Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bromide-catalyzed oxo-amination of alkenes towards the synthesis of α-amine ketones under photoelectrocatalysis conditions

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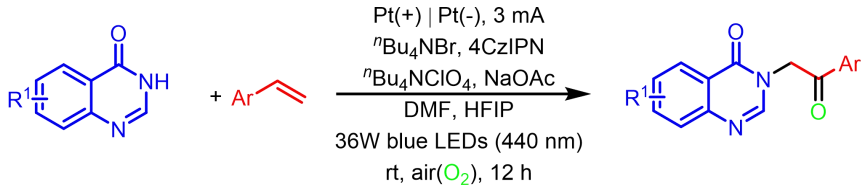
1.General information

All glassware were oven dried at 110 ℃ for several hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. **The instrument for electrolysis** was dual display potentiostat (DJS-292B) (made in China). Both of the anode electrode and cathodic electrode were platinum plates (10 mm×10 mm×0.2 mm). Thin-layer chromatography was performed with EMD silica gel 100 F254 plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid (PMA). Flash chromatography columns were packed with 60-100 mesh silica gel in petroleum (bp. 60-90 ℃). **^{1}H NMR**, **^{13}C NMR** and **^{19}F NMR** spectra were obtained on Bruker Advance III (400 MHz). Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent $CDCl_3$ (7.26 ppm), tetramethylsilane (0.00 ppm) asinternal reference for ^{1}H NMR and the deuterated solvent $CDCl_3$ (77.16 ppm) tetramethylsilane (0.00 ppm) as internal standard for ^{13}C NMR； solvent d_6-DMSO (2.50 ppm), tetramethylsilane (0.00 ppm) asinternal reference for ^{1}H NMR and the deuterated solvent d_6-DMSO (39.52 ppm) tetramethylsilane (0.00 ppm) as internal standard for ^{13}C NMR， multiplicities are as indicated: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. **High-resolution mass spectral analysis (HRMS) data** was measured on a Waters Acquity UPLC I-Class plus Xevo G2-XS (Q-TOF) mass spectrum by means of the ESI technique. **Crystallographic data** were obtained from a Bruker D8 Quest diffractometer. The compounds **1** and **2** were all purchased.

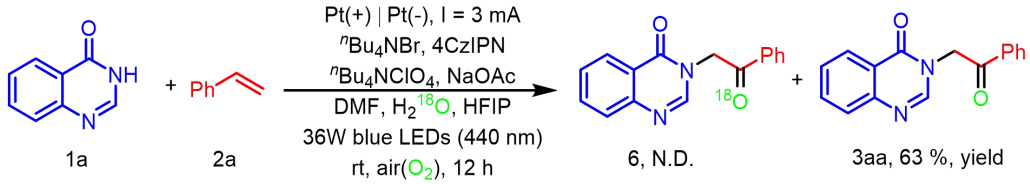
2.General procedure for the synthesis of products



General procedure for the preparation of **3**: Unless otherwise noted, reactions were conducted using: Pt plate anode (10 mm × 10 mm × 0.2 mm), Pt plate cathode (10 mm × 10 mm × 0.2 mm), constant current = 3 mA, **1** (0.2 mmol), **2** (0.4 mmol), $^{n}Bu_4NBr$ (10 mol%), 4CzIPN (2 mol%), $^{n}Bu_4NClO_4$ (0.4 mmol), NaOAc (0.4 mmol) , HFIP (0.4 mmol), DMF (3.0 mL), room temperature, undivided cell. Then stirred for 12 h. The resulting brown mixture was concentrated under a vacuum, the crude product was purified by flash column chromatography using petroleum ether/EtOAc (3:1) to give the title compounds **3**.

The control experiments.

(a)

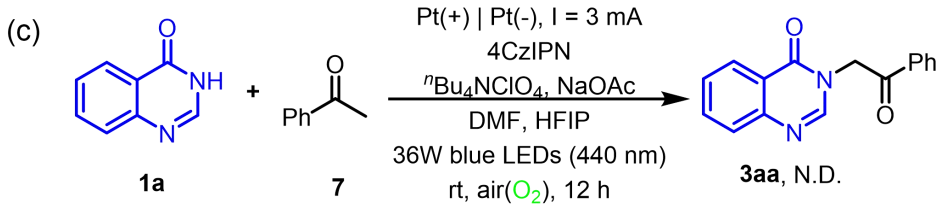


Unless otherwise noted, reactions were performed: **1a** (0.2 mmol, 29.2 mg), **2a** (0.4 mmol, 41.7 mg, 46.0 μL), $^{n}Bu_4NBr$ (10 mol%, 6.4 mg), 4CzIPN (2 mol%, 3.2 mg), $^{n}Bu_4NClO_4$ (0.4 mmol, 136.8 mg), NaOAc (0.4 mmol, 32.8 mg), HFIP (0.4 mmol, 67.2 mg, 42.0 μL), $H_2{}^{18}O$ (0.8 mmol, 16.0 mg, 16.0 μL) were added to DMF (3.0 mL) under air atmosphere at room temperature. Then stirred for 12 h. The resulting yellow mixture was concentrated under vacuum, the crude product was purified by flash column chromatography using petroleum ether/ EtOAc (3:1) to give the compound and detected by HRMS.

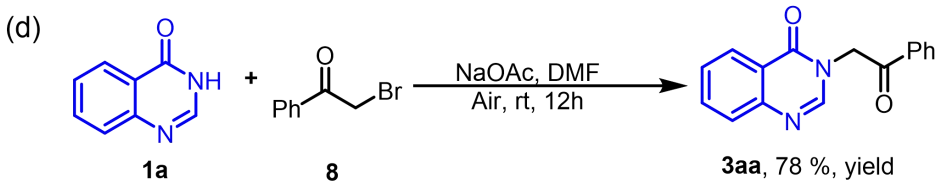
(b)

Unless otherwise noted, reactions were performed: **1a** (0.2 mmol, 29.2 mg), **2a** (0.4 mmol, 41.7 mg, 46.0 μL), $^{n}Bu_4NBr$ (10 mol%, 6.4 mg), 4CzIPN (2 mol%, 3.2 mg), $^{n}Bu_4NClO_4$ (0.4 mmol, 136.8 mg), NaOAc (0.4 mmol, 32.8 mg), HFIP (0.4 mmol, 67.2 mg, 42.0 μL), TEMPO (0.4 mmol,

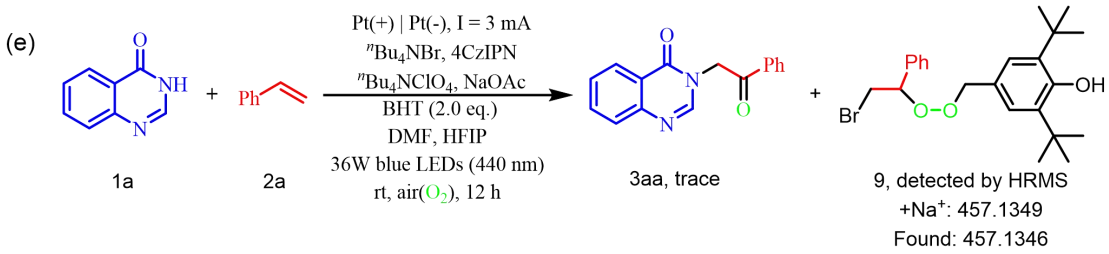
62.5 mg) (or BHT (0.4 mmol, 88.1 mg)) were added to DMF (3.0 mL) under air atmosphere at room temperature. Then stirred for 12 h. Detected by HRMS.



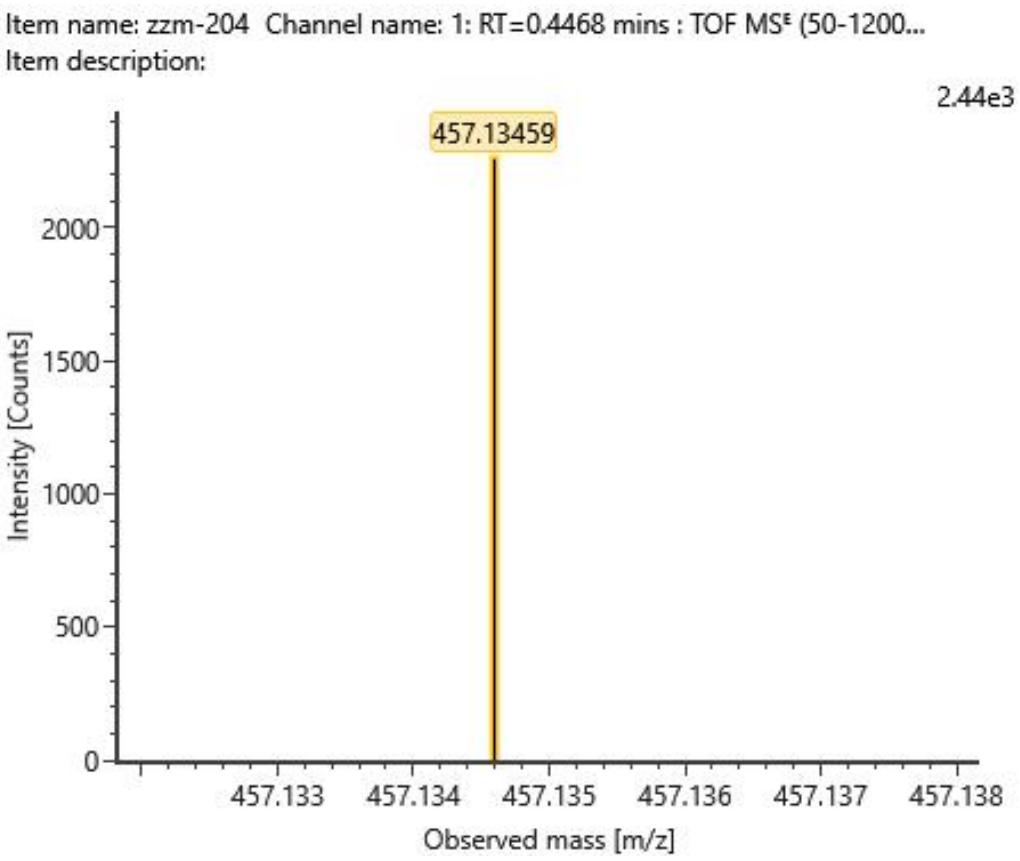
Unless otherwise noted, reactions were performed: **1a** (0.2 mmol, 29.2 mg), **7** (0.4 mmol, 48.1 mg, 47.0 μL), 4CzIPN (2 mol%, 3.2 mg), $^{n}Bu_4NClO_4$ (0.4 mmol, 136.8 mg), NaOAc (0.4 mmol, 32.8 mg), HFIP (0.4 mmol, 67.2 mg, 42.0 μL) were added to DMF (3.0 mL) under air atmosphere at room temperature. Then stirred for 12 h. Detected by HRMS.

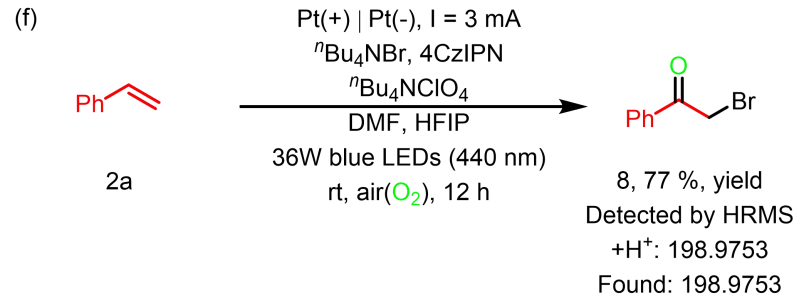


Unless otherwise noted, reactions were performed: **1a** (0.2 mmol, 29.2 mg), **8** (0.4 mmol, 79.6 mg), NaOAc (0.4 mmol, 32.8 mg) were added to DMF (3.0 mL) under air atmosphere at room temperature. Then stirred for 12 h. The resulting yellow mixture was concentrated under vacuum, the crude product was purified by flash column chromatography using petroleum ether/ EtOAc (3:1) to give the compound **3aa**.

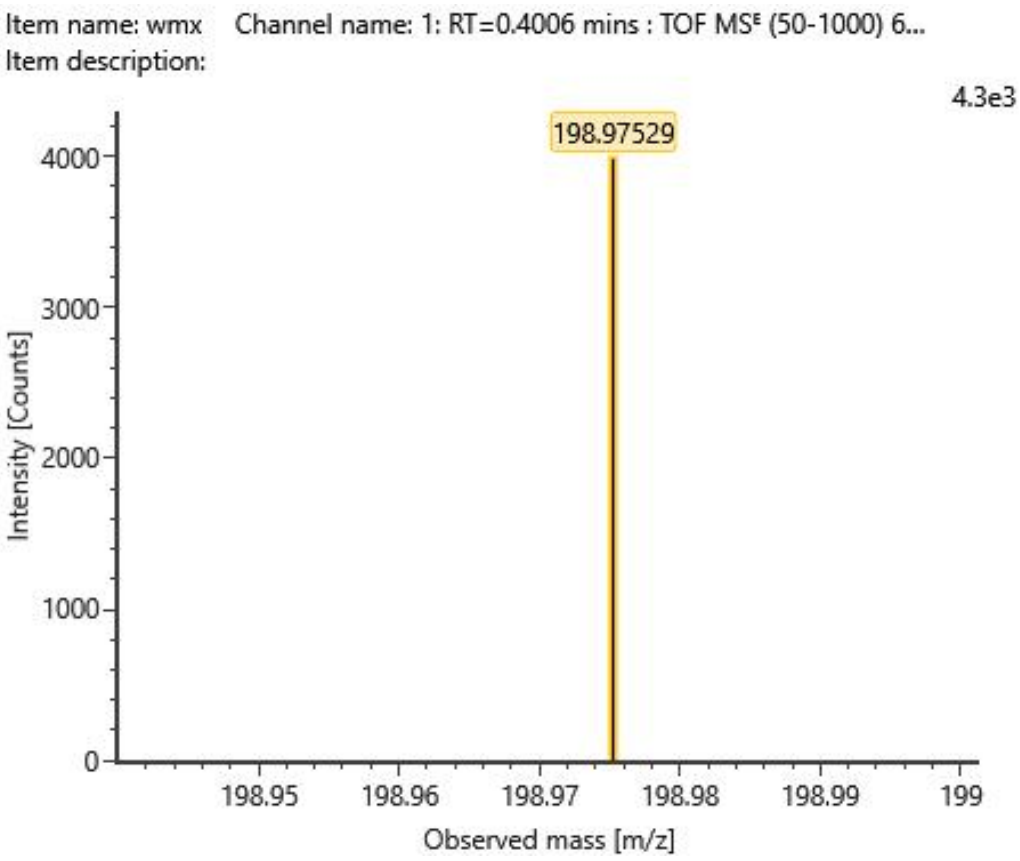


Unless otherwise noted, reactions were performed: **1a** (0.2 mmol, 29.2 mg), **2a** (0.4 mmol, 41.7 mg, 46.0 μL), $^{n}Bu_4NBr$ (10 mol%, 6.4 mg), 4CzIPN (2 mol%, 3.2 mg), $^{n}Bu_4NClO_4$ (0.4 mmol, 136.8 mg), NaOAc (0.4 mmol, 32.8 mg), HFIP (0.4 mmol, 67.2 mg, 42.0 μL), BHT (0.4 mmol, 88.1 mg) were added to DMF (3.0 mL) under air atmosphere at room temperature. Then stirred for 12 h. Detected by HRMS.

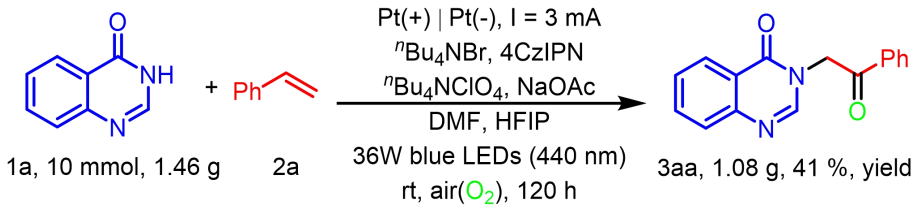




Unless otherwise noted, reactions were performed: **2a** (0.4 mmol, 41.7 mg, 46.0 μL), ^{n}Bu$_4$NBr (0.4 mmol, 128.9 mg), 4CzIPN (2 mol%, 3.2 mg), ^{n}Bu$_4$NClO$_4$ (0.4 mmol, 136.8 mg), HFIP (0.4 mmol, 67.2 mg, 42.0 μL), were added to DMF (3.0 mL) under air atmosphere at room temperature. Then stirred for 12 h. The resulting yellow mixture was concentrated under vacuum, the crude product was purified by flash column chromatography using petroleum ether/ EtOAc (30:1) to give the compound. Detected by HRMS and NMR.



Gram-scale reaction.



1a, 10 mmol, 1.46 g 2a 3aa, 1.08 g, 41 %, yield

Unless otherwise noted, reactions were performed: **1a** (10.0 mmol, 1.46 g), **2a** (20 mmol, 2.08 g, 2.3 mL), ^{n}Bu$_4$NBr (10 mol%, 322.4 mg), 4CzIPN (2 mol%, 160.0 mg), ^{n}Bu$_4$NClO$_4$ (10 mmol, 3.4 g), NaOAc (20 mmol, 0.7 g), HFIP (20 mmol, 3.36 g, 0.8 mL) were added to DMF (30 mL) under air atmosphere at room temperature. Then stirred for 120 h. The resulting yellow mixture was concentrated under vacuum, the crude product was purified by flash column chromatography using petroleum ether/ EtOAc (3:1) to give the compound **3aa**.

3.Cyclic voltammetry experiments

Before the experiment, the glassy carbon disk electrode (≈5.0 mm^2) was polished step by step with metallographic sandpaper from 28 μm to 3.5 μm, and then polished to the mirror surface with 1.0, 0.3 μm Al_2O_3 slurry on the suede in turn. After each polishing, the surface dirt was washed first, and then moved into the ultrasonic water bath for cleaning, every 2 ~ 3 min, repeated three

times, and finally followed by ultrasonic cleaning with 1 : 1 ethanol, 1 : 1 HNO_3 and distilled water. After thorough washing, the electrode was activated by cyclic voltammetry in 0.5-1.0 mol / L H_2SO_4 solution. The scan range was 1.0 ~ -1.0V, and the scan was repeated until a stable cyclic voltammogram was reached. Finally, the cyclic voltammetry curve of 1×10^{-3} mol / L $K_3Fe(CN)_6$ solution was recorded in 0.20 mol / L KNO_3 to test the electrode performance. The scanning speed was 50 mV / s and the scanning range was -0.2 ~ 0.6 V. The peak potential difference in the cyclic voltammogram obtained under laboratory conditions is below 80 mV, and as close as possible to 64 mV, the electrode can be used, otherwise the electrode should be reprocessed until it meets the requirements.

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode (≈5.0 mm^2), the counter electrode a platinum wire. The reference was an $Ag/AgNO_3$ electrode submerged in 0.1 M $^n Bu_4NClO_4$ and 0.01 M $AgNO_3$ in CH_3CN. 3 mL of DMF were poured into the electrochemical cell in all experiments. The redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured (same experimental conditions) and used to provide an internal reference. The potential values were then adjusted relative to Fc/Fc^+. The scan rate is 0.1 V/s, ranging from -0.2 V to 2.0 V.

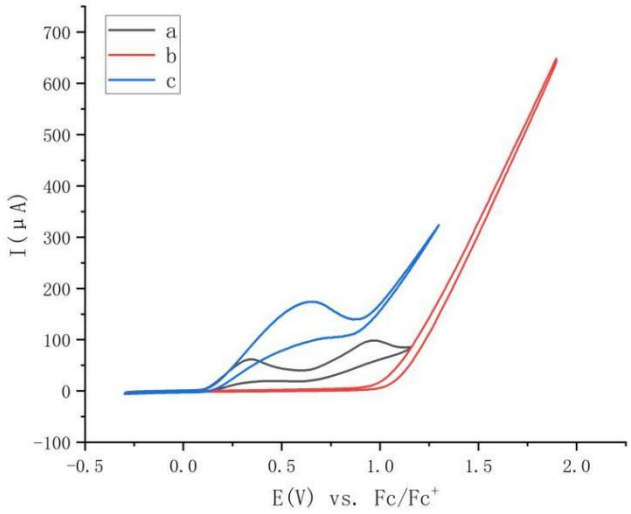


Figure S1. CV plotting convention (IUPAC)

In the **figure S1**, cyclic voltammograms of in 3 mL of DMF solution containing different compounds: (A) tetrabutylammonium perchlorate (0.4 mmol), tetrabutylammonium bromide (0.02

mmol); (B) tetrabutylammonium perchlorate (0.4 mmol), styrene (0.4 mmol); (C) tetrabutylammonium perchlorate (0.4 mmol), tetrabutylammonium bromide (0.02 mmol), styrene (0.4 mmol); with a GC disk working electrode (≈5.0 mm^2), Pt counter electrode, and $Ag/AgNO_3$ reference electrode (internal solution, 0.1 M $^nBu_4NClO_4$ and 0.01 M $AgNO_3$ in CH_3CN) at 0.1 V/s scan rate.

4.Stern-Volmer Fluorescence Quenching Experiments

Fluorescence spectra samples for the quenching experiments were prepared in a glass cuvette with a septum screw cap. 4CzIPN was irradiated at 470 nm and the emission intensity at 532 nm was observed. In a typical experiment, the emission spectrum of a 1.0×10^{-5} M solution of 4CzIPN in DMF was collected. A stock solution of $^nBu_4NBr$ (32.2 mg, 0.1 mmol) in 1 ml of DMF was prepared. Then, different amounts of this stock solution were added to a solution of the photocatalyst in DMF (1.0×10^{-5} M). As shown in **Figure S2**, a decrease of 4CzIPN luminescence was observed, suggesting that the mechanism might operate via a canonical photo-redox cycle consisting of a reductive quenching with $^nBu_4NBr$.

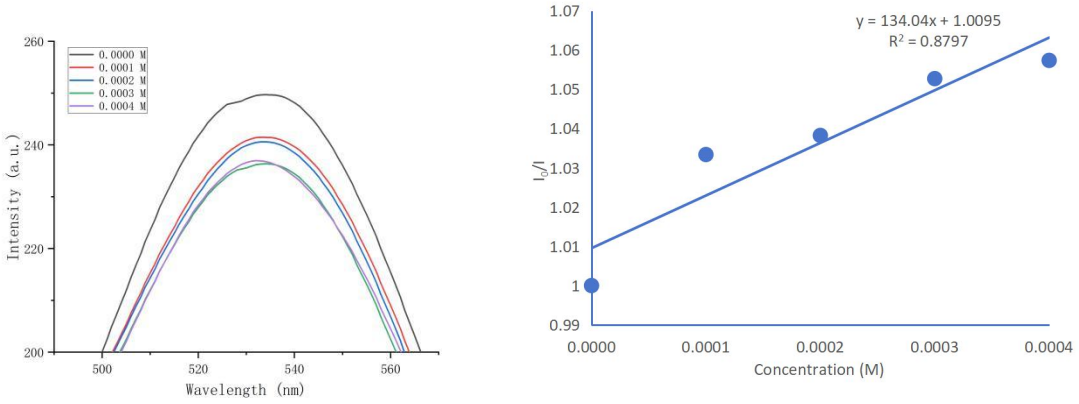


Figure S2. Stern–Volmer fluorescence quenching experiments of 4CzIPN with $^nBu_4NBr$.

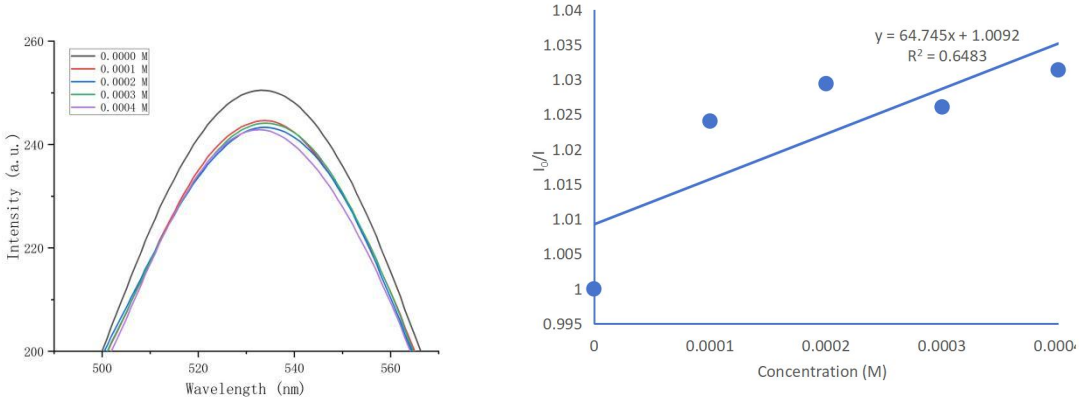


Figure S3. Stern–Volmer fluorescence quenching experiments of 4CzIPN with NaOAc.

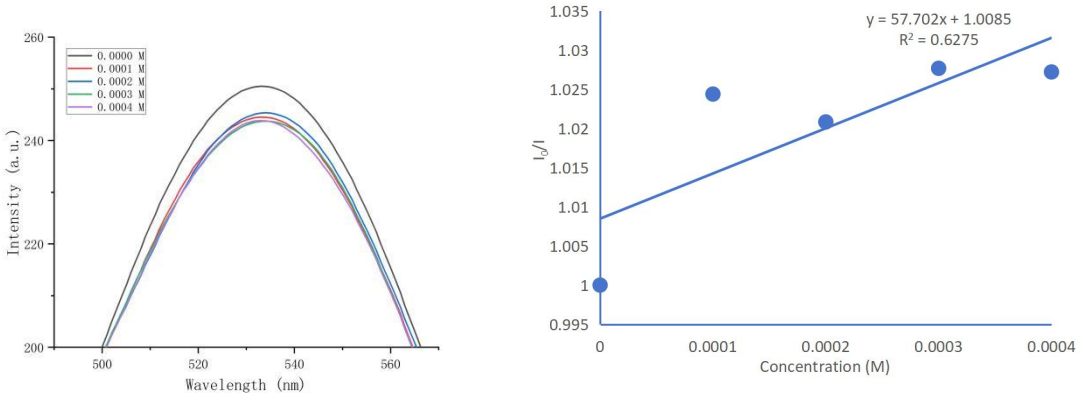
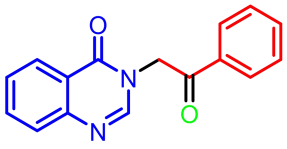


Figure S4. Stern–Volmer fluorescence quenching experiments of 4CzIPN with styrene.

4.Analytical data



3aa

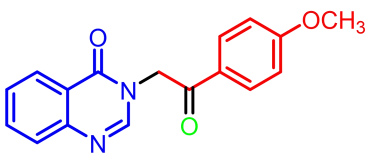
3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3aa)

According to the general procedure, **3aa** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 68% yield (35.9 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.41 (s, 1H), 8.16 (dd, J = 8.0, 1.6 Hz, 1H), 8.12-8.09 (m, 2H), 7.89-7.85 (m, 1H), 7.76-7.72 (m, 2H), 7.63-7.56 (m, 3H), 5.69 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.9, 160.2, 148.4, 148.1, 134.6, 134.3, 134.2, 129.1, 128.1, 127.4, 127.2, 126.1, 121.4, 52.2.

HRMS (ESI) calcd for $C_{16}H_{12}N_2NaO_2$: $[M+Na]^+$ 287.0791. Found: m/z 287.0793.



3ab

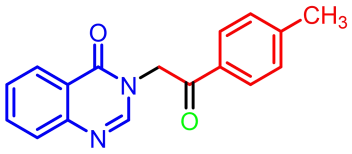
3-(2-(4-methoxyphenyl)-2-oxoethyl)quinazolin-4(3H)-one (3ab)

According to the general procedure, **3ab** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-methoxy-4-vinylbenzene **2b** (54.7 mg, 53.5 μL，0.4 mmol) in 69% yield (40.6 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29-8.26 (m, 1H), 8.02-7.99 (m, 2H), 7.98 (s, 1H), 7.79-7.72 (m, 2H), 7.51-7.47 (m, 1H), 6.98-6.96 (m, 2H), 5.38 (s, 2H), 3.88 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.1, 164.5, 161.2, 148.4, 146.9, 134.5, 130.7, 127.7, 127.5, 127.4, 126.9, 122.1, 114.3, 55.7, 51.0.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 317.0897. Found: m/z 317.0903.



3ac

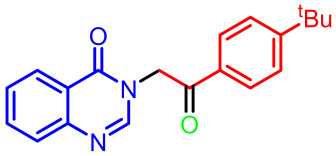
3-(2-oxo-2-(p-tolyl)ethyl)quinazolin-4(3H)-one (3ac)

According to the general procedure, **3ac** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-methoxy-4-vinylbenzene **2c** (47.3 mg, 53.0 μL，0.4 mmol) in 63% yield (35.0 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30-8.27 (m, 1H), 7.97 (s, 1H), 7.95-7.92 (m, 2H), 7.80-7.73 (m, 2H), 7.52-7.48 (m, 1H), 7.32-7.30 (m, 2H), 5.41 (s, 2H), 2.43 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.3, 161.2, 148.3, 146.8, 145.6, 134.6, 132.0, 129.8, 128.4, 127.7, 127.5, 127.0, 122.1, 51.3, 21.9.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_2$: $[M+Na]^+$ 301.0947. Found: m/z 301.0950.



3ad

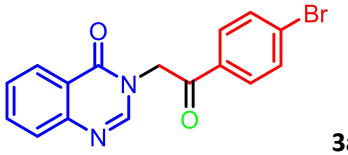
3-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)quinazolin-4(3H)-one (3ad)

According to the general procedure, **3ad** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-methoxy-4-vinylbenzene **2d** (64.1 mg, 73.5 μL，0.4 mmol) in 77% yield (49.3 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29-8.27 (m, 1H), 7.99-7.96 (m, 3H), 7.77-7.72 (m, 2H), 7.54-7.49 (m, 3H), 5.41 (s, 2H), 1.35 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.3, 161.1, 158.4, 148.3, 146.9, 134.6, 132.0, 128.3, 127.7, 127.4, 127.0, 126.1, 122.1, 51.3, 35.4, 31.1.

HRMS (ESI) calcd for $C_{20}H_{20}N_2NaO_2$: $[M+Na]^+$ 343.1417. Found: m/z 343.1416.



3ae

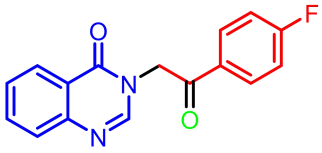
3-(2-(4-bromophenyl)-2-oxoethyl)quinazolin-4(3H)-one (3ae)

According to the general procedure, **3ae** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-bromo-4-vinylbenzene **2e** (73.2 mg, 52.5 μL，0.4 mmol) in 58% yield (39.7 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29-8.27 (m, 1H), 7.97 (s, 1H), 7.92-7.88 (m, 2H), 7.81-7.74 (m, 2H), 7.69-7.66 (m, 2H), 7.54-7.50 (m, 1H), 5.38 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.0, 161.1, 148.3, 146.5, 134.7, 133.2, 132.6, 129.9, 129.8, 127.8, 127.6, 127.0, 122.0, 51.3.

HRMS (ESI) calcd for $C_{16}H_{11}BrN_2NaO_2$: $[M+Na]^+$ 364.9896. Found: m/z 364.9896.



3af

3-(2-(4-fluorophenyl)-2-oxoethyl)quinazolin-4(3H)-one (3af)

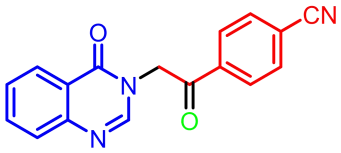
According to the general procedure, **3af** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-fluoro-4-vinylbenzene **2f** (48.9 mg, 48.0 μL，0.4 mmol) in 56% yield (31.6 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29-8.27 (m, 1H), 8.10-8.06 (m, 2H), 7.97 (s, 1H), 7.80-7.73 (m, 2H), 7.53-7.49 (m, 1H), 7.23-7.18 (m, 2H), 5.39 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.3, 166.6 (d, J = 256.0 Hz), 161.2, 148.4, 146.6, 134.7, 131.1 (d, J = 9.0 Hz), 127.8, 127.6, 126.9, 122.0, 116.6, 116.3, 51.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -102.42.

HRMS (ESI) calcd for $C_{16}H_{12}FN_2O_2$: $[M+H]^+$ 283.0877. Found: m/z 283.0868.



3ag

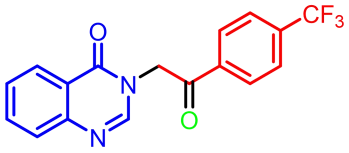
4-(2-(4-oxoquinazolin-3(4H)-yl)acetyl)benzonitrile (3ag)

According to the general procedure, **3ag** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 4-vinylbenzonitrile **2g** (51.7 mg, 48.0 μL，0.4 mmol) in 41% yield (2 3.7 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:5).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.40 (s, 1H), 8.25 (d, J = 8.0 Hz, 2H), 8.16-8.13 (m, 1H), 8.11 (d, J = 8.0 Hz, 2H), 7.90-7.86 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 5.73 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.6, 160.2, 148.2, 148.1, 137.5, 134.7, 133.1, 128.8, 127.4, 127.4, 126.1, 121.4, 118.1, 116.1, 52.6.

HRMS (ESI) calcd for $C_{17}H_{12}N_3O_2$: $[M+H]^+$ 290.0924. Found: m/z 290.0923



3ah

3-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)quinazolin-4(3H)-one (3ah)

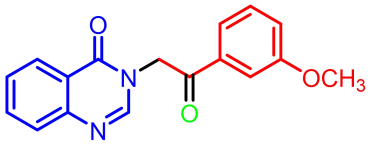
According to the general procedure, **3ah** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-(trifluoromethyl)-4-vinylbenzene **2h** (68.9 mg, 59.0 μL，0.4 mmol) i n 30% yield (19.9 mg) as a white solid (silica gel flash chromatography: petroleum ether/ EtOAc = 1:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.40 (s, 1H), 8.30 (d, J = 8.0 Hz, 2H), 8.16-8.14 (m, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.90-7.86 (m, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.60-7.56 (m, 1H), 7.74 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.6, 160.2, 148.2 (d, J = 13.0 Hz), 137.5, 134.7, 1 33.4 (q, J = 31.0 Hz), 129.1, 127.4 (d, J = 4.0 Hz), 126.1, 126.1, 126.1, 126.0, 123.7 (q, J = 272.0 Hz), 121.4, 52.5.

^{19}F NMR (376 MHz, DMSO-d_6) δ: -61.70.

HRMS (ESI) calcd for $C_{17}H_{11}F_3N_2NaO_2$: $[M+Na]^+$ 355.0665. Found: m/z 355.0671.



3ai

3-(2-(3-methoxyphenyl)-2-oxoethyl)quinazolin-4(3H)-one (3ai)

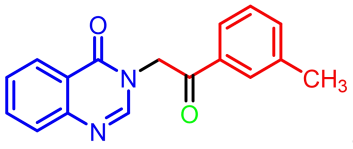
According to the general procedure, **3ai** was obtained using quinazolin-4(3H)-one **1a** (29.2

mg, 0.2 mmol) and 1-methoxy-3-vinylbenzene **2i** (56.7 mg, 55.5 μL，0.4 mmol) in 60% yield (35.3 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30-8.28 (m, 1H), 7.97 (s, 1H), 7.80-7.73 (m, 2H), 7.64-7.61 (m, 1H), 7.53-7.49 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.20-7.17 (m, 1H), 5.42 (s, 2 H), 3.85 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 161.2, 160.2, 148.3, 146.7, 135.8, 134.6, 130.2, 127.8, 127.5, 127.0, 122.0, 121.0, 120.8, 112.5, 55.6, 51.6.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 317.0897. Found: m/z 317.0903.



3aj

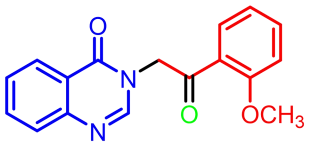
3-(2-oxo-2-(m-tolyl)ethyl)quinazolin-4(3H)-one (3aj)

According to the general procedure, **3aj** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-fluoro-4-vinylbenzene **2j** (47.3 mg, 53.5 μL，0.4 mmol) in 65% yi eld (36.2 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30-8.28 (m, 1H), 7.97 (s, 1H), 7.84-7.82 (m, 2H), 7.80-7.75 (m, 2H), 7.53-7.49 (m, 1H), 7.47-7.44 (m, 1H), 7.42-7.39 (m, 1H), 5.42 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.9, 161.2, 148.4, 146.8, 139.1, 135.2, 134.6, 134.6, 129.0, 128.8, 127.8, 127.5, 127.0, 125.5, 122.1, 51.4, 21.5.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 301.0947. Found: m/z 301.0950.



3ak

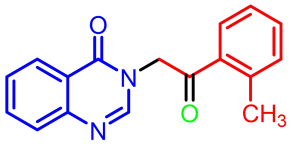
3-(2-(2-methoxyphenyl)-2-oxoethyl)quinazolin-4(3H)-one (3ak)

According to the general procedure, **3ak** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-methoxy-2-vinylbenzene **2k** (53.7 mg, 54.0 μL，0.4 mmol) in 55% yield (32.4 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30-8.27 (m, 1H), 7.97 (s, 1H), 7.93-7.91 (m, 1H), 7.78-7.72 (m, 2H), 7.57-7.52 (m, 1H), 7.50-7.46 (m, 1H), 7.06-7.01 (m, 2H), 5.36 (s, 2H), 3.99 (s, 3H),;

^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.5, 161.2, 159.7, 148.4, 147.2, 135.4, 134.4, 131.4, 127.6, 127.3, 126.9, 124.7, 122.2, 121.3, 111.7, 56.3, 55.8.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 317.0897. Found: m/z 317.0903.



3al

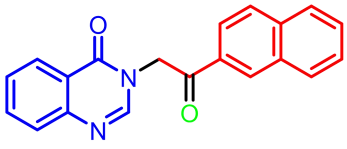
3-(2-oxo-2-(o-tolyl)ethyl)quinazolin-4(3H)-one (3al)

According to the general procedure, **3al** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 1-methyl-2-vinylbenzene **2l** (47.3 mg, 52.0 μL，0.4 mmol) in 52% yield (28.9 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31-8.28 (m, 1H), 7.98 (s, 1H), 7.90-7.88 (m, 1H), 7.80-7.73 (m, 2H), 7.53-7.45 (m, 2H), 7.37-7.30 (m, 2H), 5.30 (s, 2H), 2.53 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.6, 161.2, 148.4, 146.8, 139.9, 134.6, 134.4, 132.9, 132.6, 128.9, 127.7, 127.5, 126.9, 126.2, 122.1, 77.5, 77.2, 76.8, 53.3, 21.6.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 301.0947. Found: m/z 301.0950.



3am

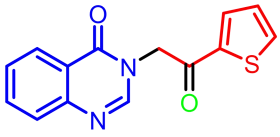
3-(2-(naphthalen-2-yl)-2-oxoethyl)quinazolin-4(3H)-one (3am)

According to the general procedure, **3am** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 2-vinylnaphthalene **2m** (61.7 mg, 0.4 mmol) in 41% yield (25.8 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59-8.58 (m, 1H), 8.31-8.28 (m, 1H), 8.05-8.02 (m, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.80-7.74 (m, 2H), 7.66-7.62 (m, 1H), 7.61-7.56 (m, 1H), 7.52-7.48 (m, 1H), 5.56 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 161.2, 148.4, 146.8, 136.2, 134.6, 132.5, 131.9, 130.3, 129.8, 129.3, 129.1, 128.0, 127.8, 127.5, 127.3, 127.0, 123.6, 122.1, 51.5.

HRMS (ESI) calcd for $C_{20}H_{14}N_2NaO_2$: $[M+Na]^+$ 337.0947. Found: m/z 337.0939.



3an

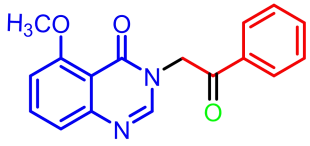
3-(2-oxo-2-(thiophen-2-yl)ethyl)quinazolin-4(3H)-one (3an)

According to the general procedure, **3an** was obtained using quinazolin-4(3H)-one **1a** (29.2 mg, 0.2 mmol) and 2-vinylthiophene **2n** (44.1 mg, 42.0 μL, 0.4 mmol) in 53% yield (28.6 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29-8.27 (m, 1H), 8.02 (s, 1H), 7.94-7.92 (m, 1H), 7.80-7.73 (m, 3H), 7.53-7.49 (m, 1H), 7.22-7.19 (m, 1H), 5.34 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.7, 161.1, 148.3, 146.6, 140.8, 135.4, 134.7, 133.0, 128.7, 127.8, 127.6, 127.0, 122.0, 51.4.

HRMS (ESI) calcd for $C_{14}H_{11}N_2O_2S$: $[M+H]^+$ 271.0536. Found: m/z 271.0537.



3ba

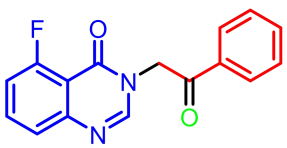
5-methoxy-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ba)

According to the general procedure, **3ba** was obtained using 5-methoxyquinazolin-4(3H)-one **1b** (35.2 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 34% yield (20.0 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-8.02 (m, 2H), 7.99 (s, 1H), 7.69-7.61 (m, 2H), 7.53-7.49 (m, 2H), 7.34-7.31 (m, 1H), 6.92 (d, J = 8.8 Hz, 1H), 5.33 (s, 2H), 3.96 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.1, 160.4, 159.3, 150.8, 147.5, 135.1, 134.7, 134.3, 129.1, 128.4, 119.8, 111.9, 108.7, 56.4, 51.3.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 317.0897. Found: m/z 317.0903.



3ca

5-fluoro-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ca)

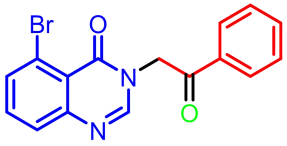
According to the general procedure, **3ca** was obtained using 5-fluoroquinazolin-4(3H)-one **1c** (32.8 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 57% yield (32.2 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.41 (s, 1H), 8.11-8.08 (m, 2H), 7.88-7.83 (m, 1H), 7.77-7.72 (m, 1H), 7.64-7.60 (m, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.36-7.31 (m, 1H), 5.63 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.8, 160.4 (d, J = 261.7 Hz), 157.2 (d, J = 4.0 Hz), 150.3, 149.3, 135.5 (d, J = 10.0 Hz), 134.3, 129.1, 128.2, 123.5 (d, J = 4.0 Hz), 113.8, 113.6, 111.0 (d, J = 6.0 Hz), 52.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ: -110.62.

HRMS (ESI) calcd for $C_{16}H_{12}FN_2O_2$: $[M+H]^+$ 283.0877. Found: m/z 283.0868.



3da

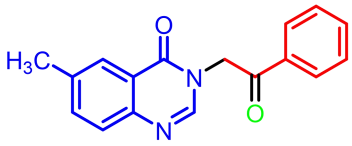
5-bromo-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3da)

According to the general procedure, **3da** was obtained using 5-bromoquinazolin-4(3H)-one **1d** (45.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 67% yield (45.8 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02-7.98 (m, 3H), 7.72 (dd, J = 7.6, 1.2 Hz, 1H), 7.67 (dd, J = 8.4, 1.2 Hz, 1H), 7.65-7.60 (m, 1H), 7.53-7.47 (m, 3H), 5.37 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 159.2, 150.6, 147.3, 134.5, 134.4, 134.3, 134.1, 129.1, 128.3, 127.8, 121.5, 120.2, 51.7.

HRMS (ESI) calcd for $C_{16}H_{11}BrN_2NaO_2$: $[M+Na]^+$ 364.9896. Found: m/z 364.9896.



3ea

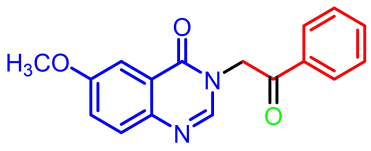
6-methyl-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ea)

According to the general procedure, **3ea** was obtained using 6-methylquinazolin-4(3H)-one **1e** (32.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 52% yield (28.9 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (s, 1H), 8.06-8.04 (m, 2H), 7.94 (s, 1H), 7.68-7.64 (m, 2H), 7.61-7.59 (m, 1H), 7.56-7.51 (m, 2H), 5.44 (s, 2H), 2.49 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.8, 161.2, 146.3, 146.0, 137.9, 136.1, 134.6, 134.5, 129.2, 128.3, 127.5, 126.4, 121.8, 51.5, 21.5.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 301.0947. Found: m/z 301.0950.



3fa

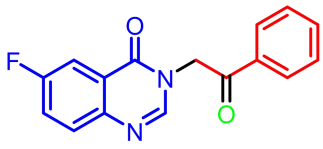
6-methoxy-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3fa)

According to the general procedure, **3fa** was obtained using 6-methoxyquinazolin-4(3H)-one **1f** (35.2 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 52% yield (30. 6 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-8.03 (m, 2H), 7.88 (s, 1H), 7.68-7.63 (m, 3H), 7.54-7.51 (m, 2H), 7.38-7.35 (m, 1H), 5.43 (s, 2H), 3.90 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 161.0, 158.9, 144.6, 142.9, 134.6, 134.4, 129.3, 1 29.1, 128.3, 124.8, 122.9, 106.3, 56.0, 51.6.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 317.0897. Found: m/z 317.0903.



3ga

6-fluoro-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ga)

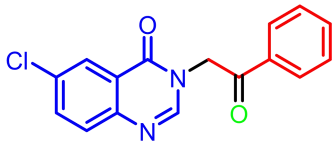
According to the general procedure, **3ga** was obtained using 6-fluoroquinazolin-4(3H)-one **1g** (32.8 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 68% yield (38. 4 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-8.02 (m, 2H), 7.94 (s, 1H), 7.91 (dd, J = 8.4, 3.2 Hz, 1H), 7.78-7.75 (m, 1H), 7.68-7.64 (m, 1H), 7.55-7.47 (m, 3H), 5.44 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.5, 161.3 (d, J = 248.0 Hz), 160.5 (d, J = 3.0 Hz), 146.0 (d, J = 3.0 Hz), 145.0 (d, J = 3.0 Hz), 134.6, 134.4, 130.2(d, J = 9.0 Hz), 129.2, 128.3, 123.3, 123.1, 168.0 (d, J = 23.0 Hz), 51.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.63.

HRMS (ESI) calcd for $C_{16}H_{12}FN_2O_2$: $[M+H]^+$ 283.0877. Found: m/z 283.0868.



3ha

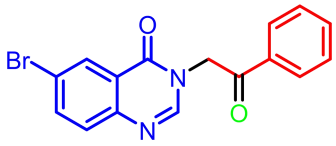
6-chloro-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ha)

According to the general procedure, **3ha** was obtained using 6-chloroquinazolin-4(3H)-one **1h** (36.1 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 69% yield (41. 1 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (d, *J* = 8.8 Hz, 1H), 8.02-8.00 (m, 2H), 7.99 (s, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 2H), 7.44 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.42 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.5, 160.5, 149.2, 148.0, 140.9, 134.6, 134.3, 129.2, 128.4, 128.3, 128.1, 127.3, 120.5, 51.5.

HRMS (ESI) calcd for $C_{16}H_{11}ClN_2NaO_2$: $[M+Na]^+$ 321.0401. Found: m/z 321.0391.



3ia

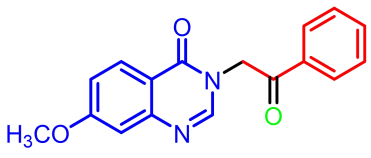
6-bromo-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ia)

According to the general procedure, **3ia** was obtained using 6-bromoquinazolin-4(3H)-one **1 i** (45.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 63% yield (43.1 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 2.0 Hz, 1H), 8.05-8.03 (m, 2H), 8.00 (s, 1H), 7.87-7.85 (m, 1H), 7.69-7.62 (m, 2H), 7.56-7.52 (m, 2H), 5.45 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.4, 160.0, 147.2, 147.1, 137.8, 134.6, 134.4, 129.6, 129.5, 129.2, 128.3, 123.4, 121.2, 51.5.

HRMS (ESI) calcd for $C_{16}H_{11}BrN_2NaO_2$: $[M+Na]^+$ 364.9896. Found: m/z 364.9896.



3ja

7-methoxy-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ja)

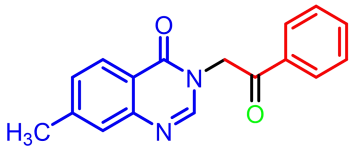
According to the general procedure, **3ja** was obtained using 7-methoxyquinazolin-4(3H)-one **1j** (35.2 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 45% yield (26.

5 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 8.8 Hz, 1H), 8.04-8.02 (m, 2H), 7.95 (s, 1H), 7.67-7.62 (m, 1H), 7.54-7.50 (m, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.08-7.05 (m, 1H), 5.41 (s, 2H), 3.92 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.0, 164.8, 160.7, 150.7, 147.4, 134.5, 134.4, 129.1, 128.5, 128.3, 117.4, 115.5, 108.6, 55.8, 51.2.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 317.0897. Found: m/z 317.0903.



3ka

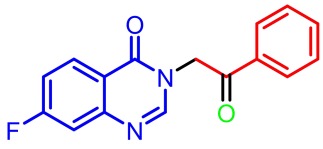
7-methyl-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ka)

According to the general procedure, **3ka** was obtained using 7-methylquinazolin-4(3H)-one **1k** (32.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 50% yield (27. 8 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.0 Hz, 1H), 8.06-8.03 (m, 2H), 7.95 (s, 1H), 7.68-7.63 (m, 1H), 7.55-7.51 (m, 3H), 7.34-7.32 (m, 1H), 5.42 (s, 2H), 2.52 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.9, 161.1, 148.5, 146.8, 145.7, 134.6, 134.4, 129.2, 129.1, 128.3, 127.5, 126.8, 119.6, 51.4, 22.1.

HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_3$: $[M+Na]^+$ 301.0947. Found: m/z 301.0950.



3la

7-fluoro-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3la)

According to the general procedure, **3la** was obtained using 7-fluoroquinazolin-4(3H)-one **1l** (32.8 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 65% yield (36.7 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

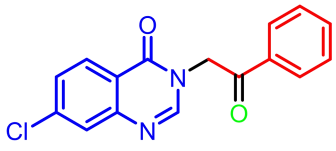
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.28 (m, 1H), 8.05-8.02 (m, 2H), 7.98 (s, 1H), 7.68-7.64 (m, 1H), 7.55-7.51 (m, 2H), 7.41-7.38 (m, 1H), 7.24-7.20 (m, 1H), 5.43 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 166.7 (d, *J* = 253.0 Hz), 160.4, 150.6 (d, *J* = 13.0 Hz), 148.0, 134.6, 134.4, 129.7 (d, *J* = 11.0 Hz), 129.2, 128.3, 118.8 (d, *J* = 3.0 Hz), 116.3 (d, *J* = 23.0

Hz), 113.2 (d, J = 21.0 Hz), 51.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -102.83.

HRMS (ESI) calcd for $C_{16}H_{12}FN_2O_2$: $[M+H]^+$ 283.0877. Found: m/z 283.0868.



3ma

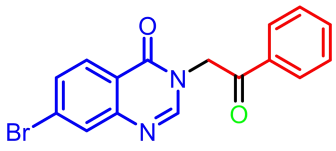
7-chloro-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ma)

According to the general procedure, **3ma** was obtained using 6-chloroquinazolin-4(3H)-one **1m** (36.1 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 62% yield (37. 0 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (d, J = 2.0 Hz, 1H), 8.04-8.02 (m, 2H), 7.96 (s, 1H), 7.72-7.70 (m, 2H), 7.67-7.64 (m, 1H), 7.55-7.51 (m, 2H), 5.44 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.4, 160.1, 147.0, 146.8, 135.0, 134.6, 134.4, 133.4, 129.4, 129.2, 128.3, 126.3, 123.1, 51.5.

HRMS (ESI) calcd for $C_{16}H_{11}ClN_2NaO_2$: $[M+Na]^+$ 321.0401. Found: m/z 321.0391.



3na

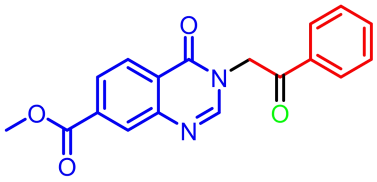
7-bromo-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3na)

According to the general procedure, **3na** was obtained using 7-bromoquinazolin-4(3H)-one **1n** (45.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 63% yield (43. 1 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, J = 8.8 Hz, 1H), 8.04-8.02 (m, 2H), 7.97 (s, 1H), 7.93 (d, J = 1.6 Hz, 1H), 7.68-7.64 (m, 1H), 7.61 (dd, J = 8.4, 2.0 Hz, 1H), 7.55-7.52 (m, 2H), 5.42 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.5, 160.7, 149.3, 147.9, 134.6, 134.4, 130.9, 130.6, 129.4, 129.2, 128.4, 128.3, 120.9, 51.5.

HRMS (ESI) calcd for $C_{16}H_{11}BrN_2NaO_2$: $[M+Na]^+$ 364.9896. Found: m/z 364.9896.



3oa

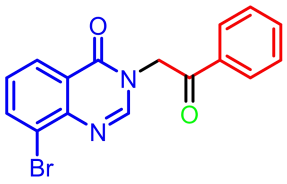
Methyl 4-oxo-3-(2-oxo-2-phenylethyl)-3,4-dihydroquinazoline-7-carboxylate (3oa)

According to the general procedure, **3oa** was obtained using methyl 4-oxo-3,4-dihydroquina zoline-7-carboxylate **1o** (40.8 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 47% yield (30.3 mg) as a white solid (silica gel flash chromatography: petroleum ethe r/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (d, *J* = 1.6 Hz, 1H), 8.33 (d, *J* =8.0 Hz, 1H), 8.11-8.09 (m, 1H), 8.05-8.04 (m, 1H), 8.03-8.01 (m, 2H), 7.68-7.63 (m, 2H), 7.55-7.51 (m, 2H), 5.45 (s, 2H), 3.98 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.5, 166.1, 160.6, 148.2, 147.5, 135.7, 134.6, 134.4, 129.6, 129.2, 128.3, 127.5, 127.3, 125.0, 52.8, 51.5.

HRMS (ESI) calcd for $C_{18}H_{15}N_2O_4$: $[M+H]^+$ 323.1026. Found: m/z 323.1036.



3pa

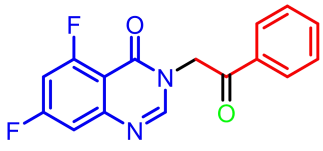
8-bromo-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3pa)

According to the general procedure, **3pa** was obtained using 8-bromoquinazolin-4(3H)-one **1p** (45.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 64% yield (43. 8 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26-8.24 (m, 1H), 8.08 (s, 1H), 8.06-8.02 (m, 3H), 7.68-7.64 (m, 1H), 7.55-7.51 (s, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 5.44 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.2, 160.6, 147.5, 146.2, 138.3, 134.6, 134.4, 129.2, 128.3, 128.1, 126.6, 123.6, 122.6, 77.5, 77.2, 76.8, 51.7.

HRMS (ESI) calcd for $C_{16}H_{11}BrN_2NaO_2$: $[M+Na]^+$ 364.9896. Found: m/z 364.9896.



3qa

5,7-difluoro-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3qa)

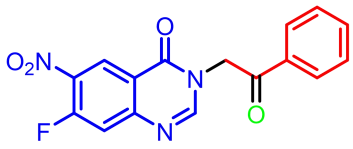
According to the general procedure, **3qa** was obtained using 5,7-difluoroquinazolin-4(3H)-one **1q** (36.4 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 55% yield (33.0 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 2:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.46 (s, 1H), 8.10-8.08 (m, 2H), 7.77-7.72 (m, 1H), 7.64-7.60 (m, 2H), 7.47-7.38 (m, 2H), 5.64 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.6, 165.1 (dd, J = 250.0, 15.0 Hz), 161.6 (dd, J = 264.0, 15.0 Hz), 156.6 (d, J = 4.0 Hz), 151.6 (d, J = 14.0 Hz), 150.4, 134.3, 134.2, 129.1, 128.1, 109.2 (dd, J = 22.0, 5.0 Hz), 108.4, 103.7 (q, J = 26.0 Hz), 52.0.

^{19}F NMR (376 MHz, DMSO-d_6) δ: -100.71 (d, J = 12.8 Hz), -105.48 (d, J = 12.4 Hz).

HRMS (ESI) calcd for $C_{16}H_{11}F_2N_2O_2$: $[M+H]^+$ 301.0783. Found: m/z 301.0778.



3ra

7-fluoro-6-nitro-3-(2-oxo-2-phenylethyl)quinazolin-4(3H)-one (3ra)

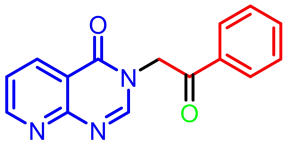
According to the general procedure, **3ra** was obtained using 7-fluoro-6-nitroquinazolin-4(3H)-one **1r** (41.8 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 41% yield (26.8 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:2).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.80 (d, J = 8.0 Hz, 1H), 8.62 (s, 1H), 8.11 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 12.0 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 2H), 5.73 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.3 158.8, 157.8 (d, J = 264.6 Hz), 153.2 (d, J = 13.5 Hz), 152.6, 136.0, 134.4, 134.1, 129.1, 128.2, 126.0, 118.0, 116.0 (d, J = 21.5 Hz), 52.6.

^{19}F NMR (376 MHz, DMSO-d_6) δ: -111.18.

HRMS (ESI) calcd for $C_{16}H_{11}FN_3O_4$: $[M+H]^+$ 328.0728. Found: m/z 328.0726.



3sa

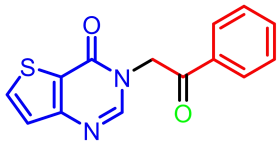
3-(2-oxo-2-phenylethyl)pyrido[2,3-d]pyrimidin-4(3H)-one (3sa)

According to the general procedure, **3sa** was obtained using pyrido[2,3-d]pyrimidin-4(3H)-one **1s** (29.4 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 45% yield (23.9 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1: 8).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.02 (dd, J = 4.4, 2.0 Hz, 1H), 8.58 (s, 1H), 8.56 (dd, J = 7.6, 2.0 Hz, 1H), 8.12-8.09 (m, 2H), 7.78-7.73 (m, 2H), 7.65-7.60 (m, 3H), 5.68 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.6, 160.7, 158.0, 156.2, 151.5, 136.0, 134.4, 134.2, 129.1, 128.2, 123.1, 116.7, 52.3.

HRMS (ESI) calcd for $C_{15}H_{11}N_3NaO_2$: $[M+Na]^+$ 288.0743. Found: m/z 288.0748.



3ta

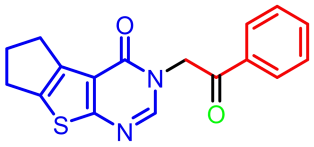
3-(2-oxo-2-phenylethyl)thieno[3,2-d]pyrimidin-4(3H)-one (3ta)

According to the general procedure, **3ta** was obtained using thieno[3,2-d]pyrimidin-4(3H)-one **1t** (30.4 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 69% yield (37.3 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1: 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04-8.02 (m, 2H), 8.00 (s, 1H), 7.80 (d, J = 5.2 Hz, 1H), 7.67-7.62 (m, 1H), 7.54-7.50 (m, 2H), 7.36 (d, J = 5.2 Hz, 1H), 5.47 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 157.4, 157.3, 148.2, 134.7, 134.5, 134.4, 129.2, 128.3, 125.4, 123.4, 51.0.

HRMS (ESI) calcd for $C_{14}H_{10}N_2NaO_2S$: $[M+Na]^+$ 293.0355. Found: m/z 293.0363.



3ua

3-(2-oxo-2-phenylethyl)-3,5,6,7-tetrahydro-4H-cyclopenta[4,5]thieno[2,3-d]pyrimidin-4-one (3ua)

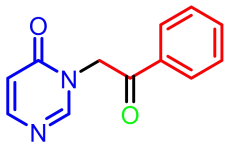
According to the general procedure, **3ua** was obtained using 3,5,6,7-tetrahydro-4H-cyclopenta[4,5]thieno[2,3-d]pyrimidin-4-one **1u** (38.4 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0

μL, 0.4 mmol) in 68% yield (42.2 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02-8.00 (m, 2H), 7.85 (s, 1H), 7.64-7.60 (m, 1H), 7.51-7.47 (m, 2H), 5.39 (s, 2H), 3.04-2.99 (m, 2H), 2.97-2.92 (m, 2H), 2.47-2.39 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.8, 167.4, 157.5, 145.7, 140.5, 140.0, 134.5, 134.4, 129.1, 128.3, 120.2, 51.1, 29.7, 29.0, 28.1.

HRMS (ESI) calcd for $C_{17}H_{15}N_2O_2S$: $[M+H]^+$ 308.0614. Found: m/z 308.0619.



3va

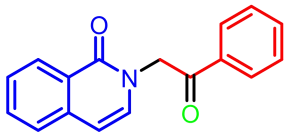
3-(2-oxo-2-phenylethyl)pyrimidin-4(3H)-one (3va)

According to the general procedure, **3va** was obtained using pyrimidin-4(3H)-one **1v** (19.2 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 68% yield (29.1 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (s, 1H), 7.96-7.94 (m, 2H), 7.88 (d, *J* = 9.2 Hz, 1 H), 7.63-7.58 (m, 1H), 7.49-7.45 (m, 2H), 6.42 (d, *J* = 6.4 Hz, 1H), 5.32 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.1, 160.6, 153.8 151.9, 134.4, 134.2, 129.0, 128.2, 11 5.8, 51.3.

HRMS (ESI) calcd for $C_{12}H_{11}N_2O_2$: $[M+H]^+$ 215.0815. Found: m/z 215.0823.



