

Visible light induced radical cascade cyclization of ortho-cyanoarylacrylamides with phosphine oxides for the preparation of phosphorylated quinoline-2,4(1*H*,3*H*)-dione

Yuan-Yuan Sun,^aJing-Cheng Song,^a Shao-Hui Yang,^a Zu-Li Wang,^{a*} En-Xuan Zhang,^b Qing-Qing Han,^a Shan Yue^a

^a College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao, 266109, P. R. China.

^b Asymchem Life Science (Tianjin) Co., Ltd., Tianjin 300457, China

1. Instrument

NMR spectra were recorded at 500 MHz for protons on JOEL JNM-ECA spectrometers. ¹H NMR chemical shifts (δ) are given in ppm relative to TMS ($\delta = 0.0$). Chemical shifts for ¹³C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard. Data Reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal), integration, coupling constant (Hz) and identification. HRMS data were obtained from Thermo fisher, Exactive . All major chemicals and solvents were obtained from commercial sources and used without further purification.

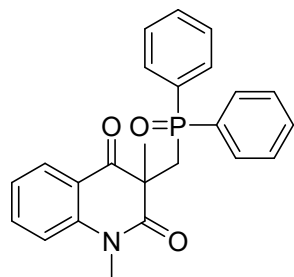
2. Typical procedure for the synthesis of phosphorylated quinoline -2,4 (1*H*,2*H*) - diones

A sealable reaction tube equipped with a magnetic stirrer bar was charged with N-(2-cyanophenyl)-N-methylmethacrylamide (0.2 mmol), HP(O)Ph₂(1.5 equiv.), LPO (2.0 equiv.), 4CzIPN(5mol%), THF (2 ml). The reaction vial was sealed under N₂ and stirred under the irradiation of white LEDs (10 W) at room temperature. After completion, it was diluted with ethyl acetate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel to afford the corresponding product.

3. The photochemical reaction apparatus



4.Characterization data of products:

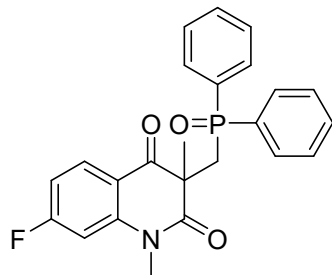


3-((diphenylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C1**):

The pure product was obtained as a white solid(68mg,84%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.00 – 7.94 (m, 1H), 7.79 – 7.64 (m, 4H), 7.63 – 7.56 (m, 1H), 7.46 (dt, $J = 24.8, 6.9$ Hz, 6H), 7.14 (dd, $J = 14.6, 7.8$ Hz, 2H), 3.44 (s, 3H), 3.39 – 3.30 (m, 2H), 1.49 (d, $J = 1.7$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 195.98 (d, $J = 1.5$ Hz), 173.26 (d, $J = 1.8$ Hz), 143.28, 135.74, 134.85, 134.06, 131.43 (d, $J = 2.7$ Hz), 130.89 (dd, $J = 15.6, 9.8$ Hz), 128.47, 128.40, 128.38, 128.31, 128.29, 122.79, 119.56, 114.88, 54.96 (d, $J = 4.1$ Hz), 36.45, 35.90, 30.01, 27.61 (d, $J = 13.9$ Hz).

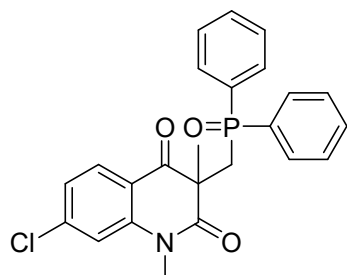


3-((diphenylphosphoryl)methyl)-7-fluoro-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C2**):

The pure product was obtained as a white solid(63mg,75%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.99 (dd, $J = 8.5, 6.7$ Hz, 1H), 7.76 – 7.60 (m, 4H), 7.54 – 7.35 (m, 6H), 6.83 (ddd, $J = 14.4, 9.6, 2.1$ Hz, 2H), 3.41 (s, 3H), 3.38 – 3.31 (m, 2H), 1.49 (d, $J = 1.9$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 194.50, 173.45, 168.47, 166.44, 145.55 (d, $J = 11.7$ Hz), 134.67 (d, $J = 4.0$ Hz), 133.87 (d, $J = 3.9$ Hz), 131.44 (dd, $J = 21.9, 6.7$ Hz), 130.93, 128.39 (d, $J = 12.0$ Hz), 116.19 (d, $J = 2.1$ Hz), 110.24, 110.07, 102.56, 102.34, 54.79 (d, $J = 4.1$ Hz), 36.56, 36.01, 30.17, 27.58 (d, $J = 13.8$ Hz).

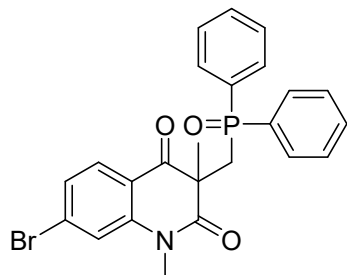


7-chloro-3-((diphenylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C3**):

The pure product was obtained as a white solid(57mg,65%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.91 (d, $J = 8.3$ Hz, 1H), 7.74 – 7.60 (m, 4H), 7.57 – 7.32 (m, 6H), 7.16 (s, 1H), 7.11 (d, $J = 8.3$ Hz, 1H), 3.44 – 3.38 (m, 3H), 3.37 – 3.29 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 194.91, 173.34, 144.24, 142.02, 134.63, 133.83, 131.53, 130.85 (dd, $J = 14.8, 9.8$ Hz), 129.85, 128.41 (d, $J = 11.1$ Hz), 123.07, 117.96, 115.21, 54.90 (d, $J = 4.1$ Hz), 36.66, 36.11, 30.13, 27.47 (d, $J = 13.8$ Hz).

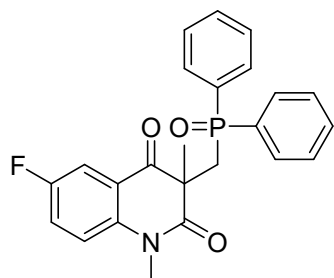


7-bromo-3-((diphenylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C4**):

The pure product was obtained as a white solid(60mg,62%).

^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J = 8.3$ Hz, 1H), 7.75 – 7.60 (m, 4H), 7.55 – 7.39 (m, 6H), 7.34 (s, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 3.41 (d, $J = 9.0$ Hz, 3H), 3.35 (tt, $J = 14.4, 7.4$ Hz, 2H), 1.48 (d, $J = 0.9$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.11, 173.29 (d, $J = 1.5$ Hz), 144.13, 134.62 (d, $J = 3.3$ Hz), 133.82 (d, $J = 3.4$ Hz), 131.54 (d, $J = 2.6$ Hz), 130.94, 130.86, 130.82, 130.76, 130.74, 129.80, 128.40 (dd, $J = 12.0, 2.2$ Hz), 126.02, 118.31, 118.14, 54.93 (d, $J = 4.1$ Hz), 36.67, 36.12, 30.13, 27.42 (d, $J = 13.8$ Hz).

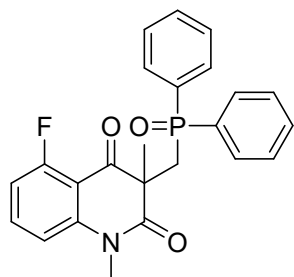


3-((diphenylphosphoryl)methyl)-6-fluoro-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C5**):

The pure product was obtained as a white solid(57mg,68%).

^1H NMR (500 MHz, CDCl_3) δ 7.76 – 7.59 (m, 5H), 7.55 – 7.39 (m, 6H), 7.31 (ddd, $J = 9.0, 7.5, 3.1$ Hz, 1H), 7.14 (dd, $J = 9.1, 4.0$ Hz, 1H), 3.43 (d, $J = 5.1$ Hz, 3H), 3.41 – 3.28 (m, 2H), 1.49 (d, $J = 2.0$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.25, 172.88 (d, $J = 1.8$ Hz), 159.38, 157.44, 139.71 (d, $J = 2.1$ Hz), 134.67 (d, $J = 4.7$ Hz), 133.87 (d, $J = 5.0$ Hz), 131.52 (d, $J = 1.5$ Hz), 130.84 (dd, $J = 19.0, 9.8$ Hz), 128.39 (dd, $J = 12.0, 4.4$ Hz), 122.75, 122.57, 120.74 (d, $J = 6.3$ Hz), 116.67 (d, $J = 7.1$ Hz), 114.20, 114.02, 54.75 (d, $J = 4.0$ Hz), 36.71, 36.16, 30.27, 27.39 (d, $J = 13.9$ Hz).

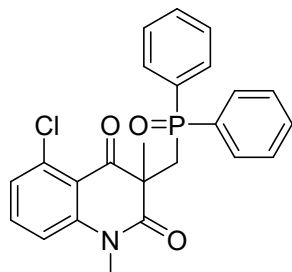


3-((diphenylphosphoryl)methyl)-5-fluoro-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C6**):

The pure product was obtained as a white solid(60mg,71%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.82 – 7.66 (m, 4H), 7.58 – 7.37 (m, 7H), 7.05 – 6.90 (m, 1H), 6.89 – 6.75 (m, 1H), 3.43 (d, $J = 20.1$ Hz, 3H), 3.32 (ddd, $J = 27.4, 14.3, 9.0$ Hz, 2H), 1.50 (s, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 193.24, 172.89 (d, $J = 1.3$ Hz), 163.66, 161.55, 144.52 (d, $J = 3.2$ Hz), 135.88 (d, $J = 11.8$ Hz), 135.09, 134.81, 134.29, 134.01, 131.44, 130.89 (dd, $J = 12.0, 9.9$ Hz), 128.39 (dd, $J = 12.0, 7.7$ Hz), 111.07, 110.90, 110.79, 110.77, 109.33 (d, $J = 9.0$ Hz), 56.06 (d, $J = 4.4$ Hz), 35.74, 35.18, 30.87, 27.03 (d, $J = 13.6$ Hz).

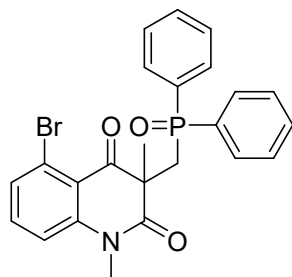


5-chloro-3-((diphenylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C7**):

The pure product was obtained as a white solid(56mg,64%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.81 – 7.61 (m, 4H), 7.55 – 7.37 (m, 7H), 7.15 (t, $J = 10.6$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 3.46 (s, 3H), 3.31 (d, $J = 9.0$ Hz, 2H), 1.48 (d, $J = 2.0$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 193.67 (d, $J = 1.2$ Hz), 172.55 (d, $J = 1.9$ Hz), 145.07, 135.99, 135.38, 134.97, 134.58, 134.15 (d, $J = 3.6$ Hz), 131.38, 131.35, 131.32, 130.88 (dd, $J = 17.0, 9.7$ Hz), 128.35 (dd, $J = 12.0, 8.8$ Hz), 126.21, 117.52, 113.84, 56.27 (d, $J = 4.6$ Hz), 35.60, 35.04, 30.97, 26.30 (d, $J = 13.4$ Hz).

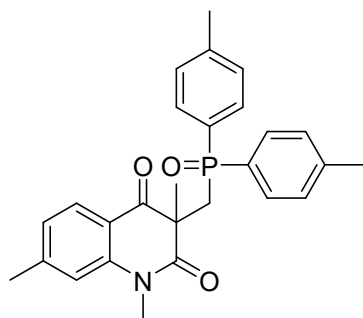


5-bromo-3-((diphenylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C8**):

The pure product was obtained as a white solid(57mg,59%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.73 (dd, $J = 19.0, 9.4$ Hz, 4H), 7.52 – 7.42 (m, 6H), 7.40 (d, $J = 7.9$ Hz, 1H), 7.34 (t, $J = 8.1$ Hz, 1H), 7.15 (d, $J = 8.3$ Hz, 1H), 3.46 (s, 3H), 3.32 (t, $J = 11.8$ Hz, 2H), 1.48 (s, 3H)

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 193.87 (d, $J = 1.4$ Hz), 172.49 (d, $J = 1.9$ Hz), 145.19, 135.36, 134.94, 134.56, 134.36, 134.14, 131.37 (t, $J = 3.0$ Hz), 130.89 (dd, $J = 15.3, 9.7$ Hz), 129.87, 128.37 (dd, $J = 12.0, 8.3$ Hz), 123.65, 118.55, 114.57, 56.02 (d, $J = 4.6$ Hz), 35.59, 35.04, 30.94, 26.20 (d, $J = 13.3$ Hz).



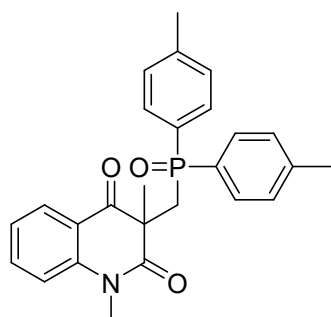
3-((di-p-tolylphosphoryl)methyl)-1,3,7-trimethylquinoline-2,4(1H,3H)-dione (**C9**):

The pure product was obtained as a white solid(82mg,92%).

$^1\text{H NMR}$ (500 MHz, DMSO) δ 7.70 (d, $J = 7.9$ Hz, 1H), 7.51 (td, $J = 12.1, 8.0$ Hz, 4H), 7.28 (d, $J = 6.2$ Hz, 4H), 7.23 (s, 1H), 7.04 (d, $J = 7.9$ Hz, 1H), 3.32 (s, 3H), 3.23 (d, $J = 9.0$ Hz, 2H), 2.46 (d, $J = 9.2$ Hz, 3H), 2.34 (s, 6H), 1.36 (d, $J = 1.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, DMSO) δ 195.39 (d, $J = 1.0$ Hz), 173.27 (d, $J = 1.5$ Hz), 147.47, 143.47, 141.51 (t, $J = 3.1$ Hz), 133.21 (d, $J = 15.7$ Hz), 132.41 (d, $J = 16.1$ Hz), 130.76 (dd, $J = 14.8, 9.9$ Hz), 129.34 (dd, $J = 12.0, 6.1$ Hz), 127.91, 123.96, 117.21, 116.30, 54.73 (d, $J = 4.0$ Hz), 36.28, 35.72, 30.07, 27.76 (d, $J = 13.7$ Hz), 22.27, 21.49.

HRMS: m/z calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 446.18759; found: 446.18796;



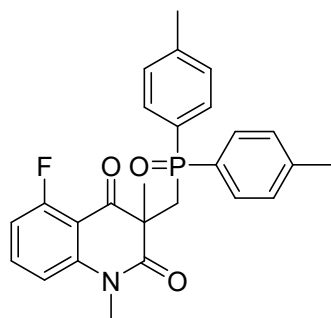
3-((di-p-tolylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C10**):

The pure product was obtained as a white solid(68mg,79%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.97 (d, $J = 7.7$ Hz, 1H), 7.63 – 7.50 (m, 5H), 7.25 – 7.18 (m, 4H), 7.13 (dd, $J = 13.1, 7.8$ Hz, 2H), 3.44 (s, 3H), 3.38 – 3.26 (m, 2H), 2.37 (s, 6H), 1.48 (d, $J = 1.7$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 196.02 (d, $J = 1.5$ Hz), 173.31 (d, $J = 1.5$ Hz), 143.31, 141.68 (dd, $J = 2.5, 1.7$ Hz), 135.66, 131.74 (d, $J = 3.6$ Hz), 130.93 (dd, $J = 14.6, 10.1$ Hz), 129.07 (dd, $J = 12.4, 1.3$ Hz), 128.45, 122.70, 119.57, 114.83, 54.91 (d, $J = 4.0$ Hz), 36.77, 36.22, 30.00, 27.61 (d, $J = 14.0$ Hz), 21.58.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 432.17188 ; found: 432.17231;



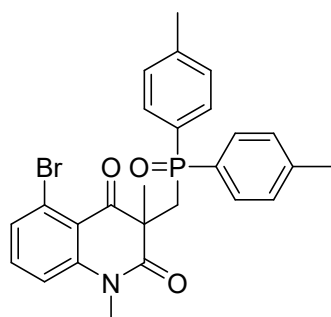
3-((di-p-tolylphosphoryl)methyl)-5-fluoro-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C11**):

The pure product was obtained as a white solid(73mg,81%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.66 – 7.45 (m, 5H), 7.24 (td, $J = 8.1, 4.0$ Hz, 4H), 6.95 (d, $J = 8.5$ Hz, 1H), 6.81 (dd, $J = 10.1, 8.6$ Hz, 1H), 3.45 (s, 3H), 3.28 (qd, $J = 14.4, 9.0$ Hz, 2H), 2.37 (d, $J = 4.6$ Hz, 6H), 1.49 (d, $J = 1.9$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 193.26, 172.92 (d, $J = 1.8$ Hz), 163.66, 161.55, 144.56 (d, $J = 3.2$ Hz), 141.73 (t, $J = 2.6$ Hz), 135.79 (d, $J = 11.8$ Hz), 131.86, 131.57, 131.04, 131.01, 130.94, 130.93, 130.86, 130.74, 129.11 (dd, $J = 12.4, 4.9$ Hz), 110.99, 110.82, 110.74, 110.71, 109.33 (d, $J = 9.0$ Hz), 55.97 (d, $J = 4.4$ Hz), 36.08, 35.52, 30.85, 27.05 (d, $J = 13.6$ Hz), 21.58.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{FNO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 450.16245 ; found: 450.16288;



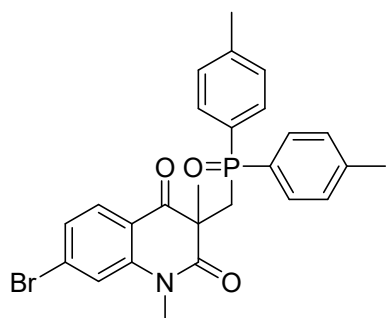
5-bromo-3-((di-p-tolylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C12**):

The pure product was obtained as a white solid(85mg,83%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (ddd, $J = 16.2, 11.7, 8.0$ Hz, 4H), 7.39 (d, $J = 7.7$ Hz, 1H), 7.33 (t, $J = 8.1$ Hz, 1H), 7.24 (d, $J = 6.0$ Hz, 4H), 7.15 (t, $J = 6.5$ Hz, 1H), 3.45 (s, 3H), 3.25 (t, $J = 13.1$ Hz, 2H), 2.41 – 2.32 (m, 6H), 1.46 (d, $J = 1.9$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 193.87 (d, $J = 1.3$ Hz), 172.52 (d, $J = 2.0$ Hz), 145.25, 141.64 (d, $J = 2.1$ Hz), 134.31, 132.15, 131.75, 131.34, 131.01, 130.93, 130.84, 129.82, 129.10 (dd, $J = 12.4, 6.7$ Hz), 123.64, 118.50, 114.55, 55.89 (d, $J = 4.5$ Hz), 35.97, 35.41, 30.92, 26.25 (d, $J = 13.3$ Hz), 21.59.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{BrNO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 510.08249 ; found: 510.08282;



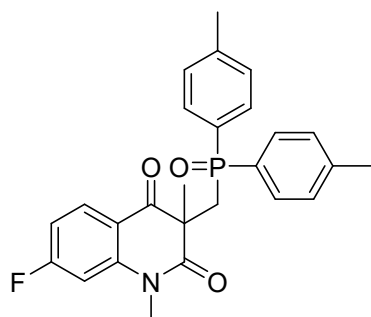
7-bromo-3-((di-p-tolylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C13**):

The pure product was obtained as a white solid(91mg,89%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.82 (d, $J = 8.3$ Hz, 1H), 7.62 – 7.47 (m, 4H), 7.32 (d, $J = 1.4$ Hz, 1H), 7.24 (ddd, $J = 10.1, 7.0, 2.3$ Hz, 5H), 3.42 (d, $J = 5.7$ Hz, 3H), 3.31 (qd, $J = 14.4, 9.0$ Hz, 2H), 2.35 (d, $J = 14.4$ Hz, 6H), 1.45 (t, $J = 10.1$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 195.14 (d, $J = 1.5$ Hz), 173.34 (d, $J = 1.7$ Hz), 144.15, 141.83 (d, $J = 2.4$ Hz), 131.49, 130.98, 130.89, 130.86, 130.78, 130.68, 129.77, 129.25, 129.17, 129.16, 129.07, 129.06, 128.99, 126.46, 125.92, 118.32, 118.09, 54.89 (d, $J = 4.0$ Hz), 36.99, 36.44, 30.12, 27.43 (d, $J = 13.7$ Hz), 21.60.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{BrNO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 510.08240 ; found: 510.08282;



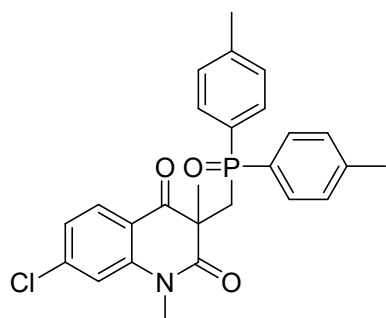
3-((di-p-tolylphosphoryl)methyl)-7-fluoro-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C14**):

The pure product was obtained as a white solid(84mg,93%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.98 (dt, $J = 18.8, 9.5$ Hz, 1H), 7.63 – 7.46 (m, 4H), 7.23 (t, $J = 5.3$ Hz, 4H), 6.82 (td, $J = 10.8, 3.4$ Hz, 2H), 3.40 (s, 3H), 3.35 – 3.26 (m, 2H), 2.35 (d, $J = 18.4$ Hz, 6H), 1.48 (t, $J = 8.1$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 194.54 (d, $J = 1.3$ Hz), 173.48 (d, $J = 1.8$ Hz), 168.45, 166.42, 145.57 (d, $J = 11.7$ Hz), 141.84, 141.83, 141.81, 131.40 (dd, $J = 20.9, 9.2$ Hz), 130.98, 130.89, 130.89, 130.80, 130.69, 130.64, 129.11 (d, $J = 12.4$ Hz), 125.76, 116.20 (d, $J = 2.3$ Hz), 110.14, 109.96, 102.50, 102.28, 54.74 (d, $J = 4.0$ Hz), 36.84, 36.29, 30.15, 27.58 (d, $J = 13.8$ Hz), 21.59.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{FNO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 450.16241 ; found: 450.16288;



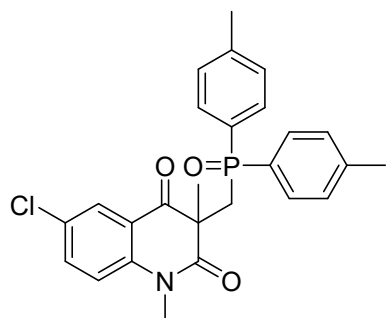
7-chloro-3-((di-p-tolylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C15**):

The pure product was obtained as a white solid(82mg,88%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.3$ Hz, 1H), 7.62 – 7.46 (m, 4H), 7.23 (d, $J = 3.3$ Hz, 4H), 7.15 (s, 1H), 7.10 (d, $J = 8.3$ Hz, 1H), 3.41 (s, 3H), 3.31 (qd, $J = 14.5, 9.1$ Hz, 2H), 2.36 (d, $J = 14.7$ Hz, 6H), 1.45 (t, $J = 10.3$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 194.94 (d, $J = 1.6$ Hz), 173.38 (d, $J = 1.9$ Hz), 144.24, 141.85 (dd, $J = 8.1, 7.2$ Hz), 131.51, 130.96, 130.88, 130.85, 130.77, 130.69, 129.82, 129.15, 129.15, 129.06, 122.95, 117.97, 115.14, 54.84 (d, $J = 4.3$ Hz), 36.96, 36.41, 30.10, 27.45 (d, $J = 13.8$ Hz), 21.58.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{ClNO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 466.13300 ; found: 466.13333;



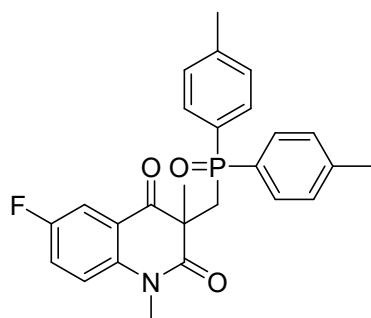
6-chloro-3-((di-p-tolylphosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C16**):

The pure product was obtained as a white solid(84mg,90%).

