Supporting Information

Visible-Light-Mediated Organoboron-Catalysed Metal-Free Dehydrogenation of *N*-Heterocycles Using Molecular Oxygen

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Contents

1. General considerations

General. Unless otherwise noted, all reactions were carried out under an O_2 atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

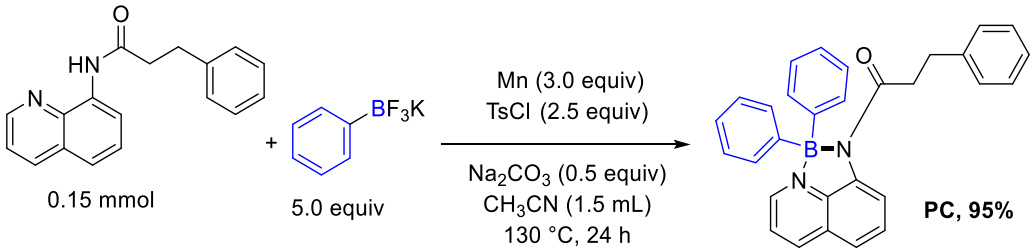
Structural analysis. NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad).

Materials. Commercial reagents and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

2. The synthesis of the photocatalyst used

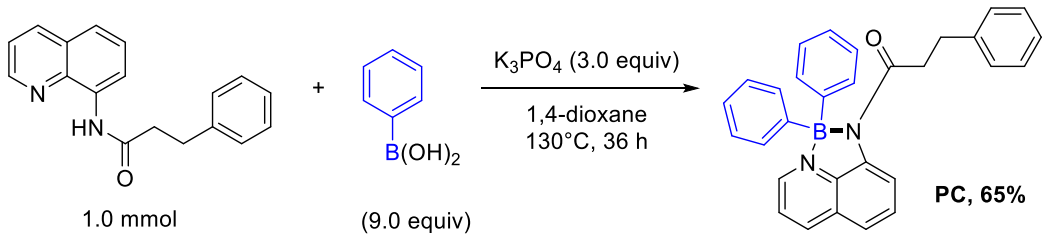
The photocatalyst was prepared via the methods that we have disclosed in the previous literatures (*Chemical Communications* **2020**, *56*, 8273; *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 13894). The preparation procedure was recorded herein, for the sake of completeness. Also, the UV-vis the UV-vis, CV and fluorescence data have been disclosed (*Chemical Communications* **2020**, *56*, 8273).

(a) Method A for the synthesis of PC



A flame-dried 25 mL reaction tube was placed with a stirring bar. Then, 3-phenyl-N-(quinolin-8-yl)propanamide (41.4 mg, 0.15 mmol, 1.0 equiv), phenyl trifluoroborate (138.0 mg, 0.75 mmol, 5.0 equiv), Mn (24.7 mg, 0.45 mmol, 3.0 equiv), 4-toluenesulfonyl chloride (71.5 mg, 0.375 mmol, 2.5 equiv), Na_2CO_3 (7.9 mg, 0.075 mmol, 0.5 equiv) and CH_3CN (1.5 mL) were added. The resulting mixture was stirred at 130 ℃ for 24 hours. Then, the reaction mixture was filtered, concentrated and purified by column chromatography (silica gel) to give 62.7 mg of the target product in 95% yield.

(b) Method B for the synthesis of PC



A flame-dried 125 mL reaction tube was placed with a stirring bar. Then, 3-phenyl-N-(quinolin-8-yl)propanamide (276.3 mg, 1.0 mmol, 1.0 equiv), phenylboronic acid (1100.0 mg, 9.0 mmol, 9.0 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 3.0 equiv) and 1,4-dioxane (15 mL) were added. The resulting mixture was stirred at

130 ℃ for 36 hours. Then, the reaction mixture was filtered, concentrated, and purified by column chromatography (silica gel) to give 286.2 mg of the target product in 65% yield.

(c) Characterization data of the photocatalyst

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 7.6 Hz, 1H), 8.43 (dd, J = 5.2, 0.8 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 8.4 Hz, 1H), 7.56−7.52 (m, 1H), 7.52−7.46 (m, 5H), 7.30−7.24 (m, 6H), 7.13 (t, J = 7.2 Hz, 2H), 7.10−7.03 (m, 1H), 6.83 (d, J = 6.8 Hz, 2H), 2.60 (dd, J = 9.5, 4.9 Hz, 2H), 2.57−2.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 142.0, 141.5, 139.5, 139.1, 137.7, 133.5, 132.6, 128.5, 128.1, 127.9, 127.6, 127.2, 125.5, 122.5, 119.0, 117.2, 39.9, 31.5.

3. General procedure for the dehydrogenation reactions

(a) General Procedure A. The procedure for the direct dehydrogenation reactions.

A flame-dried 25 mL quartz reaction tube was placed with a magnetic stir bar. Then, 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol, 1.0 equiv), PC (1.3 mg, 0.003 mmol, 1.0 mol%), solvent were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with Blue LEDs (10 W) at the bottom (**Figure S1**). Then the reaction mixture was stirred and irradiated with the Blue LEDs for 5 hours at room temperature.

Figure S1. Picture of the reactor

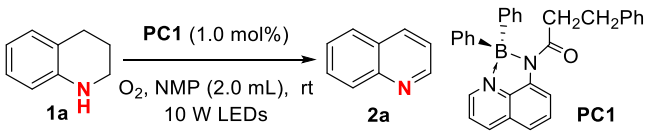
After taking the reaction tube out, 10 mL water was added to the reaction mixture. Then, the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL) and then dried over anhydrous Na_2SO_4. After concentration, the crude product was purified by column chromatography (silica gel) to give the target product, using petroleum ether/ethyl acetate as the eluent.

(b) General Procedure B. The procedure for the cascade cyclization and dehydrogenation reactions.

A flame-dried 25 mL quartz reaction tube was placed with a magnetic stir bar. Then, 2-(aminomethyl)aniline (36.7mg, 0.3 mmol, 1.0 equiv), benzaldehyde (47.8mg, 0.45 mmol, 1.5 equiv), PC (1.3 mg, 0.003 mmol, 1.0 mol%), solvent were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with Blue LEDs (10 W) at the bottom. Then the reaction mixture was stirred and irradiated with the Blue LEDs for 10 hours at room temperature. After taking the reaction tube out, 10 mL water was added to the reaction mixture. Then, the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 5.0 mL) and then dried over anhydrous Na_2SO_4. After concentration, the crude product was purified by column chromatography (silica gel) to give the target product, using petroleum ether/ethyl acetate as the eluent.

(c) Evaluation of reaction variables

Table S1 Influence of wavelength on the yields.



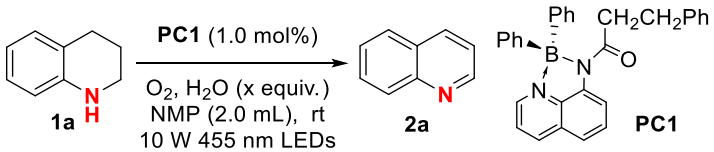
Entry	Wavelength	Isolated yield (%)
1	440 nm	71%
2	445 nm	74%
3	450 nm	66%
4	455 nm	75%
5	460 nm	70%
6	465 nm	54%
7	470 nm	38%

To investigate the influence of wavelength on the yields, we have chosen a series of LED sources to irradiate the reaction mixtures, based on the model reaction. The obtained isolated yields are listed in Table S1. The highest yield is obtained at 455nm.

It is found the yields decreased significantly when longer wavelength light is used, probably due to less absorption of the longer wavelength light.

To investigate the influence of water on the yields, based on the model reaction, two reactions with different amount of water have been performed. The obtained isolated yields are listed in Table S2. For the model reaction, 75% yield of target product was obtained in extra dry NMP solvent. Then, 10 equivalents of water were added to the model reaction, the yield was 68%. When 20 equivalents of water were used, the isolated yield dropped to 60%. It seemed the presence of water did affect the efficiency of the reaction. However, its influence was not crucial.

Table S2 Influence of water on the yields.

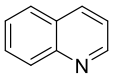


Entry	Solvent	x equiv.	Isolated yield (%)
1	extra dry NMP	0 equiv.	75%
2	extra dry NMP	10 equiv.	68%
3	extra dry NMP	20 equiv.	60%

4. Characterization data

All the obtained products are known compounds. The characterization data are in accordance with the reported literatures, which are referenced herein.

(2a) quinoline (CAS: 91-22-5)[1]



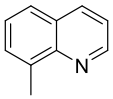
quinoline
Chemical Formula: C_9H_7N
Exact Mass: 129.0578
Molecular Weight: 129.1620

Following the General Procedure A with 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol), **2a** was obtained as colorless liquid (29.1 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.2, 1.8 Hz, 1H), 8.17−8.07 (m, 2H), 7.81 (dd, J = 8.0, 1.2 Hz, 1H), 7.74−7.68 (m, 1H), 7.57−7.50 (m, 1H), 7.38 (dd, J = 8.2, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 148.3, 136.1, 129.5, 129.5, 128.3, 127.8, 126.6, 121.1.

(2b) 8-methylquinoline (CAS: 611-32-5)[2]



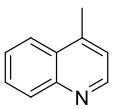
8-methylquinoline
Chemical Formula: $C_{10}H_9N$
Exact Mass: 143.0735
Molecular Weight: 143.1890

Following the General Procedure A with 8-methyl-1,2,3,4-tetrahydroquinoline (44.2 mg, 0.3 mmol), **2b** was obtained as colorless liquid (30.5 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.8 Hz, 1H), 8.13 (dd, J = 8.4, 1.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.47−7.37 (m, 2H), 2.83 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 149.3, 147.4, 137.1, 136.4, 129.7, 128.3, 126.3, 125.9, 120.9, 18.2.

(2c) 4-methylquinoline (CAS: 491-35-0)[2]



4-methylquinoline
Chemical Formula: $C_{10}H_9N$
Exact Mass: 143.0735
Molecular Weight: 143.1890

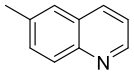
Following the General Procedure A with 4-methyl-1,2,3,4-tetrahydroquinoline (44.2 mg, 0.3 mmol), **2c** was obtained as colorless liquid (30.1 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 4.4 Hz, 1H), 8.09

(dd, *J* = 8.4, 0.4 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.21−7.64 (m, 1H), 7.56−7.48 (m, 1H), 7.18 (dd, *J* = 4.4, 0.8 Hz, 1H), 2.65 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 148.0, 144.3, 130.0, 129.1, 128.3, 126.3, 123.8, 121.9, 18.6.

(2d) 6-methylquinoline (CAS: 91-62-3)[2]



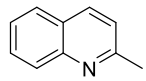
6-methylquinoline
Chemical Formula: $C_{10}H_9N$
Exact Mass: 143.0735
Molecular Weight: 143.1890

Following the General Procedure A with 6-methyl-1,2,3,4-tetrahydroquinoline (44.2 mg, 0.3 mmol), **2d** was obtained as colorless liquid (34.8 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.57−7.51 (m, 2H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 146.9, 136.4, 135.4, 131.8, 129.1, 128.3, 126.6, 121.1, 21.6.

(2e) 2-methylquinoline (CAS: 91-63-4)[1]



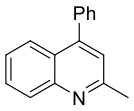
2-methylquinoline
Chemical Formula: $C_{10}H_9N$
Exact Mass: 143.0735
Molecular Weight: 143.1890

Following the General Procedure A with 2-methyl-1,2,3,4-tetrahydroquinoline (44.2 mg, 0.3 mmol), **2e** was obtained as colorless liquid (33.1 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.74 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.69−7.63 (m, 1H), 7.49−7.43 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 2.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 147.8, 136.2, 129.5, 128.6, 127.5, 126.5, 125.7, 122.0, 25.4.

(2f) 2-methyl-4-phenylquinoline (CAS: 1721-92-2)[3]



2-methyl-4-phenylquinoline
Chemical Formula: $C_{16}H_{13}N$
Exact Mass: 219.1048
Molecular Weight: 219.2870

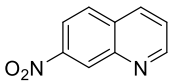
Following the General Procedure A with 2-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (67.0 mg, 0.3 mmol), **2f** was obtained as white solid (44.7 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.4, 0.4 Hz, 1H),

7.86 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.71−7.64 (m, 1H), 7.53−7.46 (m, 5H), 7.45−7.41 (m, 1H), 7.23 (s, 1H), 2.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 148.6, 148.4, 138.2, 129.5, 129.3, 129.0, 128.5, 128.3, 125.8, 125.7, 125.1, 122.2, 25.4.

(2g) 7-nitroquinoline (CAS: 613-50-3)[1]



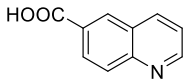
7-nitroquinoline
Chemical Formula: $C_9H_6N_2O_2$
Exact Mass: 174.04
Molecular Weight: 174.16

Following the General Procedure A with 7-nitro-1,2,3,4-tetrahydroquinoline (53.5 mg, 0.3 mmol), **2g** was obtained as yellow solid (18.8 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (dd, *J* = 4.0, 1.6 Hz, 1H), 9.01 (d, *J* = 2.4 Hz, *1H*), 8.33 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.28 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.60 (dd, *J* = 8.4, 4.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 148.1, 147.2, 135.9, 131.4, 129.5, 125.9, 124.0, 120.1.

(2h) quinoline-6-carboxylic acid (CAS: 10349-57-2)[4]



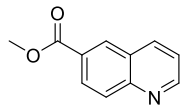
quinoline-6-carboxylic acid
Chemical Formula: $C_{10}H_7NO_2$
Exact Mass: 173.0477
Molecular Weight: 173.1710

Following the General Procedure A with 1,2,3,4-tetrahydroquinoline-6-carboxylic acid (53.2 mg, 0.3 mmol), **2h** was obtained as white solid (27.0 mg, 52%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.19 (s, 1H), 9.04 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.70 (d, *J* = 1.6 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.24 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.64 (dd, *J* = 8.2, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.5, 153.1, 149.8, 138.0, 131.4, 129.8, 129.2, 129.1, 127.7, 122.7.

(2i) methyl quinoline-6-carboxylate (CAS: 38896-30-9)[2]



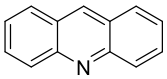
methyl quinoline-6-carboxylate
Chemical Formula: $C_{11}H_9NO_2$
Exact Mass: 187.0633
Molecular Weight: 187.1980

Following the General Procedure A with methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (57.4 mg, 0.3 mmol), **2i** was obtained as white solid (29.8 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (dd, J = 4.2, 1.8 Hz, 1H), 8.57 (d, J = 2.0 Hz, 1H), 8.28 (dd, J = 8.8, 2.0 Hz, 1H), 8.24 (dd, J = 8.4, 1.2 Hz, 1H), 8.13 (d, J = 9.2 Hz, 1H), 7.45 (dd, J = 8.4, 4.4 Hz, 1H), 3.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 152.5, 150.1, 137.4, 131.0, 129.8, 129.0, 128.1, 127.4, 121.9, 52.5.

(2j) acridine (CAS: 260-94-6)[2]



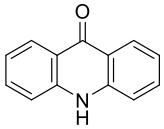
acridine
Chemical Formula: $C_{13}H_9N$
Exact Mass: 179.0735
Molecular Weight: 179.2220

Following the General Procedure A with 9,10-dihydroacridine (54.4 mg, 0.3 mmol), **2j** was obtained as white solid (27.4 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.23 (dd, J = 8.8, 0.8 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.80−7.72 (m, 2H), 7.53−7.46 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 136.0, 130.3, 129.4, 128.2, 126.6, 125.7.

(2j') acridin-9(10H)-one (CAS: 578-95-0)[5]



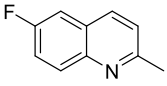
acridin-9(10*H*)-one
Chemical Formula: $C_{13}H_9NO$
Exact Mass: 195.0684
Molecular Weight: 195.2210

Following the General Procedure A with 9,10-dihydroacridine (54.4 mg, 0.3 mmol), **2j'** was obtained as white solid (15.0 mg, 26%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 8.23 (dd, J = 8.0, 1.3 Hz, 2H), 7.76 - 7.69 (m, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.29 – 7.22 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 177.2, 141.4, 133.9, 126.5, 121.5, 121.0, 117.8.

(2k) 6-fluoro-2-methylquinoline (CAS: 1128-61-6)[6]



6-fluoro-2-methylquinoline
Chemical Formula: $C_{10}H_8FN$
Exact Mass: 161.0641
Molecular Weight: 161.1794

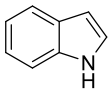
Following the General Procedure A with 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (49.6 mg, 0.3 mmol), **2k** was obtained as white solid (37.3 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.95 (m, 2H), 7.48−7.40 (m, 1H), 7.37 (dd, J = 8.8, 2.8 Hz, 1H), 7.29 (d, J = *8.4* Hz, 1H), 2.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, J = 248.5 Hz), 158.3 (d, J = 3.0 Hz), 144.9, 135.5 (d, J = 5.3 Hz), 131.0 (d, J = 9.0 Hz), 127.0 (d, J = 9.9 Hz), 122.7, 119.4 (d, J = 25.7 Hz), 110.5 (d, J = 21.5 Hz), 25.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.94.

(2l) 1H-indole (CAS: 120-72-9)[1]



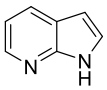
1*H*-indole
Chemical Formula: C_8H_7N
Exact Mass: 117.0578
Molecular Weight: 117.1510

Following the General Procedure A with indoline (35.8 mg, 0.3 mmol), **2l** was obtained as white solid (25.0 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.35 (dd, J = 8.2, 0.6 Hz, 1H), 7.22−7.09 (m, 3H), 6.54 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 127.9, 124.2, 122.0, 120.8, 119.9, 111.1, 102.6.

(2m) 1H-pyrrolo[2,3-b]pyridine (CAS: 271-63-6)[7]



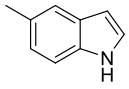
1*H*-pyrrolo[2,3-*b*]pyridine
Chemical Formula: $C_7H_6N_2$
Exact Mass: 118.0531
Molecular Weight: 118.1390

Following the General Procedure A with 2,3-dihydro-1H-pyrrolo[2,3-b]pyridine (36.0 mg, 0.3 mmol), **2m** was obtained as white solid (19.1 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 8.42−8.31 (m, 1H), 7.98 (dd, J = 8.0, 1.2 Hz, 1H), 7.40 (d, J = 3.2 Hz, 1H), 7.11 (dd, J = 7.8, 4.8 Hz, 1H), 6.52 (d, J = 3.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 142.4, 129.1, 125.3, 120.5, 115.8, 100.6.

(2n) 5-methyl-1H-indole (CAS: 916979-65-2)[7]



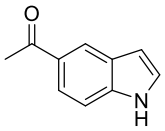
5-methyl-1*H*-indole
Chemical Formula: C_9H_9N
Exact Mass: 131.0735
Molecular Weight: 131.1780

Following the General Procedure A with 5-methylindoline (40.0 mg, 0.3 mmol), **2n** was obtained as white solid (28.3 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.48 (s, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.18−7.14 (m, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.51 (s, 1H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 129.0, 128.2, 124.3, 123.7, 120.4, 110.7, 102.1, 21.5.

(2o)1-(1H-indol-5-yl)ethan-1-one (CAS: 53330-94-2)[8]



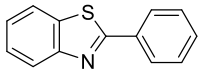
1-(1*H*-indol-5-yl)ethan-1-one
Chemical Formula: $C_{10}H_9NO$
Exact Mass: 159.0684
Molecular Weight: 159.1880

Following the General Procedure A with 1-(indolin-5-yl)ethan-1-one (48.4 mg, 0.3 mmol), **2o** was obtained as white solid (35.3 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.33 (s, 1H), 7.87 (dd, J = 8.8, 1.6 Hz, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.31−7.27 (m, 1H), 6.66 (s, 1H), 2.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 138.7, 129.8, 127.5, 126.0, 123.2, 122.2, 111.2, 104.1, 26.7.

(2p) 2-phenylbenzo[d]thiazole (CAS: 883-93-2)[9]



2-phenylbenzo[*d*]thiazole
Chemical Formula: $C_{13}H_9NS$
Exact Mass: 211.0456
Molecular Weight: 211.2820

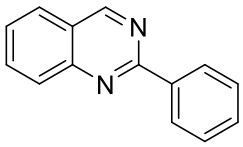
Following the General Procedure A with 2-phenyl-2,3-dihydrobenzo[d]thiazole (64.0 mg, 0.3 mmol), **2p** was obtained as white solid (58.3 mg, 92%).

Following the General Procedure B with 2-aminobenzenethiol (37.6 mg, 0.3 mmol) and benzaldehyde (47.8 mg, 0.45 mmol), **2p** was obtained as white solid (62.8 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.07 (m, 3H), 7.92−7.87 (m, 1H), 7.54−7.46 (m, 4H), 7.42−7.35 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 154.2, 135.1, 133.7, 131.0, 129.1, 127.6, 126.4, 125.2, 123.3, 121.7.

(2q) 2-phenylquinazoline (CAS: 25855-20-3)[2]



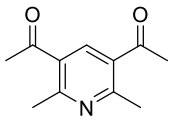
2-phenylquinazoline
Chemical Formula: $C_{14}H_{10}N_2$
Exact Mass: 206.0844
Molecular Weight: 206.2480

Following the General Procedure A with 2-phenyl-1,2,3,4-tetrahydroquinazoline (63.1 mg, 0.3 mmol), **2q** was obtained as white solid (48.3 mg, 78%). Following the General Procedure B with 2-(aminomethyl)aniline (36.7 mg, 0.3 mmol) and benzaldehyde (47.8 mg, 0.45 mmol), **2q** was obtained as white solid (49.5 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.66−8.59 (m, 2H), 8.09 (d, J = 8.8 Hz, 1H), 7.96−7.87 (m, 2H), 7.65−7.58 (m, 1H), 7.58−7.50 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 160.5, 150.8, 138.1, 134.1, 130.6, 128.7, 128.6, 127.33, 127.1, 123.6.

(2r) 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) (CAS: 24234-61-5)[10]



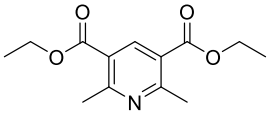
1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one)
Chemical Formula: $C_{11}H_{13}NO_2$
Exact Mass: 191.0946
Molecular Weight: 191.2300

Following the General Procedure A with 1,1'-(2,6-dimethyl-1,4-dihydropyridine-3,5-diyl) bis(ethan-1-one) (58.0 mg, 0.3 mmol), **2r** was obtained as white solid (55.7 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 2.77 (s, 6H), 2.64 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 160.2, 137.8, 130.1, 29.3, 25.0.

(2s) diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (CAS: 1149-23-1)[7]



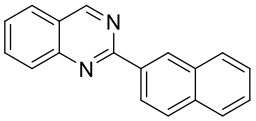
diethyl 2,6-dimethylpyridine-3,5-dicarboxylate
Chemical Formula: $C_{13}H_{17}NO_4$
Exact Mass: 251.1158
Molecular Weight: 251.2820

Following the General Procedure A with diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylat e (76.0 mg, 0.3 mmol), **2s** was obtained as white solid (69.3 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 4.35 (q, J = 7.2 Hz, 4H), 2.80 (s, 6H), 1.37 (t, J = 7.0 Hz, *6H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 162.2, 140.9, 123.0, 61.4, 24.9, 14.2.

(6a) 2-(naphthalen-2-yl)quinazoline (CAS: 2025333-94-0)[11]



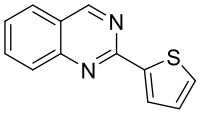
2-(naphthalen-2-yl)quinazoline
Chemical Formula: $C_{18}H_{12}N_2$
Exact Mass: 256.1000
Molecular Weight: 256.3080

Following the General Procedure B with 2-(aminomethyl)aniline (36.7 mg, 0.3 mmol) and 2-naphthaldehyde (70.3 mg, 0.45 mmol), **6a** was obtained as white solid (51.5 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 9.17 (s, 1H), 8.74 (dd, *J = 8.6, 1.8* Hz, 1H), 8.17−8.10 (m, 1H), 8.09−8.03 (m, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.94−7.86 (m, 3H), 7.62−7.52 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 160.5, 150.8, 135.4, 134.7, 134.2, 133.5, 129.3, 129.0, 128.7, 128.3, 127.8, 127.3, 127.2, 127.1, 126.3, 125.5, 123.6.

(6b) 2-(thiophen-2-yl)quinazoline (CAS: 154221-04-2)[12]



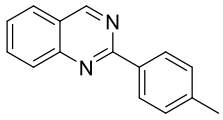
2-(thiophen-2-yl)quinazoline
Chemical Formula: $C_{12}H_8N_2S$
Exact Mass: 212.0408
Molecular Weight: 212.2700

Following the General Procedure B with 2-(aminomethyl)aniline (36.7 mg, 0.3 mmol) and thiophene-2-carbaldehyde (50.5 mg, 0.45 mmol), **6b** was obtained as white solid (42.0 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (d, *J* = 0.8 Hz, 1H), 8.15 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.89−7.83 (m, 2H), 7.58−7.49 (m, 2H), 7.19 (dd, *J* = 5.2, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 157.9, 150.6, 143.9, 134.4, 130.0, 129.3, 128.4, 128.2, 127.3, 127.0, 123.4.

(6c) 2-(p-tolyl)quinazoline (CAS: 80089-59-4)[11]



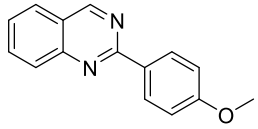
2-(*p*-tolyl)quinazoline
Chemical Formula: $C_{15}H_{12}N_2$
Exact Mass: 220.1000
Molecular Weight: 220.2750

Following the General Procedure B with 2-(aminomethyl)aniline (36.7 mg, 0.3 mmol) and 4-methylbenzaldehyde (54.1 mg, 0.45 mmol), **6c** was obtained as white solid (47.6 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, J = 0.8 Hz, 1H), 8.56−8.47 (m, 2H), 8.06 (dd, J = 8.4, 0.8 Hz, 1H), 7.93−7.82 (m, 2H), 7.57 (td, J = 7.4, 1.1 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 160.5, 150.8, 140.9, 135.3, 134.1, 129.5, 128.6, 128.6, 127.2, 127.1, 123.5, 21.6.

(6d) 2-(4-methoxyphenyl)quinazoline (CAS: 67205-04-3)[11]



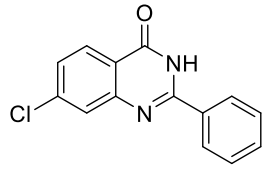
2-(4-methoxyphenyl)quinazoline
Chemical Formula: $C_{15}H_{12}N_2O$
Exact Mass: 236.0950
Molecular Weight: 236.2740

Following the General Procedure B with 2-(aminomethyl)aniline (36.7 mg, 0.3 mmol) and 4-methoxybenzaldehyde (61.3 mg, 0.45 mmol), **6d** was obtained as white solid (39.7 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, J = 0.8 Hz, 1H), 8.58 (d, J = 9.2 Hz, 2H), 8.02 (d, J = 8.8 Hz, 1H), 7.87−7.81 (m, 2H), 7.56−7.48 (m, 1H), 7.04 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 160.8, 160.4, 150.8, 134.0, 130.7, 130.2, 128.4, 127.1, 126.8, 123.3, 114.0, 55.4.

(8a) 7-chloro-2-phenylquinazolin-4(3H)-one (CAS: 7012-94-4)[11]



7-chloro-2-phenylquinazolin-4(3*H*)-one
Chemical Formula: $C_{14}H_9ClN_2O$
Exact Mass: 256.0403
Molecular Weight: 256.6890

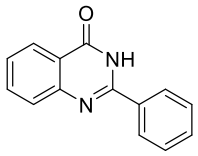
Following the General Procedure B with 2-amino-4-chlorobenzamide (51.2 mg, 0.3 mmol) and benzaldehyde (47.8 mg, 0.45 mmol), **8a** was obtained as white solid (73.9 mg, 96%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.72 (s, 1H),

8.26−8.17 (m, 3H), 7.84 (d, J = 2.0 Hz, 1H), 7.69−7.57 (m, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 162.2, 154.3, 150.3, 139.7, 132.8, 132.2, 129.1, 128.4, 128.4, 127.3, 127.1, 120.3.

(8b) 2-phenylquinazolin-4(3H)-one (CAS: 1022-45-3)[13]



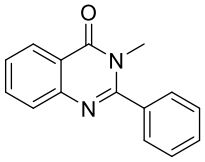
2-phenylquinazolin-4(3*H*)-one
Chemical Formula: $C_{14}H_{10}N_2O$
Exact Mass: 222.0793
Molecular Weight: 222.2470

Following the General Procedure B with 2-aminobenzamide (40.9 mg, 0.3 mmol) and benzaldehyde (47.8 mg, 0.45 mmol), **8b** was obtained as white solid (62.0 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.33 (dd, J = 8.0, 0.8 Hz, 1H), 8.30−8.24 (m, 2H), 7.87−7.77 (m, 2H), 7.62−7.56 (m, 3H), 7.54−7.47 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 151.9, 149.5, 134.9, 132.8, 131.6, 129.0, 128.0, 127.5, 126.8, 126.3, 120.8.

(8c) 3-methyl-2-phenylquinazolin-4(3H)-one (CAS: 22686-81-3)[14]



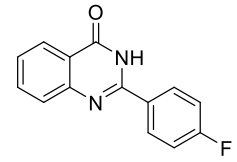
3-methyl-2-phenylquinazolin-4(3*H*)-one
Chemical Formula: $C_{15}H_{12}N_2O$
Exact Mass: 236.0950
Molecular Weight: 236.2740

Following the General Procedure B with 2-amino-N-methylbenzamide (45.1 mg, 0.3 mmol) and benzaldehyde (47.8 mg, 0.45 mmol), **8c** was obtained as white solid (46.8 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37−8.31 (m, 1H), 7.80−7.71 (m, 2H), 7.59−7.49 (m, 6H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 156.2, 147.4, 135.4, 134.3, 130.1, 128.9, 128.0, 127.5, 127.0, 126.7, 120.6, 34.3.

(8d) 2-(4-fluorophenyl)quinazolin-4(3H)-one (CAS: 190838-76-7)[11]



2-(4-fluorophenyl)quinazolin-4(3*H*)-one
Chemical Formula: $C_{14}H_9FN_2O$
Exact Mass: 240.0699
Molecular Weight: 240.2374

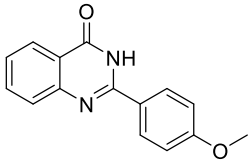
Following the General Procedure B with 2-aminobenzamide (40.9 mg, 0.3 mmol) and 4-fluorobenzaldehyde (55.9 mg, 0.45 mmol), **8d** was obtained as white solid (57.0 mg, 79%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.32−8.22 (m, 2H), 8.17 (dd, J = 8.0, 1.2 Hz, 1H), 7.89−7.81 (m, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.56−7.49 (m, 1H), 7.40 (t, J = 8.8 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 164.5 (d, J = 250.4 Hz), 162.72, 151.9, 149.1, 135.1, 130.8 (d, J = 9.1 Hz), 129.7 (d, J = 2.8 Hz), 127.9, 127.1, 126.3, 121.3, 116.1 (d, J = 22.0 Hz).

^{19}F NMR (376 MHz, DMSO-d_6) δ -109.05.

(8e) 2-(4-methoxyphenyl)quinazolin-4(3H)-one (CAS: 1152-07-4)[11]



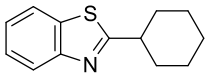
2-(4-methoxyphenyl)quinazolin-4(3*H*)-one
Chemical Formula: $C_{15}H_{12}N_2O_2$
Exact Mass: 252.0899
Molecular Weight: 252.2730

Following the General Procedure B with 2-aminobenzamide (40.9 mg, 0.3 mmol) and 4-methoxybenzaldehyde (61.3 mg, 0.45 mmol), **8e** was obtained as white solid (46.9 mg, 62%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (s, 1H), 8.20 (d, J = 9.2 Hz, 2H), 8.14 (dd, J = 8.0, 1.2 Hz, 1H), 7.85−7.79 (m, 1H), 7.71 (dd, J = 8.0, 0.4 Hz, 1H), 7.53−7.45 (m, 1H), 7.10 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 162.8, 162.4, 152.3, 149.4, 135.0, 129.9, 127.8, 126.6, 126.3, 125.3, 121.2, 114.5, 55.9.

(10a) 2-cyclohexylbenzo[d]thiazole (CAS: 40115-03-5)[15]



2-cyclohexylbenzo[*d*]thiazole
Chemical Formula: $C_{13}H_{15}NS$
Exact Mass: 217.0925
Molecular Weight: 217.3300

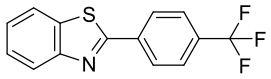
Following the General Procedure B with 2-aminobenzenethiol (37.6 mg, 0.3 mmol) and cyclohexanecarbaldehyde (55.0 mg, 0.45 mmol), **10a** was

obtained as colorless liquid (50.2 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.94 (m, 1H), 7.86−7.81 (m, 1H), 7.47−7.40 (m, 1H), 7.36−7.29 (m, 1H), 3.16−3.04 (m, 1H), 2.26−2.14 (m, 2H), 1.95−1.84 (m, 2H), 1.80−1.72 (m, 1H), 1.71−1.58 (m, 2H), 1.51−1.38 (m, 2H), 1.38−1.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 153.1, 134.6, 125.8, 124.5, 122.6, 121.6, 43.5, 33.5, 26.1, 25.8.

(10b) 2-(4-(trifluoromethyl)phenyl)benzo[d]thiazole (CAS: 134384-31-9)[16]



2-(4-(trifluoromethyl)phenyl)benzo[*d*]thiazole
Chemical Formula: $C_{14}H_8F_3NS$
Exact Mass: 279.0330
Molecular Weight: 279.2802

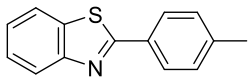
Following the General Procedure B with 2-aminobenzenethiol (37.6 mg, 0.3 mmol) and 4-(trifluoromethyl)benzaldehyde (78.4 mg, 0.45 mmol), **10b** was obtained as white solid (82.1 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 1H), 7.94−7.87 (m, 1H), 7.73 (d, J = *8.0* Hz, 2H), 7.56−7.48 (m, 1H), 7.46−7.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.03, 154.05, 136.8 (q, J = 1.5 Hz), 135.2, 132.4 (q, J = 32.9 Hz), 127.8, 126.7, 126.0 (q, J = 3.7 Hz), 125.8, 124.2 (q, J = 273.4 Hz), 123.6, 121.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84.

(10c) 2-(p-tolyl)benzo[d]thiazole (CAS: 16112-21-3)[16]



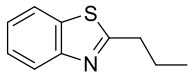
2-(*p*-tolyl)benzo[*d*]thiazole
Chemical Formula: $C_{14}H_{11}NS$
Exact Mass: 225.0612
Molecular Weight: 225.3090

Following the General Procedure B with 2-aminobenzenethiol (37.6 mg, 0.3 mmol) and 4-methylbenzaldehyde (54.1 mg, 0.45 mmol), **10c** was obtained as white solid (53.4 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.05 (m, 1H), 8.04−7.96 (m, 2H), 7.88 (dd, J = 8.0, 0.4 Hz, 1H), 7.52−7.45 (m, 1H), 7.41−7.34 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 154.2, 141.5, 135.0, 131.0, 129.7, 127.5, 126.3, 125.0, 123.1, 121.6, 21.6.

(10d) 2-propylbenzo[d]thiazole (CAS: 17229-76-4)[16]



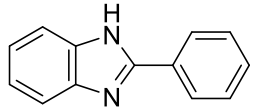
2-propylbenzo[*d*]thiazole
Chemical Formula: $C_{10}H_{11}NS$
Exact Mass: 177.0612
Molecular Weight: 177.2650

Following the General Procedure B with 2-aminobenzenethiol (37.6 mg, 0.3 mmol) and butyraldehyde (32.5 mg, 0.45 mmol), **10d** was obtained as colorless liquid (35.6 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.94 (m, 1H), 7.85−7.81 (m, 1H), 7.47−7.41 (m, 1H), 7.37−7.30 (m, 1H), 3.16−3.02 (m, 2H), 1.97−1.86 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 153.3, 135.2, 125.9, 124.6, 122.5, 121.5, 36.3, 23.1, 13.7.

(12a) 2-phenyl-1H-benzo[d]imidazole (CAS: 716-79-0)[12]



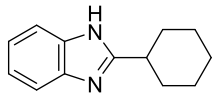
2-phenyl-1*H*-benzo[*d*]imidazole
Chemical Formula: $C_{13}H_{10}N_2$
Exact Mass: 194.0844
Molecular Weight: 194.2370

Following the General Procedure B with benzene-1,2-diamine (32.5 mg, 0.3 mmol) and benzaldehyde (47.8 mg, 0.45 mmol), **12a** was obtained as white solid (57.7 mg, 99%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.97 (s, 1H), 8.35−8.16 (m, 2H), 7.61−7.55 (m, 2H), 7.61−7.55 (m, 2H), 7.54−7.48 (m, 1H), 7.28−7.21 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 151.7, 130.7, 130.3, 129.4, 126.9, 122.6.

(12b) 2-cyclohexyl-1H-benzo[d]imidazole (CAS: 36947-70-3)[17]



2-cyclohexyl-1*H*-benzo[*d*]imidazole
Chemical Formula: $C_{13}H_{16}N_2$
Exact Mass: 200.1313
Molecular Weight: 200.2850

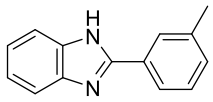
Following the General Procedure B with benzene-1,2-diamine (32.5 mg, 0.3 mmol) and

cyclohexanecarbaldehyde (55.0 mg, 0.45 mmol), **12b** was obtained as white solid (54.7 mg, 91%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.10 (s, 1H), 7.51−7.40 (m, 2H), 7.14−7.05 (m, 2H), 2.89−2.78 (m, 1H), 2.08−1.96 (m, 2H), 1.84−1.75 (m, 2H), 1.74−1.66 (m, 1H), 1.66−1.54 (m, 2H), 1.45−1.32 (m, 2H), 1.32−1.22 (m, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 159.3, 121.5, 38.2, 31.7, 26.1, 26.0.

(12c) 2-(m-tolyl)-1H-benzo[d]imidazole (CAS: 6528-83-2)[18]



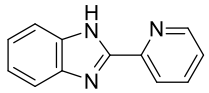
2-(*m*-tolyl)-1*H*-benzo[*d*]imidazole
Chemical Formula: $C_{14}H_{12}N_2$
Exact Mass: 208.1000
Molecular Weight: 208.2640

Following the General Procedure B with benzene-1,2-diamine (32.5 mg, 0.3 mmol) and 3-methylbenzaldehyde (54.1 mg, 0.45 mmol), **12c** was obtained as white solid (55.0 mg, 88%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.90 (s, 1H), 8.06 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.66−7.57 (m, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.25−7.18 (m, 2H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 151.8, 138.6, 130.9, 130.6, 129.3, 127.5, 124.1, 122.5, 21.5.

(12d) 2-(pyridin-2-yl)-1H-benzo[d]imidazole (CAS: 1137-68-4)[19]



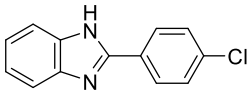
2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole
Chemical Formula: $C_{12}H_9N_3$
Exact Mass: 195.0796
Molecular Weight: 195.2250

Following the General Procedure B with benzene-1,2-diamine (32.5 mg, 0.3 mmol) and picolinaldehyde (48.2 mg, 0.45 mmol), **12d** was obtained as white solid (52.7 mg, 90%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.17 (s, 1H), 8.80−8.72 (m, 1H), 8.39 (dt, J = 7.6, 1.0 Hz, 1H), 8.02 (td, J = 7.6, 1.6 Hz, 1H), 7.89−7.57 (m, 2H), 7.56−7.50 (m, 1H), 7.27 (dd, J = 6.0, 2.8 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 151.2, 149.8, 149.0, 138.0, 125.1, 121.9.

(12e) 2-(4-chlorophenyl)-1H-benzo[d]imidazole (CAS: 1019-85-8)[12]



2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole
Chemical Formula: $C_{13}H_9ClN_2$
Exact Mass: 228.0454
Molecular Weight: 228.6790

Following the General Procedure B with benzene-1,2-diamine (32.5 mg, 0.3 mmol) and 4-chlorobenzaldehyde (63.3 mg, 0.45 mmol), **12e** was obtained as white solid (63.1 mg, 92%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 8.25−8.19 (m, 2H), 7.73−7.51 (m, 4H), 7.24 (dd, J = 6.0, 2.8 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 150.6, 135.0, 129.5, 128.6.

5. Exploration of reaction mechanism

(a) Detection of free radical

Following the General Procedure A, used 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol) as a raw material, and added TEMPO (93.7 mg, 0.6 mmol, 2.0 equiv) to the reaction mixture. 18.6 mg of the target product was obtained. The yield was 48%.

Following the General Procedure A, used 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol) as a raw material, and added TEMPO (140.6 mg, 0.9 mmol, 3.0 equiv) to the reaction mixture. 10.5 mg of the target product was obtained. The yield was 27%.

(b) Detection of superoxide radical

Following the General Procedure A, used 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol) as a raw material, and added butylated hydroxytoluene (132.2 mg, 0.6 mmol, 2.0 equiv) to the reaction mixture. 3.9 mg of the target product was obtained. The yield was 10%.

(c) Detection of peroxide species

A flame-dried 25 mL quartz reaction tube was placed with a magnetic stir bar. Then, 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol, 1.0 equiv) and solvent were added to the tube. After that, charge the tube with oxygen. The reaction tube was placed on a photocatalytic parallel reactor with Blue LEDs (10 W) at the bottom. Then the reaction mixture was stirred and irradiated with the Blue LEDs for 5 hours at room temperature. When the reaction was terminated, 2.0 mL of potassium iodide aqueous solution (0.03 g/mL) was immediately added into the reaction. Then, starch aqueous solution (0.01 g/mL) was added dropwise. It was found that no black mixture was formed.

