Supporting Information for

Visible-Light-Mediated Radical Brominative Addition / Spirocyclization / Ester Migration Cascade Reaction : Synthesis of 3-Bromocoumarins from Alkynoates

Shangbiao Feng,[a] Jinlai Li,[a] Zaimin Liu,[a] Haiyu Sun, [a] Hongliang Shi,[a] Xiaolei Wang,[a] Xingang Xie,[a] and Xuegong She [a,b,*]

[a] State Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

[b] Collaborative Innovation Center of Chemical Science and Engineering Tianjin, People's Republic of China

shexg@lzu.edu.cn

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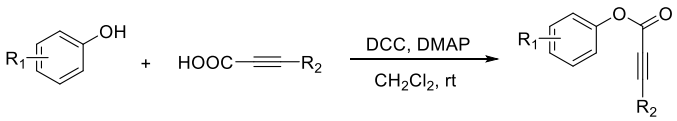
1. General information.

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 after recrystallized with petroleum ether and ethyl acetate. ^{1}H and ^{13}C NMR data were recorded on a 400 MHz or 300 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.

Wattecs Parallel Light Reactor

2. Preparation of starting materials.[1]



To a solution of the phenol (2.0 mmol, 1.0 equiv) in CH_2Cl_2 (10.0 mL) was added propiolic acid (2.2 mmol, 1.1 equiv) at 0 °C, then a mixture of DCC (3.0 mmol, 1.5 equiv) and DMAP

(0.2 mmol, 0.1 equiv) in CH_2Cl_2 (5.0 mL) was added dropwise. The resulting mixture was stirred at room temperature for 12 h. Then the crude mixture was filtered and washed with CH_2Cl_2 (10.0 mL). The combined organic phase was concentrated under reduced pressure to give a residue which was purified by a silica gel column chromatography (petroleum ether/ ethyl acetate = 10:1) to give the alkynoate products.

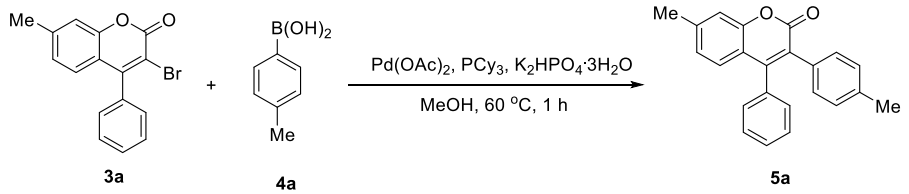
3. General procedure for the visible-light-promoted cascade reaction.(procedure 1)

To a reaction tube equipped with a magnetic stir bar was added phenyl 3-phenylpropiolate **1** (0.2 mmol, 1.0 equiv), NBS **2** (N-bromosuccinimide, 0.6 mmol, 3.0 equiv). The reaction tube was then filled with dry argon. After that, THF (2.0 mL) was injected into the tube via a syringe. Then the reaction was irradiated with an 18 W blue LED strip and stirred at room temperature from 18-20 h. The reaction was monitored by TLC to establish the consumption of starting material. 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 coumarin product.

4. Gram Scale Preparation of 3a.

To a reaction tube equipped with a magnetic stir bar was added tolyl alkynoate **1a** (1.058 g, 4.483 mmol, 1.0 equiv), NBS **2** (N-bromosuccinimide, 1.596 g, 8.966 mmol, 2.0 equiv). The reaction tube was then filled with dry argon. After that, THF (15.0 mL) was injected into the tube via a syringe. Then the reaction was irradiated with an 18 W blue LED strip and stirred at room temperature for 24 h. After it was complete, the reaction mixture was concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1 to 20:1) to afford the desired **3a** in 70% yield (0.933 g).

5. Suzuki coupling reaction of 3a.[2] (procedure 2)

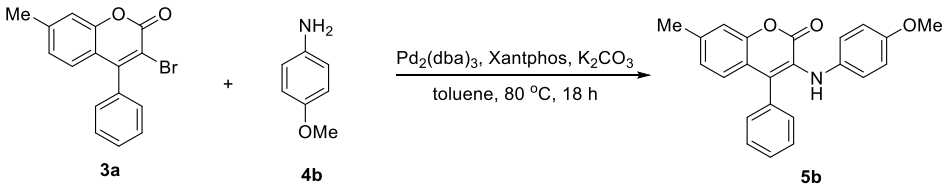


3a 4a 5a

$K_2HPO_4 \cdot 3H_2O$ (0.90 mmol, 3.0 equiv) was added to a mixture of compound **3a** (63.0 mg, 0.2 mmol, 1.0 equiv), 4-Methylphenylboronic acid **4** (41.0 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$

(2.2 mg, 5.0 mol %), and PCy_3 (5.6 mg, 10.0 mol %) in methanol (2.0 mL). The reaction mixture was stirred at 60°C for 1 h. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature and purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 5:1) to afford the product **5a** in 92% yield (60.0 mg).

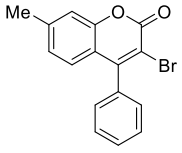
6. Buchwald-Hartwig amination of compound 3a.[2]



3a **4b** **5b**

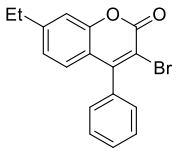
A mixture of compound **3a** (63.0 mg, 0.2 mmol, 1.0 equiv), p-anisidine **4b** (29.5 mg, 0.24 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 2.5 mol %), Xantphos (5.8 mg, 5 mol %), and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv) in toluene (2.0 mL) was stirred at 80°C for 18 h. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature and purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1) to afford the corresponding product in 69% yield (49.0 mg).

7. Characterization data for all products.



3a

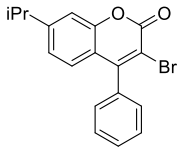
Compound **3a** was obtained as a white solid in 72% yield according to the general procedure. Mp: 191−193°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 3H), 7.32 – 7.27 (m, 2H), 7.20 (s, 1H), 6.98 (dt, J = 18.7, 4.5 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 154.6, 152.5, 143.5, 135.4, 129.2, 128.8, 128.0, 127.3, 125.9, 117.9, 116.9, 111.2, 21.6. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{16}H_{12}BrO_2$: 315.0015, found: 315.0014.



3b

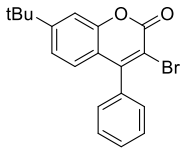
Compound **3b** was obtained as a white solid in 75% yield according to the general procedure. Mp: 157−158°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 3H), 7.32 – 7.27 (m, 2H), 7.23 (s,

1H), 7.01 (dt, *J* = 19.1, 4.8 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 154.6, 152.6, 149.7, 135.4, 129.2, 128.8, 128.1, 127.4, 124.7, 118.1, 115.7, 111.3, 28.8, 15.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{14}BrO_2$: 329.0172, found: 329.0171.



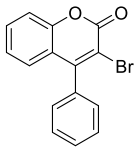
3c

Compound **3c** was obtained as a white solid in 71% yield according to the general procedure. Mp: 118−120°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 3H), 7.33 – 7.27 (m, 2H), 7.26 (s, 1H), 7.06 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 2.99 (hept, *J* = 6.9 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 154.6, 154.4, 152.7, 135.5, 129.2, 128.8, 128.1, 127.5, 123.4, 118.3, 114.4, 111.3, 34.2, 23.5. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{18}H_{16}BrO_2$: 343.0328, found: 343.0326.



3d

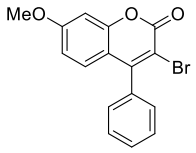
Compound **3d** was obtained as ropy oil in 68% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 3H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.22 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 156.7, 154.5, 152.5, 135.4, 129.3, 128.8, 128.1, 127.1, 122.2, 117.9, 113.6, 111.5, 35.3, 31.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{19}H_{18}BrO_2$: 357.0485, found: 357.0484.



3e

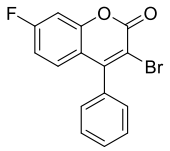
Compound **3e** was obtained as a white solid in 63% yield according to the general procedure. Mp: 154−155°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 4H), 7.41 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.22 – 7.16 (m, 1H), 7.08 (dd, *J* = 8.0, 1.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.34, 154.62, 152.48, 135.29, 132.02, 129.34, 128.85, 128.07, 127.60, 124.69, 120.35, 116.82, 112.65. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{15}H_{10}BrO_2$: 300.9859, found:

300.9863.



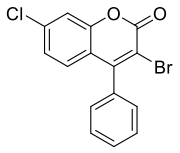
3f

Compound **3f** was obtained as a white solid in 52% yield according to the general procedure. Mp: 153−155°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 3H), 7.31 – 7.27 (m, 2H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.74 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 157.8, 154.8, 154.3, 135.6, 129.3, 128.8, 128.6, 128.1, 114.0, 112.9, 108.8, 100.6, 55.9. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{16}H_{12}BrO_3$: 330.9964, found: 330.9963.



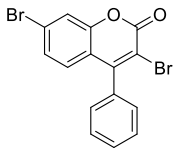
3g

Compound **3g** was obtained as a white solid in 52% yield according to the general procedure. Mp: 206−207°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 3H), 7.32 – 7.27 (m, 2H), 7.10 (ddd, *J* = 14.9, 8.8, 4.2 Hz, 2H), 6.92 (ddd, *J* = 8.9, 8.1, 2.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (165.67, 163.13, d, *J* = 254 Hz), 157.01, 154.15, (153.55, 153.42, d, *J* = 13 Hz), 135.10, 129.52, (129.43, 129.33, d, *J* = 10 Hz), 128.96, 127.99, (117.15, 117.12, d, *J* = 3 Hz), (112.93, 112.70, d, *J* = 23 Hz), (111.42, 111.39, d, *J* = 3 Hz), (104.49, 104.23, d, *J* = 26 Hz). **HRMS** (ESI): m/z $[M+NH_4]^+$ calculated for $C_{15}H_{12}BrFNO_2$: 336.0030, found: 336.0031.



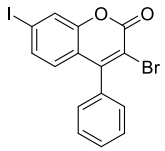
3h

Compound **3h** was obtained as a white solid in 59% yield according to the general procedure. Mp: 204−205°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 3H), 7.42 (d, *J* = 1.9 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.16 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 154.0, 152.6, 138.0, 134.9, 129.6, 129.0, 128.5, 128.0, 125.3, 119.0, 117.1, 112.6. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{15}H_9BrClO_2$: 334.9469, found: 334.9468.



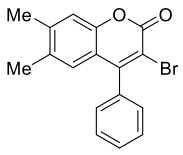
3i

Compound **3i** was obtained as a white solid in 51% yield according to the general procedure. Mp: 204−206°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 4H), 7.33 – 7.27 (m, 3H), 6.94 (d, J = 8.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 154.0, 152.5, 134.8, 129.6, 129.0, 128.6, 128.1, 128.0, 126.0, 120.0, 119.3, 112.8. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{15}H_9Br_2O_2$: 378.8964, found: 378.378.8962.



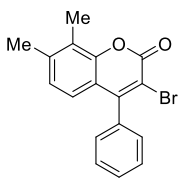
3j

Compound **3j** was obtained as a white solid in 52% yield according to the general procedure. Mp: 204−206°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, J = 1.6 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.51 (dd, J = 8.4, 1.6 Hz, 1H), 7.30 – 7.26 (m, 2H), 6.77 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 154.1, 152.2, 134.8, 134.0, 129.6, 129.0, 128.5, 128.0, 125.9, 119.9, 113.1, 97.5. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{15}H_9BrIO_2$: 462.8825, found: 462.8837.



3k

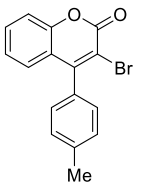
Compound **3k** was obtained as a white solid in 37% yield according to the general procedure. Mp: 181−183°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 3H), 7.31 – 7.27 (m, 2H), 7.18 (s, 1H), 6.77 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 154.6, 150.9, 142.3, 135.6, 133.6, 129.2, 128.8, 128.1, 127.5, 118.1, 117.3, 111.3, 20.2, 19.3. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{14}BrO_2$: 329.0172, found: 329.0171.



3k'

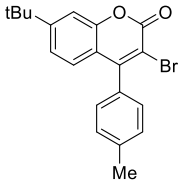
Compound **3k'** was obtained as a white solid in 33% yield according to the general procedure.

Mp: 186−189°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 3H), 7.30 – 7.26 (m, 2H), 6.98 (d, J = 8.2 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 155.1, 150.8, 142.0, 135.8, 129.1, 128.7, 128.1, 126.1, 124.7, 124.5, 118.3, 111.0, 20.4, 11.6. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{14}BrO_2$: 329.0172, found: 329.0174.



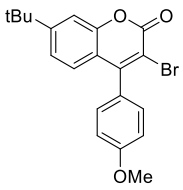
3m

Compound **3m** was obtained as a white solid in 70% yield according to the general procedure. Mp: 161−164°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 7.22 –7.10 (m, 4H), 2.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 154.8, 152.5, 139.4, 132.3, 131.9, 129.5, 128.1, 127.7, 124.6, 120.5, 116.8, 112.6, 21.4. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{16}H_{12}BrO_2$: 315.0015, found: 315.0017.



3n

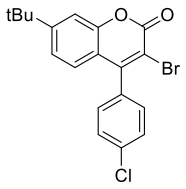
Compound **3n** was obtained as ropy oil in 65% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 1.8 Hz, 1H), 7.36 (d, J = 7.9 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.04 (d, J = 8.5 Hz, 1H), 2.47 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 156.6, 154.7, 152.5, 139.3, 132.4, 129.4, 128.0, 127.2, 122.1, 118.0, 113.5, 111.4, 35.2, 30.9, 21.4. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{20}H_{20}BrO_2$:371.0641, found: 371.0651.



3o

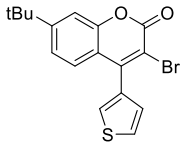
Compound **3o** was obtained as ropy oil in 66% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 1.8 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.11 – 7.04 (m, 3H), 3.91 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2, 157.8, 156.6, 154.4, 152.5, 129.7, 127.5, 127.2, 122.2, 118.1, 114.1, 113.6, 111.6, 55.4, 35.2, 30.9. **HRMS** (ESI): m/z $[M+H]^+$

calculated for $C_{20}H_{20}BrO_3$: 387.0590, found: 387.0592.



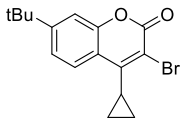
3p

Compound **3p** was obtained as a white solid in 68% yield according to the general procedure. Mp: 195−196°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.41 (d, J = 1.8 Hz, 1H), 7.28 – 7.22 (m, 3H), 6.98 (d, J = 8.5 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 157.0, 153.3, 152.5, 135.5, 133.7, 129.6, 129.2, 126.8, 122.4, 117.6, 113.7, 111.7, 35.3, 30.9. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{19}H_{17}BrClO_2$: 391.0095, found: 391.0094.



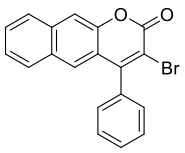
3q

Compound **3q** was obtained as a white solid in 50% yield according to the general procedure. Mp: 98−100°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 5.0, 3.0 Hz, 1H), 7.45 (dd, J = 2.9, 1.2 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.19 (s, 1H), 7.18 – 7.14 (m, 1H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 156.8, 152.4, 150.3, 134.8, 127.8, 126.9, 126.5, 126.0, 122.3, 117.8, 113.6, 111.8, 35.3, 31.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{16}BrO_2S$: 363.0049, found: 363.0048.



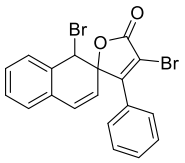
3r

Compound **3r** was obtained as ropy oil in 66% yield according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.39 – 7.31 (m, 2H), 1.89 (tt, J = 8.6, 5.9 Hz, 1H), 1.35 (s, 9H), 1.34 – 1.31 (m, 2H), 0.93 – 0.86 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 156.2, 153.5, 152.0, 125.1, 121.9, 118.2, 114.5, 113.6, 35.2, 31.0, 14.4, 9.3. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{16}H_{18}BrO_2$: 321.0485, found: 321.0487.



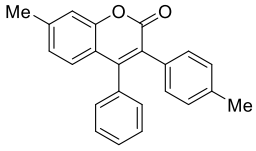
3s

Compound **3s** was obtained as a white solid in 32% yield according to the general procedure. Mp: 183−186°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 – 8.60 (m, 1H), 7.89 – 7.81 (m, 1H), 7.71 – 7.64 (m, 2H), 7.61 – 7.55 (m, 4H), 7.40 – 7.31 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 155.5, 149.7, 135.7, 134.8, 129.3, 129.1, 128.9, 128.1, 127.8, 127.5, 124.6, 122.9, 122.5, 115.6, 112.1, 100.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{19}H_{12}BrO_2$: 351.0015, found: 351.0017.



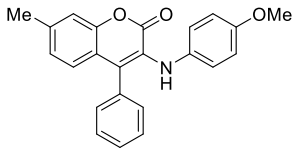
3s'

Compound **3s'** was obtained as a white solid in 50% yield according to the general procedure. Mp: 182−185°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.60 – 7.56 (m, 1H), 7.45 – 7.39 (m, 3H), 7.29 – 7.26 (m, 2H), 7.16 – 7.11 (m, 1H), 6.93 (d, *J* = 9.5 Hz, 1H), 6.09 (d, *J* = 9.5 Hz, 1H), 5.36 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 161.9, 134.1, 132.0, 130.7, 130.2, 129.5, 129.4, 129.2, 128.9, 128.8, 128.5, 127.7, 121.8, 112.1, 87.6, 53.4. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{19}H_{13}Br_2O_2$: 430.9277, found: 430.9270.



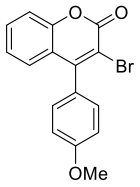
5a

Compound **5a** was obtained as a white solid in 92% yield according to the procedure. Mp: 232−234°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 3H), 7.22 (s, 1H), 7.14 – 7.09 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.04 – 6.95 (m, 5H), 2.45 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.7, 153.2, 151.3, 142.5, 137.2, 134.9, 131.0, 130.4, 129.4, 128.5, 128.2, 128.1, 127.4, 125.9, 125.2, 118.2, 116.9, 21.6, 21.2. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{23}H_{19}O_2$: 327.1380, found: 327.1381.



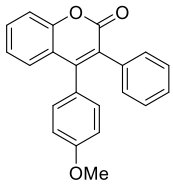
5b

Compound **5b** was obtained as a yellow solid in 69% yield according to the procedure. Mp: 148−150°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 3H), 7.20 – 7.14 (m, 3H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 8.8 Hz, 2H), 6.56 – 6.48 (m, 2H), 6.04 (s, 1H), 3.68 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 155.4, 149.6, 138.7, 134.7, 133.4, 129.4, 128.4, 128.1, 126.4, 125.5, 124.9, 122.7, 119.1, 116.6, 113.6, 55.5, 21.3. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{23}H_{20}NO_3$: 358.1438, found: 358.1439.



7

Compound **7** was obtained as a white solid in 65% yield according to the general procedure. Mp: 154−156°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 1H), 7.43 – 7.36 (m, 1H), 7.29 – 7.14 (m, 4H), 7.12 – 7.05 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.2, 157.4, 154.5, 152.4, 131.9, 129.7, 127.7, 127.2, 124.6, 120.5, 116.7, 114.1, 112.7, 55.3. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{16}H_{12}BrO_3$: 330.9964, found: 330.9966.



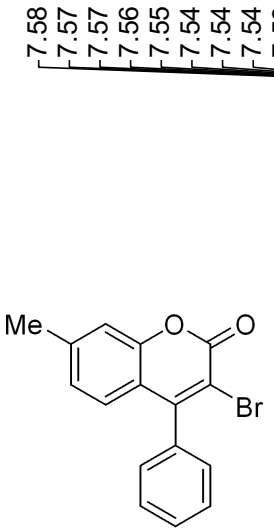
8

Compound **8** was obtained as a faint yellow solid in 90% yield according to the procedure 2. Mp: 226−228°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.41 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.24 – 7.11 (m, 6H), 7.08 – 7.00 (m, 2H), 6.87 – 6.79 (m, 2H), 3.78 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.3, 159.4, 153.2, 151.4, 134.1, 131.3, 130.77, 130.5, 127.8, 127.7, 127.5, 126.8, 126.5, 124.0, 120.7, 116.7, 113.7, 55.1. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{22}H_{17}O_3$: 329.1172, found: 329.1173.