$^1\text{H NMR}$ (500 MHz, DMSO) δ 7.78 (dd, $J = 8.9, 2.7$ Hz, 1H), 7.69 (d, $J = 2.7$ Hz, 1H), 7.55 – 7.41 (m, 5H), 7.28 (dd, $J = 7.8, 1.8$ Hz, 4H), 3.31 (s, 3H), 3.24 (dd, $J = 8.9, 6.5$ Hz, 2H), 2.34 (d, $J = 3.6$ Hz, 6H), 1.39 (d, $J = 1.7$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, DMSO) δ 195.01 (d, $J = 1.1$ Hz), 172.76 (d, $J = 1.7$ Hz), 142.31, 141.67 (dd, $J = 4.1, 2.6$ Hz), 135.85, 132.90, 132.82 (d, $J = 20.4$ Hz), 132.09, 131.93, 130.74 (dd, $J = 16.6, 10.0$ Hz), 129.40 (dd, $J = 12.1, 6.7$ Hz), 127.43, 126.68, 120.60, 118.47, 54.78 (d, $J = 4.0$ Hz), 36.90, 36.35, 30.32, 27.14 (d, $J = 13.5$ Hz), 21.50.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{ClNO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 466.13318 ; found: 466.13333;



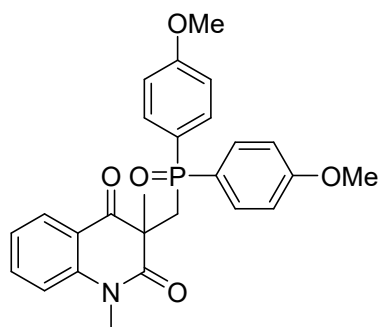
3-((di-p-tolylphosphoryl)methyl)-6-fluoro-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C17**):

The pure product was obtained as a white solid(75mg,83%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.67 – 7.47 (m, 5H), 7.34 – 7.26 (m, 1H), 7.23 (d, $J = 7.6$ Hz, 4H), 7.13 (t, $J = 9.8$ Hz, 1H), 3.44 (d, $J = 9.0$ Hz, 3H), 3.38 – 3.21 (m, 2H), 2.38 (d, $J = 10.4$ Hz, 6H), 1.53 – 1.38 (m, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 195.29, 172.91 (d, $J = 1.7$ Hz), 159.35, 157.41, 141.85 (t, $J = 2.8$ Hz), 139.74 (d, $J = 2.0$ Hz), 131.45 (d, $J = 2.1$ Hz), 130.99, 130.91, 130.86, 130.78, 130.64, 130.63, 129.12 (dd, $J = 12.4, 2.7$ Hz), 122.69, 122.51, 120.73 (d, $J = 6.3$ Hz), 116.64 (d, $J = 7.1$ Hz), 114.14, 113.96, 54.68 (d, $J = 4.0$ Hz), 37.04, 36.49, 30.26, 27.39 (d, $J = 13.8$ Hz), 21.59.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{FNO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 450.16257 ; found: 450.16288;



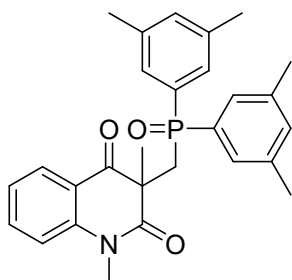
3-((bis(4-methoxyphenyl)phosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C18**):

The pure product was obtained as a white solid(85mg,92%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.97 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.66 – 7.54 (m, 5H), 7.16 – 7.10 (m, 2H), 6.95 – 6.89 (m, 4H), 3.82 (d, $J = 0.8$ Hz, 6H), 3.44 (s, 3H), 3.29 (qd, $J = 14.5, 9.2$ Hz, 2H), 1.48 (d, $J = 2.0$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 196.07 (d, $J = 1.5$ Hz), 173.36 (d, $J = 1.8$ Hz), 162.00, 161.99, 161.98, 143.30, 135.69, 132.87 (dd, $J = 16.3, 11.1$ Hz), 128.43, 126.26 (d, $J = 12.6$ Hz), 125.41 (d, $J = 12.6$ Hz), 122.71, 119.57, 114.83, 113.85 (dd, $J = 13.0, 2.0$ Hz), 55.27, 54.92 (d, $J = 4.0$ Hz), 37.15, 36.59, 30.01, 27.67 (d, $J = 13.9$ Hz).

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_5\text{P}$ $[\text{M}+\text{H}]^+$: 464.16177 ; found: 464.16214;

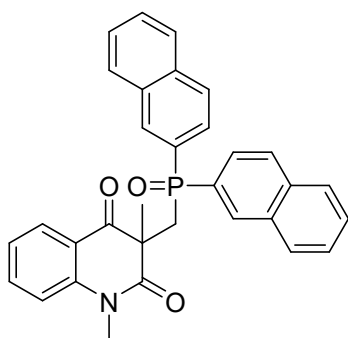


3-((bis(3,5-dimethylphenyl)phosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C19**):
The pure product was obtained as a white solid(84mg,91%).

$^1\text{H NMR}$ (500 MHz, DMSO) δ 7.81 – 7.72 (m, 2H), 7.39 (d, J = 8.3 Hz, 1H), 7.28 – 7.19 (m, 5H), 7.13 (s, 2H), 3.31 (s, 3H), 3.25 (d, J = 9.2 Hz, 2H), 2.28 (d, J = 2.4 Hz, 12H), 1.39 (d, J = 1.6 Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, DMSO) δ 195.80 (d, J = 1.3 Hz), 172.89 (d, J = 1.6 Hz), 143.41, 137.90 (dd, J = 12.3, 7.6 Hz), 136.54, 136.30 (d, J = 16.6 Hz), 135.53 (d, J = 16.8 Hz), 133.05 (t, J = 2.6 Hz), 128.14, 128.07, 128.04, 127.96, 127.83, 123.05, 119.38, 116.02, 54.70 (d, J = 4.1 Hz), 36.37, 35.83, 30.09, 27.58 (d, J = 13.8 Hz), 21.38.

HRMS: m/z calcd for $\text{C}_{28}\text{H}_{31}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 460.20309 ; found: 460.20361;

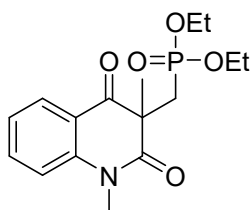


3-((di(naphthalen-2-yl)phosphoryl)methyl)-1,3-dimethylquinoline-2,4(1H,3H)-dione (**C20**):
The pure product was obtained as a white solid(91mg,90%).

$^1\text{H NMR}$ (500 MHz, DMSO) δ 8.40 – 8.27 (m, 2H), 8.08 – 7.93 (m, 6H), 7.87 – 7.72 (m, 4H), 7.62 (dt, J = 14.8, 7.0 Hz, 4H), 7.41 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 3.57 – 3.46 (m, 2H), 3.32 (s, 3H), 1.44 (t, J = 9.8 Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, DMSO) δ 195.96, 173.02 (d, J = 1.5 Hz), 143.43, 136.64, 134.38, 133.57 (d, J = 17.8 Hz), 132.79 (d, J = 18.2 Hz), 132.42 (d, J = 12.9 Hz), 131.91 (dd, J = 14.2, 8.9 Hz), 129.23, 128.69, 128.61, 128.52, 128.19 (d, J = 1.4 Hz), 127.87, 127.44 (d, J = 3.0 Hz), 126.17 (dd, J = 17.4, 10.6 Hz), 123.14, 119.38, 116.12, 55.03 (d, J = 4.1 Hz), 35.95, 35.40, 30.17, 27.64 (d, J = 13.8 Hz), 21.24.

HRMS: m/z calcd for $\text{C}_{32}\text{H}_{27}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 504.17175 ; found: 504.17231;

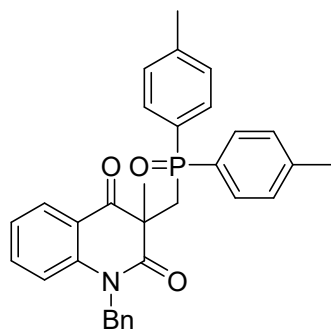


diethyl ((1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl)methyl)phosphonate (**C21**):

The pure product was obtained as a white solid(54mg,80%).

¹H NMR (500 MHz, DMSO) δ 7.91 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.78 – 7.73 (m, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.25 (t, $J = 7.5$ Hz, 1H), 3.94 – 3.78 (m, 4H), 3.41 (s, 3H), 2.61 (t, $J = 15.0$ Hz, 2H), 1.36 – 1.30 (m, 3H), 1.12 (dd, $J = 13.3, 6.9$ Hz, 6H)

¹³C NMR (126 MHz, DMSO) δ 195.87 (d, $J = 1.7$ Hz), 172.79 (d, $J = 2.2$ Hz), 143.44, 136.92, 127.84, 123.31, 119.29, 116.19, 61.44 (dd, $J = 15.3, 6.0$ Hz), 54.42 (d, $J = 3.3$ Hz), 32.84, 31.75, 30.14, 27.66 (d, $J = 18.5$ Hz), 16.46 (dd, $J = 6.2, 2.6$ Hz).



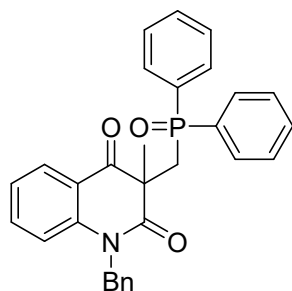
1-benzyl-3-((di-p-tolylphosphoryl)methyl)-3-methylquinoline-2,4(1H,3H)-dione (**C22**):

The pure product was obtained as a white solid(90mg,89%).

¹H NMR (500 MHz, DMSO) δ 7.86 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.57 (ddd, $J = 19.6, 11.7, 8.0$ Hz, 5H), 7.47 (d, $J = 7.5$ Hz, 2H), 7.34 – 7.28 (m, 4H), 7.28 – 7.20 (m, 3H), 7.16 (dd, $J = 12.5, 5.1$ Hz, 2H), 5.41 (d, $J = 15.8$ Hz, 1H), 5.05 (d, $J = 16.6$ Hz, 1H), 3.36 (t, $J = 9.6$ Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.46 (s, 3H).

¹³C NMR (126 MHz, DMSO) δ 195.79, 173.78 (d, $J = 1.5$ Hz), 142.22, 141.57 (dd, $J = 16.4, 2.6$ Hz), 136.88, 136.32, 133.53, 133.13, 132.73, 132.33, 130.71 (dd, $J = 10.0, 2.6$ Hz), 129.40 (dd, $J = 16.5, 12.1$ Hz), 128.90, 128.14, 127.40, 127.19, 123.18, 119.63, 116.64, 55.34, 45.43, 36.14, 35.59, 27.55 (d, $J = 13.8$ Hz), 21.49 (d, $J = 5.0$ Hz).

HRMS: m/z calcd for $C_{32}H_{31}NO_3P[M+H]^+$: 508.20325 ; found: 508.20361;



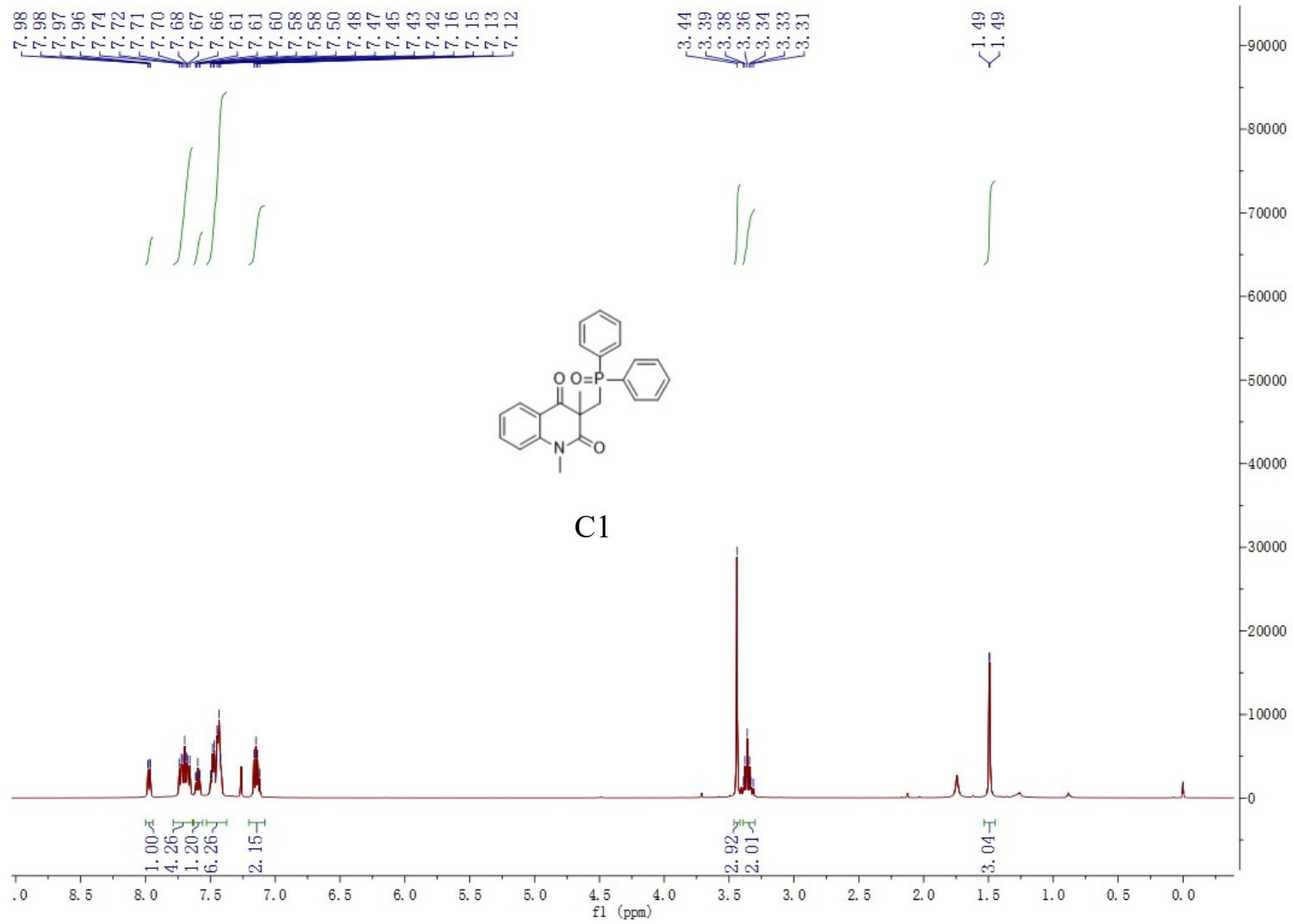
1-benzyl-3-((diphenylphosphoryl)methyl)-3-methylquinoline-2,4(1H,3H)-dione (**C23**):

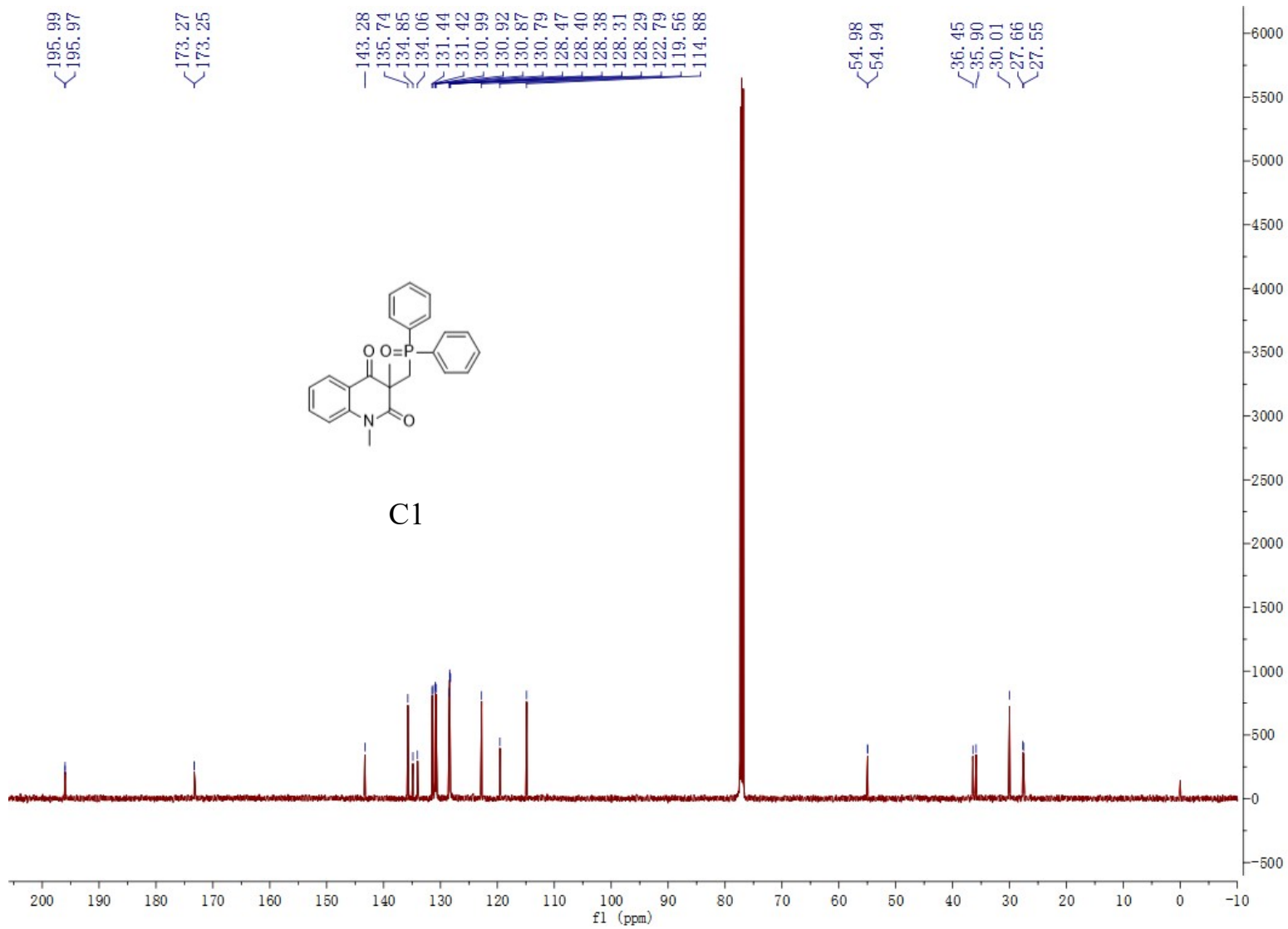
The pure product was obtained as a white solid(63mg,66%).

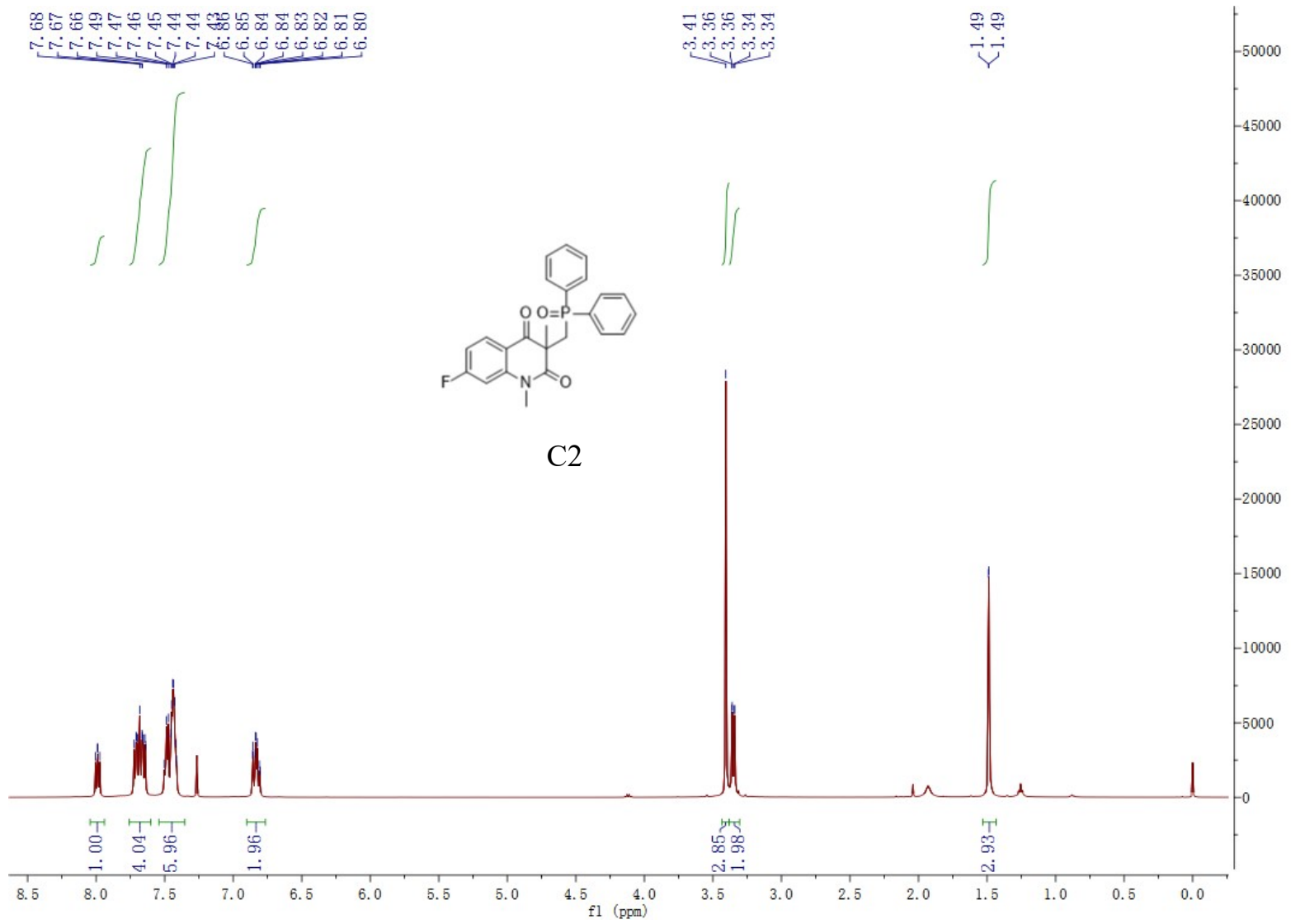
¹H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, $J = 7.7$ Hz, 1H), 7.74 (dd, $J = 11.6, 7.9$ Hz, 4H), 7.56 – 7.36 (m, 9H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 7.01 (d, $J = 8.4$ Hz, 1H), 5.28 (dd, $J = 46.5, 16.2$ Hz, 2H), 3.44 (qd, $J = 14.4, 8.9$ Hz, 2H), 1.58 (s, 3H).

