Supporting Information

CO_2-Tuned highly selective reduction of formamides to the corresponding methylamines

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General Information

All solvents were dried and distilled before use according to the standard methods. The chemicals were purchased from commercial sources (purity > 97%) and used as received unless otherwise indicated. The N-methylformanilides were prepared according to the literature procedures.[1] Carbon dioxide (99.999%) was used as received without further purification. Flash chromatography columns were packed with 200-300 mesh neutral alumina in petroleum (bp. 60-90 ^{o}C) and ethyl acetate. ^{1}H NMR (600 MHz), ^{13}C NMR (150.9 MHz) data were recorded on a BRUKER AVANCE III 600MHz instrument at 298 K with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.16 ppm, chloroform), respectively.

General procedure for hydrogenation of N-methylformanilide to N, N-dimethylaniline

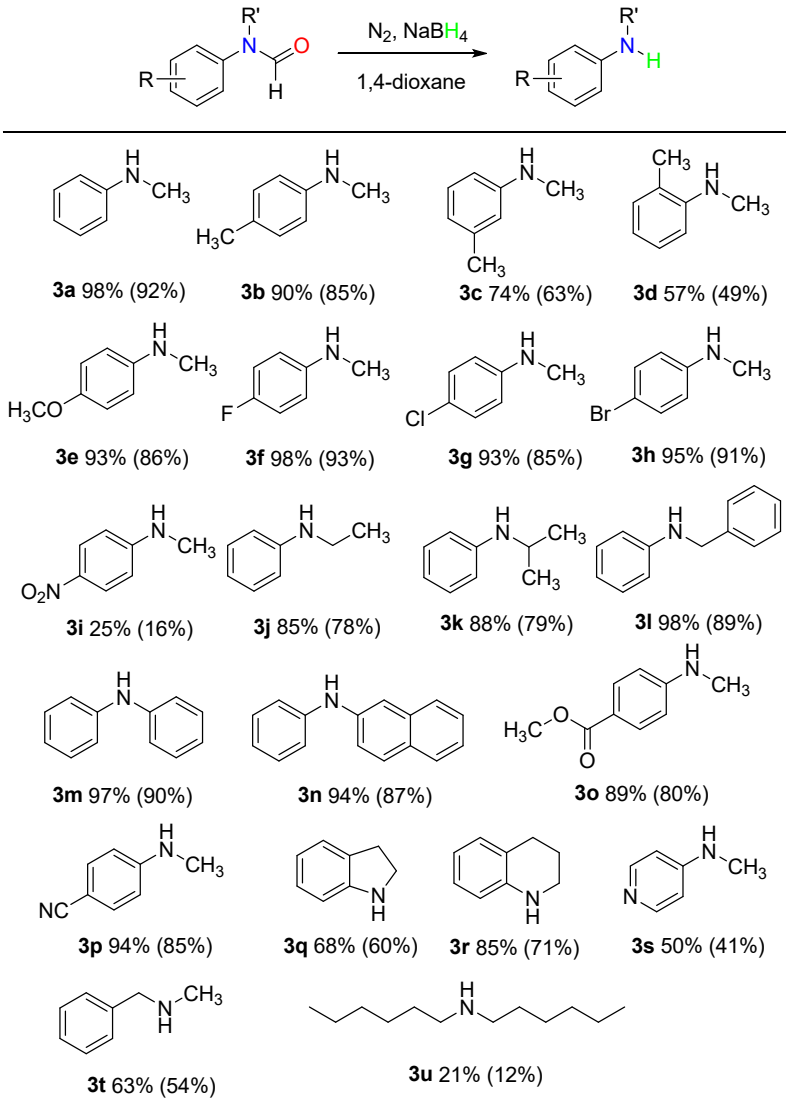
To a 25 mL sealed tube equipped with a magnetic stir bar was added $NaBH_4$ (56.7 mg, 1.5 mmol), this tube was evacuated and backfilled with CO_2 three times. Then, N-methylformanilide (67.6 mg, 0.5 mmol), 1.0 mL of 1,4-dioxane were added under the CO_2 atmosphere, and the reaction tube was sealed and stirred for 24 h at 100 °C. The reaction was carefully quenched with saturated ammonium chloride solution (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The yields were determined by using the ^{1}H NMR technique using trichloroethylene (45 μL, 0.5 mmol) as an internal standard. The crude product was purified by silica gel flash chromatography (petroleum ether/ EtOAc: 5/1). All of the products were characterized by NMR techniques.

General procedure for hydrogenation of N-methylformanilide to N-methylaniline

To a 25 mL sealed tube equipped with a magnetic stir bar was added $NaBH_4$ (56.7 mg, 1.5 mmol), this tube was evacuated and backfilled with N_2 three times. Then, N-

methylformanilide (67.6 mg, 0.5 mmol), 1.0 mL of 1,4-dioxane were added under the N_2 atmosphere, the reaction tube was sealed and stirred at 100 °C for 24 h. After completion, the reaction was carefully quenched with saturated ammonium chloride solution (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The yields were determined by using the ^1H NMR technique using trichloroethylene (45 μL, 0.5 mmol) as an internal standard. The crude product was purified by silica gel flash chromatography (petroleum ether/ EtOAc: 5/1). All of the products were characterized by NMR techniques.

Scheme S1 Substrate scope for C-N hydrogenolysis of formanilides



[a]Reaction conditions: formanilide (0.5 mmol), 1,4-dioxane (2 mL), $NaBH_4$ (1.5 mmol), 100 °C, 24 h,

the sealed tube was evacuated and backfilled with N_2three time. [b]Yield determinedby ^1H NMR spectroscopy using trichloroethylene as an internal standard. Values inparentheses refer to yields of isolatedproducts.

Isotope Labeling Experiments with $^{13}CO_2$

To a 25 mL sealed tube equipped with a magnetic stir bar was added $NaBH_4$ (56.7 mg, 1.5 mmol), this tube was evacuated and backfilled with $^{13}CO_2$ three times. Then, N-methylformanilide (67.6 mg, 0.5 mmol), 1.0 mL of 1, 4-dioxane were added at atmospheric pressure of $^{13}CO_2$ (1 atm), and the reaction tube was sealed and stirred for 24 h at 100 °C. The reaction was carefully quenched with saturated ammonium chloride solution (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product (**2a'**) was purified by silica gel flash chromatography (petroleum ether/ EtOAc: 5/1). The methyl signals of (**2a'**) were detected in the ^{13}C NMR spectrum at δ = 40.75 ppm, which is not significantly different from what did in general carbon dioxide (see Fig. S1). It indicates that the methyl group did not come from CO_2.

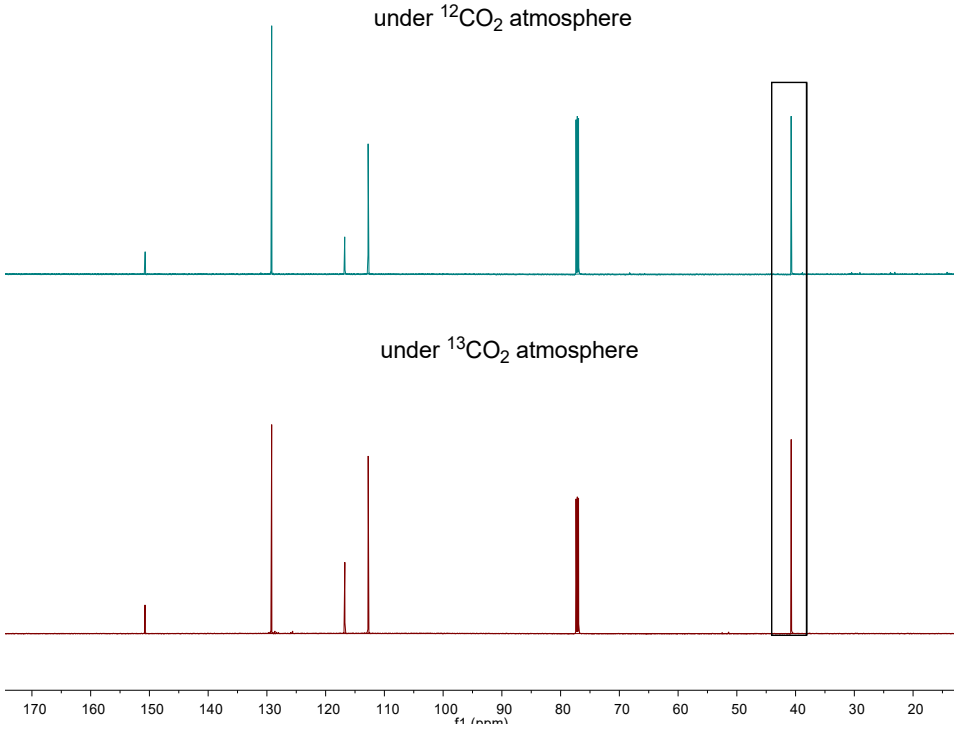


Fig. S1 ^{13}C NMR spectrum of **2a'**

Isotope Labeling Experiments with $NaBD_4$

To a 25 mL sealed tube equipped with a magnetic stir bar was added $NaBD_4$ (56.7 mg, 1.5 mmol), this tube was evacuated and backfilled with CO_2 three times. Then, N-methylformanilide (67.6 mg, 0.5 mmol), 1.0 mL of 1,4-dioxane were added under the CO_2 atmosphere, and the reaction tube was sealed and stirred for 24 h at 100 °C. The reaction was carefully quenched with saturated ammonium chloride solution (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product (**2a''**) was purified by silica gel flash chromatography (petroleum ether/ EtOAc: 5/1).

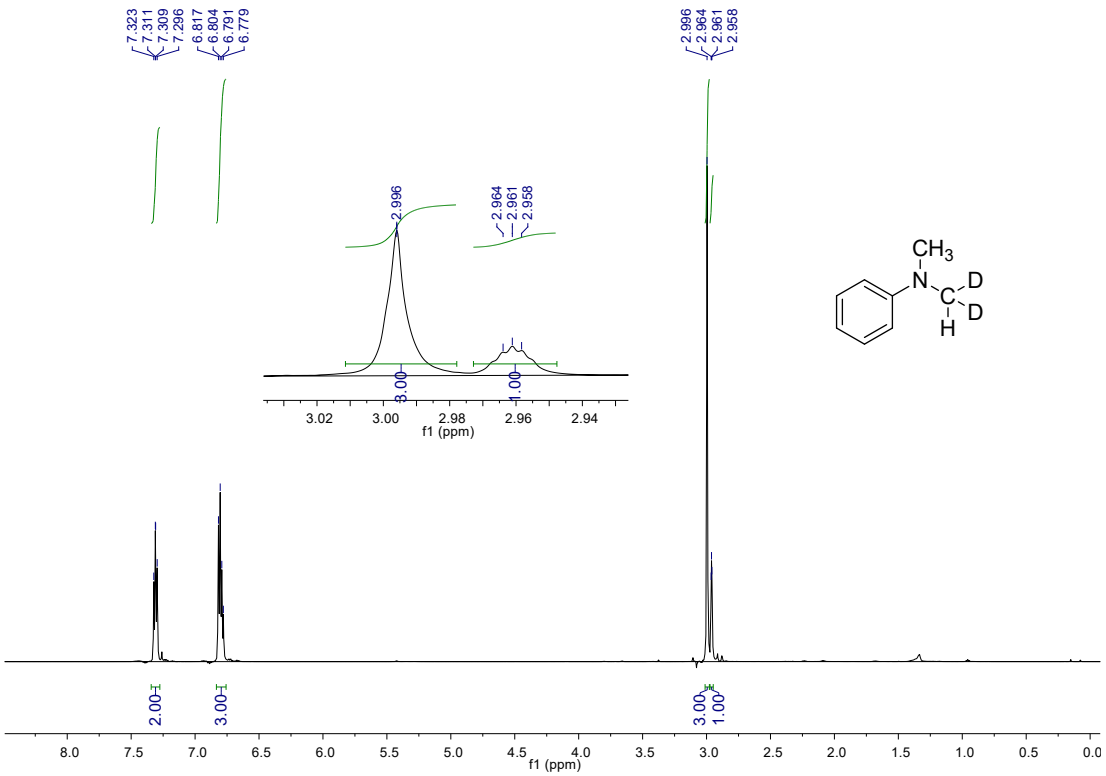


Fig. S2 ^{1}H NMR spectrum of **2a''**

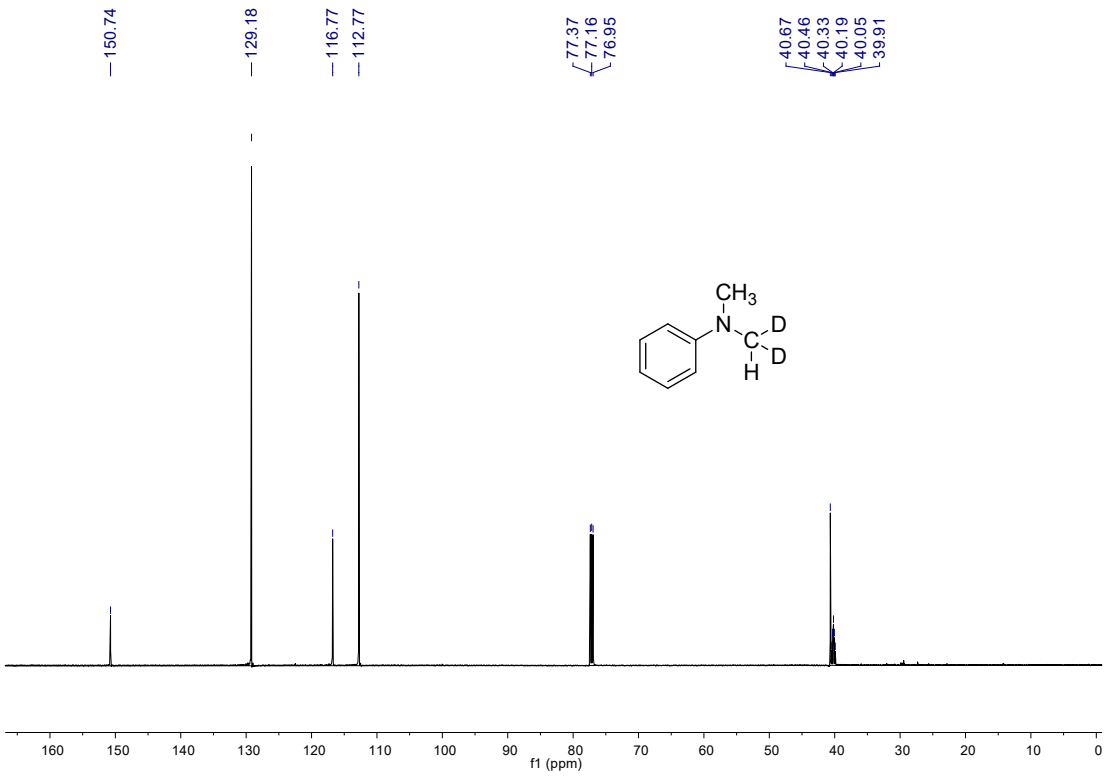


Fig. S3 ^{13}C NMR spectrum of **2a''**

Experiments under the mixed CO_2/N_2 atmosphere

To a 25 mL sealed tube equipped with a magnetic stir bar was added $NaBH_4$ (56.7 mg, 1.5 mmol), this tube was evacuated and backfilled with CO_2-N_2 three times. Then, N-methylformanilide (67.6 mg, 0.5 mmol), 1.0 mL of 1,4-dioxane were added under the CO_2-N_2 atmosphere, and the reaction tube was sealed and stirred for 24 h at 100 °C. The reaction was carefully quenched with saturated ammonium chloride solution (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was determined by using the ^1H NMR technique using trichloroethylene (45 μL, 0.5 mmol) as an internal standard. (See Fig. S4).

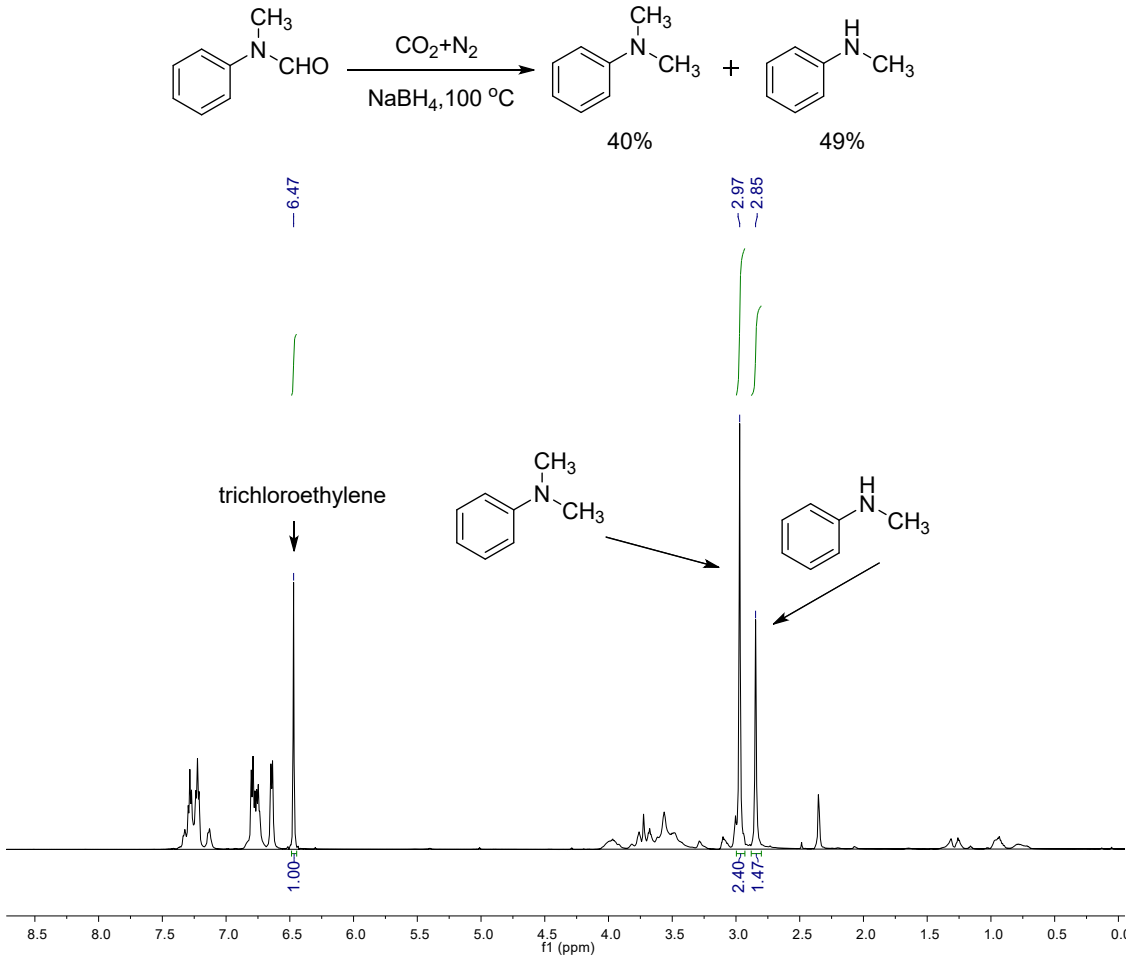


Fig. S4 ^{1}H NMR spectrum of the reaction mixture after reaction under the mixed CO_2 and N_2 atmosphere for determined the yields

Control experiment

To a 25 mL sealed tube equipped with a magnetic stir bar was added $NaBH_4$ (56.7 mg, 1.5 mmol), this tube was evacuated and backfilled with CO_2 three times. 1.0 mL of 1,4-dioxane were added, the reaction tube was sealed and stirred at 100 °C for 24 h, the reaction mixture was allowed to room temperature. Then CO_2 was replaced with N_2 atmosphere and N-methylformanilide (67.6 mg, 0.5 mmol) was added, and the reaction tube was sealed again and stirred for 24 h at 100 °C. The reaction was carefully quenched with saturated ammonium chloride solution (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The yields were determined by using the ^{1}H NMR technique using trichloroethylene (45 μL, 0.5 mmol) as an internal standard (See

Fig. S5).

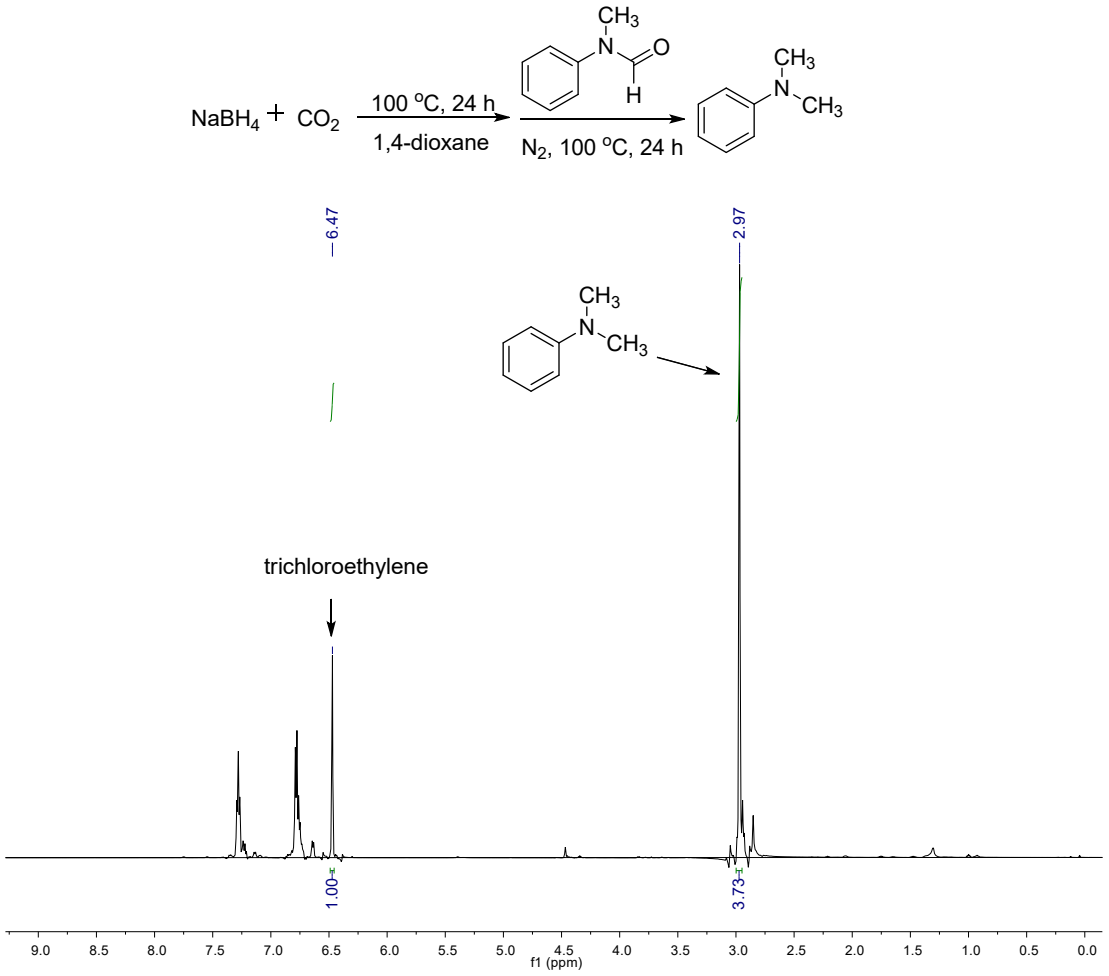


Fig. S5 ^{1}H NMR spectrum of the reaction mixture after reaction for determined the yields

The reaction of N-methylformanilide with $NaBH(OAc)_3$ under N_2 atmosphere

To a 25 mL sealed tube equipped with a magnetic stir bar was added $NaHB(OAc)_3$ (56.7 mg, 1.5 mmol), this tube was evacuated and backfilled with CO_2 three times. 2.0 mL of 1,4-dioxane, N-methylformanilide (67.6 mg, 0.5 mmol) were added, and the reaction tube was sealed and stirred for 24 h at 100 °C. The reaction was carefully quenched with saturated ammonium chloride solution (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The yields were determined by using the ^1H NMR technique using trichloroethylene (45 μL, 0.5 mmol) as an internal standard (See Fig. S6).

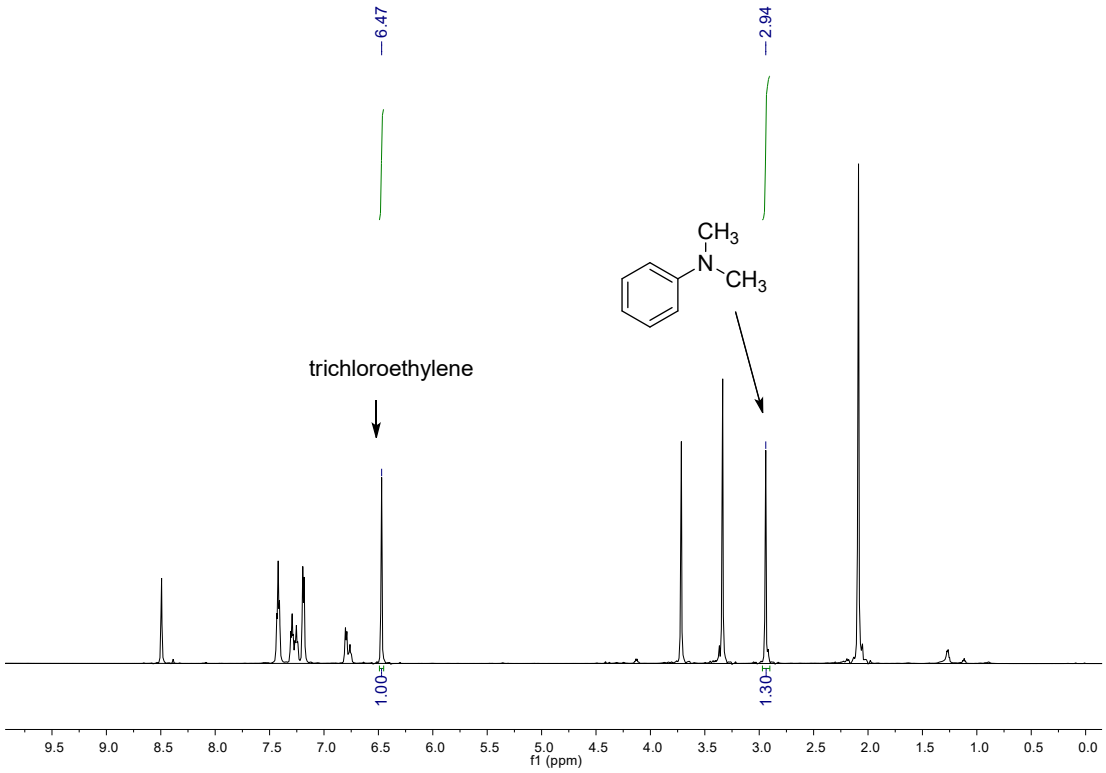
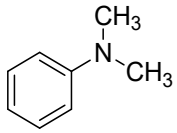


Fig. S6 ^1H NMR spectrum of the reaction mixture after reaction for determined the yields

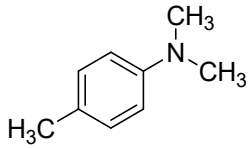
Characterization data of methylamines

(All products were identified through comparisons with the corresponding ^{1}H NMR, ^{13}C NMR data reported in the literatures.)



