

## *Supporting information*

### **Mono and Double Mizoroki-Heck Reaction of Aryl Halides with Dialkyl Vinylphosphonates using a Reusable Palladium Catalyst under Aqueous Medium**

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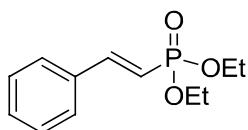
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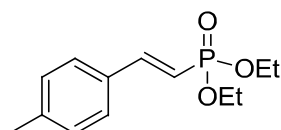
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## Spectral data of products:



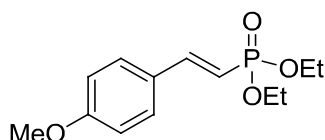
### *Diethyl cinnamylphosphonate (E)-diethyl styrylphosphonate (3a)*

Colorless oil.<sup>[1]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.30 (t, *J* = 7.1 Hz, 6H), 4.03–4.13 (m, 4H), 6.21 (t, *J* = 17.6 Hz, 1H), 7.24–7.52 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 16.2 (*J*<sub>C-P</sub> = 6.0 Hz), 61.6 (*J*<sub>C-P</sub> = 5.3 Hz), 113.6 (*J*<sub>C-P</sub> = 189.8 Hz), 127.5, 128.6, 130.0, 134.5 (*J*<sub>C-P</sub> = 23.3 Hz), 148.6 (*J*<sub>C-P</sub> = 6.8 Hz).



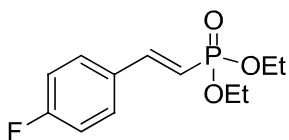
### *(2-p-Tolyvinyl)phosphonic acid diethyl ester (3b)*

Colorless oil.<sup>[2]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.30 (t, *J* = 7.1 Hz, 6H), 2.31 (s, 3H), 4.02–4.12 (m, 4H), 6.14 (t, *J* = 17.7 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.42 (dd, *J* = 17.7 Hz, *J*<sub>H-P</sub> = 22.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 16.3 (*J*<sub>C-P</sub> = 6.0 Hz), 21.3, 61.6 (*J*<sub>C-P</sub> = 5.3 Hz), 112.3 (*J*<sub>C-P</sub> = 190.5 Hz), 127.6, 129.4, 132.0 (*J*<sub>C-P</sub> = 23.3 Hz), 140.5, 148.6 (*J*<sub>C-P</sub> = 6.0 Hz)



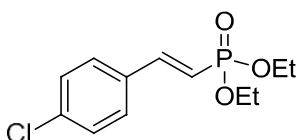
### *(E)-Diethyl 4-methoxystyrylphosphonate (3c)*

Colorless oil.<sup>[2]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.28 (t, *J* = 7.1 Hz, 6H), 3.75 (s, 3H), 4.00–4.10 (m, 4H), 6.02 (t, *J* = 17.7 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 7.37 (t, *J* = 20.1 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 16.4 (*J*<sub>C-P</sub> = 6.8 Hz), 55.3, 61.7 (*J*<sub>C-P</sub> = 5.3 Hz), 110.7 (*J*<sub>C-P</sub> = 192.0 Hz), 114.2, 127.5 (*J*<sub>C-P</sub> = 23.0 Hz), 129.3, 148.5 (*J*<sub>C-P</sub> = 6.8 Hz), 161.3.



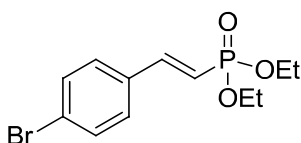
**[2-( 4-Fluorophenyl )vinyl]phosphonic acid diethyl ester (3d)**

Colorless oil.<sup>[3]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.30 (t, *J* = 7.1 Hz, 6H), 4.02–4.12 (m, 4H), 6.12 (t, *J* = 17.4 Hz, 1H), 7.43 (t, *J* = 6 Hz, 2H), 7.34–7.47 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 16.1 (*J*<sub>C-P</sub> = 6.8 Hz), 61.6 (*J*<sub>C-P</sub> = 5.3 Hz), 113.4 (*J*<sub>C-P</sub> = 192.8 Hz), 115.7 (*J*<sub>C-P</sub> = 21.8 Hz), 129.3 (*J*<sub>C-P</sub> = 8.3 Hz), 130.7, 131.0 (*J*<sub>C-P</sub> = 3.0 Hz), 147.2 (*J*<sub>C-P</sub> = 6.8 Hz), 163.6 (*J*<sub>C-F</sub> = 249.8 Hz).



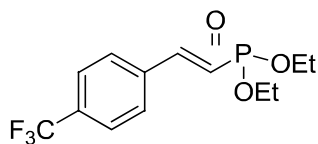
**[2-( 4-Chlorophenyl )vinyl]phosphonic acid diethyl ester (3e)**

Colorless oil.<sup>[4]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.28 (t, *J* = 7.1 Hz, 6H), 4.02–4.11 (m, 4H), 6.17 (t, *J* = 17.3 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 20.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 16.3 (*J*<sub>C-P</sub> = 6.0 Hz), 61.8 (*J*<sub>C-P</sub> = 5.3 Hz), 114.6 (*J*<sub>C-P</sub> = 190.5 Hz), 128.9 (*J*<sub>C-P</sub> = 16.5 Hz), 133.2 (*J*<sub>C-P</sub> = 23.3 Hz), 136.0, 147.1 (*J*<sub>C-P</sub> = 6.8 Hz).



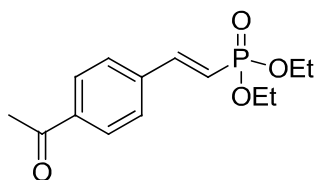
**[2-( 4-Bromophenyl )vinyl]phosphonic acid diethyl ester (3f)**

Colorless oil.<sup>[4]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.28 (t, *J* = 7.1 Hz, 6H), 4.01–4.11 (m, 4H), 6.19 (t, *J* = 17.3 Hz, 1H), 7.28–7.45 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 16.3 (*J*<sub>C-P</sub> = 6.8 Hz), 61.8 (*J*<sub>C-P</sub> = 5.3 Hz), 114.7 (*J*<sub>C-P</sub> = 190.5 Hz), 124.3, 130.0, 131.9, 133.6 (*J*<sub>C-P</sub> = 24 Hz), 147.1 (*J*<sub>C-P</sub> = 6.8 Hz).



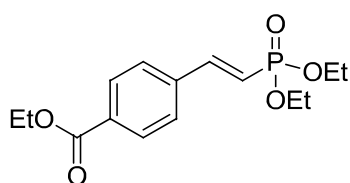
**(E)-Diethyl 4-(trifluoromethyl)styrylphosphonate (3g)**

Colorless oil.<sup>[4]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.33 (t, *J* = 7.1 Hz, 6H), 4.06–4.16 (m, 4H), 6.33 (t, *J* = 17.3 Hz, 1H), 7.42–7.62 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 15.9 (*J*<sub>C-P</sub> = 6.8 Hz), 61.6 (*J*<sub>C-P</sub> = 6.0 Hz), 116.8 (*J*<sub>C-P</sub> = 189.0 Hz), 123.4 (*J*<sub>C-P</sub> = 270.8 Hz), 125.3 (*J*<sub>C-P</sub> = 3.0 Hz), 127.5, 131.2 (*J*<sub>C-P</sub> = 32.3 Hz), 137.8 (*J*<sub>C-P</sub> = 23.3 Hz), 146.3 (*J*<sub>C-P</sub> = 6.8 Hz).



**(E)-Diethyl 4-methoxystyrylphosphonate (3h)**

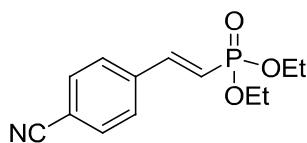
Colorless oil.<sup>[4]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.28 (t, *J* = 7.1 Hz, 6H), 2.53 (s, 3H), 4.02–4.12 (m, 4H), 6.31 (t, *J* = 17.3 Hz, 1H), 7.43 (dd, *J* = 17.4 Hz, *J*<sub>H-P</sub> = 22.2 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 16.4 (*J*<sub>C-P</sub> = 6.0 Hz), 26.7, 62.0 (*J*<sub>C-P</sub> = 6.0 Hz), 117.1 (*J*<sub>C-P</sub> = 189.8 Hz), 127.8, 128.8, 137.9, 139.0 (*J*<sub>C-P</sub> = 23.3 Hz), 147.1 (*J*<sub>C-P</sub> = 6.0 Hz), 197.3.



**(E)-Ethyl 4-(2-(diethoxyphosphoryl)vinyl)benzoate (3i)**

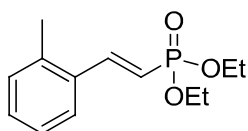
Colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.27–1.35 (m, 9H), 4.05–4.13 (m, 4H), 4.31 (q, *J* = 7.2 Hz, 2H), 6.30 (t, *J* = 17.3 Hz, 1H), 7.45 (dd, *J*<sub>H-P</sub> = 24.4 Hz, *J* = 13.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 14.1, 16.2 (*J*<sub>C-P</sub> = 6.0 Hz), 61.0, 61.8 (*J*<sub>C-P</sub> = 6.0 Hz), 116.6 (*J*<sub>C-P</sub> = 189.0 Hz), 127.4, 129.8, 131.5, 138.7 (*J*<sub>C-P</sub> = 22.5 Hz), 147.1 (*J*<sub>C-P</sub> = 6.0 Hz).

= 6.0 Hz), 165.7;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  = 19.53; HRMS calcd for  $\text{C}_{15}\text{H}_{21}\text{O}_5\text{P}$ , 312.1127; found, 312.1129.



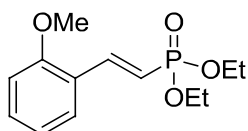
**(E)-Diethyl 4-cyanostyrylphosphonate (3j)**

Pale yellow solid. mp 86–88 °C.<sup>[4]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.22 (t,  $J$  = 7.1 Hz, 6H), 3.96–4.06 (m, 4H), 6.27 (t,  $J$  = 17.1 Hz, 1H), 7.35 (dd,  $J$  = 17.7 Hz,  $J_{\text{H-P}}$  = 22.2 Hz, 1H), 7.47 (d,  $J$  = 8.4 Hz, 2H), 7.55 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.3 ( $J_{\text{C-P}}$  = 6.0 Hz), 62.1 ( $J_{\text{C-P}}$  = 5.3 Hz), 113.2, 118.3, 118.4 ( $J_{\text{C-P}}$  = 189.0 Hz), 123.6, 128.1, 138.9 ( $J_{\text{C-P}}$  = 23.3 Hz), 146.1 ( $J_{\text{C-P}}$  = 6.8 Hz).



**(2-o-Tolylvinyl)phosphonic acid diethyl ester (3k)**

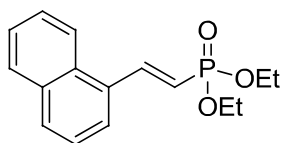
Colorless oil.<sup>[5]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.29 (t,  $J$  = 7.1 Hz, 6H), 2.36 (s, 3H), 4.03–4.12 (m, 4H), 6.12 (dd,  $J$  = 17.4 Hz,  $J_{\text{H-P}}$  = 18.6 Hz, 1H), 7.11–7.23 (m, 3H), 7.46 (d,  $J$  = 7.5 Hz, 1H), 7.71 (dd,  $J$  = 17.4 Hz,  $J_{\text{H-P}}$  = 22.5 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.2 ( $J_{\text{C-P}}$  = 6.0 Hz), 61.6 ( $J_{\text{C-P}}$  = 5.3 Hz), 115.0 ( $J_{\text{C-P}}$  = 189.0 Hz), 126.0 ( $J_{\text{C-P}}$  = 21.8 Hz), 129.8, 130.6, 133.7 ( $J_{\text{C-P}}$  = 22.5 Hz), 137.0, 146.2 ( $J_{\text{C-P}}$  = 6.8 Hz).



**(E)-Diethyl 2-methoxystyrylphosphonate (3l)**

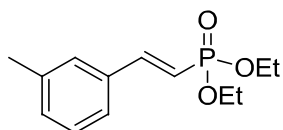
Colorless oil.<sup>[5]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.27 (t,  $J$  = 7.1 Hz, 6H), 3.77 (s, 3H), 4.00–4.09 (m, 4H), 6.27 (dd,  $J$  = 17.4 Hz,  $J_{\text{H-P}}$  = 19.5 Hz, 1H), 6.86 (d,  $J$  = 8.4 Hz, 1H), 6.91 (d,  $J$  = 7.5 Hz, 1H),

7.30 (d,  $J = 7.9$  Hz, 1H), 7.44 (d,  $J = 7.8$  Hz, 1H), 7.72 (dd,  $J = 17.7$  Hz,  $J_{\text{H-P}} = 23.7$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.2 ( $J_{\text{C-P}} = 6.8$  Hz), 55.2, 61.5 ( $J_{\text{C-P}} = 5.3$  Hz), 110.9, 113.9 ( $J_{\text{C-P}} = 189.0$  Hz), 120.4, 123.4 ( $J_{\text{C-P}} = 22.5$  Hz), 128.3, 131.3, 143.9 ( $J_{\text{C-P}} = 7.5$  Hz), 157.8.



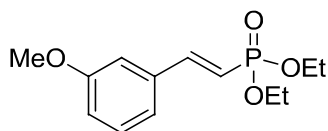
**(E)-diethyl 2-(naphthalen-1-yl)vinylphosphonate (3m)**

Colorless oil.<sup>[6]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.36 (t,  $J = 7.2$  Hz, 6H), 4.11–4.21 (m, 4H), 6.34 (dd,  $J = 17.4$  Hz,  $J_{\text{H-P}} = 18.9$  Hz, 1H), 7.42–7.56 (m, 3H), 7.69 (d,  $J = 6.9$  Hz, 1H), 7.81–7.86 (m, 2H), 8.15 (d,  $J = 8.1$  Hz, 1H), 8.30 (dd,  $J = 17.4$  Hz,  $J_{\text{H-P}} = 22.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.4 ( $J_{\text{C-P}} = 6.8$  Hz), 61.8 ( $J_{\text{C-P}} = 5.3$  Hz), 117.1 ( $J_{\text{C-P}} = 188.3$  Hz), 123.1, 124.6, 125.3, 126.1, 126.7, 128.6, 130.3, 130.9, 133.5, 132.3 ( $J_{\text{C-P}} = 22.5$  Hz), 145.7 ( $J_{\text{C-P}} = 6.8$  Hz).



**(2-m-Tolylvinyl)phosphonic acid diethyl ester (3n)**

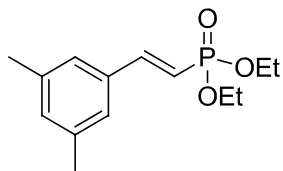
Colorless oil.<sup>[7]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.29 (t,  $J = 7.1$  Hz, 6H), 2.29 (s, 3H), 4.01–4.11 (m, 4H), 6.18 (t,  $J = 17.7$  Hz, 1H), 7.11–7.25 (m, 4H), 7.42 (dd,  $J = 15.8$  Hz,  $J_{\text{H-P}} = 17.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.2 ( $J_{\text{C-P}} = 6.8$  Hz), 21.14, 61.6 ( $J_{\text{C-P}} = 6.0$  Hz), 113.3 ( $J_{\text{C-P}} = 190.5$  Hz), 124.8, 128.4 ( $J_{\text{C-P}} = 33.8$  Hz), 130.9, 134.6 ( $J_{\text{C-P}} = 23.3$  Hz), 138.3, 148.8 ( $J_{\text{C-P}} = 6.8$  Hz).



**(E)-diethyl 3-methoxystyrylphosphonate (3o)**

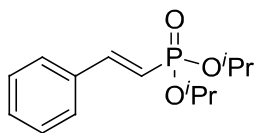
Colorless oil.<sup>[6]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.28 (t,  $J = 7.1$  Hz, 6H), 3.75 (s, 3H), 4.01–4.11 (m,

4H), 6.18 (t,  $J = 17.6$  Hz, 1H), 6.84–7.04 (m, 3H), 7.23 (t,  $J = 7.8$  Hz, 1H), 7.40 (dd,  $J = 17.4$  Hz,  $J_{\text{H-P}} = 22.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.2 ( $J_{\text{C-P}} = 6.8$  Hz), 55.1, 61.7 ( $J_{\text{C-P}} = 5.3$  Hz), 112.4, 114.0 ( $J_{\text{C-P}} = 189.8$  Hz), 115.9, 120.2, 129.7, 136.0 ( $J_{\text{C-P}} = 23.3$  Hz), 148.5 ( $J_{\text{C-P}} = 6.8$  Hz).



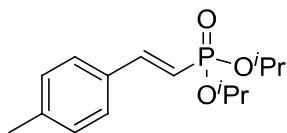
**[2-(3,5-Dimethylphenyl)vinyl]phosphonic acid diethyl ester (3p)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.30 (t,  $J = 7.1$  Hz, 6H), 2.28 (s, 6H), 4.03–4.13 (m, 4H), 6.18 (t,  $J = 17.7$  Hz, 1H), 6.97 (s, 1H), 7.07 (s, 2H), 7.41 (dd,  $J_{\text{H-P}} = 22.5$  Hz,  $J = 17.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.3 ( $J_{\text{C-P}} = 6.4$  Hz), 21.1, 61.7 ( $J_{\text{C-P}} = 5.3$  Hz), 113.2 ( $J_{\text{C-P}} = 190.0$  Hz), 125.5, 131.9, 134.7 ( $J_{\text{C-P}} = 22.9$  Hz), 138.3, 149.0 ( $J_{\text{C-P}} = 6.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  20.96; HRMS calcd for  $\text{C}_{14}\text{H}_{21}\text{O}_3\text{P}$ , 268.1288; found, 268.1282.



**(E)-Diisopropyl styrylphosphonate (4a)**

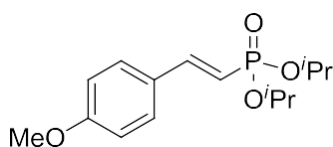
Colorless oil.  $^{181}\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.29 (d,  $J = 6.2$  Hz, 6H), 1.34 (d,  $J = 6.2$  Hz, 6H), 4.63–4.74 (m, 2H), 6.24 (t,  $J = 17.4$  Hz, 1H), 7.24–7.52 (m, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.0 ( $J_{\text{C-P}} = 5.3$  Hz), 24.1 ( $J_{\text{C-P}} = 4.5$  Hz), 70.4 ( $J_{\text{C-P}} = 6.0$  Hz), 115.5 ( $J_{\text{C-P}} = 190.5$  Hz), 127.6, 128.8, 130.0, 135.0 ( $J_{\text{C-P}} = 23.3$  Hz), 147.7 ( $J_{\text{C-P}} = 6.8$  Hz).



**(E)-Diisopropyl 4-methylstyrylphosphonate (4b)**

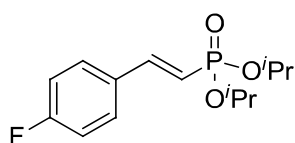
Colorless oil.  $^{181}\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.26 (d,  $J = 6.2$  Hz, 6H), 1.31 (d,  $J = 6.2$  Hz, 6H),

2.31 (s, 3H), 4.60–4.71 (m, 2H), 6.15 (t,  $J = 17.5$  Hz, 1H), 7.11–7.47 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  21.3, 23.9 ( $J_{\text{C-P}} = 4.7$  Hz), 24.0 ( $J_{\text{C-P}} = 4.1$  Hz), 70.2 ( $J_{\text{C-P}} = 5.5$  Hz), 114.1 ( $J_{\text{C-P}} = 191.0$  Hz), 127.5, 129.4, 132.2 ( $J_{\text{C-P}} = 23.2$  Hz), 140.3, 147.7 ( $J_{\text{C-P}} = 6.7$  Hz).



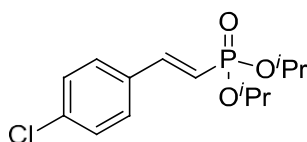
**(E)-Diisopropyl 4-methoxystyrylphosphonate (4c)**

Colorless oil.  $^{81}\text{Br}$   $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.28 (d,  $J = 6.2$  Hz, 6H), 1.33 (d,  $J = 6.2$  Hz, 6H), 3.80 (s, 3H), 4.63–4.70 (m, 2H), 6.07 (t,  $J = 17.4$  Hz, 1H), 6.85–6.88 (m, 2H), 7.33–7.46 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.0 ( $J_{\text{C-P}} = 4.8$  Hz), 24.1 ( $J_{\text{C-P}} = 4.2$  Hz), 55.3, 70.3 ( $J_{\text{C-P}} = 5.4$  Hz), 112.5 ( $J_{\text{C-P}} = 192.1$  Hz), 114.1, 127.8 ( $J_{\text{C-P}} = 23.5$  Hz), 129.2, 147.5 ( $J_{\text{C-P}} = 6.9$  Hz), 161.1.



**(E)-Diisopropyl 4-fluorostyrylphosphonate (4d)**

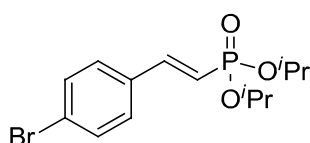
Colorless oil.  $^{81}\text{Br}$   $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.26 (d,  $J = 6.2$  Hz, 6H), 1.31 (d,  $J = 6.2$  Hz, 6H), 4.60–4.71 (m, 2H), 6.12 (t,  $J = 17.2$  Hz, 1H), 6.98–7.04 (m, 2H), 7.31–7.44 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.0 ( $J_{\text{C-P}} = 4.9$  Hz), 70.4 ( $J_{\text{C-P}} = 5.5$  Hz), 115.3 ( $J_{\text{C-P}} = 191.4$  Hz), 115.8 ( $J_{\text{C-F}} = 21.8$  Hz), 127.2 ( $J_{\text{C-F}} = 8.1$  Hz), 131.2 (dd,  $J_{\text{C-P}} = 23.6$  Hz,  $J_{\text{C-F}} = 3.2$  Hz), 146.3 ( $J_{\text{C-P}} = 6.8$  Hz), 163.6 ( $J_{\text{C-F}} = 249.1$  Hz).



**(E)-diisopropyl 4-chlorostyrylphosphonate (4e)**

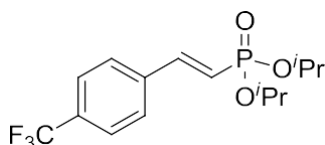


Colorless oil.<sup>[8]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.28 (d, *J* = 6.2 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 6H), 4.62–4.73 (m, 2H), 6.20 (t, *J* = 17.1 Hz, 1H), 7.29–7.45 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 24.0 (*J*<sub>C-P</sub> = 4.8 Hz), 70.5 (*J*<sub>C-P</sub> = 5.6 Hz), 116.3 (*J*<sub>C-P</sub> = 191.0 Hz), 128.9 (*J*<sub>C-P</sub> = 18.2 Hz), 133.5 (*J*<sub>C-P</sub> = 23.6 Hz), 135.9, 146.2 (*J*<sub>C-P</sub> = 6.8 Hz).



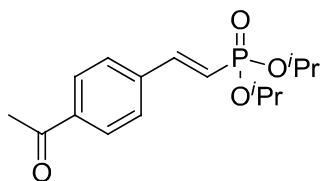
**(E)-diisopropyl 4-bromostyrylphosphonate (4f)**

Colorless oil.<sup>[9]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.27 (d, *J* = 6.2 Hz, 6H), 1.32 (d, *J* = 6.2 Hz, 6H), 4.61–4.72 (m, 2H), 6.21 (t, *J* = 17.1 Hz, 1H), 7.29–7.47 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 24.0 (*J*<sub>C-P</sub> = 4.8 Hz), 70.5 (*J*<sub>C-P</sub> = 5.6 Hz), 116.5 (*J*<sub>C-P</sub> = 190.8 Hz), 124.2, 129.0, 132.0, 133.9 (*J*<sub>C-P</sub> = 23.5 Hz), 146.2 (*J*<sub>C-P</sub> = 6.8 Hz).



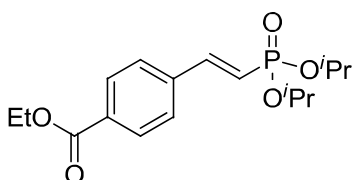
**(E)-diisopropyl 4-(trifluoromethyl)styrylphosphonate (4g)**

Colorless oil.<sup>[8]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.28 (d, *J* = 6.2 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 6H), 4.63–4.74 (m, 2H), 6.32 (t, *J* = 17.0 Hz, 1H), 7.45 (dd, *J* = 17.5 Hz, *J*<sub>H-P</sub> = 22.3 Hz, 1H), 7.53–7.60 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 24.0 (*J*<sub>C-P</sub> = 4.7 Hz), 70.7 (*J*<sub>C-P</sub> = 5.6 Hz), 118.8 (*J*<sub>C-P</sub> = 190.1 Hz), 123.8 (*J*<sub>C-F</sub> = 270.5 Hz), 125.7 (*J*<sub>C-F</sub> = 3.5 Hz), 127.7, 131.5 (*J*<sub>C-F</sub> = 32.5 Hz), 138.3 (*J*<sub>C-P</sub> = 23.2 Hz), 145.7 (*J*<sub>C-P</sub> = 6.7 Hz).



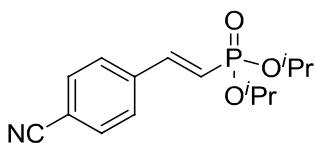
**(E)-Diisopropyl 4-acetylstyrylphosphonate (4h)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.27 (d,  $J = 6.2$  Hz, 6H), 1.32 (d,  $J = 6.2$  Hz, 6H), 2.56 (s, 3H), 4.62–4.73 (m, 2H), 6.33 (t,  $J = 17.3$  Hz, 1H), 7.44 (dd,  $J = 17.3$  Hz,  $J_{\text{H-P}} = 22.4$  Hz, 1H), 7.52 (d,  $J = 8.5$  Hz, 2H), 7.91 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.0 ( $J_{\text{C-P}} = 4.5$  Hz), 26.6, 70.7 ( $J_{\text{C-P}} = 5.6$  Hz), 118.7 ( $J_{\text{C-P}} = 190.0$  Hz), 127.7, 128.7, 137.8, 139.2 ( $J_{\text{C-P}} = 23.2$  Hz), 146.0 ( $J_{\text{C-P}} = 6.7$  Hz), 197.2;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  17.16; HRMS calcd for  $\text{C}_{16}\text{H}_{23}\text{O}_4\text{P}$ , 310.1334; found, 310.1340.



**(E)-Ethyl 4-(2-(diisopropoxyphosphoryl)vinyl)benzoate (4i)**

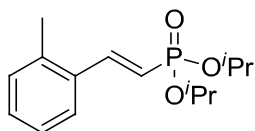
Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.29 (d,  $J = 6.2$  Hz, 6H), 1.34 (d,  $J = 6.2$  Hz, 6H), 1.36 (t,  $J = 5.7$  Hz, 3H), 4.35 (q,  $J = 7.1$  Hz, 2H), 4.64–4.73 (m, 2H), 6.33 (t,  $J = 17.3$  Hz, 1H), 7.46 (dd,  $J = 17.3$  Hz,  $J_{\text{H-P}} = 22.3$  Hz, 1H), 7.51 (d,  $J = 8.3$  Hz, 2H), 8.01 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  14.3, 24.0 ( $J_{\text{C-P}} = 4.5$  Hz), 61.1, 70.7 ( $J_{\text{C-P}} = 5.6$  Hz), 118.4 ( $J_{\text{C-P}} = 190.1$  Hz), 127.4, 130.0, 131.5, 139.0 ( $J_{\text{C-P}} = 23.2$  Hz), 146.3 ( $J_{\text{C-P}} = 6.5$  Hz), 165.9;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  17.32; HRMS calcd for  $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}$ , 340.1440; found, 340.1447.



**(E)-Diisopropyl 4-cyanostyrylphosphonate (4j)**

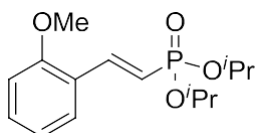
White solid. mp 64–66 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.28 (d,  $J = 6.2$  Hz, 6H), 1.33 (d,  $J = 6.2$  Hz, 6H), 4.64–4.75 (m, 2H), 6.35 (dd,  $J_{\text{H-P}} = 16.1$  Hz,  $J = 17.5$  Hz, 1H), 7.36 (dd,  $J = 17.5$  Hz,  $J_{\text{H-P}} = 22.2$  Hz, 1H), 7.54 (d,  $J = 8.4$  Hz, 2H), 7.64 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.0 ( $J_{\text{C-P}} = 4.1$  Hz), 70.9 ( $J_{\text{C-P}} = 5.7$  Hz), 113.1, 118.3, 120.1 ( $J_{\text{C-P}} = 189.9$  Hz), 128.0, 132.6, 139.2

( $J_{C-P} = 23.5$  Hz), 145.1 ( $J_{C-P} = 6.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  16.40; HRMS calcd for  $\text{C}_{15}\text{H}_{20}\text{NO}_3\text{P}$ , 293.1181; found, 293.1179.



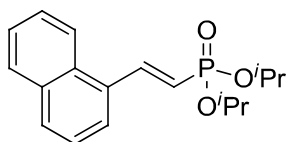
**(E)-Diisopropyl 2-methylstyrylphosphonate (4k)**

Colorless oil.<sup>[8]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.30 (d,  $J = 6.2$  Hz, 6H), 1.34 (d,  $J = 6.2$  Hz, 6H), 2.39 (s, 3H), 4.63–4.74 (m, 2H), 6.16 (dd,  $J = 17.3$  Hz,  $J_{H-P} = 18.4$  Hz, 1H), 7.14–7.24 (m, 3H), 7.48 (d,  $J = 7.9$  Hz, 1H), 7.71 (dd,  $J = 17.4$  Hz,  $J_{H-P} = 22.7$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  19.7, 24.0 ( $J_{C-P} = 4.7$  Hz), 24.1 ( $J_{C-P} = 4.1$  Hz), 70.1 ( $J_{C-P} = 5.6$  Hz), 117.0 ( $J_{C-P} = 189.8$  Hz), 126.1 ( $J_{C-P} = 19.6$  Hz), 129.7, 130.7, 134.1 ( $J_{C-P} = 22.4$  Hz), 137.0, 145.3 ( $J_{C-P} = 6.9$  Hz).



**(E)-Diisopropyl 2-methoxystyrylphosphonate (4l)**

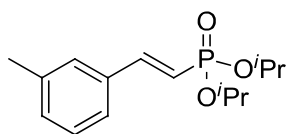
Colorless oil.<sup>[10]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.29 (d,  $J = 6.2$  Hz, 6H), 1.34 (d,  $J = 6.2$  Hz, 6H), 3.83 (s, 3H), 4.62–4.73 (m, 2H), 6.32 (dd,  $J = 17.7$  Hz,  $J_{H-P} = 19.3$  Hz, 1H), 6.86–6.95 (m, 2H), 7.24–7.33 (m, 1H), 7.45 (d,  $J = 7.7$  Hz, 1H), 7.75 (dd,  $J = 17.7$  Hz,  $J_{H-P} = 23.6$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.0 ( $J_{C-P} = 4.6$  Hz), 24.1 ( $J_{C-P} = 4.0$  Hz), 55.4, 70.2 ( $J_{C-P} = 5.4$  Hz), 111.1, 115.9 ( $J_{C-P} = 189.5$  Hz), 120.5, 123.9 ( $J_{C-P} = 23.2$  Hz), 128.3, 131.2, 143.0 ( $J_{C-P} = 7.8$  Hz), 158.0.



**(E)-Diisopropyl (2-(naphthalen-1-yl)vinyl)phosphonate (4m)**

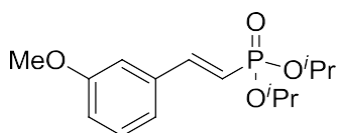
Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.34 (d,  $J = 6.0$  Hz, 6H), 1.38 (d,  $J = 6.0$  Hz, 6H),

4.70–4.81 (m, 2H), 6.36 (dd,  $J = 17.2$  Hz,  $J_{\text{H-P}} = 18.6$  Hz, 1H), 7.46–7.53 (m, 3H), 7.69 (d,  $J = 7.1$  Hz, 1H), 7.83–7.87 (m, 2H), 8.17 (d,  $J = 8.1$  Hz, 1H), 8.28 (dd,  $J = 17.2$  Hz,  $J_{\text{H-P}} = 22.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.1 ( $J_{\text{C-P}} = 4.8$  Hz), 70.5 ( $J_{\text{C-P}} = 5.5$  Hz), 118.9 ( $J_{\text{C-P}} = 188.7$  Hz), 123.3, 124.6, 125.4, 126.2, 126.8, 128.6, 130.2, 131.1, 132.7 ( $J_{\text{C-P}} = 22.8$  Hz), 133.6, 144.8 ( $J_{\text{C-P}} = 7.0$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  17.72; HRMS calcd for  $\text{C}_{18}\text{H}_{23}\text{O}_3\text{P}$ , 318.1385; found, 318.1381.



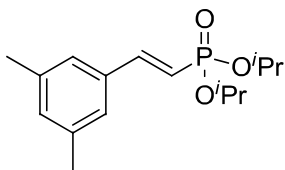
***(E)*-Diisopropyl 3-methylstyrylphosphonate (4n)**

Colorless oil.  $^{181}\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.29 (d,  $J = 6.2$  Hz, 6H), 1.34 (d,  $J = 6.2$  Hz, 6H), 2.34 (s, 3H), 4.63–4.73 (m, 2H), 6.22 (t,  $J = 17.5$  Hz, 1H), 7.15–7.28 (m, 4H), 7.43 (dd,  $J = 17.5$  Hz,  $J_{\text{H-P}} = 22.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  21.3, 24.0 ( $J_{\text{C-P}} = 4.8$  Hz), 24.1 ( $J_{\text{C-P}} = 4.1$  Hz), 70.4 ( $J_{\text{C-P}} = 5.4$  Hz), 115.2 ( $J_{\text{C-P}} = 190.6$  Hz), 124.9, 128.2, 128.7, 130.8, 135.0 ( $J_{\text{C-P}} = 22.9$  Hz), 138.4, 148.0 ( $J_{\text{C-P}} = 6.6$  Hz).



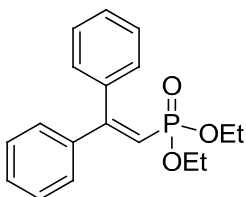
***(E)*-Diisopropyl 3-methoxystyrylphosphonate (4o)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.29 (d,  $J = 6.2$  Hz, 6H), 1.34 (d,  $J = 6.2$  Hz, 6H), 3.80 (s, 3H), 4.65–4.74 (m, 2H), 6.23 (t,  $J = 17.4$  Hz, 1H), 6.87–7.07 (m, 3H), 7.27 (t,  $J = 8.2$  Hz, 1H), 7.42 (dd,  $J = 17.4$  Hz,  $J_{\text{H-P}} = 22.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.0 ( $J_{\text{C-P}} = 4.9$  Hz), 24.1 ( $J_{\text{C-P}} = 4.3$  Hz), 55.3, 70.5 ( $J_{\text{C-P}} = 5.5$  Hz), 112.6, 115.9 ( $J_{\text{C-P}} = 190.6$  Hz), 115.8, 120.3, 130.0, 136.4 ( $J_{\text{C-P}} = 23.2$  Hz), 147.7 ( $J_{\text{C-P}} = 6.7$  Hz), 159.8;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  18.31; HRMS calcd for  $\text{C}_{15}\text{H}_{23}\text{O}_4\text{P}$ , 298.1334; found, 298.1336.



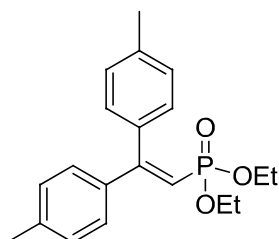
**(E)-diisopropyl 3,5-dimethylstyrylphosphonate (4p)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.28 (d,  $J = 6.2$  Hz, 6H), 1.33 (d,  $J = 6.2$  Hz, 6H), 2.29 (s, 6H), 4.61–4.72 (m, 2H), 6.20 (t,  $J = 17.5$  Hz, 1H), 6.98 (s, 1H), 7.08 (s, 2H), 7.39 (dd,  $J = 17.5$  Hz,  $J_{\text{H-P}} = 22.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  21.1, 24.0 ( $J_{\text{C-P}} = 4.7$  Hz), 24.1 ( $J_{\text{C-P}} = 4.1$  Hz), 70.3 ( $J_{\text{C-P}} = 5.4$  Hz), 115.0 ( $J_{\text{C-P}} = 190.5$  Hz), 125.4, 131.1, 134.9 ( $J_{\text{C-P}} = 22.9$  Hz), 138.3, 148.0 ( $J_{\text{C-P}} = 6.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  18.74; HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{O}_3\text{P}$ , 296.1541; found, 296.1542.



**Diethyl (2,2-diphenylethenyl)phosphonate (6a)**

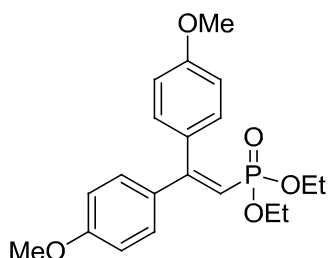
Colorless oil.  $^{91}\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.09 (t,  $J = 7.1$  Hz, 6H), 3.74–3.93 (m, 4H), 6.15 (d,  $J_{\text{H-P}} = 15.3$  Hz, 1H), 7.23–7.35 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.0 ( $J_{\text{C-P}} = 6.8$  Hz), 61.4 ( $J_{\text{C-P}} = 6.0$  Hz), 114.6 ( $J_{\text{C-P}} = 192.0$  Hz), 127.7, 128.0, 128.2, 128.5, 129.2, 129.6, 138.7 ( $J_{\text{C-P}} = 7.5$  Hz), 141.3 ( $J_{\text{C-P}} = 21.8$  Hz), 160.0 ( $J_{\text{C-P}} = 6.0$  Hz).



**Diethyl (2,2-di-p-tolylvinyl)phosphonate (6b)**

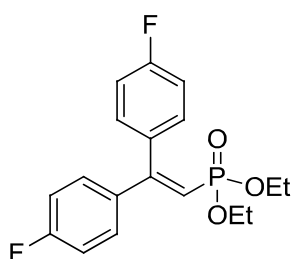
Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.10 (t,  $J = 7.1$  Hz, 6H), 2.31 (s, 3H), 2.34 (s, 3H),

3.76–3.93 (m, 4H), 6.07 (d,  $J_{\text{H-P}} = 15.7$  Hz, 1H), 7.07 (d,  $J = 8.2$  Hz, 2H), 7.14 (d,  $J = 8.6$  Hz, 4H), 7.24 (d,  $J = 8.2$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.0 ( $J_{\text{C-P}} = 6.7$  Hz), 21.1, 21.2, 61.3 ( $J_{\text{C-P}} = 5.9$  Hz), 112.9 ( $J_{\text{C-P}} = 192.2$  Hz), 128.1, 128.3, 128.9, 129.6, 136.0 ( $J_{\text{C-P}} = 7.4$  Hz), 138.4, 138.8 ( $J_{\text{C-P}} = 22.3$  Hz), 139.4, 160.2 ( $J_{\text{C-P}} = 6.3$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  18.39; HRMS calcd for  $\text{C}_{20}\text{H}_{25}\text{O}_3\text{P}$ , 344.1541; found, 344.1536.



**Diethyl (2,2-bis(4-methoxyphenyl)vinyl)phosphonate (6c)**

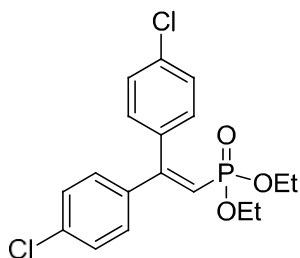
Colorless oil. $^{[11]}$   $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.10 (t,  $J = 7.1$  Hz, 6H), 3.75–3.88 (m, 10H), 5.95 (d,  $J_{\text{H-P}} = 15.6$  Hz, 1H), 6.78 (d,  $J = 8.9$  Hz, 2H), 6.85 (d,  $J = 8.8$  Hz, 2H), 7.17 (d,  $J = 8.9$  Hz, 2H), 7.28 (d,  $J = 8.7$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.0 ( $J_{\text{C-P}} = 6.7$  Hz), 61.3 ( $J_{\text{C-P}} = 5.9$  Hz), 111.3 ( $J_{\text{C-P}} = 192.7$  Hz), 113.0, 113.4, 129.7, 131.2, 134.2 ( $J_{\text{C-P}} = 22.5$  Hz), 159.5, 159.6, 159.9, 160.5.



