

## Supporting Information

### MICROWAVE-ASSISTED AND SOLVENT-FREE SYNTHESIS OF QUINOLINE DERIVATIVES AND THEIR FLUORESCENCE PROPERTIES

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## 1. General Information

Elemental analyses were performed on an Elementar Vario EL III. IR spectra were recorded on a Specode 75 model (Carl Zeiss, Jena, Germany) using KBr as the sample holder. <sup>1</sup>H NMR spectra were recorded on a Varian Inova 400 and 600 MHz instrument with chemical shifts reported relative to tetramethylsilane (TMS). <sup>13</sup>C NMR spectra were recorded on a Varian Inova 151 MHz instrument with chemical shifts reported relative to tetramethylsilane (TMS). GC-MS spectra were determined on a Varian 3800 spectrometer. All materials were weighed in the air. Flash column chromatography was performed with silica gel (100–200 mesh). Fluorescence spectra were recorded using a Hitachi F-7000 spectrofluorophotometer. Fluorescence scans were recorded from 200 nm to 700 nm. Kitchen microwave oven (MI-231A, Wmax : 800W, Midea Group, China). All measurements were carried out at room temperature. All reagents were commercially available, and were used without further purification.

## 2. General procedure for the synthesis of **3a–3g**

2-Aminobenzophenone (0.01 mol),  $\alpha$ -methylene ketones (0.012 mol), and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (0.91 g, 0.5 mmol) were added to a mortar, ground (homogenized), and then transferred to a sealed glass tube with rubber stopper, and were then irradiated for 8 min in a microwave oven with wattage power set at 320 W. After being cooled to room temperature in a water bath, water (10 mL) was added to the reaction mixture, and the suspension was treated with 10% NaOH and extracted with ethyl acetate (3×10 mL). The organic phase was dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to yield the crude product, and was then purified by (silica gel) column chromatography (petroleum ether : ethyl acetate = 3 : 1 as an eluent) to yield pure products.

**Ethyl 2-methyl-4-phenylquinoline-3-carboxylate (3a):** a pale yellow granular crystals (2.63 g, 90%); mp 99–101 °C; IR(KBr)  $\nu$  3057, 2985, 1728, 1580, 1502, 1406, 1286, 1235, 1065, 769 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.02 (t, *J* = 7.8 Hz, 3H), 2.85 (s, 3H), 4.15 (m, 2H), 7.26–7.47 (m, 6H), 7.58 (d, 1H), 7.78 (t, 1H), 8.23 (d, *J* = 7.6 Hz, 1H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  168.55, 154.76, 147.76, 146.46, 135.86, 130.61, 130.21, 129.31, 129.04, 128.84, 128.30, 127.56, 126.70, 126.45, 125.30, 61.47, 23.93, 13.90, 13.64; MS (70 eV) *m/z* (%): 292.2 (M+1, 100), 293.2 (25), 264.1 (18). Anal. Calcd for C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub>: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.31; H, 5.87; N, 4.82.

**1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (3b):** a yellow flaky crystals (2.33 g, 89%); mp 104–106 °C; IR(KBr)  $\nu$  3057, 2959, 1697, 1572, 1445, 1405, 1217, 756, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.13 (s, 3H), 2.85 (s, 3H), 7.22–7.49 (m, 6H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 7.3 Hz, 1H), 8.23 (d, *J*

= 8.6 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  199.19 , 151.02 , 140.22 , 134.09 , 131.15 , 129.38 , 129.06 , 128.28 , 128.11 , 118.28 , 117.32–117.25 , 116.90 , 116.63 , 116.06 , 115.18 ; MS (70 eV)  $m/z$  (%): 262.1 (  $M+1$ , 100 ), 218.1 (76), 204 (7). Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{NO}$ : C, 82.73; H, 5.79; N, 5.36. Found C, 82.75; H, 5.78; N, 5.34.

**3,3-Dimethyl-9-phenyl-3,4-dihydroacridin-1(2H)-one (3c):** a yellow powder (2.48 g, 82%); mp 190–192 °C; IR(KBr)  $\nu$  3057, 2959, 1715, 1600, 1565, 1210, 736  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.12 (s, 6H), 2.37 (s, 2H), 3.26 (s, 2H), 7.18–7.26 (m, 2H), 7.46–7.62 (m, 4H), 7.76 (m, 2H), 8.16 (d,  $J$  = 8 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  198.09 , 161.28 , 151.14 , 149.14 , 137.73 , 131.97 , 131.55 , 128.78 , 128.55 , 128.25 , 127.86 , 127.55 , 122.84 , 54.36 , 48.55–48.46 , 32.39 , 28.57 , 28.39 ; MS (70 eV)  $m/z$  (%) 302.2 (  $M+1$ , 100 ), 303.2 (23), 324.2 (18). Anal. Calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$ : C, 83.69; H, 6.35; N, 4.65. Found C, 83.68; H, 6.34; N 4.66.

**2,4-Diphenylquinoline (3d):** a yellow granular crystals (1.91 g, 68%); mp 106–107 °C; IR(KBr)  $\nu$  3052, 1586, 1551, 1447  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.44 (m, 2H), 7.46–7.53 (m, 7H), 7.69 (t,  $J$  = 7.5 Hz, 1H), 7.78 (s, 1H), 7.830 (d,  $J$  = 3.0 Hz, 1H), 8.06 (d,  $J$  = 8.0 Hz, 2H), 8.12 (d,  $J$  = 9.0 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  150.89 , 140.08 , 134.63 , 134.46 , 133.95 , 131.00 , 129.24 , 128.92 , 128.14 , 127.99 , 127.47 , 118.14 , 117.45 , 117.19 , 116.75 , 115.93 , 115.48 , 115.04 ; MS (70 eV)  $m/z$  (%) 282.1 ( $M+1$ , 100), 283.1 (3), 202 (15). Anal. Calcd for  $\text{C}_{21}\text{H}_{15}\text{N}$ : C, 89.65; H, 5.37; N, 4.98. Found C, 89.68; H, 5.36; N, 4.87.

**2-(4-Chlorophenyl)-4-phenylquinoline (3e):** a pale yellow needle-like crystals (2.23 g, 71%); mp 97–100 °C; IR(KBr)  $\nu$  3054, 1591, 1545, 1487, 1416, 1094, 769, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38–7.49 (m, 8H), 7.69–7.76 (m, 2H), 7.89 (d,  $J$  = 8.0 Hz, 1H), 8.06 (d,  $J$  = 8.4 Hz, 2H), 8.12 (d,  $J$  = 8.4 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  155.43 , 149.32 , 148.68 , 138.17 , 137.95 , 135.48 , 130.01 , 129.52 , 129.38 , 128.90 , 128.80 , 128.69 , 128.61 , 128.44 , 126.43 , 125.74 , 125.40 , 119.02 , 118.59–118.51 ; MS (70 eV)  $m/z$  (%) 316.2 ( $M+1$ , 100), 317.2 (22), 318.2 (33). Anal. Calcd for  $\text{C}_{21}\text{H}_{14}\text{ClN}$ : C, 79.87; H, 4.47; N, 4.44. Found C, 79.85; H, 4.45; N, 4.46.

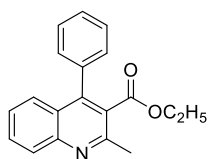
**2-(4-Bromophenyl)-4-phenylquinoline (3f):** a pale yellow needle-like crystals (2.72 g, 76%); mp 126–128 °C; IR(KBr)  $\nu$  3051, 1590, 1544, 1486, 1416, 1356, 1072, 1008, 829, 768, 701  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.71 (m, 10H), 7.79 (d,  $J$  = 8.1 Hz, 1H), 8.01 (d,  $J$  = 8.7 Hz, 2H), 8.14 (d,  $J$  = 8.4 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  155.69 , 149.56 , 148.91 , 138.62 , 138.38 , 132.27 , 131.92 , 130.24 , 129.74 , 129.61 , 129.33 , 129.14 , 128.83 , 128.62 , 126.67 , 126.00 , 125.62 , 124.09 , 119.18 , 118.75 ; MS (70 eV)  $m/z$  (%) 360 ( $M+1$ , 100), 361 (24), 362 (98). Anal. Calcd for  $\text{C}_{21}\text{H}_{14}\text{BrN}$ : C, 70.01; H, 3.92; N, 3.92. Found: C, 69.78; H, 3.96; N, 3.93.

**2-(4-Methoxyphenyl)-4-phenylquinoline (3g):** a colorless needle-like crystals (1.89 g, 61%); mp 83–84

°C; IR(KBr)  $\nu$  3052, 1587, 1551, 1480, 1448, 743, 701, 643  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 8.4$  Hz, 1H), 8.20–8.19 (dd,  $J = 2.1$  Hz, 2H), 7.90 (d,  $J = 8.4$  Hz, 1H), 7.79 (s, 1H), 7.72 (t,  $J = 8.3$  Hz, 1H), 7.59–7.51 (m, 5H), 7.45 (t,  $J = 7.6$  Hz, 1H), 7.08–7.04 (m, 2H), 3.88 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.95, 156.52, 149.09, 148.94, 138.62, 138.62, 132.31, 129.63, 129.02, 128.70, 125.62, 119.00, 114.53, 114.13, 55.49; MS (70 eV)  $m/z$  (%) 312.2 (M+1, 100), 313.2 (23). Anal. Calcd for  $\text{C}_{22}\text{H}_{17}\text{NO}$ : C, 84.86; H, 5.50; N, 4.50. Found: C, 84.92; H, 5.52; N, 4.48.

