Supplementary information

Synthesis of Benzyl Esters from Available Alcohols Catalyzed by TBAI via C(sp^3)-H Bond Functionalization

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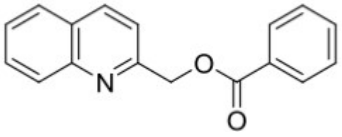
1. Instrument

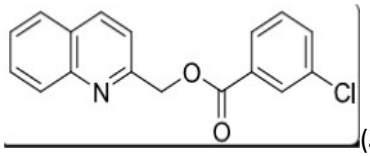
Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. $CDCl_3$ was purchased from Energy Chemical. NMR spectra were recorded at 500 MHz BRUKER spectrometers. ^1H NMR chemical shifts (δ) are given in ppm relative to TMS (δ = 0.0). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard at room temperature. All major chemicals and solvents were obtained from commercial sources and used without further purification.

2. Synthesis of *tert*-butyl peresters catalysed by Bu_4NI: Under air, alcohols (1 mmol), 2-alkyl azaarenes (0.5 mmol), TBAI (0.2 mmol), TBHP (4.0 mmol), water (2 mL) were mixed in a screw cap vial. The mixture was stirred at 90℃ in a closed reaction vessel. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel to give the desired product.

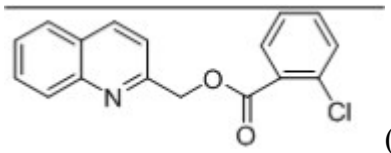
4. Characterization data of products:



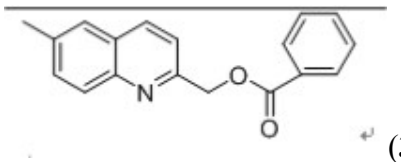
(**3a**) quinolin-2-ylmethyl benzoate: $C_{17}H_{13}NO_2$ Yellow liquid .^1H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.00 (m, 4H), 7.87 – 7.79 (m, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.50 – 7.39 (m, 2H), 5.65 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.30 (s), 156.41 (s), 147.69 (s), 137.05 (s), 133.25 (s), 130.20 (s), 129.86 (s), 129.20 (s), 128.48 (s), 127.62 (d, *J* = 6.0 Hz), 126.71 (s), 119.40 (s), 67.90 (s).



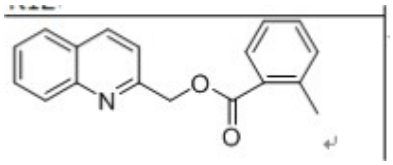
(**3b**)quinolin-2-ylmethyl 3-chlorobenzoate: $C_{17}H_{12}ClNO_2$ (White solid).^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.56 (t, *J* = 14.5 Hz, 3H), 7.39 (t, *J* = 6.1 Hz, 1H), 5.65 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.11 (s), 155.92 (s), 147.72 (s), 137.13 (s), 134.66 (s), 133.79 (s), 133.28 (s), 131.62 (s), 130.12 – 129.73 (m), 129.24 (s), 128.00 (s), 127.67 (s), 126.81 (s), 119.44 (s), 68.25 (s).



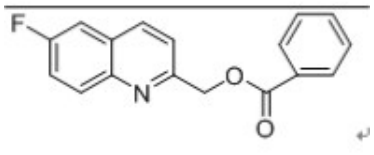
(**3c**) quinolin-2-ylmethyl 2-chlorobenzoate: $C_{17}H_{12}ClNO_2$ (Yellow solid).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 1H), 8.04 – 7.86 (m, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 (s, 2H), 7.20 – 6.98 (m, 2H), 5.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.32 (s), 155.92 (s), 137.08 (s), 134.02 (s), 132.84 (s), 131.77 (s), 131.20 (s), 129.83 (d, *J* = 17.7 Hz), 129.21 (s), 127.64 (d, *J* = 5.2 Hz), 126.72 (d, *J* = 11.0 Hz), 119.55 (s), 68.36 (s).



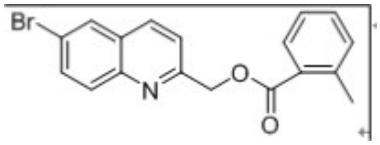
(**3d**) (6-methylquinolin-2-yl)methyl benzoate: $C_{18}H_{15}NO_2$ (Yellow solid).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 6.7 Hz, 2H), 8.08 (t, *J* = 10.3 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.53 (dd, *J* = 25.7, 16.2 Hz, 4H), 7.46 (d, *J* = 6.6 Hz, 2H), 5.64 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.31 (s), 155.40 (s), 146.27 (s), 136.62 (s), 136.38 (s), 133.22 (s), 132.17 (s), 129.90 (d, *J* = 8.9 Hz), 128.83 (s), 128.47 (s), 127.65 (s), 126.49 (s), 119.48 (s), 67.95 (s), 21.58 (s).



(**3e**) quinolin-2-ylmethyl 2-methylbenzoate:Yellow liquid . IR (KBr):1722, 1606, 1580, 1509 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 1H), 8.02 (t, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 5.7 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.66 (s, 1H), 7.49 (d, *J* = 6.6 Hz, 2H), 7.35 (s, 1H), 7.19 (s, 3H), 5.56 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.10 (s), 156.52 (s), 147.65 (s), 140.68 (s), 137.07 (s), 132.30 (s), 131.81 (s), 130.85 (s), 129.89 (s), 129.16 (d, *J* = 2.1 Hz), 127.61 (d, *J* = 9.5 Hz), 126.70 (s), 125.81 (s), 119.42 (s), 67.67 (s), 21.88 (s). HRMS (ESI) m/z calcd for **$C_{18}H_{15}NO_2$** [M+H]$^+$**278.11740**, found **278.11756**.

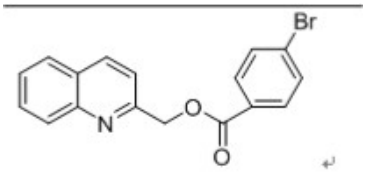


(**3f**) (6-fluoroquinolin-2-yl)methyl benzoate: $C_{17}H_{12}FNO_2$ (Yellow solid). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.01 (m, 4H), 7.57 (d, *J* = 4.6 Hz, 2H), 7.45 (dt, *J* = 25.5, 12.9 Hz, 4H), 5.64 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.25 (s), 161.52 (s), 159.54 (s), 155.80 (d, *J* = 2.7 Hz), 144.76 (s), 136.35 (d, *J* = 5.4 Hz), 133.29 (s), 131.72 (d, *J* = 9.1 Hz), 129.83 (d, *J* = 5.0 Hz), 128.50 (s), 128.17 (d, *J* = 10.1 Hz), 120.18 (d, *J* = 3.8 Hz), 119.96 (s), 110.73 (s), 110.63 (d, *J* = 21.7 Hz).

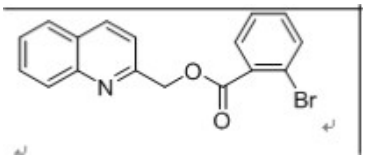


(**3g**) (6-bromoquinolin-2-yl)methyl 2-methylbenzoate : White solid. mp **110.1-111.5** °C; IR (KBr):715, 1592, 1491, 1457 cm^{-1}.^{1}H NMR (500

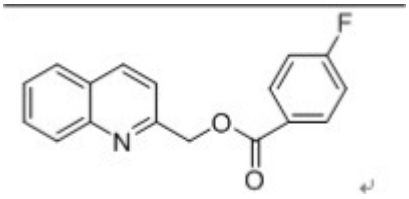
MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.88 (dd, *J* = 12.8, 5.5 Hz, 2H), 7.70 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.18 (dd, *J* = 7.9, 4.4 Hz, 2H), 5.52 (s, 2H), 2.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.02 (s), 157.05 (s), 146.24 (s), 140.72 (s), 135.98 (s), 133.31 (s), 132.38 (s), 131.85 (s), 130.88 (d, *J* = 14.5 Hz), 129.67 (s), 129.01 (s), 128.62 (s), 125.83 (s), 120.55 (s), 120.20 (s), 67.45 (s), 21.88 (s). HRMS (ESI) m/z calcd for **$C_{18}H_{14}BrNO_2$** [M+H] $^+$**356.02756**, found **356.02807**.



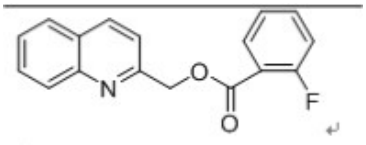
(**3h**) quinolin-2-ylmethyl 4-bromobenzoate: White solid. mp **143.1.4-144.5** °C; IR (KBr):1721, 1590, 1506, 1448 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.04 – 7.95 (m, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.56 (ddd, *J* = 8.5, 6.1, 2.1 Hz, 2H), 5.65 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.61 (s), 156.02 (s), 147.70 (s), 137.12 (s), 131.86 (s), 131.38 (s), 129.96 (s), 129.23 (s), 128.75 (s), 128.45 (s), 127.64 (d, *J* = 6.7 Hz), 126.81 (s), 119.46 (s), 68.14 (s). HRMS (ESI) m/z calcd for **$C_{17}H_{12}BrNO_2$** [M+H] $^+$**342.01208**, found **342.01242**.



(**3i**) quinolin-2-ylmethyl 2-bromobenzoate: White solid. mp **88.5-89.8** °C; IR (KBr):1729, 1618, 1588, 1505 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 5.1 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.71 – 7.57 (m, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.47 (s, 1H), 7.36 – 7.21 (m, 2H), 5.59 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.78 (s), 155.83 (s), 147.67 (s), 137.06 (s), 134.48 (s), 132.84 (s), 131.73 (d, *J* = 11.5 Hz), 129.90 (s), 129.22 (s), 127.63 (d, *J* = 5.7 Hz), 127.25 (s), 126.77 (s), 121.97 (s), 119.61 (s), 68.42 (s). HRMS (ESI) m/z calcd for **$C_{17}H_{12}BrNO_2$** [M+H] $^+$**342.01210**, found **342.01242**.

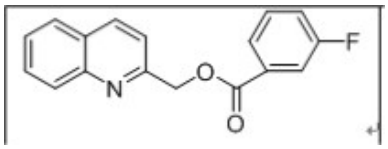


(**3j**) quinolin-2-ylmethyl 4-fluorobenzoate : $C_{17}H_{12}FNO_2$ (White solid).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.13 (m, 3H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.77 (m, 1H), 7.73 (t, *J* = 7.1 Hz, 1H), 7.57 (dd, *J* = 22.3, 7.7 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 2H), 5.64 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.97 (s), 165.33 (s), 164.95 (s), 156.18 (s), 147.70 (s), 137.08 (s), 132.44 (d, *J* = 9.4 Hz), 129.92 (s), 129.21 (s), 127.63 (d, *J* = 6.4 Hz), 126.77 (s), 119.43 (s), 115.74 (s), 115.57 (s), 68.01 (s).

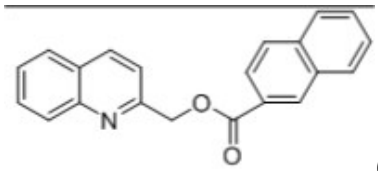


(**3k**) quinolin-2-ylmethyl 2-fluorobenzoate: Yellow solid. mp **51.2-52.1** °C; IR (KBr):1735, 1613, 1581, 1490 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.97 (s, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.66 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.48 (s, 2H), 7.23 – 7.13 (m, 1H), 7.10 (t, *J* = 9.0 Hz, 1H), 5.60 (s, 2H). ^{13}C

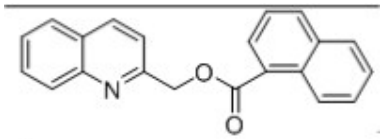
NMR (126 MHz, $CDCl_3$) δ 163.03 (d, *J* = 3.6 Hz), 162.15 (s), 160.08 (s), 155.12 (s), 146.58 (s), 136.08 (s), 133.80 (d, *J* = 9.0 Hz), 131.35 (s), 128.84 (s), 128.09 (s), 126.59 (d, *J* = 8.9 Hz), 125.66 (s), 123.06 (d, *J* = 3.9 Hz), 118.28 (s), 117.34 (d, *J* = 9.7 Hz), 116.14 (s), 115.96 (s), 67.05 (s).
HRMS (ESI) m/z calcd for **$C_{17}H_{12}FNO_2$** [M+H] $^+$**282.09233**, found **282.09248**.



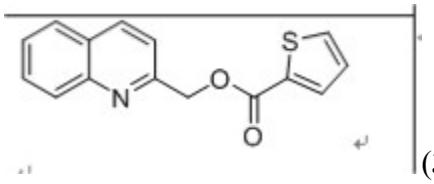
(**3l**) quinolin-2-ylmethyl 3-fluorobenzoate: White solid. mp **56.4-57.5** °C; IR (KBr):1794, 1594, 1508, 1487 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 6.3 Hz, 1H), 7.68 (d, *J* = 6.4 Hz, 2H), 7.60 (s, 1H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.24 (m, 1H), 7.15 (d, *J* = 6.7 Hz, 1H), 5.54 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.14 (d, *J* = 3.0 Hz), 163.54 (s), 161.58 (s), 155.95 (s), 147.66 (s), 137.11 (s), 131.98 (d, *J* = 7.5 Hz), 130.15 (d, *J* = 7.7 Hz), 129.92 (s), 129.18 (s), 127.63 (d, *J* = 10.2 Hz), 126.78 (s), 125.60 (d, *J* = 3.0 Hz), 120.41 (s), 120.24 (s), 119.37 (s), 116.80 (s), 116.62 (s), 68.18 (s).
HRMS (ESI) m/z calcd for **$C_{17}H_{12}FNO_2$** [M+H] $^+$**282.09238**, found **282.09248**.



(**3m**) quinolin-2-ylmethyl 2-naphthoate: $C_{21}H_{15}NO_2$ (White solid).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.09 – 7.98 (m, 2H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.80 (t, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 6.8 Hz, 1H), 7.58 – 7.40 (m, 4H), 5.64 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.47 (s), 156.45 (s), 147.73 (s), 137.10 (s), 135.71 (s), 132.54 (s), 131.48 (s), 129.90 (s), 129.44 (s), 129.24 (s), 128.37 (d, *J* = 16.8 Hz), 127.94 – 127.56 (m), 127.10 (s), 126.74 (s), 125.37 (s), 119.52 (s), 68.04 (s).

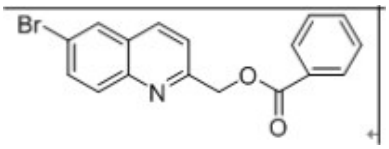


(**3n**) quinolin-2-ylmethyl 1-naphthoate: White solid. mp 74.8-75.6 °C; IR (KBr):1720, 1576, 1508, 1446 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 5.5 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.1 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.73 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.40 (m, 3H), 5.75 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.14 (s), 155.50 (s), 146.78 (s), 136.13 (s), 132.95 (s), 132.79 (s), 130.60 (s), 129.66 (s), 128.94 (s), 128.27 (s), 127.64 (s), 126.99 (s), 126.68 (d, *J* = 6.8 Hz), 125.74 (d, *J* = 5.0 Hz), 125.37 (s), 124.95 (s), 123.58 (s), 118.48 (s), 66.94 (s).
HRMS (ESI) m/z calcd for $C_{21}H_{15}NO_2$ [M+H] $^+$ 314.11725, found 314.11756.

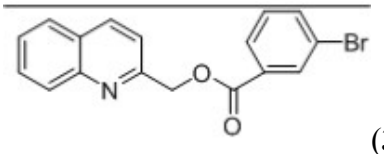


(**3o**) quinolin-2-ylmethyl thiophene-2-carboxylate: $C_{15}H_{11}NO_2S$ (White solid). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 6.5 Hz, 1H), 7.64 – 7.50 (m, 3H), 7.13 (d, *J* = 3.3 Hz, 1H), 5.63 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.89 (s), 156.20 (s), 147.64 (s),

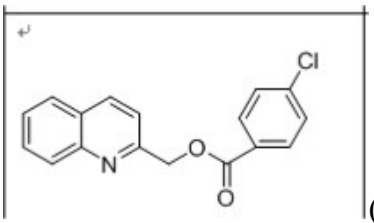
137.10 (s), 134.02 (s), 133.27 (s), 132.87 (s), 129.89 (s), 129.17 (s), 127.90 (s), 127.63 (d, *J* = 5.2 Hz), 126.73 (s), 119.33 (s), 67.86 (s).



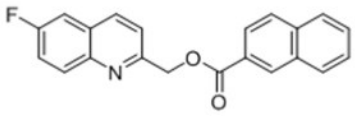
(**3p**) (6-bromoquinolin-2-yl)methyl benzoate: $C_{17}H_{12}BrNO_2$ (Yellow solid). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 14.8, 7.3 Hz, 3H), 8.02 – 7.92 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 6.2 Hz, 2H), 7.47 (s, 2H), 5.64 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.25 (s), 156.96 (s), 146.27 (s), 136.01 (s), 133.34 (s), 130.96 (s), 130.21 (s), 129.87 (s), 129.68 (s), 128.59 (d, *J* = 18.6 Hz), 120.60 (s), 120.22 (s), 67.66 (s).



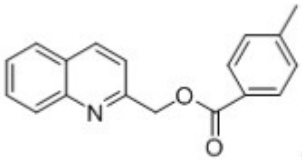
(**3q**) quinolin-2-ylmethyl 3-bromobenzoate: $C_{17}H_{12}BrNO_2$ (White solid).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 8.07 (dd, *J* = 20.8, 7.6 Hz, 2H), 7.83 (t, *J* = 13.6 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.31 (dd, *J* = 17.5, 10.2 Hz, 1H), 5.65 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.97 (s), 155.90 (s), 147.72 (s), 137.11 (s), 136.19 (s), 132.81 (s), 131.81 (s), 129.99 (d, *J* = 15.6 Hz), 129.25 (s), 128.44 (s), 127.64 (d, *J* = 5.9 Hz), 126.80 (s), 122.58 (s), 119.44 (s), 68.26 (s).



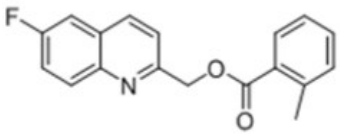
(**3r**) quinolin-2-ylmethyl 4-chlorobenzoate: $C_{17}H_{12}ClNO_2$ (White solid).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.07 – 7.92 (m, 3H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.66 (s, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 5.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.46 (s), 156.06 (s), 139.76 (s), 131.25 (s), 129.94 (s), 129.23 (s), 128.85 (s), 128.33 (s), 127.63 (d, *J* = 4.8 Hz), 126.80 (s), 119.44 (s), 68.11 (s).



(**3s**) (6-fluoroquinolin-2-yl)methyl 2-naphthoate: White solid. mp **133.5-134.8** °C; IR (KBr):1716, 1605, 1507, 1469 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.22 – 8.01 (m, 3H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (t, *J* = 8.2 Hz, 2H), 7.69 – 7.37 (m, 5H), 5.70 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46 (s), 161.55 (s), 159.57 (s), 155.82 (d, *J* = 2.8 Hz), 144.79 (s), 136.44 (d, *J* = 5.4 Hz), 135.70 (s), 132.50 (s), 131.75 (d, *J* = 9.2 Hz), 131.49 (s), 129.43 (s), 128.31 (dd, *J* = 23.5, 14.7 Hz), 127.82 (s), 126.98 (s), 126.78 (s), 125.32 (s), 120.28 (d, *J* = 13.0 Hz), 120.03 (s), 110.75 (s), 110.58 (s), 67.86 (s). HRMS (ESI) m/z calcd for $\mathbf{C_{21}H_{14}FNO_2}$ $[M+H]^+$ **332.10776**, found **332.10813**.

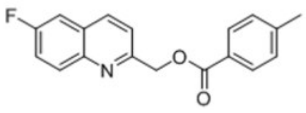


(**3t**) quinolin-2-ylmethyl 4-methylbenzoate: $C_{18}H_{15}NO_2$ (White solid). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (t, *J* = 17.6 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 6.6 Hz, 1H), 7.48 (dd, *J* = 14.1, 7.6 Hz, 2H), 7.18 (d, *J* = 5.0 Hz, 2H), 5.57 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.36 (s), 156.60 (s), 147.68 (s), 143.99 (s), 137.02 (s), 129.88 (d, *J* = 7.9 Hz), 129.20 (s), 127.62 (d, *J* = 6.1 Hz), 127.14 (s), 126.67 (s), 119.40 (s), 67.73 (s), 21.70 (s).



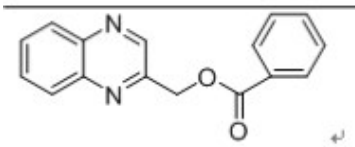
(**3u**) (6-fluoroquinolin-2-yl)methyl 2-methylbenzoate:

Yellow solid. mp **73.8-75.2** °C; IR (KBr):1716, 1604, 1510, 1456 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.11 – 8.03 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.49 (td, *J* = 8.8, 2.8 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.26 (t, *J* = 6.9 Hz, 2H), 5.61 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.07 (s), 161.51 (s), 159.54 (s), 155.89 (d, *J* = 2.8 Hz), 144.76 (s), 140.69 (s), 136.35 (d, *J* = 5.3 Hz), 132.34 (s), 131.95 – 131.60 (m), 130.83 (s), 129.07 (s), 128.15 (d, *J* = 10.2 Hz), 125.82 (s), 120.20 (d, *J* = 4.5 Hz), 119.97 (s), 110.73 (s), 110.56 (s), 77.32 (s), 77.06 (s), 76.81 (s), 67.52 (s), 21.87 (s). HRMS (ESI) m/z calcd for **$C_{18}H_{14}FNO_2$** [M+H] $^+$ **296.10792**, found **296.10813**.

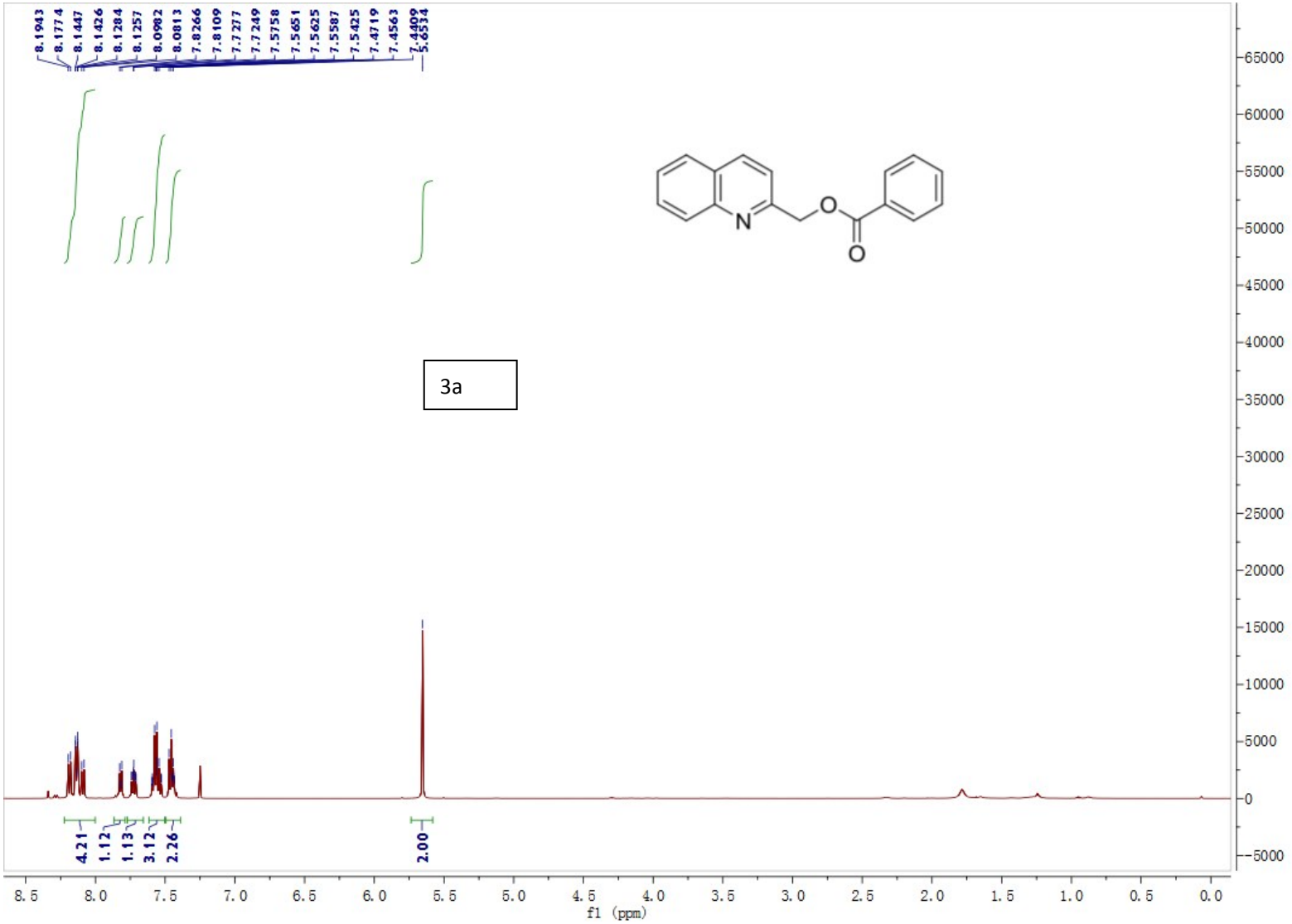


(**3v**) (6-fluoroquinolin-2-yl)methyl 4-methylbenzoate:

White solid. mp **94.2-95.8** °C; IR (KBr):1720, 1610, 1509, 1449 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.08 (dd, *J* = 9.2, 5.3 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.49 (td, *J* = 8.8, 2.8 Hz, 1H), 7.43 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.31 – 7.24 (m, 2H), 5.62 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.34 (s), 161.51 (s), 159.53 (s), 155.97 (d, *J* = 2.8 Hz), 144.74 (s), 144.07 (s), 136.35 (d, *J* = 5.4 Hz), 131.70 (d, *J* = 9.2 Hz), 130.24 (s), 129.90 (s), 129.22 (s), 128.16 (d, *J* = 10.0 Hz), 127.03 (s), 120.19 (d, *J* = 5.8 Hz), 119.97 (s), 110.72 (s), 110.55 (s), 67.57 (s), 21.72 (s). HRMS (ESI) m/z calcd for **$C_{18}H_{14}FNO_2$** [M+H] $^+$ **296.10803**, found **296.10813**.