Following the General Procedure A with 1,2,3,4-tetrahydroquinoline (40.0 mg, 0.3 mmol). When the reaction was terminated, 2.0 mL of potassium iodide aqueous solution (0.03 g/mL) was immediately added into the reaction. Then, starch aqueous solution (0.01 g/mL) was added dropwise. The reaction mixture turned into black.

6. References

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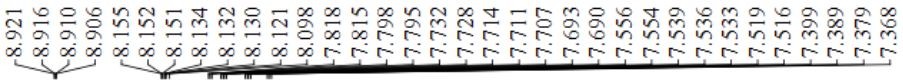
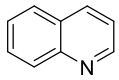
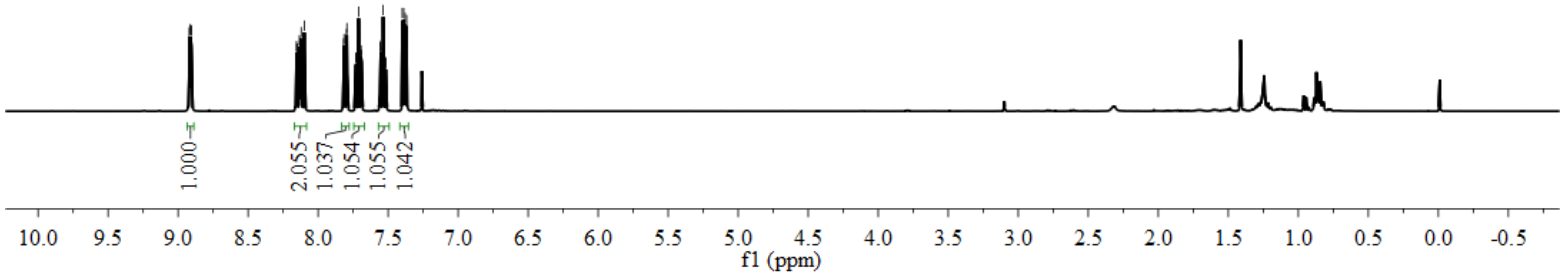
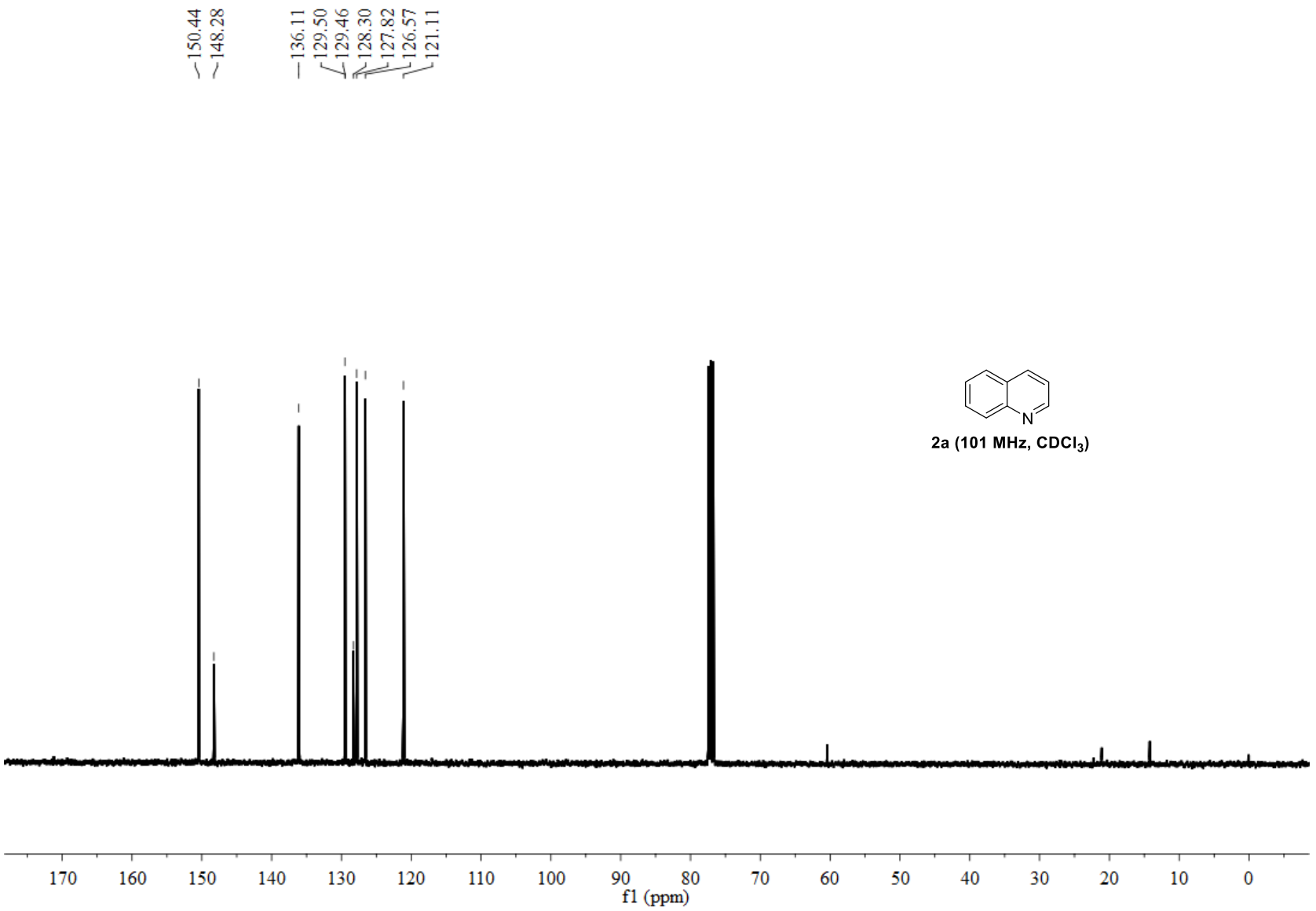
7. Copies of NMR spectra

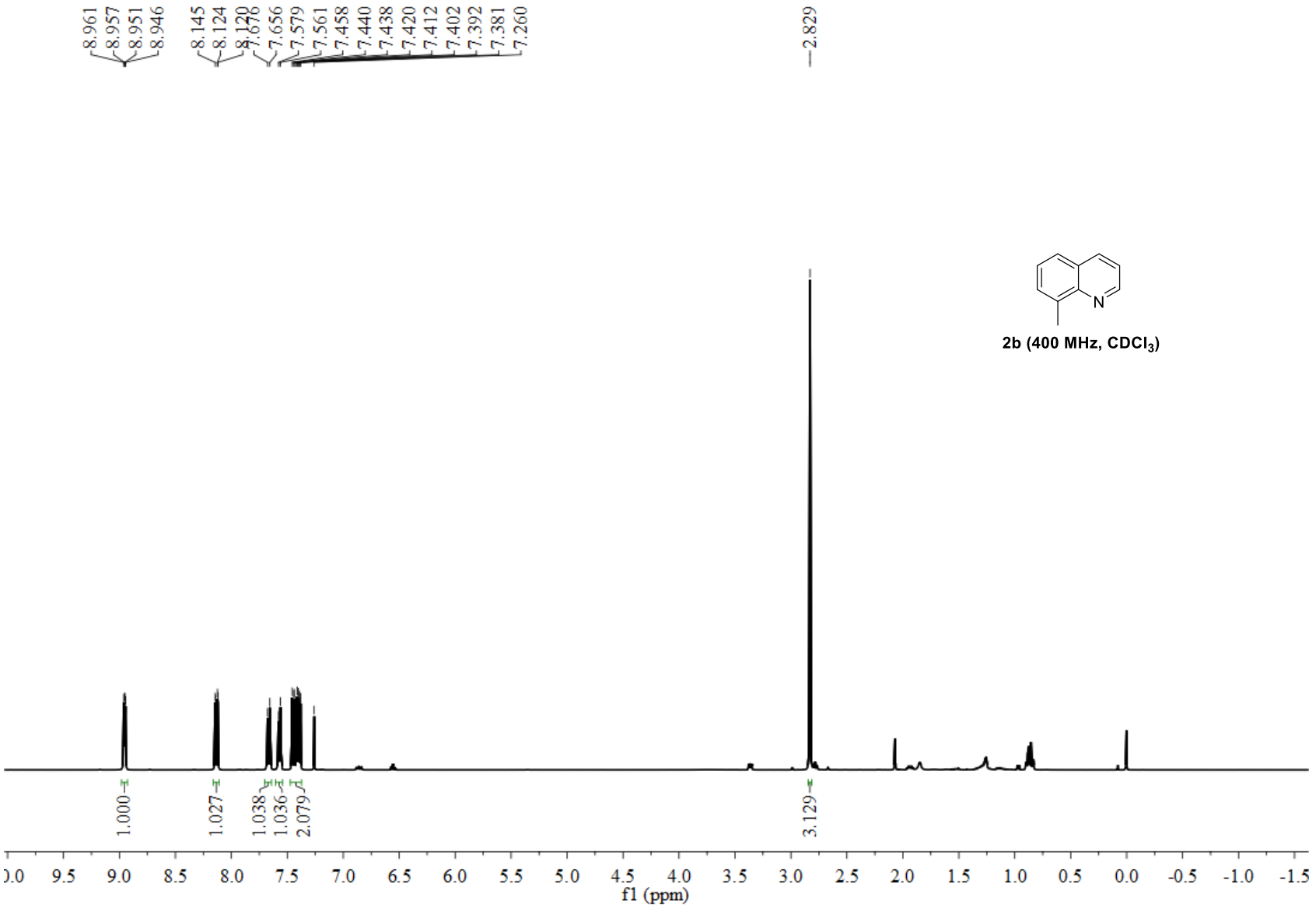




2a (400 MHz, $CDCl_3$)




150.44
148.28
136.11
129.50
129.46
128.30
127.82
126.57
121.11
N
2a (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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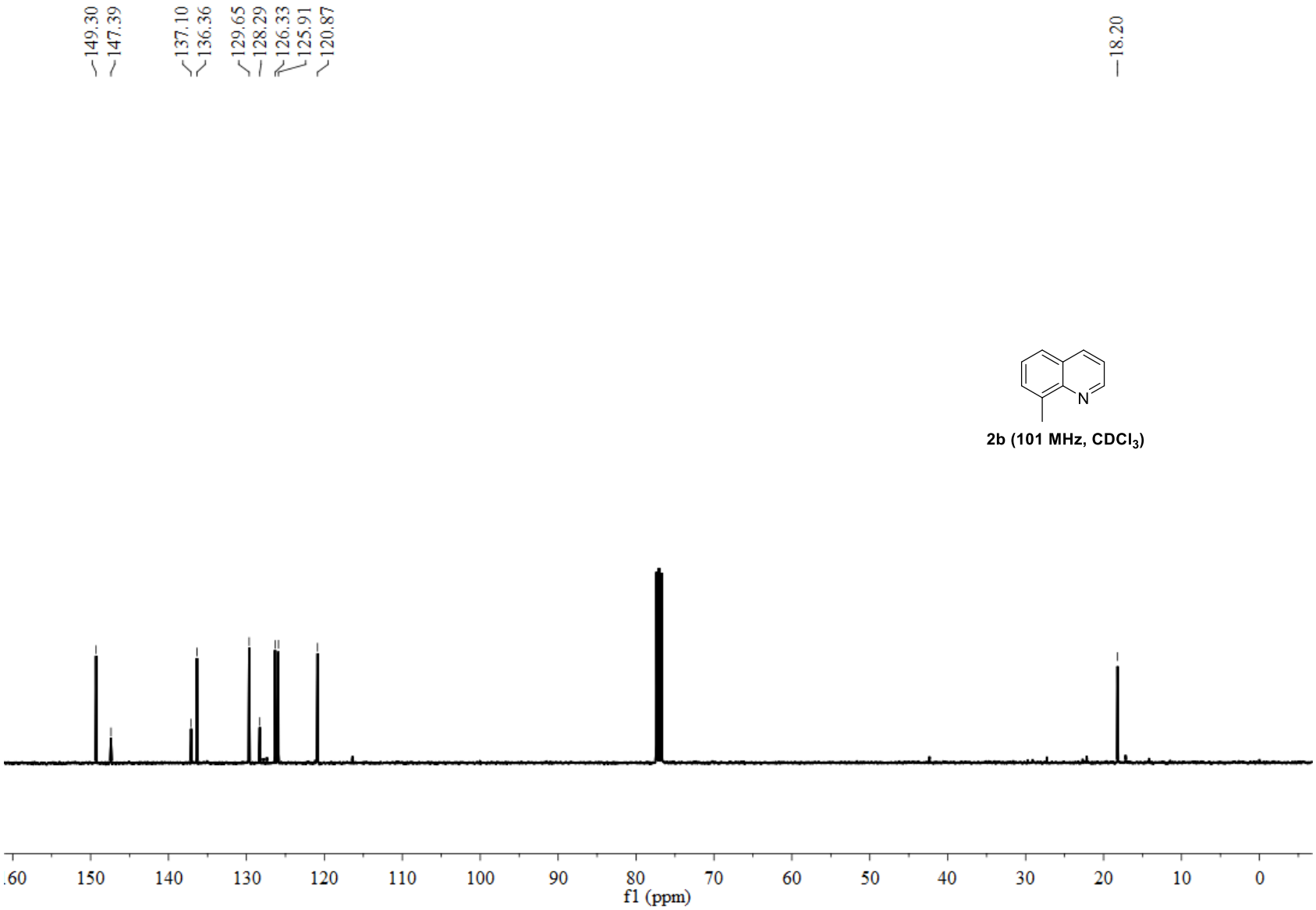
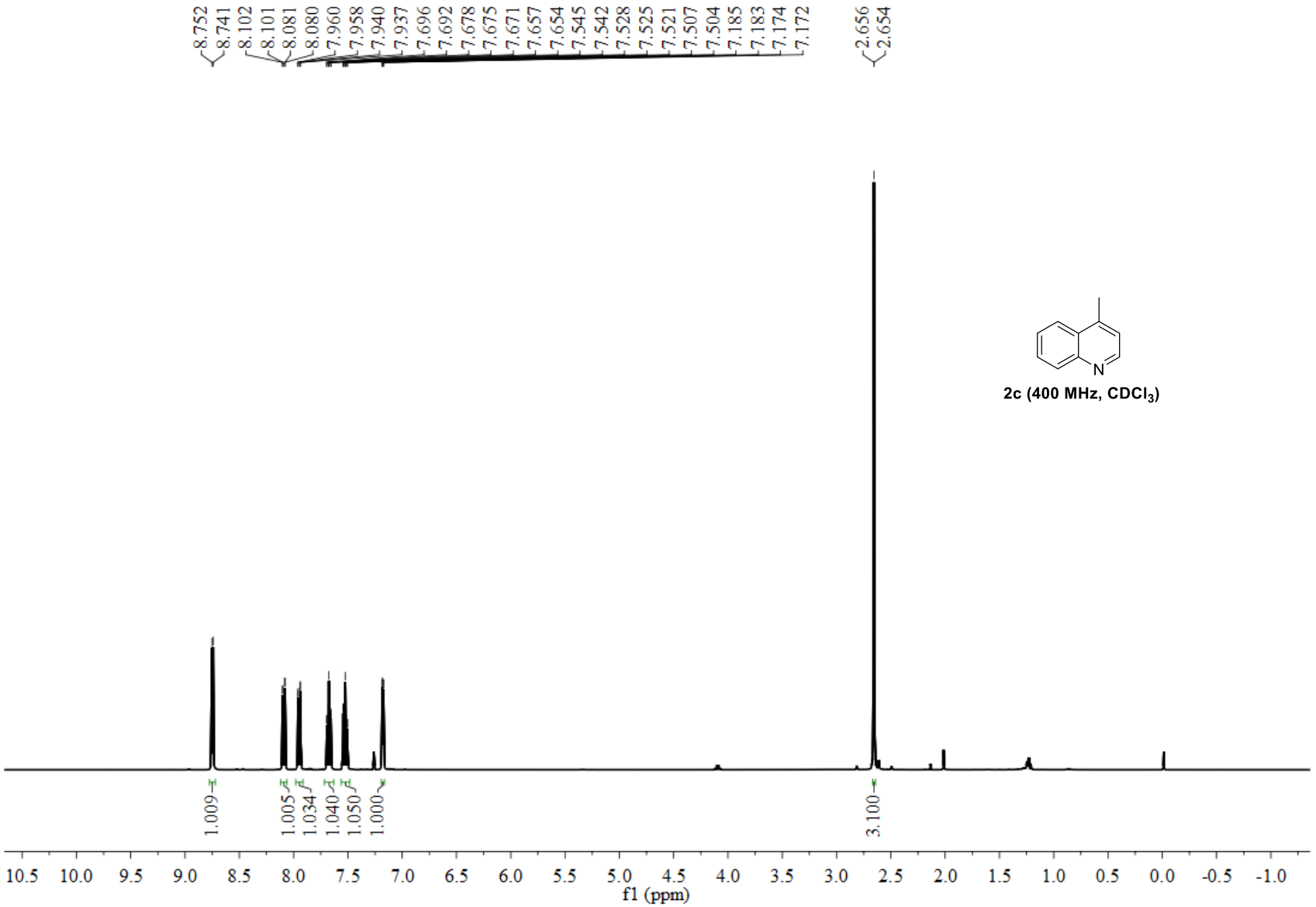
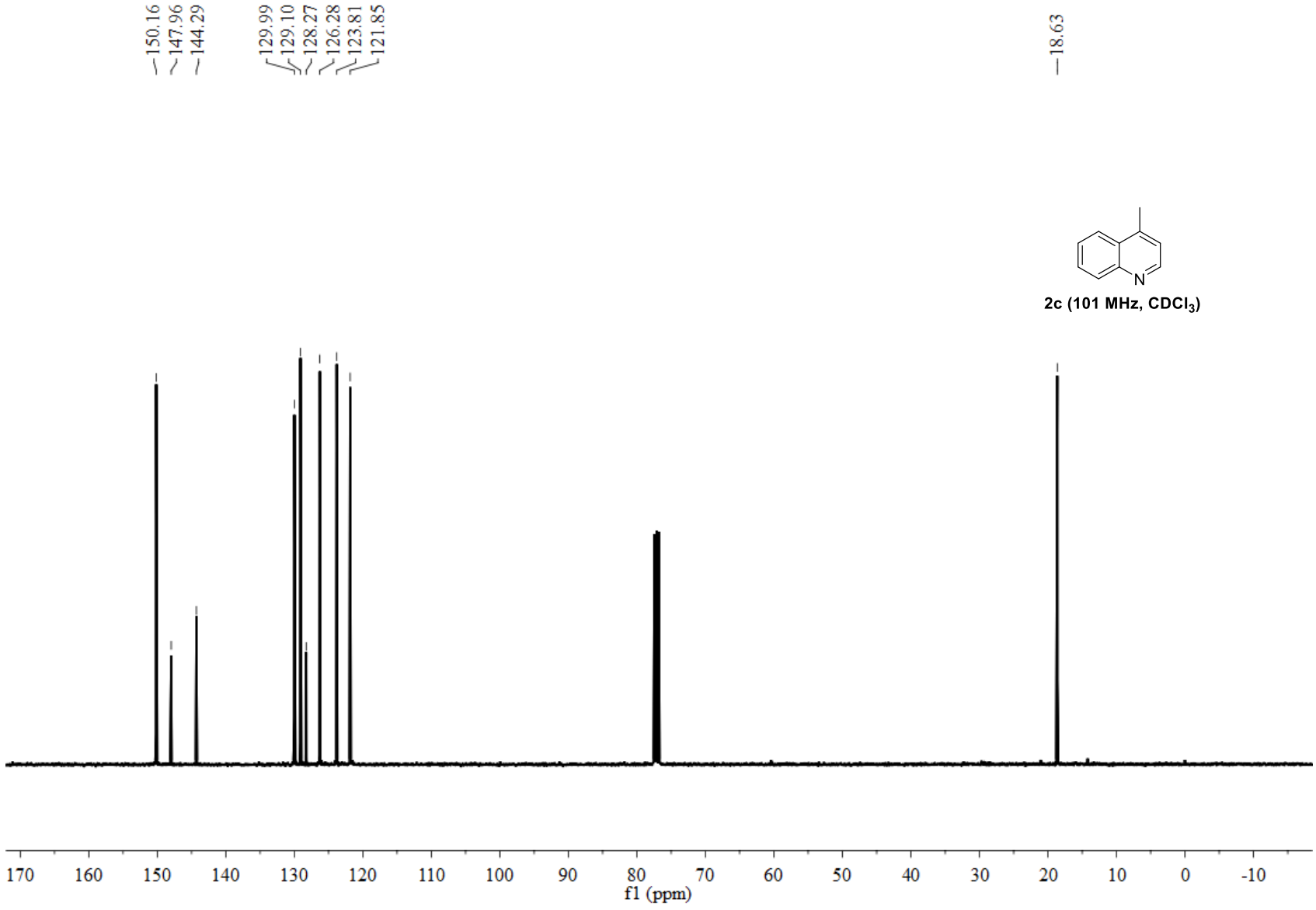
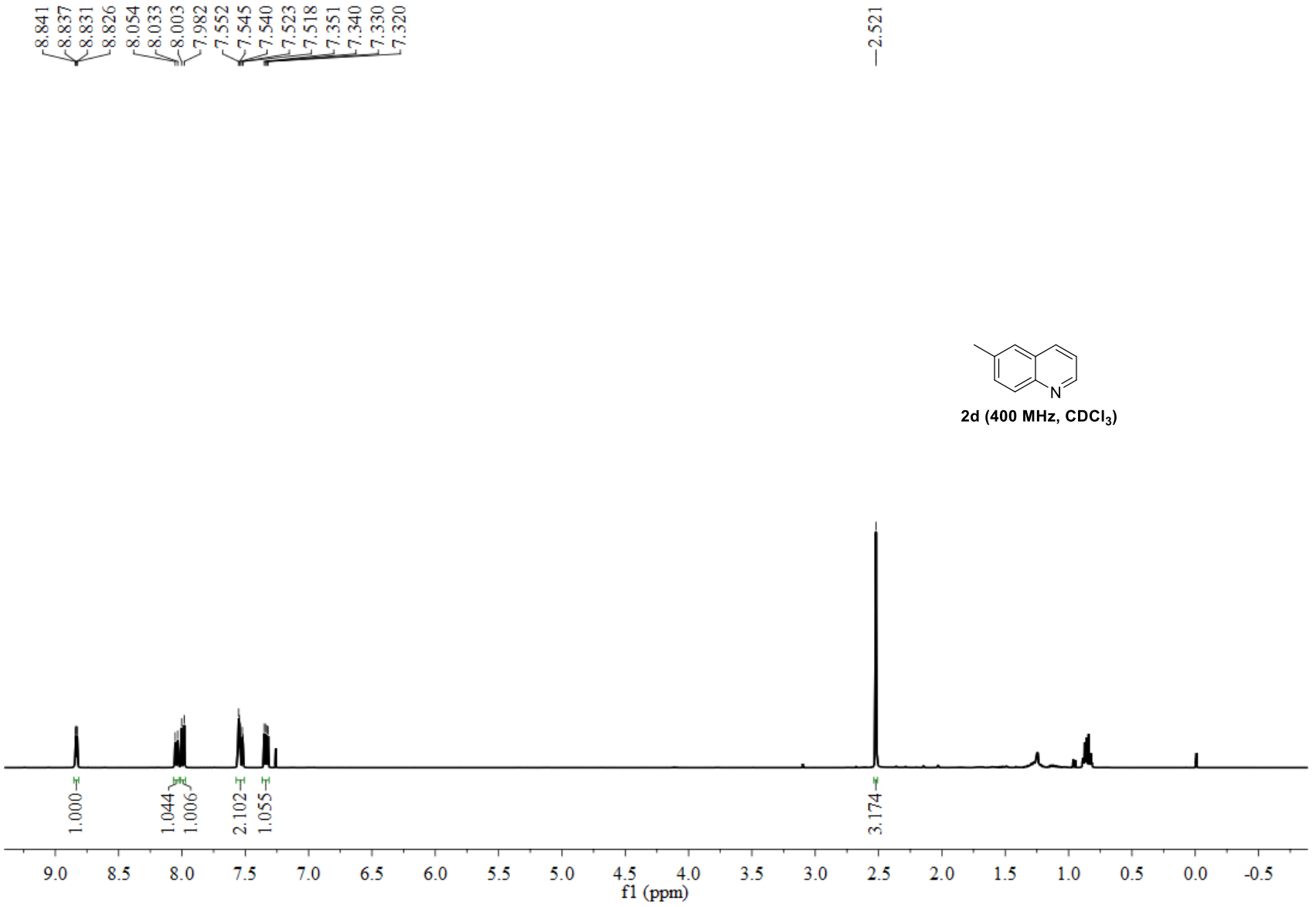


2b (101 MHz, $CDCl_3$)

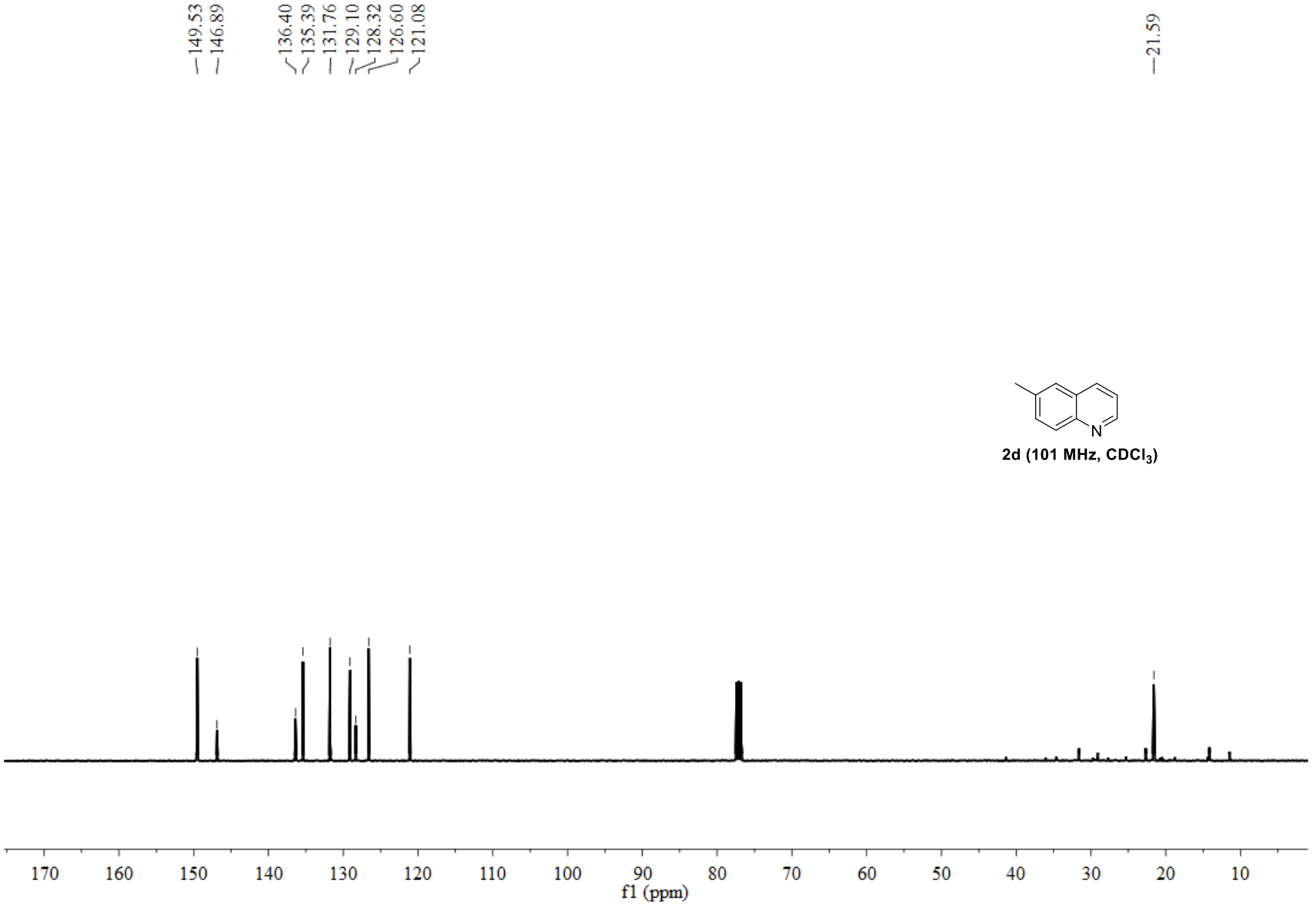


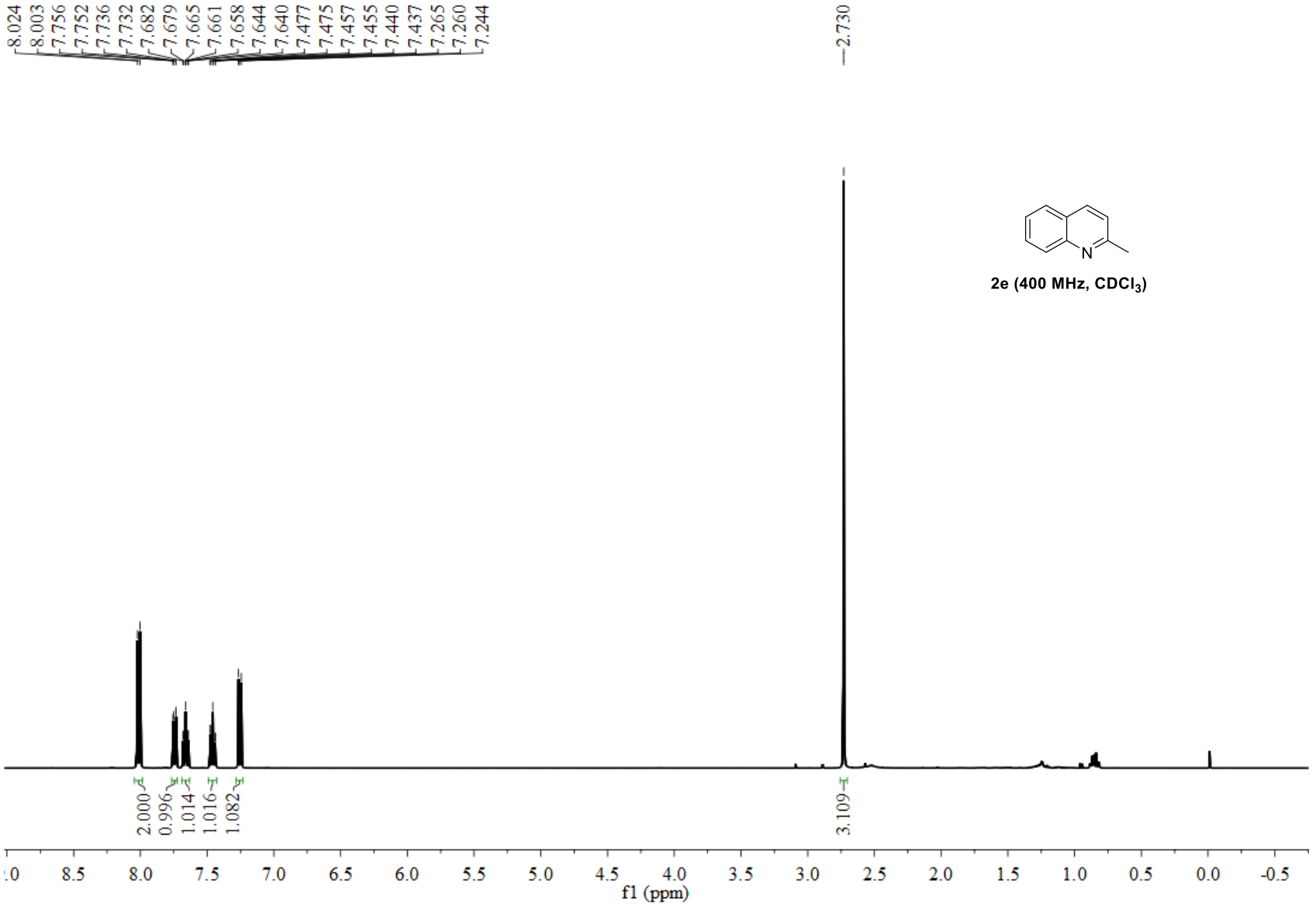
2c (400 MHz, $CDCl_3$)


150.16
147.96
144.29
129.99
129.10
128.27
126.28
123.81
121.85
18.63
N
2c (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2d (400 MHz, $CDCl_3$)


149.53
146.89
136.40
135.39
131.76
129.10
128.32
126.60
121.08
21.59
N
2d (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



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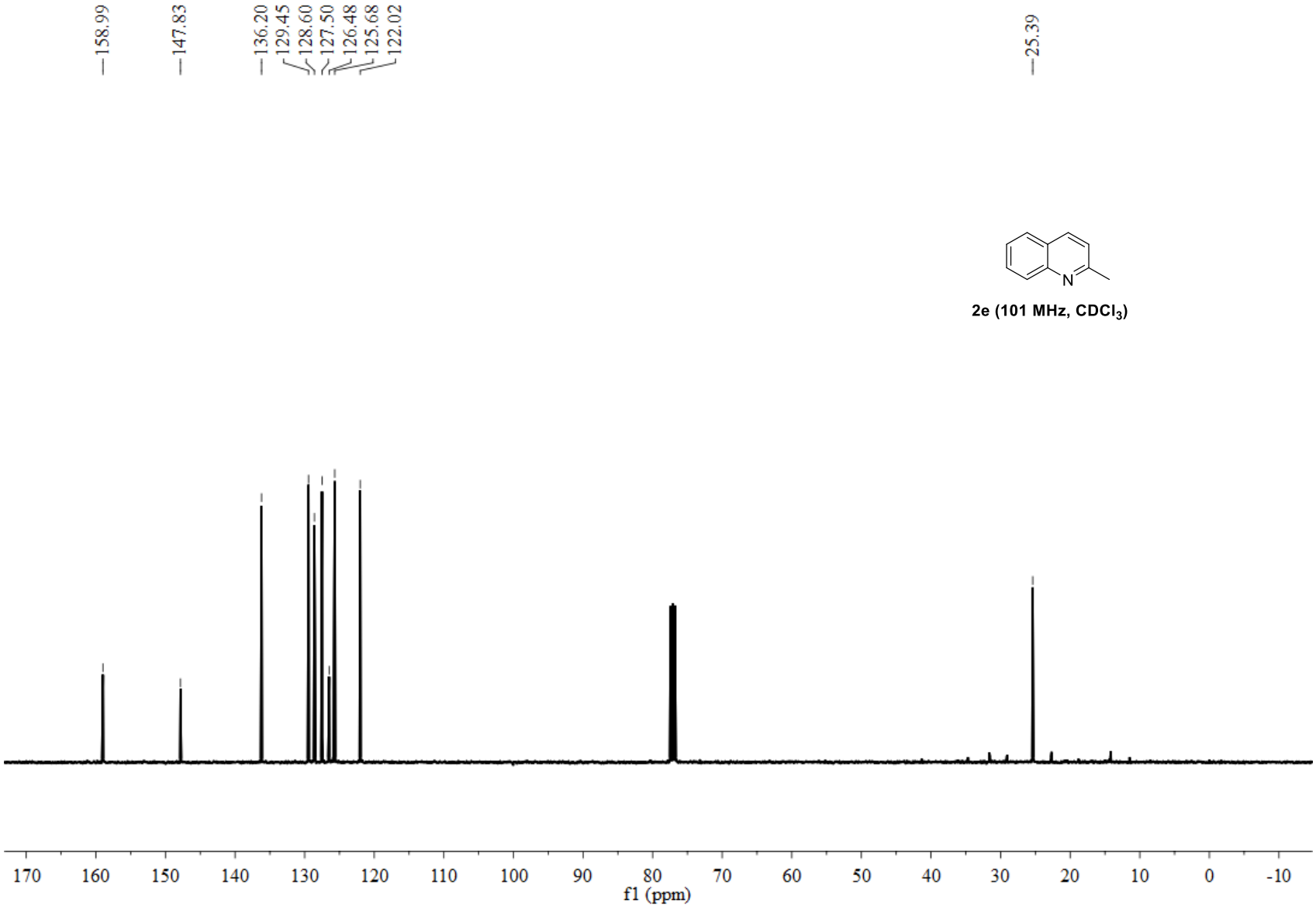
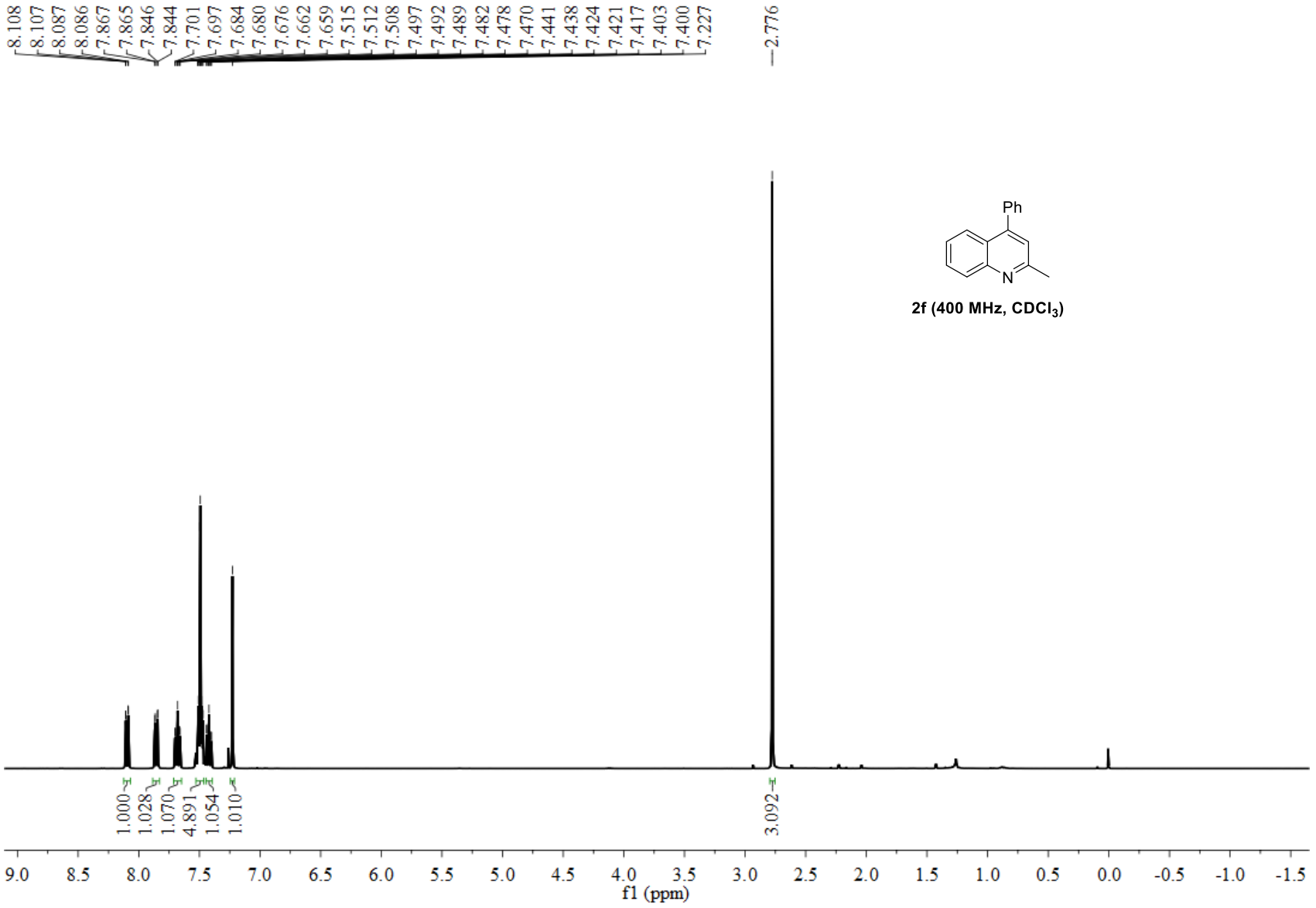


2e (101 MHz, $CDCl_3$)