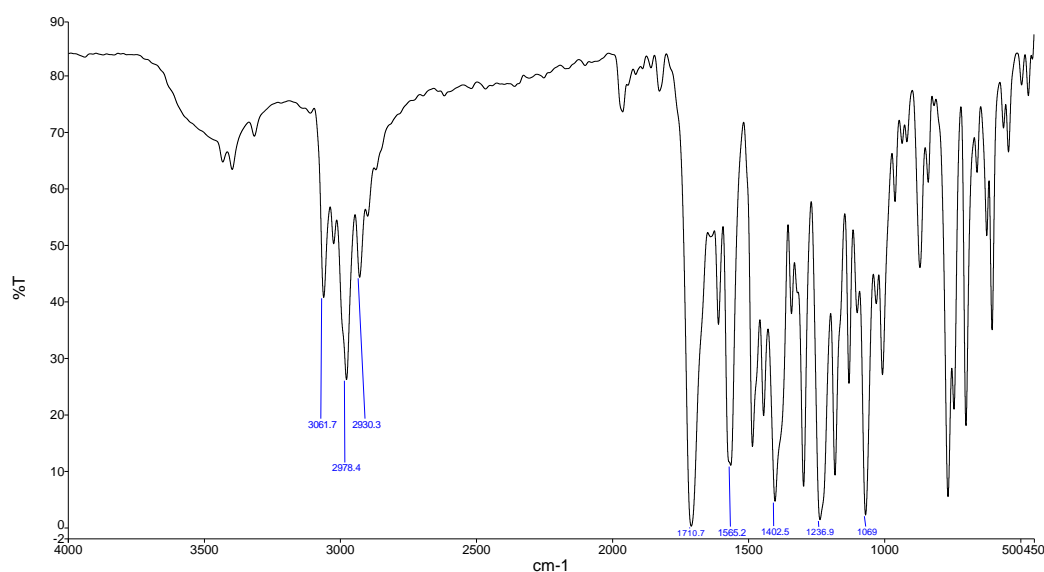
### 3. Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR, MS and IR

**3a:**



MW: 291.35

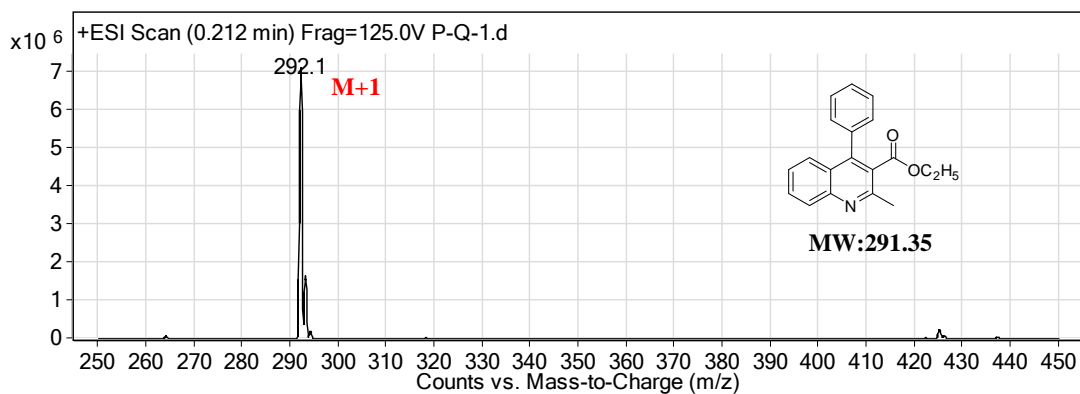
IR: 3062, 2978, 2930, 1711, 1565, 1403, 1236, 1068  $\text{cm}^{-1}$ .



The IR of 3a

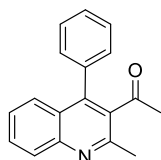
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.06 (d,  $J = 8.4$  Hz, 1H), 7.73–7.67 (m, 1H), 7.56 (d,  $J = 7.8$  Hz, 1H), 7.48–7.44 (m, 3H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.34 (dd,  $J = 6.4, 3.1$  Hz, 2H), 4.04 (q,  $J = 7.1$  Hz, 2H), 2.77 (s, 3H), 0.93 (t,  $J = 7.1$  Hz, 3H).





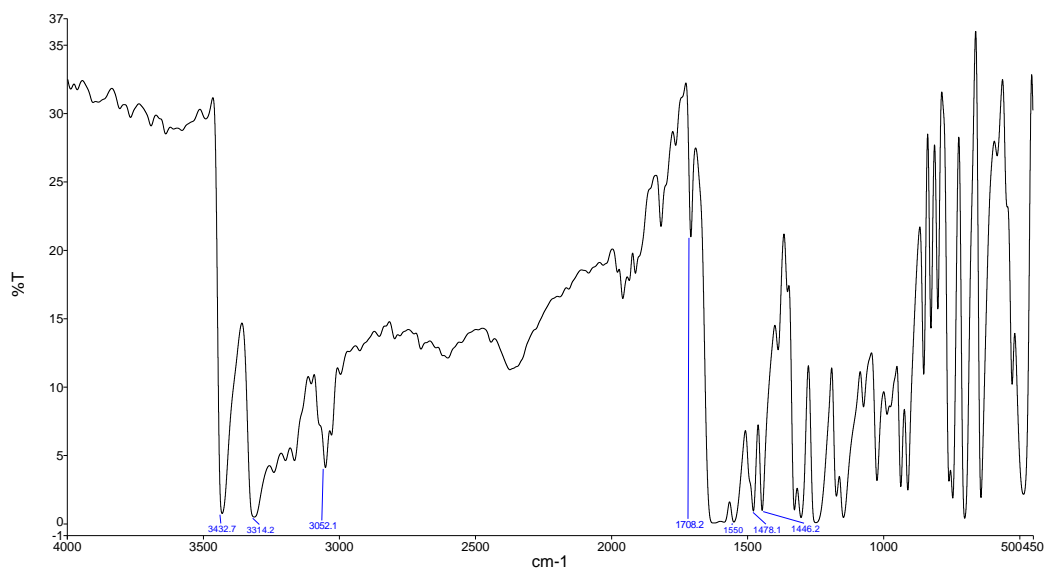
The MS of 3a

**3b**



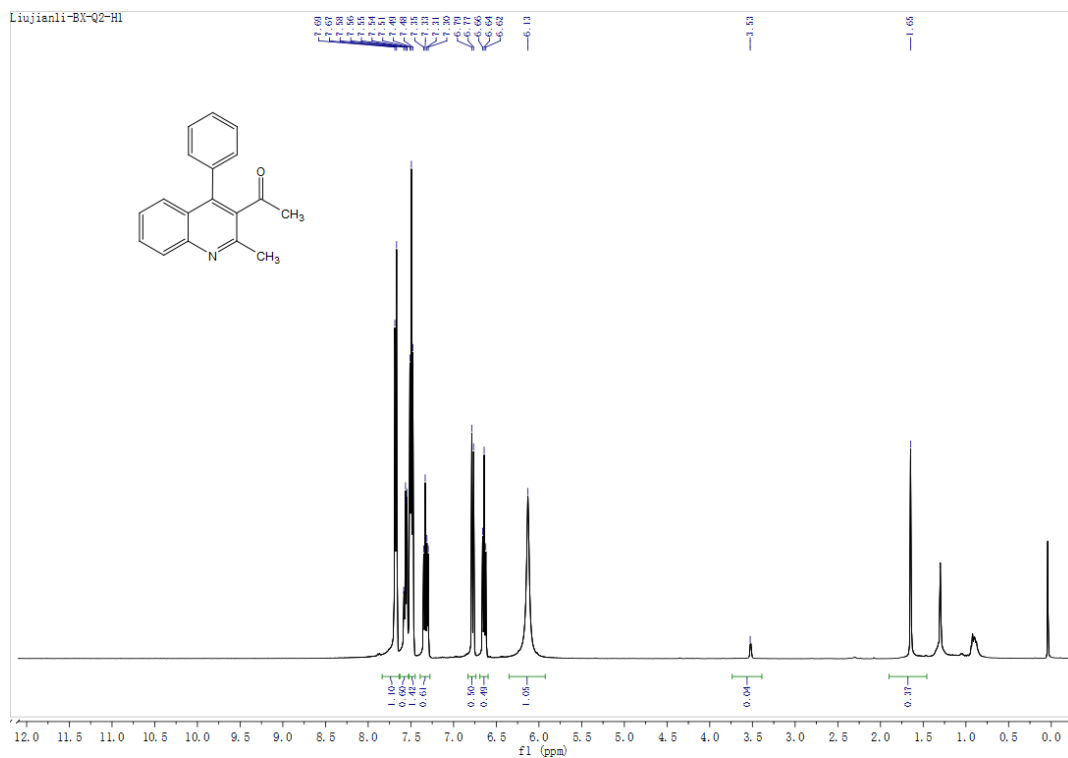
MW: 261.32

IR: 3433, 3314, 3052, 1708, 1550, 1478, 1466  $\text{cm}^{-1}$ .



