

## *Supporting Information*

# **Iron-Catalyzed Clean Dehydrogenative Coupling of Alcohols with P(O)-H Compounds: a New Protocol for ROH Phosphorylation**

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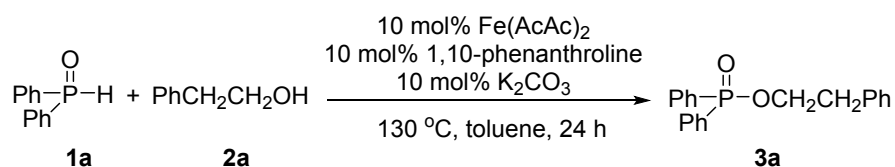
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## 1. General information

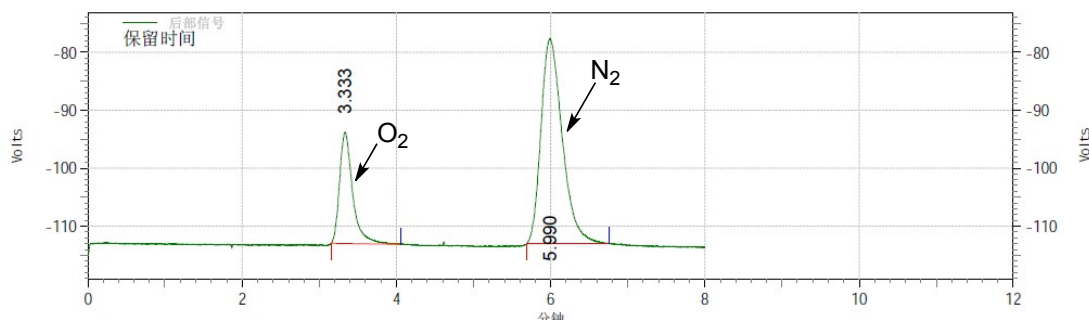
All reactions were carried out in oven-dried Schlenk tubes under N<sub>2</sub> atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. Column chromatography was performed using Silica Gel 60 (particle size 37–54 μm). The pure products were obtained by means of column chromatography. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR data were acquired on a Bruker-400 spectrometer (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C, and 162 MHz for <sup>31</sup>P NMR spectroscopy). Chemical shifts for <sup>1</sup>H NMR are referred to internal Me<sub>4</sub>Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for <sup>31</sup>P NMR were relative to H<sub>3</sub>PO<sub>4</sub> (85% solution in D<sub>2</sub>O, 0 ppm). HRMS were conducted in the Analytical Center at Hunan University, China.

## 2. Typical procedure for the iron-catalyzed cross dehydrogenative coupling of P(O)-H compounds with alcohols

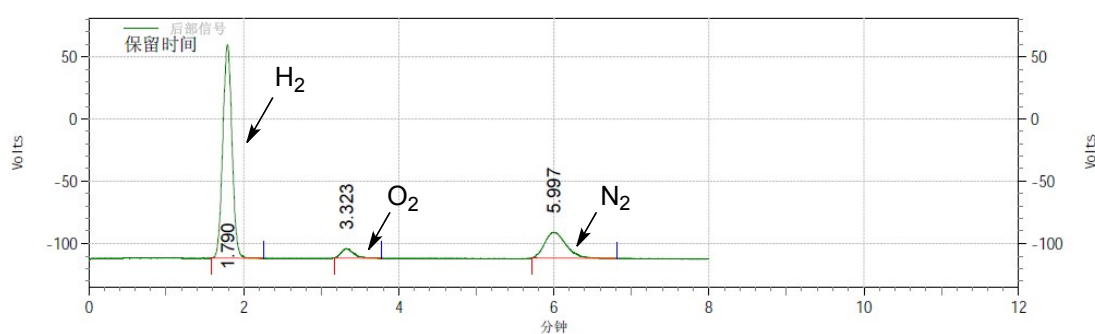


Under the dinitrogen atmosphere (1 atm), 0.24 mmol 2-phenylethanol **2a**, 0.2 mmol diphenylphosphine oxide **1a**, 10 mol% Fe(AcAc)<sub>2</sub>, 10 mol% 1,10-phenanthroline, 10% K<sub>2</sub>CO<sub>3</sub> and 1 mL toluene were charged into a 25 mL sealed tube and the mixture was heated at 130 °C until the starting material was consumed (ca. 24 hours). After removal of the volatiles in vacuum, the residues were passed through a short silica chromatography (particle size 37-54 μm, ethyl acetate/pether as eluent) to afford analytically pure **3a** in 95% isolated yield.

### 3. Detection of dihydrogen generated in the iron-catalyzed cross dihydrogenative coupling of diphenylphosphine oxide with 2-phenylethanol by GC.



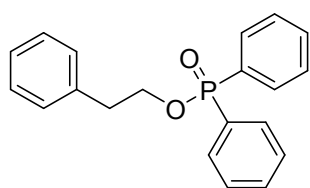
The reference (air)



Sample of the reaction after 24 h

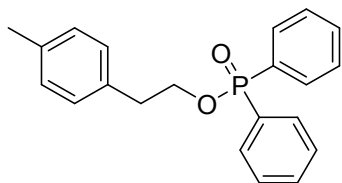
Agilent Technologies 7820A GC system, TCD detector, AE.5A column, oven temperature: 50 °C, carrier: Ar, 45 mL/min. The pick time was checked by standard samples.

### 4. Characterization and analytical data of products 3

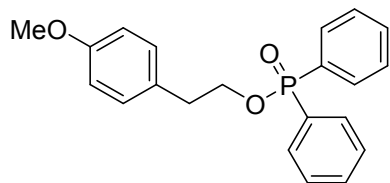


**Phenethyl diphenylphosphinate (3a).**<sup>11</sup> White solid; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.73-7.68 (m, 4H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.39-7.35 (m, 4H), 7.29-7.17 (m, 5H), 4.21 (dt,  $J = 7.2$  Hz, 7.2 Hz, 2H), 3.02 (t,  $J = 7.2$  Hz, 2H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  137.5, 132.1 (d,  $J_{C-P} = 2.6$  Hz), 131.6 (d,  $J_{C-P} = 10.1$  Hz), 131.4 (d,  $J_{C-P} = 134.9$  Hz), 129.1, 128.5, 128.5 (d,  $J_{C-P} = 13.1$  Hz), 126.7, 85.4 (d,  $J_{C-P} = 5.9$  Hz), 37.1

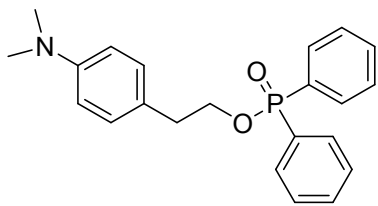
(d,  $J_{C-P} = 6.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.46.



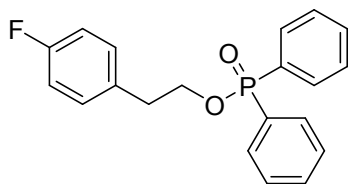
**4-Methylphenethyl diphenylphosphinate (3b).** White solid; m.p.: 60.3–61.2 °C;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.73-7.69 (m, 4H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.41-7.37 (m, 4H), 7.09 (b, 4H), 4.19 (dt,  $J = 6.8$  Hz, 6.8 Hz, 2H), 3.00 (t,  $J = 6.8$  Hz, 2H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  136.2, 134.4, 132.1 (d,  $J_{C-P} = 2.8$  Hz), 131.6 (d,  $J_{C-P} = 10.1$  Hz), 131.5 (d,  $J_{C-P} = 136.2$  Hz), 129.2, 129.0, 128.5 (d,  $J_{C-P} = 13.0$  Hz), 65.6 (d,  $J_{C-P} = 6.0$  Hz), 36.7 (d,  $J_{C-P} = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.46.  $\text{C}_{21}\text{H}_{21}\text{O}_2\text{P}$ . HRMS: Cal. 336.1279. Found 335.1183 (M-H).



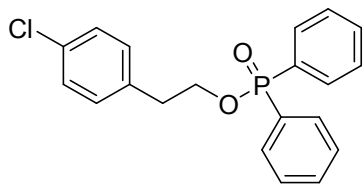
**4-Methoxyphenethyl diphenylphosphinate (3c).** Colorless oil;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.74-7.69 (m, 4H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.43-7.38 (m, 4H), 7.11 (d,  $J = 8.4$  Hz, 2H), 6.82 (d,  $J = 8.4$  Hz, 2H), 4.18 (dt,  $J = 7.2$  Hz, 7.2 Hz, 2H), 3.79 (s, 3H), 2.98 (t,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  158.4, 132.1 (d,  $J_{C-P} = 2.8$  Hz), 131.6 (d,  $J_{C-P} = 10.0$  Hz), 131.5 (d,  $J_{C-P} = 136.1$  Hz), 130.1, 129.5, 128.5 (d,  $J_{C-P} = 13.1$  Hz), 65.6 (d,  $J_{C-P} = 6.0$  Hz), 55.3, 36.2 (d,  $J_{C-P} = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.45.  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{P}$ . HRMS: Cal. 352.1228. Found 352.1206.



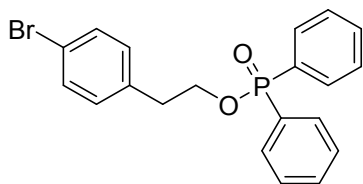
**4-(dimethylamino)phenethyl diphenylphosphinate (3d).** Yellow solid; m.p.: 111.8–112.7 °C;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.76–7.71 (m, 4H), 7.50–7.38 (m, 6H), 7.07 (d,  $J = 8.5$  Hz, 2H), 6.68 (d,  $J = 8.5$  Hz, 2H), 4.16 (dt,  $J = 6.8$  Hz, 6.8 Hz, 2H), 2.95 (t,  $J = 6.8$  Hz, 2H), 2.92 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  149.6, 132.0 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.4, 131.4 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.1 (d,  $J_{\text{C-P}} = 136.1$  Hz), 130.7, 128.4 (d,  $J_{\text{C-P}} = 13.1$  Hz), 120.4, 64.8 (d,  $J_{\text{C-P}} = 6.0$  Hz), 36.3 (d,  $J_{\text{C-P}} = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.28.  $\text{C}_{22}\text{H}_{24}\text{NO}_2\text{P}$ . HRMS: Cal. 365.1539. Found 365.1525.



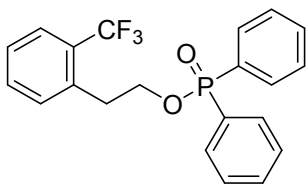
**4-Fluorophenethyl diphenylphosphinate (3e).** Colorless oil;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.72–7.67 (m, 4H), 7.51–7.47 (m, 2H), 7.42–7.39 (m, 4H), 7.15 (dd,  $J = 6.4$  Hz, 6.4 Hz, 2H), 6.97 (dd,  $J = 8.4$  Hz, 8.4 Hz, 2H), 4.19 (dt,  $J = 6.8$  Hz, 6.8 Hz, 2H), 3.00 (t,  $J = 6.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  161.8 (d,  $J_{\text{C-F}} = 243.0$  Hz), 133.2 (d,  $J_{\text{C-F}} = 3.2$  Hz), 132.2 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.3 (d,  $J_{\text{C-P}} = 136.1$  Hz), 130.5 (d,  $J_{\text{C-F}} = 7.9$  Hz), 128.5 (d,  $J_{\text{C-P}} = 13.0$  Hz), 65.3 (d,  $J_{\text{C-P}} = 6.0$  Hz), 36.3 (d,  $J_{\text{C-P}} = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.72.  $\text{C}_{20}\text{H}_{18}\text{FO}_2\text{P}$ . HRMS: Cal. 340.1028. Found 340.1006.



**4-Chlorophenethyl diphenylphosphinate (3f).** Yellow solid; m.p.: 65.2–66.3 °C;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.63–7.58 (m, 4H), 7.41 (t,  $J = 7.2$  Hz, 2H), 7.34–7.32 (m, 4H), 7.17 (d,  $J = 8.0$  Hz, 2H), 7.04 (d,  $J = 8.0$  Hz, 2H), 4.12 (dt,  $J = 6.8$  Hz, 6.8 Hz, 2H), 2.91 (t,  $J = 6.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  135.0, 131.4, 132.1 (d,  $J_{\text{C-P}} = 2.7$  Hz), 130.5 (d,  $J_{\text{C-P}} = 10.1$  Hz), 130.2 (d,  $J_{\text{C-P}} = 136.2$  Hz), 129.4, 127.6, 127.5 (d,  $J_{\text{C-P}} = 12.7$  Hz), 64.0 (d,  $J_{\text{C-P}} = 5.8$  Hz), 35.4 (d,  $J_{\text{C-P}} = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.82.

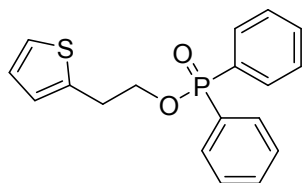


**4-Bromophenethyl diphenylphosphinate (3g).** Colorless oil;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.71–7.66 (m, 4H), 7.49 (t,  $J = 7.2$  Hz, 2H), 7.42–7.37 (m, 6H), 7.06 (d,  $J = 8.0$  Hz, 2H), 4.19 (dt,  $J = 6.8$  Hz, 6.8 Hz, 2H), 2.97 (t,  $J = 6.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  136.6, 132.2 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.5, 131.3 (d,  $J_{\text{C-P}} = 136.1$  Hz), 130.9, 128.5 (d,  $J_{\text{C-P}} = 13.1$  Hz), 120.5, 64.9 (d,  $J_{\text{C-P}} = 6.0$  Hz), 36.5 (d,  $J_{\text{C-P}} = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.77.

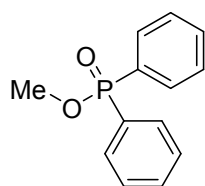


**2-(Trifluoromethyl)phenethyl diphenylphosphinate (3h).** Colorless oil;  $^1\text{H}$  NMR

(400 MHz CDCl<sub>3</sub>):  $\delta$  7.77-7.72 (m, 4H), 7.62 (d,  $J = 7.6$  Hz, 1H), 7.52-7.30 (m, 9H), 4.24 (dt,  $J = 7.2$  Hz, 7.2 Hz, 2H), 3.25 (t,  $J = 7.2$  Hz, 2H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  135.8 (b), 132.2 (d,  $J_{C-P} = 2.8$  Hz), 132.1 (b), 131.7 (b), 131.6 (d,  $J_{C-P} = 10.1$  Hz), 131.2 (d,  $J_{C-P} = 136.2$  Hz), 129.0 (q,  $J_{C-F} = 29.6$  Hz), 128.5 (d,  $J_{C-P} = 13.0$  Hz), 126.9, 126.1 (q,  $J_{C-F} = 5.7$  Hz), 124.4 (q,  $J_{C-F} = 272.2$  Hz), 64.7 (d,  $J_{C-P} = 4.9$  Hz), 33.8 (db,  $J_{C-P} = 8.4$  Hz). <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  32.05. C<sub>21</sub>H<sub>18</sub>F<sub>3</sub>O<sub>2</sub>P. HRMS: Cal. 390.0997. Found 390.0980.

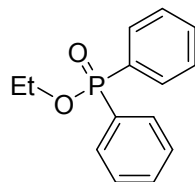


**2-(Thiophen-2-yl)ethyl diphenylphosphinate (3i).** Colorless oil; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.79-7.74 (m, 4H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.43-7.39 (m, 4H), 7.15 (d,  $J = 4.8$  Hz, 1H), 6.93 (dd,  $J = 3.6$  Hz, 4.8 Hz, 1H), 6.85 (d,  $J = 3.6$  Hz, 1H), 4.22 (dt,  $J = 6.4$  Hz, 6.4 Hz, 2H), 3.24 (t,  $J = 6.4$  Hz, 2H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  139.5, 132.2 (d,  $J_{C-P} = 2.8$  Hz), 131.6 (d,  $J_{C-P} = 10.2$  Hz), 131.3 (d,  $J_{C-P} = 136.1$  Hz), 128.6 (d,  $J_{C-P} = 13.1$  Hz), 126.9, 125.9, 124.1, 65.0 (d,  $J_{C-P} = 5.9$  Hz), 31.3 (d,  $J_{C-P} = 7.1$  Hz). <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  31.86. C<sub>18</sub>H<sub>17</sub>O<sub>2</sub>PS. HRMS: Cal. 328.0687. Found 328.0670.

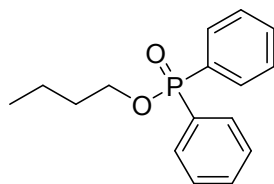


**Methyl diphenylphosphinate (3j)**<sup>12</sup>. Colorless oil; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$

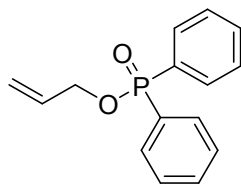
7.76-7.71 (m, 4H), 7.46-7.35 (m, 6H), 3.69 (d,  $J = 11.2$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  132.2 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.7 (d,  $J_{\text{C-P}} = 10.0$  Hz), 131.0 (d,  $J_{\text{C-P}} = 138.5$  Hz), 51.6 (d,  $J_{\text{C-P}} = 6.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  33.29.



**Ethyl diphenylphosphinate (3k).**<sup>13</sup> Colorless oil;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.85-7.79 (m, 4H), 7.52-7.42 (m, 6H), 4.11 (dq,  $J = 7.2$  Hz, 7.2 Hz, 2H), 1.36 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  132.1 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 136.3$  Hz), 131.6 (d,  $J_{\text{C-P}} = 10.0$  Hz), 128.5 (d,  $J_{\text{C-P}} = 13.0$  Hz), 61.1 (d,  $J_{\text{C-P}} = 5.9$  Hz), 16.5 (d,  $J_{\text{C-P}} = 6.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.34.



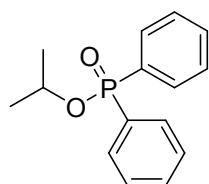
**n-Butyl diphenylphosphinate (3l).**<sup>12</sup> White solid;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.83-7.79 (m, 4H), 7.53-7.42 (m, 6H), 4.03 (dt,  $J = 6.8$  Hz, 6.8 Hz, 2H), 1.74-1.67 (m, 2H), 1.48-1.39 (m, 2H), 0.91 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  132.1 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.7 (d,  $J_{\text{C-P}} = 136.4$  Hz), 131.6 (d,  $J_{\text{C-P}} = 10.0$  Hz), 128.5 (d,  $J_{\text{C-P}} = 13.0$  Hz), 64.7 (d,  $J_{\text{C-P}} = 6.1$  Hz), 32.6 (d,  $J_{\text{C-P}} = 6.6$  Hz), 18.9, 13.6.  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  31.12.



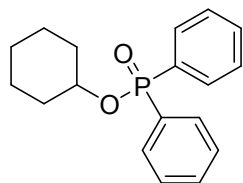
**Allyl diphenylphosphinate (3m).**<sup>13</sup> Colorless oil;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$



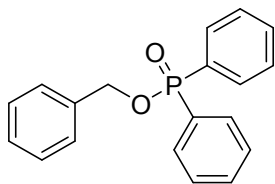
7.85-7.81 (m, 4H), 7.54-7.43 (m, 6H), 6.02-5.92 (m, 1H), 5.36 (d,  $J = 17.2$  Hz, 1H), 5.23 (d,  $J = 10.4$  Hz, 1H), 4.54 (dd,  $J = 6.4$  Hz, 6.4 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  133.0 (d,  $J_{\text{C-P}} = 7.2$  Hz), 132.2 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.3 (d,  $J_{\text{C-P}} = 136.3$  Hz), 128.6 (d,  $J_{\text{C-P}} = 13.1$  Hz), 117.9, 65.4 (d,  $J_{\text{C-P}} = 5.4$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  32.28.



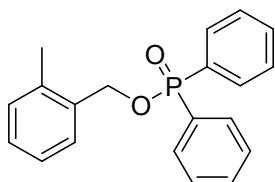
***i*-Propyl diphenylphosphinate (3n).**<sup>14</sup> White solid;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.84-7.79 (m, 4H), 7.52-7.41 (m, 6H), 4.73-4.62 (m, 1H), 1.35 (d,  $J = 6.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  132.4 (d,  $J_{\text{C-P}} = 136.3$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 10.0$  Hz), 128.4 (d,  $J_{\text{C-P}} = 13.0$  Hz), 70.3 (d,  $J_{\text{C-P}} = 6.0$  Hz), 24.3 (d,  $J_{\text{C-P}} = 4.1$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  29.82.



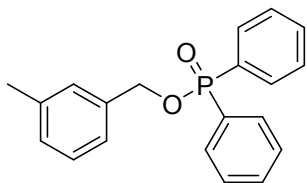
**Cyclohexyl diphenylphosphinate (3o).**<sup>15</sup> White solid;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.84-7.79 (m, 4H), 7.51-7.41 (m, 6H), 4.47-4.38 (m, 1H), 1.91-1.88 (m, 2H), 1.75-1.72 (m, 2H), 1.65-1.56 (m, 2H), 1.48-1.43 (m, 1H), 1.34-1.22 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  132.6 (d,  $J_{\text{C-P}} = 136.4$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 10.0$  Hz), 128.4 (d,  $J_{\text{C-P}} = 13.0$  Hz), 74.9 (d,  $J_{\text{C-P}} = 6.2$  Hz), 33.9 (d,  $J_{\text{C-P}} = 3.7$  Hz), 25.2, 23.6.  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  29.66.



**Benzyl diphenylphosphinate (3p).**<sup>16</sup> White solid; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.76-7.71 (m, 4H), 7.41-7.16 (m, 11H), 4.96 (d,  $J$  = 6.8 Hz, 2H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  136.4 (d,  $J_{C-P}$  = 7.4 Hz), 132.3 (d,  $J_{C-P}$  = 2.7 Hz), 131.7 (d,  $J_{C-P}$  = 10.2 Hz), 131.4 (d,  $J_{C-P}$  = 136.1 Hz), 128.6 (d,  $J_{C-P}$  = 13.1 Hz), 128.6, 128.3, 127.9, 66.3 (d,  $J_{C-P}$  = 5.4 Hz). <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  30.32.



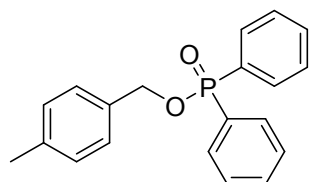
**2-Methylbenzyl diphenylphosphinate (3q).**<sup>16</sup> White solid; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.85-7.80 (m, 4H), 7.51 (t,  $J$  = 7.2 Hz, 2H), 7.45-7.40 (m, 4H), 7.31 (d,  $J$  = 7.2 Hz, 1H), 7.26-7.15 (m, 3H), 5.08 (d,  $J$  = 6.0 Hz, 2H), 2.32 (s, 3H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  136.7, 134.4 (d,  $J_{C-P}$  = 7.7 Hz), 132.2 (d,  $J_{C-P}$  = 2.8 Hz), 131.7 (d,  $J_{C-P}$  = 10.1 Hz), 131.4 (d,  $J_{C-P}$  = 135.9 Hz), 130.3, 128.7, 128.6 (d,  $J_{C-P}$  = 13.1 Hz), 128.5, 126.0, 64.6 (d,  $J_{C-P}$  = 5.4 Hz), 18.8. <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  32.21.



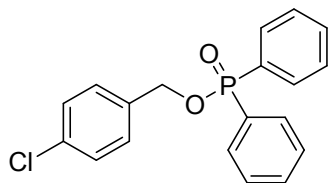
**3-Methylbenzyl diphenylphosphinate (3r).** White solid; m.p.: 100.0–100.5 °C; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.86-7.81 (m, 4H), 7.54-7.42 (m, 6H), 7.26-7.11 (m, 4H), 5.03 (d,  $J$  = 6.8 Hz, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  138.2, 136.2 (d,  $J_{C-P}$  = 7.5 Hz), 132.2 (d,  $J_{C-P}$  = 2.7 Hz), 131.7 (d,  $J_{C-P}$  = 10.1 Hz), 131.4 (d,  $J_{C-P}$  =

135.9 Hz), 129.1, 128.7, 128.5 (d,  $J_{C-P} = 13.2$  Hz), 125.0, 66.4 (d,  $J_{C-P} = 5.6$  Hz), 21.4.

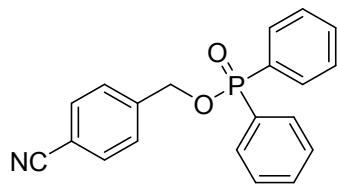
$^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  32.23.  $\text{C}_{20}\text{H}_{19}\text{O}_2\text{P}$ . HRMS: Cal. 322.1123. Found 322.1115.



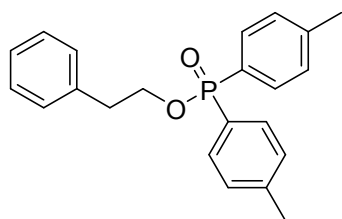
**4-Methylbenzyl diphenylphosphinate (3s).**<sup>16</sup> White solid;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.85-7.80 (m, 4H), 7.50-7.42 (m, 6H), 7.25 (d,  $J = 7.2$  Hz, 2H), 7.14 (d, 8.0 Hz, 2H), 5.02 (d,  $J = 6.4$  Hz, 2H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  138.1, 133.4 (d,  $J_{C-P} = 7.5$  Hz), 132.2, 131.7 (d,  $J_{C-P} = 10.1$  Hz), 131.5 (d,  $J_{C-P} = 135.0$  Hz), 129.2, 128.5 (d,  $J_{C-P} = 13.1$  Hz), 128.1, 66.3 (d,  $J_{C-P} = 5.6$  Hz), 21.2.  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  32.09.



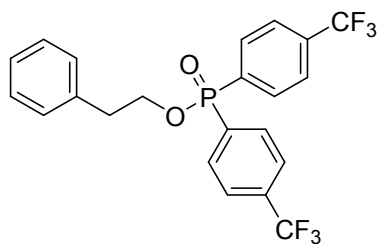
**4-Chlorobenzyl diphenylphosphinate (3t).**<sup>16</sup> White solid;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.84-7.79 (m, 4H), 7.53 (t,  $J = 7.2$  Hz, 2H), 7.47-7.43 (m, 4H), 7.33-7.28 (m, 4H), 5.03 (d,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  134.9 (d,  $J_{C-P} = 7.2$  Hz), 134.2, 132.3 (d,  $J_{C-P} = 2.8$  Hz), 131.7 (d,  $J_{C-P} = 10.2$  Hz), 131.2 (d,  $J_{C-P} = 135.8$  Hz), 129.3, 128.8, 128.6 (d,  $J_{C-P} = 13.2$  Hz), 65.5 (d,  $J_{C-P} = 5.4$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  32.68.



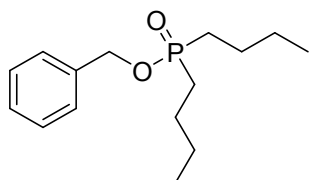
**4-Cyanobenzyl diphenylphosphinate (3u).**<sup>16</sup> White solid; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.85-7.80 (m, 4H), 7.64 (d,  $J$  = 8.0 Hz, 2H), 7.56 (t,  $J$  = 7.2 Hz, 2H), 7.49-7.45 (m, 6H), 5.11 (d,  $J$  = 7.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  141.7 (d,  $J_{C-P}$  = 7.1 Hz), 132.6 (d,  $J_{C-P}$  = 2.8 Hz), 132.4, 131.6 (d,  $J_{C-P}$  = 10.3 Hz), 130.8 (d,  $J_{C-P}$  = 136.0 Hz), 128.7 (d,  $J_{C-P}$  = 13.1 Hz), 128.0, 118.6, 112.1, 65.1 (d,  $J_{C-P}$  = 5.2 Hz). <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  33.43.



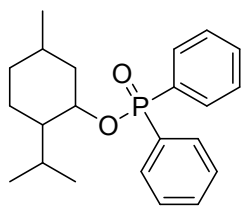
**Phenethyl di-*p*-tolylphosphinate (3v).** Colorless oil; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.61-7.56 (m, 4H), 7.29-7.17 (m, 9H), 4.19 (dt,  $J$  = 6.8 Hz, 6.8 Hz, 2H), 3.01 (t,  $J$  = 6.8 Hz, 2H), 2.33 (s, 6H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  142.5 (d,  $J_{C-P}$  = 2.8 Hz), 137.6, 131.6 (d,  $J_{C-P}$  = 10.4 Hz), 129.2 (d,  $J_{C-P}$  = 13.8 Hz), 129.2, 128.5, 128.4 (d,  $J_{C-P}$  = 138.8 Hz), 126.6, 65.2 (d,  $J_{C-P}$  = 6.0 Hz), 37.1 (d,  $J_{C-P}$  = 6.9 Hz), 21.6 (d,  $J_{C-P}$  = 1.0 Hz). <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  32.44. C<sub>22</sub>H<sub>23</sub>O<sub>2</sub>P. HRMS: Cal. 350.1436. Found 350.1422.



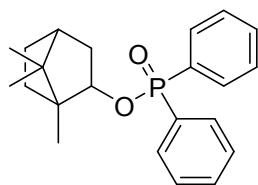
**Phenethyl bis(4-(trifluoromethyl)phenyl)phosphinate (3w).** White solid; m.p.: 90.5–91.3 °C;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.81-7.76 (m, 4H), 7.68-7.65 (m, 4H), 7.34-7.24 (m, 3H), 7.20 (d,  $J = 6.8$  Hz, 2H), 4.29 (dt,  $J = 6.8$  Hz, 6.8 Hz, 2H), 3.07 (t,  $J = 6.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  137.2, 134.9 (d,  $J_{\text{C-P}} = 135.7$  Hz), 134.2 (dq,  $J_{\text{C-P}} = 3.0$  Hz,  $J_{\text{C-F}} = 32.6$  Hz), 132.1 (d,  $J_{\text{C-P}} = 10.5$  Hz), 129.1, 128.6, 126.9, 125.5 (dq,  $J_{\text{C-P}} = 9.5$  Hz,  $J_{\text{C-F}} = 3.7$  Hz), 123.4 (q,  $J_{\text{C-F}} = 271.3$  Hz), 66.1 (d,  $J_{\text{C-P}} = 6.0$  Hz), 36.9 (d,  $J_{\text{C-P}} = 7.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  27.66.  $\text{C}_{22}\text{H}_{17}\text{F}_6\text{O}_2\text{P}$ . HRMS: Cal. 458.0870. Found 457.0789(M-H).



**Benzyl dibutylphosphinate (3x).** Yellow oil;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.38-7.27 (m, 5H), 5.03 (d,  $J = 8.0$  Hz, 2H), 1.78-1.67 (m, 4H), 1.59-1.49 (m, 4H), 1.42-1.33 (m, 4H), 0.81 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  137.0 (d,  $J_{\text{C-P}} = 5.7$  Hz), 128.6, 128.2, 127.8, 65.5 (d,  $J_{\text{C-P}} = 6.1$  Hz), 27.9 (d,  $J_{\text{C-P}} = 88.6$  Hz), 24.0 (d,  $J_{\text{C-P}} = 8.4$  Hz), 23.9 (d,  $J_{\text{C-P}} = 3.1$  Hz), 13.55.  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  59.33.

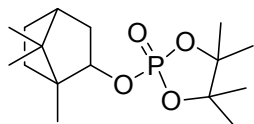


**Benzyl dibutylphosphinate (3y).**<sup>17</sup> White solid; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.83-7.73 (m, 4H), 7.50-7.39 (m, 6H), 4.27-4.18 (m, 1H), 2.16-2.07 (m, 2H), 1.62-1.60 (m, 2H), 1.46-1.34 (m, 2H), 1.23-1.18 (m, 1H), 0.98-0.92 (m, 1H), 0.87-0.78 (m, 7H), 0.51 (d,  $J = 1.7$  Hz, 3H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  133.0 (d,  $J_{C-P} = 137.1$  Hz), 132.3 (d,  $J_{C-P} = 137.9$  Hz), 131.8 (d,  $J_{C-P} = 2.8$  Hz), 131.7 (d,  $J_{C-P} = 2.8$  Hz), 131.6 (d,  $J_{C-P} = 3.8$  Hz), 131.5 (d,  $J_{C-P} = 3.6$  Hz), 128.2 (d,  $J_{C-P} = 13.0$  Hz), 128.2 (d,  $J_{C-P} = 13.0$  Hz), 77.1 (d,  $J_{C-P} = 7.0$  Hz), 48.8 (d,  $J_{C-P} = 6.3$  Hz), 43.5, 34.0, 31.5, 25.5, 22.6, 21.9, 21.1, 15.2. <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  29.41.