**Diethyl (2,2-bis(4-fluorophenyl)vinyl)phosphonate (6d)**

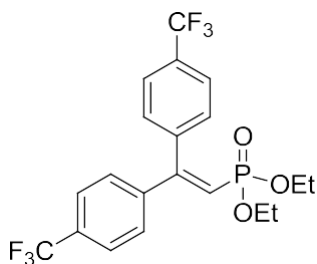
Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.13 (t,  $J = 7.1$  Hz, 6H), 3.77–3.98 (m, 4H), 6.08 (d,  $J_{\text{H-P}} = 14.8$  Hz, 1H), 6.95–7.08 (m, 4H), 7.19–7.24 (m, 2H), 7.31–7.36 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.1 ( $J_{\text{C-P}} = 6.6$  Hz), 61.5 ( $J_{\text{C-P}} = 6.0$  Hz), 114.9 ( $J_{\text{C-P}} = 192.3$  Hz), 114.9 ( $J_{\text{C-F}} = 21.4$  Hz), 115.3 ( $J_{\text{C-F}} = 21.5$  Hz), 130.0 ( $J_{\text{C-P}} = 8.4$  Hz), 131.6 ( $J_{\text{C-P}} = 7.1$  Hz), 134.5 ( $J_{\text{C-P}} = 7.5$  Hz), 137.4

( $J_{C-P} = 22.4$  Hz), 157.8 ( $J_{C-P} = 6.1$  Hz), 163.0 ( $J_{C-F} = 247.1$  Hz), 163.4 ( $J_{C-F} = 248.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  17.27; HRMS calcd for  $\text{C}_{18}\text{H}_{19}\text{F}_2\text{O}_3\text{P}$ , 352.1032; found, 352.1040.



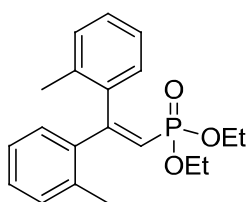
**Diethyl (2,2-bis(4-chlorophenyl)vinyl)phosphonate (6e)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.13 (t,  $J = 7.1$  Hz, 6H), 3.80–3.96 (m, 4H), 6.13 (d,  $J_{H-P} = 14.5$  Hz, 1H), 7.15 (d,  $J = 8.6$  Hz, 2H), 7.24–7.29 (m, 4H), 7.34 (d,  $J = 8.5$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.1 ( $J_{C-P} = 6.6$  Hz), 61.6 ( $J_{C-P} = 5.5$  Hz), 115.8 ( $J_{C-P} = 191.8$  Hz), 128.1, 128.6, 129.3, 131.0, 134.9, 135.6, 136.7 ( $J_{C-P} = 7.5$  Hz), 139.4 ( $J_{C-P} = 22.2$  Hz), 157.3 ( $J_{C-P} = 5.9$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  16.82; HRMS calcd for  $\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{O}_3\text{P}$ , 384.0449; found, 384.0450.



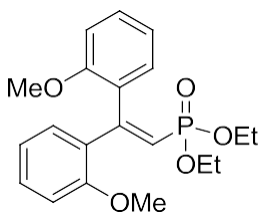
**Diethyl (2,2-bis(4-(trifluoromethyl)phenyl)vinyl)phosphonate (6g)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.12 (t,  $J = 7.1$  Hz, 6H), 3.80–3.97 (m, 4H), 6.30 (d,  $J_{H-P} = 14.1$  Hz, 1H), 7.34 (d,  $J = 8.2$  Hz, 2H), 7.47 (d,  $J = 8.0$  Hz, 2H), 7.57 (d,  $J = 8.2$  Hz, 2H), 7.65 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.0 ( $J_{C-P} = 6.5$  Hz), 61.8 ( $J_{C-P} = 6.0$  Hz), 118.5 ( $J_{C-P} = 191.1$  Hz), 123.7 ( $J_{C-F} = 270.5$  Hz), 123.9 ( $J_{C-F} = 270.6$  Hz), 125.0 ( $J_{C-F} = 3.6$  Hz), 125.5 ( $J_{C-F} = 3.7$  Hz), 128.3, 130.0, 130.9 ( $J_{C-F} = 32.5$  Hz), 131.4 ( $J_{C-F} = 32.5$  Hz), 141.8 ( $J_{C-P} = 7.1$  Hz), 144.0 ( $J_{C-P} = 22.0$  Hz), 156.7 ( $J_{C-P} = 5.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  15.73; HRMS calcd for  $\text{C}_{20}\text{H}_{19}\text{F}_6\text{O}_3\text{P}$ , 452.0976; found, 452.0982.



**Diethyl (2,2-di-*o*-tolylvinyl)phosphonate (6k)**

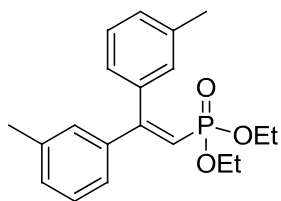
Pale yellow solid. mp 82–84 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.10 (t,  $J = 7.1$  Hz, 6H), 1.99 (s, 3H), 2.32 (s, 3H), 3.68–3.93 (m, 4H), 5.94 (d,  $J_{\text{H-P}} = 17.6$  Hz, 1H), 7.02–7.10 (m, 3H), 7.15–7.17 (m, 2H) 7.20–7.24 (m, 2H), 7.44–7.47 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.1 ( $J_{\text{C-P}} = 6.5$  Hz), 20.0, 21.0, 61.4 ( $J_{\text{C-P}} = 6.1$  Hz), 120.0 ( $J_{\text{C-P}} = 189.0$  Hz), 125.1, 125.6, 128.2, 128.4, 129.5, 130.0, 130.7, 131.2, 135.3, 135.7, 139.3 ( $J_{\text{C-P}} = 7.4$  Hz), 140.8 ( $J_{\text{C-P}} = 22.0$  Hz), 160.0 ( $J_{\text{C-P}} = 5.0$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  16.91; HRMS calcd for  $\text{C}_{20}\text{H}_{25}\text{O}_3\text{P}$ , 344.1541; found, 344.1548.



**Diethyl (2,2-bis(2-methoxyphenyl)vinyl)phosphonate (6l)**

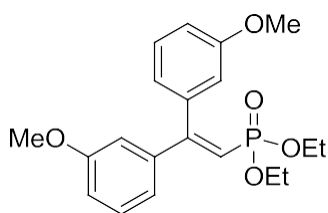
Pale yellow solid. mp 68–70 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.11 (t,  $J = 7.1$  Hz, 6H), 3.61 (s, 3H), 3.70 (s, 3H), 3.74–3.93 (m, 4H), 6.33 (d,  $J_{\text{H-P}} = 17.9$  Hz, 1H), 6.78–6.85 (m, 3H), 6.93 (t,  $J = 7.5$  Hz, 1H), 7.04 (d,  $J = 7.6$  Hz, 1H), 7.17–7.29 (m, 2H), 7.34 (d,  $J = 7.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.1 ( $J_{\text{C-P}} = 6.7$  Hz), 55.6, 61.2 ( $J_{\text{C-P}} = 5.7$  Hz), 110.6, 111.5, 119.1 ( $J_{\text{C-P}} = 187.4$  Hz), 119.8, 120.1, 129.1 ( $J_{\text{C-P}} = 7.7$  Hz) 129.3, 129.4, 130.4, 130.7, 131.2, 154.4 ( $J_{\text{C-P}} = 5.2$  Hz), 156.5, 157.0;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  17.77; HRMS calcd for  $\text{C}_{20}\text{H}_{25}\text{O}_5\text{P}$ , 376.1440; found, 376.1436.





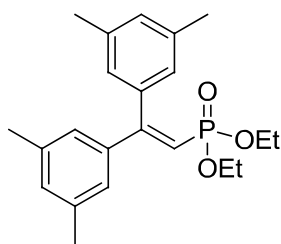
**Diethyl (2,2-di-*m*-tolylvinyl)phosphonate (6n)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.13 (t,  $J = 7.1$  Hz, 6H), 2.31 (s, 3H), 2.35 (s, 3H), 3.76–3.96 (m, 4H), 6.11 (d,  $J_{\text{H-P}} = 15.8$  Hz, 1H), 7.04–7.29 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.2 ( $J_{\text{C-P}} = 6.8$  Hz), 21.4, 61.5 ( $J_{\text{C-P}} = 5.9$  Hz), 114.4 ( $J_{\text{C-P}} = 192$  Hz), 125.5, 126.9, 127.7, 128.2, 128.8, 129.3, 130.2, 130.3, 137.3, 138.0, 138.9 ( $J_{\text{C-P}} = 7.4$  Hz), 141.6 ( $J_{\text{C-P}} = 22.1$  Hz), 160.6 ( $J_{\text{C-P}} = 6.0$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  18.06; HRMS calcd for  $\text{C}_{20}\text{H}_{25}\text{O}_3\text{P}$ , 344.1541; found, 344.1548.



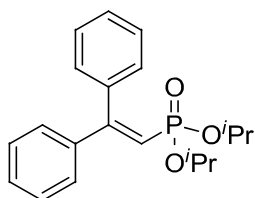
**Diethyl (2,2-bis(3-methoxyphenyl)vinyl)phosphonate (6o)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.11 (t,  $J = 7.1$  Hz, 6H), 3.74–3.94 (m, 10H), 6.14 (d,  $J_{\text{H-P}} = 15.5$  Hz, 1H), 6.79–6.91 (m, 5H), 6.98 (s, 1H), 7.18–7.28 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.2 ( $J_{\text{C-P}} = 6.7$  Hz), 55.3, 61.6 ( $J_{\text{C-P}} = 5.9$  Hz), 115.0 ( $J_{\text{C-P}} = 192.0$  Hz), 113.9, 114.8, 115.0, 120.8, 122.1, 128.9, 129.2, 140.1 ( $J_{\text{C-P}} = 7.5$  Hz), 142.6, 142.9, 159.0, 159.4, 159.8 ( $J_{\text{C-P}} = 6.0$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  17.74; HRMS calcd for  $\text{C}_{20}\text{H}_{25}\text{O}_5\text{P}$ , 376.1440; found, 376.1440.



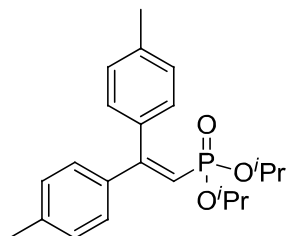
**Diethyl (2,2-bis(3,5-dimethylphenyl)vinyl)phosphonate (6p)**

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.11 (t,  $J = 7.1$  Hz, 6H), 2.24 (s, 6H), 2.29 (s, 6H), 3.74–3.93 (m, 4H), 6.06 (d,  $J_{\text{H-P}} = 16.3$  Hz, 1H), 6.87 (s, 2H), 6.96 (d,  $J = 5.9$  Hz, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.2 ( $J_{\text{C-P}} = 6.8$  Hz), 21.3, 61.4 ( $J_{\text{C-P}} = 5.9$  Hz), 114.0 ( $J_{\text{C-P}} = 192.1$  Hz), 126.1, 127.4, 1230.2, 131.0, 137.1, 137.8, 138.9 ( $J_{\text{C-P}} = 7.2$  Hz), 141.8 ( $J_{\text{C-P}} = 22.0$  Hz), 161.1 ( $J_{\text{C-P}} = 6.1$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  18.32; HRMS calcd for  $\text{C}_{22}\text{H}_{29}\text{F}_6\text{O}_3\text{P}$ , 372.1850; found, 372.1854.



**Diisopropyl (2,2-diphenylvinyl)phosphonate (7a)**

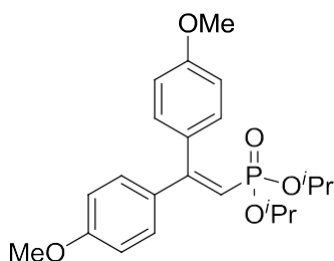
Colorless oil.<sup>[12]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.08 (d,  $J = 6.2$  Hz, 6H), 1.19 (d,  $J = 6.2$  Hz, 6H), 4.47–4.58 (m, 2H), 6.14 (d,  $J_{\text{H-P}} = 15.5$  Hz, 1H), 7.25–7.38 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  23.7 ( $J_{\text{C-P}} = 5.0$  Hz), 24.0 ( $J_{\text{C-P}} = 3.9$  Hz), 70.3 ( $J_{\text{C-P}} = 6.1$  Hz), 116.5 ( $J_{\text{C-P}} = 192.9$  Hz), 127.7, 128.2, 128.5, 129.1, 130.0, 139.0 ( $J_{\text{C-P}} = 7.3$  Hz), 142.0 ( $J_{\text{C-P}} = 22.1$  Hz), 159.4 ( $J_{\text{C-P}} = 6.0$  Hz).



**Diisopropyl (2,2-di-p-tolylvinyl)phosphonate (7b)**

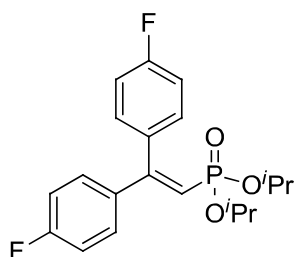
Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.09 (d,  $J = 6.2$  Hz, 6H), 1.20 (d,  $J = 6.2$  Hz, 6H), 2.32 (s, 3H), 2.35 (s, 3H), 4.47–4.58 (m, 2H), 6.05 (d,  $J_{\text{H-P}} = 15.7$  Hz, 1H), 7.08 (d,  $J = 8.2$  Hz, 2H), 7.14 (d,  $J = 8.0$  Hz, 4H), 7.25 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  21.2, 21.3, 23.7 ( $J_{\text{C-P}} = 5.1$  Hz), 24.0 ( $J_{\text{C-P}} = 3.8$  Hz), 70.2 ( $J_{\text{C-P}} = 6.1$  Hz), 115.0 ( $J_{\text{C-P}} = 193.1$  Hz), 128.3, 128.3, 129.0, 130.0, 136.3 ( $J_{\text{C-P}} = 7.4$  Hz), 138.4, 139.5 ( $J_{\text{C-P}} = 24.3$  Hz), 160.0 ( $J_{\text{C-P}} = 5.8$  Hz);  $^{31}\text{P}$  NMR

(CDCl<sub>3</sub>, 162 MHz):  $\delta$  16.08; HRMS calcd for C<sub>22</sub>H<sub>29</sub>O<sub>3</sub>P, 372.1854; found, 372.1860.



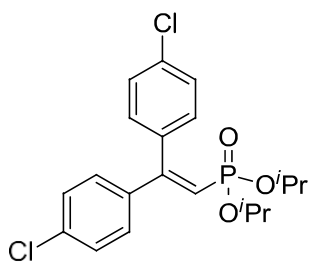
***Diisopropyl (2,2-bis(4-methoxyphenyl)vinyl)phosphonate (7c)***

Colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  1.10 (d,  $J$  = 6.2 Hz, 6H), 1.21 (d,  $J$  = 6.2 Hz, 6H), 3.78 (s, 3H), 3.81 (s, 3H), 4.48–4.58 (m, 2H), 5.96 (d,  $J_{\text{H-P}}$  = 15.5 Hz, 1H), 6.80 (d,  $J$  = 8.7 Hz, 2H), 6.86 (d,  $J$  = 8.6 Hz, 2H), 7.18 (d,  $J$  = 8.7 Hz, 2H), 7.32 (d,  $J$  = 8.6 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  23.8 ( $J_{\text{C-P}}$  = 5.0 Hz), 24.0 ( $J_{\text{C-P}}$  = 3.8 Hz), 55.3, 55.3, 70.2 ( $J_{\text{C-P}}$  = 6.1 Hz), 113.4 ( $J_{\text{C-P}}$  = 193.7 Hz), 113.0, 113.5, 129.8, 131.6, 134.9 ( $J_{\text{C-P}}$  = 22.6 Hz), 159.0 ( $J_{\text{C-P}}$  = 6.0 Hz), 160.0, 160.5; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  15.39; HRMS calcd for C<sub>22</sub>H<sub>29</sub>O<sub>5</sub>P, 404.1753; found, 404.1759.



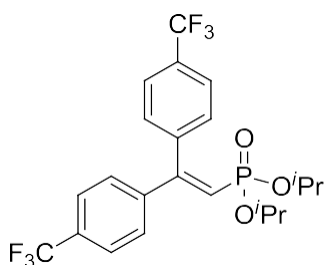
***Diisopropyl (2,2-bis(4-fluorophenyl)vinyl)phosphonate (7d)***

Colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  1.11 (d,  $J$  = 6.2 Hz, 6H), 1.20 (d,  $J$  = 6.2 Hz, 6H), 4.46–4.61 (m, 2H), 6.07 (d,  $J_{\text{H-P}}$  = 14.8 Hz, 1H), 6.95–7.06 (m, 4H), 7.18–7.24 (m, 2H), 7.32–7.37 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  23.8 ( $J_{\text{C-P}}$  = 4.9 Hz), 24.0 ( $J_{\text{C-P}}$  = 3.8 Hz), 70.5 ( $J_{\text{C-P}}$  = 6.2 Hz), 114.8 ( $J_{\text{C-F}}$  = 21.4 Hz), 115.3 ( $J_{\text{C-F}}$  = 21.5 Hz), 116.8 ( $J_{\text{C-P}}$  = 192.0 Hz), 130.1 ( $J_{\text{C-P}}$  = 8.4 Hz), 131.9 ( $J_{\text{C-P}}$  = 8.1 Hz), 134.8 ( $J_{\text{C-P}}$  = 7.1 Hz), 137.9 ( $J_{\text{C-P}}$  = 22.4 Hz), 157.1 ( $J_{\text{C-P}}$  = 5.6 Hz), 163.0 ( $J_{\text{C-F}}$  = 246.8 Hz), 163.4 ( $J_{\text{C-F}}$  = 248.4 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  15.04; HRMS calcd for C<sub>20</sub>H<sub>23</sub>F<sub>2</sub>O<sub>3</sub>P, 380.1353; found, 380.1353.



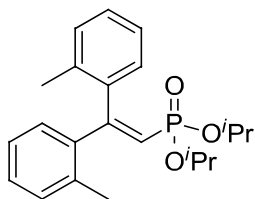
***Diisopropyl (2,2-bis(4-chlorophenyl)vinyl)phosphonate (7e)***

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.12 (d,  $J = 6.2$  Hz, 6H), 1.21 (d,  $J = 6.2$  Hz, 6H), 4.49–4.60 (m, 2H), 6.12 (d,  $J_{\text{H-P}} = 14.5$  Hz, 1H), 7.15 (d,  $J = 8.6$  Hz, 2H), 7.24–7.35 (m, 4H), 7.27 (d,  $J = 8.6$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  23.8 ( $J_{\text{C-P}} = 4.9$  Hz), 24.0 ( $J_{\text{C-P}} = 3.8$  Hz), 70.7 ( $J_{\text{C-P}} = 6.0$  Hz), 117.7 ( $J_{\text{C-P}} = 192.7$  Hz), 128.1, 128.6, 130.0, 131.4, 134.9, 135.6, 137.1 ( $J_{\text{C-P}} = 7.3$  Hz), 140.0 ( $J_{\text{C-P}} = 22.4$  Hz), 156.8 ( $J_{\text{C-P}} = 5.7$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  14.57; HRMS calcd for  $\text{C}_{20}\text{H}_{23}\text{Cl}_2\text{O}_3\text{P}$ , 412.0762; found, 412.0754.



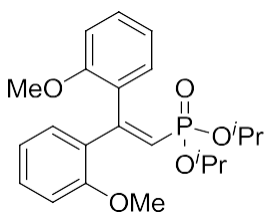
***Diisopropyl (2,2-bis(4-(trifluoromethyl)phenyl)vinyl)phosphonate (7g)***

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.10 (d,  $J = 6.2$  Hz, 6H), 1.19 (d,  $J = 6.2$  Hz, 6H), 4.50–4.61 (m, 2H), 6.28 (d,  $J_{\text{H-P}} = 14.1$  Hz, 1H), 7.33 (d,  $J = 8.1$  Hz, 2H), 7.47 (d,  $J = 8.2$  Hz, 2H), 7.57 (d,  $J = 8.2$  Hz, 2H), 7.63 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  23.7 ( $J_{\text{C-P}} = 4.7$  Hz), 23.9 ( $J_{\text{C-P}} = 3.9$  Hz), 70.9 ( $J_{\text{C-P}} = 6.2$  Hz), 120.3 ( $J_{\text{C-P}} = 191.8$  Hz), 124.0 ( $J_{\text{C-F}} = 270.7$  Hz), 123.8 ( $J_{\text{C-F}} = 268.2$  Hz), 124.9 ( $J_{\text{C-F}} = 3.7$  Hz), 125.5 ( $J_{\text{C-F}} = 3.6$  Hz), 128.4, 130.3, 130.9 ( $J_{\text{C-F}} = 32.5$  Hz), 131.7 ( $J_{\text{C-F}} = 32.3$  Hz), 142.0 ( $J_{\text{C-P}} = 6.1$  Hz), 144.5 ( $J_{\text{C-P}} = 22.3$  Hz), 156.0 ( $J_{\text{C-P}} = 4.7$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  13.54; HRMS calcd for  $\text{C}_{22}\text{H}_{23}\text{F}_6\text{O}_3\text{P}$ , 480.1289; found, 480.1293.



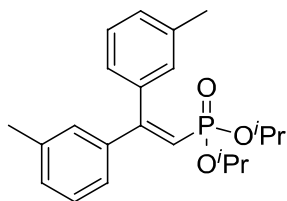
***Diisopropyl (2,2-di-*o*-tolylvinyl)phosphonate (7k)***

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.07 (d,  $J = 6.2$  Hz, 6H), 1.17 (d,  $J = 6.2$  Hz, 6H), 1.97 (s, 3H), 2.31 (s, 3H), 4.41–4.56 (m, 2H), 5.91 (d,  $J_{\text{H-P}} = 17.7$  Hz, 1H), 7.02–7.11 (m, 3H), 7.14–7.24 (m, 4H) 7.46–7.49 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  20.2, 21.1, 23.7 ( $J_{\text{C-P}} = 5.1$  Hz), 24.0 ( $J_{\text{C-P}} = 3.9$  Hz), 70.2 ( $J_{\text{C-P}} = 6.3$  Hz), 121.6 ( $J_{\text{C-P}} = 190.2$  Hz), 125.0, 125.7, 128.1, 128.3, 129.6, 130.0, 131.0, 131.1, 135.4, 135.9, 139.6 ( $J_{\text{C-P}} = 7.1$  Hz), 141.2 ( $J_{\text{C-P}} = 22.0$  Hz), 159.4 ( $J_{\text{C-P}} = 4.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  14.63; HRMS calcd for  $\text{C}_{22}\text{H}_{29}\text{O}_3\text{P}$ , 372.1854; found, 372.1859.



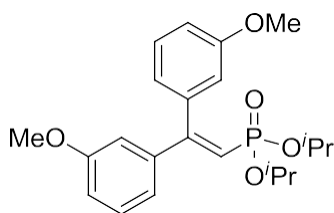
***Diisopropyl (2,2-bis(2-methoxyphenyl)vinyl)phosphonate (7l)***

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.12 (d,  $J = 6.2$  Hz, 6H), 1.18 (d,  $J = 6.2$  Hz, 6H), 3.60 (s, 3H), 3.70 (s, 3H), 4.46–4.57 (m, 2H), 6.29 (d,  $J_{\text{H-P}} = 17.6$  Hz, 1H), 6.78–6.85 (m, 3H), 6.92 (t,  $J = 7.5$  Hz, 1H), 7.04 (d,  $J = 7.6$  Hz, 1H), 7.17–7.28 (m, 2H), 7.36 (d,  $J = 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  23.7 ( $J_{\text{C-P}} = 4.8$  Hz), 24.0 ( $J_{\text{C-P}} = 3.8$  Hz), 55.5, 55.7, 69.9 ( $J_{\text{C-P}} = 5.9$  Hz), 110.8, 111.6, 120.7 ( $J_{\text{C-P}} = 188.2$  Hz), 120.0, 120.2, 129.2, 129.3, 129.5 ( $J_{\text{C-P}} = 7.5$  Hz) 130.4, 131.1, 131.4, 153.7 ( $J_{\text{C-P}} = 5.0$  Hz), 156.9 ( $J_{\text{C-P}} = 23.4$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  15.36; HRMS calcd for  $\text{C}_{22}\text{H}_{29}\text{O}_5\text{P}$ , 404.1753; found, 404.1746.



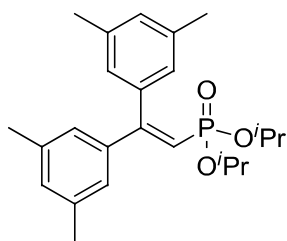
***Diisopropyl (2,2-di-m-tolylvinyl)phosphonate (7n)***

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.09 (d,  $J = 6.2$  Hz, 6H), 1.19 (d,  $J = 6.2$  Hz, 6H), 2.29 (s, 3H), 2.33 (s, 3H), 4.46–4.57 (m, 2H), 6.09 (d,  $J_{\text{H-P}} = 15.9$  Hz, 1H), 7.01–7.25 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  21.3, 21.3, 23.7 ( $J_{\text{C-P}} = 5.0$  Hz), 24.0 ( $J_{\text{C-P}} = 3.8$  Hz), 70.2 ( $J_{\text{C-P}} = 6.1$  Hz), 116.1 ( $J_{\text{C-P}} = 193.1$  Hz), 125.5, 127.1, 127.5, 128.0, 128.8, 129.1, 129.9, 130.6, 137.1, 137.8, 139.0 ( $J_{\text{C-P}} = 7.2$  Hz), 142.1 ( $J_{\text{C-P}} = 22.2$  Hz), 159.9 ( $J_{\text{C-P}} = 5.7$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  16.04; HRMS calcd for  $\text{C}_{22}\text{H}_{29}\text{O}_3\text{P}$ , 372.1854; found, 372.1860.



***Diisopropyl (2,2-bis(3-methoxyphenyl)vinyl)phosphonate (7o)***

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.09 (d,  $J = 6.2$  Hz, 6H), 1.19 (d,  $J = 6.2$  Hz, 6H), 3.74 (s, 3H), 3.79 (s, 3H), 4.48–4.59 (m, 2H), 6.12 (d,  $J_{\text{H-P}} = 15.6$  Hz, 1H), 6.79–6.90 (m, 5H), 7.01–7.02 (m, 1H), 7.17–7.25 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  23.8 ( $J_{\text{C-P}} = 4.8$  Hz), 24.0 ( $J_{\text{C-P}} = 3.6$  Hz), 55.3, 70.5 ( $J_{\text{C-P}} = 6.1$  Hz), 113.9, 114.6, 114.7, 115.3, 116.8 ( $J_{\text{C-P}} = 192.5$  Hz), 120.9, 122.5, 128.7, 129.2, 140.2 ( $J_{\text{C-P}} = 7.3$  Hz), 143.3 ( $J_{\text{C-P}} = 22.1$  Hz), 159.2 ( $J_{\text{C-P}} = 5.1$  Hz), 159.4;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  15.45; HRMS calcd for  $\text{C}_{22}\text{H}_{29}\text{O}_5\text{P}$ , 404.1753; found, 404.1747.



***Diisopropyl (2,2-bis(3,5-dimethylphenyl)vinyl)phosphonate (7p)***

Colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.10 (d,  $J = 6.2$  Hz, 6H), 1.19 (d,  $J = 6.2$  Hz, 6H), 2.25 (s, 6H), 2.28 (s, 6H), 4.44–4.59 (m, 2H), 6.04 (d,  $J_{\text{H-P}} = 16.2$  Hz, 1H), 6.86 (s, 2H), 6.96 (s, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  21.3, 23.8 ( $J_{\text{C-P}} = 5.0$  Hz), 24.0 ( $J_{\text{C-P}} = 3.9$  Hz), 70.2 ( $J_{\text{C-P}} = 6.1$  Hz), 115.8 ( $J_{\text{C-P}} = 192.9$  Hz), 126.2, 127.8, 130.0, 130.8, 136.9, 137.7, 139.1 ( $J_{\text{C-P}} = 7.2$  Hz), 142.3 ( $J_{\text{C-P}} = 22.1$  Hz), 160.4 ( $J_{\text{C-P}} = 5.6$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz):  $\delta$  16.07; HRMS calcd for  $\text{C}_{24}\text{H}_{33}\text{O}_3\text{P}$ , 400.2167; found, 400.2176.

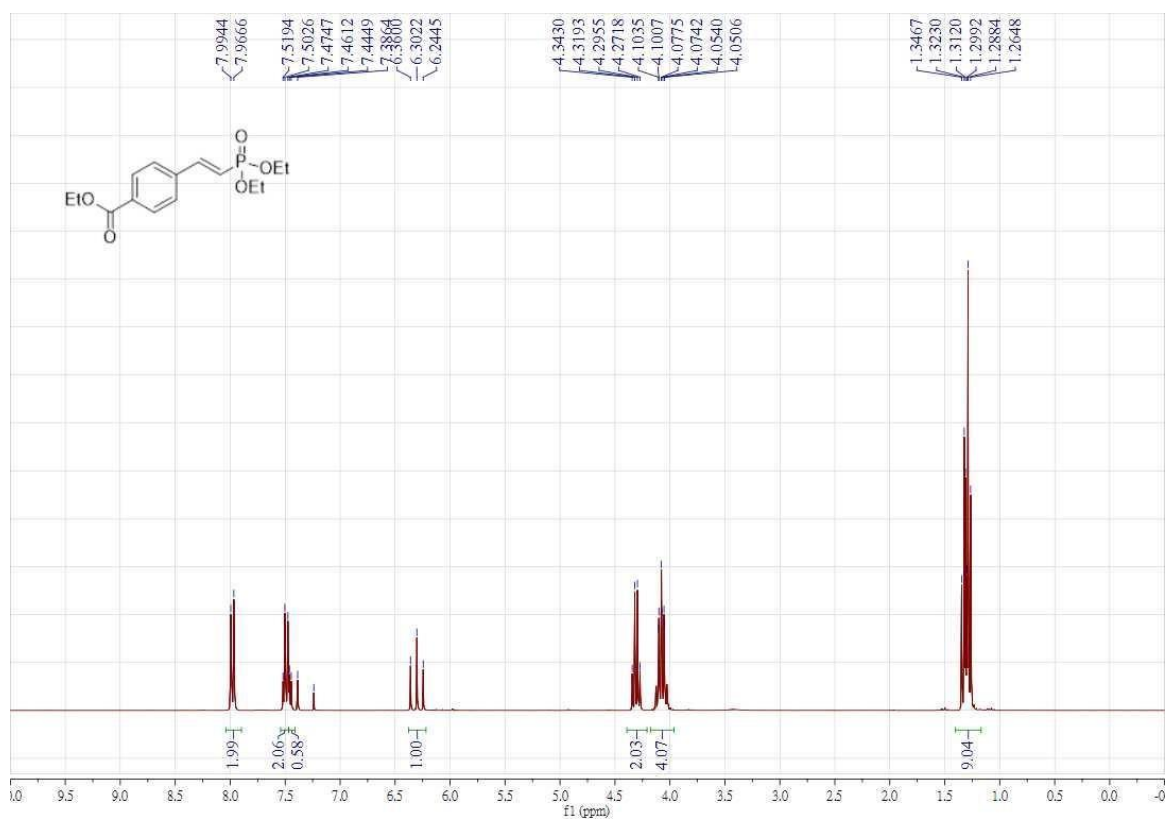
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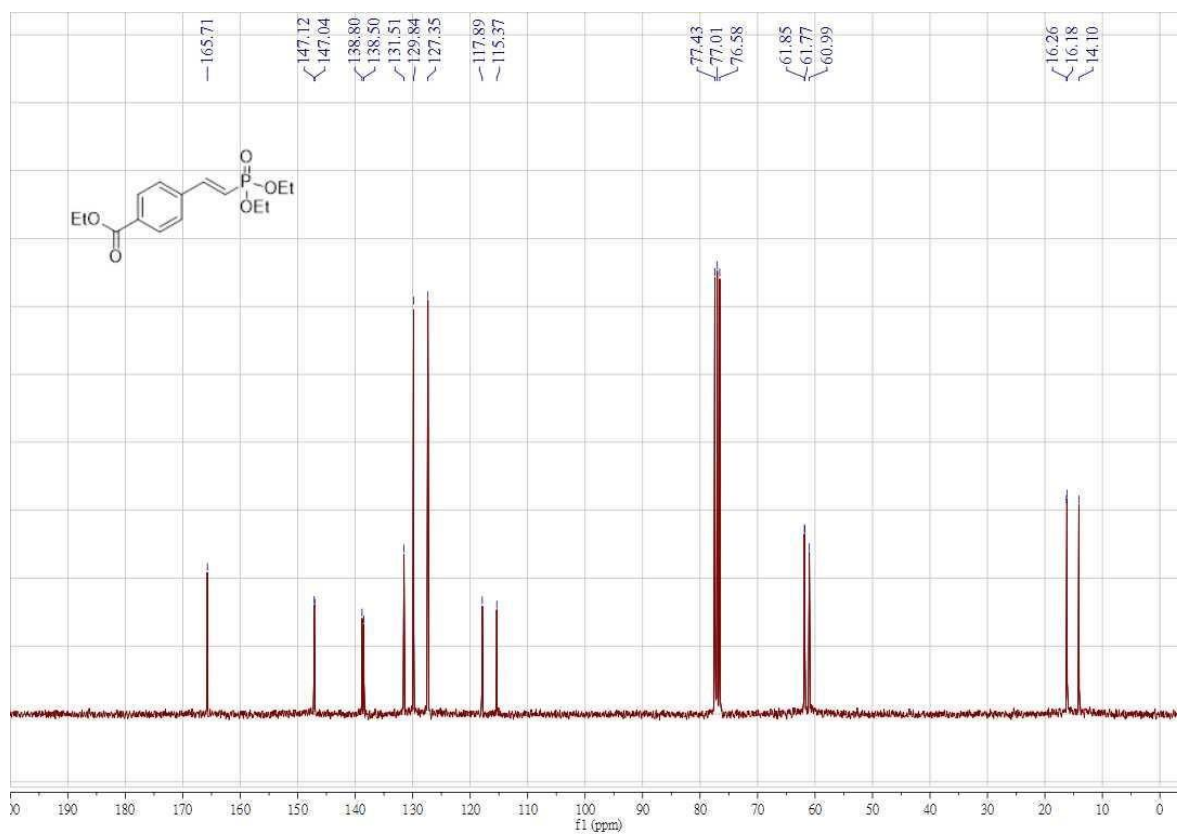


# Copies of $^1\text{H}$ , $^{13}\text{C}$ , and $^{31}\text{P}$ NMR for unknown compounds

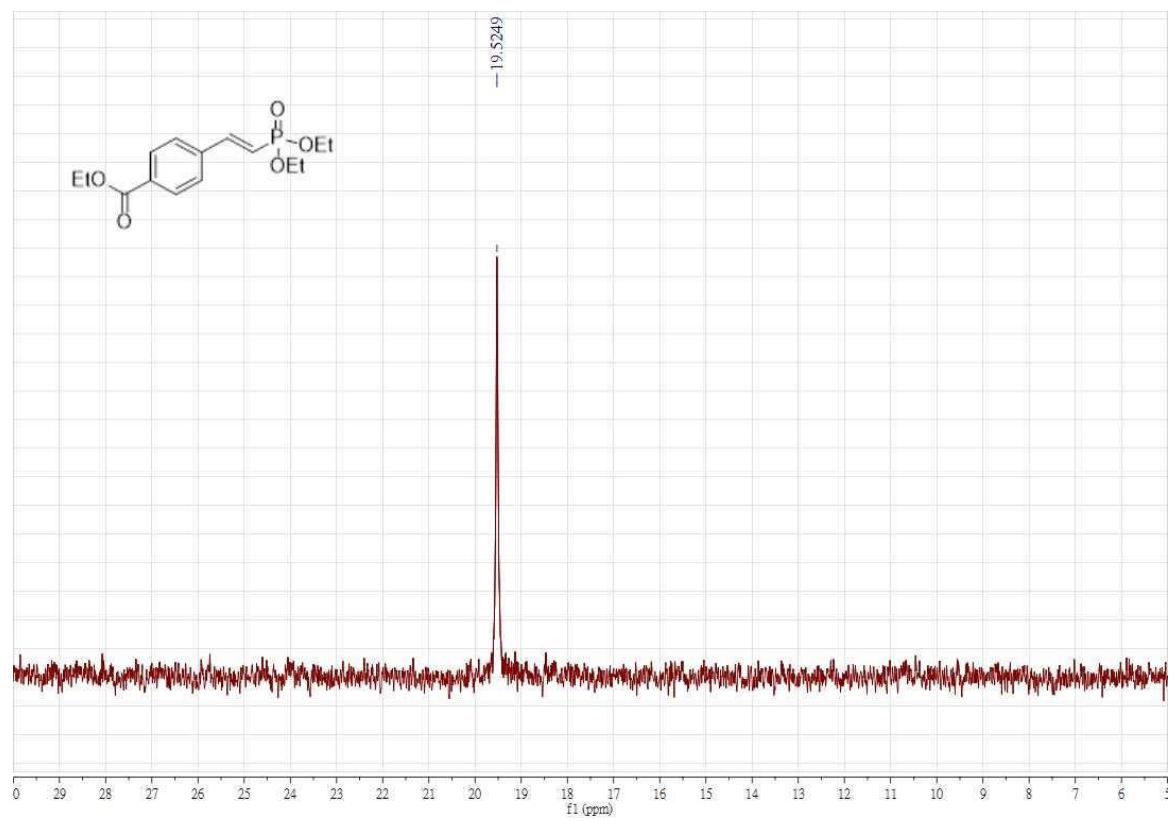
## $^1\text{H}$ NMR spectrum of compound **3i**



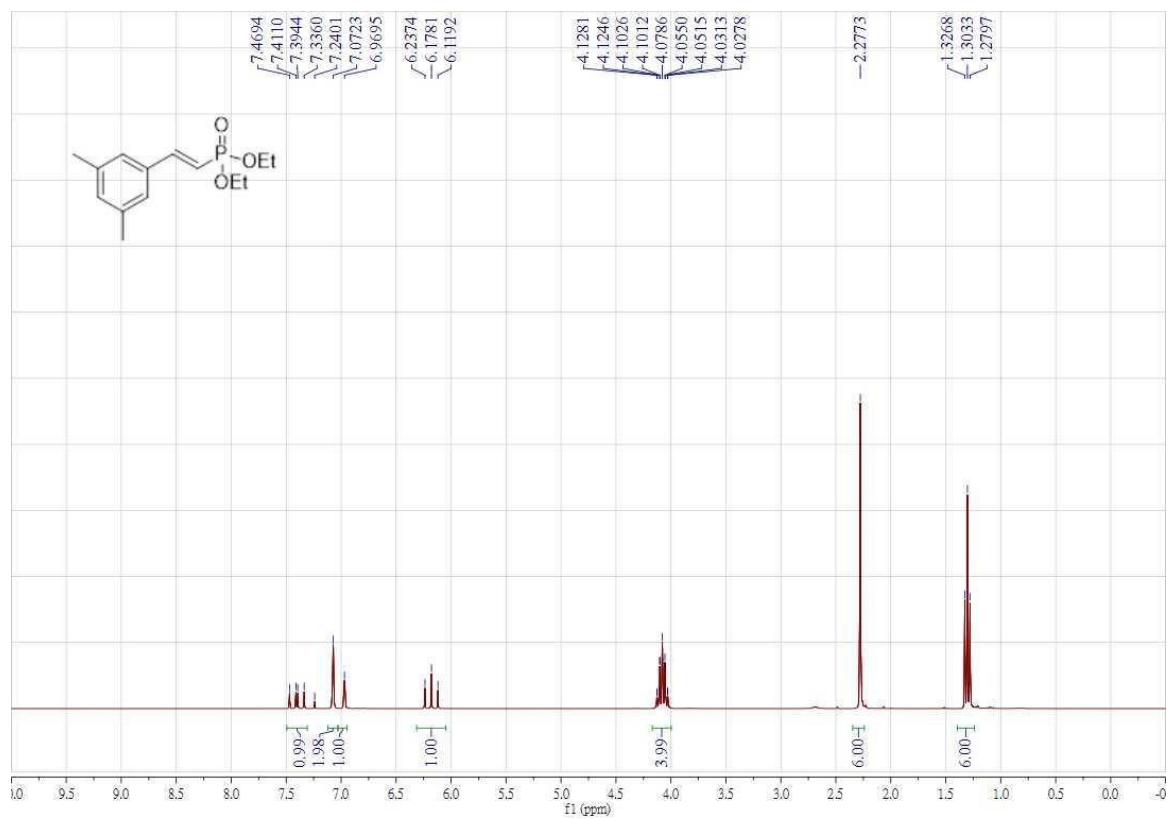
## $^{13}\text{C}$ NMR spectrum of compound **3i**



