Supporting Information for

Visible-Light-mediated Radical Insertion/Cyclization Cascade Reaction: Synthesis of Phenanthridines and Isoquinolines from Isocyanides

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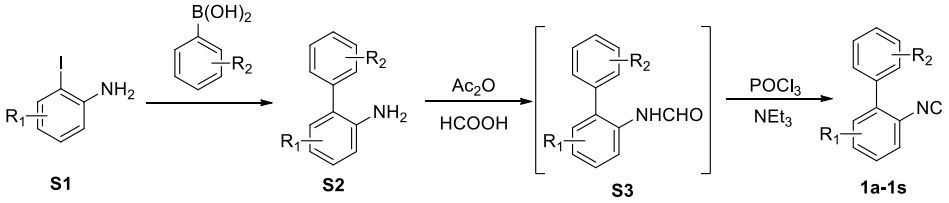
1. General information.

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. All syntheses of complex were carried out under argon atmosphere on Wattecs Parallel Reactor. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. Melting points were determined with a digital Koffer apparatus and were uncorrected. ^{1}H and ^{13}C NMR data were recorded on a 400 MHz spectrometer using $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High-resolution mass spectra (HRMS) were obtained on a FT-ICR spectrometer.

2. Preparation of starting materials.

Isocyanides **1a-1s** were prepared according to the previously reported procedure.[1]



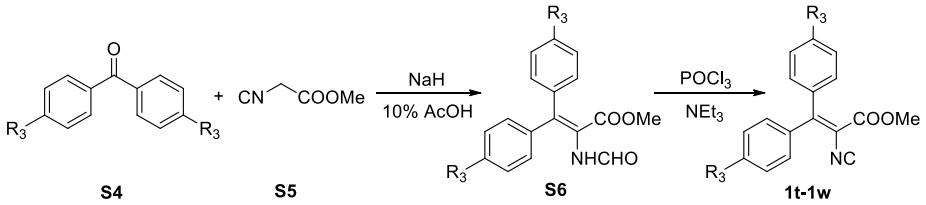
2-iodoaniline **S1** (10 mmol, 1.0 equiv), phenylboronic acid (12 mmol, 1.2 equiv) were added to a dry Schlenk flask. The flask was evacuated and backfilled with pure N_2 for 3 times. DME (10 mL) and aqueous solution of K_2CO_3 (2 M, 20 mL) were added with syringe and the mixture was stirred for 30 min at room temperature under N_2 atmosphere. To the stirred mixture, $PdCl_2(PPh_3)_2$ (0.2 mmol, 140 mg, 0.02 equiv) in DME (10 mL) was added with syringe at room temperature and the mixture was stirred at 80 °C for 12 hours under N_2 atmosphere (monitored by TLC). After the reaction was complete, the mixture was then cooled to room temperature and diluted with EtOAc (20 mL). The aqueous layer was extracted with EtOAc for 3 times (20 mL × 3). Then the organic phase was combinated and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 30:1) to give the amine **S2**.

To an oven-dried three necked flask equipped with a dropping funnel, **S2** (15 mmol, 1.0 equiv) and THF (30 mL) were added under N_2 atmosphere and cooled to 0 °C. Acetic formic

anhydride, which was prepared from the reaction of acetic anhydride (3.8 mL) with formic acid (1.7 mL) at 55 °C for 2 hours, was transferred to the dropping funnel and dropped to the solution of **S2** at 0 °C. After the addition was complete, the mixture was warmed to room temperature and stirred for 2 hours. Then, the mixture was quenched by sat. aqueous solution of $NaHCO_3$ and extracted with EtOAc three times. The extract was dried over Na_2SO_4 and concentrated under reduced pressure to give formamide **S3**. This material was used for the subsequent dehydration without further purification.

To an oven-dried three necked flask equipped with a dropping funnel, **S3 (**2 mmol, 1.0 equiv**) in** THF (5 mL), and NEt_3 (10 mmol, 5 equiv) were added under N_2 atmosphere . $POCl_3$ (4 mmol, 2 equiv) was added dropwise at 0 °C, the mixture was stirred for 2 hours at 0 °C and at room temperature over night after the addition was complete. Then, the mixture was quenched by sat. aqueous solution of $NaHCO_3$ and stirred for 1 hour. The mixture was extracted with CH_2Cl_2 three times, dried over $MgSO_4$ and evaporated under reduced pressure. The compound was purified by column chromatography (petroleum ether /EtOAc = 20/1) to give **1a-1s**.

Isocyanides **1t-1w** were prepared according to the previously reported procedure.[2]



S4 **S5** **S6** **1t-1w**

A mixture of benzophenone (**S4**, 10.0 mmol) and methyl isocyanoacetate (**S5**, 10.0 mmol) in THF (10 ml) was added dropwise to a suspension of NaH (60% in oil) (12.0 mmol, 1.2 equiv) in THF (10.0 ml) at room temperature. After stirring for 2 h at room temperature, 10% AcOH was added to the mixture at 0 °C until there is no hydrogen release. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 three times and the extract was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. Further recrystallization in MeOH afforded the product **S6**.

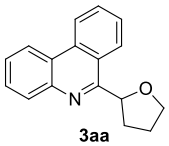
THF (10.0 mL), NEt_3 (40 mmol, 8.0 equiv) and **S6** (5.0 mmol) were added to an oven-dried three necked flask under N_2 atmosphere and cooled to 0°C. $POCl_3$ (10.0 mmol, 2.0 equiv) was added dropwise and the mixture was stirred for 2h at 0 °C after the addition was

completed. Then the mixture was quenched by sat. Na_2CO_3 and stirred for another 1 h. The mixture was extracted with CH_2Cl_2 three times, dried over Na_2SO_4 and concentracted under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 20/1) to give **1t**-**1w**.

3. General procedure for the radical insertion /cyclization reaction.

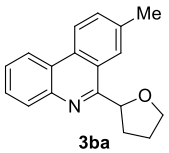
To a reaction tube equipped with a magnetic stir bar was added isocyanide (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (5 mol%, 7.5 mg), $KHCO_3$(0.4 mmol, 40 mg), the flask was evacuated and backfilled with Ar for 3 times. Then *t*-BuOOH (5.5 M in decane) (0.8 mmol, 0.15 ml), MeCN (1.0 mL), THF (3.0 mL) were added. The reaction was irradiated with a 18 W blue LED strip and stirred at ambient temperature from 12-18 hours. After it was complete, the reaction mixture was concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography to afford the desired phenanthridines or isoquinolines products.

4. Characterization data for all products.



3aa

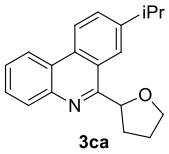
Compound **3aa** was obtained as a white solid in 68% yield according to the general procedure. Mp: 104−106°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.75 – 7.59 (m, 3H), 5.77 (t, *J* = 6.9 Hz, 1H), 4.20 (dd, *J* = 14.4, 7.5 Hz, 1H), 4.06 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.83 – 2.65 (m, 1H), 2.41 (dt, *J* = 12.8, 7.7 Hz, 1H), 2.27 – 2.05 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 143.2, 133.2, 130.4, 130.2, 128.4, 127.1, 126.8, 126.5, 124.8, 124.1, 122.3, 121.8, 79.6, 69.0, 29.9, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{16}NO$: 250.1226, found: 250.1232.



3ba

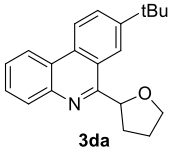
Compound **3ba** was obtained as colorless oil in 60% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (t, *J* = 8.1 Hz, 2H), 8.22 – 8.14 (m, 2H), 7.71 – 7.57 (m, 3H),

5.76 (t, *J* = 6.9 Hz, 1H), 4.19 (dd, *J* = 14.4, 7.5 Hz, 1H), 4.07 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.77 (ddd, *J* = 15.1, 13.0, 6.8 Hz, 1H), 2.60 (s, 3H), 2.45 – 2.34 (m, 1H), 2.27 – 2.05 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 158.8, 142.9, 137.1, 132.0, 131.1, 130.4, 128.0, 126.7, 125.9, 125.0, 124.2, 122.2, 121.6, 79.3, 69.0, 29.8, 26.0, 22.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO$: 264.1383, found: 264.1387.



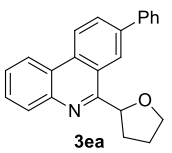
3ca

Compound **3ca** was obtained as colorless oil in 66% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.60 – 8.48 (m, 2H), 8.24 (d, *J* = 1.2 Hz, 1H), 7.76 – 7.58 (m, 3H), 5.79 (t, *J* = 6.9 Hz, 1H), 4.23 (dd, *J* = 14.4, 7.6 Hz, 1H), 4.08 (dd, *J* = 14.1, 7.9 Hz, 1H), 3.18 (m, *J* = 6.9 Hz, 1H), 2.71 (ddd, *J* = 15.4, 13.5, 6.9 Hz, 1H), 2.48 – 2.37 (m, 1H), 2.28 – 2.07 (m, 2H), 1.39 (dd, *J* = 6.9, 1.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.2, 147.8, 143.0, 131.5, 130.3, 129.4, 128.0, 126.7, 124.9, 124.2, 123.4, 122.4, 121.7, 79.6, 69.0, 34.4, 30.2, 26.0, 24.1, 23.9. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{20}H_{22}NO$: 292.1696, found: 292.1694.



3da

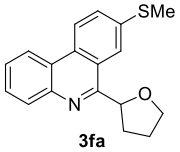
Compound **3da** was obtained as colorless oil in 70% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.57 (d, *J* = 8.7 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 1.8 Hz, 1H), 8.17 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.91 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.72 – 7.57 (m, 2H), 5.78 (t, *J* = 7.1 Hz, 1H), 4.26 (dd, *J* = 14.4, 7.6 Hz, 1H), 4.09 (dd, *J* = 14.2, 7.9 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.51 – 2.40 (m, 1H), 2.28 – 2.08 (m, 2H), 1.47 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.5, 150.0, 143.0, 131.1, 130.3, 128.6, 128.0, 126.7, 124.5, 124.0, 122.1, 121.9, 121.7, 80.0, 69.0, 35.1, 31.3, 30.5, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{21}H_{24}NO$: 306.1852, found: 306.1850.



3ea

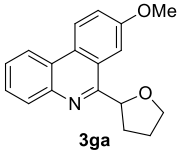
Compound **3ea** was obtained as a white solid in 65% yield according to the general procedure. Mp: 150−152°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.69 (d, *J* = 8.6 Hz, 1H), 8.64 (d, *J* =

1.3 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.06 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.73 (dd, *J* = 17.2, 7.3 Hz, 3H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 5.82 (t, *J* = 6.9 Hz, 1H), 4.21 (dd, *J* = 14.5, 7.5 Hz, 1H), 4.08 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.78 (dt, *J* = 15.2, 6.9 Hz, 1H), 2.44 (dt, *J* = 12.7, 7.7 Hz, 1H), 2.30 – 2.05 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.4, 143.2, 140.6, 139.9, 132.3, 130.4, 129.5, 129.0, 128.5, 127.7, 127.5, 127.0, 125.1, 124.7, 123.9, 122.9, 121.9, 79.7, 69.0, 30.1, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{23}H_{20}NO$: 326.1539, found: 326.1541.



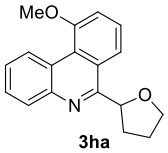
3fa

Compound **3fa** was obtained as a white solid in 61% yield according to the general procedure. Mp: 84−86°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.49 (dd, *J* = 16.9, 8.4 Hz, 2H), 8.26 (d, *J* = 1.8 Hz, 1H), 8.15 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.73 – 7.58 (m, 3H), 5.70 (t, *J* = 6.9 Hz, 1H), 4.18 (dd, *J* = 14.4, 7.6 Hz, 1H), 4.06 (dt, *J* = 14.2, 7.2 Hz, 1H), 2.75 (ddt, *J* = 13.6, 8.4, 6.9 Hz, 1H), 2.63 (s, 3H), 2.45 – 2.34 (m, 1H), 2.26 – 2.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 158.3, 142.9, 138.0, 130.7, 130.4, 129.2, 128.2, 127.0, 125.2, 123.9, 122.8, 122.7, 121.6, 79.8, 69.0, 29.9, 26.0, 15.8. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NOS$: 296.1104, found: 296.1102.



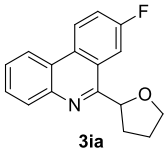
3ga

Compound **3ga** was obtained as a white solid in 84% yield according to the general procedure. Mp: 121−122°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.54 (d, *J* = 9.1 Hz, 1H), 8.48 – 8.42 (m, 1H), 8.19 – 8.12 (m, 1H), 7.82 (d, *J* = 2.5 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.45 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.70 (t, *J* = 6.9 Hz, 1H), 4.18 (dd, *J* = 14.5, 7.5 Hz, 1H), 4.06 (dd, *J* = 14.1, 7.8 Hz, 1H), 3.99 (s, 3H), 2.78 (ddd, *J* = 15.3, 13.5, 6.8 Hz, 1H), 2.48 – 2.33 (m, 1H), 2.29 – 2.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 158.4, 158.3, 142.4, 130.3, 127.6, 127.4, 126.9, 126.1, 124.2, 123.9, 121.3, 120.7, 106.9, 79.9, 68.9, 55.5, 29.7, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO_2$: 280.1332, found: 280.1331.



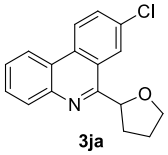
3ha

Compound **3ha** was obtained as colorless ropy oil in 40% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.75 – 7.58 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 5.77 (t, *J* = 6.8 Hz, 1H), 4.20 (dd, *J* = 14.2, 7.6 Hz, 1H), 4.14 (s, 3H), 4.06 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.81 – 2.70 (m, 1H), 2.41 (dt, *J* = 12.7, 7.3 Hz, 1H), 2.25 – 2.05 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 158.4, 143.8, 130.2, 127.8, 127.3, 126.9, 126.7, 123.8, 123.8, 118.6, 111.3, 79.6, 69.0, 55.8, 29.9, 25.9. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO_2$: 280.1332, found: 280.1334.



3ia

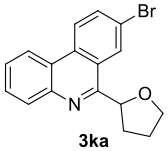
Compound **3ia** was obtained as a white solid in 56% yield according to the general procedure. Mp: 104−106°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 9.1, 5.4 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.13 (dd, *J* = 10.2, 2.6 Hz, 1H), 7.68 (dtd, *J* = 15.0, 7.1, 1.3 Hz, 2H), 7.58 (ddd, *J* = 9.0, 8.1, 2.6 Hz, 1H), 5.65 (t, *J* = 7.0 Hz, 1H), 4.18 (dd, *J* = 14.4, 7.6 Hz, 1H), 4.06 (dt, *J* = 14.3, 7.2 Hz, 1H), 2.83 – 2.71 (m, 1H), 2.46 – 2.36 (m, 1H), 2.27 – 2.08 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (162.42, 159.96, d, *J* = 246 Hz), 158.35, 142.87, 130.52, (129.97, 129.95, d, *J* = 2 Hz), 128.34, 127.26, (126.18, 126.09, d, *J* = 9 Hz), (124.82, 124.73, d, *J* = 9 Hz), 123.68, 121.61, (119.57, 119.33, d, *J* = 24 Hz), (111.56, 111.34, d, *J* = 22 Hz), 79.95, 68.98, 29.60, 25.93. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.75. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{15}FNO$: 268.1132, found: 268.1133.



3ja

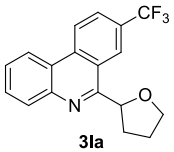
Compound **3ja** was obtained as colorless oil in 53% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.9 Hz, 1H), 8.48 – 8.43 (m, 2H), 8.16 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.73 (ddd, *J* = 9.3, 8.6, 1.7 Hz, 2H), 7.67 – 7.61 (m, 1H), 5.65 (t, *J* = 6.9 Hz, 1H), 4.15 (dd, *J* = 14.4, 7.6 Hz, 1H), 4.06 (td, *J* = 7.9, 6.3 Hz, 1H), 2.79 (ddt, *J* = 13.7, 8.4, 6.9 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.27 – 2.06 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 143.1, 133.1,

131.6, 130.8, 130.5, 128.8, 127.3, 126.1, 125.8, 124.0, 123.5, 121.7, 79.6, 69.0, 29.6, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{15}ClNO$: 284.0837, found: 284.0838.



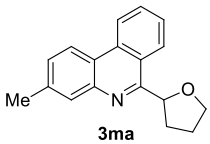
3ka

Compound **3ka** was obtained as colorless oil in 52% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.9 Hz, 1H), 8.47 (d, *J* = 8.7 Hz, 2H), 8.17 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.89 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.67 – 7.61 (m, 1H), 5.65 (t, *J* = 6.9 Hz, 1H), 4.16 (dd, *J* = 14.4, 7.5 Hz, 1H), 4.06 (dt, *J* = 14.2, 7.2 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.45 – 2.33 (m, 1H), 2.27 – 2.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 143.1, 133.4, 131.9, 130.5, 129.3, 128.9, 127.3, 126.2, 124.1, 123.5, 121.7, 121.3, 79.6, 69.0, 29.6, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{15}BrNO$: 328.0332, found: 328.0333.



3la

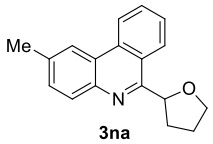
Compound **3la** was obtained as colorless oil in 58% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.71 (d, *J* = 8.7 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H), 8.26 – 8.17 (m, 1H), 8.04 – 7.97 (m, 1H), 7.82 – 7.74 (m, 1H), 7.72 – 7.65 (m, 1H), 5.72 (t, *J* = 6.9 Hz, 1H), 4.15 (dd, *J* = 14.5, 7.5 Hz, 1H), 4.07 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.82 (dt, *J* = 15.3, 7.0 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.28 – 2.09 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 143.8, 135.5, 130.6, 129.7, 128.8 (q, *J* = 30.0 Hz), 127.5, 126.1 (q, *J* = 3.0 Hz), 124.4 (q, *J* = 4.0 Hz), 124.3, 124.1 (q, *J* = 271.0 Hz), 123.3, 123.1, 122.2, 79.8, 69.1, 29.7, 26.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.14. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{15}F_3NO$: 318.1100, found: 318.1102.



3ma

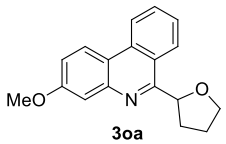
Compound **3ma** was obtained as colorless oil in 64% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.3 Hz, 1H), 8.43 (d, *J* = 8.3 Hz, 2H), 7.99 (s, 1H), 7.81 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.3, 1.3 Hz, 1H), 5.76 (t, *J* = 6.9 Hz, 1H), 4.20 (dd, *J* = 14.4, 7.6 Hz, 1H), 4.06 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.58 (s, 3H), 2.46 – 2.36 (m, 1H), 2.26 – 2.06 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2,

143.3, 138.6, 133.3, 130.2, 130.0, 128.6, 126.7, 126.4, 124.5, 122.1, 121.7, 121.6, 79.6, 68.96, 30.0, 26.0, 21.5. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO$: 264.1383, found: 264.1382.



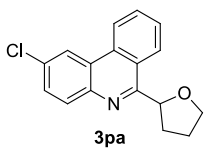
3na

Compound **3na** was obtained as colorless oil in 60% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.32 (s, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.71 – 7.63 (m, 1H), 7.53 (dd, *J* = 8.3, 1.5 Hz, 1H), 5.75 (t, *J* = 6.9 Hz, 1H), 4.20 (dd, *J* = 14.3, 7.6 Hz, 1H), 4.06 (dd, *J* = 14.2, 7.9 Hz, 1H), 2.73 (ddd, *J* = 15.4, 13.7, 6.9 Hz, 1H), 2.61 (s, 3H), 2.46 – 2.36 (m, 1H), 2.26 – 2.06 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2, 141.5, 136.7, 133.0, 130.1, 130.0, 127.0, 126.4, 124.8, 123.9, 122.3, 121.5, 79.6, 68.9, 30.0, 26.0, 22.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO$: 264.1383, found: 264.1381.



3oa

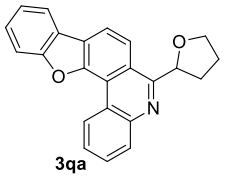
Compound **3oa** was obtained as pale yellow oil in 60% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.2 Hz, 1H), 8.43 (d, *J* = 9.0 Hz, 1H), 8.38 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.4 Hz, 1H), 7.61 (q, *J* = 6.5 Hz, 2H), 7.30 – 7.26 (m, 1H), 5.77 (t, *J* = 7.1 Hz, 1H), 4.25 (dd, *J* = 14.5, 7.5 Hz, 1H), 4.08 (dd, *J* = 14.2, 7.8 Hz, 1H), 3.99 (s, 3H), 2.64 (dt, *J* = 15.5, 7.0 Hz, 1H), 2.45 (dt, *J* = 12.6, 7.4 Hz, 1H), 2.26 – 2.08 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.0, 159.9, 144.9, 133.5, 130.3, 126.3, 126.1, 123.7, 123.0, 121.9, 118.1, 117.9, 110.2, 79.6, 69.0, 55.6, 30.5, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO_2$: 280.1332, found: 280.1334.



3pa

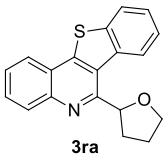
Compound **3pa** was obtained as a white solid in 68% yield according to the general procedure. Mp: 122−124°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.3 Hz, 1H), 8.50 (d, *J* = 2.2 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.74 (t, *J* =

7.6 Hz, 1H), 7.65 (dd, *J* = 8.7, 2.2 Hz, 1H), 5.76 (t, *J* = 6.9 Hz, 1H), 4.20 (dd, *J* = 14.3, 7.6 Hz, 1H), 4.07 (dd, *J* = 14.2, 7.9 Hz, 1H), 2.71 (dt, *J* = 15.3, 6.7 Hz, 1H), 2.43 (dt, *J* = 12.6, 7.6 Hz, 1H), 2.27 – 2.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.6, 141.7, 132.7, 132.3, 131.9, 130.6, 129.0, 127.9, 126.6, 125.2, 124.9, 122.4, 121.6, 79.4, 69.0, 29.9, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{15}ClNO$: 284.0837, found: 284.0841.



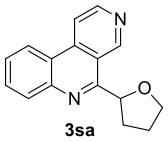
3qa

Compound **3qa** was obtained as a white solid in 78% yield according to the general procedure. Mp: 160−162°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 9.66 – 9.58 (m, 1H), 8.45 (d, *J* = 8.6 Hz, 1H), 8.32 – 8.26 (m, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.11 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.88 – 7.77 (m, 3H), 7.64 – 7.57 (m, 1H), 7.50 – 7.44 (m, 1H), 5.86 (t, *J* = 6.9 Hz, 1H), 4.24 (dd, *J* = 14.3, 7.7 Hz, 1H), 4.11 (td, *J* = 7.9, 6.3 Hz, 1H), 2.82 (ddt, *J* = 13.0, 8.5, 6.7 Hz, 1H), 2.55 – 2.41 (m, 1H), 2.30 – 2.10 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 158.9, 156.6, 152.4, 149.2, 143.6, 130.1, 128.7, 127.8, 127.3, 127.0, 125.0, 124.4, 123.5, 123.4, 122.2, 121.4, 121.0, 119.5, 112.1, 79.8, 69.1, 30.1, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{23}H_{18}NO_2$: 340.1332, found: 340.1331.



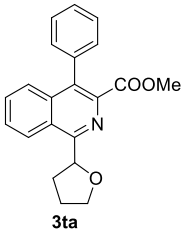
3ra

Compound **3ra** was obtained as a pale yellow solid in 40% yield according to the general procedure. Mp: 124−126°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.61 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.12 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.74 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.56 – 7.50 (m, 1H), 5.98 (dd, *J* = 7.2, 5.2 Hz, 1H), 4.21 (dd, *J* = 14.0, 7.8 Hz, 1H), 4.13 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.02 (ddd, *J* = 18.0, 8.4, 5.6 Hz, 1H), 2.49 – 2.37 (m, 1H), 2.33 – 2.10 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 155.7, 147.3, 143.7, 139.0, 135.1, 134.0, 130.4, 129.2, 127.5, 126.9, 126.2, 125.7, 125.5, 123.6, 122.9, 79.4, 69.0, 28.7, 25.8. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{19}H_{16}NOS$: 306.0947, found: 306.0948.



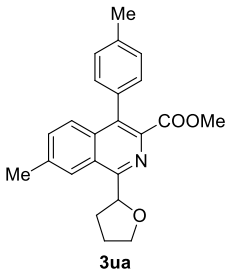
3sa

Compound **3sa** was obtained as colorless oil in 70% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.91 (d, *J* = 5.7 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.36 (d, *J* = 5.7 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.82 (dd, *J* = 11.3, 3.9 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 5.76 (t, *J* = 7.0 Hz, 1H), 4.20 (dd, *J* = 14.5, 7.5 Hz, 1H), 4.08 (dd, *J* = 14.3, 7.9 Hz, 1H), 2.75 (dt, *J* = 15.5, 7.1 Hz, 1H), 2.53 – 2.39 (m, 1H), 2.29 – 2.10 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 150.7, 148.2, 144.5, 138.1, 130.7, 130.5, 127.4, 122.4, 122.0, 119.8, 115.5, 79.8, 69.1, 30.1, 25.9. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{16}H_{15}N_2O$: 251.1179, found: 251.1181.



3ta

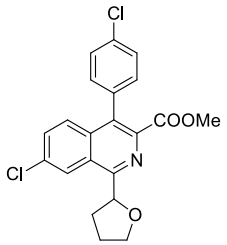
Compound **3ta** was obtained as colorless oil in 75% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.61 (m, 3H), 7.53 – 7.43 (m, 3H), 7.38 – 7.29 (m, 2H), 5.73 (t, *J* = 7.0 Hz, 1H), 4.16 (dd, *J* = 14.5, 7.5 Hz, 1H), 4.05 (td, *J* = 7.9, 6.1 Hz, 1H), 3.67 (s, 3H), 2.81 (ddd, *J* = 15.6, 12.5, 7.2 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.29 – 2.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 158.8, 140.4, 136.3, 136.2, 133.5, 130.3, 129.8, 129.6, 128.2, 128.2, 128.1, 127.9, 127.2, 127.0, 125.7, 79.8, 69.0, 52.2, 29.8, 26.1. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{21}H_{20}NO_3$: 334.1438, found: 334.1437.



3ua

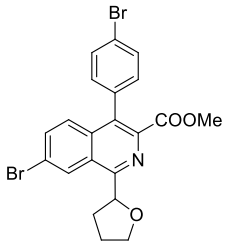
Compound **3ua** was obtained as colorless oil in 85% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.44 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 5.72 (t, *J* = 7.0 Hz, 1H), 4.14 (dd, *J* = 14.5, 7.5 Hz, 1H),

4.04 (td, *J* = 7.9, 6.0 Hz, 1H), 3.70 (s, 3H), 2.83 (dt, *J* = 15.5, 7.1 Hz, 1H), 2.57 (s, 3H), 2.45 (s, 3H), 2.43 – 2.33 (m, 1H), 2.30 – 2.19 (m, 1H), 2.19 – 2.07 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 167.9, 157.6, 139.5, 138.4, 137.4, 134.6, 133.7, 133.3, 132.4, 129.6, 129.4, 128.9, 128.8, 127.5, 126.9, 124.5, 79.5, 69.0, 52.2, 29.5, 26.2, 22.1, 21.4. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{23}H_{24}NO_3$: 362.1751, found: 362.1750.



3va

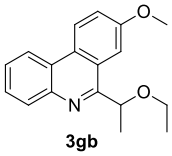
Compound **3va** was obtained as pale yellow oil in 60% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.55 (d, *J* = 1.9 Hz, 1H), 7.58 (dd, *J* = 9.1, 2.0 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.26 – 7.20 (m, 2H), 5.63 (t, *J* = 7.0 Hz, 1H), 4.13 (dd, *J* = 14.6, 7.5 Hz, 1H), 4.05 (td, *J* = 7.9, 6.2 Hz, 1H), 3.72 (s, 3H), 2.79 (ddd, *J* = 15.6, 12.6, 7.3 Hz, 1H), 2.46 – 2.34 (m, 1H), 2.28 – 2.09 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 167.2, 158.4, 140.4, 136.9, 134.6, 134.6, 134.3, 134.1, 132.3, 131.5, 131.1, 130.8, 128.6, 128.4, 128.0, 125.2, 79.8, 69.1, 52.4, 29.7, 26.1. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{21}H_{18}Cl_2NO_3$: 402.0658, found: 402.0657.



3wa

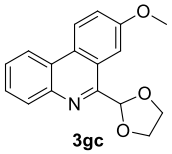
Compound **3wa** was obtained as pale yellow oil in 55% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.73 (d, *J* = 1.9 Hz, 1H), 7.71 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.63 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.23 – 7.13 (m, 2H), 5.63 (t, *J* = 7.0 Hz, 1H), 4.12 (dd, *J* = 14.7, 7.4 Hz, 1H), 4.05 (dt, *J* = 14.1, 7.1 Hz, 1H), 3.72 (s, 3H), 2.80 (ddd, *J* = 15.5, 12.7, 7.3 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.28 – 2.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 167.2, 158.4, 140.4, 134.7, 134.6, 134.1, 132.3, 131.6, 131.4, 131.2, 128.5, 128.4, 128.3, 123.1, 122.5, 79.7, 69.1, 52.4, 29.6, 26.1. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{21}H_{18}Br_2NO_3$:

489.9648, found: 489.9649.



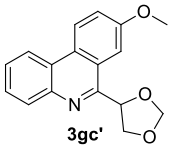
3gb

Compound **3gb** was obtained as colorless oil in 71% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 9.1 Hz, 1H), 8.50 – 8.45 (m, 1H), 8.37 (d, *J* = 2.6 Hz, 1H), 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.64 (ddt, *J* = 8.3, 7.0, 3.6 Hz, 2H), 7.48 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.18 (q, *J* = 6.8 Hz, 1H), 3.99 (s, 3H), 3.59 (tt, *J* = 14.0, 7.0 Hz, 1H), 3.52 – 3.39 (m, 1H), 1.78 (d, *J* = 6.8 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0, 158.3, 142.5, 129.9, 127.9, 127.6, 127.0, 125.3, 124.2, 123.9, 121.4, 121.4, 106.7, 82.1, 64.52, 55.5, 21.2, 15.6. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{20}NO_2$: 282.1489, found: 282.1487.



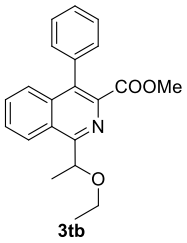
3gc

Compound **3gc** was obtained as a white solid in 55% yield according to the general procedure. Mp: 140−142°C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 9.1 Hz, 1H), 8.49 – 8.45 (m, 1H), 8.24 – 8.20 (m, 1H), 7.85 (d, *J* = 2.6 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.46 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.46 (s, 1H), 4.40 – 4.32 (m, 2H), 4.28 – 4.18 (m, 2H), 3.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3, 153.7, 142.1, 130.6, 127.9, 127.6, 125.3, 124.7, 123.9, 121.4, 121.2, 106.6, 104.3, 65.5, 55.4. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{16}NO_3$: 282.1125, found: 282.1126.



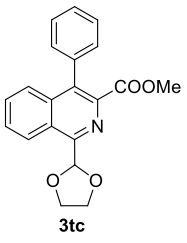
3gc'

Compound **3gc'** was obtained as a white solid in 16% yield according to the general procedure. Mp: 130−132°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 9.1 Hz, 1H), 8.50 – 8.44 (m, 1H), 8.19 – 8.11 (m, 1H), 7.86 (d, *J* = 2.6 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.49 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.79 – 5.71 (m, 1H), 5.27 (s, 1H), 5.21 (s, 1H), 4.89 (dd, *J* = 8.2, 6.3 Hz, 1H), 4.44 (dd, *J* = 8.0, 7.3 Hz, 1H), 4.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6, 155.2, 142.1, 130.4, 127.8, 127.7, 127.4, 126.2, 124.3, 124.1, 121.4, 121.2, 106.5, 95.9, 67.6, 55.5. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{16}NO_3$: 282.1125, found: 282.1127.



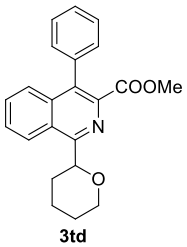
3tb

Compound **3tb** was obtained as colorless ropy oil in 81% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 – 8.92 (m, 1H), 7.69 – 7.60 (m, 3H), 7.52 – 7.44 (m, 3H), 7.38 – 7.32 (m, 2H), 5.22 (q, *J* = 6.8 Hz, 1H), 3.67 (s, 3H), 3.65 – 3.57 (m, 1H), 3.45 (dq, *J* = 9.2, 7.0 Hz, 1H), 1.78 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 161.5, 140.6, 136.4, 136.1, 133.3, 130.4, 129.7, 129.7, 128.1, 127.9, 127.9, 127.0, 126.4, 125.9, 81.5, 64.7, 52.3, 21.7, 15.5. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{21}H_{22}NO_3$:336.1594, found: 336.1592.



3tc

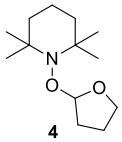
Compound **3tc** was obtained as a white solid in 65% yield according to the general procedure. Mp: 128−130°C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 – 8.53 (m, 1H), 7.71 – 7.63 (m, 3H), 7.53 – 7.46 (m, 3H), 7.36 – 7.30 (m, 2H), 6.42 (s, 1H), 4.41 (td, *J* = 6.6, 4.3 Hz, 2H), 4.22 (td, *J* = 6.5, 4.2 Hz, 2H), 3.70 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 154.0, 140.2, 136.7, 136.0, 135.4, 130.6, 129.6, 128.5, 128.2, 128.0, 127.1, 126.7, 125.5, 104.8, 65.5, 52.4. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{20}H_{18}NO_4$: 336.1230, found: 336.1229.



3td

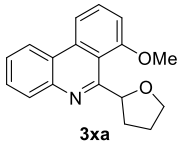
Compound **3td** was obtained as colorless oil in 70% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.57 (m, 3H), 7.53 – 7.42 (m, 3H), 7.36 – 7.28 (m, 2H), 5.18 (dd, *J* = 11.3, 2.2 Hz, 1H), 4.24 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.79 (td, *J* = 11.6, 2.1 Hz, 1H), 3.67 (s, 3H), 2.32 (ddd, *J* = 15.3, 12.5, 4.2 Hz, 1H), 2.09 (t, *J* = 10.2 Hz, 2H),

1.96 – 1.78 (m, 2H), 1.73 – 1.65 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 159.2, 140.5, 136.5, 136.2, 133.6, 130.3, 129.8, 129.6, 128.2, 128.1, 128.0, 127.8, 127.0, 126.8, 126.3, 81.4, 69.3, 52.3, 30.3, 26.0, 23.7. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{22}H_{22}NO_3$: 348.1594, found: 348.1593.



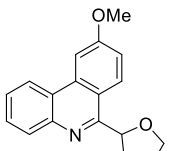
4

Compound **4** was obtained as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.36 (dd, *J* = 5.3, 1.7 Hz, 1H), 3.84 (ddt, *J* = 12.6, 8.2, 6.4 Hz, 2H), 2.03 – 1.87 (m, 3H), 1.77 (ddd, *J* = 10.8, 9.8, 6.1 Hz, 1H), 1.57 – 1.38 (m, 5H), 1.31 (d, *J* = 10.1 Hz, 1H), 1.22 (s, 3H), 1.14 – 0.99 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 109.6, 66.6, 60.1, 58.6, 40.1, 39.7, 33.9, 33.3, 31.2, 23.9, 20.4, 20.0, 17.2. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{13}H_{26}NO_2$: 228.1958, found: 228.1955.