**Benzyl dibutylphosphinate (3z).** Colorless oil; <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  7.84-7.78 (m, 4H), 7.52-7.42 (m, 6H), 4.59 (tb,  $J = 8.8$  Hz, 1H), 2.23-2.09 (m, 2H), 1.78-1.72 (m, 1H), 1.64 (t,  $J = 4.4$  Hz, 1H), 1.37-1.26 (m, 4H), 0.86 (s, 3H), 0.85 (s, 3H), 0.78 (s, 3H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta$  132.7 (d,  $J_{C-P} = 136.2$  Hz), 132.2 (d,  $J_{C-P} = 137.0$  Hz), 131.9 (d,  $J_{C-P} = 2.2$  Hz), 131.9 (d,  $J_{C-P} = 2.4$  Hz), 131.7 (d,  $J_{C-P} = 10.0$  Hz), 131.7 (d,  $J_{C-P} = 10.0$  Hz), 128.4 (d,  $J_{C-P} = 13.0$  Hz), 128.4 (d,  $J_{C-P} = 13.0$  Hz), 81.7 (d,  $J_{C-P} = 5.6$  Hz), 49.9 (d,  $J_{C-P} = 5.2$  Hz), 47.6, 45.0, 37.5, 28.1, 26.8, 19.9, 18.8, 13.4. <sup>31</sup>P NMR (162 MHz CDCl<sub>3</sub>):  $\delta$  30.46. C<sub>22</sub>H<sub>27</sub>O<sub>2</sub>P. HRMS: Cal. 354.1749. Found

354.1731.



**4,4,5,5-tetramethyl-2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)-1,3,2-**

**dioxaphospholane 2-oxide (3aa).** Colorless oil;  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  4.71-4.67 (m, 1H), 2.35-2.29 (m, 1H), 1.91-1.84 (m, 1H), 1.75-1.70 (m, 1H), 1.67-1.63 (m, 2H), 1.45 (s, 6H), 1.41 (s, 6H), 1.29-1.20 (m, 2H), 0.90 (s, 3H), 0.86 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta$  88.1 (d,  $J_{\text{C-P}} = 6.1$  Hz), 85.1 (d,  $J_{\text{C-P}} = 6.2$  Hz), 49.6 (d,  $J_{\text{C-P}} = 5.9$  Hz), 47.7, 44.8, 37.0 (d,  $J_{\text{C-P}} = 2.9$  Hz), 28.0, 26.7, 24.2 (d,  $J_{\text{C-P}} = 1.1$  Hz), 24.1 (d,  $J_{\text{C-P}} = 1.3$  Hz), 23.7 (d,  $J_{\text{C-P}} = 5.0$  Hz), 23.6 (d,  $J_{\text{C-P}} = 5.1$  Hz), 19.9, 18.8, 13.2.  $^{31}\text{P}$  NMR (162 MHz  $\text{CDCl}_3$ ):  $\delta$  12.65.  $\text{C}_{16}\text{H}_{29}\text{O}_4\text{P}$ . HRMS: Cal. 316.1803. Found 316.1791.

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6. Copies of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra

