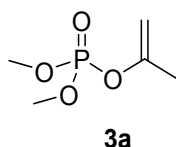


**Regioselective O/C Phosphorylation of α -Chloroketones: A
General Method for the Synthesis of Enol Phosphates and β -
Ketophosphonates via Perkow/Arbuzov Reaction**

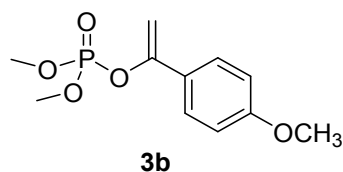
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Yongbiao Guo*, Enxue Shi*

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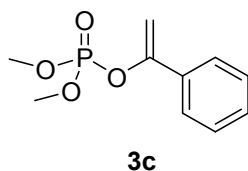
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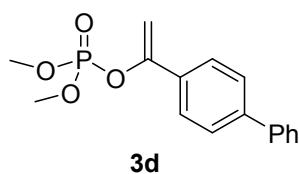
dimethyl prop-1-en-2-yl phosphate (3a). Colorless oil, yield 75%; ¹H NMR(600 MHz, CDCl₃): δ (ppm) 4.72 (s, 1H), 4.48 (s, 1H), 3.78 (d, J = 11.3 Hz, 6H), 1.91 (s, 3H). ¹³C NMR(151 MHz, CDCl₃): δ (ppm) 152.0 (d, J = 8.4 Hz), 98.1 (d, J = 4.9 Hz), 54.5 (d, J = 6.2 Hz) (2), 20.5 (d, J = 5.0 Hz). ³¹P NMR(243 MHz, CDCl₃): δ (ppm) -4.6. HRMS (m/z) calcd for C₅H₁₂O₄P[M+H]⁺ 167.04732, found 167.04636.



1-(4-methoxyphenyl)vinyl dimethyl phosphate (3b). Colorless oil, yield 88%; ¹H NMR(600 MHz, CDCl₃): δ (ppm) 7.68-7.41 (m, 1H), 6.87 (d, J = 8.9 Hz, 1H), 5.16 (t, J = 2.7 Hz, 1H), 5.12-5.04 (m, 1H). 3.83 (d, J = 11.3 Hz, 6H), 3.80 (s, 3H). ¹³C NMR(151 MHz, CDCl₃): δ (ppm) 160.2, 152.0 (d, J = 7.8 Hz), 126.6, 113.7, 95.6 (d, J = 3.6 Hz), 55.2, 54.8 (d, J = 6.1 Hz) (2). ³¹P NMR(243 MHz, CDCl₃): δ (ppm) -4.0. HRMS (m/z) calcd for C₁₁H₁₆O₅P[M+H]⁺ 259.07354, found 259.07237.

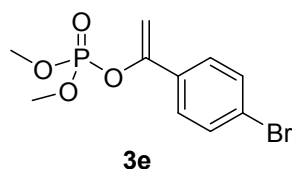


dimethyl (1-phenylvinyl) phosphate (3c). Colorless oil, yield 90%; ¹H NMR(600 MHz, CDCl₃): δ (ppm) 7.64-7.53 (m, 2H), 7.40-7.29 (m, 3H), 5.29 (t, J = 2.8 Hz, 1H), 5.21 (dd, J = 2.9, 2.2 Hz, 1H), 3.83 (d, J = 11.3 Hz, 6H). ¹³C NMR(151 MHz, CDCl₃): δ (ppm) 152.1 (d, J = 7.8 Hz), 133.9 (d, J = 6.8 Hz), 129.1, 128.3 (2), 125.0 (2), 97.3 (d, J = 3.5 Hz), 54.78 (d, J = 6.1 Hz) (2). ³¹P NMR(243 MHz, CDCl₃): δ (ppm) -4.0. HRMS (m/z) calcd for C₁₀H₁₄O₄P[M+H]⁺ 229.06297, found 229.06194.

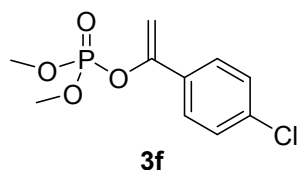


1-([1,1'-biphenyl]-4-yl)vinyl dimethyl phosphate (3d). Colorless oil, yield 95%; ¹H NMR(600 MHz, CDCl₃): δ (ppm) 7.67 (d, J = 8.4 Hz, 2H), 7.64-7.56 (m, 3H), 7.45 (t,

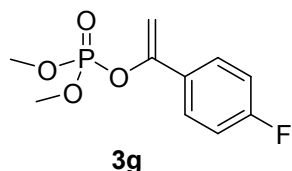
$J = 7.7$ Hz, 2H), 7.37 (t, $J = 7.4$ Hz, 1H), 5.36 (t, $J = 2.8$ Hz, 1H), 5.30-5.21 (m, 1H), 3.88 (d, $J = 11.3$ Hz, 6H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 152.0 (d, $J = 7.7$ Hz), 142.0, 140.3, 132.9 (d, $J = 6.8$ Hz), 128.8, 127.7, 127.1 (2), 127.0 (2), 125.6 (2), 97.4 (d, $J = 3.6$ Hz), 54.9 (d, $J = 6.1$ Hz) (2). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) -4.0. HRMS (m/z) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 305.09427, found 305.09266.



1-(4-bromophenyl)vinyl dimethyl phosphate (3e). Colorless oil, yield 94%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.48 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 8.7$ Hz, 2H), 5.29 (t, $J = 2.8$ Hz, 1H), 5.24-5.21 (m, 1H), 3.84 (d, $J = 11.3$ Hz, 6H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 151.2 (d, $J = 7.6$ Hz), 132.9 (d, $J = 6.8$ Hz), 131.5 (2), 126.6 (2), 123.2, 97.9 (d, $J = 3.6$ Hz), 54.8 (d, $J = 6.1$ Hz) (2). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) -4.0. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{BrO}_4\text{P}[\text{M}+\text{H}]^+$ 306.97348, found 306.97174.

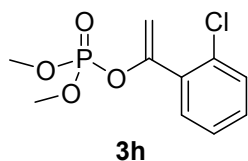


1-(4-chlorophenyl)vinyl dimethyl phosphate (3f). Colorless oil, yield 95%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.52-7.44 (m, 2H), 7.36-7.26 (m, 2H), 5.30-5.14 (m, 2H), 3.81 (d, $J = 11.4$ Hz, 6H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 151.1 (d, $J = 7.6$ Hz), 135.0, 132.4 (d, $J = 6.8$ Hz), 128.5 (2), 126.4 (2), 97.8 (d, $J = 3.6$ Hz), 54.8 (d, $J = 6.1$ Hz) (2). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) -4.0. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_4\text{P}[\text{M}+\text{H}]^+$ 263.02400, found 263.02278.

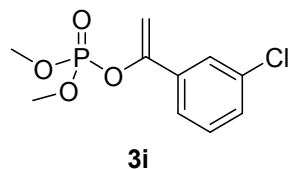


1-(4-fluorophenyl)vinyl dimethyl phosphate (3g). Colorless oil, yield 93%; ^1H NMR (600 MHz, CDCl_3): δ (ppm) 7.64-7.48 (m, 2H), 7.05 (t, $J = 8.7$ Hz, 2H), 5.24 (t, $J = 2.8$ Hz, 1H), 5.21-5.19 (m, 1H), 3.86 (d, $J = 11.3$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 163.2 (d, $J = 2489.2$ Hz), 151.31 (d, $J = 7.7$ Hz), 130.2 (dd, $J = 6.8$, 3.3 Hz), 127.1 (d, $J = 8.4$ Hz) (2), 115.3 ($J = 21.8$ Hz) (2), 97.2 (dd, $J = 3.6$, 1.5 Hz),

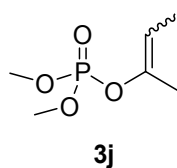
54.9, 54.8. ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -4.1. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{FO}_4\text{P}[\text{M}+\text{H}]^+$ 247.05355, found 247.05234.



1-(2-chlorophenyl)vinyl dimethyl phosphate (3h). Colorless oil, yield 91%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.48-7.46 (m, 1H), 7.40-7.38 (m, 1H), 7.30-7.23 (m, 2H), 5.51-5.29 (m, 1H), 5.16-4.94 (m, 1H), 3.77 (d, $J = 11.3$ Hz, 6H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 150.3 (d, $J = 7.8$ Hz), 134.1 (d, $J = 6.2$ Hz), 132.4, 130.7, 130.2, 130.0, 126.6, 103.28 (d, $J = 4.3$ Hz). 54.8 (d, $J = 6.3$ Hz) (2). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -4.7. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_4\text{P}[\text{M}+\text{H}]^+$ 263.02400, found 263.02275.



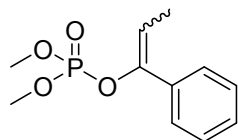
1-(3-chlorophenyl)vinyl dimethyl phosphate (3i). Colorless oil, yield 94%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.54 (t, $J = 1.7$ Hz, 1H), 7.46 (dt, $J = 7.3, 1.6$ Hz, 1H), 7.34-7.27 (m, 2H), 5.33-5.29 (m, 1H), 5.26 (dd, $J = 3.1, 2.1$ Hz, 1H), 3.85 (d, $J = 11.3$ Hz, 6H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 150.9 (d, $J = 7.9$ Hz), 135.8 (d, $J = 7.3$ Hz), 134.5, 129.7, 129.1, 125.2, 123.3, 98.5 (d, $J = 4.0$ Hz), 54.9 (d, $J = 6.3$ Hz) (2). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -4.1. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_4\text{P}[\text{M}+\text{H}]^+$ 263.02400, found 263.02279.



dimethyl pent-2-en-3-yl phosphate (3j, major). Colorless oil, yield 70% (**major + minor**); ^1H NMR(600 MHz, CDCl_3): δ (ppm) 5.27-5.23 (m, 1H), 3.75 (d, $J = 11.3$ Hz, 6H), 1.86 (s, 3H), 1.57-1.54 (m, 3H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 145.1 (d, $J = 8.9$ Hz), 109.2 (d, $J = 5.6$ Hz), 54.5 (d, $J = 6.3$ Hz) (2), 15.6 (d, $J = 3.5$ Hz), 11.8 (d, $J = 0.7$ Hz). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -3.7. HRMS (m/z) calcd for $\text{C}_6\text{H}_{14}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 181.06297, found 181.06192.

dimethyl pent-2-en-3-yl phosphate (3j, minor). Colorless oil, yield 70% (**major +**

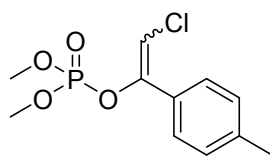
minor); ^1H NMR(600 MHz, CDCl_3): δ (ppm) 4.83 (q, $J = 7.2$ Hz, 1H), 3.78(d, $J = 11.3$ Hz, 6H), 1.93 (s, 3H), 1.58-1.56 (m, 3H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 144.6 (d, $J = 8.4$ Hz), 109.5 (d, $J = 7.9$ Hz), 54.5 (d, $J = 6.3$ Hz) (2), 20.2, 10.5 (d, $J = 1.7$ Hz). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -3.9. HRMS (m/z) calcd for $\text{C}_6\text{H}_{14}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 181.06297, found 181.06192.



3k

dimethyl (1-phenylprop-1-en-1-yl) phosphate (3k, major). Colorless oil, yield 90% (**major + minor**); ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.49-7.47 (m, 2H), 7.33-7.30 (m, 2H), 7.27-7.25 (m, 1H), 5.65 (qd, $J = 7.2, 3.0$ Hz, 1H), 3.71 (d, $J = 11.3$ Hz, 6H), 1.87 (dd, $J = 7.2, 3.0$ Hz, 3H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 146.6 (d, $J = 9.1$ Hz), 135.4 (d, $J = 1.5$ Hz), 128.4, 128.2 (2), 125.1 (2), 112.2 (d, $J = 6.5$ Hz), 54.6 (d, $J = 6.3$ Hz) (2), 11.6 (d, $J = 1.8$ Hz). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -3.3. HRMS (m/z) calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 243.07862, found 243.07732.

dimethyl (1-phenylprop-1-en-1-yl) phosphate (3k, minor). Colorless oil, yield 90% (**major + minor**); ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.45-7.43 (m, 2H), 7.37-7.35 (m, 2H), 7.33-7.30 (m, 1H), 5.73 (qd, $J = 7.2, 3.0$ Hz, 1H), 3.70 (d, $J = 11.3$ Hz, 6H), 1.74 (dd, $J = 7.2, 3.0$ Hz, 3H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 146.2 (d, $J = 9.1$ Hz), 133.8 (d, $J = 1.5$ Hz), 128.5, 128.1 (2), 128.0 (2), 125.1, 111.8 (d, $J = 6.5$ Hz), 54.5 (d, $J = 6.3$ Hz) (2), 12.8 (d, $J = 1.8$ Hz). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -3.4. HRMS (m/z) calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 243.07862, found 243.07732.

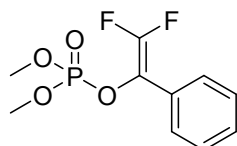


3l

2-chloro-1-(p-tolyl)vinyl dimethyl phosphate (3l, major). Colorless oil, yield 95% (**major + minor**); ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.38 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.14 (d, $J = 2.2$ Hz, 1H), 3.79 (d, $J = 11.5$ Hz, 6H), 2.35 (s, 3H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 148.3 (d, $J = 8.4$ Hz), 139.7, 130.2, 129.3 (2), 125.7 (2), 105.6 (d, $J = 8.0$ Hz), 55.0 (d, $J = 6.0$ Hz) (2), 21.3. ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -3.6. HRMS (m/z) calcd for $\text{C}_{11}\text{H}_{15}\text{Cl O}_4\text{P}[\text{M}+\text{H}]^+$ 277.03965, found 277.03848.

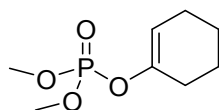
2-chloro-1-(p-tolyl)vinyl dimethyl phosphate (3l, minor). Colorless oil, yield 95%

(**major + minor**); ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.60 (d, $J = 8.2$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.43 (d, $J = 2.2$ Hz, 1H), 3.75 (d, $J = 11.5$ Hz, 6H), 2.37 (s, 3H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 147.4 (d, $J = 8.4$ Hz), 139.8, 130.2, 128.8 (2), 128.2 (2), 107.9 (d, $J = 8.0$ Hz), 54.9 (d, $J = 6.0$ Hz) (2), 21.4. ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -3.5. HRMS (m/z) calcd for $\text{C}_{11}\text{H}_{15}\text{Cl O}_4\text{P}[\text{M}+\text{H}]^+$ 277.03965, found 277.03848.



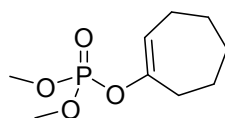
3m

2,2-difluoro-1-phenylvinyl dimethyl phosphate (3m). Colorless oil, yield 90%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.51 (d, $J = 8.3$ Hz, 2H), 7.41 (t, $J = 7.7$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 3.77 (d, $J = 11.4$ Hz, 6H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 154.8 (ddd, $J = 291.8, 287.9, 7.6$ Hz), 134.2 (d, $J = 243.3$ Hz), 130.1, 128.9 (2), 128.6 (2), 126.3 (dd, $J = 5.6, 3.5$ Hz), 55.0 (d, $J = 6.0$ Hz) (2). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) -1.59 (dd, $J = 10.0, 6.9$ Hz). HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4\text{F}_2\text{P}[\text{M}+\text{H}]^+$ 265.04413, found 265.04277.



3n

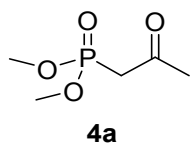
cyclohex-1-en-1-yl dimethyl phosphate (3n). Colorless oil, yield 85%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 5.49-5.38 (m, 1H), 3.77 (d, $J = 11.3$ Hz, 6H), 2.24-2.11 (m, 2H), 2.11-1.99 (m, 2H), 1.69 (dtd, $J = 9.1, 6.2, 3.1$ Hz, 2H), 1.52 (dtd, $J = 9.2, 6.1, 3.0$ Hz, 2H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 147.5 (d, $J = 9.0$ Hz), 110.7 (d, $J = 5.5$ Hz), 54.5 (d, $J = 6.4$ Hz) (2), 27.5 (d, $J = 4.2$ Hz), 23.5 (d, $J = 1.0$ Hz), 22.6, 21.4. ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) -4.0. HRMS (m/z) calcd for $\text{C}_8\text{H}_{16}\text{O}_5\text{P}[\text{M}+\text{H}]^+$ 207.07862, found 207.07862.



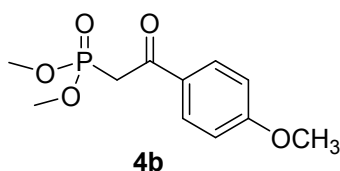
3o

cyclohept-1-en-1-yl dimethyl phosphate (3o). Colorless oil, yield 81%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 5.60 (td, $J = 6.5, 2.5$ Hz, 1H), 3.77 (d, $J = 11.3$ Hz, 6H), 2.45-2.34 (m, 2H), 2.04 (dt, $J = 6.2, 5.3$ Hz, 2H), 1.67 (dt, $J = 11.3, 5.2$ Hz, 2H), 1.61 (dt, J

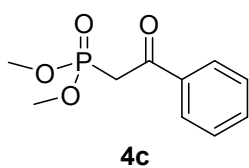
= 8.3, 5.7 Hz, 2H), 1.55 (dt, $J = 8.0, 5.9$ Hz, 2H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 13C NMR (151 MHz, CDCl_3) δ 152.0 (d, $J = 9.5$ Hz), 115.4 (d, $J = 5.4$ Hz), 54.5 (d, $J = 6.3$ Hz) (2), 33.2 (d, $J = 3.7$ Hz), 30.5, 26.8 (d, $J = 0.8$ Hz), 25.0, 24.7 (d, $J = 0.8$ Hz). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) -3.8. HRMS (m/z) calcd for $\text{C}_9\text{H}_{18}\text{O}_5\text{P}[\text{M}+\text{H}]^+$ 221.09427, found 221.09304.



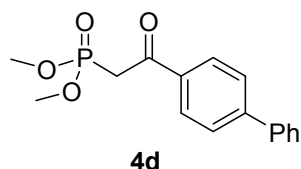
dimethyl (2-oxopropyl)phosphonate (4a). Colorless oil, yield 85%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 3.76 (d, $J = 11.2$ Hz, 6H), 3.08 (d, $J = 22.8$ Hz, 2H), 2.30 (s, 3H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 199.7 (d, $J = 6.2$ Hz), 53.0 (d, $J = 6.5$ Hz) (2), 42.1 (d, $J = 127.8$ Hz), 31.4. ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) 22.4. HRMS (m/z) calcd for $\text{C}_5\text{H}_{12}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 167.04732, found 167.04636.



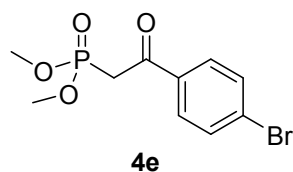
dimethyl (2-(4-methoxyphenyl)-2-oxoethyl)phosphonate (4b). Colorless oil, yield 90%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 7.94 (dd, $J = 8.8, 1.0$ Hz, 2H), 7.00-6.82 (m, 2H), 3.83 (d, $J = 1.2$ Hz, 3H), 3.73 (d, $J = 11.3$ Hz, 6H), 3.57 (s, 1H), 3.53 (s, 1H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 190.0 (d, $J = 6.4$ Hz), 164.0, 131.3 (2), 129.3 (d, $J = 2.2$ Hz), 113.8 (2), 55.4, 53.0 (d, $J = 6.5$ Hz) (2), 37.1 (d, $J = 131.0$ Hz). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) 23.3. HRMS (m/z) calcd for $\text{C}_{11}\text{H}_{16}\text{O}_5\text{P}[\text{M}+\text{H}]^+$ 259.07354, found 259.07238.



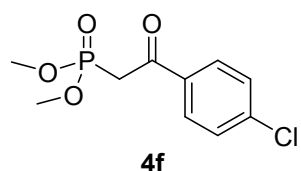
dimethyl (2-oxo-2-phenylethyl)phosphonate (4c). Colorless oil, yield 85%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 8.00-7.97 (m, 2H), 7.60-7.56 (m, 1H), 7.49-7.45 (m, 2H), 3.77 (d, $J = 11.3$ Hz, 6H), 3.65 (s, 1H), 3.61 (s, 1H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 191.7 (d, $J = 6.6$ Hz), 136.3 (d, $J = 2.5$ Hz), 133.8, 128.9 (2), 128.7 (2), 53.1 (d, $J = 6.5$ Hz) (2), 37.4 (d, $J = 131.5$ Hz). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) 22.8. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 229.06297, found 229.06176.



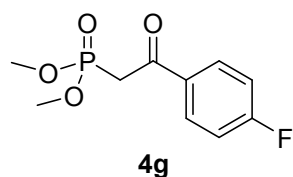
1-([1,1'-biphenyl]-4-yl)vinyl dimethyl phosphate (4d). Colorless oil, yield 83%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 8.01 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.56 (dd, $J = 8.2, 1.1$ Hz, 2H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.34 (d, $J = 7.4$ Hz, 1H), 3.73 (d, $J = 11.3$ Hz, 6H), 3.62 (s, 1H), 3.59 (s, 1H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 191.2 (d, $J = 6.6$ Hz), 146.5, 139.6, 135.0, 129.6 (2), 129.0 (2), 128.4, 127.3 (2), 127.2 (2), 53.2 (d, $J = 6.5$ Hz) (2), 37.5 (d, $J = 131.0$ Hz). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) 22.9. HRMS (m/z) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 305.09427, found 305.09279.



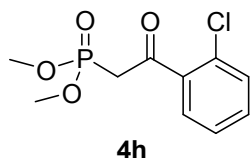
dimethyl (2-(4-bromophenyl)-2-oxoethyl)phosphonate (4e). Colorless oil, yield 85%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 8.11-7.76 (m, 2H), 7.70-7.53 (m, 2H), 3.74 (d, $J = 11.3$ Hz, 6H), 3.59 (s, 1H), 3.55 (s, 1H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 190.7 (d, $J = 6.6$ Hz), 134.9 (d, $J = 2.2$ Hz), 131.9 (2), 130.4 (2), 129.1, 53.1 (d, $J = 6.6$ Hz) (2), 37.5 (d, $J = 130.7$ Hz). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) 22.2. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{BrO}_4\text{P}[\text{M}+\text{H}]^+$ 306.97348, found 306.97215.



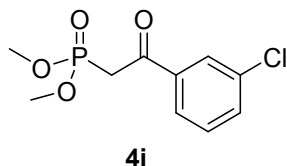
dimethyl (2-(4-chlorophenyl)-2-oxoethyl)phosphonate (4f). Colorless oil, yield 85%; ^1H NMR(600 MHz, CDCl_3): δ (ppm) 8.03-7.74 (m, 2H), 7.64-7.31 (m, 2H), 3.72 (d, $J = 11.3$ Hz, 6H), 3.56 (s, 1H), 3.52 (s, 1H). ^{13}C NMR(151 MHz, CDCl_3): δ (ppm) 190.5 (d, $J = 6.6$ Hz), 140.4, 134.6 (d, $J = 2.2$ Hz), 130.4 (2), 129.0 (2), 53.21 (d, $J = 6.5$ Hz) (2), 37.6 (d, $J = 130.8$ Hz). ^{31}P NMR(243 MHz, CDCl_3): δ (ppm) 22.3. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_4\text{P}[\text{M}+\text{H}]^+$ 263.02400, found 263.02286.



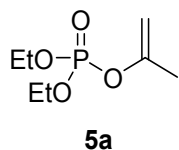
dimethyl (2-(4-fluorophenyl)-2-oxoethyl)phosphonate (4g). Colorless oil, yield 93%; ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.01 (dd, $J = 8.8, 5.3$ Hz, 2H), 7.11 (t, $J = 8.6$ Hz, 2H), 3.74 (d, $J = 11.3$ Hz, 6H), 3.60 (s, 1H), 3.56 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 190.1 (d, $J = 6.5$ Hz), 166.0 (d, $J = 256.3$ Hz), 132.7 (t, $J = 2.5$ Hz), 131.7 (d, $J = 9.6$ Hz) (2), 115.8 (d, $J = 22.0$ Hz) (2), 53.1 (d, $J = 6.6$ Hz) (2), 37.46 (d, $J = 130.8$ Hz). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) 22.5. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{FO}_4\text{P}[\text{M}+\text{H}]^+$ 247.05355, found 247.05225.



dimethyl (2-(2-chlorophenyl)-2-oxoethyl)phosphonate (4h). Colorless oil, yield 67%; ^1H NMR (600 MHz, CDCl_3): δ (ppm) 7.59 (dd, $J = 4.6, 3.7$ Hz, 1H), 7.42 (dd, $J = 4.9, 1.3$ Hz, 2H), 7.38-7.32 (m, 1H), 3.76 (d, $J = 11.3$ Hz, 6H), 3.74 (s, 1H), 3.70 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 194.2 (d, $J = 7.0$ Hz), 138.4 (d, $J = 2.3$ Hz), 132.4, 131.1, 130.6, 129.9, 127.0, 53.1 (d, $J = 6.5$ Hz), 41.1 (d, $J = 130.2$ Hz). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) 22.0. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_4\text{P}[\text{M}+\text{H}]^+$ 263.02400, found 263.02278.

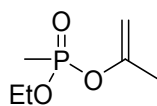


dimethyl (2-(3-chlorophenyl)-2-oxoethyl)phosphonate (4i). Colorless oil, yield 70%; ^1H NMR (600 MHz, CDCl_3): δ (ppm) 7.94 (t, $J = 1.9$ Hz, 1H), 7.88-7.82 (m, 1H), 7.53 (ddd, $J = 8.0, 2.1, 0.9$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 3.76 (d, $J = 11.3$ Hz, 6H), 3.61 (s, 1H), 3.57 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 13C NMR (151 MHz, CDCl_3) δ 190.5 (d, $J = 6.7$ Hz), 137.7 (d, $J = 2.3$ Hz), 135.0, 133.6, 130.0, 128.8, 127.1, 53.2 (d, $J = 6.6$ Hz) (2), 37.53 (d, $J = 131.2$ Hz). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) 22.1. HRMS (m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_4\text{P}[\text{M}+\text{H}]^+$ 263.02400, found 263.02268.



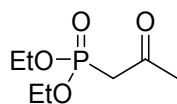
diethyl prop-1-en-2-yl phosphate (5a). Colorless oil, yield 77%; ^1H NMR (600 MHz, CDCl_3): δ (ppm) 4.72 (t, $J = 1.8$ Hz, 1H), 4.45 (d, $J = 0.7$ Hz, 1H), 4.21-4.06 (m, 4H),

1.90 (s, 3H), 1.31 (td, $J = 7.1, 0.7$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 152.0 (d, $J = 8.5$ Hz), 97.9 (d, $J = 4.9$ Hz), 64.1 (d, $J = 6.1$ Hz) (2), 20.6 (d, $J = 5.1$ Hz), 15.9 (d, $J = 6.8$ Hz) (2). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) -6.8. HRMS (m/z) calcd for $\text{C}_7\text{H}_{16}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 195.07862, found 195.07755.



5b

ethyl prop-1-en-2-yl methylphosphonate (5b). Colorless oil, yield 85%; ^1H NMR (600 MHz, CDCl_3): δ (ppm) 4.68 (t, $J = 1.9$ Hz, 1H), 4.46-4.41 (m, 1H), 4.20-4.00 (m, 2H), 1.88 (s, 3H), 1.51 (d, $J = 17.6$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 152.0 (d, $J = 9.2$ Hz), 98.0 (d, $J = 5.0$ Hz), 61.91 (d, $J = 6.5$ Hz), 21.14 (d, $J = 3.9$ Hz), 16.17 (d, $J = 6.3$ Hz), 11.1 (d, $J = 145.0$ Hz), 10.6. ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) 26.4. HRMS (m/z) calcd for $\text{C}_6\text{H}_{14}\text{O}_3\text{P}[\text{M}+\text{H}]^+$ 165.06806, found 165.06712.



6a

diethyl (2-oxopropyl)phosphonate (6a). Colorless oil, yield 86%; ^1H NMR (600 MHz, CDCl_3): δ (ppm) 4.31-4.01 (m, 4H), 3.04 (d, $J = 22.9$ Hz, 2H), 2.27 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3): δ (ppm) 199.8 (d, $J = 6.1$ Hz), 62.5 (d, $J = 6.5$ Hz) (2), 31.3, 16.17 (d, $J = 6.3$ Hz) (2). ^{31}P NMR (243 MHz, CDCl_3): δ (ppm) 19.7. HRMS (m/z) calcd for $\text{C}_7\text{H}_{16}\text{O}_4\text{P}[\text{M}+\text{H}]^+$ 195.07862, found 195.07751.