3xa

Compound **3xa** was obtained as colorless oil in 52% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.70 (dt, *J* = 11.4, 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.30 (dd, *J* = 8.1, 3.7 Hz, 1H), 4.51 (dd, *J* = 13.8, 7.7 Hz, 1H), 4.14 (q, *J* = 7.4 Hz, 1H), 4.02 (s, 3H), 2.50 (dq, *J* = 12.4, 8.3 Hz, 1H), 2.09 (ddd, *J* = 16.6, 8.3, 4.4 Hz, 1H), 1.94 (qd, *J* = 12.1, 5.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 157.8, 143.2, 135.7, 130.7, 130.4, 128.5, 126.4, 123.1, 122.2, 115.7, 114.8, 108.2, 81.5, 69.3, 55.6, 32.6, 24.5. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO_2$: 280.1332, found: 280.1331.



3xa'

Compound **3xa'** was obtained as colorless oil in 30% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.9 Hz, 1H), 8.38 (d, *J* = 9.1 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 2.5 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.63 – 7.59 (m, 1H), 7.29 (dd, *J* = 9.1, 2.5 Hz, 1H), 5.70 (t, *J* = 7.0 Hz, 1H), 4.20 (dd, *J* = 14.3, 7.6 Hz, 1H), 4.09 – 4.01 (m, 4H), 2.72 (dt, *J* =

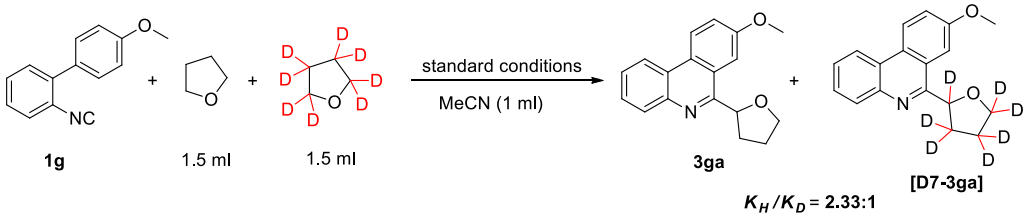
15.5, 7.0 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.26 – 2.08 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.9, 158.8, 143.7, 135.5, 130.4, 128.5, 128.4, 126.3, 123.9, 121.8, 119.8, 117.2, 103.0, 79.8, 68.94, 55.5, 30.0, 26.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{18}NO_2$: 280.1332, found: 280.1331.

Reference:

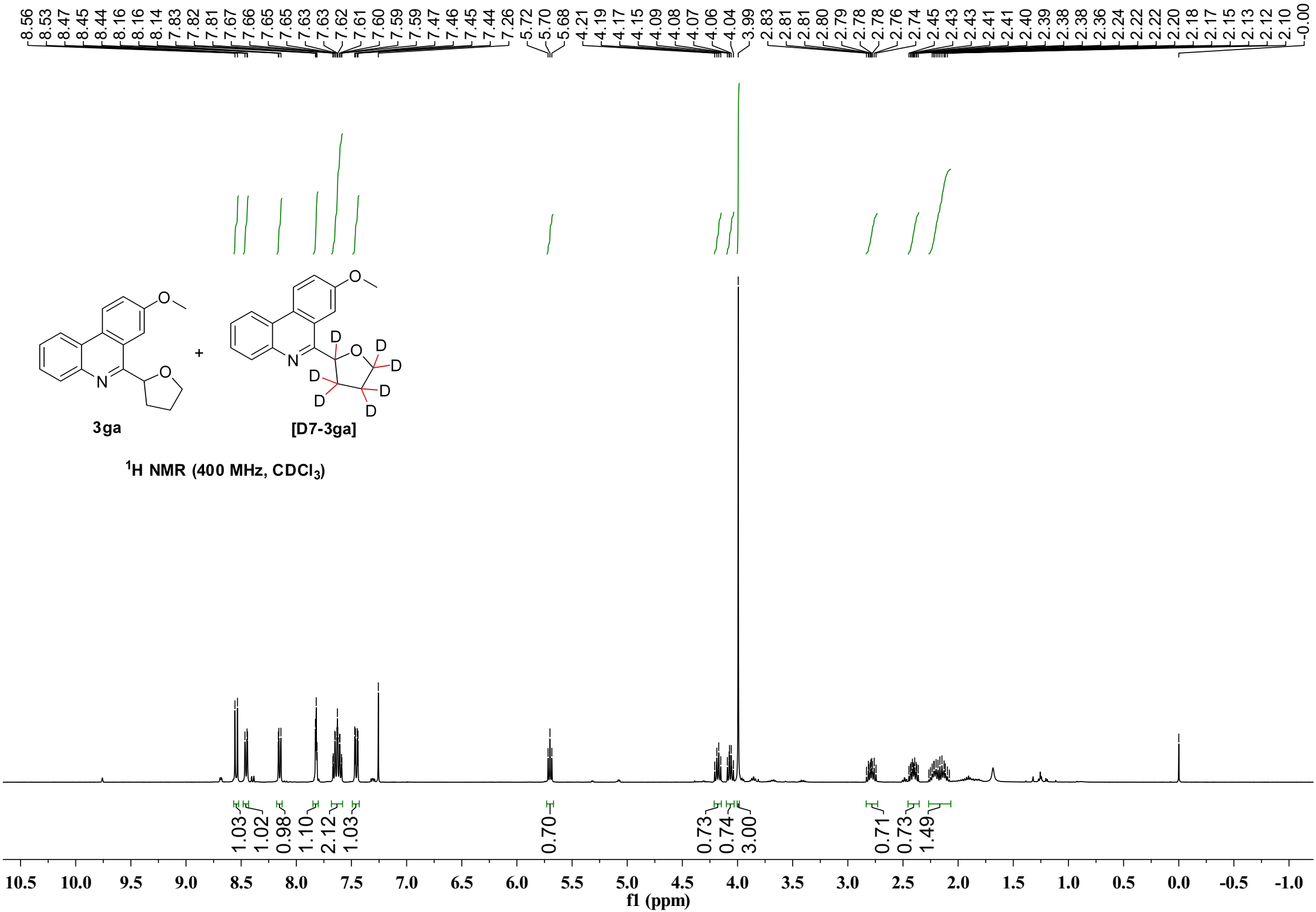
[1] Rong, J.; Deng, L.; Tan, P.; Ni, C.; Gu, Y.; Hu, J. *Angew. Chem. Int. Ed.* **2016**, 55,2743.

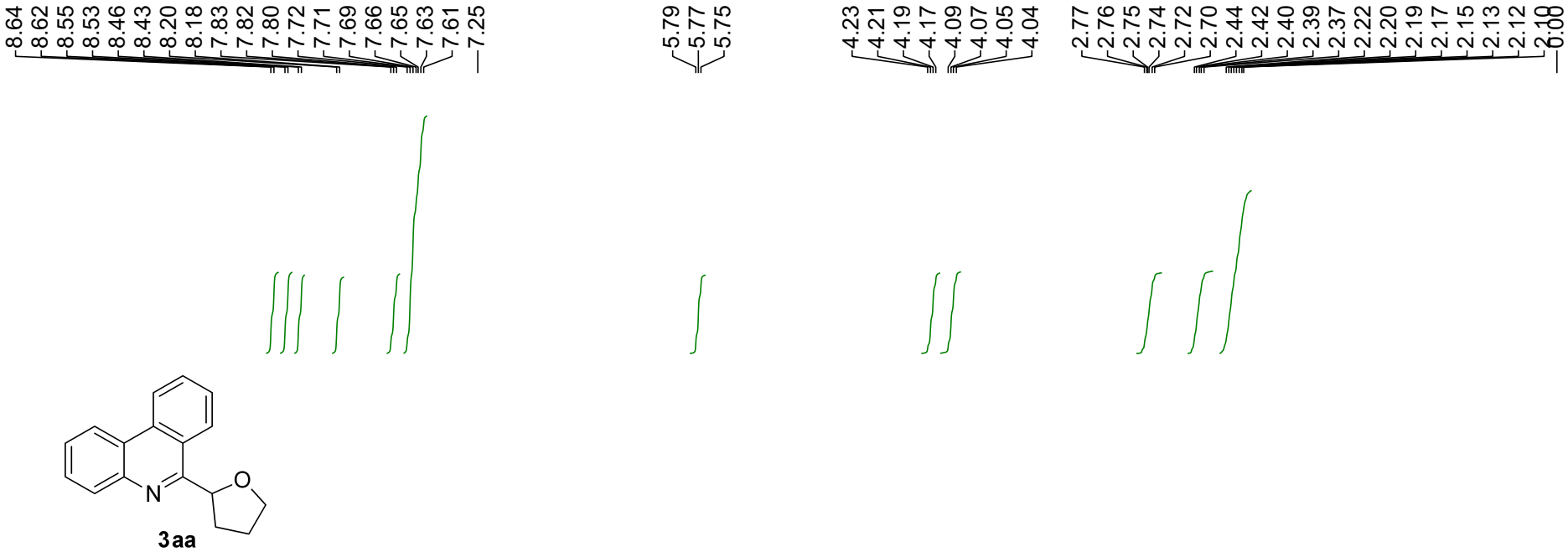
[2] Jiang, H.; Cheng, Y.; Wang, R.; Zhang, Y.; Yu, S. *Chem. Comm.* **2014**, 50, 6164.

5. Kinetic isotope effect experiment.



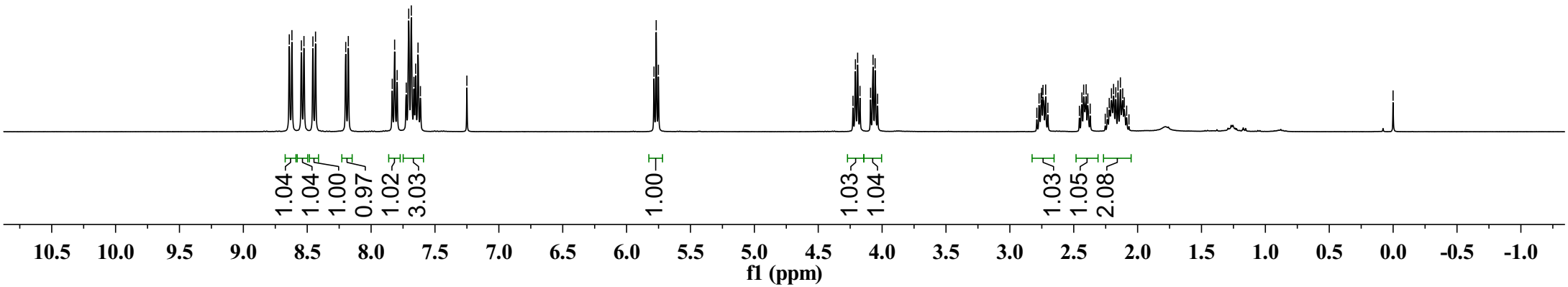
To a reaction tube equipped with a magnetic stir bar was added isocyanide **1g** (0.2 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (5 mol%, 7.5 mg), $KHCO_3$(0.4 mmol, 40 mg), the flask was evacuated and backfilled with Ar for 3 times. Then *t*-BuOOH (5.5 M in decane) (0.8 mmol, 0.15 ml), MeCN (1.0 mL), THF (1.5 mL) and D8-THF (1.5 mL) was added. The reaction was irradiated with a 18 W blue LED strip and stirred at ambient temperature from 12 hours. After it was complete, the reaction mixture was concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography to afford the desired product.

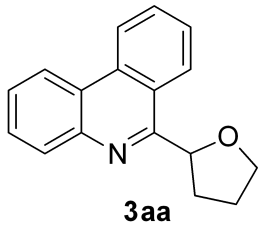

8.56 8.53 8.47 8.45 8.44 8.16 8.16 8.14 7.83 7.82 7.81 7.67 7.66 7.65 7.65 7.63 7.63 7.62 7.61 7.60 7.59 7.59 7.47 7.46 7.45 7.44 7.26
5.72 5.70 5.68
4.21 4.19 4.17 4.15 4.09 4.08 4.07 4.06 4.04 3.99
2.83 2.81 2.81 2.80 2.79 2.78 2.78 2.76 2.74 2.45 2.43 2.43 2.41 2.41 2.40 2.39 2.38 2.38 2.36 2.24 2.22 2.22 2.20 2.18 2.17 2.15 2.13 2.12 2.10 -0.00
O
N
O
+
D
O
D
D
D
D
D
D
D
3ga
[D7-3ga]
1H NMR (400 MHz, CDCl3)
1.03 1.02 0.98 1.10 2.12 1.03 0.70 0.73 0.74 3.00 0.71 0.73 1.49
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)



3aa

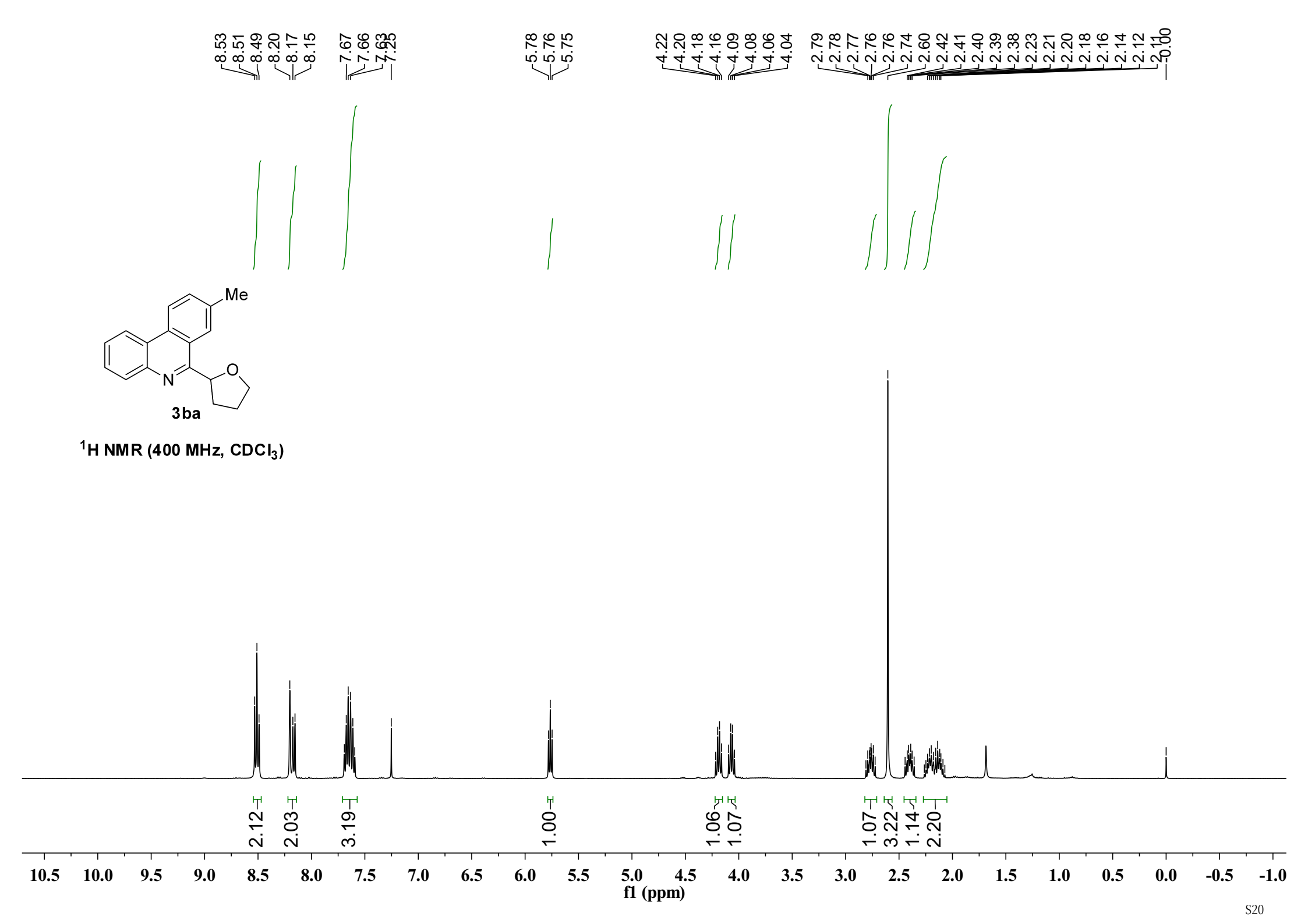
^{1}H NMR (400 MHz, $CDCl_3$)

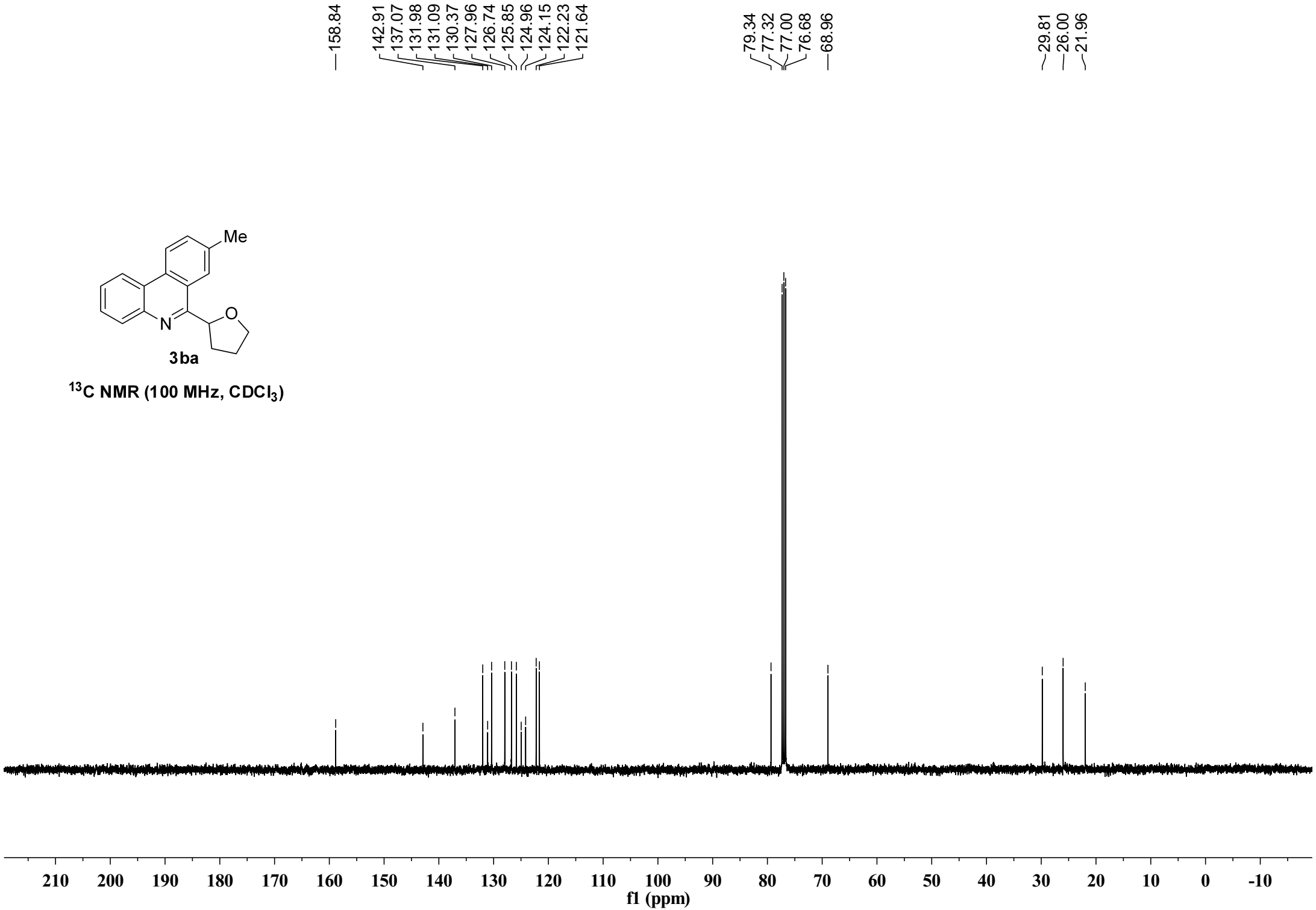


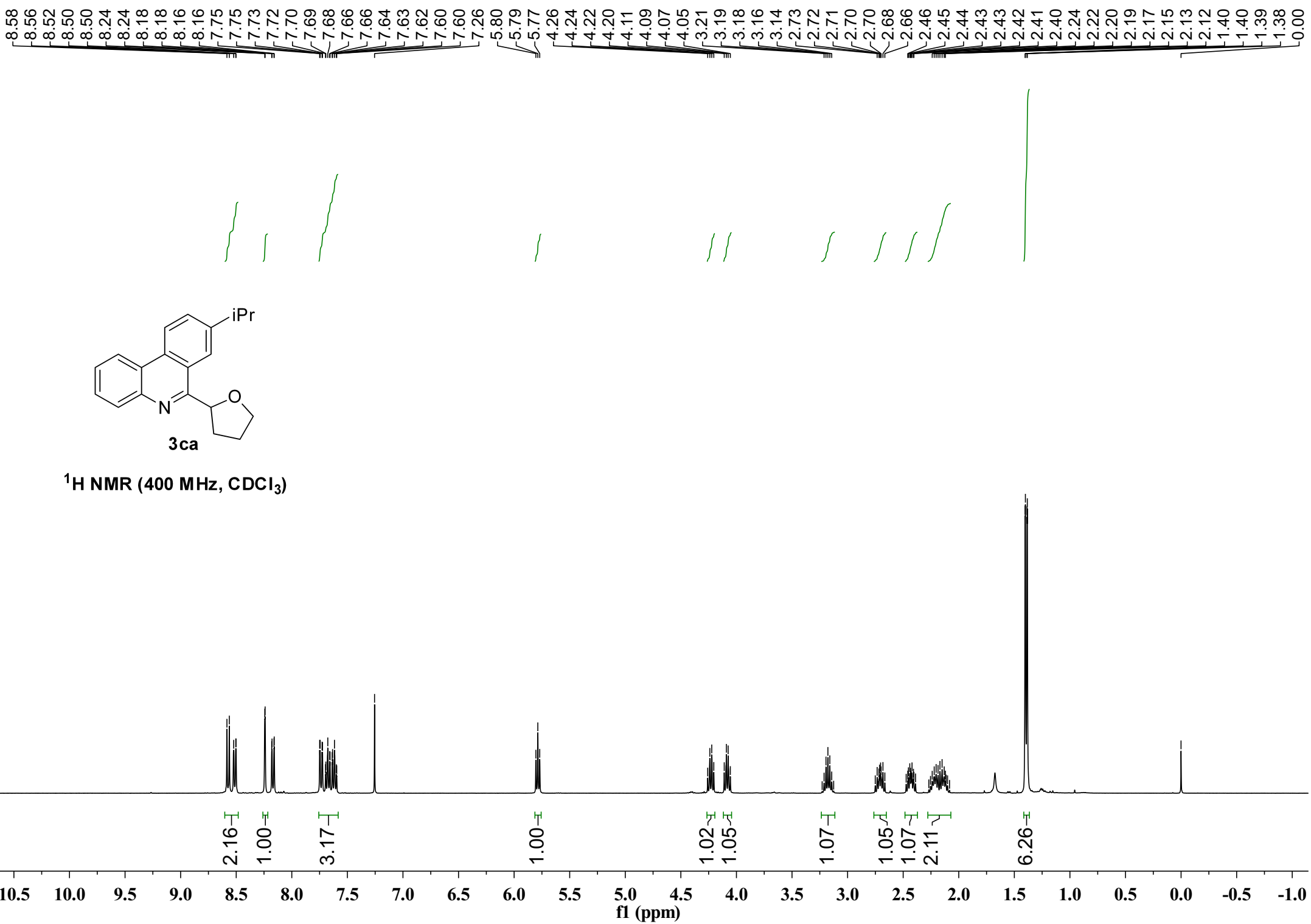


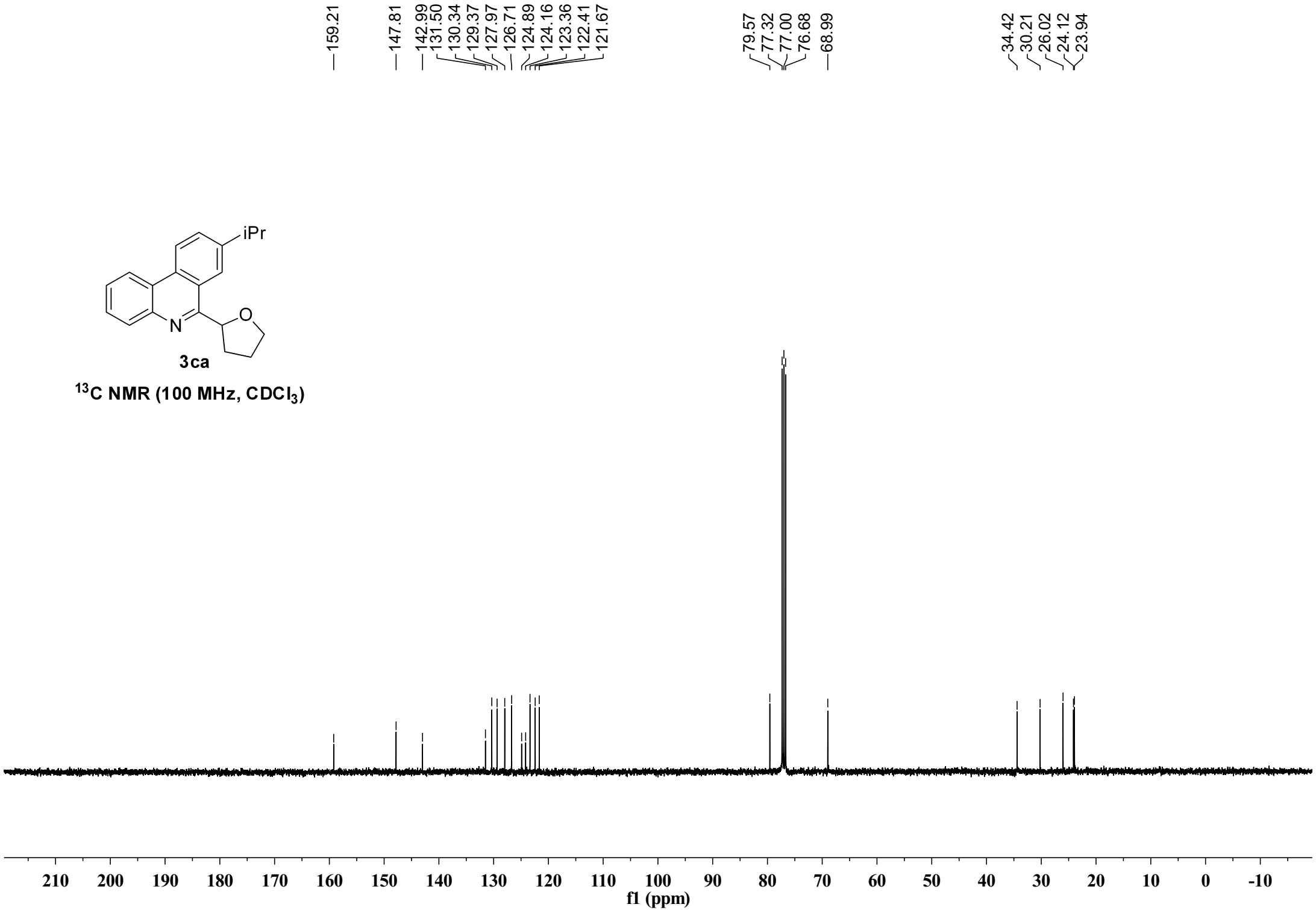
3aa

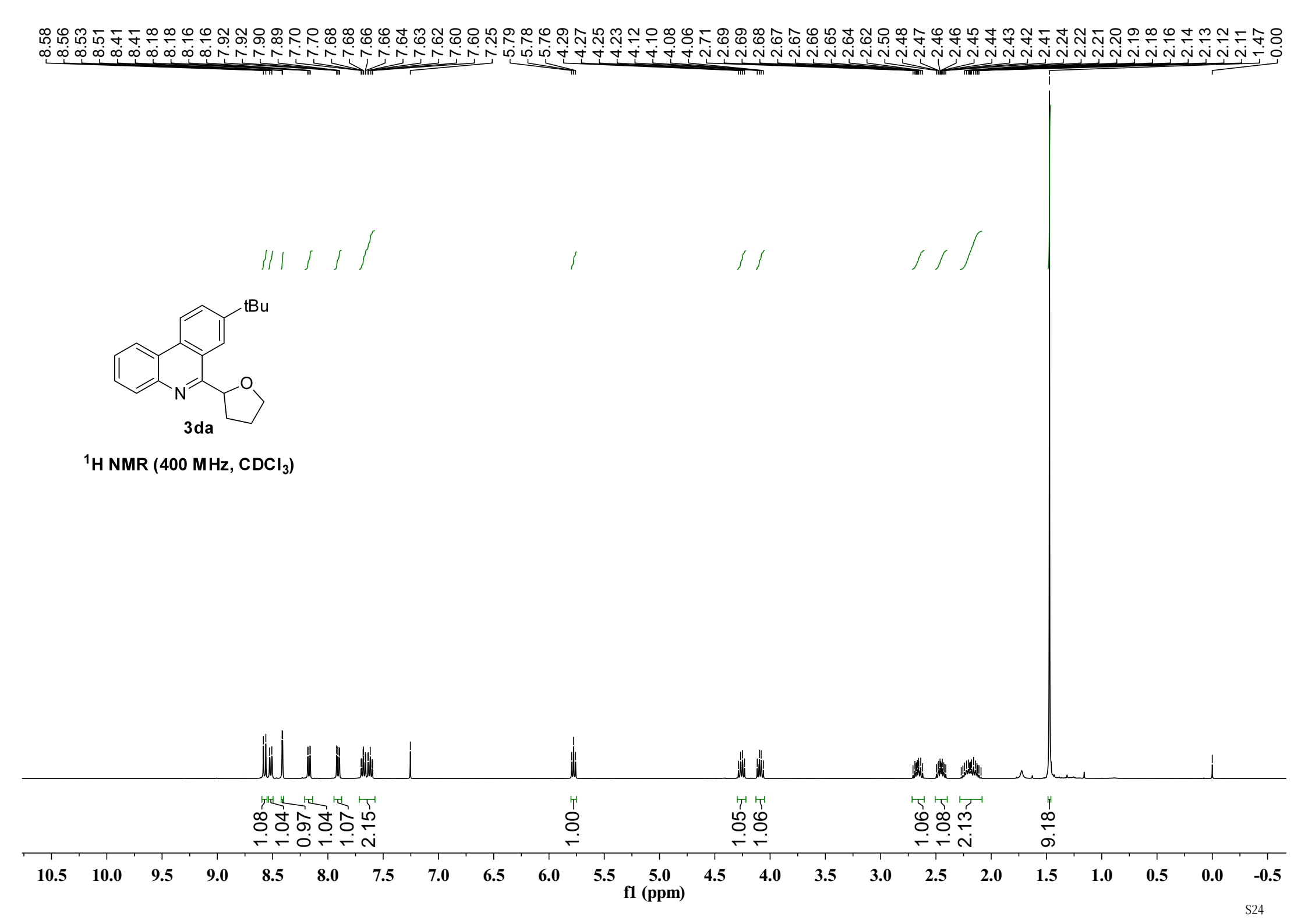
^{13}C NMR (100 MHz, $CDCl_3$)

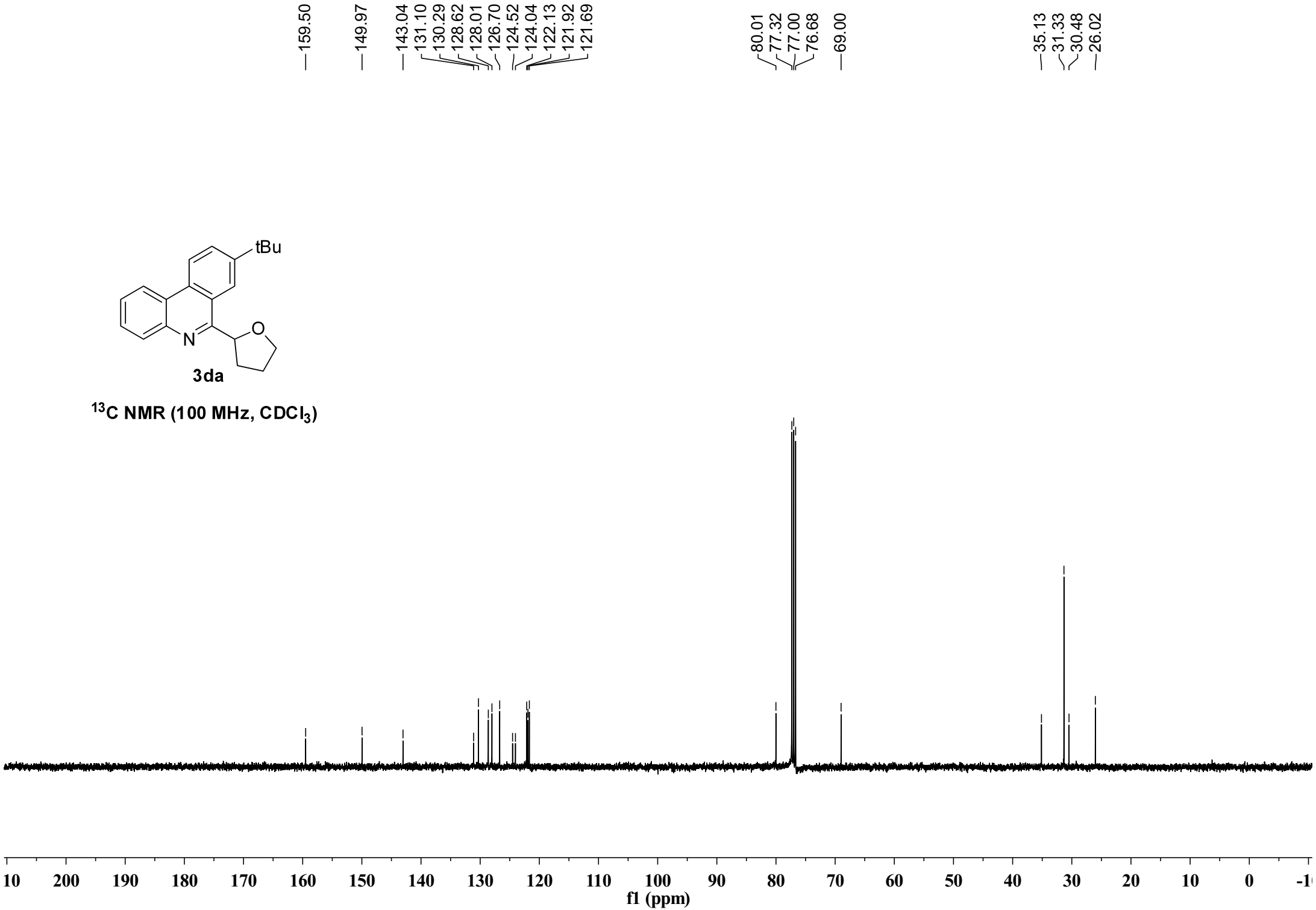

8.53
8.51
8.49
8.20
8.17
8.15
7.67
7.66
7.63
7.25
5.78
5.76
5.75
4.22
4.20
4.18
4.16
4.09
4.08
4.06
4.04
2.79
2.78
2.77
2.76
2.76
2.74
2.60
2.42
2.41
2.40
2.39
2.38
2.23
2.21
2.20
2.18
2.16
2.14
2.12
2.11
0.00
Me
N
O
3ba
1H NMR (400 MHz, CDCl3)
2.12
2.03
3.19
1.00
1.06
1.07
1.07
3.22
1.14
2.20
10.5
10.0
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)