3wa

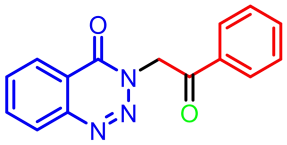
2-(2-oxo-2-phenylethyl)isoquinolin-1(2H)-one (3wa)

According to the general procedure, **3wa** was obtained using isoquinolin-1(2H)-one **1w** (29.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 23% yield (12.1 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 8:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43-8.40 (m, 1H), 8.07-8.05 (m, 2H), 7.95-7.61 (m, 2H), 7.56-7.47 (m, 4H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 5.45 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.0, 162.4, 137.5, 135.0, 134.1, 132.6, 132.1, 129.0, 128.3, 128.1, 127.1, 126.2, 126.1, 106.6, 54.4.

HRMS (ESI) calcd for $C_{17}H_{14}NO_2$: $[M+H]^+$ 264.1019. Found: m/z 264.1026.



3xa

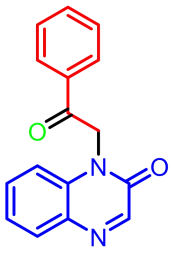
3-(2-oxo-2-phenylethyl)benzo[d][1,2,3]triazin-4(3H)-one (3xa)

According to the general procedure, **3xa** was obtained using benzo[d][1,2,3]triazin-4(3H)-on e **1x** (29.4 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 34% yield (1 7.5 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35-8.32 (m, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.05-8.03 (m, 2H), 7.98-7.93 (m, 1H), 7.82-7.78 (m, 1H), 7.65-7.60 (m, 1H), 7.53-7.49 (m, 2H), 5.90 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.1, 155.8, 144.5, 135.1, 134.6, 134.2, 132.6, 129.0, 128.6, 128.2, 125.2, 119.8, 77.5, 77.2, 76.8, 55.6.

HRMS (ESI) calcd for $C_{15}H_{12}N_3O_2$: $[M+H]^+$ 266.0924. Found: m/z 266.0923.



3ya

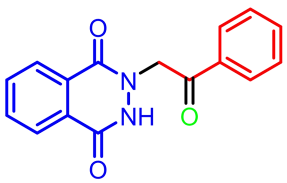
1-(2-oxo-2-phenylethyl)quinoxalin-2(1H)-one (3ya)

According to the general procedure, **3ya** was obtained using quinoxalin-2(1H)-one **1y** (29.2 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 58% yield (30.6 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (s, 1H), 8.08-8.06 (m, 2H), 7.93-7.91 (m, 1H), 7.70-7.66 (m, 1H), 7.58-7.54 (m, 2H), 7.51-7.46 (m, 1H), 7.37-7.32 (m, 1H), 6.99-6.97 (m, 1H), 5.74 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.9, 154.9, 149.9, 134.6, 133.6, 132.8, 131.3, 130.9, 129.2, 128.3, 124.0, 113.8, 48.2.

HRMS (ESI) calcd for $C_{16}H_{12}N_2NaO_2$: $[M+Na]^+$ 287.0791. Found: m/z 287.0793.



3za

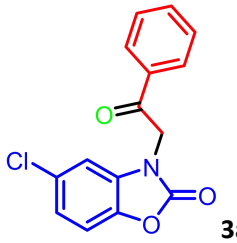
2-(2-oxo-2-phenylethyl)-2,3-dihydrophthalazine-1,4-dione (3za)

According to the general procedure, **3za** was obtained using 2,3-dihydrophthalazine-1,4-dione **1z** (32.4 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 41% yield (23.0 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 2:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.87 (s,1H), 8.24-8.22 (m, 1H), 8.08-8.06 (m, 1H), 8.04-7.97 (m, 3H), 7.72-7.67 (m, 1H), 7.59-7.55 (m, 2H), 5.80 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 193.6, 158.8, 148.8, 134.2, 134.0, 133.8, 132.5, 129.0, 128.7, 127.8, 126.3, 124.2, 123.5, 68.6.

HRMS (ESI) calcd for $C_{16}H_{12}N_2NaO_3$: $[M+Na]^+$ 303.0740. Found: m/z 303.0731.



3a'a

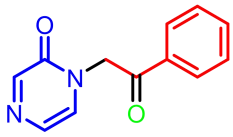
5-chloro-3-(2-oxo-2-phenylethyl)benzo[d]oxazol-2(3H)-one (3a'a)

According to the general procedure, **3a'a** was obtained using 5-chlorobenzo[d]oxazol-2(3H) -one **1a'** (38.4 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 73% yiel d (41.9 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1: 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03-8.00 (m, 2H), 7.70-7.66 (m, 1H), 7.57-7.53 (m, 2H), 7.17-7.15 (m, 1H), 7.11-7.09 (m, 1H), 6.83 (d, J = 2.0 Hz, 1H), 5.23 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.4, 154.6, 141.3, 134.7, 134.0, 132.2, 129.7, 129.3, 128.3, 122.8, 111.2, 109.4, 48.2.

HRMS (ESI) calcd for $C_{15}H_{11}ClNO_3$: $[M+H]^+$ 310.0241. Found: m/z 310.0247.



3b'a

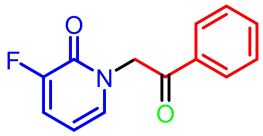
1-(2-oxo-2-phenylethyl)pyrazin-2(1H)-one (3b'a)

According to the general procedure, **3b'a** was obtained using pyrazin-2(1H)-one **1b'** (19.2 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 70% yield (30.0 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 1.6 Hz, 1H), 8.00-7.97 (m, 2H), 7.67-7.62 (m, 1H), 7.54-7.49 (m, 2H), 7.36 (d, *J* = 4.4 Hz, 1H), 7.04 (dd, *J* = 4.4, 1.2 Hz, 1H), 5.34 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.8, 155.9, 149.7, 134.6, 134.3, 129.5, 129.2, 128.3, 123.8, 77.5, 77.2, 76.8, 53.8.

HRMS (ESI) calcd for $C_{12}H_{11}N_2O_2$: $[M+H]^+$ 215.0815. Found: m/z 215.0823.



3c'a

3-fluoro-1-(2-oxo-2-phenylethyl)pyridin-2(1H)-one (3c'a)

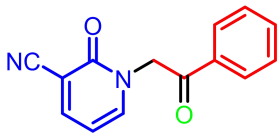
According to the general procedure, **3c'a** was obtained using 3-fluoropyridin-2(1H)-one **1c'** (22.6 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 63% yield (29.1 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00-7.97 (m, 2H), 7.64-7.60 (m, 1H), 7.51-7.47 (m, 2H), 7.15-7.10 (m, 1H), 7.06-7.03 (m, 1H), 6.16-6.11 (m, 1H), 5.43 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 156.3 (d, *J* = 26.0 Hz), 152.5 (d, *J* = 248.0 Hz), 134.5, 134.3, 133.7 (d, *J* = 5.0 Hz), 129.0, 128.2, 120.8 (d, *J* = 16.0 Hz), 103.9 (d, *J* = 6.0 Hz), 54.4 (d, *J* = 2.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -130.47.

HRMS (ESI) calcd for $C_{13}H_{11}FNO_2$: $[M+H]^+$ 254.0588. Found: m/z 254.0596.



3d'a

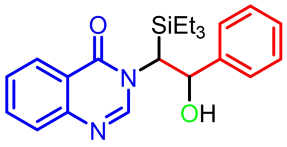
2-oxo-1-(2-oxo-2-phenylethyl)-1,2-dihydropyridine-3-carbonitrile (3d'a)

According to the general procedure, **3d'a** was obtained using 2-oxo-1,2-dihydropyridine-3-carbonitrile **1d'** (24.0 mg, 0.2 mmol) and styrene **2a** (41.7 mg, 46.0 μL, 0.4 mmol) in 65% yield (30.9 mg) as a white solid (silica gel flash chromatography: petroleum ether/EtOAc = 3:1)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.25 (dd, *J* = 7.2, 2.0 Hz, 1H), 8.16-8.14 (m, 1H), 8.07-8.05 (m, 2H), 7.76-7.71 (m, 1H), 7.62-7.59 (m, 2H), 6.54-6.50 (m, 1H), 5.67 (s, 2H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.1, 159.3, 149.1, 146.2, 134.3, 134.2, 129.1, 128.1, 116.28, 105.6, 102.7, 55.8.

HRMS (ESI) calcd for $C_{14}H_{10}N_2NaO_2$: $[M+Na]^+$ 261.0634. Found: m/z 261.0641.



4

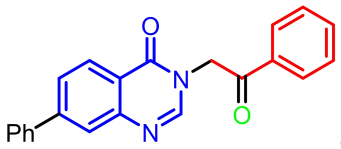
3-(2-hydroxy-2-phenyl-1-(triethylsilyl)ethyl)quinazolin-4(3H)-one (4)

General procedure for the preparation of **4:** Reactions were performed: **3aa** (0.2 mmol, 52.8 mg), triethylsilane (0.4 mmol, 46.5 mg, 64.0 μL), $Pd(OAc)_2$ (1 mol%) were added to DMF (3.0 mL) under air atmosphere at 80℃. Then stirred for 3h. The resulting yellow mixture was concentrated under vacuum, the crude product was purified by flash column chromatography using petroleum ether/ EtOAc (30:1) to give the compound **4** in 89% yield (67.7 mg) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12-8.10 (m, 1H), 7.81 (s, 1H), 7.55-7.48 (m, 2H), 7.30-7.22 (m, 3H), 7.16-7.12 (m, 2H), 7.10-7.05 (m, 1H), 4.88 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.22 (dd, *J* = 13.6, 3.2 Hz, 1H), 3.41 (dd, *J* = 13.2, 9.2 Hz, 1H), 0.48 (t, *J* = 8.0 Hz, 9H), 0.17-0.11 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.3, 148.2, 147.6, 141.5, 134.2, 128.5, 128.1, 127.4, 127.1, 126.5, 125.9, 121.9, 72.0, 55.3, 6.4, 4.4.

HRMS (ESI) calcd for $C_{22}H_{28}N_2NaO_2Si$: $[M+Na]^+$ 403.1812. Found: m/z 403.1815.



5

3-(2-oxo-2-phenylethyl)-7-phenylquinazolin-4(3H)-one (5)

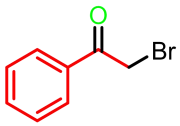
General procedure for the preparation of **5:** Reactions were performed: **3na** (0.2 mmol, 68.6 mg), phenylboronic acid (0.4 mmol, 48.8 mg), $Pd(PPh_3)_4$ (1 mol%) ,K_3PO_4 (0.4 mmol, 84.9 mg), H_2O (1.0 mL) were added to DMSO (2.0 mL) under N_2 atmosphere at 100℃. Then stirred for 5h. The resulting yellow mixture was concentrated under vacuum, the crude product was purified by flash column chromatography using petroleum ether/ EtOAc (1:1) to give the compound **5** in 83% yield (56.5 mg) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 8.0 Hz, 1H), 8.05-8.02 (m, 2H), 8.01 (s, 1H), 7.96 (s, 1H), 7.75-7.73 (m, 1H), 7.71-7.69 (m, 2H), 7.66-7.62 (m, 1H), 7.54-7.48 (m, 4H), 7.45-7.41 (m, 1H), 5.44 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.8, 161.0, 148.7, 147.4, 147.2, 139.6, 134.4, 134.4, 129.2,

129.1, 128.6, 128.3, 127.6, 127.4, 126.6, 125.7, 120.7, 51.4.

HRMS (ESI) calcd for $C_{22}H_{17}N_2O_2$: $[M+H]^+$ 341.1285. Found: m/z 341.1291.



8

2-bromo-1-phenylethan-1-one (8)

General procedure for the preparation of **8:** Reactions were performed: **2a** (0.4 mmol, 41.7 mg, 46.0 µL), ^{n}Bu$_4$NBr (0.4 mmol, 128.9 mg), 4CzIPN (2 mol%, 3.2 mg), ^{n}Bu$_4$NClO$_4$ (0.4 mmol, 136.8 mg), HFIP (0.4 mmol, 67.2 mg, 42.0 µL), were added to DMF (3.0 mL) under air atmosphere at room temperature. Then stirred for 12 h. The resulting yellow mixture was concentrated under vacuum, the crude product was purified by flash column chromatography using petroleum ether/ EtOAc (30:1) to give the compound **8** in 77 % yield (61.0 mg) as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.95 (m, 2H), 7.61-7.57 (m, 1H), 7.49-7.45 (m, 2H), 4.45 (s, 2H).

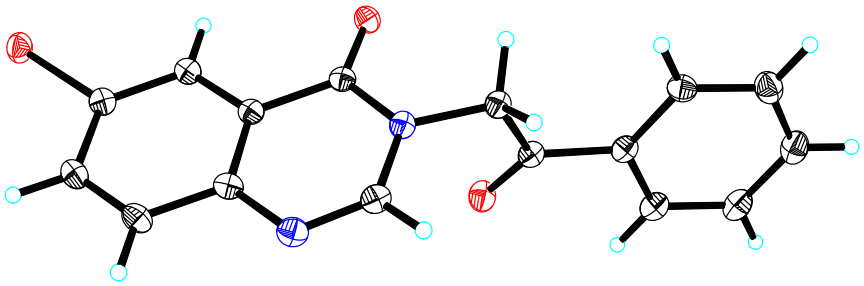
^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.3, 134.0, 134.0, 128.9, 128.9, 31.1.

HRMS (ESI) calcd for C_8H_8BrO: $[M+H]^+$ 198.9753. Found: m/z 198.9753.

Crystal of 3ia

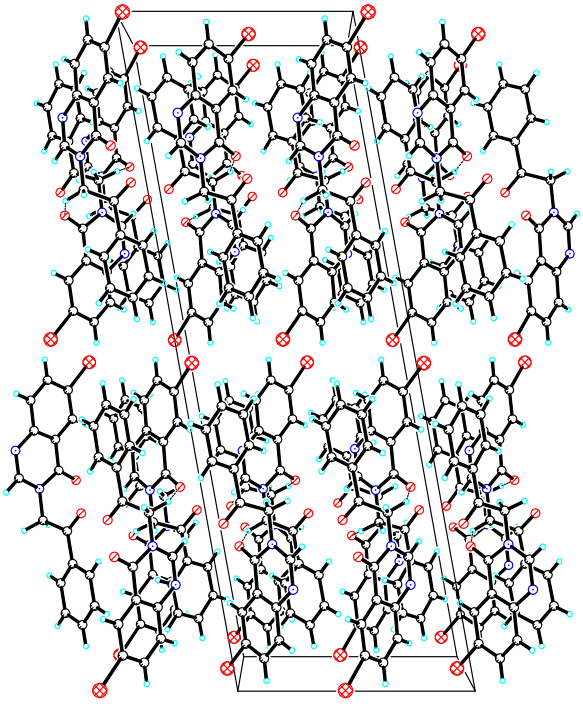
The crystal of **3ia** suitable for crystallographic analysis was grown from $CHCl_3$ by slow crystallization in 10 mL flat bottom bottle.

Crystal data for md_zxjb1: $C_{16}H_{11}BrN_2O_2$, M = 343.18, a = 29.6679(9) Å, b = 9.0807(3) Å, c = 10.2318(3) Å, α = 90°, β = 100.2330(10)°, γ = 90°, V = 2712.65(15) Å^3, T = 150.(2) K, space group $C12/c1$, Z = 8, μ(Cu Kα) = 4.188 mm^{-1}, 12466 reflections measured, 2658 independent reflections (R_{int} = 0.0612). The final R_1 values were 0.0559 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1413 ($I > 2\sigma(I)$). The final R_1 values were 0.0580 (all data). The final $wR(F^2)$ values were 0.1449 (all data). The goodness of fit on F^2 was 1.061.



View of a molecule of md_zxjb1.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of md_zxjb1.

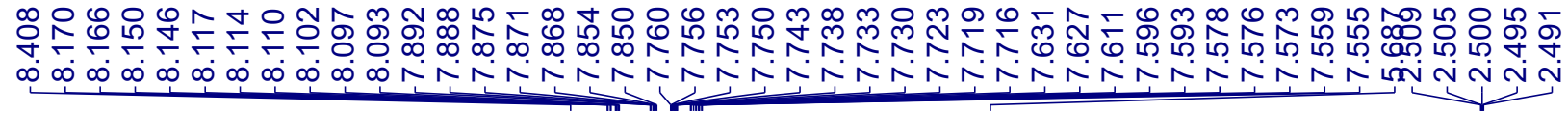
Hydrogen-bonds are shown as dashed lines.

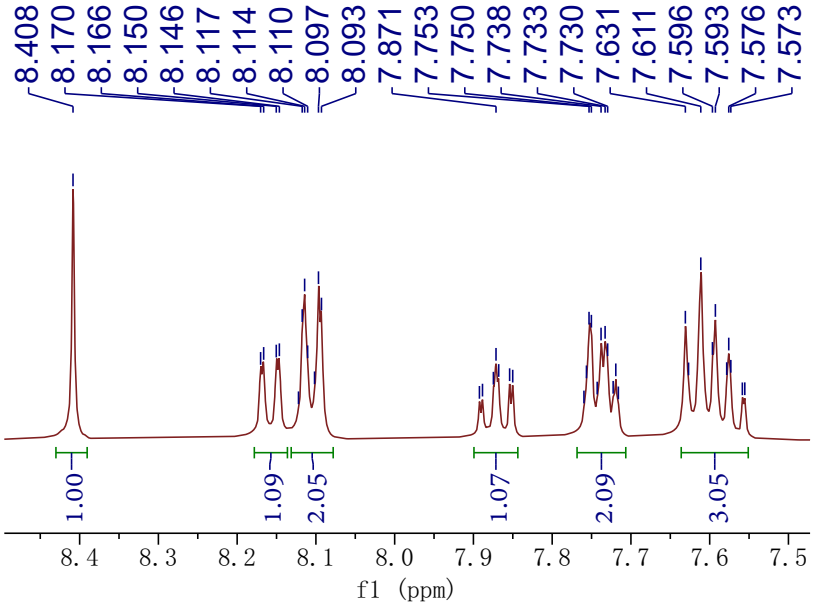
Table 1. Crystal data and structure refinement for md_zxjb1_0m.

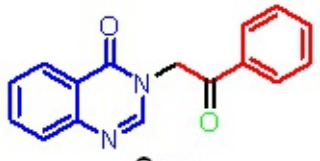
Identification code	global	
Empirical formula	C16 H11 Br N2 O2	
Formula weight	343.18	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 29.6679(9) Å	α= 90°.
	b = 9.0807(3) Å	β= 100.2330(10)°.
	c = 10.2318(3) Å	γ = 90°.
Volume	2712.65(15) $Å^3$	
Z	8	

Density (calculated)	1.681 Mg/m^3	
Absorption coefficient	4.188 mm^{-1}	
F(000)	1376	
Crystal size	0.400 x 0.360 x 0.180 mm^3	
Theta range for data collection	3.03 to 72.00°.	
Index ranges	-36<=h<=32, -11<=k<=10, -12<=l<=12	
Reflections collected	12466	
Independent reflections	2658 [R(int) = 0.0612]	
Completeness to theta = 72.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.52 and 0.22	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2658 / 0 / 191	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.1413	
R indices (all data)	R1 = 0.0580, wR2 = 0.1449	
Extinction coefficient	0.0031(3)	
Largest diff. peak and hole	1.828 and -0.993 $e.Å^{-3}$	

5 Copies of NMR spectra

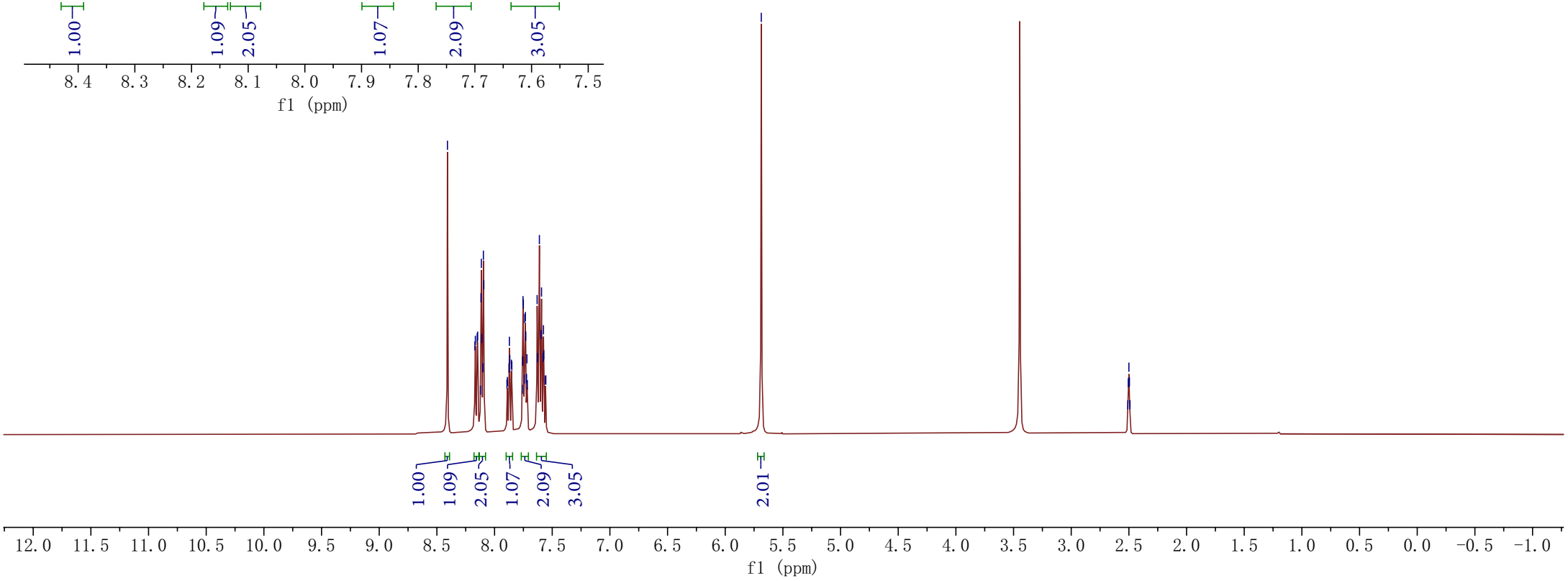


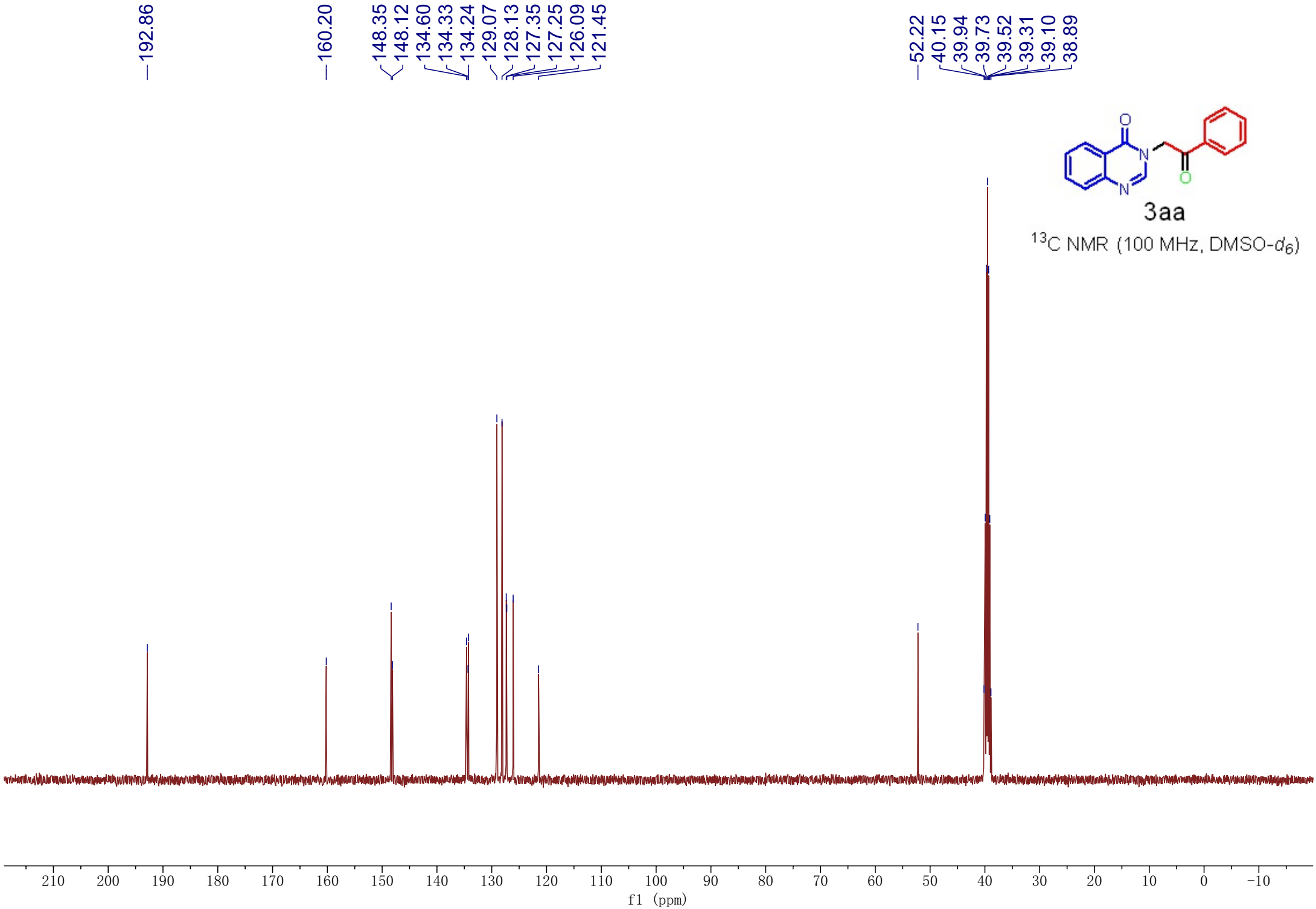




3aa

^{1}H NMR (400 MHz, DMSO-d_6)

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127.35
127.25
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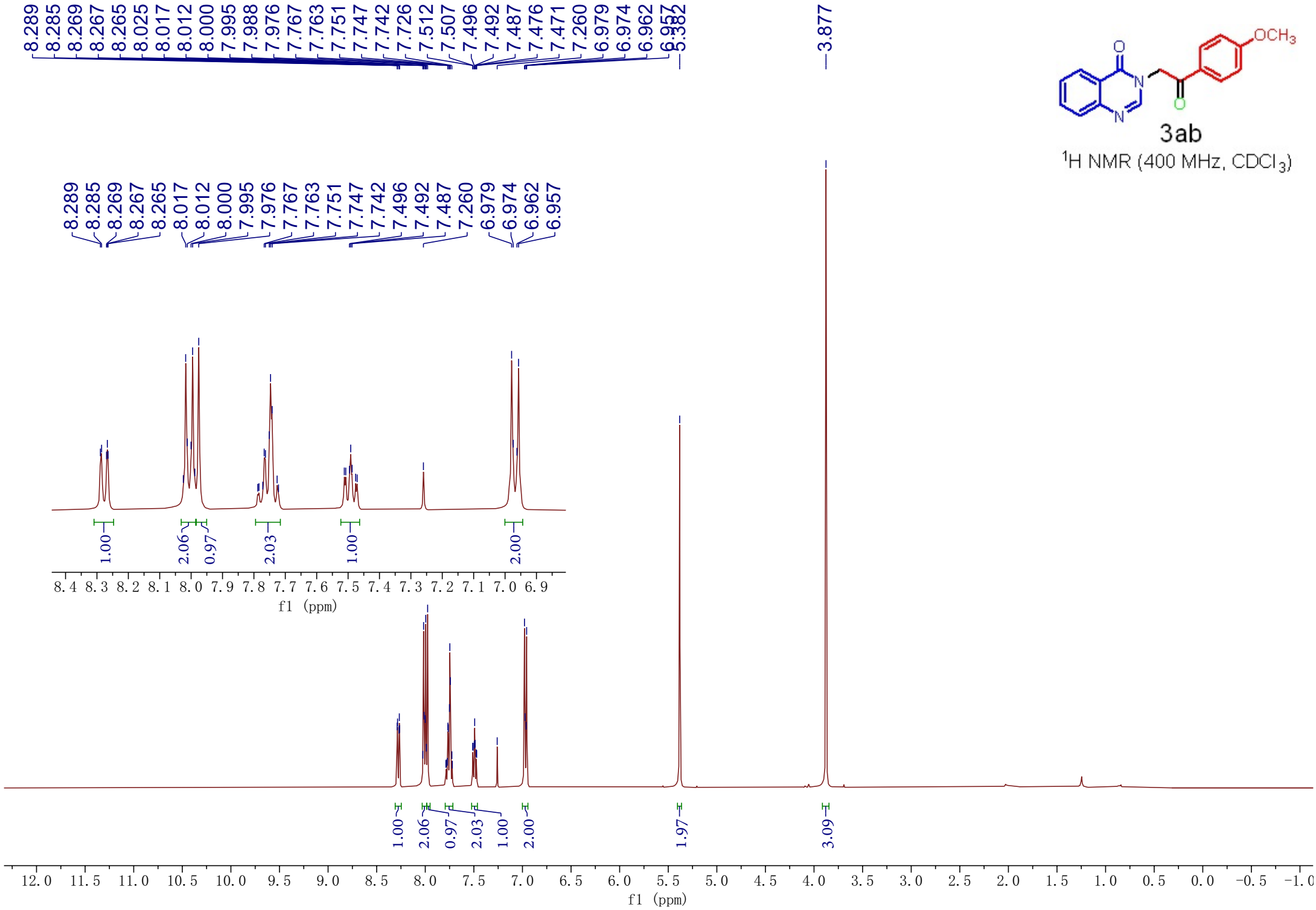
52.22
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
N
N
O
3aa
13C NMR (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.507
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N
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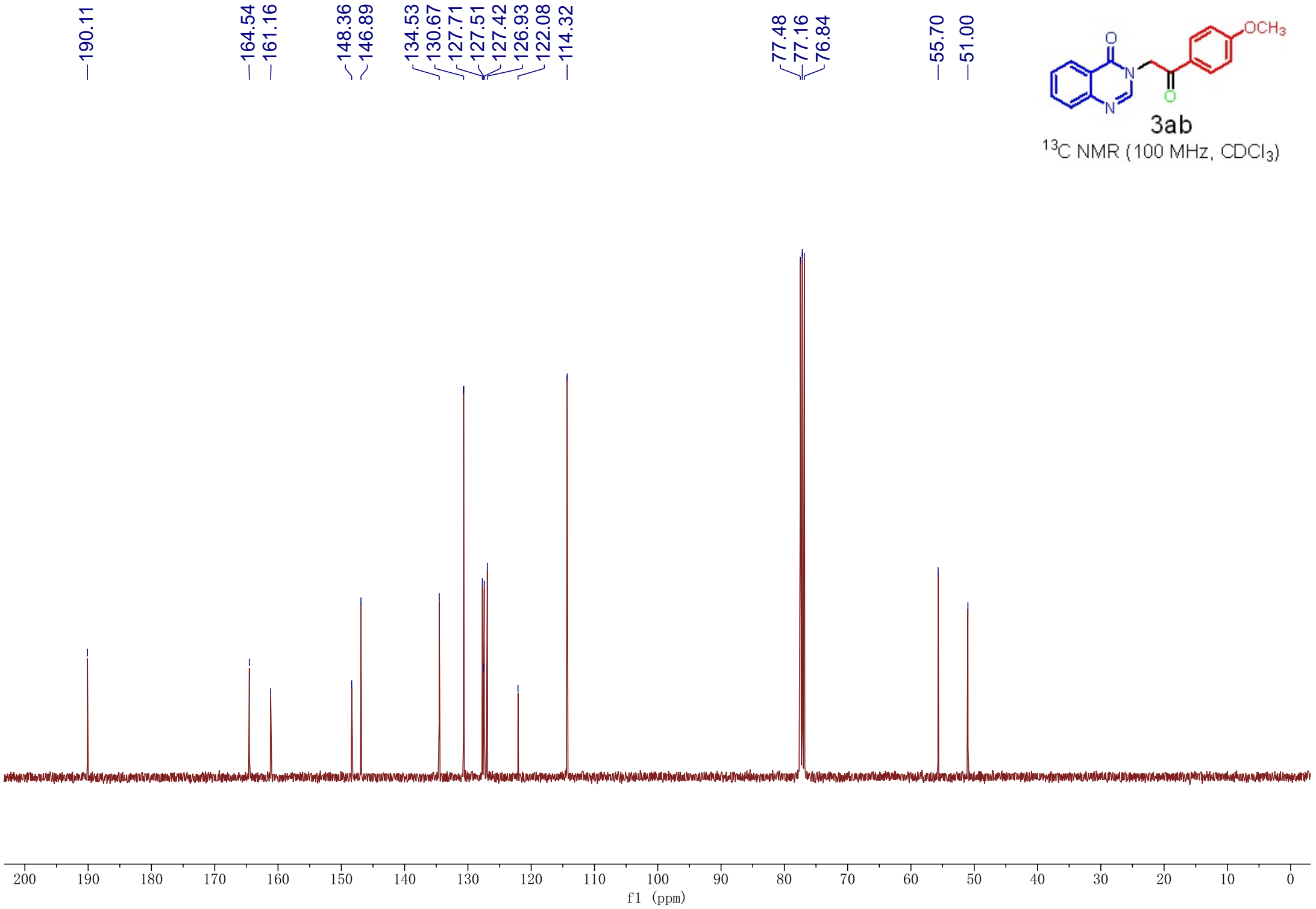
f1 (ppm)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180
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50
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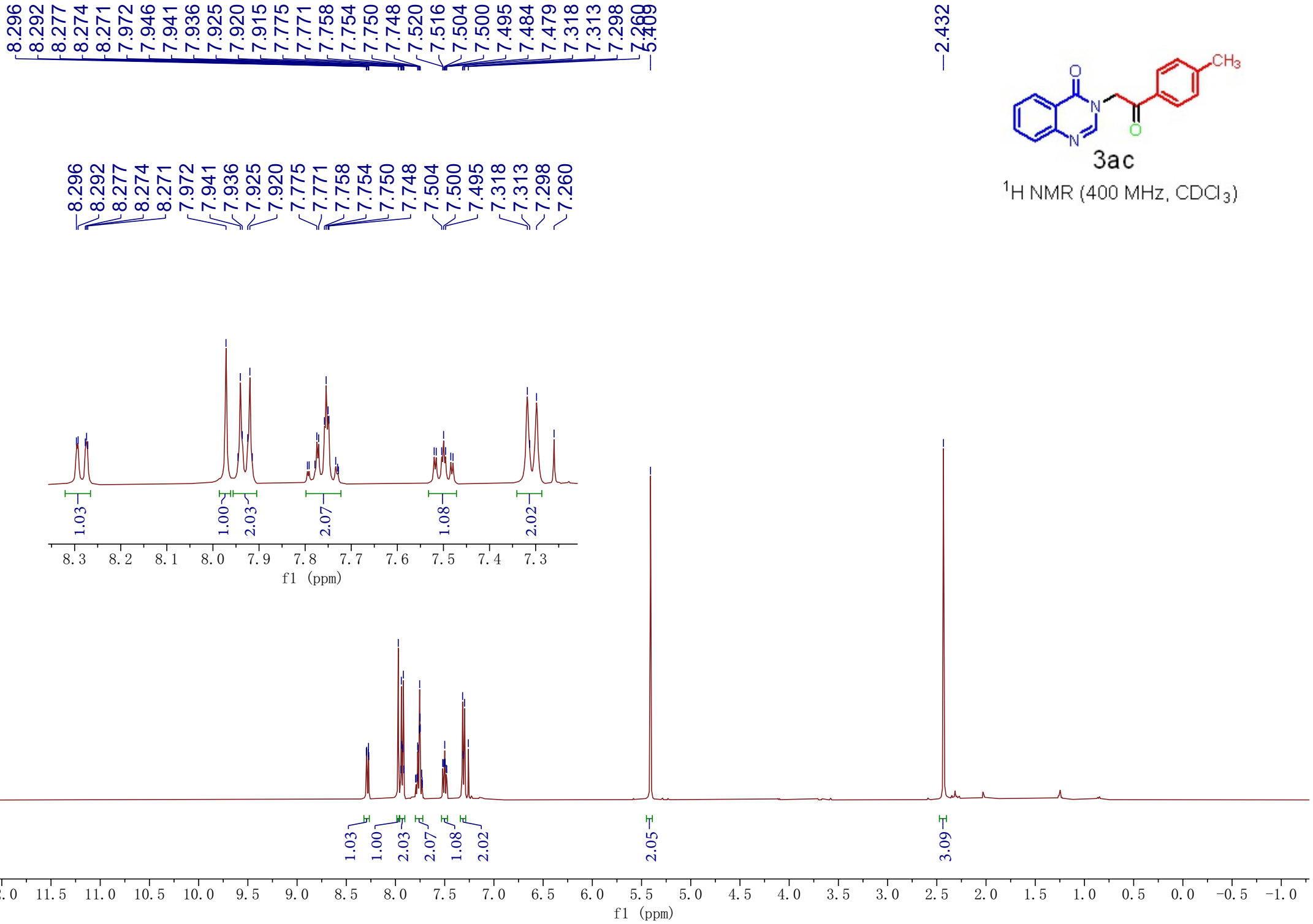
f1 (ppm)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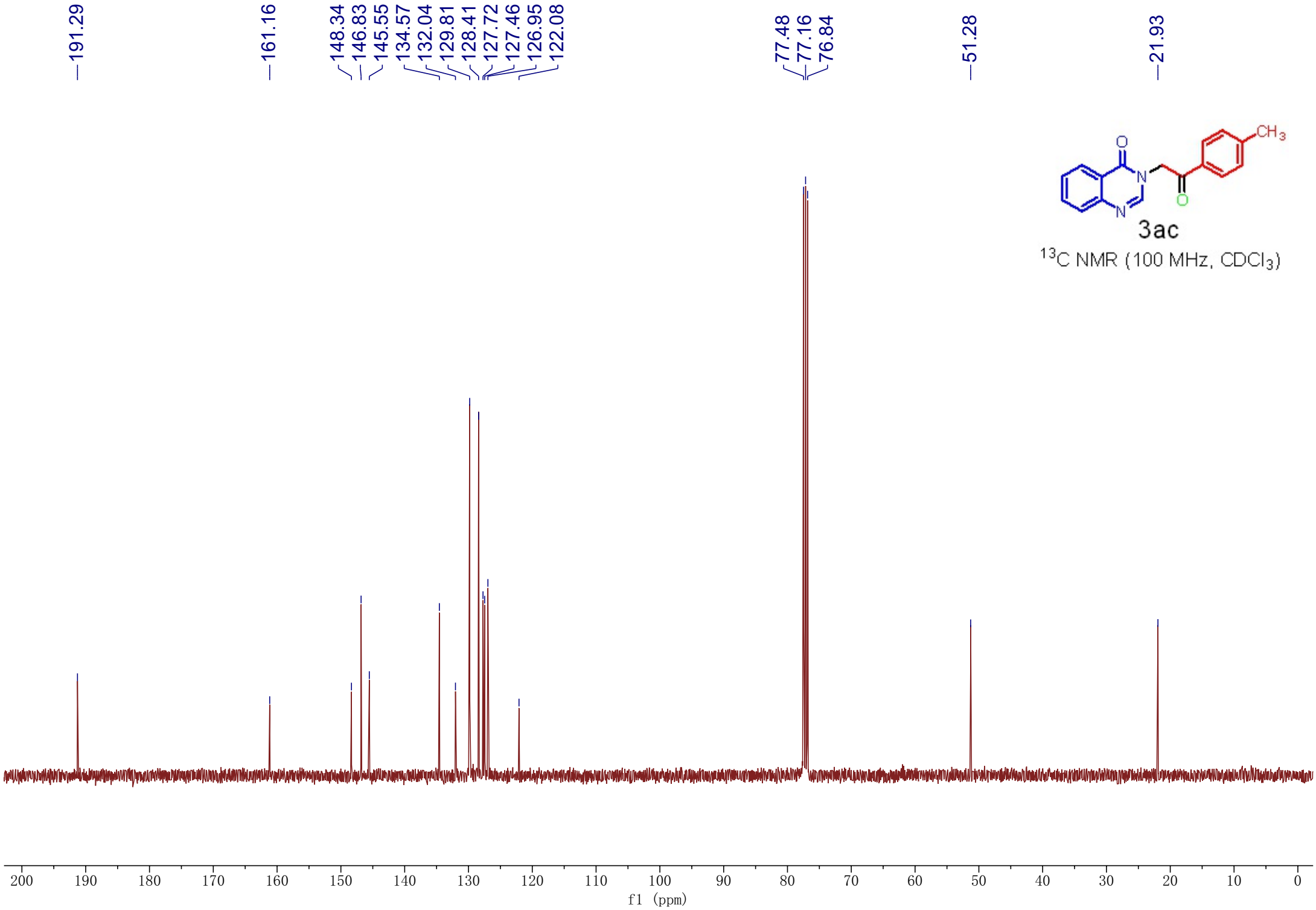
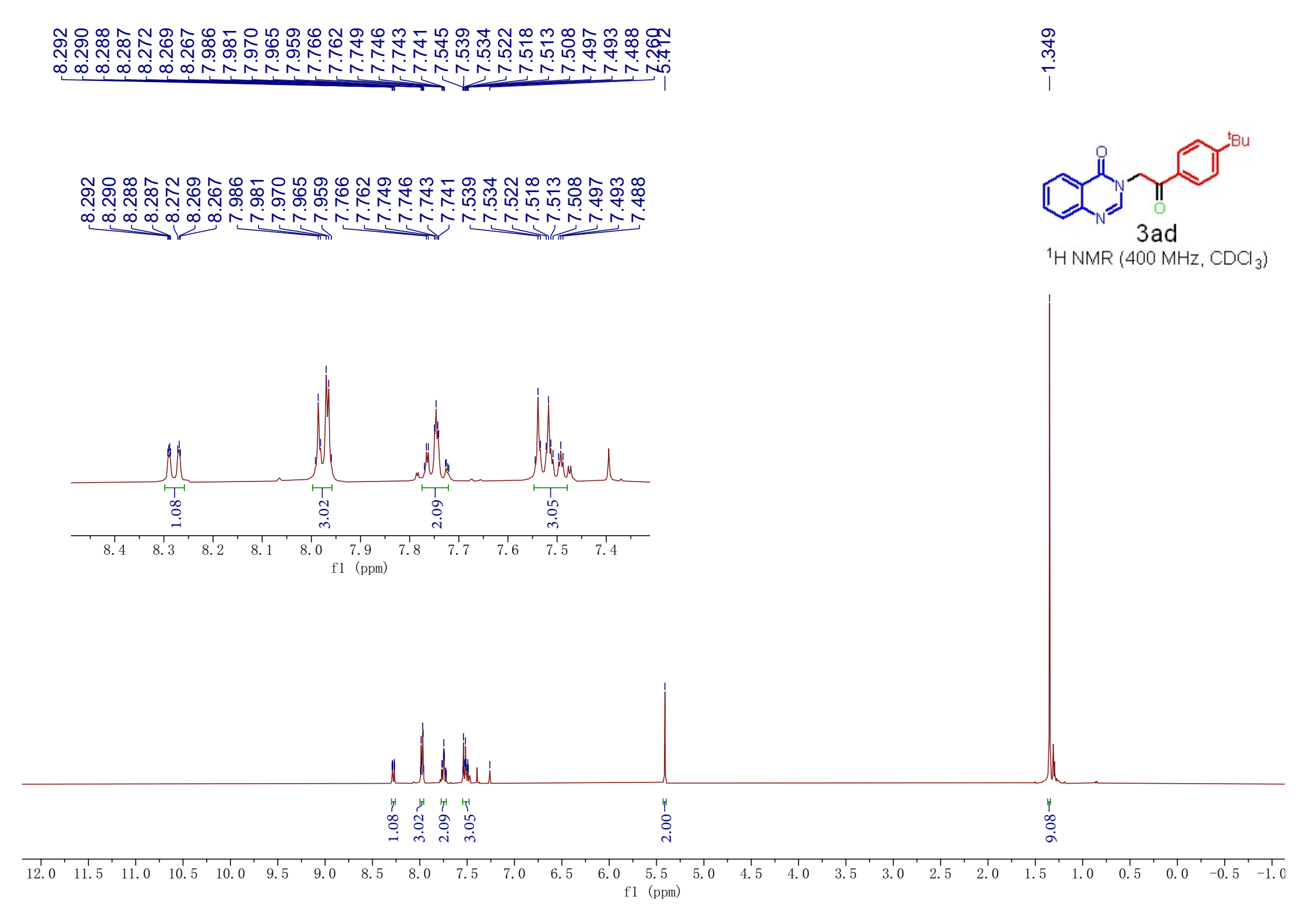
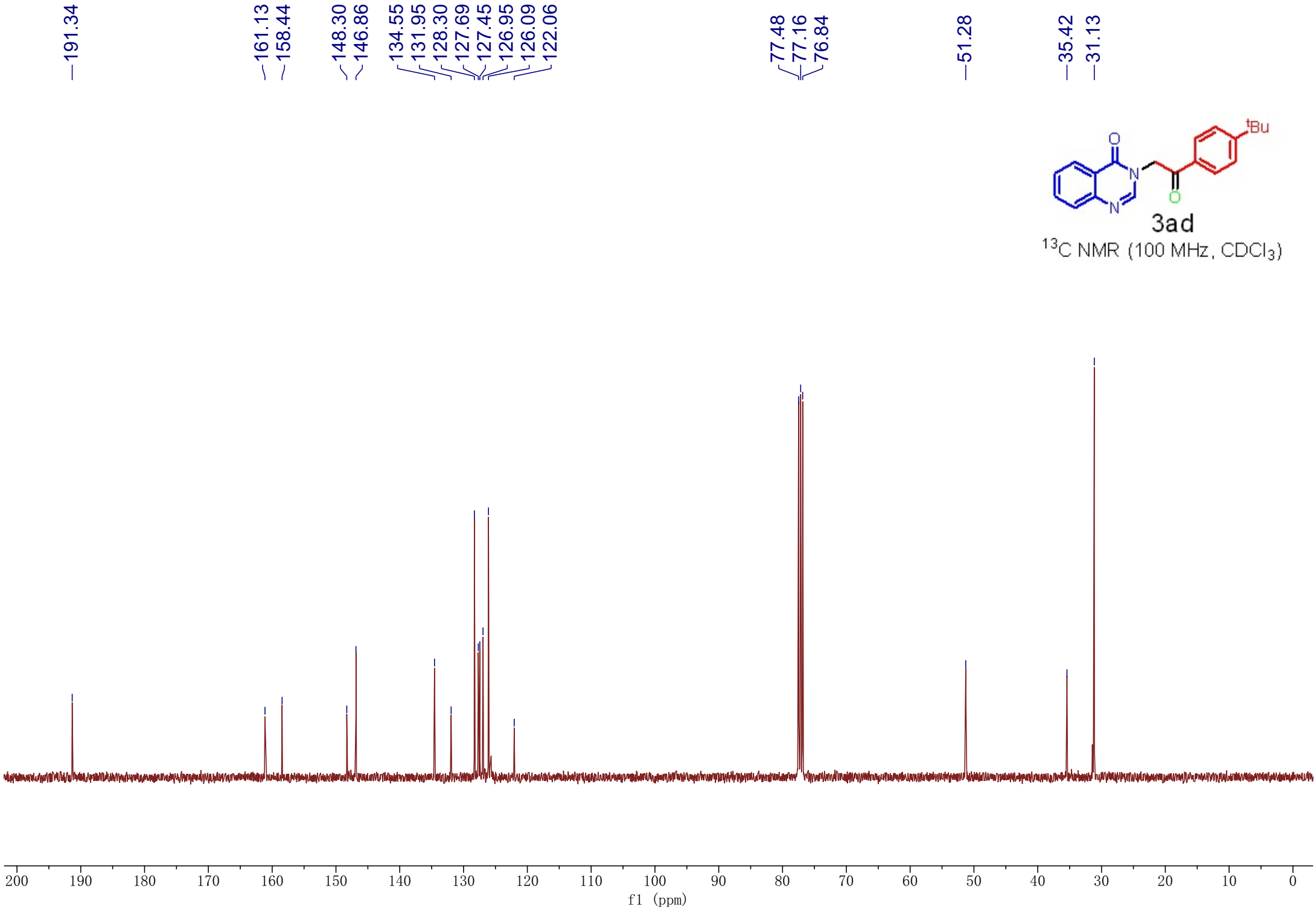
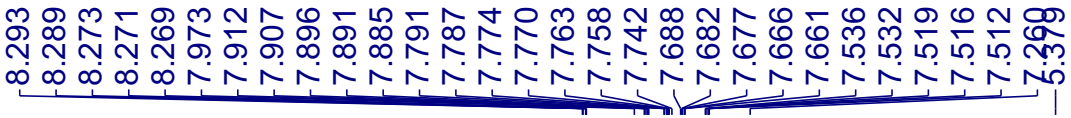
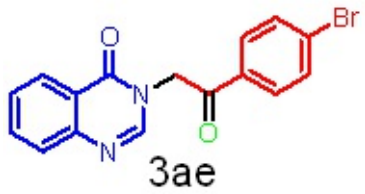
7.298
7.260
2.432
3ac
1H NMR (400 MHz, CDCl3)
1.03
1.00
2.03
2.07
1.08
2.02
2.05
3.09
f1 (ppm)


191.29
161.16
148.34
146.83
145.55
134.57
132.04
129.81
128.41
127.72
127.46
126.95
122.08
77.48
77.16
76.84
51.28
21.93
CH3
O
N
N
O
3ac
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.292
8.290
8.288
8.287
8.272
8.269
8.267
7.986
7.981
7.970
7.965
7.959
7.766
7.762
7.749
7.746
7.743
7.741
7.545
7.539
7.534
7.522
7.518
7.513
7.508
7.497
7.493
7.488
7.260
5.412
1.349
tBu
O
N
N
O
3ad
1H NMR (400 MHz, CDCl3)
1.08
3.02
2.09
3.05
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)
1.08
3.02
2.09
3.05
2.00
9.08
12.0
11.5
11.0
10.5
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
-1.0
f1 (ppm)

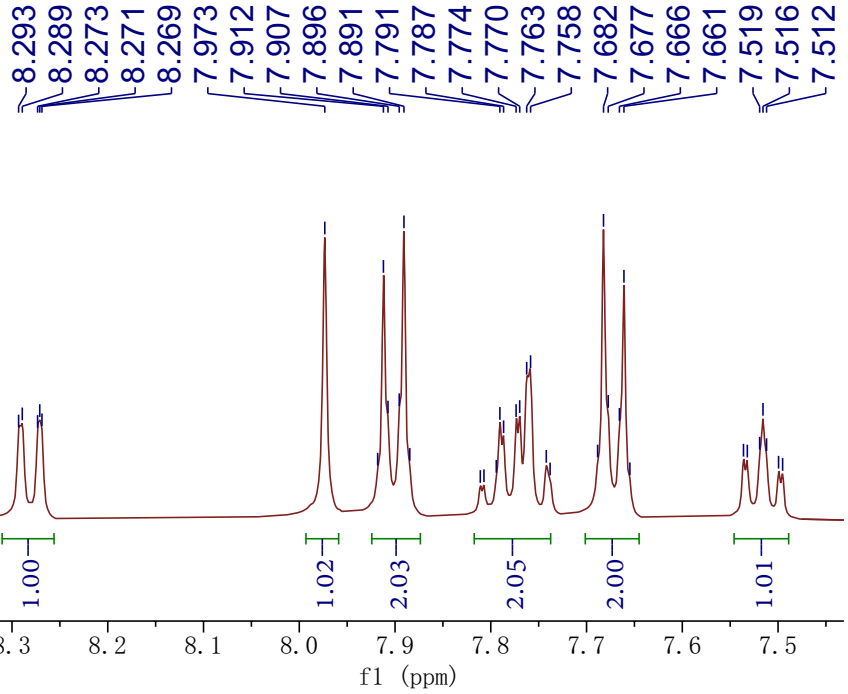

191.34
161.13
158.44
148.30
146.86
134.55
131.95
128.30
127.69
127.45
126.95
126.09
122.06
77.48
77.16
76.84
51.28
35.42
31.13
tBu
O
N
N
O
3ad
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

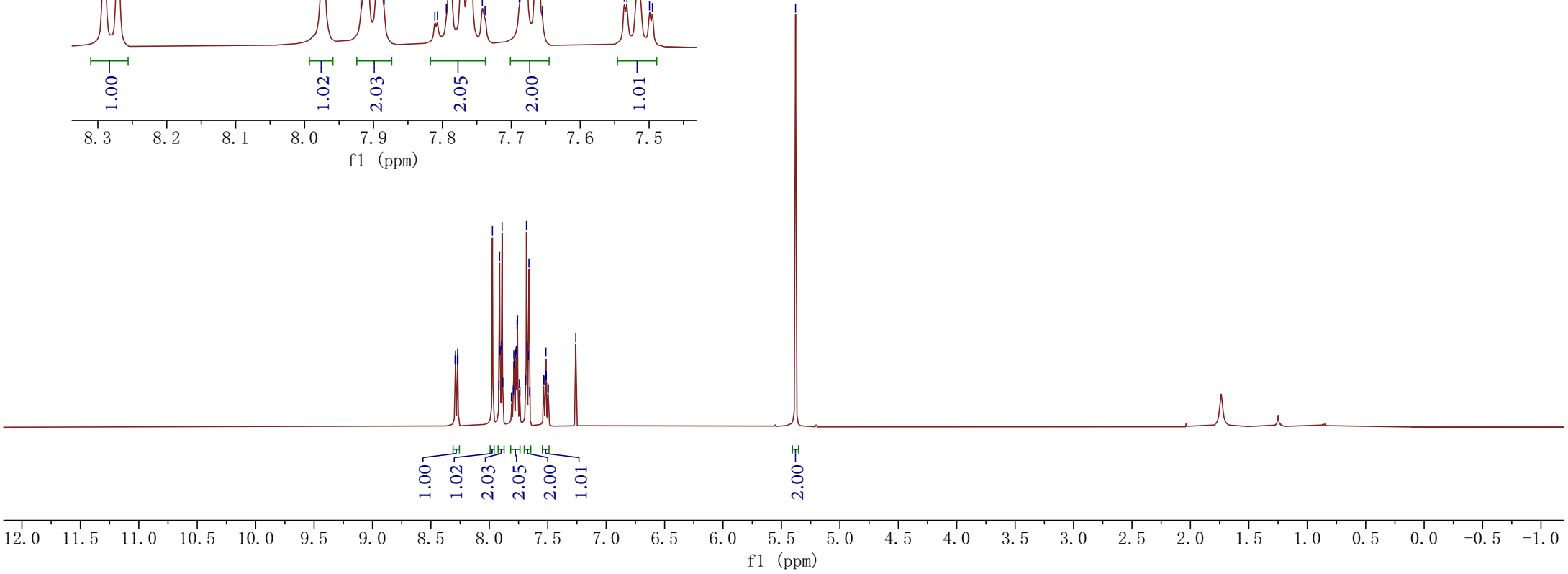


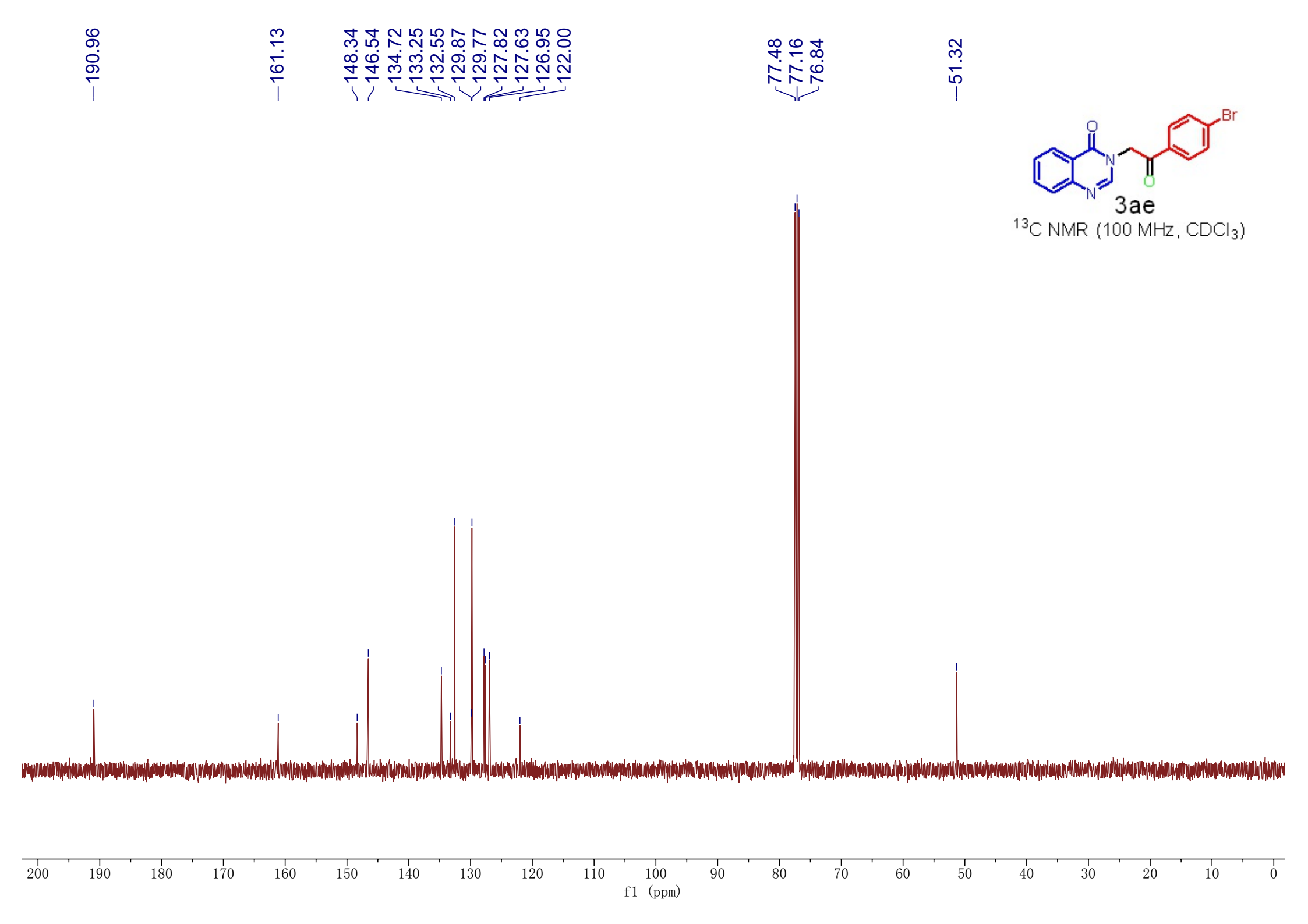


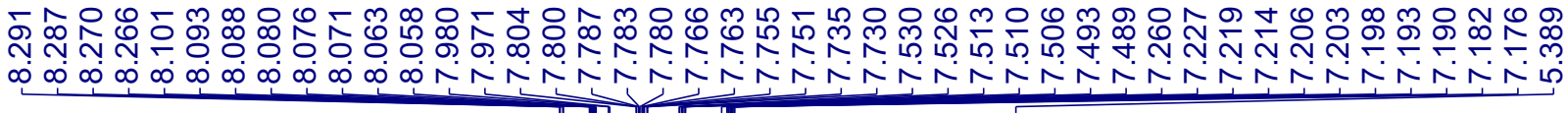
3ae

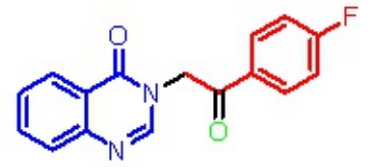
^{1}H NMR (400 MHz, $CDCl_3$)





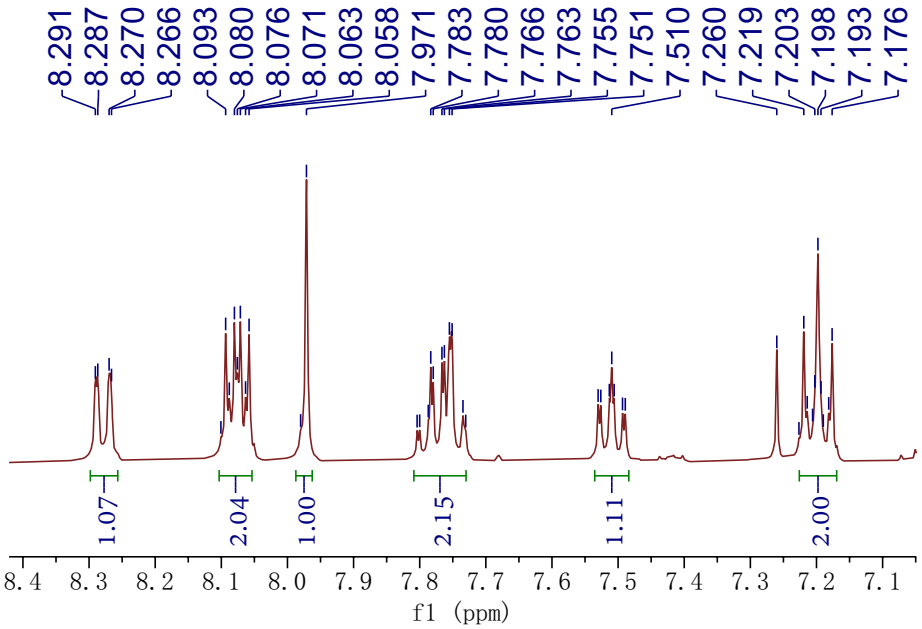

190.96
161.13
148.34
146.54
134.72
133.25
132.55
129.87
129.77
127.82
127.63
126.95
122.00
77.48
77.16
76.84
51.32
Br
O
N
N
O
3ae
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

