Electronic Supplementary Information

TBHP-mediated denitrogenative synthesis of pyridine carboxamides from pyridine carbohydrazides and amines in water

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General considerations

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All reactions were performed in a screw-capped vial. All reaction temperatures correspond to oil bath temperatures. The proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained using 400, 500 or 600 MHz and 100, 125, or 150 MHz, respectively, with Me_4Si as an internal standard and are reported in δ units. The coupling constants (*J* values) are reported in hertz (Hz). Column chromatography was performed on silica gel (60−120 or 100−200 mesh). HRMS was obtained using the electron spray ionization (ESI) technique and as a time-of-flight mass analyzer. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer. New compounds were characterized by melting point, ^{1}H NMR, ^{13}C NMR and HRMS data.

I. Experimental Procedure

General procedure for the synthesis of amides (3a-3an): In an oven-dried screw-cap vial equipped with magnetic stir bar, carbohydrazides (0.5 mmol) and the corresponding amines (1 mmol) were taken and dissolved in water (2 mL). To the reaction mixture, TBHP (2 equiv) and TBAI (10 mol%) were added and it was stirred at 40 °C for 0.5-1 h. After significant consumption of the starting material, monitored through TLC, the reaction mixture was extracted using ethyl acetate (3 x 50 mL). The combined organic layers were dried over sodium sulphate and concentrated under reduced pressure. The crude concentrate was then loaded onto the column, which upon chromatographic separation (100–200 mesh silica, ethyl acetate /hexane = 1:4 ~ 3:2) afforded the desired product.

General procedure for gram scale synthesis of *N*-phenylisonicotinamide (3a): In an oven-dried screw-cap vial equipped with magnetic stir bar, 4-pyridine carbohydrazide **1a** (7 mmol, 960 mg) and aniline **2a** (14 mmol, 1.3 g) were taken and dissolved in water (20 mL). To the reaction mixture, TBHP (2 equiv, 2.8 mL) and TBAI (10 mol%, 258.6 mg) were added and it was stirred at 40 °C for 1 h. After significant consumption of the starting material, monitored through TLC, the reaction mixture was extracted using ethyl acetate. The combined organic layers were dried over sodium sulphate and concentrated under reduced pressure. The crude concentrate was then loaded onto the column, which upon chromatographic separation (100–200 mesh silica, ethyl acetate /hexane = 1:4) afforded the desired product **3a** in 75% yield (1.04 g).

General procedure for the synthesis of TEMPO adducts (4a-4c): In an oven-dried screw-cap vial equipped with magnetic stir bar, carbohydrazides (0.5 mmol), aniline (1 mmol) and TEMPO (8 equiv)

were taken and dissolved in DCE (2 mL). To the reaction mixture, TBHP (2 equiv) and TBAI (10 mol%) were added and it was stirred at 40 °C for 1 h. After monitoring the TLC, the reaction mixture was extracted using ethyl acetate (3 x 50 mL). The combined organic layers were dried over sodium sulphate and concentrated under reduced pressure. The crude concentrate was then loaded onto the column, which upon chromatographic separation (100–200 mesh silica, ethyl acetate /hexane = 1:9) afforded the desired product.

General procedure for the synthesis of *tert*-butyloxy esters (5a-5c): In an oven-dried screw-cap vial equipped with magnetic stir bar, carbohydrazides (0.5 mmol), along with TBHP (2 equiv) and TBAI (10 mol%) were taken and dissolved in DCE (2 mL). The reaction mixture was stirred at 40 °C for 1 h. After monitoring the TLC, the reaction mixture was extracted using ethyl acetate (3 x 50 mL). The combined organic layers were dried over sodium sulphate and concentrated under reduced pressure. The crude concentrate was then loaded onto the column, which upon chromatographic separation (100–200 mesh silica, ethyl acetate /hexane = 1:4) afforded the desired product.

General procedure for the synthesis of isonicotinic acid (6a): In an oven-dried screw-cap vial equipped with magnetic stir bar, 4-pyridine carbohydrazide **1a** (0.5 mmol), along with TBHP (2 equiv) and TBAI (10 mol%) were taken and dissolved in water (2 mL). The reaction mixture was stirred at 40 °C for 1 h. After monitoring the TLC, the reaction mixture was concentrated under reduced pressure. The crude concentrate was then loaded onto the column, which upon chromatographic separation (100–200 mesh silica, ethyl acetate /hexane = 9:1) afforded the desired product as white solid in 64% yield.

II. Computational Data

Computational Details

Radical philicities were calculated as previously described[1] using the hybrid functional B3LYP[2] with the triple-ζ basis set 6-311+G(d,p) in the gas phase. The calculations were performed with Gaussian16.[3]

Determination of Radical Philicities

The global electrophilicity index ω was derived from vertical ionization potentials (IP) and electron affinities (EA) at the B3LYP/6-311+G(d,p) level of theory using the following equation:

$$IP = E(\text{Cation}) - E(\text{Radical}) \quad \text{(eq. S1)}$$

$$EA = E(\text{Radical}) - E(\text{Anion}) \quad \text{(eq. S2)}$$

$$\mu = -\frac{IP + EA}{2} \quad \text{(eq. S3)}$$

$$\eta = IP - EA \quad \text{(eq. S4)}$$

$$\omega = \frac{\mu^2}{2\eta} \quad \text{(eq. S5)}$$

2-Pyridine Acyl Radical

E(Radical) –361.051724303 hartree
E(Cation) –360.751006942 hartree
E(Anion) –361.056015961 hartree

Cartesian Coordinates Radical (B3LYP):

O	-3.07043	-0.00710	-0.00013
C	-1.90939	-0.01857	0.00001
C	-0.54470	-0.00246	-0.00002
N	0.07758	-1.23516	0.00009
C	1.40043	-1.22046	0.00012
C	2.19195	-0.06268	0.00007
C	1.54395	1.18583	-0.00004
C	0.17081	1.24345	-0.00008
H	1.87371	-2.19925	0.00021
H	3.27128	-0.13804	0.00011
H	2.12032	2.10406	-0.00010
H	-0.36318	2.18540	-0.00017

3-Pyridine Acyl Radical

E(Radical) –361.053958876 hartree
E(Cation) –360.746069982 hartree
E(Anion) –361.06480069 hartree

Cartesian Coordinates Radical (B3LYP):

O	3.08957	0.00209	0.00002

C	1.92524	0.03187	0.00001
C	0.57784	0.03956	0.00001
C	-0.16392	-1.21223	-0.00003
N	-1.47083	-1.26262	-0.00005
C	-2.18264	-0.11244	-0.00002
C	-1.56822	1.14959	0.00002
C	-0.19759	1.25756	0.00003
H	0.37781	-2.15298	-0.00006
H	-3.26124	-0.21309	-0.00003
H	-2.17934	2.04475	0.00005
H	0.29779	2.21946	0.00007

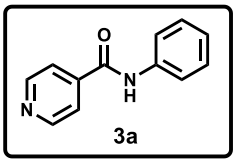
4-Pyridine Acyl Radical

E(Radical) –361.051676798 hartree
E(Cation) –360.738823971 hartree
E(Anion) –361.066793328 hartree

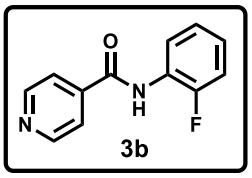
Cartesian Coordinates Radical (B3LYP):

O	3.09905	-0.00001	-0.00012
C	1.93631	0.00002	-0.00011
C	0.58363	0.00002	-0.00001
C	-0.16861	-1.22686	0.00001
C	-1.54344	-1.14528	0.00006
N	-2.25460	-0.00002	0.00008
C	-1.54347	1.14526	0.00007
C	-0.16863	1.22687	0.00002
H	0.33320	-2.18544	-0.00001
H	-2.12557	-2.06262	0.00008
H	-2.12562	2.06258	0.00008
H	0.33315	2.18547	-0.00000

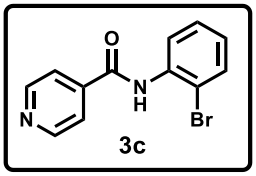
III. Characterization data of substrates:



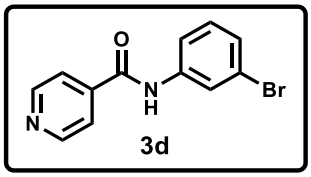
***N*-phenylisonicotinamide (3a)**[4] was obtained in 77% yield (76.3 mg) as light brown solid. The compound **3a** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.50 (bs, 1H), 8.79 (d, J = 4.9 Hz, 2H), 7.87-7.77 (m, 4H), 7.38 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.9, 150.7, 142.2, 137.3, 129.3, 125.4, 121.1, 120.6.



***N*-(2-fluorophenyl)isonicotinamide (3b)**[5] was obtained in 65% yield (70.2 mg) as brown solid. The compound **3b** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.43 (bs, 1H), 8.80 (d, J = 6 Hz, 2H), 7.88 (d, J = 5.8 Hz, 2 H), 7.63 (t, J = 7.8 Hz, 1 H), 7.35–7.31 (m, 2H), 7.28–7.23 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 157.5, 155.0, 150.8, 141.4, 127.6, 125.6, 125.4, 124.9, 124.8, 122.1, 116.5, 116.3.

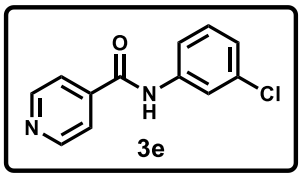


***N*-(2-bromophenyl)isonicotinamide (3c)**[6] was obtained in 62% yield (85.9 mg) as light brown solid. The compound **3c** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (dd, J = 4.6, 1.4 Hz, 2H), 8.44 (bs, 1H), 8.40 (dd, J = 8.2, 0.8 Hz, 1H), 7.67 (dd, J = 4.4, 1.6 Hz, 2H), 7.51 (dd, J = 8.0, 1.4 Hz, 1H), 7.32-7.29 (m, 1H), 7.00-6.97 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 150.8, 141.5, 135.0, 132.3, 128.5, 126.0, 121.9, 120.7, 114.0.



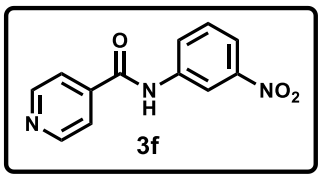
***N*-(3-bromophenyl)isonicotinamide (3d)** was obtained in 65% yield (90.1 mg) as brown solid (m.p. = 184-186 °C). The compound **3d** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (bs, 1H), 8.80 (d, J = 5.8 Hz, 2H), 8.09 (s, 1H), 7.86 (d, J = 5.8 Hz, 2H), 7.76–7.75 (m, 1H), 7.35–7.33 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.7, 150.8, 142.0, 140.6, 131.2, 127.3, 123.2, 122.0, 121.9, 119.6.

HRMS (ESI) m/z calculated for $C_{12}H_9BrN_2O$ $[M+H]^+$ 276.9971, found 276.9975.

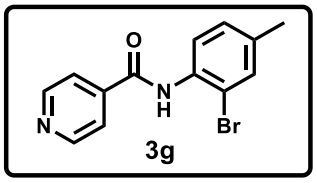


***N*-(3-chlorophenyl)isonicotinamide (3e)** was obtained in 65% yield (75.6 mg) as light brown solid (m.p. = 155-157 °C). The compound **3e** was purified with chromatography on silica gel (hexane/ethyl acetate = 13:7). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.65 (bs, 1H), 8.80 (d, J = 6 Hz, 2H), 7.97–7.96 (m, 1H), 7.86 (d, J = 6.0 Hz, 2H), 7.71 (d, J = 9.2 Hz, 1H), 7.40 (t, J = 8.1, 16.2 Hz, 1H), 7.20 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.2, 150.3, 141.5, 140.0, 133.0, 130.4, 123.8, 121.5, 119.8, 118.7.

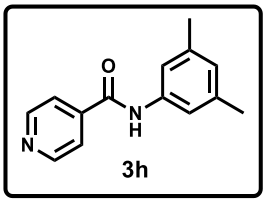
HRMS (ESI) m/z calculated for $C_{12}H_9ClN_2O$ $[M+H]^+$ 233.0476, found 233.0478.



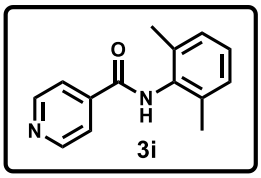
***N*-(3-nitrophenyl)isonicotinamide (3f)**[7] was obtained in 50% yield (60.8 mg) as brown solid. The compound **3f** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.92 (bs, 1H), 8.82 (d, J = 6.0 Hz, 2H), 8.78–8.77 (m, 1H), 8.18 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 4.5 Hz, 2H), 7.67 (t, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.9, 150.8, 148.3, 141.7, 140.2, 130.6, 126.7, 122.0, 119.1, 114.9.



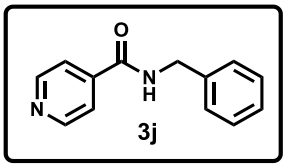
***N*-(2-bromo-4-methylphenyl)isonicotinamide (3g)** was obtained in 68% yield (98.9 mg) as white solid (m.p. = 101-103 °C). The compound **3g** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (d, J = 5.9 Hz, 2 H), 8.41 (bs, 1H), 8.34 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 5.9 Hz, 2H), 7.42 (s, 1H), 7.19 (d, J = 8.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 150.8, 141.6, 136.2, 132.6, 132.4, 129.2, 121.8, 120.7, 113.9, 20.6.
HRMS (ESI) m/z calculated for $C_{13}H_{11}BrN_2O$ $[M+H]^+$ 291.0128, found 291.0126.



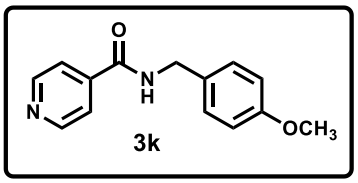
***N*-(3,5-dimethylphenyl)isonicotinamide (3h)**[8] was obtained in 70% yield (79.2 mg) as light brown solid. The compound **3h** was purified with chromatography on silica gel (hexane/ethyl acetate = 13:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 4.5 Hz, 2H), 8.02 (bs, 1H), 7.70 (d, J = 5.9 Hz, 2H), 7.28 (s, 2H), 6.85 (s, 1H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 150.7, 142.2, 138.9, 137.0, 127.0, 120.9, 118.2, 21.4.



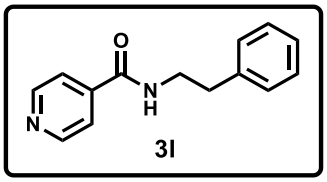
***N*-(2,6-dimethylphenyl)isonicotinamide (3i)**[9] was obtained in 70% yield (79.2 mg) as light brown solid. The compound **3i** was purified with chromatography on silica gel (hexane/ethyl acetate = 13:7). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.06 (bs, 1H), 8.79 (d, J = 5.8 Hz, 2H), 7.89 (d, J = 5.7 Hz, 2H), 7.16–7.12 (m, 3H), 2.19 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.4, 150.3, 141.3, 135.4, 134.6, 127.8, 126.9, 121.4, 17.9.



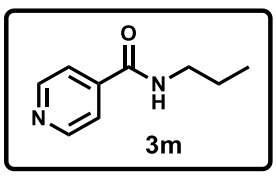
***N*-benzylisonicotinamide (3j)**[10] was obtained in 72% yield (76.4 mg) as white solid. The compound **3j** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.54–7.50 (m, 1H), 7.46–7.42 (m, 2H), 7.38–7.37 (m, 3H), 7.33–7.31 (m, 1H), 6.59 (bs, 1H), 4.66 (d, J = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 137.2, 133.3, 130.5, 127.8, 127.5, 126.9, 126.6, 125.9, 43.1.



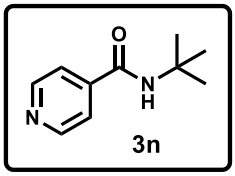
***N*-(4-methoxybenzyl)isonicotinamide (3k)**[11] was obtained in 87% yield (105.4 mg) as white solid. The compound **3k** was purified with chromatography on silica gel (hexane/ethyl acetate = 2:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.24 (bs, 1H), 8.67 (d, J = 5.5 Hz, 2H), 7.75 (d, J = 5.5 Hz, 2H), 7.21 (d, J = 8.5, 2H), 6.85 (d, J = 8.5, 2H), 4.39 (d, J = 5.9, 2H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.0, 158.8, 150.7, 141.8, 131.5, 129.2, 121.7, 114.2, 55.5,42.7.



***N*-phenethylisonicotinamide (3l)**[12] was obtained in 91% yield (102.9 mg) as light yellow solid. The compound **3l** was purified with chromatography on silica gel (hexane/ethyl acetate = 2:3). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.83 (bs, 1H), 8.68-8.66 (m, 2H), 7.69-7.67 (m, 2H), 7.26-7.15 (m, 5H), 3.47-3.46 (m, 2H), 2.83-2.80 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 150.7, 141.9, 139.8, 129.2, 128.8, 126.7, 121.7, 41.4, 35.4.

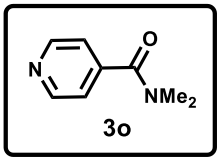


***N*-propylisonicotinamide (3m)**[13] was obtained in 85% yield (69.8 mg) as white solid. The compound **3m** was purified with chromatography on silica gel (hexane/ethyl acetate = 2:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.74 (bs, 1H), 8.66 (d, J = 6.0 Hz, 2H), 7.70 (d, J = 5.6 Hz, 2H), 3.18 (q, J = 6.7 Hz, 2H), 1.52-1.47 (m, 2H), 0.84 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.0, 150.7, 142.1, 121.7, 41.5, 22.7, 11.9.



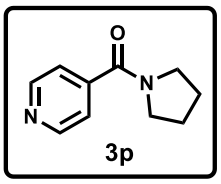
3n

***N*-(t-butyl)isonicotinamide (3n)**[14] was obtained in 89% yield (79.3 mg) as white solid. The compound **3n** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64-8.63 (m, 2H), 8.02 (bs, 1H), 7.66-7.65 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.2, 150.4, 143.2, 121.9, 51.6, 28.9.



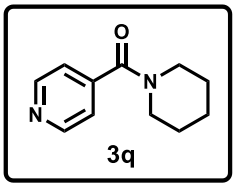
3o

***N,N*-dimethylisonicotinamide (3o)**[15] was obtained in 92% yield (69.0 mg) as white solid. The compound **3o** was purified with chromatography on silica gel (hexane/ethyl acetate = 1:4). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.62 (d, J = 5 Hz, 2H), 7.34 (d, J = 5.5 Hz, 2H), 2.95 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.4, 150.4, 144.5, 121.7, 39.1, 35.0.

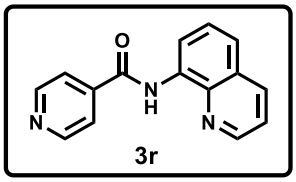


3p

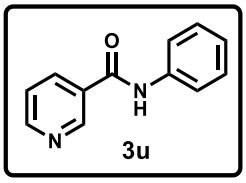
Pyridin-4-yl(pyrrolidin-1-yl)methanone (3p)[16] was obtained in 90% yield (79.3 mg) as yellow oil. The compound **3p** was purified with chromatography on silica gel (hexane/ethyl acetate = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 5.6 Hz, 2H), 7.32 (d, J = 5.7 Hz, 2H), 3.57 (t, J = 6.7 Hz, 2H), 3.30 (t, J = 6.6 Hz, 2H), 1.92-1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 150.0, 144.6, 121.2, 49.2, 46.2, 26.3, 24.3.



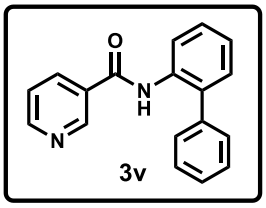
Piperidin-1-yl(pyridin-4-yl)methanone (3q)[17] was obtained in 93% yield (88.4 mg) as yellow oil. The compound **3q** was purified with chromatography on silica gel (hexane/ethyl acetate = 2:3). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.60 (d, J = 5.1 Hz, 2H), 7.31 (d, J = 5.4 Hz, 2H), 3.55-3.54 (m, 2H), 3.15-3.13 (m, 2H), 1.56-1.55 (m, 2H), 1.54-1.51 (m, 2H), 1.40 (s, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.0, 150.5, 144.5, 121.4, 48.2, 42.6, 26.3, 25.6, 24.4.



***N*-(quinolin-8-yl)isonicotinamide (3r)**[18] was obtained in 63% yield (78.5 mg) as light orange solid. The compound **3r** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.72 (s, 1H), 8.95-8.94 (m, 1H), 8.83 (d, J = 5.8 Hz, 2H), 8.65 (d, J = 7.5 Hz, 1H), 8.43 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 5.5 Hz, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.65-7.62 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.1, 150.6, 149.2, 141.3, 138.4, 136.6, 133.5, 127.8, 126.8, 123.0, 122.3, 120.9, 117.4.

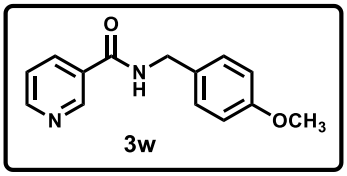


***N*-phenylnicotinamide (3u)**[19] was obtained in 72% yield (71.3 mg) as brown solid. The compound **3u** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:2). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.40 (s, 1H), 9.07 (s, 1H), 8.73 (d, J = 4.6 Hz, 1H), 8.26-8.24 (m, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.54-7.51 (m, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.5, 152.6, 149.2, 139.3, 135.9, 131.1, 129.2, 124.5, 124.0, 120.8.

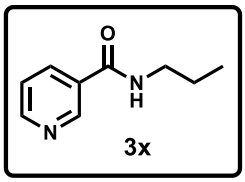


***N*-([1,1'-biphenyl]-2-yl)nicotinamide (3v)** was obtained in 69% yield (94.6 mg) as white solid (m.p. = 170-172 °C). The compound **3v** was purified with chromatography on silica gel (hexane/ethyl acetate = 13:7). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.08 (s, 1H), 8.89 (s, 1H), 8.67 (d, J = 4.4 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H), 7.48-7.45 (m, 2H), 7.42-7.34 (m, 7H), 7.27 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.8, 152.5, 149.0, 139.6, 138.9, 135.7, 134.9, 130.8, 130.6, 129.1, 128.9, 128.8, 128.4, 127.7, 127.5, 124.0.

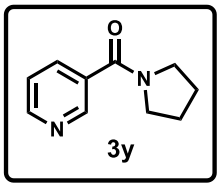
HRMS (ESI) m/z calculated for $C_{18}H_{14}N_2O$ $[M+H]^+$ 275.1179, found 275.1188.



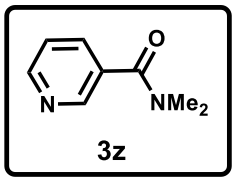
***N*-(4-methoxybenzyl)nicotinamide (3w)**[20] was obtained in 56% yield (67.8 mg) as white solid. The compound **3w** was purified with chromatography on silica gel (hexane/ethyl acetate = 1:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.14 (t, J = 5.5 Hz, 1H), 8.99 (s, 1H), 8.67 (d, J = 4.4 Hz, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.48-7.45 (m, 1H), 7.22 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.39 (d, J = 5.4 Hz, 2H), 3.69 (d, J = 4.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 158.7, 152.4, 148.9, 135.5, 131.7, 130.3, 129.1, 123.9, 114.2, 55.5, 42.6.



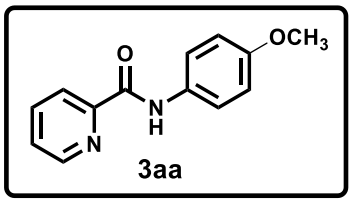
***N*-propylnicotinamide (3x)**[21] was obtained in 68% yield (55.8 mg) as white solid. The compound **3x** was purified with chromatography on silica gel (hexane/ethyl acetate = 2:3). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.95 (s, 1H), 8.65-8.61 (m, 2H), 8.13 (d, J = 7.8 Hz, 1H), 7.46-7.44 (m, 1H), 3.19 (q, J = 6.6 Hz, 2H), 1.52-1.47 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 152.2, 148.8, 135.3, 130.6, 123.9, 41.5, 22.8, 11.9.



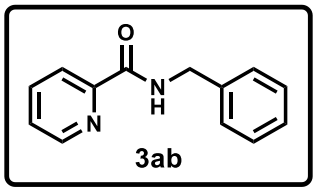
Pyridin-3-yl(pyrrolidin-1-yl)methanone (3y)[22] was obtained in 85% yield (74.8 mg) as yellow oil. The compound **3y** was purified with chromatography on silica gel (hexane/ethyl acetate = 1:4). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.66 (s, 1H), 8.60 (d, J = 4.3 Hz, 1H), 7.89-7.87 (m, 1H), 7.43-7.41 (m, 1H), 3.44-3.42 (m, 2H), 3.36-3.34 (m, 2H), 1.84-1.76 (m, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.5, 151.0, 148.3, 135.2, 133.4, 123.8, 49.2, 46.5, 26.4, 24.4.



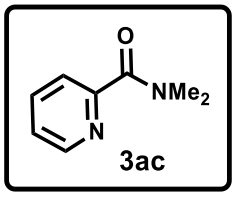
***N,N*-dimethylnicotinamide (3z)**[23] was obtained in 90% yield (67.5 mg) as yellow oil. The compound **3z** was purified with chromatography on silica gel (hexane/ethyl acetate = 1:4). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.59-8.57 (m, 2H), 7.80 (d, J = 7.8 Hz, 1H), 7.43-7.41 (m, 1H), 2.96-2.93 (m, 3H), 2.87 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.4, 150.7, 148.1, 135.2, 132.7, 123.9, 35.3, 29.5.



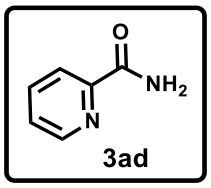
***N*-(4-methoxyphenyl)picolinamide (3aa)**[24] was obtained in 62% yield (70.7 mg) as off-white solid. The compound **3aa** was purified with chromatography on silica gel (hexane/ethyl acetate = 19:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.50 (s, 1H), 8.67 (d, J = 4.4 Hz, 1H), 8.11 (d, J = 7.4 Hz, 1H), 8.00 (t, J = 7.5 Hz, 1H), 7.79 (d, J = 8.7 Hz, 2H), 7.61-7.58 (m, 1H), 6.89 (d, J = 9.1 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.5, 156.2, 150.5, 148.8, 138.5, 132.0, 127.2, 122.7, 122.2, 114.3, 55.6.



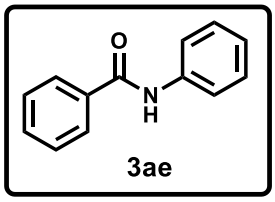
***N*-benzylpicolinamide (3ab)**[24] was obtained in 78% yield (82.7 mg) as off-white solid. The compound **3ab** was purified with chromatography on silica gel (hexane/ethyl acetate = 9:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.31 (s, 1H), 8.61 (d, J = 4.4 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.95 (t, J = 7.6 Hz, 1H), 7.57-7.54 (m, 1H), 7.29-7.25 (m, 4H), 7.19-7.17 (m, 1H), 4.47 (d, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.4, 150.5, 148.9, 140.0, 138.3, 128.7, 127.8, 127.2, 127.0, 122.5, 42.9.



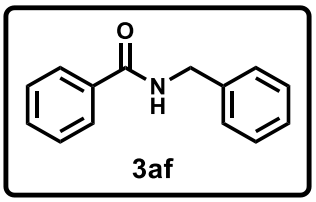
***N,N*-dimethylpicolinamide (3ac)**[15] was obtained in 83% yield (62.3 mg) as yellow oil. The compound **3ac** was purified with chromatography on silica gel (hexane/ethyl acetate = 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 4.4 Hz, 1H), 7.81-7.77 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.35-7.32 (m, 1H), 3.14 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 154.4, 148.2, 137.0, 124.3, 123.5, 39.0, 35.7.



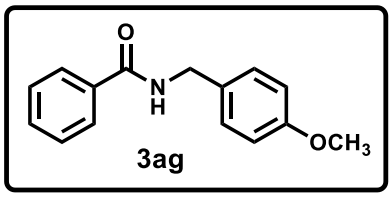
Picolinamide (3ad)[25] was obtained in 88% yield (53.7 mg) as white solid. The compound **3ad** was purified with chromatography on silica gel (hexane/ethyl acetate = 3:2). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.58-8.57 (m, 1H), 8.11 (s, 1H), 8.01-7.99 (m, 1H), 7.94-7.91 (m, 1H), 7.64 (s. 1H), 7.54-7.52 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.5, 150.7, 148.9, 138.1, 126.9, 122.4.



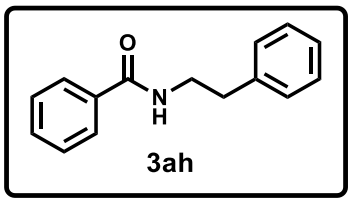
***N*-phenylbenzamide (3ae)**[10] was obtained in 72% yield (71.0 mg) as white solid. The compound **3ae** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (bs, 1H), 7.85 (d, J = 7.7 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 6.6 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.35 (t, J = 6.9 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 138.0, 135.0, 131.9, 129.1, 128.8, 127.1, 124.6, 120.3.



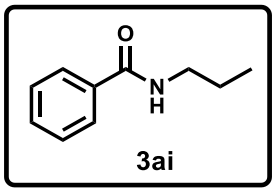
***N*-benzylbenzamide (3af)**[10] was obtained in 75% yield (79.2 mg) as light-yellow solid. The compound **3af** was purified with chromatography on silica gel (hexane/ethyl acetate = 9:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.01 (s, 1H), 7.86-7.85 (m, 2H), 7.51-7.48 (m, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.29-7.28 (m, 4H), 7.21-7.19 (m, 1H), 4.45 (d, J = 5.9 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.7, 140.2, 134.8, 131.7, 128.8, 128.8, 127.8, 127.7, 127.2, 43.1.



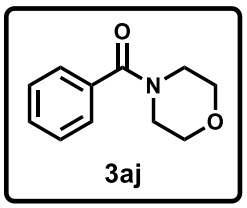
***N*-(4-methoxybenzyl)benzamide (3ag)**[10] was obtained in 87% yield (104.9 mg) as white solid. The compound **3ag** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.48 (t, J = 7.1 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.27-7.24 (m, 2H), 6.87-6.86 (m, 2H), 6.43 (bs, 1H), 4.56 (d, J = 5.3 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 154.4, 129.7, 126.8, 125.5, 124.6, 123.8, 122.2, 109.4, 50.6, 38.9.



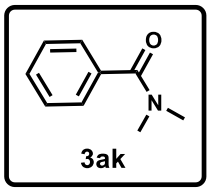
***N*-phenethylbenzamide (3ah)**[26] was obtained in 91% yield (79.2 mg) as off-white solid. The compound **3ah** was purified with chromatography on silica gel (hexane/ethyl acetate = 17:3). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (s, 1H), 7.78 (d, J = 7.3 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.20 (d, J = 7.1 Hz, 2H), 7.16 (t, J = 6.9 Hz, 1H), 3.44 (q, J = 6.6 Hz, 2H), 2.81 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.6, 140.0, 135.1, 131.5, 129.1, 128.8, 128.7, 127.6, 126.6, 41.4, 35.6.



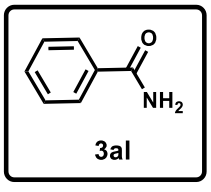
***N*-propylbenzamide (3ai)**[19] was obtained in 85% yield (69.3 mg) as white solid. The compound **3ai** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.1 Hz, 2H), 7.43-7.42 (m, 1H), 7.37-7.35 (m, 2H), 6.59 (bs, 1H), 3.36-3.35 (m, 2H), 1.61-1.56 (m, 2H), 0.94-0.91 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 134.9, 131.3, 128.5, 126.9, 41.8, 22.9, 11.5.



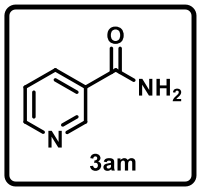
Morpholino(phenyl)methanone (3aj)[10] was obtained in 93% yield (88.9 mg) as colorless oil. The compound **3aj** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.34 (m, 5H), 3.71-3.56 (m, 6H), 3.38 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 135.3, 129.9, 128.6, 127.1, 66.9, 48.3, 42.6.



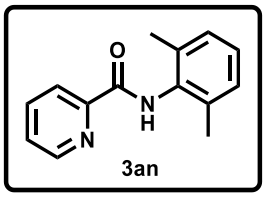
***N*,*N*-dimethylbenzamide (3ak)**[27] was obtained in 92% yield (68.6 mg) as white solid. The compound **3ak** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 5H), 3.07 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 136.2, 129.5, 128.3, 127.0, 39.5, 35.3.



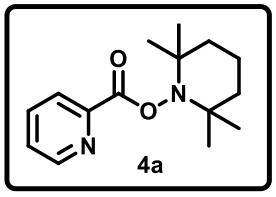
Benzamide (3al)[19] was obtained in 82% yield (49.6 mg) as white solid. The compound **3al** was purified with chromatography on silica gel (hexane/ethyl acetate = 7:3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 6.30 (bs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 133.4, 132.1, 128.7, 127.4.



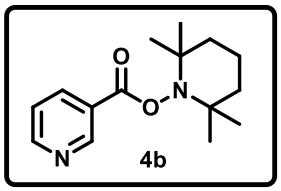
Nicotinamide (3am)[28] was obtained in 78% yield (47.6 mg) as white solid. The compound **3am** was purified with chromatography on silica gel (hexane/ethyl acetate = 1:4). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.99 (s, 1H), 8.66 (d, J = 4.7 Hz, 1H), 8.17-8.14 (m, 2H), 7.59 (s, 1H), 7.46-7.44 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.9, 152.4, 149.2, 135.6, 130.1, 123.9.



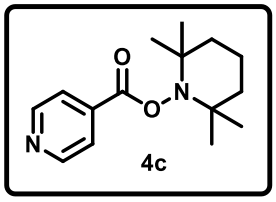
***N*-(2,6-dimethylphenyl)picolinamide (3an)**[24] was obtained in 65% yield (73.5 mg) as white solid. The compound **3an** was purified with chromatography on silica gel (hexane/ethyl acetate = 19:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.62 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.90-7.87 (m, 1H), 7.49-7.48 (m, 1H), 7.12 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 149.8, 148.2, 137.6, 135.4, 133.8, 128.2, 127.2, 126.5, 122.6, 18.7.



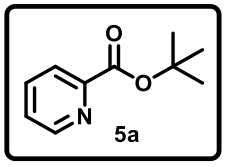
2,2,6,6-tetramethylpiperidin-1-yl picolinate (4a)[29] was obtained in 60% yield (78.7 mg) as white solid. The compound **4a** was purified with chromatography on silica gel (hexane/ethyl acetate = 9:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78-8.77 (m, 1H), 8.05 (t, J = 7.8 Hz, 1H), 7.85-7.81 (m, 1H), 7.48-7.44 (m, 1H), 1.77-1.65 (m, 3H), 1.58-1.57 (m, 2H), 1.45-1.42 (m, 1H), 1.27 (d, J = 7.2 Hz, 6H), 1.13 (d, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 150.1, 147.8, 136.7, 126.6, 124.6, 60.4, 38.9, 31.8, 20.7, 16.8.



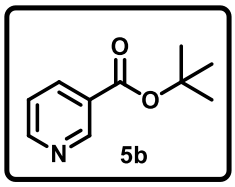
2,2,6,6-tetramethylpiperidin-1-yl nicotinate (4b) was obtained in 72% yield (94.4 mg) as white solid (m.p. = 89-91 ^{o}C). The compound **4b** was purified with chromatography on silica gel (hexane/ethyl acetate = 9:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.78-8.77 (m, 1H), 8.32-8.30 (m, 1H), 7.41-7.39 (m, 1H), 1.74-1.65 (m, 3H), 1.58-1.56 (m, 2H), 1.45-1.43 (m, 1H), 1.24 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 153.4, 150.5, 137.2, 125.6, 123.4, 60.5, 39.0, 31.9, 20.8, 16.9.
HRMS (ESI) m/z calculated for $C_{15}H_{22}N_2O_2$ $[M+H]^+$ 263.1760, found 263.1764.



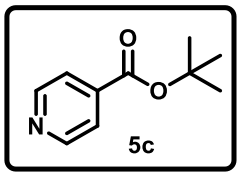
2,2,6,6-tetramethylpiperidin-1-yl isonicotinate (4c)[30] was obtained in 80% yield (104.4 mg) as colorless solid. The compound **4c** was purified with chromatography on silica gel (hexane/ethyl acetate = 9:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, J = 5.8 Hz, 2H), 7.84 (d, J = 6 Hz, 2H), 1.76-1.65 (m, 3H), 1.58-156 (m, 2H), 1.45-1.42 (m, 1H), 1.24 (s, 6H), 1.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 150.5, 136.9, 122.8, 60.6, 39.0, 31.8, 20.7, 16.8.



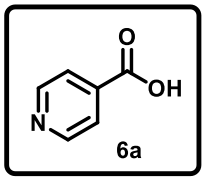
***tert*-butyl picolinate (5a)**[31] was obtained in 76% yield (68 mg) as colorless oil. The compound **5a** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 4.4 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.52–7.49 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 150.0, 146.6, 137.0, 127.2, 125.0, 84.4, 26.2.



***tert*-butyl nicotinate (5b)**[32] was obtained in 78% yield (69.8 mg) as colorless oil. The compound **5b** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.1 (s, 1H), 8.77 (d, J = 4.6 Hz, 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.41–7.38 (m, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 153.7, 149.9, 136.6, 123.9, 123.5, 84.4, 26.1.



***tert*-butyl isonicotinate (5c)**[33] was obtained in 80% yield (71.6 mg) as yellow oil. The compound **5c** was purified with chromatography on silica gel (hexane/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 5.9 Hz, 2H), 7.73 (d, J = 6 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 150.7, 134.9, 122.3, 84.6, 26.1.



Isonicotinic acid (6a)[34] was obtained in 64% yield (39.3 mg) as white solid. The compound **6a** was purified with chromatography on silica gel (hexane/ethyl acetate = 1:9). ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.63 (bs, 1H), 8.74 (d, J = 6 Hz, 2H), 7.77 (d, J = 6 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 166.6, 151.0, 138.6, 123.2.

IV. References

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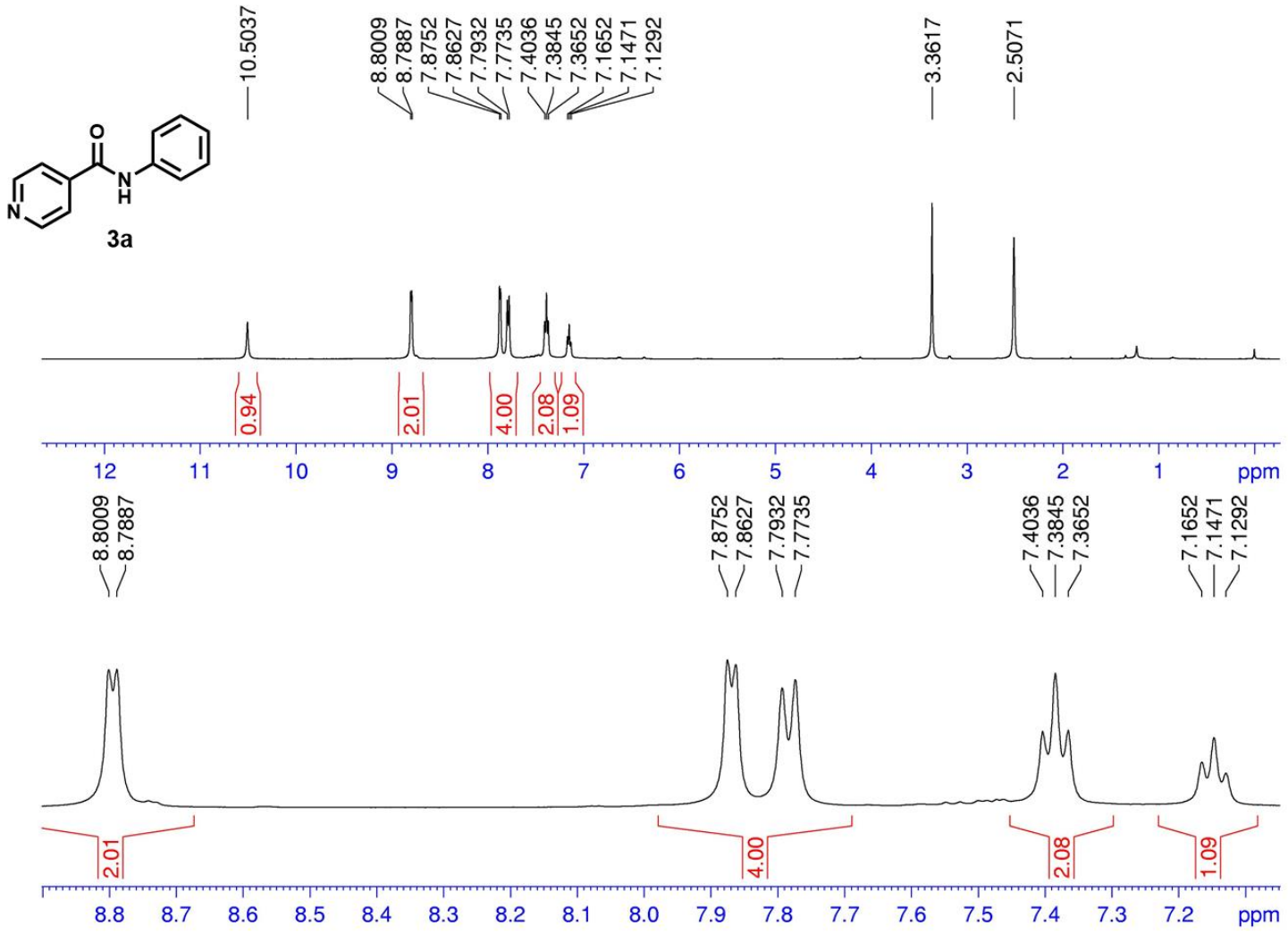
34. The NMR spectra is in accordance with the standard sample procured from Sigma Aldrich.