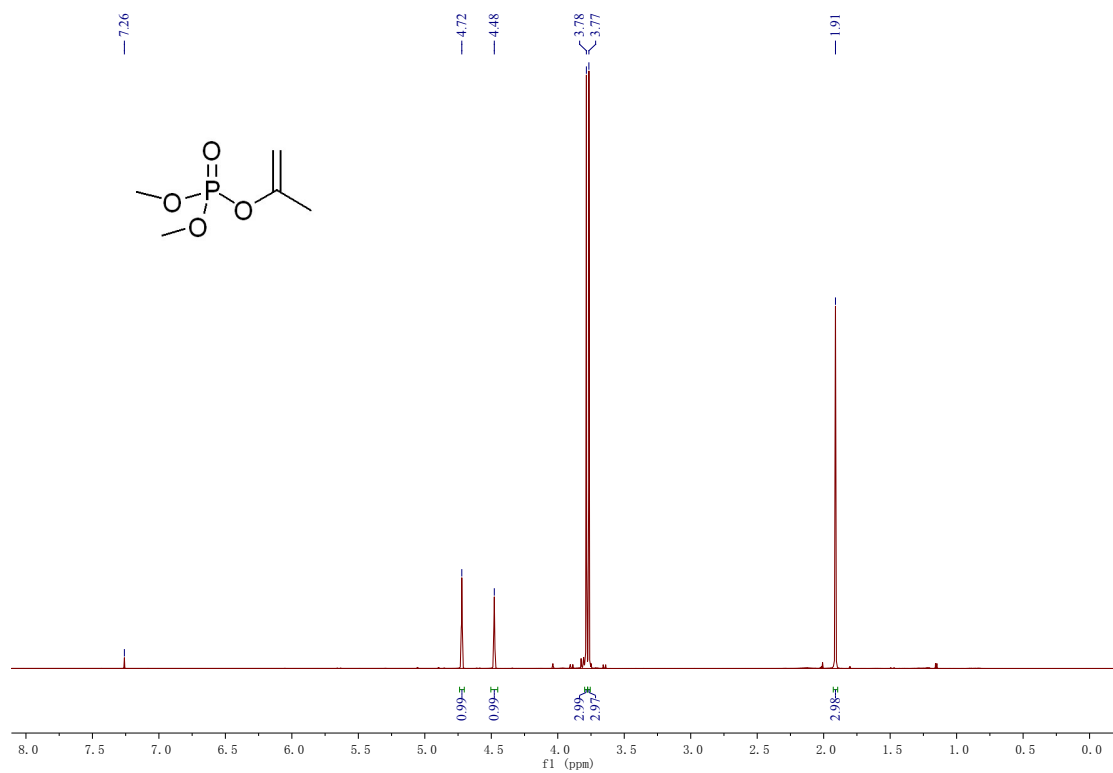


Fig.S 1 ¹H NMR of compound 3a

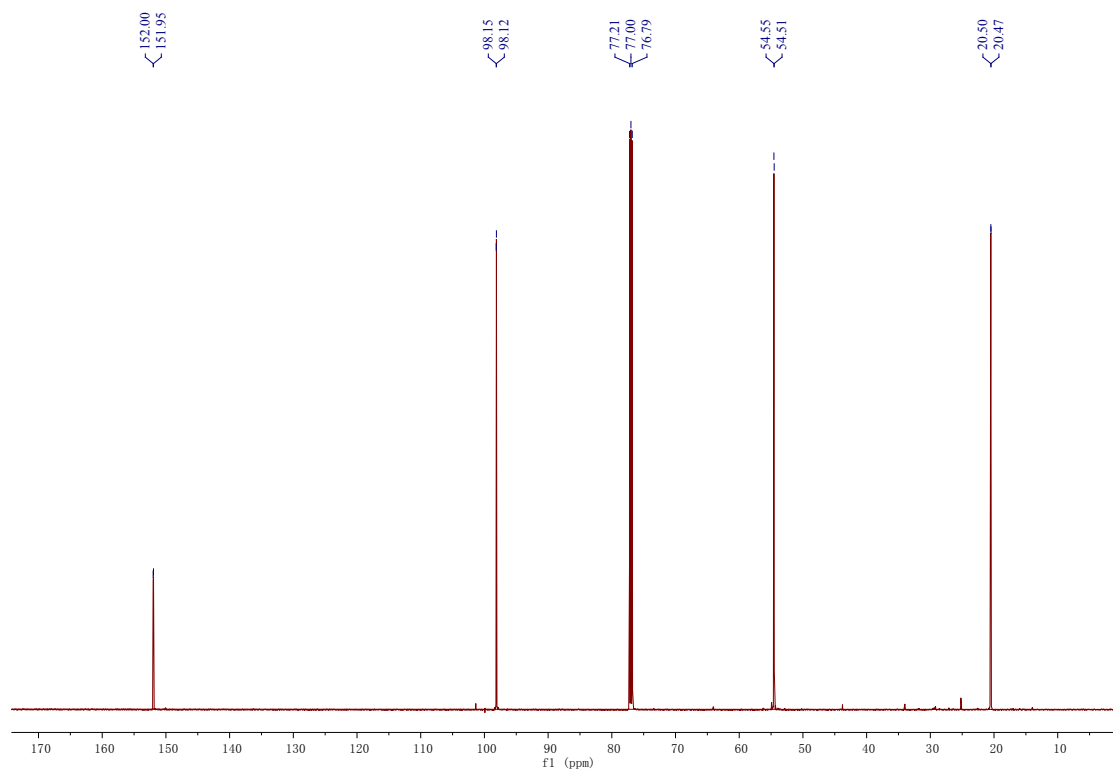


Fig.S 2 ¹³C NMR of compound 3a

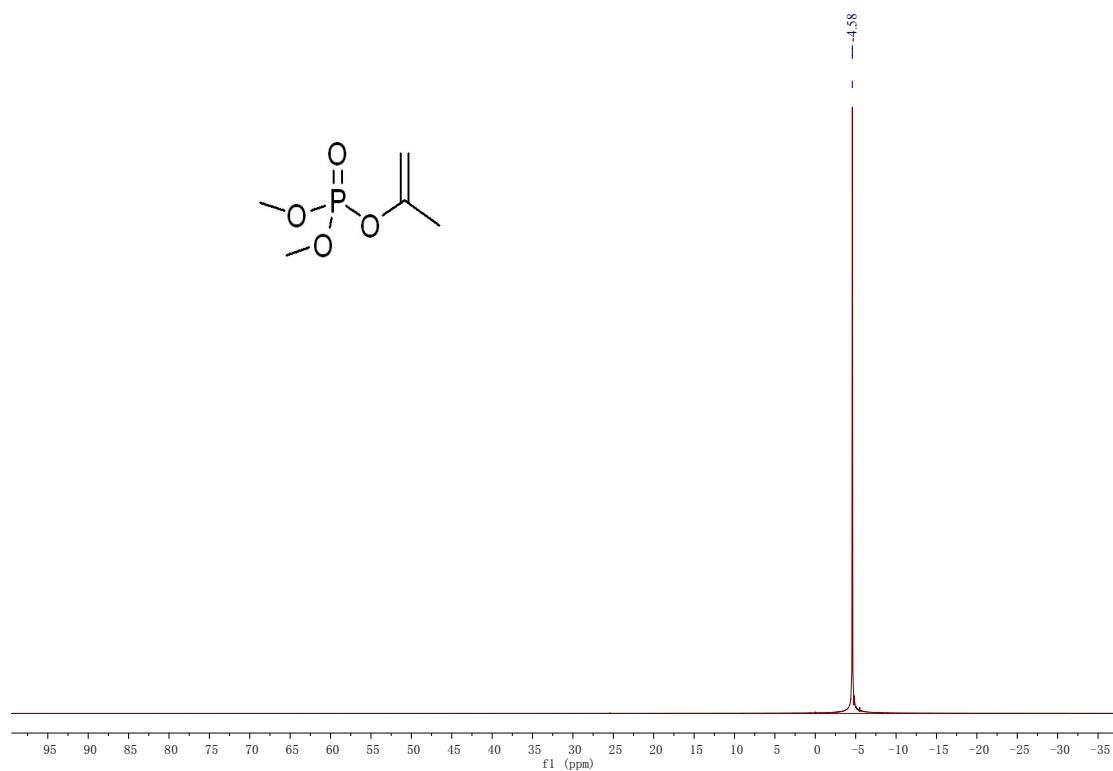


Fig.S 3 ^{31}P NMR of compound **3a**

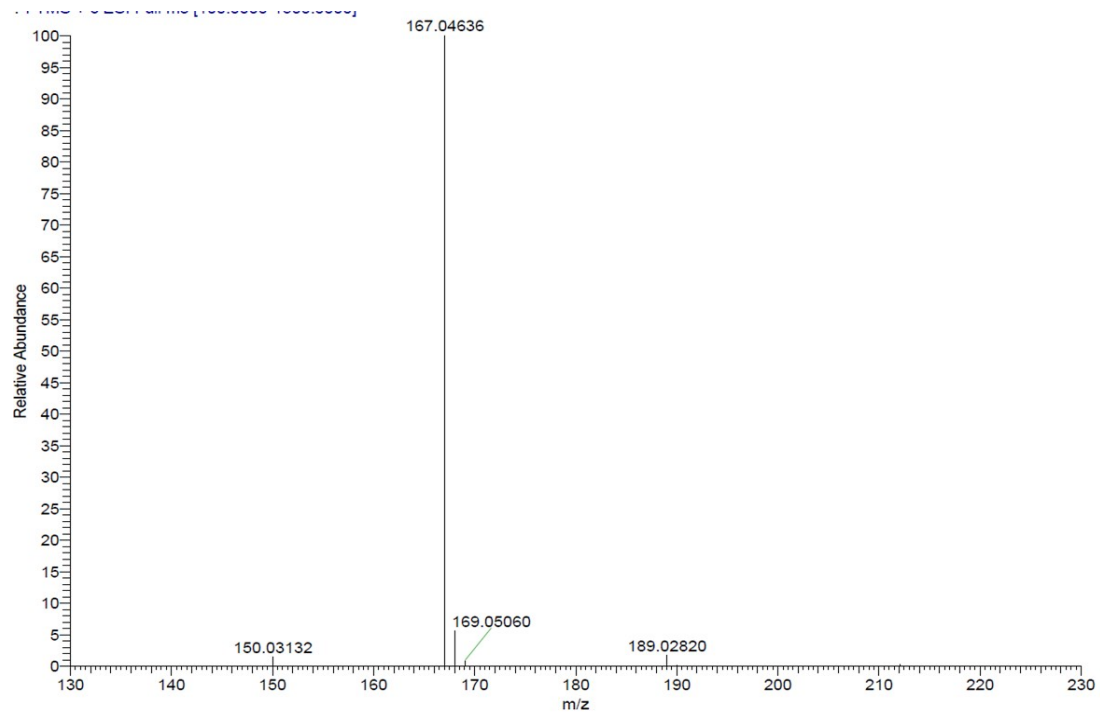


Fig.S 4 HRMS of compound **3a**

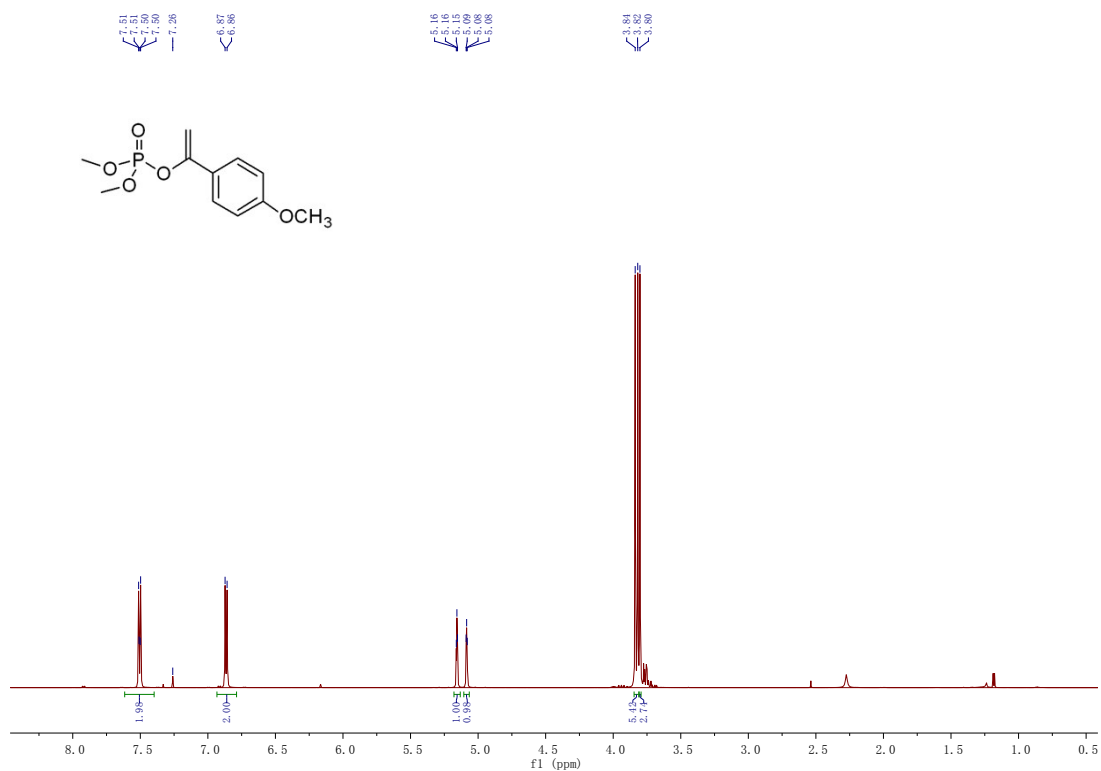


Fig.S 5 ¹H NMR of compound **3b**

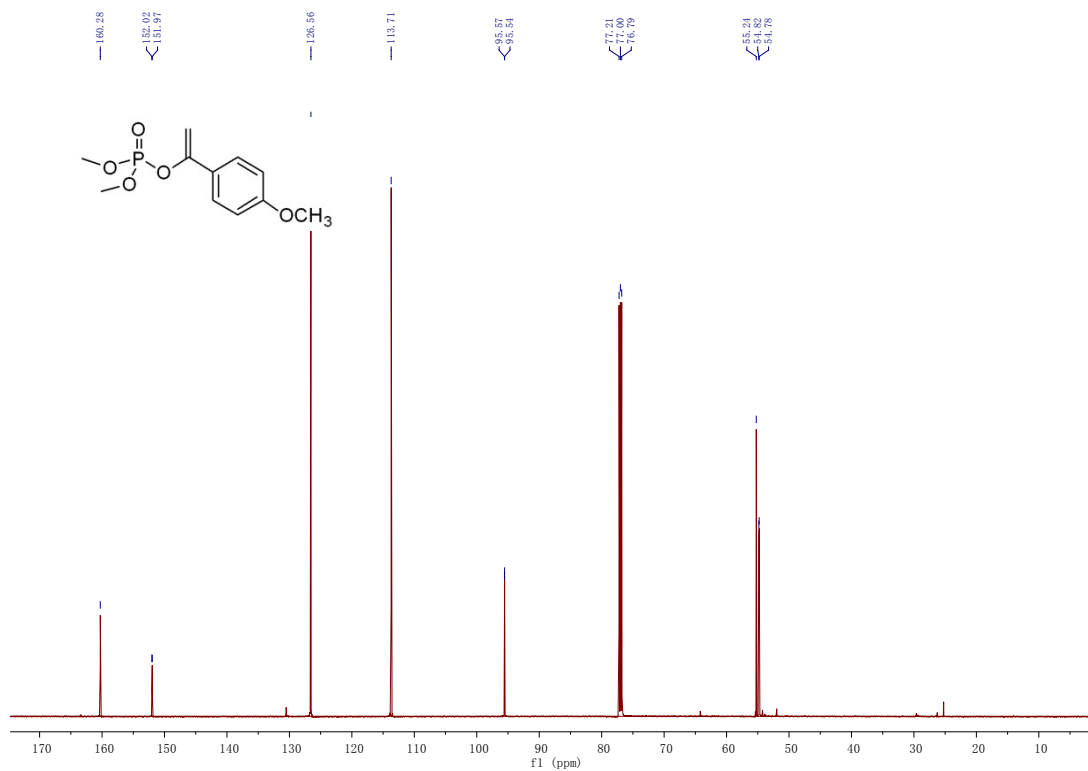


Fig.S 6 ¹³C NMR of compound **3b**

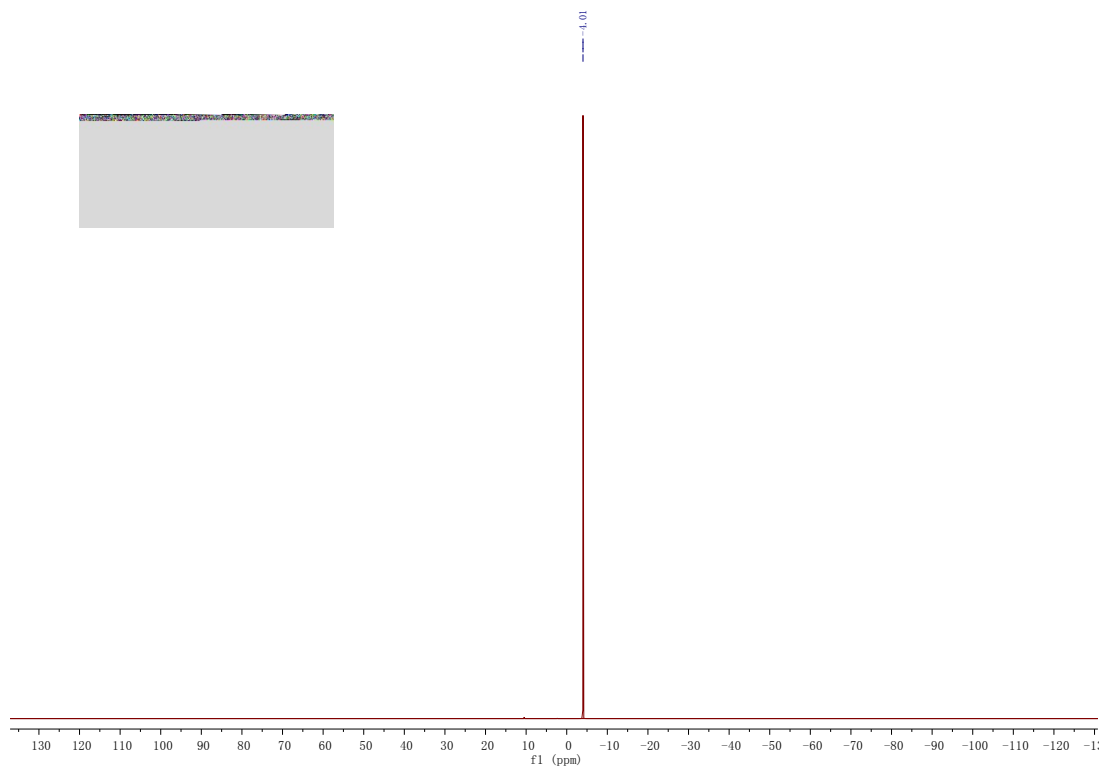


Fig.S 7 ^{31}P NMR of compound **3b**

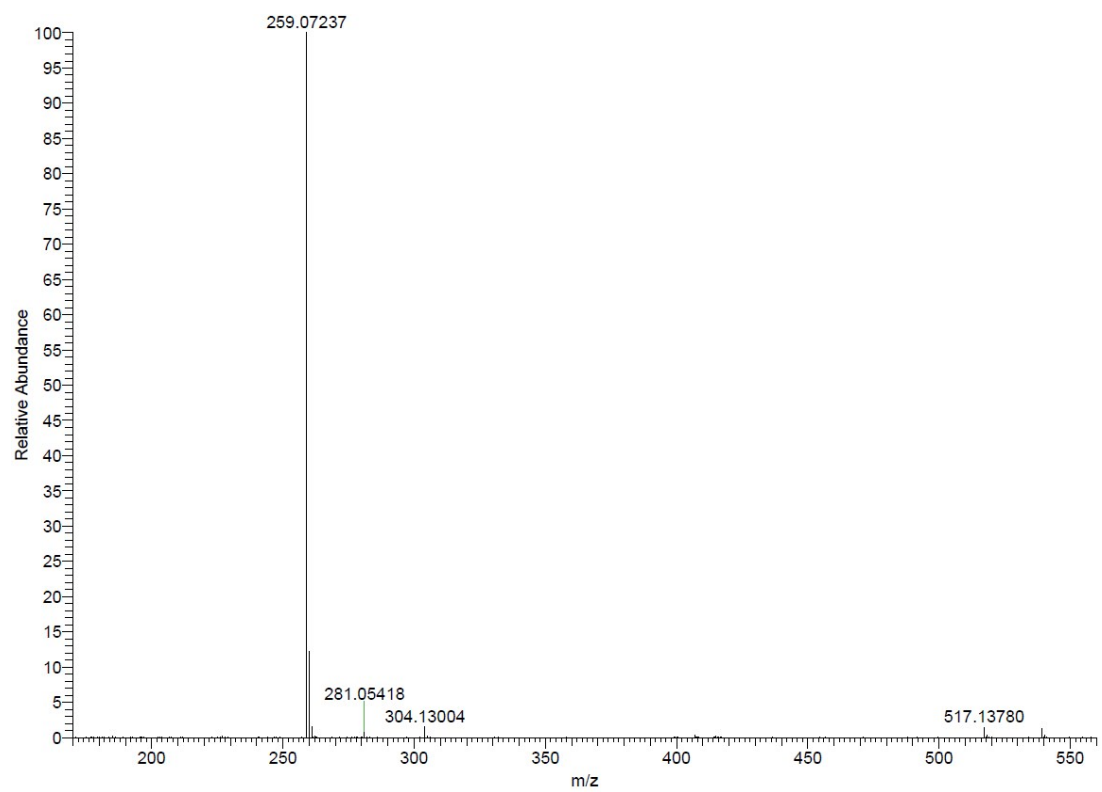


Fig.S 8 HRMS of compound **3b**

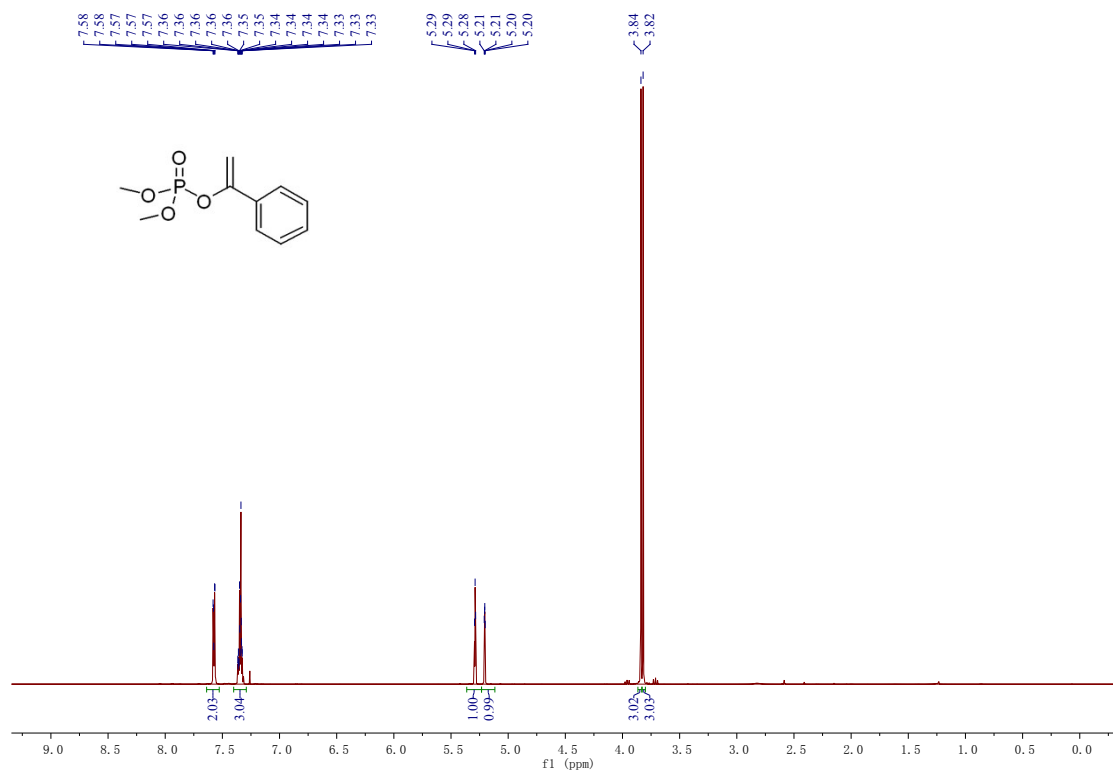


Fig.S 9 ¹H NMR of compound 3c

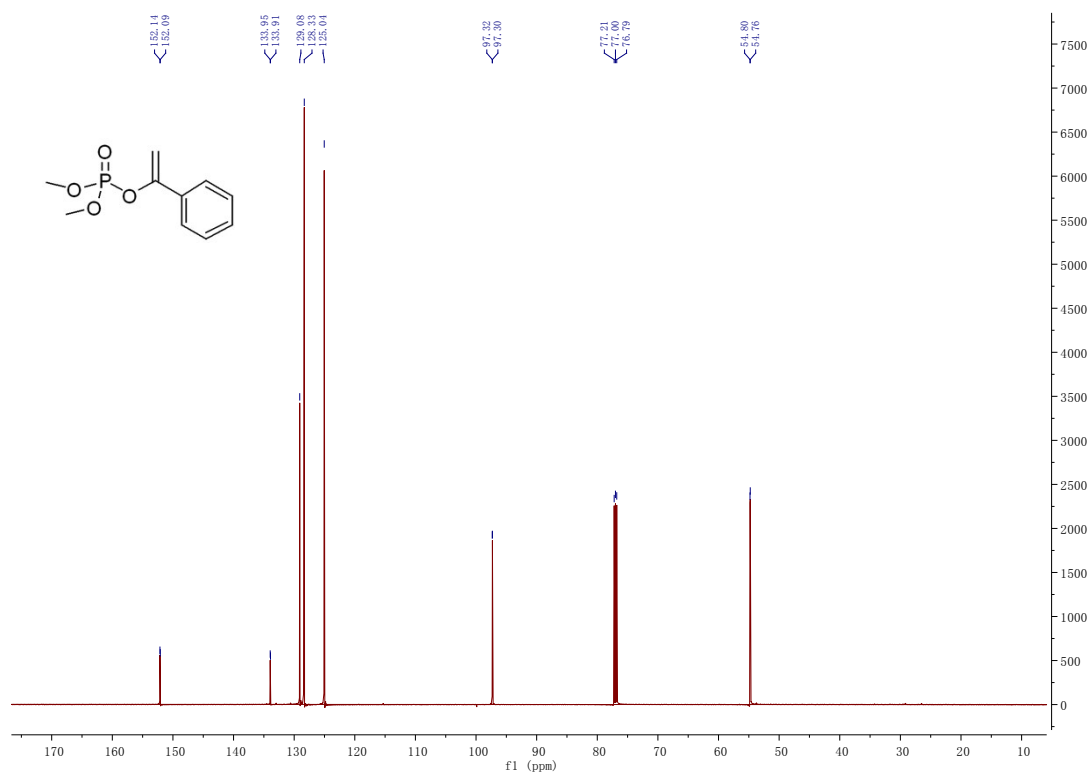


Fig.S 10 ¹³C NMR of compound 3c

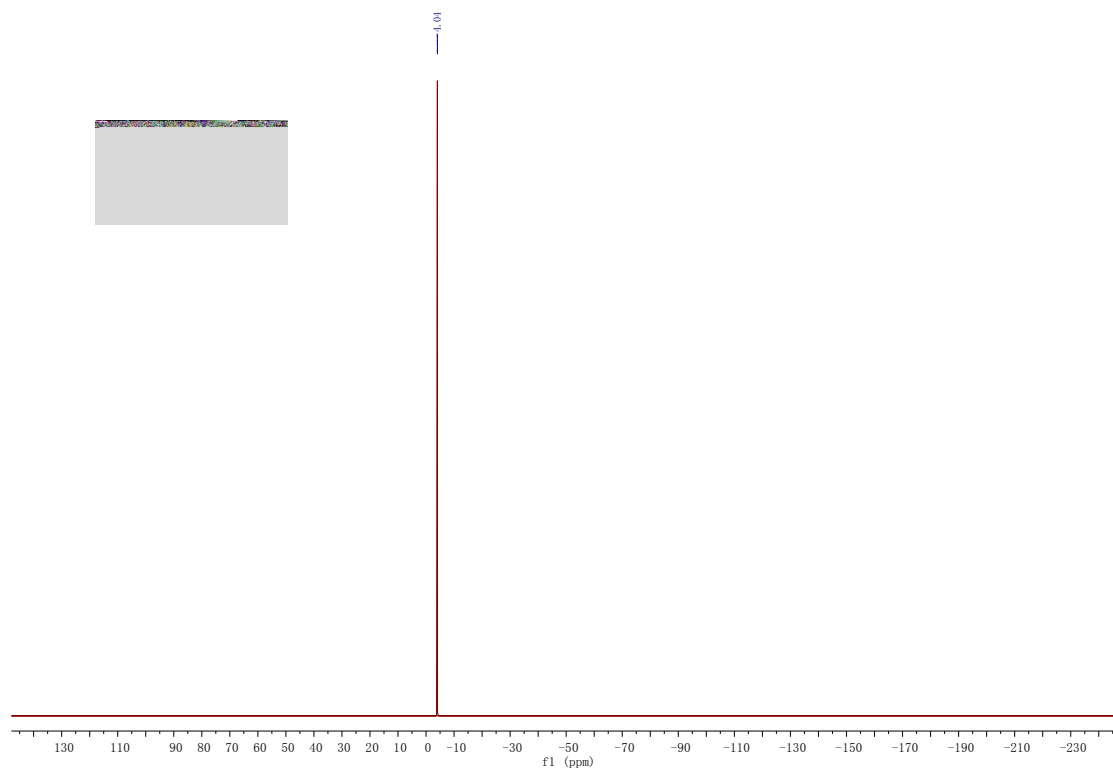


Fig.S 11 ^{31}P NMR of compound **3c**

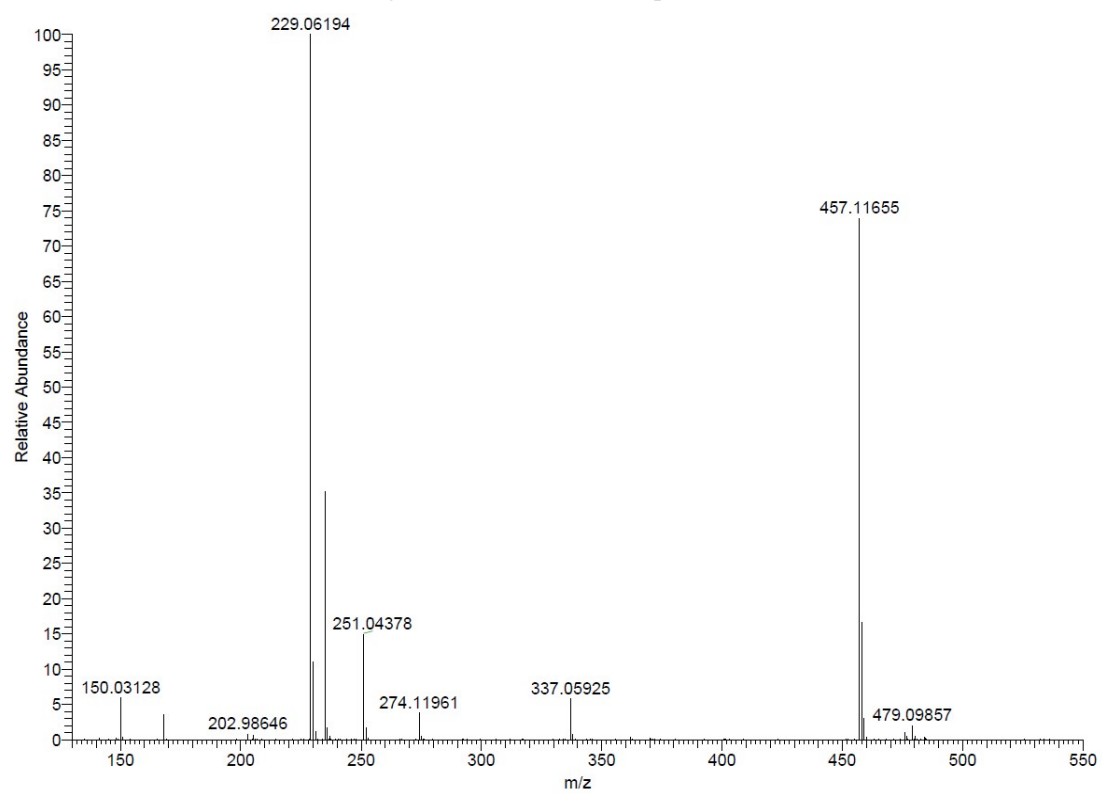


Fig.S 12 HRMS of compound **3c**

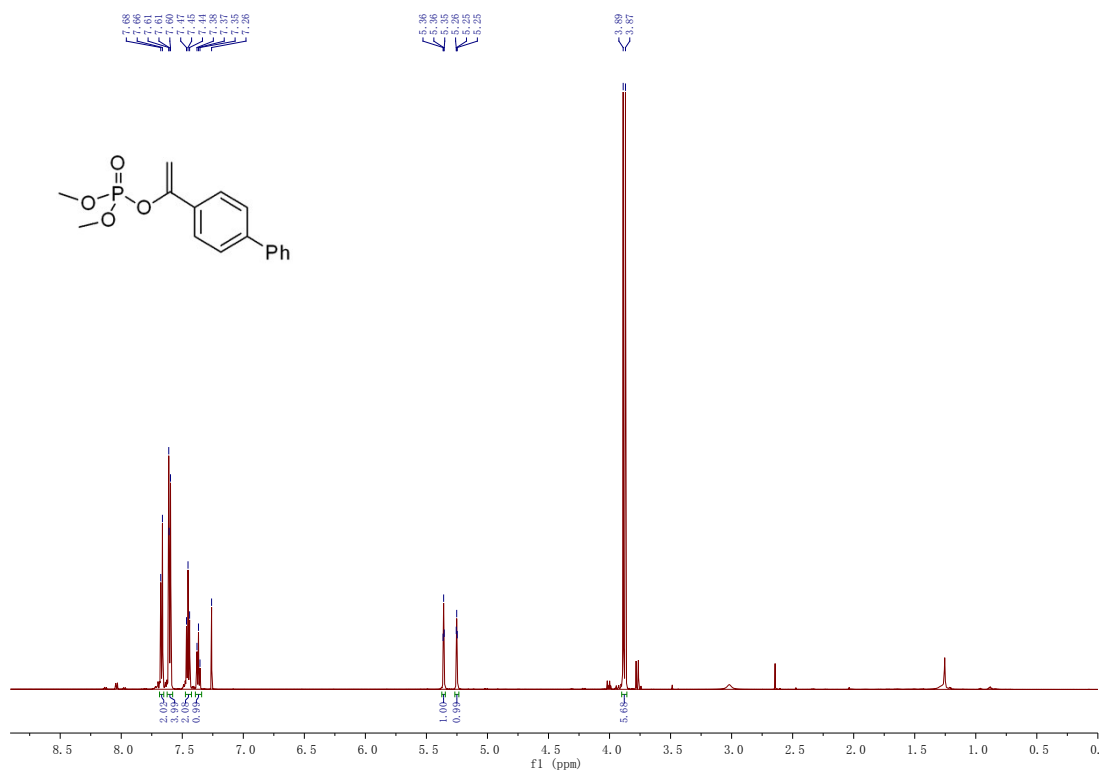


Fig.S 13 ¹H NMR of compound 3d

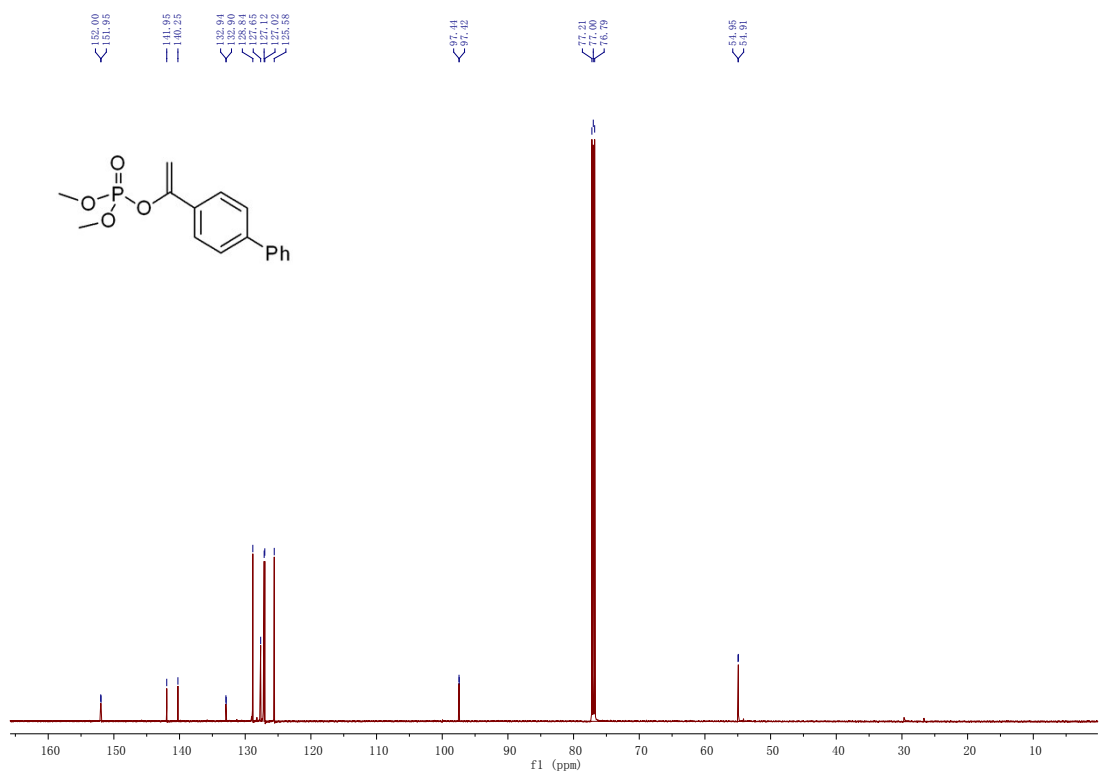


Fig.S 14 ¹³C NMR of compound 3d

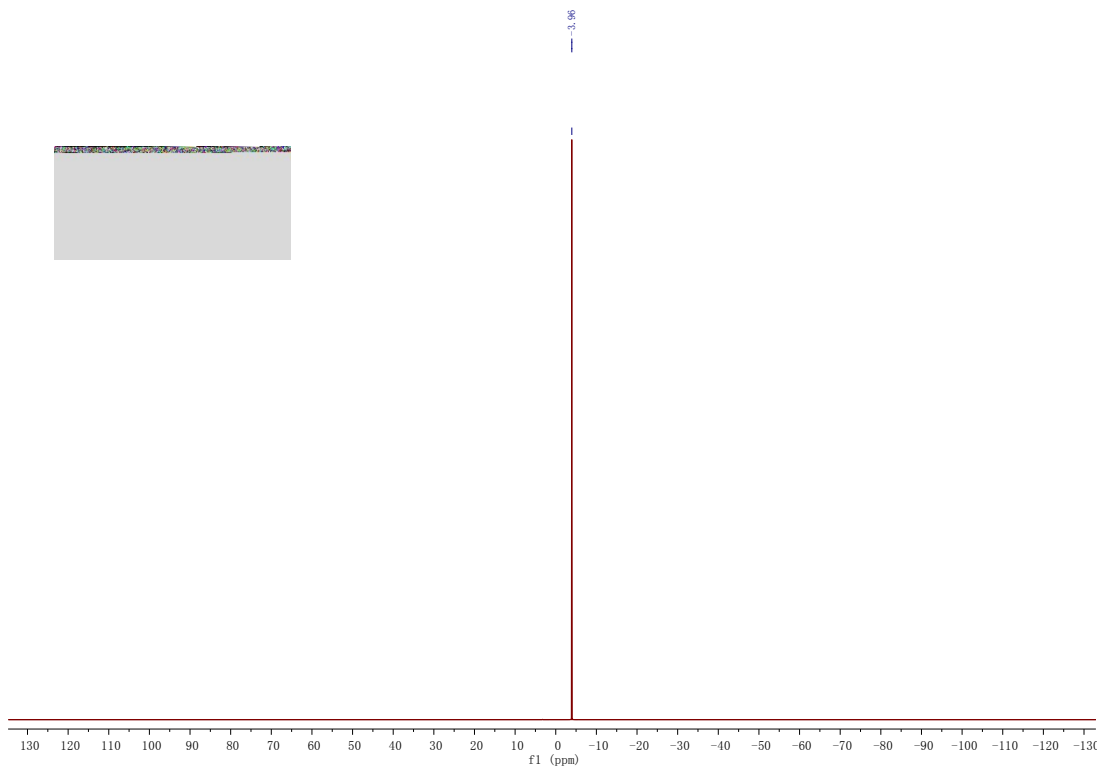