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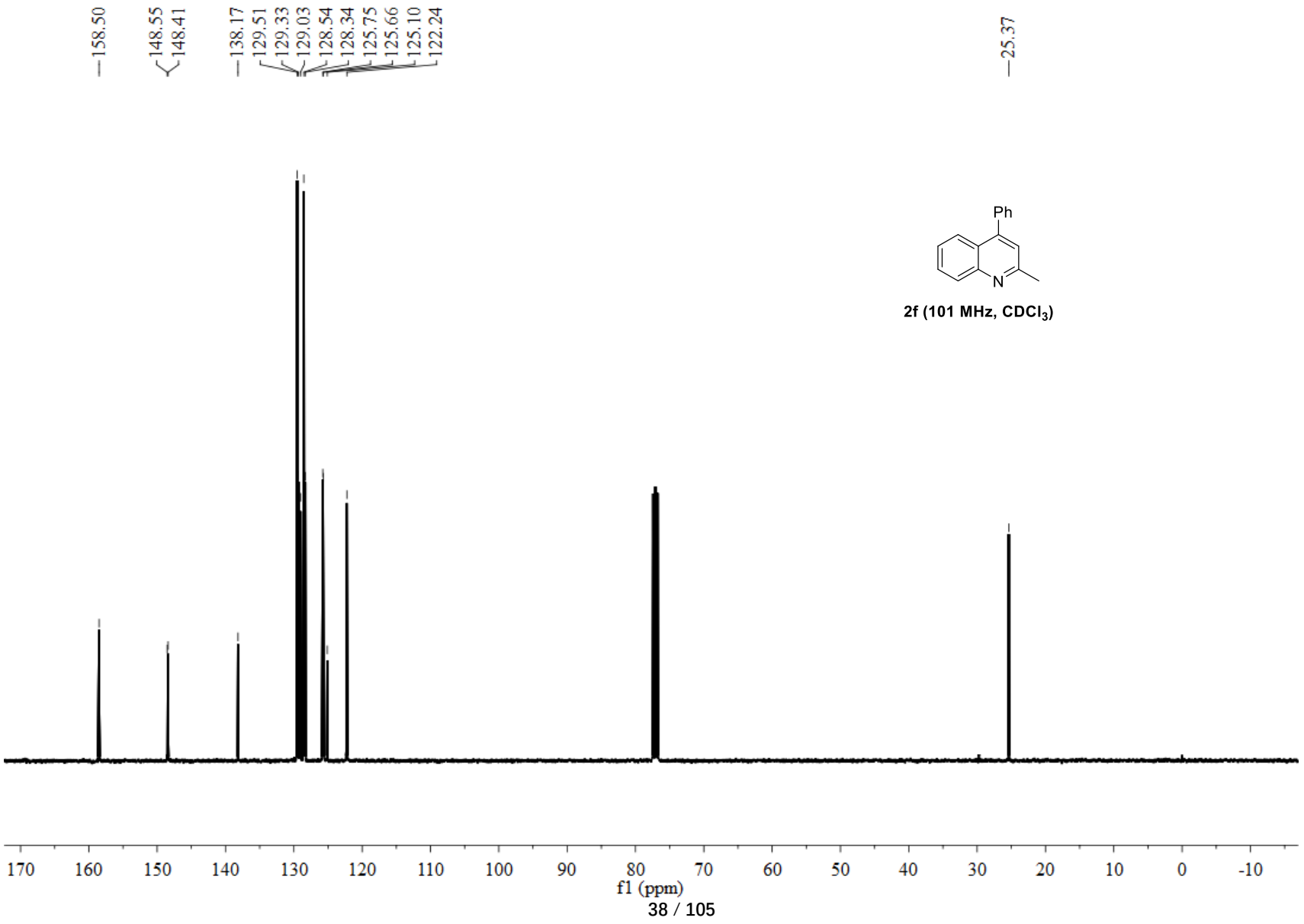

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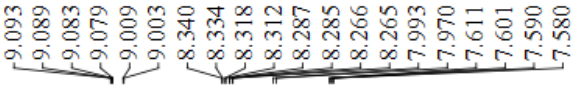
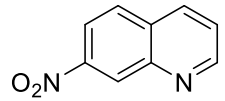
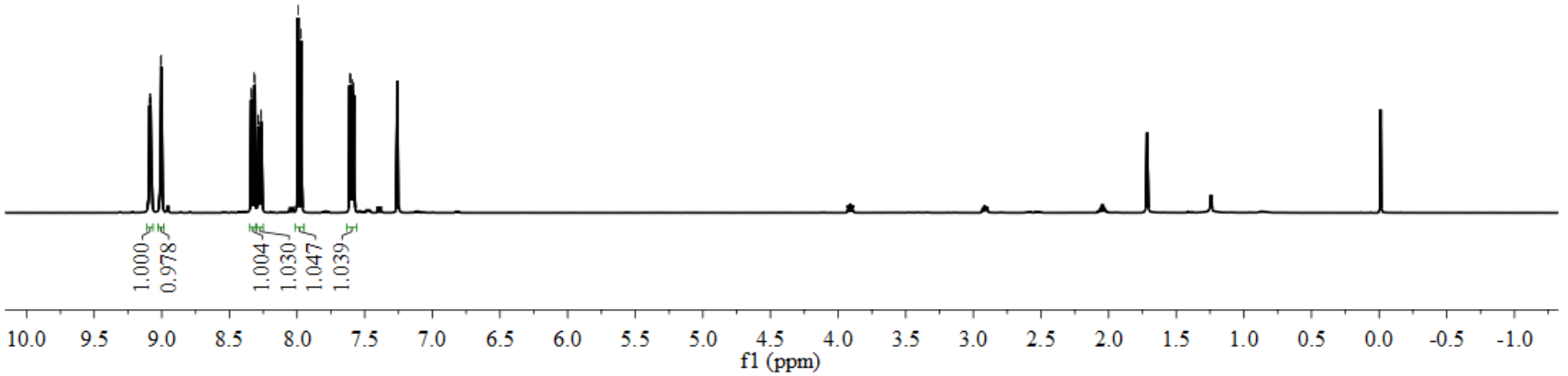
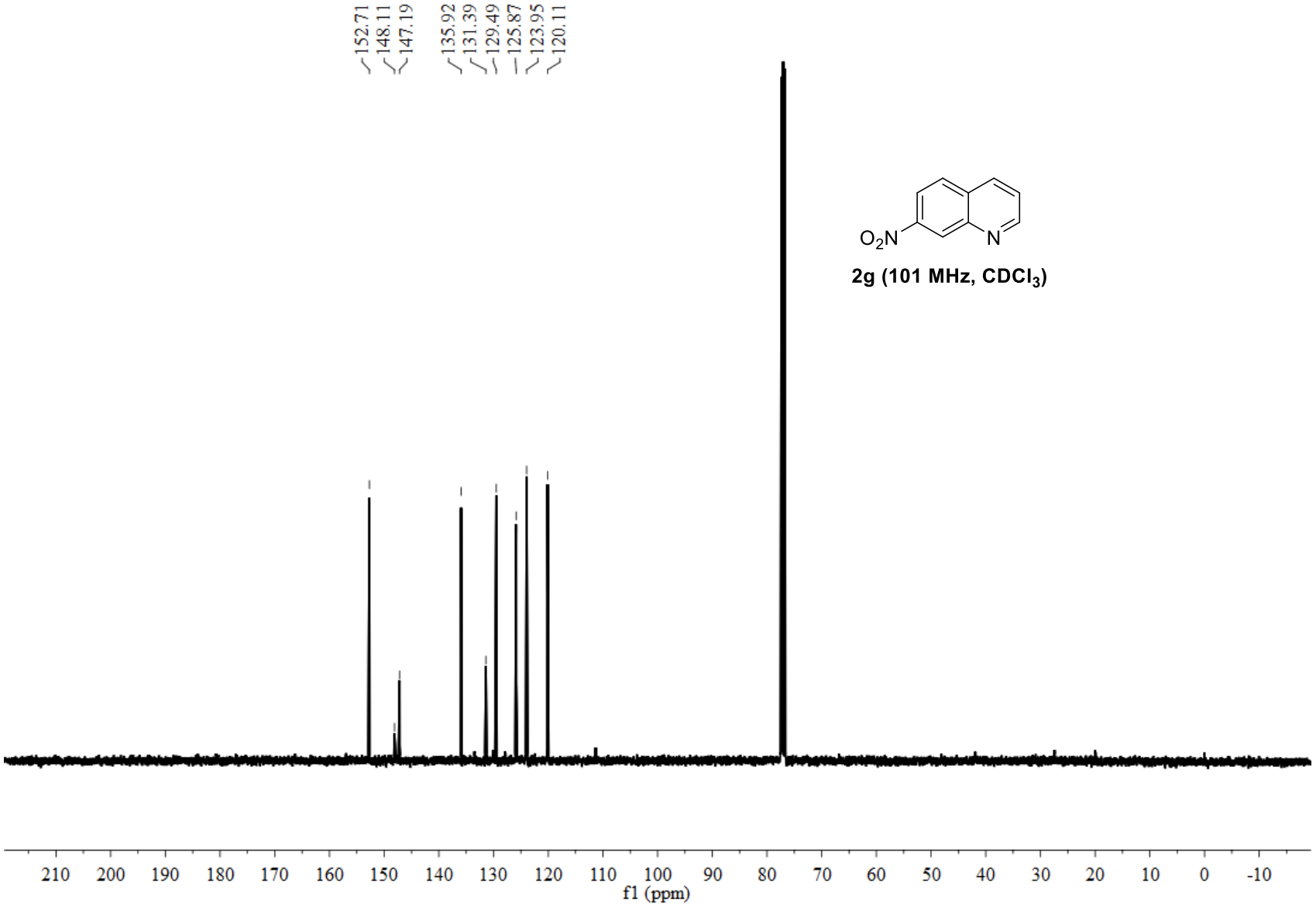
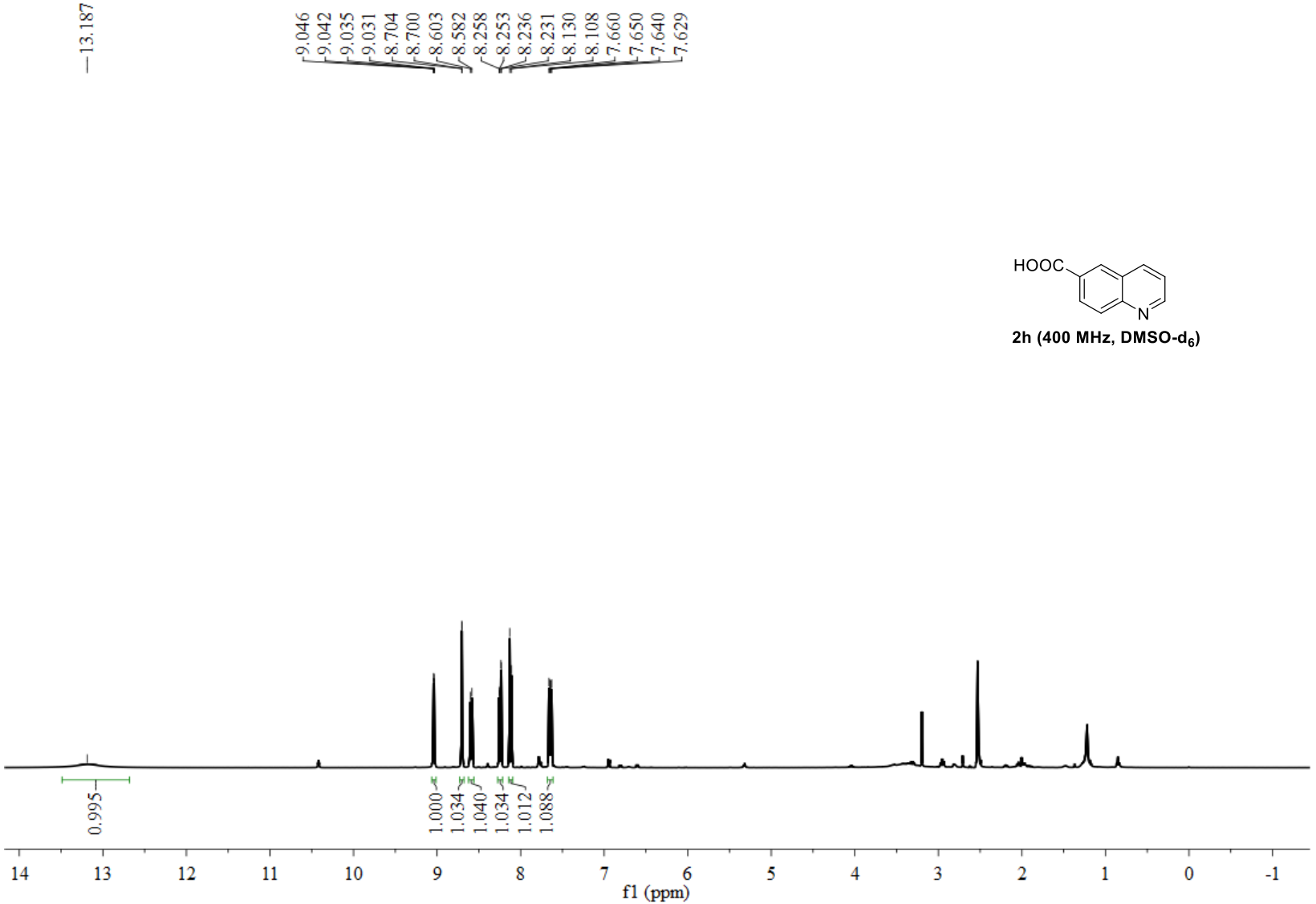


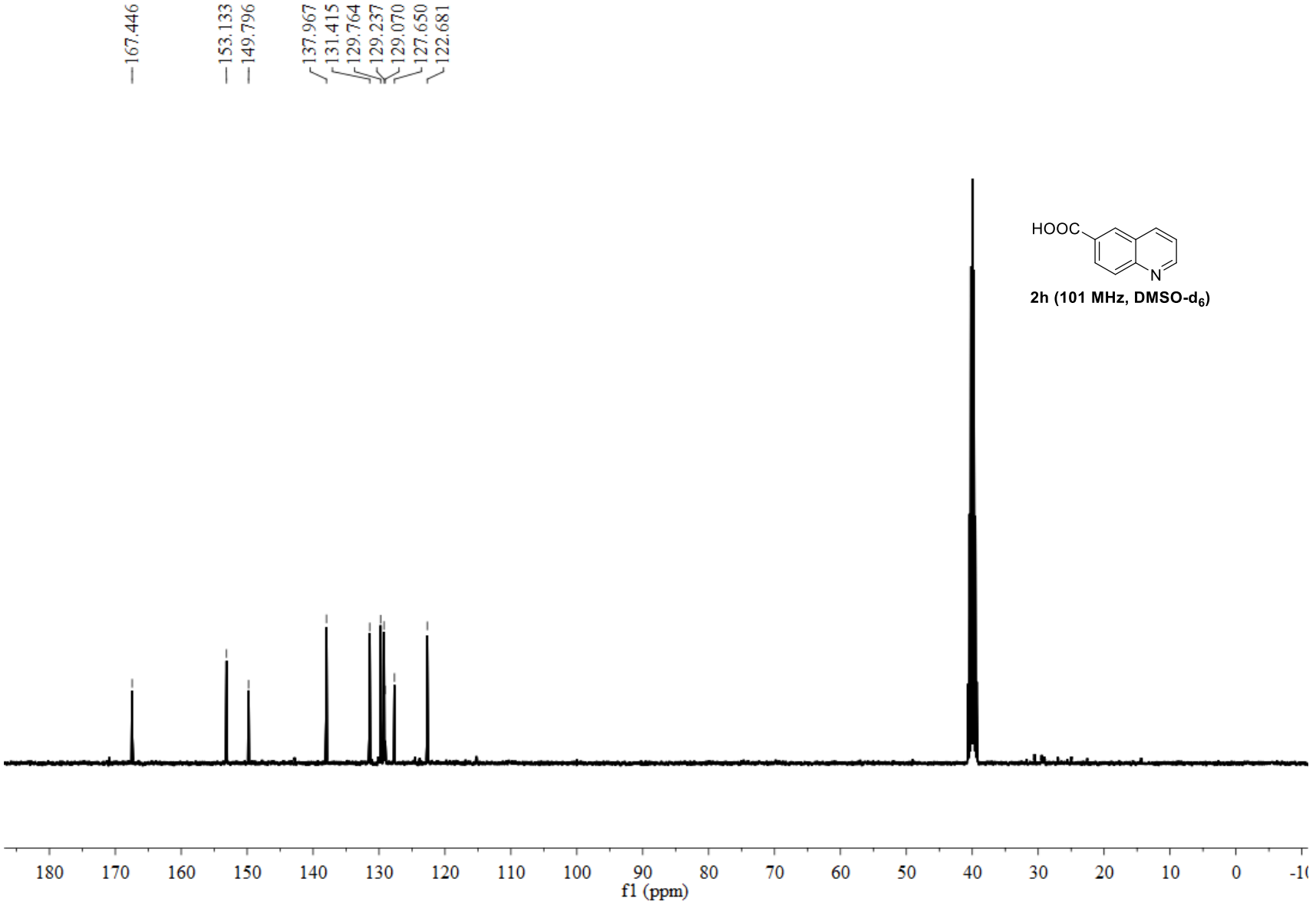


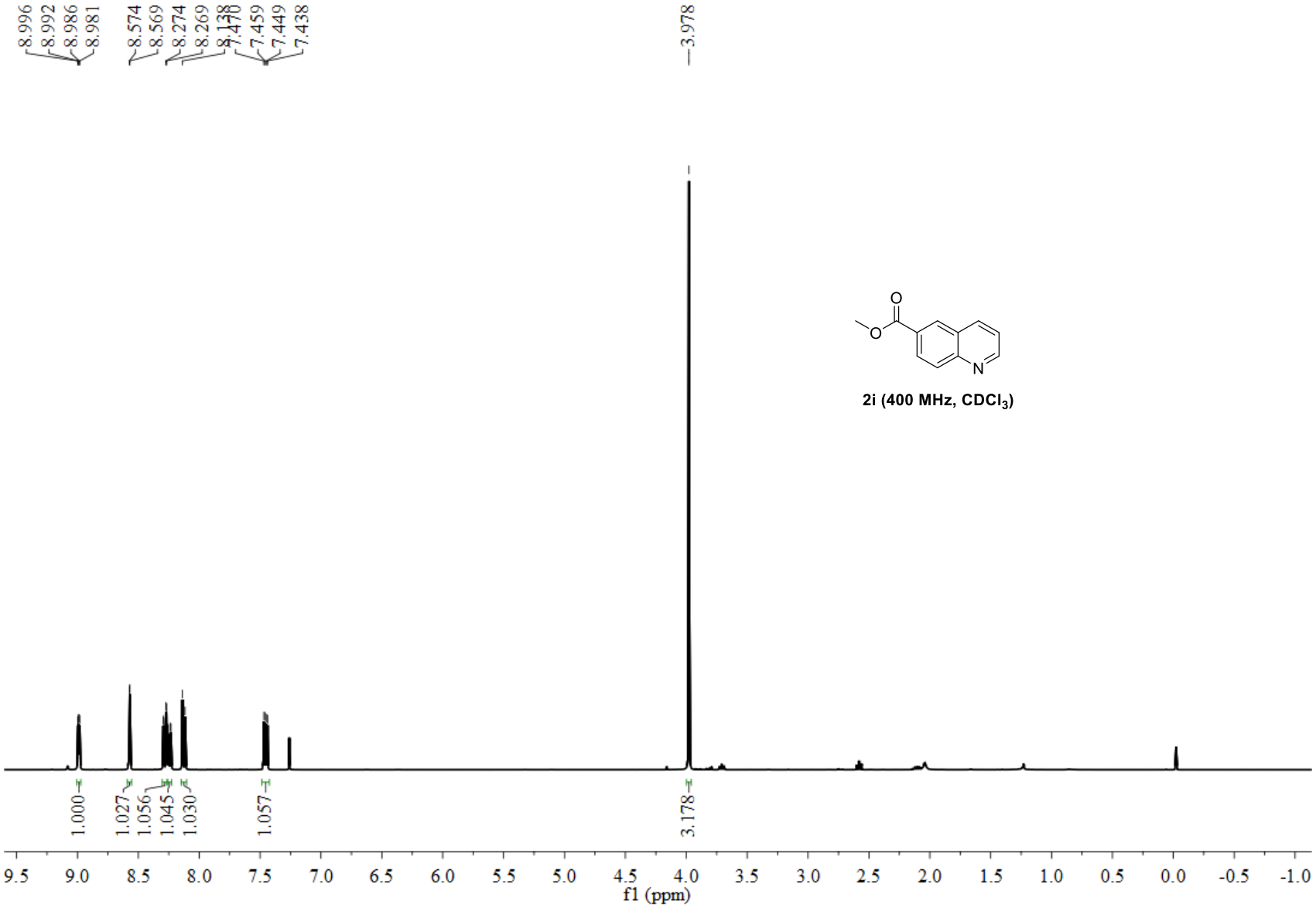
2g (400 MHz, $CDCl_3$)



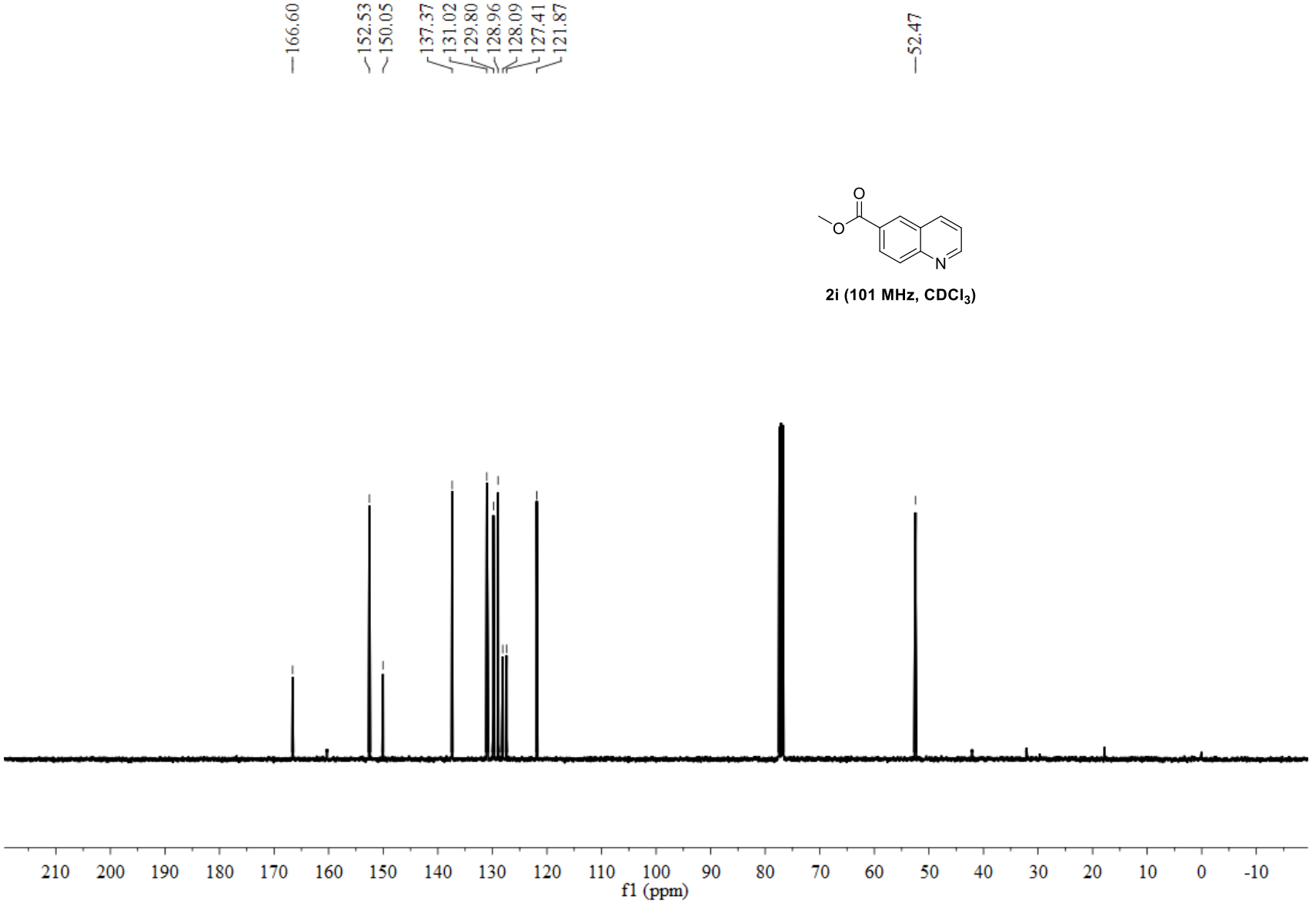

152.71
148.11
147.19
135.92
131.39
129.49
125.87
123.95
120.11
O2N
N
2g (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


13.187
9.046
9.042
9.035
9.031
8.704
8.700
8.603
8.582
8.258
8.253
8.236
8.231
8.130
8.108
7.660
7.650
7.640
7.629
HOOC
N
2h (400 MHz, DMSO-d6)
0.995
1.000
1.034
1.040
1.034
1.012
1.088
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

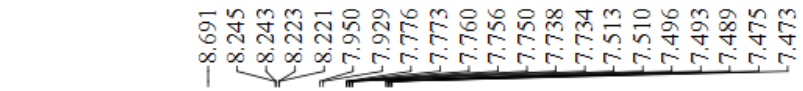

167.446
153.133
149.796
137.967
131.415
129.764
129.237
129.070
127.650
122.681
HOOC
N
2h (101 MHz, DMSO-d6)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

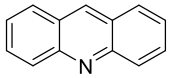


2i (400 MHz, $CDCl_3$)

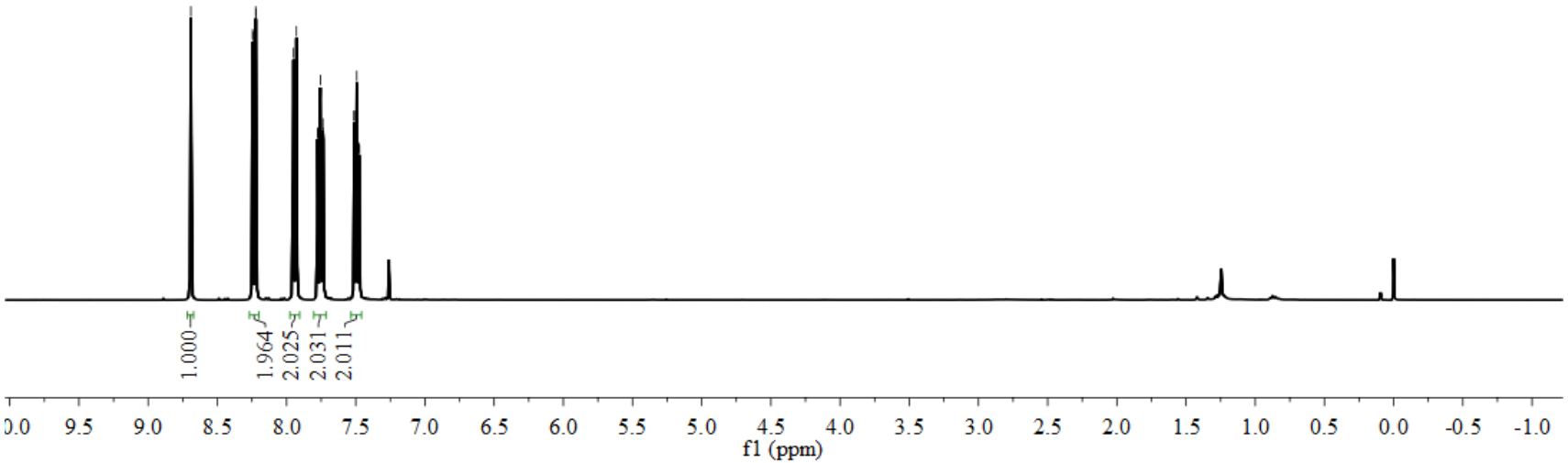


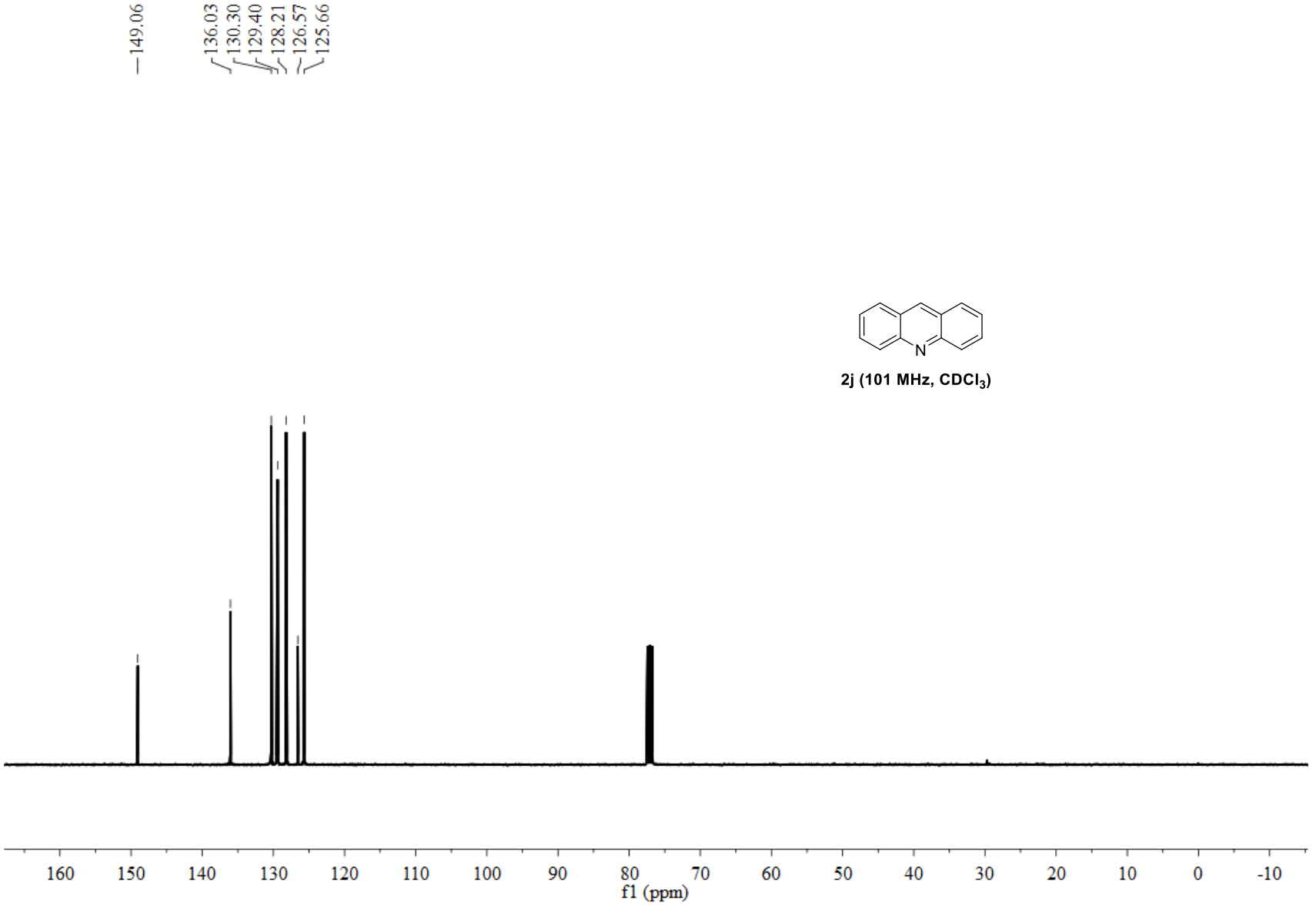
2i (101 MHz, $CDCl_3$)

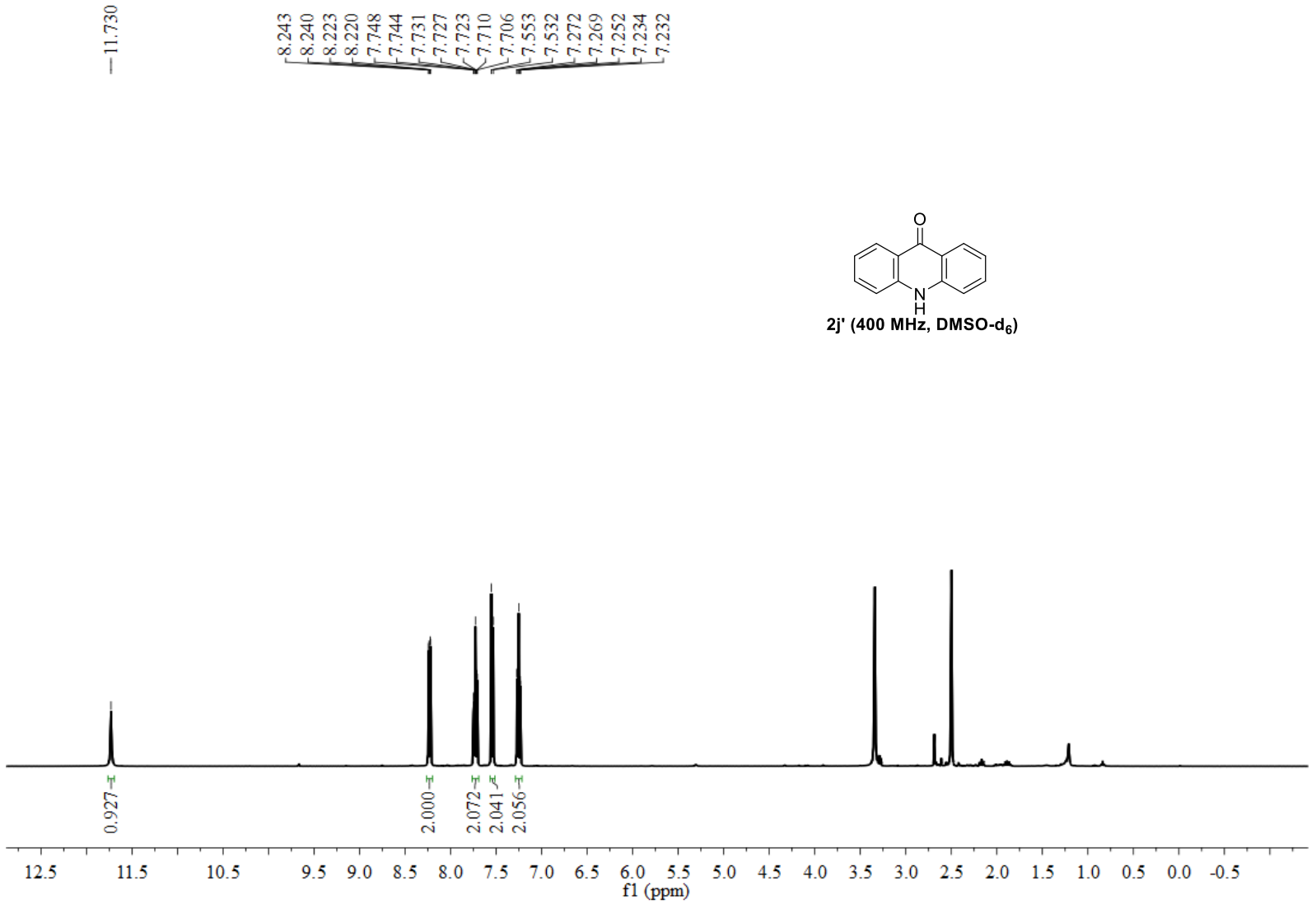




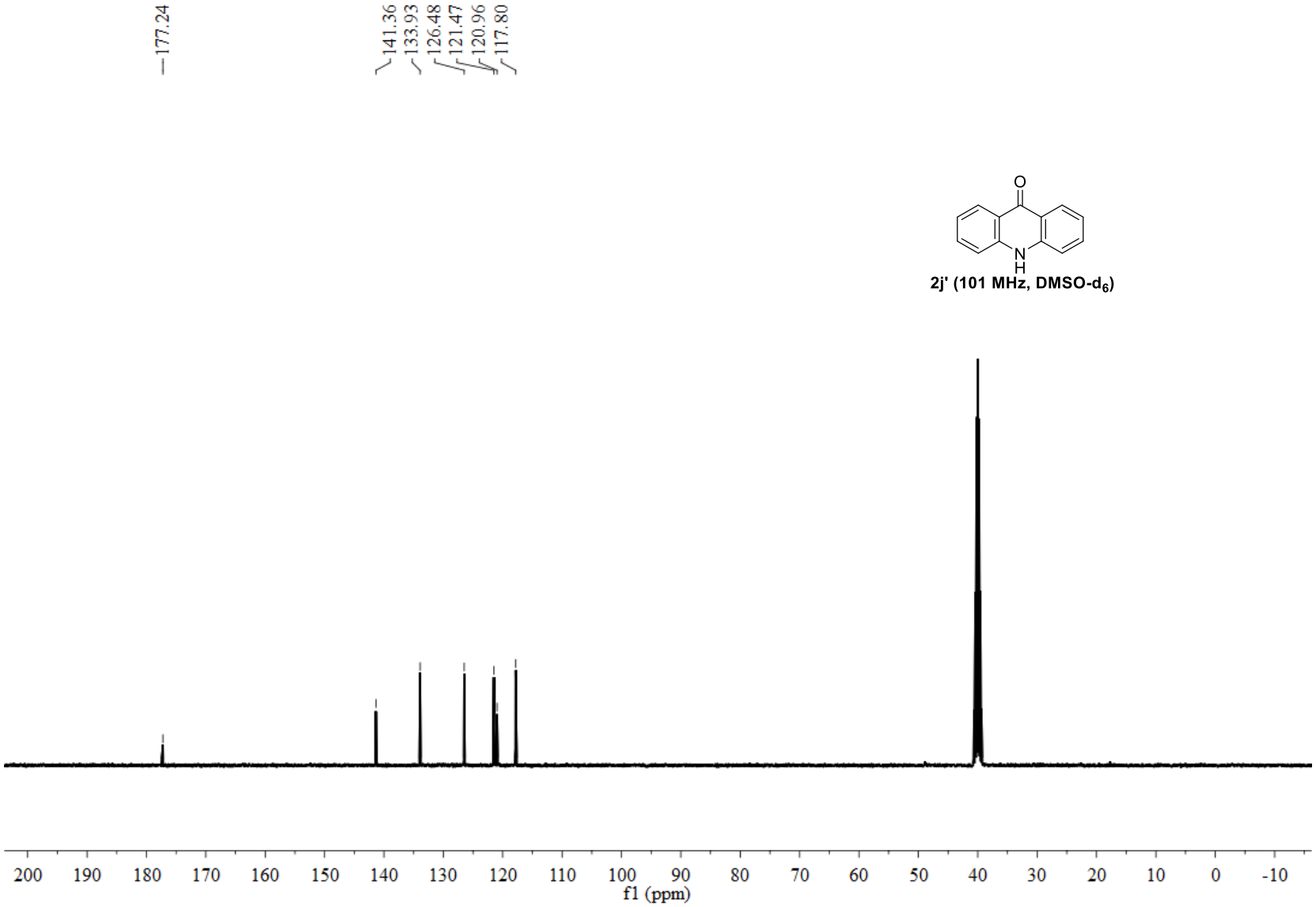
2j (400 MHz, $CDCl_3$)

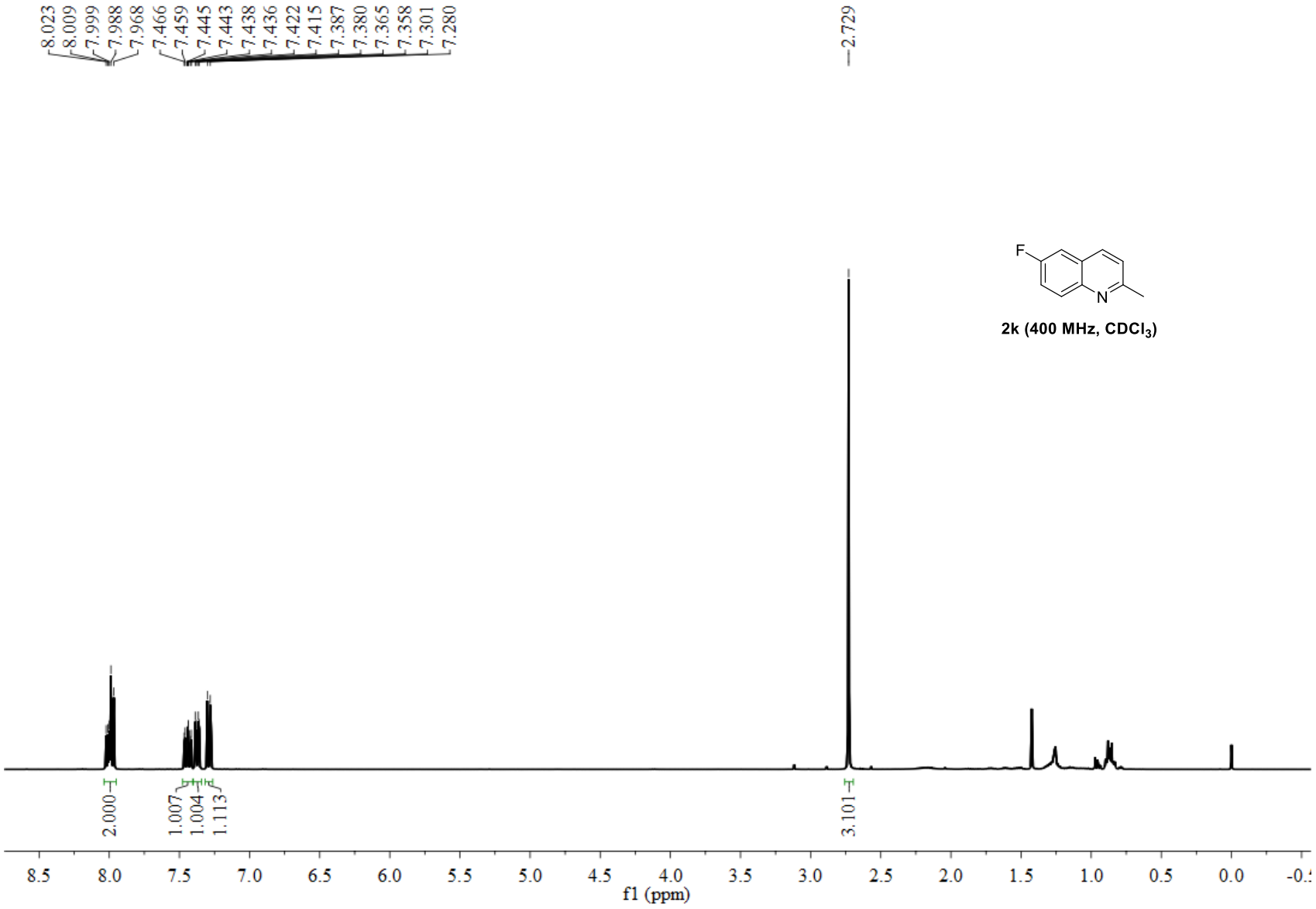


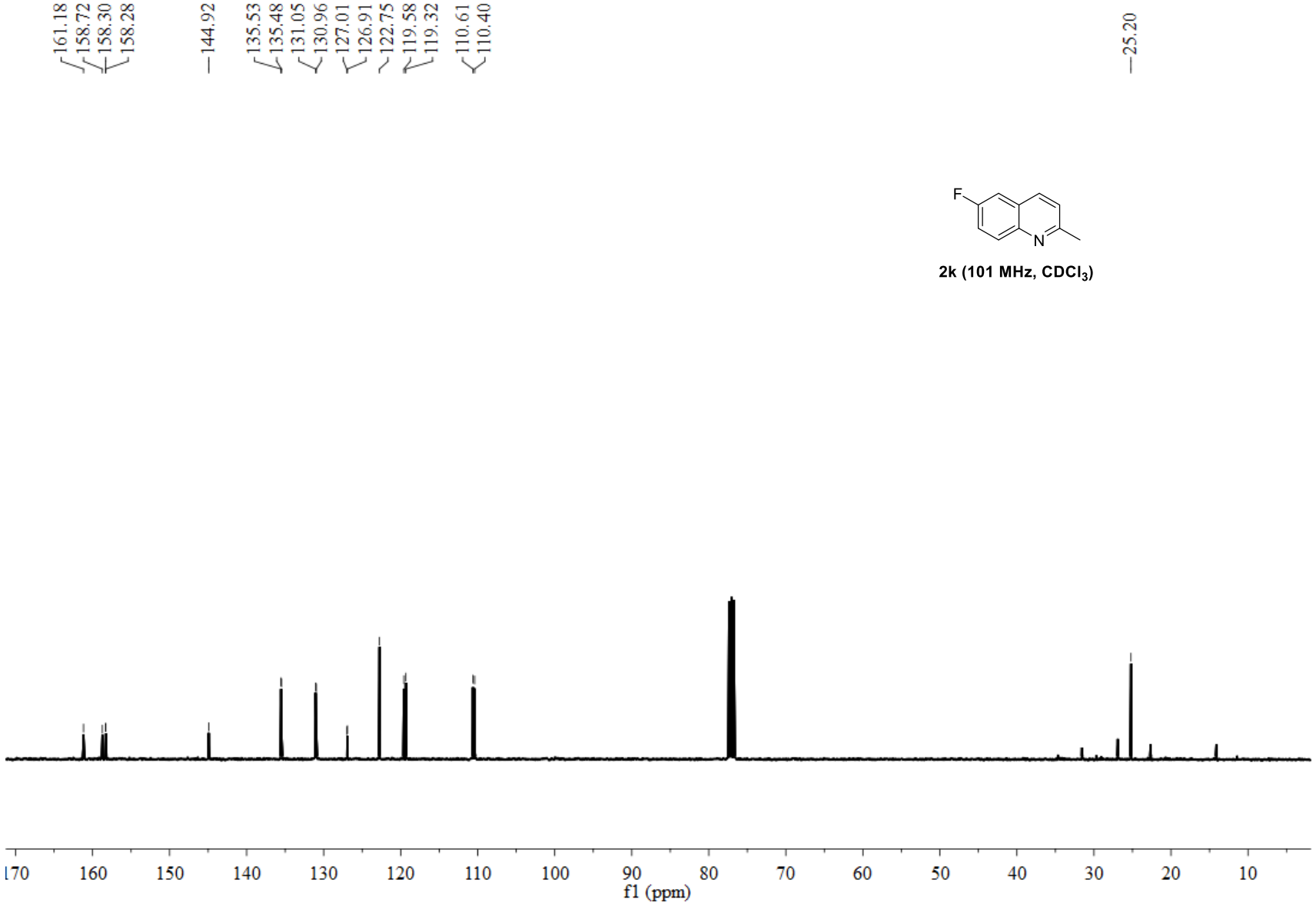

149.06
136.03
130.30
129.40
128.21
126.57
125.66
N
2j (101 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



