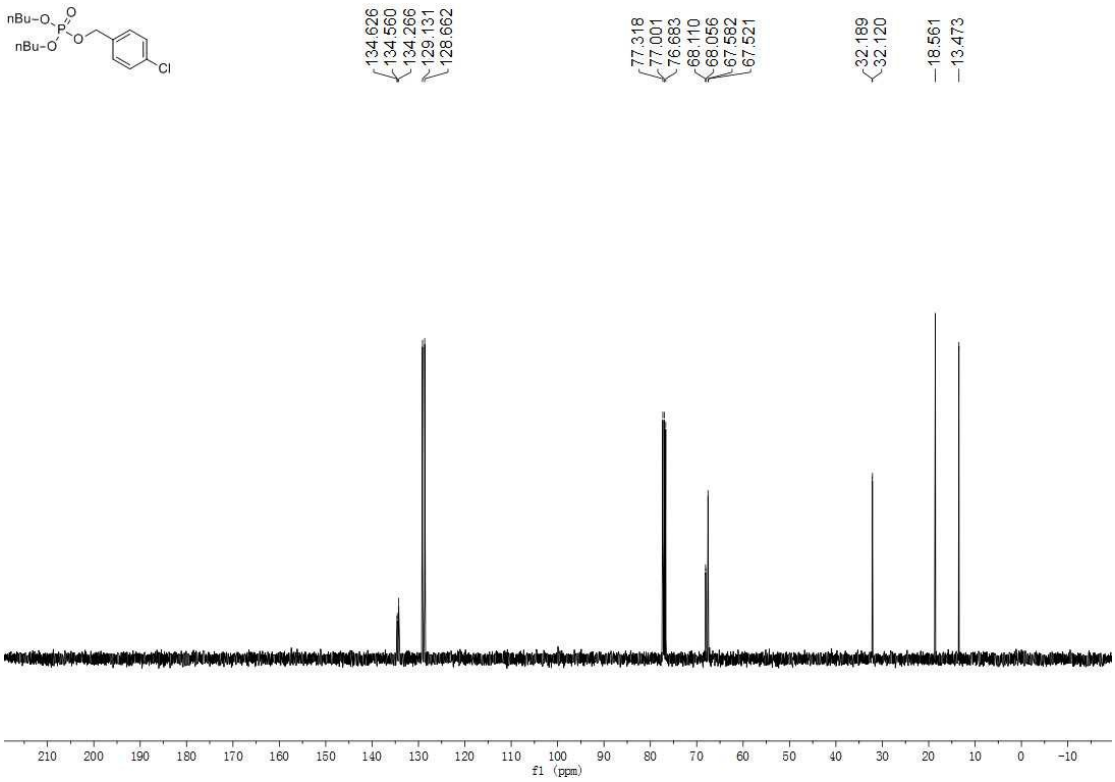
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4c**



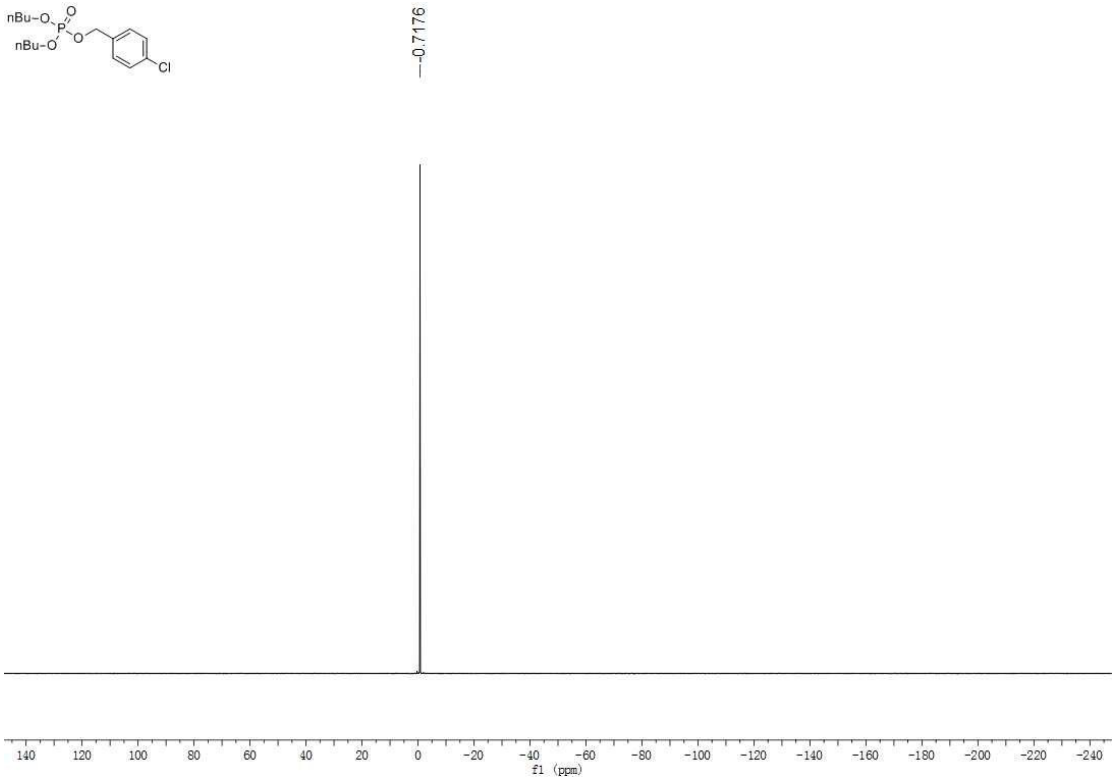
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4c**