(**3w**)quinoxalin-2-ylmethyl benzoate: $C_{16}H_{12}N_2O_2$ (Yellow solid).^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.12 (dd, *J* = 11.4, 6.8 Hz, 4H), 7.79 (d, *J* = 4.2 Hz, 2H), 7.59 (s, 1H), 7.47 (s, 2H), 5.70 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.16 (s), 151.03 (s), 144.21 (s), 142.22 (s), 141.84 (s), 133.45 (s), 130.45 (s), 130.16 (s), 129.89 (s), 129.54 – 129.22 (m), 128.55 (s), 66.03 (s).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7.4563
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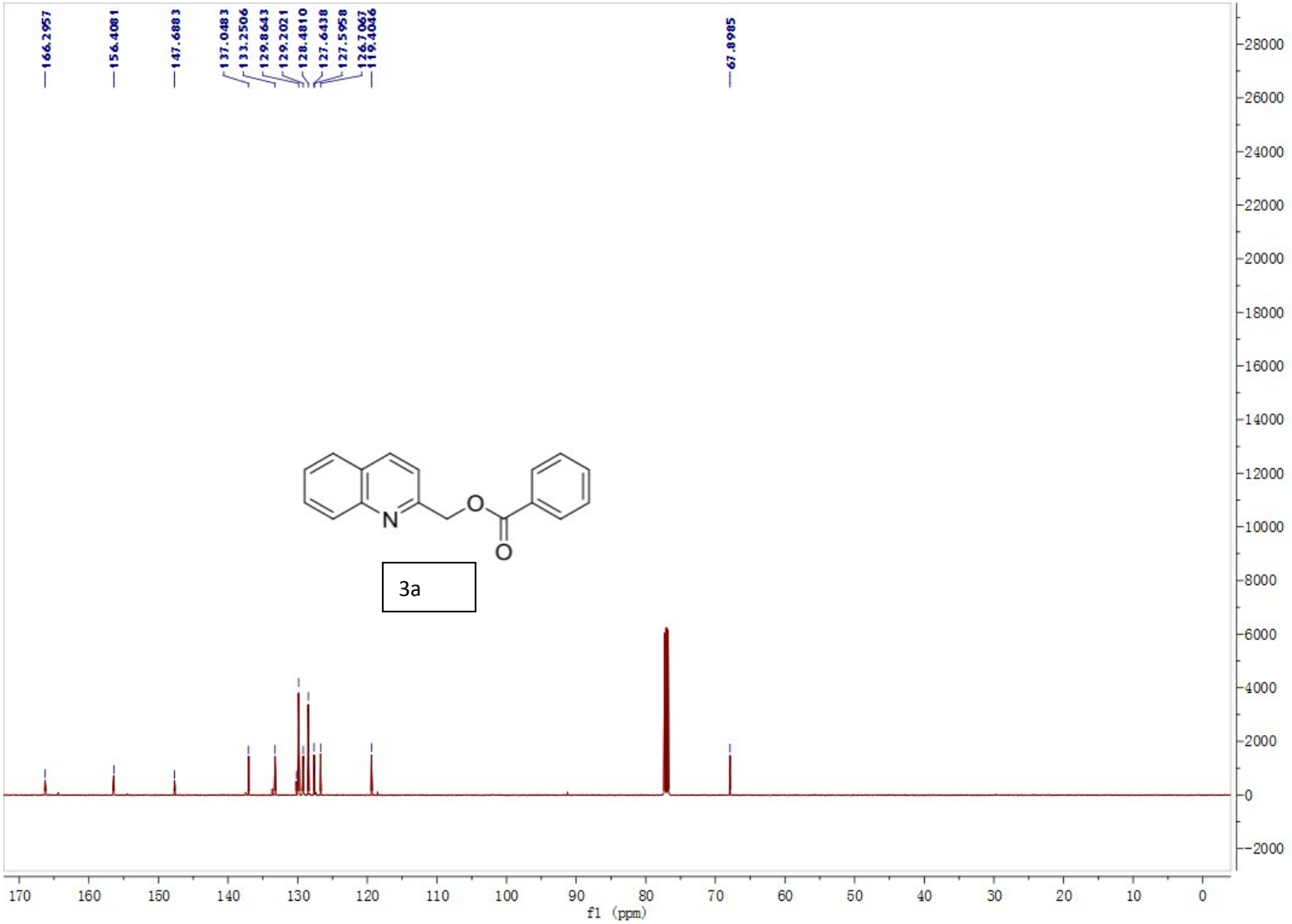
f1 (ppm)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24000
22000
20000
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16000
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12000
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8000
6000
4000
2000
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160
150
140
130
120
110
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90
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70
60
50
40
30
20
10
0
f1 (ppm)