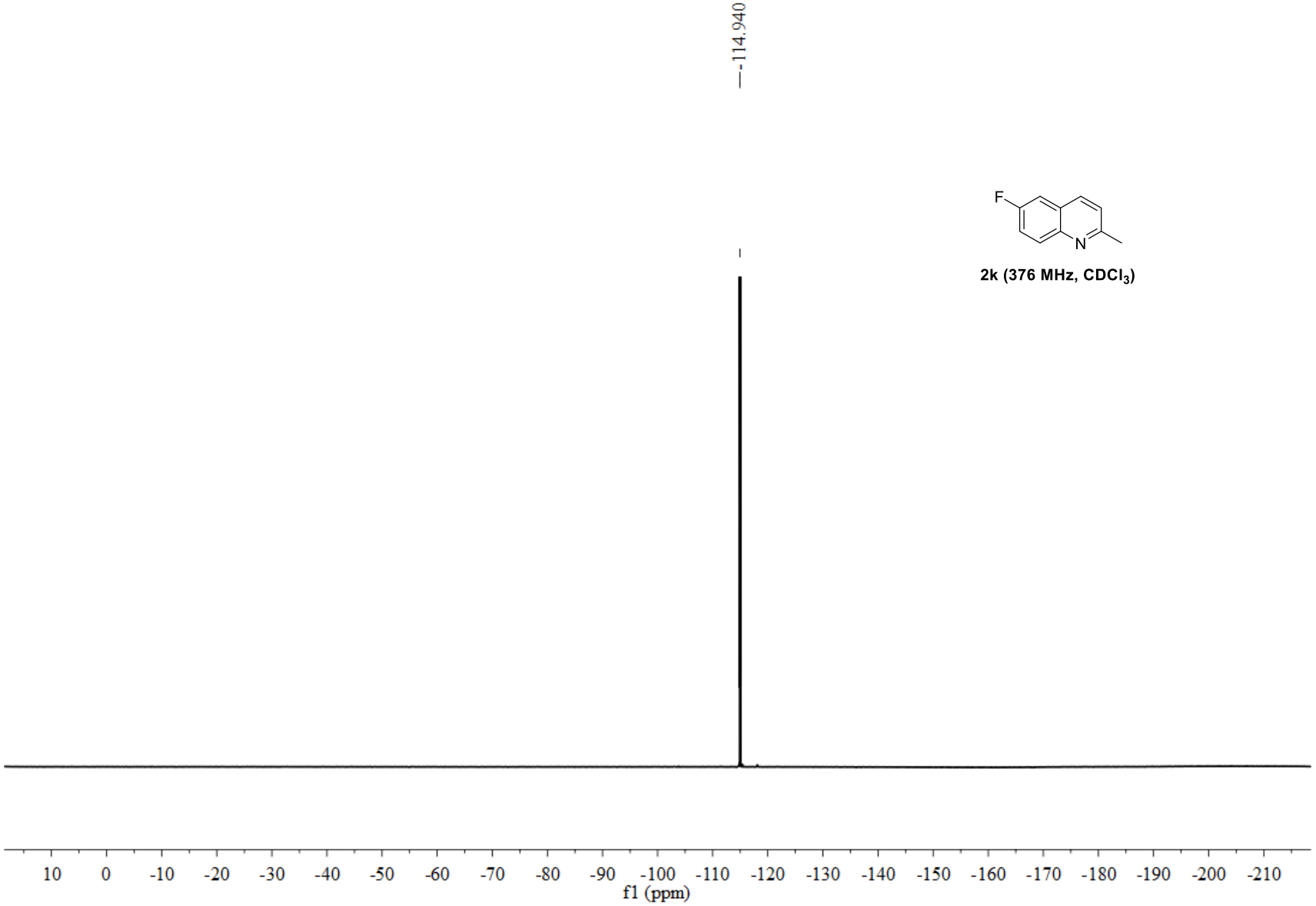
2j' (400 MHz, DMSO-d_6)


177.24
141.36
133.93
126.48
121.47
120.96
117.80
O
N
H
2j' (101 MHz, DMSO-d6)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

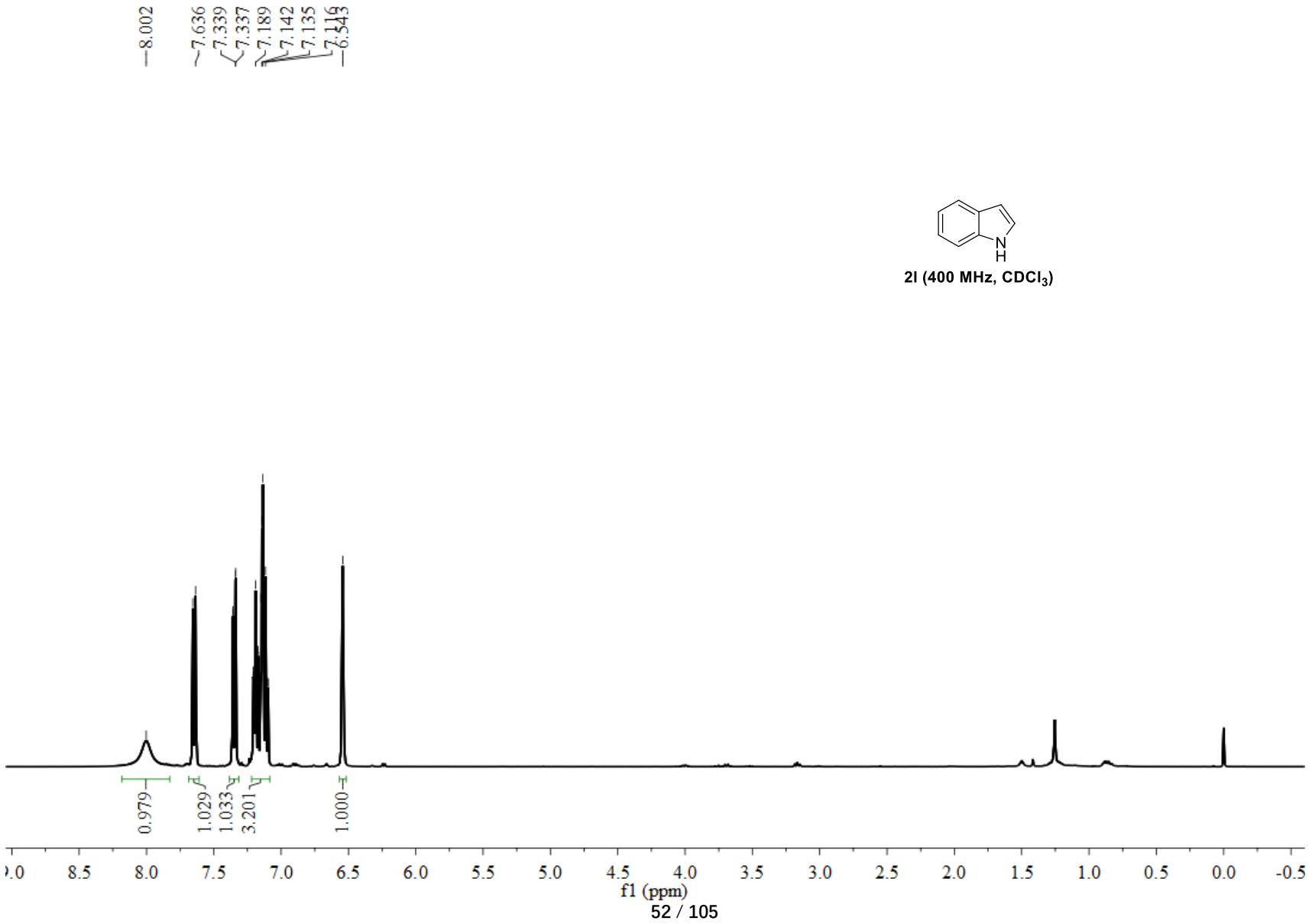

8.023
8.009
7.999
7.988
7.968
7.466
7.459
7.445
7.443
7.438
7.436
7.422
7.415
7.387
7.380
7.365
7.358
7.301
7.280
2.729
F
N
2k (400 MHz, CDCl3)
2.000
1.007
1.004
1.113
3.101
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



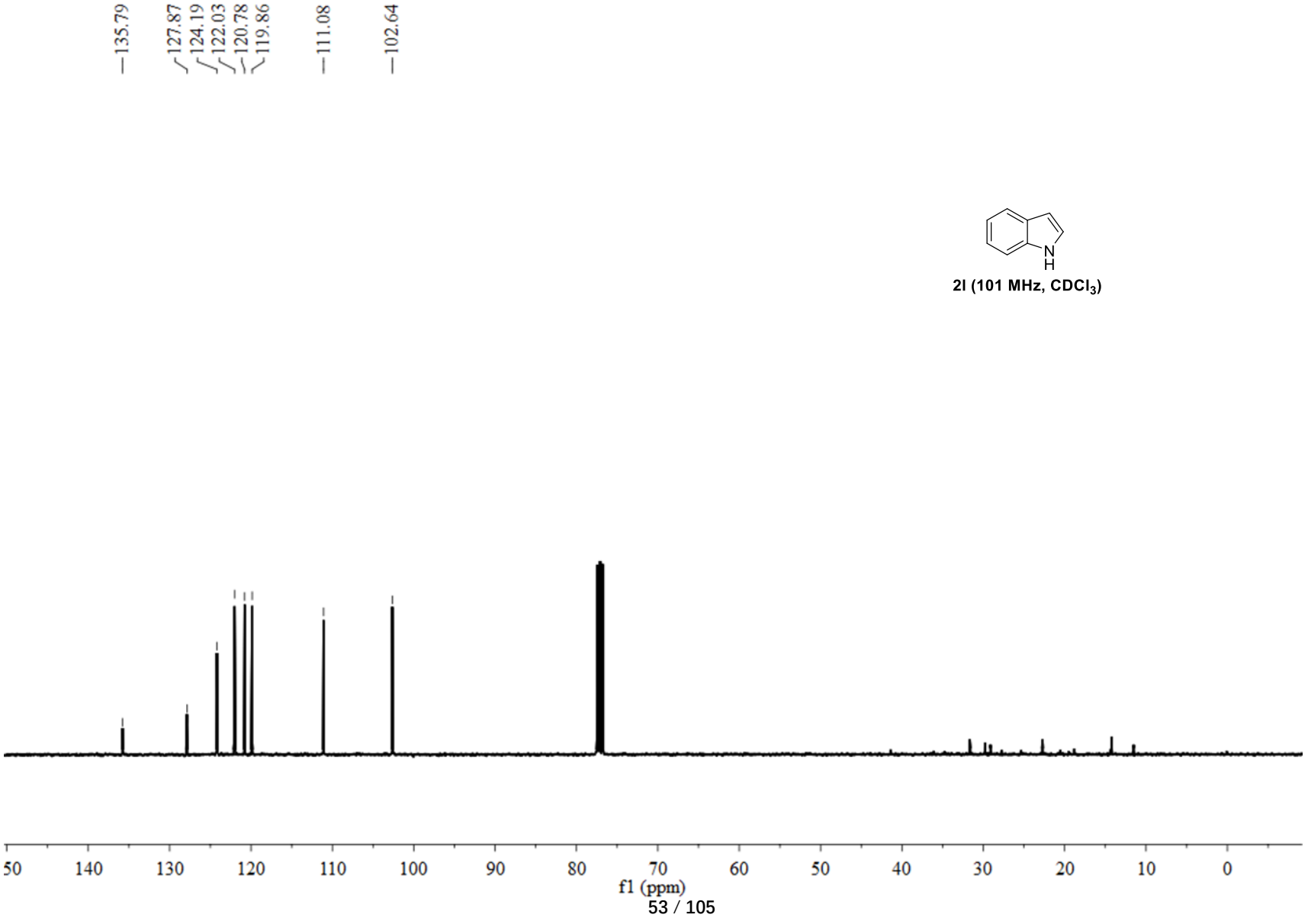
2k (101 MHz, $CDCl_3$)

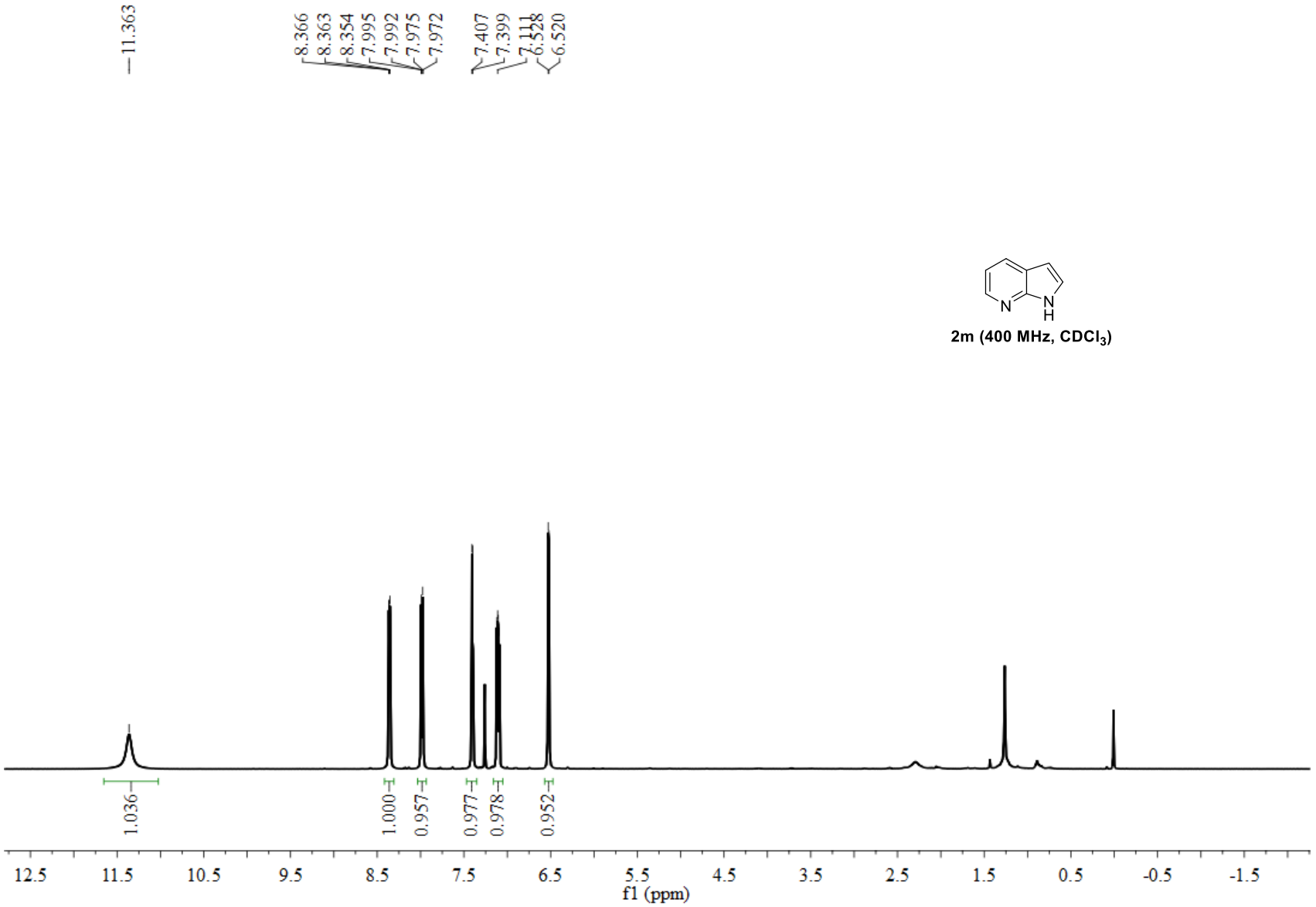


2k (376 MHz, $CDCl_3$)

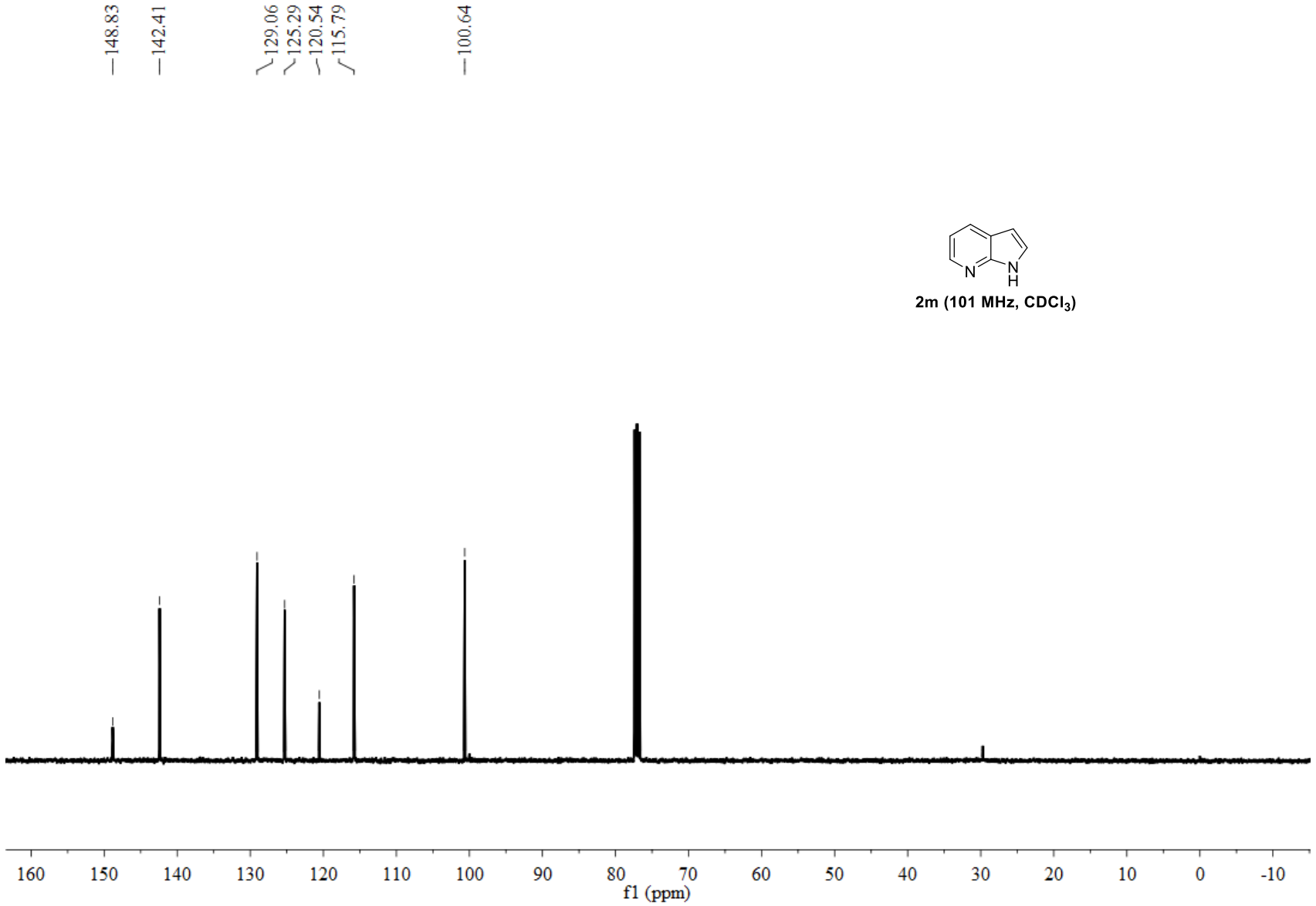


2l (400 MHz, $CDCl_3$)

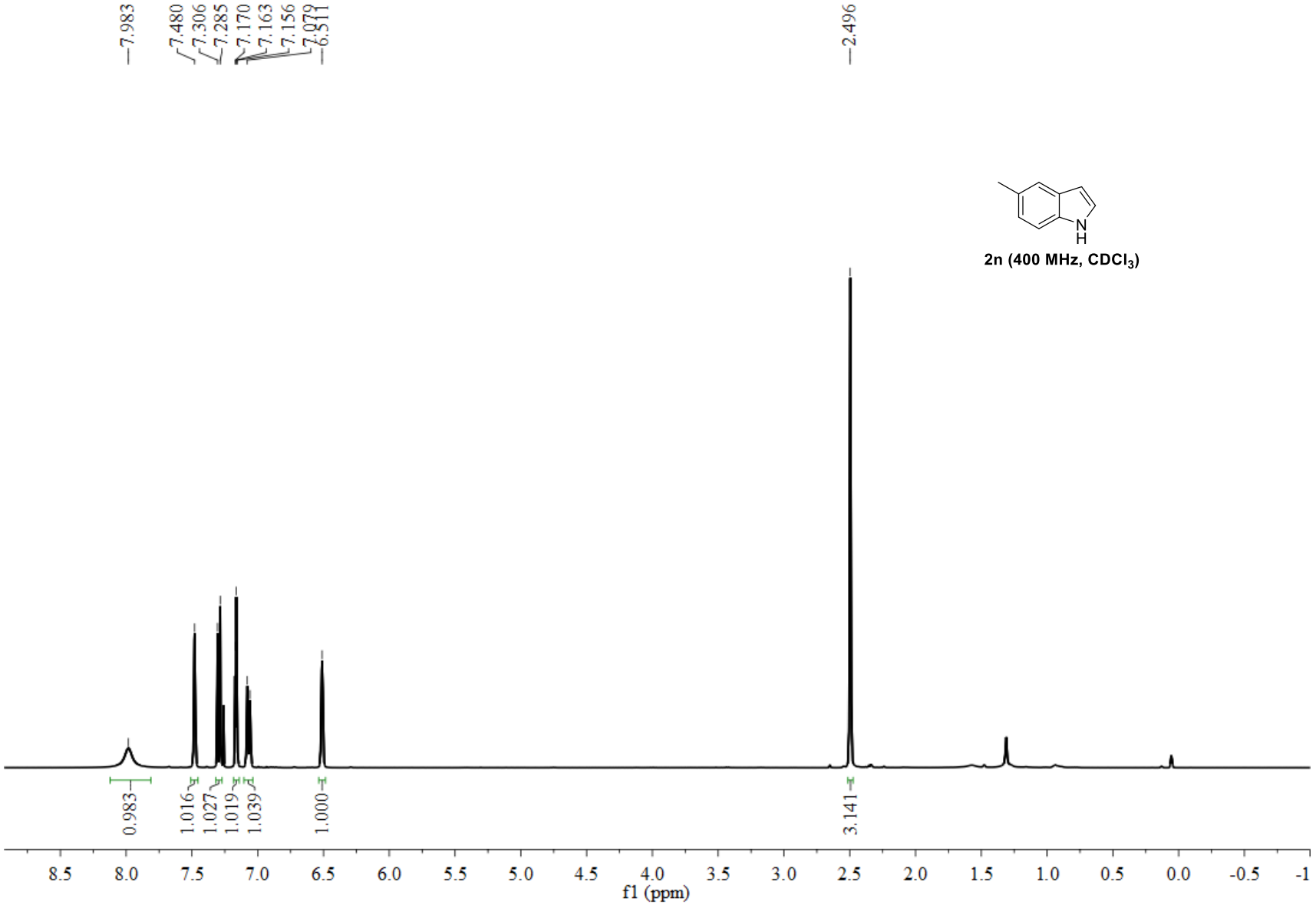

135.79
127.87
124.19
122.03
120.78
119.86
111.08
102.64
N
H
2l (101 MHz, CDCl3)
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



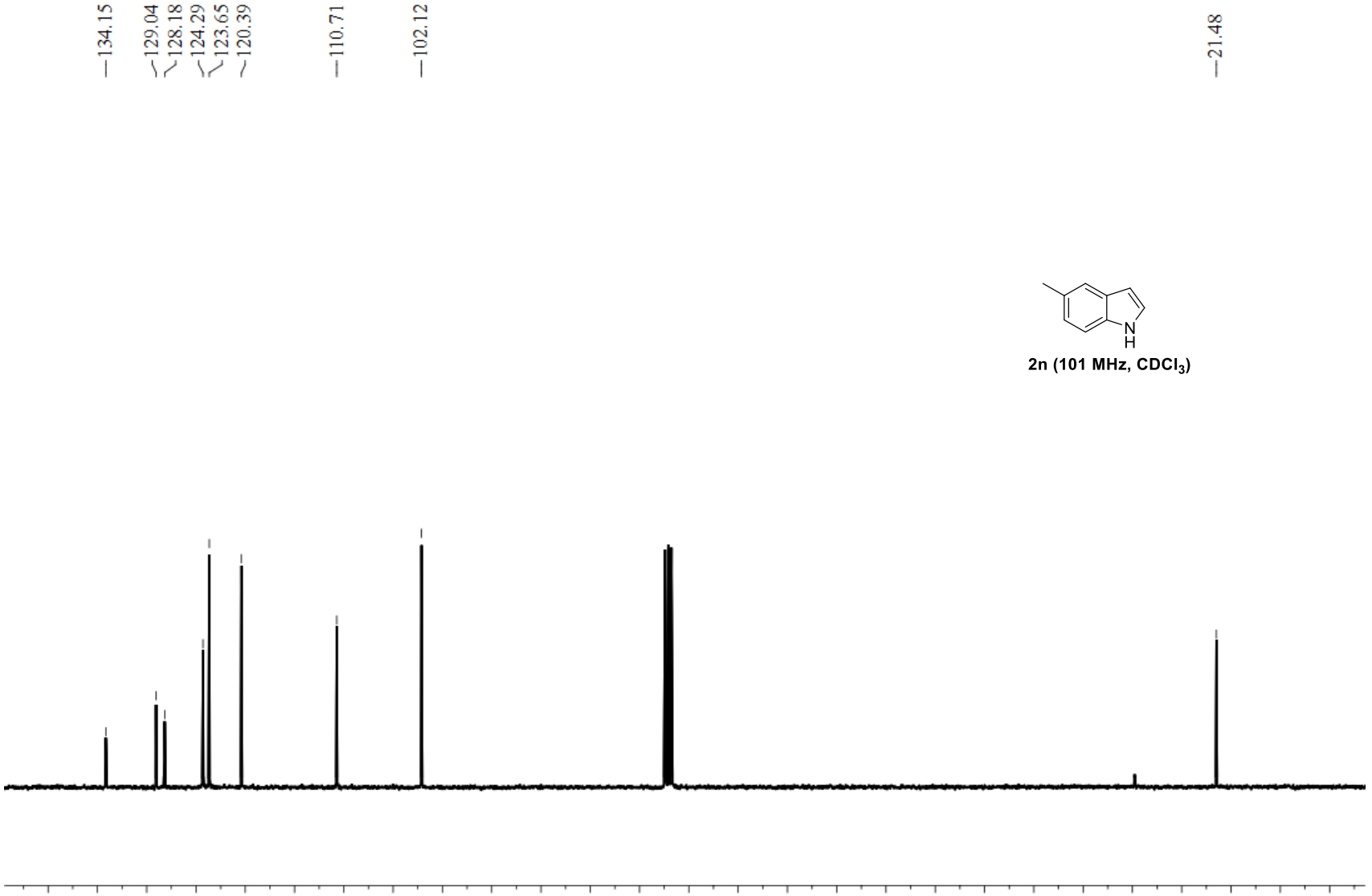
2m (400 MHz, $CDCl_3$)



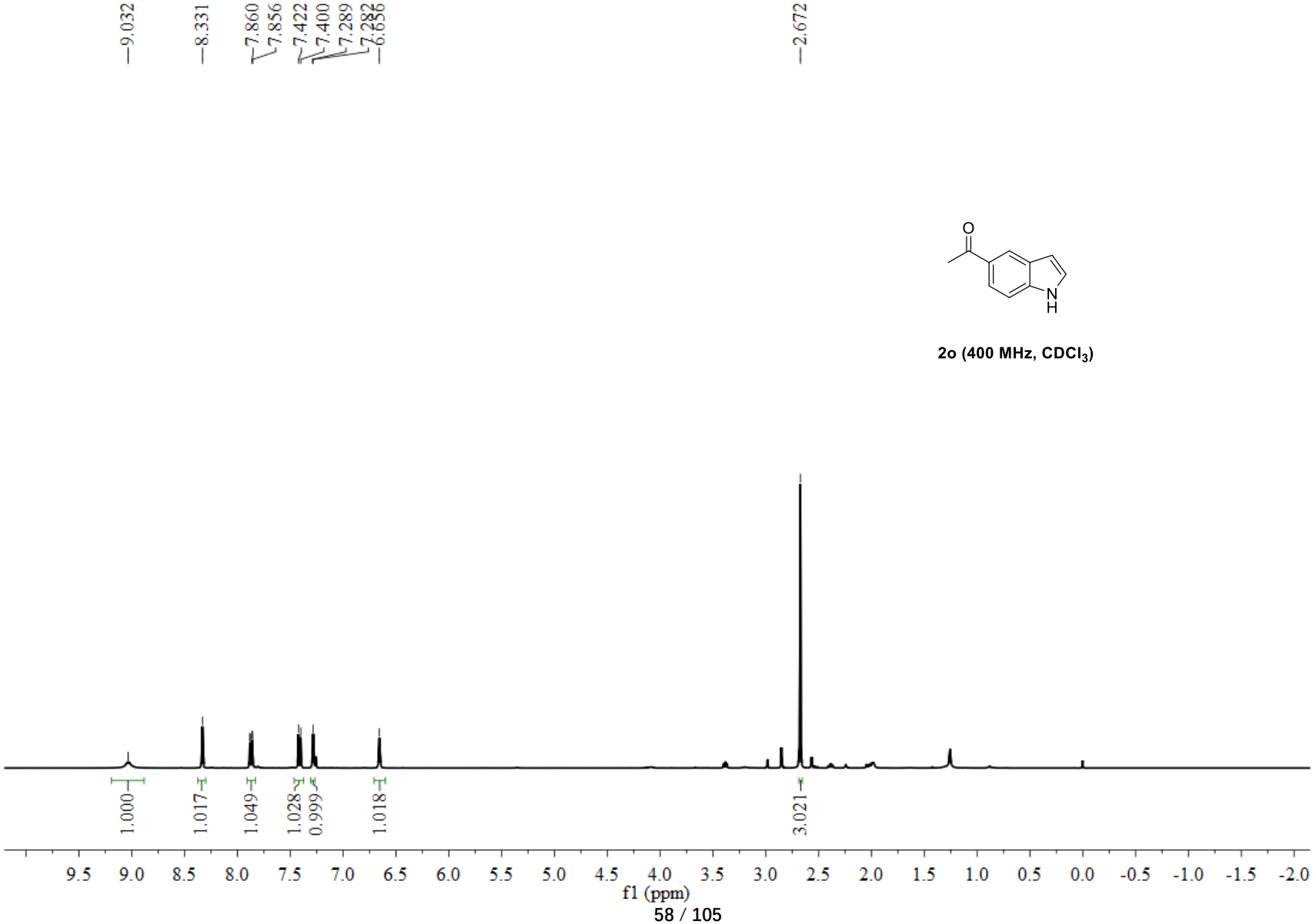
2m (101 MHz, $CDCl_3$)



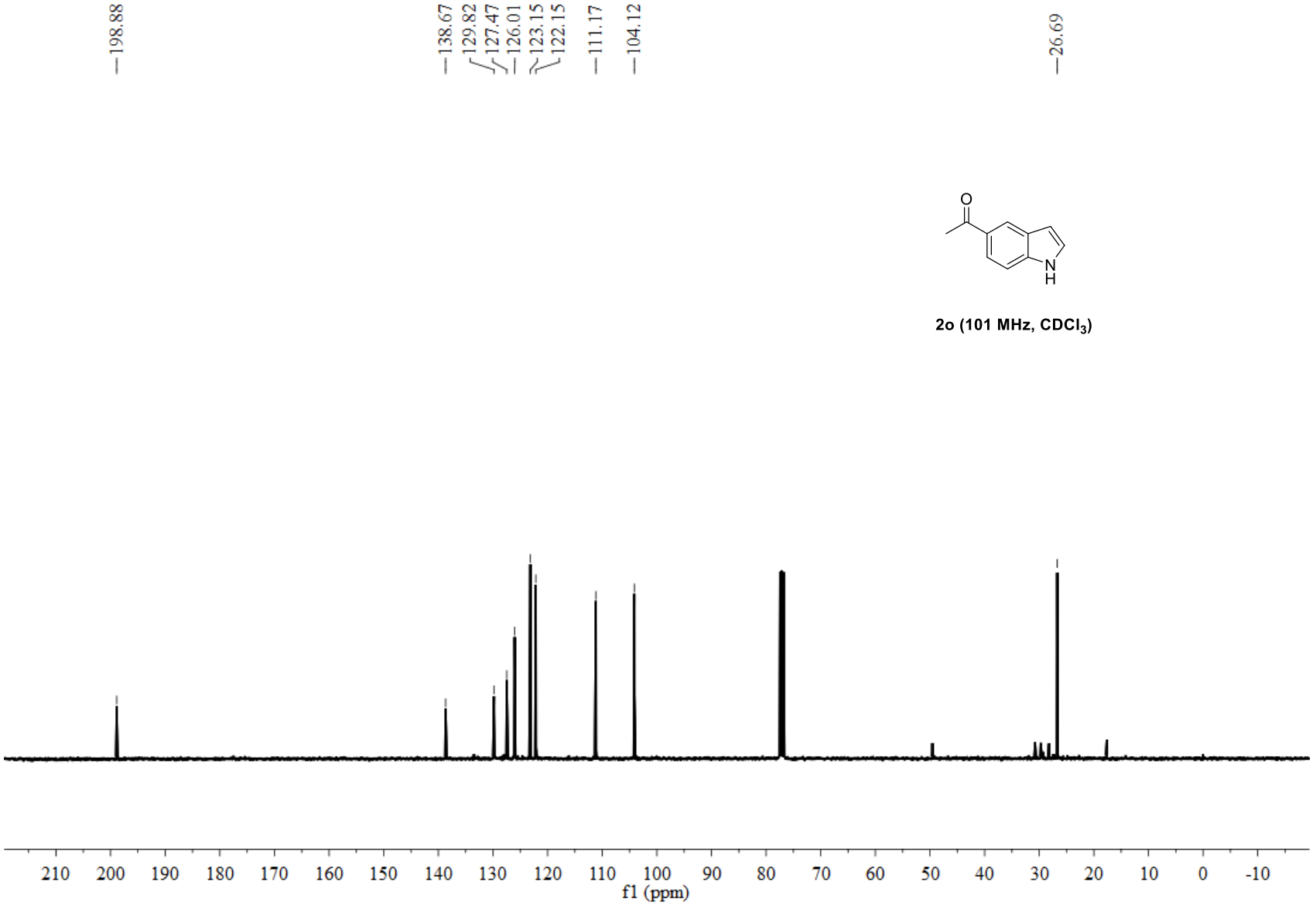
2n (400 MHz, $CDCl_3$)



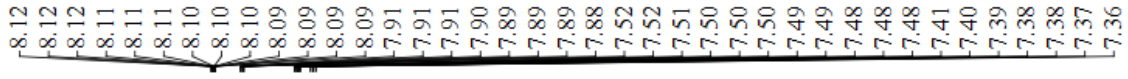
2n (101 MHz, $CDCl_3$)

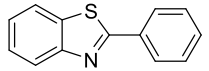


2o (400 MHz, $CDCl_3$)