V. Copies of NMR spectra of substrates

3a ^{1}H NMR (400 MHz, $CDCl_3$)



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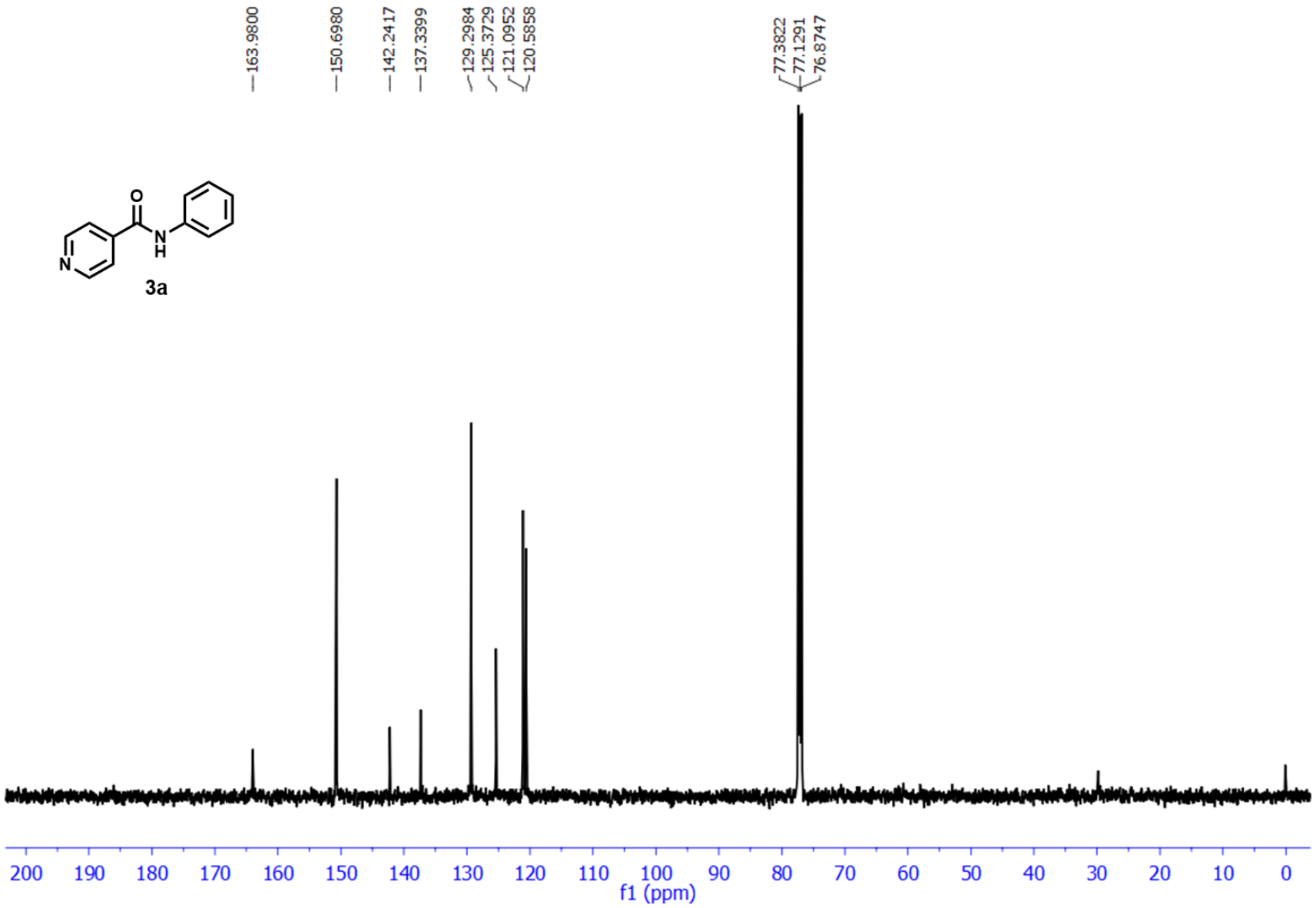

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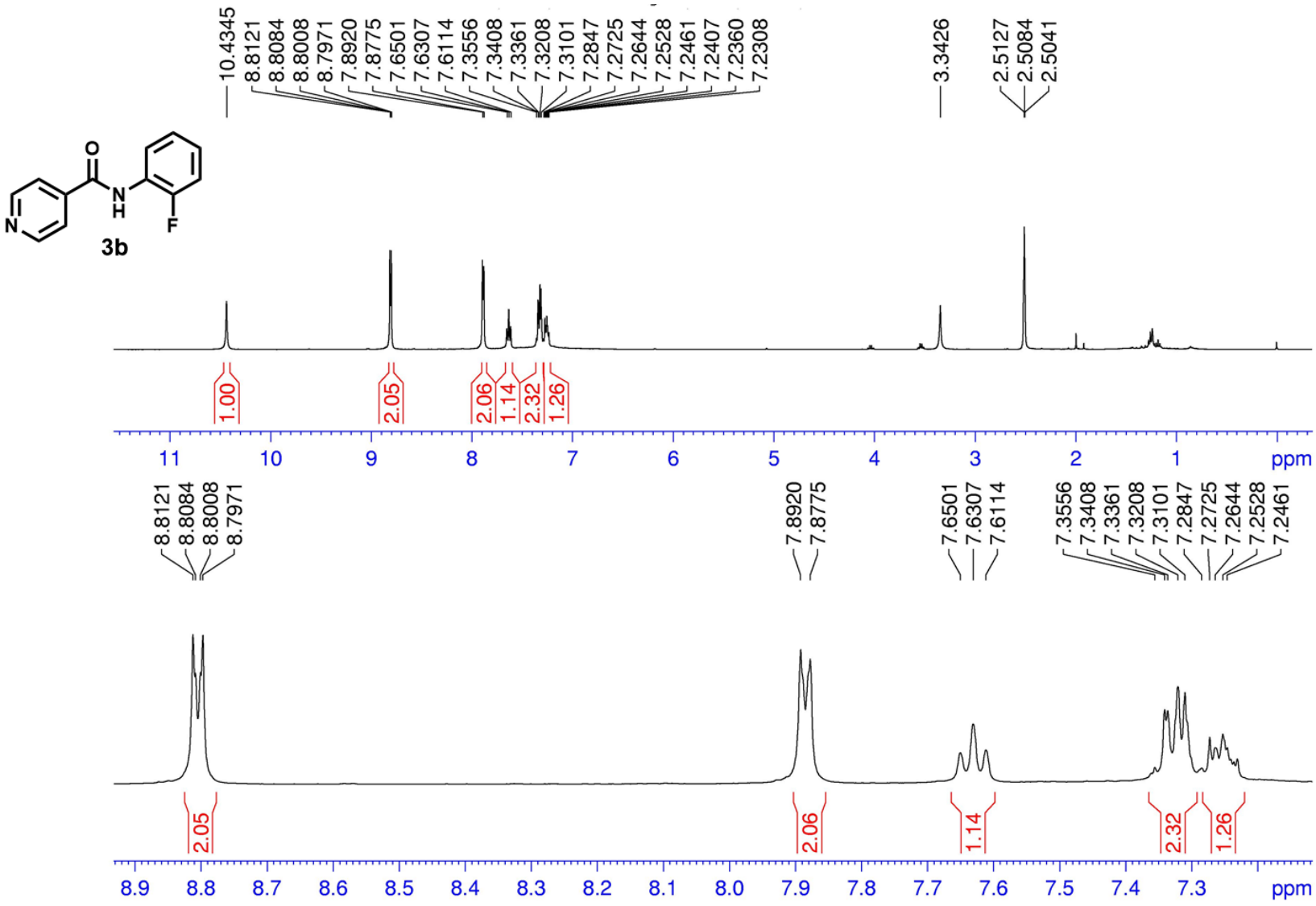

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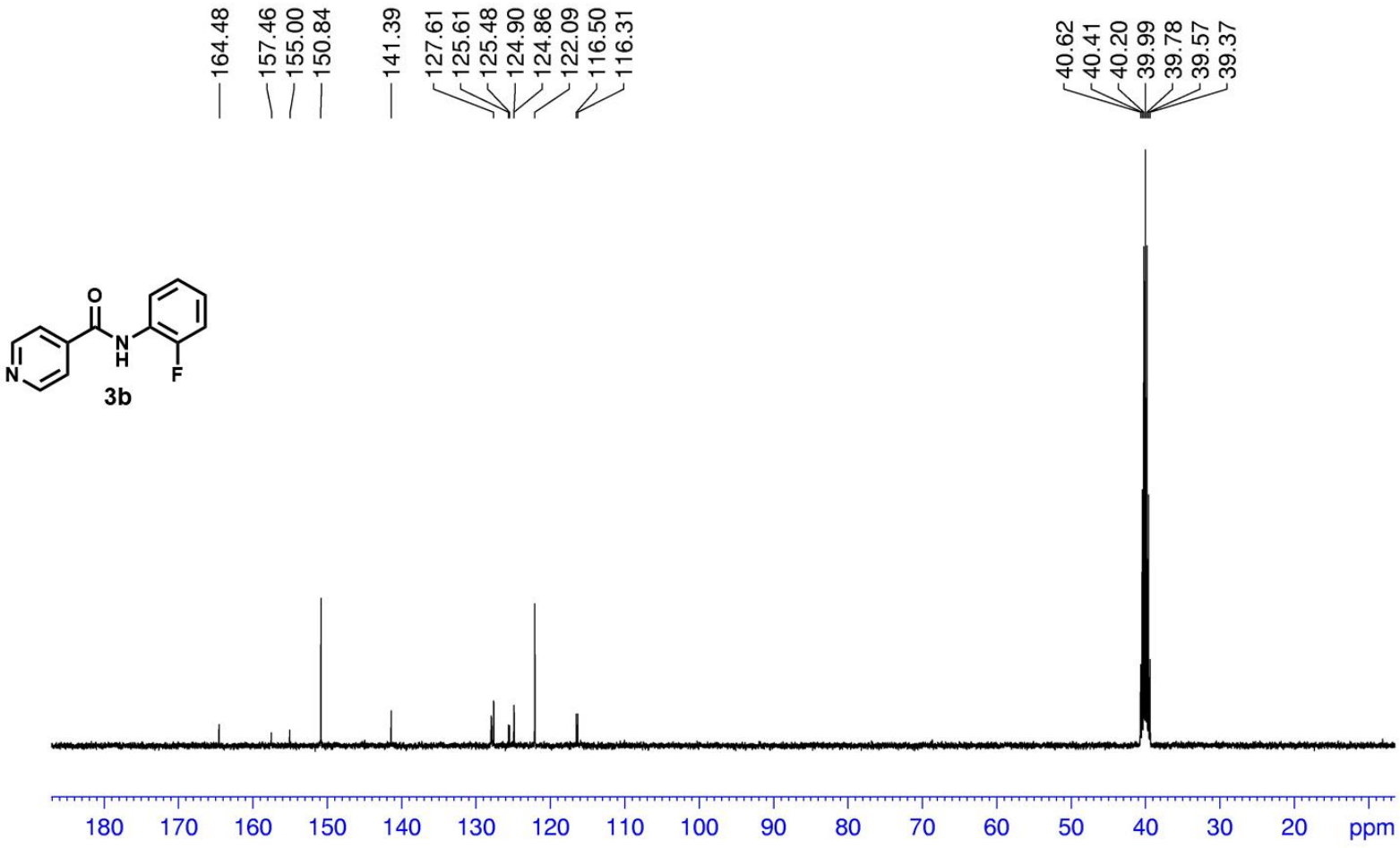

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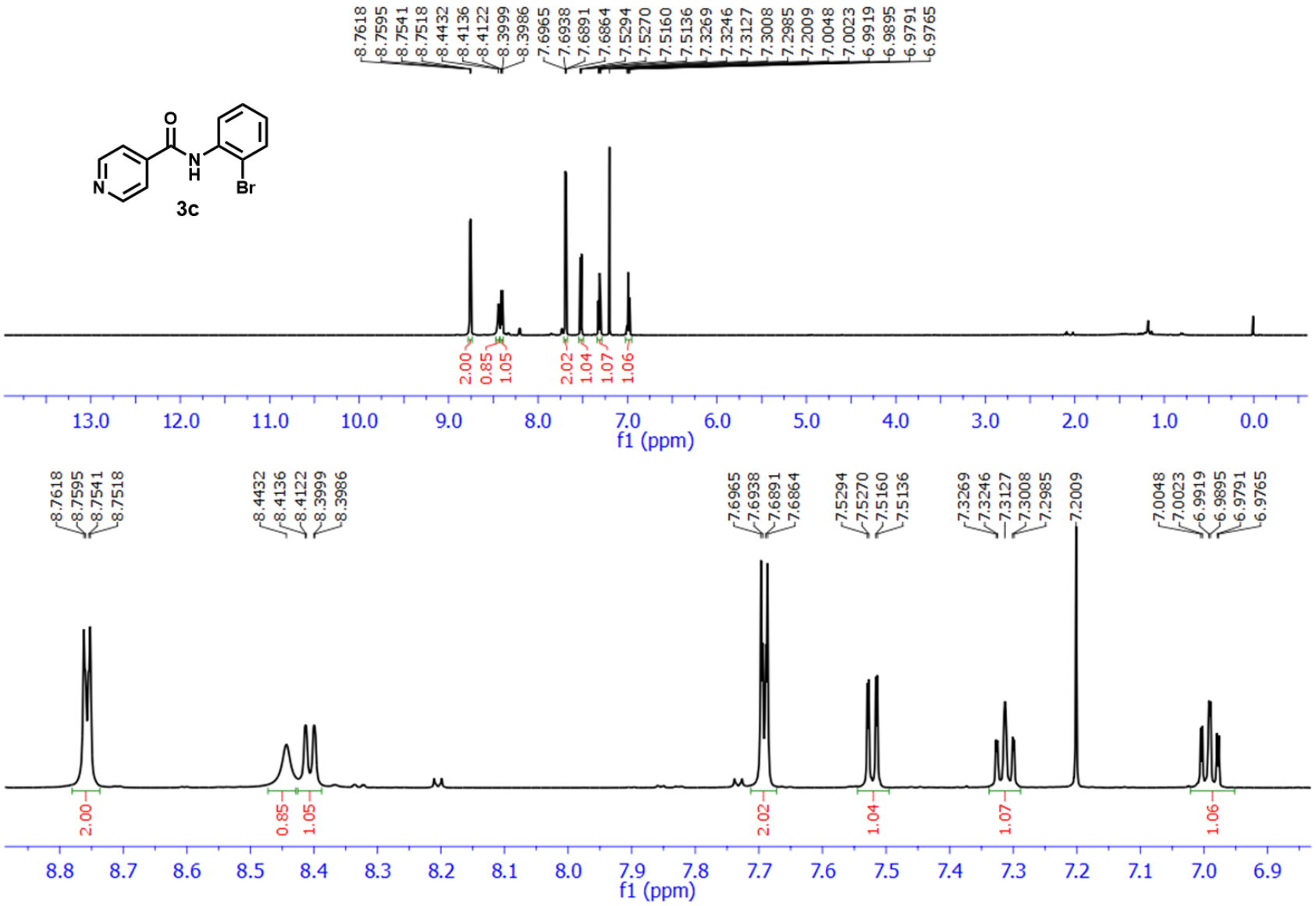

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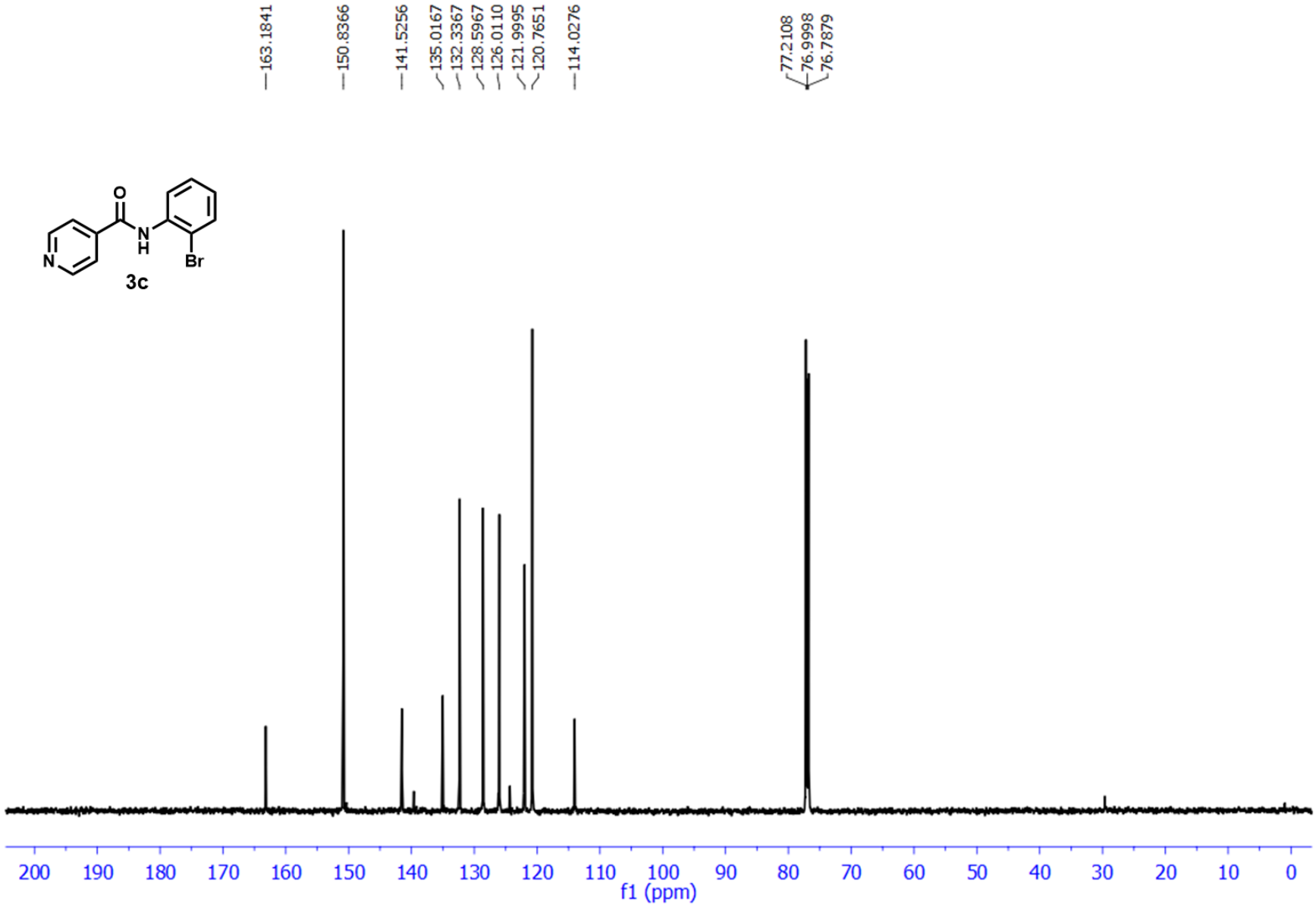

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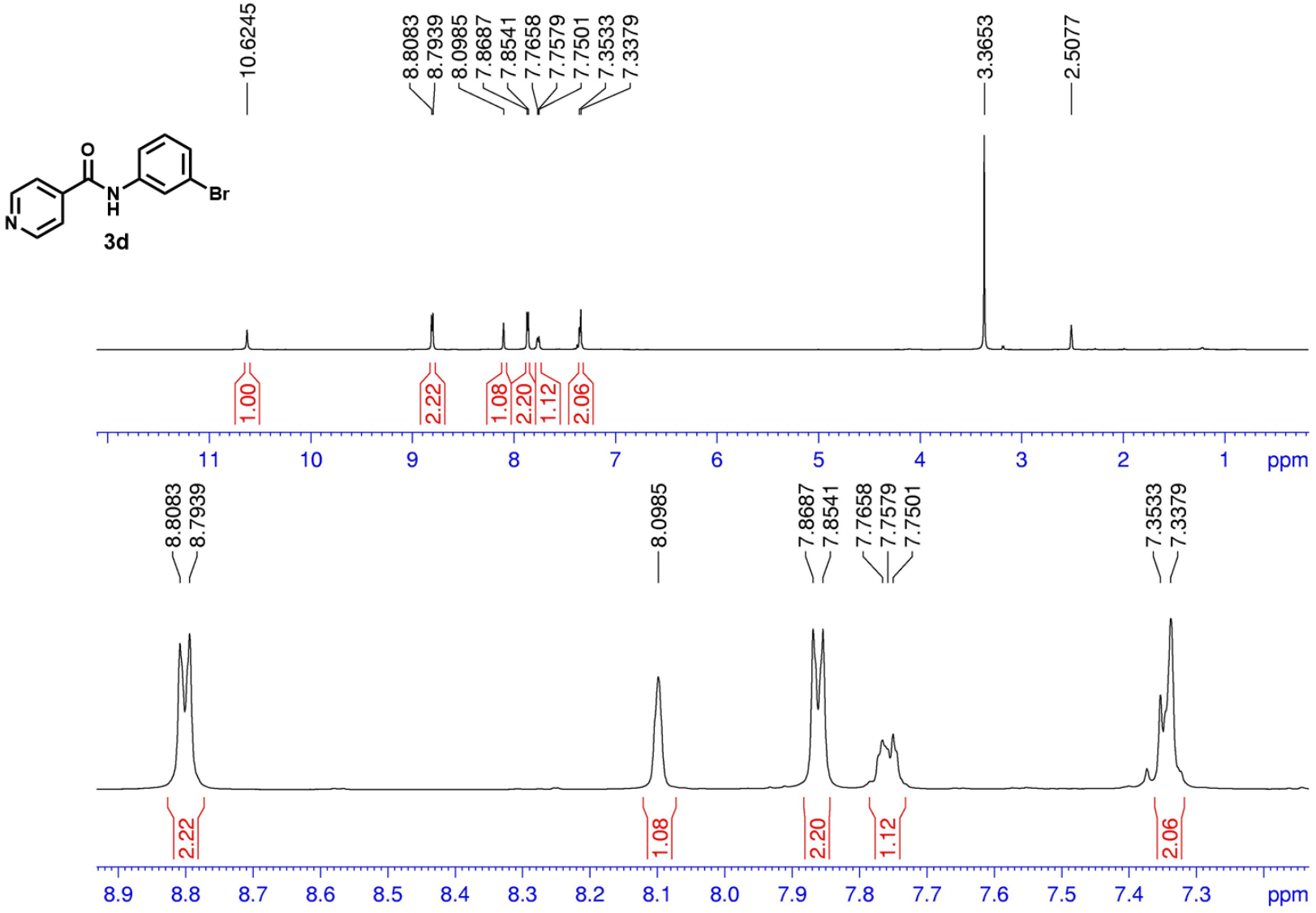

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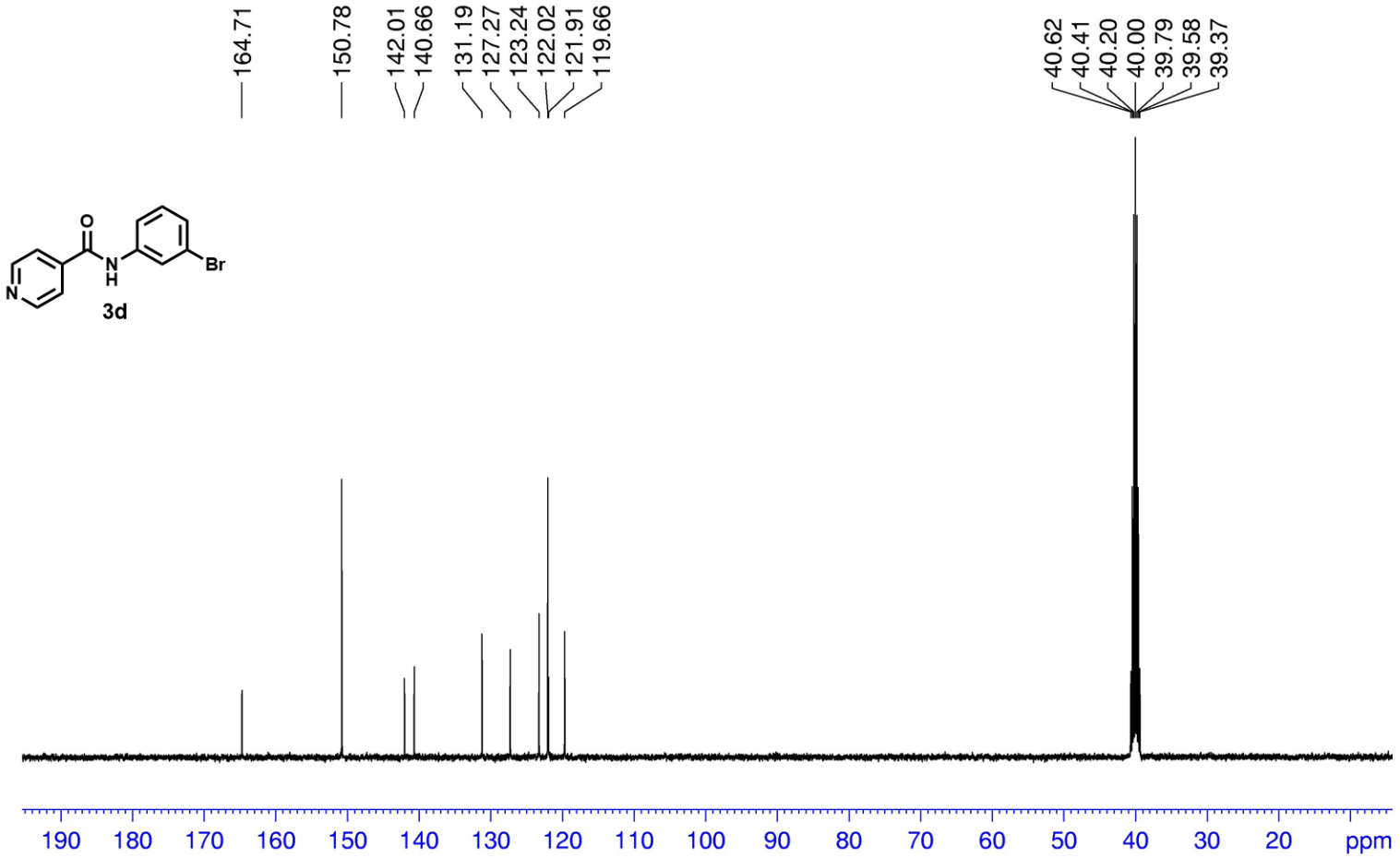

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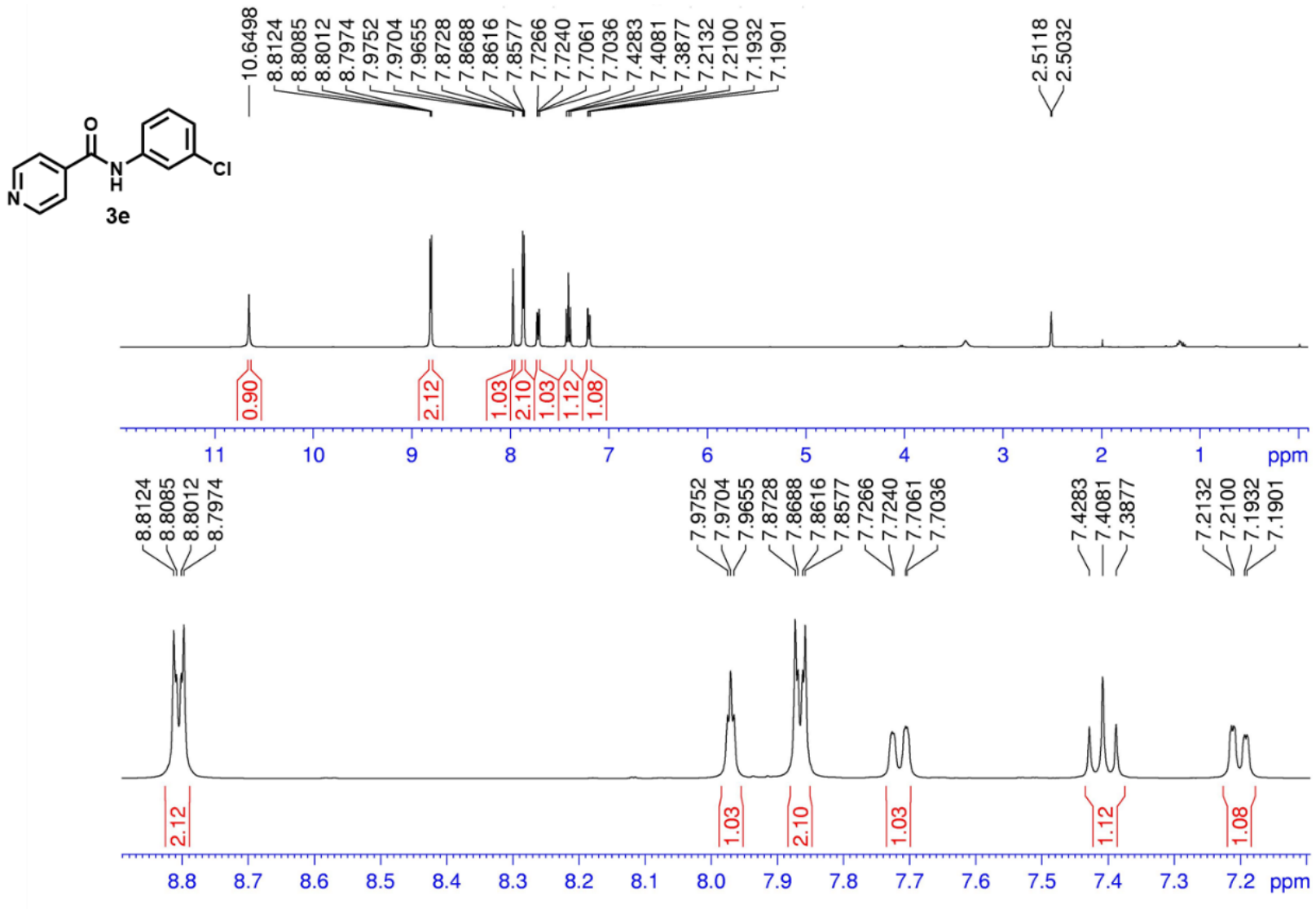
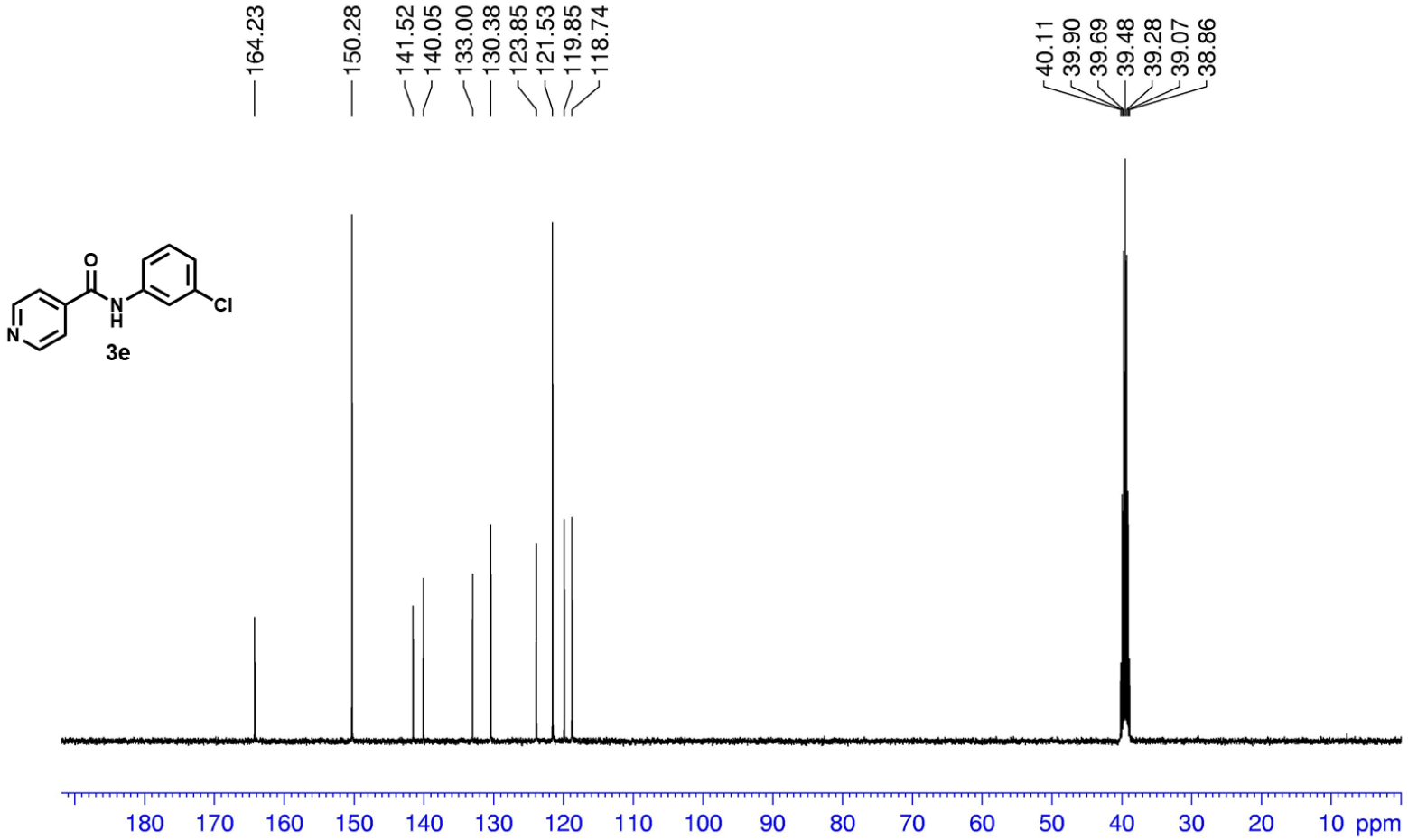


3e ^{13}C {1H} NMR (100 MHz, DMSO-d_6)



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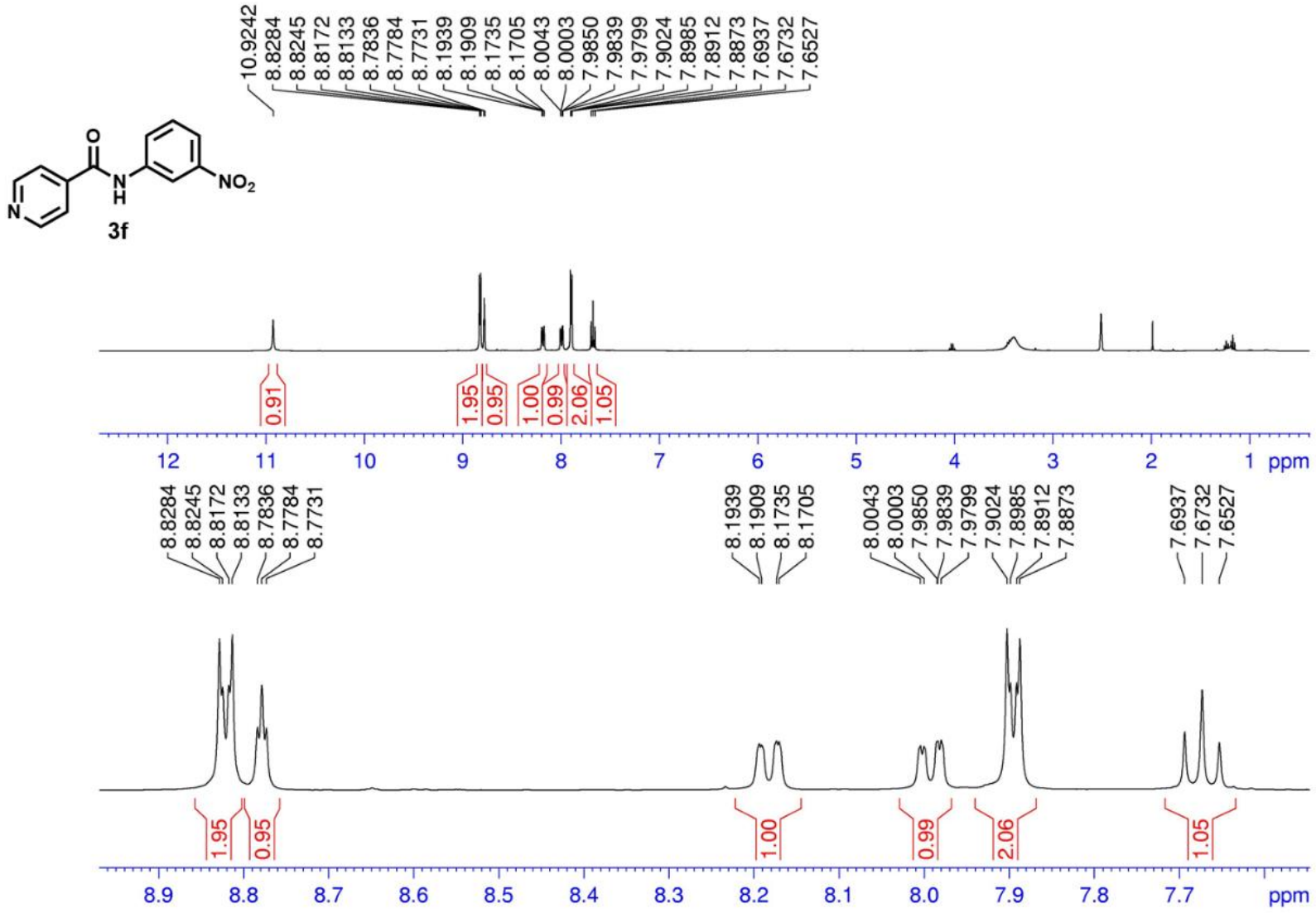
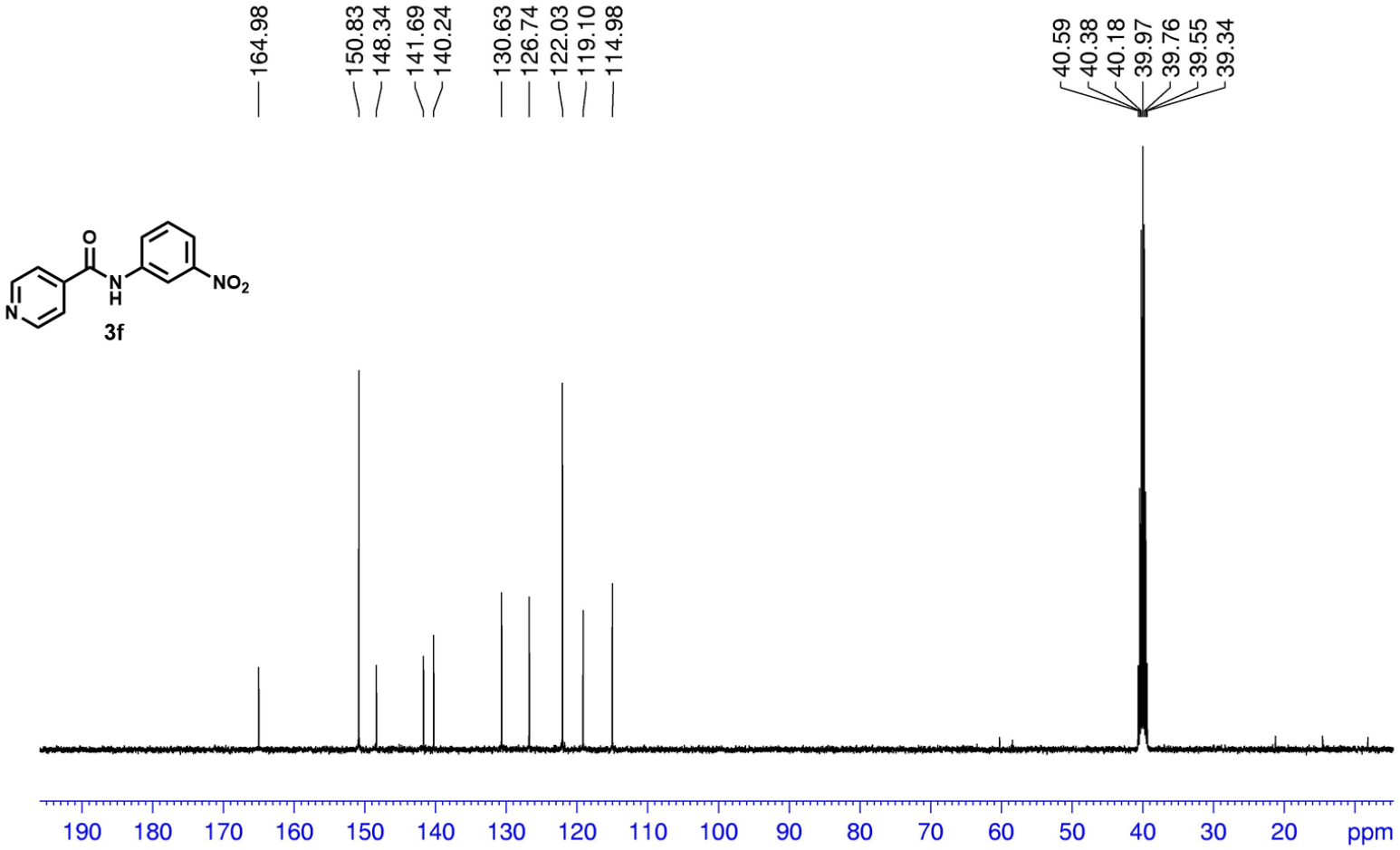


3f ^{13}C {1H} NMR (100 MHz, DMSO-d_6)



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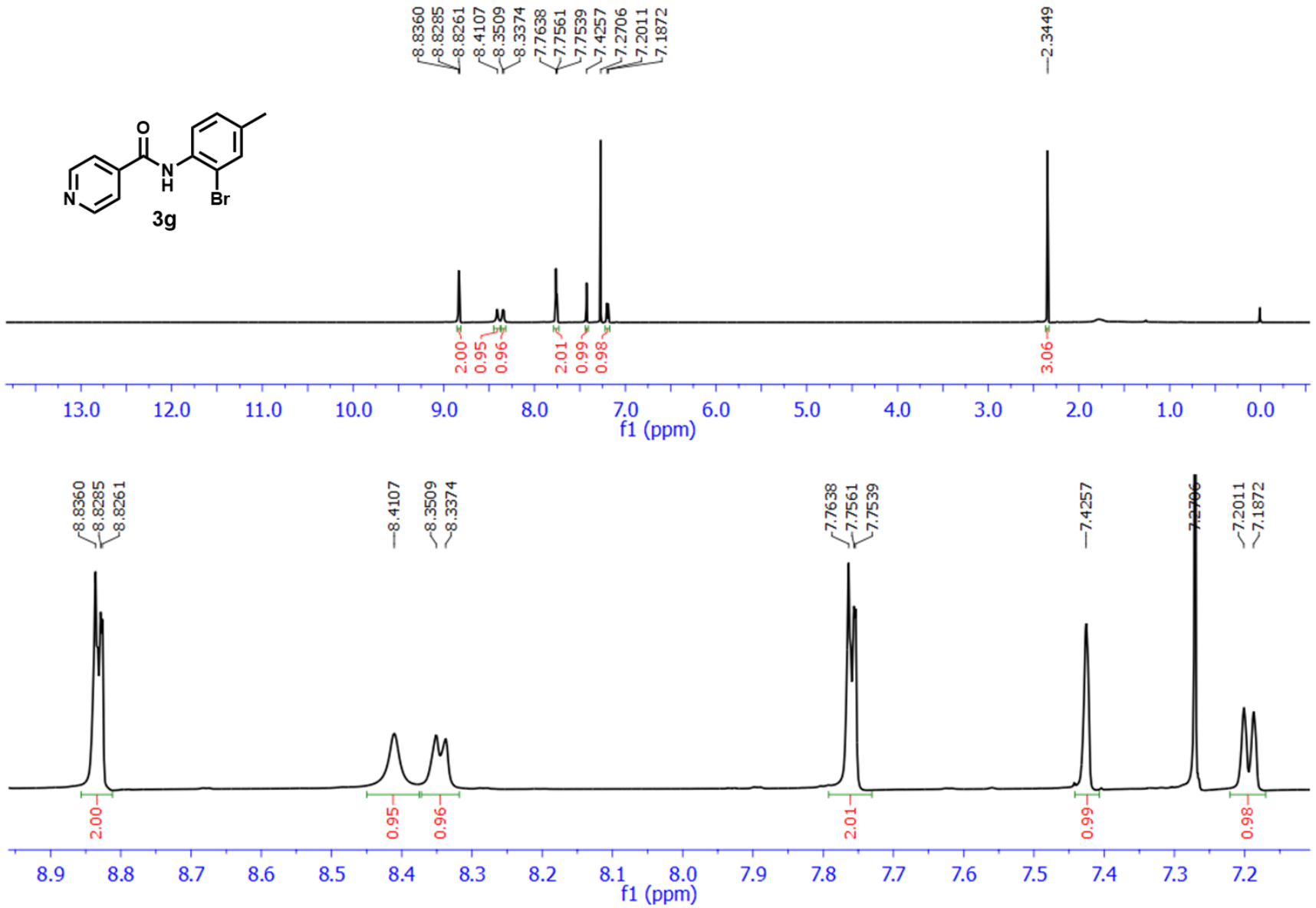

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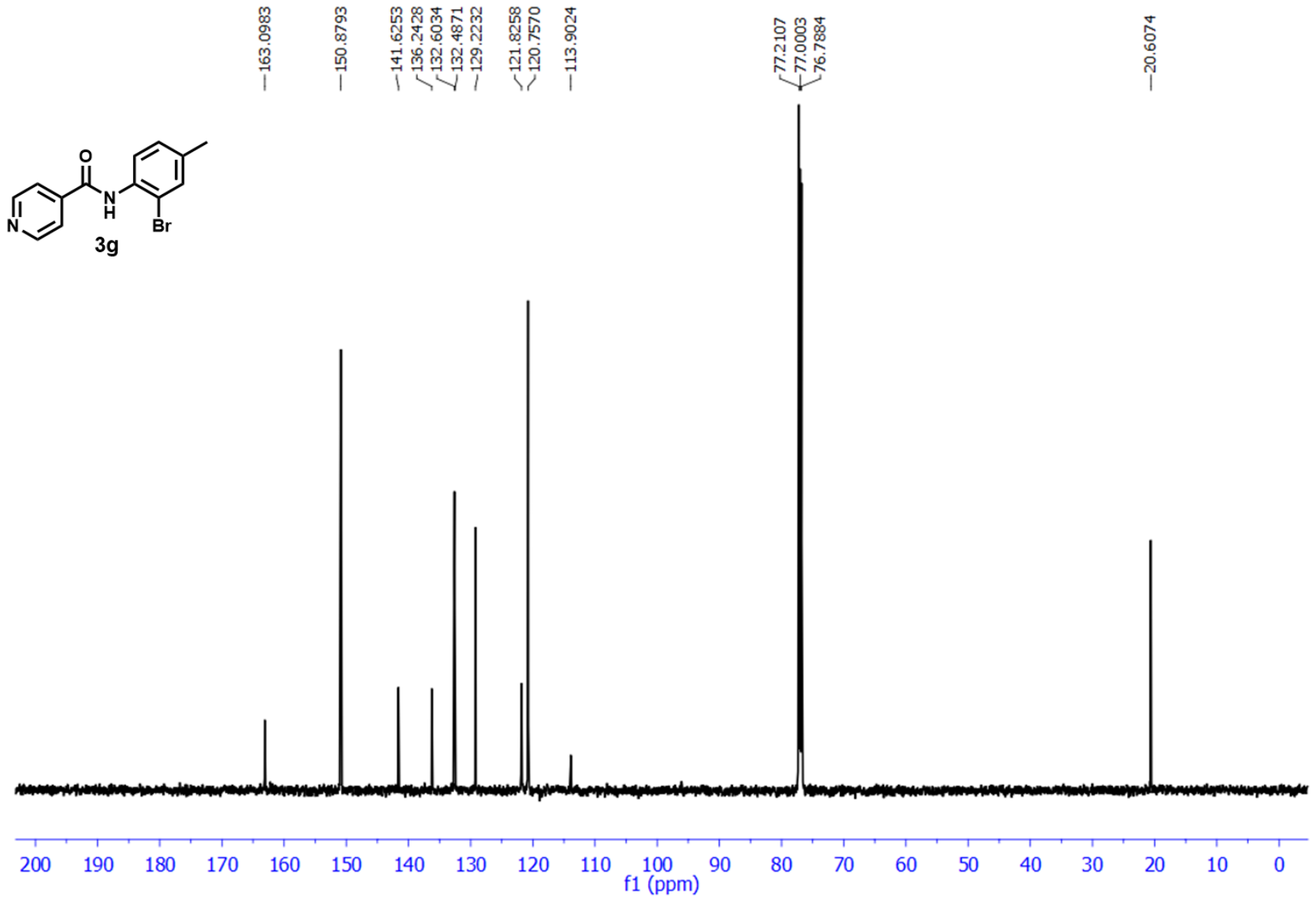