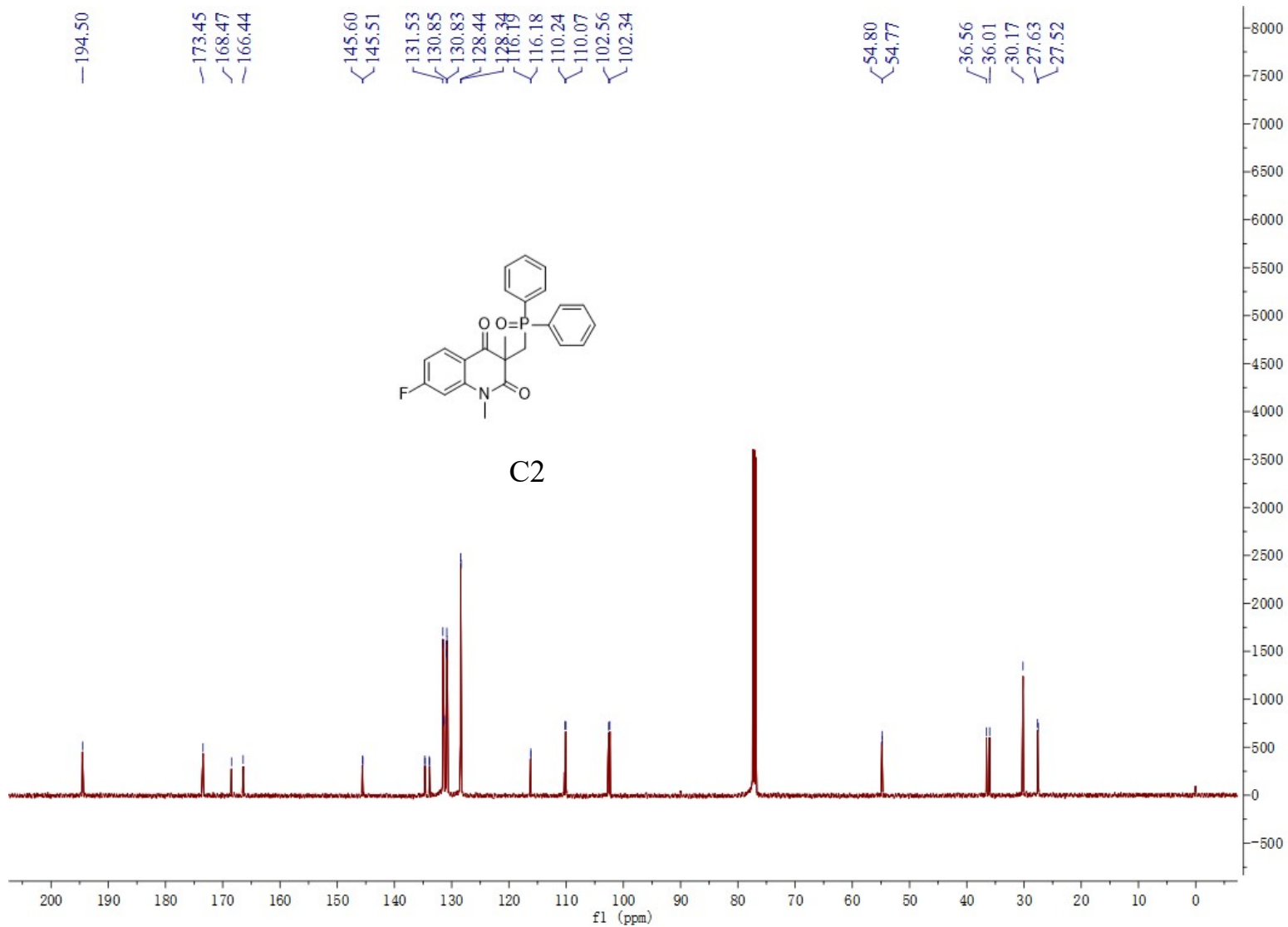
^{13}C NMR (126 MHz, CDCl_3) δ 195.94 (d, $J = 1.2$ Hz), 173.87 (d, $J = 1.9$ Hz), 142.41, 136.32, 135.62, 135.13, 134.81, 134.34, 134.01, 131.45 (dd, $J = 8.5, 2.7$ Hz), 130.92 (dd, $J = 9.8, 2.4$ Hz), 128.84, 128.44 (dd, $J = 27.6, 15.0$ Hz), 127.14, 126.43, 122.91, 119.72, 115.85, 55.48 (d, $J = 4.3$ Hz), 46.42, 36.14, 35.59, 27.56 (d, $J = 13.8$ Hz).