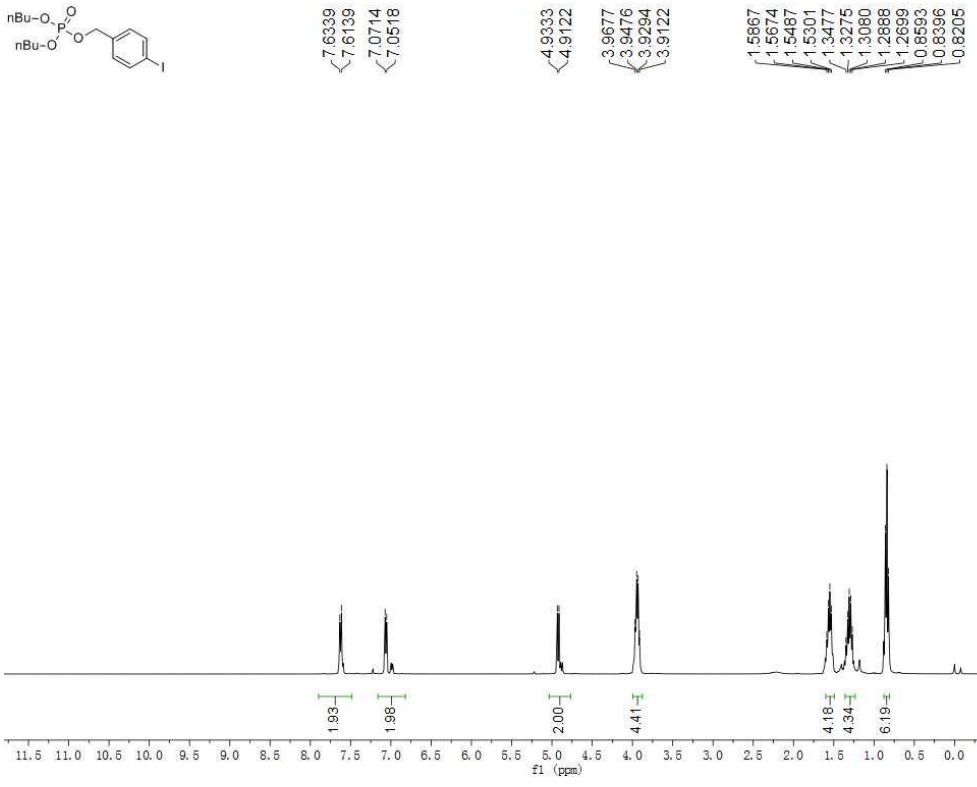
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4d**



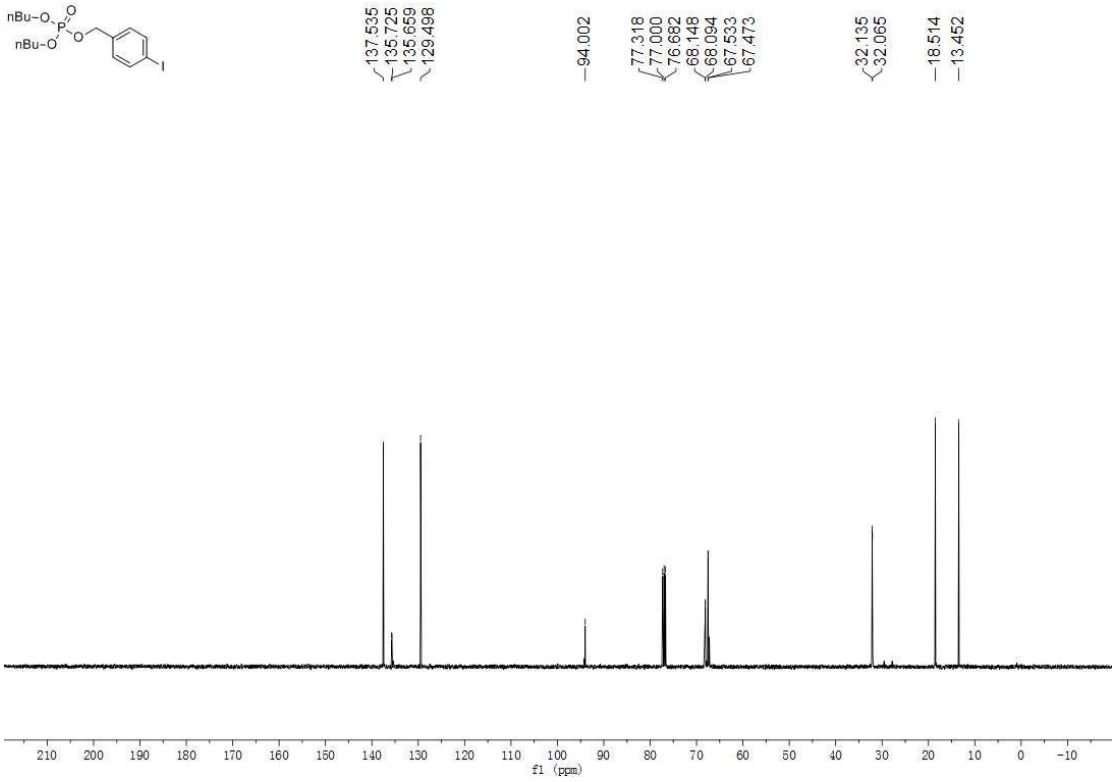
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4d**