Reference:

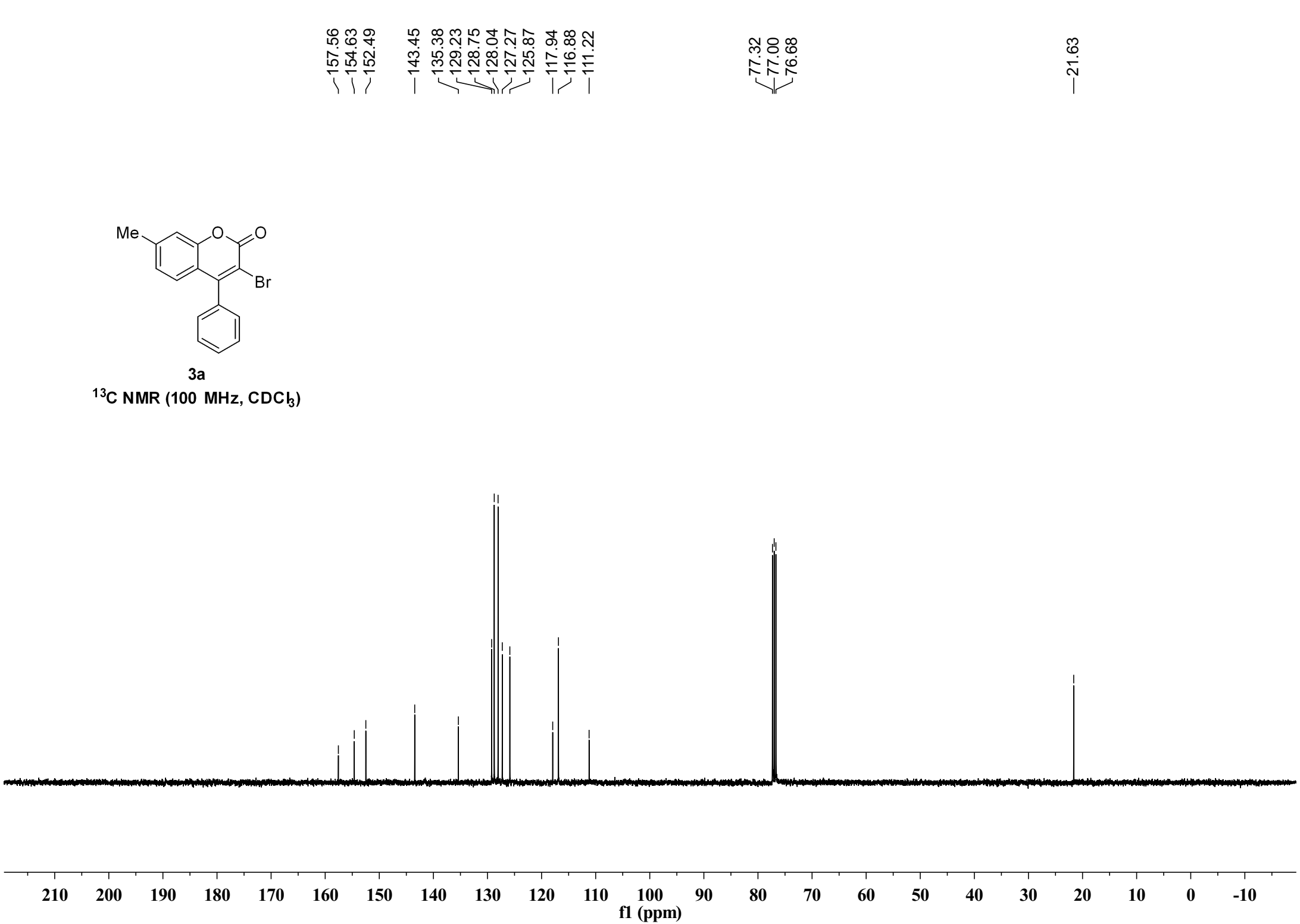
[1] Hua, H.-L.; He, Y.-T.; Qiu, Y.-F.; Li, Y.-X.; Song, B.; Gao, P.; Song, X.-R.; Guo, D.-H.; Liu, X.-Y.; Liang, Y.-M. *Chem. Eur. J.***2015**, *21*, 1468.

[2] Zhang, L.; Meng, T.; Fan, R.; Wu, J. *J. Org. Chem.* **2007**, *72*, 7279.