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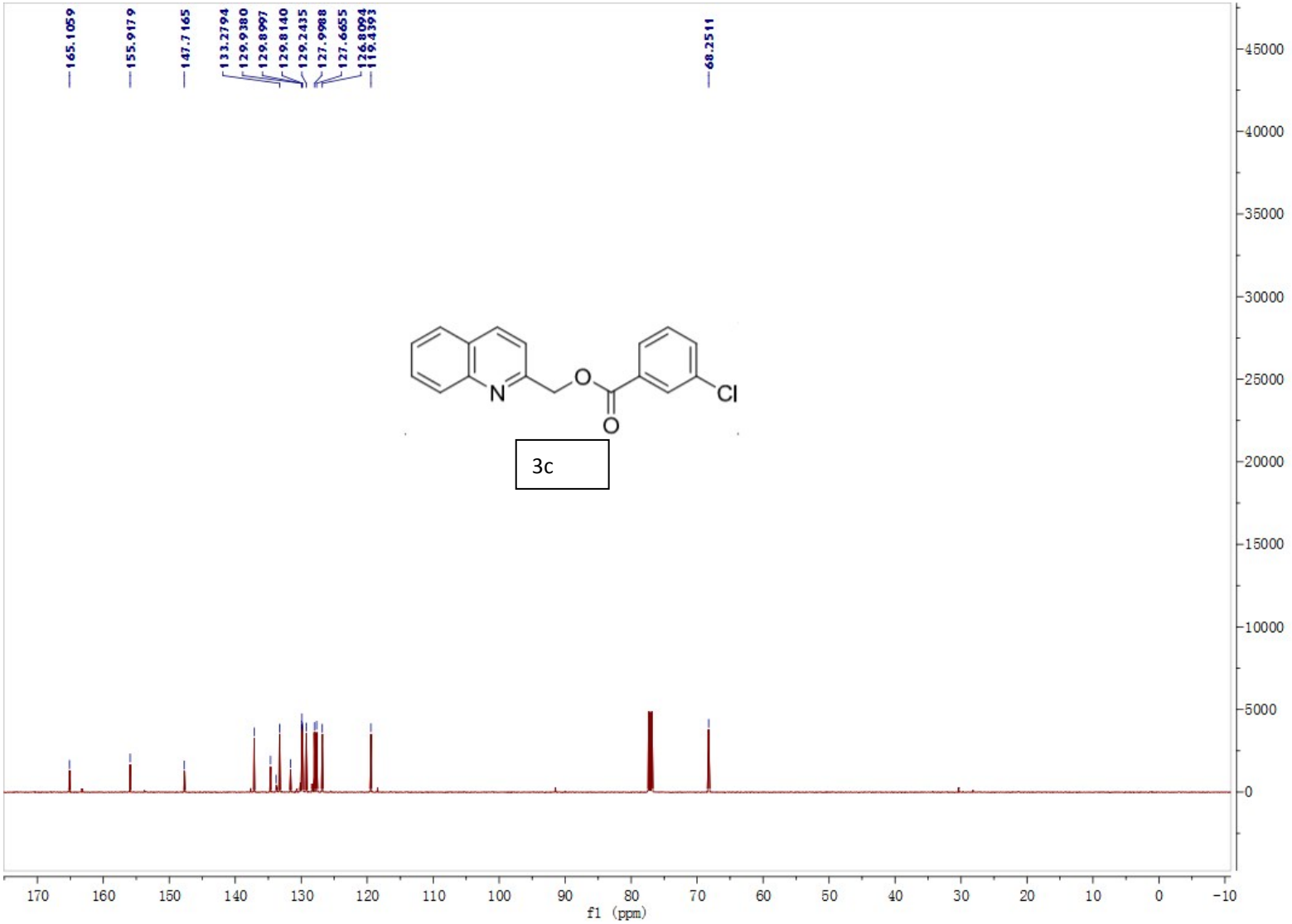
f1 (ppm)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O
O
Cl
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40000
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30000
25000
20000
15000
10000
5000
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40
30
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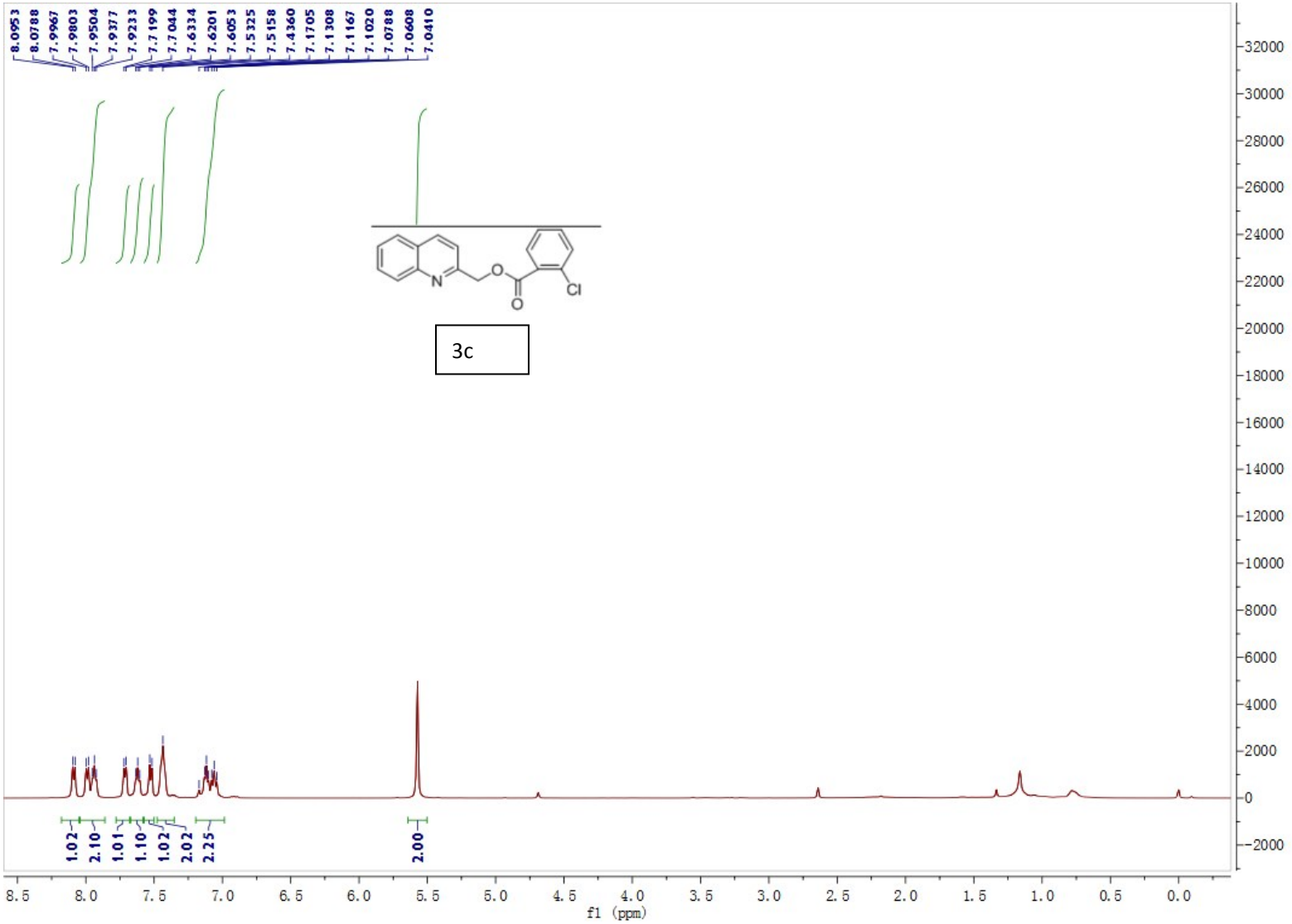
f1 (ppm)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7.5325
7.5158
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7.0410
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1.01
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2.02
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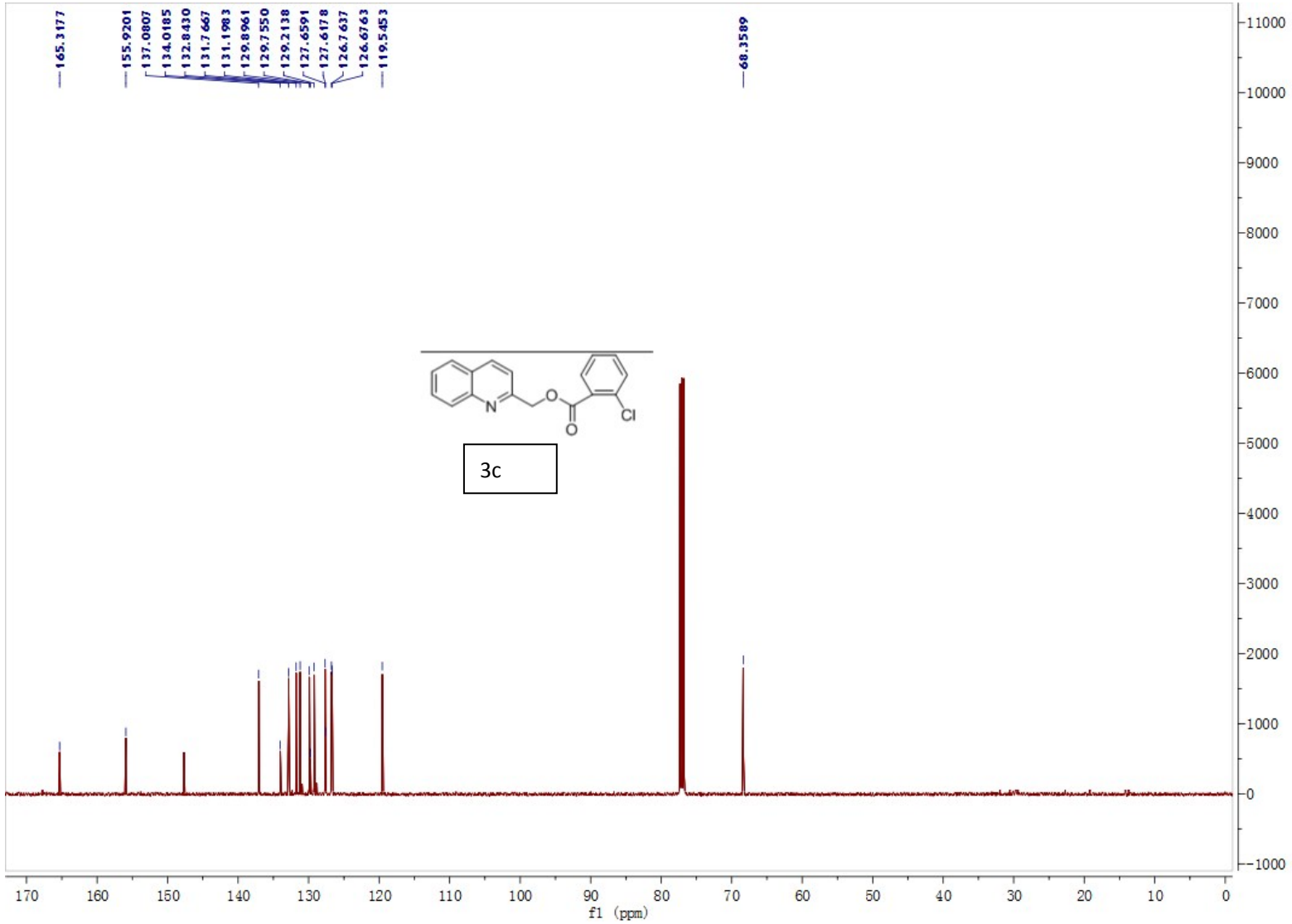
2.00
f1 (ppm)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68.3589
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O
Cl
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9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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110
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50
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30
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10
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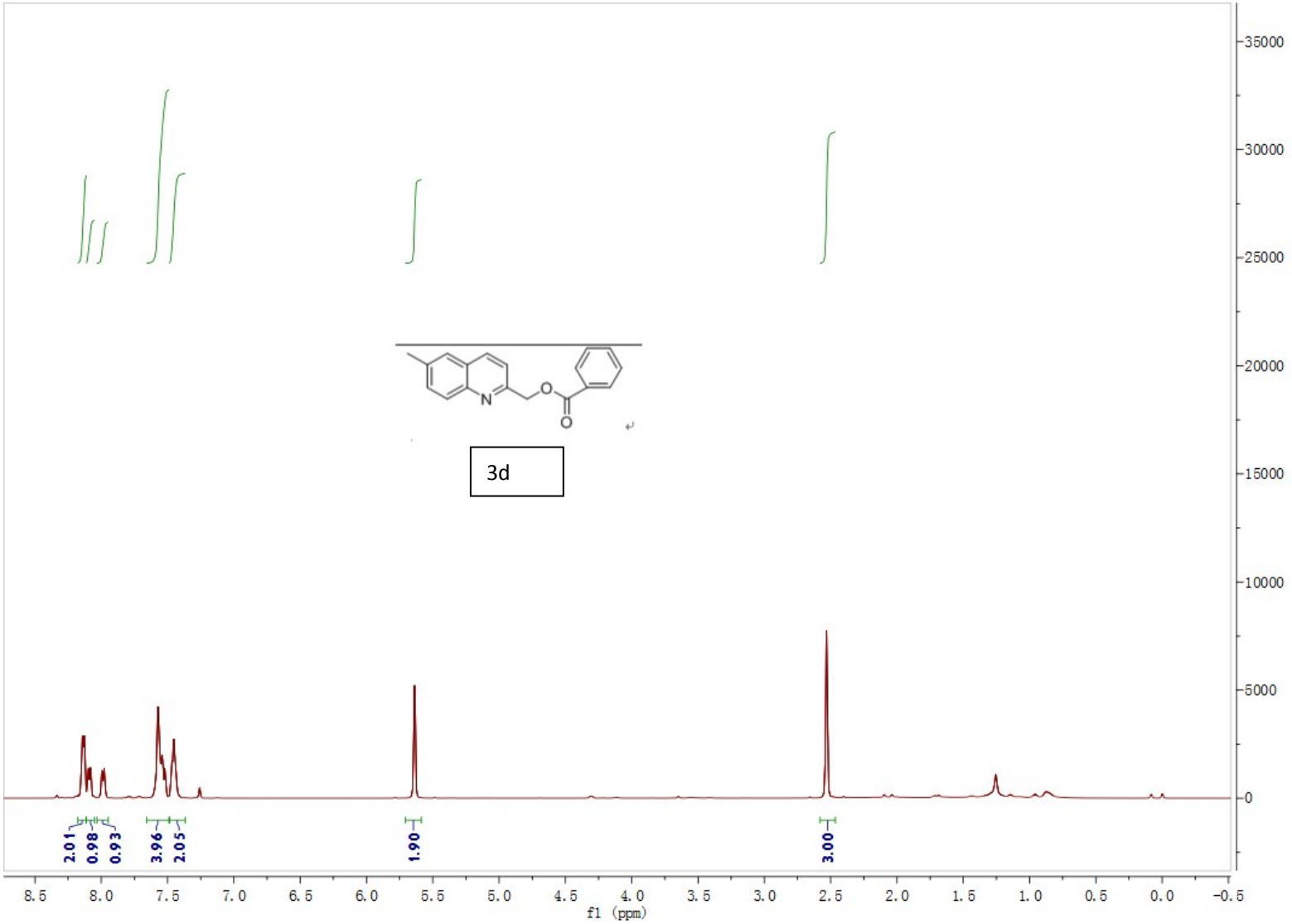
f1 (ppm)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1.90
3.00
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5.0
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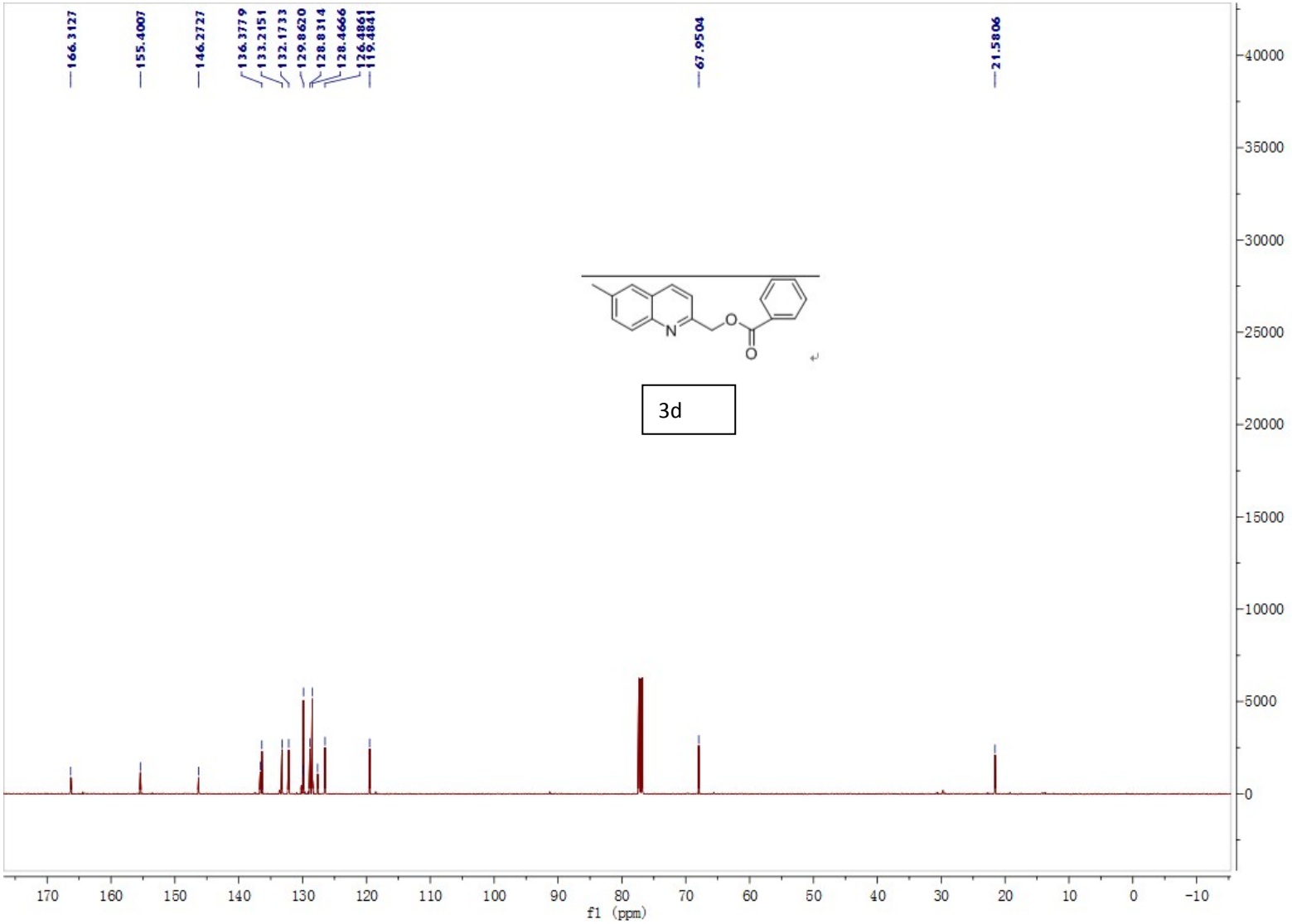
-0.5
f1 (ppm)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67.9504
21.5806
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O
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30000
25000
20000
15000
10000
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80
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30
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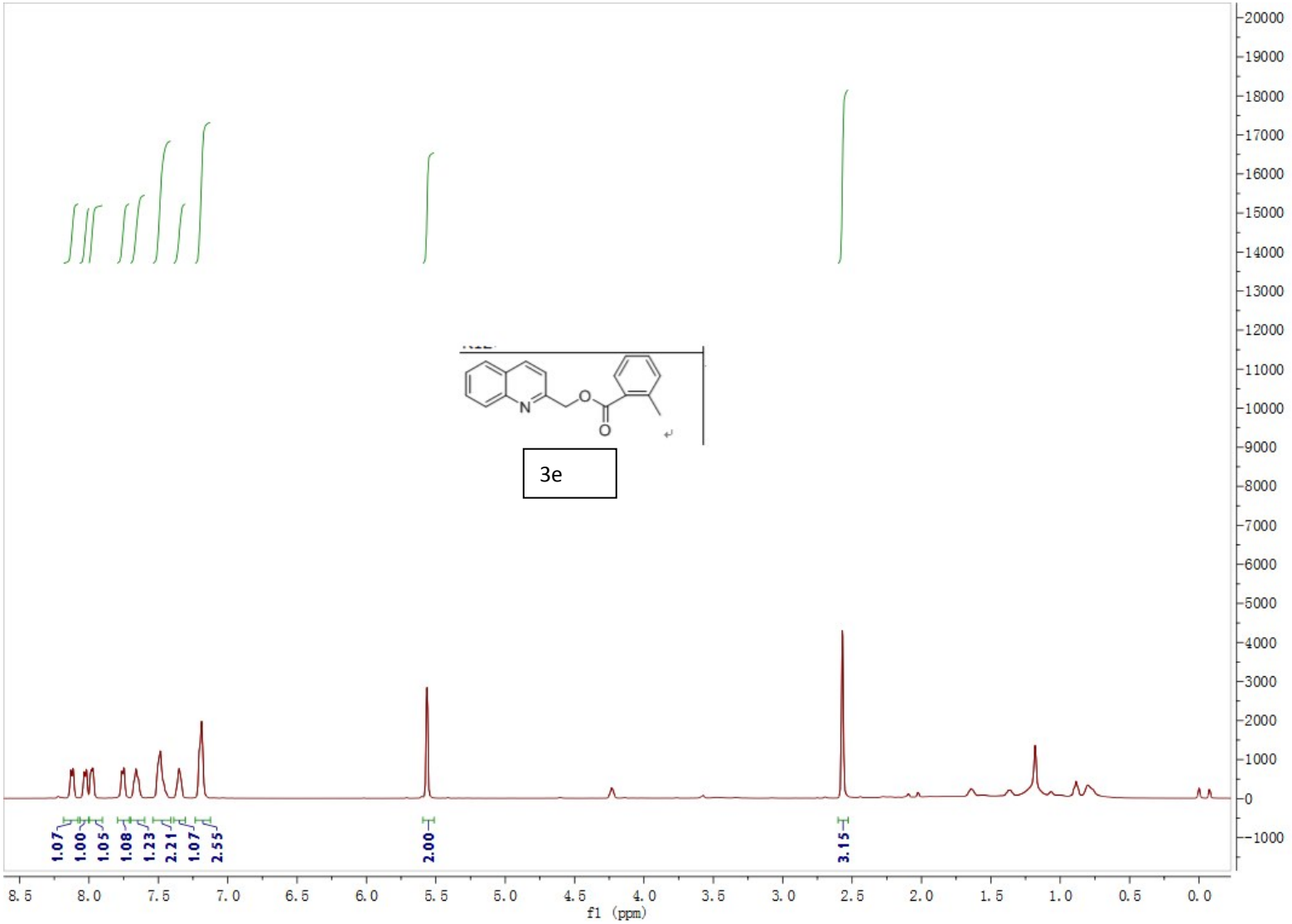
f1 (ppm)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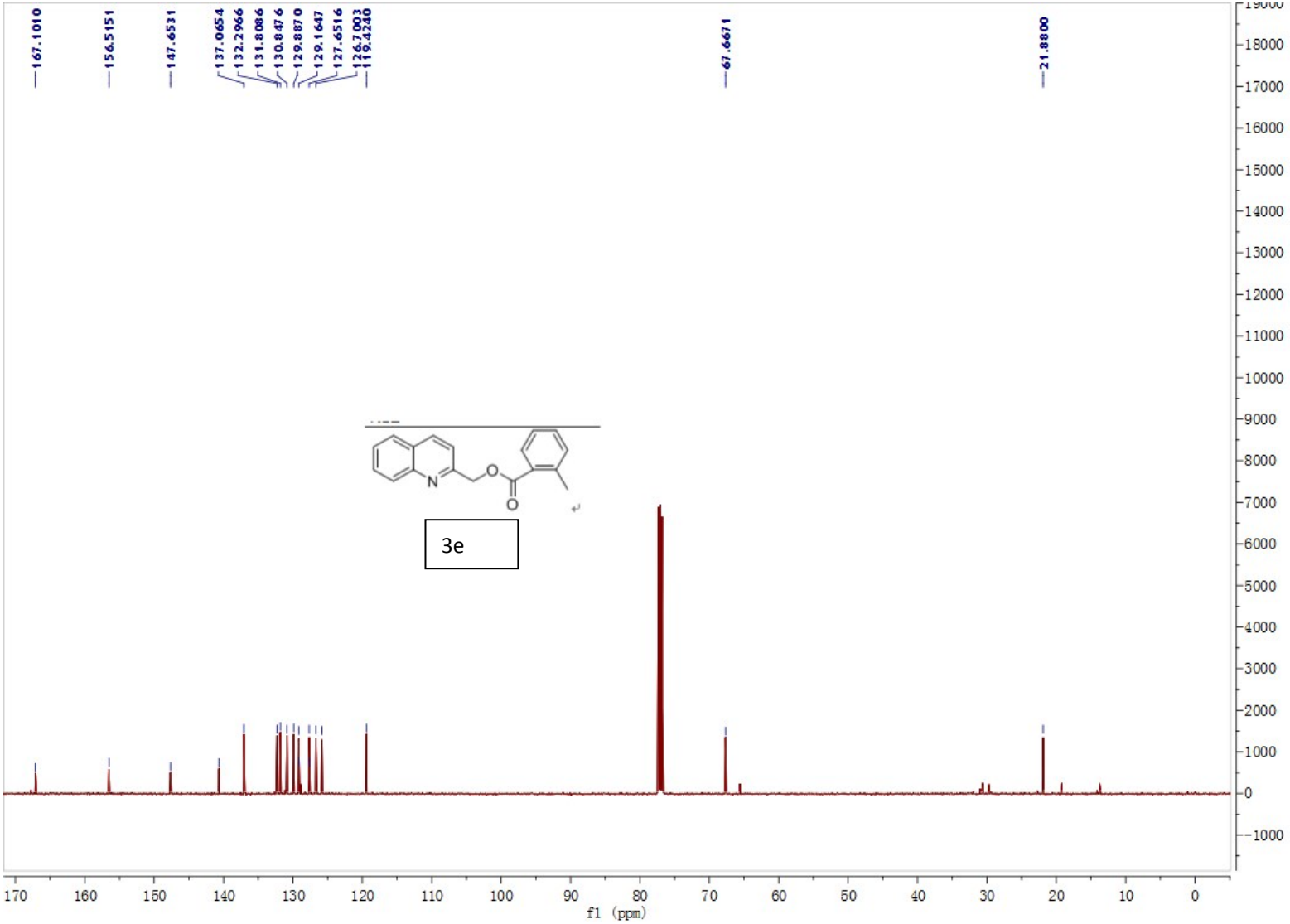
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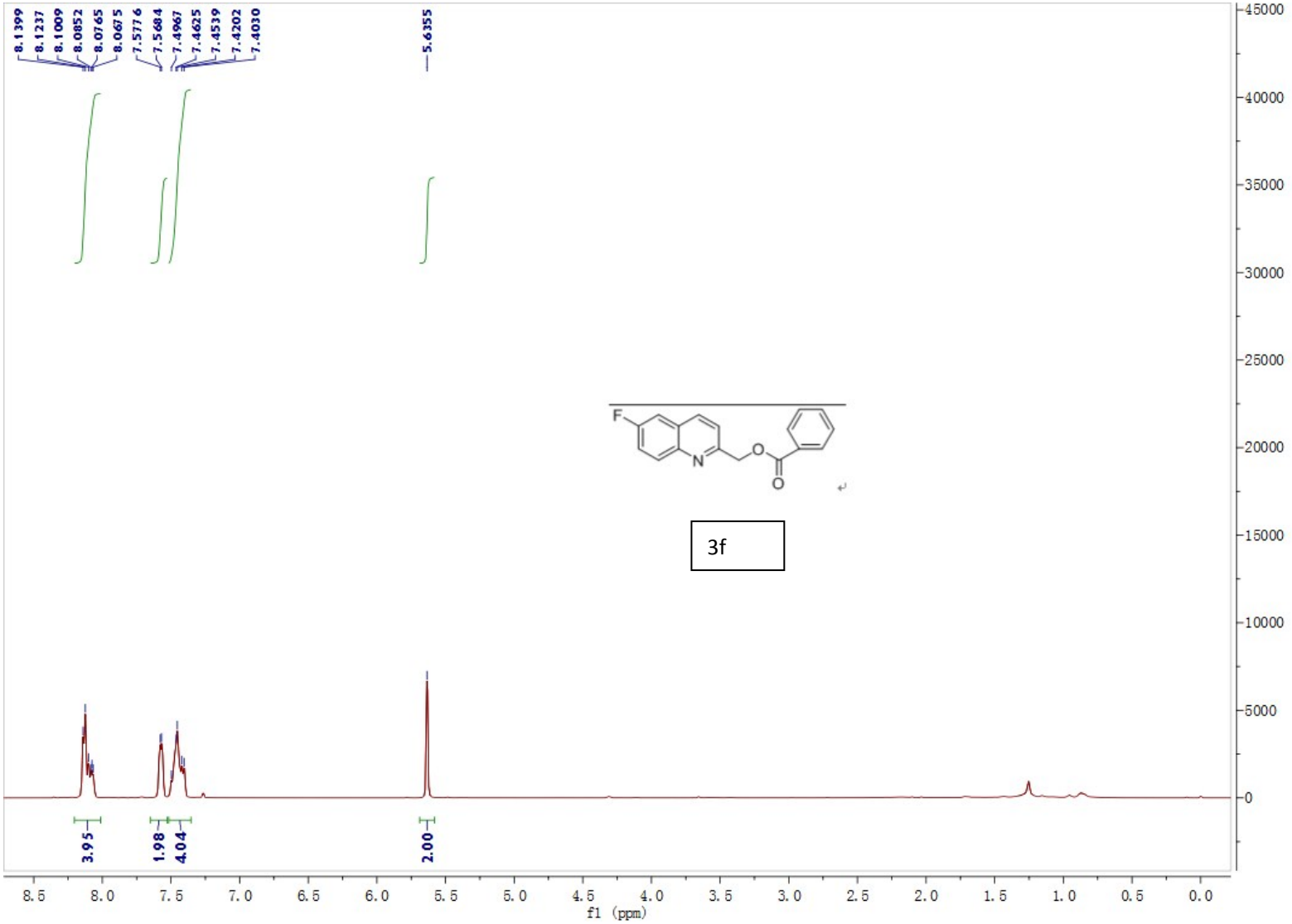
3e
f1 (ppm)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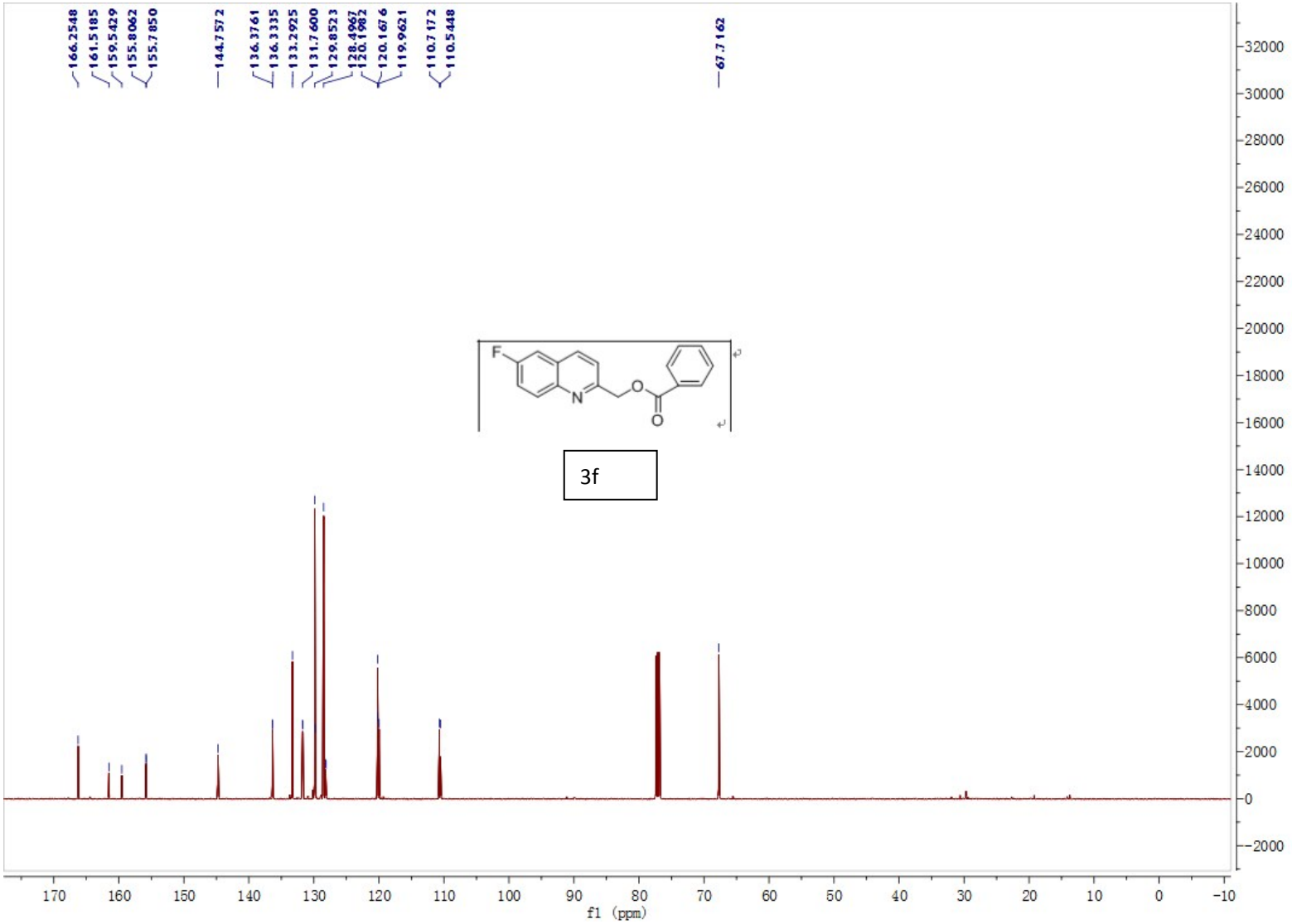
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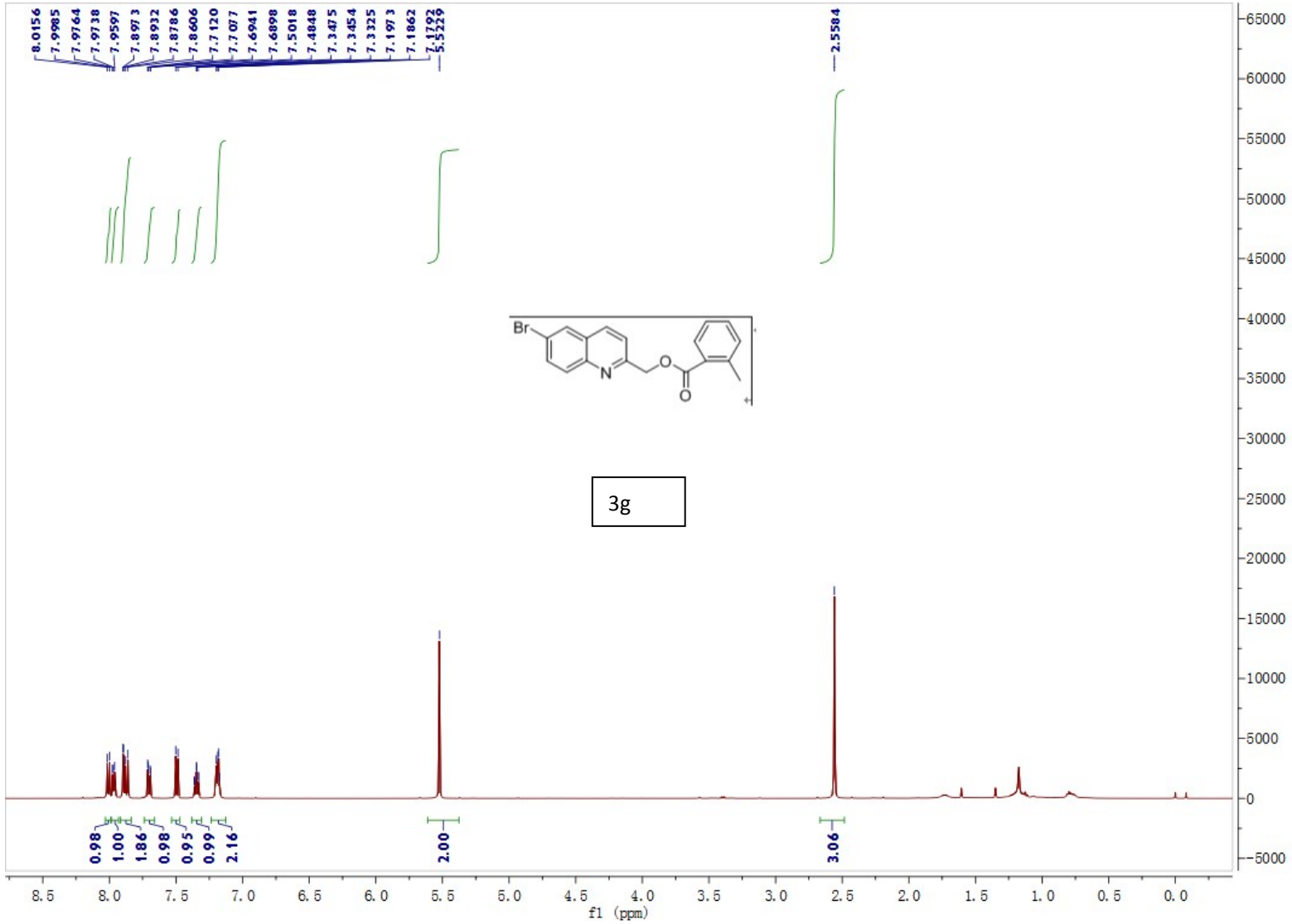
f1 (ppm)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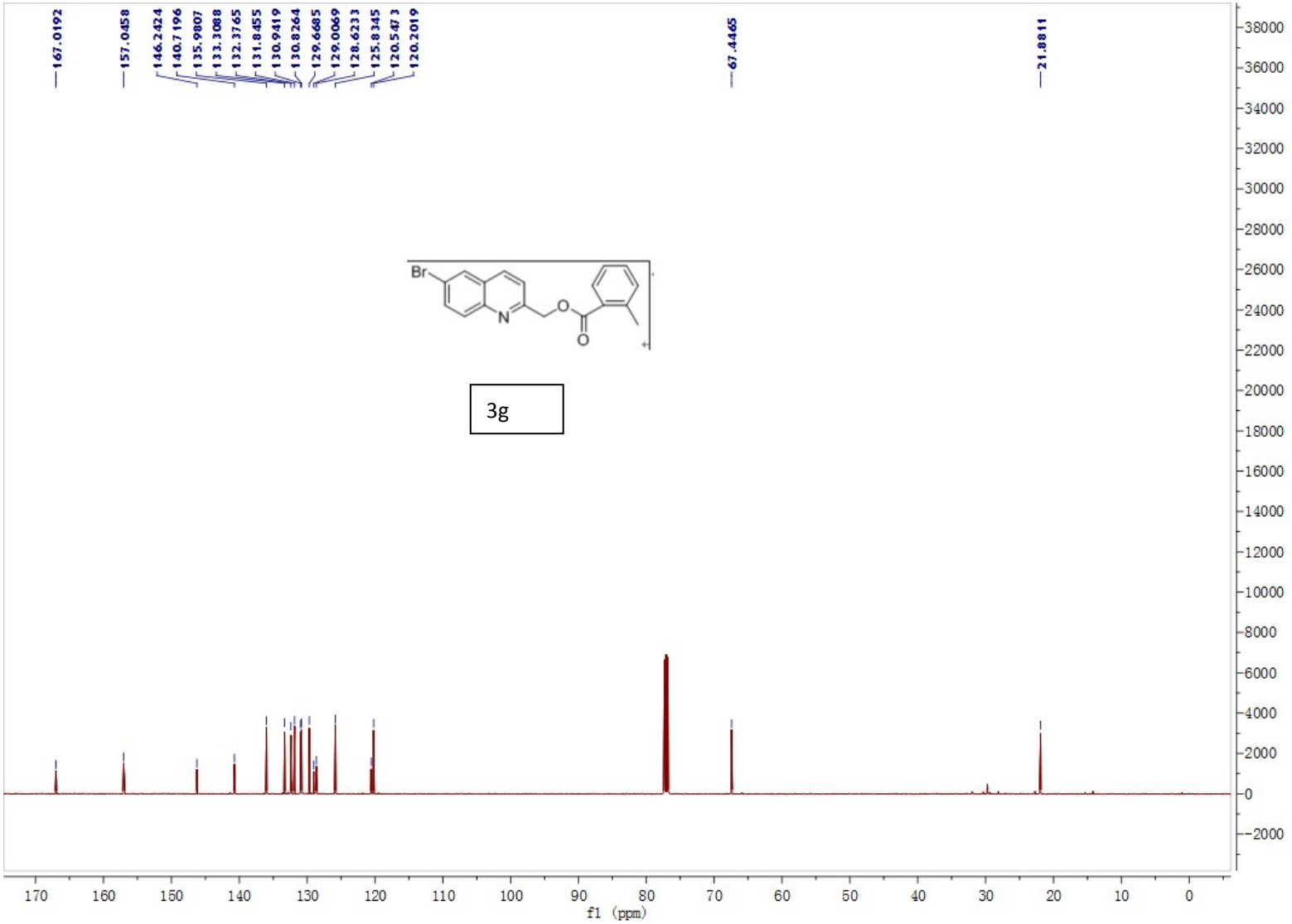
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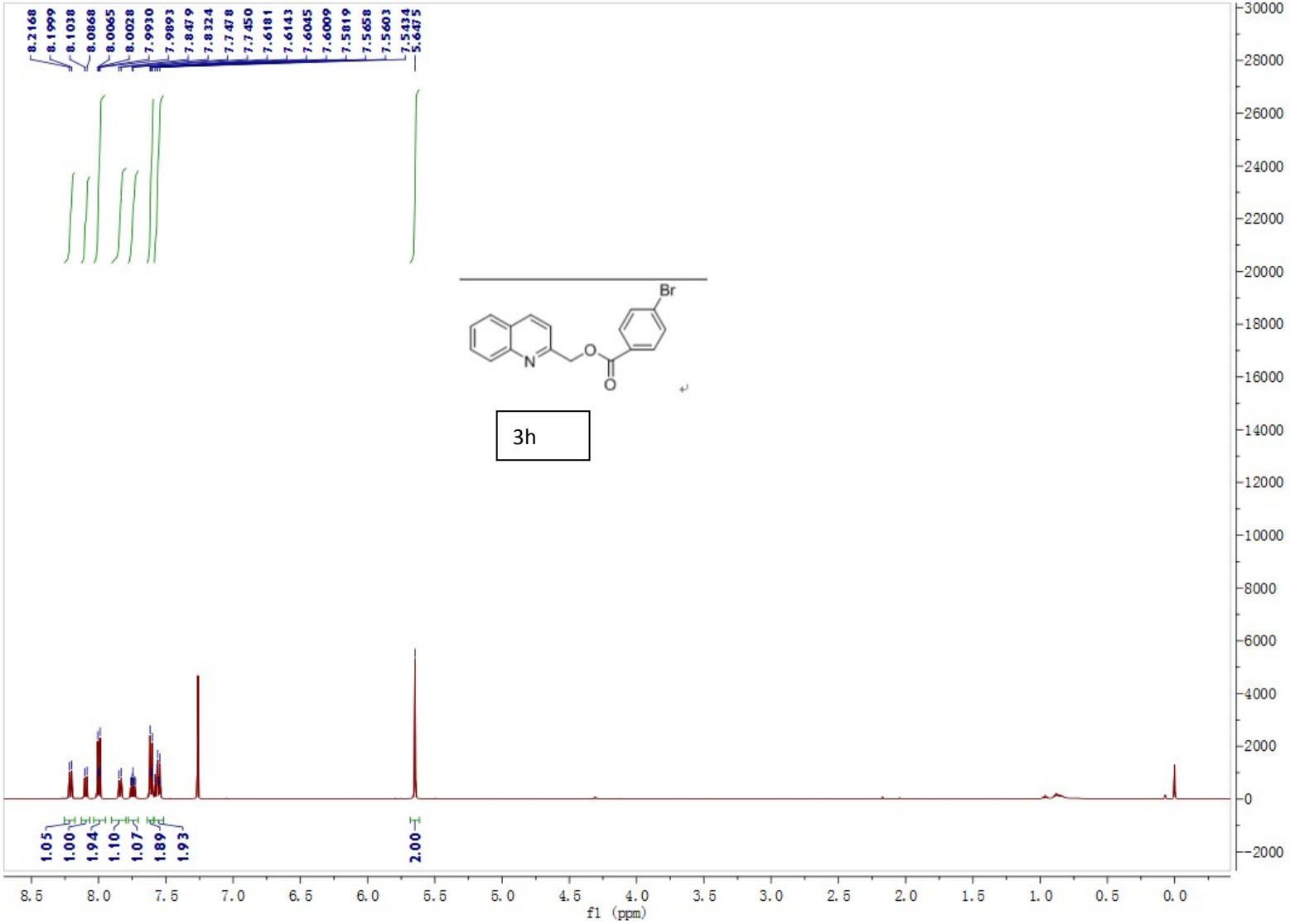
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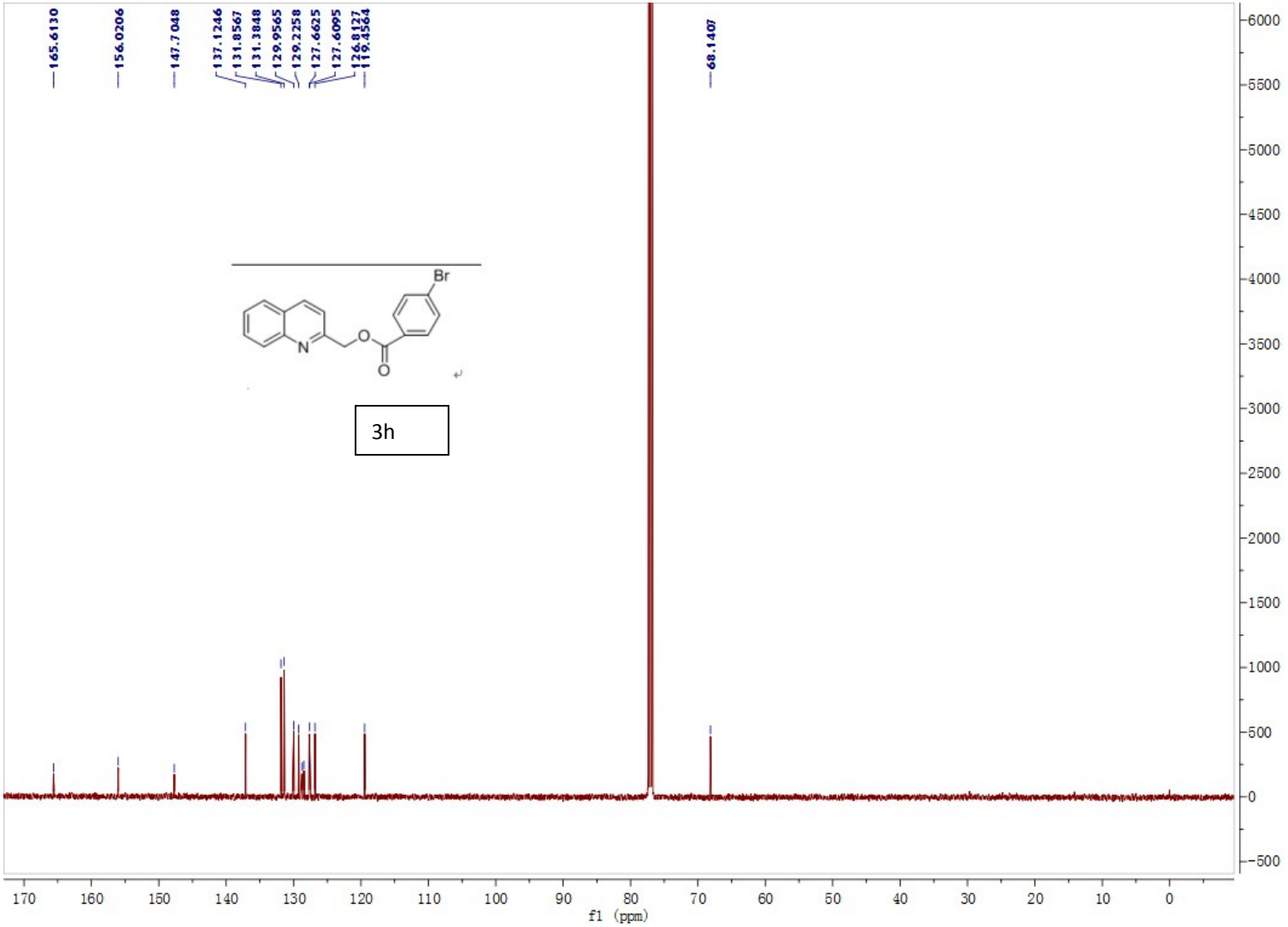
2.00
f1 (ppm)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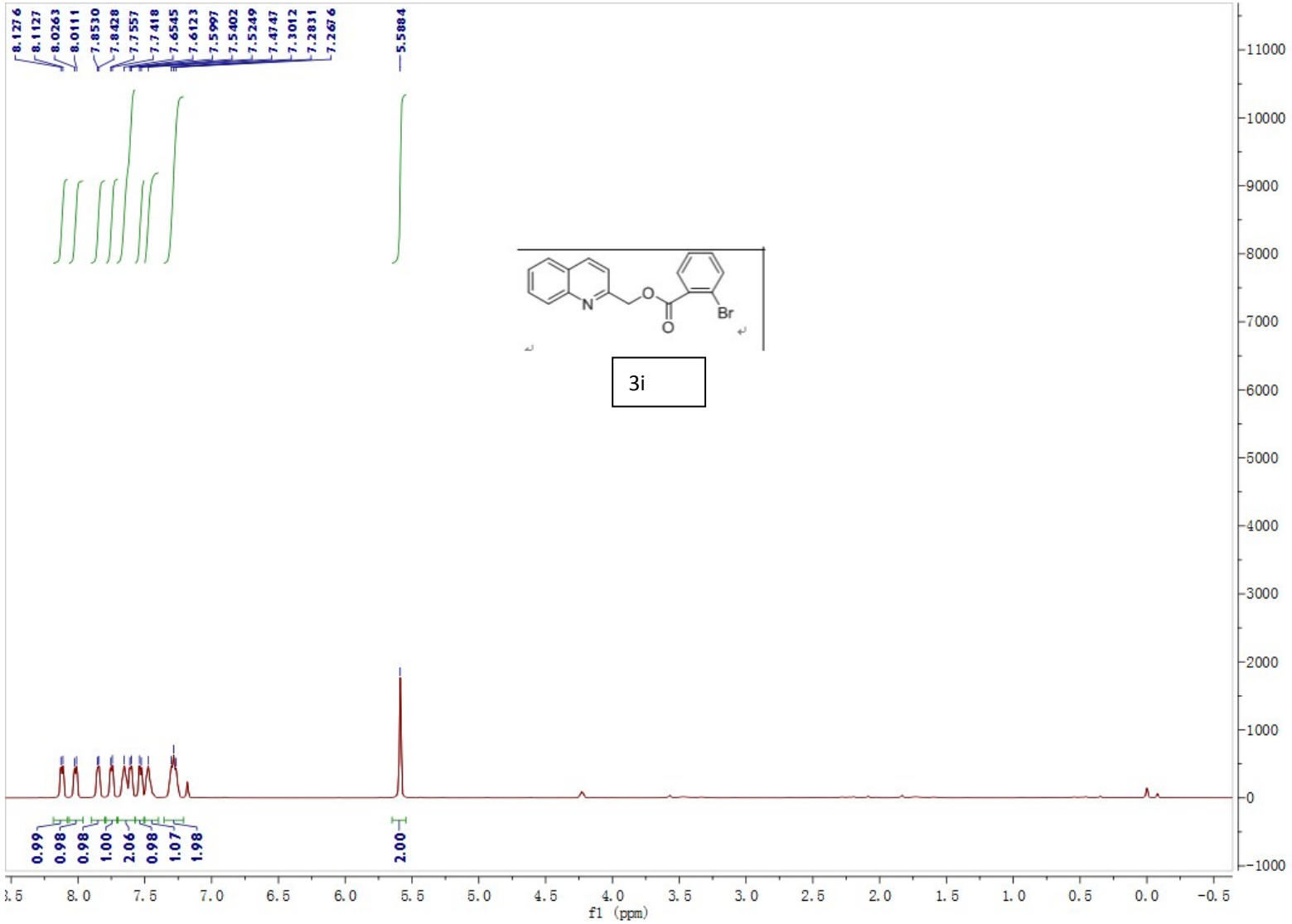
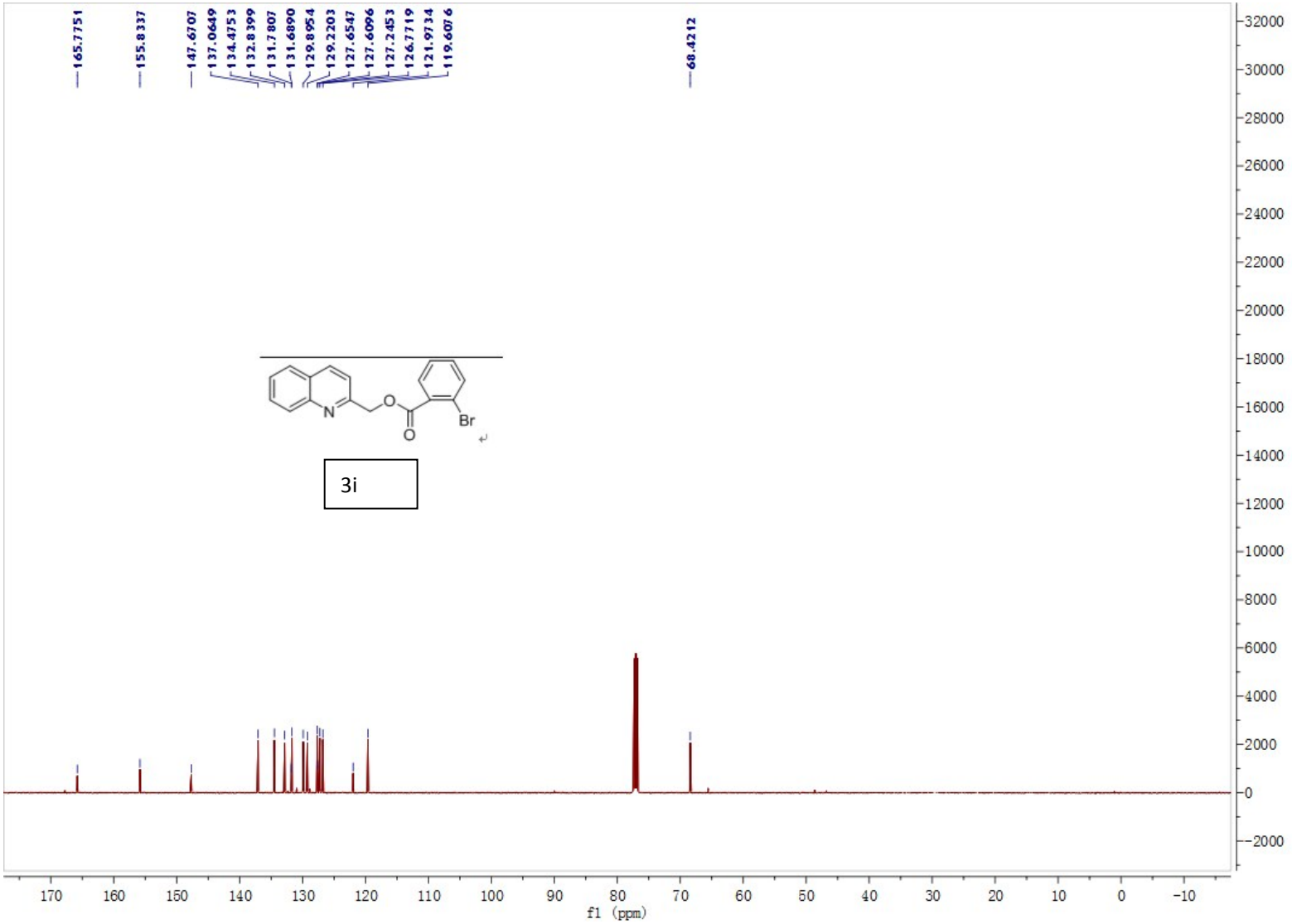
156.0206
147.7048
137.1246
131.8567
131.3848
129.9565
129.2258
127.6625
127.6095
126.8127
119.4564
68.1407
Br
N
O
O
3h
f1 (ppm)