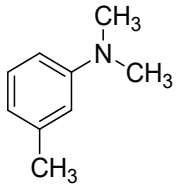
N, N-Dimethylaniline (2a)[15]

Colorless oil, yield: 84%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.7 Hz, 2H), 6.76 (dd, *J* = 17.4, 7.9 Hz, 3H), 2.97 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.72 (s), 129.18 (s), 116.75 (s), 112.77 (s), 40.75 (s).



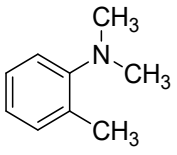
N, N-Dimethyl-p-toluidine (2b)[15]

Colorless oil, yield: 66%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 7.9 Hz, 2H), 2.92 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.88 (s), 129.72 (s), 126.34 (s), 113.40 (s), 41.26 (s), 20.39 (s).



N, N-Dimethyl-m-toluidine (2c)[15]

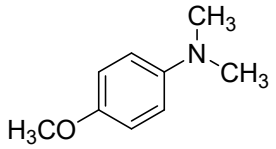
Colorless liquid, yield: 54%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 9.0 Hz, 3H), 2.94 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.81 (s), 138.88 (s), 129.07 (s), 117.87 (s), 113.66 (s), 110.11 (s), 40.90 (s), 22.04 (s).



N, N-Dimethyl-o-toluidine (2d)[15]

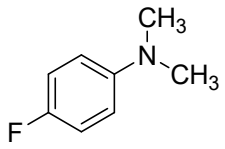
Colorless liquid, yield: 39%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 6.9 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.1 Hz, 1H), 2.74 (s, 6H), 2.37 (s, 3H). ^{13}C NMR

(151 MHz, $CDCl_3$) δ 152.77 (s), 132.20 (s), 131.27 (s), 126.55 (s), 122.69 (s), 118.44 (s), 44.35 (s), 18.50 (s).



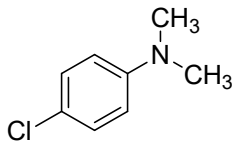
4-Methoxy-N, N-dimethylaniline (2e)[15]

White solid, yield: 89%, ^1H NMR (600 MHz, $CDCl_3$) δ 6.86 (d, J = 9.1 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H), 2.88 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.16 (s), 145.76 (s), 115.10 (s), 114.72 (s), 55.86 (s), 42.02 (s).



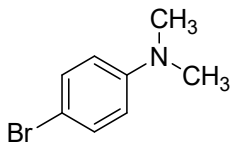
4-Fluoro-N, N-dimethylaniline (2f)[15]

White solid, yield: 85%, ^1H NMR (600 MHz, $CDCl_3$) δ 6.96 (t, J = 8.8 Hz, 2H), 6.72-6.67 (m, 2H), 2.91 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.50 (s), 154.94 (s), 147.61 (s), 115.57 (s), 115.43 (s), 114.07 (d, J = 7.3 Hz), 41.52 (s).



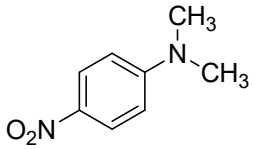
4-Chloro-N, N-dimethylaniline (2g)[15]

White solid, yield: 92%, ^1H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 8.9 Hz, 2H), 2.90 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.22 (s), 128.89 (s), 121.47 (s), 113.73 (s), 40.76 (s).



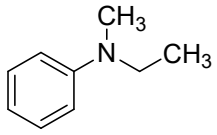
4-Bromo-N, N-dimethylaniline (2h)[15]

White solid, yield: 94%, ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, J = 8.7 Hz, 2H), 6.60 (d, J = 7.2 Hz, 2H), 2.93 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.57 (s), 131.77 (s), 114.19 (s), 108.57 (s), 40.68 (s).



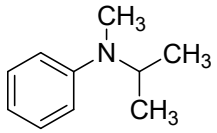
4-Nitro-N, N-dimethylaniline (2i)[15]

Yellow solid, yield: 33%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.11 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.32 (s), 137.02 (s), 126.26 (s), 110.33 (s), 40.41 (s).



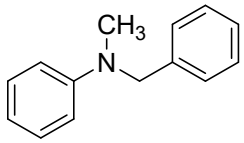
N-Ethyl-N-methylaniline (2j)[15]

Colorless liquid, yield: 88%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 3.39 (q, *J* = 7.1 Hz, 2H), 2.89 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.17 (s), 129.29 (s), 116.19 (s), 112.54 (s), 46.95 (s), 37.59 (s), 11.29 (s).



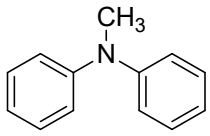
N-Isopropyl-N-methylaniline (2k)[15]

Colorless liquid, yield: 77%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 4.15 (dt, *J* = 13.2, 6.6 Hz, 1H), 2.78 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.30 (s), 129.23 (s), 116.49 (s), 113.40 (s), 48.99 (s), 29.87 (s), 19.43 (s).



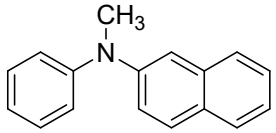
N-Benzyl-N-methylaniline (2l)[15]

Colorless oil, yield: 71%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 5H), 6.91 – 6.82 (m, 3H), 4.65 (s, 2H), 3.13 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.78 (s), 139.09 (s), 129.27 (s), 128.64 (s), 126.94 (s), 126.80 (s), 116.61 (s), 112.41 (s), 56.67 (s), 38.58 (s).



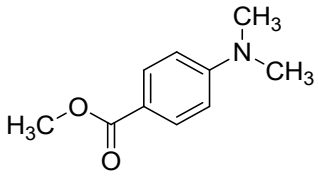
N-Methyl-N-phenylaniline (2m)[15]

Colorless oil, yield: 89%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.1 Hz, 4H), 7.07 (d, *J* = 7.7 Hz, 4H), 7.00 (t, *J* = 7.3 Hz, 2H), 3.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.10 (s), 129.31 (s), 121.38 (s), 120.55 (s), 40.37 (s).



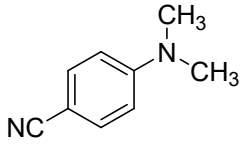
N-Methyl-N-phenylnaphthalen-2-amine (2n)[15]

Colorless oil, yield: 85%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 13.7, 8.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.41-7.35 (m, 4H), 7.28 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.09 (s), 146.61 (s), 134.77 (s), 129.42 (s), 129.25 (s), 128.71 (s), 127.66 (s), 126.86 (s), 126.39 (s), 123.88 (s), 122.15 (s), 121.88 (s), 121.52 (s), 114.73 (s), 40.78 (s).



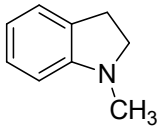
Methyl 4-dimethylaminobenzoate (2o)[15]

White solid, yield: 91%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H), 3.01 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.55 (s), 153.30 (s), 131.28 (s), 116.91 (s), 110.70 (s), 51.53 (s), 40.08 (s).



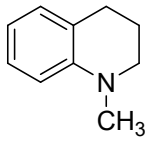
4-(N, N-Dimethylamino)benzonitrile (2p)[15]

White solid, yield: 82%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.51 (s), 133.47 (s), 120.87 (s), 111.48 (s), 97.34 (s), 40.04 (s).



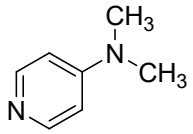
1-methylindoline (2q)[15]

Colorless oil, yield: 87%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (s, 2H), 6.71 (t, *J* = 7.0 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 3.31 (t, *J* = 8.0 Hz, 2H), 2.97 (t, *J* = 7.9 Hz, 2H), 2.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.39 (s), 130.47 (s), 127.44 (s), 124.40 (s), 118.02 (s), 107.47 (s), 56.29 (s), 36.48 (s), 28.85 (s).



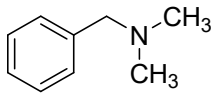
1-Methyl-1,2,3,4-tetrahydroquinoline (2r)[15]

Colorless oil, yield: 83%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 4.1 Hz, 1H), 7.01 (s, 1H), 6.66 (s, 2H), 3.27 (d, *J* = 3.3 Hz, 2H), 2.93 (s, 3H), 2.82 (d, *J* = 4.1 Hz, 2H), 2.04 (d, *J* = 4.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.84 (s), 128.92 (s), 127.14 (s), 122.94 (s), 116.29 (s), 111.05 (s), 51.37 (s), 39.23 (s), 27.89 (s), 22.55 (s).



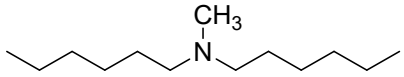
4-Dimethylaminopyridine (2s)[15]

White solid, yield: 52%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.9 Hz, 2H), 6.47 (d, *J* = 6.1 Hz, 2H), 3.08 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.69 (s), 146.88 (s), 106.47 (s), 39.59 (s).



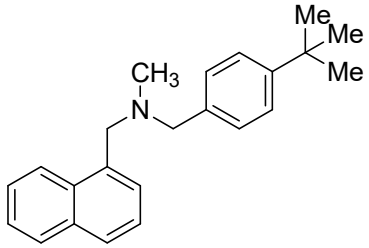
N, N-Dimethylbenzylamine (2t)[15]

Colorless oil, yield: 69%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 5.0 Hz, 3H), 7.32 (d, *J* = 5.0 Hz, 2H), 3.98 (s, 2H), 2.50 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.31 (s), 131.27 (s), 129.23 (s), 128.57 (s), 67.58 (s), 49.71 (s).



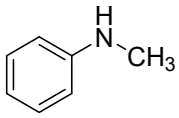
N-Methyldihexylamine (2u)[15]

Colorless oil, yield: 62%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.69 (tt, *J* = 20.6, 10.5 Hz, 4H), 2.50 (s, 3H), 1.69-1.57 (m, 5H), 1.27 (d, *J* = 31.0 Hz, 12H), 0.88 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 61.40 (s), 49.45 (s), 31.60 (s), 27.05 (s), 23.38 (s), 22.67 (s), 14.10 (s).



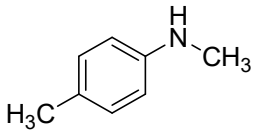
Butenafine

White solid, yield: 78%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.56-7.48 (m, 3H), 7.47-7.41 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.97 (s, 2H), 3.62 (s, 2H), 2.25 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.97 (s), 136.43 (s), 135.21 (s), 134.03 (s), 132.67 (s), 128.92 (s), 128.48 (s), 128.00 (s), 127.51 (s), 125.72 (d, *J* = 16.6 Hz), 125.20 (s), 125.03 (s), 77.37 (s), 77.16 (s), 76.95 (s), 62.18 (s), 60.57 (s), 42.52 (s), 34.59 (s), 31.56 (s).



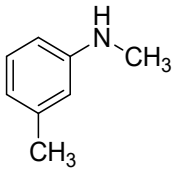
N-methylaniline (3a)[2]

Colorless oil, yield: 92%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.12 (m, 2H), 6.70 (t, *J* = 7.1 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 2H), 3.63 (s, 1H), 2.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.40 (s), 129.26 (s), 117.27 (s), 112.46 (s), 30.76 (s).



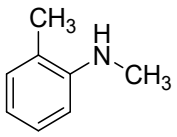
N-Methyl-p-toluidine (3b)[2]

Colorless oil, yield: 81%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.6 Hz, 2H), 6.57 (d, *J* = 7.7 Hz, 2H), 2.83 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.18 (s), 129.82 (s), 126.68 (s), 112.78 (s), 31.27 (s), 20.52 (s).



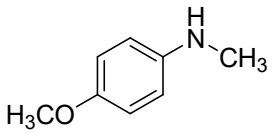
N-Methyl-m-toluidine (3c)[3]

Colorless oil, yield: 63%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (s, 1H), 6.59 (d, *J* = 6.2 Hz, 1H), 6.48 (s, 2H), 2.86 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.49 (s), 139.06 (s), 129.17 (s), 118.28 (s), 113.26 (s), 109.71 (s), 30.86 (s), 21.74 (s).



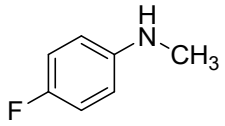
N-Methyl-o-toluidine (3d)[2]

Colorless oil, yield: 49%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, *J* = 6.9 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 1H), 6.72 (d, *J* = 7.1 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 2.93 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.32 (s), 130.00 (s), 127.29 (s), 122.01 (s), 116.93 (s), 109.20 (s), 30.88 (s), 17.52 (s).



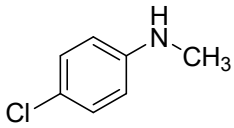
N-Methyl-p-anisidine (3e)[2]

White solid, yield: 86%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 3H), 2.81 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 152.19 (s), 143.80 (s), 115.00 (s), 113.79 (s), 55.98 (s), 31.77 (s).



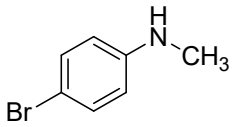
4-Fluoro-N-methylaniline (3f)[4]

Colorless oil, yield: 63%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 (t, *J* = 8.3 Hz, 2H), 6.55 (dd, *J* = 8.2, 3.9 Hz, 2H), 2.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.68 (s), 155.12 (s), 145.82 (s), 115.79 (s), 115.64 (s), 113.23 (d, *J* = 7.4 Hz), 31.45 (s).



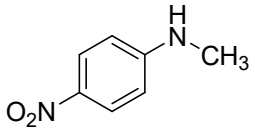
4-Chloro-N-methylaniline (3g) [2]

Colorless oil, yield: 63%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 8.6 Hz, 2H), 2.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.97 (s), 129.10 (s), 121.85 (s), 113.52 (s), 30.91 (s).



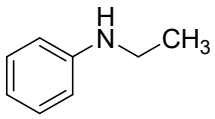
4-Bromo-N-methylaniline (3h)[5]

Colorless oil, yield: 63%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 8.7 Hz, 2H), 2.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.23 (s), 131.97 (s), 114.14 (s), 109.01 (s), 30.89 (s).



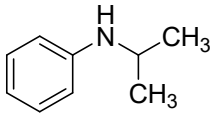
N-Methyl-4-nitroaniline (3i)[2]

Yellow solid, yield: 86%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.1 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 2.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.28 (s), 138.04 (s), 126.54 (s), 110.86 (s), 30.29 (s).



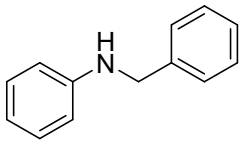
N-Ethylaniline (3j)[2]

Colorless oil, yield: 78%.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 6.5 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 3.18 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.55 (s), 129.33 (s), 117.30 (s), 112.84 (s), 38.55 (s), 15.00 (s).



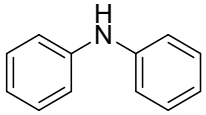
N-Isopropylaniline (3k)[6]

Colorless oil, yield: 79%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.7 Hz, 2H), 6.70 (d, *J* = 6.9 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 3.65 (dd, *J* = 12.4, 6.2 Hz, 1H), 3.46 (s, 1H), 1.23 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.62 (s), 129.39 (s), 117.04 (s), 113.32 (s), 44.29 (s), 23.14 (s).



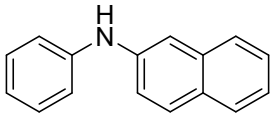
N-Benzylaniline (3l)[7]

White solid, yield: 89%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.32 (m, 4H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 4.34 (s, 2H), 4.04 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.26 (s), 139.54 (s), 129.40 (s), 128.77 (s), 127.65 (s), 127.37 (s), 117.68 (s), 112.95 (s), 48.43 (s).



Diphenylamine (3m)[8]

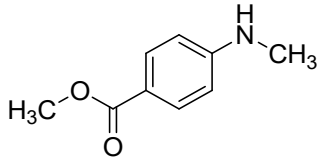
White solid, yield: 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (s, 4H), 7.10 (s, 4H), 6.95 (d, *J* = 5.7 Hz, 2H), 5.75 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.20 (s), 129.49 (s), 121.14 (s), 117.92 (s).



N-Phenyl-2-naphthylamine (3n)[9]

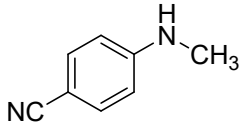
White solid, yield: 87%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.45 (s, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 (q, *J* = 7.6 Hz, 3H), 7.23 (d, *J*

= 8.7 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 5.90 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.57 (s), 129.31 (d, *J* = 4.6 Hz), 127.78 (s), 126.60 (d, *J* = 4.1 Hz), 123.63 (s), 121.54 (s), 120.17 (s), 118.38 (s), 111.66 (s).



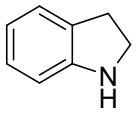
Methyl 4-(methylamino)benzoate (3o)[10]

White solid, yield: 80%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.19 (s, 1H), 3.85 (s, 3H), 2.88 (d, *J* = 4.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.54 (s), 153.00 (s), 131.65 (s), 118.31 (s), 111.21 (s), 51.69 (s), 30.29 (s).



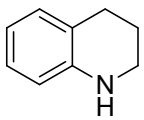
4-(Methylamino)benzonitrile (3p)[11]

White solid, yield: 85%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 2.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.23 (s), 133.79 (s), 120.69 (s), 111.98 (s), 98.71 (s), 30.14 (s).



Indoline (3q)[11]

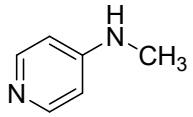
Colorless oil, yield: 60%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.05 (s, 1H), 6.74 (d, *J* = 4.3 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 3.76 (s, 1H), 3.56 (t, *J* = 8.3 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.67 (s), 129.40 (s), 127.28 (s), 124.70 (s), 118.71 (s), 109.52 (s), 47.41 (s), 29.90 (s).



1,2,3,4-Tetrahydroquinoline (3r)[12]

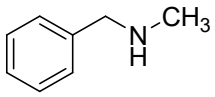
Colorless oil, yield: 71%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 13.7, 7.3 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 3.84 (s, 1H), 3.36-3.30 (m, 2H), 2.81

(t, *J* = 6.3 Hz, 2H), 2.02-1.96 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.84 (s), 129.58 (s), 126.78 (s), 121.48 (s), 116.97 (s), 114.25 (s), 42.03 (s), 27.03 (s), 22.23 (s).



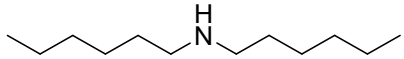
4-(Methylamino)pyridine (3s)[2]

White solid, yield: 41%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 5.3 Hz, 2H), 6.43 (d, *J* = 5.4 Hz, 2H), 4.26 (s, 1H), 2.85 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.33 (s), 150.04 (s), 107.35 (s), 29.53 (s).



N-methyl-1-phenylmethanamine (3t)[13]

Colorless oil, yield: 54%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.29 (m, 4H), 7.28-7.24 (m, 1H), 3.75 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.29 (s), 128.49 (s), 128.28 (s), 127.06 (s), 56.22 (s), 36.18 (s).



Di-n-hexylamine (3u)[14]

Colorless oil, yield: 12%. ^{1}H NMR (600 MHz, CDCl3) δ 2.56 (t, *J* = 7.3 Hz, 4H), 1.49-1.37 (m, 4H), 1.27 (s, 12H), 0.86 (d, J = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 50.33 (s), 31.94 (s), 30.31 (s), 27.25 (s), 22.76 (s), 14.19 (s).

References

[1] T. Leischner, L. Artús Suarez, A. Spannenberg, K. Junge, A. Nova and M. Beller, *Chem. Sci.*, 2019, **10**, 10566-10576.

[2] J. Jiao, X-R. Zhang, N-H. Chang, J. Wang, J-F.Wei, X-Y. Shi, Z-G. Chen, *J. Org. Chem.* **2011**, 76, 1180-1183.

[3] I.l Gonza´lez, J. Mosquera, C. Guerrero, R. Rodrı´guez, and J. Cruces. *Org. Lett.,* **2009**, 11(8), 1677-1680.

[4] N. Sun, S. Wang, W. Mo, B. Hu, Z. Shen, X. Hu. *Tetrahedron*, **2010**, 66, 7142-7148.

[5] M. Verma, K.N. Singh, E. D. Clercq, *Heterocycles*, **2006**, 68(1), 11-22.

[6] K. Shimizu, K. Ohshima, Y. Tai, M. Tamurab and A. Satsuma. *Catal. Sci. Technol.,* **2012**, 2, 730-738.

[7] D.B. Bagal, R.A. Watile, M.V. Khedkar, K.P. Dhake and B.M. Bhanage, *Catal. Sci. Technol.*, **2012**, 2, 354-358.

[8] Z. Garkani-Nejad and M. Poshteh-Shirani, *Can. J. Chem.*, **2011**, 89, 598-607.

[9] C. Cazorla, E. Pfordt, M. Duclos, E. Me′tay and M. Lemaire, *Green Chem.*, **2011**, 13, 2482-2488.

[10] A. L. Pera, A. Leggio and A.Liguori, *Tetrahedron*, **2006**, 62, 6100-6106.

[11] A. Kulkarni, W. Zhou, and B. Torok. *Org. Lett.*, **2011**, 13(19), 5124-5127.

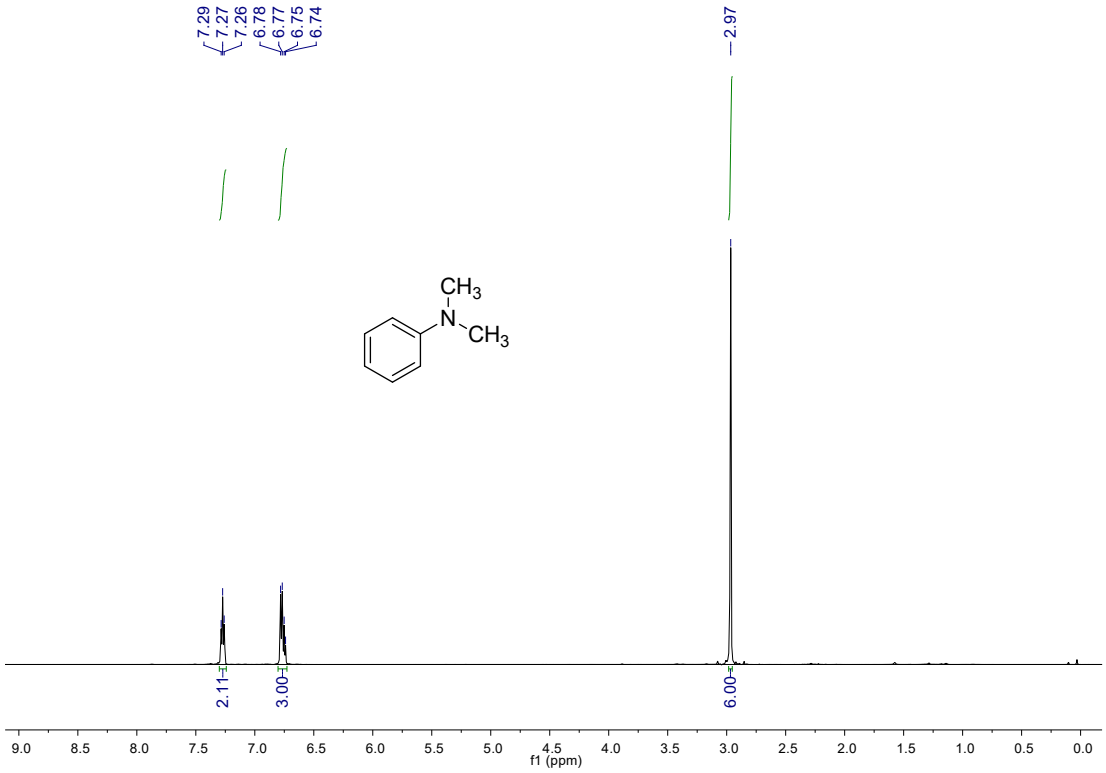
[12] F. Nador, Y. Moglie, C. Vitale, M. Yus, F. Alonso, G. Radivoy. *Tetrahedron*, **2010**, 66, 4318-4325.

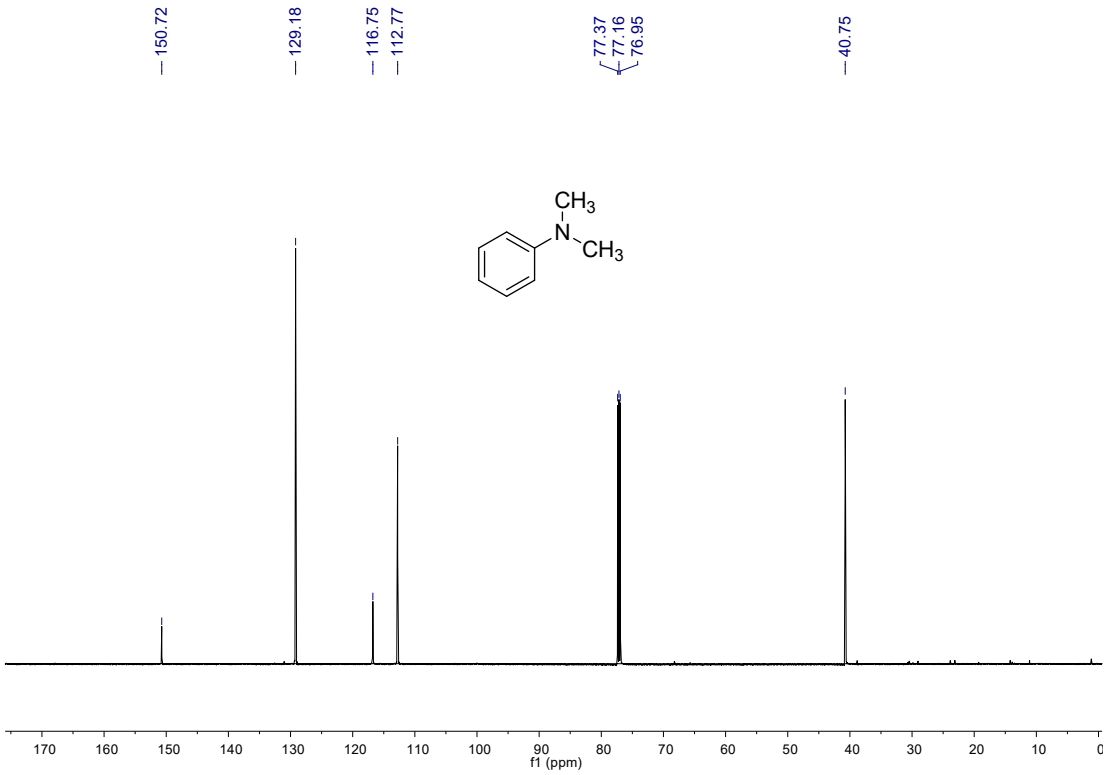
[13] B. Cho and S. Kang, Tetrahedron, **2005**, 61, 5725-5734.