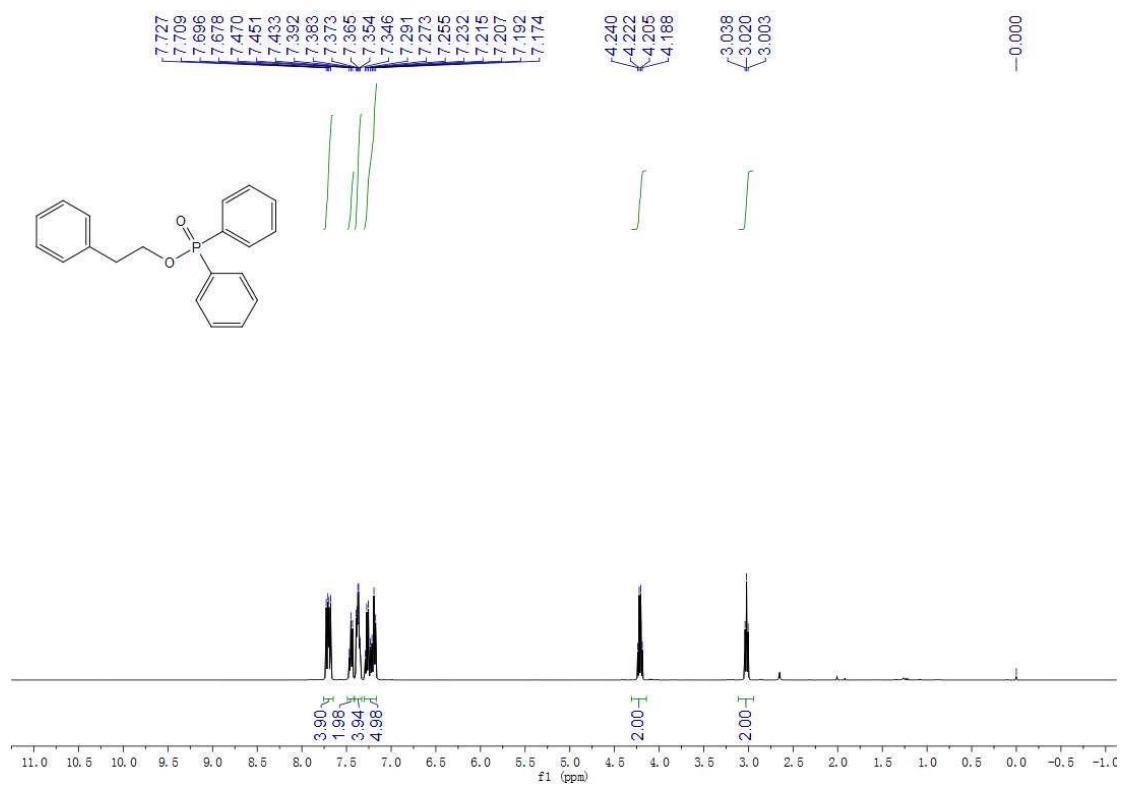


Figure 1. 3a- $^1\text{H}$  NMR

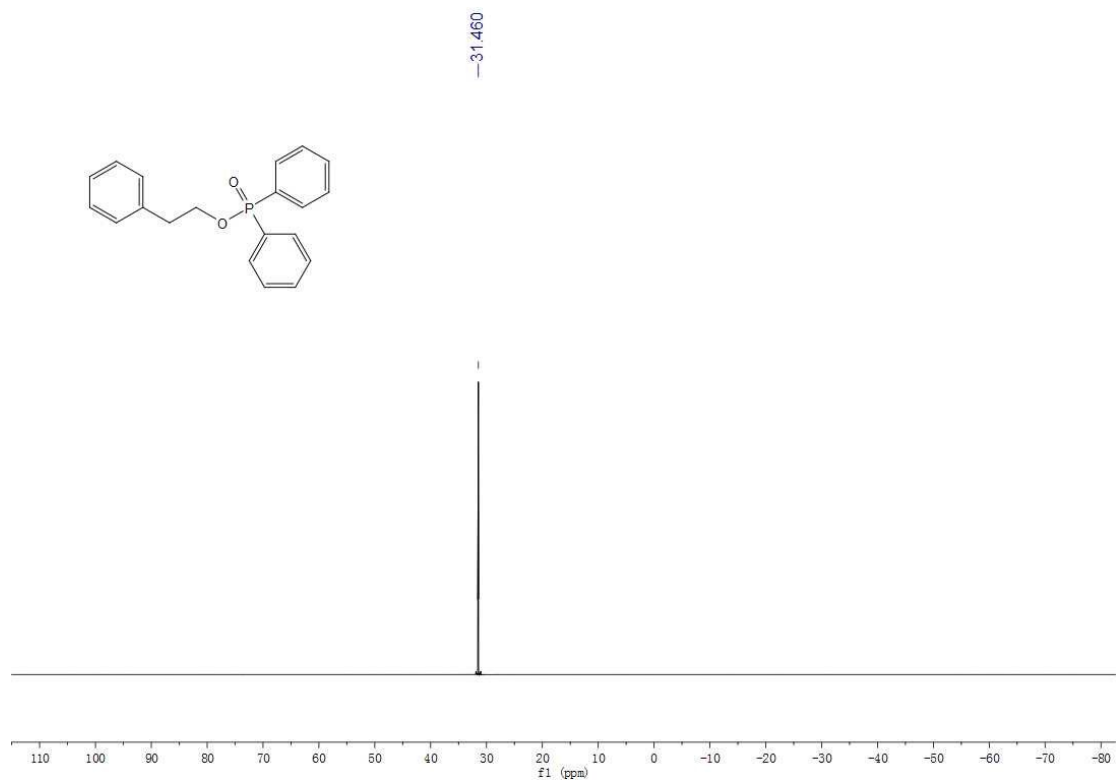


Figure 2. 3a- $^{31}\text{P}$  NMR

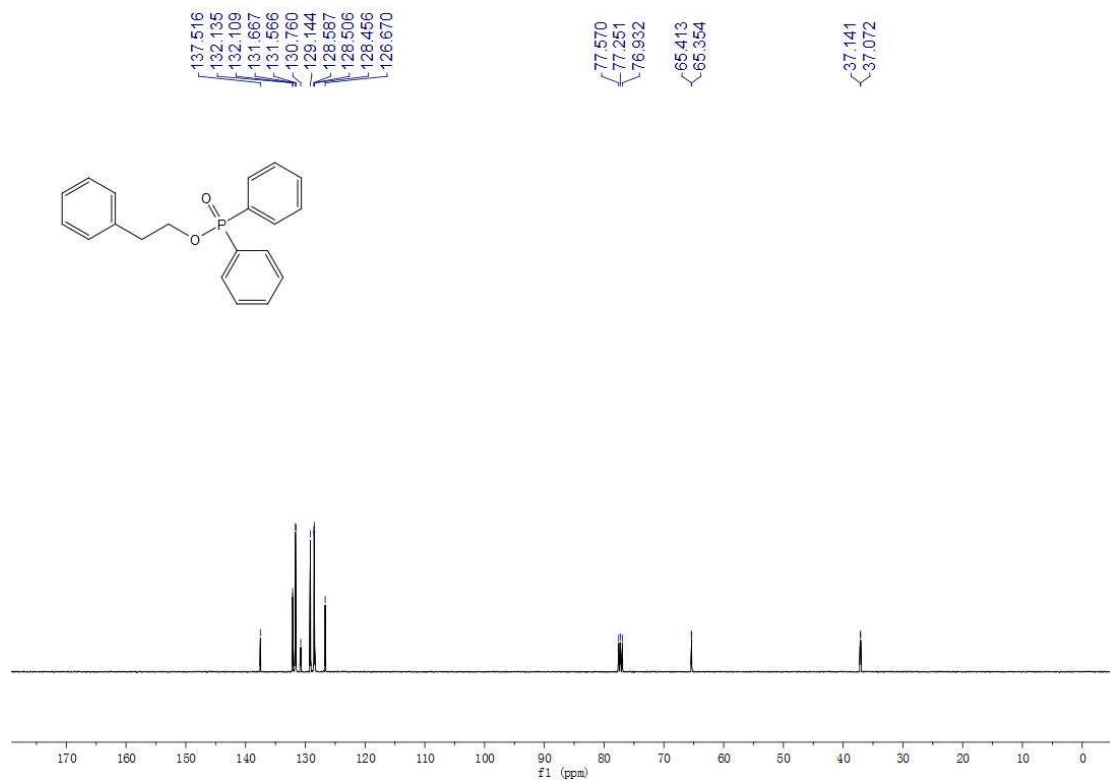


Figure 3. 3a- $^{13}\text{C}$  NMR

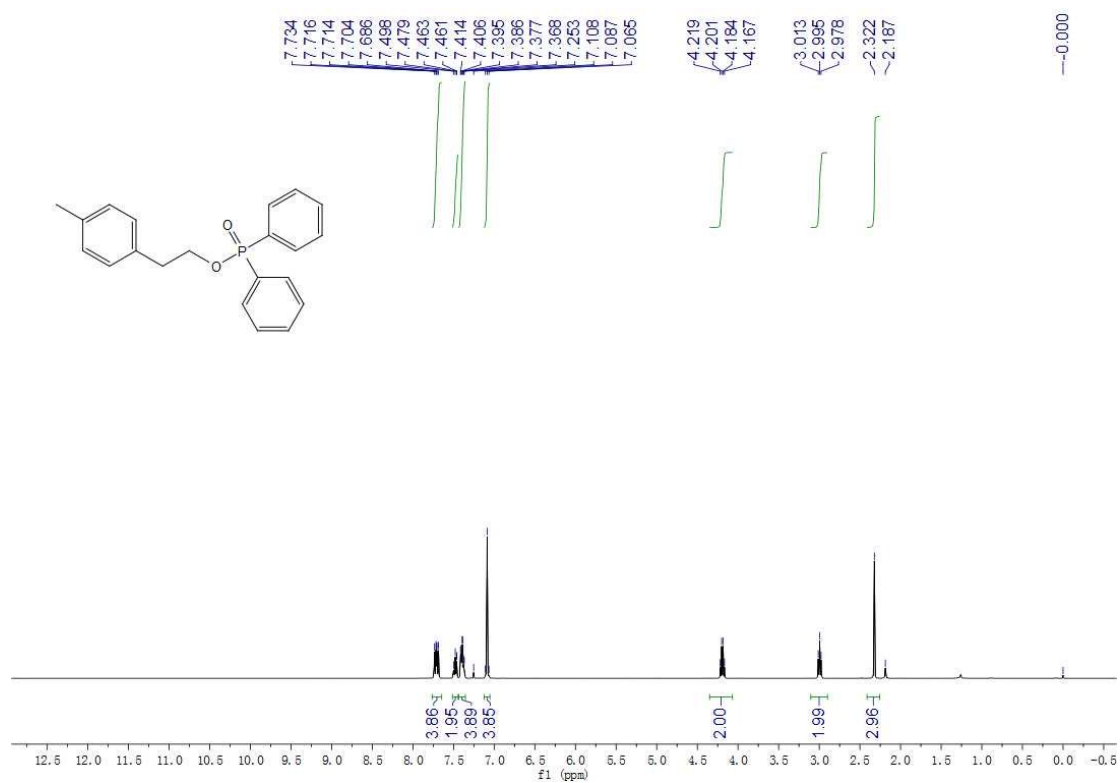


Figure 4. 3b- $^1\text{H}$  NMR

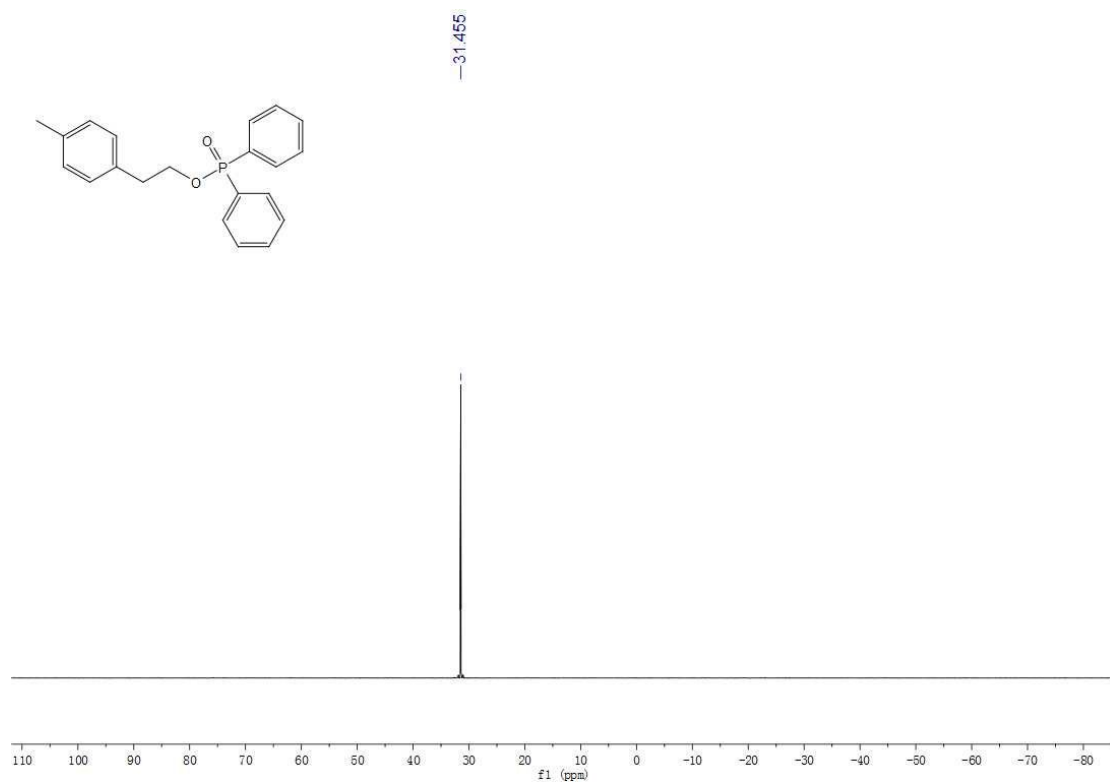


Figure 5. 3b-<sup>31</sup>P NMR

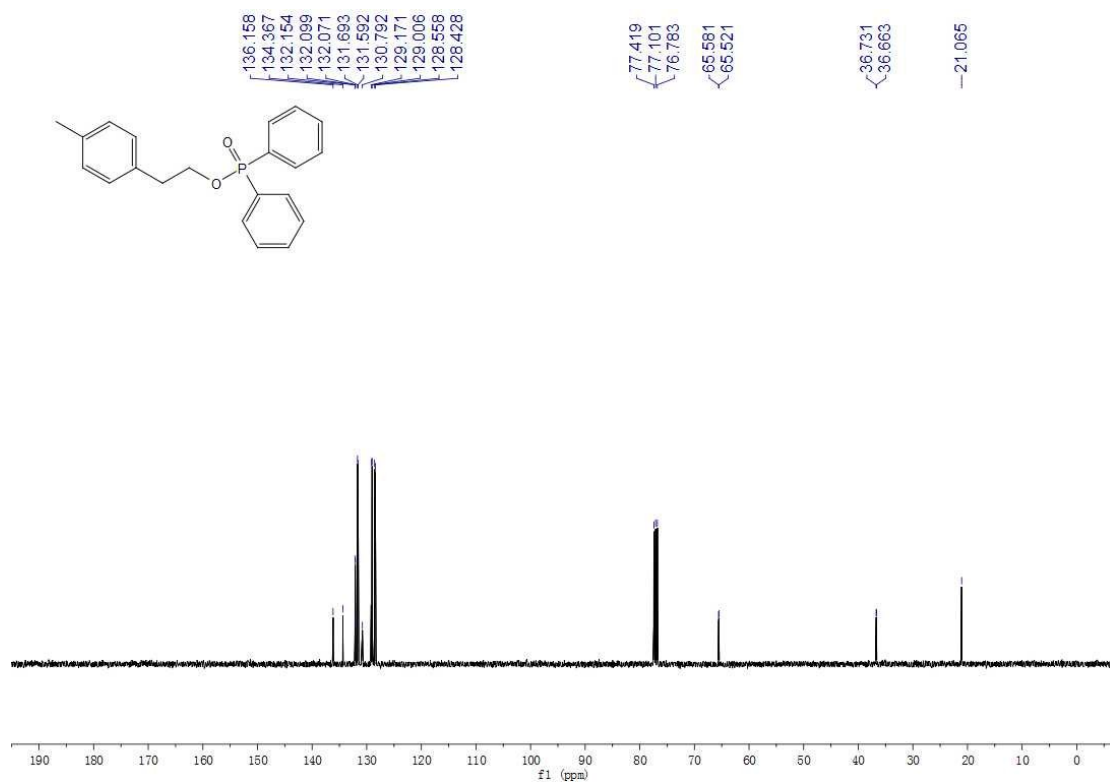


Figure 6. 3b-<sup>13</sup>C NMR

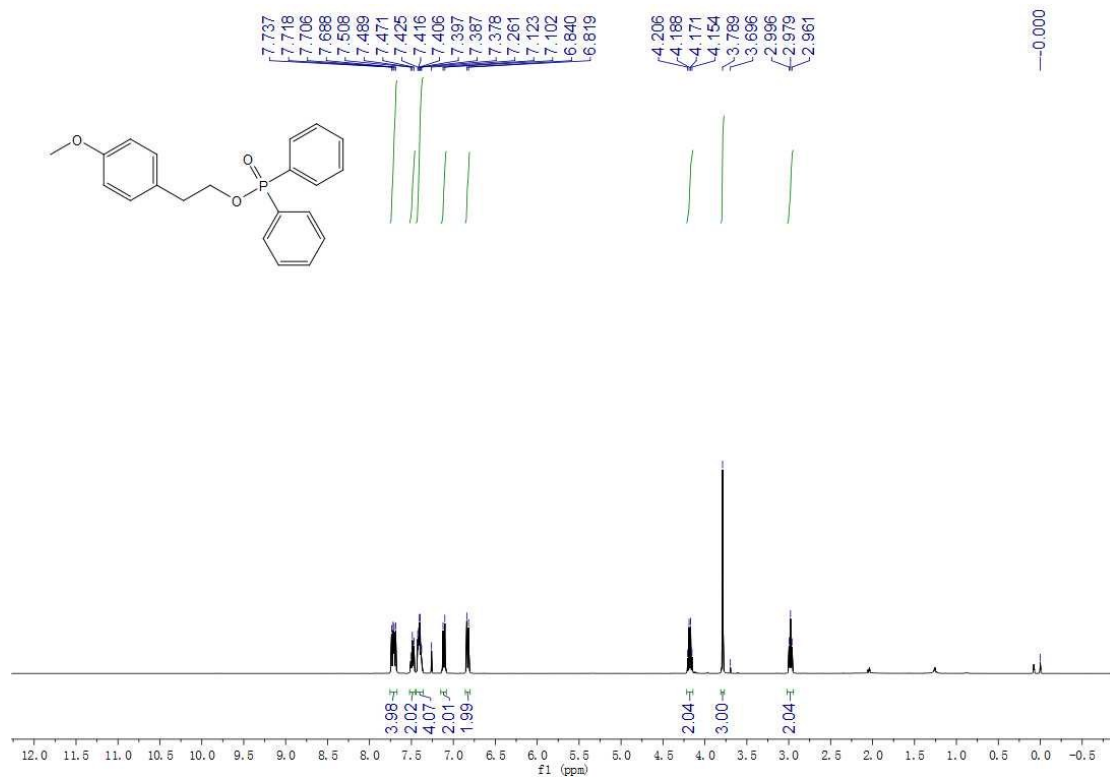


Figure 7. 3c-<sup>1</sup>H NMR

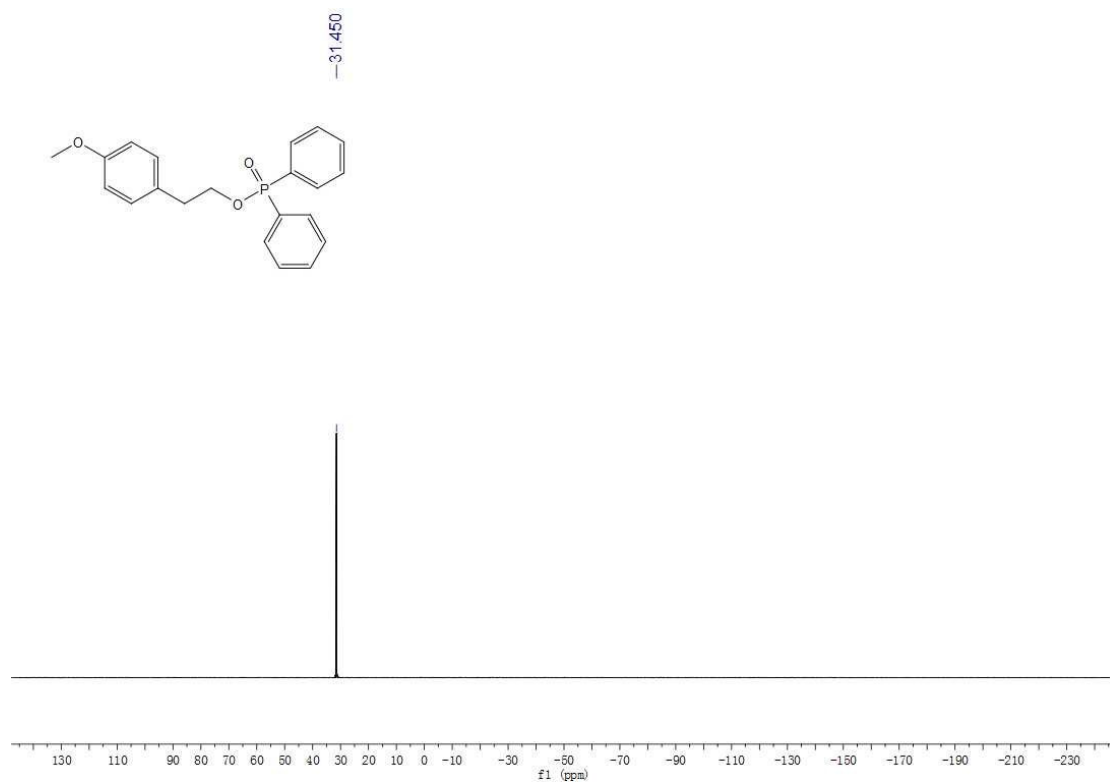


Figure 8. 3c-<sup>31</sup>P NMR

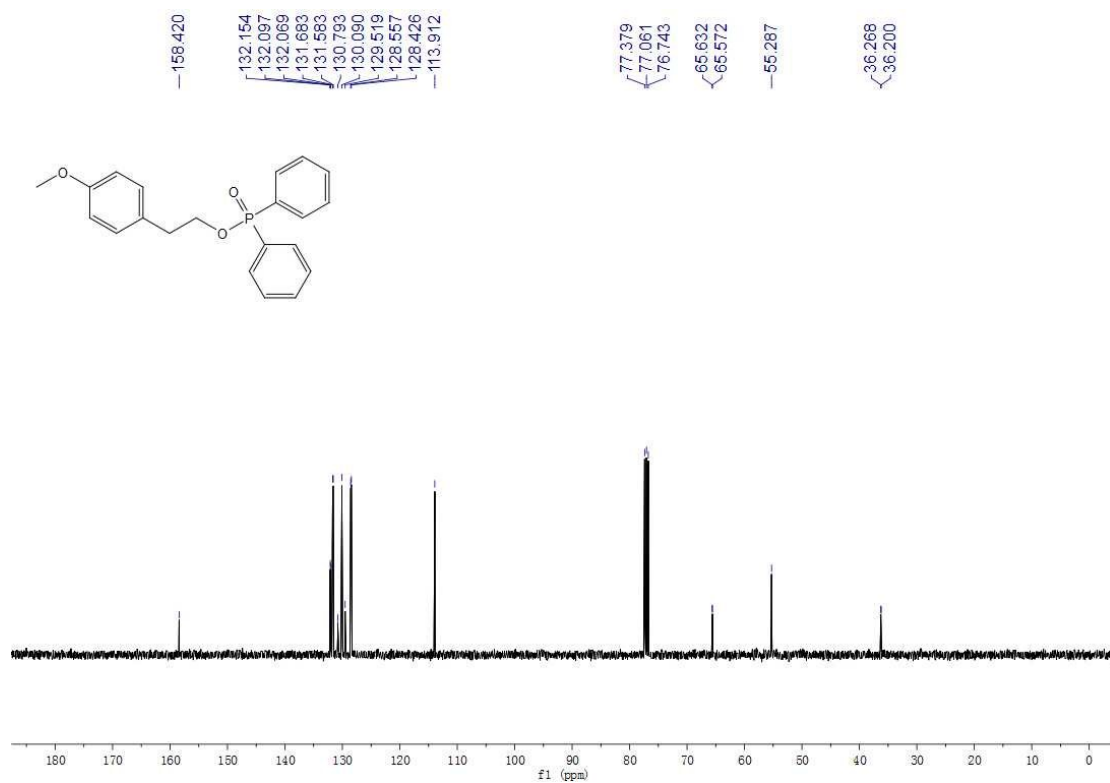


Figure 9. 3c- $^{13}\text{C}$  NMR

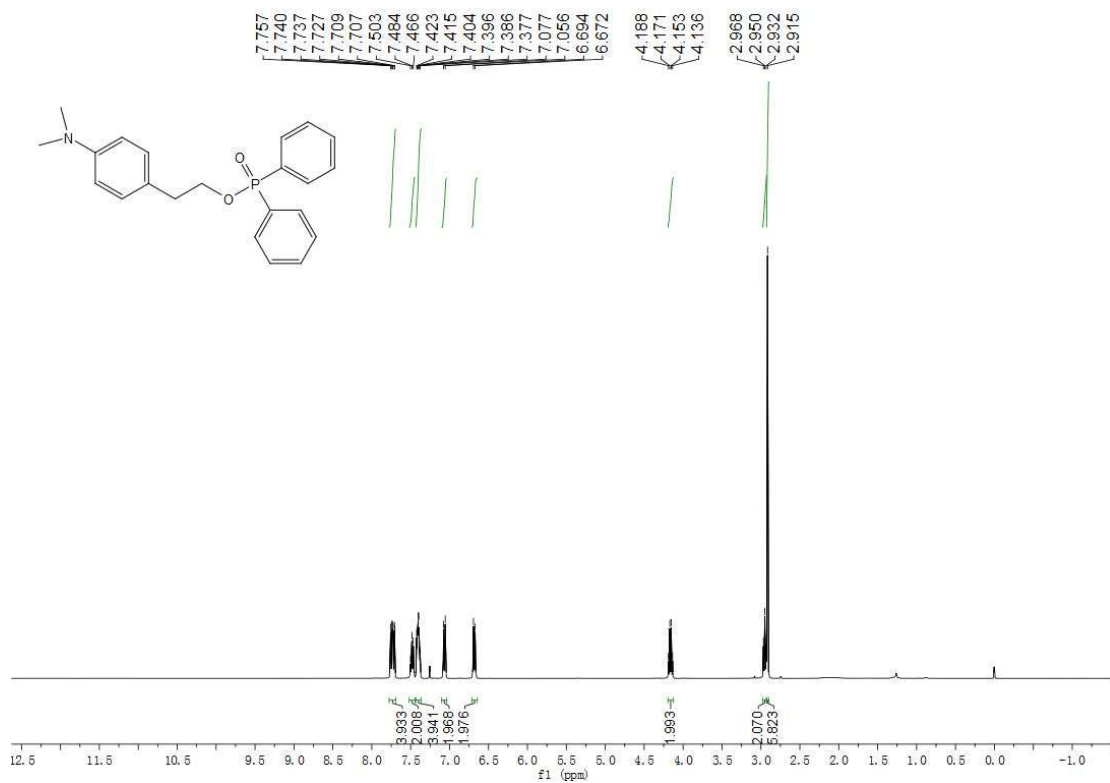


Figure 10. 3d- $^1\text{H}$  NMR

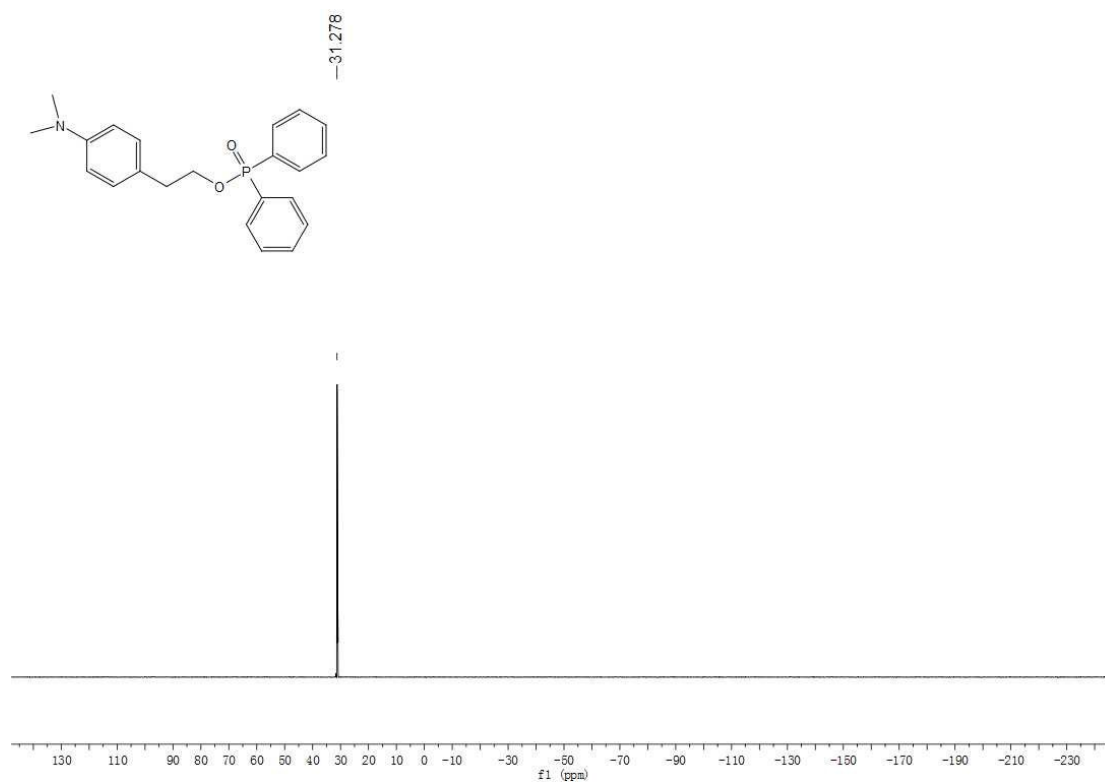


Figure 11. 3d- $^{31}\text{P}$  NMR

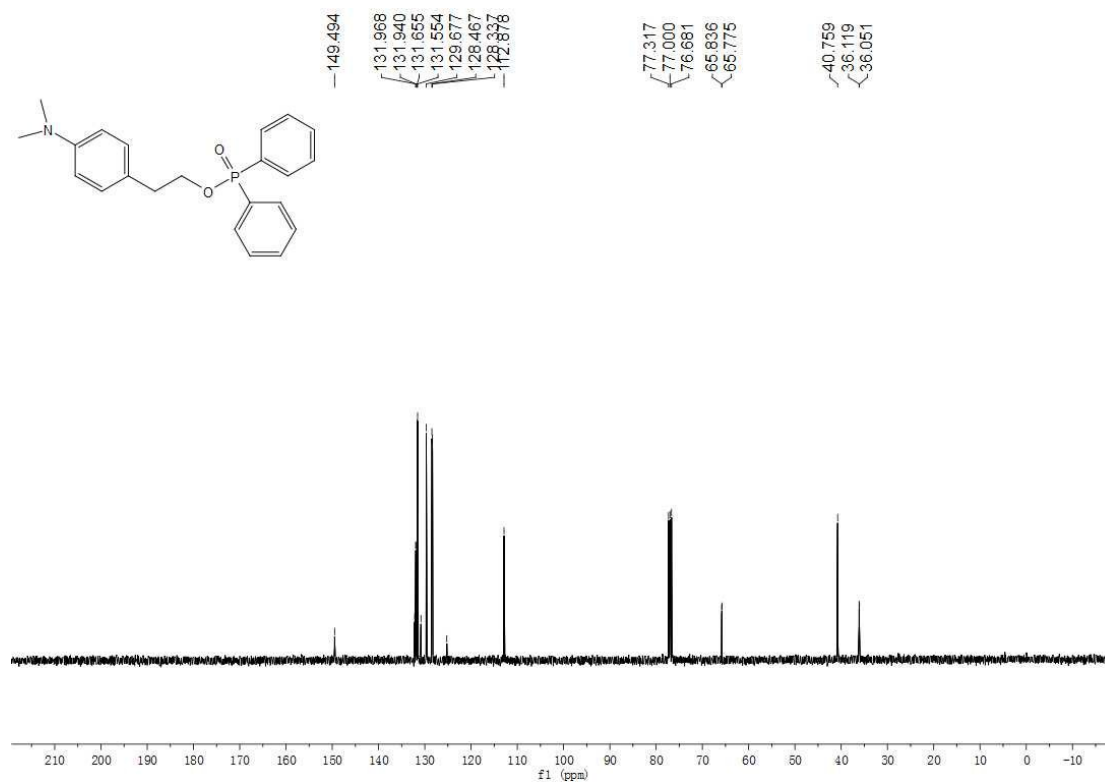


Figure 12. 3d- $^{13}\text{C}$  NMR

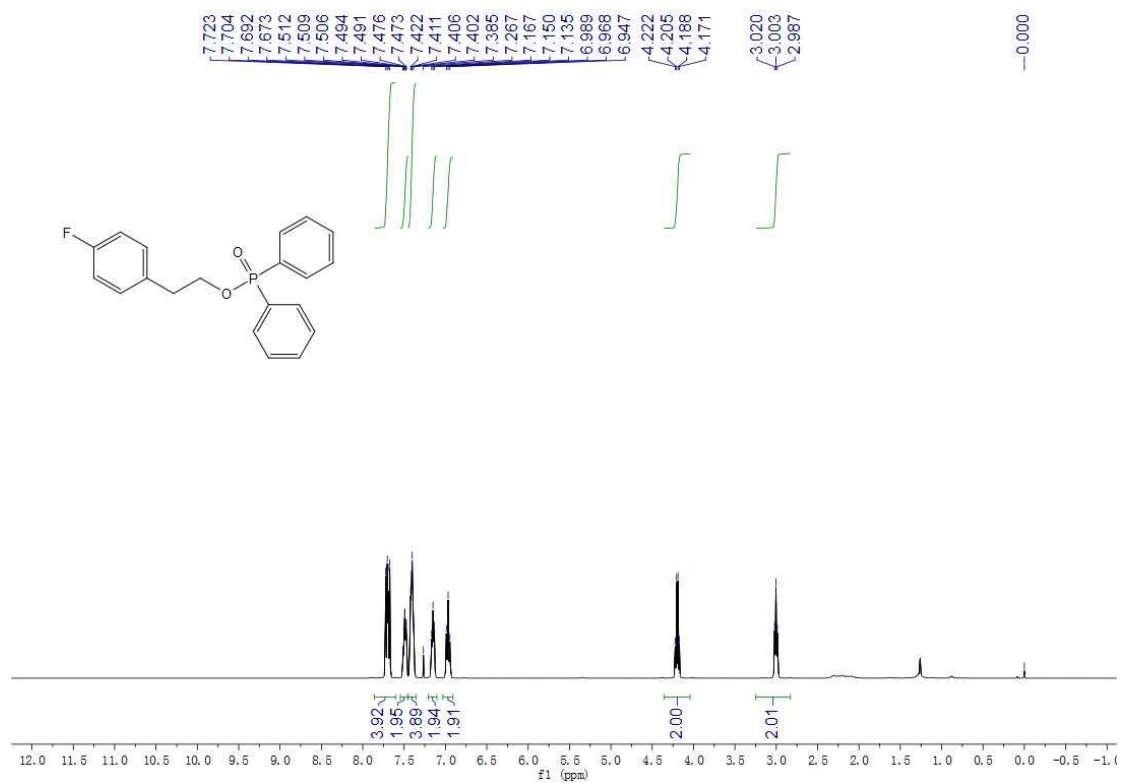


Figure 13.  $^3\text{e}$ - $^1\text{H}$  NMR

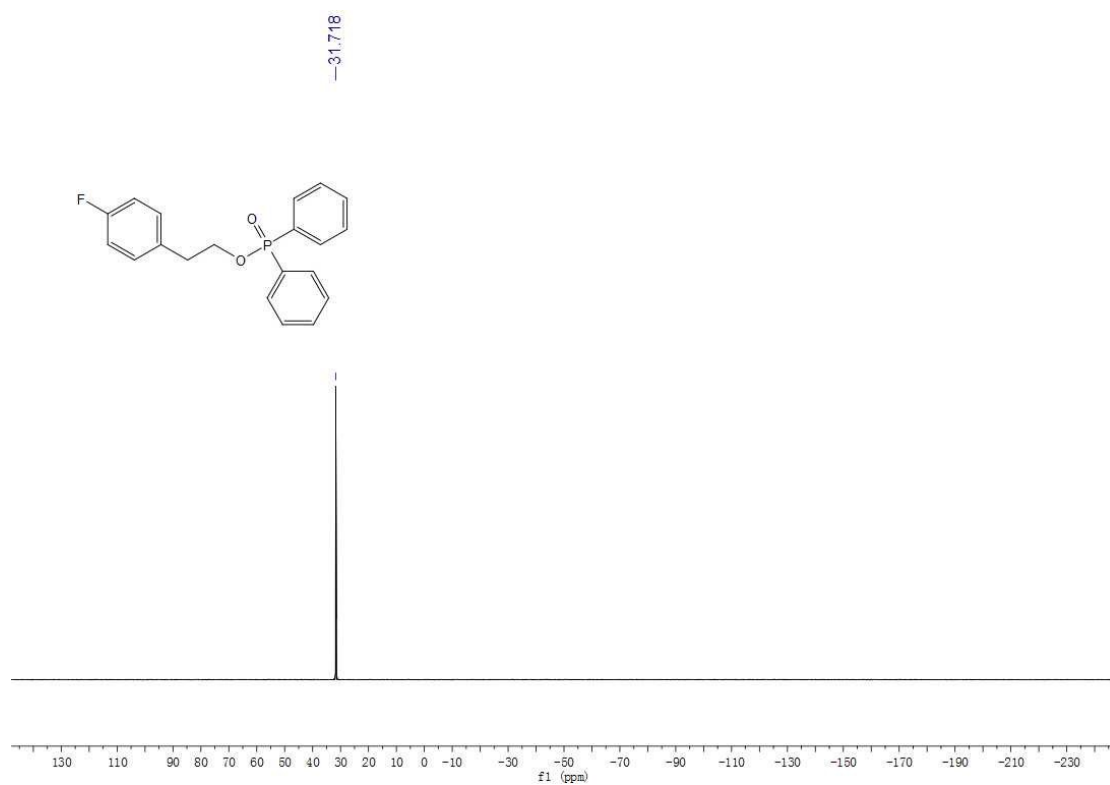


Figure 14.  $^3\text{e}$ - $^{31}\text{P}$  NMR

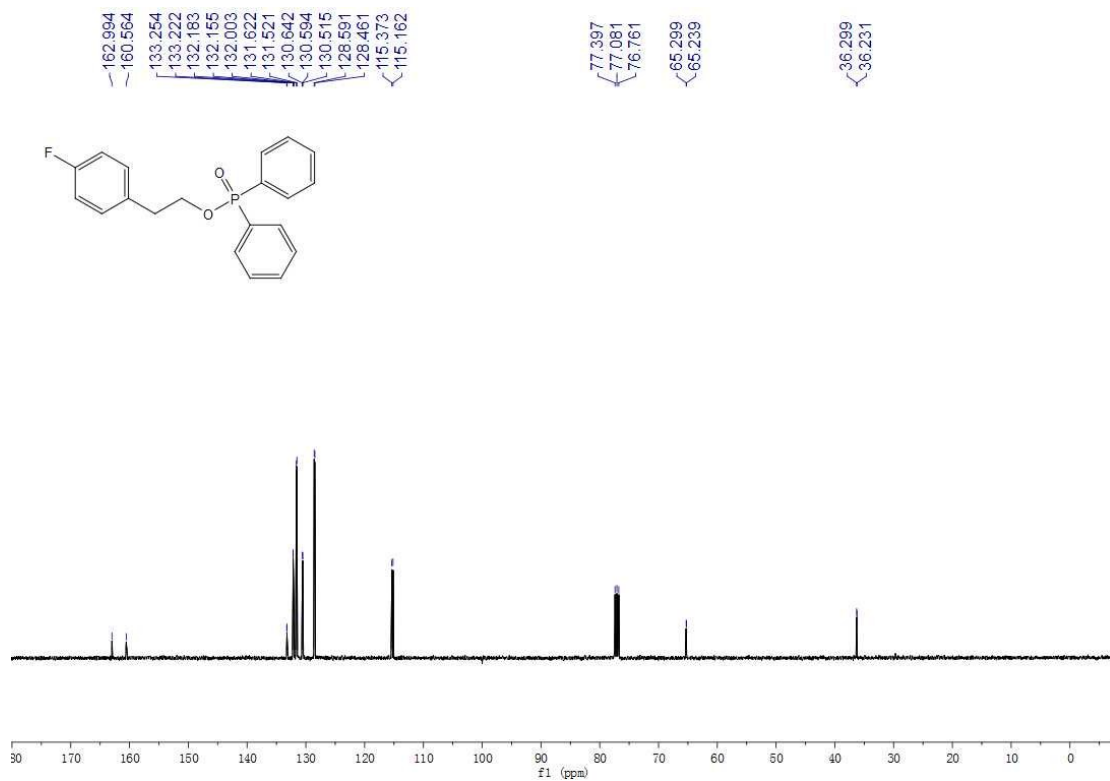