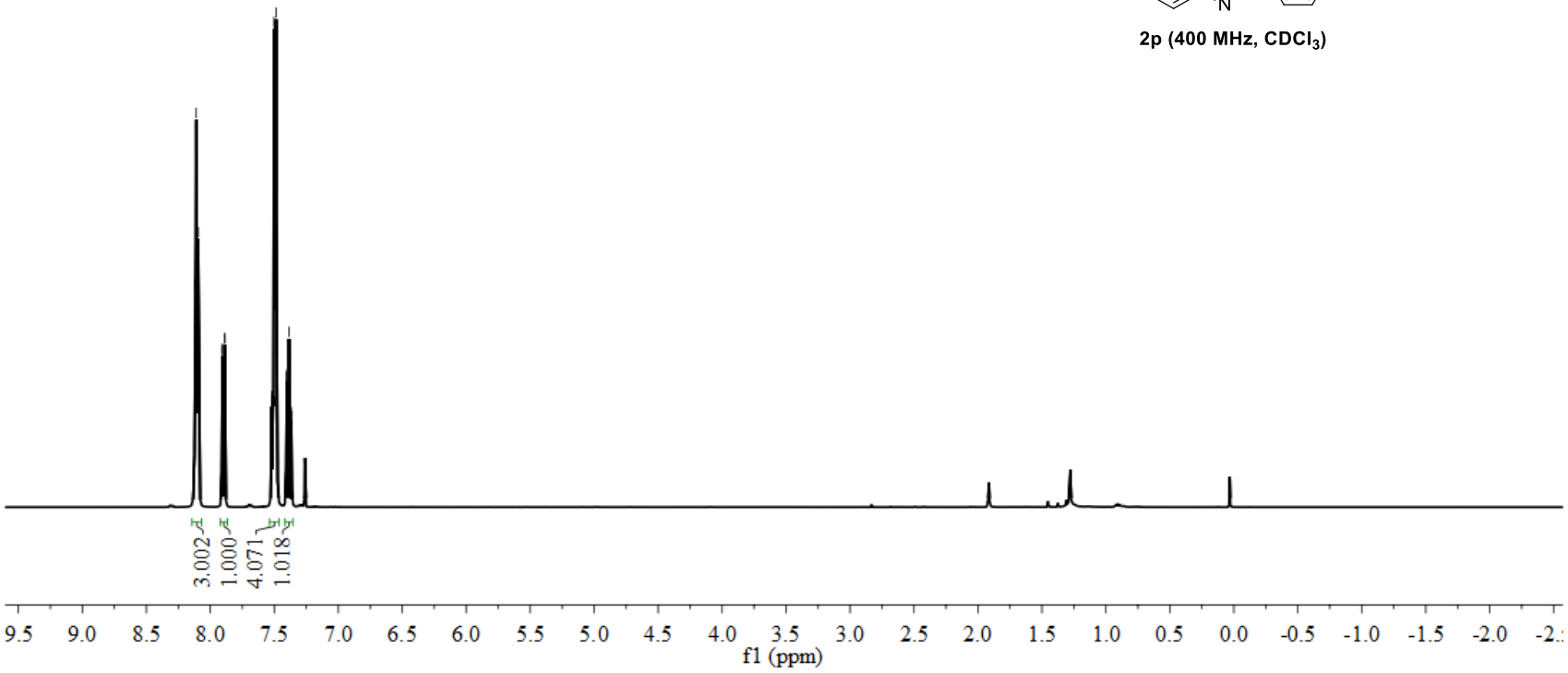


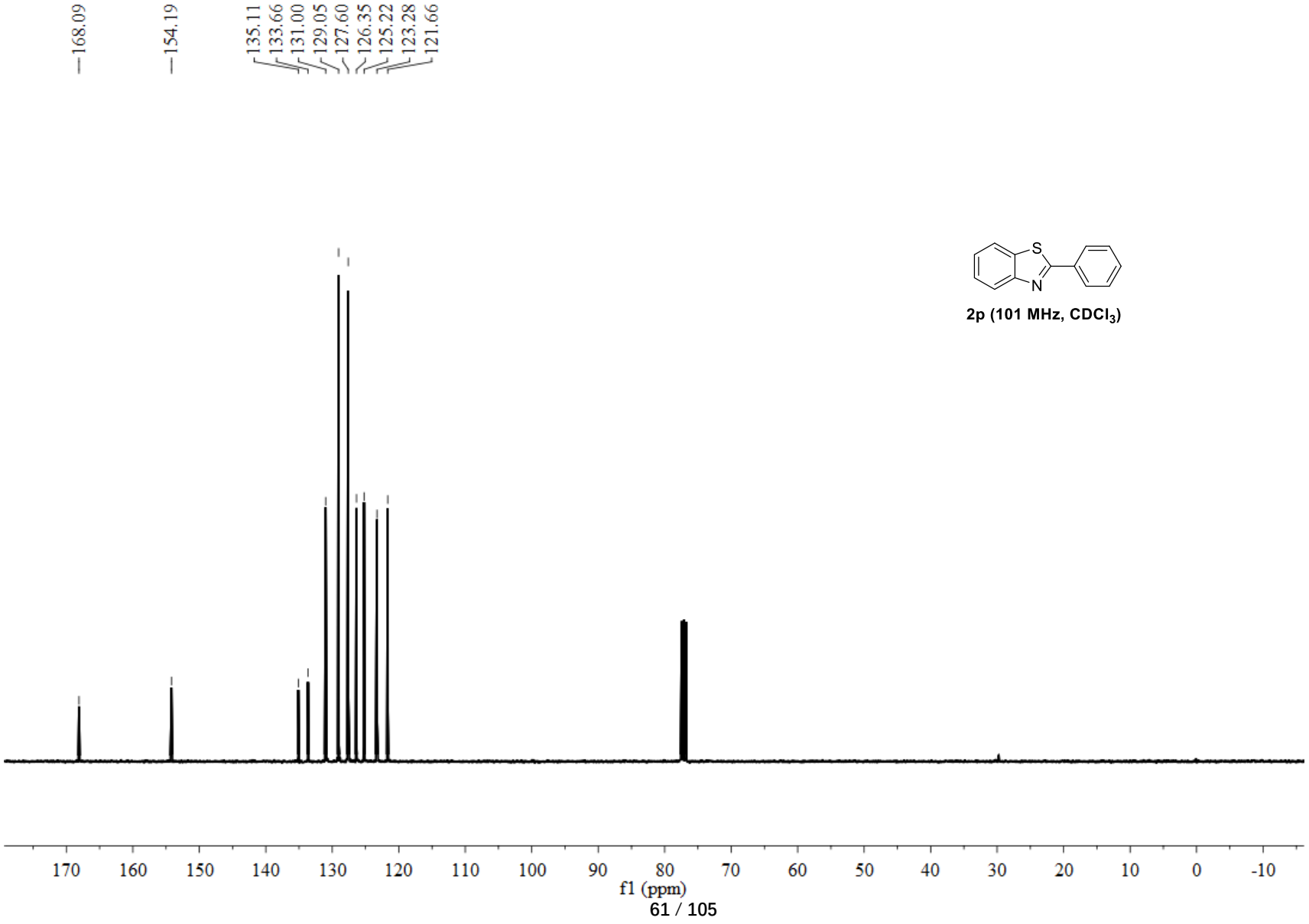
2o (101 MHz, $CDCl_3$)



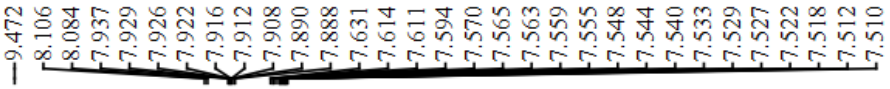


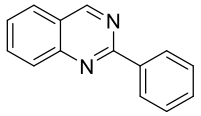
2p (400 MHz, $CDCl_3$)



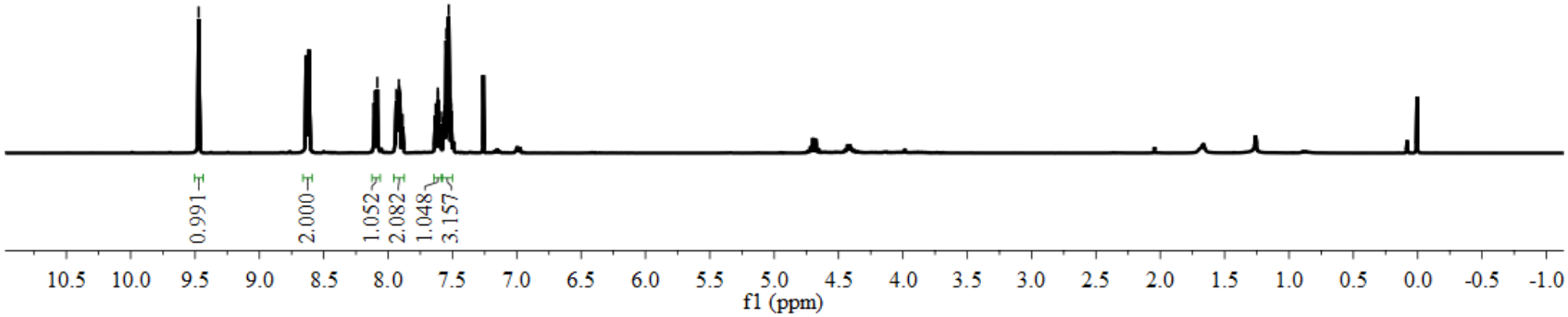


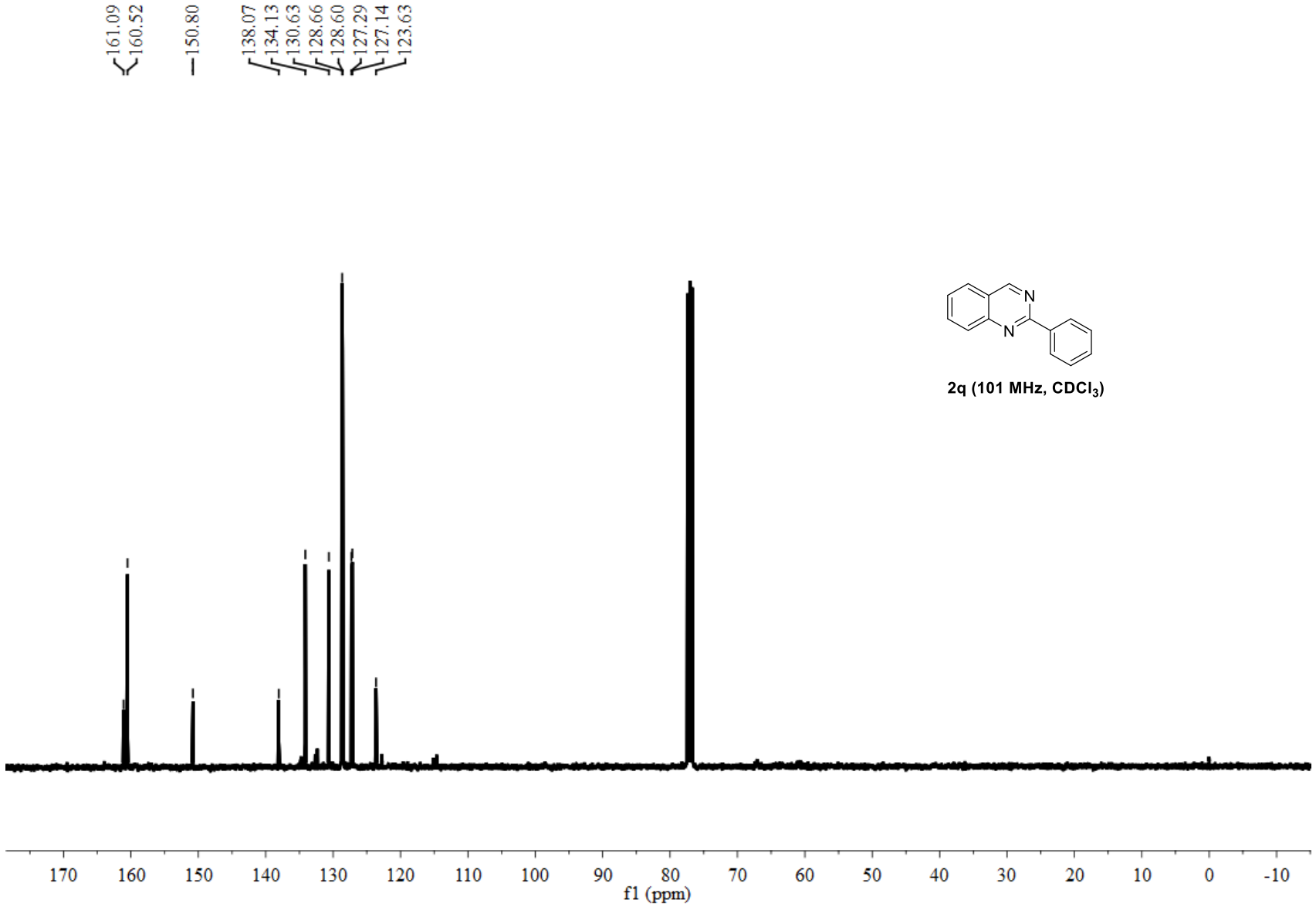
2p (101 MHz, $CDCl_3$)



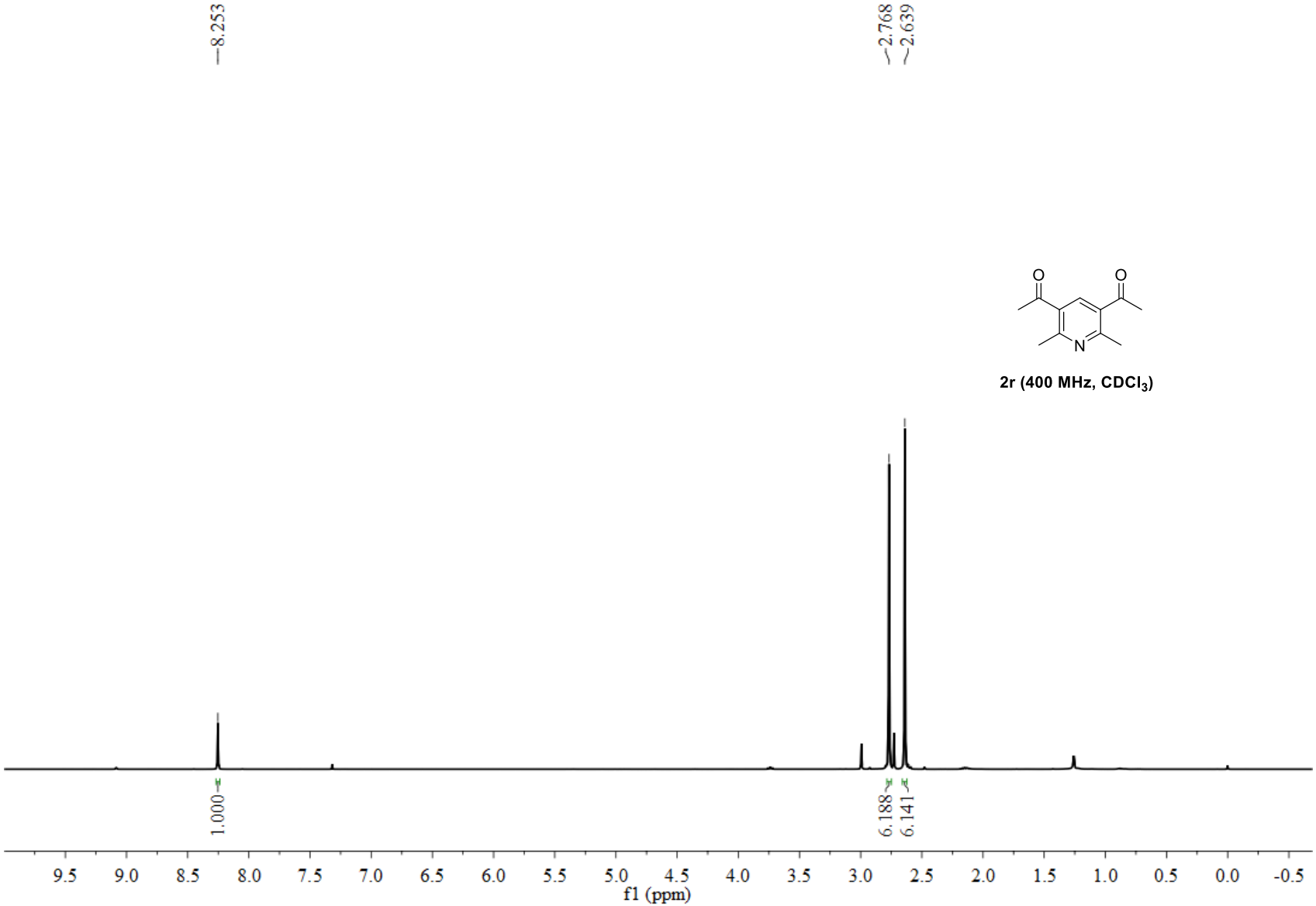


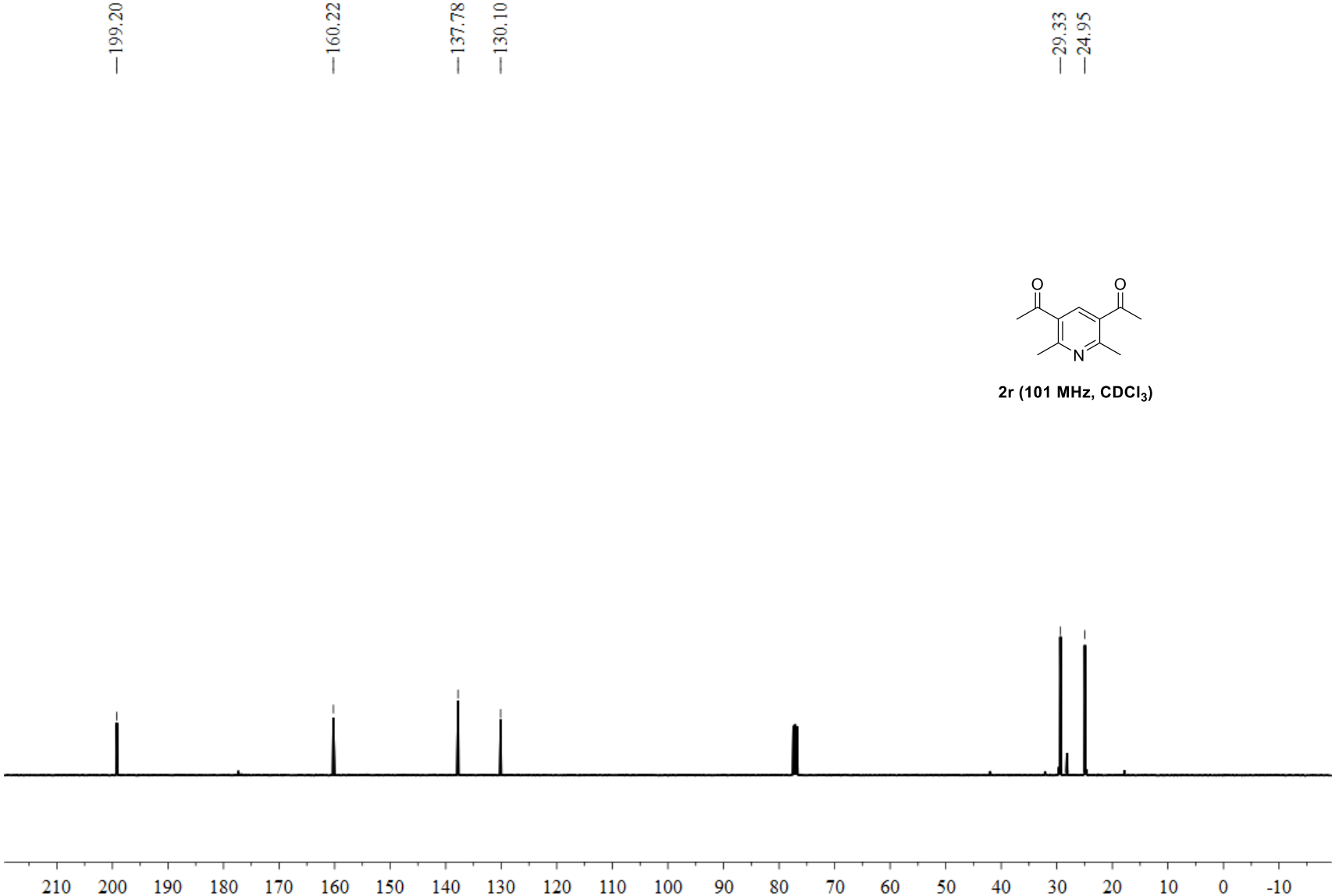
2q (400 MHz, $CDCl_3$)



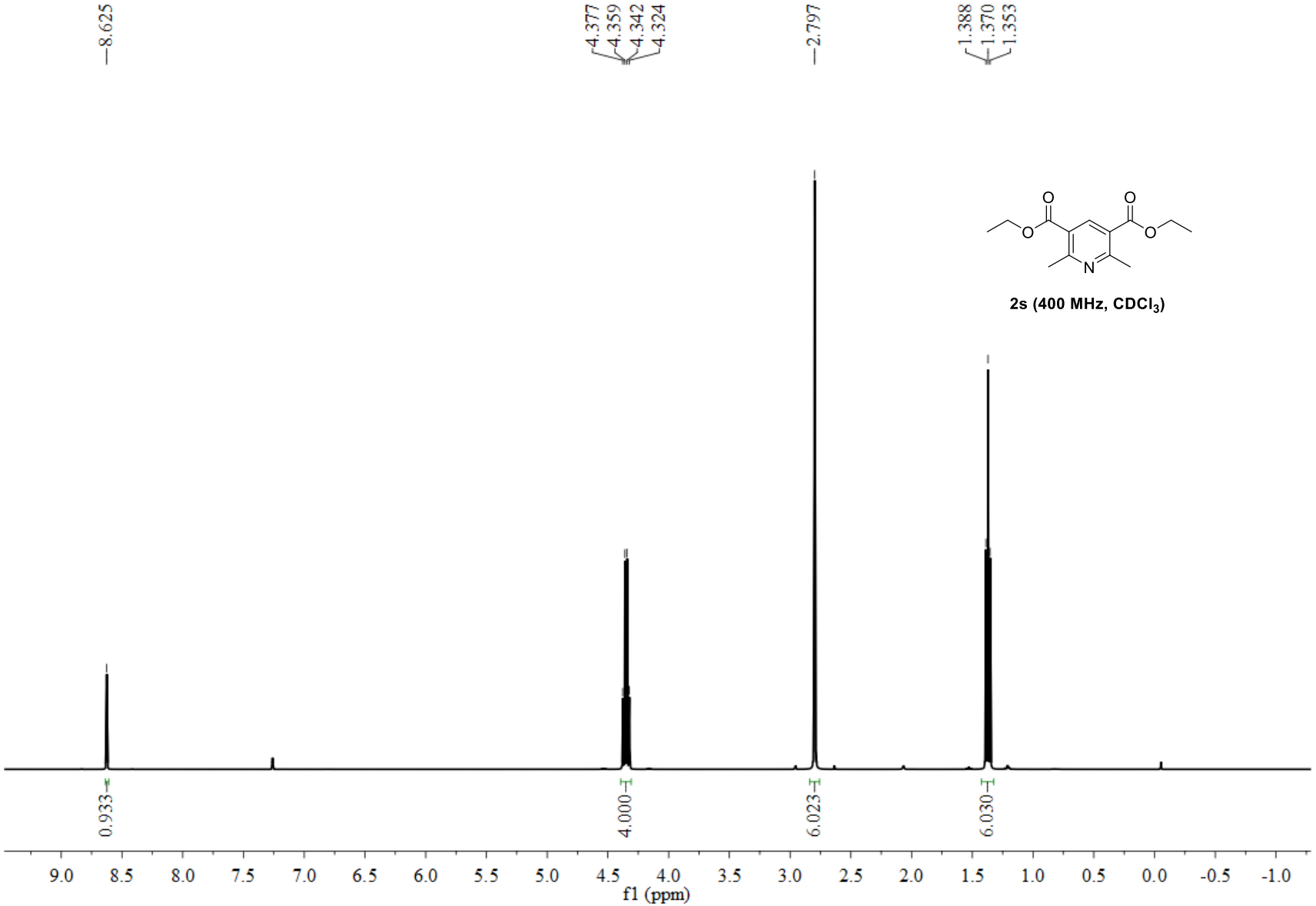


2q (101 MHz, $CDCl_3$)

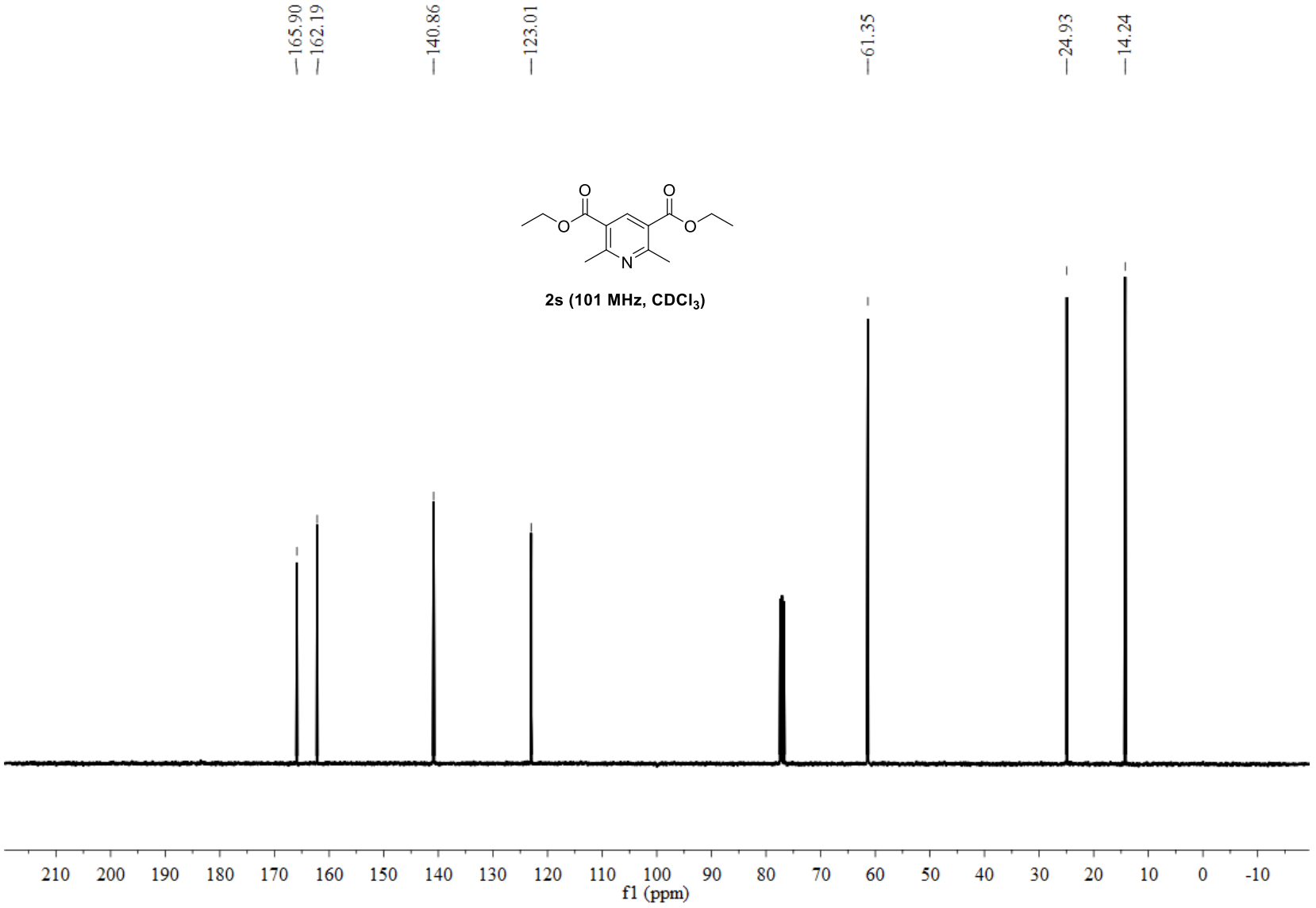

8.253
2.768
2.639
O
O
N
2r (400 MHz, CDCl3)
1.000
6.188
6.141
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

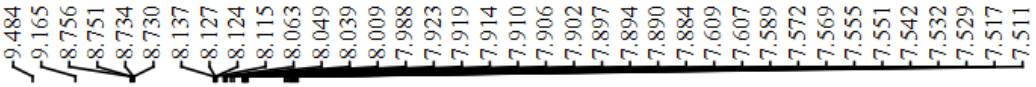


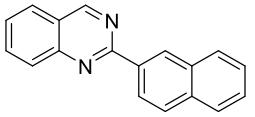
2r (101 MHz, $CDCl_3$)



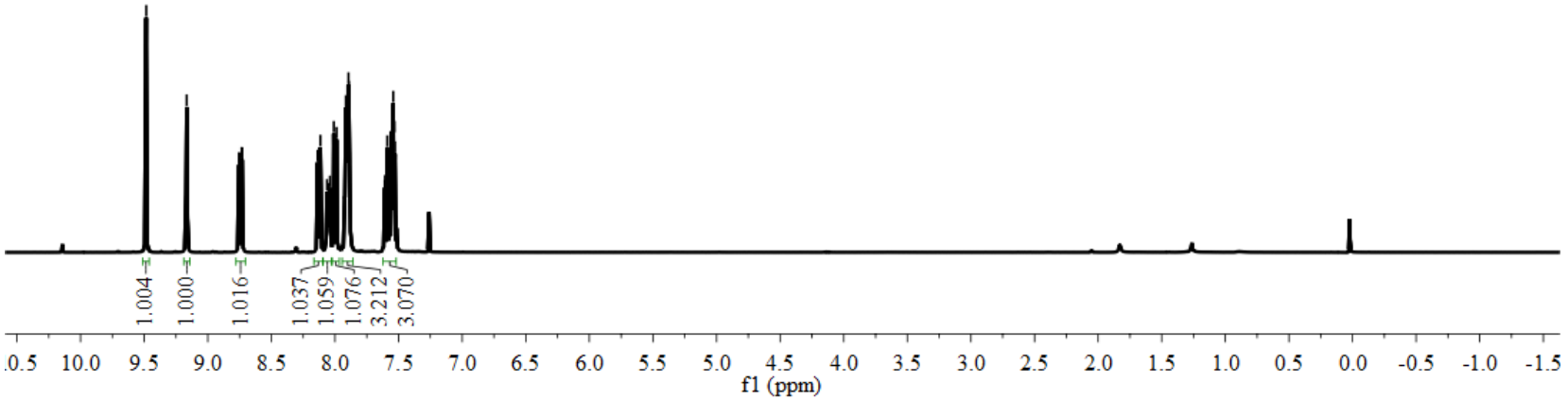
2s (400 MHz, $CDCl_3$)

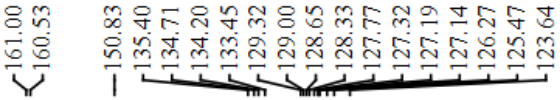

165.90
162.19
140.86
123.01
61.35
24.93
14.24
O
O
O
O
N
2s (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

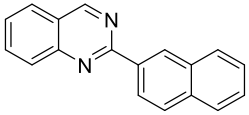




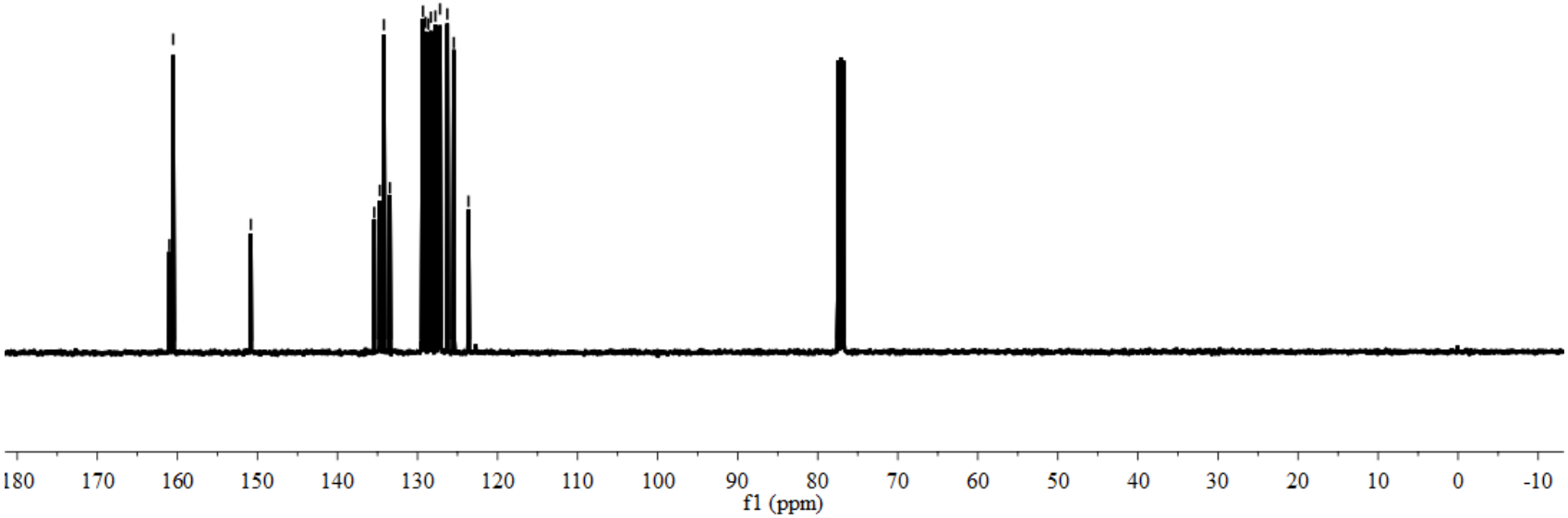
6a (400 MHz, $CDCl_3$)

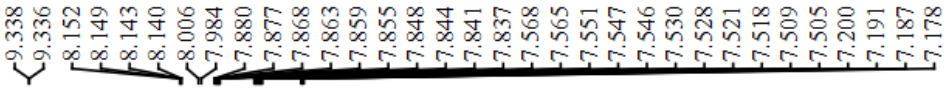


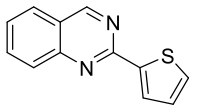




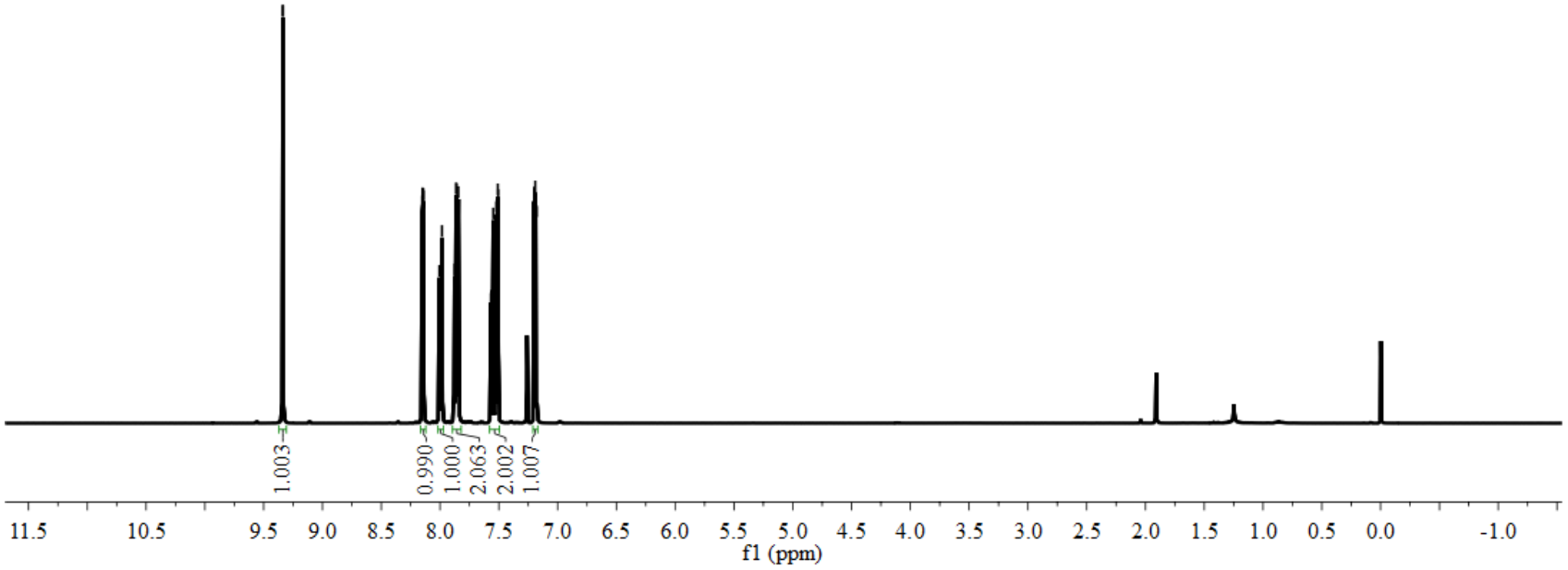
6a (101 MHz, $CDCl_3$)

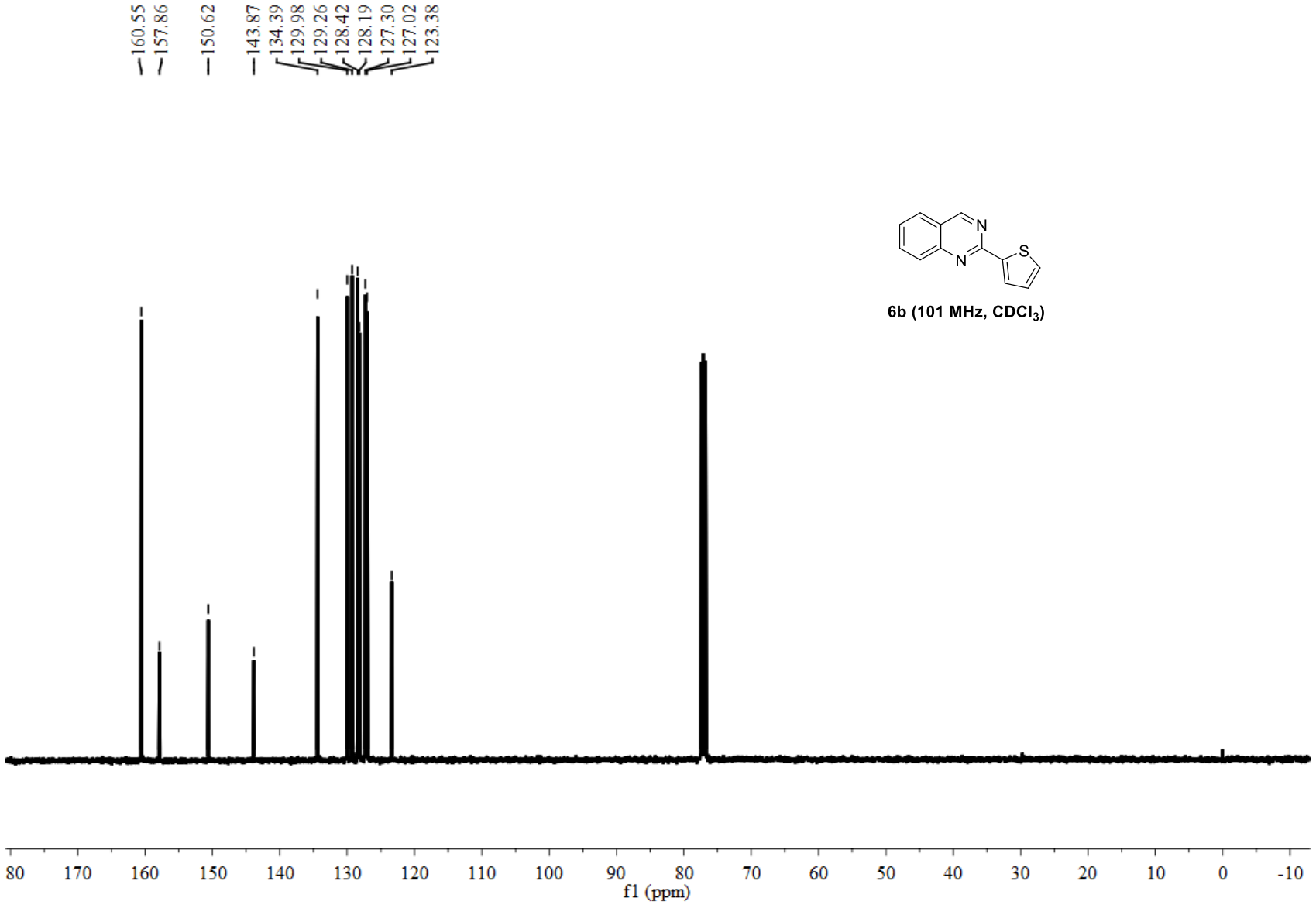




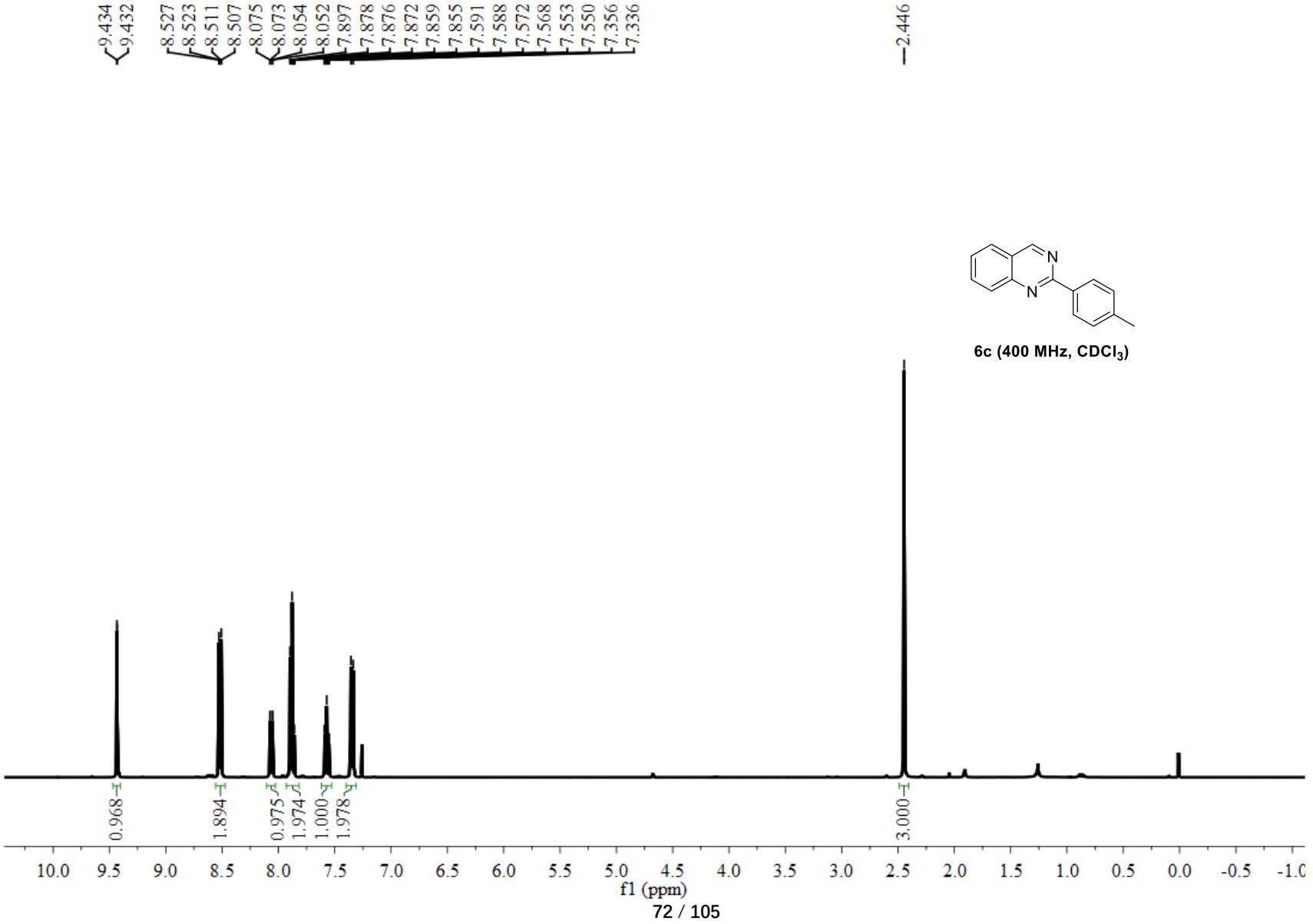


6b (400 MHz, $CDCl_3$)