[14] R. Yamaguchi, M. Zhu, S. Kawagoe, K. Fujita. *Synthesis*, **2009**, 7, 1220-1223.

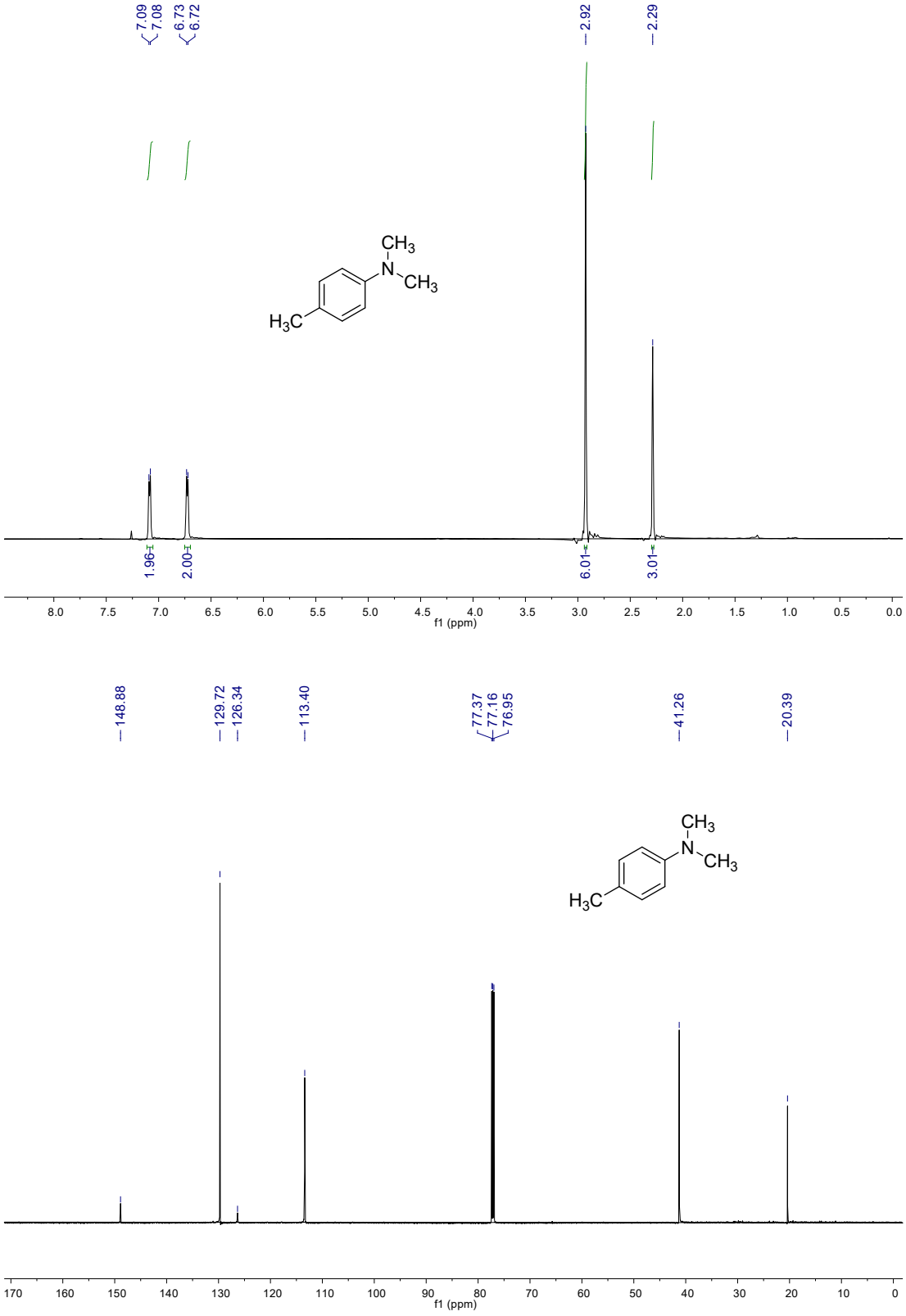
[15] Z. Guo, B. Zhang, X. Wei and C. Xi, *ChemSusChem*, **2018**, 11, 2296-2299.

^{1}H and ^{13}C NMR Spectra of Methylamines





^{1}H and ^{13}C NMR Spectra of **2a**



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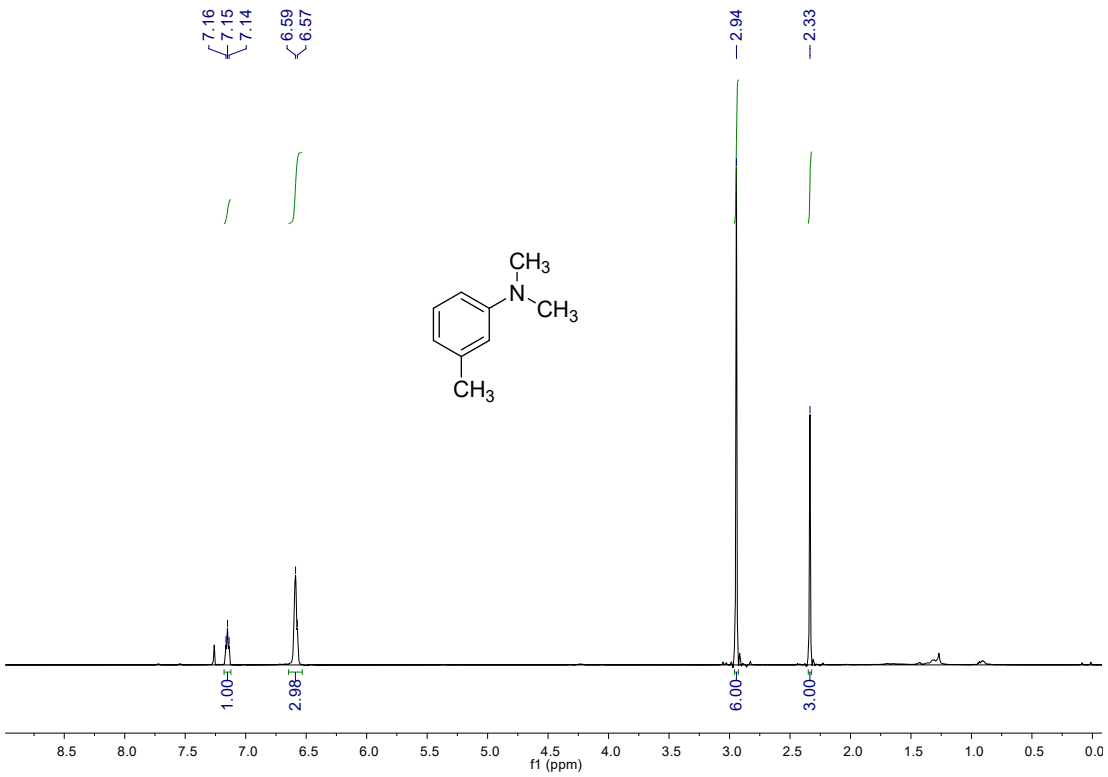
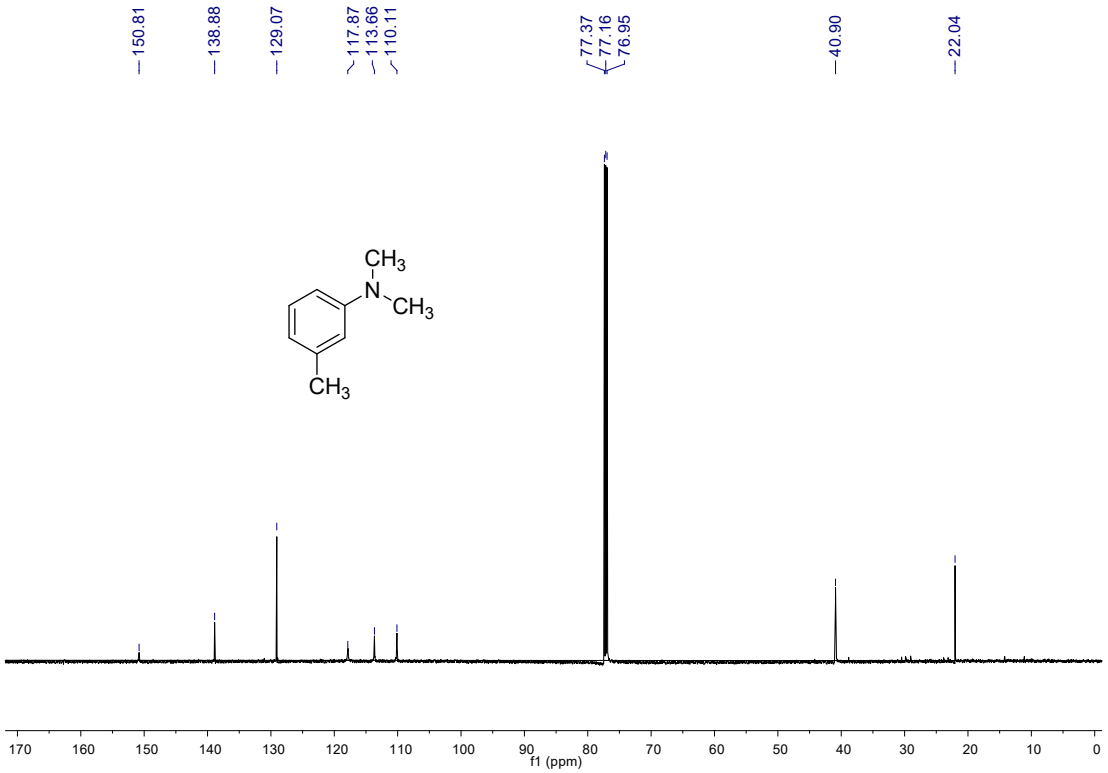
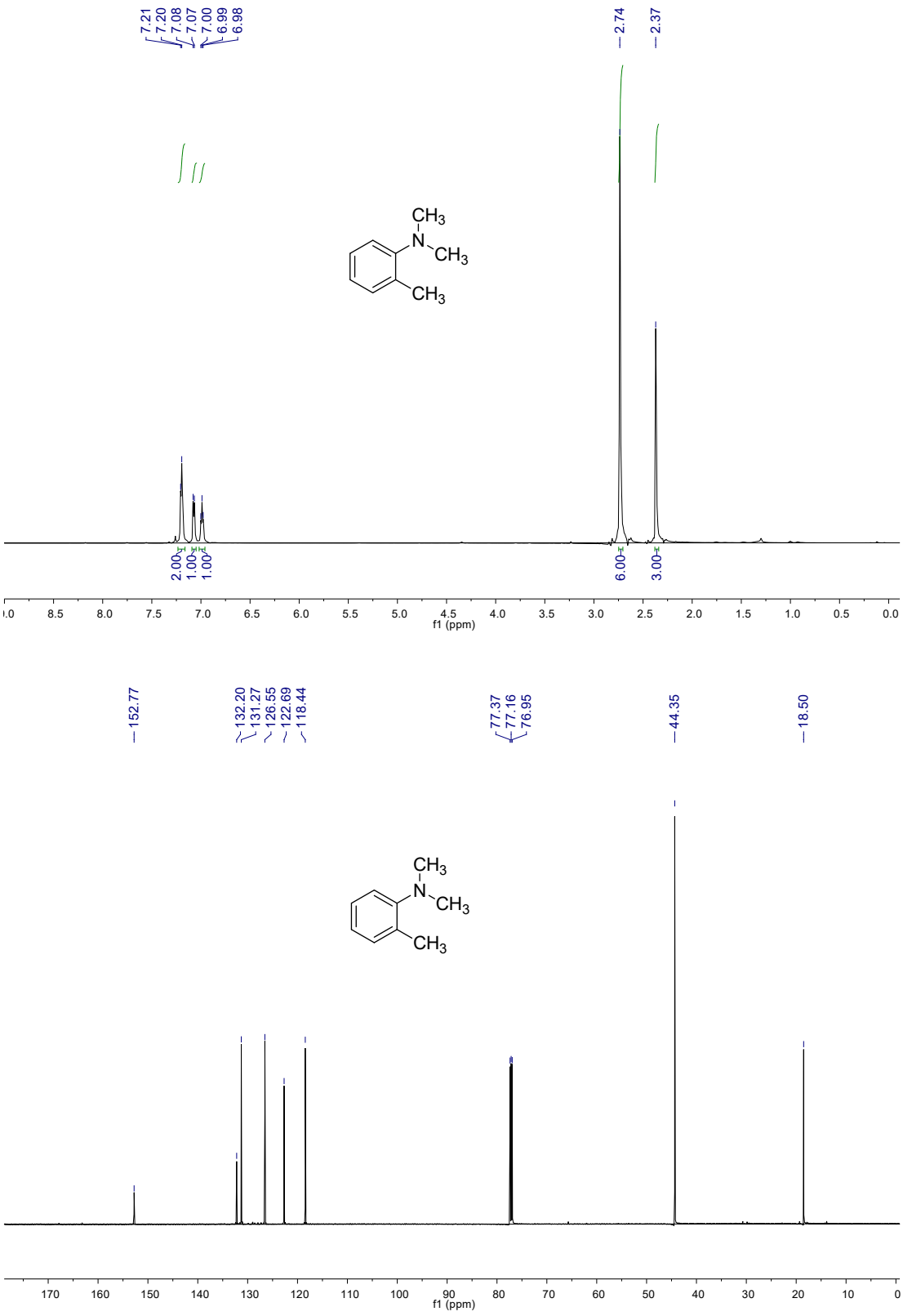




^{1}H and ^{13}C NMR Spectra of **2c**



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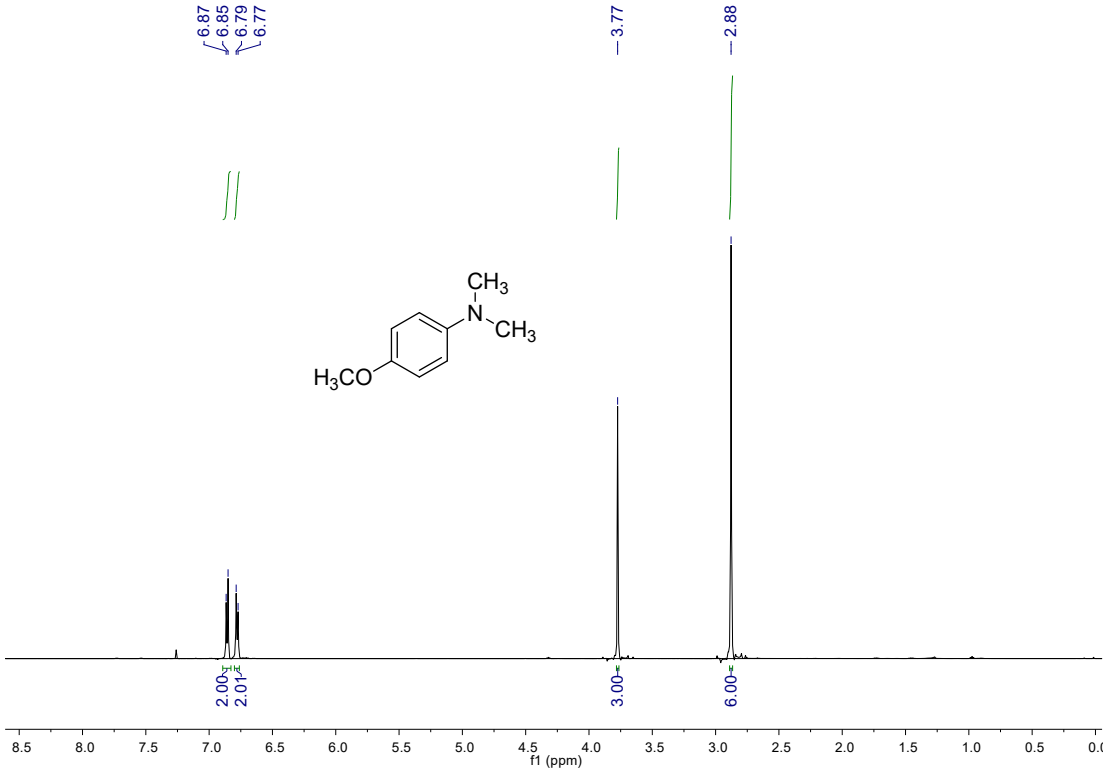
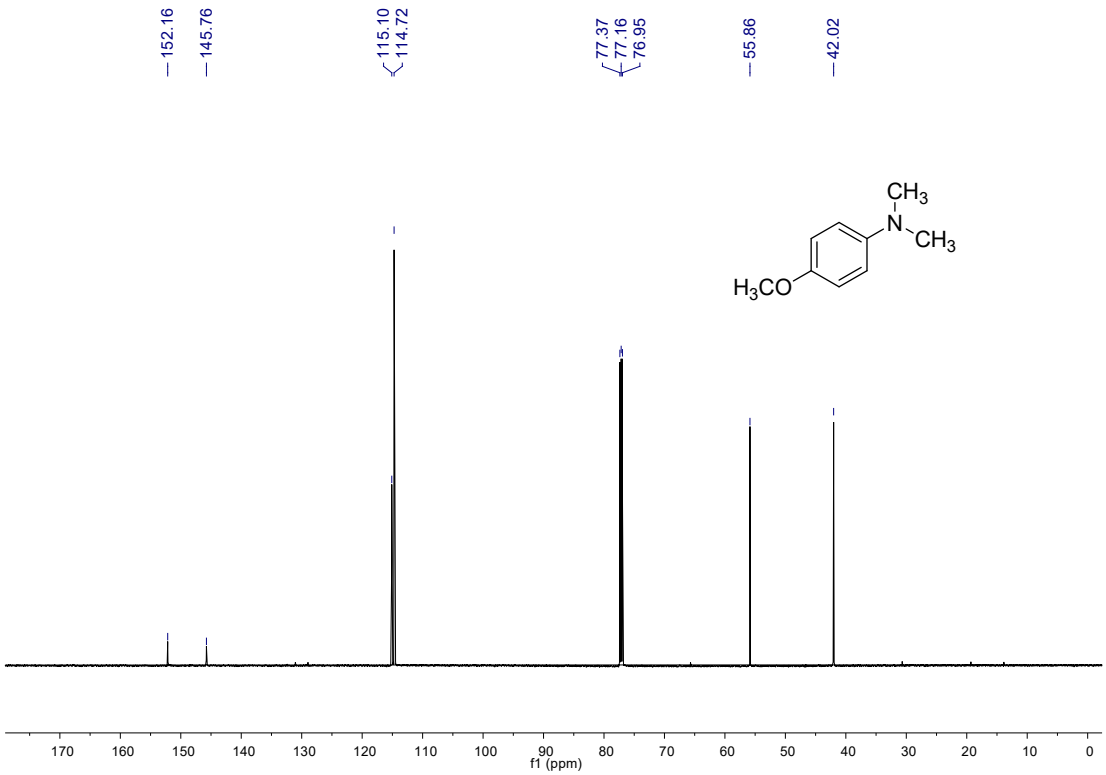
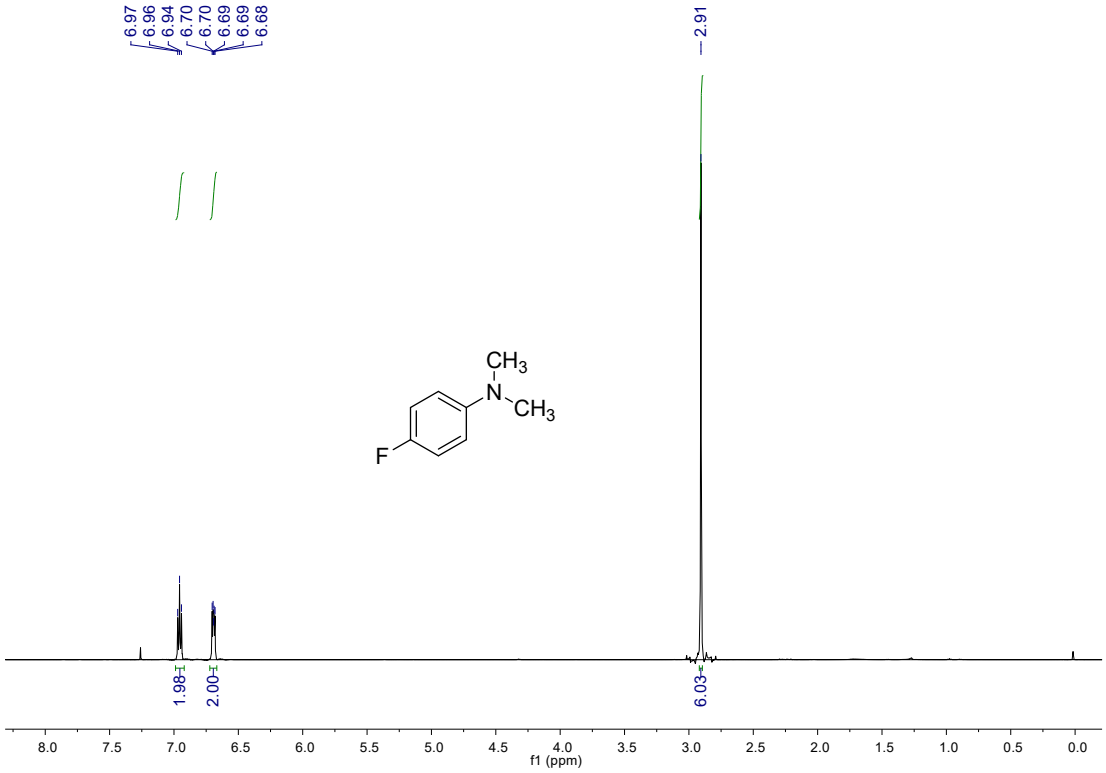
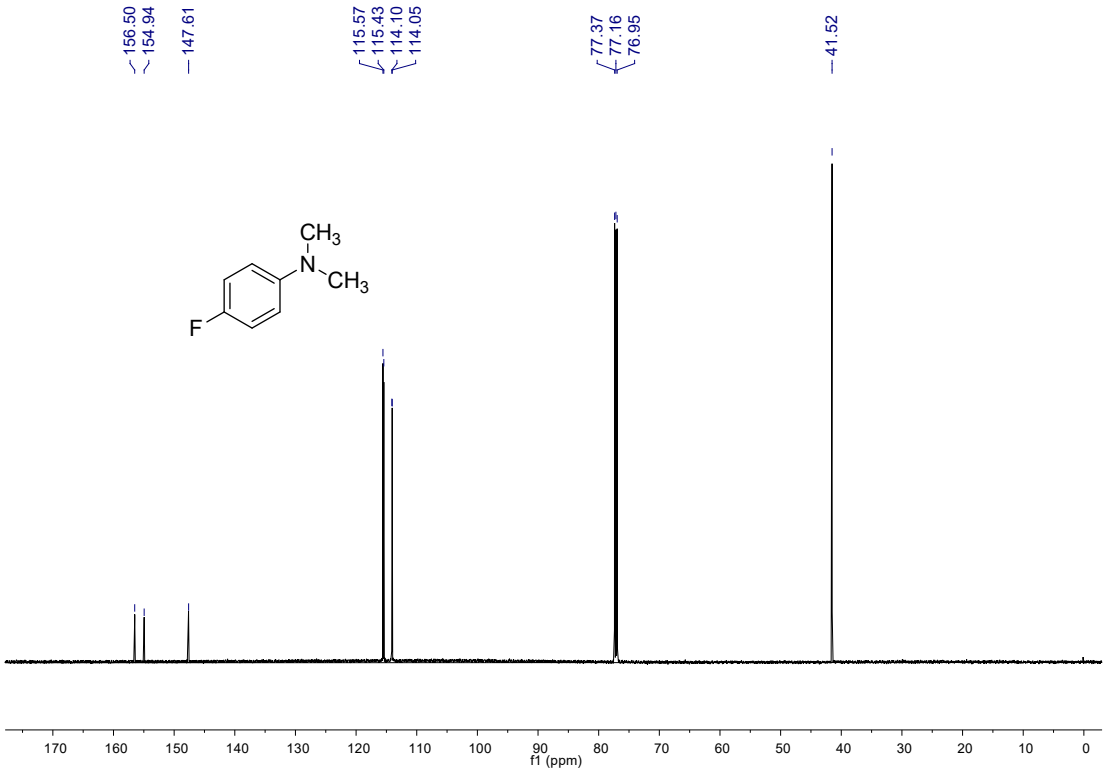