Figure 15. 3e-<sup>13</sup>C NMR

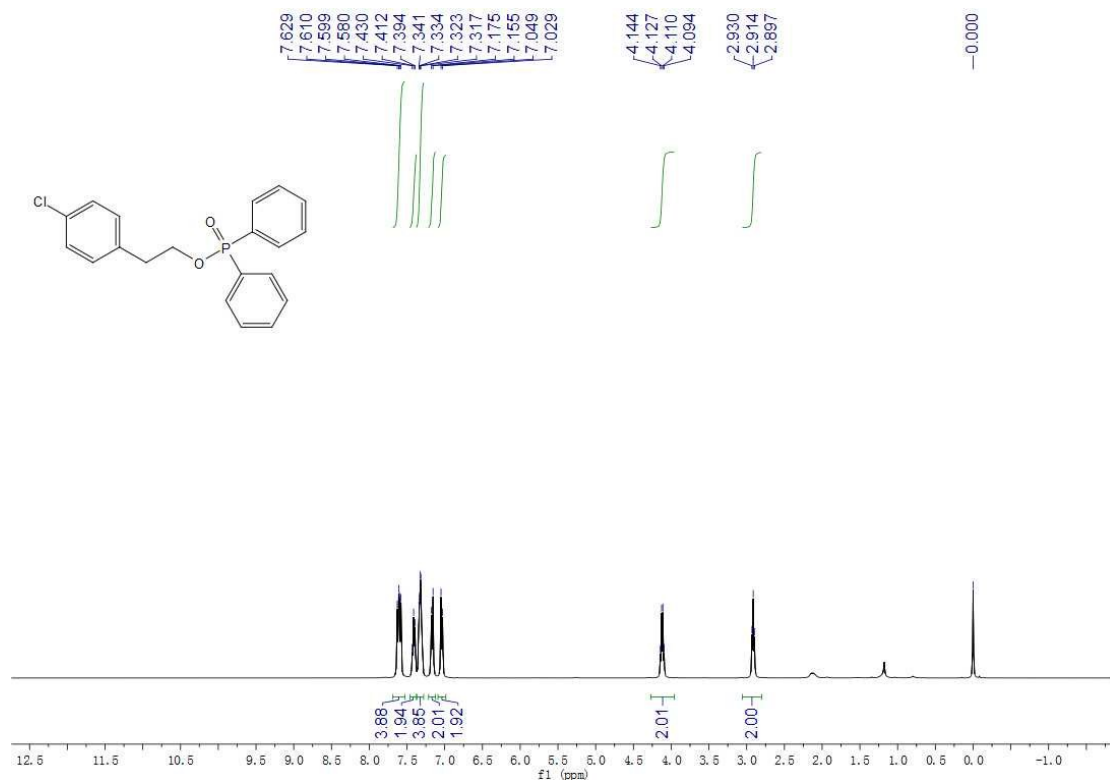


Figure 16. 3f-<sup>1</sup>H NMR



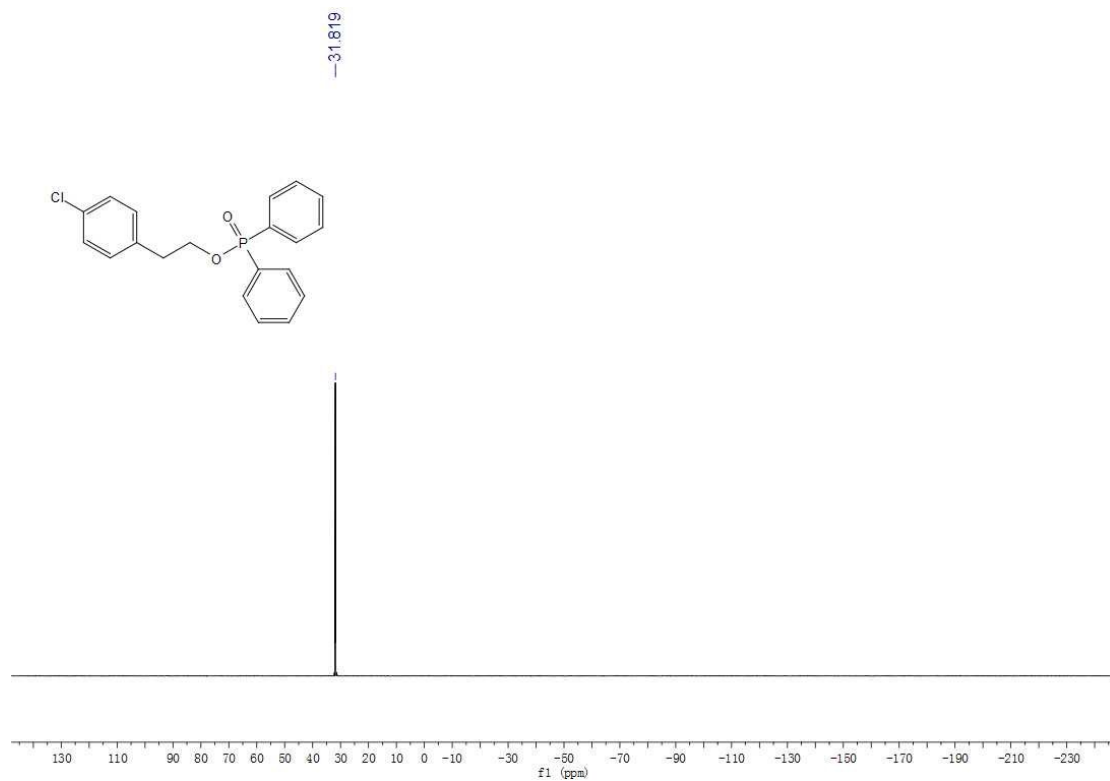


Figure 17. 3f-<sup>31</sup>P NMR

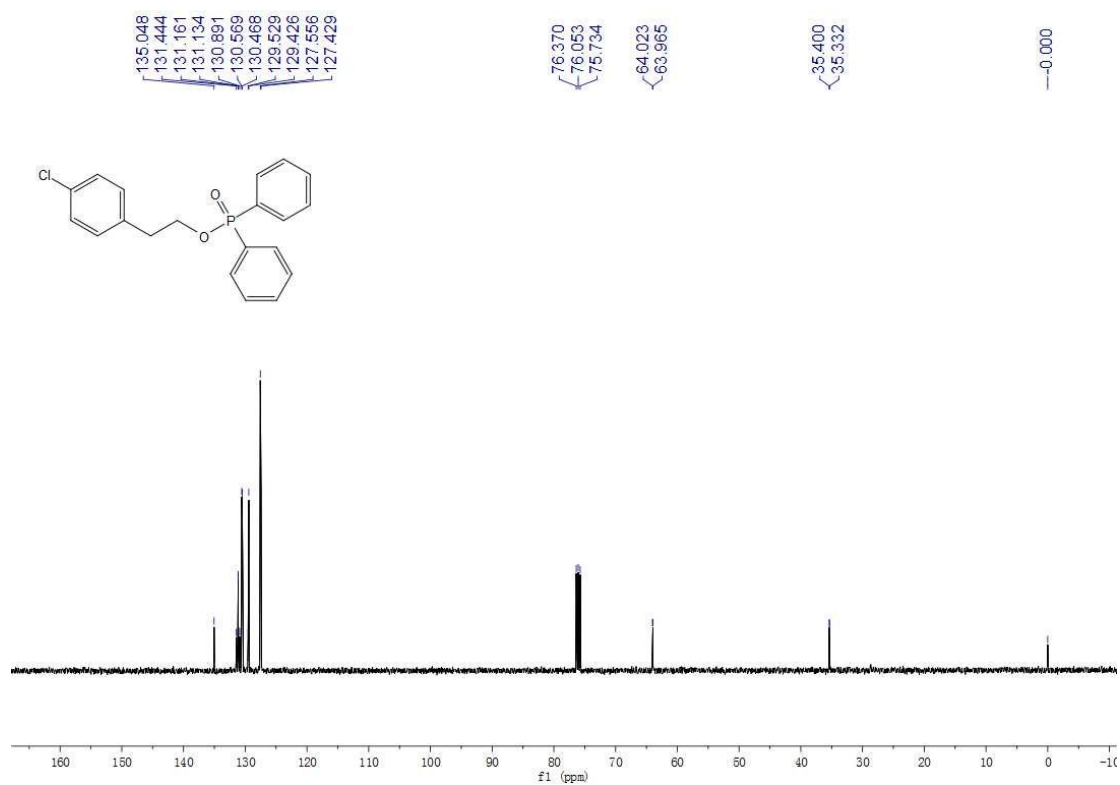


Figure 18. 3f-<sup>13</sup>C NMR

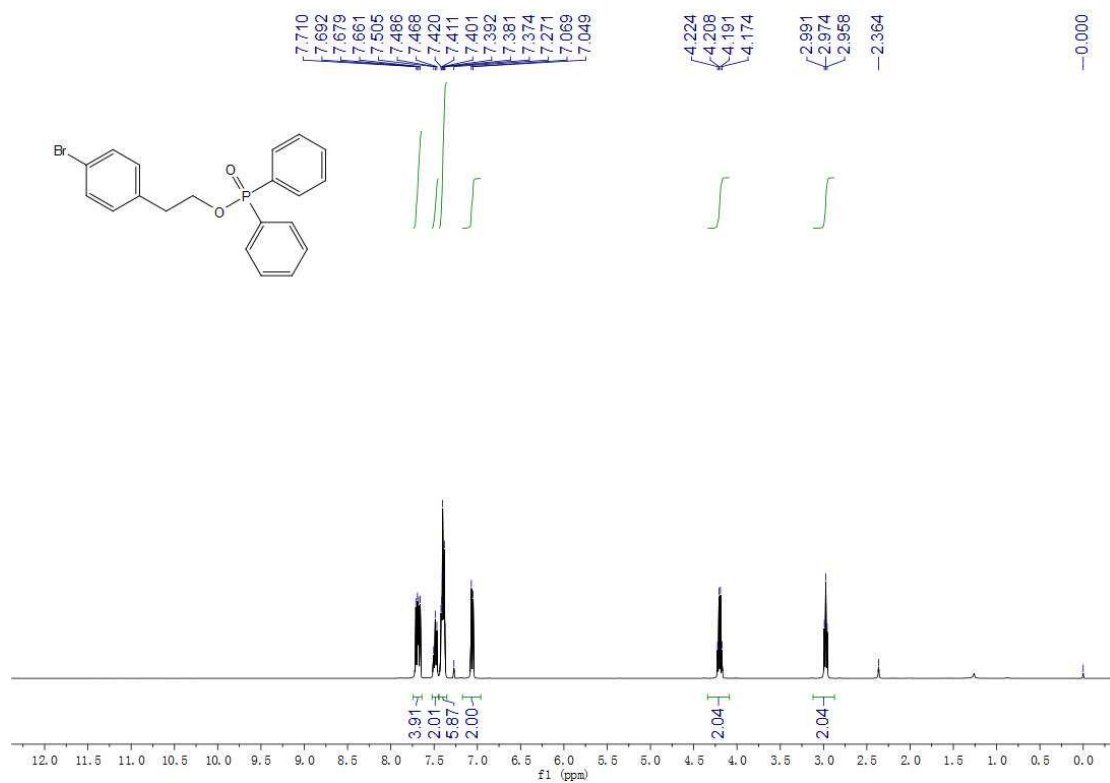


Figure 19.  $^3\text{g-}^1\text{H}$  NMR

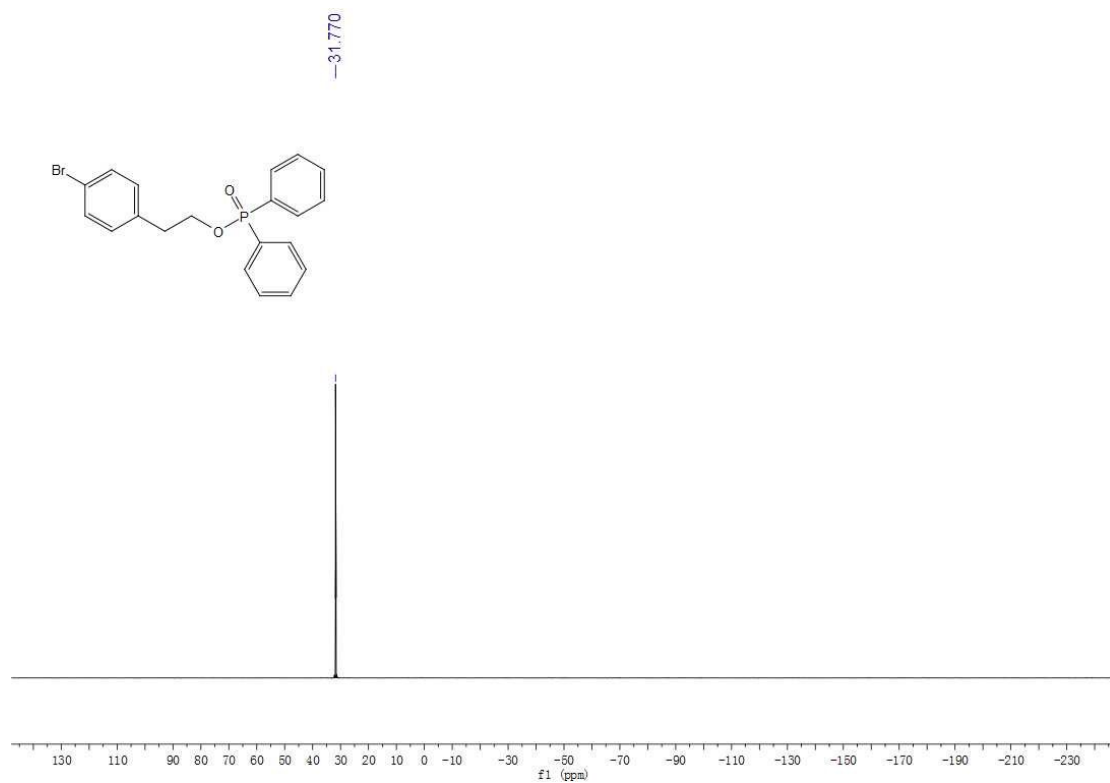


Figure 20.  $^3\text{g-}^{31}\text{P}$  NMR

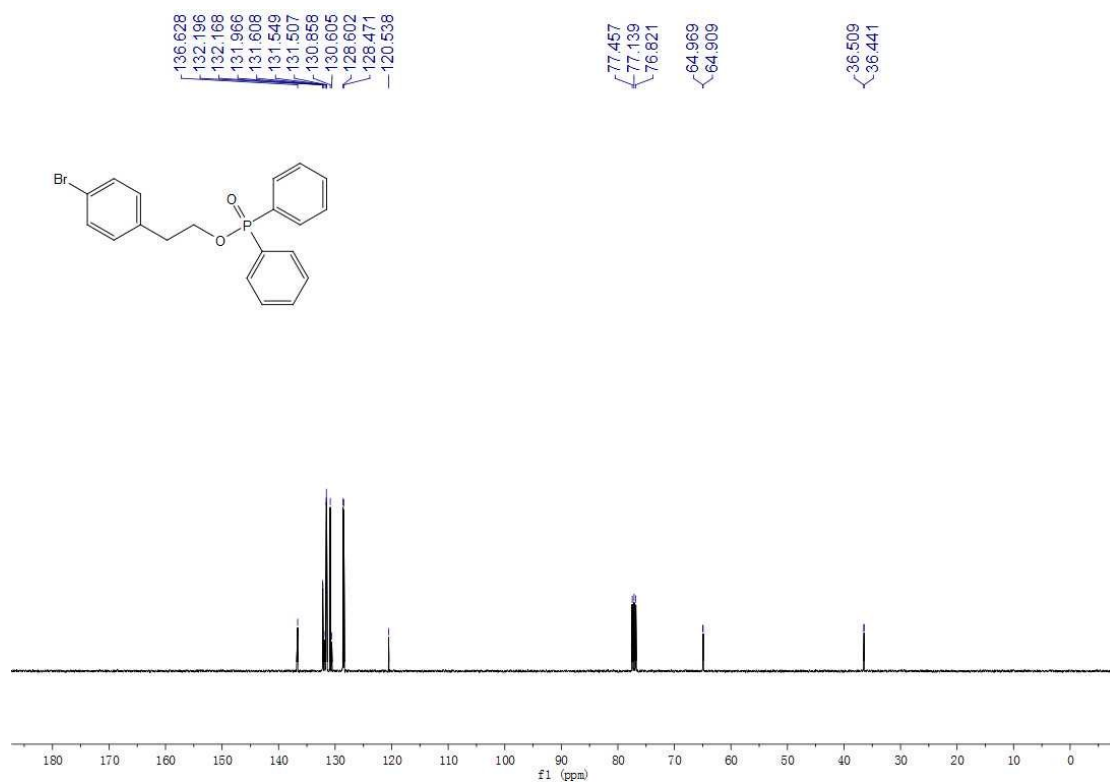


Figure 21. <sup>3g</sup>-<sup>13</sup>C NMR

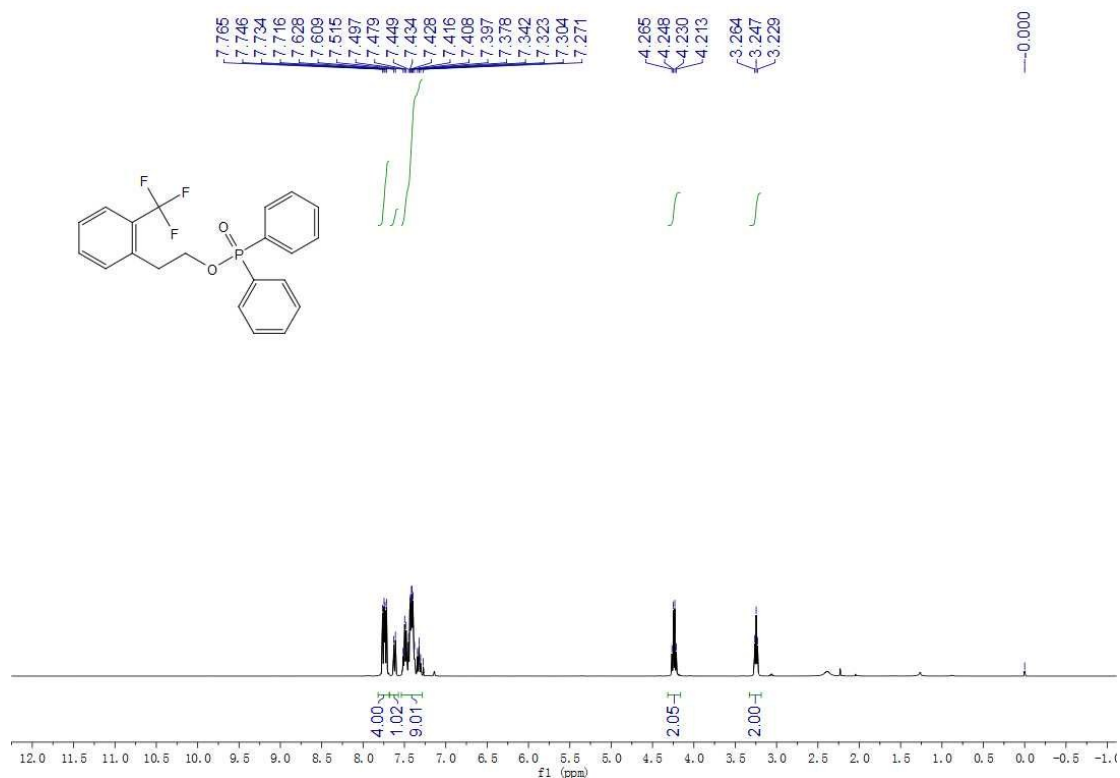


Figure 22. <sup>3h</sup>-<sup>1</sup>H NMR

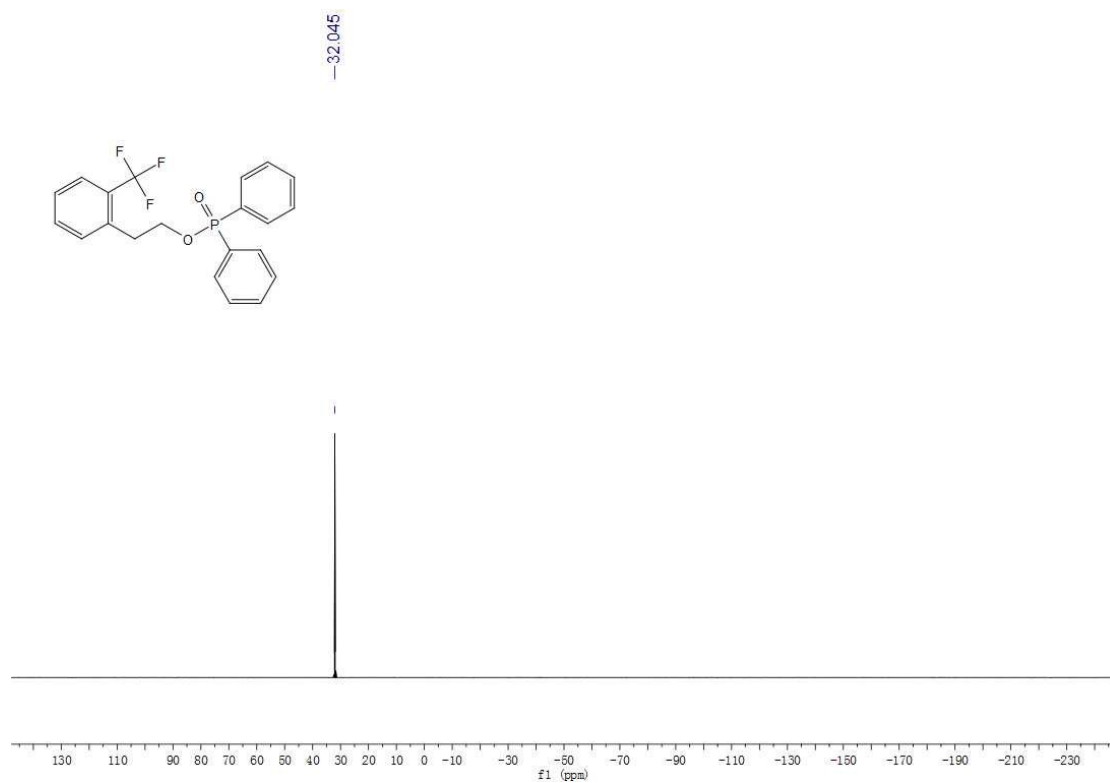


Figure 23.  $3\text{h-}^{31}\text{P}$  NMR

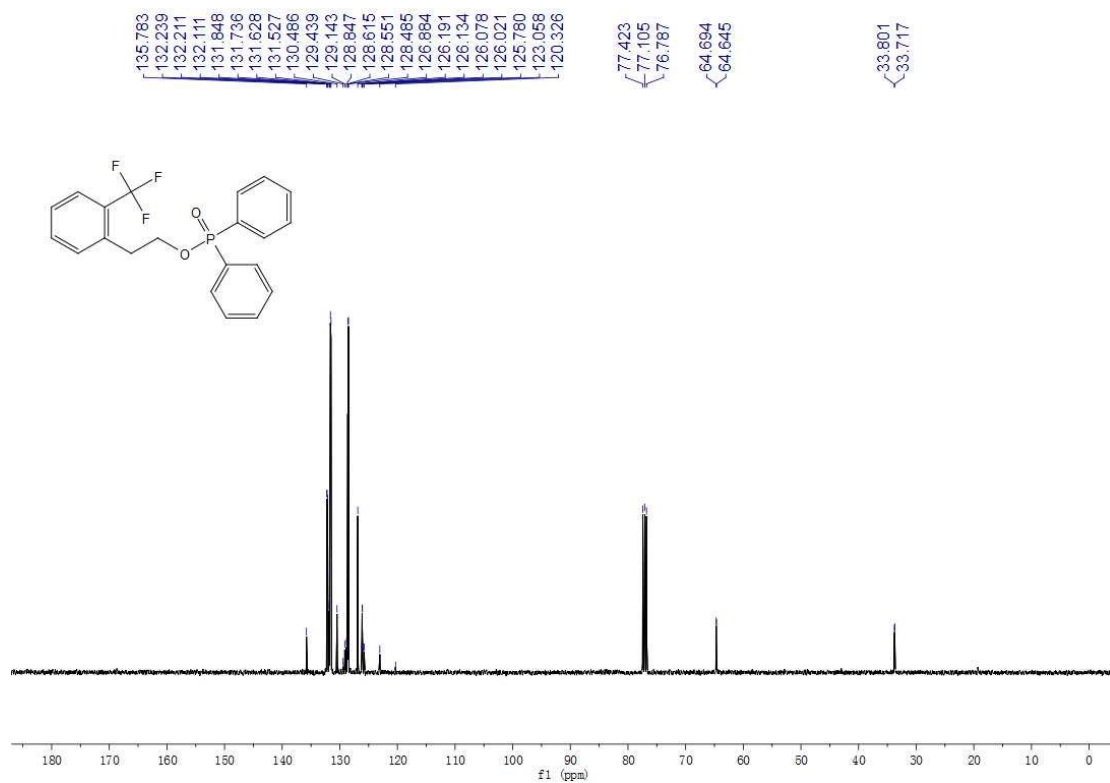


Figure 24.  $3\text{h-}^{13}\text{C}$  NMR

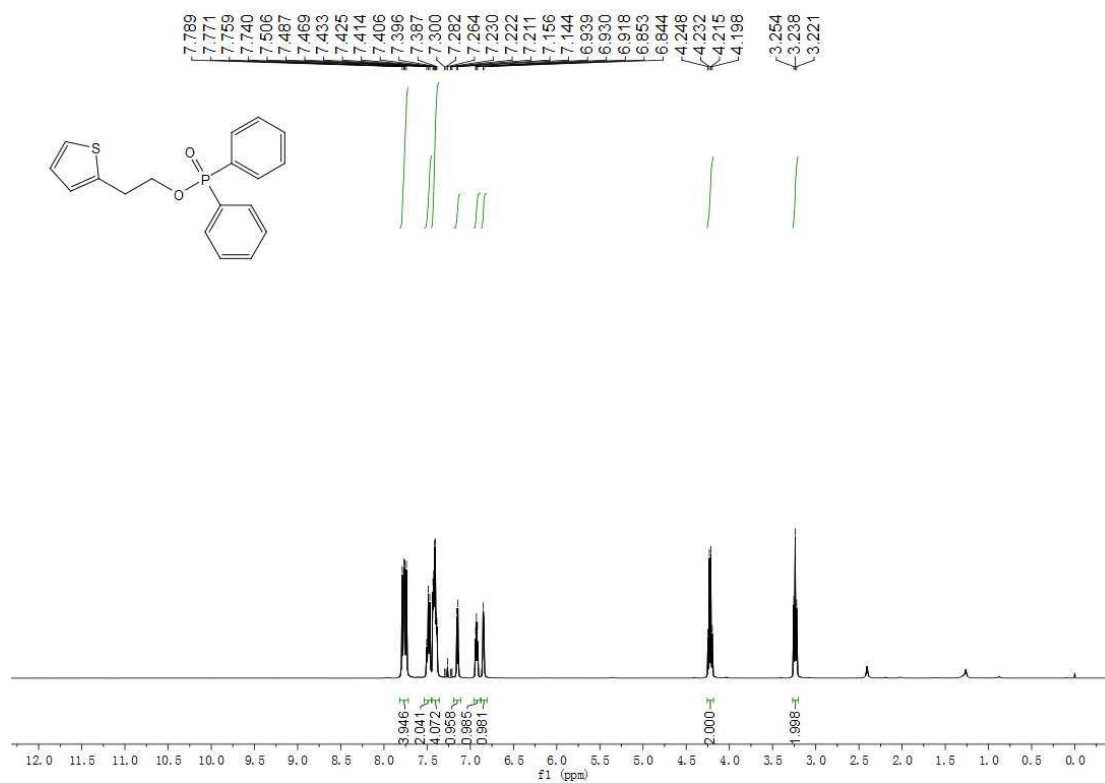


Figure 25. <sup>31</sup>H NMR

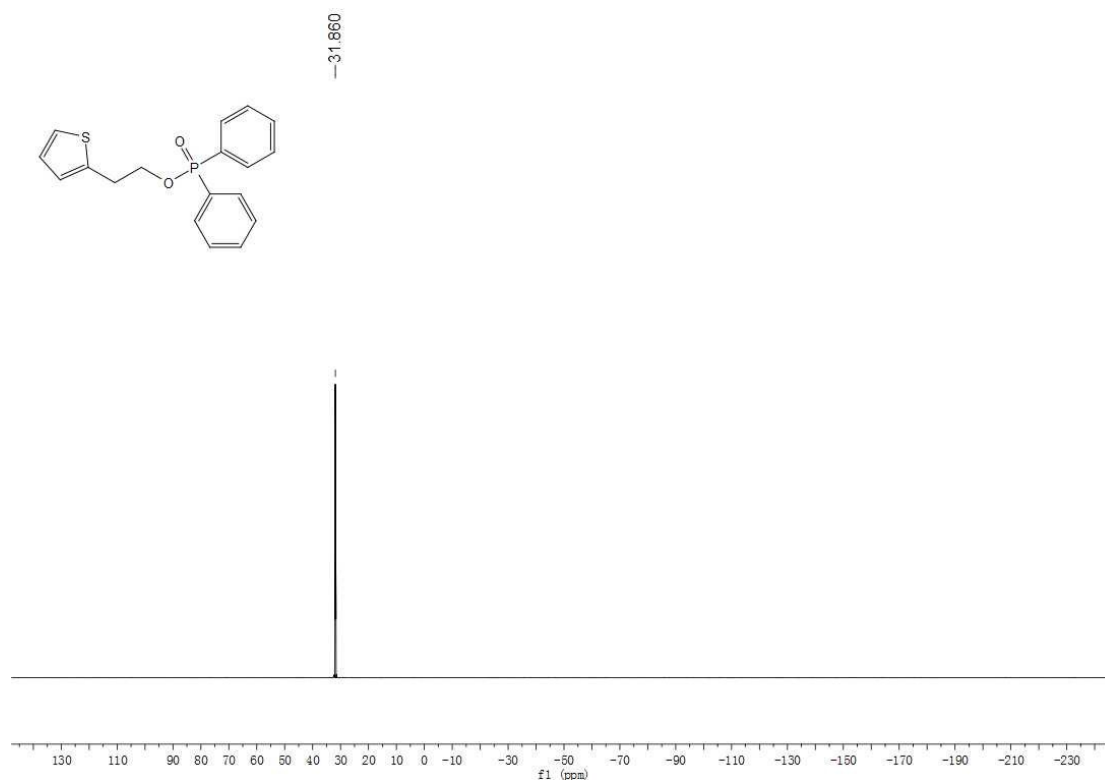


Figure 26. <sup>31</sup>P NMR

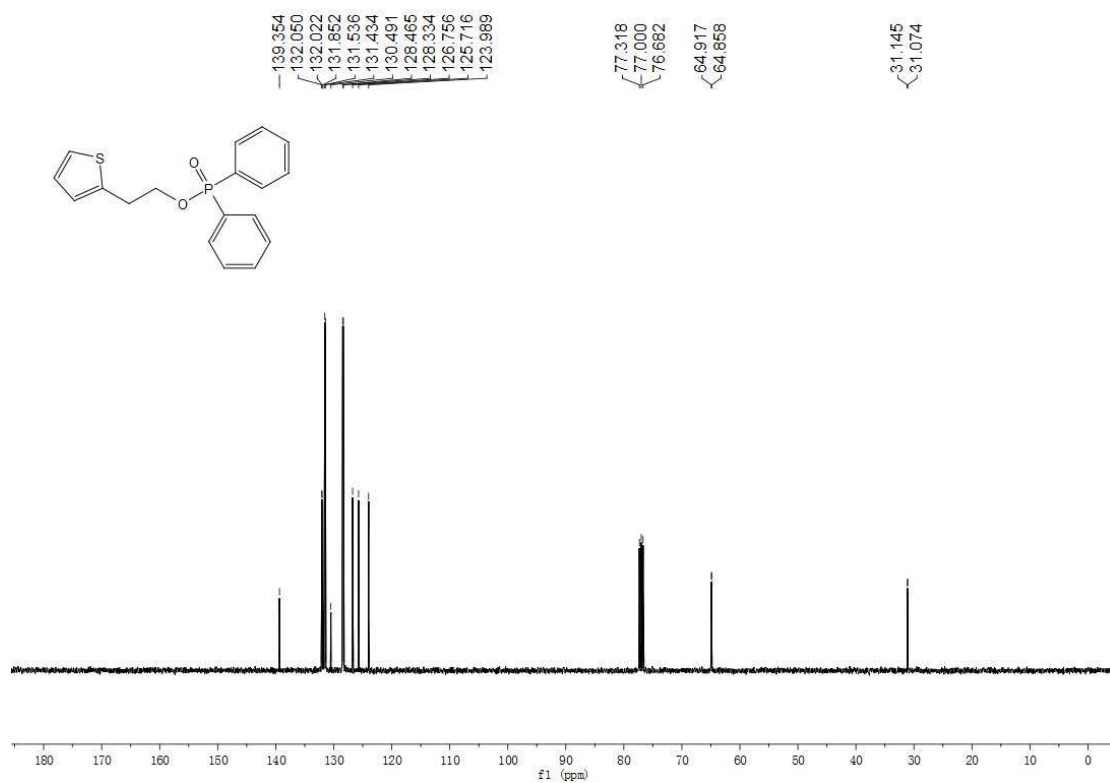


Figure 27.  $^{13}\text{C}$  NMR

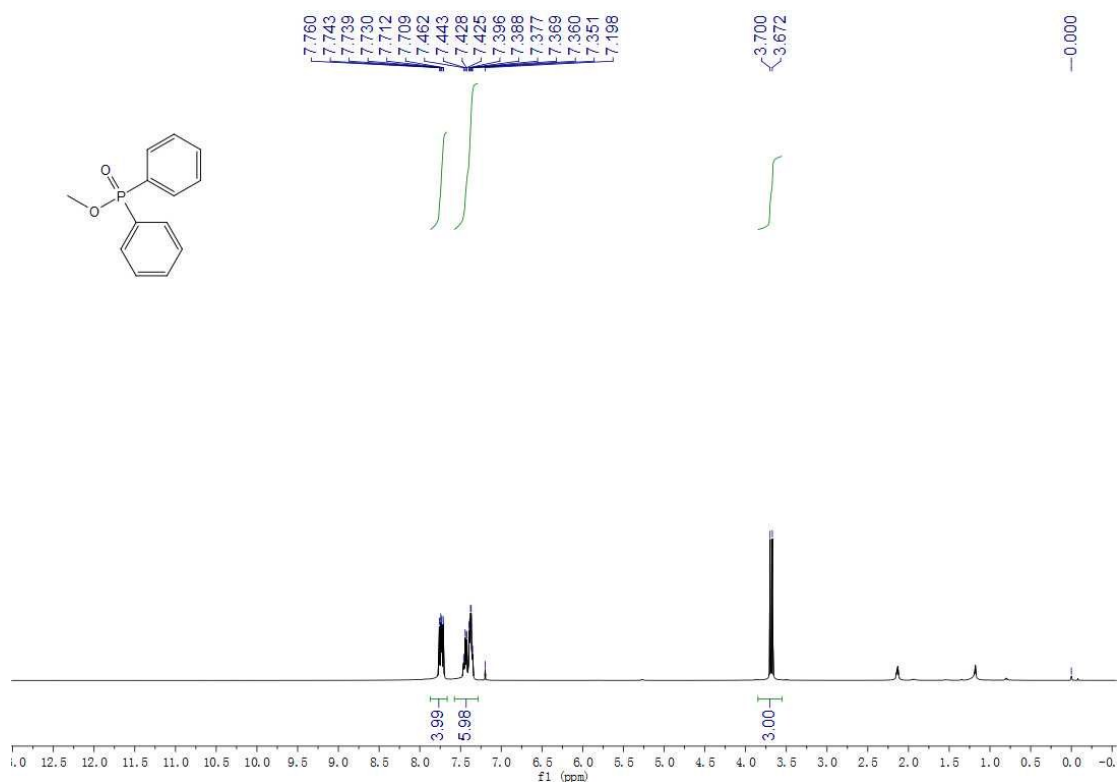


Figure 28.  $^1\text{H}$  NMR

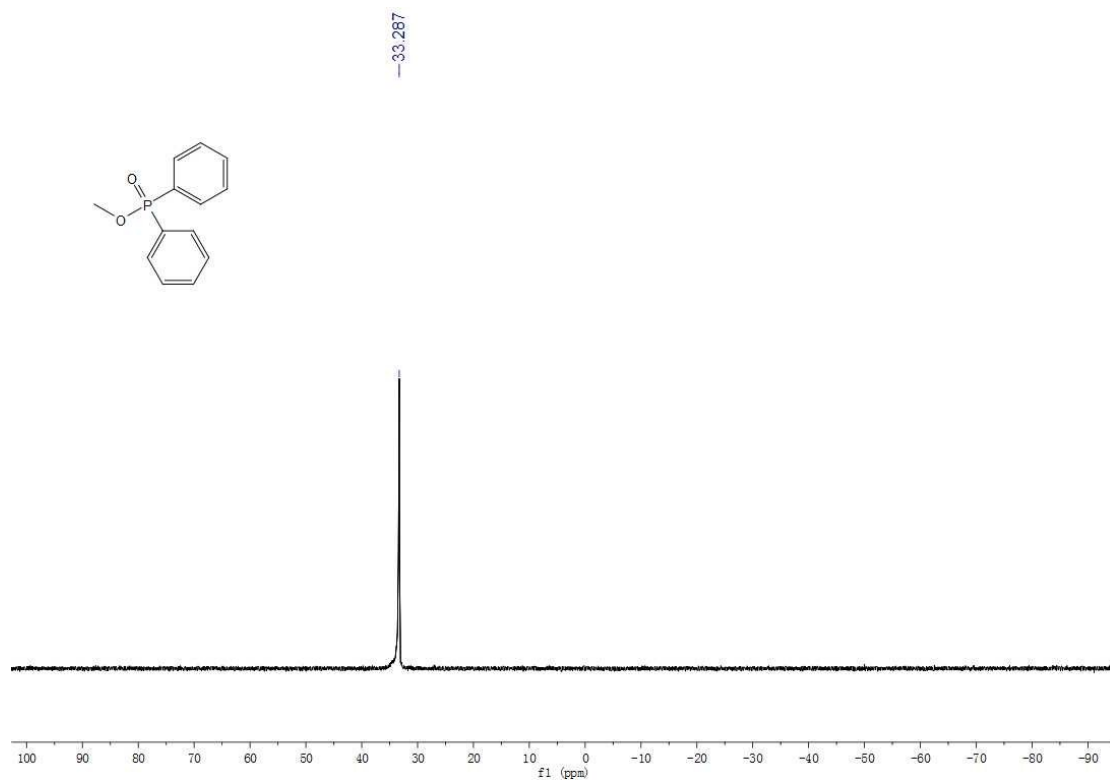


Figure 29.  $^{31}\text{P}$  NMR

