Supporting Information

Metal-free C3-H acylation of quinoxalin-2(1*H*)-ones with α-oxo-carboxylic acids

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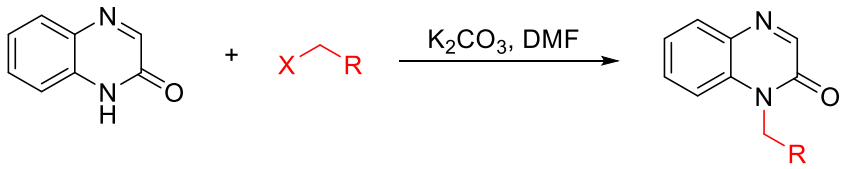
1 General Procedure.

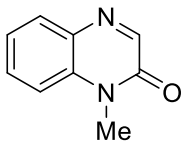
^{1}H NMR spectra were recorded on a Bruker DPX600 spectrometer at 600 MHz or a Bruker DPX500 spectrometer at 500 MHz. ^{13}C NMR spectra were recorded on a Bruker DPX600 spectrometer at 600 MHz or a Bruker DPX500 spectrometer at 151 MHz or 125 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts. HRMS spectra were obtained on a Thermo Q Exactive spectrometer. Melting points (MP) were determined by SGW X-4A. Compounds **1b-1i** and **2b-2k** were prepared using literature methods.[1,5,7] All other chemicals were purchased from Chemical Co. and used as received unless otherwise specified.

2 General procedure for the synthesis of starting materials (1b-1g).[1]



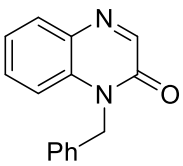
A typical procedure: To a stirred solution of quinoxalin-2(*1H*)-ones (3 mmol) in DMF (10 mL) was added the corresponding halide (1.6 equiv.) and potassium carbonate (1.2 equiv.) at room temperature overnight. Then the resulting mixture was added with water, and extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product **1b** to **1g**.

1-Methylquinoxalin-2(1*H*)-one (1b):



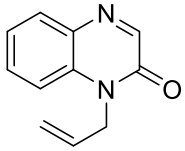
White solid. Yield: 73%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.24 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H) (aromatic *H*), 3.61 (s, 3H) (C*H*$_3$). ^{13}C NMR (151 MHz, DMSO-d_6): δ 154.31 (*C*O), 150.04, 133.11, 132.63, 131.05, 129.53, 123.42, 114.84 (aromatic *C*), 28.54 (*C*H$_3$). This is a known structure. These data are similar to the reported one.[2]

1-Benzylquinoxalin-2(1*H*)-one (1c):



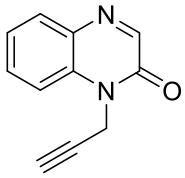
White solid. Yield: 68%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.36 (s, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.28 – 7.24 (m, 3H) (aromatic *H*), 5.49 (s, 2H) (C*H*$_2$). ^{13}C NMR (151 MHz, DMSO-d_6): δ 154.51 (*C*O), 150.35, 135.69, 132.98, 132.24, 131.04, 129.84, 128.71, 127.37, 126.80, 123.63, 115.21 (aromatic *C*), 44.45 (*C*H$_2$). This is a known structure. These data are similar to the reported one.[2]

1-Allylquinoxalin-2(1*H*)-one (1d):



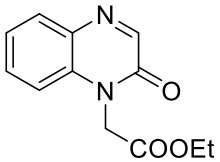
White solid. Yield: 66%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.28 (s, 1H), 7.85 (dd, J = 7.9, 1.2 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.41 – 7.36 (m, 1H) (aromatic *H*), 5.98 – 5.90 (m, 1H), 5.17 (dd, J = 10.5, 1.5 Hz, 1H), 5.05 (dd, J = 17.3, 1.5 Hz, 1H) (olefinic *H*), 4.90 – 4.84 (m, 2H) (CH_2). ^{13}C NMR (151 MHz, DMSO-d_6): δ 153.96 (*C*O), 150.20, 132.85, 132.20, 131.43, 131.01, 129.75, 123.52 (aromatic *C*), 117.11, 115.20 (olefinic *C*), 43.36 (*C*H$_2$). This is a known structure. These data are similar to the reported one.[2]

1-(2-Propynyl)quinoxalin-2(1*H*)-one (1e):



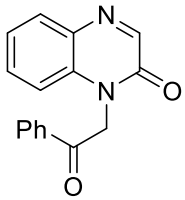
Yellow solid. Yield: 79%. MP: 162.2-163.8 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.29 (s, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H) (aromatic *H*), 5.07 (d, J = 2.5 Hz, 2H) (CH_2), 3.36 (t, J = 2.4 Hz, 1H) (alkynyl *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 153.32 (*C*O), 150.04, 132.83, 131.45, 131.18, 129.82, 123.91, 115.08 (aromatic *C*), 77.83, 75.25 (alkynyl *C*), 30.83 (*C*H$_2$). HRMS (ESI): *m/z* calcd for $C_{11}H_8N_2O$ $[M+H]^+$: 185.0709. Found: 185.0708. This is a known structure without NMR spectra.[3]

Ethyl 2-(2-oxoquinoxalin-1(2*H*)-yl)acetate (1f):



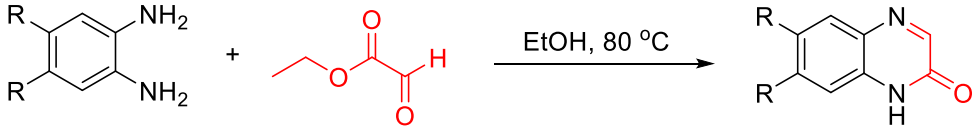
White solid. Yield: 66%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.32 (s, 1H), 8.01 – 7.78 (m, 1H), 7.71 – 7.62 (m, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.46 – 7.33 (m, 1H) (aromatic *H*), 5.10 (s, 2H) , 4.17 (q, J = 7.1 Hz, 2H) (CH_2), 1.21 (t, J = 7.1 Hz, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 167.39, 154.06 (*C*O), 149.81, 132.65, 132.40, 131.30, 129.87, 123.85, 114.72 (aromatic *C*), 61.44, 43.23 (*C*H$_2$), 13.99 (*C*H$_3$). This is a known structure. These data are similar to the reported one.[3]

1-Acetophenylquinoxalin-2(1*H*)-one (1g):



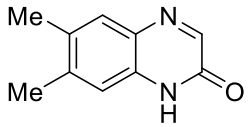
Yellow solid. Yield: 65%. MP: 178.1-182.1 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.35 (s, 1H), 8.15 (d, J = 7.5 Hz, 2H), 7.90 (dd, J = 8.0, 1.5 Hz, 1H), 7.77 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H) (aromatic *H*), 5.93 (s, 2H) (CH_2).^{13}C NMR (151 MHz, DMSO-d_6): δ 192.18, 154.17(*C*O), 149.77, 134.37, 134.29, 132.83, 132.73, 131.21, 129.80, 128.97, 128.33, 123.67, 115.02 (aromatic *C*), 48.63 (*C*H$_2$). HRMS (ESI): *m/z* calcd for $C_{16}H_{12}N_2O_2$ $[M+H]^+$: 265.0972. Found: 265.0971. This is a known structure without NMR spectra.[4]

3 General procedure for the synthesis of starting materials (1h-1i).[5]



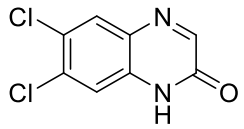
To ethanol (8 ml) suspension solution of *o*-arylenediamine (2 mmol) was added ethyl 2-oxoacetate (2.4 equiv, 50% toluene solution). The reaction system was stirred and heated to refluxing at 80 °C for 1 h, Then the reaction was cooled. The precipitate was filtered and washed with ethanol, and finally dried to give quinoxalin-2(*1H*)-one **1h-1i**.

6,7-Dimethylquinoxalin-2(1*H*)-one (1h):



Brown solid. Yield: 73%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.30 (s, 1H) (N*H*), 8.06 (s, 1H), 7.54 (s, 1H), 7.06 (s, 1H) (aromatic *H*), 2.30 (s, 3H), 2.28 (s, 3H) (CH_3). ^{13}C NMR was unable to be collected due to low solubility. This is a known structure. These data are similar to the reported one.[6]

6,7-Dichloroquinoxalin-2(1*H*)-one (1i):

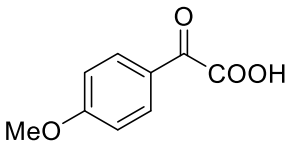


Brown solid. Yield: 75%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.55 (s, 1H) (N*H*), 8.21 (s, 1H), 8.12 – 7.93 (m, 1H), 7.73 – 7.20 (m, 1H) (aromatic *H*). ^{13}C NMR was unable to be collected due to low solubility. This is a known structure. These data are similar to the reported one.[6]

4 General procedure for the synthesis of starting materials (2b-2k).[7]

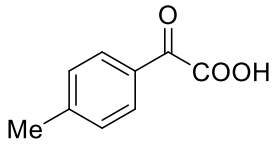
In a dry, 35mL Schlenk tube equipped with a stir bar was added selenium dioxide (SeO_2, 1.5 equiv). Then under an atmosphere of nitrogen, the substituted aryl-methylketone (3.0 mmol) were added followed by anhydrous pyridine (10 mL). The reaction mixture was heated in an oil bath to 110 ^{o}C for 4 h. Then the solution containing precipitated selenium was filtered, and the residue was washed with ethyl acetate. Pyridine was removed on a rotary evaporator, and the residue was treated with 1 N NaOH (3 mL) and water (20 mL). The resulting aqueous layer was extracted with ethyl acetate (3*20 mL). The aqueous layers were acidified using 1N HCl (4.0 mL), and water (20 mL) was added. The mixture was extracted with ethyl acetate (3*20 mL), and the combined organic layers were dried (anhydrous Na_2SO_4), and concentrated on a rotary evaporator. The crude arylglyoxylic acid products were purified by silica-gel column chromatography using ethyl acetate and petrol ether as solvent system for elution or used directly without purification.

2-(4-Methoxyphenyl)-2-oxoacetic acid (2b):



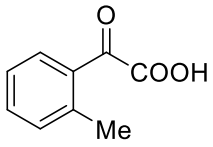
White solid. Yield: 80%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.90 (d, J = 7.7 Hz, 2H), 7.53 – 6.64 (m, 2H) (aromatic *H*), 3.88 (s, 3H) (OCH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 187.17 (*C*O), 166.54 (*C*OOH), 164.72, 132.06, 124.75, 114.75 (aromatic *C*), 55.85 (O*C*H$_3$). This is a known structure. These data are similar to the reported one.[8]

2-Benzyl-2-oxoacetic acid (2c):



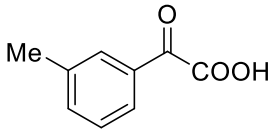
White solid. Yield: 71%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.83 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H) (aromatic H), 2.41 (s, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 188.34 (CO), 166.35 (COOH), 146.11, 129.90, 129.60, 129.46 (aromatic C), 21.42 (CH$_3$). This is a known structure. These data are similar to the reported one.[9]

2-(2-Methyl)phenyl-2-oxoacetic acid (2d):



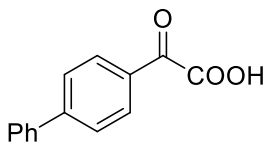
Yellow oil. Yield: 92%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.71 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.45 – 7.39 (m, 2H) (aromatic H), 2.53 (s, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 190.98 (CO), 166.58 (COOH), 140.05, 133.84, 132.33, 131.99, 130.91, 126.39 (aromatic C), 20.81 (CH$_3$). This is a known structure. These data are similar to the reported one.[9]

2-(3-Methylphenyl)-2-oxoacetic acid (2e):



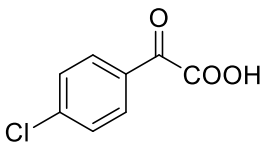
White solid. Yield: 87%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.73 (s, 2H), 7.59 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H) (aromatic H), 2.40 (s, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 188.93 (CO), 166.32 (COOH), 138.92, 135.88, 131.96, 129.55, 129.23, 126.88 (aromatic C), 20.79 (CH$_3$). This is a known structure. These data are similar to the reported one.[8]

2-Biphenyl-2-oxoacetic acid (2f):



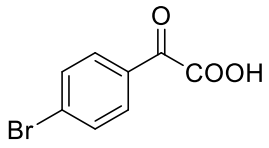
White solid. Yield: 77%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.02 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 7.3 Hz, 1H) (aromatic H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 188.17 (CO), 166.11 (COOH), 146.40, 138.51, 130.72, 130.24, 129.21, 128.86, 127.47, 127.18 (aromatic C). This is a known structure. These data are similar to the reported one.[10]

2-(4-Chlorophenyl)-2-oxoacetic acid (2g):



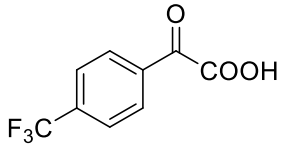
White solid. Yield: 60%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.96 (d, J = 8.4 Hz, 2H), 7.69 (m, 2H) (aromatic H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 187.36 (CO), 165.49 (COOH), 140.11, 131.41, 130.79, 129.49 (aromatic C). This is a known structure. These data are similar to the reported one.[9]

2-(4-bromophenyl)-2-oxoacetic acid (2h):



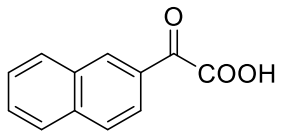
White solid. Yield: 86%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.88 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H) (aromatic H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 187.57 (CO), 165.45 (COOH), 132.43, 131.41, 131.09, 129.45 (aromatic C). This is a known structure. These data are similar to the reported one.[8]

2-oxo-2-(4-(trifluoromethyl)phenyl)acetic acid (2i):



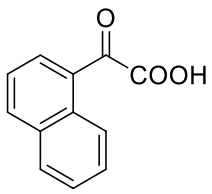
White solid. Yield: 67%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.16 (d, J = 8.1 Hz, 2H), 7.98 (d, J = 8.1 Hz, 2H) (aromatic H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 187.44 (CO), 164.97 (COOH), 135.44, 133.87 (d, $^3J_{C\text{-}F}$ = 32.3 Hz), 130.46, 126.15 (q, $^4J_{C\text{-}F}$ = 3.7 Hz), 123.58 (d, $^2J_{C\text{-}F}$ = 272.9 Hz) (aromatic C). This is a known structure. These data are similar to the reported one.[8]

2-(β-naphthoyl)acetic acid (2j):



Yellow solid. Yield: 94%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.60 (s, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.96 (dd, J = 8.6, 1.6 Hz, 1H), 7.75 (t, J = 7.1 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H) (aromatic H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 188.78 (CO), 166.26 (COOH), 135.86, 132.88, 131.98, 130.04, 129.80, 129.31, 129.19, 127.92, 127.48, 123.39 (aromatic C). This is a known structure. These data are similar to the reported one.[11]

2-(α-naphthoyl)acetic acid (2k):

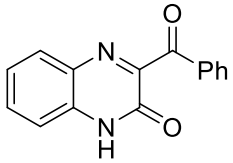


Yellow solid. Yield: 65%. ^{1}H NMR (600 MHz, DMSO-d_6): δ ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.91 (d, J = 8.6 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.82 – 7.55 (m, 3H). (aromatic H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.28 (CO), 166.53 (COOH), 135.81, 134.13, 133.62, 130.12, 129.33, 129.11, 127.54, 127.12, 125.04, 124.76 (aromatic C). This is a known structure. These data are similar to the reported one.[12]

5 General procedure for the synthesis of product (3a-3t).

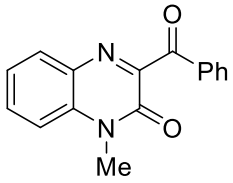
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2.0 equiv) and PIDA (0.45 mmol, 1.5 equiv). Then, the resulting mixture was evacuated, and purged with nitrogen for 3 times. The reaction mixture was stirred at 80 ^{o}C for 0.5 h - 1.5 h. After that, 20 mL sat. $NaHCO_3$ aq. was added to the reaction mixture, and the resulting solution was extracted with ethyl acetate (20 mL* 3). The combined organic phase was dried over Na_2SO_4, and then removed under reduced pressure with a rotary evaporator. The crude residue was purified by silica gel column chromatography with ethyl acetate and petrol ether or dichloromethane and ethyl acetate as eluent to give the pure product **3**.

3-Benzoylquinoxalin-2(1*H*)-one (3a):



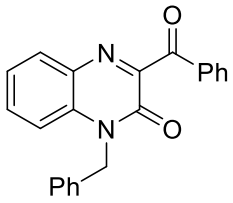
Yellow solid. Yield: 87%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.87 (s, 1H) (N*H*), 7.97 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.4 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 8.2 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H) (aromatic *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.49, 156.30 (*C*O), 153.42, 134.66, 134.59, 132.71, 131.79, 131.25, 129.69, 129.14, 129.06, 123.86, 115.94 (aromatic *C*). This is a known structure. These data are similar to the reported one.[3]

3-Benzoyl-1-methylquinoxalin-2(1*H*)-one (3b):



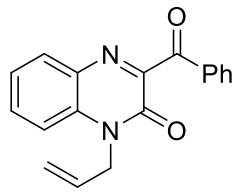
Pale yellow solid. Yield: 87%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.98 – 7.96 (m, 2H), 7.89 (dd, J = 8.0, 1.5 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.70 (d, J = 8.5 Hz, 1H), 7.57 (t, J = 7.9 Hz, 2H), 7.48 – 7.45 (m, 1H) (aromatic *H*), 3.67 (s, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.28, 154.82 (*C*O), 152.89, 134.67, 134.46, 133.94, 132.03, 131.72, 129.90, 129.72, 129.03, 123.98, 115.25 (aromatic *C*), 28.99 (*C*H$_3$). This is a known structure. These data are similar to the reported one.[3]

3-Benzoyl-1-benzylquinoxalin-2(1*H*)-one (3c):



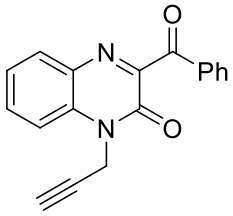
Yellow solid. Yield: 88%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.04 (d, J = 7.9 Hz, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.1 Hz, 1H), 7.59 (m, 3H), 7.44 (t, J = 7.6 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.28 (t, J = 6.6 Hz, 1H) (aromatic *H*), 5.54 (s, 2H) (CH_2). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.07, 154.86 (*C*O), 153.07, 135.47, 134.74, 134.45, 133.09, 132.09, 132.03, 130.24, 129.81, 129.08, 128.80, 127.50, 126.89, 124.20, 115.53 (aromatic *C*), 45.00 (*C*H$_2$). This is a known structure. These data are similar to the reported one.[3]

1-Allyl-3-benzoylquinoxalin-2(1*H*)-one (3d):



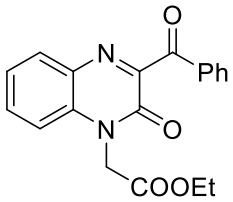
Yellow solid. Yield: 69%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.99 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.9 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.63 (d, J = 8.5 Hz, 1H), 7.58 (t, J = 7.8 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H) (aromatic *H*), 6.01 – 5.95 (m, 1H), 5.24 – 5.16 (m, 2H) (olefinic *H*), 4.93 (d, J = 5.3 Hz, 2H) (CH_2). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.14, 154.79 (*C*O), 152.51, 134.72, 134.45, 133.04, 132.02, 131.91, 131.33, 130.11, 129.76, 129.06 (aromatic *C*), 124.08, 117.46, 115.54 (olefinic *C*), 43.90 (*C*H$_2$). This is a known structure. These data are similar to the reported one.[3]

3-Benzoyl-1-(2-propynyl)quinoxalin-2(1*H*)-one (3e):



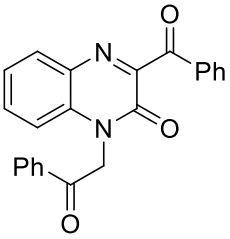
Yellow solid. Yield: 79%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.07 – 7.94 (m, 2H), 7.92 (dd, J = 8.0, 1.3 Hz, 1H), 7.87 – 7.80 (m, 1H), 7.77 – 7.70 (m, 2H), 7.58 (t, J = 7.8 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H) (aromatic *H*), 5.13 (d, J = 2.5 Hz, 2H) (CH_2), 3.43 (t, J = 2.5 Hz, 1H) (alkynyl *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.80, 154.58 (*C*O), 151.95, 134.81, 134.31, 132.31, 132.24, 131.86, 130.21, 129.81, 129.08, 124.47, 115.41 (aromatic *C*), 77.66, 75.64 (alkynyl *C*), 31.35 (*C*H$_2$). This is a known structure. These data are similar to the reported one.[3]

Ethyl 2-(3-benzoyl-2-oxoquinoxalin-1(2*H*)-yl)acetate (3f):



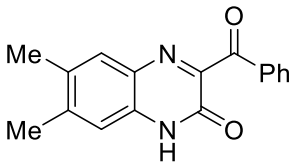
Yellow solid. Yield: 90%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.94 (d, J = 8.0 Hz, 3H), 7.81 – 7.71 (m, 2H), 7.69 (d, J = 8.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H) (aromatic *H*), 5.18 (s, 2H), 4.19 (q, J = 7.1 Hz, 2H) (CH_2), 1.22 (t, J = 7.1 Hz, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.72, 167.22, 154.39 (*C*O), 152.61, 134.85, 134.31, 133.17, 132.39, 131.68, 130.27, 129.64, 129.14, 124.45, 115.09 (aromatic *C*), 61.58 (*C*H$_2$), 43.67, 14.00 (*C*H$_3$). This is a known structure. These data are similar to the reported one.[3]

1-Acetylphenyl-3-benzoylquinoxalin-2(1*H*)-one (3g):



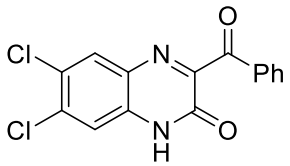
Yellow solid. Yield: 79%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.17 – 8.15 (m, 2H), 7.97 – 7.95 (m, 3H), 7.78 – 7.74 (m, 2H), 7.72 – 7.70 (m, 1H), 7.66 – 7.58 (m, 5H), 7.47 – 7.50 (m, 1H) (aromatic *H*), 6.01 (s, 2H) (CH_2). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.03, 191.85, 154.37 (*C*O), 152.67, 134.81, 134.37, 134.29, 133.59, 132.30, 131.76, 130.20, 129.60, 129.15, 129.00, 128.40, 124.31, 115.39 (aromatic *C*), 49.08 (*C*H$_2$). This is a known structure. These data are similar to the reported one.[3]

3-Benzoyl-6,7-dimethylquinoxalin-2(1*H*)-one (3h):



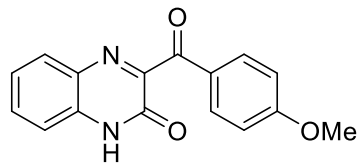
White solid. Yield: 77%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.75 (s, 1H) (N*H*), 7.93 (d, J = 8.3 Hz, 2H), 7.73 (t, J = 7.8 Hz, 1H), 7.60 (s, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.16 (s, 1H) (aromatic *H*), 2.36 (s, 3H), 2.30 (s, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.58, 154.80 (*C*O), 153.46, 141.80, 134.78, 134.50, 132.77, 130.77, 129.75, 129.62, 129.00, 128.83, 115.81 (aromatic *C*), 19.95, 18.87 (CH_3). This is a known structure. These data are similar to the reported one.[3]

3-Benzoyl-6,7-dichloroquinoxalin-2(1*H*)-one (3i):



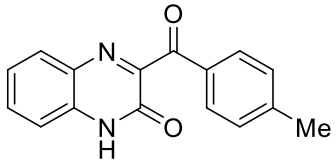
Yellow solid. Yield: 71%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 13.00 (s, 1H) (N*H*), 8.17 (s, 1H), 8.00 (d, J = 7.3 Hz, 2H), 7.75 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.9 Hz, 2H), 7.55 (s, 1H) (aromatic *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.86, 157.66 (*C*O), 153.07, 134.87, 134.29, 133.81, 132.67, 130.72, 130.13, 129.79, 129.06, 125.61, 116.93 (aromatic *C*). This is a known structure. These data are similar to the reported one.[13]

3-(4-Methoxybenzoyl)-quinoxalin-2(1*H*)-one (3j):



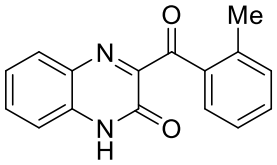
White solid. Yield: 93%. MP: 242.7-243.5 ºC. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.81 (s, 1H) (N*H*), 7.93 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 7.9 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.53 – 7.27 (m, 2H), 7.08 (d, J = 8.8 Hz, 2H) (aromatic *H*), 3.87 (s, 3H) (CH_3).^{13}C NMR (151 MHz, DMSO-d6): δ 190.75, 164.27 (*C*O), 156.65, 153.39, 132.63, 132.19, 131.55, 131.21, 129.03, 127.59, 123.75, 115.85, 114.34 (aromatic *C*), 55.74 (O*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{16}H_{12}N_2O_3$ $[M+H]^+$: 281.0921. Found: 281.0914.