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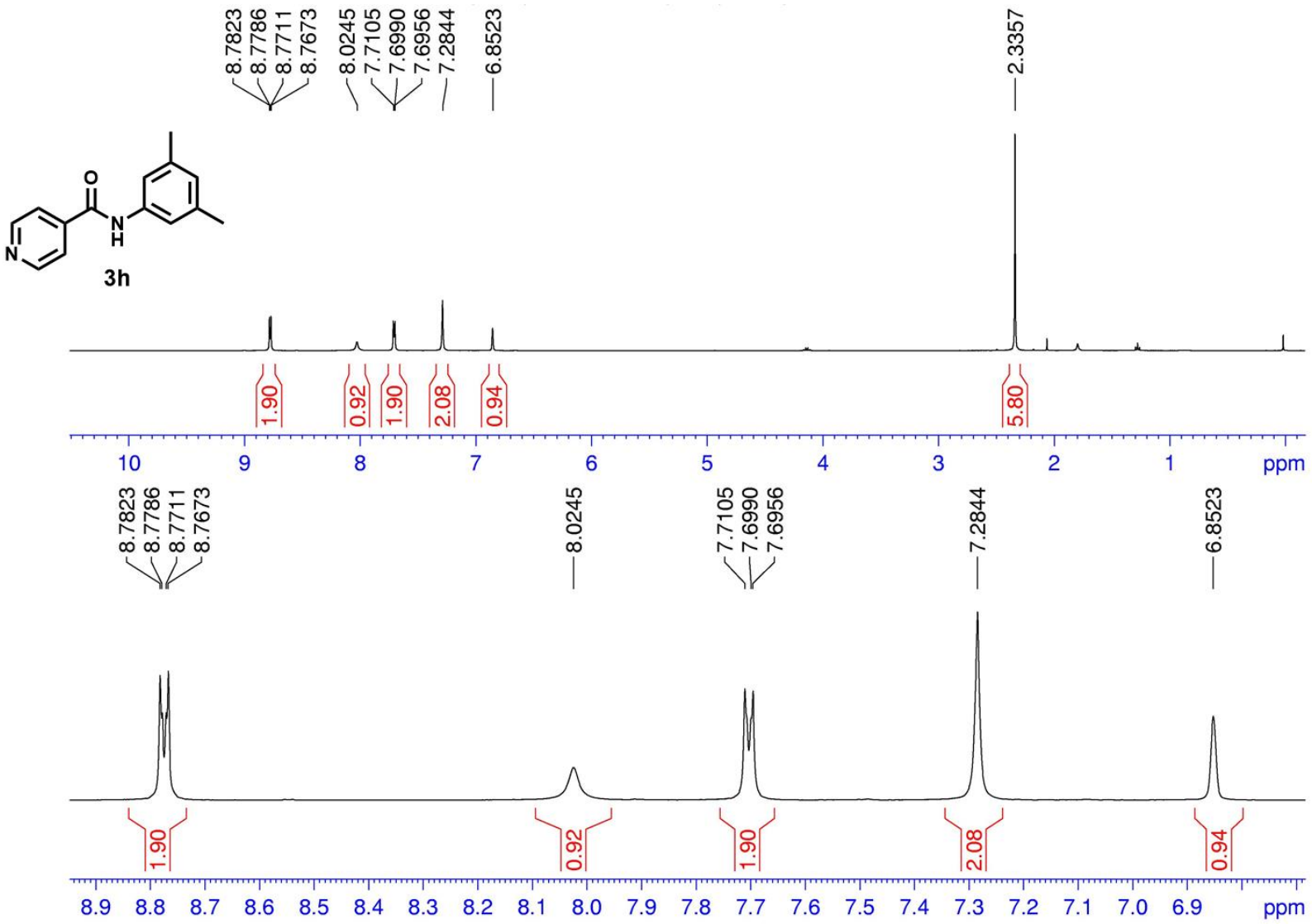
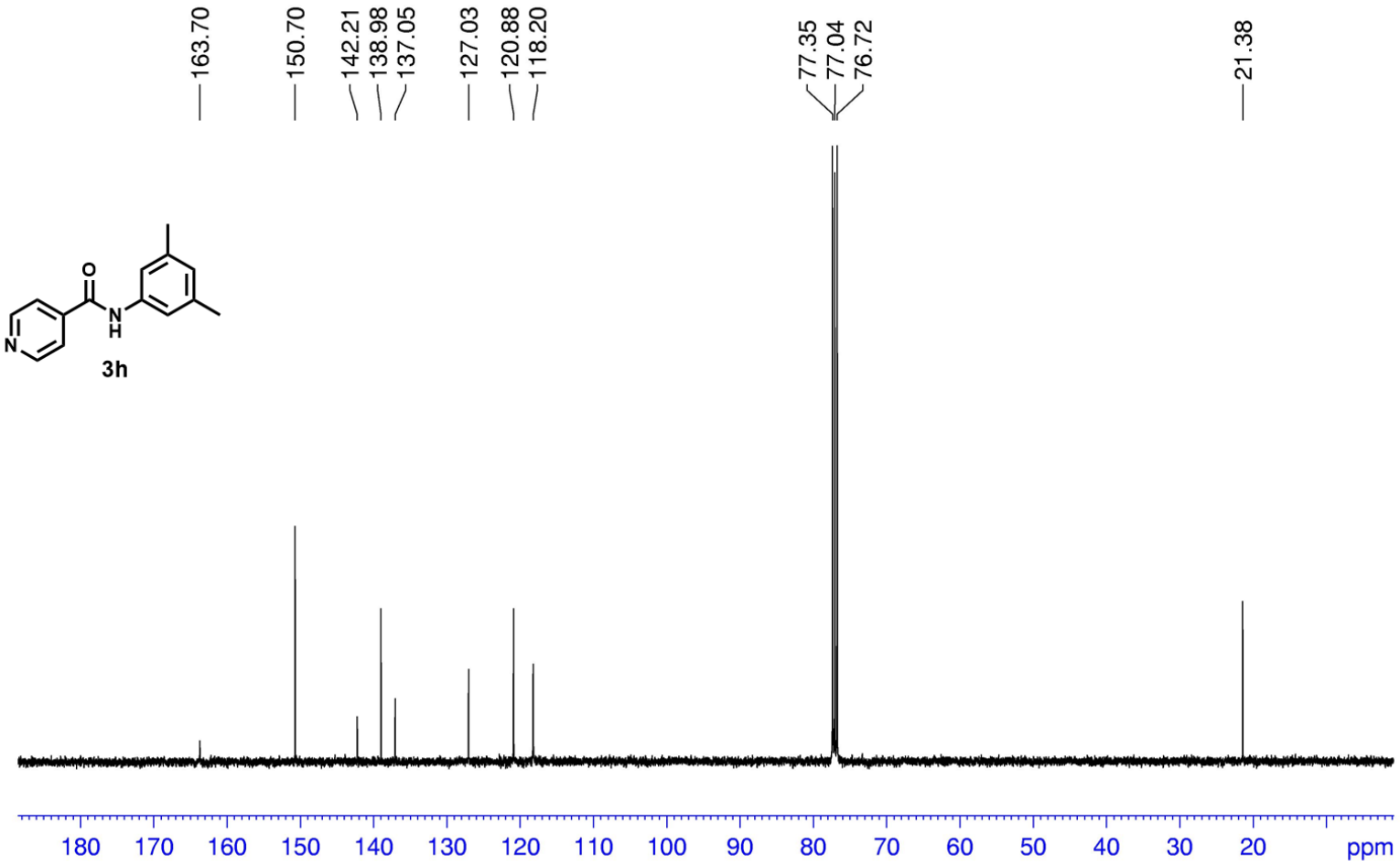
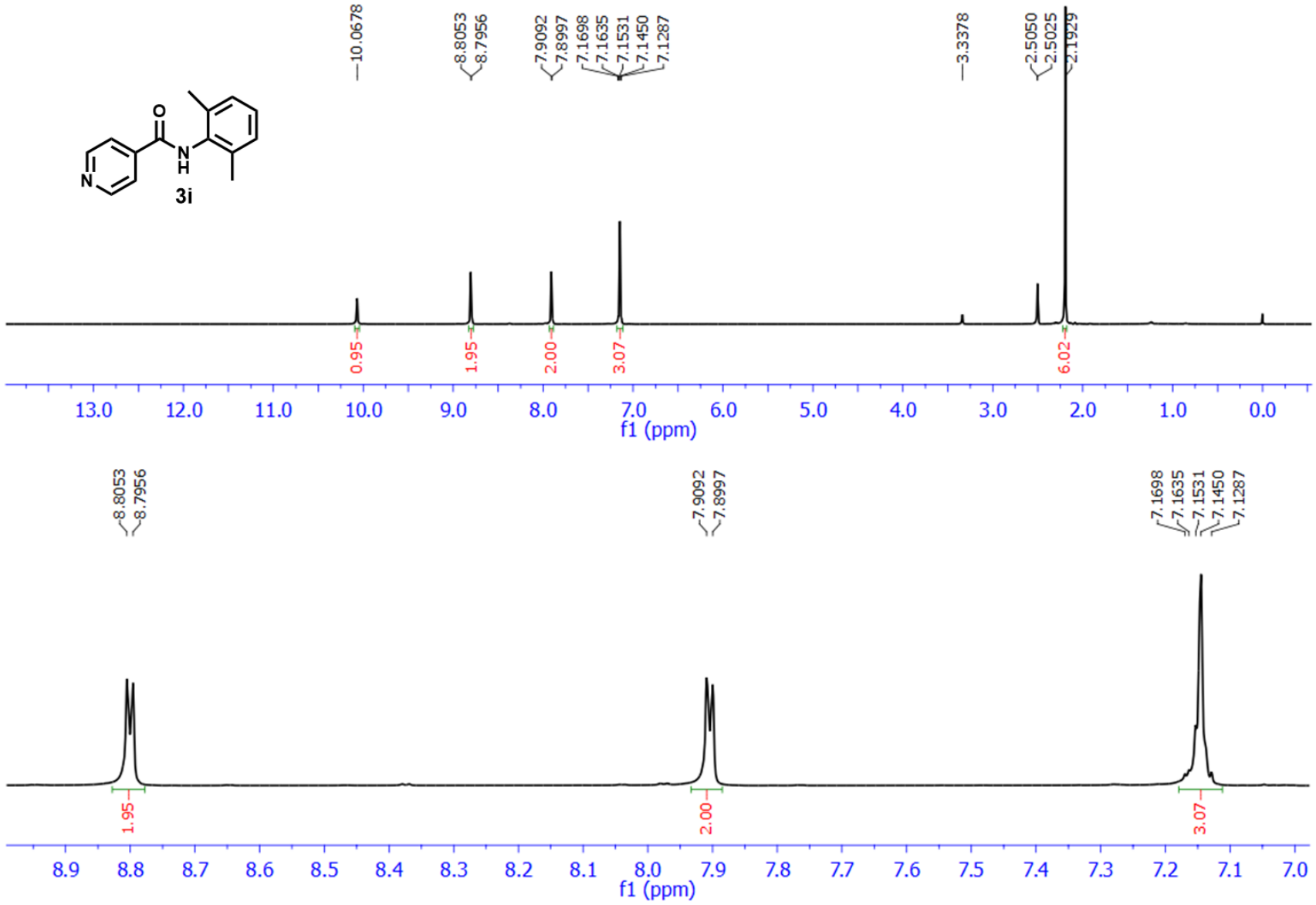


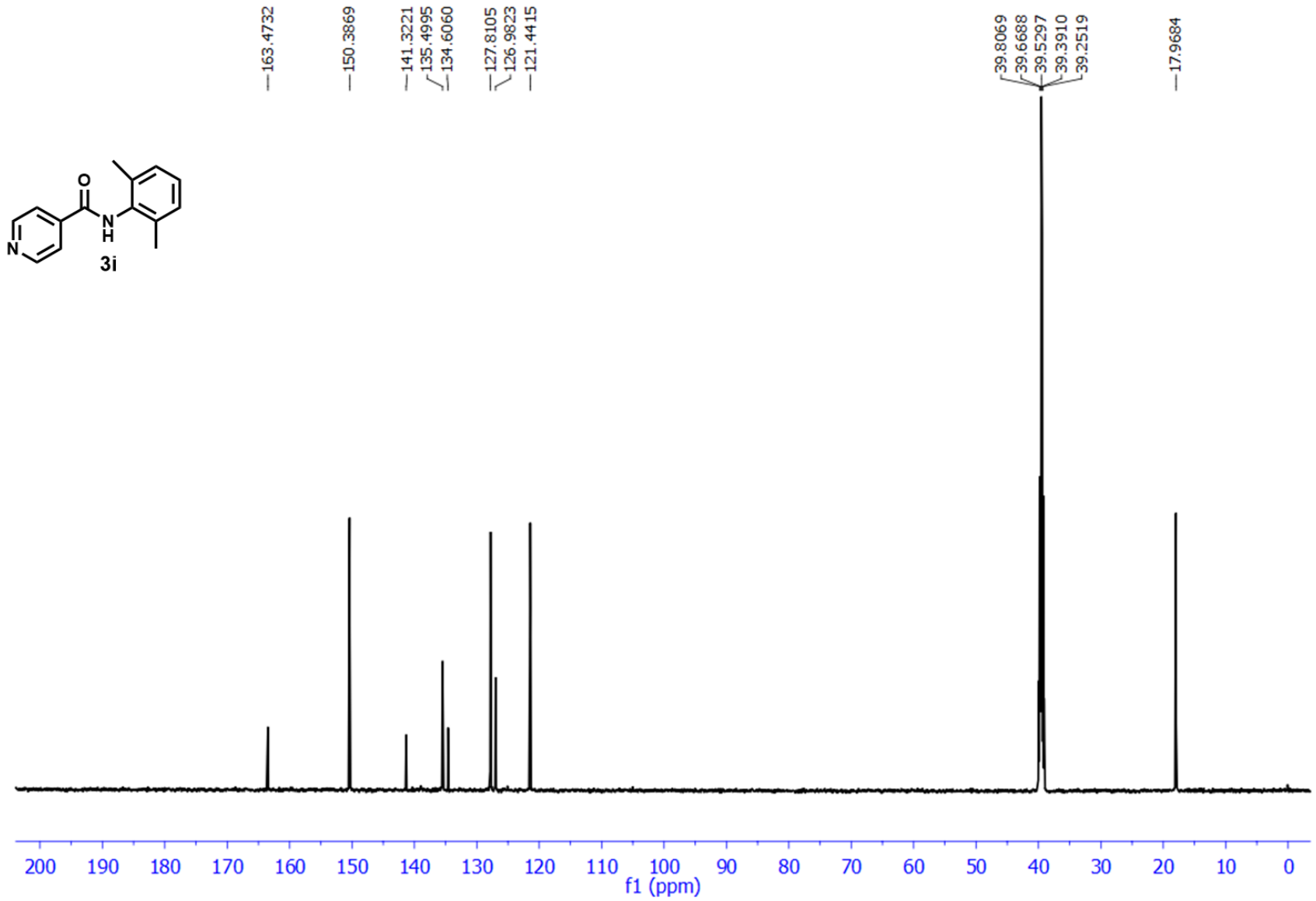
3h ^{13}C {1H} NMR (100 MHz, $CDCl_3$)



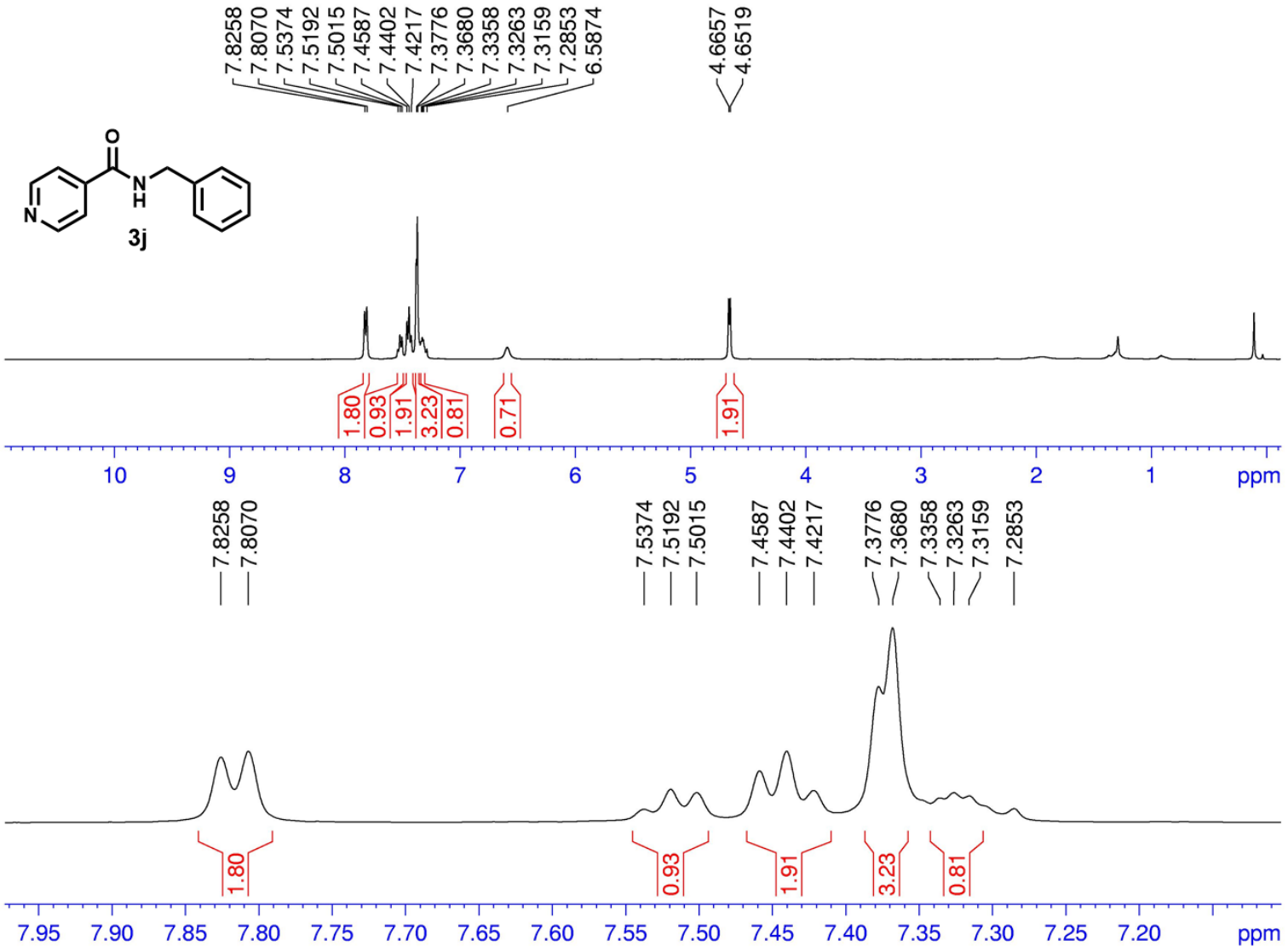
3i ^{1}H NMR (600 MHz, DMSO-d_6)



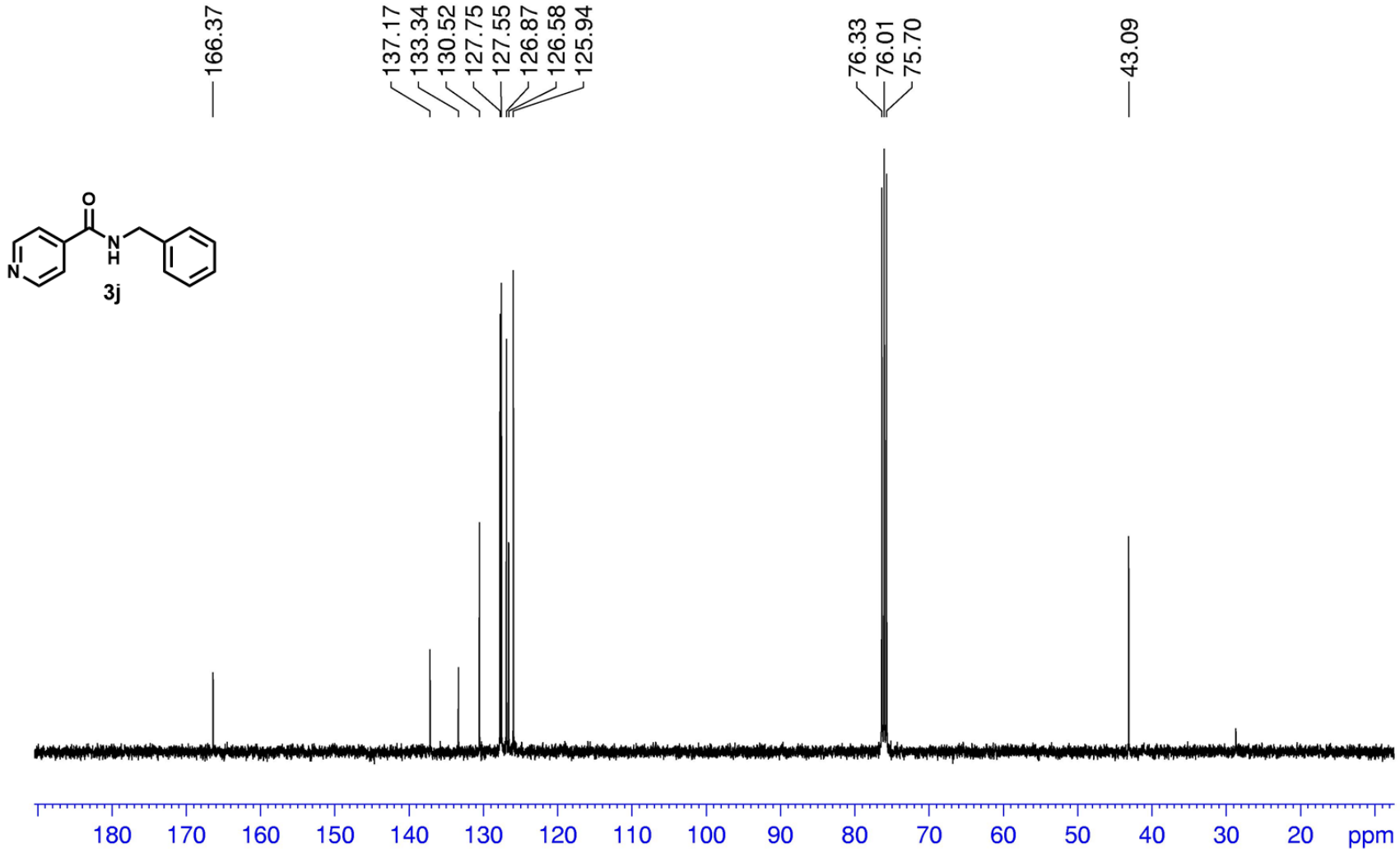
3i ^{13}C {1H} NMR (150 MHz, DMSO-d_6)



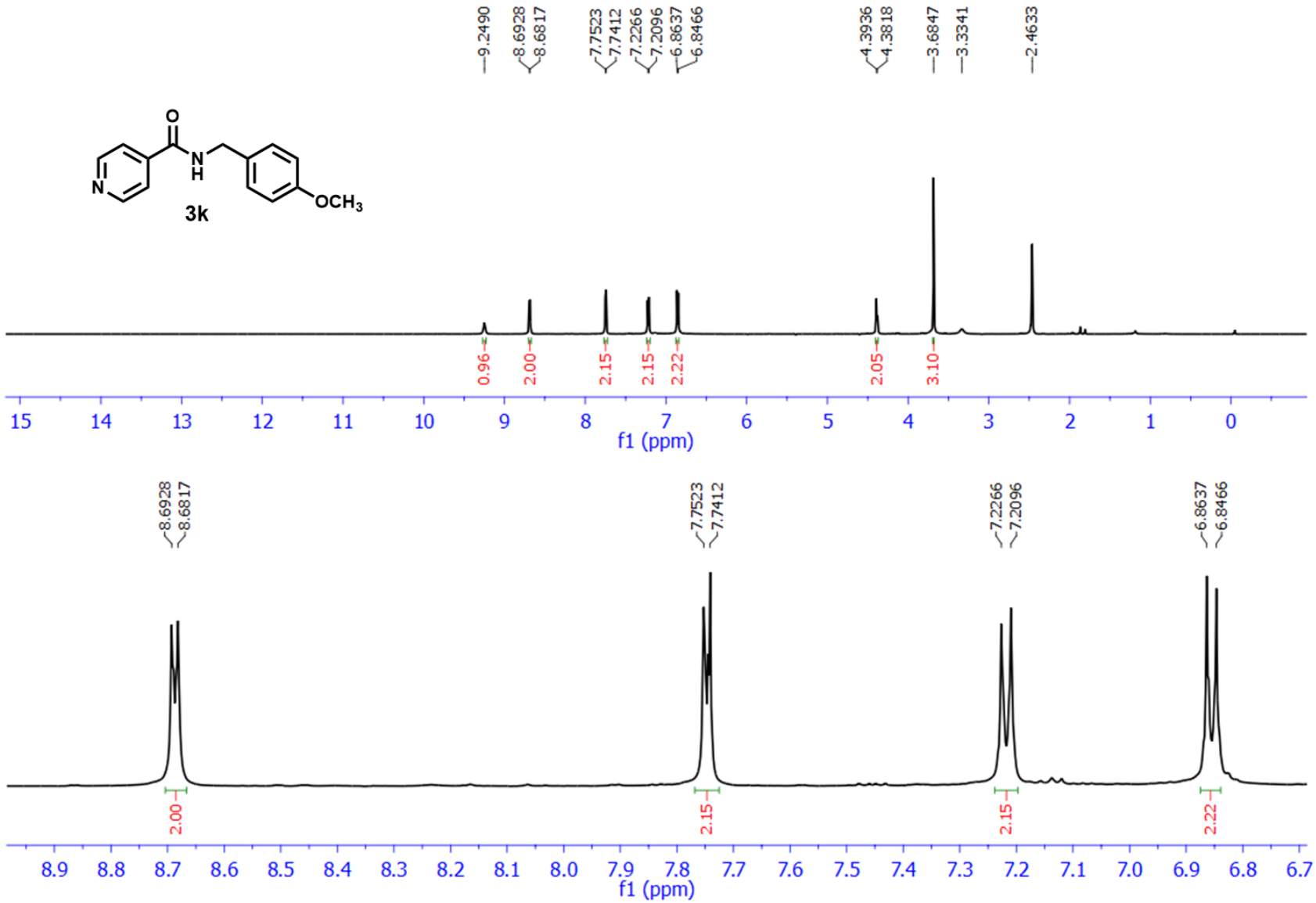
3j ^{1}H NMR (400 MHz, $CDCl_3$)



3j ^{13}C {1H} NMR (100 MHz, $CDCl_3$)

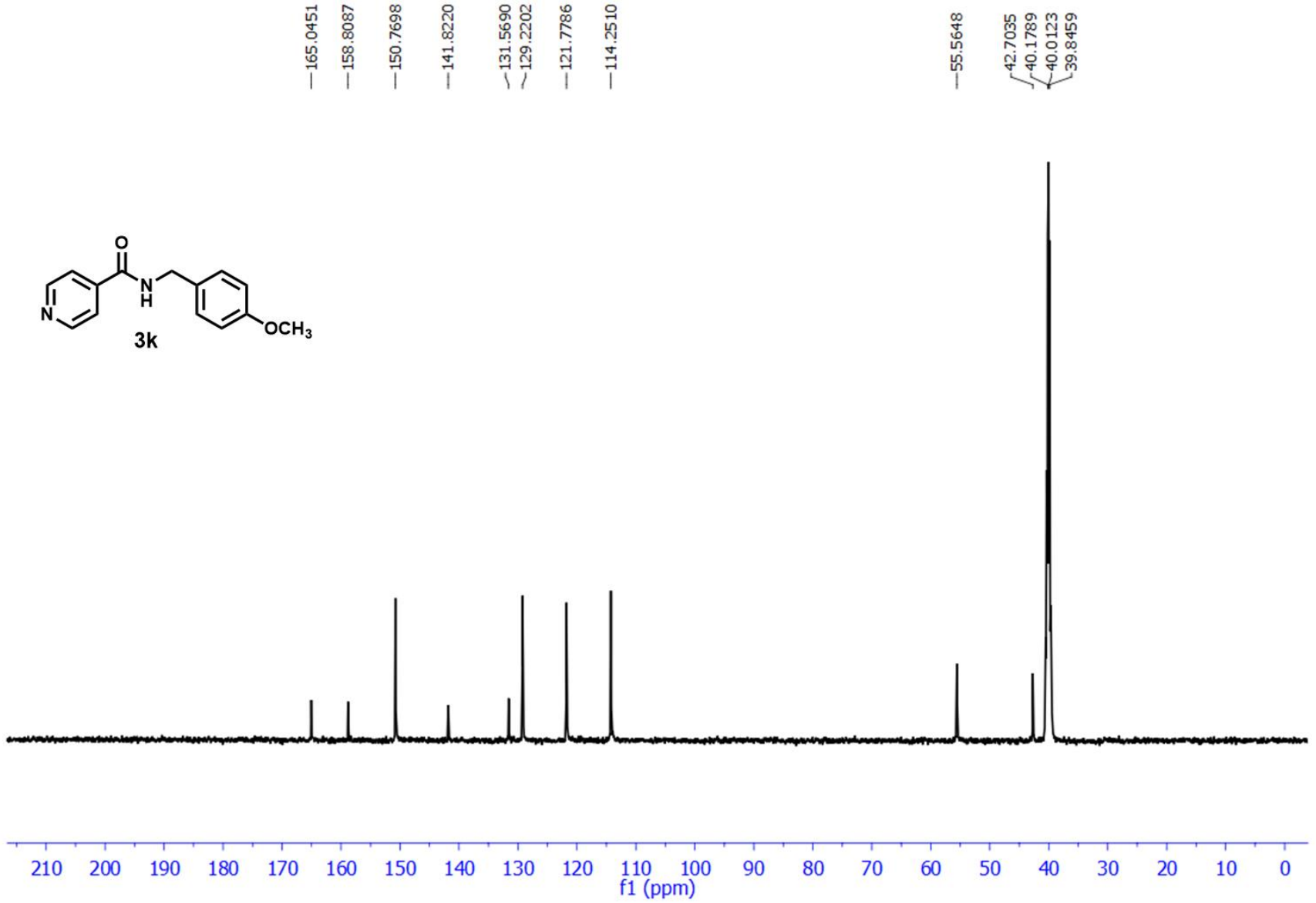


3k ^{1}H NMR (500 MHz, DMSO-d_6)

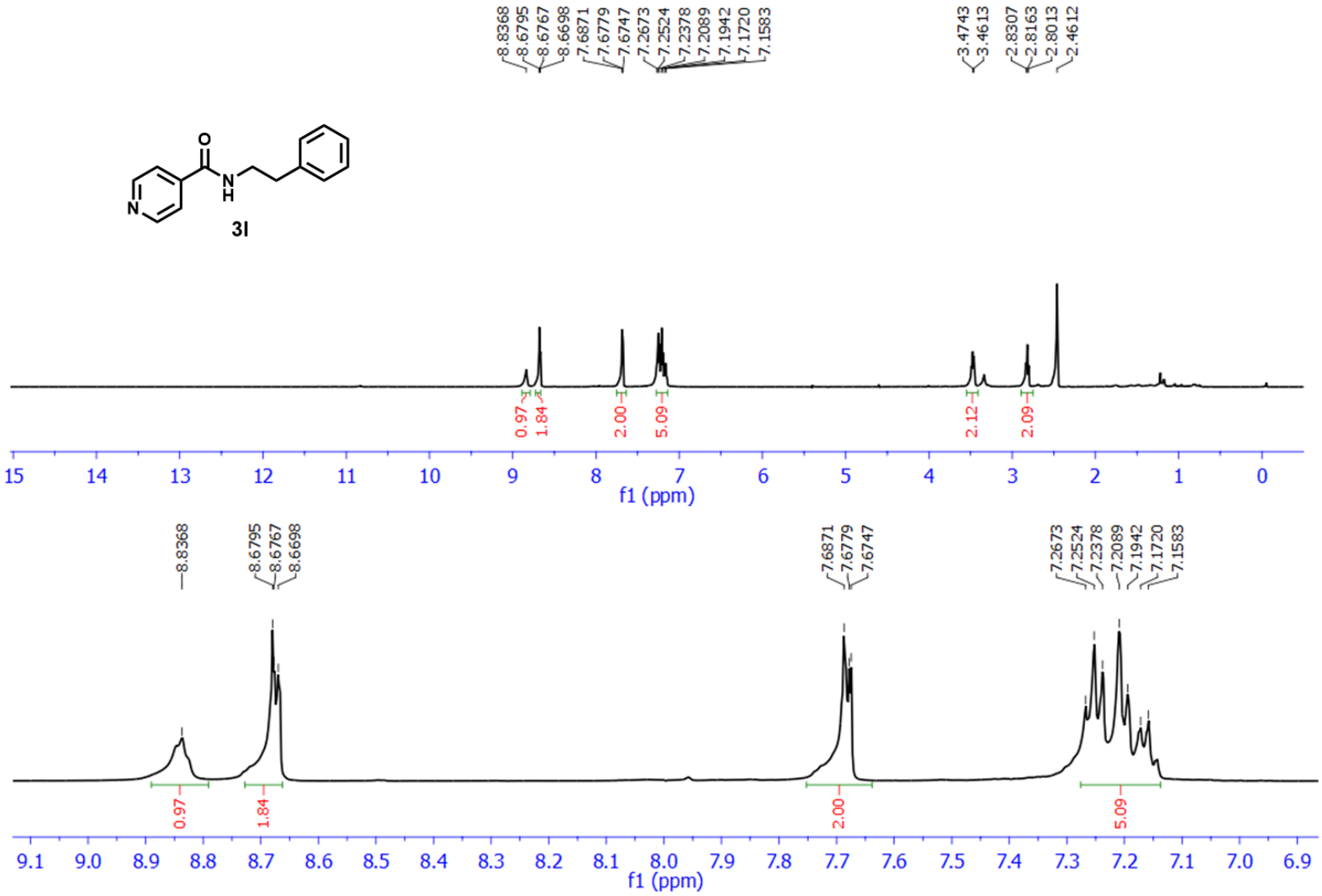


3k

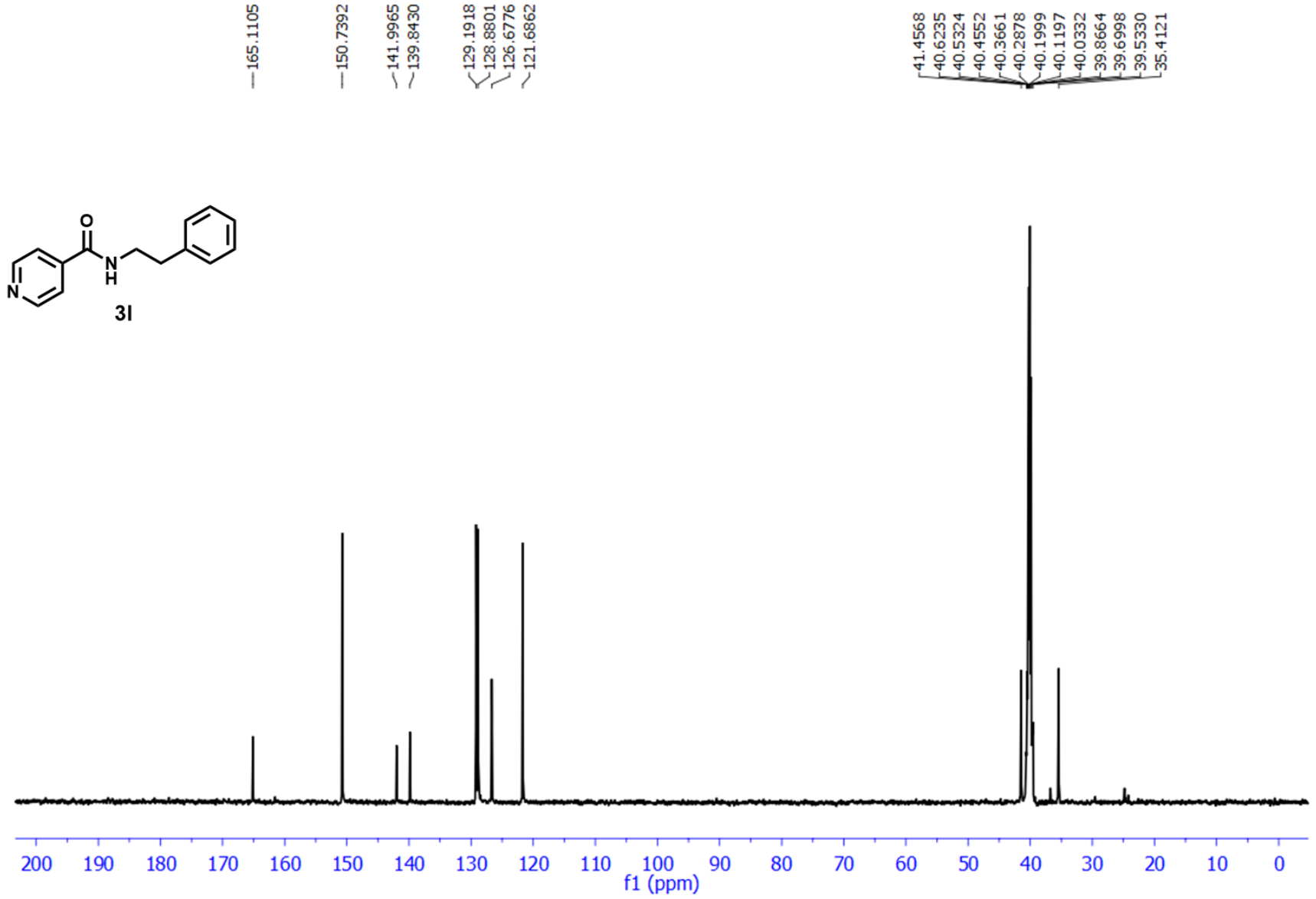
3k ^{13}C {1H} NMR (125 MHz, $CDCl_3$)



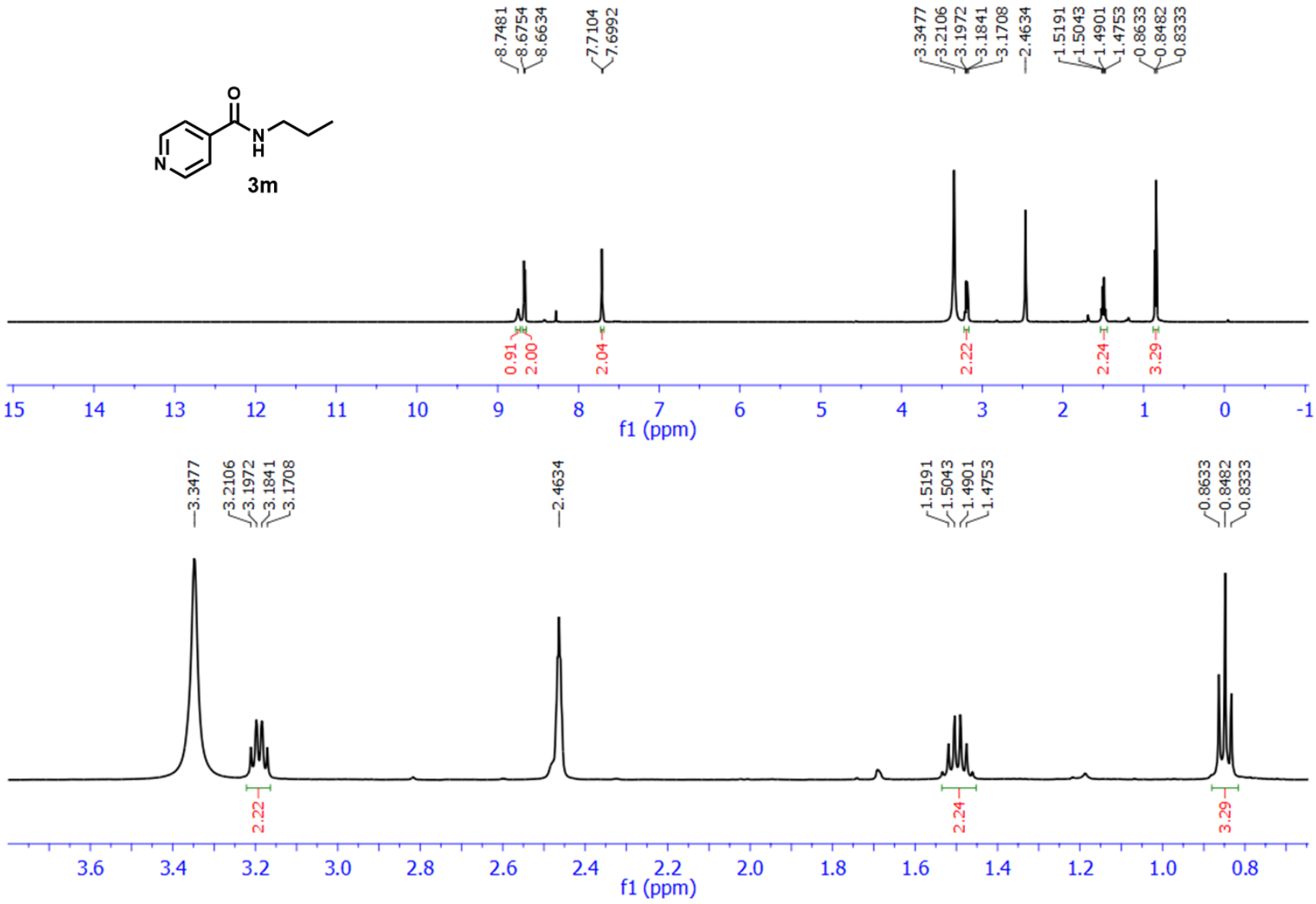
3l ^{1}H NMR (500 MHz, DMSO-d_6)



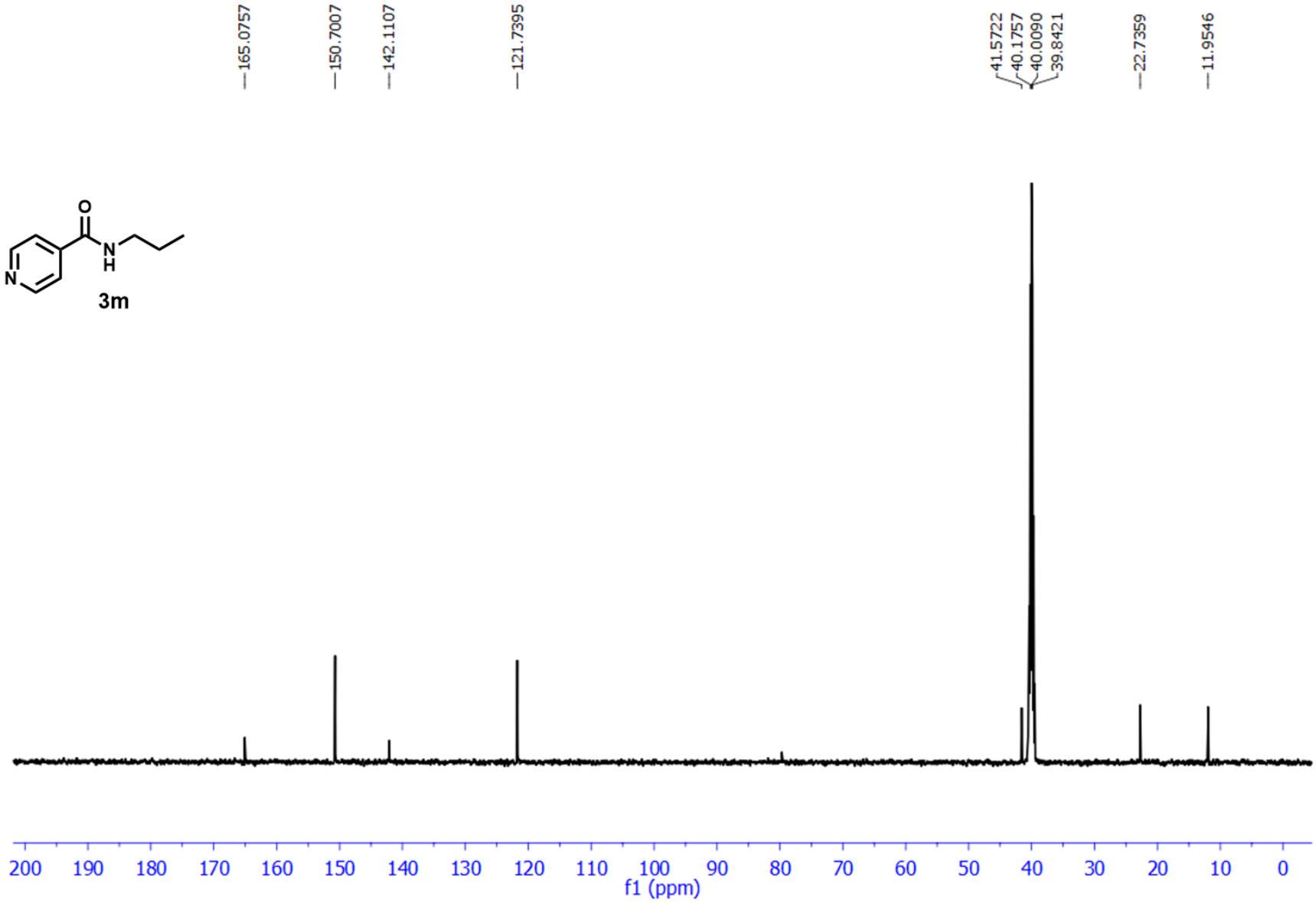
3l ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



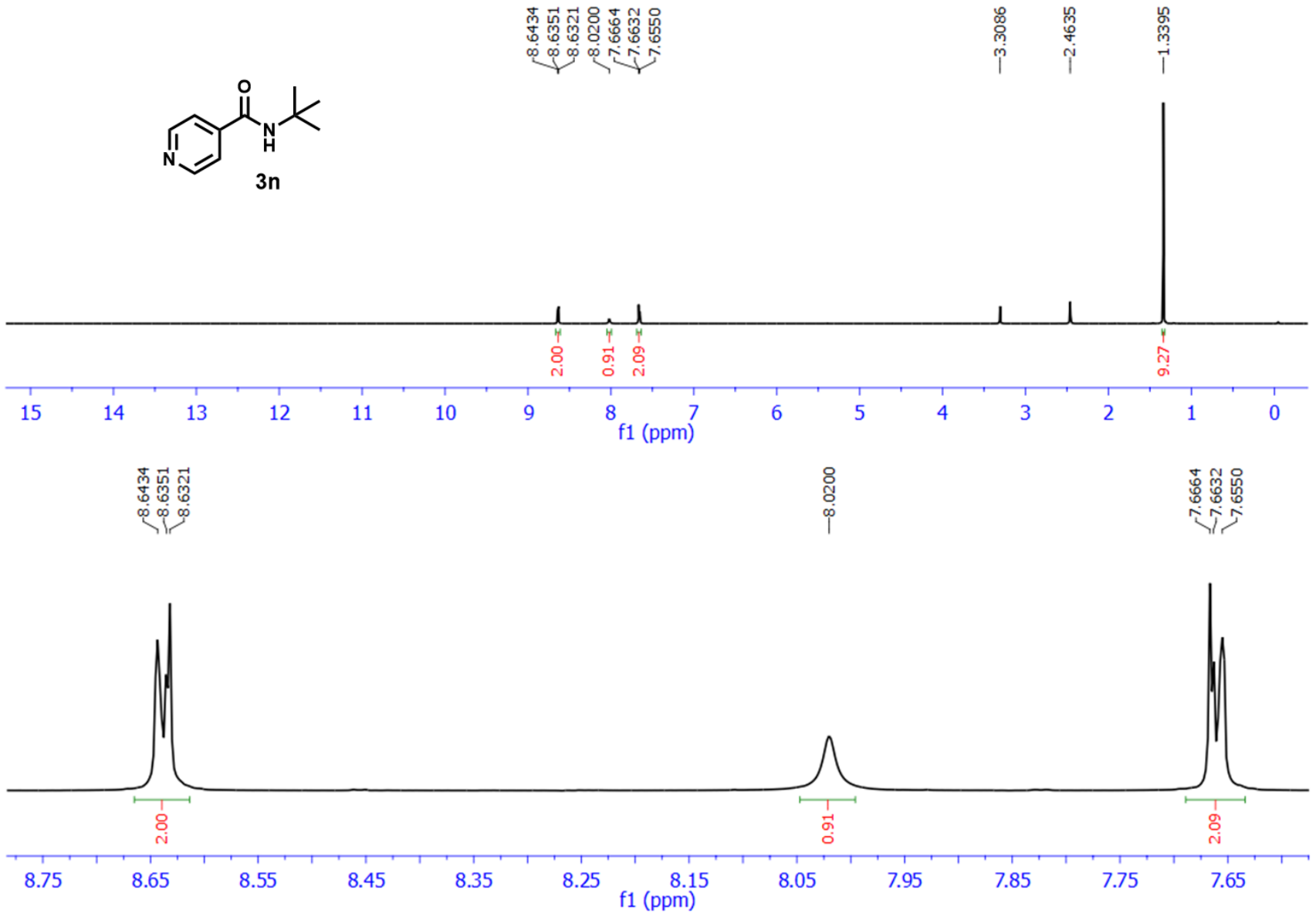
3m ^{1}H NMR (500 MHz, DMSO-d_6)