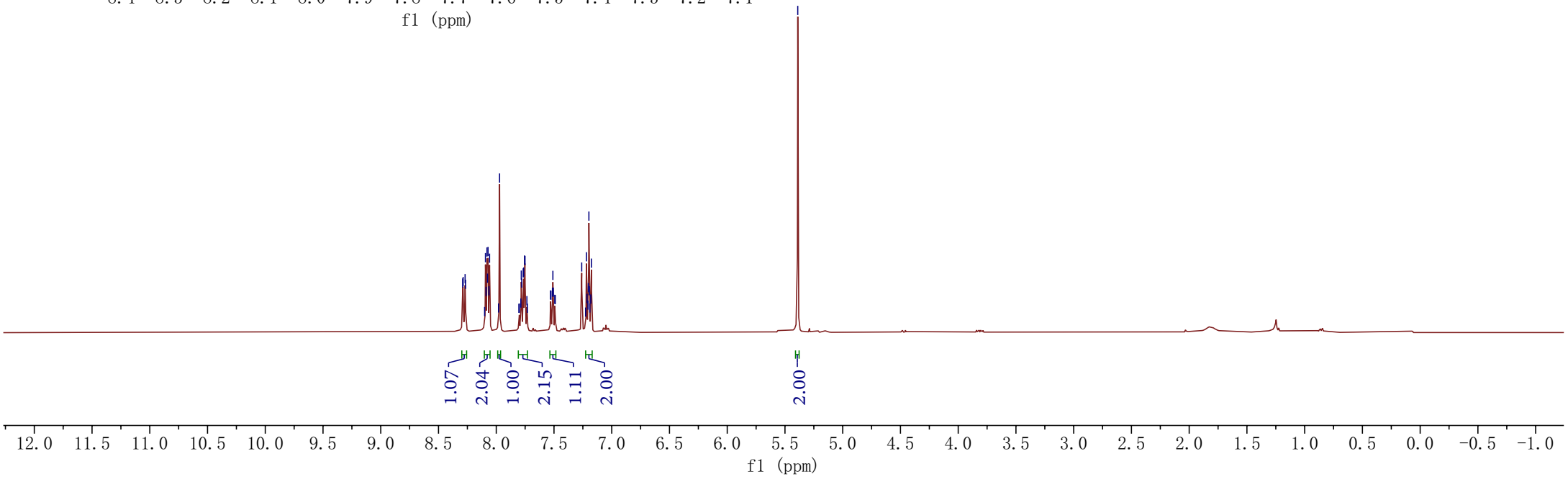


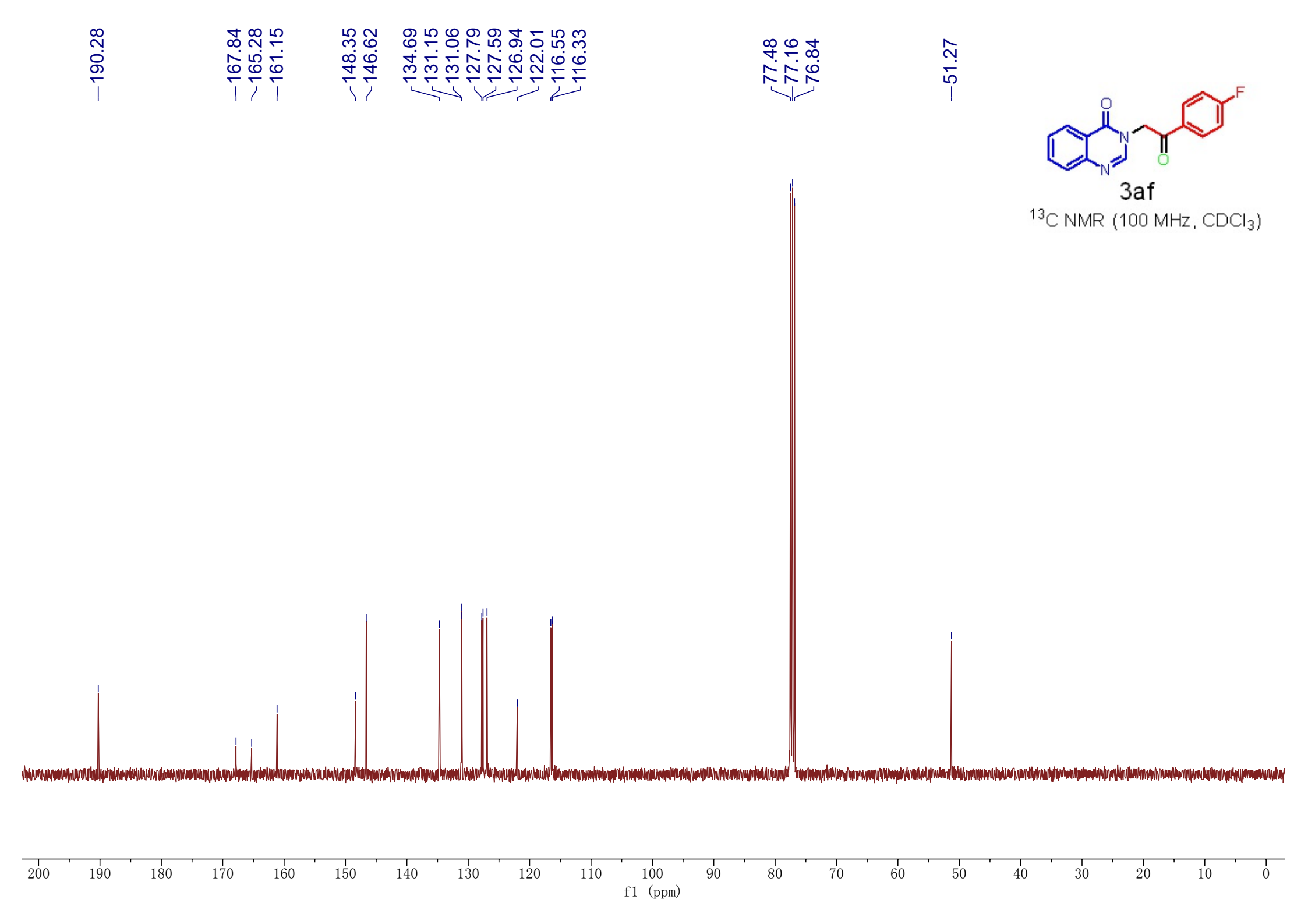


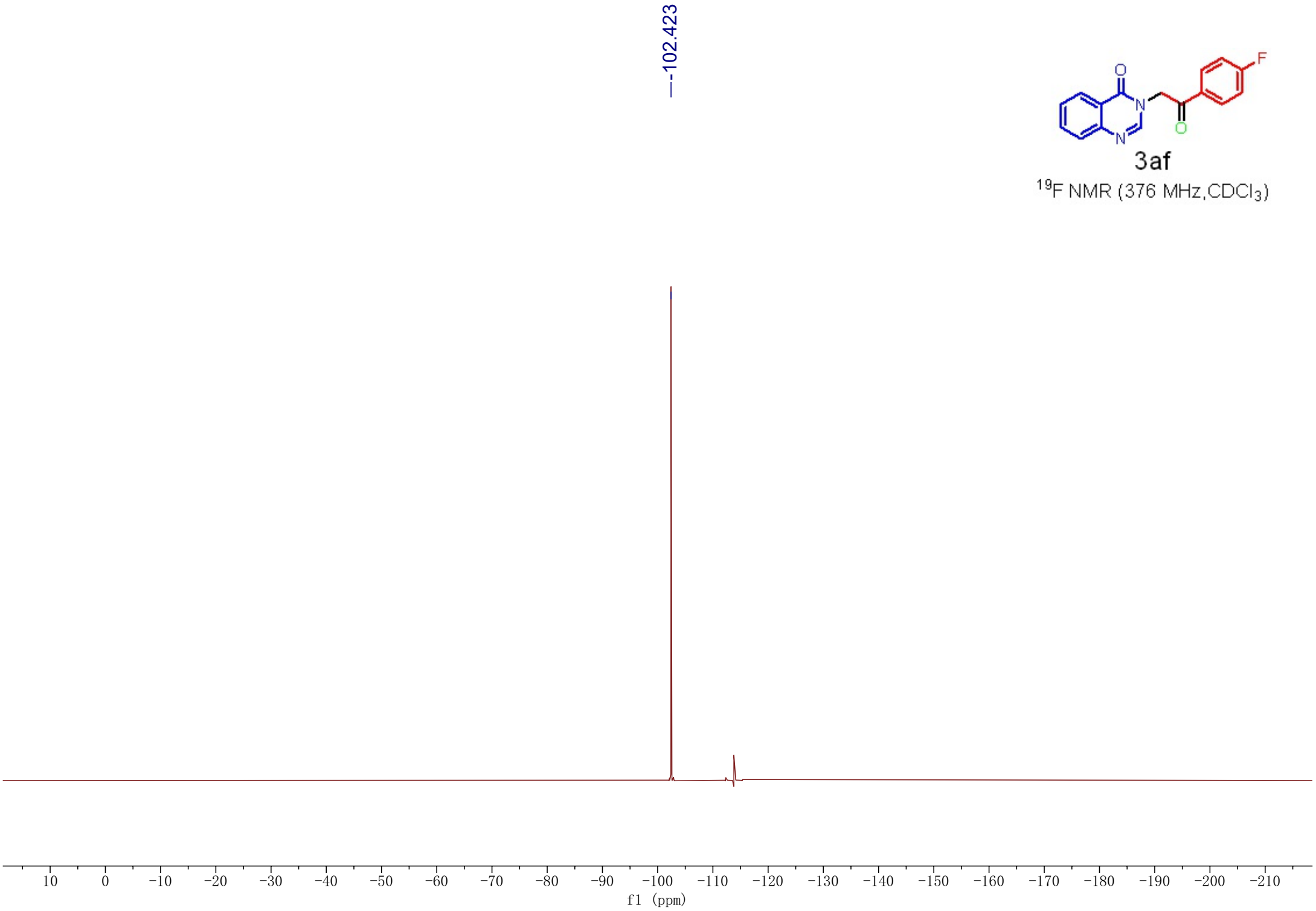
3af

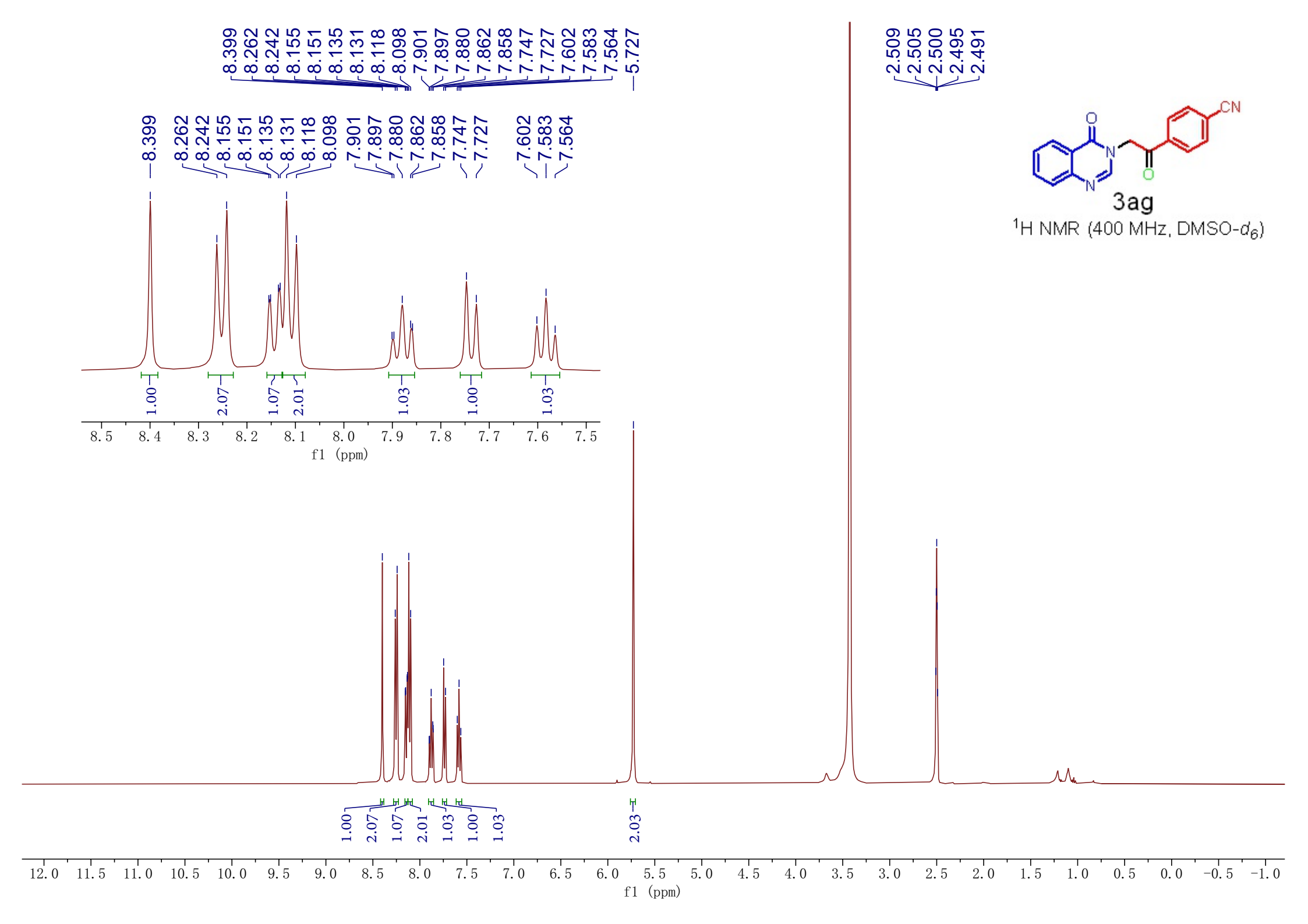
^{1}H NMR (400 MHz, $CDCl_3$)

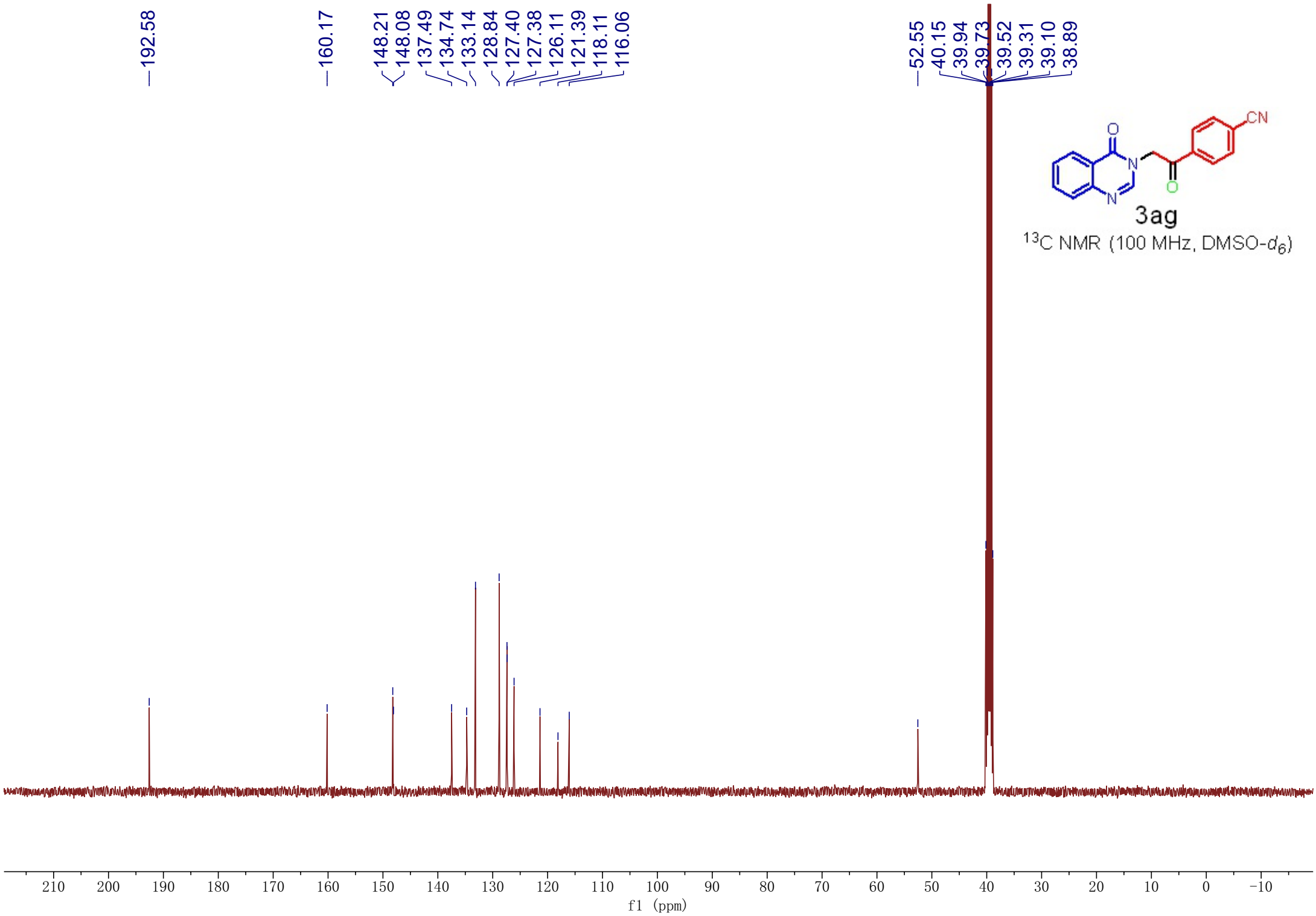


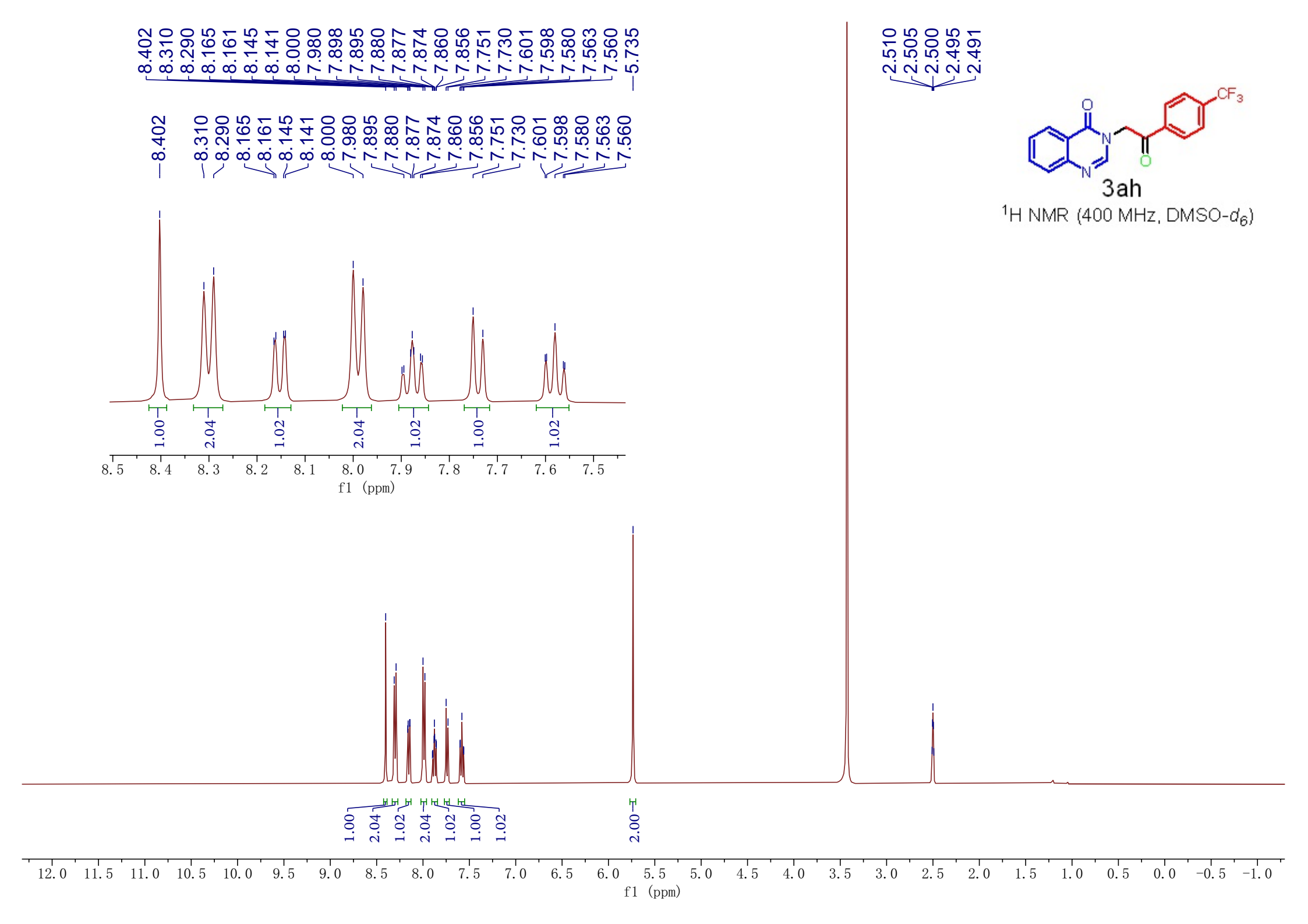


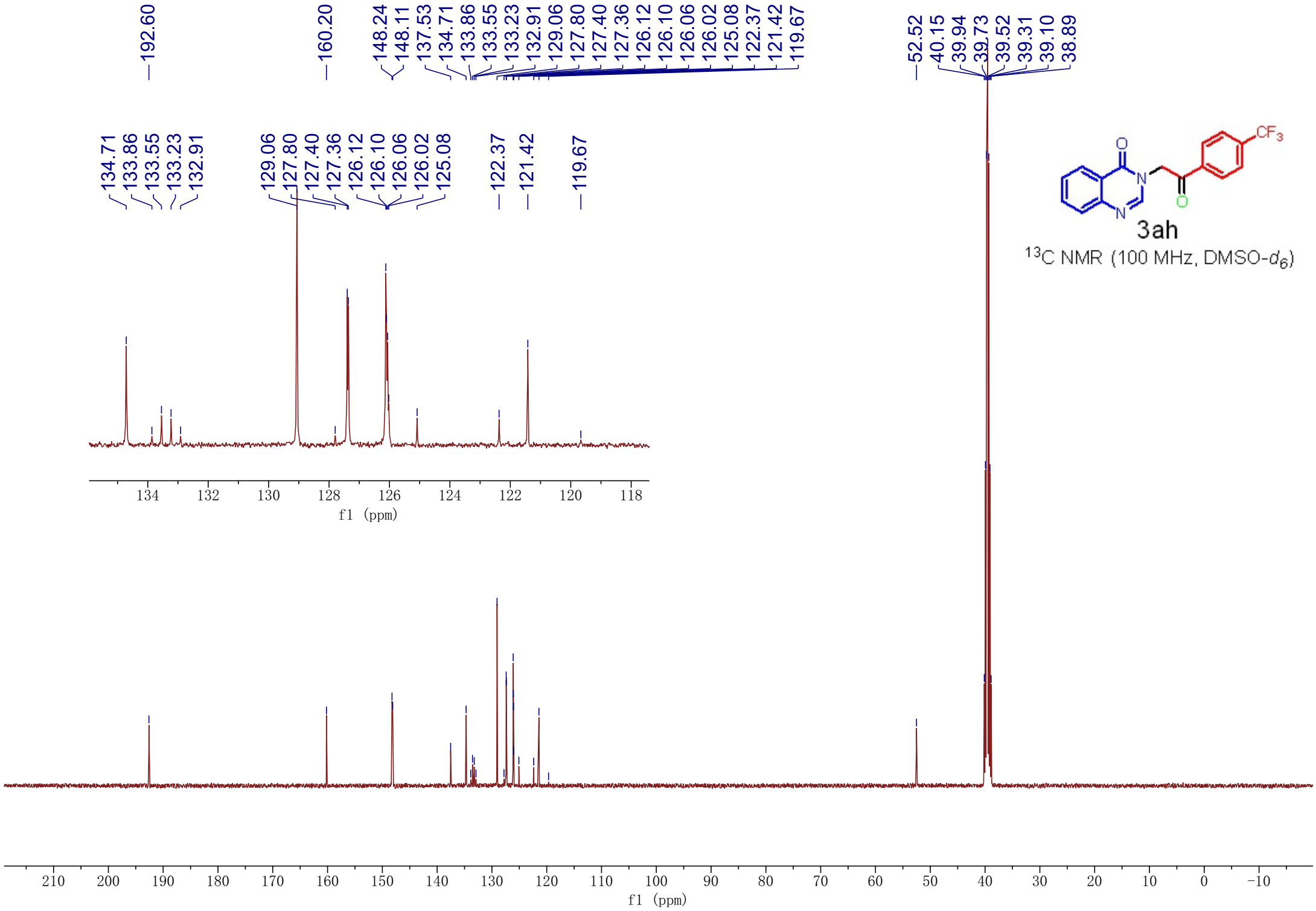

190.28
167.84
165.28
161.15
148.35
146.62
134.69
131.15
131.06
127.79
127.59
126.94
122.01
116.55
116.33
77.48
77.16
76.84
51.27
O
N
N
O
F
3af
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

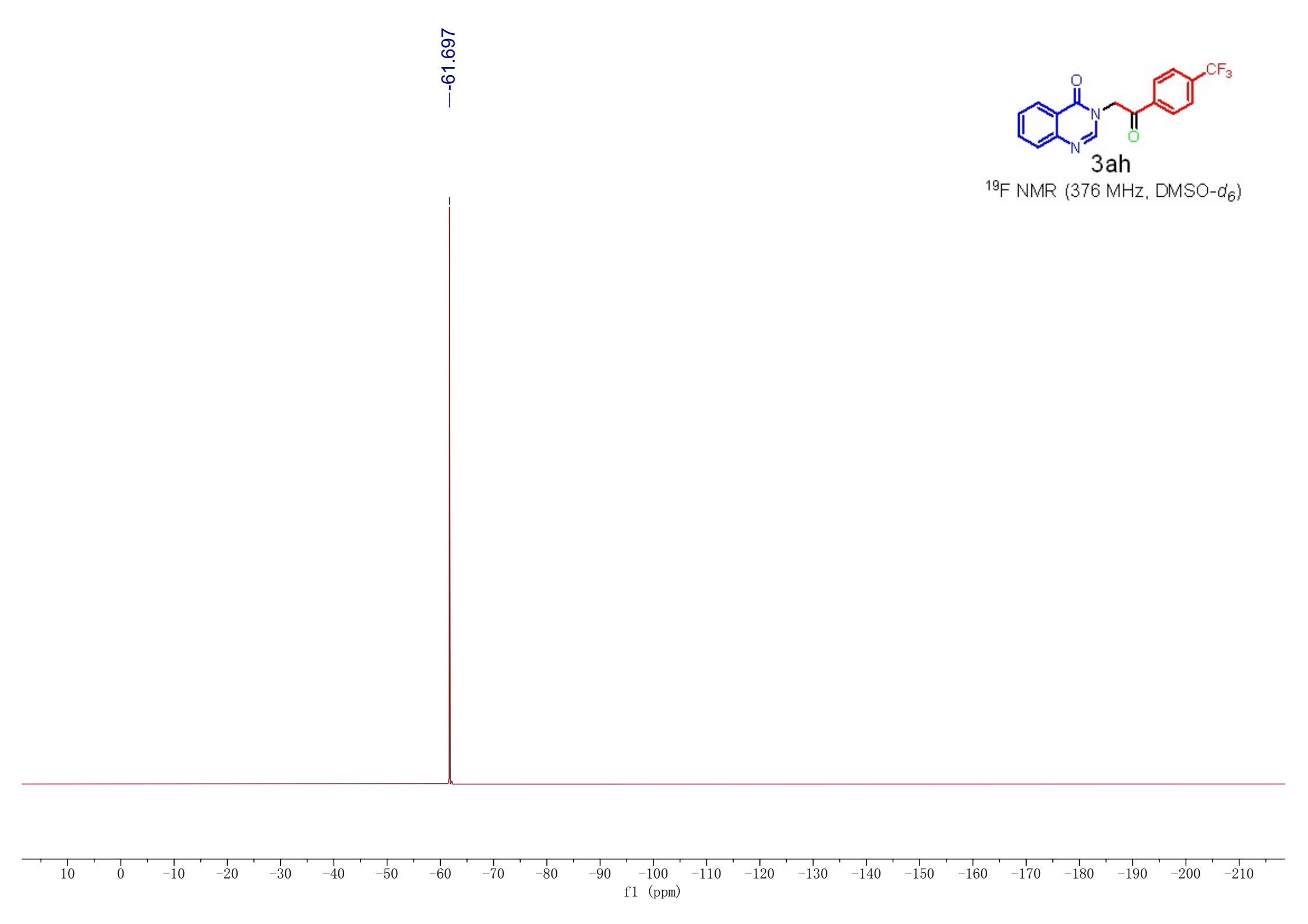

-102.423
O
N
N
O
F
3af
^{19}F NMR (376 MHz,$CDCl_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

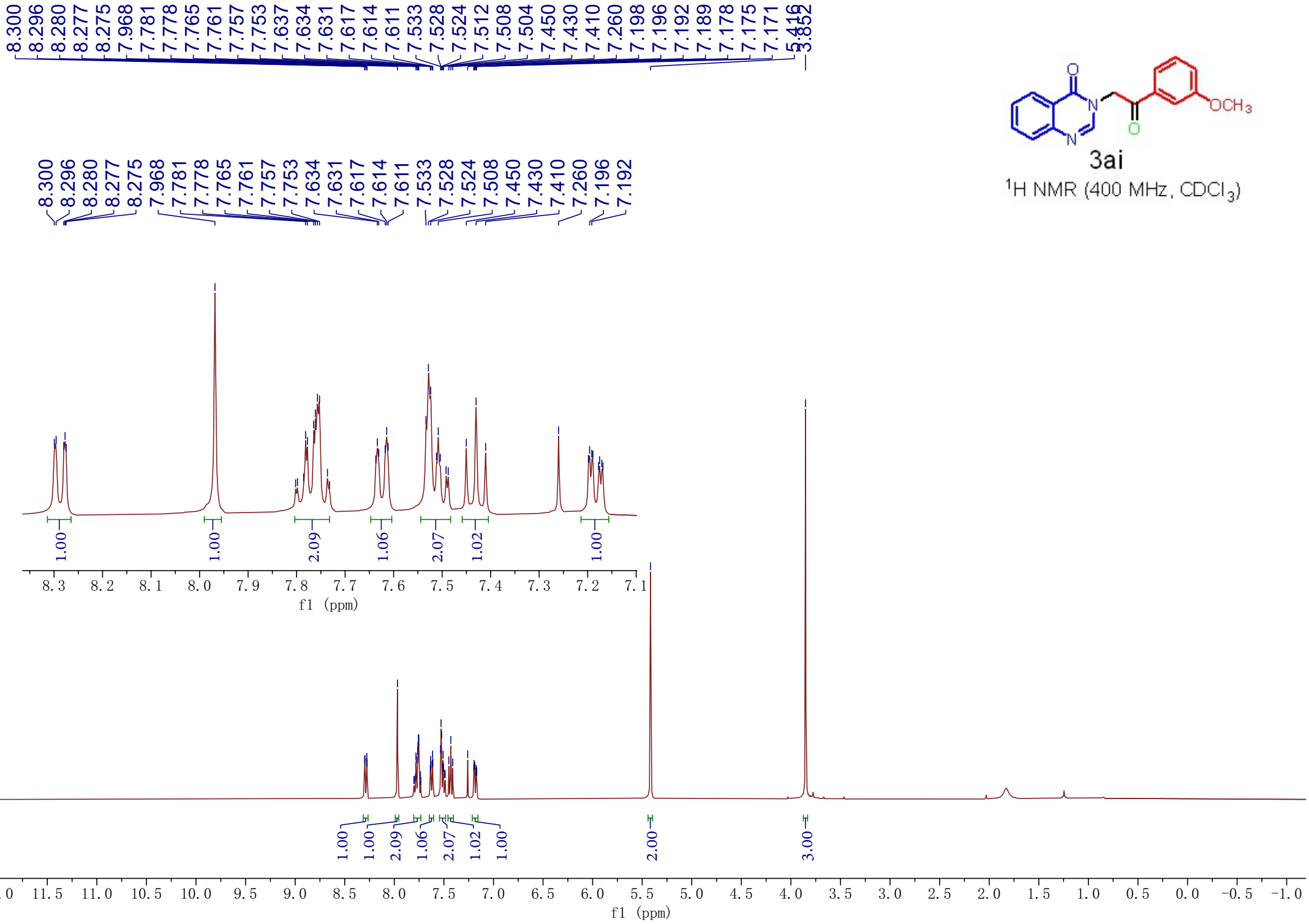

8.399
8.262
8.242
8.155
8.151
8.135
8.131
8.118
8.098
7.901
7.897
7.880
7.862
7.858
7.747
7.727
7.602
7.583
7.564
5.727
2.509
2.505
2.500
2.495
2.491
1.00
2.07
1.07
2.01
1.03
1.00
1.03
2.03
f1 (ppm)
CN
O
N
N
O
3ag
1H NMR (400 MHz, DMSO-d6)

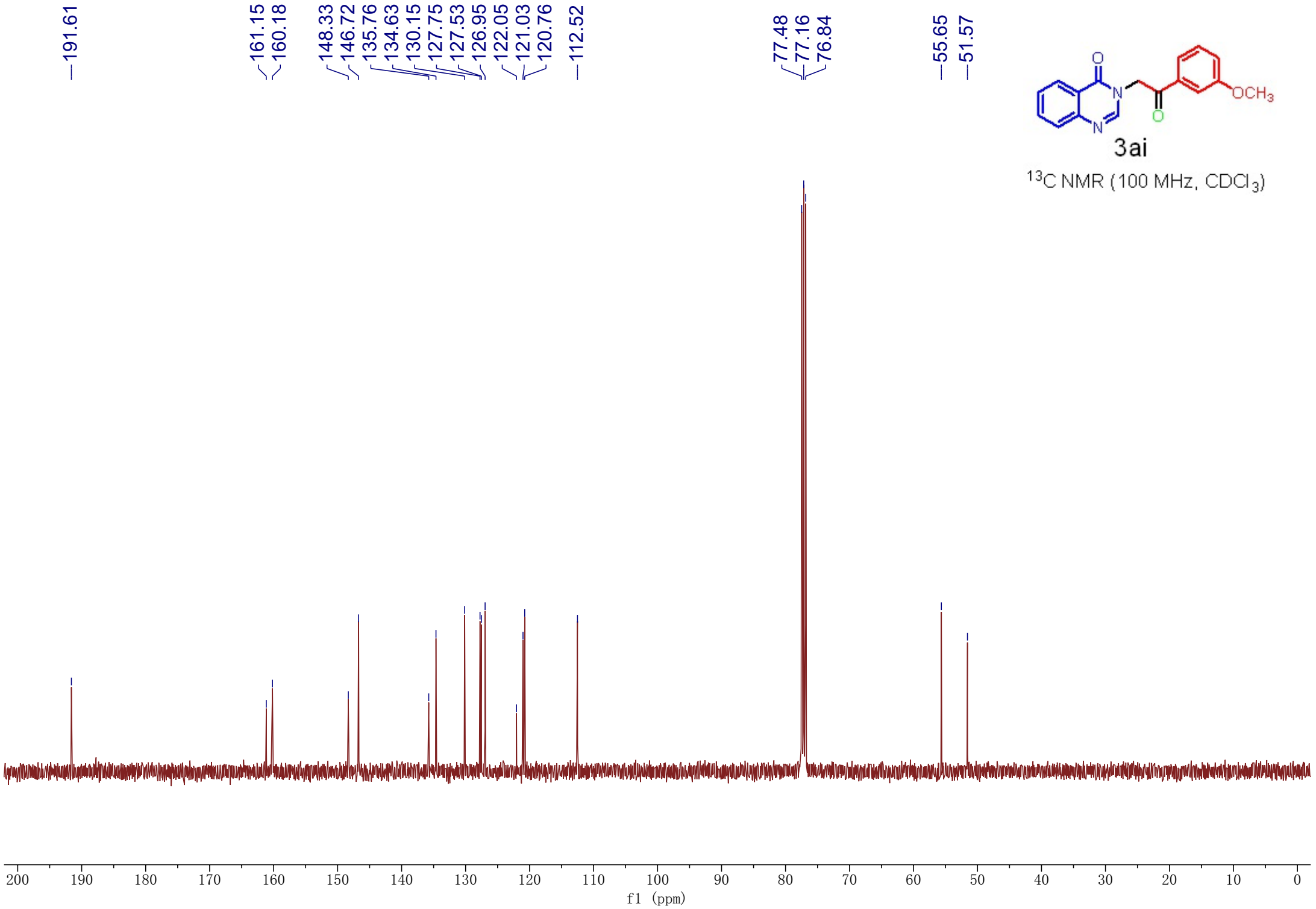

192.58
160.17
148.21
148.08
137.49
134.74
133.14
128.84
127.40
127.38
126.11
121.39
118.11
116.06
52.55
40.15
39.94
39.73
39.52
39.31
39.10
38.89
CN
O
N
N
O
3ag
13C NMR (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

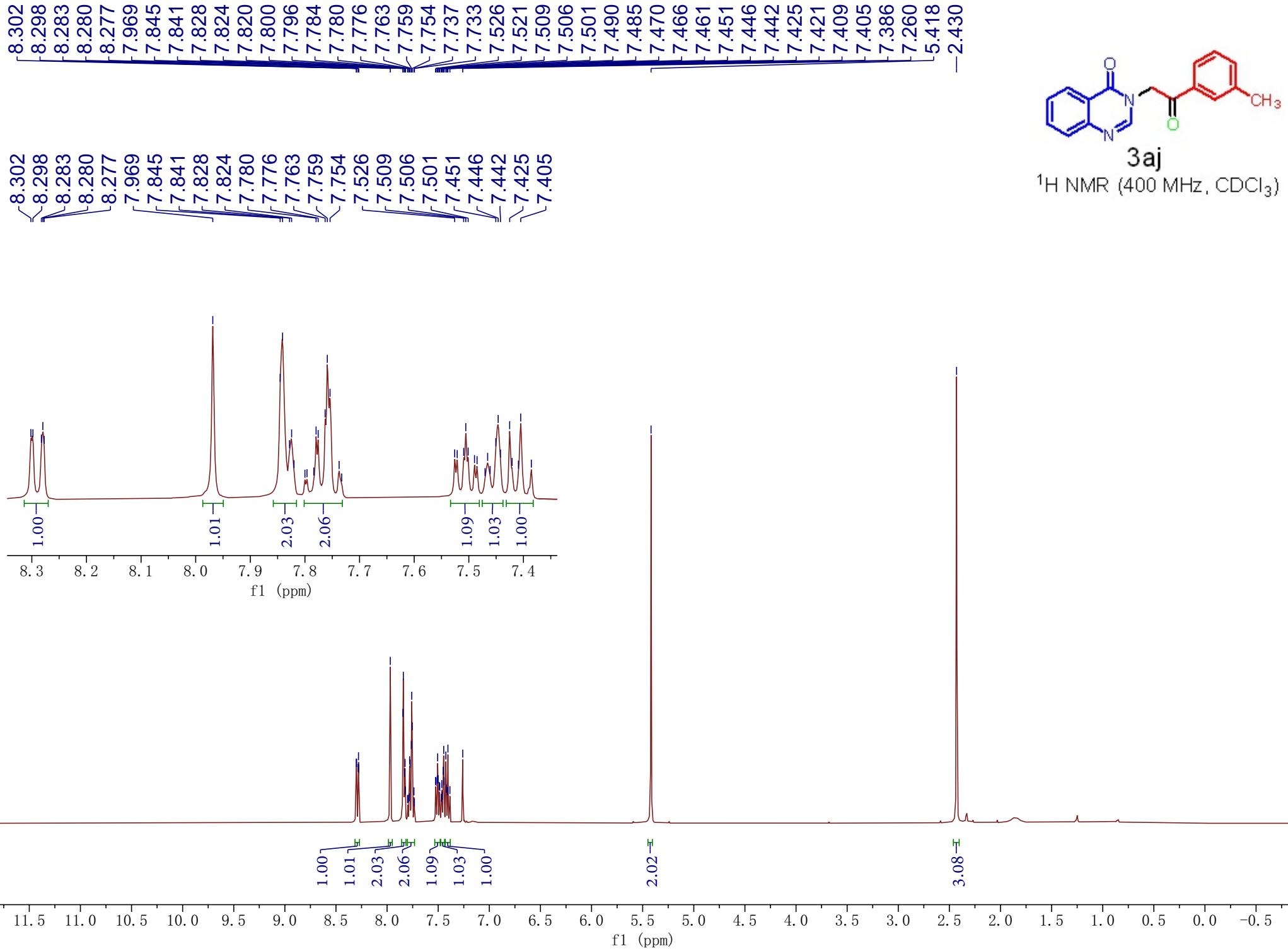

8.402
8.310
8.290
8.165
8.161
8.145
8.141
8.000
7.980
7.898
7.895
7.880
7.877
7.874
7.860
7.856
7.751
7.730
7.601
7.598
7.580
7.563
7.560
5.735
2.510
2.505
2.500
2.495
2.491
1.00
2.04
1.02
2.04
1.02
1.00
1.02
2.00
f1 (ppm)
3ah
^{1}H NMR (400 MHz, DMSO-d_6)

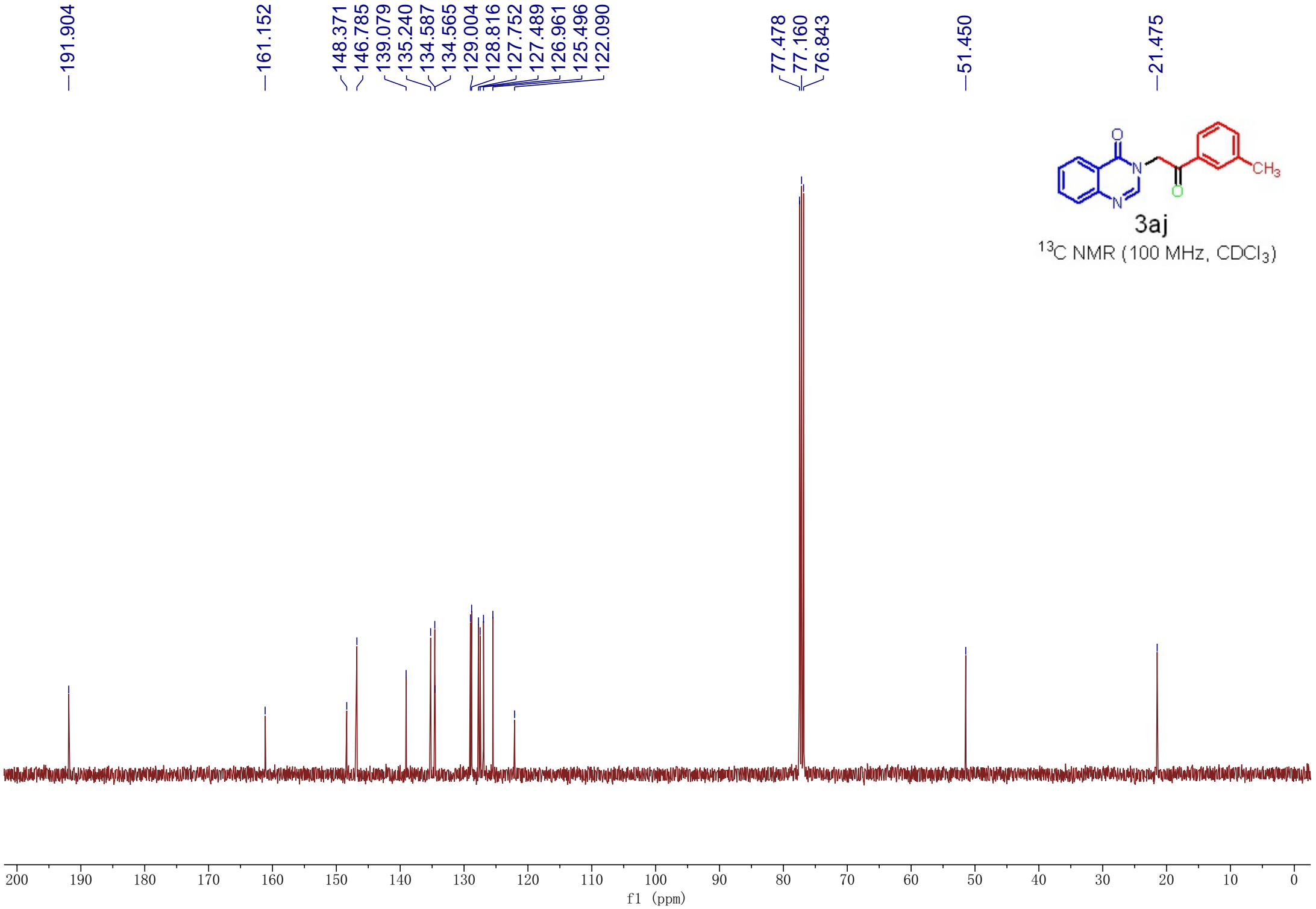

192.60
160.20
148.24
148.11
137.53
134.71
133.86
133.55
133.23
132.91
129.06
127.80
127.40
127.36
126.12
126.10
126.06
126.02
125.08
122.37
121.42
119.67
52.52
40.15
39.94
39.73
39.52
39.31
39.10
38.89
f1 (ppm)
CF3
O
N
N
O
3ah
13C NMR (100 MHz, DMSO-d6)

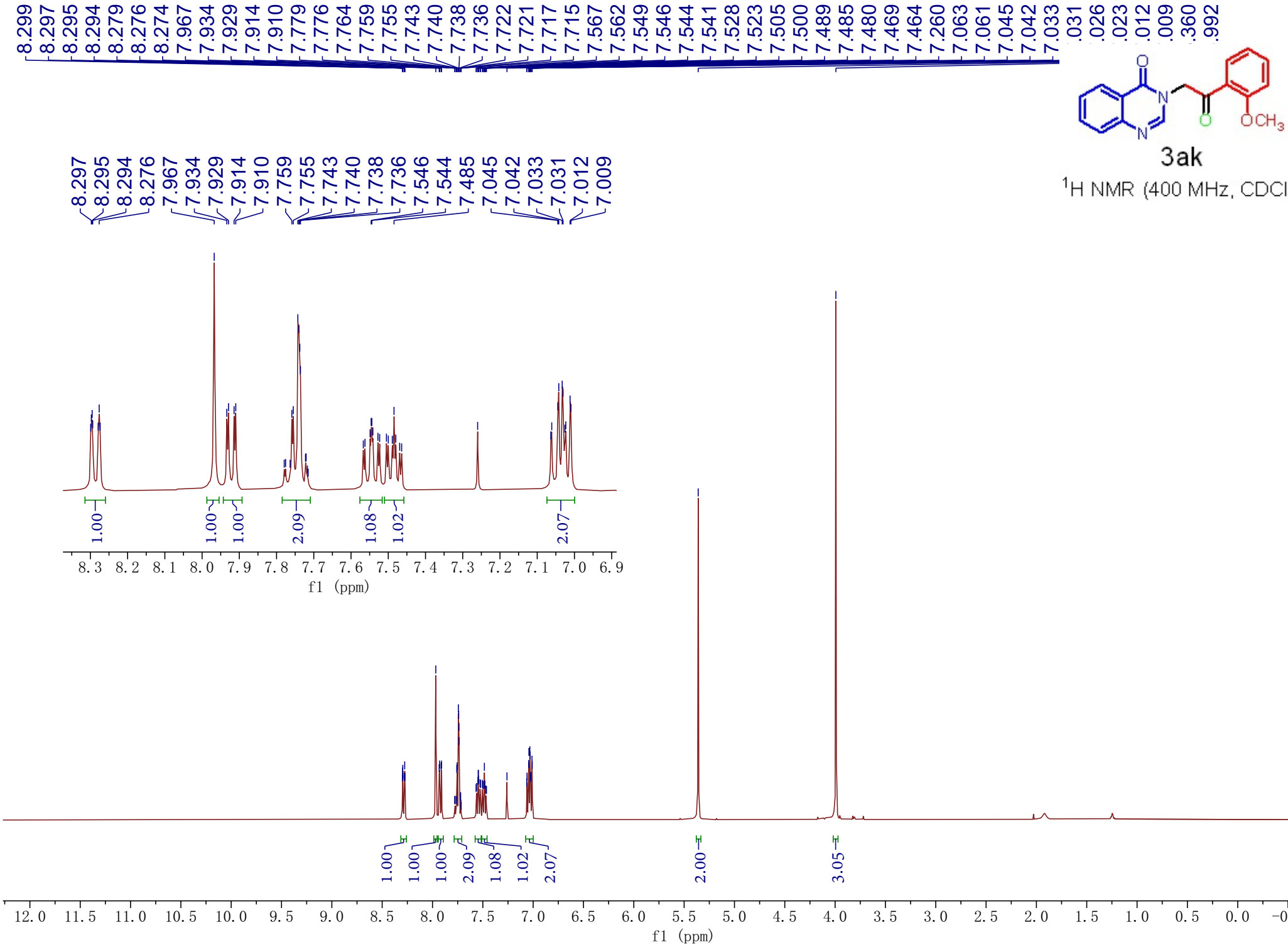

-61.697
CF3
O
N
N
O
3ah
19F NMR (376 MHz, DMSO-d6)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

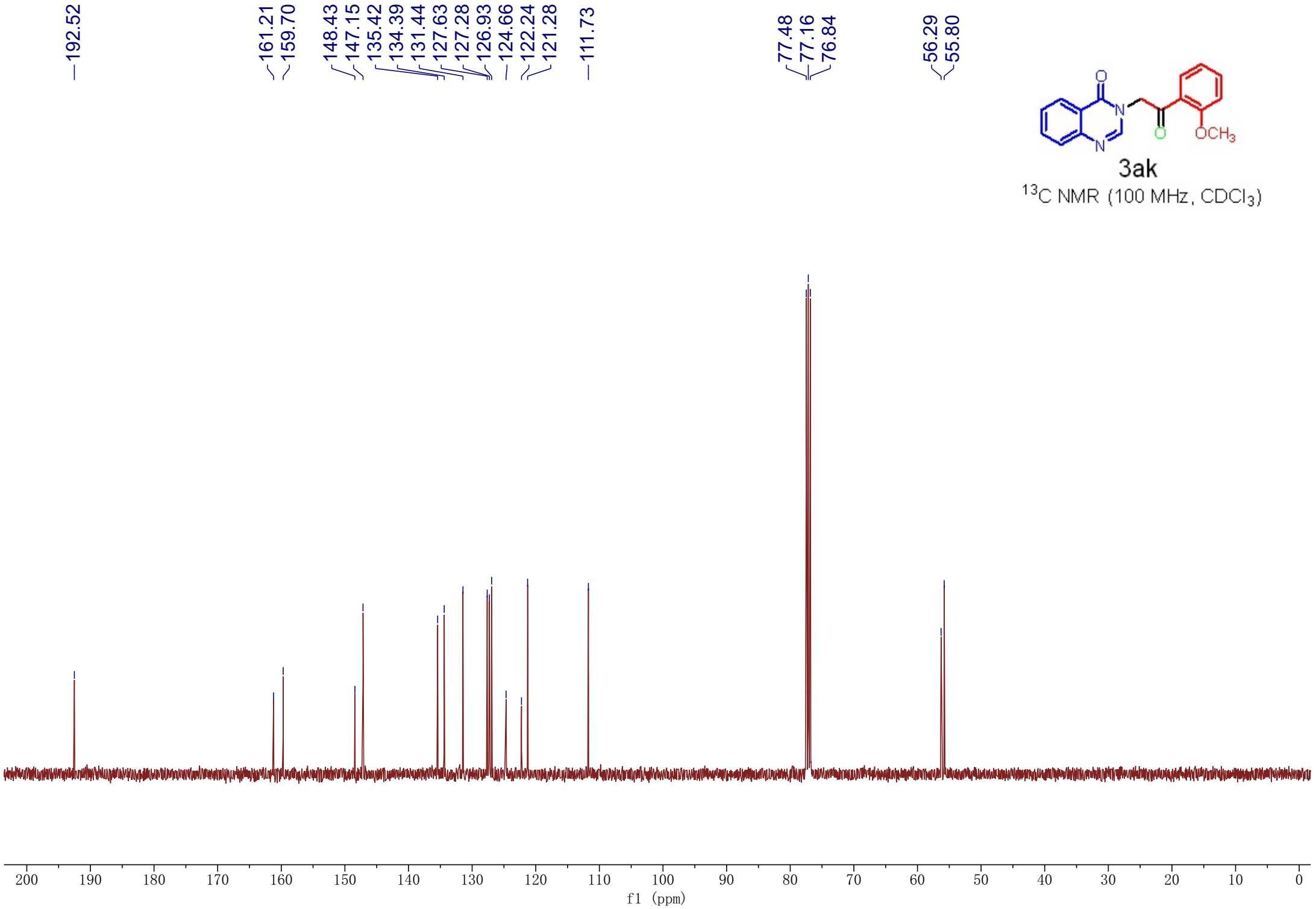

8.300
8.296
8.280
8.277
8.275
7.968
7.781
7.778
7.765
7.761
7.757
7.753
7.637
7.634
7.631
7.617
7.614
7.611
7.533
7.528
7.524
7.512
7.508
7.504
7.450
7.430
7.410
7.260
7.198
7.196
7.192
7.189
7.178
7.175
7.171
5.416
3.852
O
N
N
O
OCH3
3ai
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.09
1.06
2.07
1.02
1.00
f1 (ppm)
2.00
3.00
f1 (ppm)

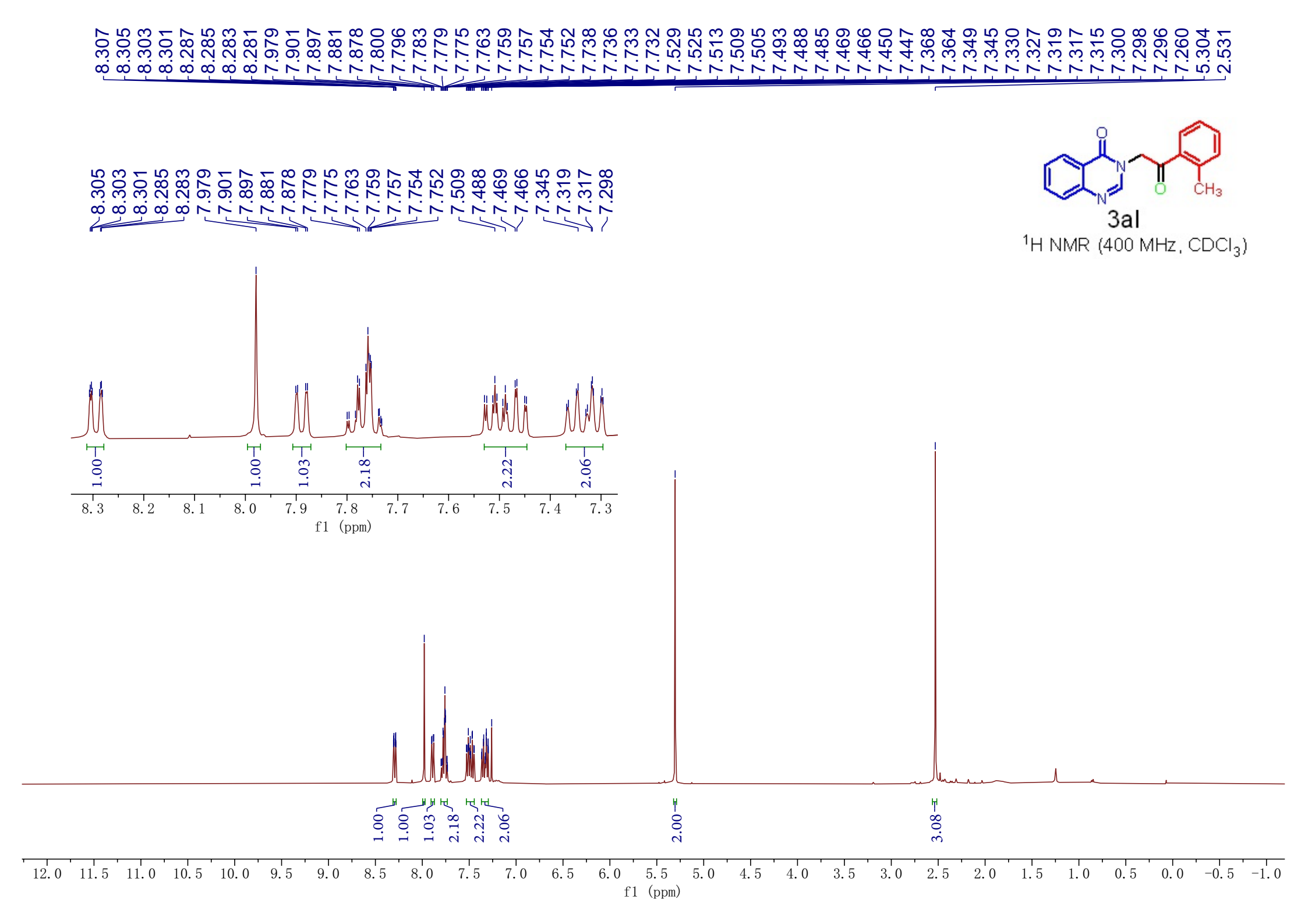

191.61
161.15
160.18
148.33
146.72
135.76
134.63
130.15
127.75
127.53
126.95
122.05
121.03
120.76
112.52
77.48
77.16
76.84
55.65
51.57
O
N
N
O
OCH3
3ai
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

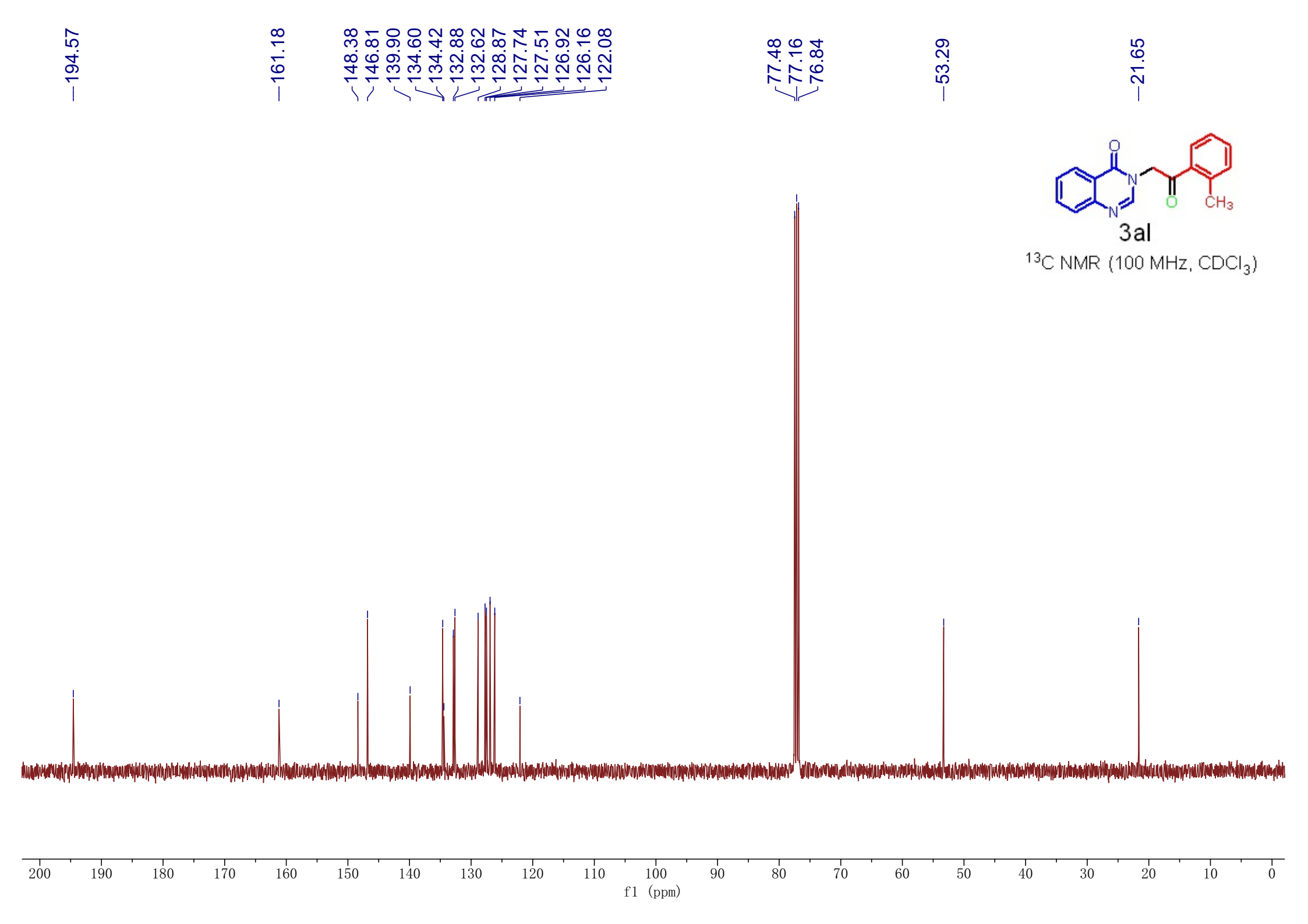

8.302
8.298
8.283
8.280
8.277
7.969
7.845
7.841
7.828
7.824
7.820
7.800
7.796
7.784
7.780
7.776
7.763
7.759
7.754
7.737
7.733
7.526
7.521
7.509
7.506
7.501
7.490
7.485
7.470
7.466
7.461
7.451
7.446
7.442
7.425
7.421
7.409
7.405
7.386
7.260
5.418
2.430
O
N
N
O
CH3
3aj
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.03
2.06
1.09
1.03
1.00
2.02
3.08
f1 (ppm)