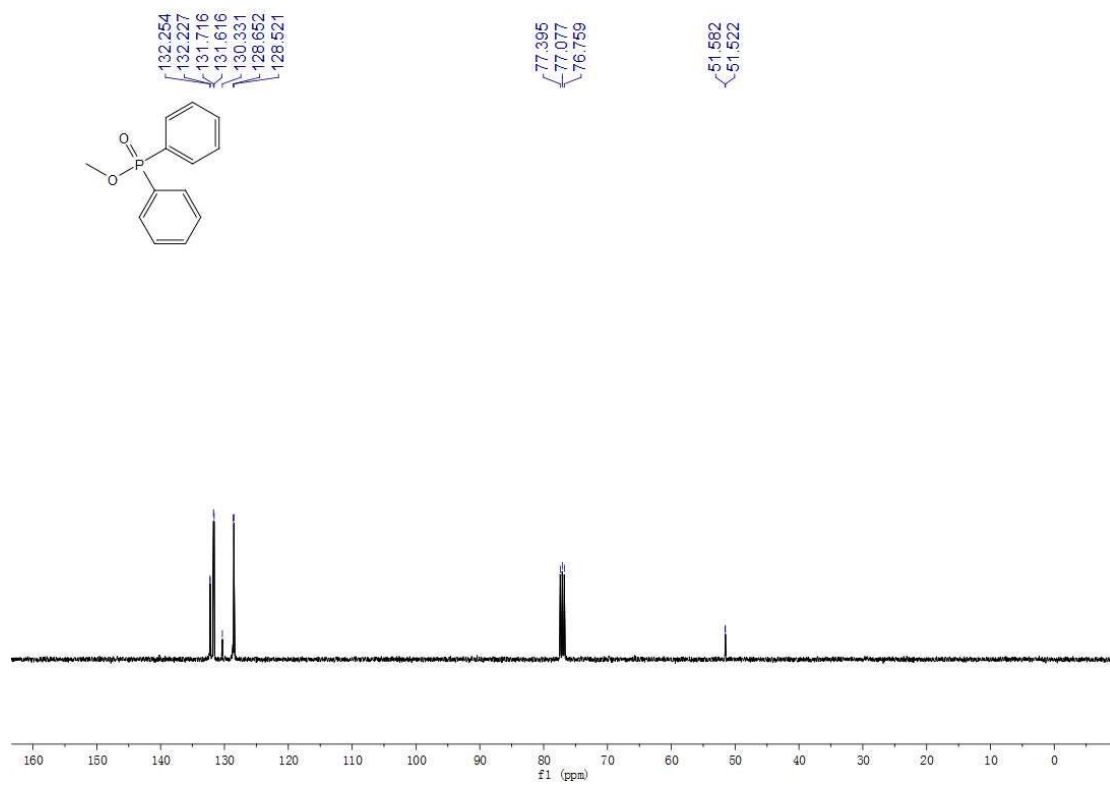


Figure 30.  $^{13}\text{C}$  NMR

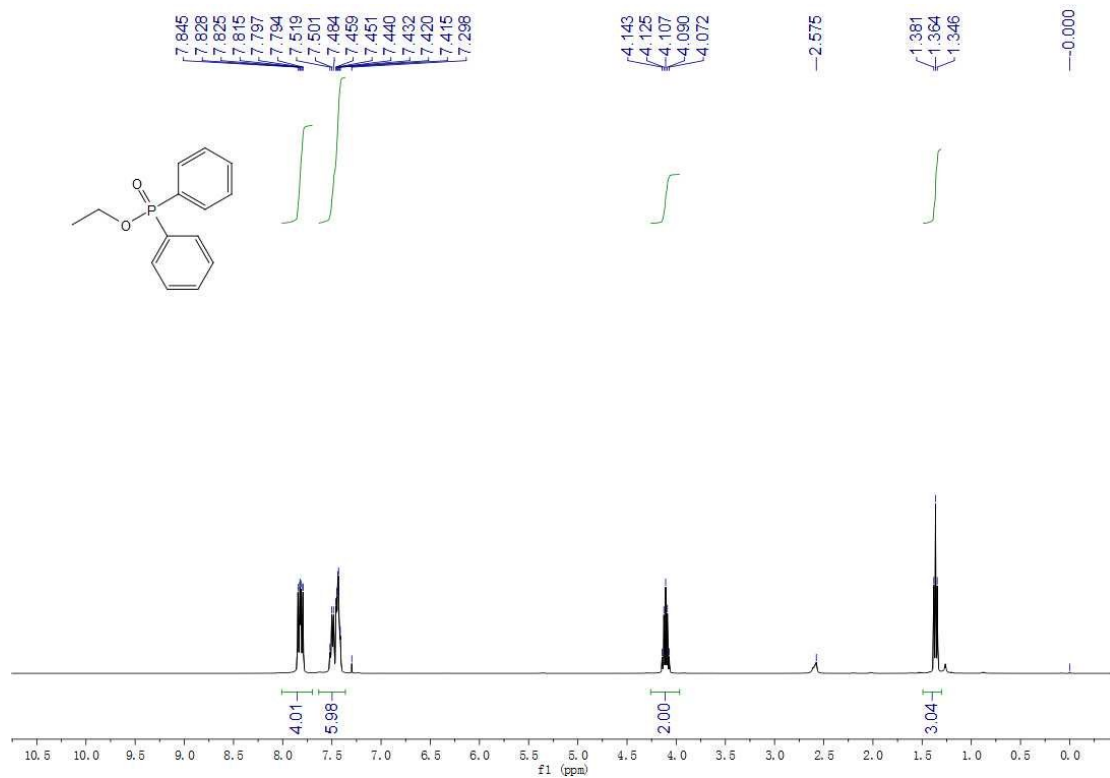


Figure 31.  $3k$ - $^1\text{H}$  NMR

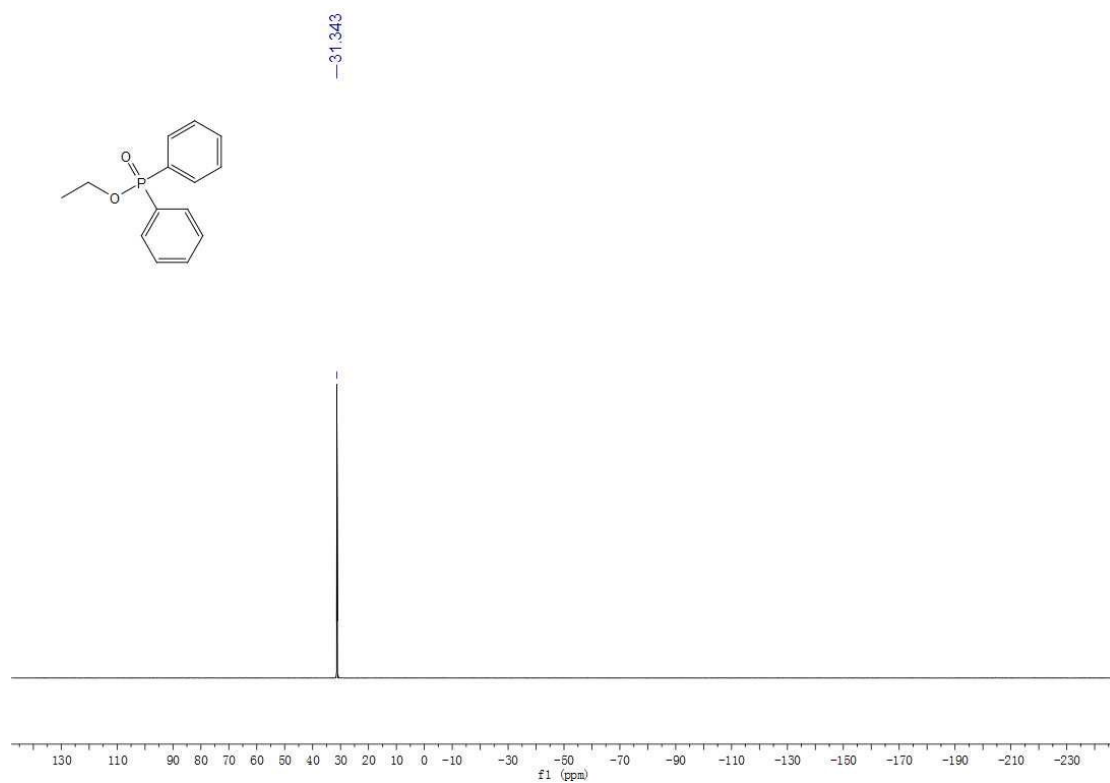


Figure 32.  $3k$ - $^{31}\text{P}$  NMR



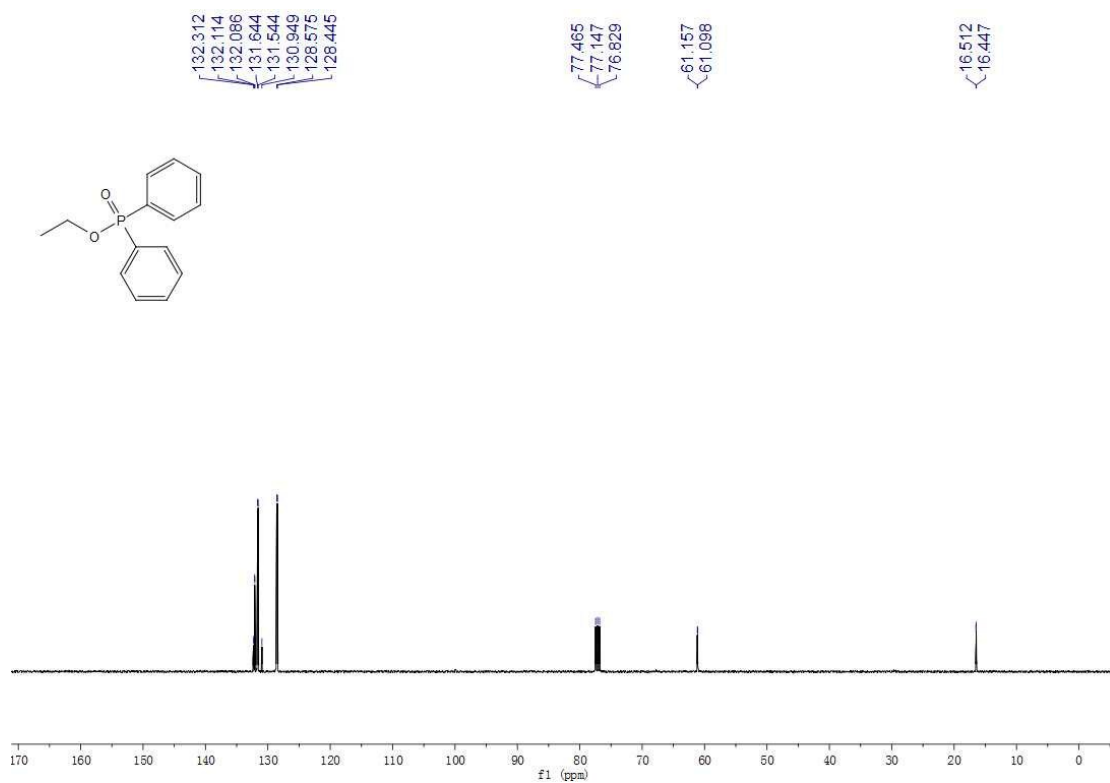


Figure 33. 3k-<sup>13</sup>C NMR

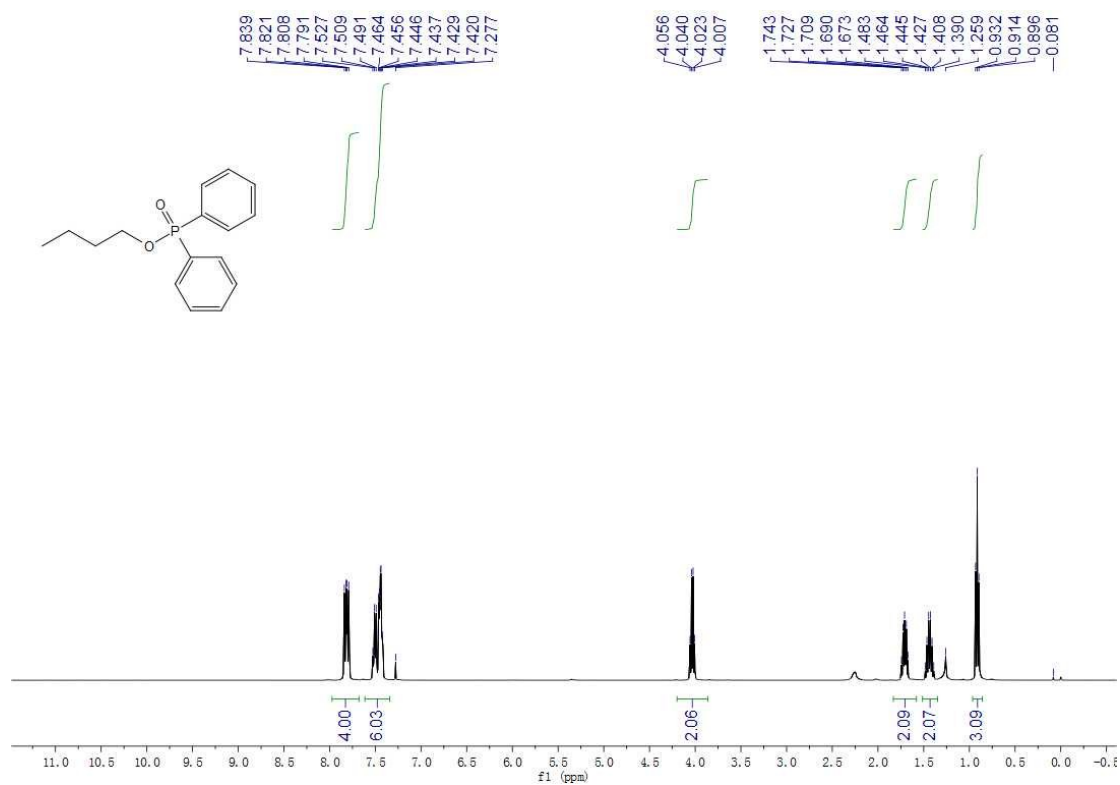


Figure 34. 3l-<sup>1</sup>H NMR

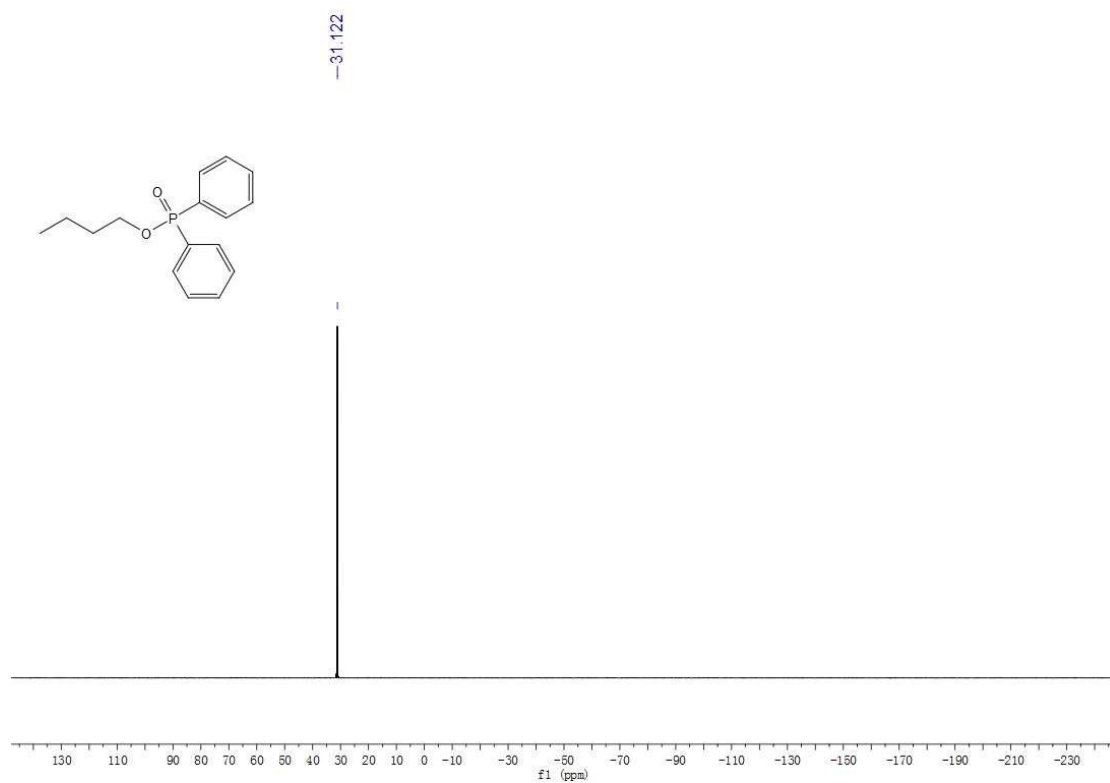


Figure 35.  $^{31}\text{P}$  NMR

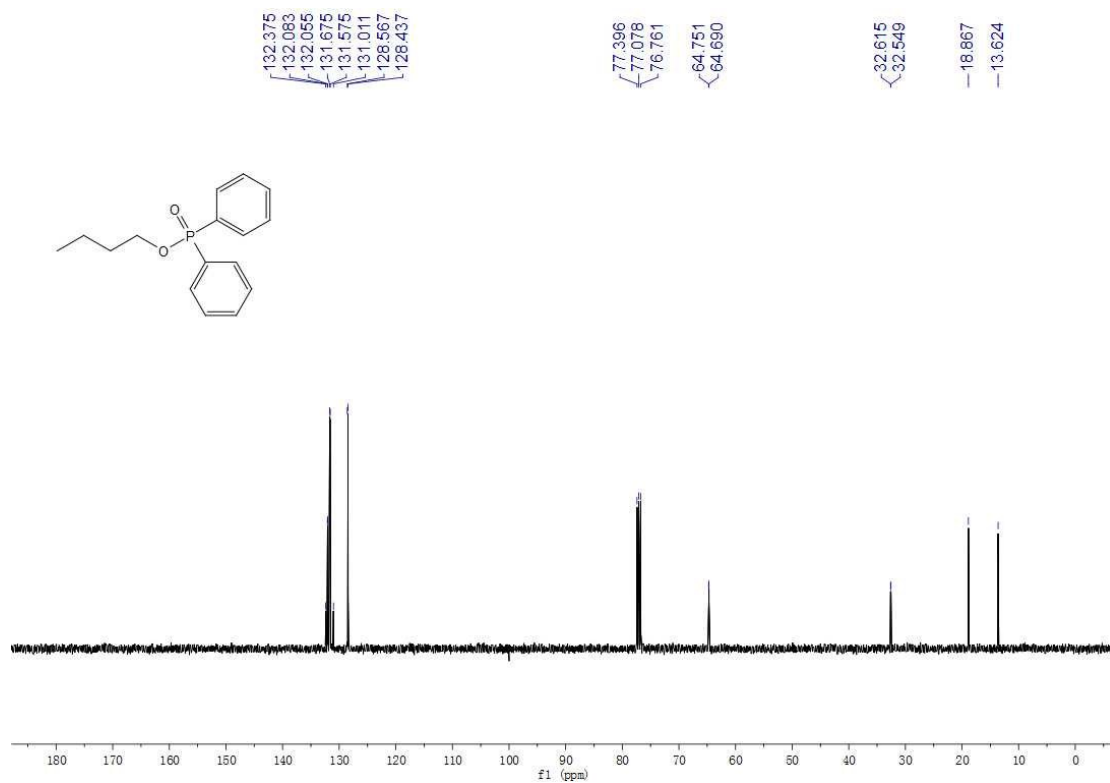


Figure 36.  $^{13}\text{C}$  NMR

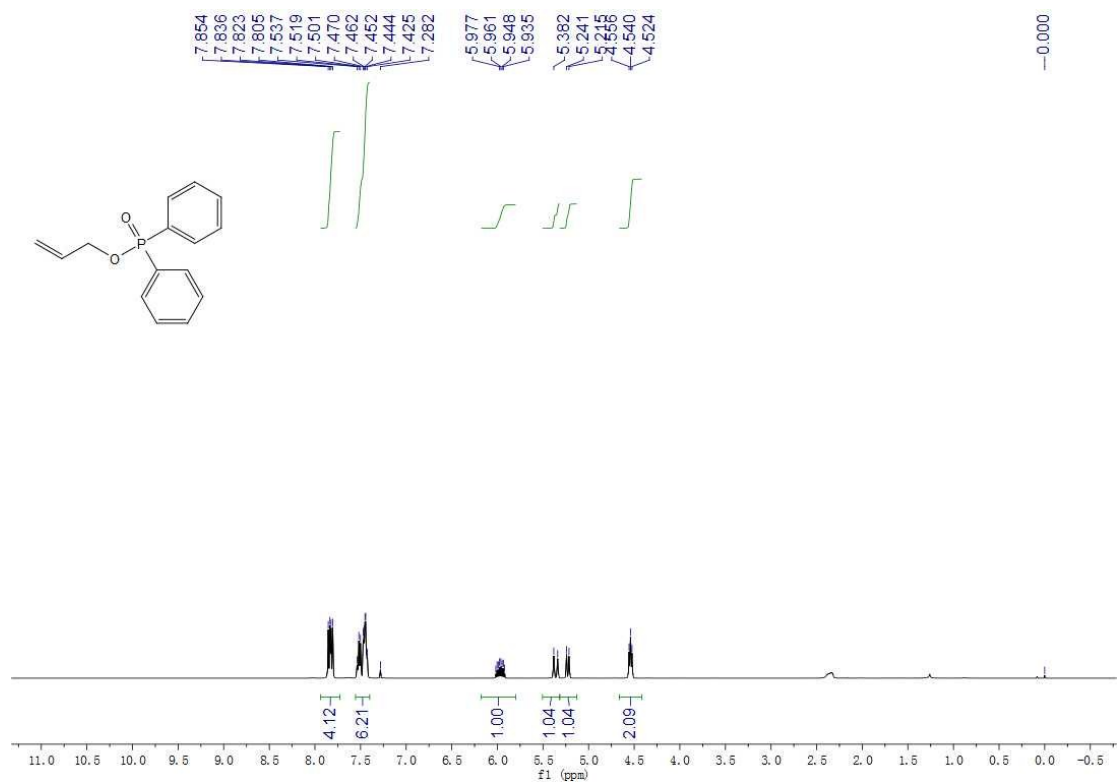


Figure 37.  $3m\text{-}^1\text{H}$  NMR

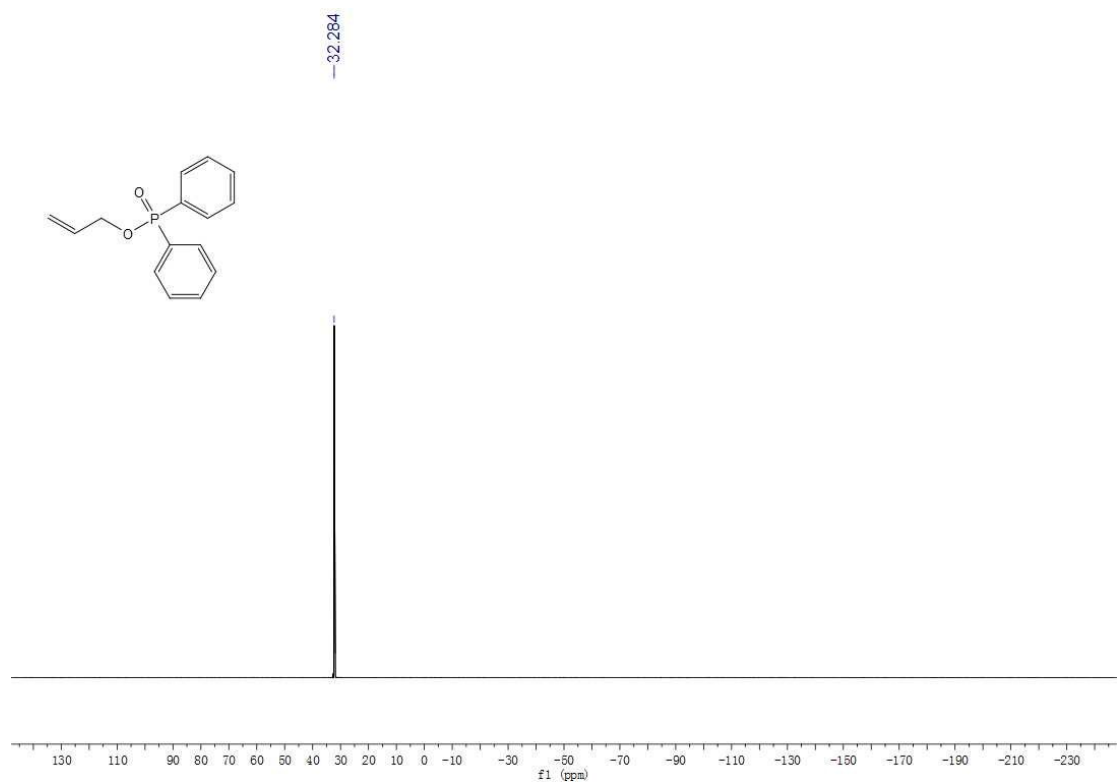
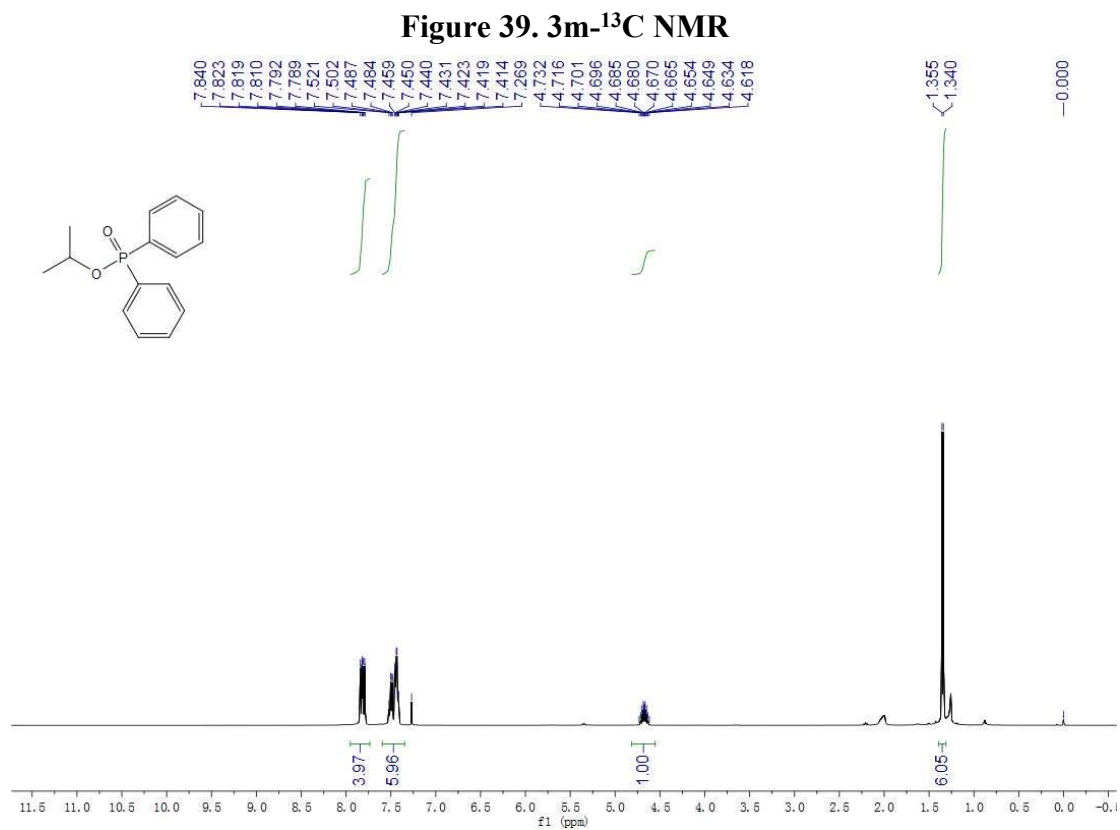
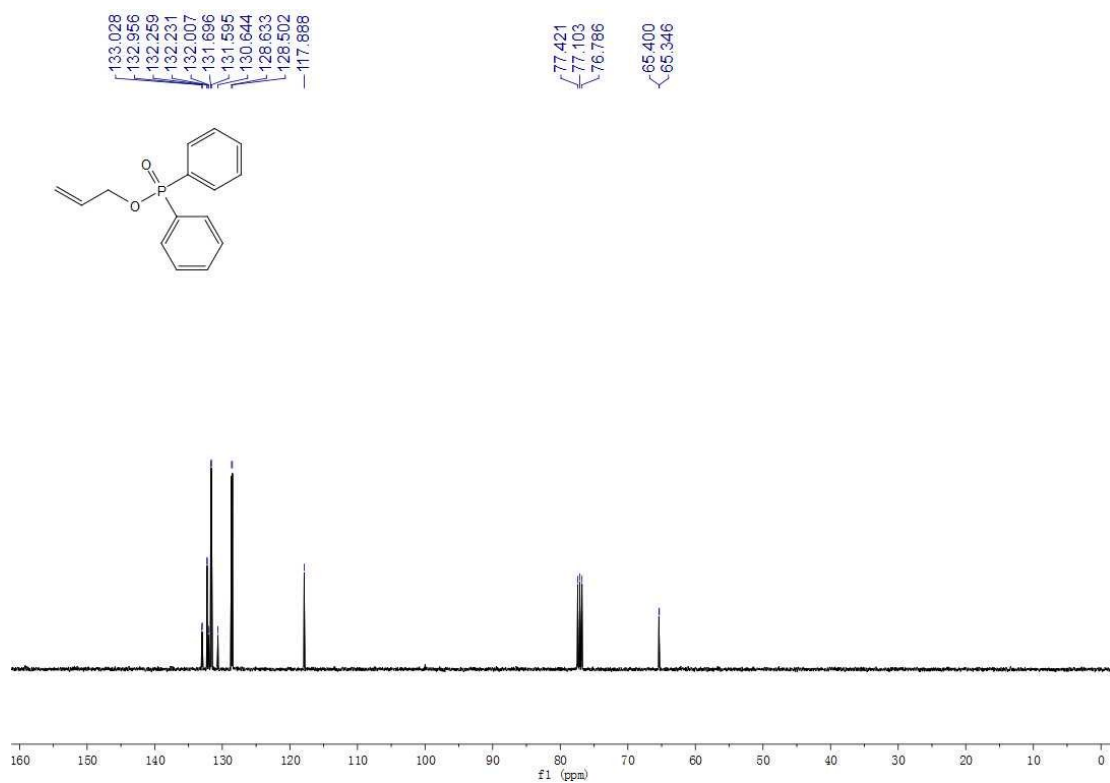


Figure 38.  $3m\text{-}^{31}\text{P}$  NMR



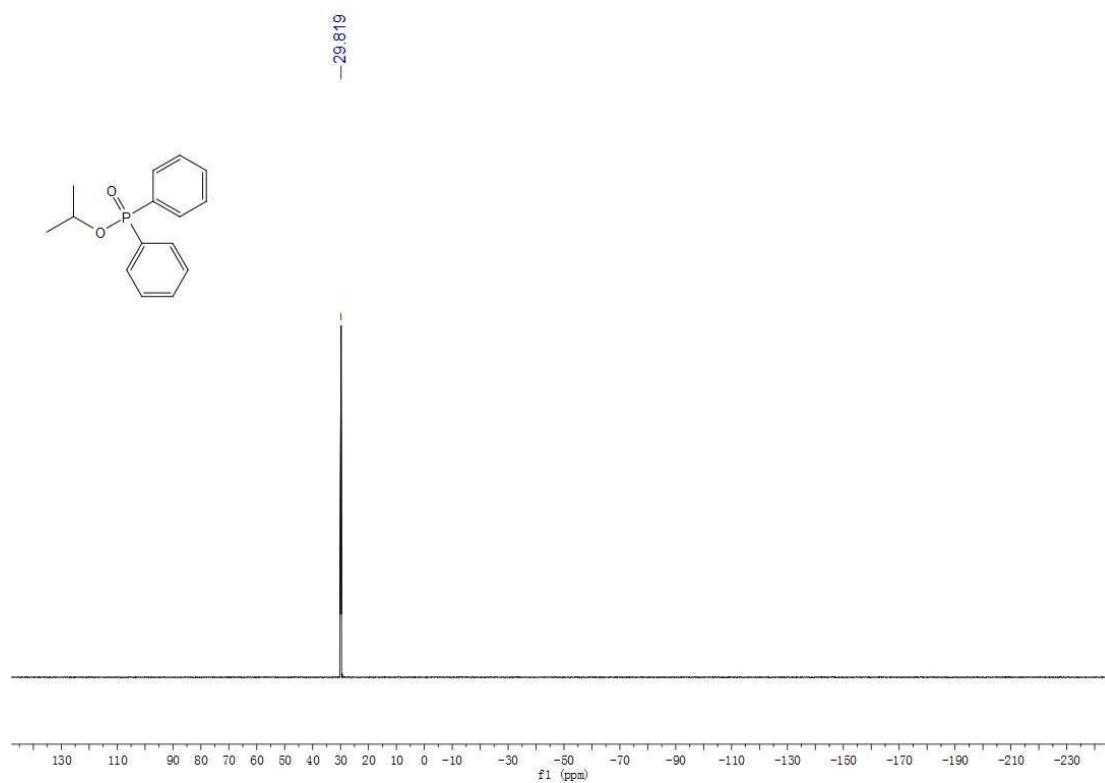


Figure 41. 3n-<sup>31</sup>P NMR

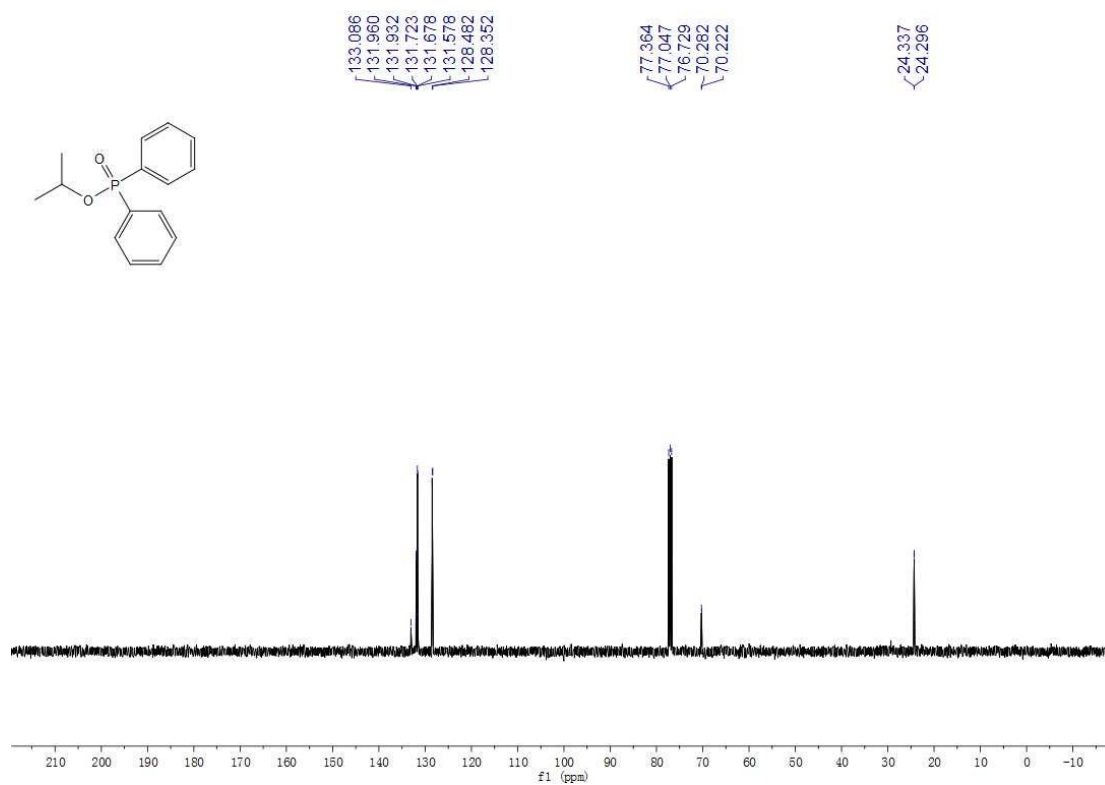


Figure 42. 3n-<sup>13</sup>C NMR

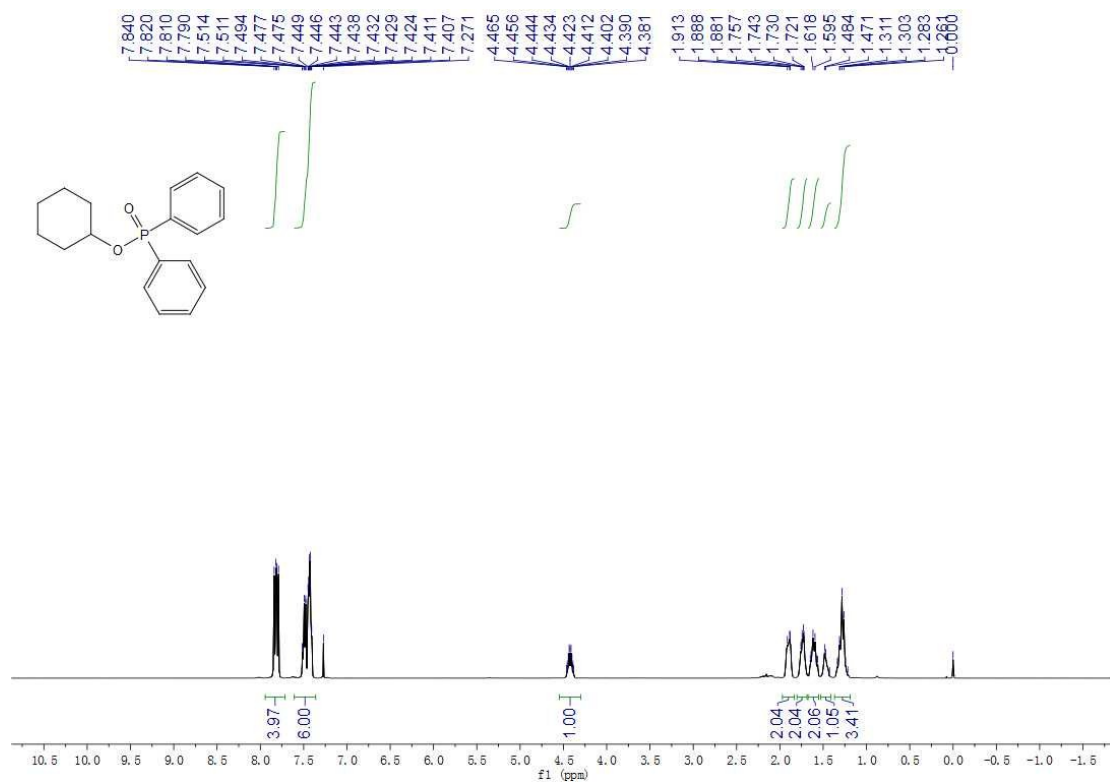


Figure 43.  $30\text{-}^1\text{H}$  NMR

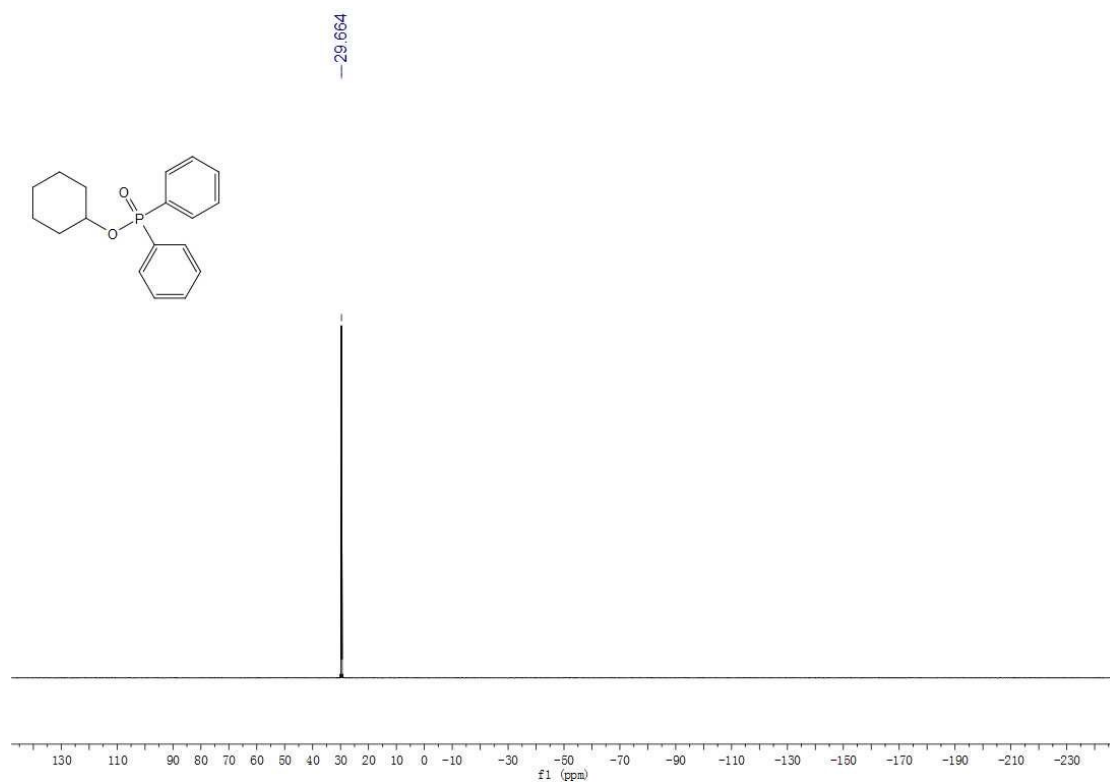
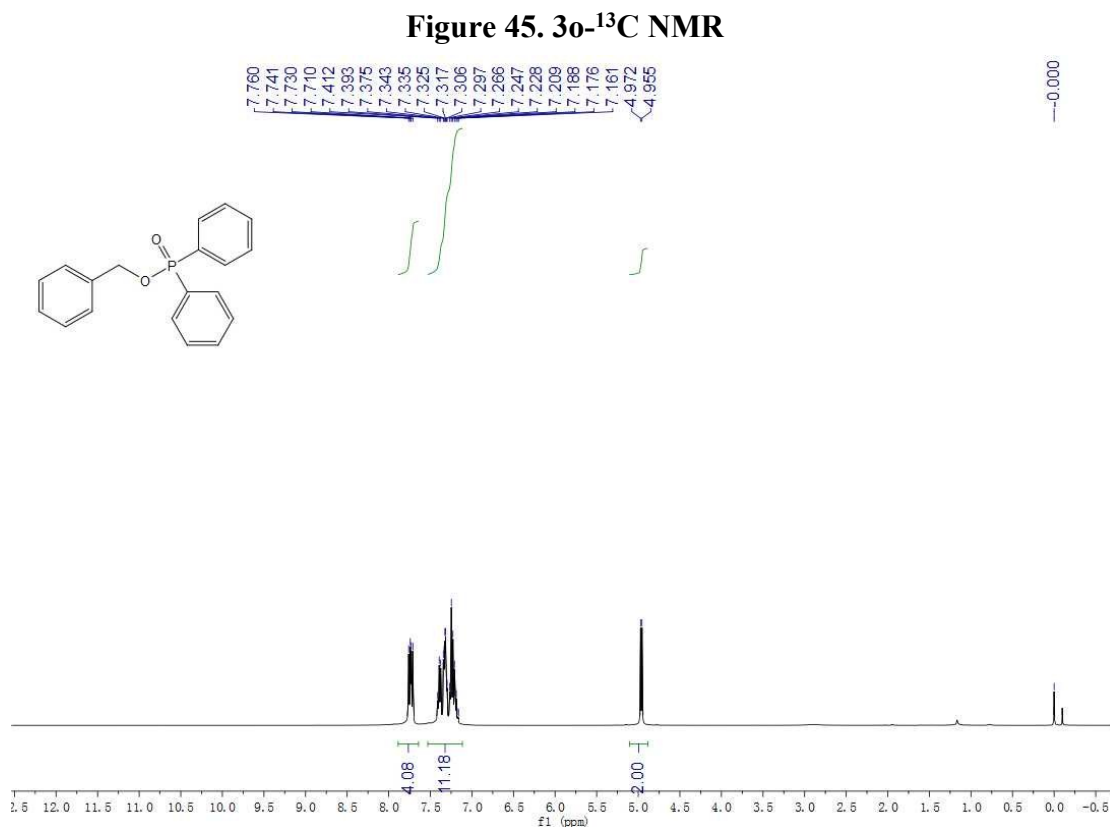
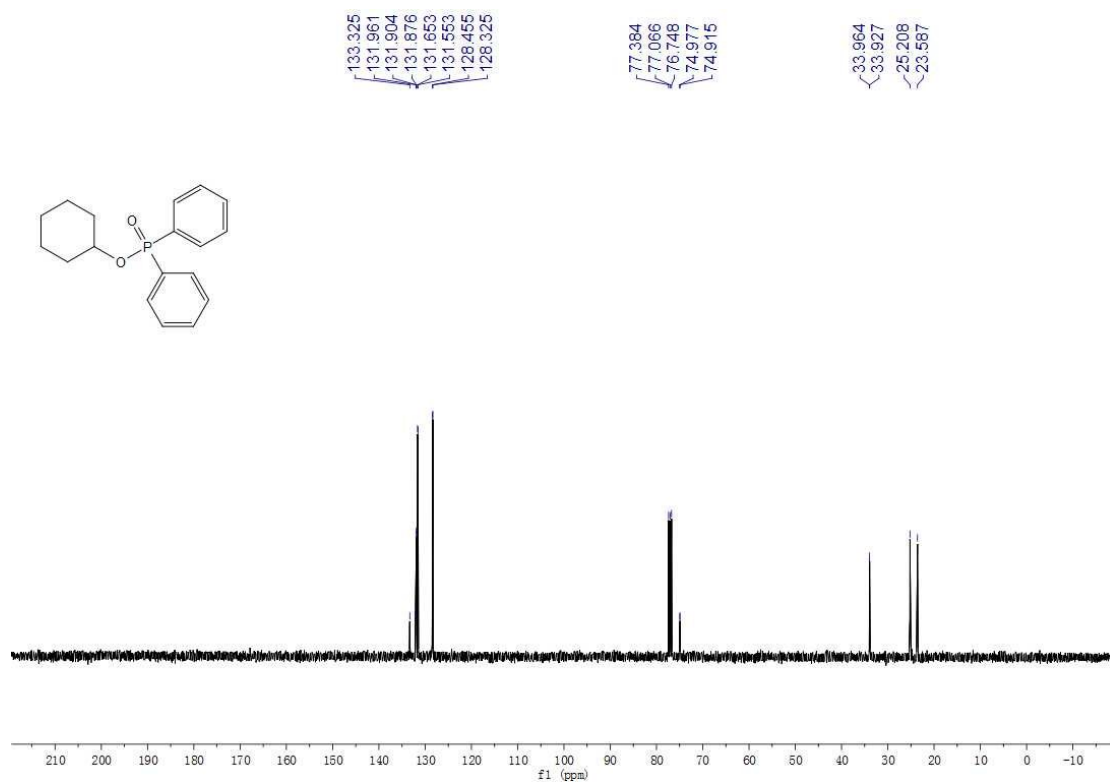