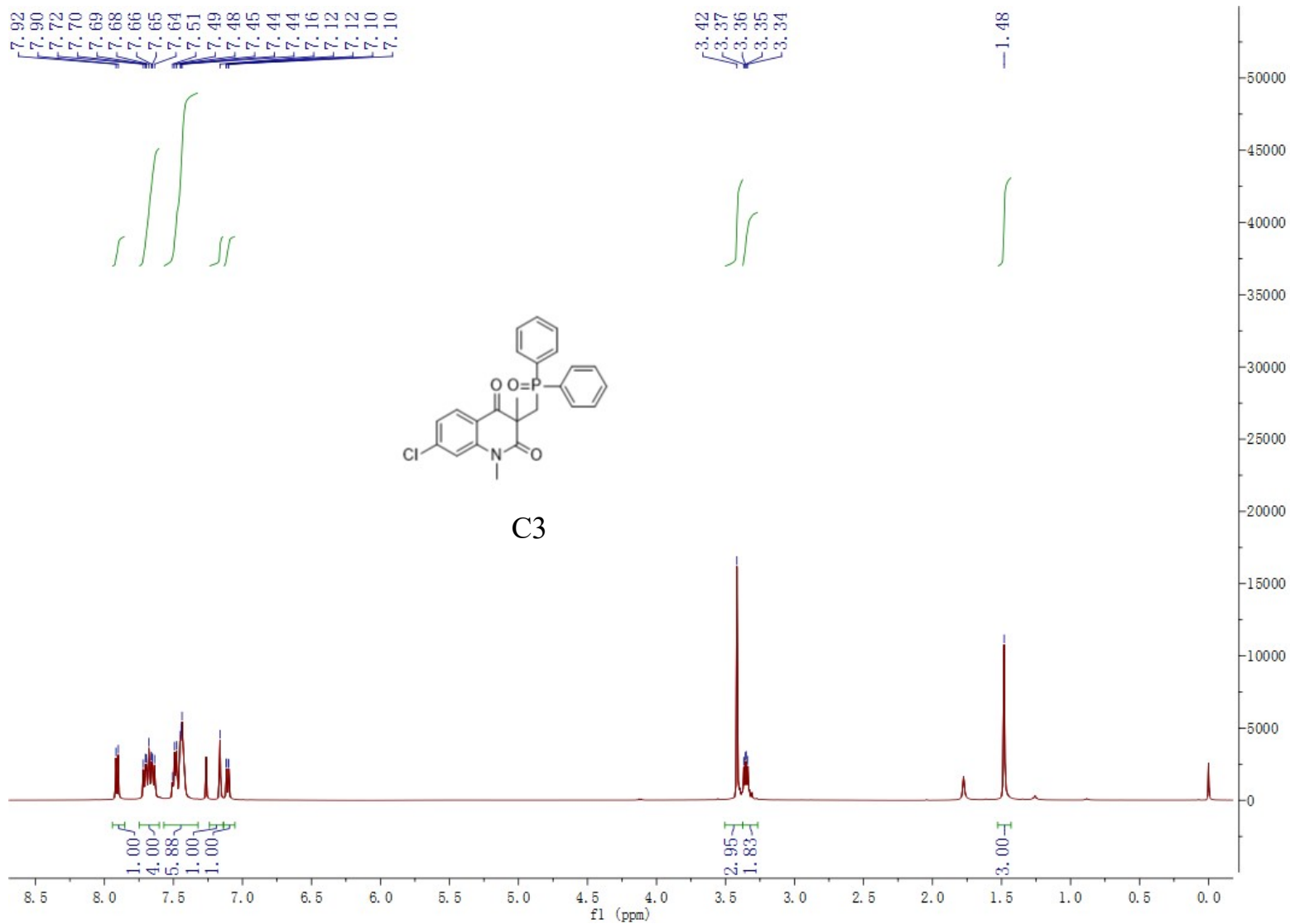
5. ^1H and ^{13}C NMR spectral copie

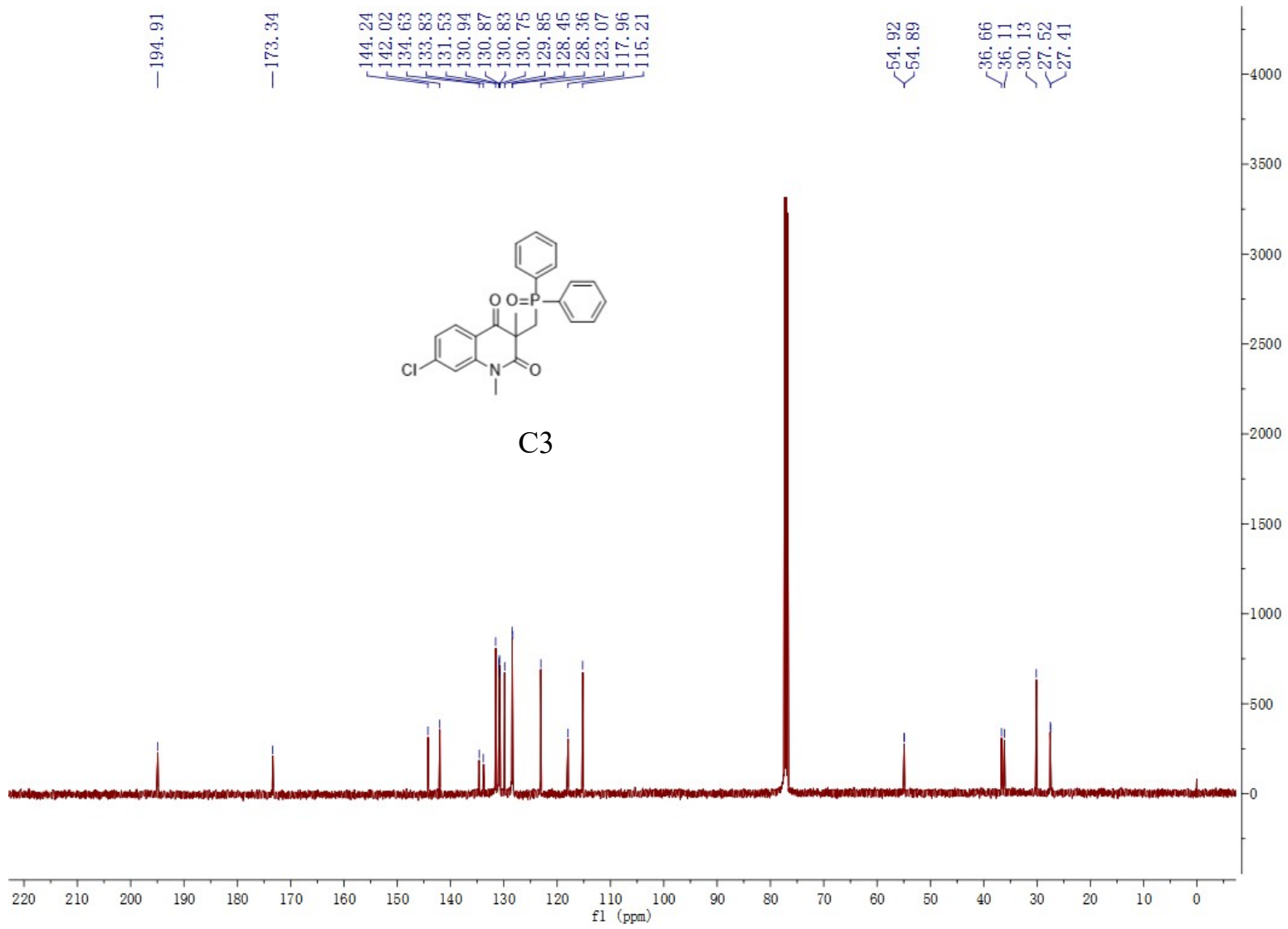


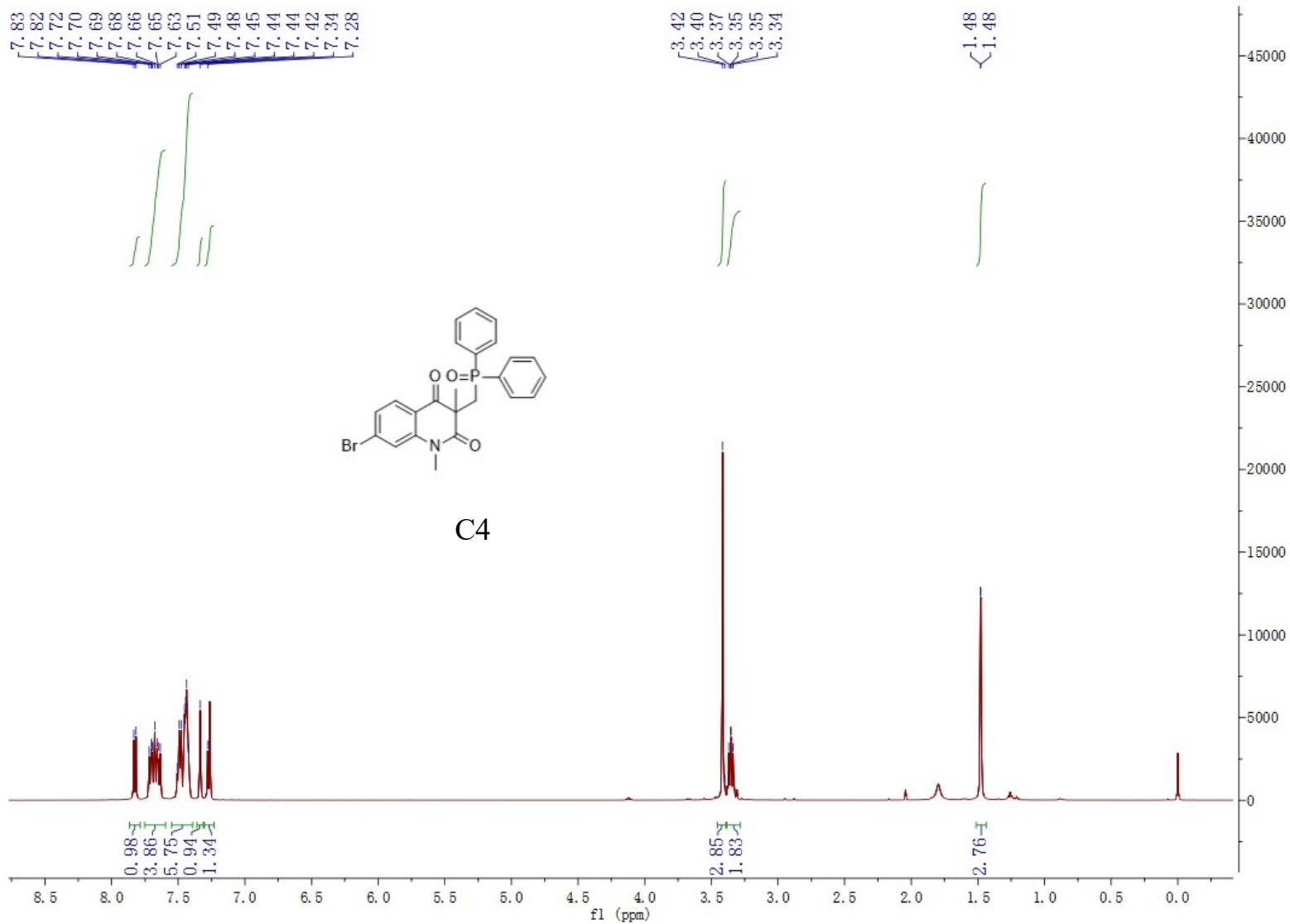


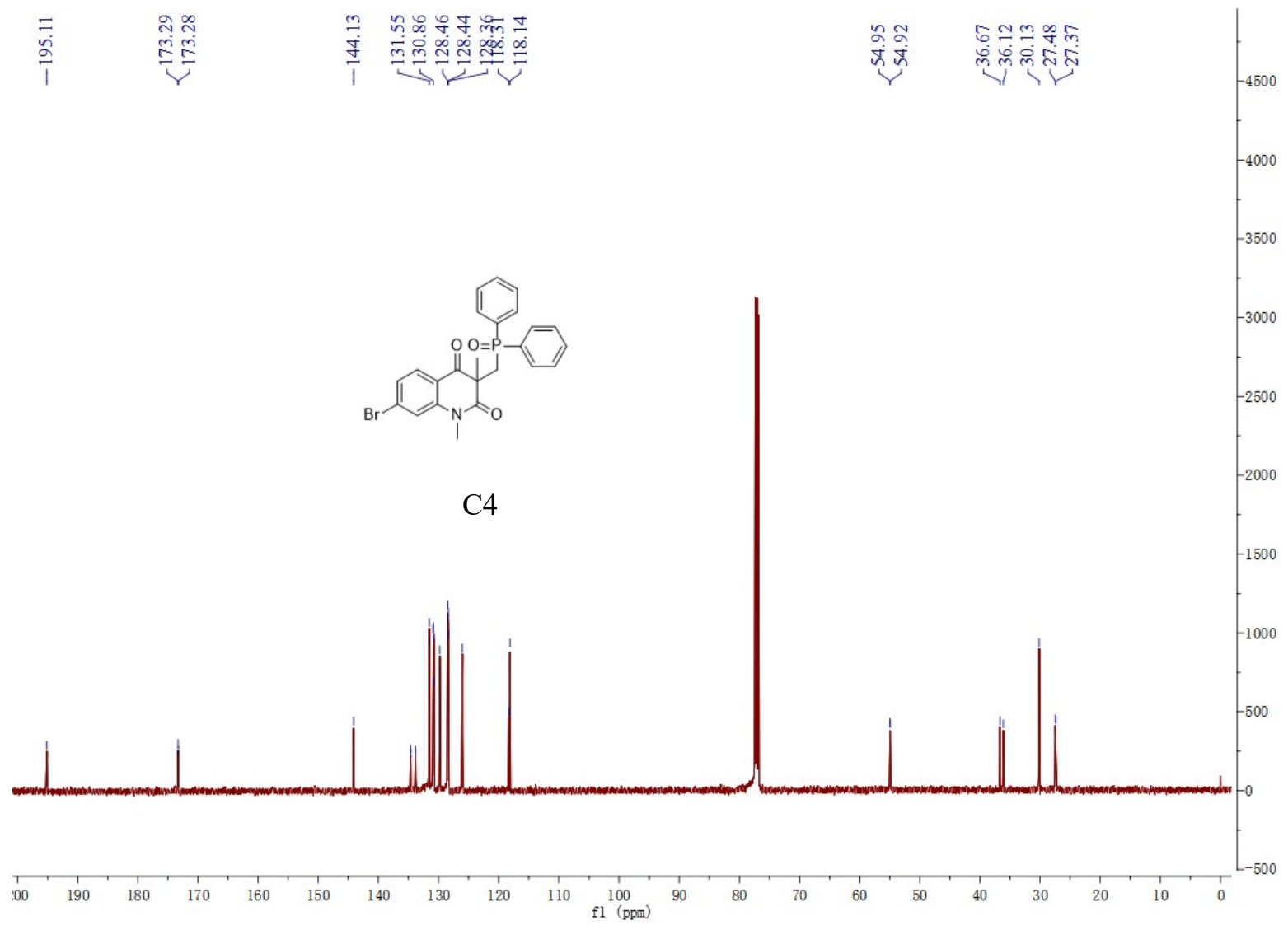


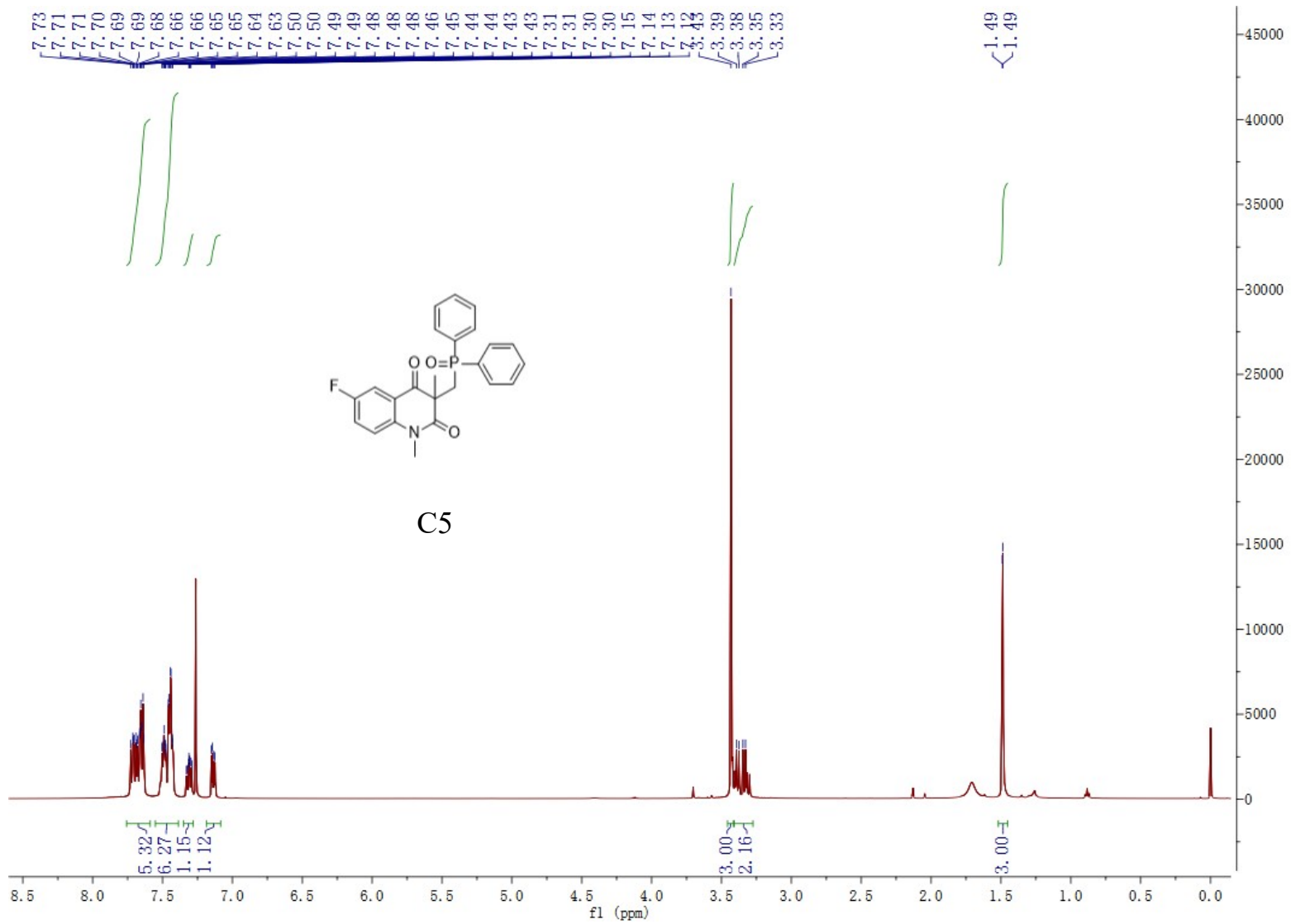


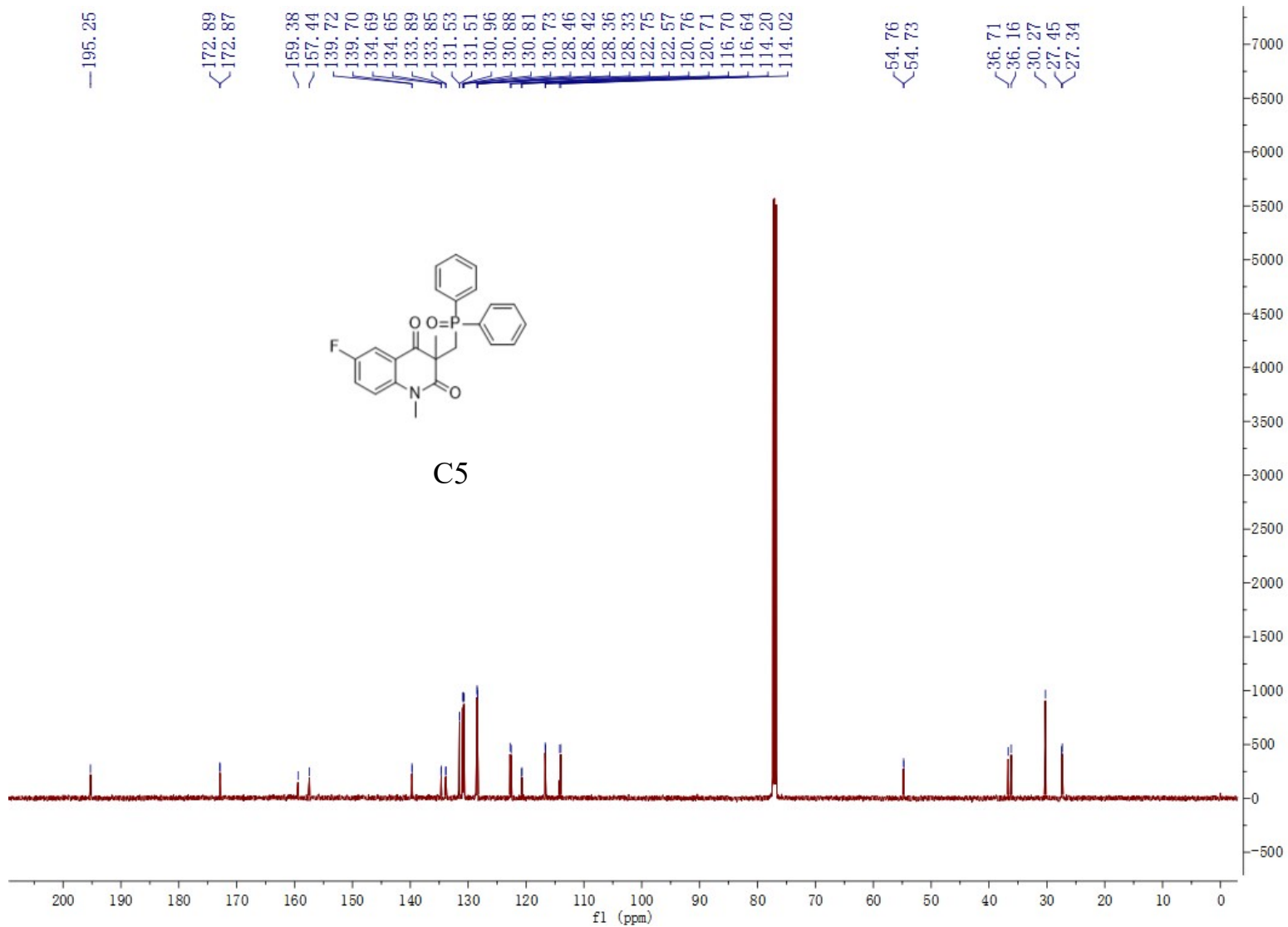


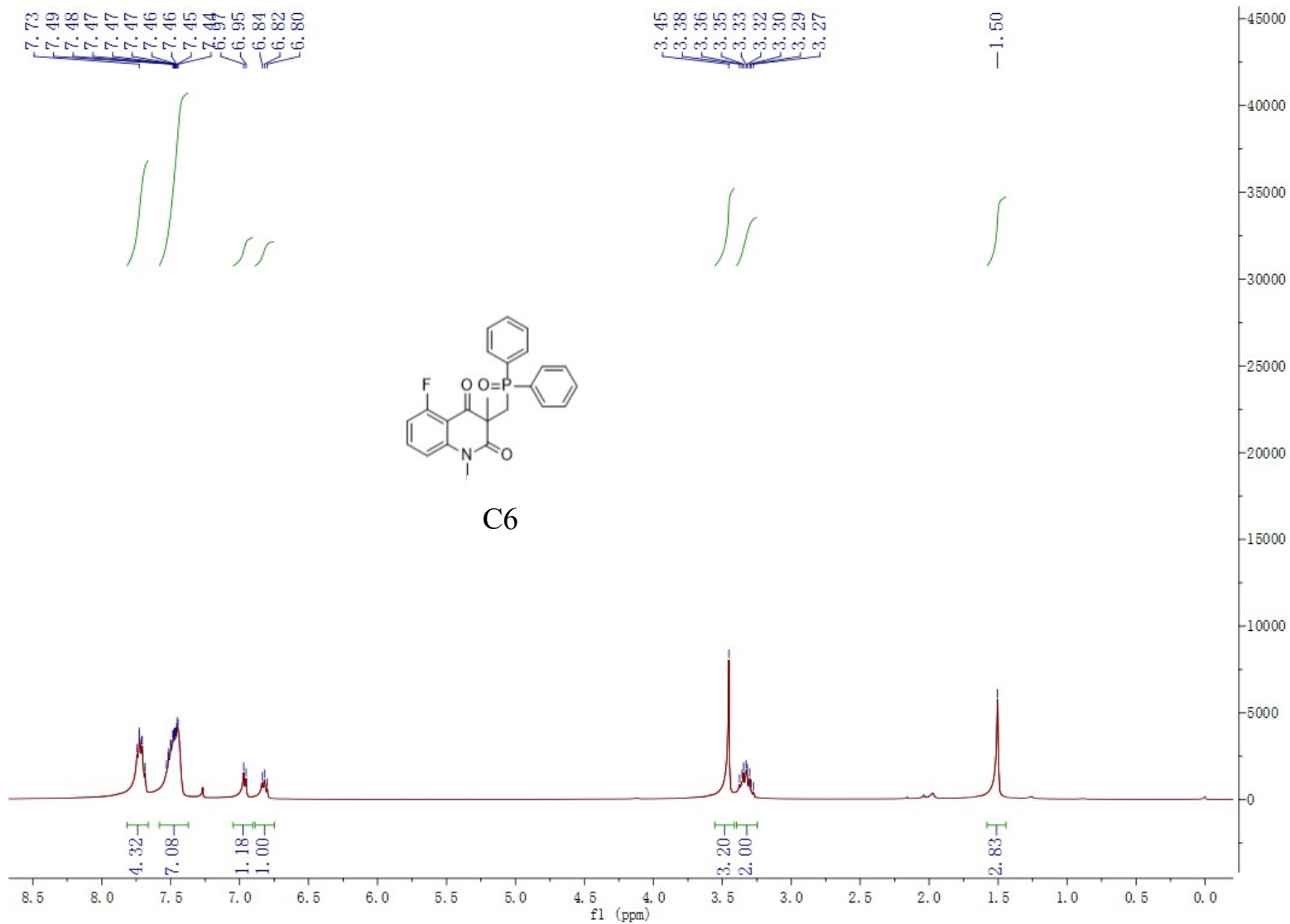