8.1276
8.1127
8.0263
8.0111
7.8530
7.8428
7.7557
7.7418
7.6545
7.6123
7.5997
7.5402
7.5249
7.4747
7.3012
7.2831
7.2676
5.5884
N
O
O
Br
3i
0.99
0.98
0.98
1.00
2.06
0.98
1.07
1.98
2.00
f1 (ppm)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147.6707
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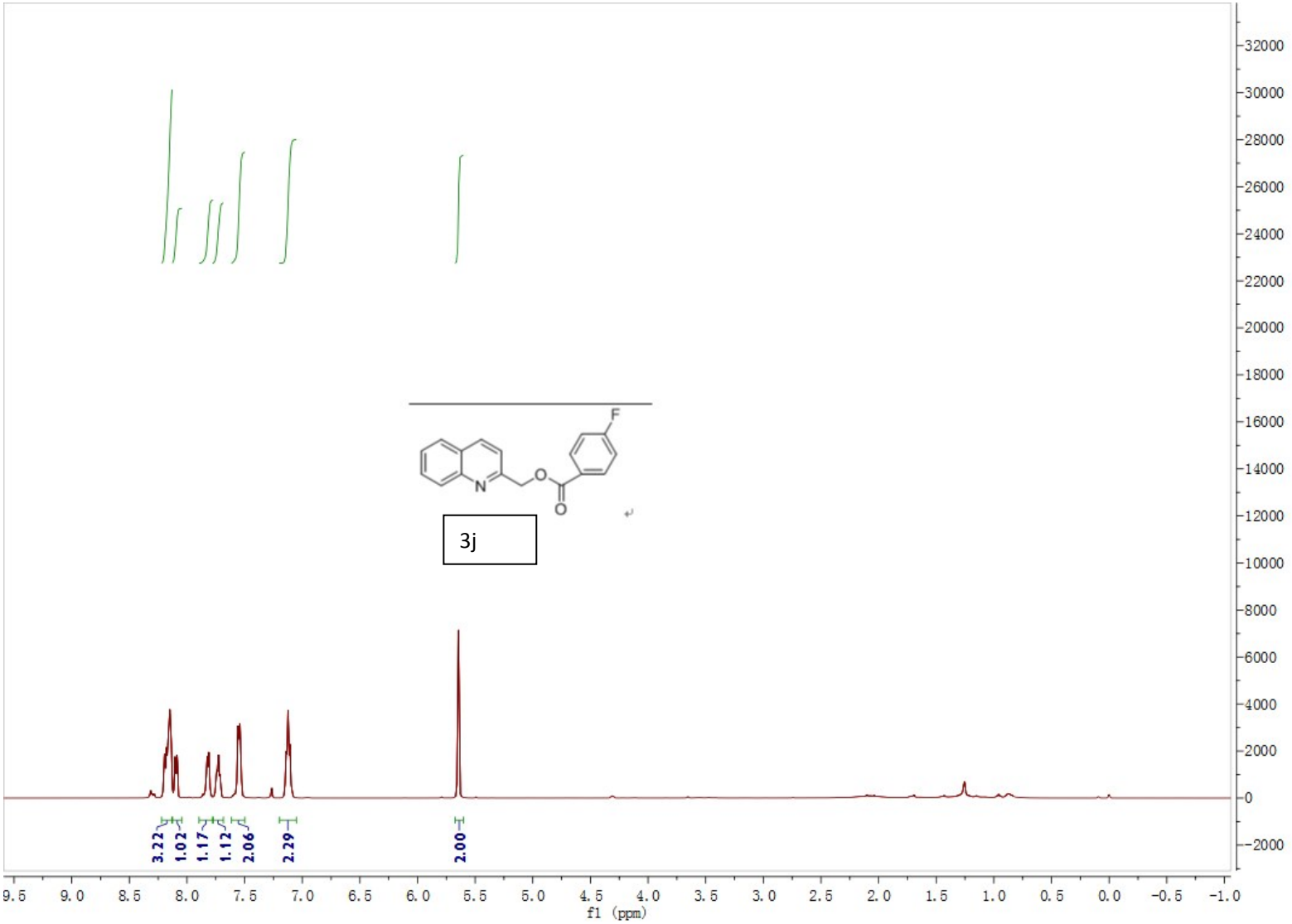
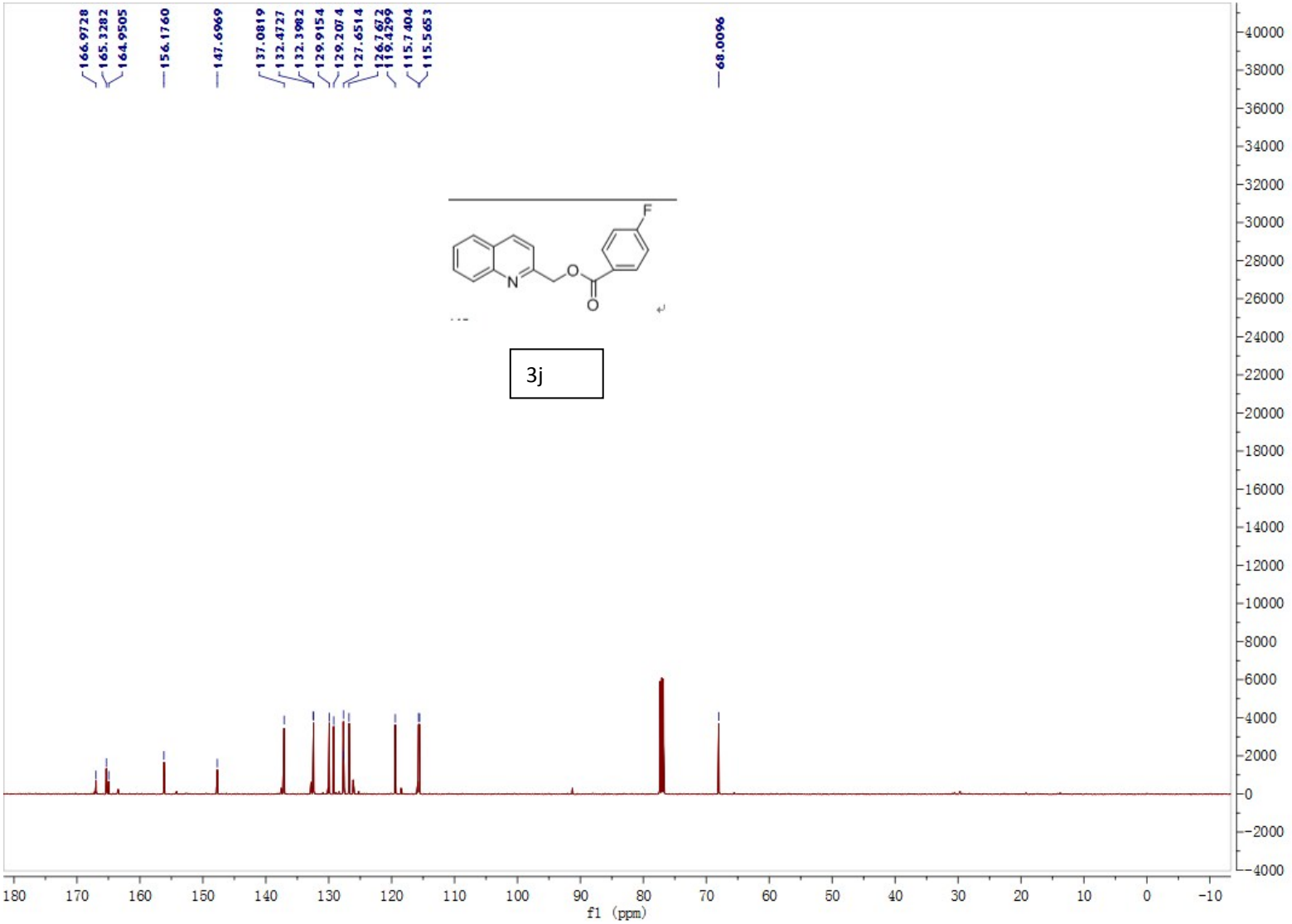
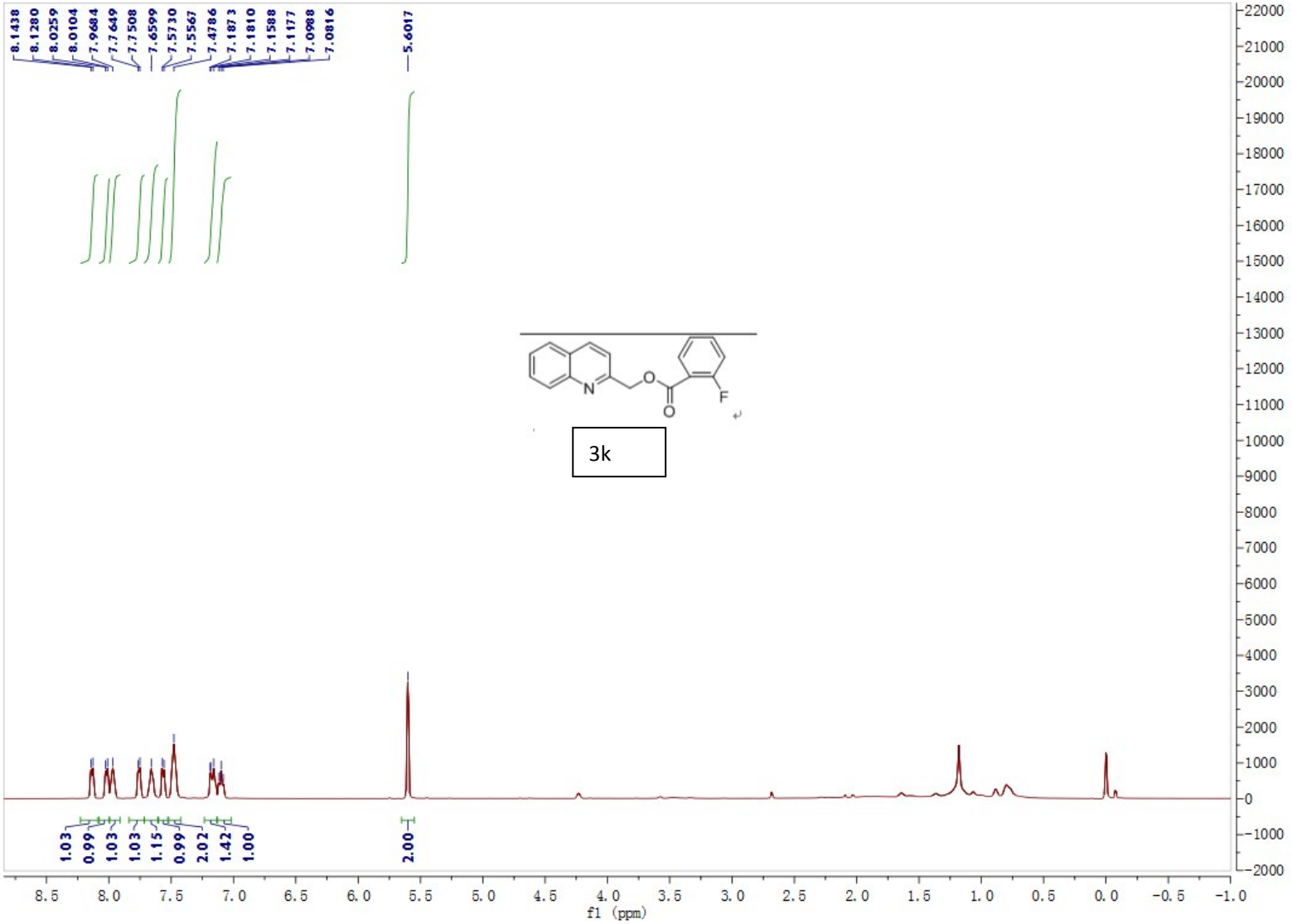
134.4753
132.8399
131.7807
131.6890
129.8954
129.2203
127.6547
127.6096
127.2453
126.7719
121.9734
119.6076
68.4212
N
O
O
Br
3i
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
N
O
O
3j
3.22
1.02
1.17
1.12
2.06
2.29
2.00
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