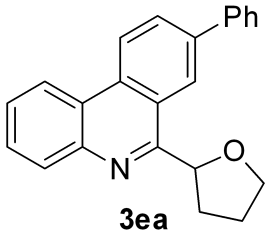

158.84
142.91
137.07
131.98
131.09
130.37
127.96
126.74
125.85
124.96
124.15
122.23
121.64
79.34
77.32
77.00
76.68
68.96
29.81
26.00
21.96
Me
N
O
3ba
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.58 8.56 8.52 8.50 8.50 8.24 8.24 8.18 8.18 8.16 8.16 7.75 7.75 7.73 7.72 7.70 7.69 7.68 7.66 7.66 7.64 7.63 7.62 7.60 7.60 7.26 5.80 5.79 5.77 4.26 4.24 4.22 4.20 4.11 4.09 4.07 4.05 3.21 3.19 3.18 3.16 3.14 2.73 2.72 2.71 2.70 2.70 2.68 2.66 2.46 2.45 2.44 2.43 2.43 2.42 2.41 2.40 2.24 2.22 2.20 2.19 2.17 2.15 2.13 2.12 1.40 1.40 1.39 1.38 0.00
iPr
N
O
3ca
1H NMR (400 MHz, CDCl3)
2.16 1.00 3.17 1.00 1.02 1.05 1.07 1.05 1.07 2.11 6.26
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)


159.21
147.81
142.99
131.50
130.34
129.37
127.97
126.71
124.89
124.16
123.36
122.41
121.67
79.57
77.32
77.00
76.68
68.99
34.42
30.21
26.02
24.12
23.94
iPr
N
O
3ca
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)

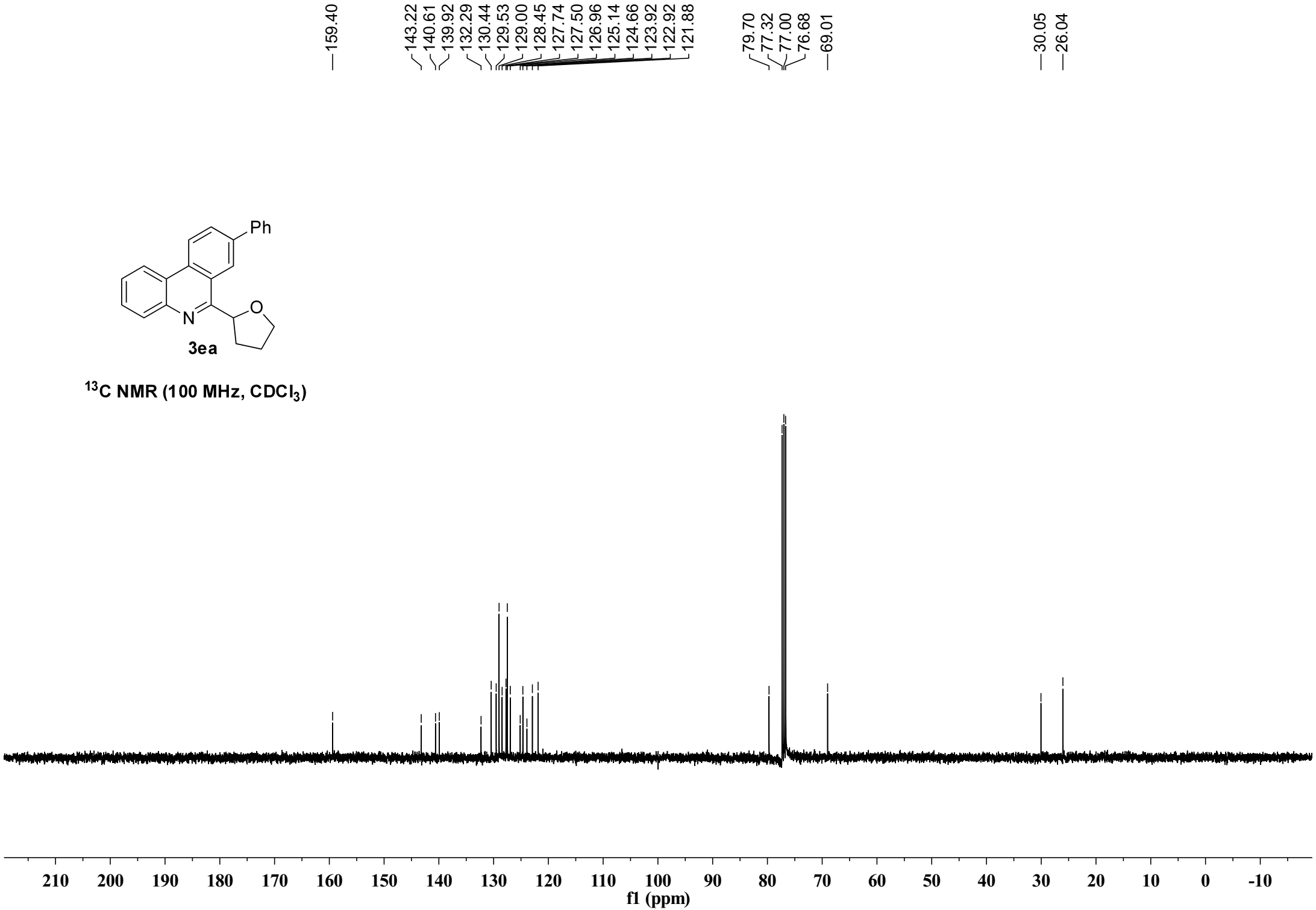

8.58 8.56 8.53 8.51 8.41 8.41 8.18 8.18 8.16 8.16 7.92 7.92 7.90 7.89 7.70 7.70 7.68 7.68 7.66 7.66 7.64 7.63 7.62 7.60 7.60 7.25
5.79 5.78 5.76 4.29 4.27 4.25 4.23 4.12 4.10 4.08 4.06 2.71 2.69 2.69 2.68 2.67 2.67 2.66 2.65 2.64 2.62 2.50 2.48 2.47 2.46 2.46 2.45 2.44 2.43 2.42 2.41 2.24 2.22 2.21 2.20 2.19 2.18 2.16 2.14 2.13 2.12 2.11 1.47 0.00
tBu
N
O
3da
1H NMR (400 MHz, CDCl3)
1.08 1.04 0.97 1.04 1.07 2.15 1.00 1.05 1.06 1.06 1.08 2.13 9.18
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)

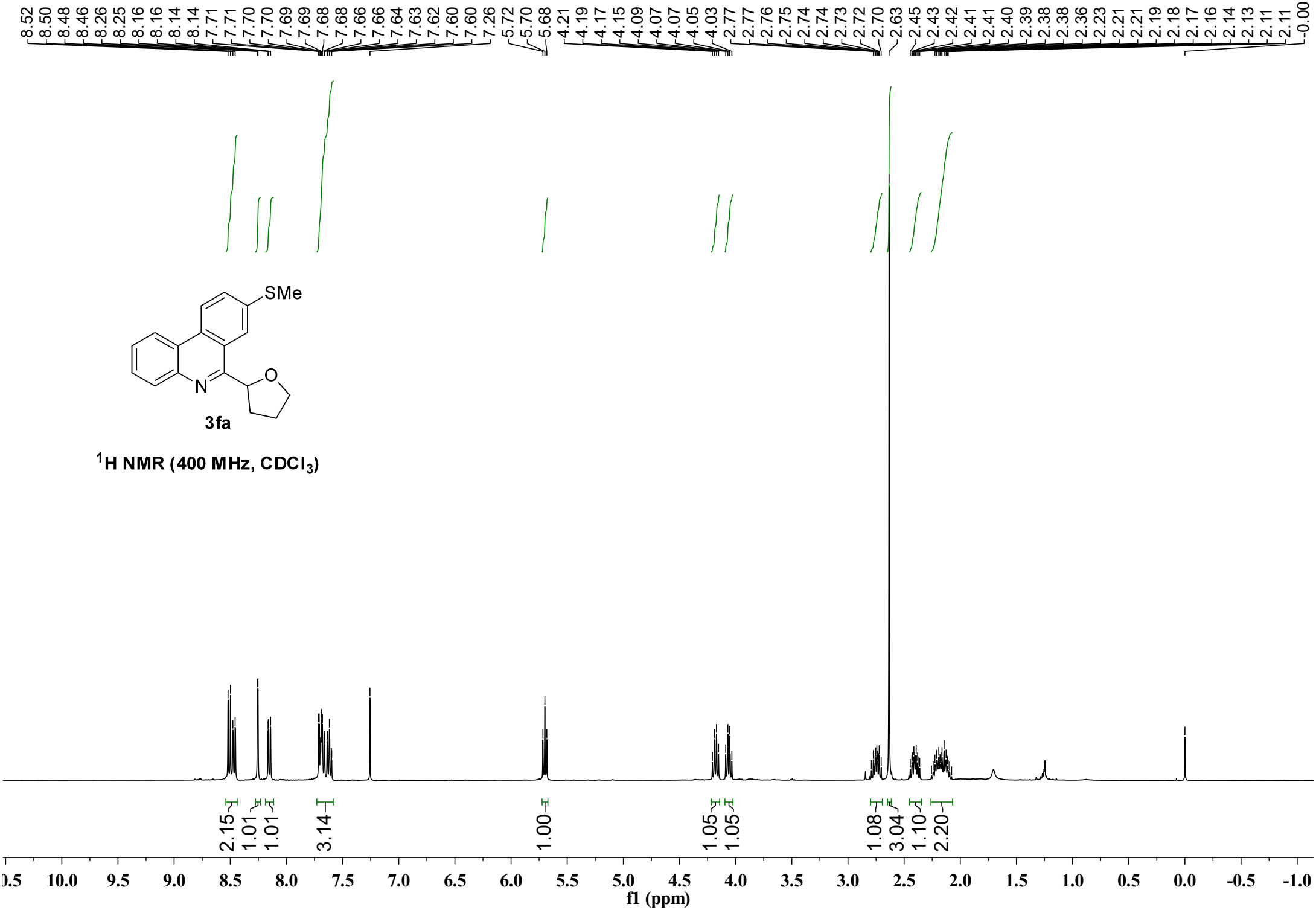

159.50
149.97
143.04
131.10
130.29
128.62
128.01
126.70
124.52
124.04
122.13
121.92
121.69
80.01
77.32
77.00
76.68
69.00
35.13
31.33
30.48
26.02
tBu
N
O
3da
13C NMR (100 MHz, CDCl3)
f1 (ppm)

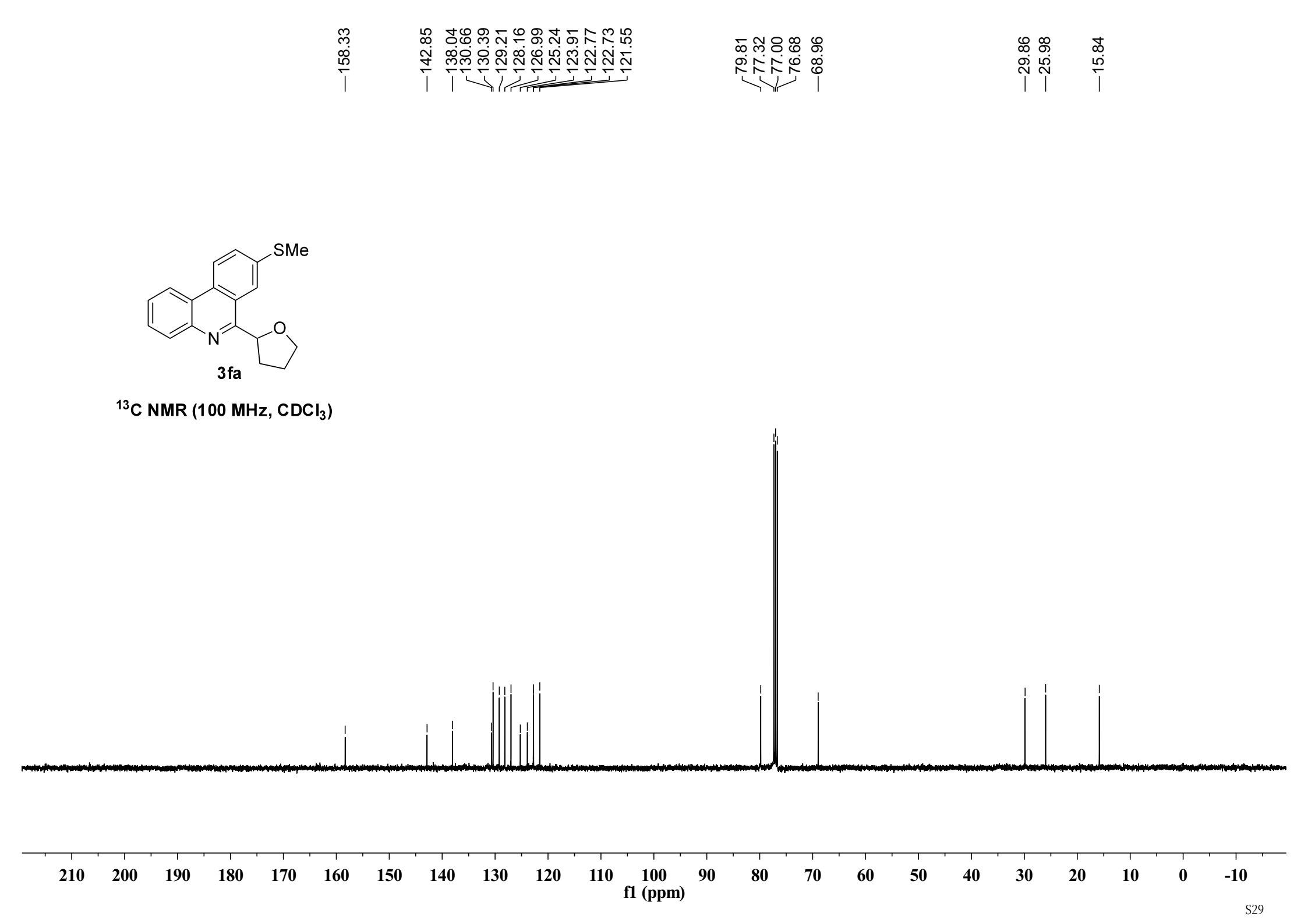


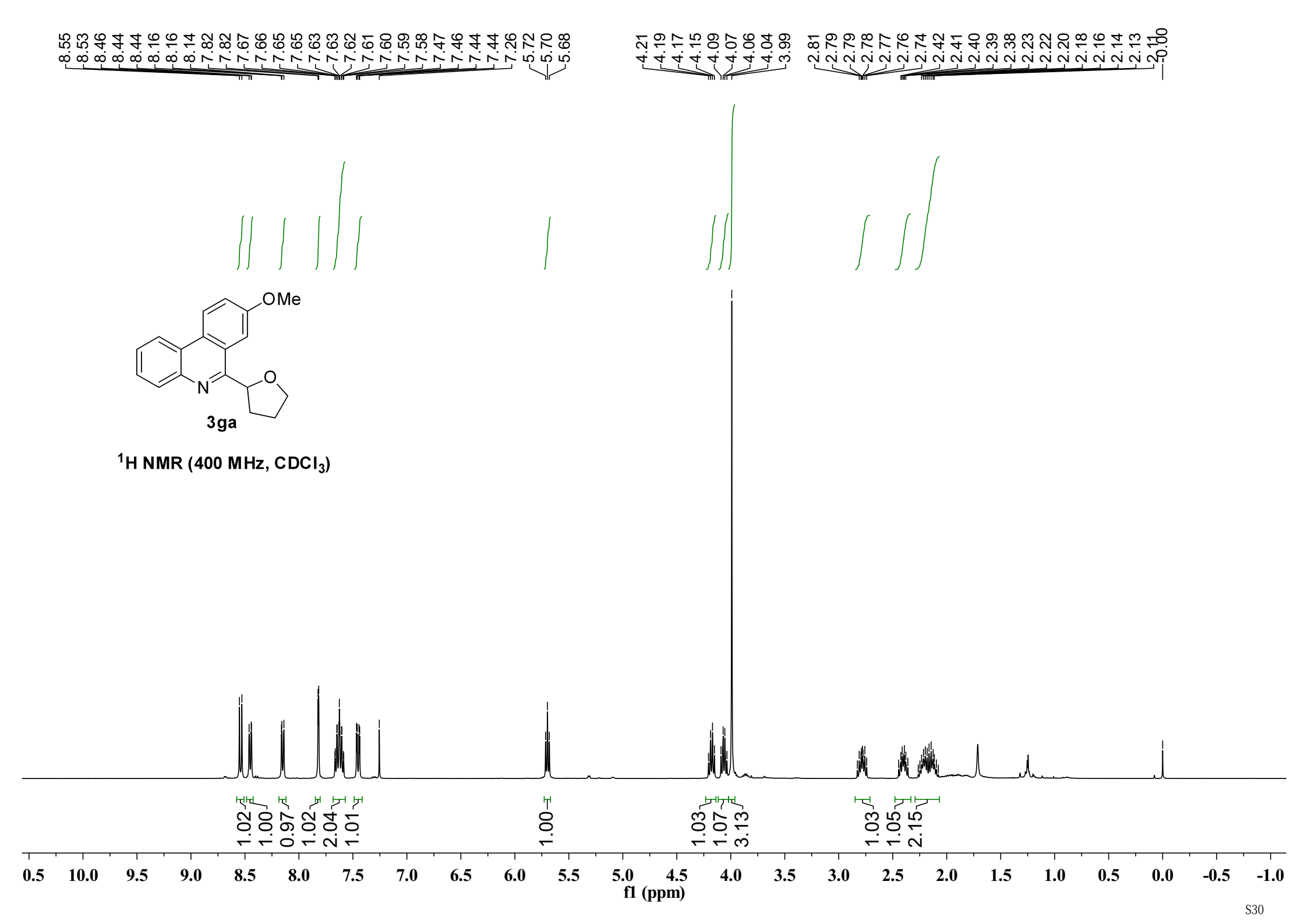
3ea

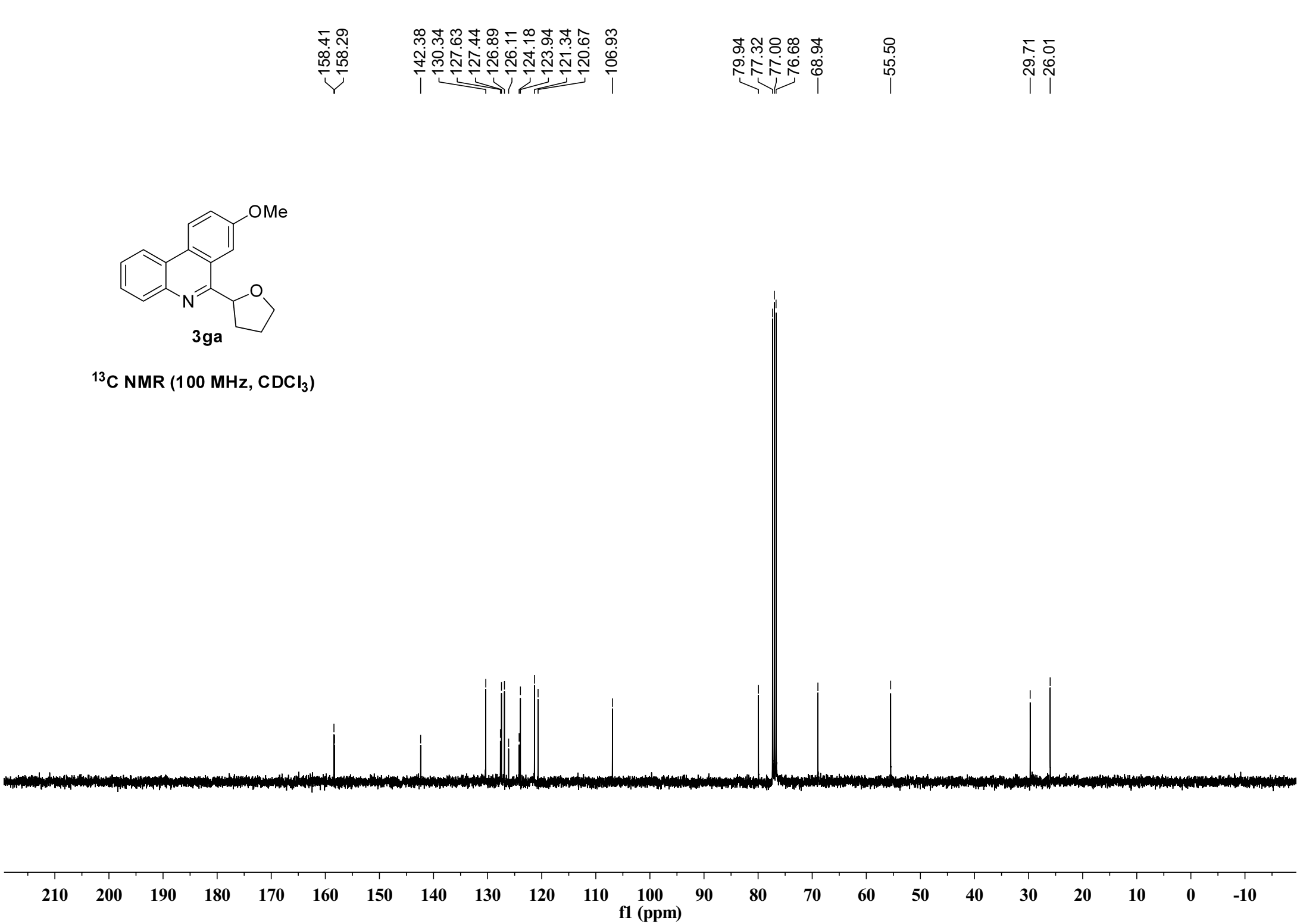
^{1}H NMR (400 MHz, $CDCl_3$)

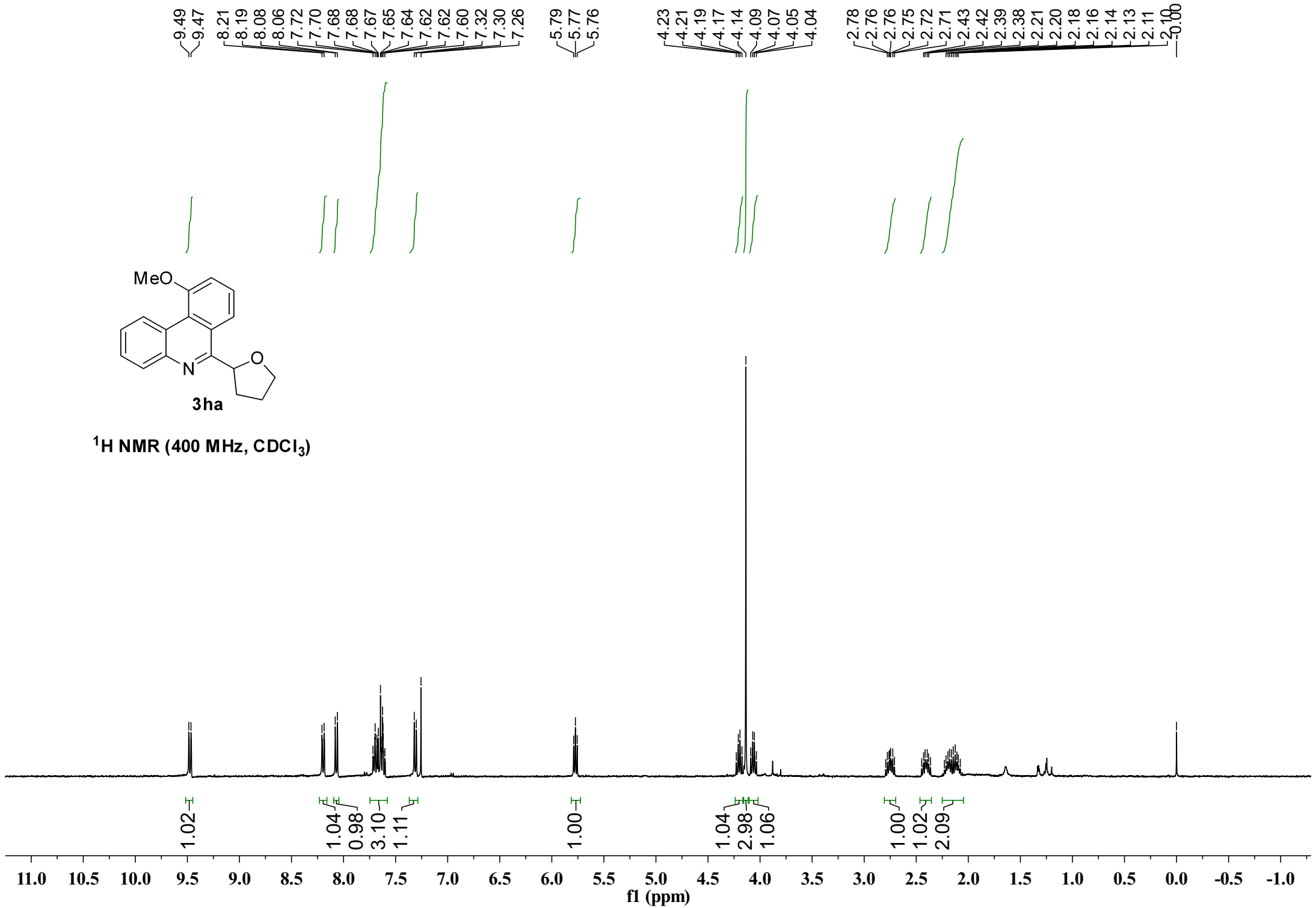

159.40
143.22
140.61
139.92
132.29
130.44
129.53
129.00
128.45
127.74
127.50
126.96
125.14
124.66
123.92
122.92
121.88
79.70
77.32
77.00
76.68
69.01
30.05
26.04
Ph
N
O
3ea
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

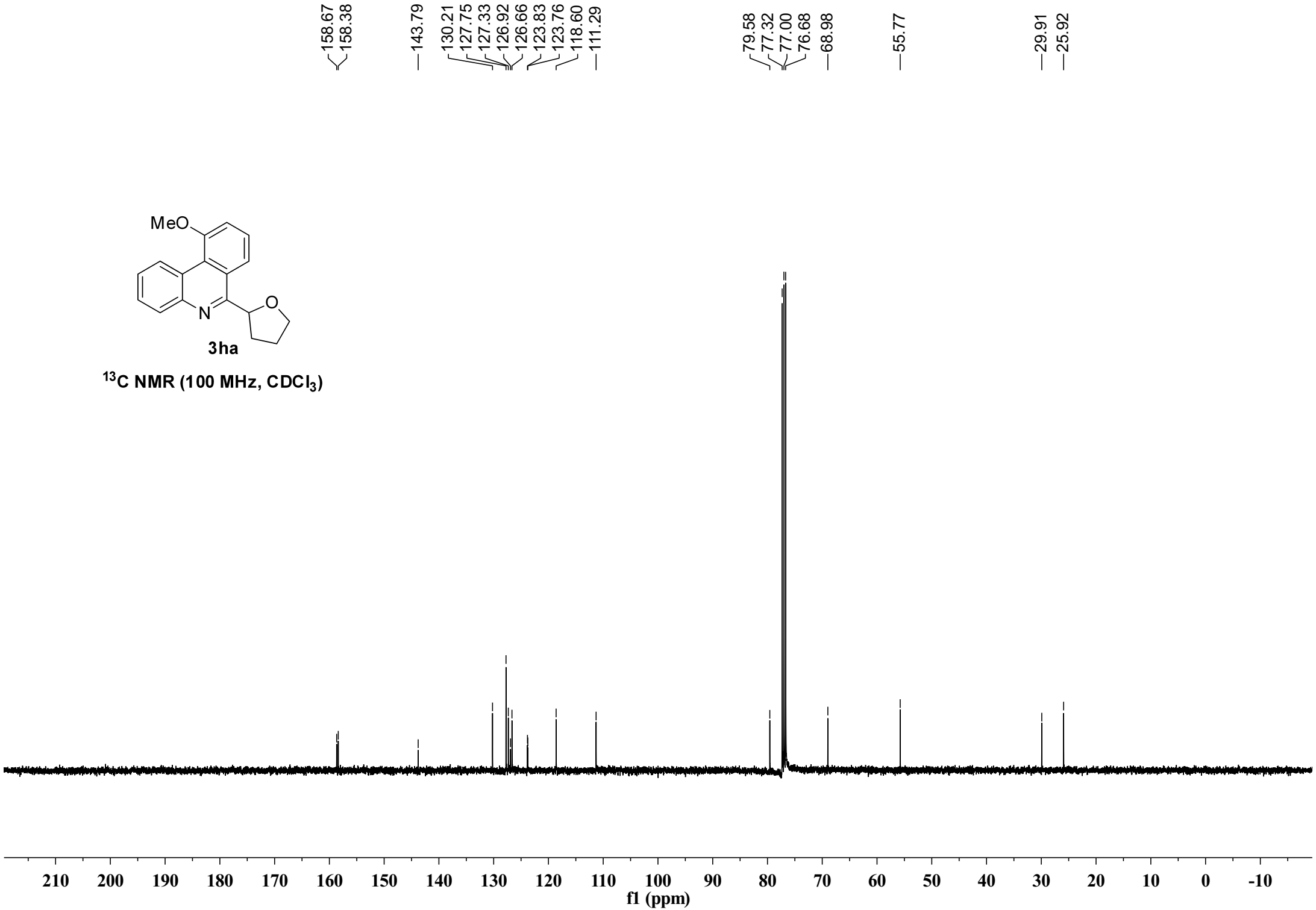

SMe
N
O
3fa
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

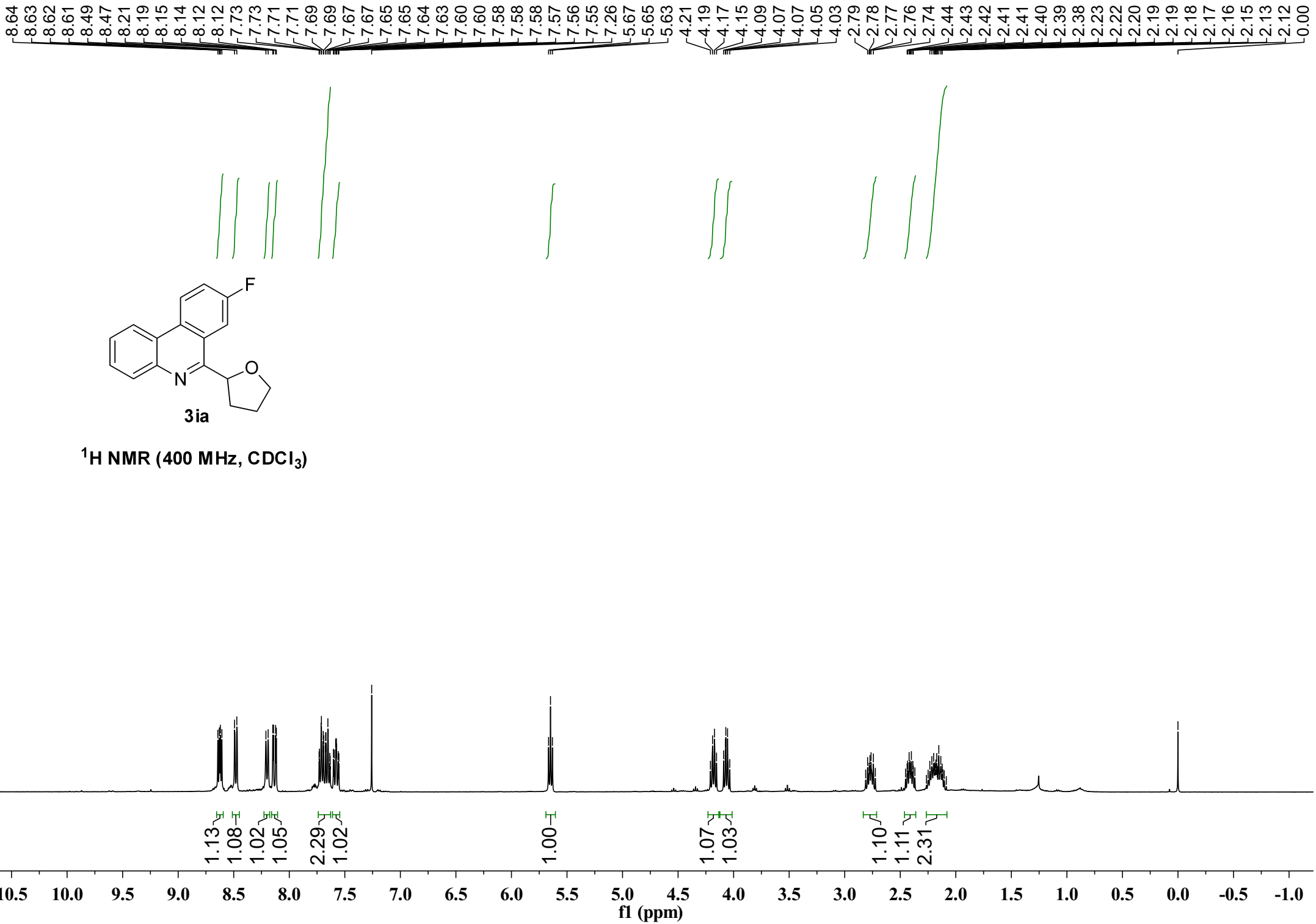

158.33
142.85
138.04
130.66
130.39
129.21
128.16
126.99
125.24
123.91
122.77
122.73
121.55
79.81
77.32
77.00
76.68
68.96
29.86
25.98
15.84
SMe
N
O
3fa
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

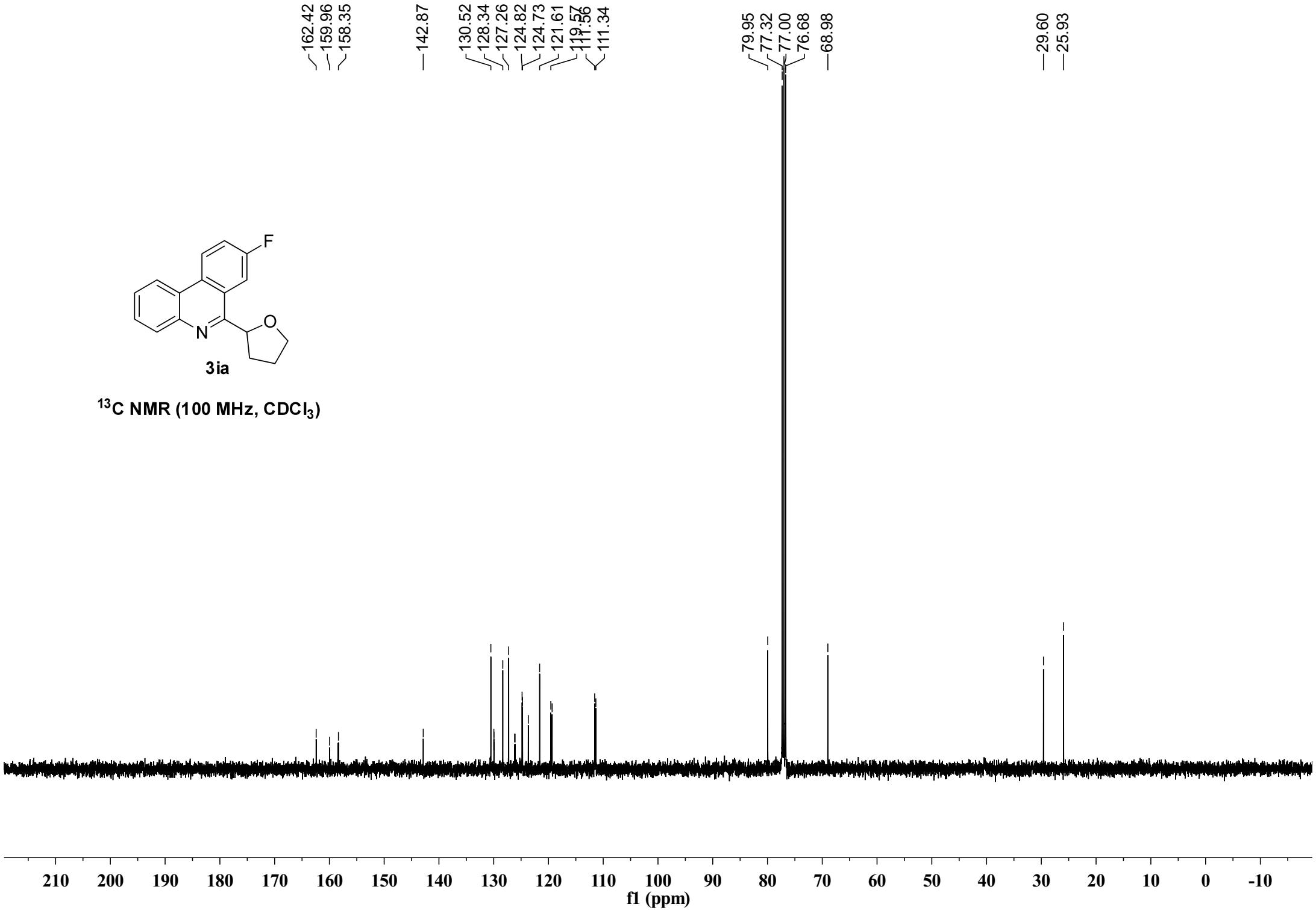

8.55
8.53
8.46
8.44
8.44
8.16
8.16
8.14
7.82
7.82
7.67
7.66
7.65
7.65
7.63
7.63
7.62
7.61
7.60
7.59
7.58
7.47
7.46
7.44
7.44
7.26
5.72
5.70
5.68
4.21
4.19
4.17
4.15
4.09
4.07
4.06
4.04
3.99
2.81
2.79
2.79
2.78
2.77
2.76
2.74
2.42
2.41
2.40
2.39
2.38
2.23
2.22
2.20
2.18
2.16
2.14
2.13
2.11
0.00
OMe
N
O
3ga
1H NMR (400 MHz, CDCl3)
1.02
1.00
0.97
1.02
2.04
1.01
1.00
1.03
1.07
3.13
1.03
1.05
2.15
0.5
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)