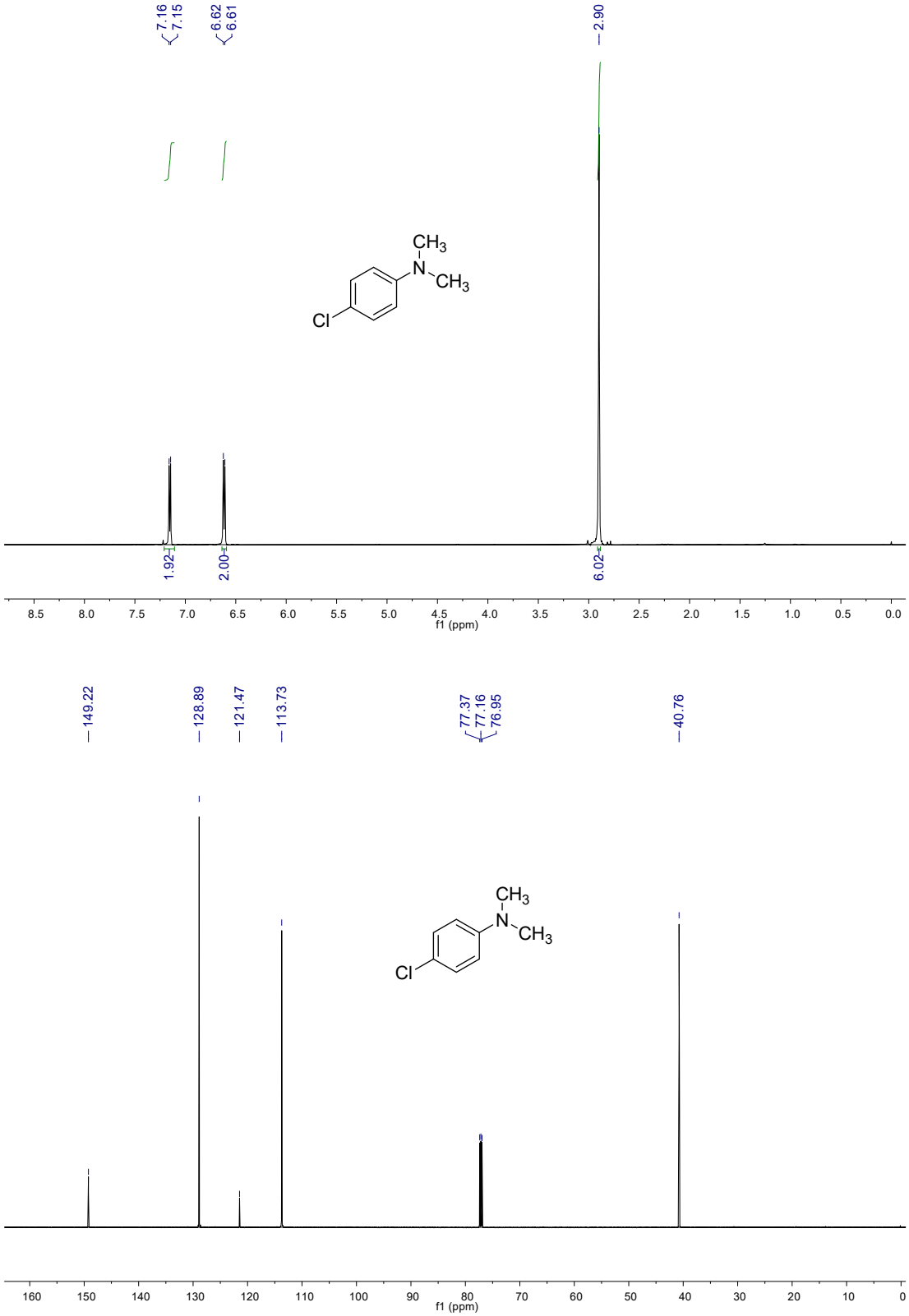


^{1}H and ^{13}C NMR Spectra of **2e**





^{1}H and ^{13}C NMR Spectra of **2f**



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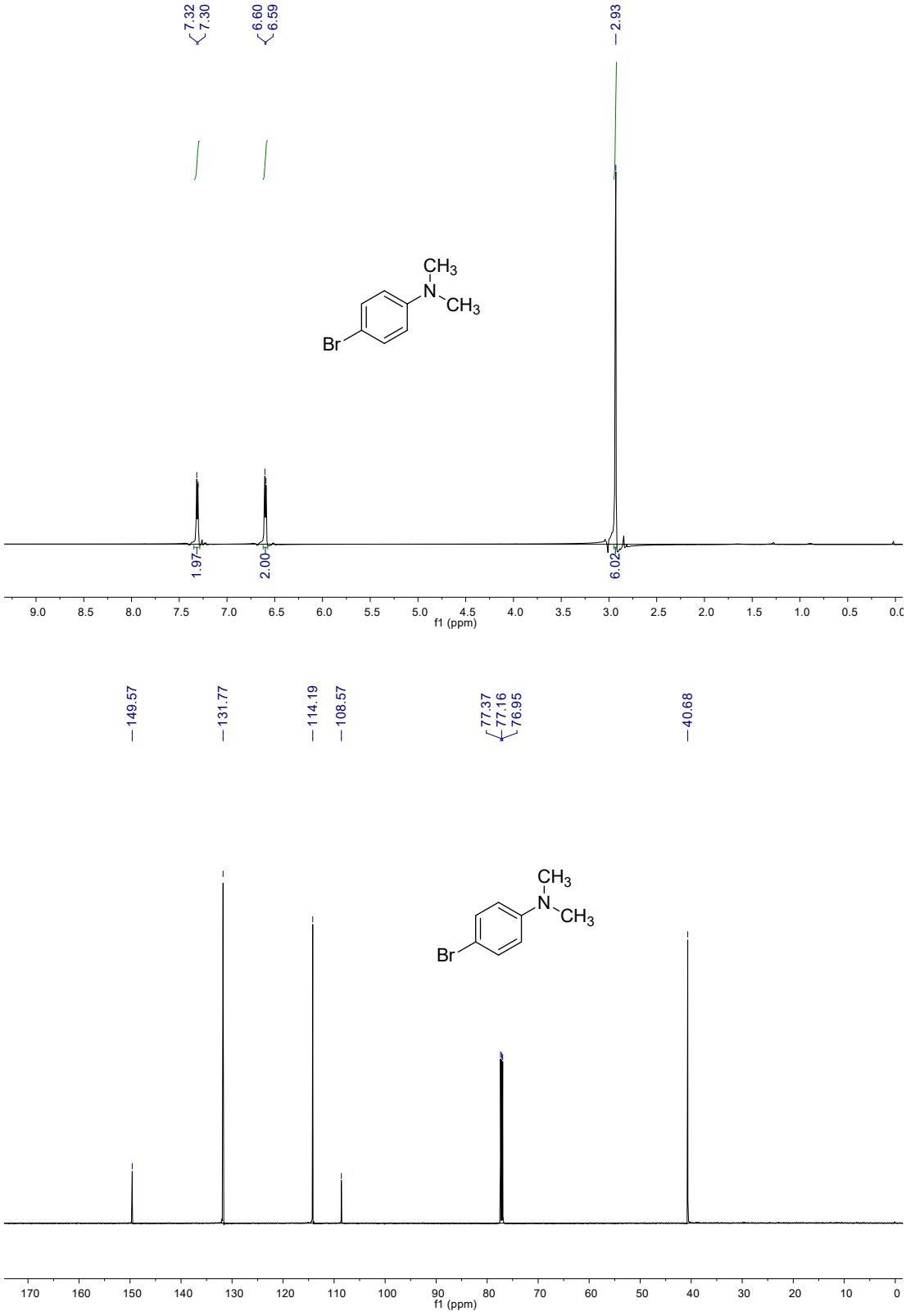
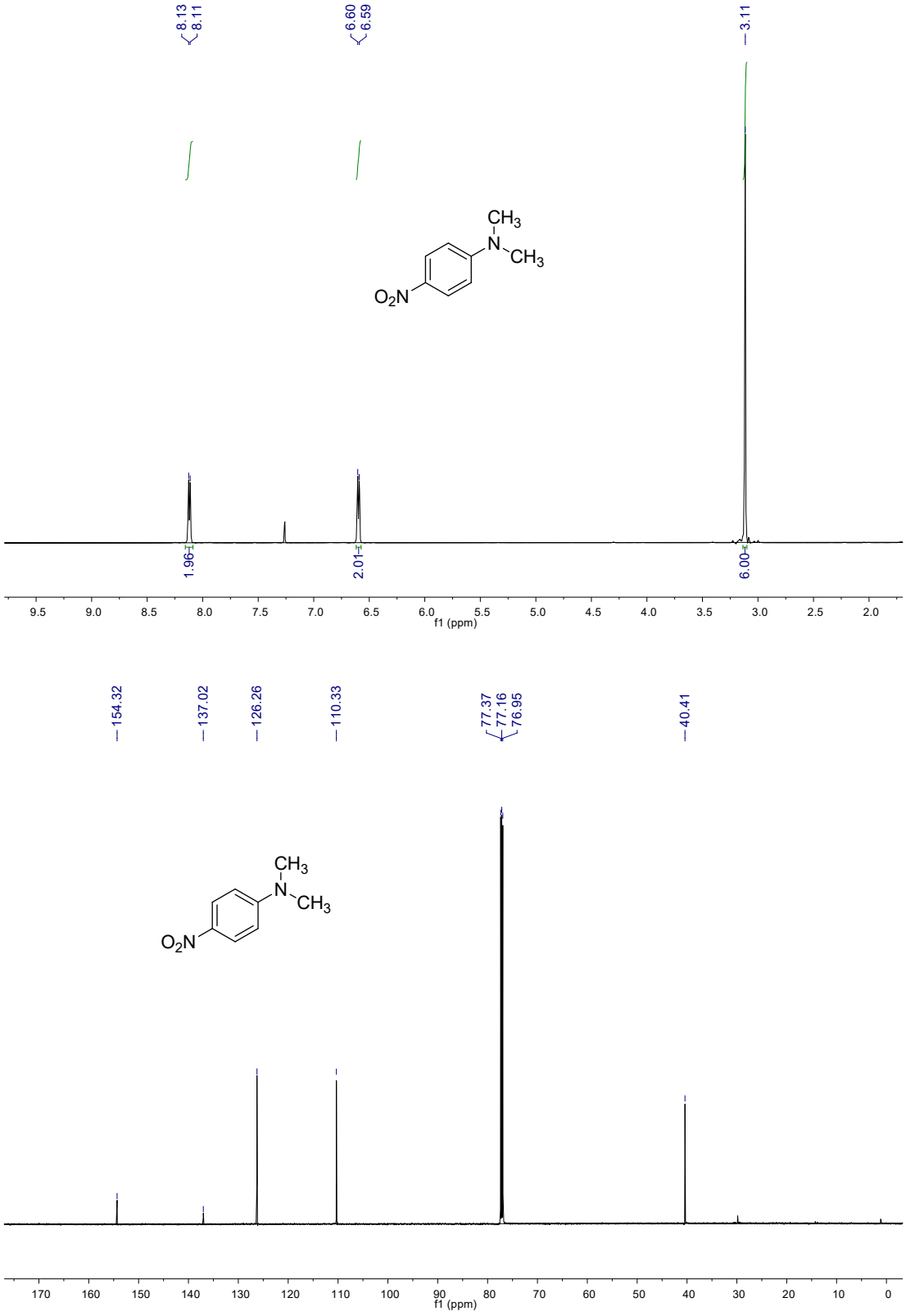
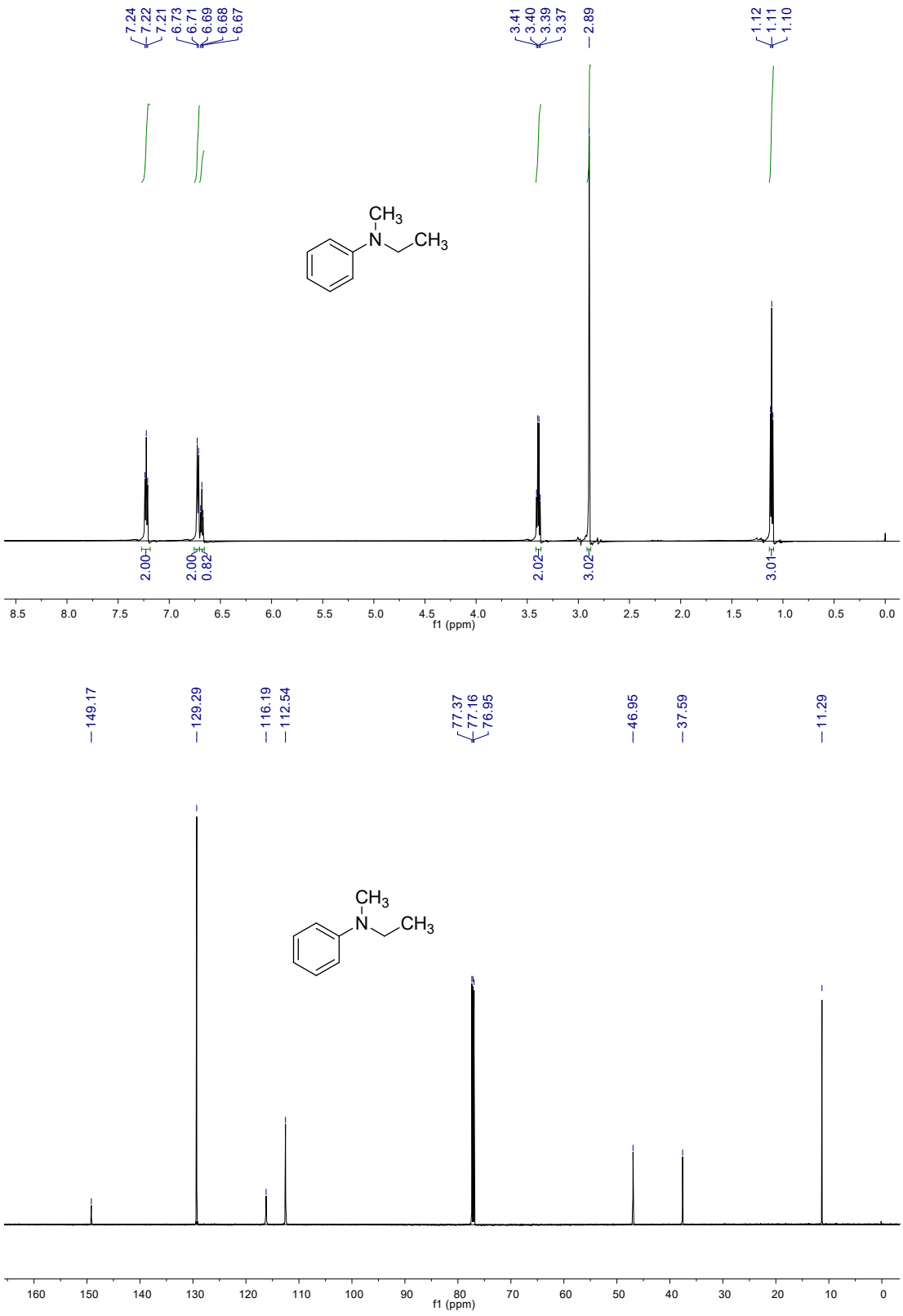


^{1}H and ^{13}C NMR Spectra of **2h**



^{1}H and ^{13}C NMR Spectra of **2i**



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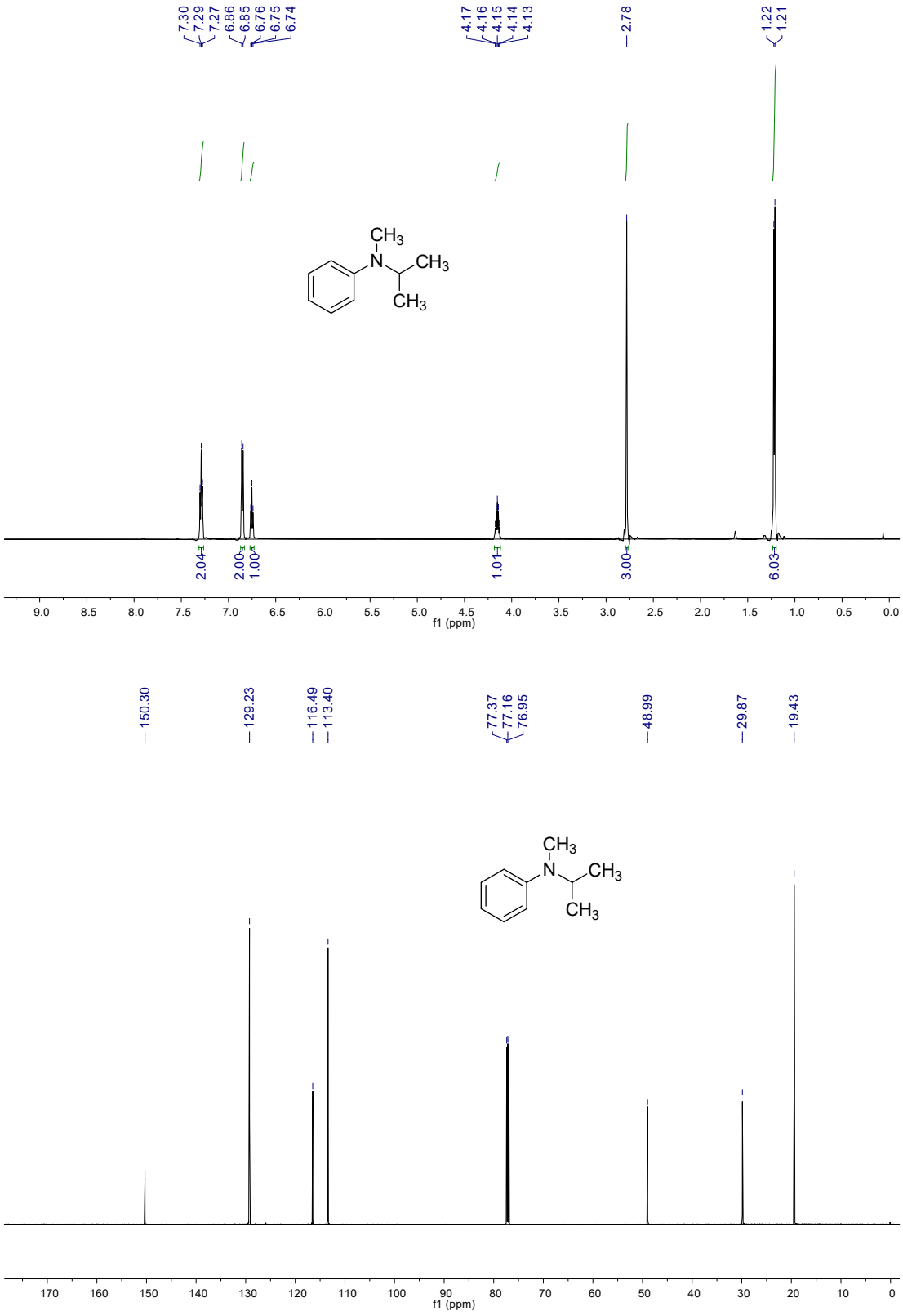

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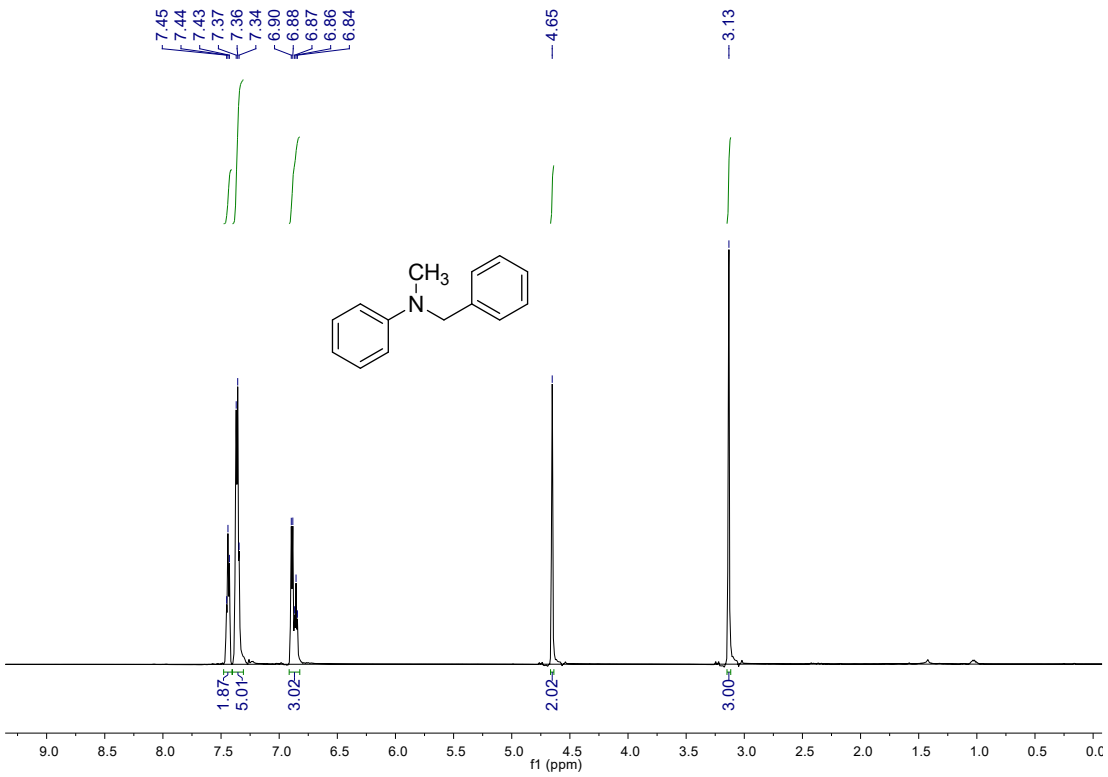
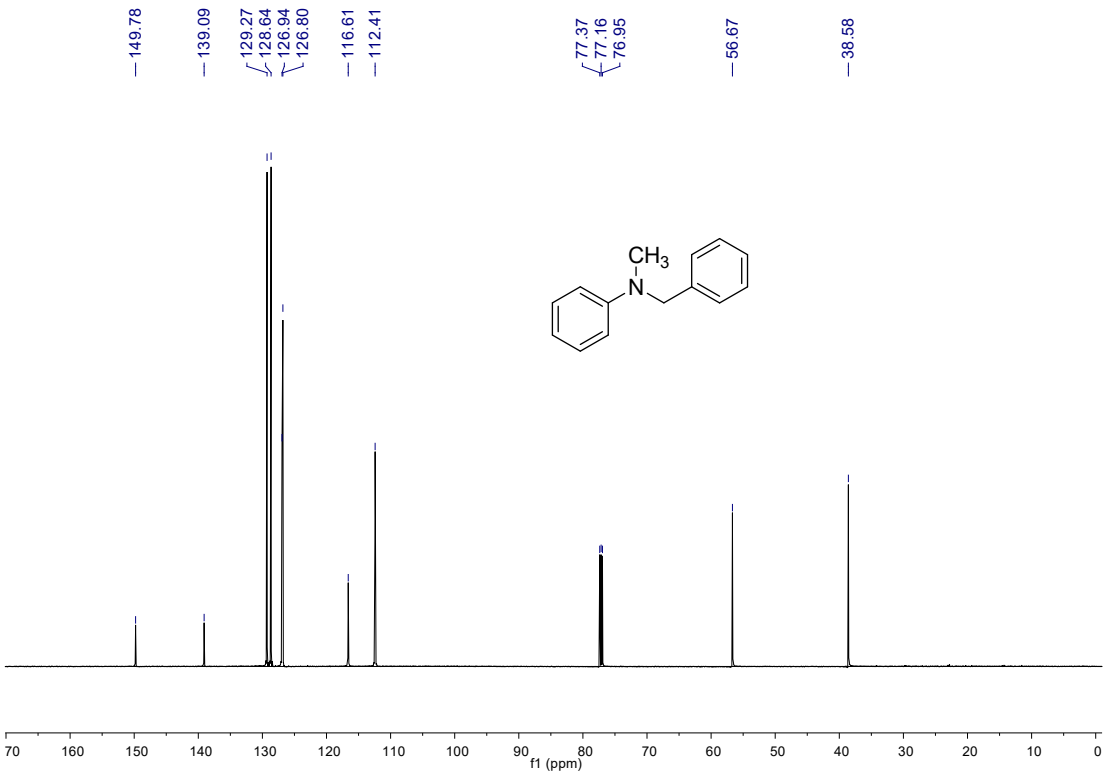
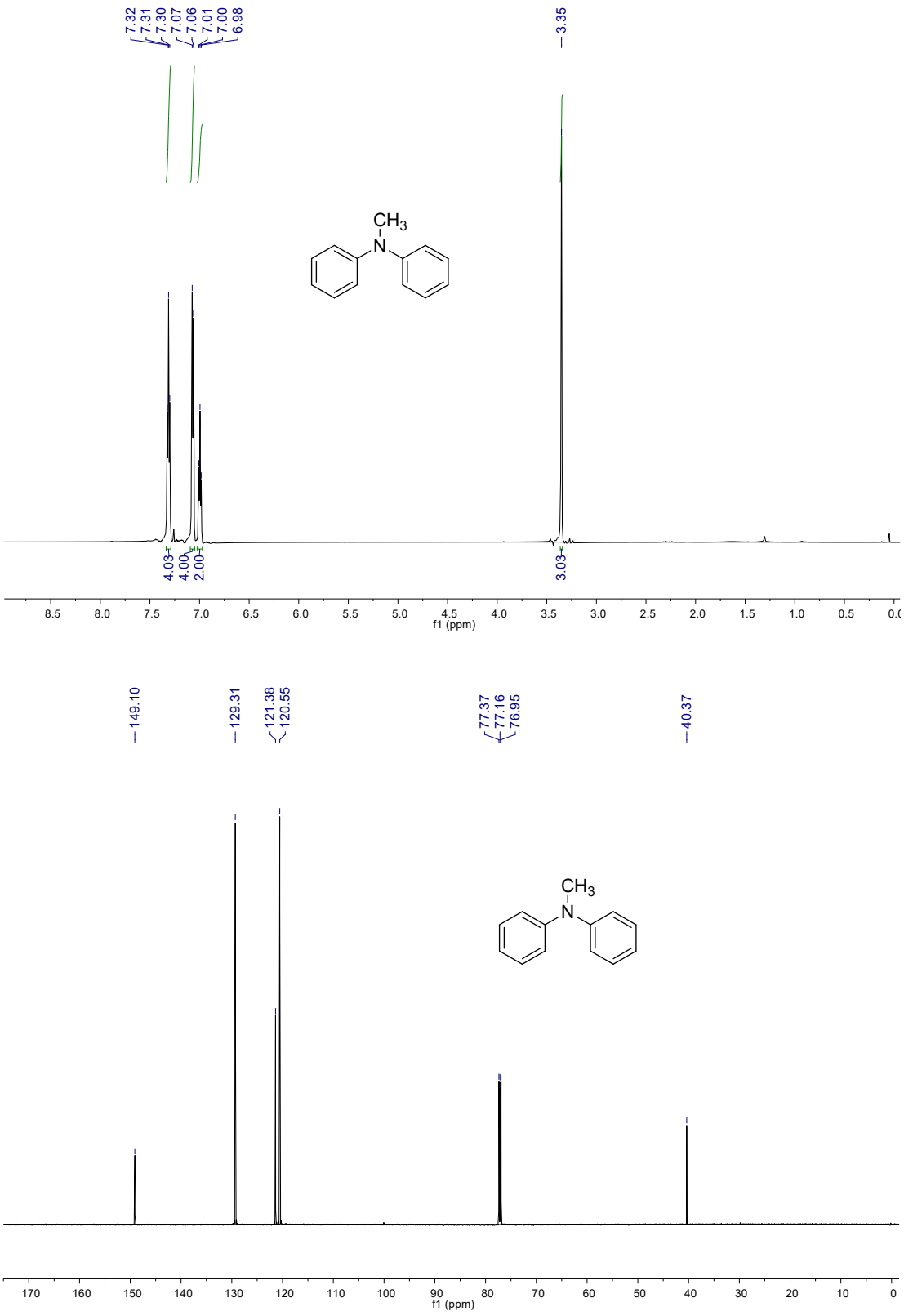
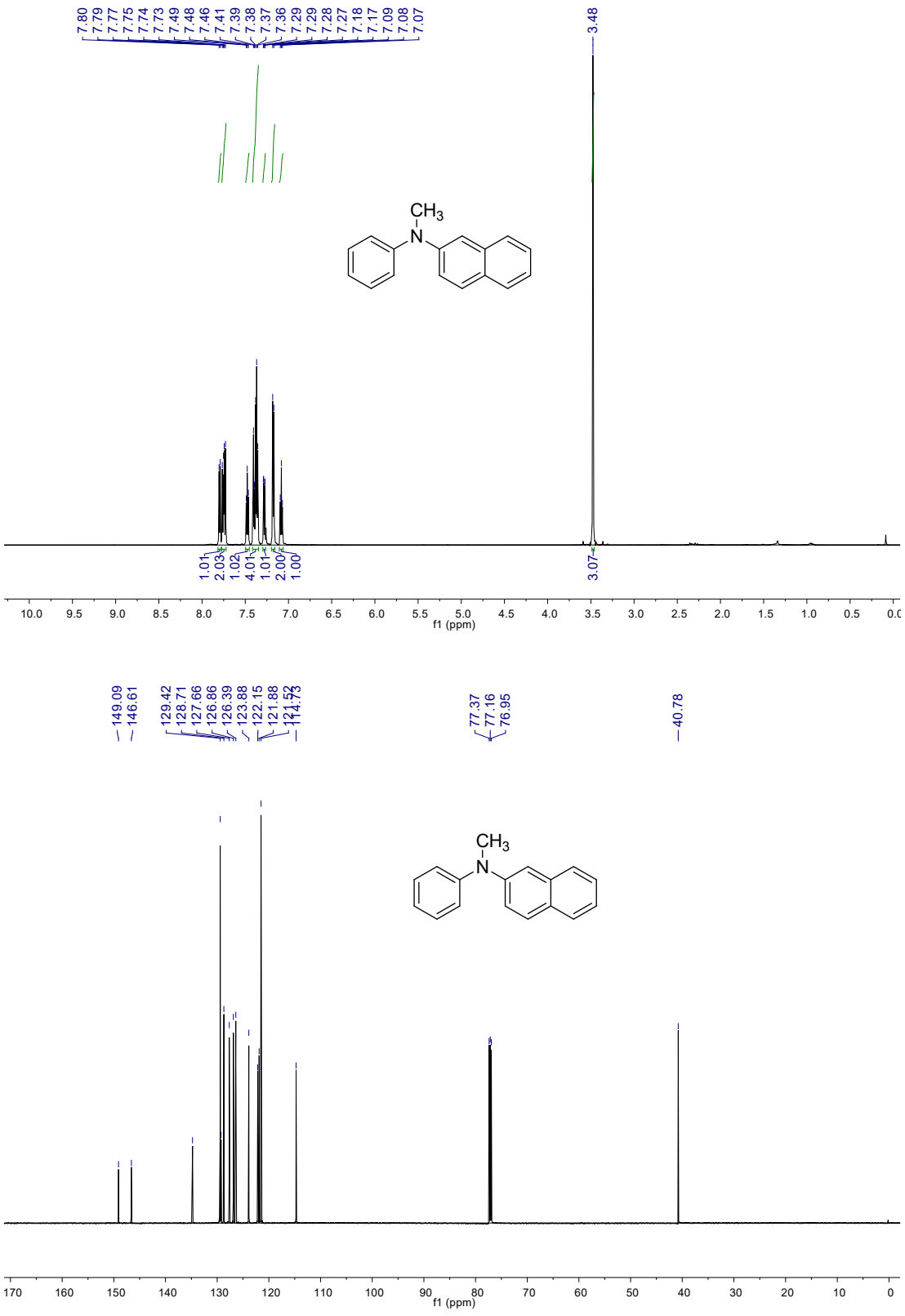