166.9728
165.3282
164.9505
156.1760
147.6969
137.0819
132.4727
132.3982
129.9154
129.2074
127.6514
126.7672
119.4299
115.7404
115.5653
68.0096
F
N
O
O
3j
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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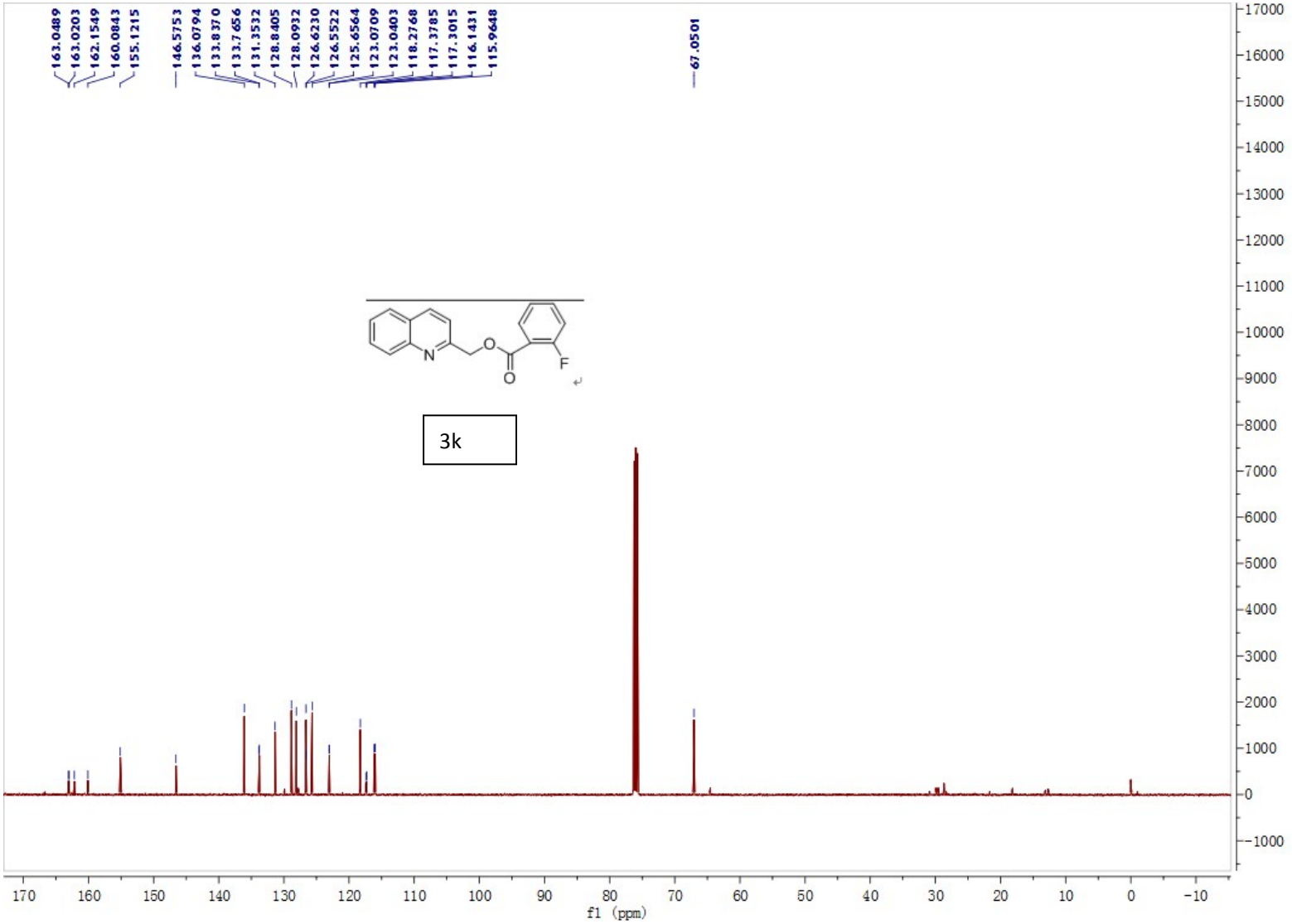
8.1280
8.0259
8.0104
7.9684
7.7649
7.7508
7.6599
7.5730
7.5567
7.4786
7.1873
7.1810
7.1588
7.1177
7.0908
7.0816
5.6017
N
O
O
F
3k
1.03
0.99
1.03
1.03
1.15
0.99
2.02
1.42
1.00
2.00
f1 (ppm)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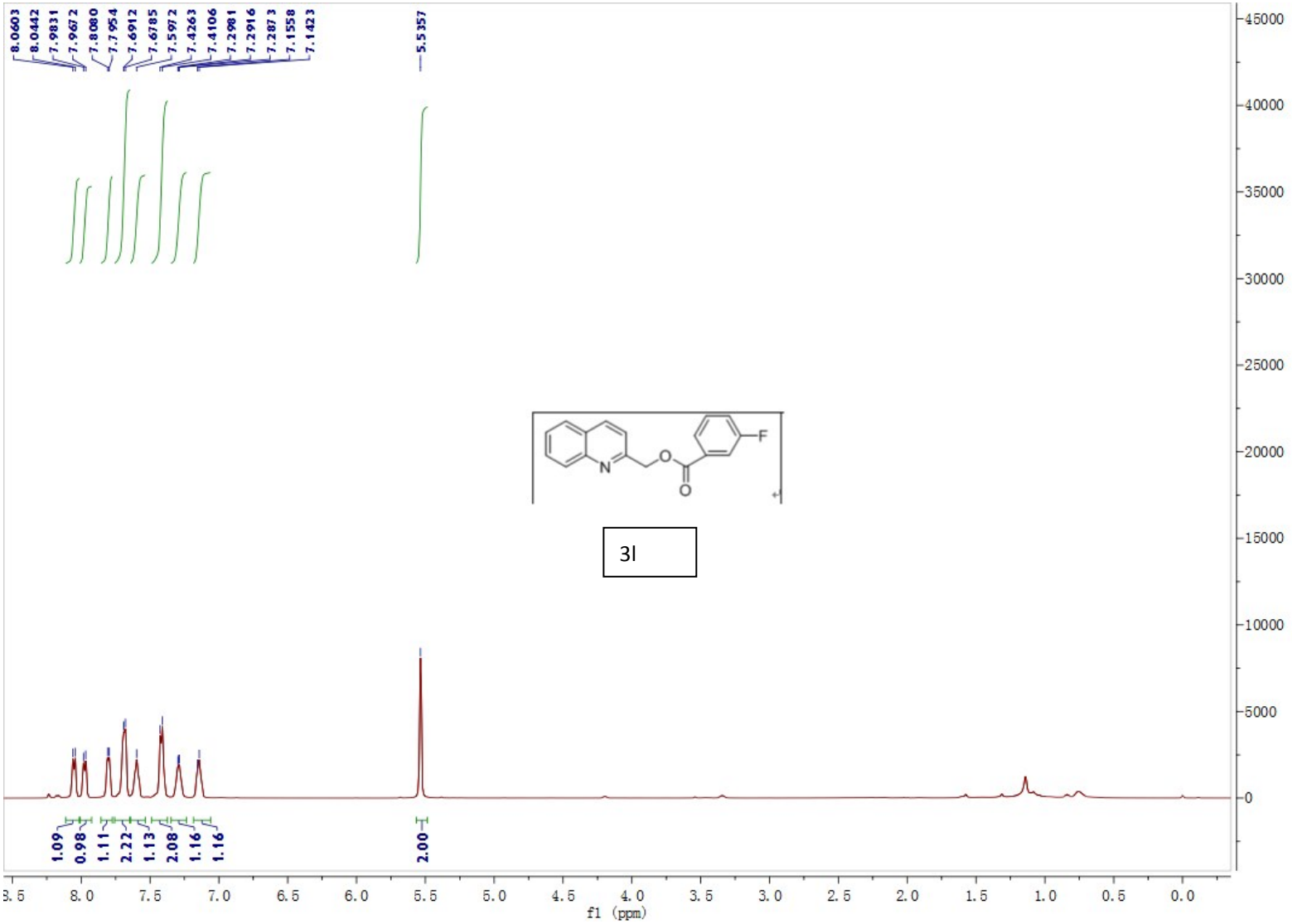
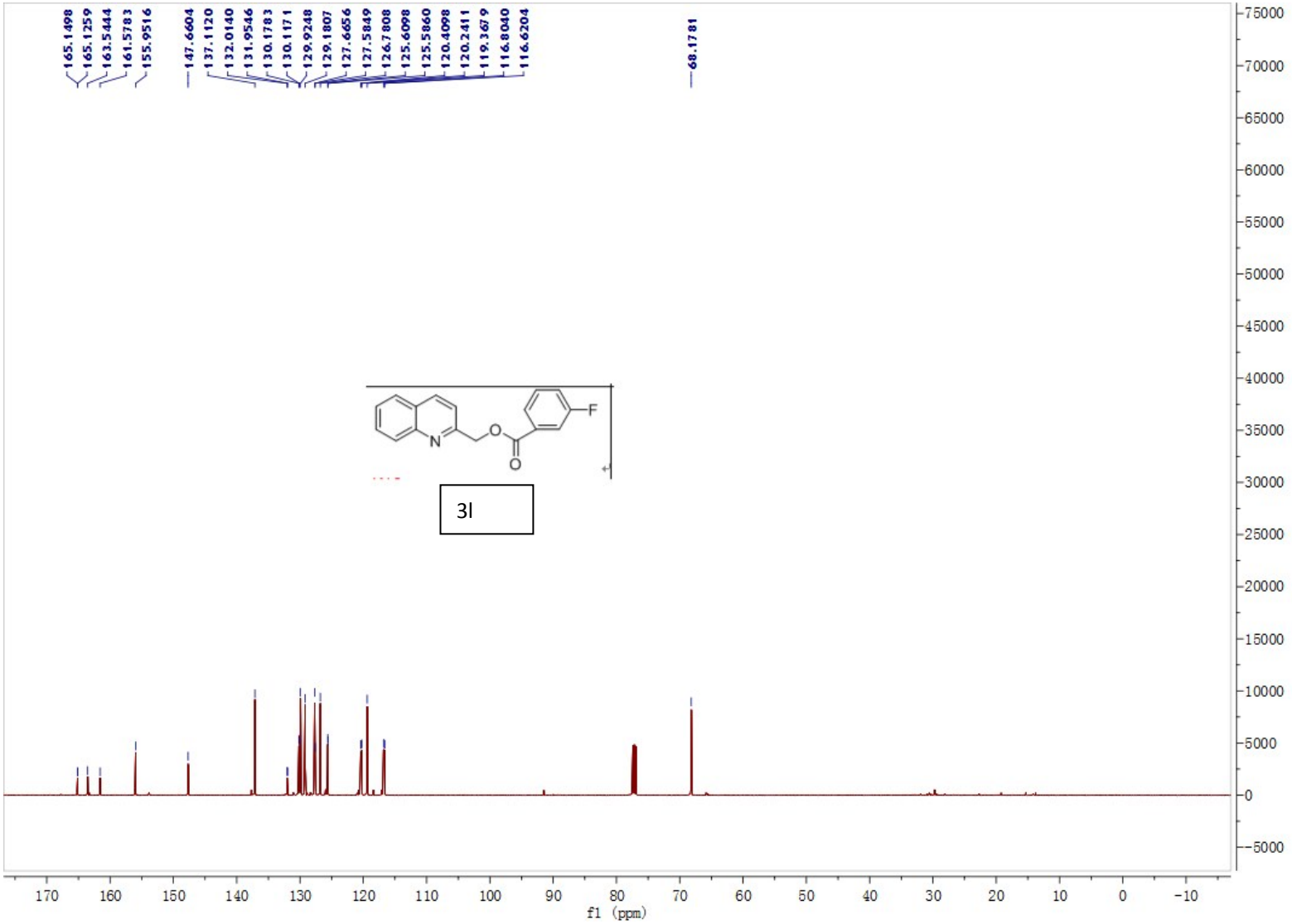
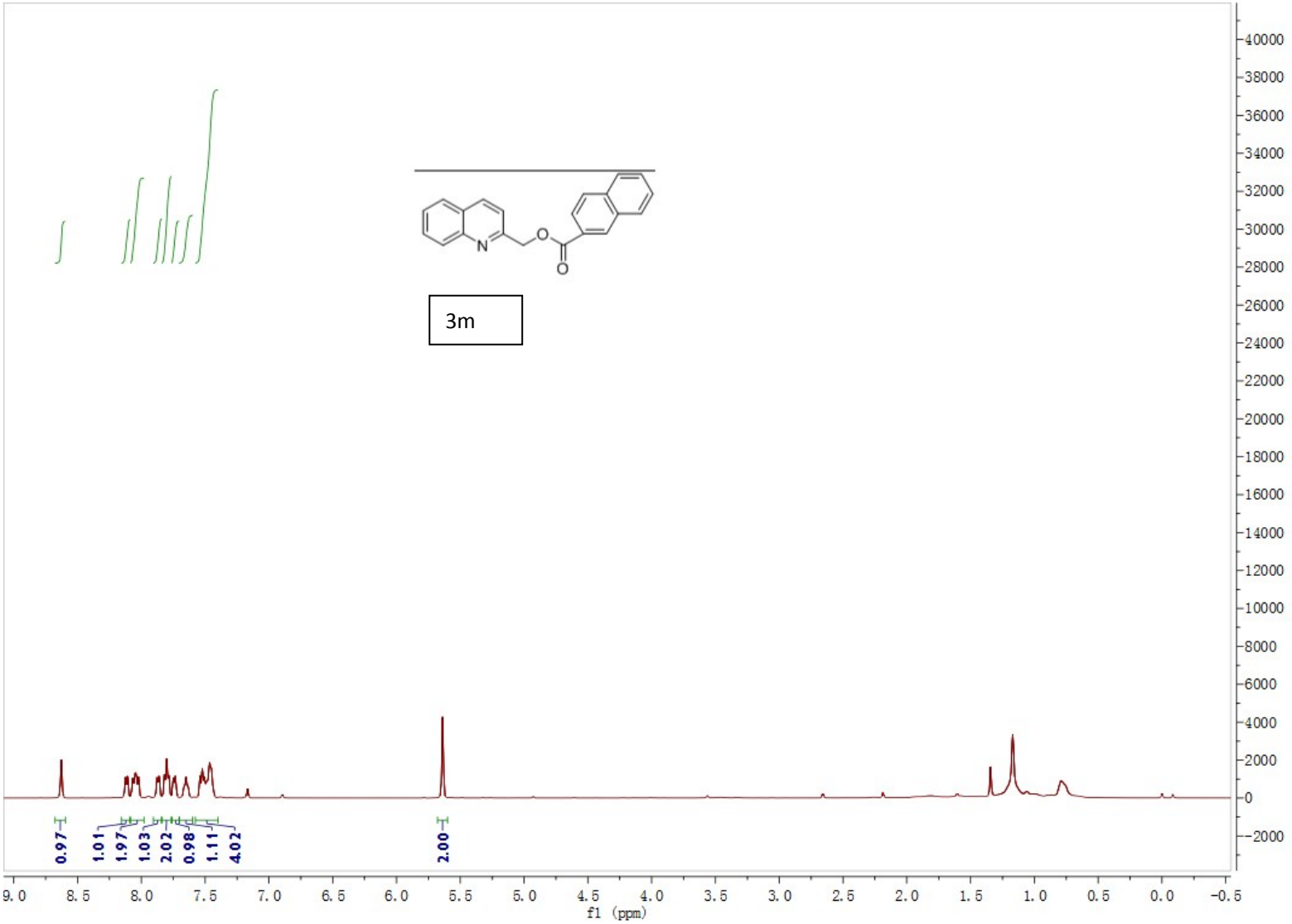
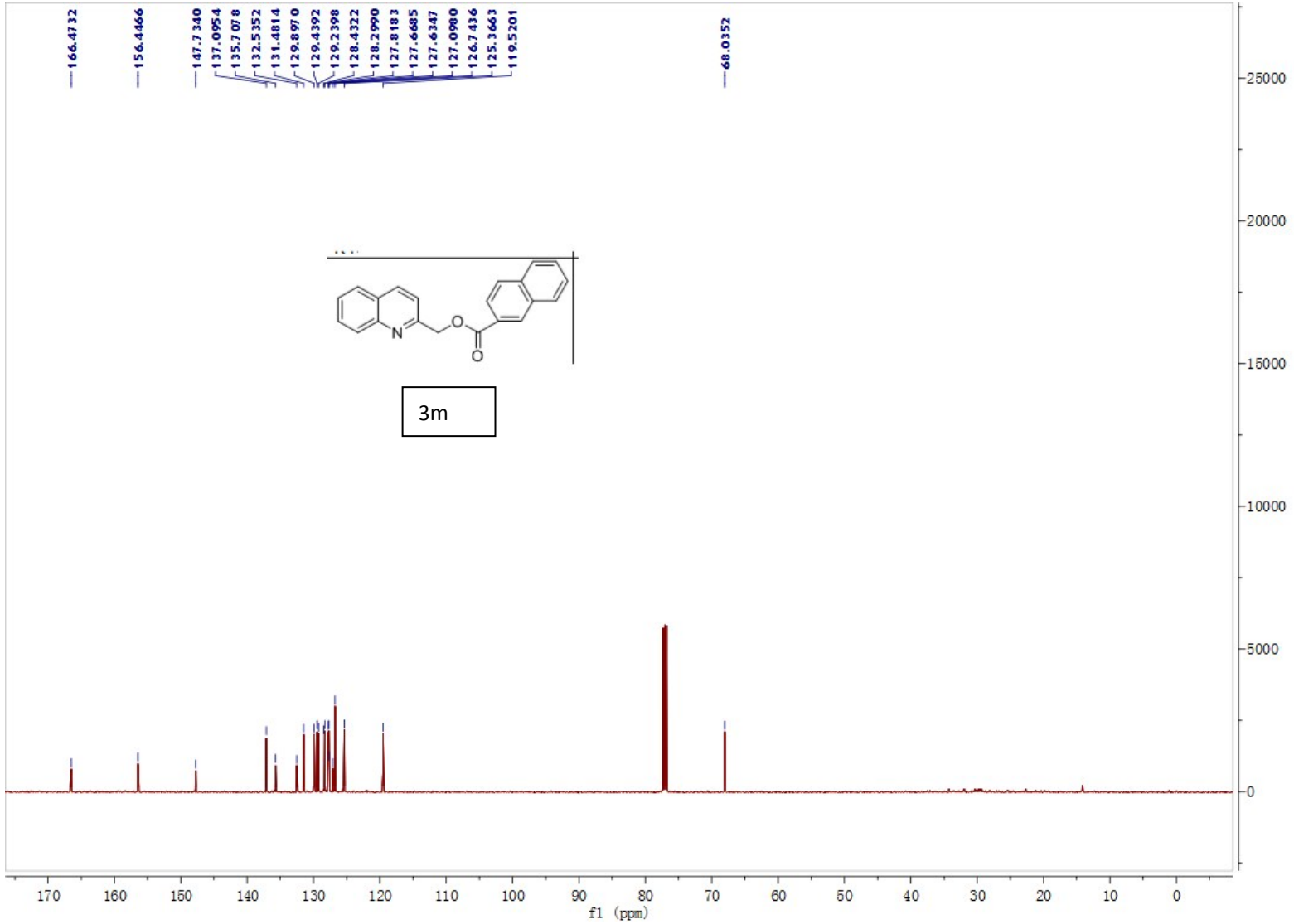
163.0203
162.1549
160.0843
155.1215
146.5753
136.0794
133.8370
133.7656
131.3532
128.8405
128.0932
126.6230
126.5522
125.6564
123.0709
123.0403
118.2768
117.3785
117.3015
116.1431
115.9648
67.0501
N
O
O
F
3k
f1 (ppm)

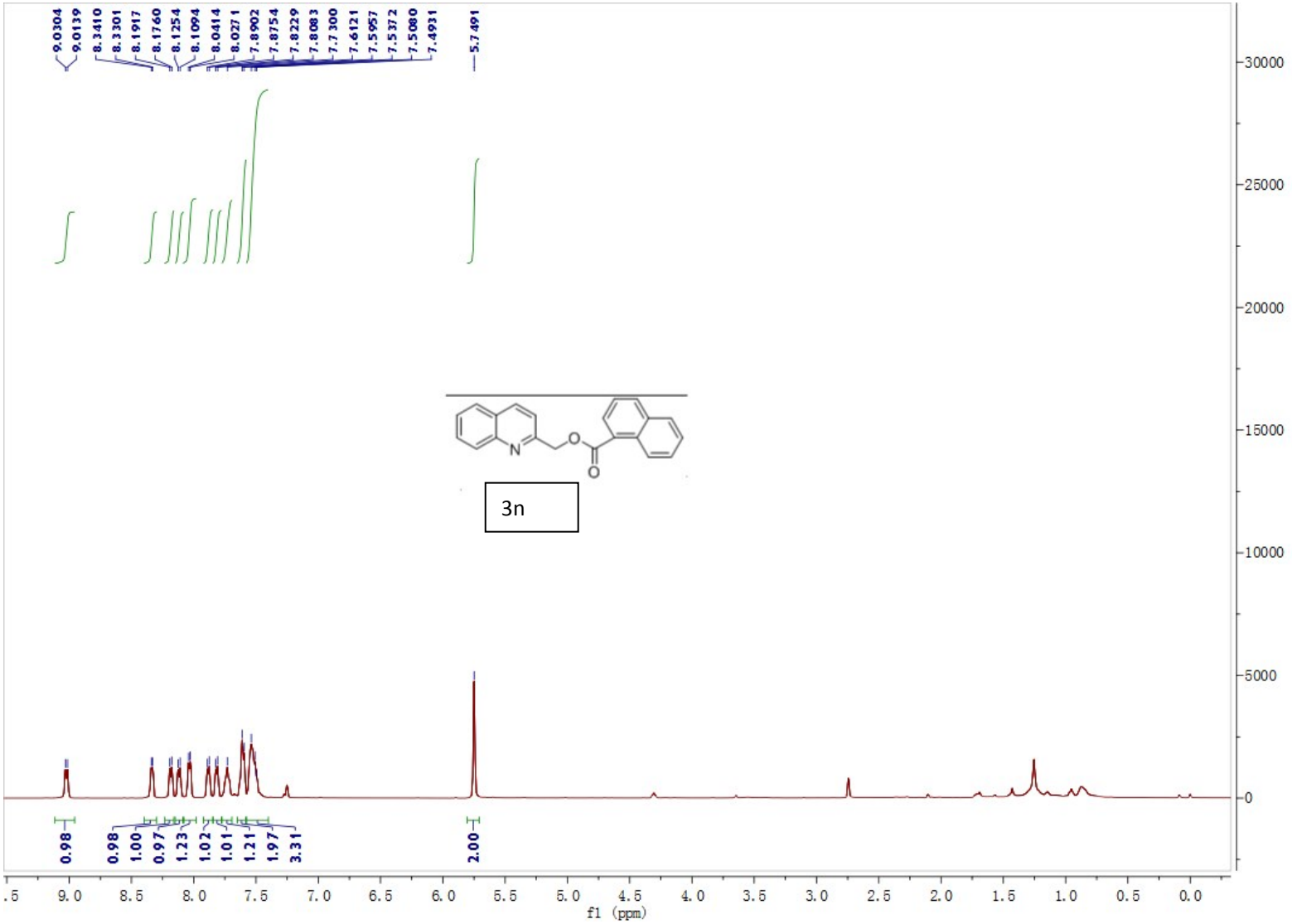

8.0603
8.0442
7.9831
7.9672
7.8080
7.7954
7.6912
7.6785
7.5972
7.4263
7.4106
7.2981
7.2916
7.2873
7.1558
7.1423
5.5357
F
N
O
O
3l
1.09
0.98
1.11
2.22
1.13
2.08
1.16
1.16
2.00
f1 (ppm)


165.1498
165.1259
163.5444
161.5783
155.9516
147.6604
137.1120
132.0140
131.9546
130.1783
130.1171
129.9248
129.1807
127.6656
127.5849
126.7808
125.6098
125.5860
120.4098
120.2411
119.3679
116.8040
116.6204
68.1781
F
N
O
O
3l
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