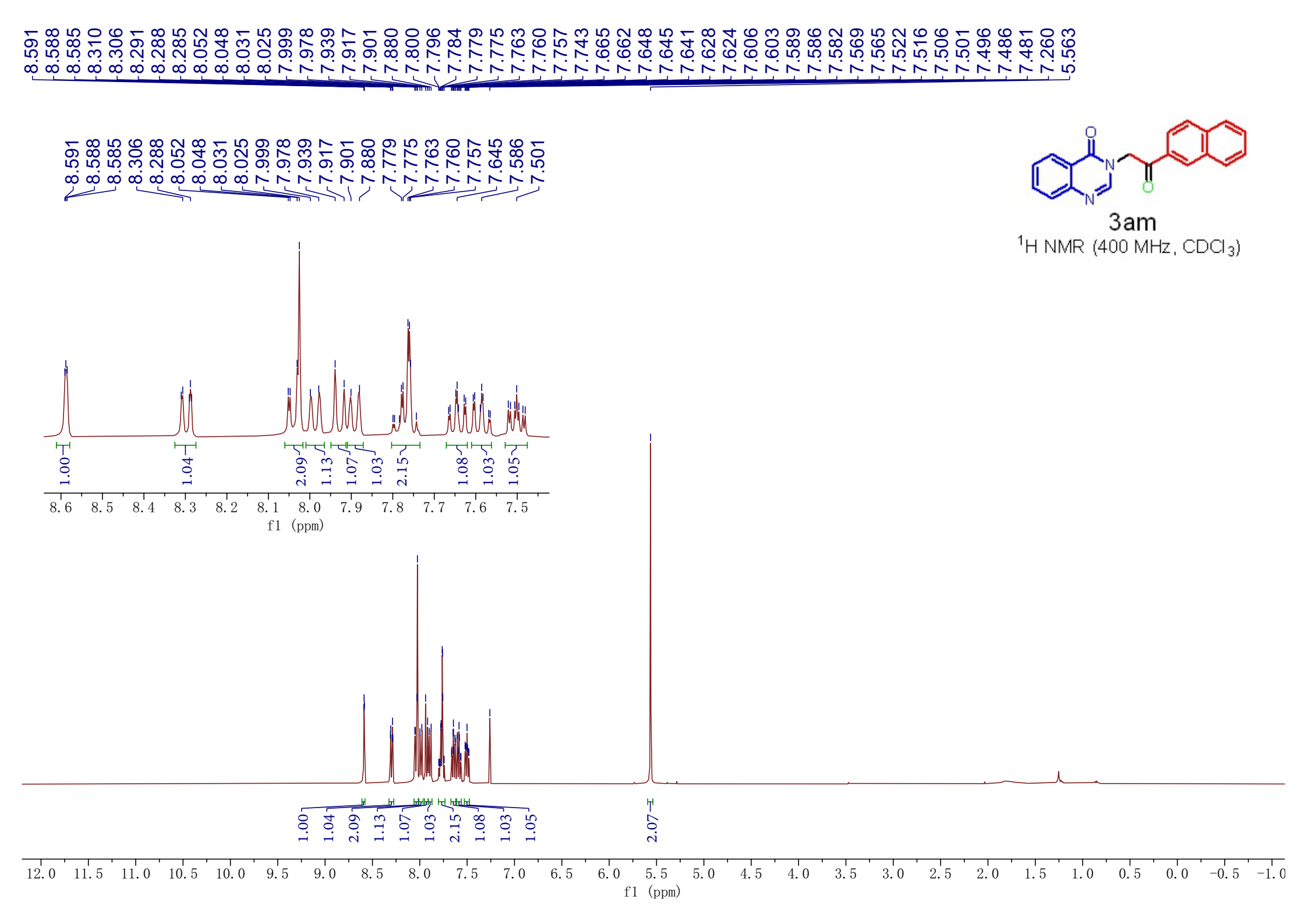

191.904
161.152
148.371
146.785
139.079
135.240
134.587
134.565
129.004
128.816
127.752
127.489
126.961
125.496
122.090
77.478
77.160
76.843
51.450
21.475
O
N
N
O
CH3
3aj
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

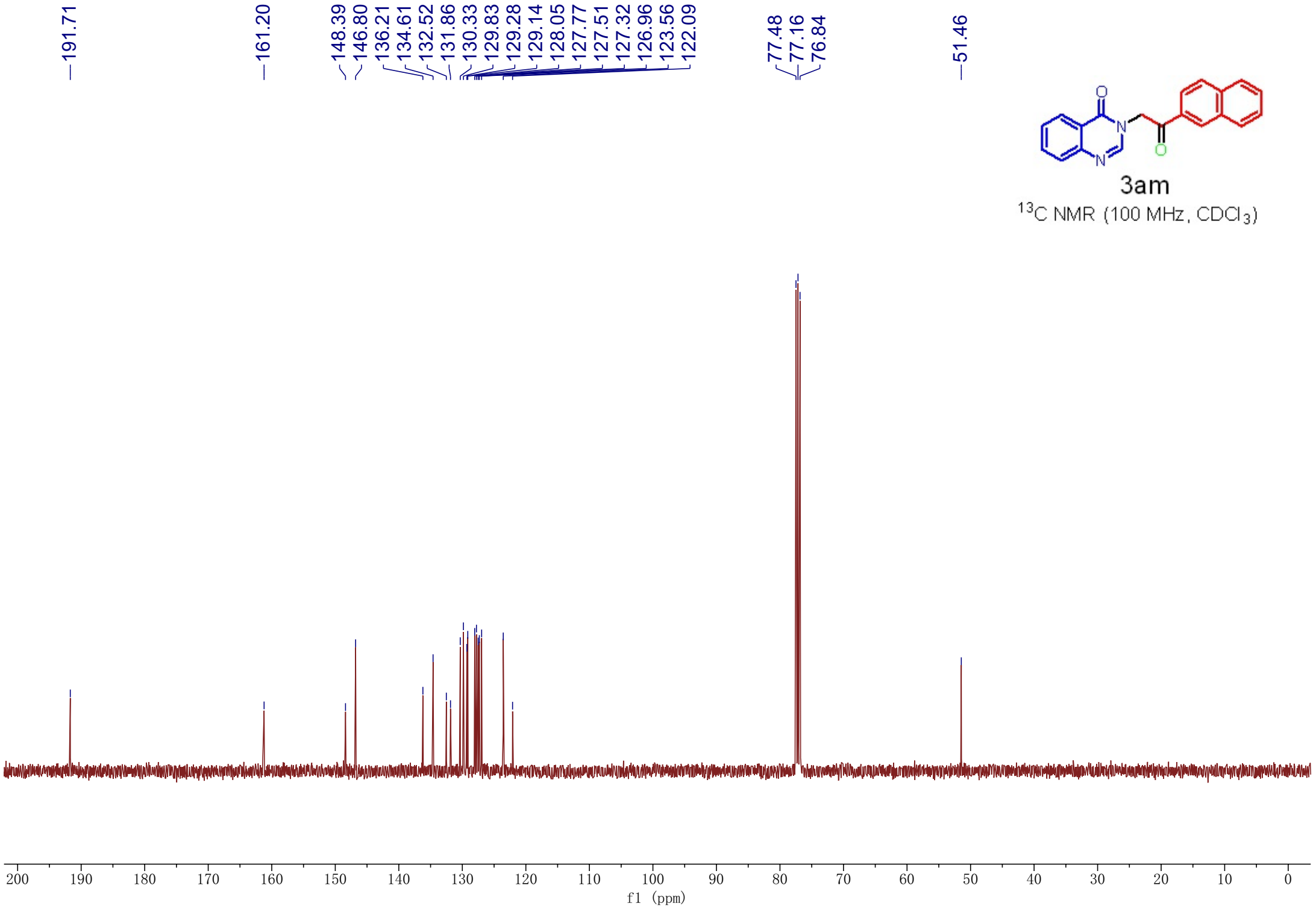

8.299 8.297 8.295 8.294 8.279 8.276 8.274 7.967 7.934 7.929 7.914 7.910 7.779 7.776 7.764 7.759 7.755 7.743 7.740 7.738 7.736 7.722 7.721 7.717 7.715 7.567 7.562 7.549 7.546 7.544 7.541 7.528 7.523 7.505 7.500 7.489 7.485 7.480 7.469 7.464 7.260 7.063 7.061 7.045 7.042 7.033 .031 .026 .023 .012 .009 .360 .992
O
N
N
O
OCH3
3ak
1H NMR (400 MHz, CDCl3)
8.297 8.295 8.294 8.276 7.967 7.934 7.929 7.914 7.910 7.759 7.755 7.743 7.740 7.738 7.736 7.546 7.544 7.485 7.045 7.042 7.033 7.031 7.012 7.009
1.00 1.00 1.00 2.09 1.08 1.02 2.07
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.00 1.00 1.00 2.09 1.08 1.02 2.07 2.00 3.05
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

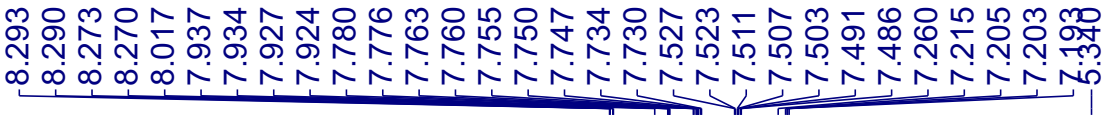

192.52
161.21
159.70
148.43
147.15
135.42
134.39
131.44
127.63
127.28
126.93
124.66
122.24
121.28
111.73
77.48
77.16
76.84
56.29
55.80
O
N
N
O
OCH3
3ak
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

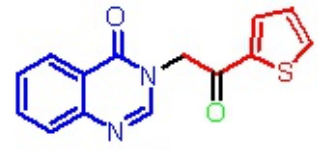

8.307
8.305
8.303
8.301
8.287
8.285
8.283
8.281
7.979
7.901
7.897
7.881
7.878
7.800
7.796
7.783
7.779
7.775
7.763
7.759
7.757
7.754
7.752
7.738
7.736
7.733
7.732
7.529
7.525
7.513
7.509
7.505
7.493
7.488
7.485
7.469
7.466
7.450
7.447
7.368
7.364
7.349
7.345
7.330
7.327
7.319
7.317
7.315
7.300
7.298
7.296
7.260
5.304
2.531
O
N
N
O
CH3
3aI
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.03
2.18
2.22
2.06
2.00
3.08
f1 (ppm)


194.57
161.18
148.38
146.81
139.90
134.60
134.42
132.88
132.62
128.87
127.74
127.51
126.92
126.16
122.08
77.48
77.16
76.84
53.29
21.65
O
N
N
O
CH3
3al
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.591
8.588
8.585
8.310
8.306
8.291
8.288
8.285
8.052
8.048
8.031
8.025
7.999
7.978
7.939
7.917
7.901
7.880
7.800
7.796
7.784
7.779
7.775
7.763
7.760
7.757
7.743
7.665
7.662
7.648
7.645
7.641
7.628
7.624
7.606
7.603
7.589
7.586
7.582
7.569
7.565
7.522
7.516
7.506
7.501
7.496
7.486
7.481
7.260
5.563
3am
1H NMR (400 MHz, CDCl3)
1.00
1.04
2.09
1.13
1.07
1.03
2.15
1.08
1.03
1.05
2.07
f1 (ppm)

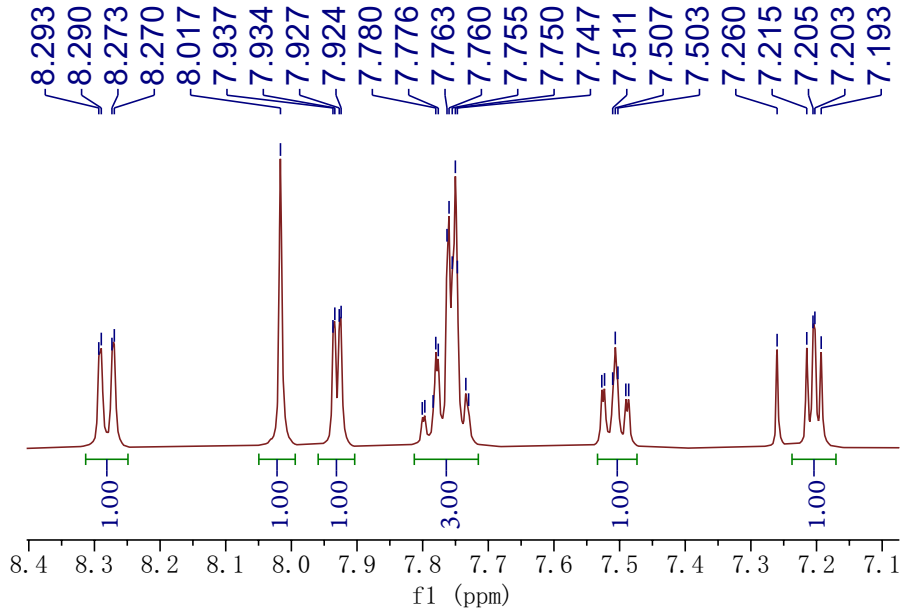

191.71
161.20
148.39
146.80
136.21
134.61
132.52
131.86
130.33
129.83
129.28
129.14
128.05
127.77
127.51
127.32
126.96
123.56
122.09
77.48
77.16
76.84
51.46
O
N
N
O
3am
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

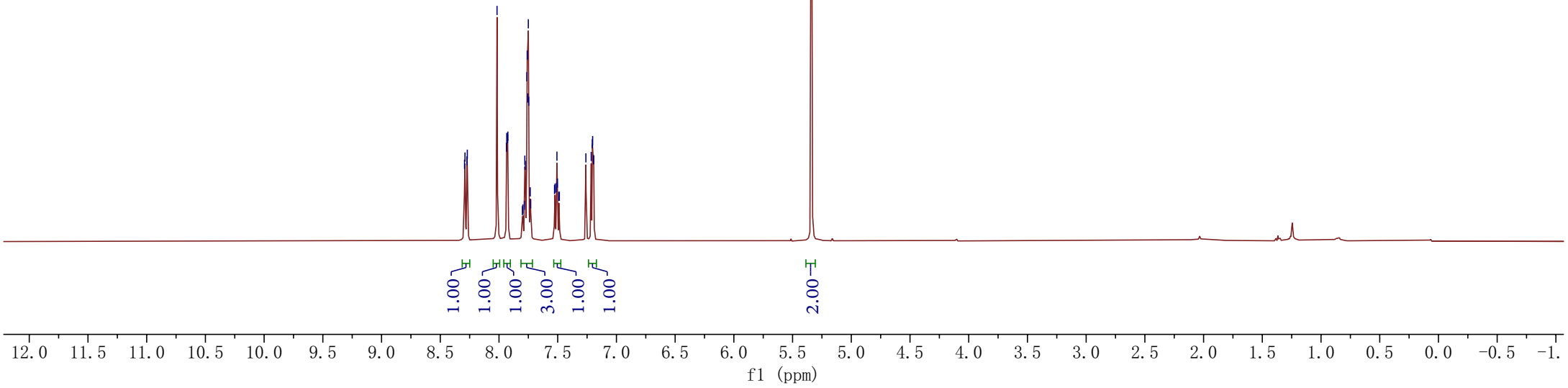


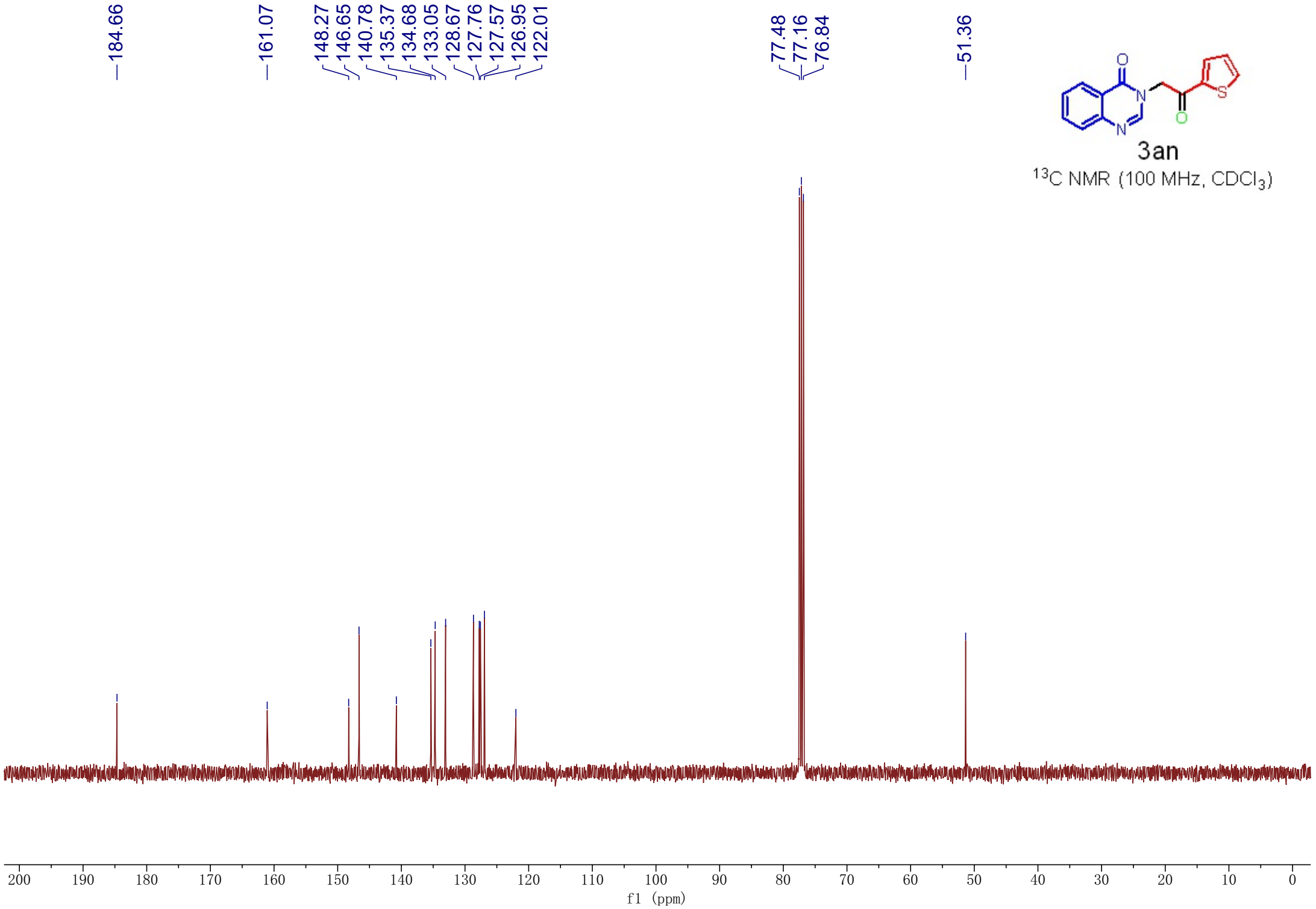


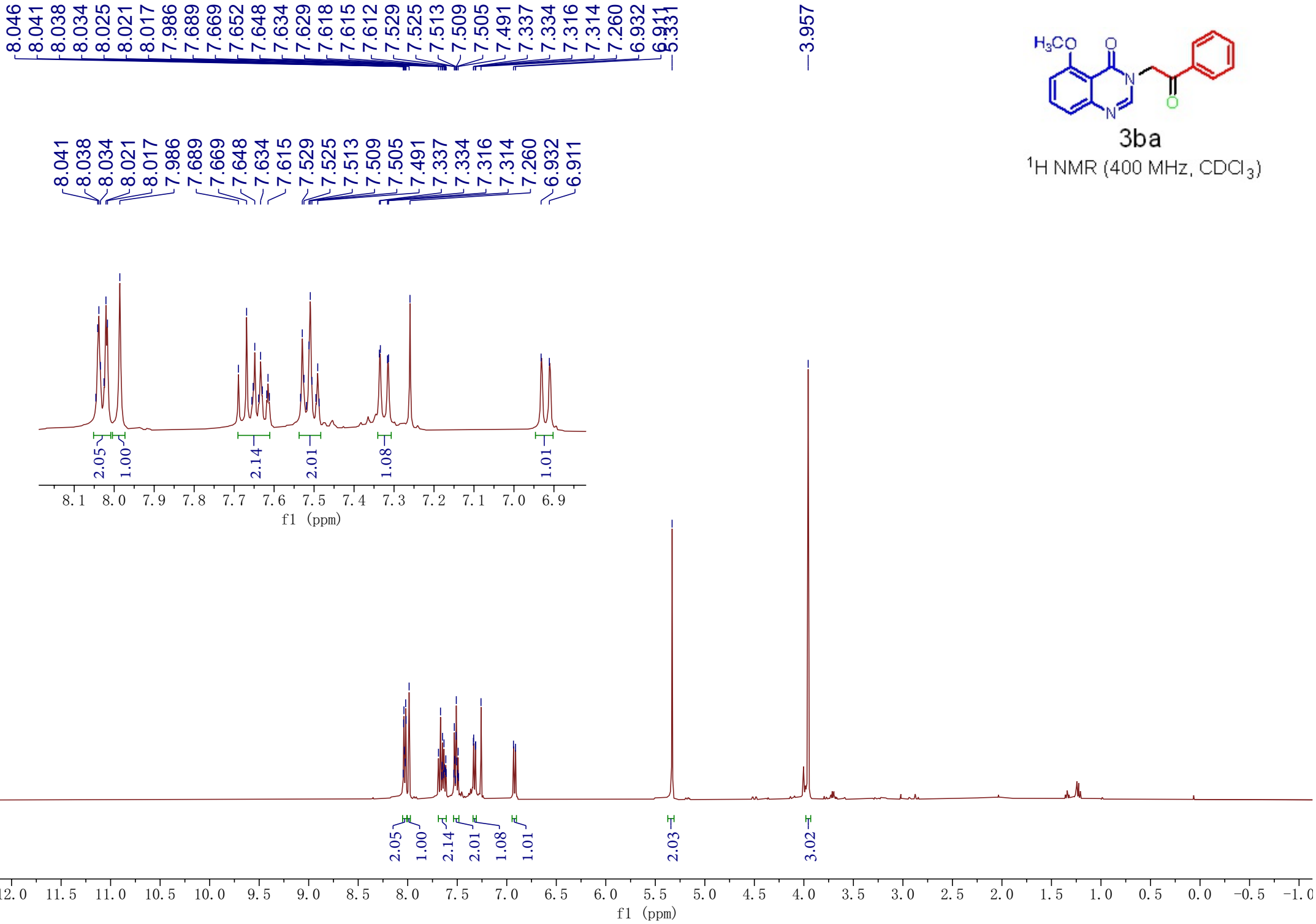
3an

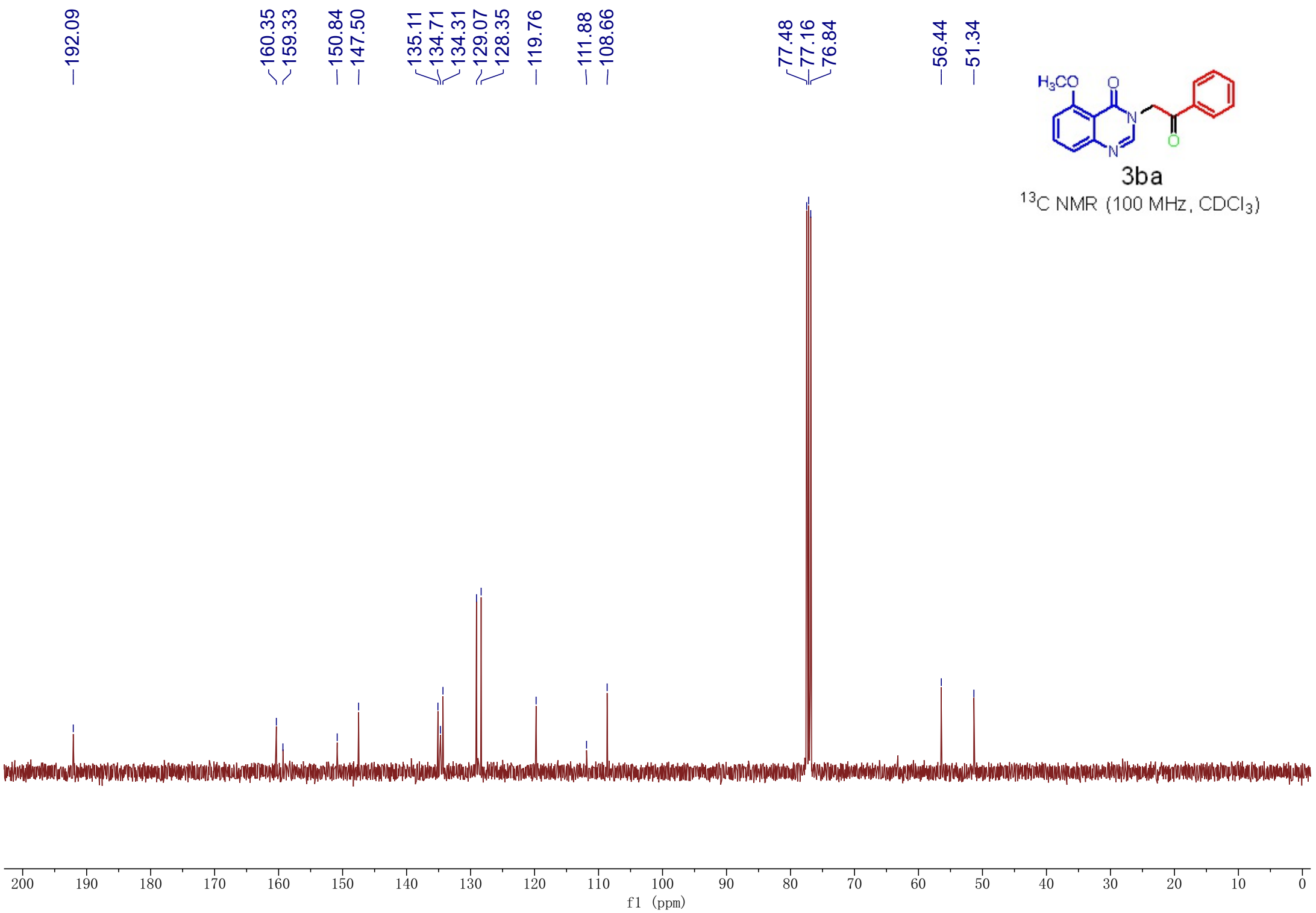
^{1}H NMR (400 MHz, $CDCl_3$)

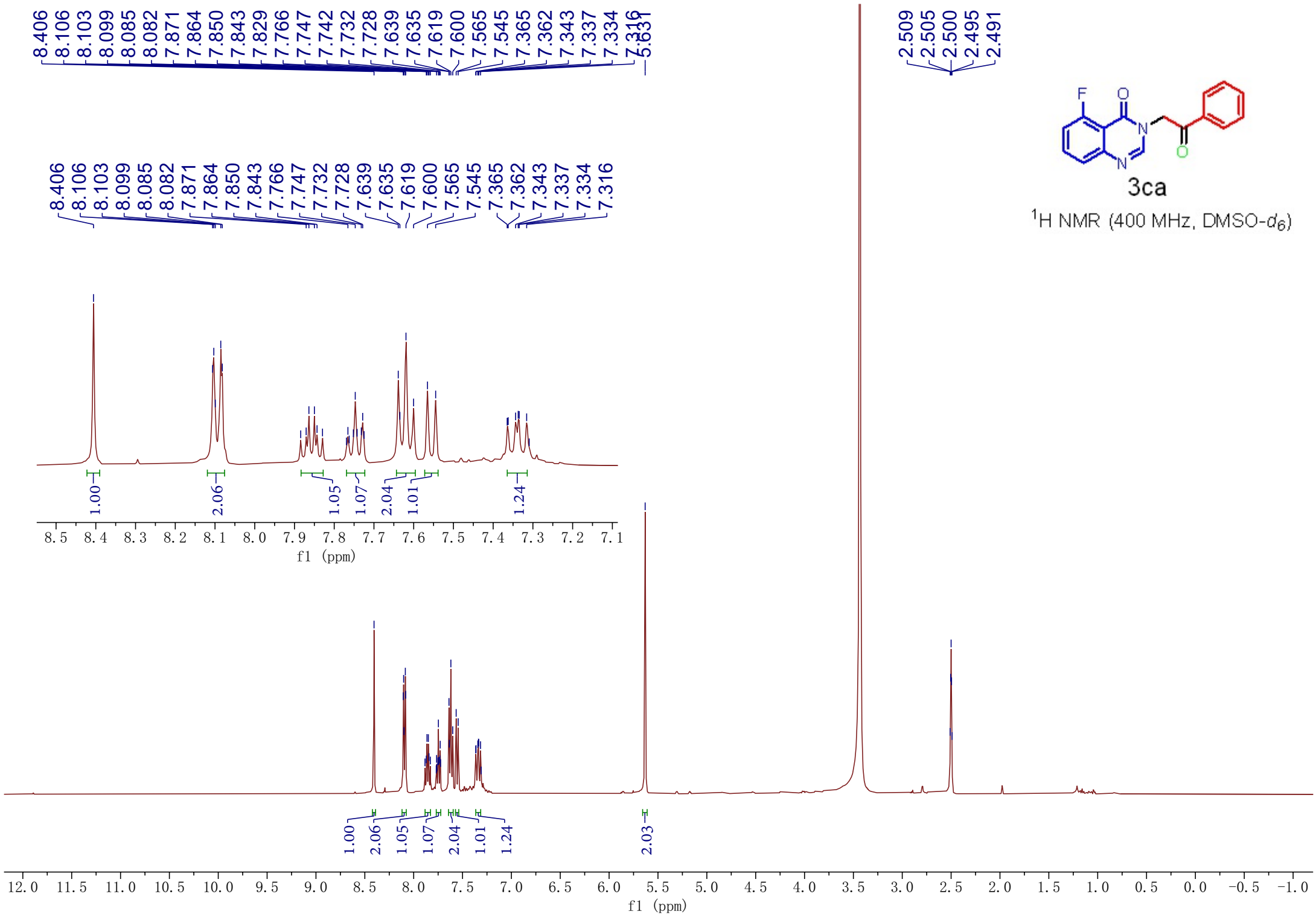


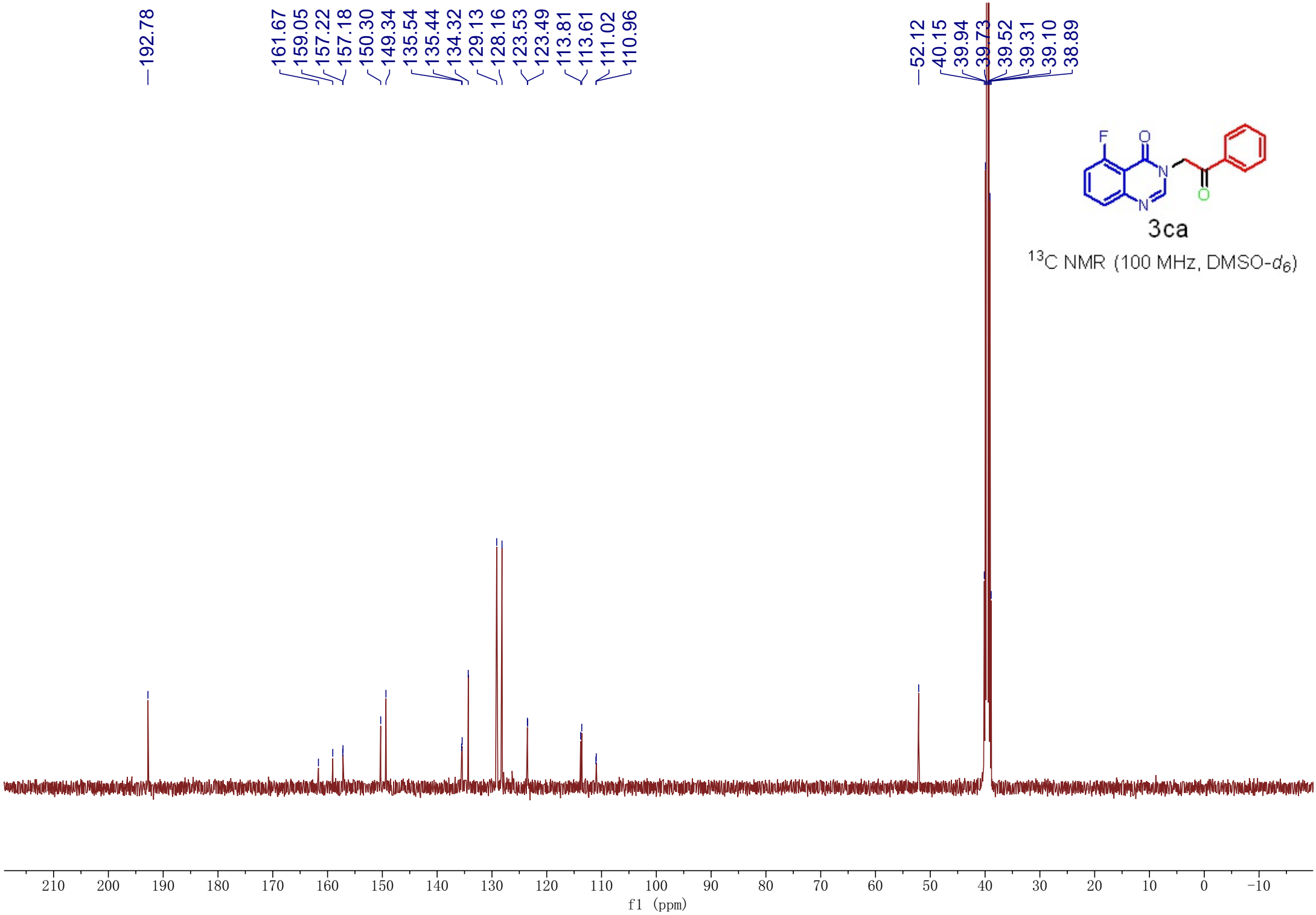


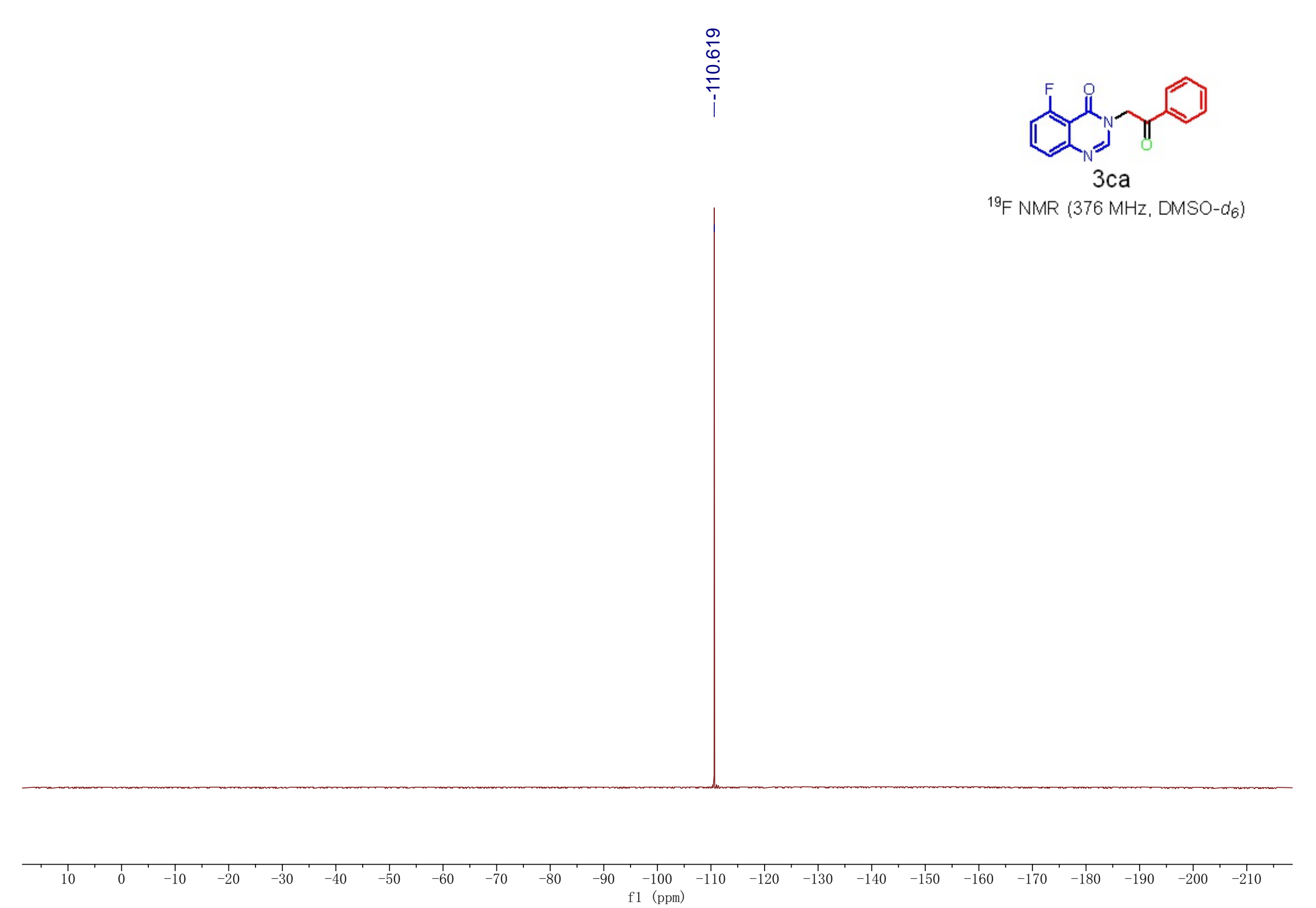

184.66
161.07
148.27
146.65
140.78
135.37
134.68
133.05
128.67
127.76
127.57
126.95
122.01
77.48
77.16
76.84
51.36
O
N
N
S
O
3an
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

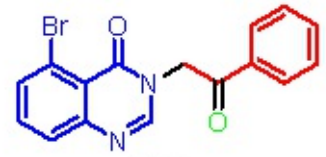

8.046
8.041
8.038
8.034
8.025
8.021
8.017
7.986
7.689
7.669
7.652
7.648
7.634
7.629
7.618
7.615
7.612
7.529
7.525
7.513
7.509
7.505
7.491
7.337
7.334
7.316
7.314
7.260
6.932
6.911
5.331
3.957
H3CO
O
N
N
O
3ba
1H NMR (400 MHz, CDCl3)
2.05
1.00
2.14
2.01
1.08
1.01
f1 (ppm)
2.03
3.02


192.09
160.35
159.33
150.84
147.50
135.11
134.71
134.31
129.07
128.35
119.76
111.88
108.66
77.48
77.16
76.84
56.44
51.34
H3CO
O
N
N
O
3ba
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.406
8.106
8.103
8.099
8.085
8.082
7.871
7.864
7.850
7.843
7.829
7.766
7.747
7.742
7.732
7.728
7.639
7.635
7.619
7.600
7.565
7.545
7.365
7.362
7.343
7.337
7.334
7.316
5.631
2.509
2.505
2.500
2.495
2.491
F
O
N
N
O
3ca
1H NMR (400 MHz, DMSO-d6)
1.00
2.06
1.05
1.07
2.04
1.01
1.24
2.03
f1 (ppm)

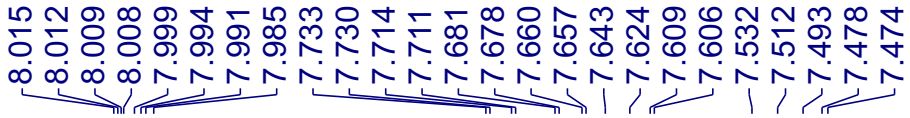

192.78
161.67
159.05
157.22
157.18
150.30
149.34
135.54
135.44
134.32
129.13
128.16
123.53
123.49
113.81
113.61
111.02
110.96
52.12
40.15
39.94
39.73
39.52
39.31
39.10
38.89
F
O
N
N
O
3ca
13C NMR (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

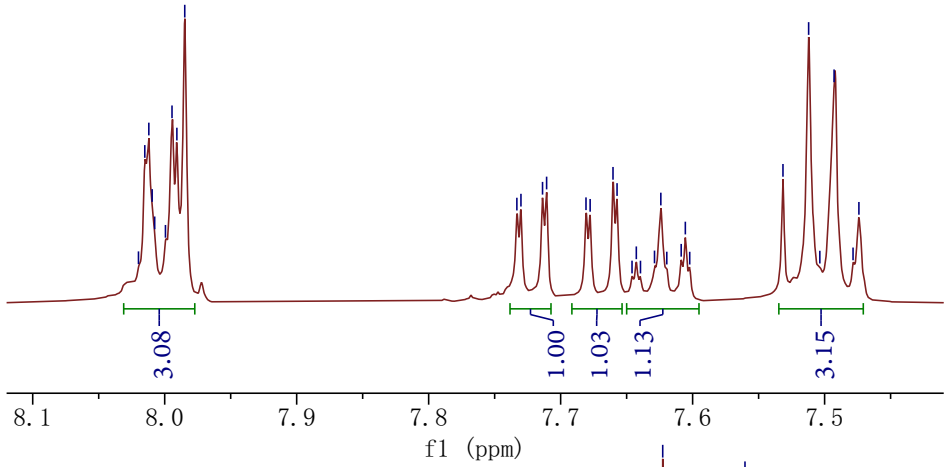

-110.619
F
O
N
N
O
3ca
^{19}F NMR (376 MHz, DMSO-d_6)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

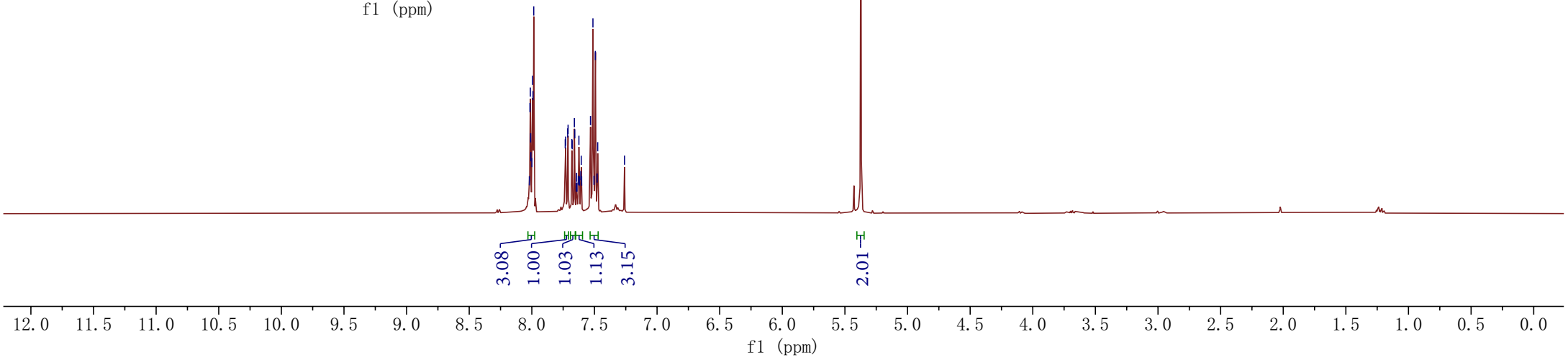


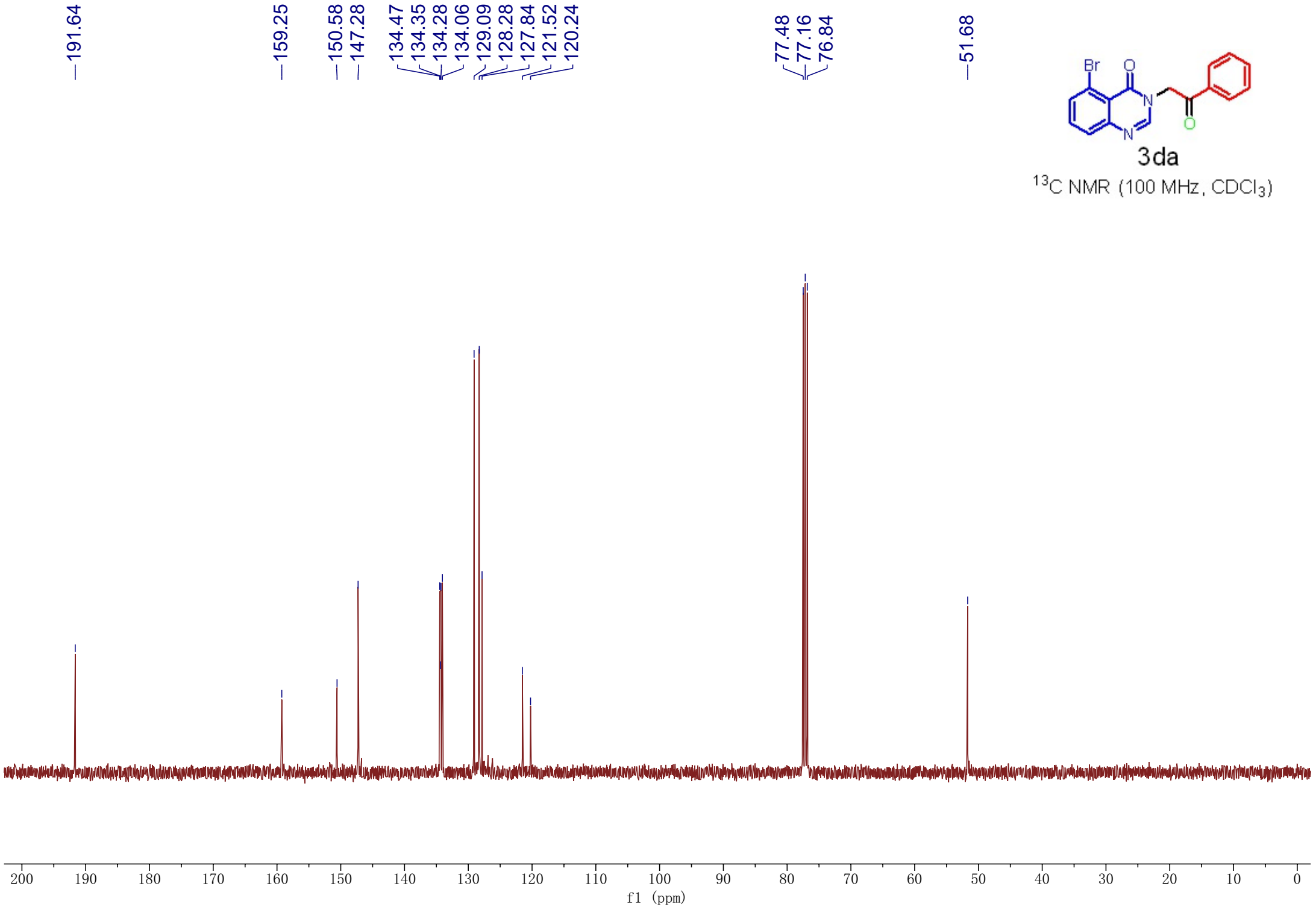
3da

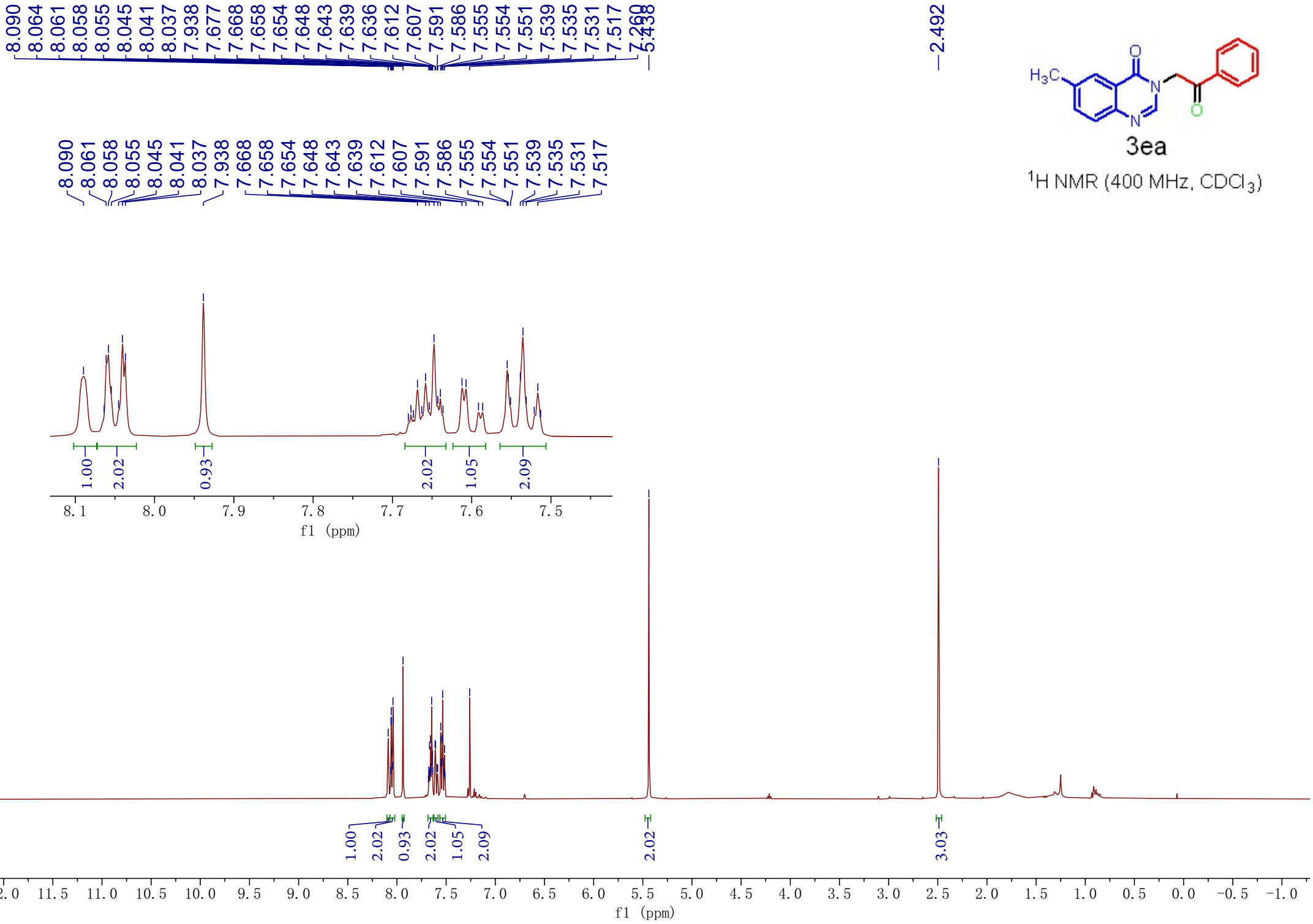
^{1}H NMR (400 MHz, $CDCl_3$)

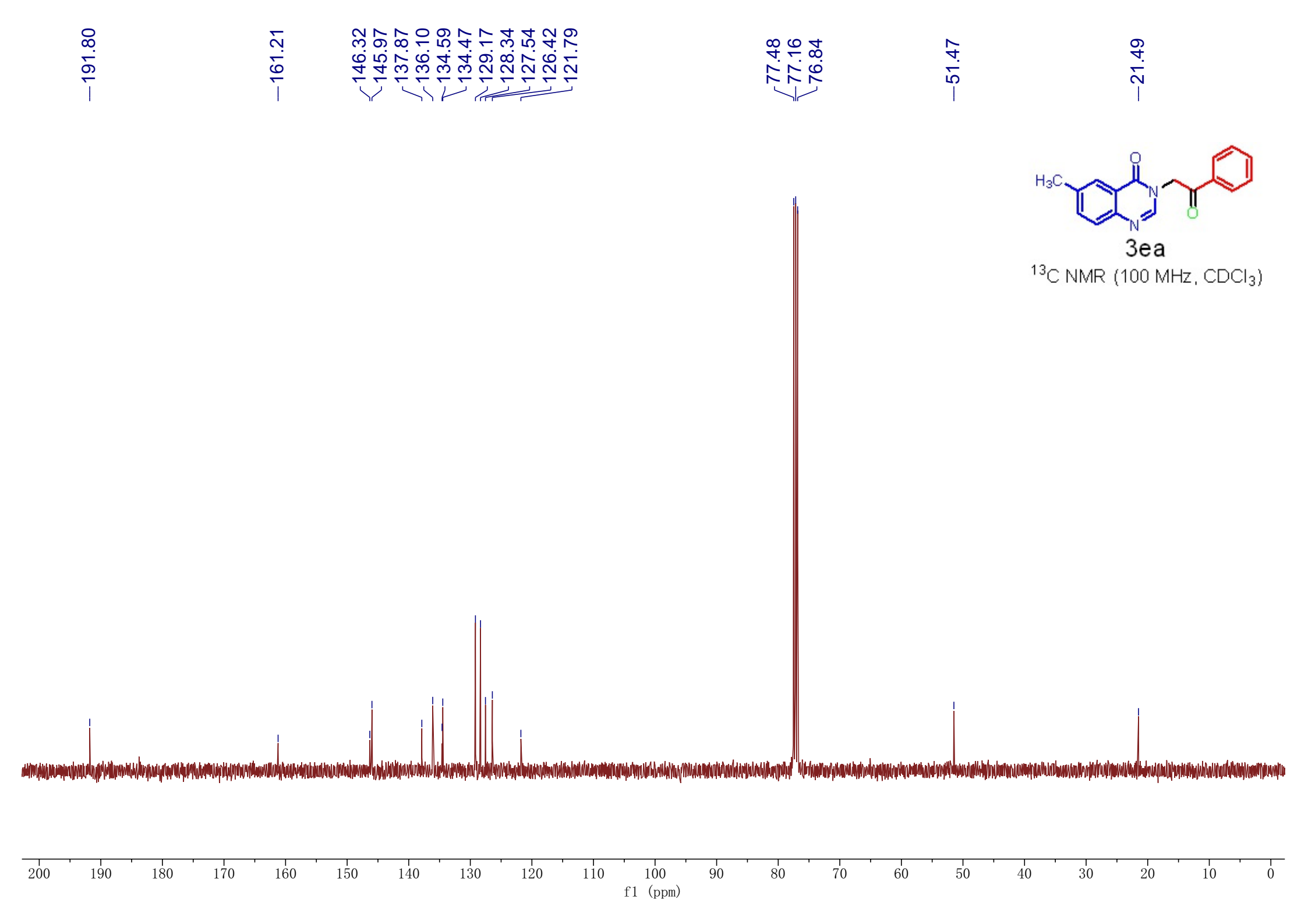


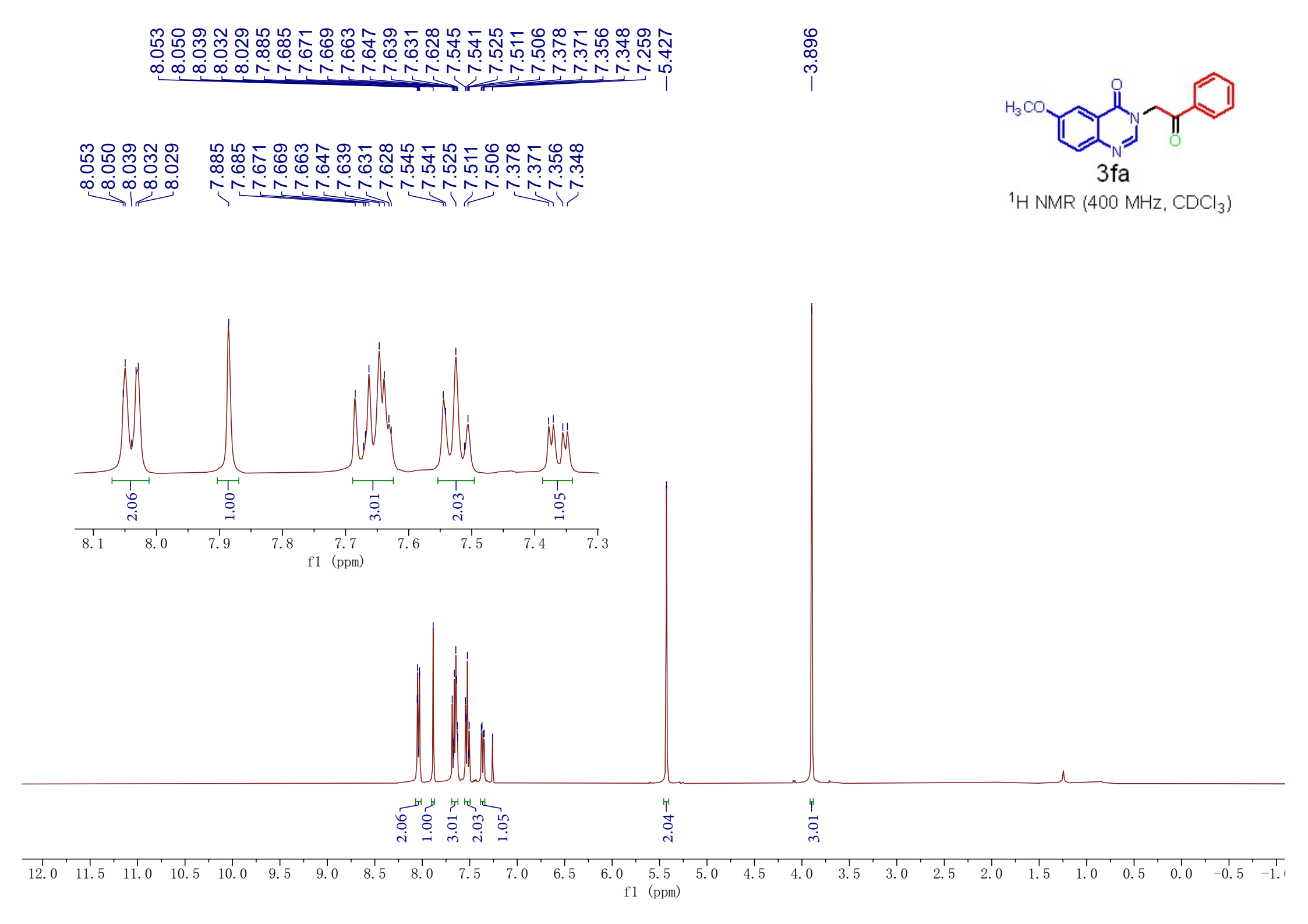


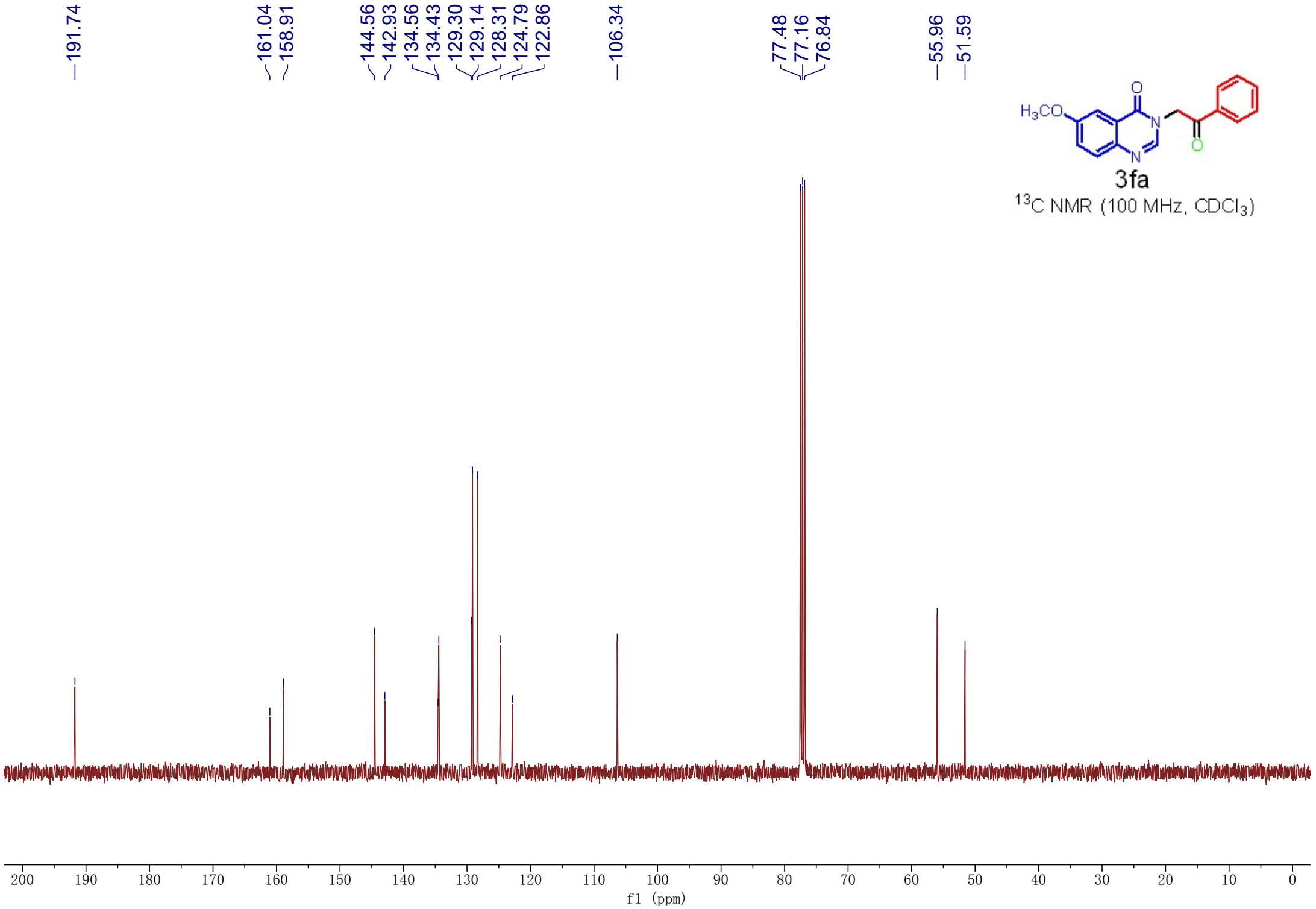


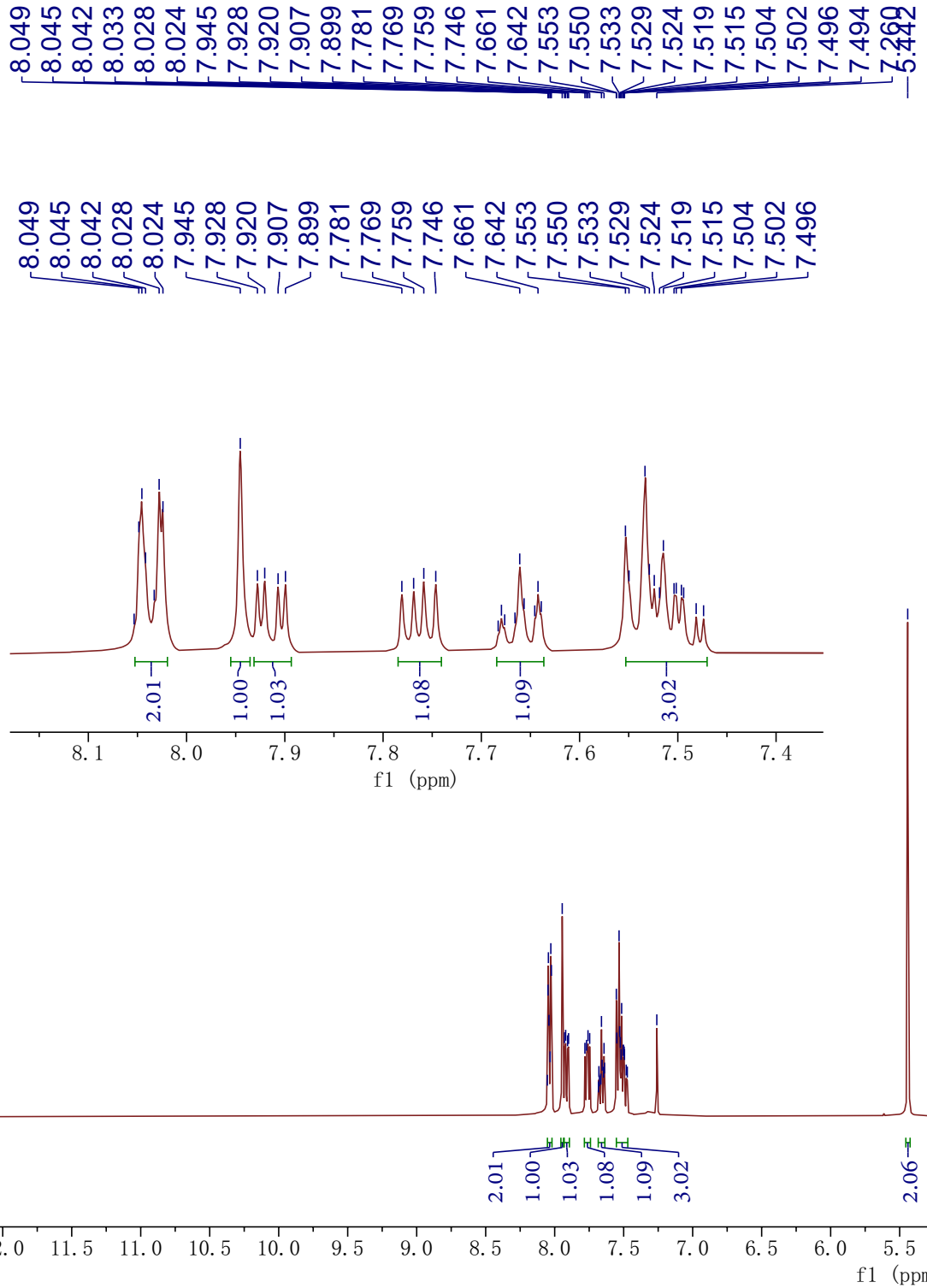

191.64
159.25
150.58
147.28
134.47
134.35
134.28
134.06
129.09
128.28
127.84
121.52
120.24
77.48
77.16
76.84
51.68
Br
O
N
N
O
3da
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