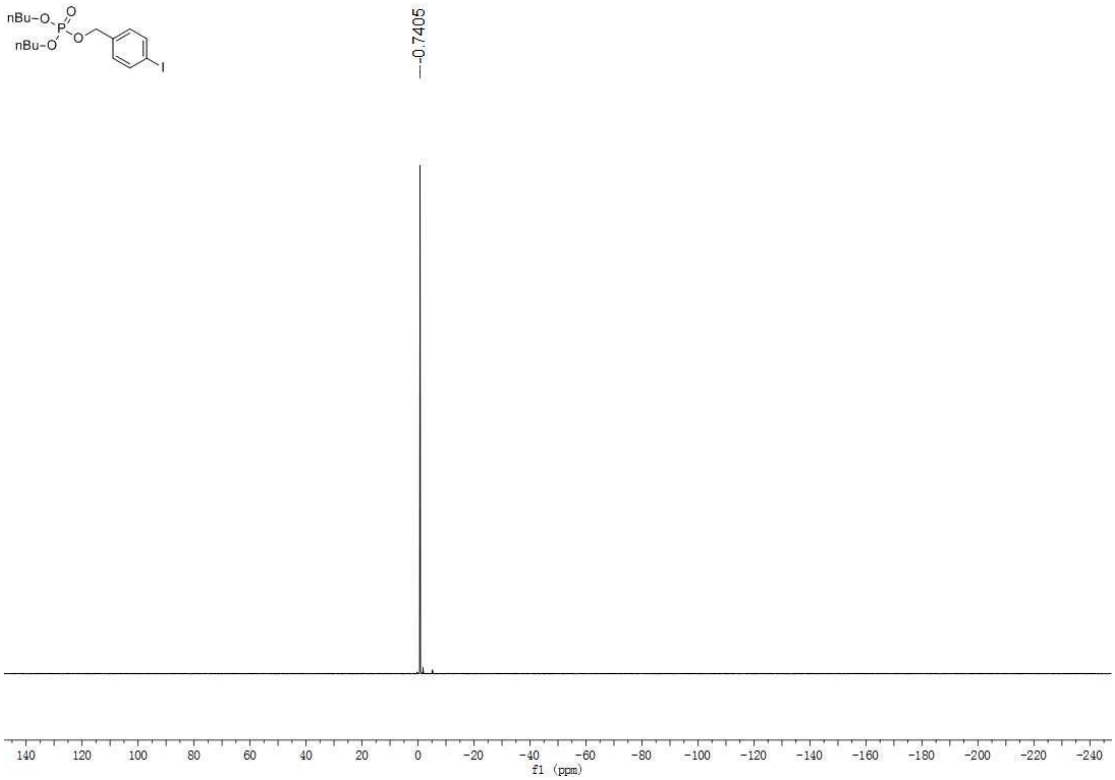
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4d**



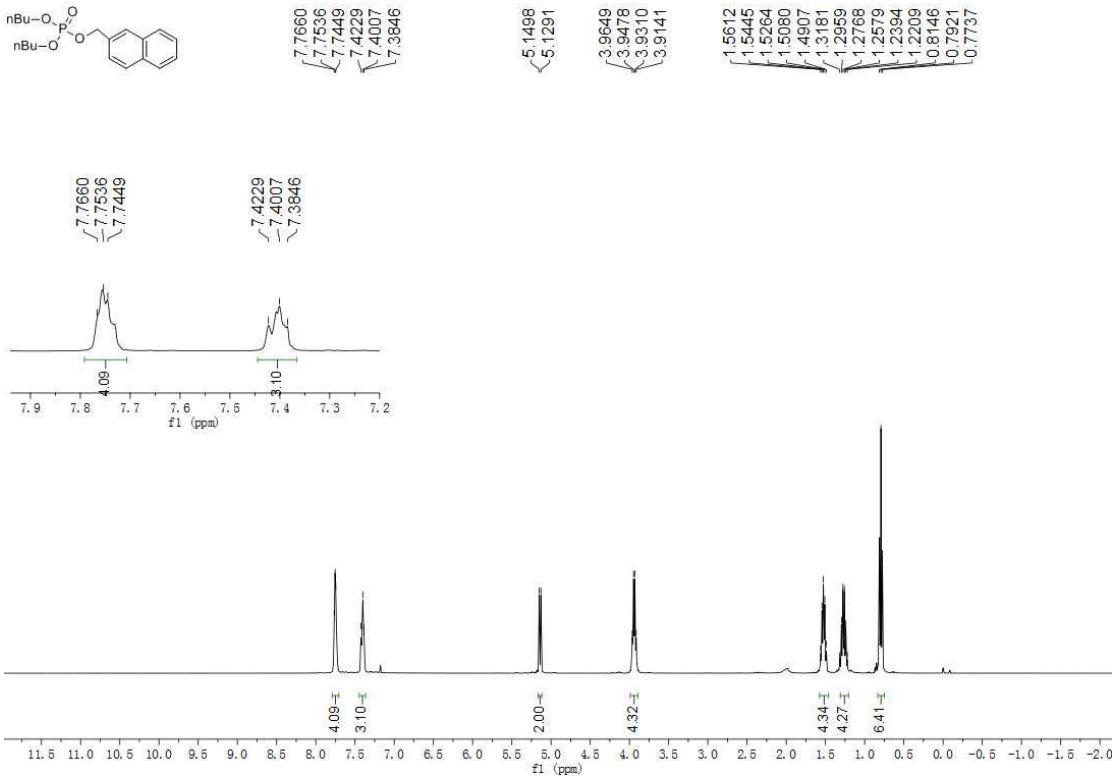
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4e**



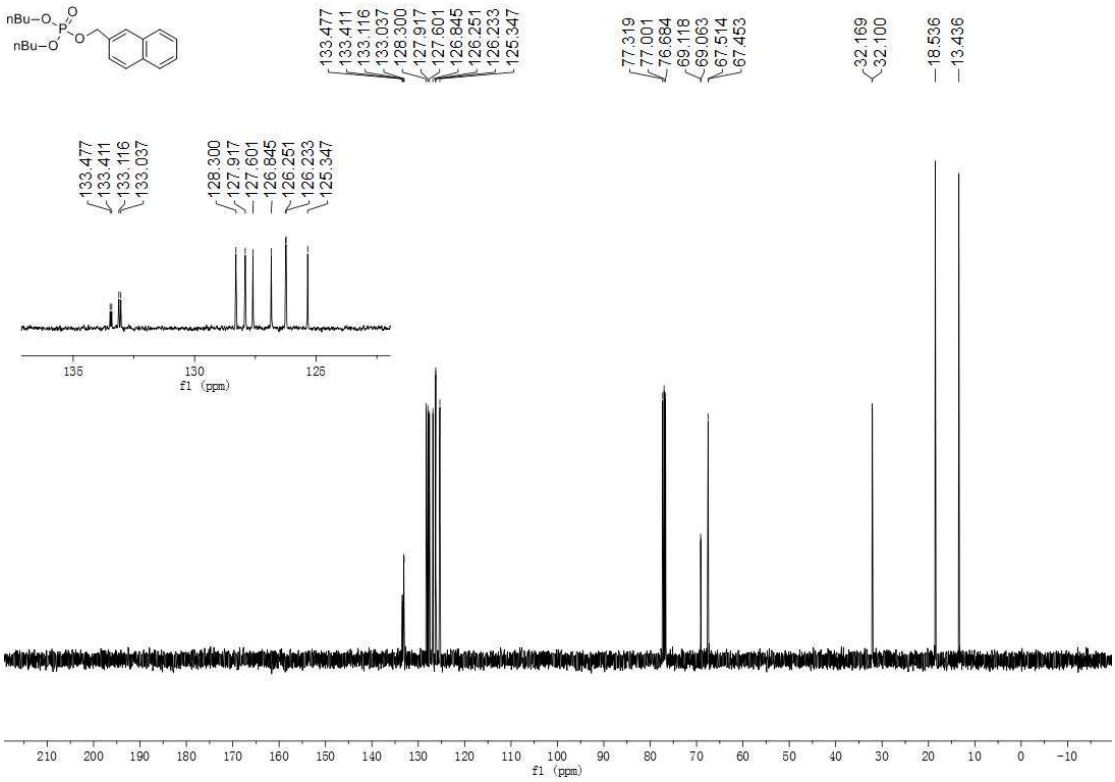
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4e**