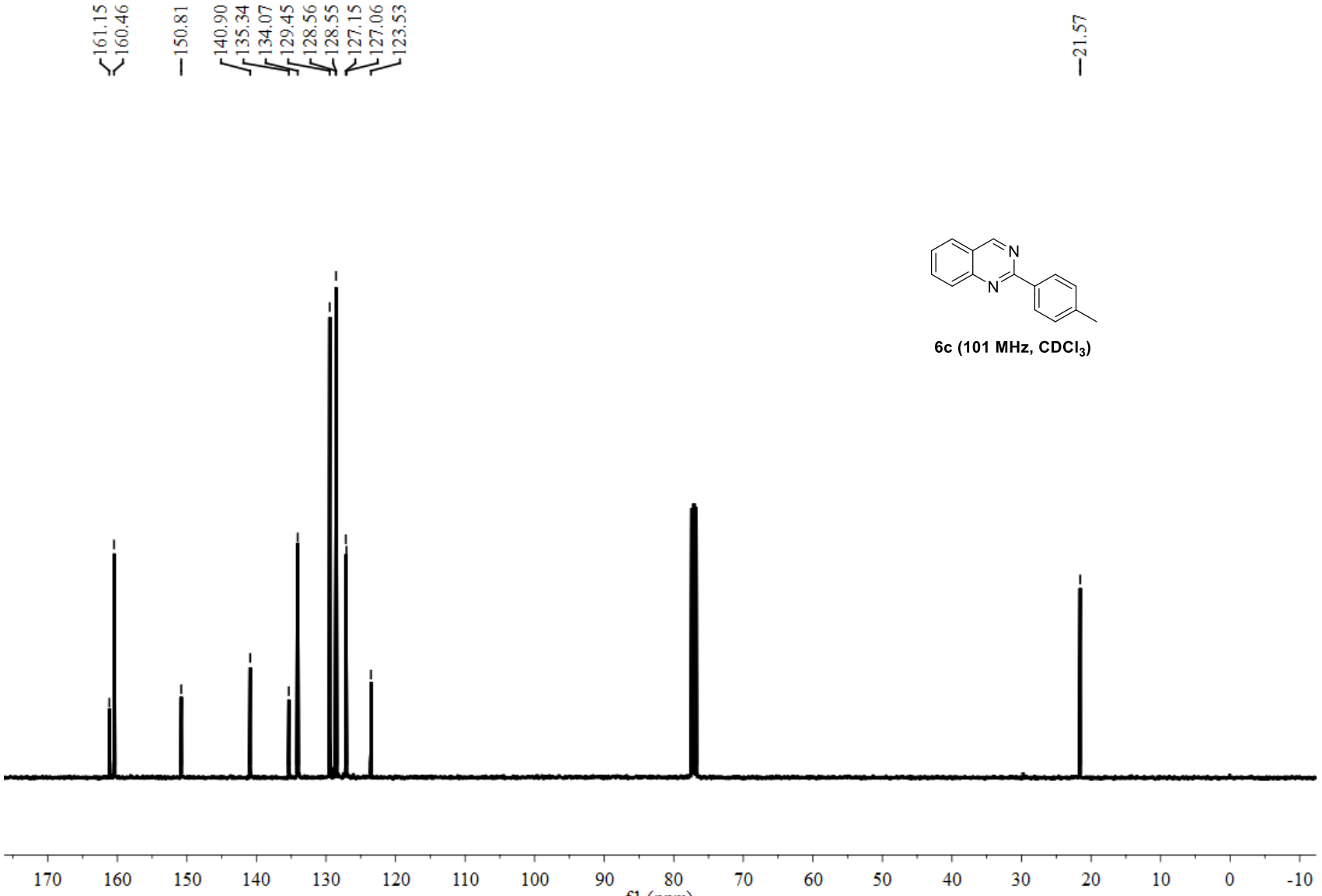




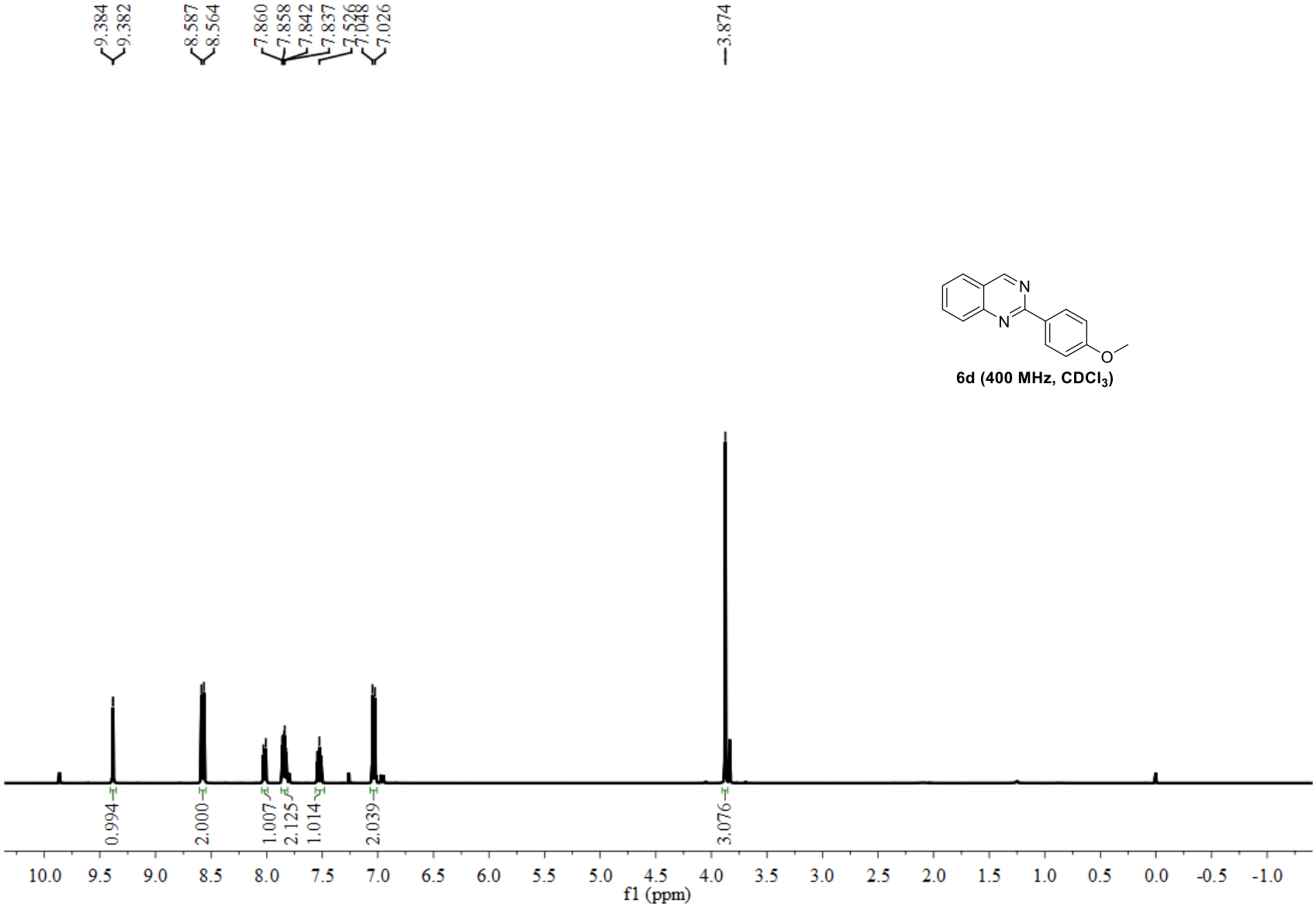
6b (101 MHz, $CDCl_3$)



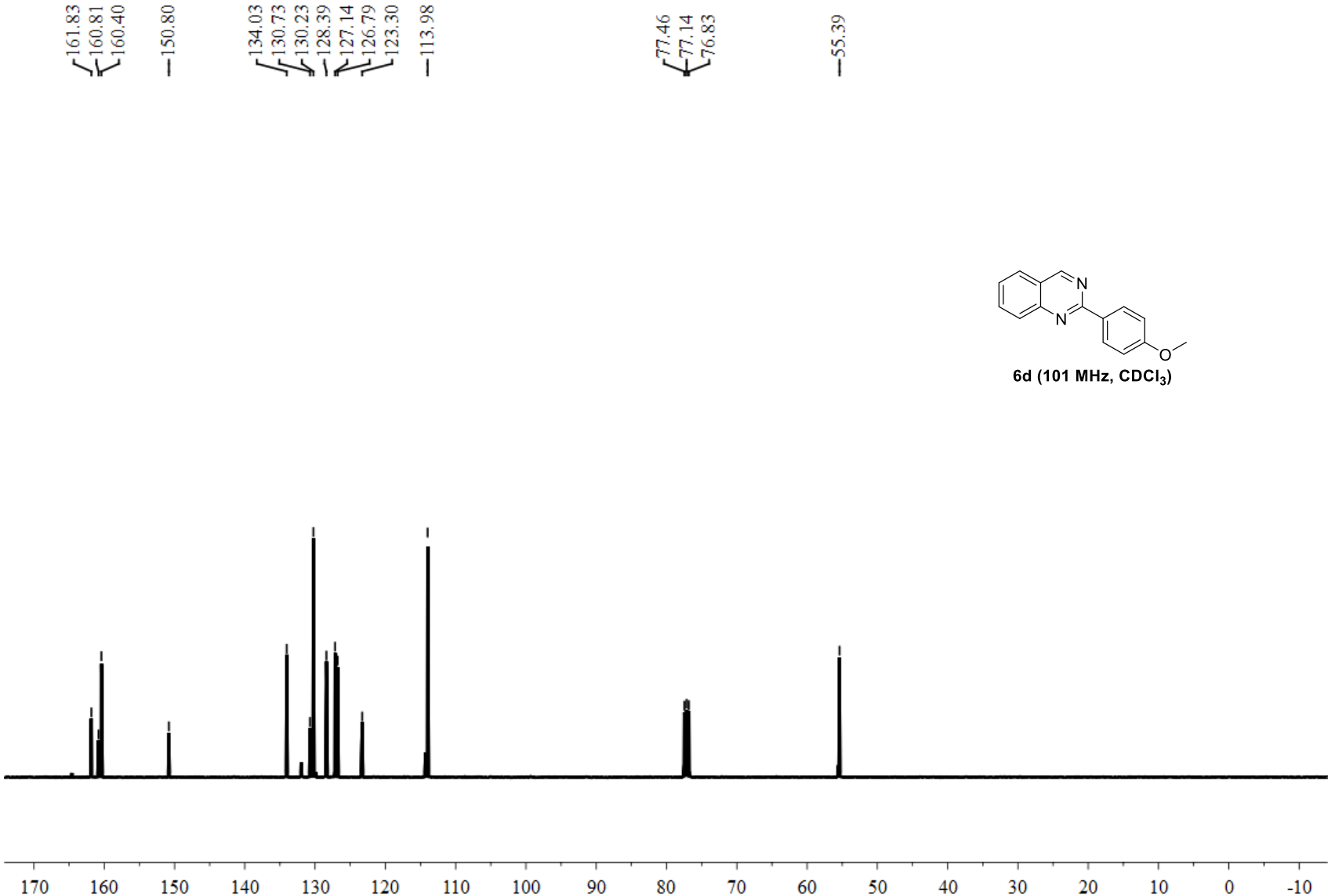
6c (400 MHz, $CDCl_3$)



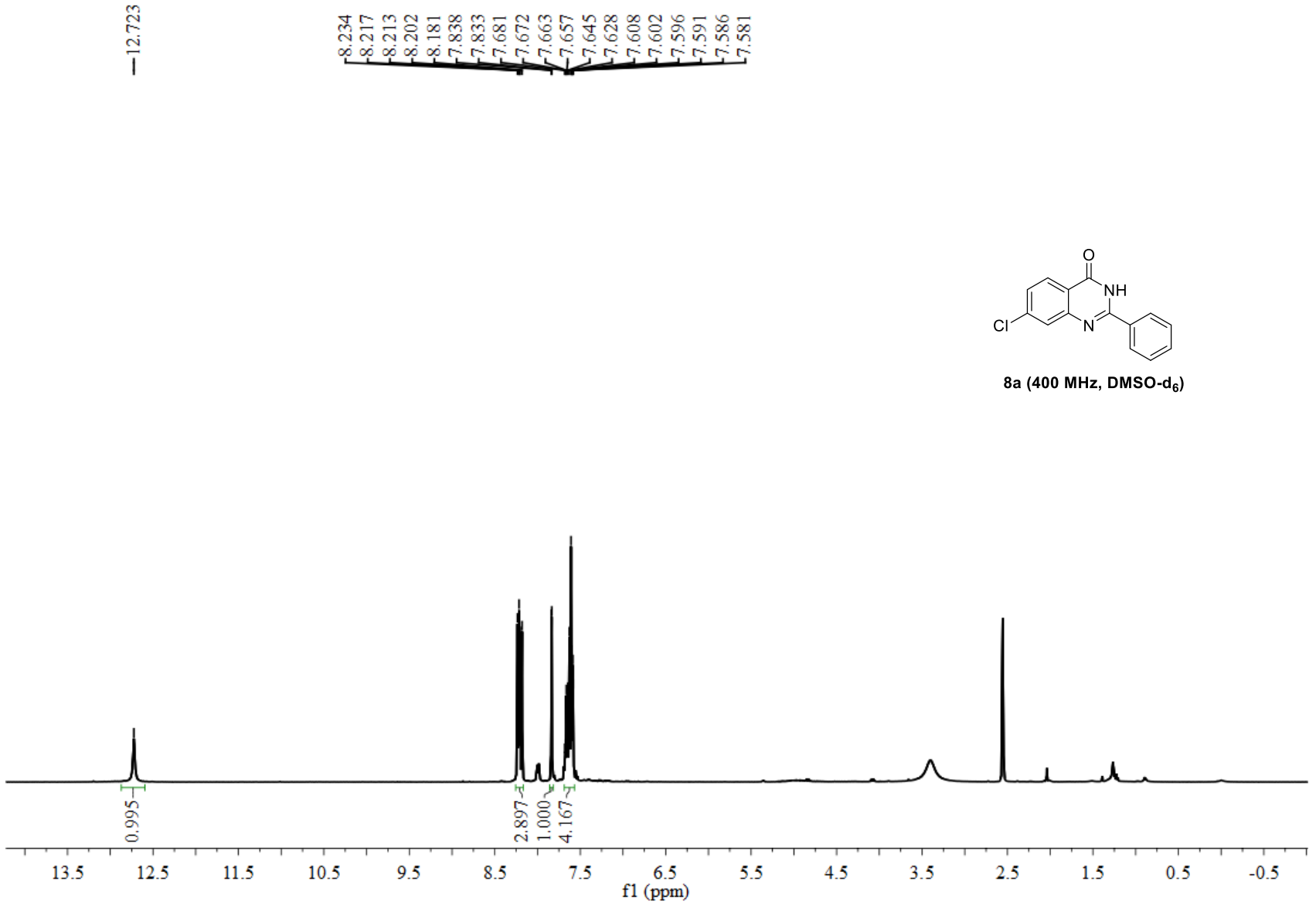
6c (101 MHz, $CDCl_3$)



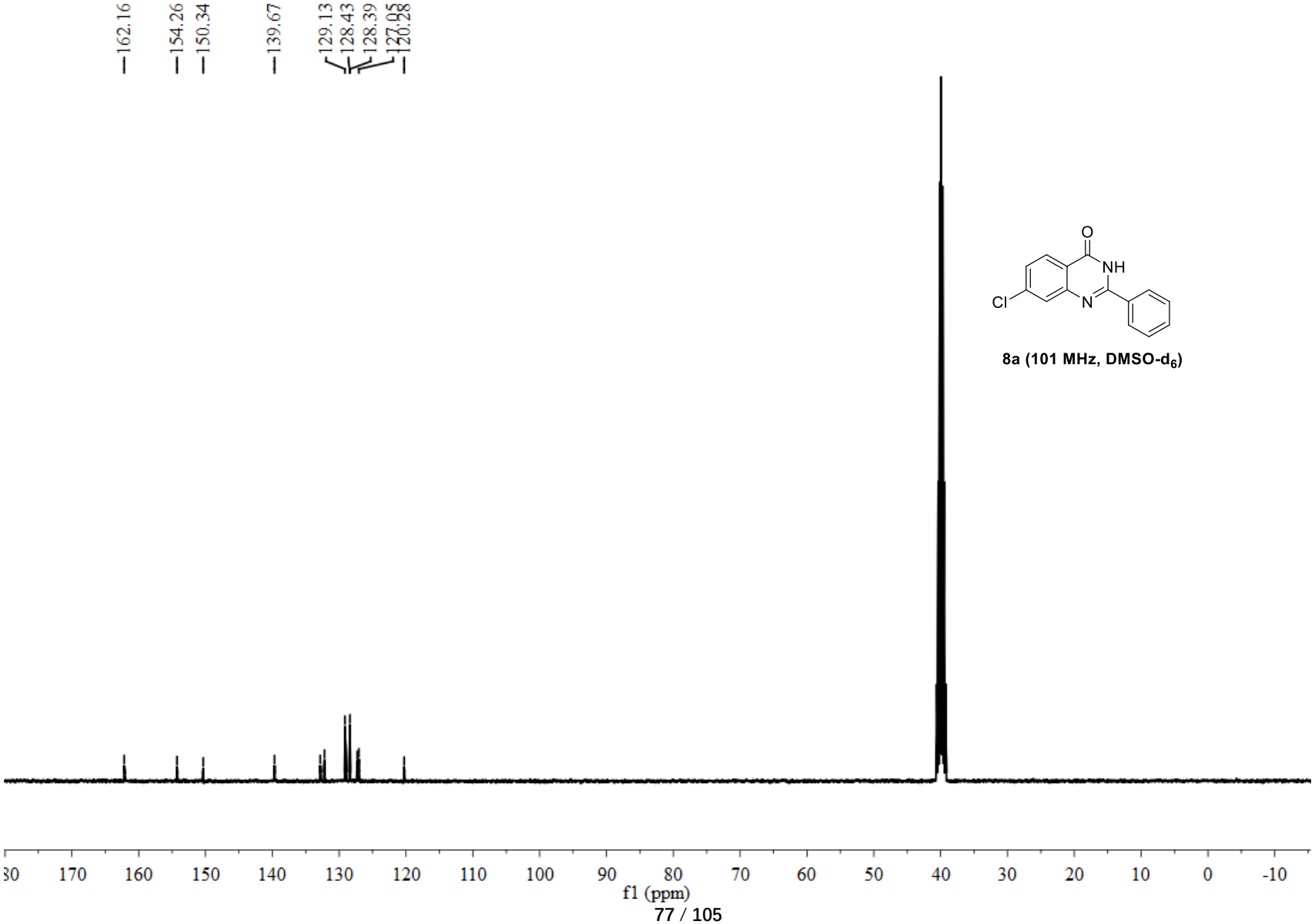
6d (400 MHz, $CDCl_3$)

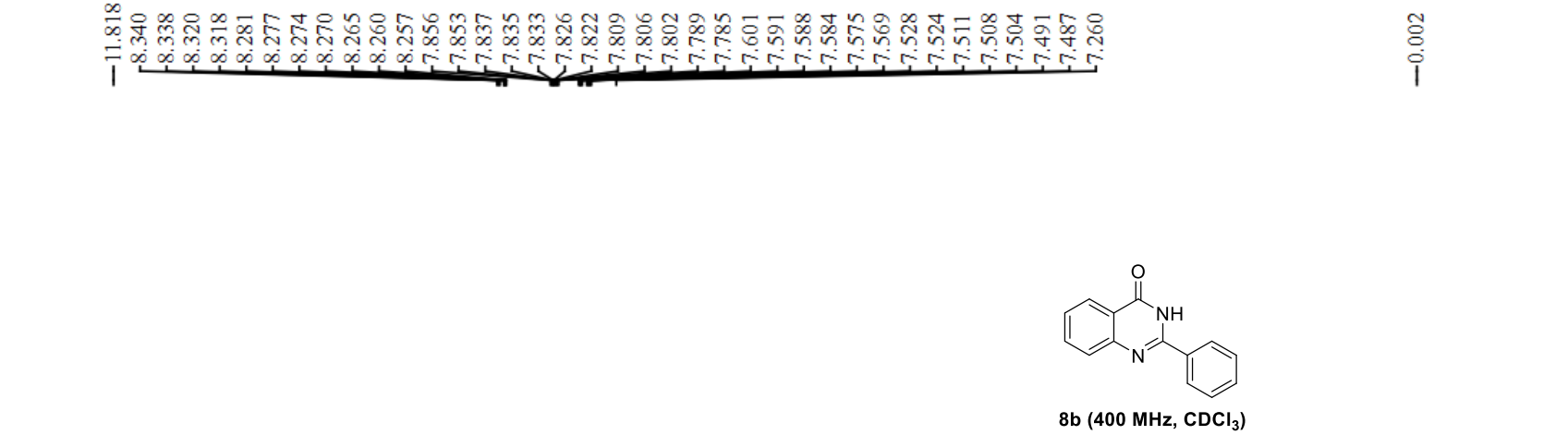


6d (101 MHz, $CDCl_3$)

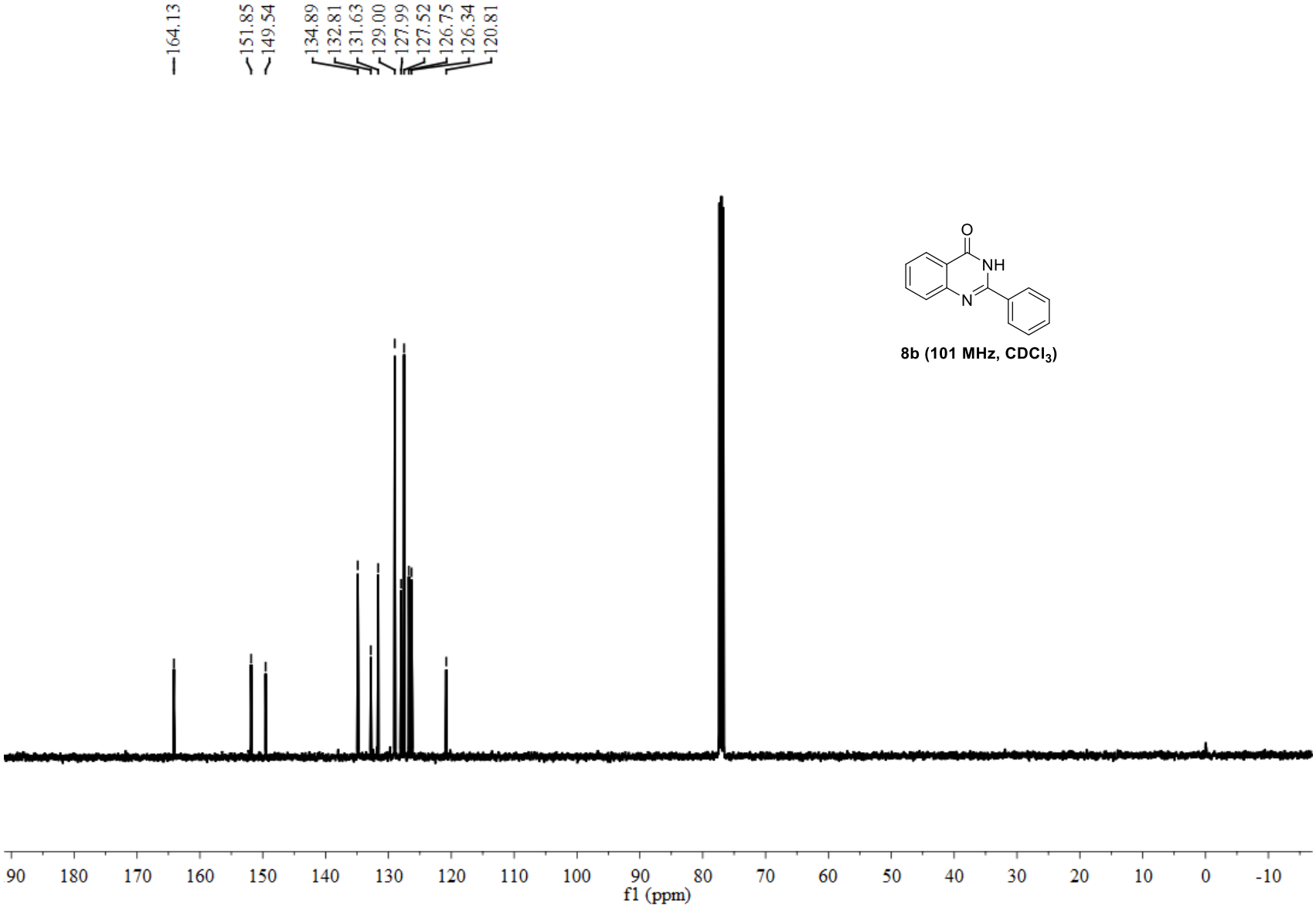


8a (400 MHz, DMSO-d_6)

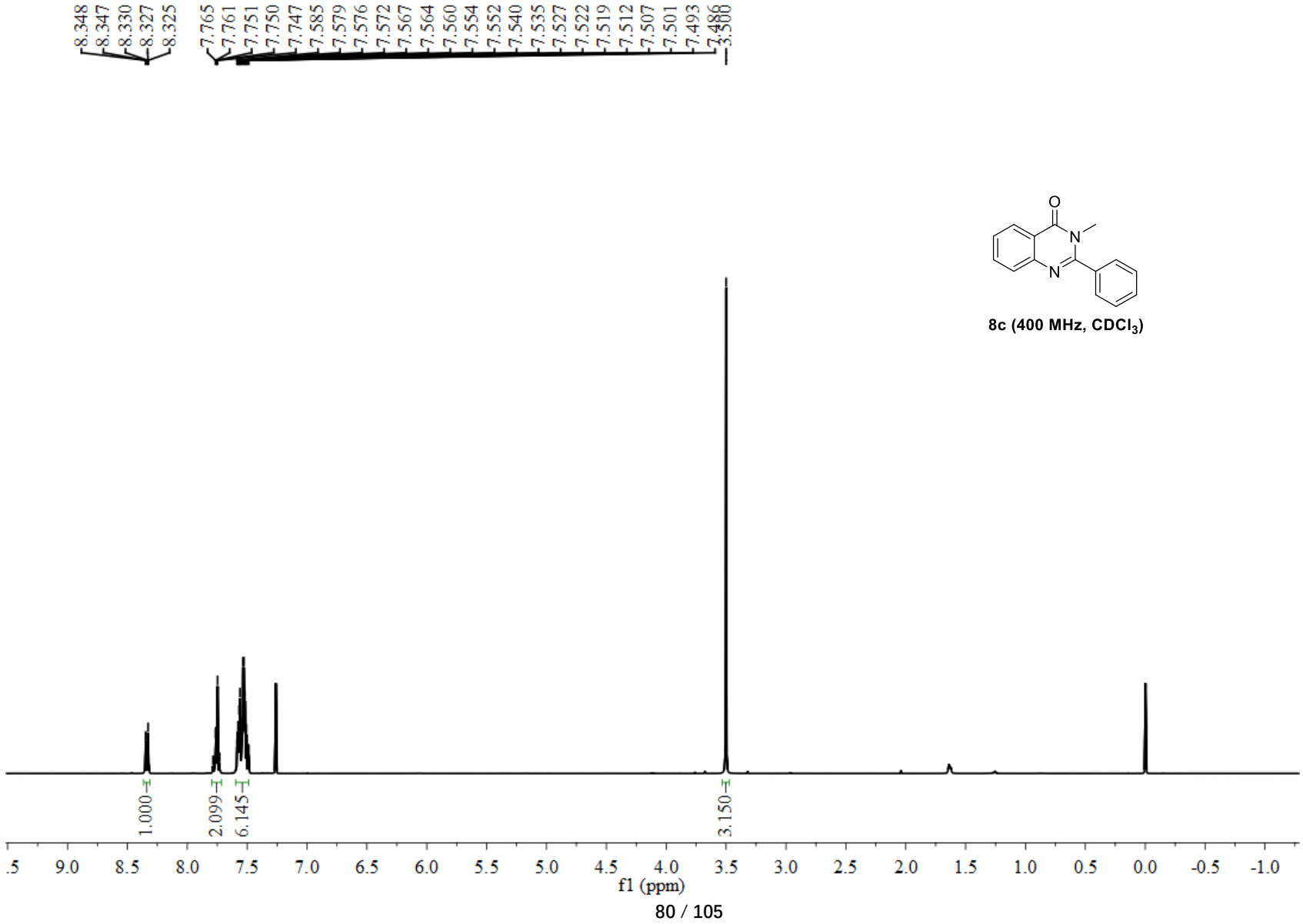

162.16
154.26
150.34
139.67
129.13
128.43
128.39
127.95
120.28
O
NH
Cl
N
8a (101 MHz, DMSO-d6)
f1 (ppm)

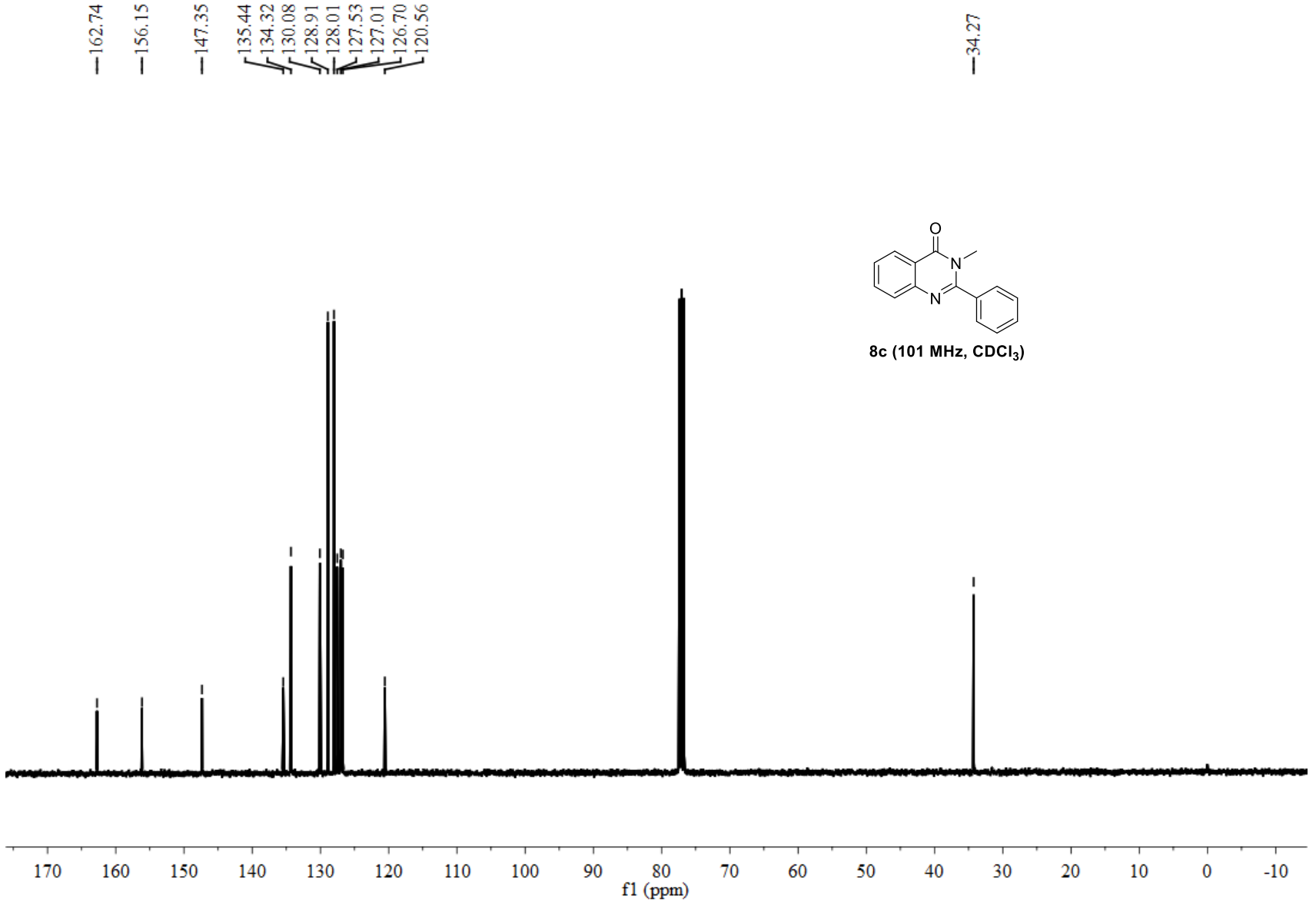


8b (400 MHz, $CDCl_3$)

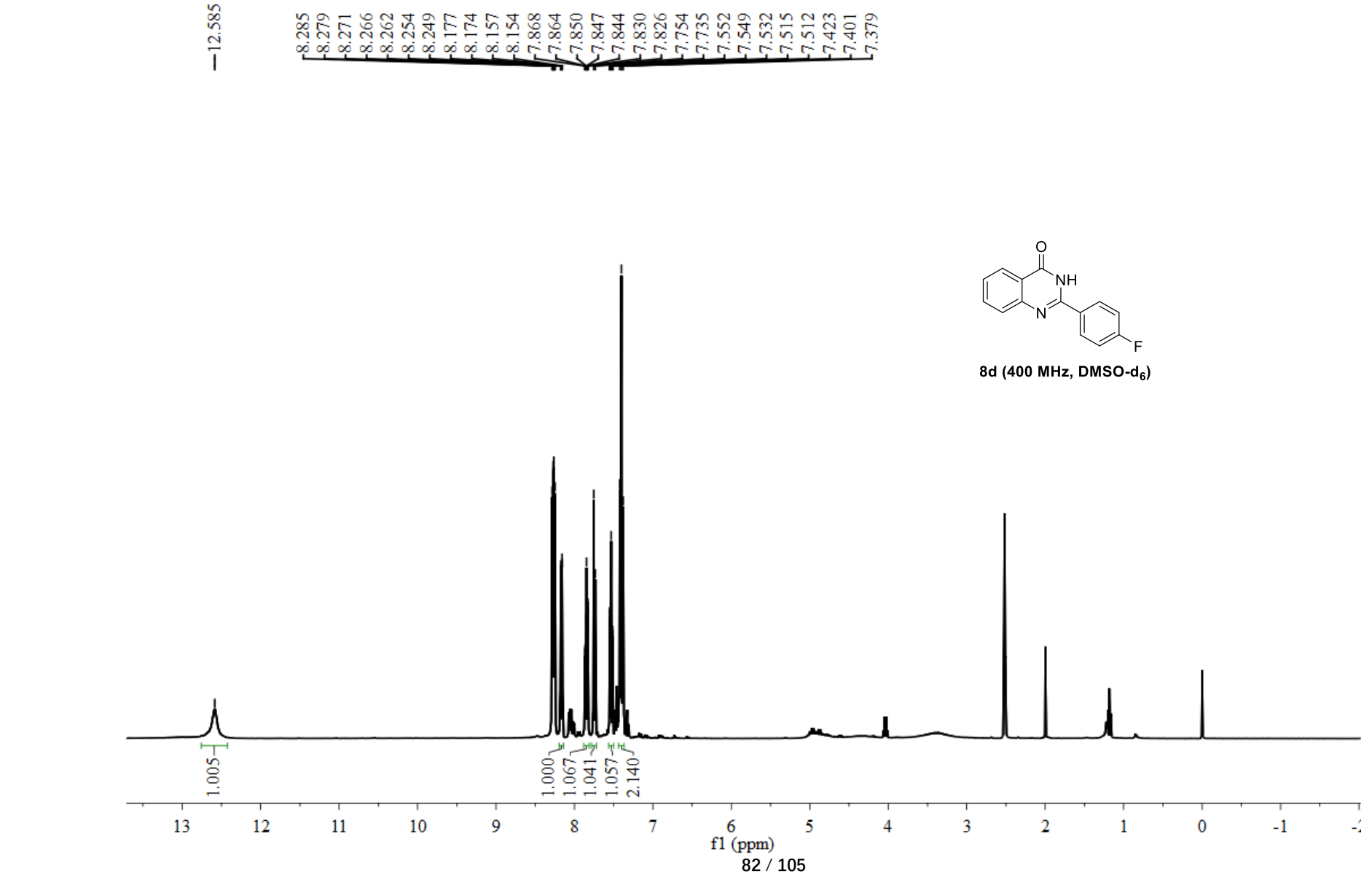


8b (101 MHz, $CDCl_3$)

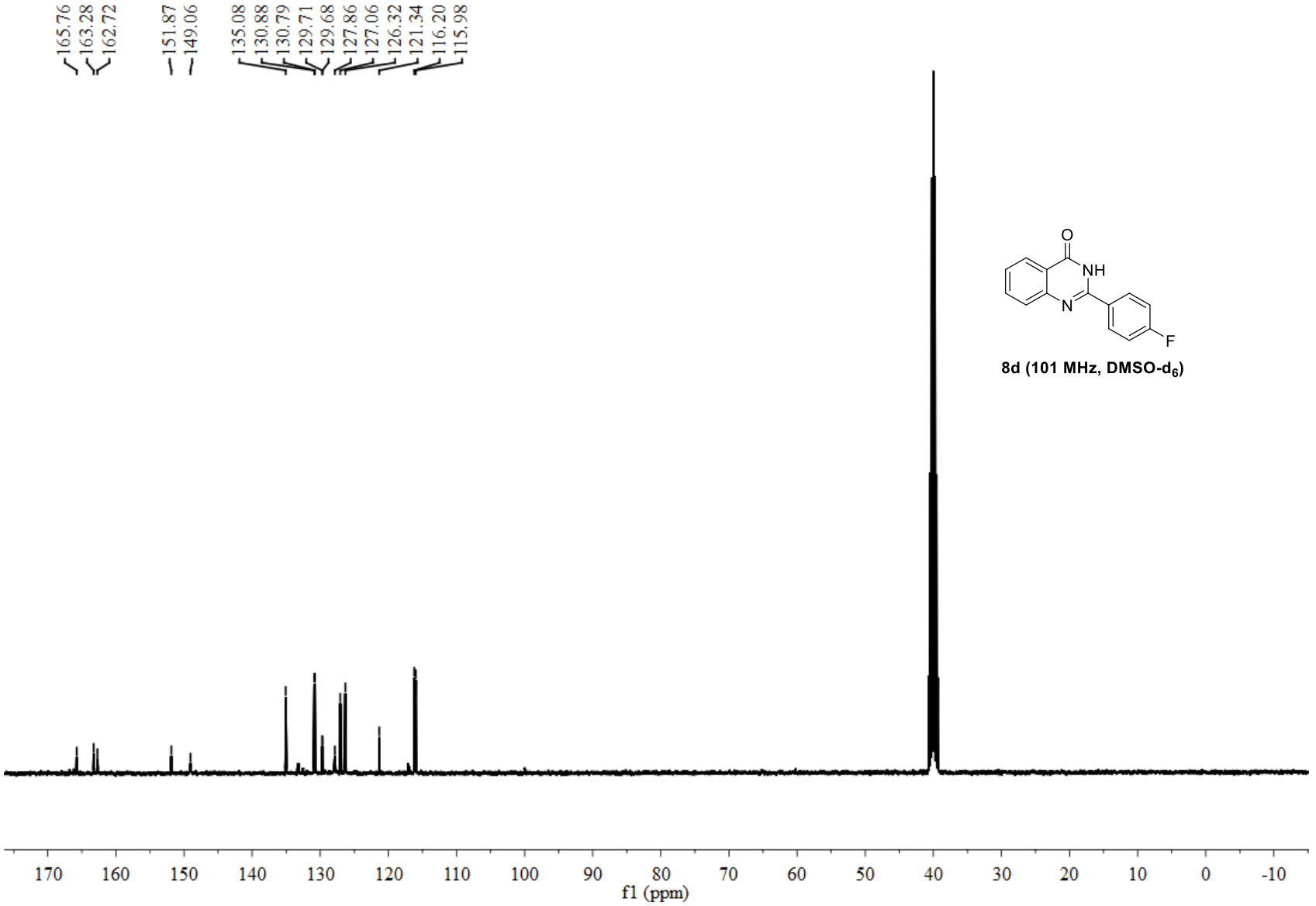

8.348
8.347
8.330
8.327
8.325
7.765
7.761
7.751
7.750
7.747
7.585
7.579
7.576
7.572
7.567
7.564
7.560
7.554
7.552
7.540
7.535
7.527
7.522
7.519
7.512
7.507
7.501
7.493
3.500
O
N
N
8c (400 MHz, CDCl3)
1.000
2.099
6.145
3.150
f1 (ppm)