^{1}H and ^{13}C NMR Spectra of **2l**



^{1}H and ^{13}C NMR Spectra of **2m**



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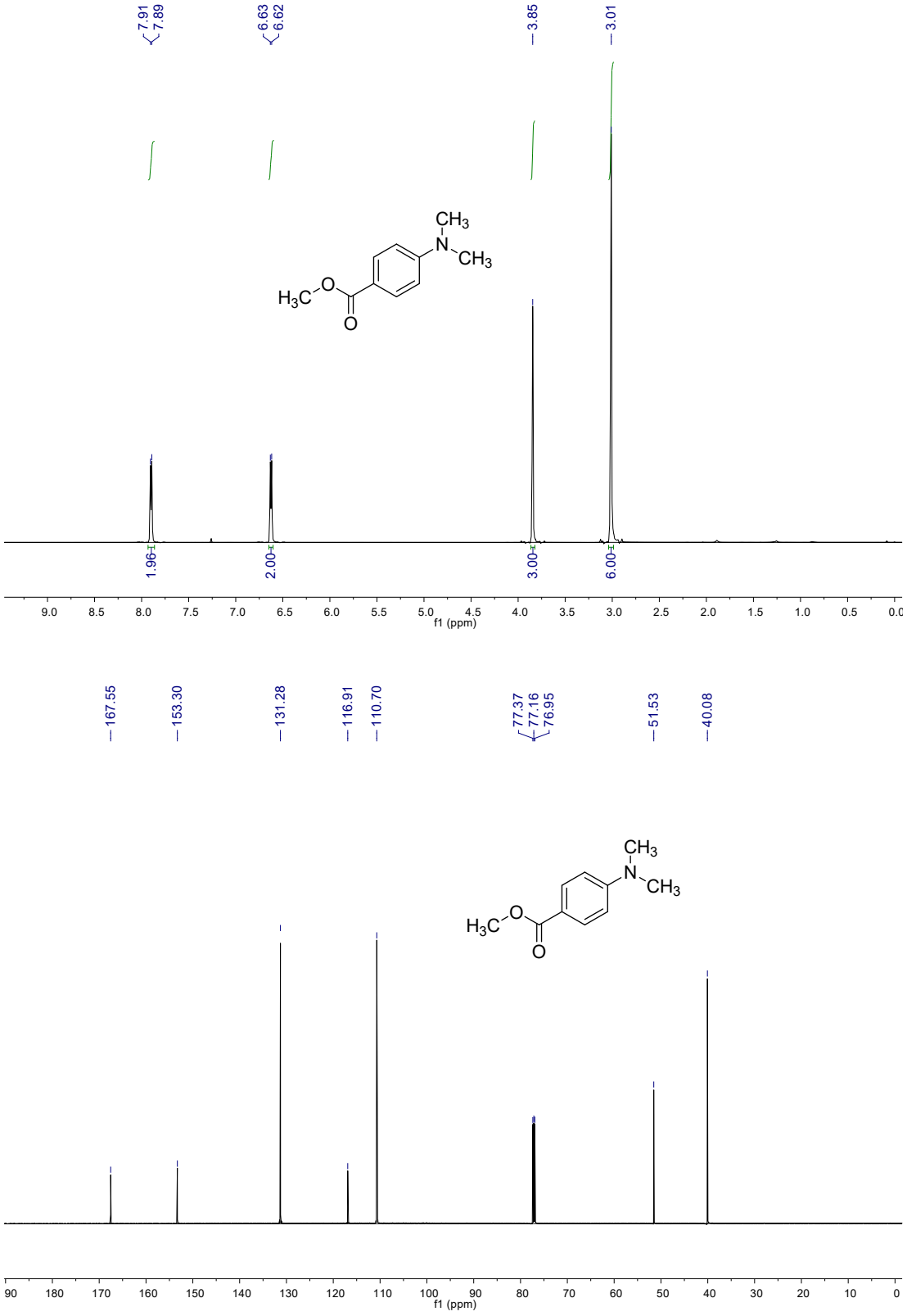
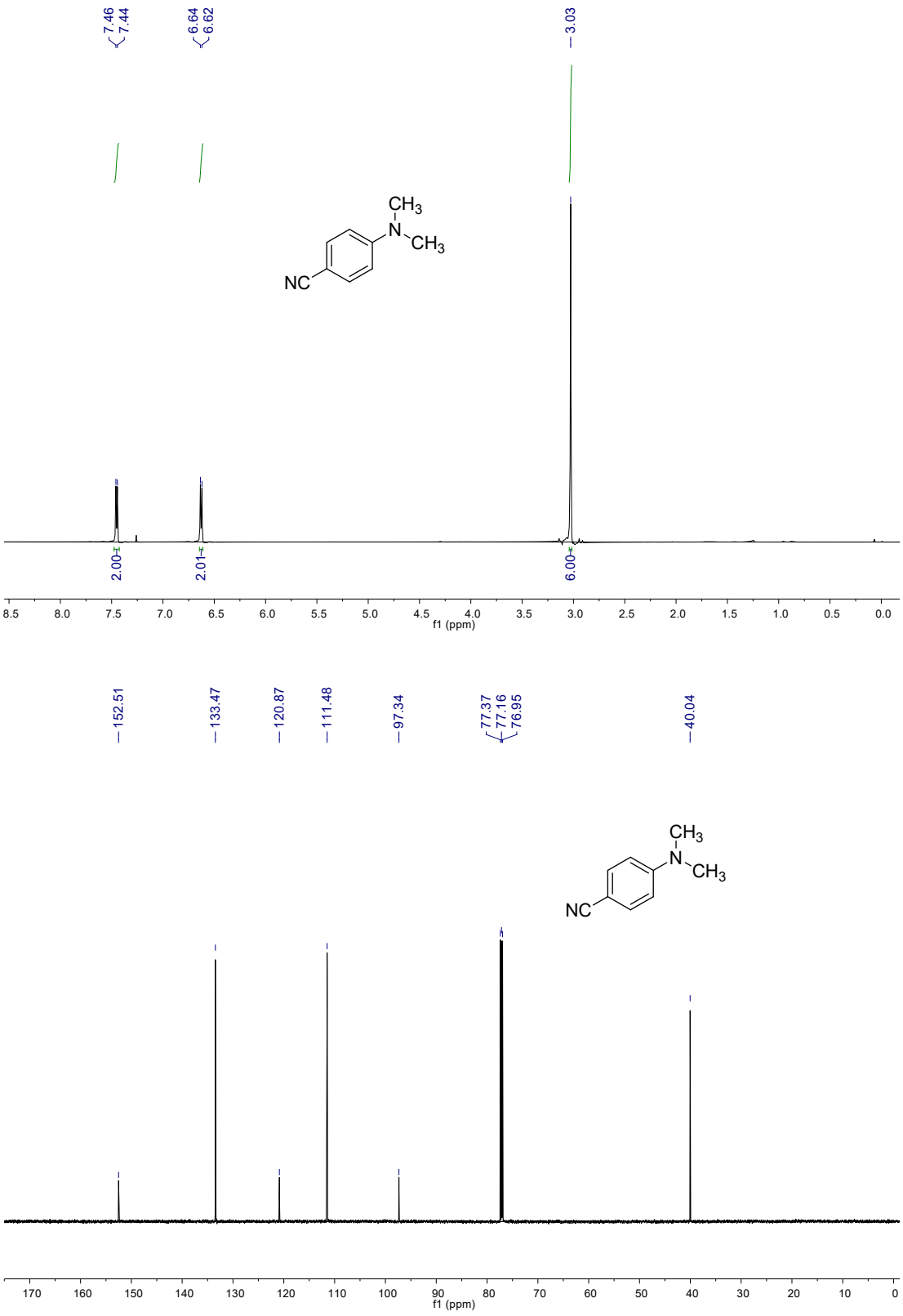
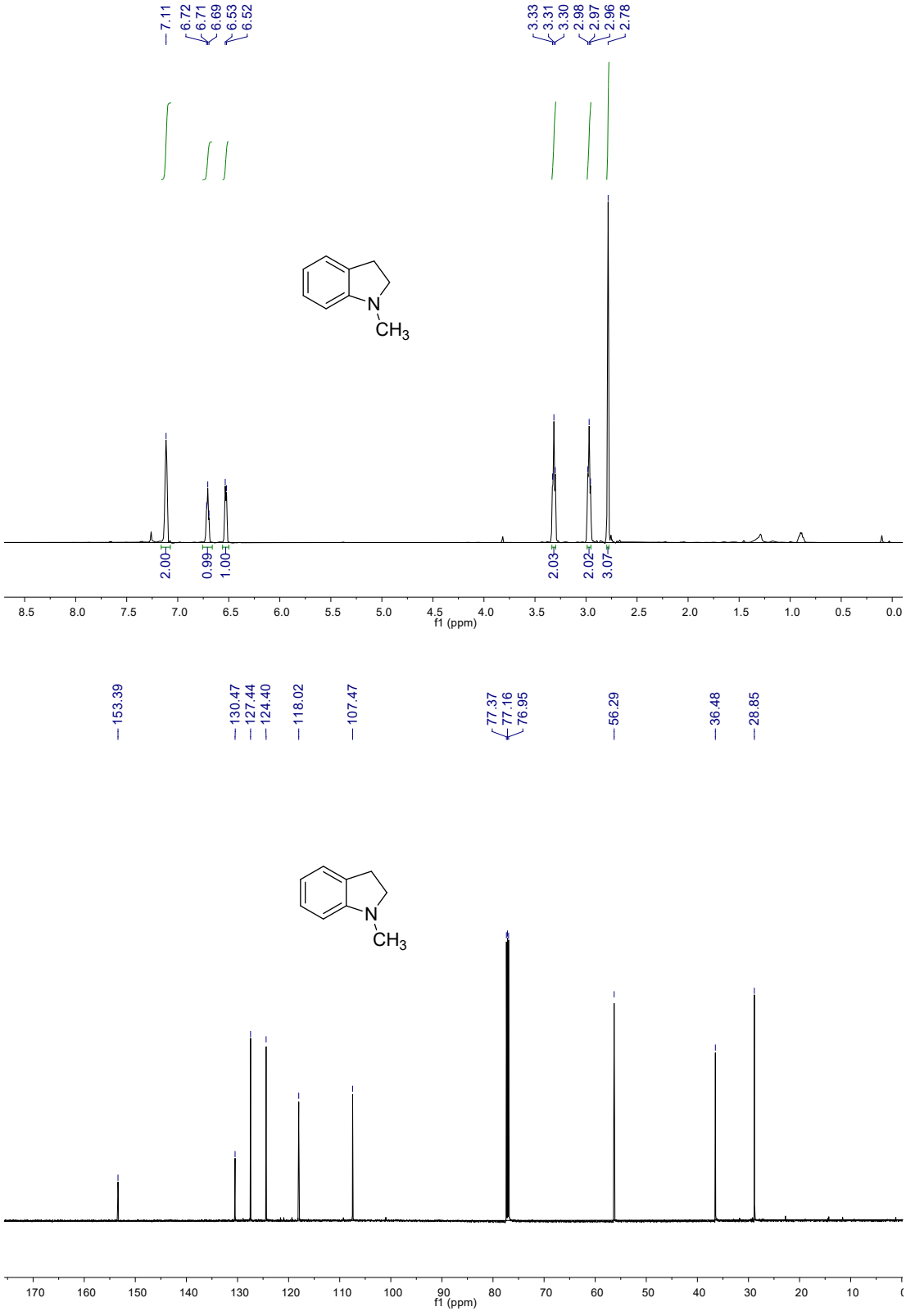


^{1}H and ^{13}C NMR Spectra of **2o**



^{1}H and ^{13}C NMR Spectra of **2p**



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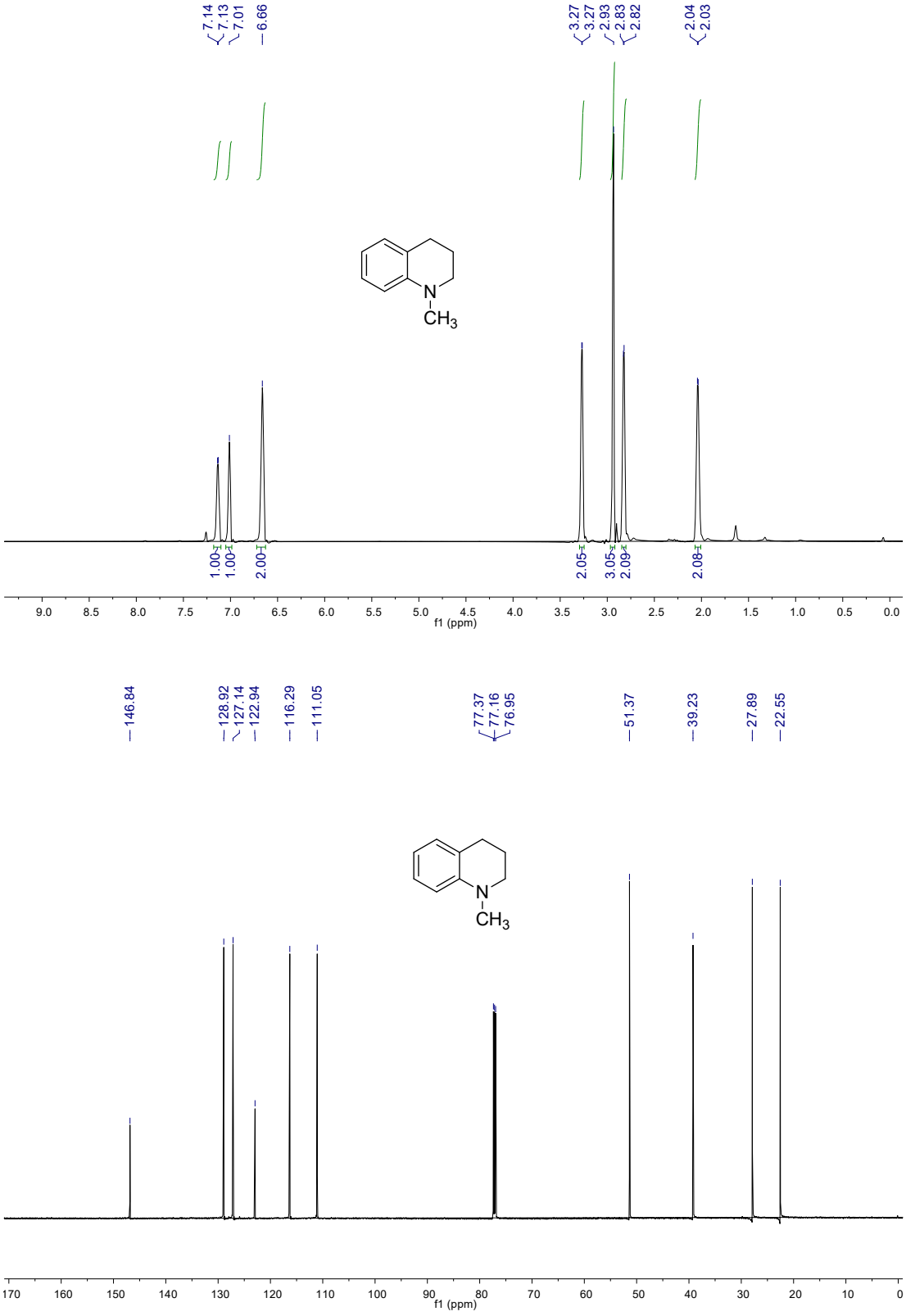

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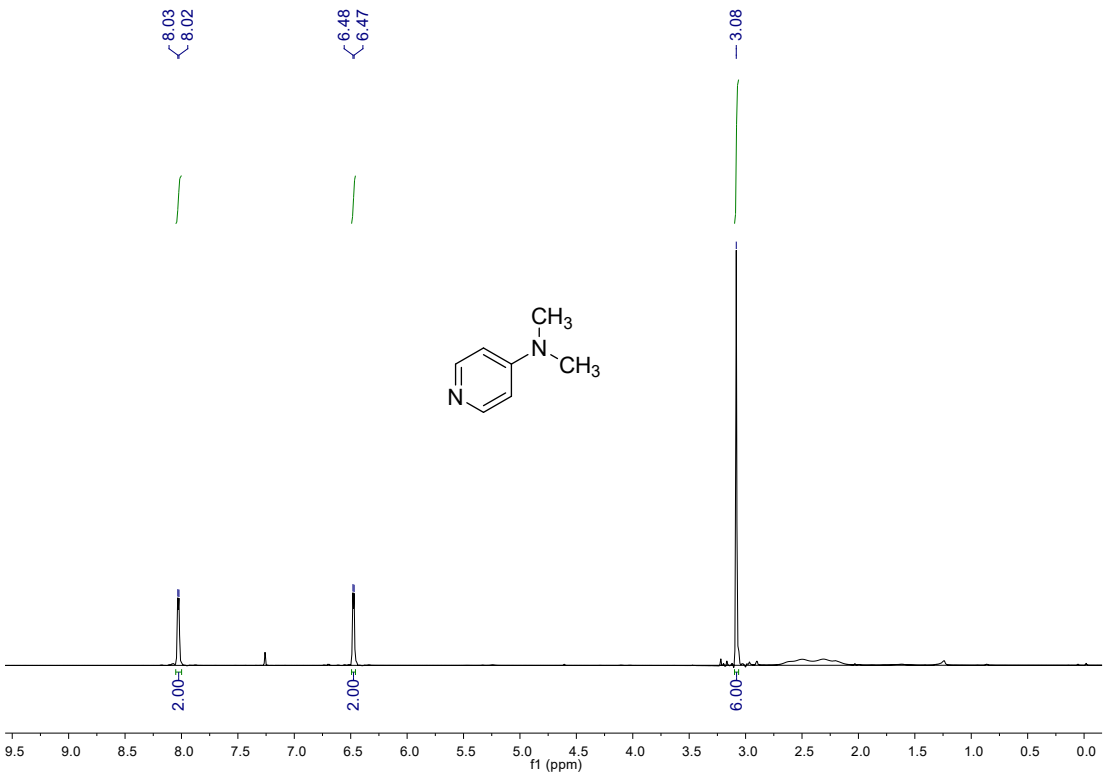
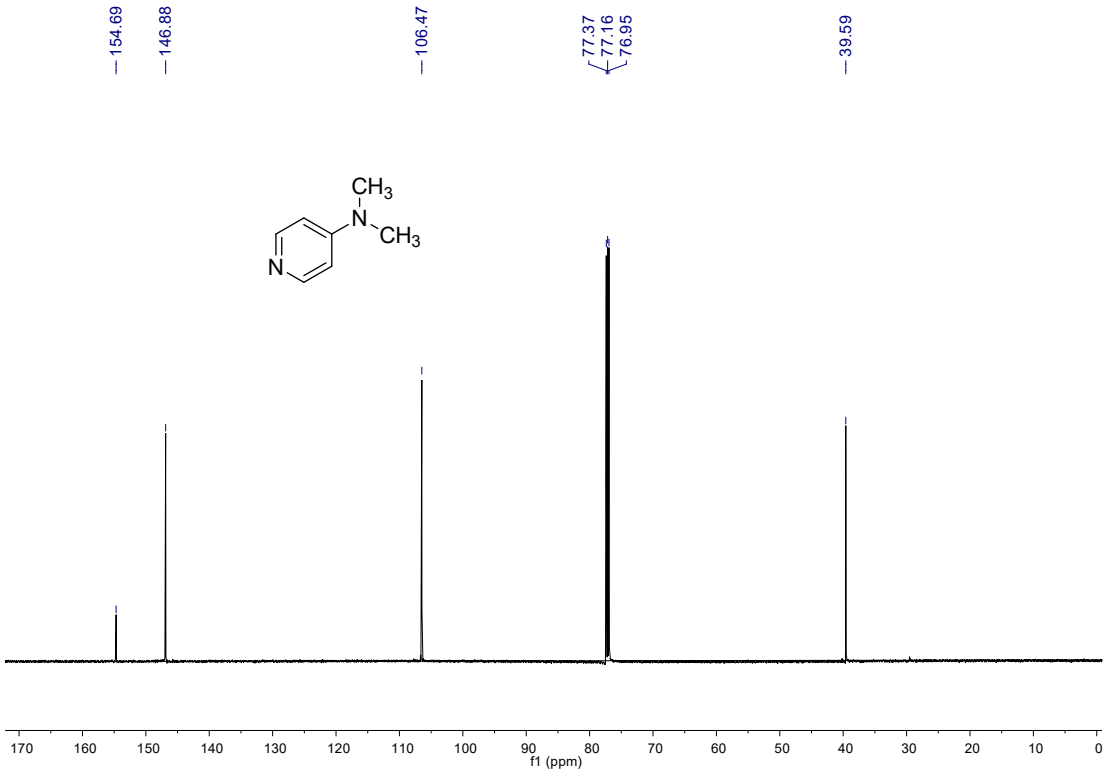
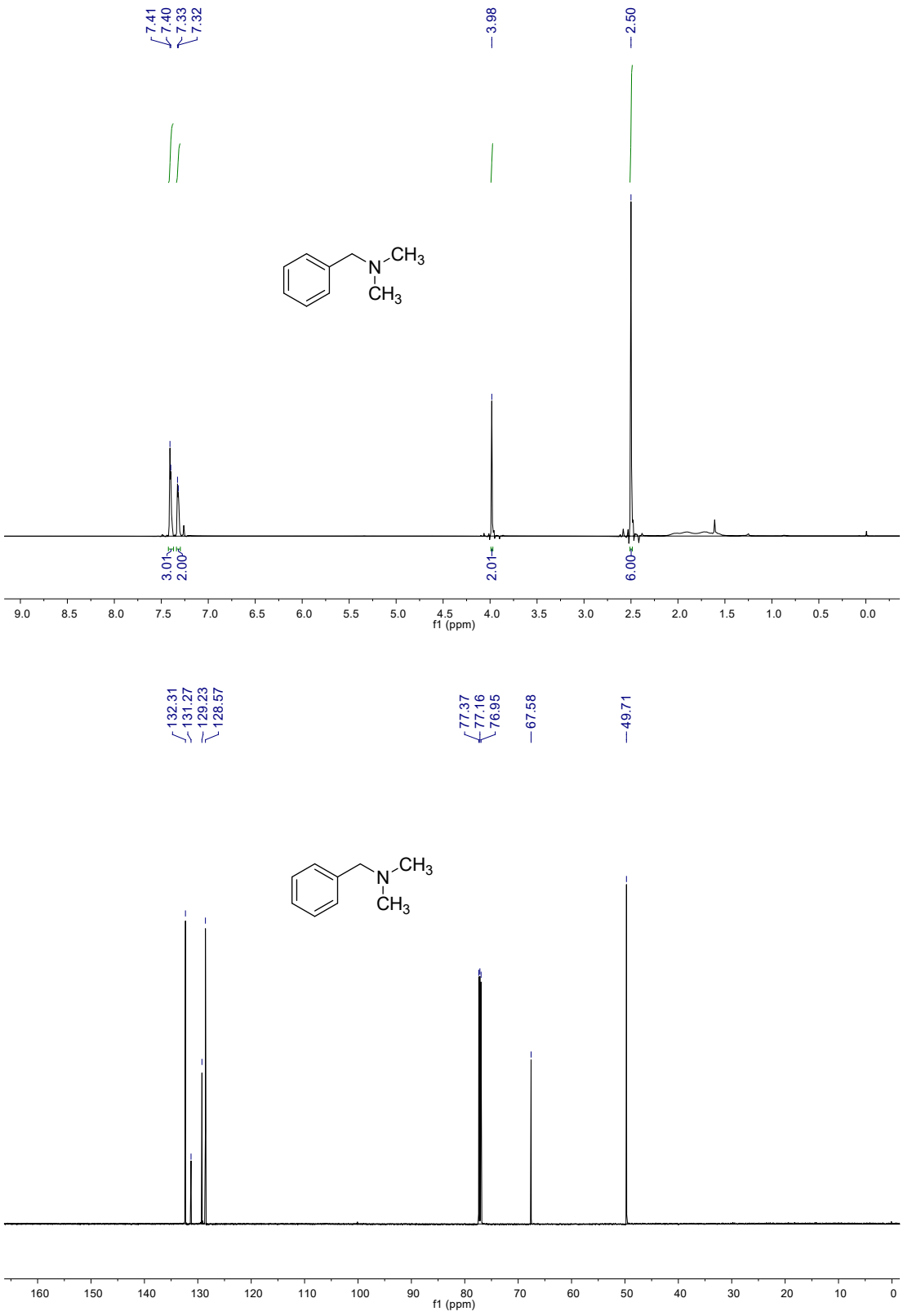