3-(4-Methylbenzoyl)-quinoxalin-2(1*H*)-one (3k):



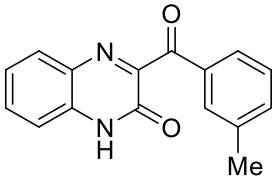
Yellow solid. Yield: 71%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.84 (s, 1H) (N*H*), 7.85 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.44 – 7.30 (m, 4H) (aromatic *H*), 2.41 (s, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.99, 156.50 (*C*O), 153.39, 145.39, 132.67, 132.20, 131.67, 131.23, 129.80, 129.59, 129.09, 123.81, 115.91 (aromatic *C*), 21.37 (*C*H$_3$). This is a known structure. These data are similar to the reported one.[14]

3-(2-methylbenzoyl)-quinoxalin-2(1*H*)-one (3l):



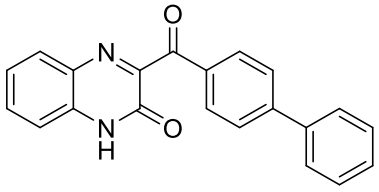
White solid. Yield: 84%. MP: 202.1-204.6 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) : δ 12.84 (s, 1H) (N*H*), 7.81 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.32 (d, J = 7.5 Hz, 1H) (aromatic *H*), 2.57 (s, 3H) (CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 194.35, 156.99 (*C*O), 153.28, 139.43, 133.94, 133.23, 132.65, 132.43, 132.10, 131.70, 131.14, 129.09, 126.13, 123.82, 115.86 (aromatic *C*), 21.13 (*C*H$_3$). HRMS (ESI): m/z calcd for $C_{16}H_{12}N_2O_2$ $[M+H]^+$: 265.0972. Found: 265.0966.

3-(3-Methylbenzoyl)-quinoxalin-2(1*H*)-one (3m):



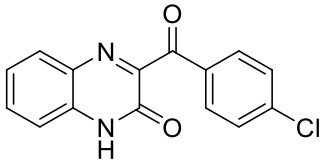
Yellow solid. Yield: 64%. MP: 182.0-182.7 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.84 (s, 1H) (N*H*), 7.83 (d, *J* = 7.9 Hz, 1H), 7.78 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.34 (m, 2H) (aromatic *H*), 2.37 (s, 3H) (C*H*$_3$). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.63, 156.49 (*C*O), 153.37, 138.58, 135.27, 134.65, 132.67, 131.66, 131.24, 129.87, 129.10, 128.89, 126.90, 123.79, 115.90 (aromatic *C*), 20.71 (*C*H$_3$). HRMS (ESI): m/z calcd for $C_{16}H_{12}N_2O_2$ $[M+H]^+$: 265.0972. Found: 265.0966. This is a known structure. These data are similar to the reported one.[15]

3-(1-Biphenylcarbonyl)quinoxalin-2(1*H*)-one (3n):



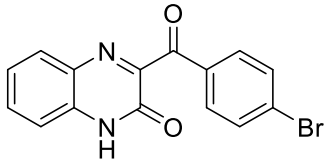
Yellow solid. Yield: 71%. MP: 287.3-290 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.88 (s, 1H) (N*H*), 8.05 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.48 – 7.36 (m, 3H) (aromatic *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.98, 156.27 (*C*O), 153.43, 145.93, 138.72, 133.43, 132.74, 131.79, 131.27, 130.41, 129.16, 128.69, 127.24, 127.16, 123.85, 115.94 (aromatic *C*). HRMS (ESI): m/z calcd for $C_{21}H_{14}N_2O_2$ $[M+H]^+$: 327.1128. Found: 327.1121.

3-(4-Chlorobenzoyl)-quinoxalin-2(1*H*)-one (3o):



Yellow solid. Yield: 35%. MP: 250.4-252.1 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.87 (s, 1H) (N*H*), 8.01 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.64 (m, 3H), 7.42 – 7.35 (m, 2H) (aromatic *H*). ^{13}C NMR (126 MHz, DMSO-d_6): δ 191.39, 155.66 (*C*O), 153.40, 139.66, 133.32, 132.82, 131.94, 131.58, 131.26, 129.23, 129.20, 123.87, 115.93 (aromatic *C*). HRMS (ESI): m/z calcd for $C_{15}H_9ClN_2O_2$ $[M+H]^+$: 285.0425. Found: 285.0424. This is a known structure without spectra.[16]

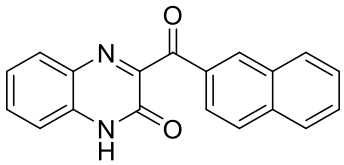
3-(4-Bromobenzoyl)-quinoxalin-2(1*H*)-one (3p):



Pale yellow solid. Yield: 43%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.88 (s, 1H) (N*H*), 7.93 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.32 (m, 2H) (aromatic *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.61, 155.62 (*C*O), 153.39, 133.64, 132.81, 132.17, 131.95, 131.60, 131.25, 129.20, 128.99, 123.87, 115.93 (aromatic *C*). This is a known structure.

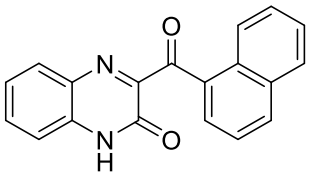
These data are similar to the reported one.[14]

3-(β-naphthoyl)-quinoxalin-2(1*H*)-one (3r):



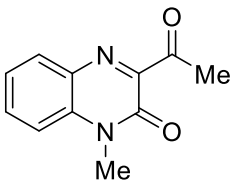
Yellow solid. Yield: 24%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.90 (s, 1H) (N*H*), 8.63 (s, 1H), 8.17 – 8.08 (m, 2H), 8.07 – 7.99 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H) (aromatic *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.60, 156.56 (*C*O), 153.54, 135.65, 133.32, 132.80, 132.12, 131.99, 131.72, 131.40, 129.84, 129.45, 129.19, 128.84, 127.84, 127.20, 123.82, 123.48, 115.93 (aromatic *C*). HRMS (ESI): m/z calcd for $C_9H_{12}N_2O_2$ $[M+H]^+$: 301.0965. Found: 301.0972.

3-(α-Naphthoyl)-quinoxalin-2(1*H*)-one (3s):



Yellow solid. Yield: 70%. MP: decomposed. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.88 (s, 1H) (N*H*), 9.01 (d, *J* = 8.6 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.08 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.72 – 7.64 (m, 2H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.33 (m, 1H) (aromatic *H*).^{13}C NMR (151 MHz, DMSO-d_6): δ 194.45, 157.05 (*C*O), 153.47, 135.05, 134.13, 133.60, 132.77, 131.72, 131.24, 130.69, 130.10, 129.15, 129.02, 128.92, 126.89, 125.12, 124.94, 123.82, 115.87 (aromatic *C*). HRMS (ESI): m/z calcd for $C_9H_{12}N_2O_2$ $[M+H]^+$: 301.0965. Found: 301.0972.

1-methyl-3-methoxyquinoxalin-2(1*H*)-one (3t):

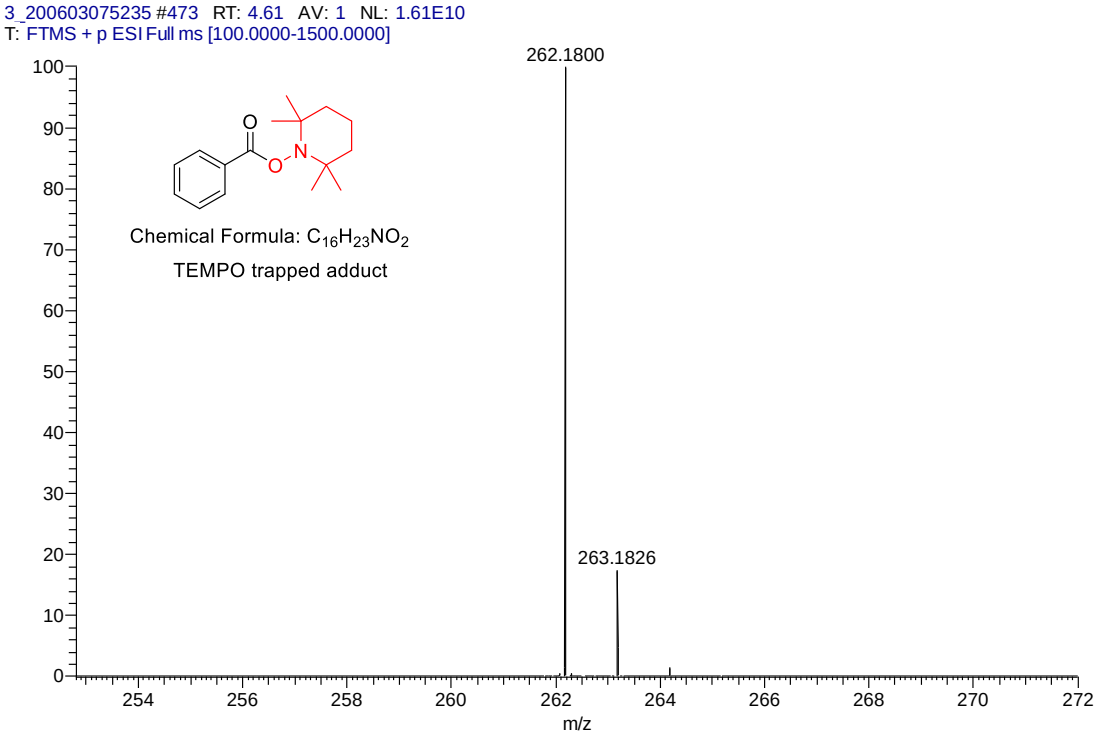


Yellow solid. Yield: 36%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 – 7.68 (m, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.32 (m, 1H) (aromatic *H*), 3.64 (s, 3H), 2.58 (s, 3H) (C*H*$_3$). ^{13}C NMR (151 MHz, DMSO-d_6): δ 198.67, 152.93 (*C*O), 152.24, 134.18, 132.48, 131.22, 130.23, 123.94, 115.08 (aromatic *C*), 28.90, 28.55 (*C*H$_3$). This is a known structure. These data are similar to the reported one.[13]

6 Radical trapping experiment.

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2.0 equiv), PIDA (0.45 mmol, 1.5 equiv) and TEMPO (1 equiv or 2 equiv). Then, the resulting mixture was evacuated, and purged with nitrogen for 3 times. The reaction mixture was stirred at 80 ^{o}C for 0.5 h. Then the reaction mixture was concentrated, and analyzed by HRMS.

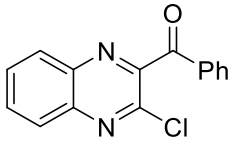
Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
$C_{16}H_{23}NO_2$	$[M+H]^+$	262.1800	262.1802	-0.76



7 **Synthesis of potential antitumor agent.**[16]

A mixture of **3a** (0.5 mmol) and an excess of $POCl_3$ (1.25 mmol) was stirred under heating at 120 °C for 3 h. On cooling, the mixture was taken up with ice, and the aqueous solution was extracted with ethyl acetate for three times. The combined organic phase was dried over Na_2SO_4, and then removed under reduced pressure with a rotary evaporator. The crude residue was purified by silica gel column chromatography with ethyl acetate and petrol ether as eluent to give the pure product **4a** as a yellow solid.

3-Benzoyl-2-chloroquinoxaline (4a):

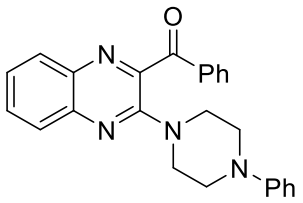


Yellow solid. Yield: 76%. ^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.17 – 8.10 (m, 2H), 8.93 – 7.88 (m, 3H), 7.86 (t, J = 7.5 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H) (aromatic *H*). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.32 (*C*O), 149.89, 142.89, 141.67, 139.30, 135.16, 134.26, 132.81, 131.65, 130.38, 129.21, 129.16, 128.21 (aromatic *C*). This is a known structure. These data are similar to the reported one.[16]

A mixture of chloroquinoxaline (**4a**, 0.3 mmol) and 1-phenylpiperazine (1.5mmol) was stirred under heating at 100 °C for 2 h. On cooling, the mixture was taken up with water, and the aqueous solution was extracted with ethyl acetate for three times. The

combined organic phase was dried over Na_2SO_4, and then removed under reduced pressure with a rotary evaporator. The crude residue was purified by silica gel column chromatography with ethyl acetate and petrol ether to give the pure product **5a** as a yellow solid.

3-Benzoyl-2-(4-phenylpiperazine)quinoxaline (5a):



Yellow solid. Yield: 89%. ^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.61 (m, 2H), 7.59 – 7.42 (m, 3H), 7.35 – 7.13 (m, 2H), 7.03 – 6.76 (m, 3H) (aromatic *H*), 3.70 (t, *J* = 5.1 Hz, 4H), 3.18 (t, *J* = 5.1 Hz, 4H) (CH_2). ^{13}C NMR (151 MHz, DMSO-d_6): δ 192.76 (*C*O), 151.40, 150.57, 144.14, 140.97, 135.28, 134.88, 134.48, 131.58, 130.47, 129.00, 128.95, 128.74, 126.31, 126.06, 119.06, 115.42 (aromatic *C*), 47.49, 47.29 (CH_2). This is a known structure. These data are similar to the reported one.[16]

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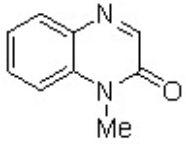


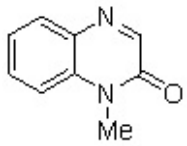
1b

8.24
7.84
7.82
7.69
7.67
7.66
7.60
7.58
7.41
7.39
7.38
3.61
3.35
2.51
2.50
2.50
2.50
2.49

0.87
0.95
1.08
1.06
1.00
3.17

f1 (ppm)

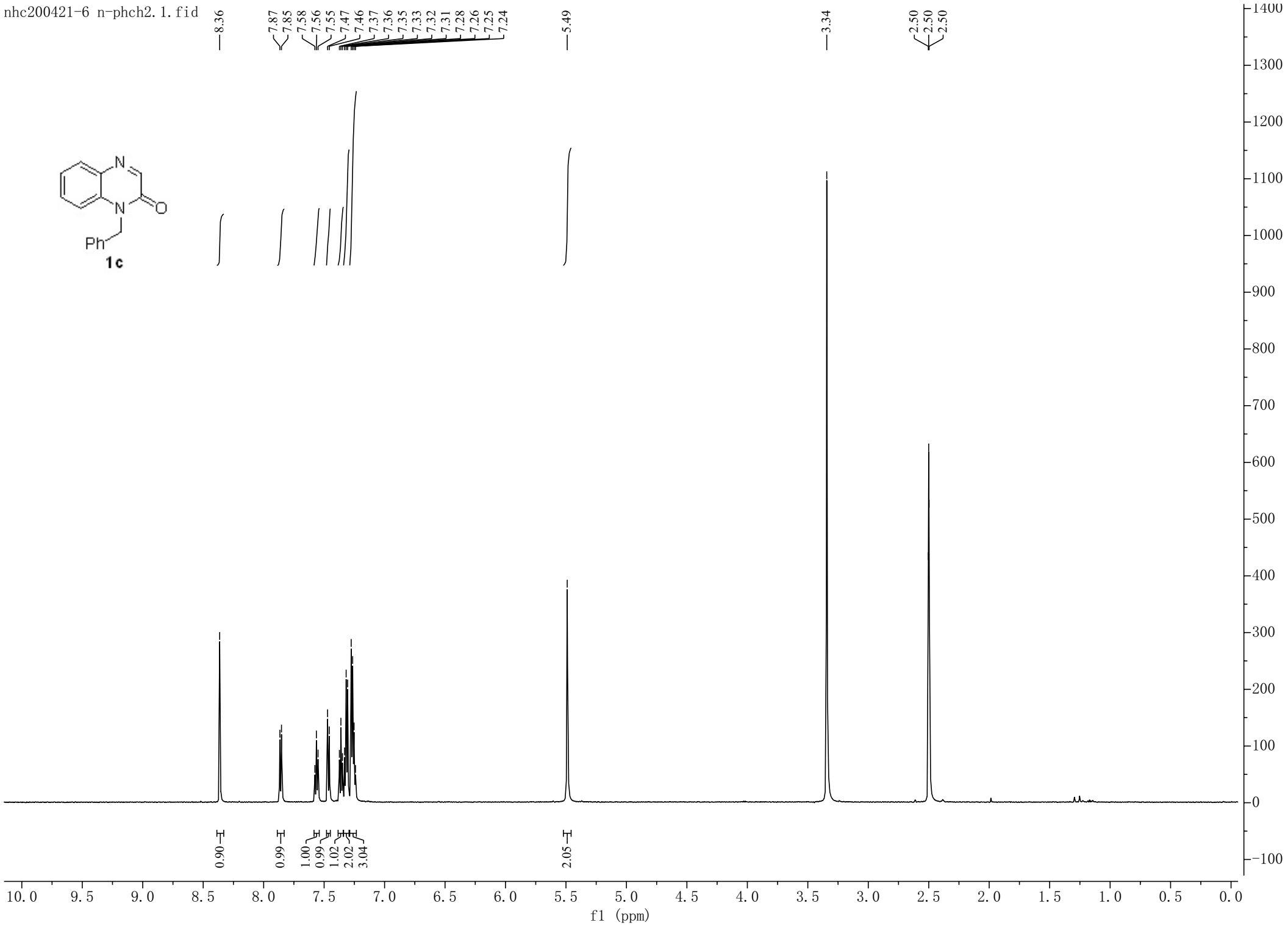
SIIA-NHC200723-11.1.fid



1b

154.31
150.04
133.11
132.63
131.05
129.53
123.42
114.84
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
28.54

f1 (ppm)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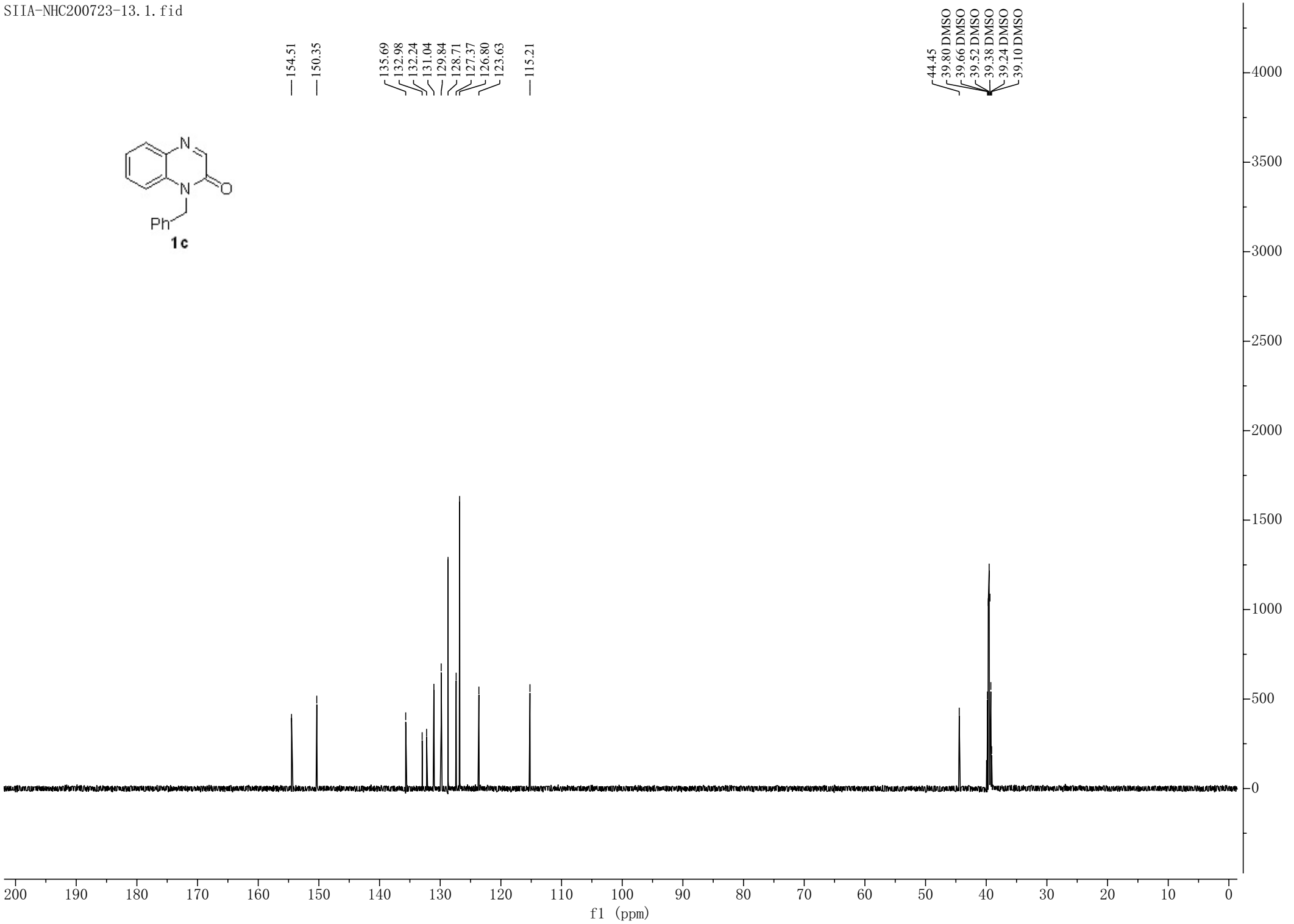
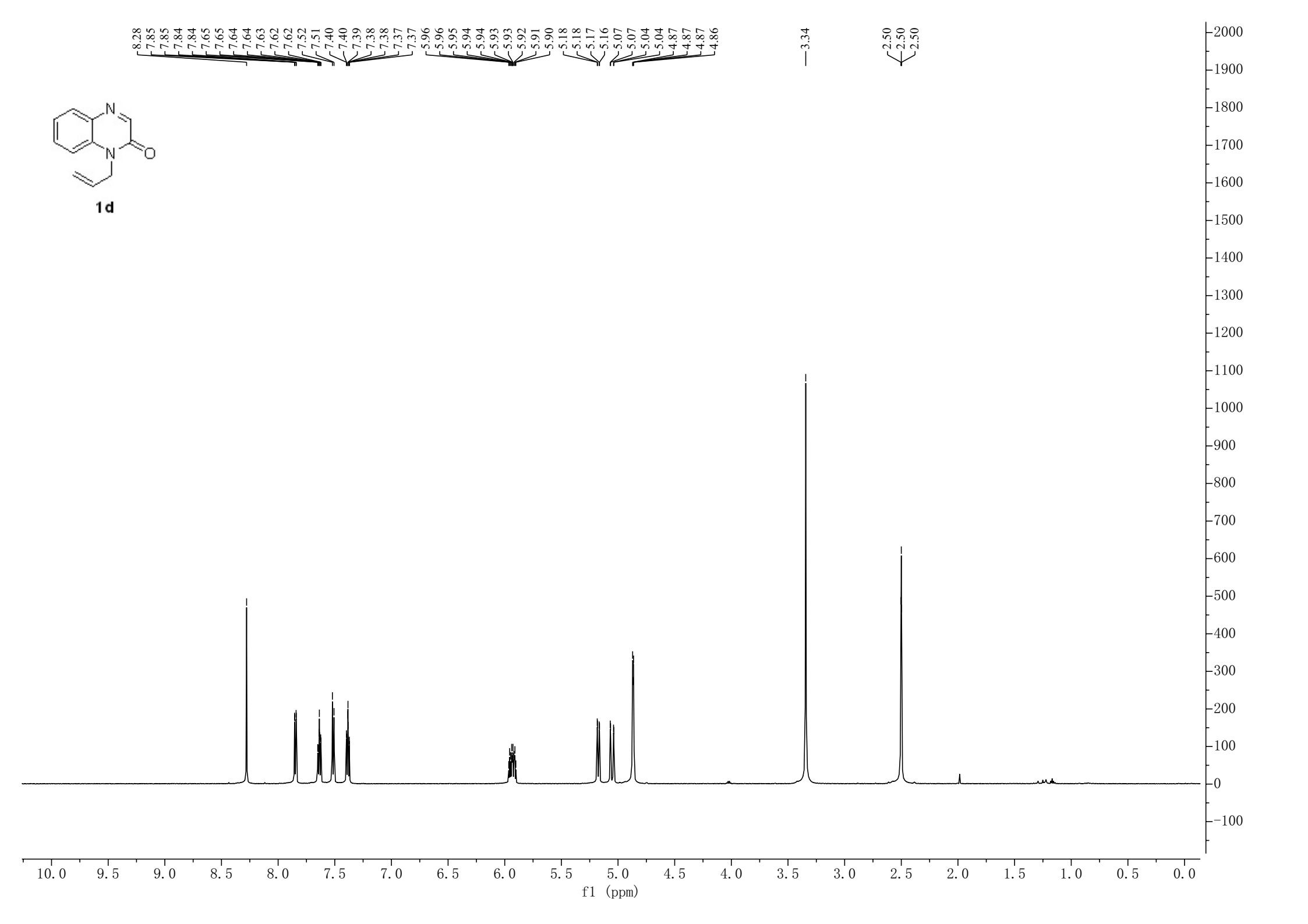
7.85
7.58
7.56
7.55
7.47
7.46
7.37
7.36
7.35
7.33
7.32
7.31
7.28
7.26
7.25
7.24
5.49
3.34
2.50
2.50
2.50
N
N
O
Ph
1c
0.90
0.99
1.00
0.99
1.02
2.02
3.04
2.05
f1 (ppm)

SIIA-NHC200723-13.1.fid

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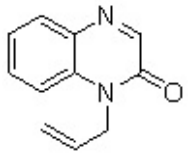
7.84
7.84
7.65
7.65
7.64
7.64
7.63
7.62
7.62
7.52
7.51
7.40
7.40
7.39
7.38
7.38
7.37
7.37
5.96
5.96
5.95
5.94
5.94
5.93
5.93
5.92
5.91
5.90
5.18
5.18
5.17
5.16
5.07
5.07
5.04
5.04
4.87
4.87
4.86
3.34
2.50
2.50
2.50
N
N
O
1d
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10.0
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)