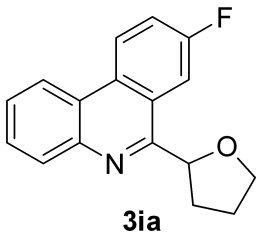

158.41
158.29
142.38
130.34
127.63
127.44
126.89
126.11
124.18
123.94
121.34
120.67
106.93
79.94
77.32
77.00
76.68
68.94
55.50
29.71
26.01
OMe
N
O
3ga
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.49
9.47
8.21
8.19
8.08
8.06
7.72
7.70
7.68
7.68
7.67
7.65
7.64
7.62
7.62
7.60
7.32
7.30
7.26
5.79
5.77
5.76
4.23
4.21
4.19
4.17
4.14
4.09
4.07
4.05
4.04
2.78
2.76
2.76
2.75
2.72
2.71
2.43
2.42
2.39
2.38
2.21
2.20
2.18
2.16
2.14
2.13
2.11
2.10
0.00
MeO
N
O
3ha
1H NMR (400 MHz, CDCl3)
1.02
1.04
0.98
3.10
1.11
1.00
1.04
2.98
1.06
1.00
1.02
2.09
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)


158.67
158.38
143.79
130.21
127.75
127.33
126.92
126.66
123.83
123.76
118.60
111.29
79.58
77.32
77.00
76.68
68.98
55.77
29.91
25.92
MeO
N
O
3ha
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)

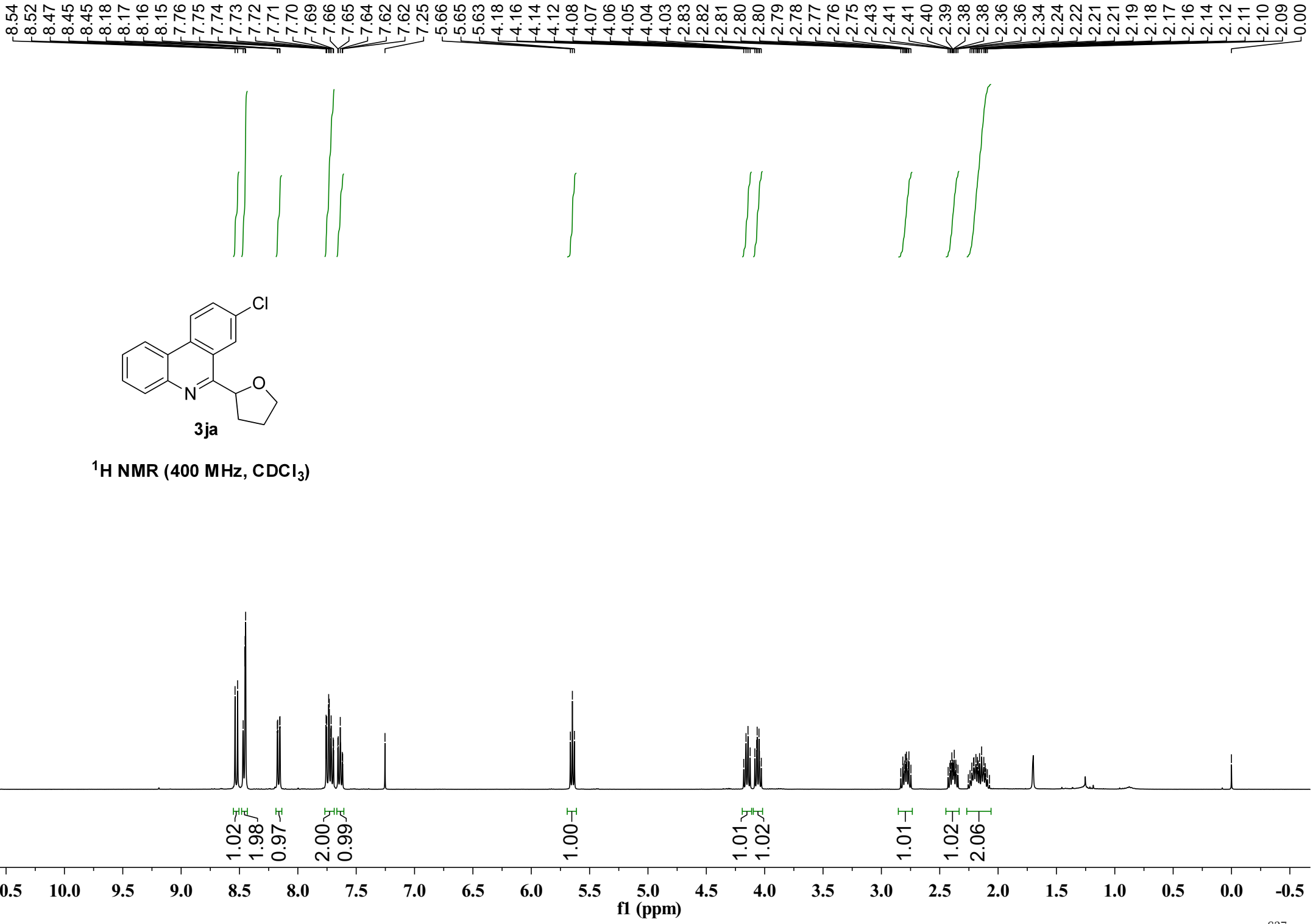

8.64 8.63 8.62 8.61 8.49 8.47 8.21 8.19 8.15 8.14 8.12 8.12 7.73 7.73 7.71 7.71 7.69 7.69 7.67 7.67 7.65 7.65 7.64 7.63 7.60 7.60 7.58 7.58 7.58 7.57 7.56 7.55 7.26 5.67 5.65 5.63 4.21 4.19 4.17 4.15 4.09 4.07 4.07 4.05 4.03 2.79 2.78 2.77 2.76 2.74 2.44 2.43 2.42 2.41 2.41 2.40 2.39 2.38 2.23 2.22 2.20 2.19 2.19 2.18 2.17 2.16 2.15 2.13 2.12 0.00
F
N
O
3ia
1H NMR (400 MHz, CDCl3)
1.13 1.08 1.02 1.05 2.29 1.02 1.00 1.07 1.03 1.10 1.11 2.31
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)

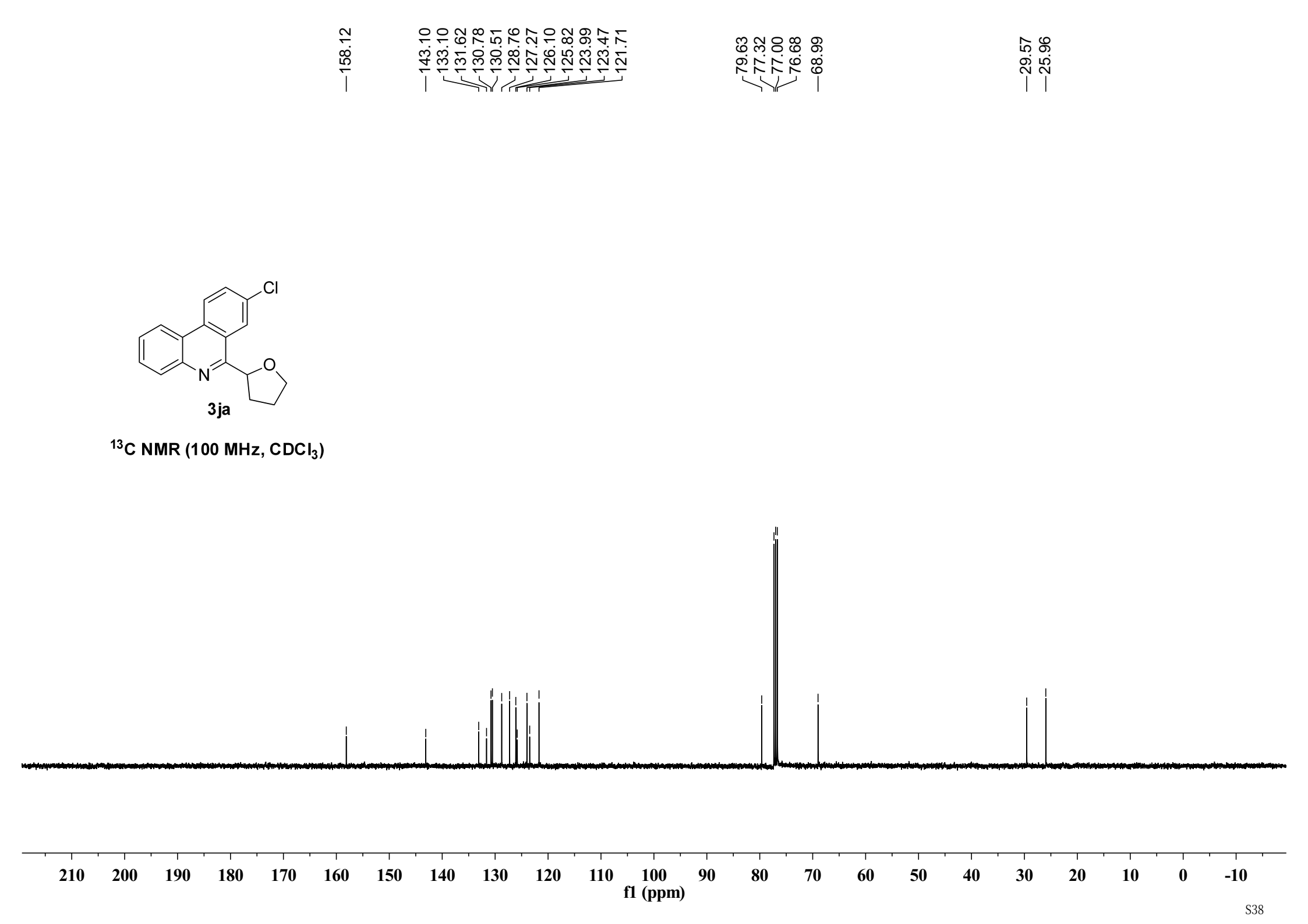

162.42
159.96
158.35
142.87
130.52
128.34
127.26
124.82
124.73
121.61
119.57
111.56
111.34
79.95
77.32
77.00
76.68
68.98
29.60
25.93
F
N
O
3ia
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

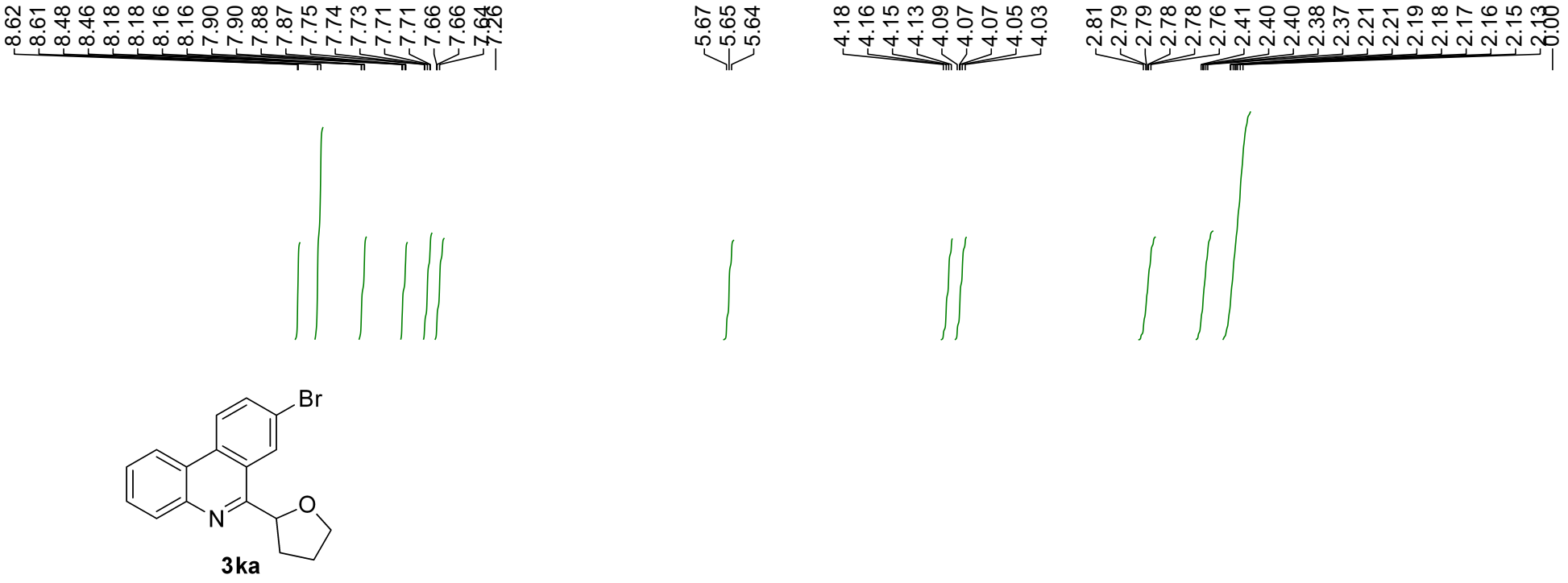


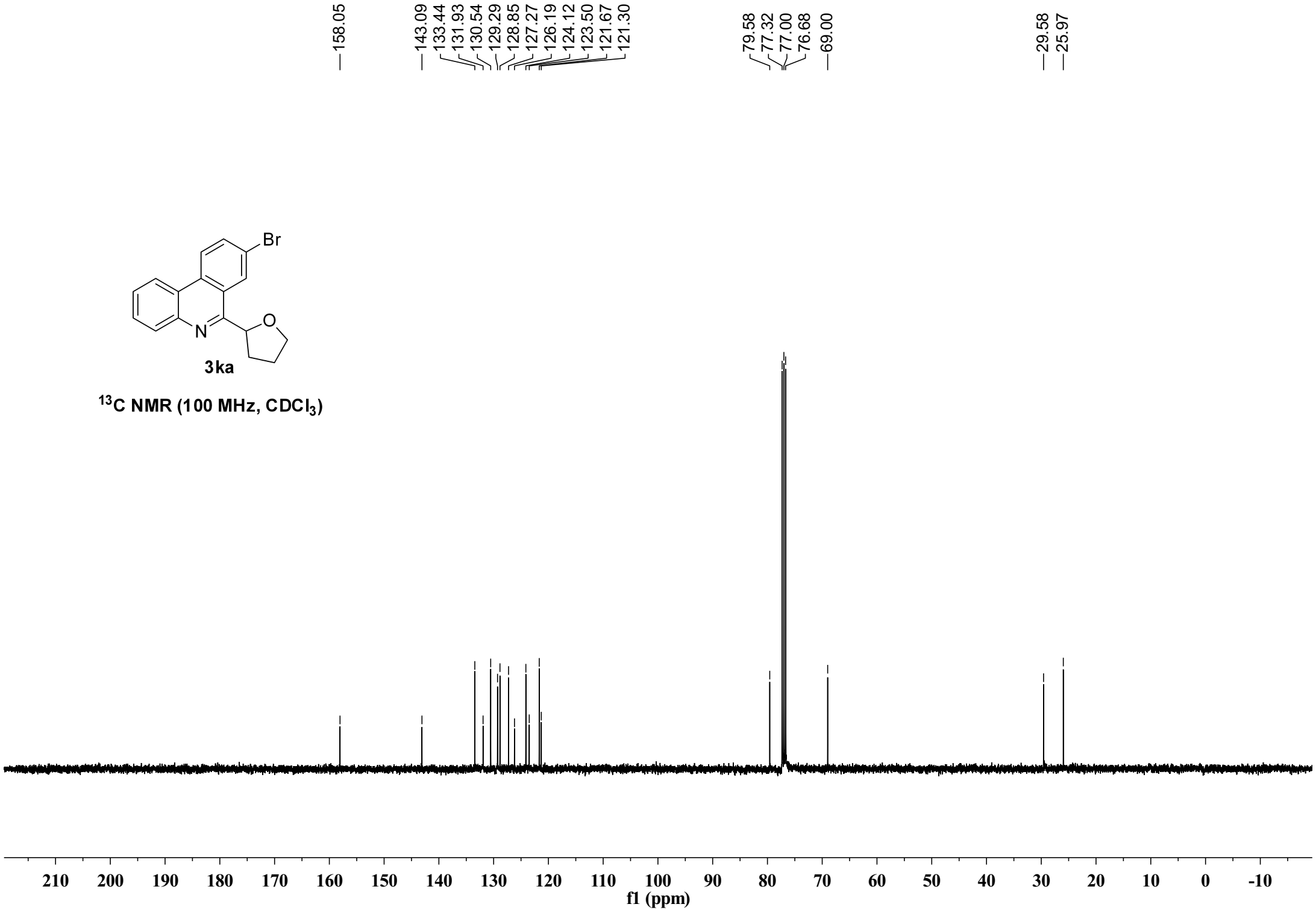
3ia

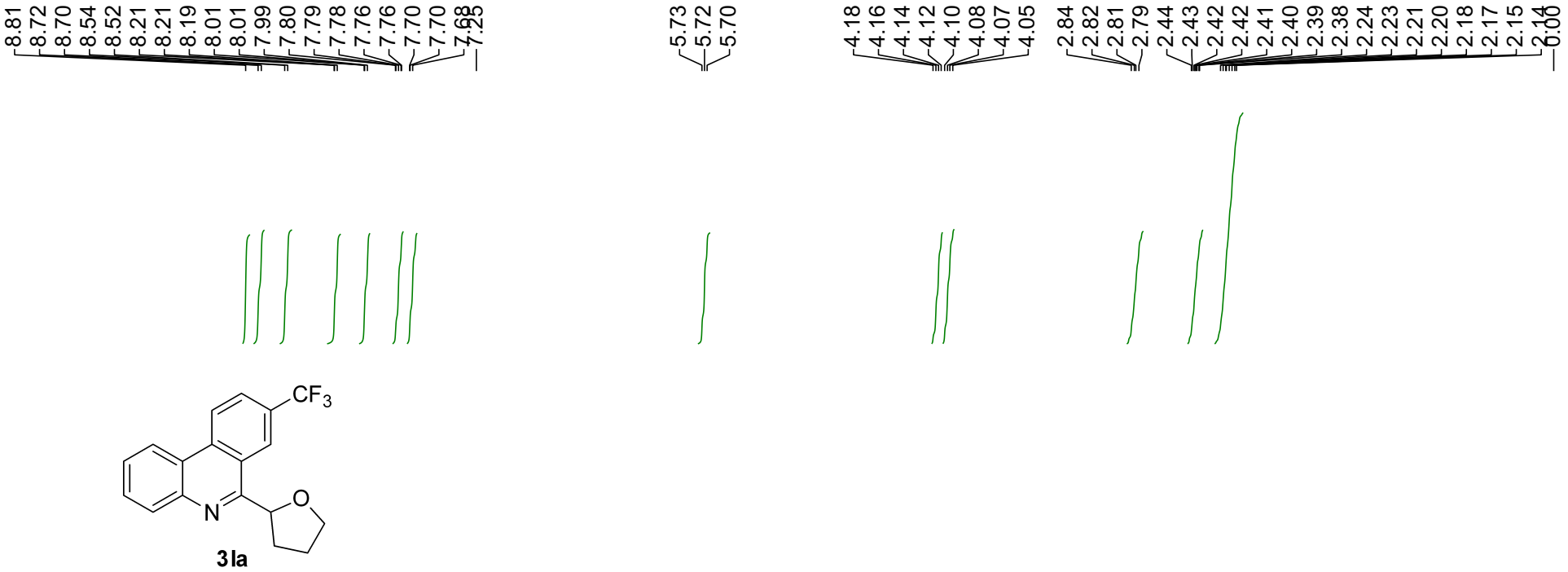
^{19}F NMR (376 MHz, $CDCl_3$)


8.54 8.52 8.47 8.45 8.45 8.18 8.17 8.16 8.15 7.76 7.75 7.74 7.73 7.72 7.71 7.70 7.69 7.66 7.65 7.64 7.62 7.62 7.25
5.66 5.65 5.63 4.18 4.16 4.14 4.12 4.08 4.07 4.06 4.05 4.04 4.03 2.83 2.82 2.81 2.80 2.80 2.79 2.78 2.77 2.76 2.75 2.43 2.41 2.41 2.40 2.39 2.38 2.38 2.36 2.36 2.34 2.24 2.22 2.21 2.21 2.19 2.18 2.17 2.16 2.14 2.12 2.11 2.10 2.09 0.00
Cl
N
O
3ja
1H NMR (400 MHz, CDCl3)
1.02 1.98 0.97 2.00 0.99 1.00 1.01 1.02 1.01 1.02 2.06
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)


158.12
143.10
133.10
131.62
130.78
130.51
128.76
127.27
126.10
125.82
123.99
123.47
121.71
79.63
77.32
77.00
76.68
68.99
29.57
25.96
Cl
N
O
3ja
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)

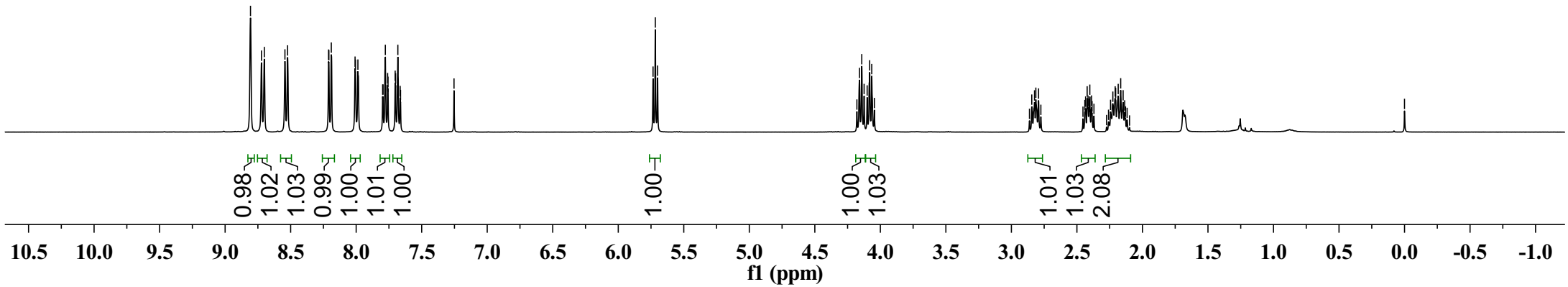

8.62
8.61
8.48
8.46
8.18
8.18
8.16
8.16
7.90
7.90
7.88
7.87
7.75
7.74
7.73
7.71
7.71
7.66
7.66
7.64
7.26
5.67
5.65
5.64
4.18
4.16
4.15
4.13
4.09
4.07
4.07
4.05
4.03
2.81
2.79
2.79
2.78
2.78
2.76
2.41
2.40
2.40
2.38
2.37
2.21
2.21
2.19
2.18
2.17
2.16
2.15
2.13
0.00
Br
N
O
3ka
1H NMR (400 MHz, CDCl3)
0.98
2.13
1.03
0.98
1.07
1.02
1.00
1.02
1.03
1.03
1.09
2.29
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)

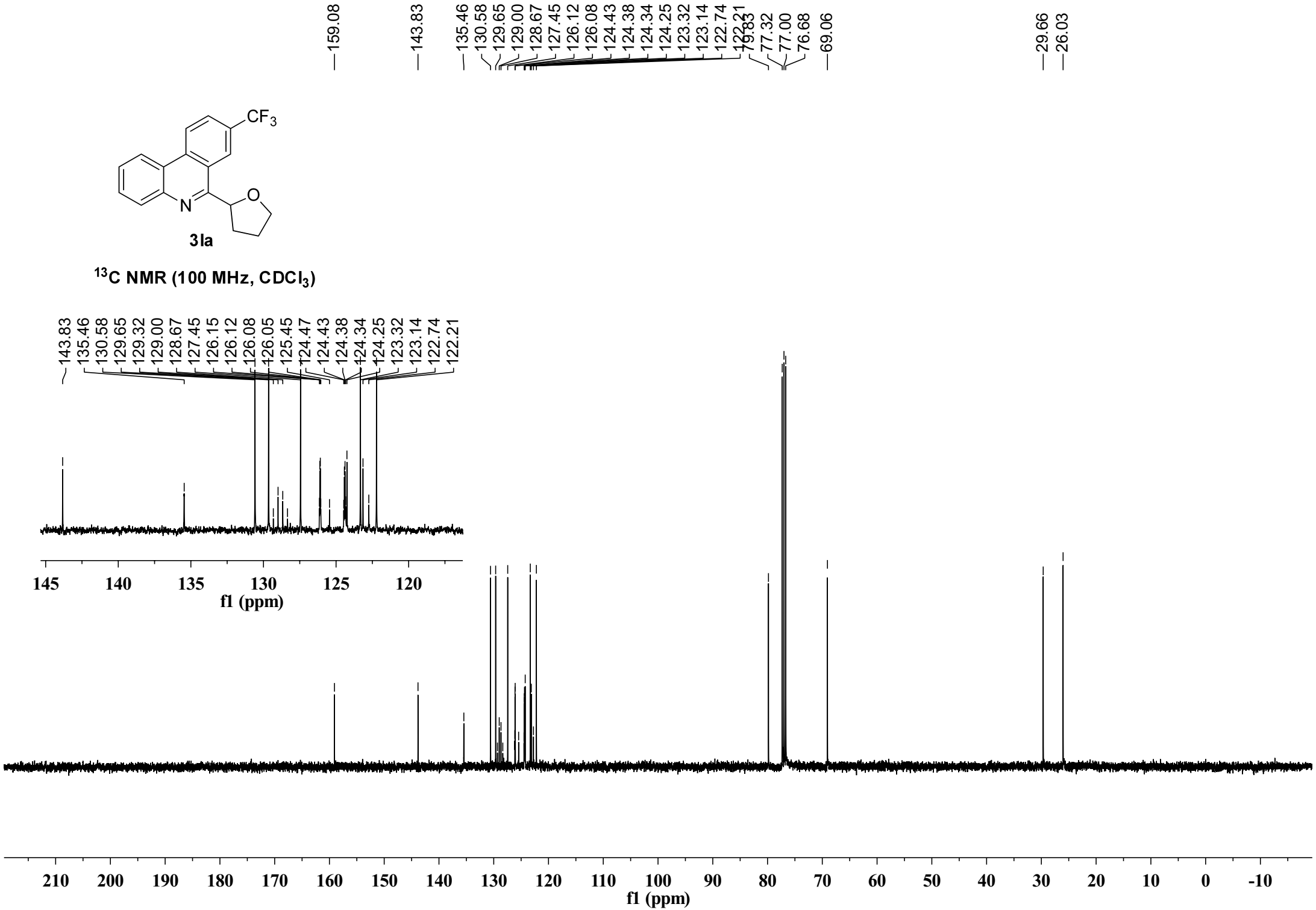

158.05
143.09
133.44
131.93
130.54
129.29
128.85
127.27
126.19
124.12
123.50
121.67
121.30
79.58
77.32
77.00
76.68
69.00
29.58
25.97
Br
N
O
3ka
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

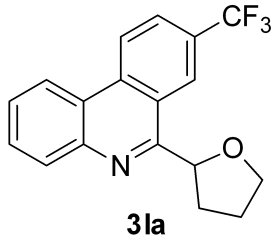


3la

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

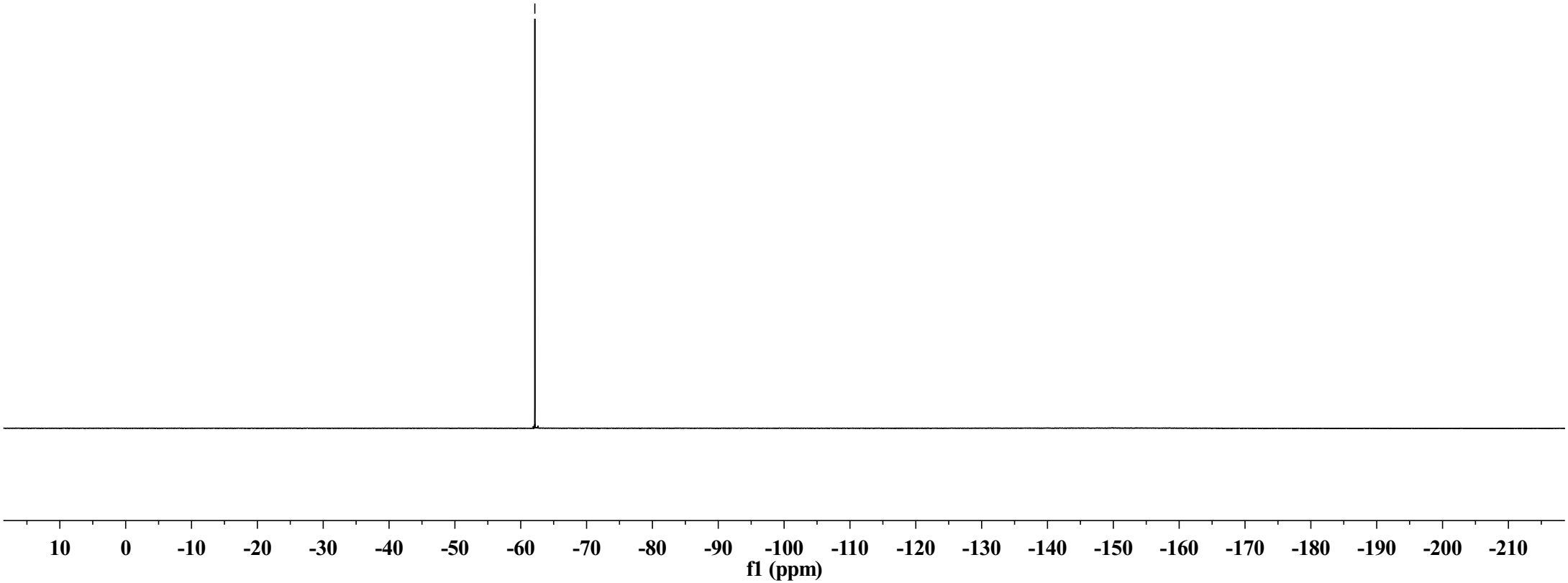


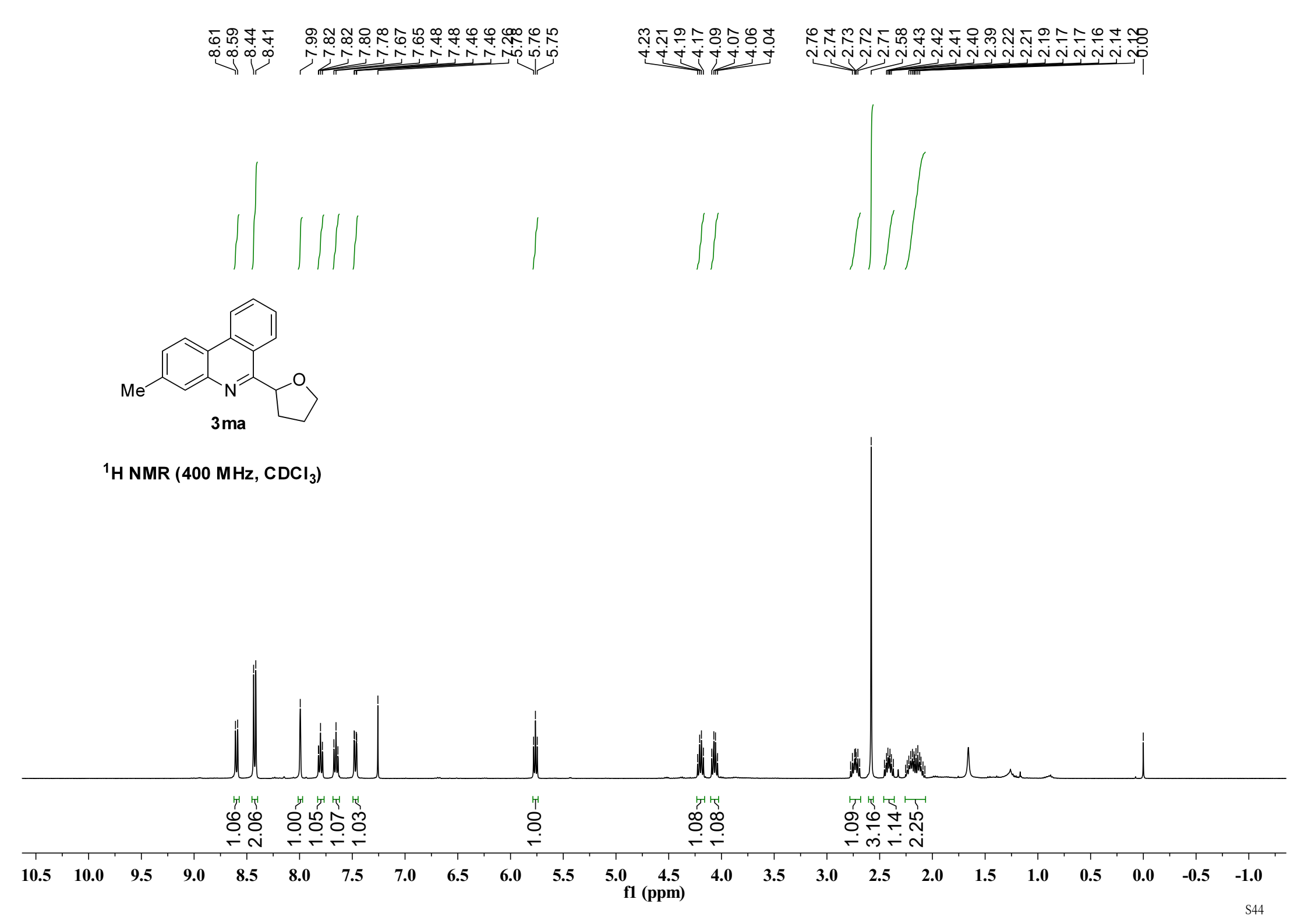

159.08
143.83
135.46
130.58
129.65
129.00
128.67
127.45
126.12
126.08
124.43
124.38
124.34
124.25
123.32
123.14
122.74
122.21
77.32
77.00
76.68
69.06
29.66
26.03
CF3
N
O
3la
13C NMR (100 MHz, CDCl3)
143.83
135.46
130.58
129.65
129.32
129.00
128.67
127.45
126.15
126.12
126.08
126.05
125.45
124.47
124.43
124.38
124.34
124.25
123.32
123.14
122.74
122.21
145
140
135
130
125
120
f1 (ppm)
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)