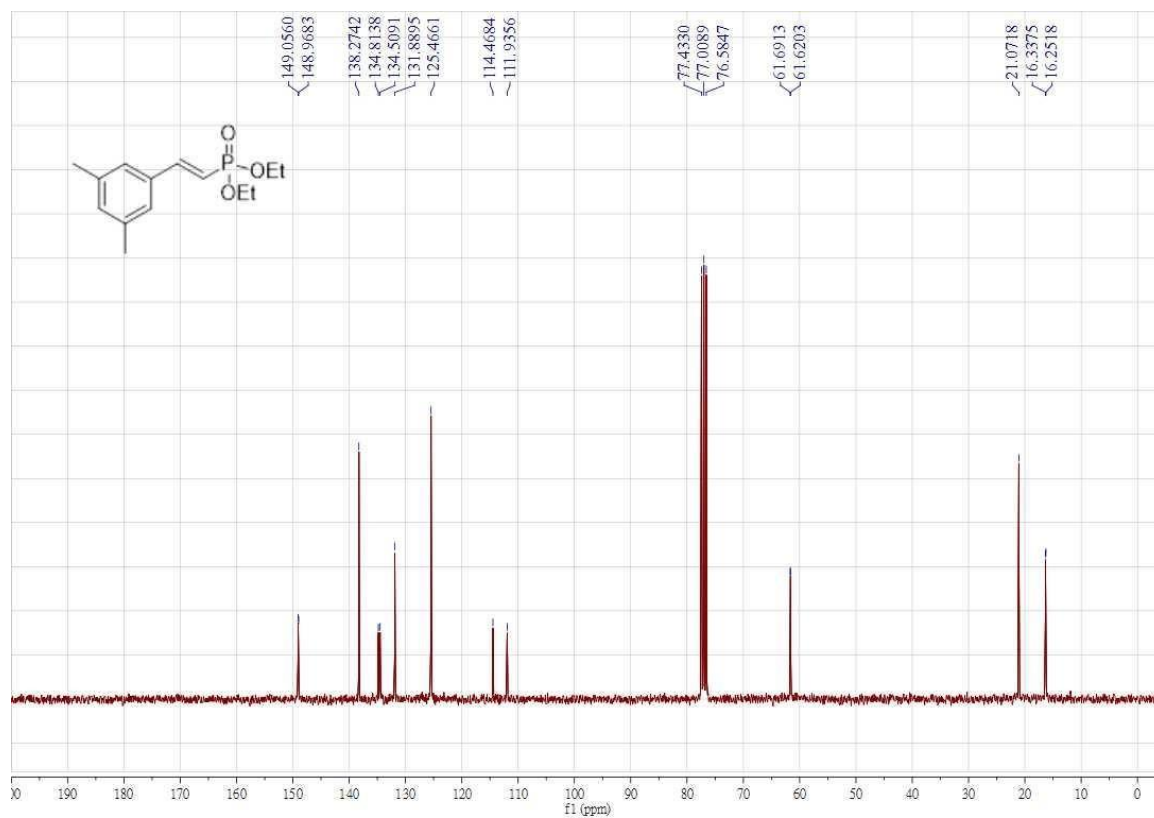
$^{31}\text{P}$  NMR spectrum of compound **3i**



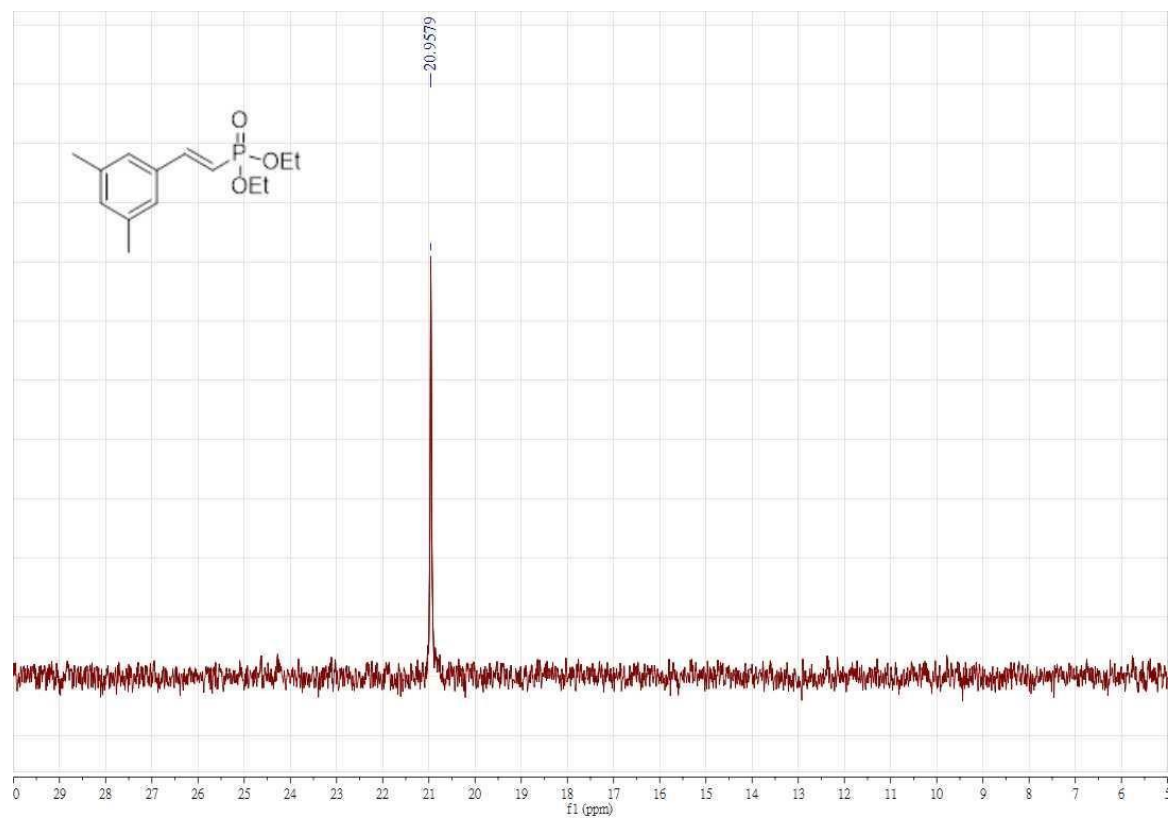
<sup>1</sup>H NMR spectrum of compound **3p**



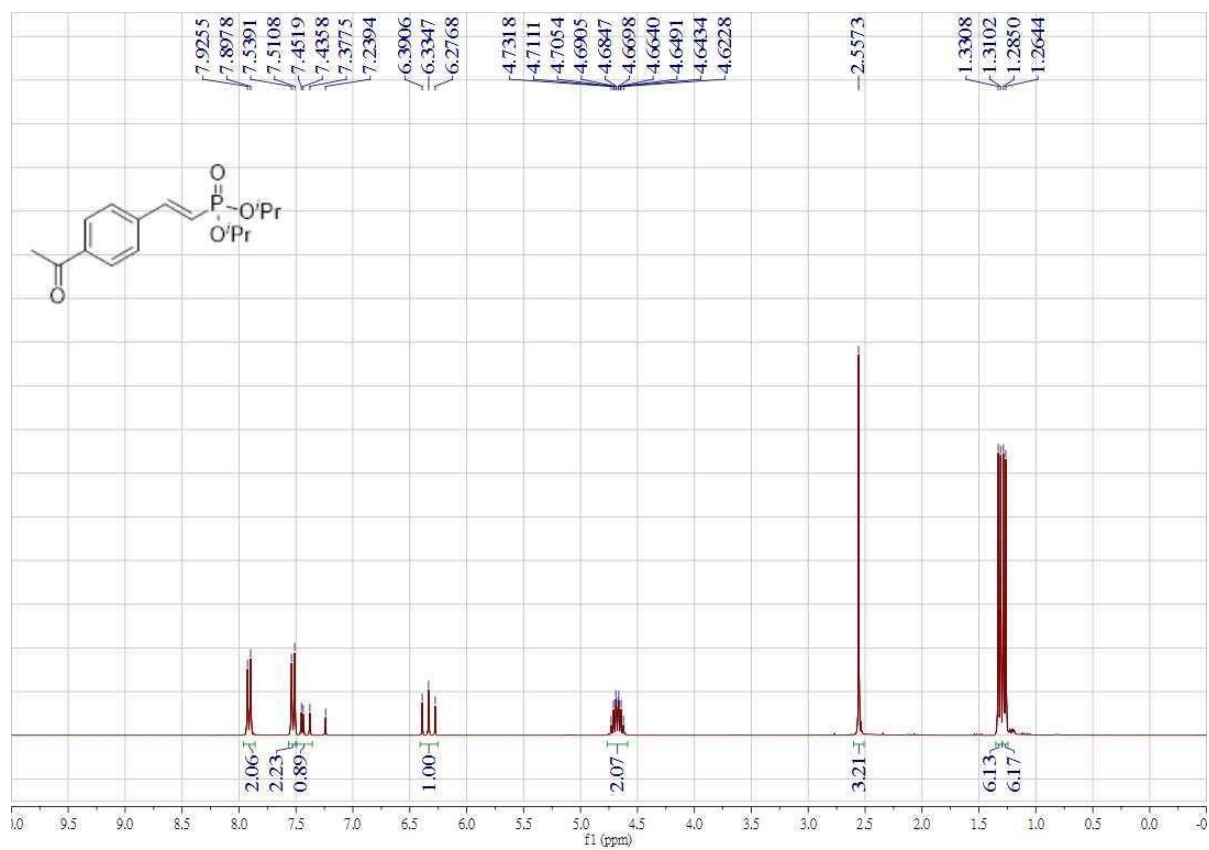
<sup>13</sup>C NMR spectrum of compound **3p**



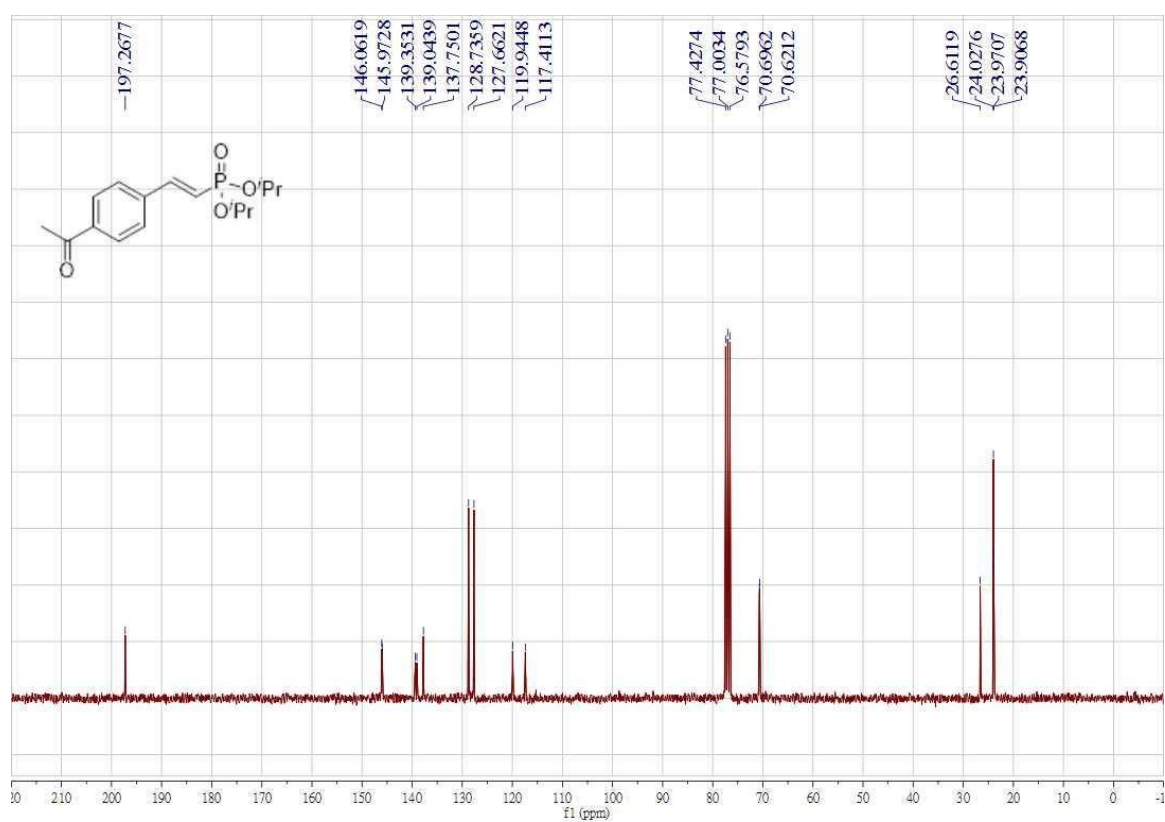
<sup>31</sup>P NMR spectrum of compound **3p**



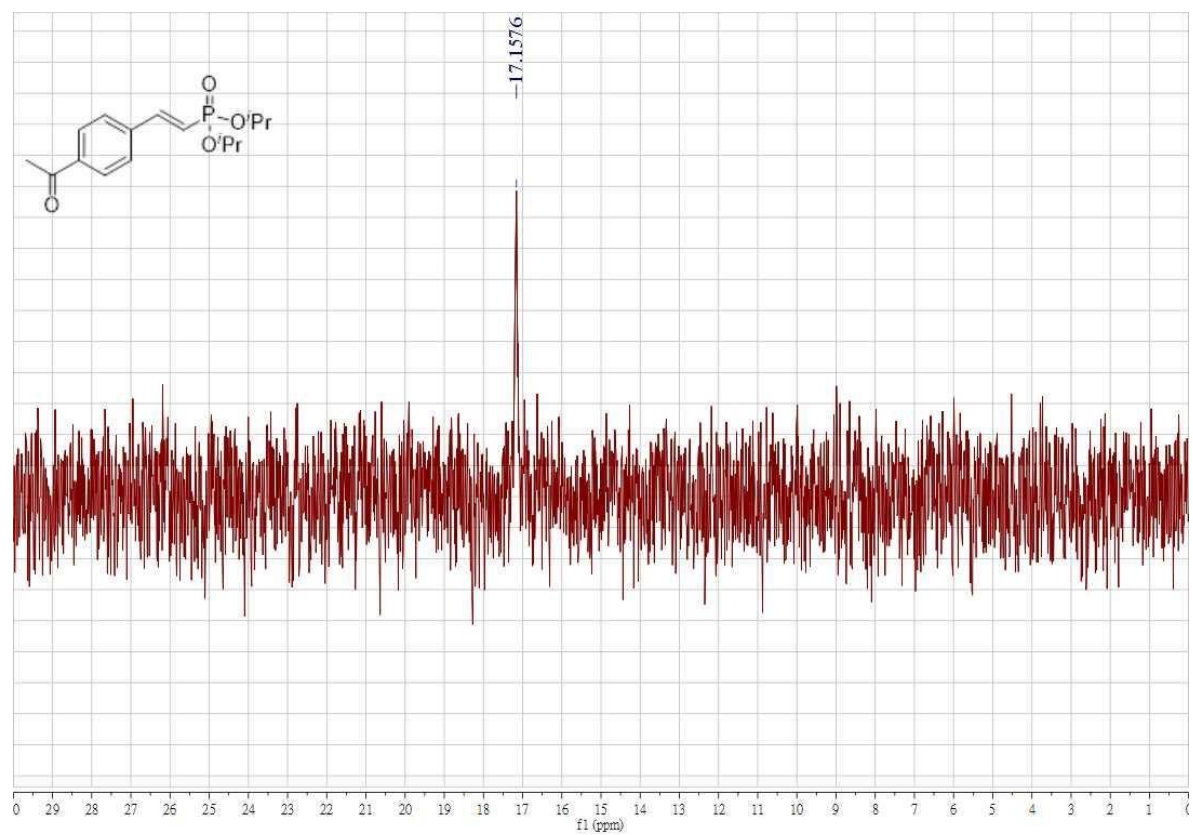
<sup>1</sup>H NMR spectrum of compound **4h**



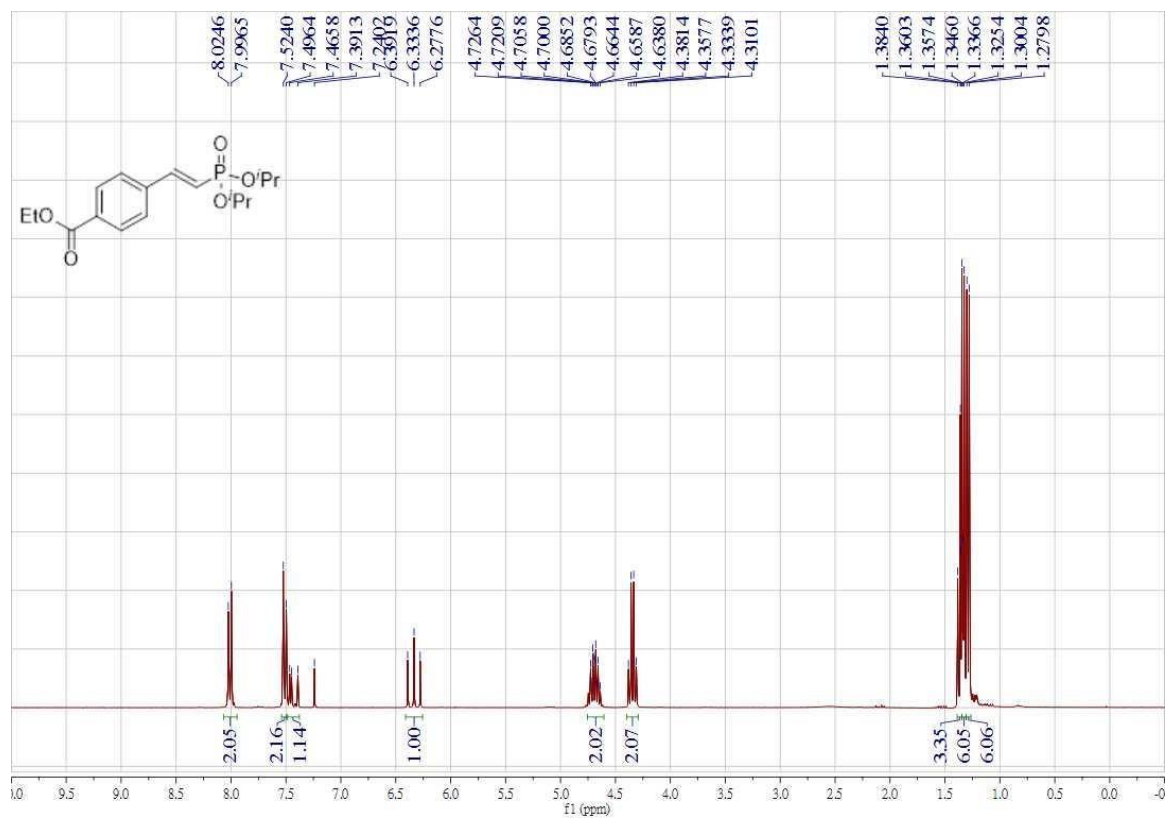
<sup>13</sup>C NMR spectrum of compound **4h**



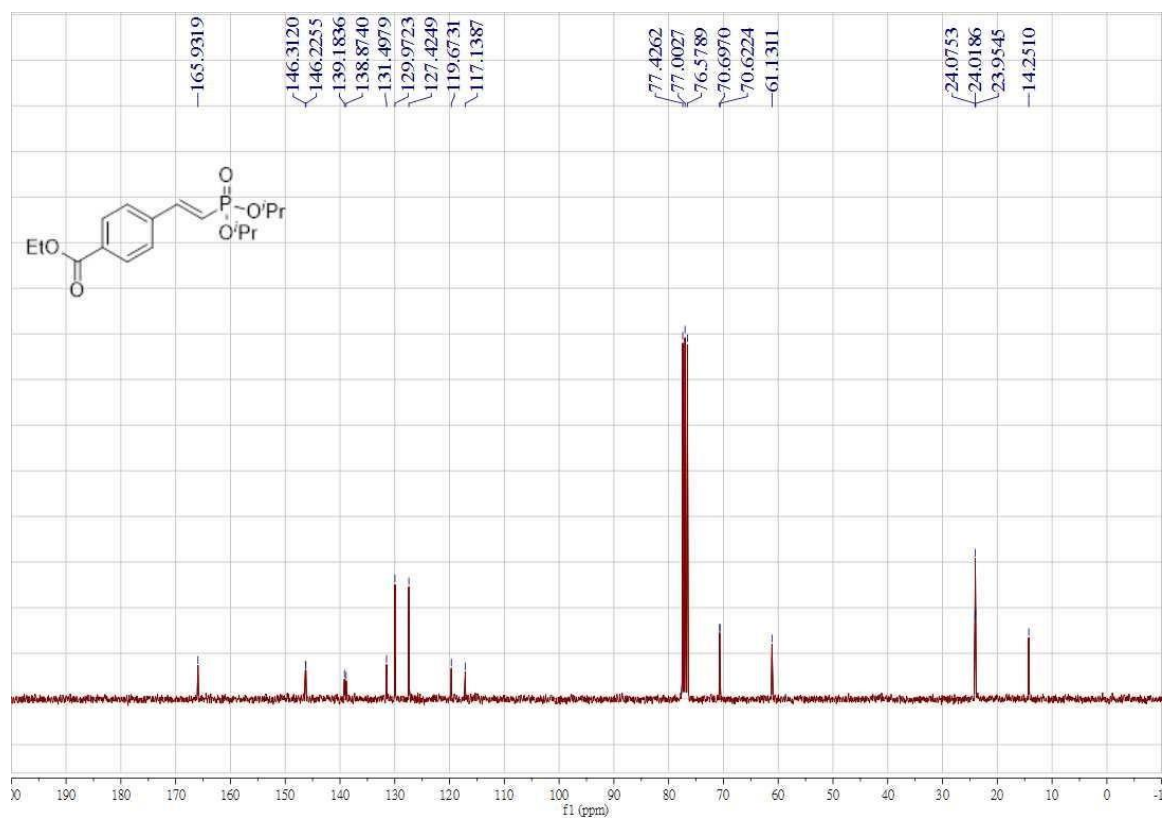
$^{31}\text{P}$  NMR spectrum of compound **4h**



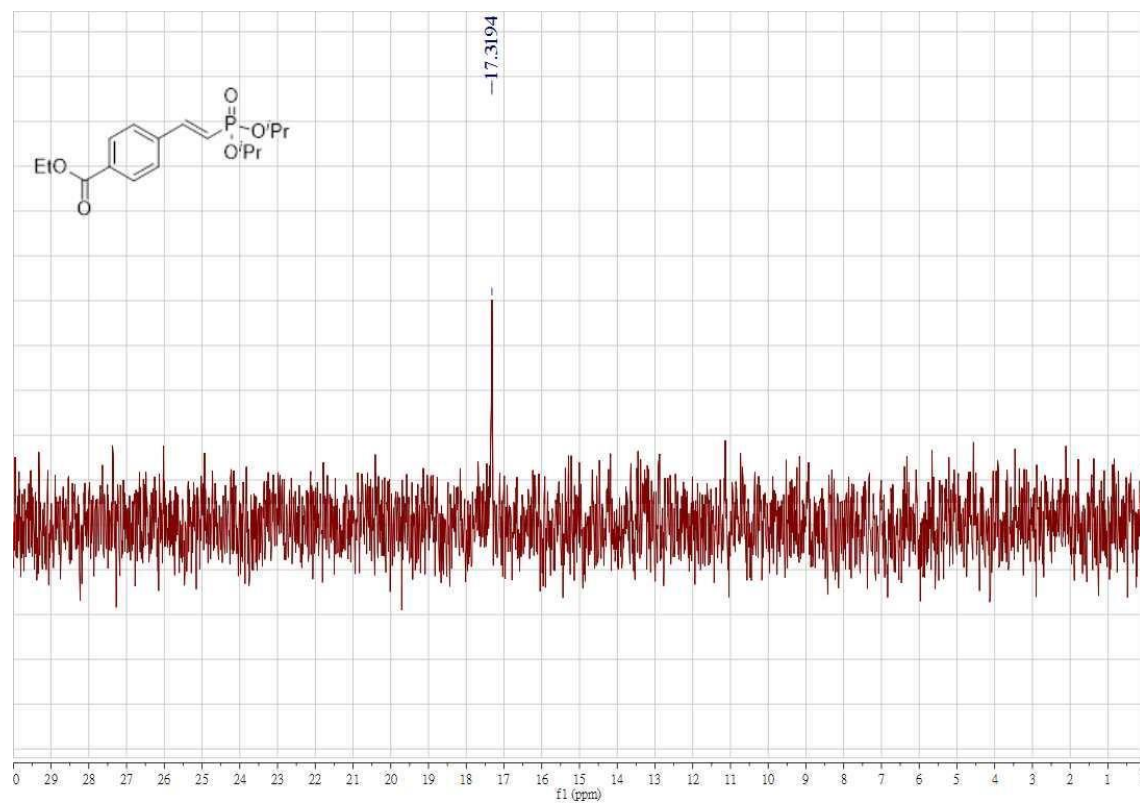
<sup>1</sup>H NMR spectrum of compound **4i**



<sup>13</sup>C NMR spectrum of compound **4i**

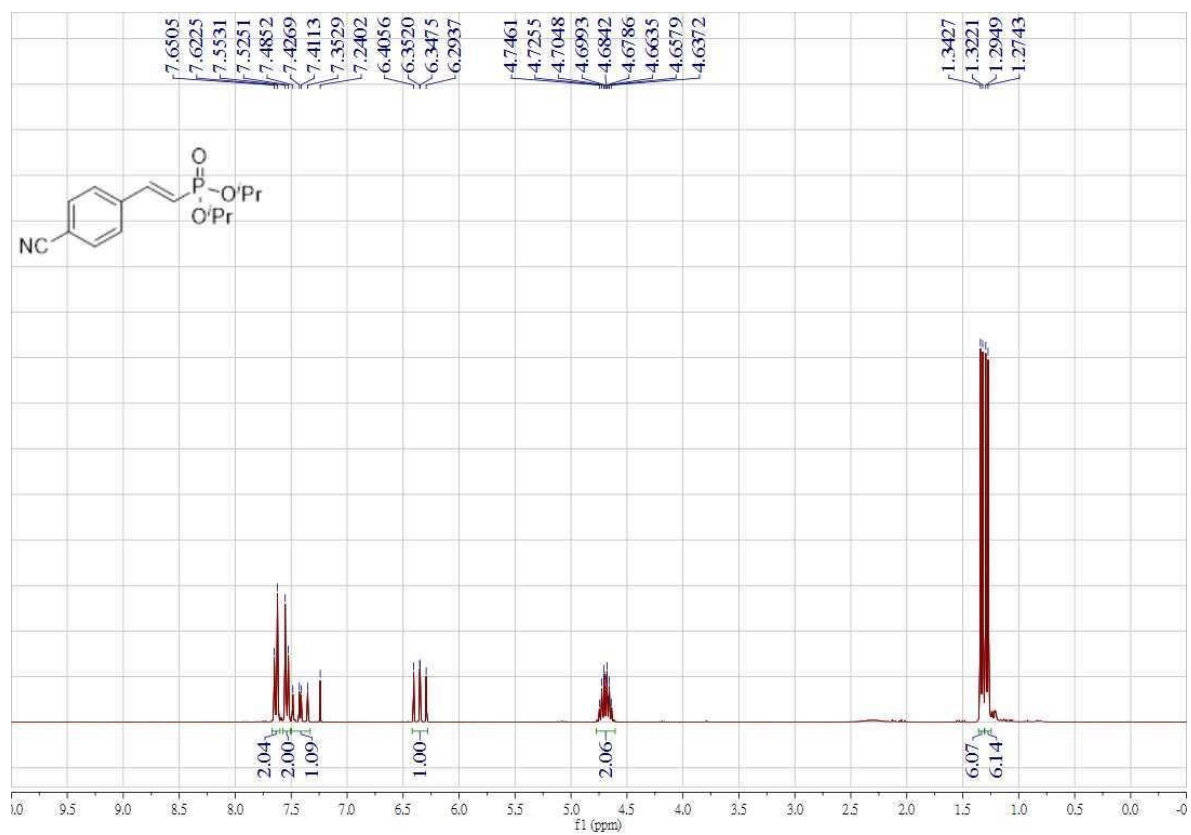


$^{31}\text{P}$  NMR spectrum of compound **4i**

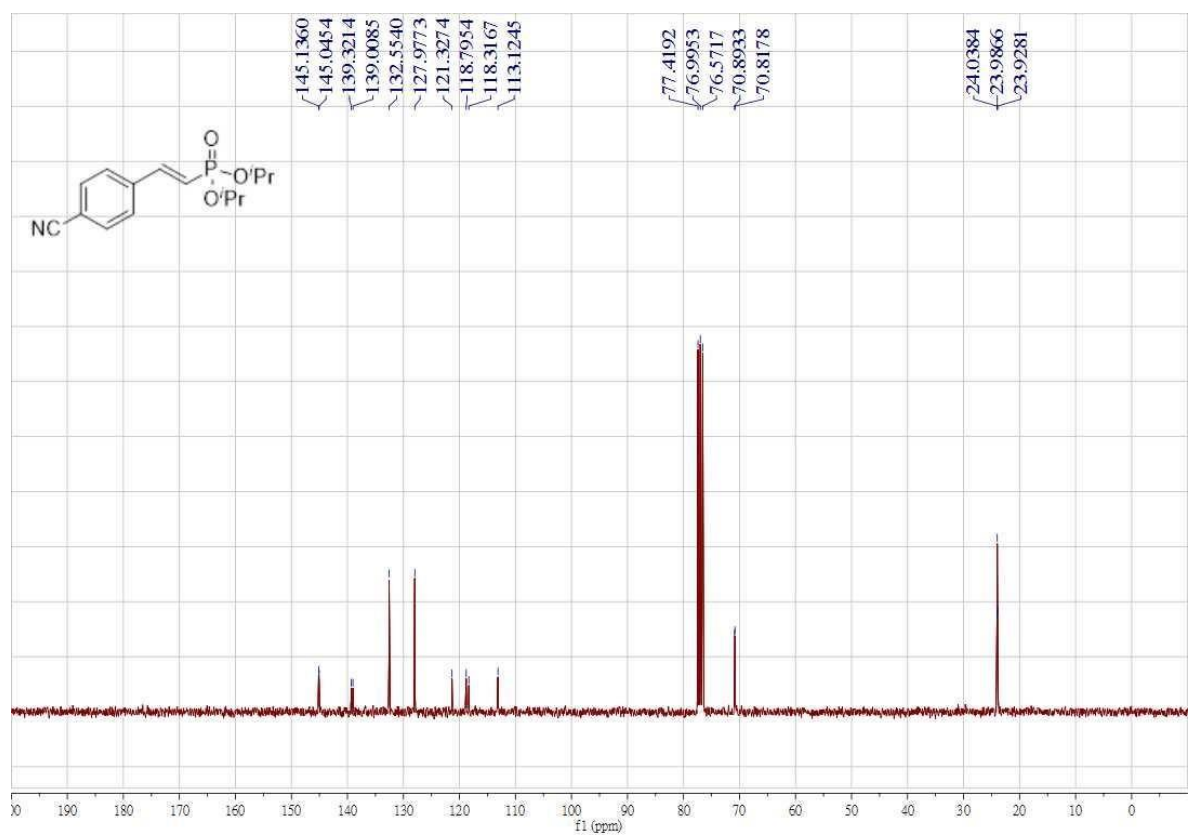




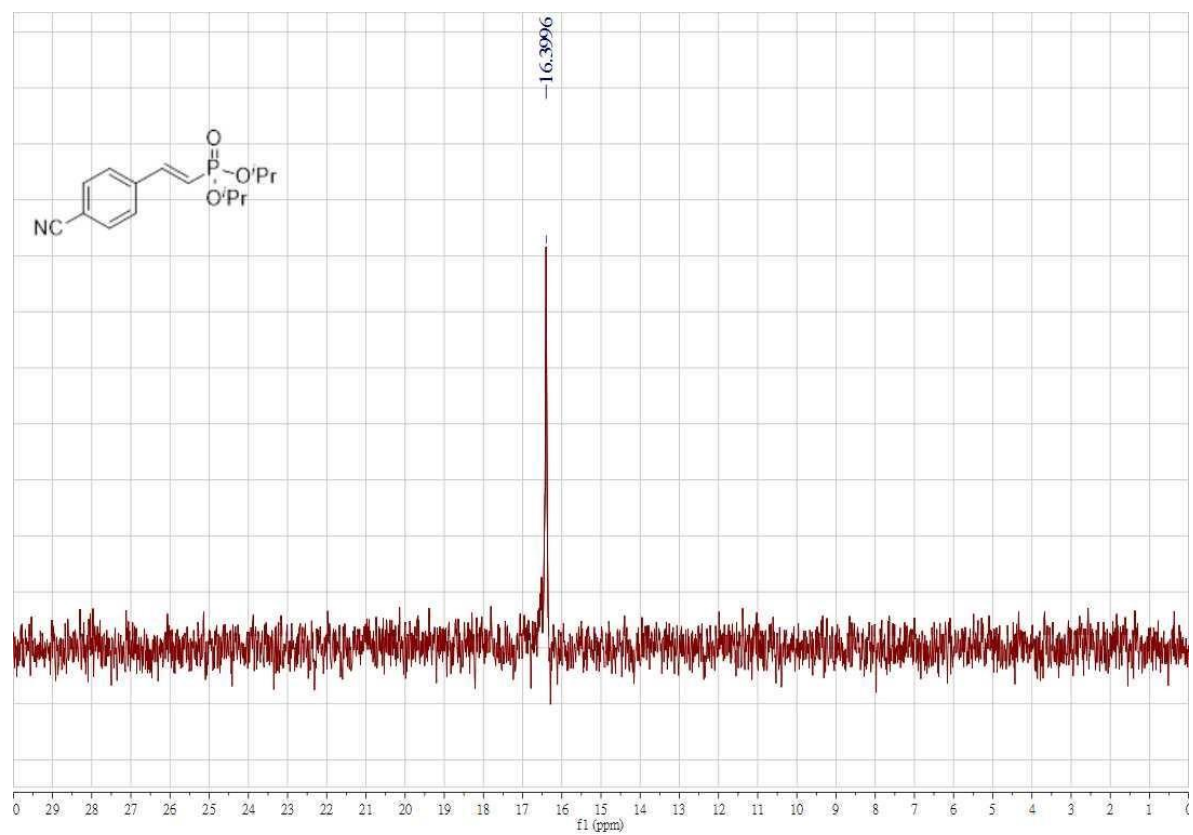
<sup>1</sup>H NMR spectrum of compound **4j**



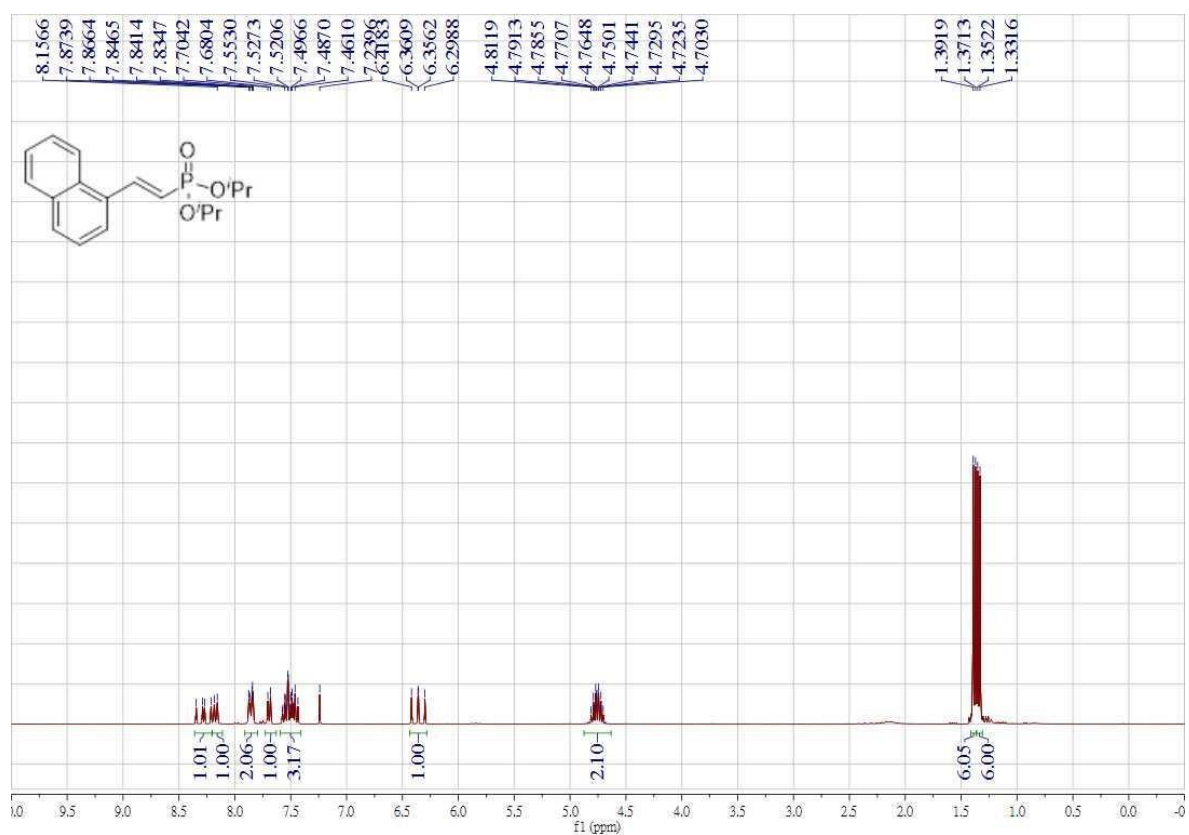
<sup>13</sup>C NMR spectrum of compound **4j**