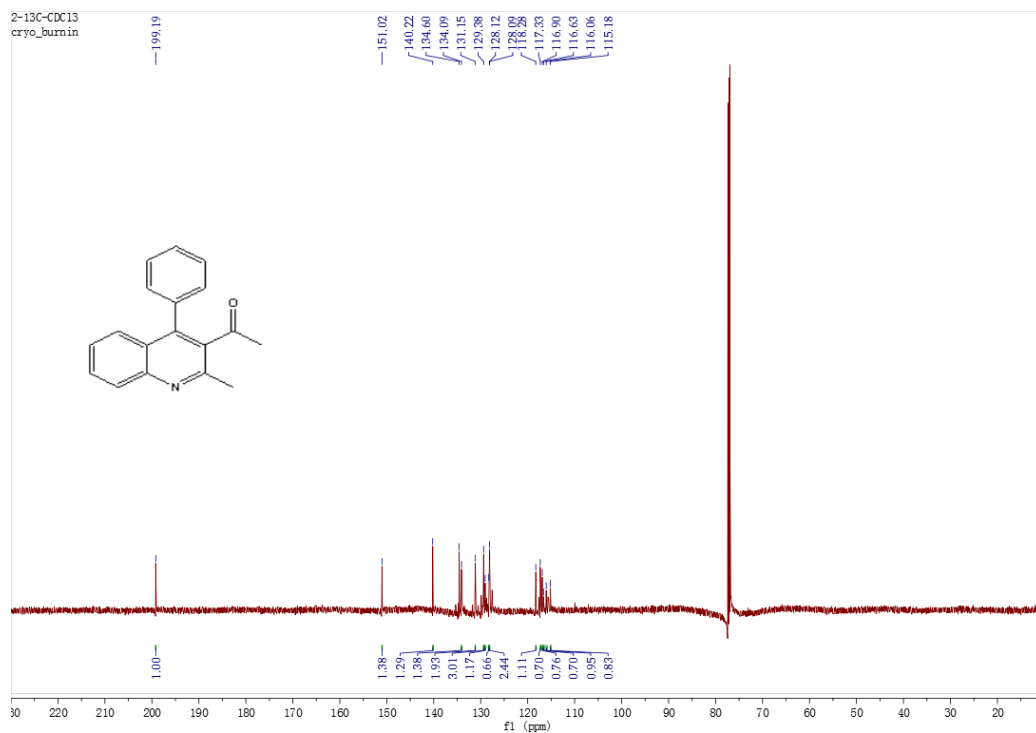
The IR of 3b

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.68 (d,  $J = 8.0$  Hz, 1H), 7.64–7.08 (m, 3H), 6.92–6.55 (m, 1H), 6.13 (s, 1H), 3.53 (s, 1H), 1.65 (s, 1H).



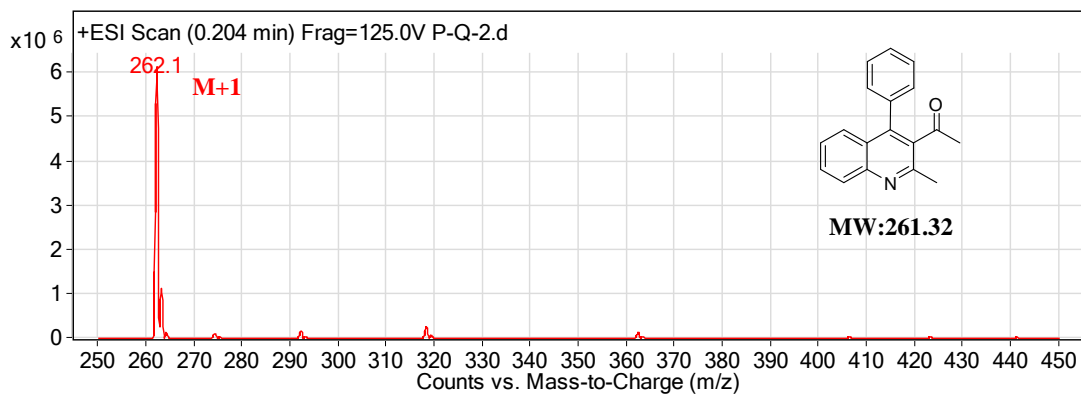
The  $^1\text{H}$  NMR of 3b

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  199.19, 151.02, 140.22, 134.09, 131.15, 129.38, 129.06, 128.28, 128.11, 118.28, 117.32–117.25, 116.90, 116.63, 116.06, 115.18.



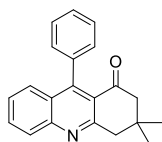
The  $^{13}\text{C}$  NMR of 3b

MS (70 eV) m/z (%): 262.1 ( M+1, 100 ), 218.1 (76), 204 (7).



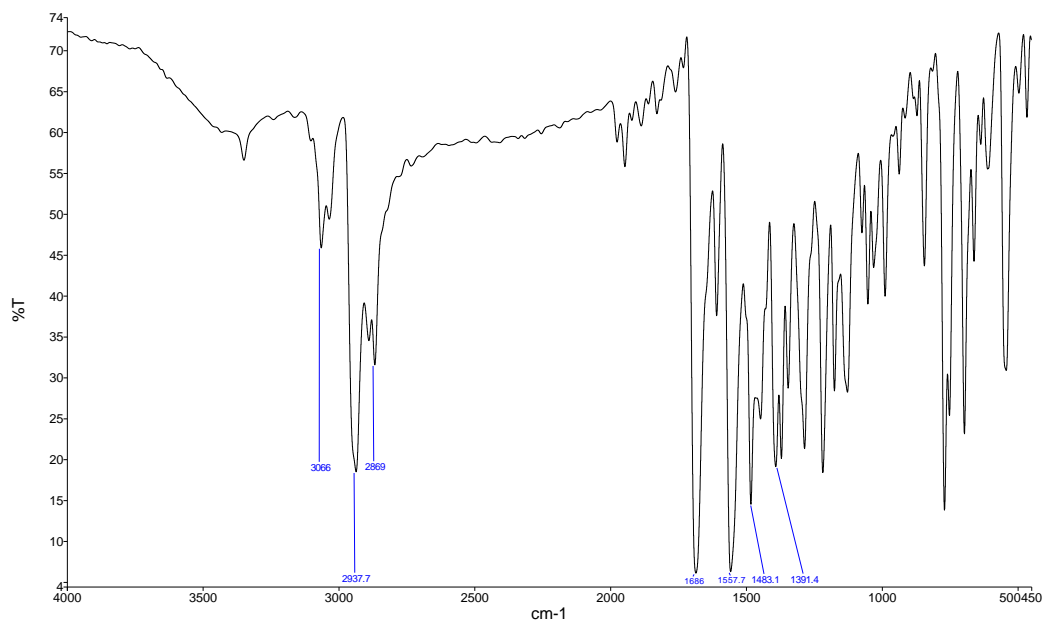
The MS of 3b

3c



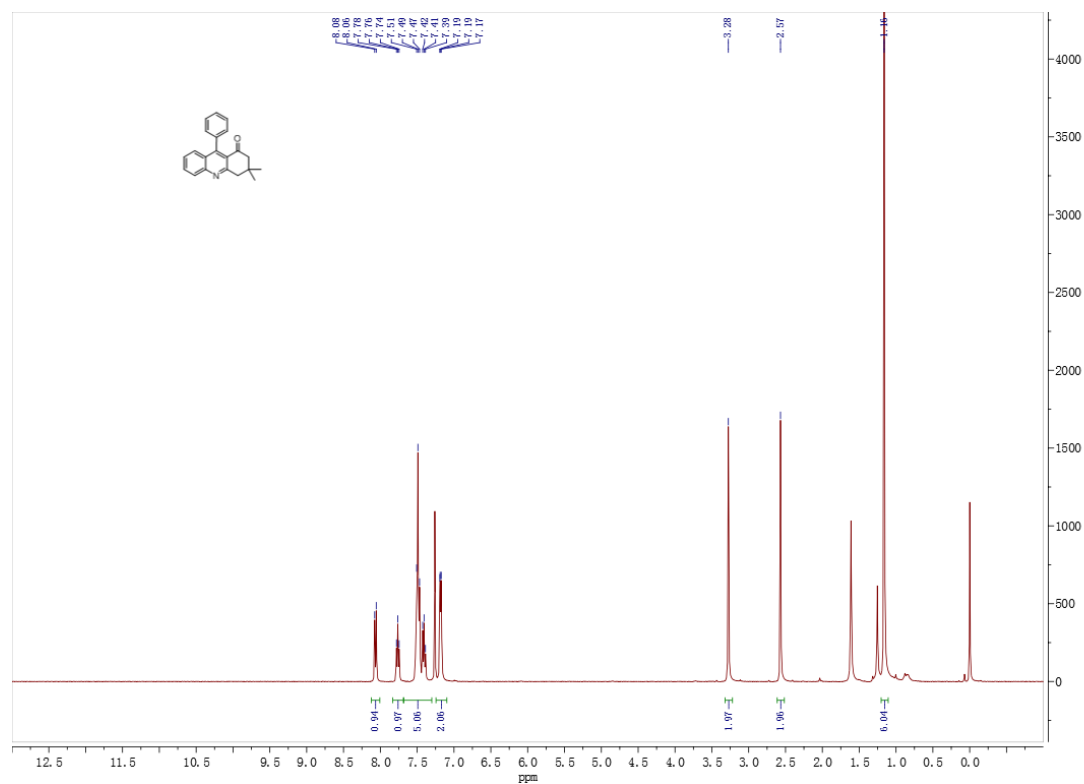
MW: 301.39

IR: 3066, 2938, 2869, 1686, 1558, 1438, 1391 cm<sup>-1</sup>.