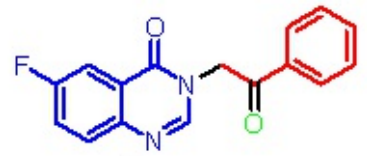

8.090
8.064
8.061
8.058
8.055
8.045
8.041
8.037
7.938
7.677
7.668
7.658
7.654
7.648
7.643
7.639
7.636
7.612
7.607
7.591
7.586
7.555
7.554
7.551
7.539
7.535
7.531
7.517
7.260
5.438
2.492
3ea
1H NMR (400 MHz, CDCl3)
1.00
2.02
0.93
2.02
1.05
2.09
2.02
3.03
f1 (ppm)


191.80
161.21
146.32
145.97
137.87
136.10
134.59
134.47
129.17
128.34
127.54
126.42
121.79
77.48
77.16
76.84
51.47
21.49
H3C
O
N
N
O
3ea
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.053
8.050
8.039
8.032
8.029
7.885
7.685
7.671
7.669
7.663
7.647
7.639
7.631
7.628
7.545
7.541
7.525
7.511
7.506
7.378
7.371
7.356
7.348
7.259
5.427
3.896
H3CO
O
N
N
O
3fa
1H NMR (400 MHz, CDCl3)
2.06
1.00
3.01
2.03
1.05
2.04
3.01
f1 (ppm)

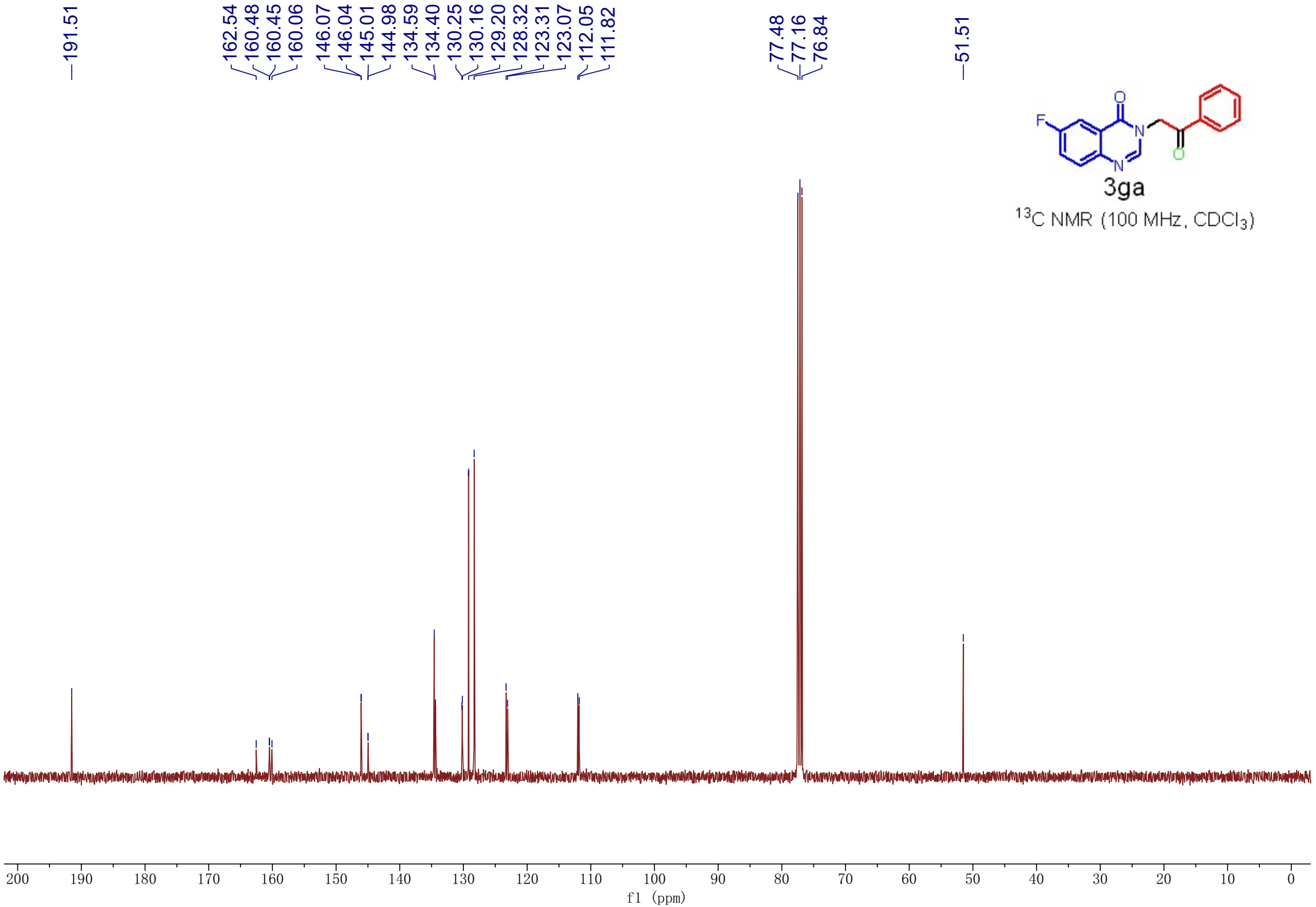

191.74
161.04
158.91
144.56
142.93
134.56
134.43
129.30
129.14
128.31
124.79
122.86
106.34
77.48
77.16
76.84
55.96
51.59
H3CO
O
N
N
O
3fa
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

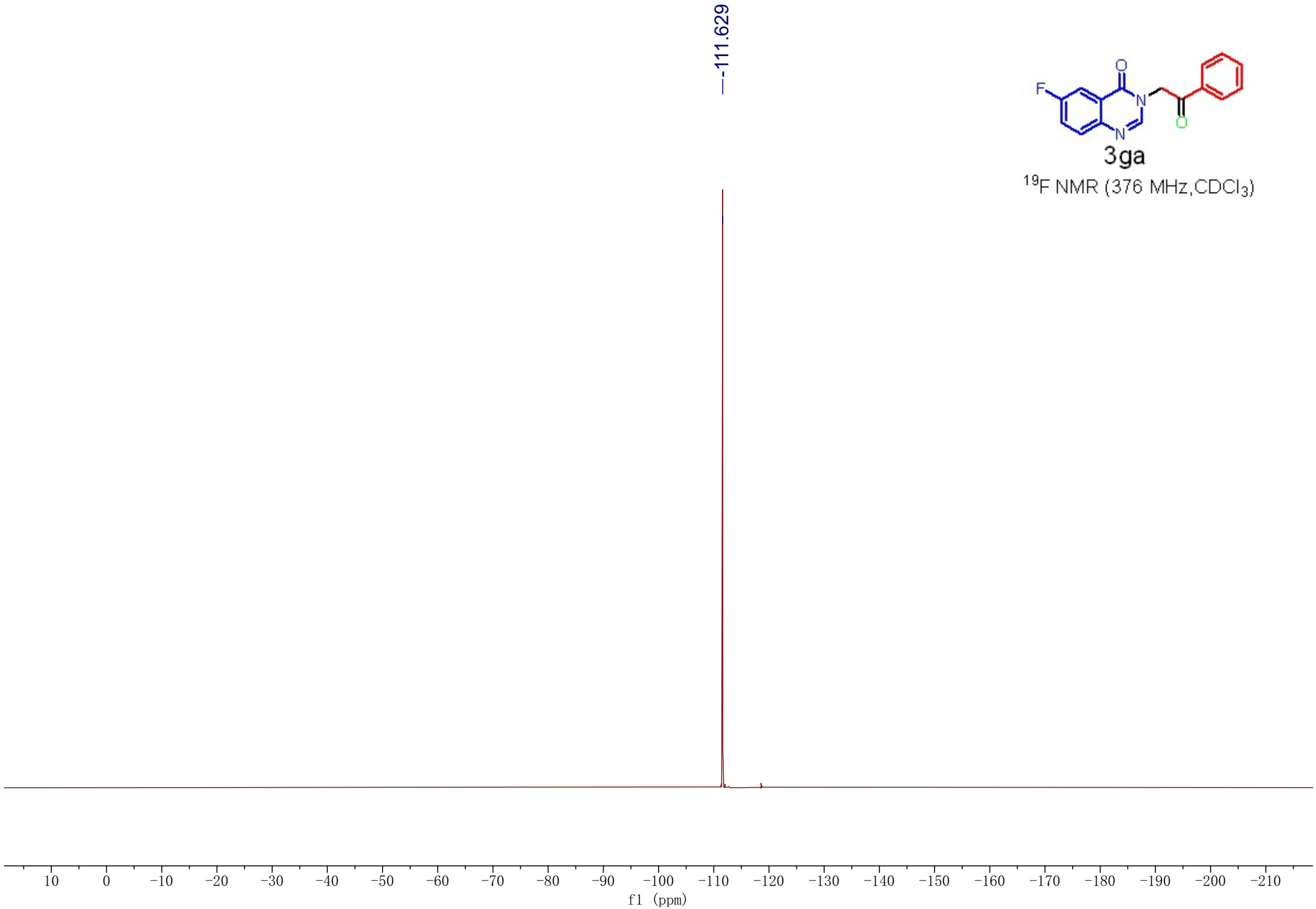


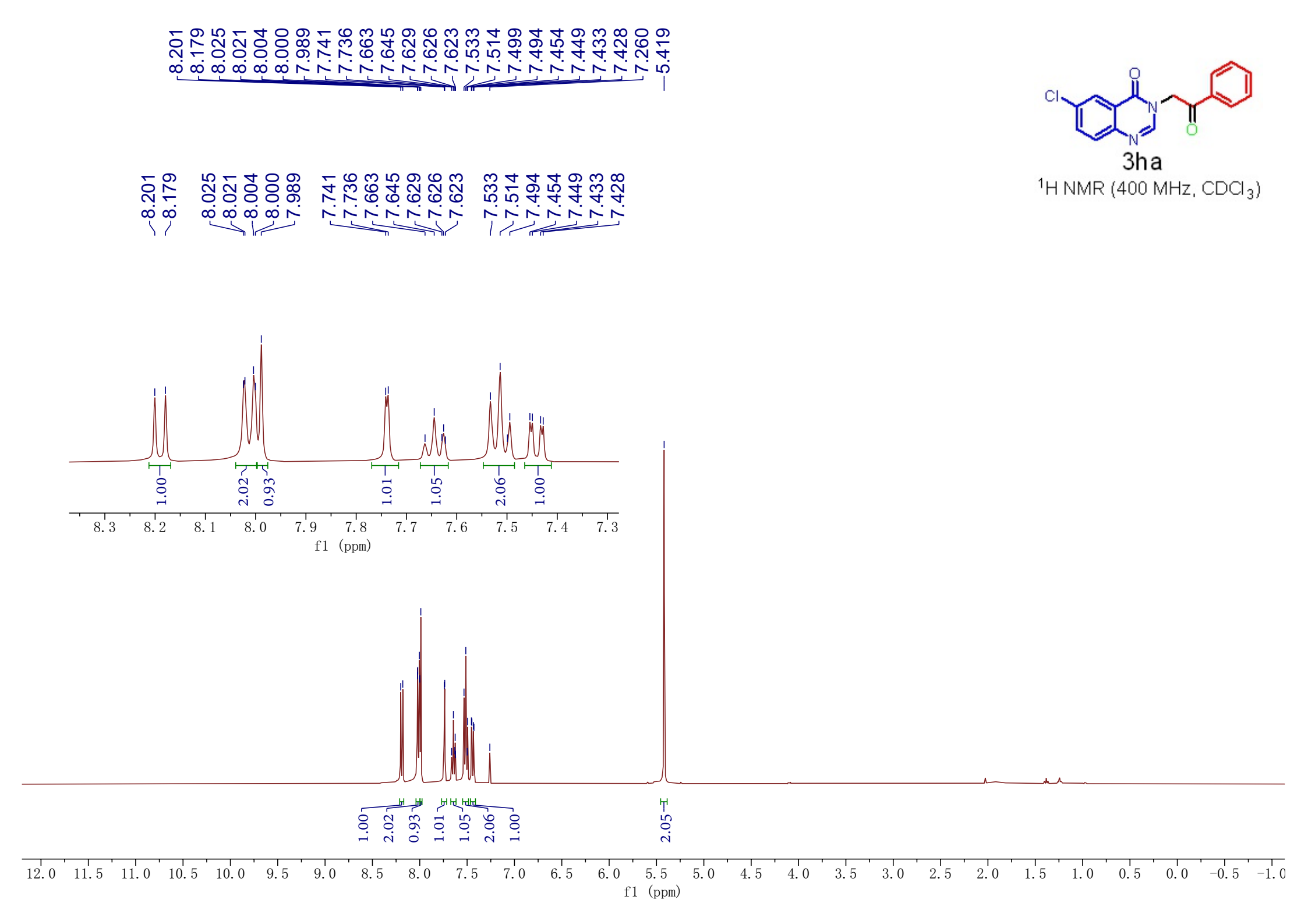


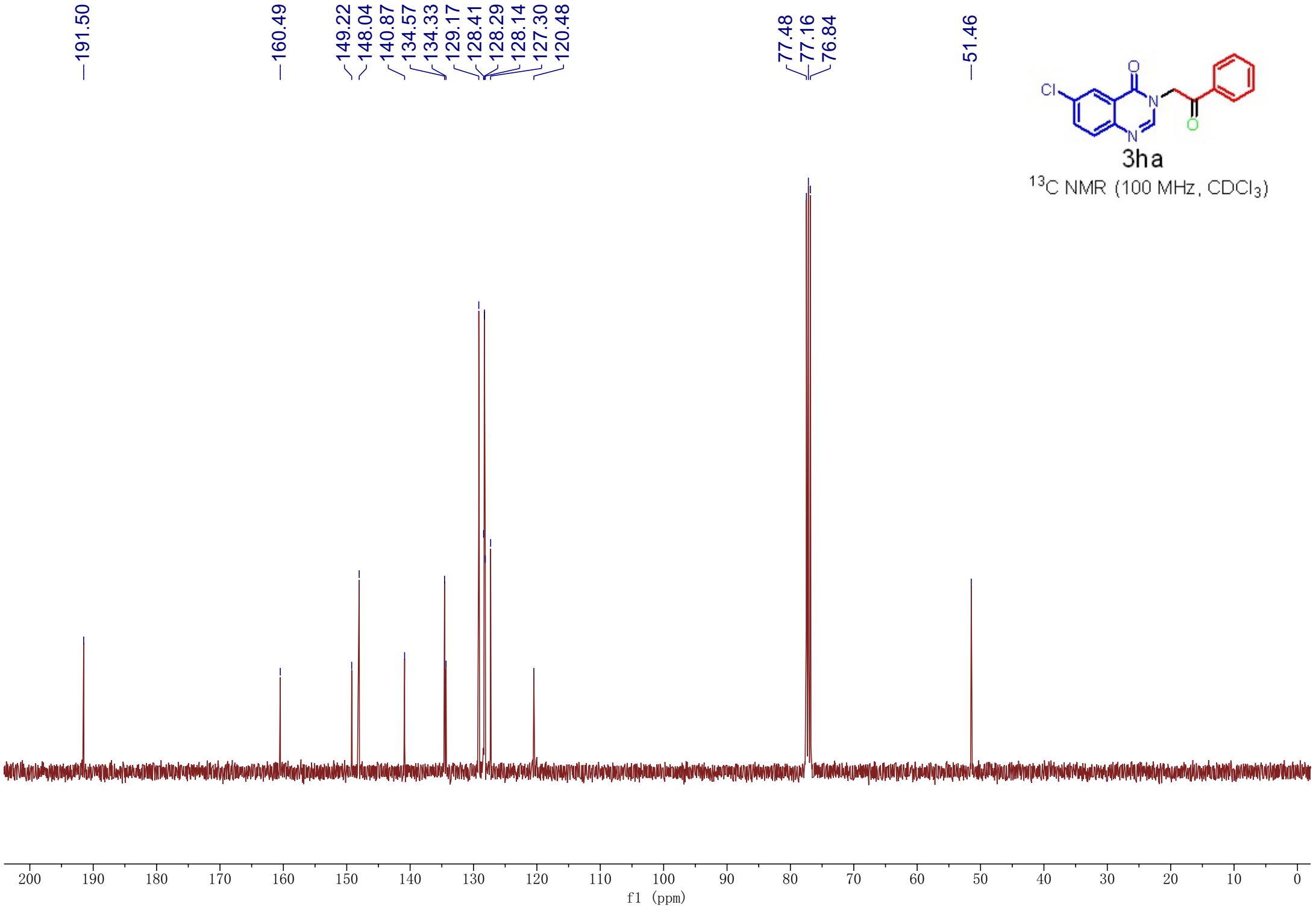
3ga

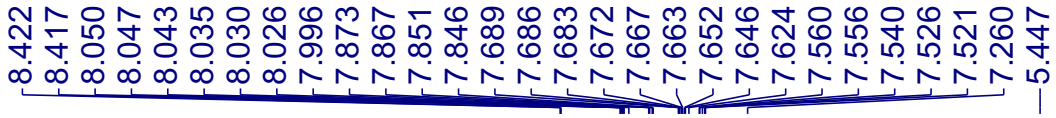
^{1}H NMR (400 MHz, $CDCl_3$)

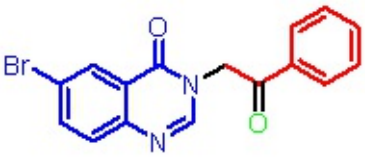

191.51
162.54
160.48
160.45
160.06
146.07
146.04
145.01
144.98
134.59
134.40
130.25
130.16
129.20
128.32
123.31
123.07
112.05
111.82
77.48
77.16
76.84
51.51
F
O
N
N
O
3ga
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-111.629
F
O
N
N
O
3ga
^{19}F NMR (376 MHz,$CDCl_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.201
8.179
8.025
8.021
8.004
8.000
7.989
7.741
7.736
7.663
7.645
7.629
7.626
7.623
7.533
7.514
7.499
7.494
7.454
7.449
7.433
7.428
7.260
5.419
Cl
O
N
N
O
3ha
1H NMR (400 MHz, CDCl3)
1.00
2.02
0.93
1.01
1.05
2.06
1.00
2.05
f1 (ppm)

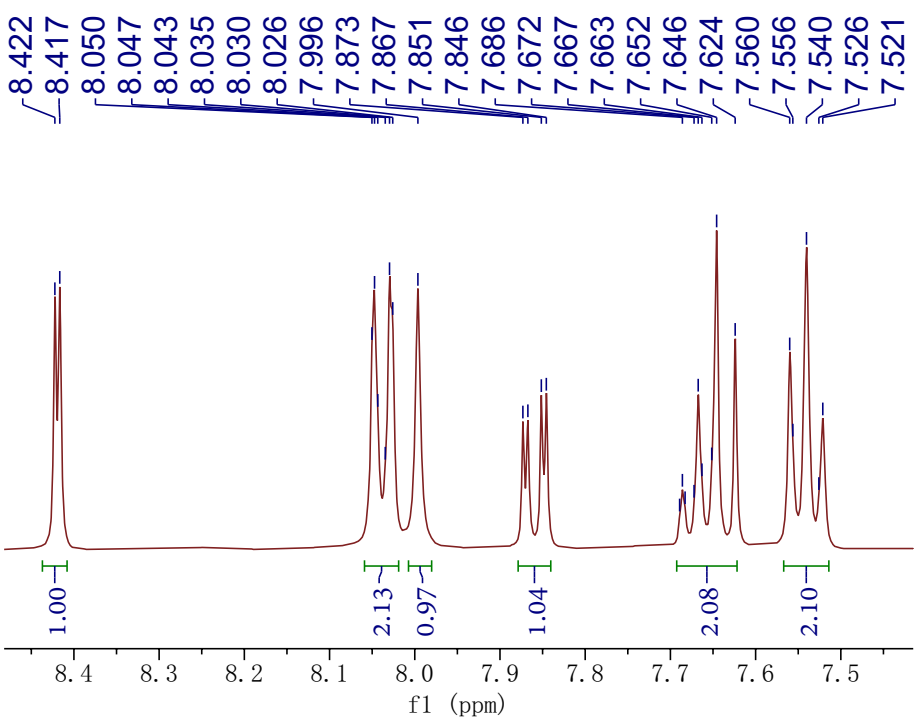

191.50
160.49
149.22
148.04
140.87
134.57
134.33
129.17
128.41
128.29
128.14
127.30
120.48
77.48
77.16
76.84
51.46
Cl
O
N
N
O
3ha
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

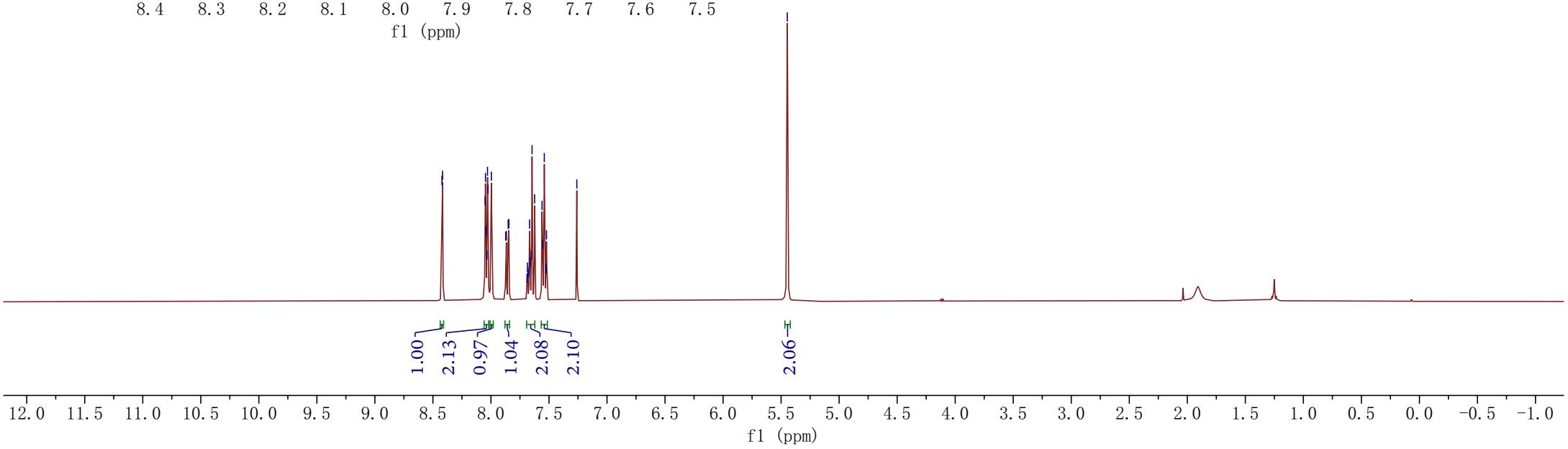


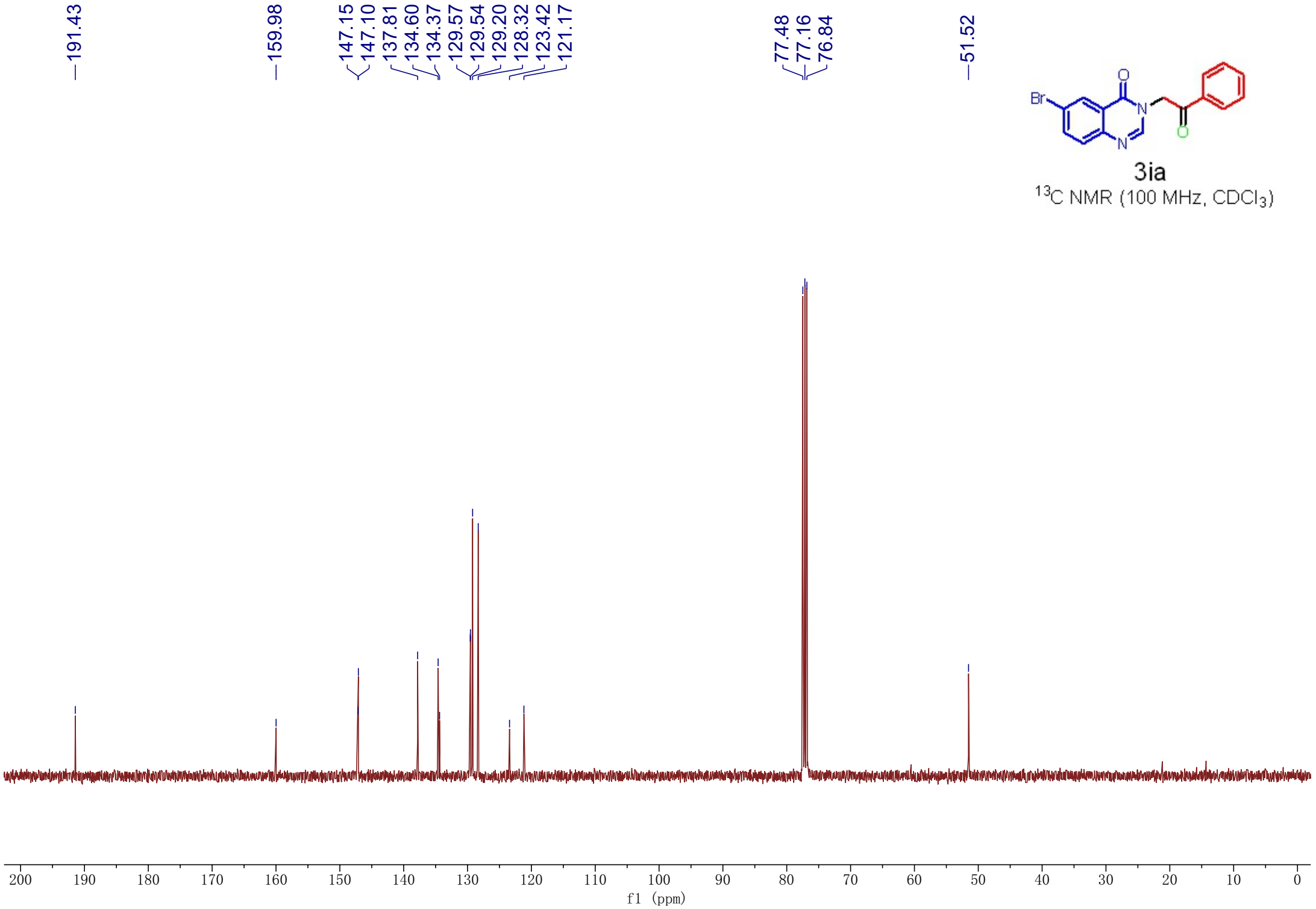


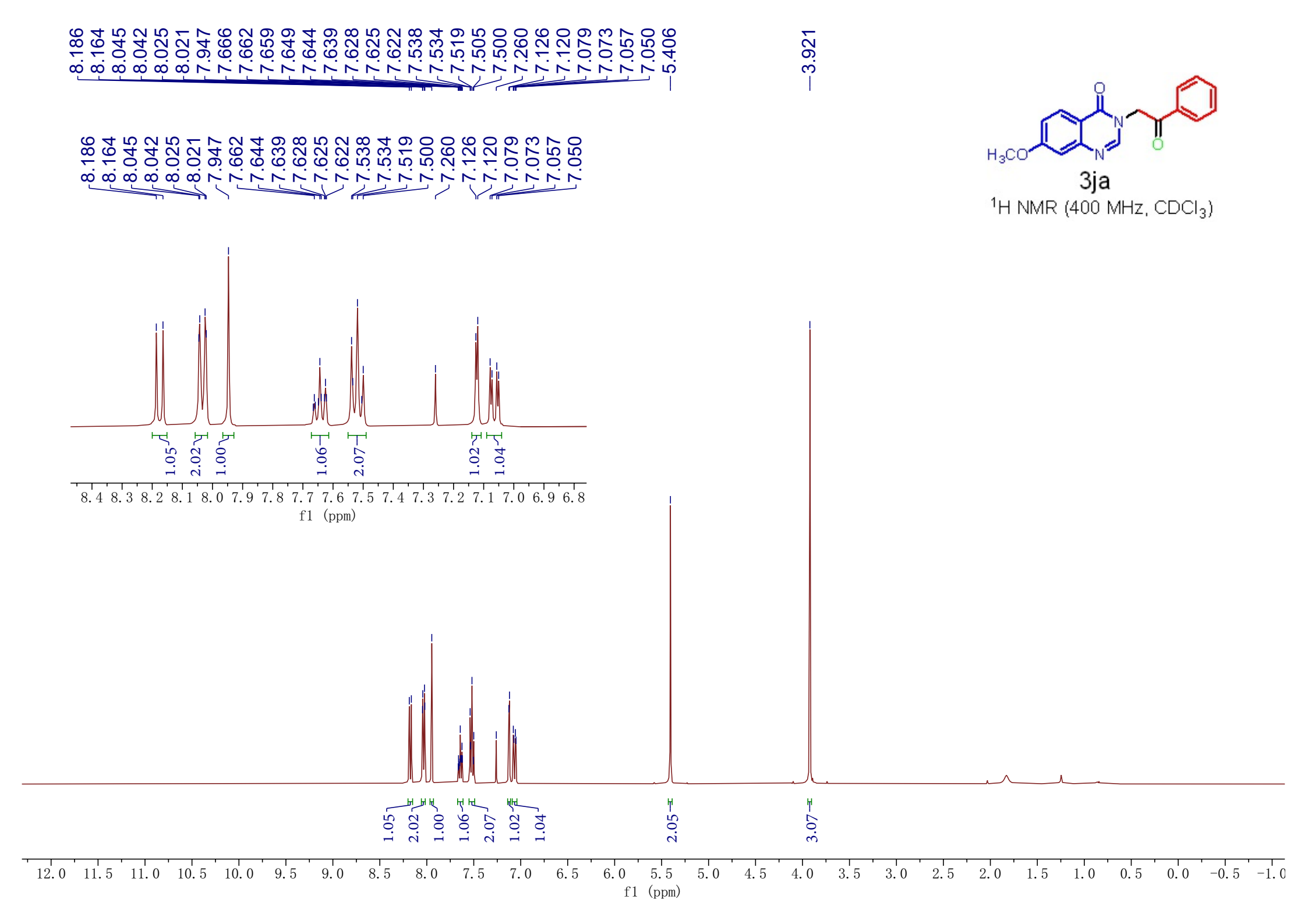
3ia

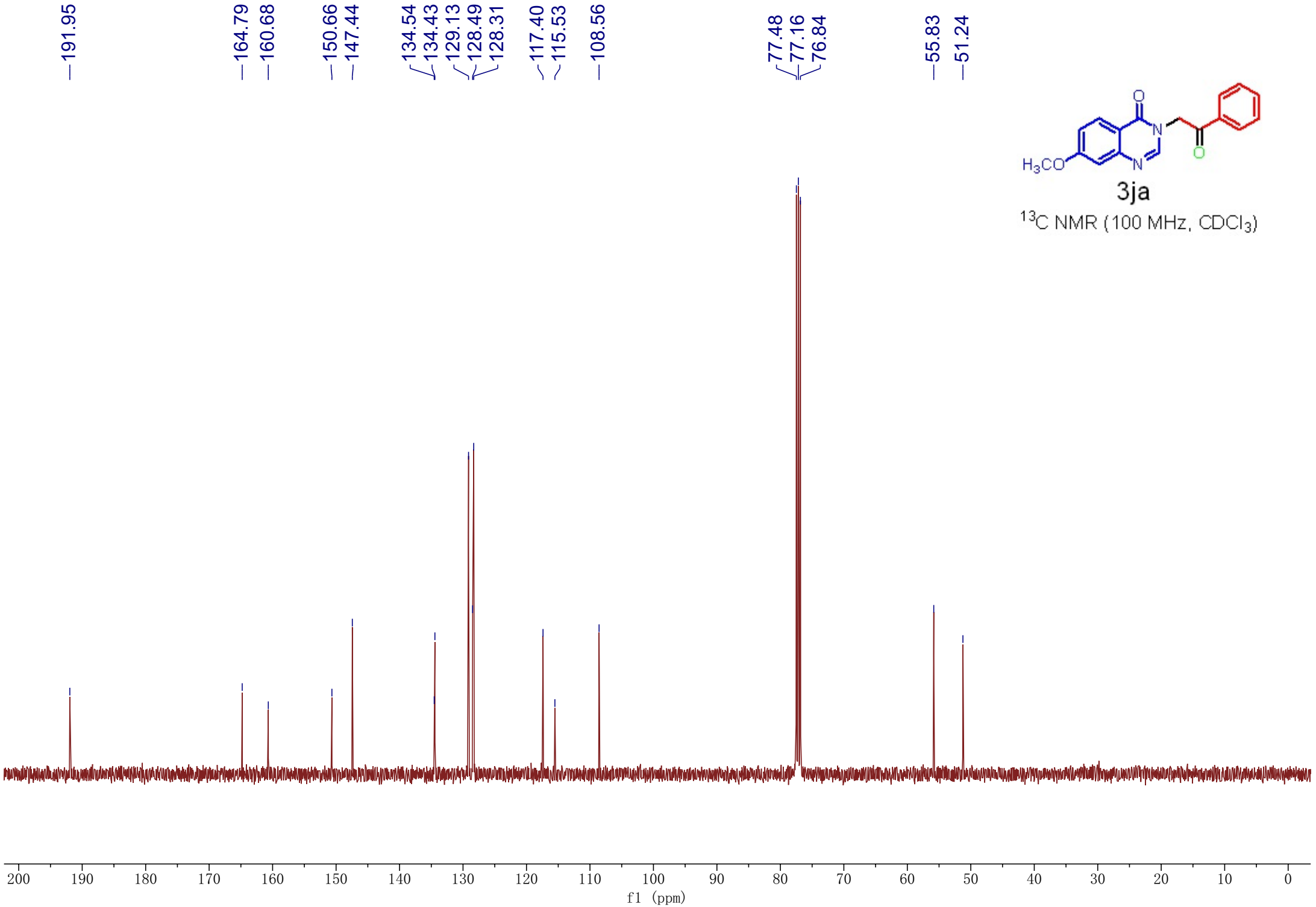
^{1}H NMR (400 MHz, $CDCl_3$)

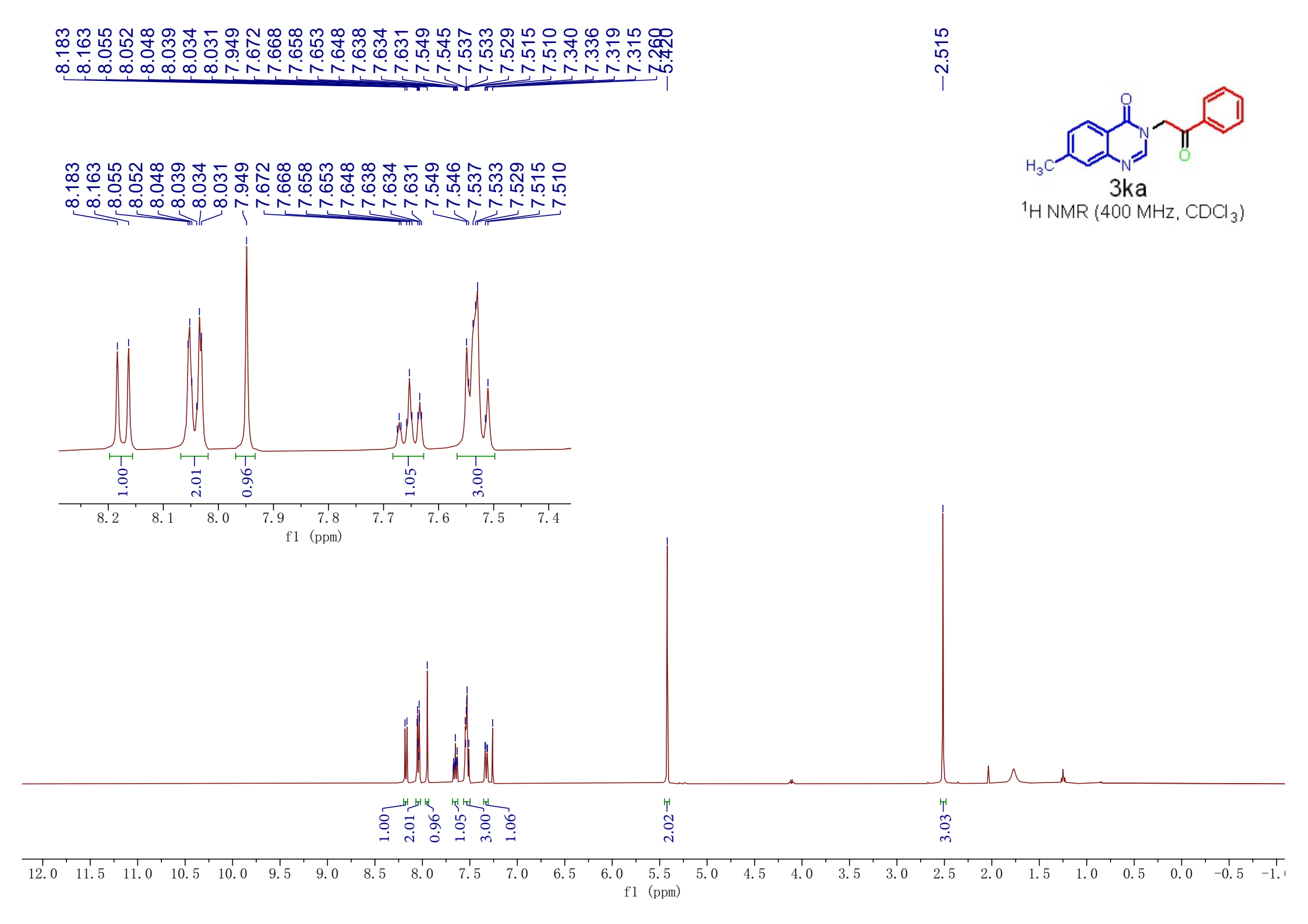


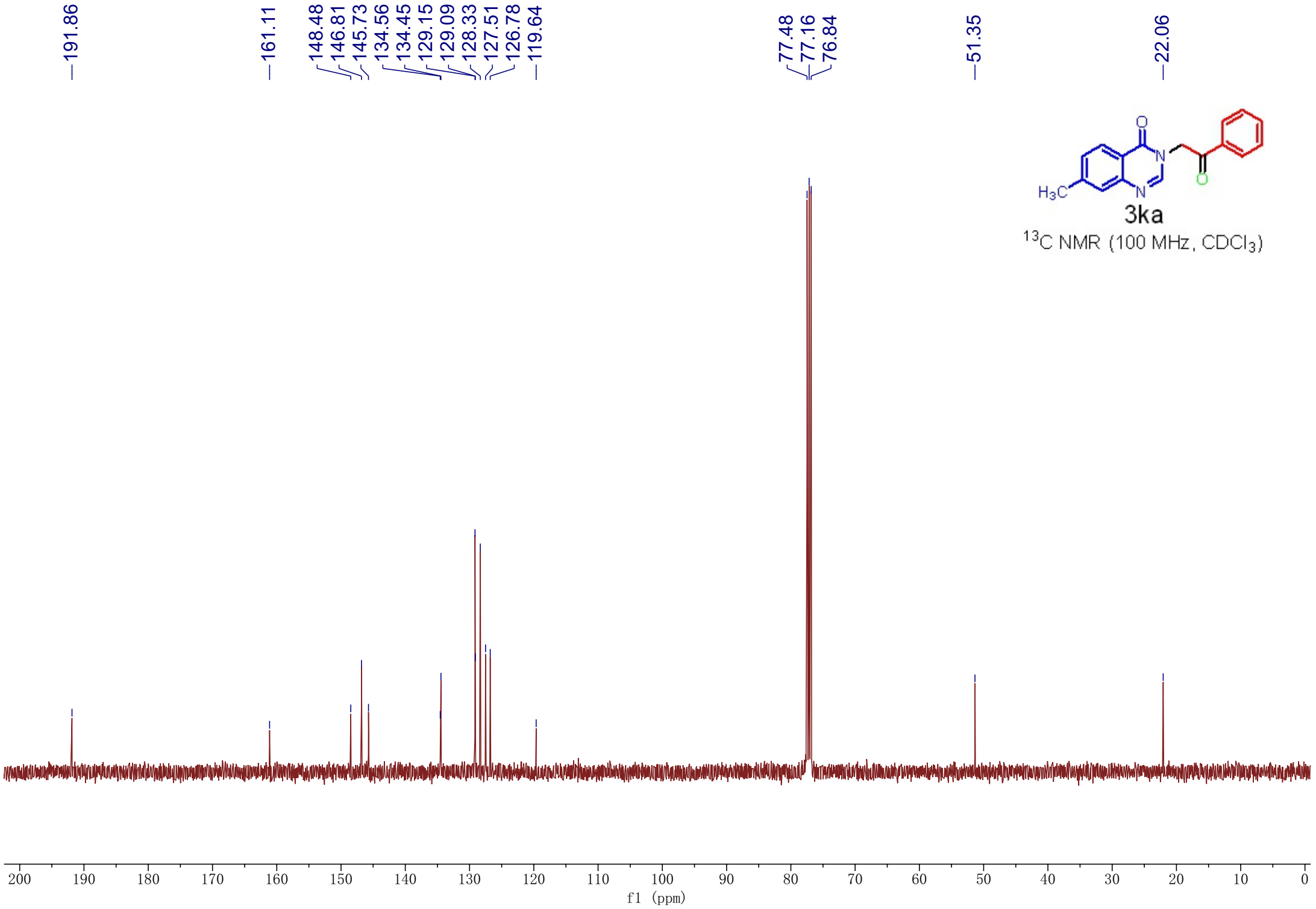


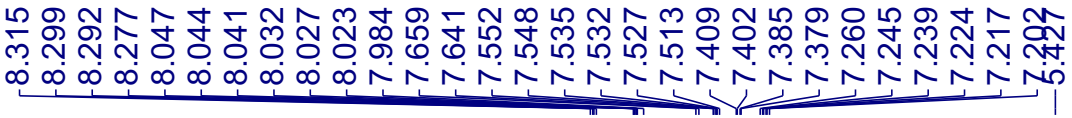

191.43
159.98
147.15
147.10
137.81
134.60
134.37
129.57
129.54
129.20
128.32
123.42
121.17
77.48
77.16
76.84
51.52
Br
O
N
N
O
3ia
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

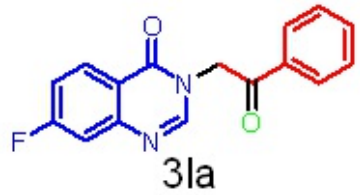

8.186
8.164
8.045
8.042
8.025
8.021
7.947
7.666
7.662
7.659
7.649
7.644
7.639
7.628
7.625
7.622
7.538
7.534
7.519
7.505
7.500
7.260
7.126
7.120
7.079
7.073
7.057
7.050
5.406
3.921
O
N
N
O
H3CO
3ja
1H NMR (400 MHz, CDCl3)
1.05
2.02
1.00
1.06
2.07
1.02
1.04
2.05
3.07
f1 (ppm)


191.95
164.79
160.68
150.66
147.44
134.54
134.43
129.13
128.49
128.31
117.40
115.53
108.56
77.48
77.16
76.84
55.83
51.24
H3CO
O
N
N
O
3ja
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.183
8.163
8.055
8.052
8.048
8.039
8.034
8.031
7.949
7.672
7.668
7.658
7.653
7.648
7.638
7.634
7.631
7.549
7.545
7.537
7.533
7.529
7.515
7.510
7.340
7.336
7.319
7.315
7.260
5.420
2.515
3ka
1H NMR (400 MHz, CDCl3)
1.00
2.01
0.96
1.05
3.00
1.06
2.02
3.03
f1 (ppm)

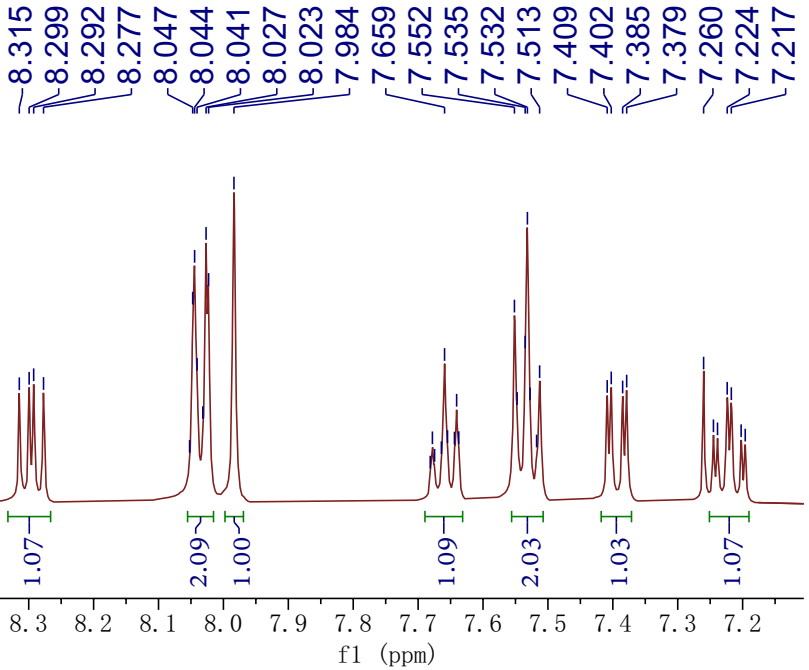

191.86
161.11
148.48
146.81
145.73
134.56
134.45
129.15
129.09
128.33
127.51
126.78
119.64
77.48
77.16
76.84
51.35
22.06
O
N
N
O
H3C
3ka
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

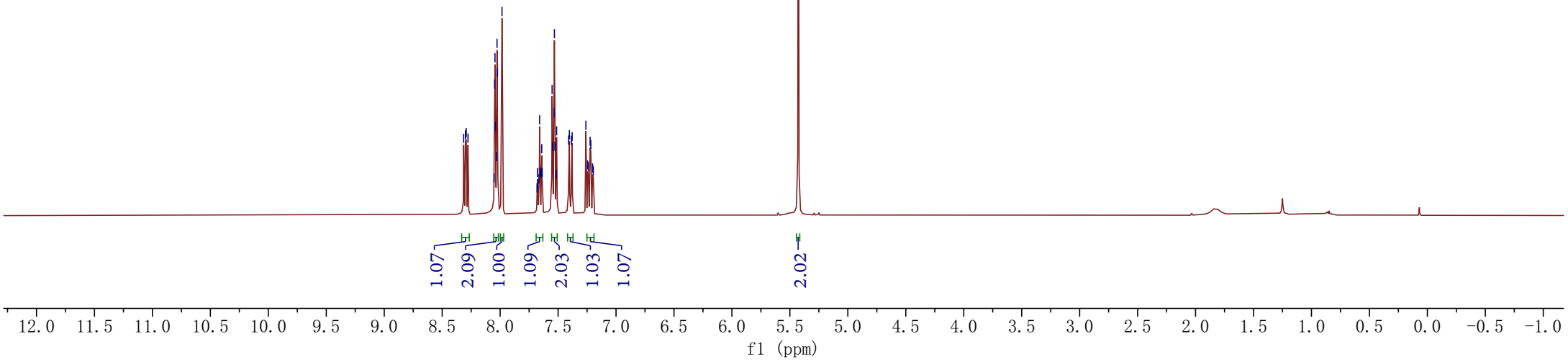


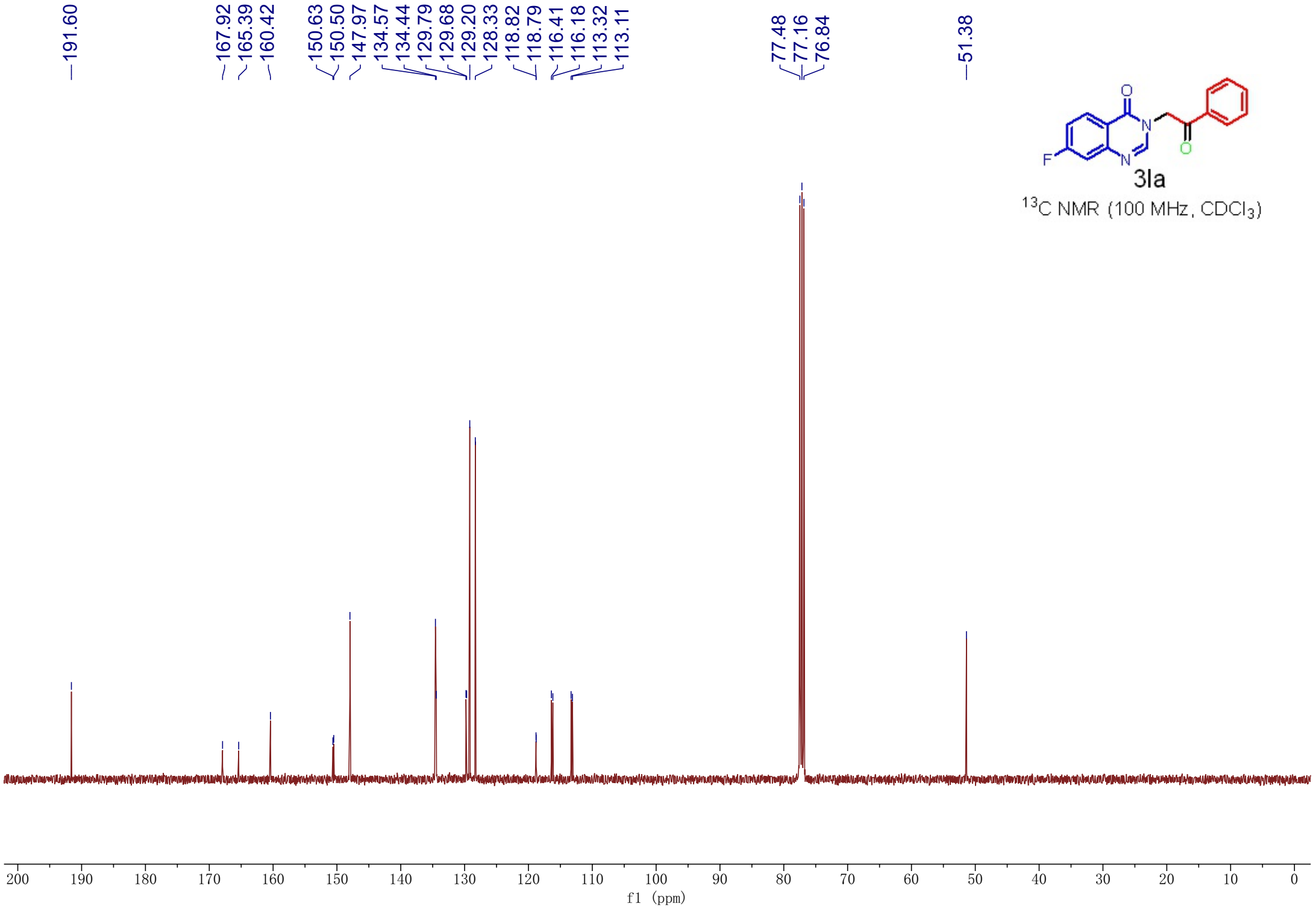


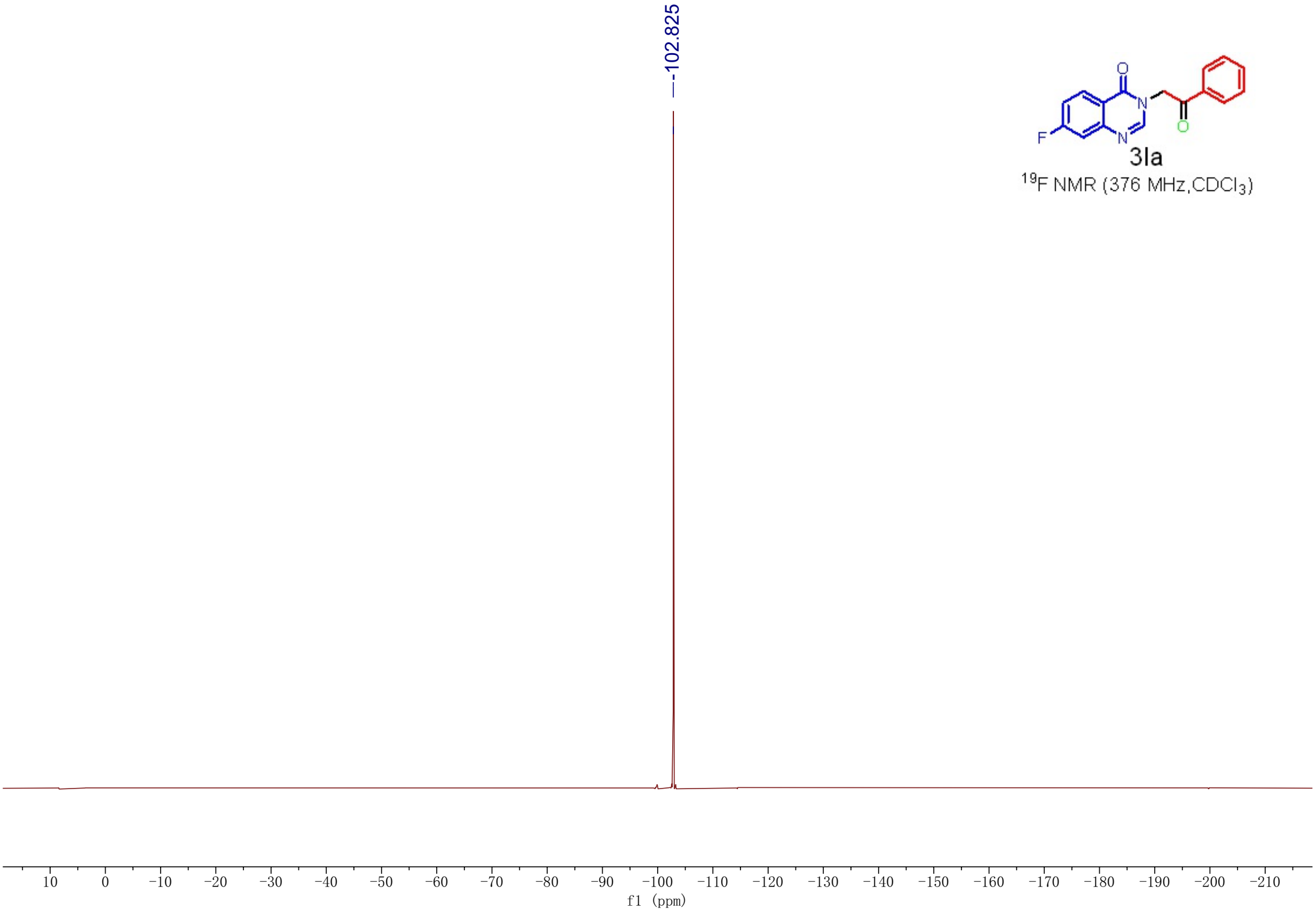
3la

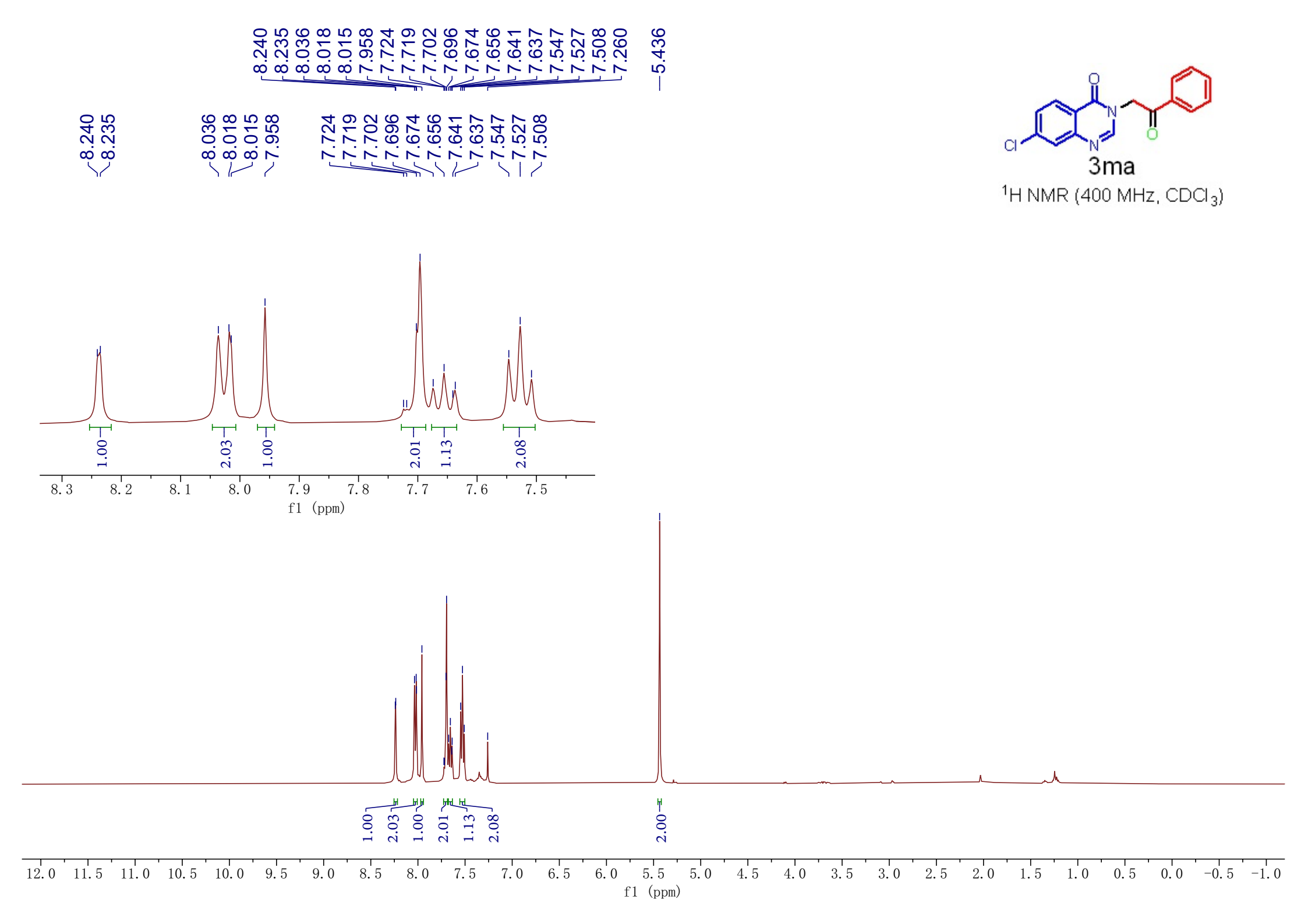
^{1}H NMR (400 MHz, $CDCl_3$)