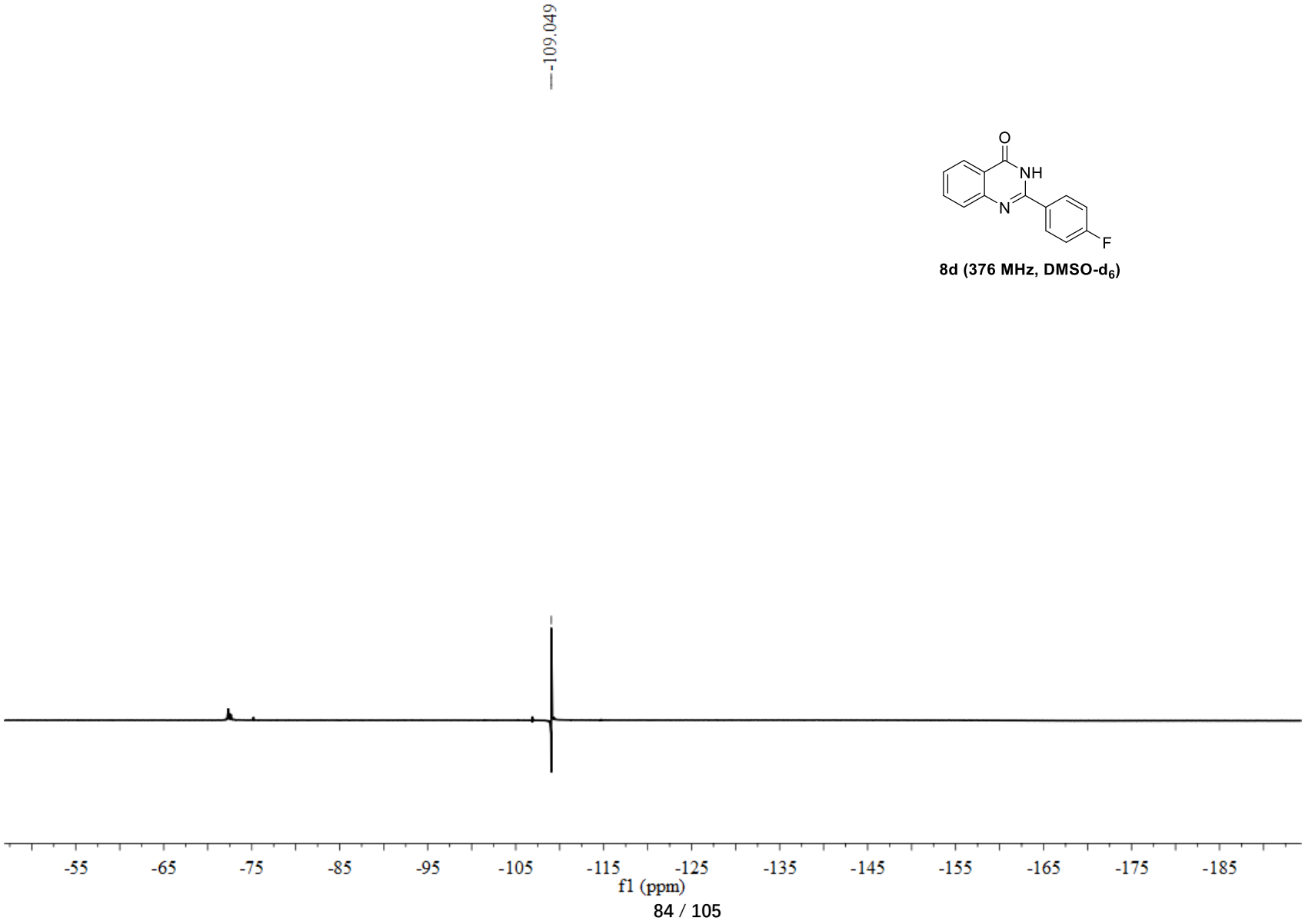


8c (101 MHz, $CDCl_3$)

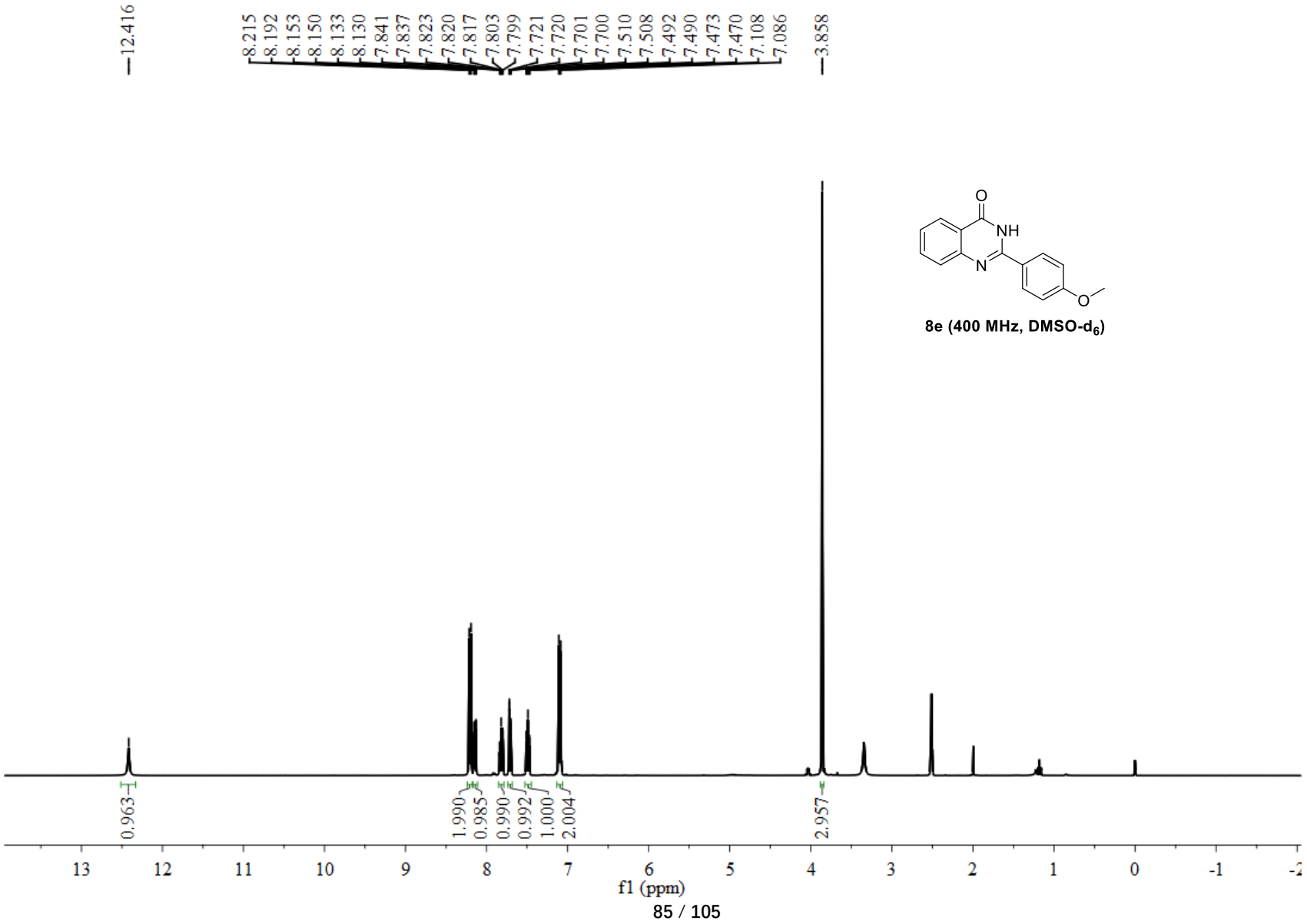


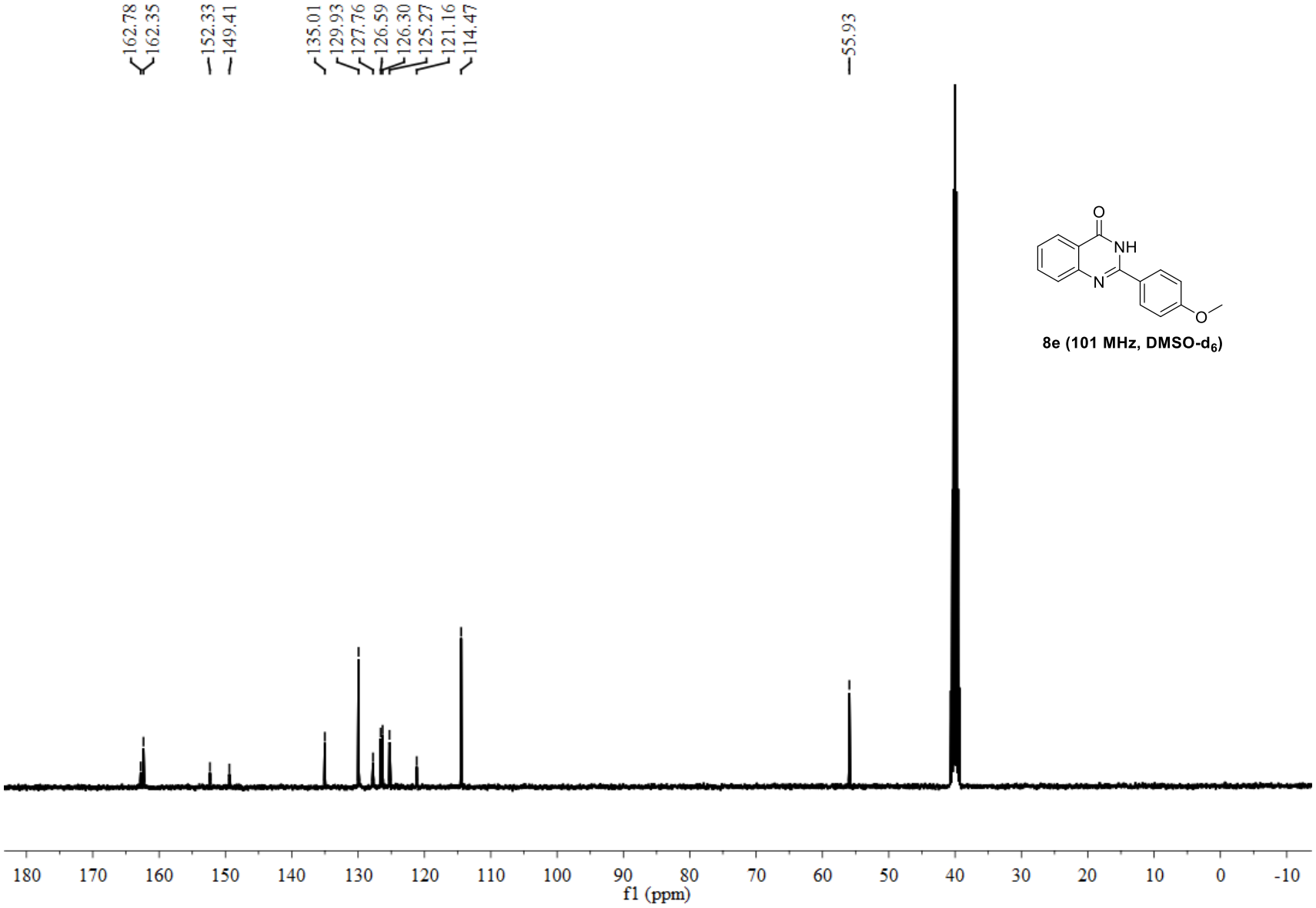
8d (400 MHz, DMSO-d_6)


165.76
163.28
162.72
151.87
149.06
135.08
130.88
130.79
129.71
129.68
127.86
127.06
126.32
121.34
116.20
115.98
O
NH
N
F
8d (101 MHz, DMSO-d6)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

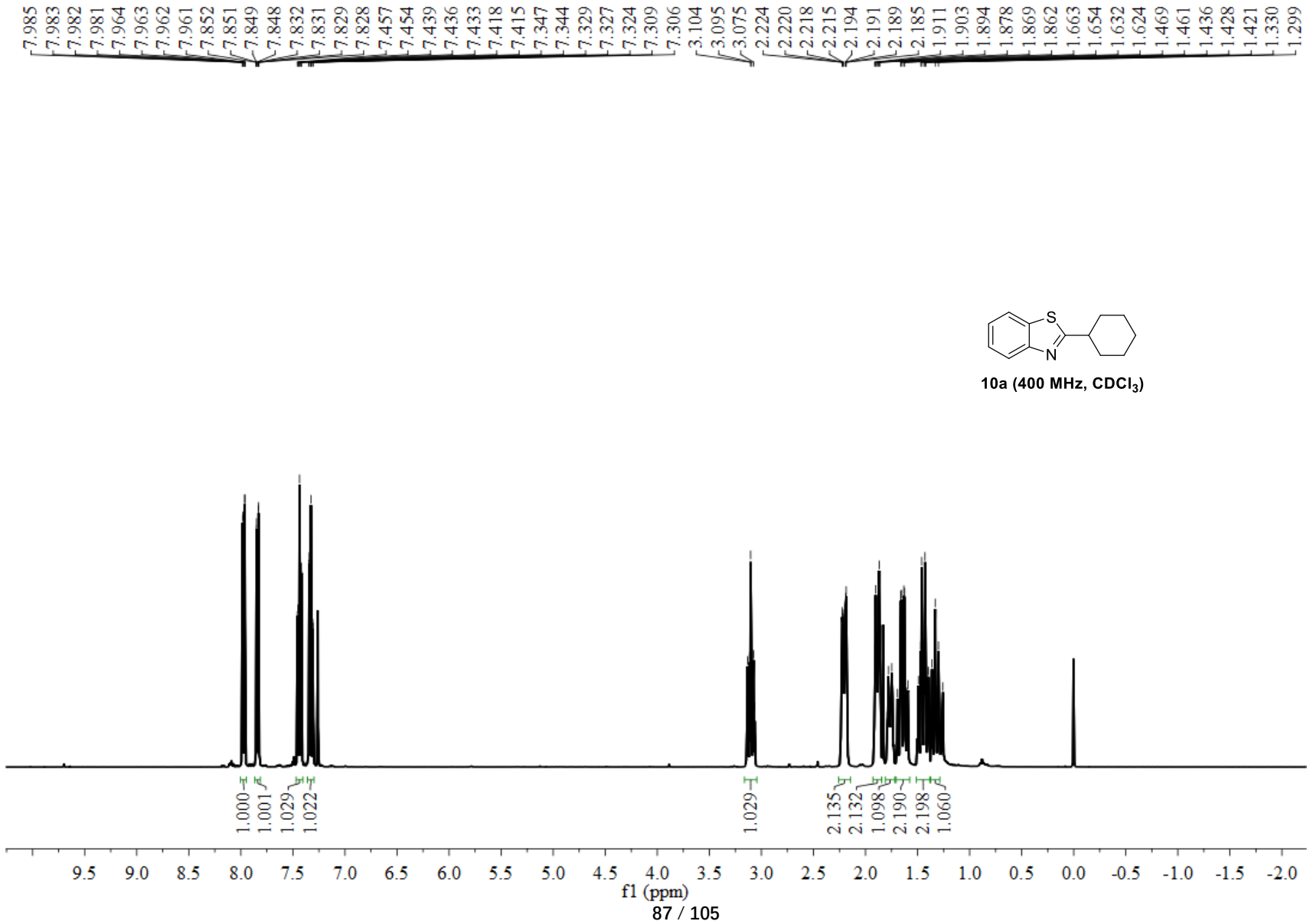


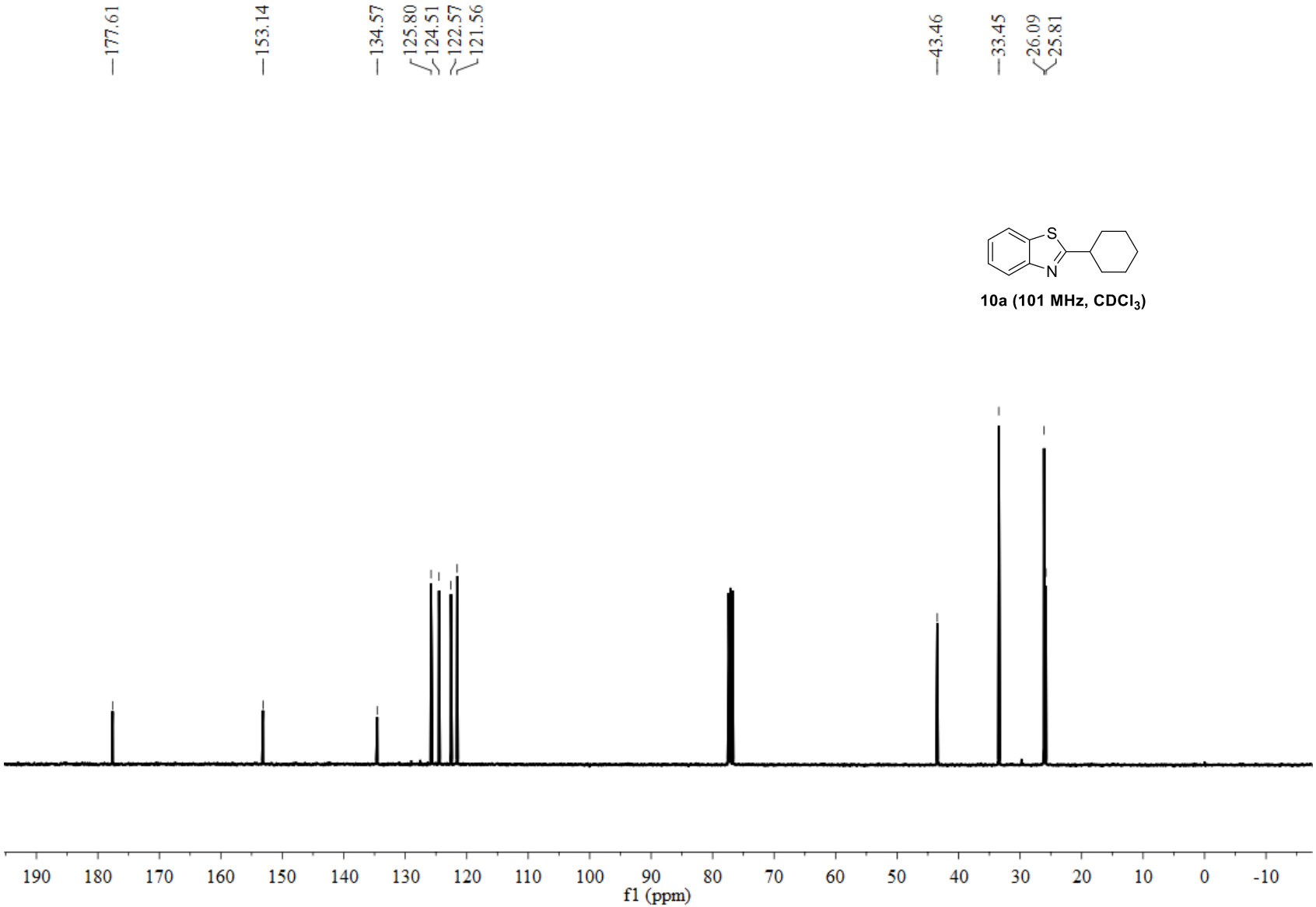
8d (376 MHz, DMSO-d_6)


12.416
8.215
8.192
8.153
8.150
8.133
8.130
7.841
7.837
7.823
7.820
7.817
7.803
7.799
7.721
7.720
7.701
7.700
7.510
7.508
7.492
7.490
7.473
7.470
7.108
7.086
3.858
O
NH
N
O
8e (400 MHz, DMSO-d6)
0.963
1.990
0.985
0.990
0.992
1.000
2.004
2.957
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

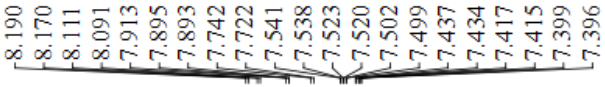


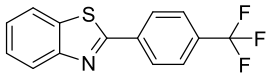
8e (101 MHz, DMSO-d_6)


7.985
7.983
7.982
7.981
7.964
7.963
7.962
7.961
7.852
7.851
7.849
7.848
7.832
7.831
7.829
7.828
7.457
7.454
7.439
7.436
7.433
7.418
7.415
7.347
7.344
7.329
7.327
7.324
7.309
7.306
3.104
3.095
3.075
2.224
2.220
2.218
2.215
2.194
2.191
2.189
2.185
1.911
1.903
1.894
1.878
1.869
1.862
1.663
1.654
1.632
1.624
1.469
1.461
1.436
1.428
1.421
1.330
1.299
S
N
10a (400 MHz, CDCl3)
1.000
1.001
1.029
1.022
1.029
2.135
2.132
1.098
2.190
2.198
1.060
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
-1.5
-2.0
f1 (ppm)

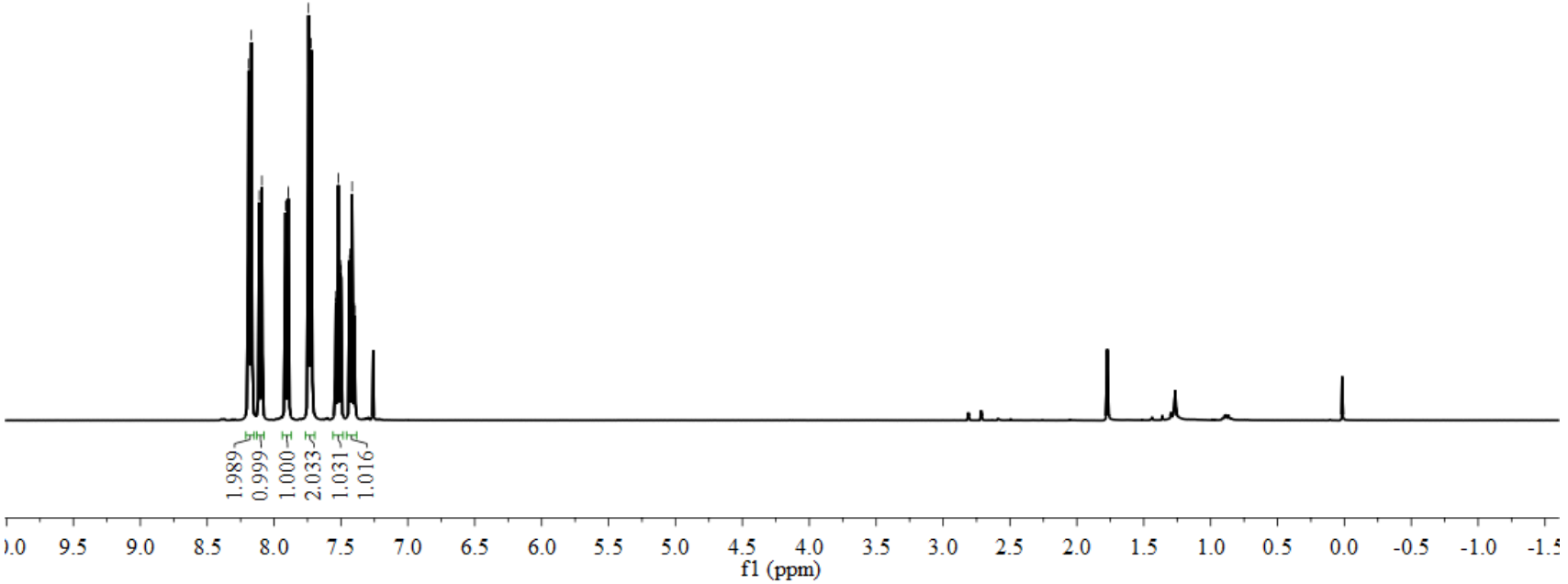


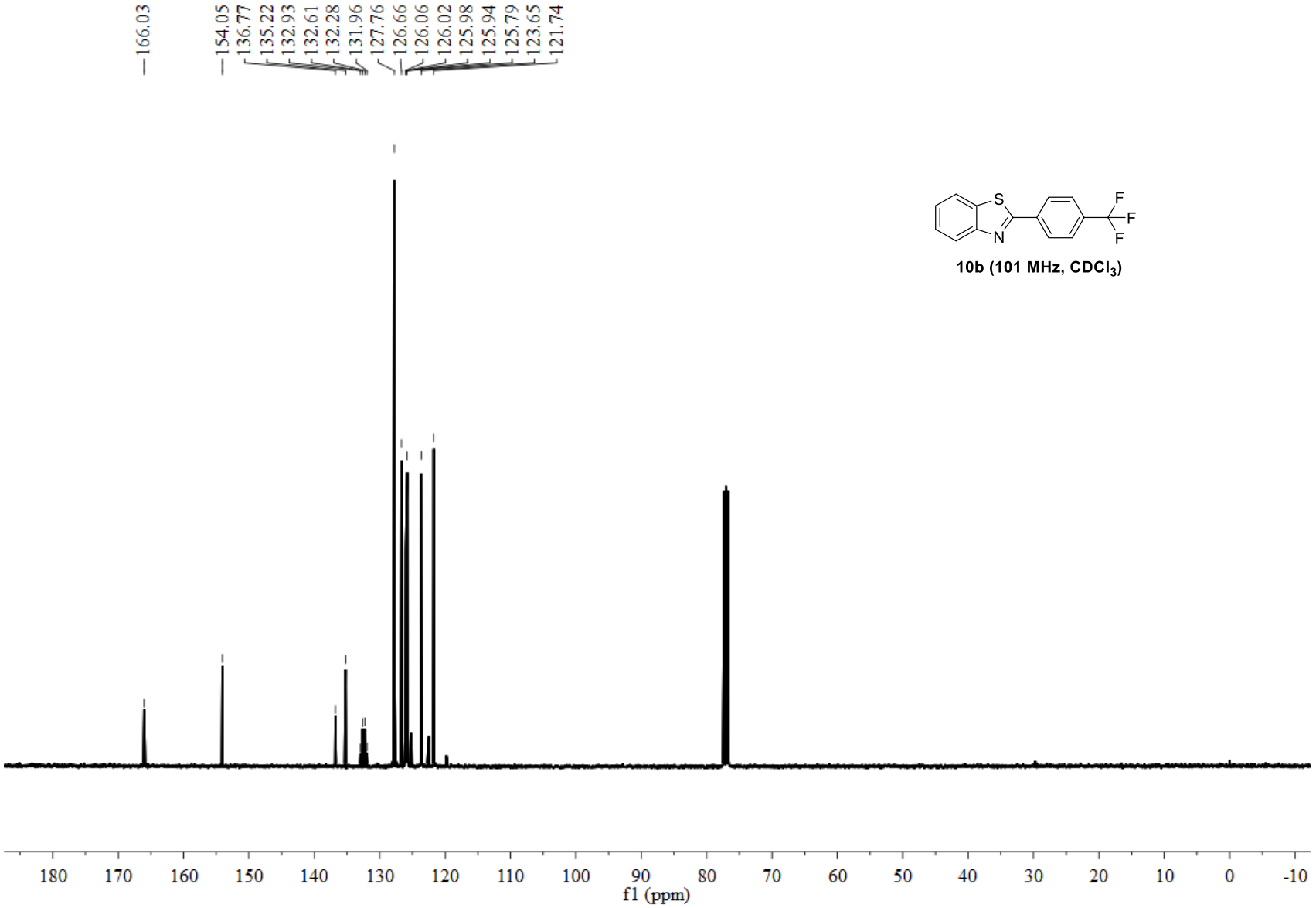
10a (101 MHz, $CDCl_3$)



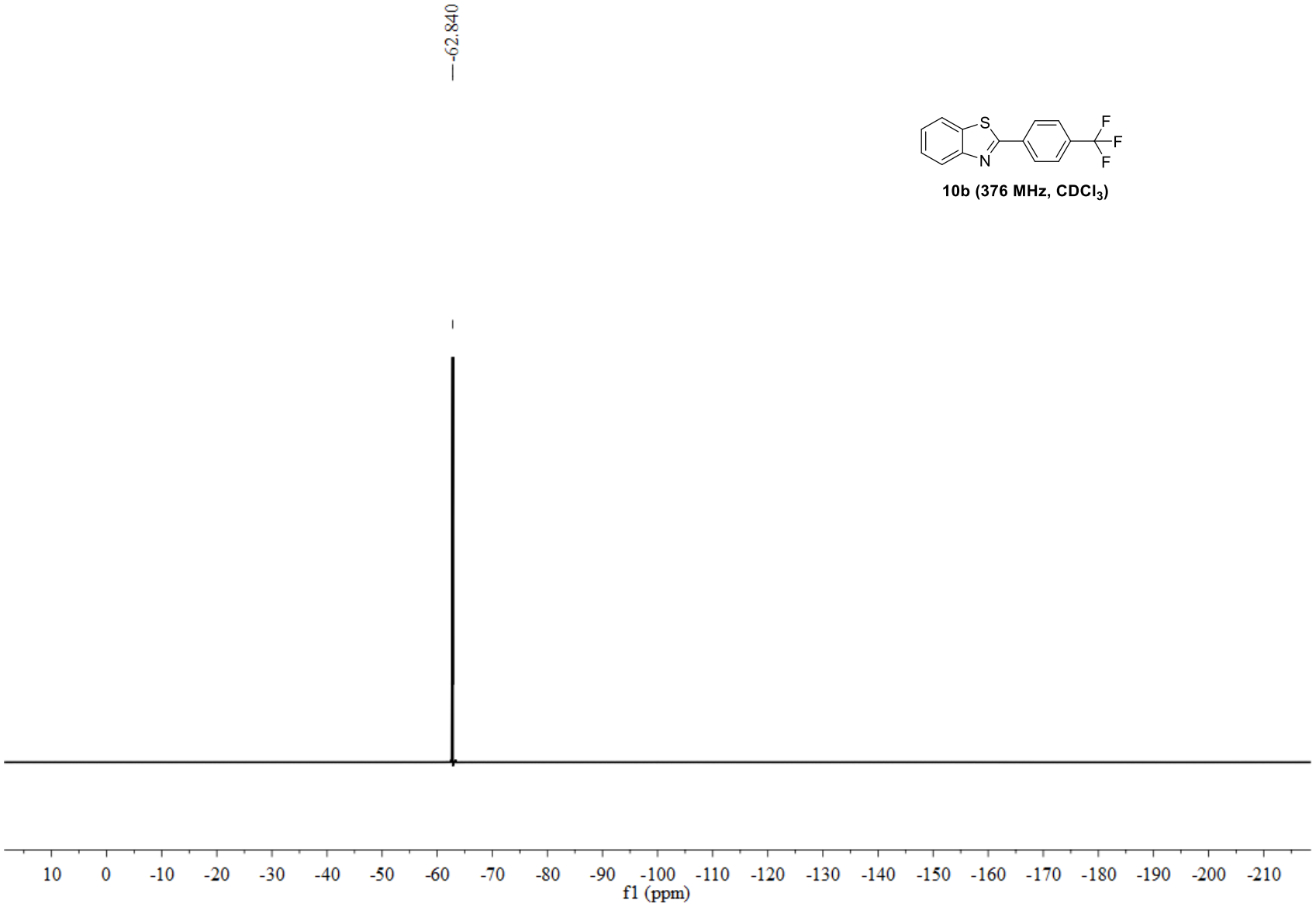


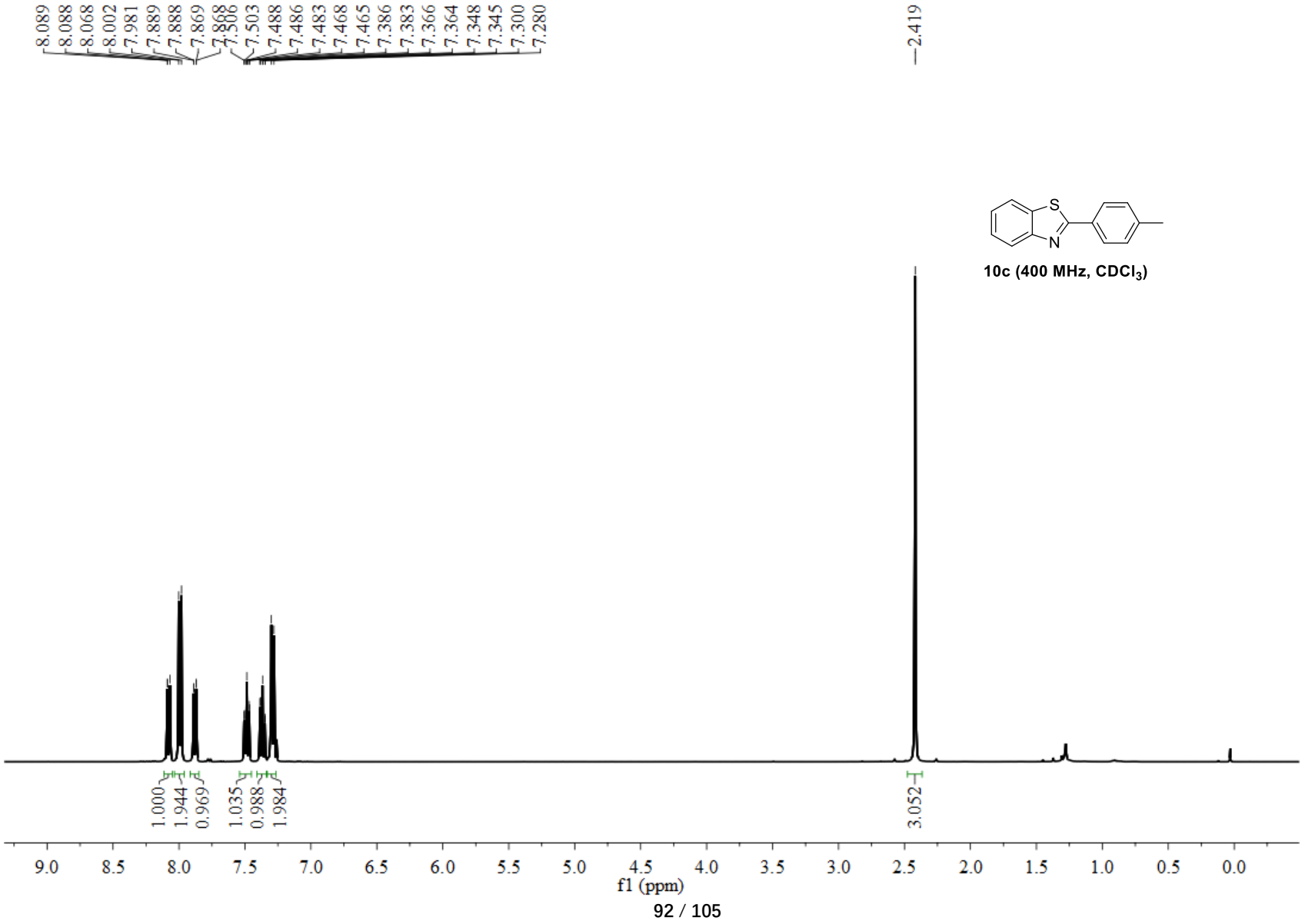
10b (400 MHz, $CDCl_3$)

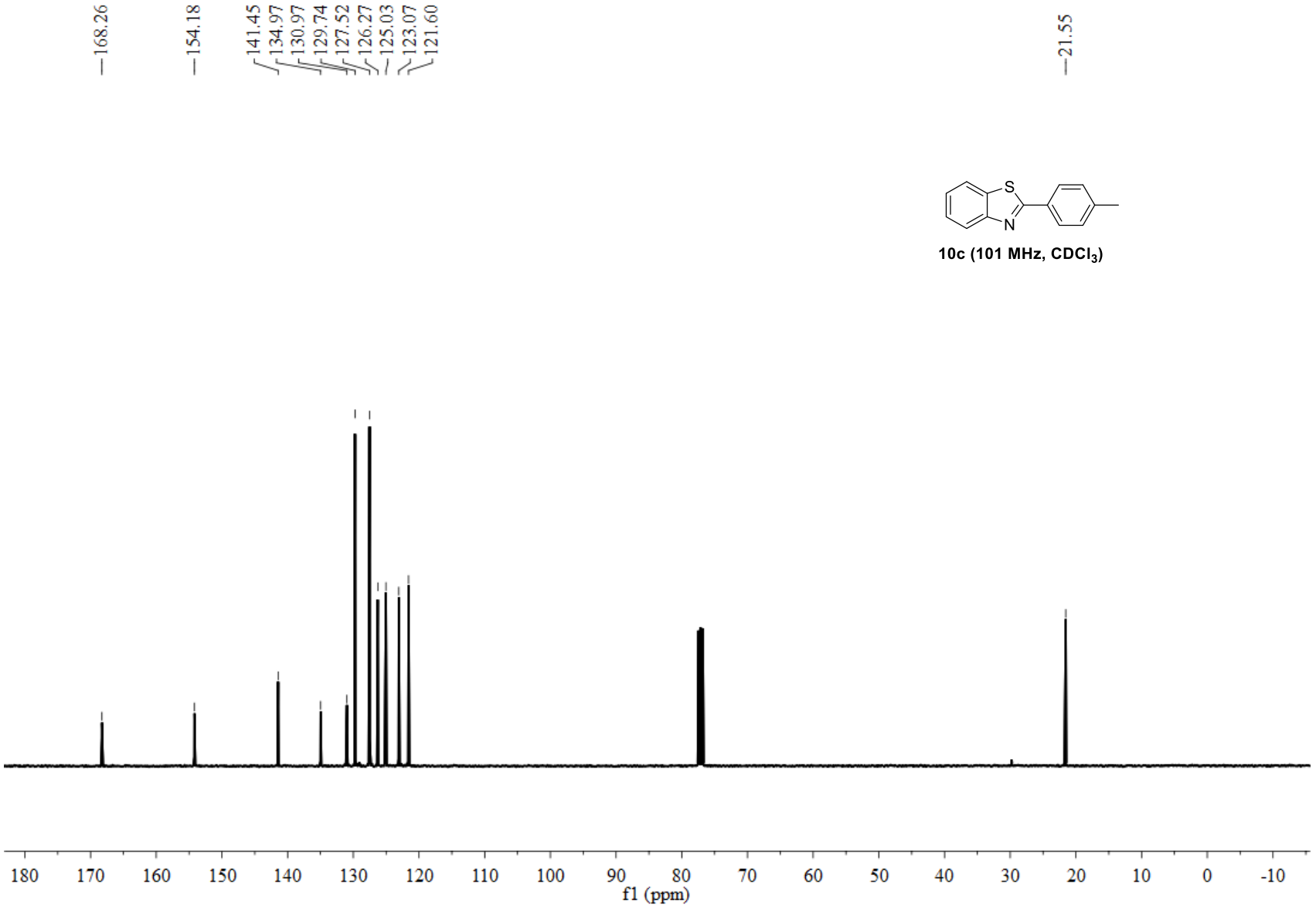




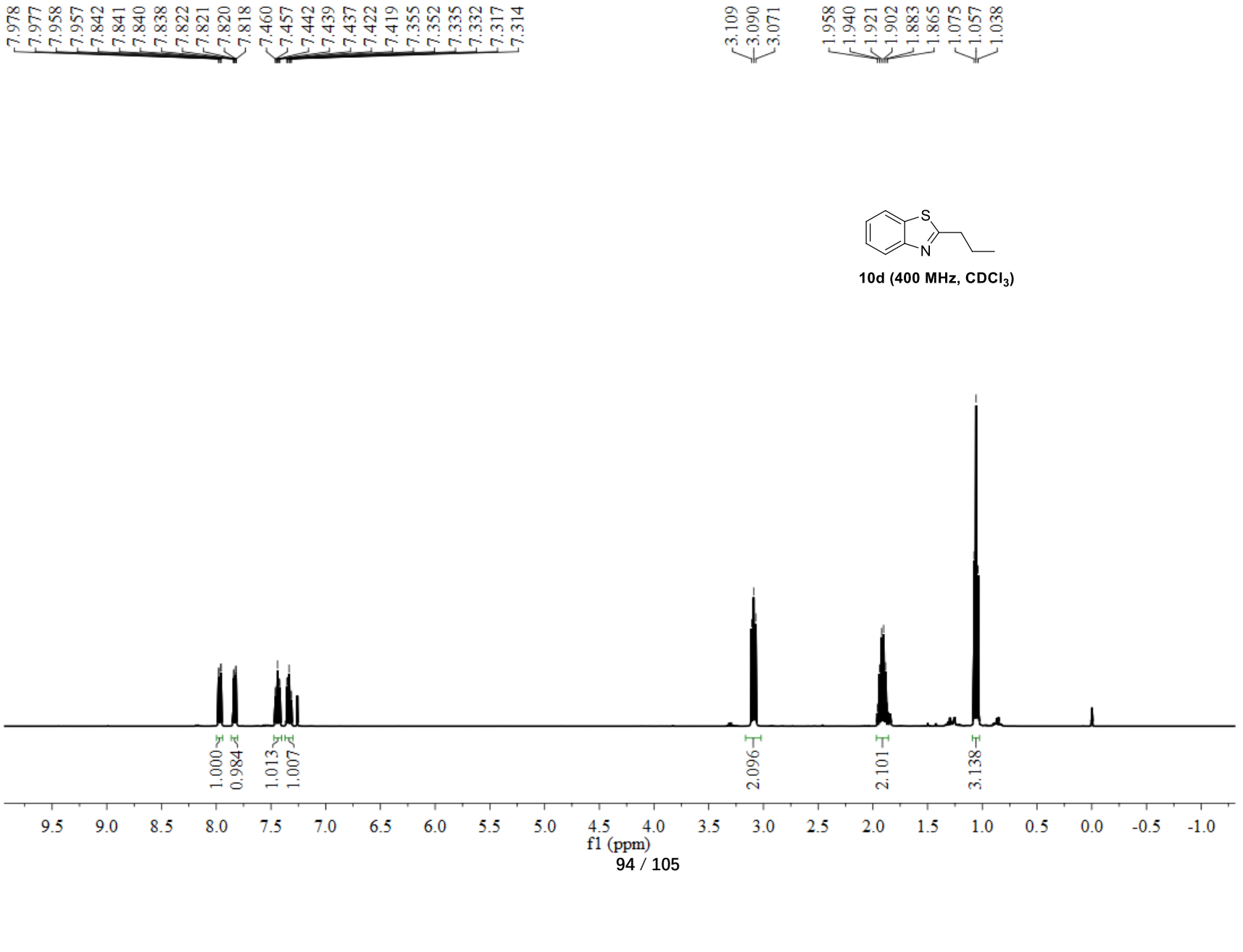
10b (101 MHz, $CDCl_3$)