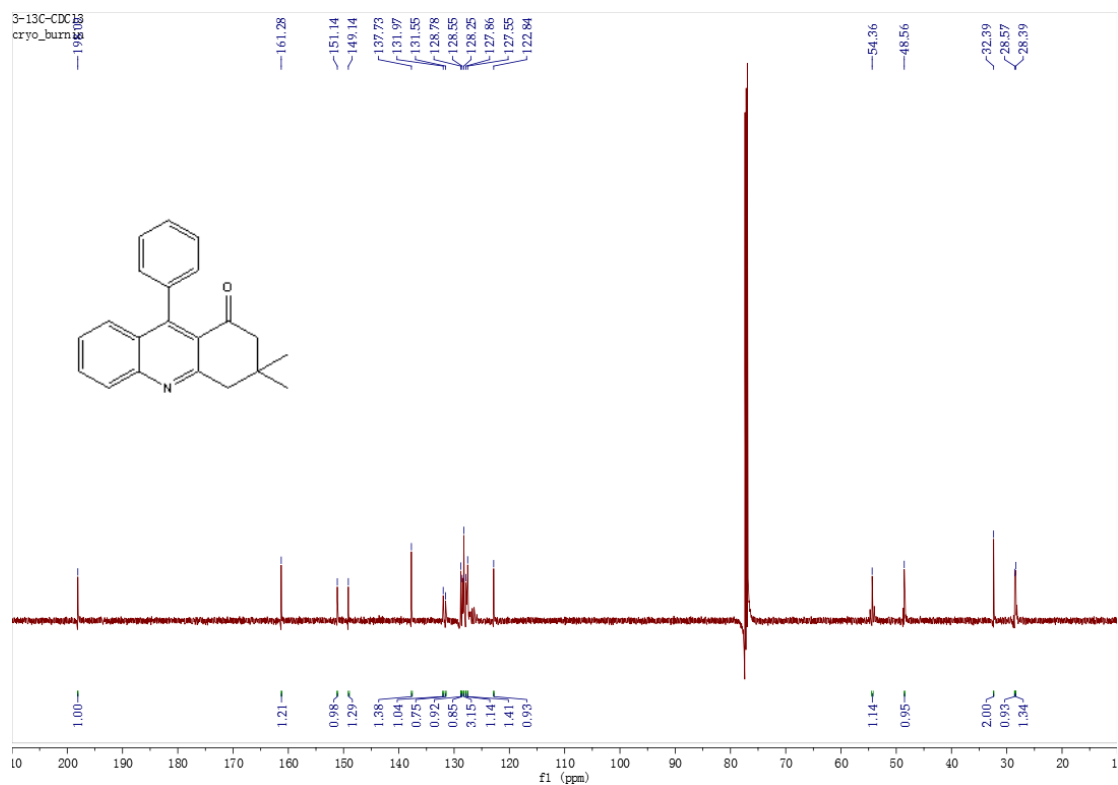
The IR of 3c

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.45 (dt, *J* = 14.9, 7.3 Hz, 5H), 7.2–7.10 (m, 2H), 3.28 (s, 2H), 2.57 (s, 2H), 1.16 (s, 6H).



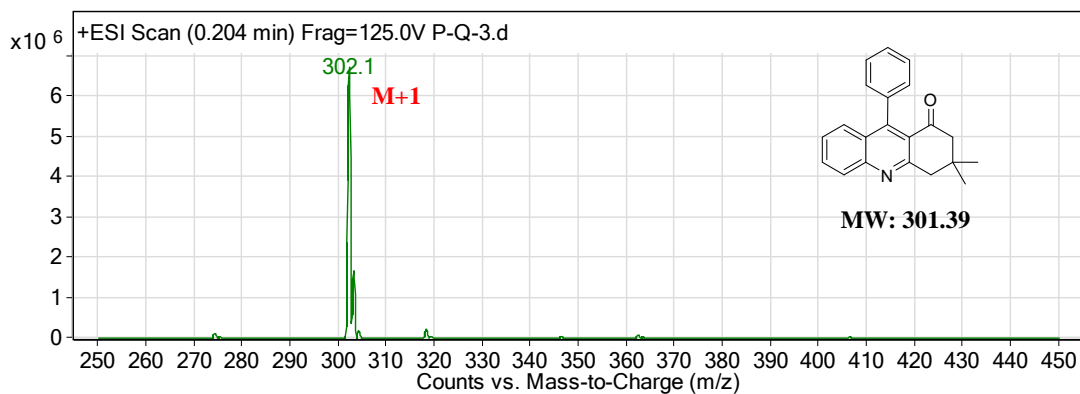
The <sup>1</sup>H NMR of 3c

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 150.89, 140.08, 134.63, 134.46, 133.95, 131.00, 129.24, 128.92, 128.14, 127.99, 127.47, 118.14, 117.45, 117.19, 116.75, 115.93, 115.48, 115.04.



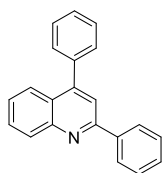
The <sup>13</sup>C NMR of 3c

MS (70 eV) m/z (%): 302.2 ( M+1, 100 ), 303.2 (23), 324.2 (18).