SIIA-NHC200723-12.1.fid

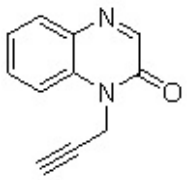
153.96
150.20
132.85
132.20
131.43
131.01
129.75
123.52
117.11
115.20
43.36



1d

f1 (ppm)

n-alkynyl.1.fid

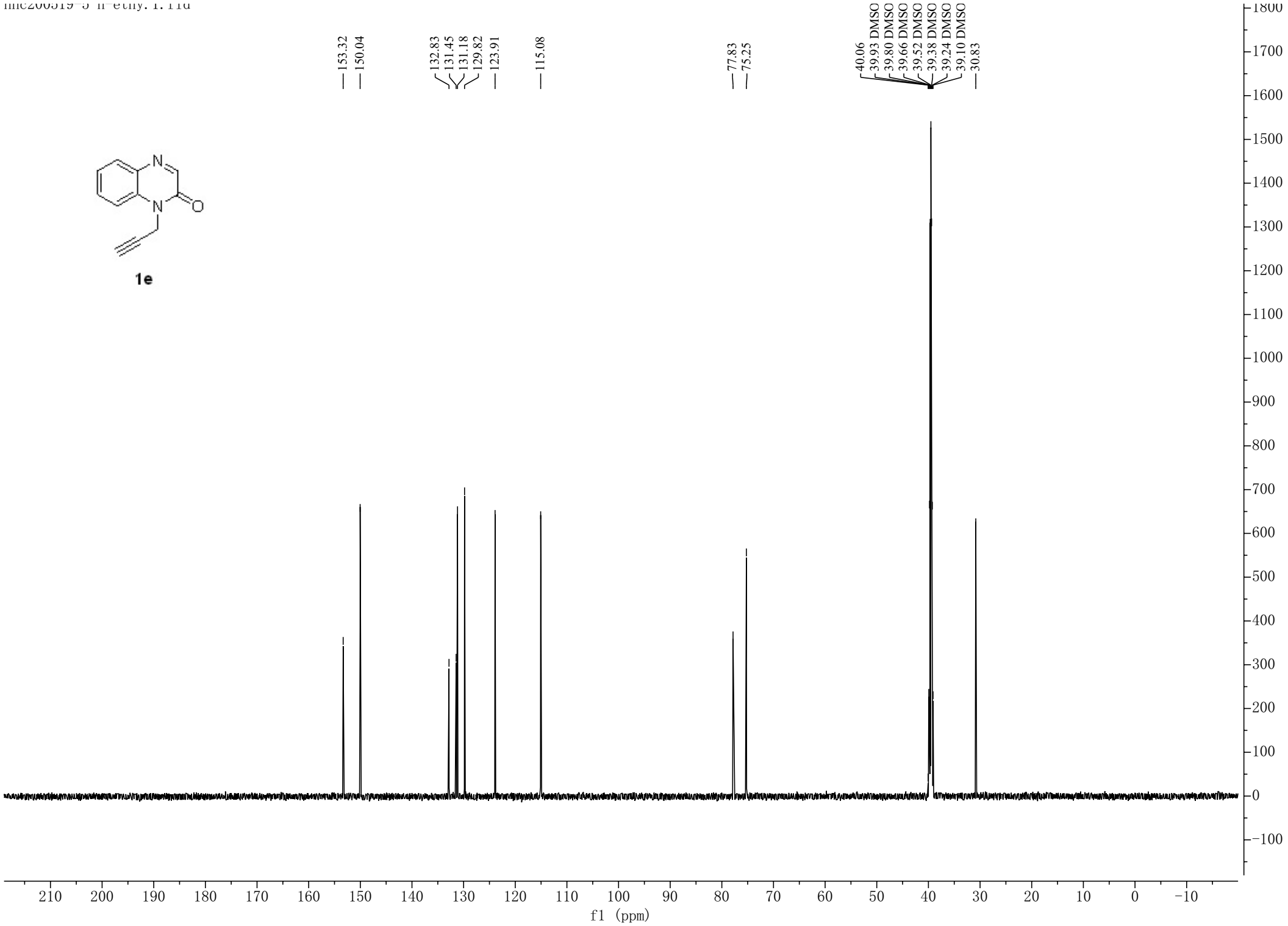


1e

8.29
7.88
7.86
7.73
7.72
7.71
7.65
7.64
7.45
7.43
7.42
5.07
5.07
3.36
3.36
3.35
3.34
2.50
2.50

0.87
1.00
1.06
1.07
1.05
2.13
0.96

f1 (ppm)


153.32
150.04
132.83
131.45
131.18
129.82
123.91
115.08
77.83
75.25
40.06
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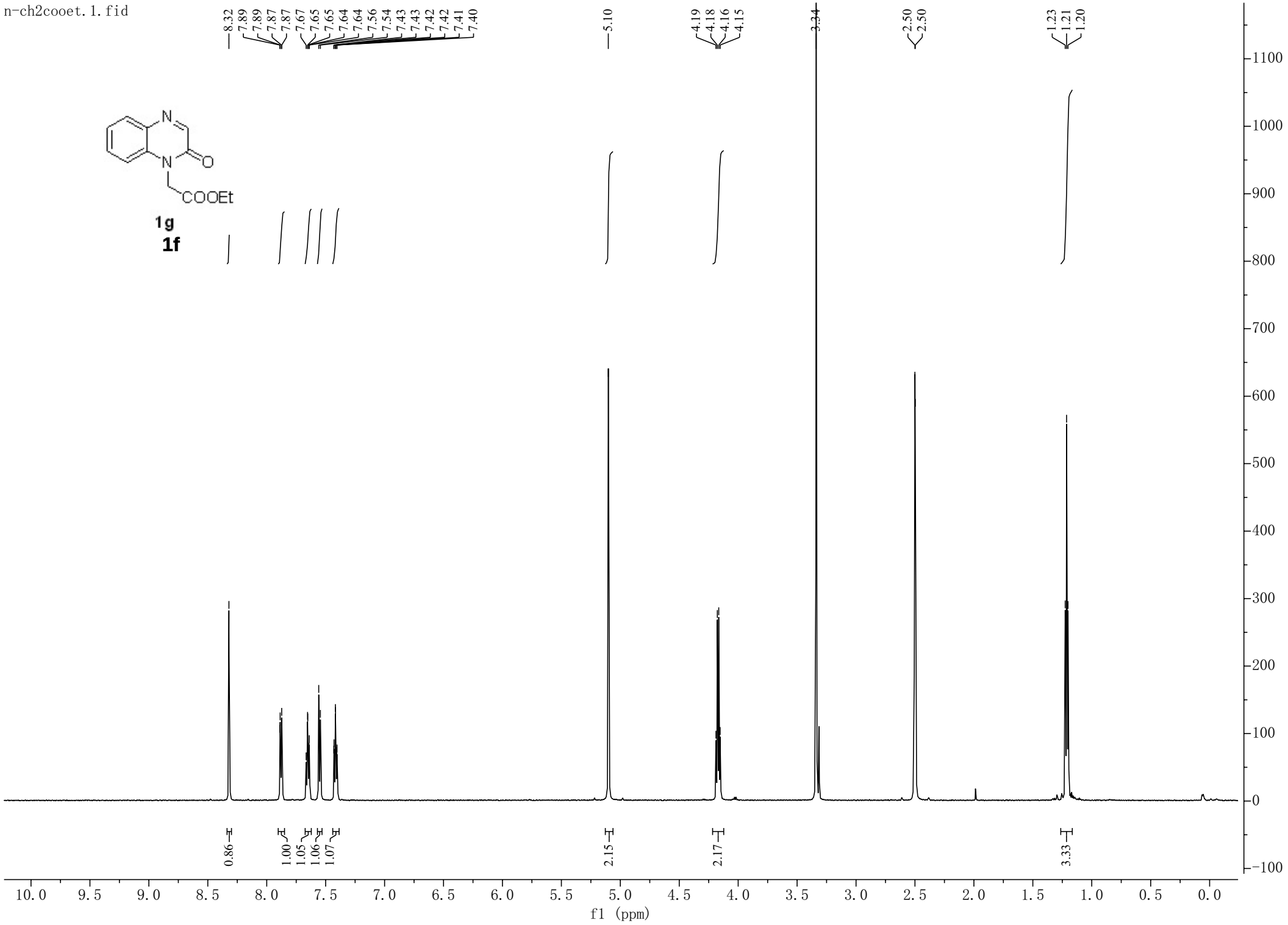
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
30.83
1e
f1 (ppm)


n-ch2cooet.1.fid
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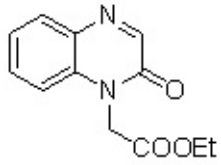
7.89
7.89
7.87
7.87
7.67
7.65
7.65
7.64
7.64
7.56
7.54
7.43
7.43
7.42
7.42
7.41
7.40
5.10
4.19
4.18
4.16
4.15
3.34
2.50
2.50
1.23
1.21
1.20
N
N
O
COOEt
1g
1f
0.86
1.00
1.05
1.06
1.07
2.15
2.17
3.33
f1 (ppm)

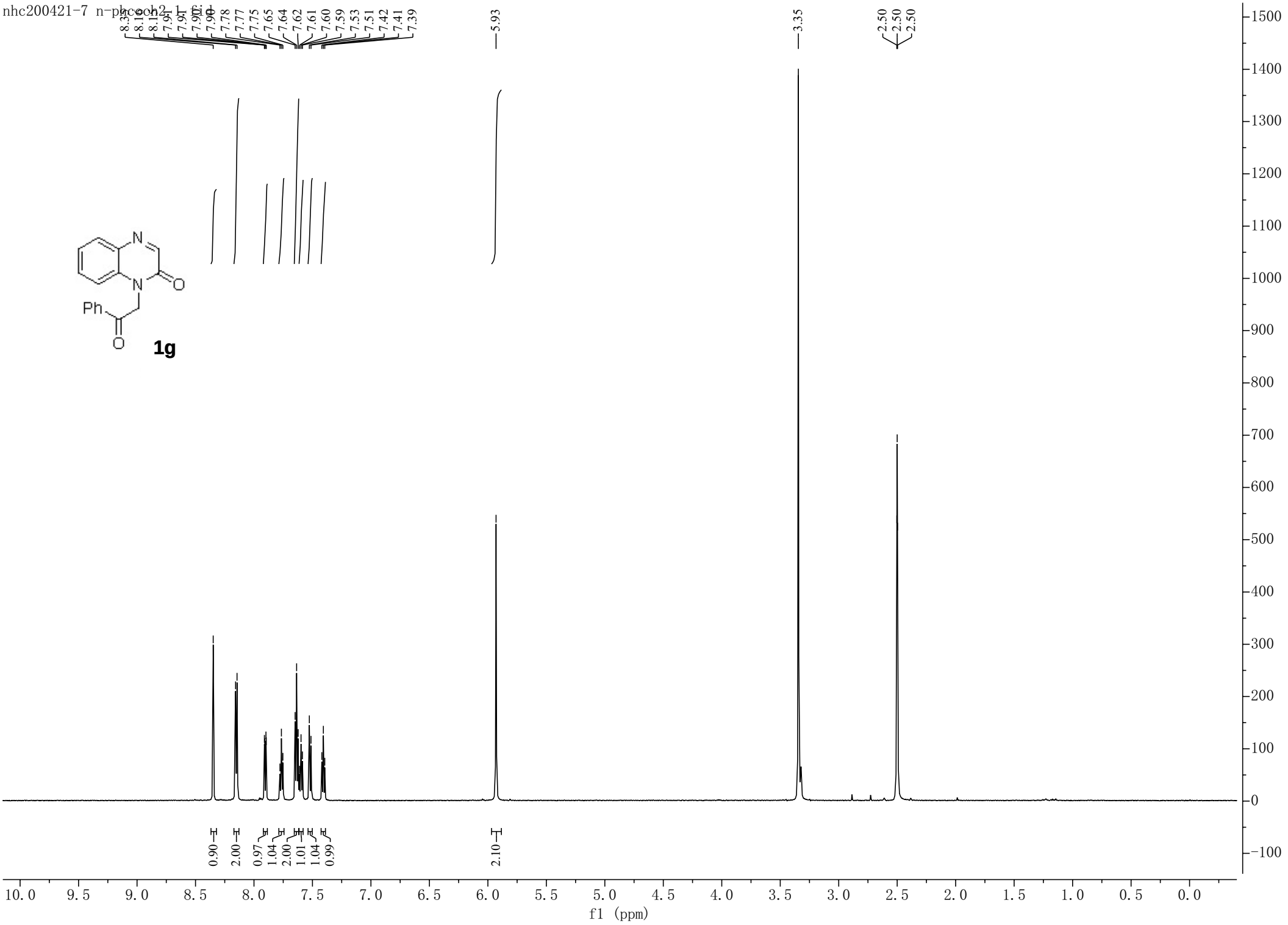
SIIA-NHC200723-14.1.fid



1g **1f**

167.39
154.06
149.81
132.65
132.40
131.30
129.87
123.85
114.72
61.44
43.23
39.52 DMSO
39.38 DMSO
39.24 DMSO
13.99

f1 (ppm)


nhc200421-7 n-phcooch2
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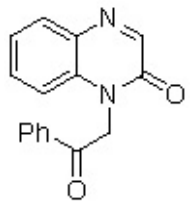
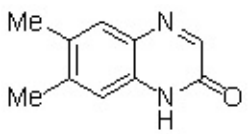
8.14
8.13
7.91
7.90
7.90
7.90
7.78
7.77
7.75
7.65
7.64
7.62
7.61
7.60
7.59
7.53
7.51
7.42
7.41
7.39
5.93
3.35
2.50
2.50
2.50
Ph
O
O
1g
0.90
2.00
0.97
1.04
2.00
1.01
1.04
0.99
2.10
f1 (ppm)

nhc200519-4-n-phco.1.fid



1g

7,8-me.1.fid

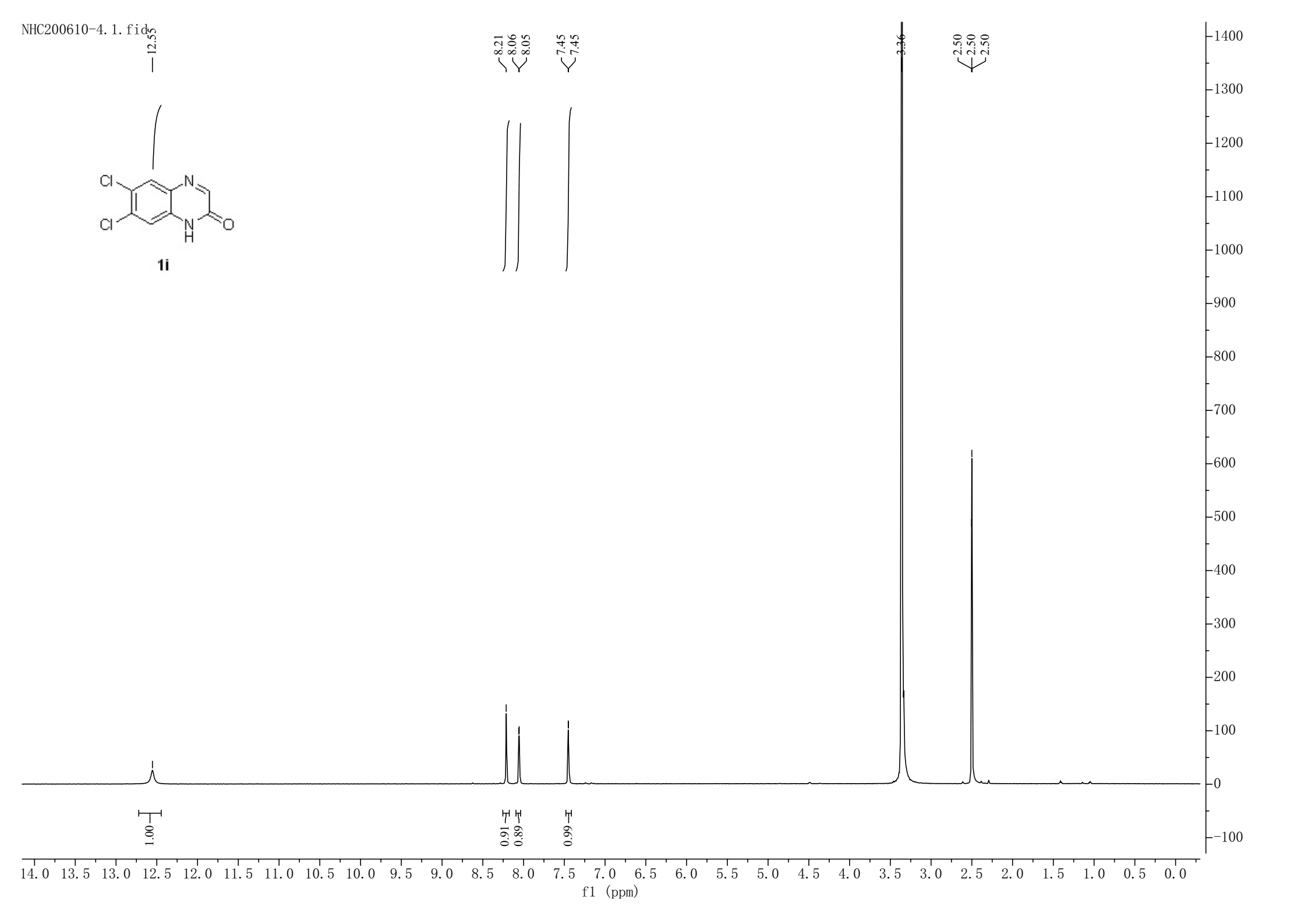


1h

12.39
8.06
7.54
7.06
3.34
2.50
2.30
2.28

1.16
1.00
1.21
1.22
3.09
3.00

f1 (ppm)


NHC200610-4.1.fid
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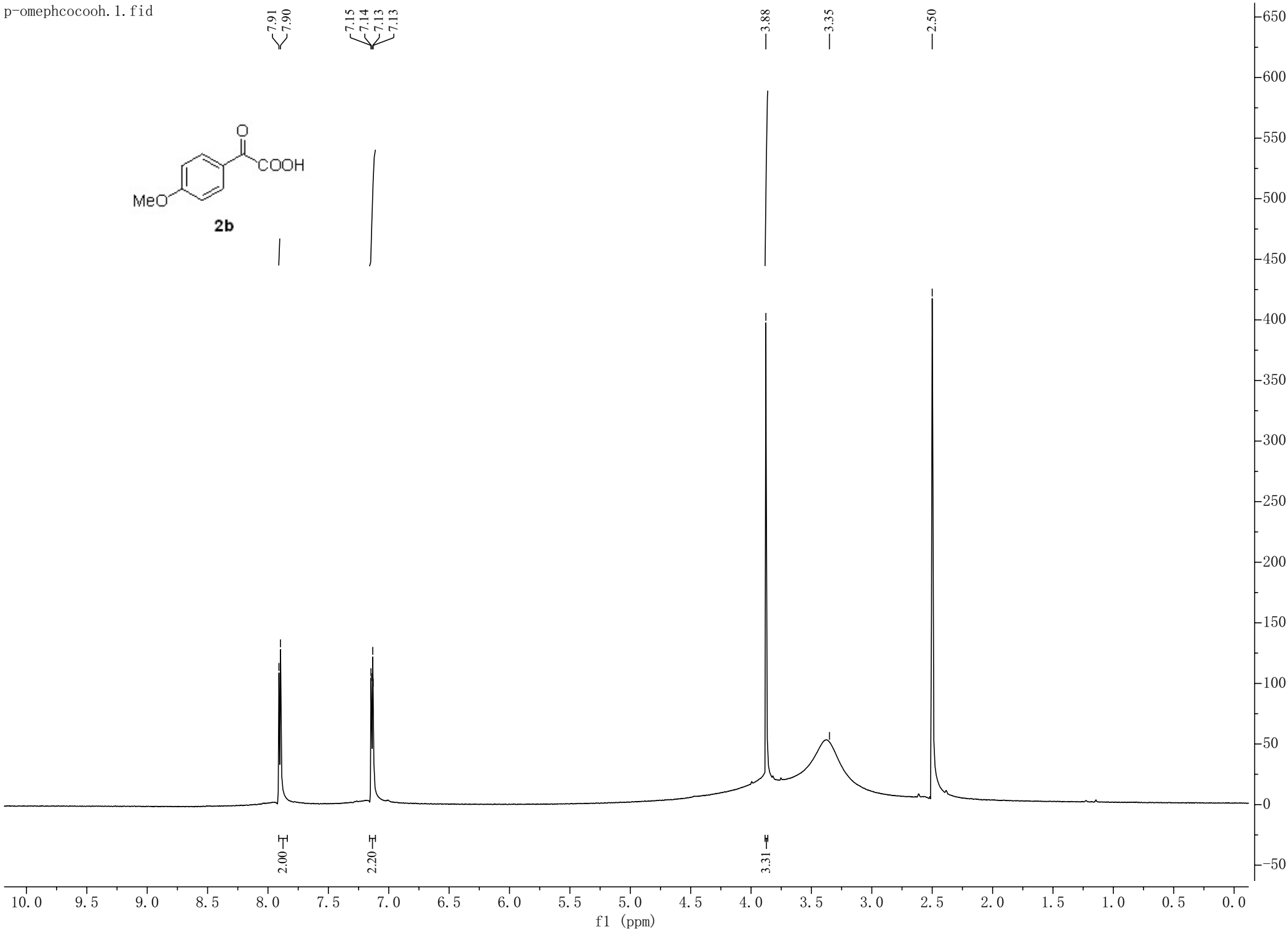
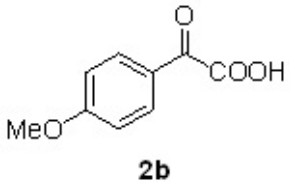
8.21
8.06
8.05
7.45
7.45
3.36
2.50
2.50
2.50
Cl
Cl
N
N
H
O
1i
1.00
0.91
0.89
0.99
f1 (ppm)


p-omephcocooh.1.fid
7.91
7.90
7.15
7.14
7.13
7.13
3.88
3.35
2.50
O
COOH
MeO
2b
2.00
2.20
3.31
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
10.0
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)

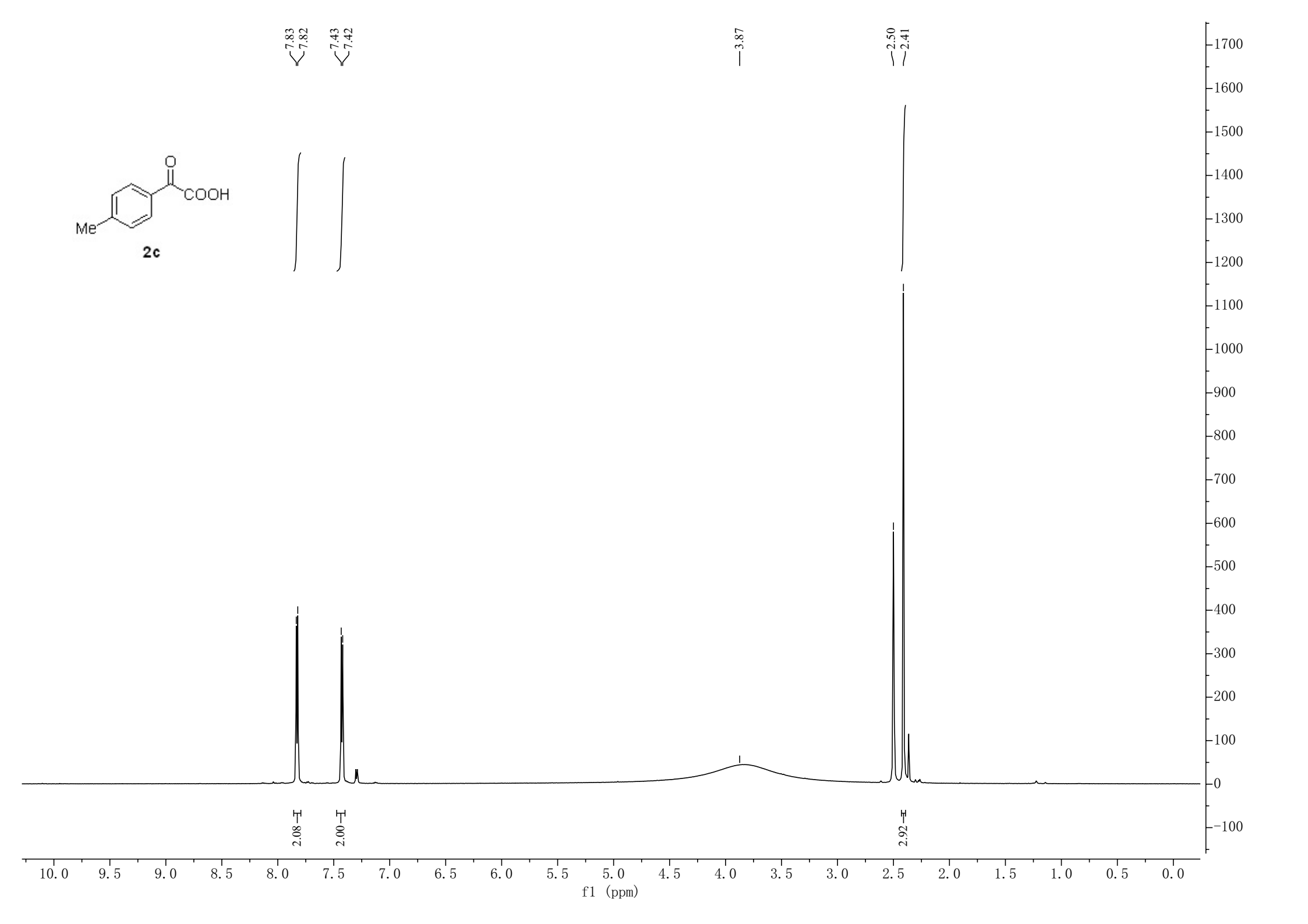
SIIA-NHC200723-8.1.fid



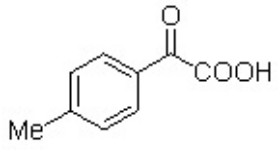
2b

187.17
166.54
164.72
132.06
124.75
114.75
55.85
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO