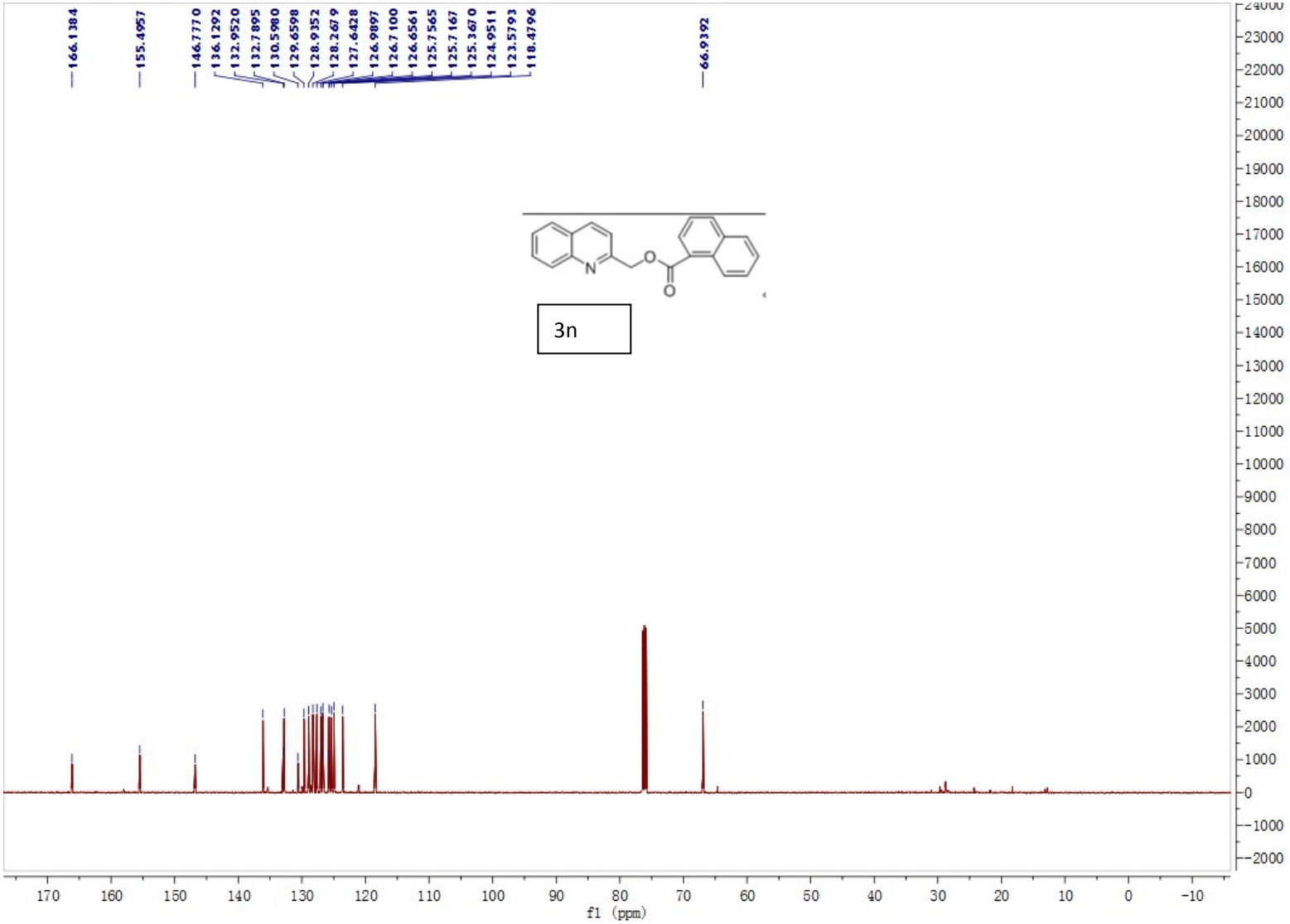

3m
0.97
1.01
1.97
1.03
2.02
0.98
1.11
4.02
2.00
f1 (ppm)


166.4732
156.4466
147.7340
137.0954
135.7078
132.5352
131.4814
129.8970
129.4392
129.2398
128.4322
128.2990
127.8183
127.6685
127.6347
127.0980
126.7436
125.3663
119.5201
68.0352
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3m


9.0304
9.0139
8.3410
8.3301
8.1917
8.1760
8.1254
8.1094
8.0414
8.0271
7.8902
7.8754
7.8229
7.8083
7.7300
7.6121
7.5957
7.5372
7.5080
7.4931
5.7491
30000
25000
20000
15000
10000
5000
0
0.98
0.98
1.00
0.97
1.23
1.02
1.01
1.21
1.97
3.31
2.00
f1 (ppm)

3n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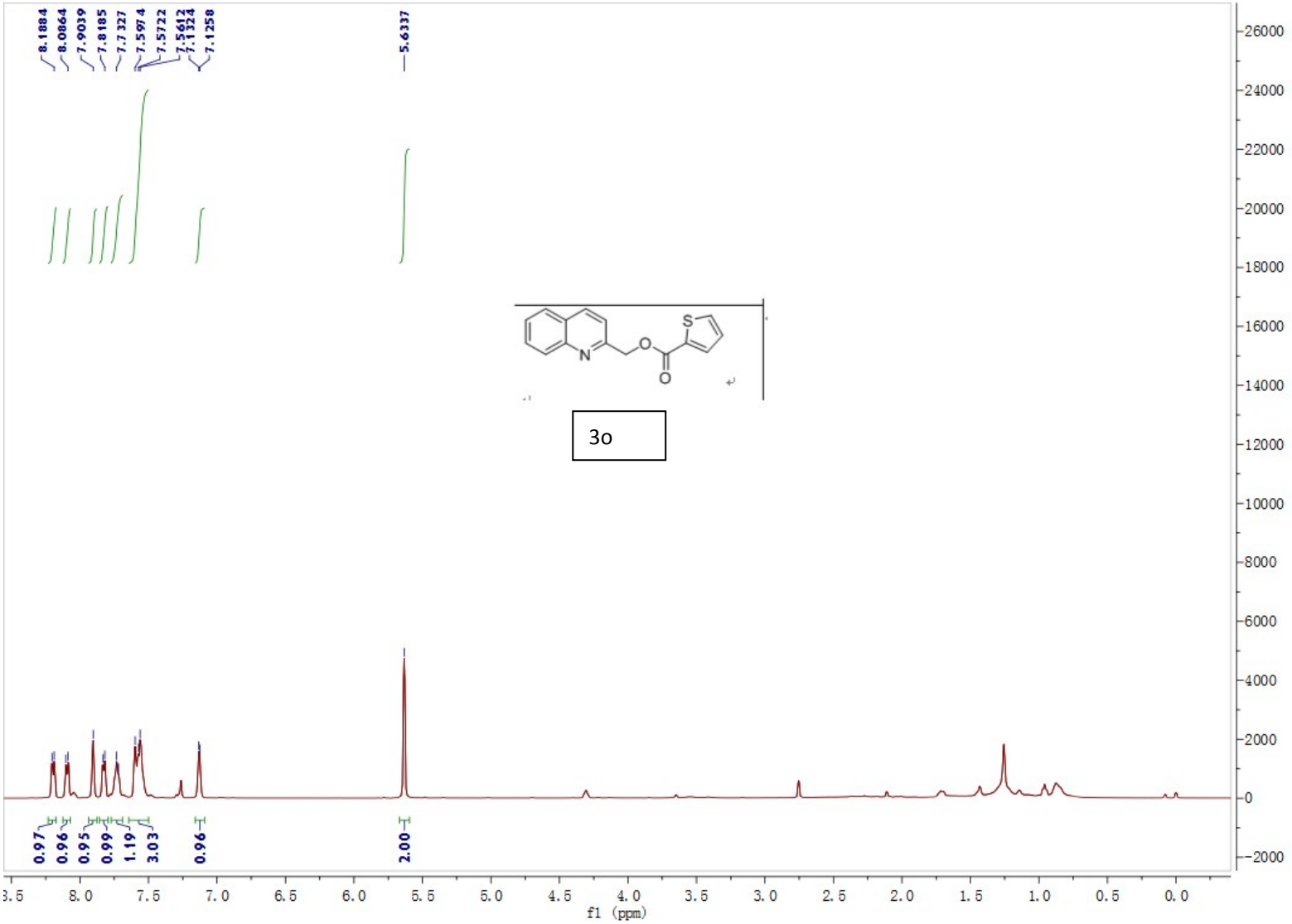
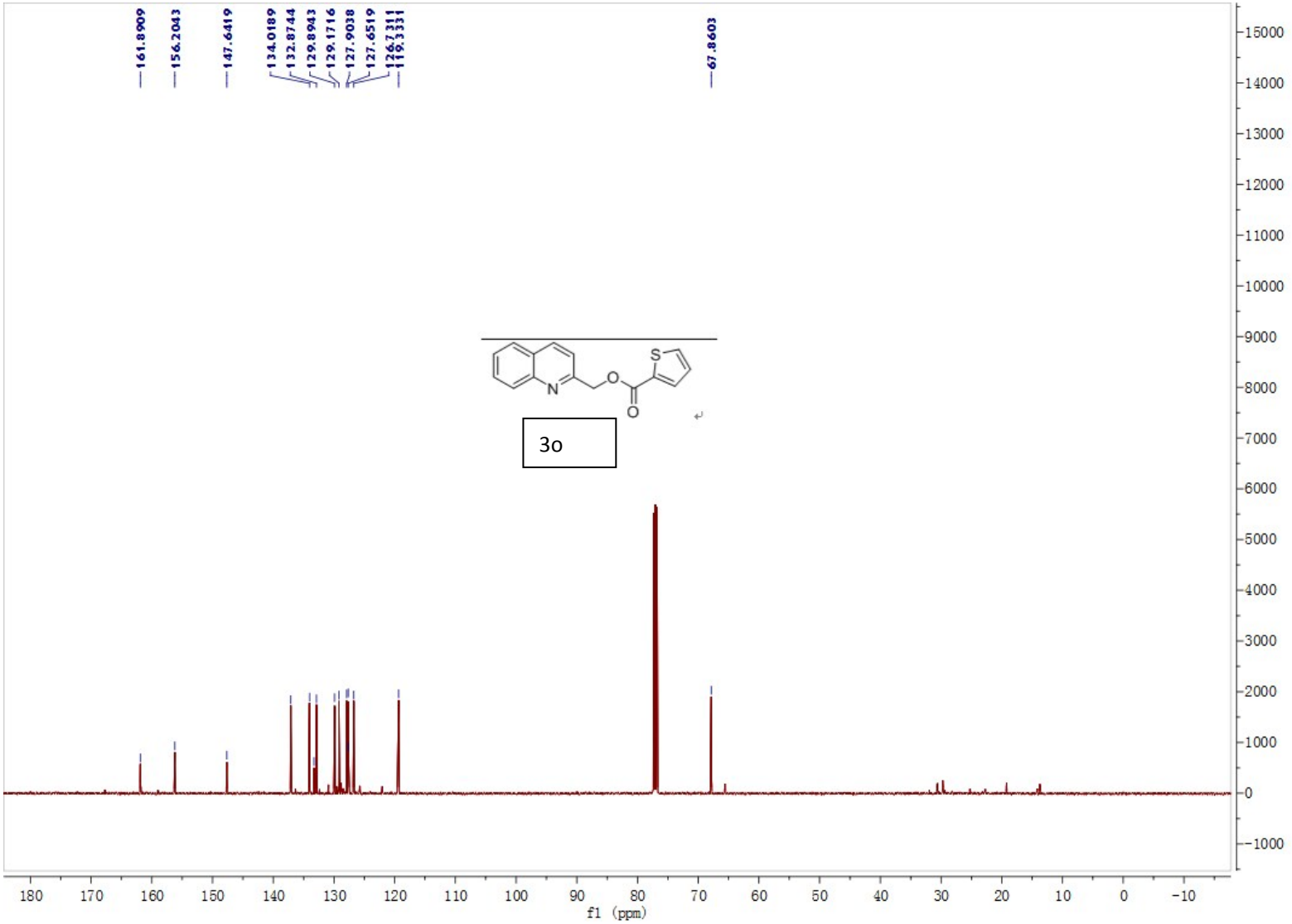
155.4957
146.7770
136.1292
132.9520
132.7895
130.5980
129.6598
128.9352
128.2679
127.6428
126.9897
126.7100
126.6561
125.7565
125.7167
125.3670
124.9511
123.5793
118.4796
66.9392
N
O
O
3n
f1 (ppm)


8.1884
8.0864
7.9039
7.8185
7.7327
7.5974
7.5722
7.5612
7.1324
7.1258
5.6337
0.97
0.96
0.95
0.99
1.19
3.03
0.96
2.00
f1 (ppm)