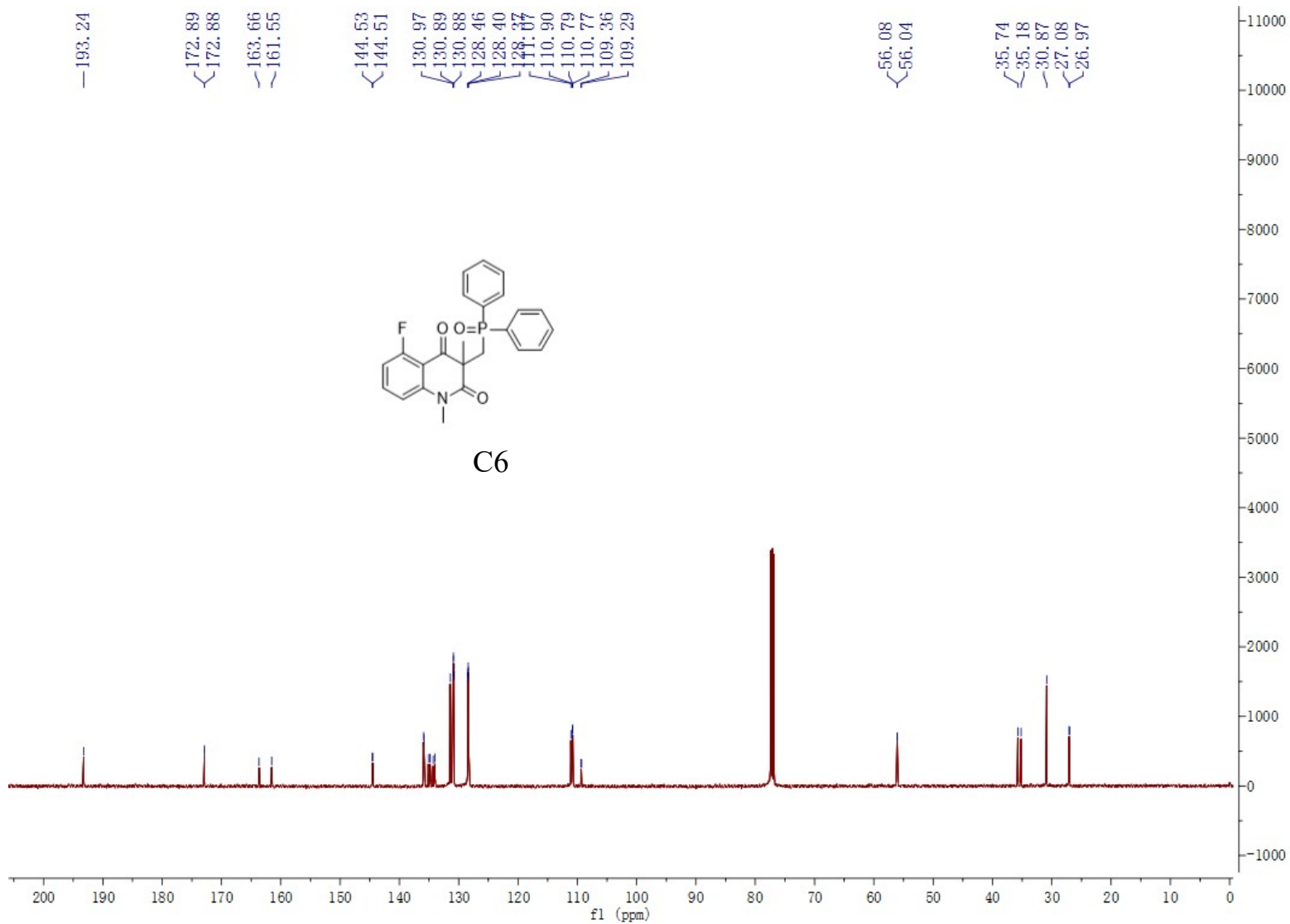


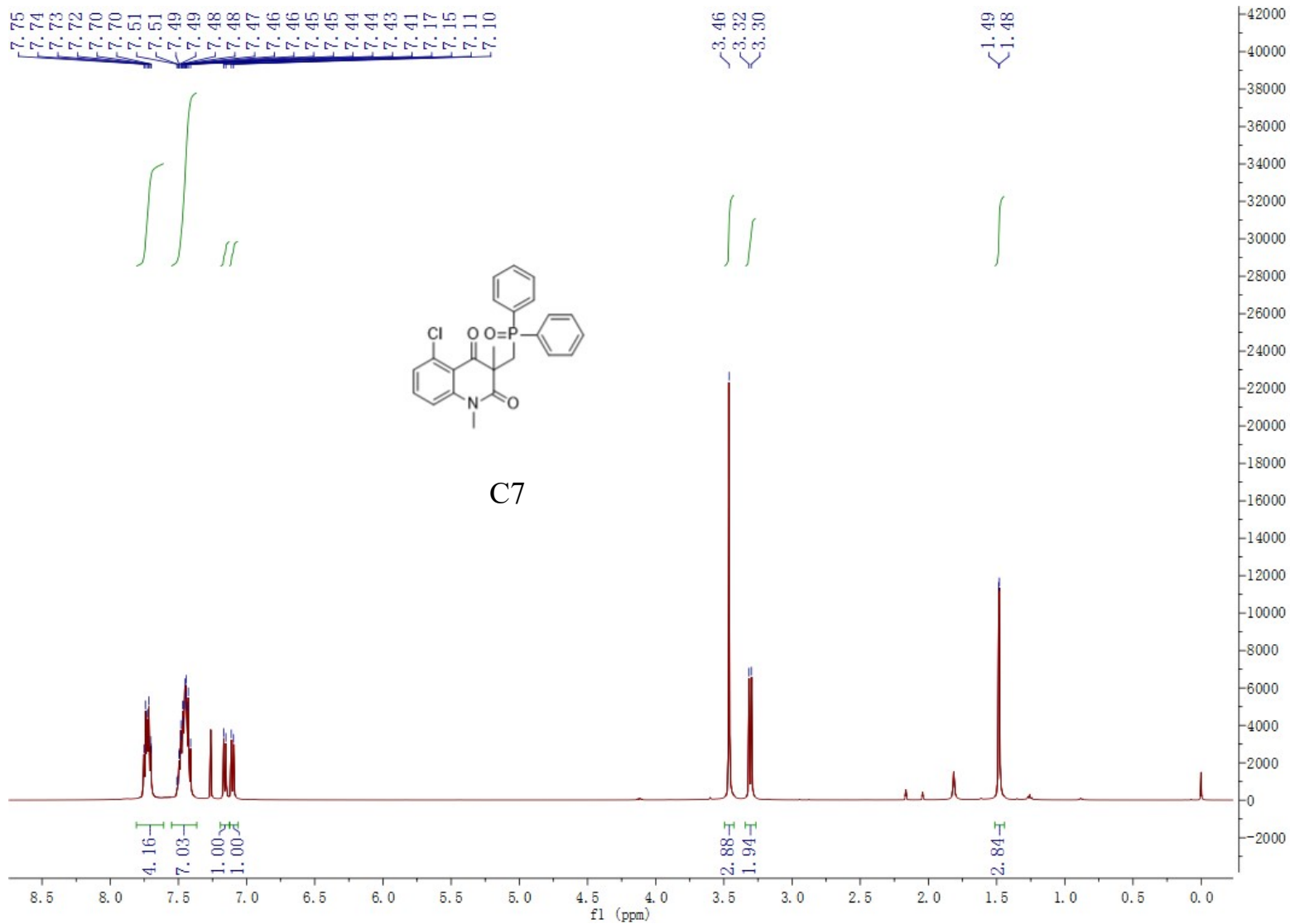


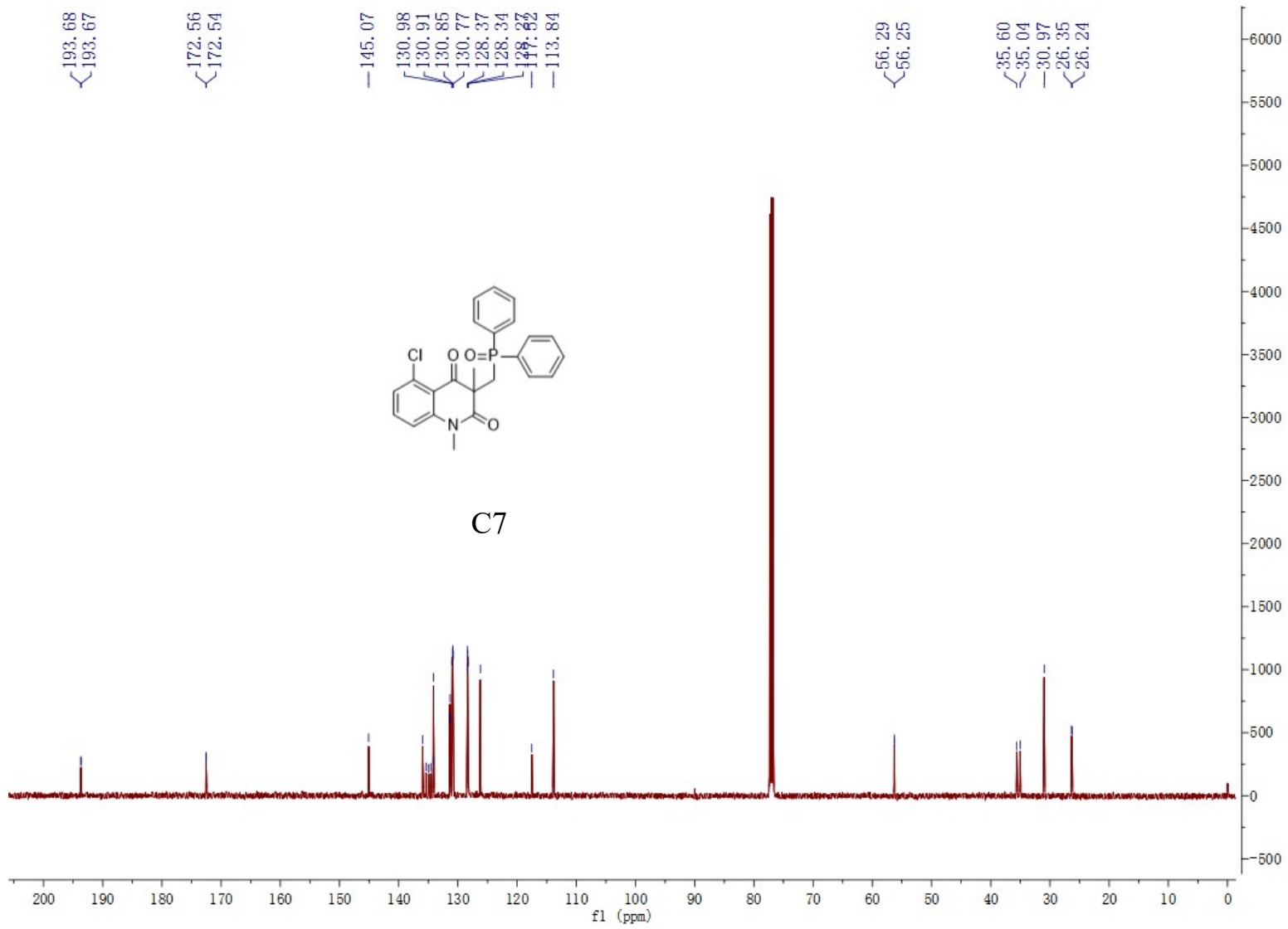


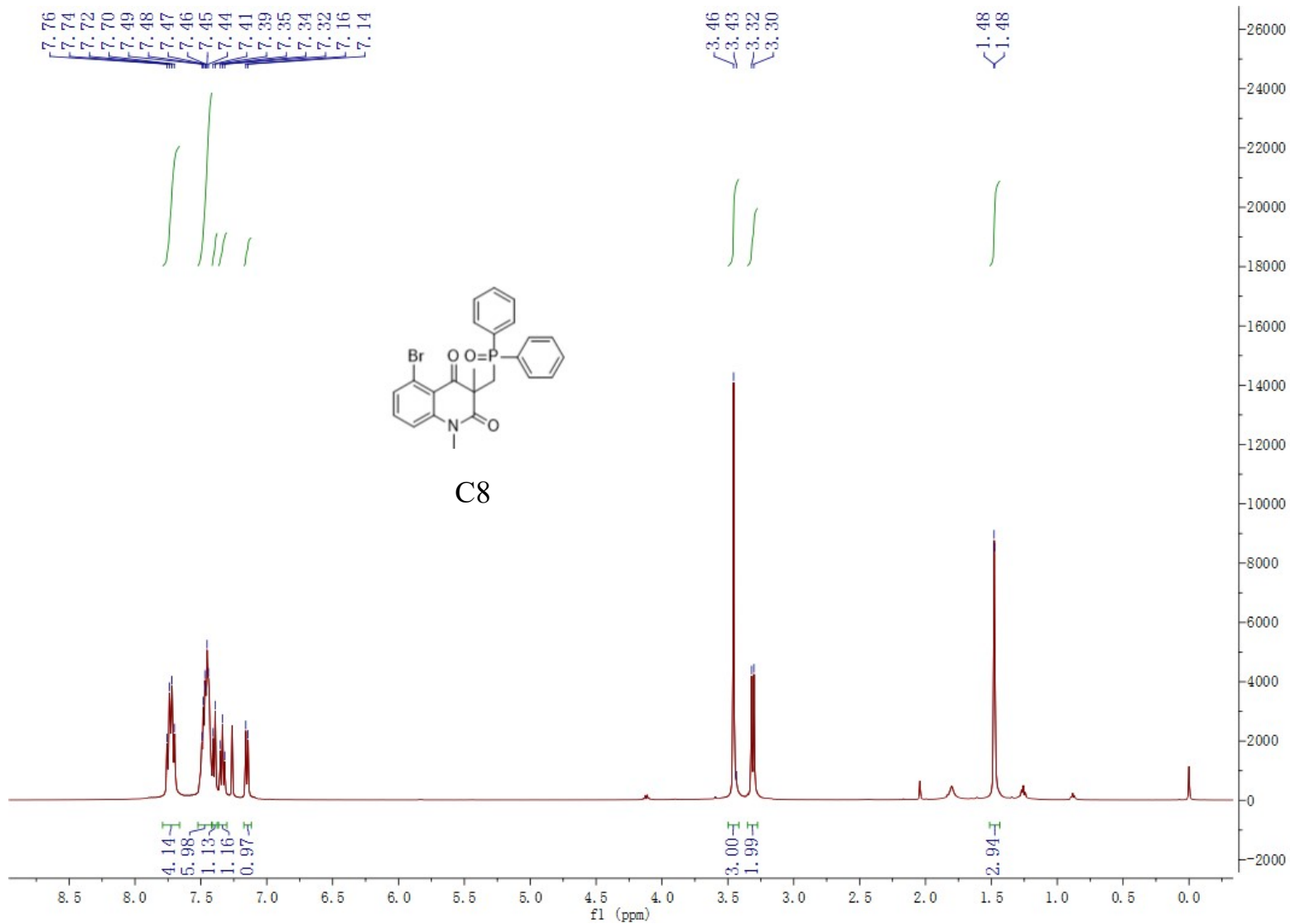


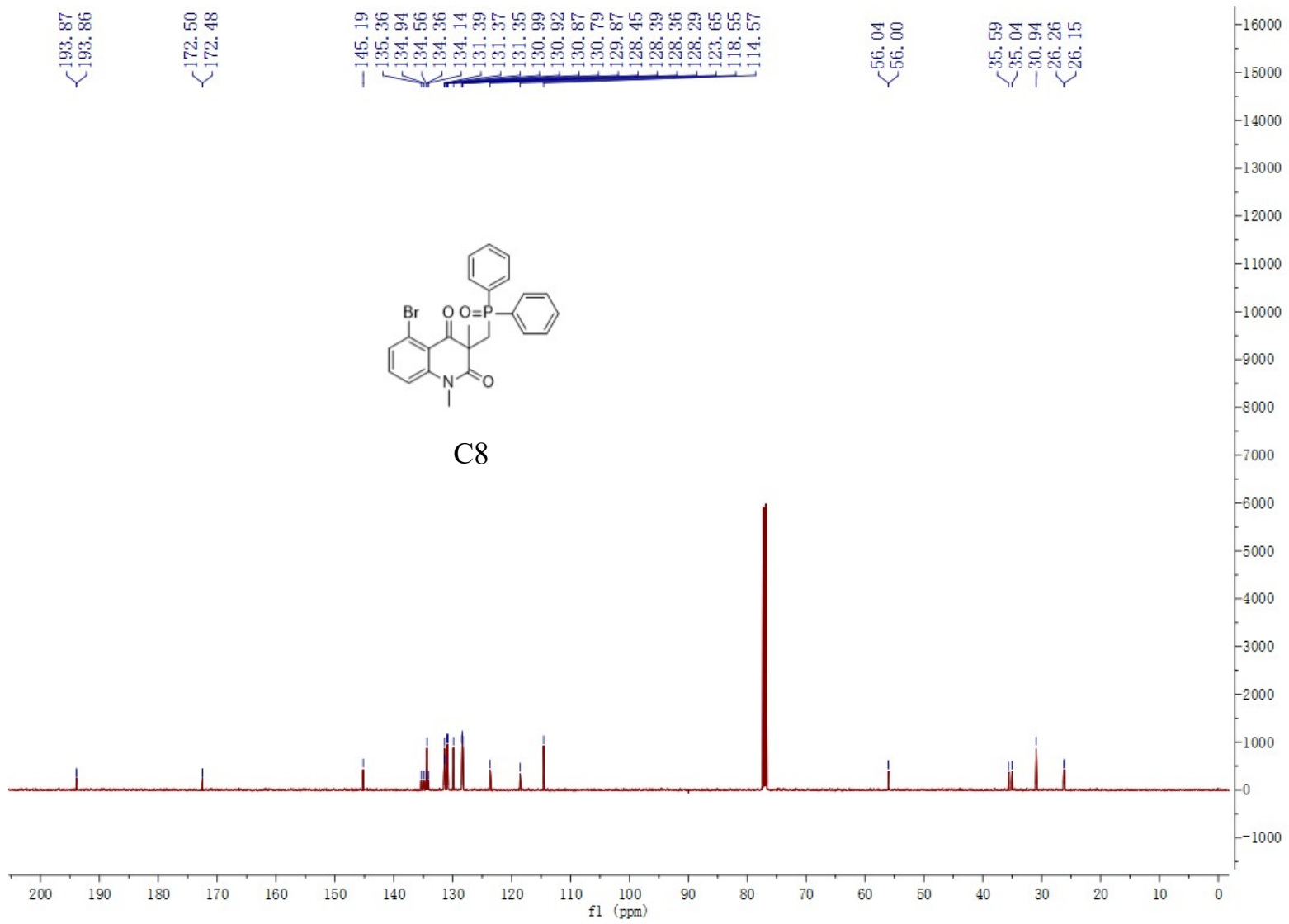


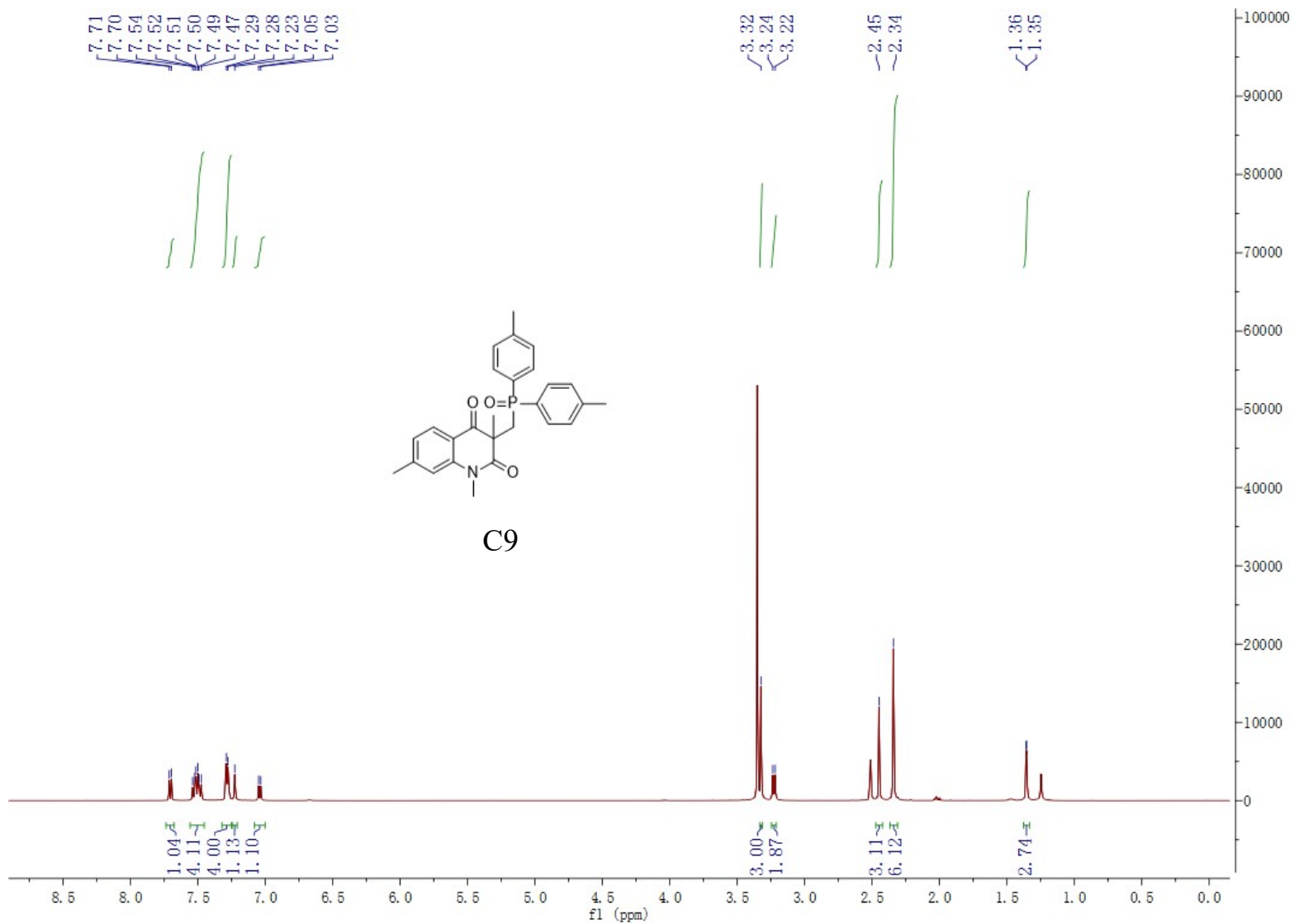


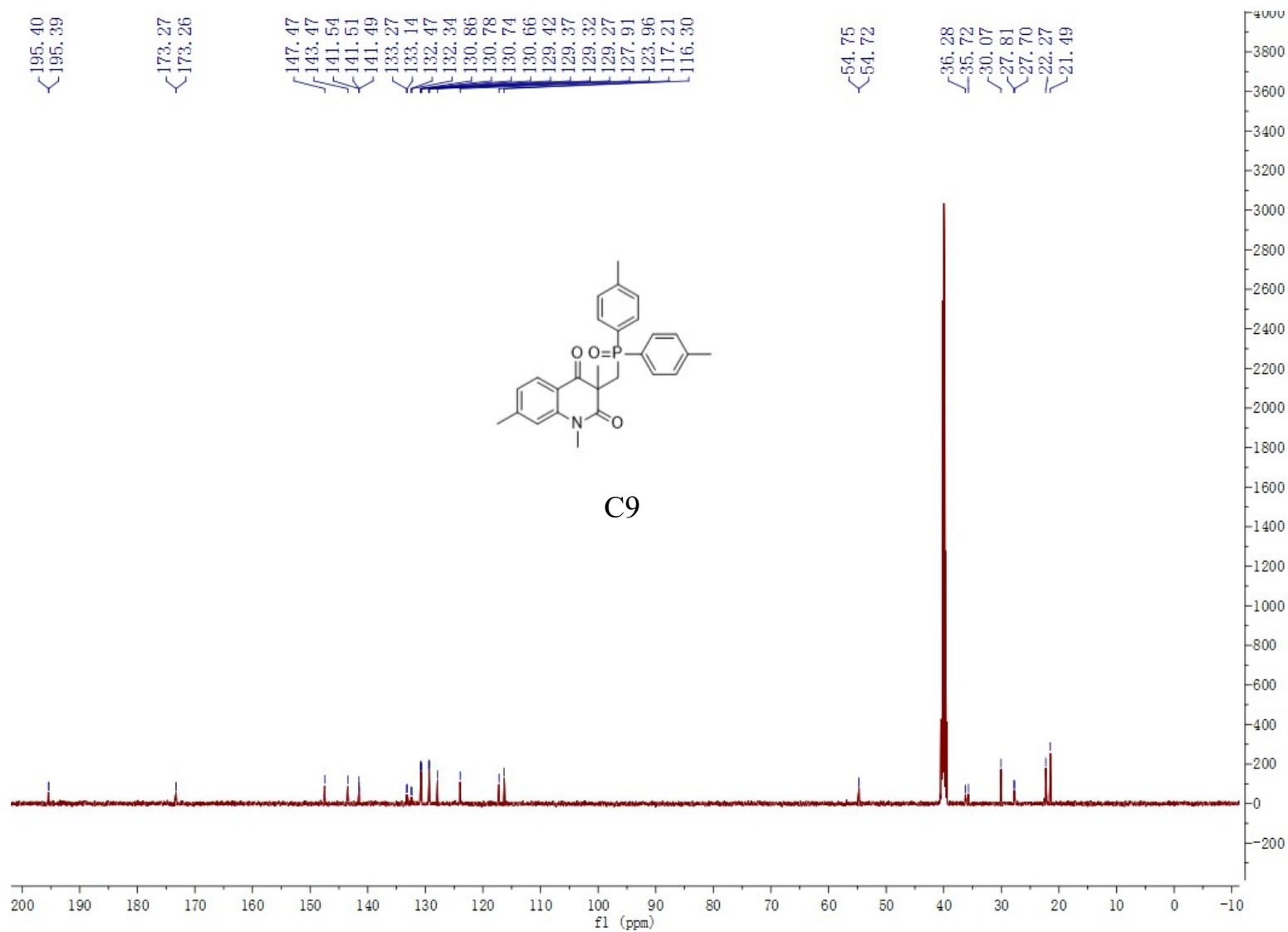


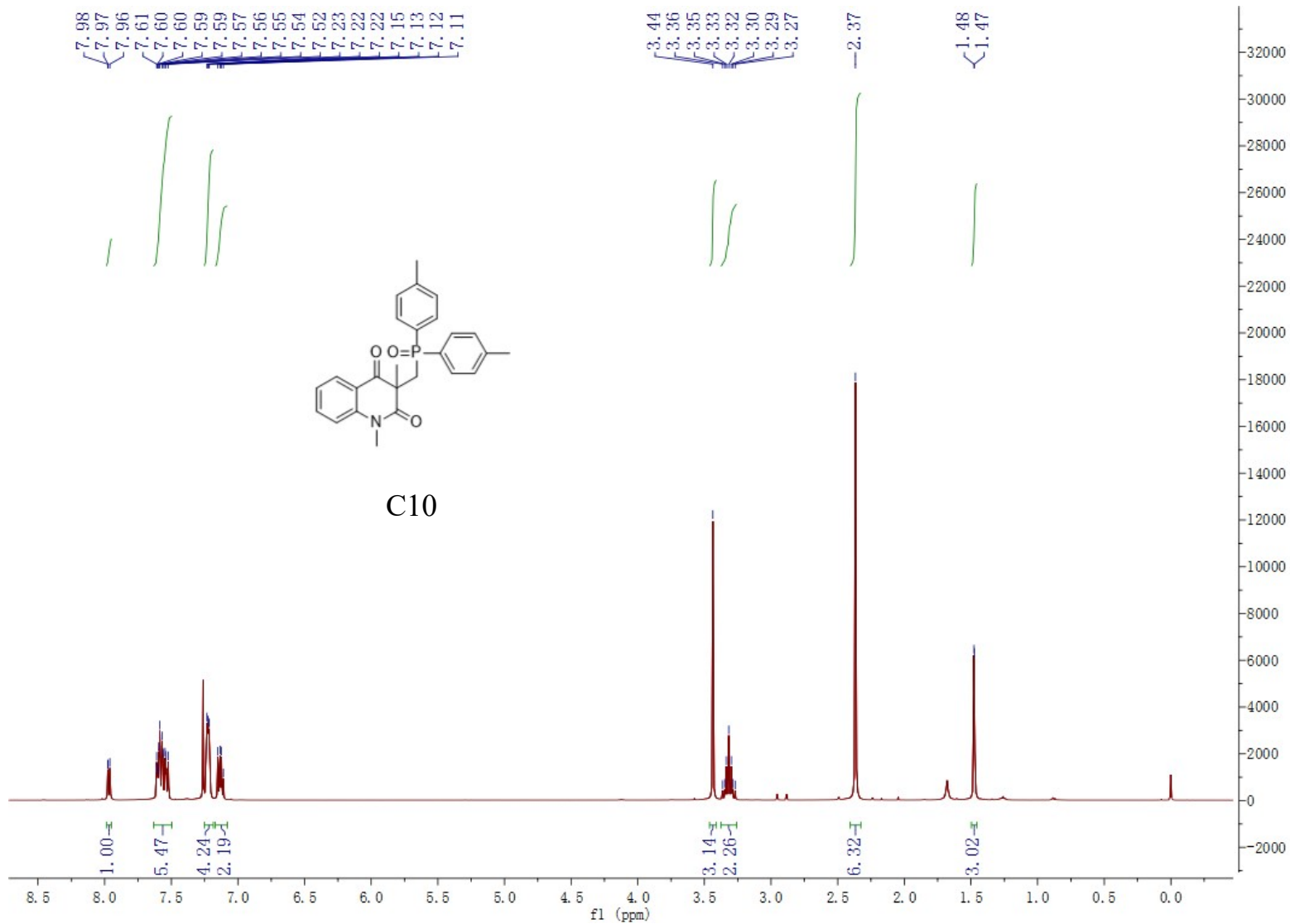


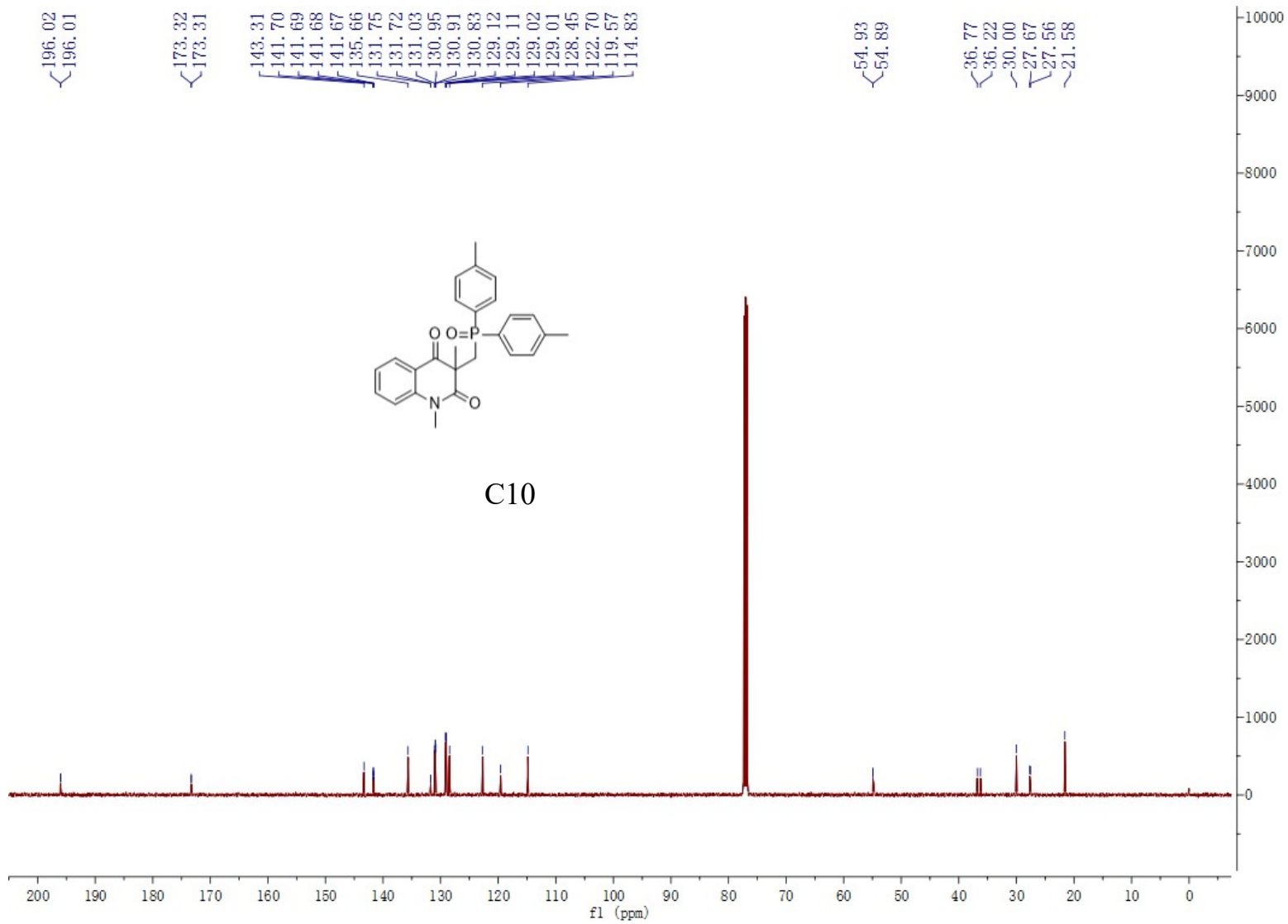