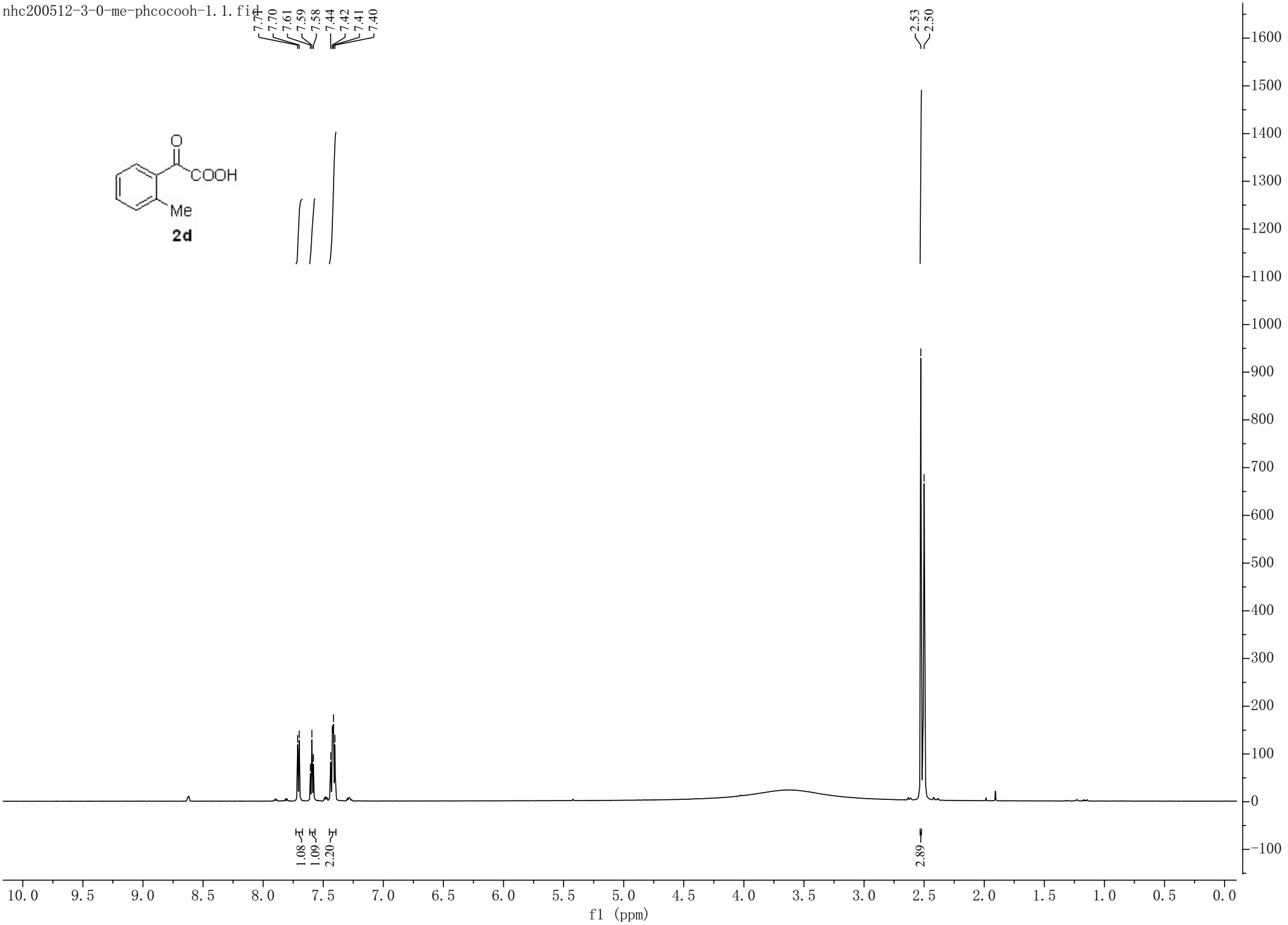
f1 (ppm)


7.83
7.82
7.43
7.42
3.87
2.50
2.41
O
COOH
Me
2c
2.08
2.00
2.92
f1 (ppm)

SIIA-NHC200723-10.1.fid



2c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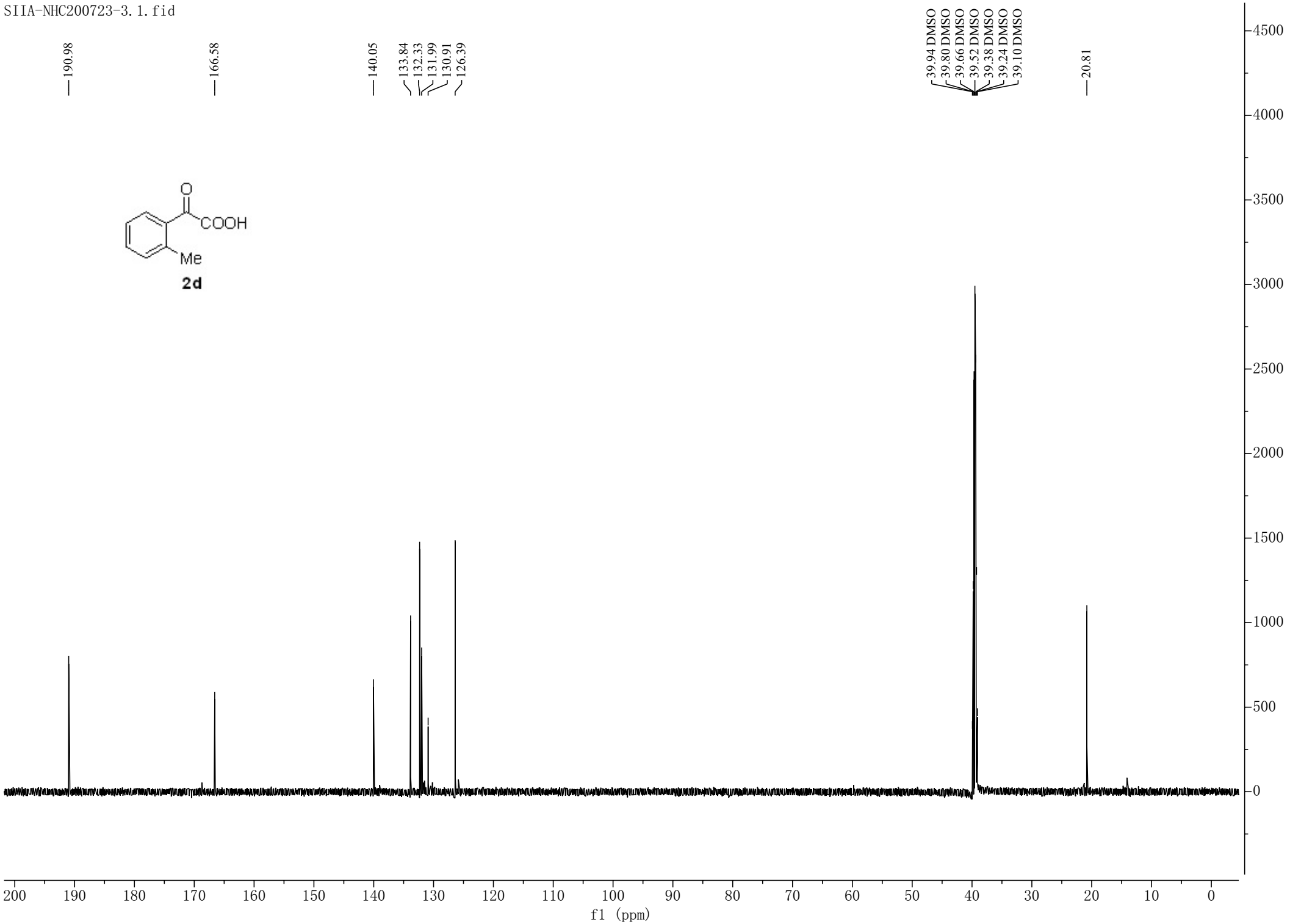
7.74
7.70
7.61
7.59
7.58
7.44
7.42
7.41
7.40
2.53
2.50
O
COOH
Me
2d
1.08
1.09
2.20
2.89
f1 (ppm)

SIIA-NHC200723-3.1.fid



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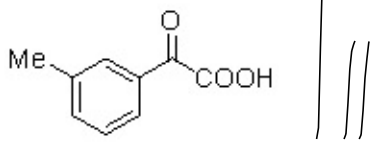
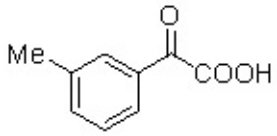
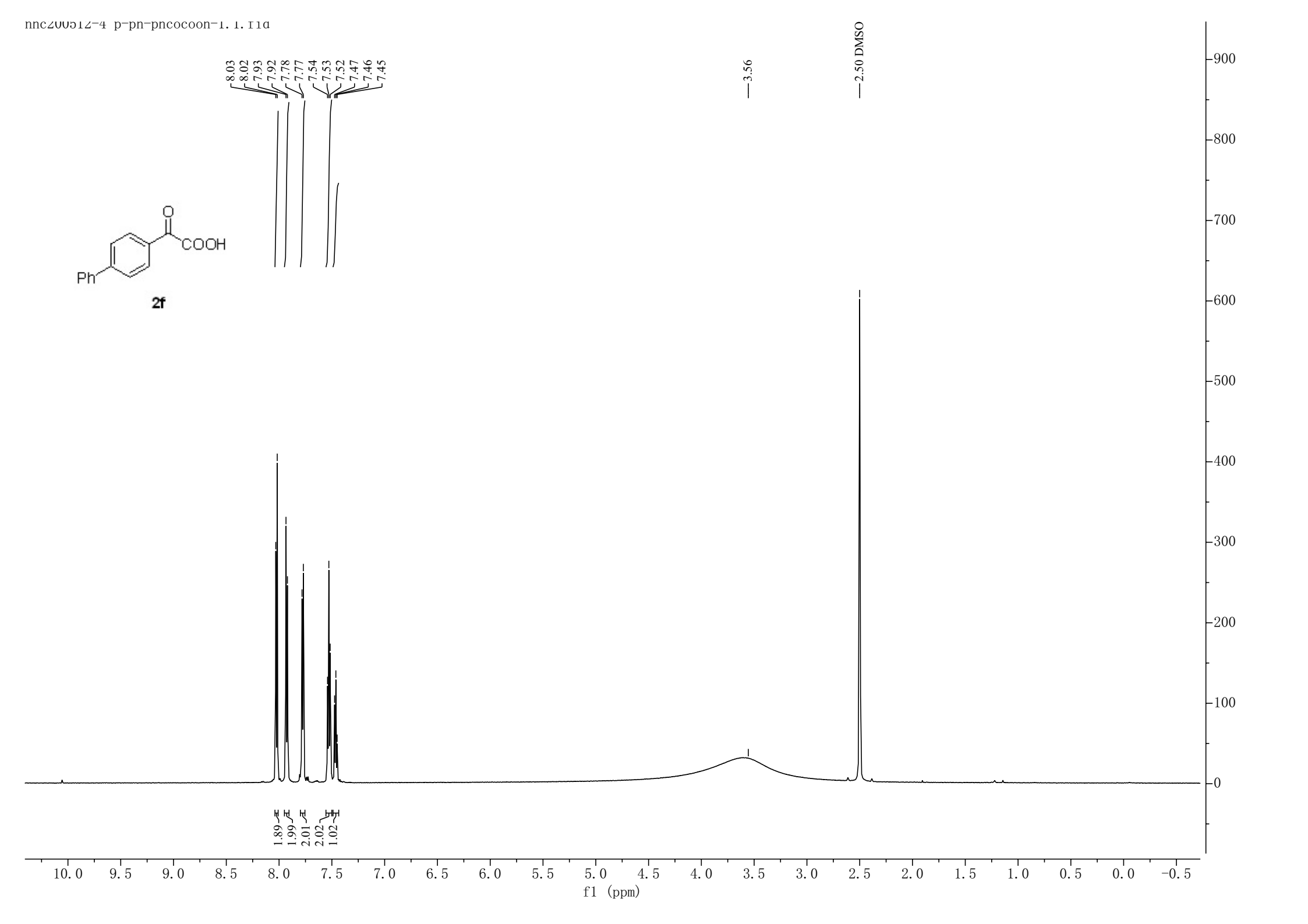


2e

SIIA-NHC200723-4.1.fid

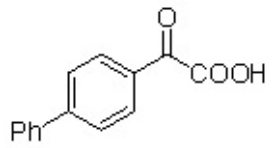


2e


nnc200512-4 p-pn-pncocoon-1.1.11d
8.03
8.02
7.93
7.92
7.78
7.77
7.54
7.53
7.52
7.47
7.46
7.45
3.56
2.50 DMSO
O
COOH
Ph
2f
1.89
1.99
2.01
2.02
1.02
f1 (ppm)

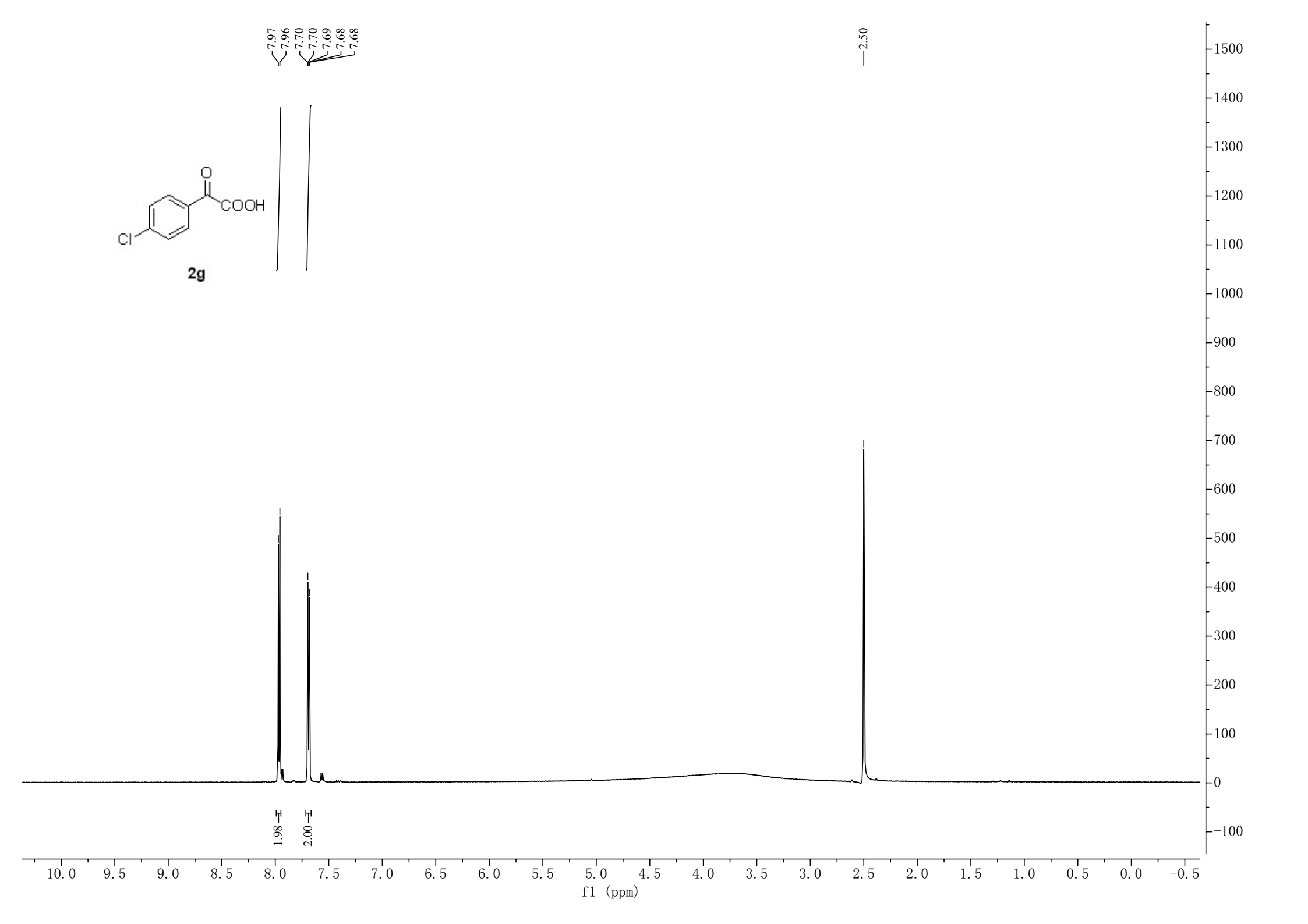
SIIA-NHC200728-1.1.fid

188.18
166.11
146.40
138.51
130.72
130.24
129.21
128.86
127.47
127.18
39.93
39.80
39.66
39.52
39.38
39.24
39.10

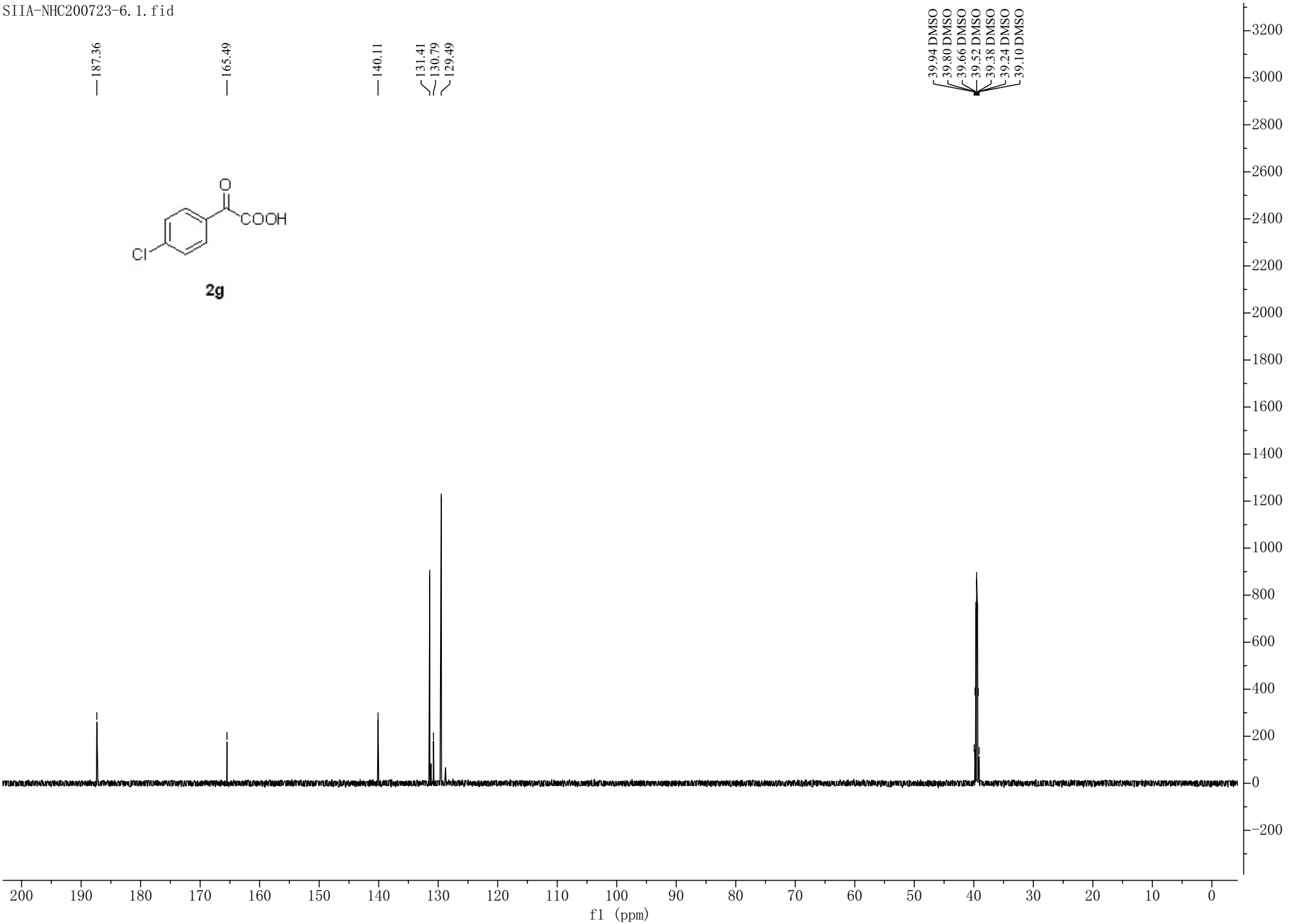


2f

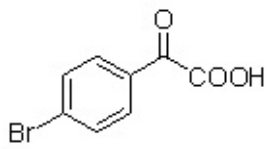
f1 (ppm)


7.97
7.96
7.70
7.70
7.69
7.68
7.68
2.50
O
COOH
Cl
2g
1.98
2.00
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.0
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
f1 (ppm)

SIIA-NHC200723-6.1.fid



p-brphcocooh.1.fid



2h

7.89
7.87
7.84
7.83

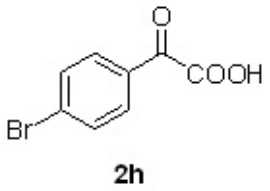
3.77

2.50
2.50
2.50

1.95
2.00

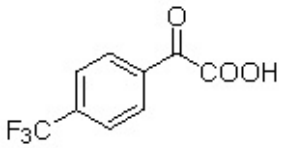
f1 (ppm)