3o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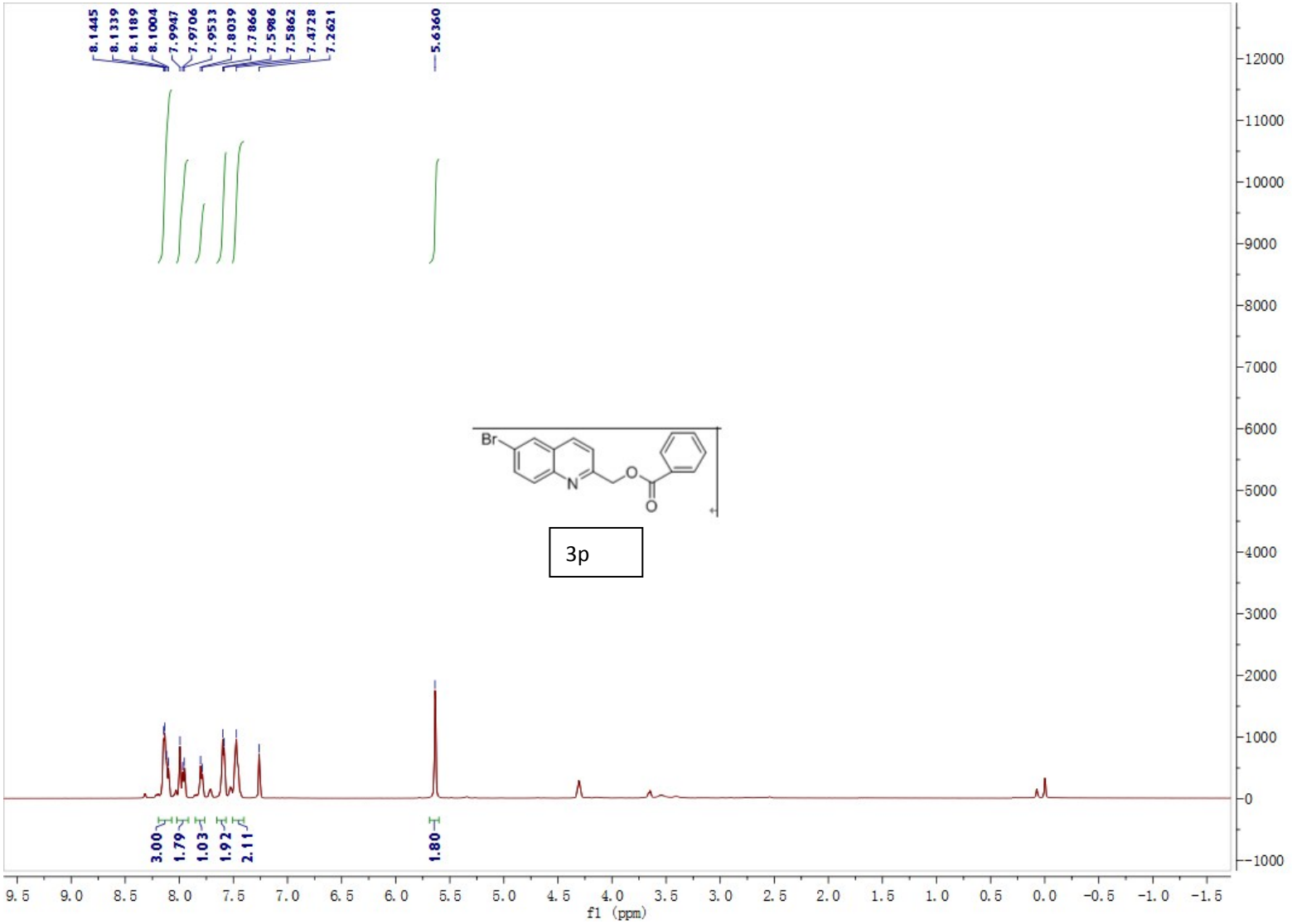
156.2043
147.6419
134.0189
132.8744
129.8943
129.1716
127.9038
127.6519
126.7311
119.3331
67.8603
N
O
O
S
3o
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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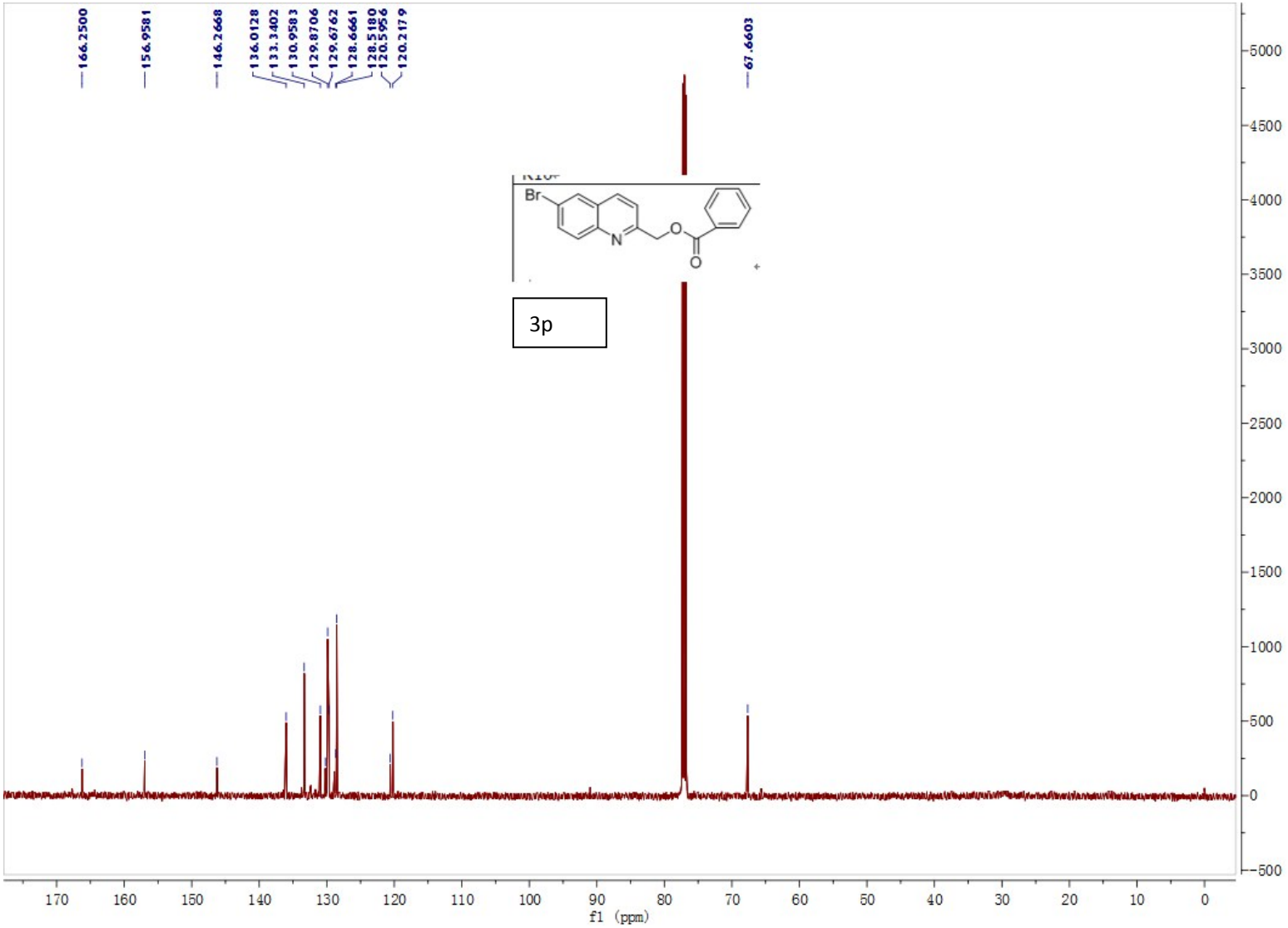
8.1339
8.1189
8.1004
7.9947
7.9706
7.9533
7.8039
7.7866
7.5986
7.5862
7.4728
7.2621
5.6360
Br
N
O
O
3p
3.00
1.79
1.03
1.92
2.11
1.80
f1 (ppm)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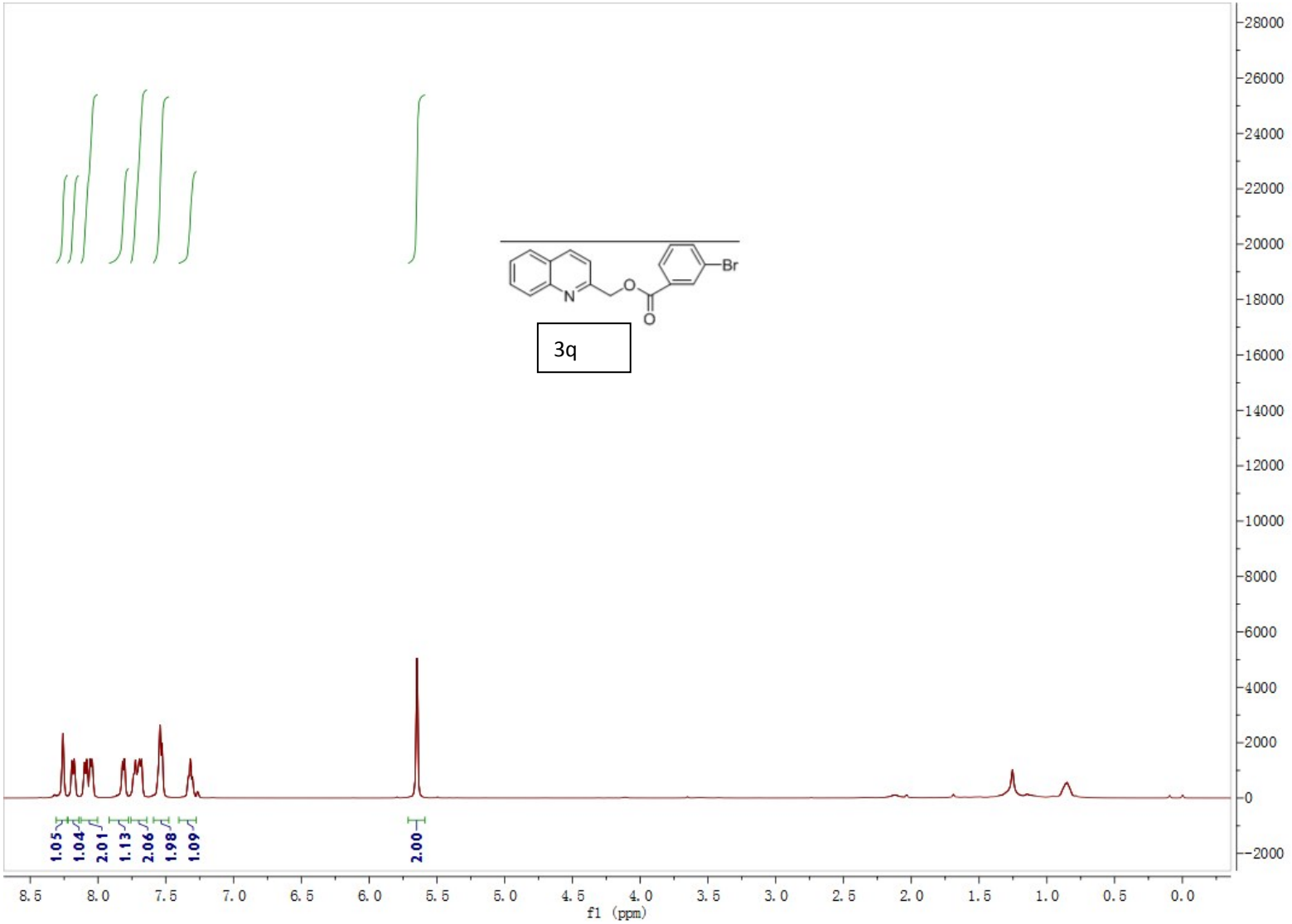
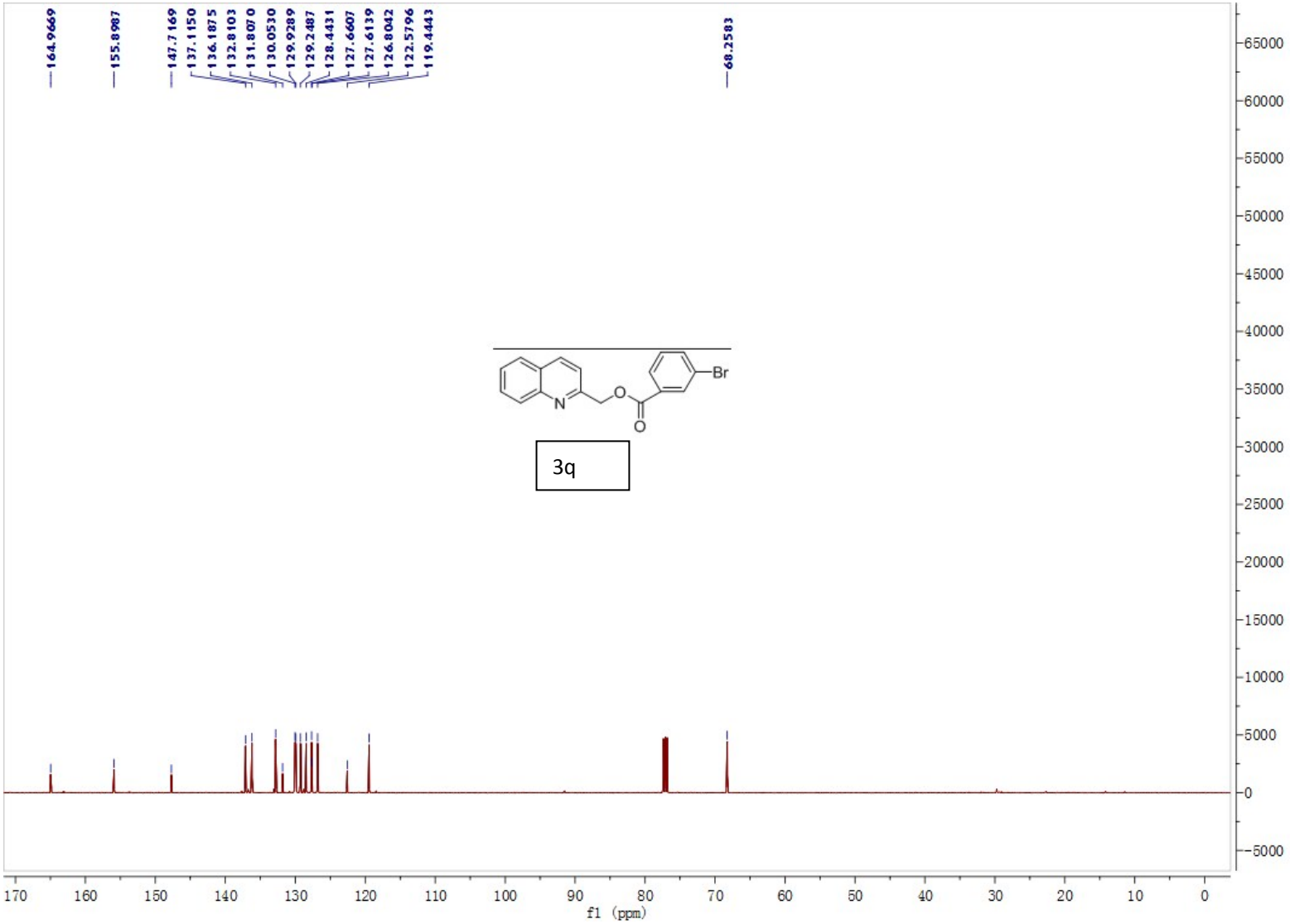
146.2668
136.0128
133.3402
130.9583
129.8706
129.6762
128.6661
128.5180
120.5956
120.2179
67.6603
Br
N
O
O
3p
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
O
N
O
3q
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.05
1.04
2.01
1.13
2.06
1.98
1.09
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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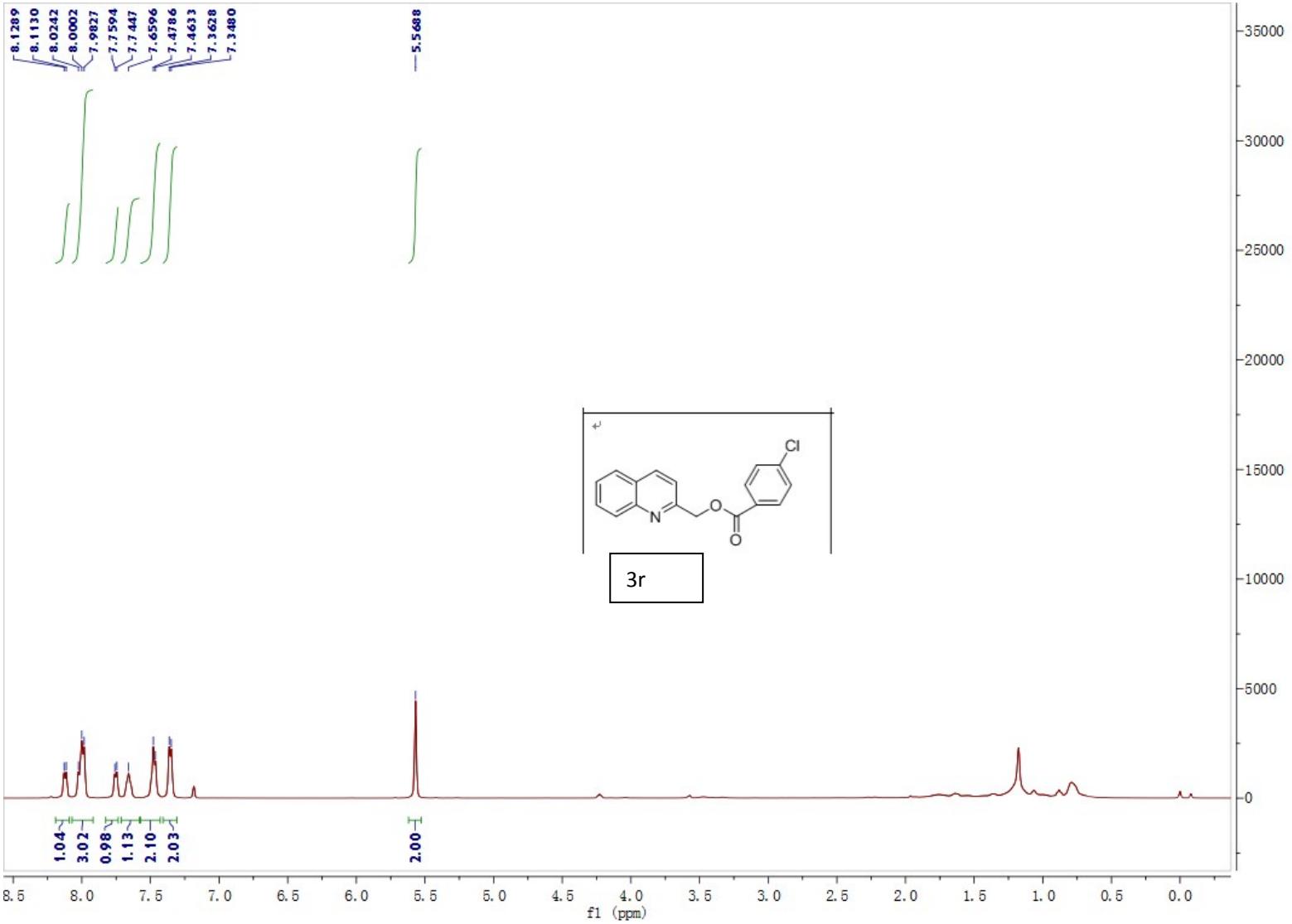
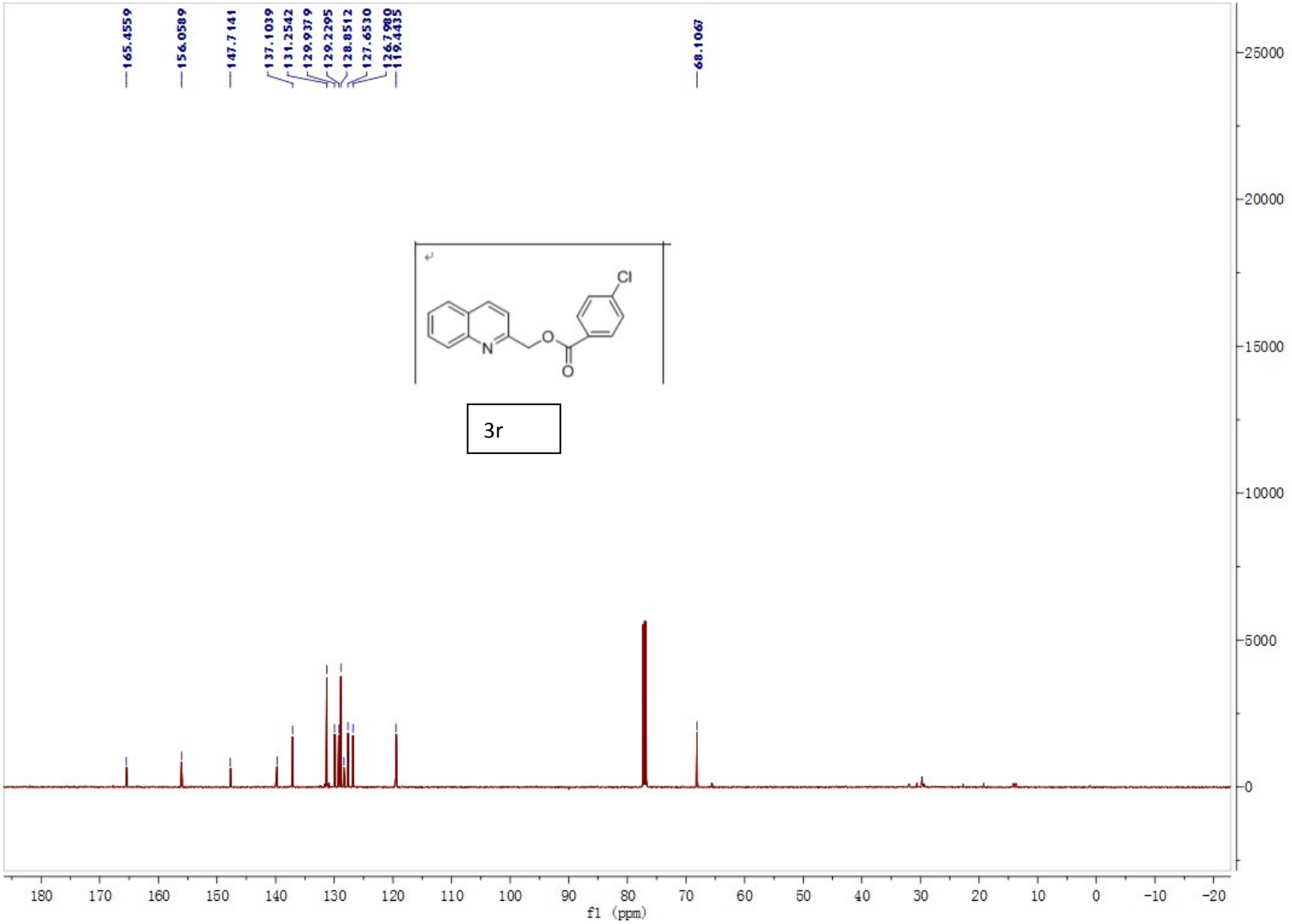
147.7169
137.1150
136.1875
132.8103
131.8070
130.0530
129.9289
129.2487
128.4431
127.6607
127.6139
126.8042
122.5796
119.4443
68.2583
Br
N
O
O
3q
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.1289
8.1130
8.0242
8.0002
7.9827
7.7594
7.7447
7.6596
7.4786
7.4633
7.3628
7.3480
5.5688
Cl
N
O
O
3r
1.04
3.02
0.98
1.13
2.10
2.03
2.00
f1 (ppm)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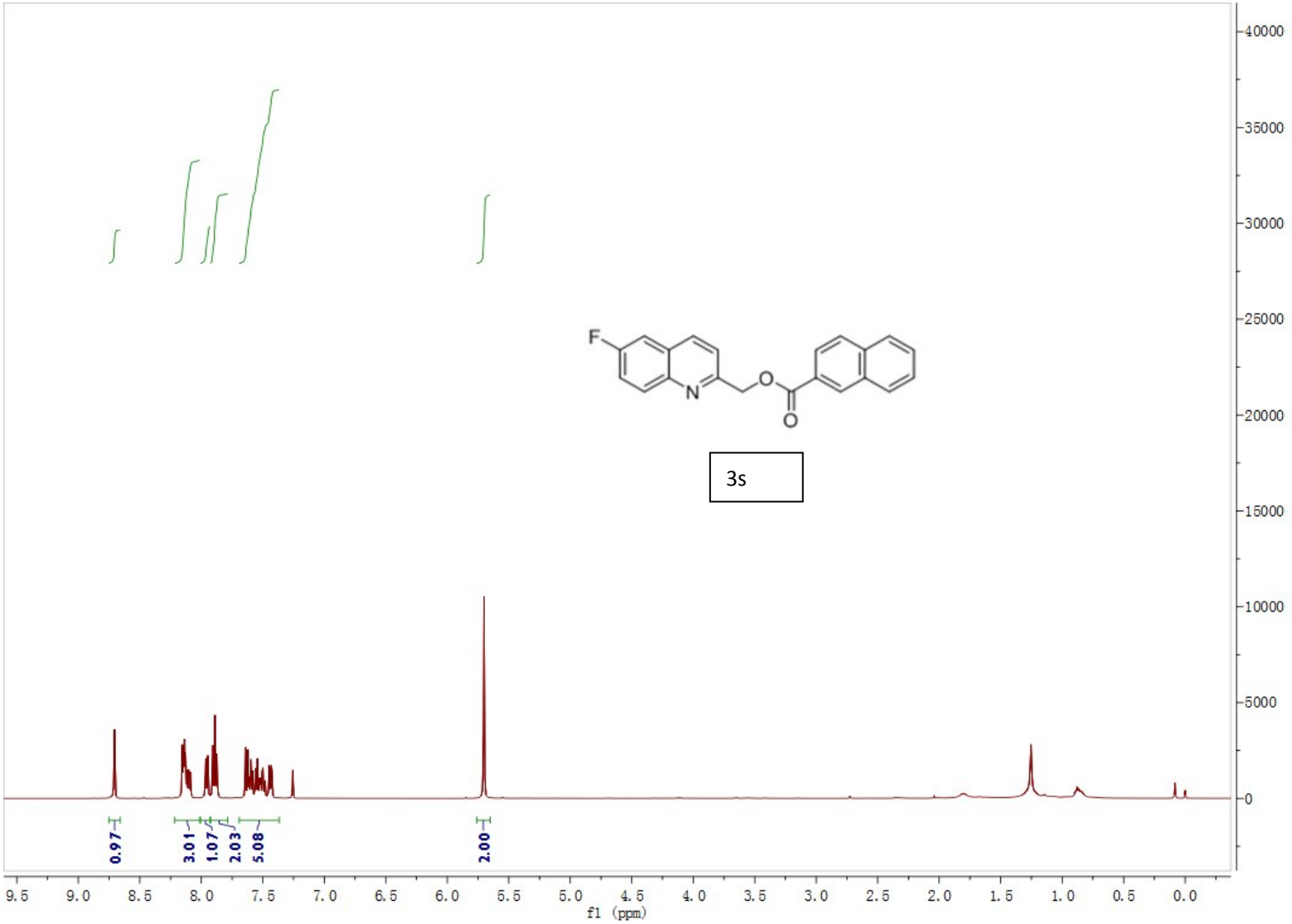
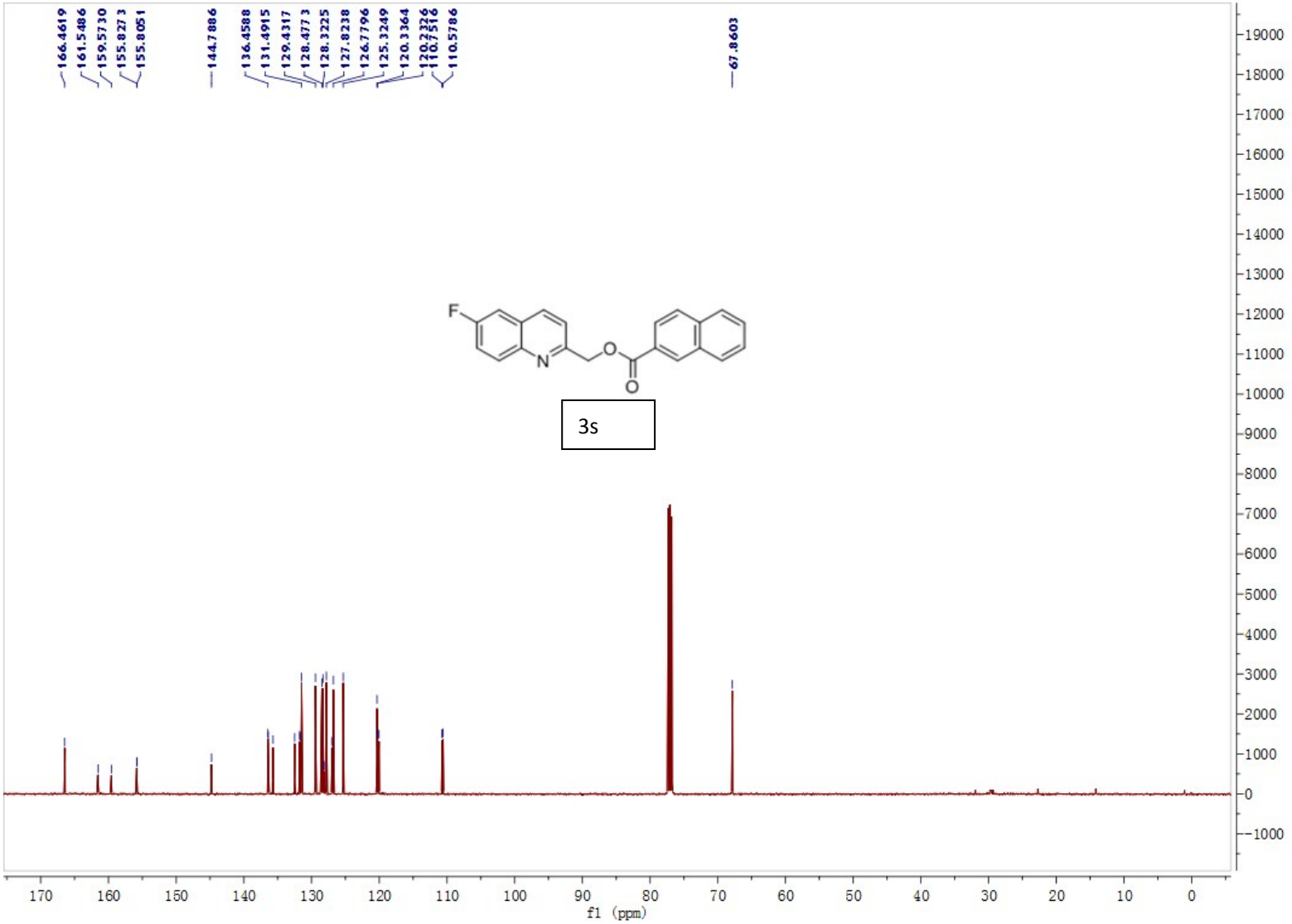
156.0589
147.7141
137.1039
131.2542
129.9379
129.2295
128.8512
127.6530
126.7980
119.4435
68.1067
Cl
N
O
O
3r
25000
20000
15000
10000
5000
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


F
N
O
O
3s
40000
35000
30000
25000
20000
15000
10000
5000
0
0.97
3.01
1.07
2.03
5.08
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.4619
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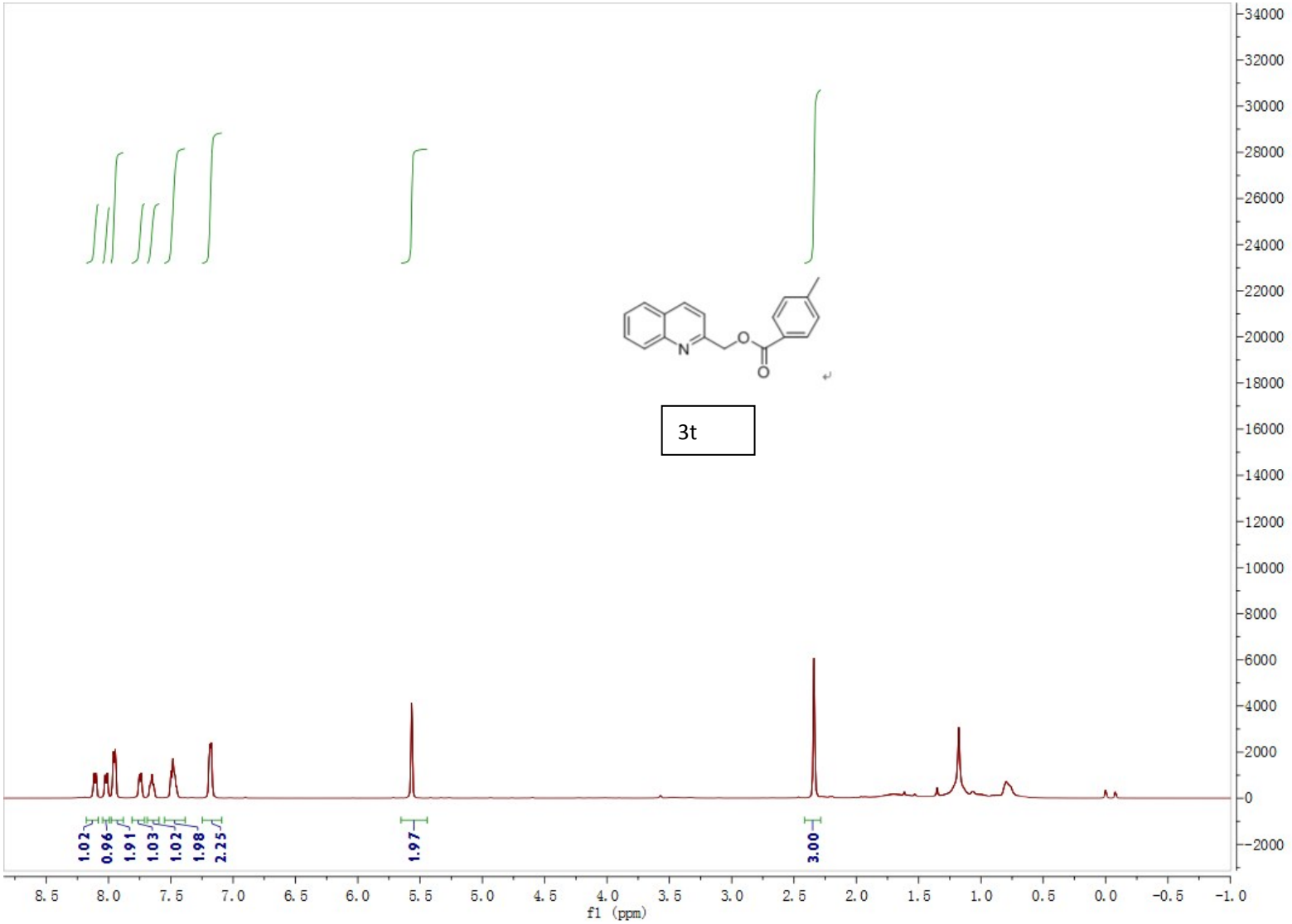
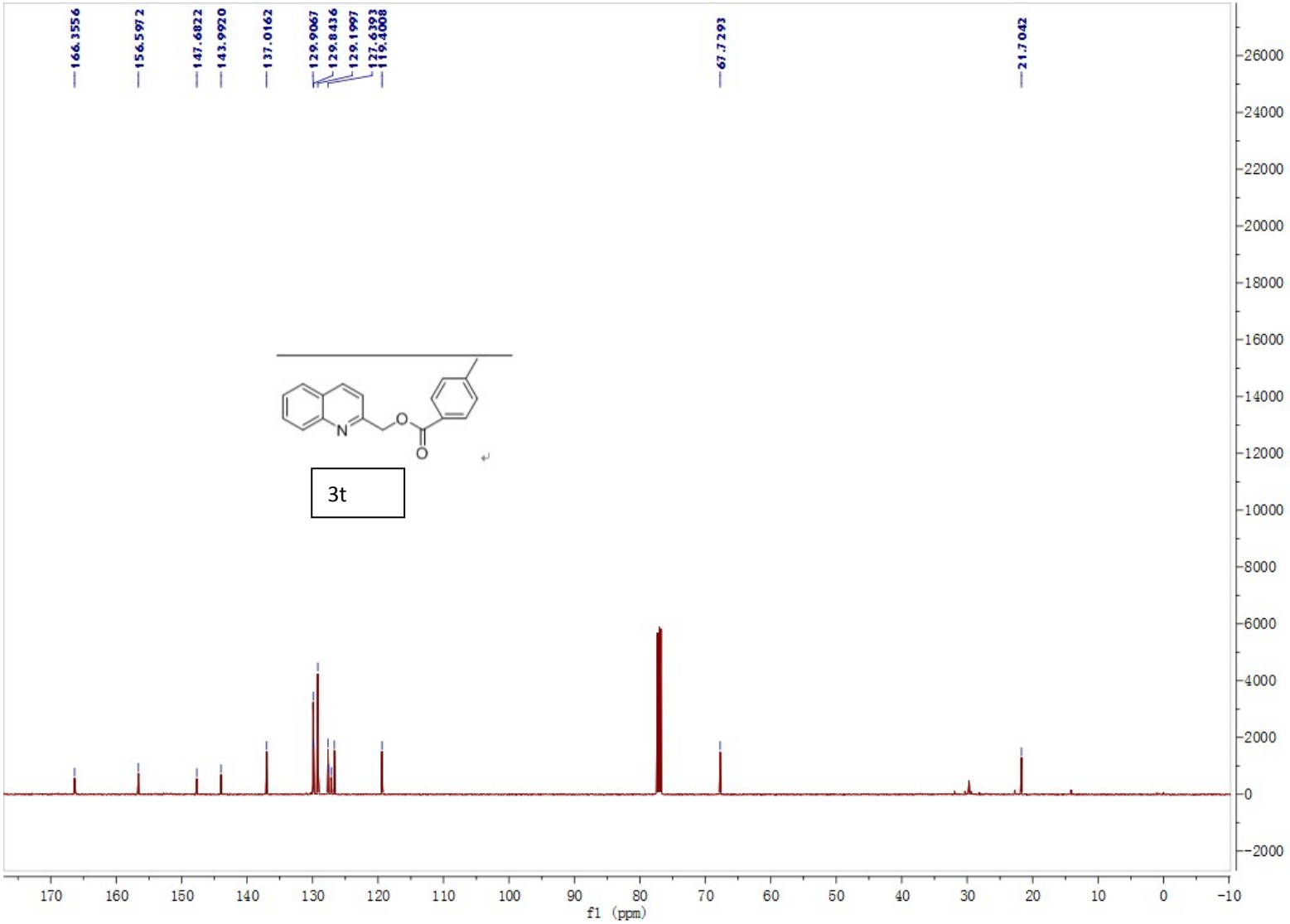
159.5730
155.8273
155.8051
144.7886
136.4588
131.4915
129.4317
128.4773
128.3225
127.8238
126.7796
125.3249
120.3364
120.2326
110.7516
110.5786
67.8603
F
N
O
O
3s
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3t
1.02
0.96
1.91
1.03
1.02
1.98
2.25
1.97
3.00
f1 (ppm)