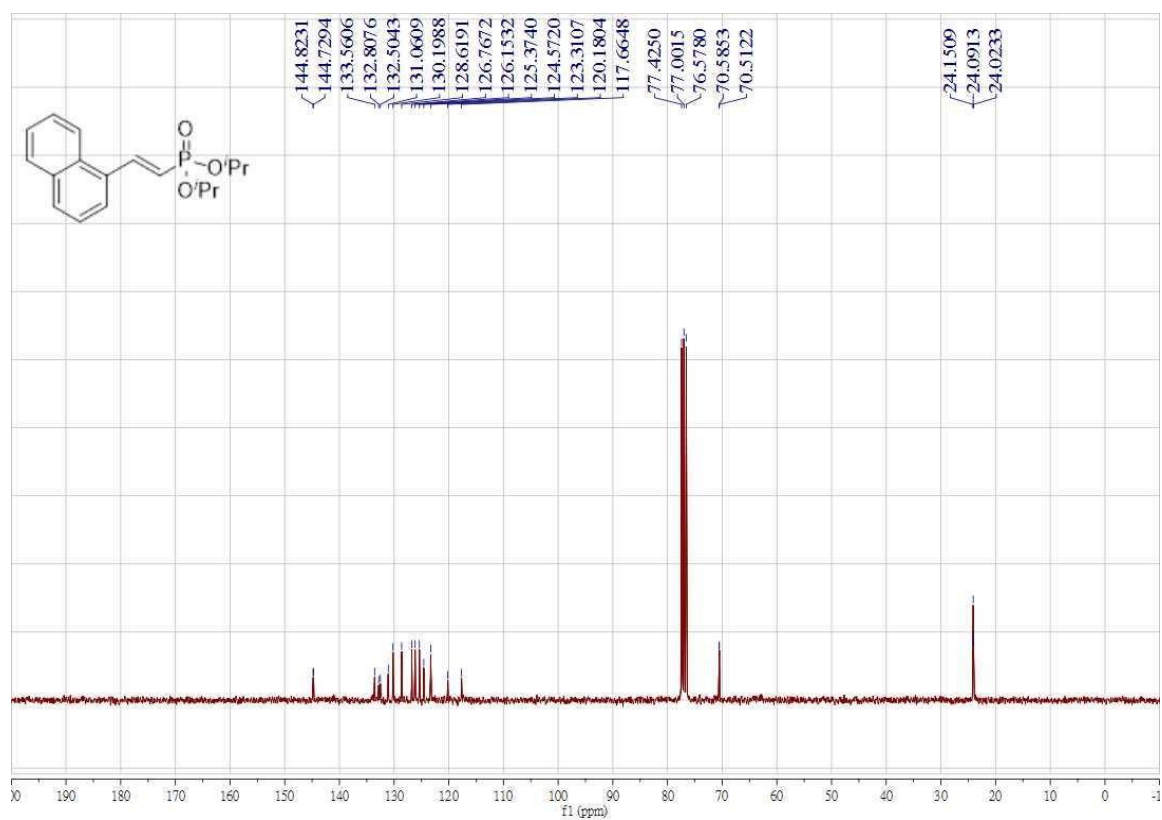
$^{31}\text{P}$  NMR spectrum of compound **4j**



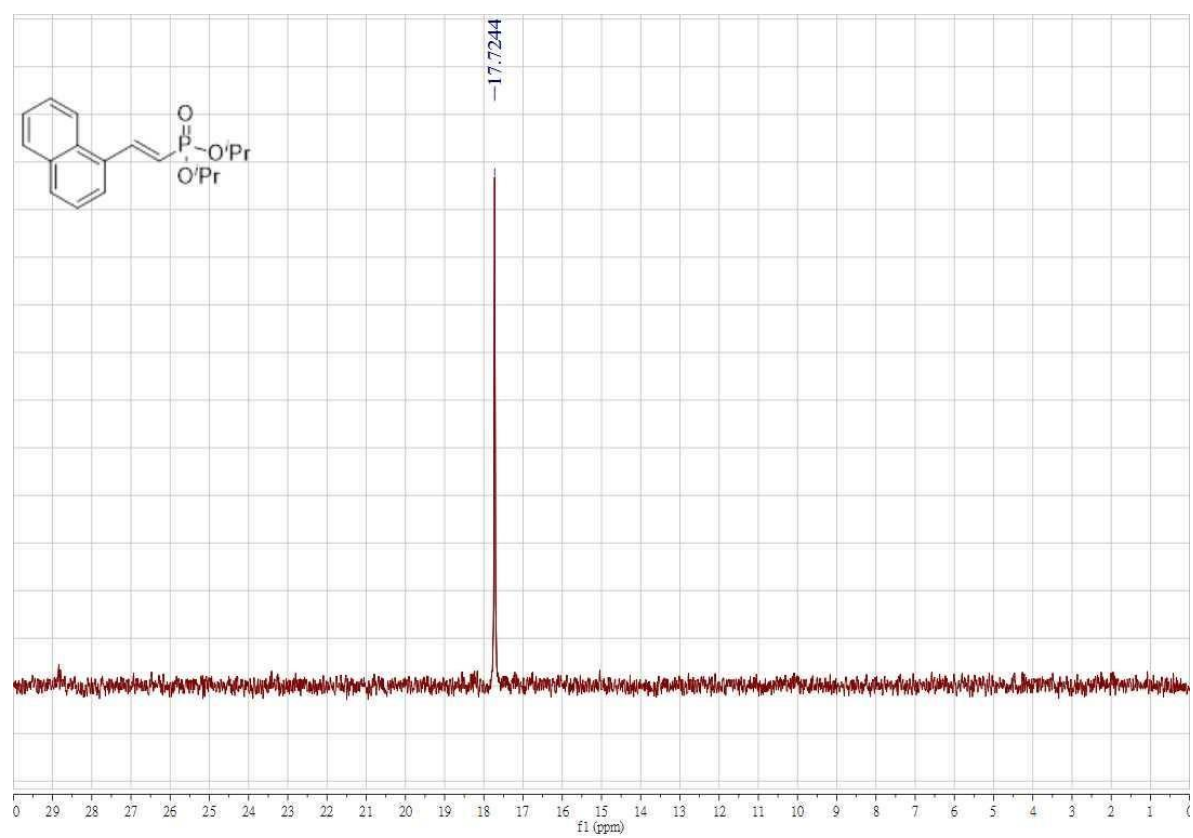
<sup>1</sup>H NMR spectrum of compound **4m**



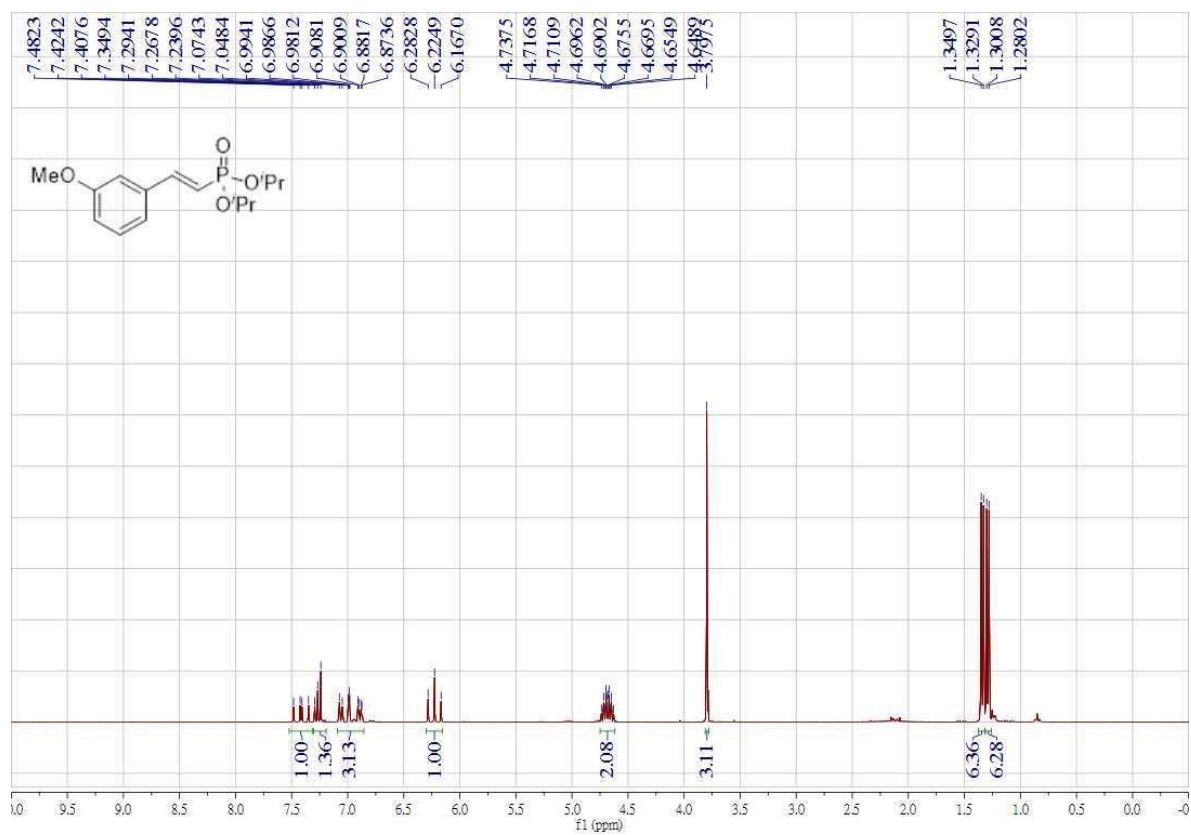
<sup>13</sup>C NMR spectrum of compound **4m**



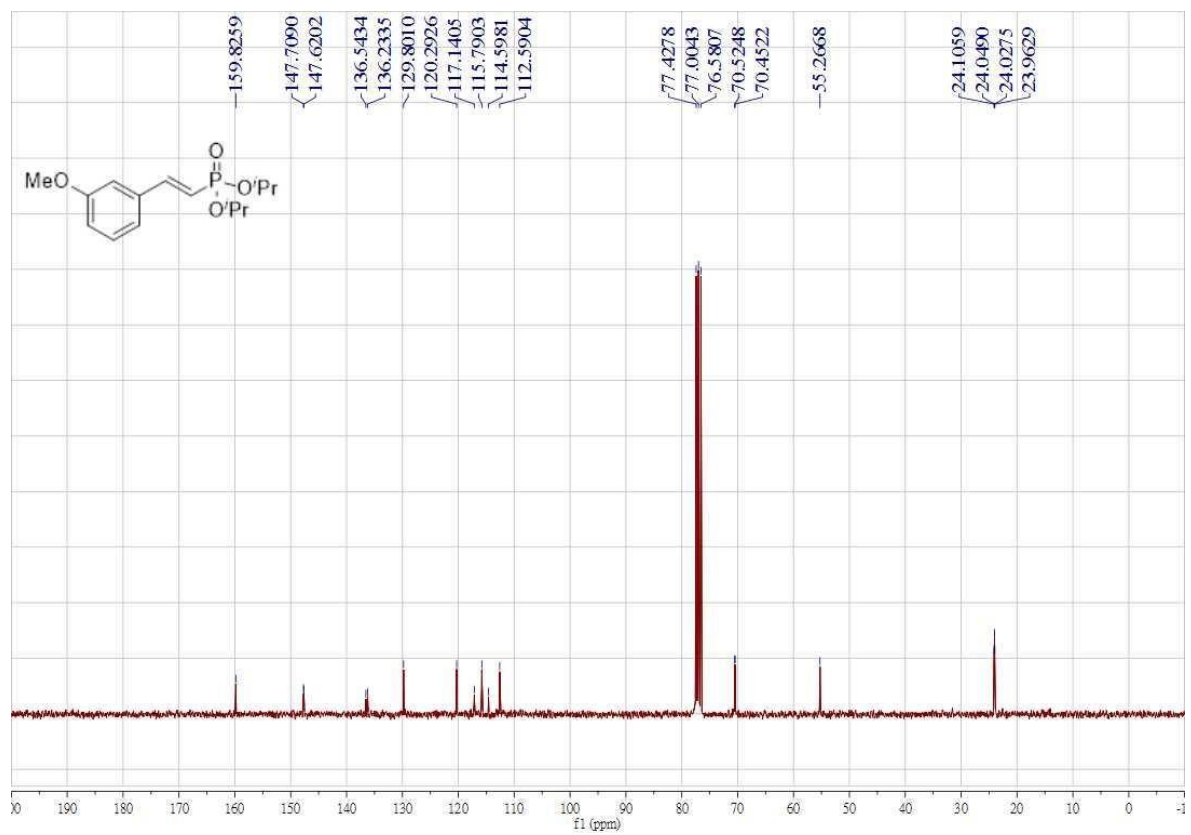
$^{31}\text{P}$  NMR spectrum of compound **4m**



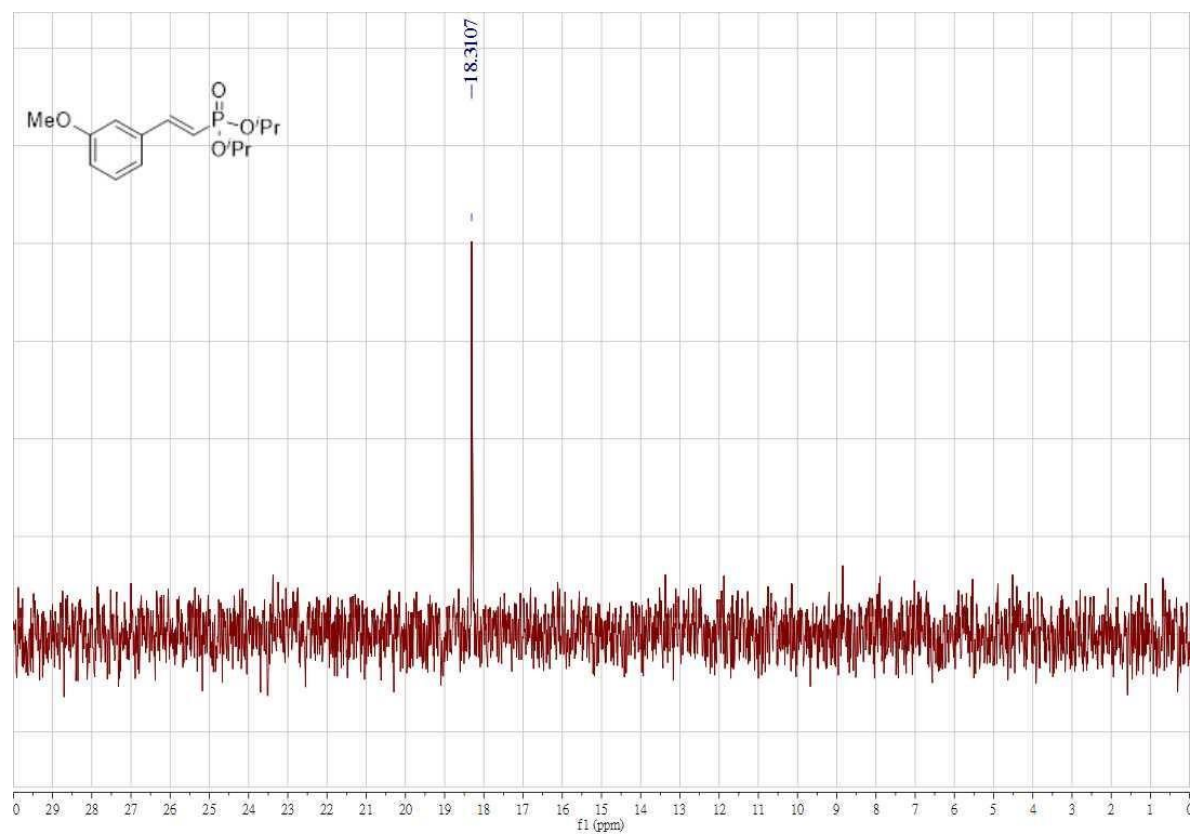
### <sup>1</sup>H NMR spectrum of compound **4o**



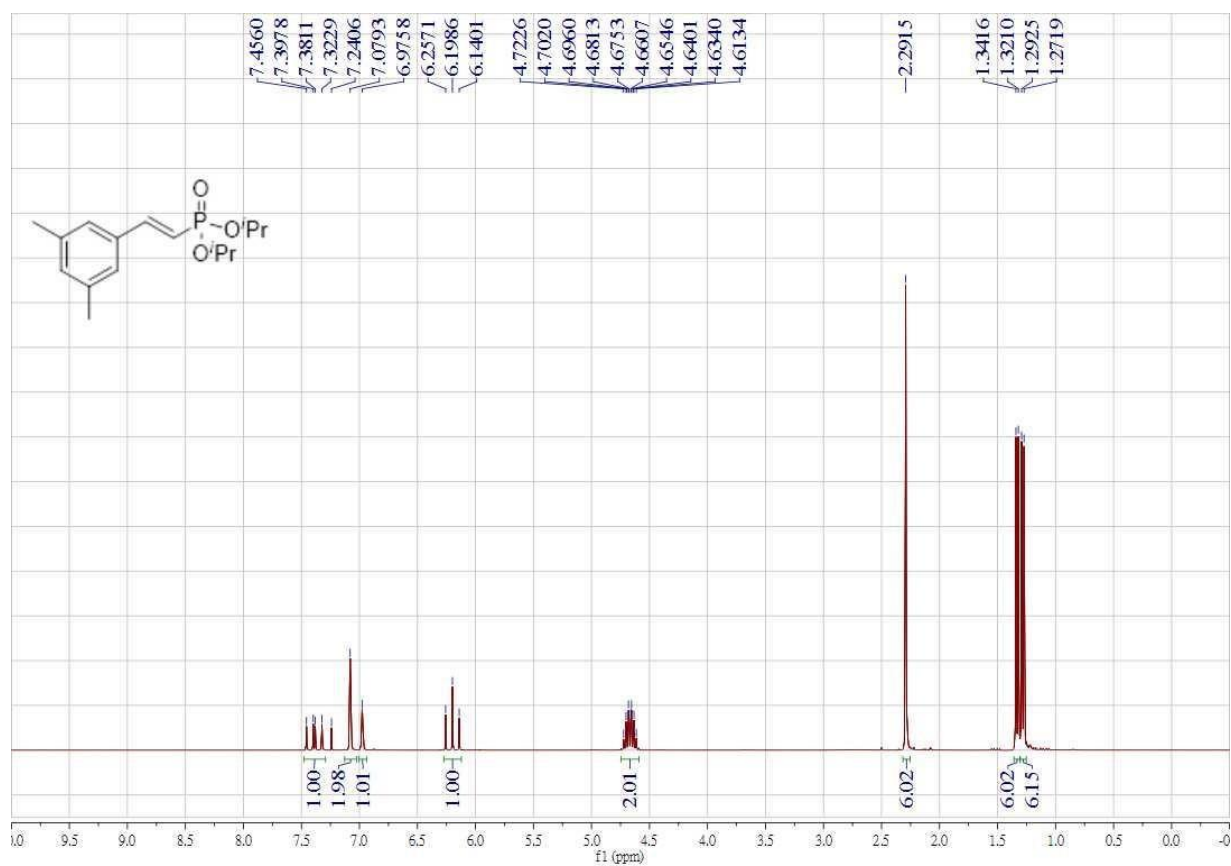
### <sup>13</sup>C NMR spectrum of compound **4o**



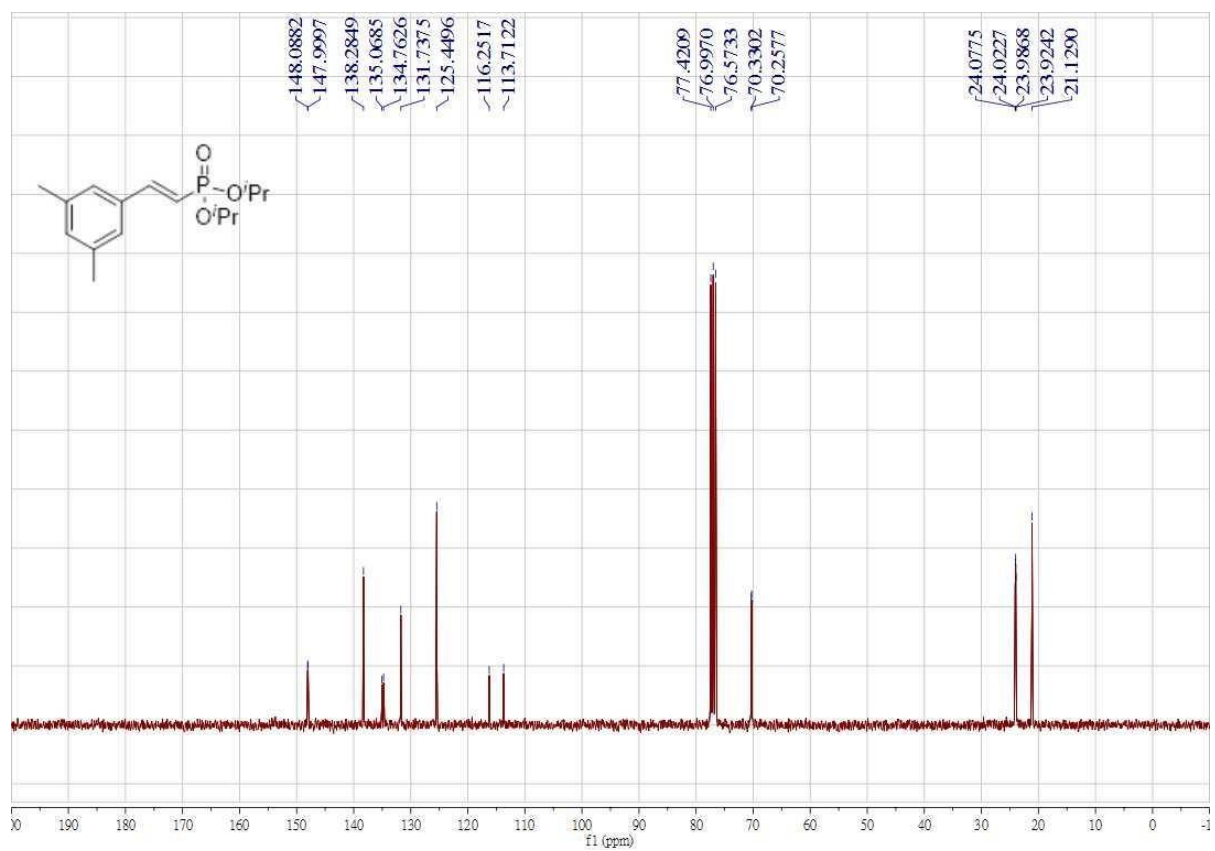
$^{31}\text{P}$  NMR spectrum of compound **4o**



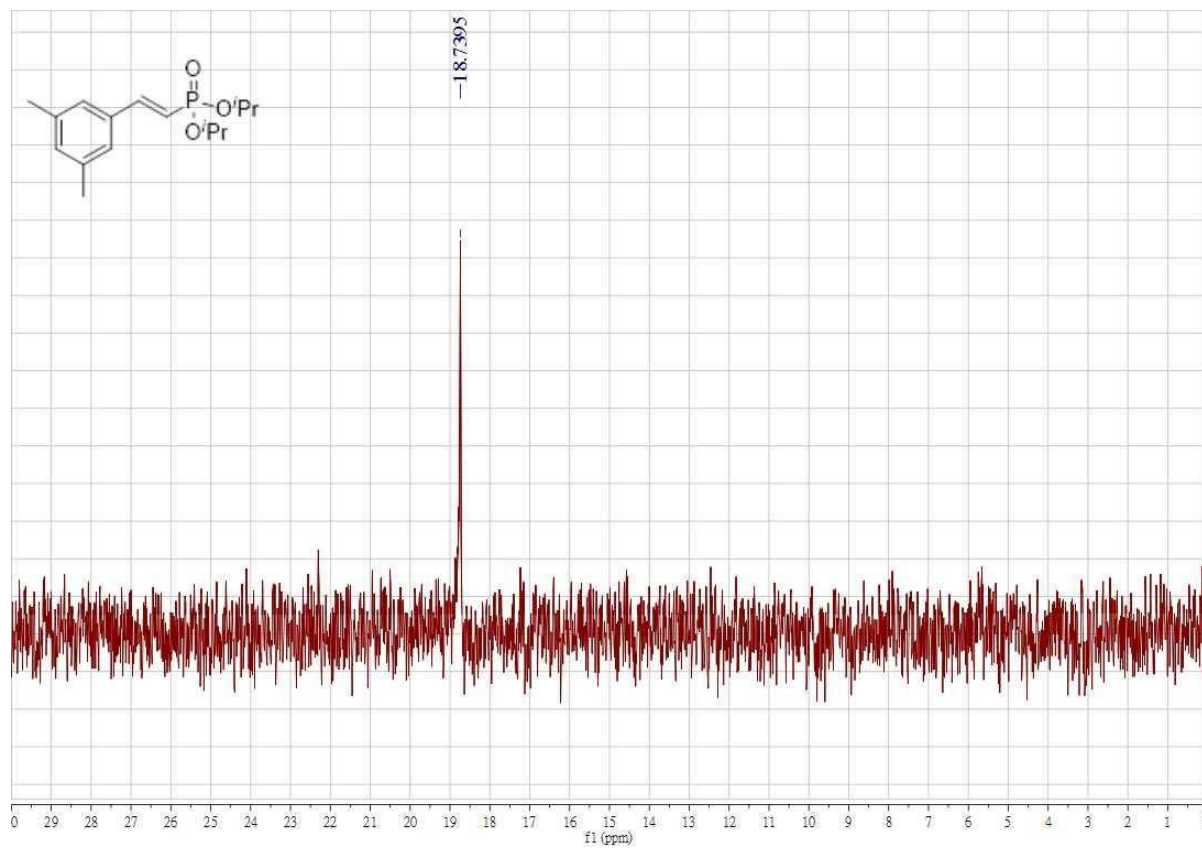
<sup>1</sup>H NMR spectrum of compound **4p**



<sup>13</sup>C NMR spectrum of compound **4p**

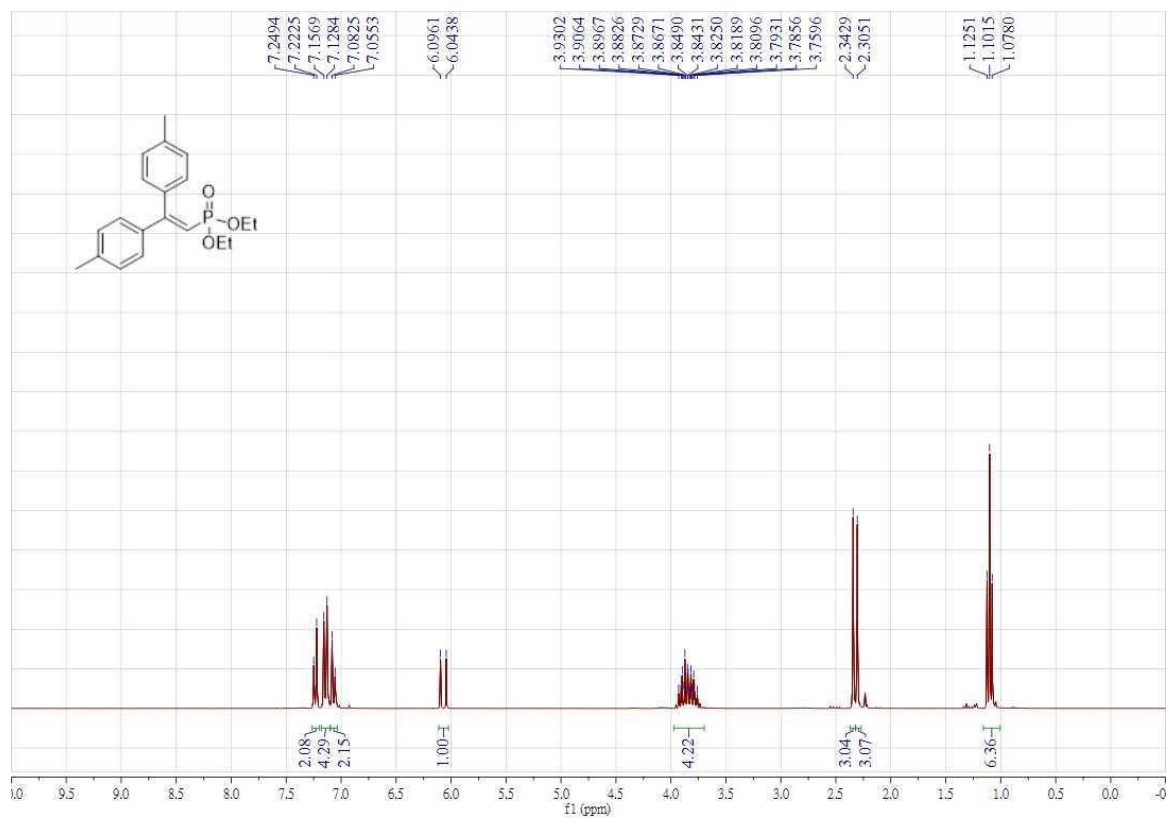


$^{31}\text{P}$  NMR spectrum of compound **4p**

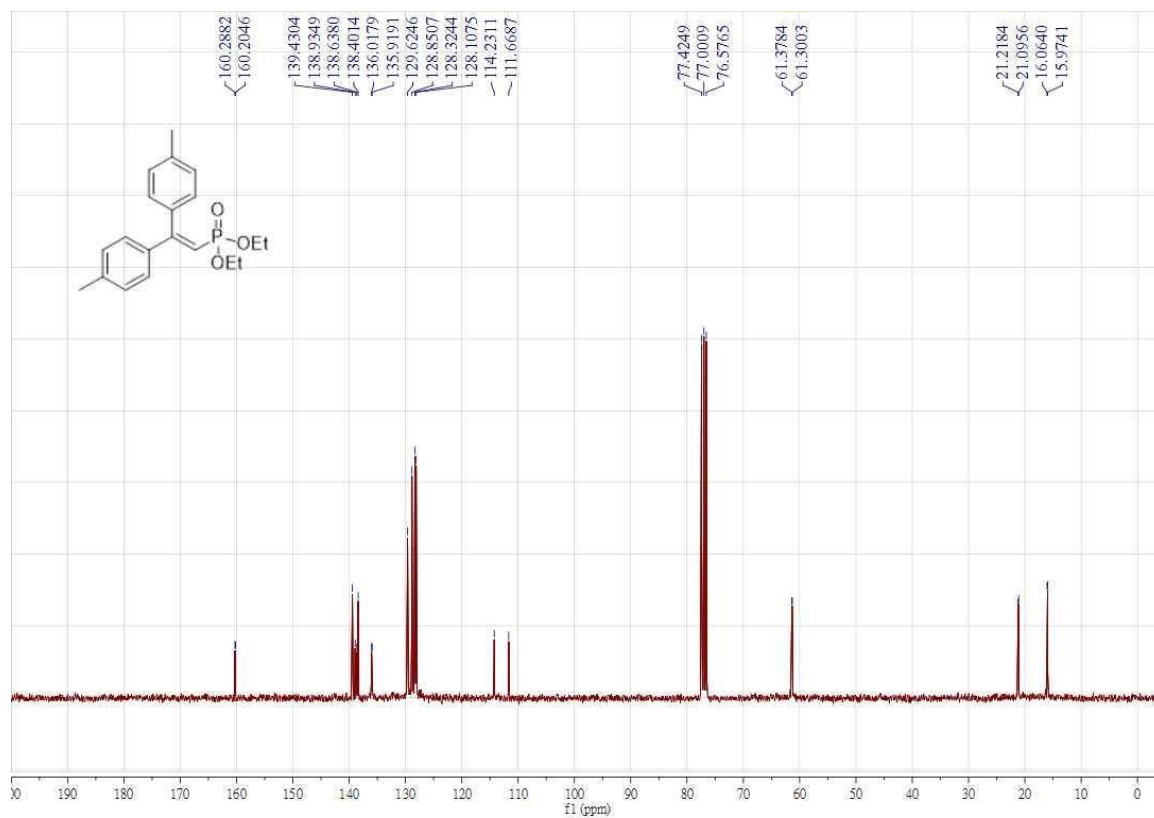




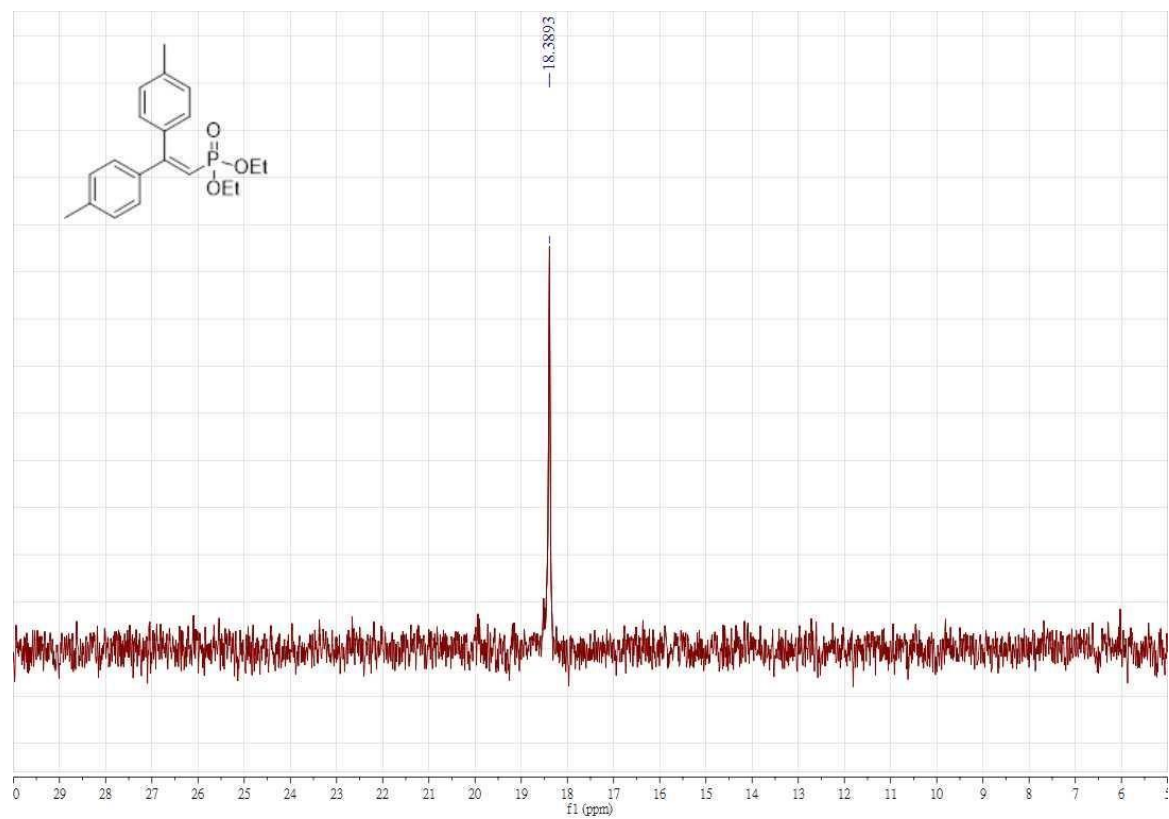
<sup>1</sup>H NMR spectrum of compound **6b**



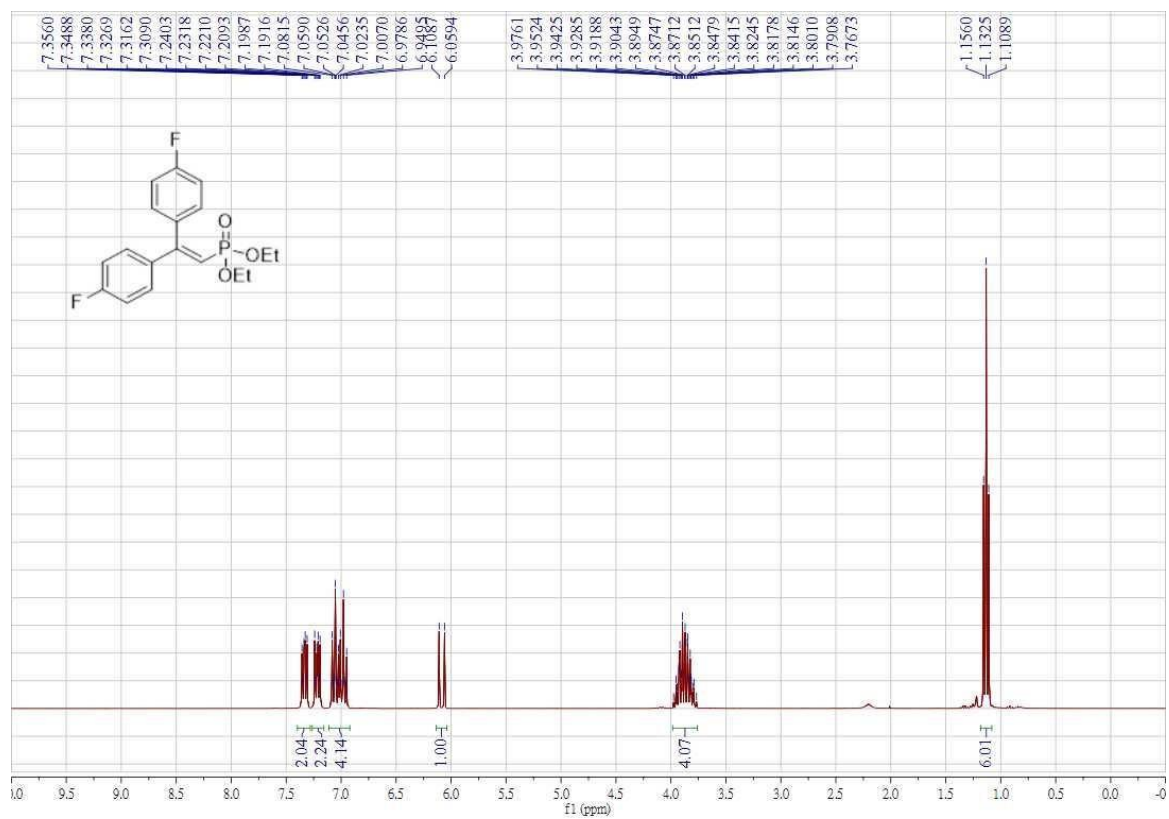
<sup>13</sup>C NMR spectrum of compound **6b**



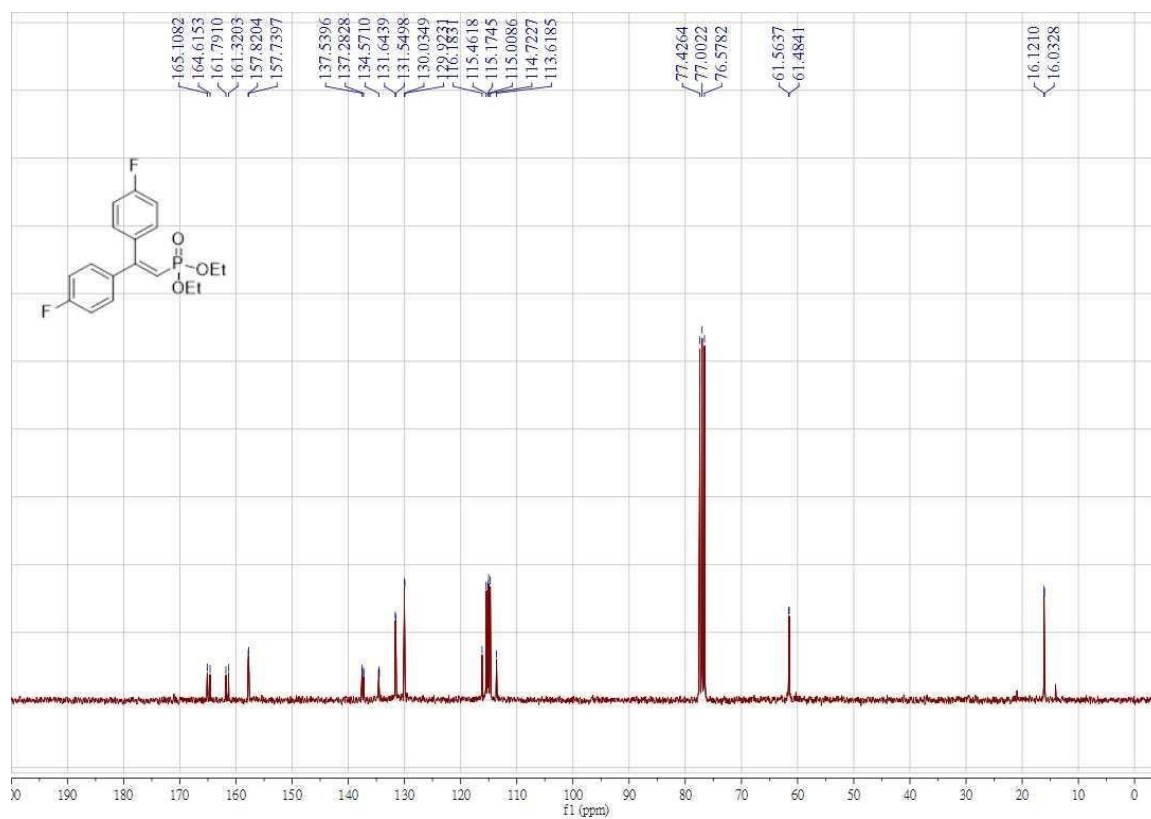
$^{31}\text{P}$  NMR spectrum of compound **6b**