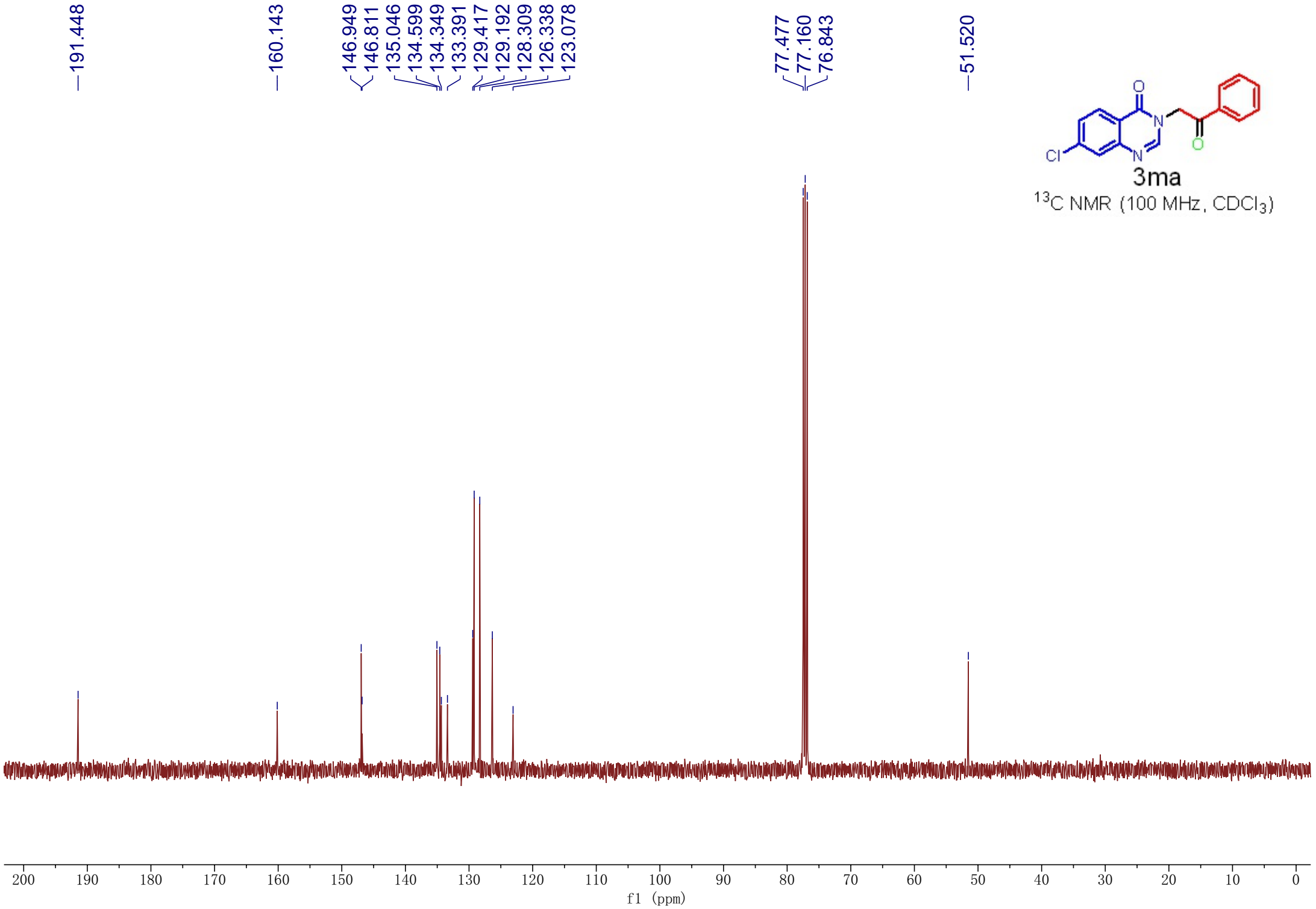


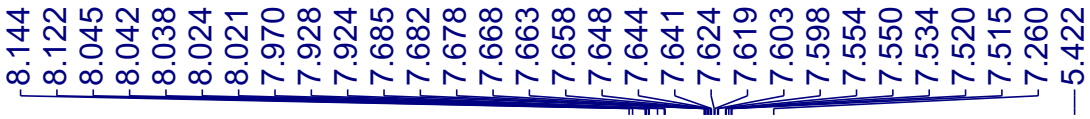


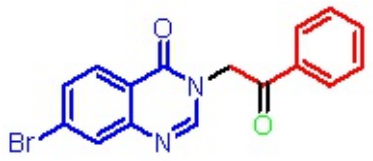

191.60
167.92
165.39
160.42
150.63
150.50
147.97
134.57
134.44
129.79
129.68
129.20
128.33
118.82
118.79
116.41
116.18
113.32
113.11
77.48
77.16
76.84
51.38
O
N
N
F
O
3la
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-102.825
O
N
F
N
O
3la
^{19}F NMR (376 MHz,$CDCl_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.240
8.235
8.036
8.018
8.015
7.958
7.724
7.719
7.702
7.696
7.674
7.656
7.641
7.637
7.547
7.527
7.508
7.260
5.436
Cl
N
N
O
O
3ma
1H NMR (400 MHz, CDCl3)
1.00
2.03
1.00
2.01
1.13
2.08
2.00
f1 (ppm)

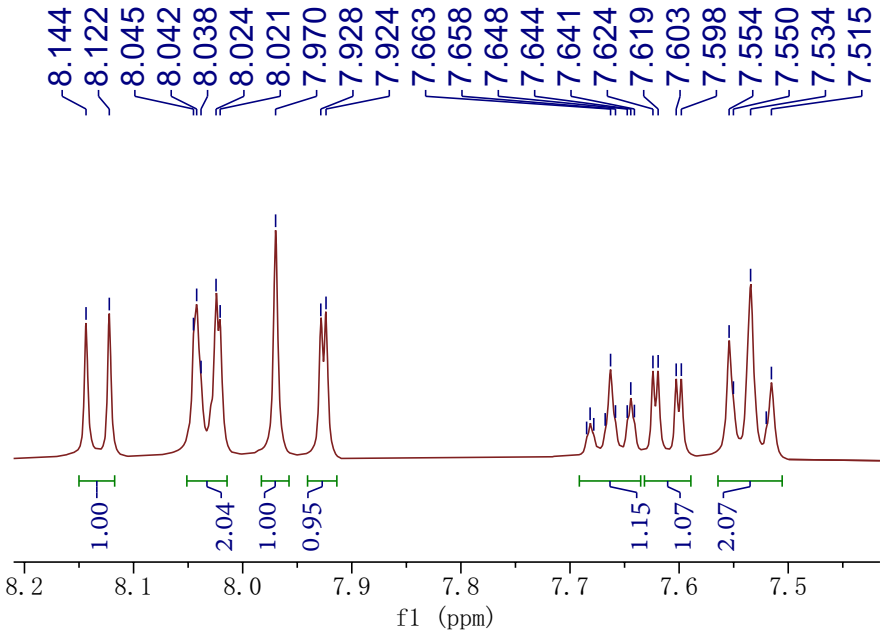

191.448
160.143
146.949
146.811
135.046
134.599
134.349
133.391
129.417
129.192
128.309
126.338
123.078
77.477
77.160
76.843
51.520
O
N
N
Cl
O
3ma
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

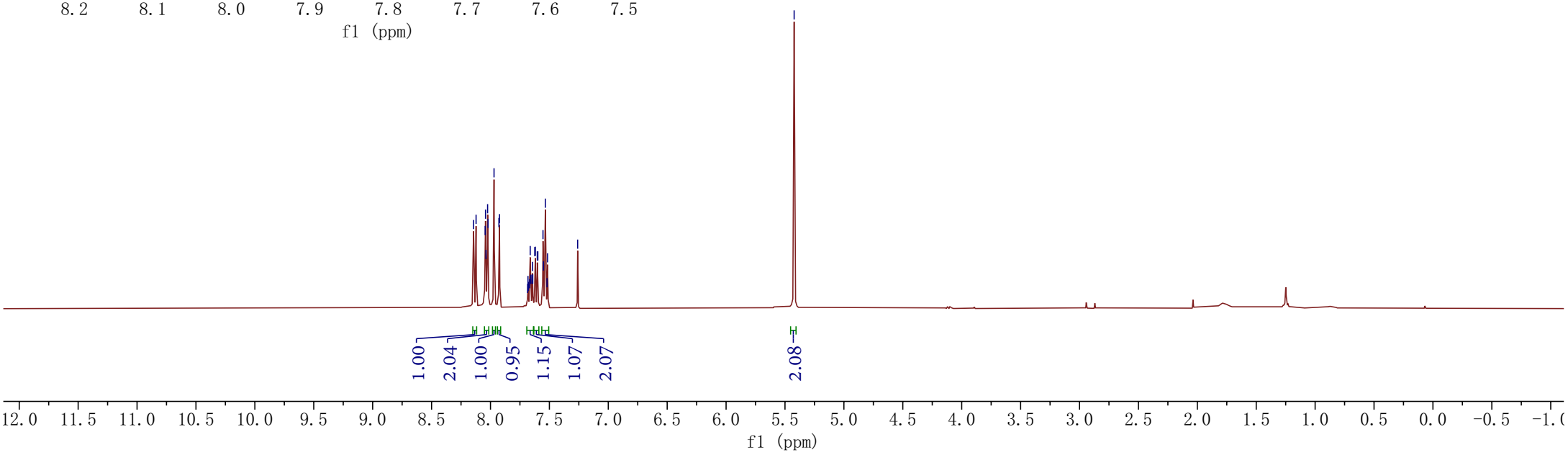


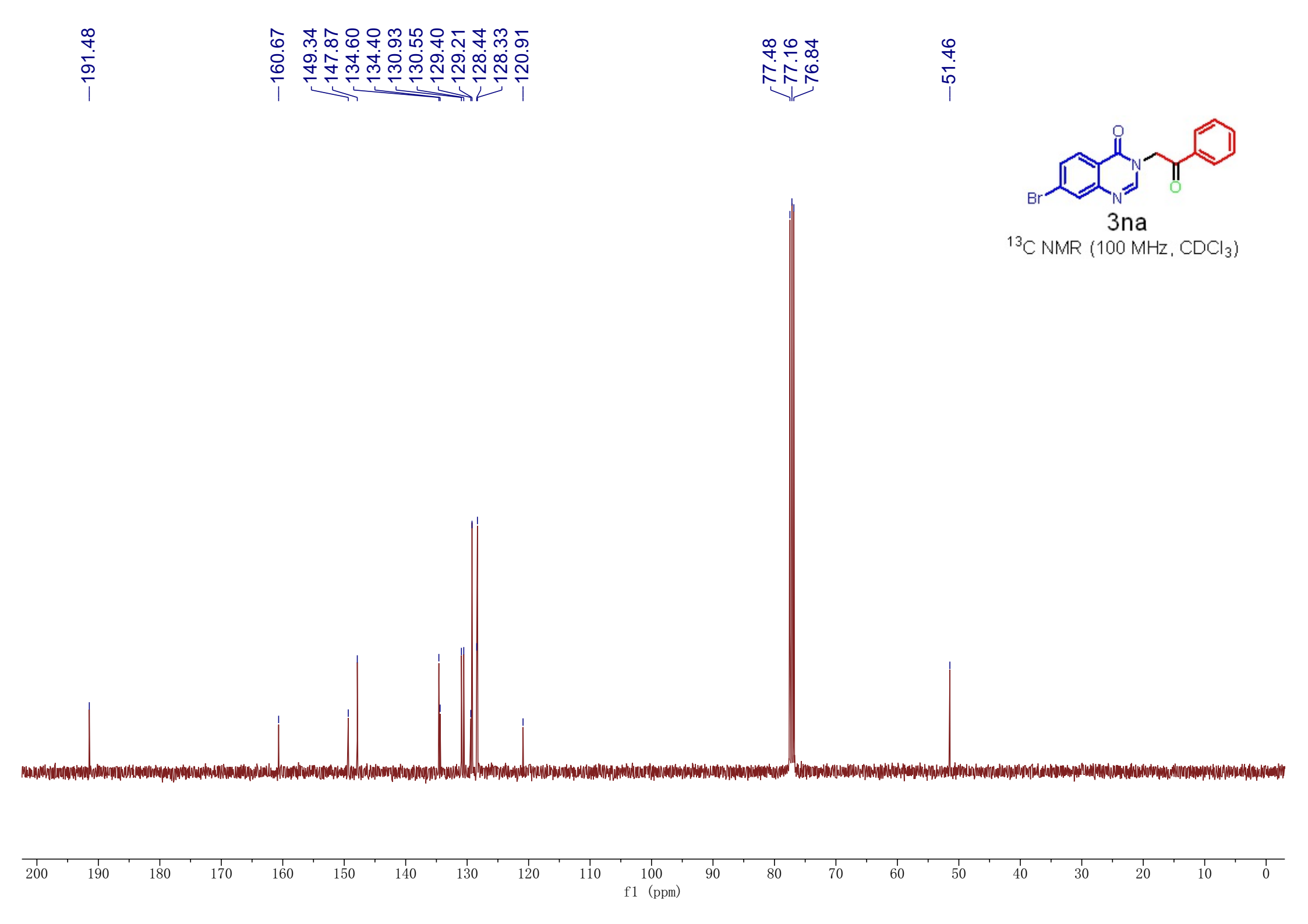


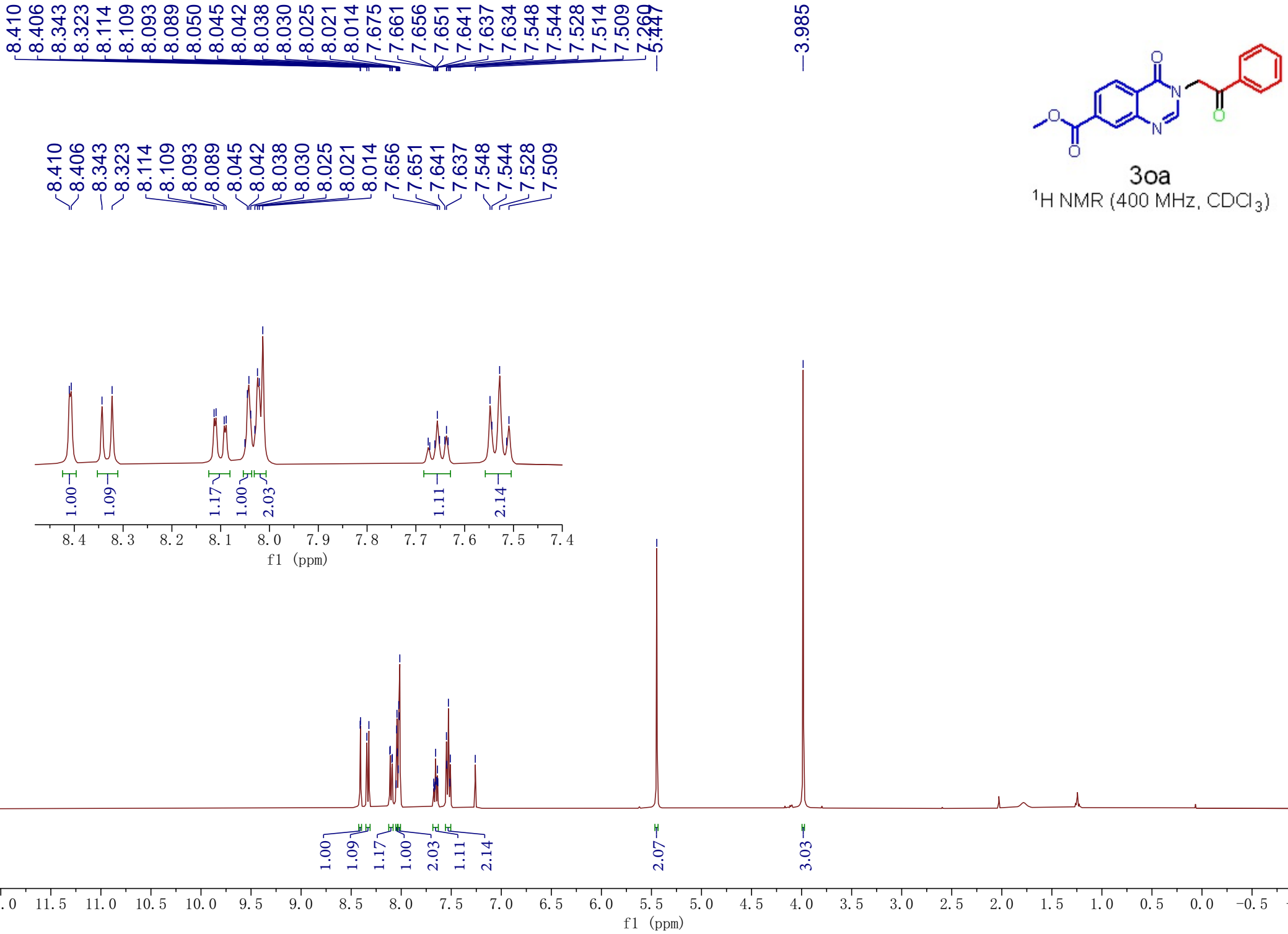
3na

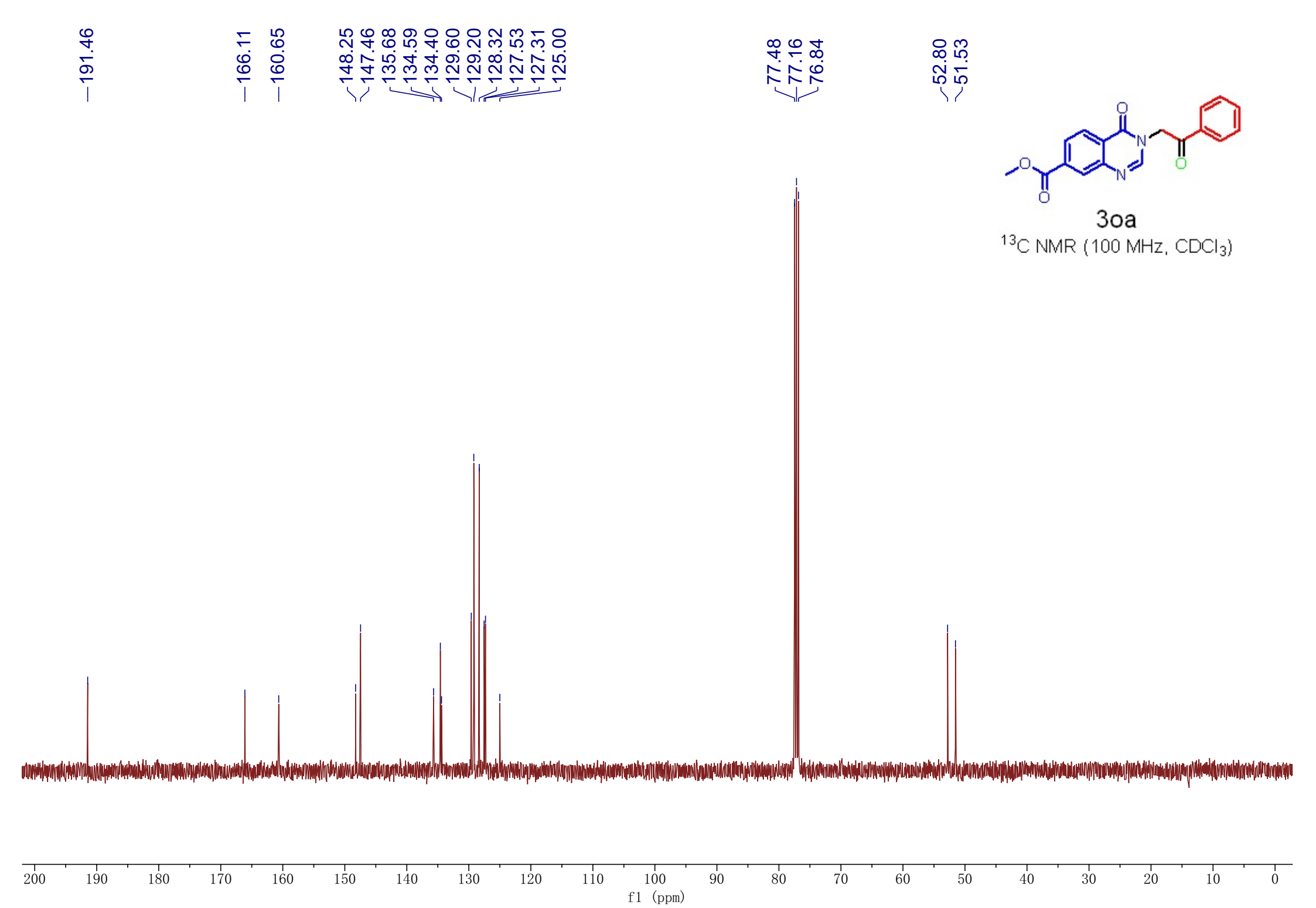
^{1}H NMR (400 MHz, $CDCl_3$)

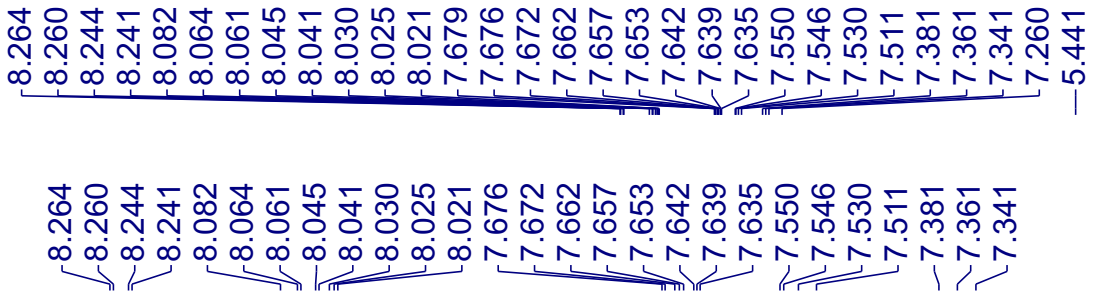


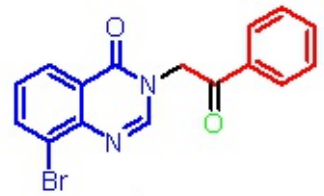



191.48
160.67
149.34
147.87
134.60
134.40
130.93
130.55
129.40
129.21
128.44
128.33
120.91
77.48
77.16
76.84
51.46
O
N
N
Br
O
3na
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.410
8.406
8.343
8.323
8.114
8.109
8.093
8.089
8.050
8.045
8.042
8.038
8.030
8.025
8.021
8.014
7.675
7.661
7.656
7.651
7.641
7.637
7.634
7.548
7.544
7.528
7.514
7.509
7.269
5.447
3.985
3oa
1H NMR (400 MHz, CDCl3)
1.00
1.09
1.17
1.00
2.03
1.11
2.14
2.07
3.03
f1 (ppm)

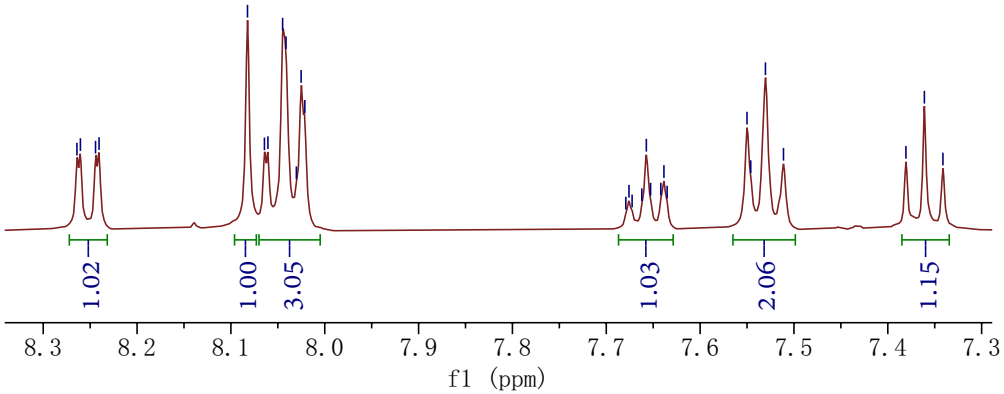

191.46
166.11
160.65
148.25
147.46
135.68
134.59
134.40
129.60
129.20
128.32
127.53
127.31
125.00
77.48
77.16
76.84
52.80
51.53
O
N
N
O
O
O
3oa
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

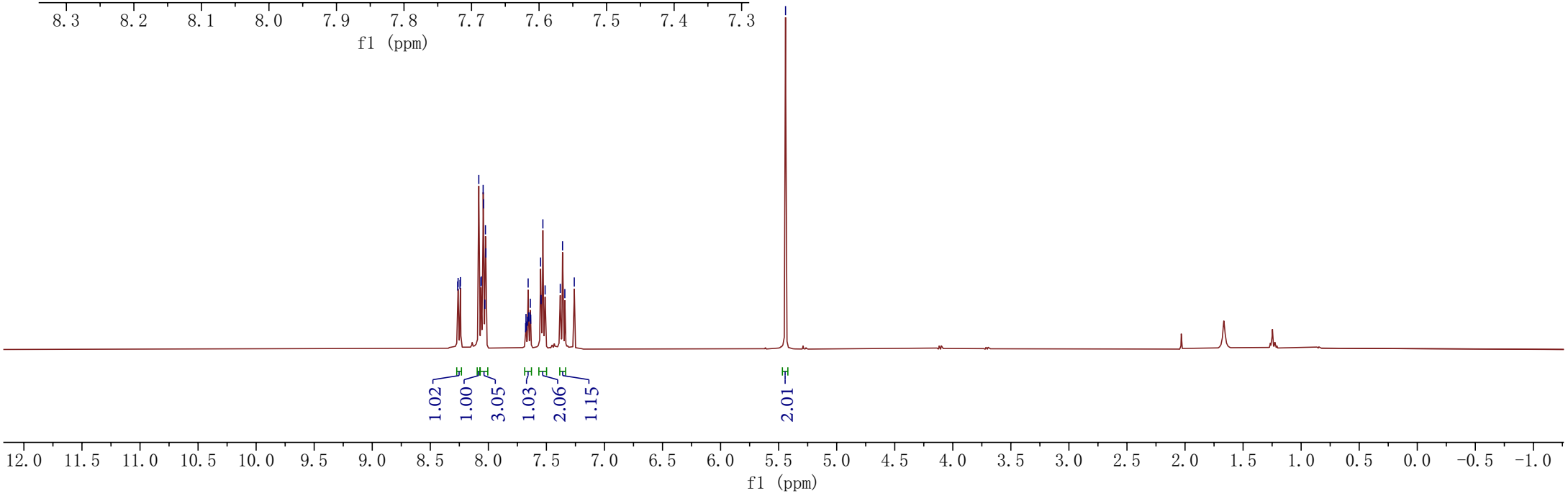


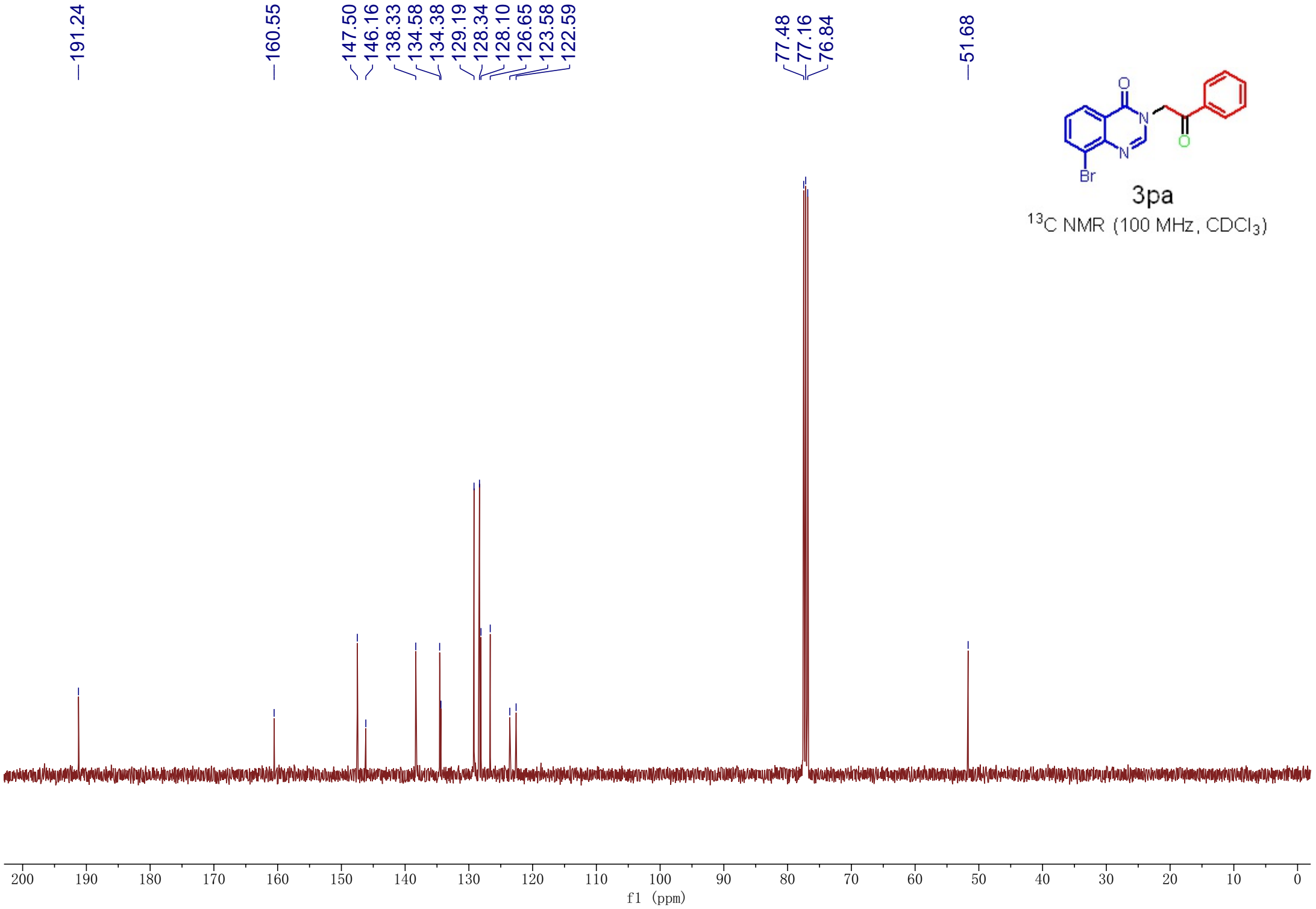


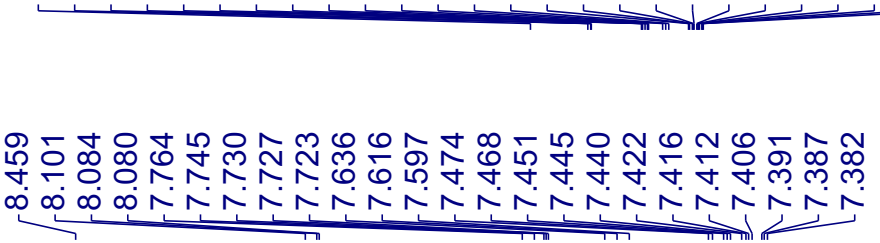
3pa

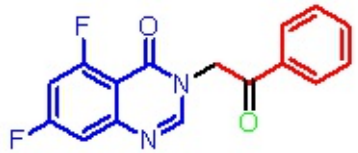
^{1}H NMR (400 MHz, $CDCl_3$)





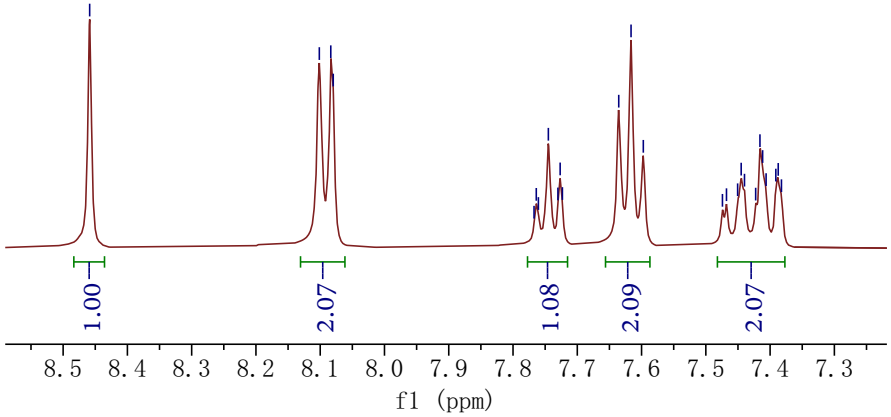

191.24
160.55
147.50
146.16
138.33
134.58
134.38
129.19
128.34
128.10
126.65
123.58
122.59
77.48
77.16
76.84
51.68
O
N
N
O
Br
3pa
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

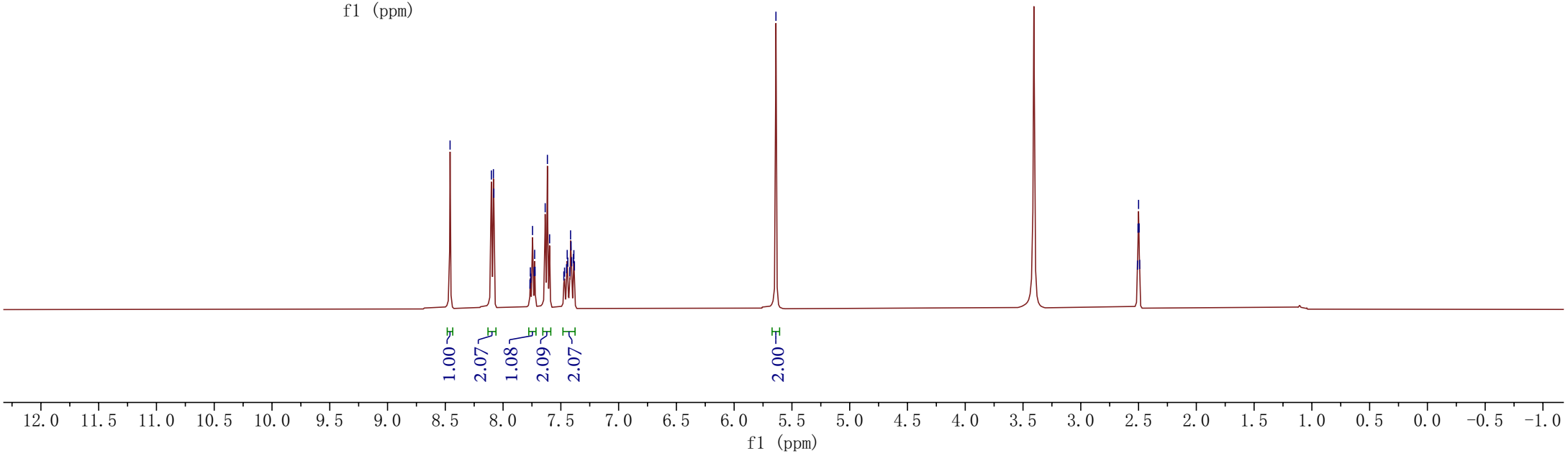


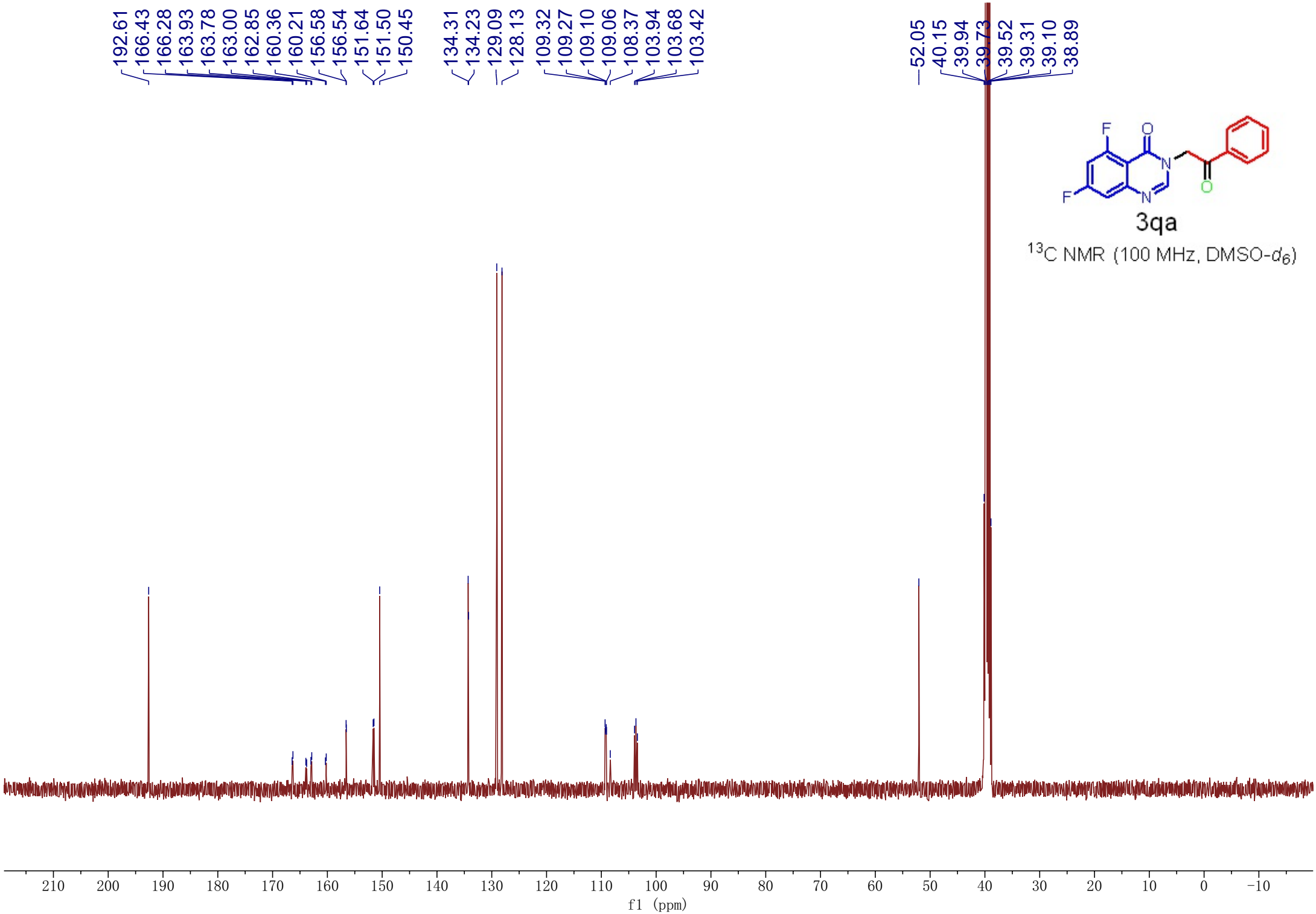


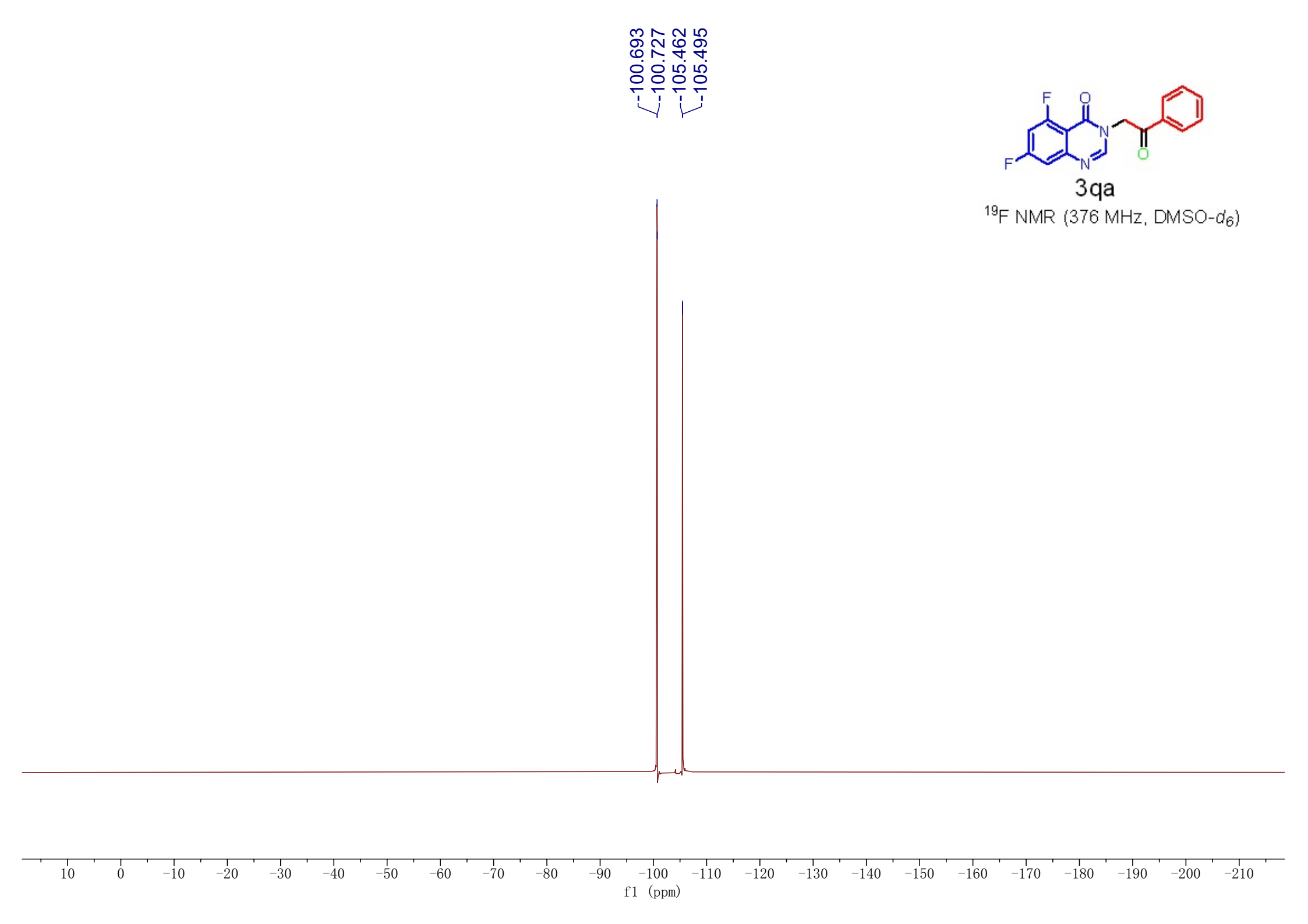
3qa

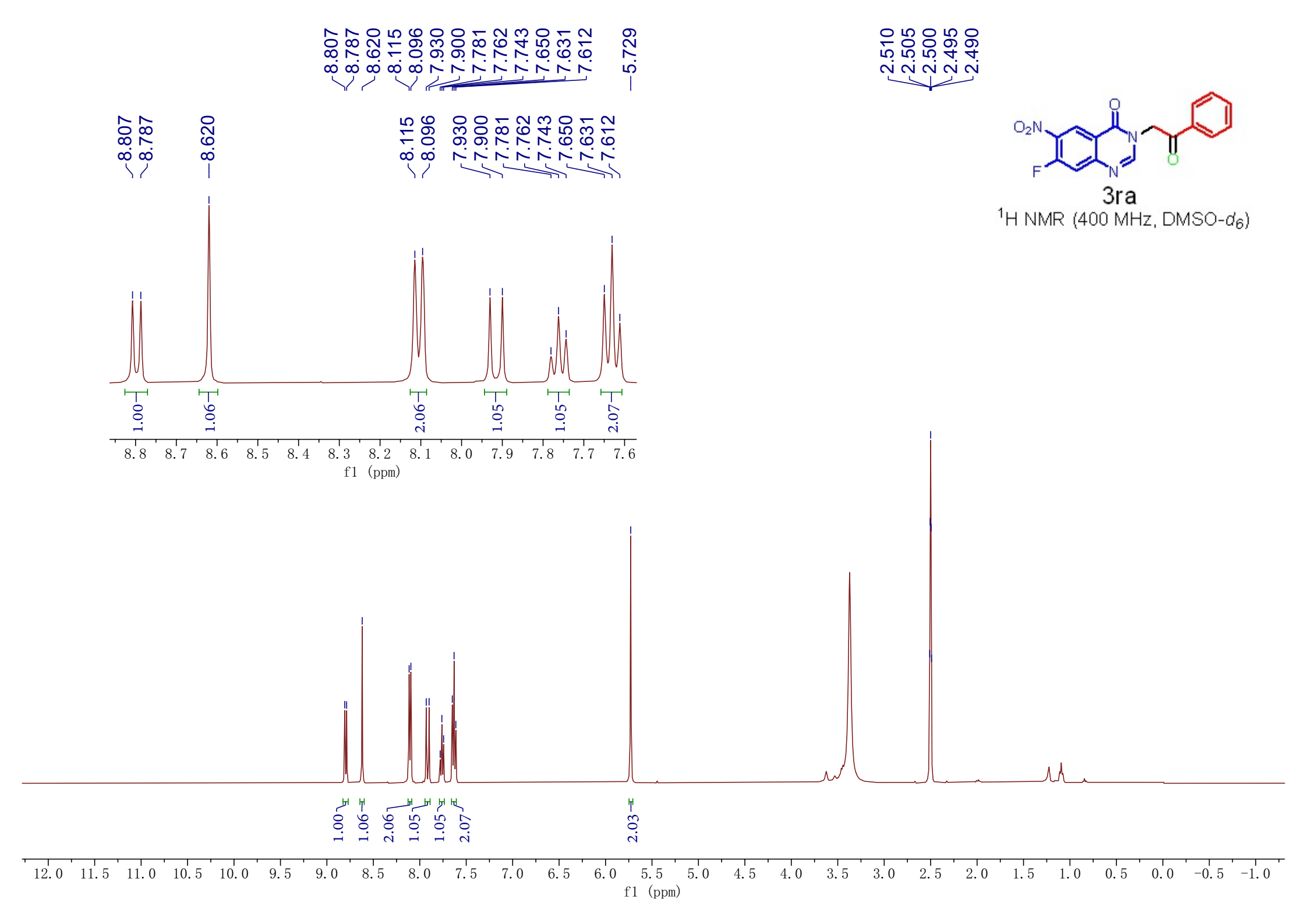
^{1}H NMR (400 MHz, DMSO-d_6)

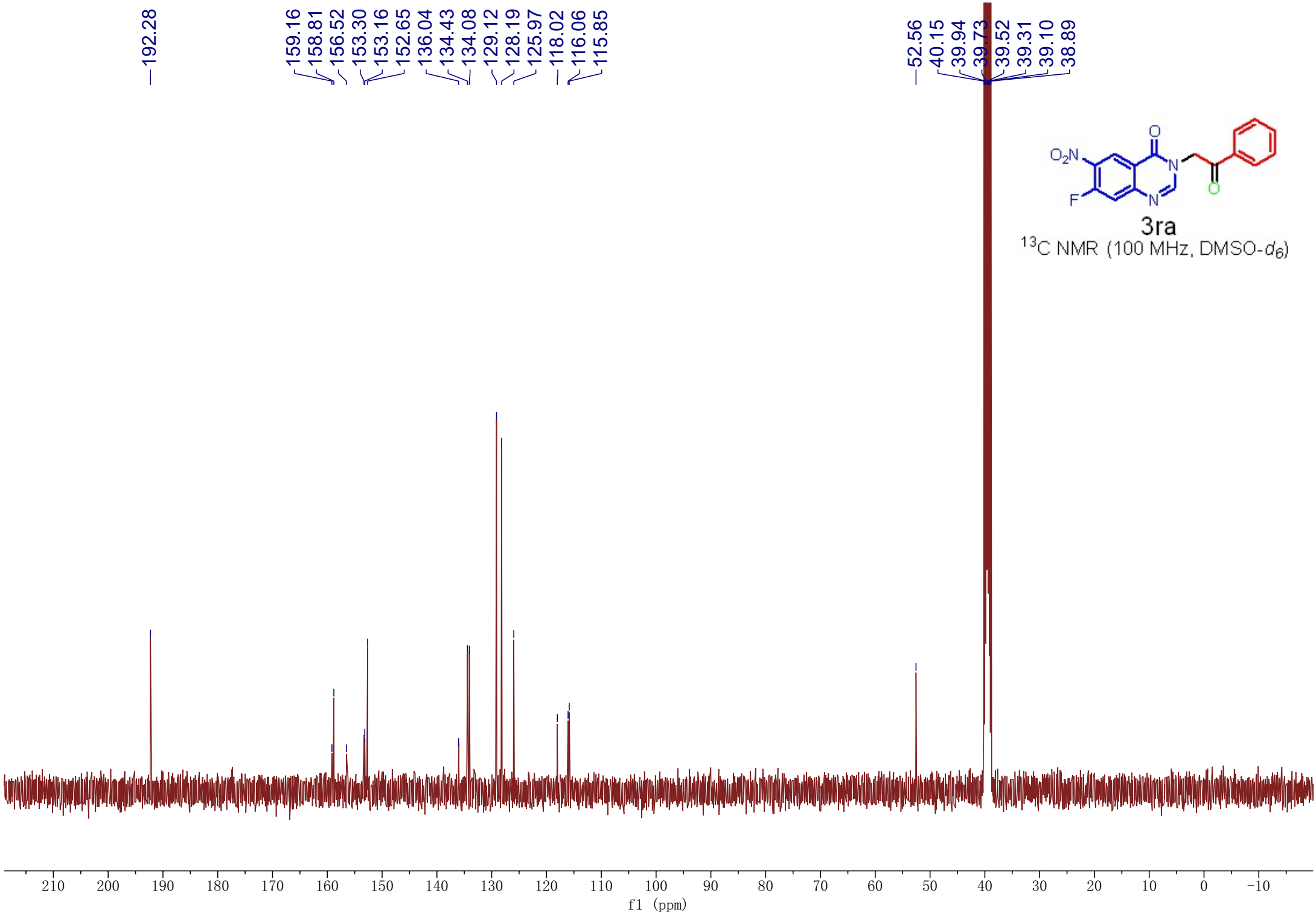


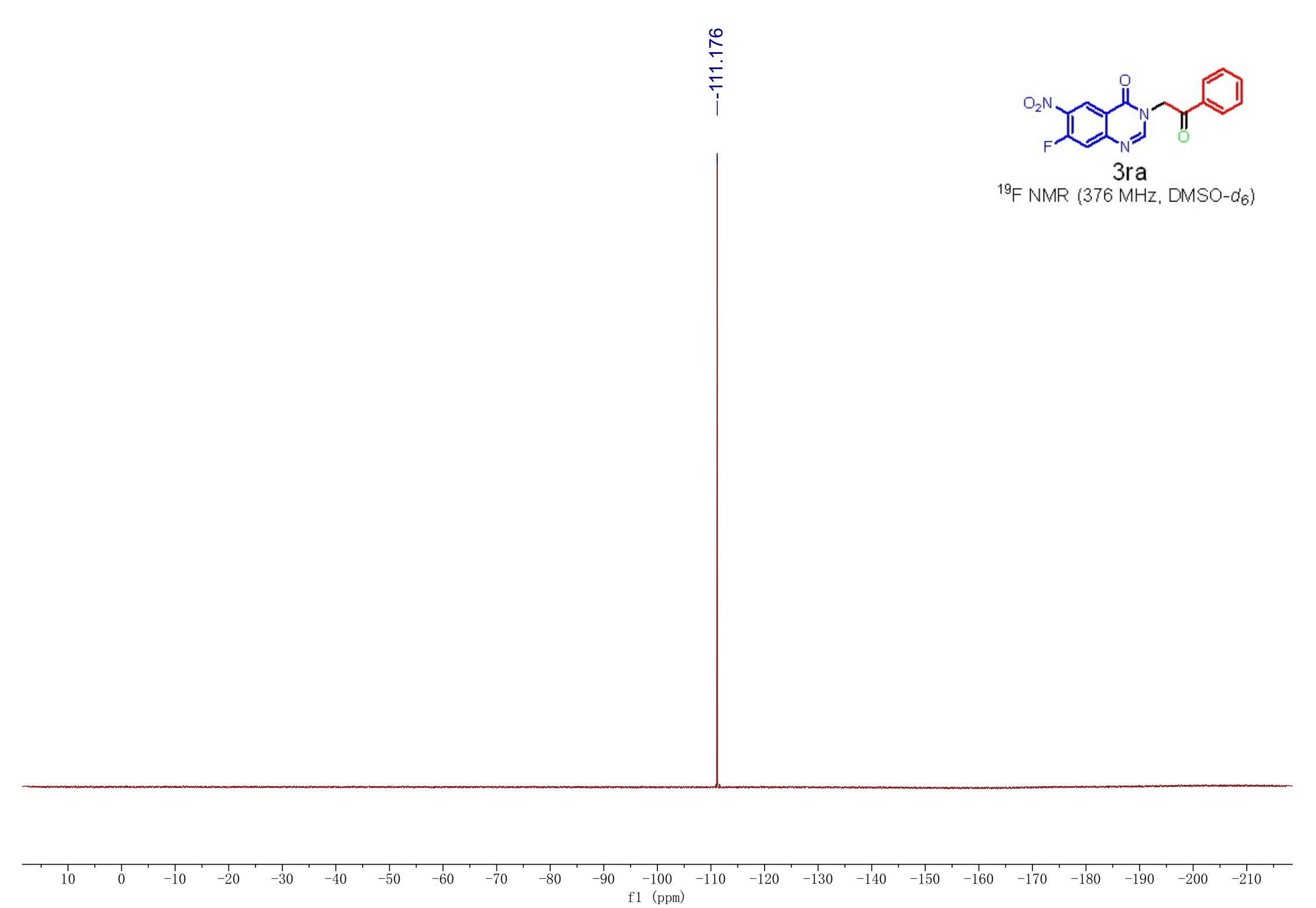


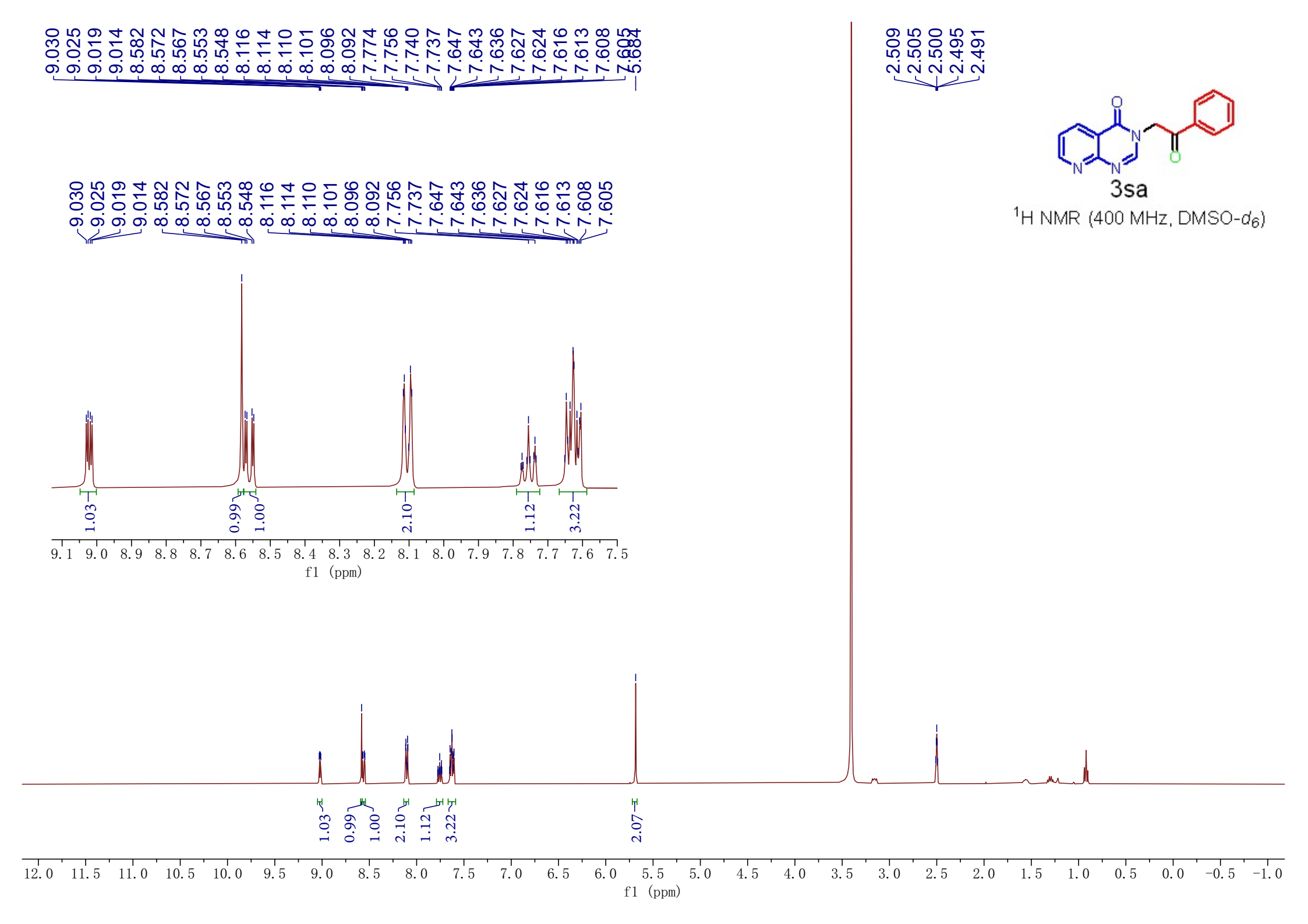

192.61
166.43
166.28
163.93
163.78
163.00
162.85
160.36
160.21
156.58
156.54
151.64
151.50
150.45
134.31
134.23
129.09
128.13
109.32
109.27
109.10
109.06
108.37
103.94
103.68
103.42
52.05
40.15
39.94
39.73
39.52
39.31
39.10
38.89
F
O
N
F
N
O
3qa
^{13}C NMR (100 MHz, DMSO-d_6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

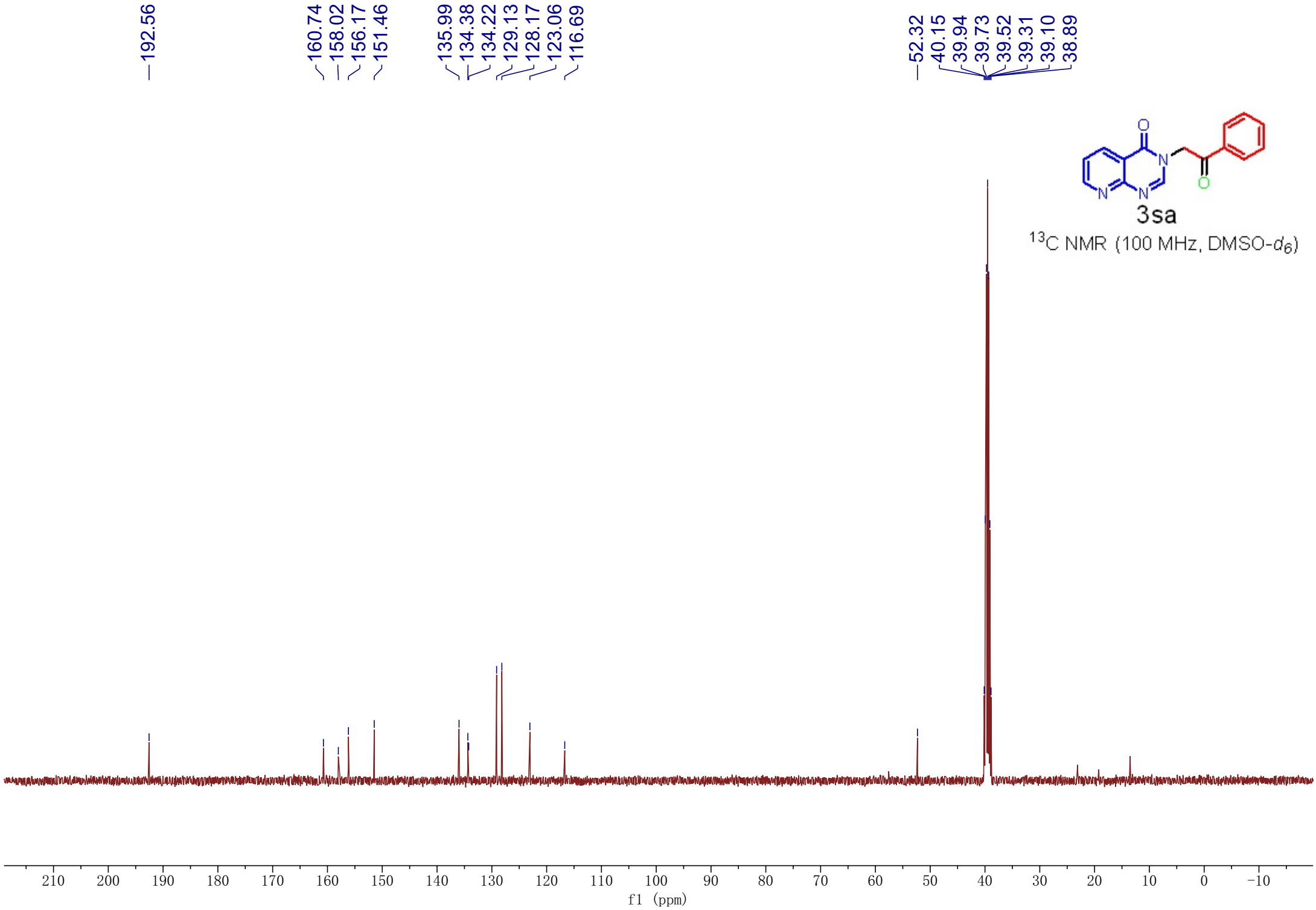

-100.693
-100.727
-105.462
-105.495
F
O
N
F
O
N
3qa
^{19}F NMR (376 MHz, DMSO-d_6)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