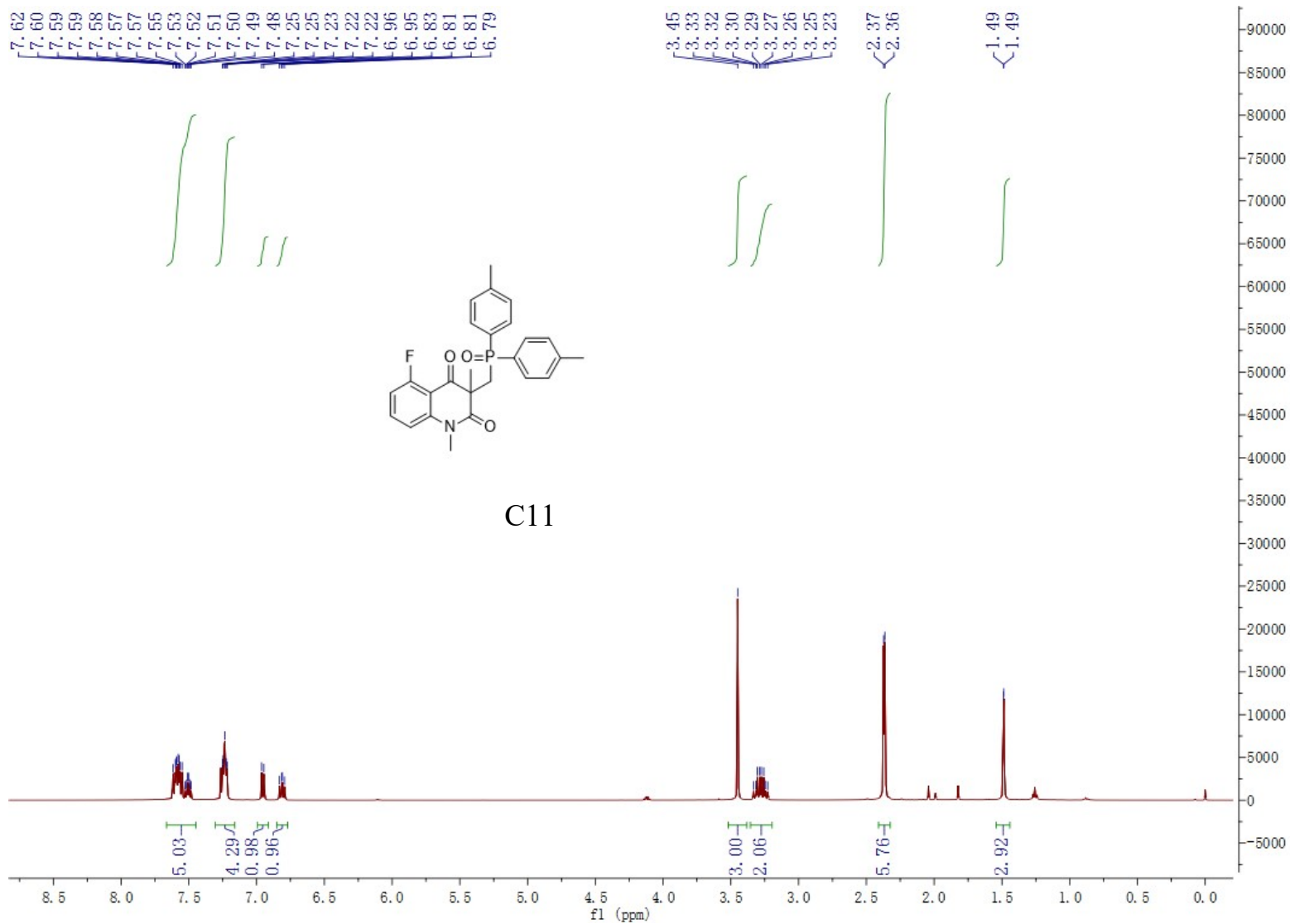




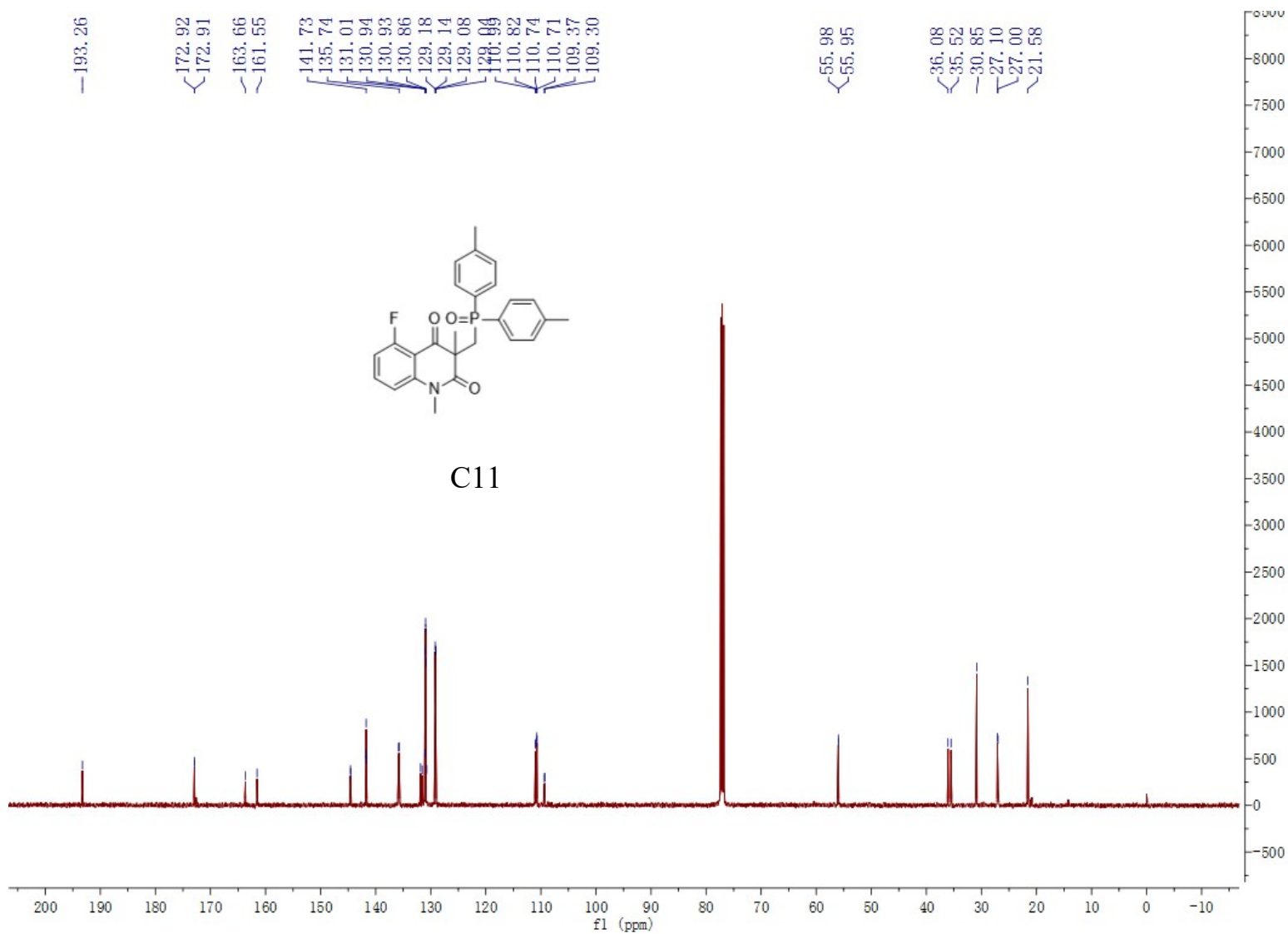


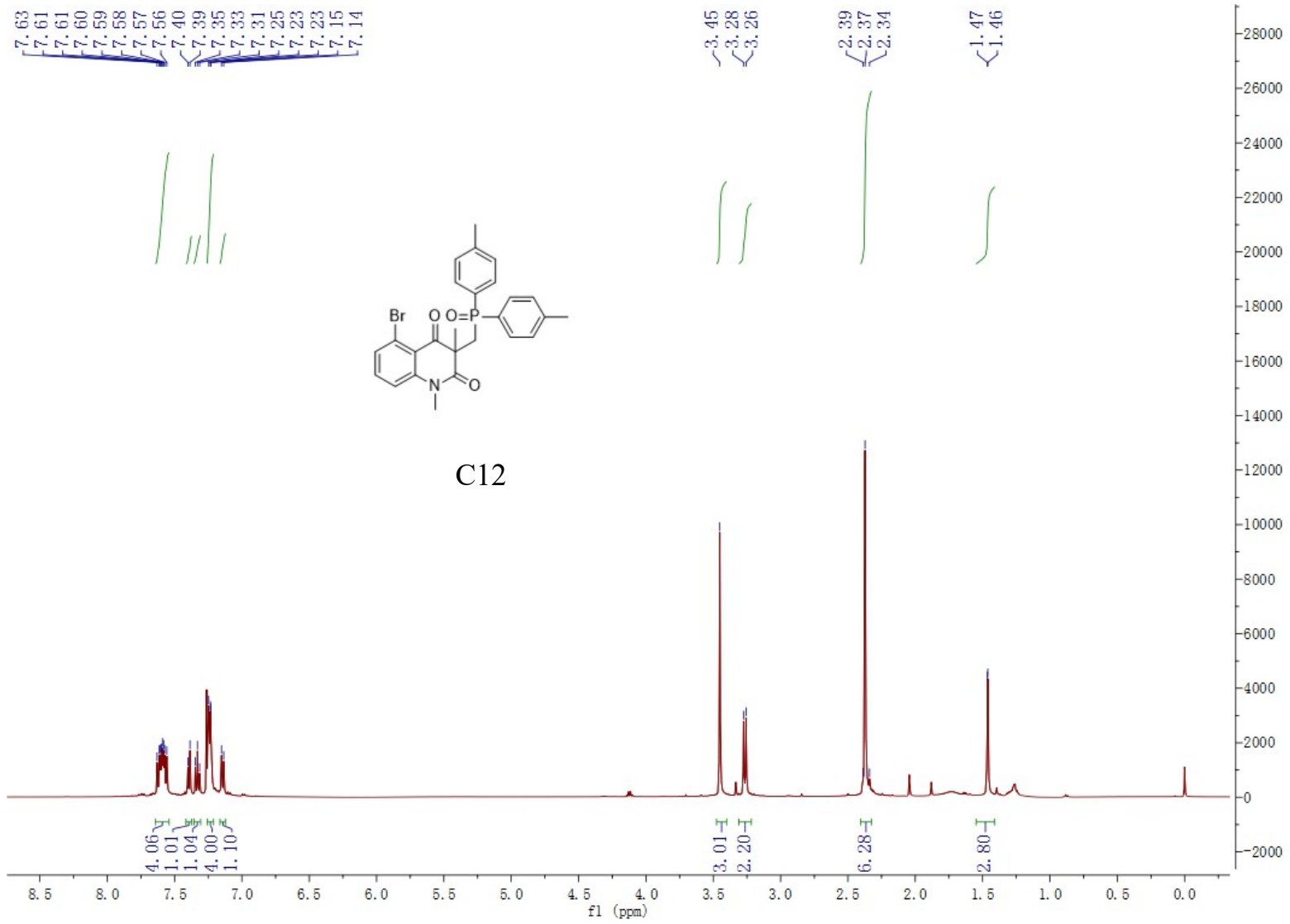


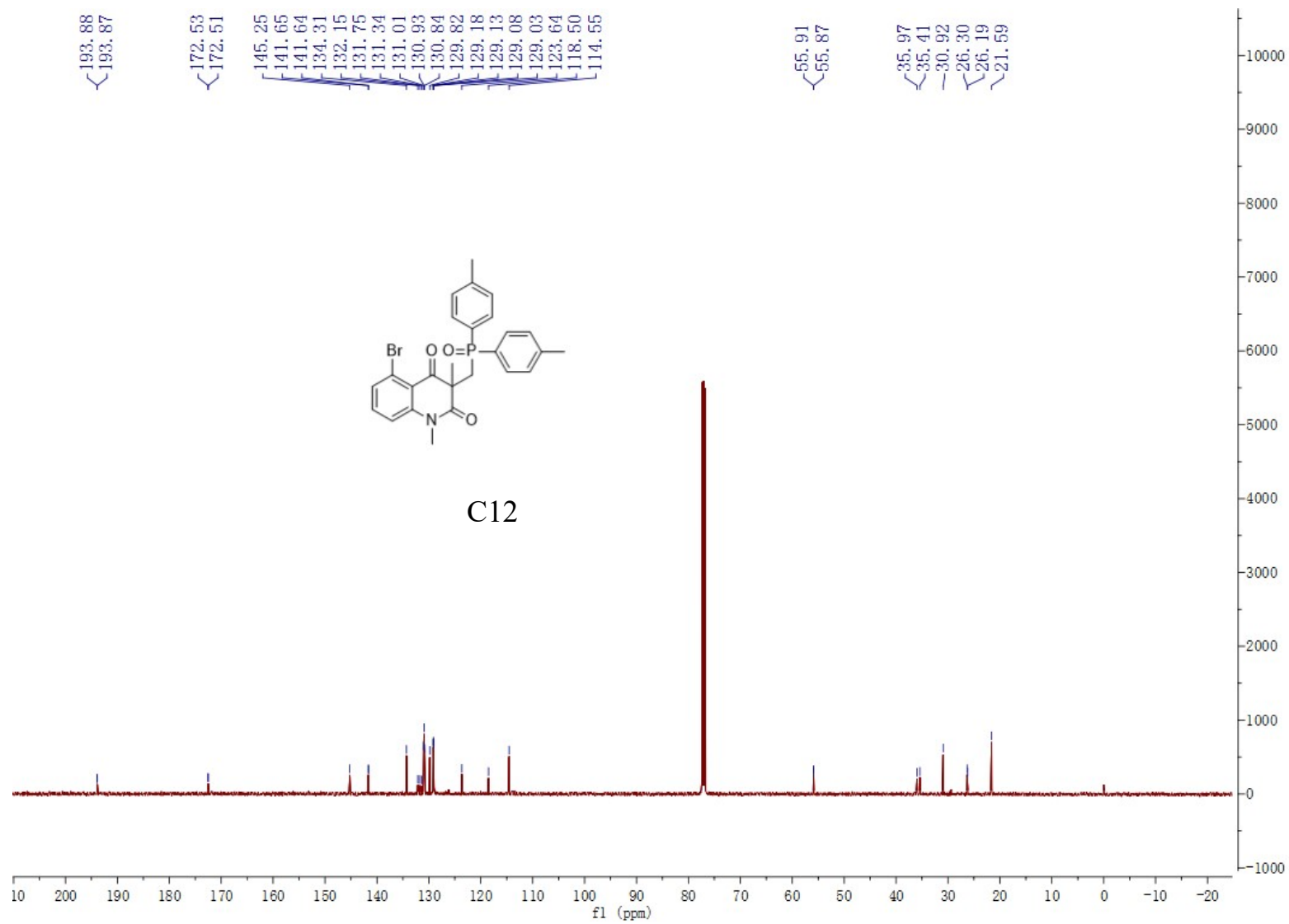


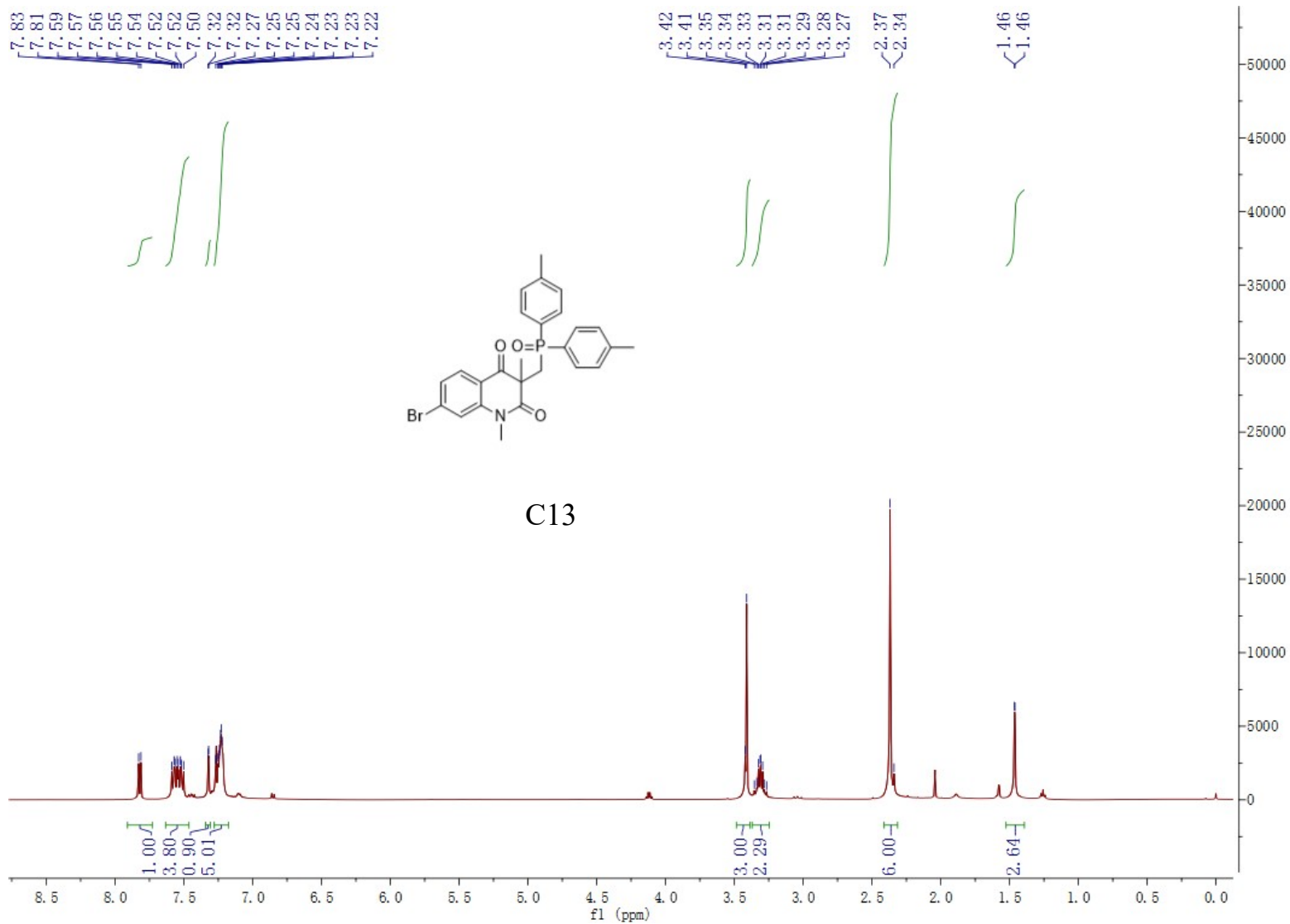


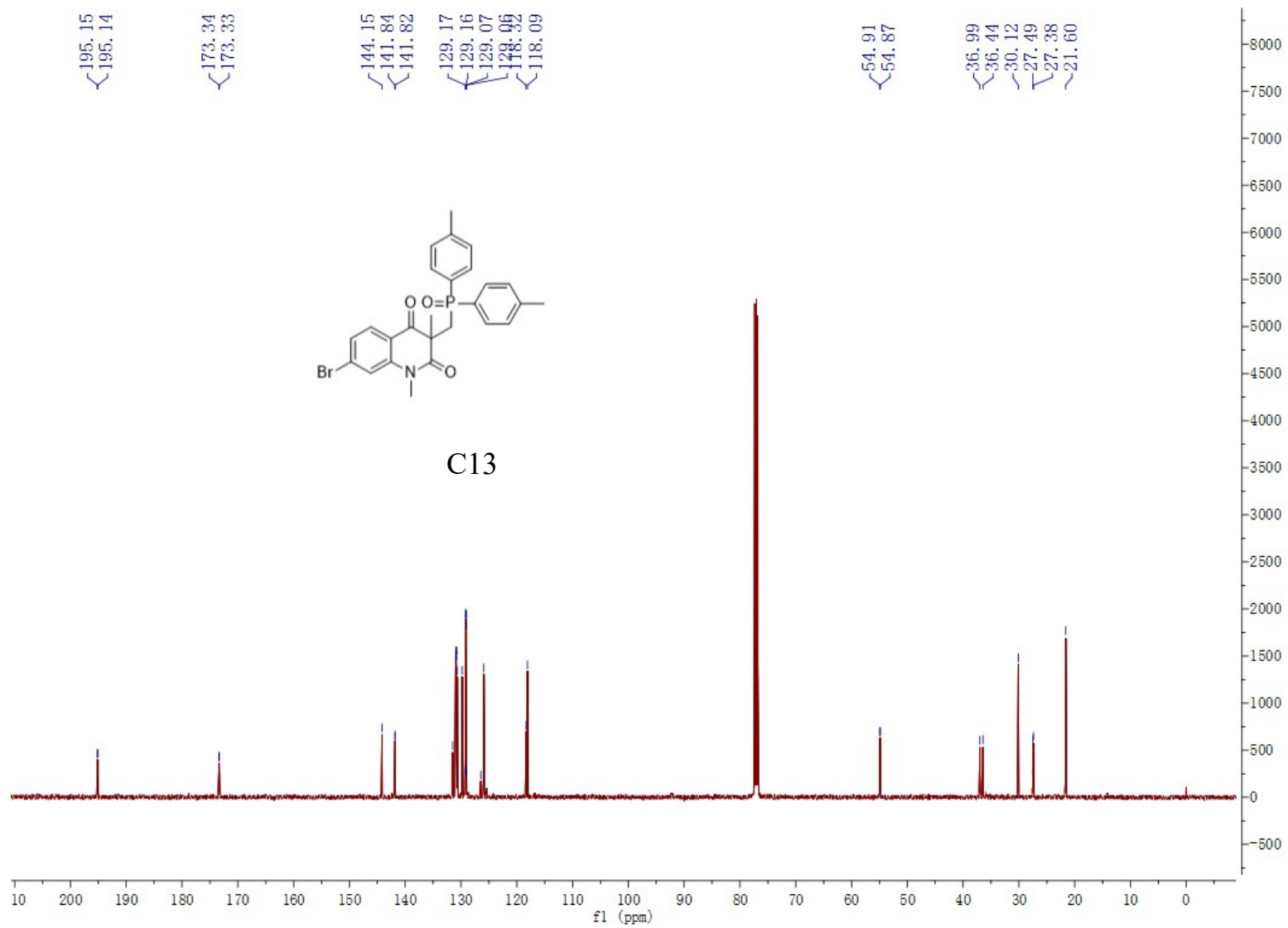
C11

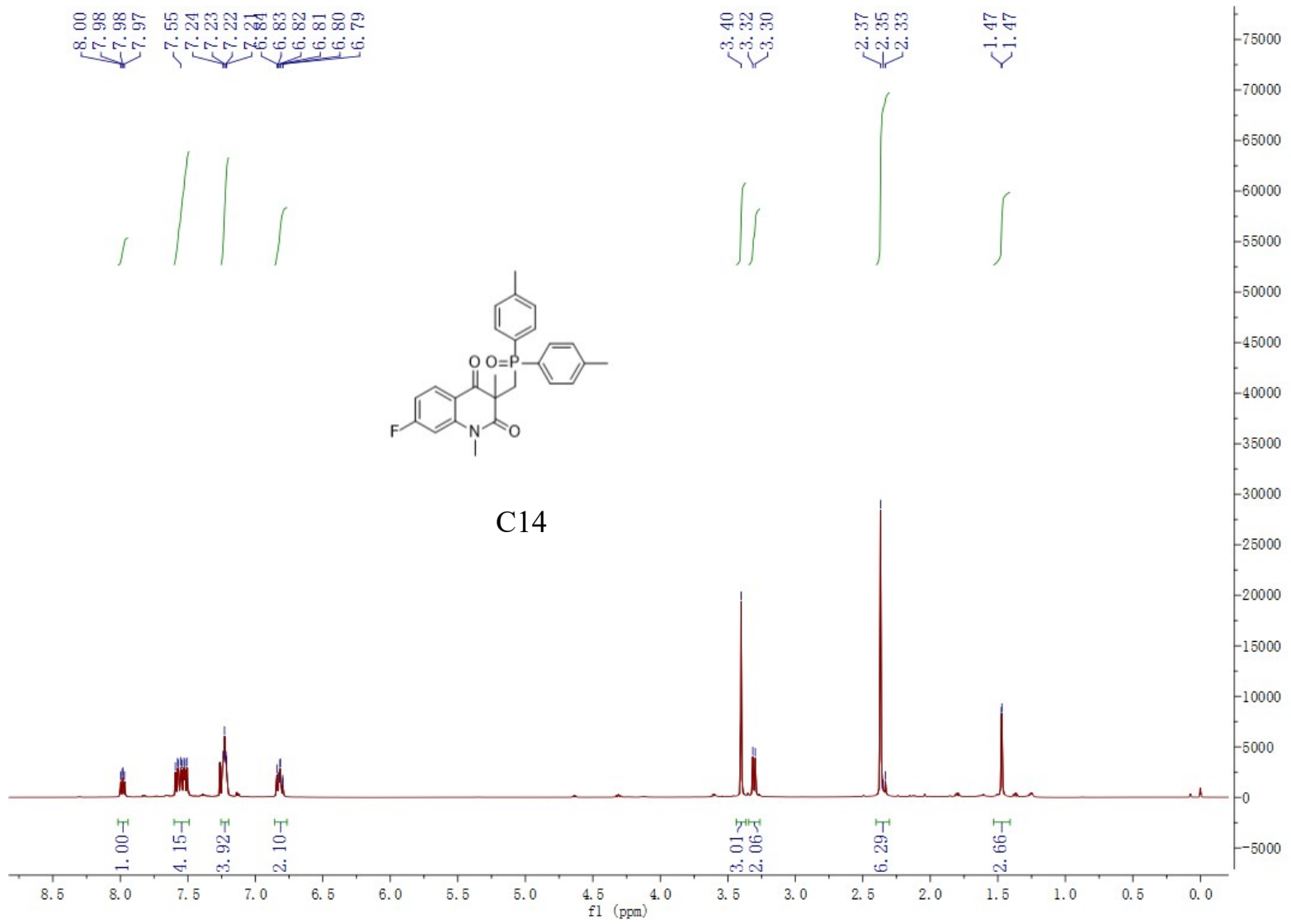




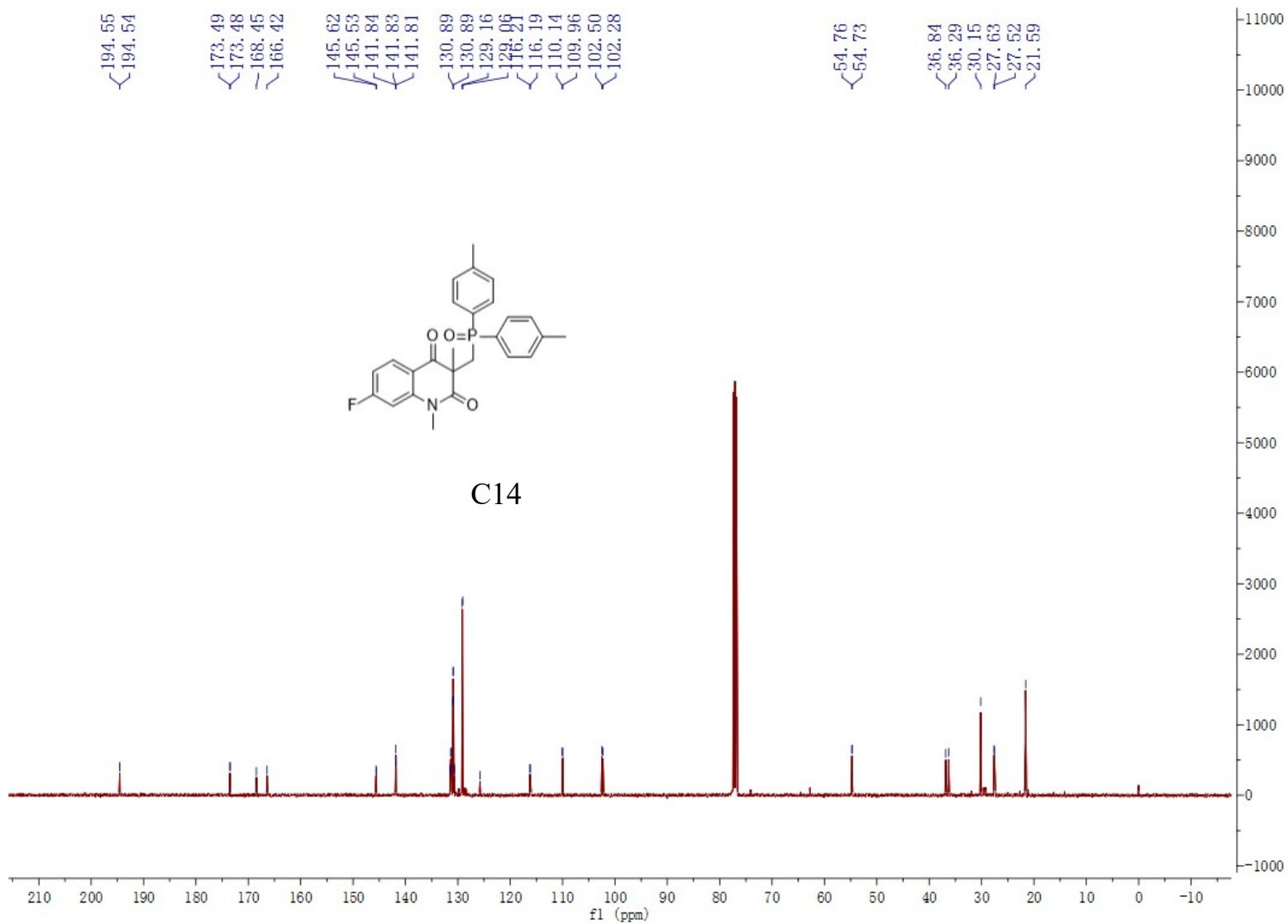