Figure 44.  $30\text{-}^{31}\text{P}$  NMR



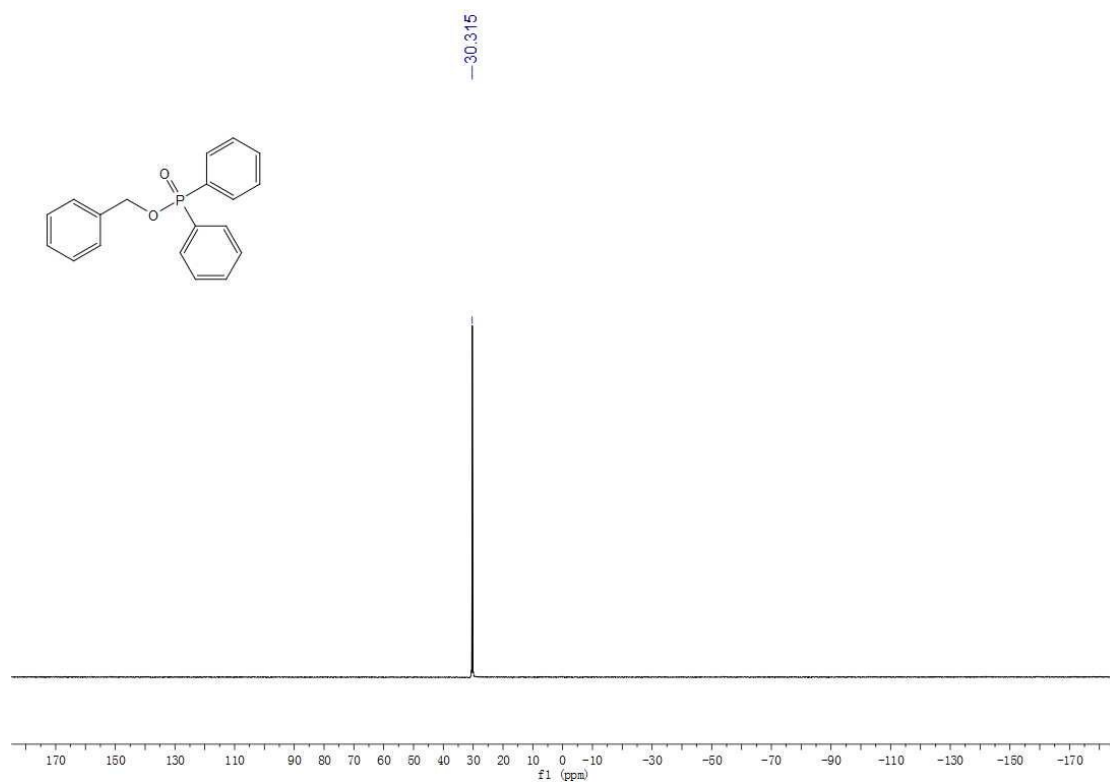


Figure 47.  $31\text{P}$  NMR

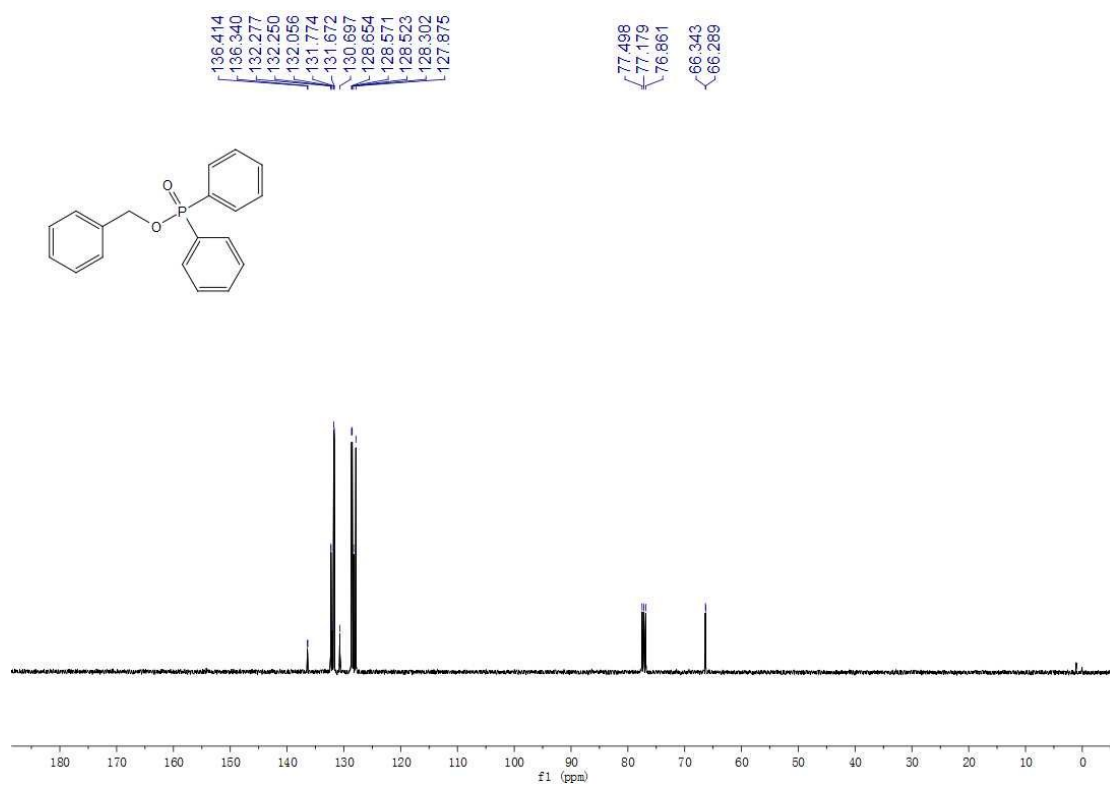


Figure 48.  $13\text{C}$  NMR



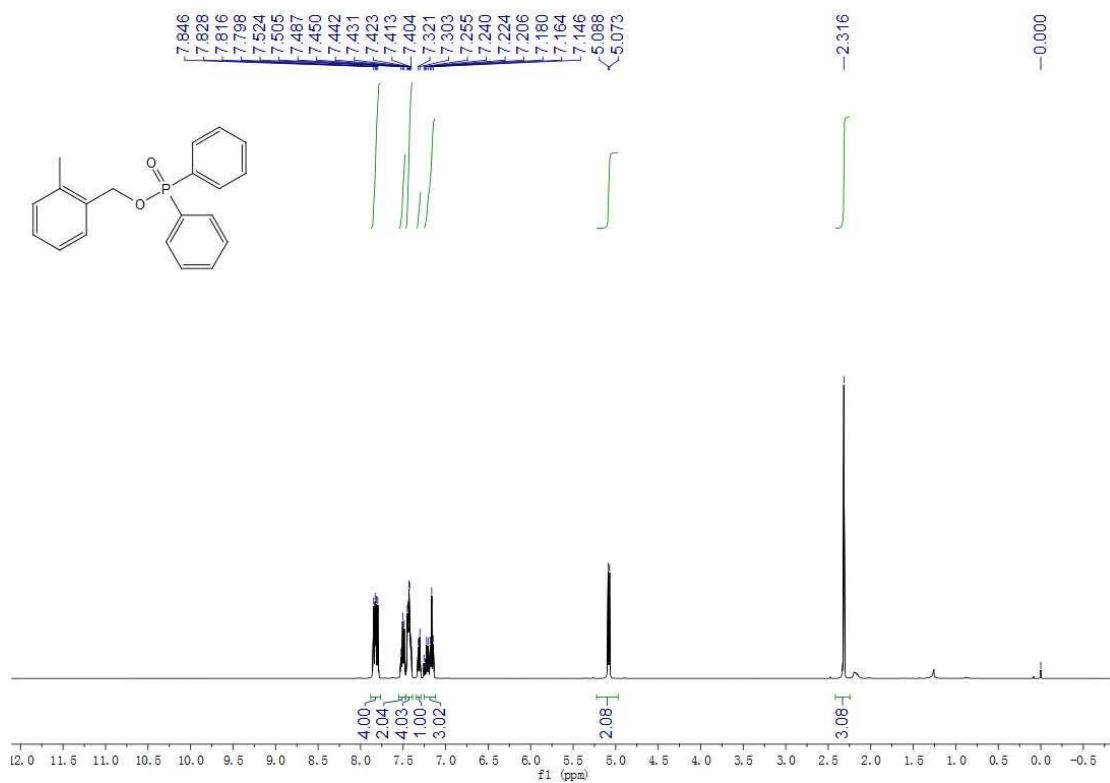


Figure 49. 3q-<sup>1</sup>H NMR

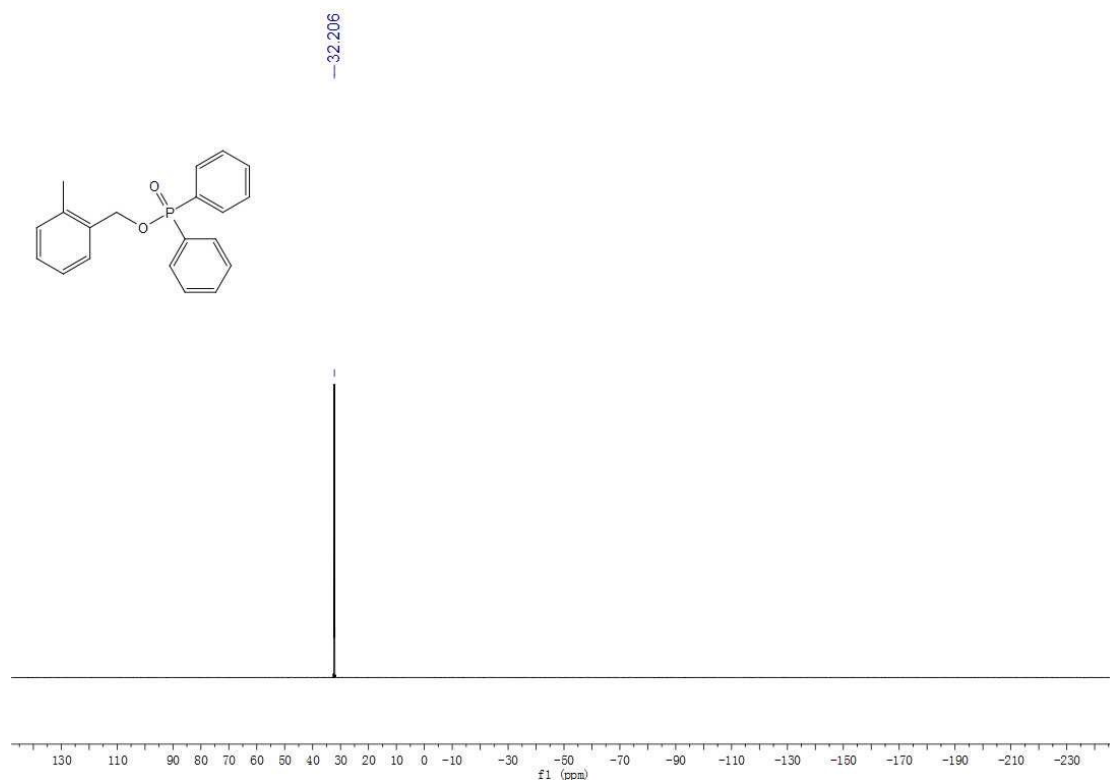


Figure 50. 3q-<sup>31</sup>P NMR

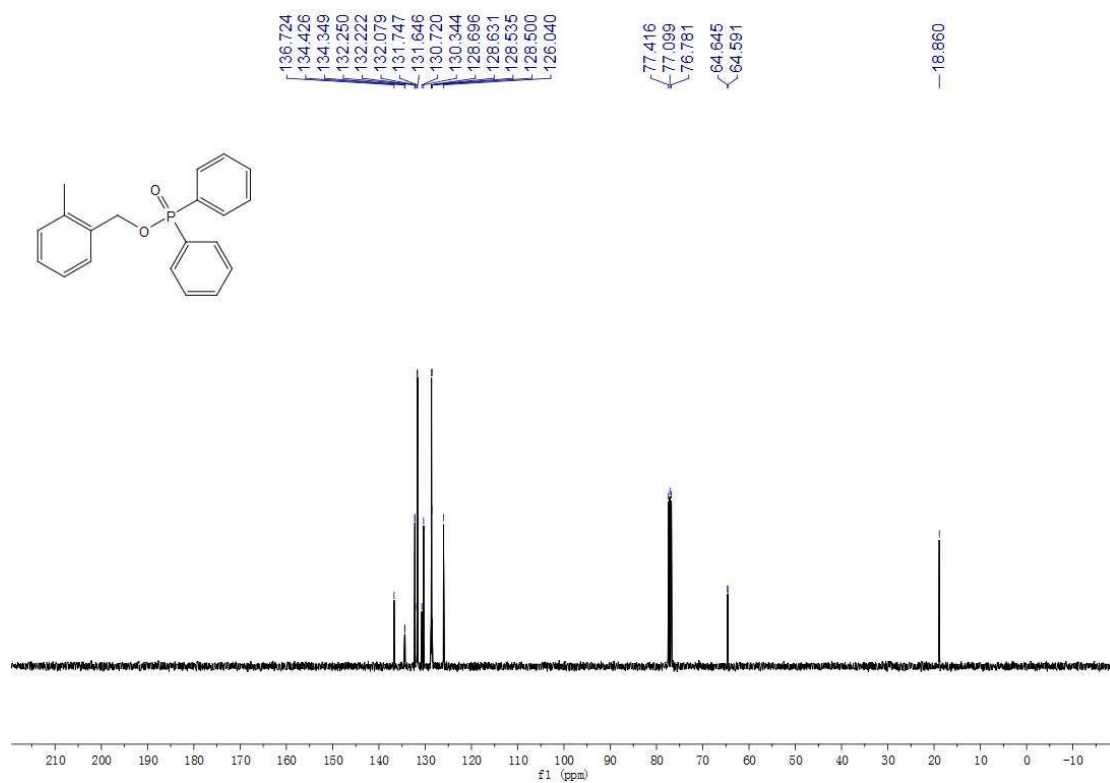


Figure 51. 3q- $^{13}\text{C}$  NMR

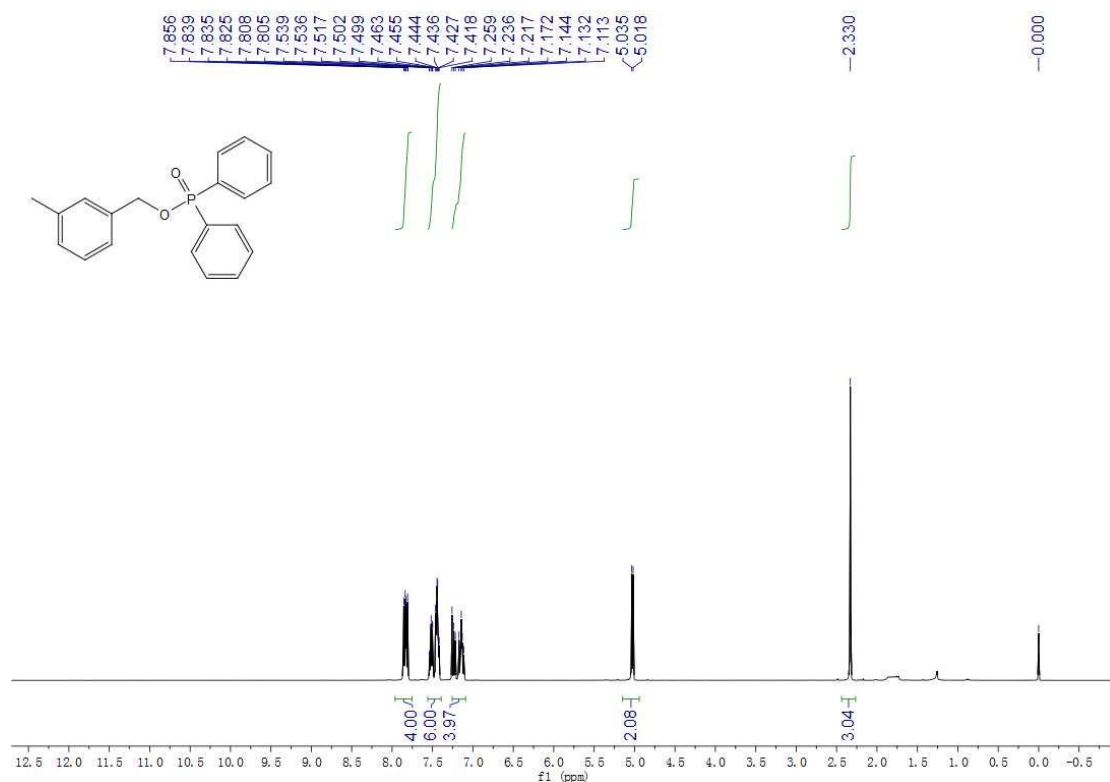


Figure 52. 3r- $^1\text{H}$  NMR

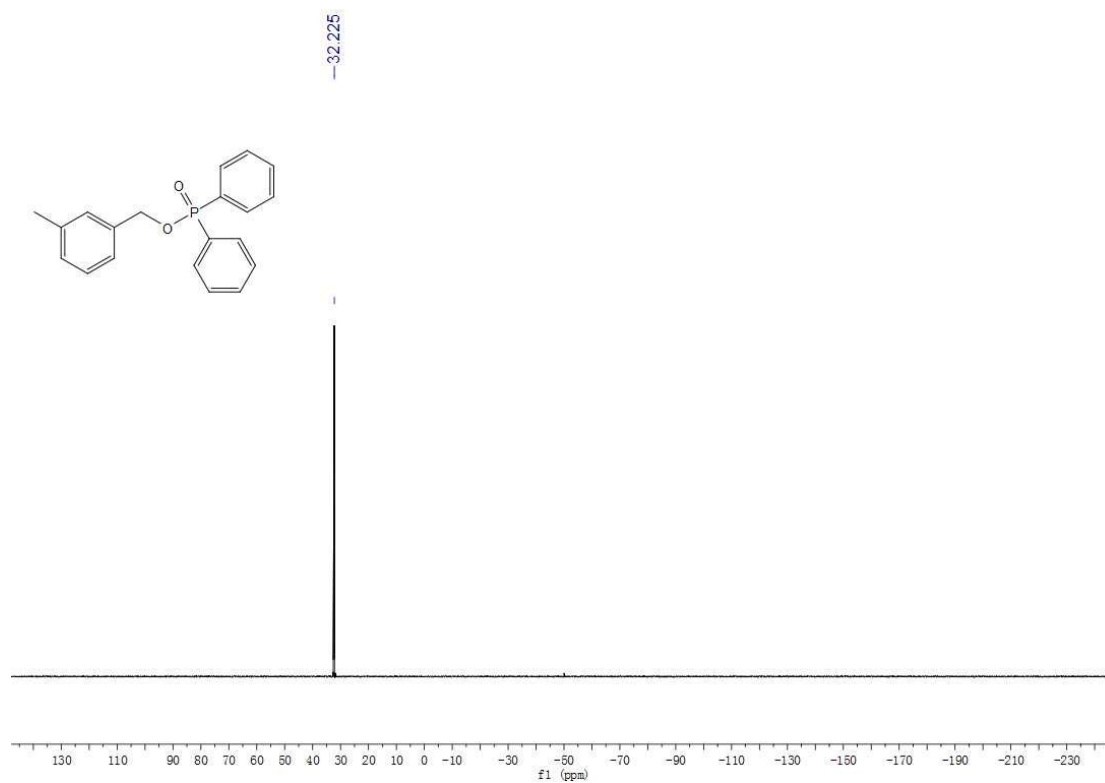


Figure 53.  $3r$ - $^{31}\text{P}$  NMR

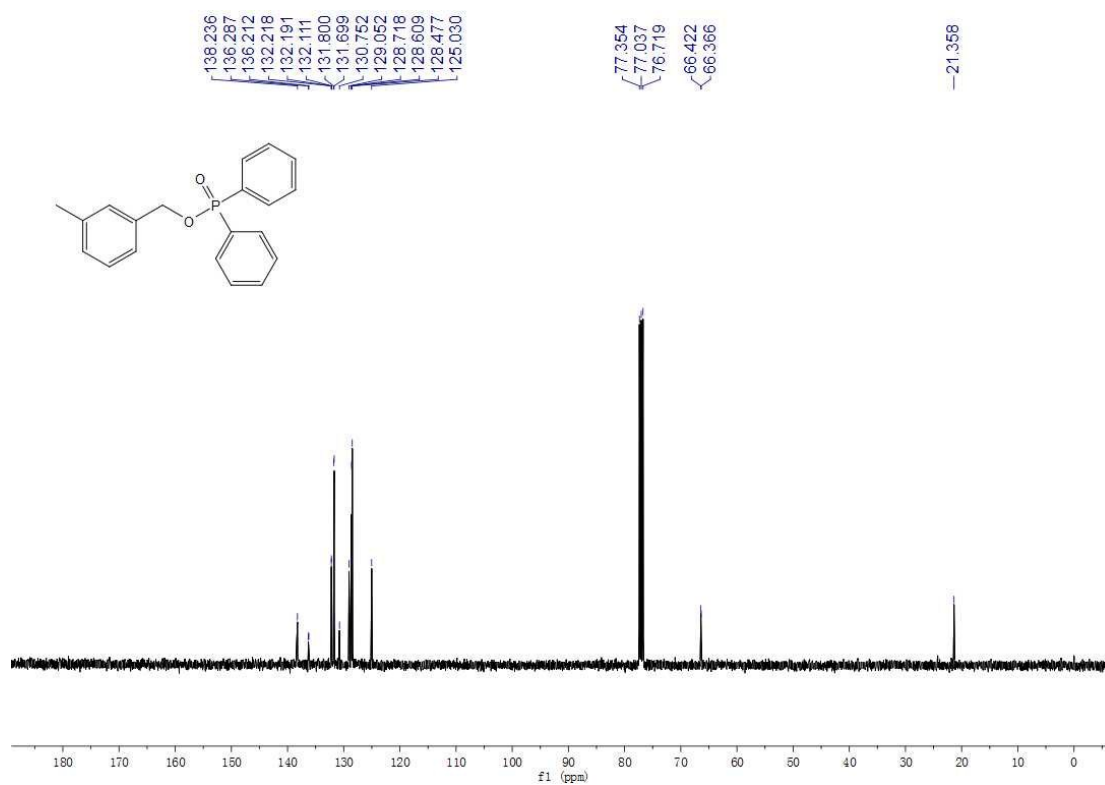


Figure 54.  $3r$ - $^{13}\text{C}$  NMR

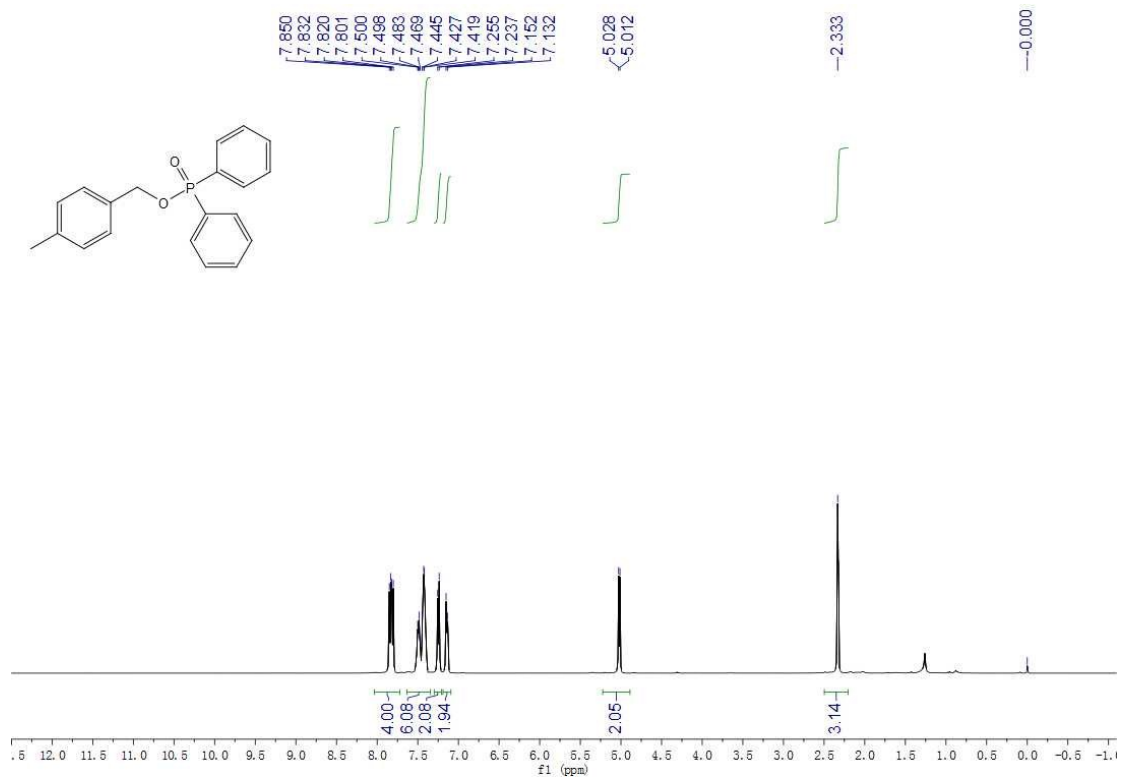


Figure 55.  $3s\text{-}^1\text{H}$  NMR

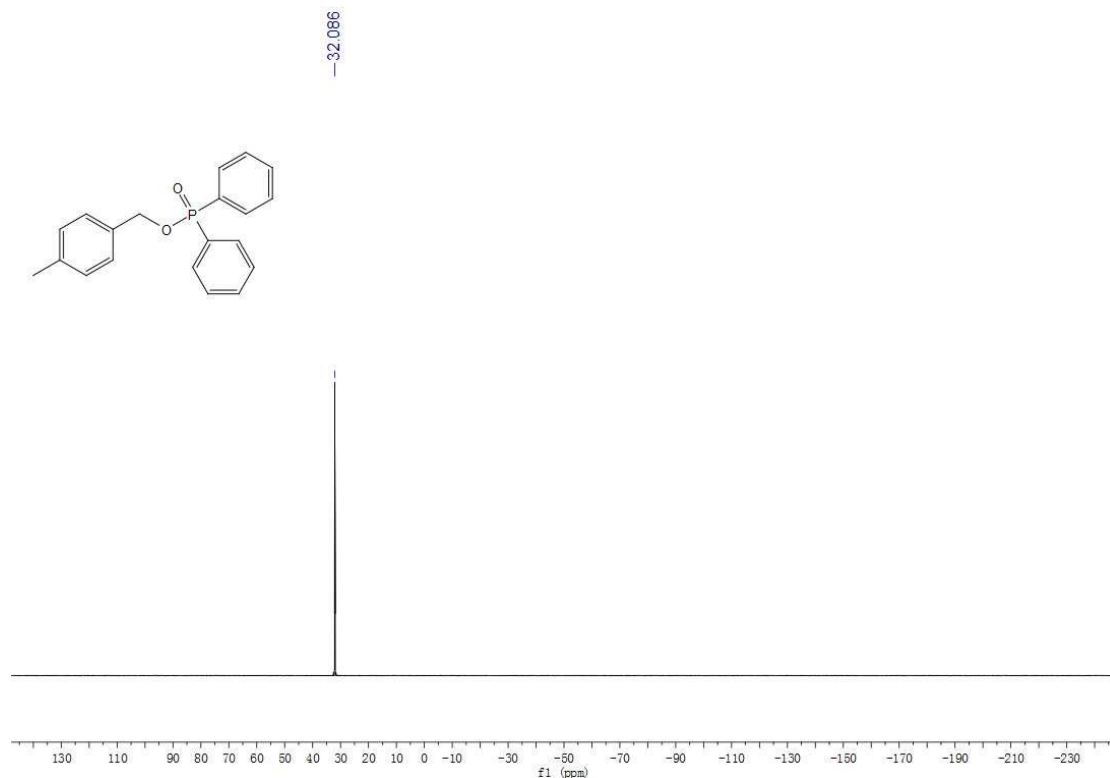


Figure 56.  $3s\text{-}^{31}\text{P}$  NMR

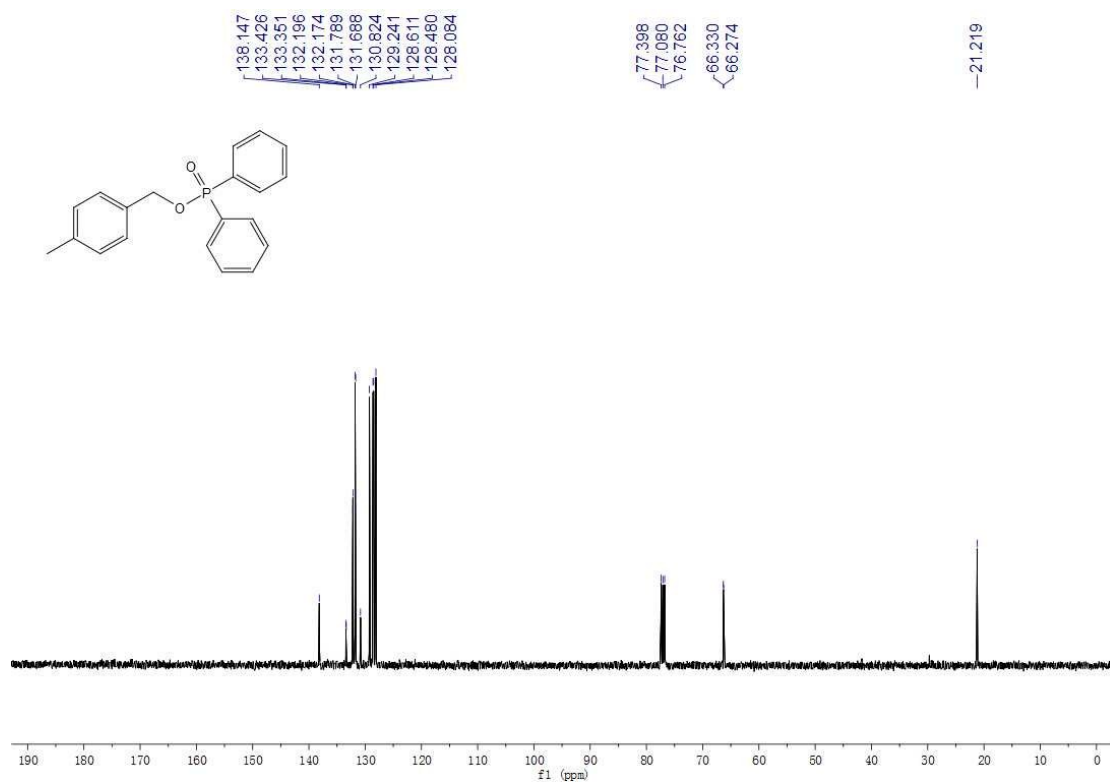


Figure 57.  $^{13}\text{C}$ -NMR

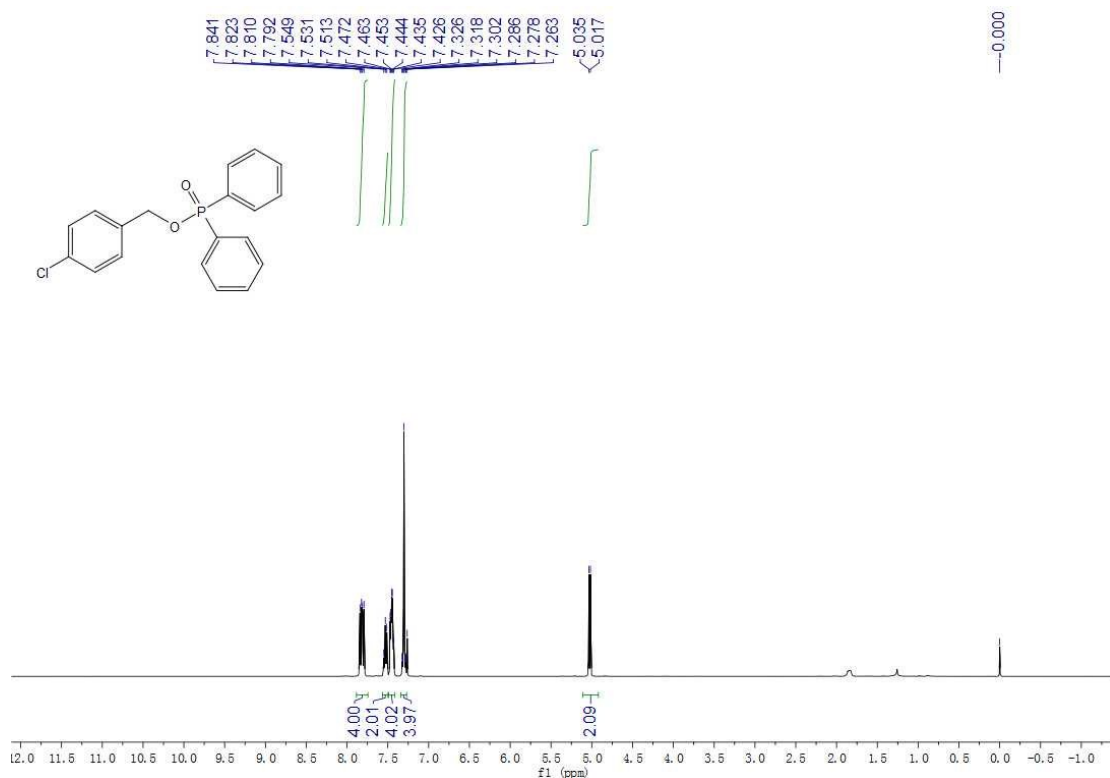