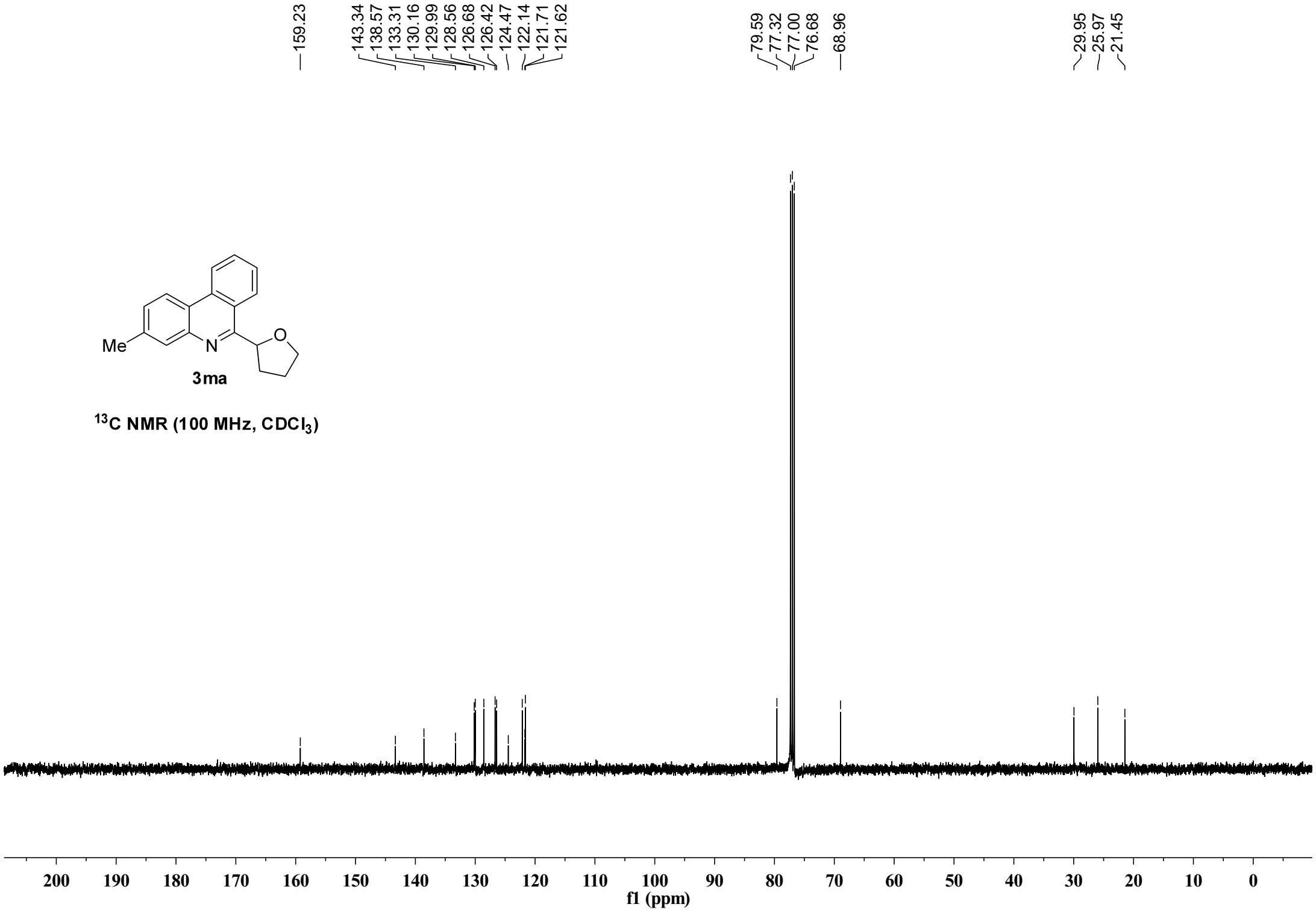


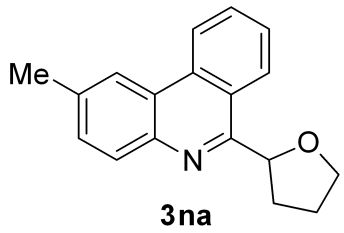
3la

^{19}F NMR (376 MHz, $CDCl_3$)



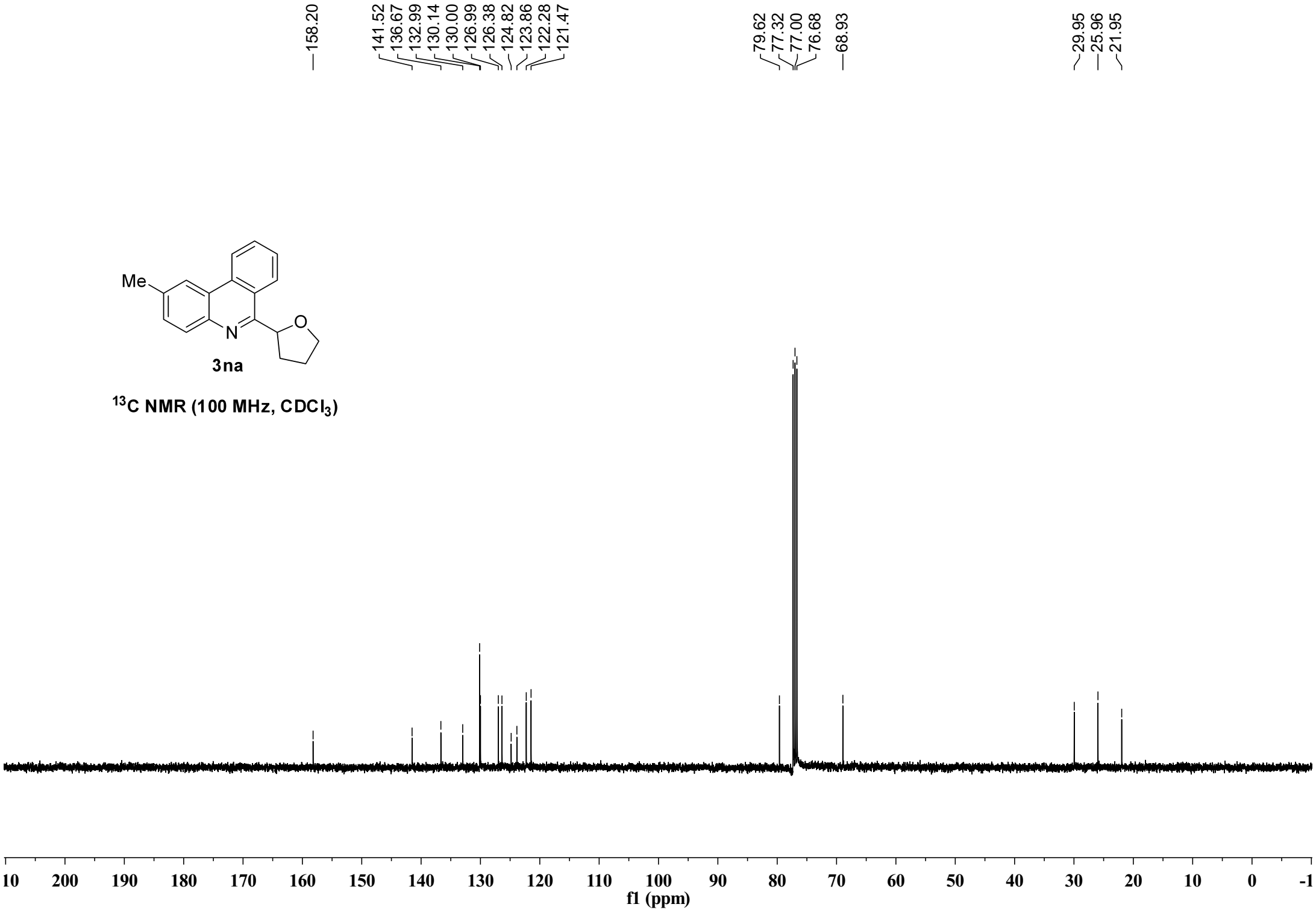

8.61
8.59
8.44
8.41
7.99
7.82
7.82
7.80
7.78
7.67
7.65
7.48
7.48
7.46
7.46
7.26
5.78
5.76
5.75
4.23
4.21
4.19
4.17
4.09
4.07
4.06
4.04
2.76
2.74
2.73
2.72
2.71
2.58
2.43
2.42
2.41
2.40
2.39
2.22
2.21
2.19
2.17
2.17
2.16
2.14
2.12
0.00
Me
N
O
3ma
1H NMR (400 MHz, CDCl3)
1.06
2.06
1.00
1.05
1.07
1.03
1.00
1.08
1.08
1.09
3.16
1.14
2.25
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)

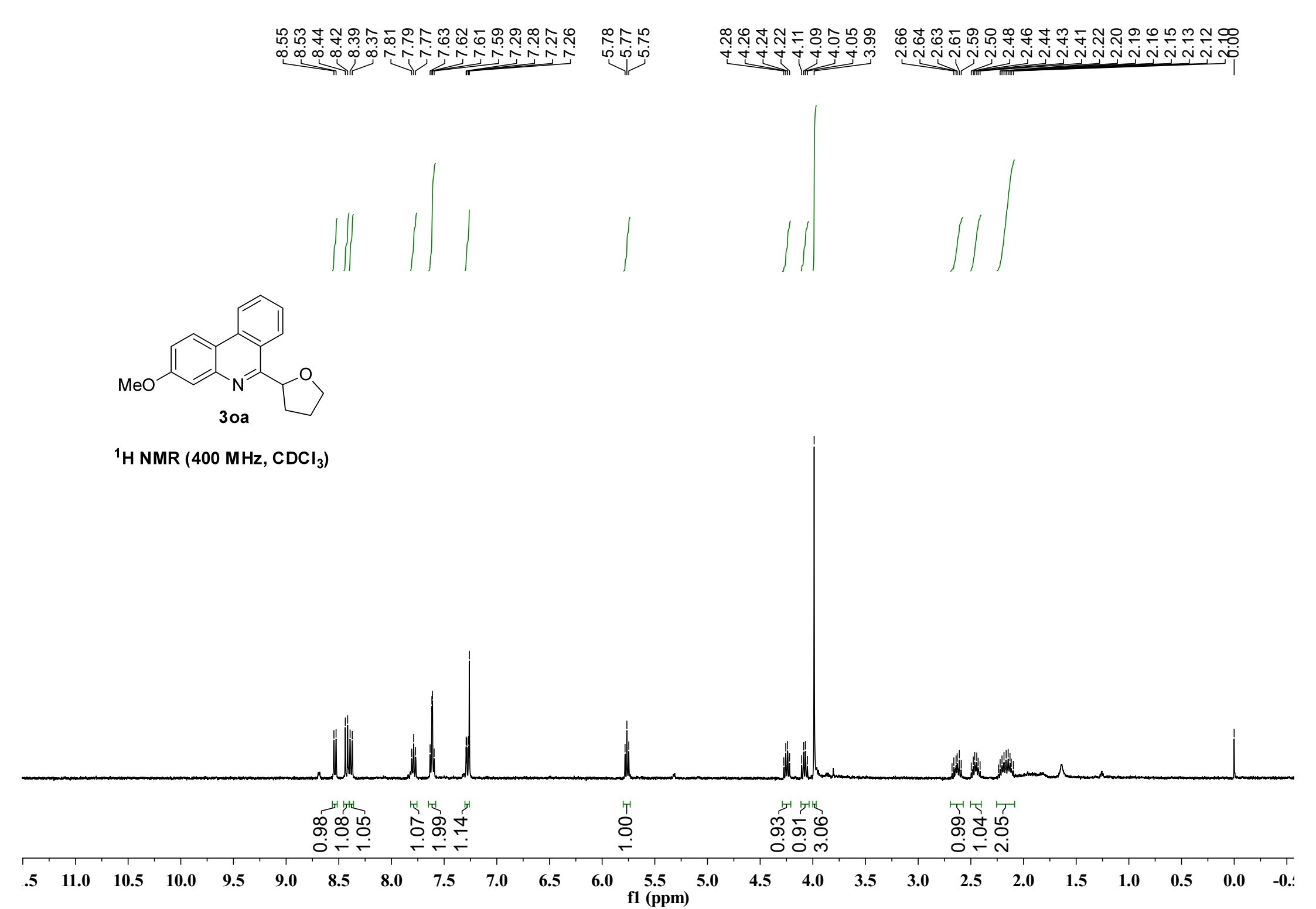

159.23
143.34
138.57
133.31
130.16
129.99
128.56
126.68
126.42
124.47
122.14
121.71
121.62
79.59
77.32
77.00
76.68
68.96
29.95
25.97
21.45
Me
N
O
3ma
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

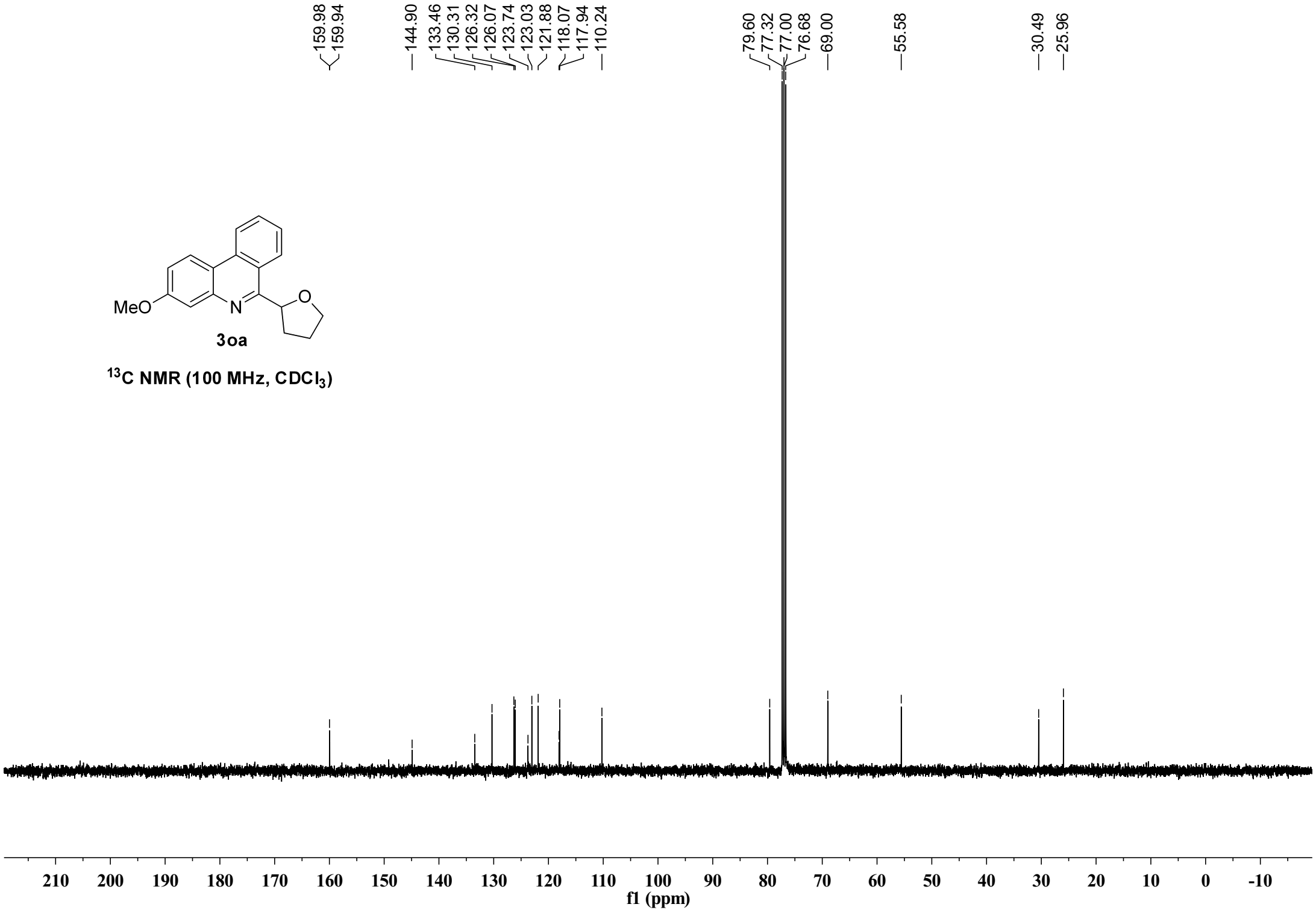


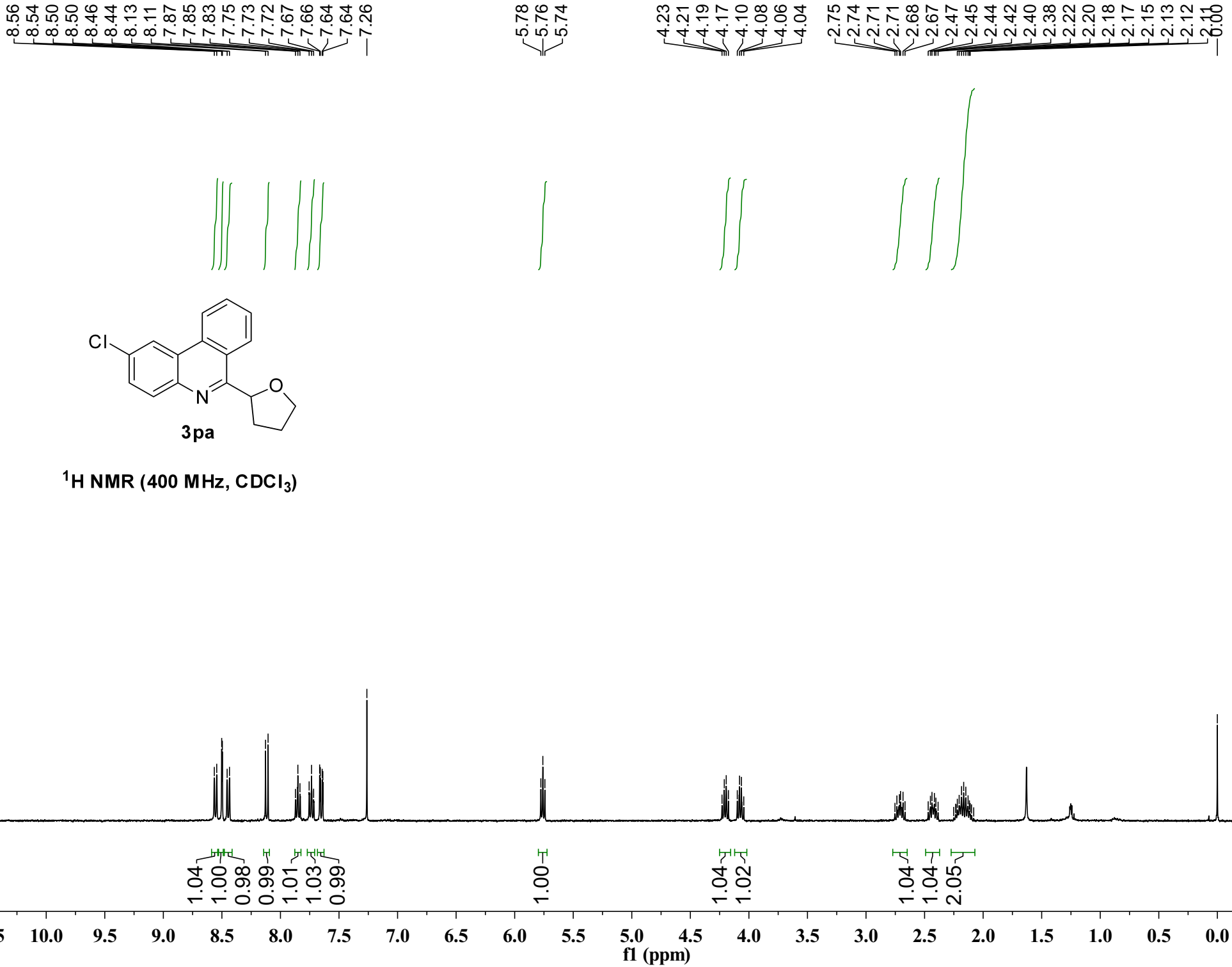
3na

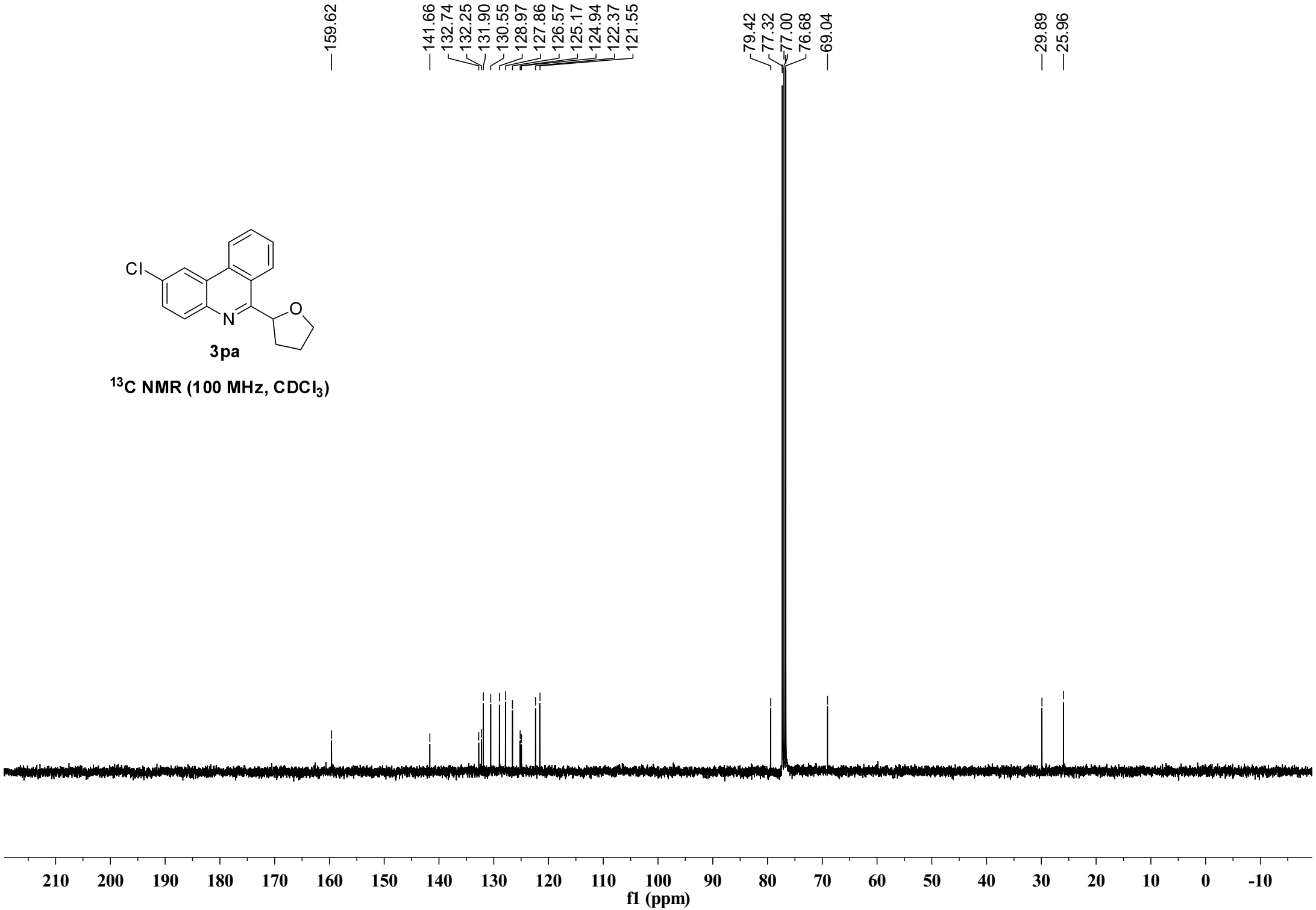
^{1}H NMR (400 MHz, $CDCl_3$)

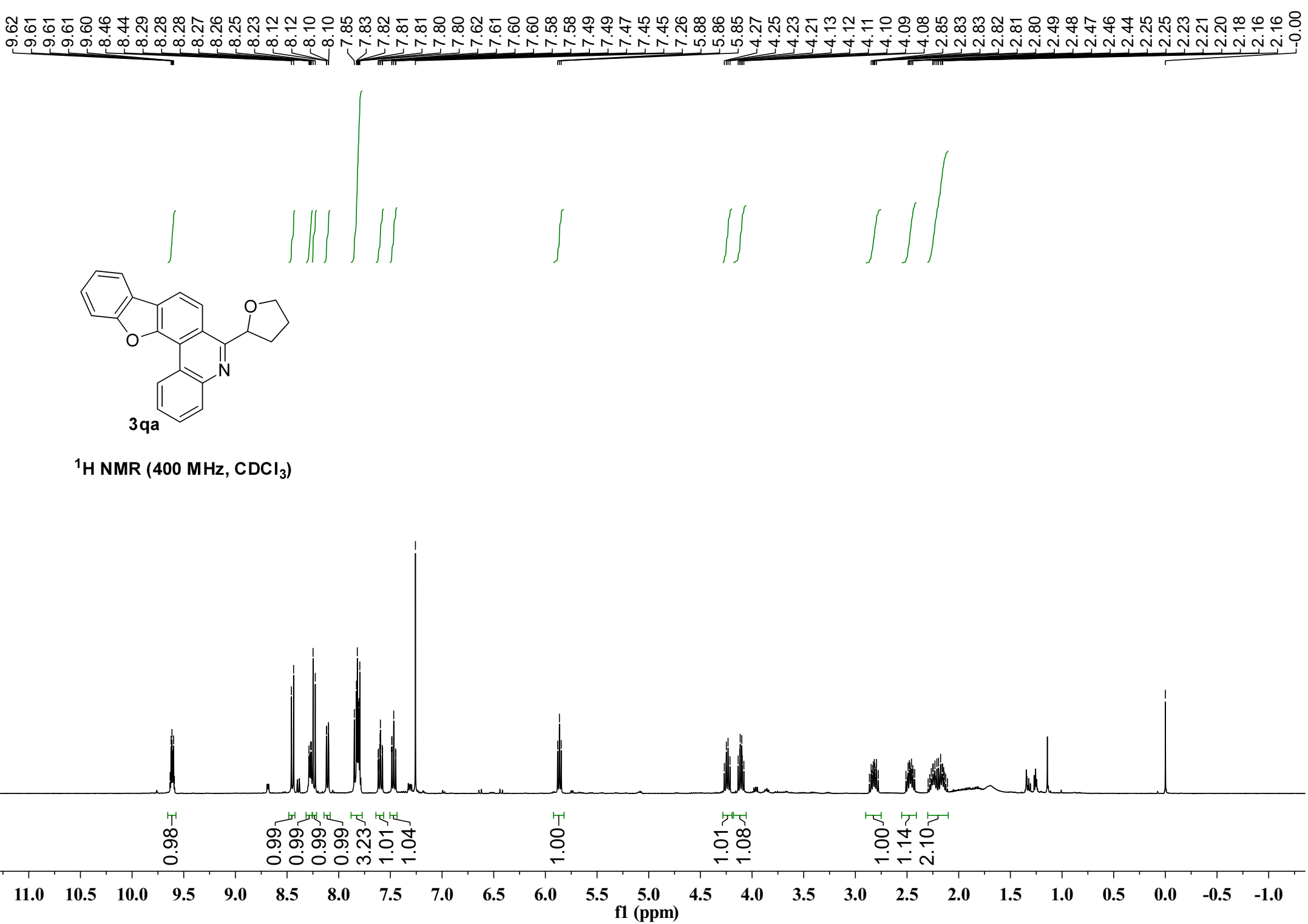

158.20
141.52
136.67
132.99
130.14
130.00
126.99
126.38
124.82
123.86
122.28
121.47
79.62
77.32
77.00
76.68
68.93
29.95
25.96
21.95
Me
N
O
3na
13C NMR (100 MHz, CDCl3)
f1 (ppm)

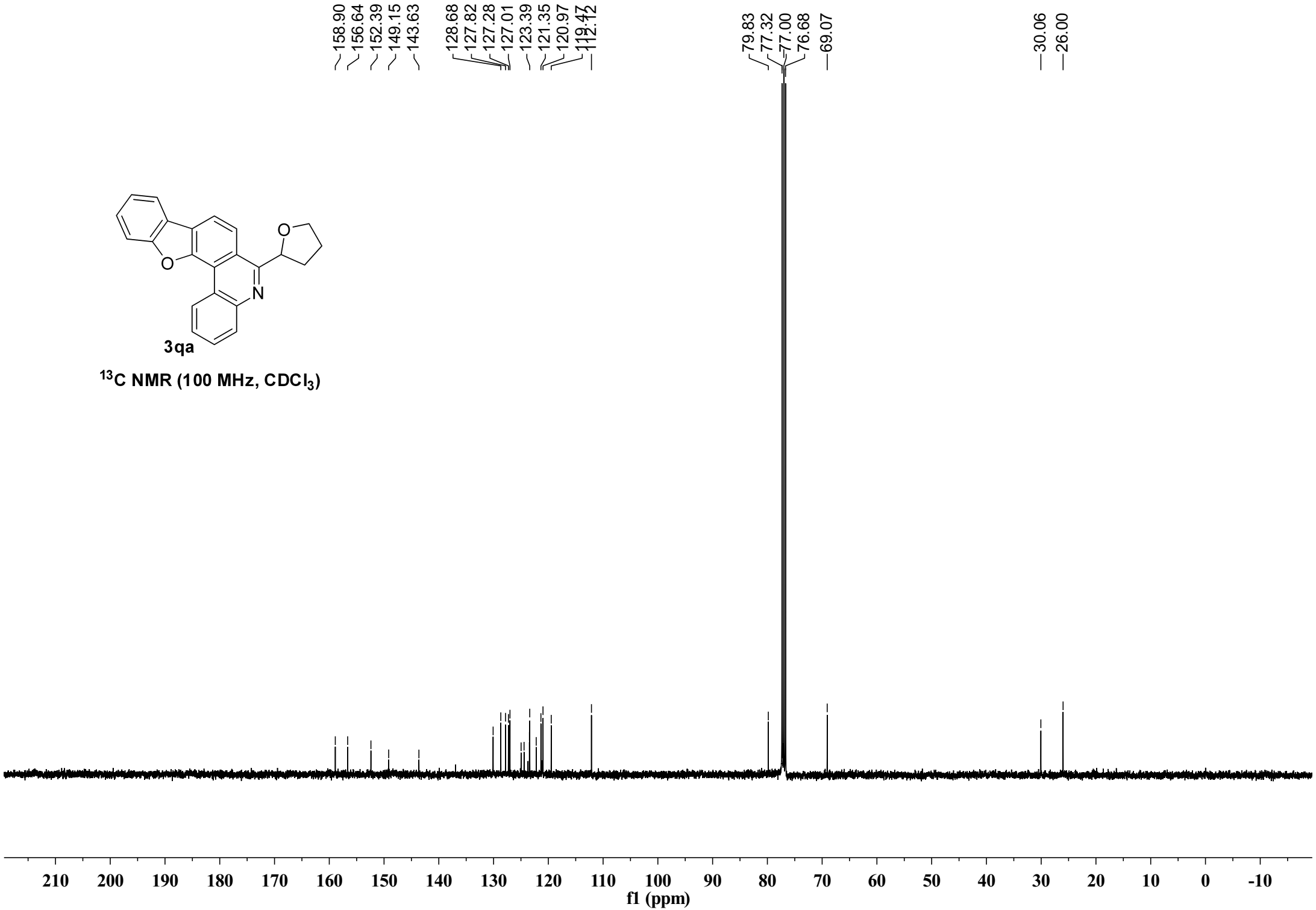

8.55
8.53
8.44
8.42
8.39
8.37
7.81
7.79
7.77
7.63
7.62
7.61
7.59
7.29
7.28
7.27
7.26
5.78
5.77
5.75
4.28
4.26
4.24
4.22
4.11
4.09
4.07
4.05
3.99
2.66
2.64
2.63
2.61
2.59
2.50
2.48
2.46
2.44
2.43
2.41
2.22
2.20
2.19
2.16
2.15
2.13
2.12
2.10
2.00
MeO
N
O
3oa
1H NMR (400 MHz, CDCl3)
0.98
1.08
1.05
1.07
1.99
1.14
1.00
0.93
0.91
3.06
0.99
1.04
2.05
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
f1 (ppm)

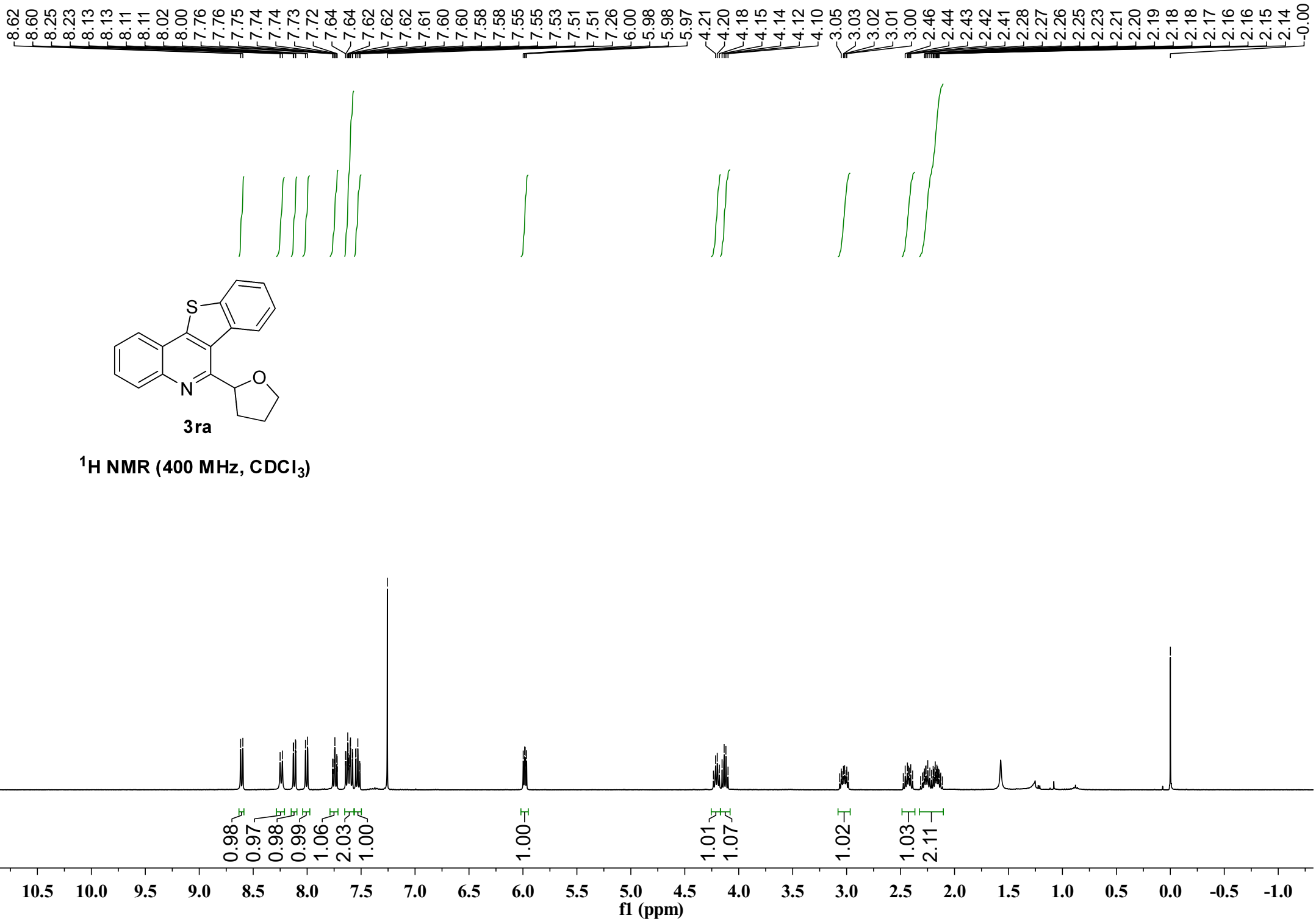

159.98
159.94
144.90
133.46
130.31
126.32
126.07
123.74
123.03
121.88
118.07
117.94
110.24
79.60
77.32
77.00
76.68
69.00
55.58
30.49
25.96
MeO
N
O
3oa
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