166.3556
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147.6822
143.9920
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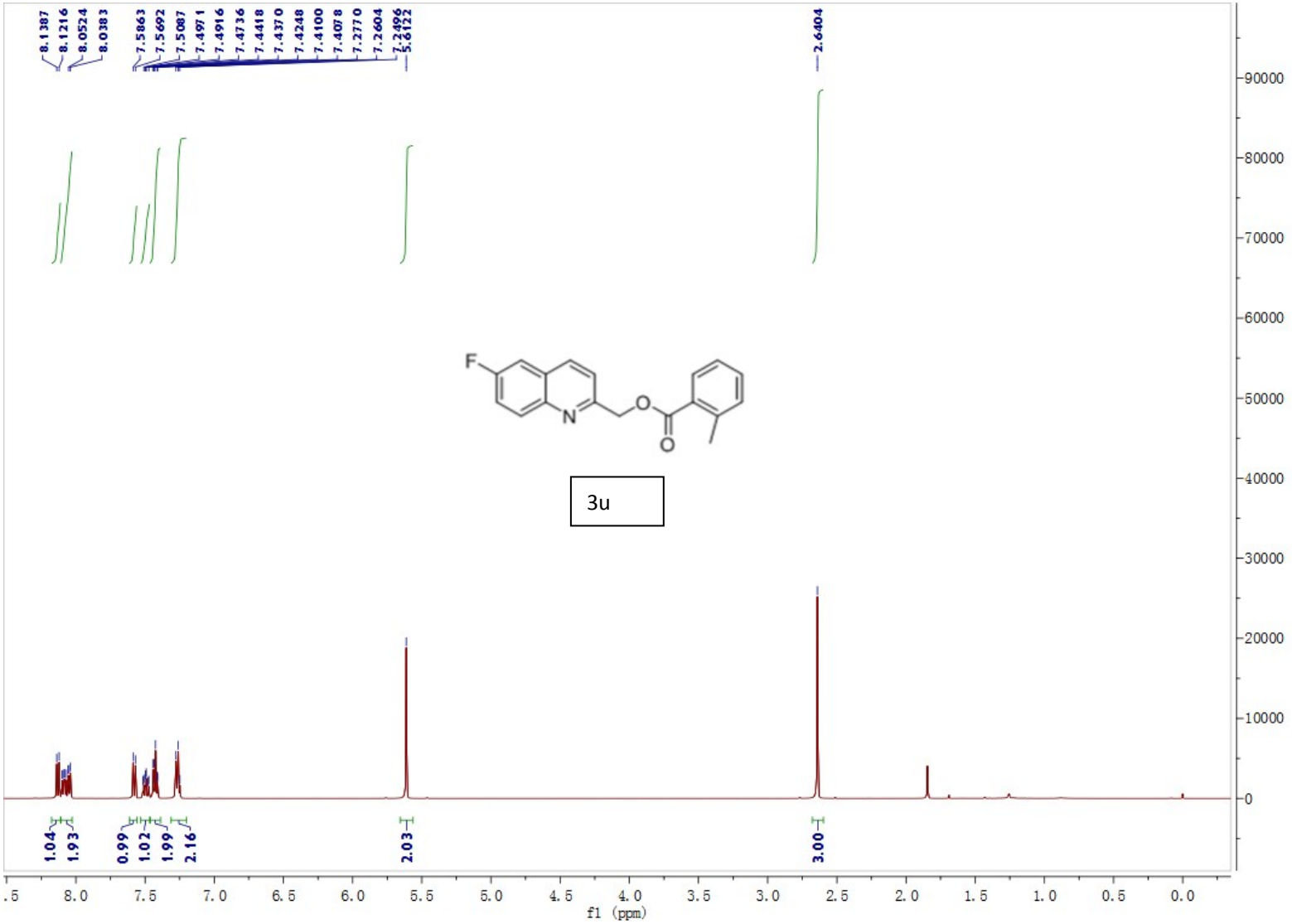
129.9067
129.8436
129.1997
127.6393
119.4008
67.7293
21.7042
3t
f1 (ppm)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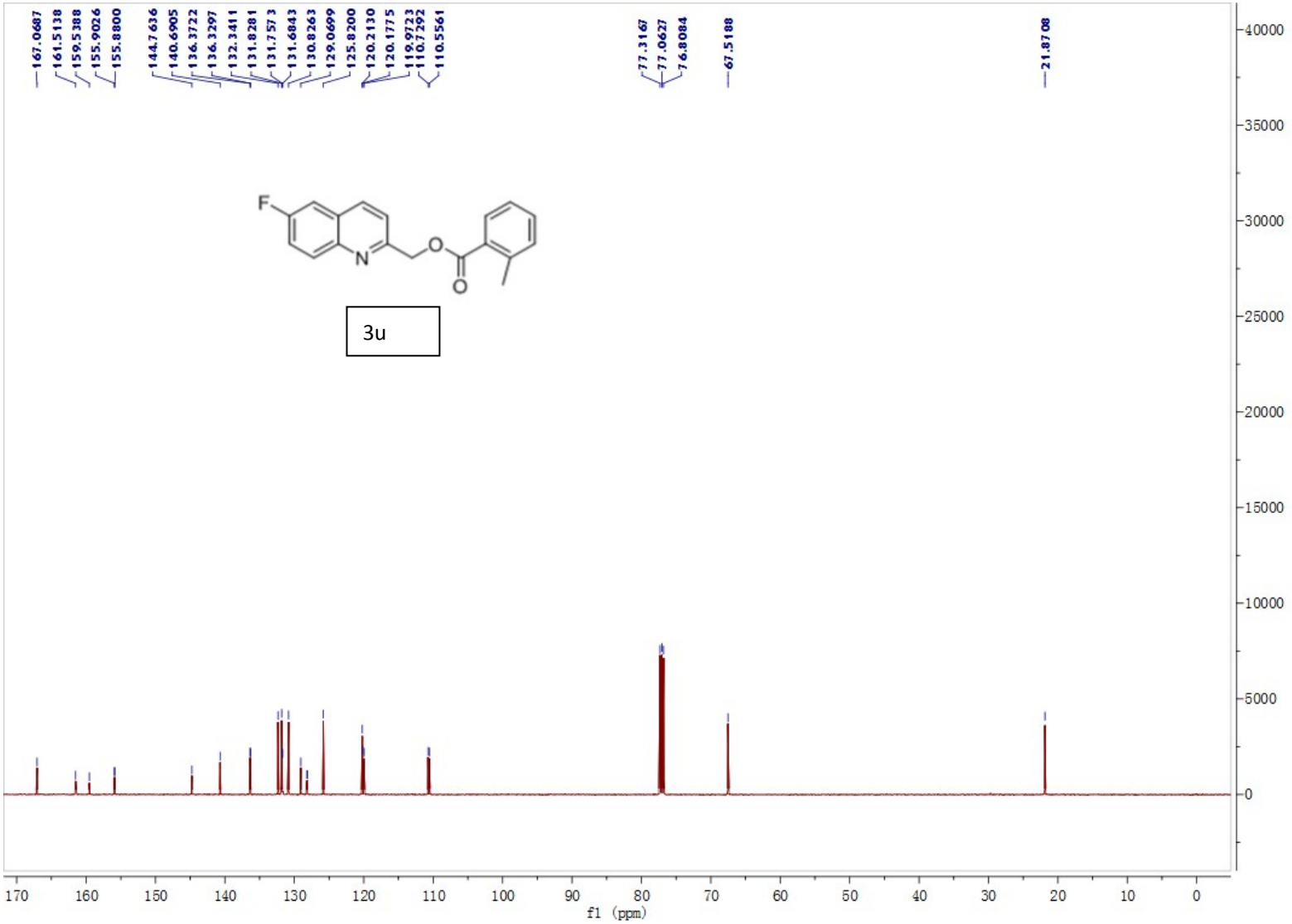
8.1216
8.0524
8.0383
7.5863
7.5692
7.5087
7.4971
7.4916
7.4736
7.4418
7.4370
7.4248
7.4100
7.4078
7.2770
7.2604
7.2496
5.6122
2.6404
F
N
O
O
3u
1.04
1.93
0.99
1.02
1.99
2.16
2.03
3.00
f1 (ppm)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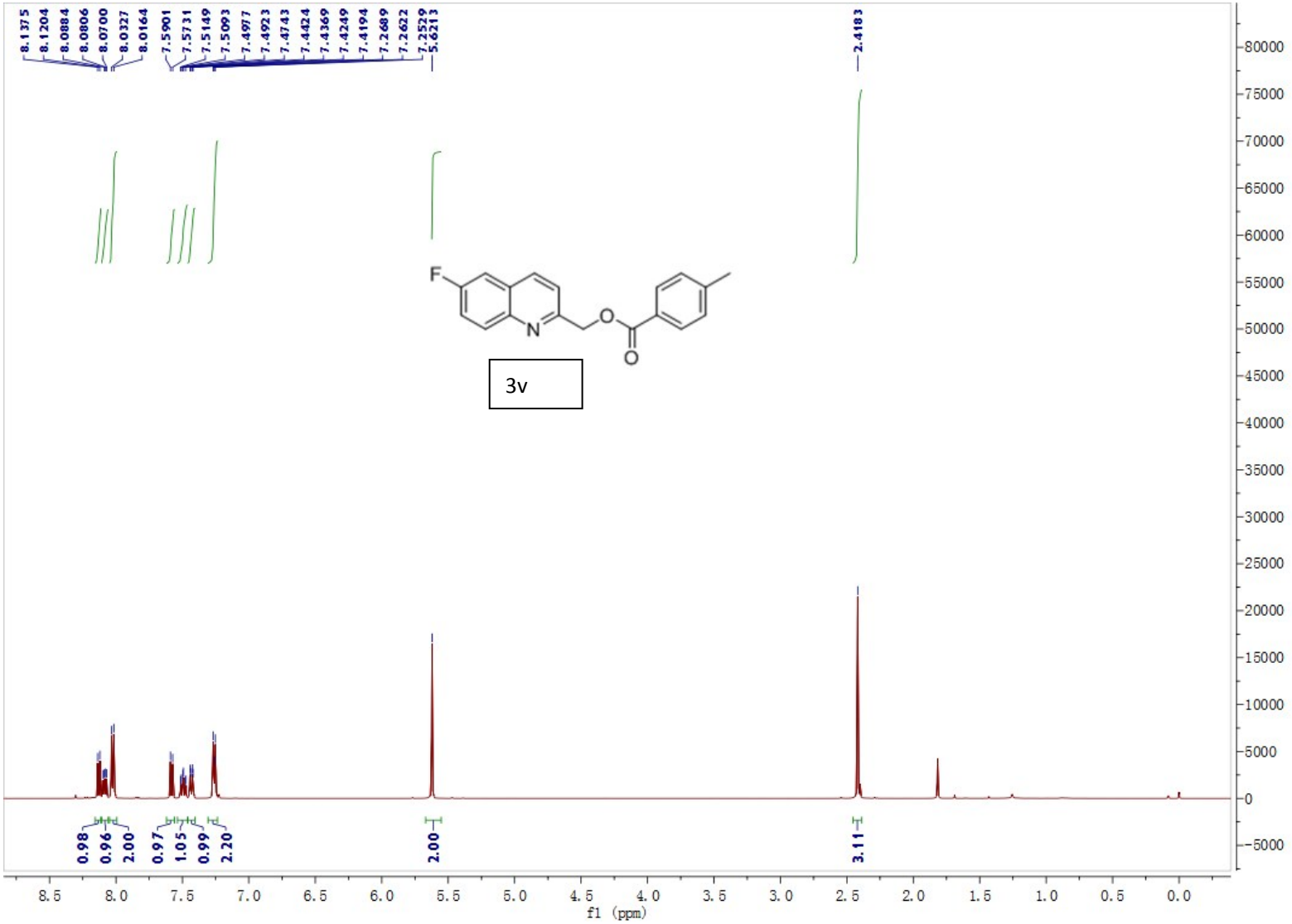
159.5388
155.9026
155.8800
144.7636
140.6905
136.3722
136.3297
132.3411
131.8281
131.7573
131.6843
130.8263
129.0699
125.8200
120.2130
120.1775
119.9723
110.7292
110.5561
77.3167
77.0627
76.8084
67.5188
21.8708
F
N
O
O
3u
40000
35000
30000
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.1204
8.0884
8.0806
8.0700
8.0327
8.0164
7.5901
7.5731
7.5149
7.5093
7.4977
7.4923
7.4743
7.4424
7.4369
7.4249
7.4194
7.2689
7.2622
7.2529
5.6213
2.4183
F
N
O
O
3v
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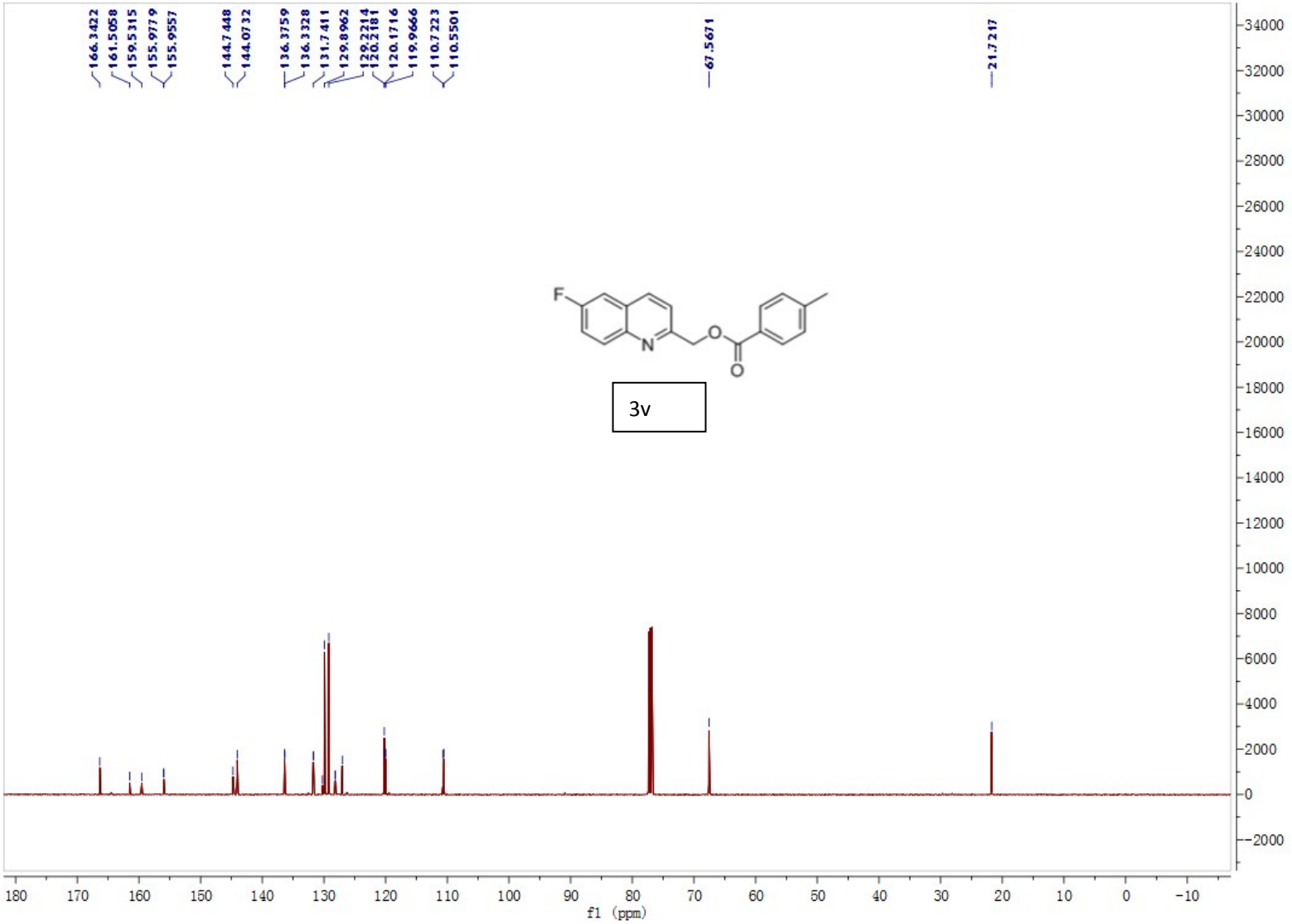
0.96
2.00
0.97
1.05
0.99
2.20
2.00
3.11
f1 (ppm)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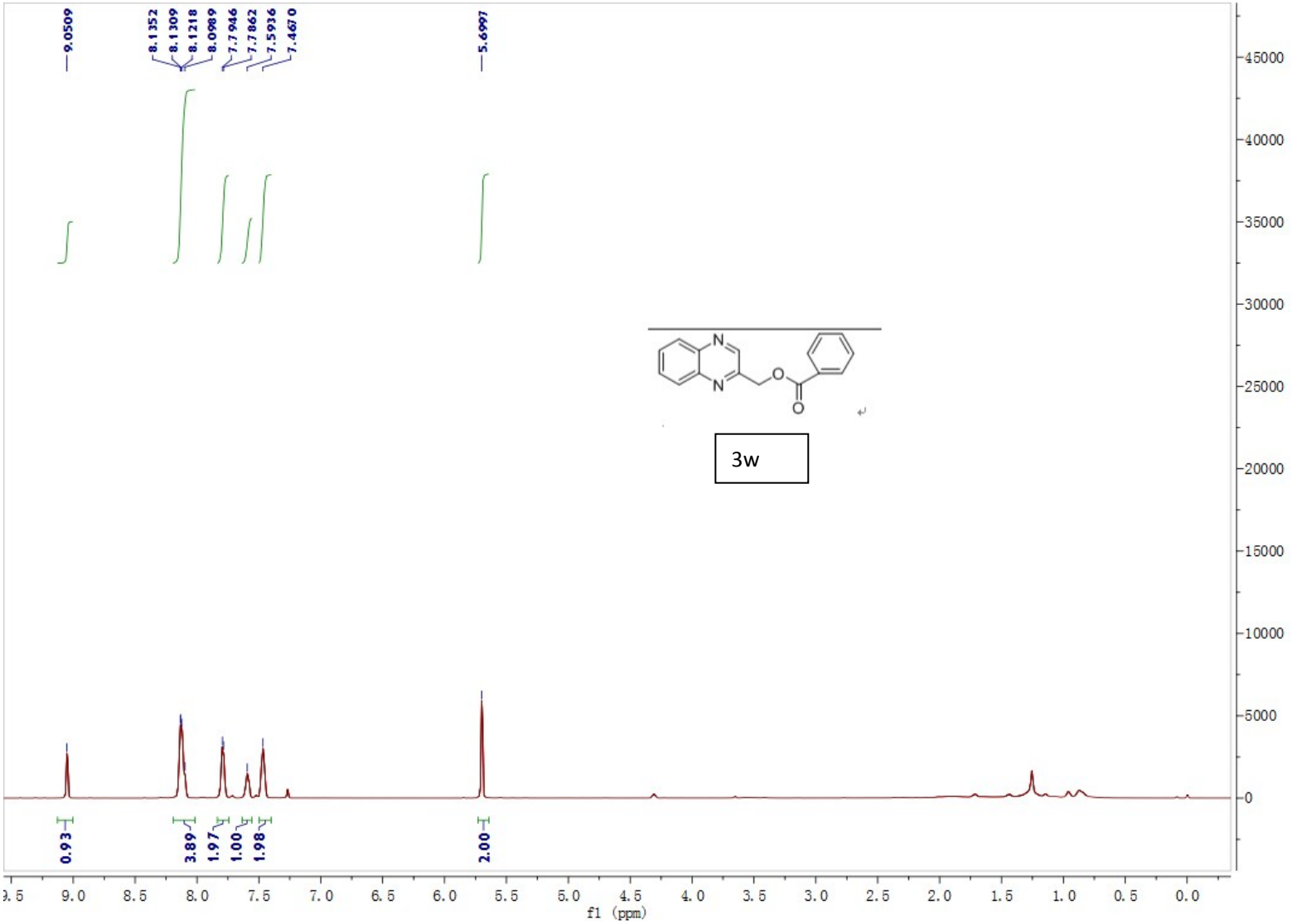
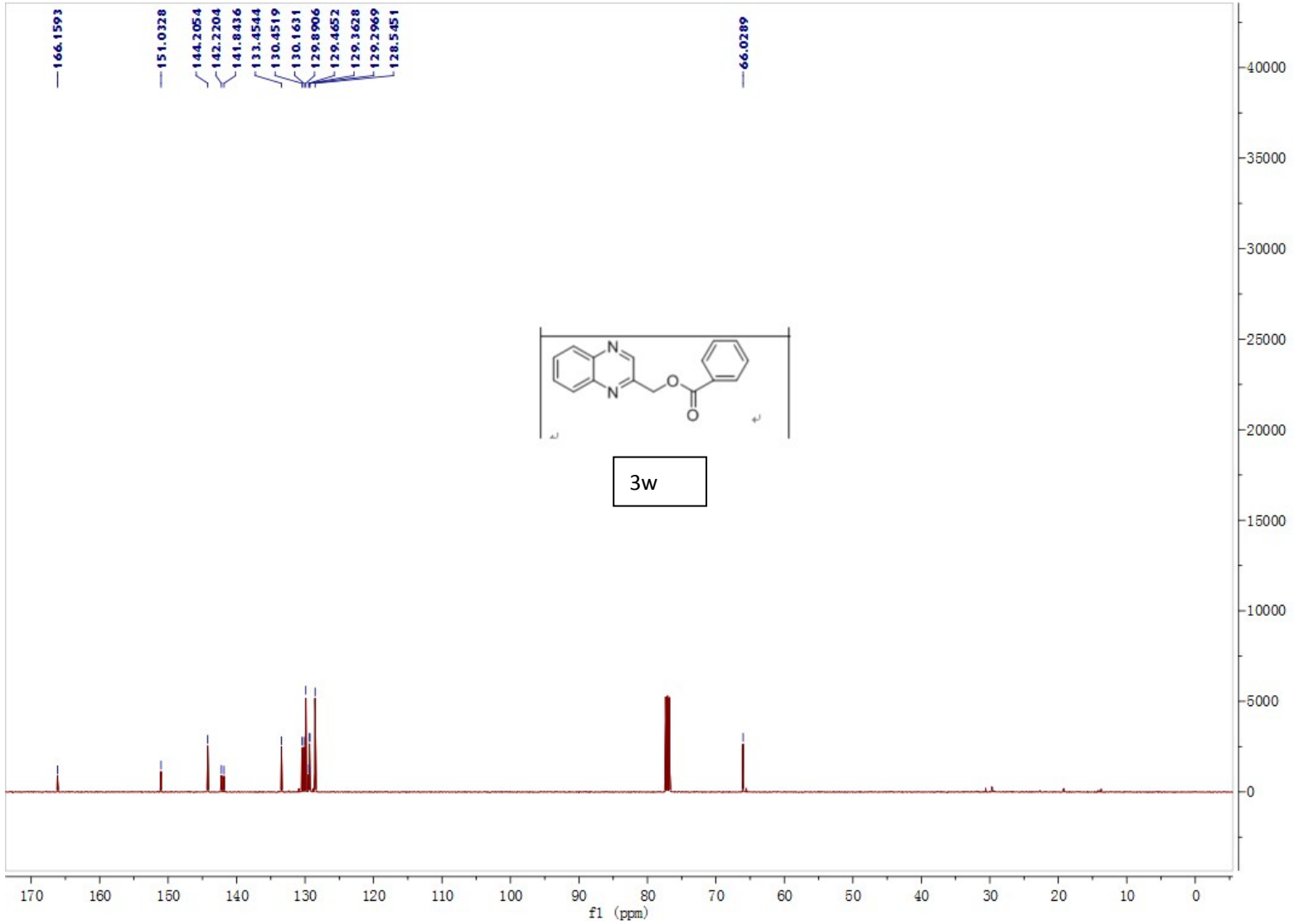
159.5315
155.9779
155.9557
144.7448
144.0732
136.3759
136.3328
131.7411
129.8962
129.2214
120.2181
120.1716
119.9666
110.7223
110.5501
67.5671
21.7217
F
N
O
O
3v
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.0509
8.1352
8.1309
8.1218
8.0989
7.7946
7.7862
7.5936
7.4670
5.6997
3w
0.93
3.89
1.97
1.00
1.98
2.00
f1 (ppm)


166.1593
151.0328
144.2054
142.2204
141.8436
133.4544
130.4519
130.1631
129.8906
129.4652
129.3628
129.2969
128.5451
66.0289
N
N
O
O
3w
40000
35000
30000
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)