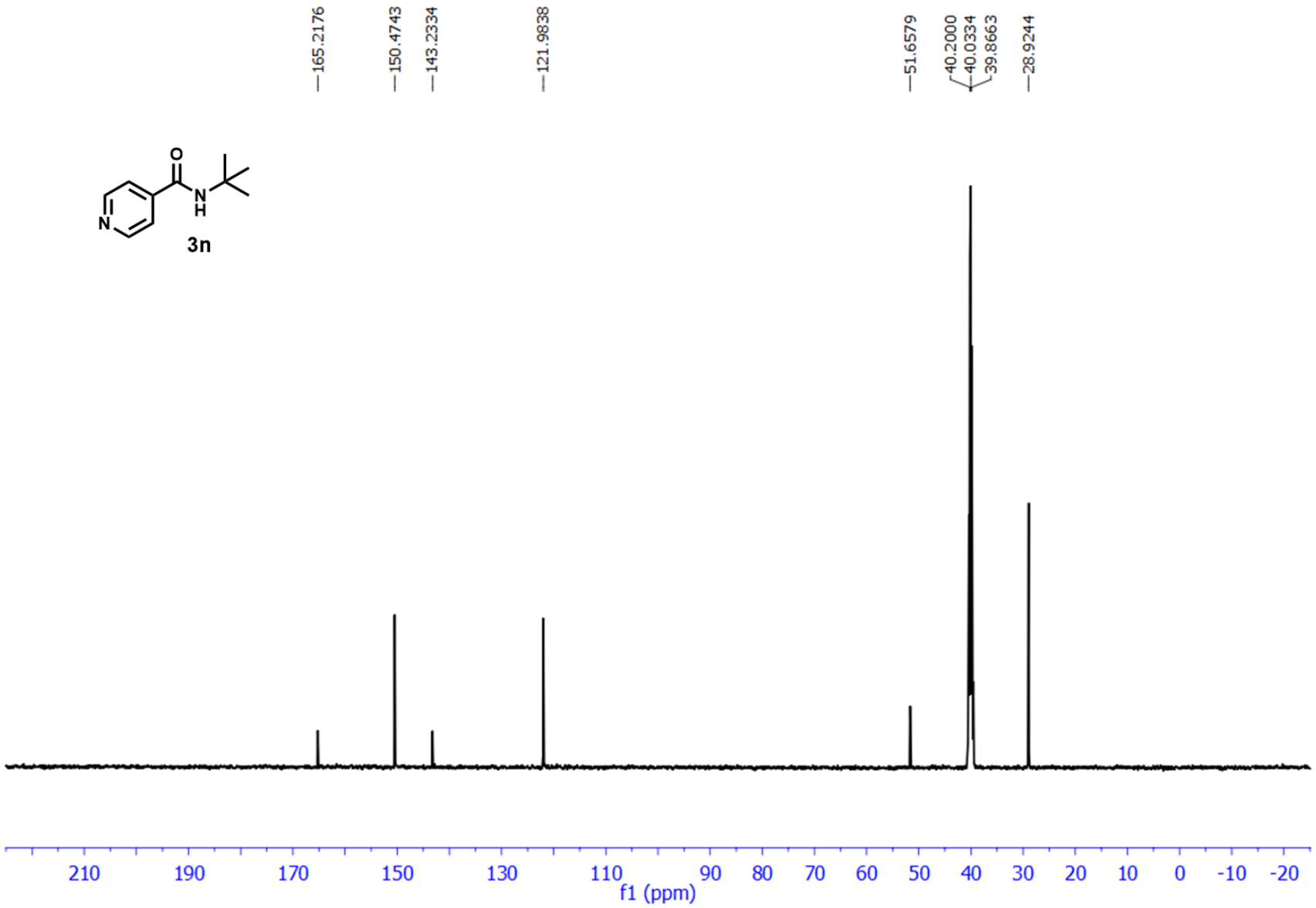
3m ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



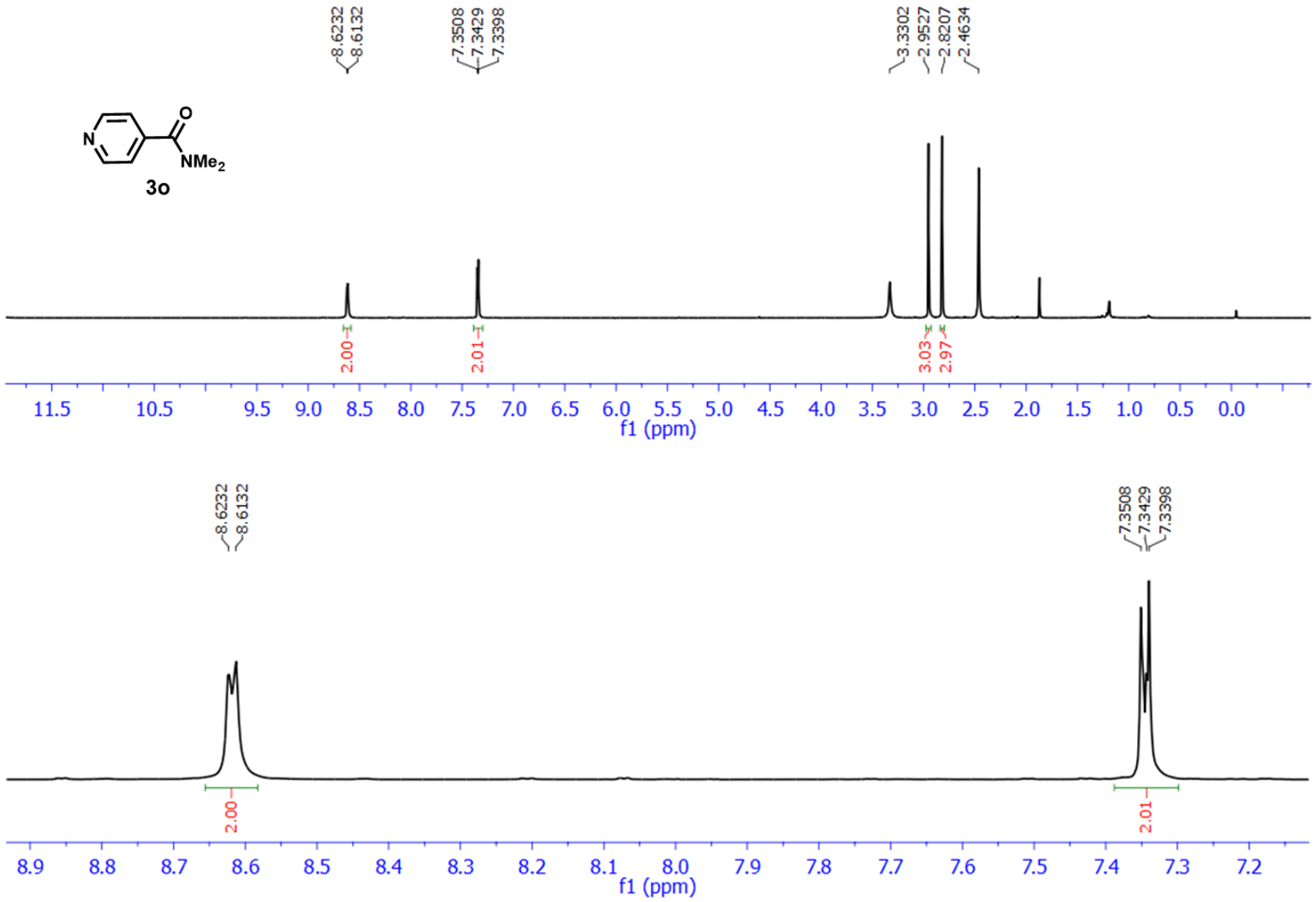
3n ^{1}H NMR (500 MHz, DMSO-d_6)



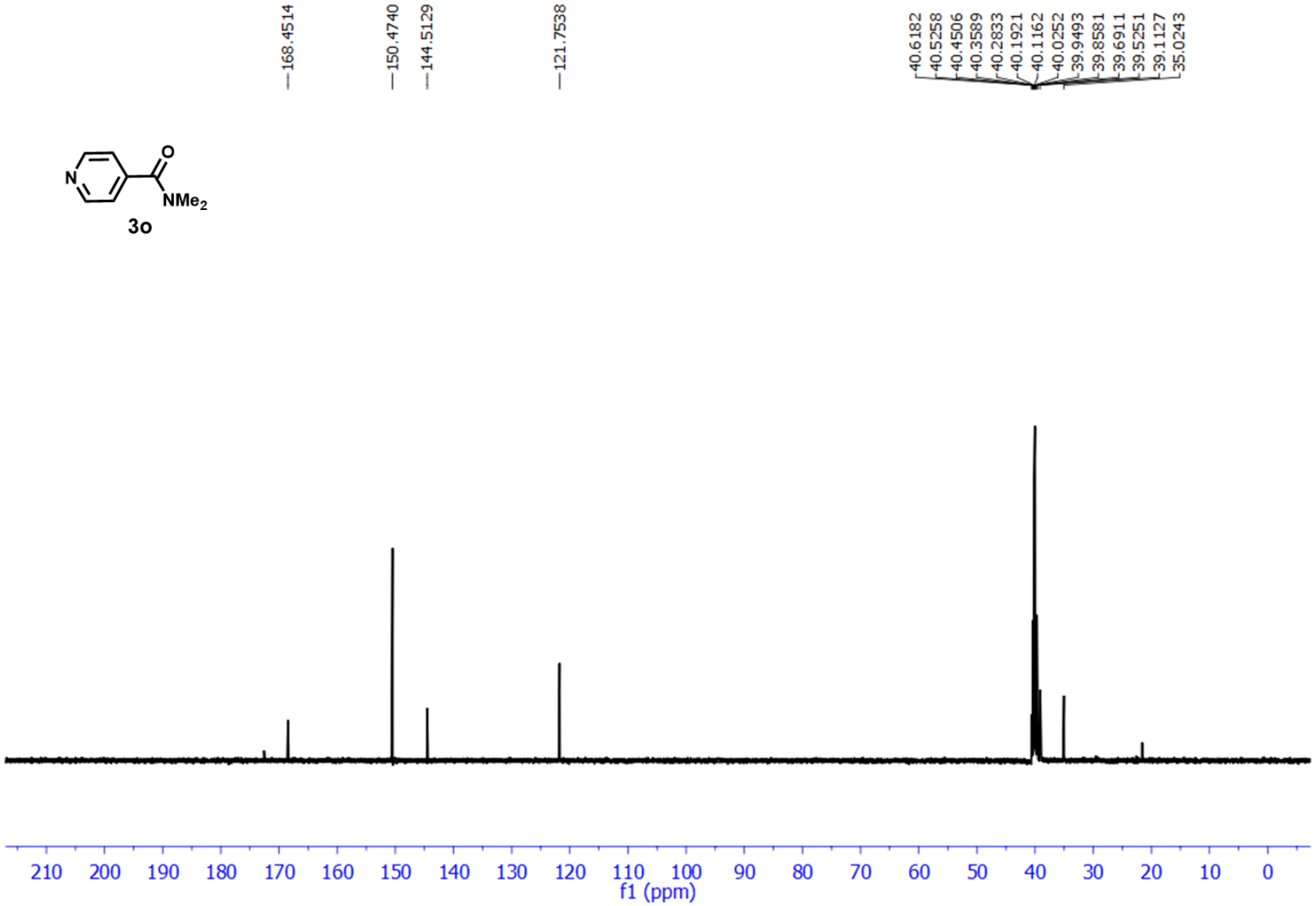
3n ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



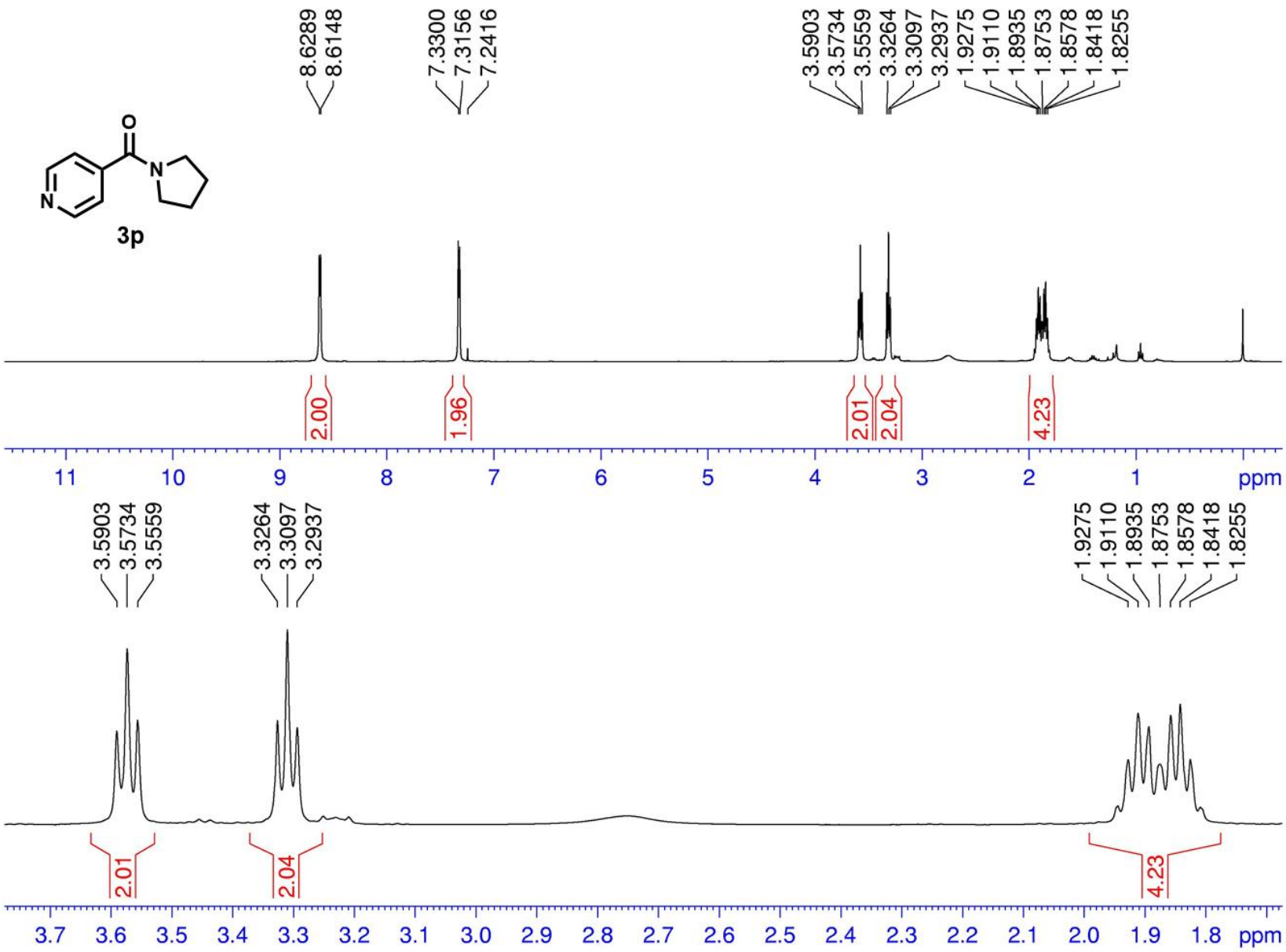
3o ^{1}H NMR (500 MHz, DMSO-d_6)



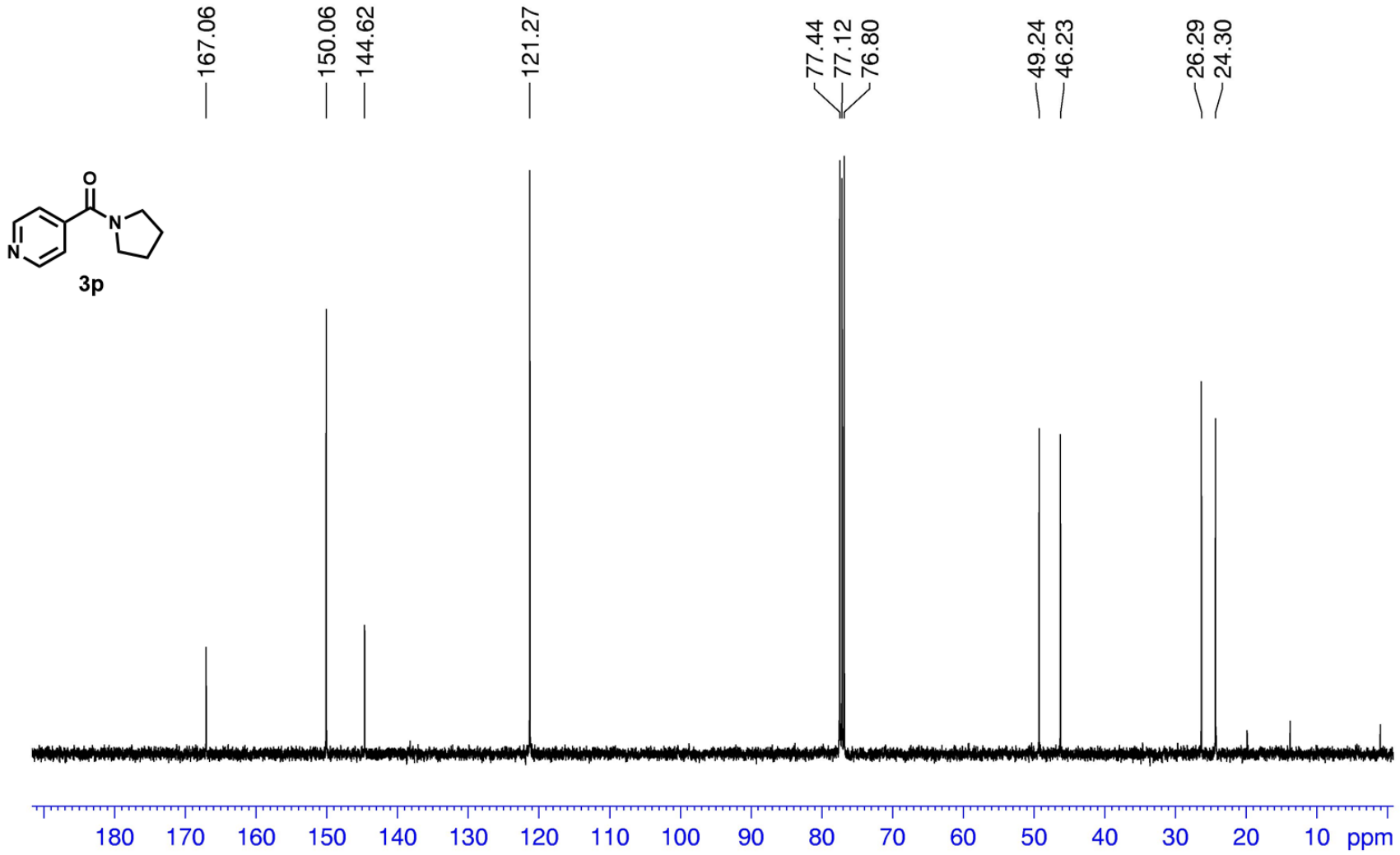
3o ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



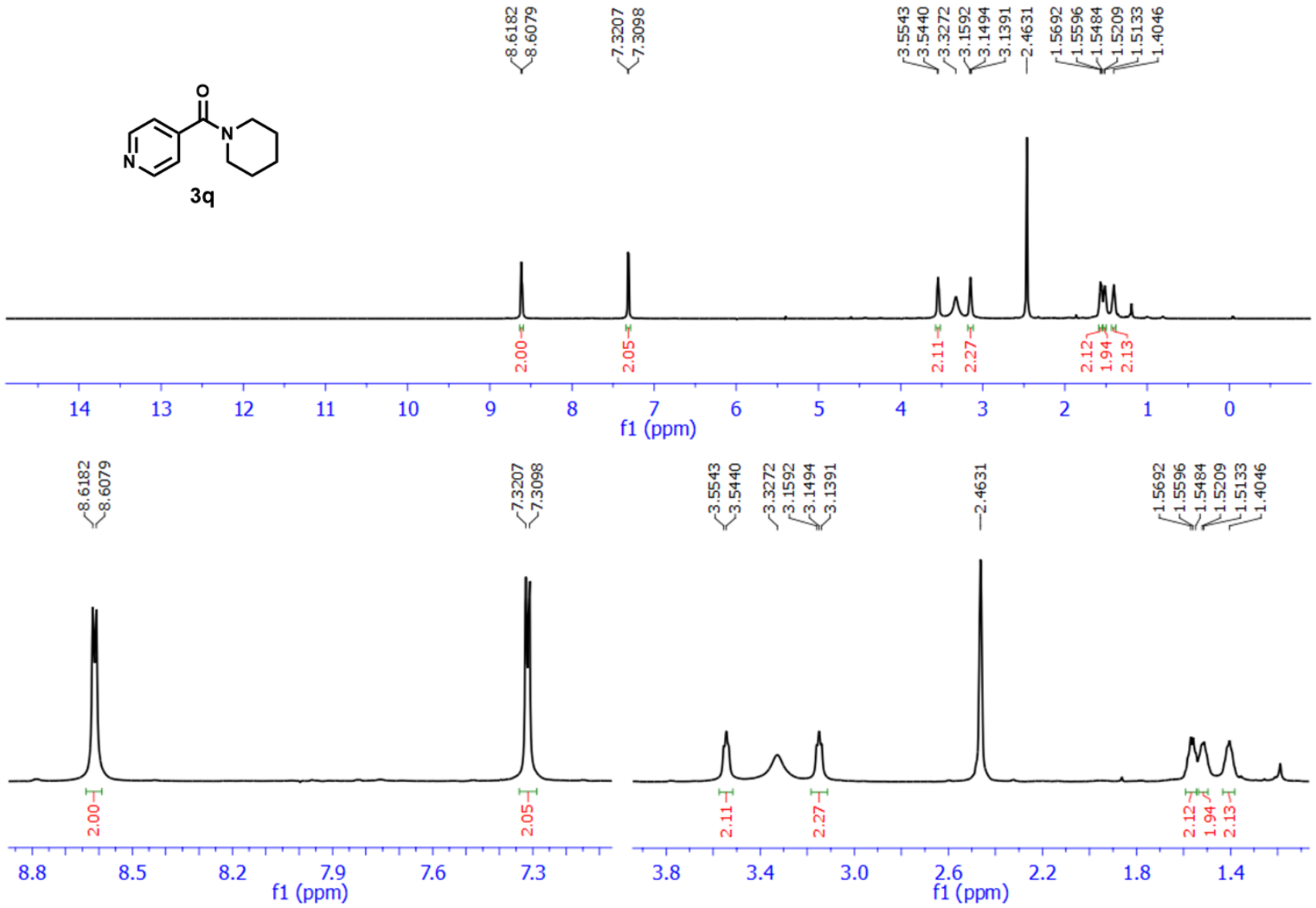
3p ^{1}H NMR (400 MHz, $CDCl_3$)



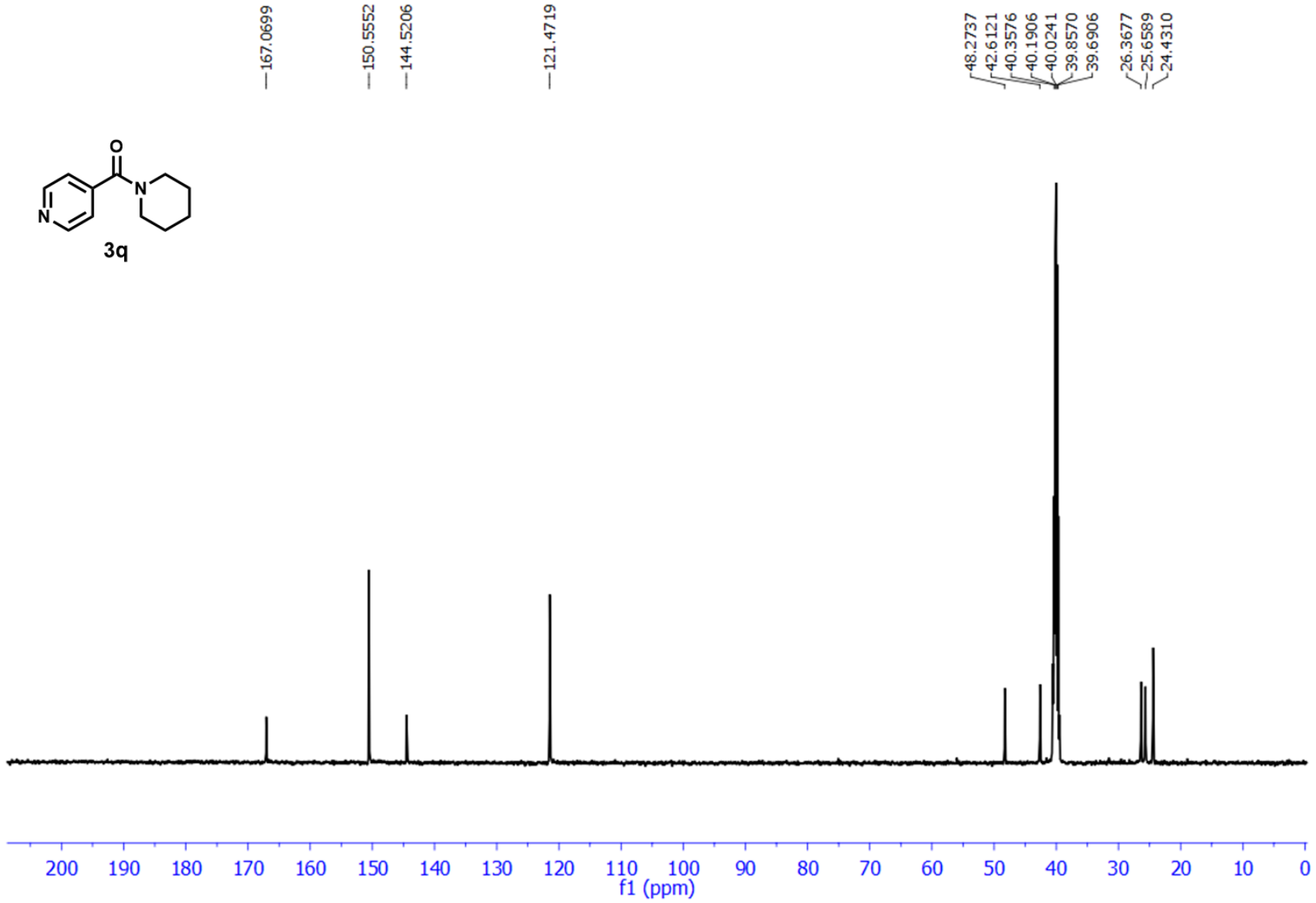
3p ^{13}C {1H} NMR (100 MHz, $CDCl_3$)



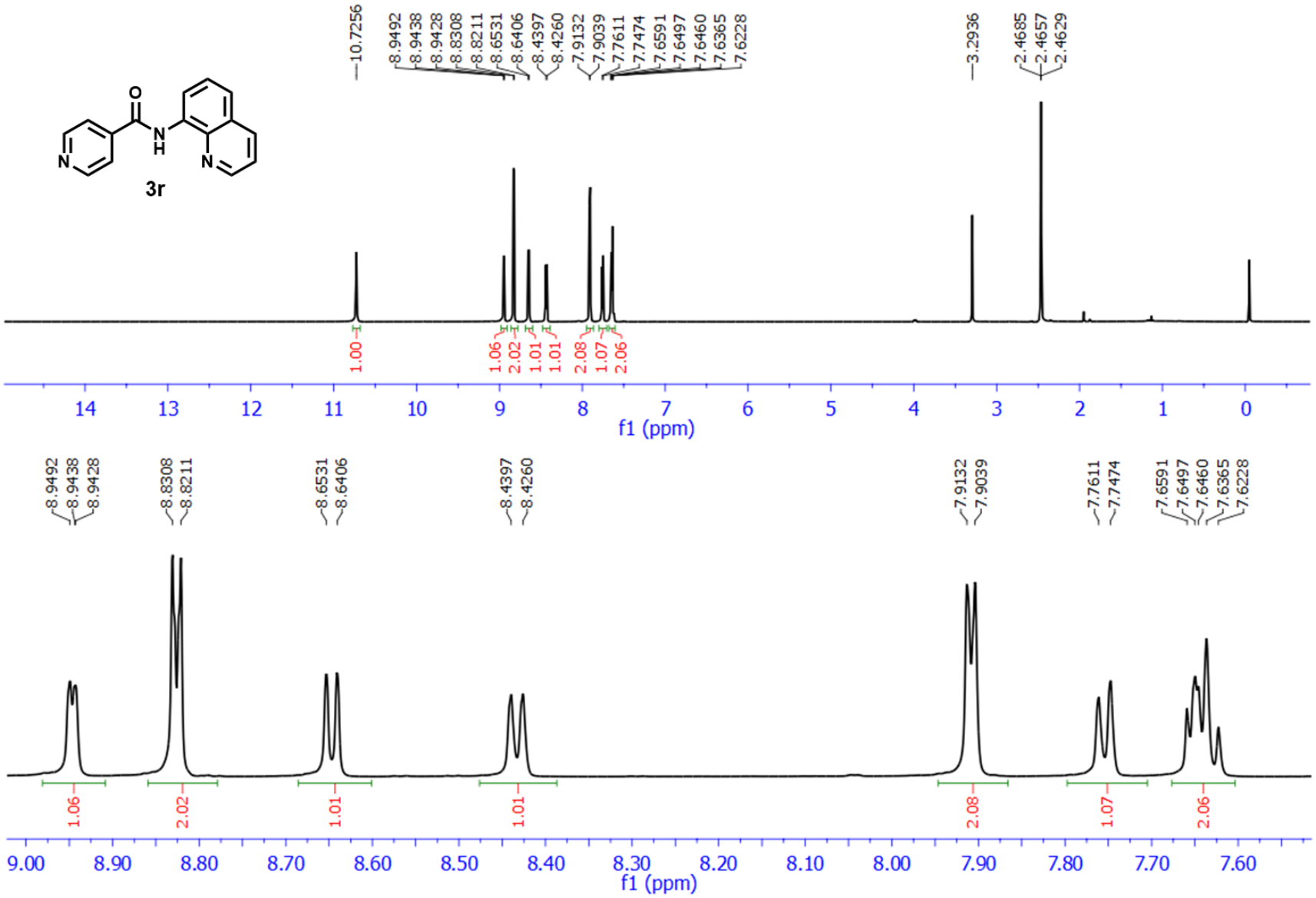
3q ^{1}H NMR (500 MHz, DMSO-d_6)



3q ^{13}C {1H} NMR (125 MHz, DMSO-d_6)

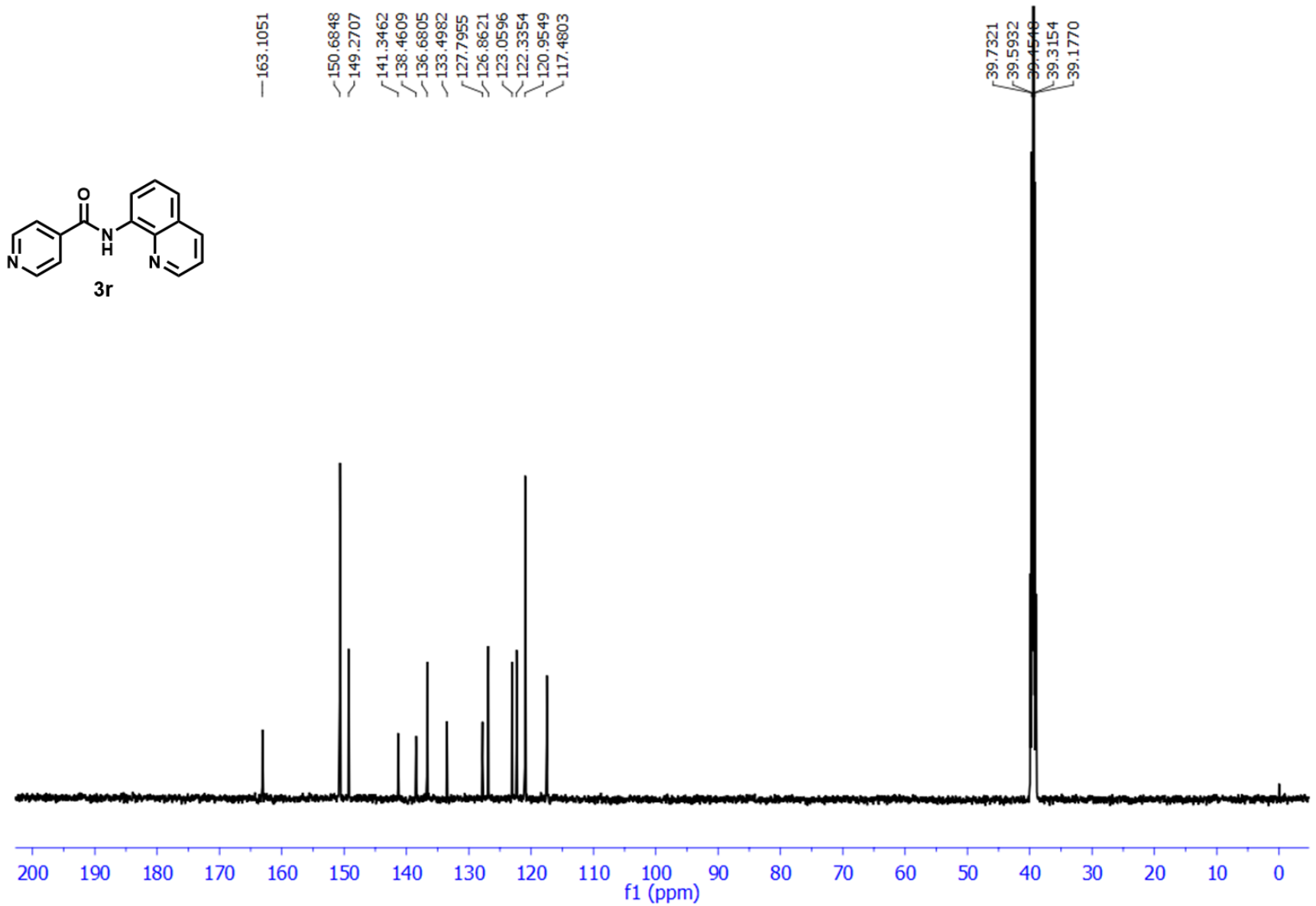


3r ^{1}H NMR (600 MHz, DMSO-d_6)

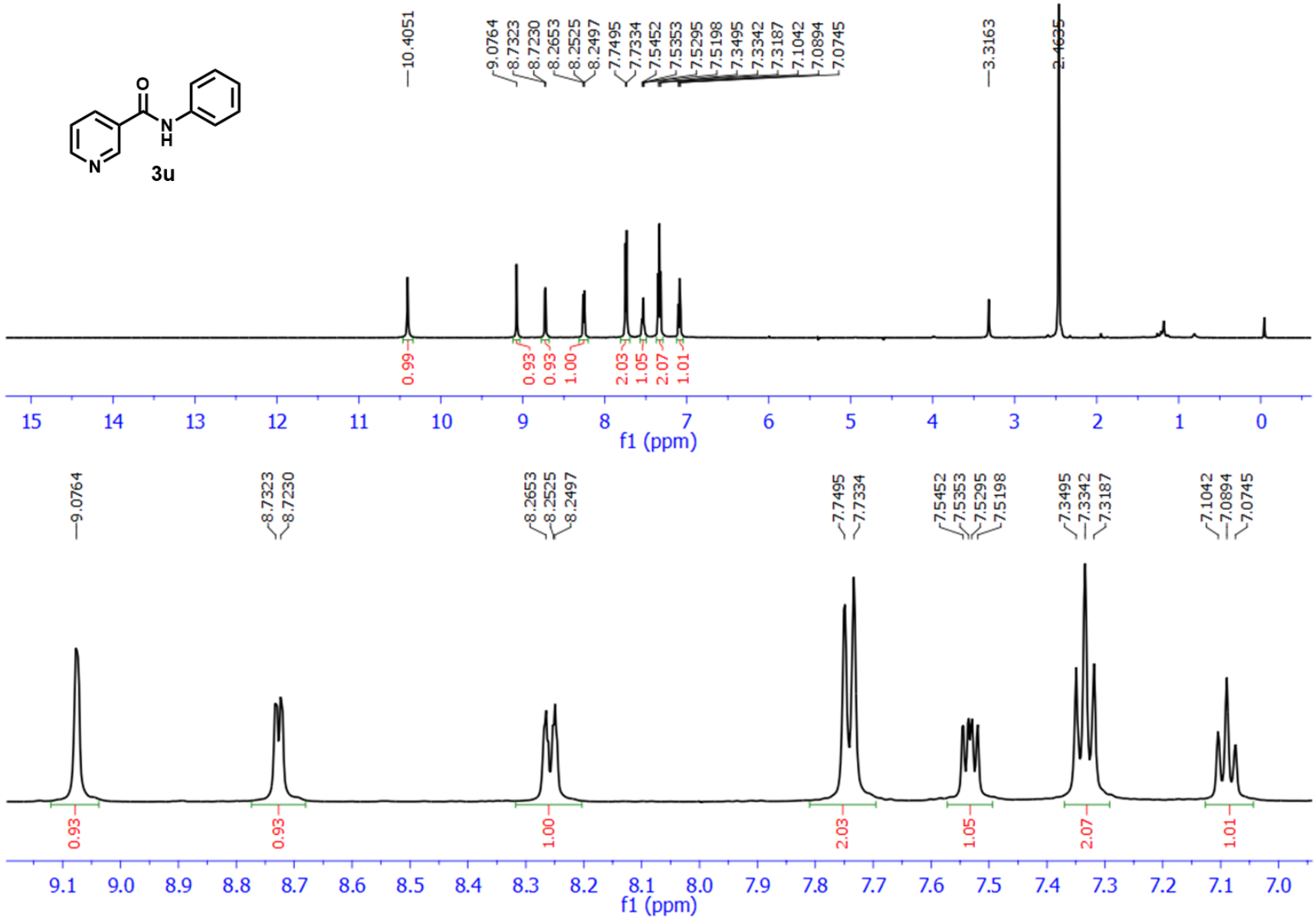


3r

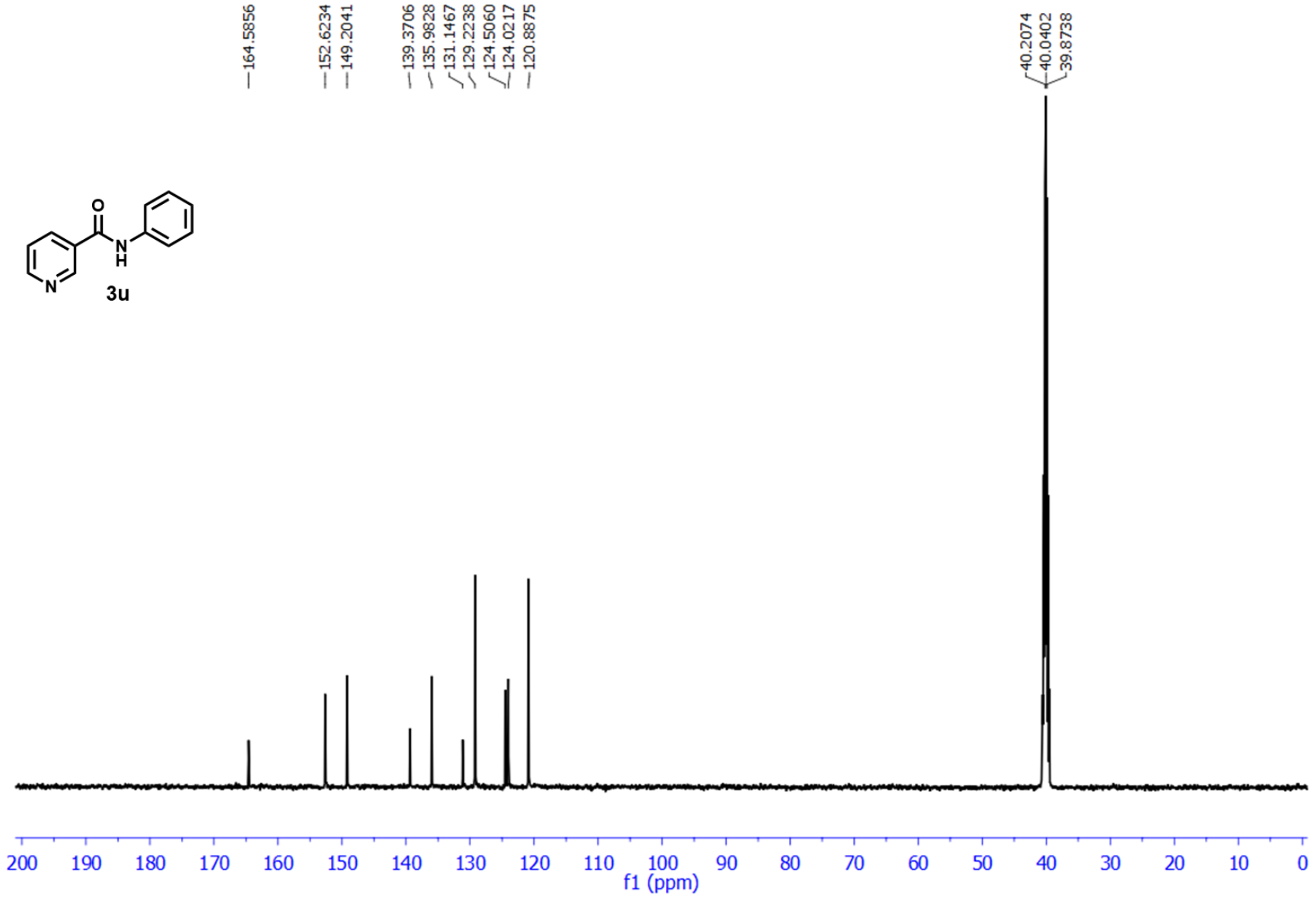
3r ^{13}C {1H} NMR (150 MHz, DMSO-d_6)



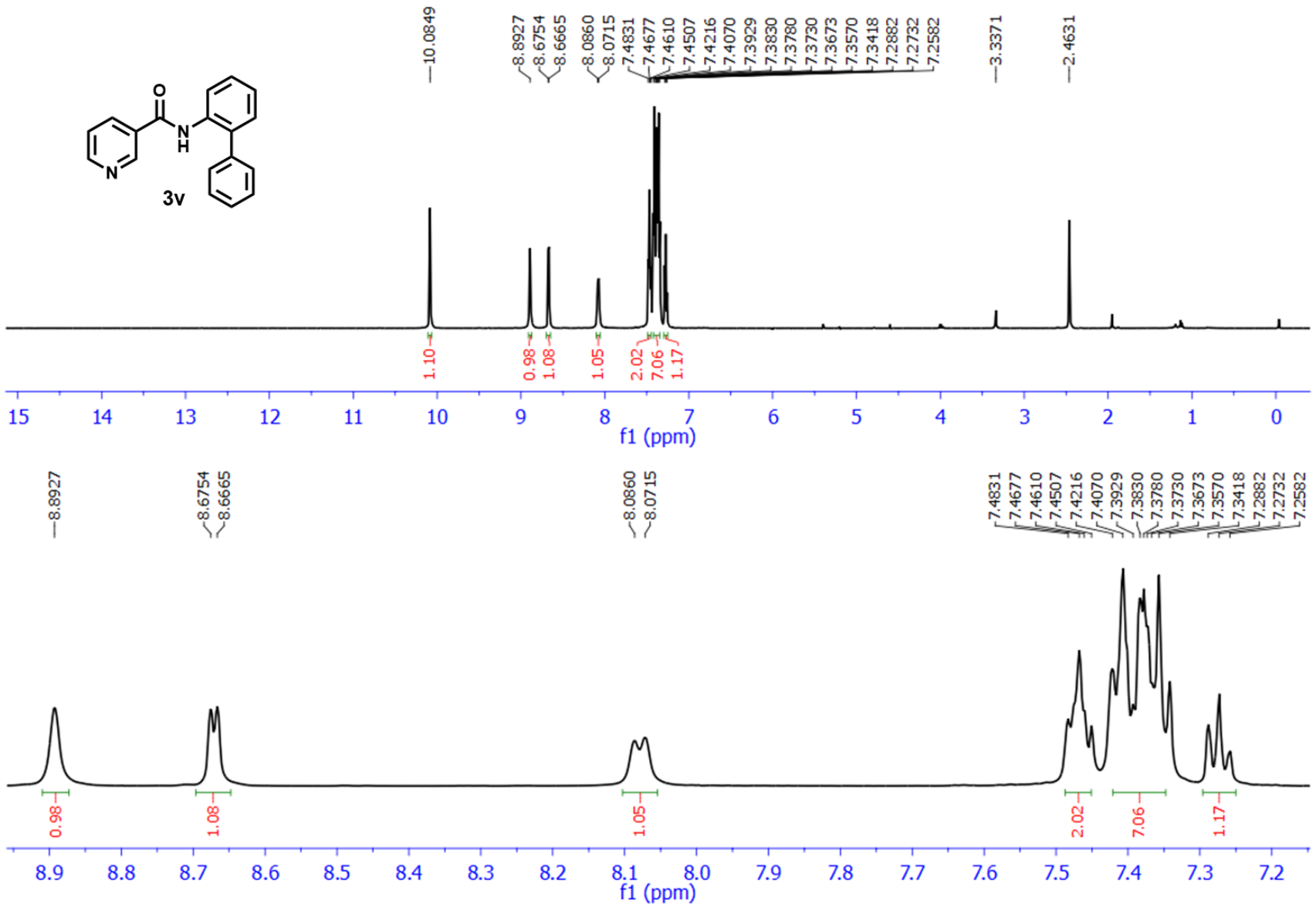
3u ^{1}H NMR (500 MHz, DMSO-d_6)



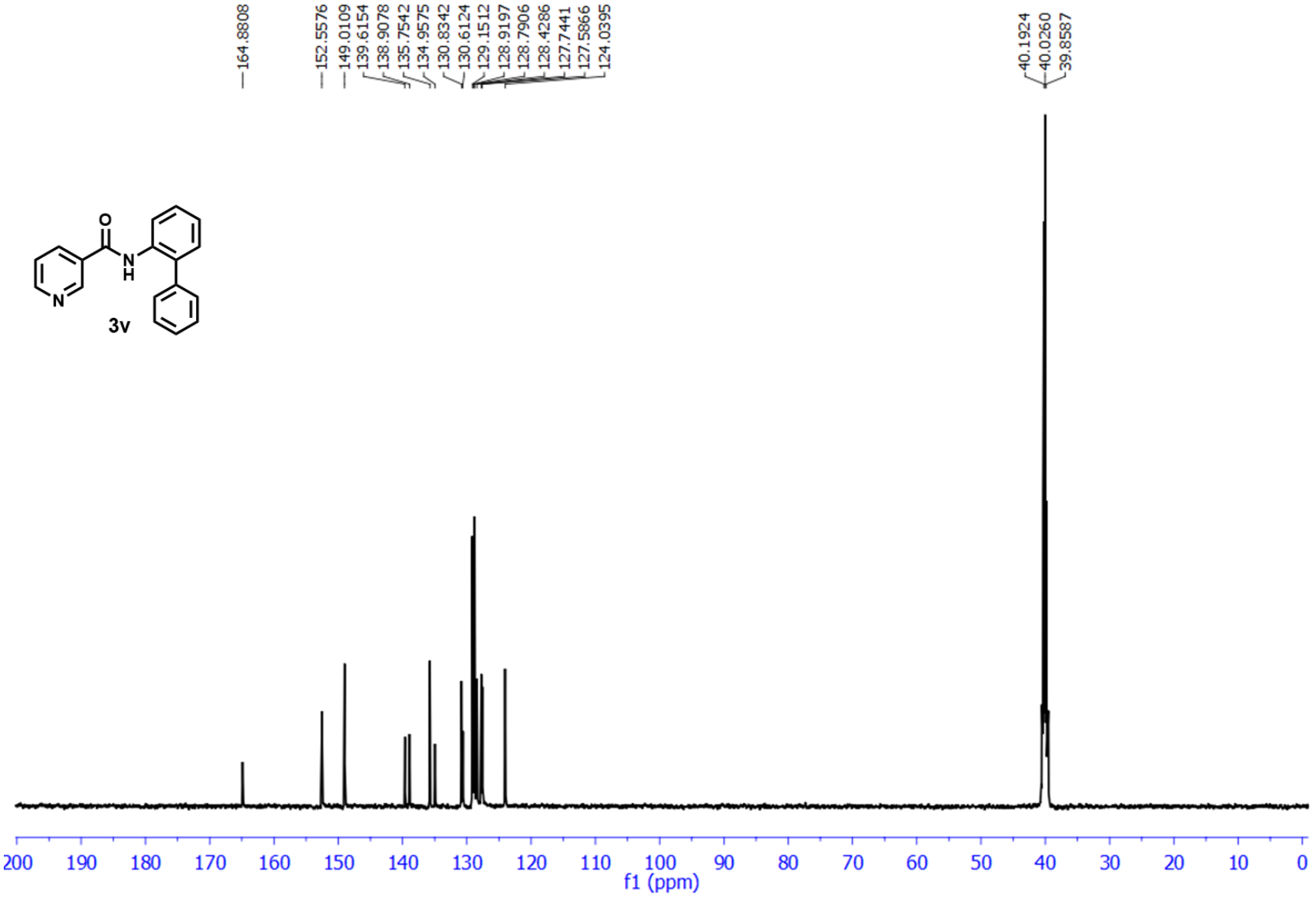
3u ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