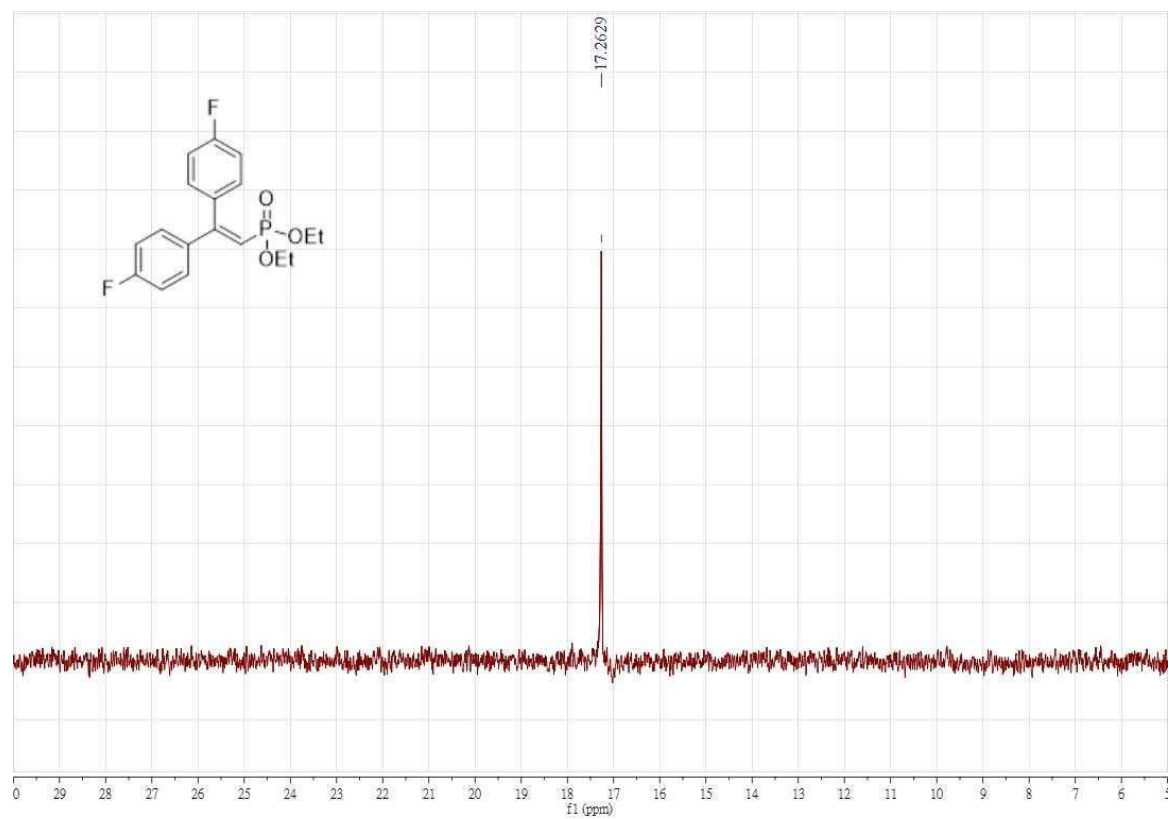
# <sup>1</sup>H NMR spectrum of compound 6d



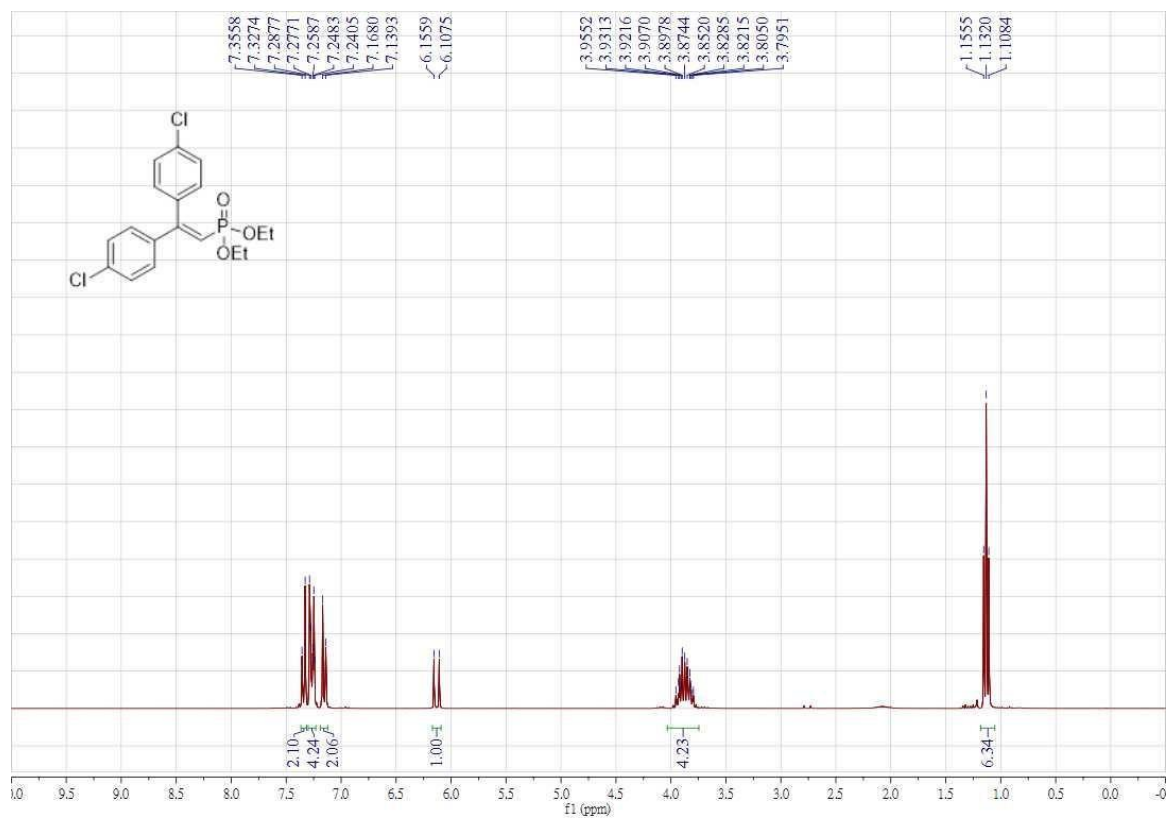
# <sup>13</sup>C NMR spectrum of compound 6d



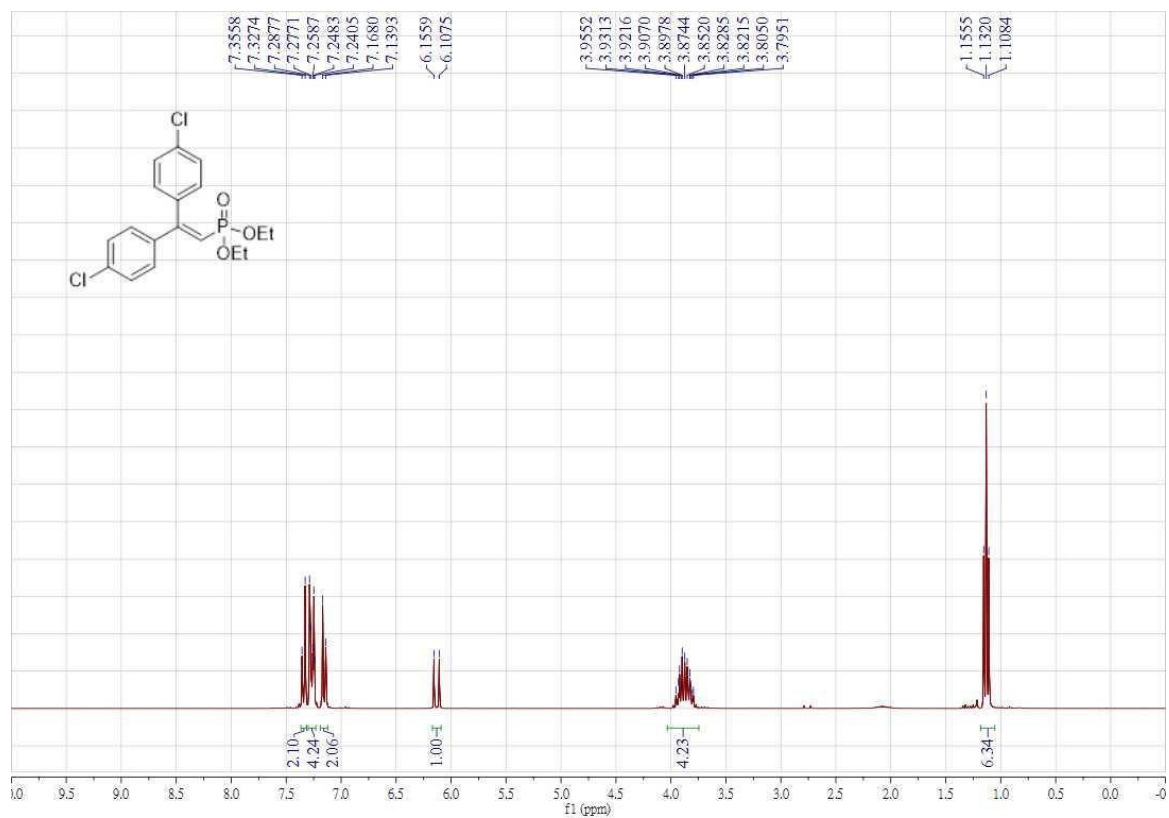
$^{31}\text{P}$  NMR spectrum of compound **6d**



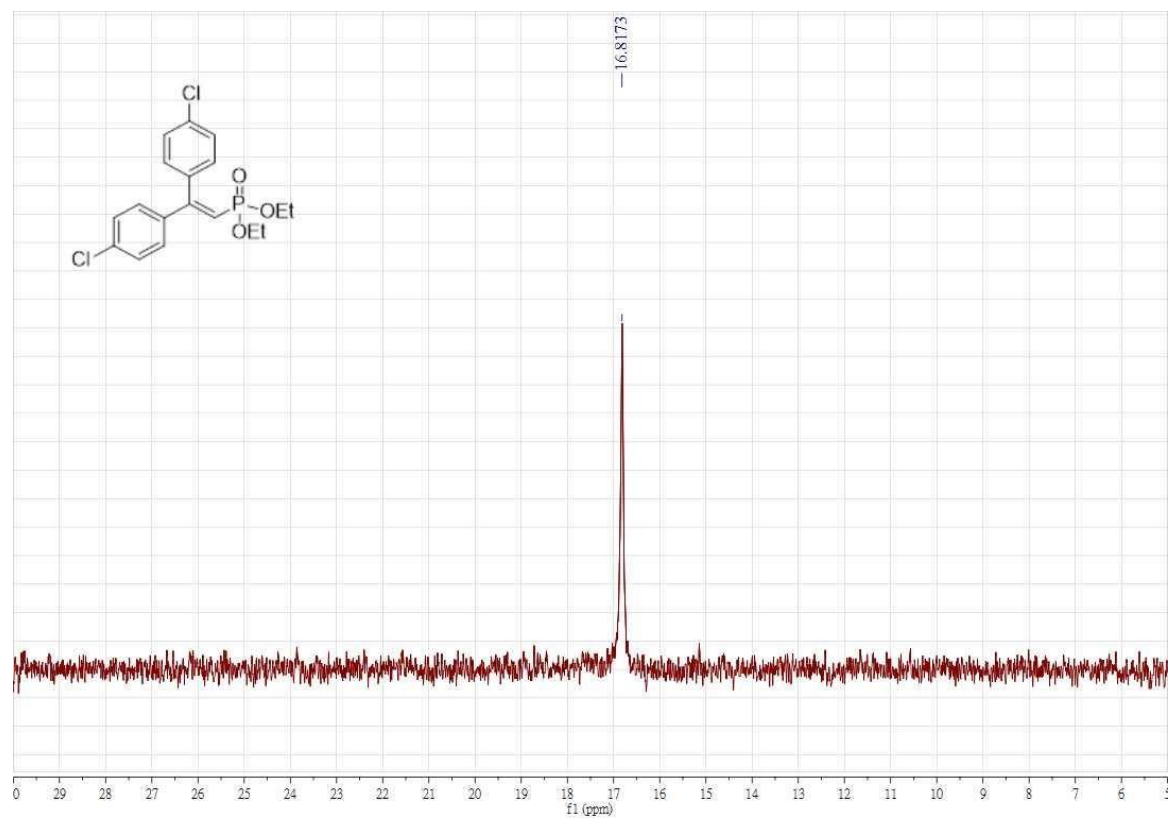
<sup>1</sup>H NMR spectrum of compound **6e**



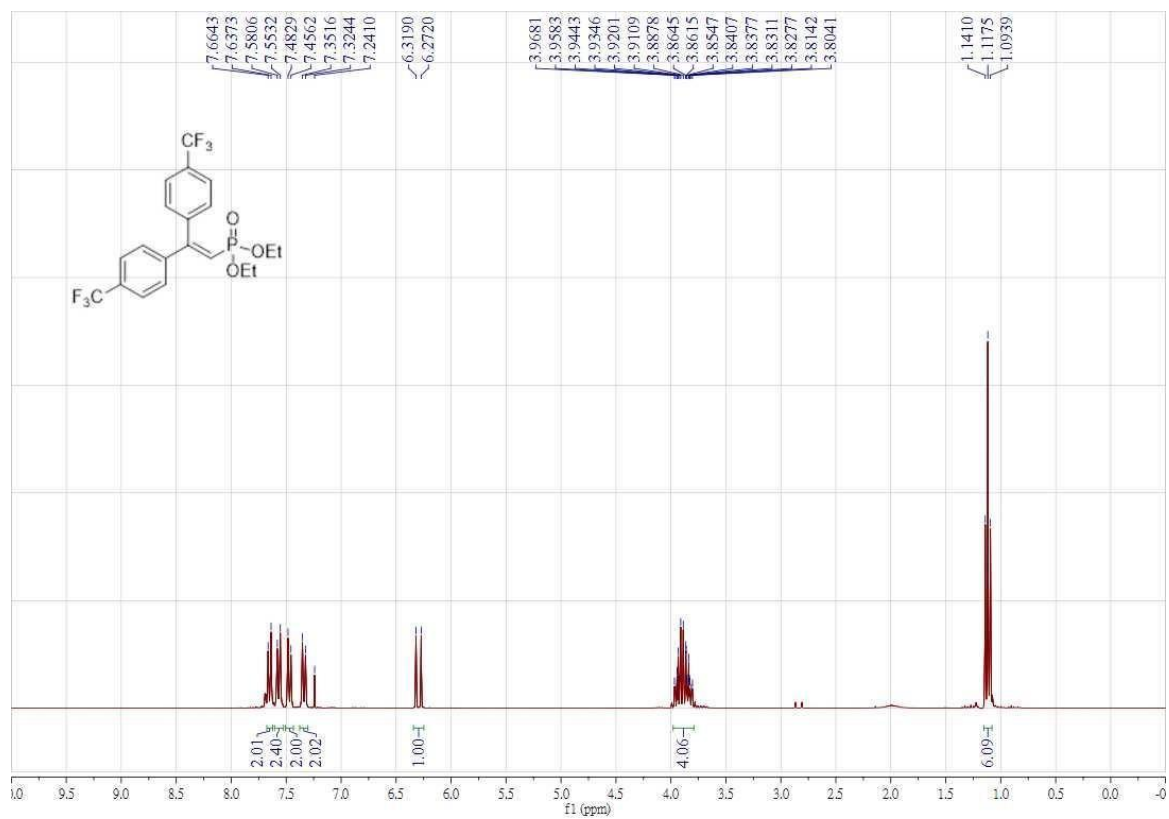
<sup>13</sup>C NMR spectrum of compound **6e**



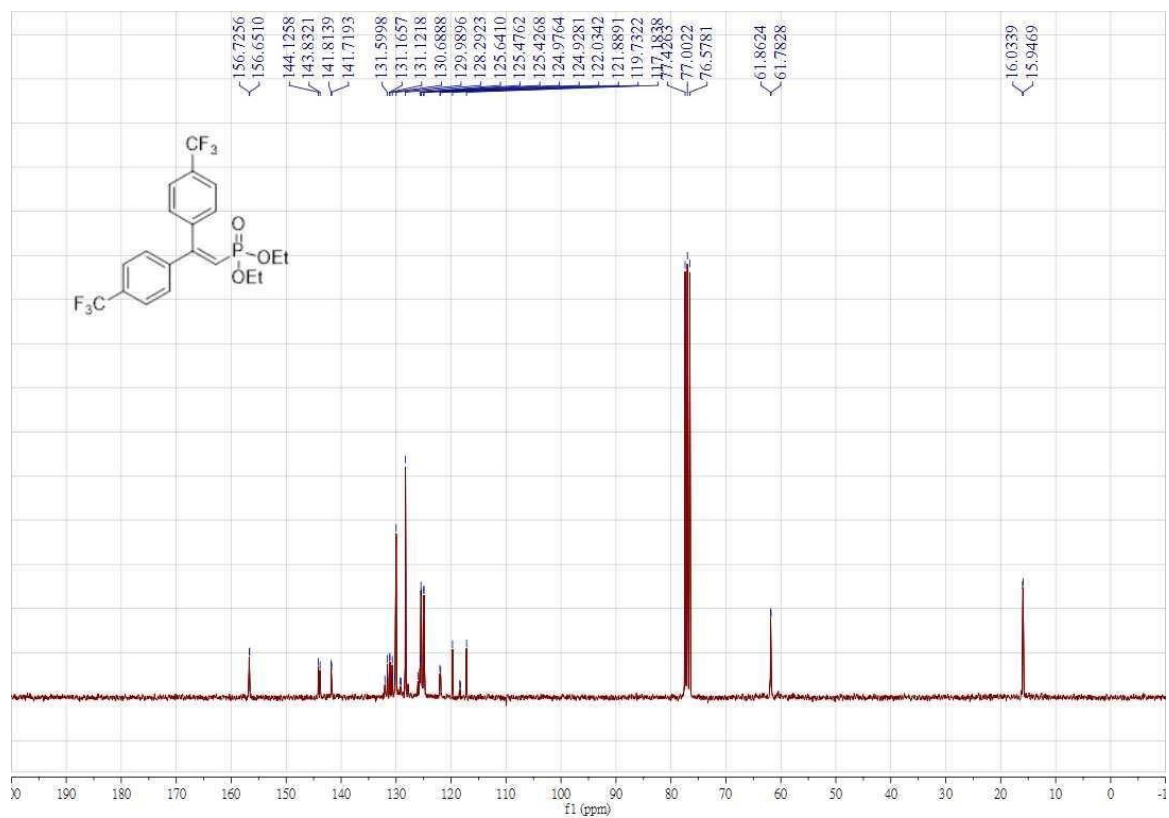
$^{31}\text{P}$  NMR spectrum of compound **6e**



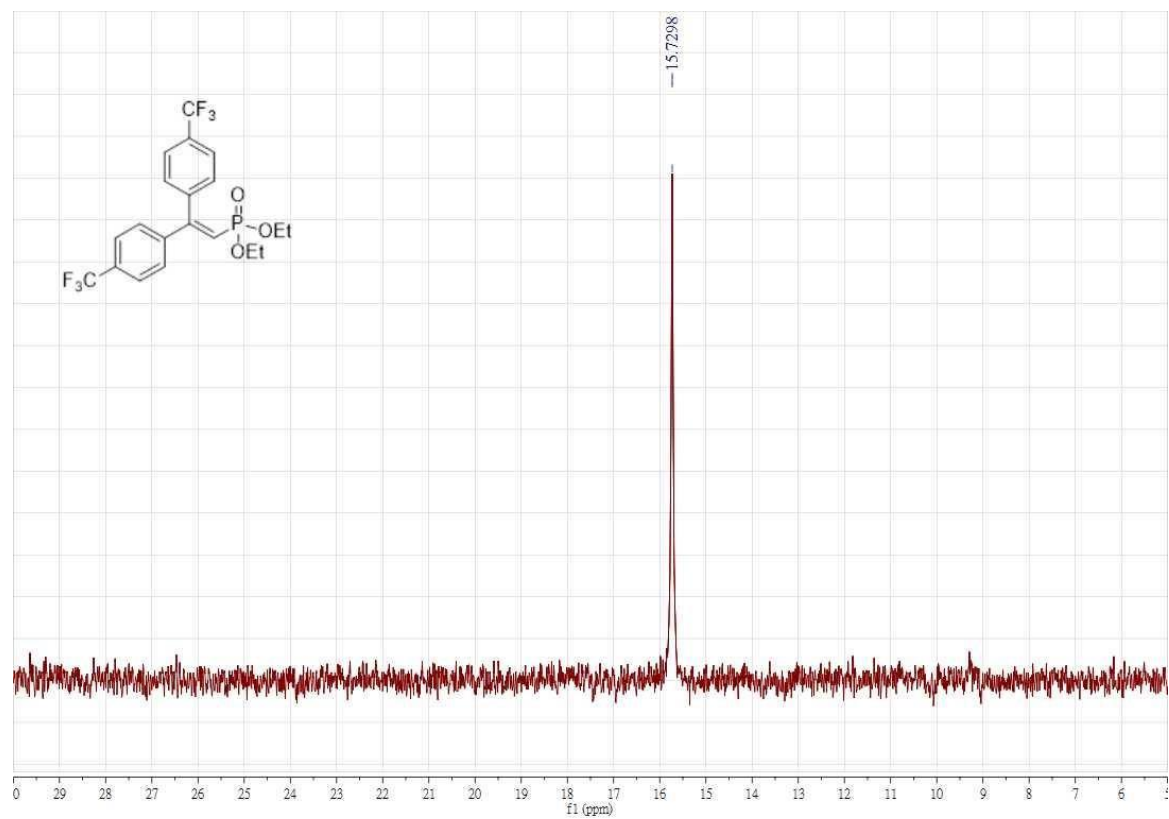
<sup>1</sup>H NMR spectrum of compound **6g**



<sup>13</sup>C NMR spectrum of compound **6g**

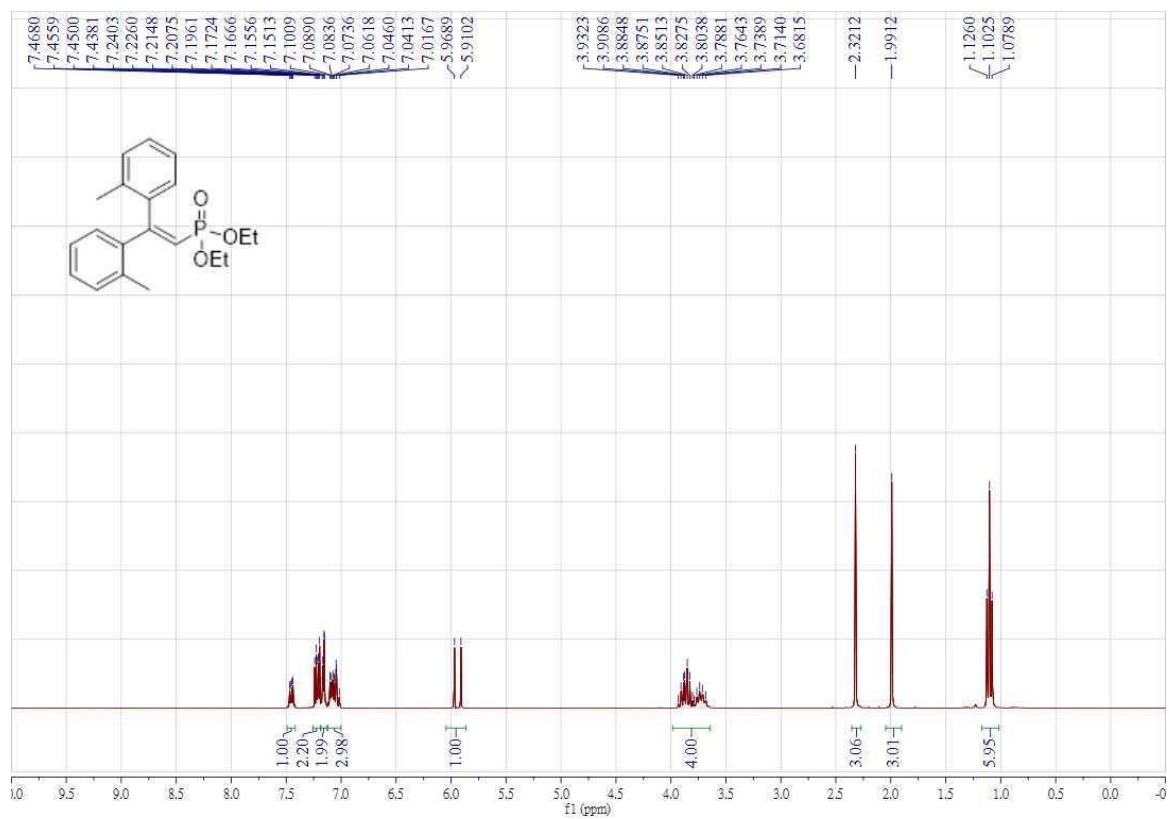


$^{31}\text{P}$  NMR spectrum of compound **6g**

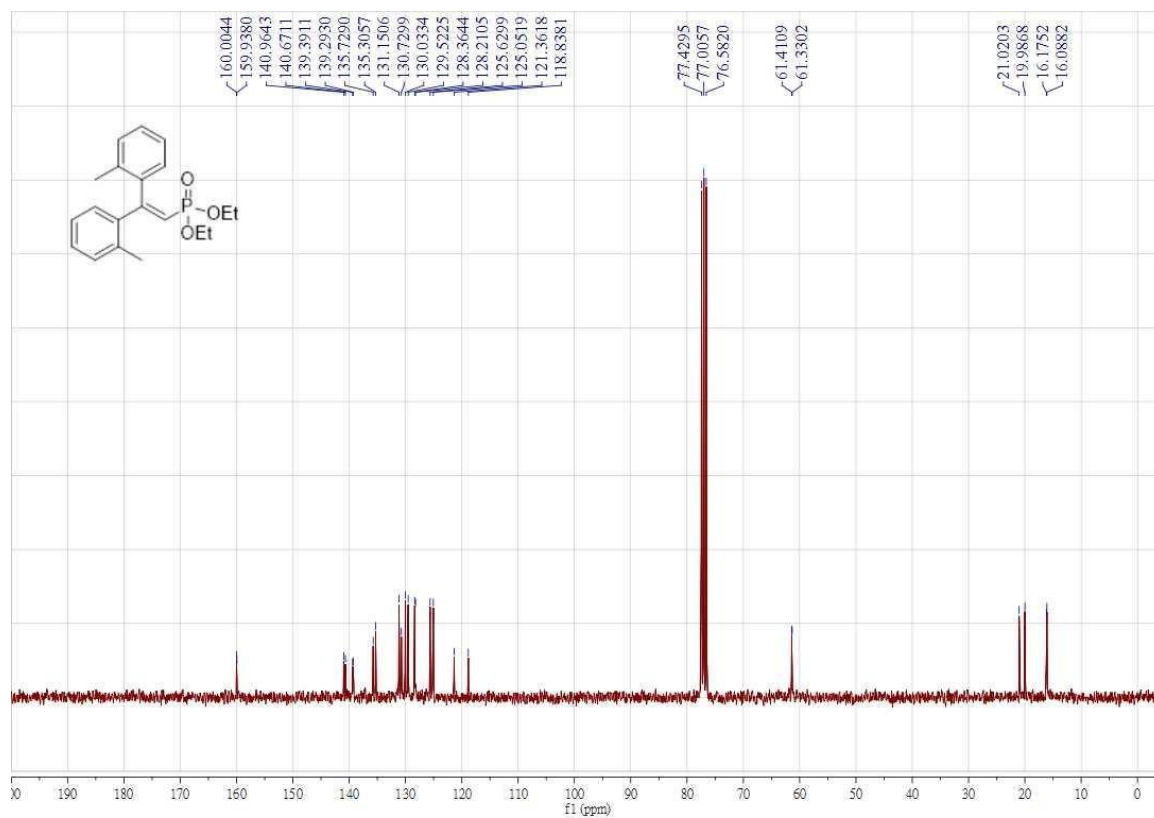




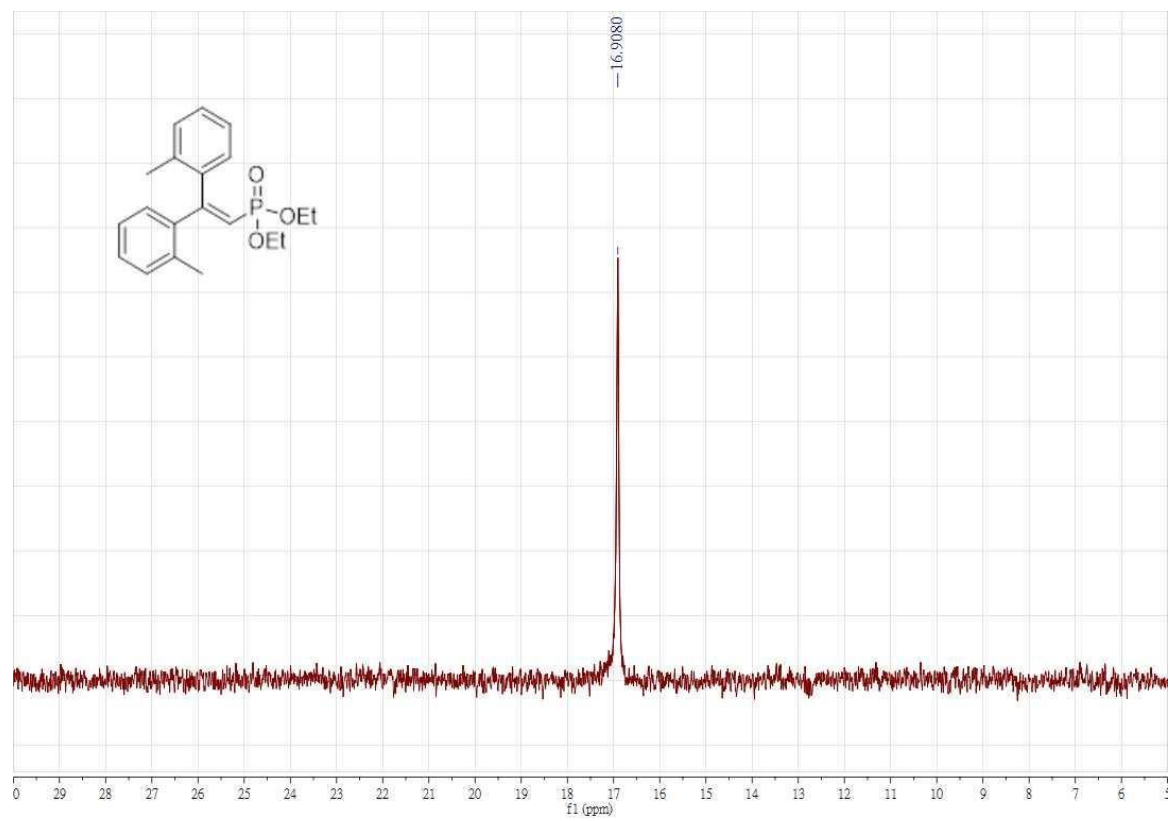
<sup>1</sup>H NMR spectrum of compound **6k**



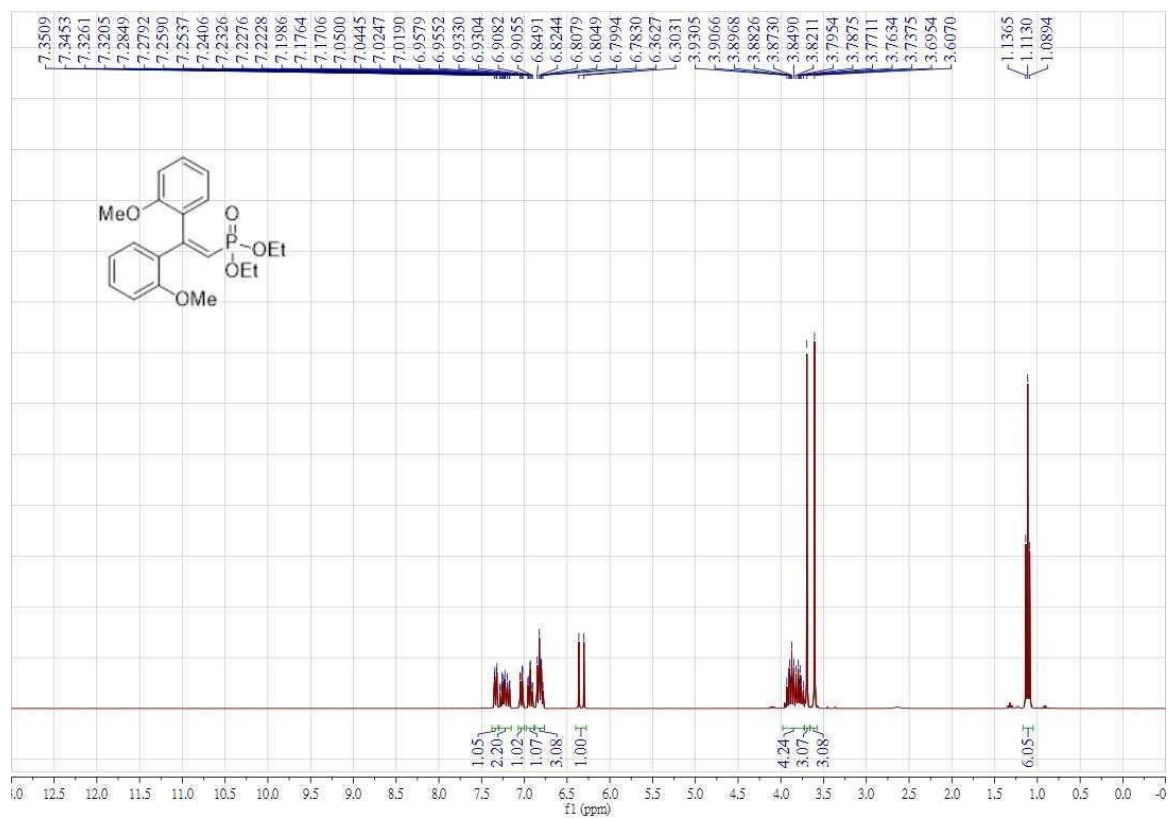
<sup>13</sup>C NMR spectrum of compound **6k**



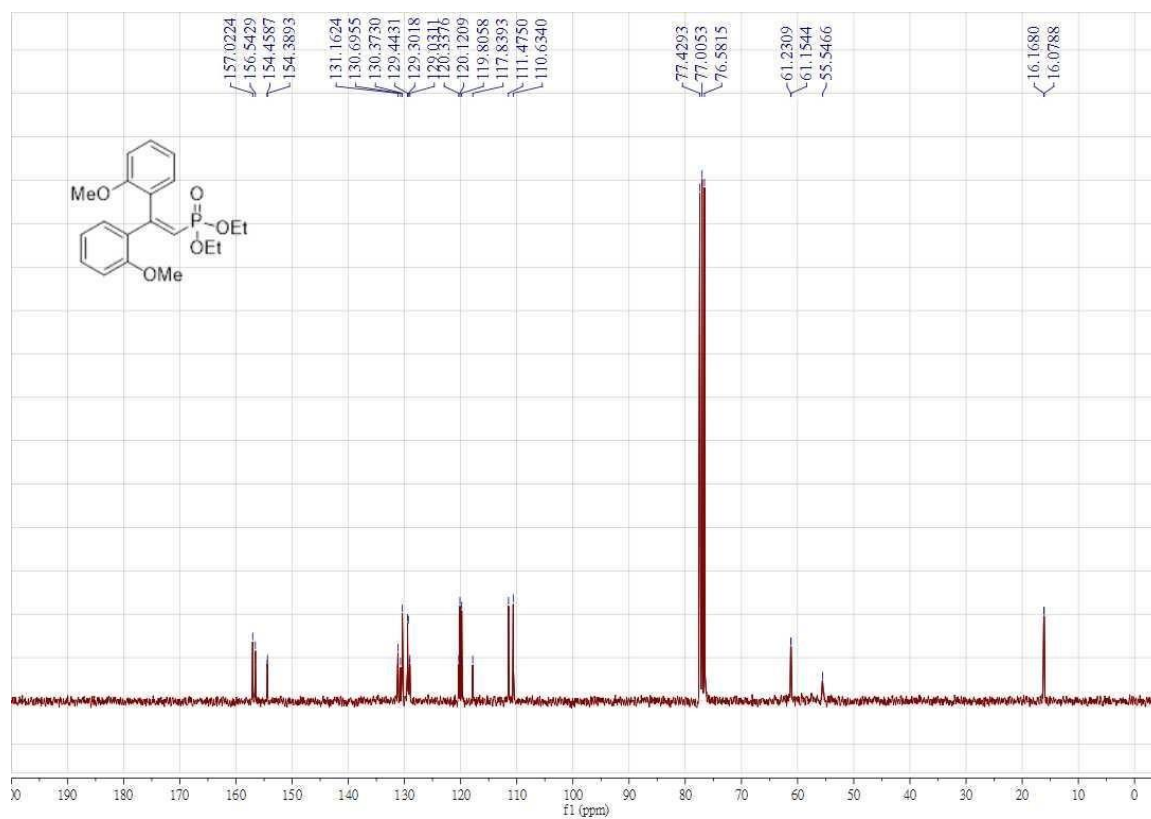
$^{31}\text{P}$  NMR spectrum of compound **6k**



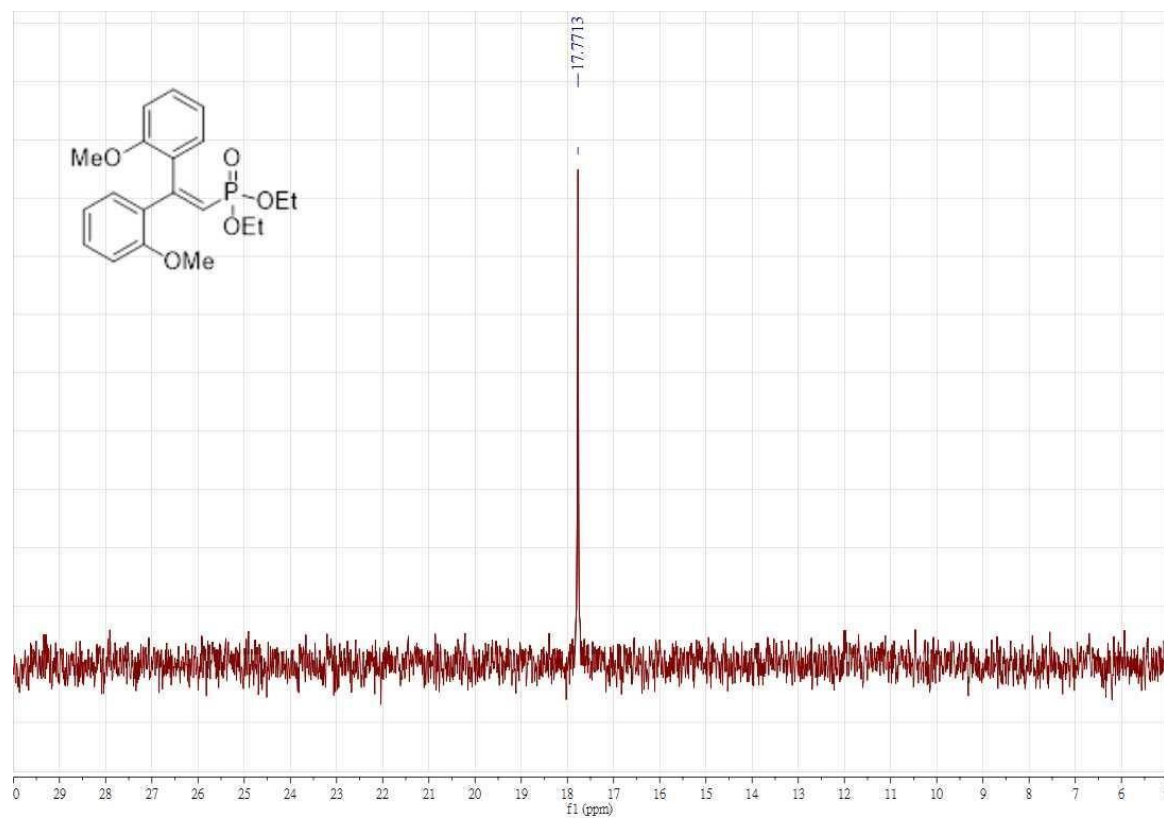
# <sup>1</sup>H NMR spectrum of compound **6l**