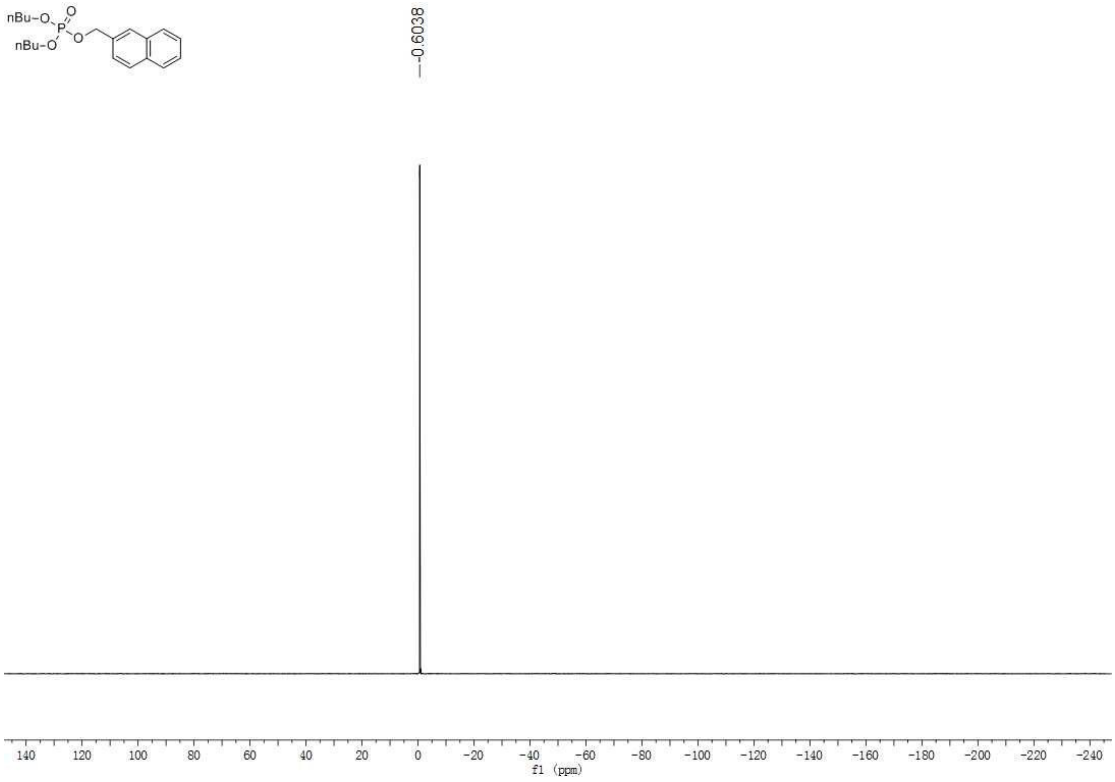
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4e**



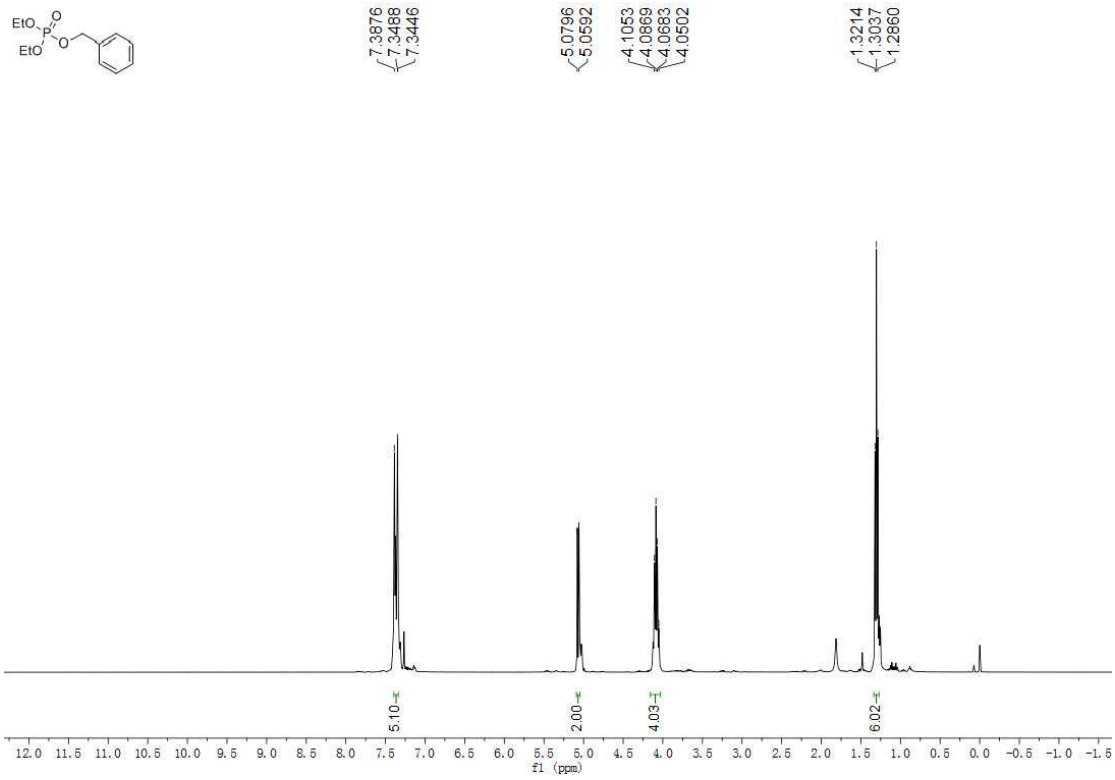
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4f**