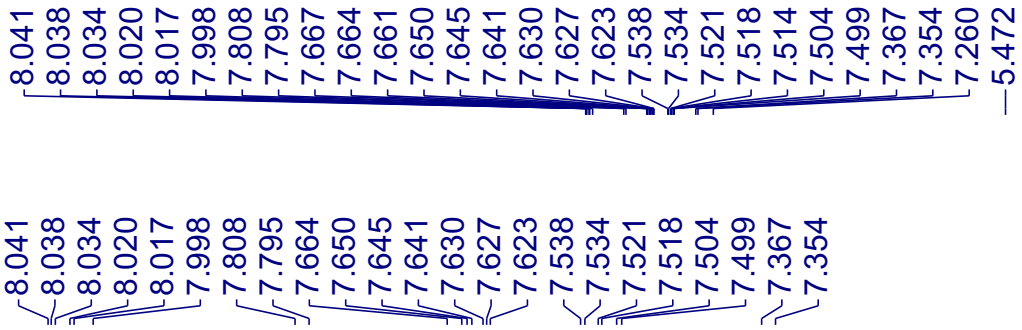

8.807
8.787
8.620
8.115
8.096
7.930
7.900
7.781
7.762
7.743
7.650
7.631
7.612
5.729
2.510
2.505
2.500
2.495
2.490
1.00
1.06
2.06
1.05
1.05
2.07
2.03
f1 (ppm)
O2N
F
O
N
3ra
1H NMR (400 MHz, DMSO-d6)

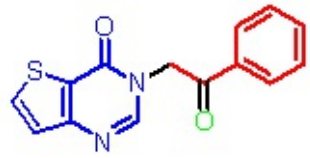

192.28
159.16
158.81
156.52
153.30
153.16
152.65
136.04
134.43
134.08
129.12
128.19
125.97
118.02
116.06
115.85
52.56
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O2N
F
O
N
N
O
3ra
13C NMR (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-111.176
O2N
F
O
N
N
O
3ra
19F NMR (376 MHz, DMSO-d6)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


9.030
9.025
9.019
9.014
8.582
8.572
8.567
8.553
8.548
8.116
8.114
8.110
8.101
8.096
8.092
7.774
7.756
7.740
7.737
7.647
7.643
7.636
7.627
7.624
7.616
7.613
7.608
7.605
5.684
2.509
2.505
2.500
2.495
2.491
3sa
1H NMR (400 MHz, DMSO-d6)
1.03
0.99
1.00
2.10
1.12
3.22
2.07
f1 (ppm)

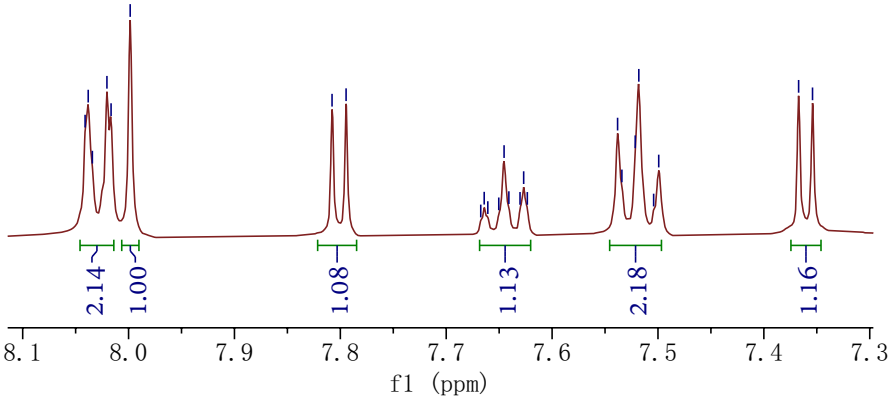

192.56
160.74
158.02
156.17
151.46
135.99
134.38
134.22
129.13
128.17
123.06
116.69
52.32
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
N
N
N
O
3sa
13C NMR (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

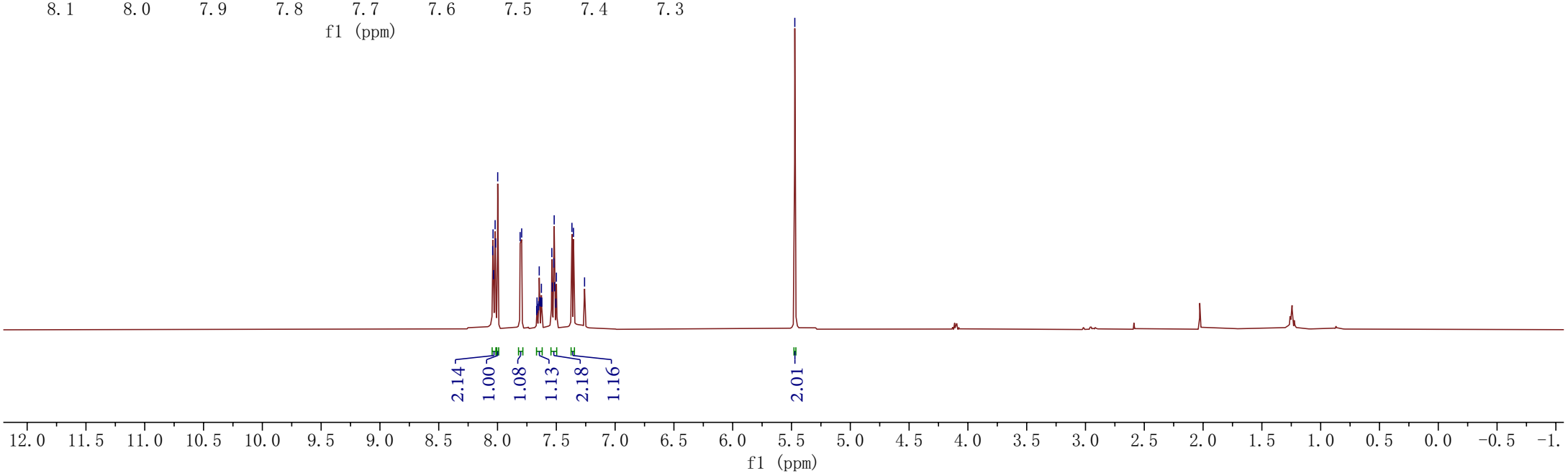


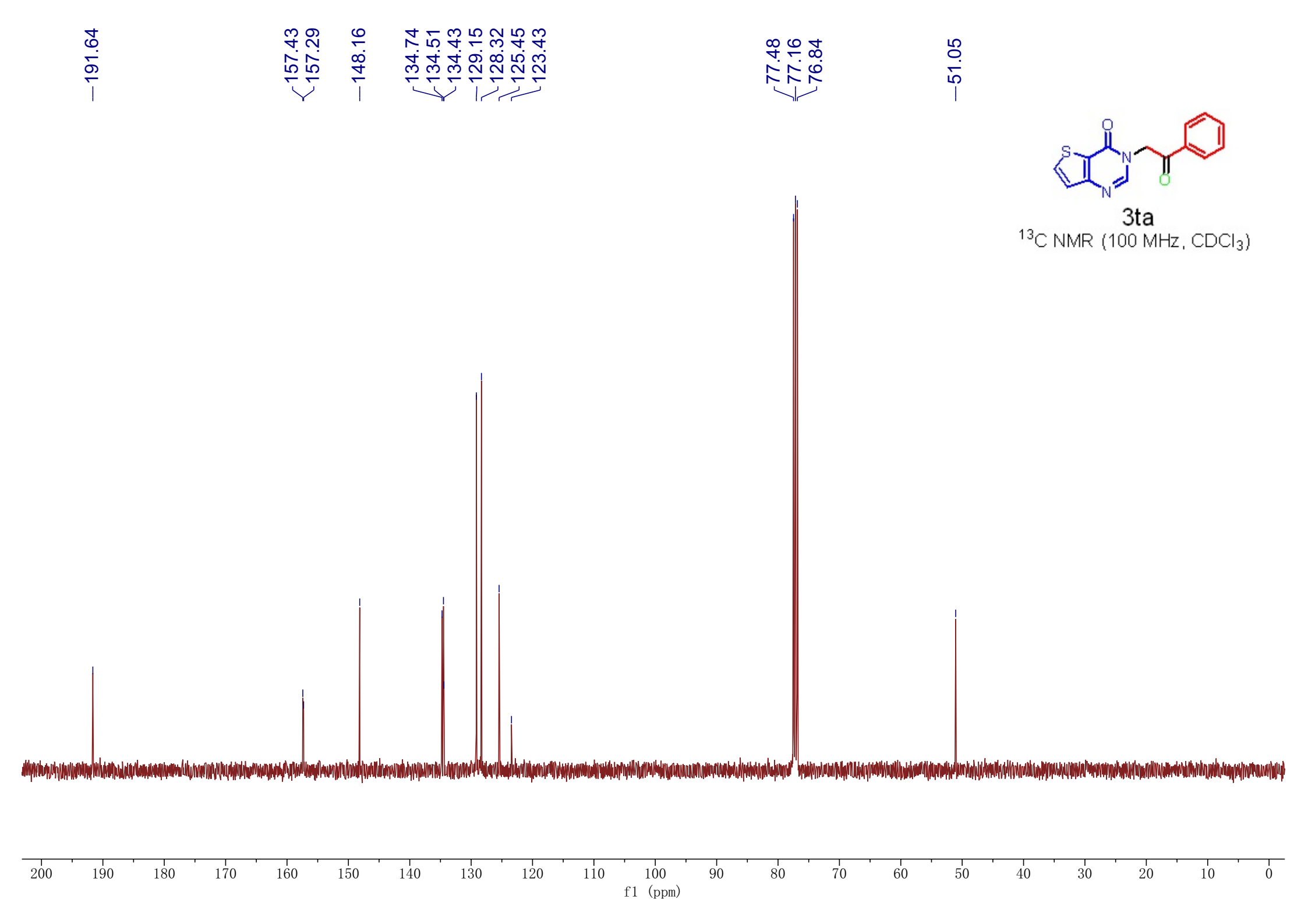


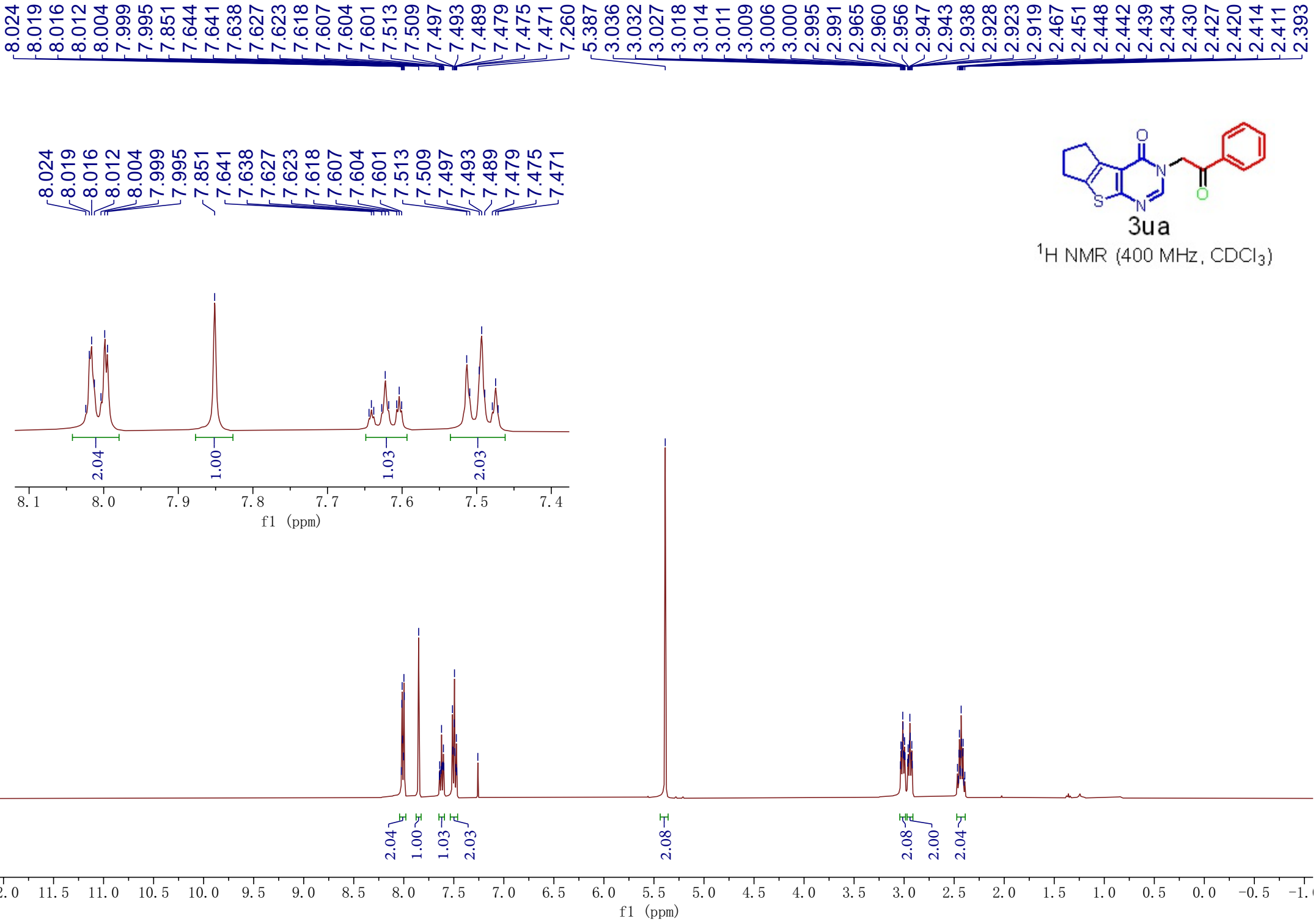
3ta

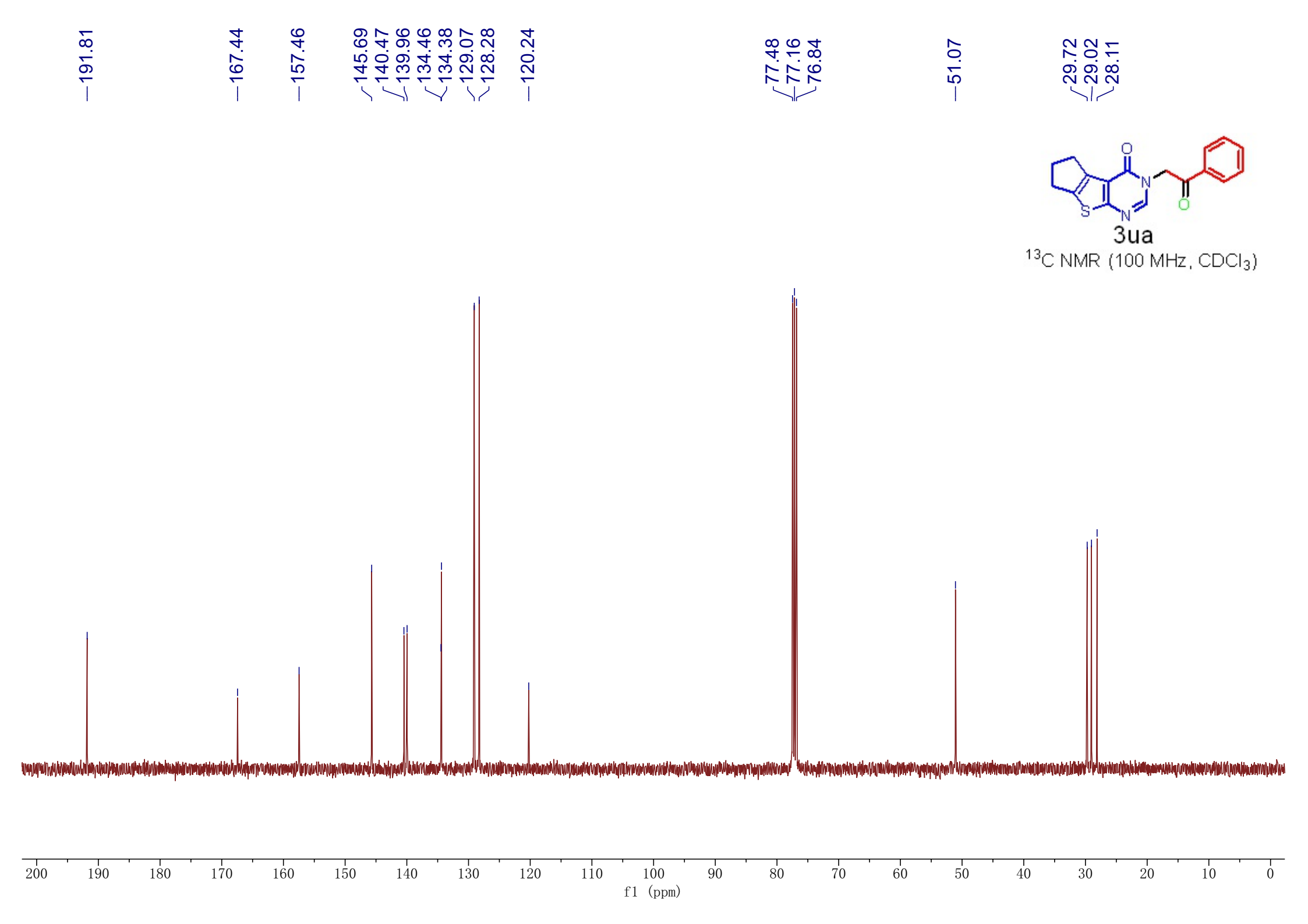
^{1}H NMR (400 MHz, $CDCl_3$)

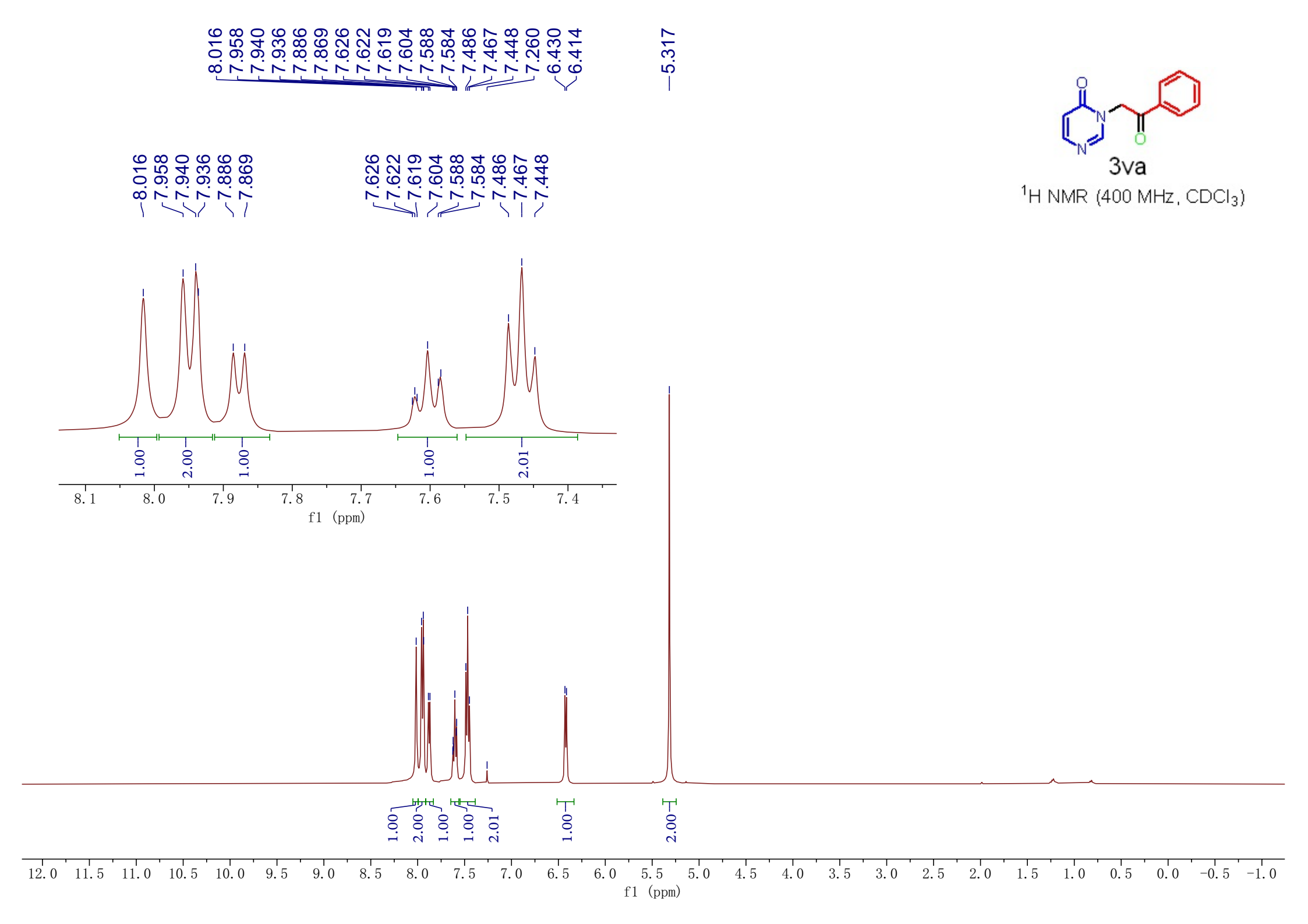


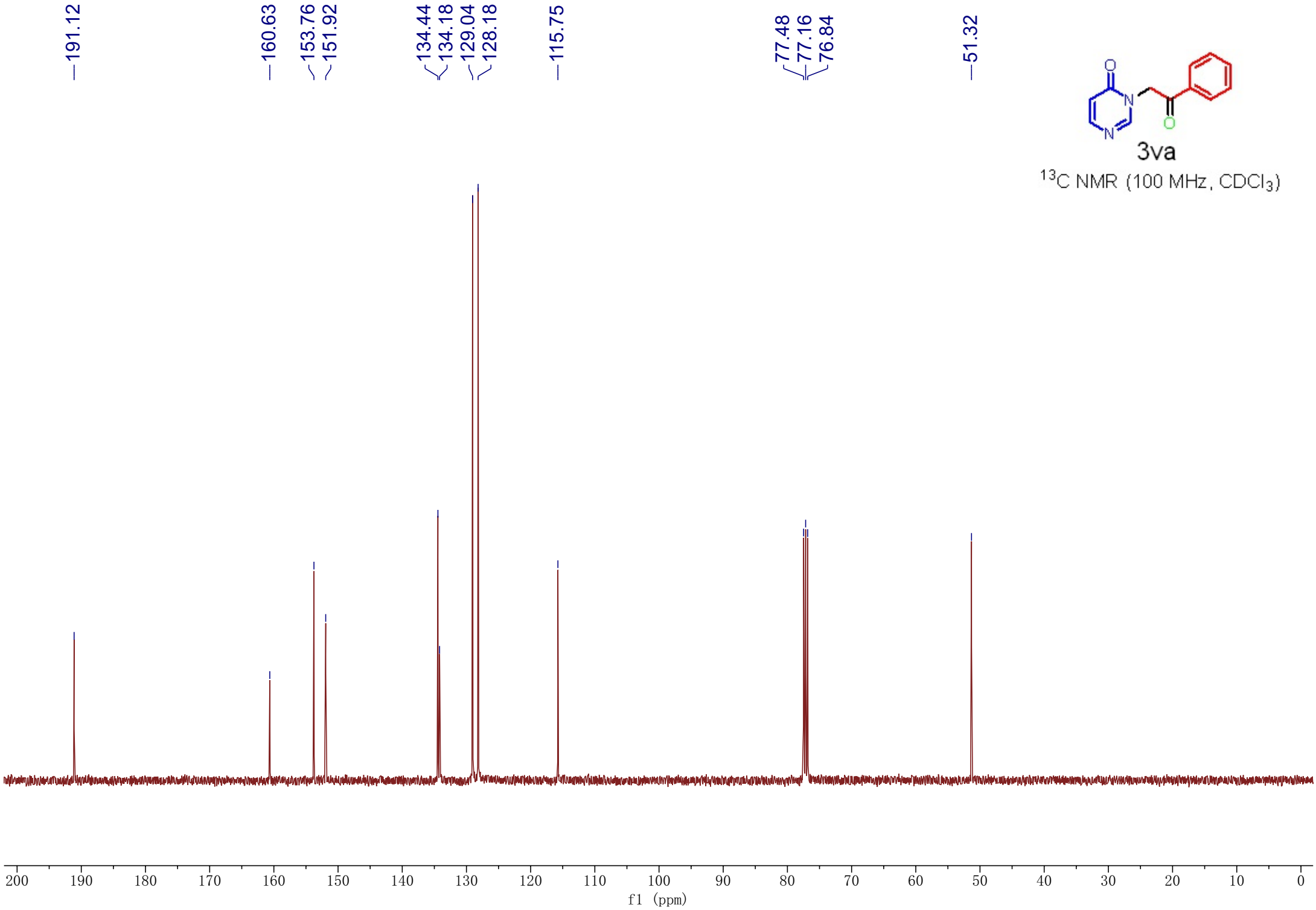


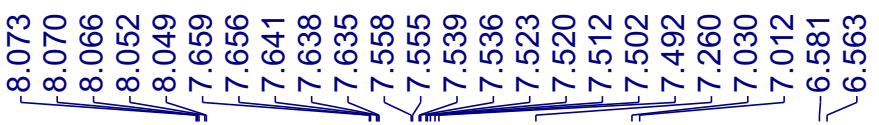

191.64
157.43
157.29
148.16
134.74
134.51
134.43
129.15
128.32
125.45
123.43
77.48
77.16
76.84
51.05
3ta
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

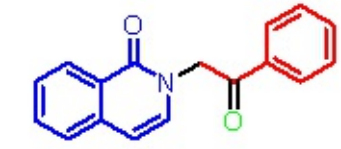

8.024 8.019 8.016 8.012 8.004 7.999 7.995 7.851 7.644 7.641 7.638 7.627 7.623 7.618 7.607 7.604 7.601 7.513 7.509 7.497 7.493 7.489 7.479 7.475 7.471 7.260
5.387 3.036 3.032 3.027 3.018 3.014 3.011 3.009 3.006 3.000 2.995 2.991 2.965 2.960 2.956 2.947 2.943 2.938 2.928 2.923 2.919 2.467 2.451 2.448 2.442 2.439 2.434 2.430 2.427 2.420 2.414 2.411 2.393
O
N
S
N
O
3ua
1H NMR (400 MHz, CDCl3)
2.04
1.00
1.03
2.03
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
2.04
1.00
1.03
2.03
2.08
2.08
2.00
2.04
12.0 11.5 11.0 10.5 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)


191.81
167.44
157.46
145.69
140.47
139.96
134.46
134.38
129.07
128.28
120.24
77.48
77.16
76.84
51.07
29.72
29.02
28.11
O
N
S
N
O
3ua
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.016
7.958
7.940
7.936
7.886
7.869
7.626
7.622
7.619
7.604
7.588
7.584
7.486
7.467
7.448
7.260
6.430
6.414
5.317
3va
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
2.00
1.00
1.00
2.01
1.00
2.00
f1 (ppm)

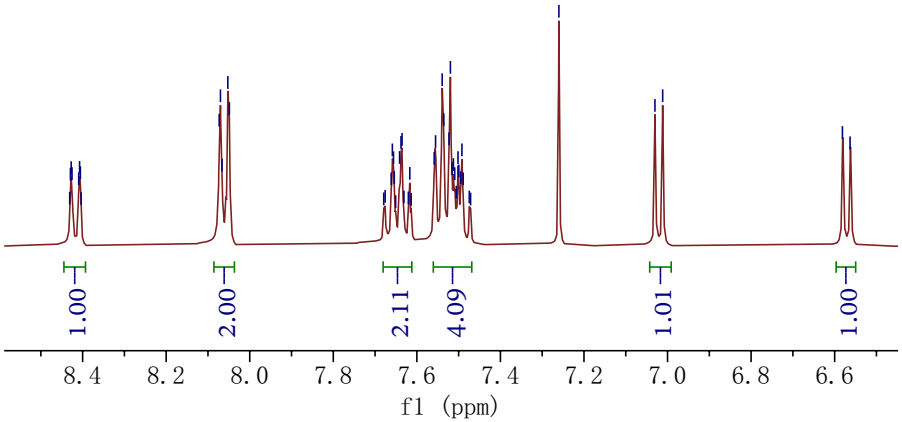

191.12
160.63
153.76
151.92
134.44
134.18
129.04
128.18
115.75
77.48
77.16
76.84
51.32
O
N
N
O
3va
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

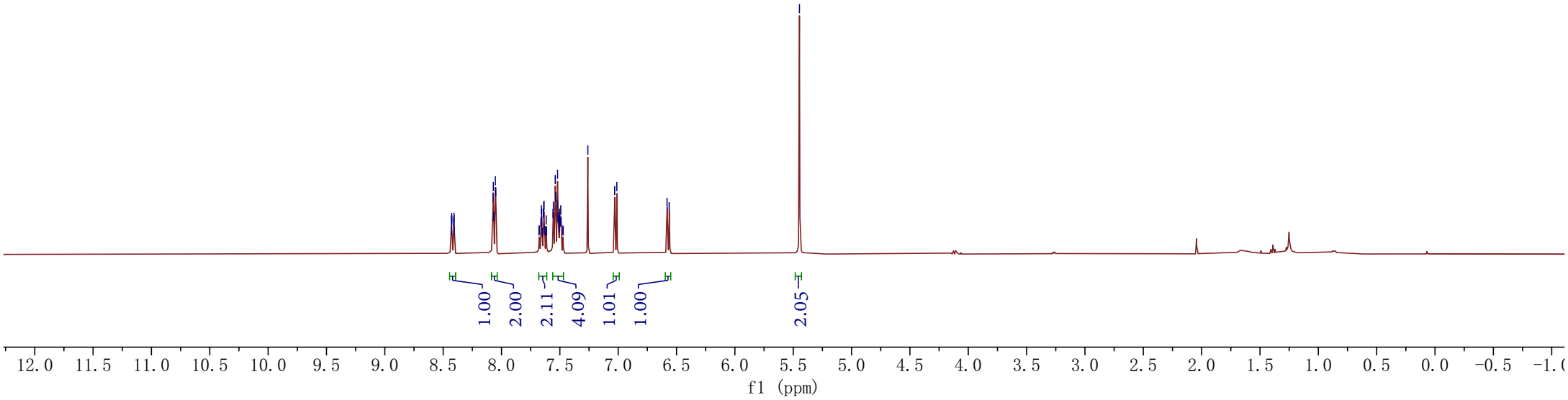


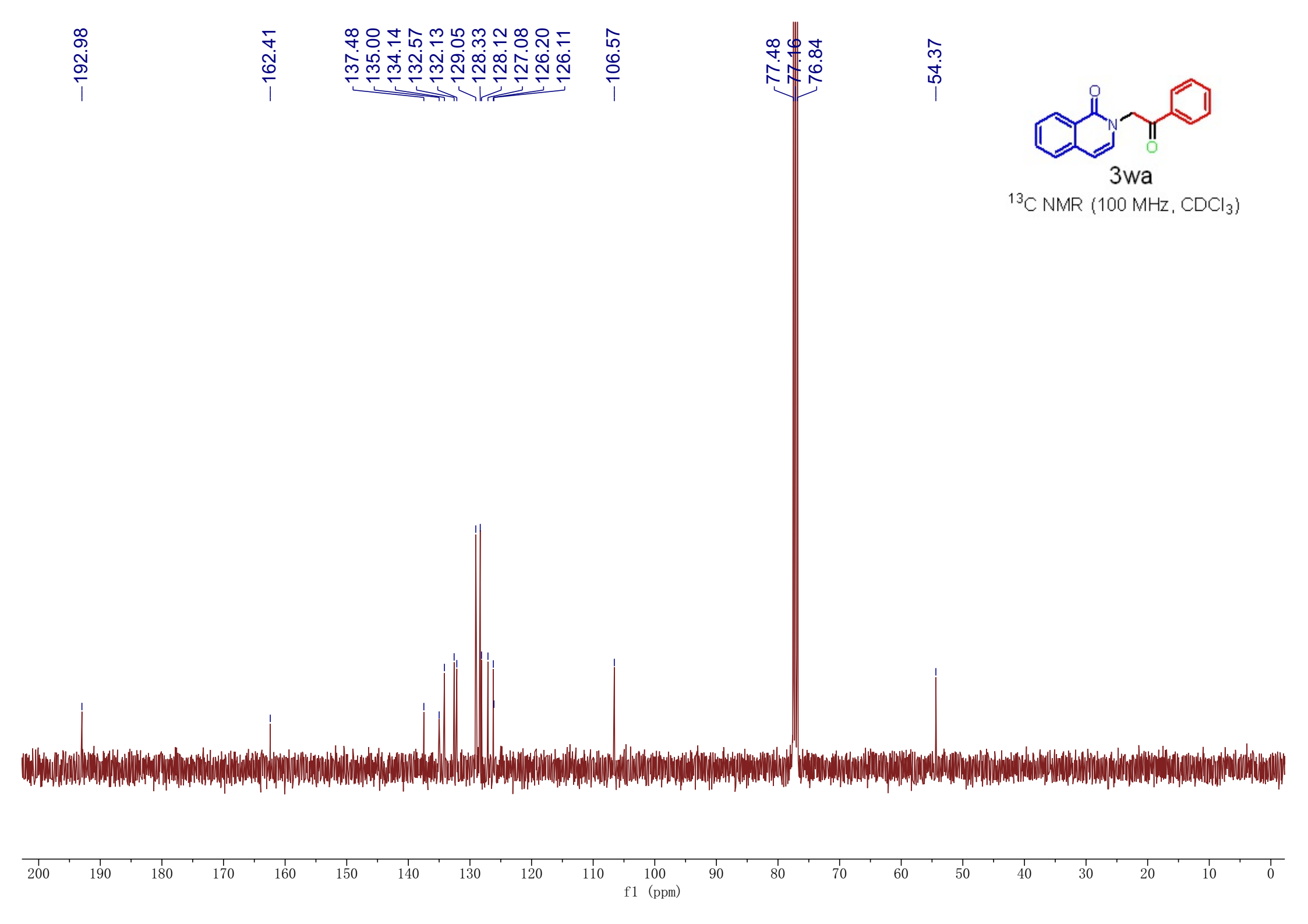


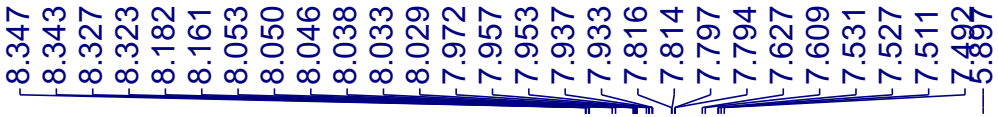
3wa

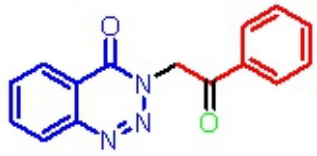
^{1}H NMR (400 MHz, $CDCl_3$)





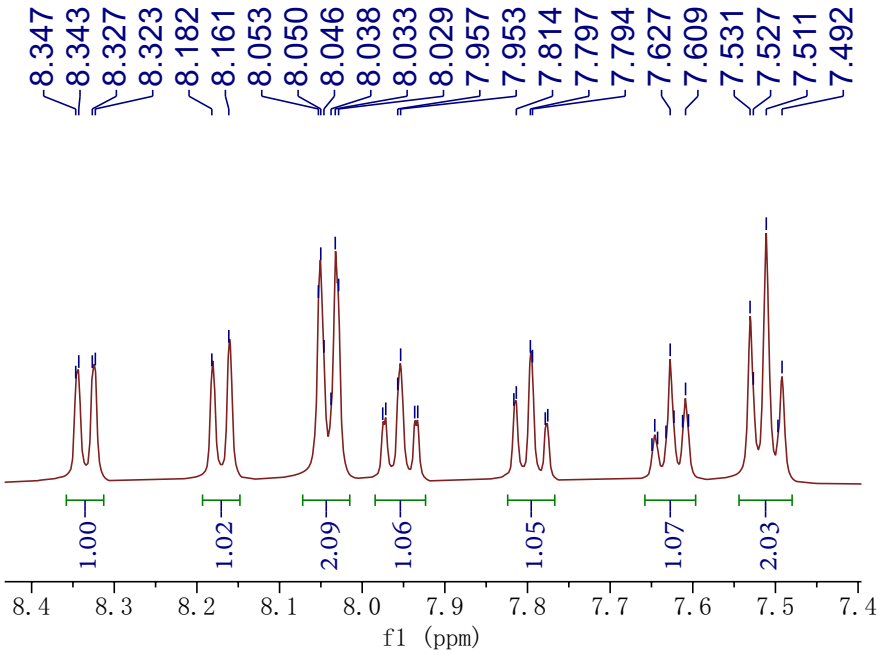

192.98
162.41
137.48
135.00
134.14
132.57
132.13
129.05
128.33
128.12
127.08
126.20
126.11
106.57
77.48
77.16
76.84
54.37
O
N
O
3wa
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

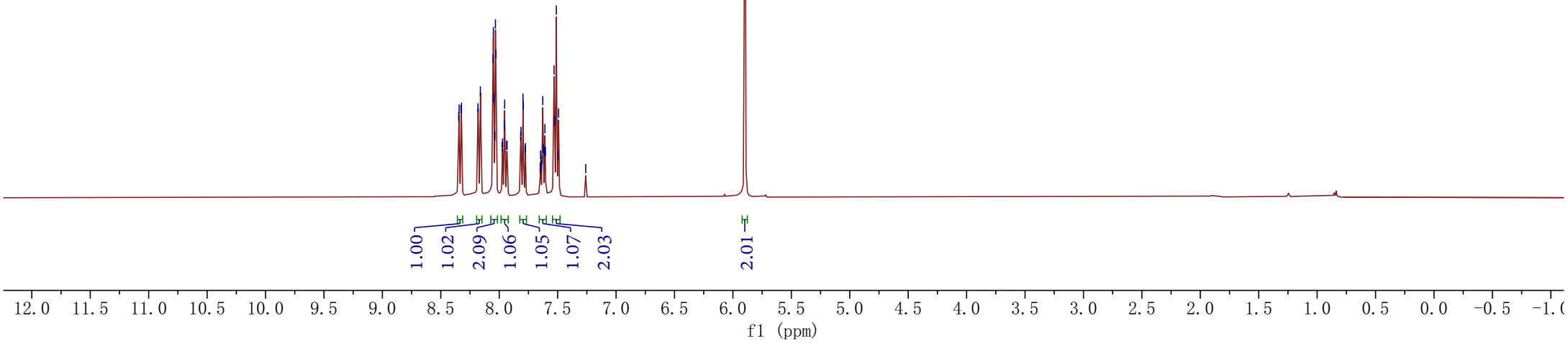


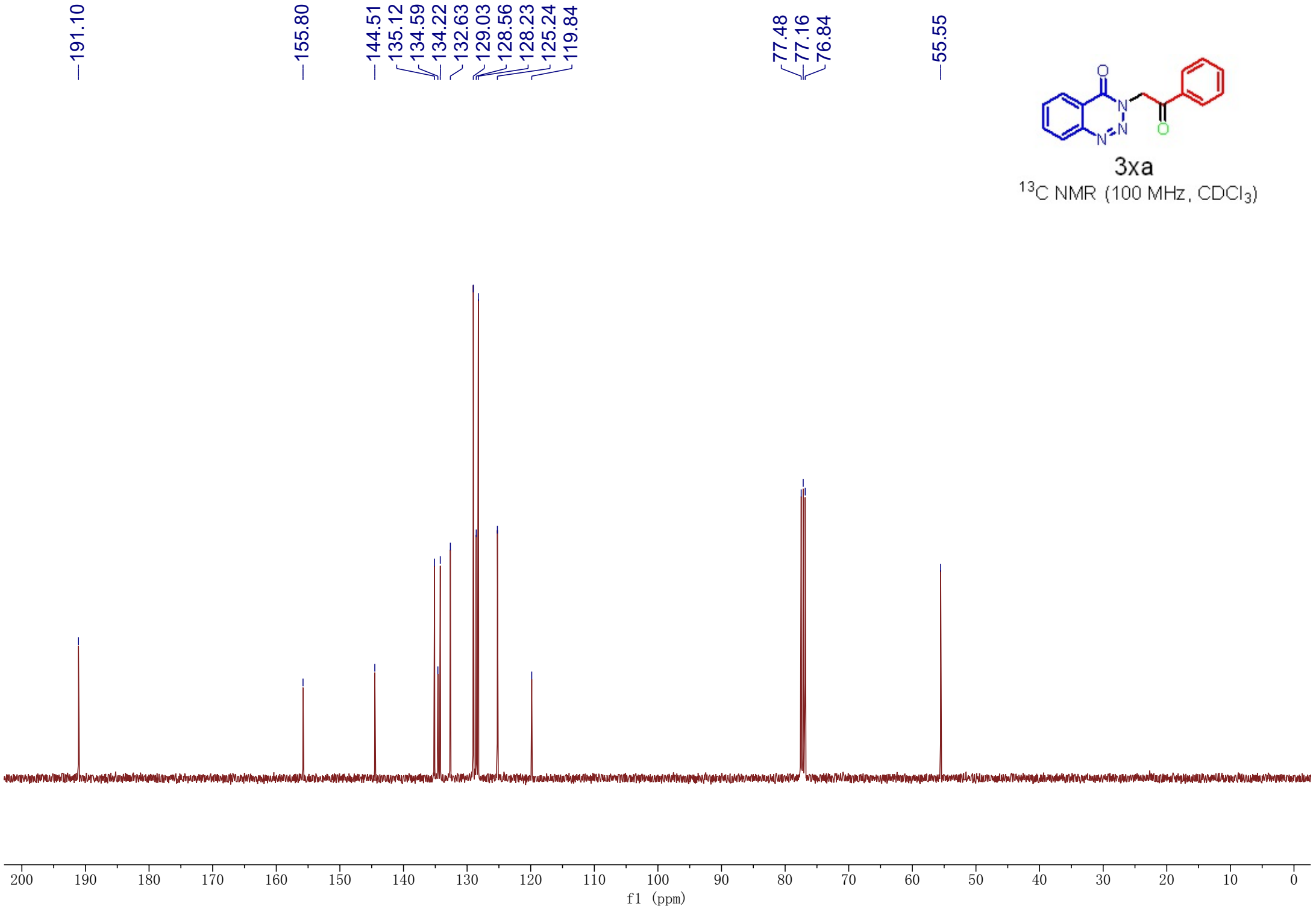


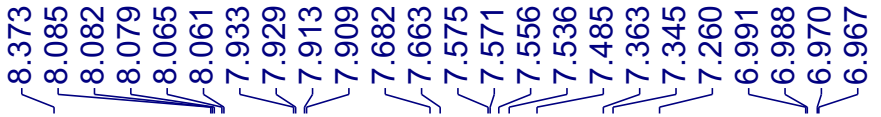
3xa

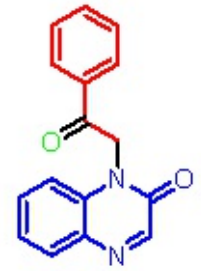
^{1}H NMR (400 MHz, $CDCl_3$)





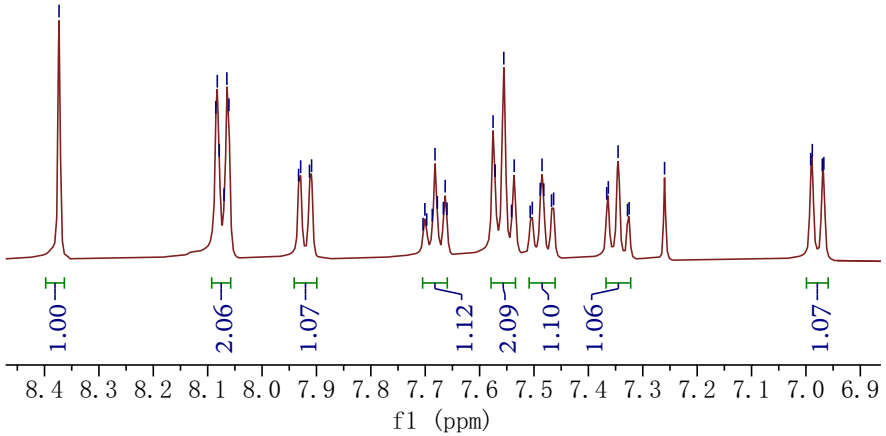

191.10
155.80
144.51
135.12
134.59
134.22
132.63
129.03
128.56
128.23
125.24
119.84
77.48
77.16
76.84
55.55
O
N
N
N
O
3xa
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

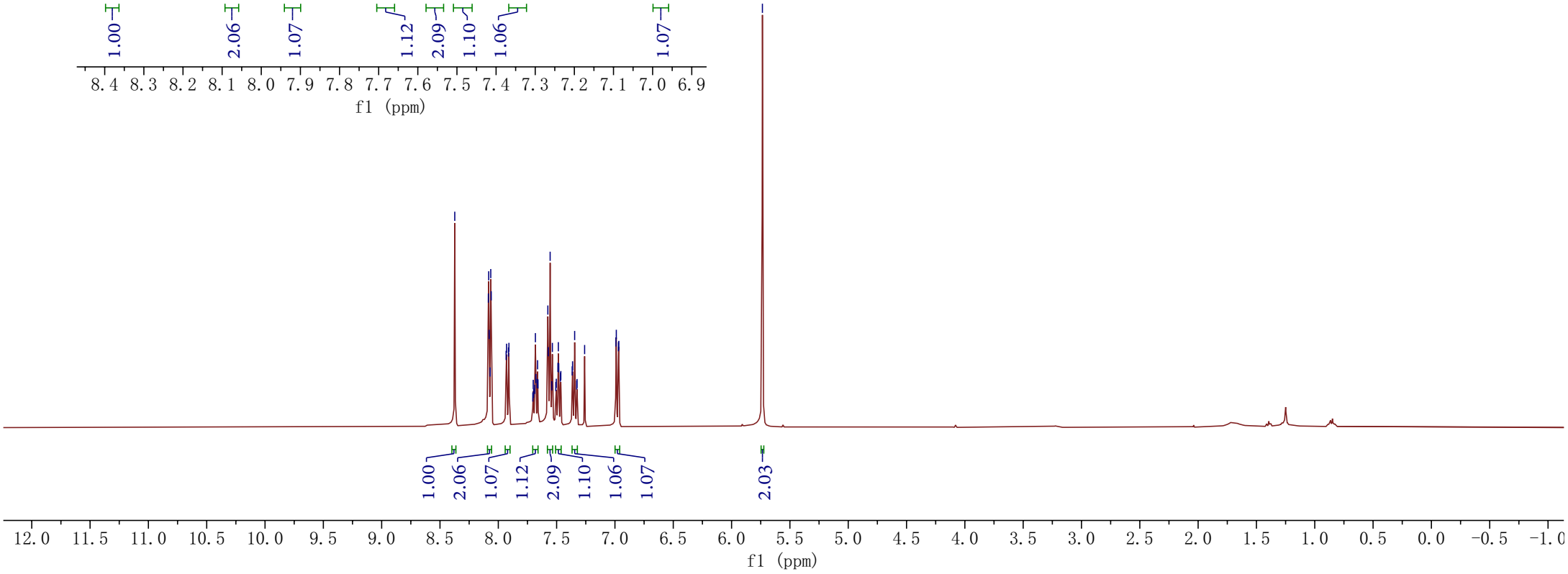


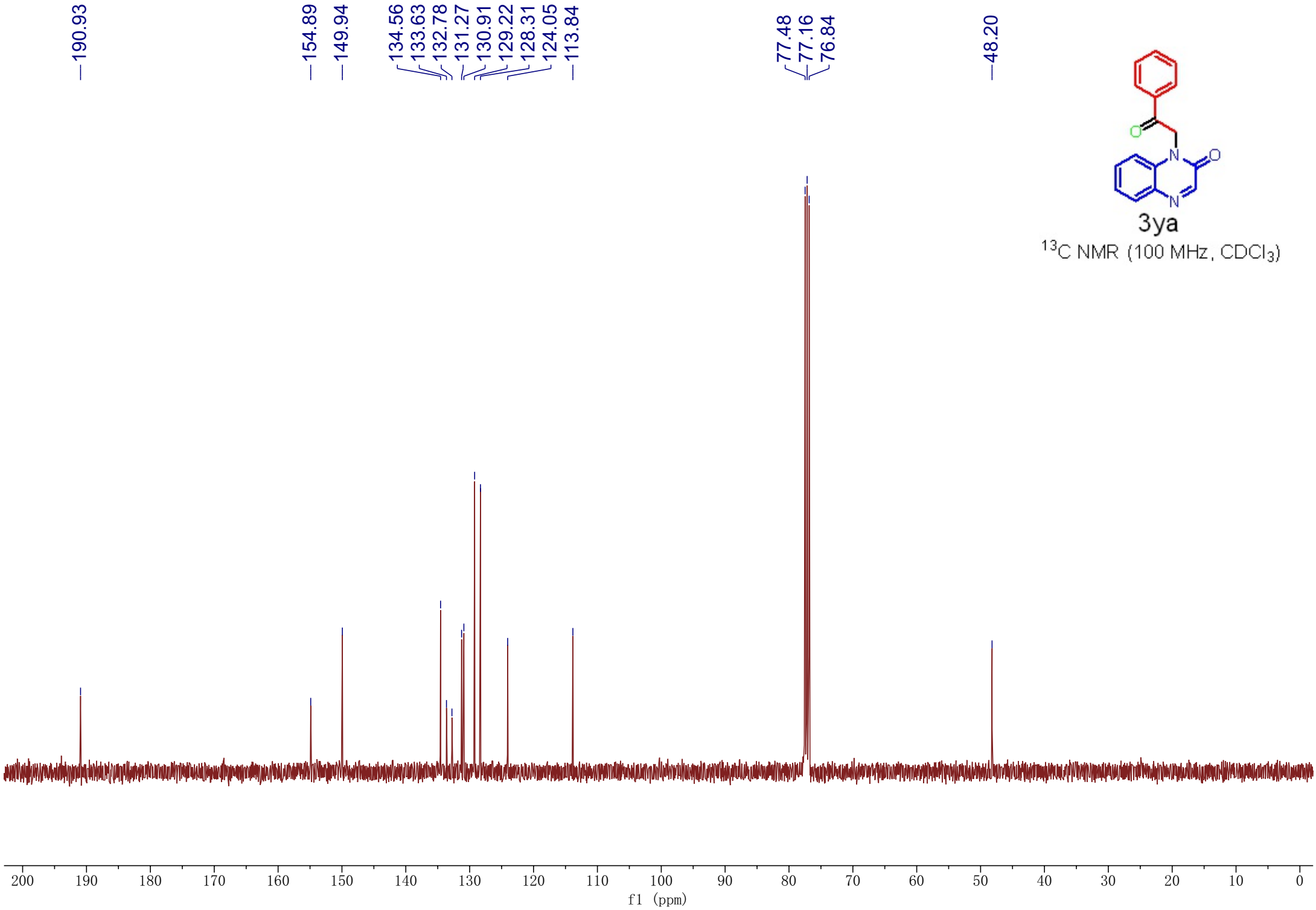


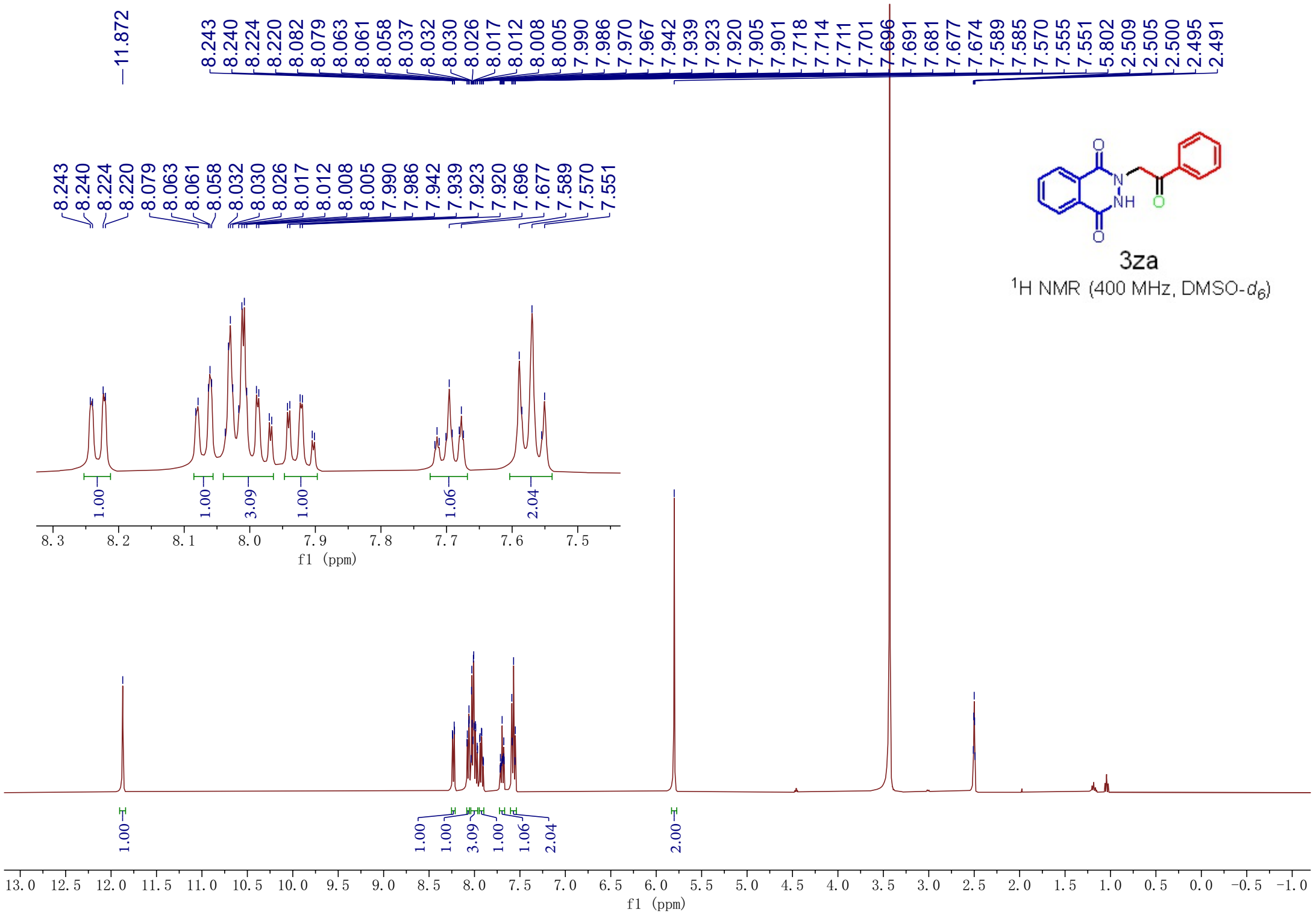
3ya

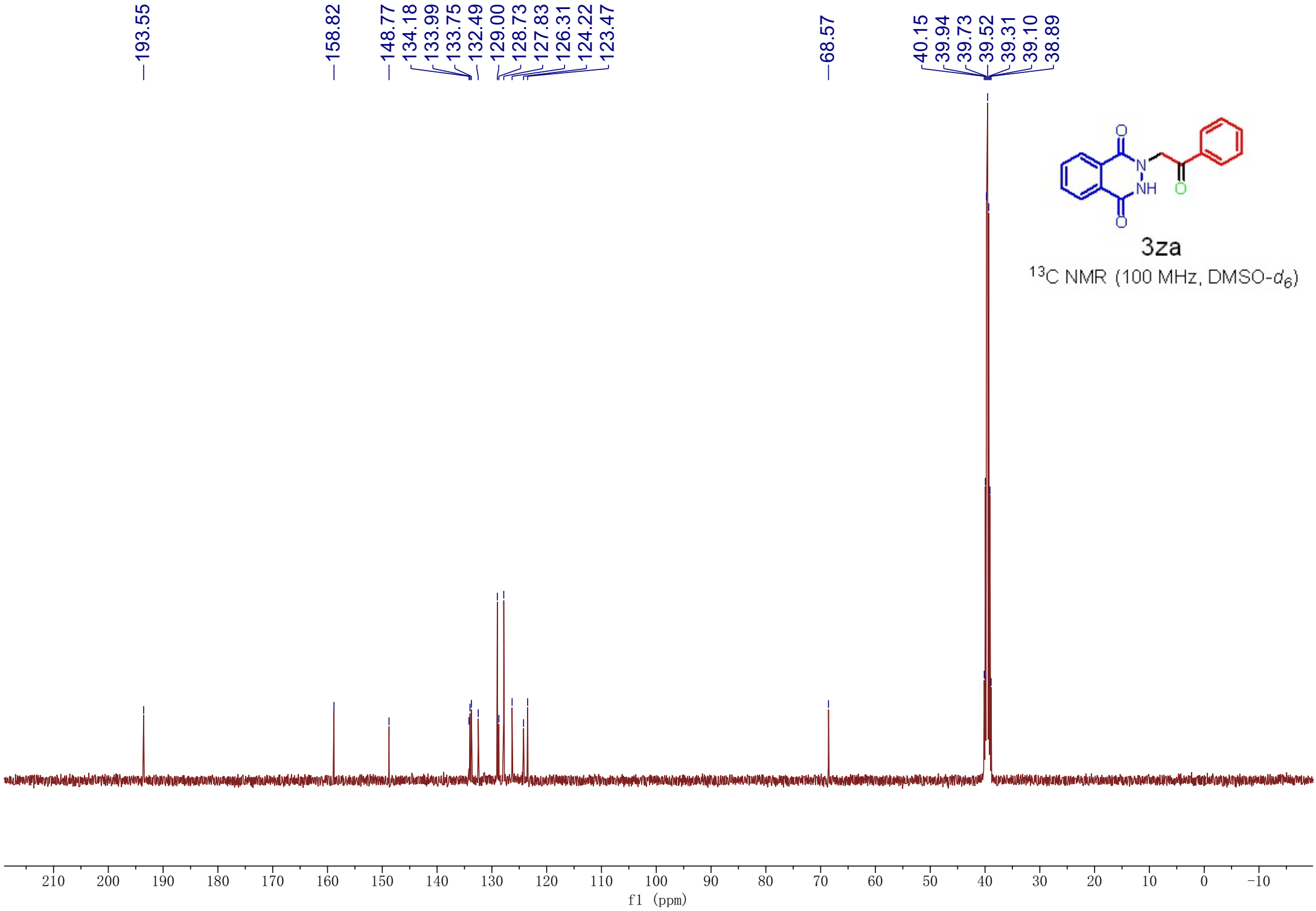
^{1}H NMR (400 MHz, $CDCl_3$)

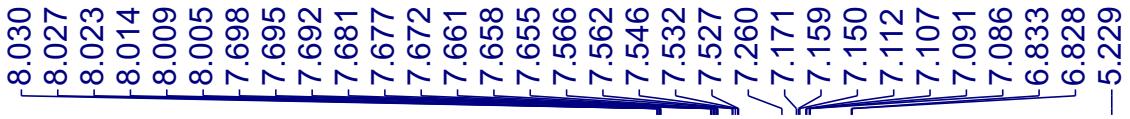





190.93
154.89
149.94
134.56
133.63
132.78
131.27
130.91
129.22
128.31
124.05
113.84
77.48
77.16
76.84
48.20
O
N
O
N
3ya
^{13}C NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

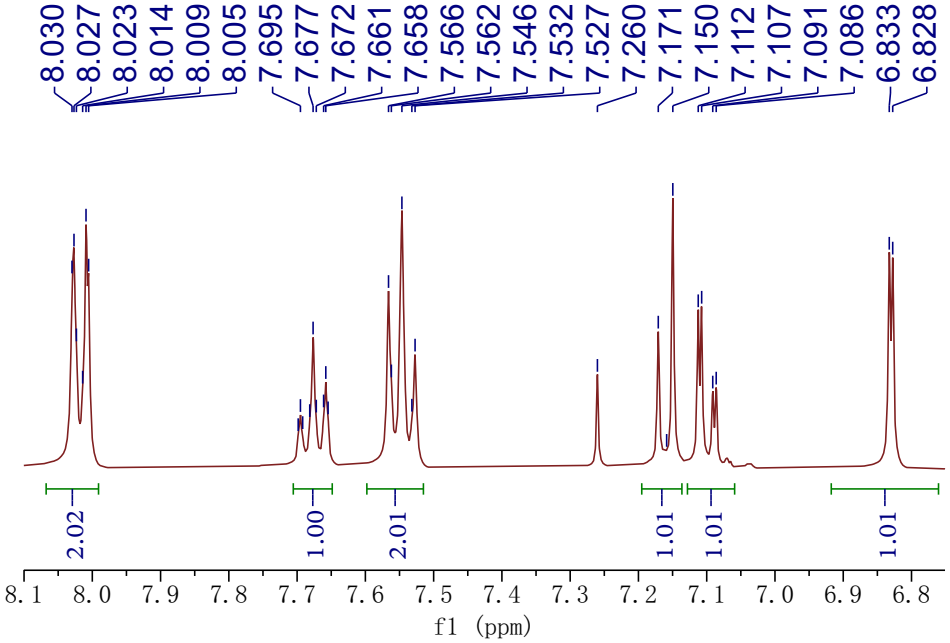

11.872
8.243
8.240
8.224
8.220
8.082
8.079
8.063
8.061
8.058
8.037
8.032
8.030
8.026
8.017
8.012
8.008
8.005
7.990
7.986
7.970
7.967
7.942
7.939
7.923
7.920
7.905
7.901
7.718
7.714
7.711
7.701
7.696
7.691
7.681
7.677
7.674
7.589
7.585
7.570
7.555
7.551
5.802
2.509
2.505
2.500
2.495
2.491
3za
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)
f1 (ppm)