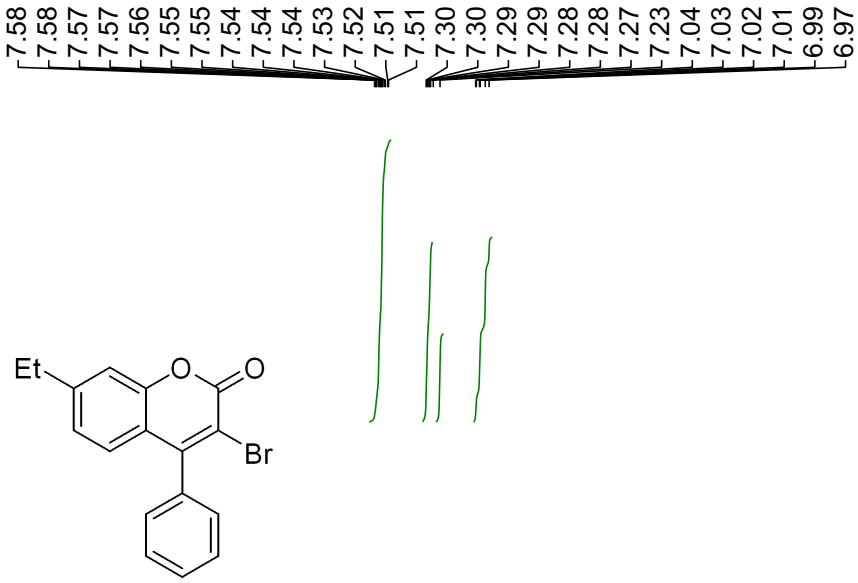
3a

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



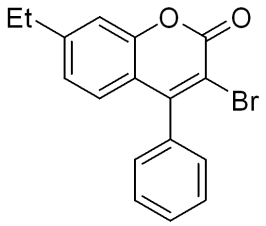
3a

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



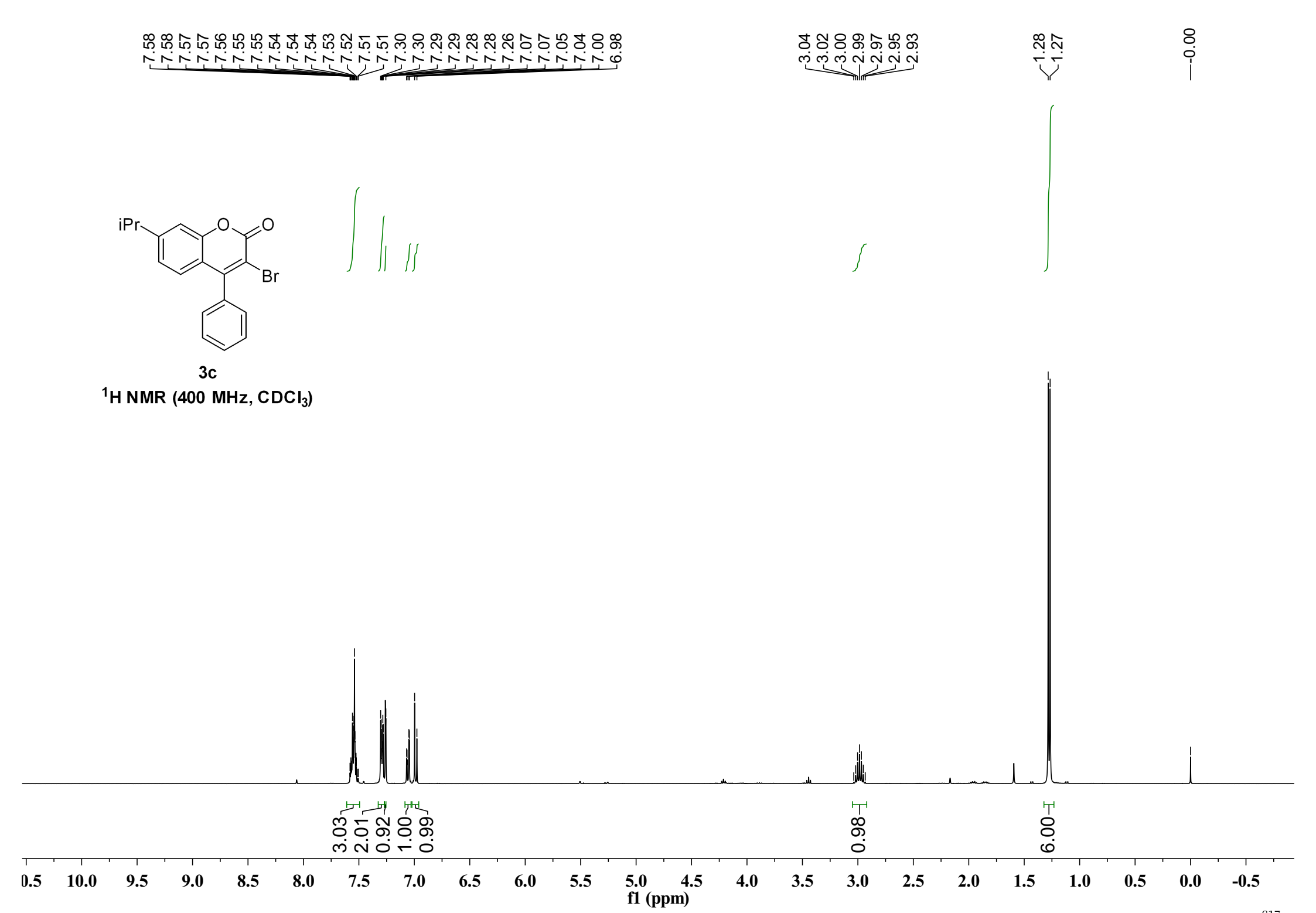
3b

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



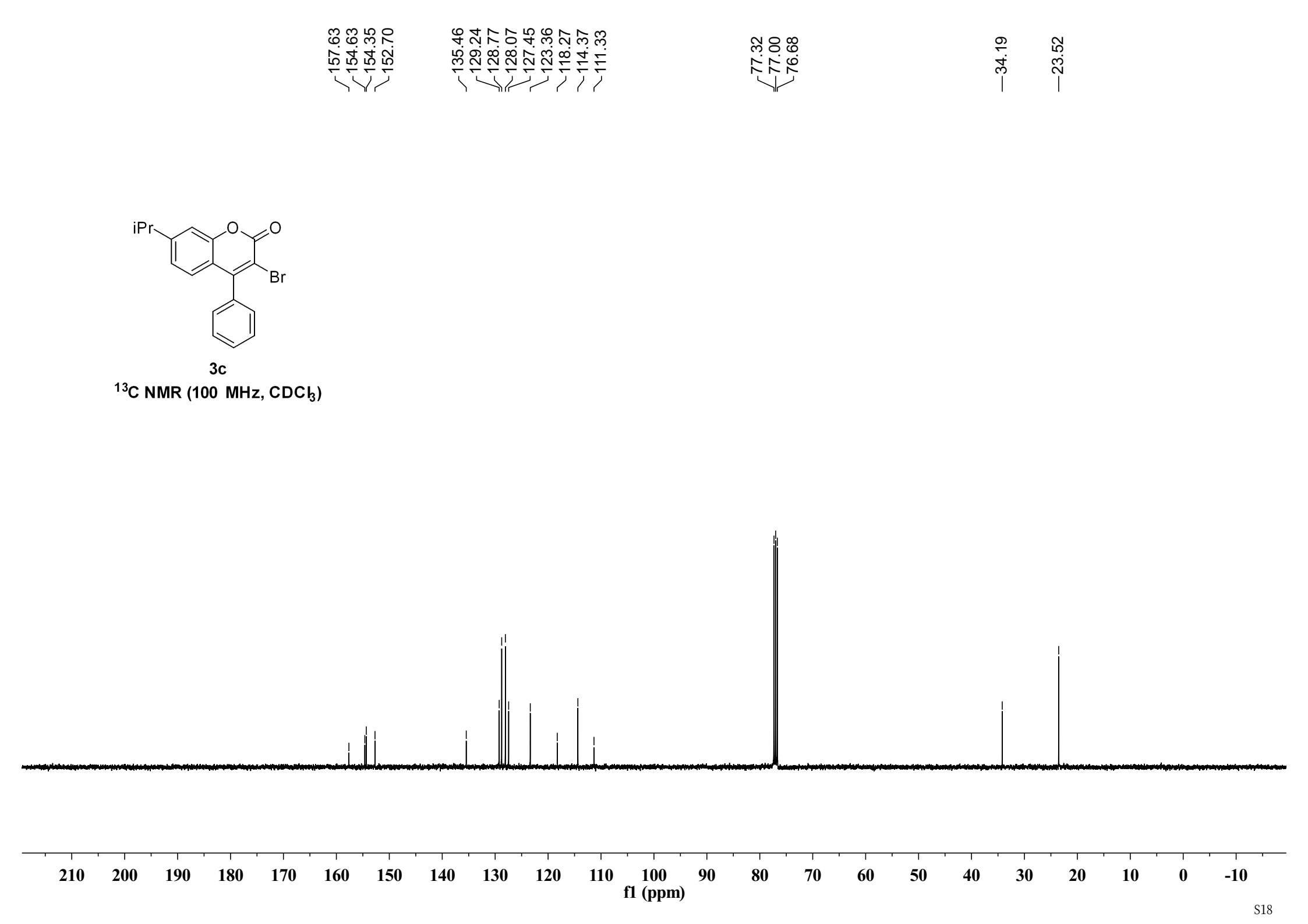
3b

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



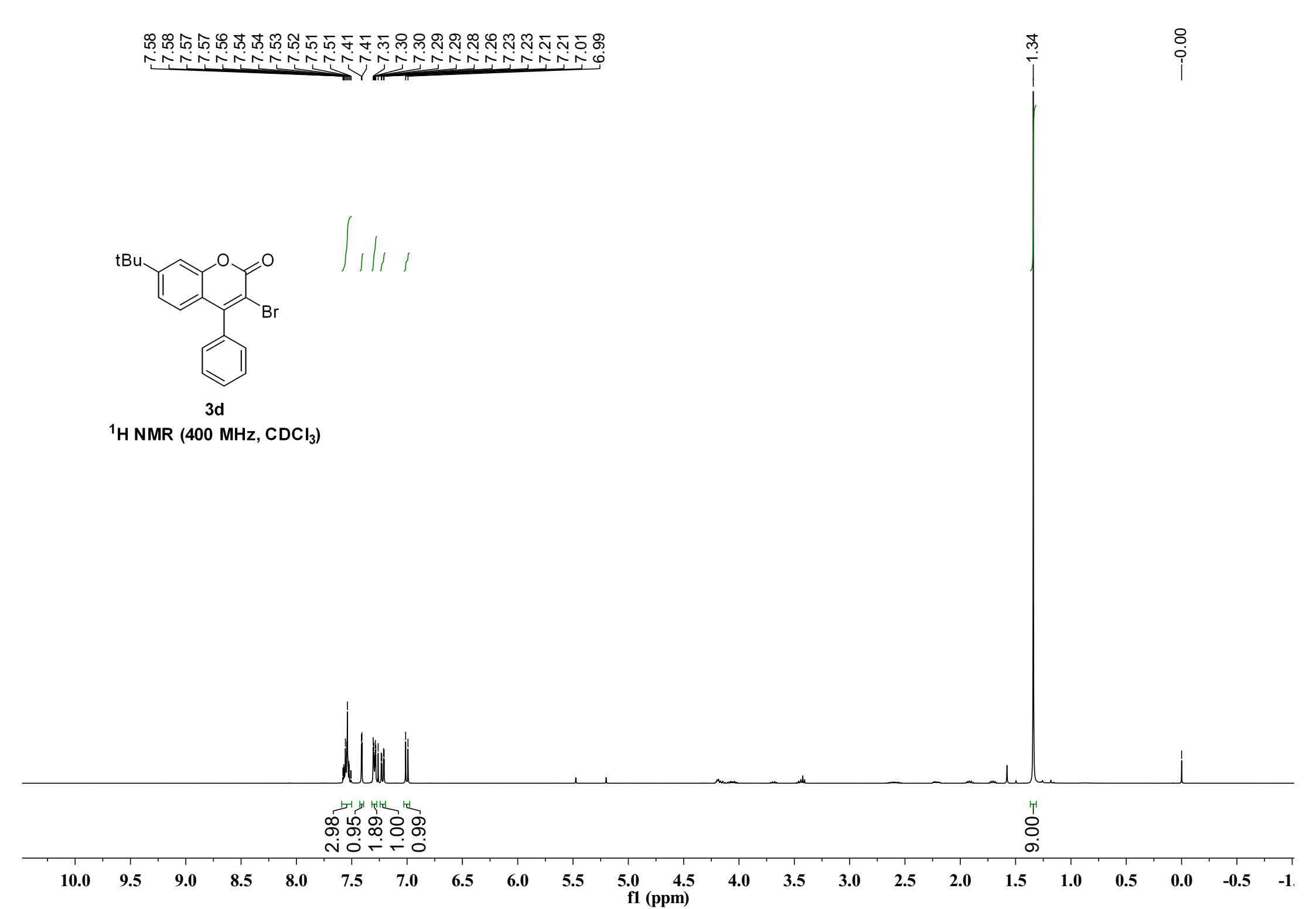
3c

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



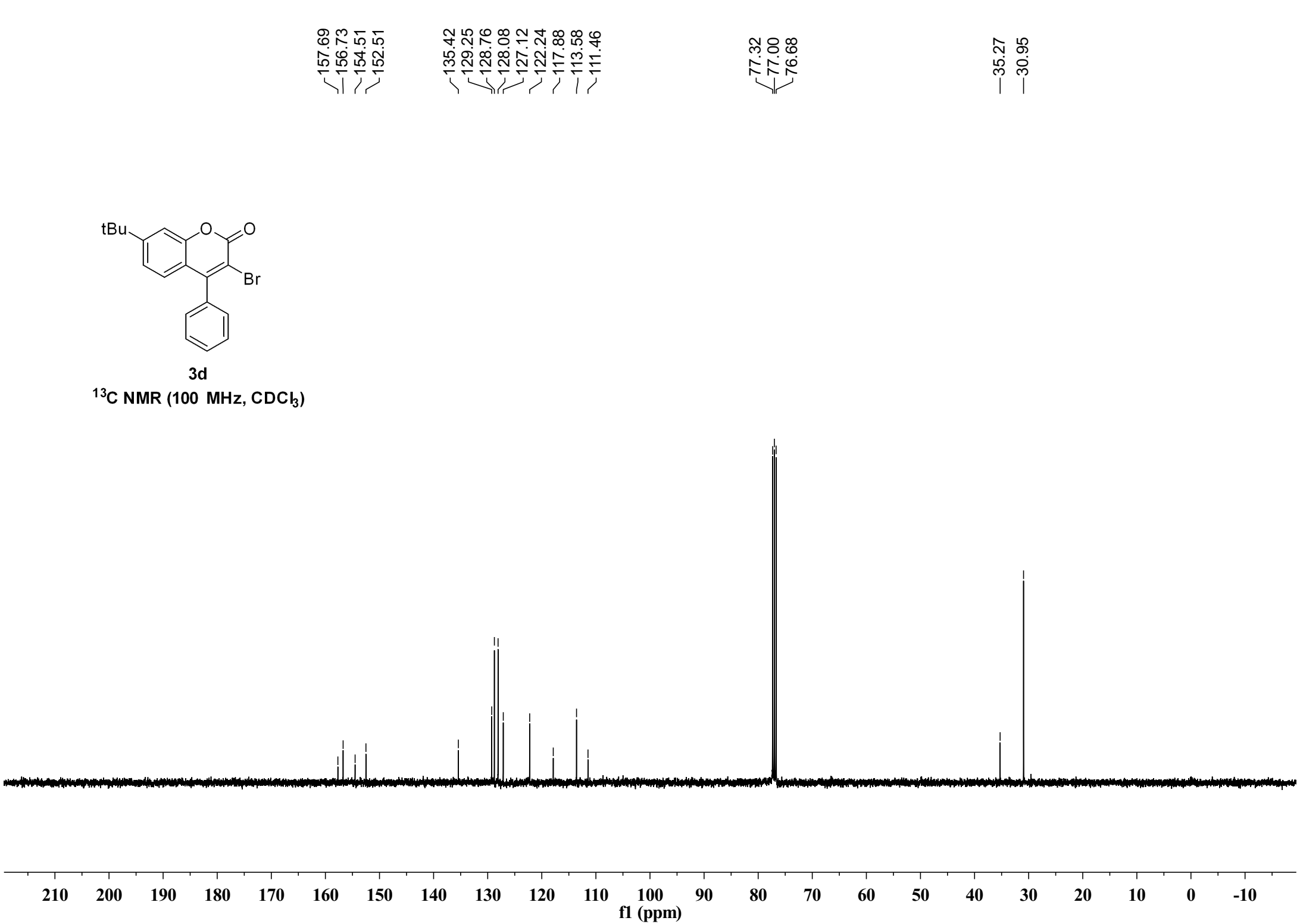
3c

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



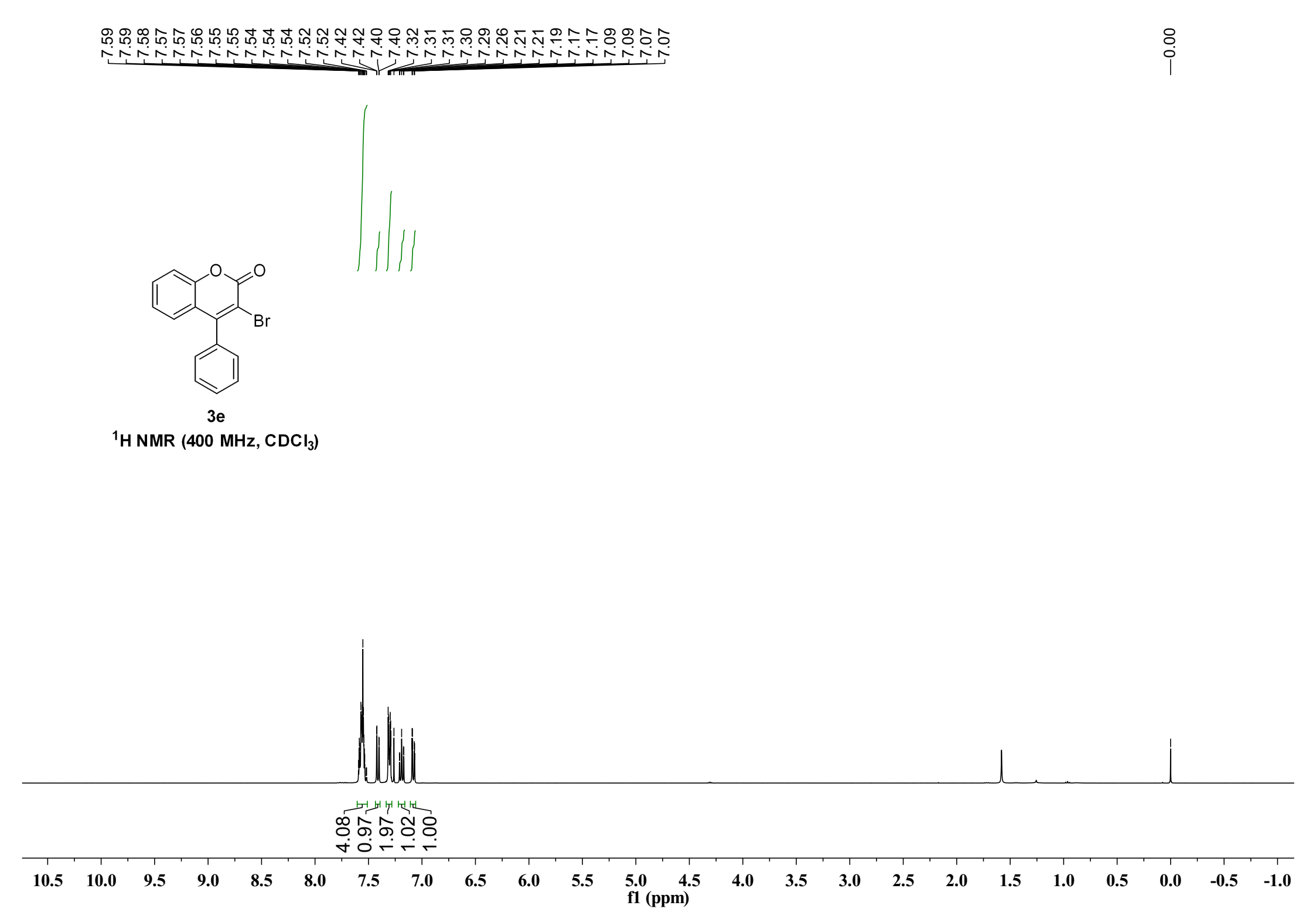
3d

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



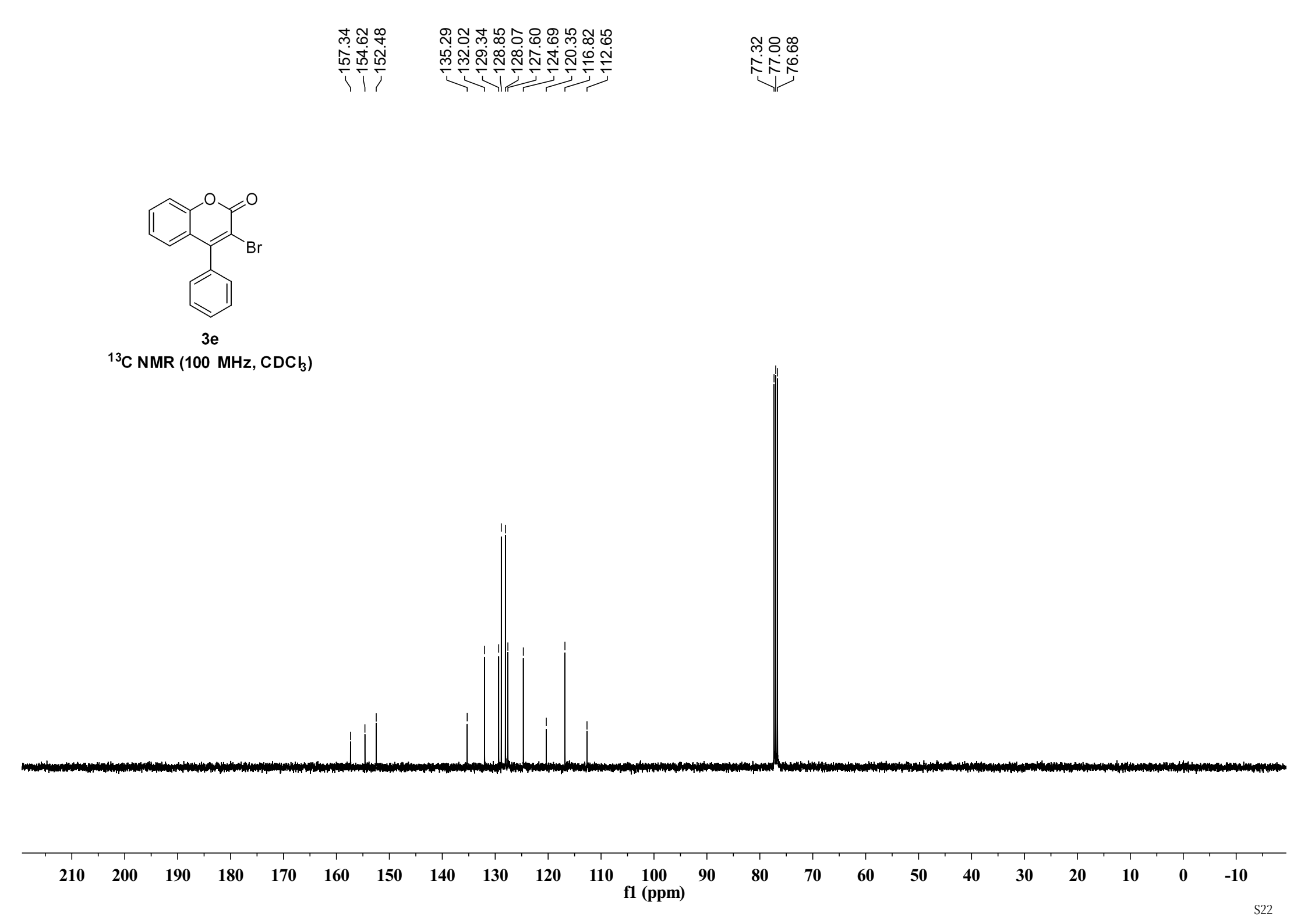
3d

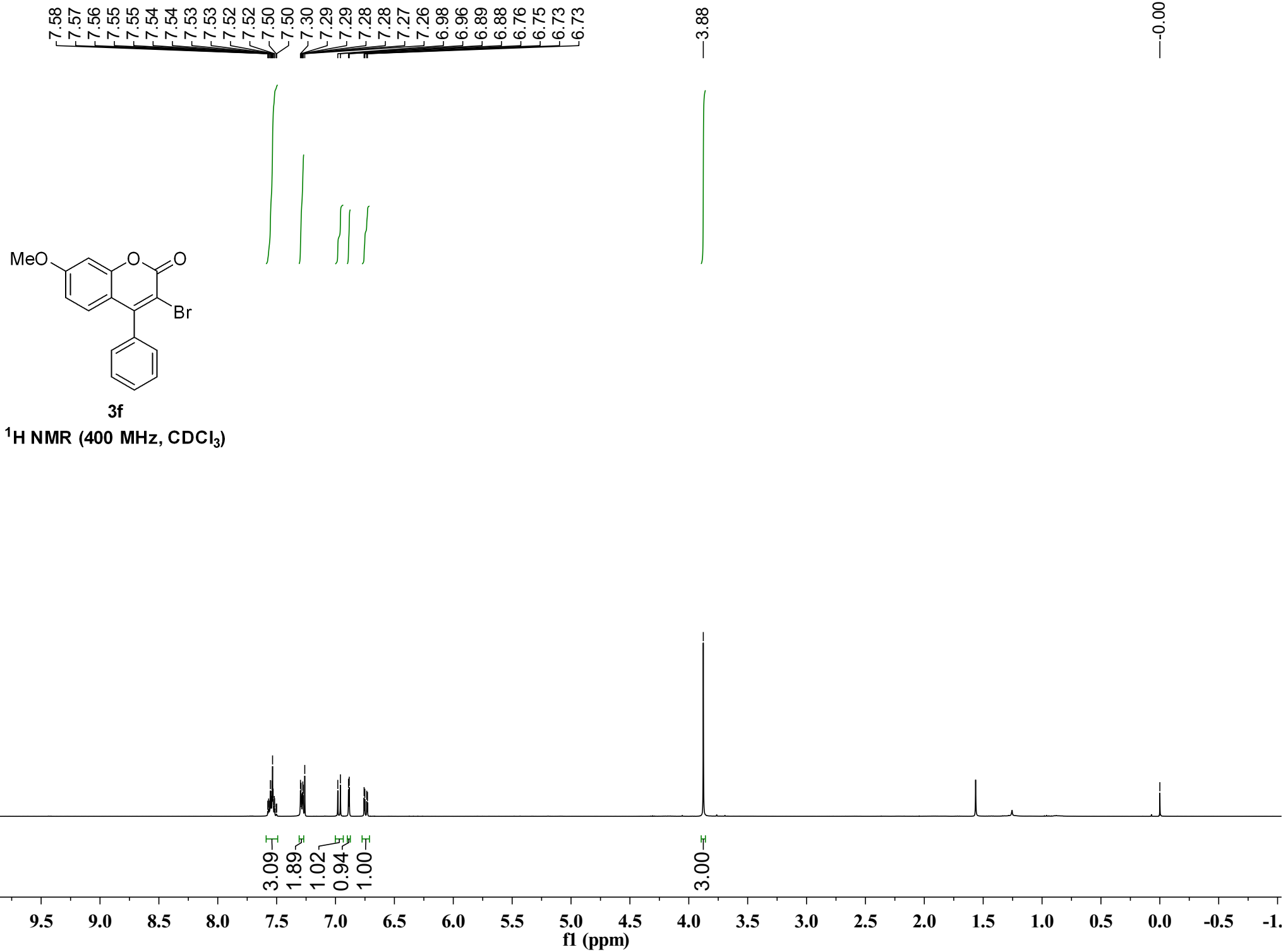
^{13}C NMR (100 MHz, $CDCl_3$)



3e

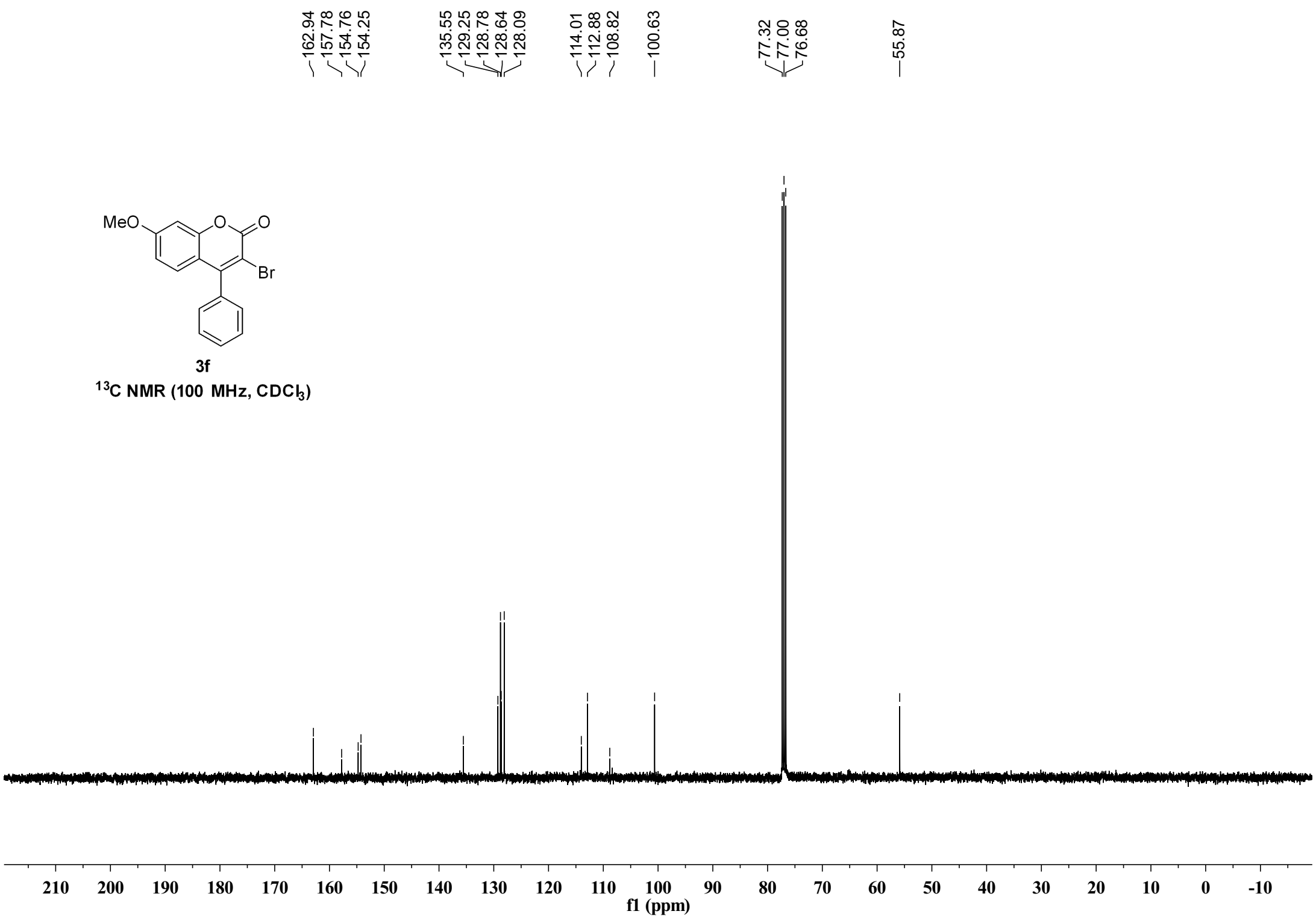
^{1}H NMR (400 MHz, $CDCl_3$)

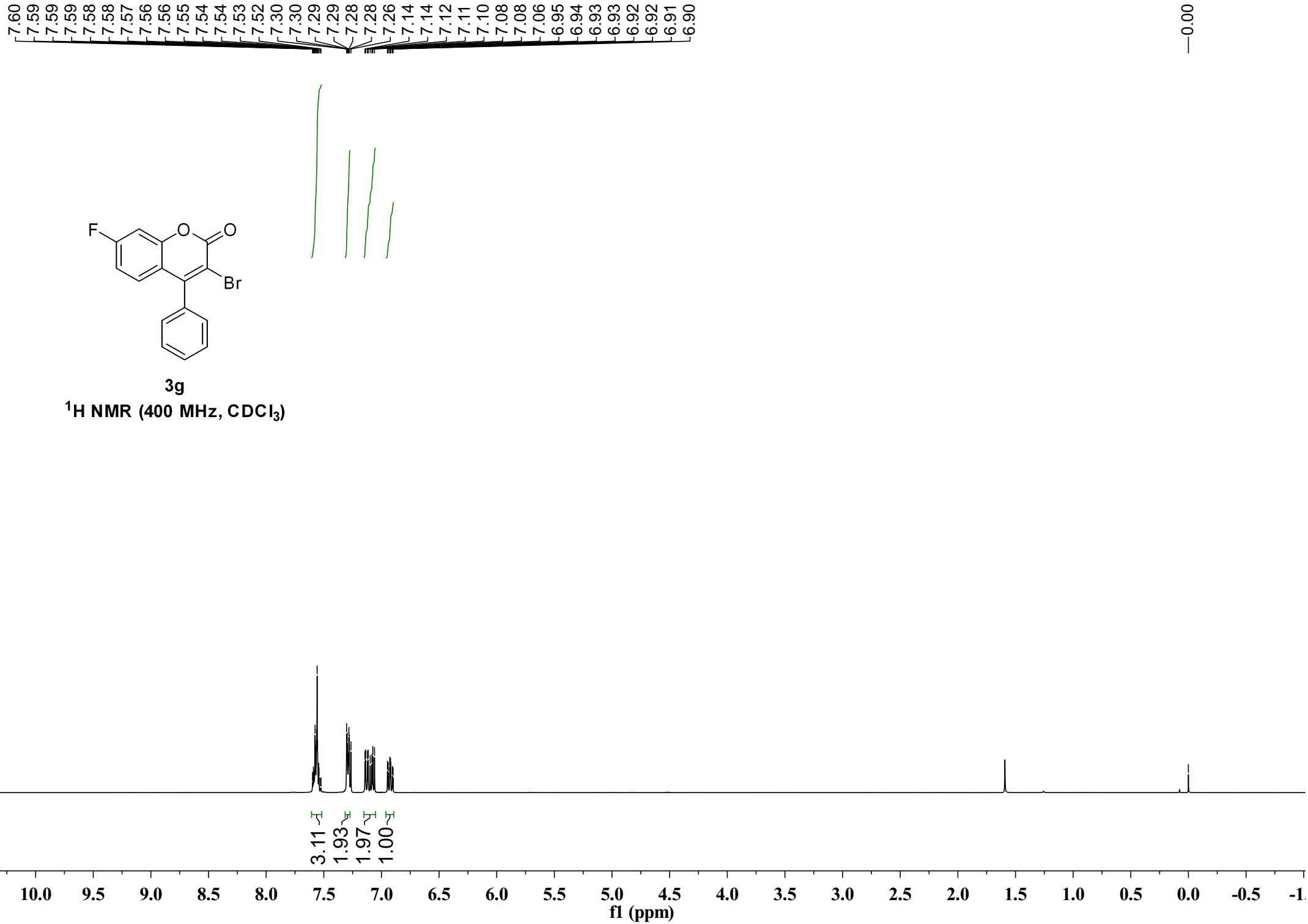

157.34
154.62
152.48
135.29
132.02
129.34
128.85
128.07
127.60
124.69
120.35
116.82
112.65
77.32
77.00
76.68
O
O
Br
3e
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3f

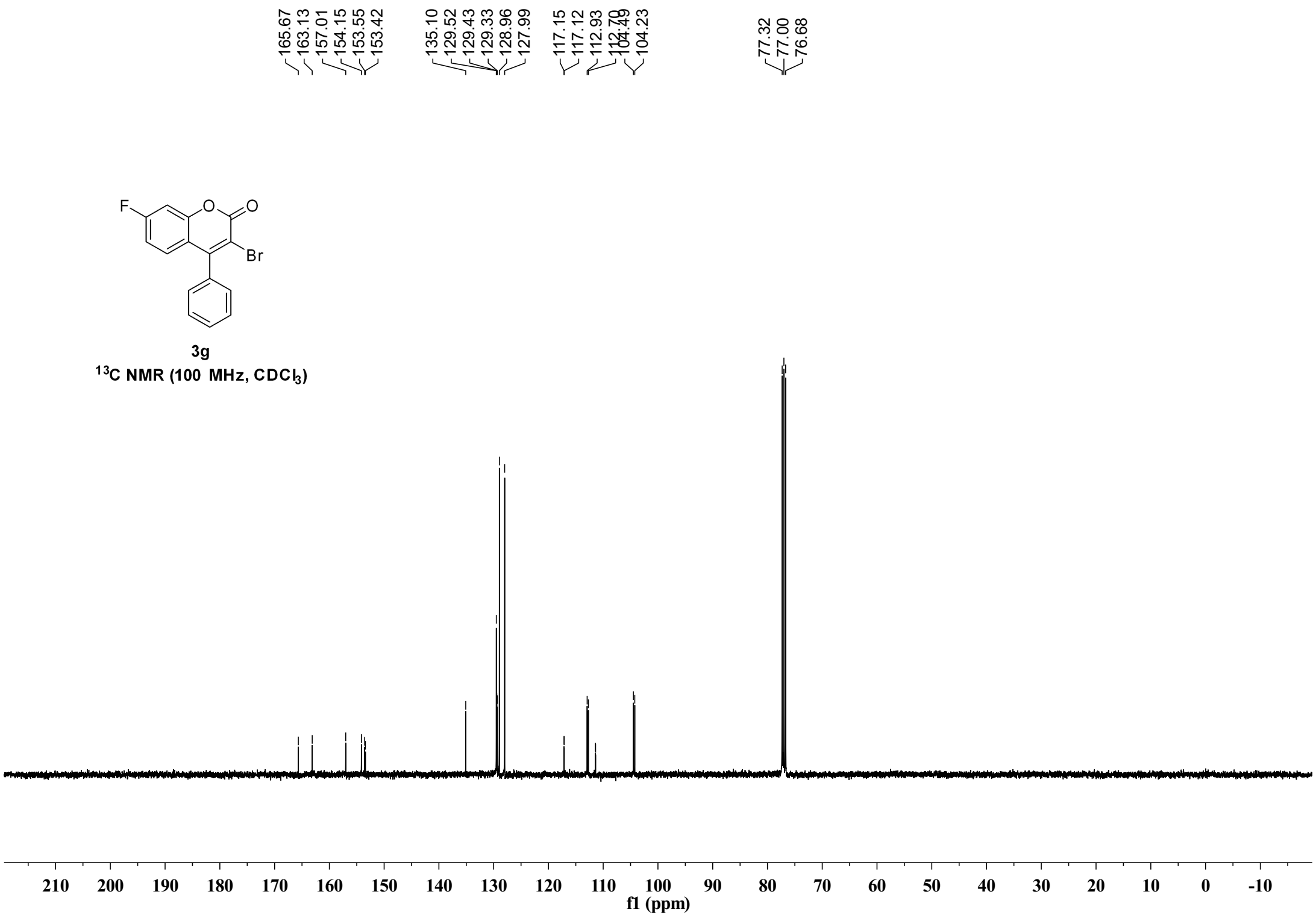
^{1}H NMR (400 MHz, $CDCl_3$)