Fig.S 15 ^{31}P NMR of compound **3d**

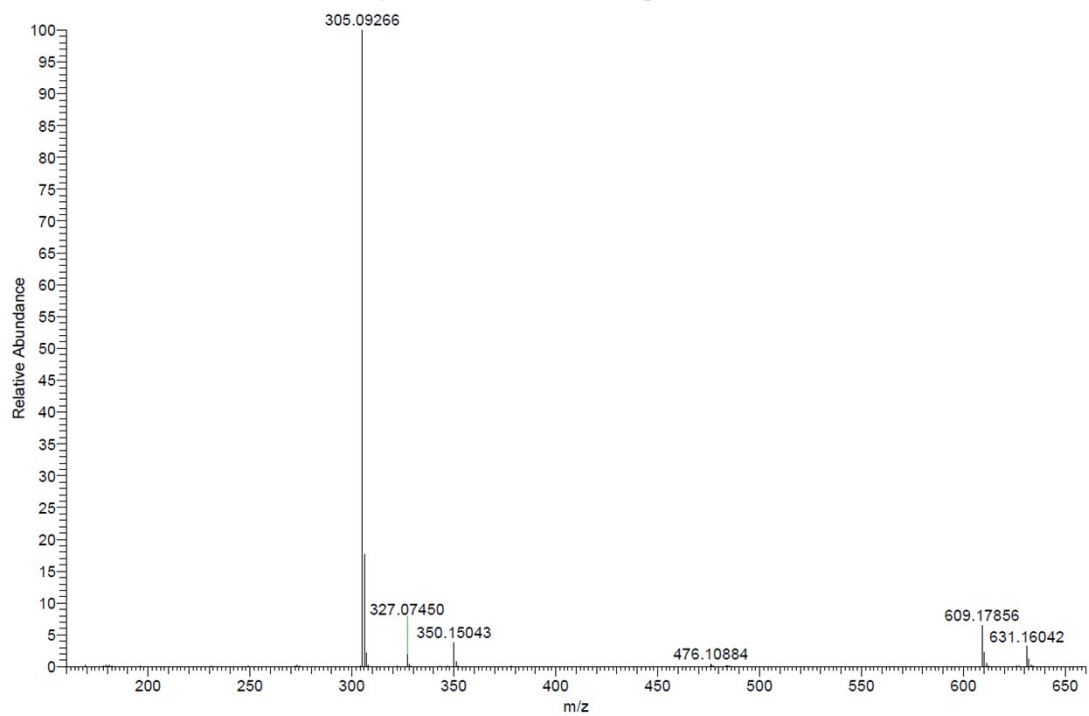


Fig.S 16 HRMS of compound **3d**

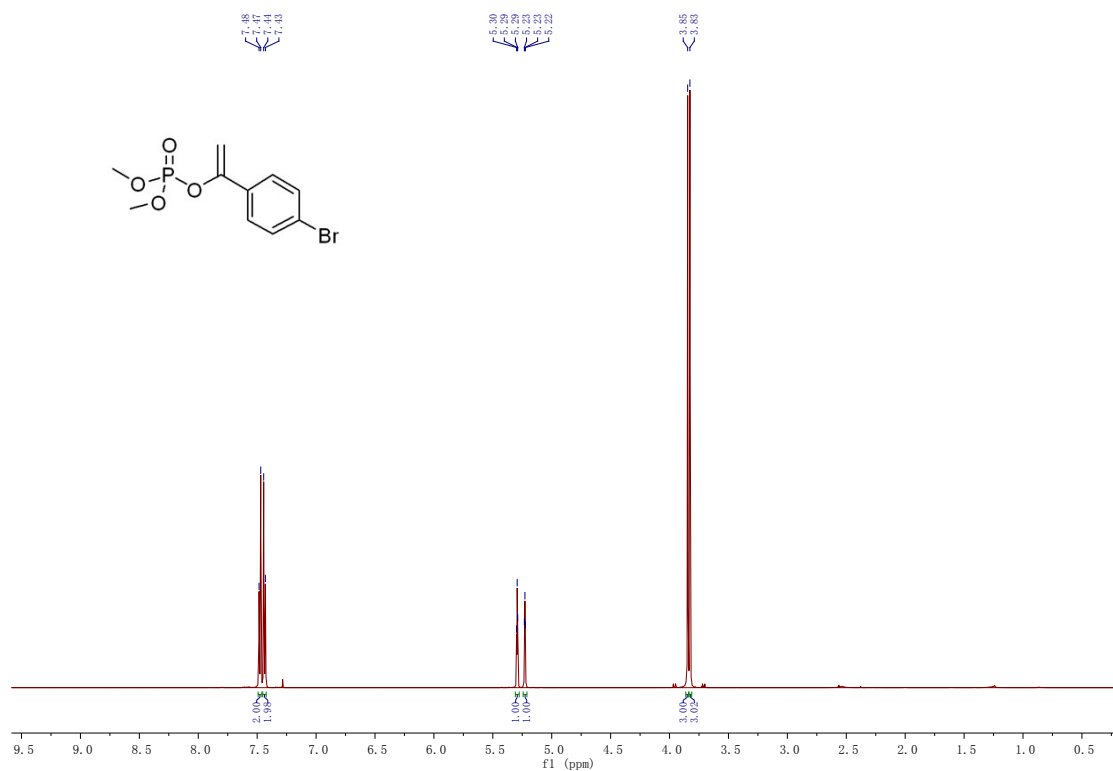


Fig.S 17 ¹H NMR of compound 3e

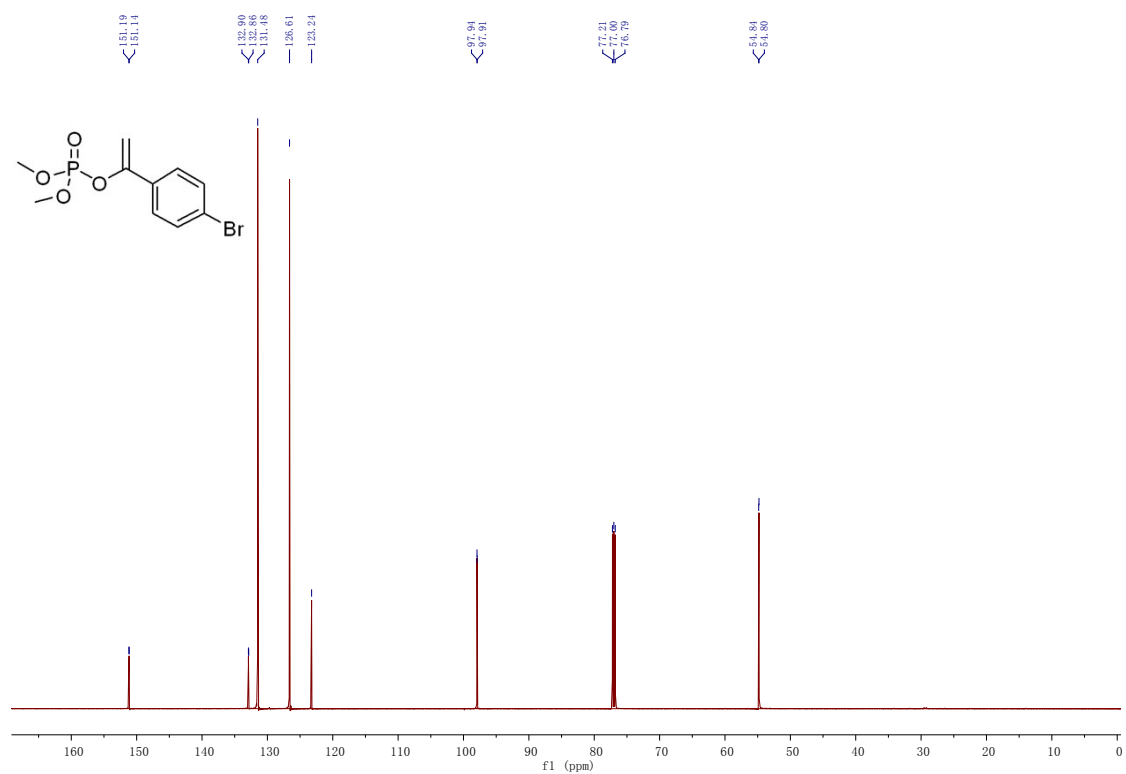


Fig.S 18 ¹³C NMR of compound 3e

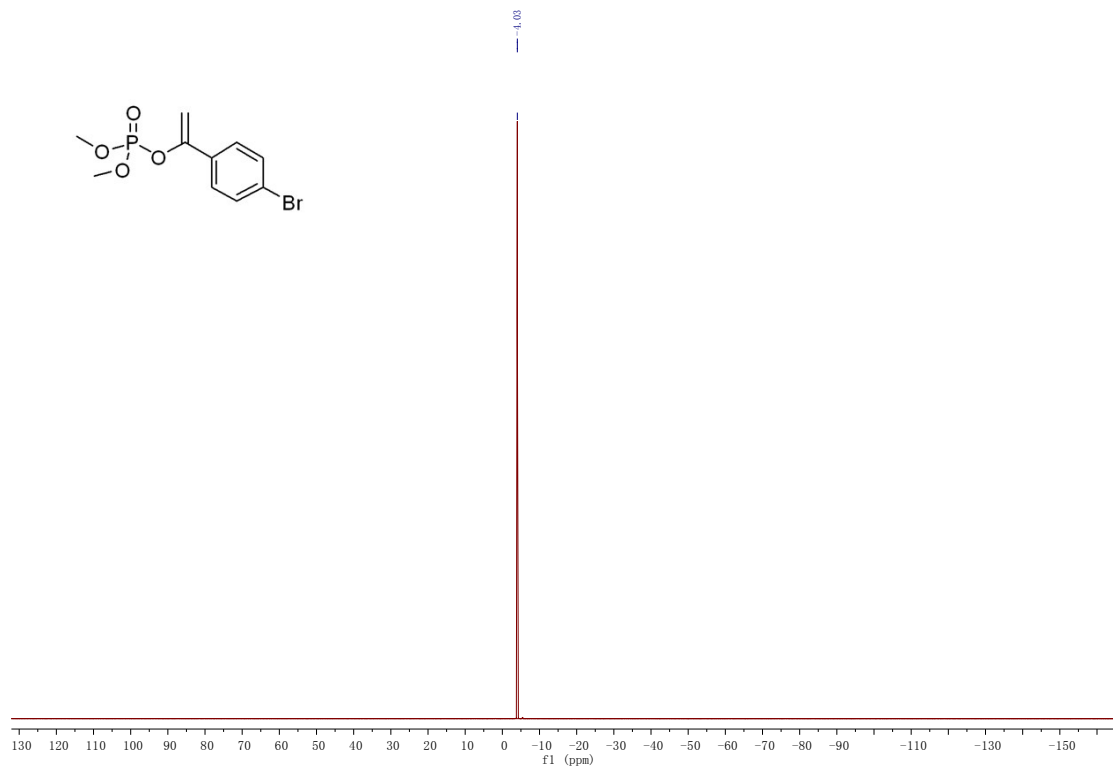


Fig.S 19 ³¹P NMR of compound **3e**

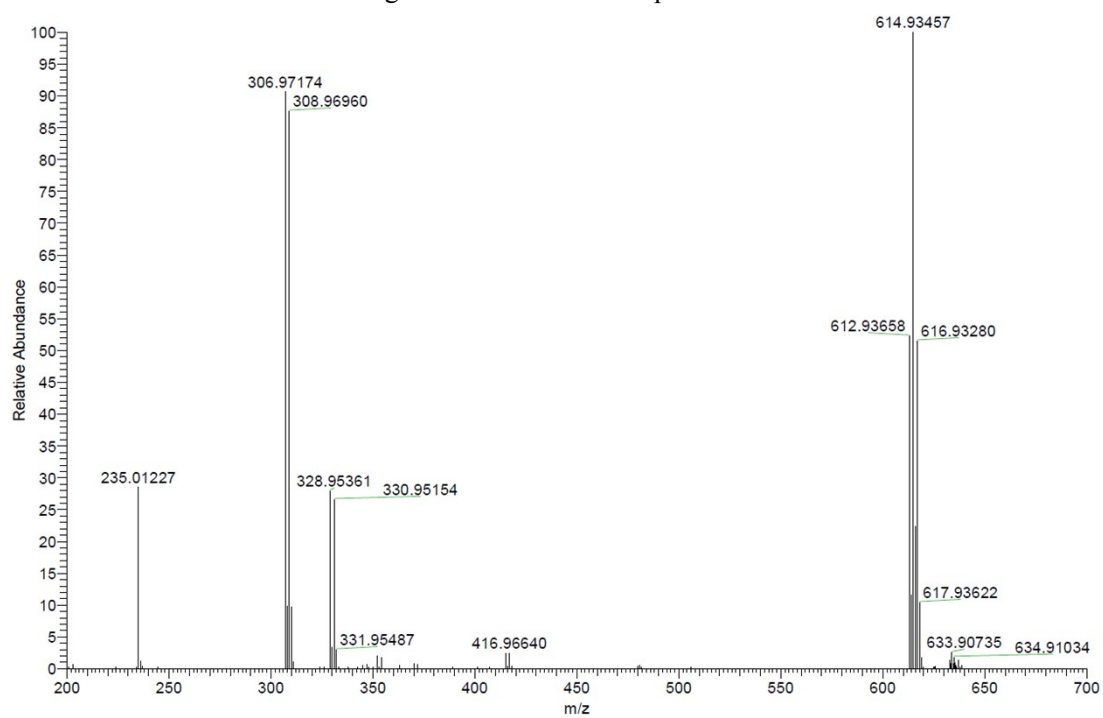


Fig.S 20 HRMS of compound **3e**

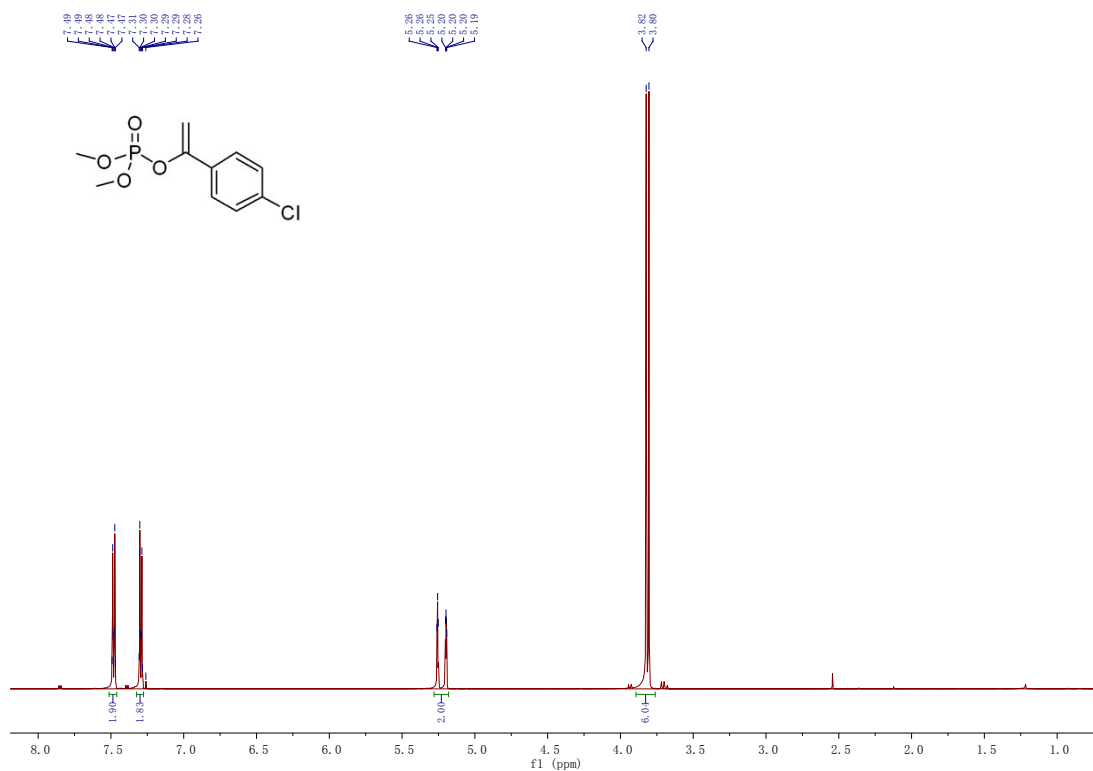


Fig.S 21 ¹H NMR of compound 3f

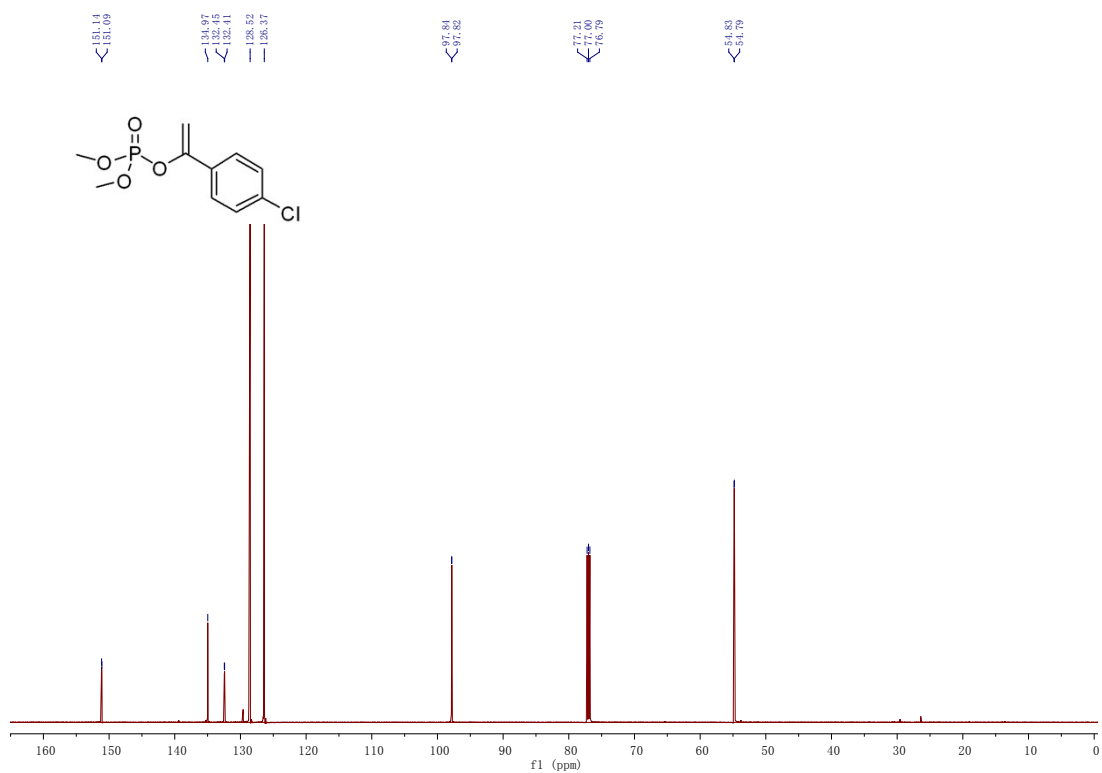


Fig.S 22 ¹³C NMR of compound 3f

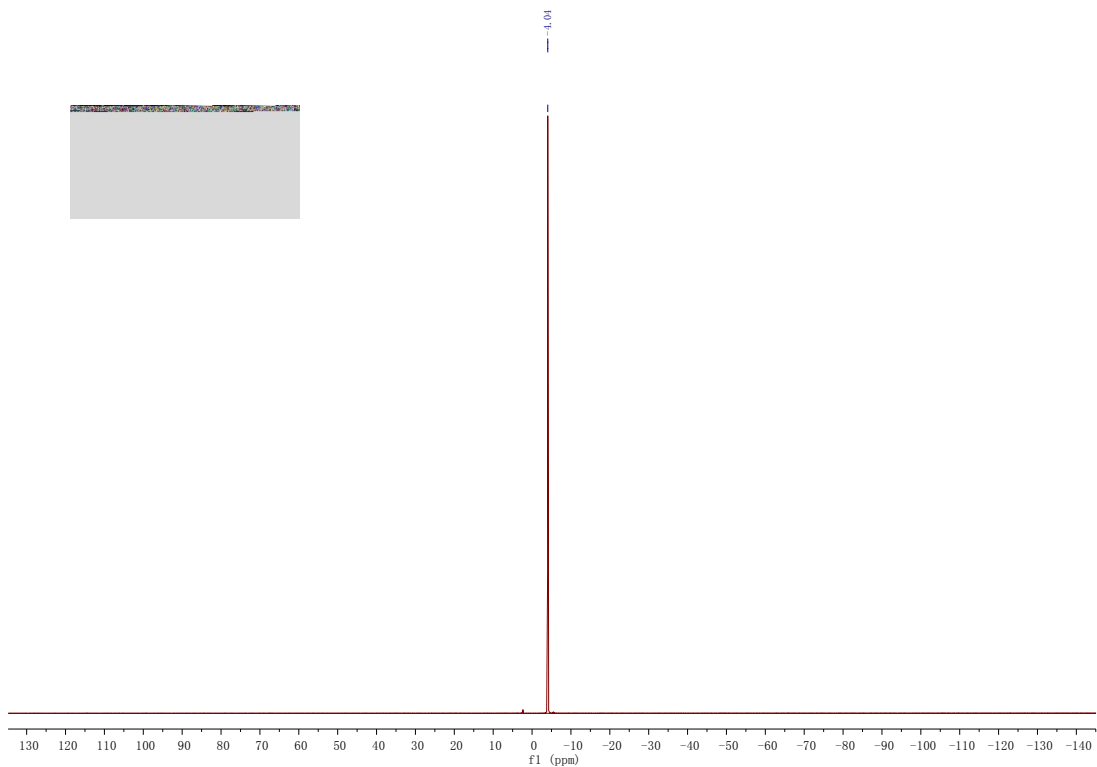


Fig.S 23 ^{31}P NMR of compound **3f**

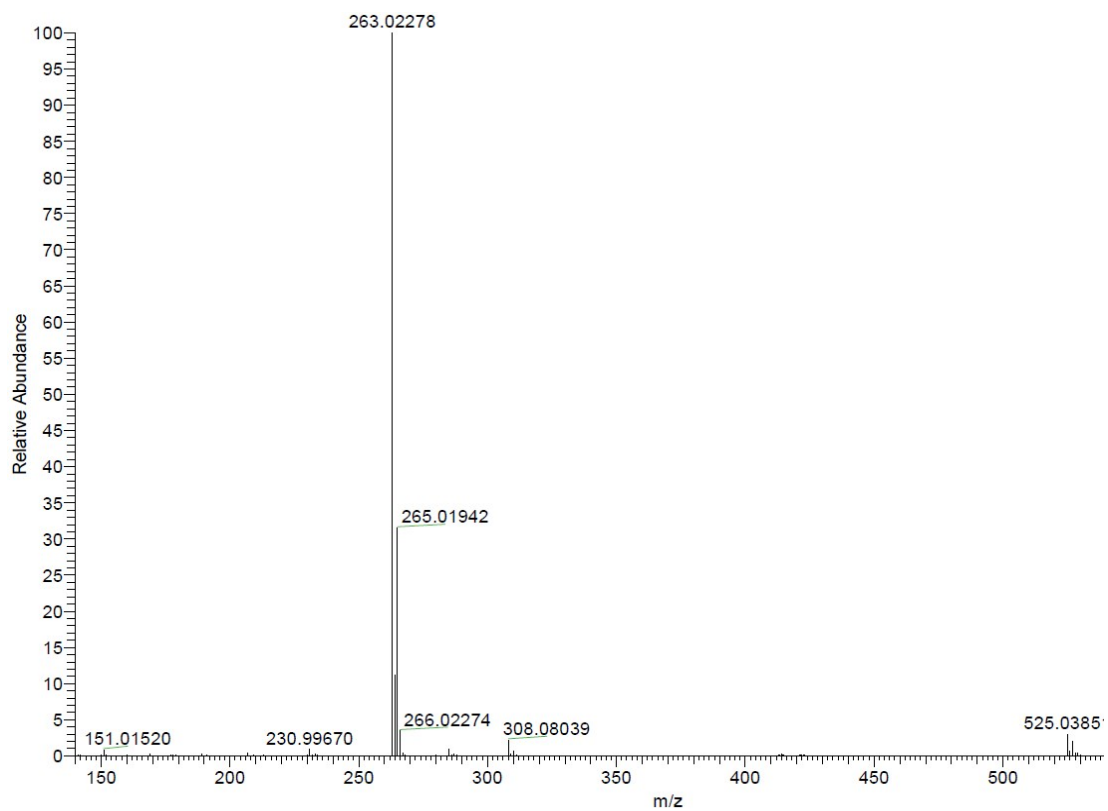


Fig.S 24 HRMS of compound **3f**

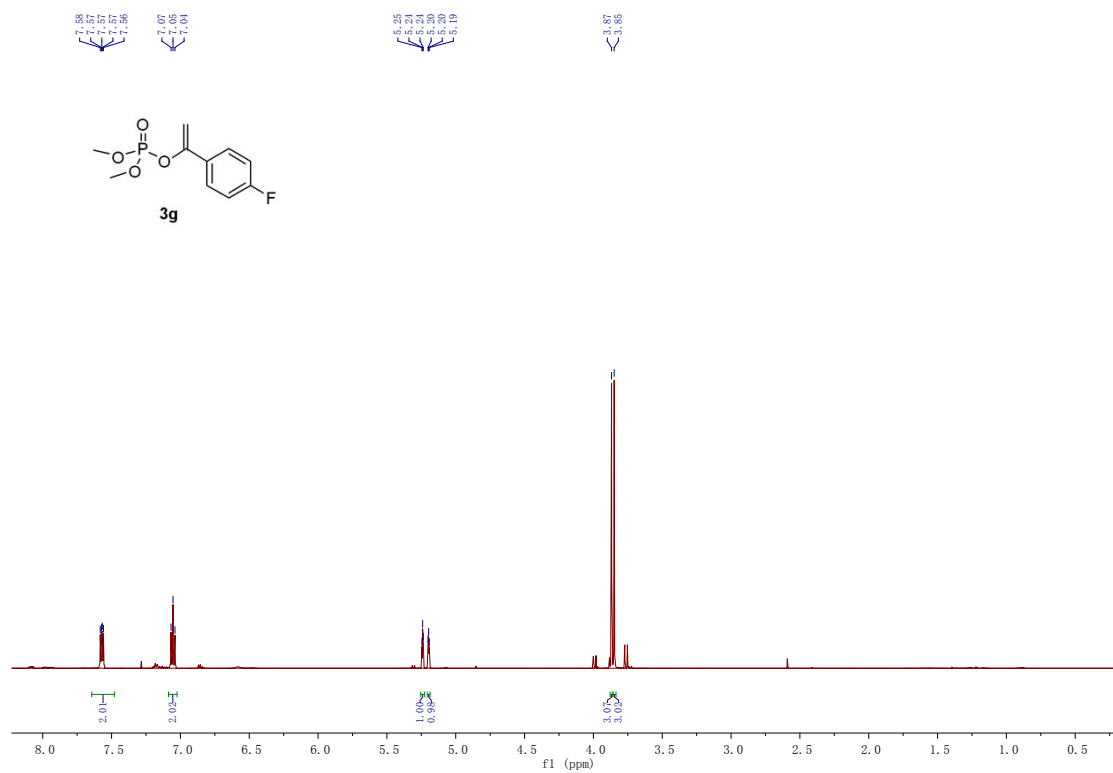


Fig.S 25 ¹H NMR of compound **3g**

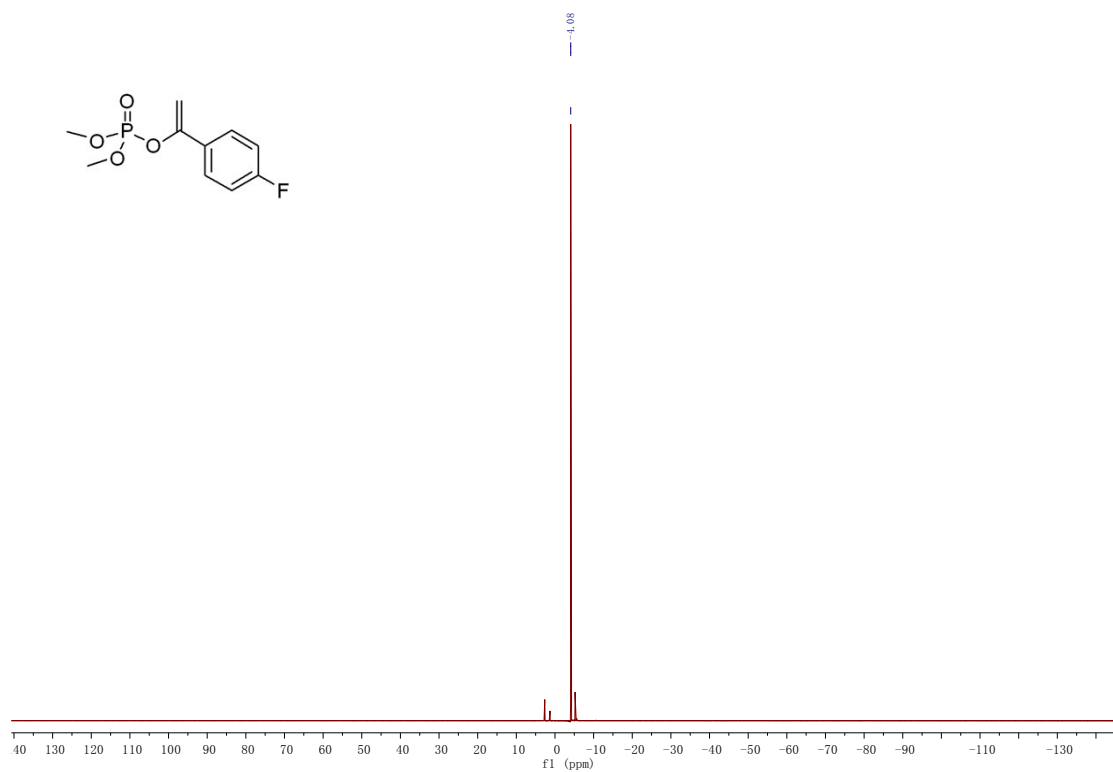


Fig.S 26 ¹³C NMR of compound **3g**

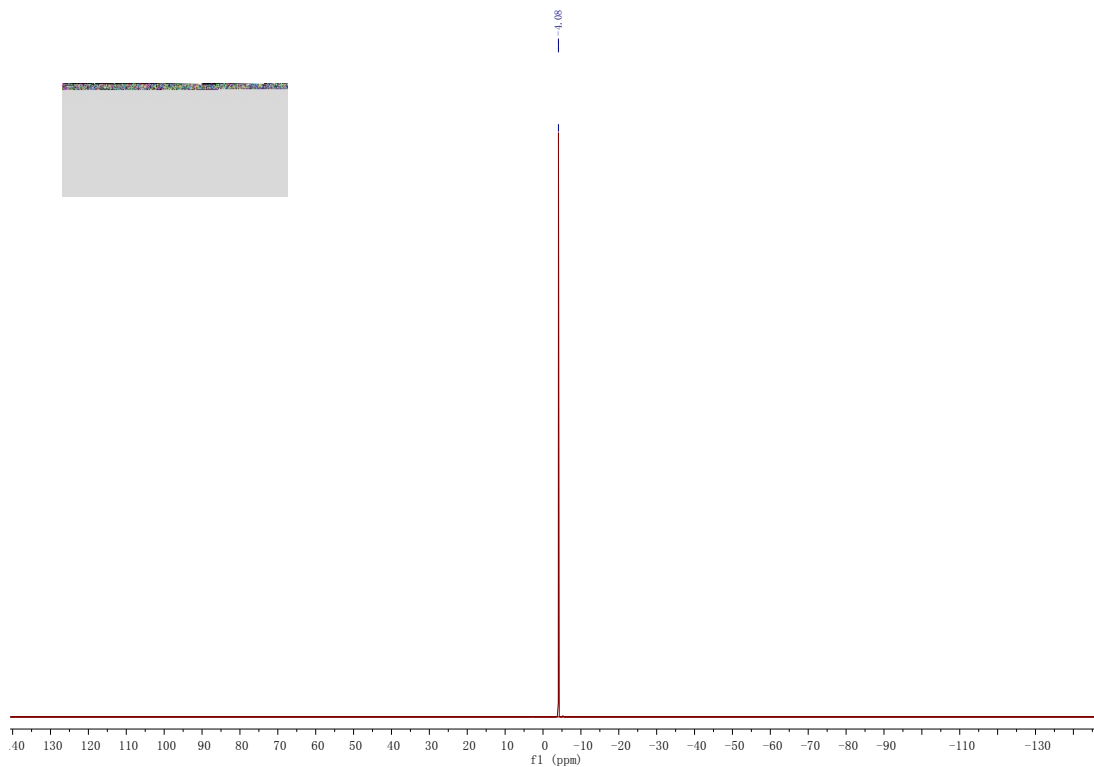


Fig.S 27 ^{31}P NMR of compound **3g**

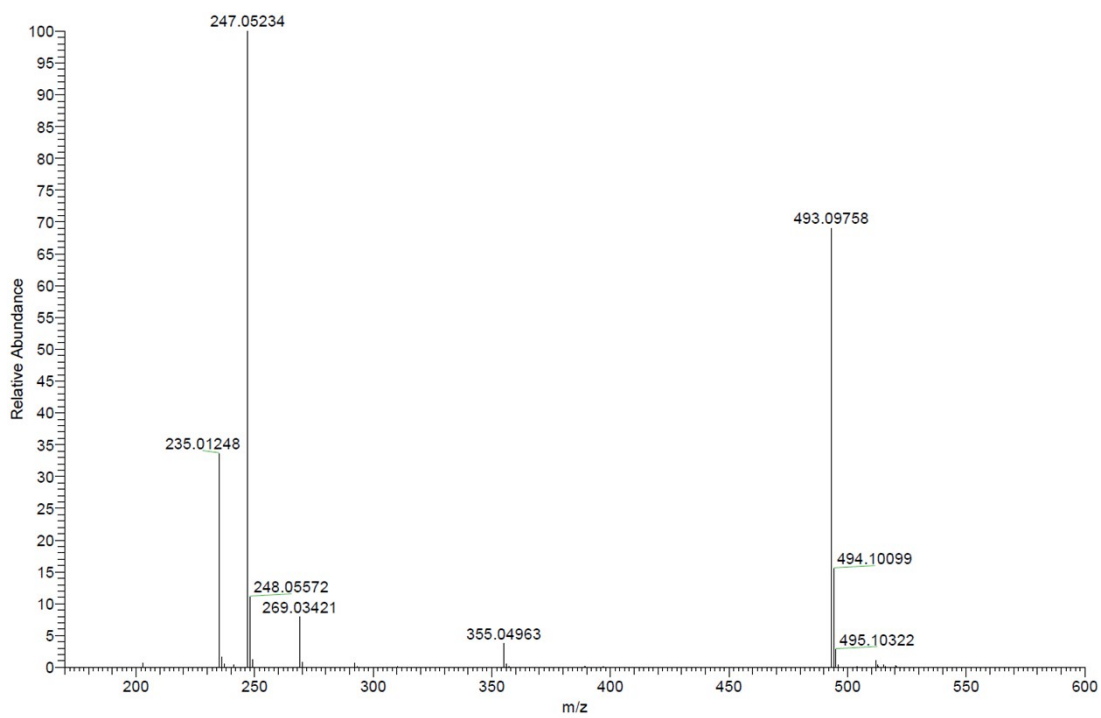


Fig.S 28 HRMS of compound **3g**

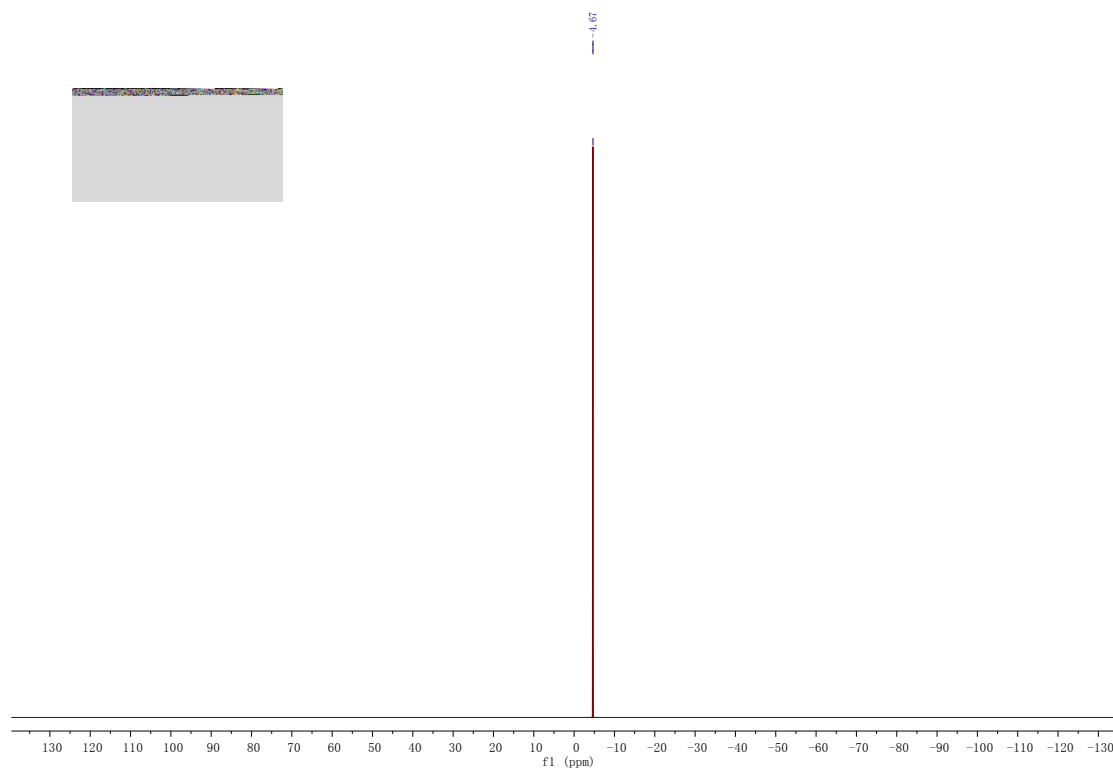


Fig.S 31 ^{31}P NMR of compound **3h**