Figure 58.  $^1\text{H}$ -NMR

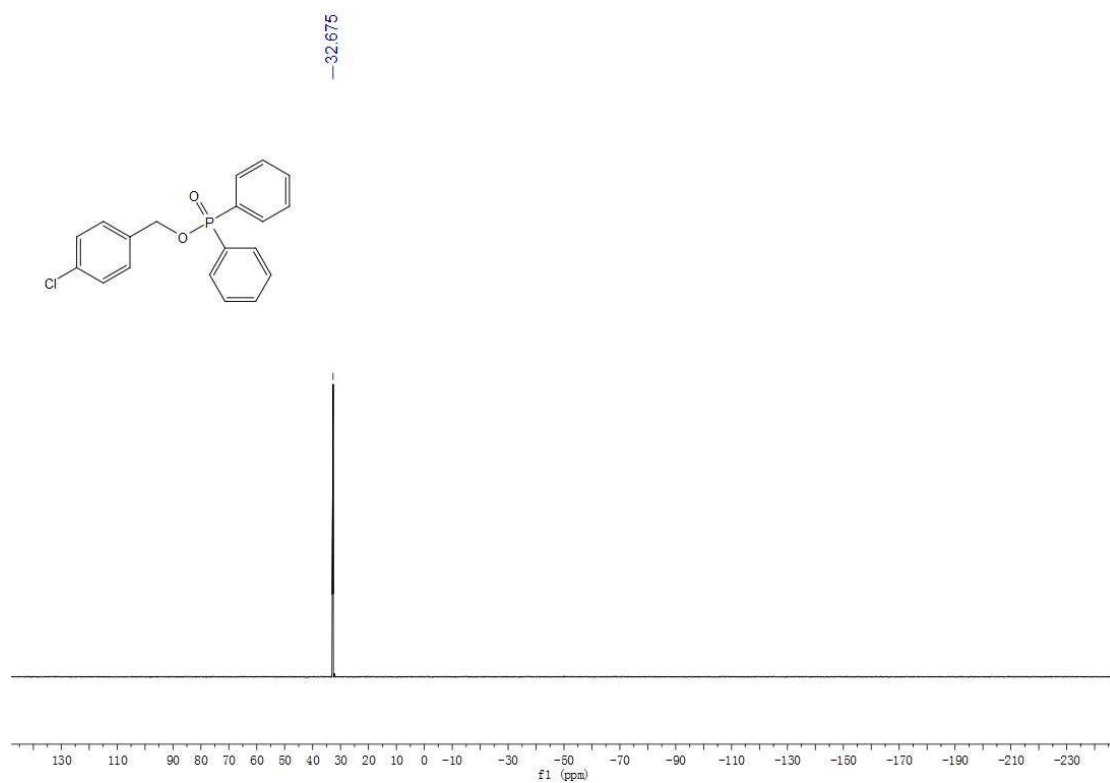


Figure 59.  $3t$ - $^{31}\text{P}$  NMR

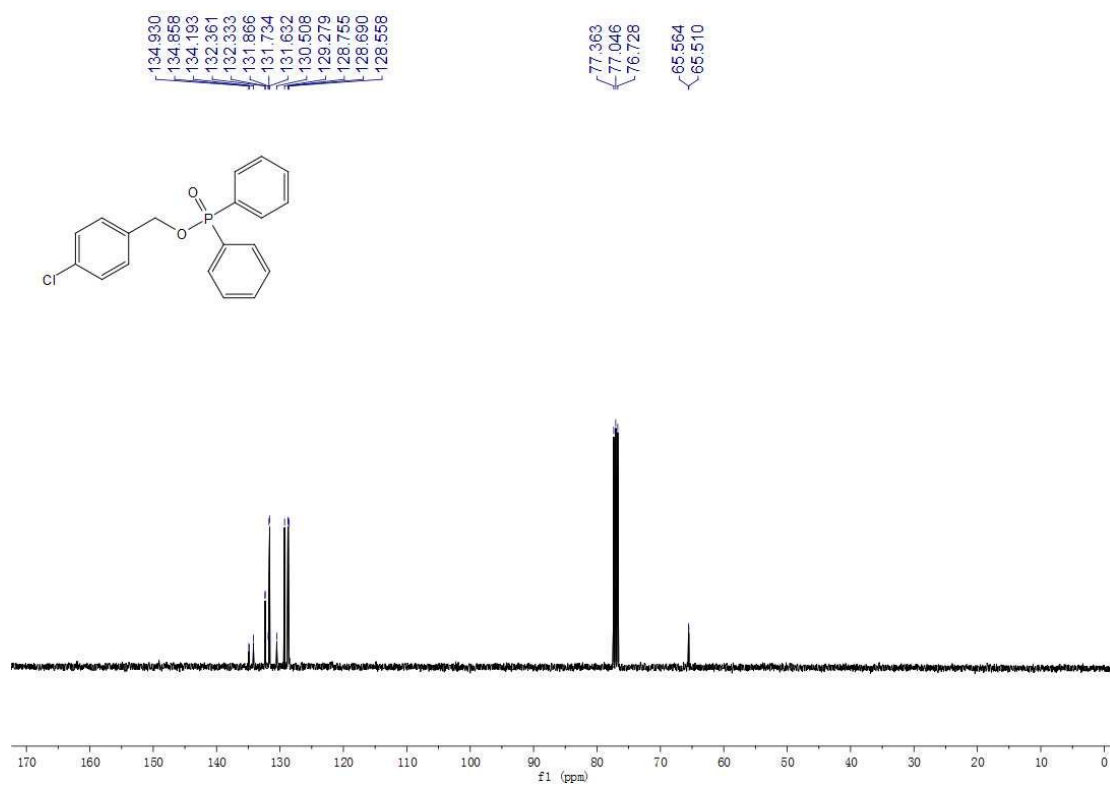


Figure 60.  $3t$ - $^{13}\text{C}$  NMR

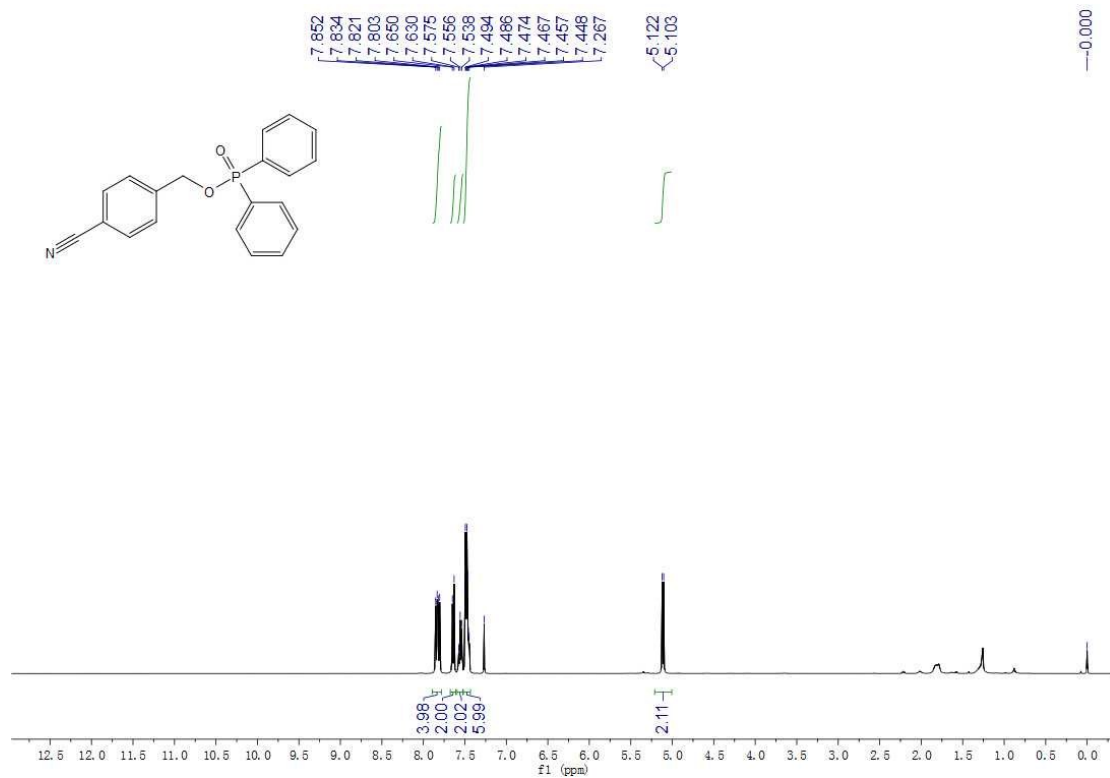


Figure 61.  $^3\text{u-}^1\text{H}$  NMR

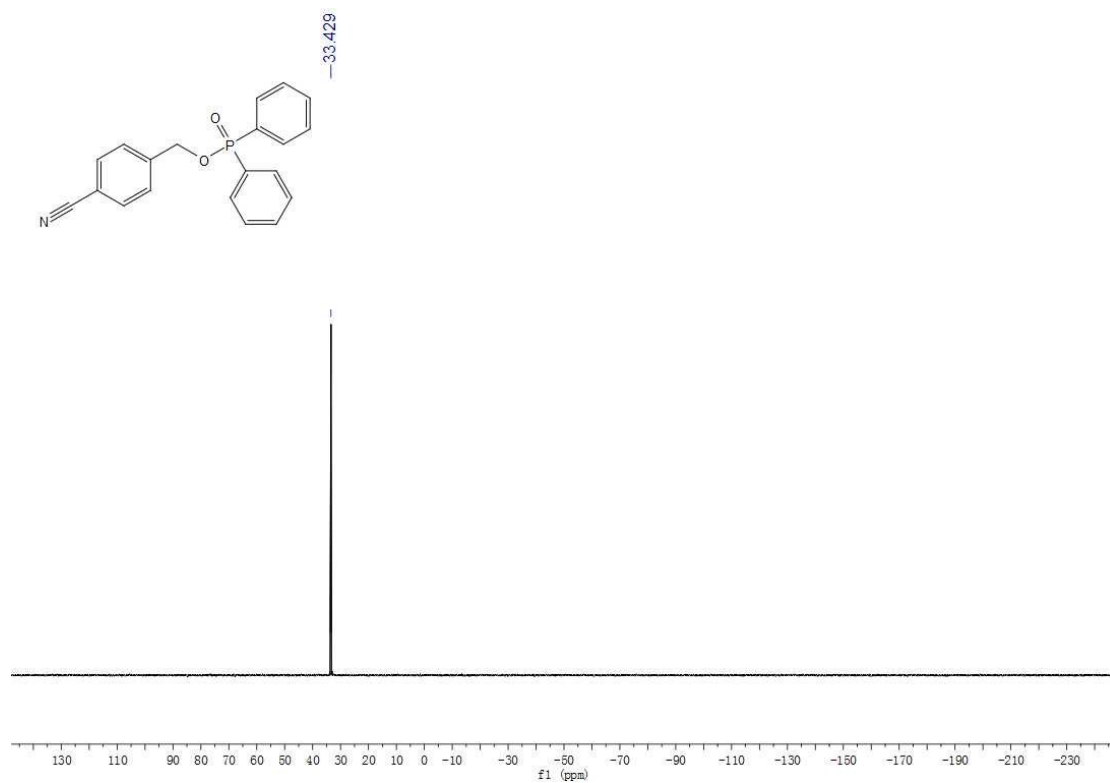


Figure 62.  $^3\text{u-}^{31}\text{P}$  NMR

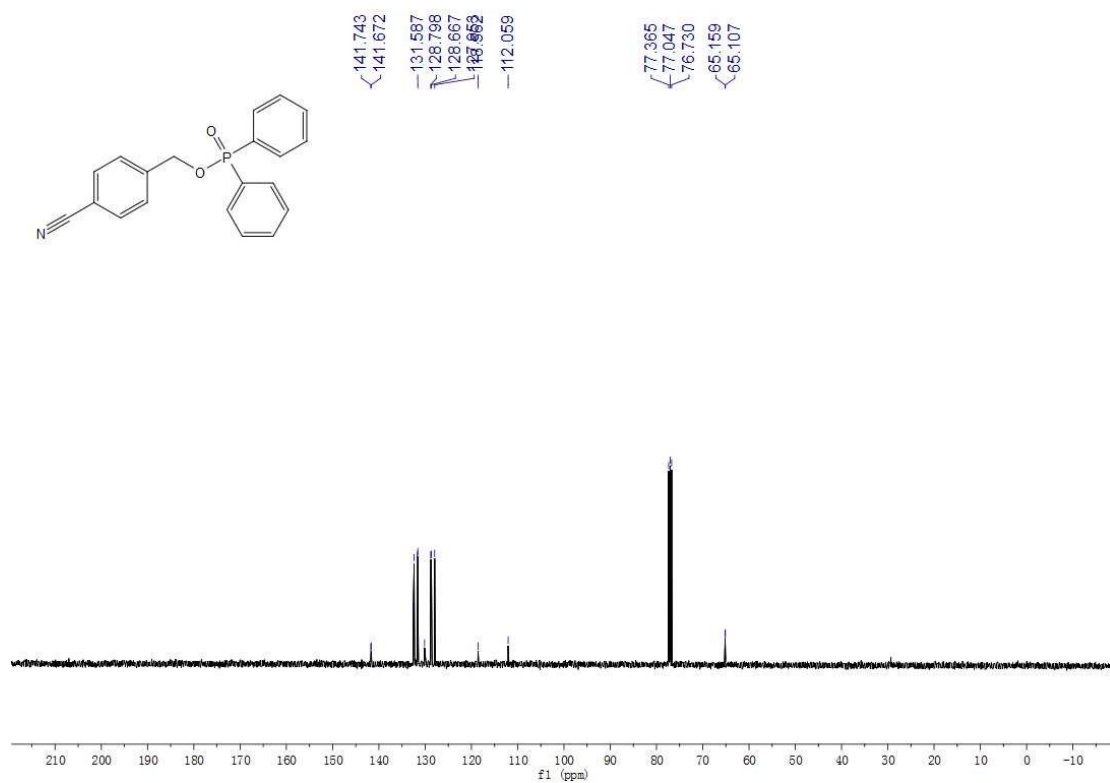


Figure 63.  $3u$ - $^{13}\text{C}$  NMR

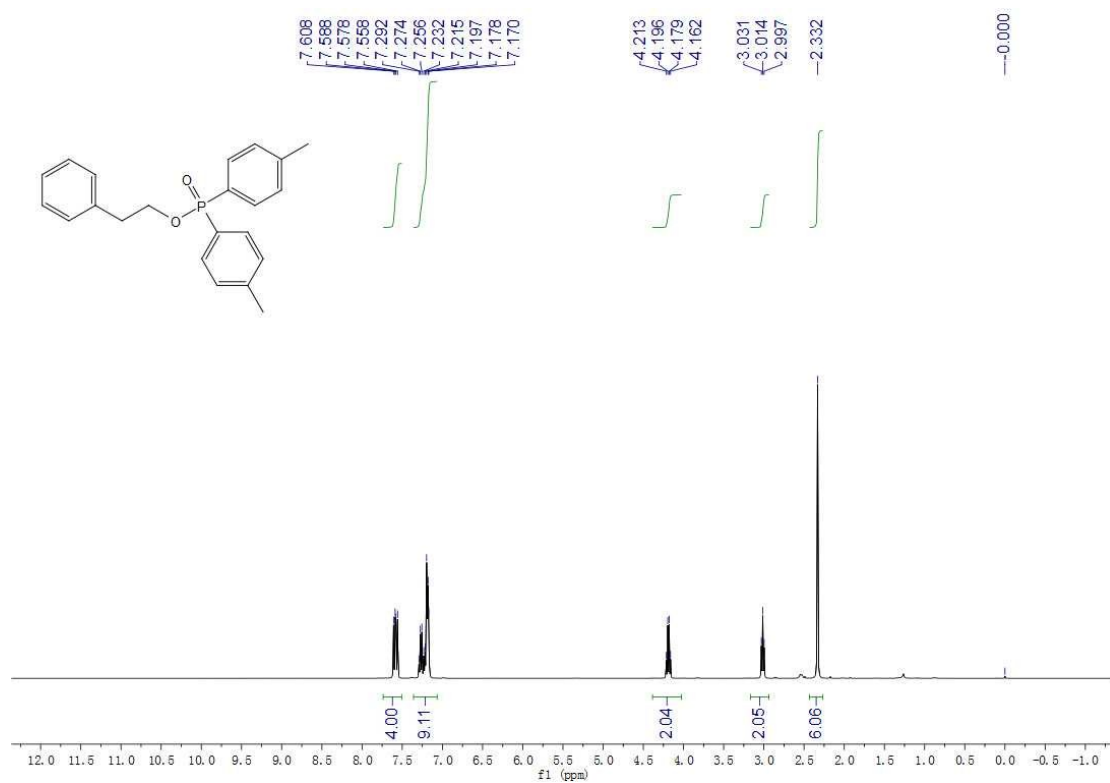


Figure 64.  $3v$ - $^1\text{H}$  NMR



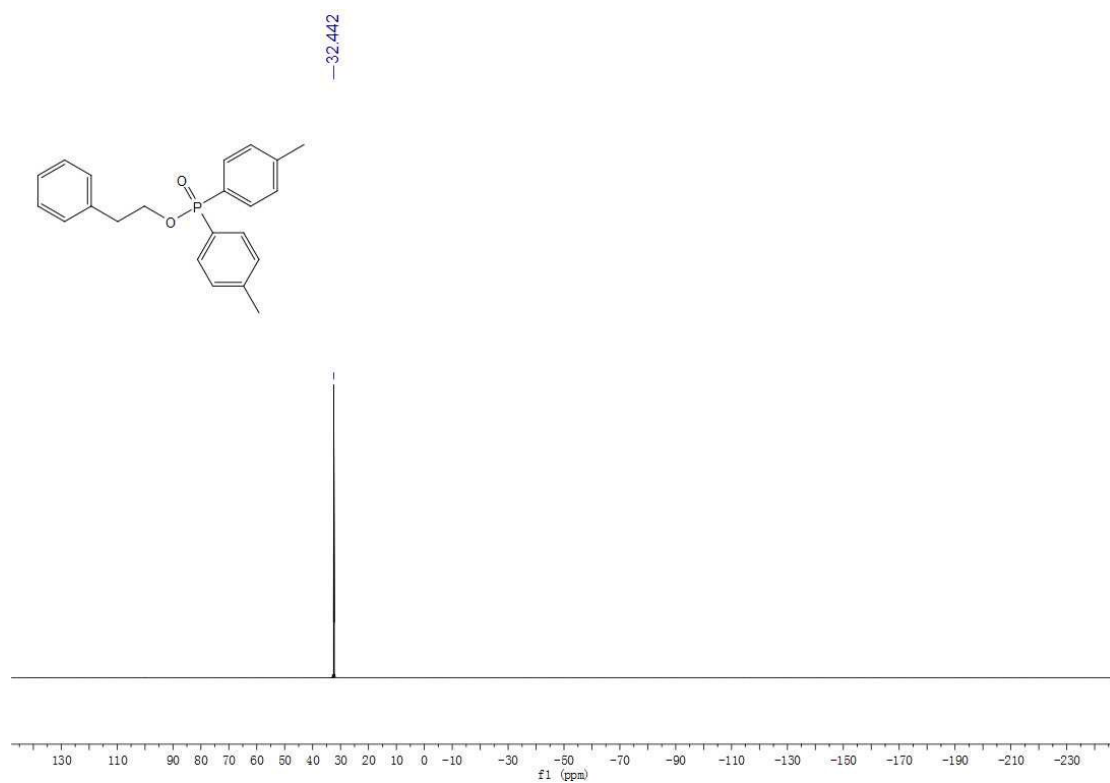


Figure 65.  $3\nu$ - $^{31}\text{P}$  NMR

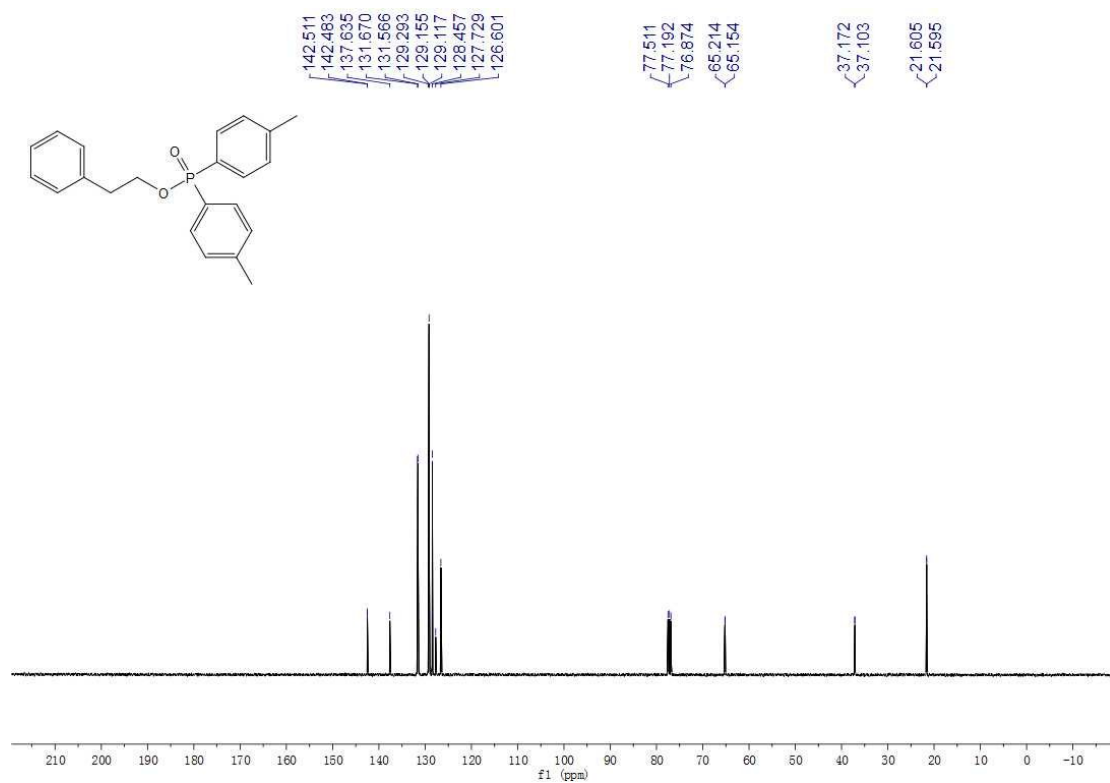


Figure 66.  $3\nu$ - $^{13}\text{C}$  NMR

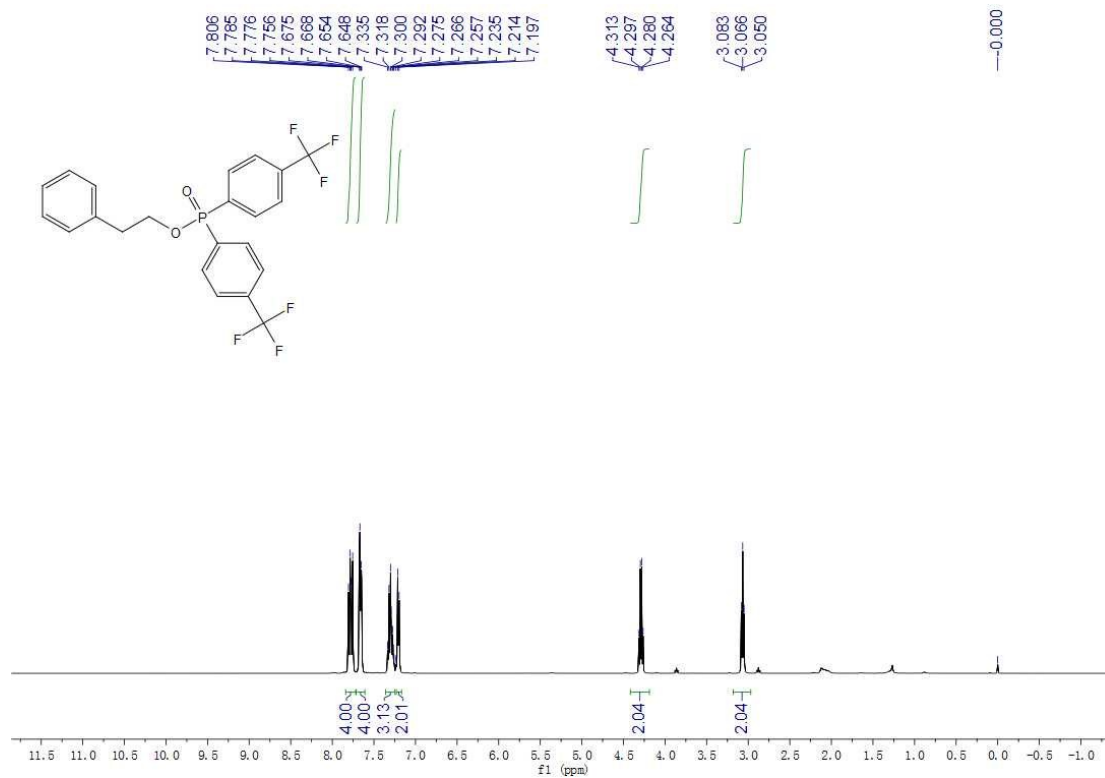


Figure 67. 3w-<sup>1</sup>H NMR

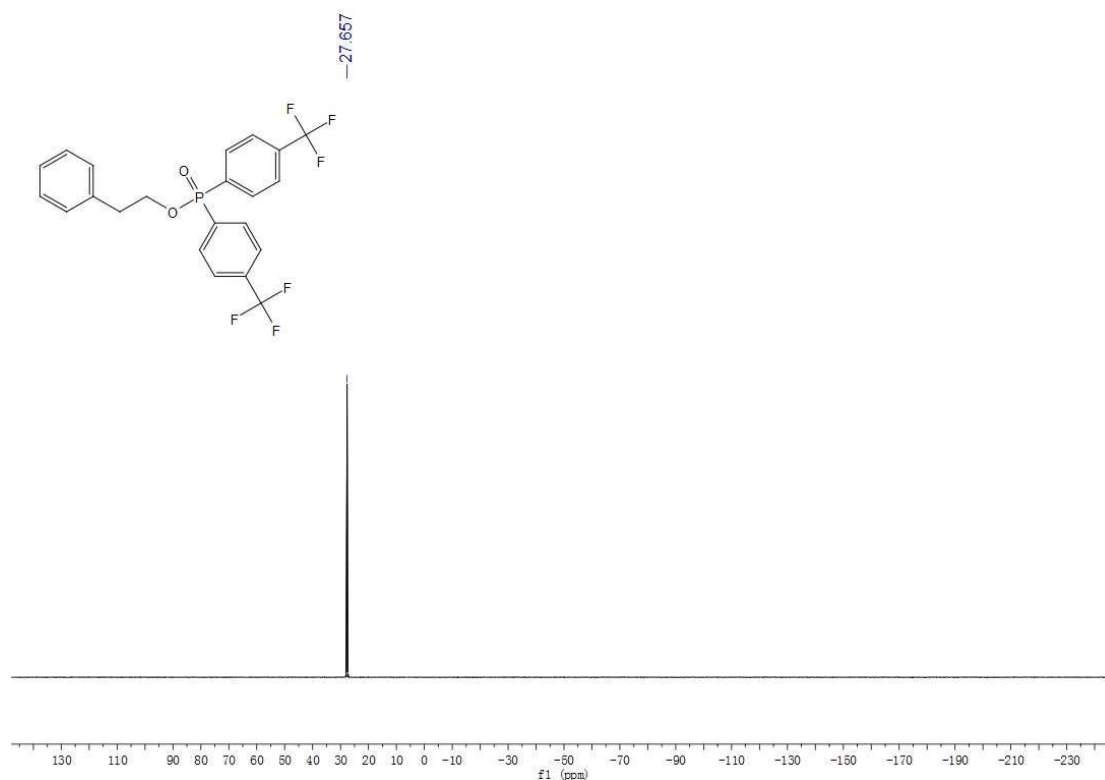


Figure 68. 3w-<sup>31</sup>P NMR

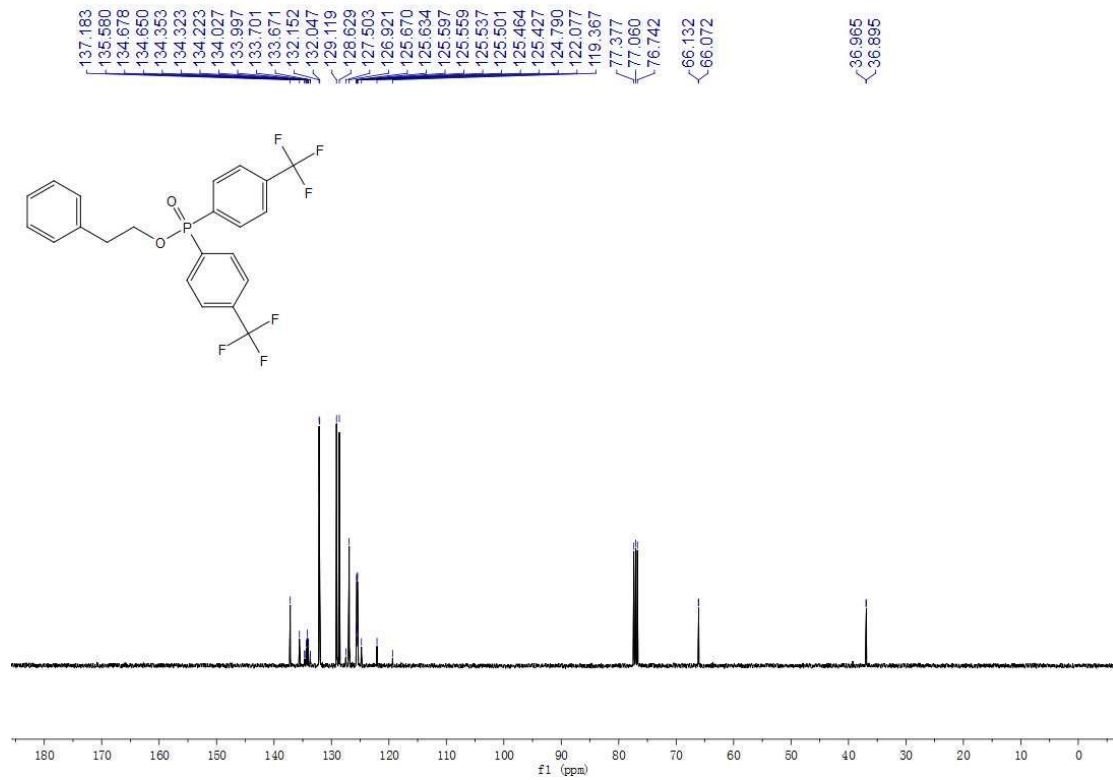


Figure 69.  $3\text{w-}^{13}\text{C}$  NMR