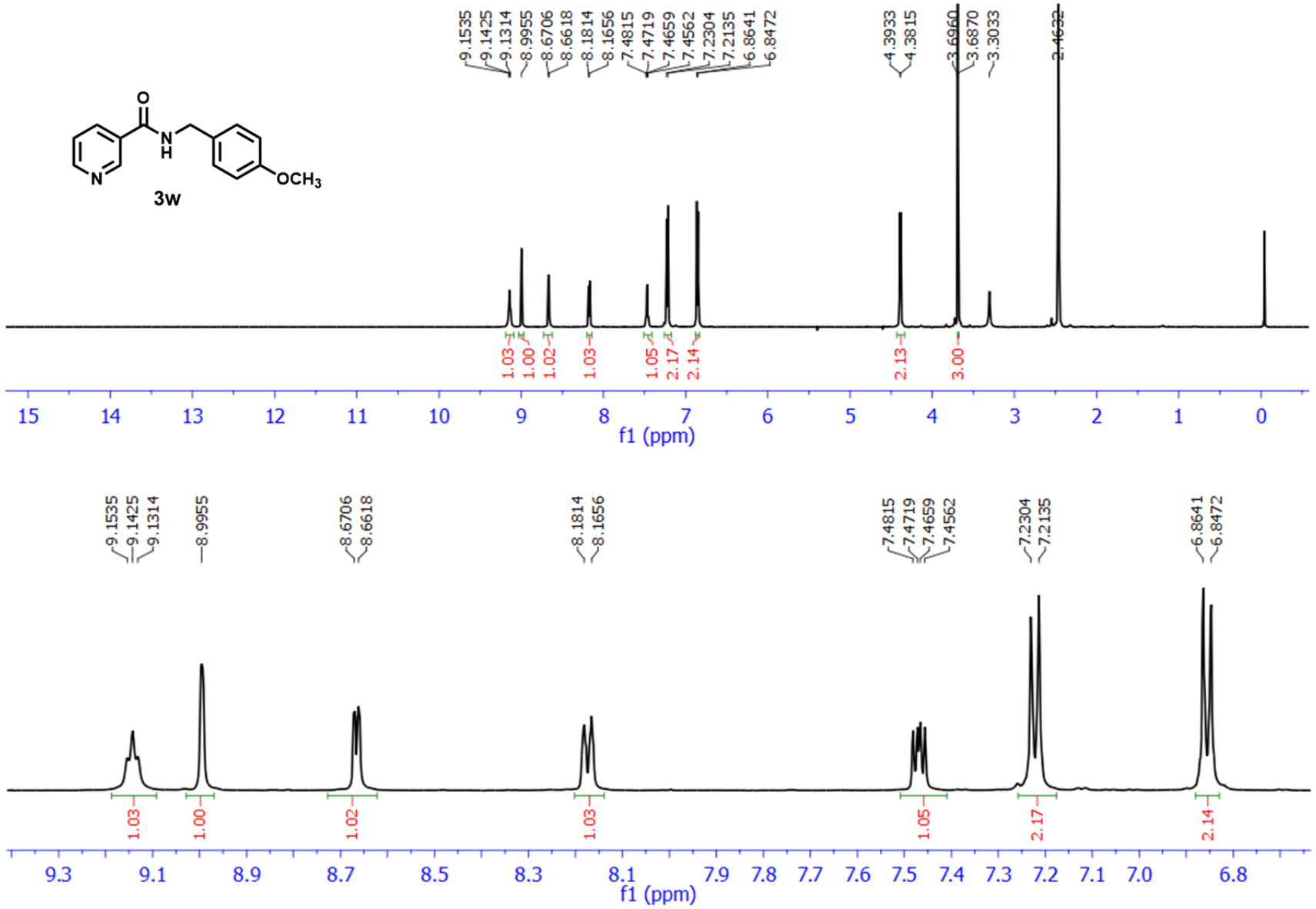
3v ^{1}H NMR (500 MHz, DMSO-d_6)



3v ^{13}C {1H} NMR (125 MHz, DMSO-d_6)

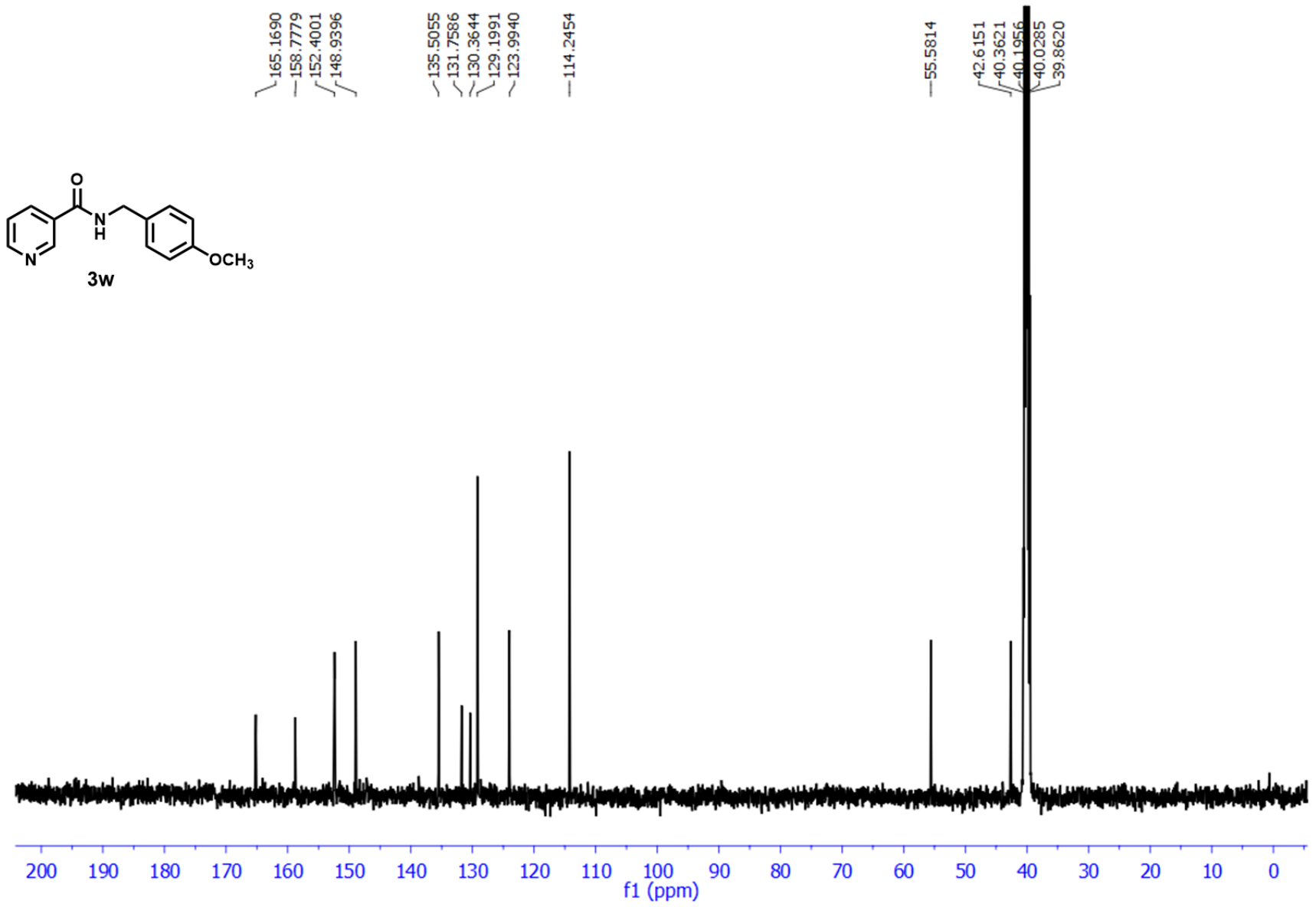


3w ^{1}H NMR (500 MHz, DMSO-d_6)

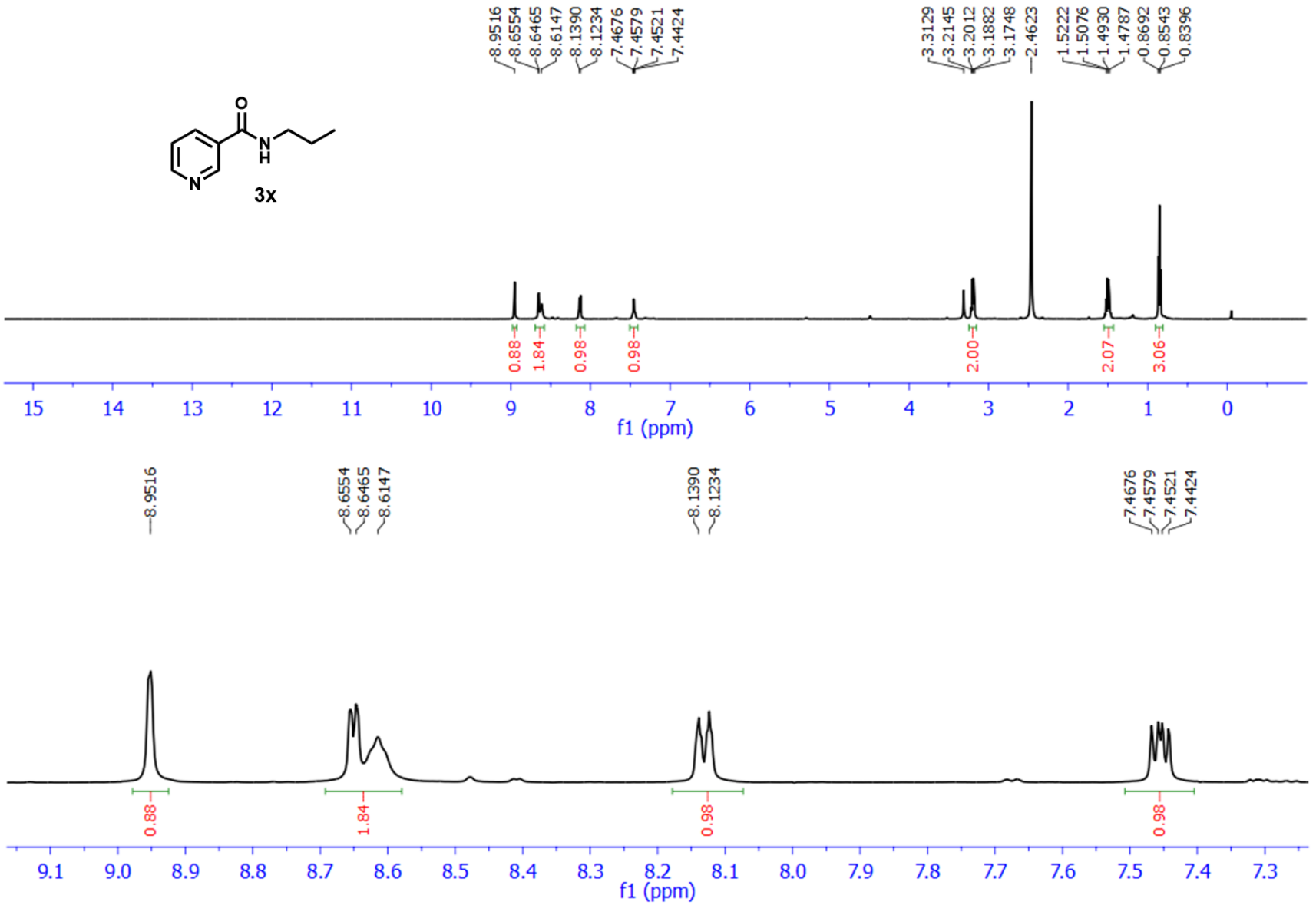


3W

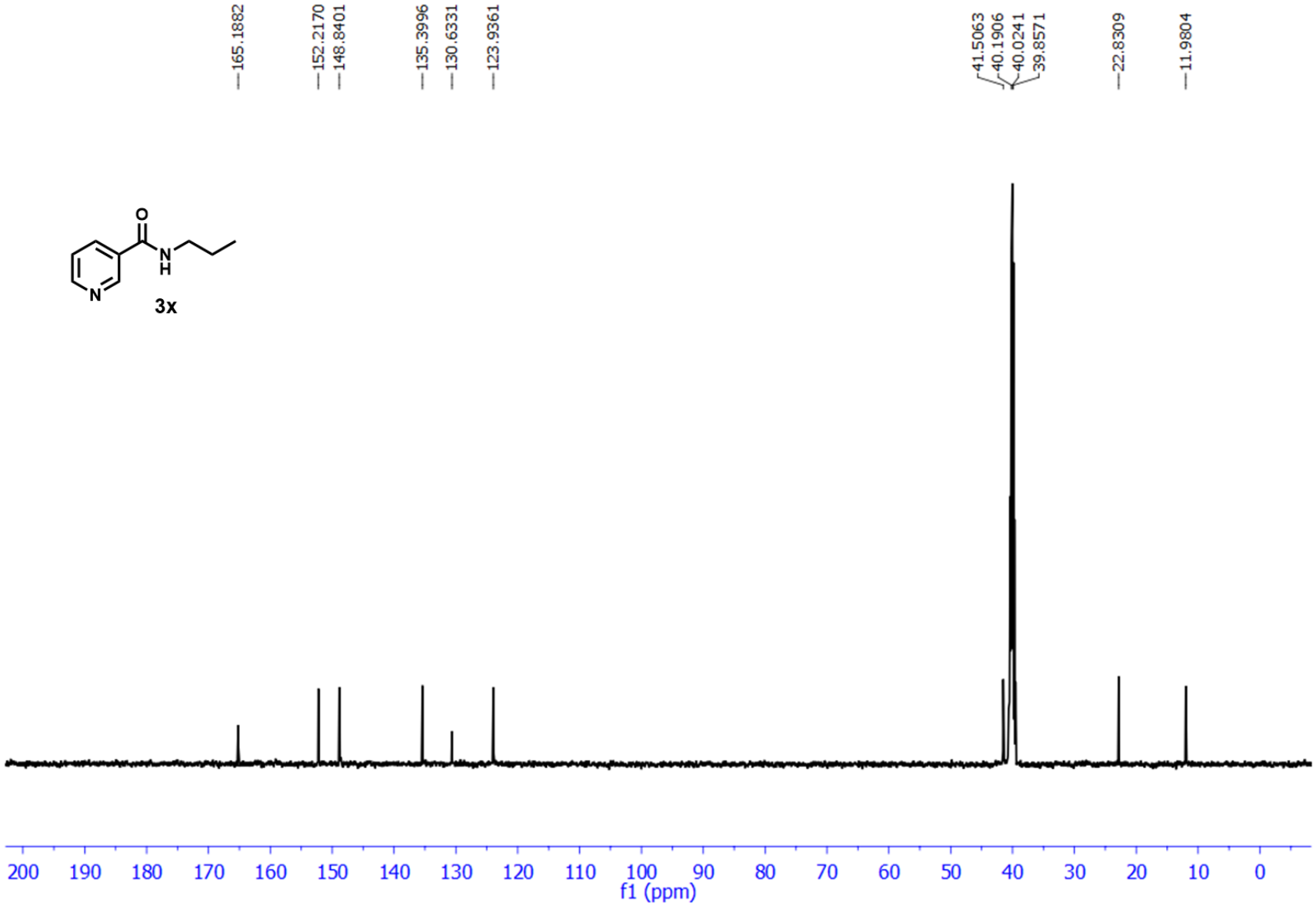
3w ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



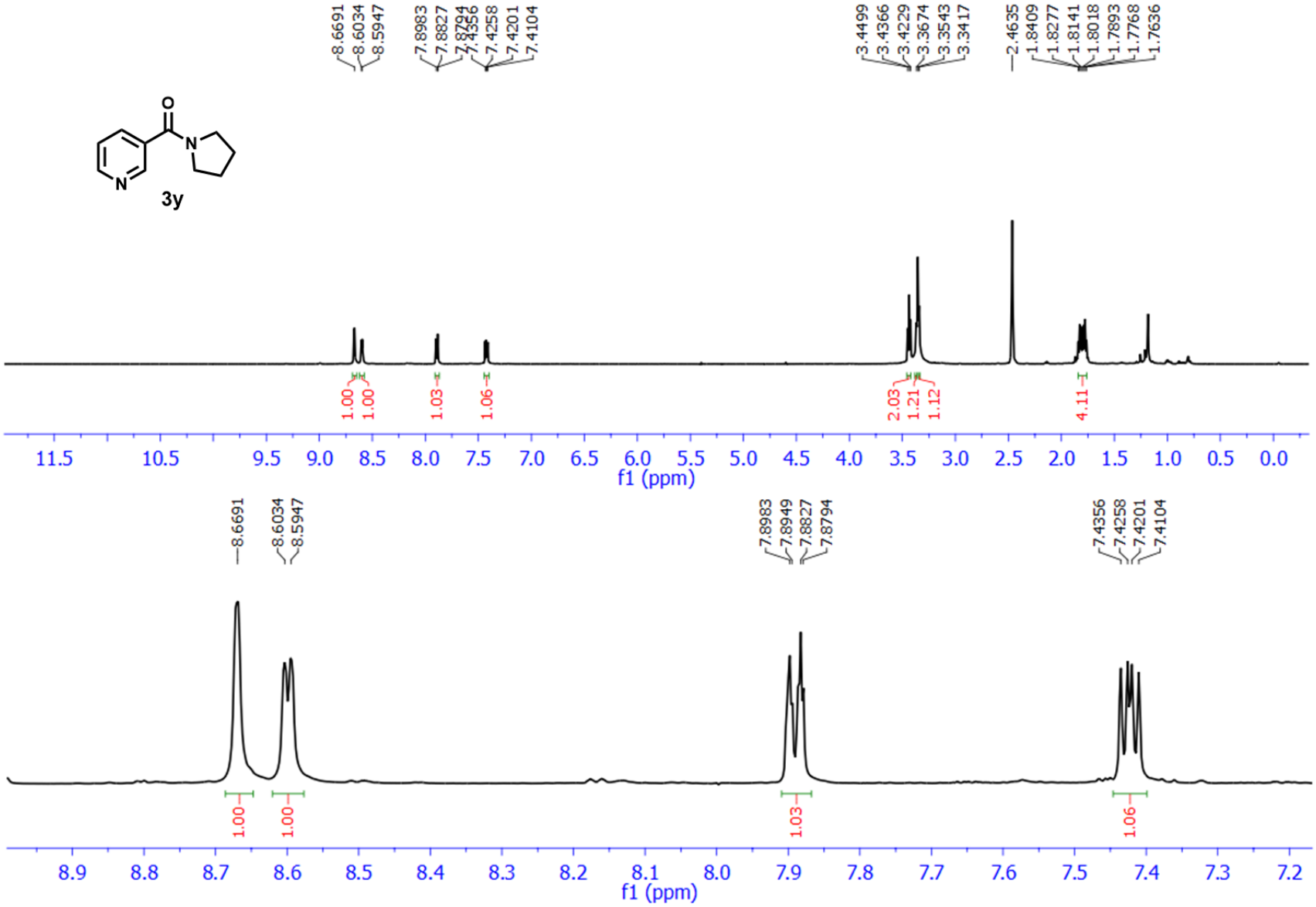
3x ^{1}H NMR (500 MHz, DMSO-d_6)



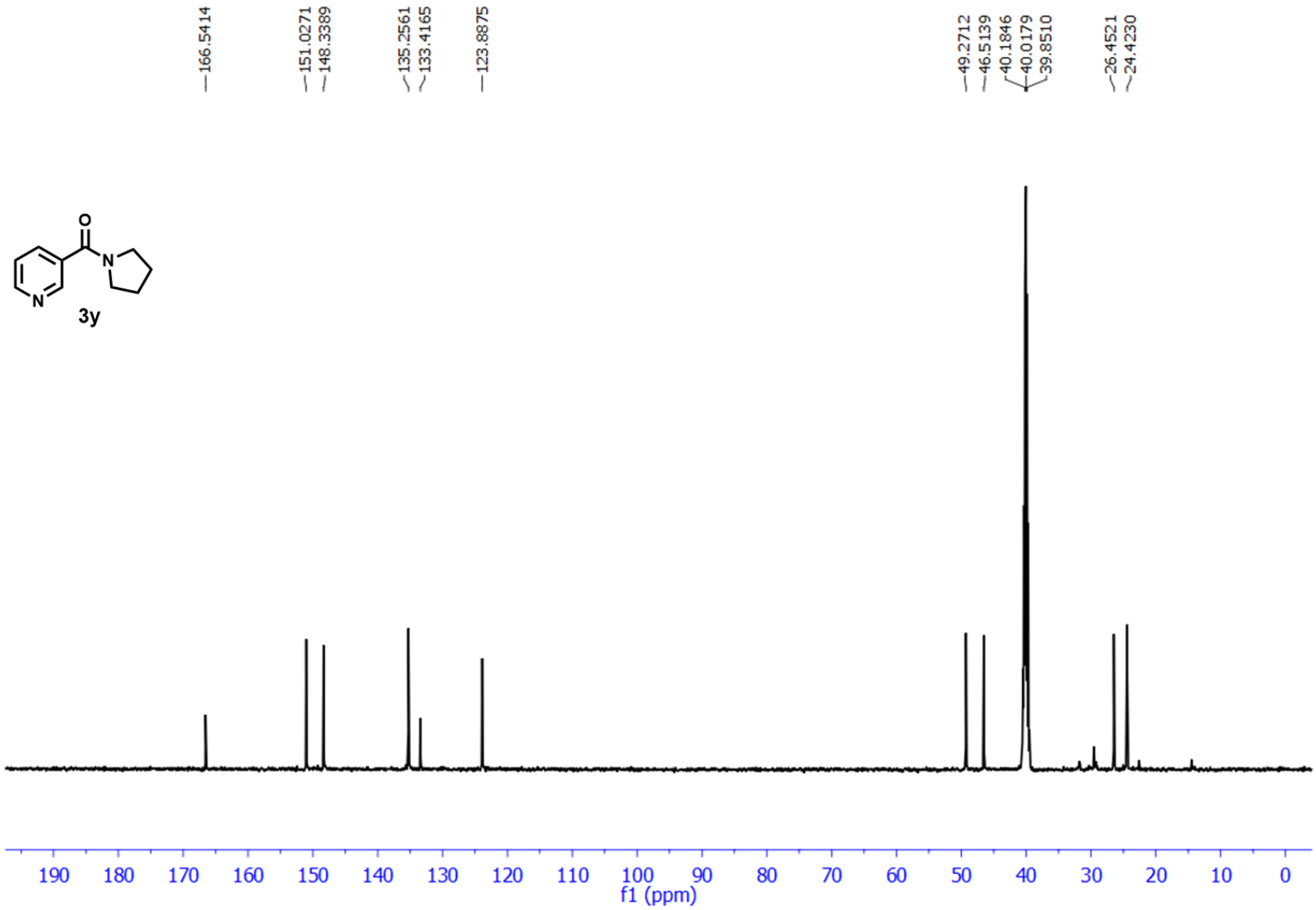
3x ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



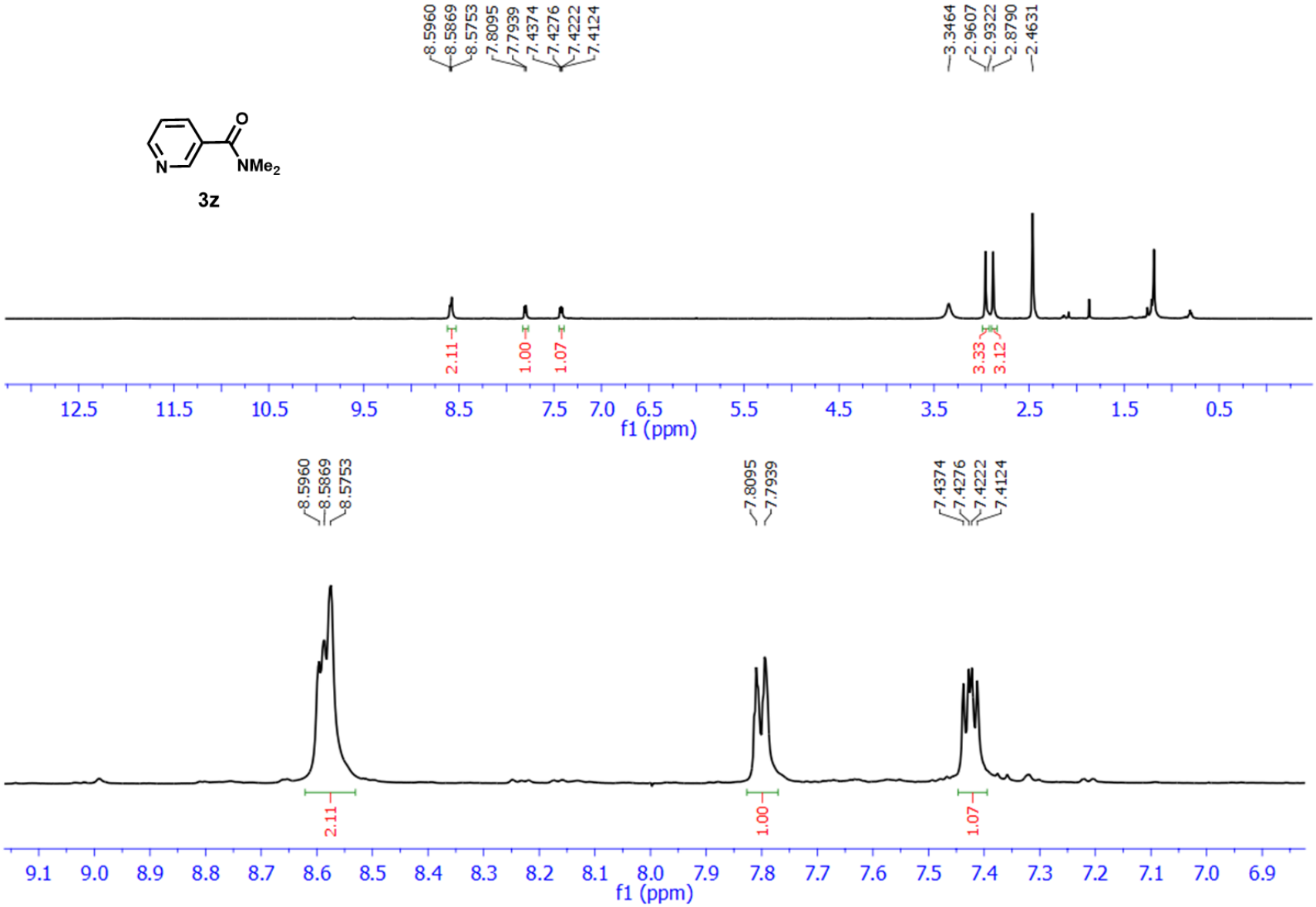
3y ^{1}H NMR (500 MHz, DMSO-d_6)



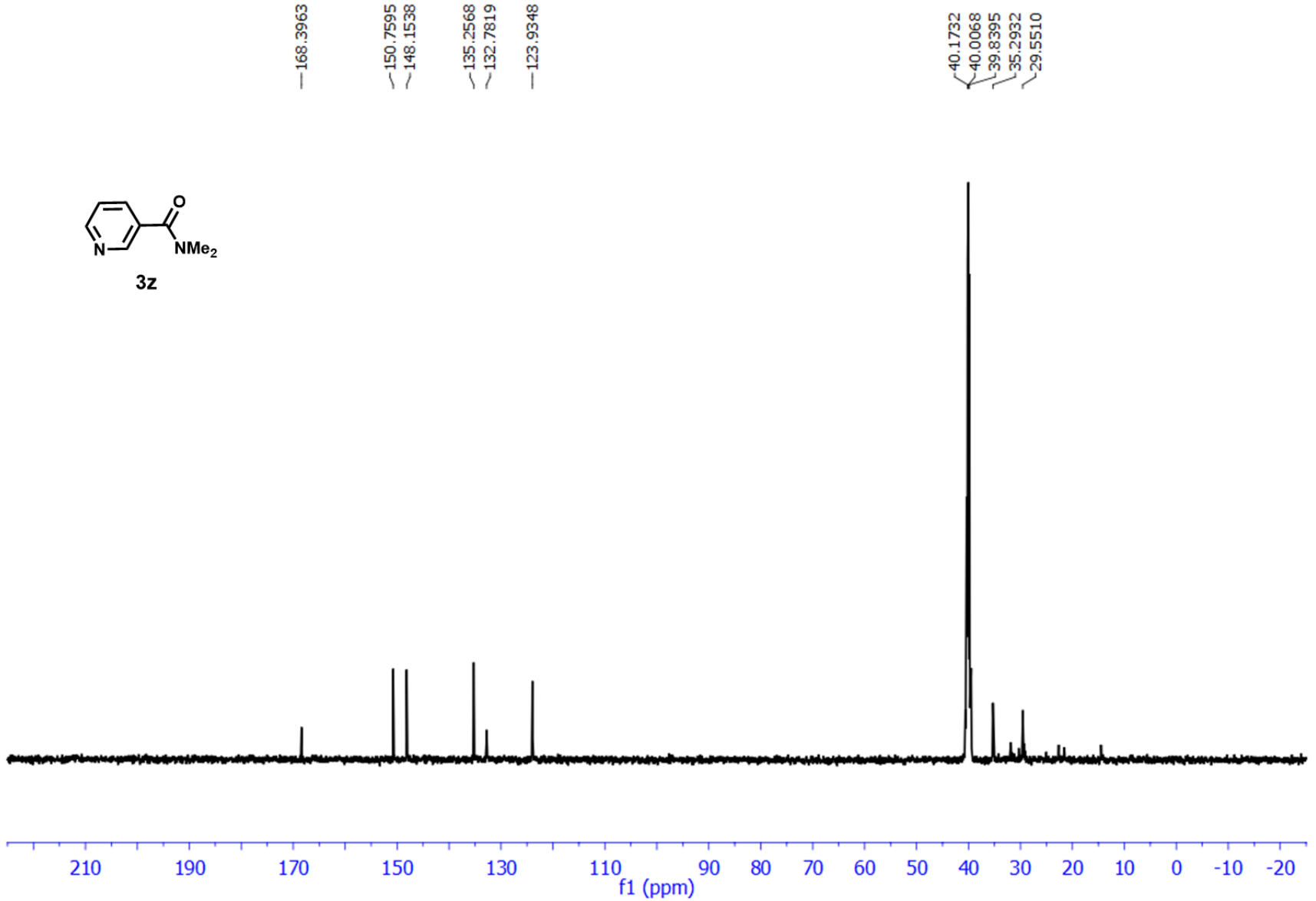
3y ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



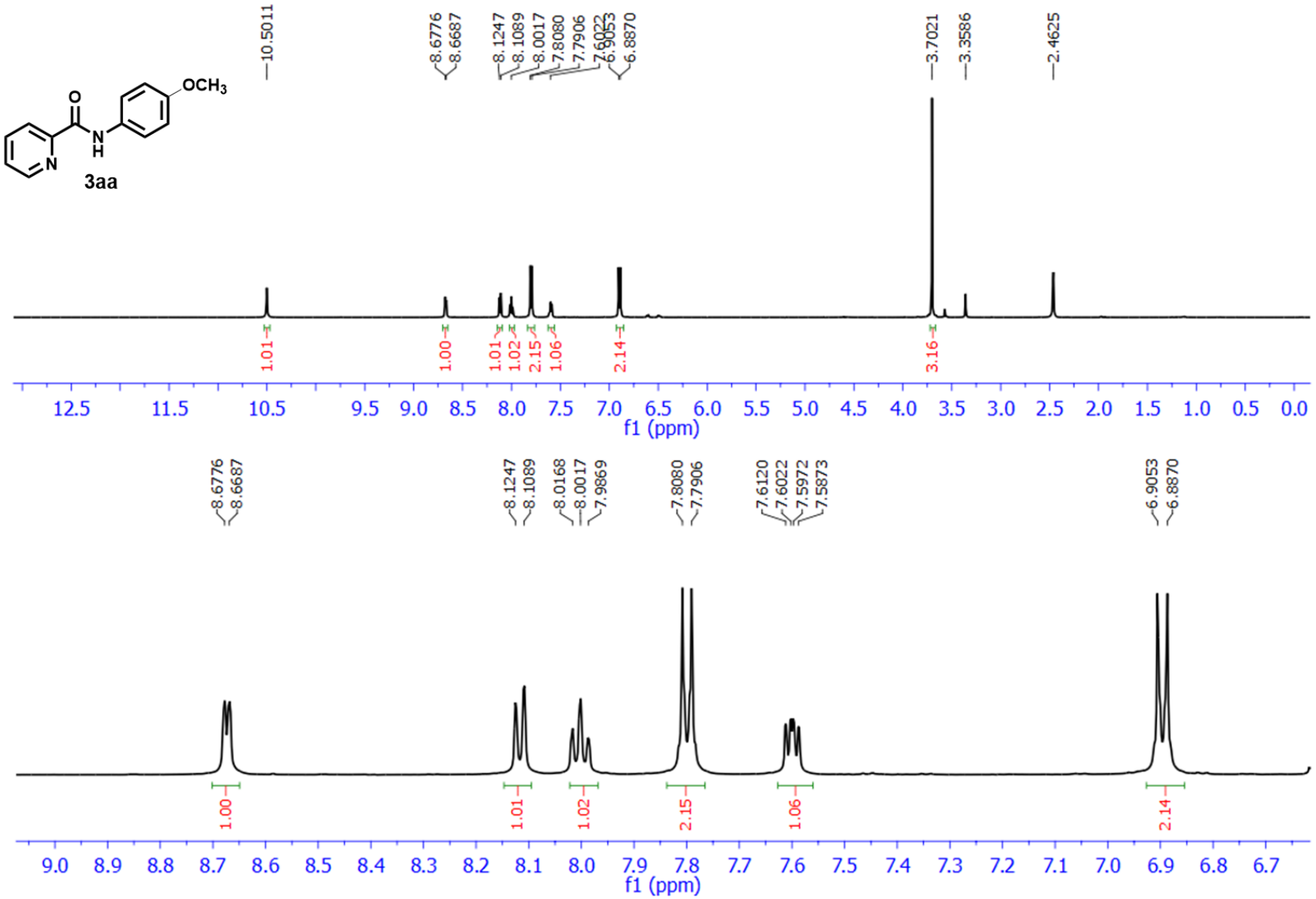
3z ^{1}H NMR (500 MHz, DMSO-d_6)



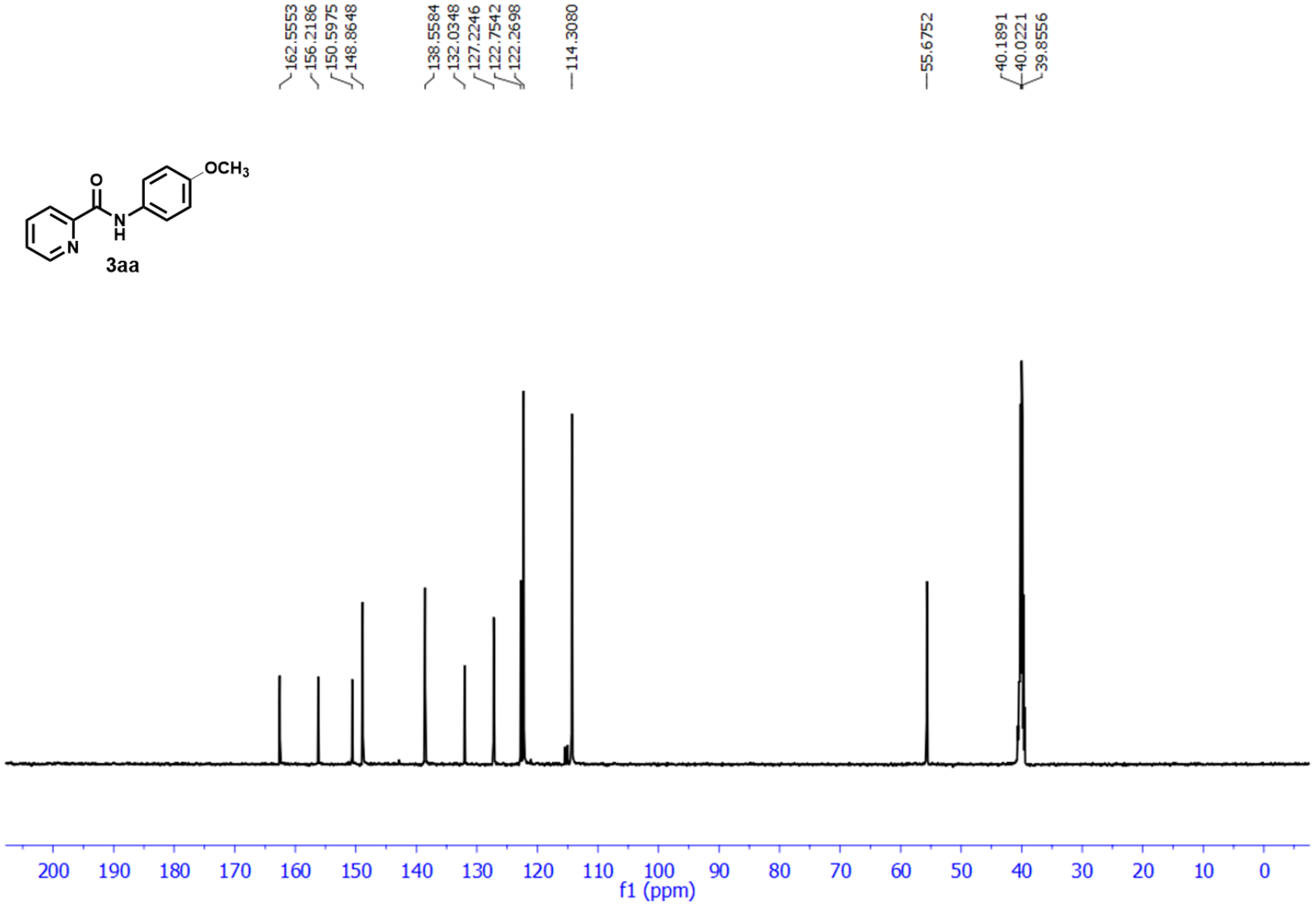
3z ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



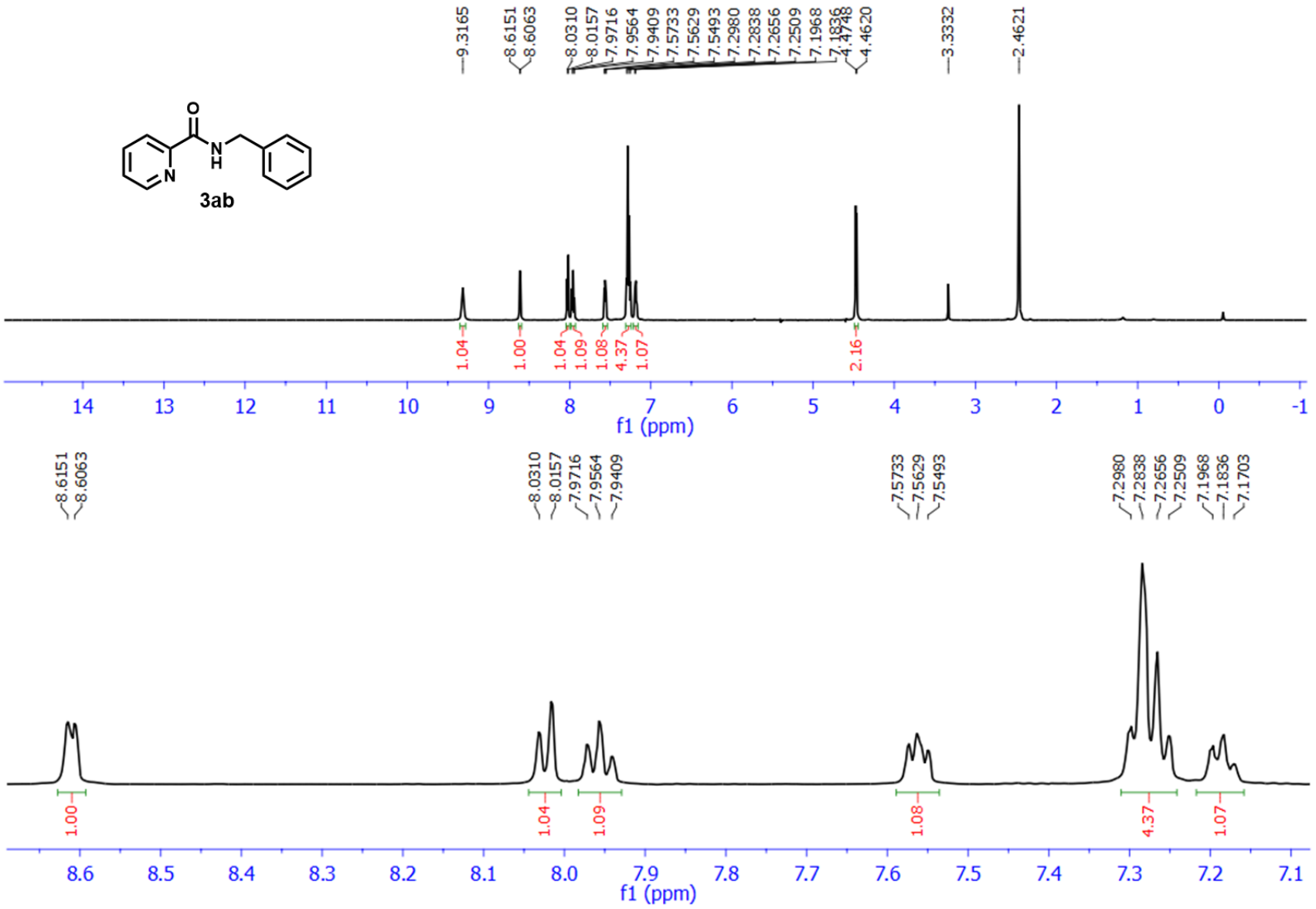
3aa ^{1}H NMR (500 MHz, DMSO-d_6)



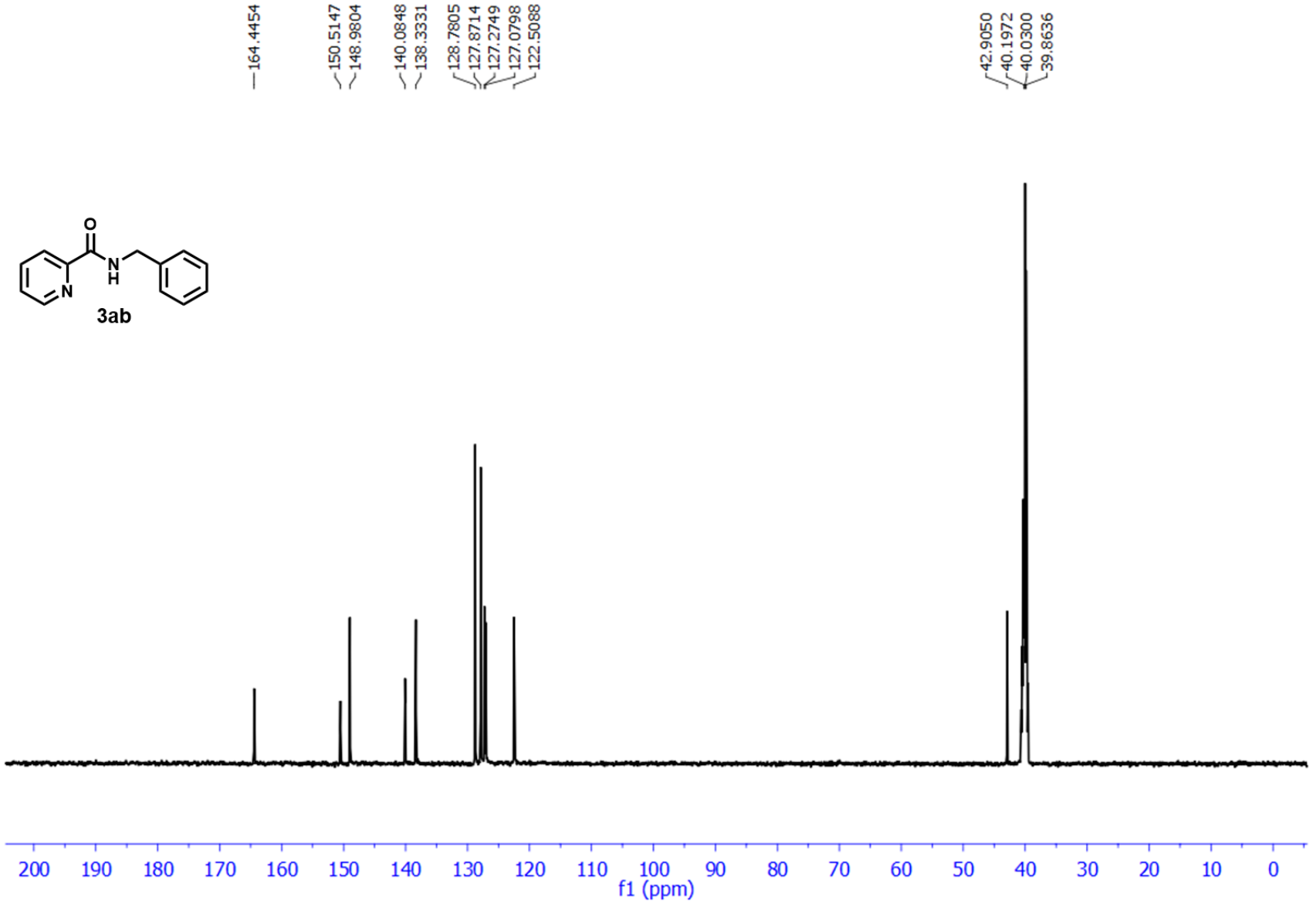
3aa ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