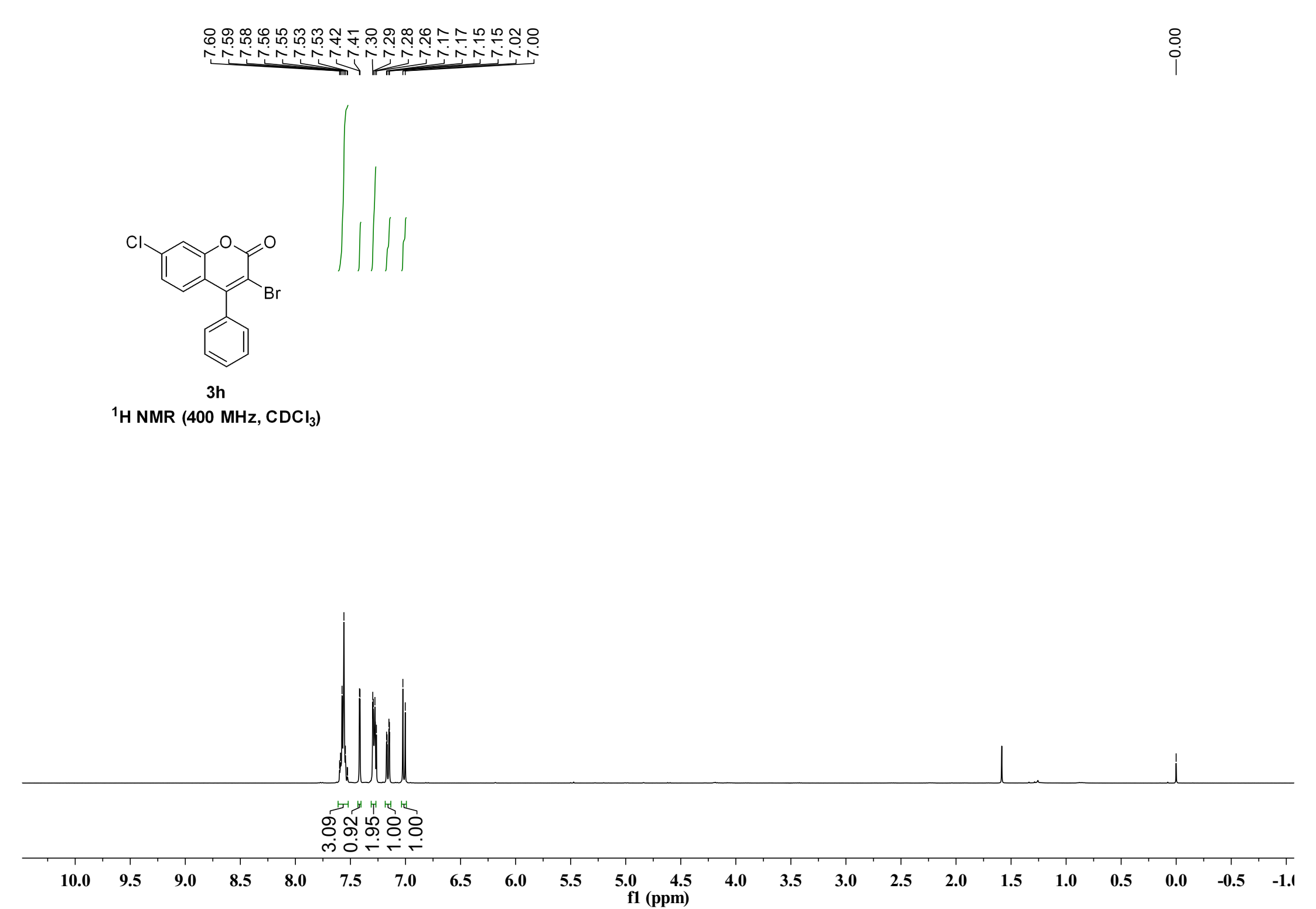

162.94
157.78
154.76
154.25
135.55
129.25
128.78
128.64
128.09
114.01
112.88
108.82
100.63
77.32
77.00
76.68
55.87
MeO
O
O
Br
3f
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3g

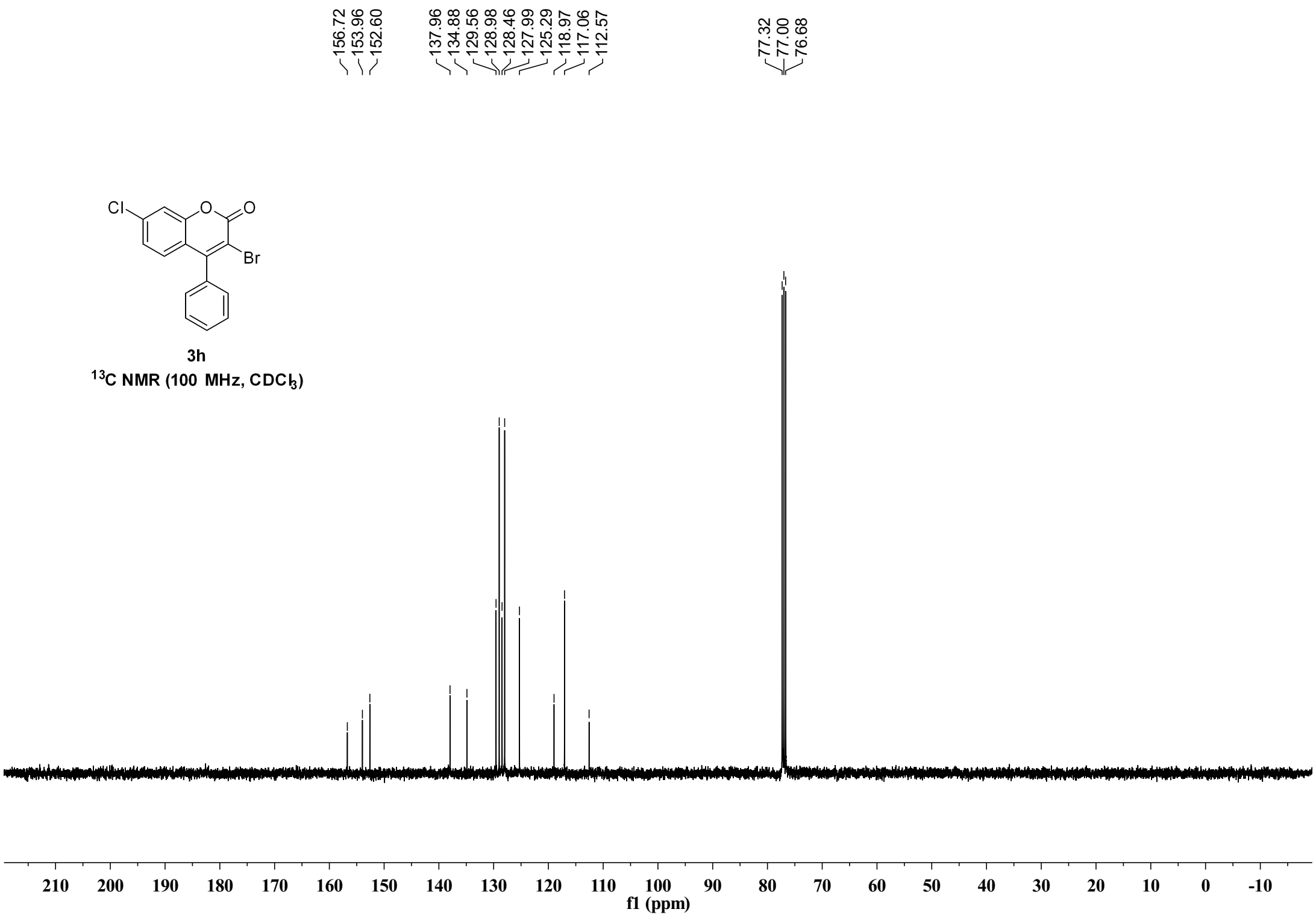
^{1}H NMR (400 MHz, $CDCl_3$)

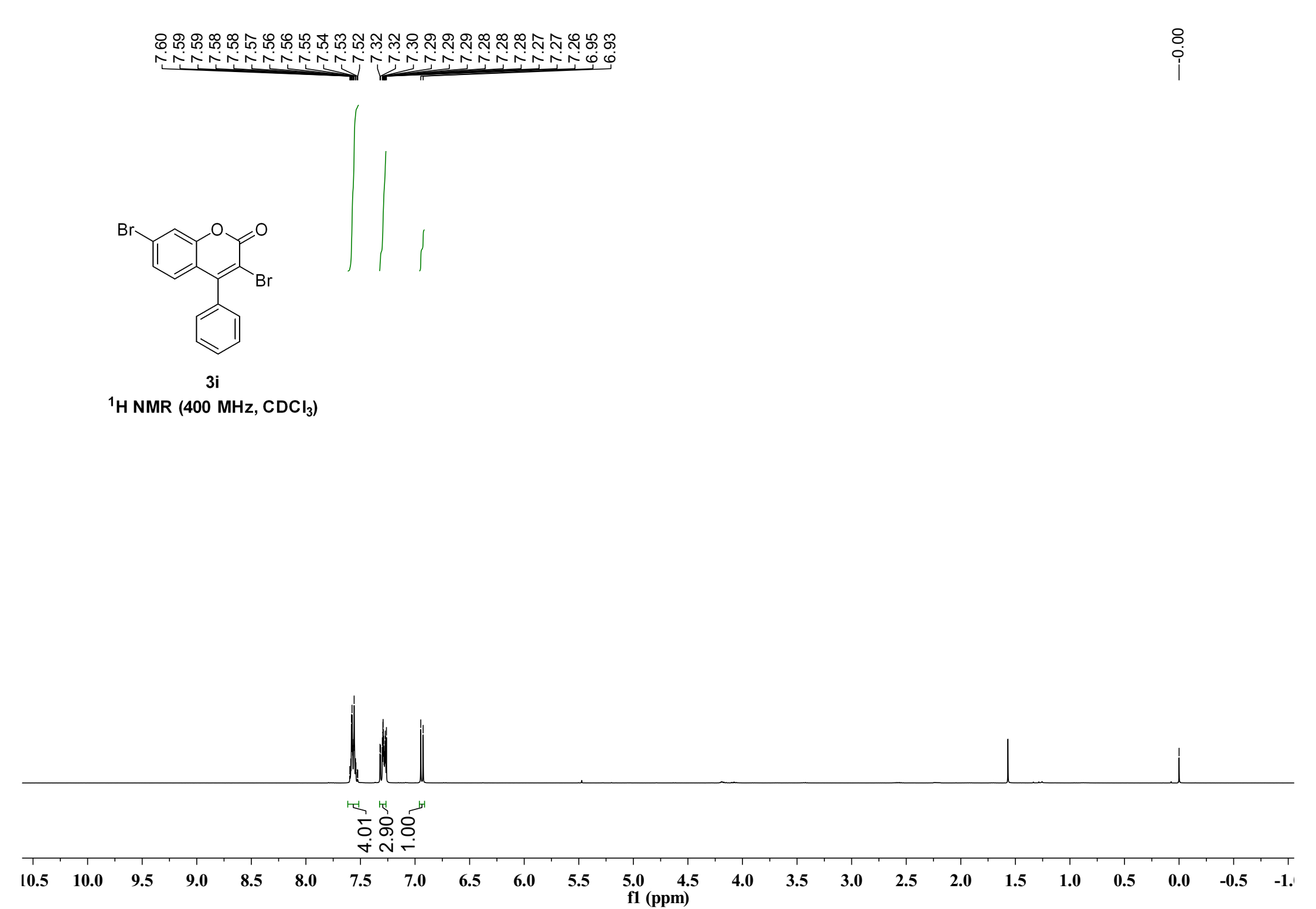

165.67
163.13
157.01
154.15
153.55
153.42
135.10
129.52
129.43
129.33
128.96
127.99
117.15
117.12
112.93
112.70
104.49
104.23
77.32
77.00
76.68
F
O
O
Br
3g
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3h

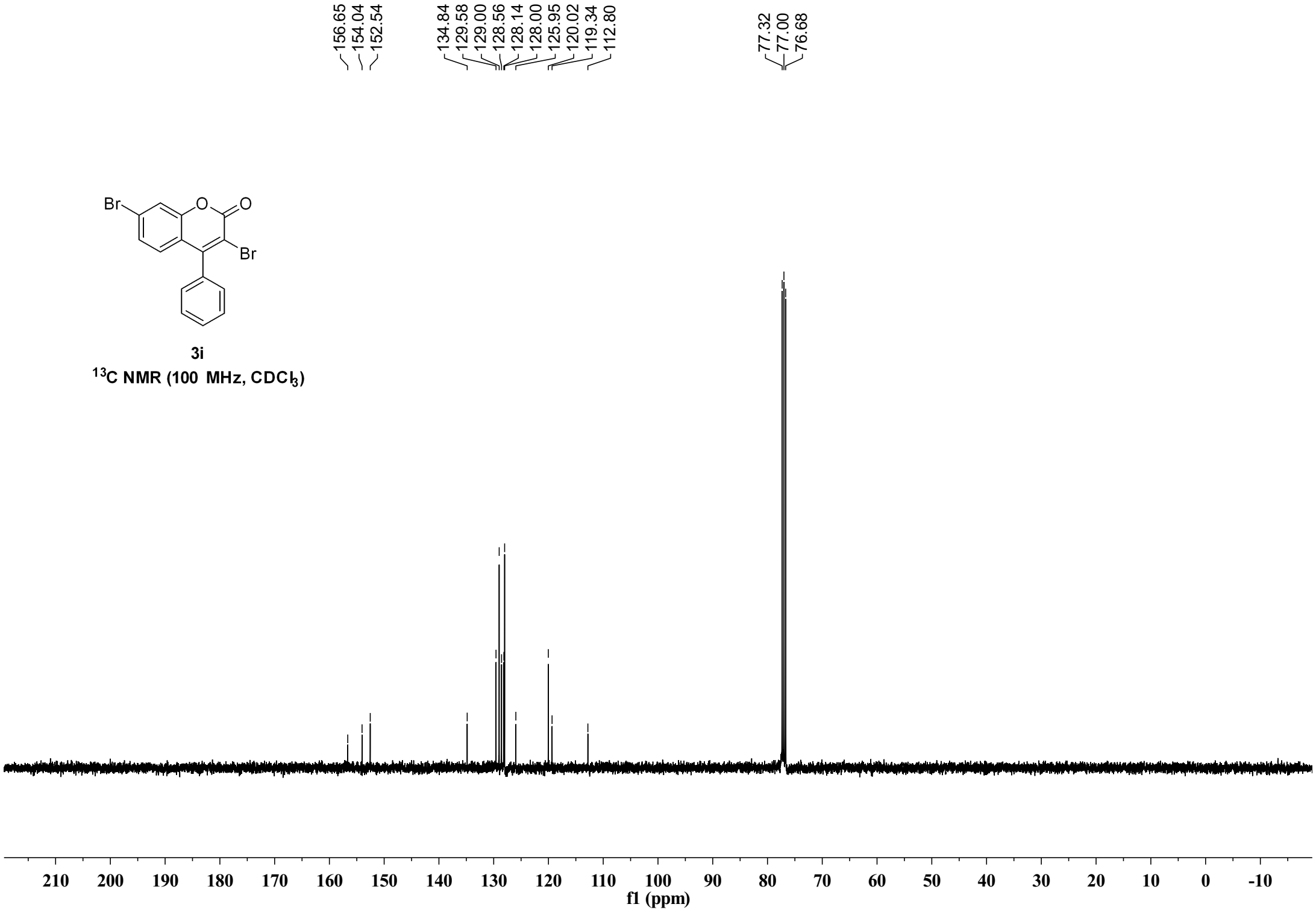
^{1}H NMR (400 MHz, $CDCl_3$)

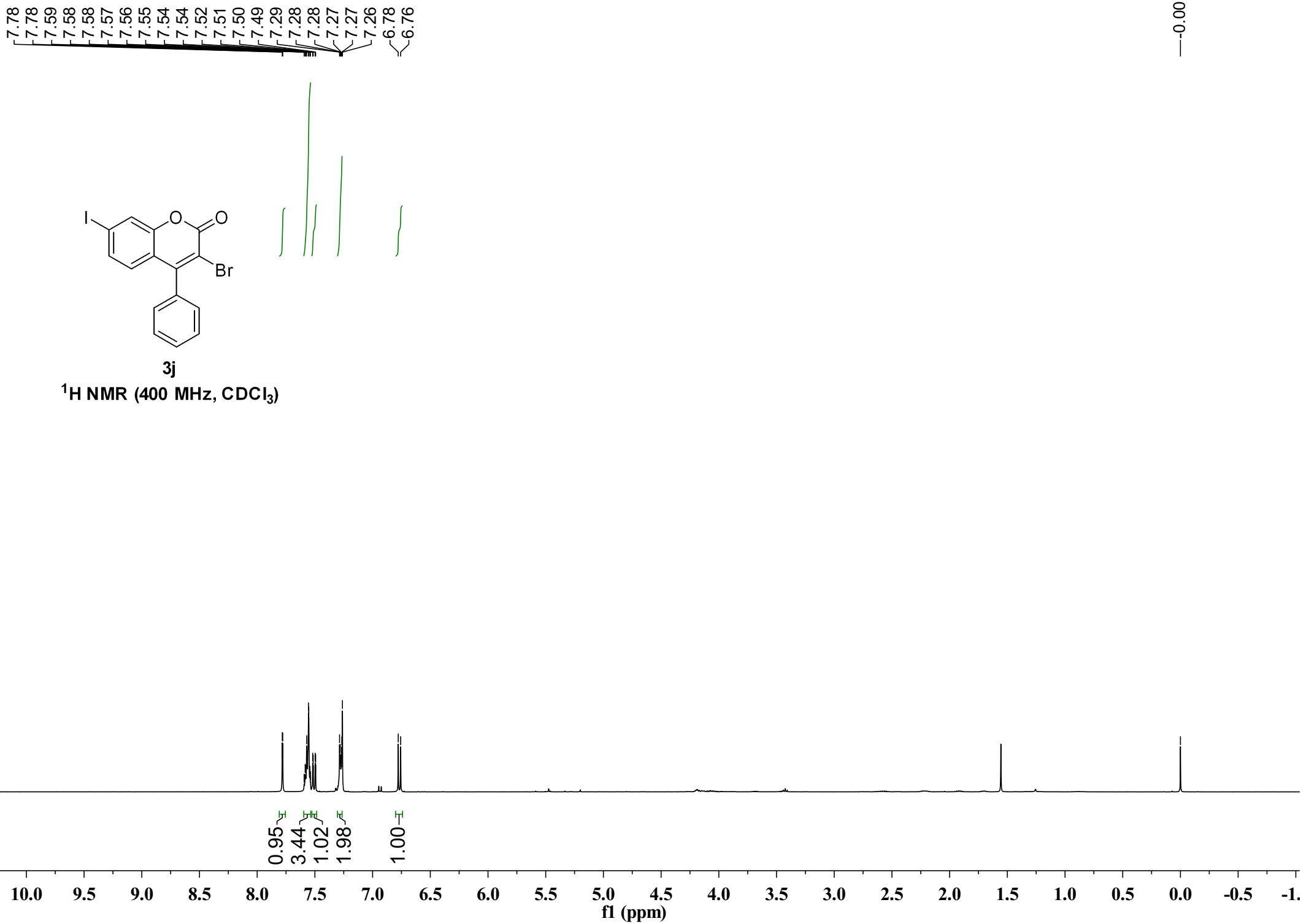

156.72
153.96
152.60
137.96
134.88
129.56
128.98
128.46
127.99
125.29
118.97
117.06
112.57
77.32
77.00
76.68
Cl
O
O
Br
3h
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3i