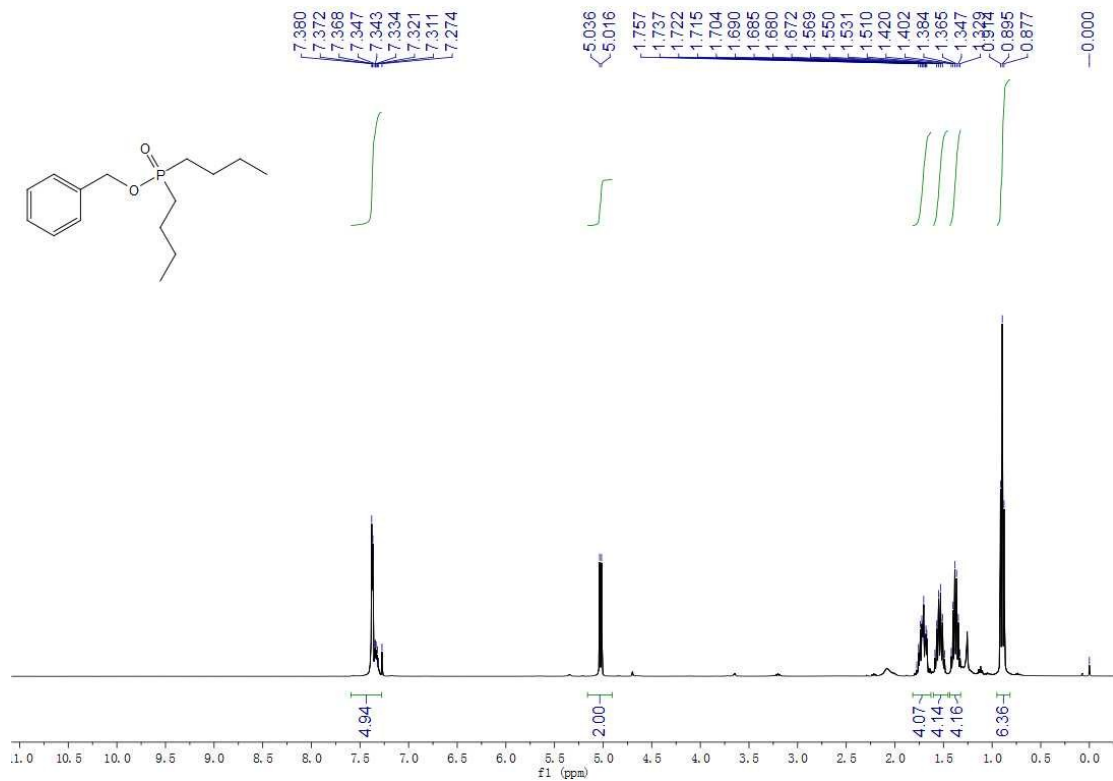


Figure 70.  $3\text{x-}^1\text{H}$  NMR

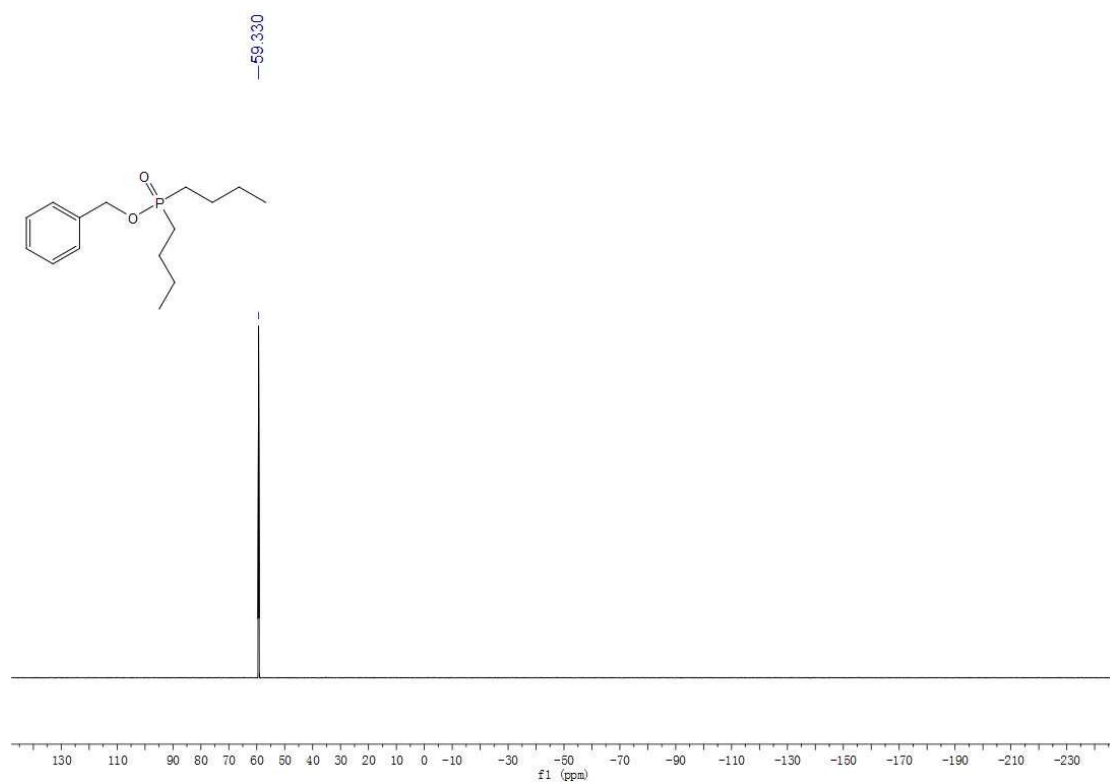


Figure 71.  $3x$ - $^{31}\text{P}$  NMR

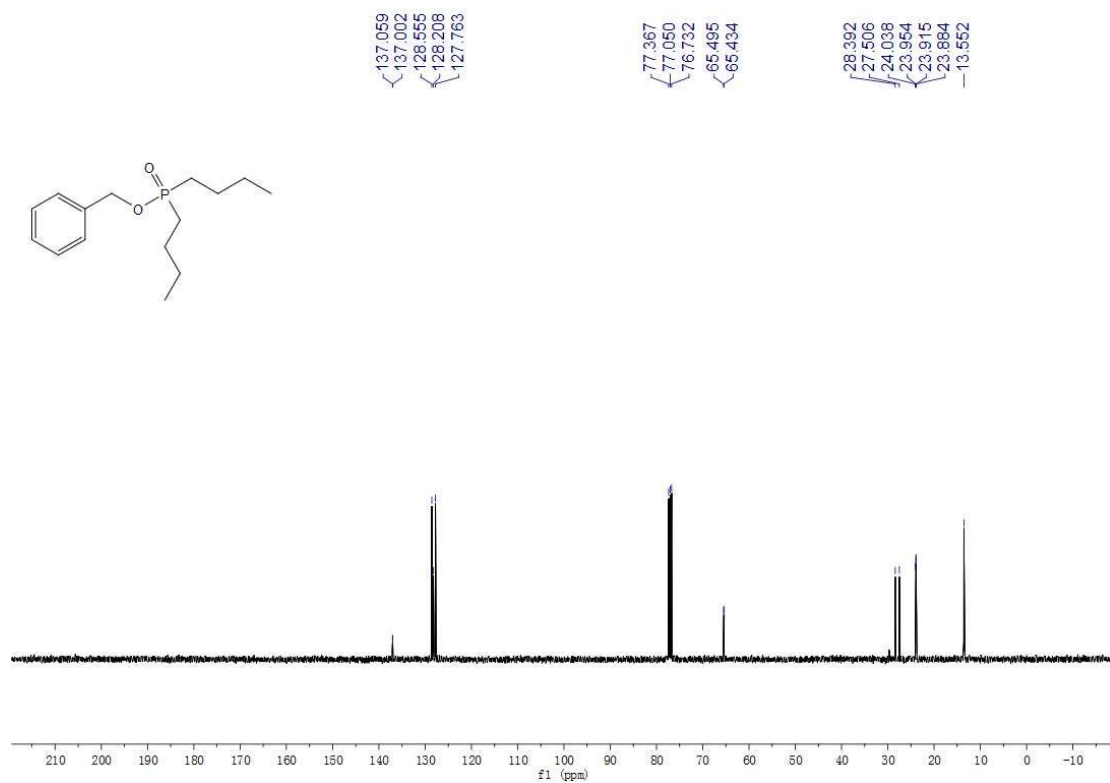


Figure 72.  $3x$ - $^{13}\text{C}$  NMR

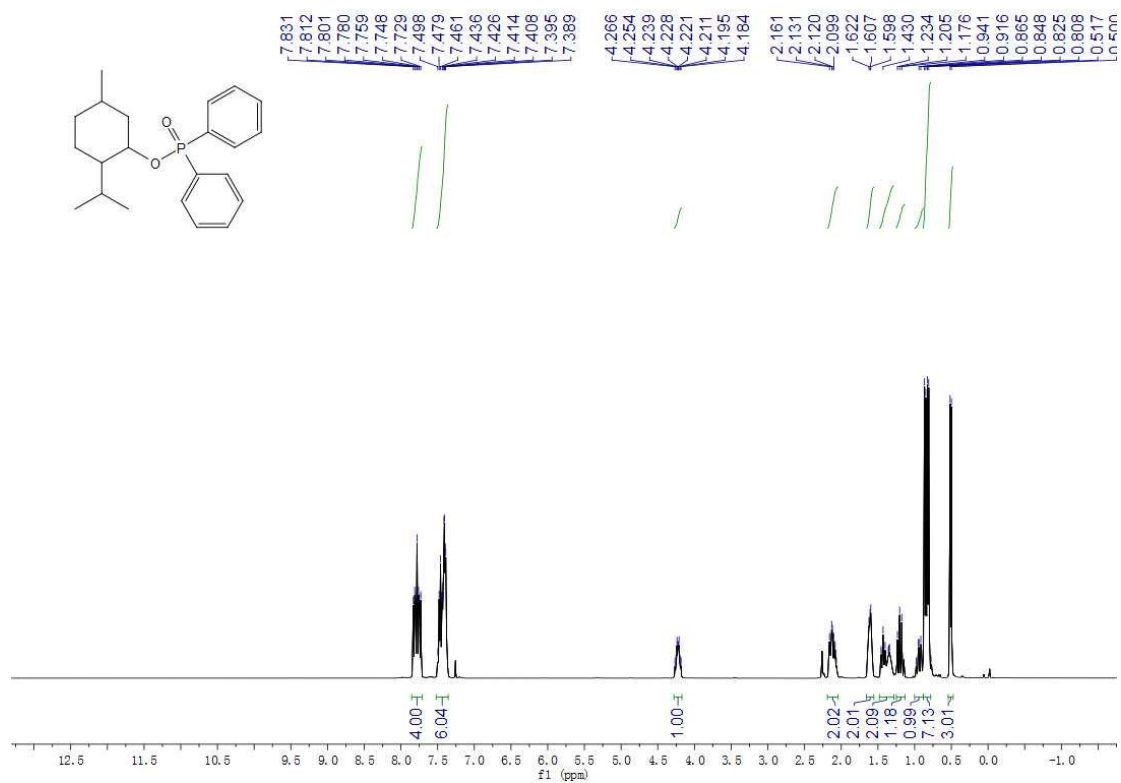


Figure 73. <sup>3</sup>y-<sup>1</sup>H NMR

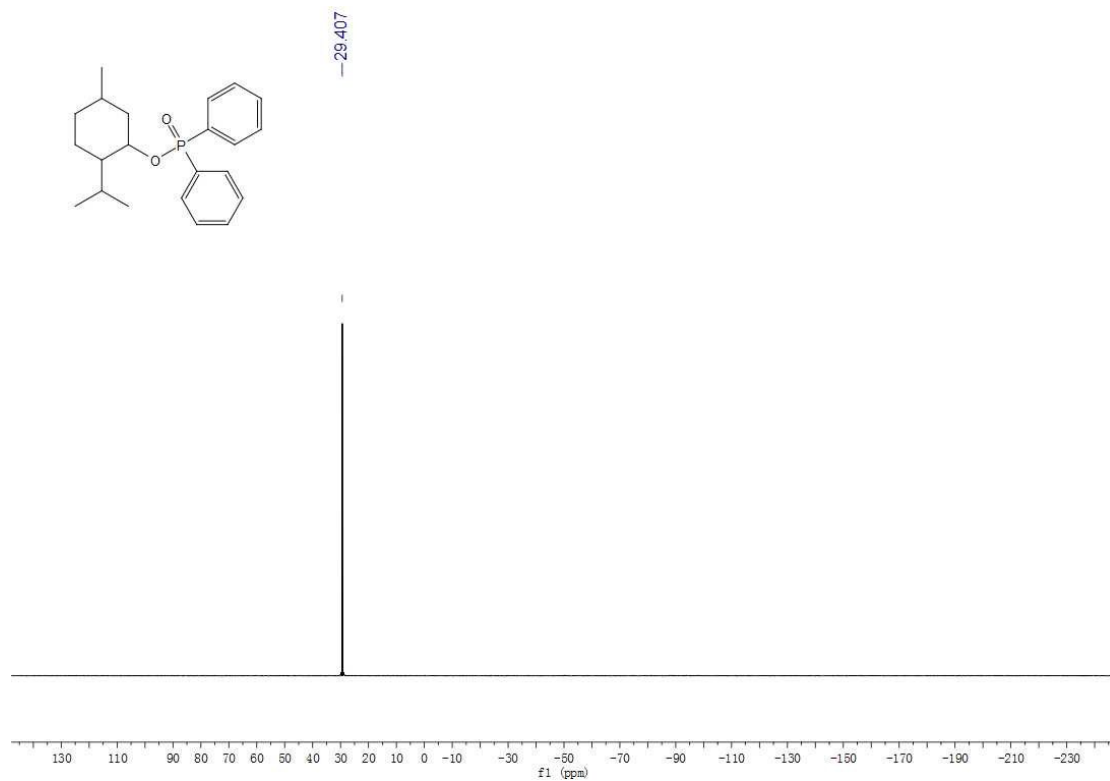


Figure 74. <sup>3</sup>y-<sup>31</sup>P NMR

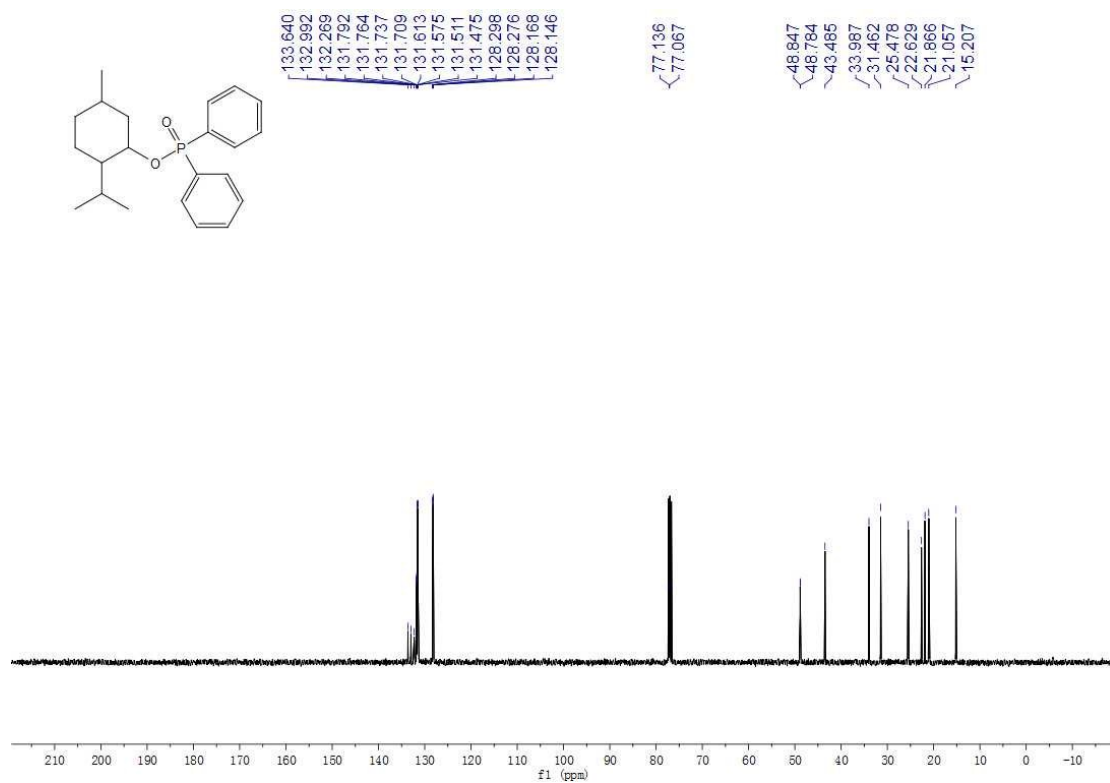


Figure 75. 3y-<sup>13</sup>C NMR

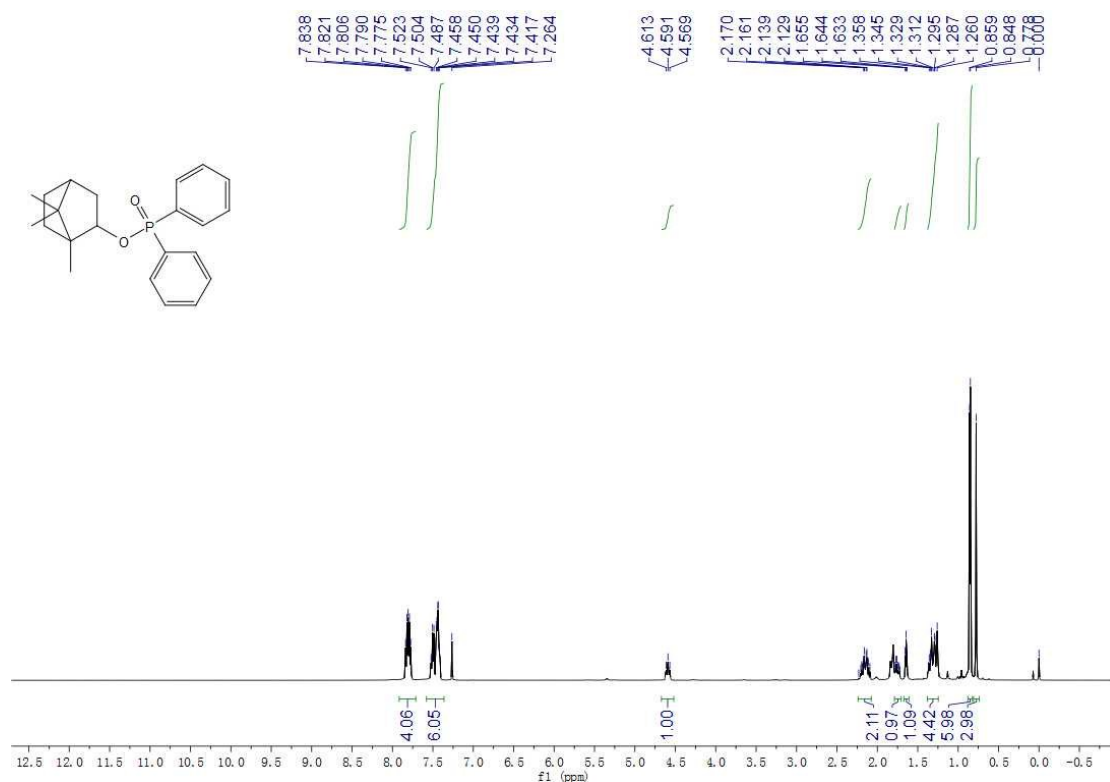


Figure 76. 3z-<sup>1</sup>H NMR

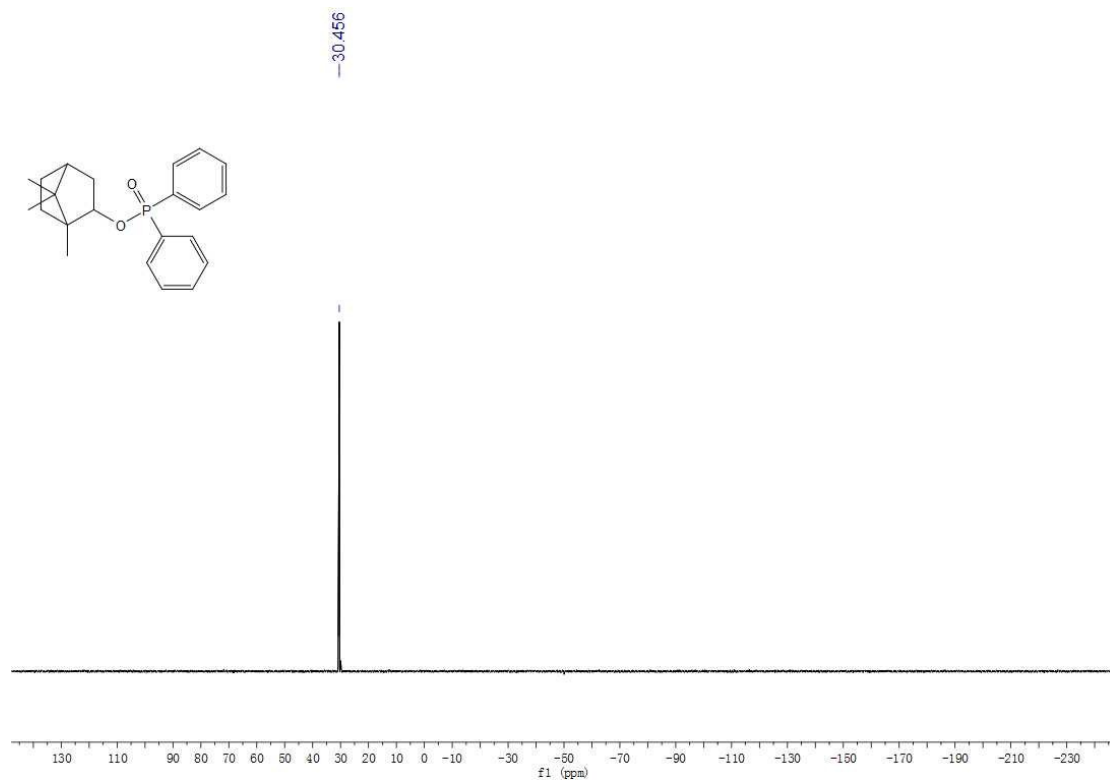


Figure 77.  $3z$ - $^{31}\text{P}$  NMR

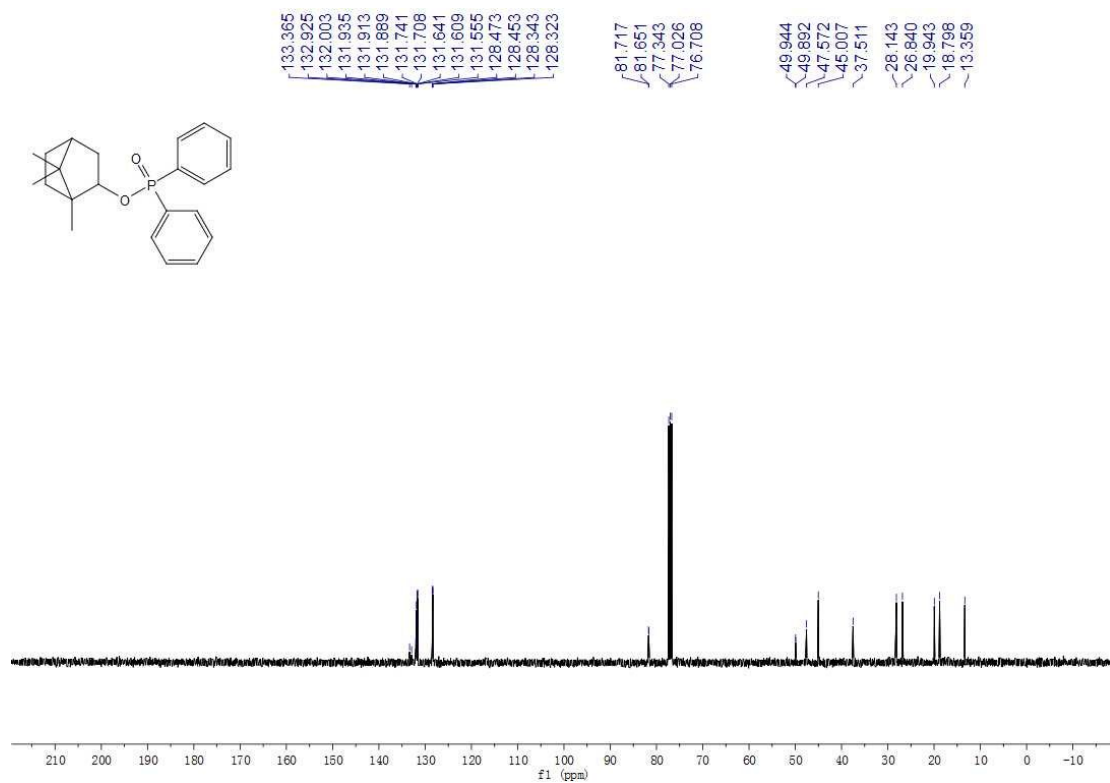


Figure 78.  $3z$ - $^{13}\text{C}$  NMR

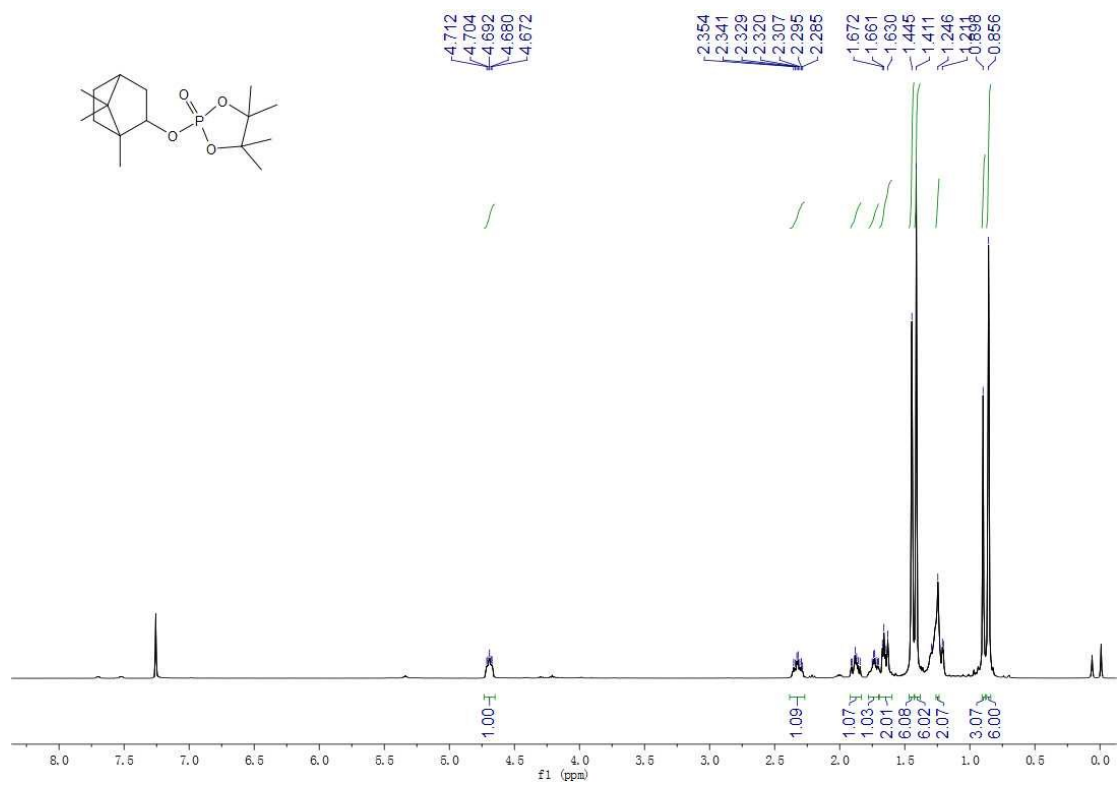


Figure 79. 3aa-<sup>1</sup>H NMR

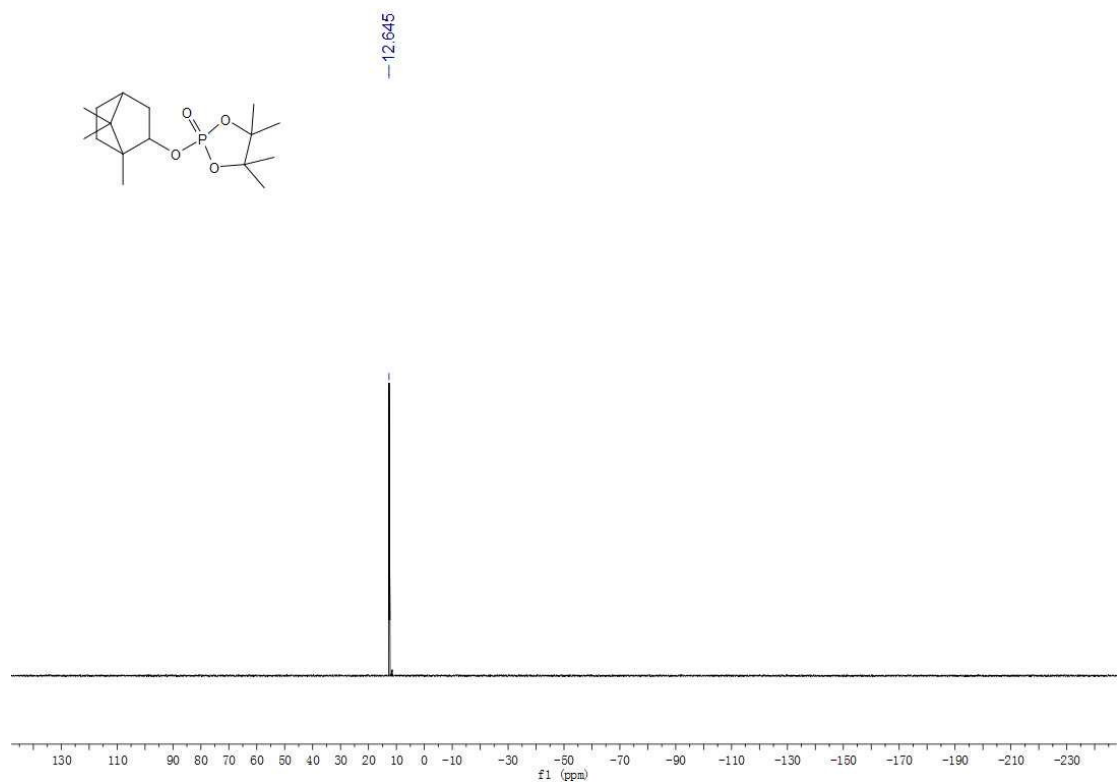


Figure 80. 3aa-<sup>31</sup>P NMR



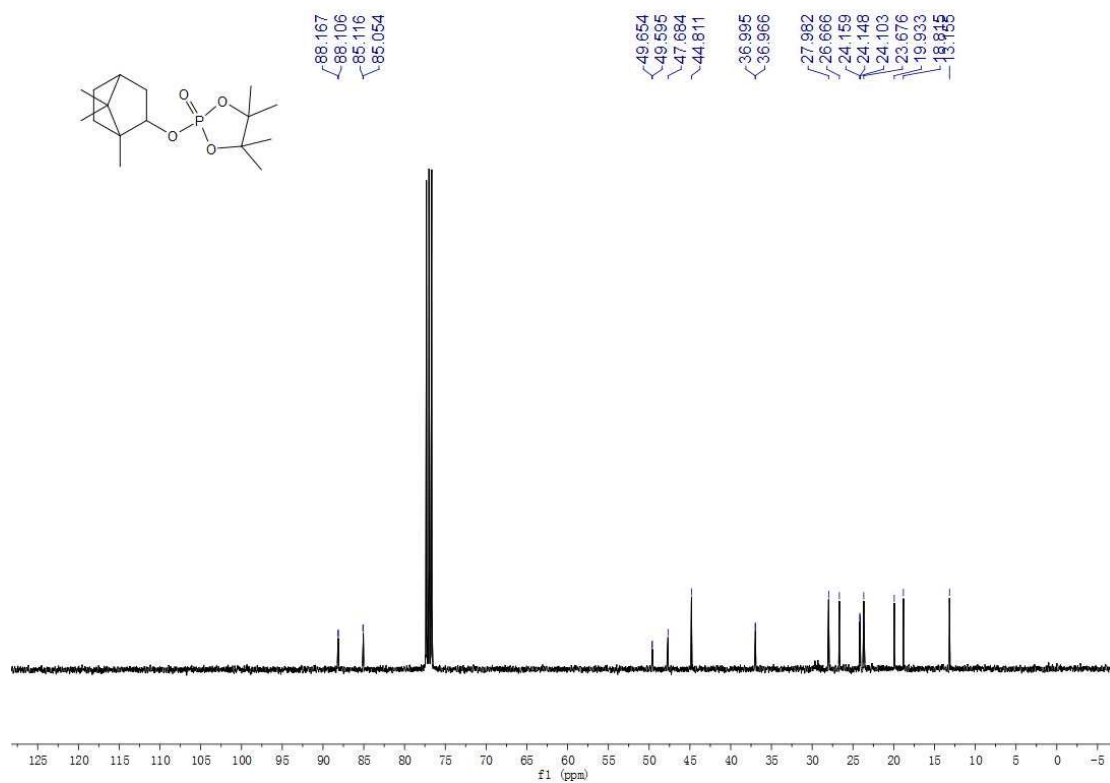


Figure 81. 3aa-<sup>13</sup>C NMR