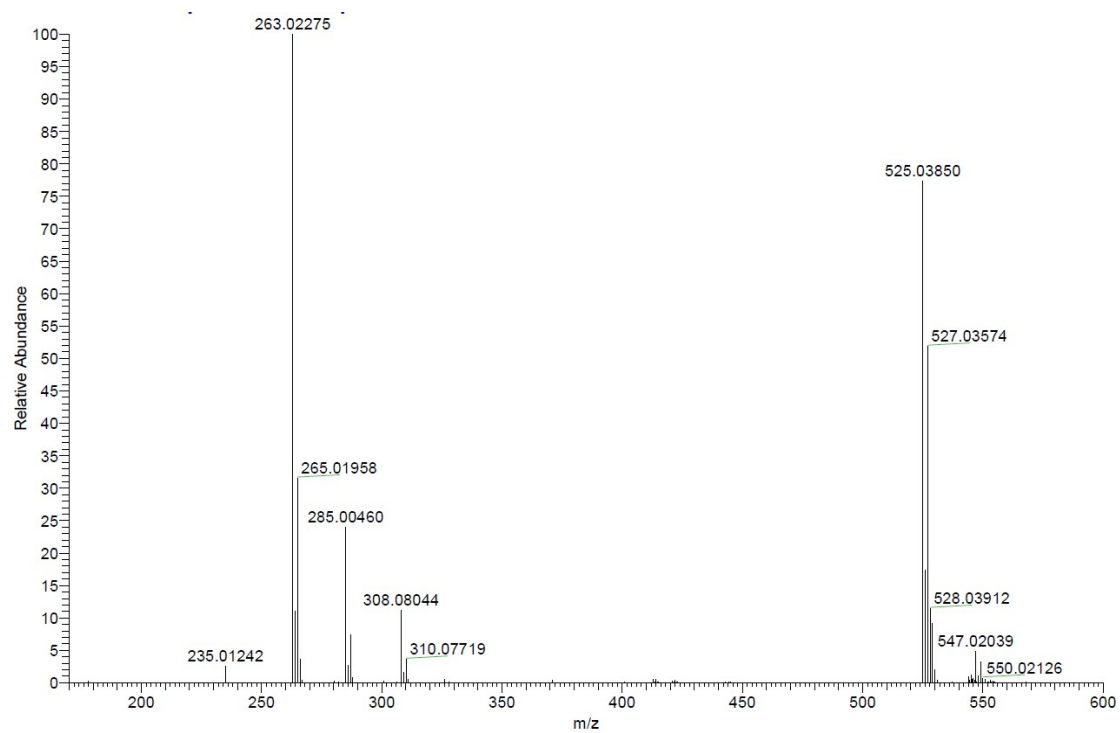


Fig.S 32 HRMS of compound **3h**

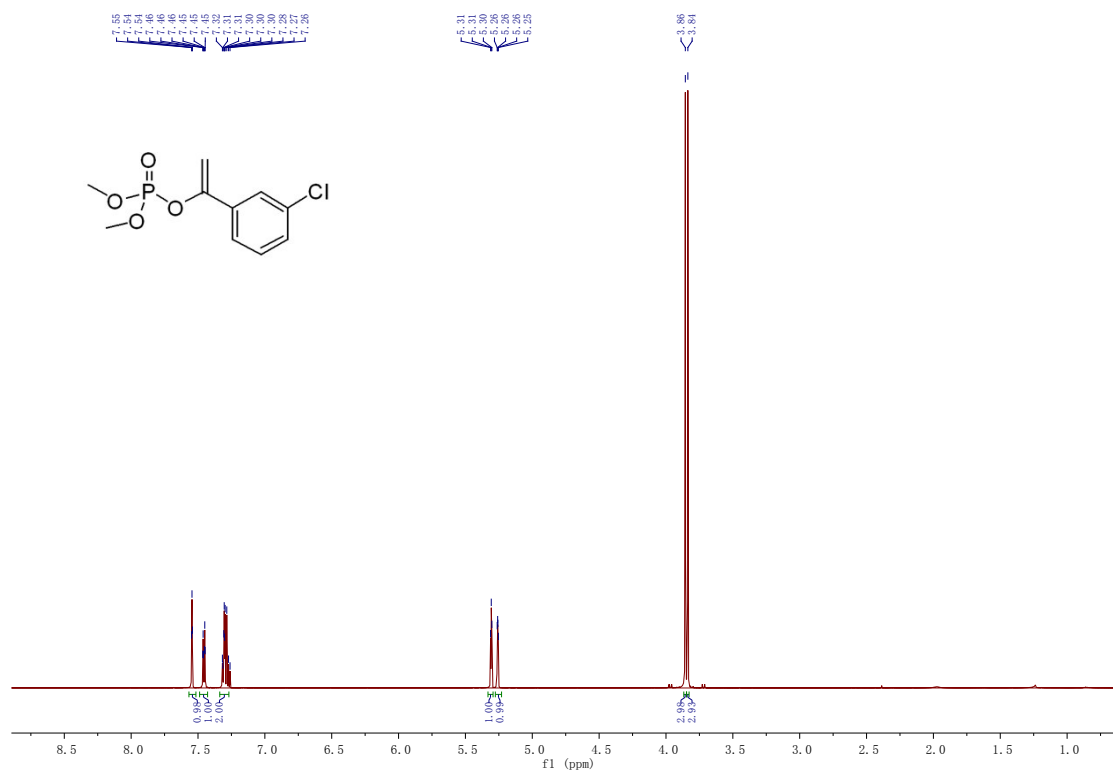


Fig.S 33 ¹H NMR of compound 3i

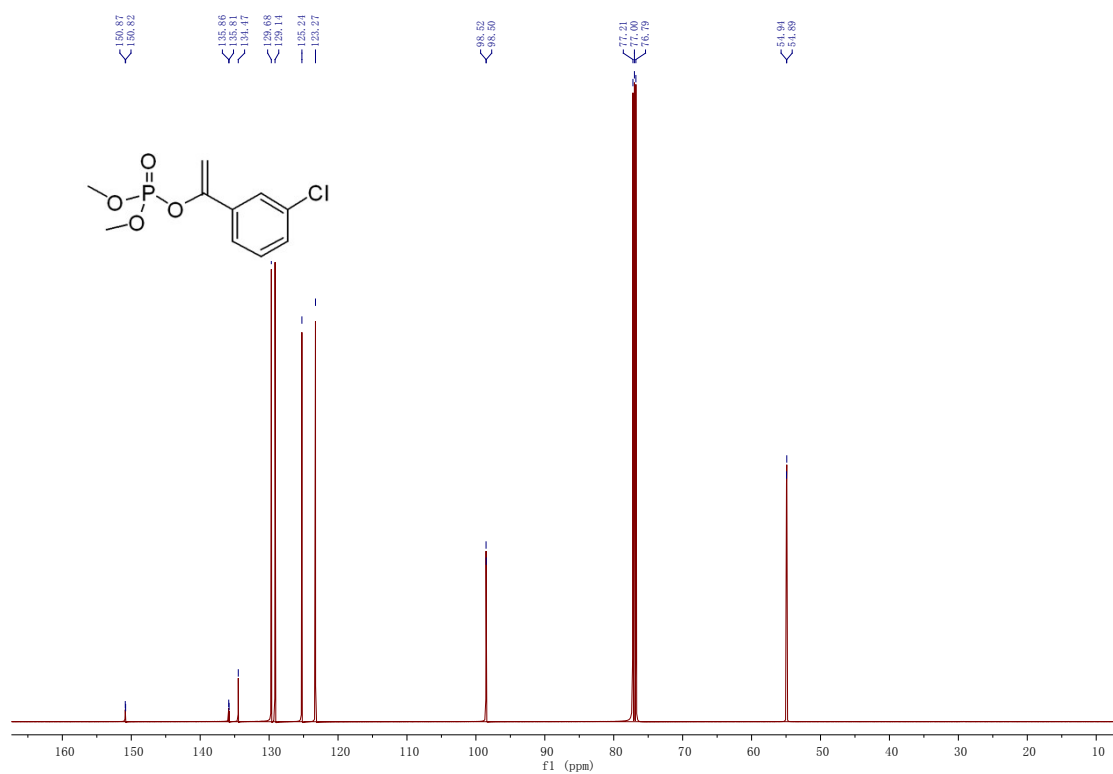


Fig.S 34 ¹³C NMR of compound 3i

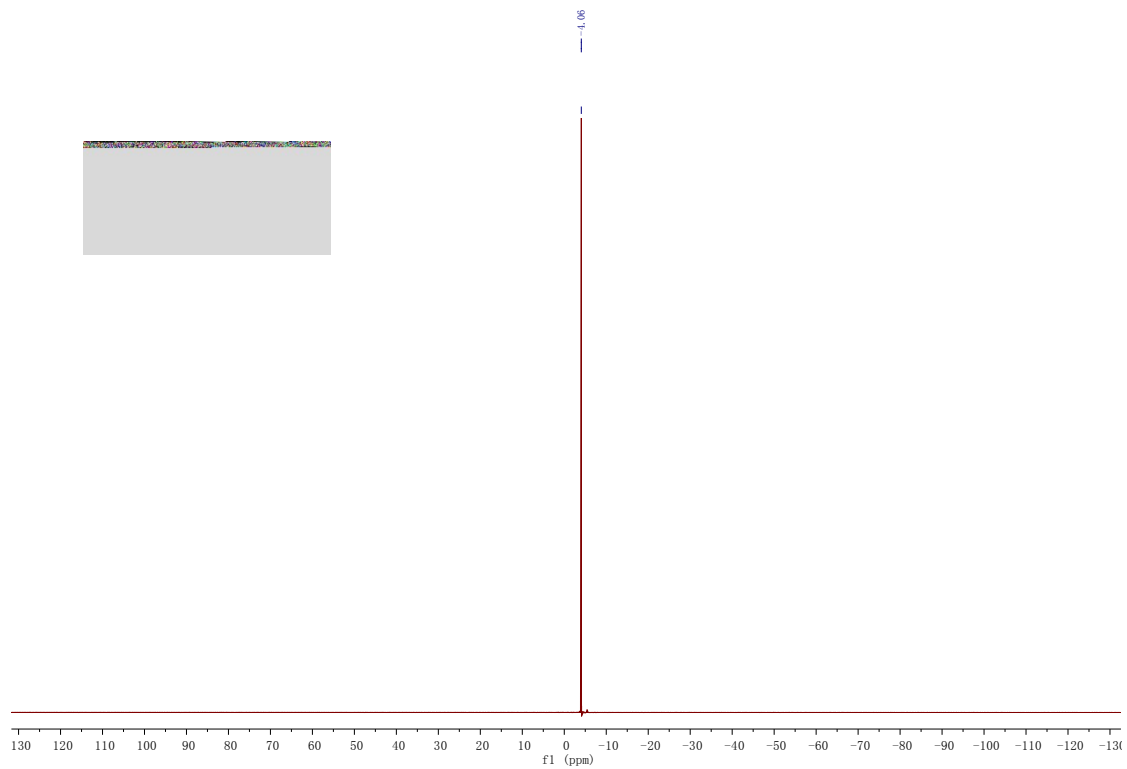


Fig.S 35 ^{31}P NMR of compound **3i**

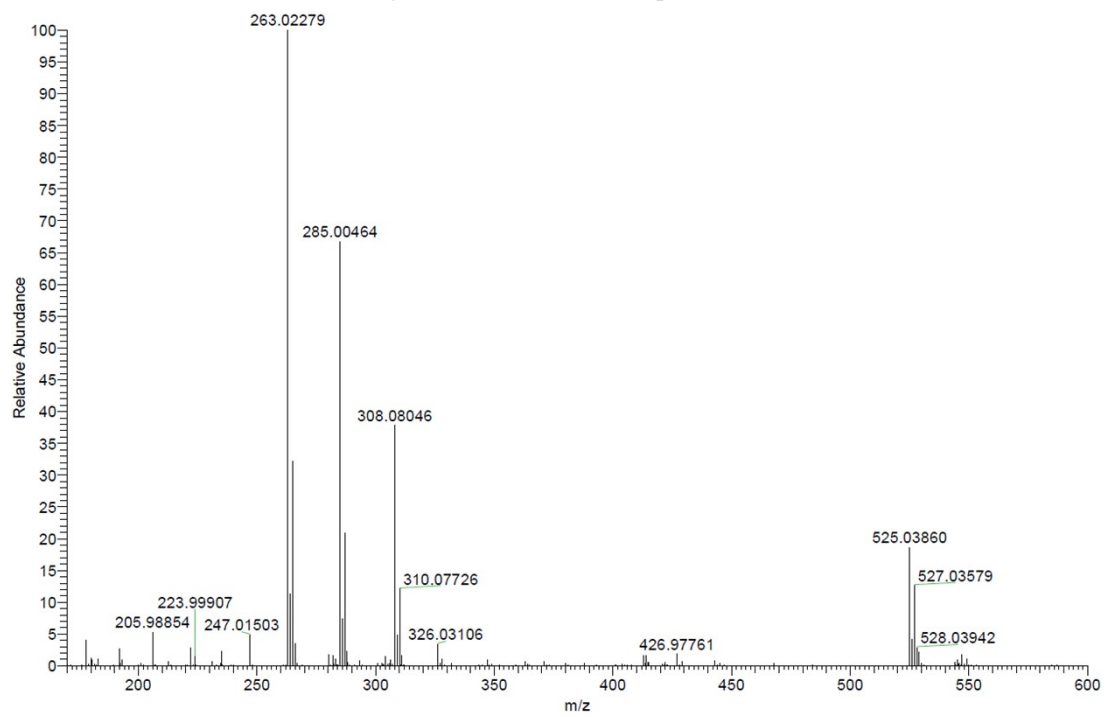


Fig.S 36 HRMS of compound **3i**

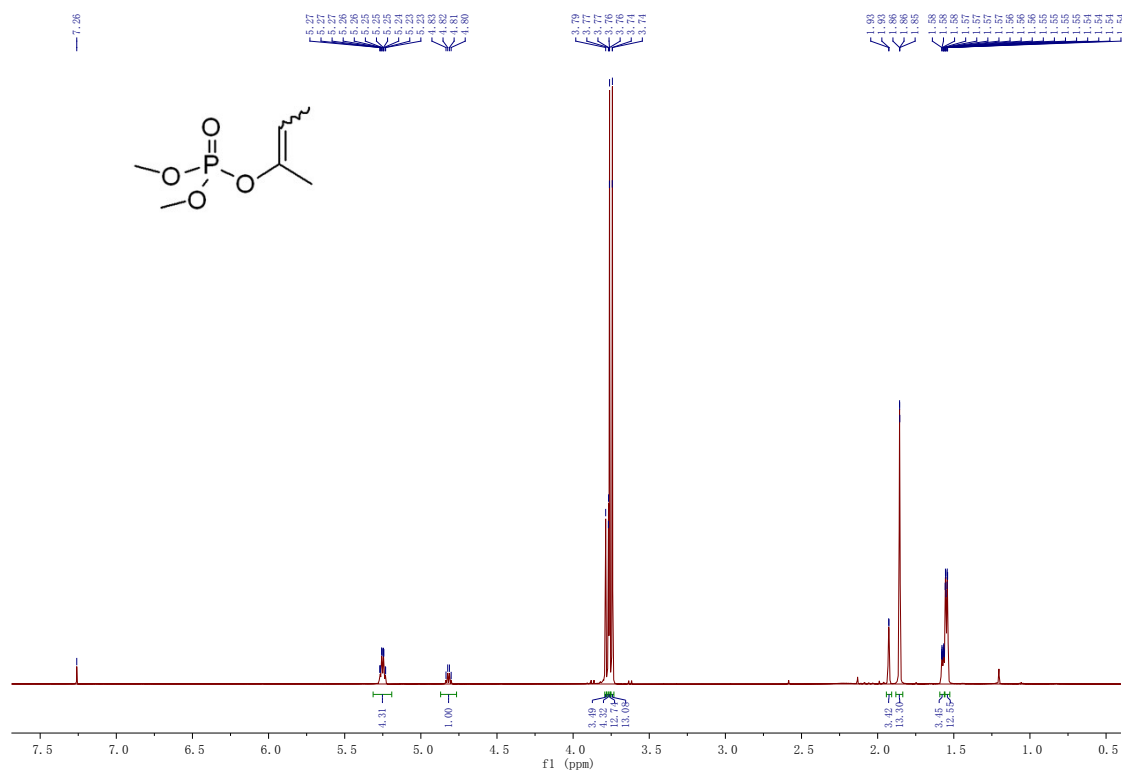


Fig.S 37 ¹H NMR of compound **3j**

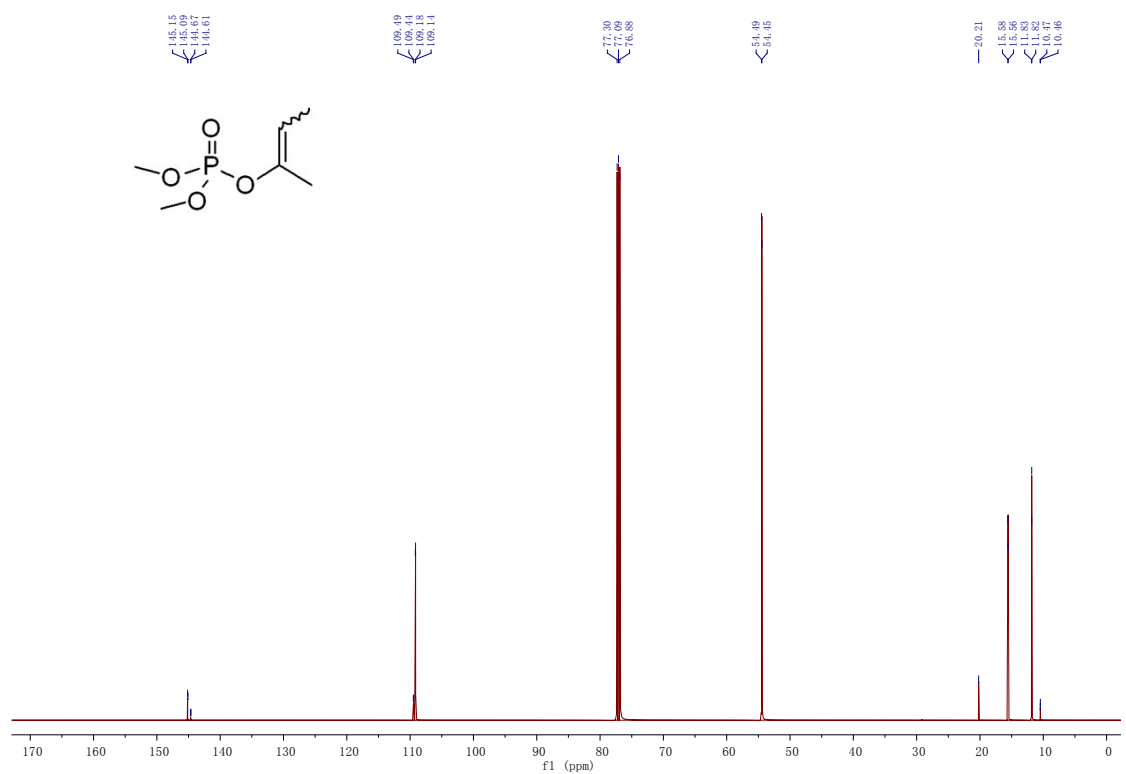


Fig.S 38 ¹³C NMR of compound **3j**

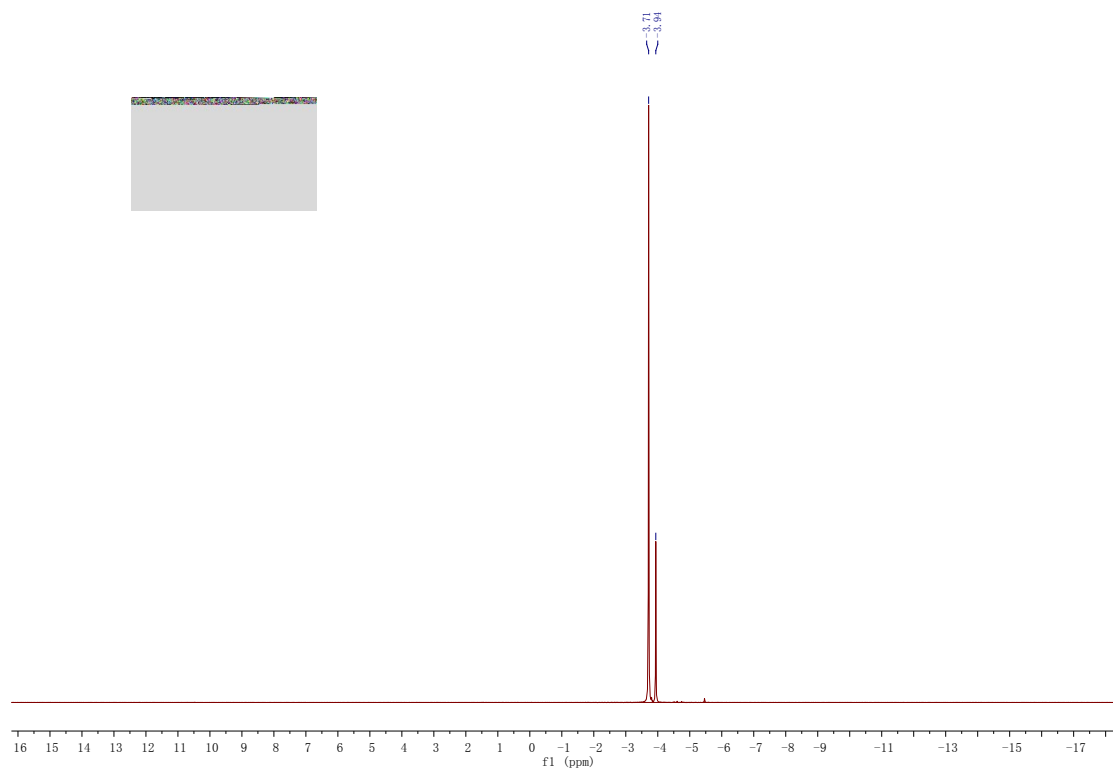


Fig.S 39 ^{31}P NMR of compound **3j**

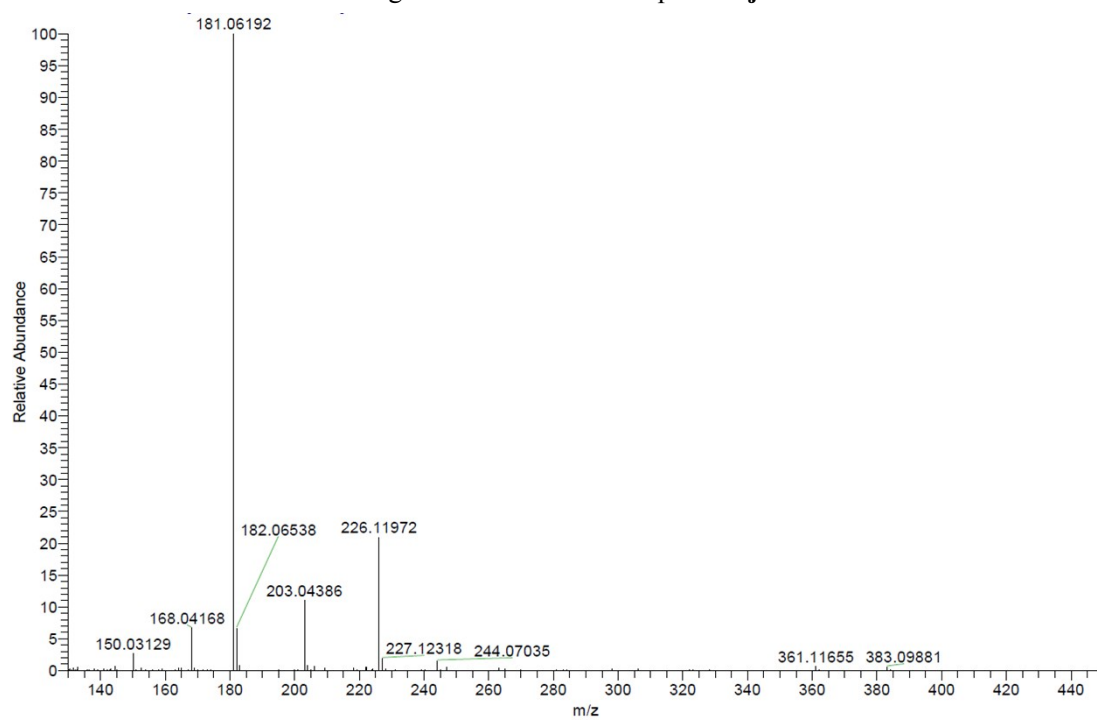


Fig.S 40 HRMS of compound **3j**

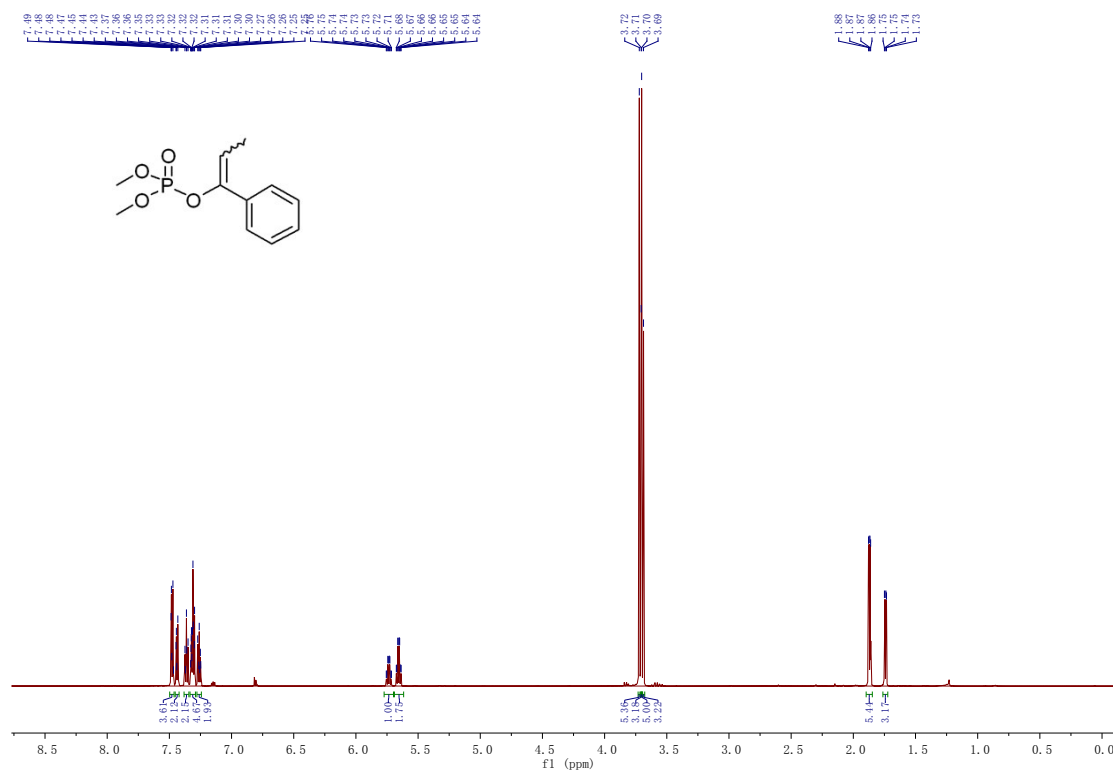


Fig.S 41 ¹H NMR of compound 3k

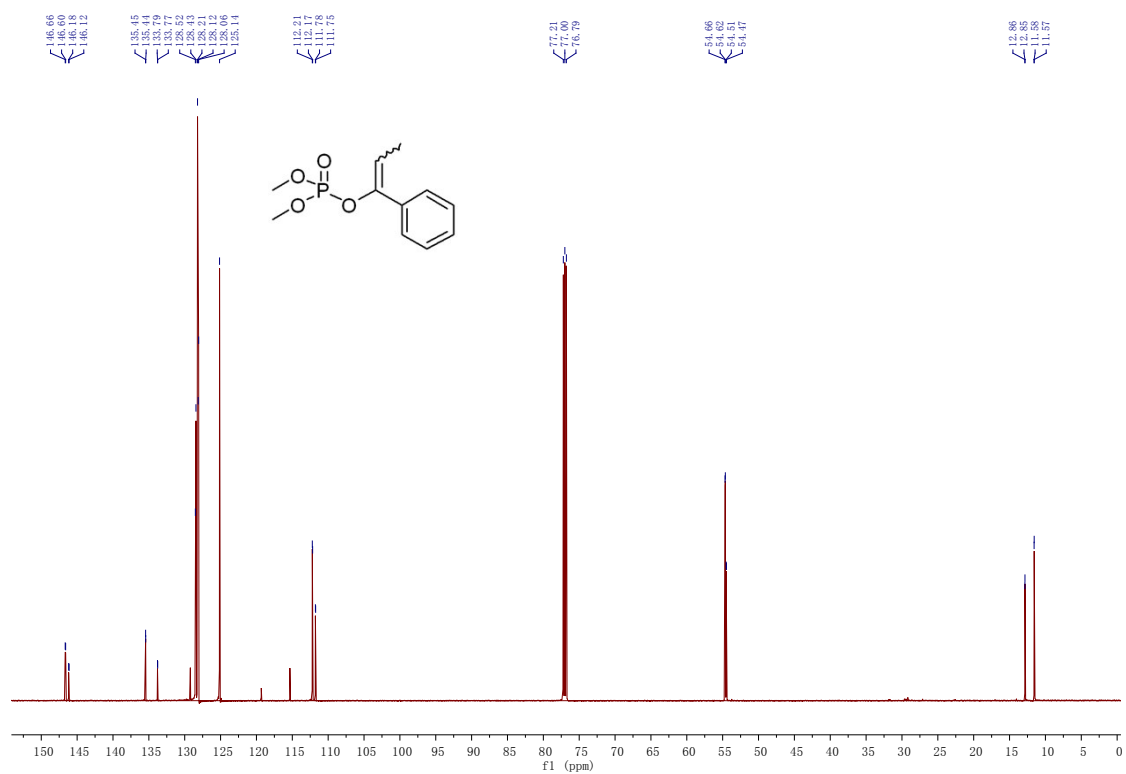


Fig.S 42 ¹³C NMR of compound 3k

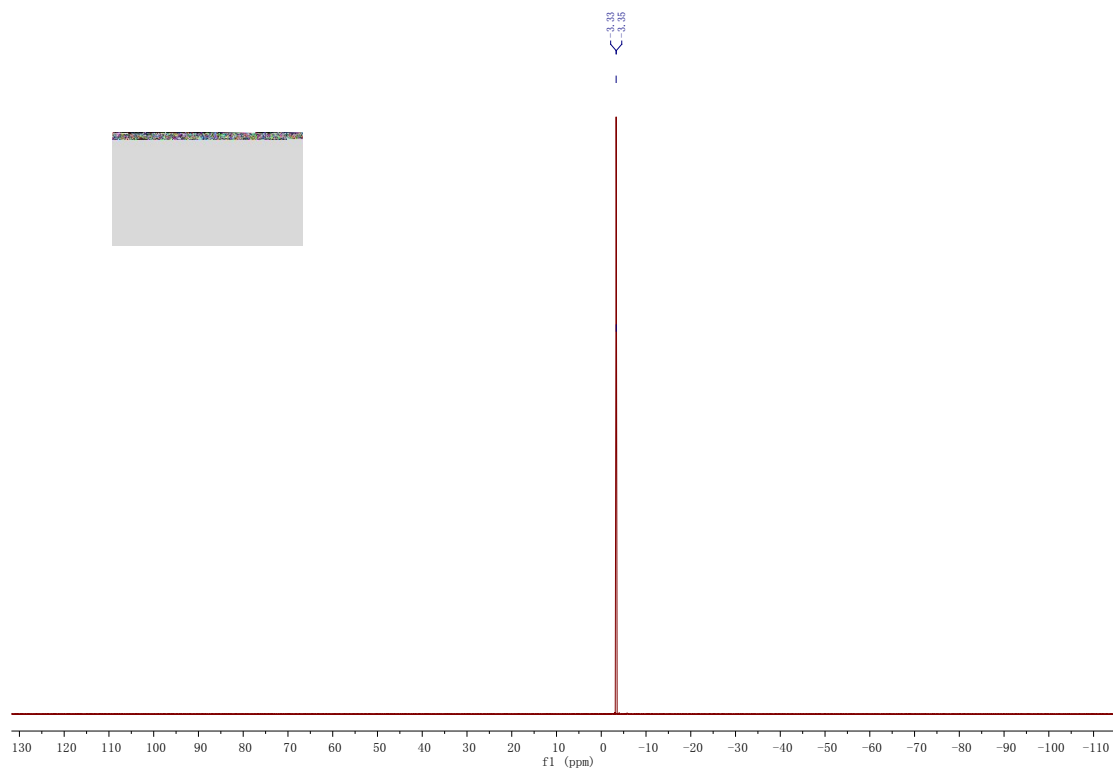


Fig.S 43 ^{31}P NMR of compound **3k**

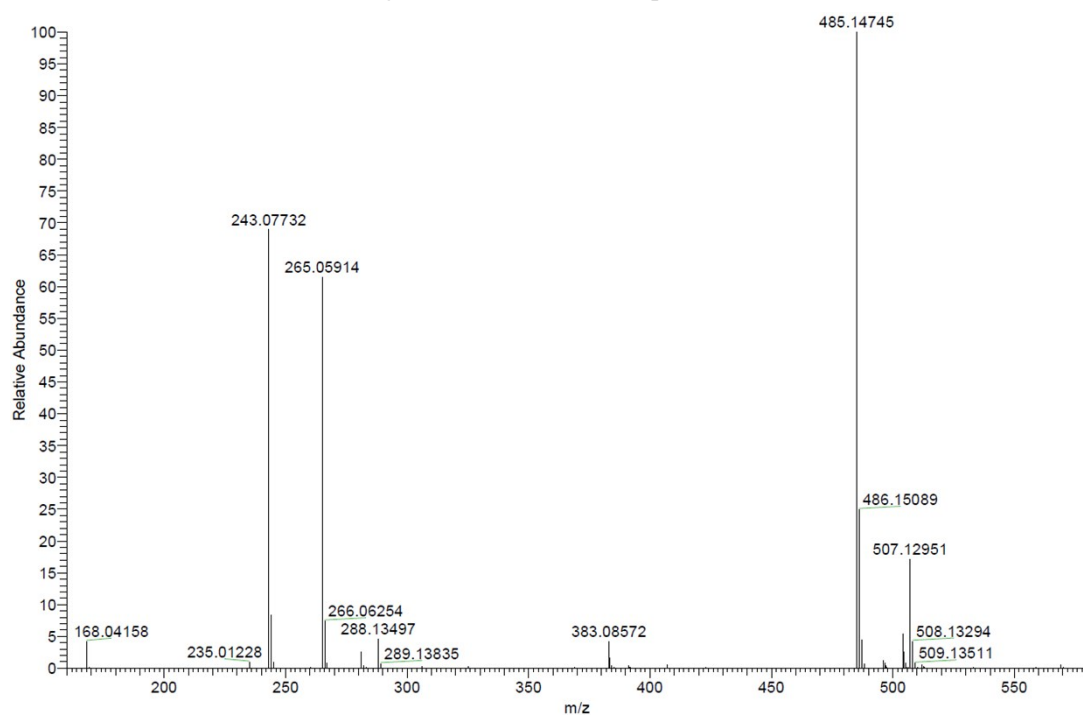


Fig.S 44 HRMS of compound **3k**

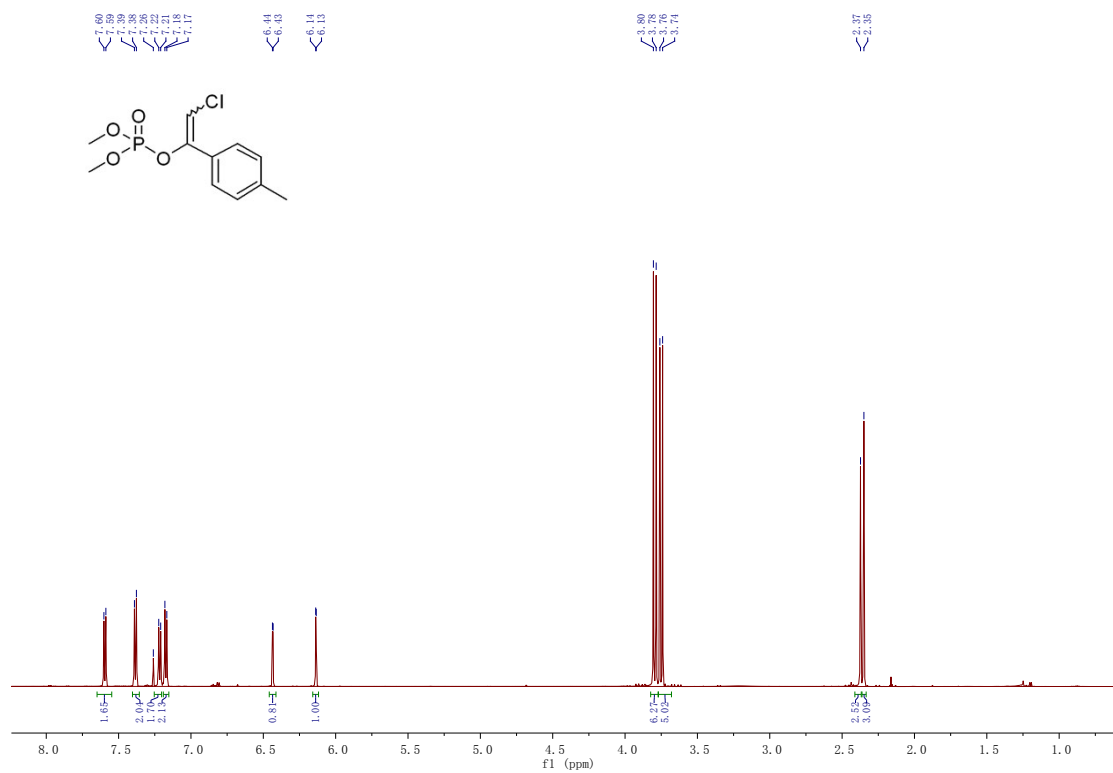


Fig.S 45 ¹H NMR of compound 31

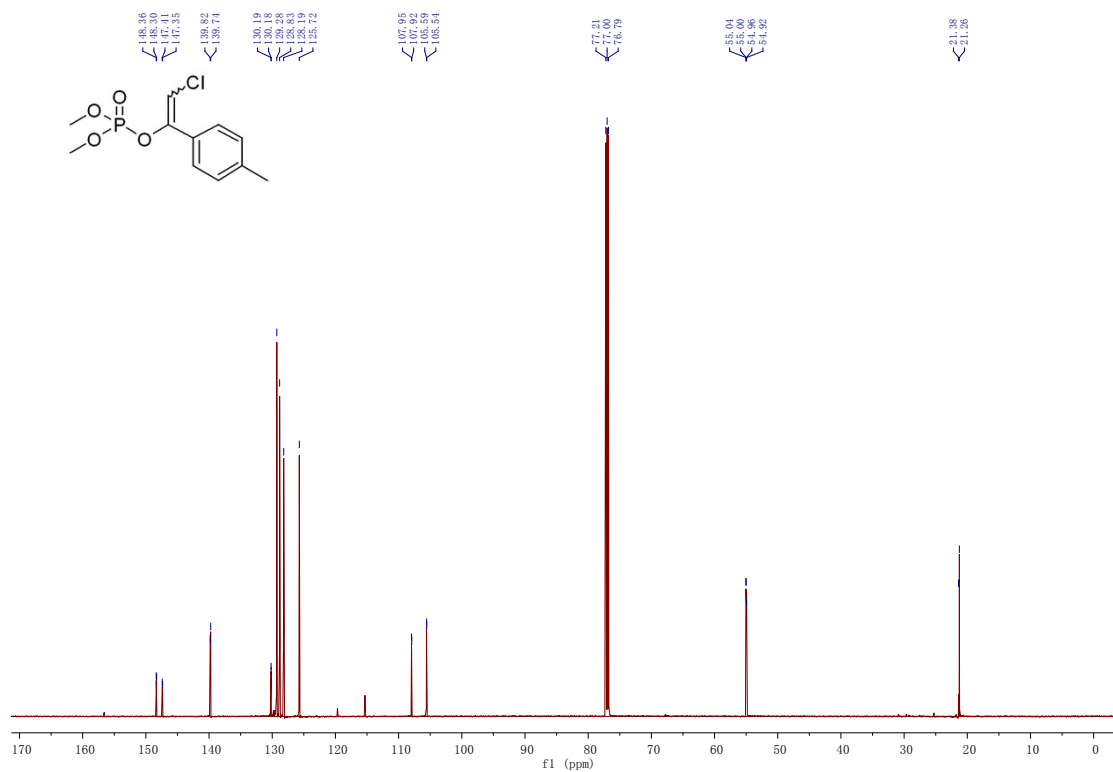