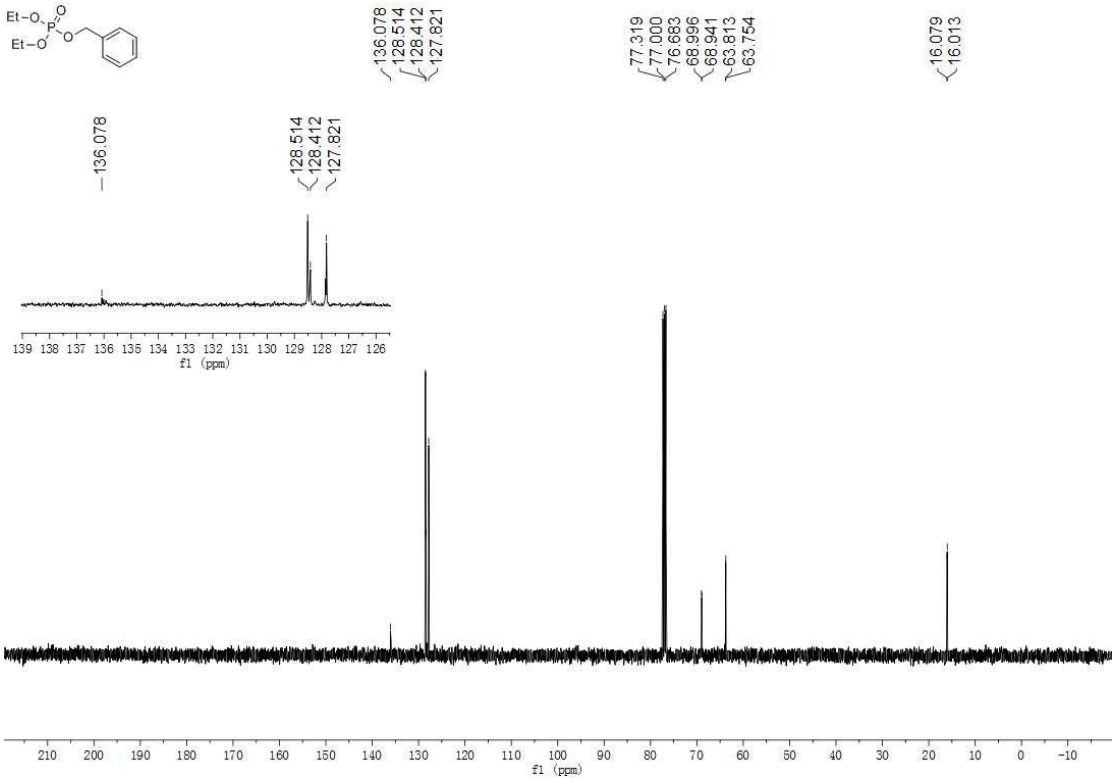
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4f** [4]



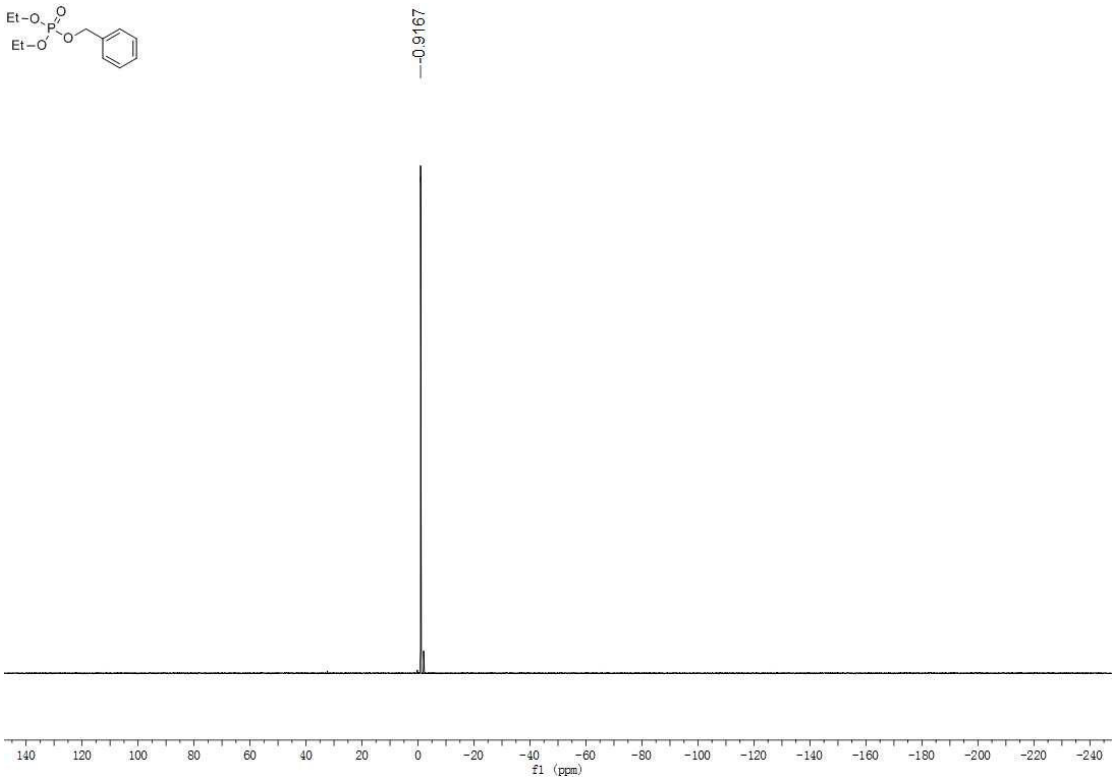
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4f**