SIIA-NHC200723-7.1.fid



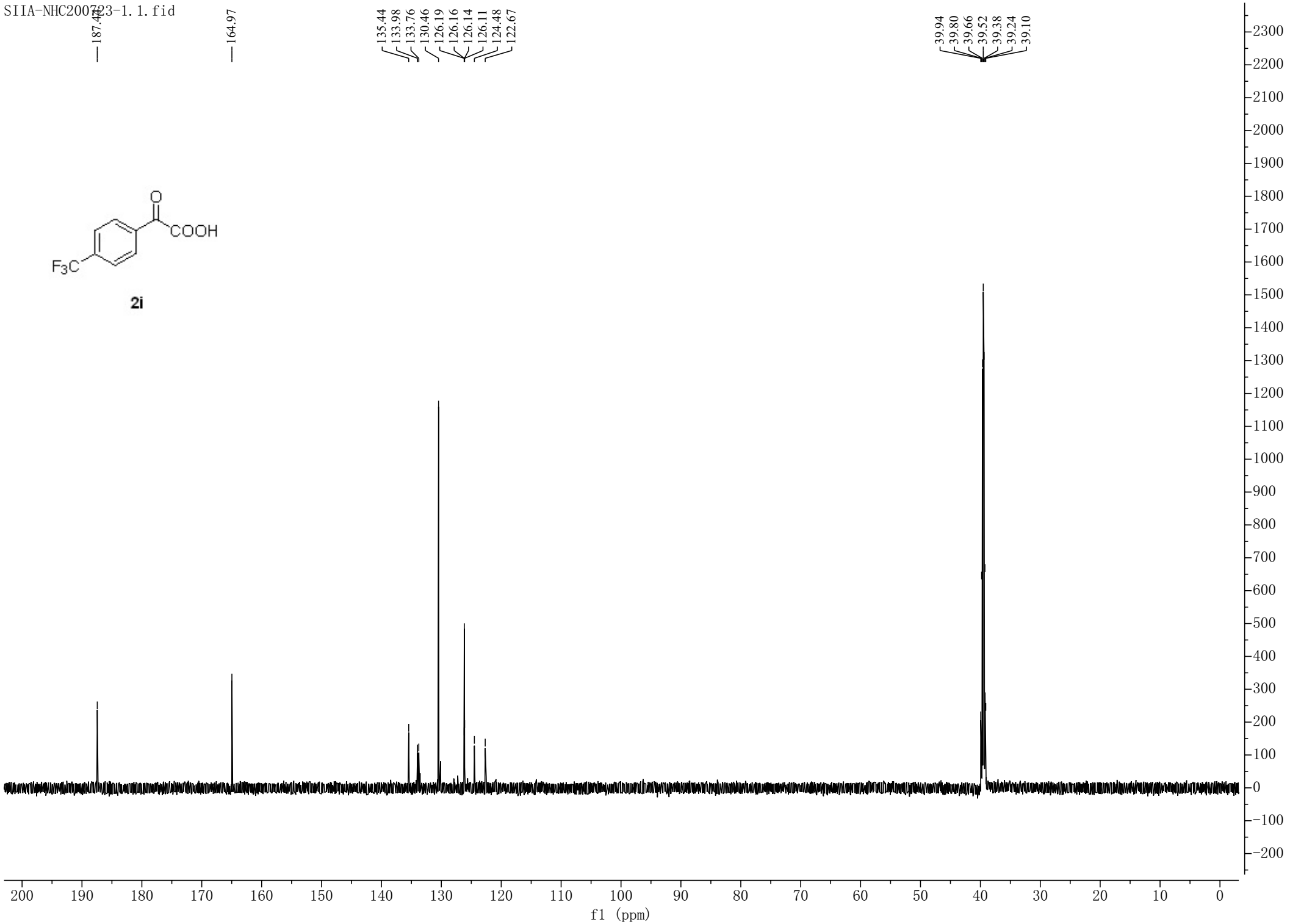
2h

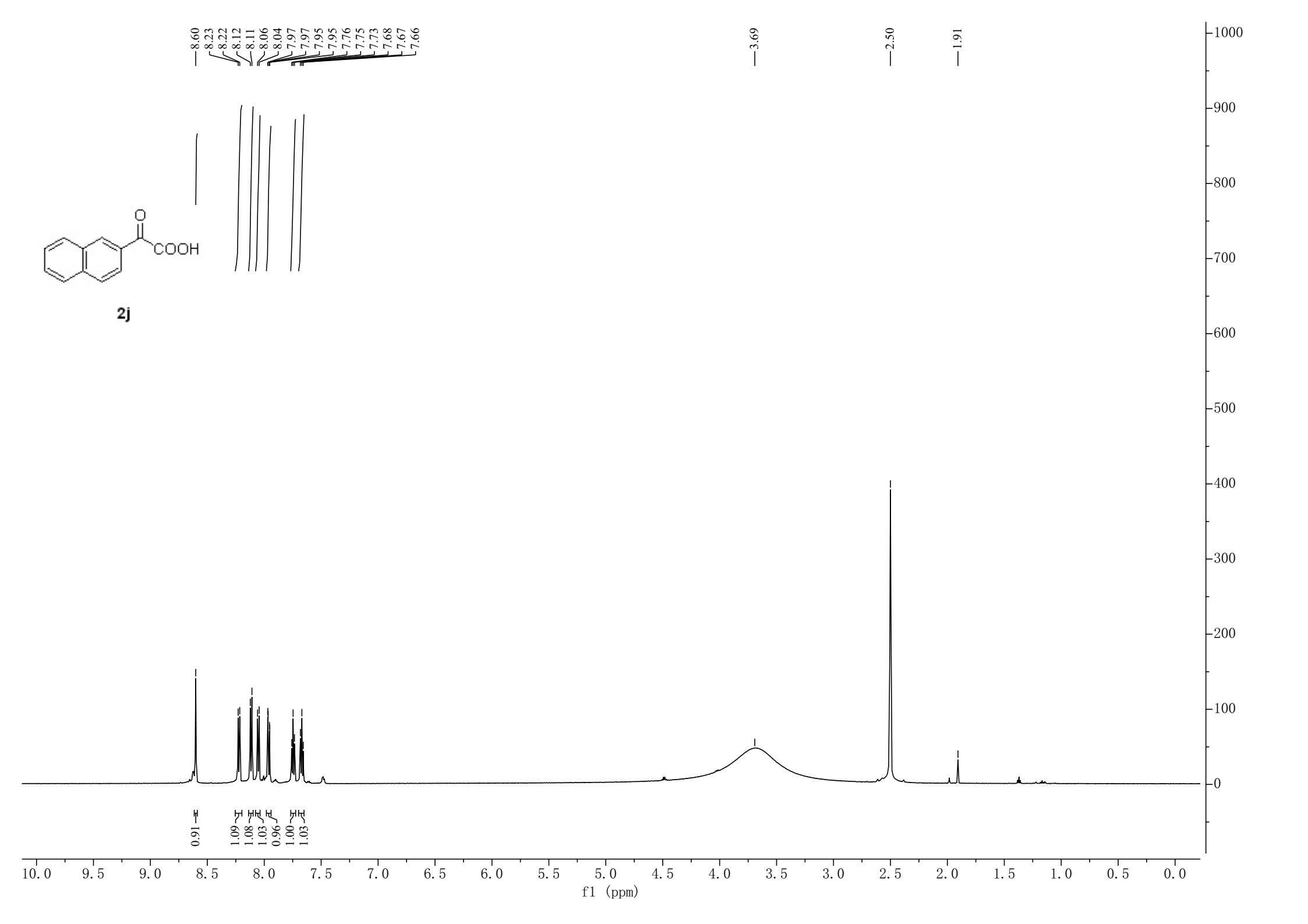
p-cf3phcocooh.1.fid



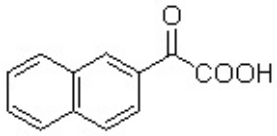
2i

8.17
8.15
7.99
7.98
3.38
2.50
1.98
2.00
f1 (ppm)


SIIA-NHC200723-1.1.fid
187.44
164.97
135.44
133.98
133.76
130.46
126.19
126.16
126.14
126.11
124.48
122.67
39.94
39.80
39.66
39.52
39.38
39.24
39.10
O
COOH
F3C
2i
f1 (ppm)


8.60
8.23
8.22
8.12
8.11
8.06
8.04
7.97
7.97
7.95
7.95
7.76
7.75
7.73
7.68
7.67
7.66
3.69
2.50
1.91
O
COOH
2j
0.91
1.09
1.08
1.03
0.96
1.00
1.03
f1 (ppm)

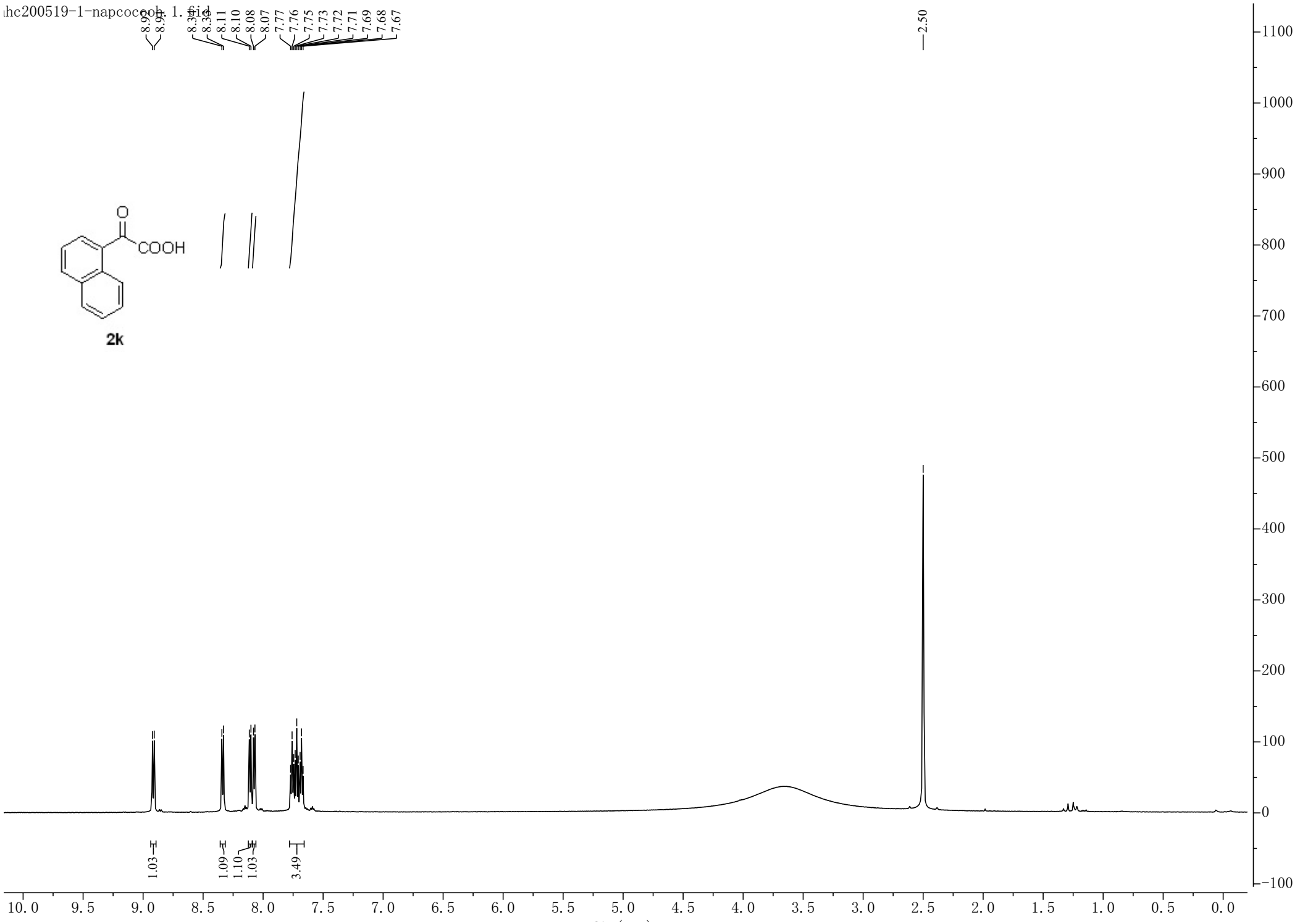
SIIA-NHC200723-2.1.fid



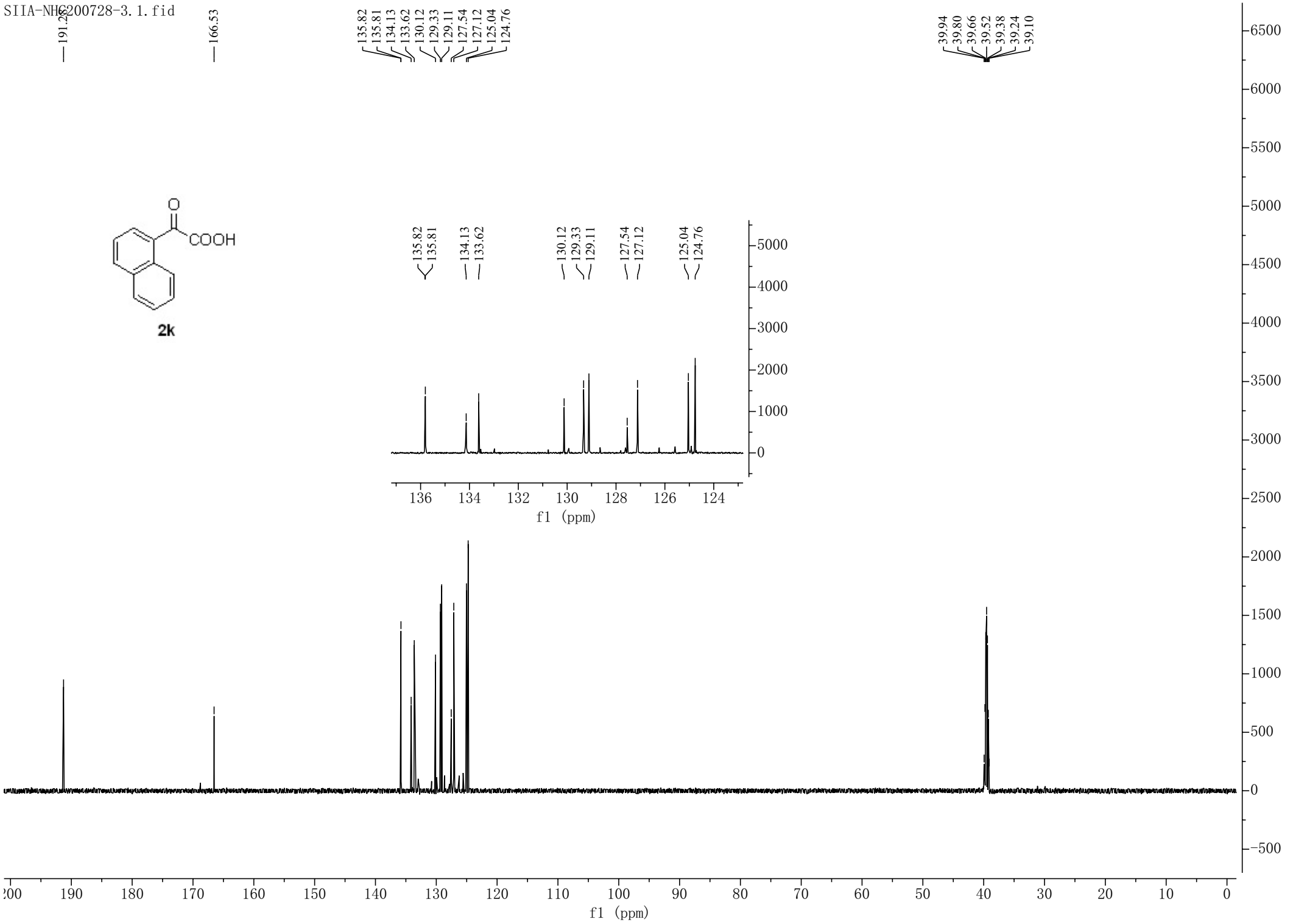
2j

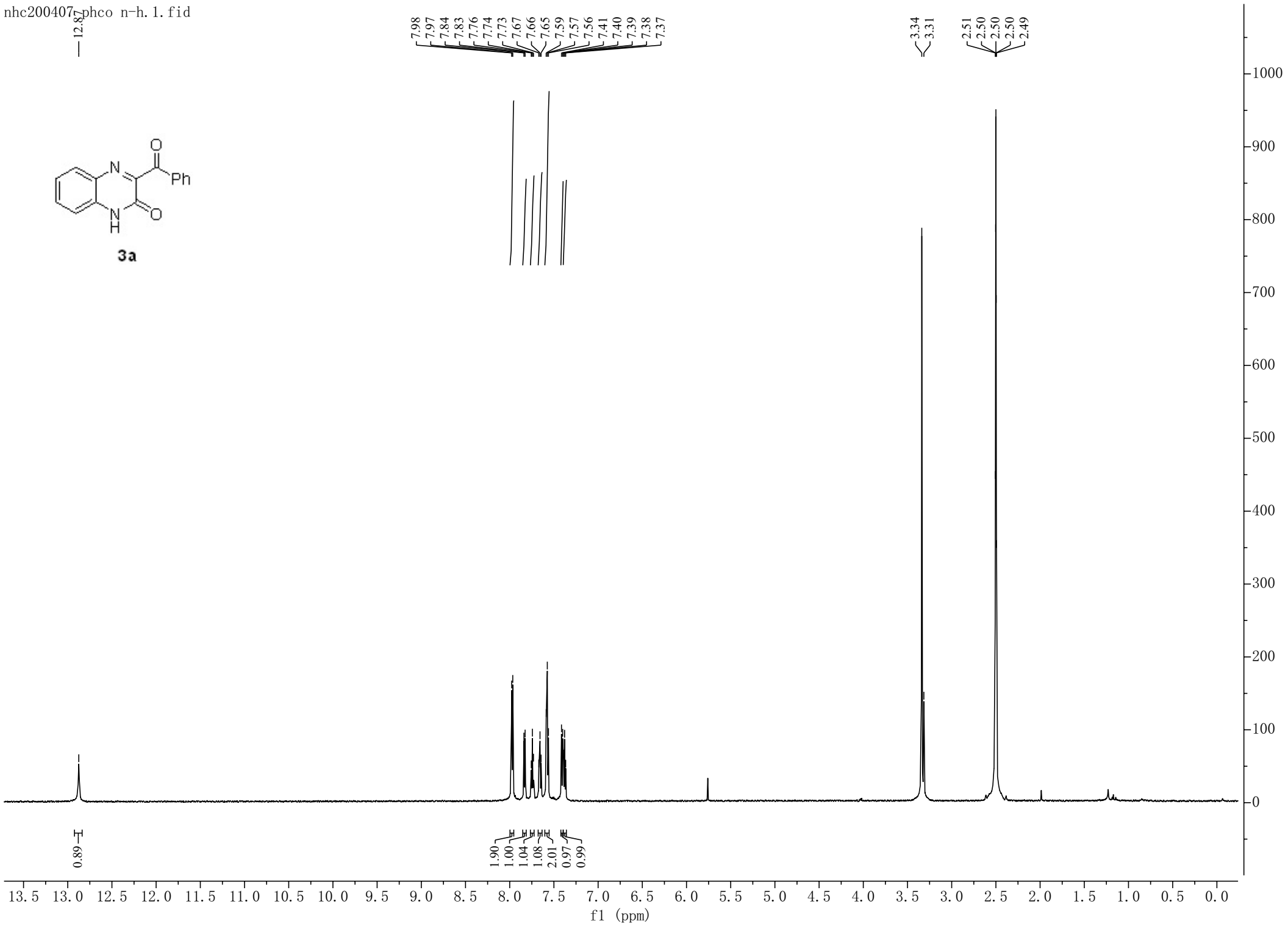
188.78
166.26
135.86
132.88
131.98
130.04
129.80
129.31
129.19
127.92
127.48
123.39
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO

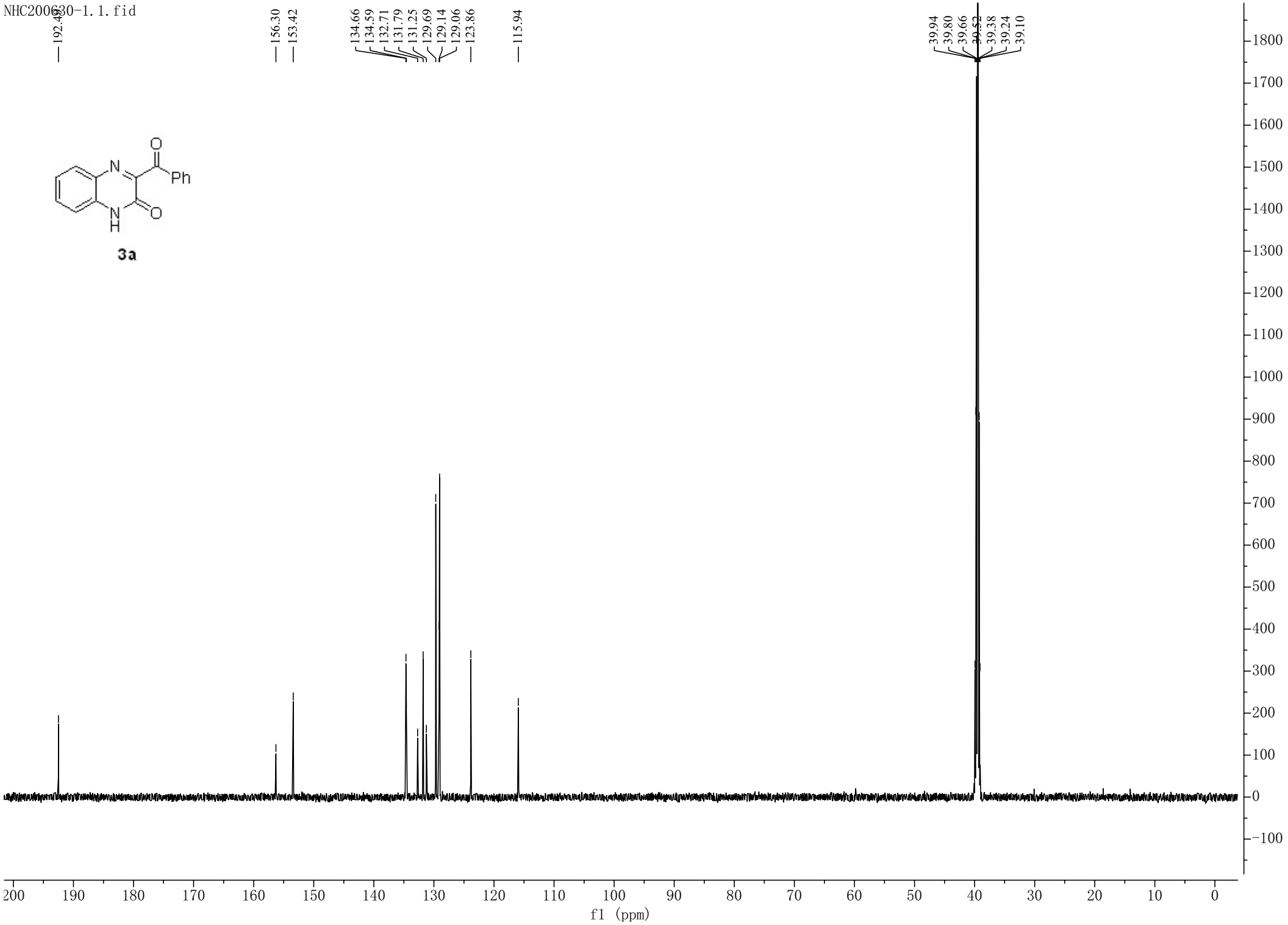
f1 (ppm)

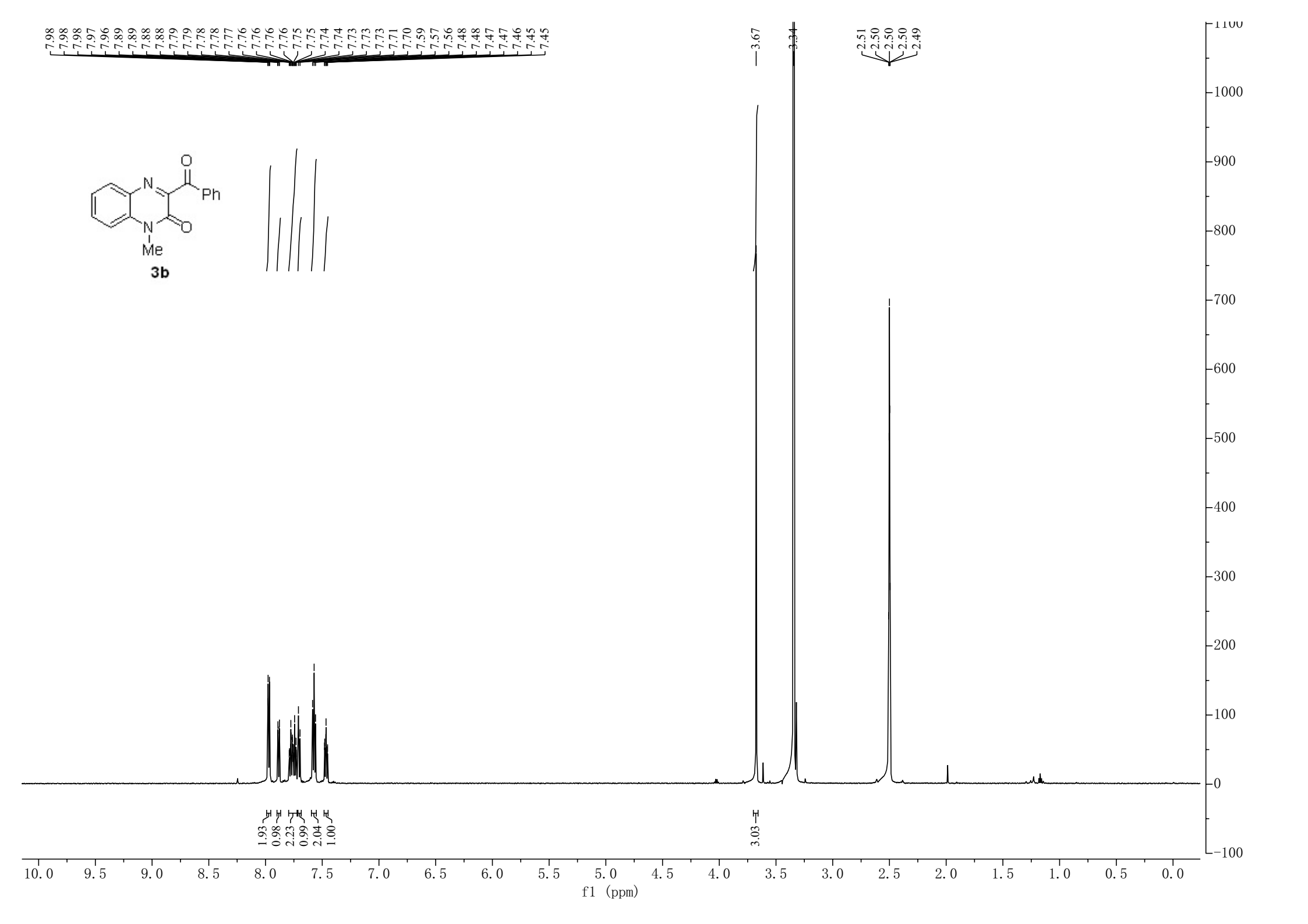

hc200519-1-napcoocooh-1.fid
8.93
8.92
8.34
8.33
8.11
8.10
8.08
8.07
7.77
7.76
7.75
7.73
7.72
7.71
7.69
7.68
7.67
2.50
O
COOH
2k
1.03
1.09
1.10
1.03
3.49
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