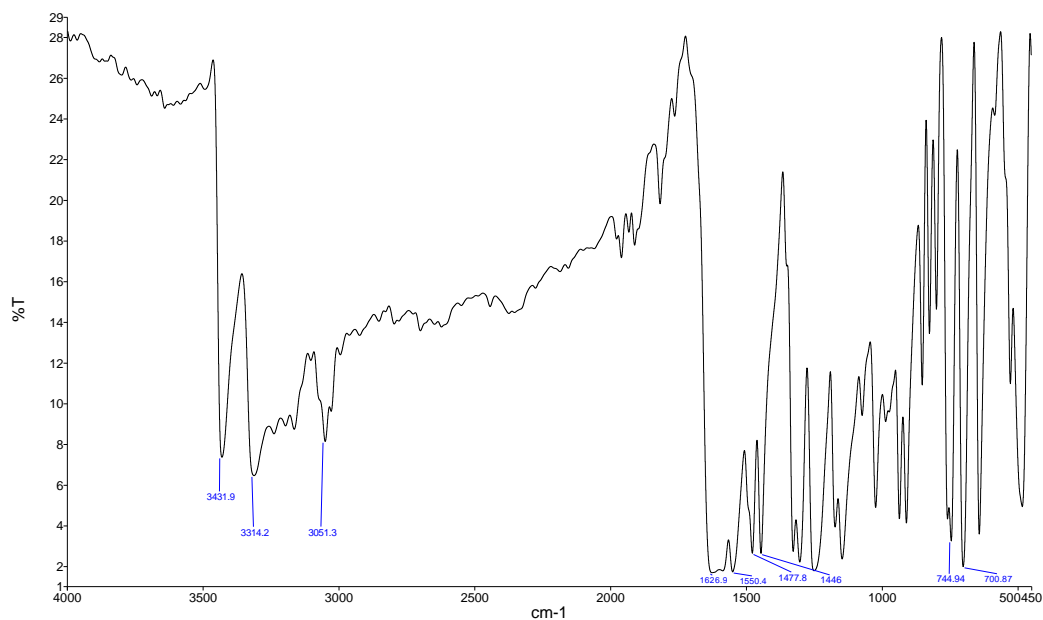
The MS of 3c

**3d**



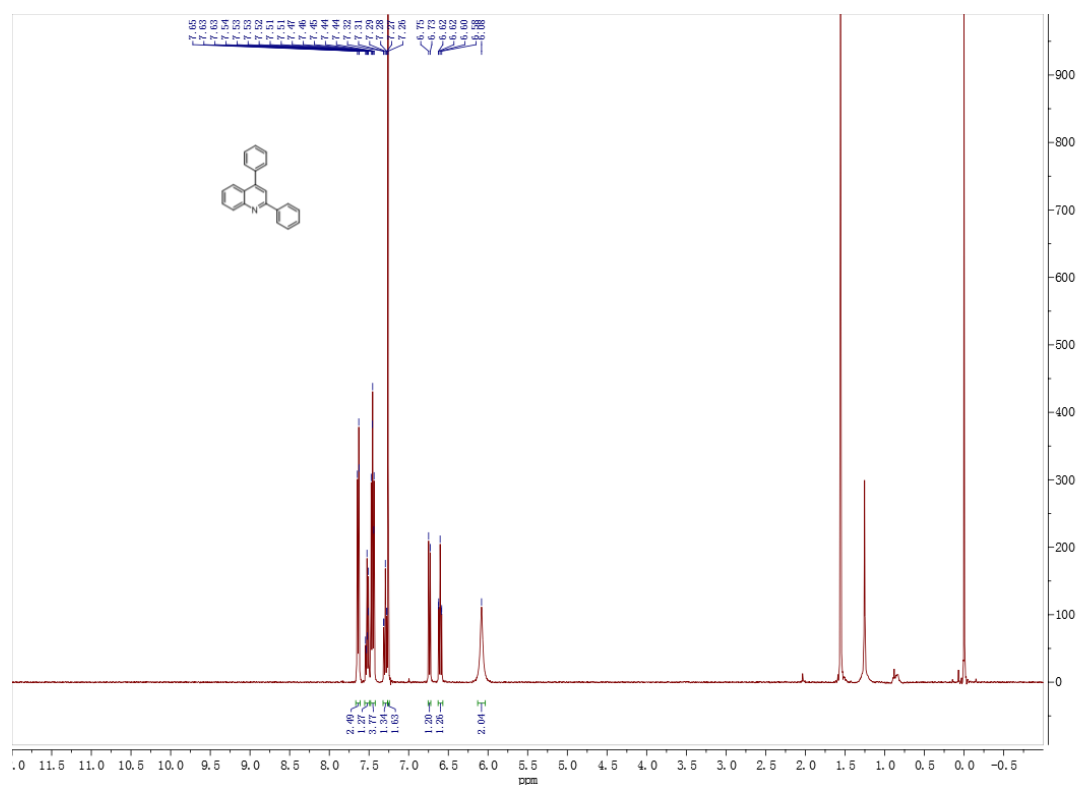
MW: 281.36

IR: 3432, 3314, 3051, 1633, 1551, 1479, 1448 cm<sup>-1</sup>.



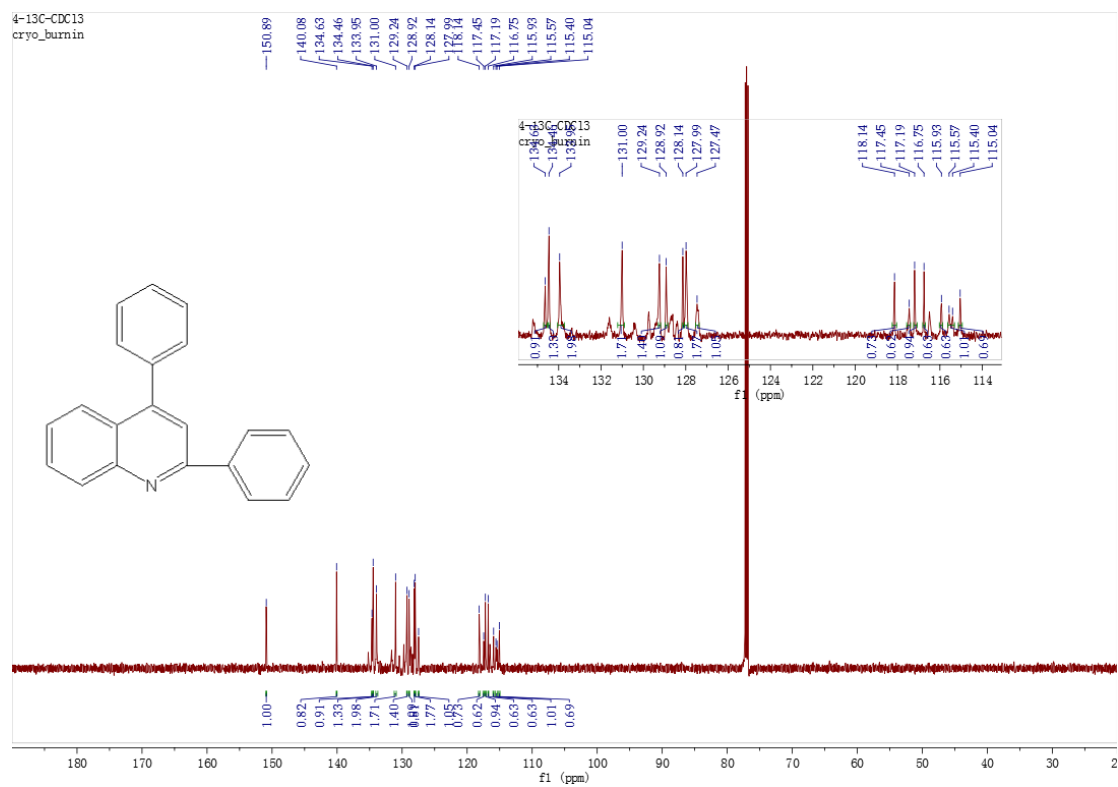
The IR of 3d

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.67–7.61 (m, 2H), 7.55–7.49 (m, 1H), 7.48–7.42 (m, 4H), 7.32–7.26 (m, 1H), 7.26 (s, 2H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.63–6.57 (m, 1H), 6.08 (s, 2H).



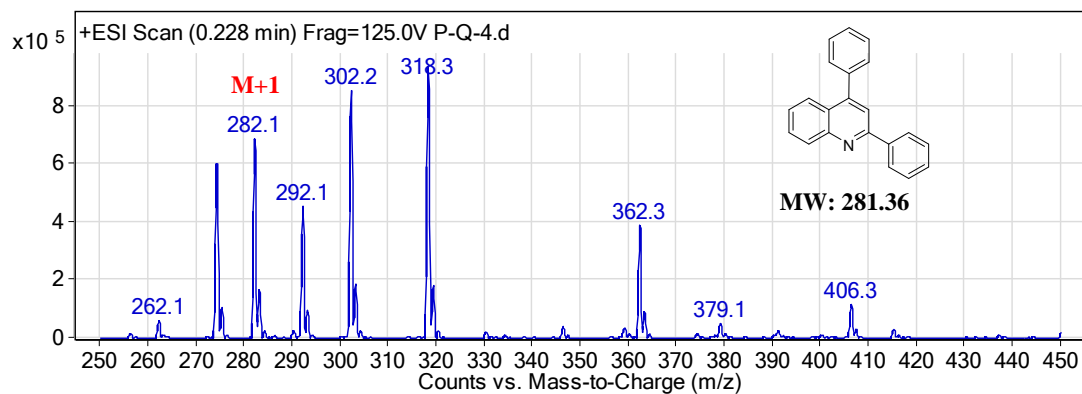
The  $^1\text{H}$  NMR of 3d

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  150.89, 140.08, 134.63, 134.46, 133.95, 131.00, 129.24, 128.92, 128.14, 127.99, 127.47, 118.14, 117.45, 117.19, 116.75, 115.93, 115.48, 115.04.



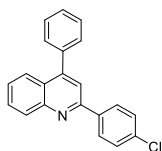
The  $^{13}\text{C}$  NMR of 3d

MS (70 eV) m/z (%): 282.1 (M+1, 100), 283.1 (3), 202 (15).