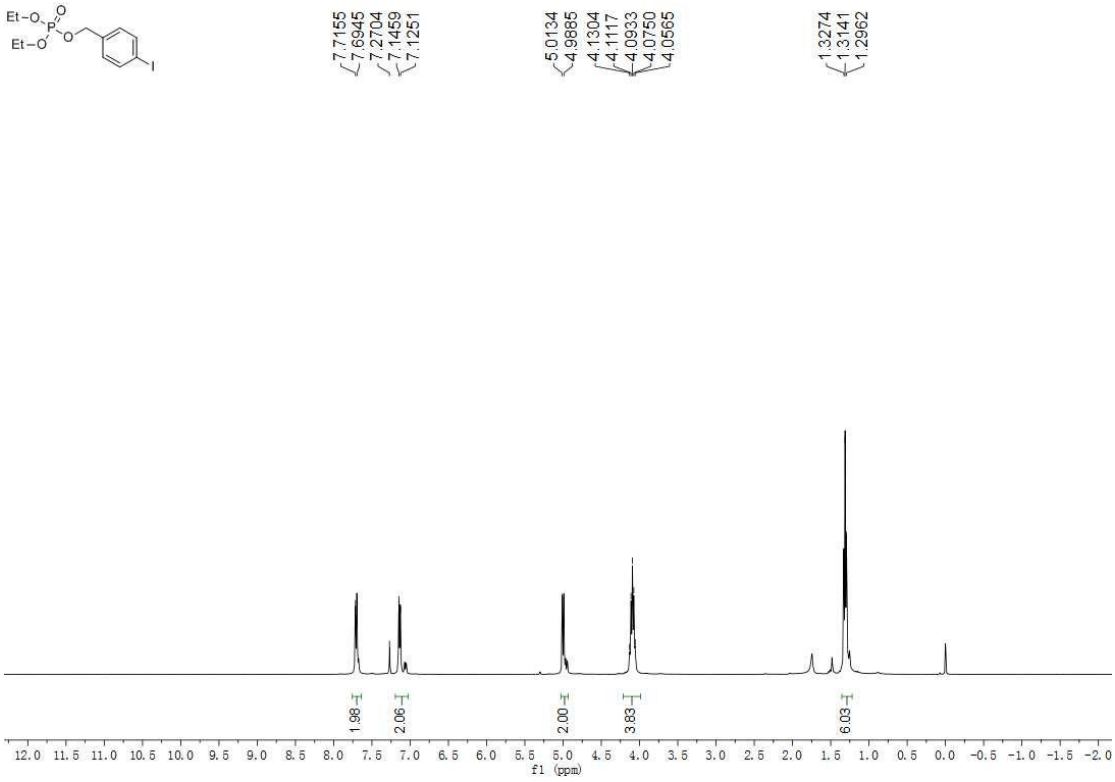
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4g** [3]



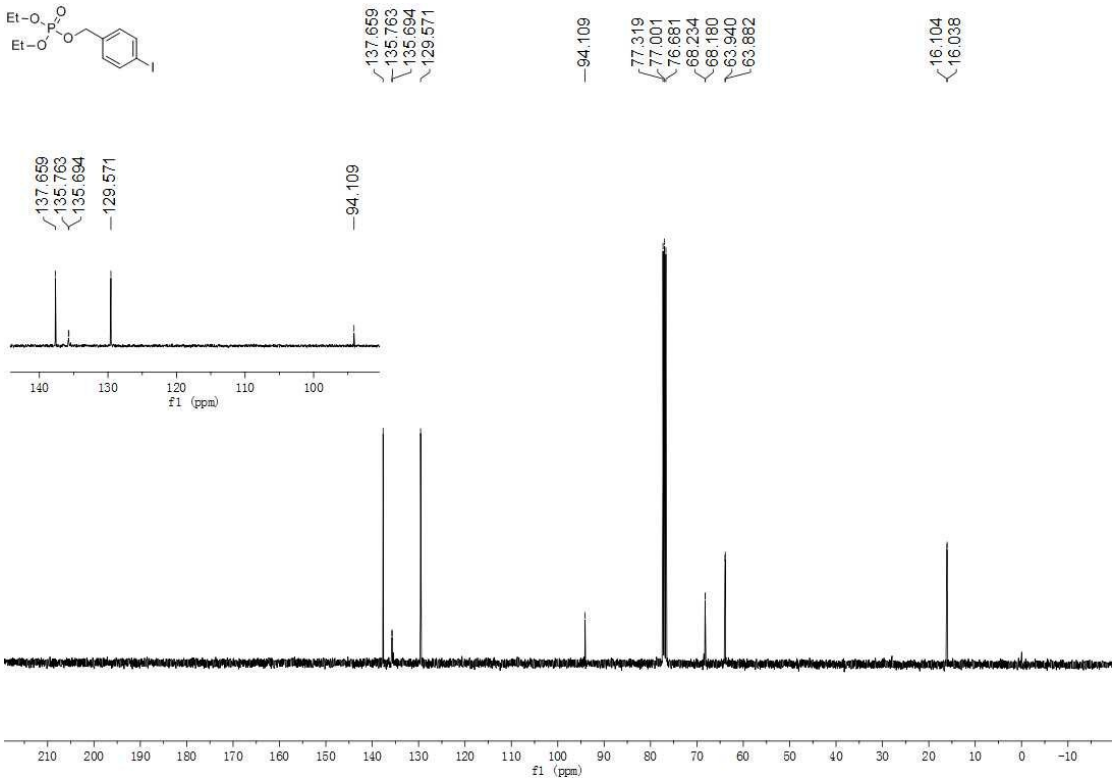
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4g** [3]