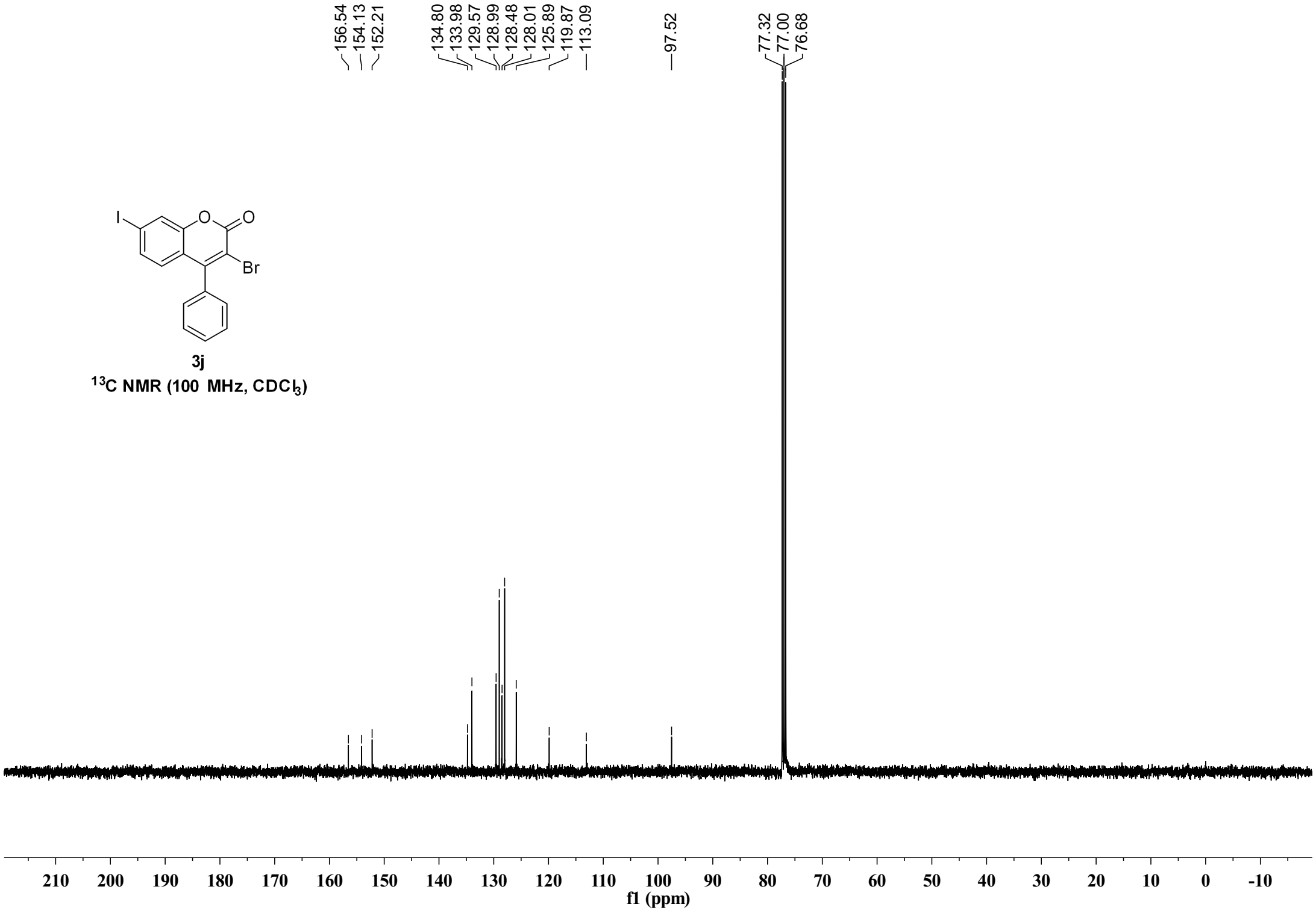
^{1}H NMR (400 MHz, $CDCl_3$)


156.65
154.04
152.54
134.84
129.58
129.00
128.56
128.14
128.00
125.95
120.02
119.34
112.80
77.32
77.00
76.68
Br
O
O
Br
3i
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)



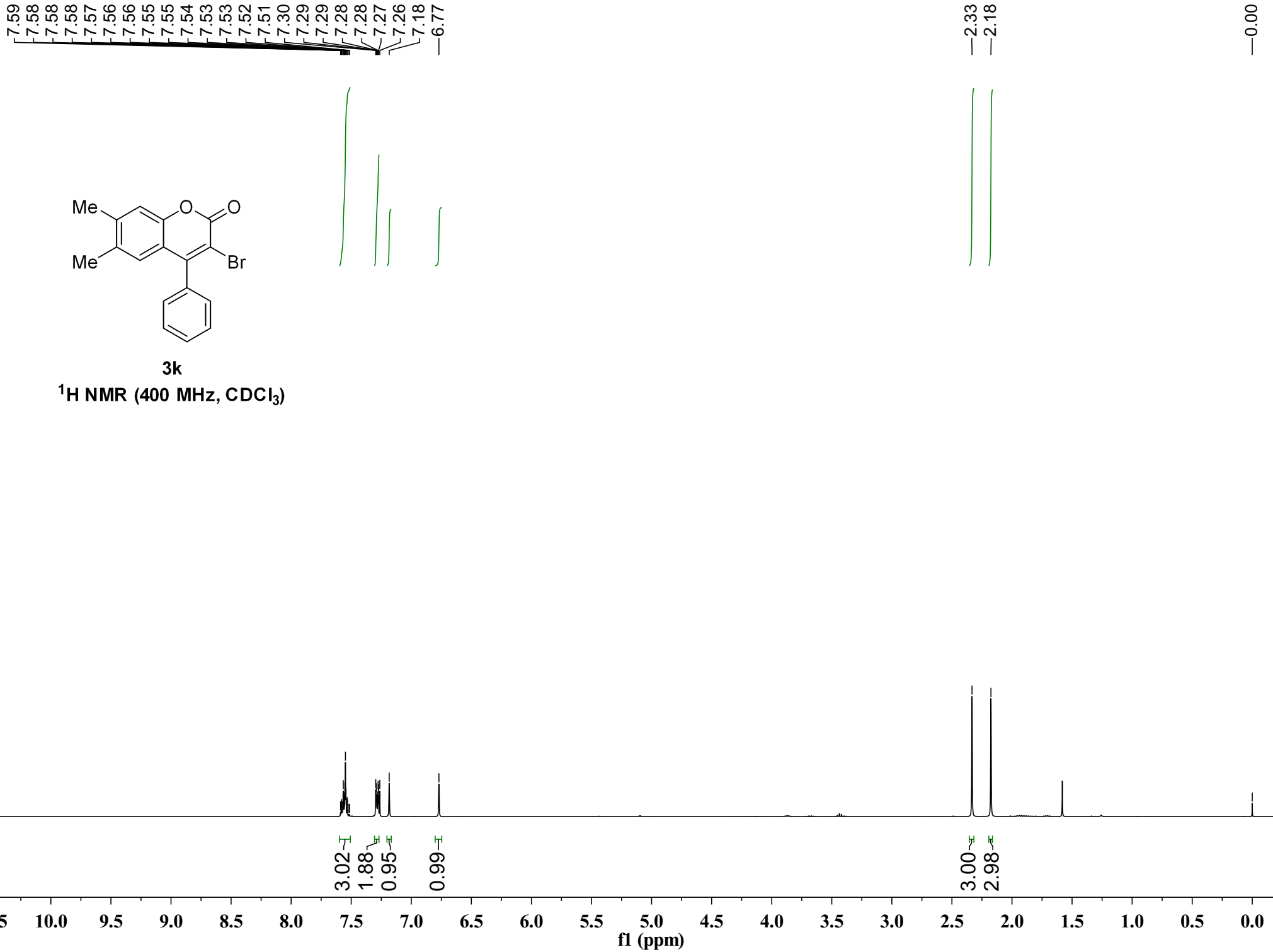
3j

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



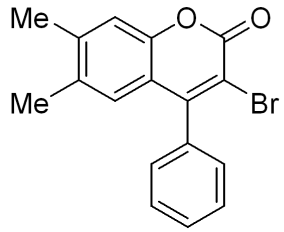
3j

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



3k

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



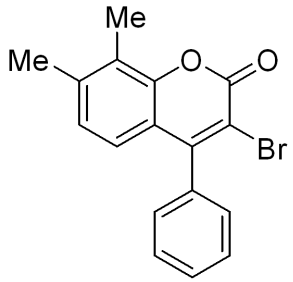
3k

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

157.76
154.62
150.90
142.34
135.59
133.57
129.19
128.77
128.08
127.45
118.05
117.31
111.30
77.32
77.00
76.68
20.23
19.26

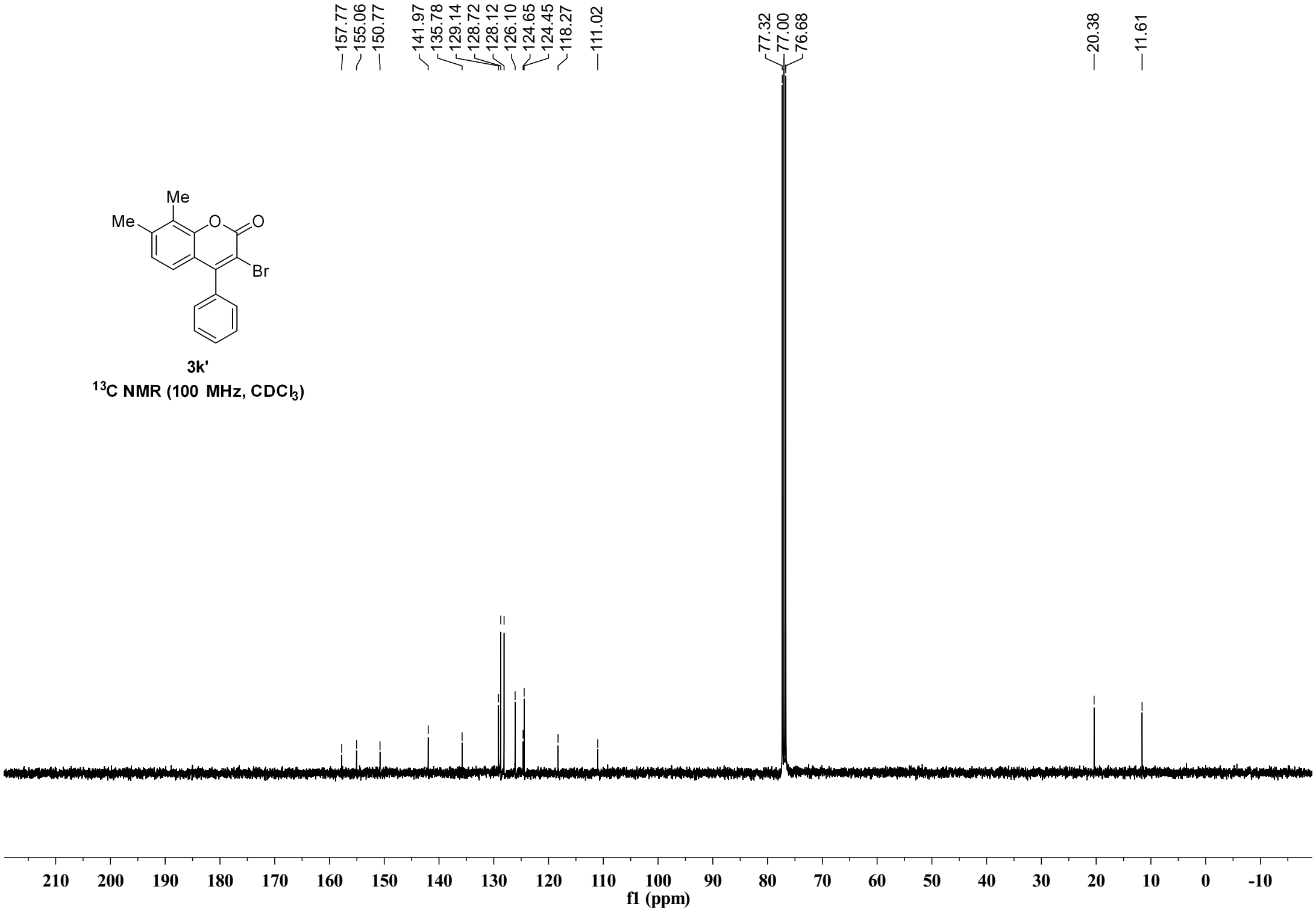
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



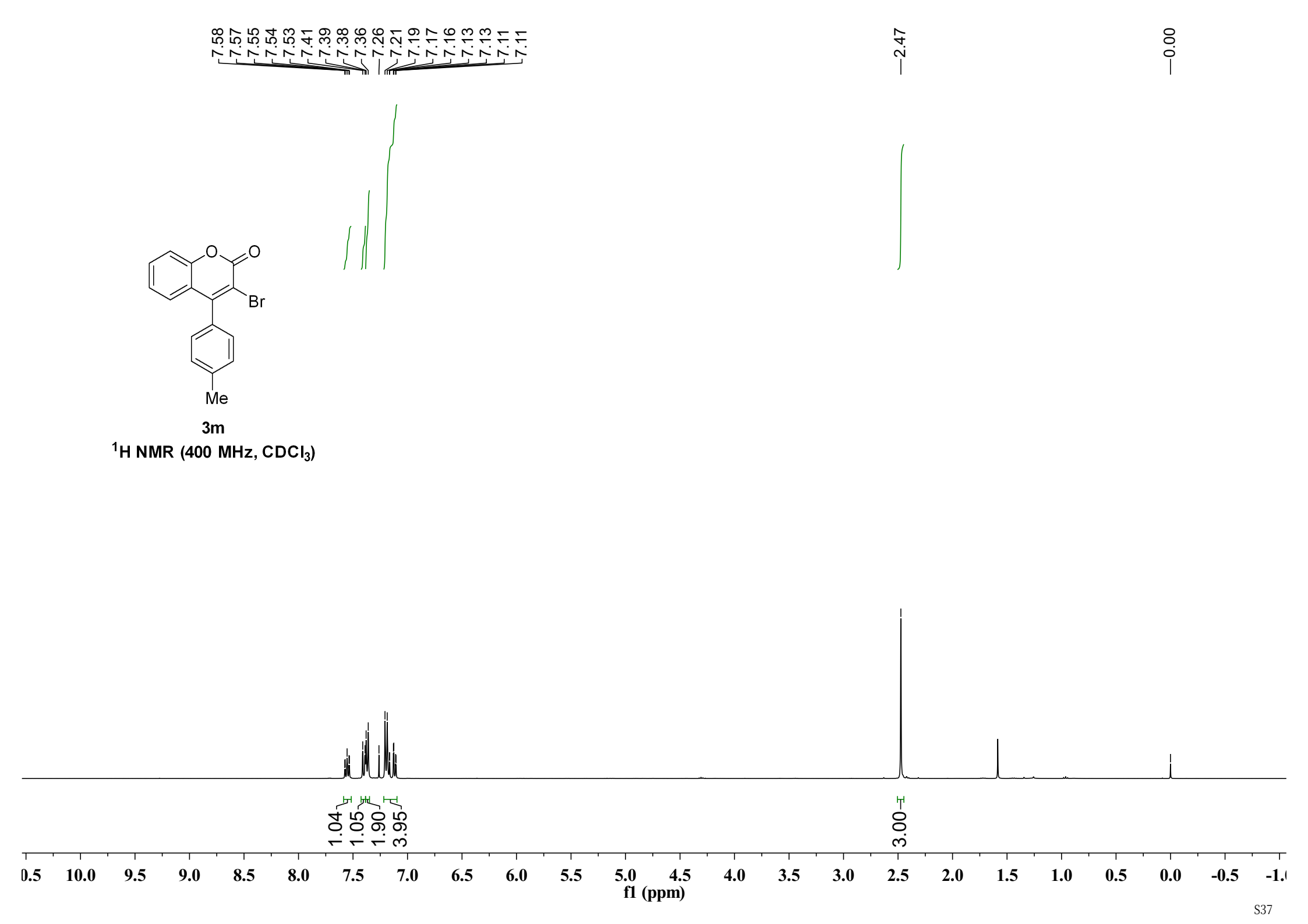
3k'

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



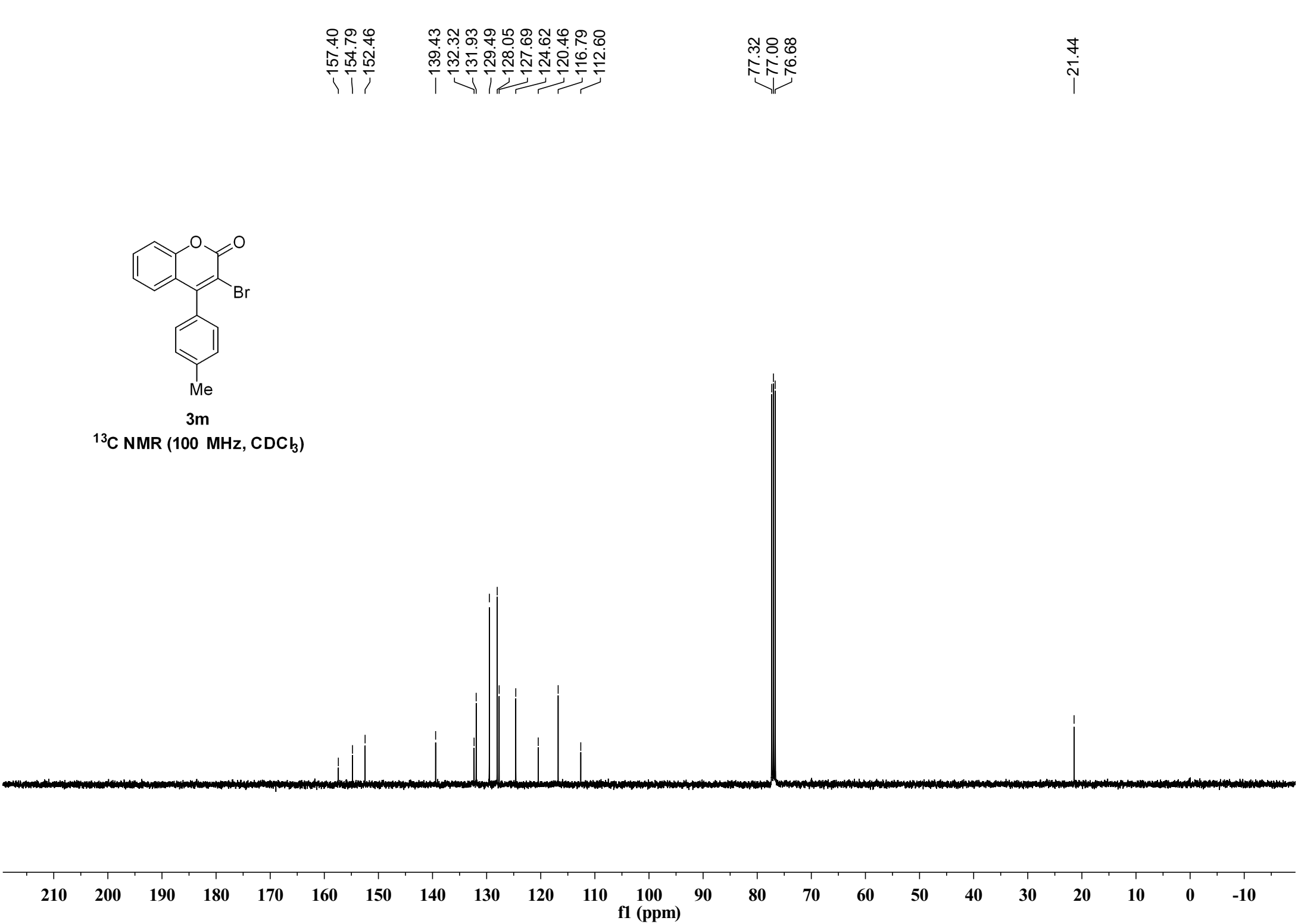
3k'

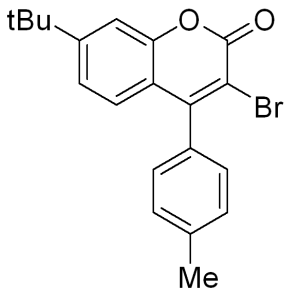
^{13}C NMR (100 MHz, $CDCl_3$)



3m

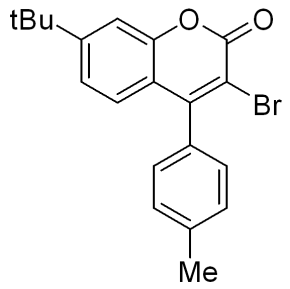
^{1}H NMR (400 MHz, $CDCl_3$)


157.40
154.79
152.46
139.43
132.32
131.93
129.49
128.05
127.69
124.62
120.46
116.79
112.60
77.32
77.00
76.68
21.44
O
O
Br
Me
3m
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)