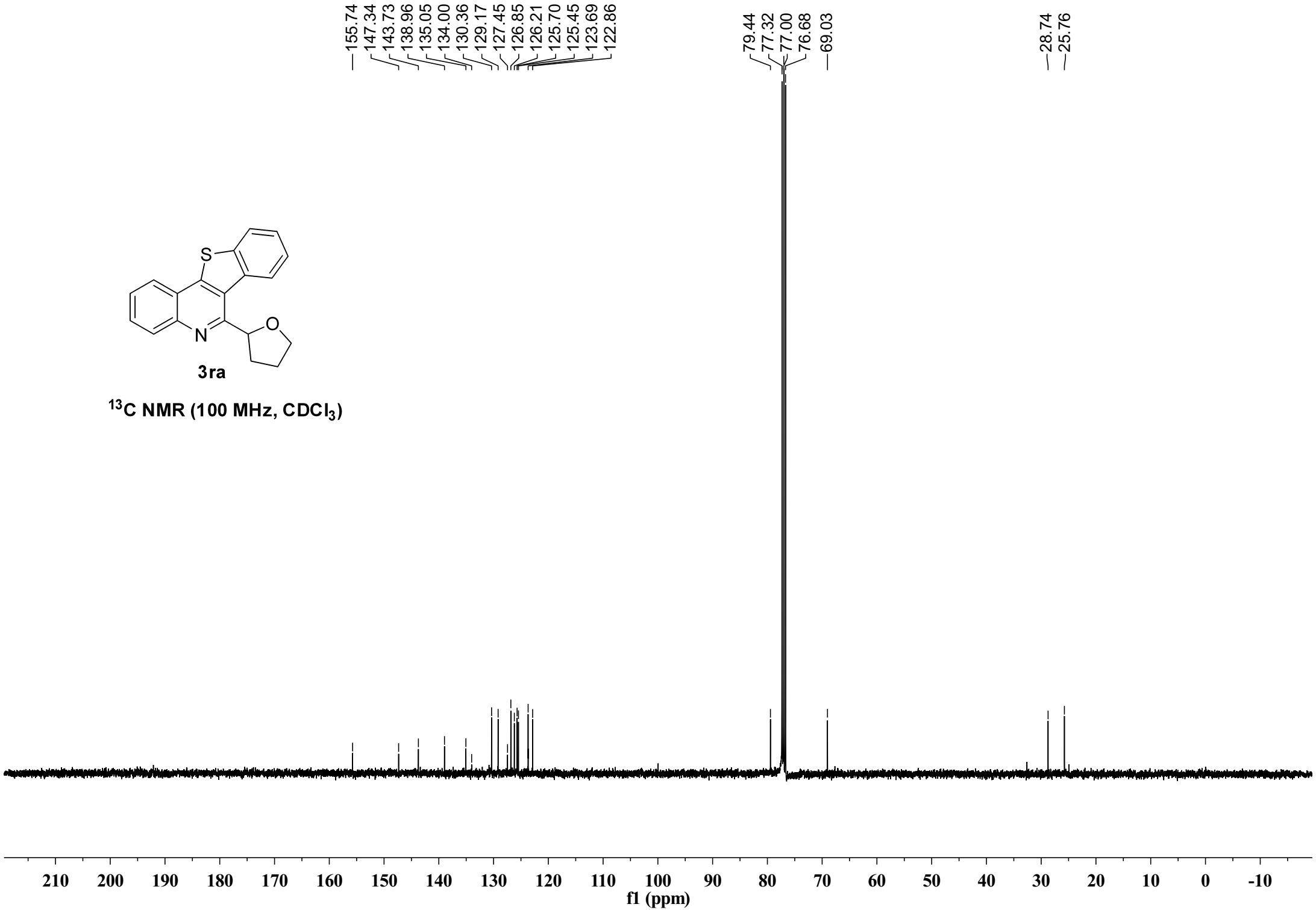

8.56
8.54
8.50
8.50
8.46
8.44
8.13
8.11
7.87
7.85
7.83
7.75
7.73
7.72
7.67
7.66
7.64
7.64
7.26
5.78
5.76
5.74
4.23
4.21
4.19
4.17
4.10
4.08
4.06
4.04
2.75
2.74
2.71
2.71
2.68
2.67
2.47
2.45
2.44
2.42
2.40
2.38
2.22
2.20
2.18
2.17
2.15
2.13
2.12
2.11
0.00
Cl
N
O
3pa
1H NMR (400 MHz, CDCl3)
1.04
1.00
0.98
0.99
1.01
1.03
0.99
1.00
1.04
1.02
1.04
1.04
2.05
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)

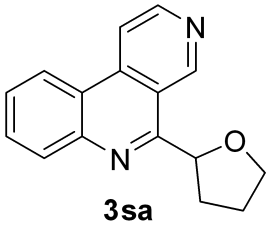

159.62
141.66
132.74
132.25
131.90
130.55
128.97
127.86
126.57
125.17
124.94
122.37
121.55
79.42
77.32
77.00
76.68
69.04
29.89
25.96
Cl
N
O
3pa
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.62 9.61 9.61 9.61 9.60 8.46 8.44 8.29 8.28 8.28 8.27 8.26 8.25 8.23 8.12 8.12 8.10 8.10 7.85 7.83 7.82 7.81 7.81 7.80 7.80 7.62 7.61 7.60 7.60 7.58 7.58 7.49 7.49 7.47 7.45 7.45 7.26 5.88 5.86 5.85 4.27 4.25 4.23 4.21 4.13 4.12 4.11 4.10 4.09 4.08 2.85 2.83 2.83 2.82 2.81 2.80 2.49 2.48 2.47 2.46 2.44 2.25 2.25 2.23 2.21 2.20 2.18 2.16 2.16 -0.00
O
O
N
3qa
1H NMR (400 MHz, CDCl3)
0.98 0.99 0.99 0.99 0.99 3.23 1.01 1.04 1.00 1.01 1.08 1.00 1.14 2.10
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)


158.90
156.64
152.39
149.15
143.63
128.68
127.82
127.28
127.01
123.39
121.35
120.97
79.83
77.32
77.00
76.68
69.07
30.06
26.00
O
O
N
3qa
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)

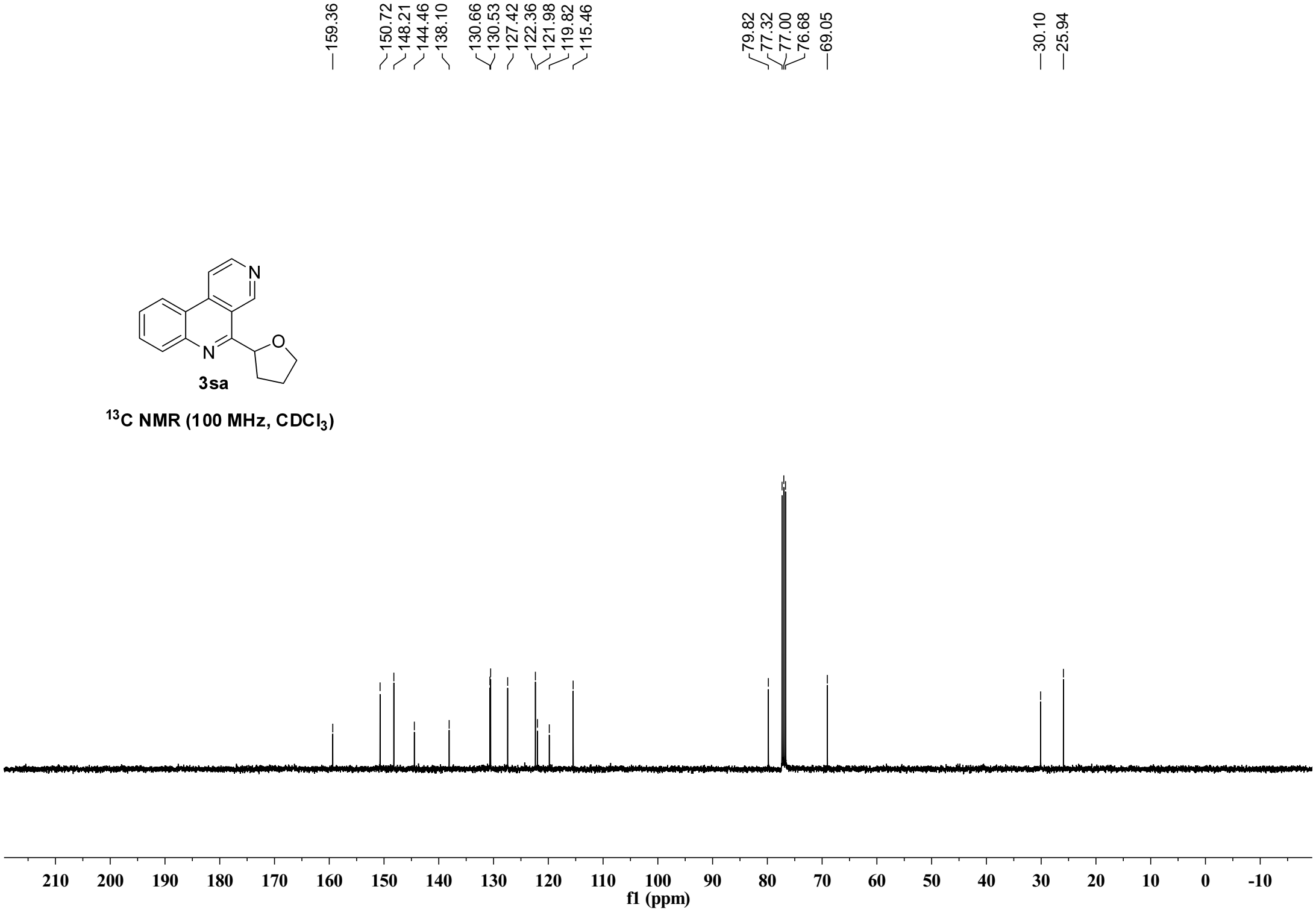

8.62 8.60 8.25 8.23 8.13 8.13 8.11 8.11 8.02 8.00 7.76 7.76 7.75 7.74 7.74 7.73 7.72 7.64 7.64 7.62 7.62 7.62 7.61 7.60 7.60 7.58 7.58 7.55 7.55 7.53 7.51 7.51 7.26 6.00 5.98 5.98 5.97 4.21 4.20 4.18 4.15 4.14 4.12 4.10 3.05 3.03 3.02 3.01 3.00 2.46 2.44 2.43 2.42 2.41 2.28 2.27 2.26 2.25 2.23 2.21 2.20 2.19 2.18 2.18 2.17 2.16 2.16 2.15 2.14 -0.00
S
N
O
3ra
1H NMR (400 MHz, CDCl3)
0.98 0.97 0.98 0.99 1.06 2.03 1.00 1.00 1.01 1.07 1.02 1.03 2.11
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)

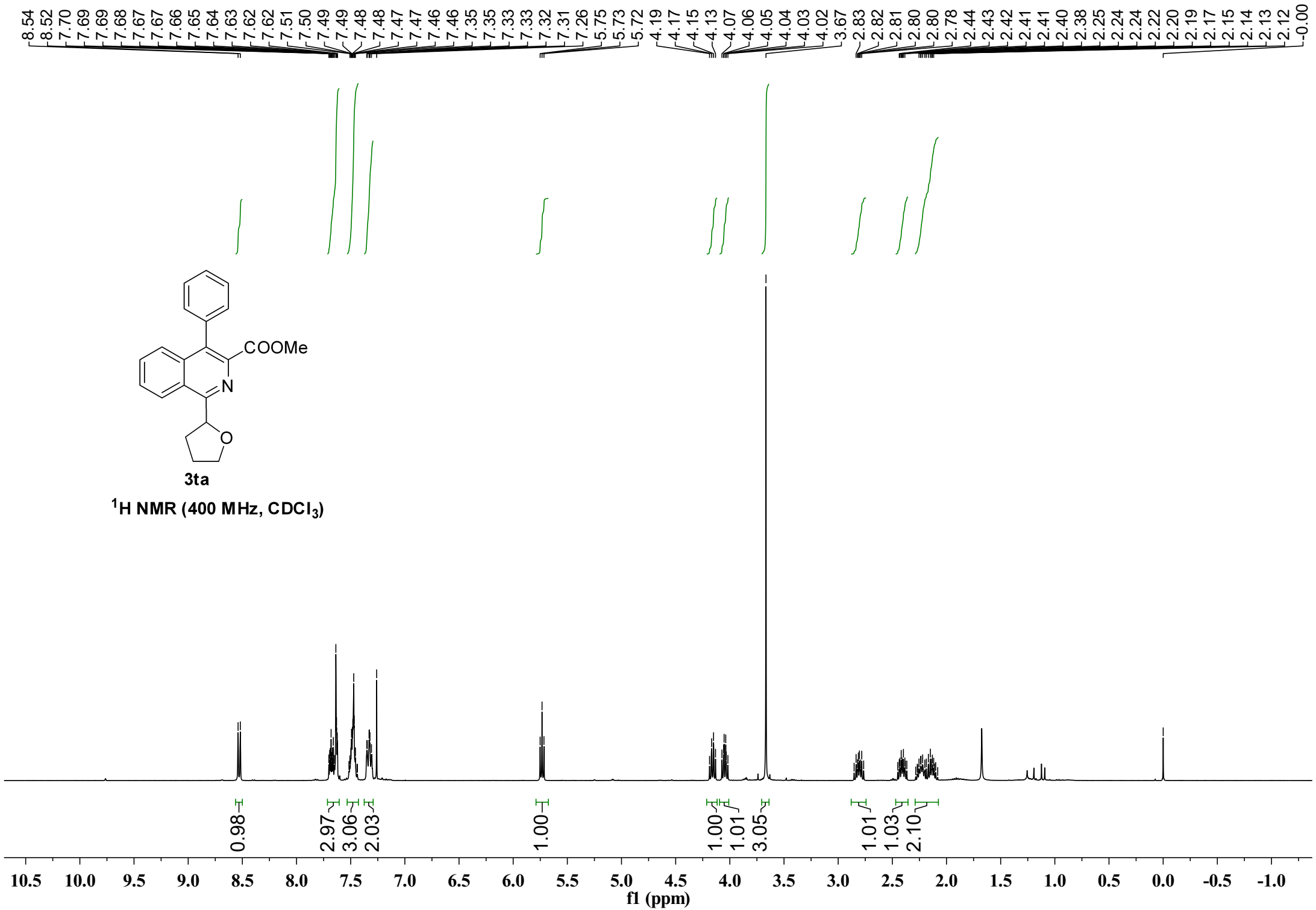

155.74
147.34
143.73
138.96
135.05
134.00
130.36
129.17
127.45
126.85
126.21
125.70
125.45
123.69
122.86
79.44
77.32
77.00
76.68
69.03
28.74
25.76
S
N
O
3ra
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

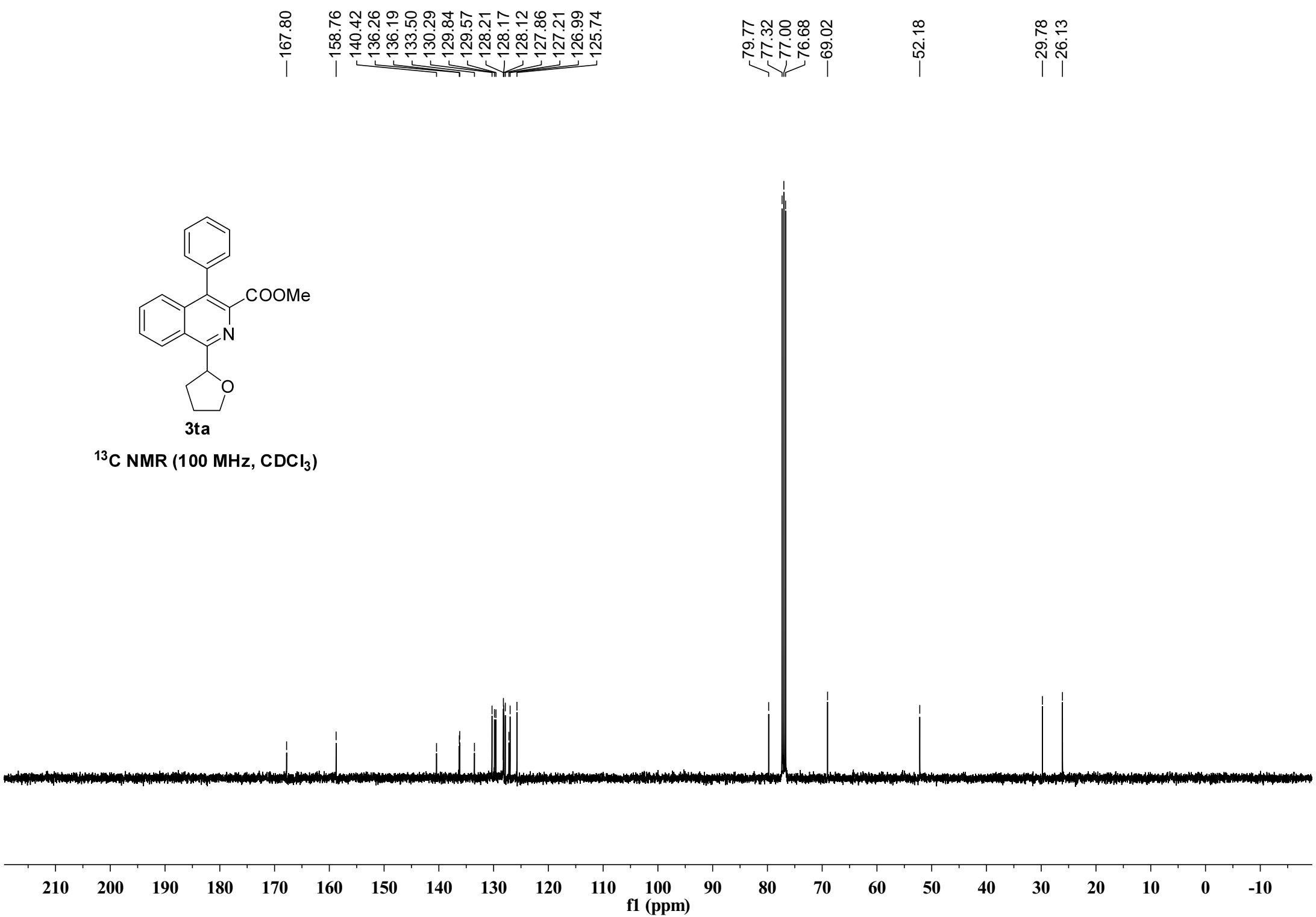


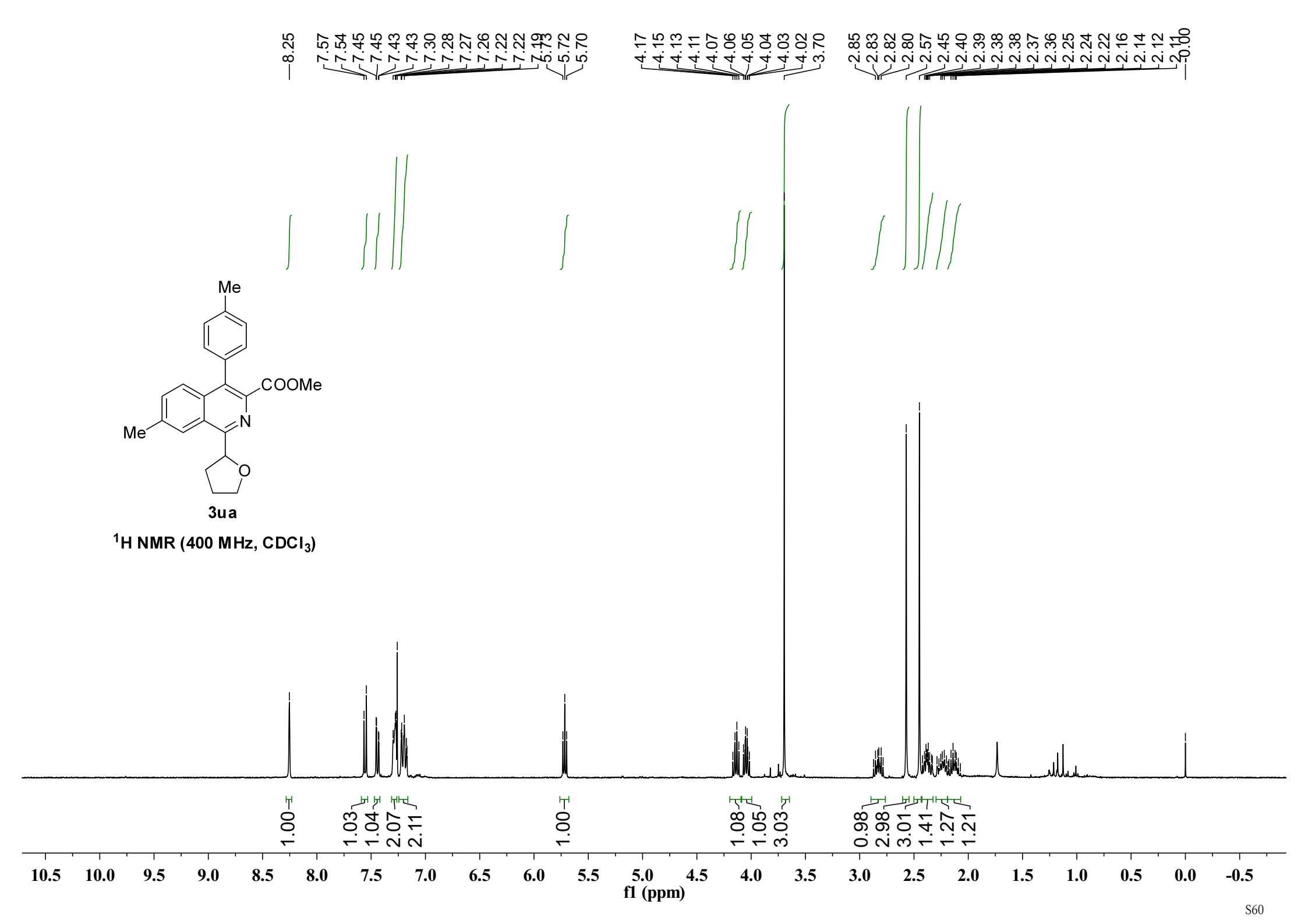
3sa

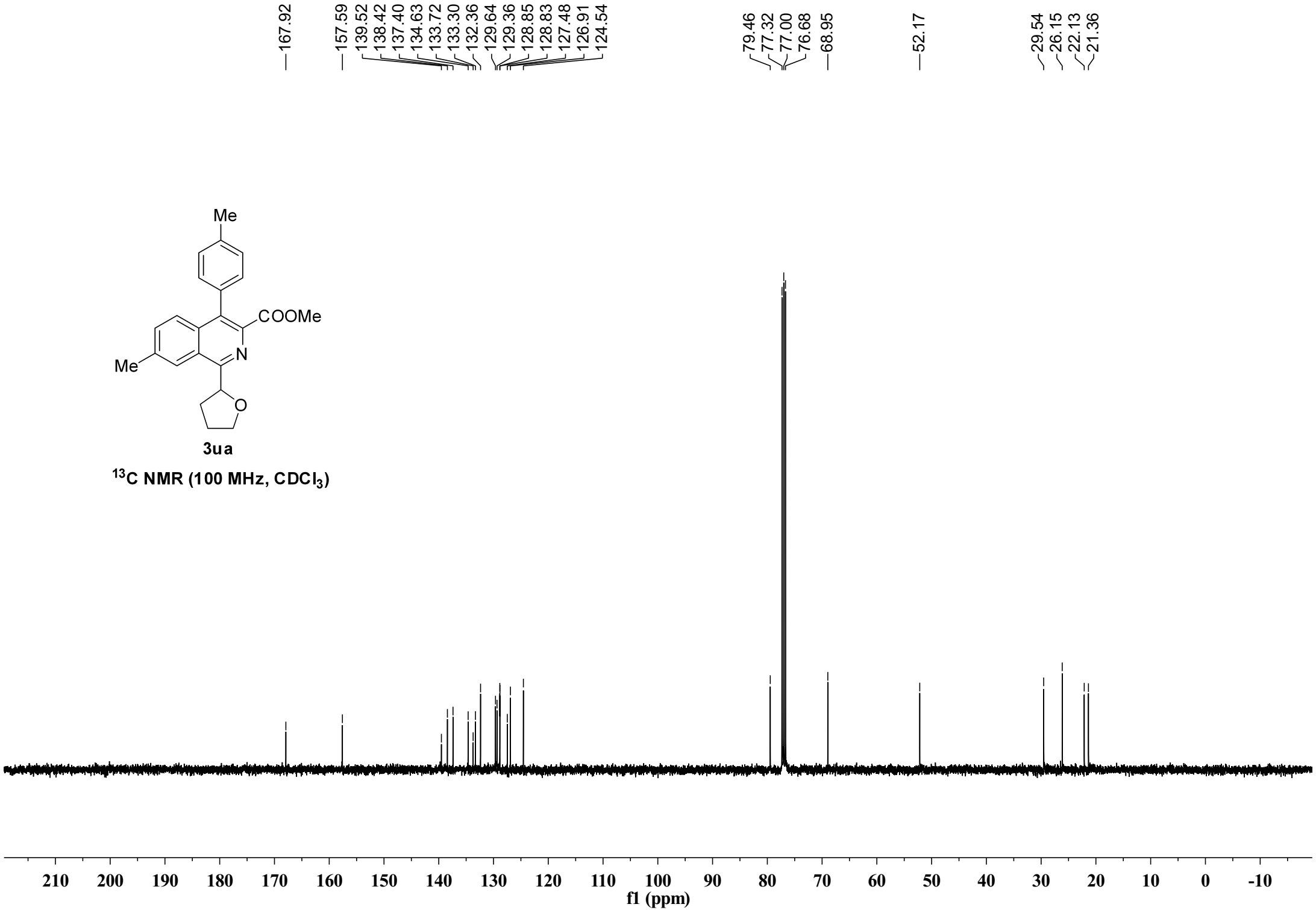
^{1}H NMR (400 MHz, $CDCl_3$)

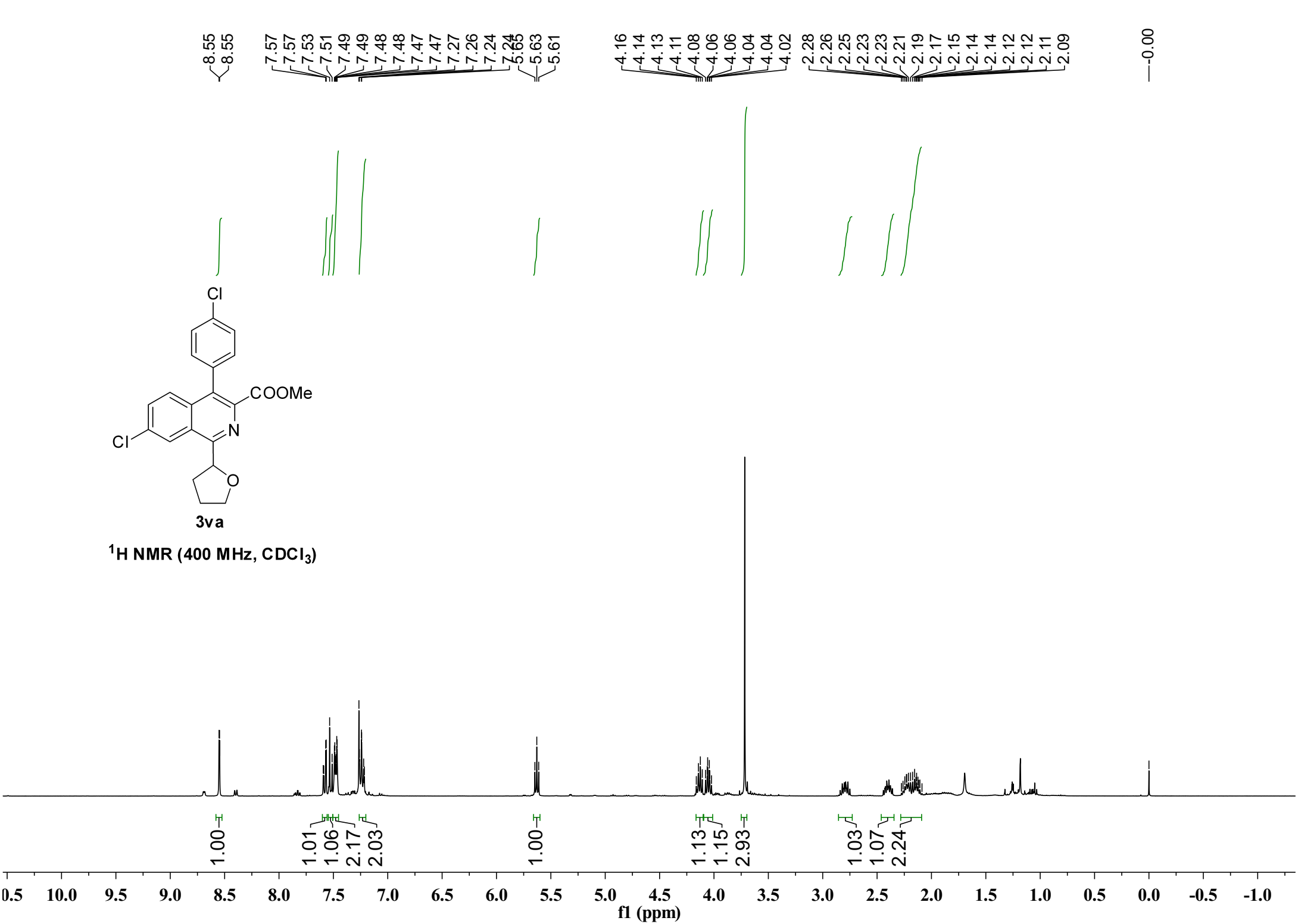

159.36
150.72
148.21
144.46
138.10
130.66
130.53
127.42
122.36
121.98
119.82
115.46
79.82
77.32
77.00
76.68
69.05
30.10
25.94
N
N
O
3sa
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.54 8.52 7.70 7.69 7.69 7.68 7.67 7.67 7.66 7.65 7.64 7.63 7.62 7.62 7.51 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.35 7.35 7.33 7.33 7.32 7.31 7.26 5.75 5.73 5.72 4.19 4.17 4.15 4.13 4.07 4.06 4.05 4.04 4.03 4.02 3.67 2.83 2.82 2.81 2.80 2.80 2.78 2.44 2.43 2.42 2.41 2.41 2.40 2.38 2.25 2.24 2.24 2.22 2.20 2.19 2.17 2.15 2.14 2.13 2.12 -0.00
COOMe
N
O
3ta
1H NMR (400 MHz, CDCl3)
0.98 2.97 3.06 2.03 1.00 1.00 1.01 3.05 1.01 1.03 2.10
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)


167.80
158.76
140.42
136.26
136.19
133.50
130.29
129.84
129.57
128.21
128.17
128.12
127.86
127.21
126.99
125.74
79.77
77.32
77.00
76.68
69.02
52.18
29.78
26.13
COOMe
N
O
3ta
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)

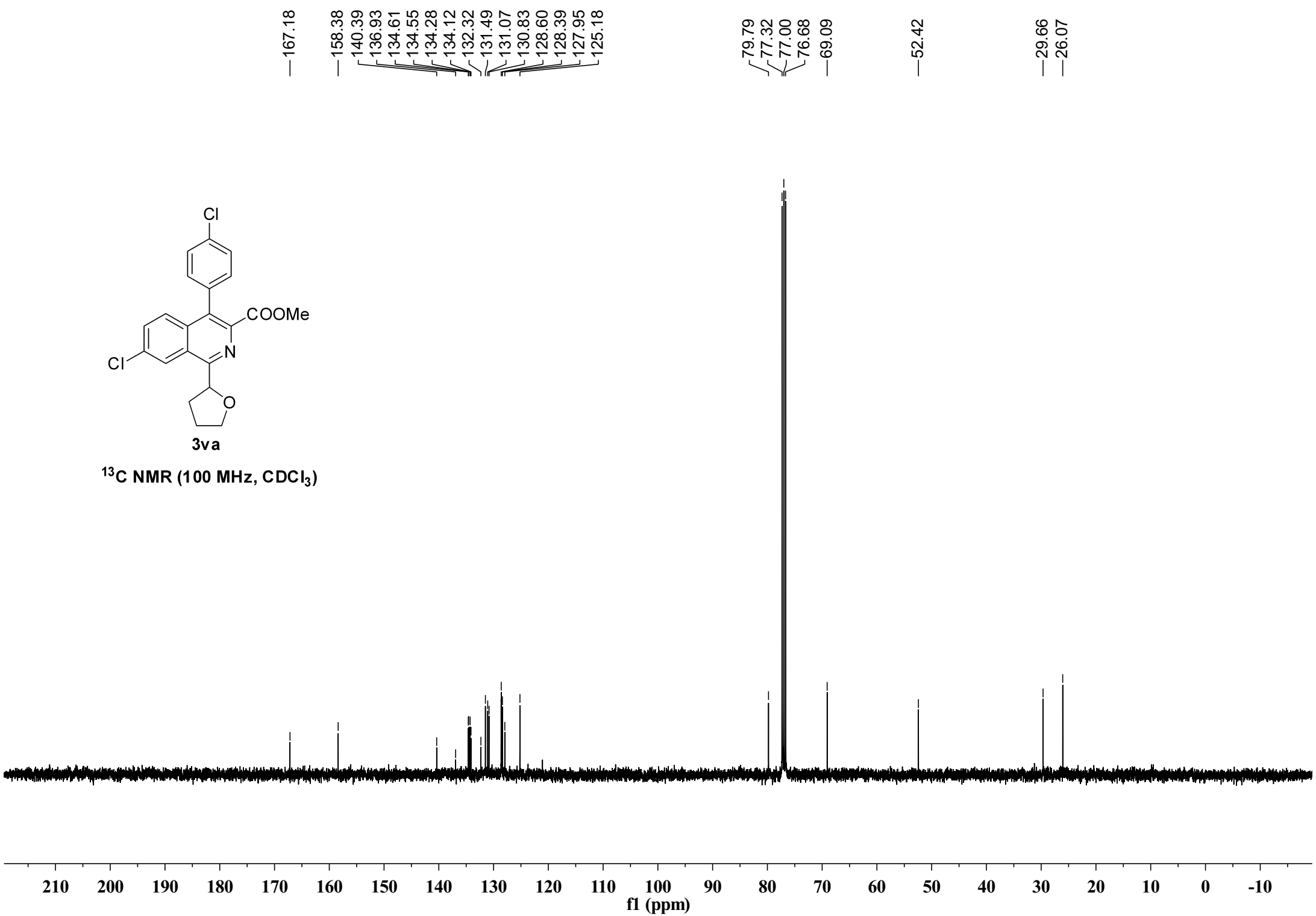

8.25
7.57
7.54
7.45
7.45
7.43
7.43
7.30
7.28
7.27
7.26
7.22
7.22
7.19
5.73
5.72
5.70
4.17
4.15
4.13
4.11
4.07
4.06
4.05
4.04
4.03
4.02
3.70
2.85
2.83
2.82
2.80
2.57
2.45
2.40
2.39
2.38
2.38
2.37
2.36
2.25
2.24
2.22
2.16
2.14
2.12
2.11
0.00
Me
COOMe
N
Me
O
3ua
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.04
2.07
2.11
1.00
1.08
1.05
3.03
0.98
2.98
3.01
1.41
1.27
1.21
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)