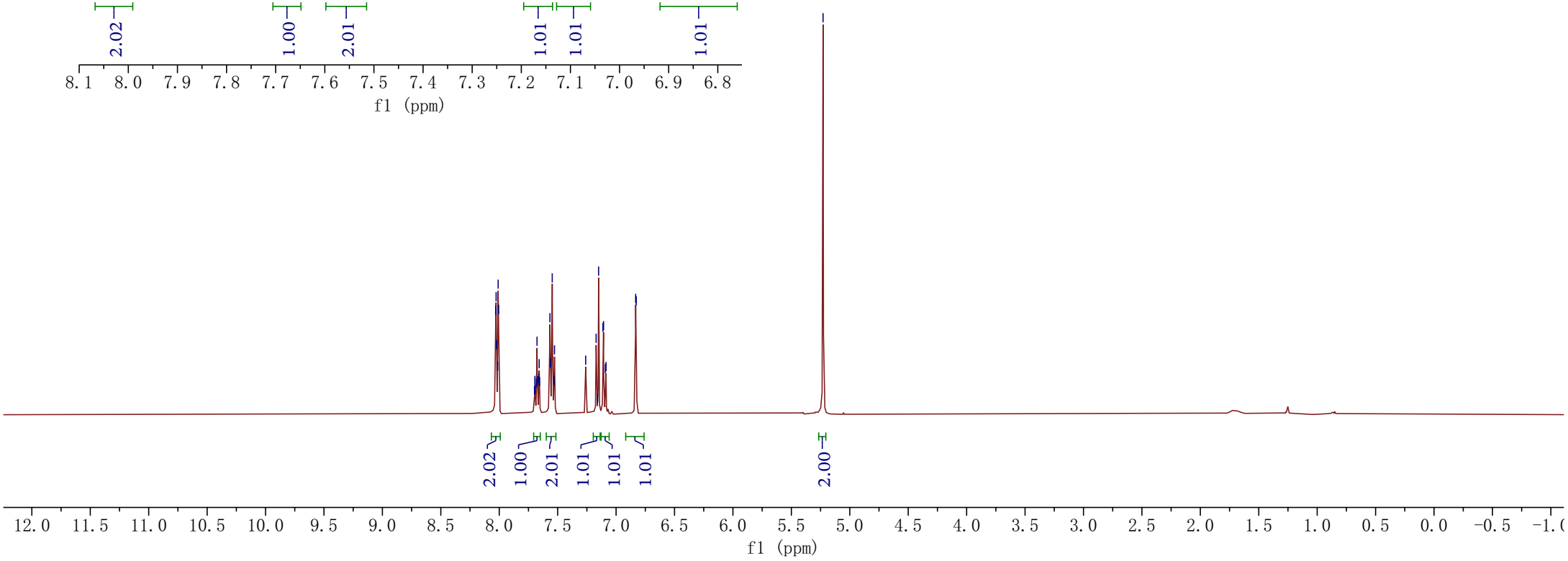

193.55
158.82
148.77
134.18
133.99
133.75
132.49
129.00
128.73
127.83
126.31
124.22
123.47
68.57
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
N
NH
O
O
3za
13C NMR (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

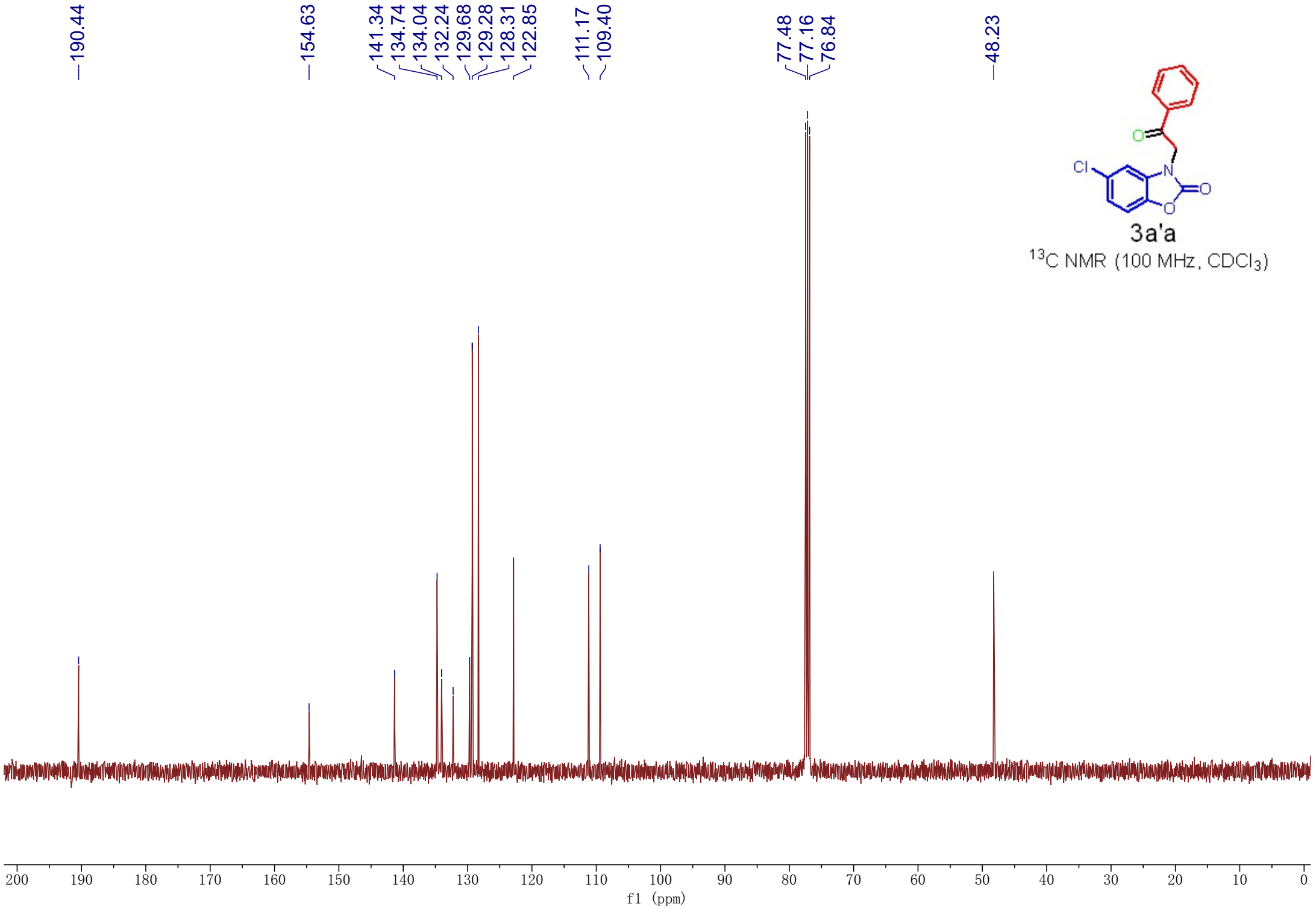


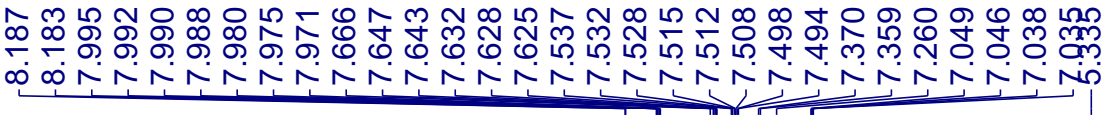
3a'a

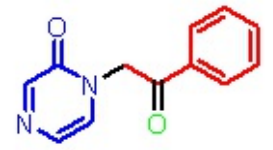
^{1}H NMR (400 MHz, $CDCl_3$)





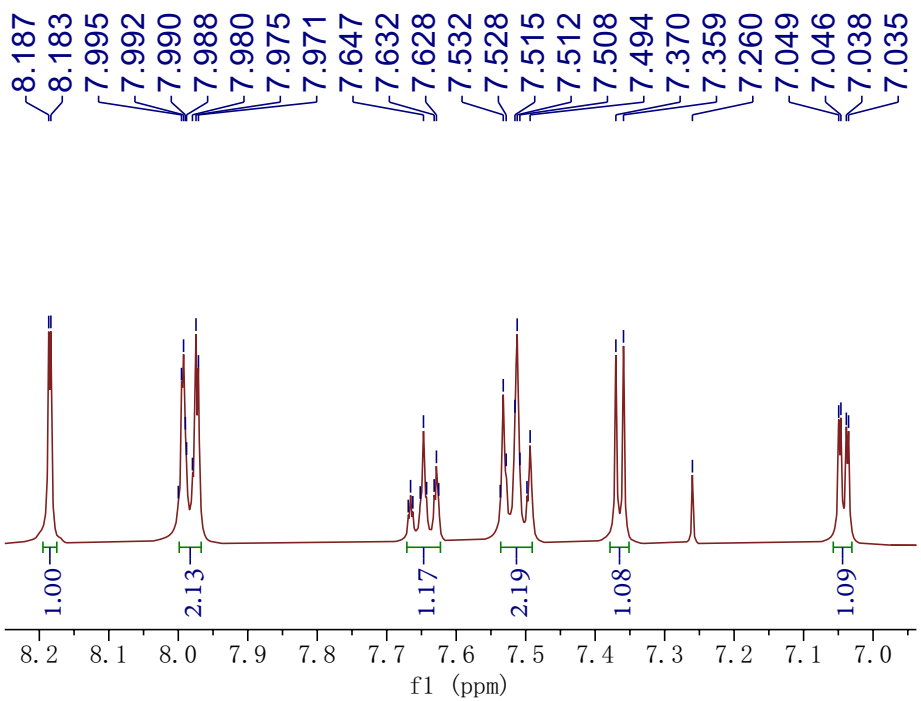

190.44
154.63
141.34
134.74
134.04
132.24
129.68
129.28
128.31
122.85
111.17
109.40
77.48
77.16
76.84
48.23
Cl
O
N
O
O
3a'a
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

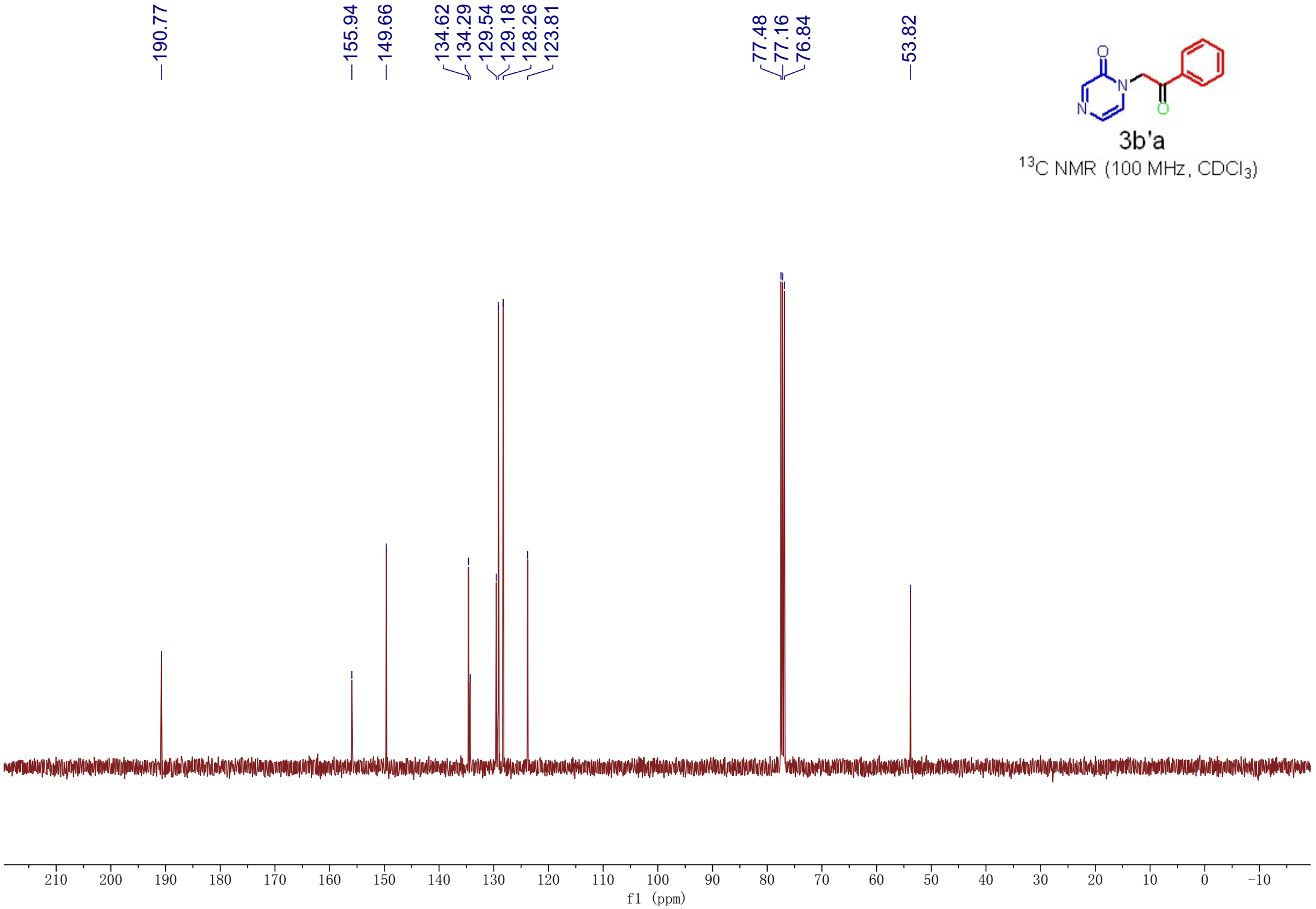


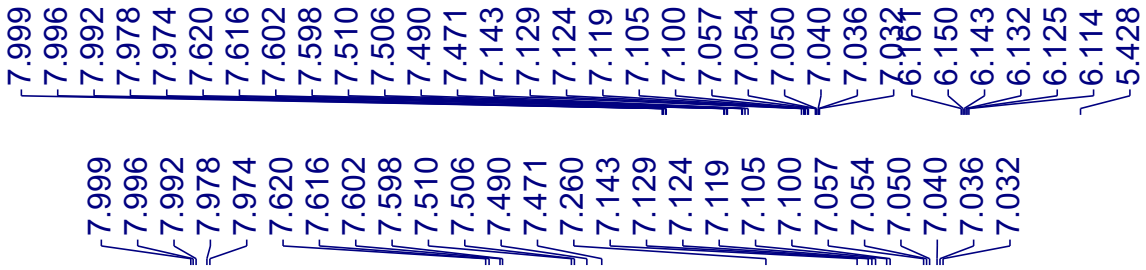


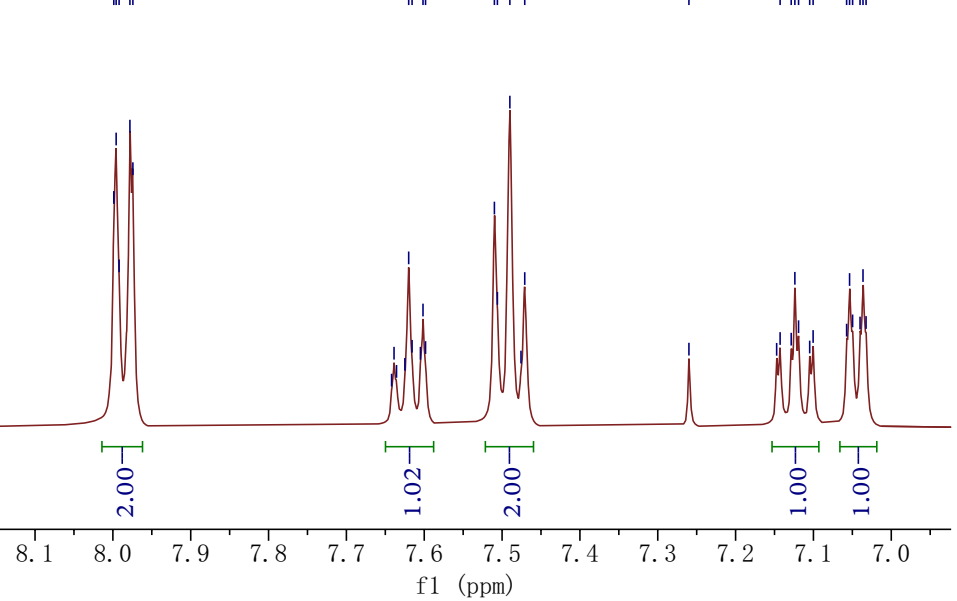
3b'a

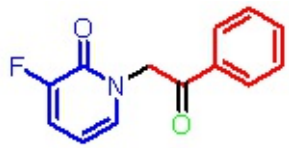
^{1}H NMR (400 MHz, $CDCl_3$)




190.77
155.94
149.66
134.62
134.29
129.54
129.18
128.26
123.81
77.48
77.16
76.84
53.82
O
N
N
O
3b'a
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

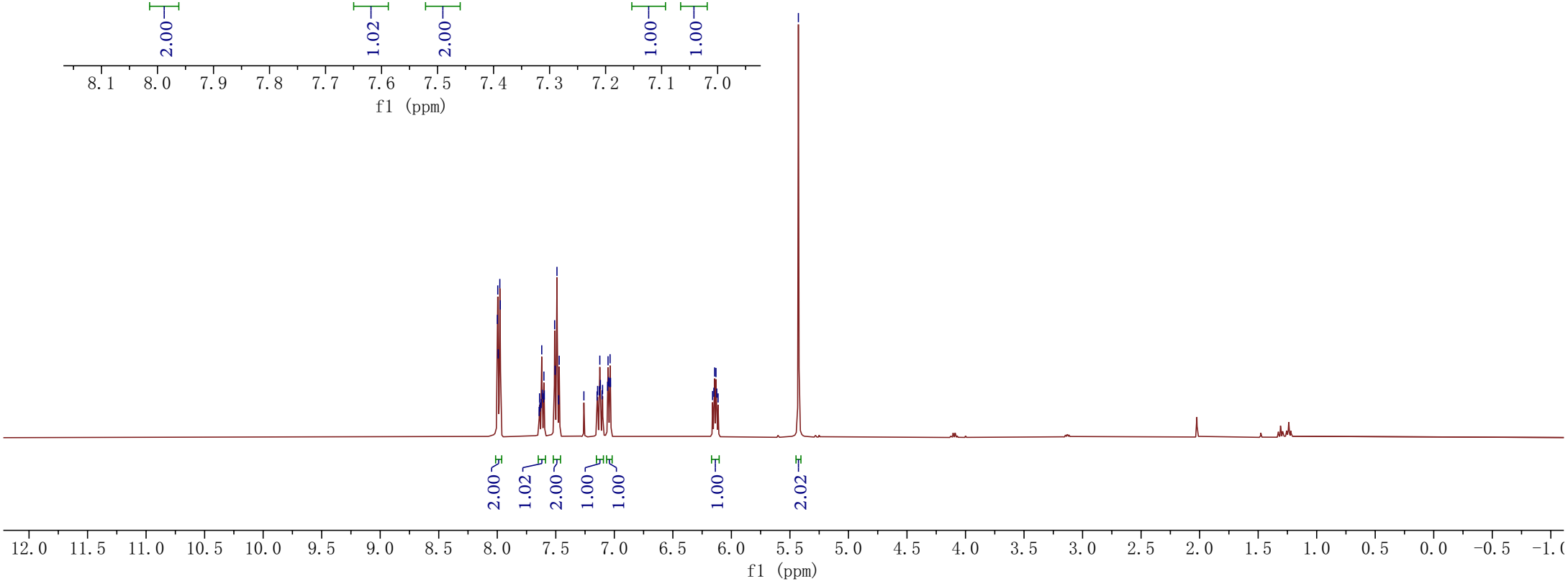


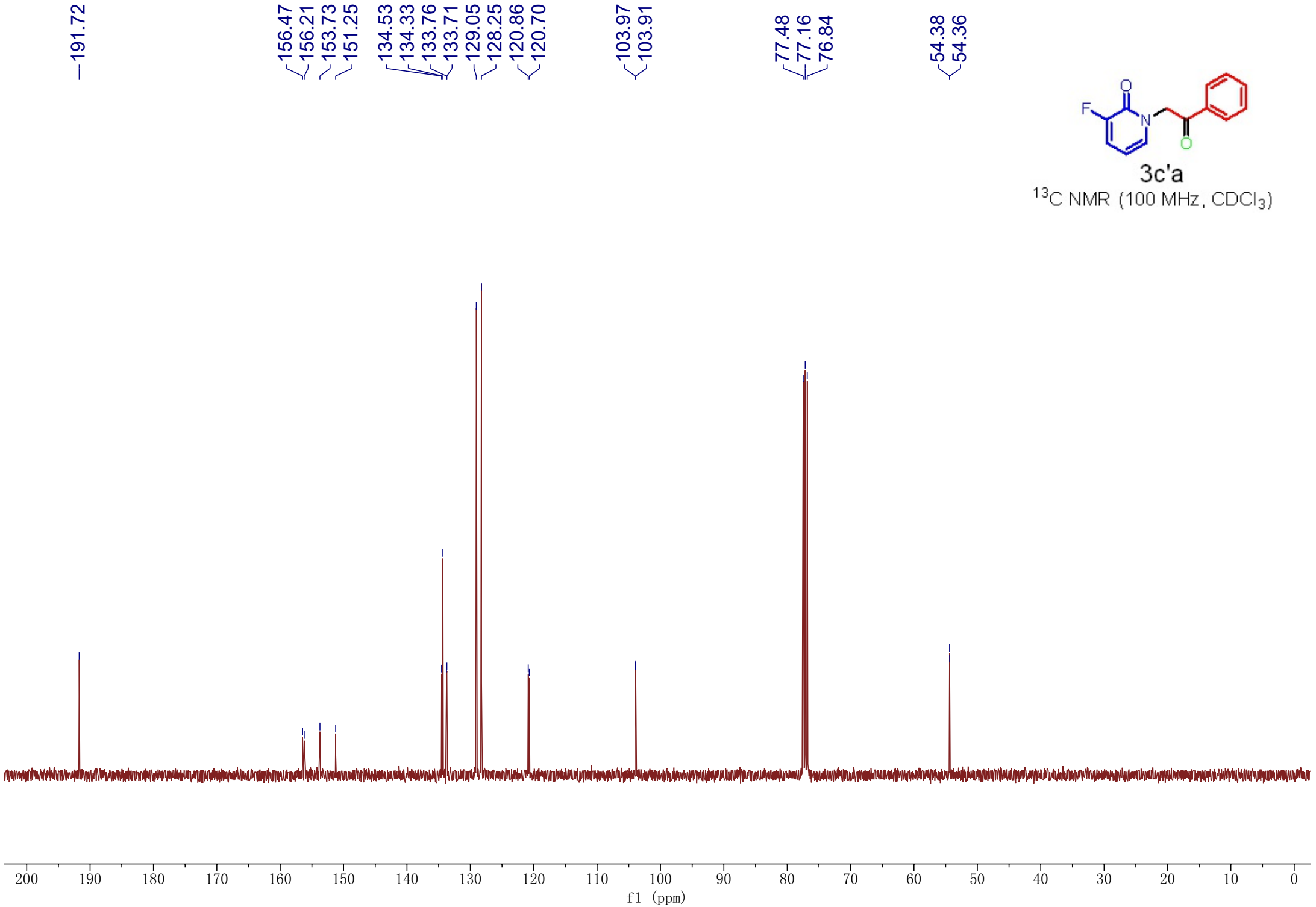


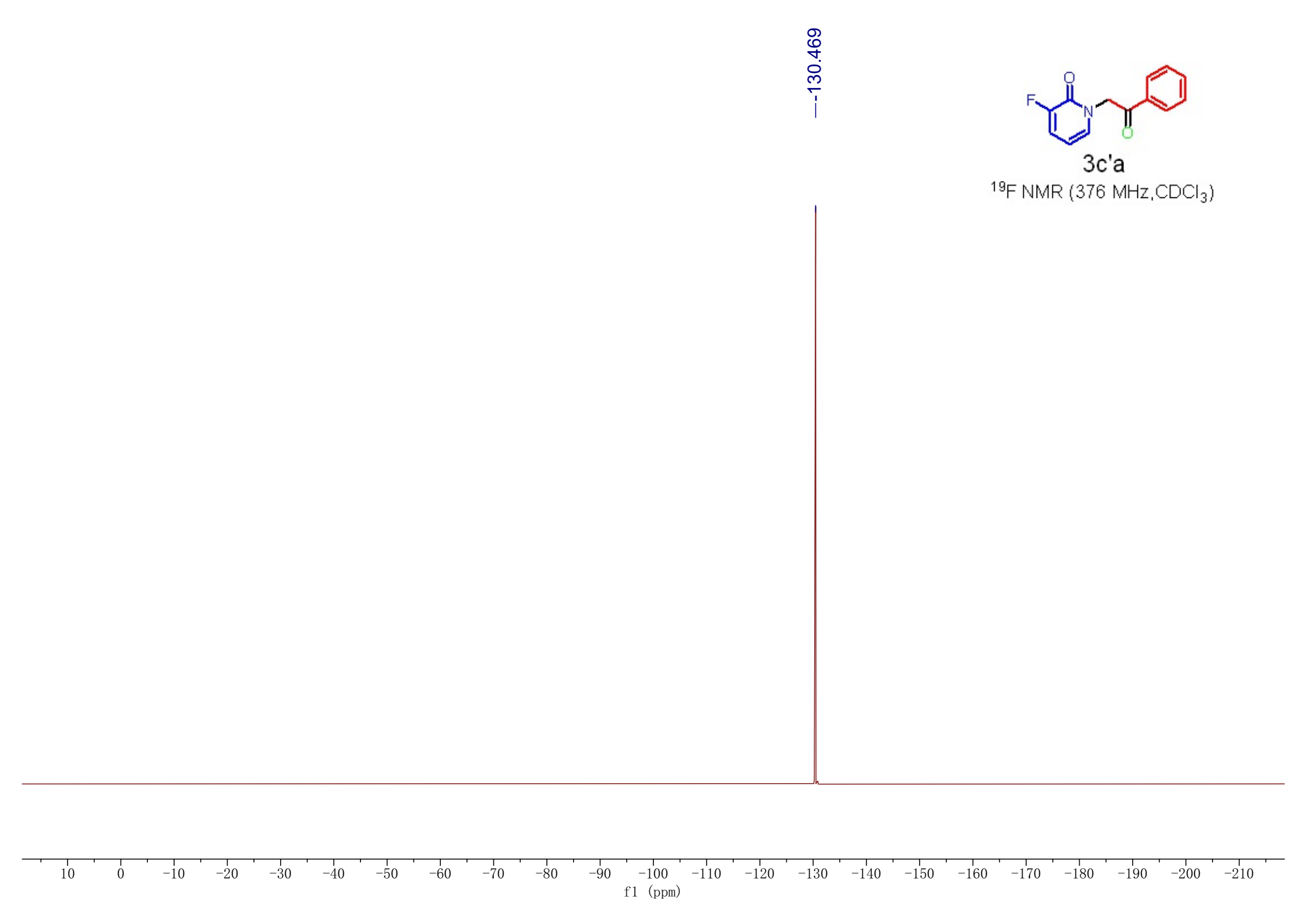


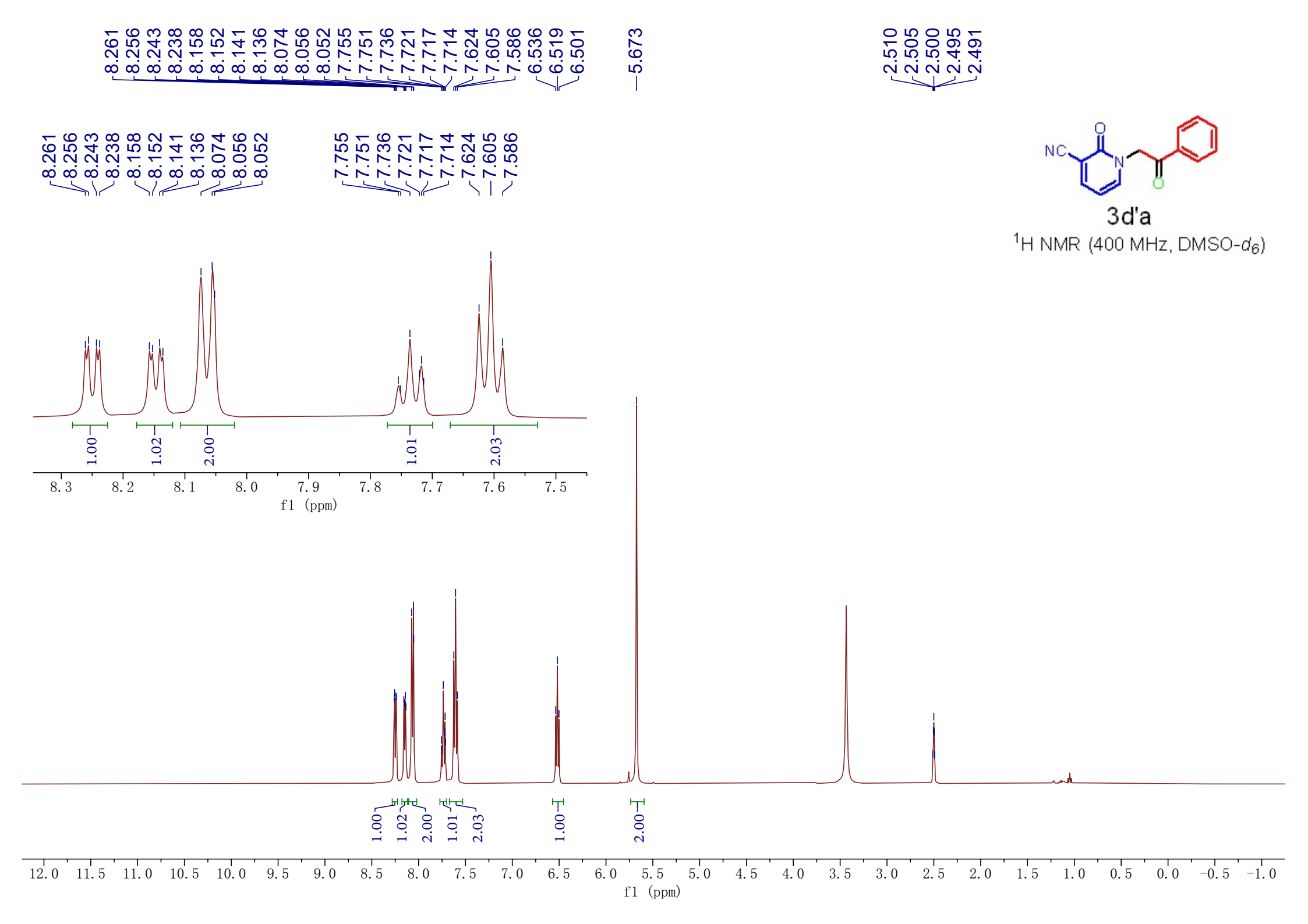
3c'a

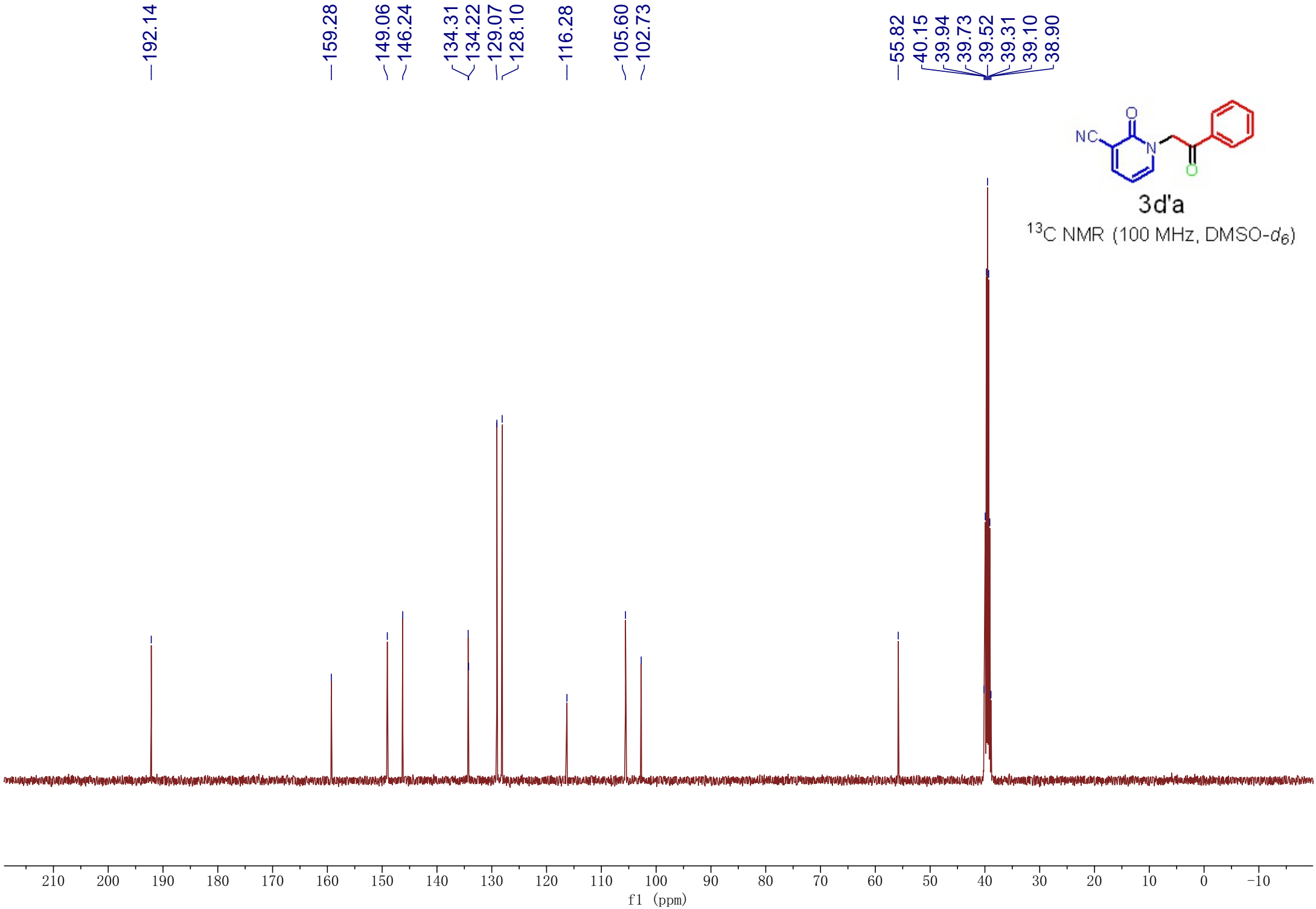
^{1}H NMR (400 MHz, $CDCl_3$)

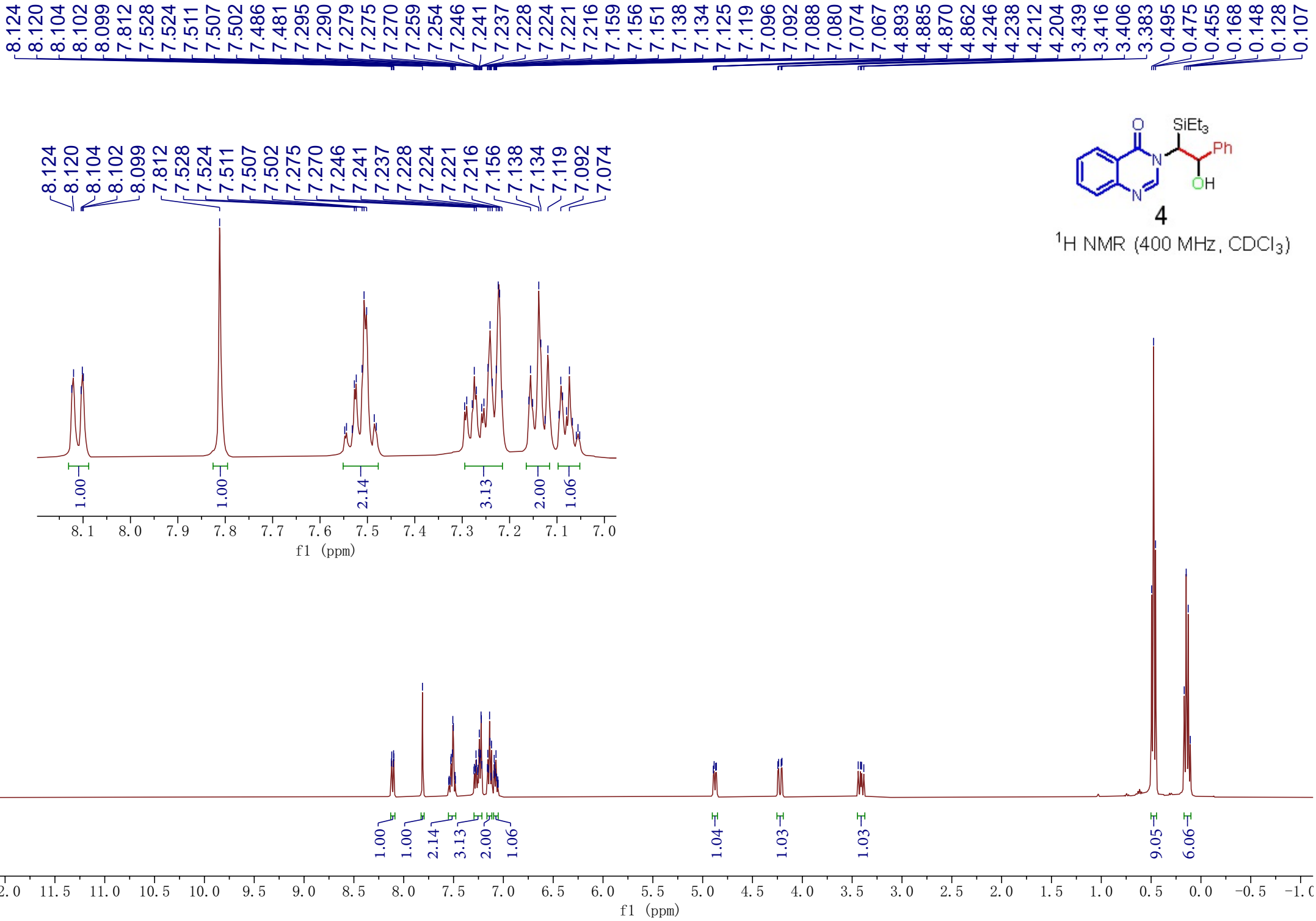


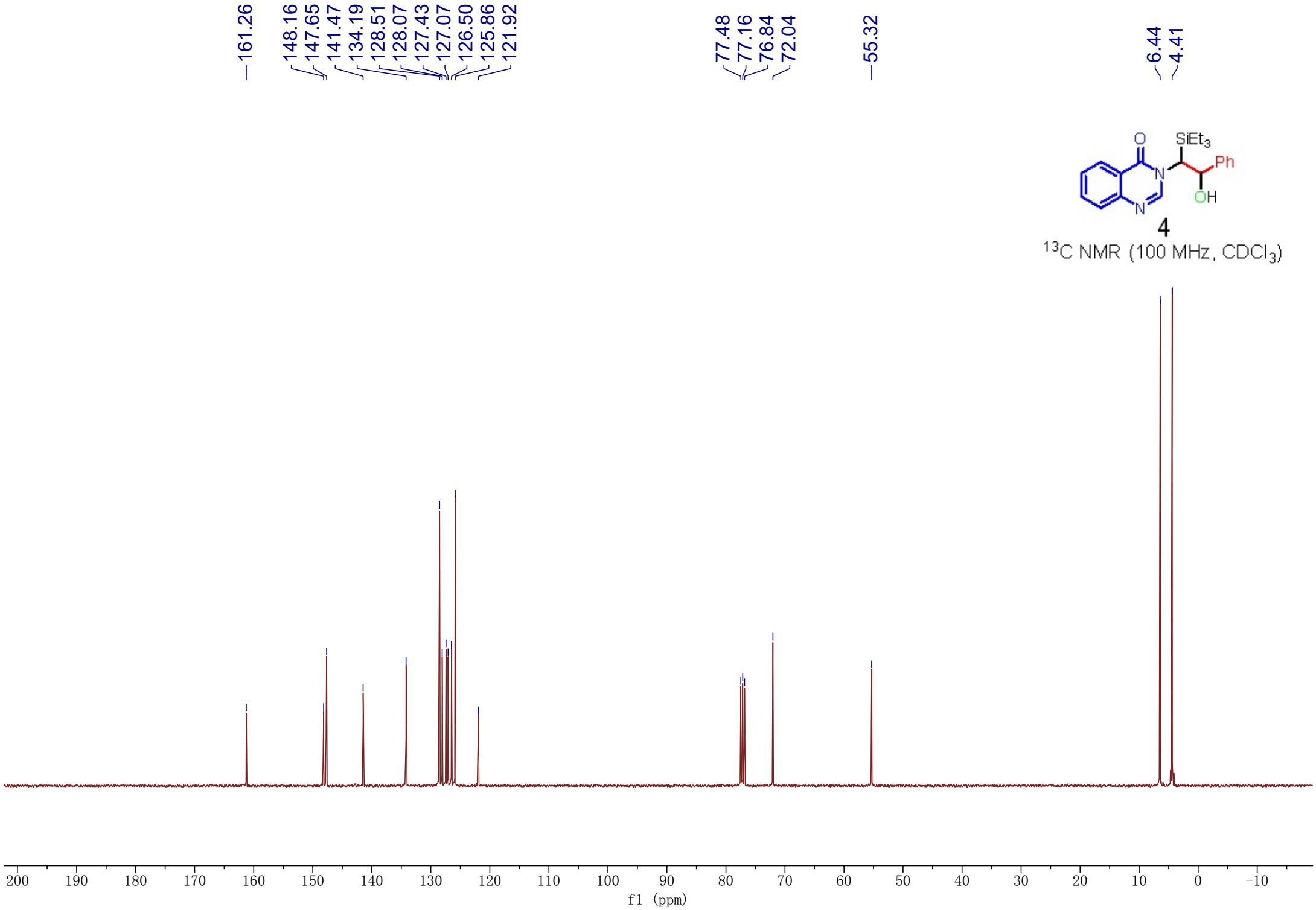

191.72
156.47
156.21
153.73
151.25
134.53
134.33
133.76
133.71
129.05
128.25
120.86
120.70
103.97
103.91
77.48
77.16
76.84
54.38
54.36
F
O
N
O
3c'a
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

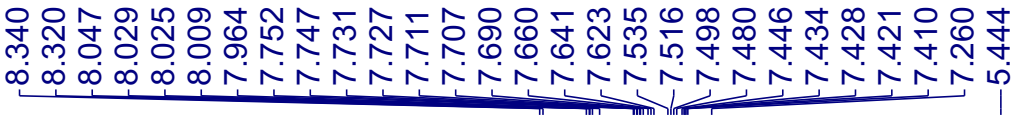

-130.469
F
O
N
O
3c'a
^{19}F NMR (376 MHz,$CDCl_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

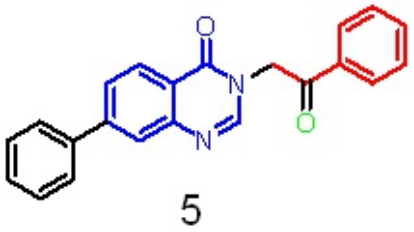

8.261
8.256
8.243
8.238
8.158
8.152
8.141
8.136
8.074
8.056
8.052
7.755
7.751
7.736
7.721
7.717
7.714
7.624
7.605
7.586
6.536
6.519
6.501
5.673
2.510
2.505
2.500
2.495
2.491
NC
O
N
O
3d'a
1H NMR (400 MHz, DMSO-d6)
1.00
1.02
2.00
1.01
2.03
1.00
2.00
f1 (ppm)


192.14
159.28
149.06
146.24
134.31
134.22
129.07
128.10
116.28
105.60
102.73
55.82
40.15
39.94
39.73
39.52
39.31
39.10
38.90
NC
O
N
O
3d'a
13C NMR (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.124 8.120 8.104 8.102 8.099 7.812 7.528 7.524 7.511 7.507 7.502 7.486 7.481 7.295 7.290 7.279 7.275 7.270 7.259 7.254 7.246 7.241 7.237 7.228 7.224 7.221 7.216 7.159 7.156 7.151 7.138 7.134 7.125 7.119 7.096 7.092 7.088 7.080 7.074 7.067 4.893 4.885 4.870 4.862 4.246 4.238 4.212 4.204 3.439 3.416 3.406 3.383 0.495 0.475 0.455 0.168 0.148 0.128 0.107
8.124 8.120 8.104 8.102 8.099 7.812 7.528 7.524 7.511 7.507 7.502 7.275 7.270 7.246 7.241 7.237 7.228 7.224 7.221 7.216 7.156 7.138 7.134 7.119 7.092 7.074
1.00 1.00 2.14 3.13 2.00 1.06
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
O SiEt3 Ph OH N N
4
1H NMR (400 MHz, CDCl3)
1.00 1.00 2.14 3.13 2.00 1.06 1.04 1.03 1.03 9.05 6.06
12.0 11.5 11.0 10.5 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 -1.0
f1 (ppm)

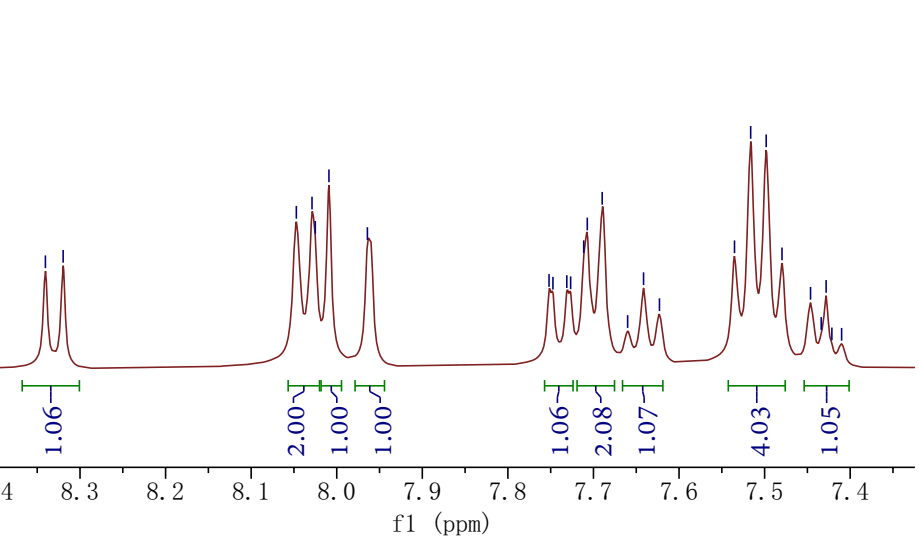

161.26
148.16
147.65
141.47
134.19
128.51
128.07
127.43
127.07
126.50
125.86
121.92
77.48
77.16
76.84
72.04
55.32
6.44
4.41
O
SiEt3
Ph
OH
N
N
4
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

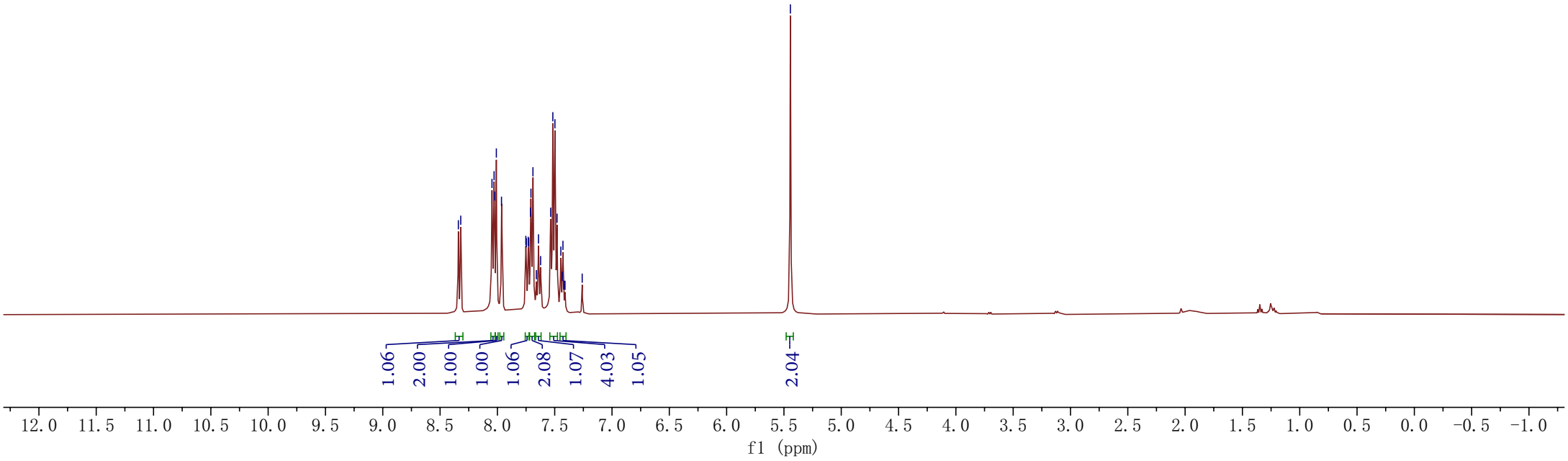


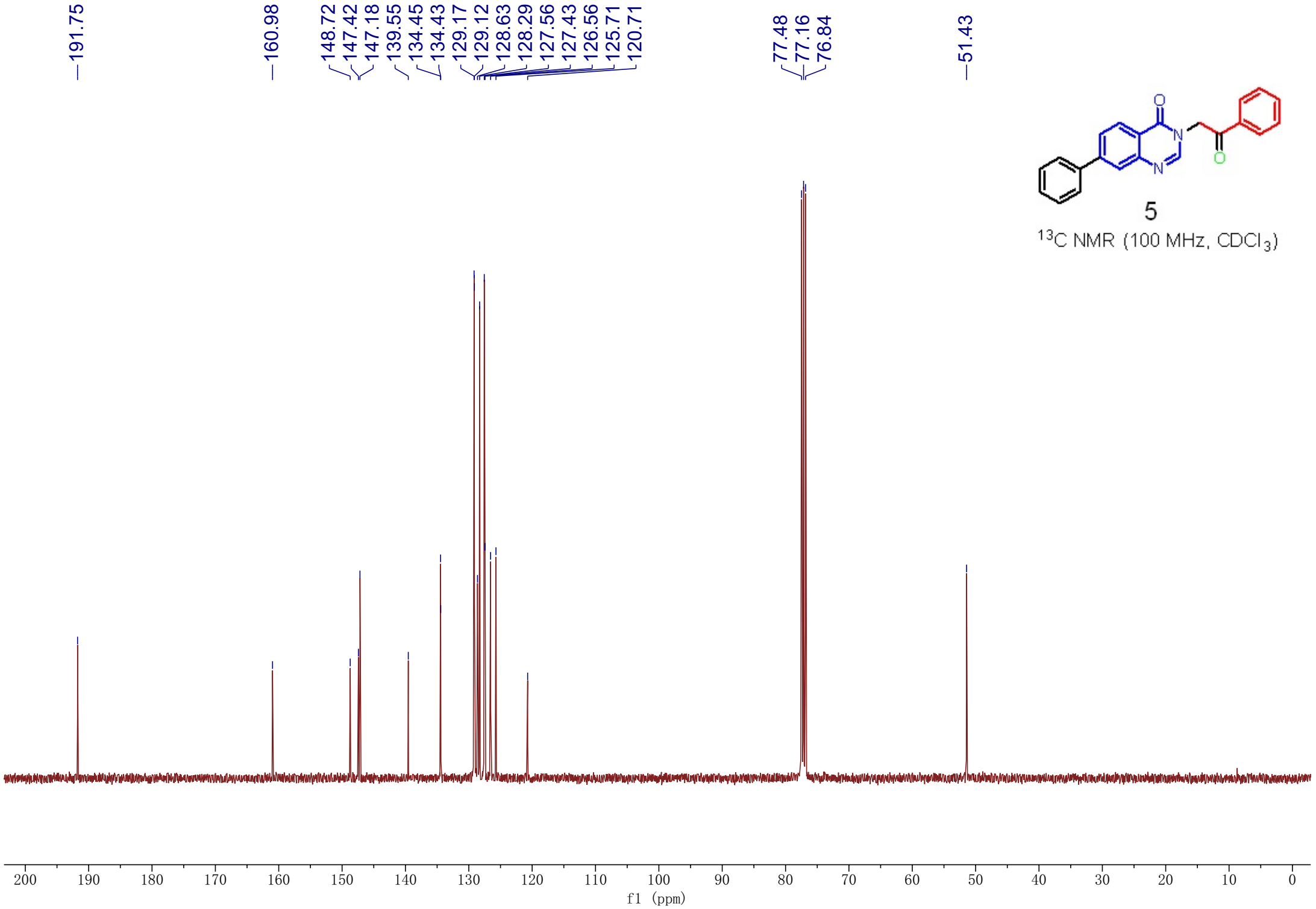


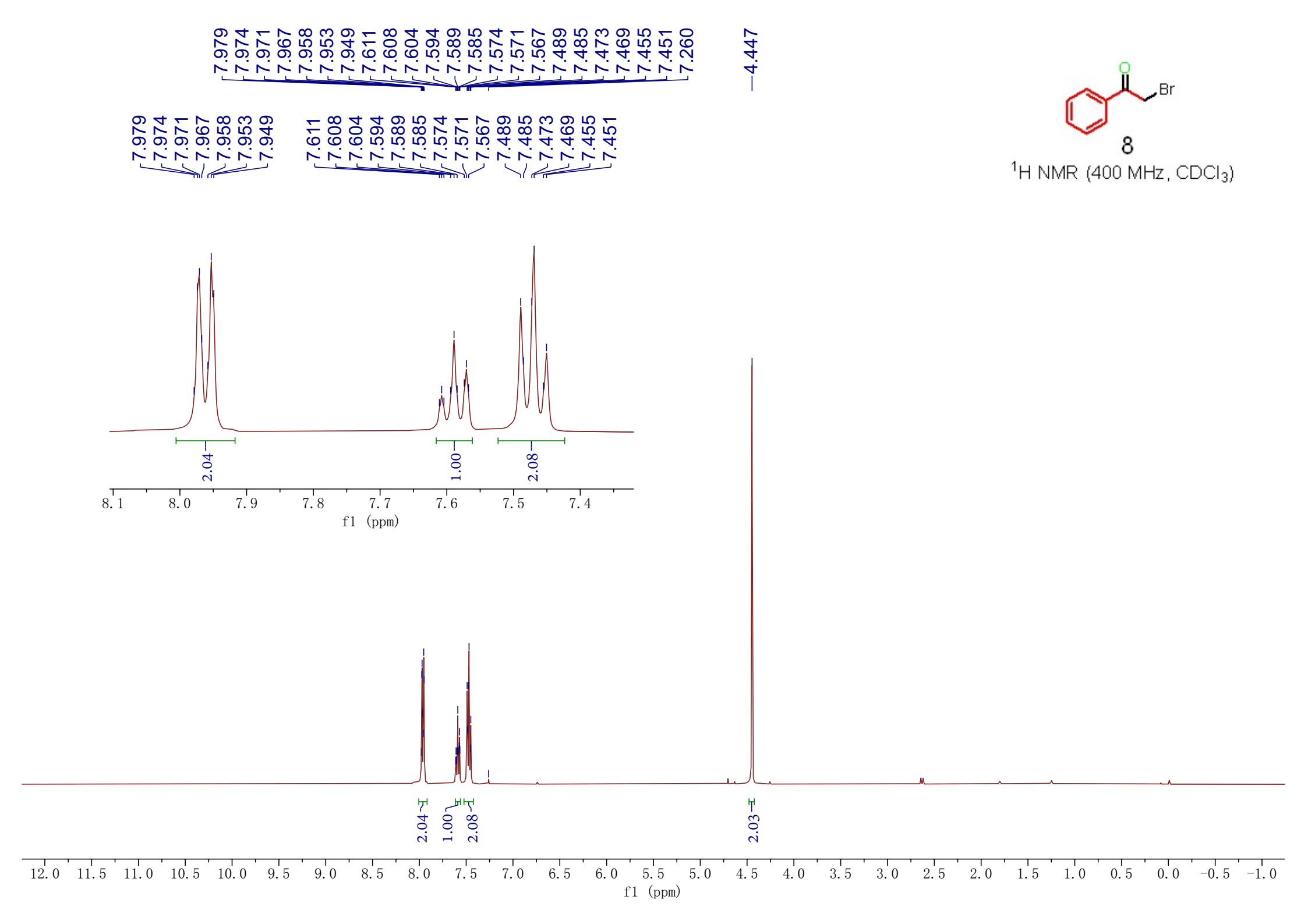
5

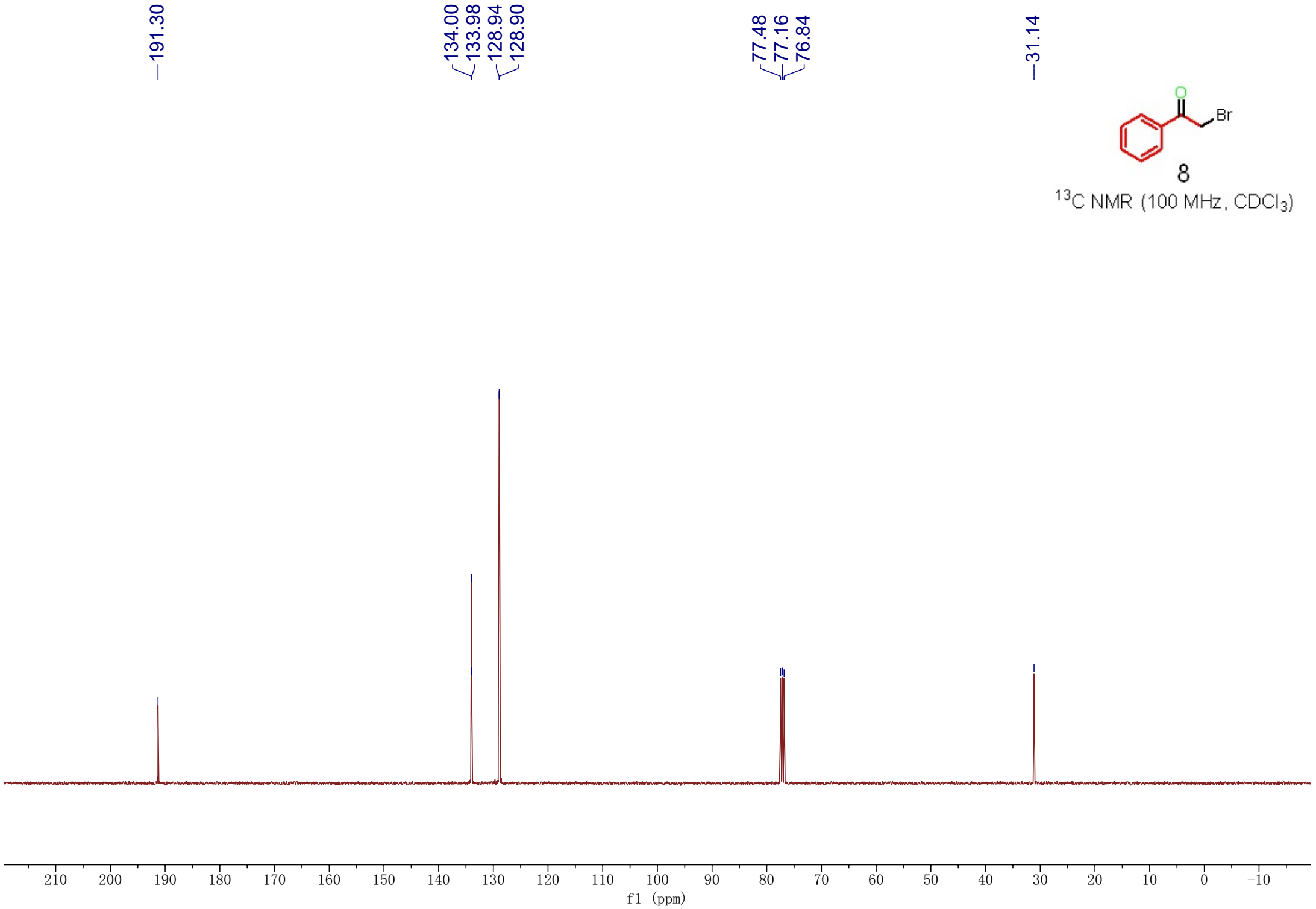
^{1}H NMR (400 MHz, $CDCl_3$)






191.75
160.98
148.72
147.42
147.18
139.55
134.45
134.43
129.17
129.12
128.63
128.29
127.56
127.43
126.56
125.71
120.71
77.48
77.16
76.84
51.43
O
N
N
O
5
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.979
7.974
7.971
7.967
7.958
7.953
7.949
7.611
7.608
7.604
7.594
7.589
7.585
7.574
7.571
7.567
7.489
7.485
7.473
7.469
7.455
7.451
7.260
4.447
Br
8
1H NMR (400 MHz, CDCl3)
2.04
1.00
2.08
f1 (ppm)
2.03
f1 (ppm)


191.30
134.00
133.98
128.94
128.90
77.48
77.16
76.84
31.14
Br
O
8
^{13}C NMR (100 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)