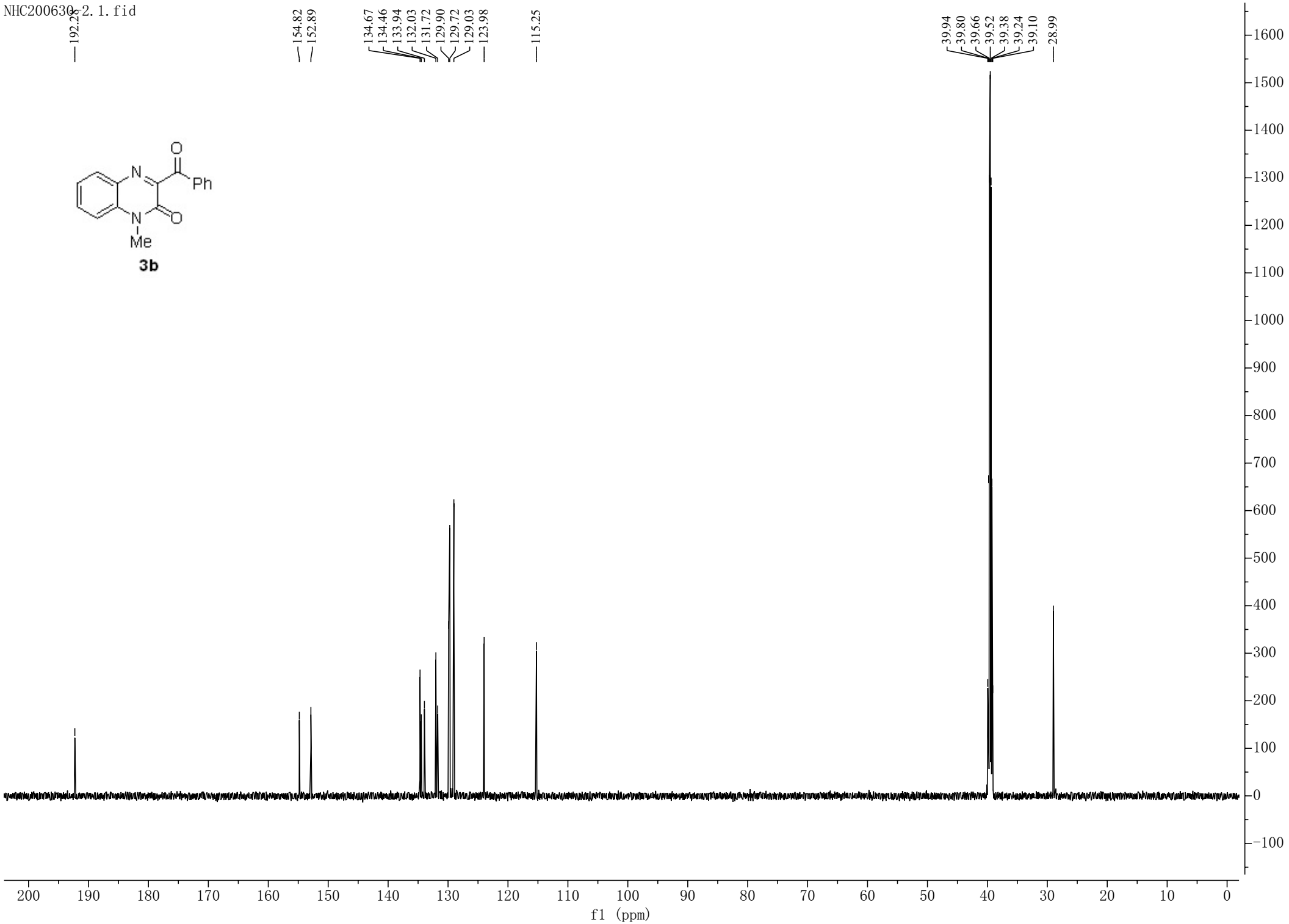
SIIA-NHC200728-3.1.fid

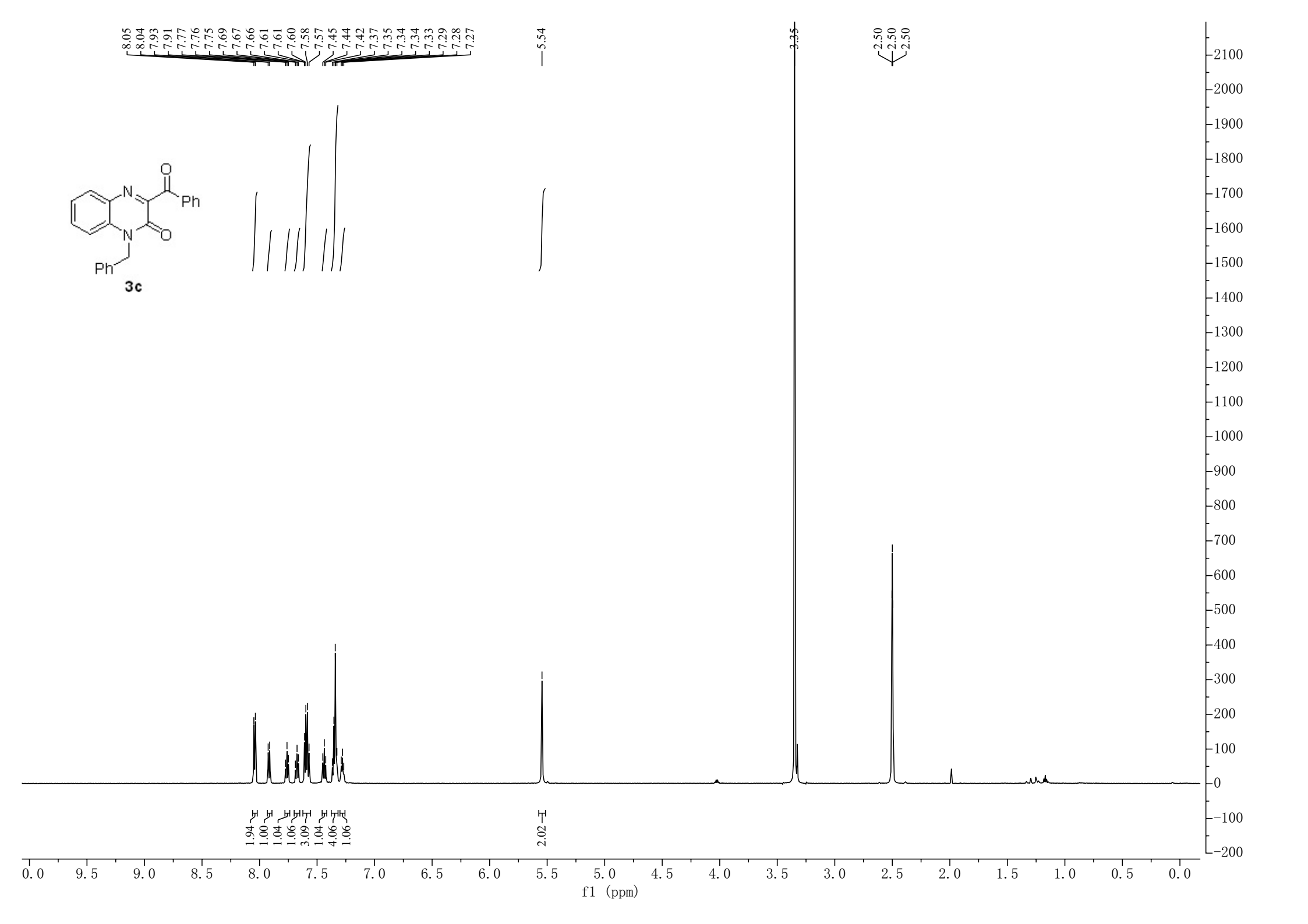



nhc200407_phco n-h.1.fid
12.87
7.98
7.97
7.84
7.83
7.76
7.74
7.73
7.67
7.66
7.65
7.59
7.57
7.56
7.41
7.40
7.39
7.38
7.37
3.34
3.31
2.51
2.50
2.50
2.50
2.49
O
N
Ph
N
H
O
3a
0.89
1.90
1.00
1.04
1.08
2.01
0.97
0.99
f1 (ppm)

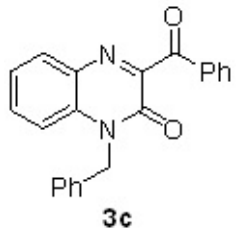

NHC200630-1.1.fid
192.48
156.30
153.42
134.66
134.59
132.71
131.79
131.25
129.69
129.14
129.06
123.86
115.94
39.94
39.80
39.66
39.52
39.38
39.24
39.10
O
N
Ph
O
N
H
3a
f1 (ppm)


7.98
7.98
7.98
7.97
7.96
7.89
7.89
7.88
7.88
7.79
7.79
7.78
7.78
7.77
7.76
7.76
7.76
7.76
7.75
7.75
7.74
7.74
7.73
7.73
7.73
7.71
7.70
7.59
7.57
7.56
7.48
7.47
7.47
7.46
7.45
7.45
3.67
3.34
2.51
2.50
2.50
2.50
2.49
O
Ph
N
N
O
Me
3b
1.93
0.98
2.23
0.99
2.04
1.00
3.03
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10.0
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)


NHC200630-2.1.fid
192.26
154.82
152.89
134.67
134.46
133.94
132.03
131.72
129.90
129.72
129.03
123.98
115.25
39.94
39.80
39.66
39.52
39.38
39.24
39.10
28.99
O
N
Ph
O
N
Me
3b
f1 (ppm)


8.05
8.04
7.93
7.91
7.77
7.76
7.75
7.69
7.67
7.66
7.61
7.61
7.60
7.58
7.57
7.45
7.44
7.42
7.37
7.35
7.34
7.34
7.33
7.29
7.28
7.27
5.54
3.35
2.50
2.50
2.50
O
N
Ph
N
O
Ph
3c
1.94
1.00
1.04
1.06
3.09
1.04
4.06
1.06
2.02
f1 (ppm)

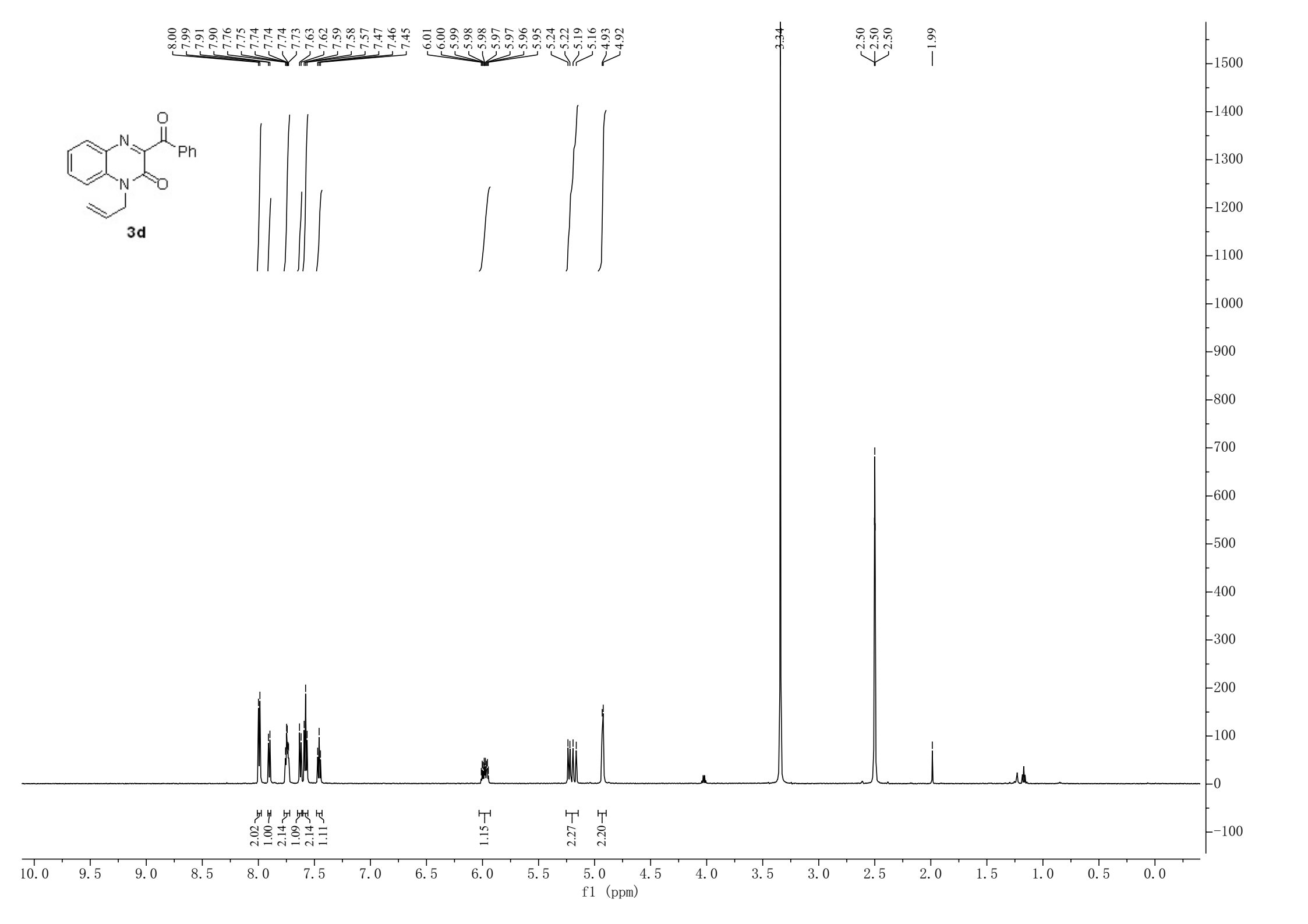
NHC200630-5.1.fid

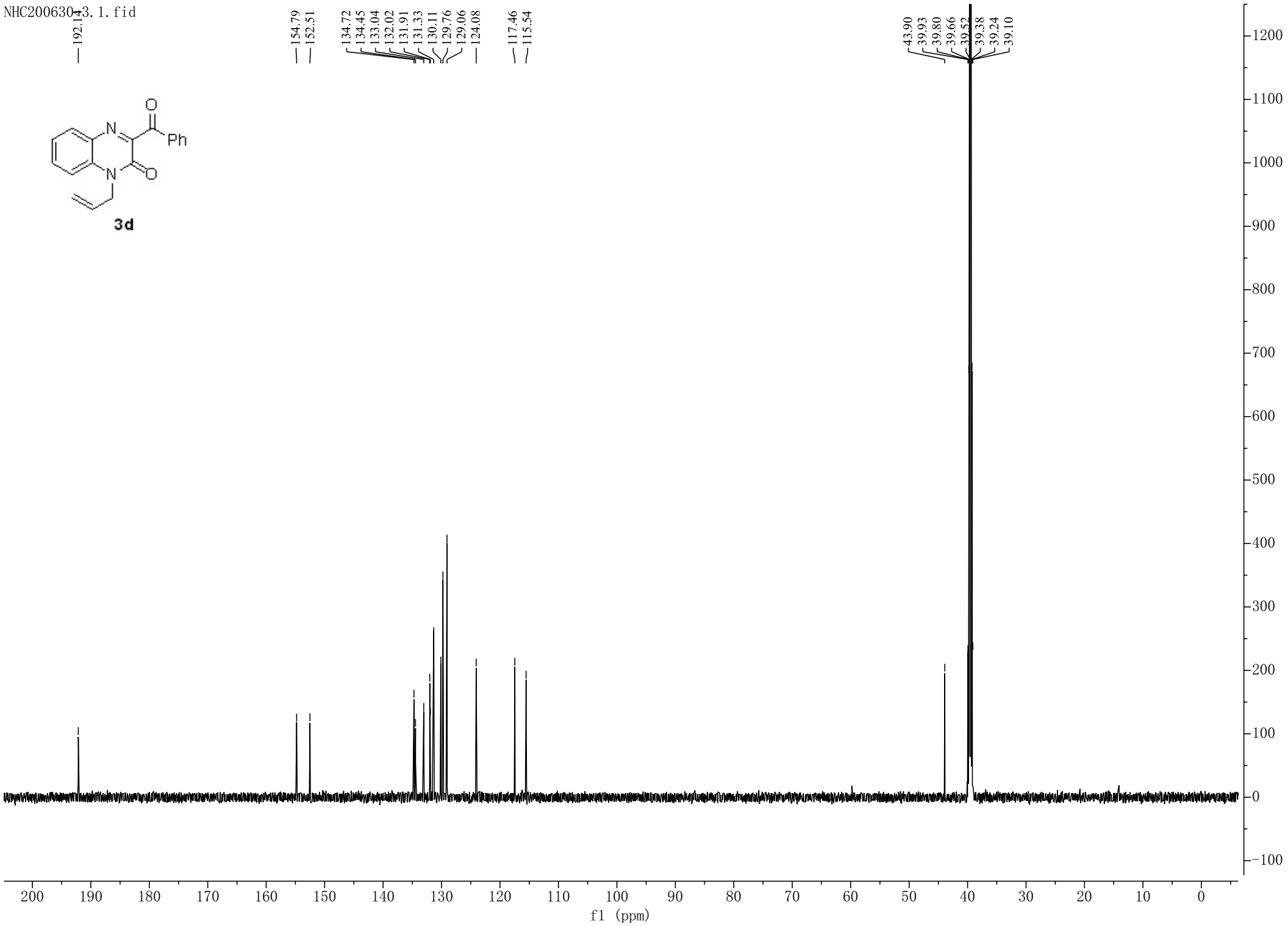


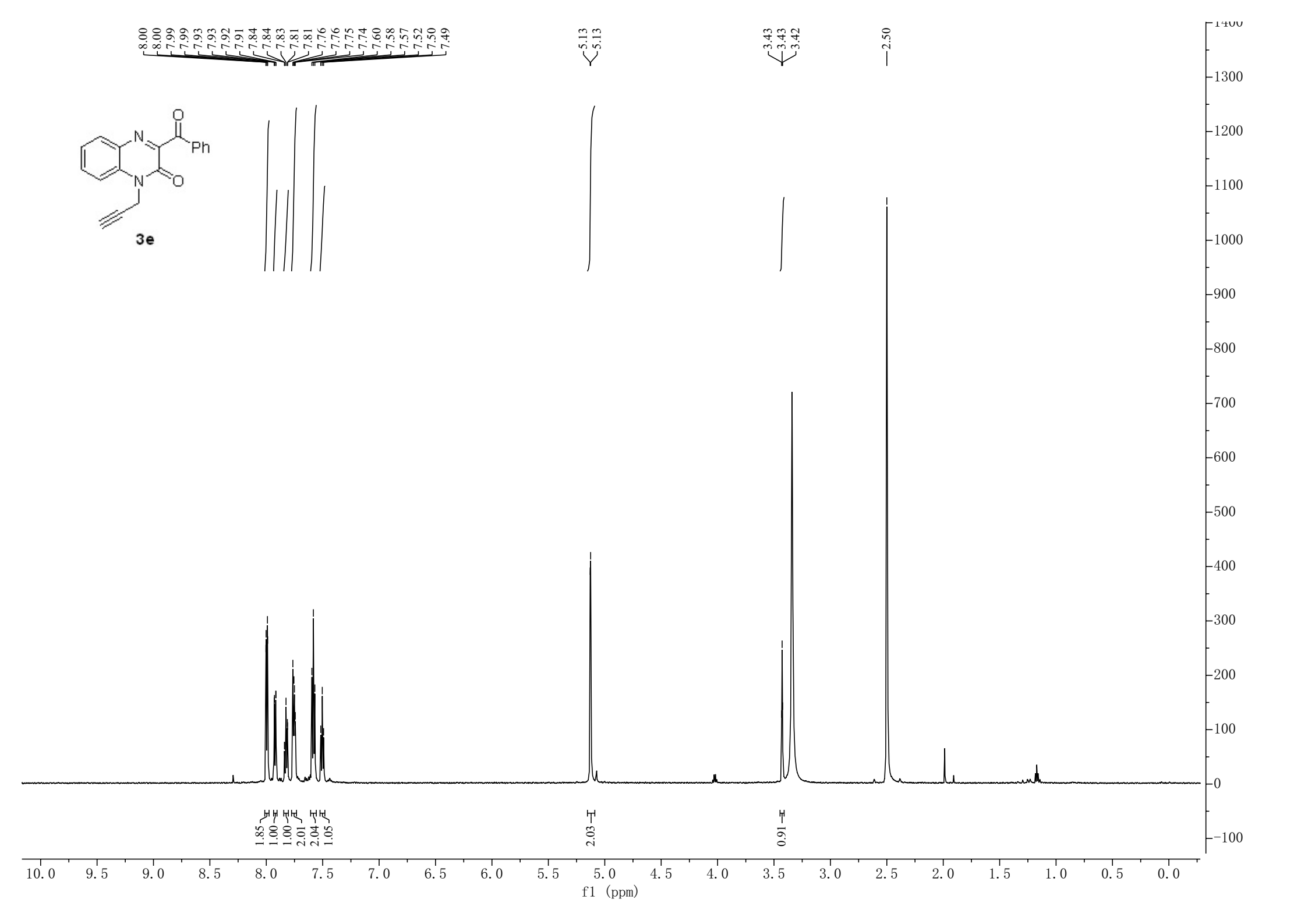
3c

192.07
154.86
153.07
135.47
134.74
134.45
133.09
132.09
132.03
130.24
129.81
129.08
128.80
127.50
126.89
124.20
115.53
45.00
40.06
39.93 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO

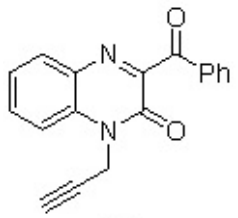
f1 (ppm)


8.00
7.99
7.91
7.90
7.76
7.75
7.74
7.74
7.74
7.73
7.63
7.62
7.59
7.58
7.57
7.47
7.46
7.45
6.01
6.00
5.99
5.98
5.98
5.97
5.97
5.96
5.95
5.24
5.22
5.19
5.16
4.93
4.92
3.34
2.50
2.50
2.50
1.99
O
N
Ph
N
O
3d
2.02
1.00
2.14
1.09
2.14
1.11
1.15
2.27
2.20
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10.0
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)


NHC200630-3.1.fid
192.14
154.79
152.51
134.72
134.45
133.04
132.02
131.91
131.33
130.11
129.76
129.06
124.08
117.46
115.54
43.90
39.93
39.80
39.66
39.52
39.38
39.24
39.10
O
N
Ph
N
O
3d
f1 (ppm)


8.00
8.00
7.99
7.99
7.93
7.93
7.92
7.91
7.84
7.84
7.83
7.81
7.81
7.76
7.76
7.75
7.74
7.60
7.58
7.57
7.52
7.50
7.49
5.13
5.13
3.43
3.43
3.42
2.50
O
N
Ph
O
N
3e
1.85
1.00
1.00
2.01
2.04
1.05
2.03
0.91
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10.0
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)

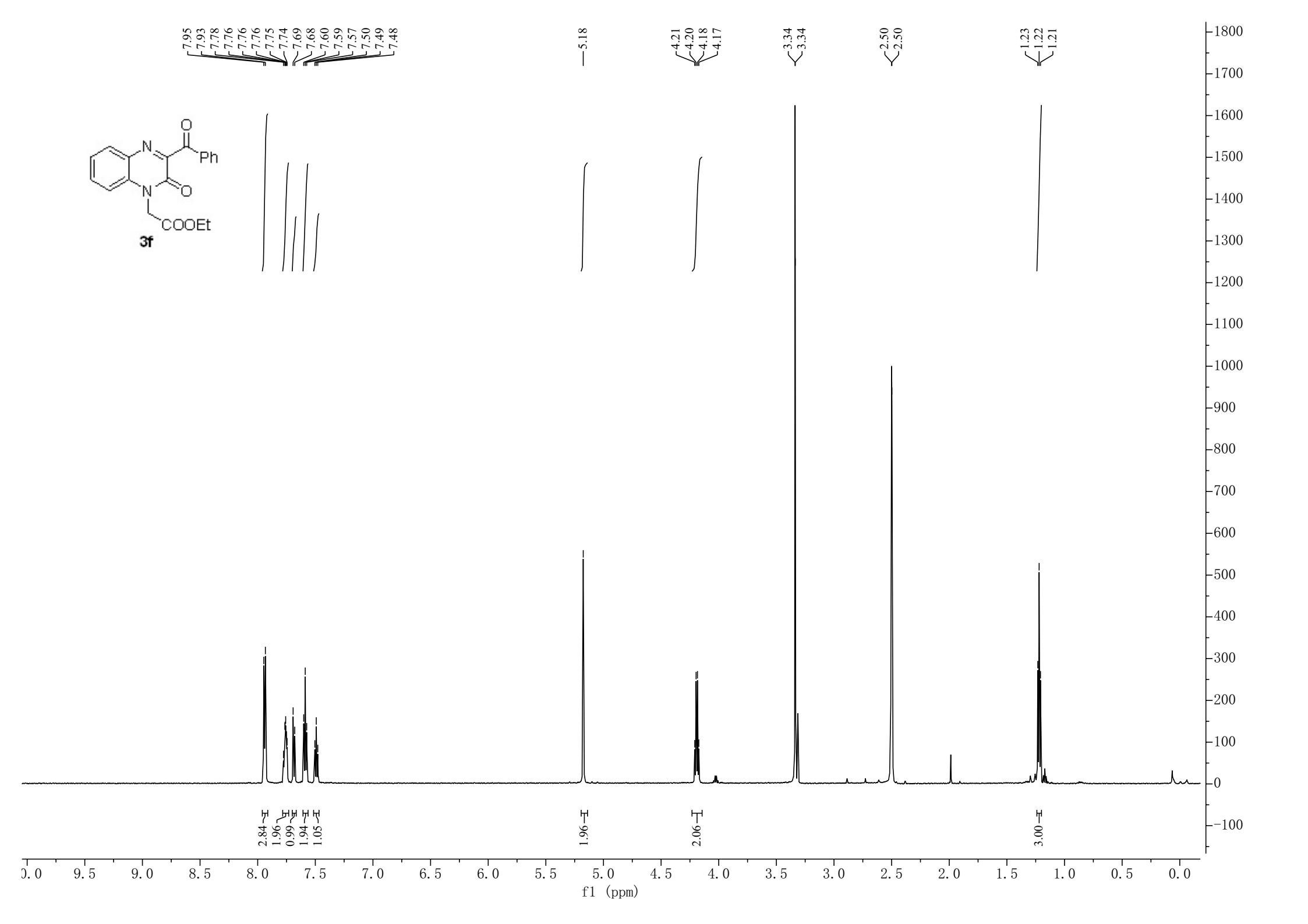
NHC200630-6.1.fid



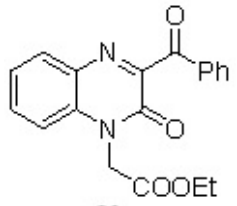
3e

191.80
154.58
151.95
134.81
134.31
132.31
132.24
131.86
130.21
129.81
129.08
124.47
115.41
77.66
75.64
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
31.35

f1 (ppm)


7.95
7.93
7.78
7.76
7.76
7.76
7.75
7.74
7.69
7.68
7.60
7.59
7.57
7.50
7.49
7.48
5.18
4.21
4.20
4.18
4.17
3.34
3.34
2.50
2.50
1.23
1.22
1.21
O
N
Ph
O
N
O
COOEt
3f
2.84
1.96
0.99
1.94
1.05
1.96
2.06
3.00
f1 (ppm)