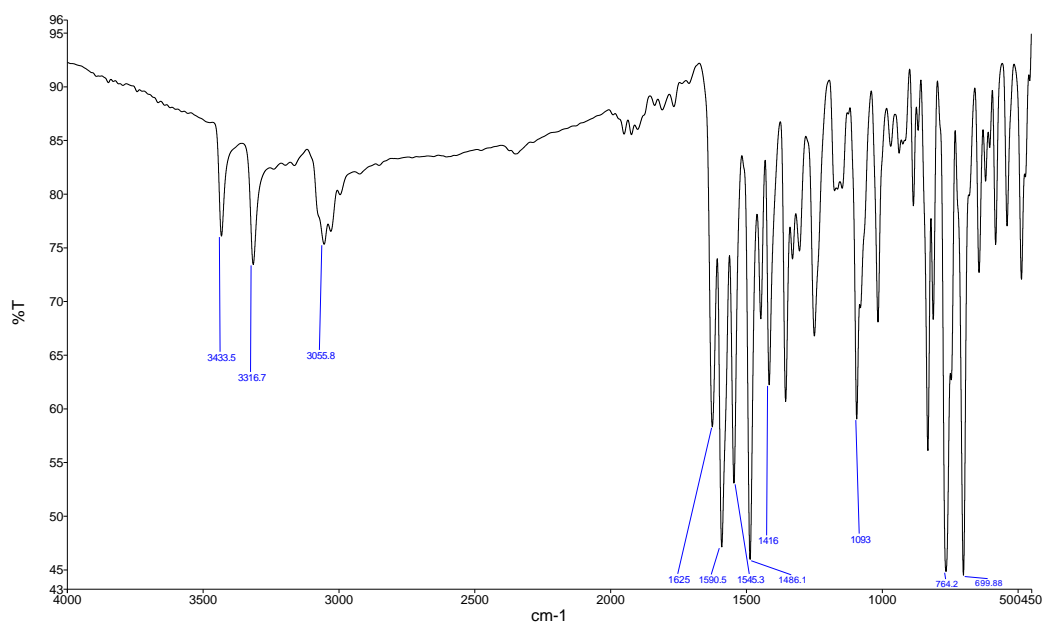
The MS of 3d

3e



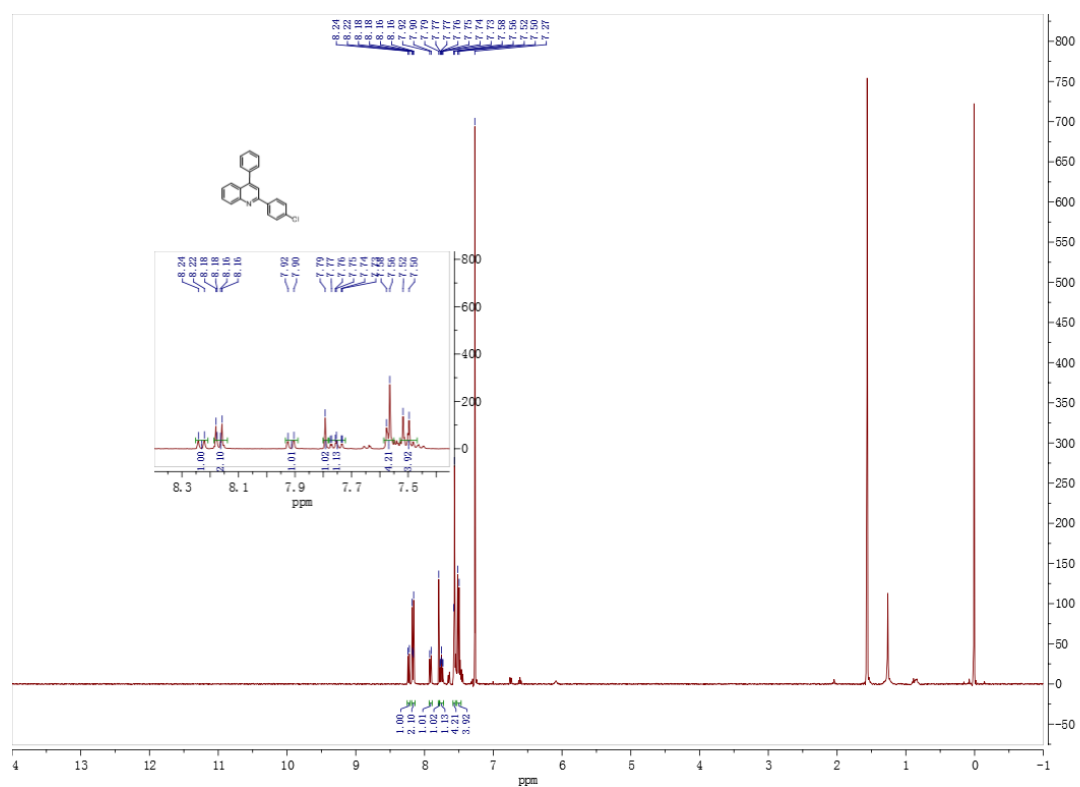
MW: 315.80

IR: 3434, 3317, 3056, 1627, 1590, 1550, 1478, 1446, 745, 700 cm<sup>-1</sup>.



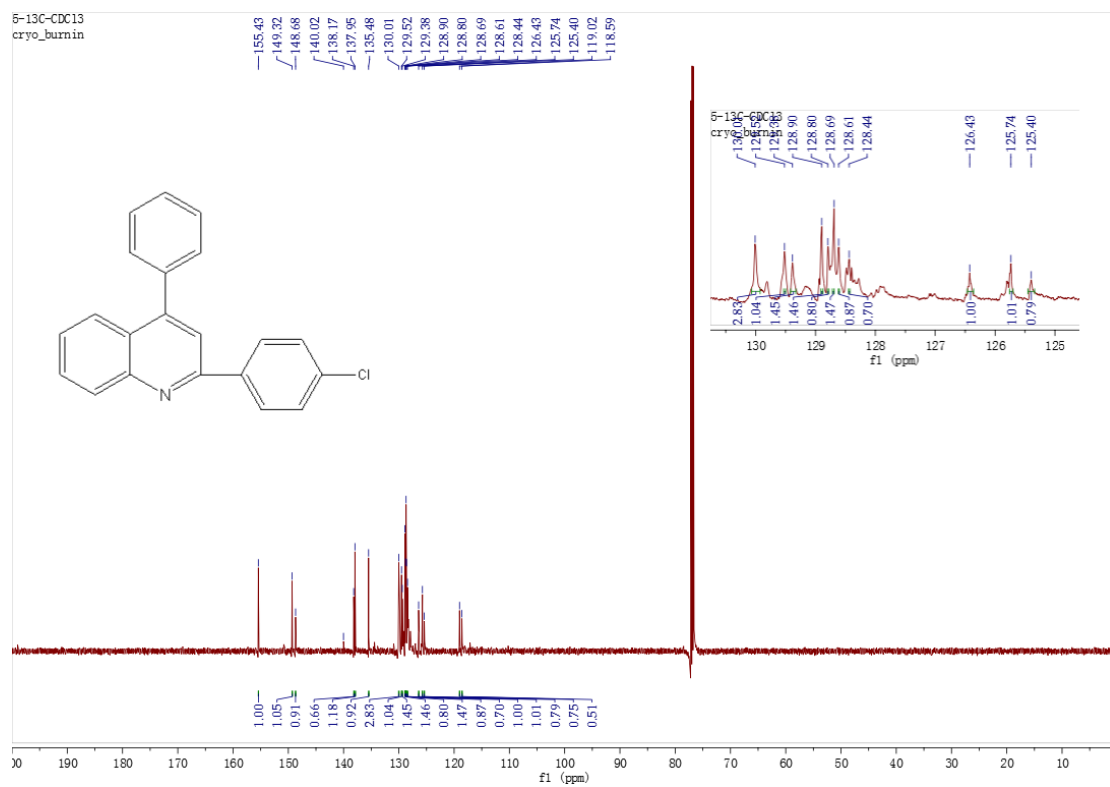
The IR of 3e

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.19–8.14 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.79 (s, 1H), 7.78–7.72 (m, 1H), 7.57 (d, *J* = 4.6 Hz, 4H), 7.51 (d, *J* = 8.6 Hz, 4H).



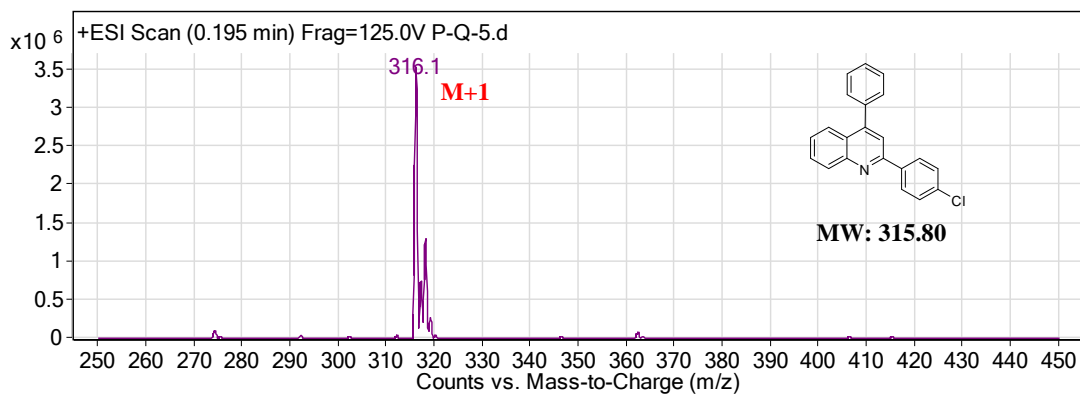
The <sup>1</sup>H NMR of 3e

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 155.43, 149.32, 148.68, 138.17, 137.95, 135.48, 130.01, 129.52, 129.38, 128.90, 128.80, 128.69, 128.61, 128.44, 126.43, 125.74, 125.40, 119.02, 118.59.



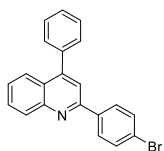
The <sup>13</sup>C NMR of 3e

MS (70 eV) m/z (%): 316.2 (M+1, 100), 317.2 (22), 318.2 (33).