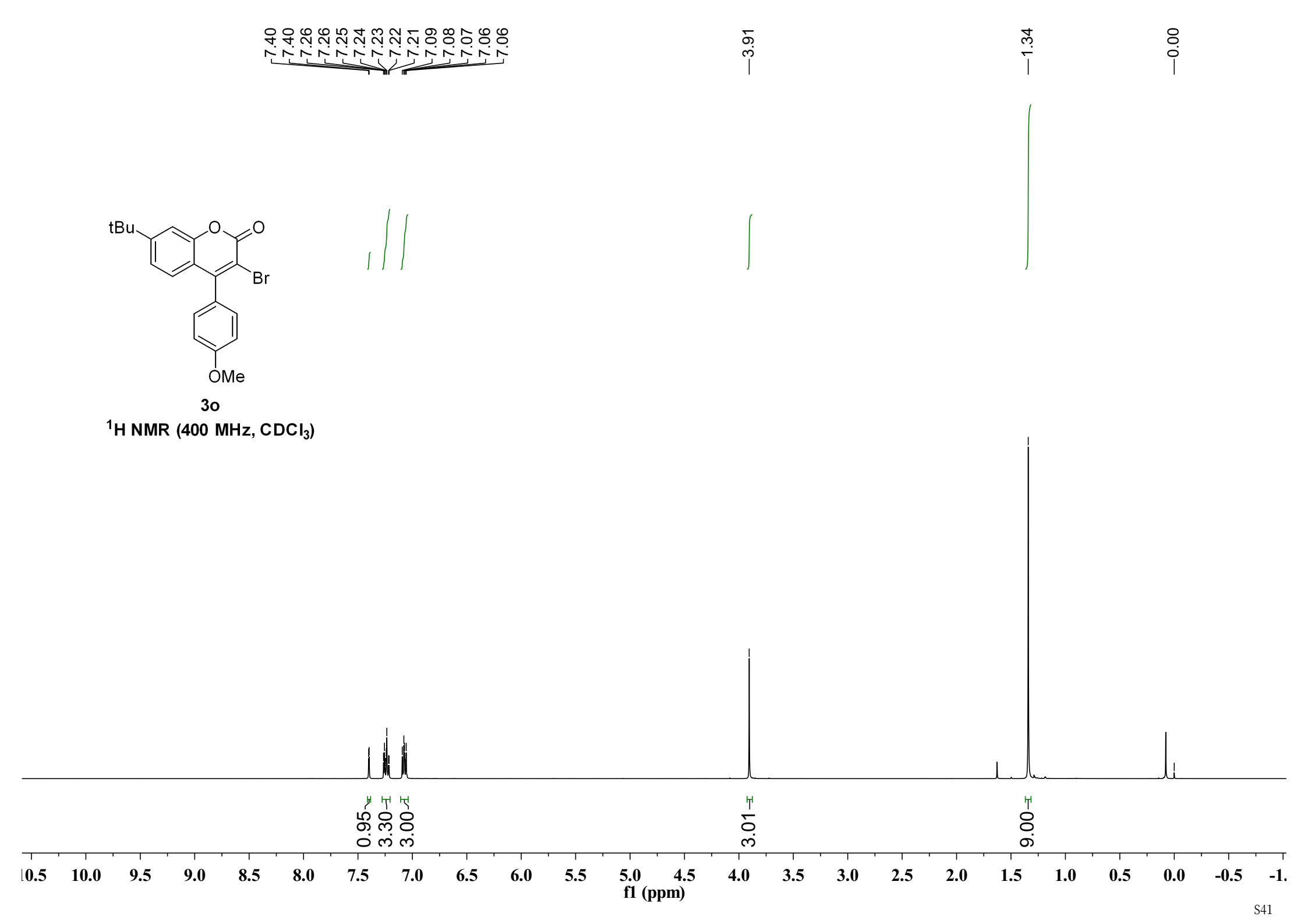
3n

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



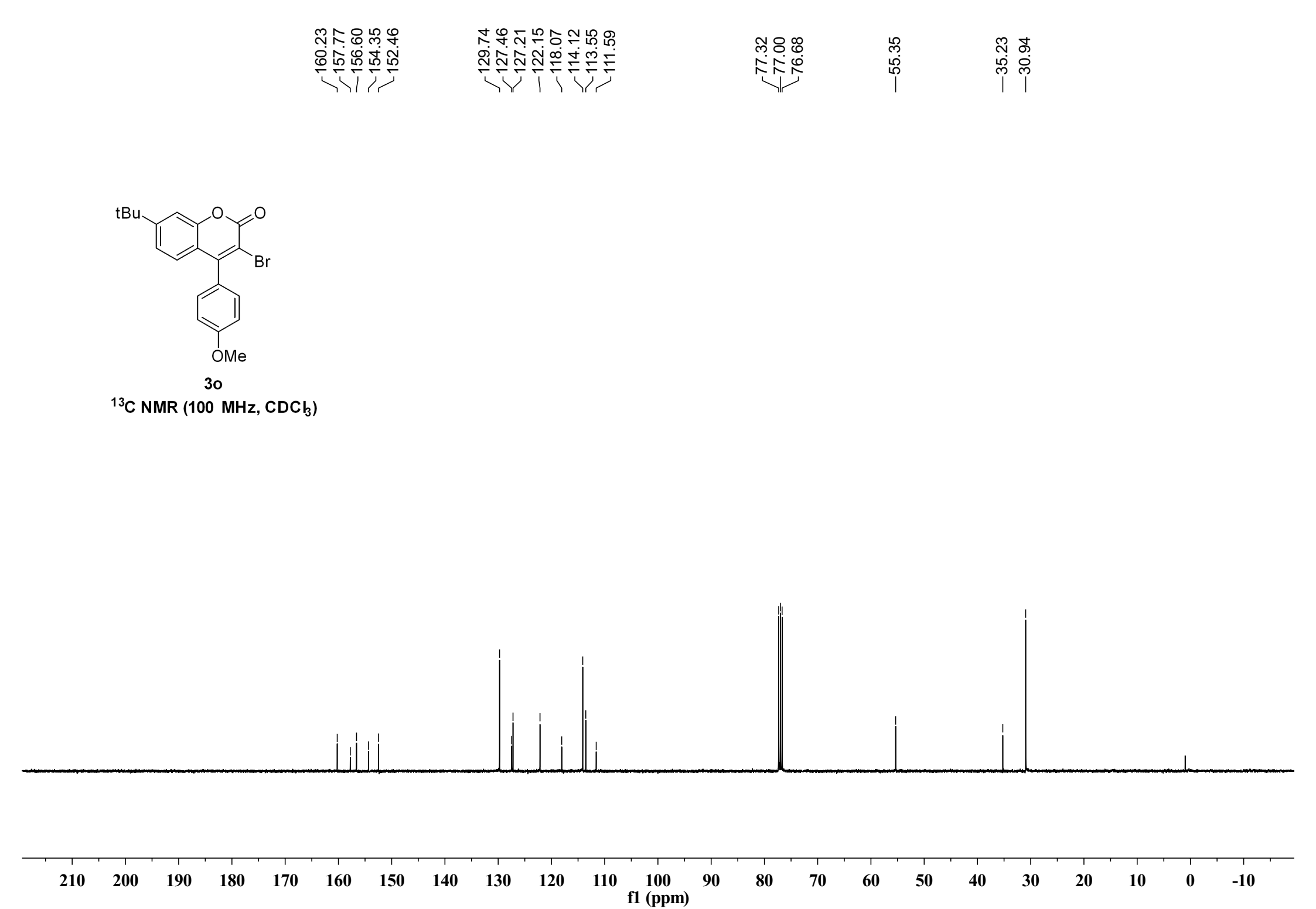
3n

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



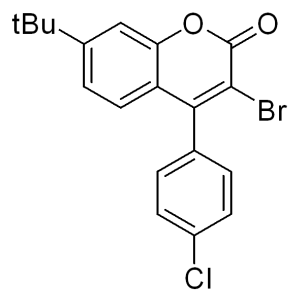
3o

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



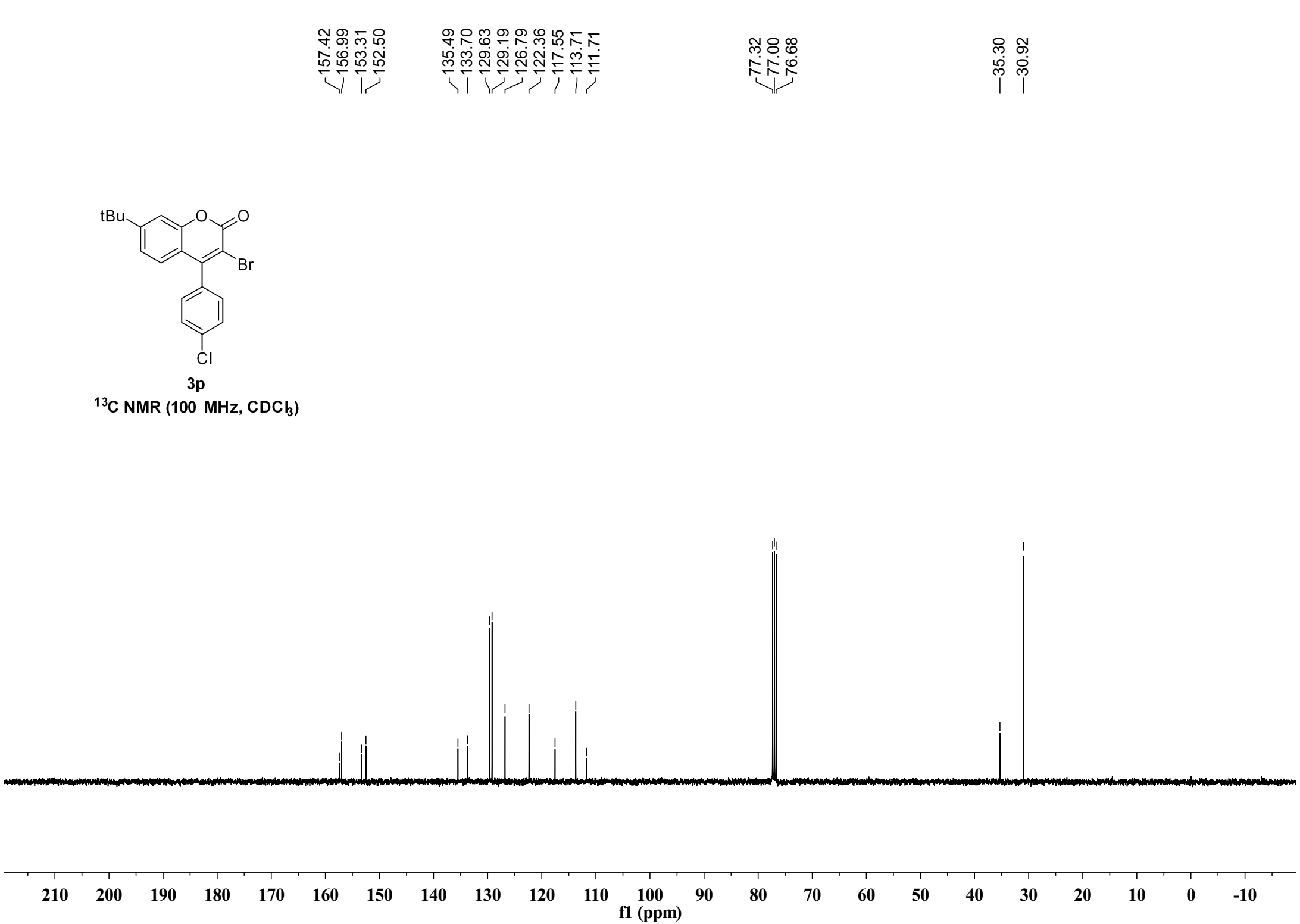
3o

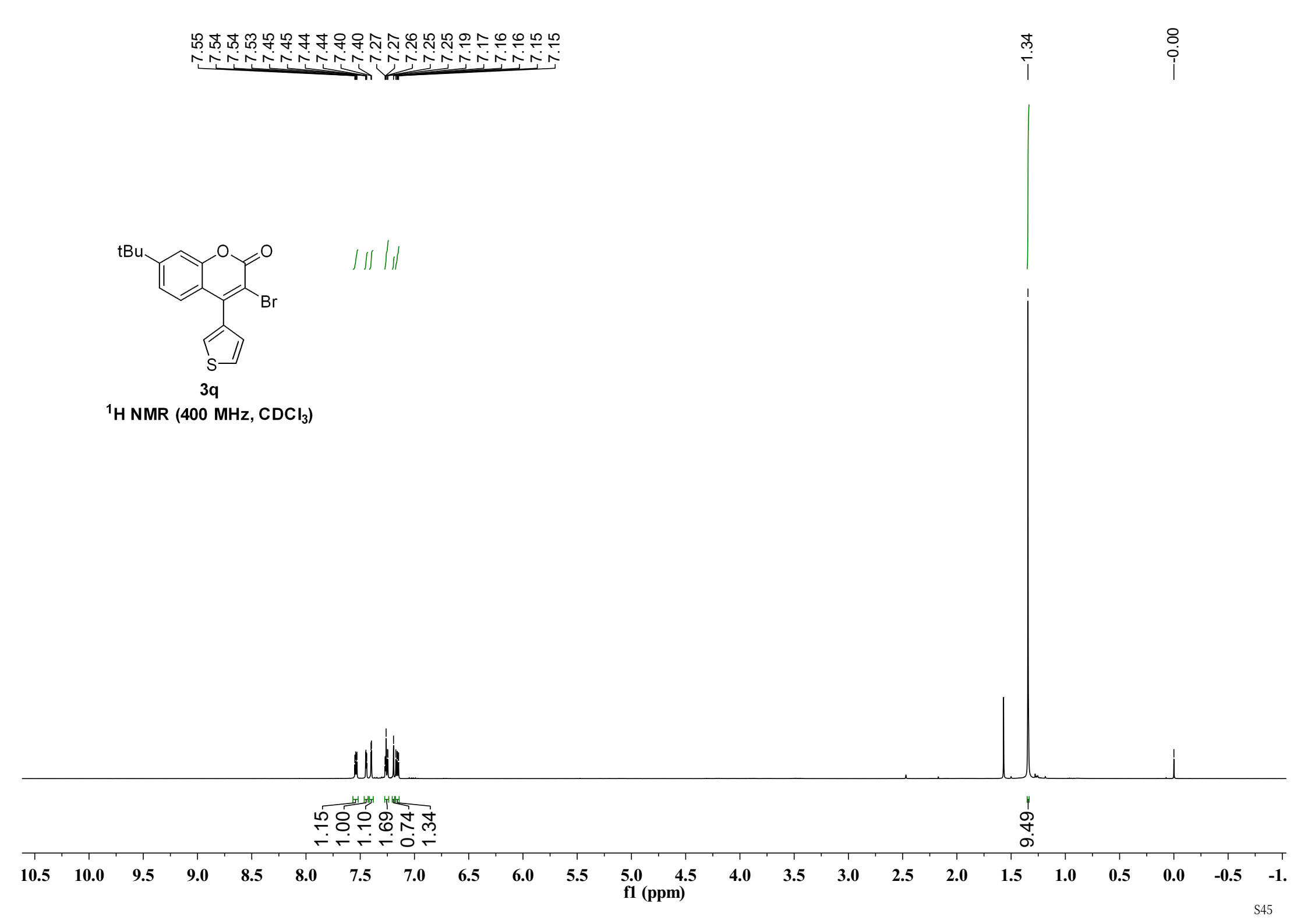
^{13}C NMR (100 MHz, $CDCl_3$)



3p

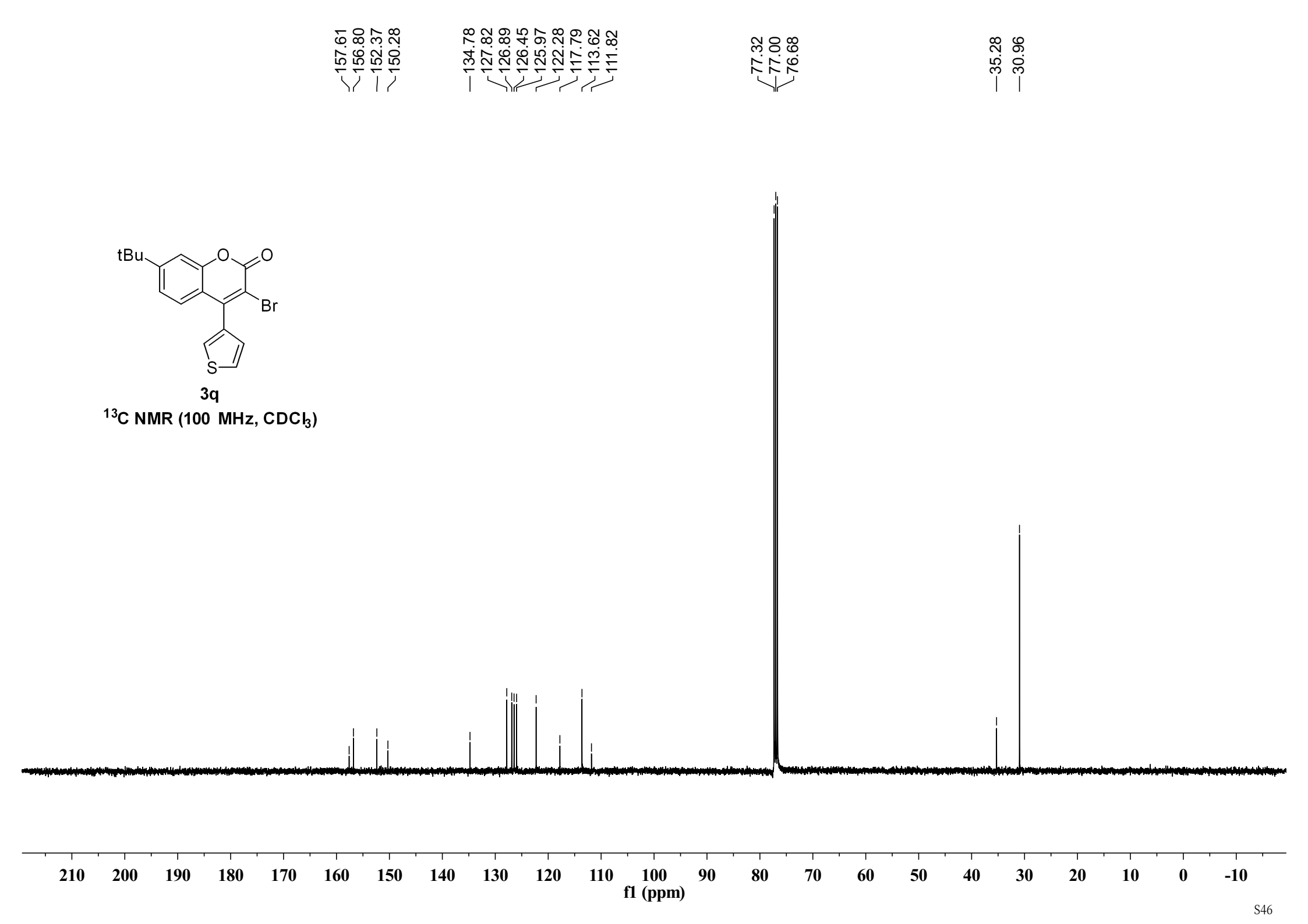
^{1}H NMR (400 MHz, $CDCl_3$)

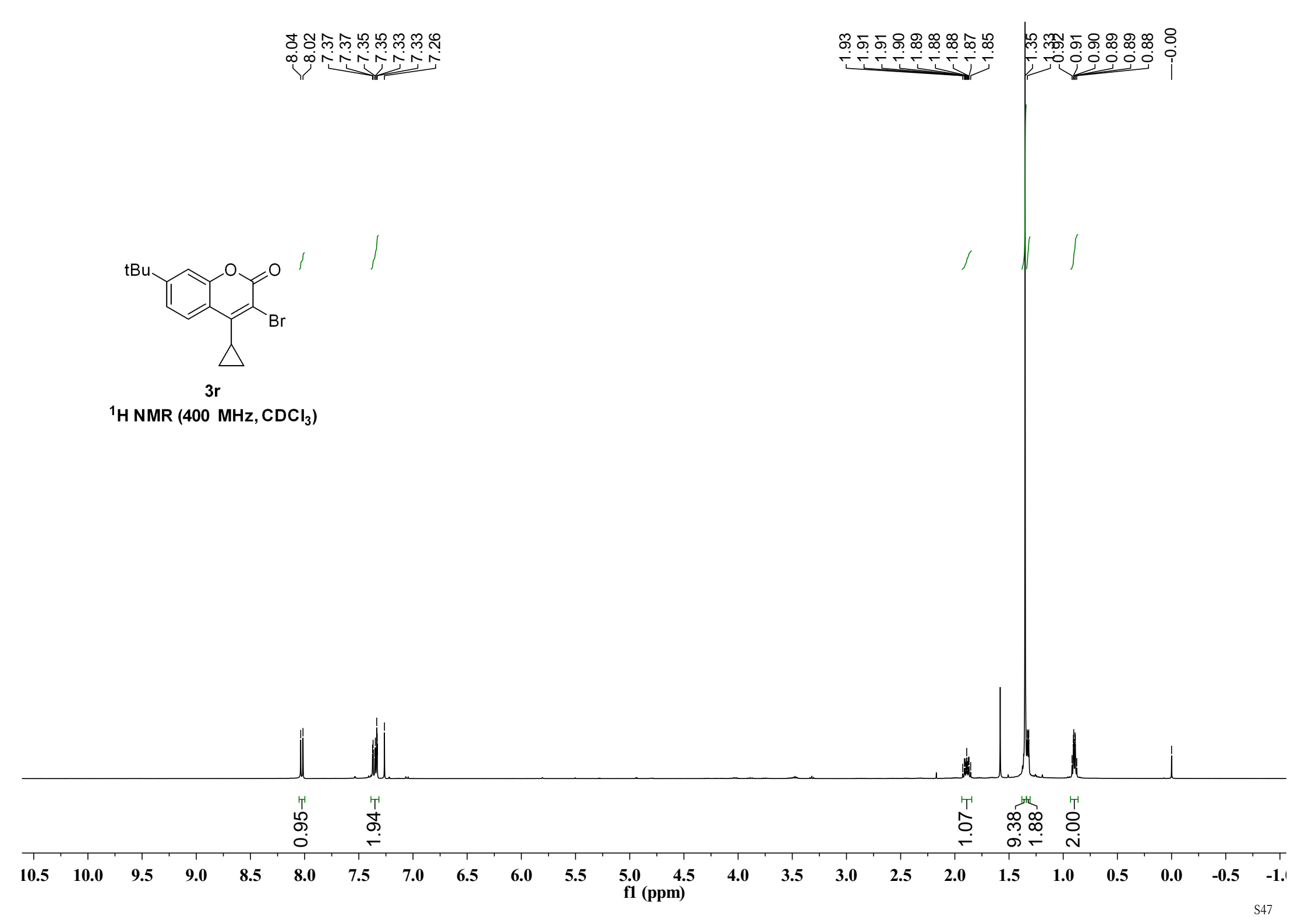

157.42
156.99
153.31
152.50
135.49
133.70
129.63
129.19
126.79
122.36
117.55
113.71
111.71
77.32
77.00
76.68
35.30
30.92
tBu
O
O
Br
Cl
3p
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