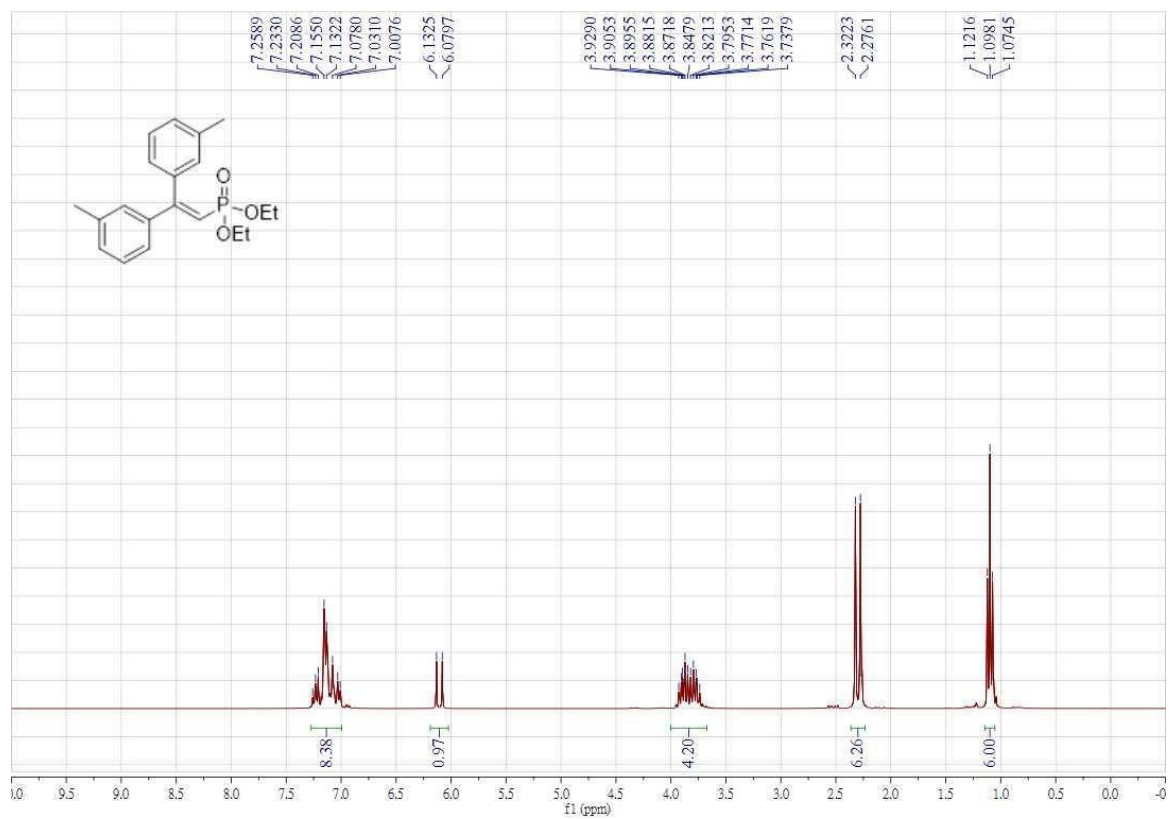
# <sup>13</sup>C NMR spectrum of compound **6l**



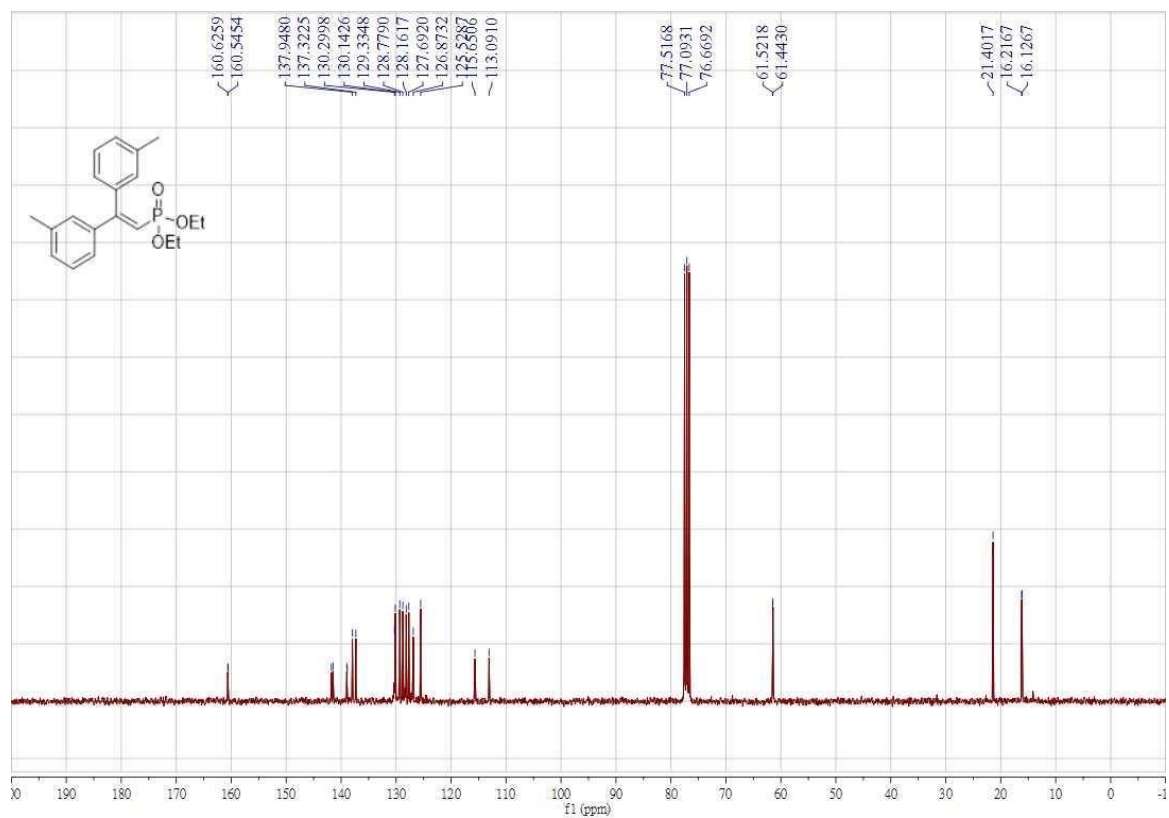
$^{31}\text{P}$  NMR spectrum of compound **6l**



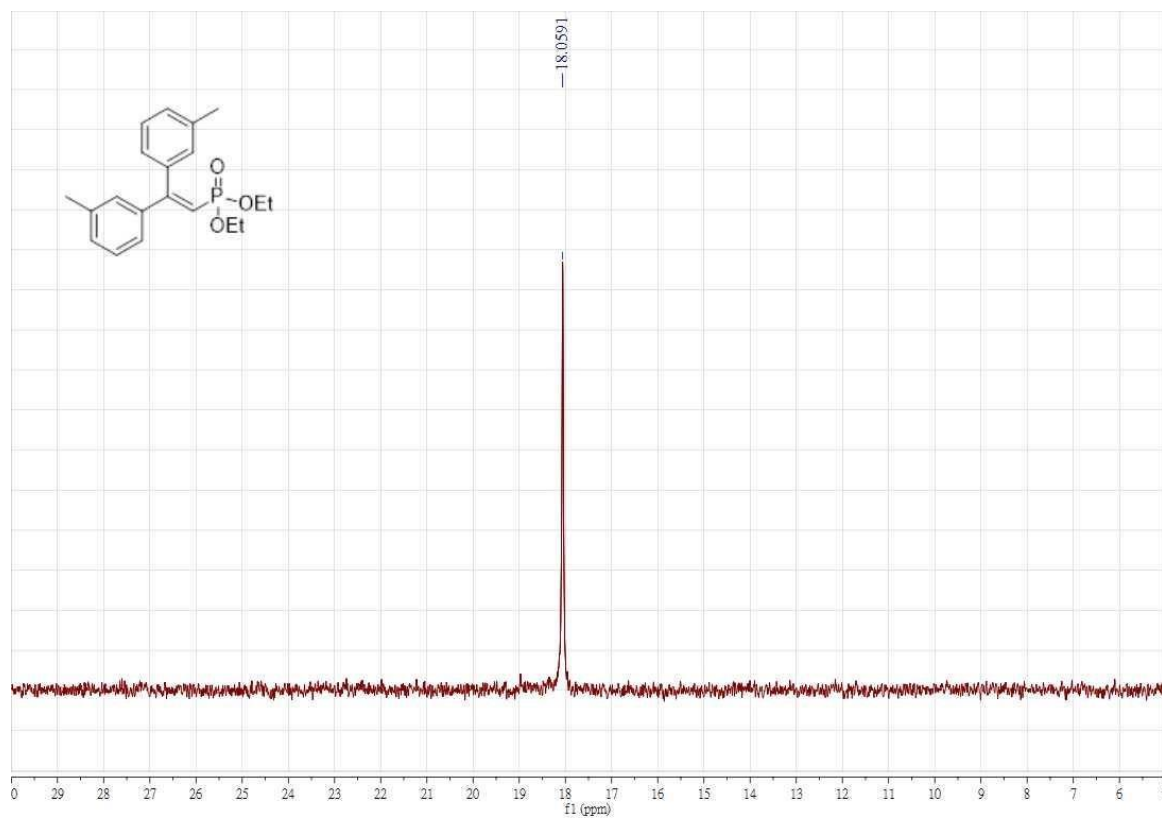
<sup>1</sup>H NMR spectrum of compound **6n**



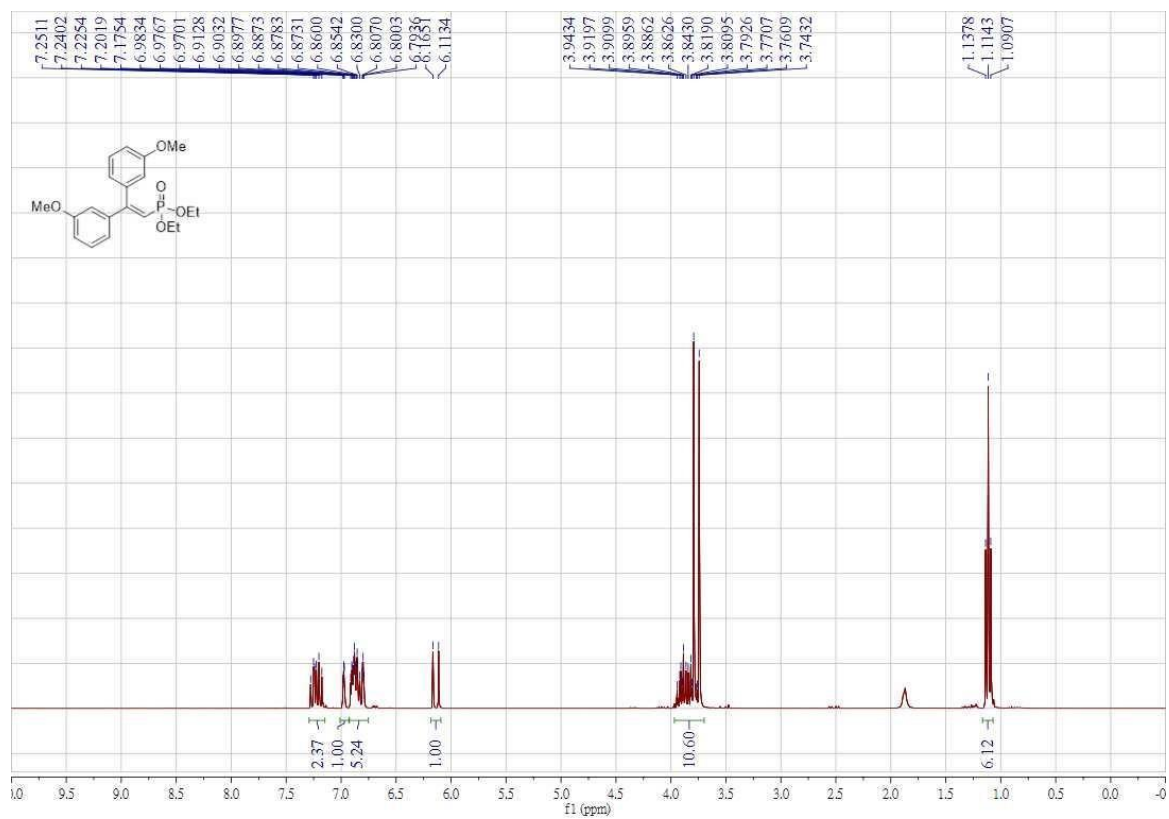
<sup>13</sup>C NMR spectrum of compound **6n**



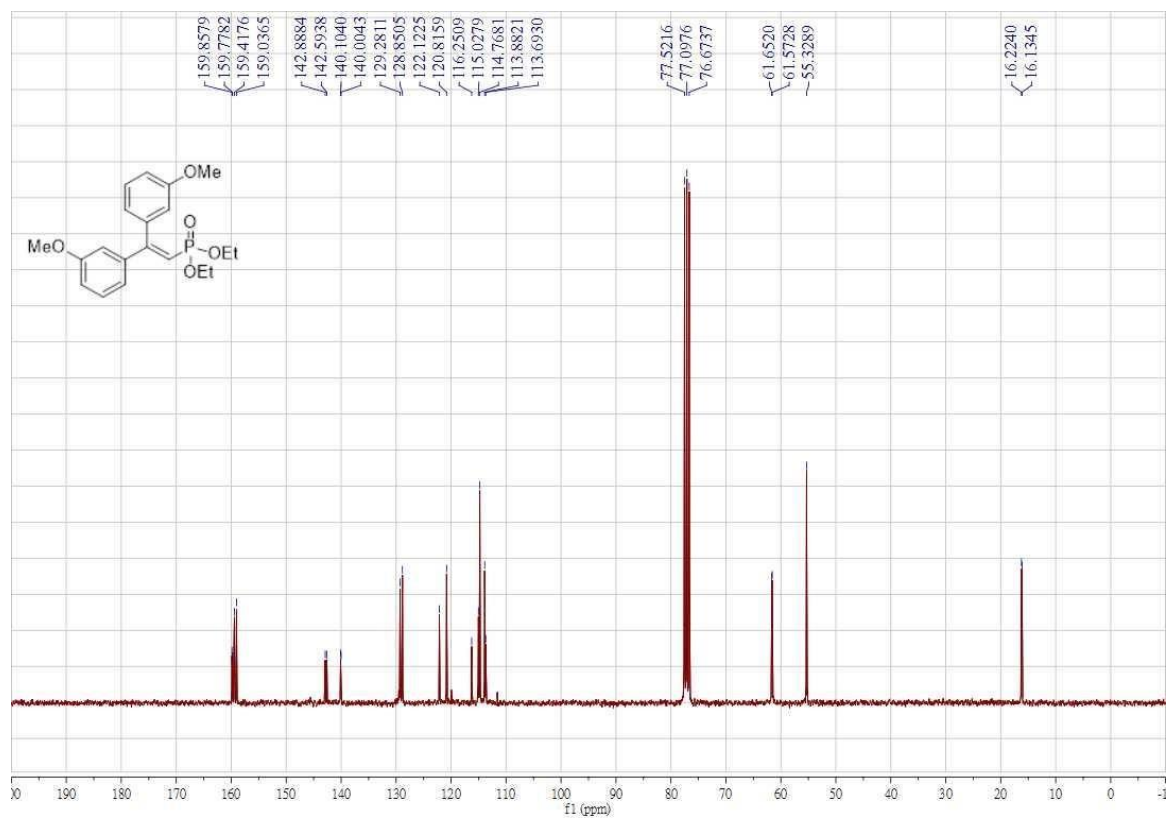
$^{31}\text{P}$  NMR spectrum of compound **6n**



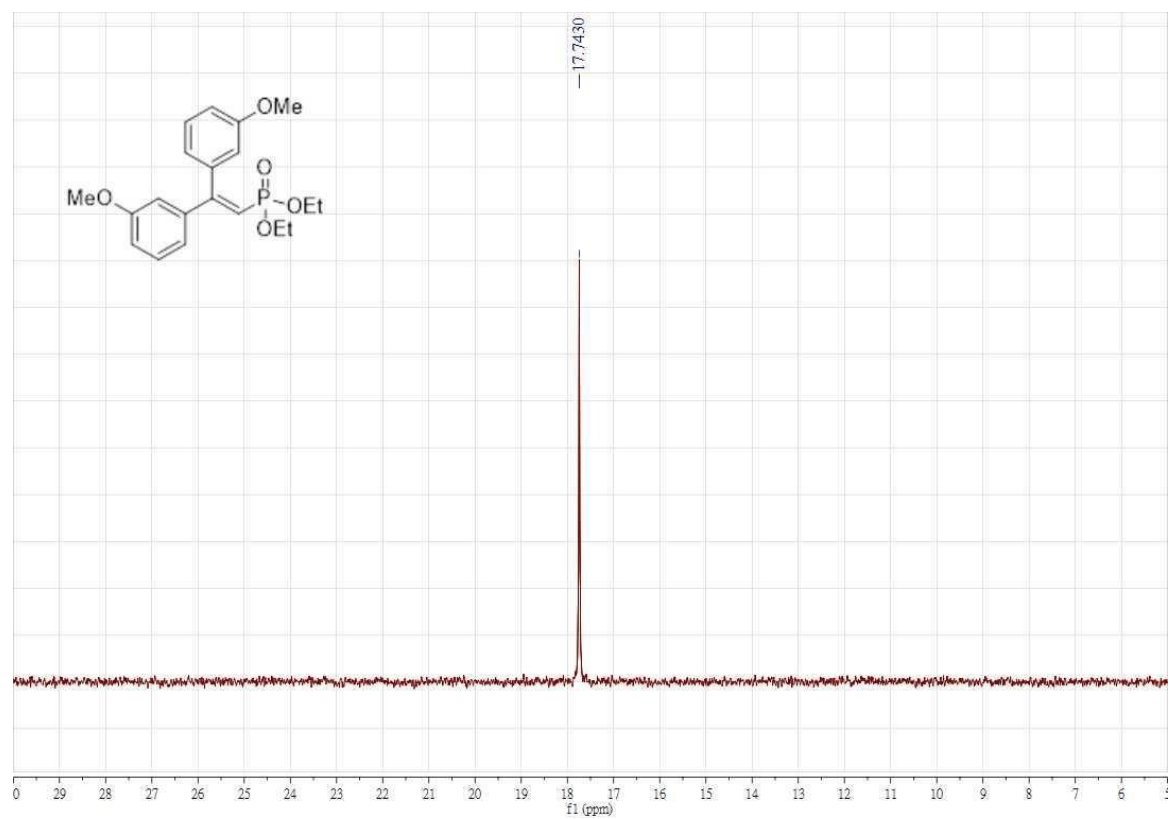
# <sup>1</sup>H NMR spectrum of compound 60



# <sup>13</sup>C NMR spectrum of compound 60

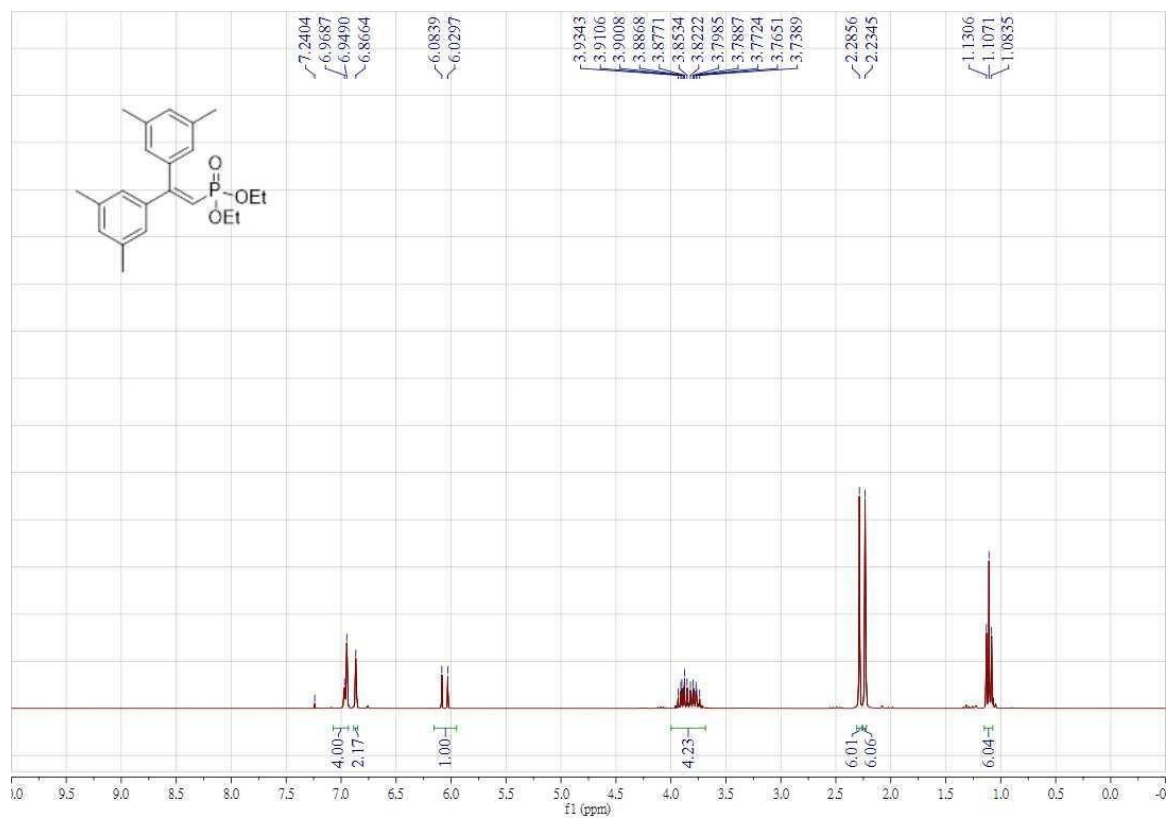


$^{31}\text{P}$  NMR spectrum of compound **60**

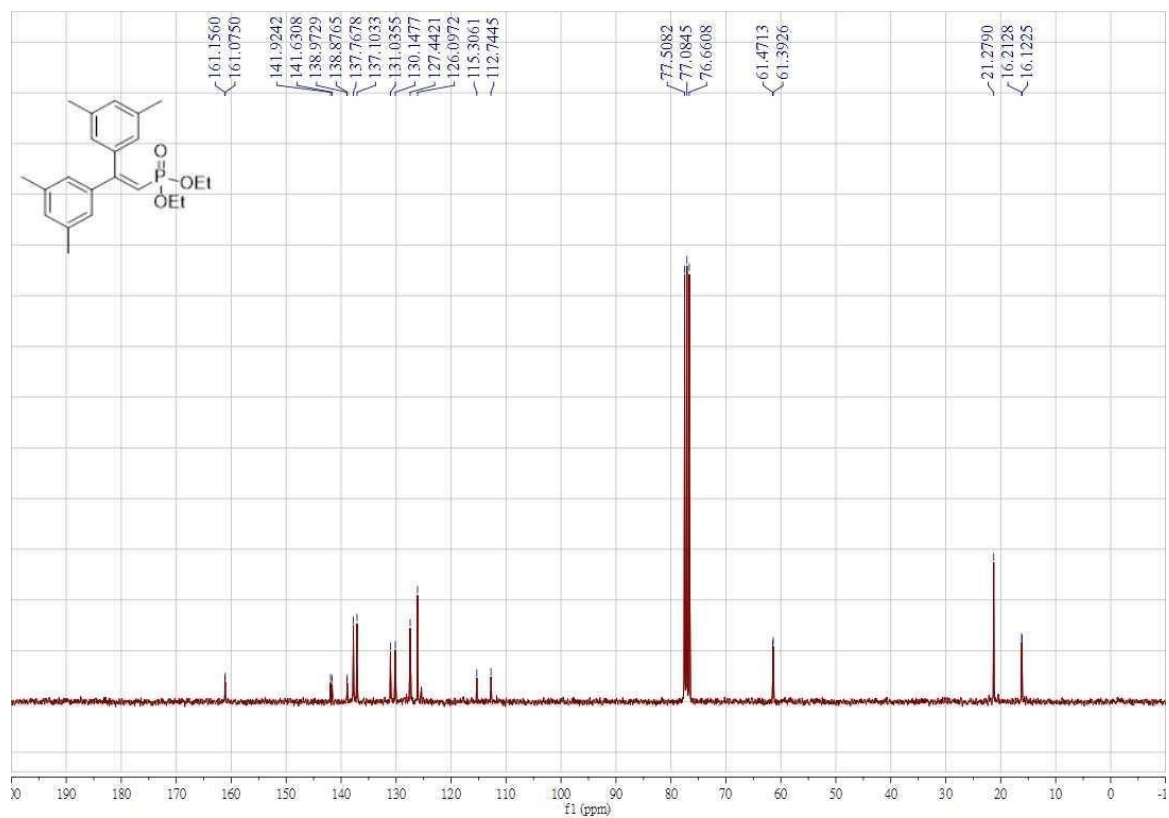




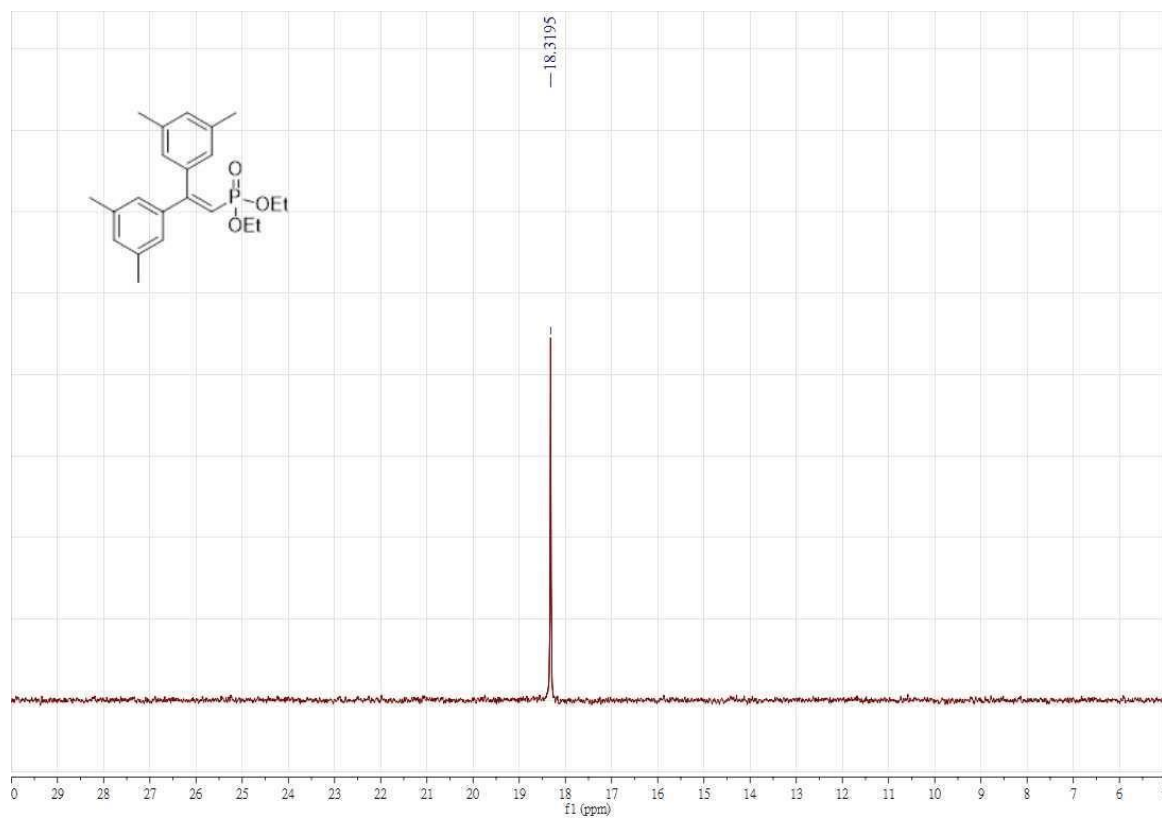
<sup>1</sup>H NMR spectrum of compound **6p**



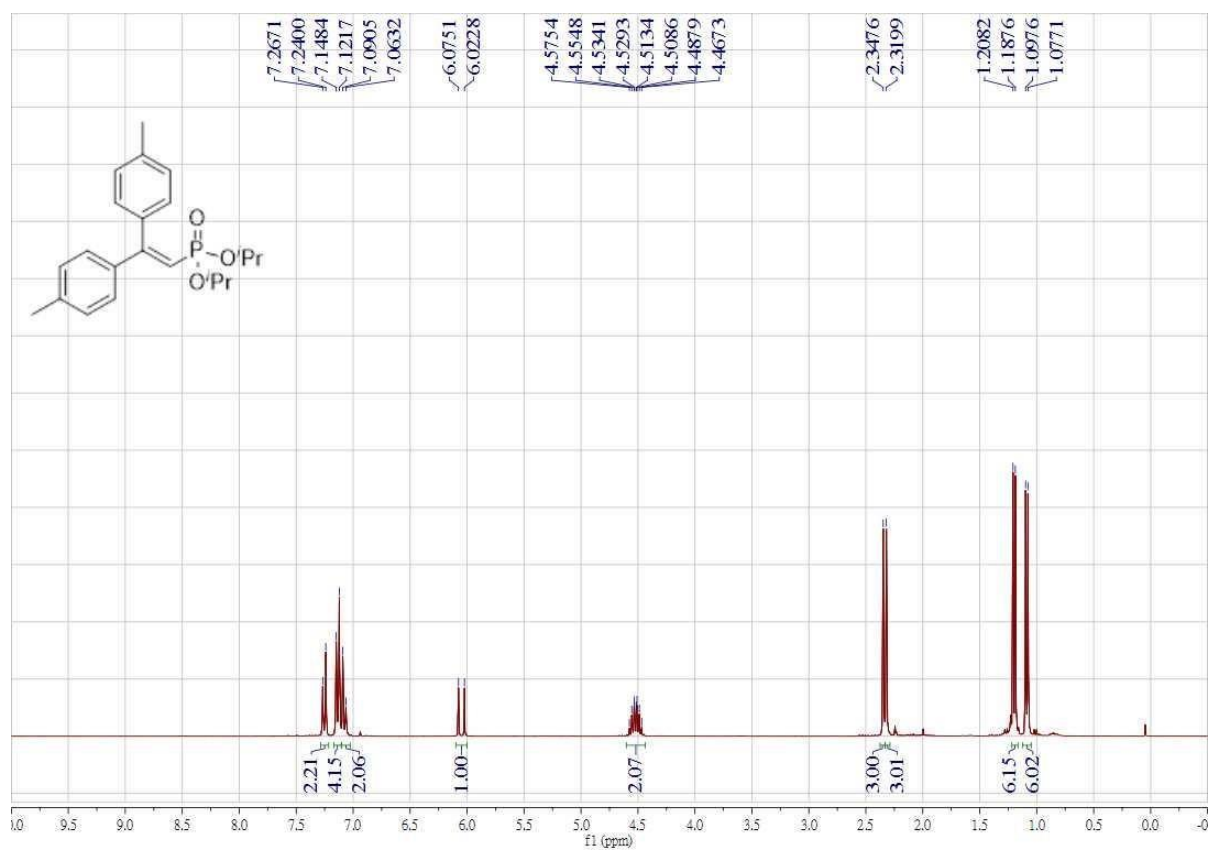
<sup>13</sup>C NMR spectrum of compound **6p**



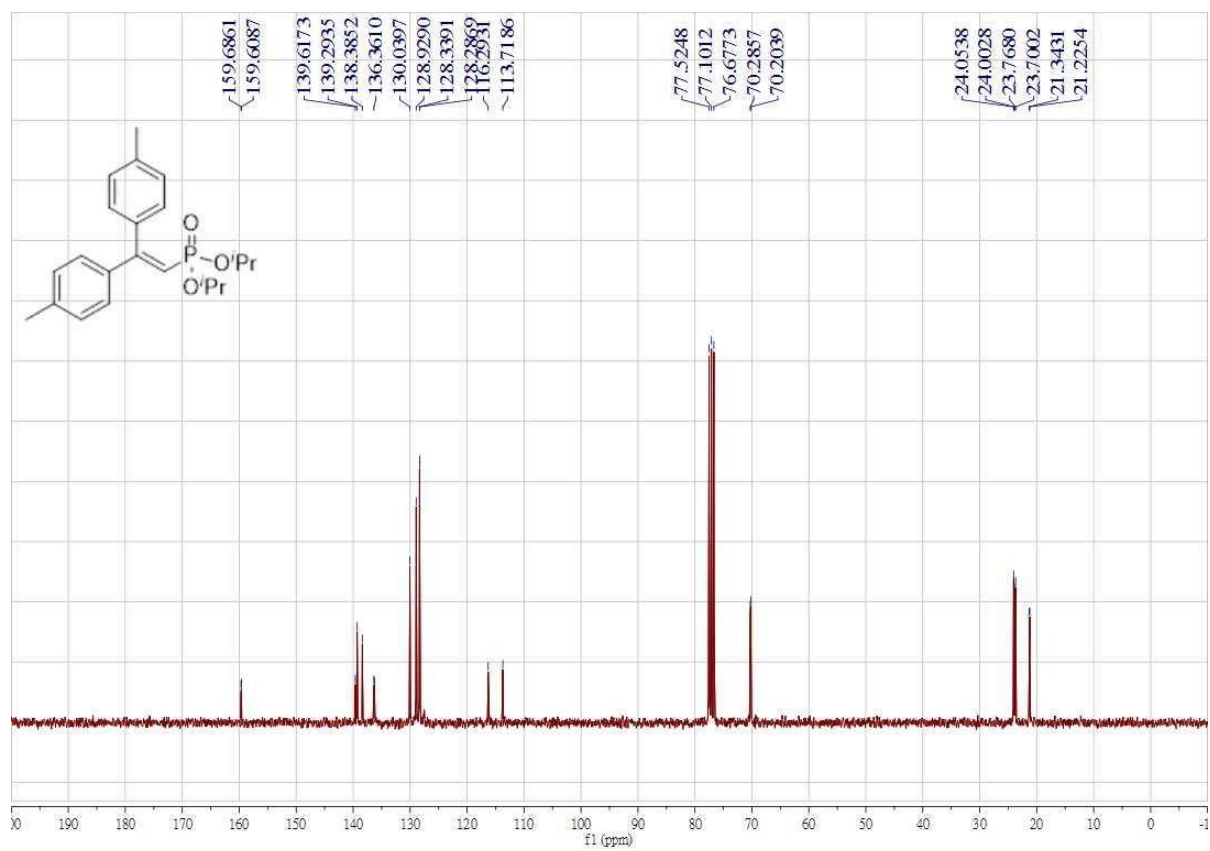
$^{31}\text{P}$  NMR spectrum of compound **6p**



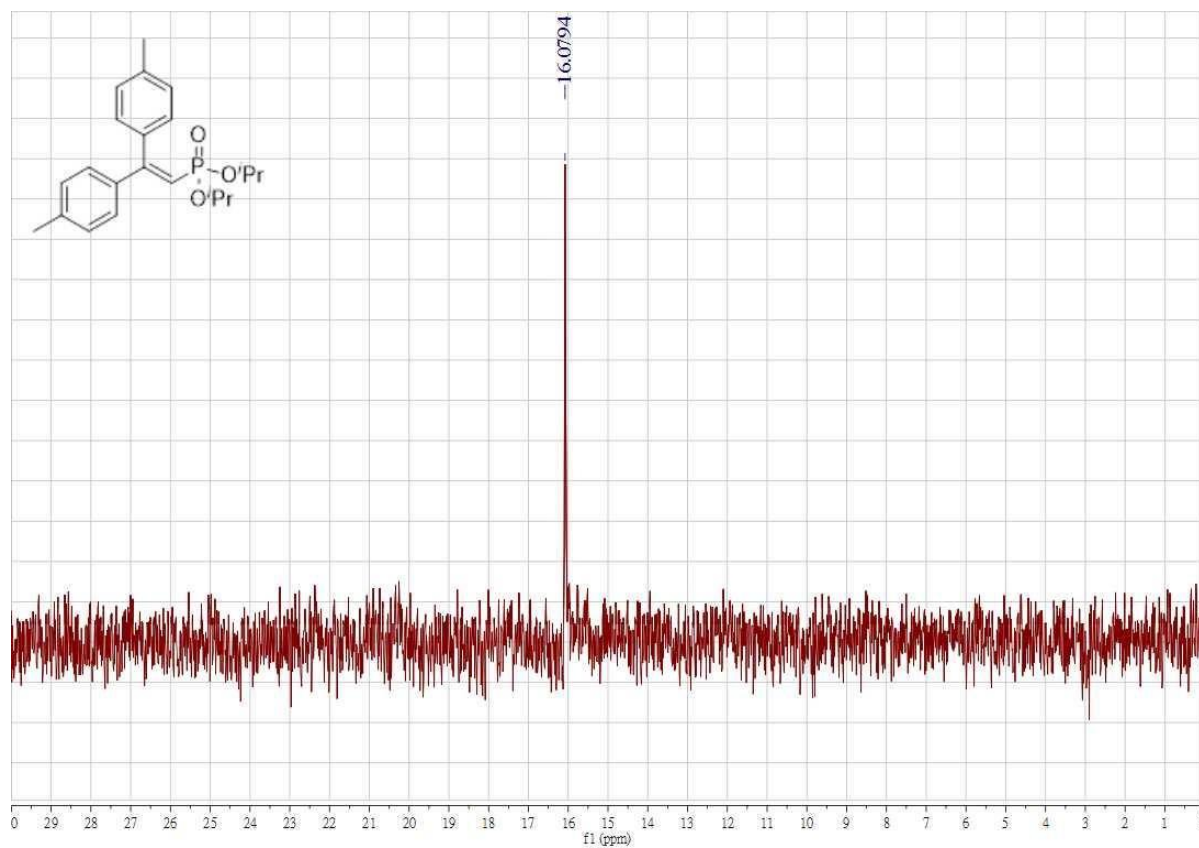
### <sup>1</sup>H NMR spectrum of compound **7b**