-62.840
S
N
F
F
F
10b (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

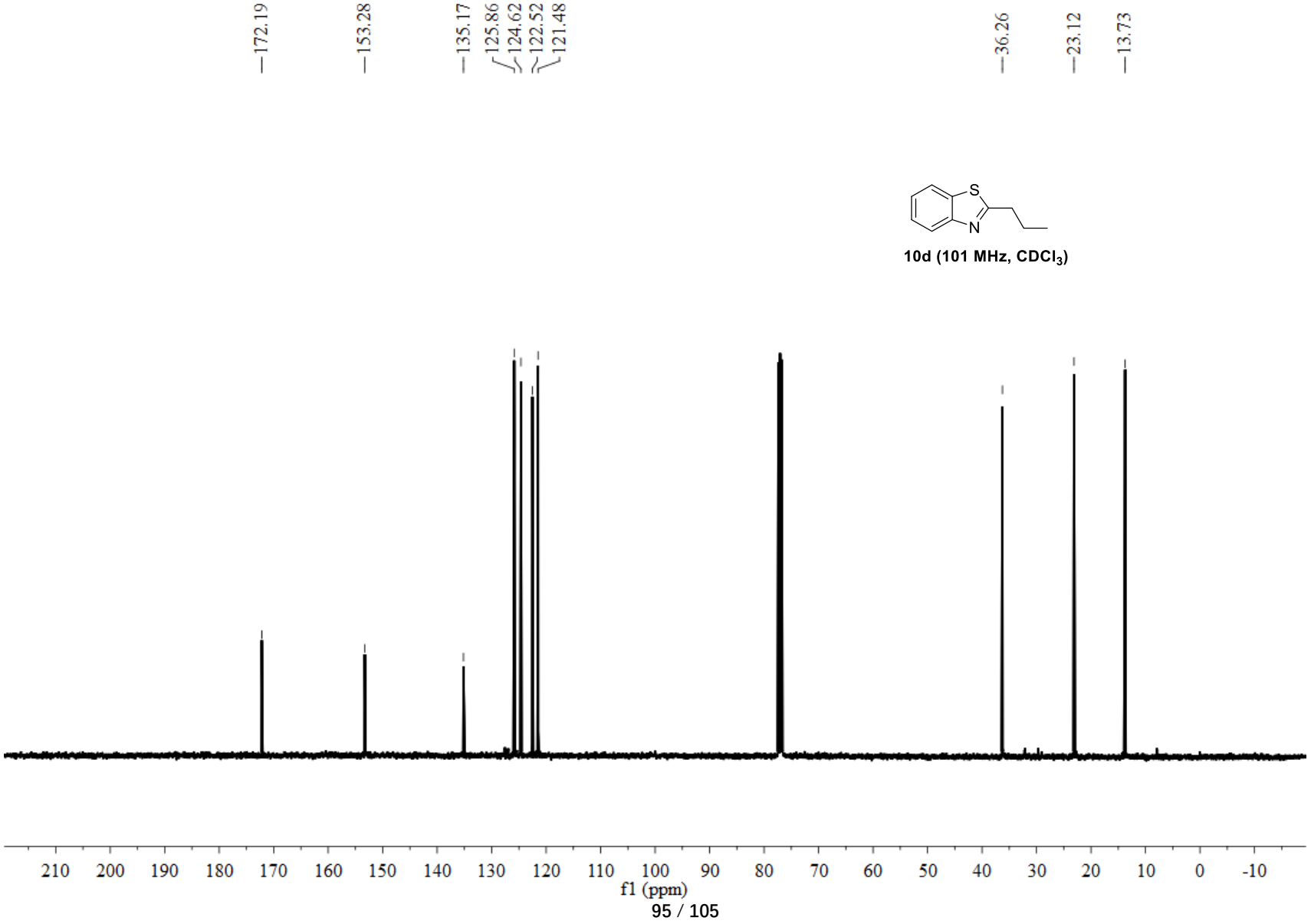

8.089
8.088
8.068
8.002
7.981
7.889
7.888
7.869
7.868
7.506
7.503
7.488
7.486
7.483
7.468
7.465
7.386
7.383
7.366
7.364
7.348
7.345
7.300
7.280
2.419
S
N
10c (400 MHz, CDCl3)
1.000
1.944
0.969
1.035
0.988
1.984
3.052
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

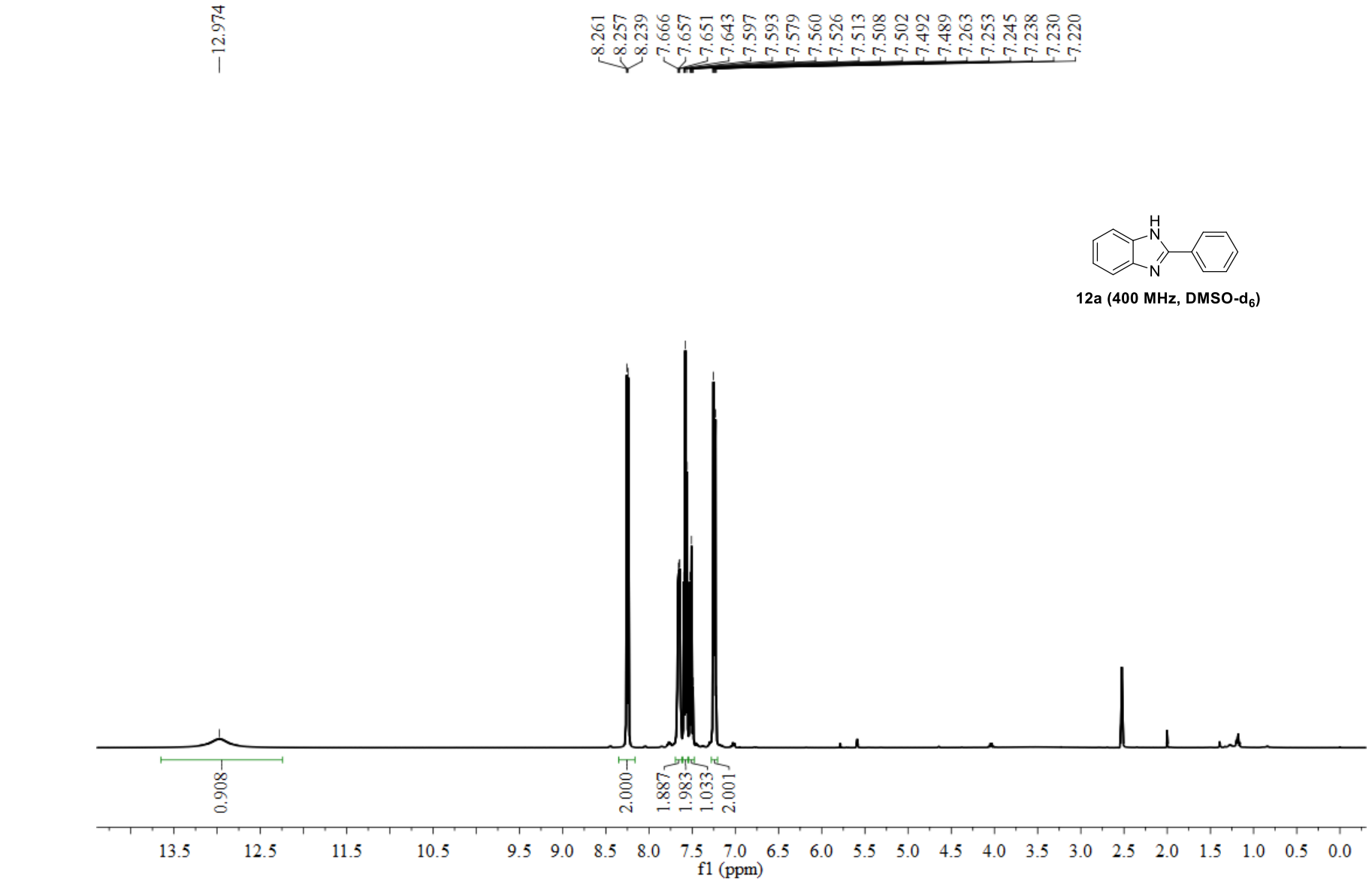


10c (101 MHz, $CDCl_3$)

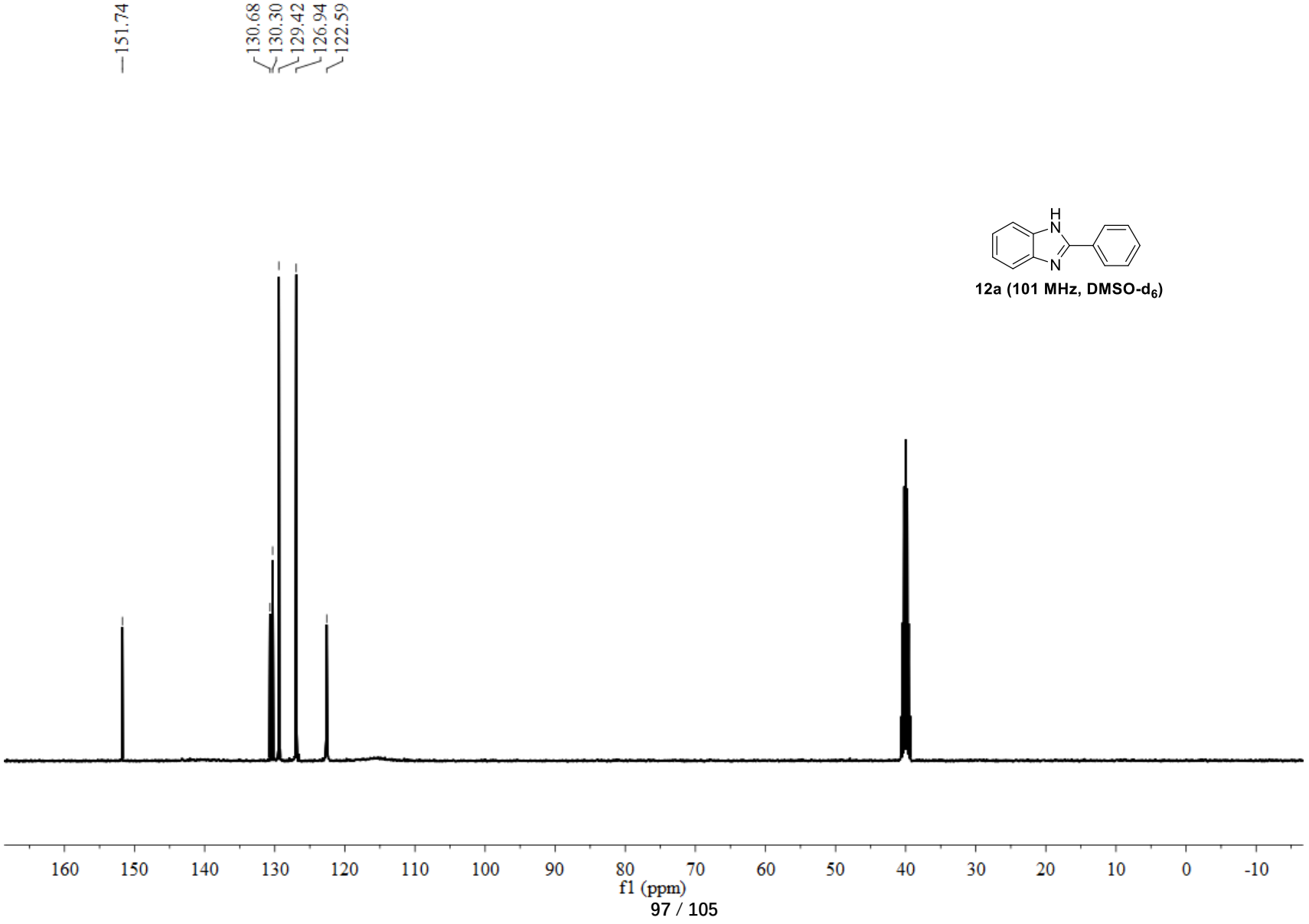


10d (400 MHz, $CDCl_3$)

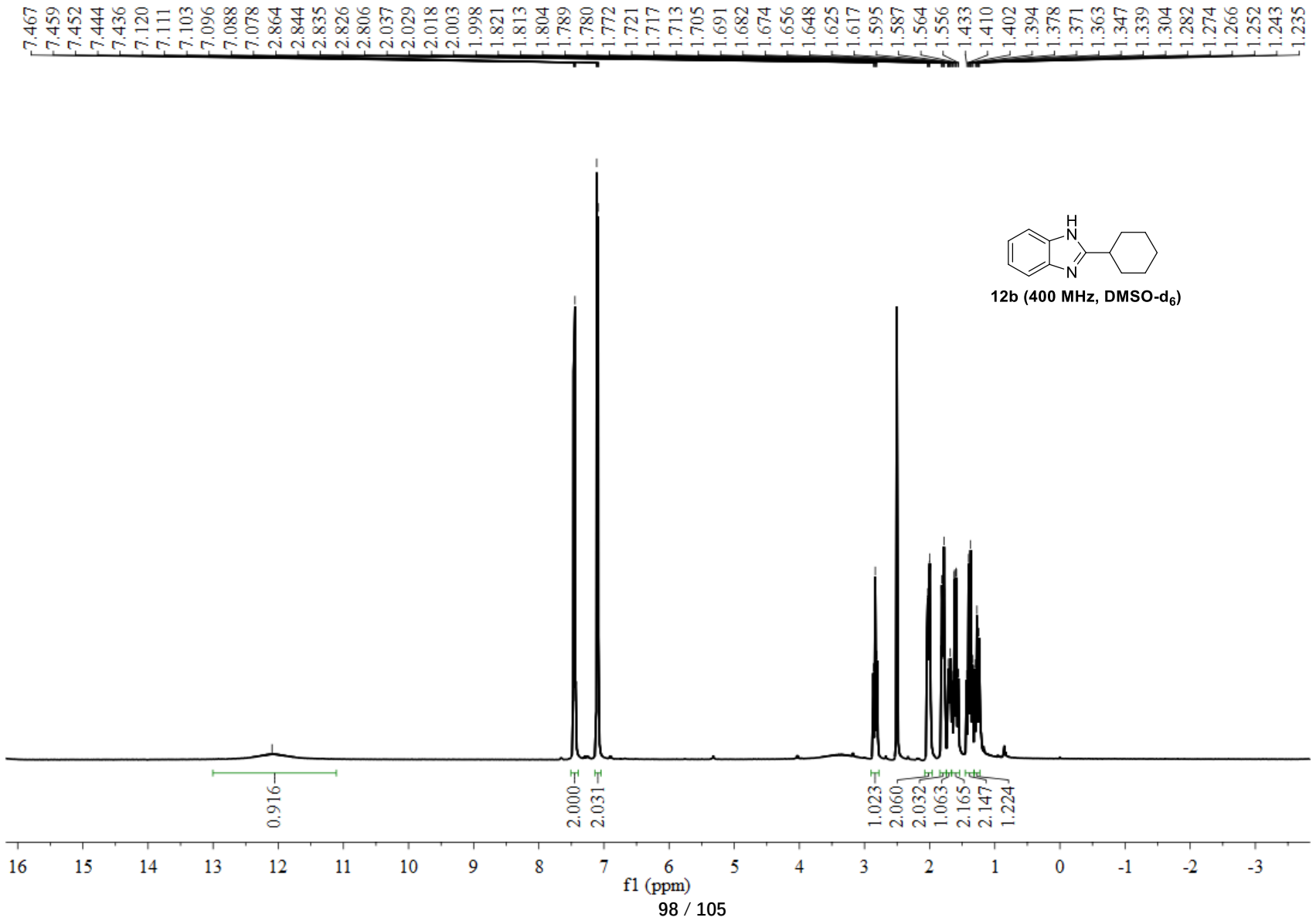

172.19
153.28
135.17
125.86
124.62
122.52
121.48
36.26
23.12
13.73
S
N
10d (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

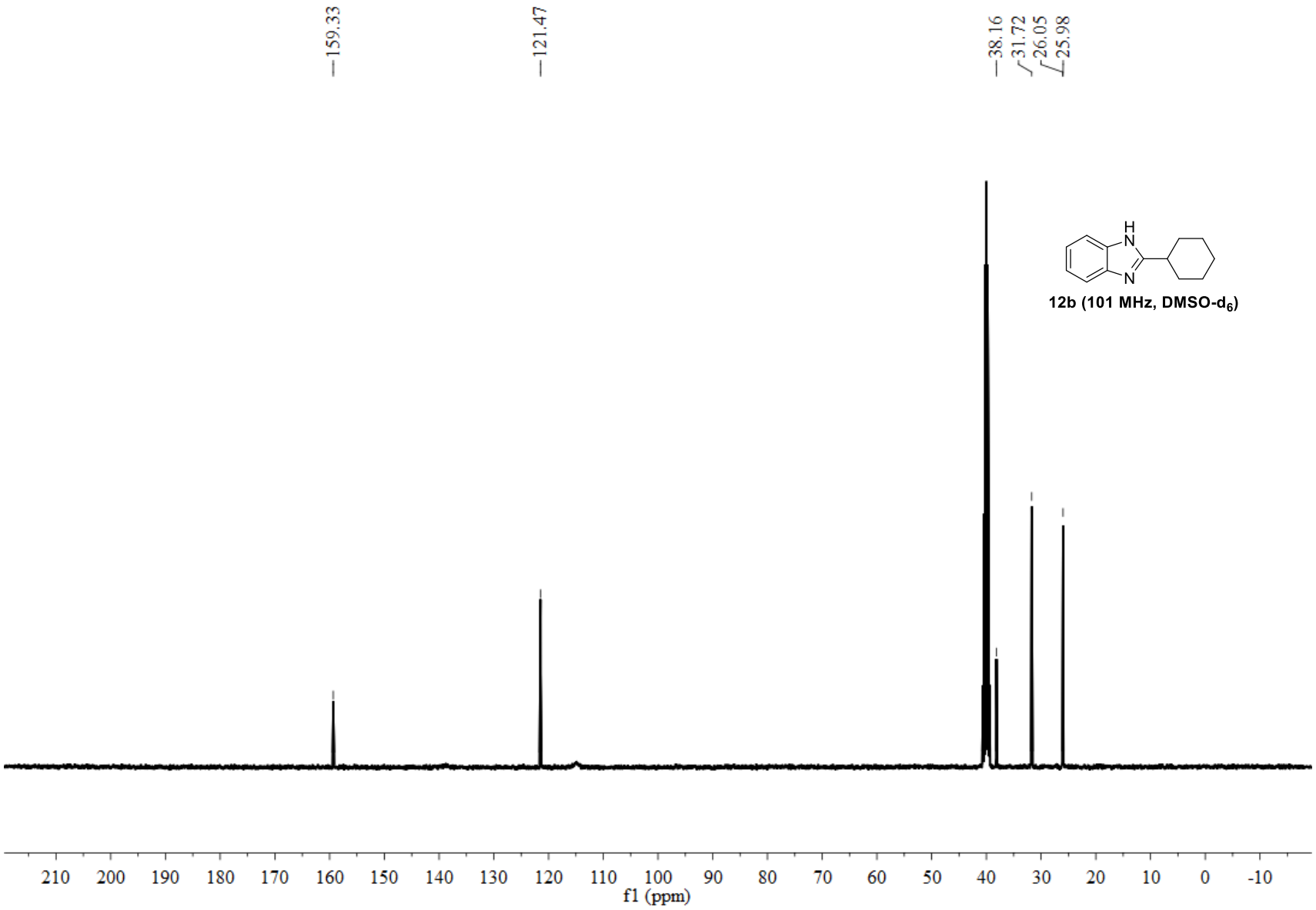


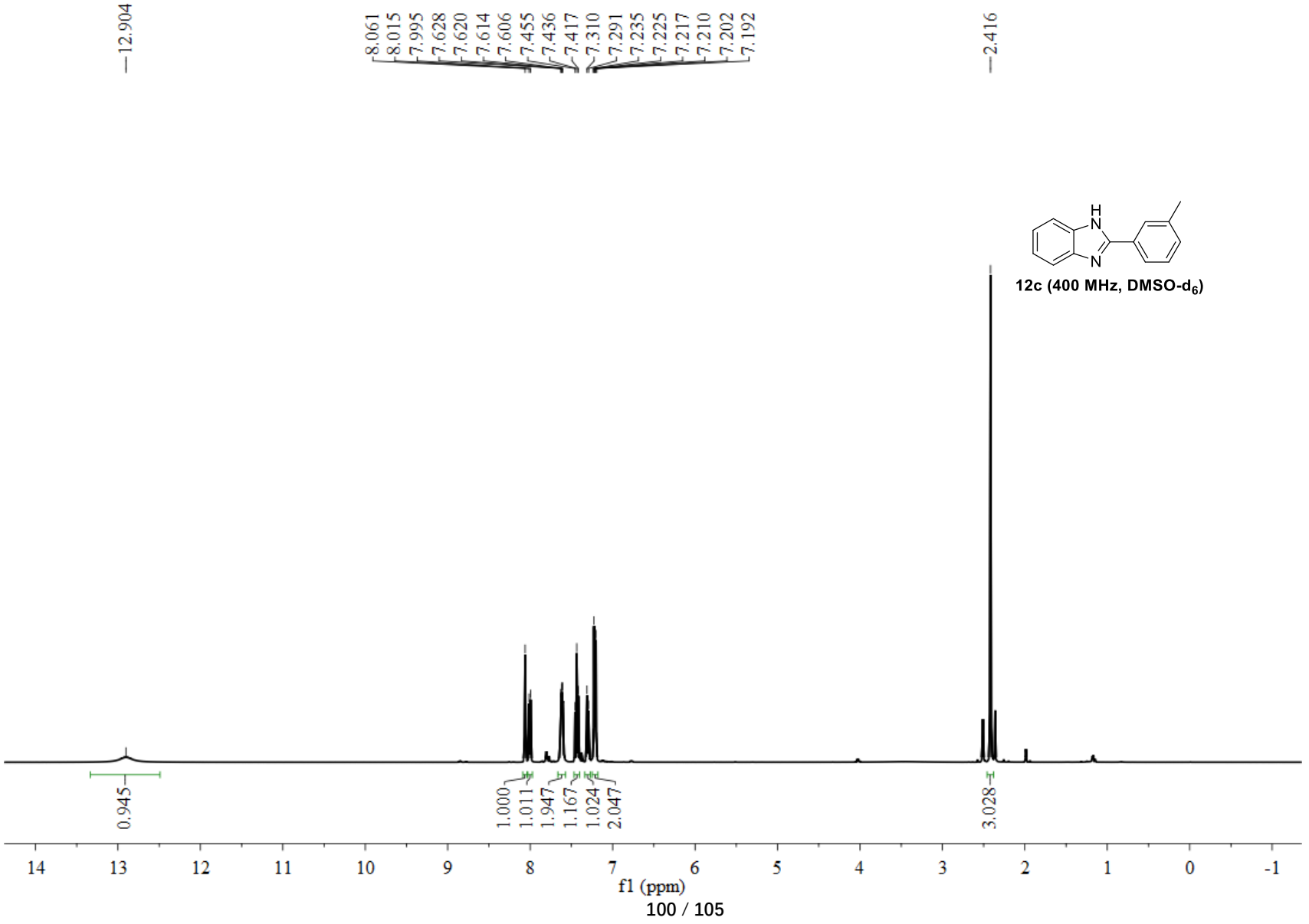
12a (400 MHz, DMSO-d_6)

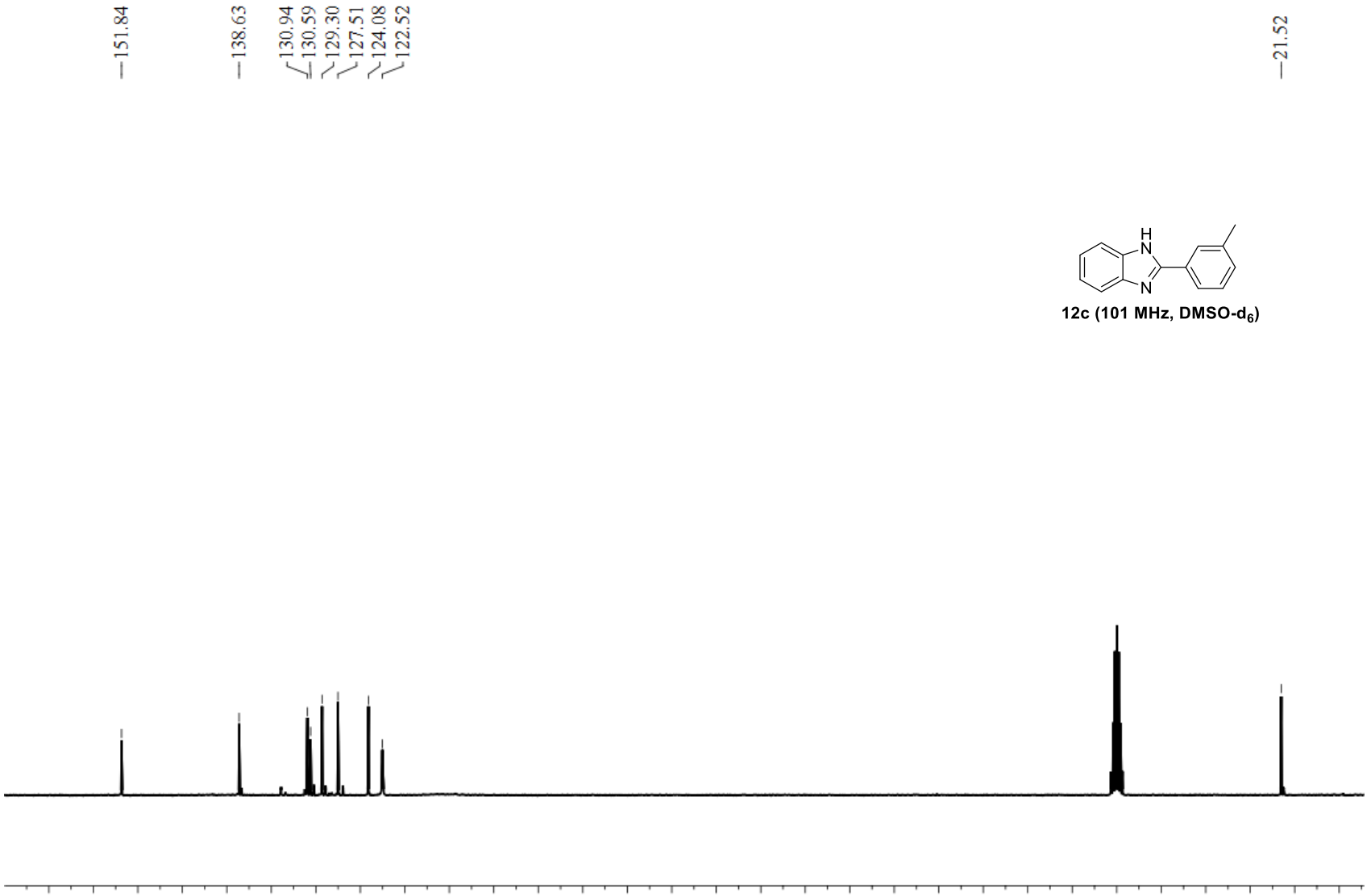


12a (101 MHz, DMSO-d_6)

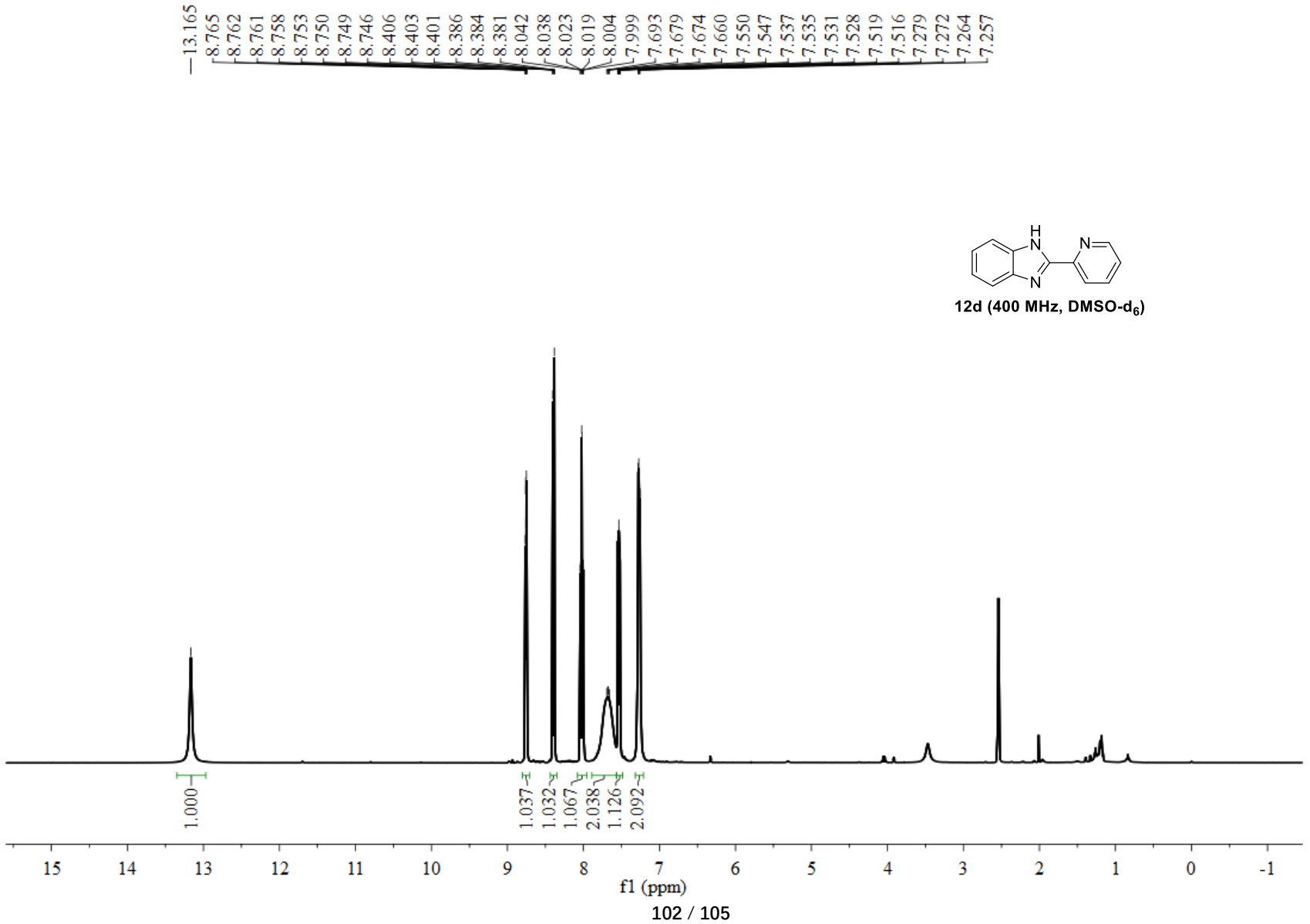

7.467
7.459
7.452
7.444
7.436
7.120
7.111
7.103
7.096
7.088
7.078
2.864
2.844
2.835
2.826
2.806
2.037
2.029
2.018
2.003
1.998
1.821
1.813
1.804
1.789
1.780
1.772
1.721
1.717
1.713
1.705
1.691
1.682
1.674
1.656
1.648
1.625
1.617
1.595
1.587
1.564
1.556
1.433
1.410
1.402
1.394
1.378
1.371
1.363
1.347
1.339
1.304
1.282
1.274
1.266
1.252
1.243
1.235
12b (400 MHz, DMSO-d6)
0.916
2.000
2.031
1.023
2.060
2.032
1.063
2.165
2.147
1.224
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

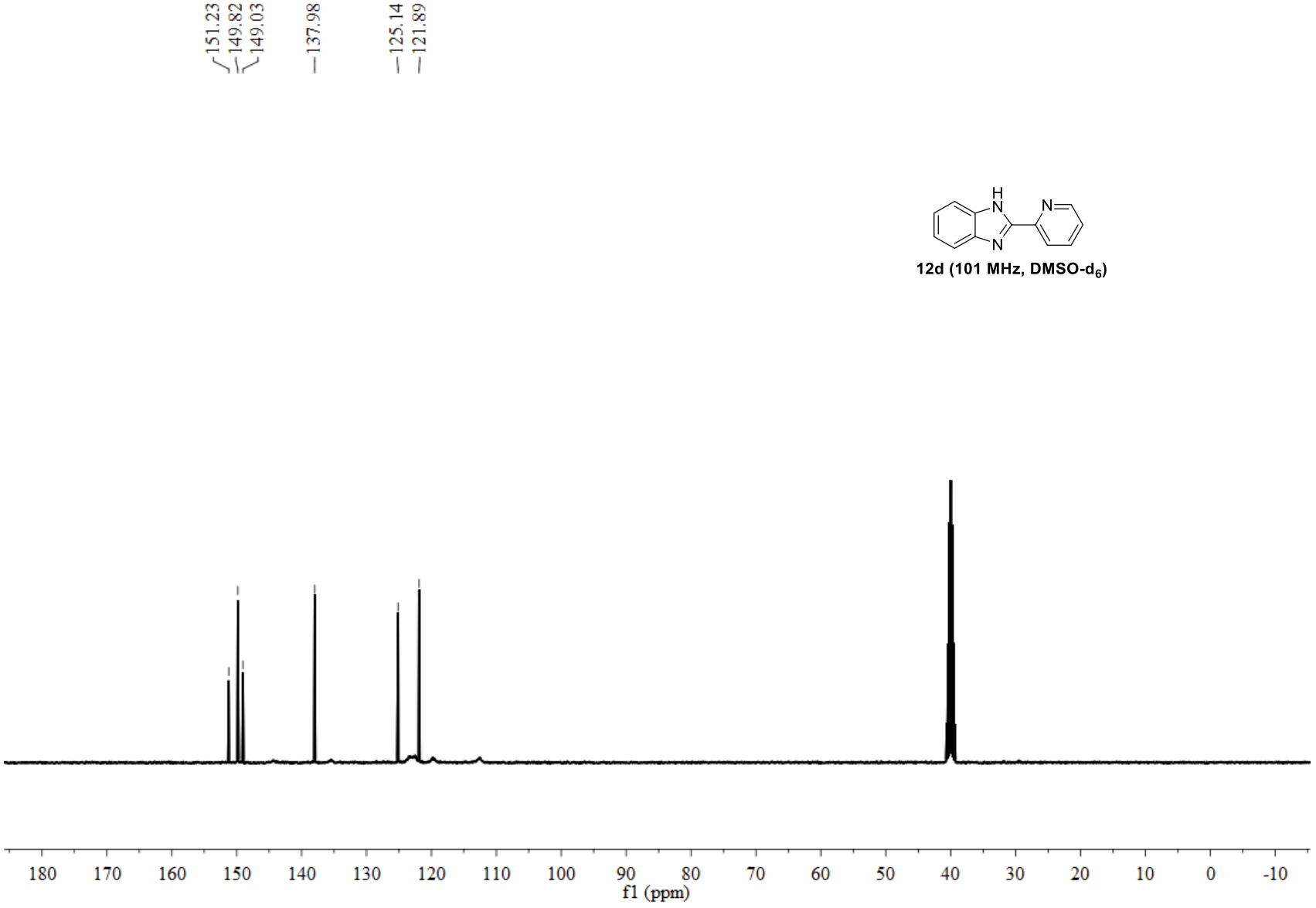

159.33
121.47
38.16
31.72
26.05
25.98
H
N
N
12b (101 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


12.904
8.061
8.015
7.995
7.628
7.620
7.614
7.606
7.455
7.436
7.417
7.310
7.291
7.235
7.225
7.217
7.210
7.202
7.192
2.416
12c (400 MHz, DMSO-d6)
0.945
1.000
1.011
1.947
1.167
1.024
2.047
3.028
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

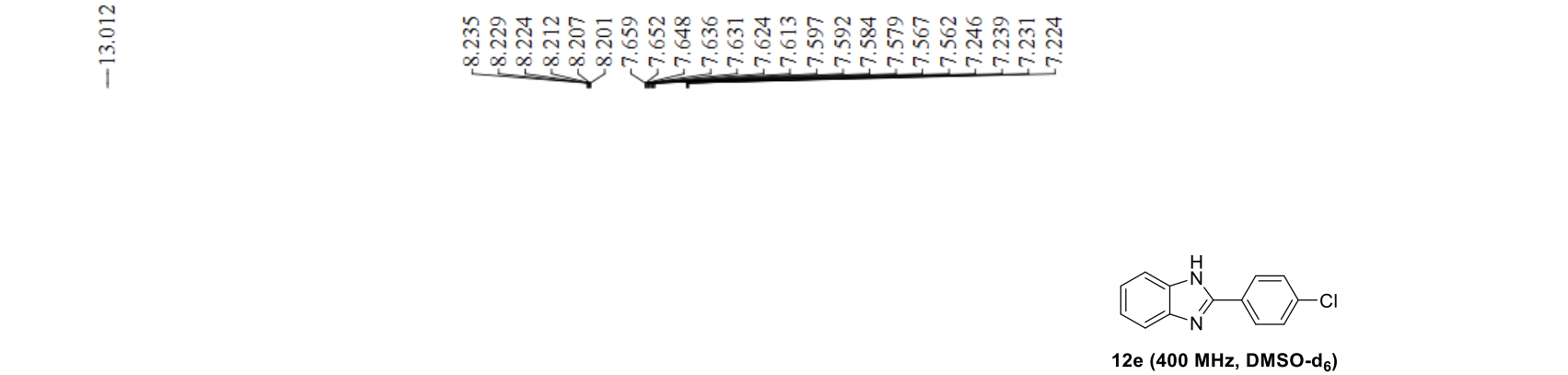


12c (101 MHz, DMSO-d_6)

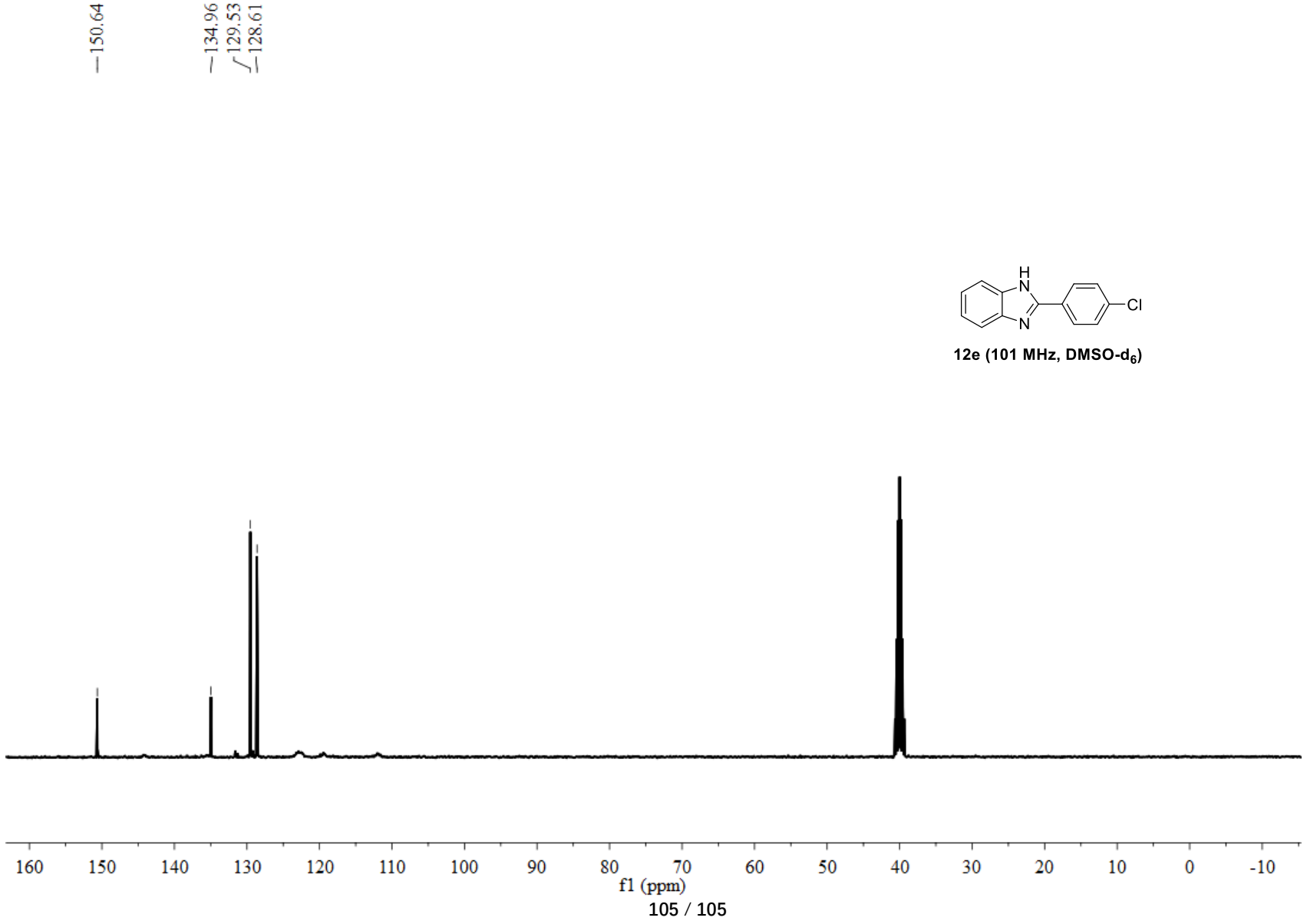

13.165
8.765
8.762
8.761
8.758
8.753
8.750
8.749
8.746
8.406
8.403
8.401
8.386
8.384
8.381
8.042
8.038
8.023
8.019
8.004
7.999
7.693
7.679
7.674
7.660
7.550
7.547
7.537
7.535
7.531
7.528
7.519
7.516
7.279
7.272
7.264
7.257
H
N
N
N
12d (400 MHz, DMSO-d6)
1.000
1.037
1.032
1.067
2.038
1.126
2.092
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



12d (101 MHz, DMSO-d_6)



12e (400 MHz, DMSO-d_6)



12e (101 MHz, DMSO-d_6)