Fig.S 46 ¹³C NMR of compound 31

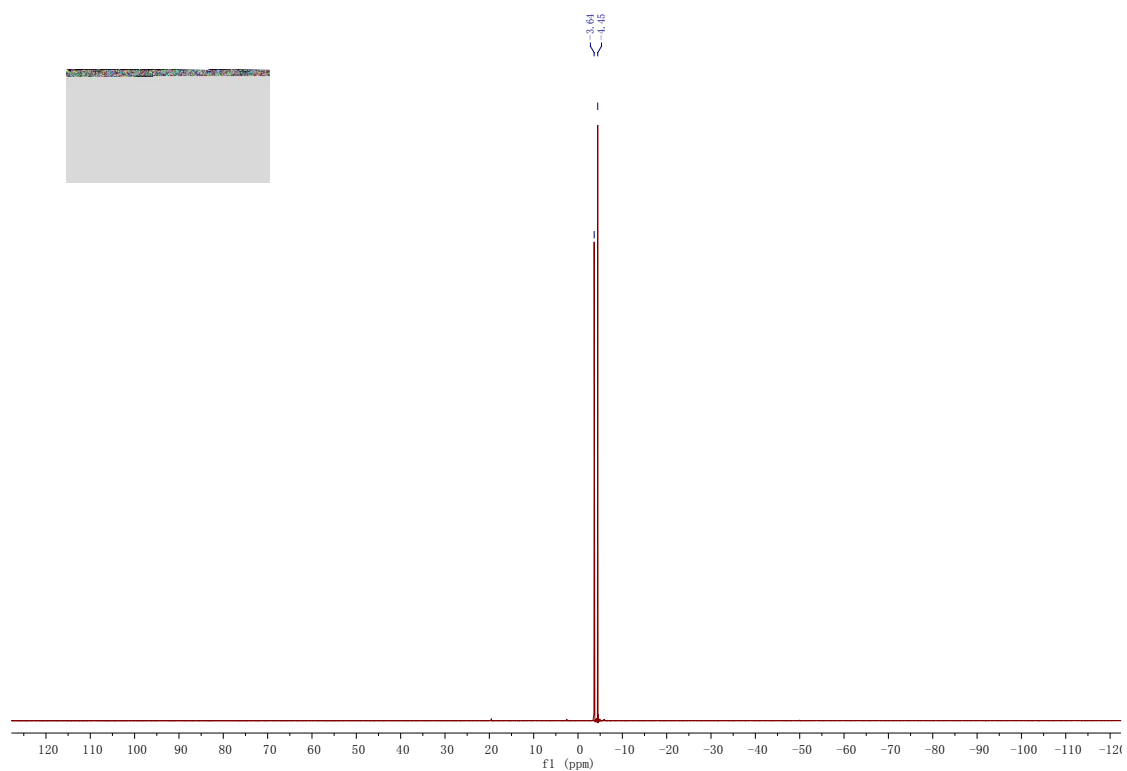


Fig.S 47 ^{31}P NMR of compound **31**

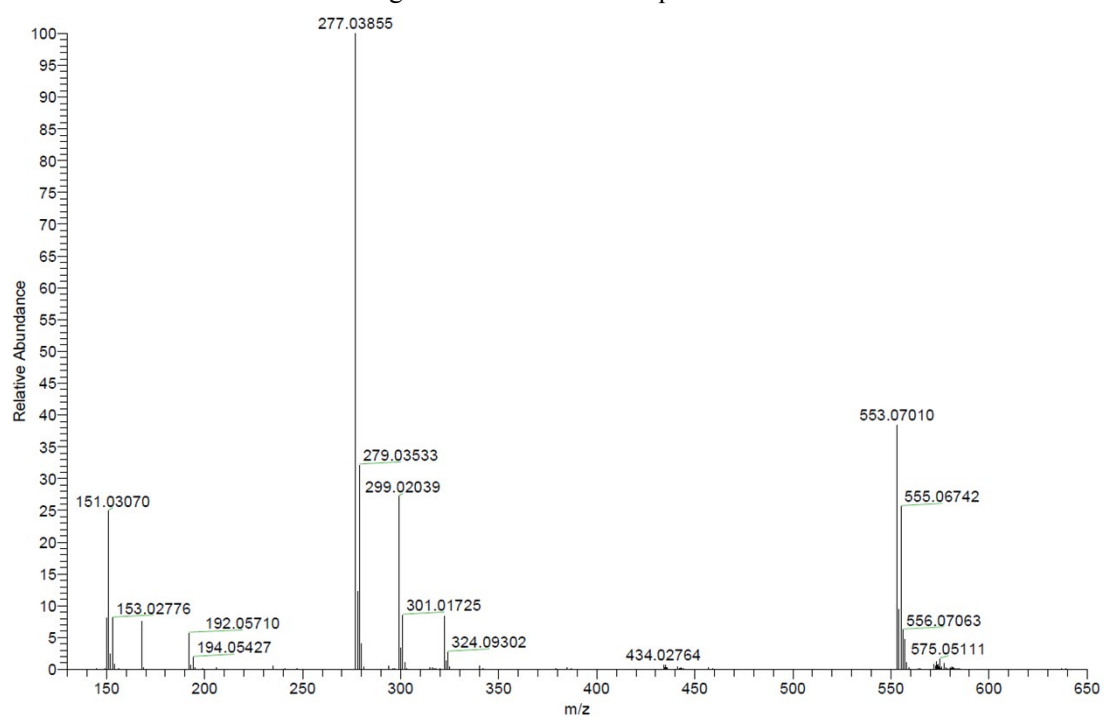


Fig.S 48 HRMS of compound **31**

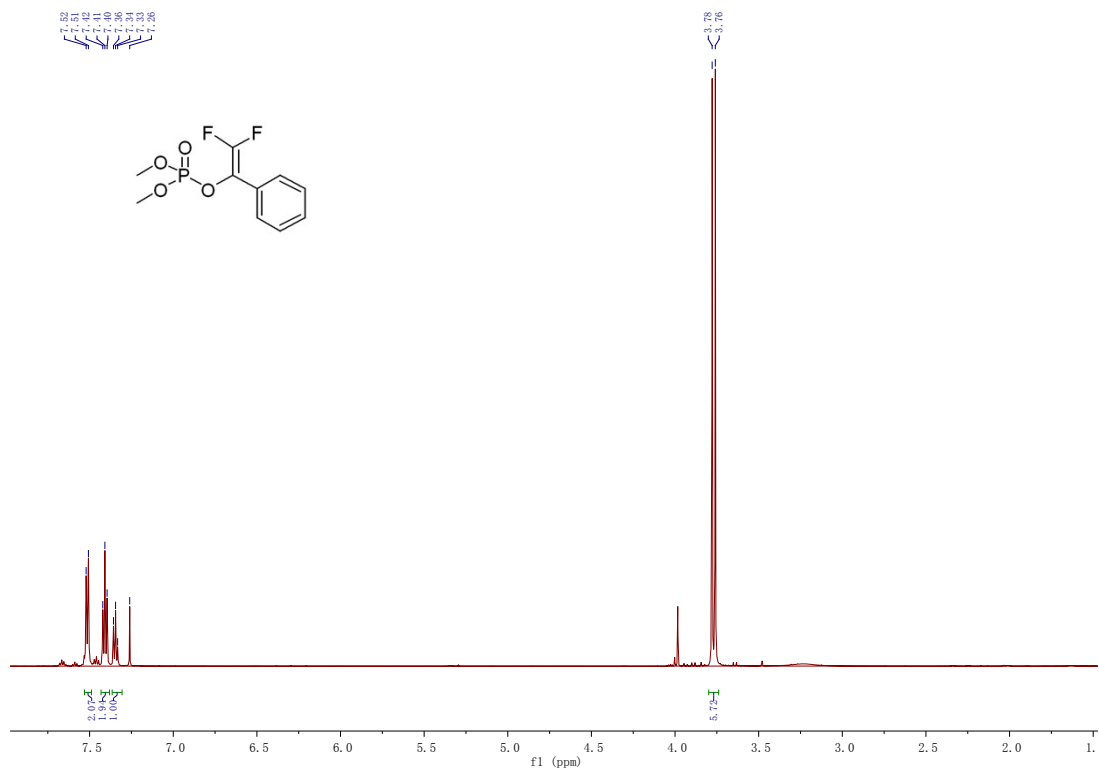


Fig.S 49 ¹H NMR of compound **3m**

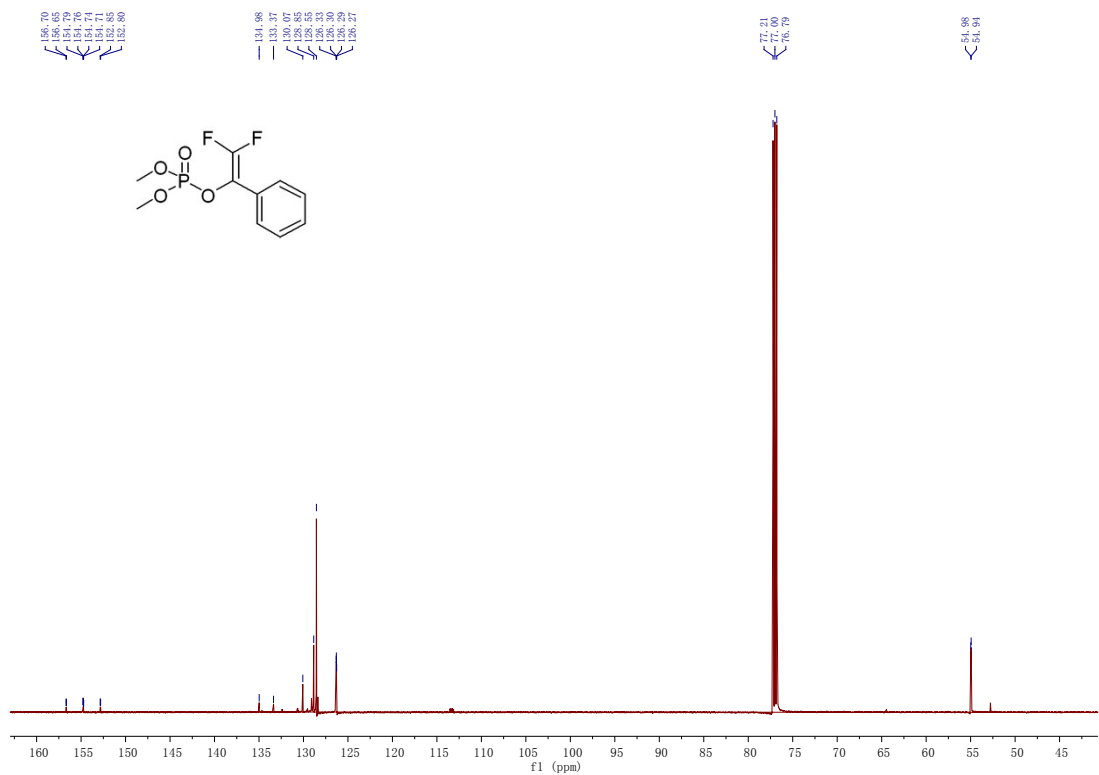


Fig.S 50 ¹³C NMR of compound **3m**

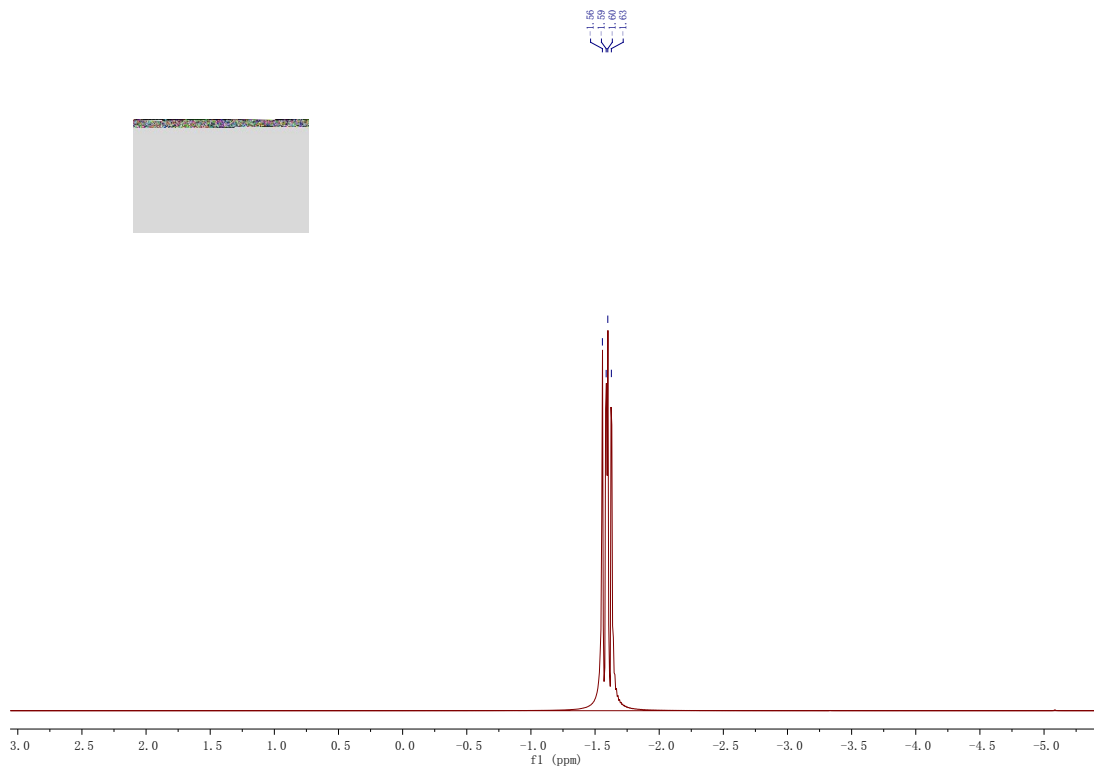


Fig.S 51 ^{31}P NMR of compound **3m**

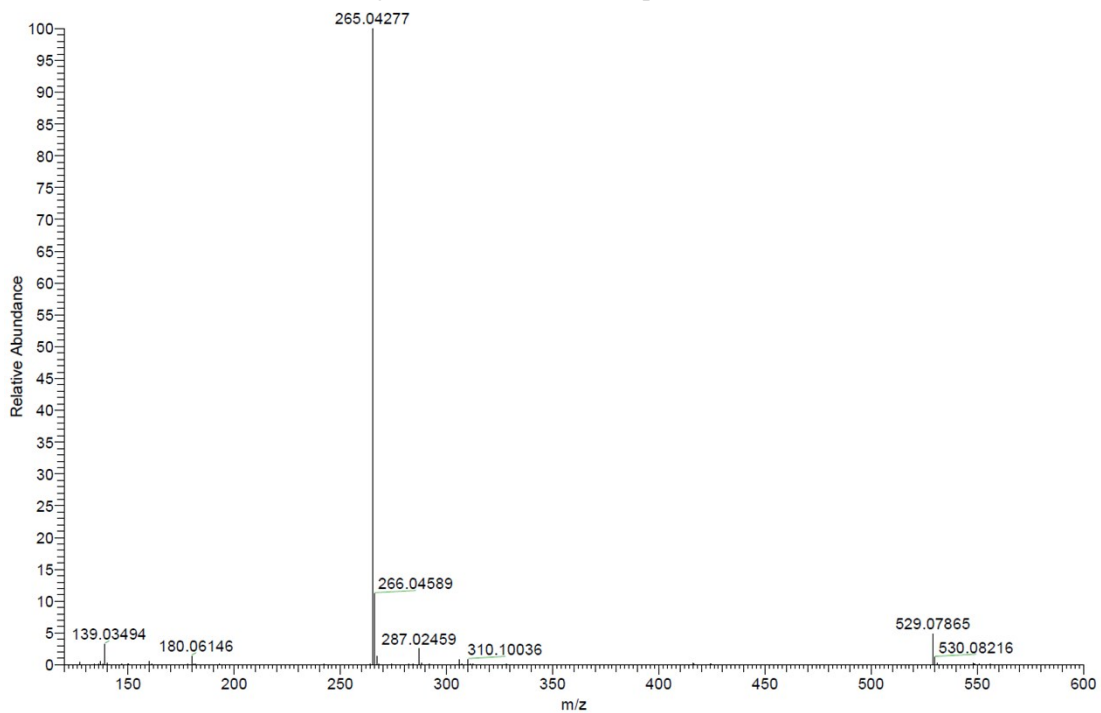


Fig.S 52 HRMS of compound **3m**

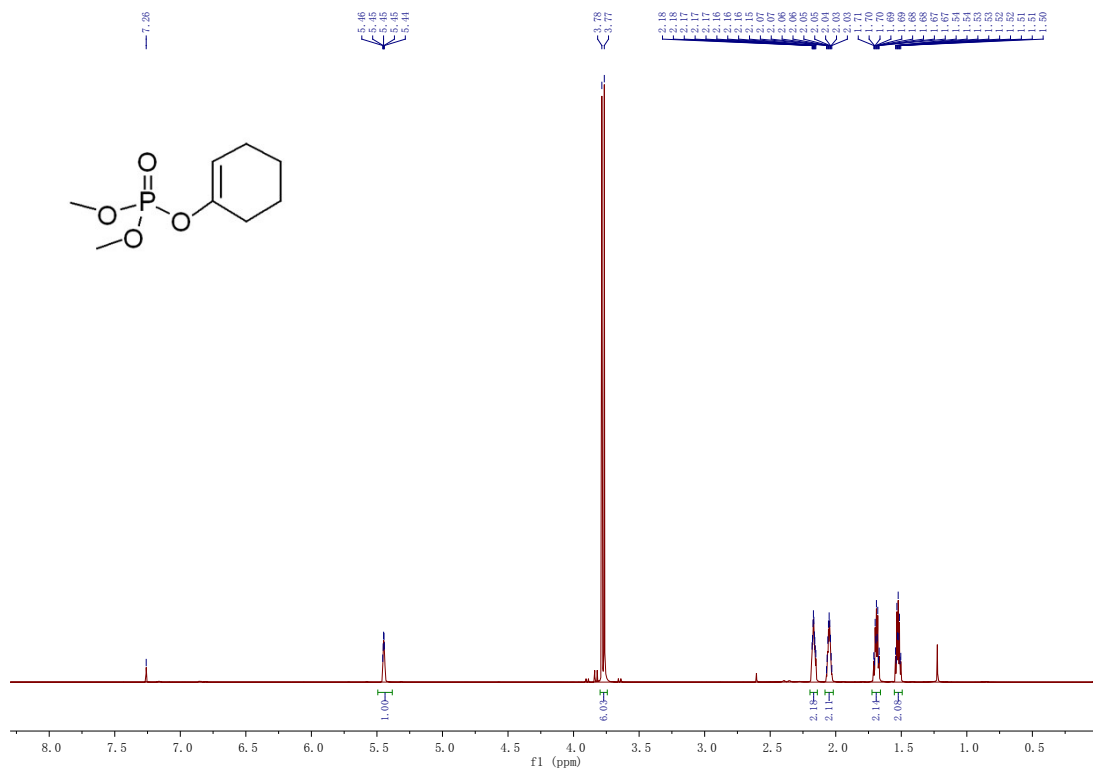


Fig.S 53 ¹H NMR of compound 3n

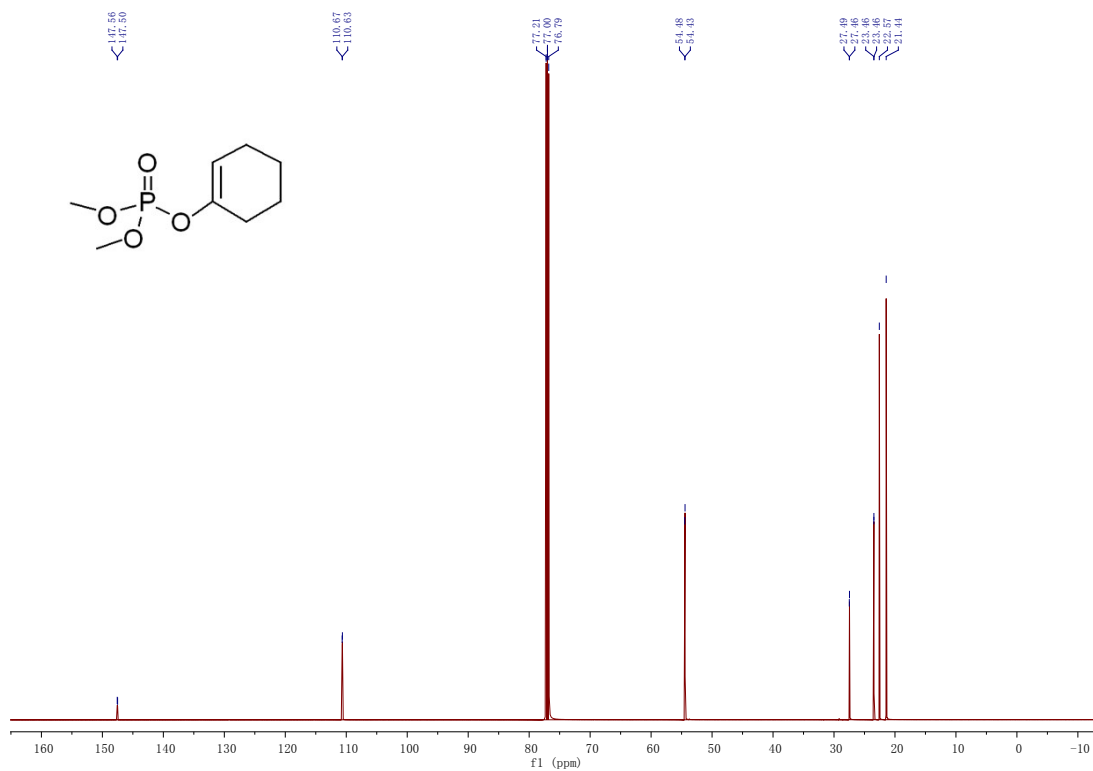


Fig.S 54 ¹³C NMR of compound 3n

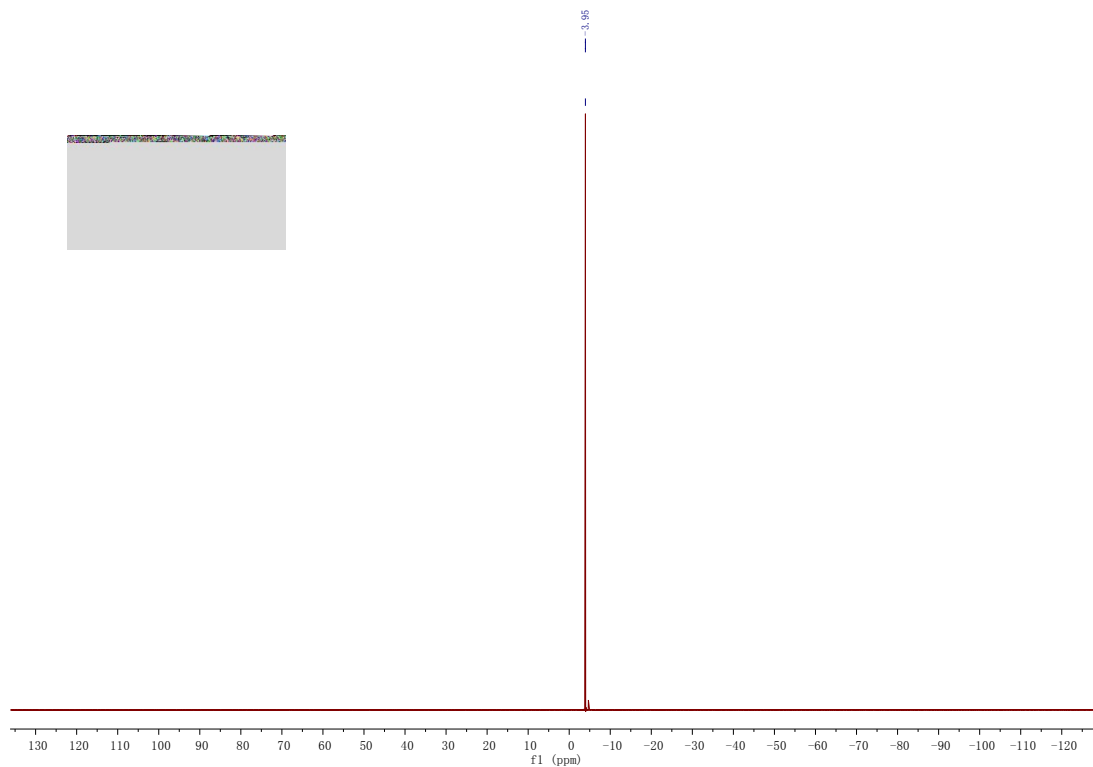


Fig.S 55 ^{31}P NMR of compound **3n**

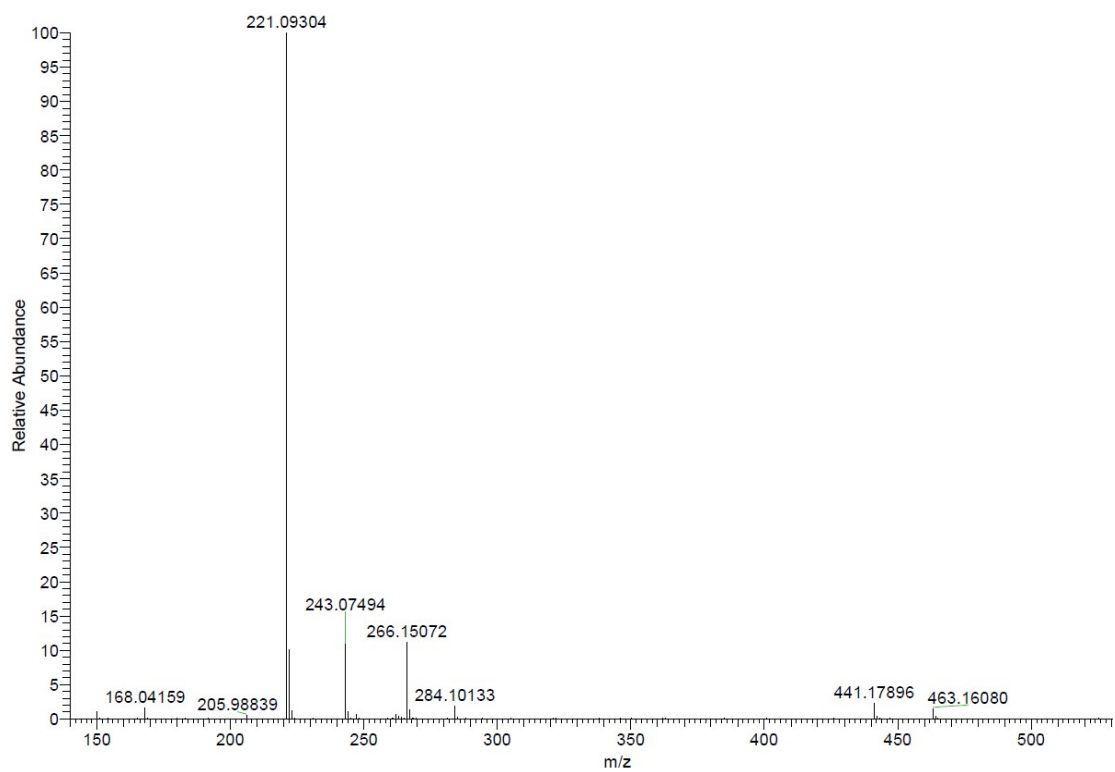


Fig.S 56 HRMS of compound **3n**

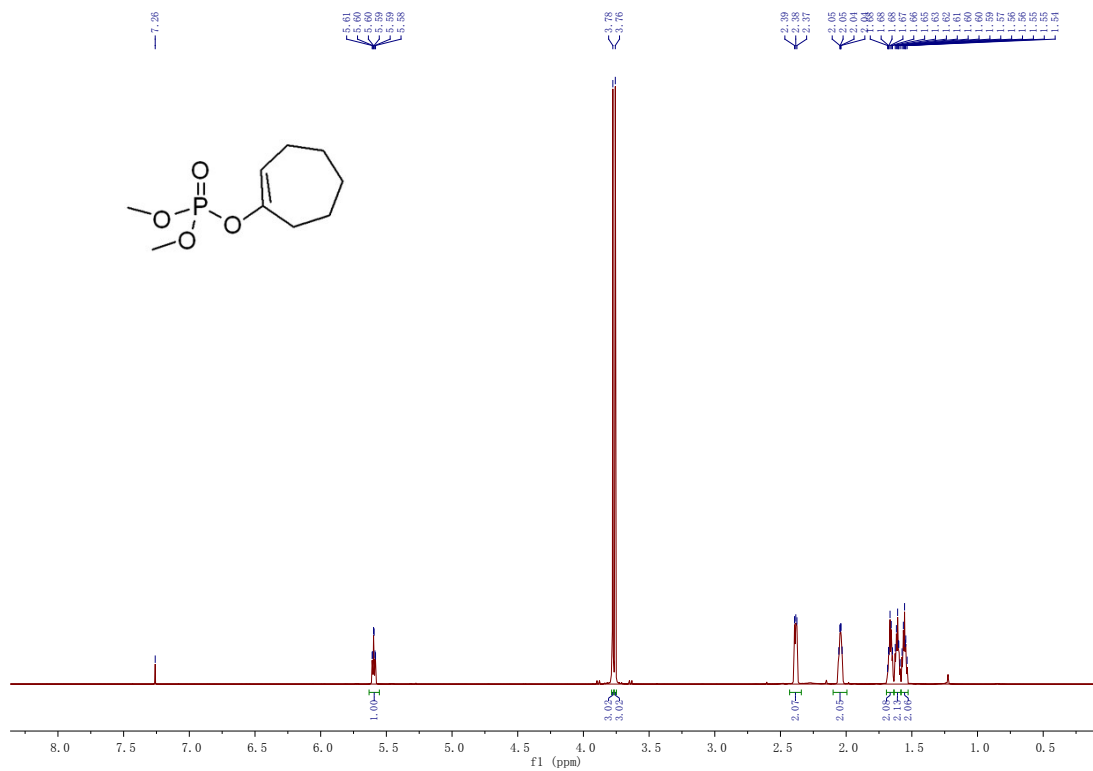


Fig.S 57 ¹H NMR of compound 30

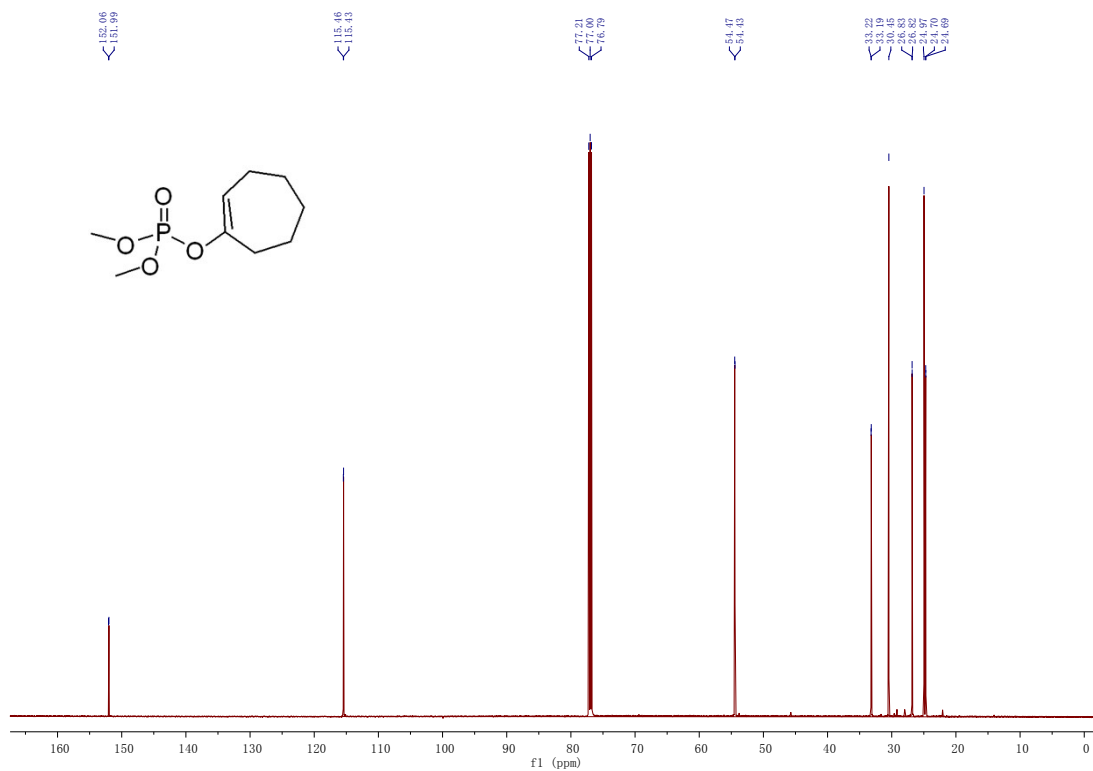


Fig.S 58 ¹³C NMR of compound 30

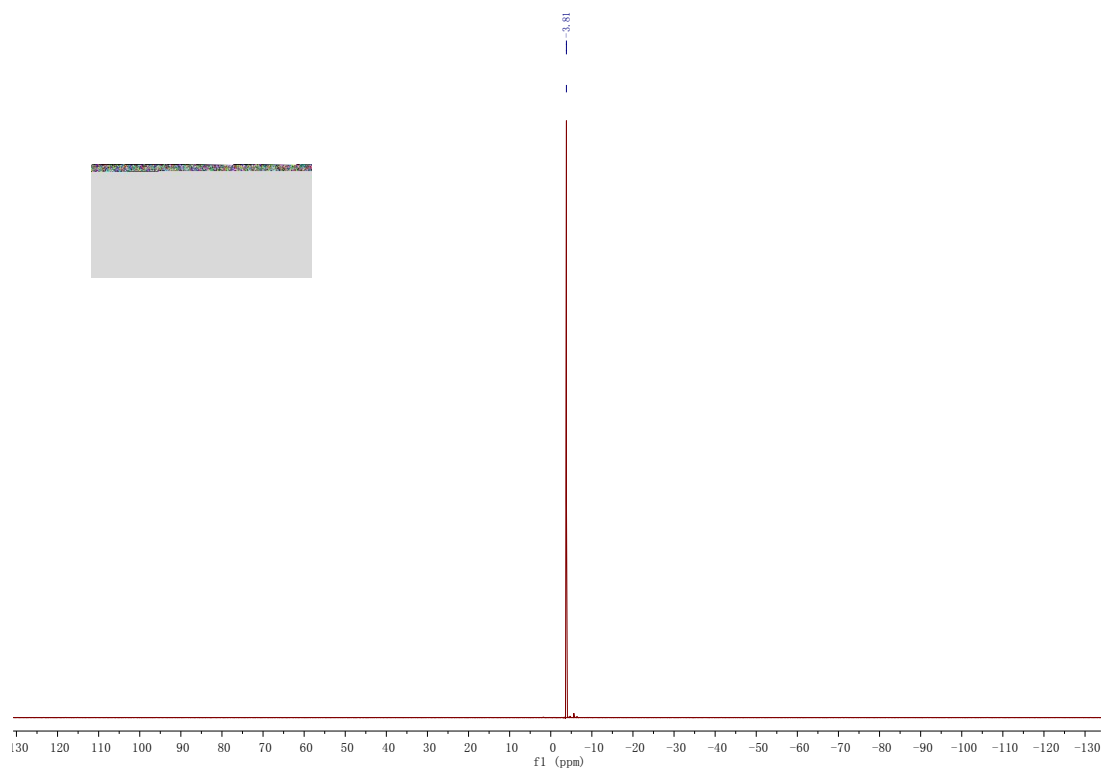


Fig.S 59 ^{31}P NMR of compound **3o**

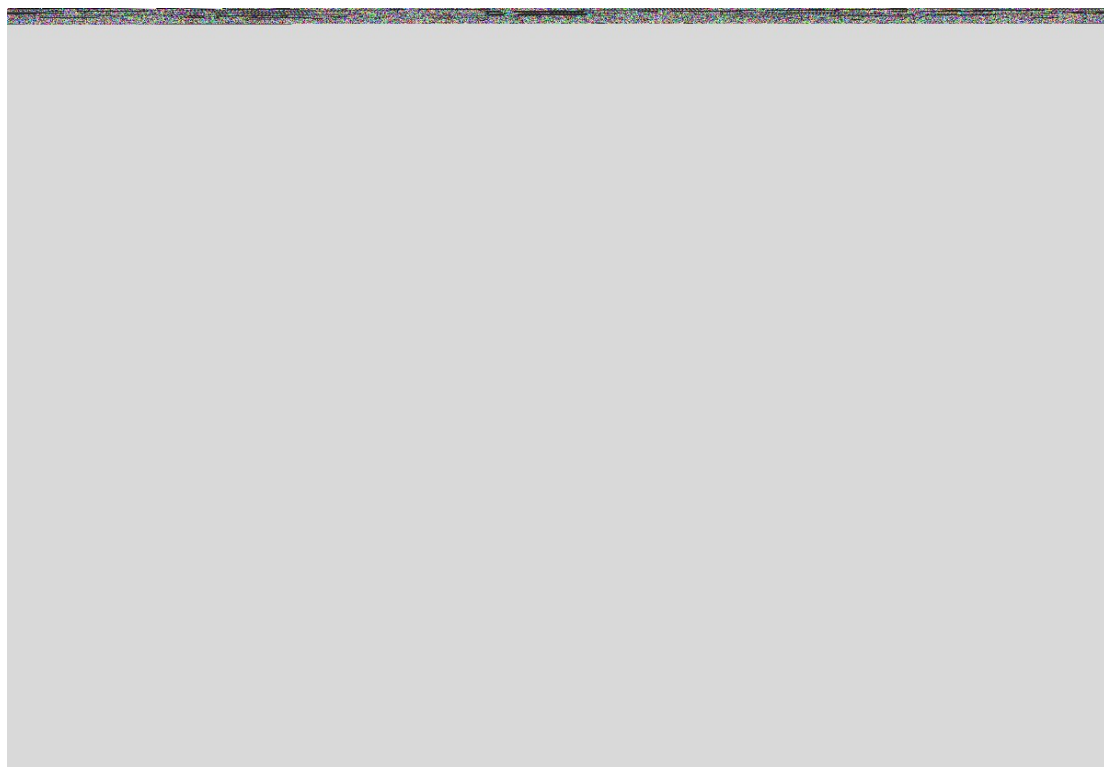


Fig.S 60 HRMS of compound **3o**