^{1}H and ^{13}C NMR Spectra of **2s**



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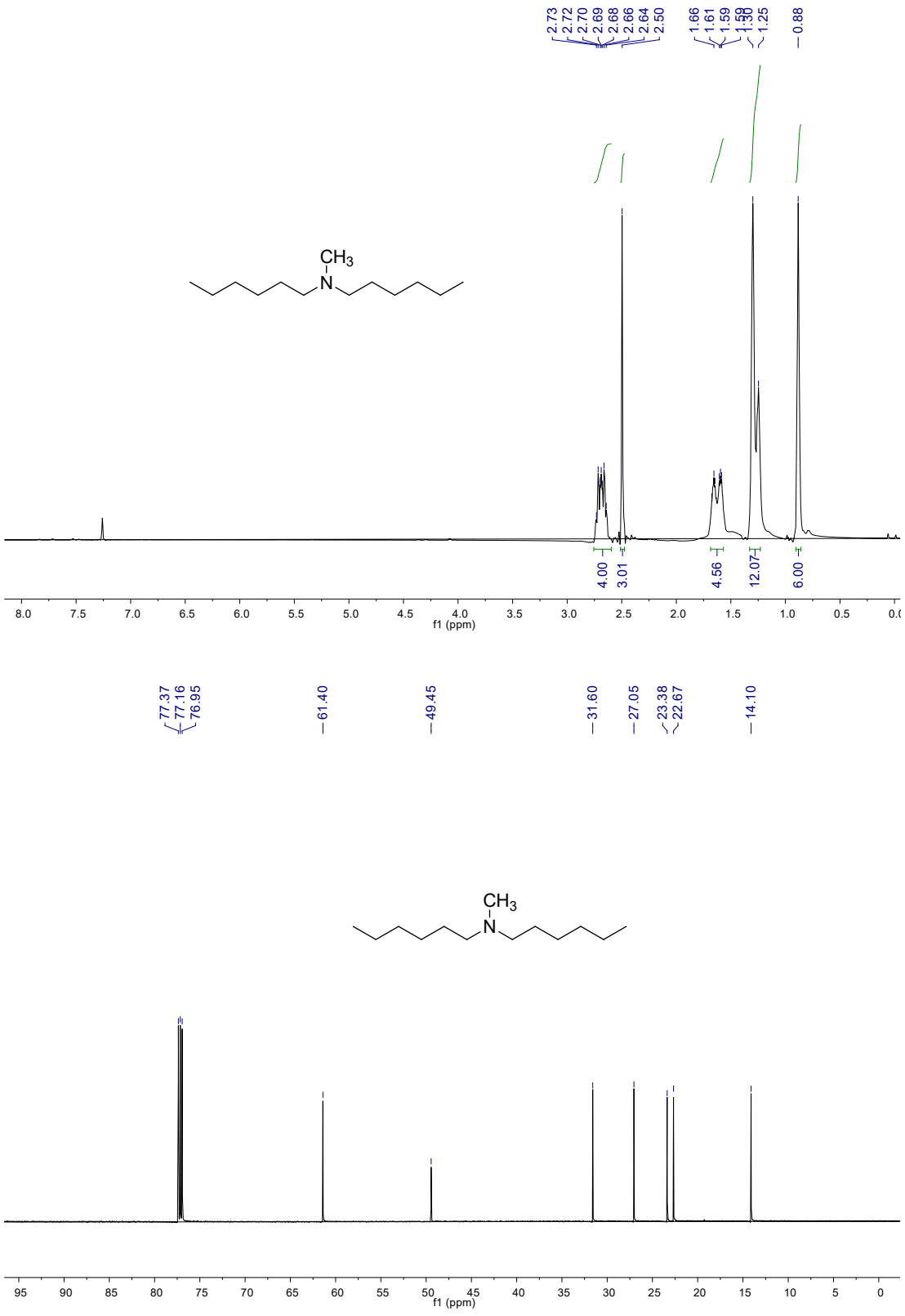

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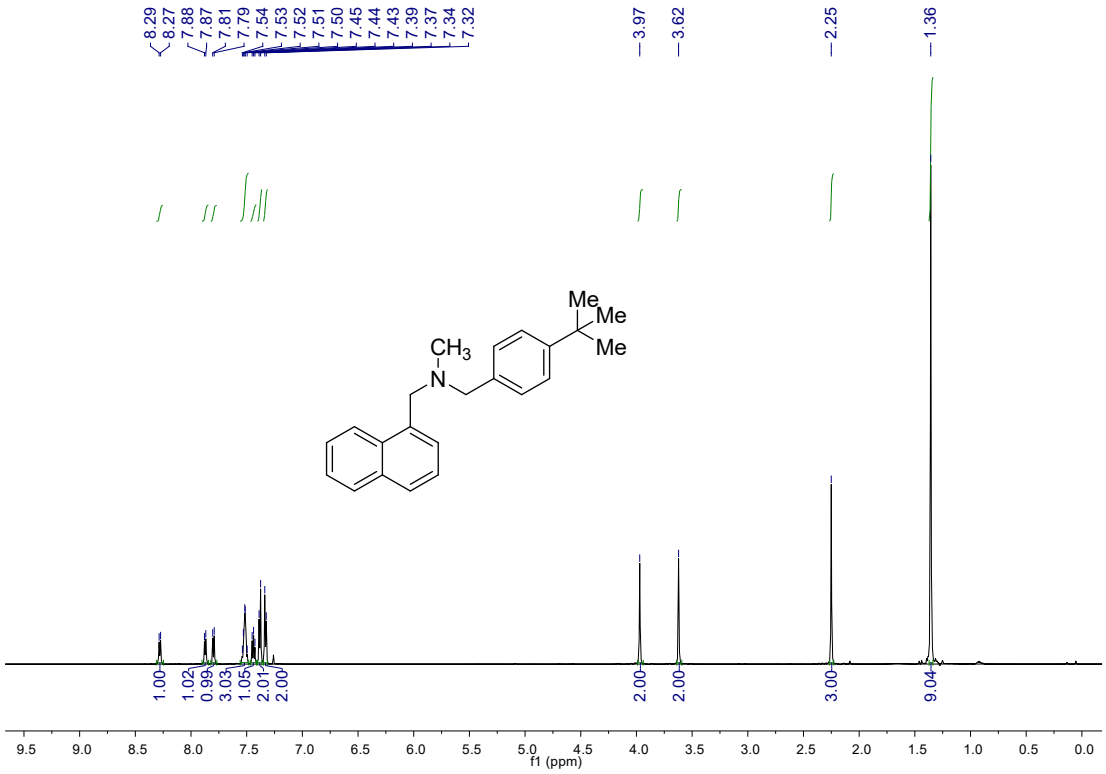
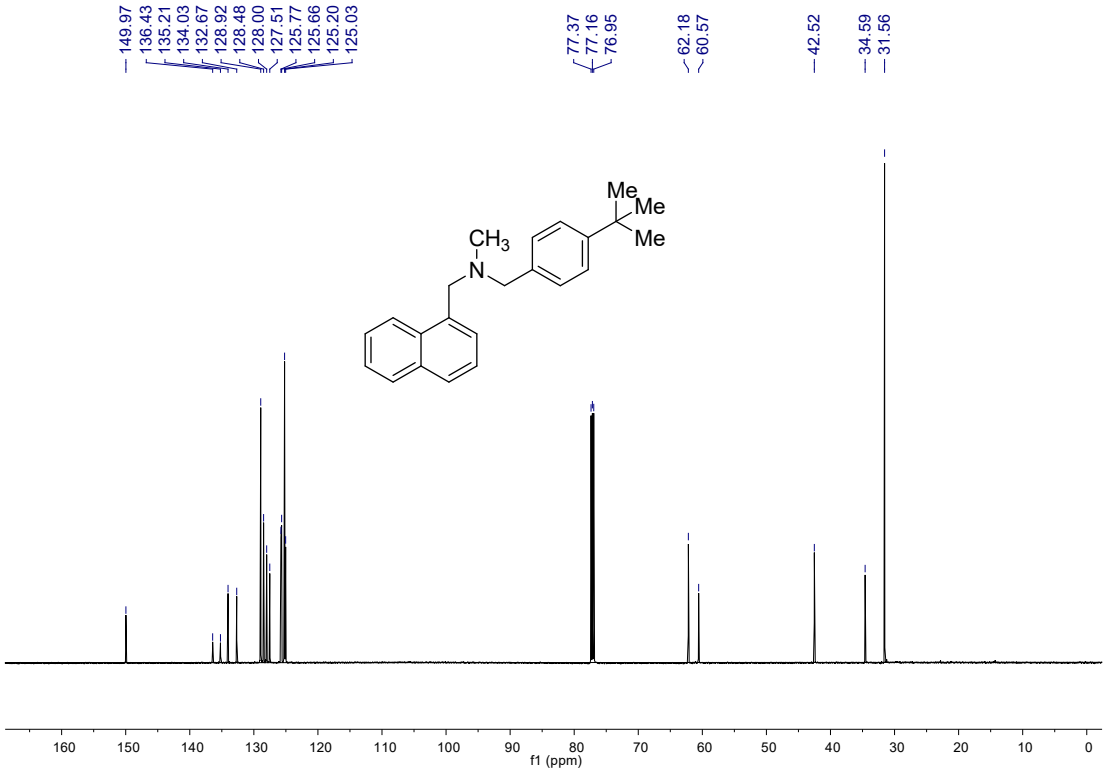
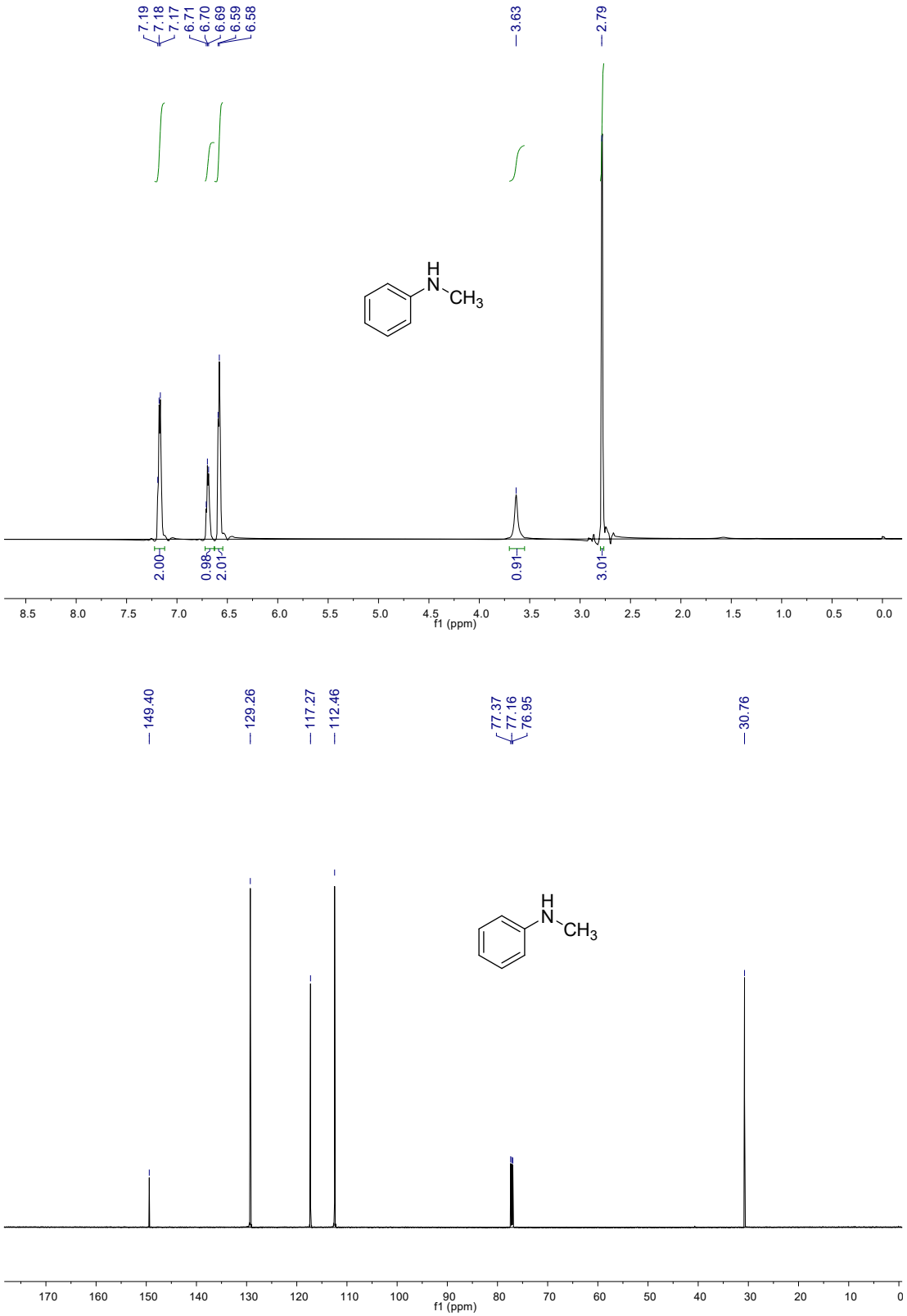
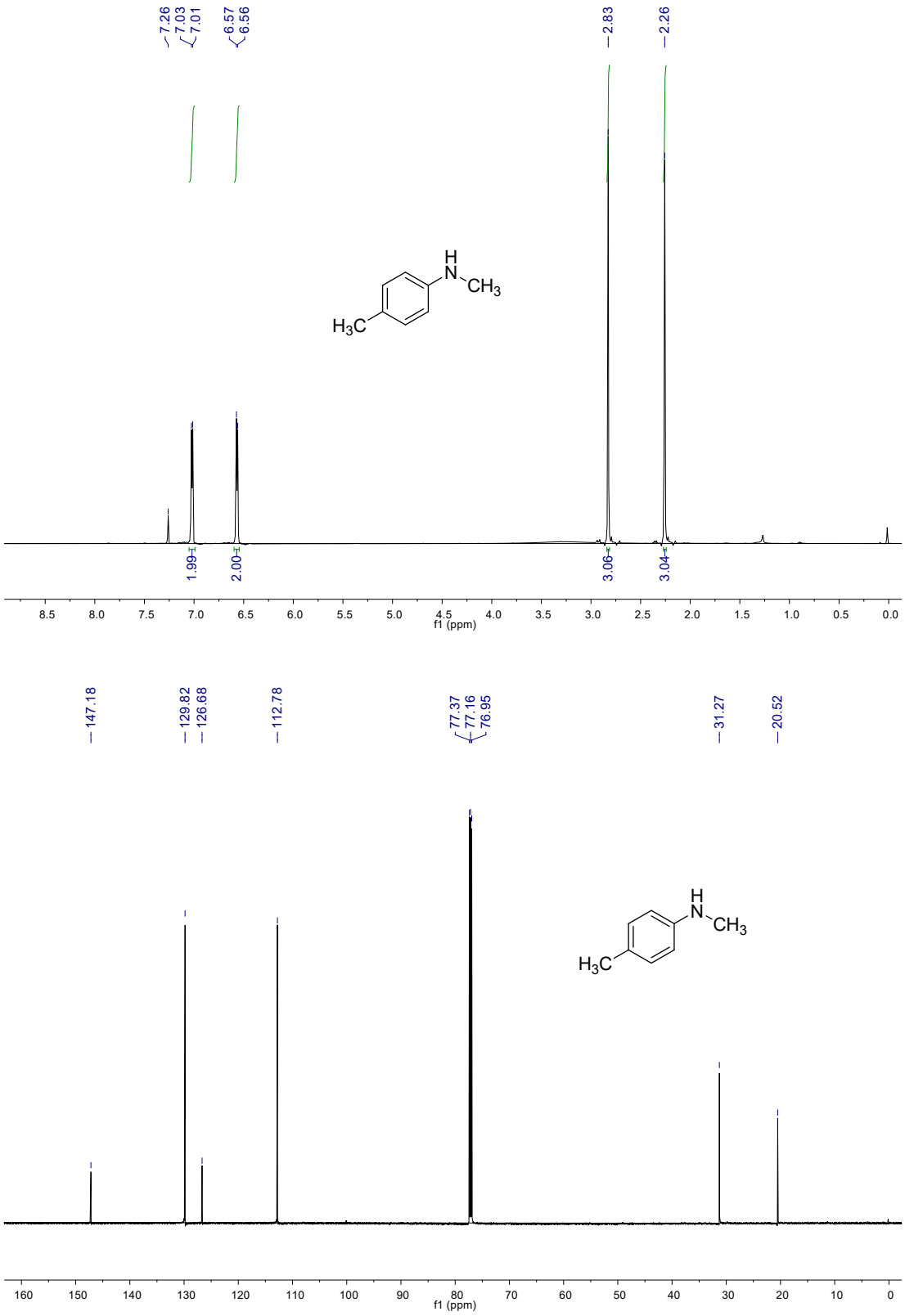




^{1}H and ^{13}C NMR Spectra of Butenafine



^{1}H and ^{13}C NMR Spectra of **3a**



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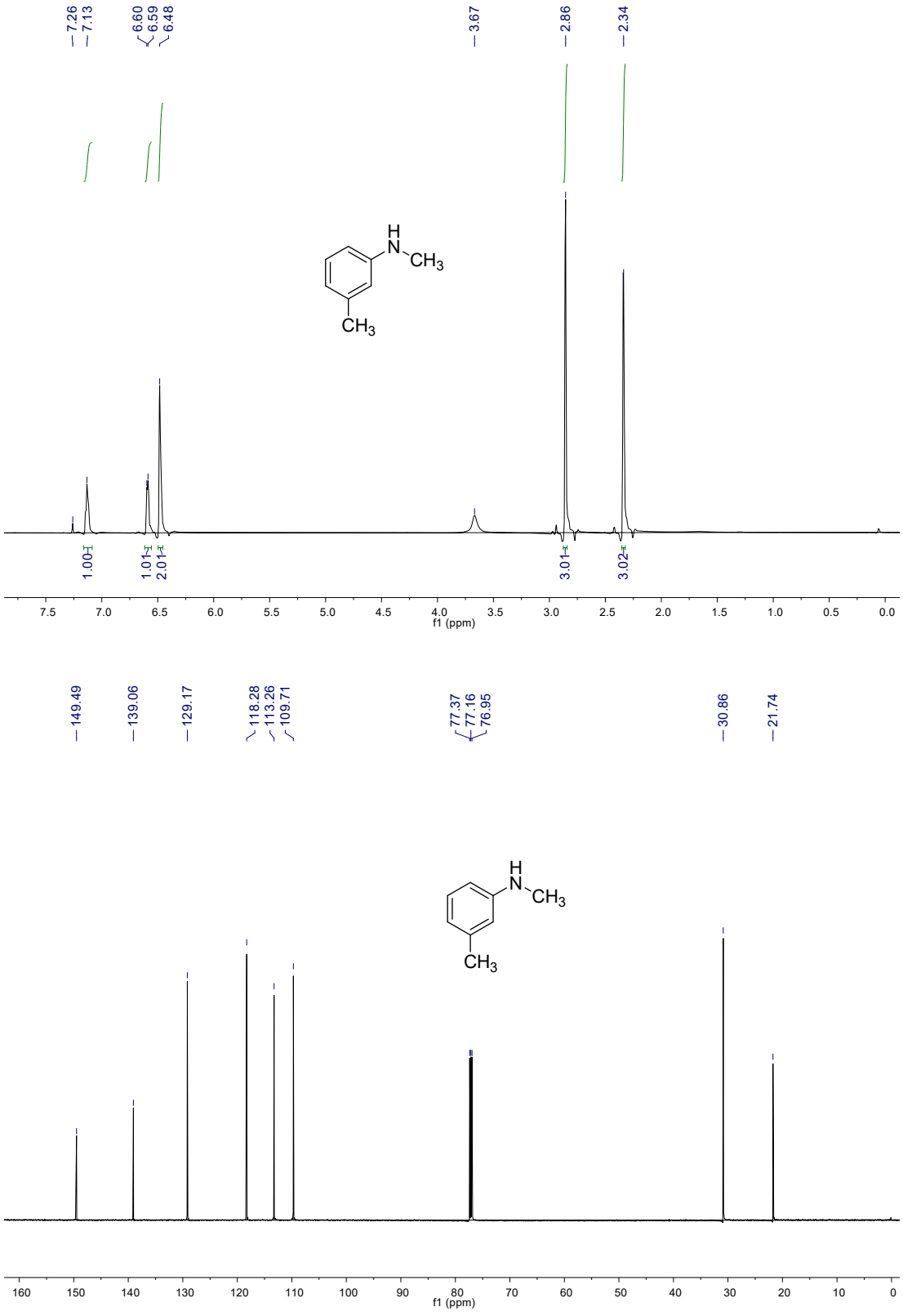

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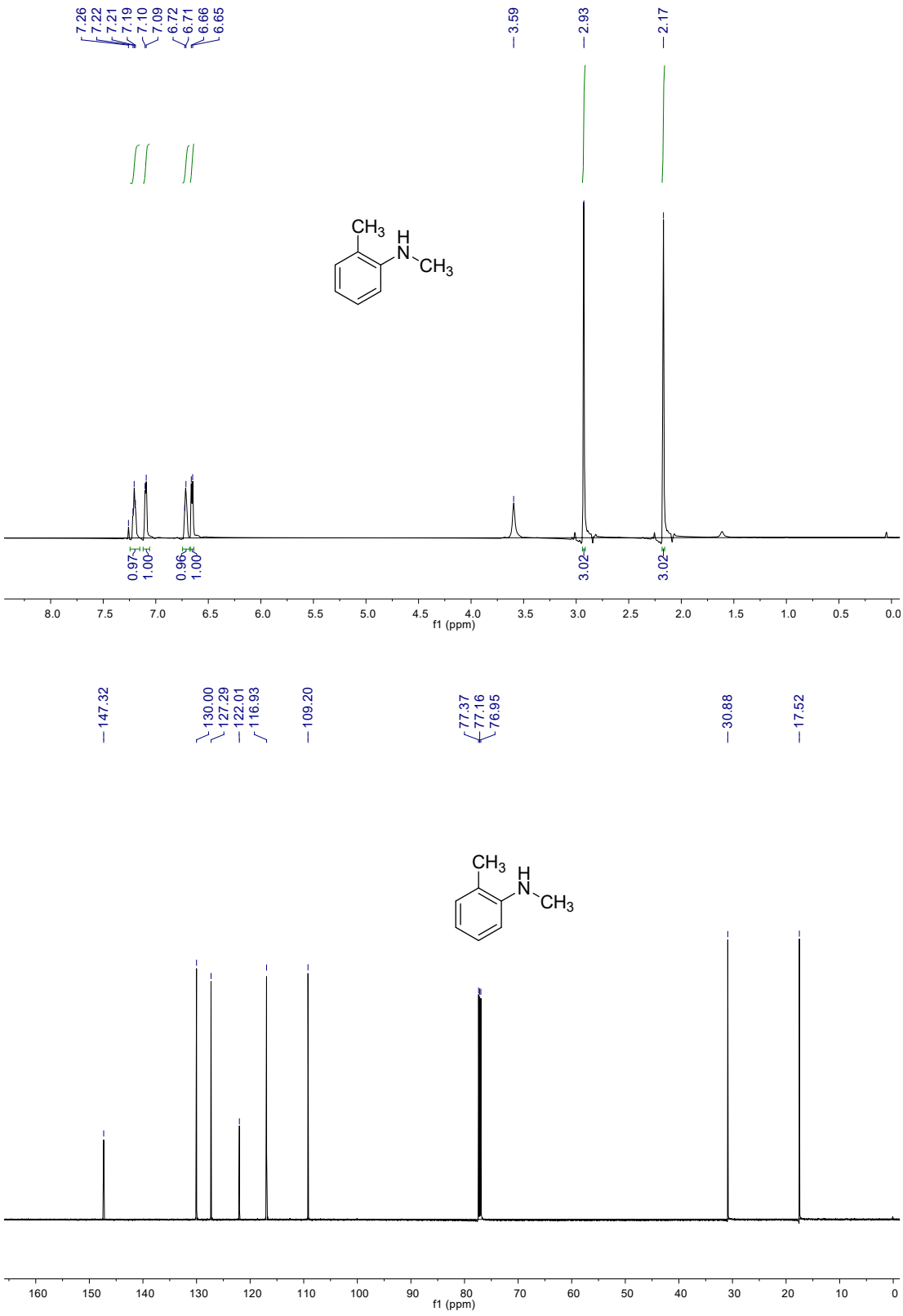
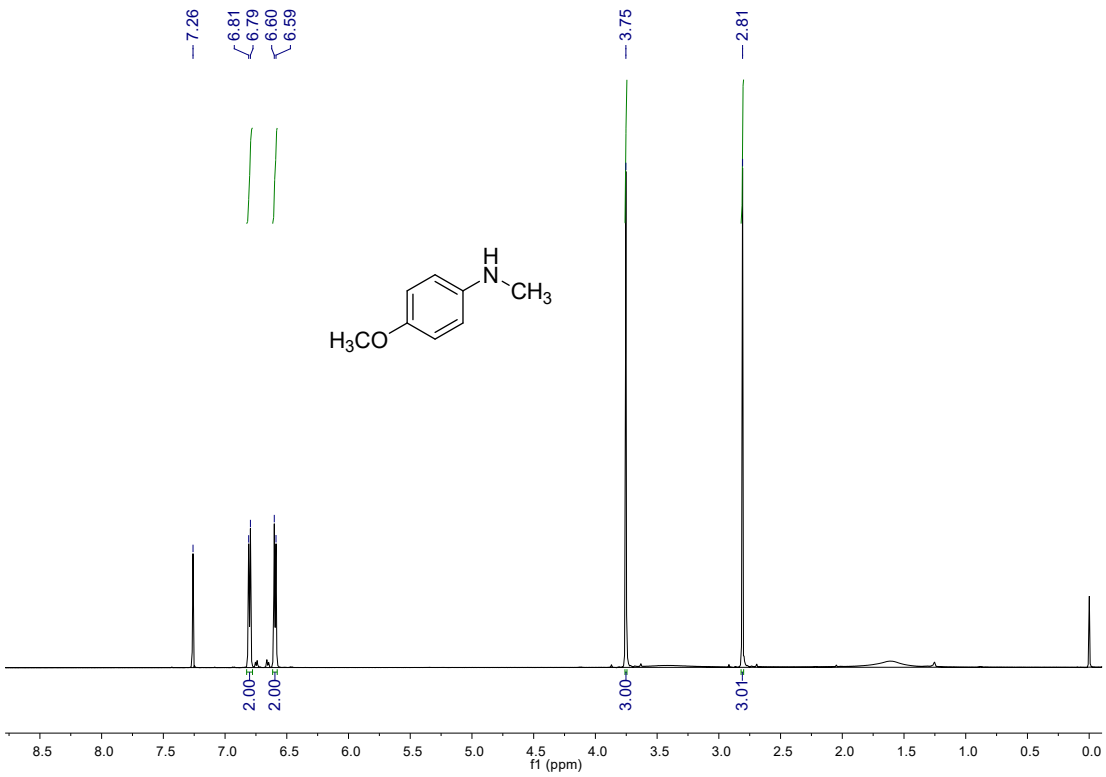
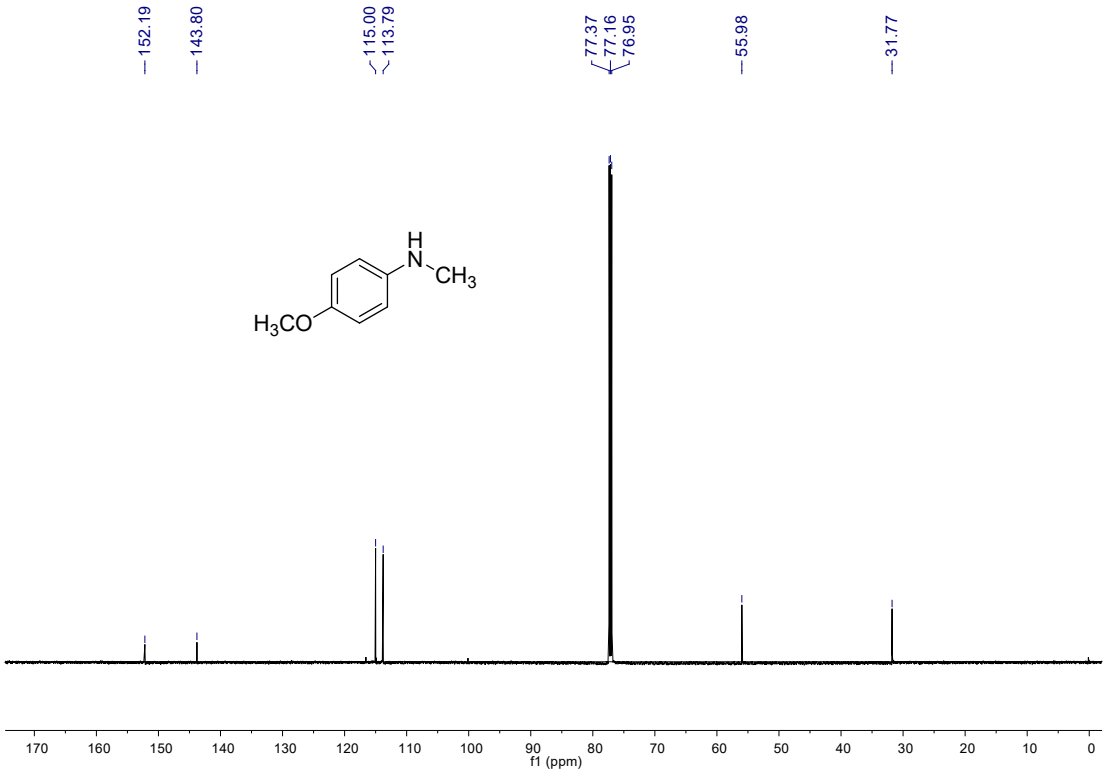