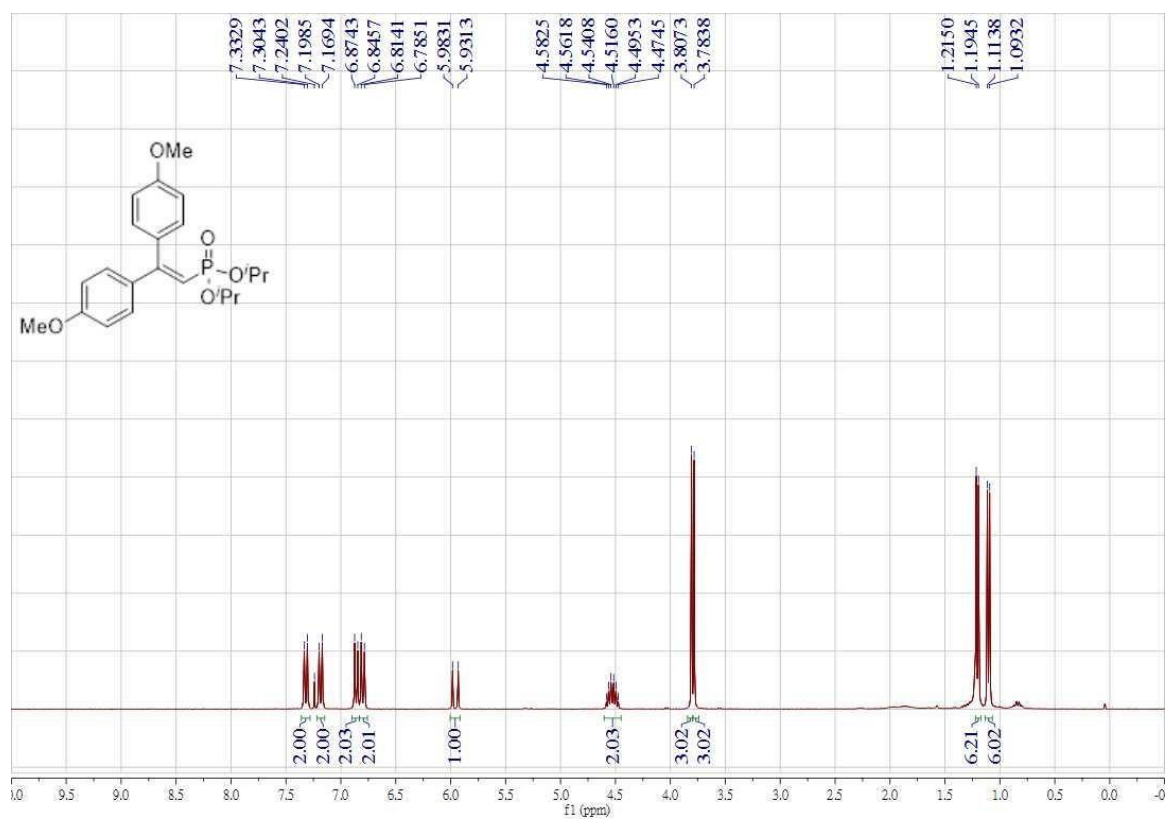
### <sup>13</sup>C NMR spectrum of compound **7b**



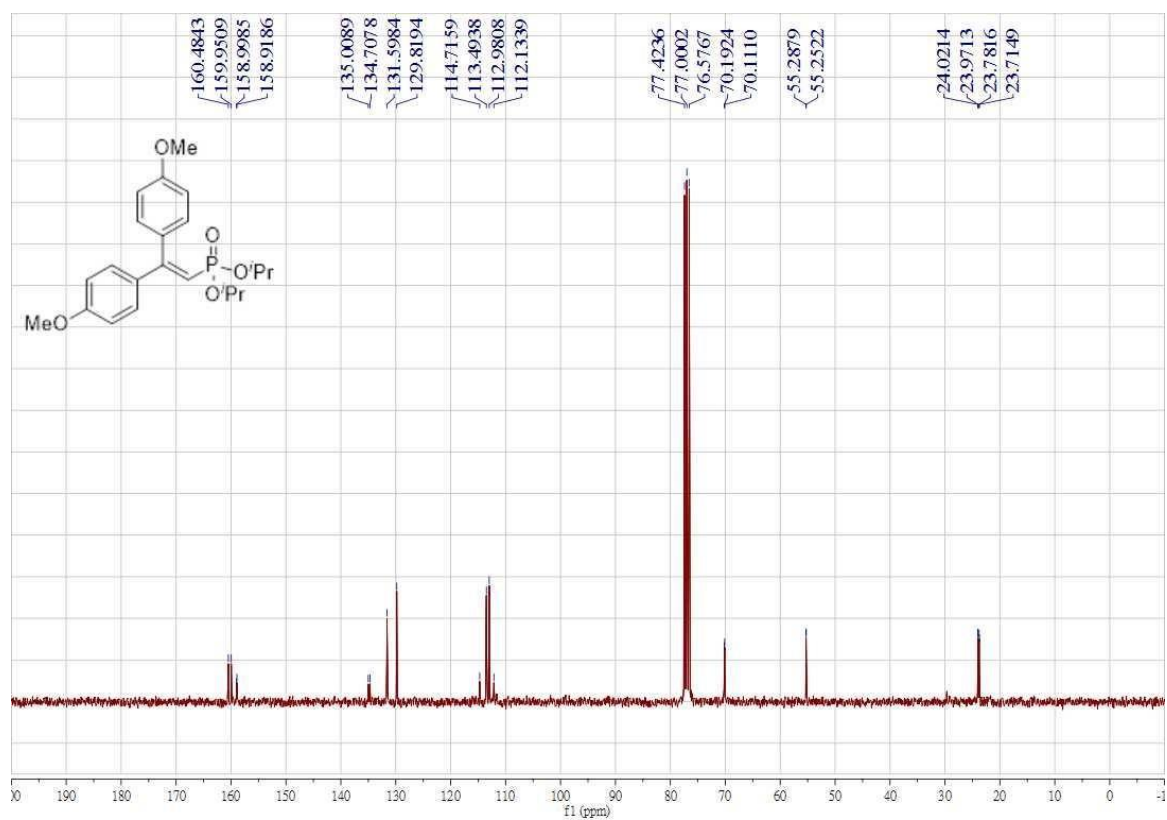
<sup>31</sup>P NMR spectrum of compound **7b**



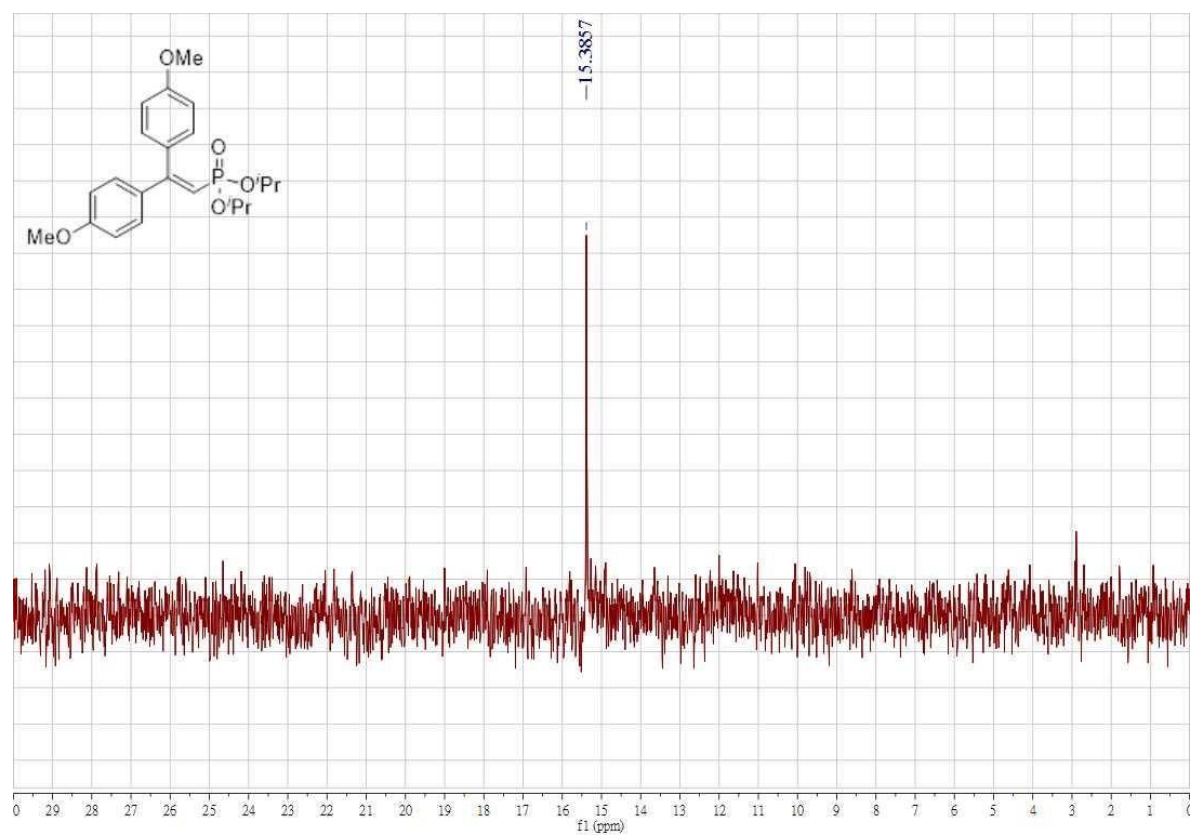
<sup>1</sup>H NMR spectrum of compound **7c**



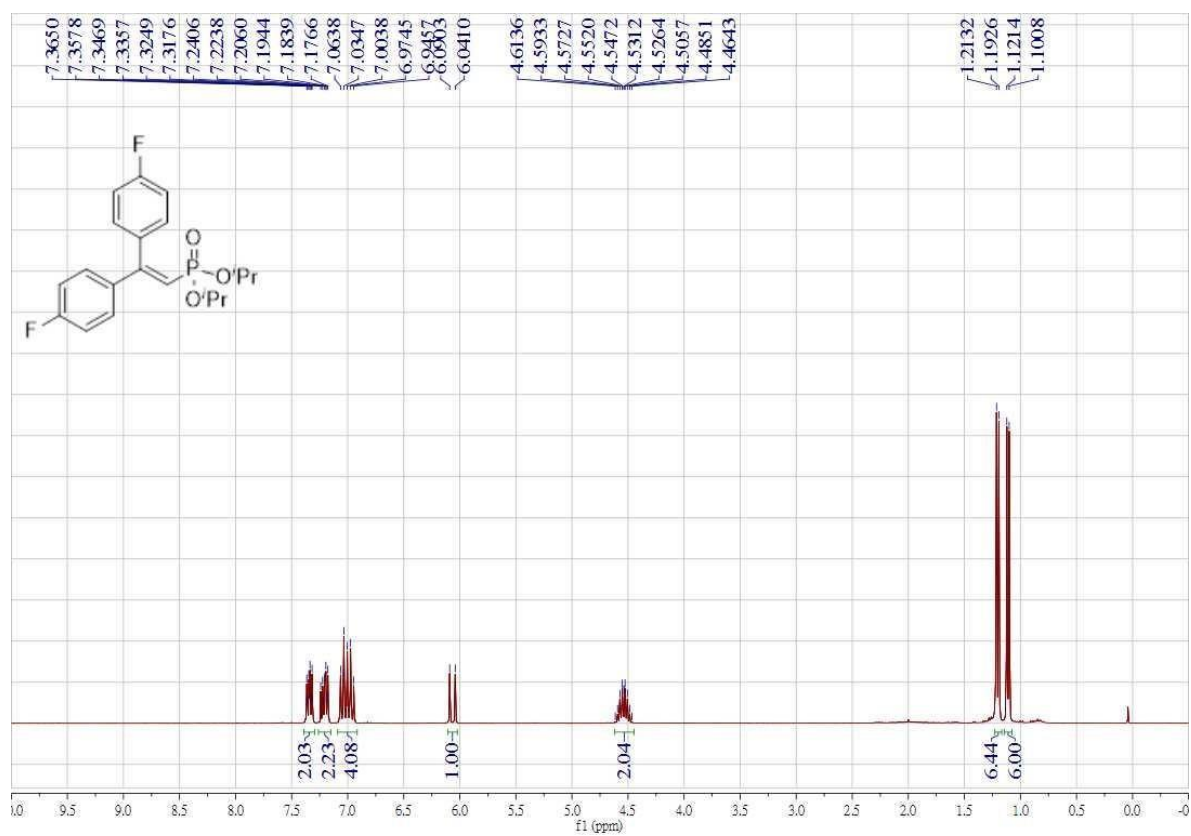
<sup>13</sup>C NMR spectrum of compound **7c**



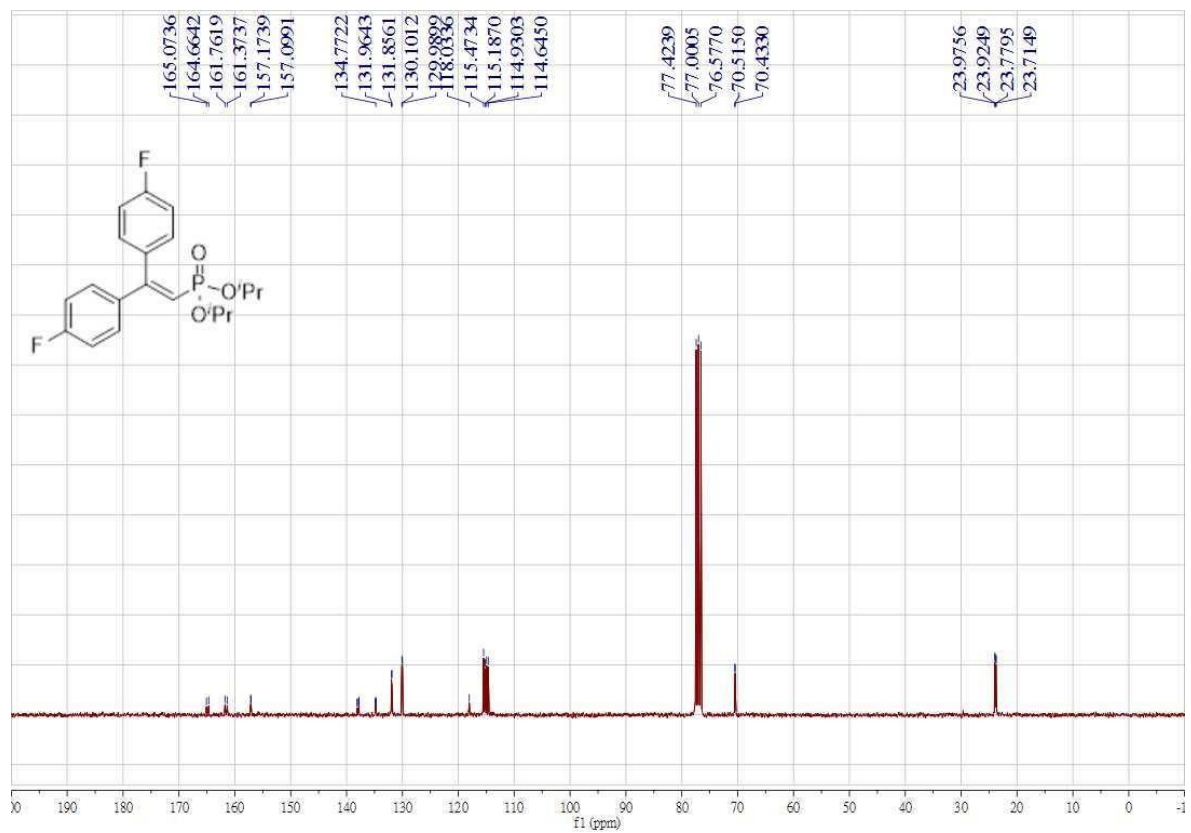
$^{31}\text{P}$  NMR spectrum of compound **7c**



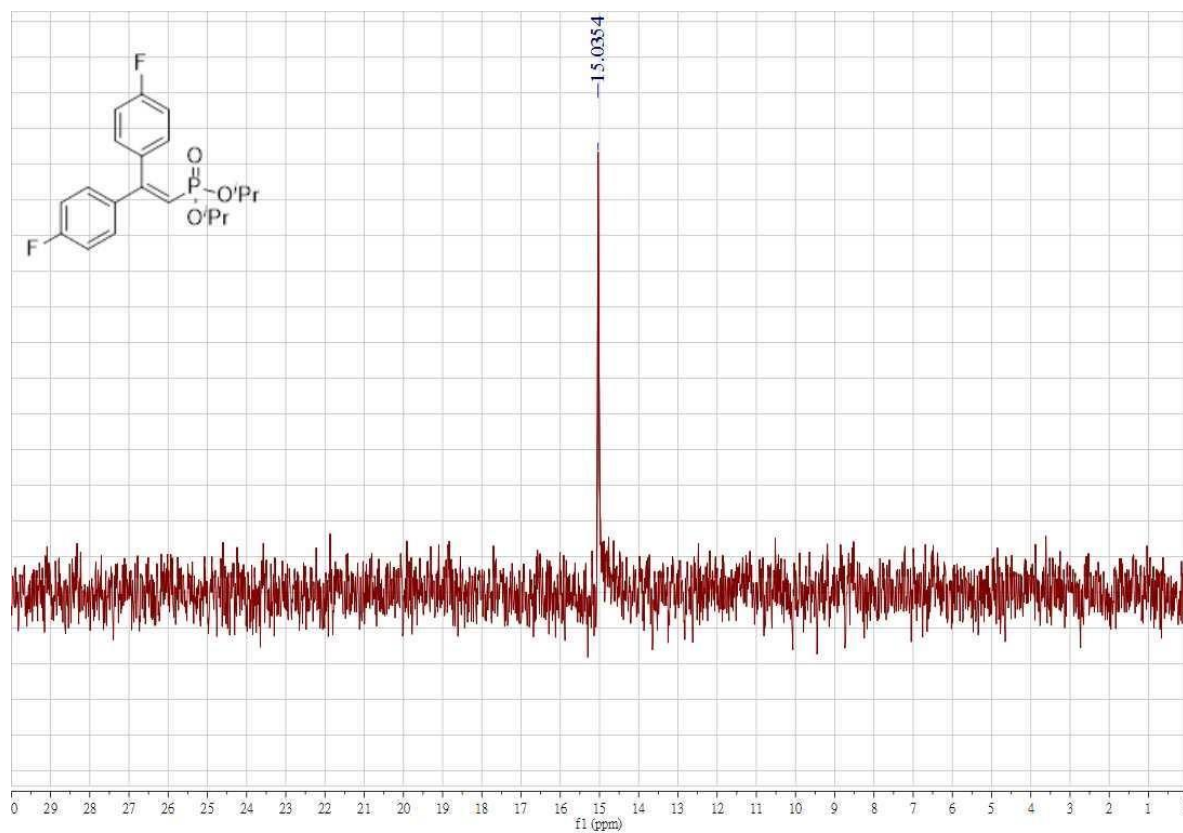
<sup>1</sup>H NMR spectrum of compound **7d**



<sup>13</sup>C NMR spectrum of compound **7d**

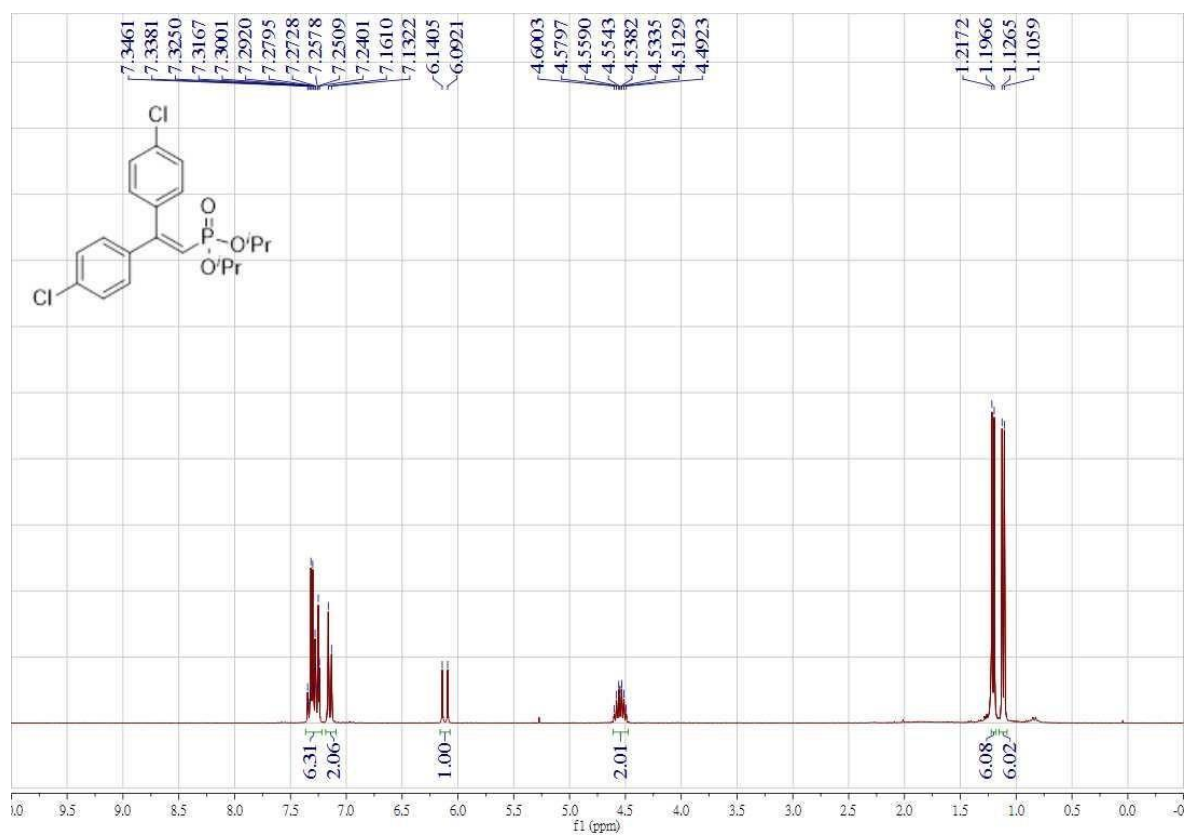


$^{31}\text{P}$  NMR spectrum of compound **7d**

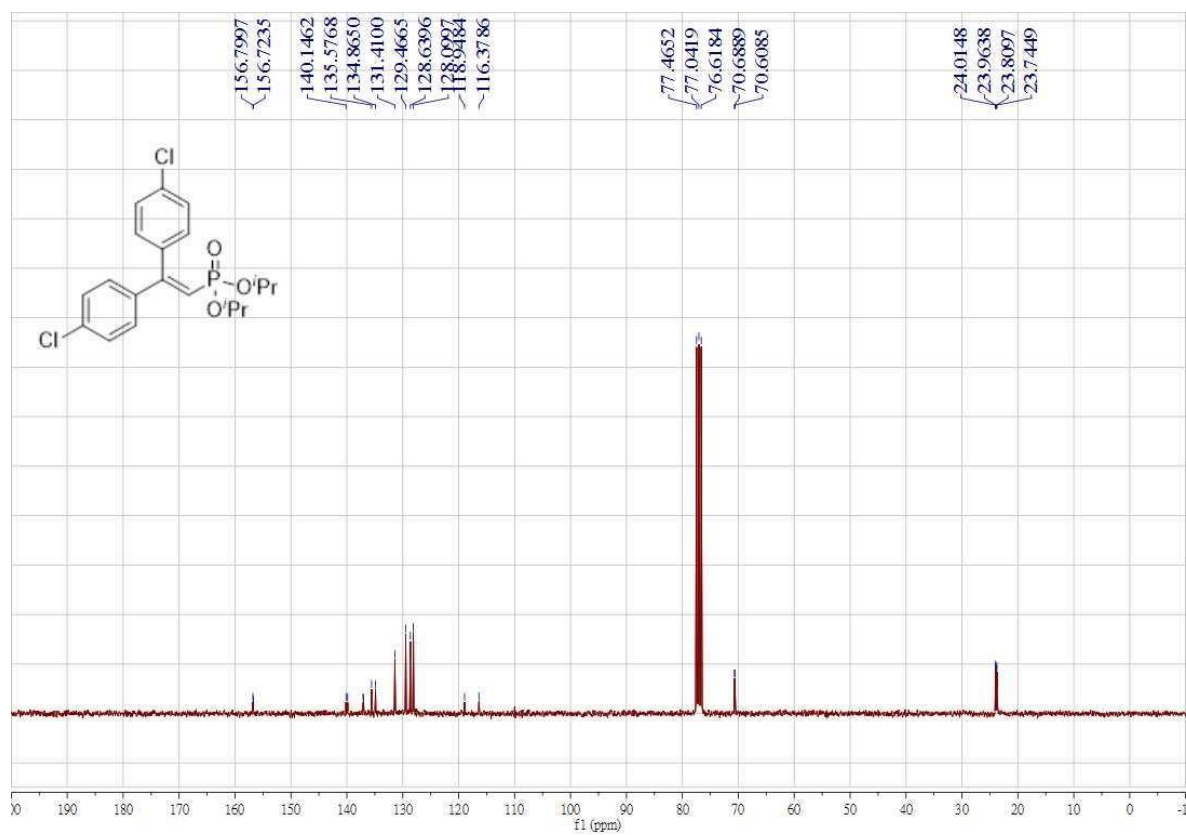




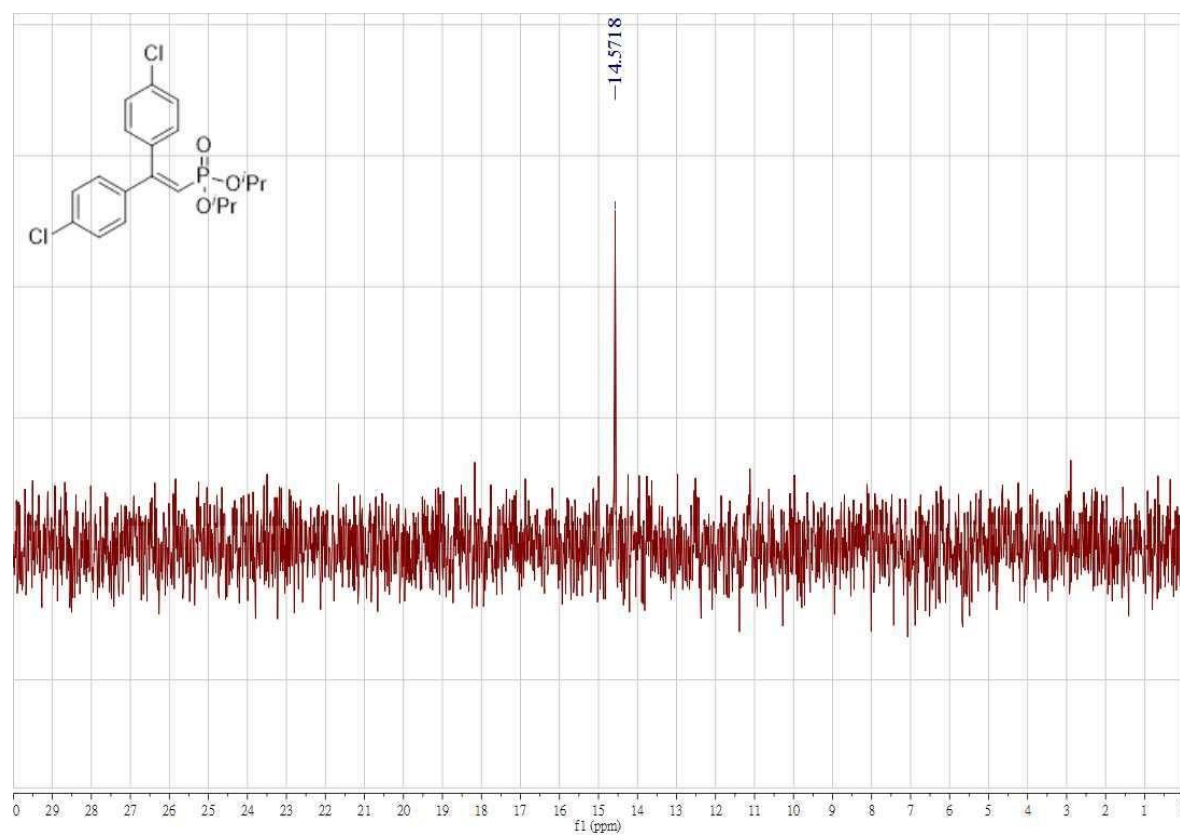
<sup>1</sup>H NMR spectrum of compound **7e**



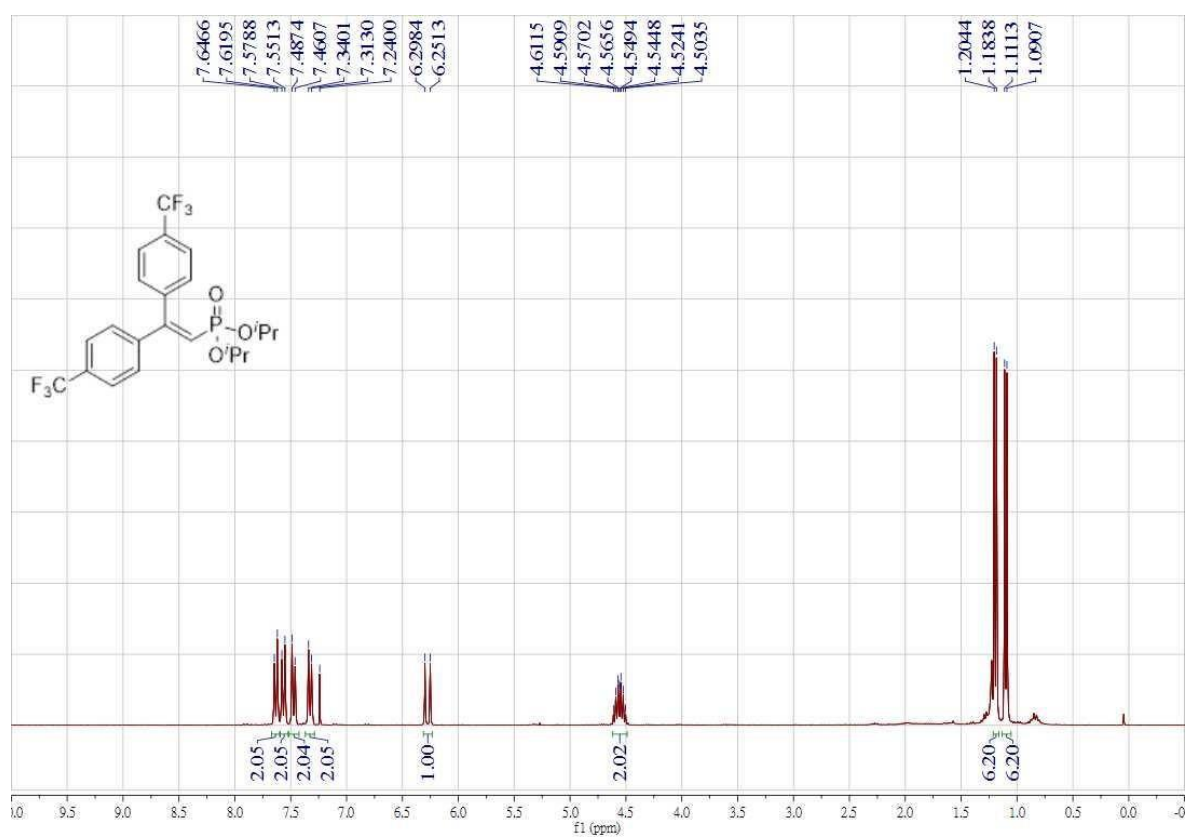
<sup>13</sup>C NMR spectrum of compound **7e**



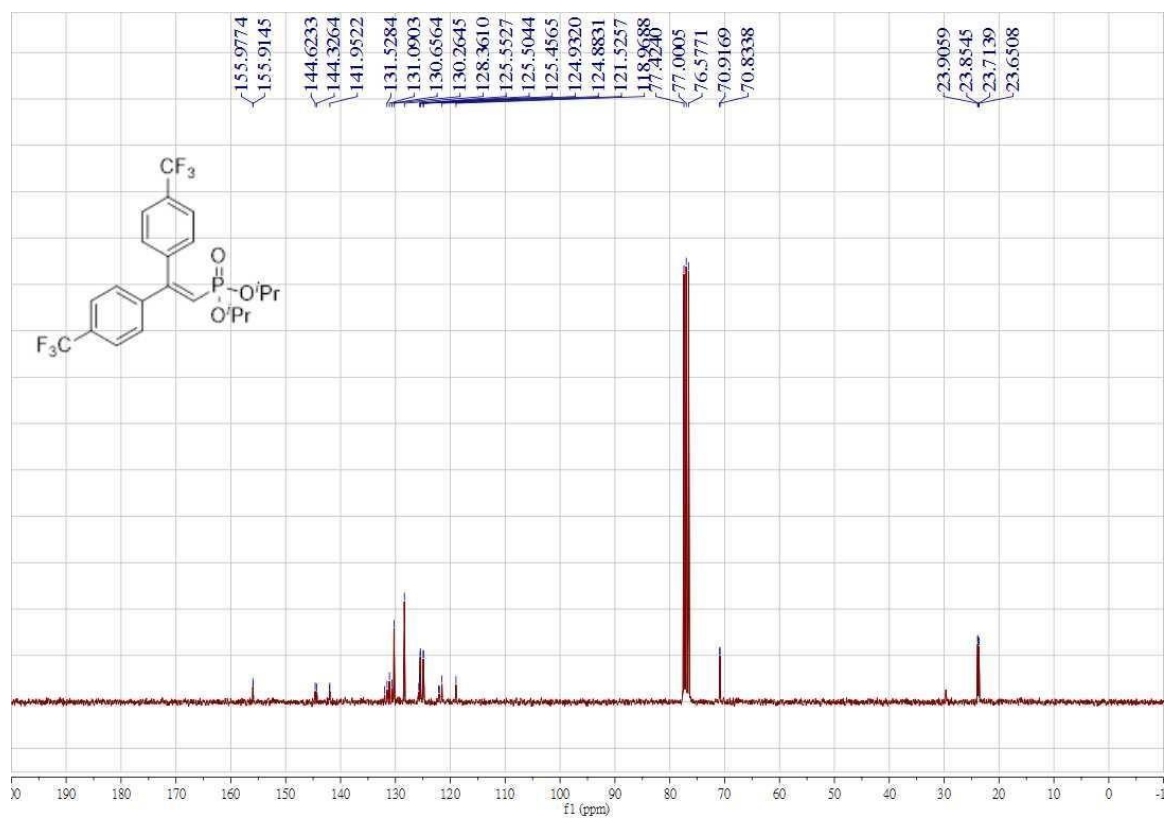
$^{31}\text{P}$  NMR spectrum of compound **7e**



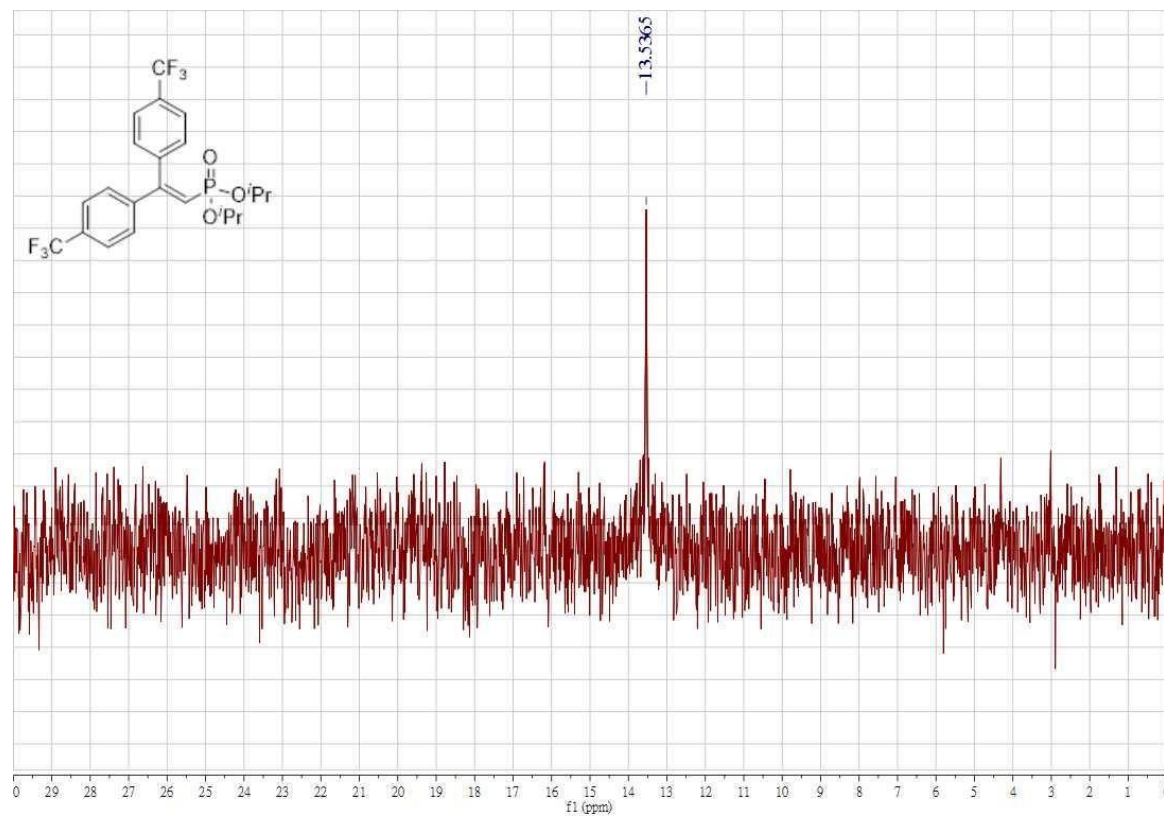
<sup>1</sup>H NMR spectrum of compound **7g**



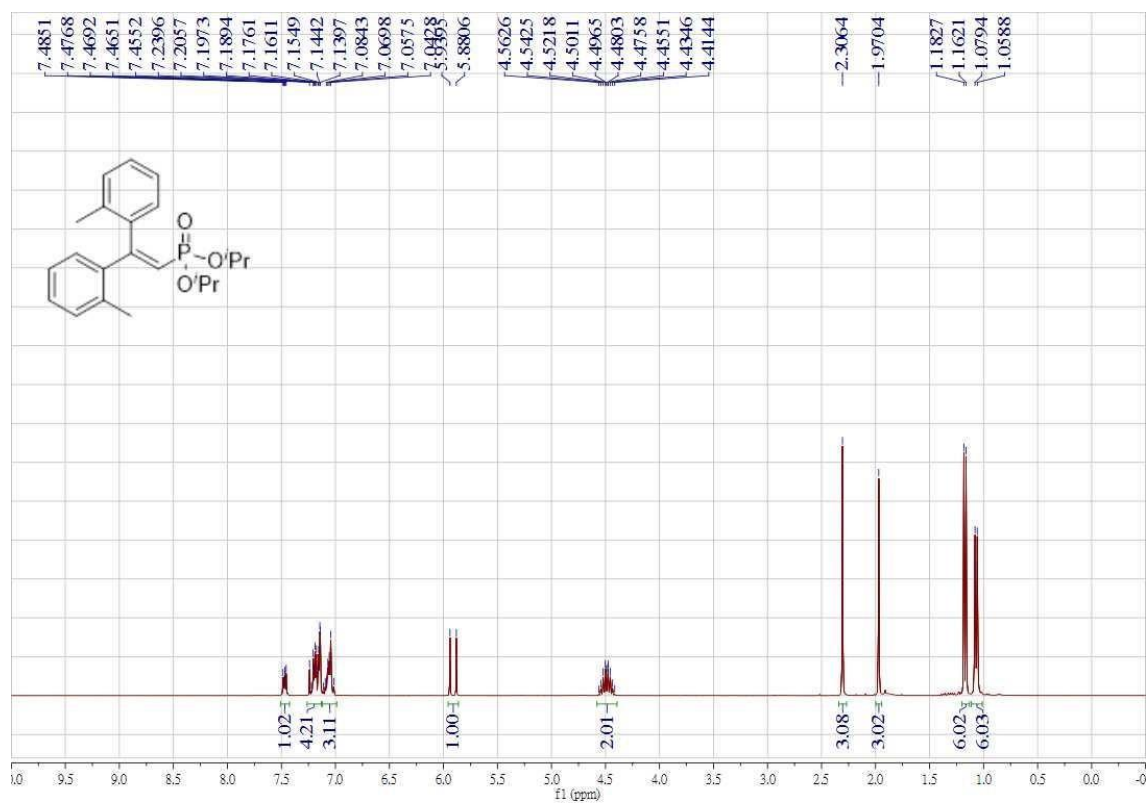
<sup>13</sup>C NMR spectrum of compound **7g**