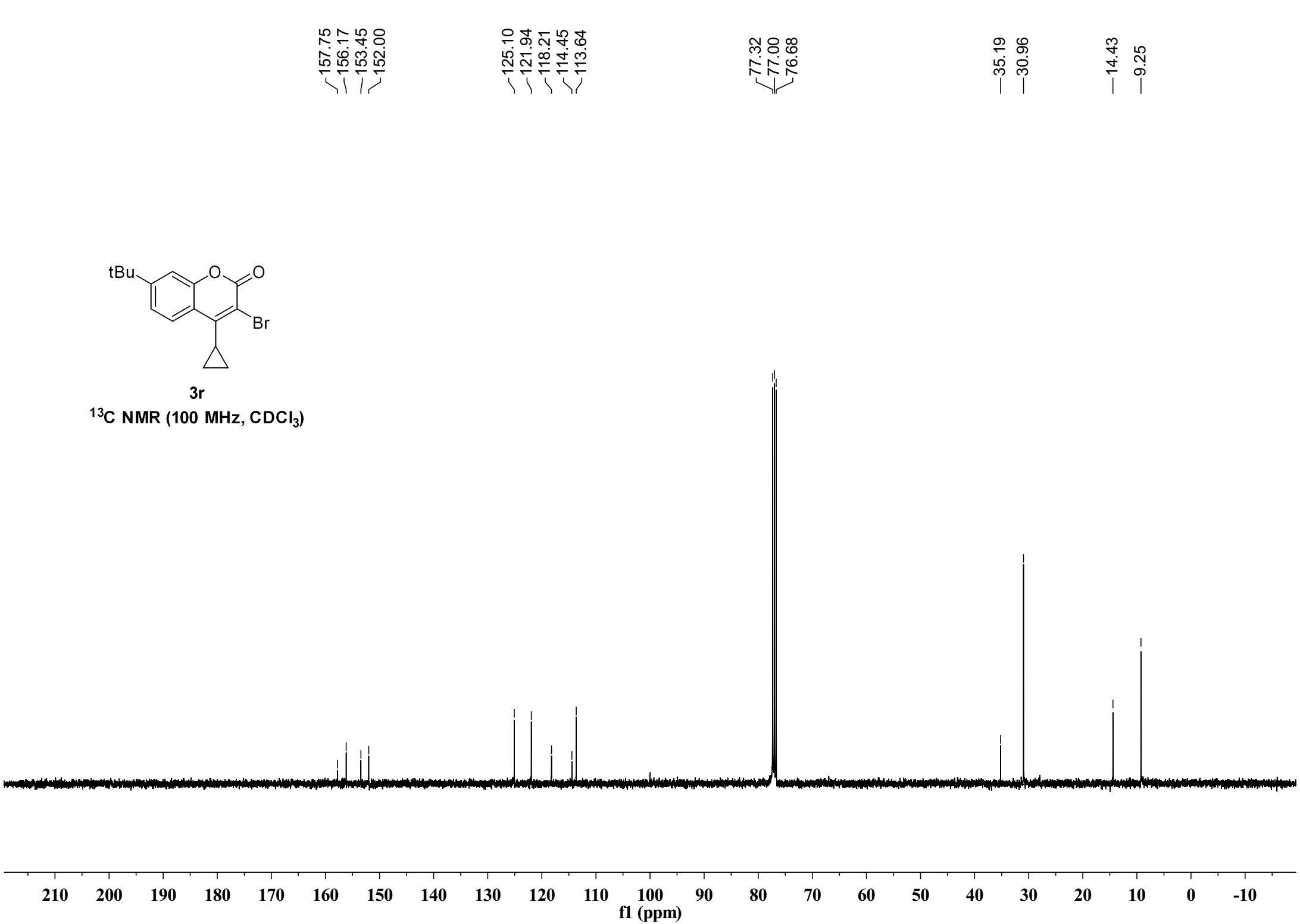


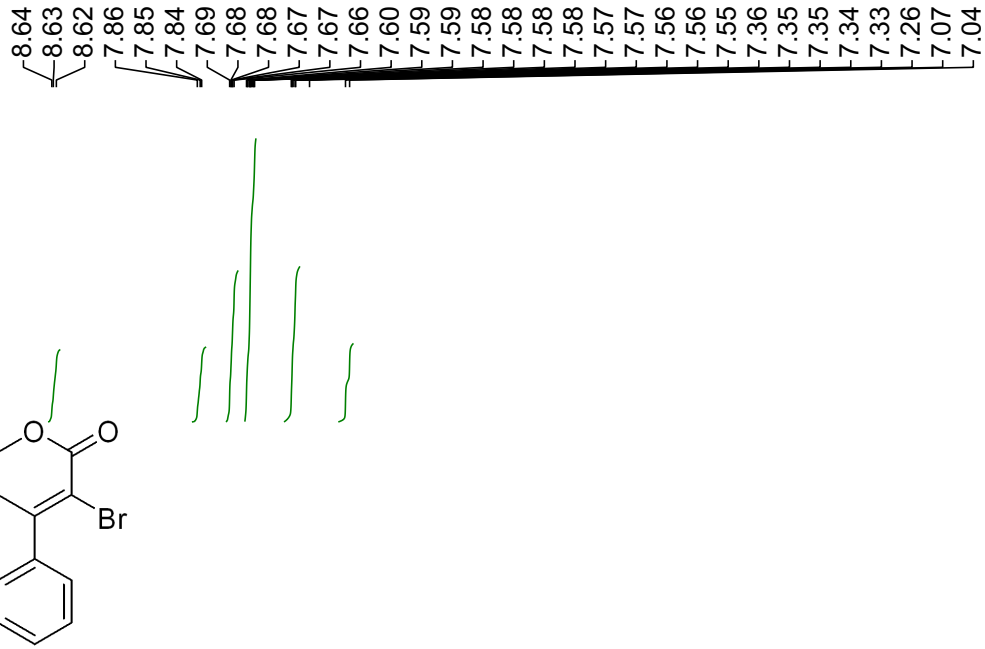
3q

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


157.61
156.80
152.37
150.28
134.78
127.82
126.89
126.45
125.97
122.28
117.79
113.62
111.82
77.32
77.00
76.68
35.28
30.96
tBu
O
O
Br
S
3q
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)

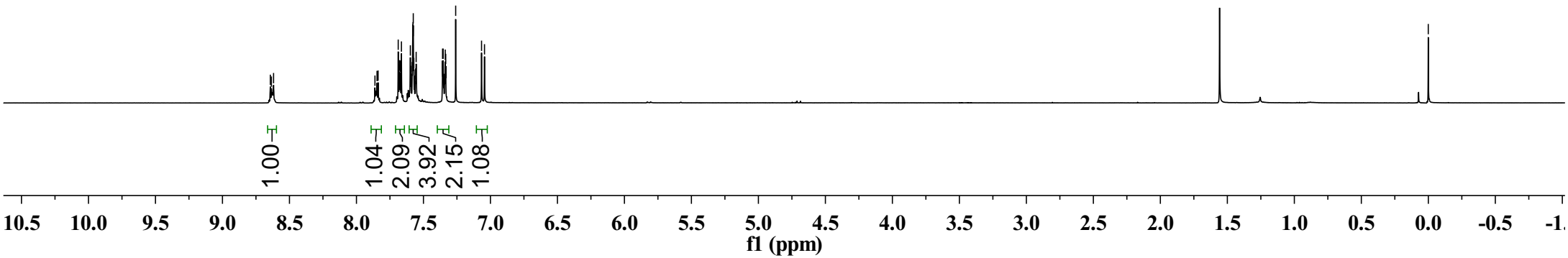

8.04
8.02
7.37
7.37
7.35
7.35
7.33
7.33
7.26
1.93
1.91
1.91
1.90
1.89
1.88
1.88
1.87
1.85
1.35
1.33
0.92
0.91
0.90
0.89
0.89
0.88
-0.00
tBu
O
O
Br
3r
1H NMR (400 MHz, CDCl3)
0.95
1.94
1.07
9.38
1.88
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

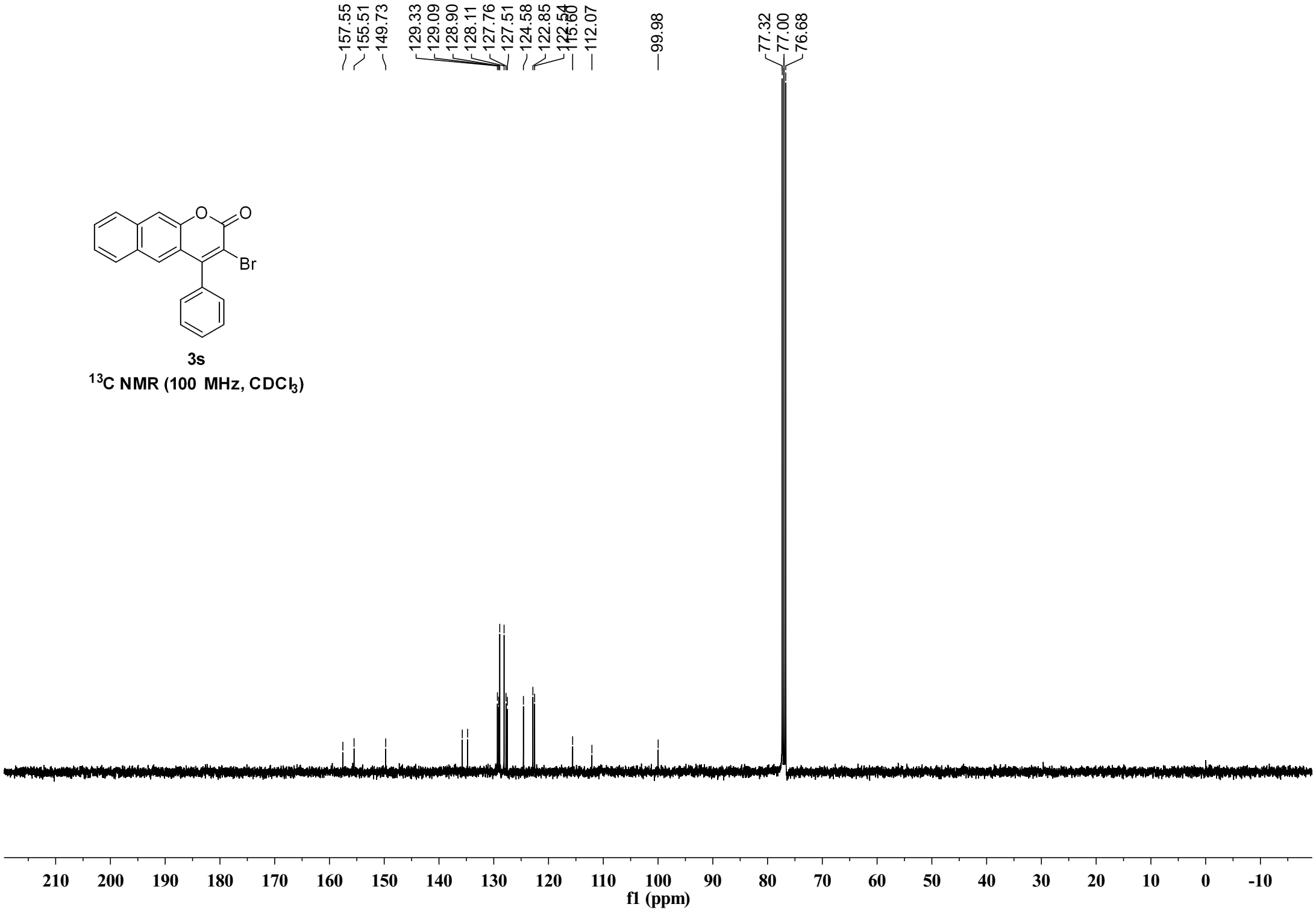

157.75
156.17
153.45
152.00
125.10
121.94
118.21
114.45
113.64
77.32
77.00
76.68
35.19
30.96
14.43
9.25
tBu
O
O
Br
3r
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3s

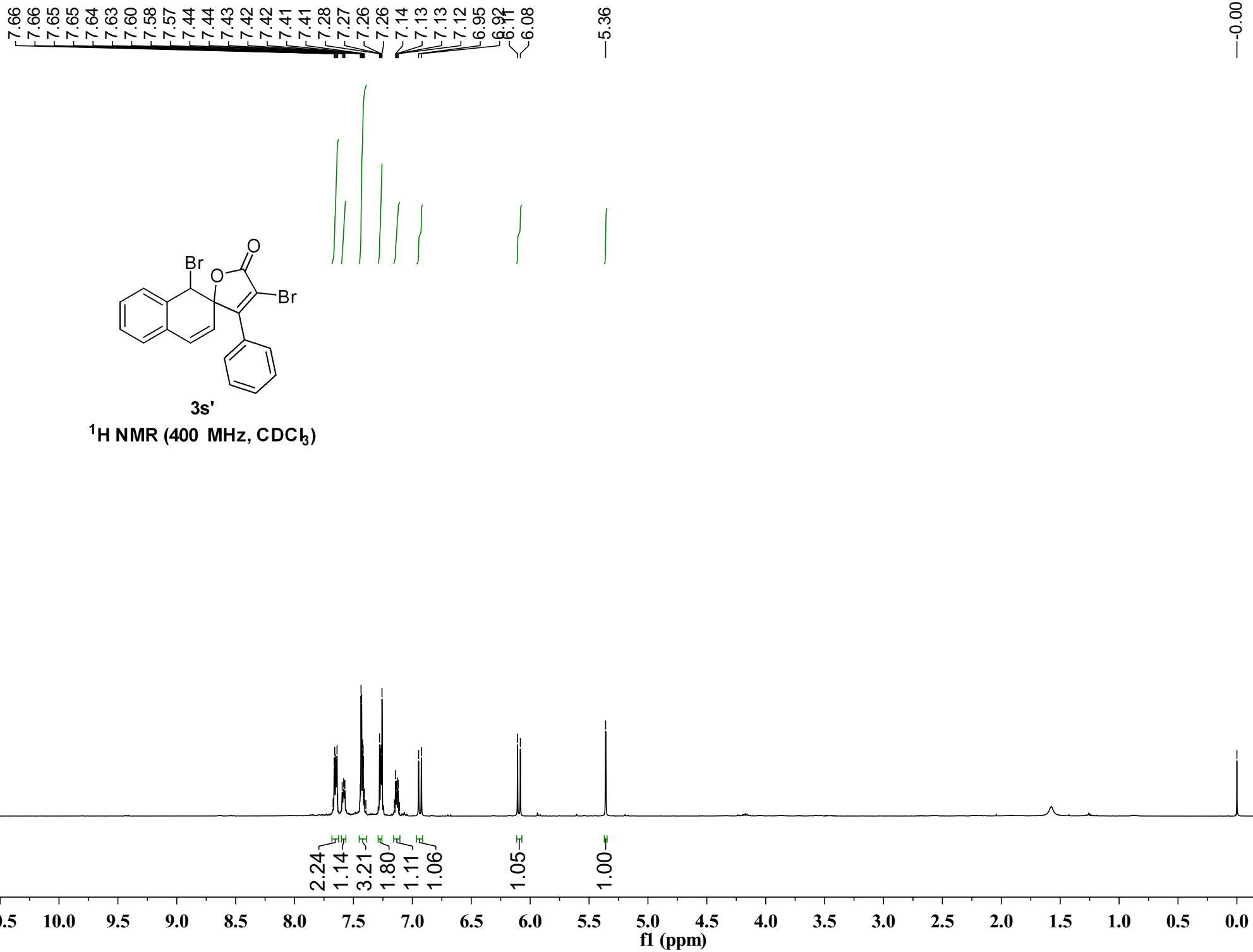
^{1}H NMR (400 MHz, $CDCl_3$)