^{1}H and ^{13}C NMR Spectra of **3d**





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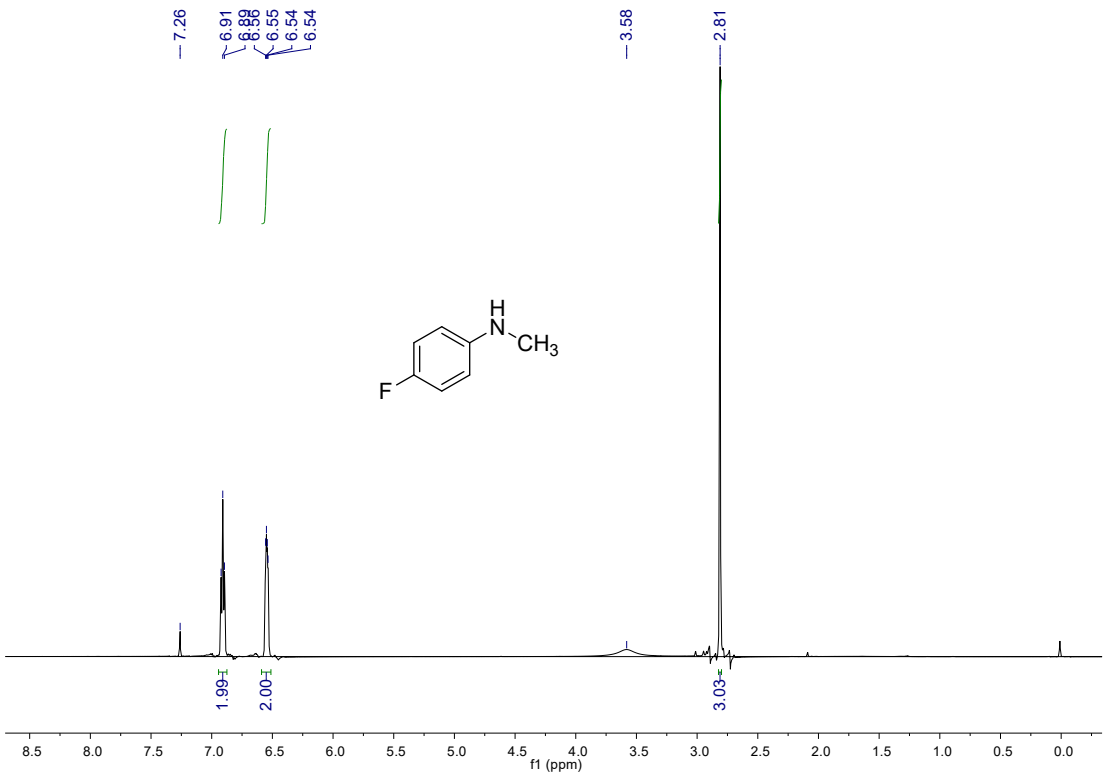

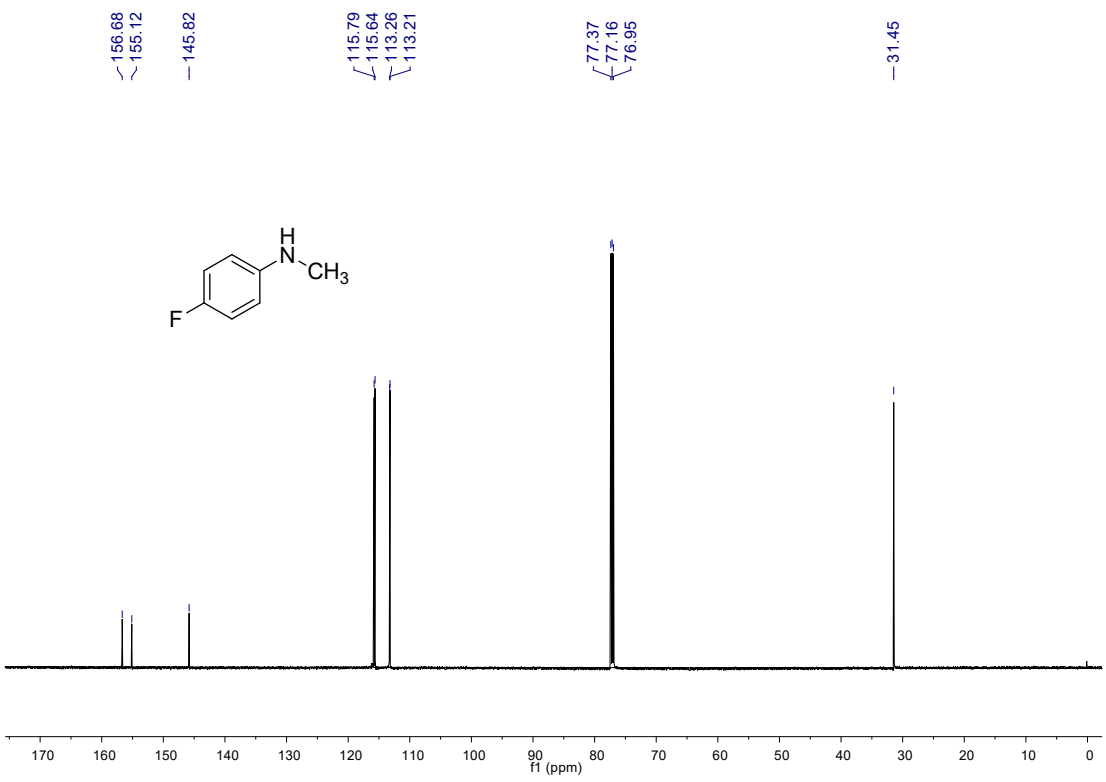

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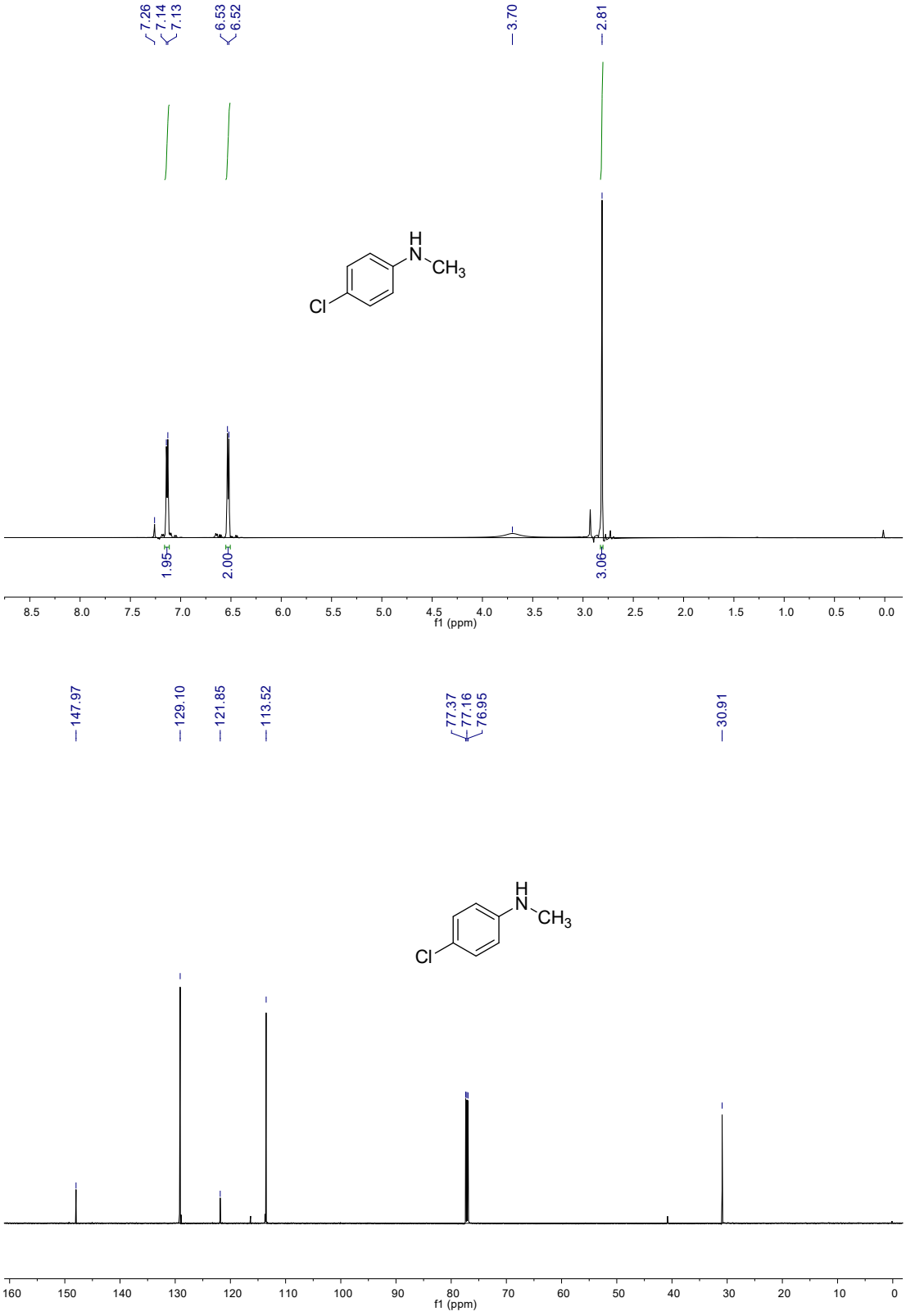

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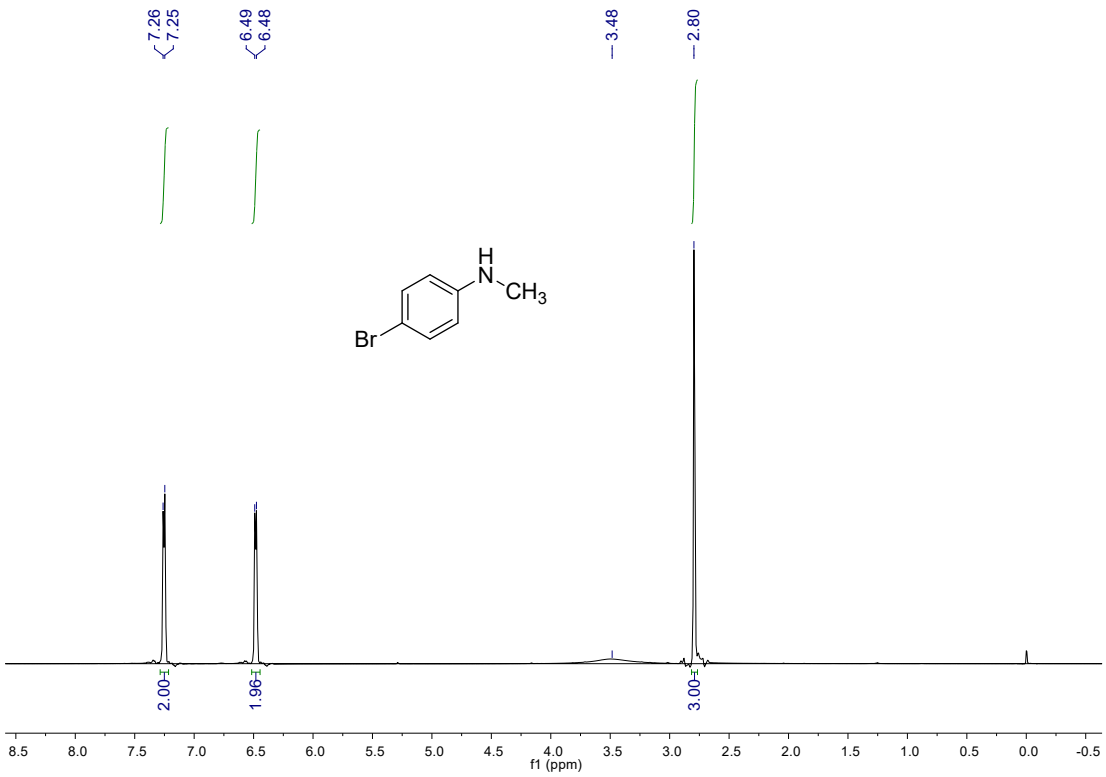

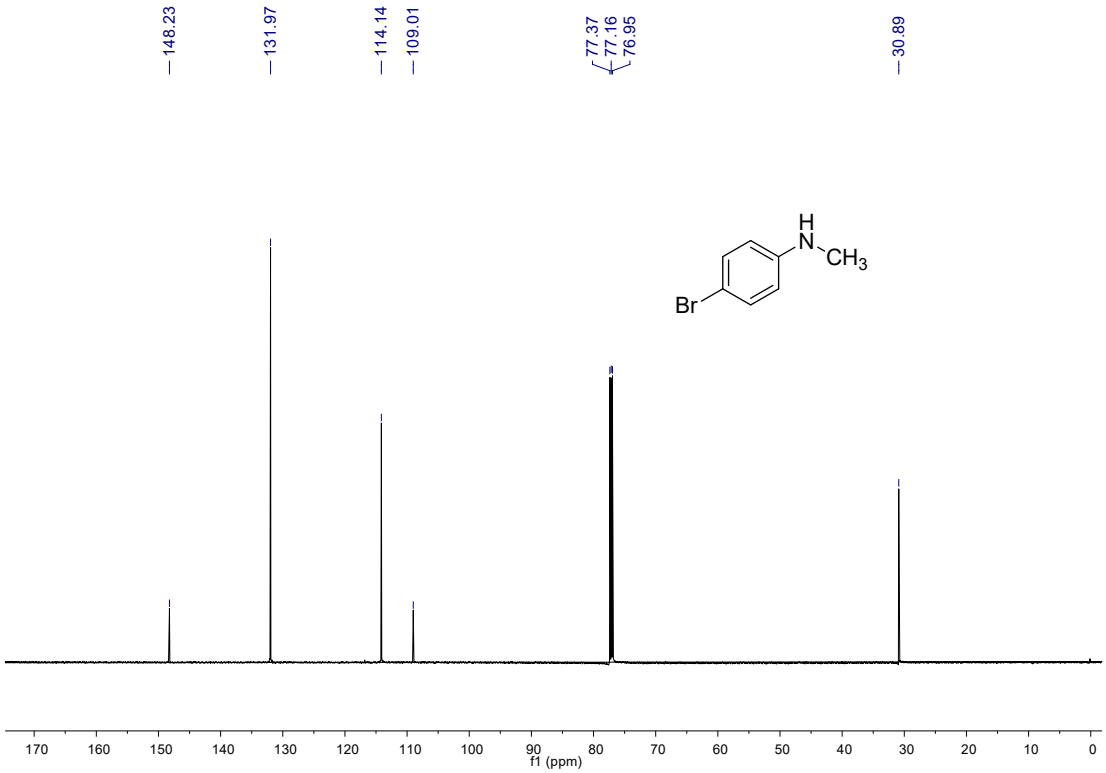

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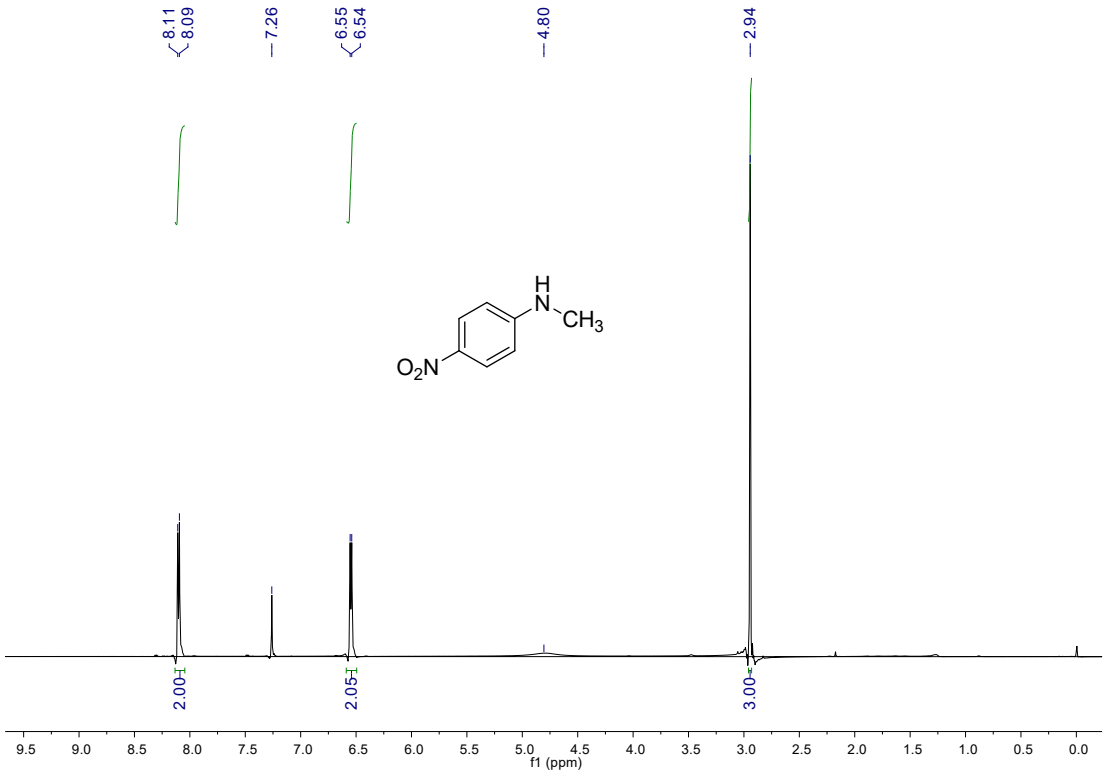
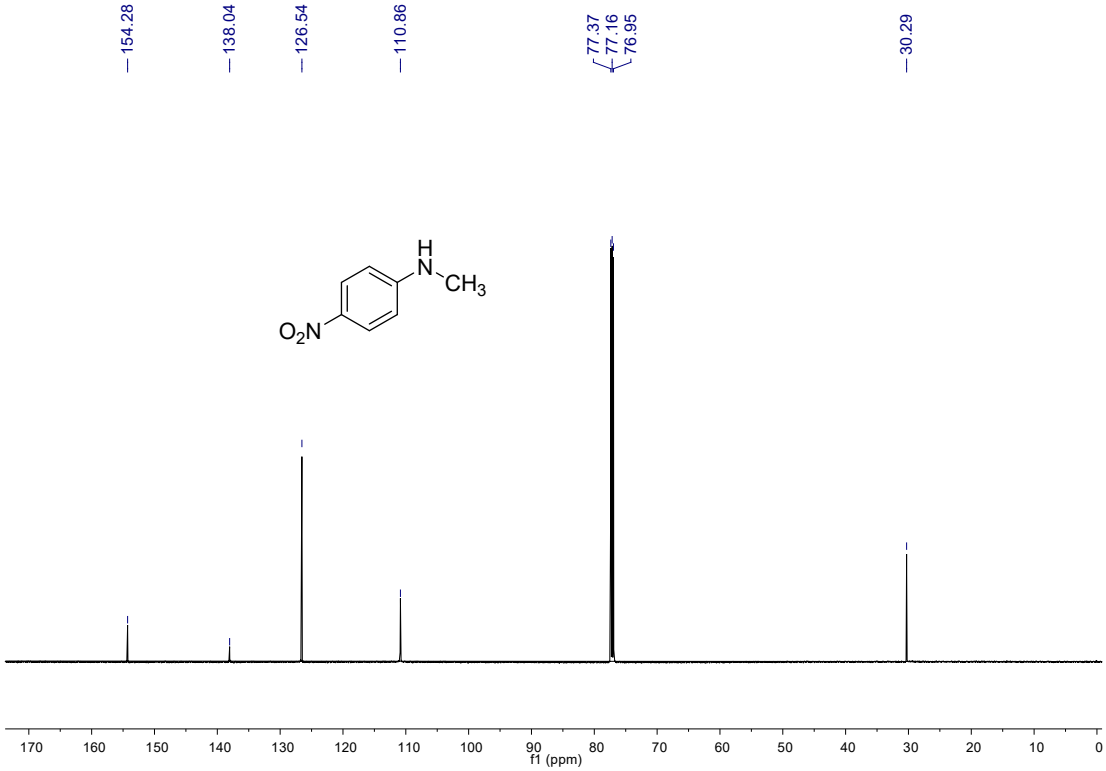
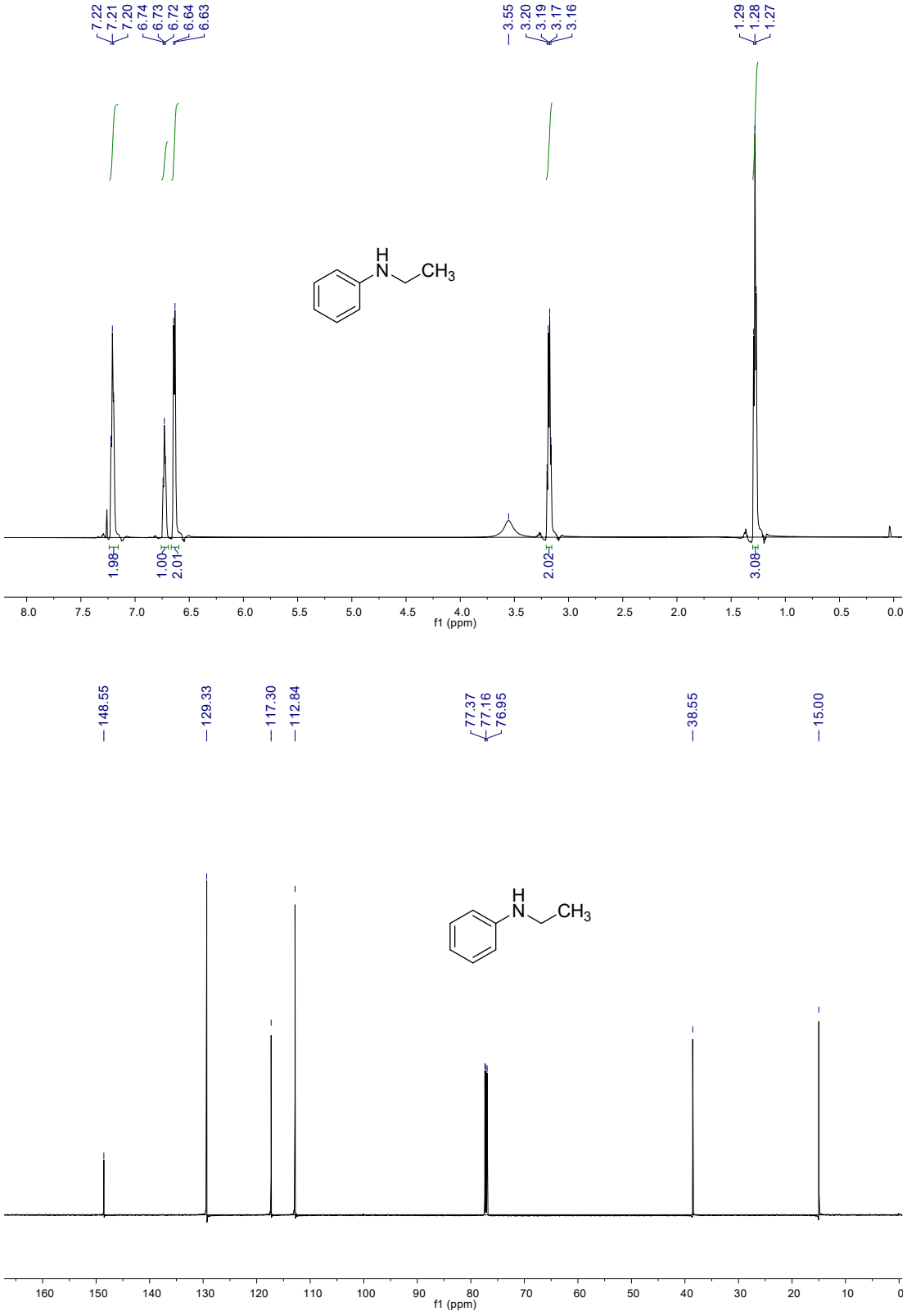