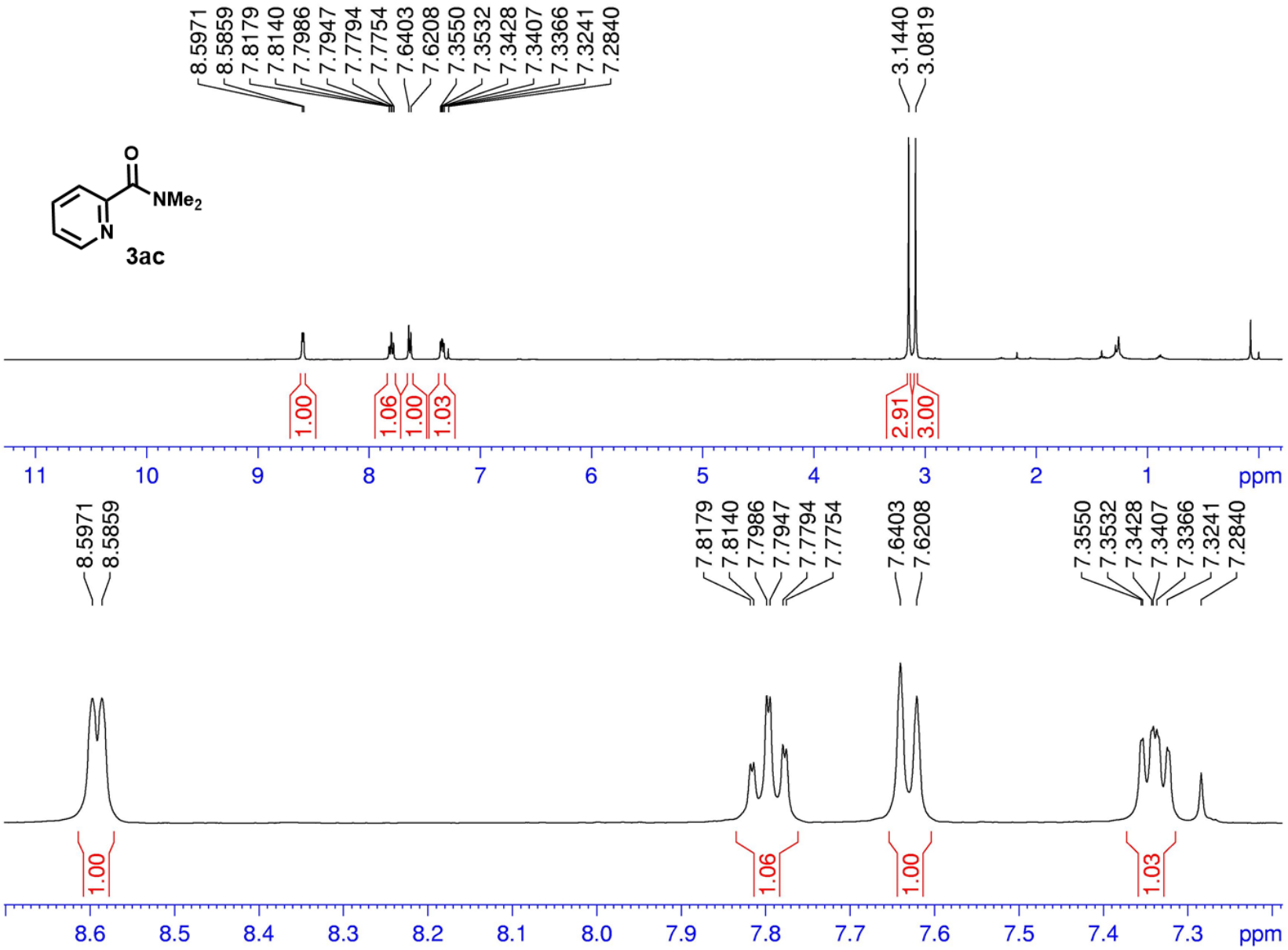
3ab ^{1}H NMR (500 MHz, DMSO-d_6)



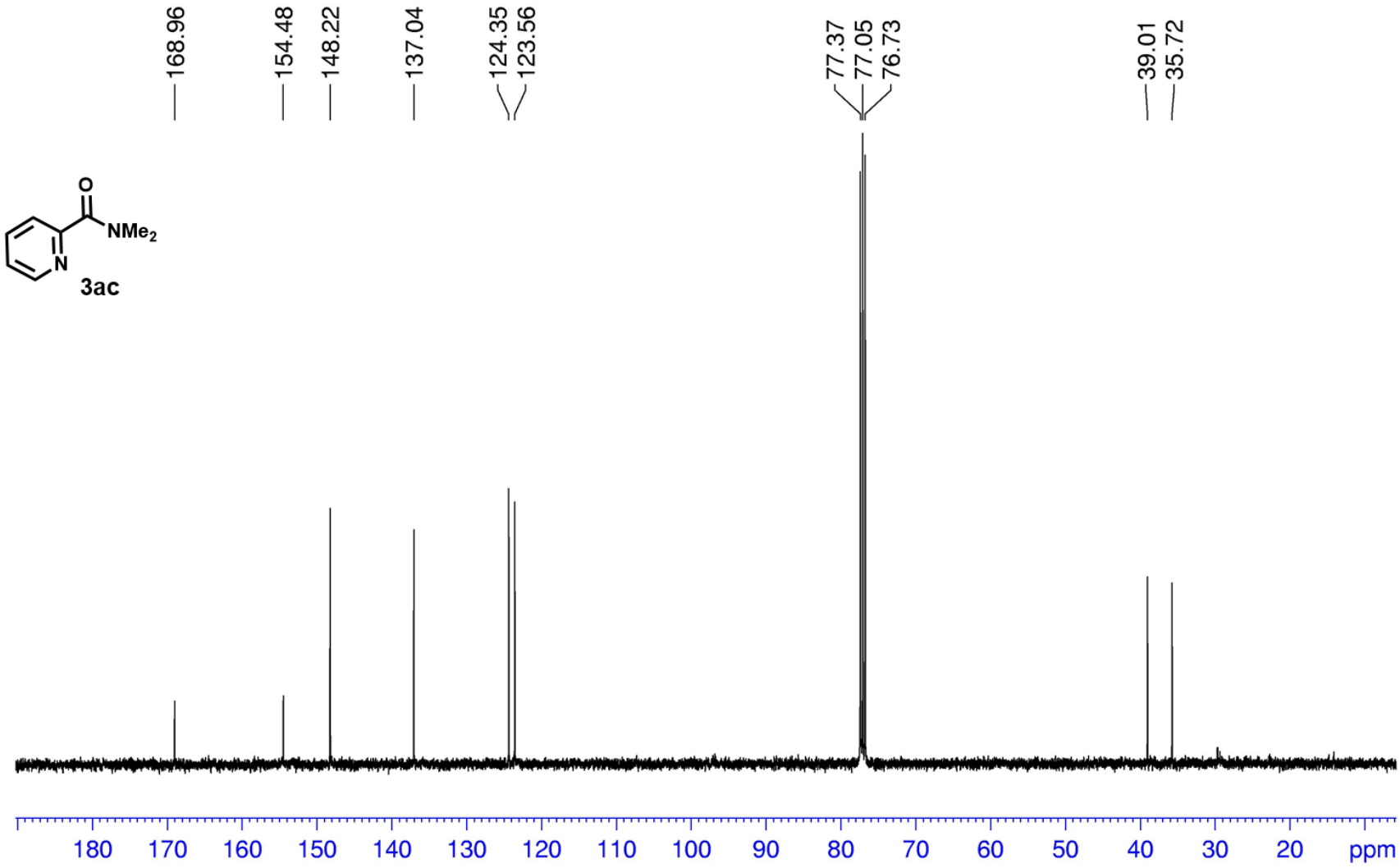
3ab ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



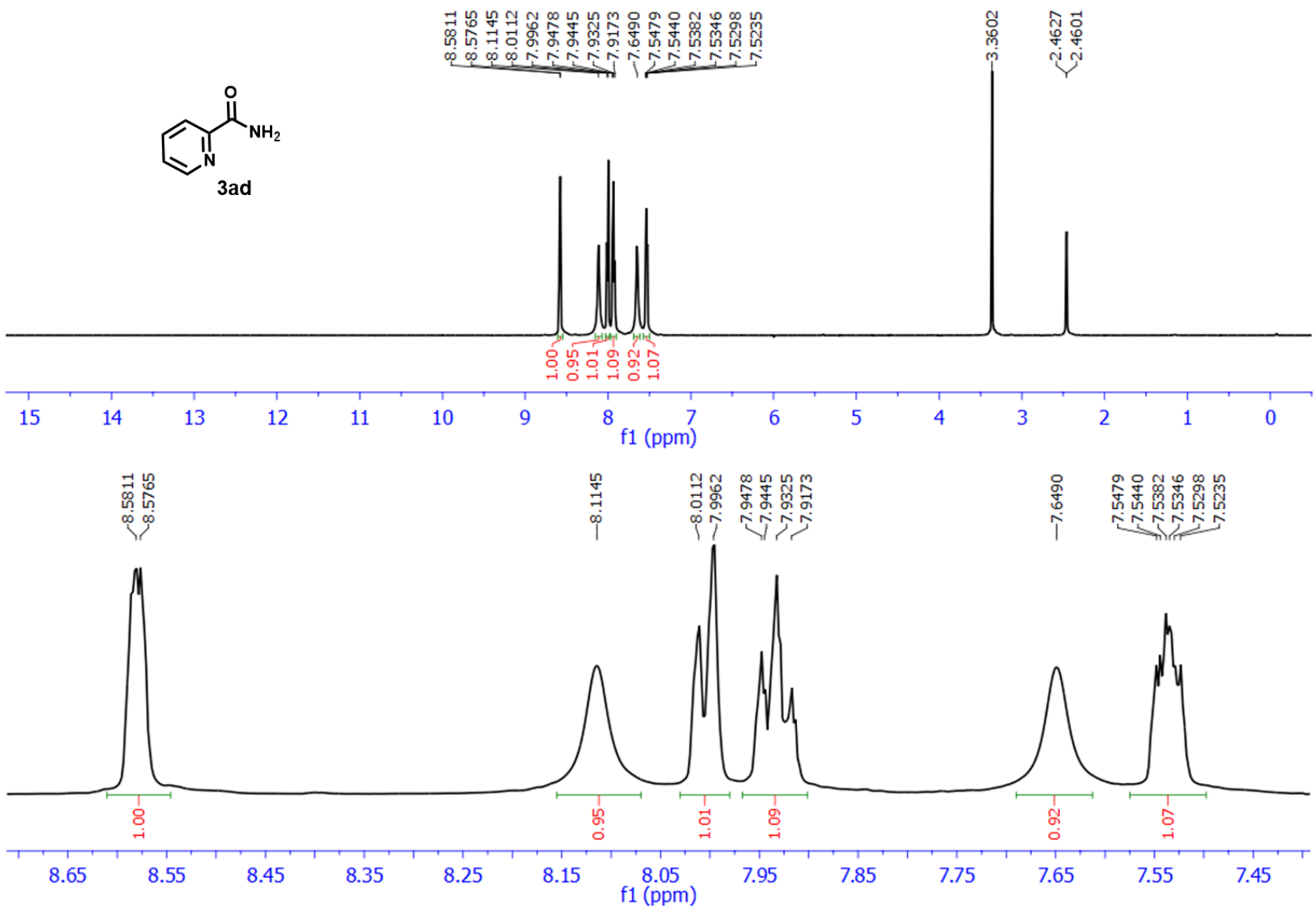
3ac ^{1}H NMR (400 MHz, $CDCl_3$)



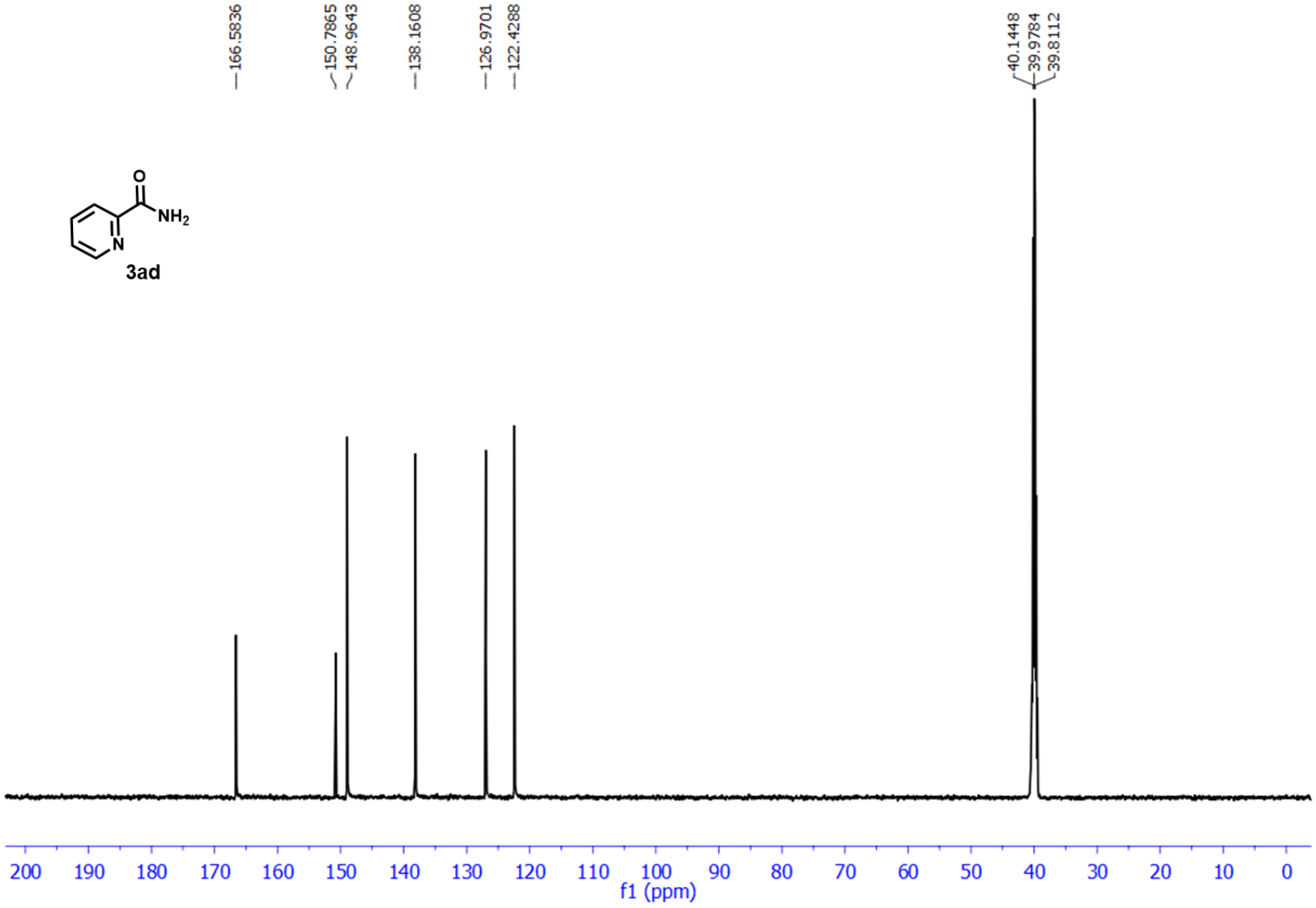
3ac ^{13}C {1H} NMR (100 MHz, $CDCl_3$)



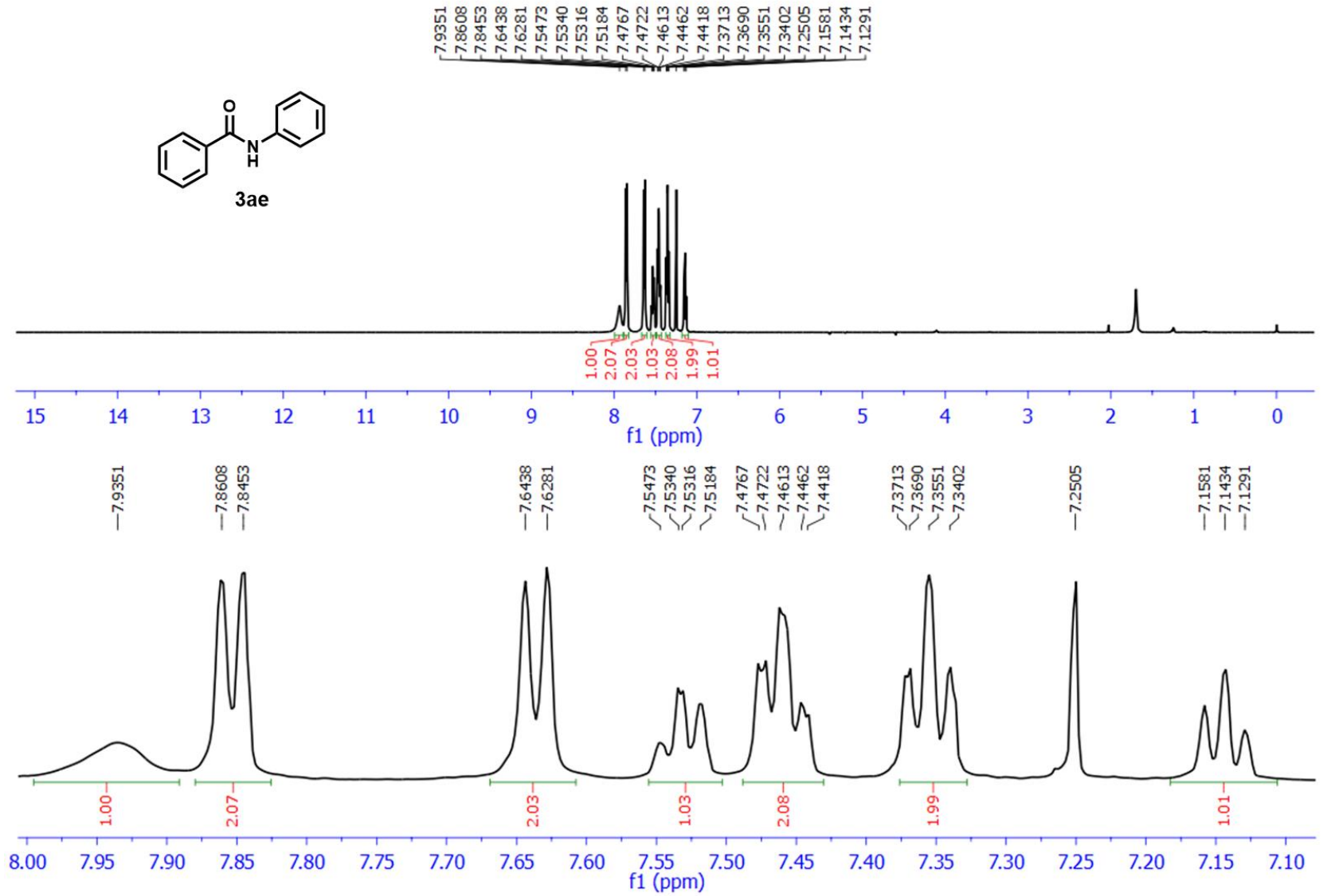
3ad ^{1}H NMR (500 MHz, DMSO-d_6)



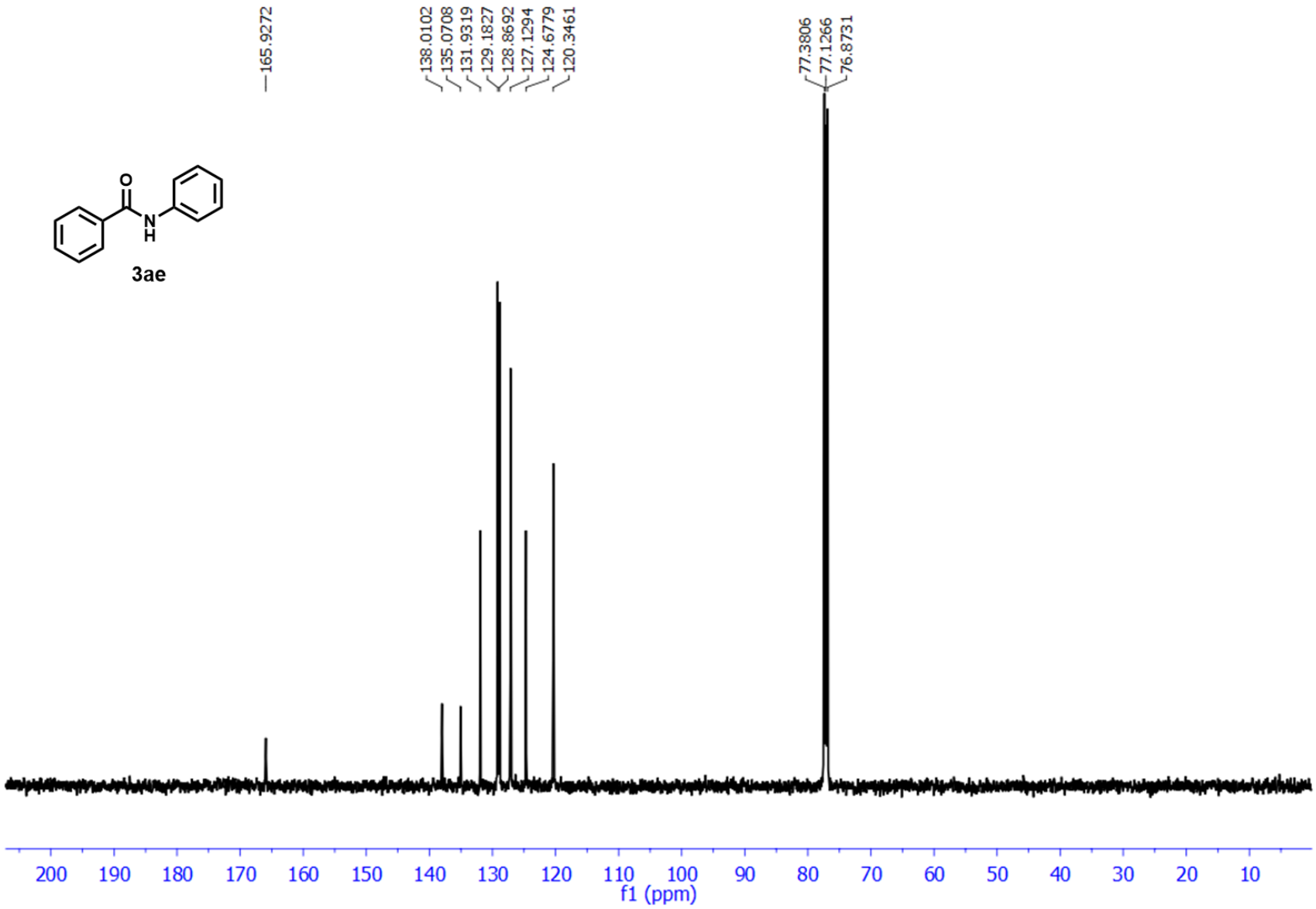
3ad ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



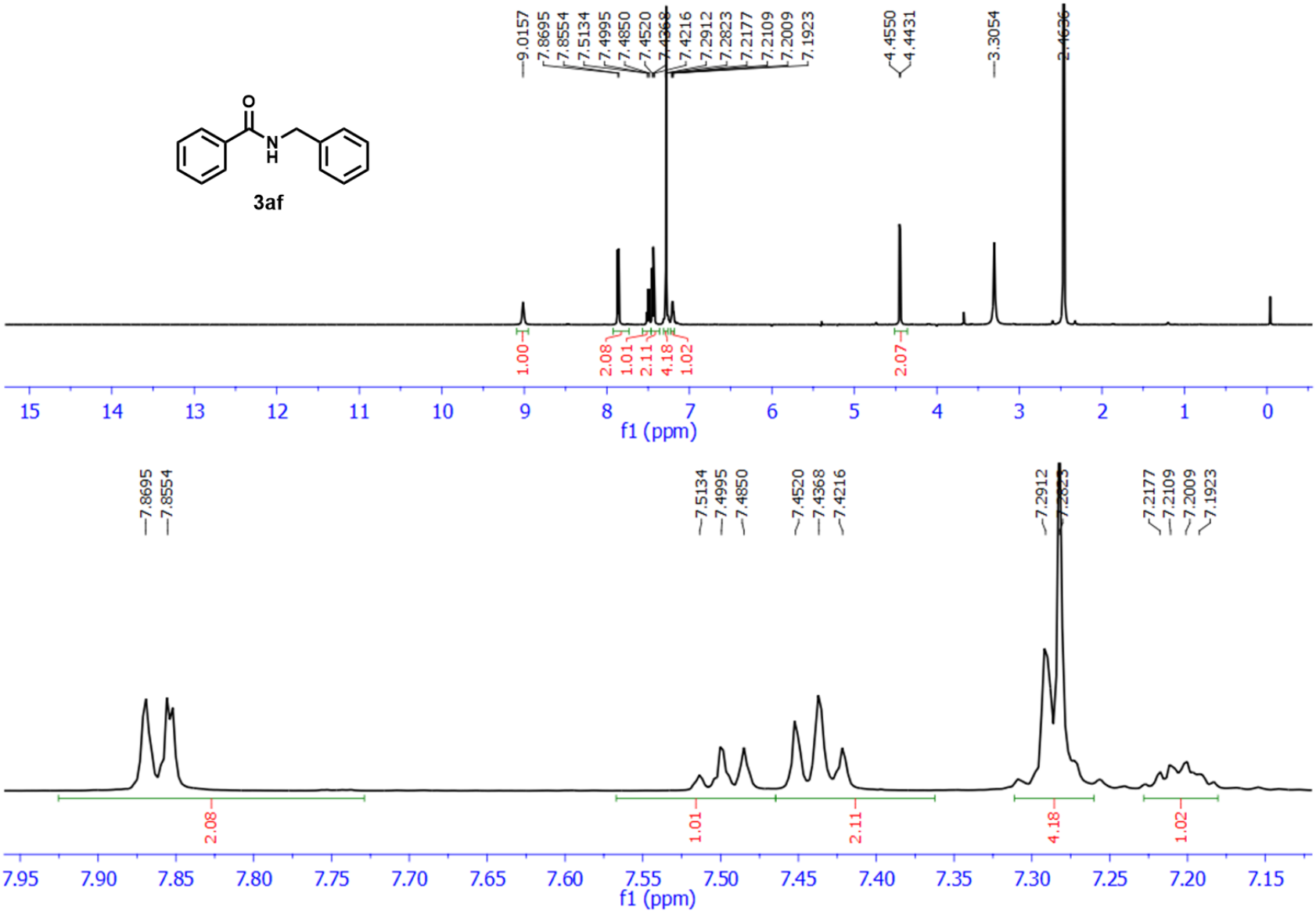
3ae ^{1}H NMR (500 MHz, $CDCl_3$)



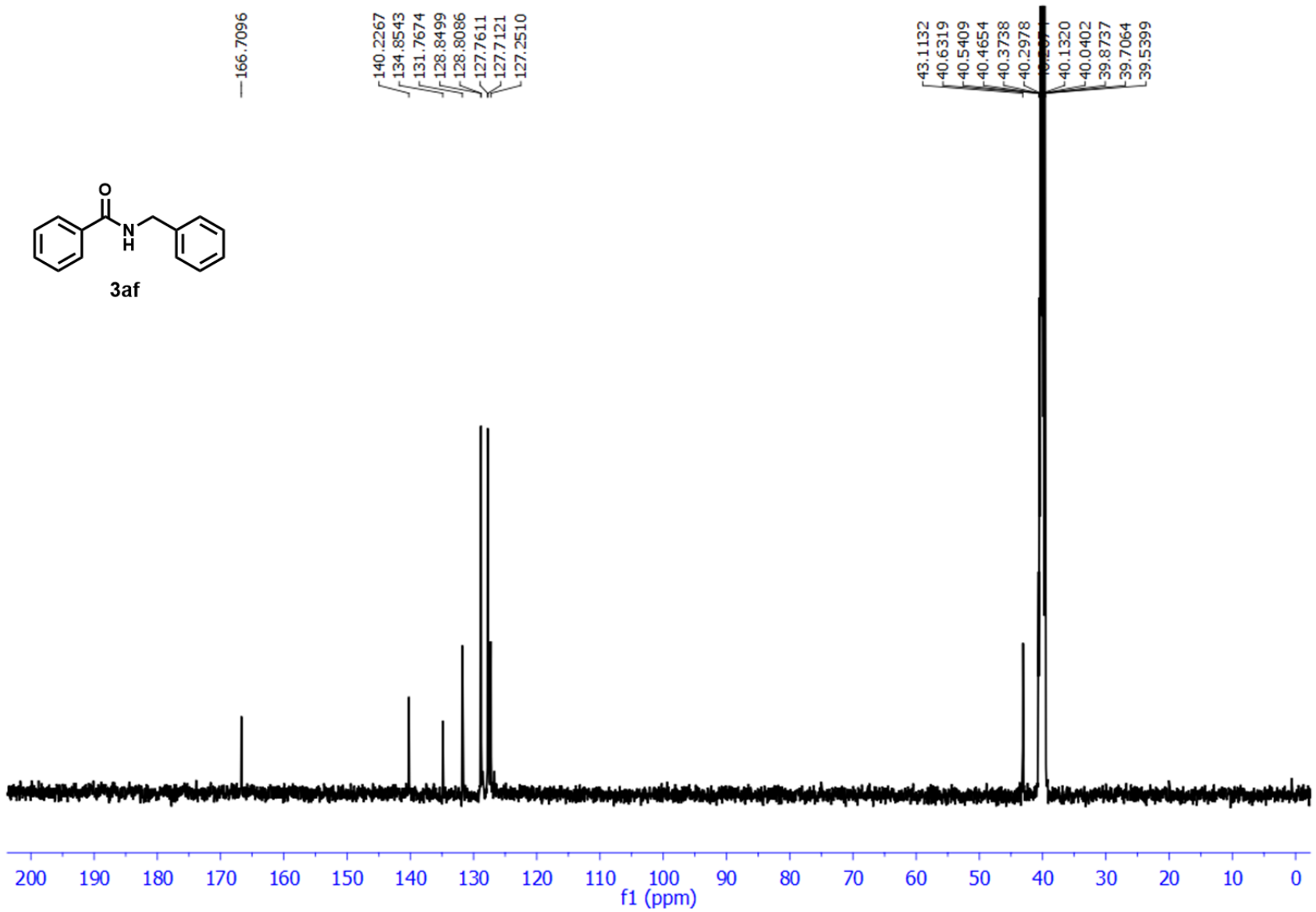
3ae ^{13}C {1H} NMR (125 MHz, $CDCl_3$)



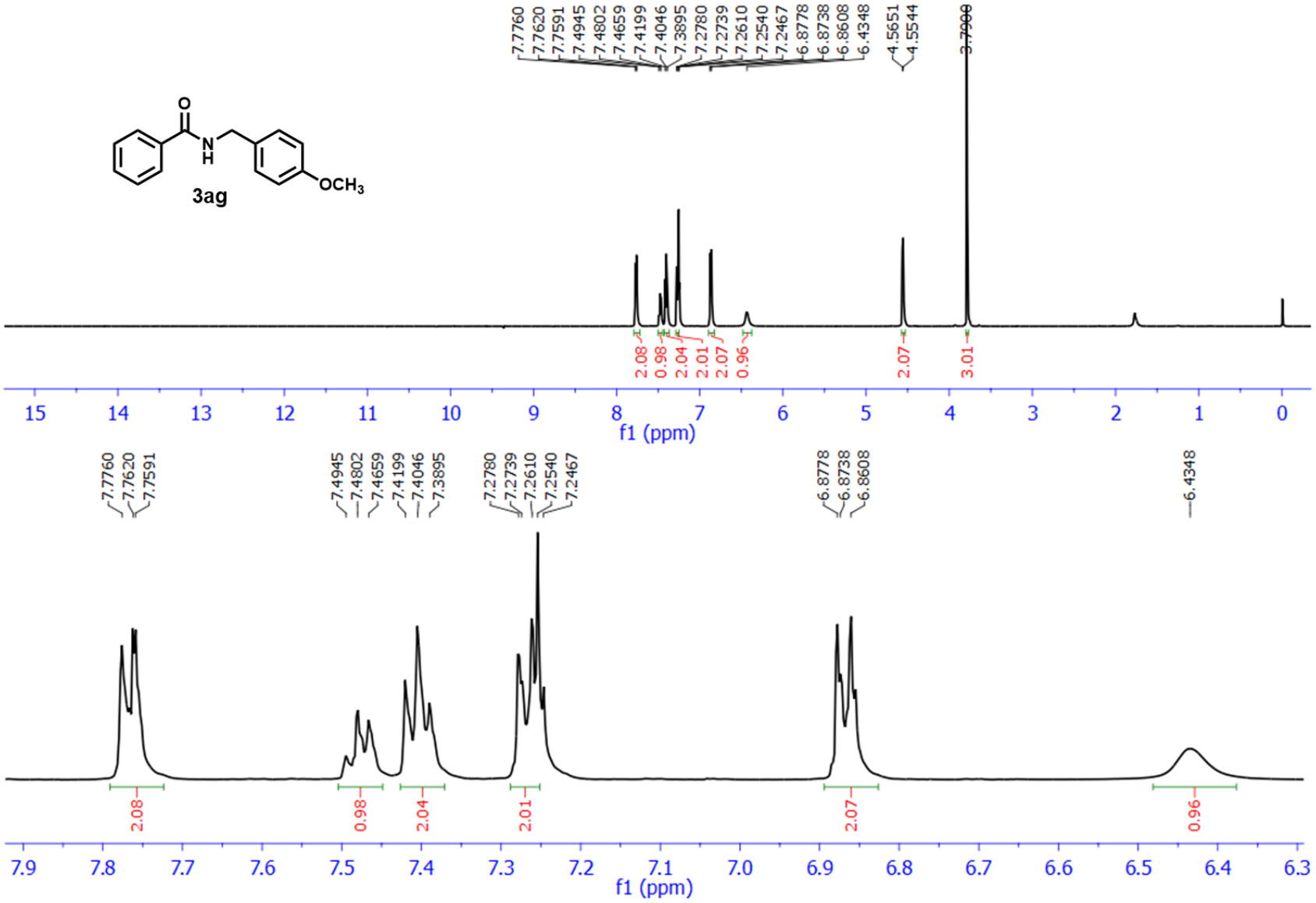
3af ^{1}H NMR (500 MHz, DMSO-d_6)



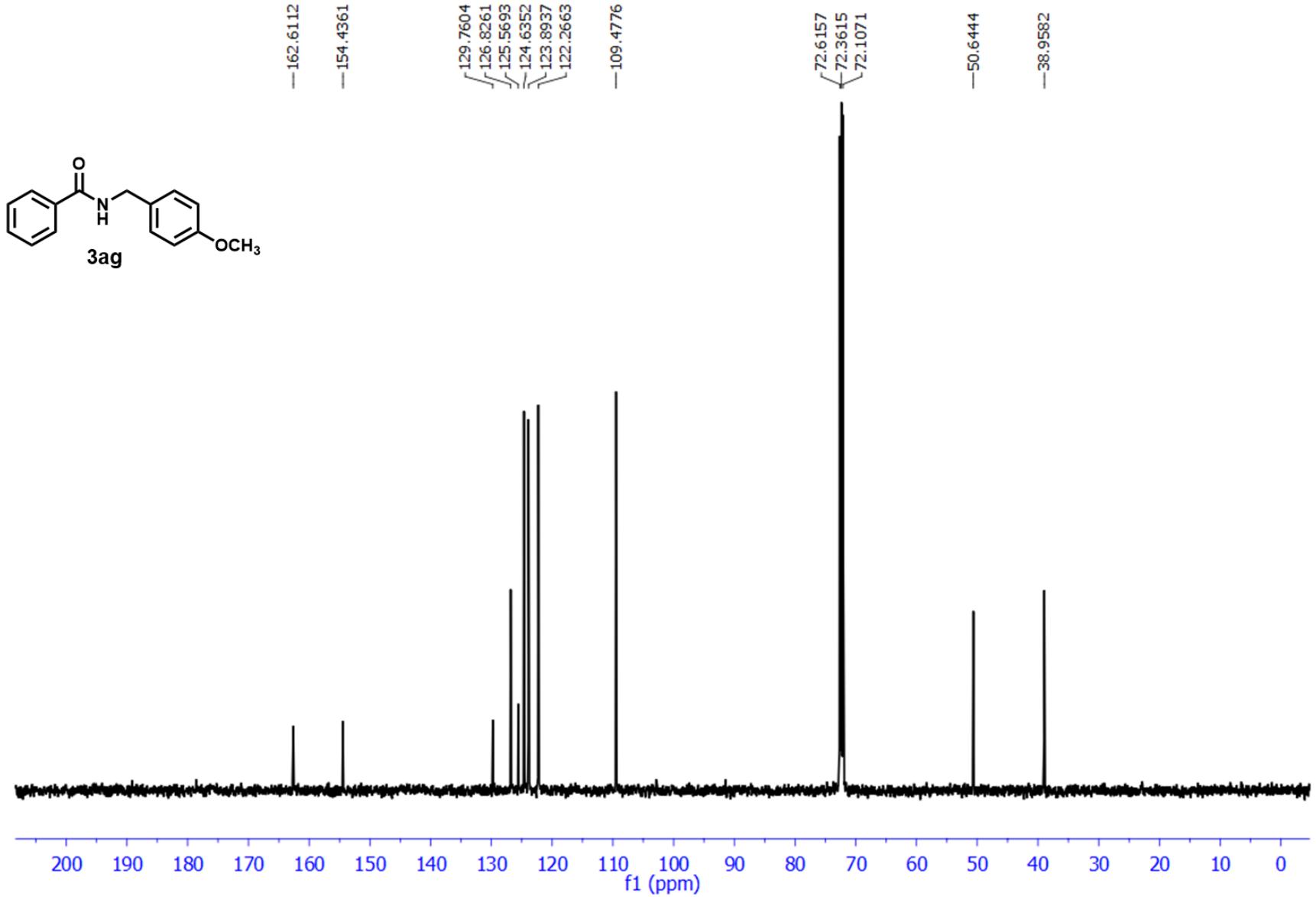
3af ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



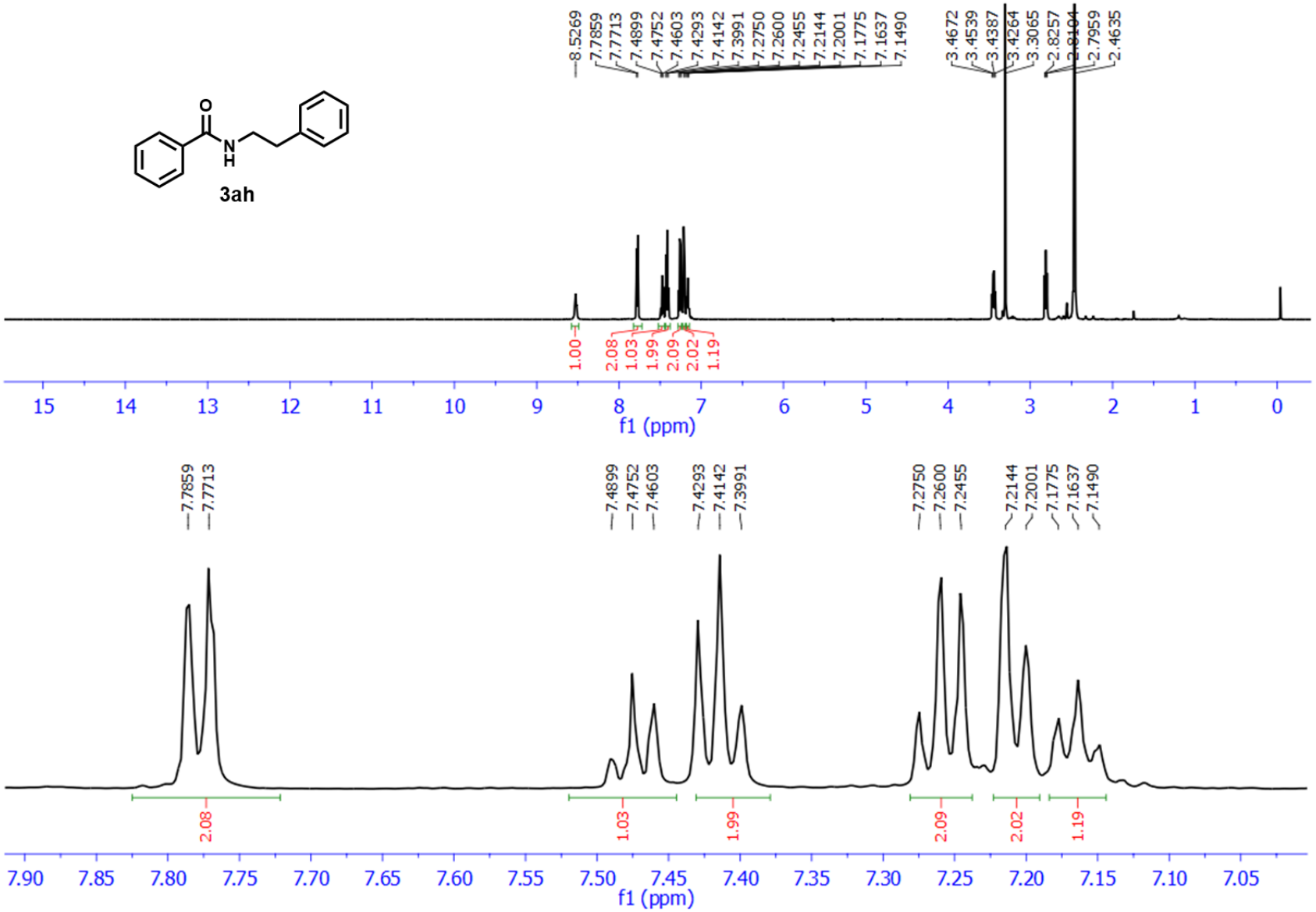
3ag ^{1}H NMR (500 MHz, $CDCl_3$)



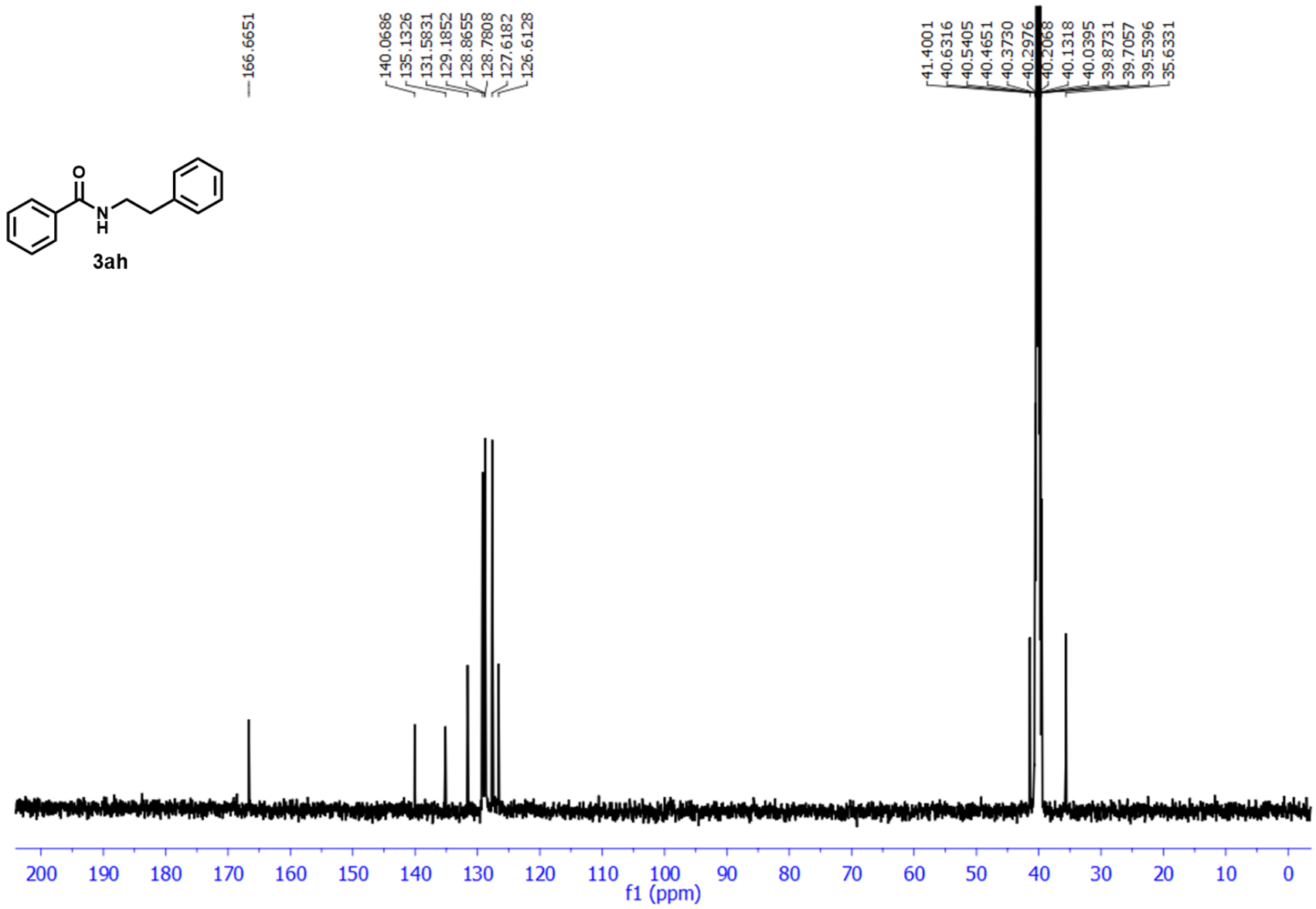
3ag ^{13}C {1H} NMR (125 MHz, $CDCl_3$)