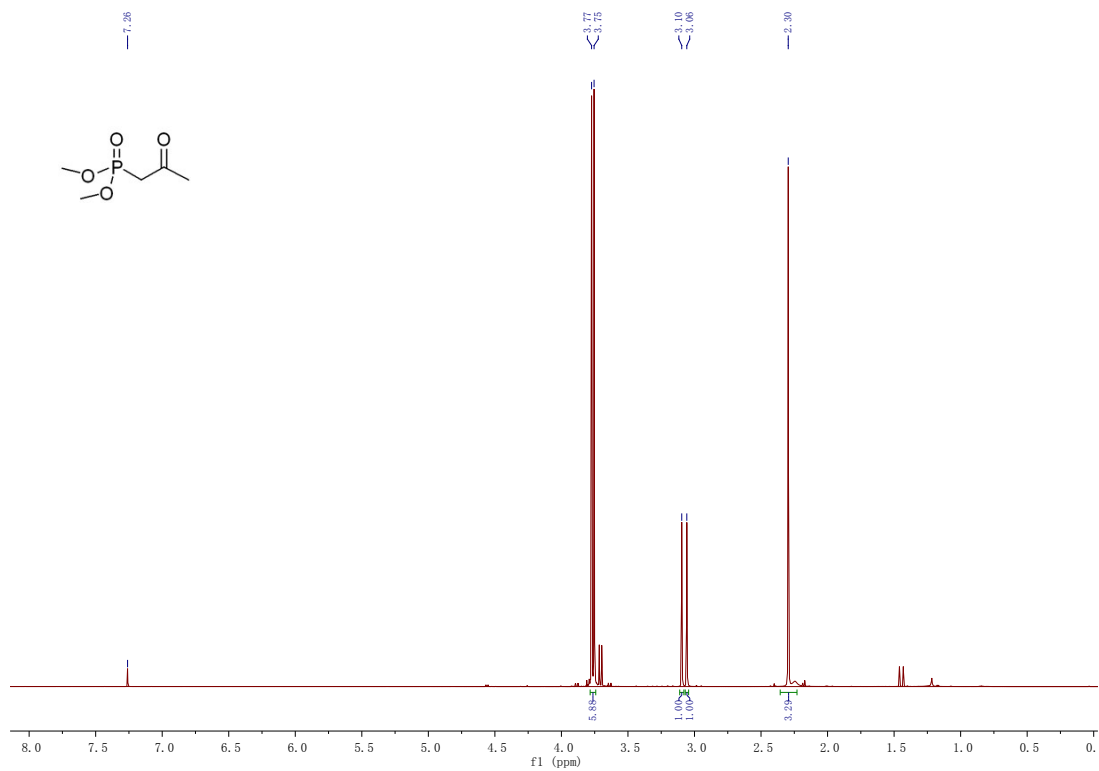


Fig.S 61 ¹H NMR of compound 4a

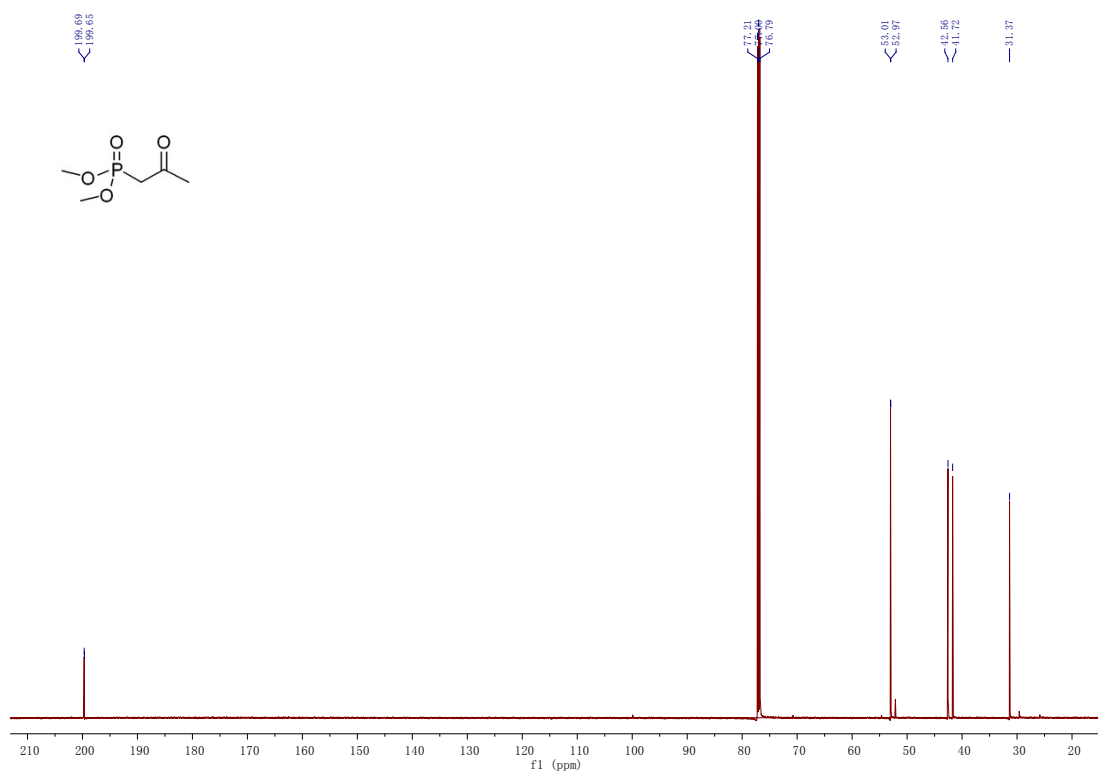


Fig.S 62 ¹³C NMR of compound 4a

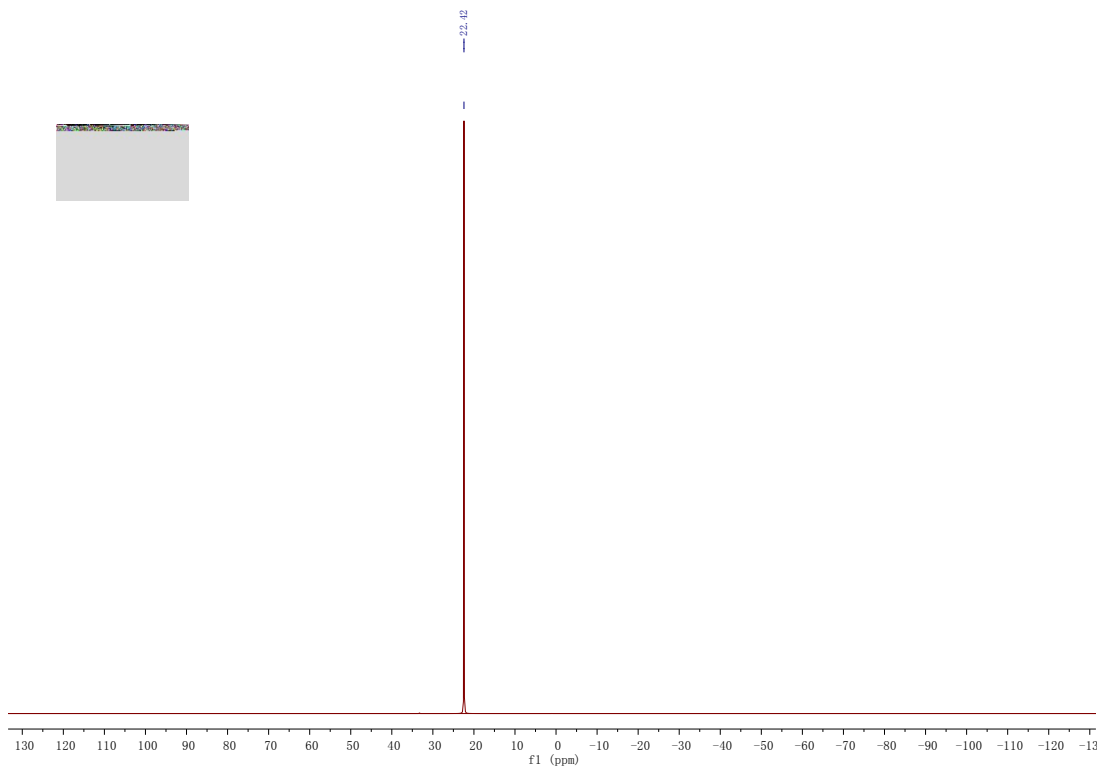


Fig.S 63 ^{31}P NMR of compound 4a

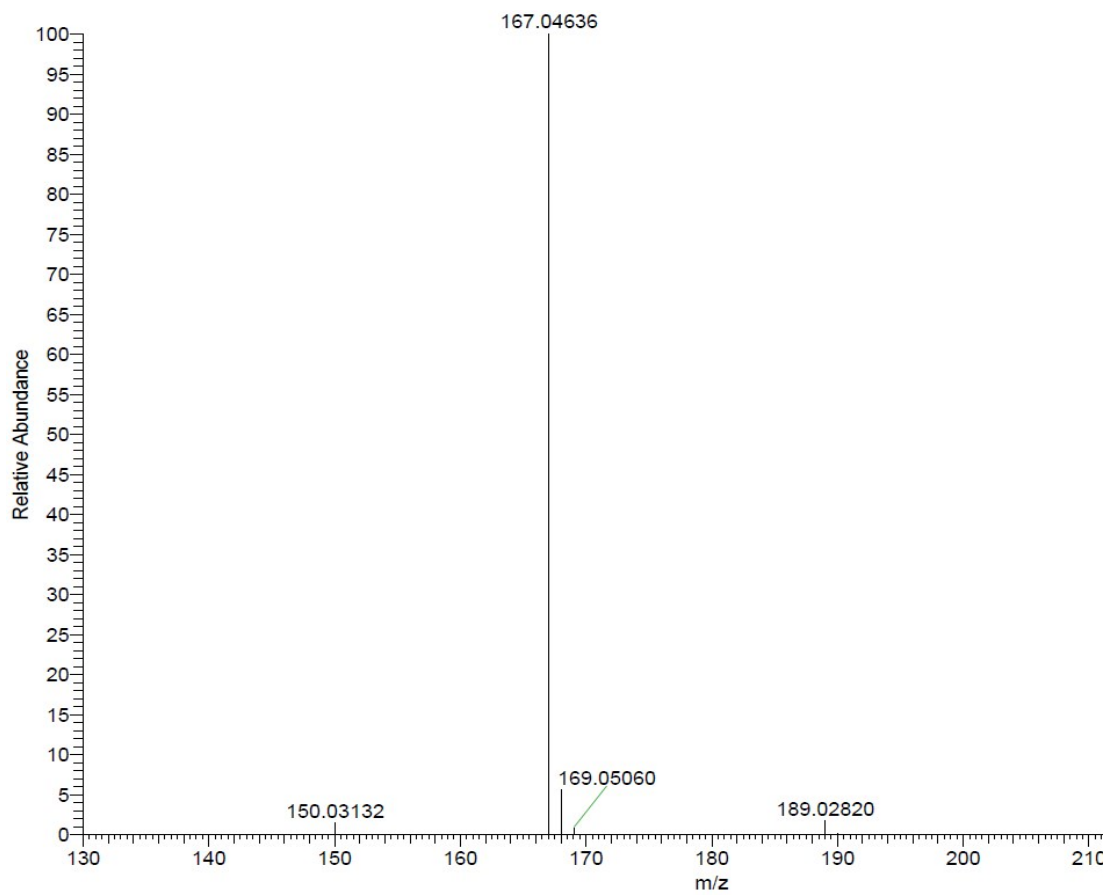


Fig.S 64 HRMS of compound 4a

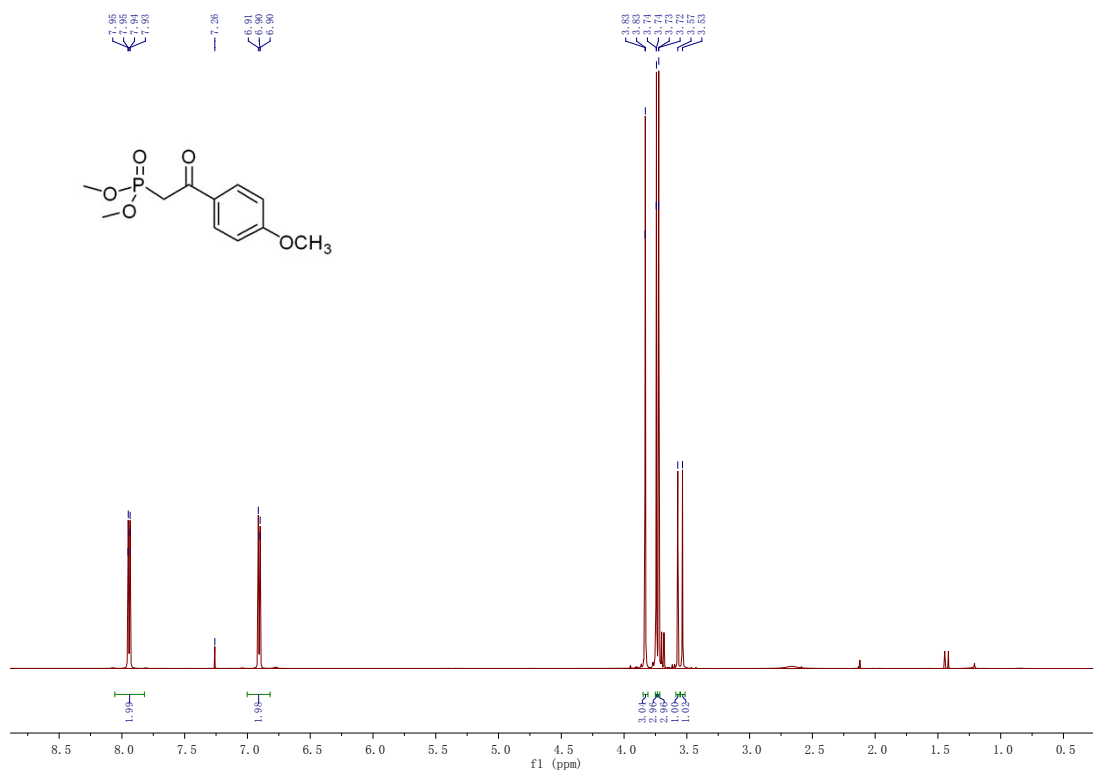


Fig.S 65 ¹H NMR of compound 4b

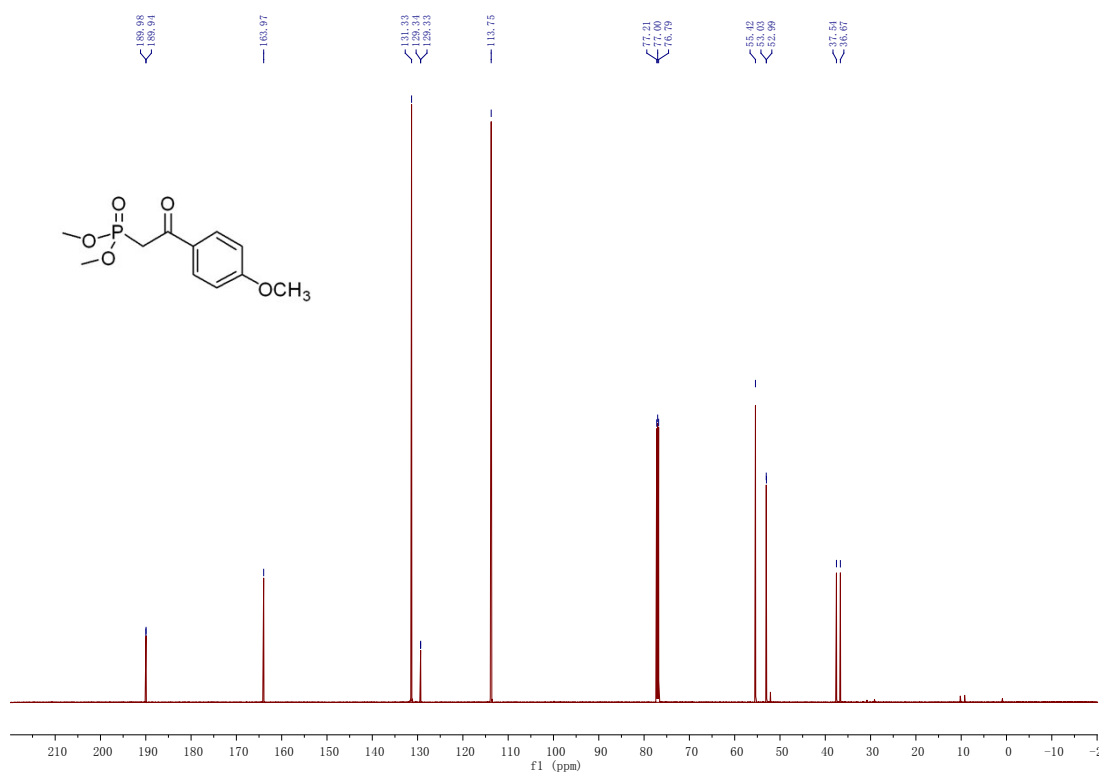


Fig.S 66 ¹³C NMR of compound 4b

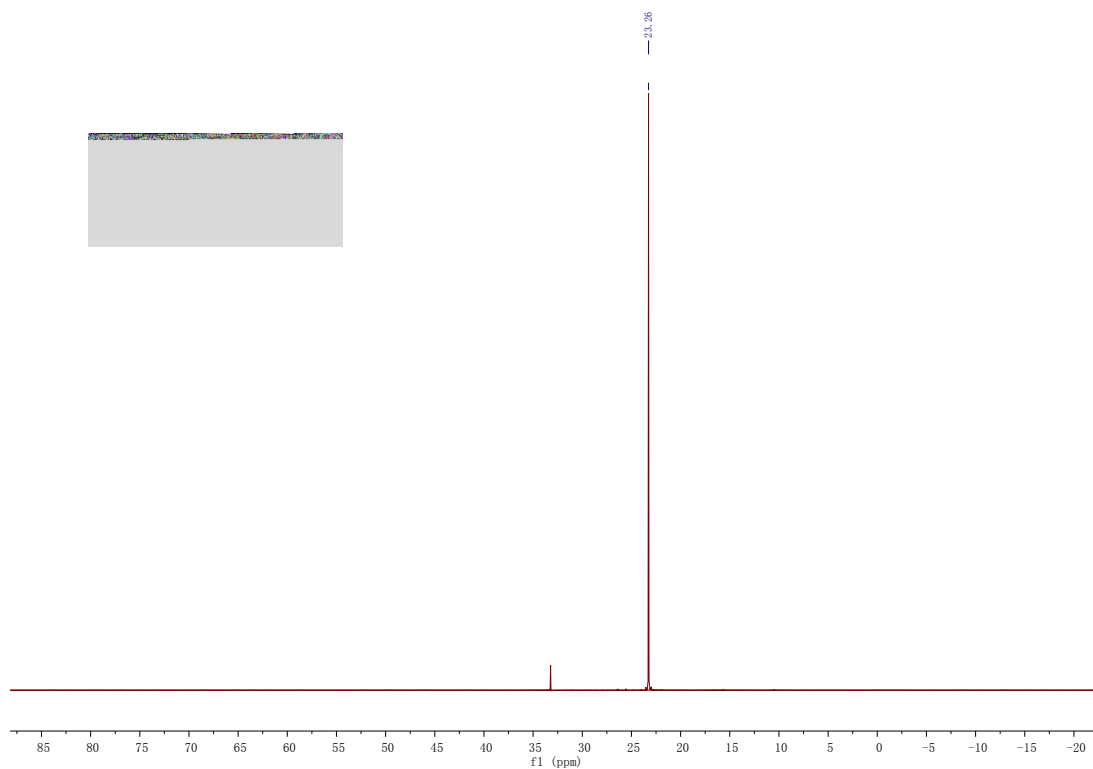


Fig.S 67 ^{31}P NMR of compound **4b**

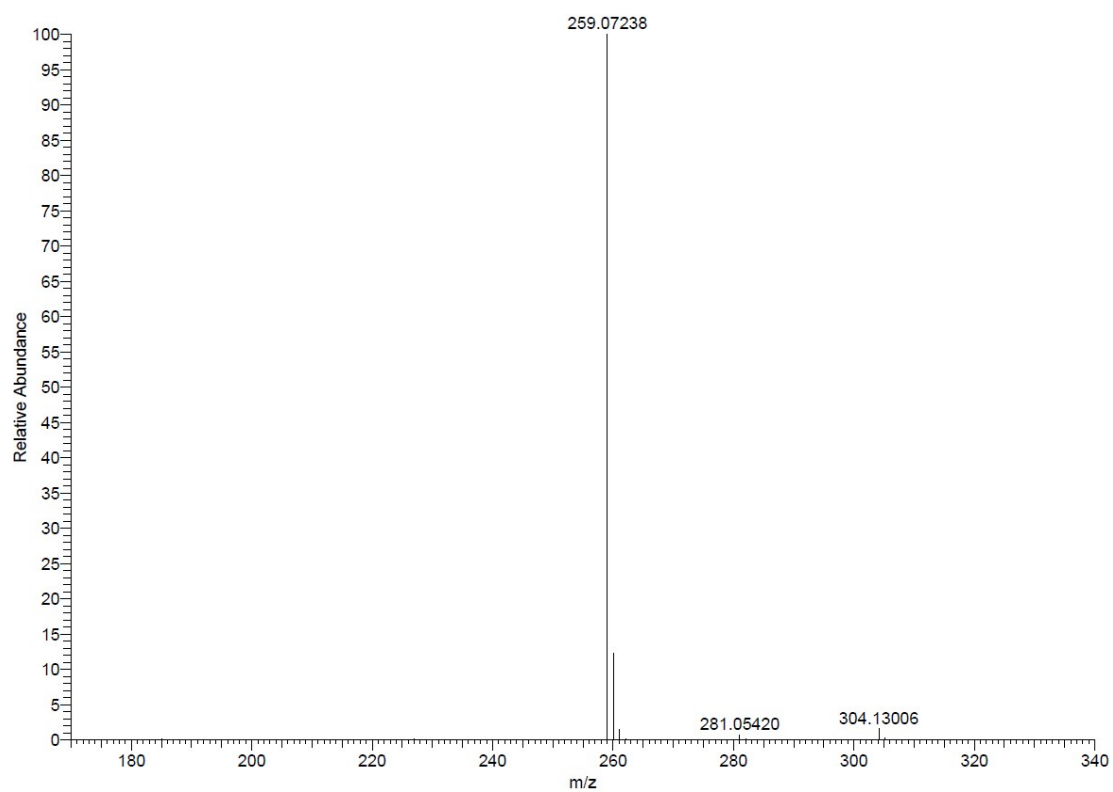


Fig.S 68 HRMS of compound **4b**

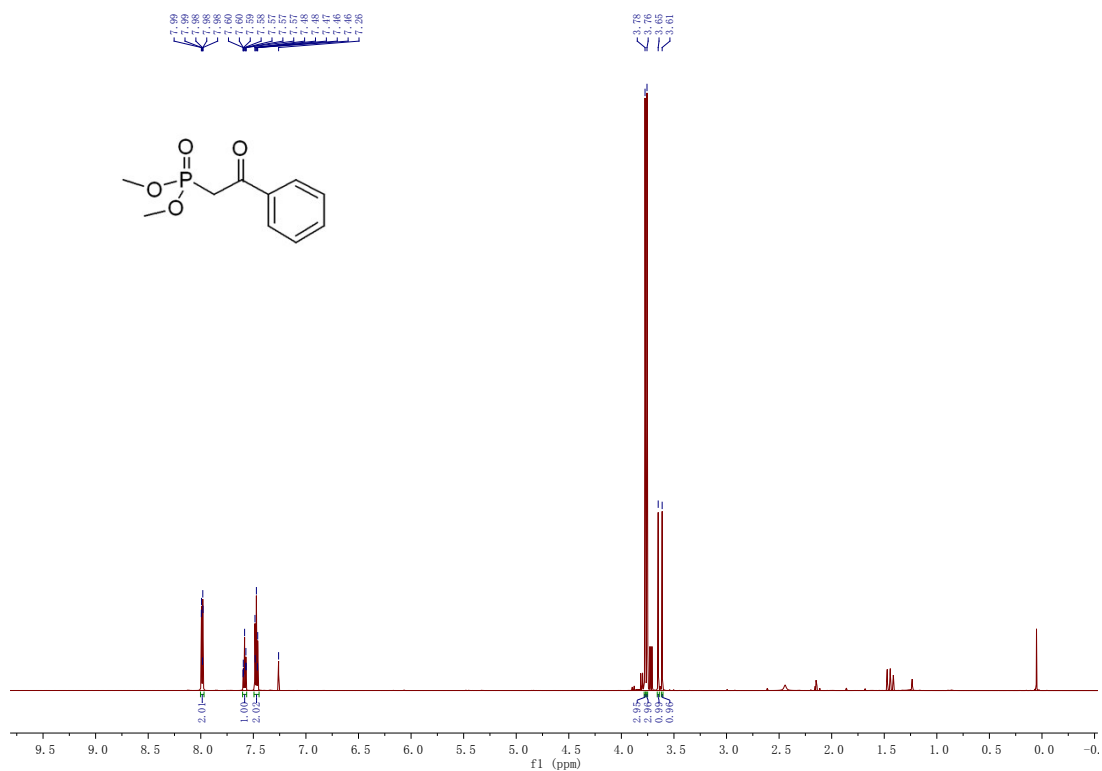


Fig.S 69 ¹H NMR of compound 4c



Fig.S 70 ¹³C NMR of compound 4c

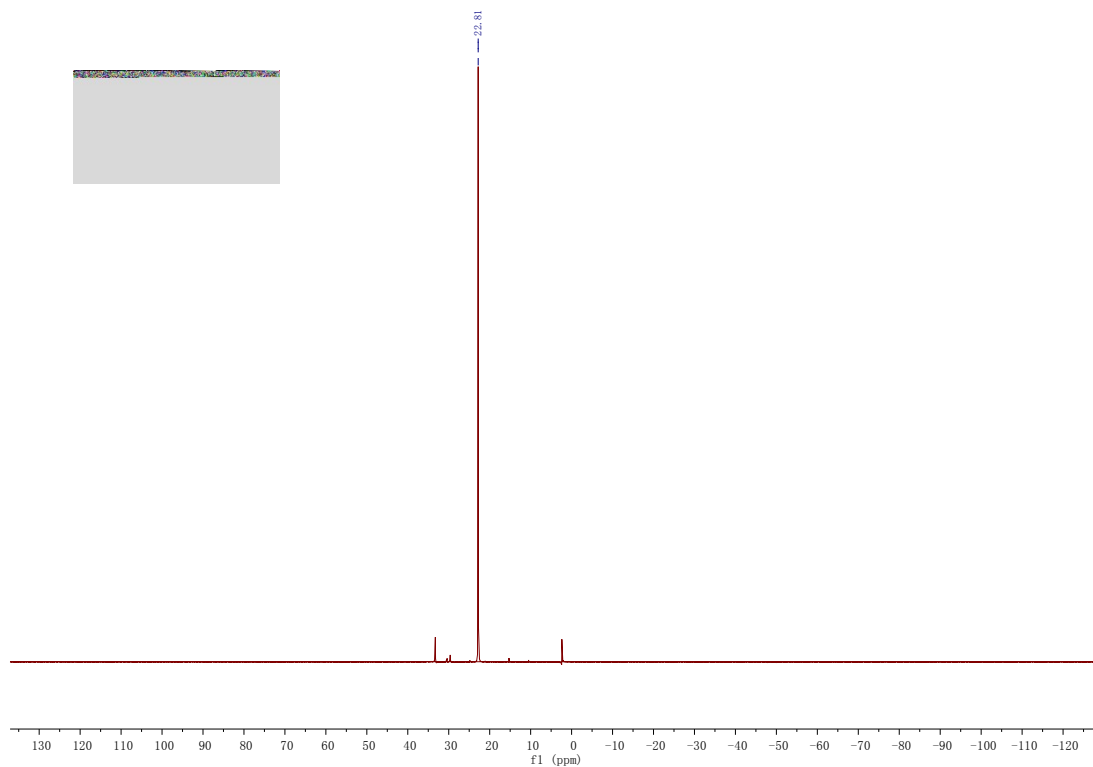


Fig.S 71 ^{31}P NMR of compound **4c**

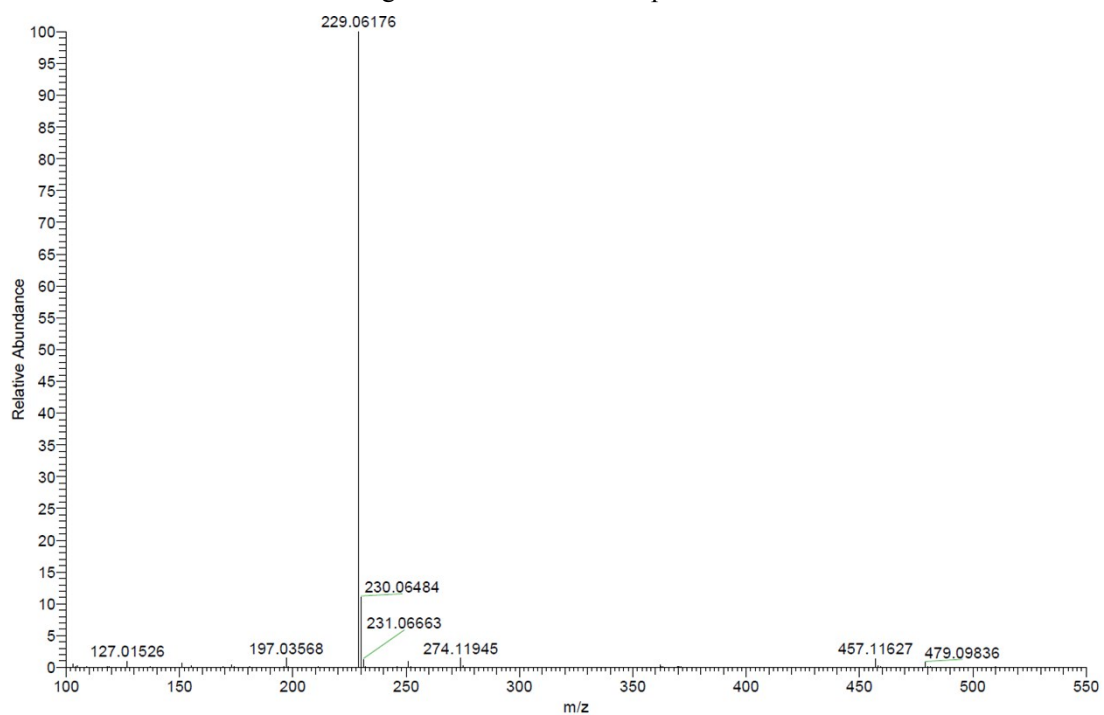


Fig.S 72 HRMS of compound **4c**

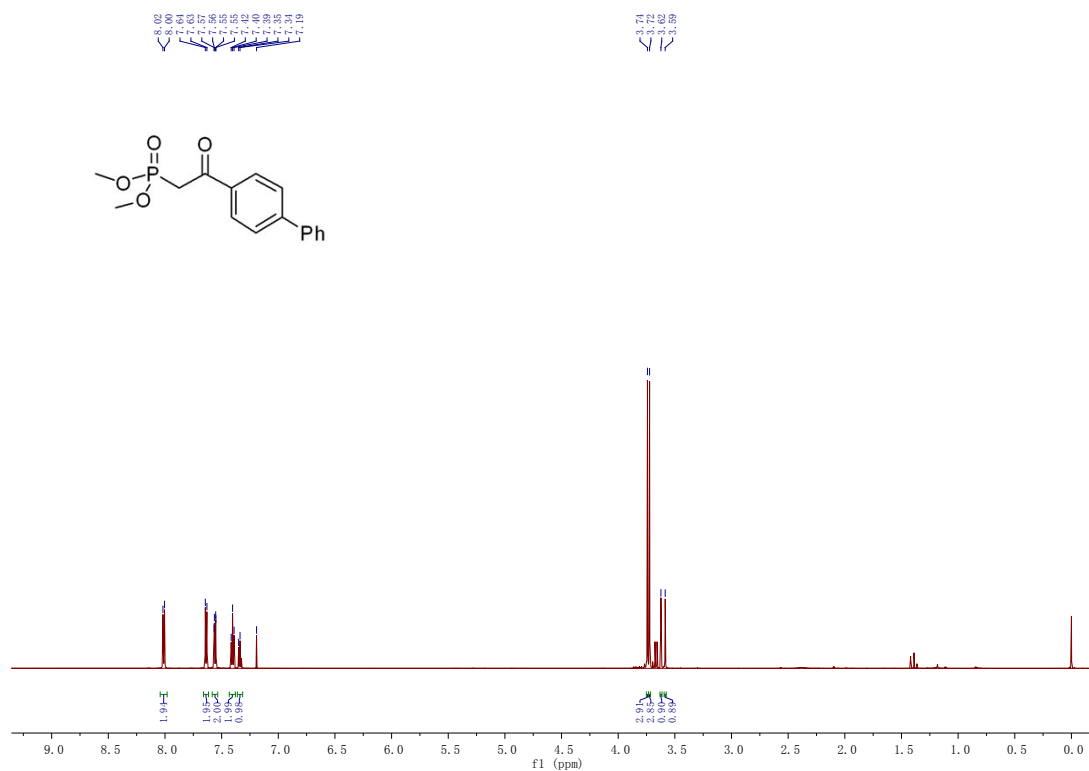


Fig.S 73 ^1H NMR of compound **4d**

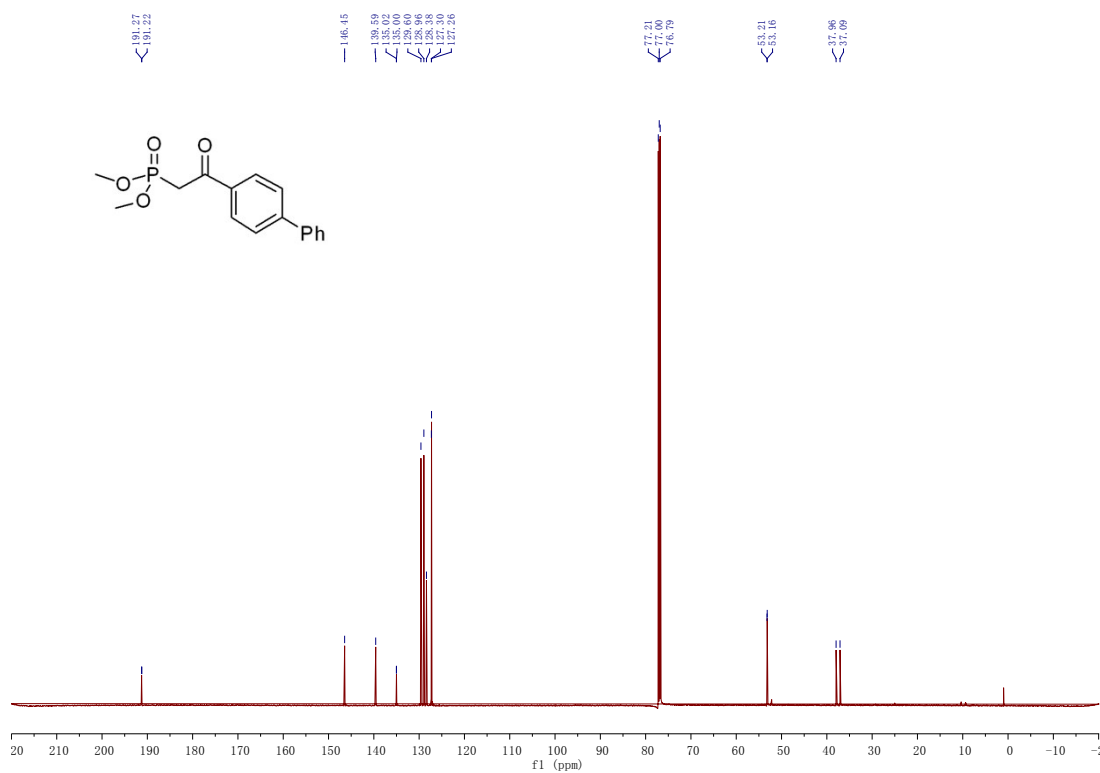


Fig.S 74 ^{13}C NMR of compound **4d**

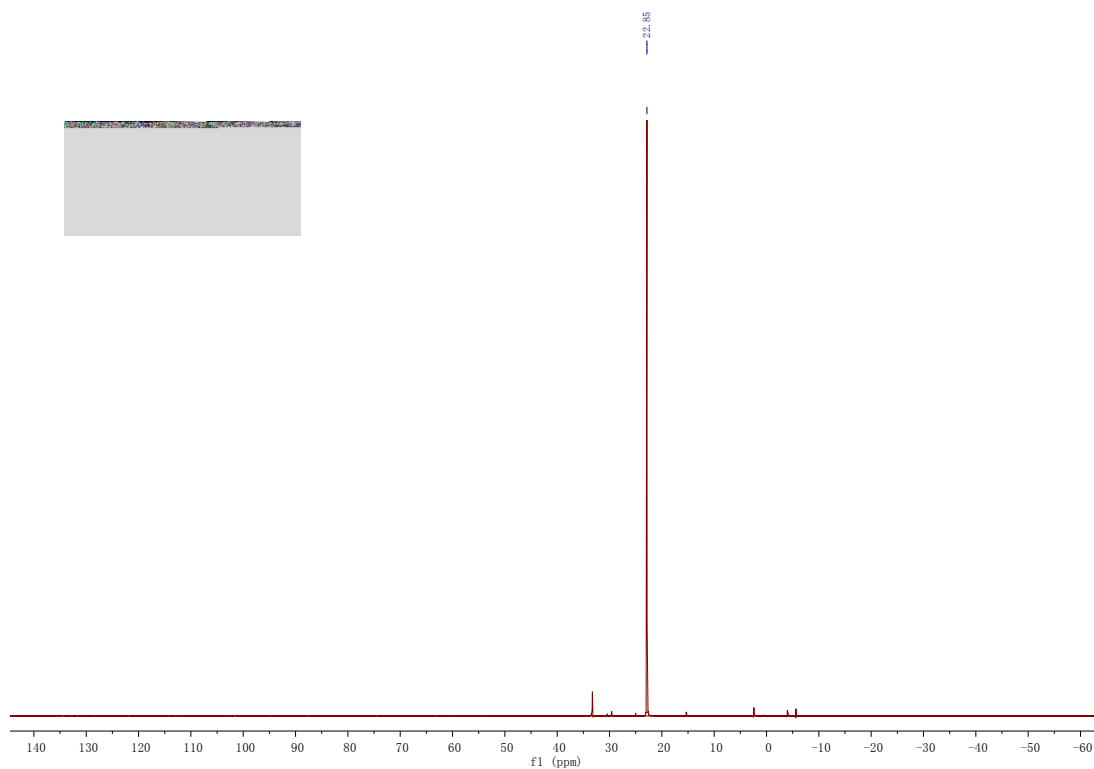


Fig.S 75 ^{31}P NMR of compound **4d**

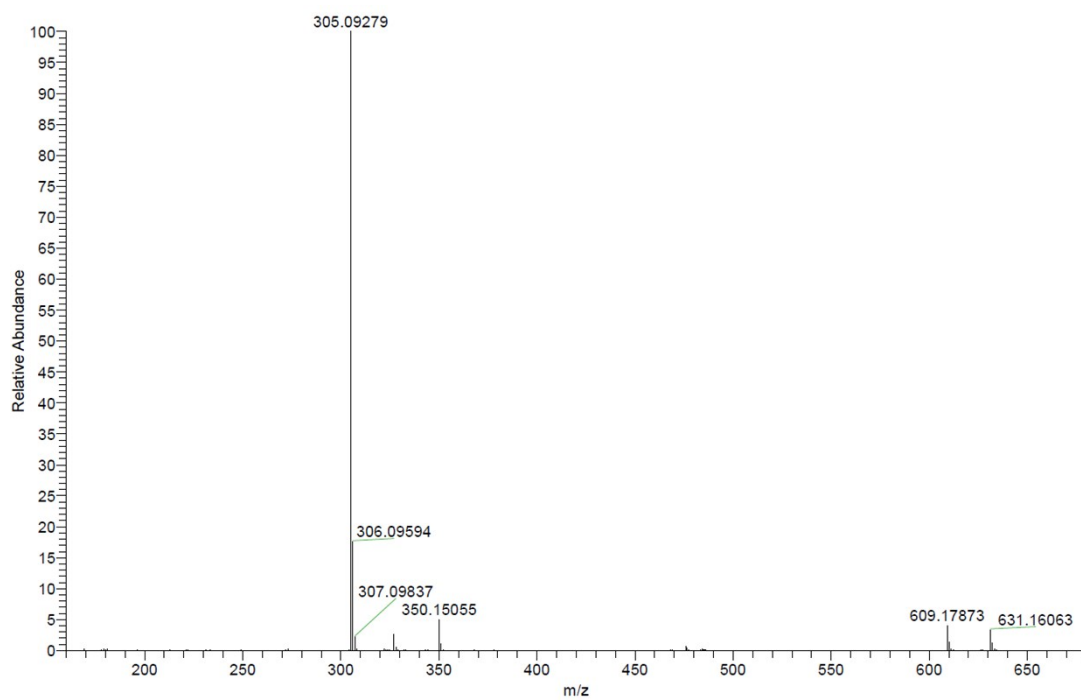