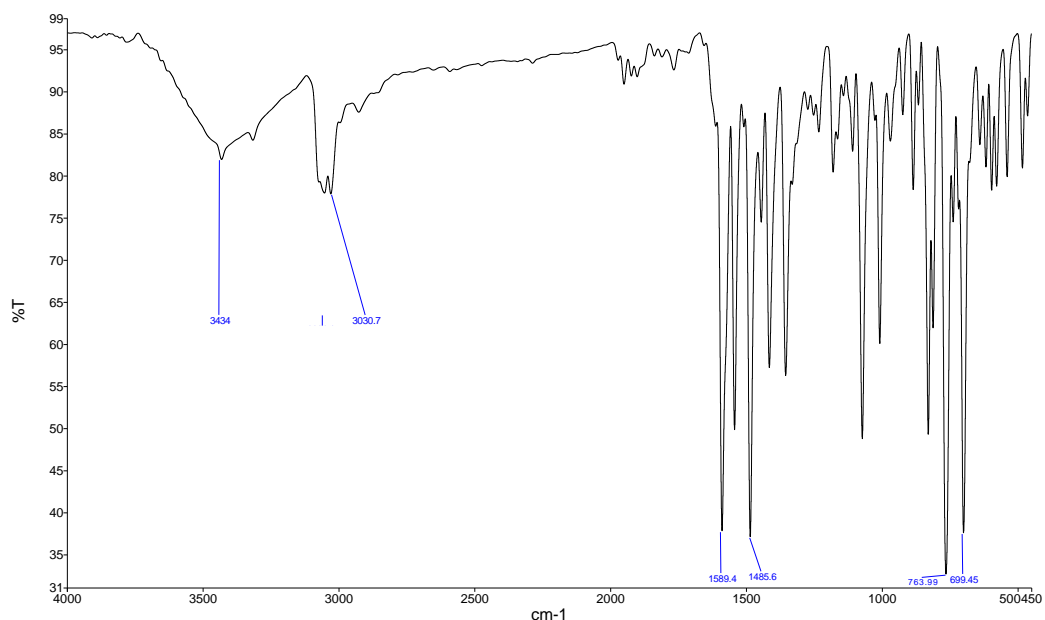
The MS of 3e

3f



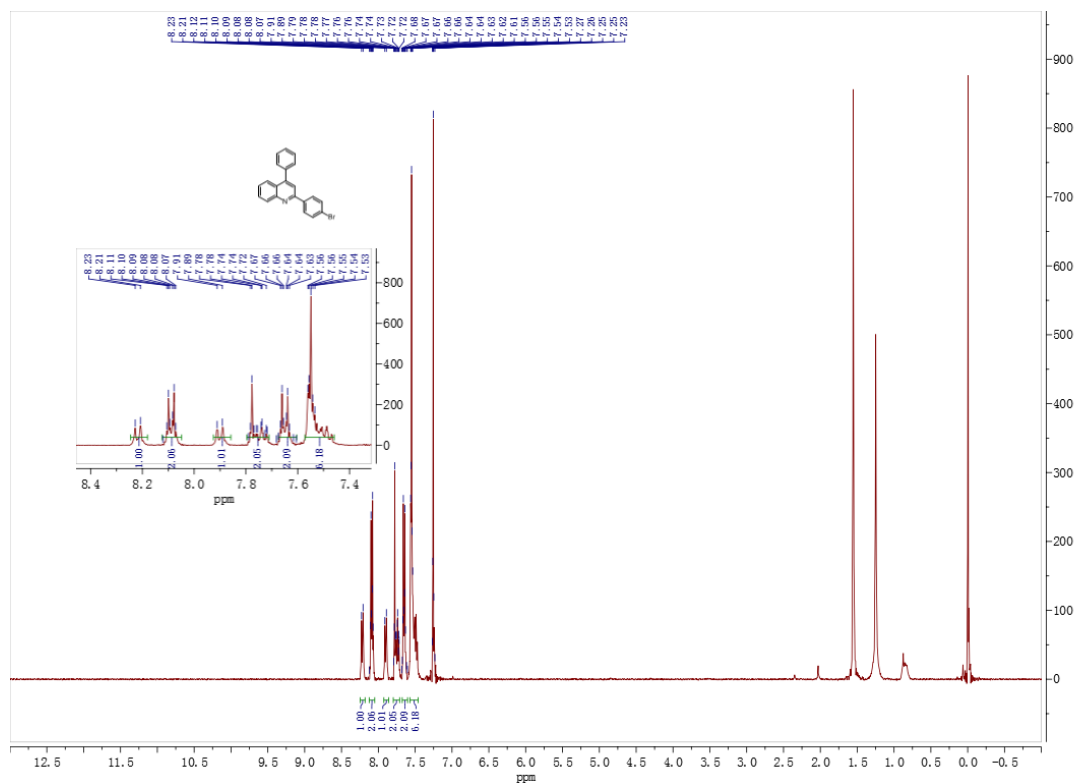
MW: 360.25

IR: 3434, 3054, 3031, 1589, 1486, 764, 700 cm<sup>-1</sup>.



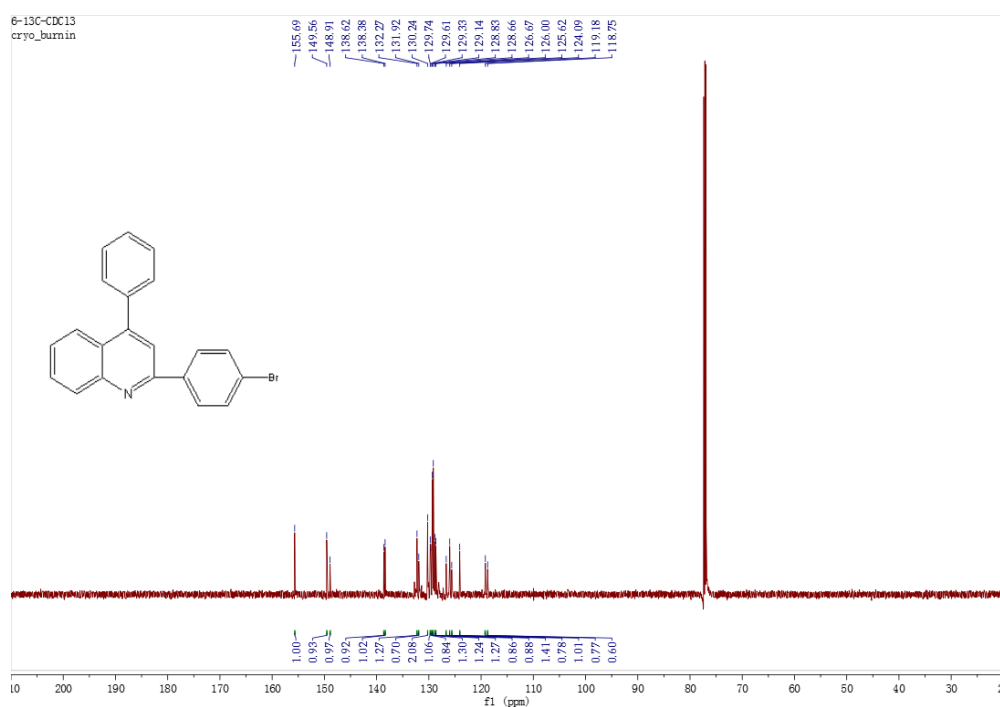
The IR of 3f

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.12–8.05 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.80–7.71 (m, 2H), 7.68–7.60 (m, 2H), 7.57–7.46 (m, 6H).



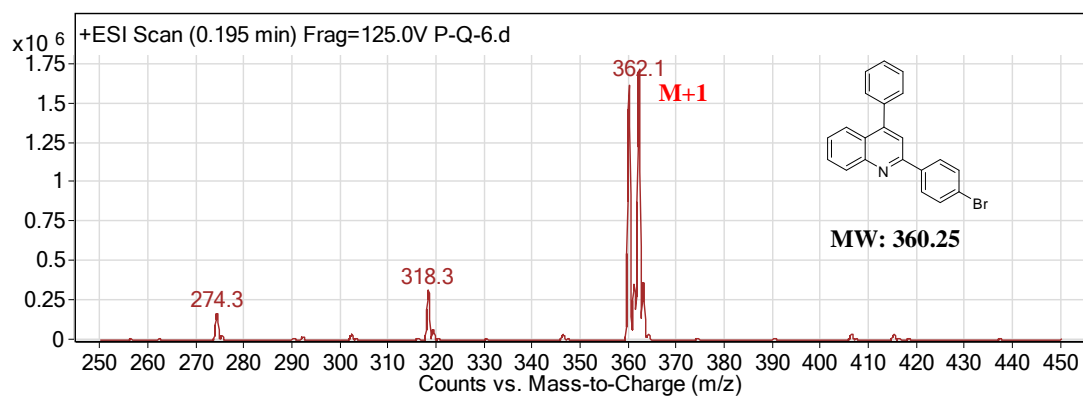
The <sup>1</sup>H NMR of 3f

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 155.69, 149.56, 148.91, 138.62, 138.38, 132.27, 131.92, 130.24, 129.74, 129.61, 129.33, 129.14, 128.83, 128.62, 126.67, 126.00, 125.62, 124.09, 119.18, 118.75.