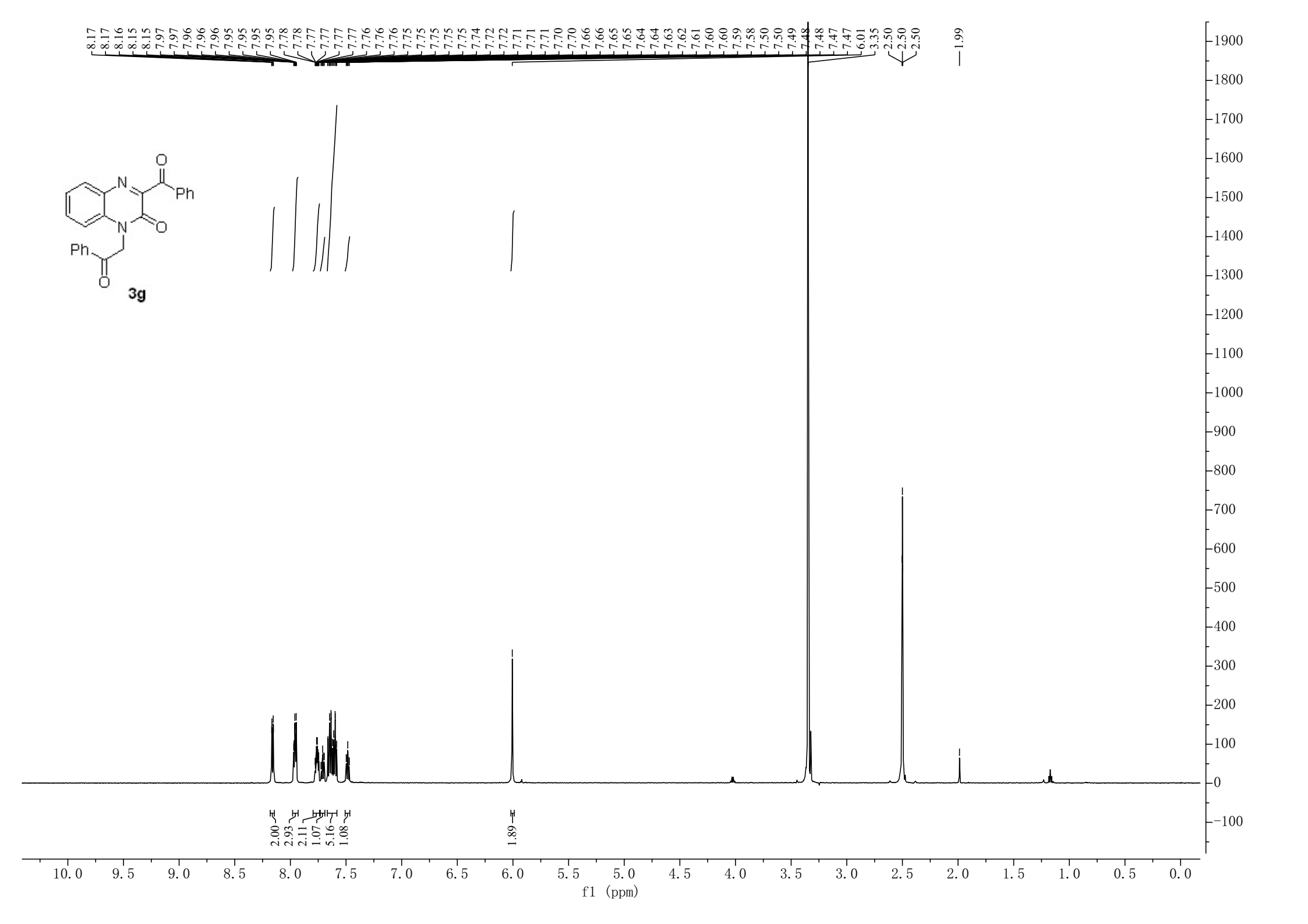
NHC200630-11.1.fid



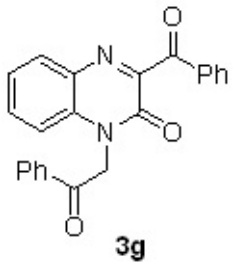
3f

191.72
167.22
154.39
152.61
134.85
134.31
133.17
132.39
131.68
130.27
129.64
129.14
124.45
115.09
61.58
43.67
40.06
39.93 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
14.00

f1 (ppm)


3g
f1 (ppm)

NHC200630-4.1.fid

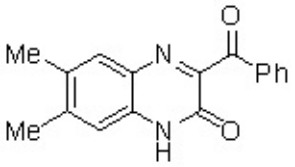


3g

192.05
191.82
154.37
152.67
134.81
134.37
134.29
133.59
132.30
131.76
130.20
129.60
129.15
129.00
128.40
124.31
115.39
49.08
39.93
39.80
39.66
39.52
39.38
39.24
39.10

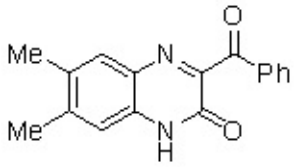
f1 (ppm)

nhc200428-7 phco 7,8-me.1.fid



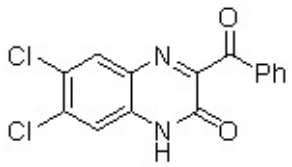
3h

NHC200630-9.1.fid



3h

nhc200428-8 pdco 7,8-cl.1.fid



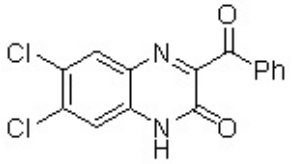
3i

13.00
8.17
8.00
7.99
7.77
7.75
7.74
7.59
7.58
7.57
7.55
3.34
2.50
2.50
2.50

1.08
0.80
2.00
1.09
2.14
1.00

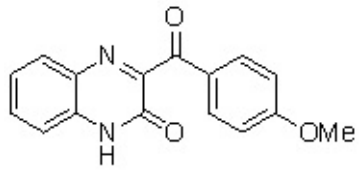
f1 (ppm)

NHC200630-10.1.fid



3i

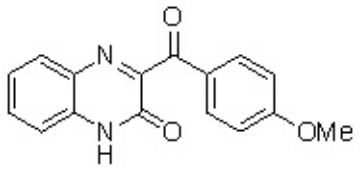
nhc200512-8 p-omephco nh.1.fid



3j

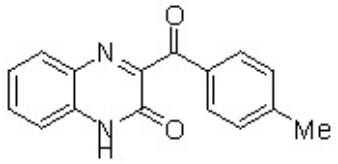
f1 (ppm)

nhc-200602-6.1.fid



3j

nhc200428-10 p-me-phco n-h.1.fid



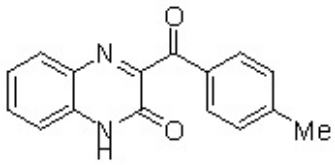
3k

12.85
7.86
7.85
7.83
7.81
7.66
7.65
7.63
7.41
7.39
7.38
7.37
7.36
3.34
2.50
2.50
2.41

0.99
1.82
1.00
1.00
4.03
2.97

f1 (ppm)

SIIA-NHC200708-1.1.fid



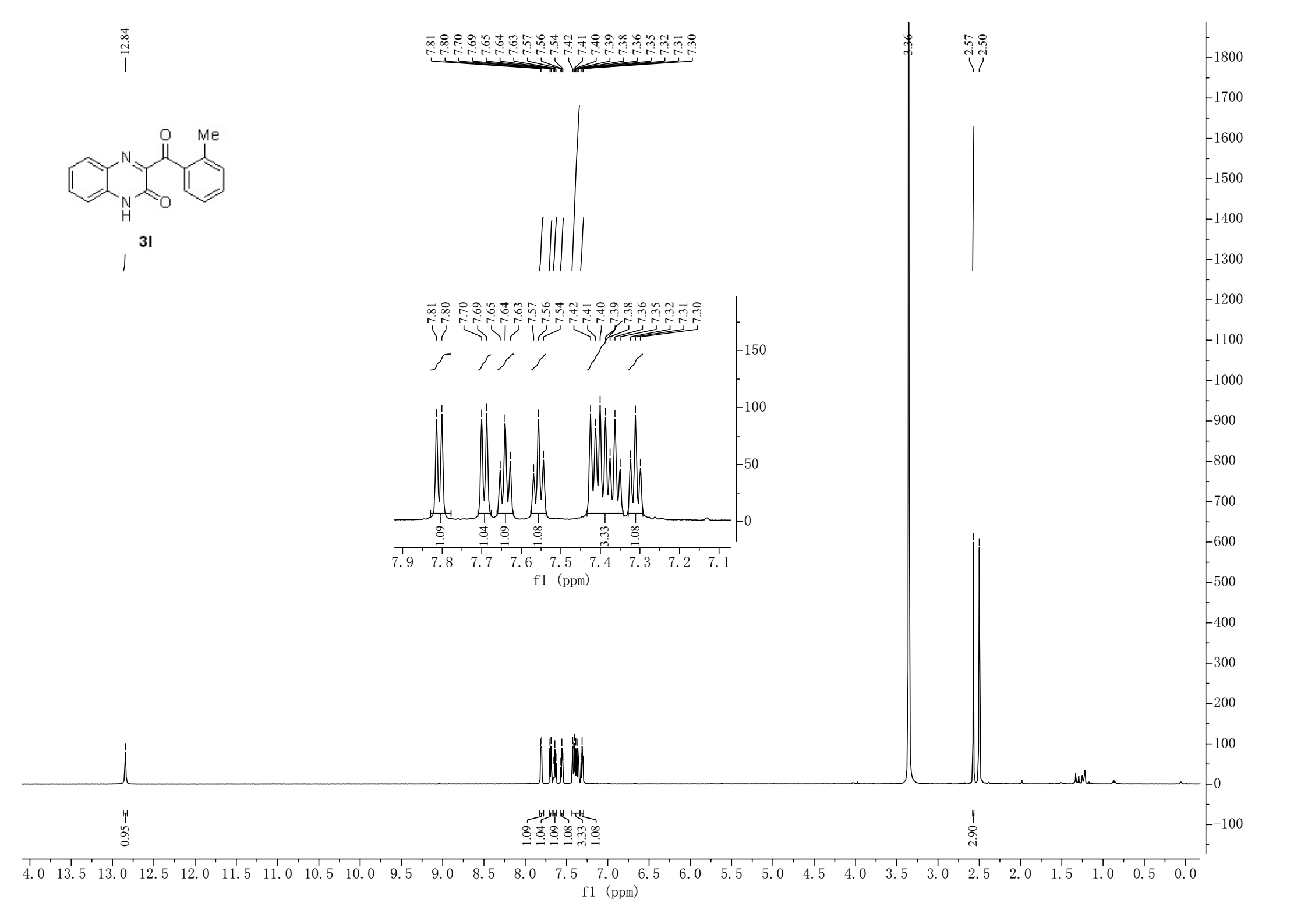
3k

191.98
156.50
153.38
145.38
132.66
132.19
131.67
131.22
129.79
129.58
129.08
123.79
115.89
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
21.37

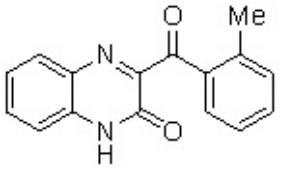
3500
3000
2500
2000
1500
1000
500
0

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


12.84
7.81
7.80
7.70
7.69
7.65
7.64
7.63
7.57
7.56
7.54
7.42
7.41
7.40
7.39
7.38
7.36
7.35
7.32
7.31
7.30
3.36
2.57
2.50
O
Me
N
O
N
H
3l
1.09
1.04
1.09
1.08
3.33
1.08
2.90
f1 (ppm)

nhc-200602-10.1.fid

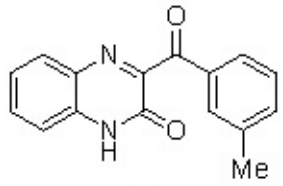


3l

194.35
156.99
153.28
139.43
133.94
133.23
132.65
132.43
132.10
131.70
131.14
129.09
126.13
123.82
115.86
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
21.13

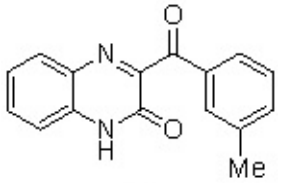
f1 (ppm)

nhc200512-11-m-me-ph nh.1.fid



3m

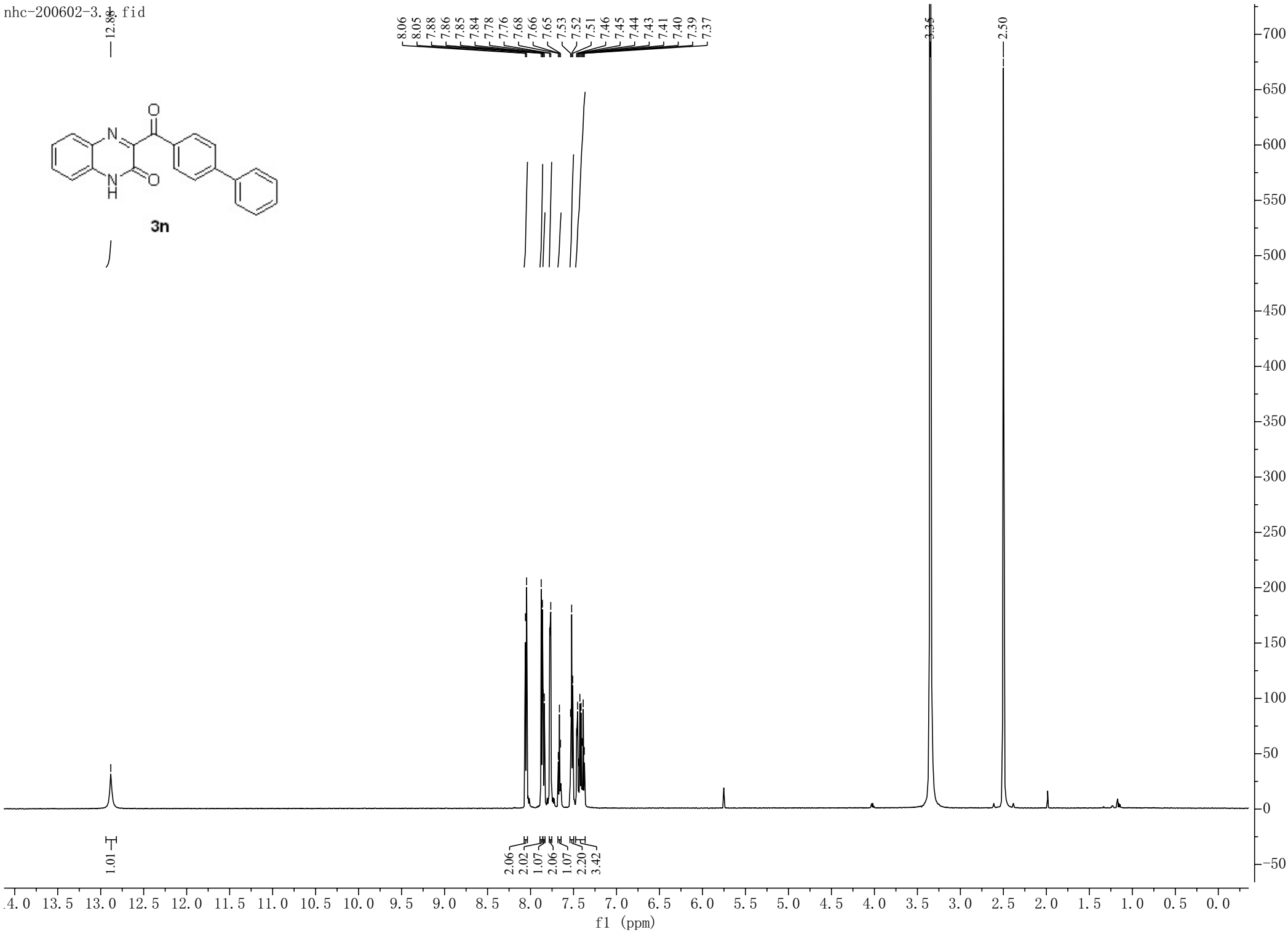
nhc-200602-9.1.fid

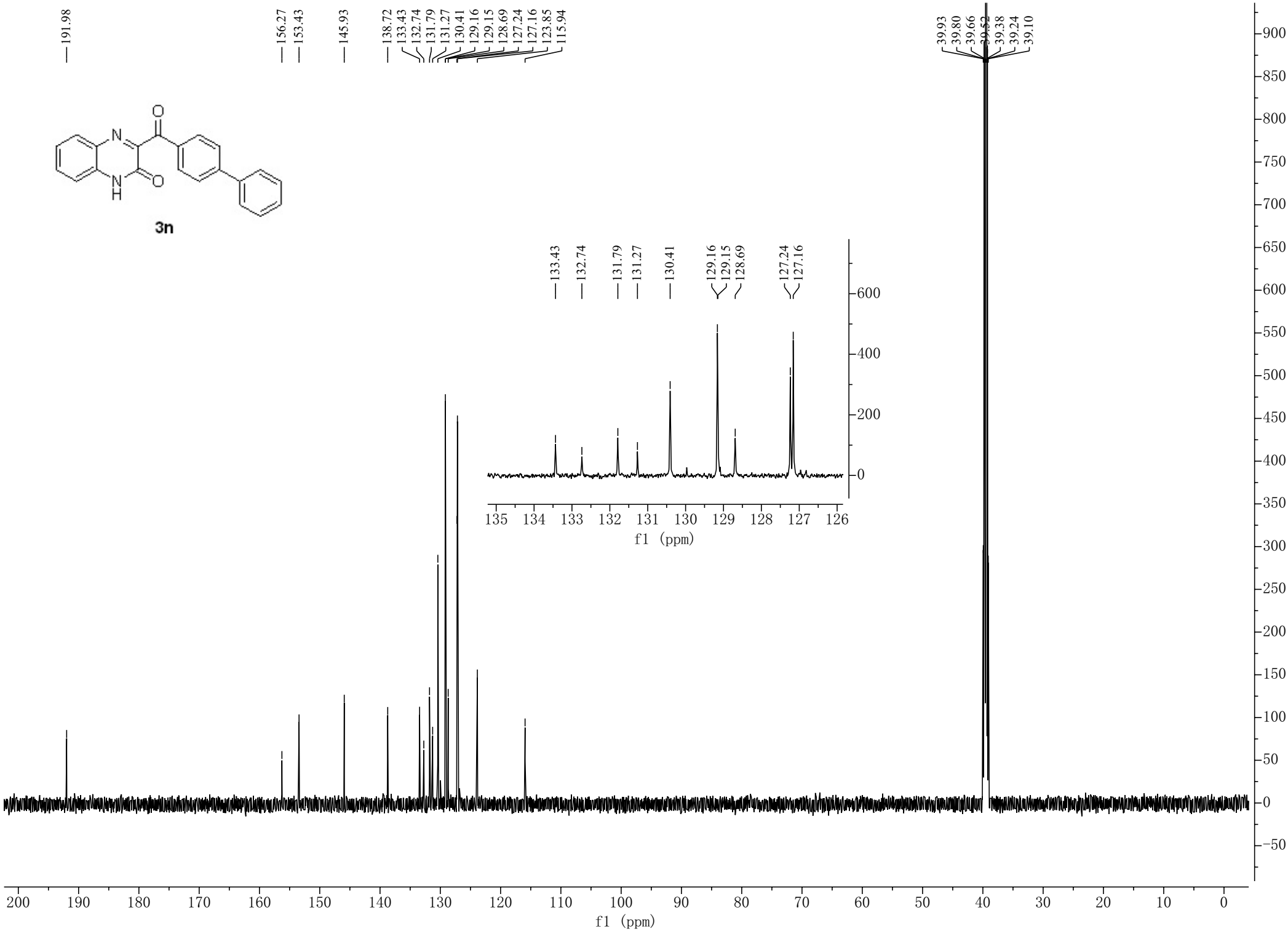


3m

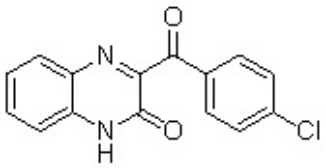
192.63
156.49
153.37
138.58
135.27
134.65
132.67
131.66
131.24
129.87
129.10
128.89
126.90
123.79
115.90
40.06
39.93 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
20.71

f1 (ppm)


nhc-200602-3.1.fid
12.88
8.06
8.05
7.88
7.86
7.85
7.84
7.78
7.76
7.68
7.66
7.65
7.53
7.52
7.51
7.46
7.45
7.44
7.43
7.41
7.40
7.39
7.37
3.35
2.50
3n
1.01
2.06
2.02
1.07
2.06
1.07
2.20
3.42
f1 (ppm)


191.98
156.27
153.43
145.93
138.72
133.43
132.74
131.79
131.27
130.41
129.16
129.15
128.69
127.24
127.16
123.85
115.94
39.93
39.80
39.66
39.52
39.38
39.24
39.10
O
N
N
H
O
3n
f1 (ppm)
f1 (ppm)

nhc200512-9 p-cl-phco nh.1.fid

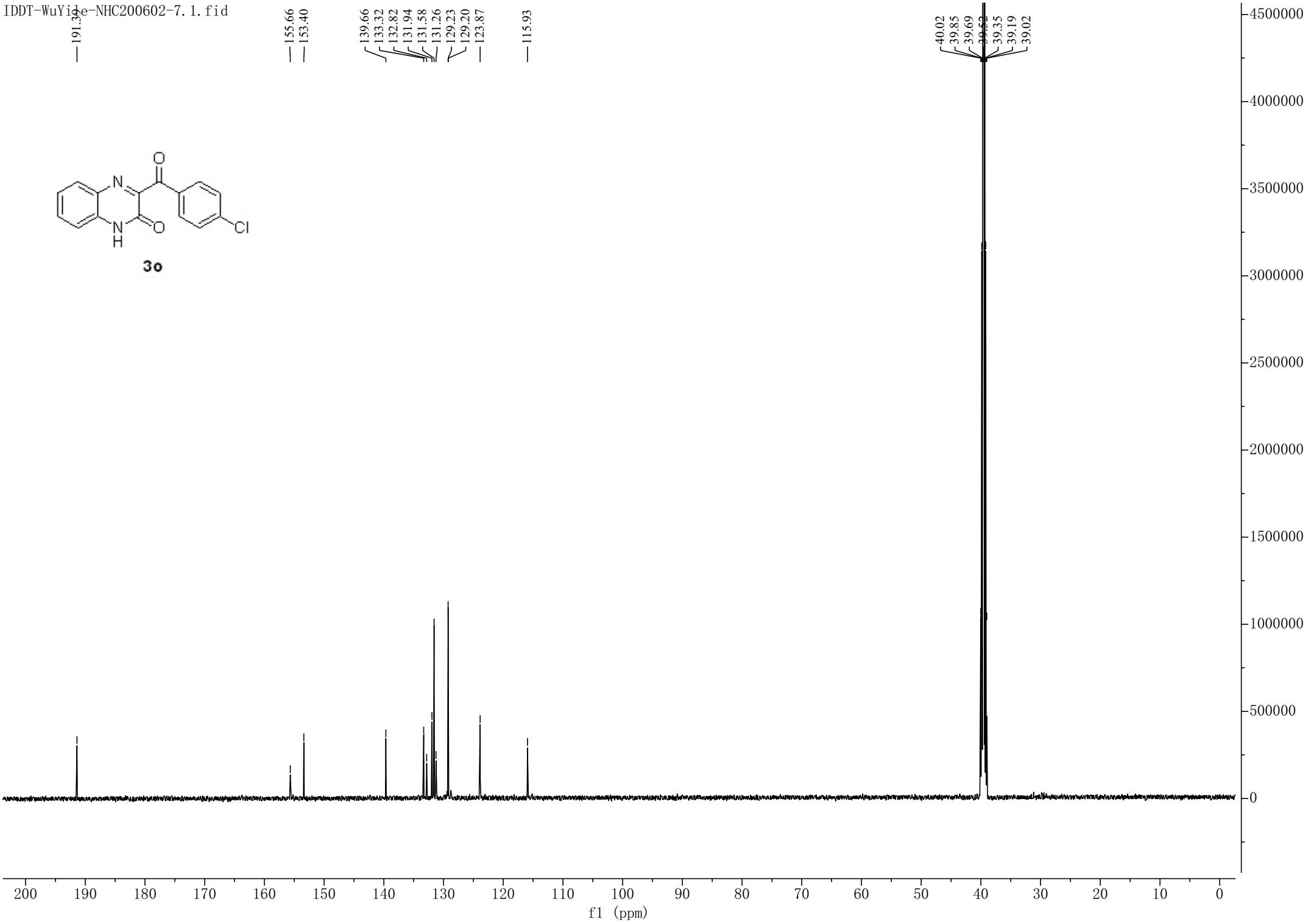


3o

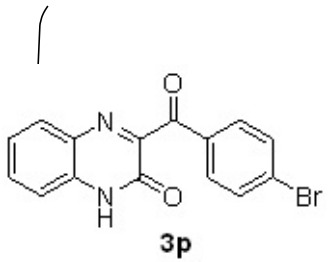
12.83
8.02
8.00
7.83
7.82
7.67
7.66
7.65
7.64
7.41
7.40
7.39
7.38
7.37
3.36
2.50

1.00
1.95
0.98
3.18
2.26

f1 (ppm)