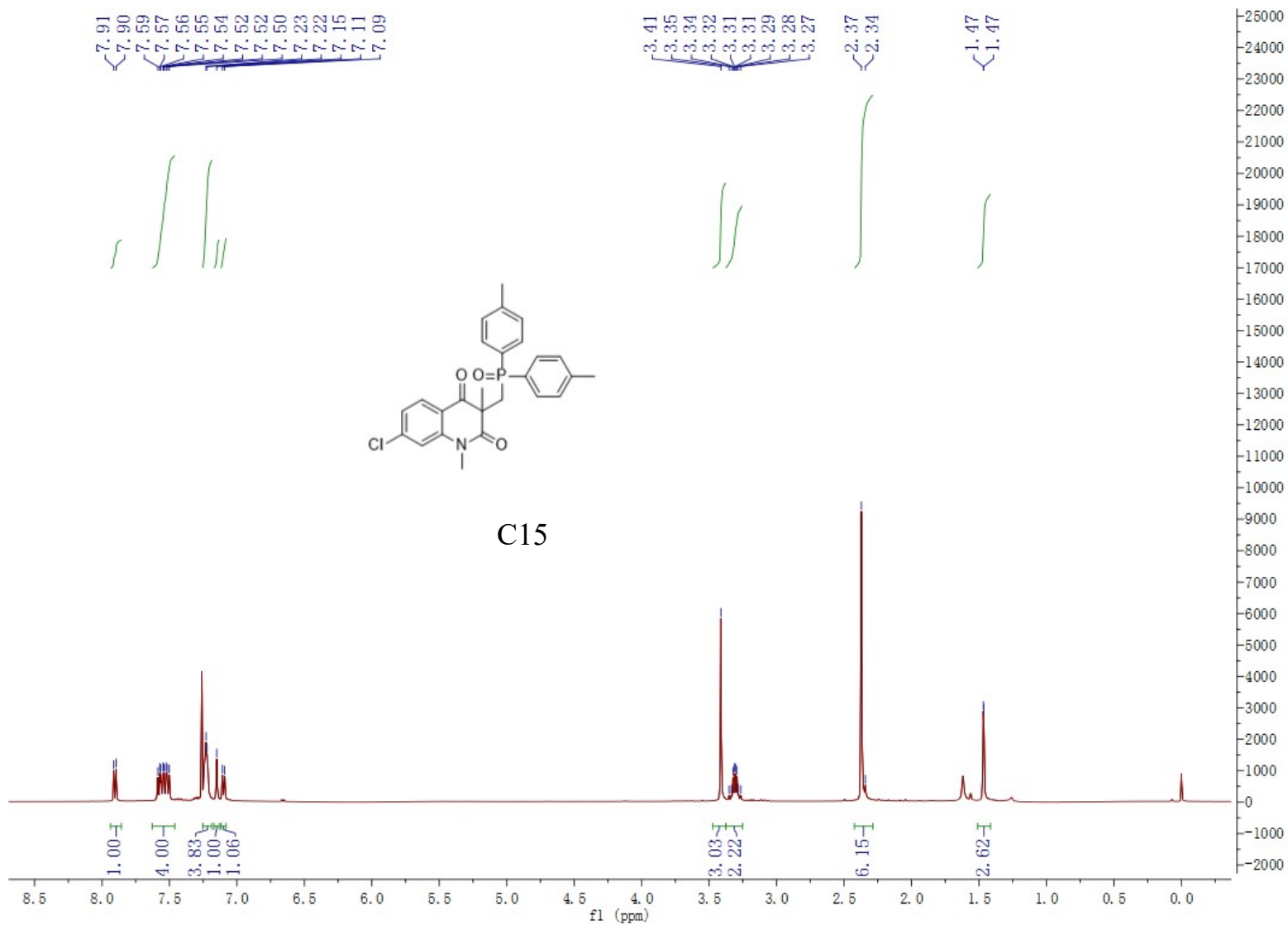


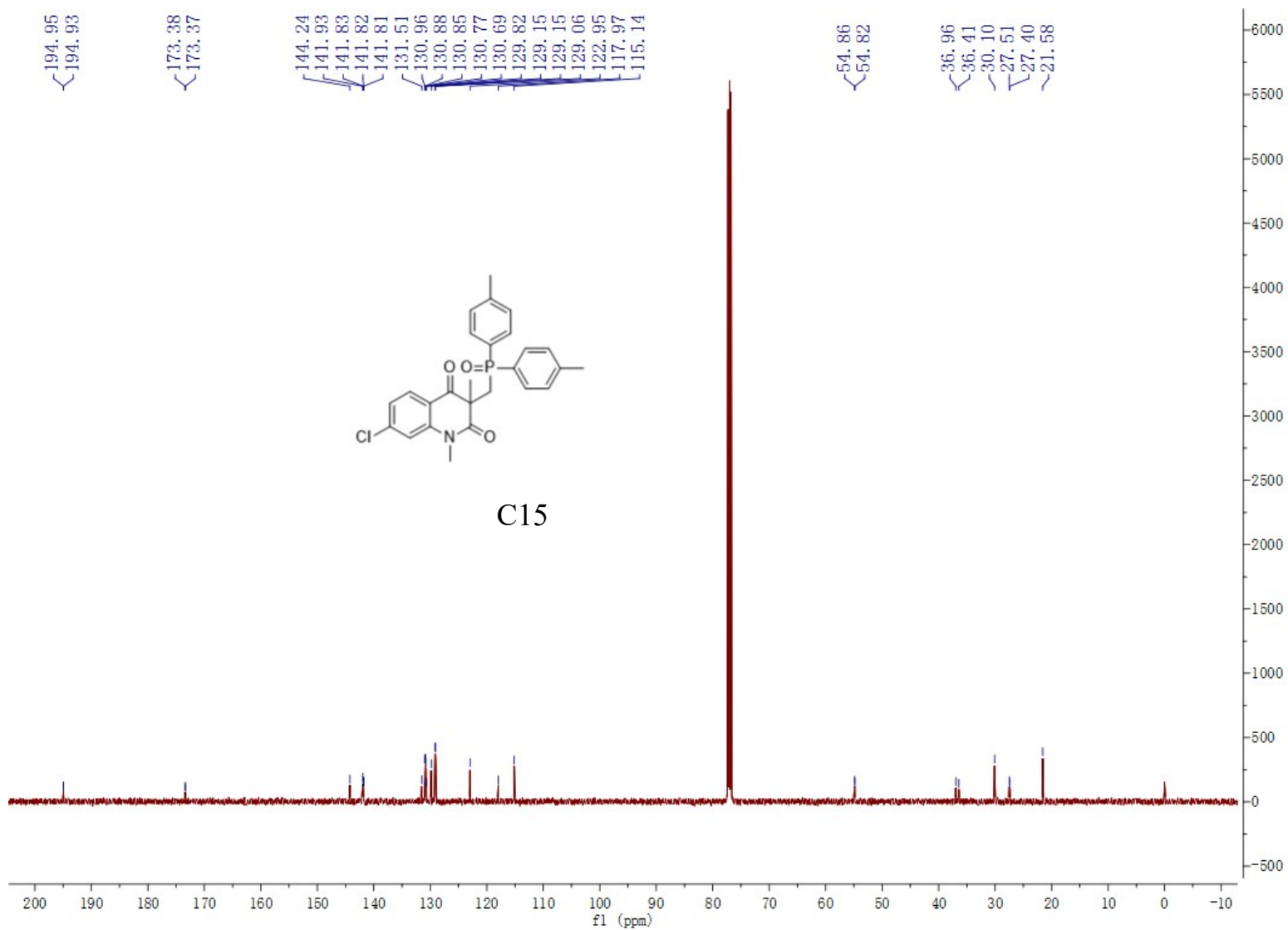


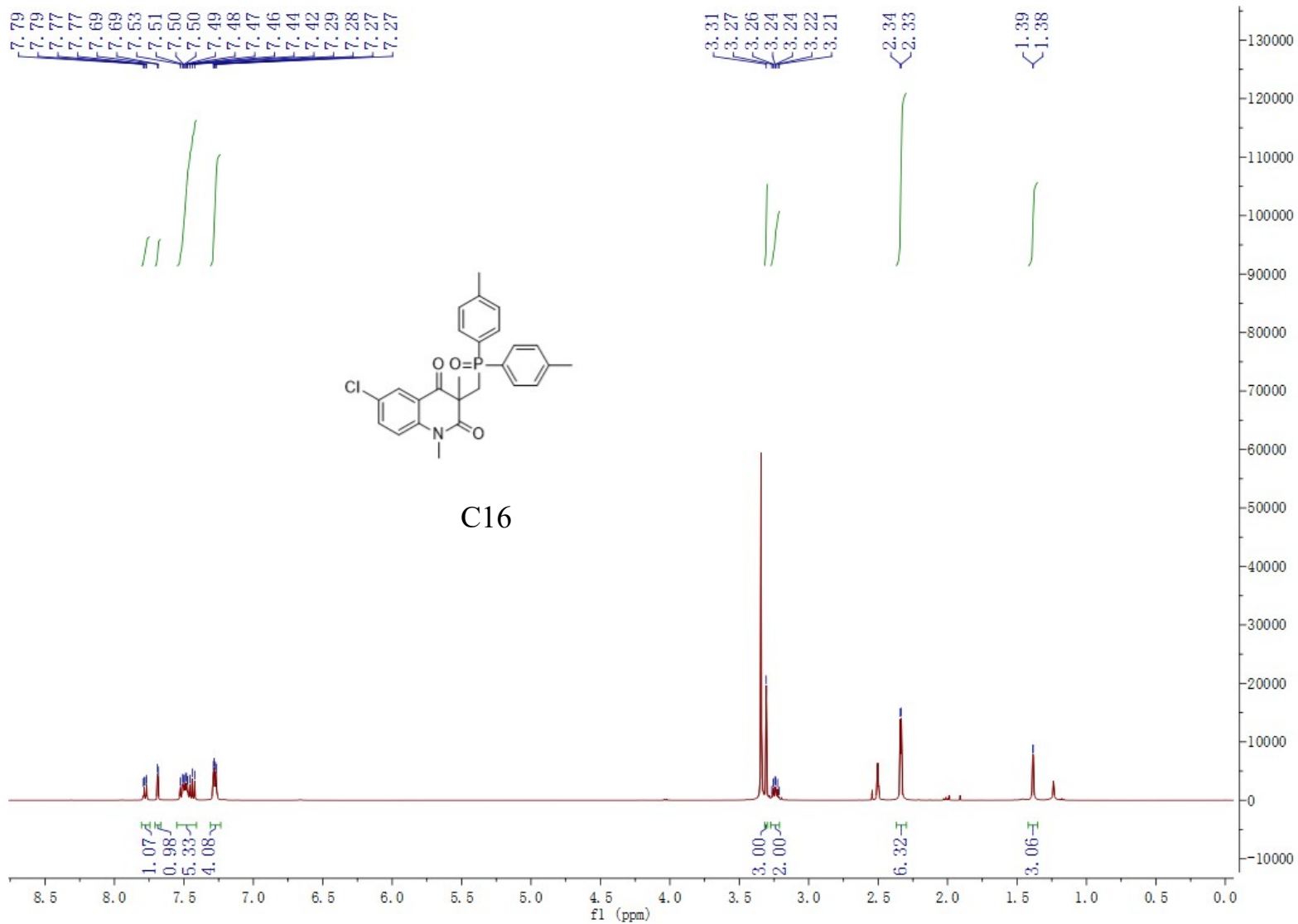


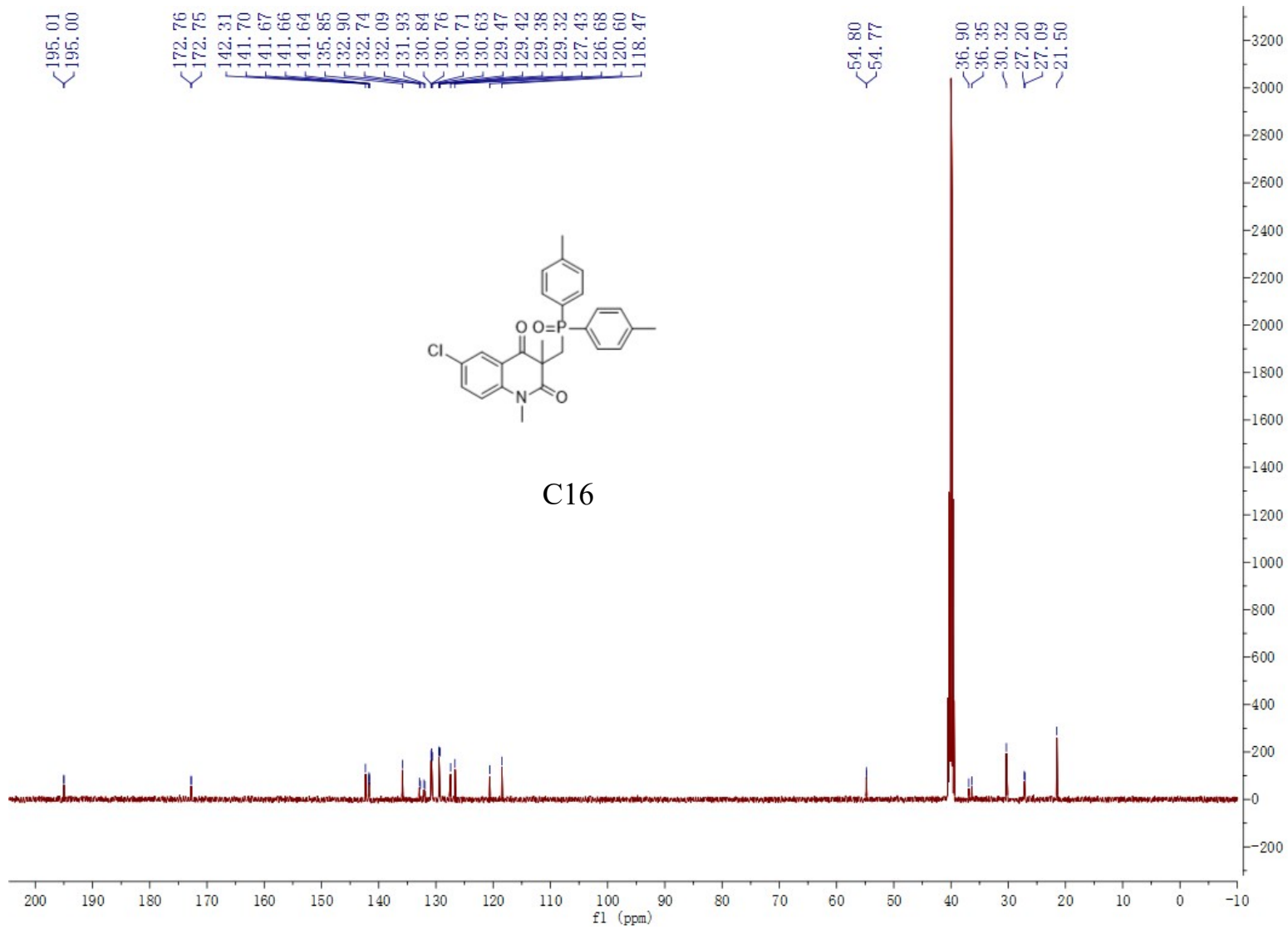
C14

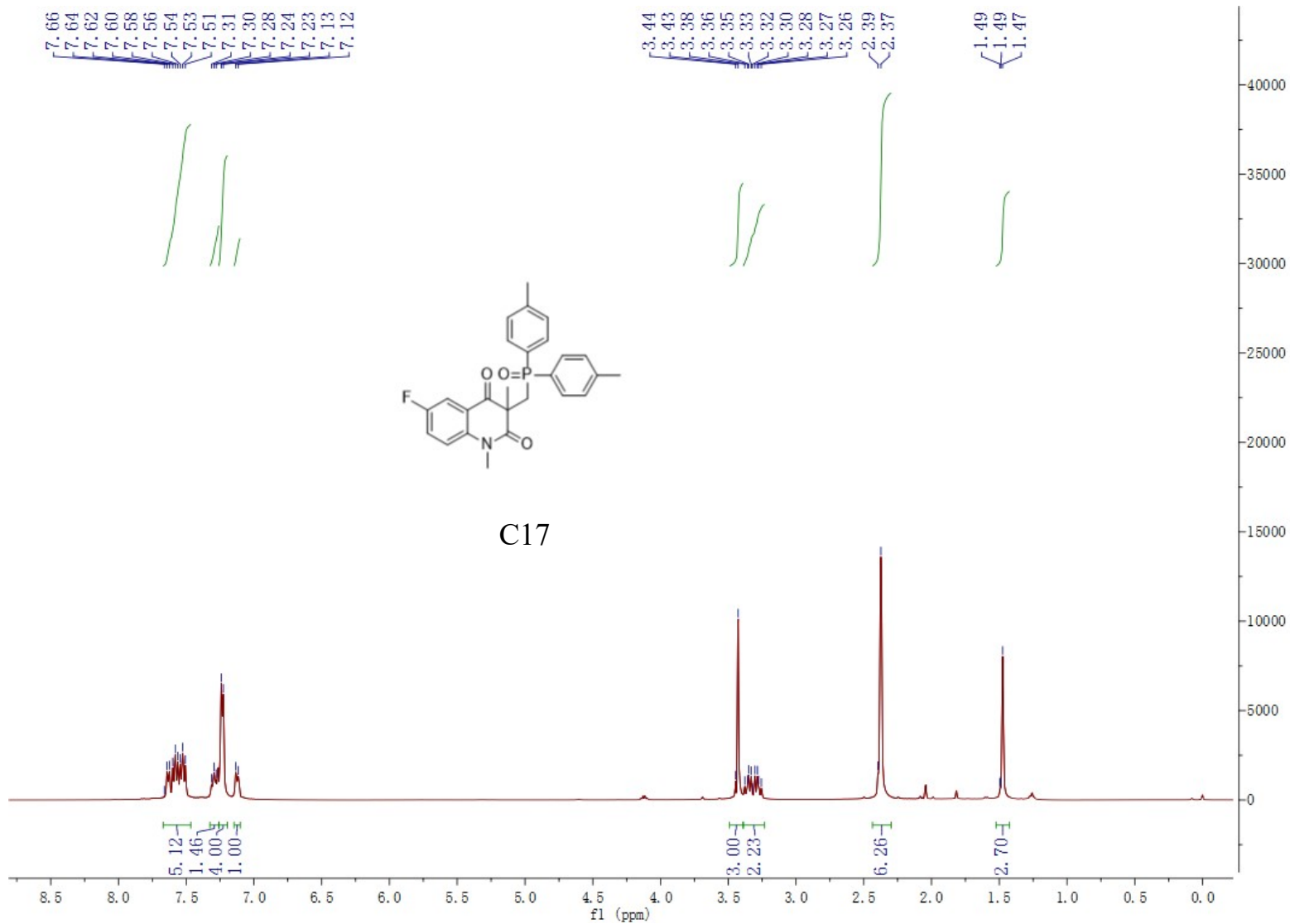


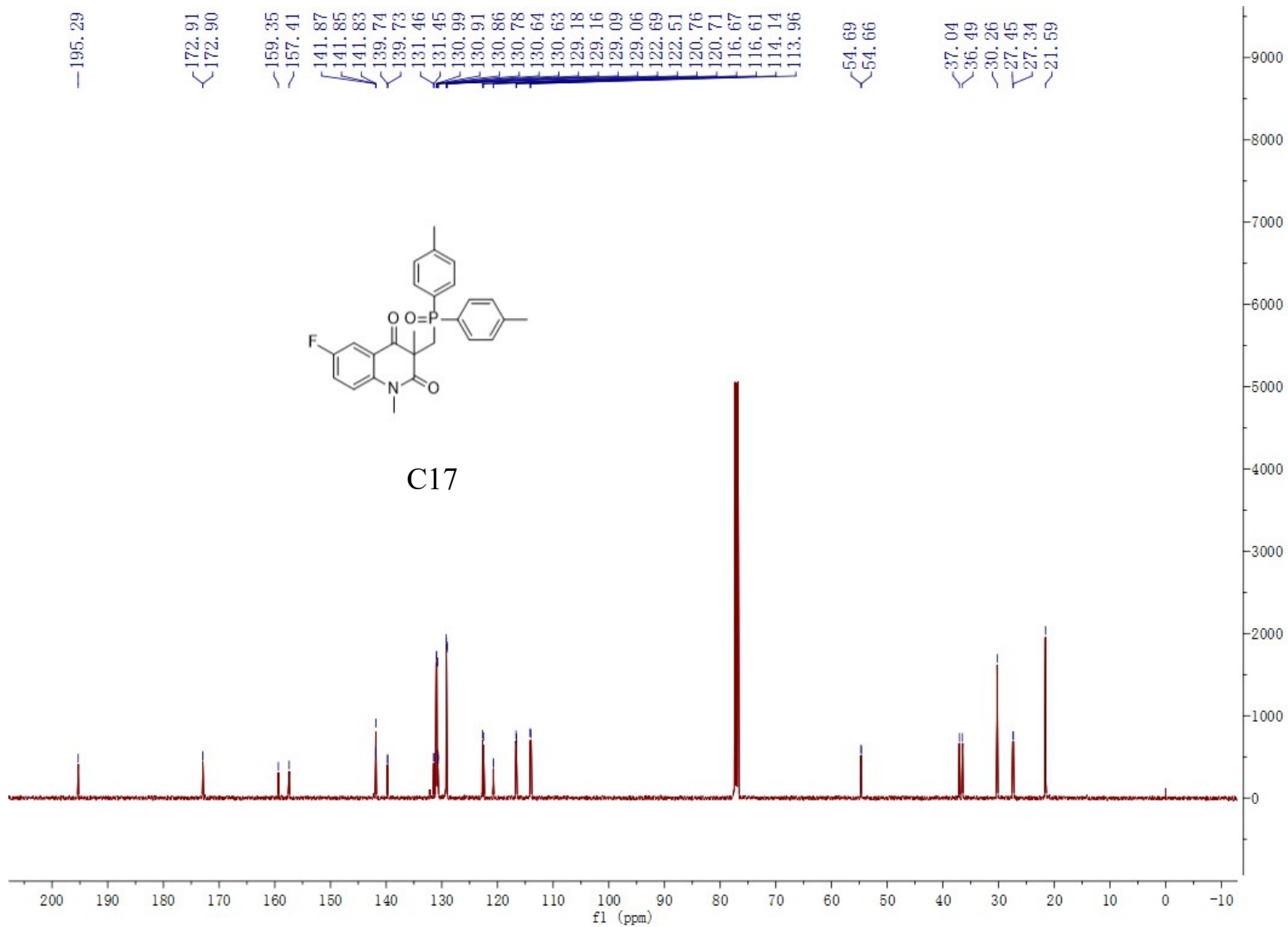


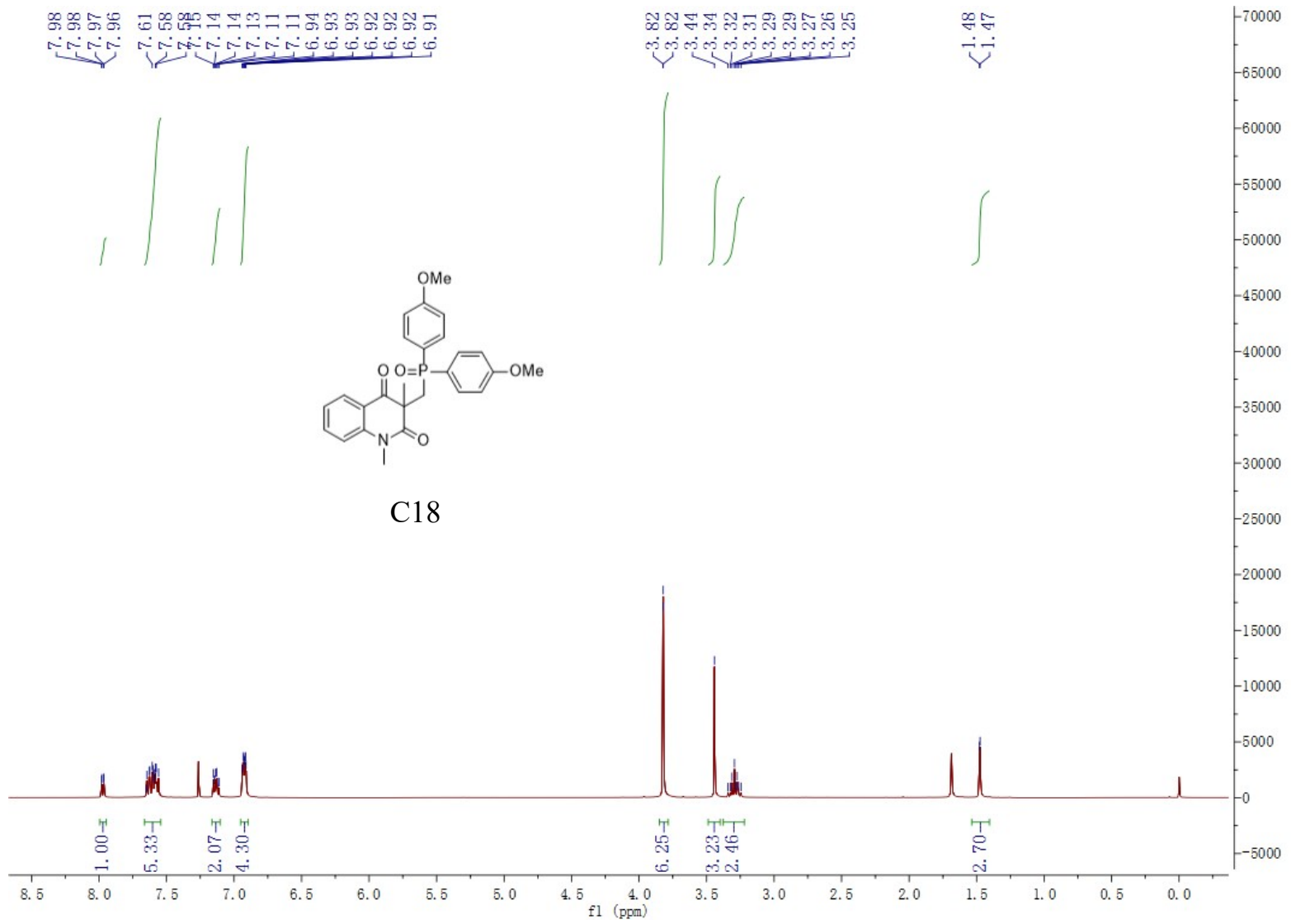


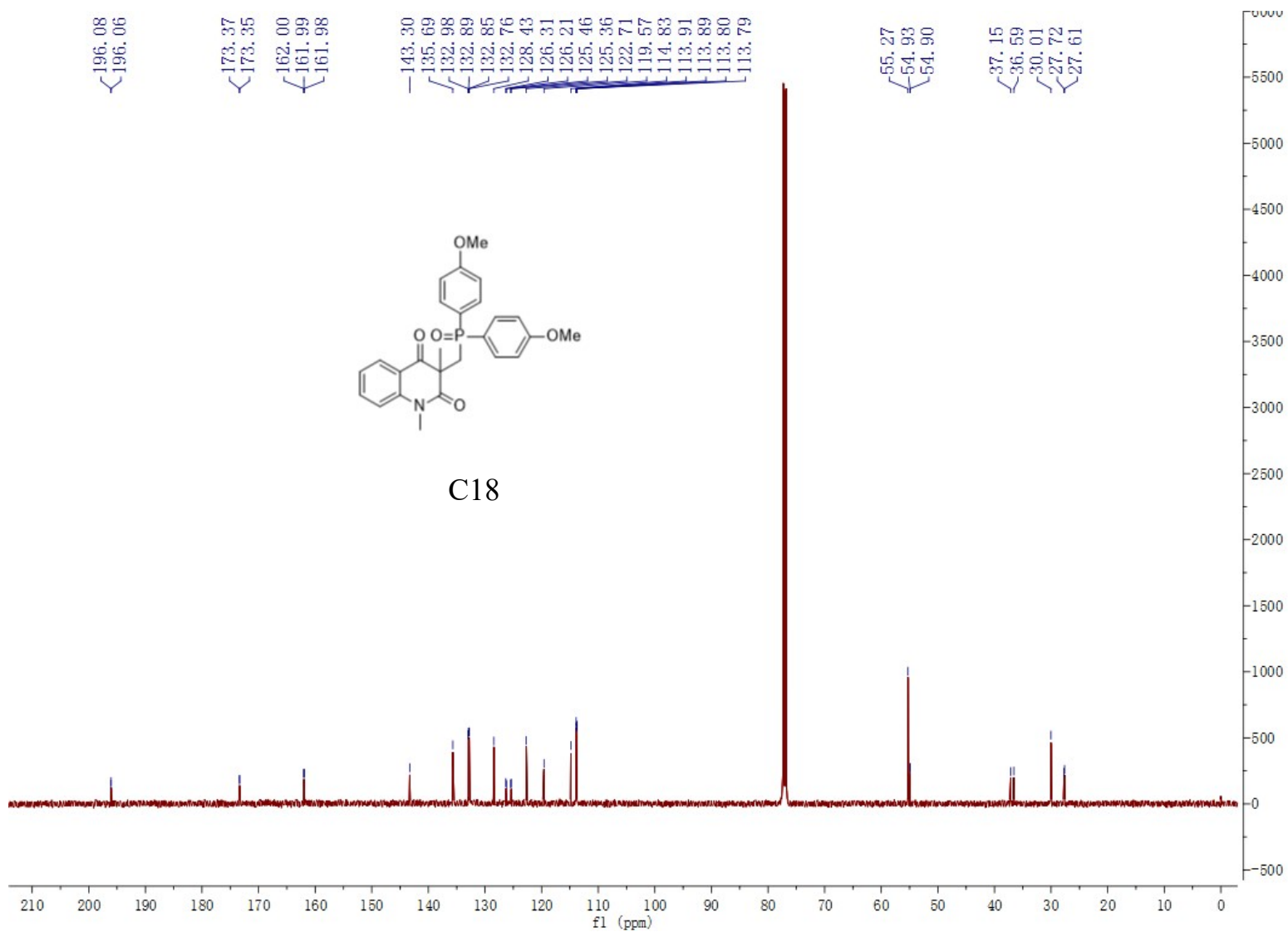