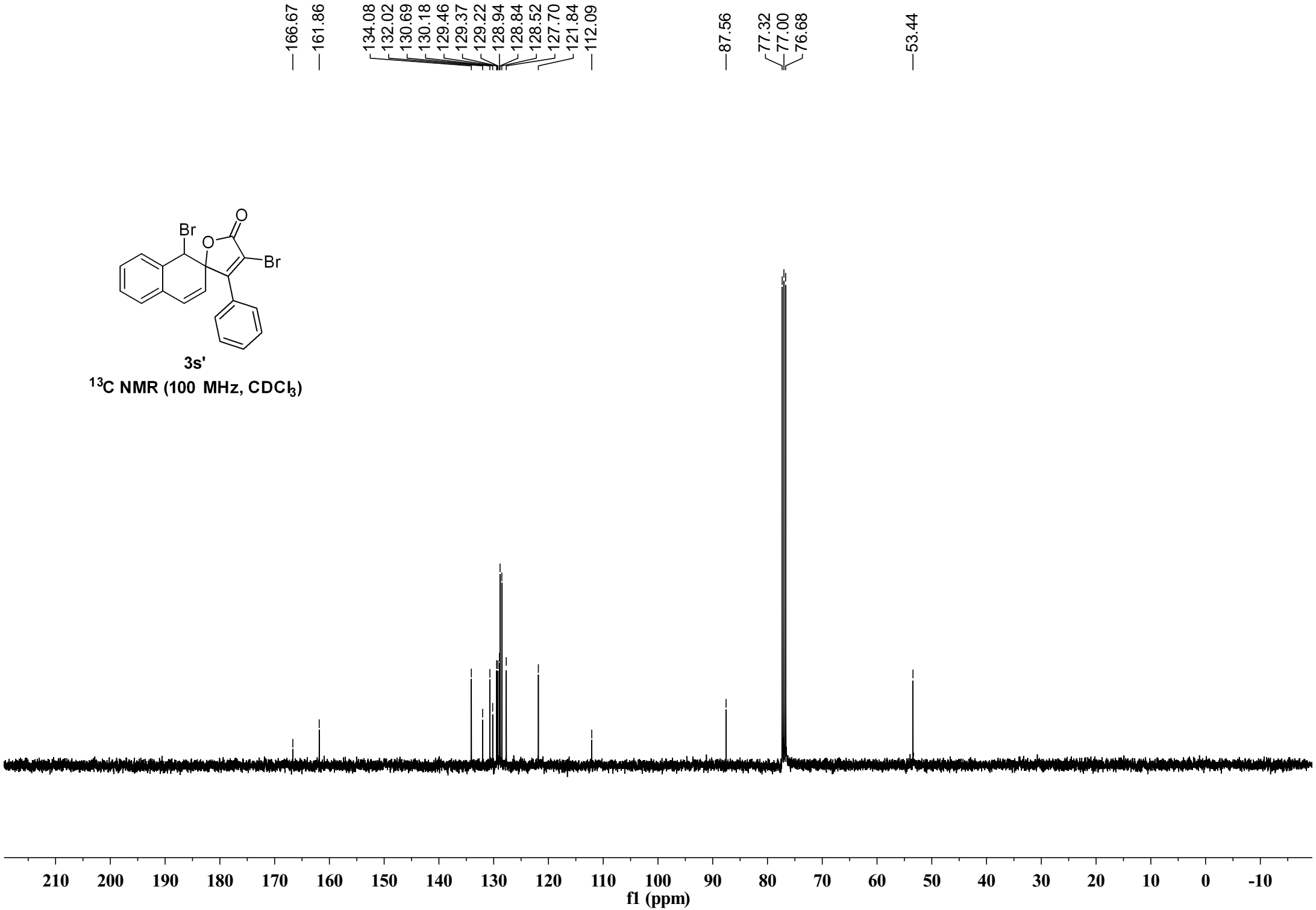
3s

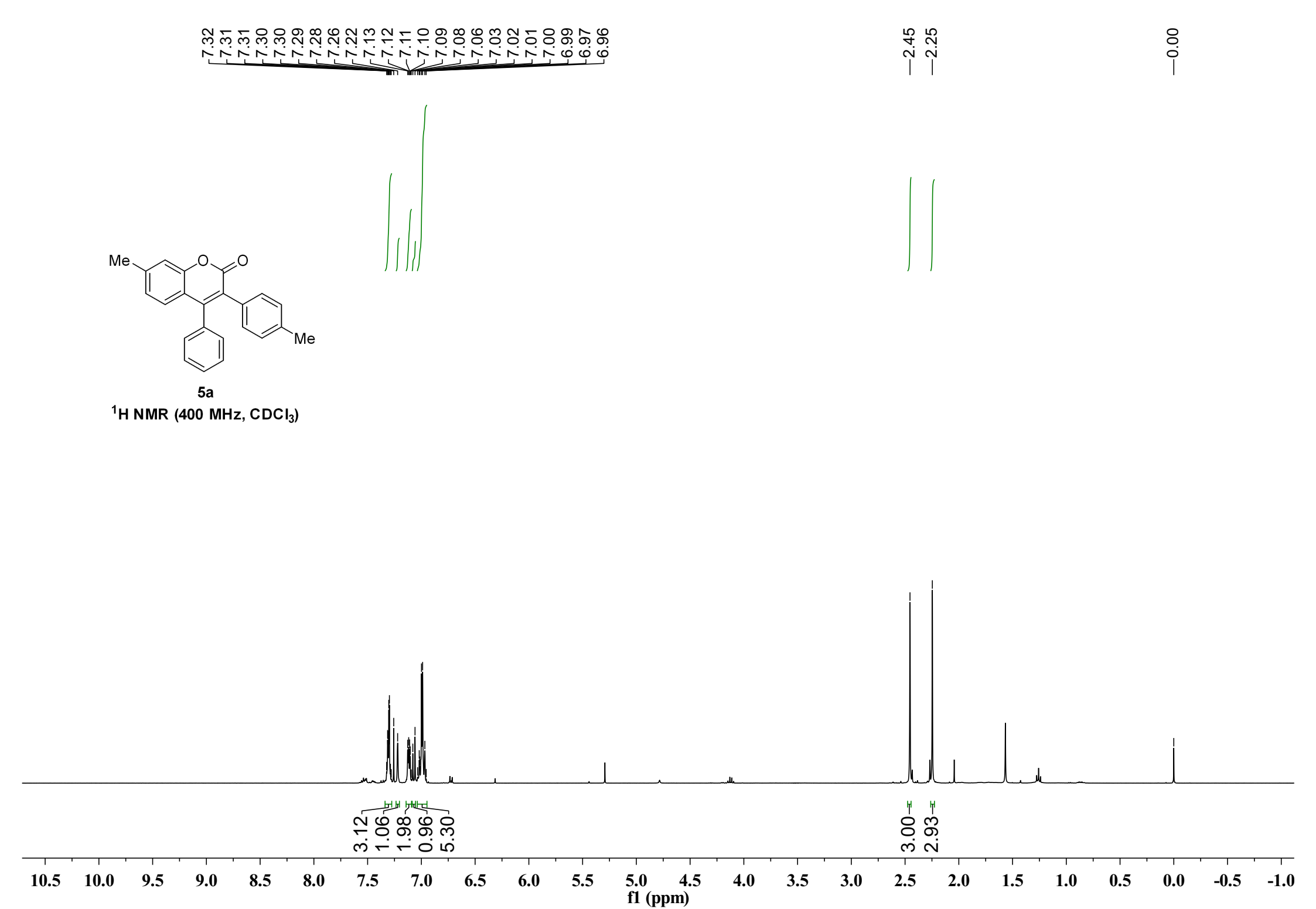
^{13}C NMR (100 MHz, $CDCl_3$)



3s'

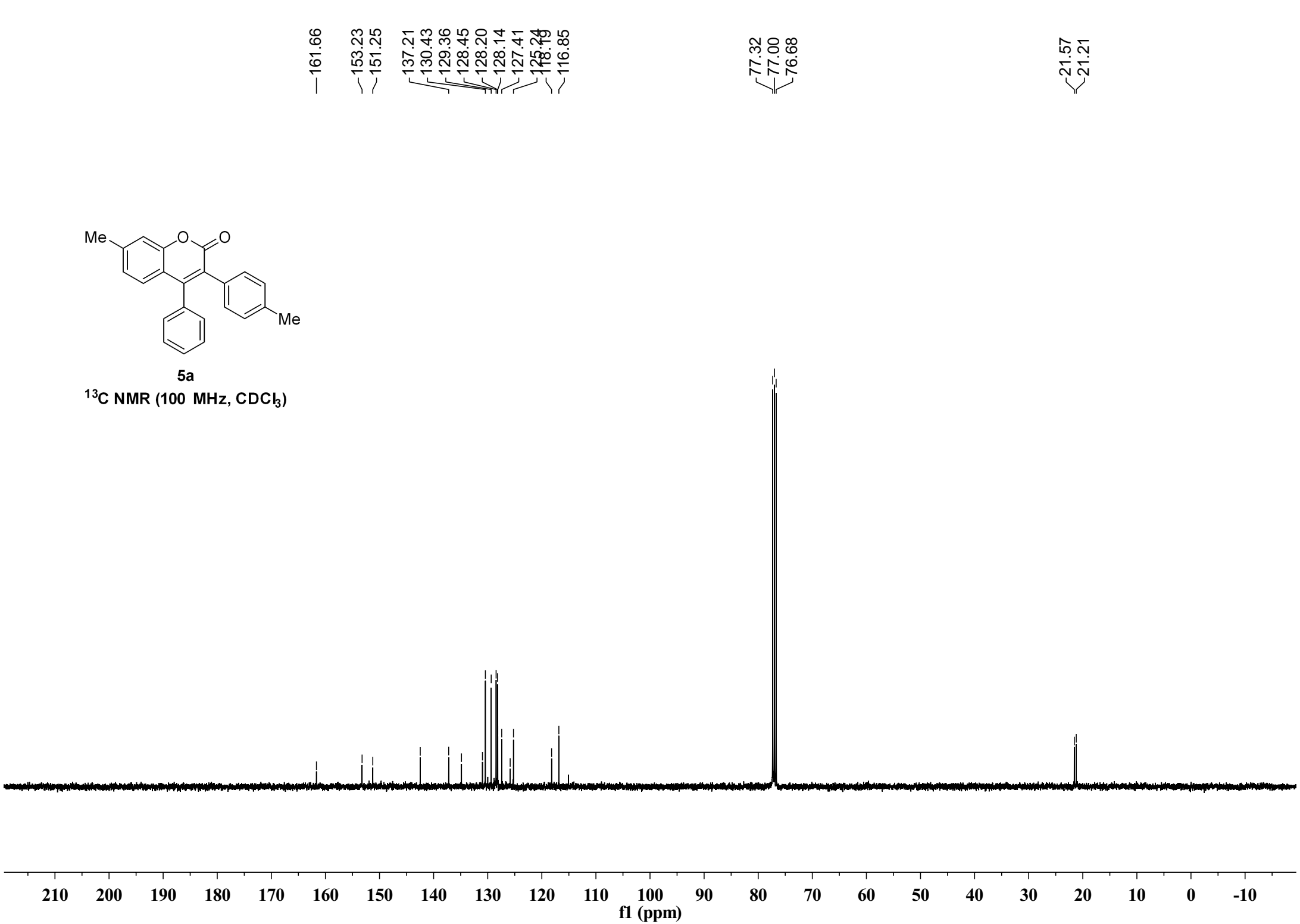
^{1}H NMR (400 MHz, $CDCl_3$)

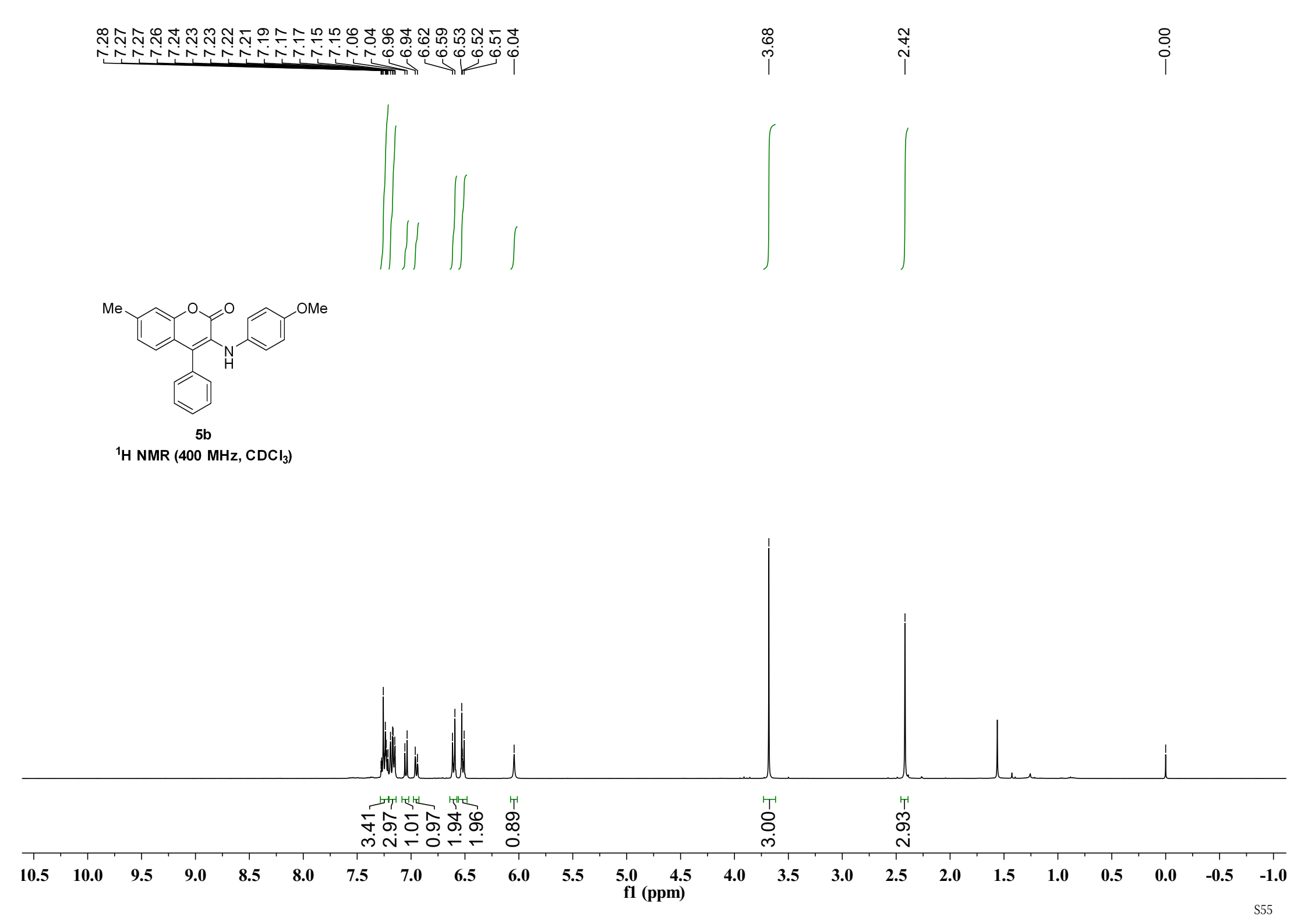

166.67
161.86
134.08
132.02
130.69
130.18
129.46
129.37
129.22
128.94
128.84
128.52
127.70
121.84
112.09
87.56
77.32
77.00
76.68
53.44
Br
O
O
Br
3s'
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5a

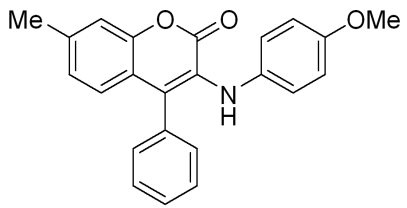
^{1}H NMR (400 MHz, $CDCl_3$)


161.66
153.23
151.25
137.21
130.43
129.36
128.45
128.20
128.14
127.41
125.24
118.19
116.85
77.32
77.00
76.68
21.57
21.21
Me
O
O
Me
5a
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)



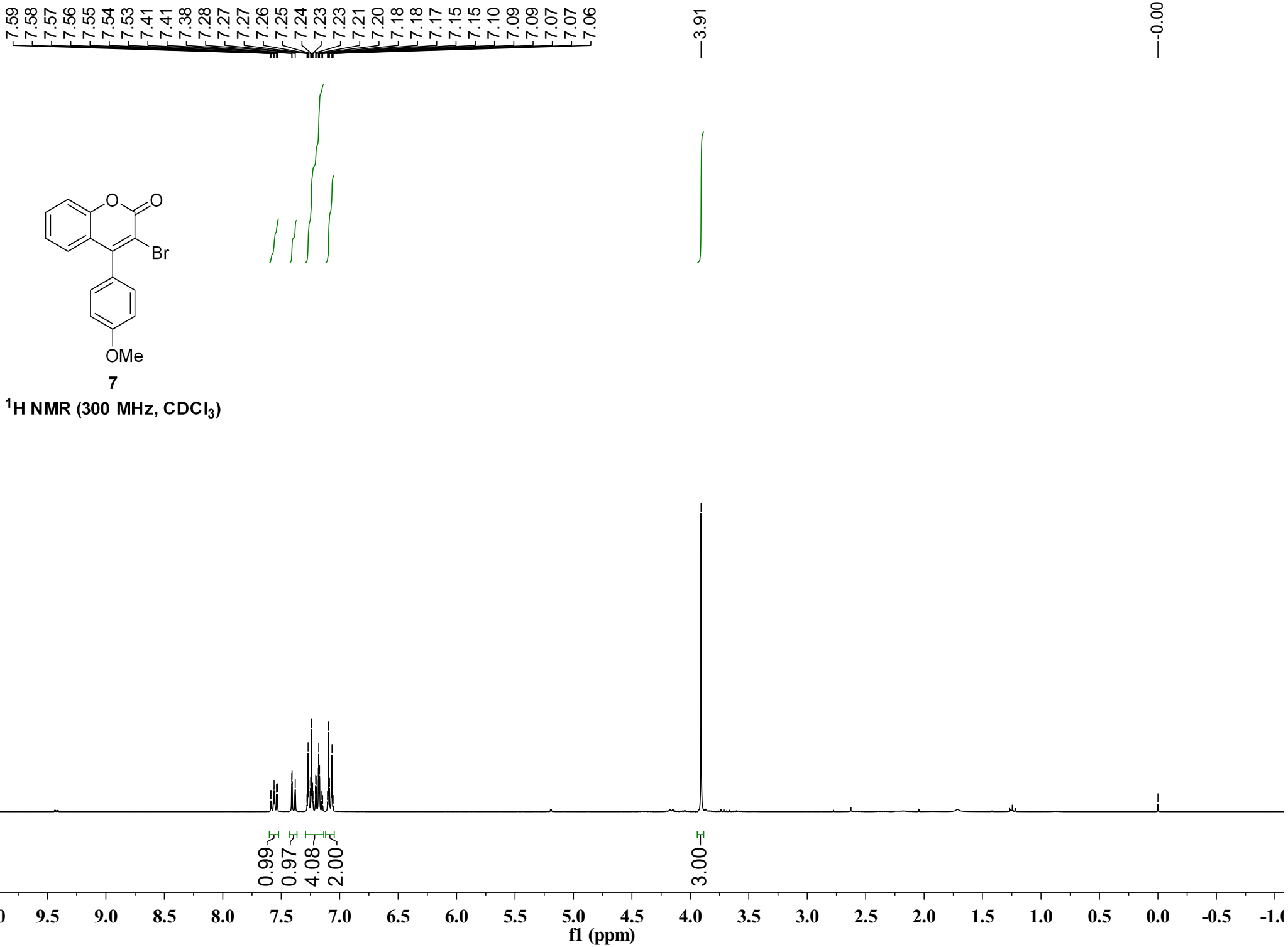
5b

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



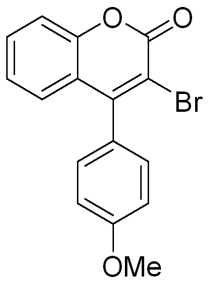
5b

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



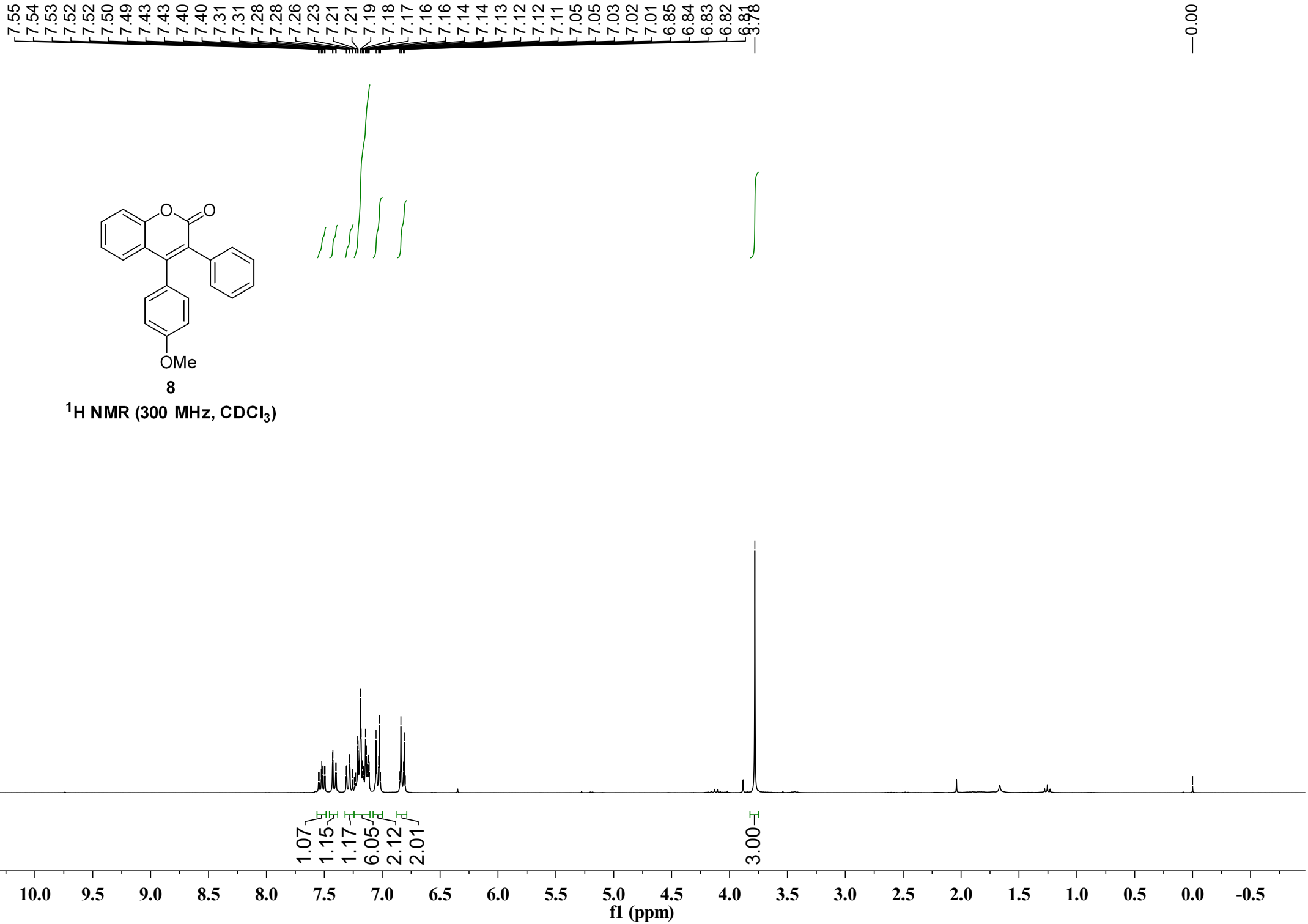
7

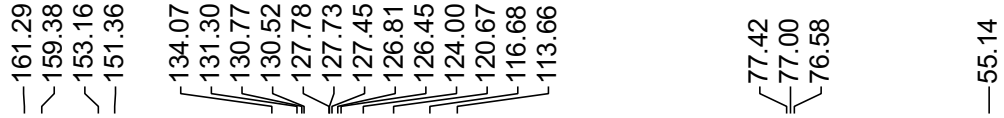
^{1}H NMR (300 MHz, $CDCl_3$)

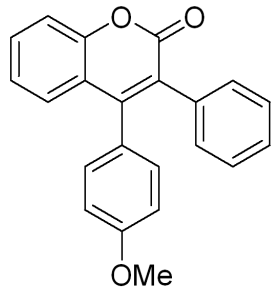


7

^{13}C NMR (75 MHz, $CDCl_3$)


7.55
7.54
7.53
7.52
7.52
7.50
7.49
7.43
7.43
7.40
7.40
7.31
7.31
7.28
7.28
7.26
7.23
7.21
7.21
7.19
7.18
7.17
7.16
7.16
7.14
7.14
7.13
7.12
7.12
7.11
7.05
7.05
7.03
7.02
7.01
6.85
6.84
6.83
6.82
6.81
3.78
0.00
O
O
OMe
8
1H NMR (300 MHz, CDCl3)
1.07
1.15
1.17
6.05
2.12
2.01
3.00
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)





8

^{13}C NMR (75 MHz, $CDCl_3$)