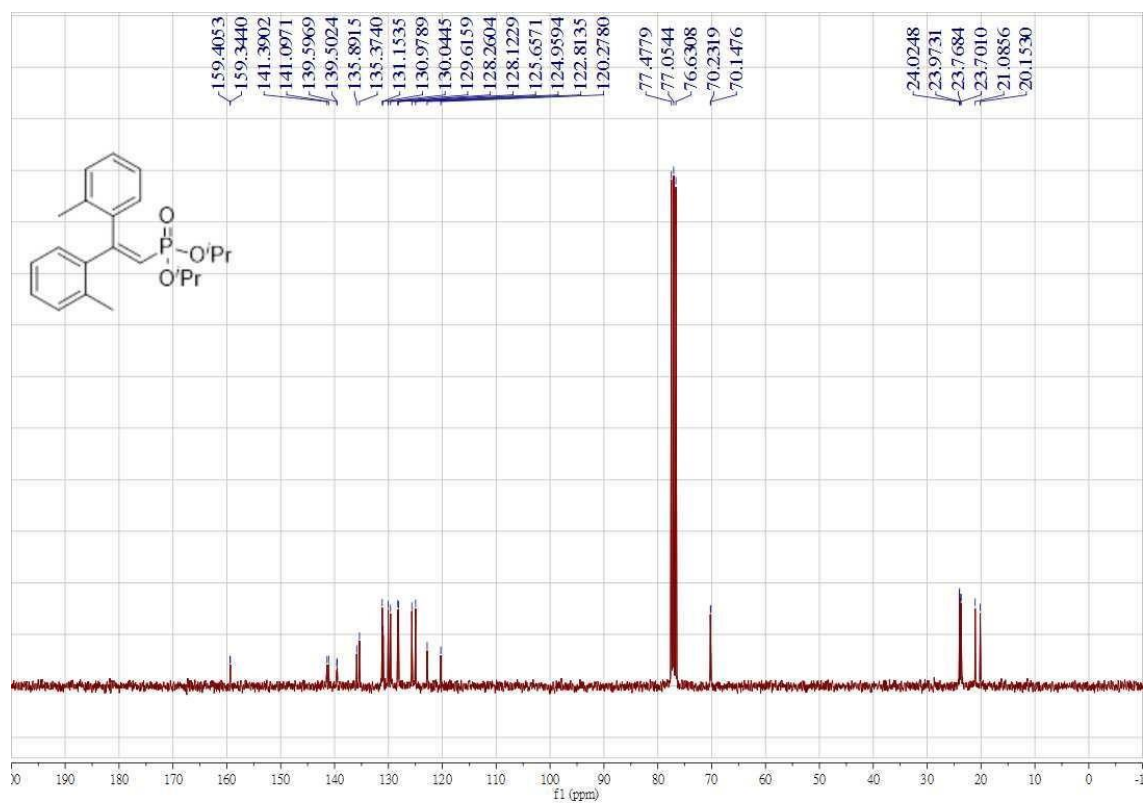
$^{31}\text{P}$  NMR spectrum of compound **7g**



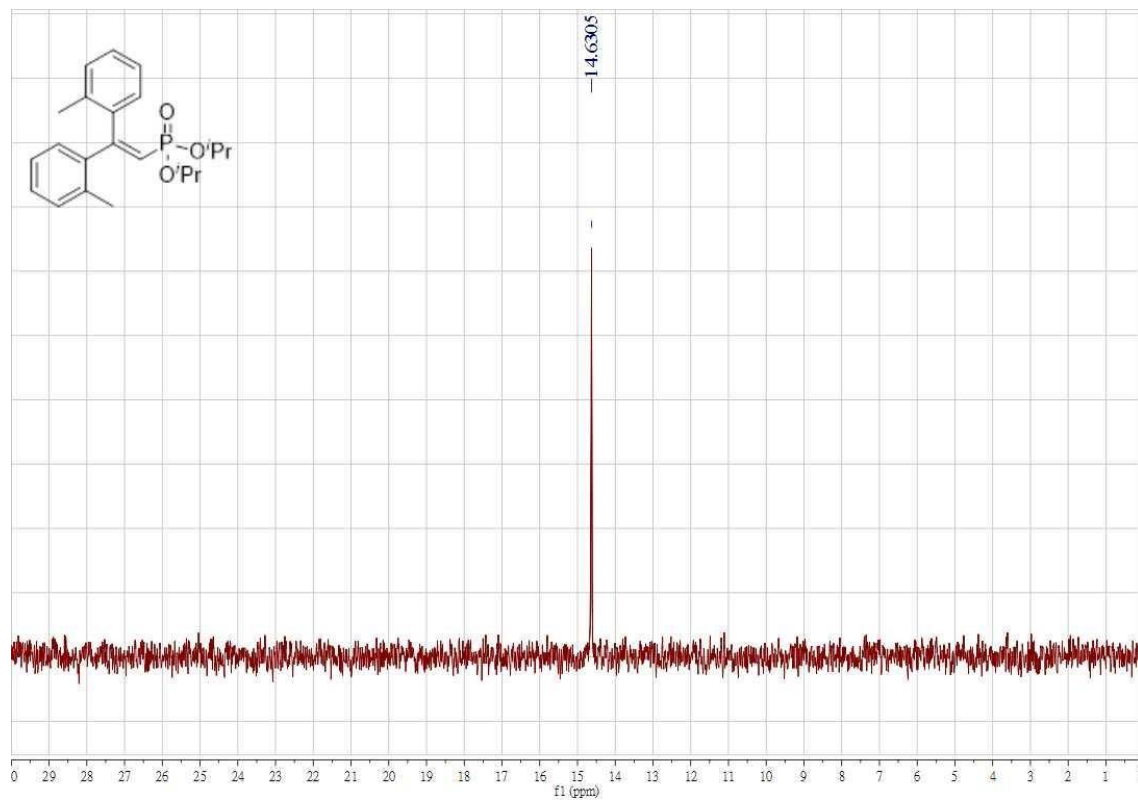
<sup>1</sup>H NMR spectrum of compound **7k**



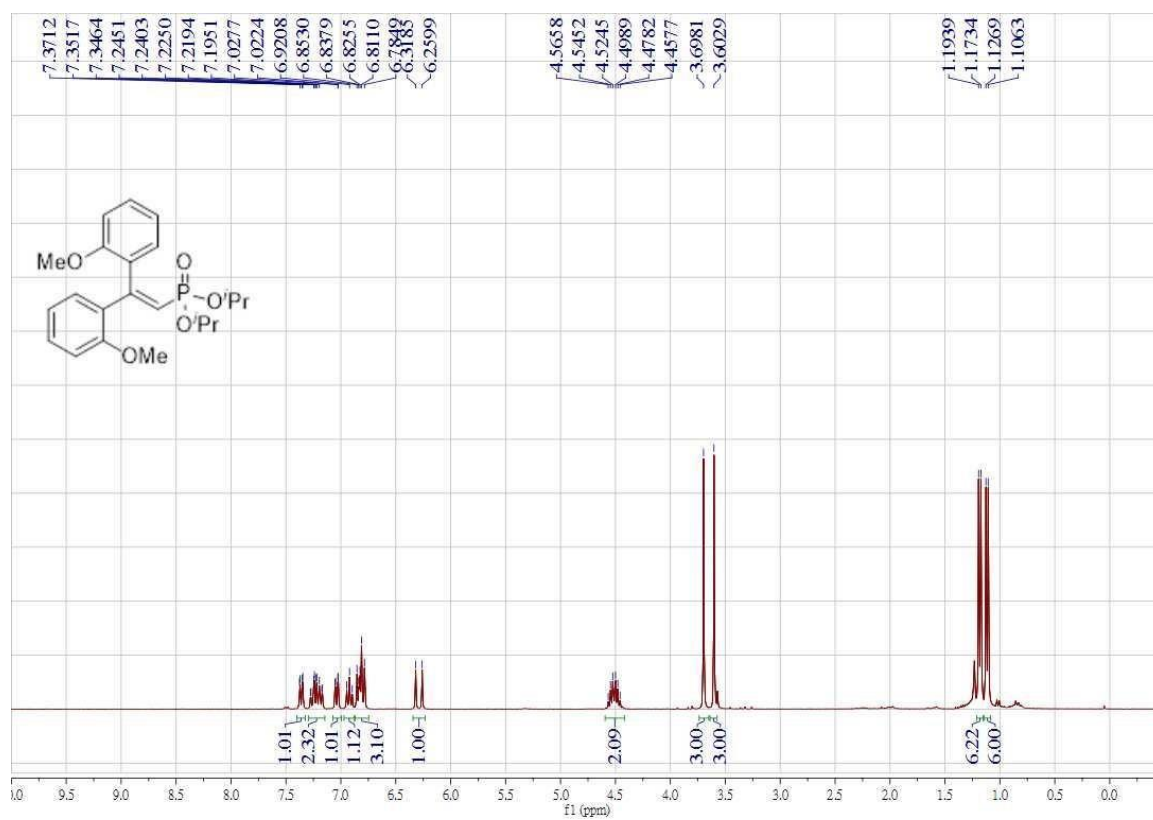
<sup>13</sup>C NMR spectrum of compound **7k**



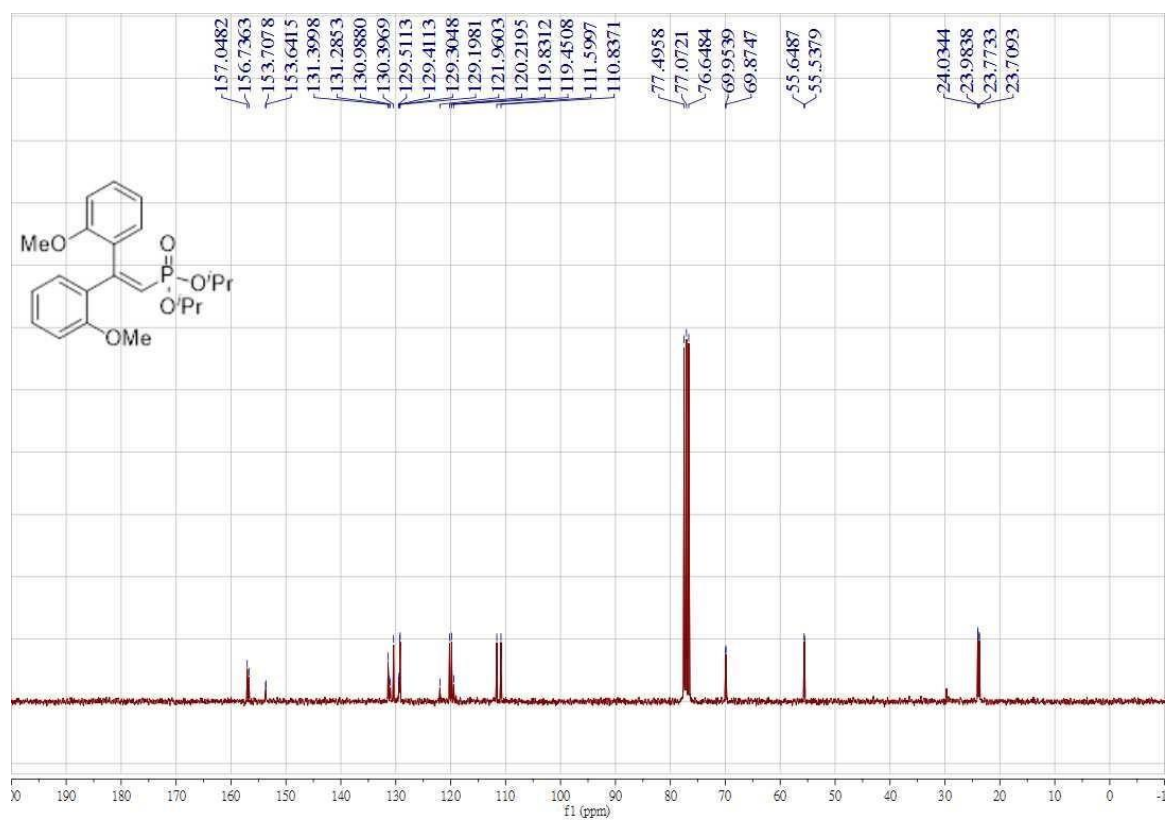
$^{31}\text{P}$  NMR spectrum of compound **7k**



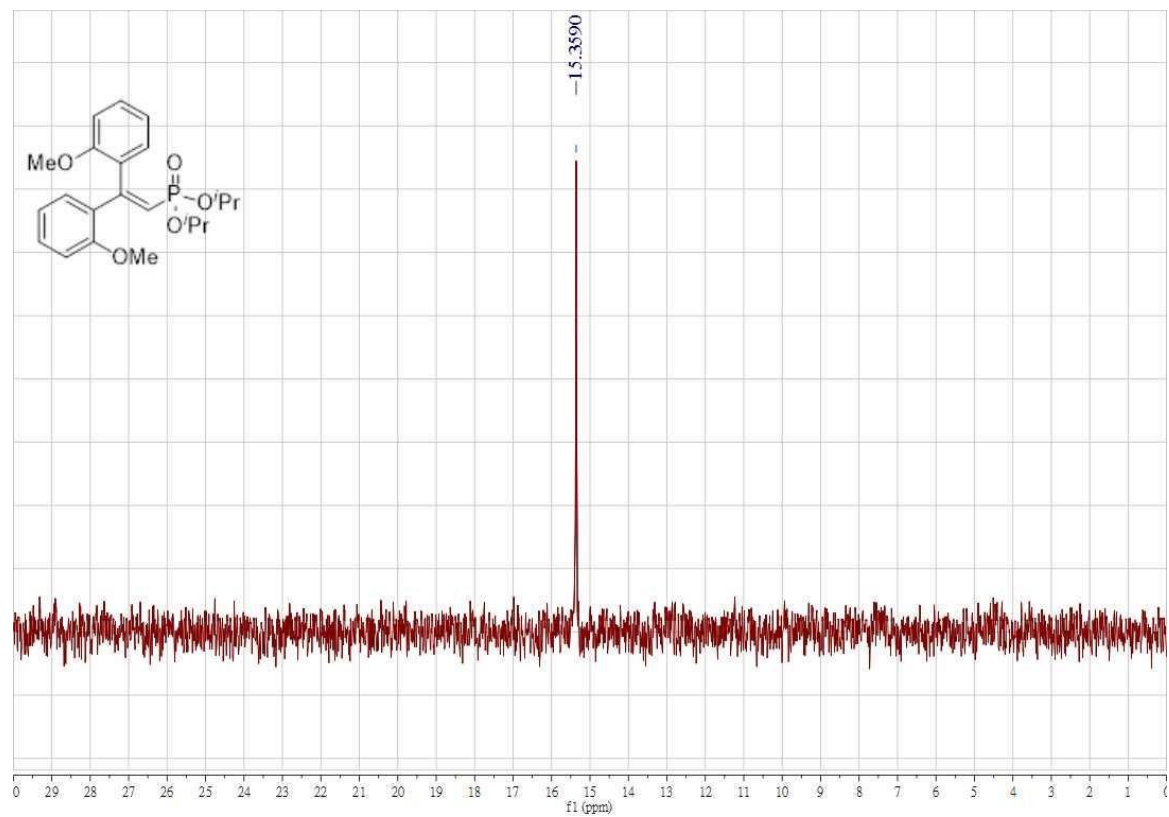
<sup>1</sup>H NMR spectrum of compound **71**



<sup>13</sup>C NMR spectrum of compound **71**

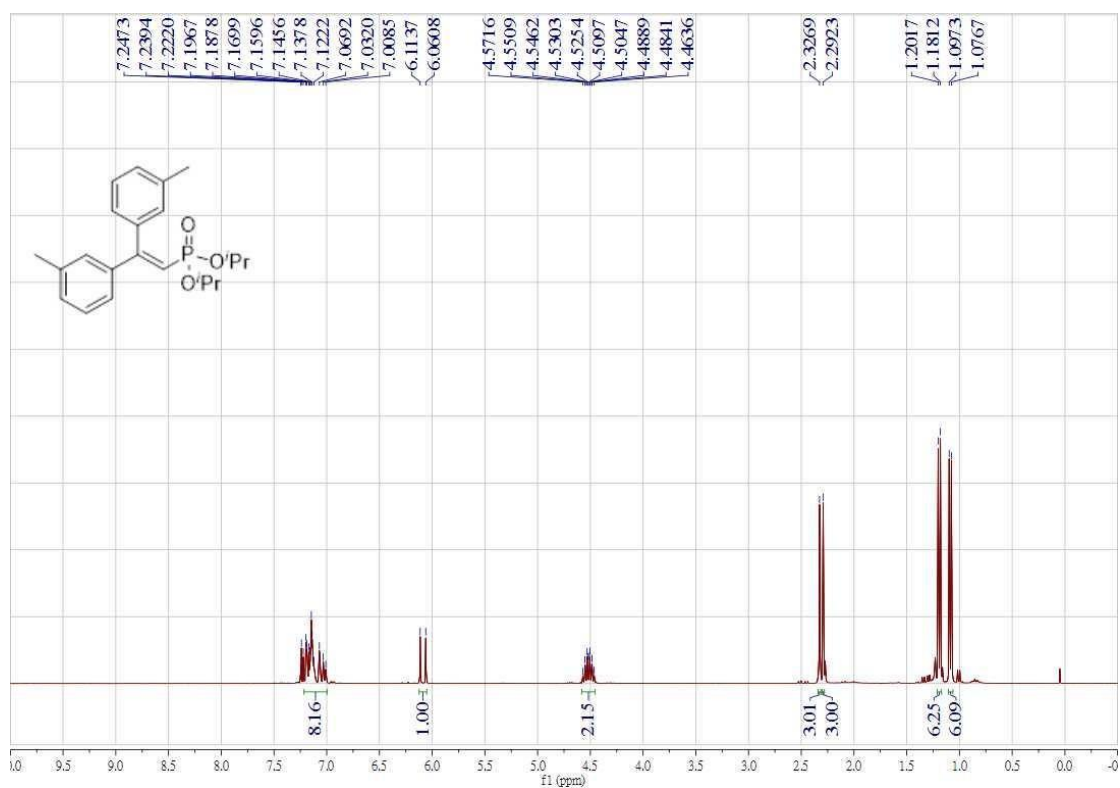


$^{31}\text{P}$  NMR spectrum of compound **7I**

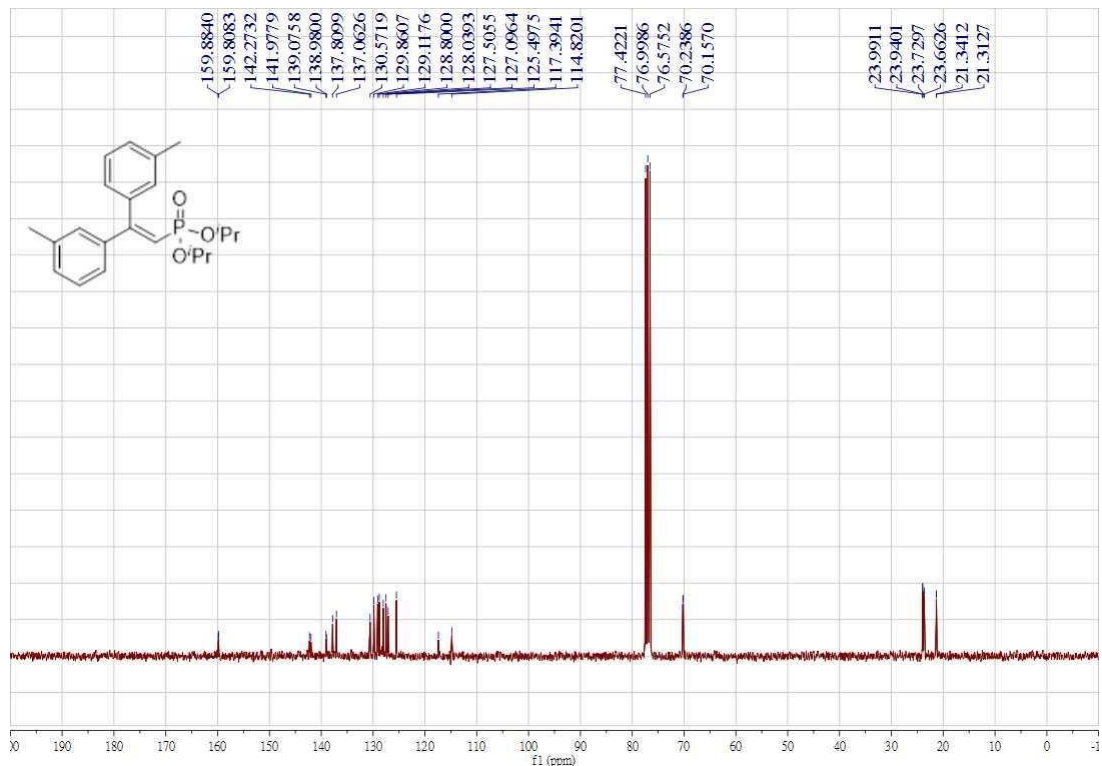




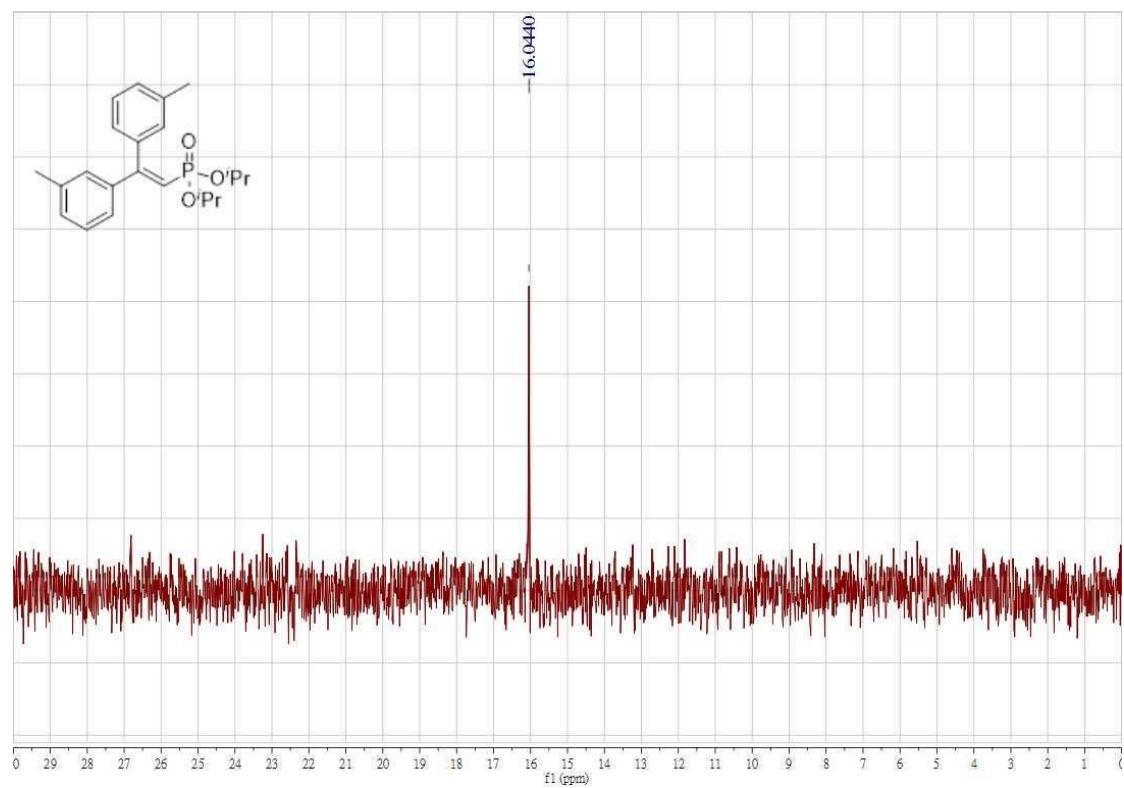
<sup>1</sup>H NMR spectrum of compound **7n**



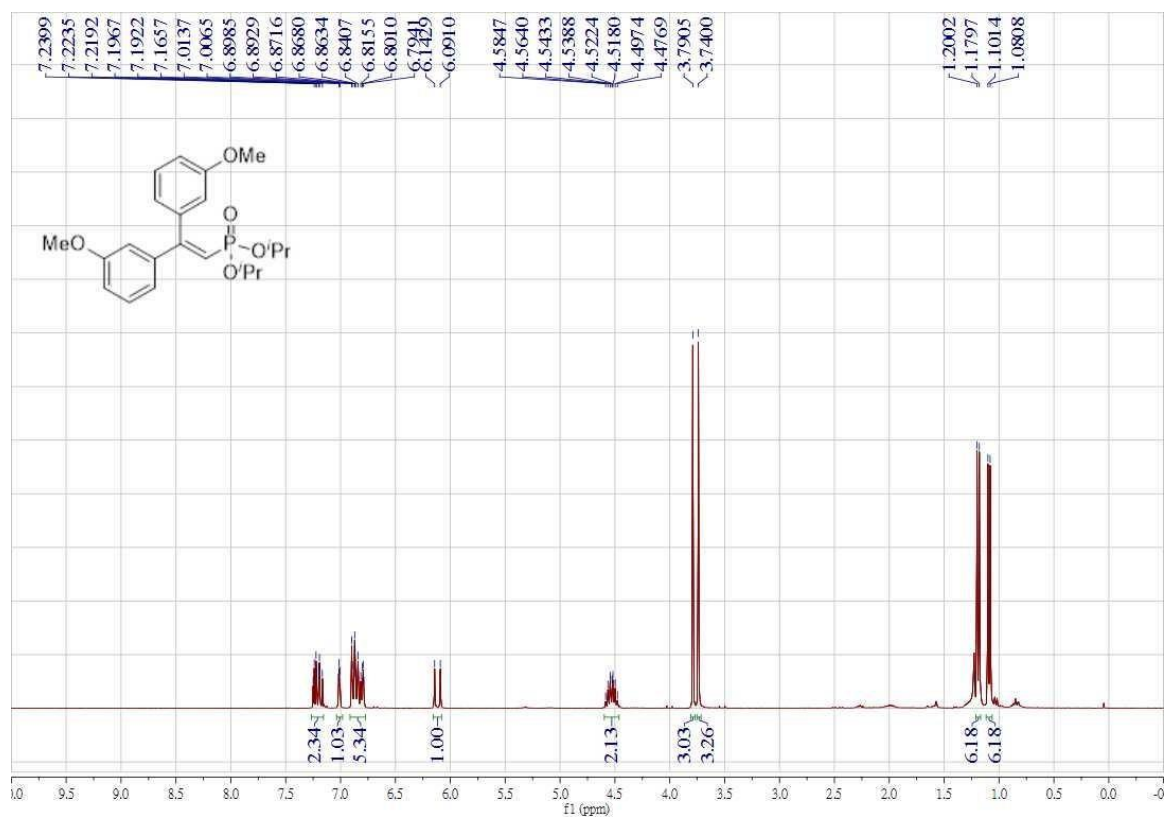
<sup>13</sup>C NMR spectrum of compound **7n**



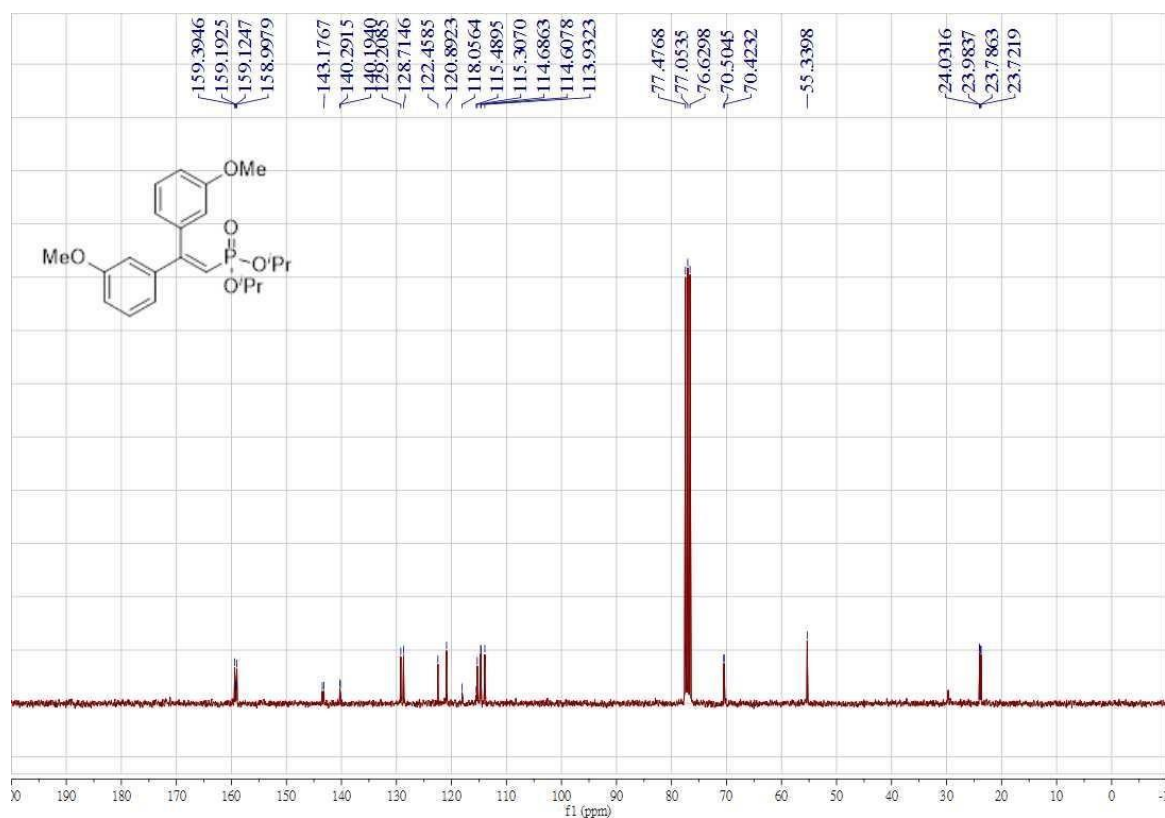
$^{31}\text{P}$  NMR spectrum of compound **7n**



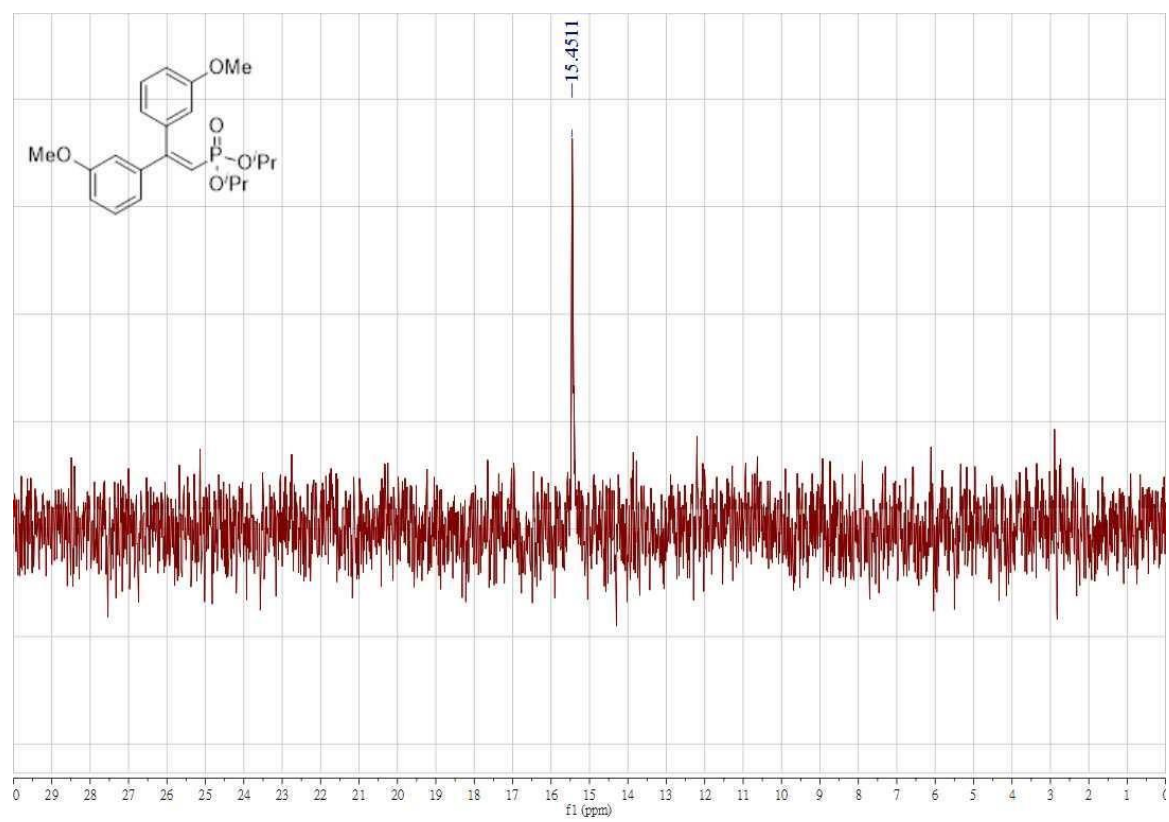
<sup>1</sup>H NMR spectrum of compound **7o**



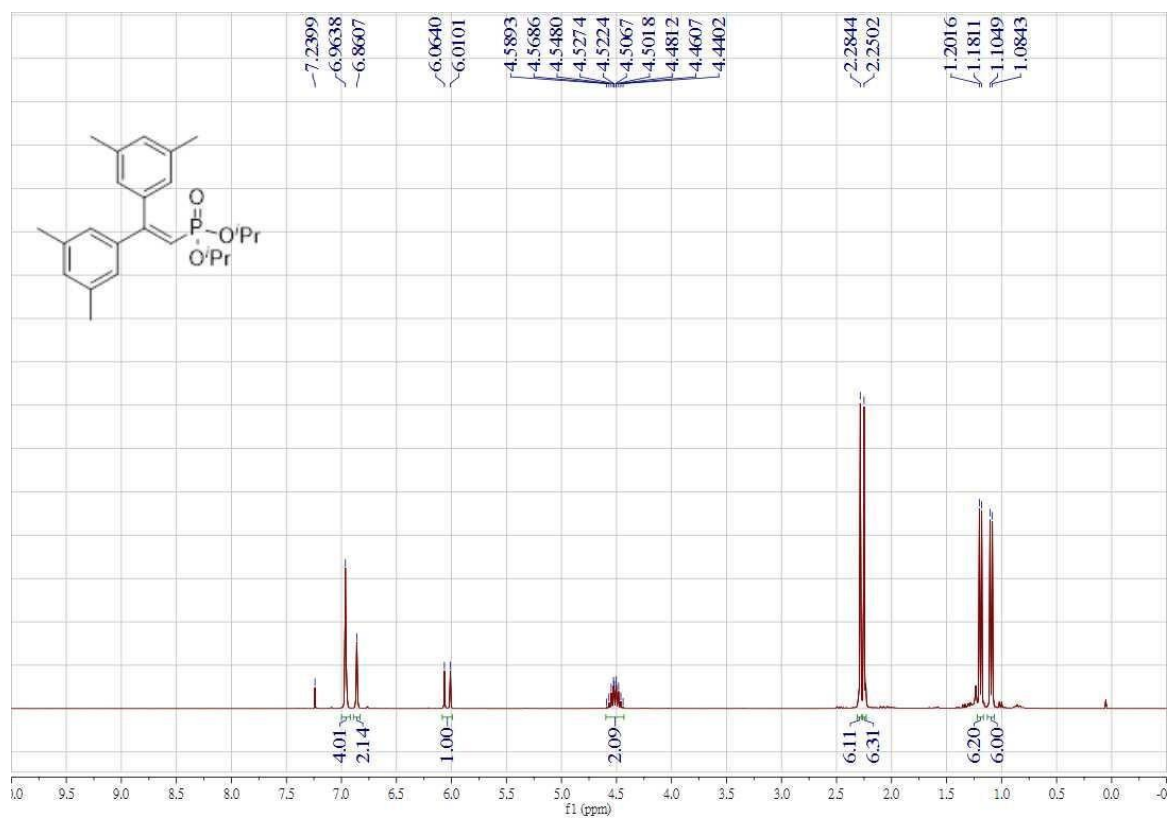
<sup>13</sup>C NMR spectrum of compound **7o**



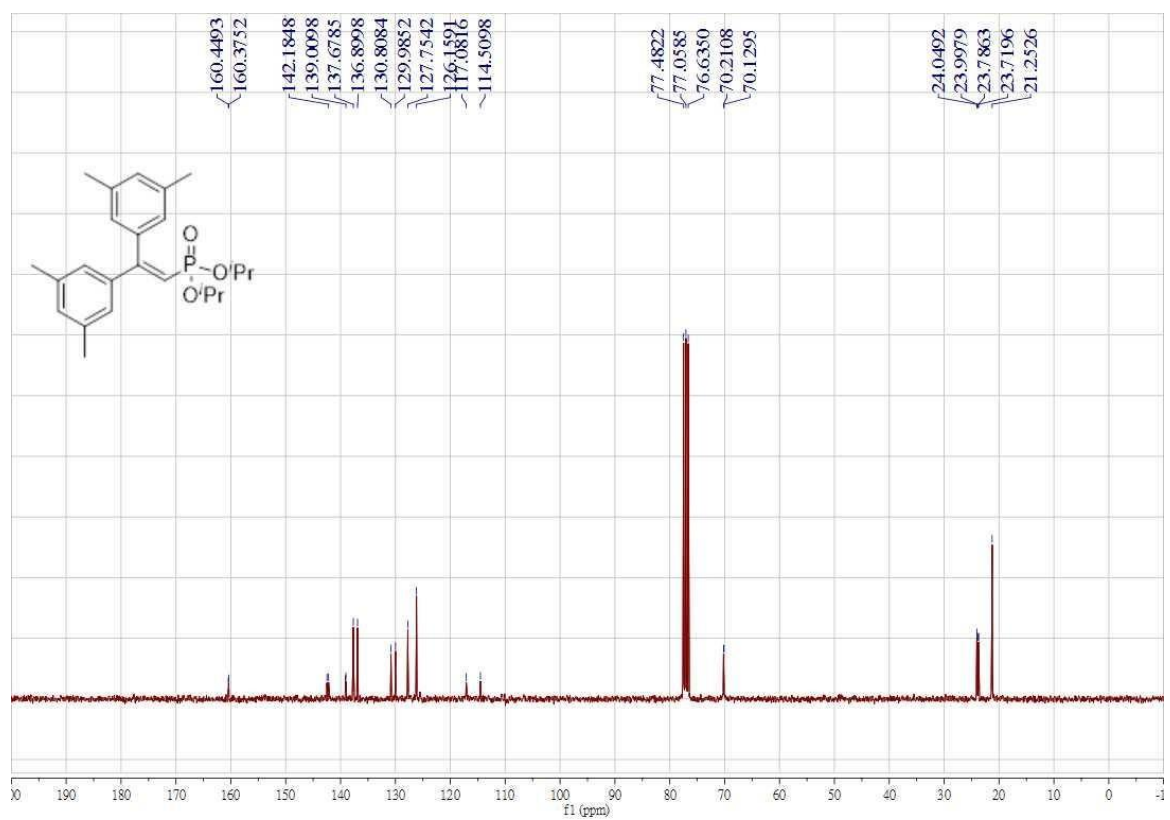
$^{31}\text{P}$  NMR spectrum of compound **7o**



<sup>1</sup>H NMR spectrum of compound **7p**



<sup>13</sup>C NMR spectrum of compound **7p**



<sup>31</sup>P NMR spectrum of compound **7p**