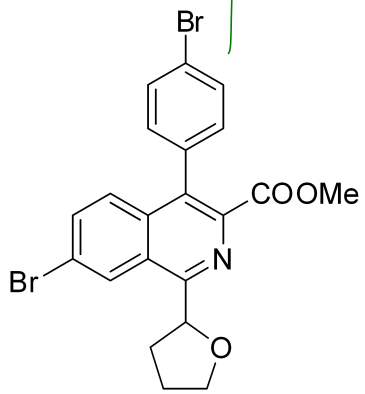

167.92
157.59
139.52
138.42
137.40
134.63
133.72
133.30
132.36
129.64
129.36
128.85
128.83
127.48
126.91
124.54
79.46
77.32
77.00
76.68
68.95
52.17
29.54
26.15
22.13
21.36
Me
COOMe
N
Me
O
3ua
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3va

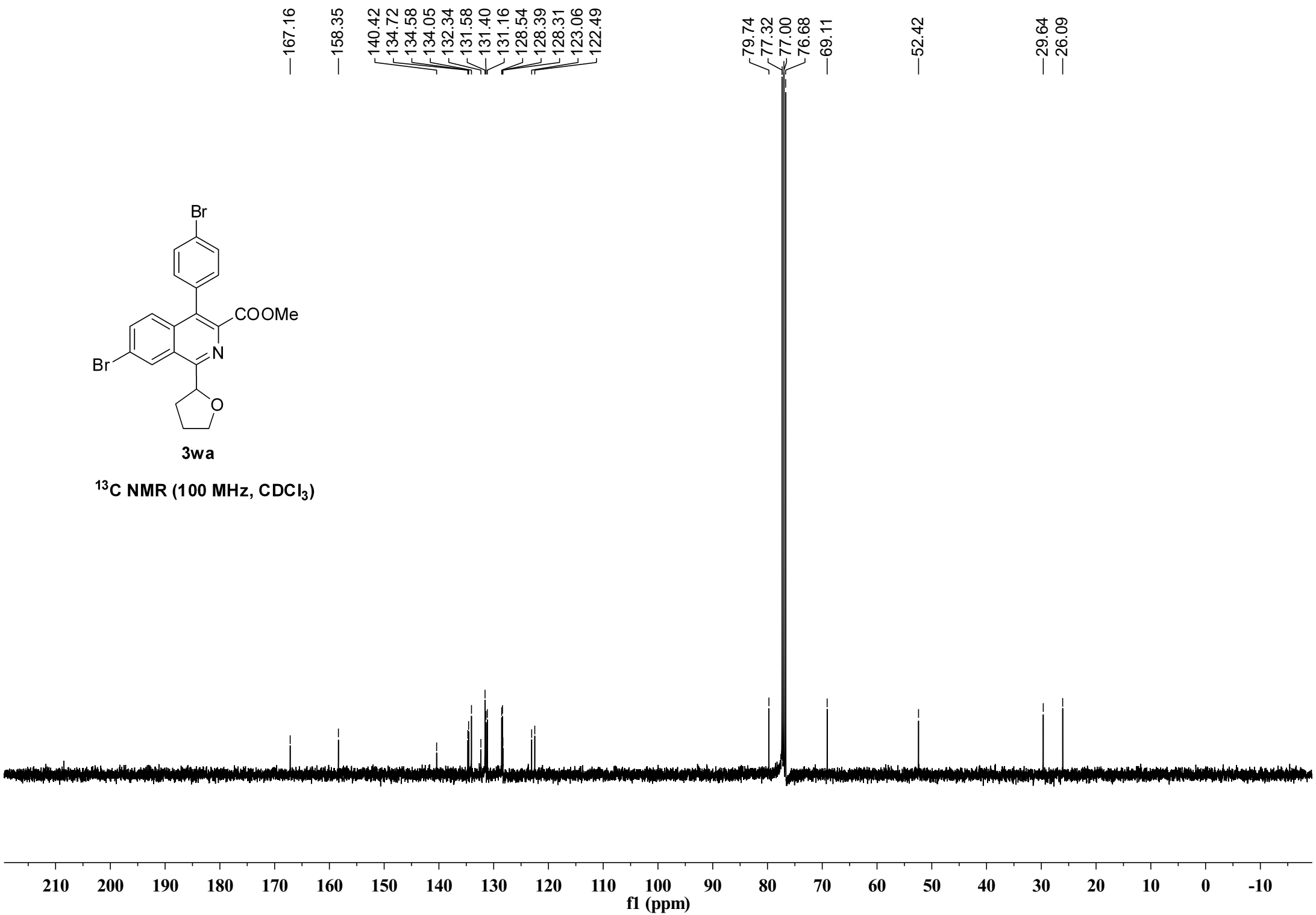
^{1}H NMR (400 MHz, $CDCl_3$)

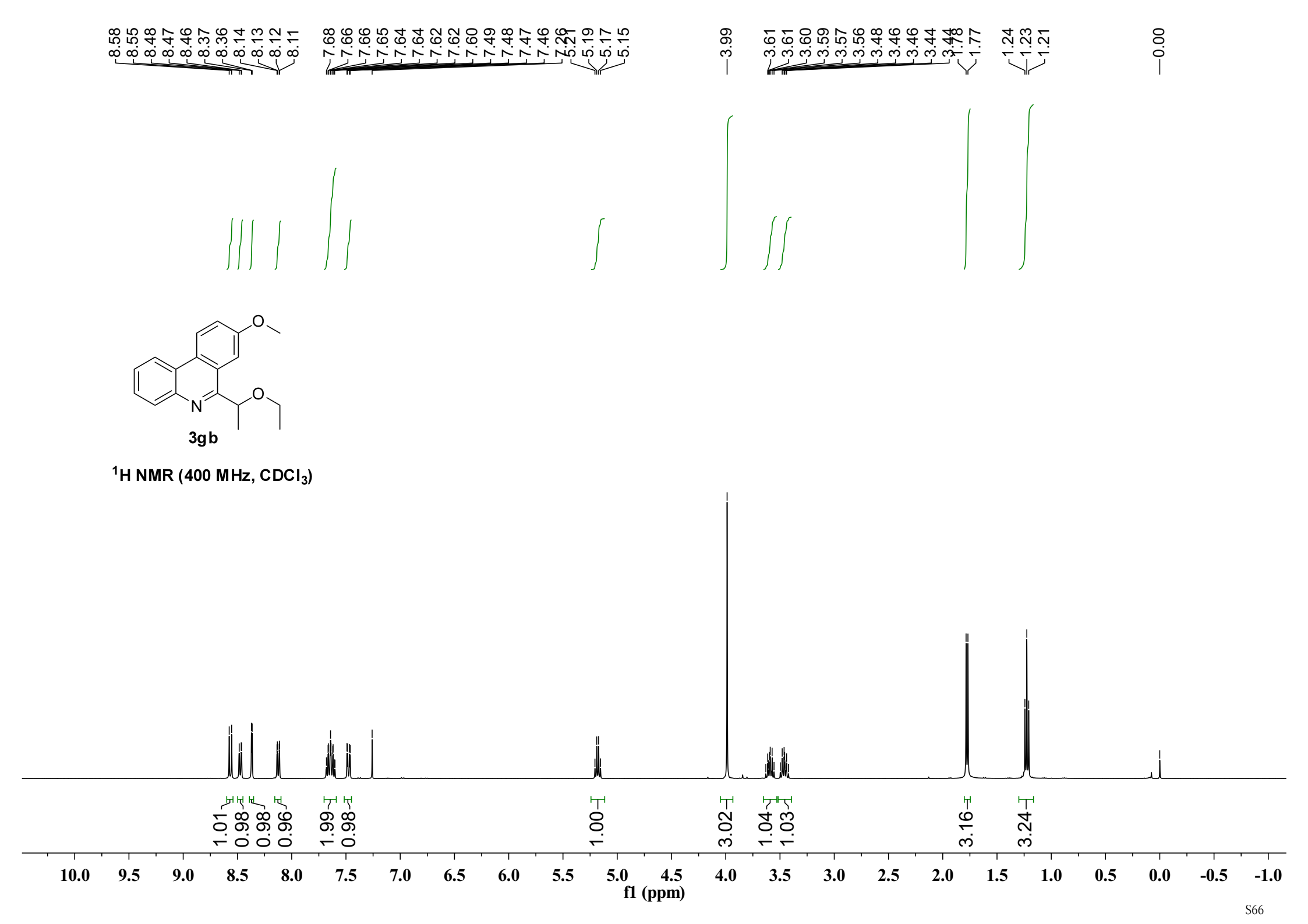

167.18
158.38
140.39
136.93
134.61
134.55
134.28
134.12
132.32
131.49
131.07
130.83
128.60
128.39
127.95
125.18
79.79
77.32
77.00
76.68
69.09
52.42
29.66
26.07
Cl
COOMe
N
Cl
O
3va
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

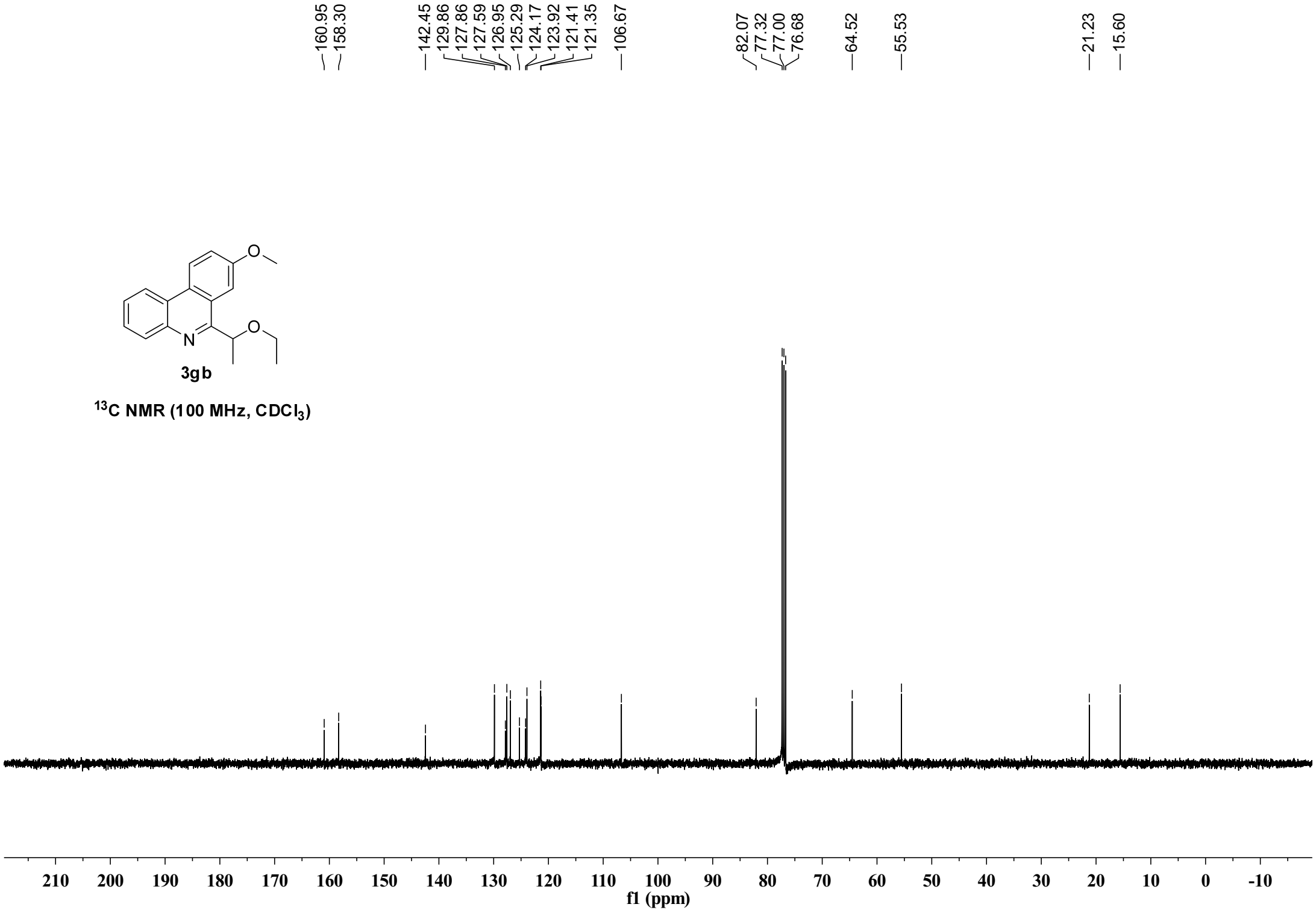


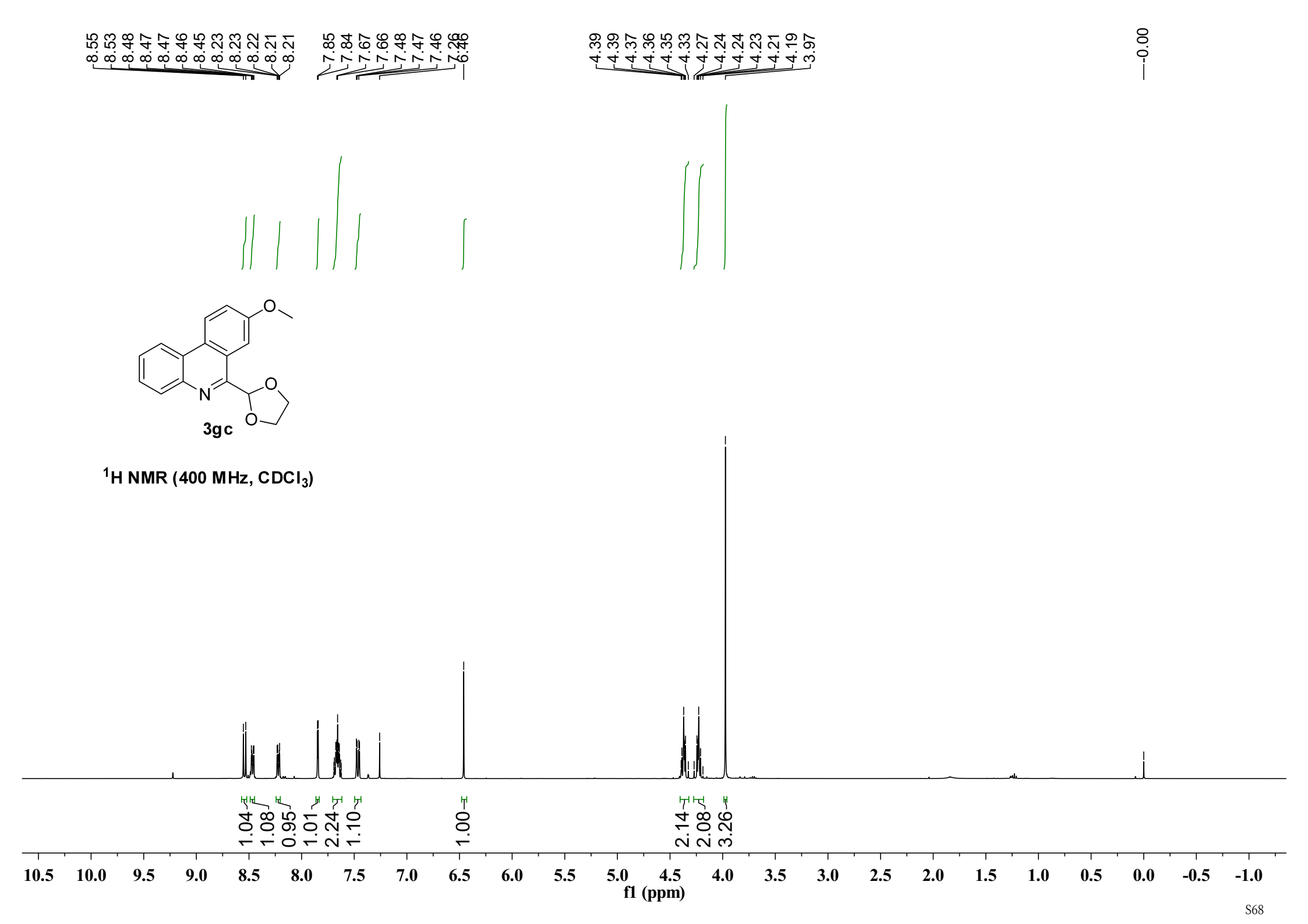
3wa

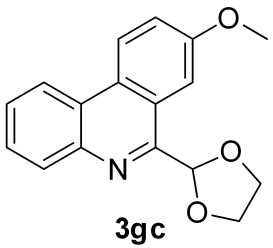
^{1}H NMR (400 MHz, $CDCl_3$)


167.16
158.35
140.42
134.72
134.58
134.05
132.34
131.58
131.40
131.16
128.54
128.39
128.31
123.06
122.49
79.74
77.32
77.00
76.68
69.11
52.42
29.64
26.09
Br
COOMe
N
Br
O
3wa
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)


8.58
8.55
8.48
8.47
8.46
8.37
8.36
8.14
8.13
8.12
8.11
7.68
7.66
7.66
7.65
7.64
7.64
7.62
7.62
7.60
7.49
7.48
7.47
7.46
7.26
5.21
5.19
5.17
5.15
3.99
3.61
3.61
3.60
3.59
3.57
3.56
3.48
3.46
3.46
3.44
3.44
1.78
1.77
1.24
1.23
1.21
0.00
O
O
N
3gb
1H NMR (400 MHz, CDCl3)
1.01
0.98
0.98
0.96
1.99
0.98
1.00
3.02
1.04
1.03
3.16
3.24
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)

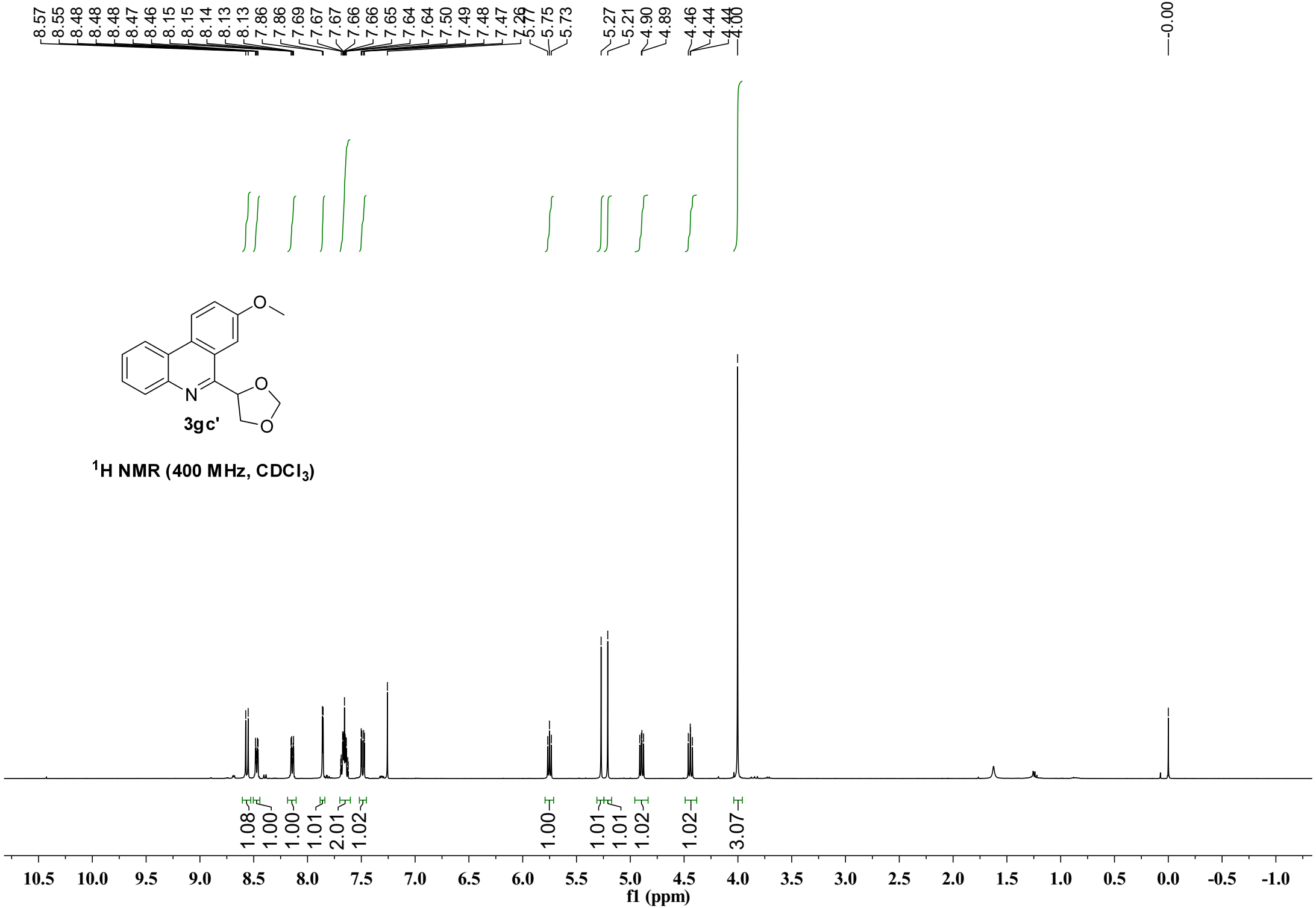

160.95
158.30
142.45
129.86
127.86
127.59
126.95
125.29
124.17
123.92
121.41
121.35
106.67
82.07
77.32
77.00
76.68
64.52
55.53
21.23
15.60
O
N
O
3gb
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

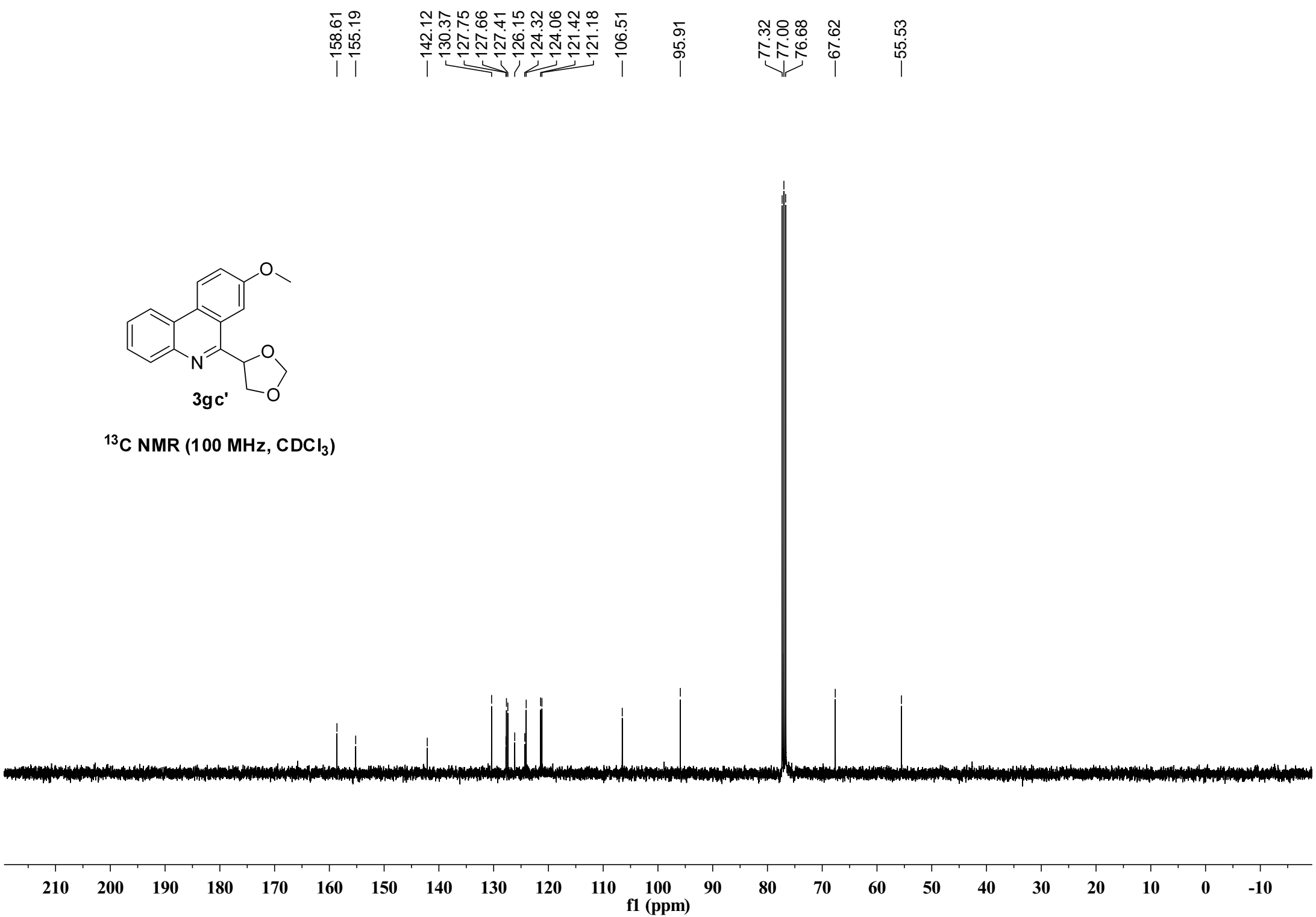

8.55
8.53
8.48
8.47
8.47
8.46
8.45
8.23
8.23
8.22
8.21
8.21
7.85
7.84
7.67
7.66
7.48
7.47
7.46
7.26
6.46
4.39
4.39
4.37
4.36
4.35
4.33
4.27
4.24
4.24
4.23
4.21
4.19
3.97
0.00
O
N
O
O
3gc
1H NMR (400 MHz, CDCl3)
1.04
1.08
0.95
1.01
2.24
1.10
1.00
2.14
2.08
3.26
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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)

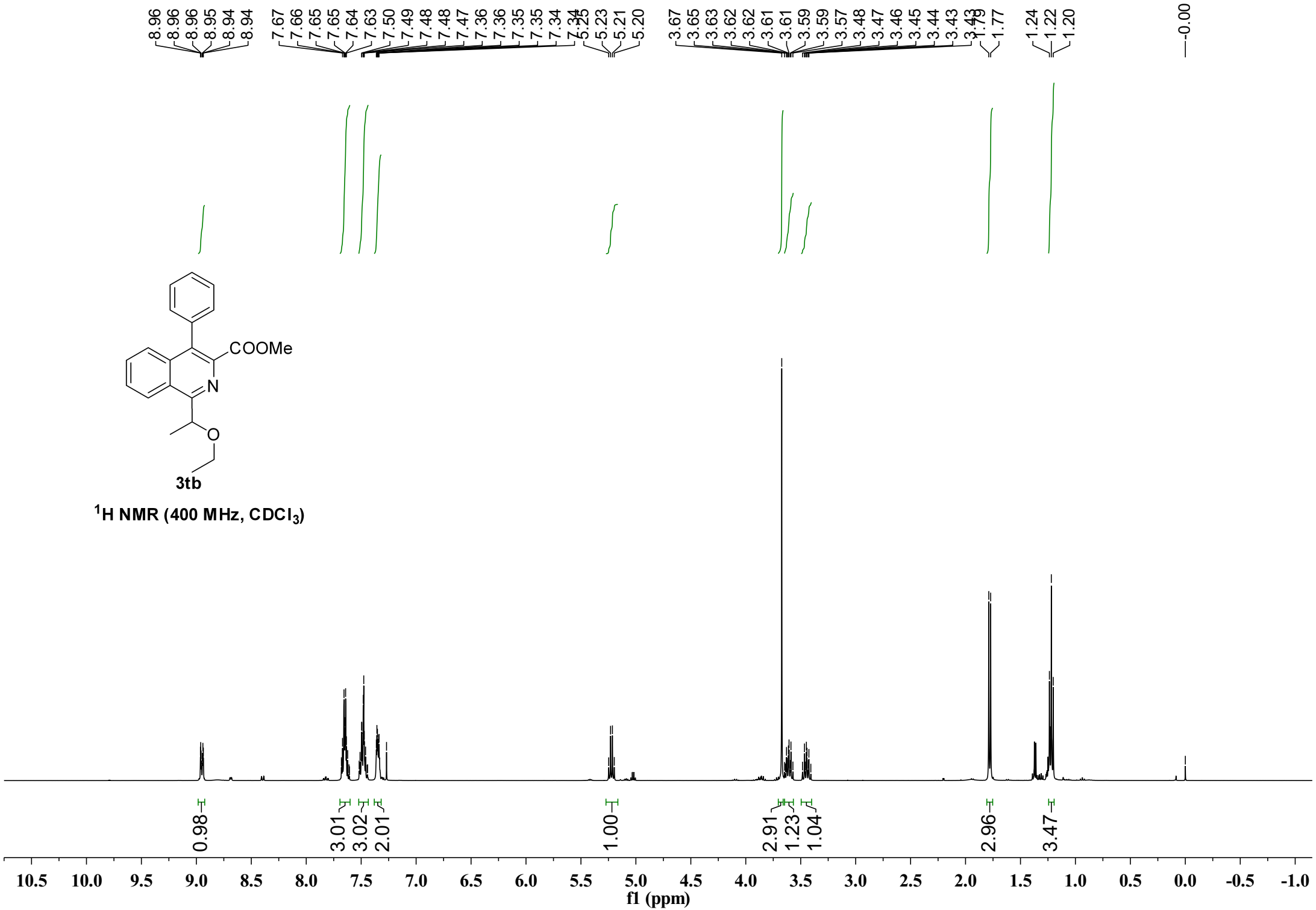


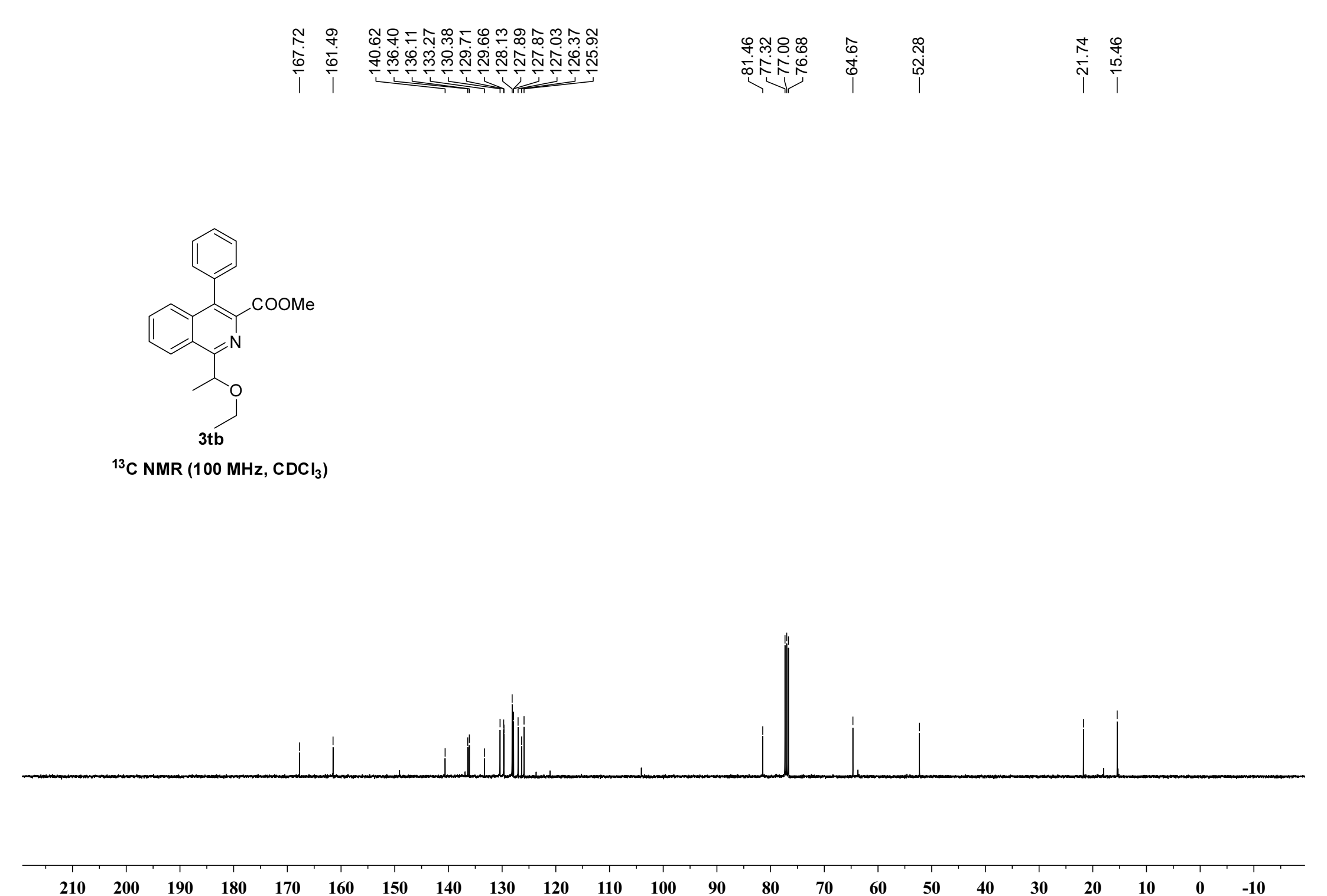
3gc

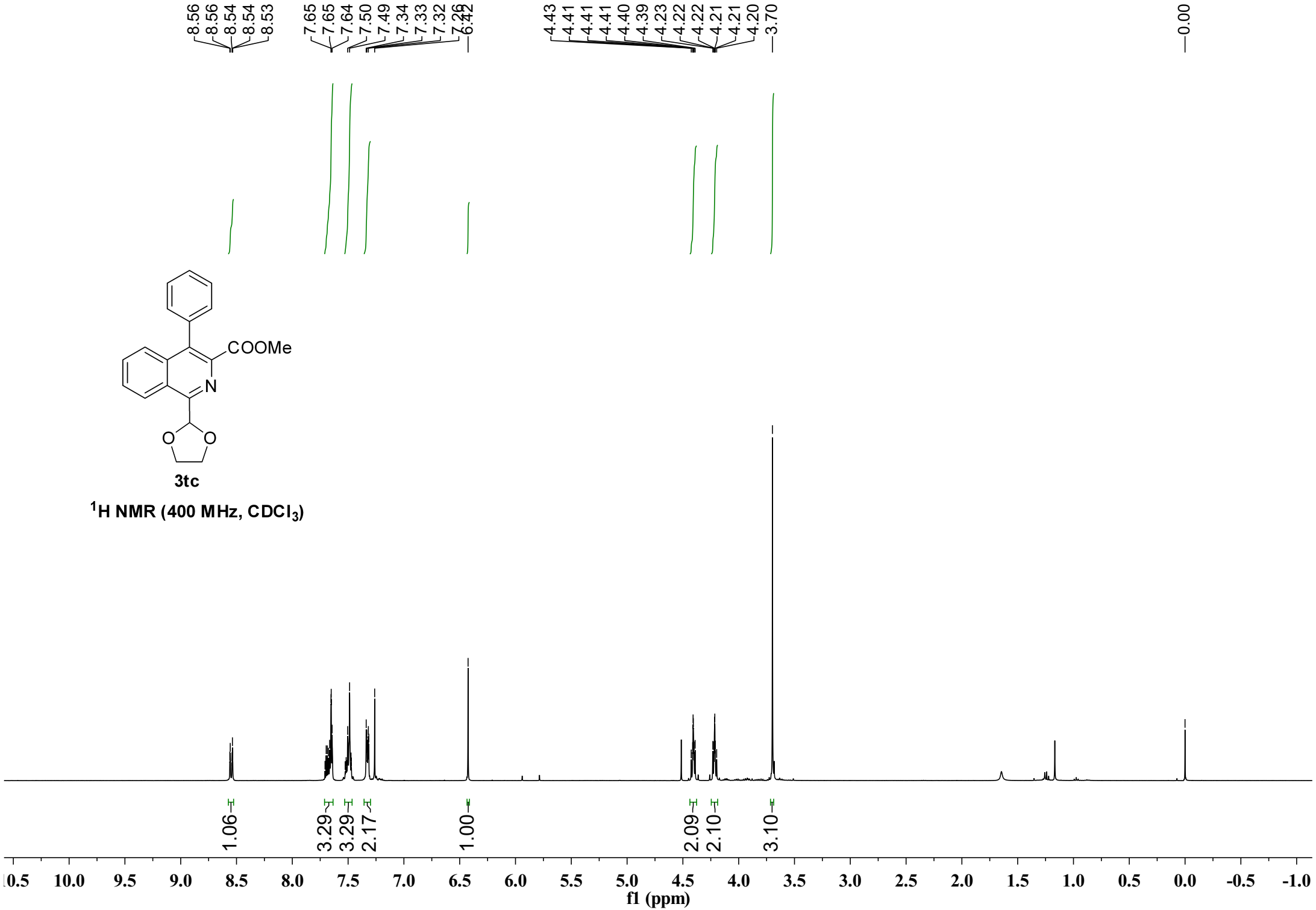
^{13}C NMR (100 MHz, $CDCl_3$)