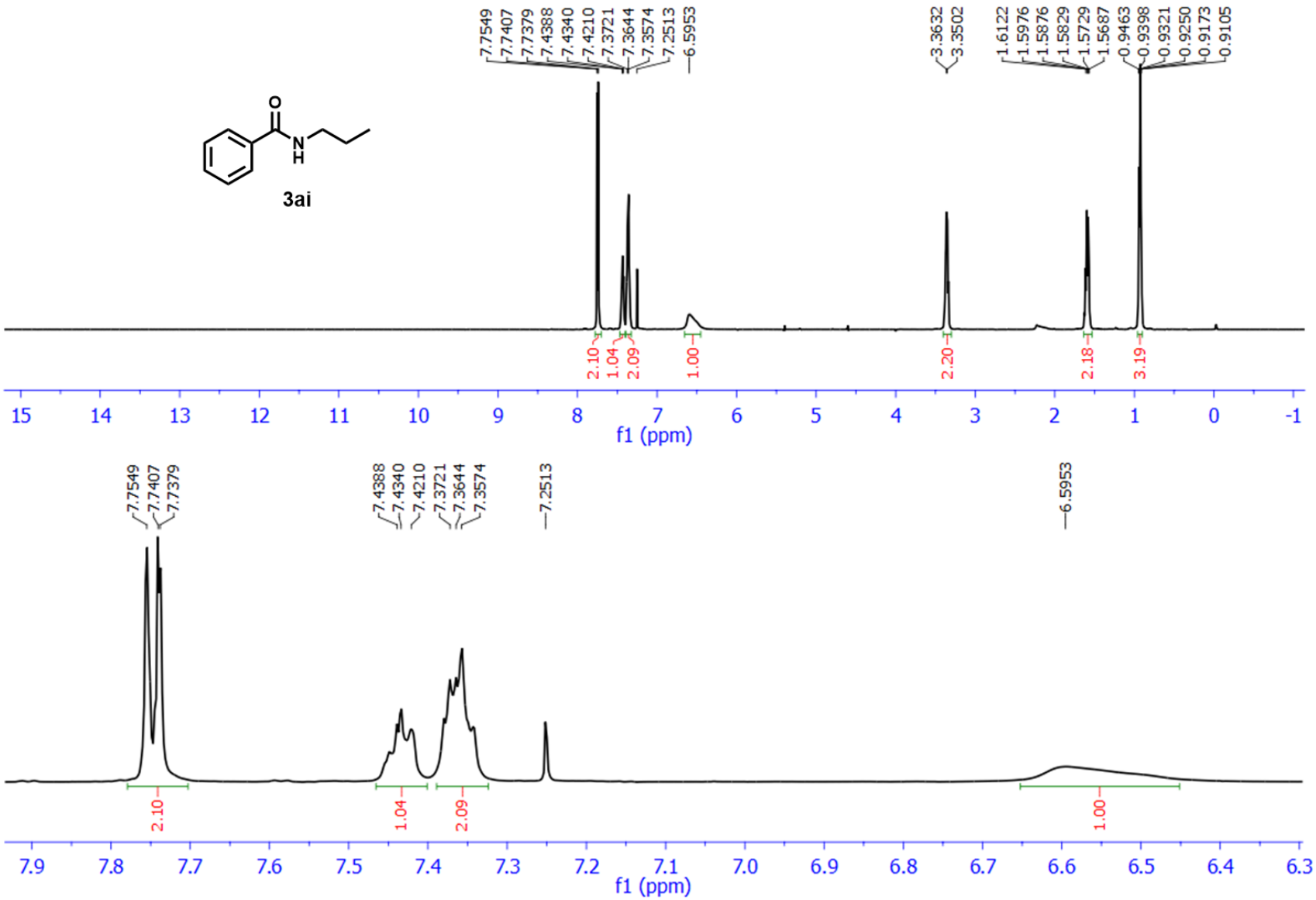
3ah ^{1}H NMR (500 MHz, DMSO-d_6)



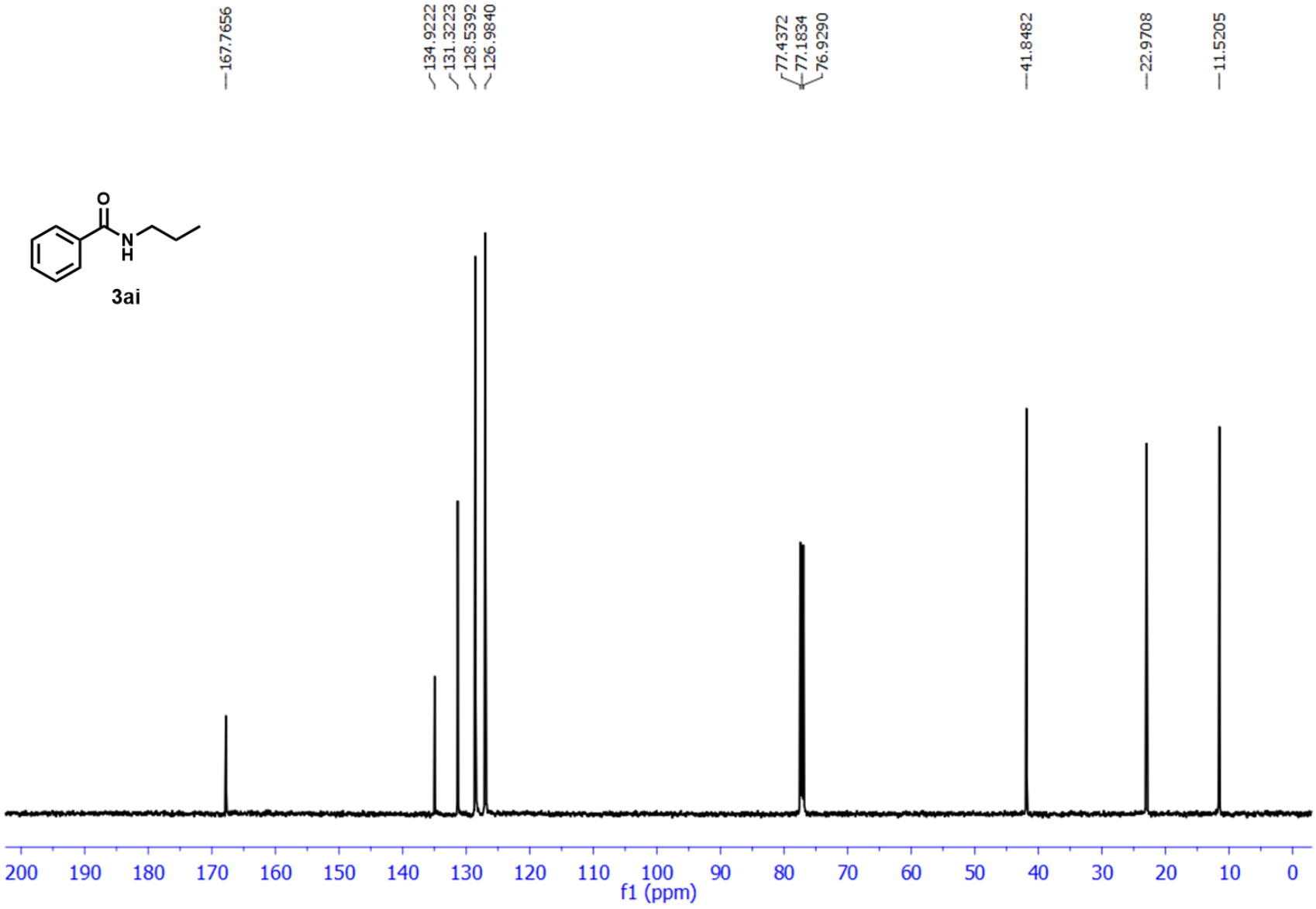
3ah ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



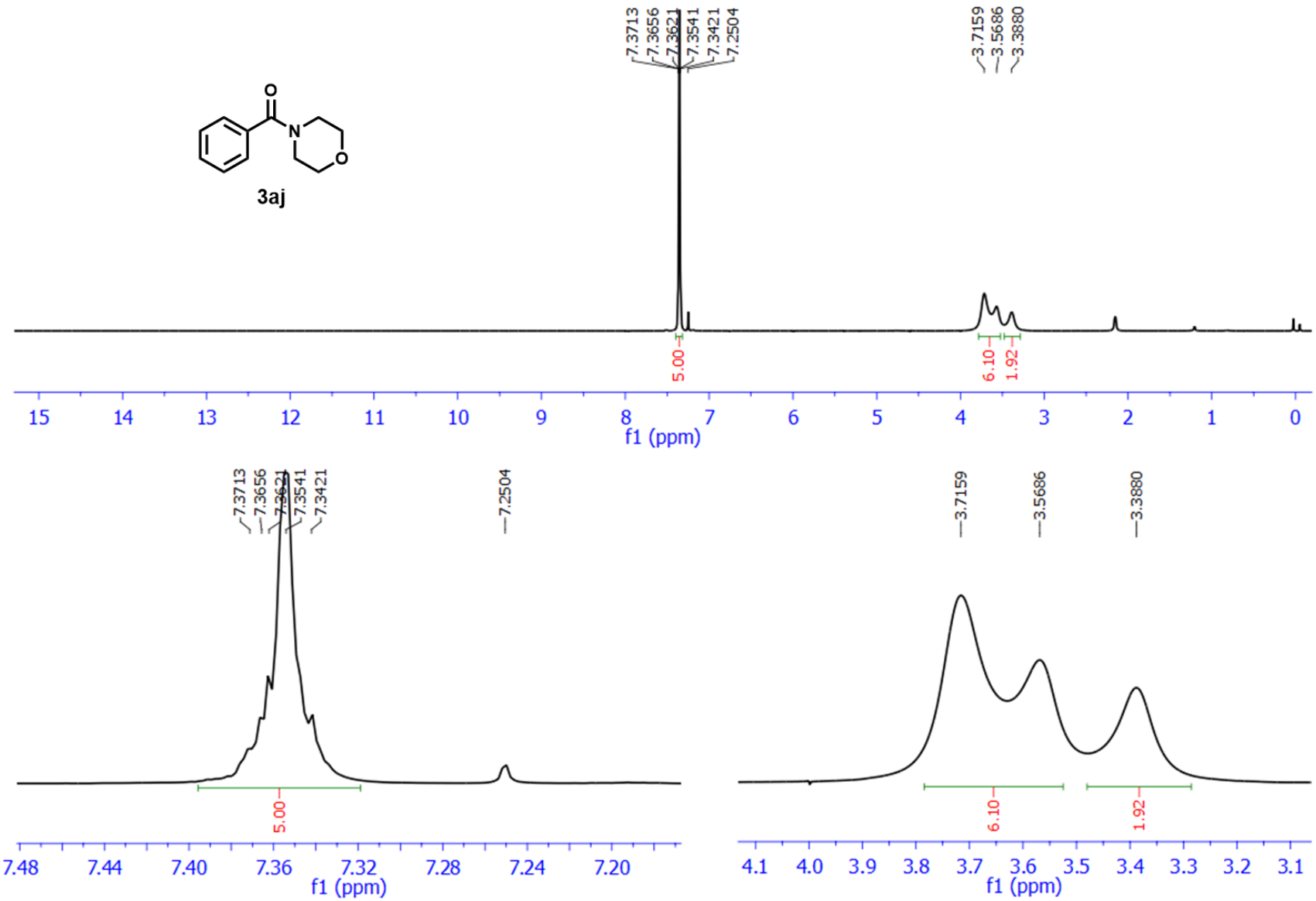
3ai ^{1}H NMR (500 MHz, $CDCl_3$)



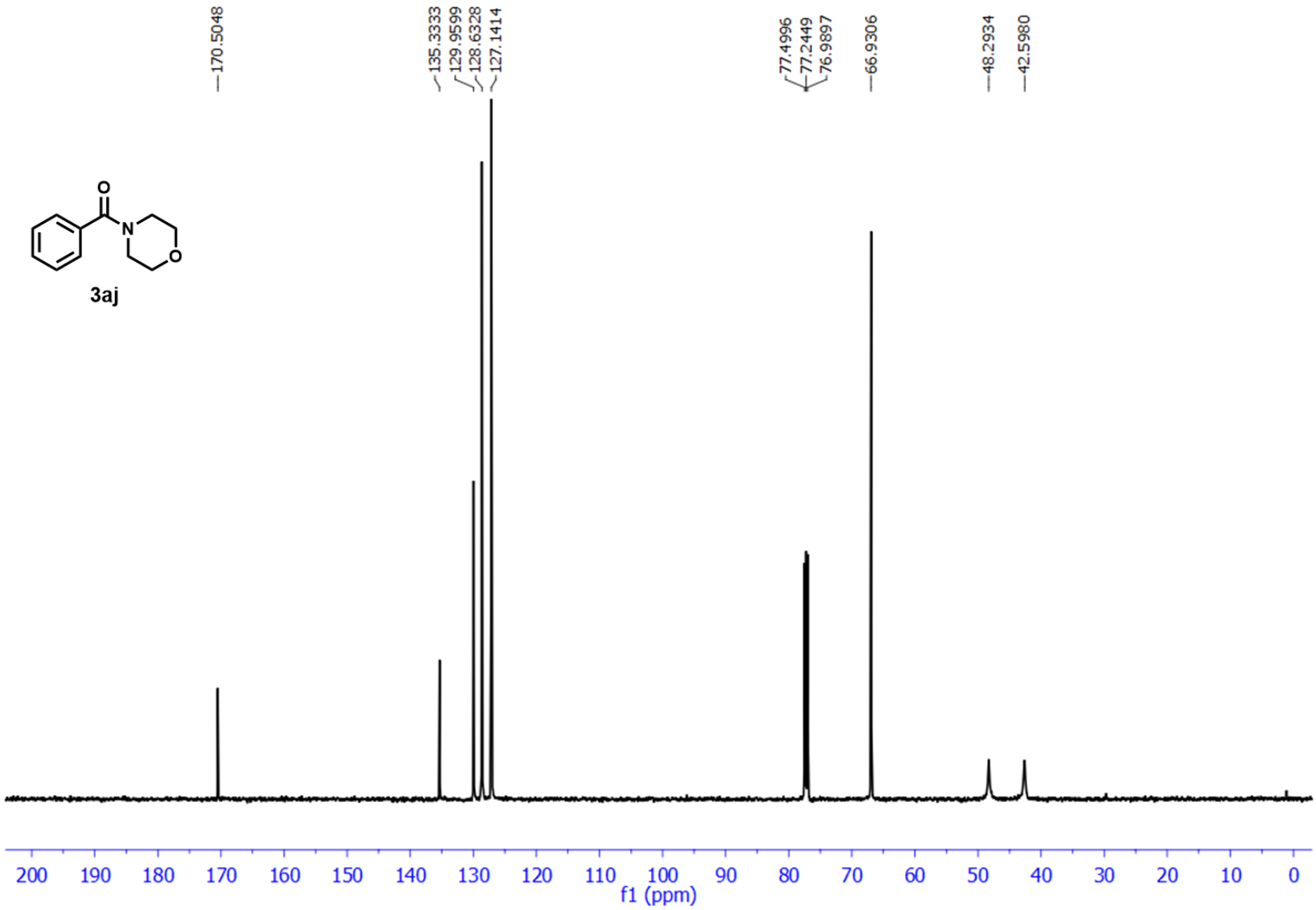
3ai ^{13}C {1H} NMR (125 MHz, $CDCl_3$)



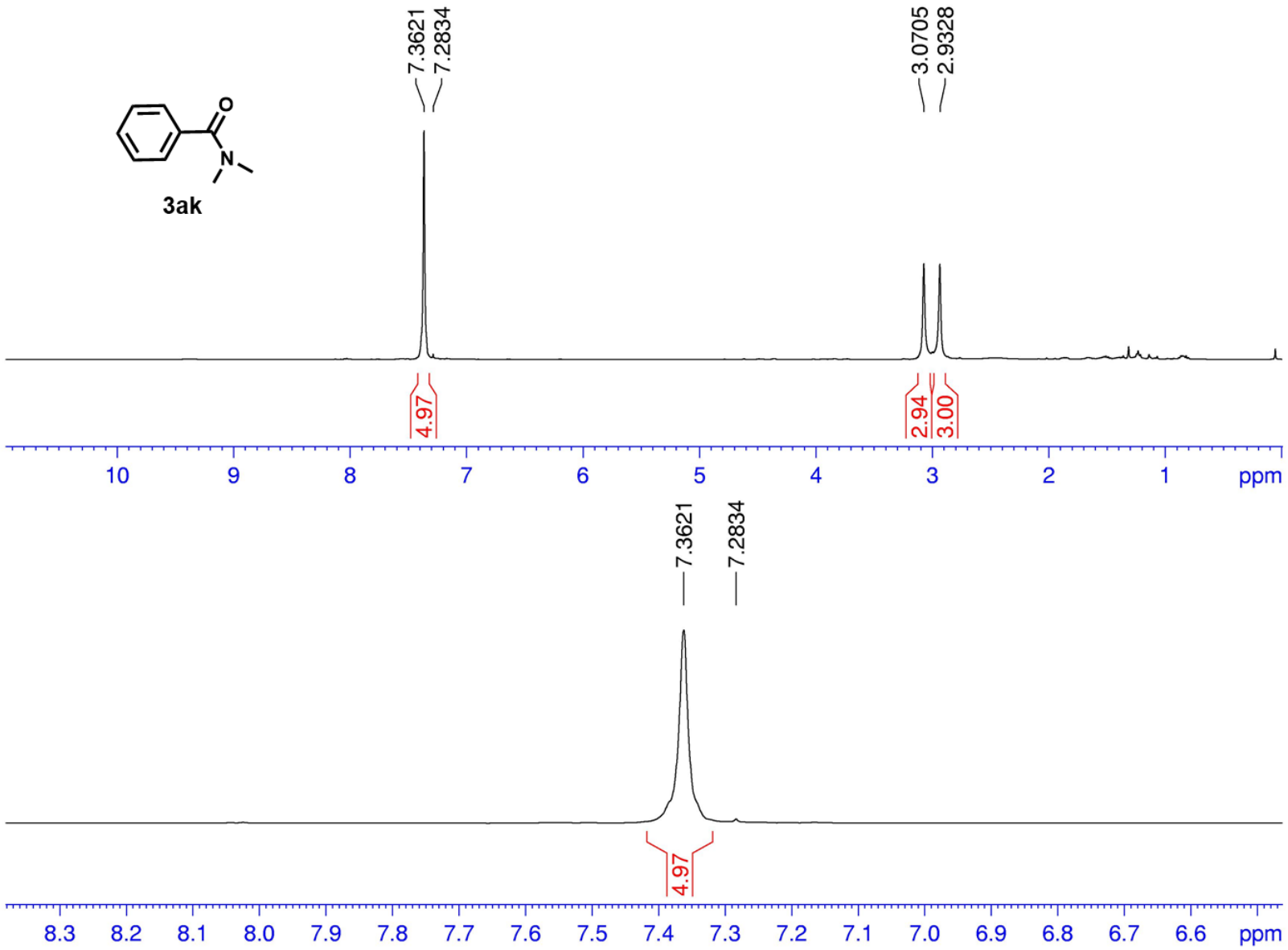
3aj ^{1}H NMR (500 MHz, $CDCl_3$)



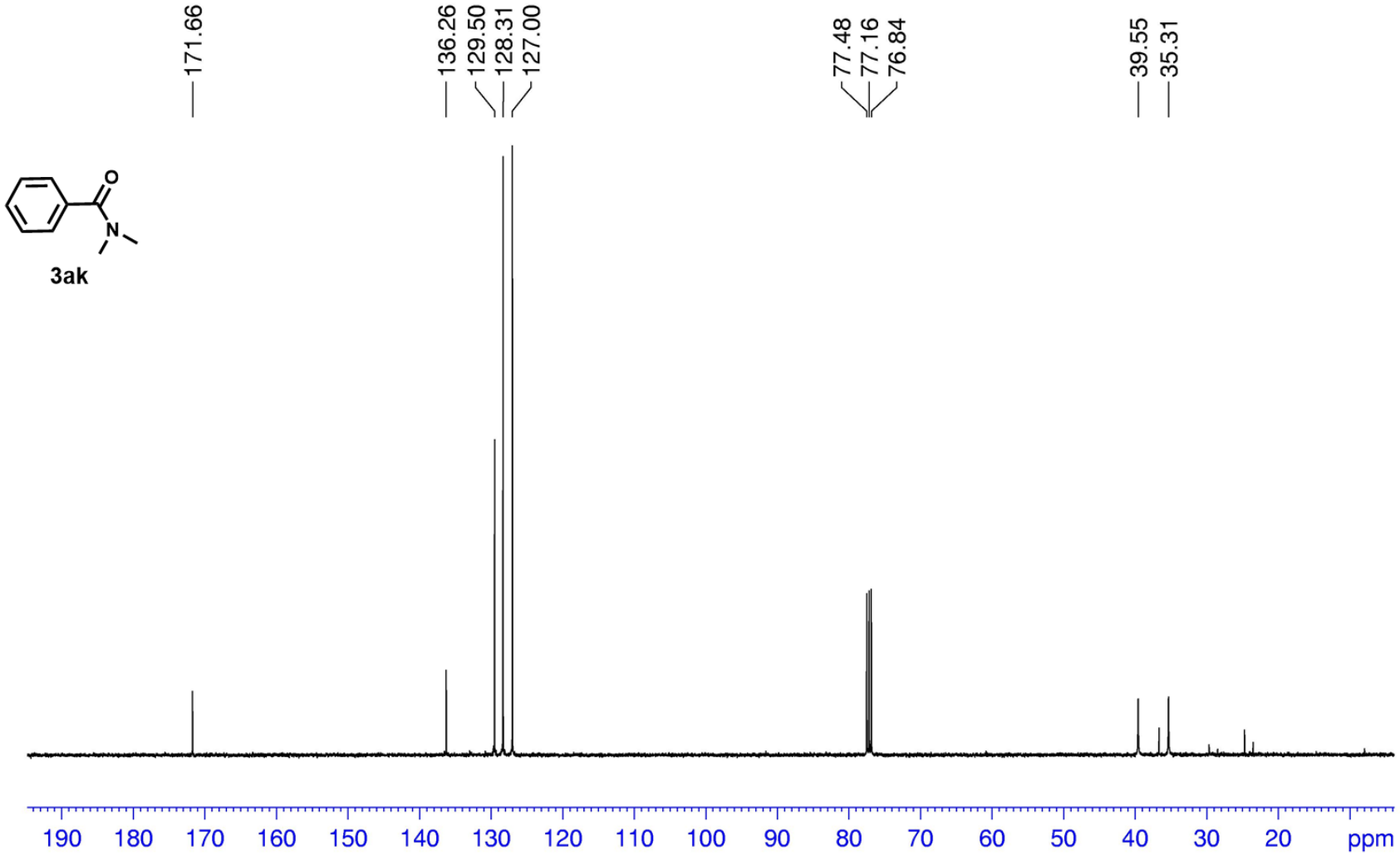
3aj ^{13}C {1H} NMR (125 MHz, $CDCl_3$)



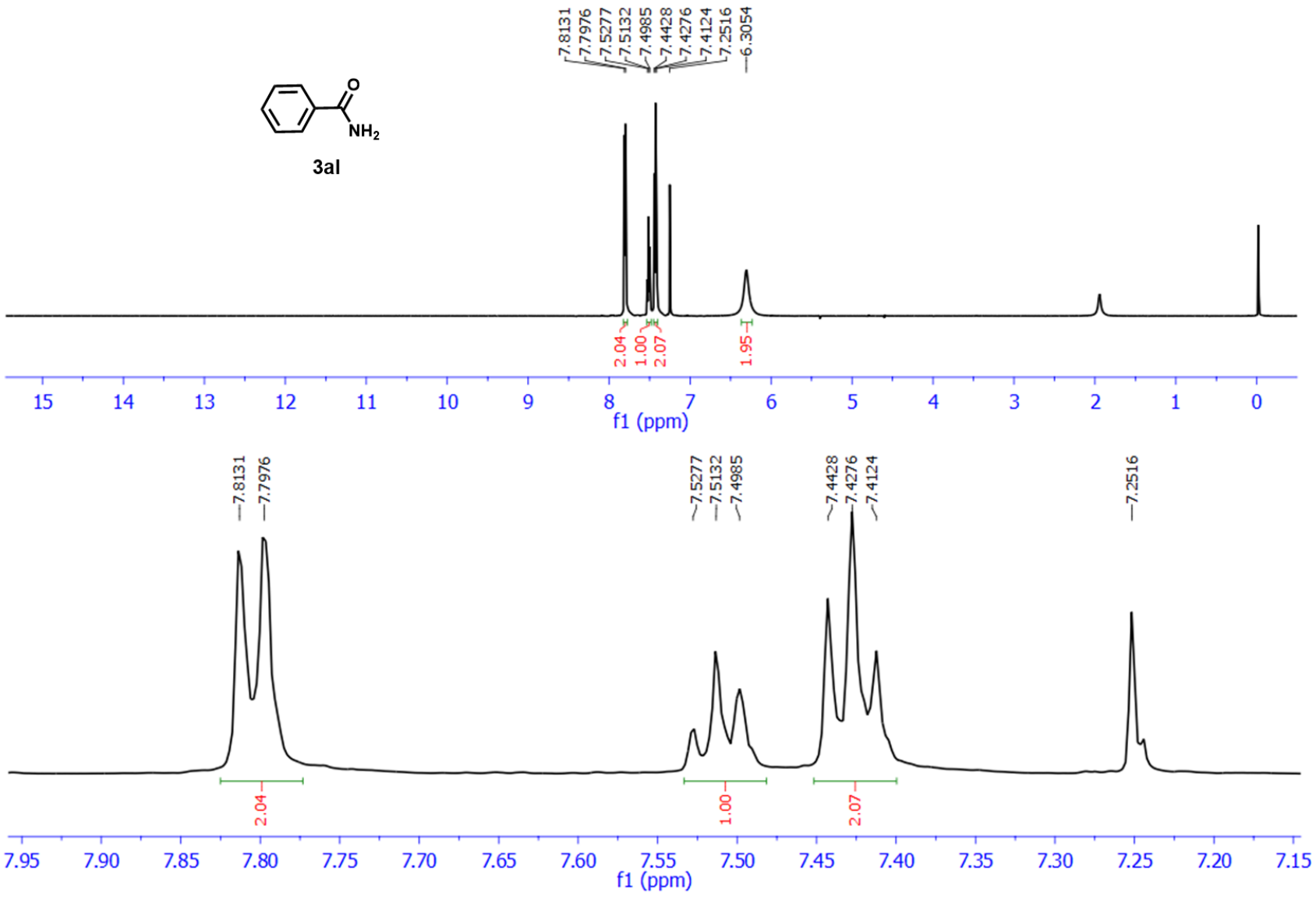
3ak ^{1}H NMR (400 MHz, $CDCl_3$)



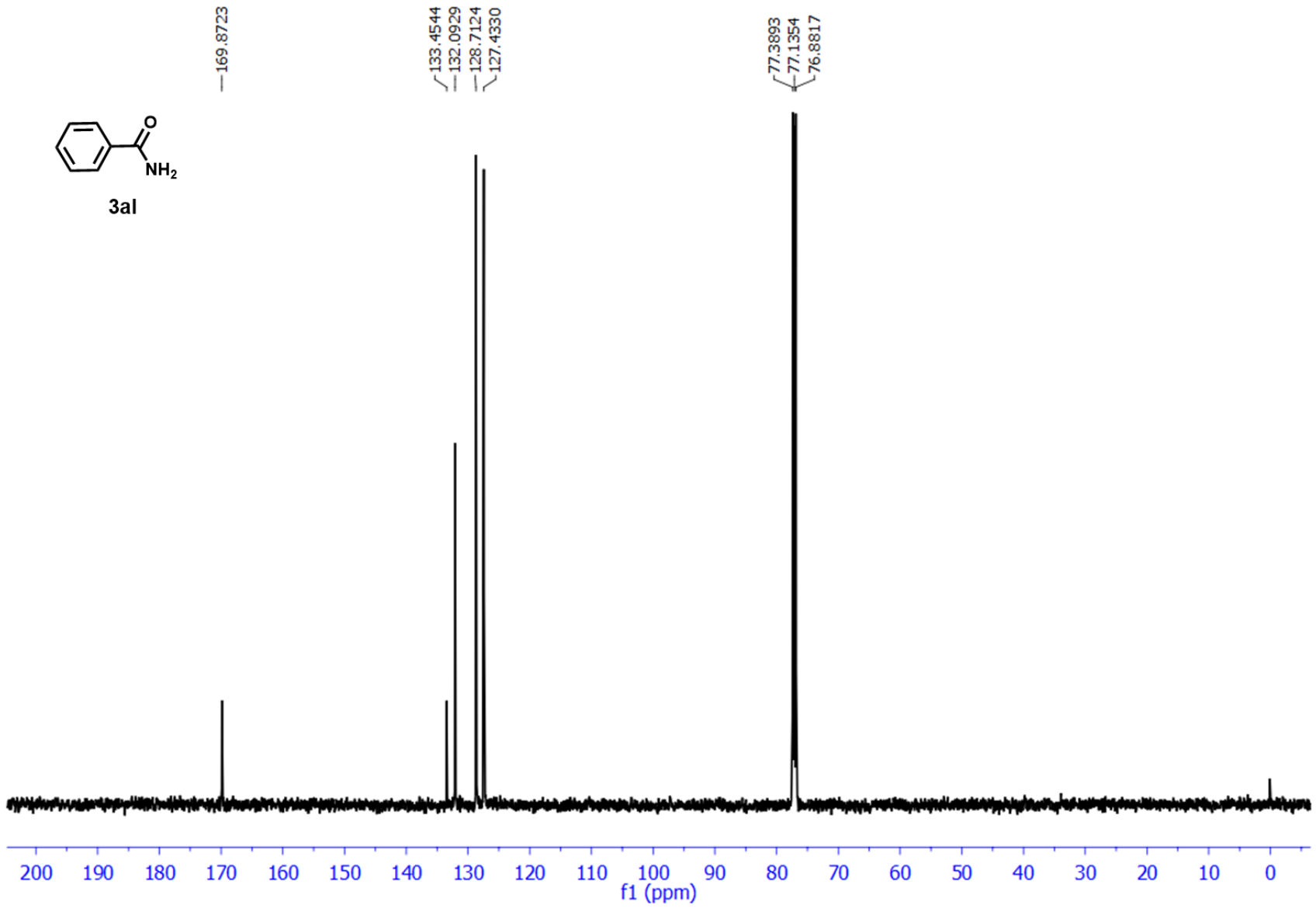
3ak ^{13}C {1H} NMR (100 MHz, $CDCl_3$)



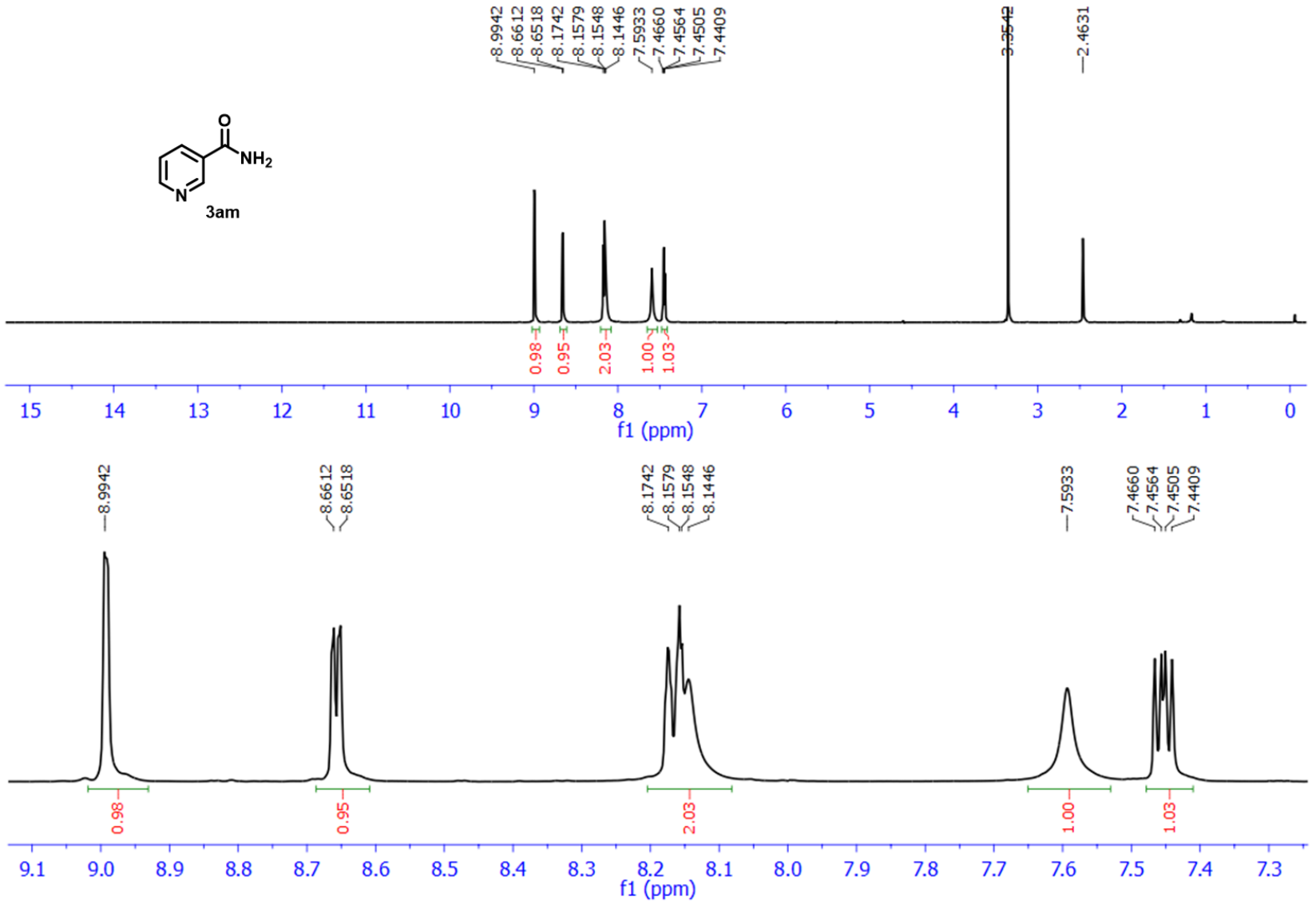
3al ^{1}H NMR (500 MHz, $CDCl_3$)



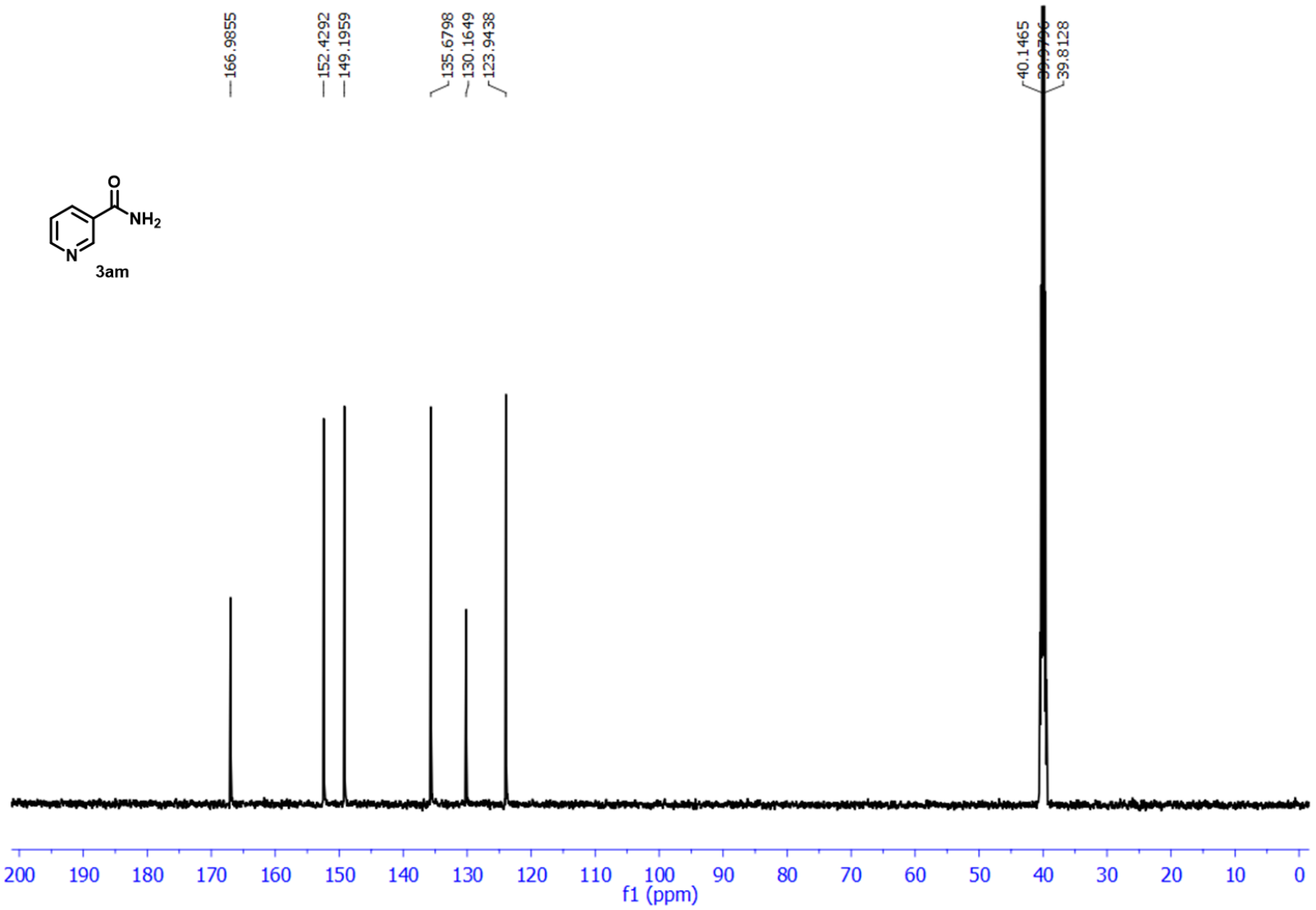
3al ^{13}C {1H} NMR (125 MHz, $CDCl_3$)



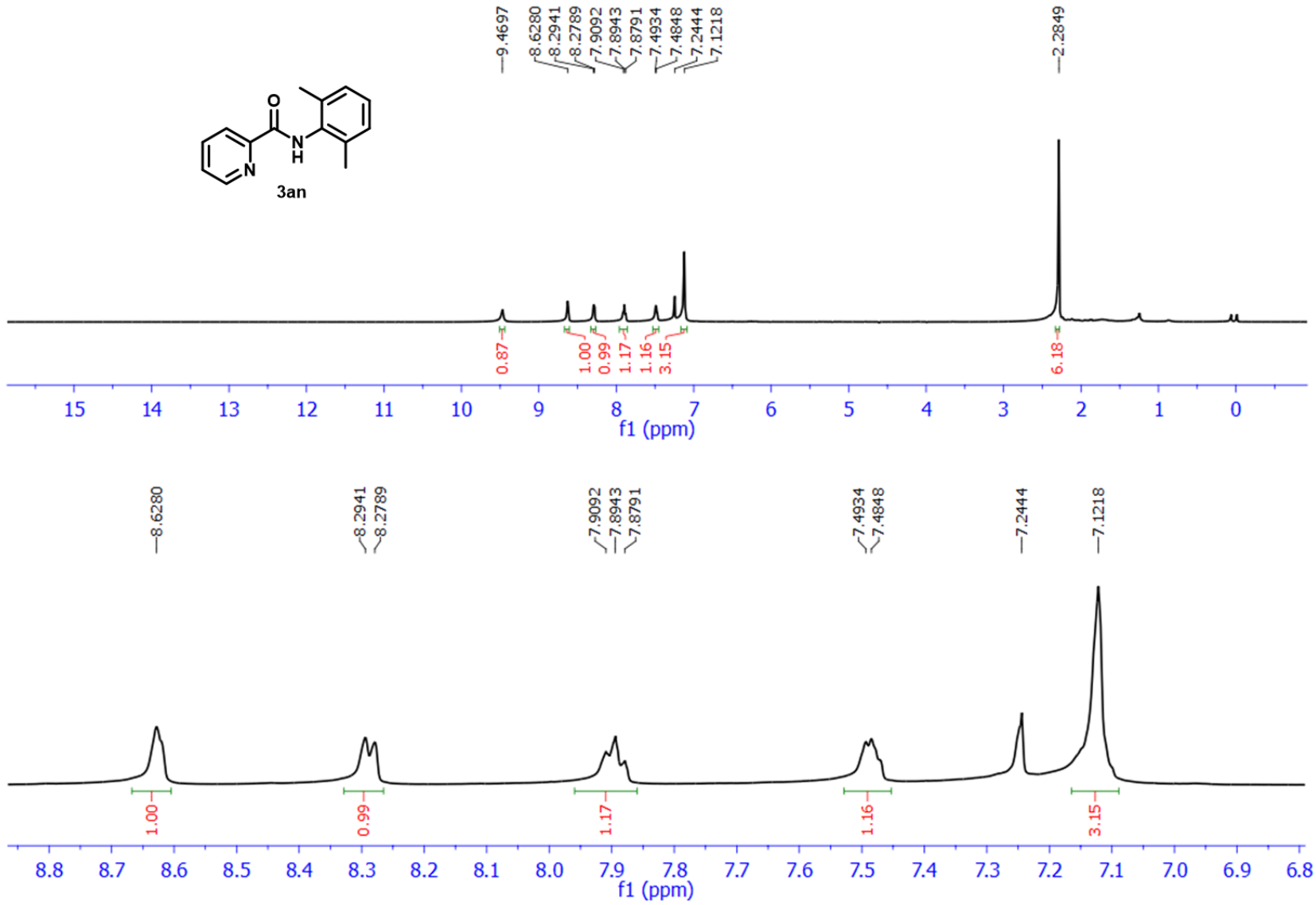
3am ^{1}H NMR (500 MHz, DMSO-d_6)



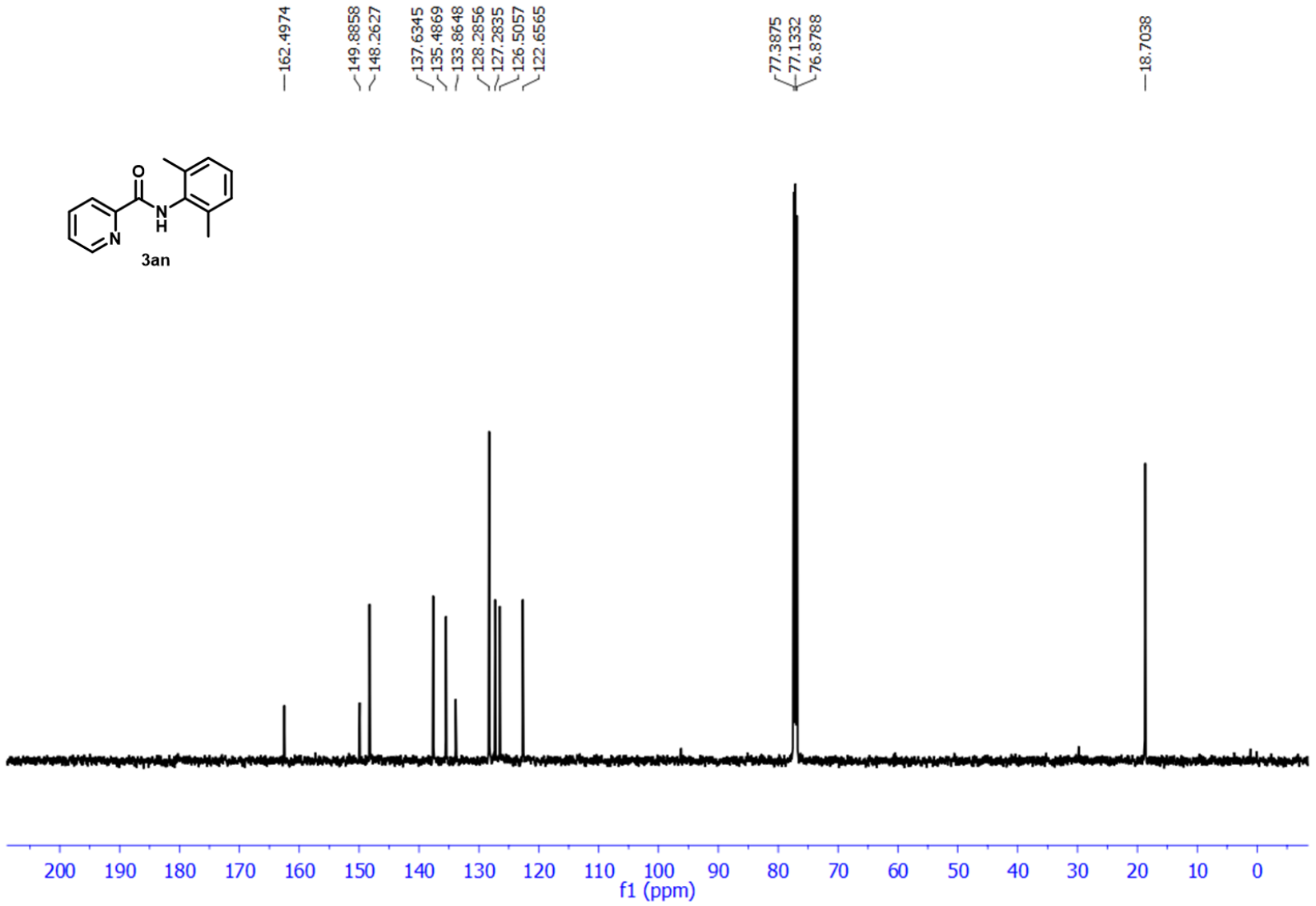
3am ^{13}C {1H} NMR (125 MHz, DMSO-d_6)



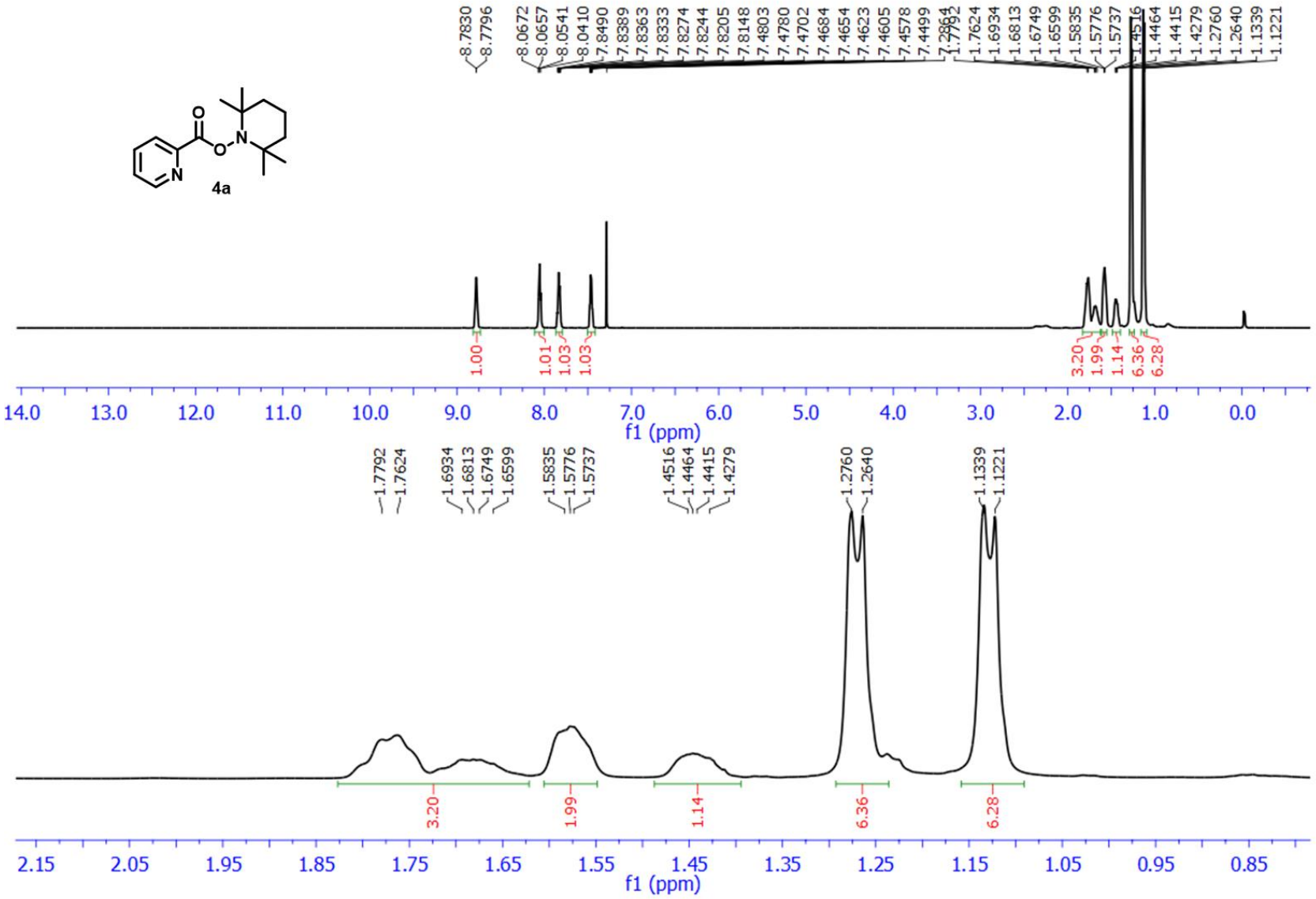
3an ^{1}H NMR (500 MHz, $CDCl_3$)