Fig.S 76 HRMS of compound **4d**

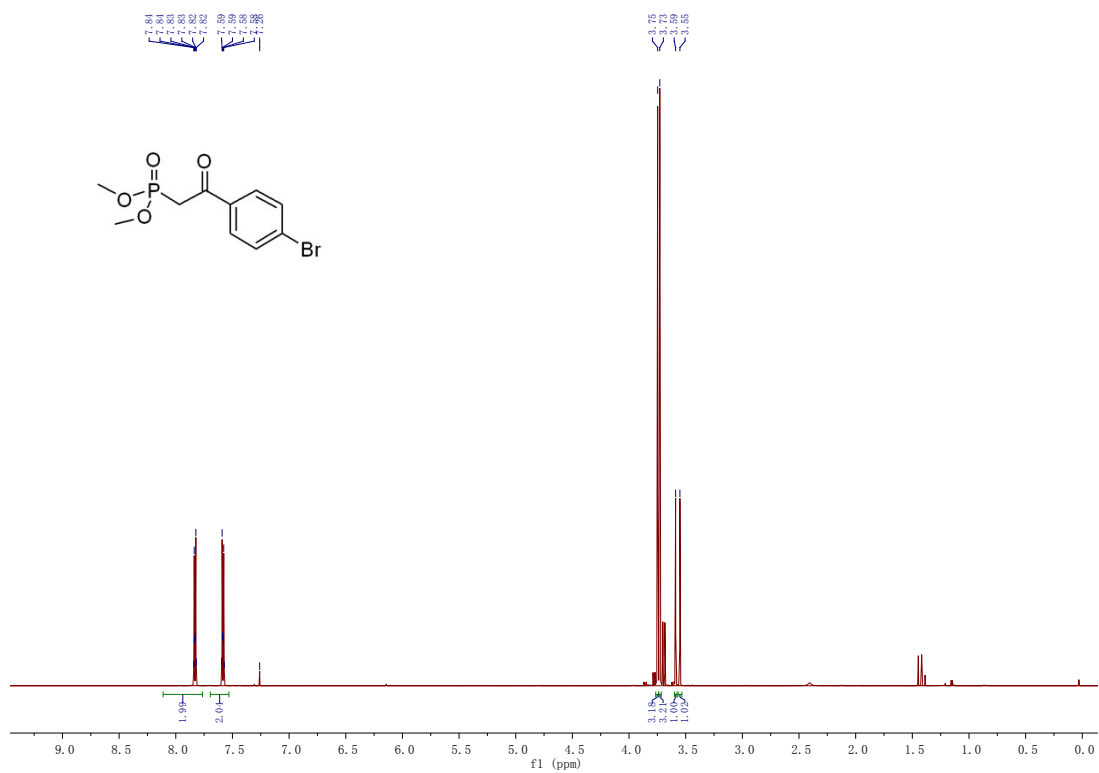


Fig.S 77 ¹H NMR of compound 4e

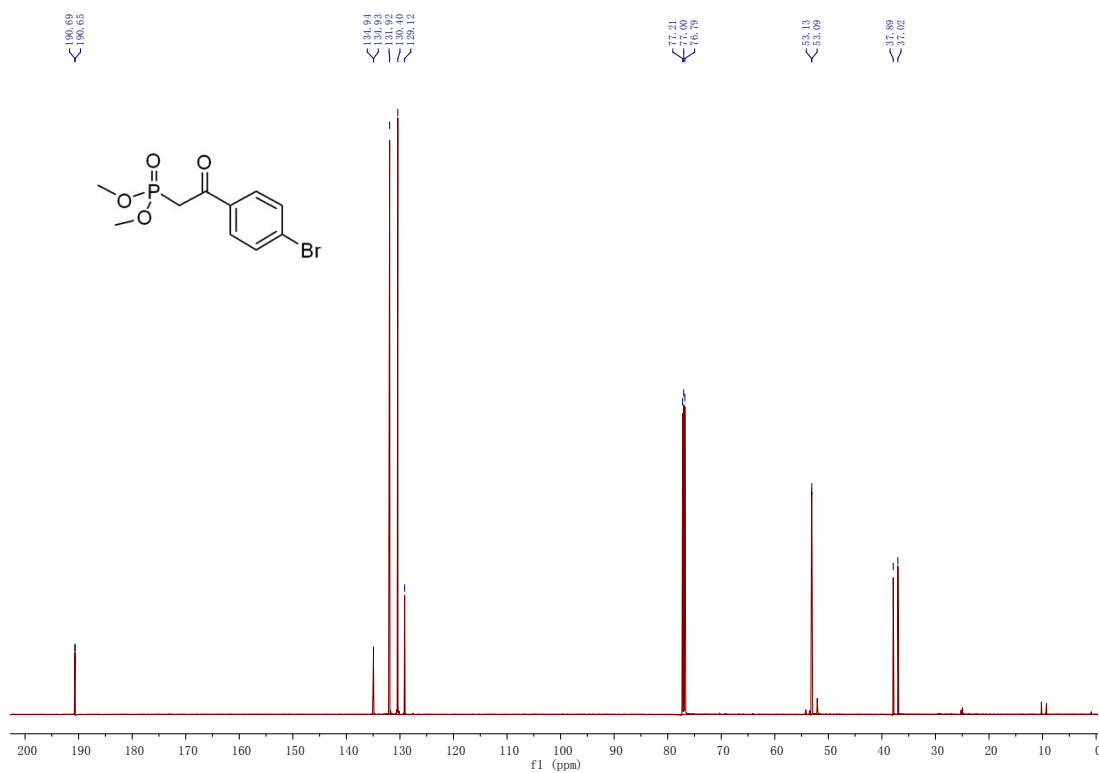


Fig.S 78 ¹³C NMR of compound 4e

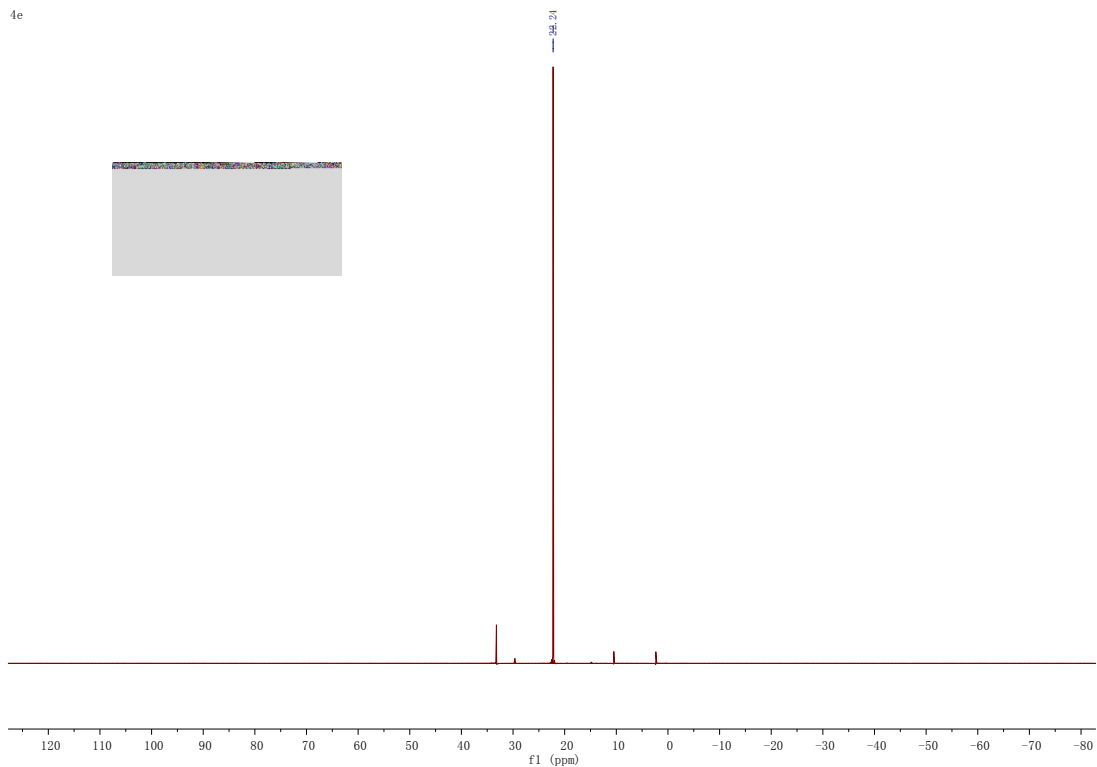


Fig.S 79 ^{31}P NMR of compound 4e

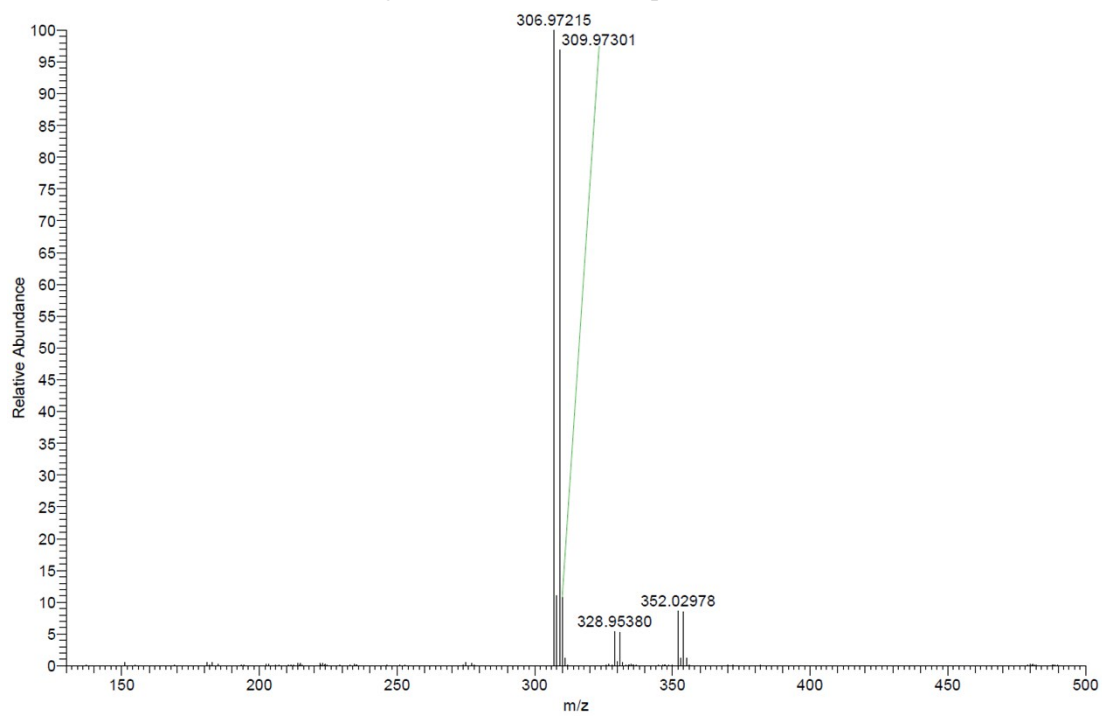


Fig.S 80 HRMS of compound 4e

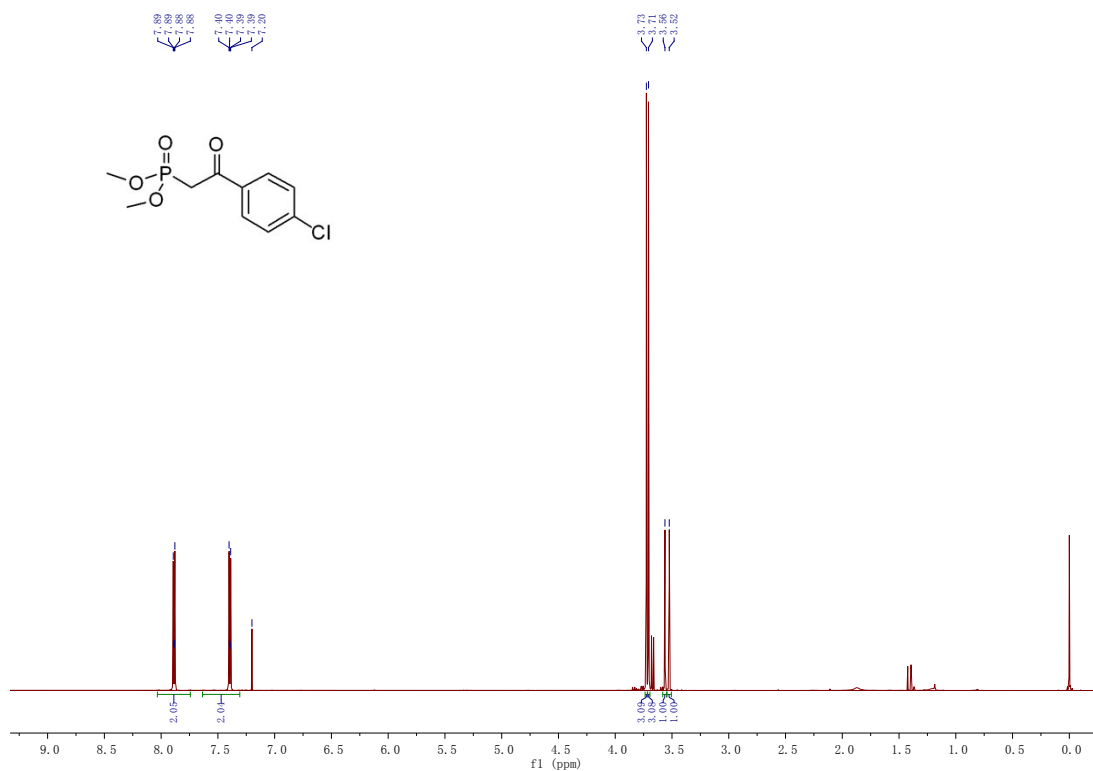


Fig.S 81 ¹H NMR of compound 4f

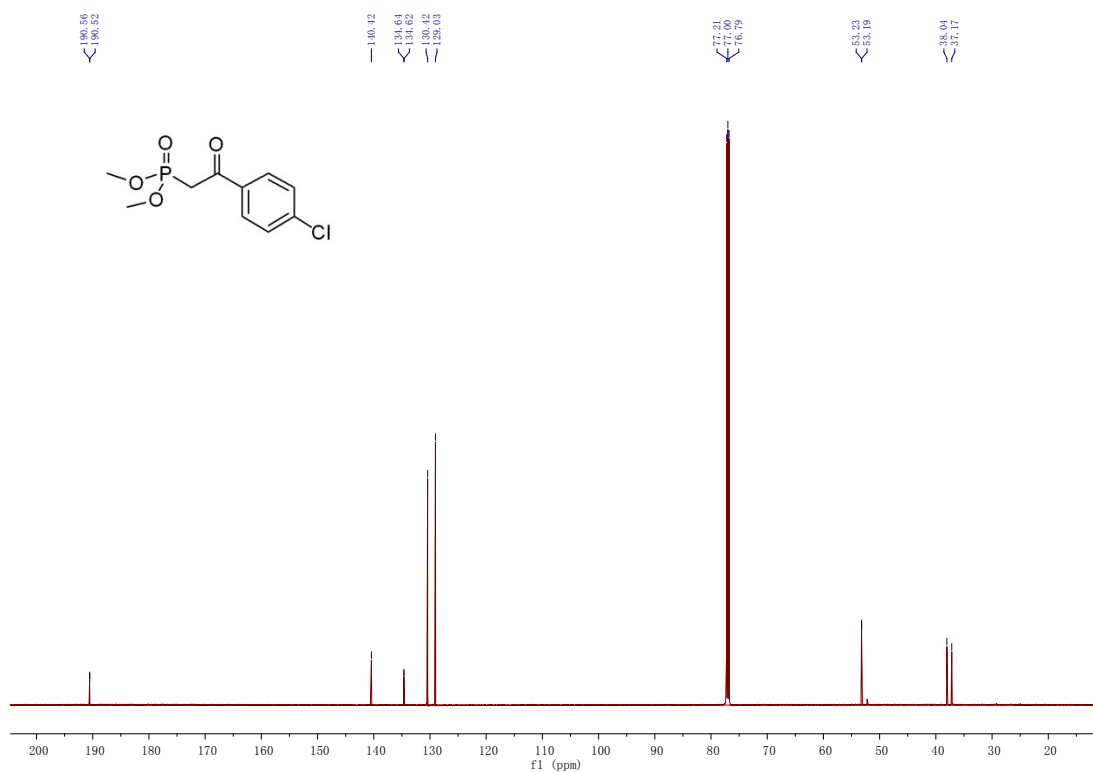


Fig.S 82 ¹³C NMR of compound 4f

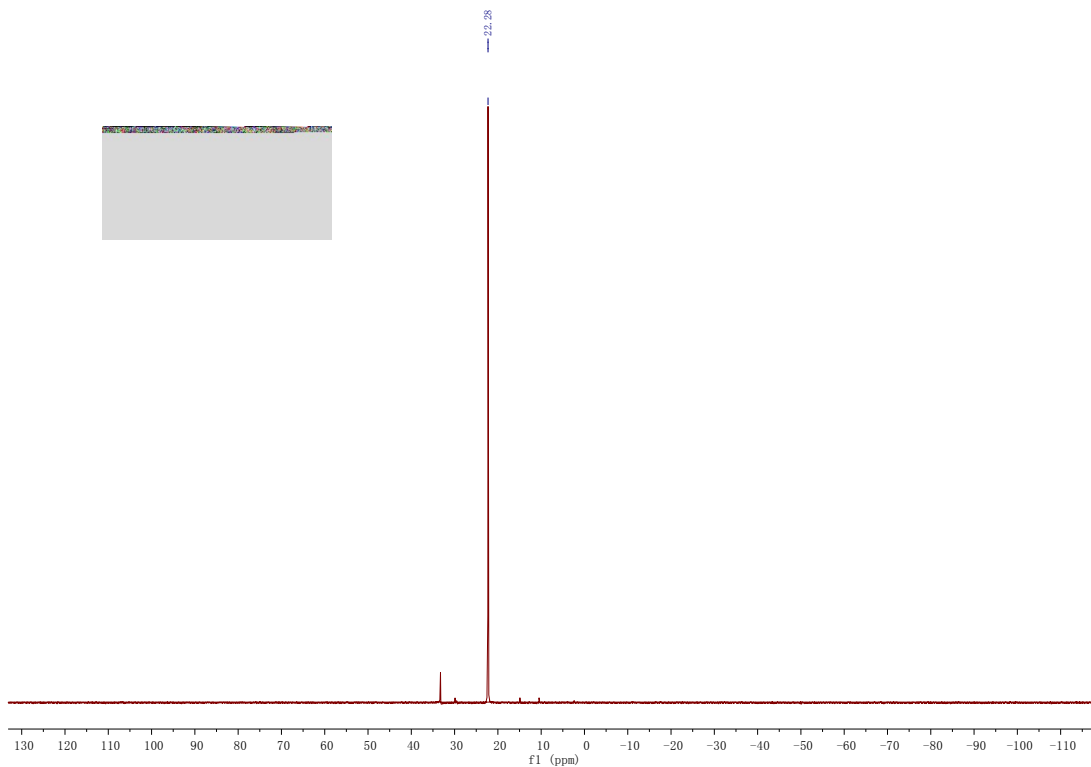


Fig.S 83 ^{31}P NMR of compound **4f**

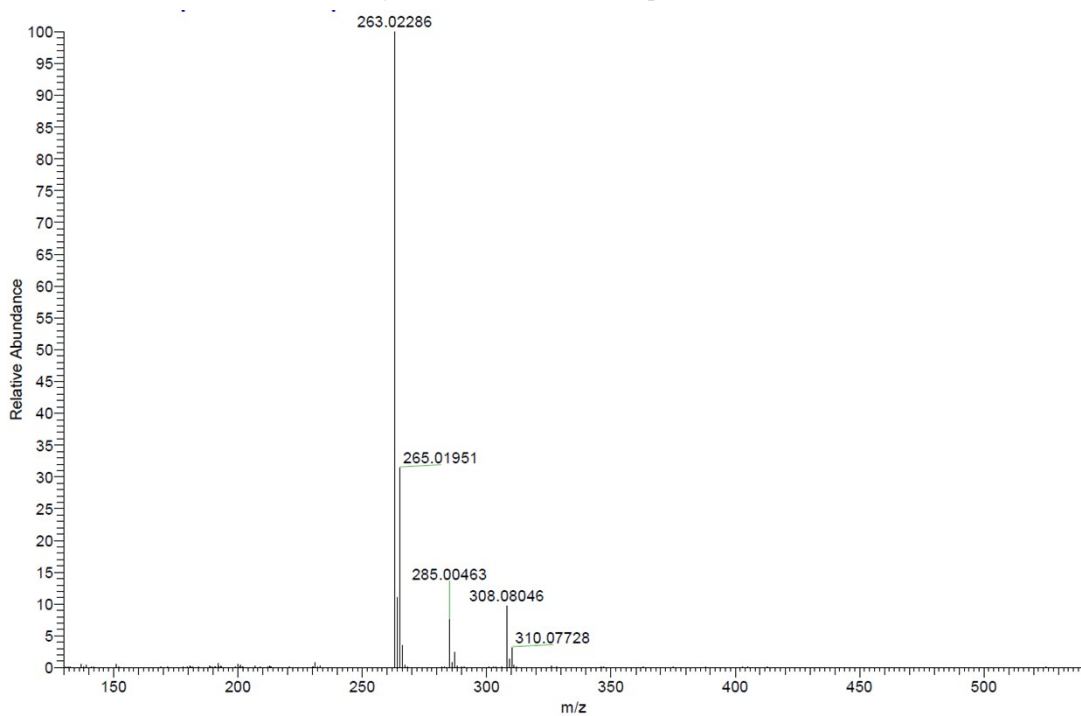


Fig.S 84 HRMS of compound **4f**



Fig.S 85 ¹H NMR of compound 4g

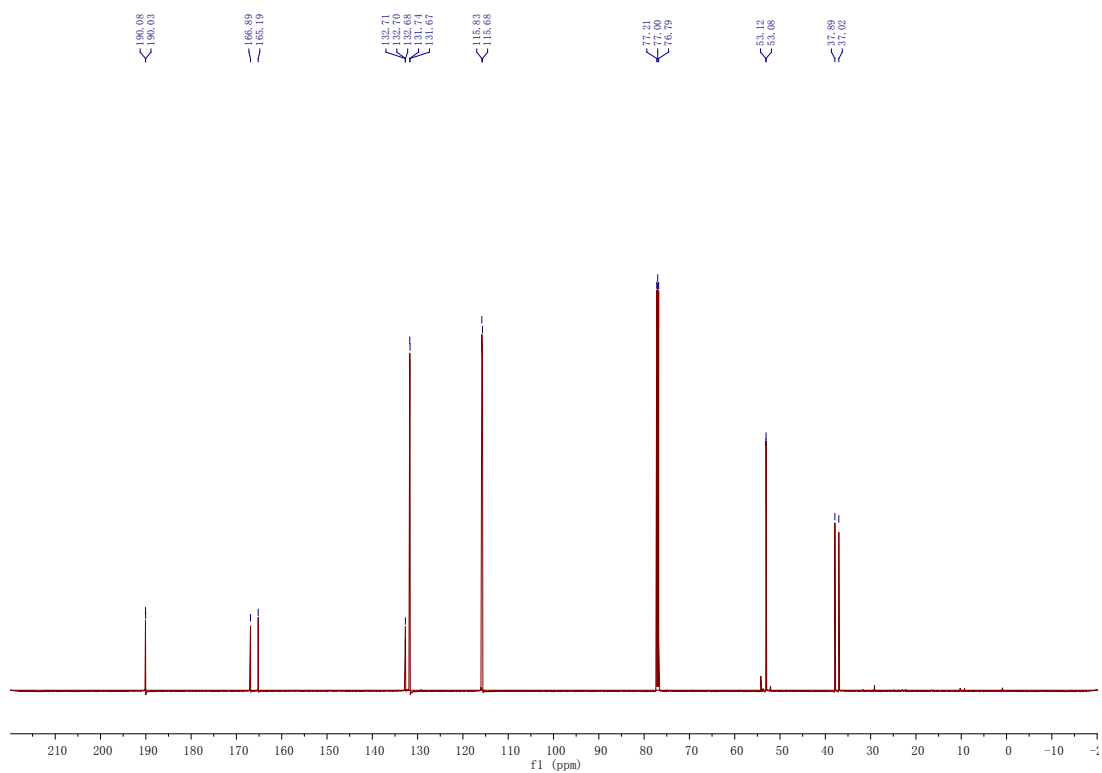


Fig.S 86 ¹³C NMR of compound 4g

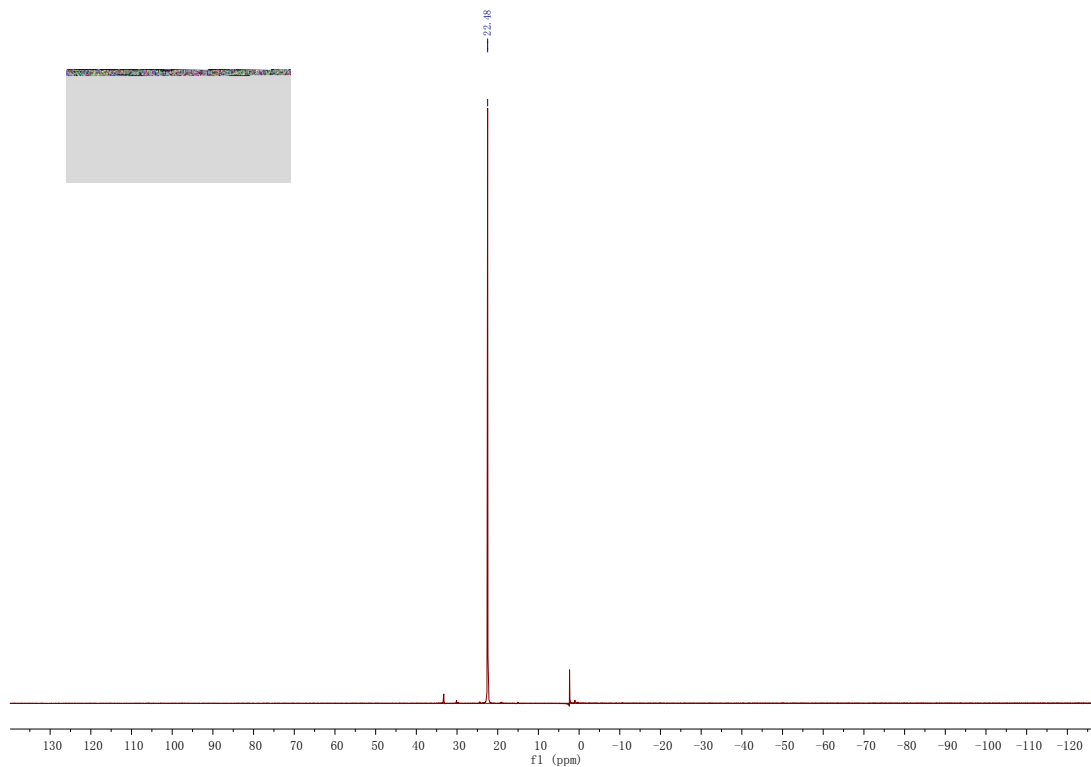


Fig.S 87 ^{31}P NMR of compound **4g**

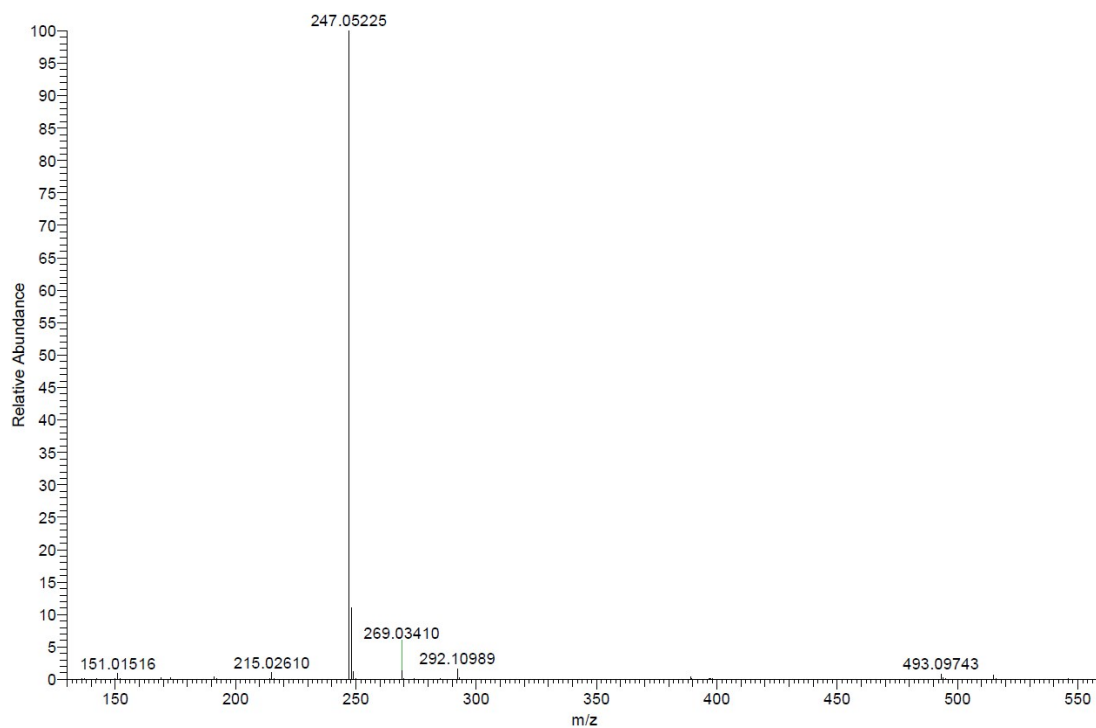


Fig.S 88 HRMS of compound **4g**

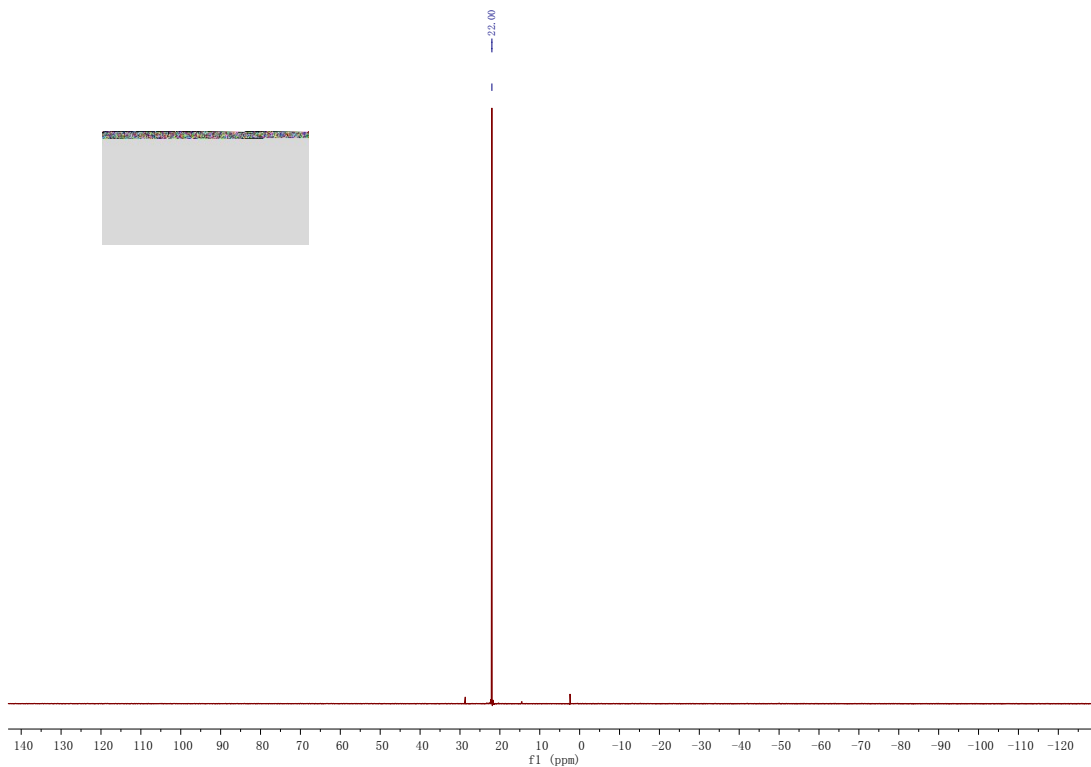


Fig.S 91 ^{31}P NMR of compound **4h**

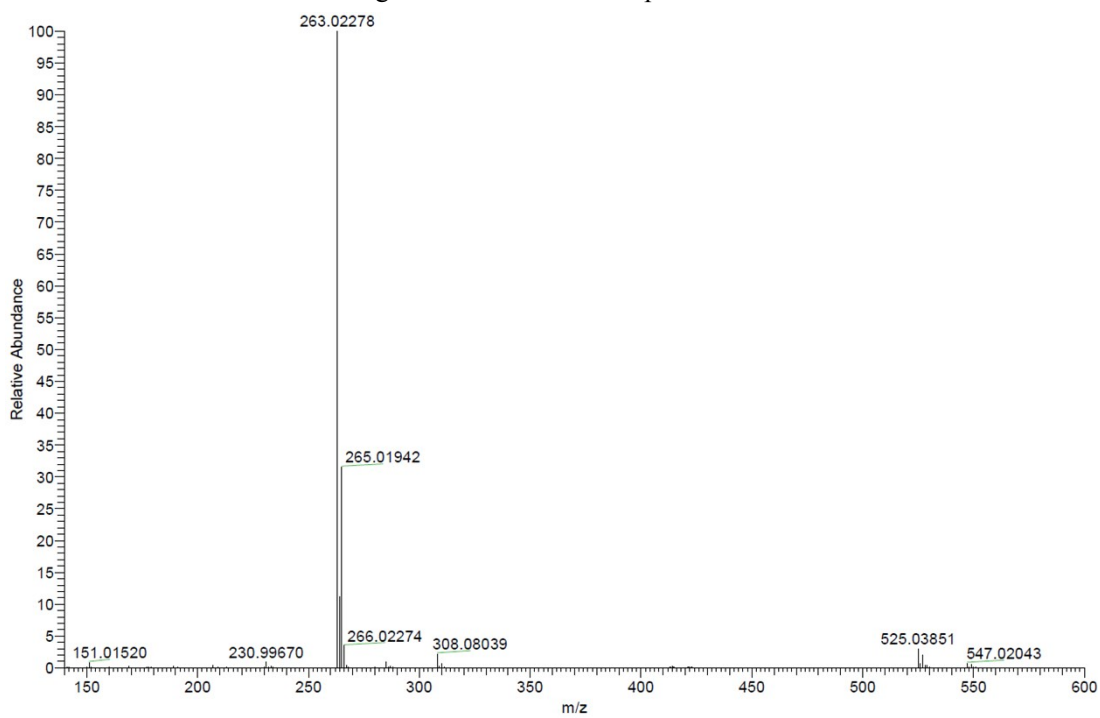
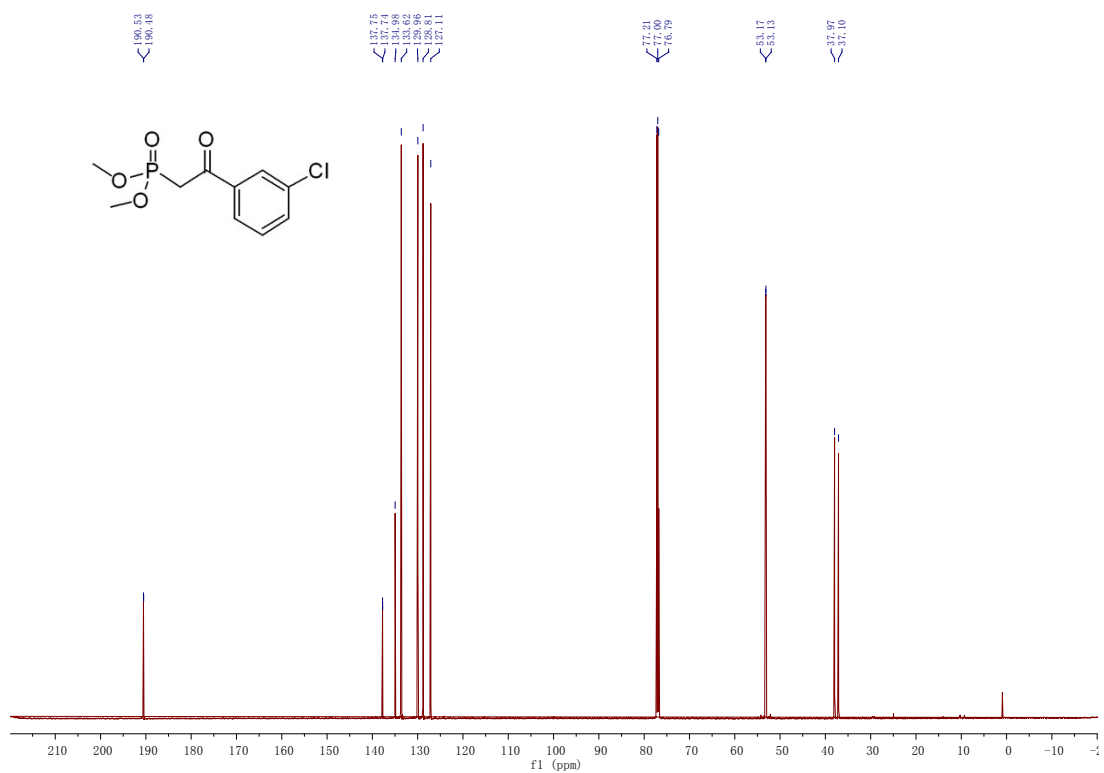
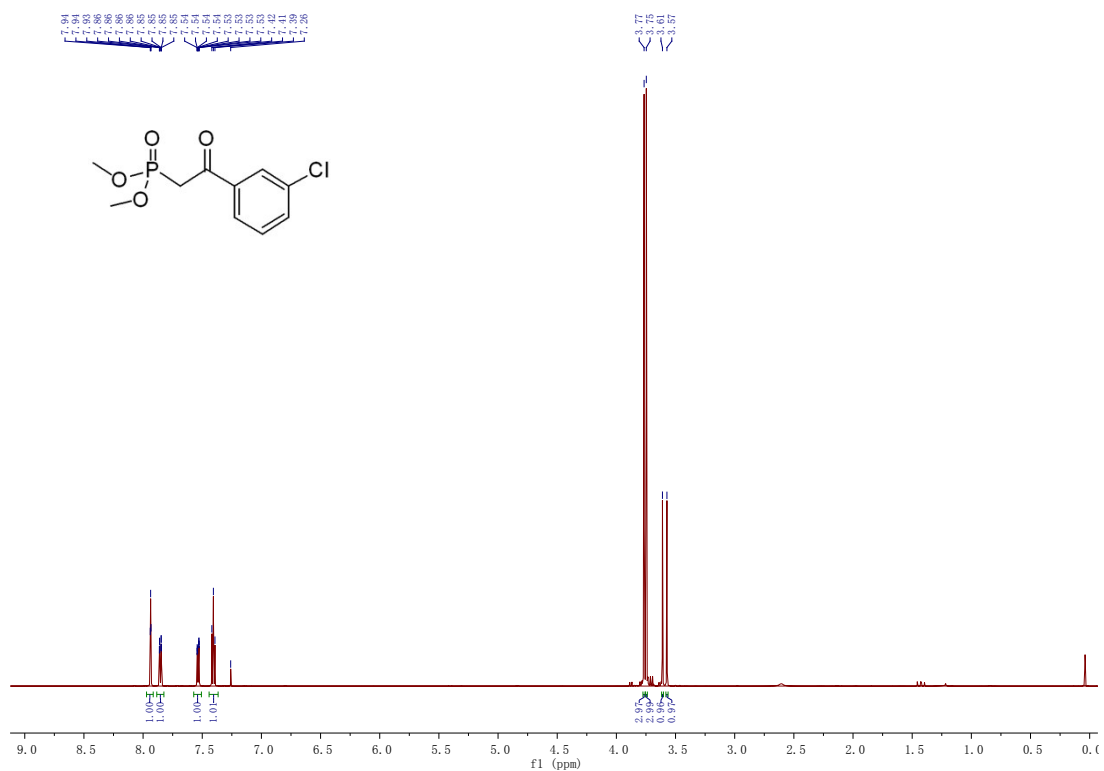