8.57
8.55
8.48
8.48
8.48
8.47
8.46
8.15
8.15
8.14
8.13
8.13
7.86
7.86
7.69
7.67
7.67
7.66
7.66
7.65
7.64
7.64
7.50
7.49
7.48
7.47
7.26
5.77
5.75
5.73
5.27
5.21
4.90
4.89
4.46
4.44
4.44
4.00
-0.00
O
O
N
O
O
3gc'
1H NMR (400 MHz, CDCl3)
1.08
1.00
1.00
1.01
2.01
1.02
1.00
1.01
1.01
1.02
1.02
3.07
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)


158.61
155.19
142.12
130.37
127.75
127.66
127.41
126.15
124.32
124.06
121.42
121.18
106.51
95.91
77.32
77.00
76.68
67.62
55.53
O
N
O
O
3gc'
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)

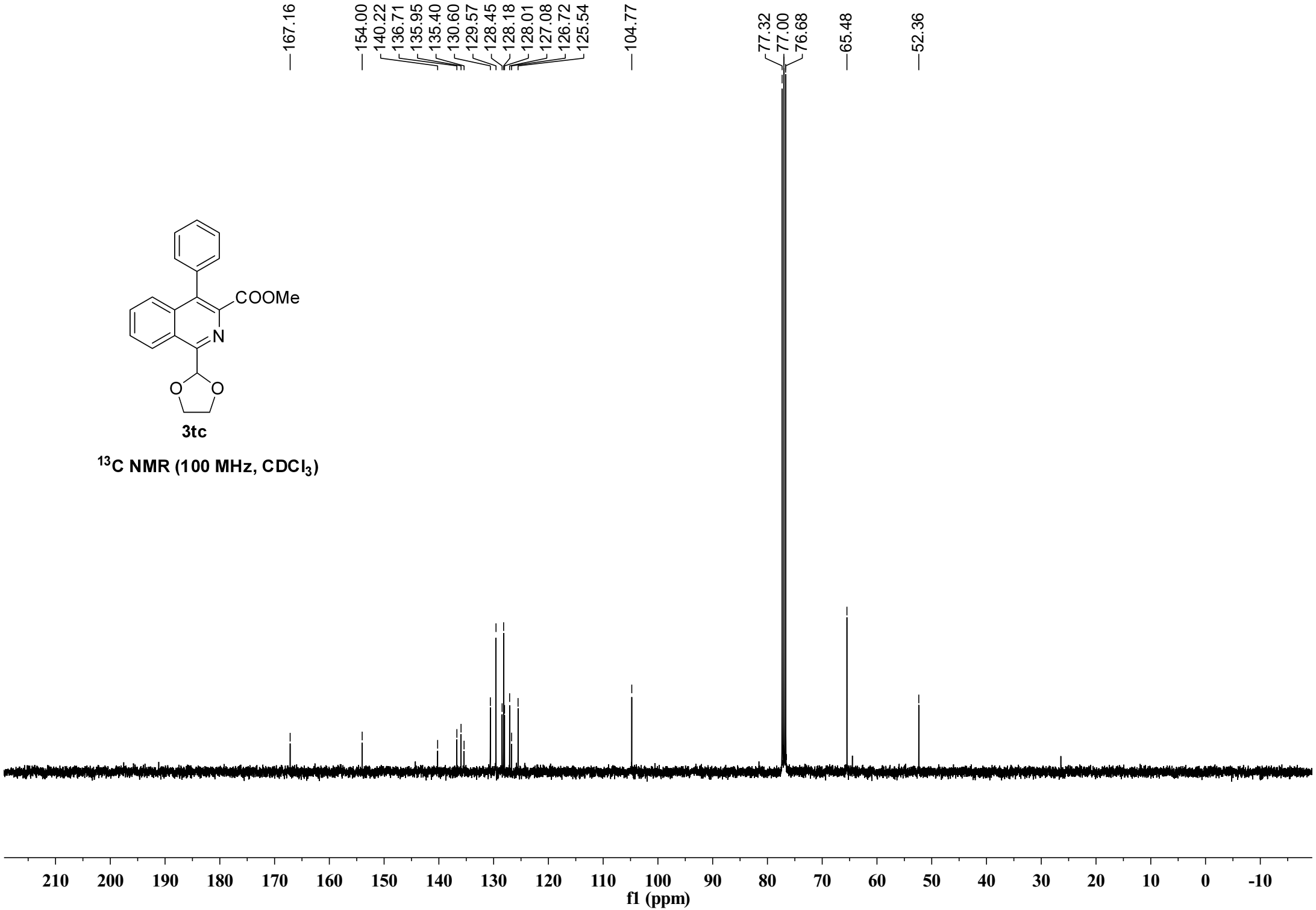

8.96
8.96
8.96
8.95
8.94
8.94
7.67
7.66
7.65
7.65
7.64
7.63
7.50
7.49
7.48
7.48
7.47
7.36
7.36
7.35
7.35
7.34
7.34
5.25
5.23
5.21
5.20
3.67
3.65
3.63
3.62
3.62
3.61
3.61
3.59
3.59
3.57
3.48
3.47
3.46
3.45
3.44
3.43
3.43
1.79
1.77
1.24
1.22
1.20
-0.00
COOMe
N
O
3tb
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
3.01
3.02
2.01
1.00
2.91
1.23
1.04
2.96
3.47
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)

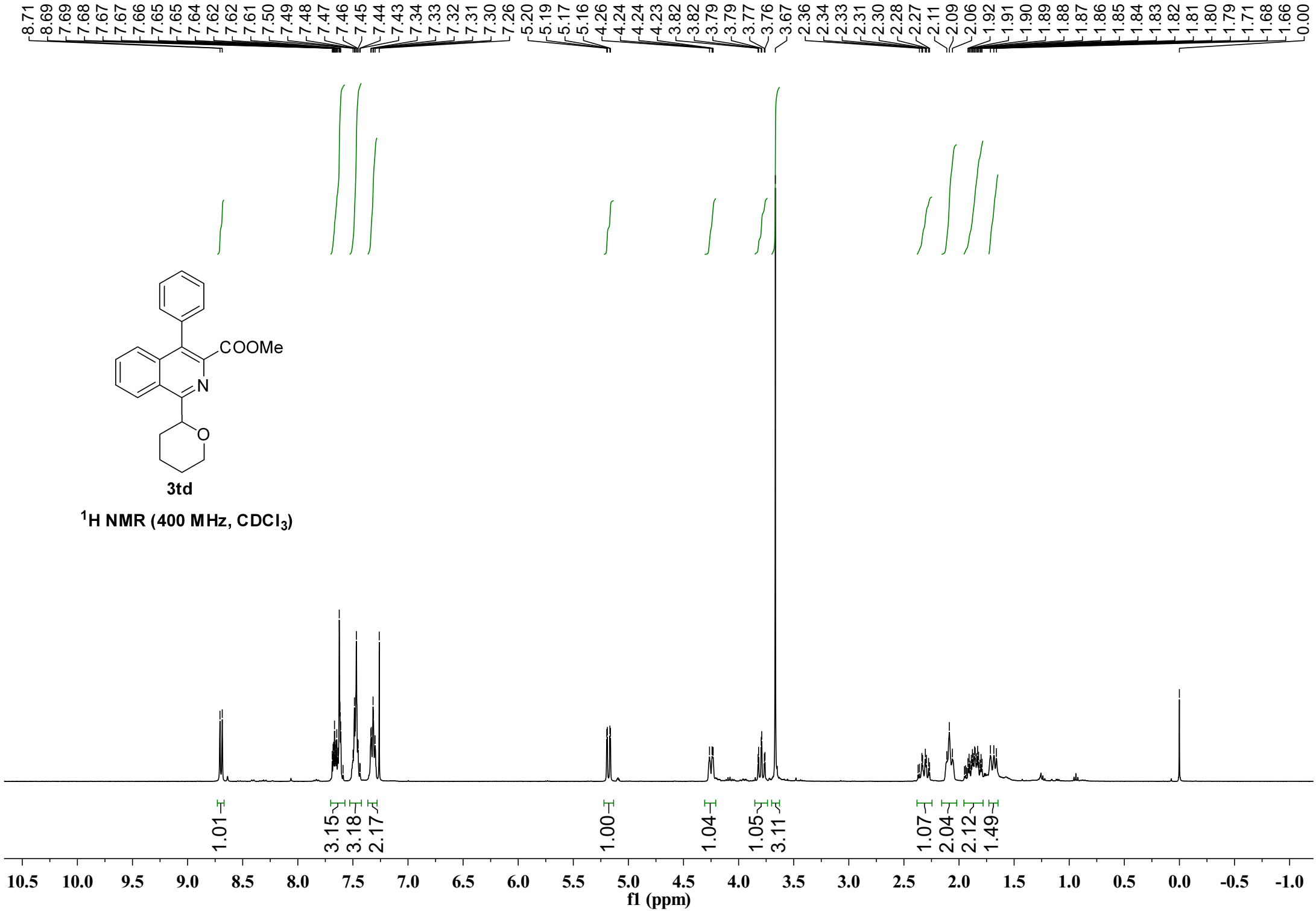

167.72
161.49
140.62
136.40
136.11
133.27
130.38
129.71
129.66
128.13
127.89
127.87
127.03
126.37
125.92
81.46
77.32
77.00
76.68
64.67
52.28
21.74
15.46
COOMe
N
O
3tb
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

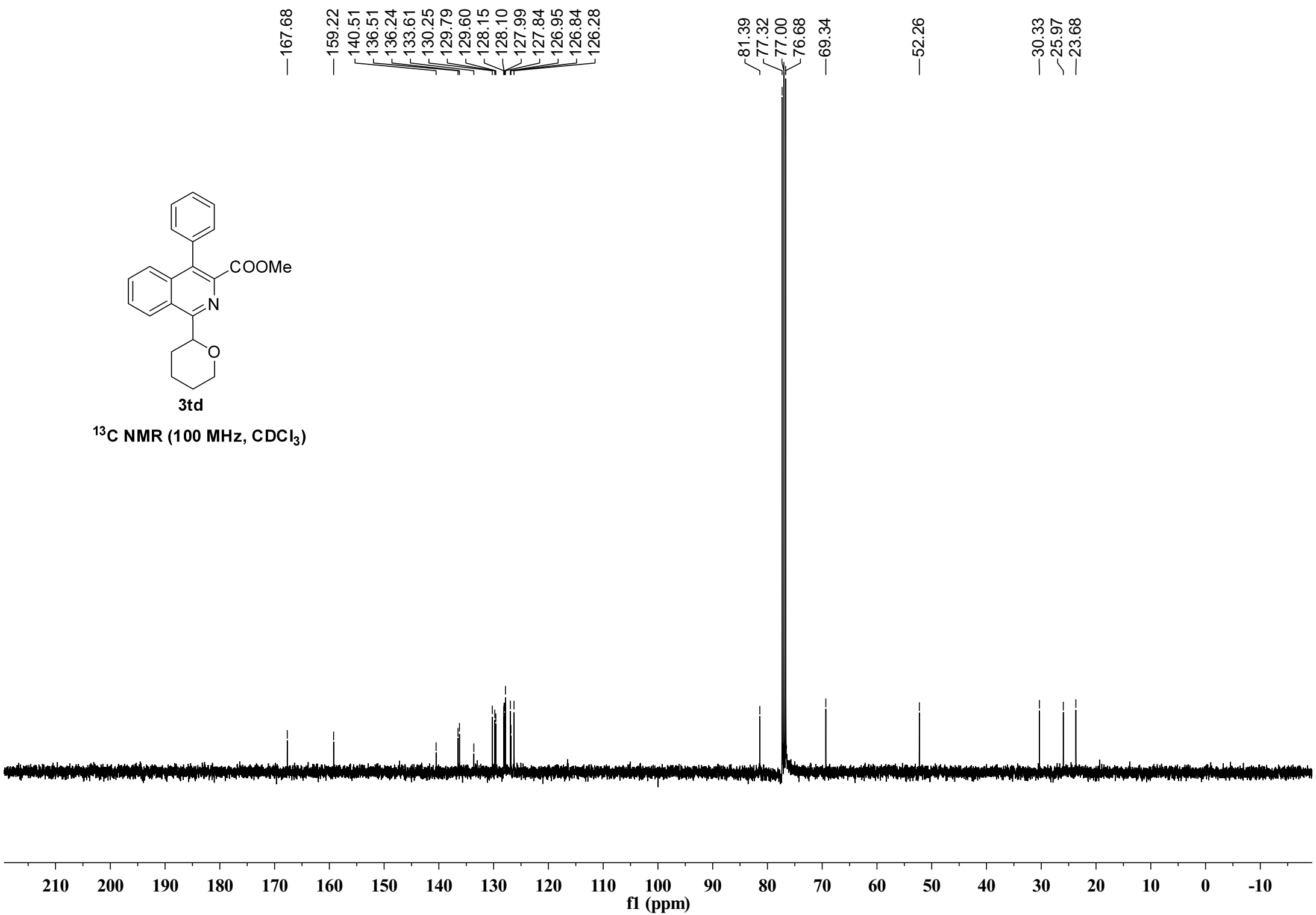


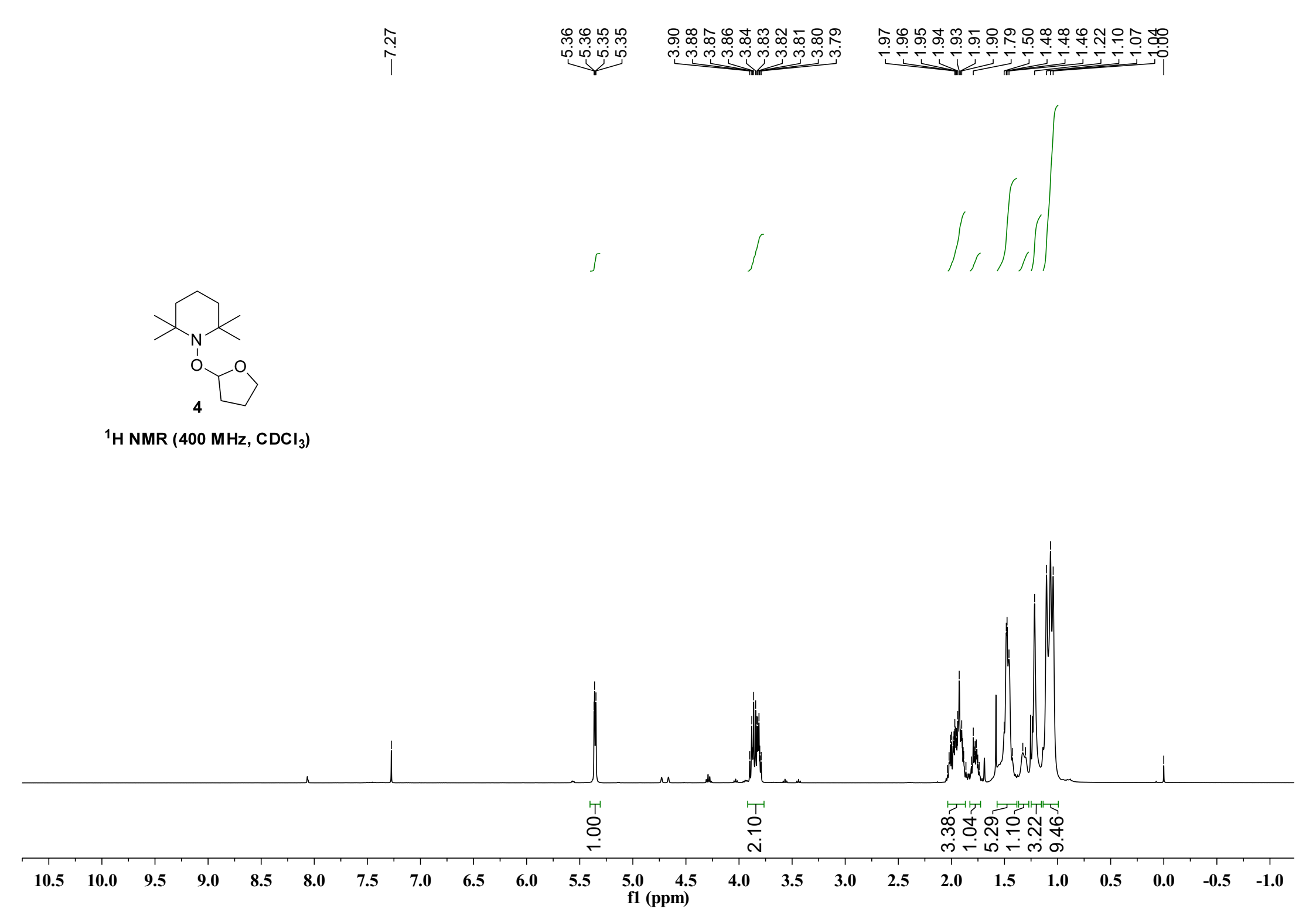
3tc

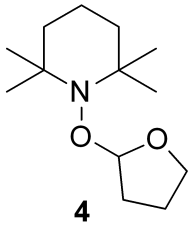
^{1}H NMR (400 MHz, $CDCl_3$)


167.16
154.00
140.22
136.71
135.95
135.40
130.60
129.57
128.45
128.18
128.01
127.08
126.72
125.54
104.77
77.32
77.00
76.68
65.48
52.36
COOMe
N
O
O
3tc
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)


8.71 8.69 7.69 7.68 7.67 7.67 7.66 7.65 7.65 7.64 7.62 7.62 7.61 7.50 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.34 7.33 7.32 7.31 7.30 7.26
5.20 5.19 5.17 5.16 4.26 4.24 4.24 4.23 3.82 3.82 3.79 3.79 3.77 3.76 3.67
2.36 2.34 2.33 2.31 2.30 2.28 2.27 2.11 2.09 2.06 1.92 1.91 1.90 1.89 1.88 1.87 1.86 1.85 1.84 1.83 1.82 1.81 1.80 1.79 1.71 1.68 1.66 0.00
COOMe
N
O
3td
1H NMR (400 MHz, CDCl3)
1.01 3.15 3.18 2.17 1.00 1.04 1.05 3.11 1.07 2.04 2.12 1.49
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)

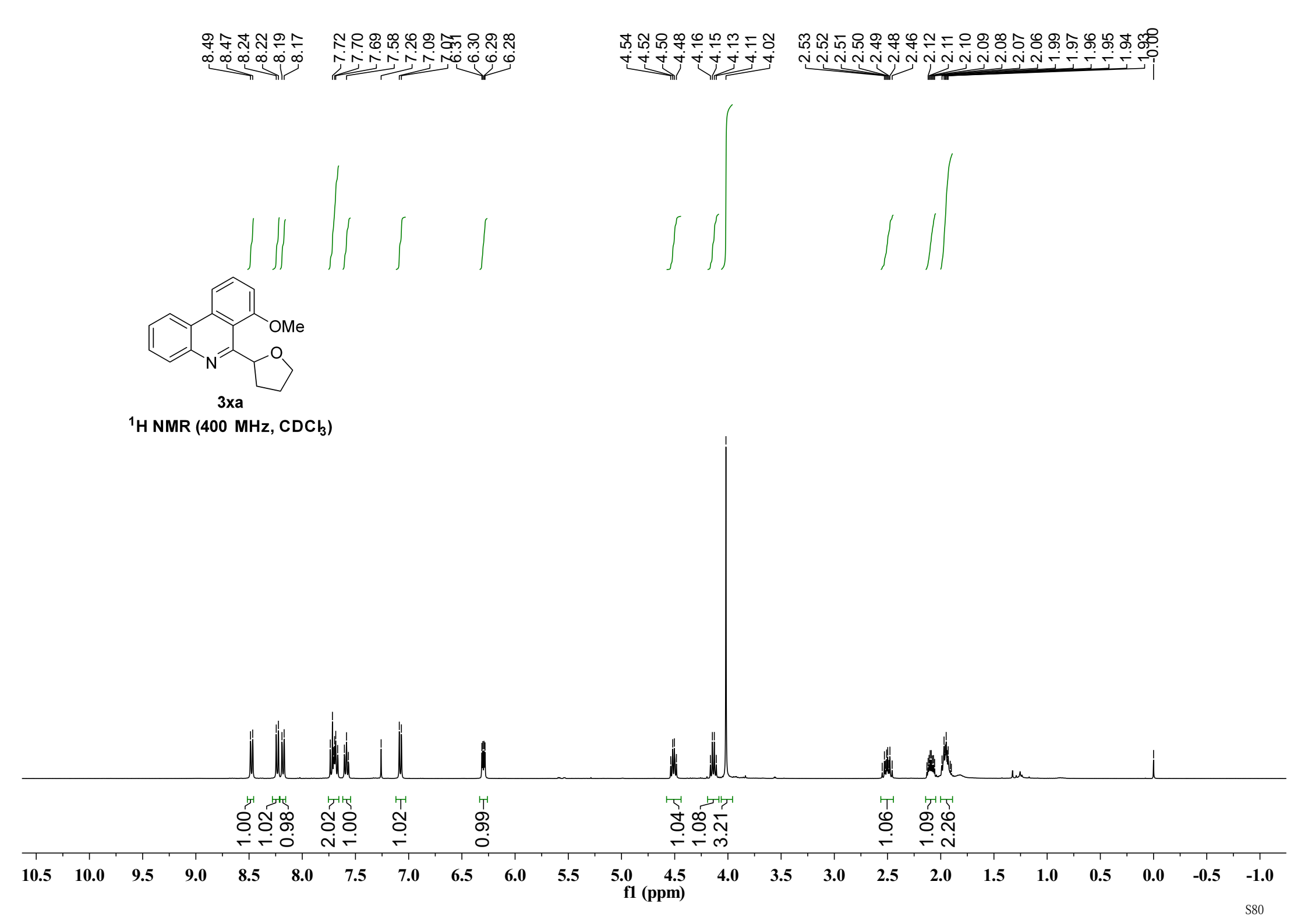

167.68
159.22
140.51
136.51
136.24
133.61
130.25
129.79
129.60
128.15
128.10
127.99
127.84
126.95
126.84
126.28
81.39
77.32
77.00
76.68
69.34
52.26
30.33
25.97
23.68
COOMe
N
O
3td
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.27
5.36
5.36
5.35
5.35
3.90
3.88
3.87
3.86
3.84
3.83
3.82
3.81
3.80
3.79
1.97
1.96
1.95
1.94
1.93
1.91
1.90
1.79
1.50
1.48
1.48
1.46
1.22
1.10
1.07
1.04
0.00
N
O
O
4
1H NMR (400 MHz, CDCl3)
1.00
2.10
3.38
1.04
5.29
1.10
3.22
9.46
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)



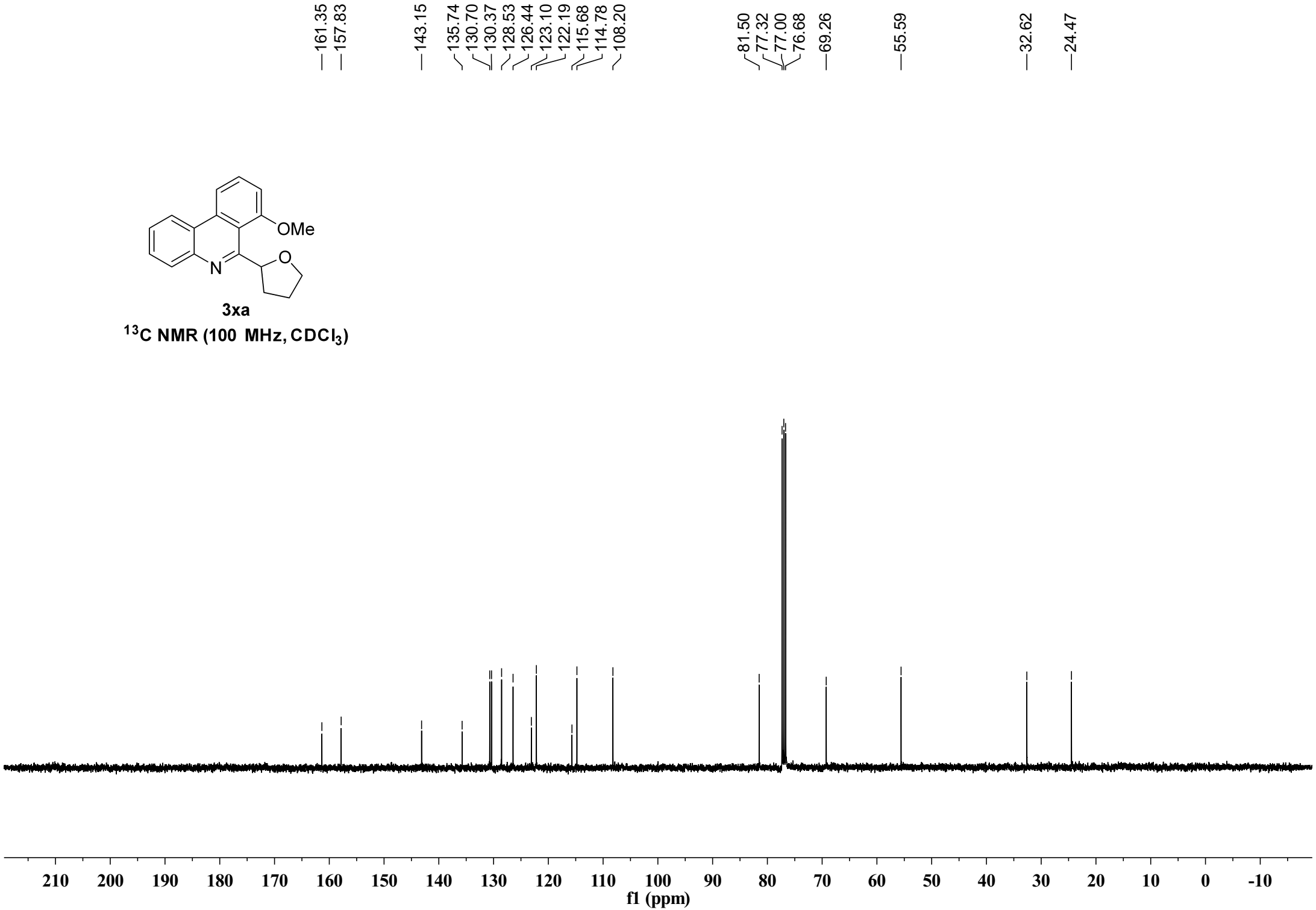
4

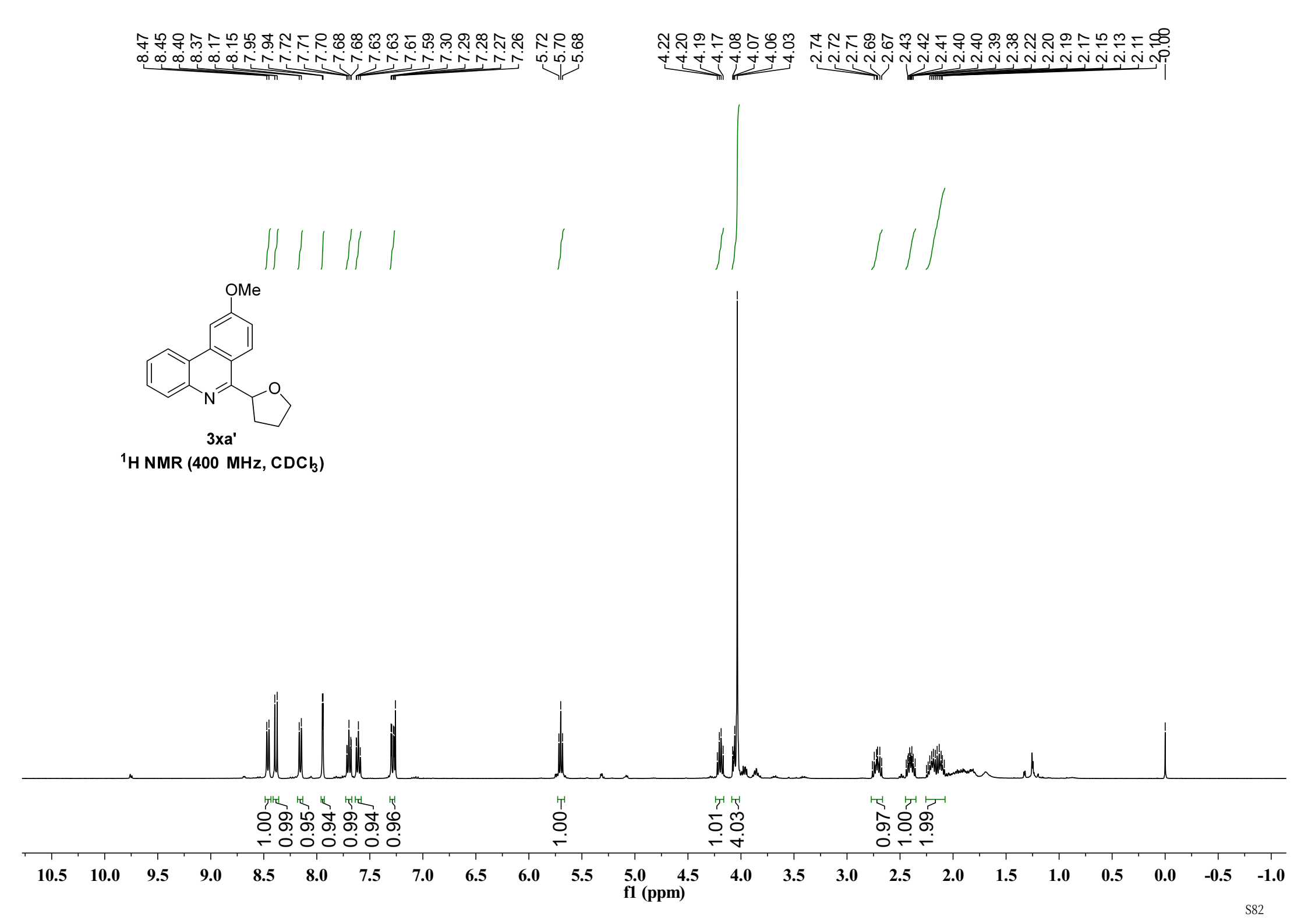
^{13}C NMR (100 MHz, $CDCl_3$)

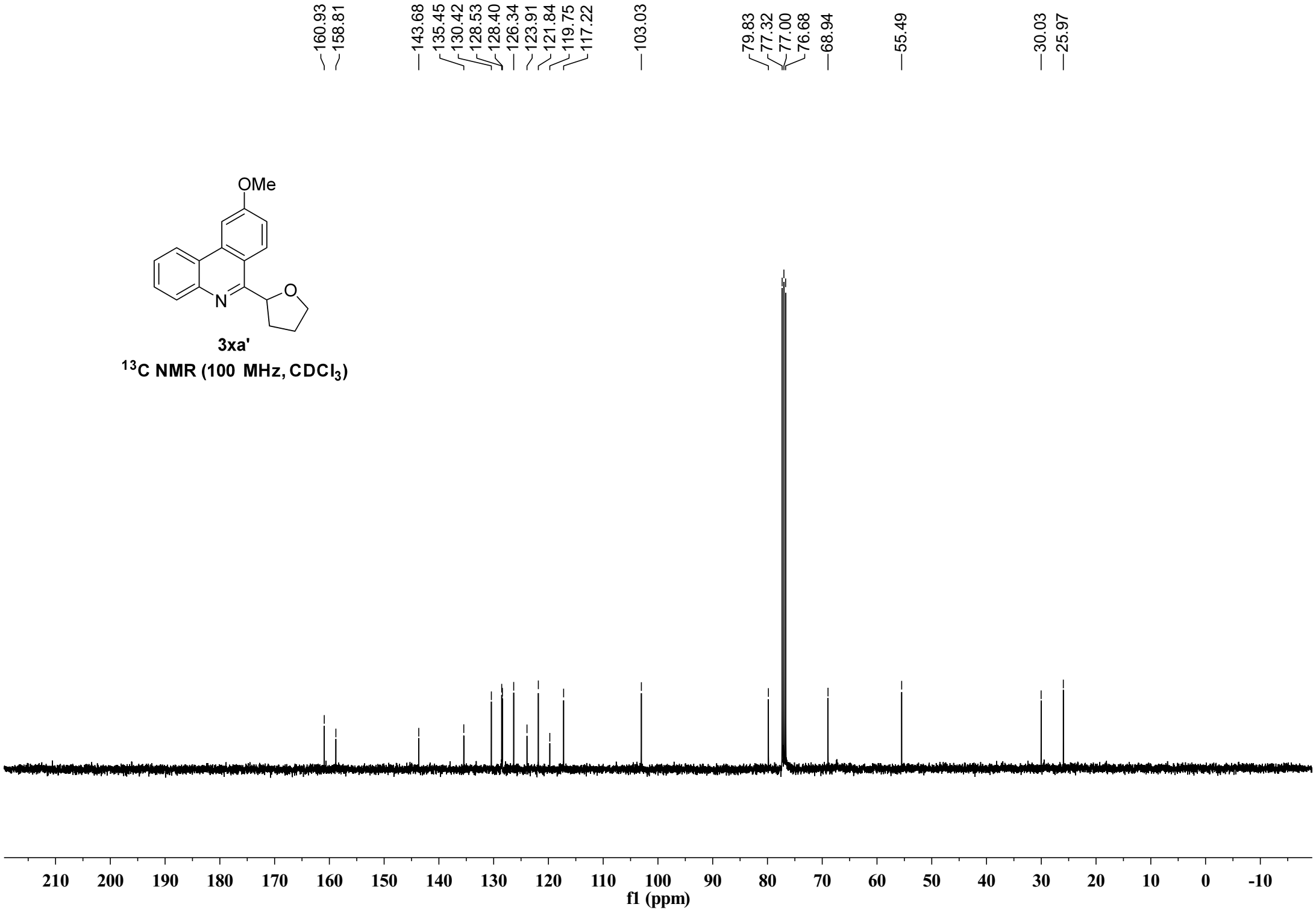


3xa

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


161.35
157.83
143.15
135.74
130.70
130.37
128.53
126.44
123.10
122.19
115.68
114.78
108.20
81.50
77.32
77.00
76.68
69.26
55.59
32.62
24.47
OMe
N
O
3xa
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)


8.47
8.45
8.40
8.37
8.17
8.15
7.95
7.94
7.72
7.71
7.70
7.68
7.68
7.63
7.63
7.61
7.59
7.30
7.29
7.28
7.27
7.26
5.72
5.70
5.68
4.22
4.20
4.19
4.17
4.08
4.07
4.06
4.03
2.74
2.72
2.71
2.69
2.67
2.43
2.42
2.41
2.40
2.40
2.39
2.38
2.22
2.20
2.19
2.17
2.15
2.13
2.11
2.10
0.00
OMe
O
N
3xa'
1H NMR (400 MHz, CDCl3)
1.00
0.99
0.95
0.94
0.99
0.94
0.96
1.00
1.01
4.03
0.97
1.00
1.99
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)


160.93
158.81
143.68
135.45
130.42
128.53
128.40
126.34
123.91
121.84
119.75
117.22
103.03
79.83
77.32
77.00
76.68
68.94
55.49
30.03
25.97
OMe
N
O
3xa'
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)