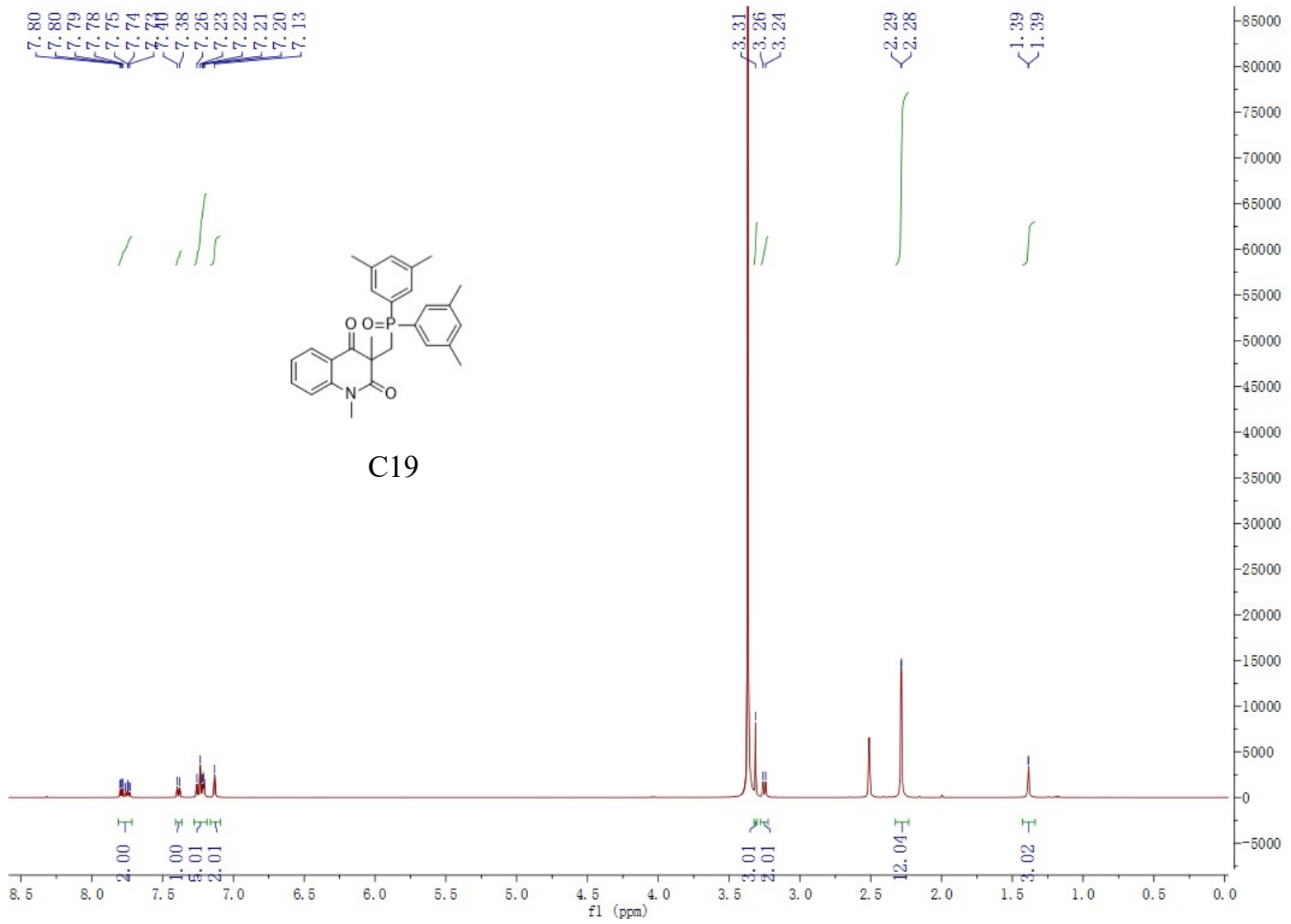


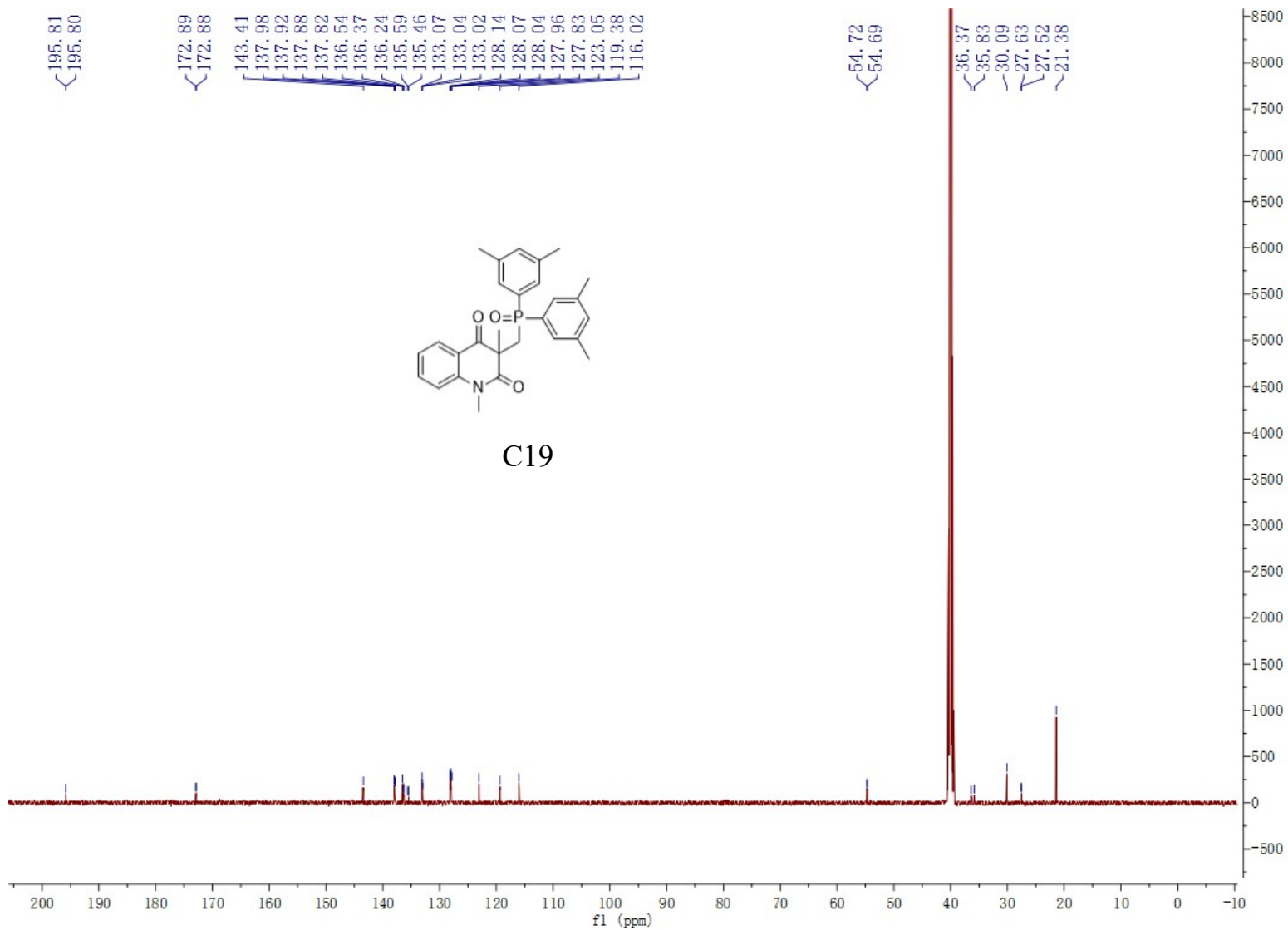


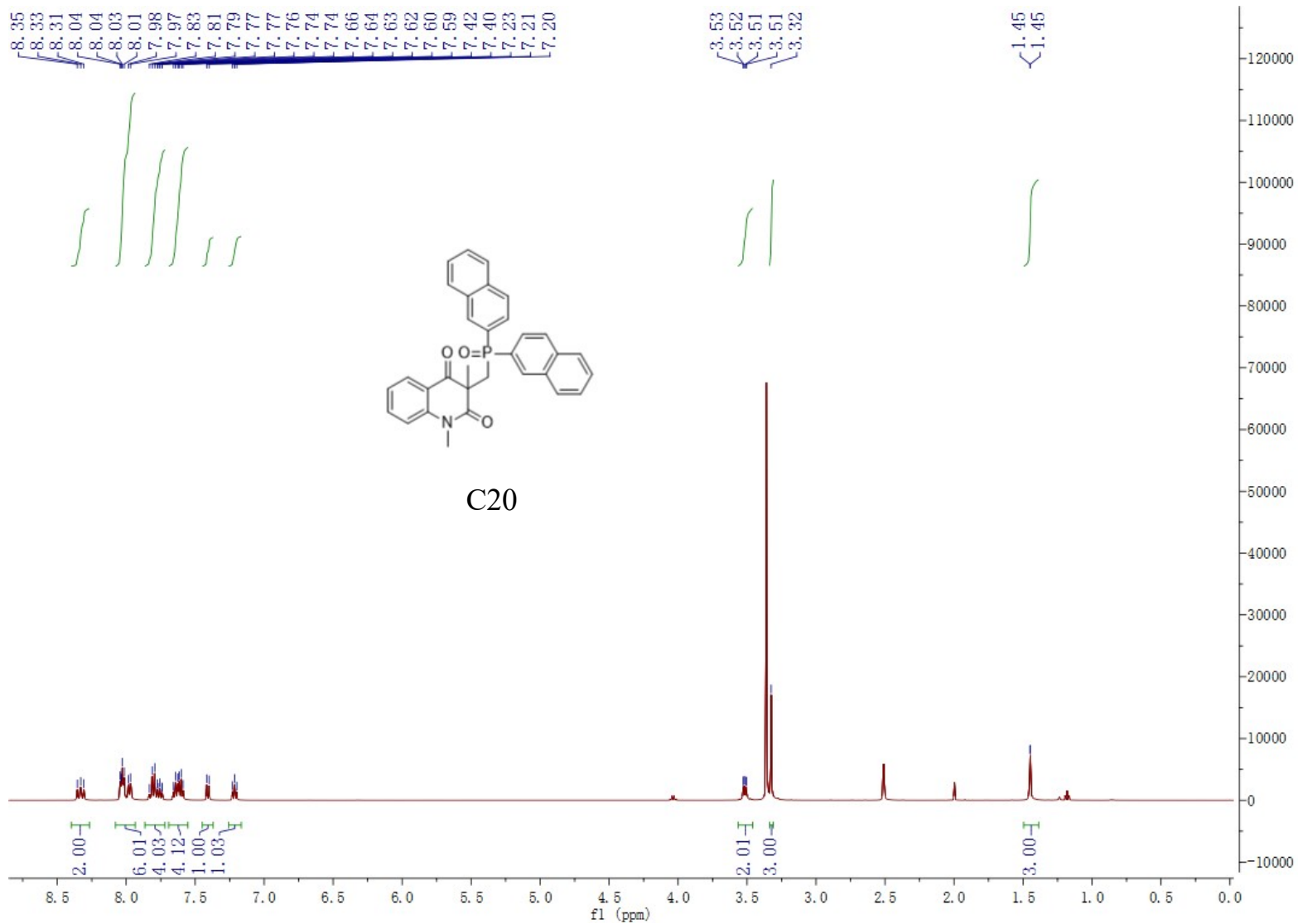


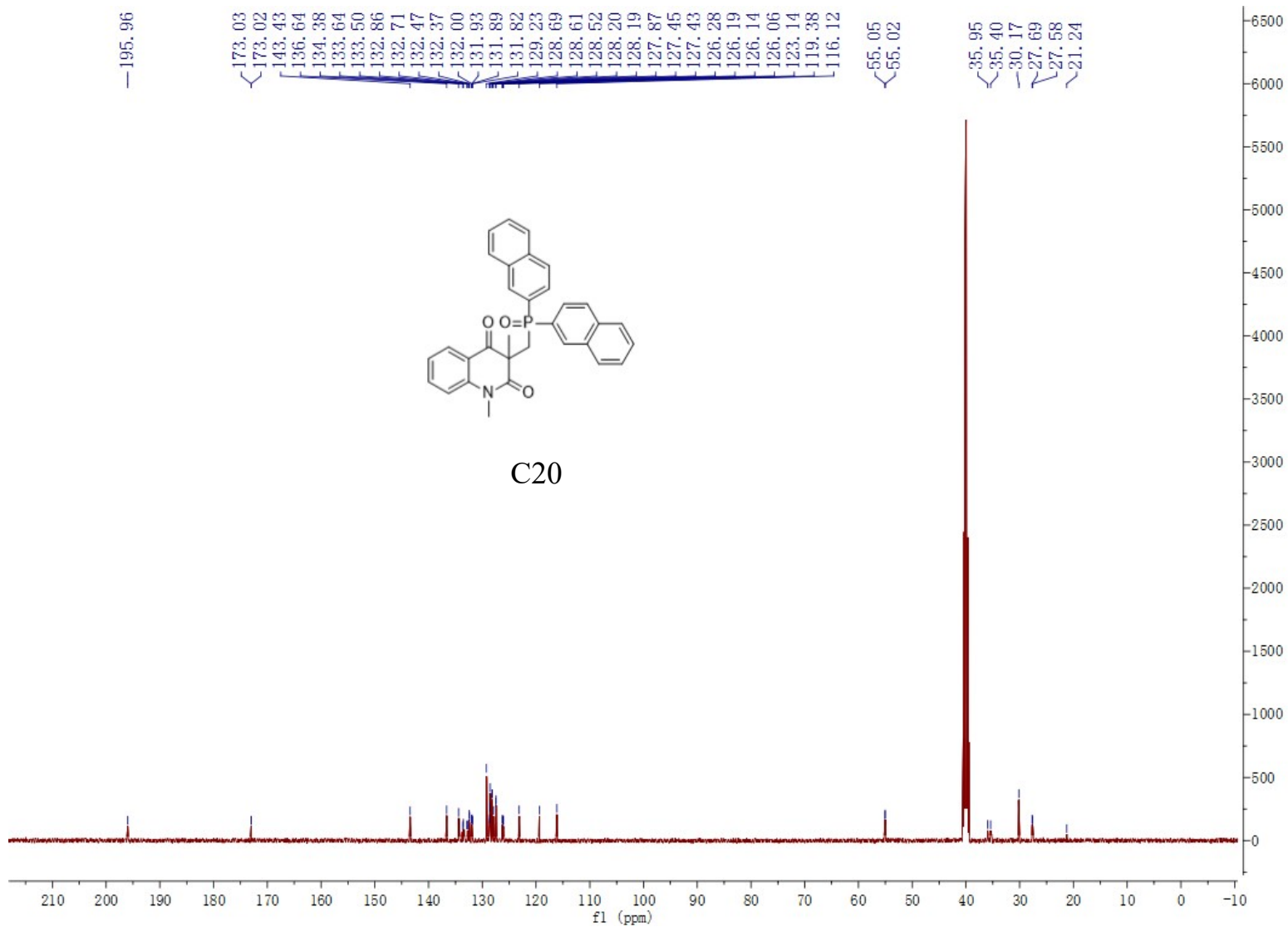


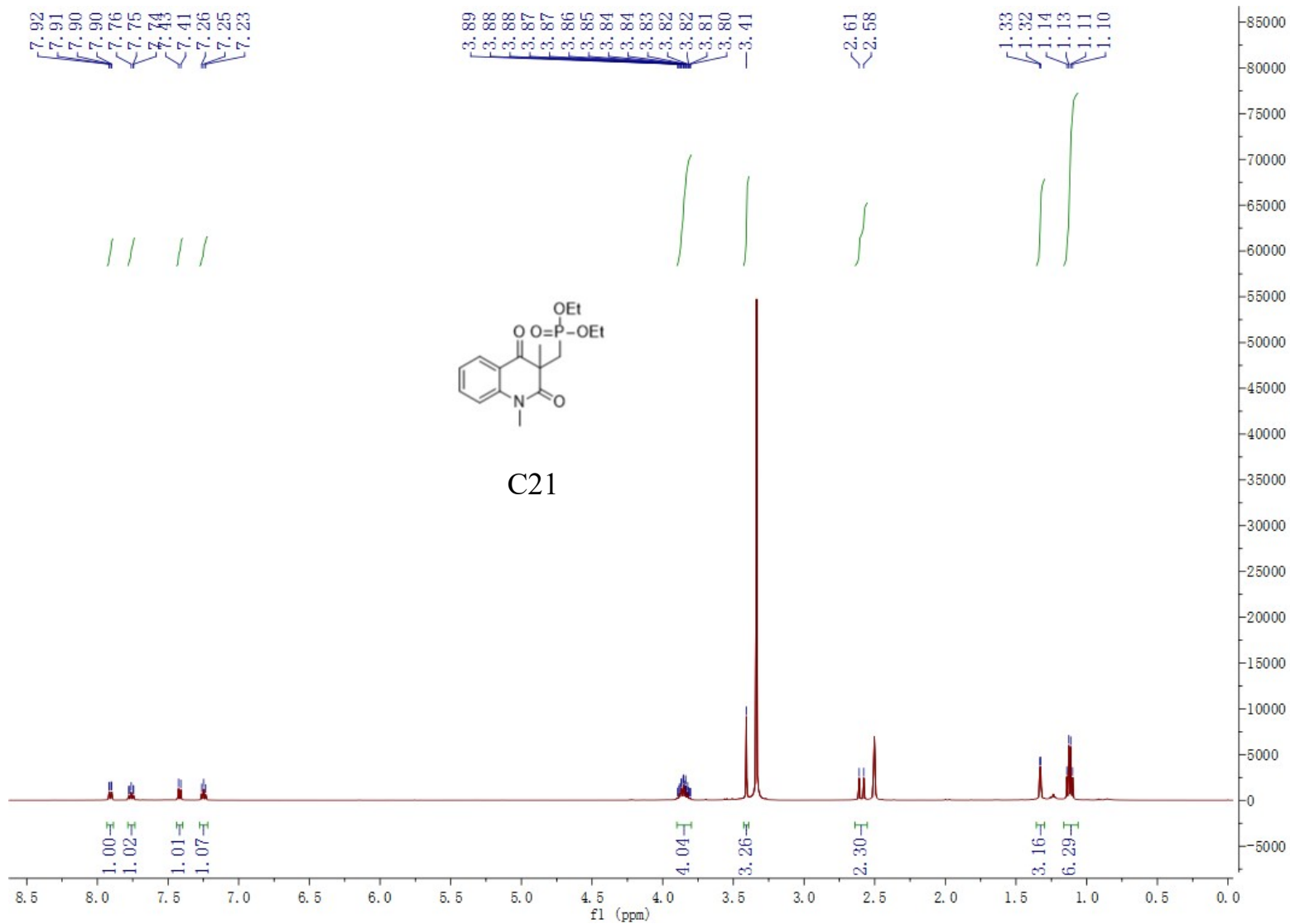


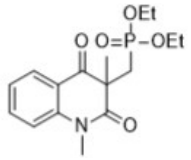
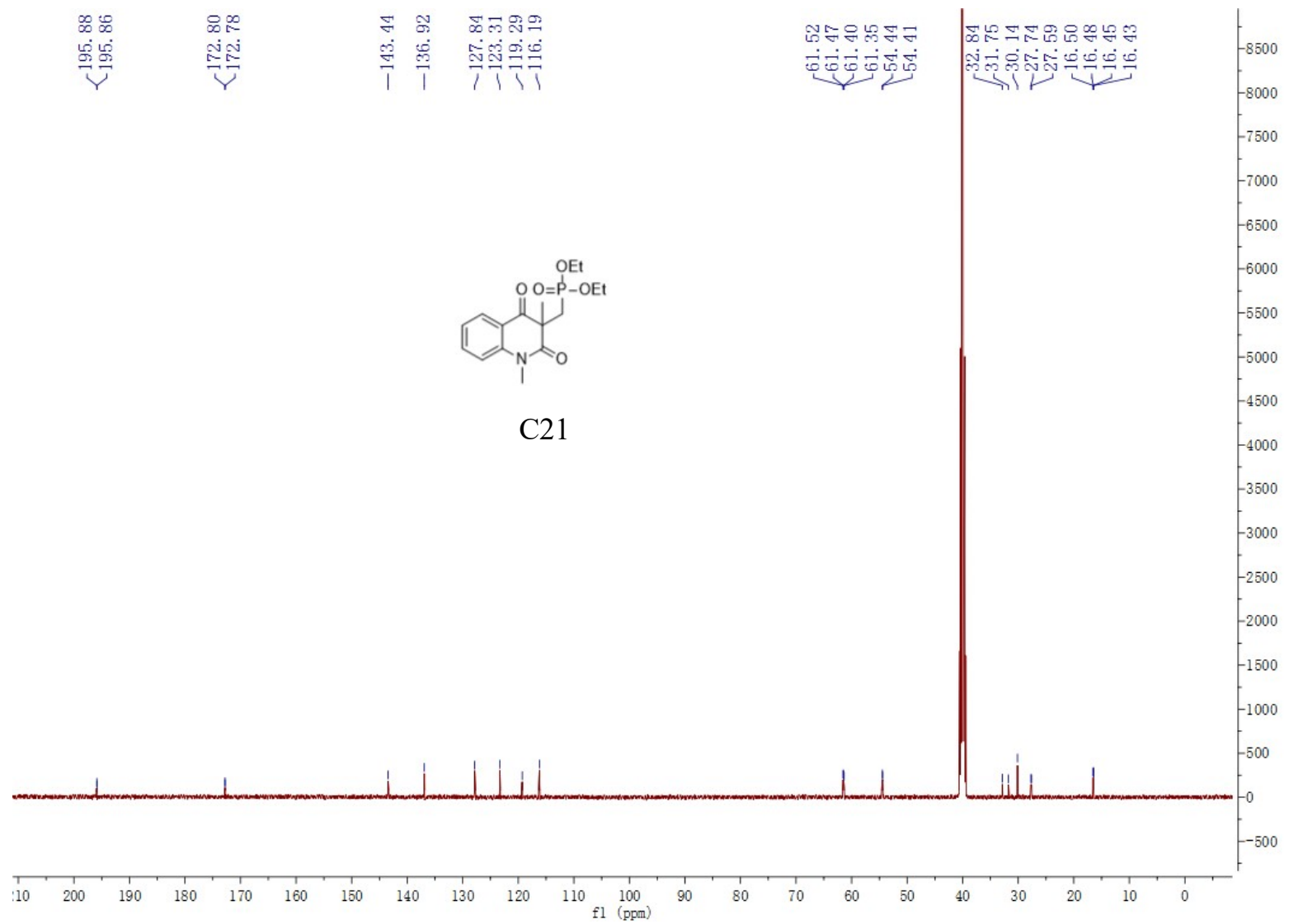












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