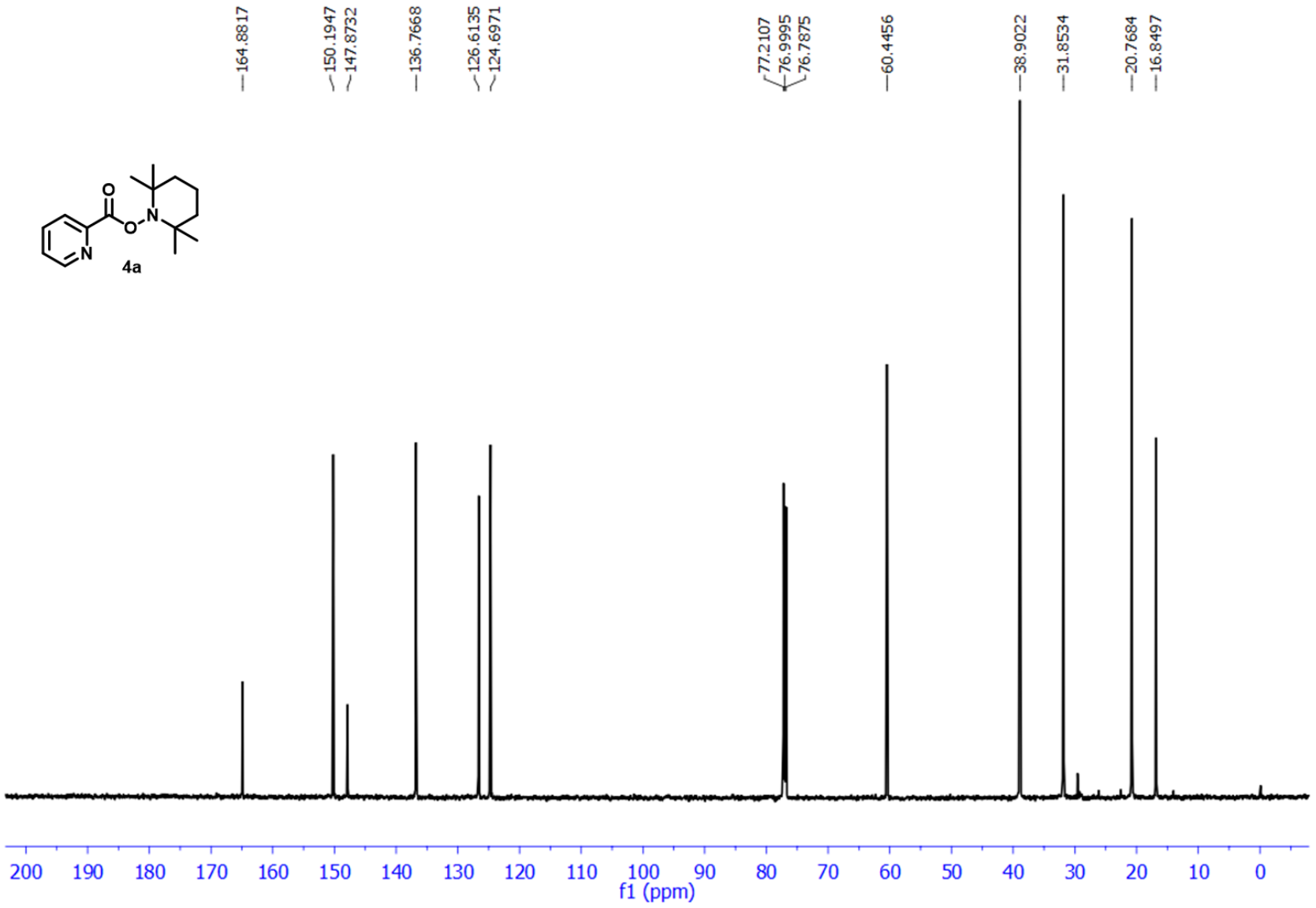
3an ^{13}C {1H} NMR (125 MHz, $CDCl_3$)



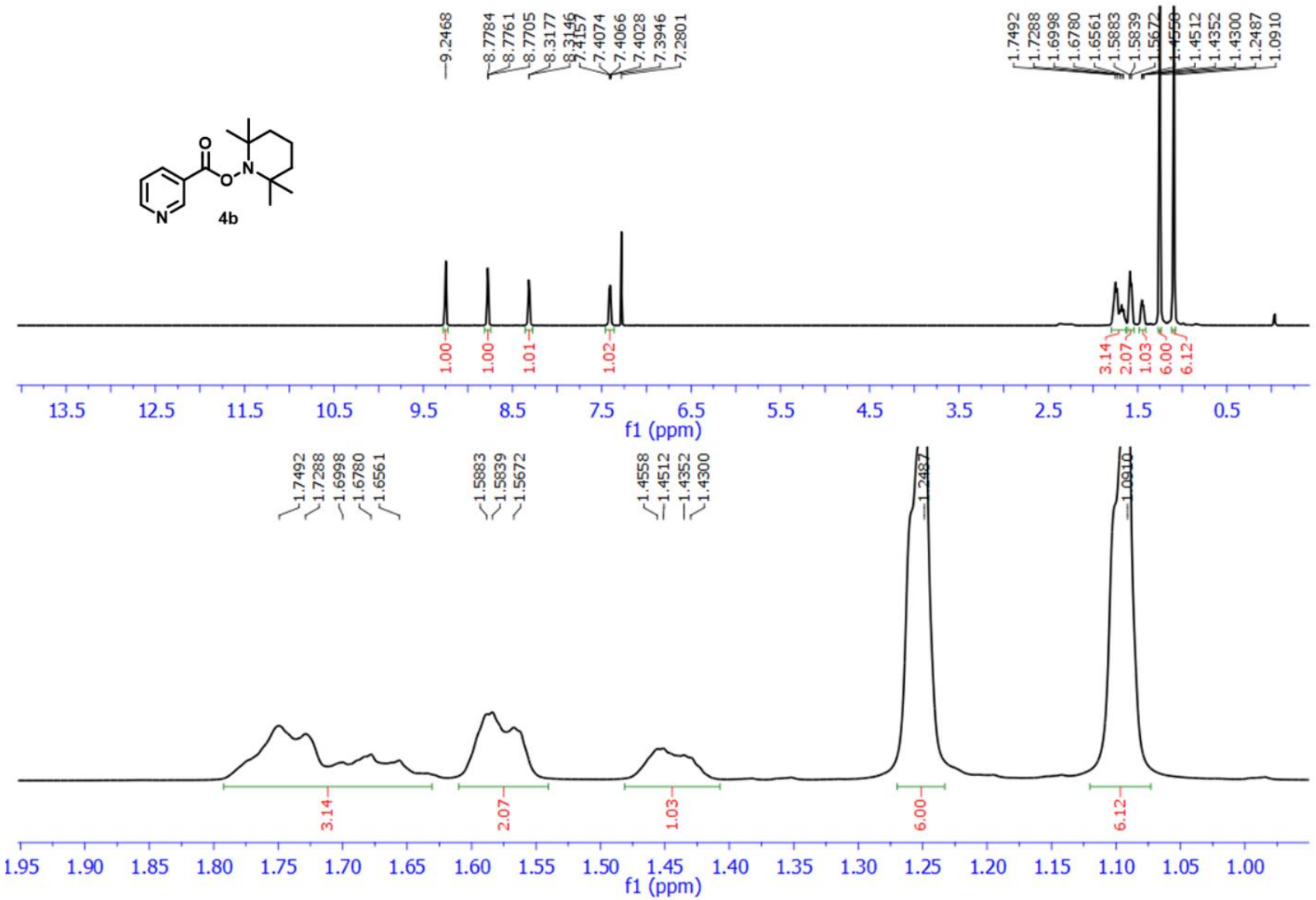
4a ^{1}H NMR (600 MHz, $CDCl_3$)



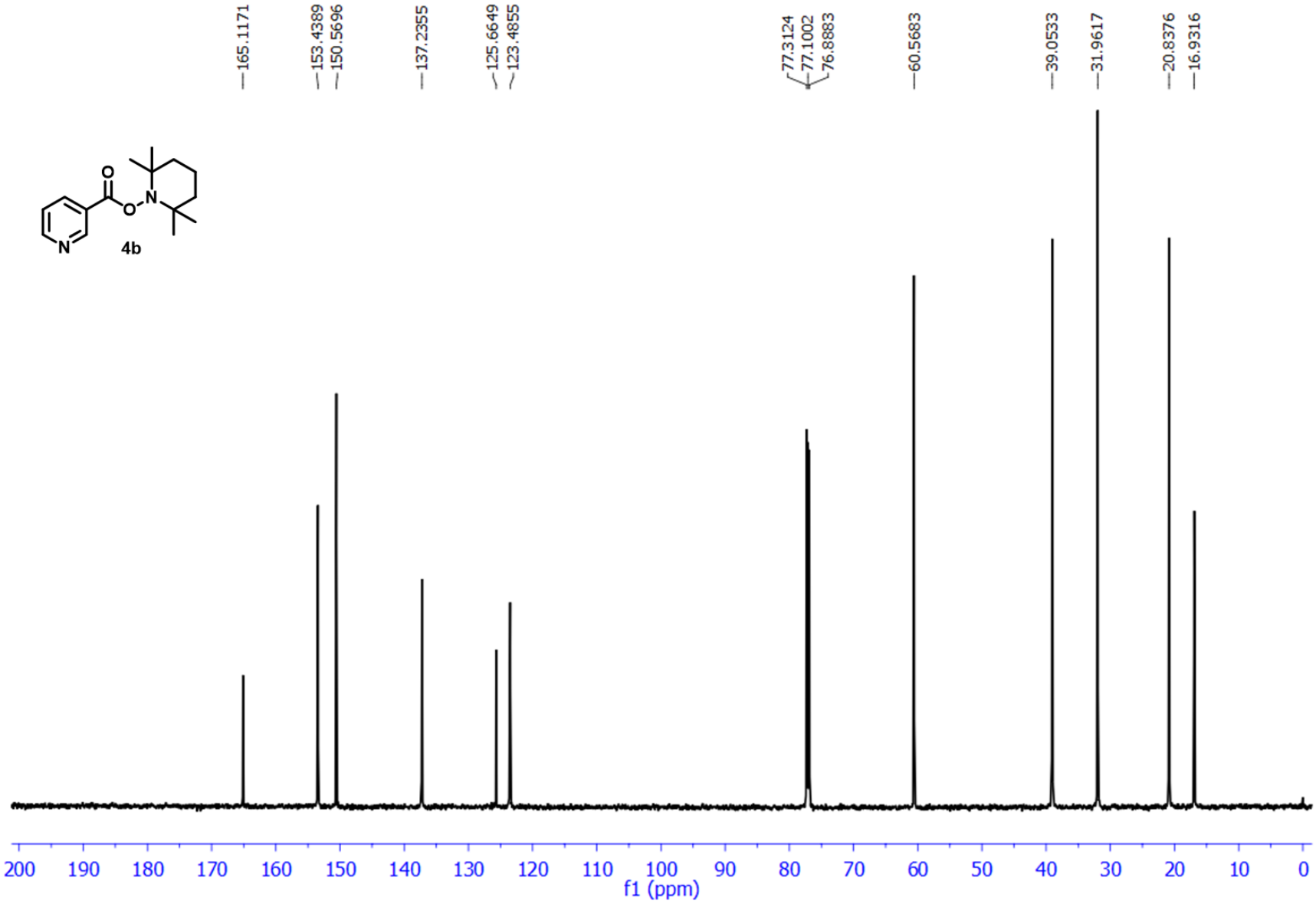
4a ^{13}C {1H} NMR (150 MHz, $CDCl_3$)



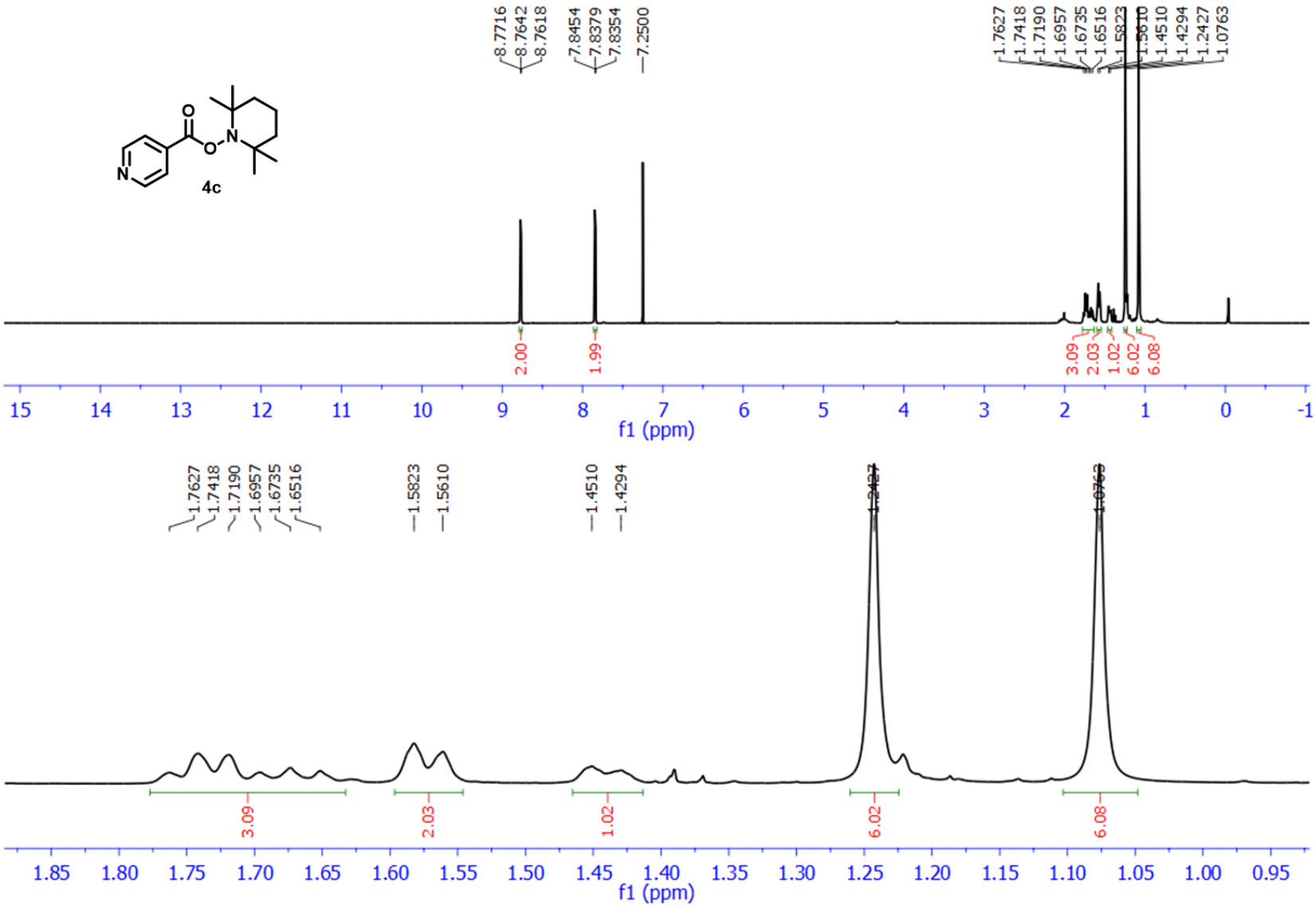
4b ^{1}H NMR (600 MHz, $CDCl_3$)



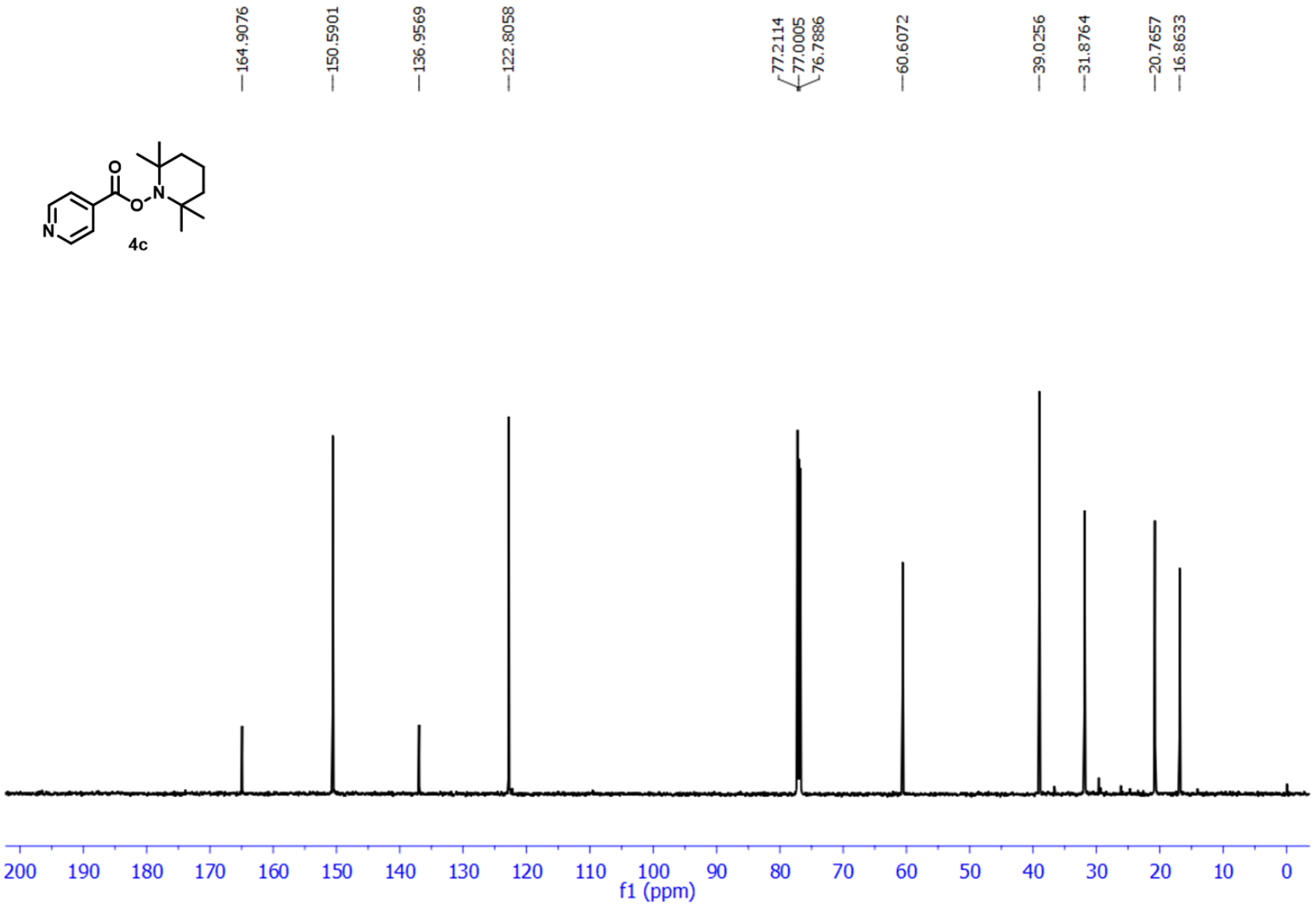
4b ^{13}C {1H} NMR (150 MHz, $CDCl_3$)



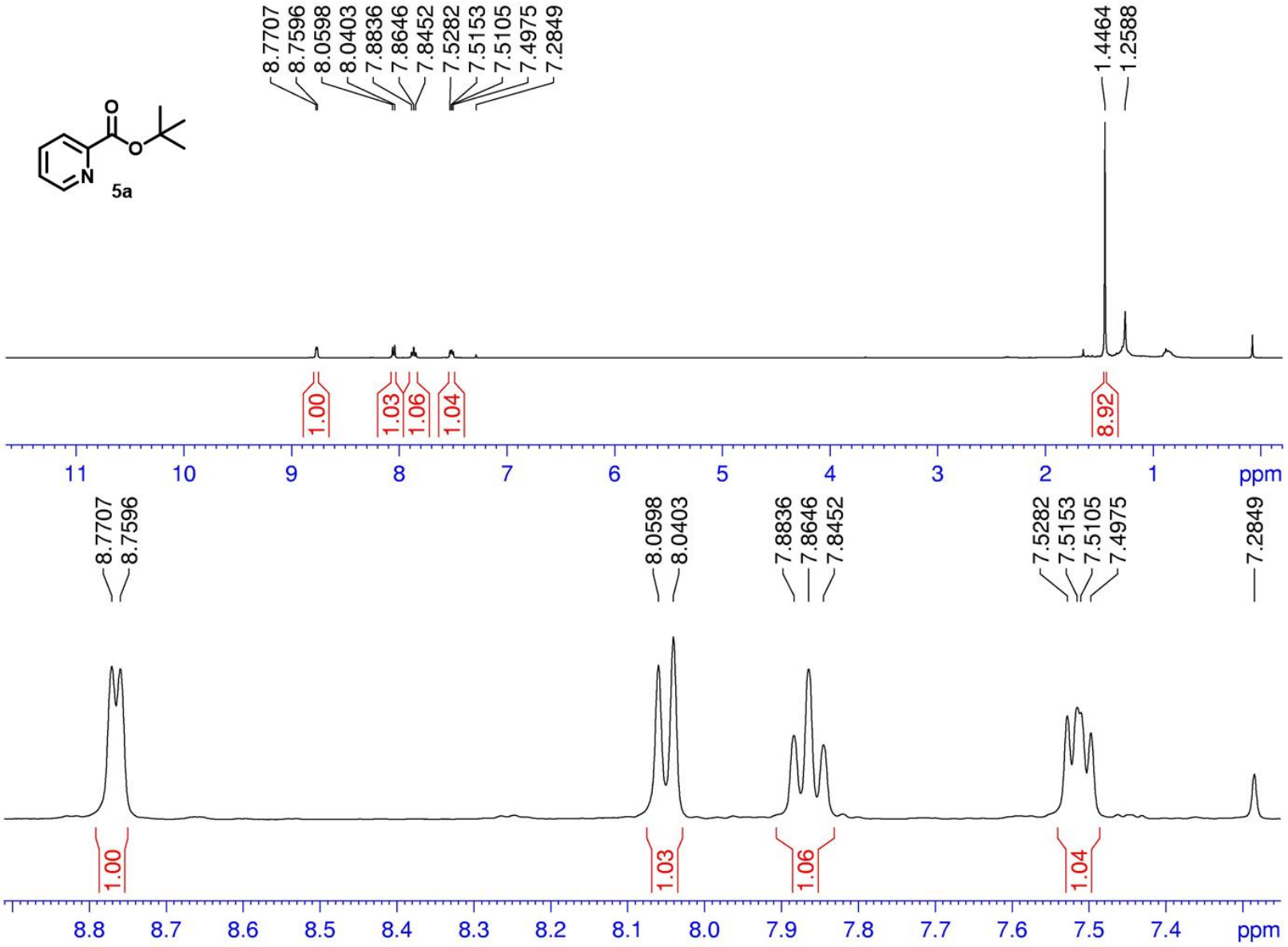
4c ^{1}H NMR (600 MHz, $CDCl_3$)



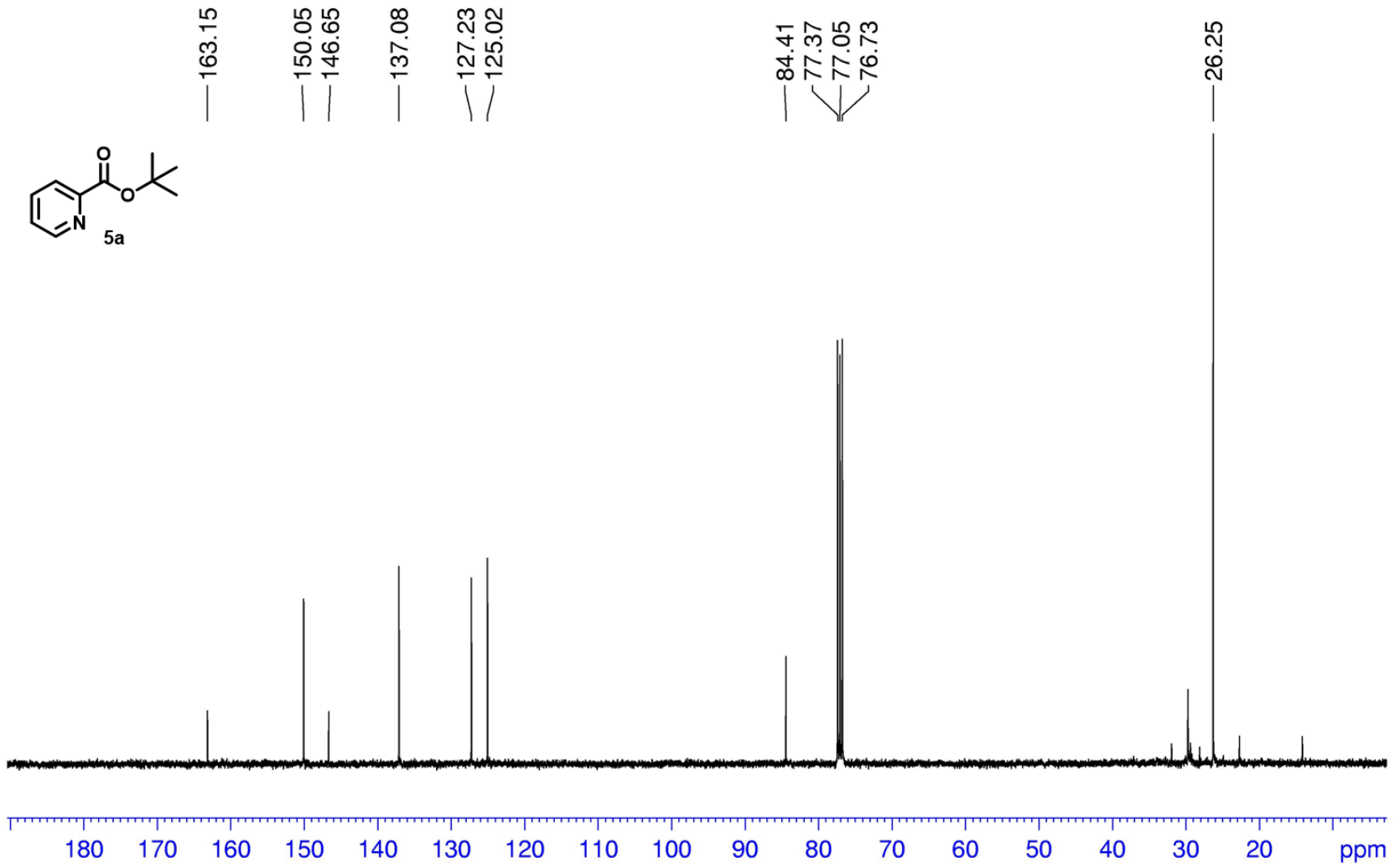
4c ^{13}C {1H} NMR (150 MHz, $CDCl_3$)



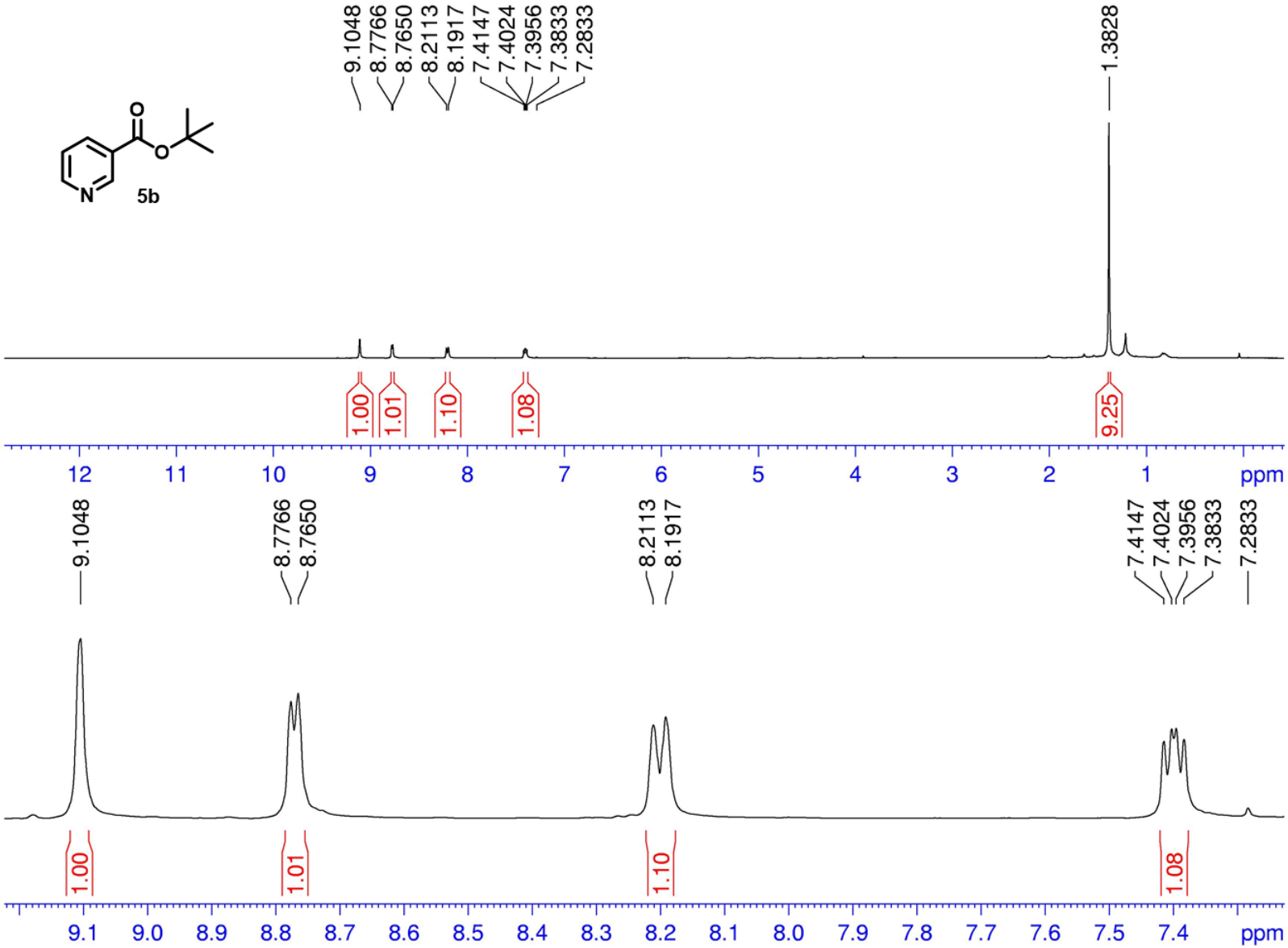
5a ^{1}H NMR (400 MHz, $CDCl_3$)



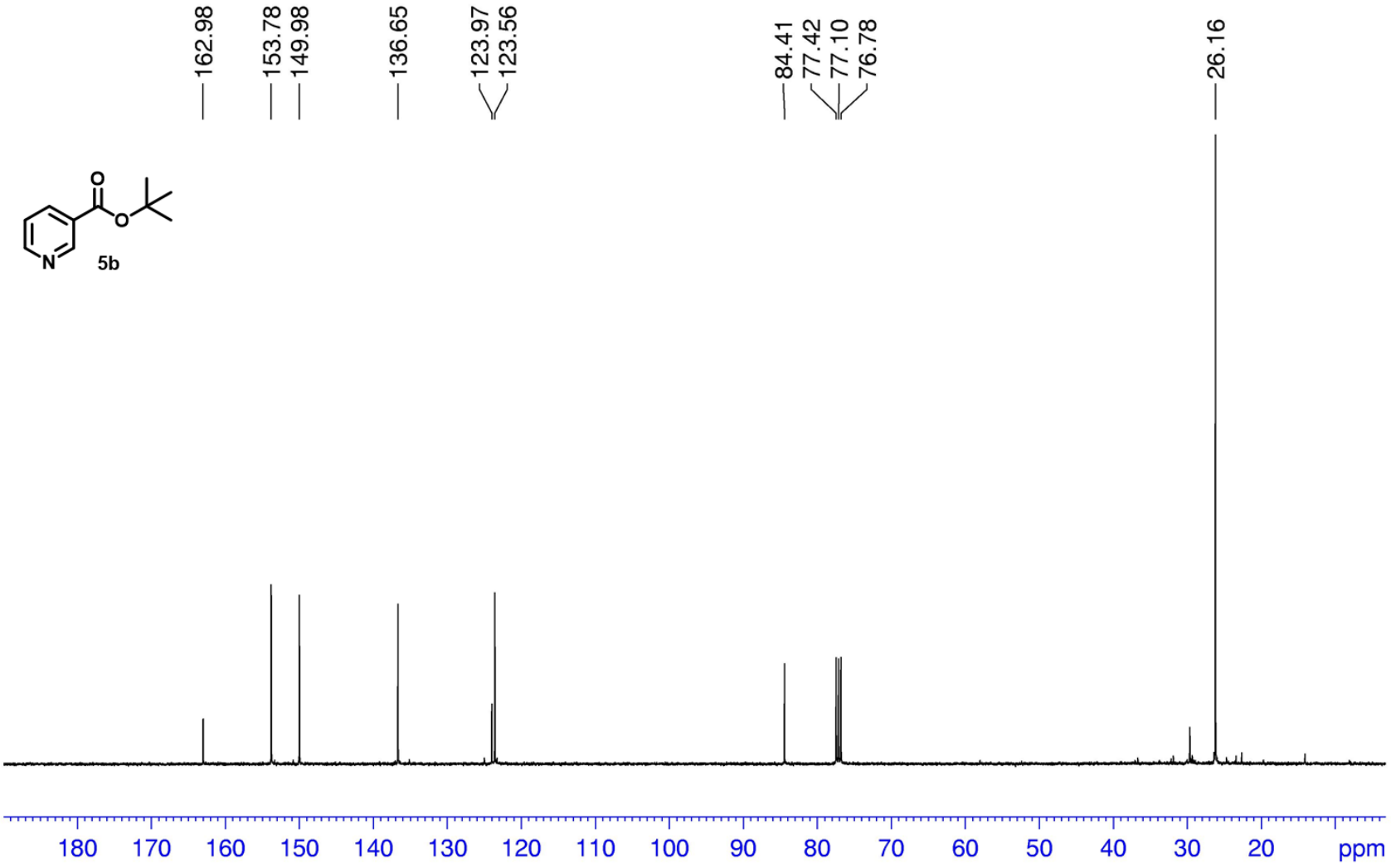
5a ^{13}C {1H} NMR (100 MHz, $CDCl_3$)



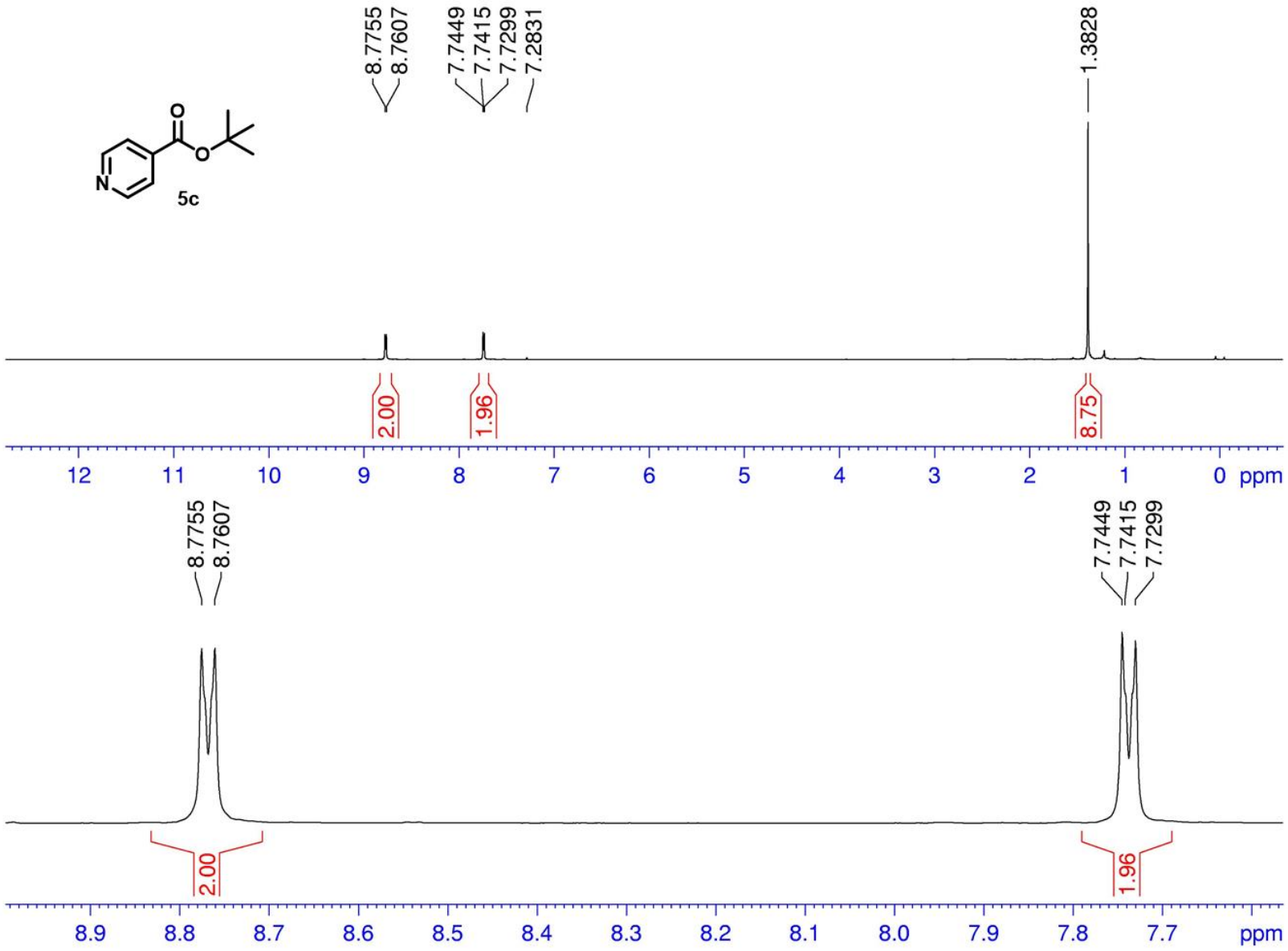
5b ^{1}H NMR (400 MHz, $CDCl_3$)



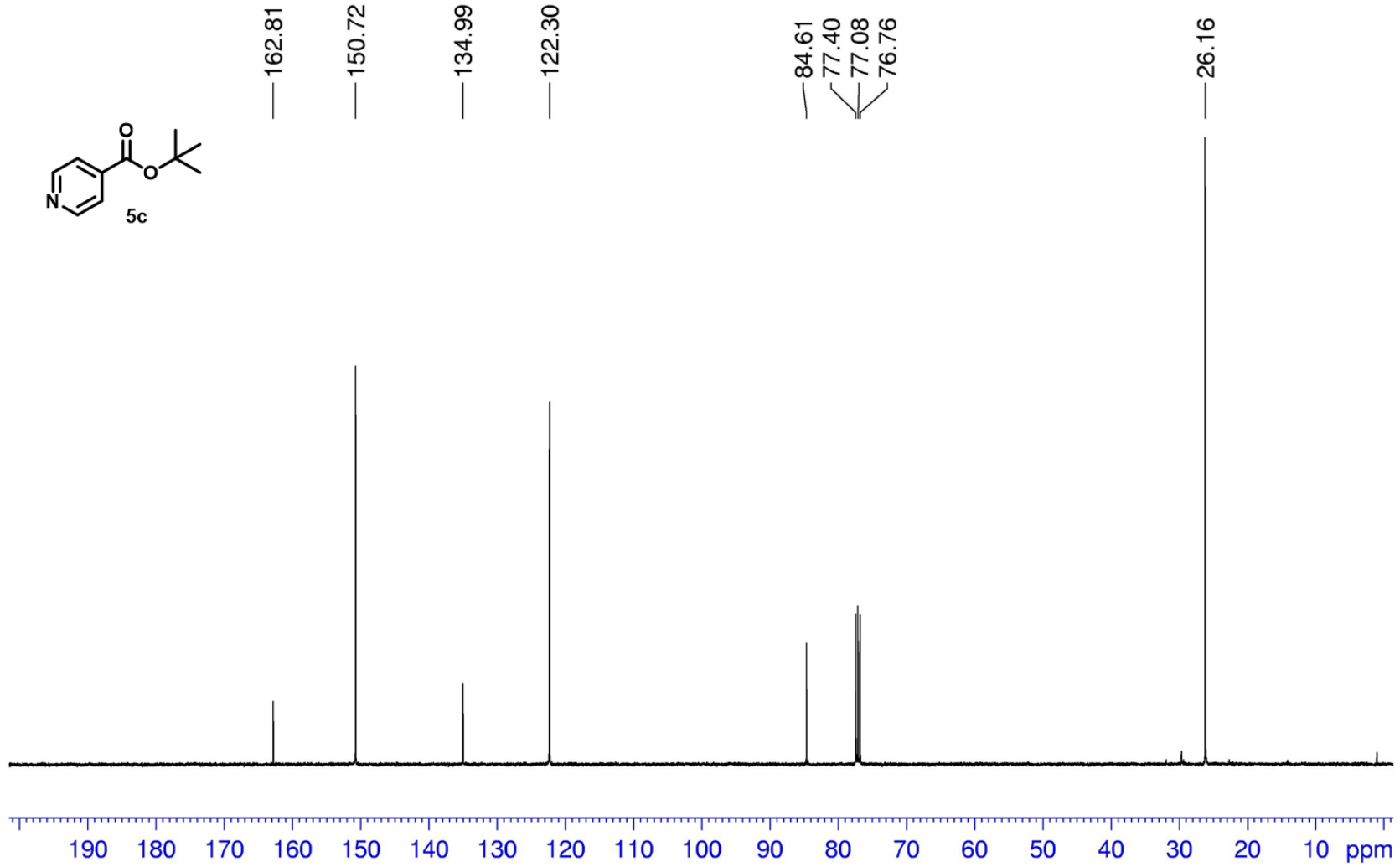
5b ^{13}C {1H} NMR (100 MHz, $CDCl_3$)



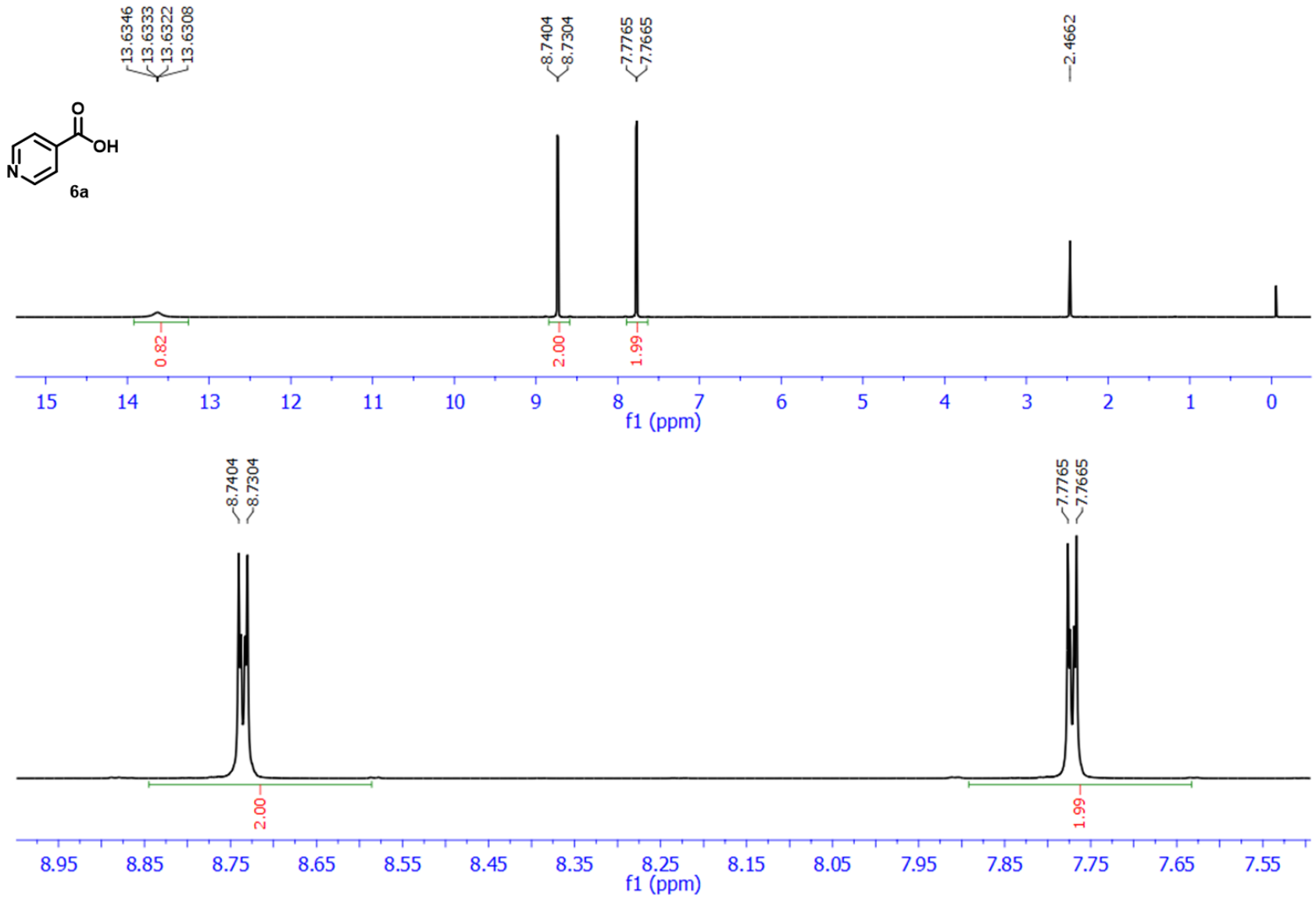
5c ^{1}H NMR (400 MHz, $CDCl_3$)



5c ^{13}C {1H} NMR (100 MHz, $CDCl_3$)



6a ^{1}H NMR (600 MHz, DMSO-d_6)



6a ^{13}C {1H} NMR (150 MHz, DMSO-d_6)