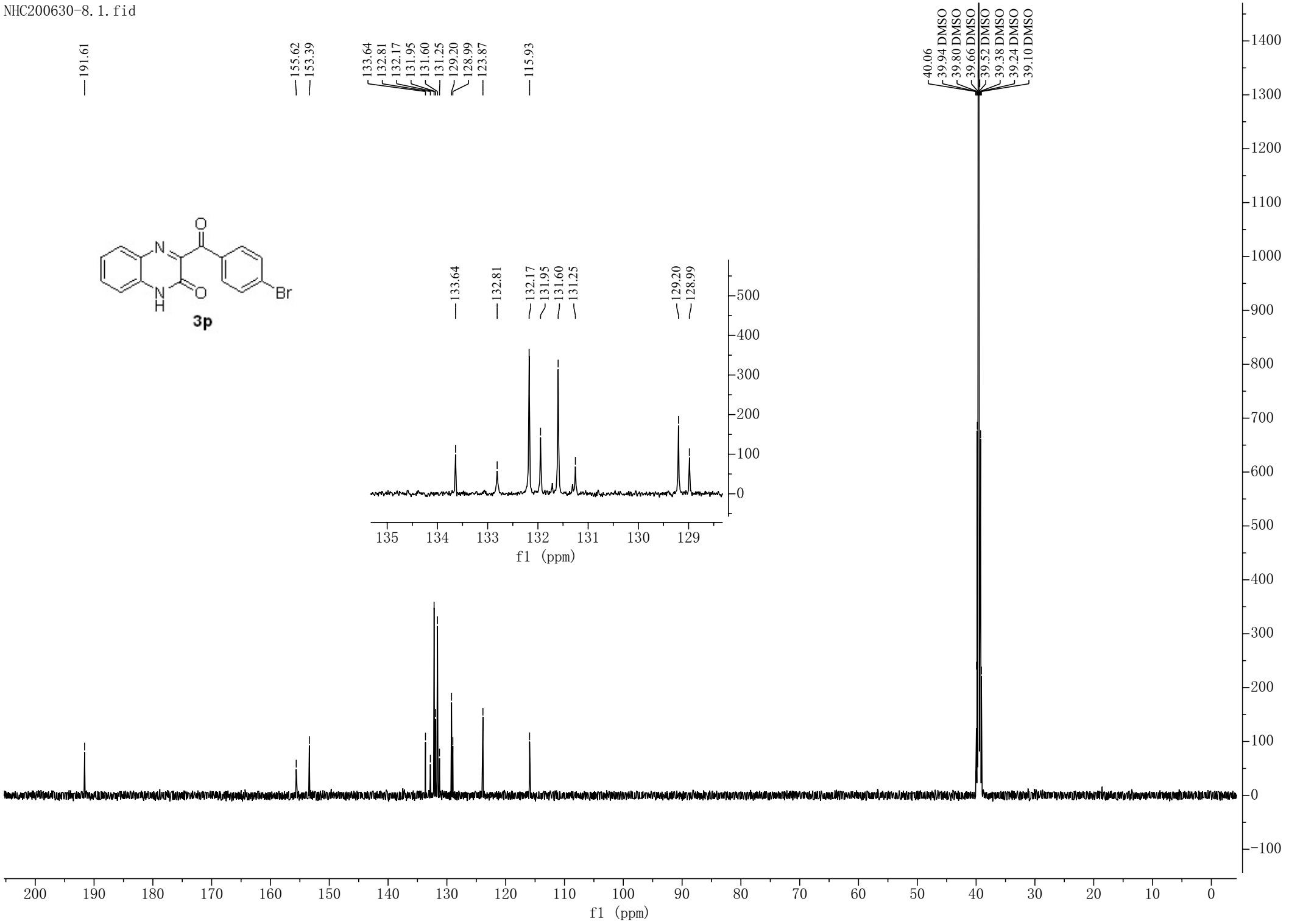

IDDT-WuYide-NHC200602-7.1.fid
191.39
155.66
153.40
139.66
133.32
132.82
131.94
131.58
131.26
129.23
129.20
123.87
115.93
40.02
39.85
39.69
39.52
39.35
39.19
39.02
O
N
N
H
O
O
Cl
3o
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

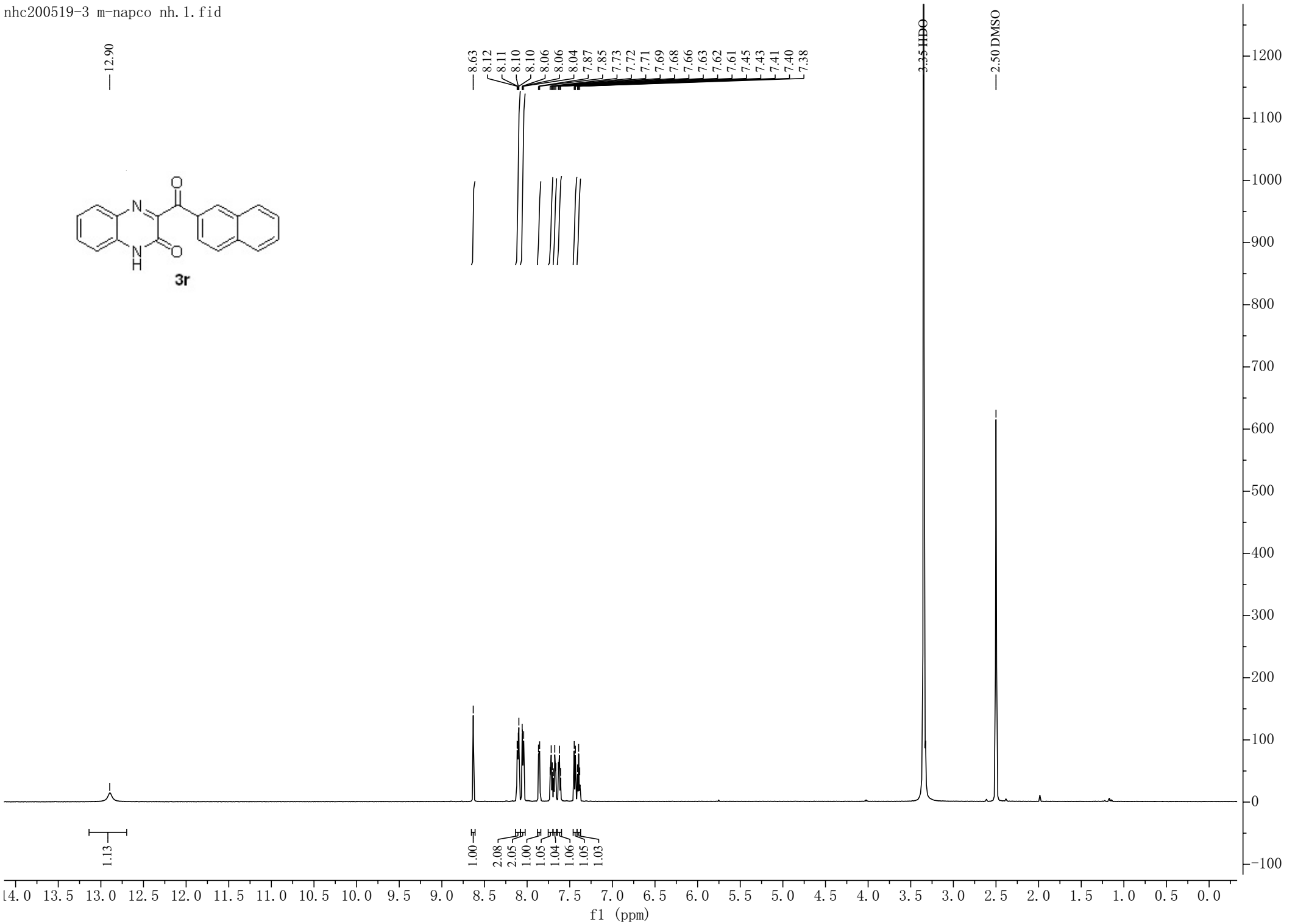
nhc200428-11 pybr-phco n-h.1.fid

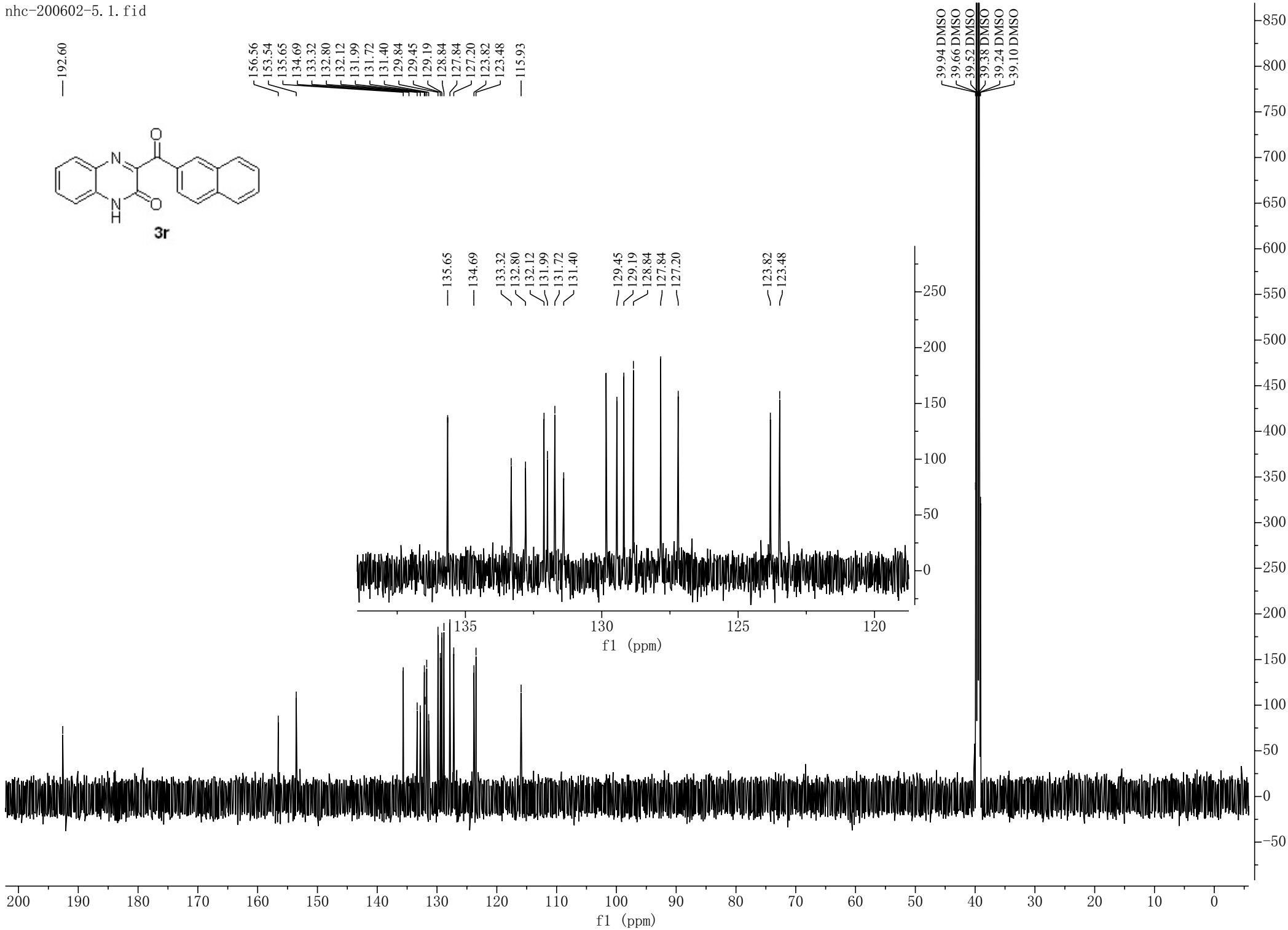


3p

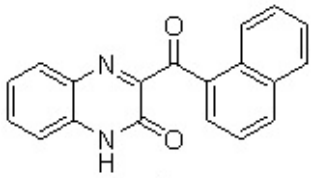
NHC200630-8.1.fid




nhc200519-3 m-napco nh.1.fid
12.90
8.63
8.12
8.11
8.10
8.10
8.06
8.06
8.04
7.87
7.85
7.73
7.72
7.71
7.69
7.68
7.66
7.63
7.62
7.61
7.45
7.43
7.41
7.40
7.38
3.35 HDO
2.50 DMSO
3r
1.13
1.00
2.08
2.05
1.00
1.05
1.04
1.06
1.05
1.03
f1 (ppm)

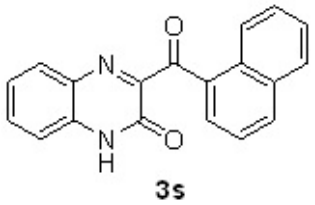

nhc-200602-5.1.fid
192.60
156.56
153.54
135.65
134.69
133.32
132.80
132.12
131.99
131.72
131.40
129.84
129.45
129.19
128.84
127.84
127.20
123.82
123.48
115.93
39.94 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
3r
f1 (ppm)

nhc200512-10-o-nap-co nh.1.fid

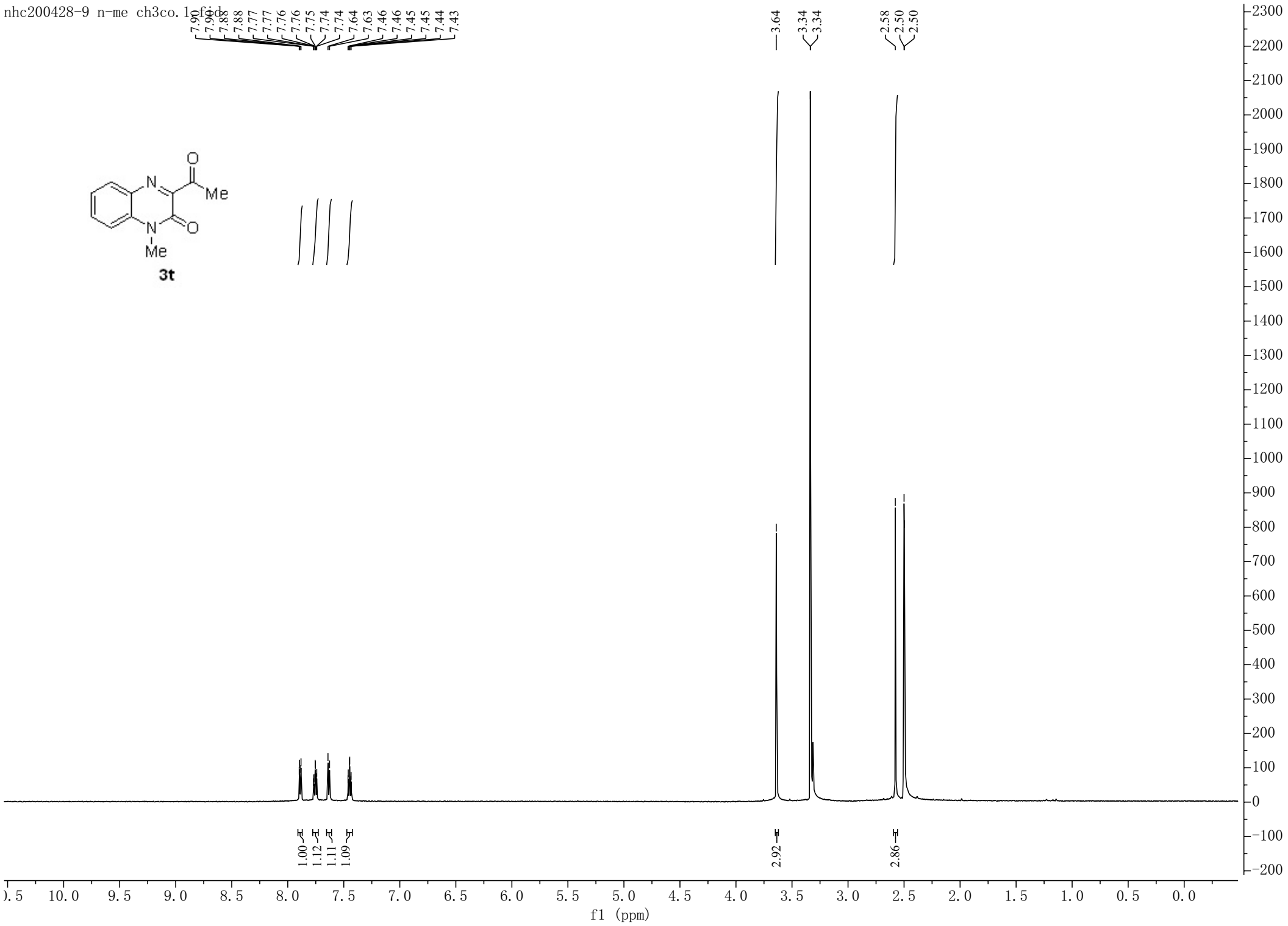


3s

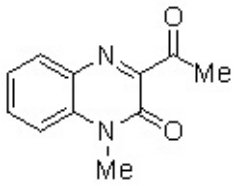
nhc200512-10-o-nap-co nh.1.fid



3s


nhc200428-9 n-me ch3co.1r.fid
7.90
7.90
7.88
7.88
7.77
7.77
7.76
7.76
7.75
7.74
7.74
7.64
7.63
7.46
7.46
7.45
7.45
7.44
7.43
3.64
3.34
3.34
2.58
2.50
2.50
O
N
Me
O
N
Me
3t
1.00
1.12
1.11
1.09
2.92
2.86
f1 (ppm)

SIIA-NHC200708-2.1.fid

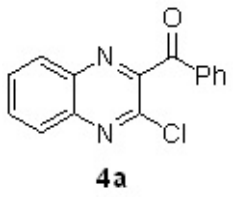


3t

198.67
152.93
152.24
134.18
132.48
131.22
130.23
123.94
115.08
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
28.90
28.55

f1 (ppm)

nhc-200602-1.1.fid



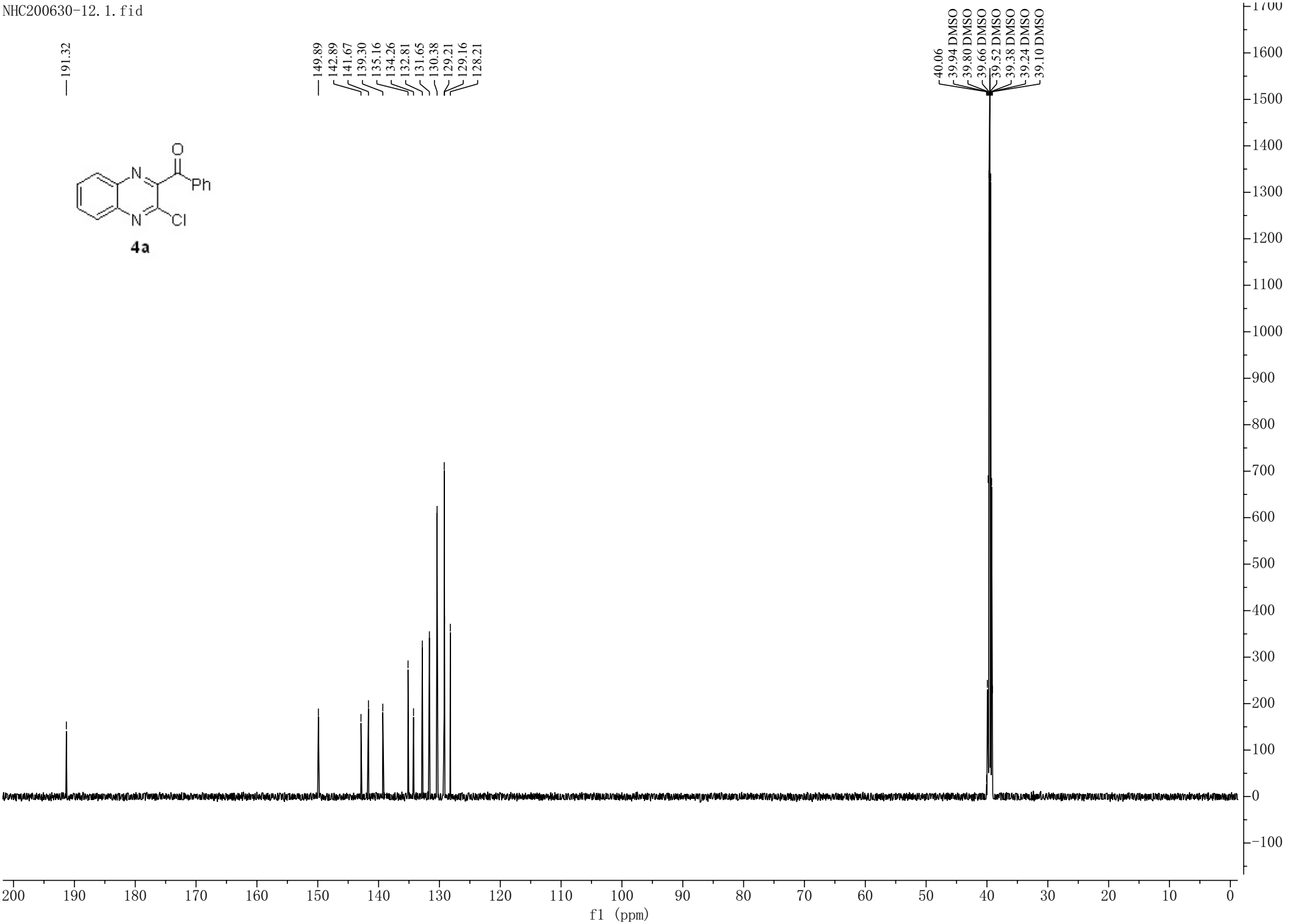
4a

8.16
8.15
8.13
8.12
7.93
7.92
7.91
7.89
7.87
7.86
7.85
7.69
7.68
7.67
7.53
7.52
7.51
7.26 CDCl3
1.57

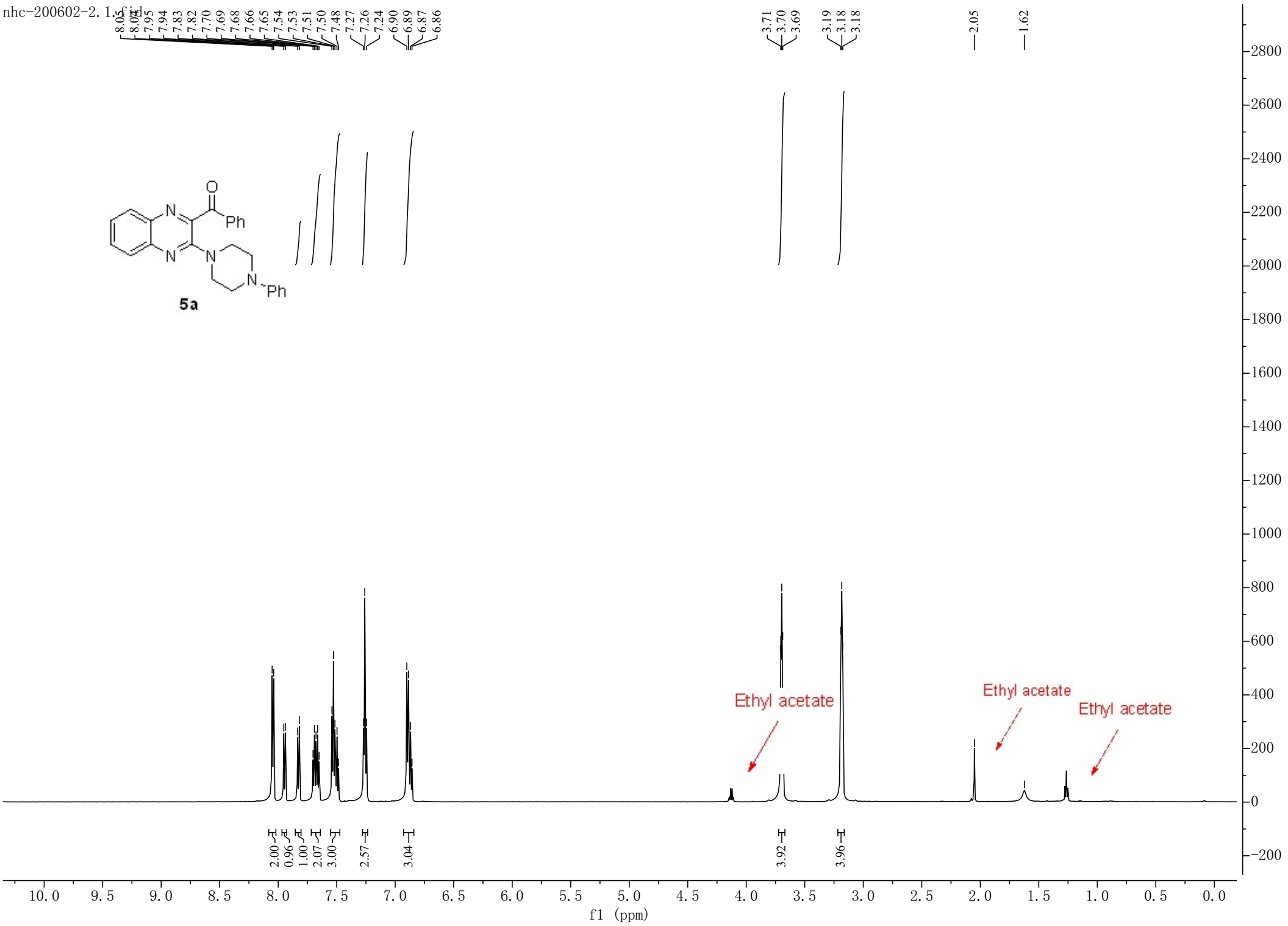
1.91
2.87
1.00
1.00
1.99

f1 (ppm)

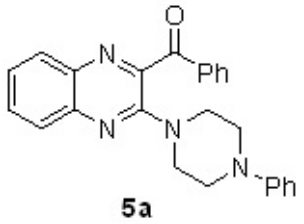
NHC200630-12.1.fid



nhc-200602-2.1.fid



NHC200630-13.1.fid



5a

192.76
151.40
150.57
144.14
140.97
135.28
134.88
134.48
131.58
130.47
129.00
128.95
128.74
126.31
126.06
119.06
115.42
47.49
47.29
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO

f1 (ppm)