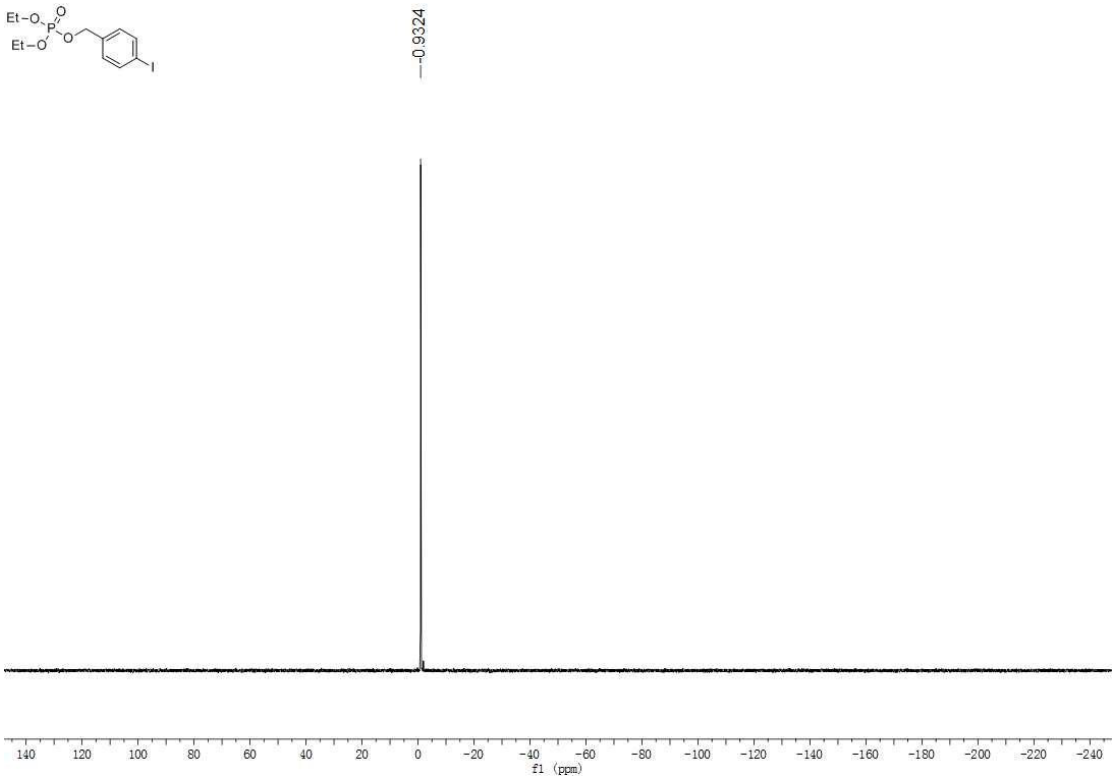
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4g**



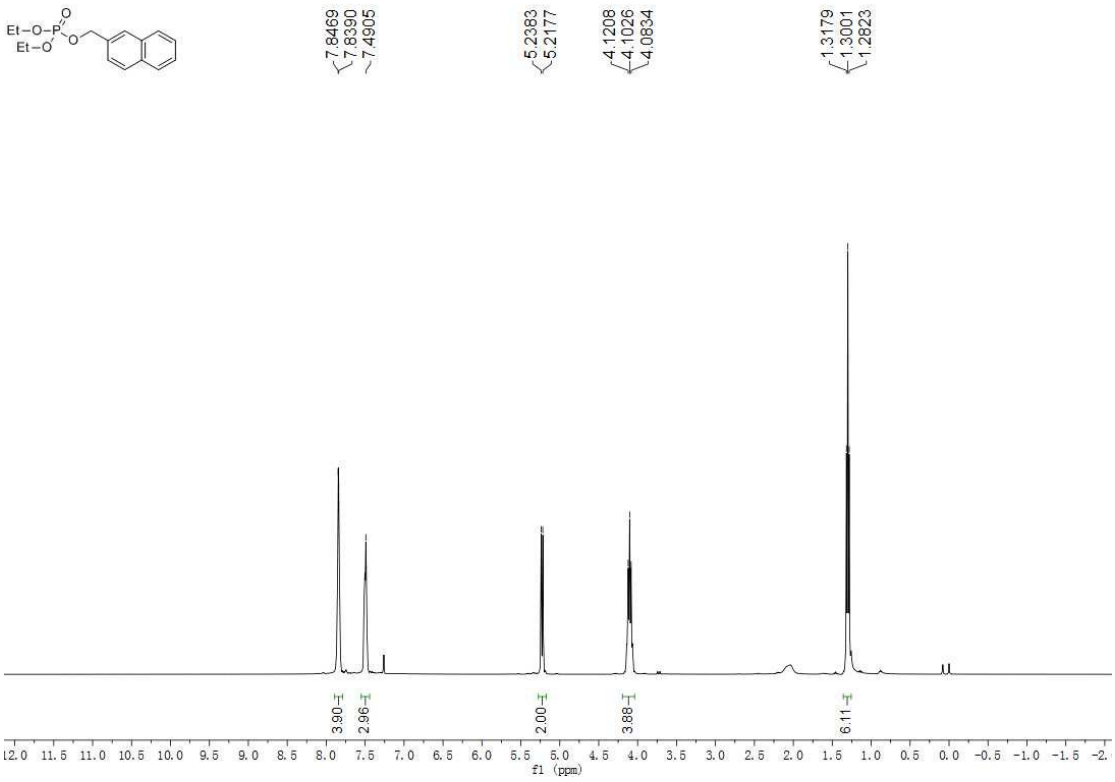
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4h**