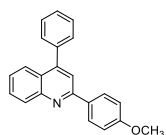
The <sup>13</sup>C NMR of 3f

MS (70 eV) m/z (%): 360 (M+1, 100), 361 (24), 362 (98).



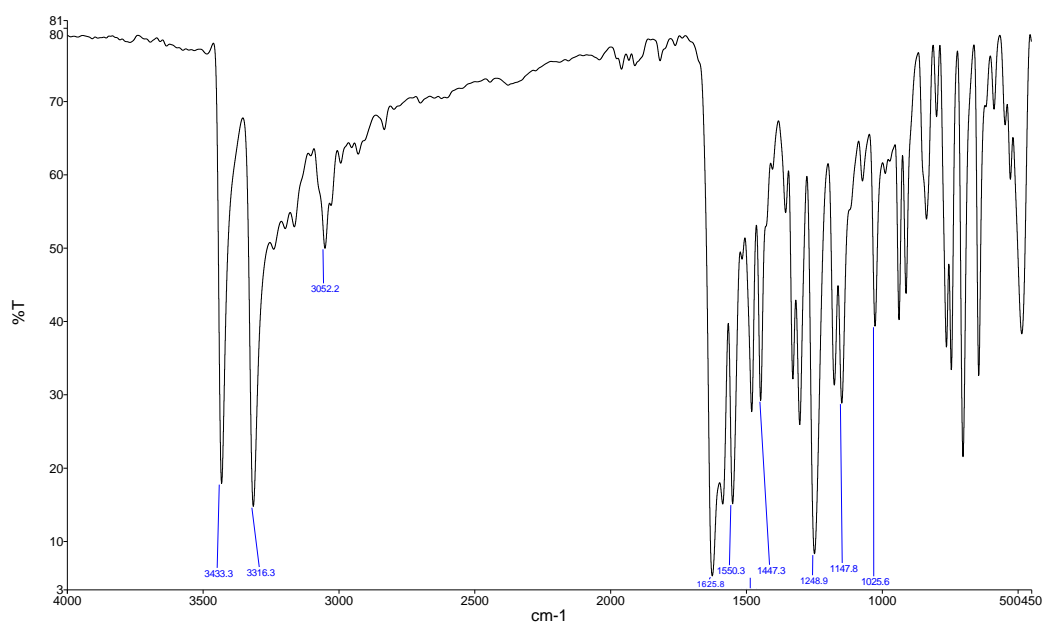
The MS of 3f

3g



MW: 311.38

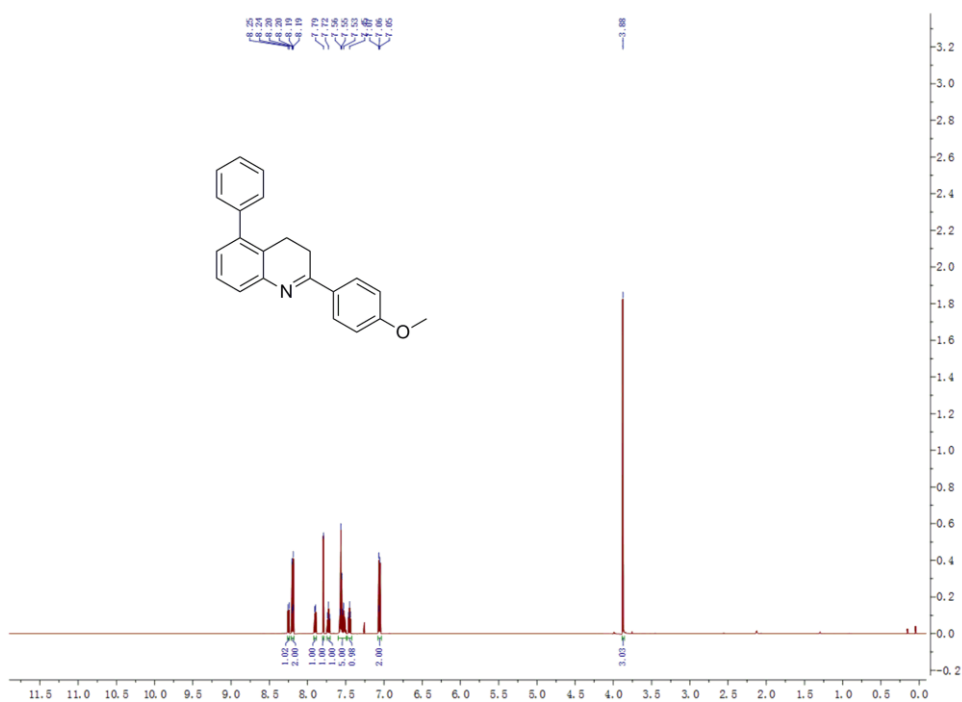
IR: 3433, 3316, 3052, 1626, 1550, 1480, 1447, 1249, 1148, 1026 cm<sup>-1</sup>.



The IR of 3g

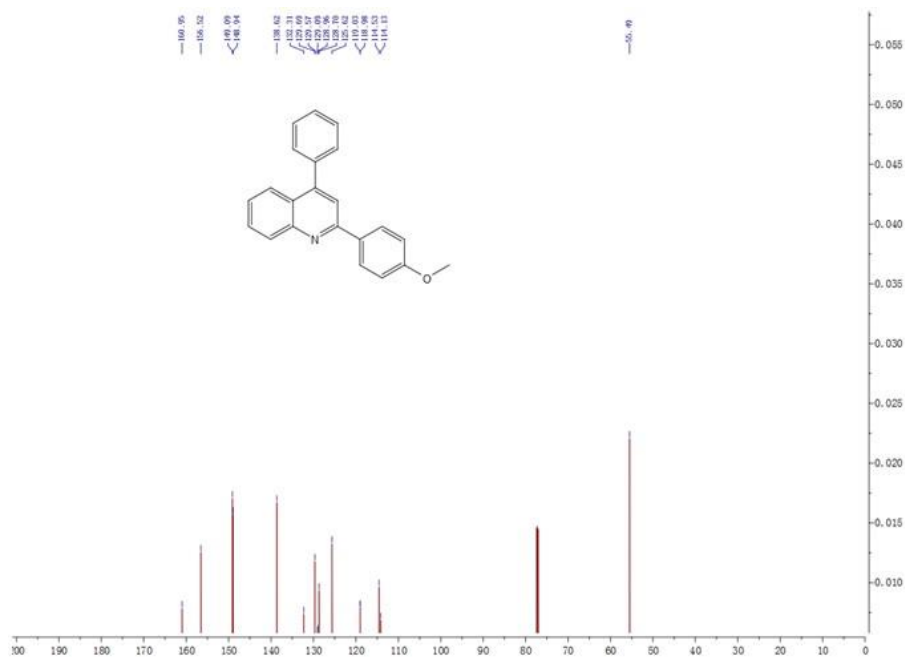
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.20–8.19 (dd, *J* = 2.1 Hz, 2H), 7.90 (d, *J* = 8.4

Hz, 1H), 7.79 (s, 1H), 7.72 (t,  $J = 8.3$  Hz, 1H), 7.59–7.51 (m, 5H), 7.45 (t,  $J = 7.6$  Hz, 1H), 7.08–7.04 (m, 2H), 3.88 (s, 3H);



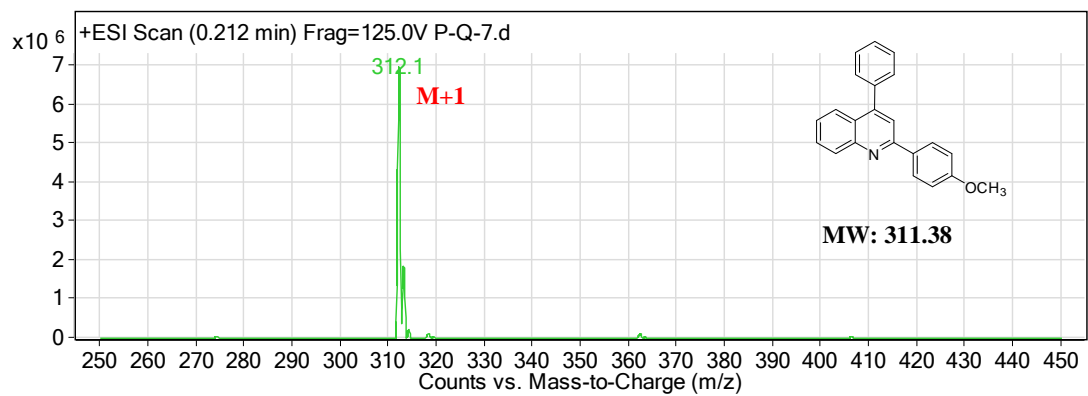
The  $^1\text{H}$  NMR of 3g

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.95, 156.52, 149.09, 148.94, 138.62, 138.62, 132.31, 129.63, 129.02, 128.70, 125.62, 119.00, 114.53, 114.13, 55.49.



The  $^{13}\text{C}$  NMR of 3g

MS (70 eV) m/z (%): 312.2 (M+1, 100), 313.2 (23).



The MS of 3g