Fig.S 92 HRMS of compound **4h**



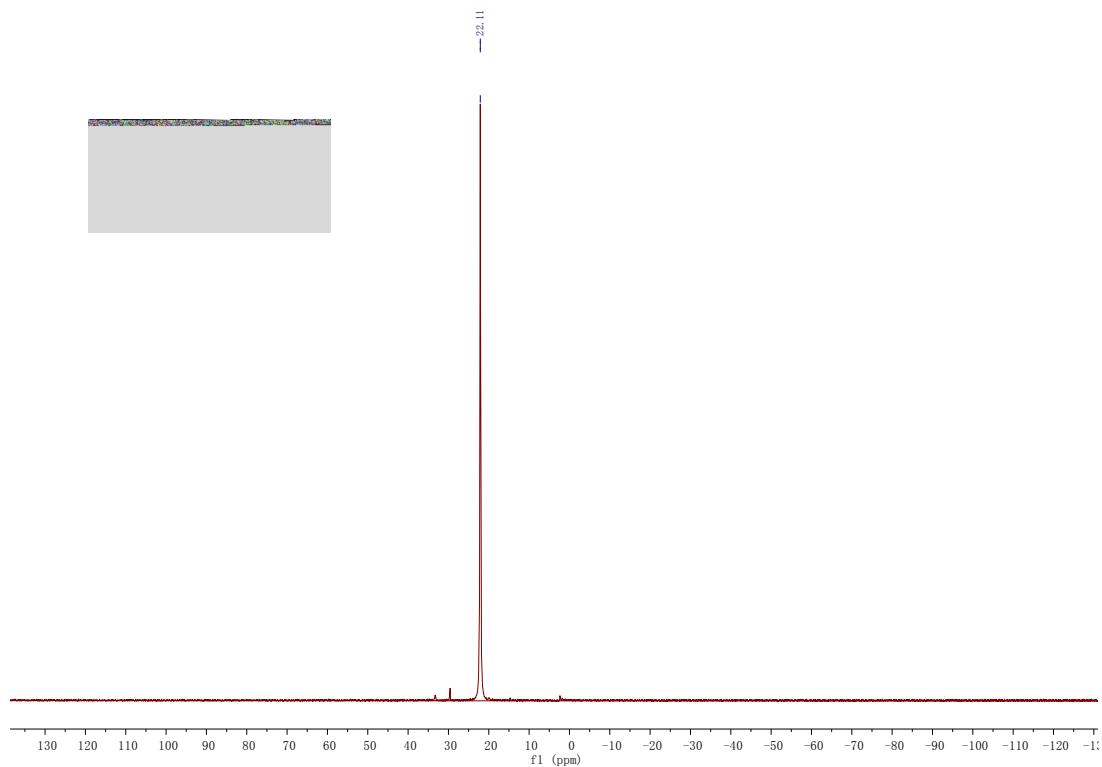


Fig.S 95 ^{31}P NMR of compound **4i**

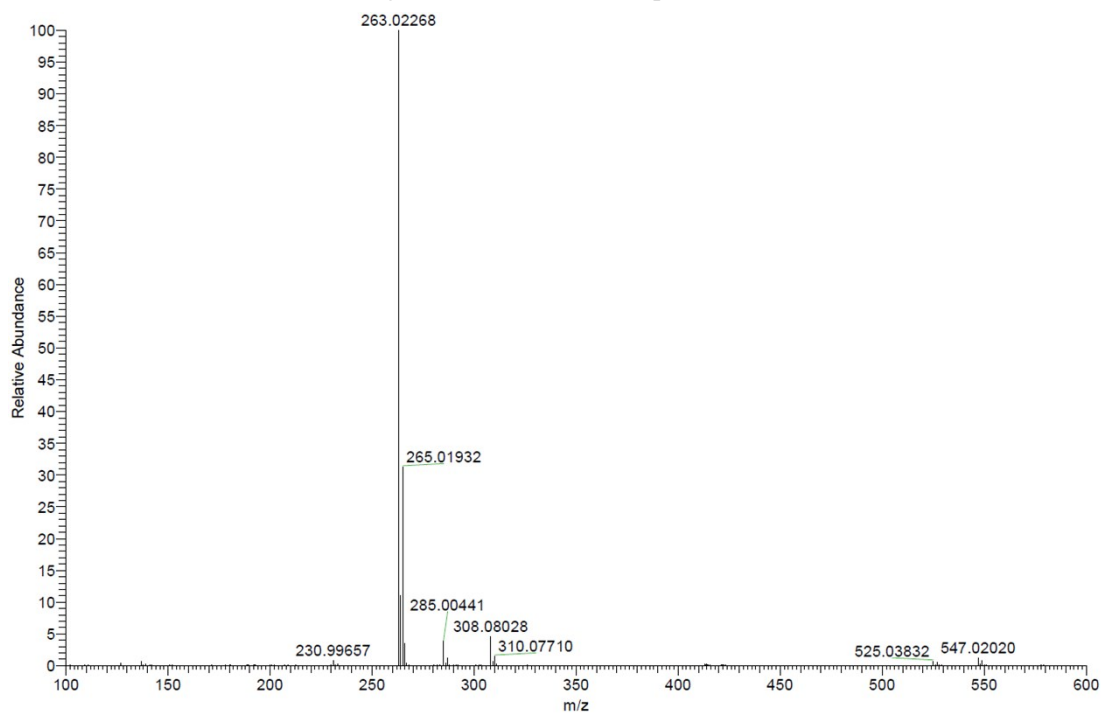


Fig.S 96 HRMS of compound **4i**

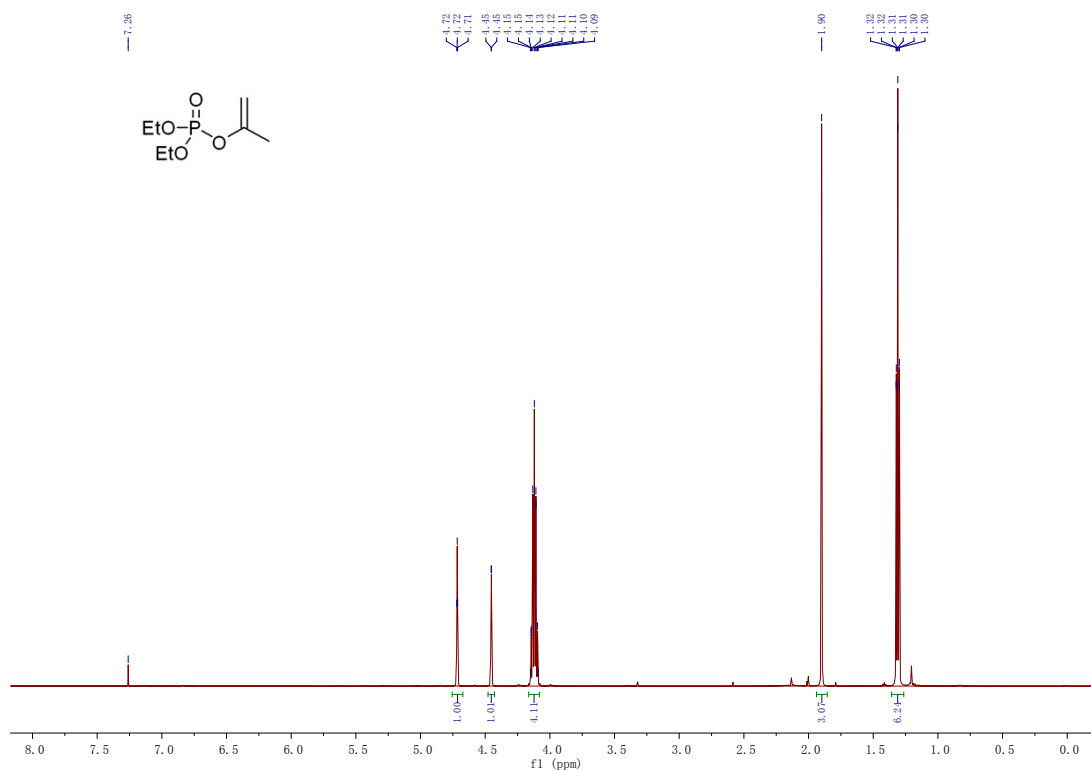


Fig.S 97 ¹H NMR of compound 5a

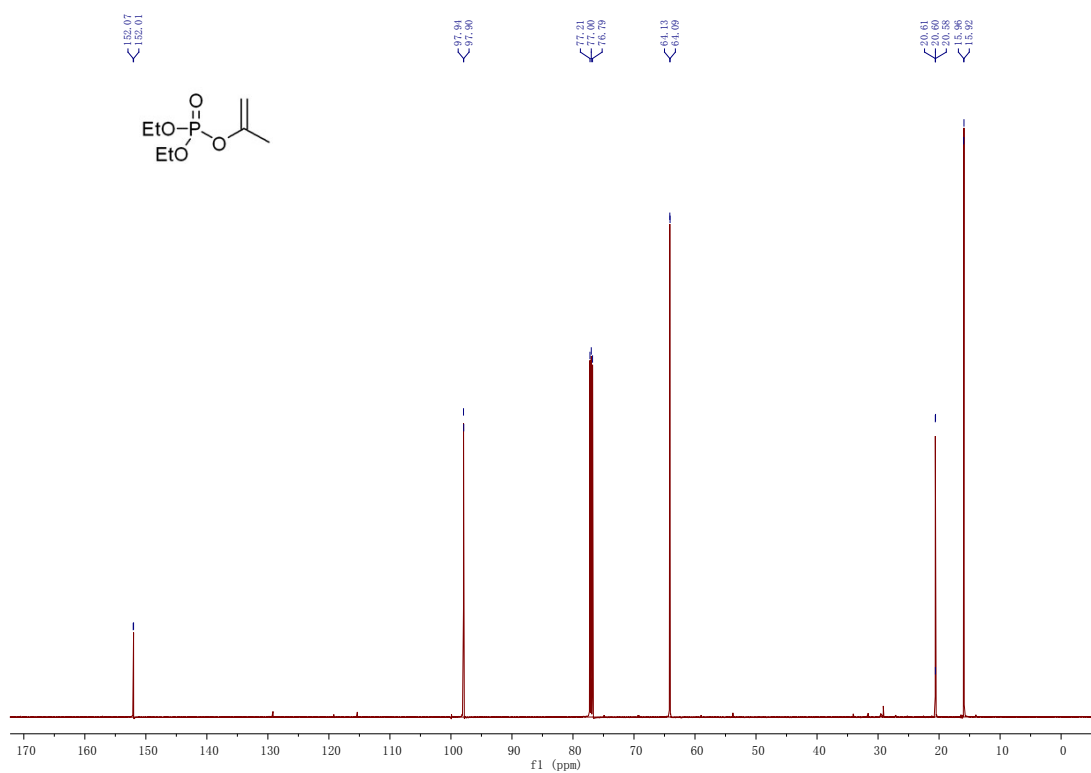


Fig.S 98 ¹³C NMR of compound 5a

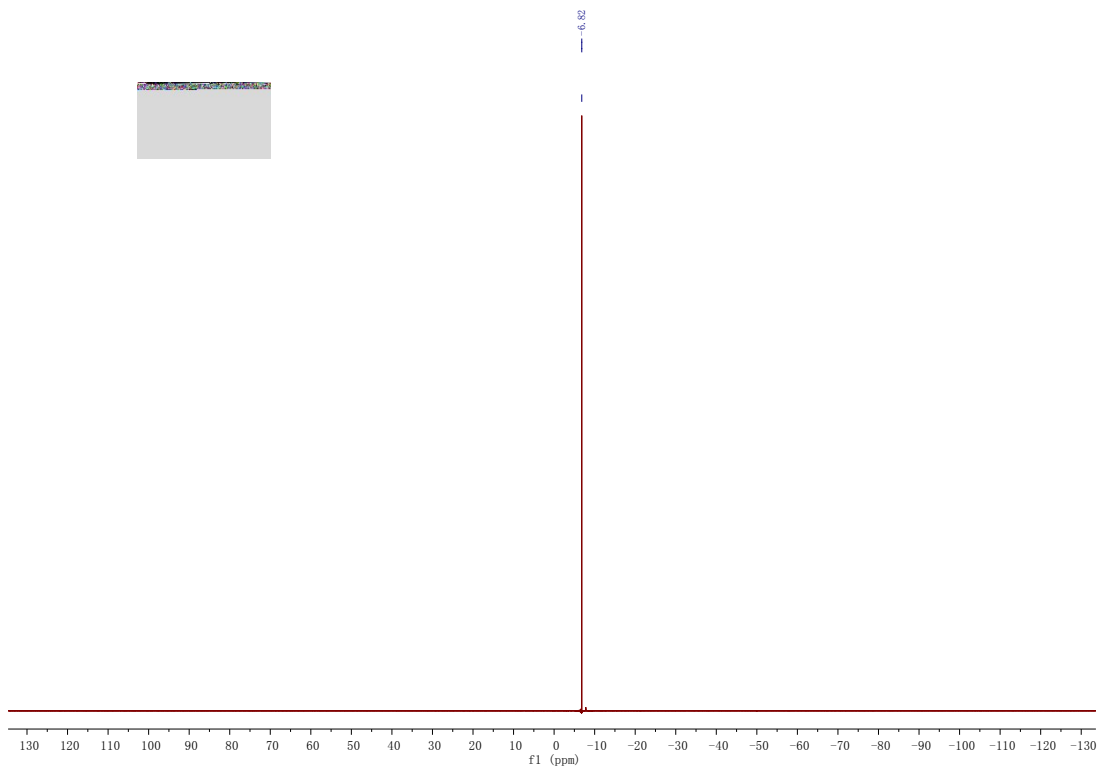


Fig.S 99 ^{31}P NMR of compound **5a**

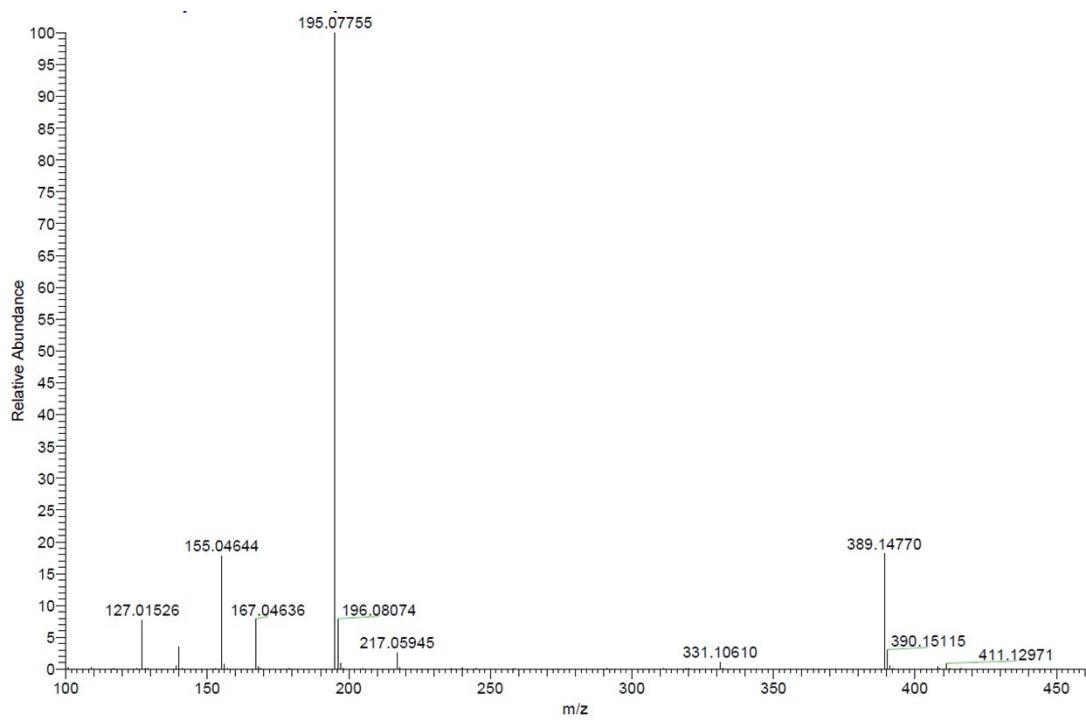


Fig.S 100 HRMS of compound **5a**

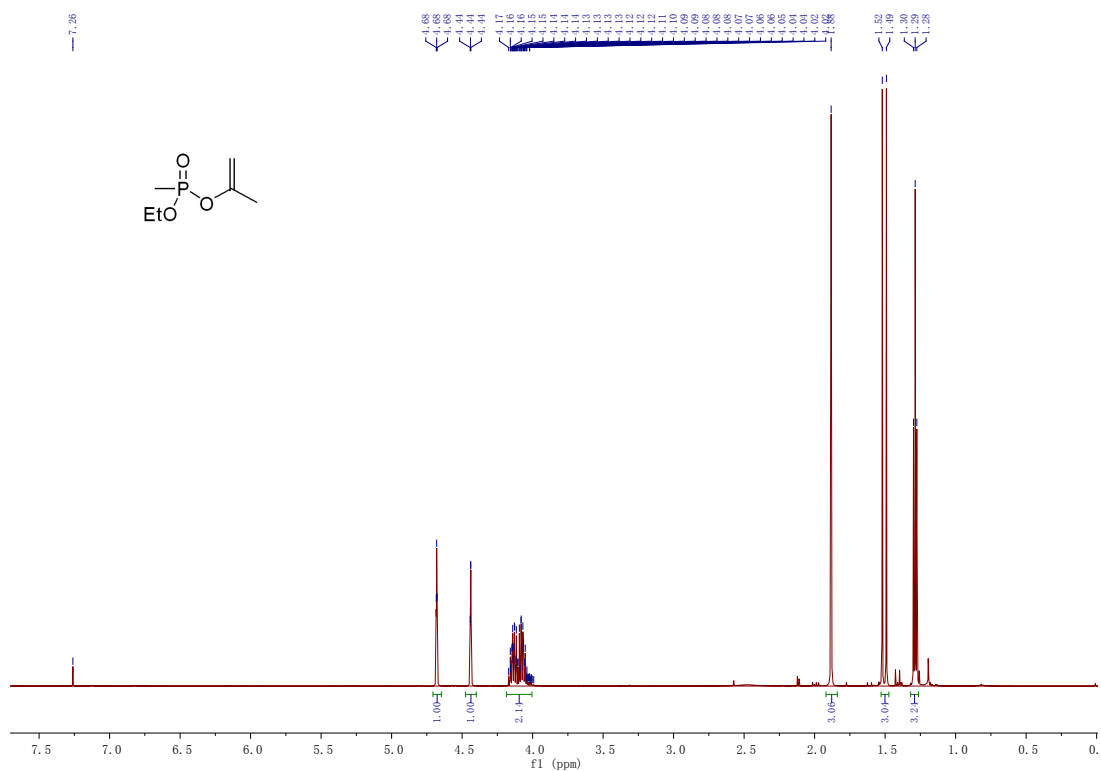


Fig.S 101 ^1H NMR of compound **5b**

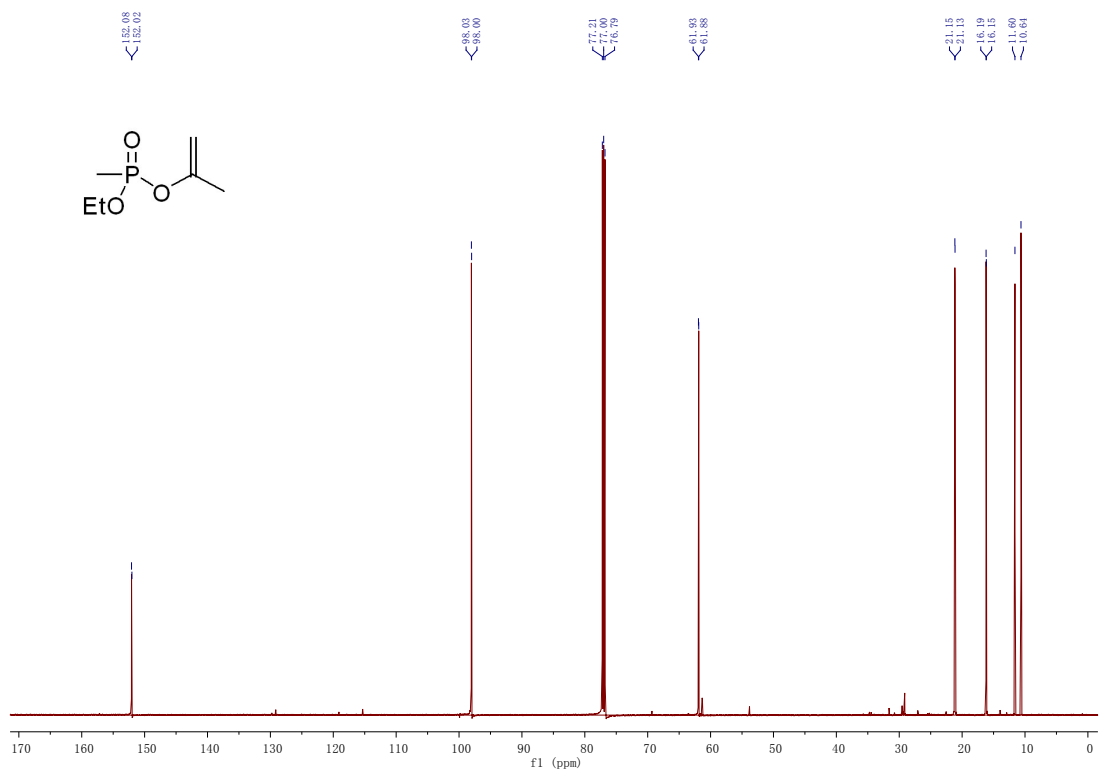


Fig.S 102 ^{13}C NMR of compound **5b**

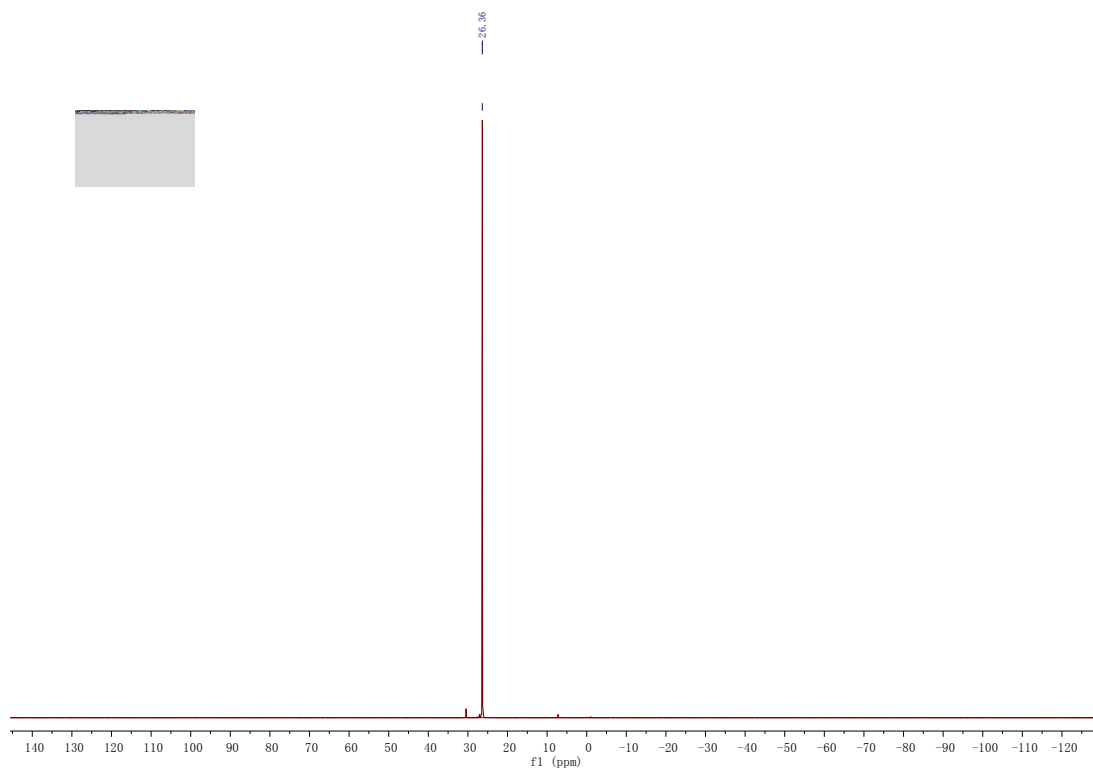


Fig.S 103 ^{31}P NMR of compound **5b**

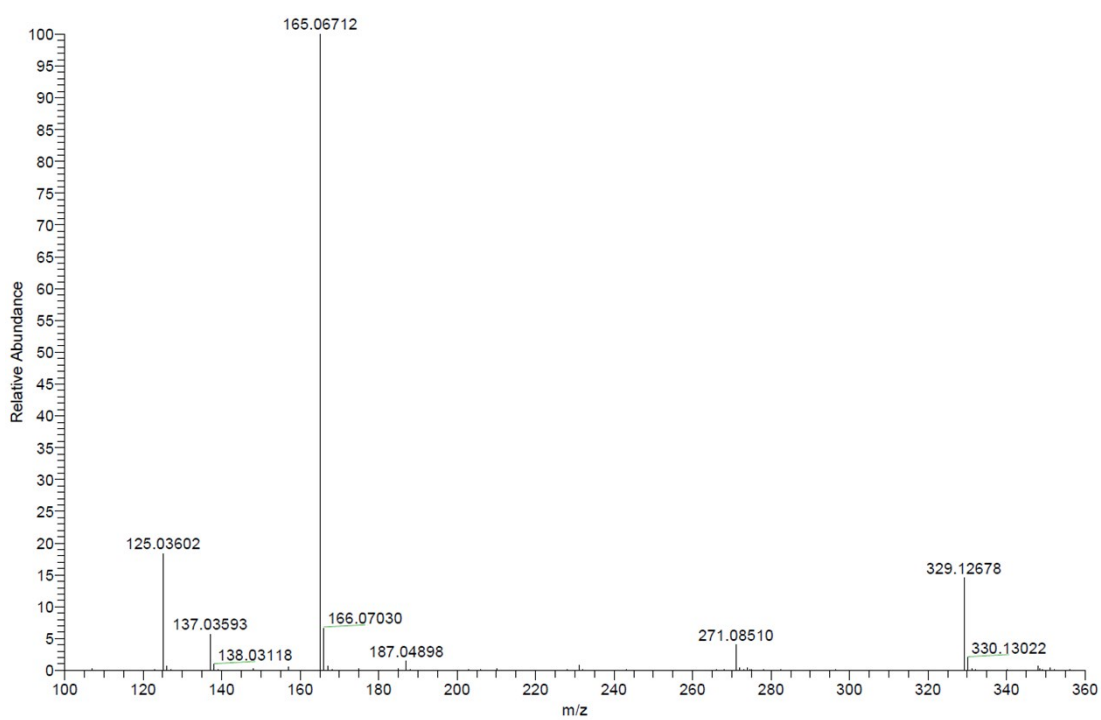


Fig.S 104 HRMS of compound **5b**

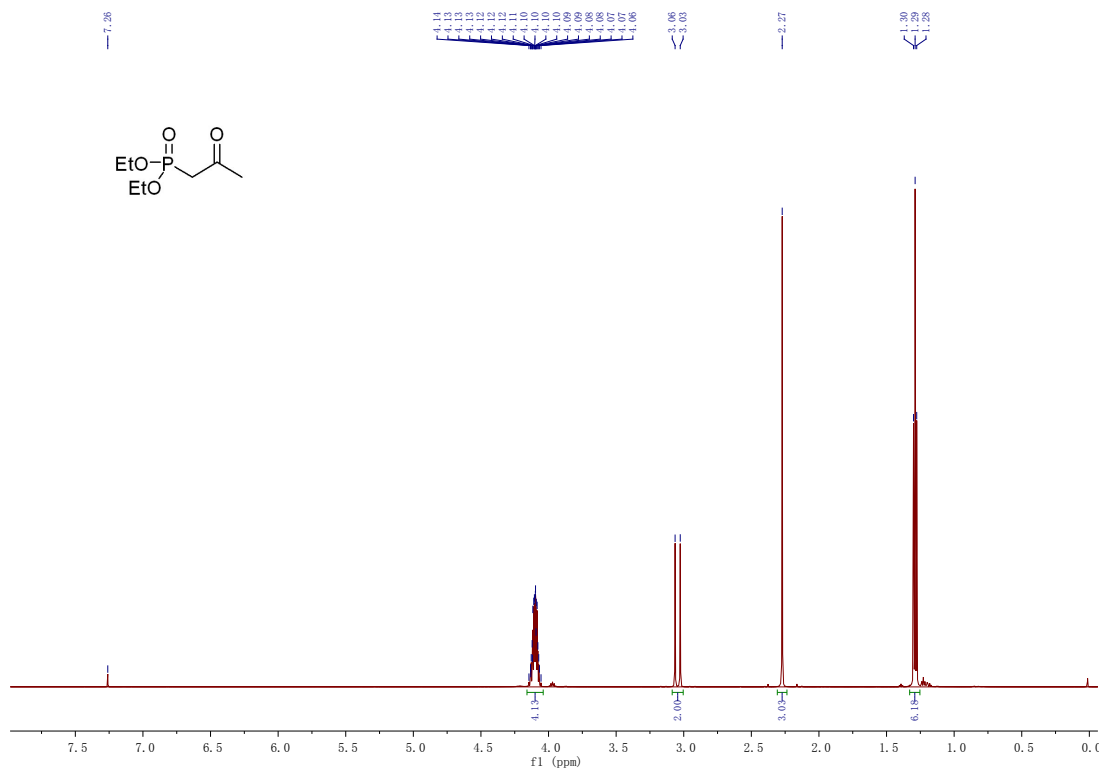


Fig.S 105 ^1H NMR of compound **6a**

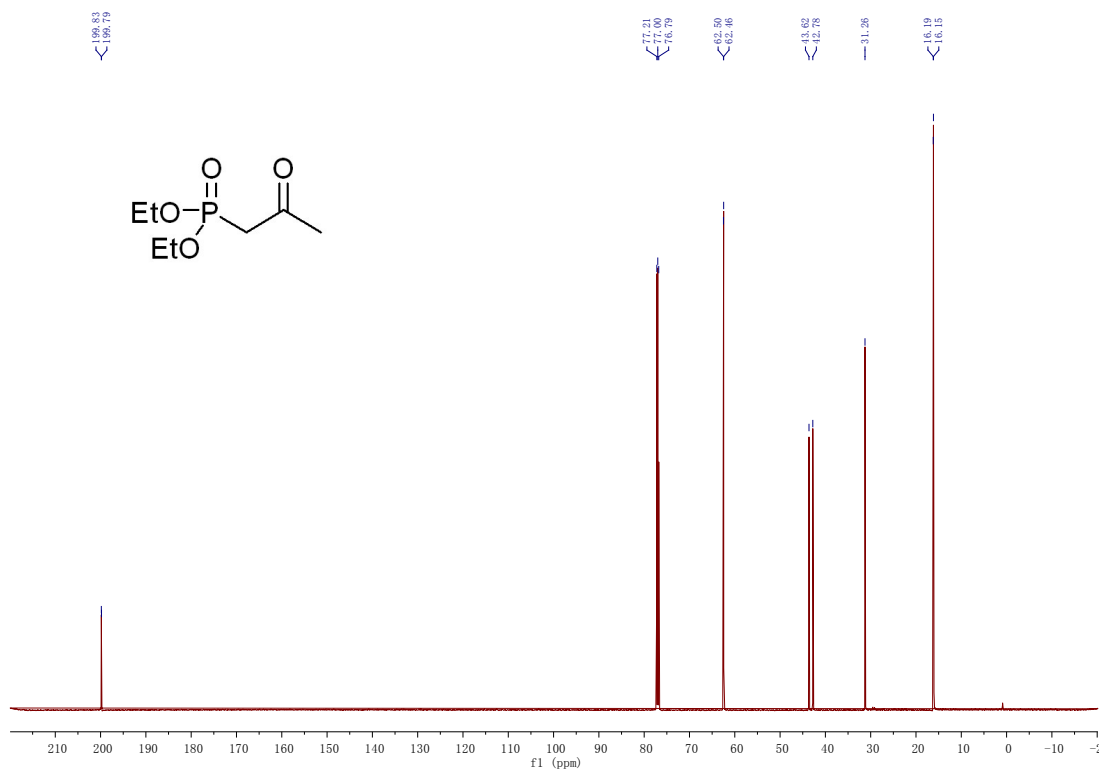


Fig.S 106 ^{13}C NMR of compound **6a**

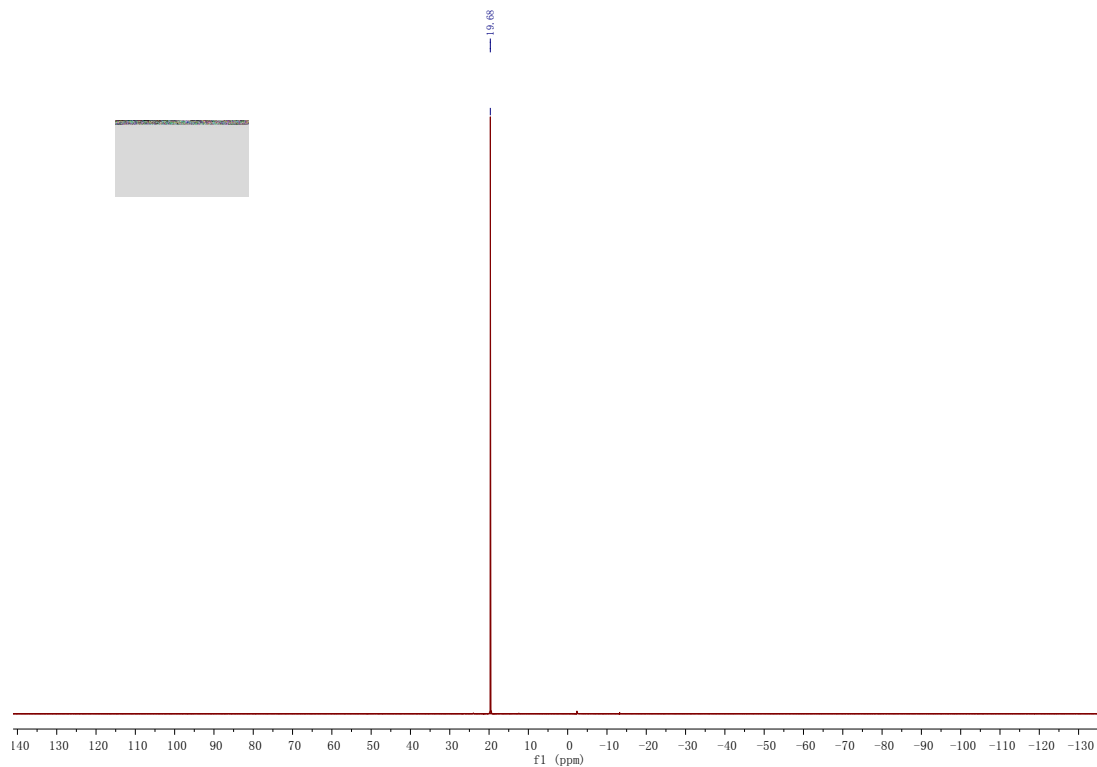


Fig.S 107 ^{31}P NMR of compound **6a**

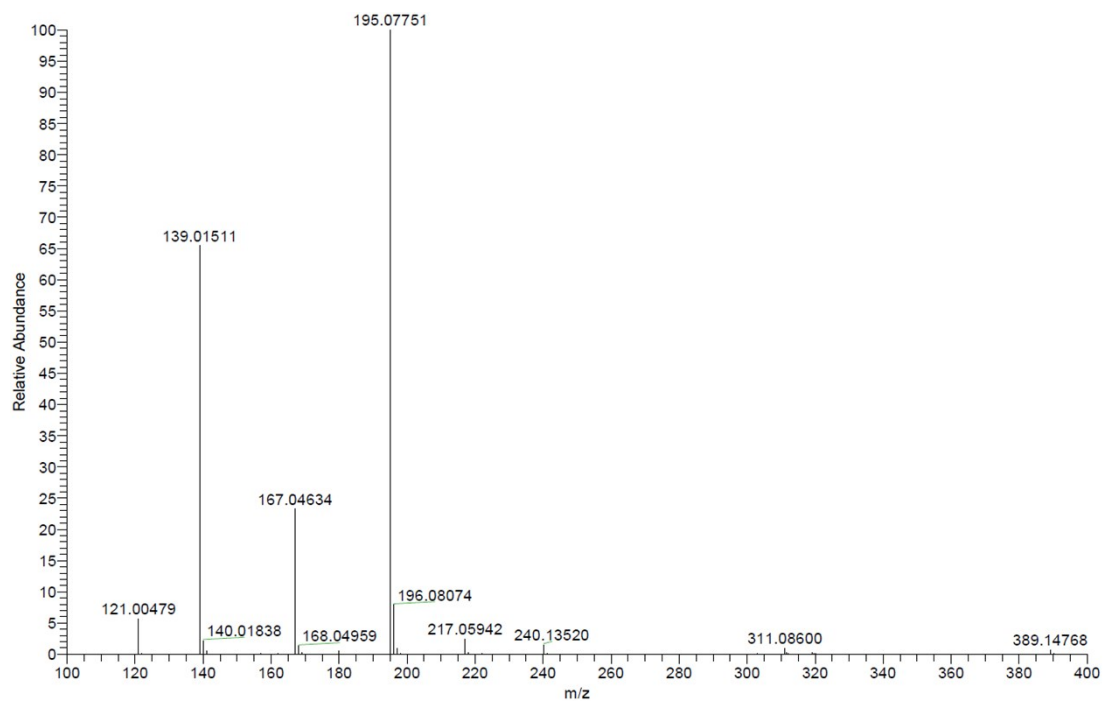


Fig.S 108 HRMS of compound **6a**