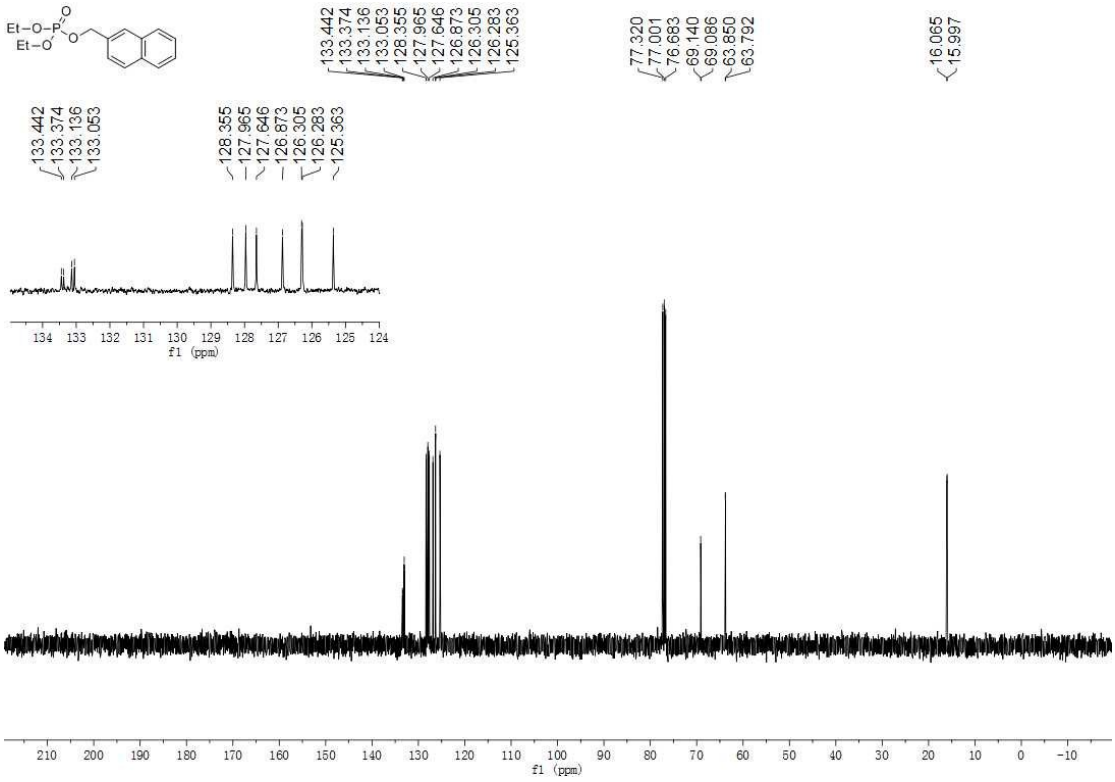
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4h**



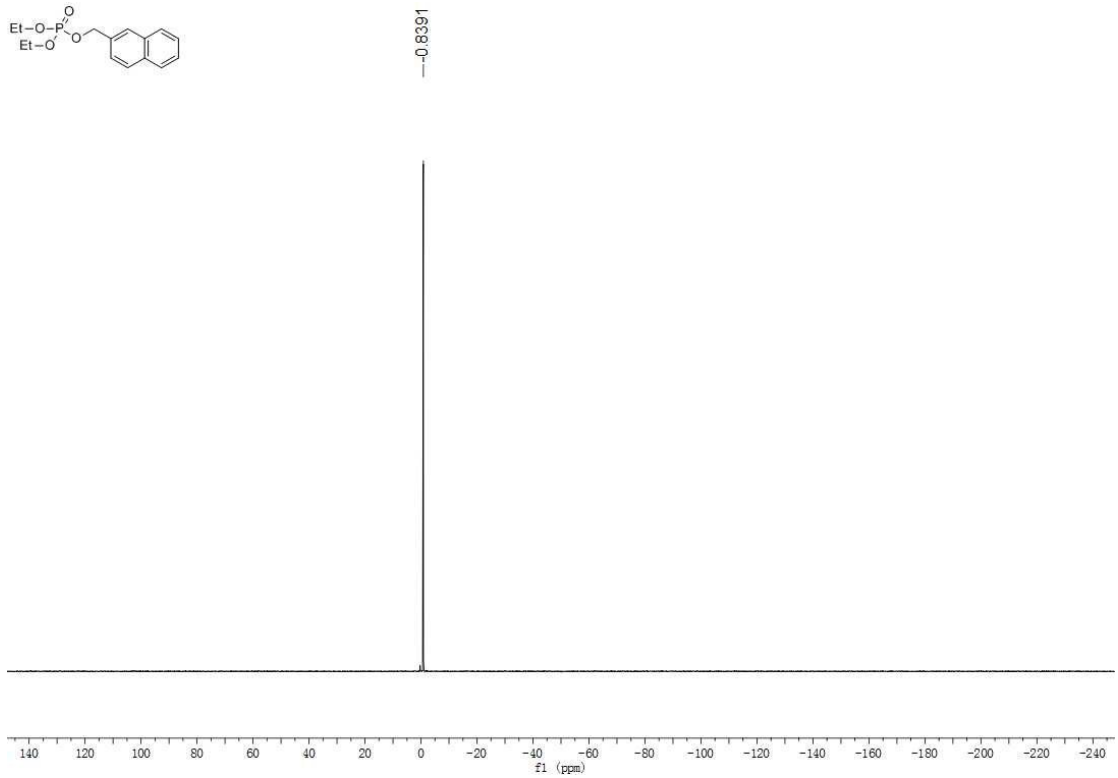
^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4h**



^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **4i**



^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound **4i**



^{31}P NMR (162MHz, $CDCl_3$) spectrum of compound **4i**

References:

1. S. I. Murahashi, N. Miyaguchi, S. Noda, T. Naota, A. Fujii, Y. Inubushi and N. Komiya, *Eur. J. Org. Chem.,* 2011, 5355–5365.
2. B. Xiong, G. Wang, C. Zhou, Y. Liu, P. Zhang and K. Tang, *J. Org. Chem.*, 2018, **83**, 993–999.
3. J. Xu, P. Zhang, X. Li, Y. Gao, J. Wu, G. Tang and Y. Zhao, *Adv. Synth. Catal.*, 2014, **356**, 3331–3335.
4. B. Xiong, Q. Ye, X. Feng, L. Zhu, T. Chen, Y. Zhou, C.-T. Au and S.-F. Yin, *Tetrahedron*, 2014, **70**, 9057-9063.