^{1}H and ^{13}C NMR Spectra of **3i**



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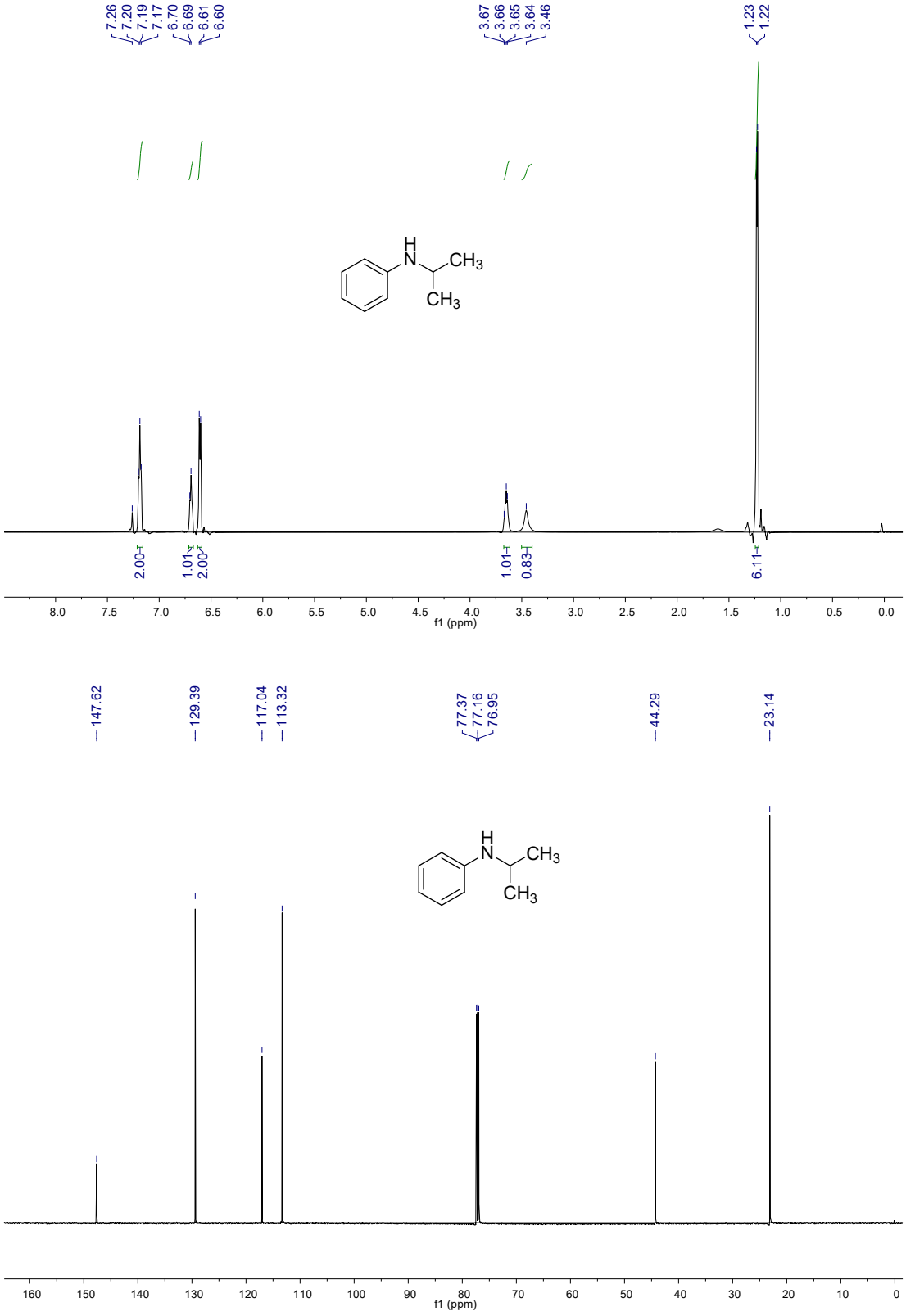

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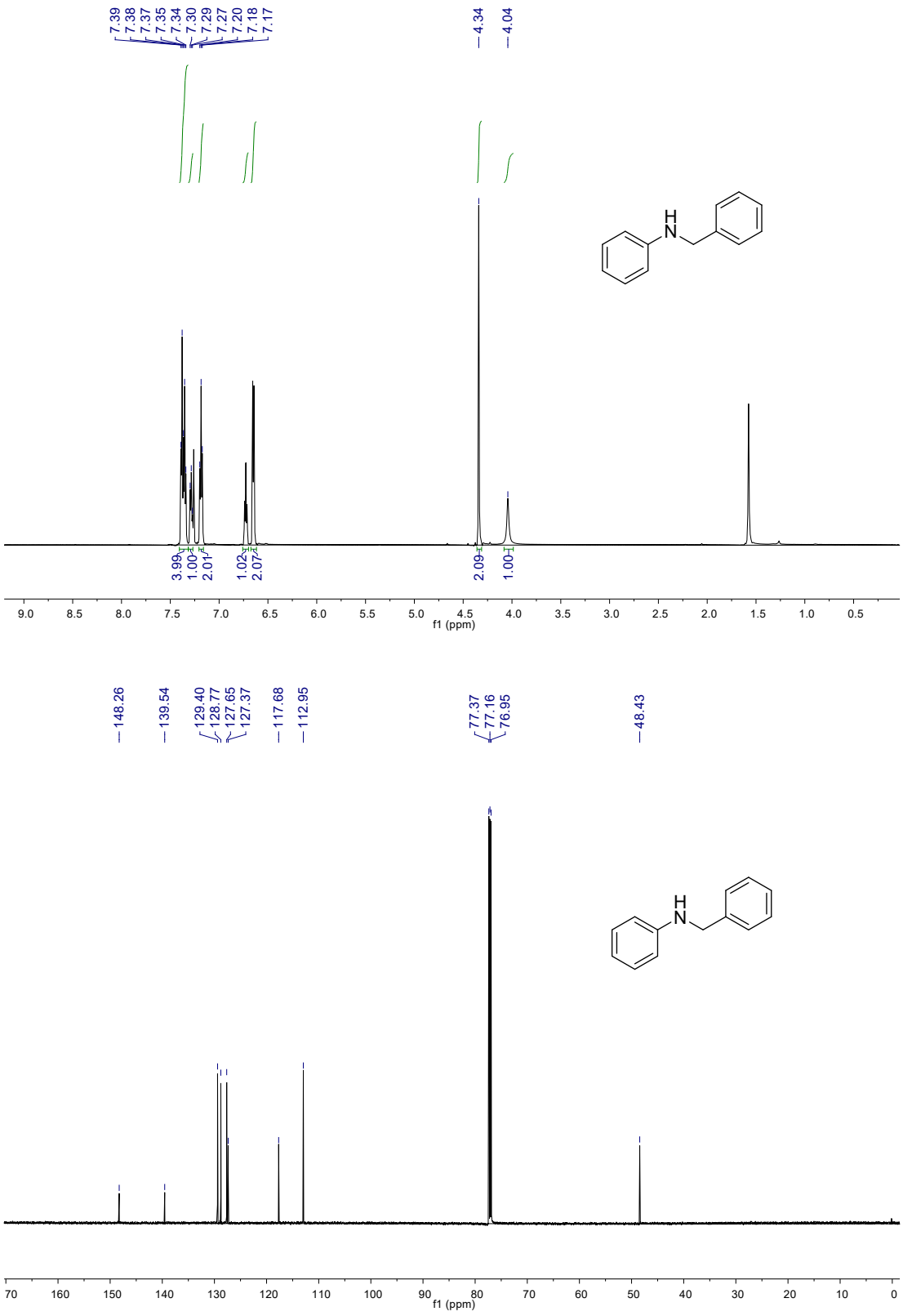

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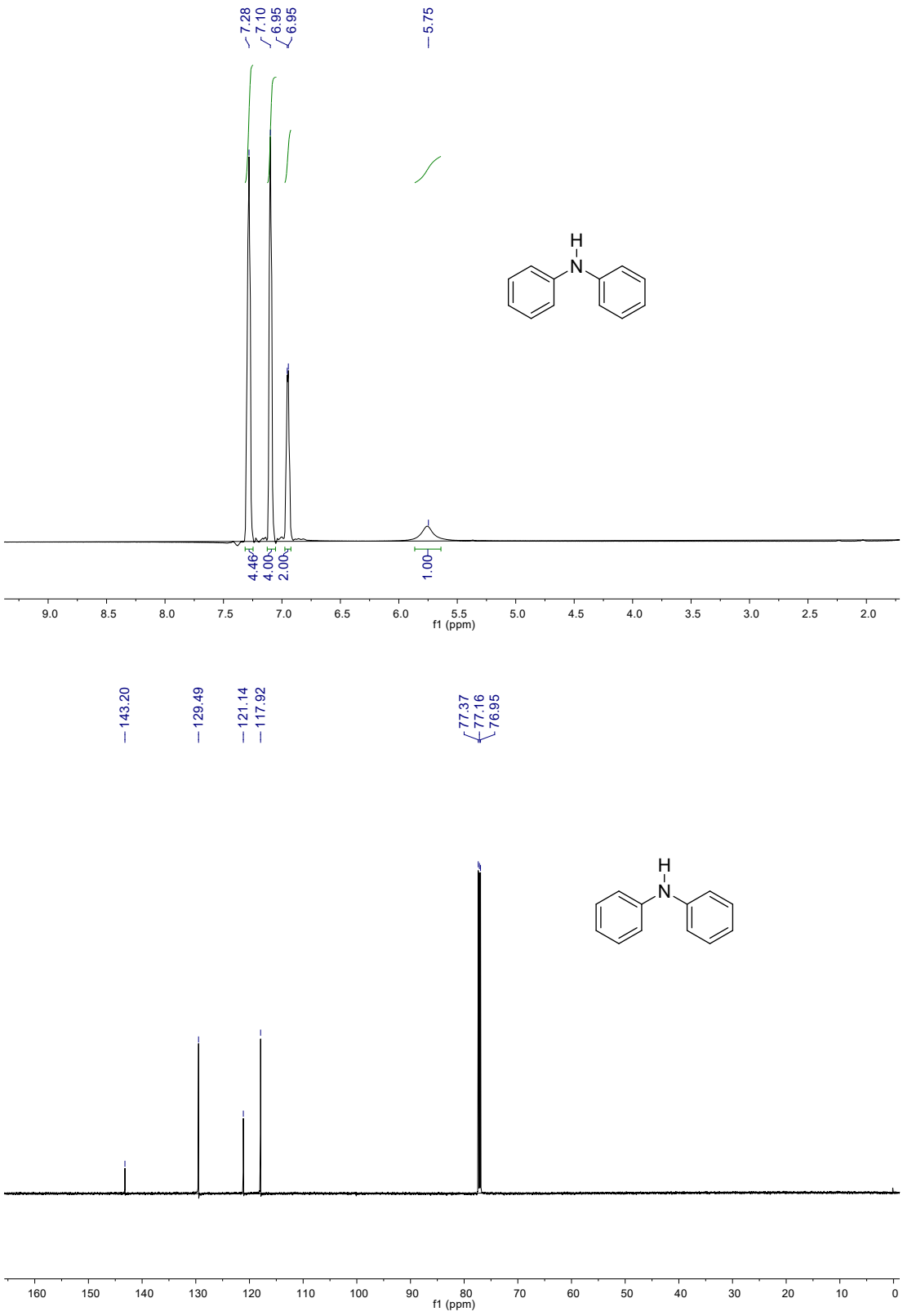

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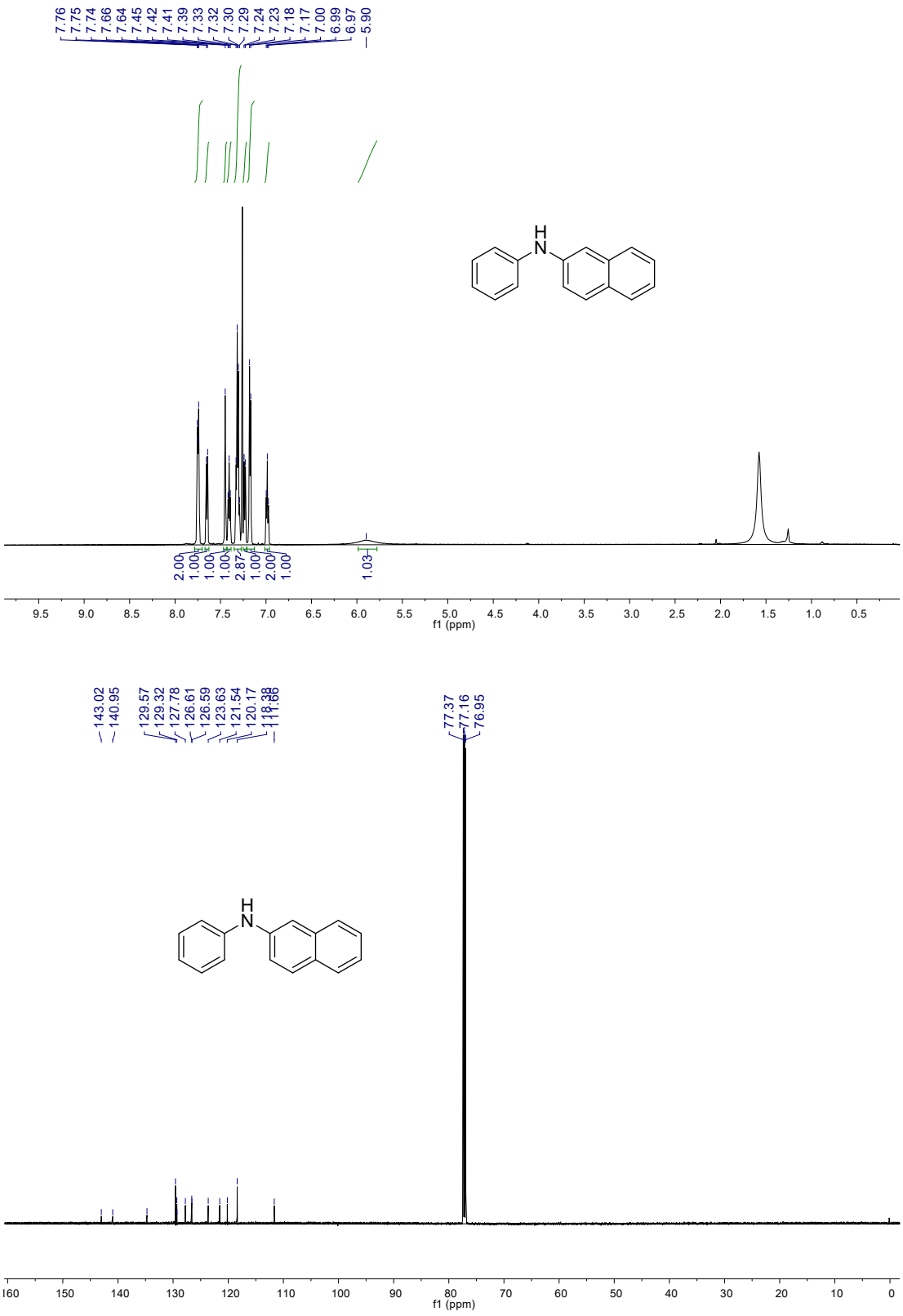

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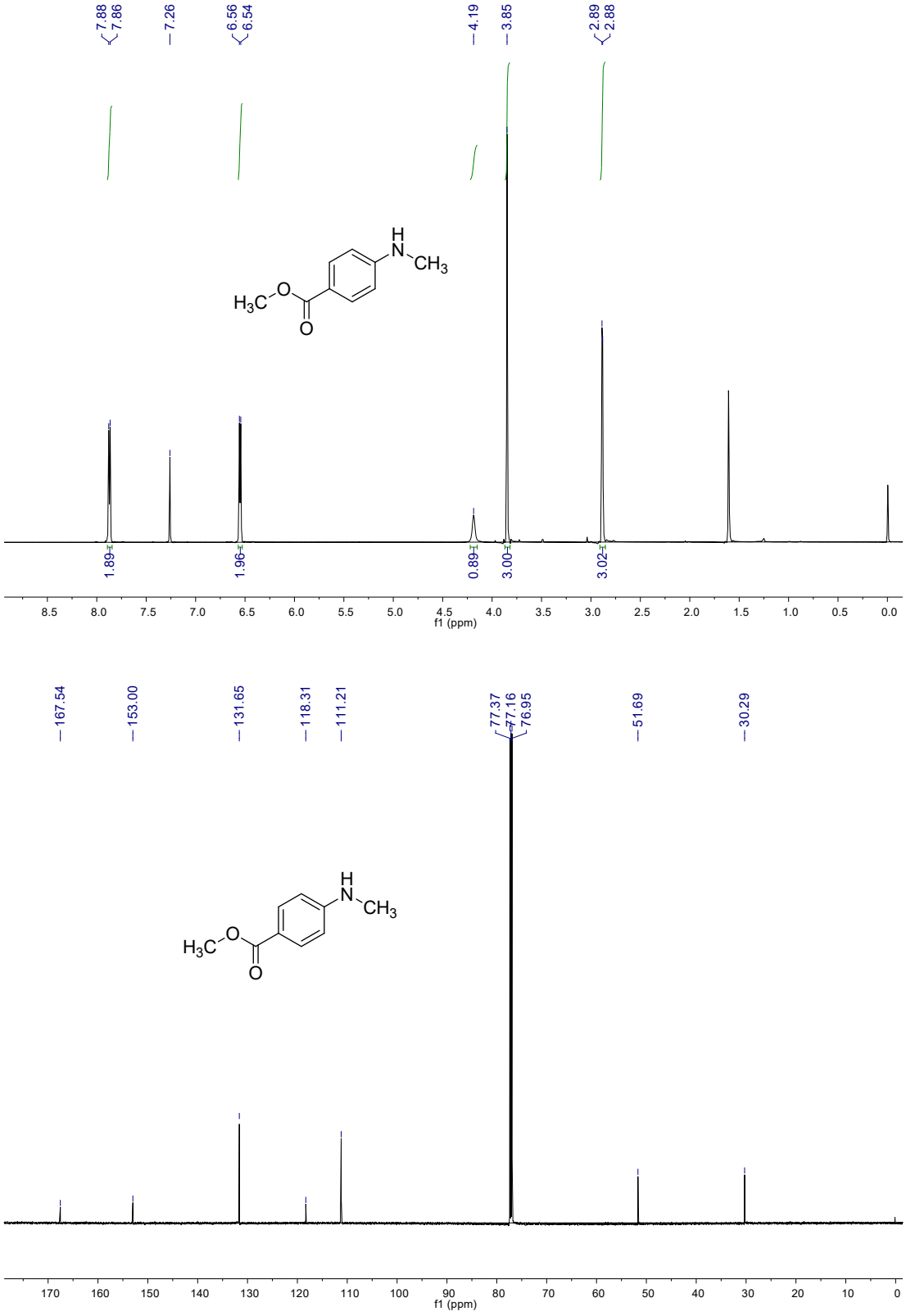
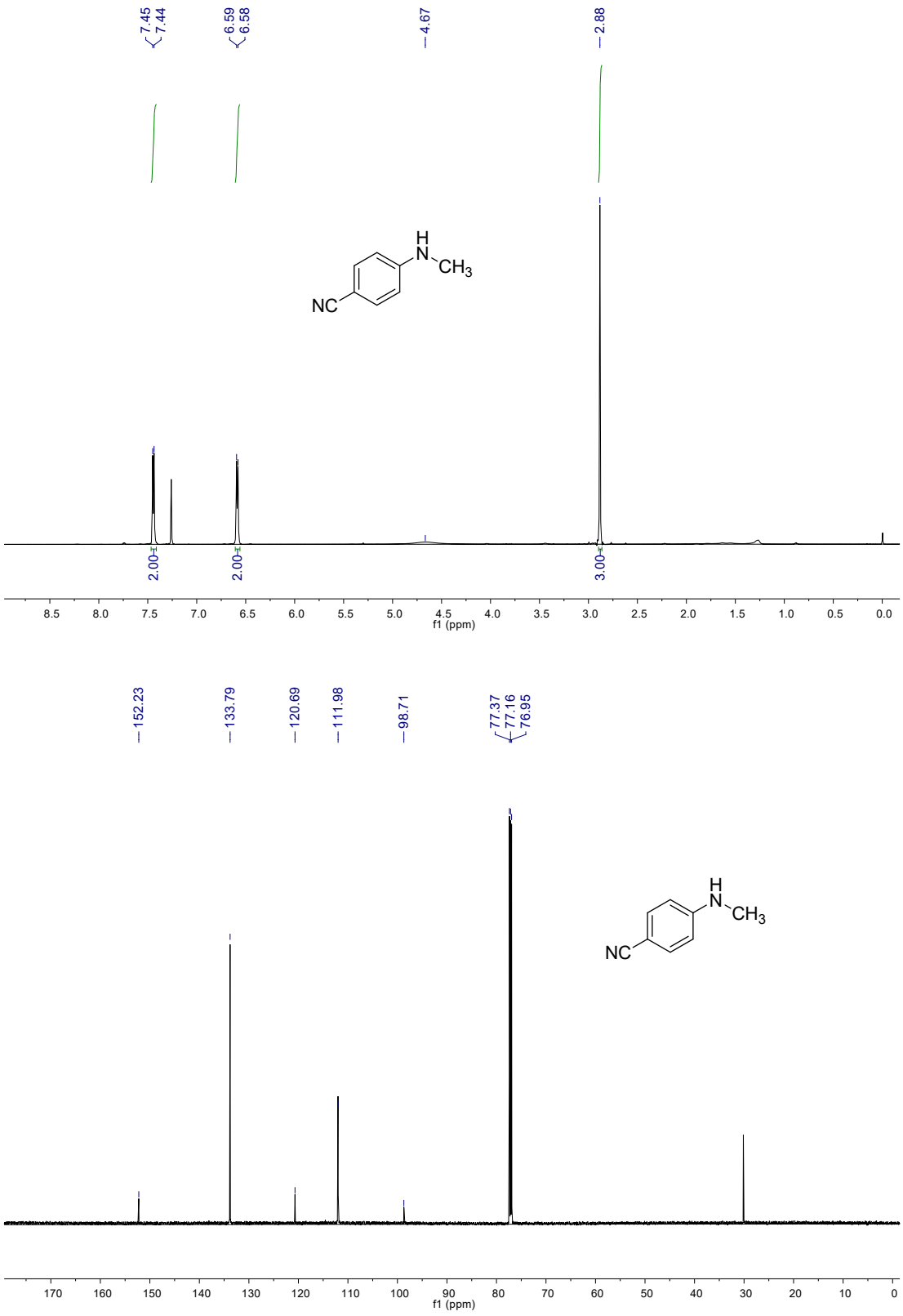
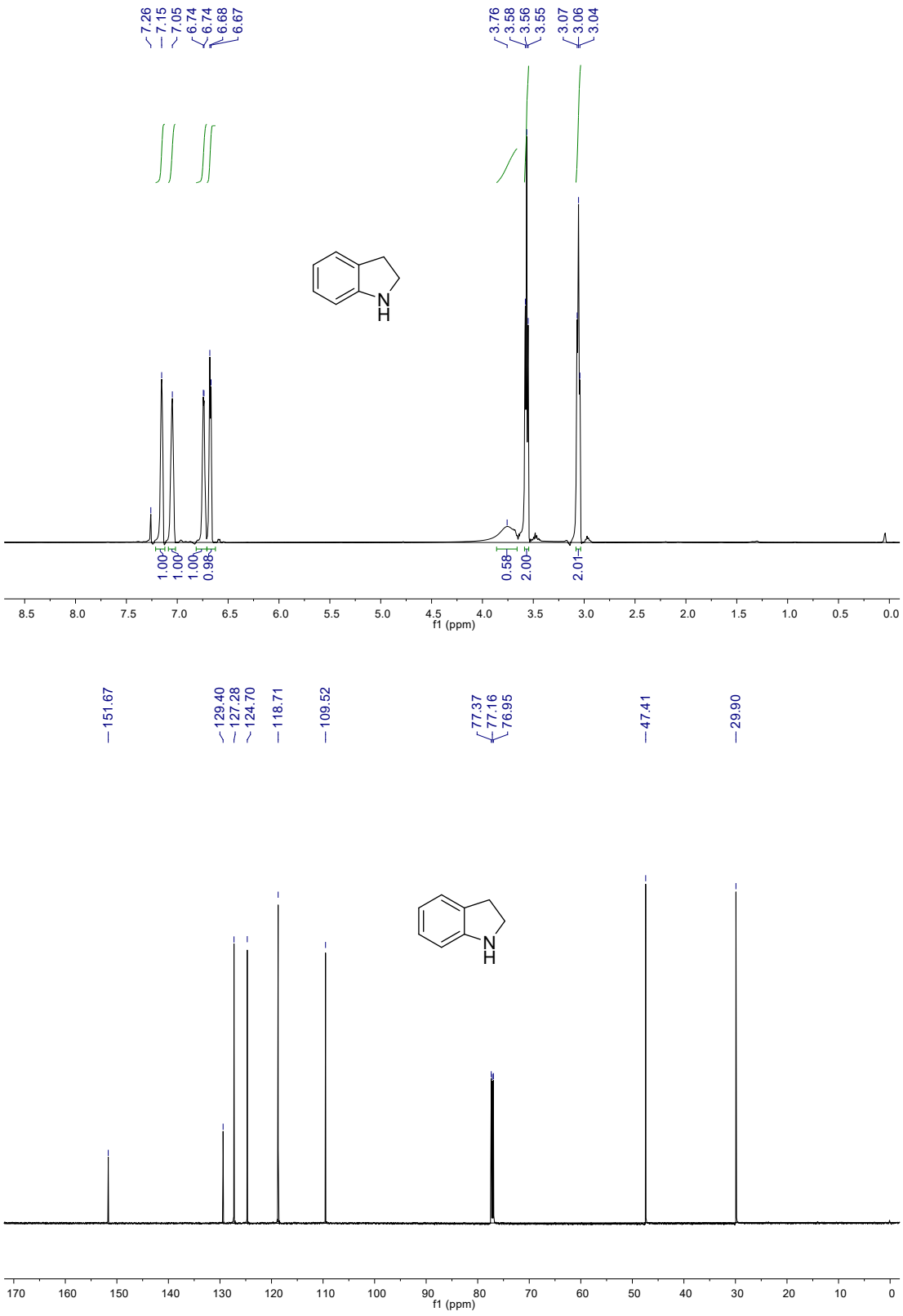


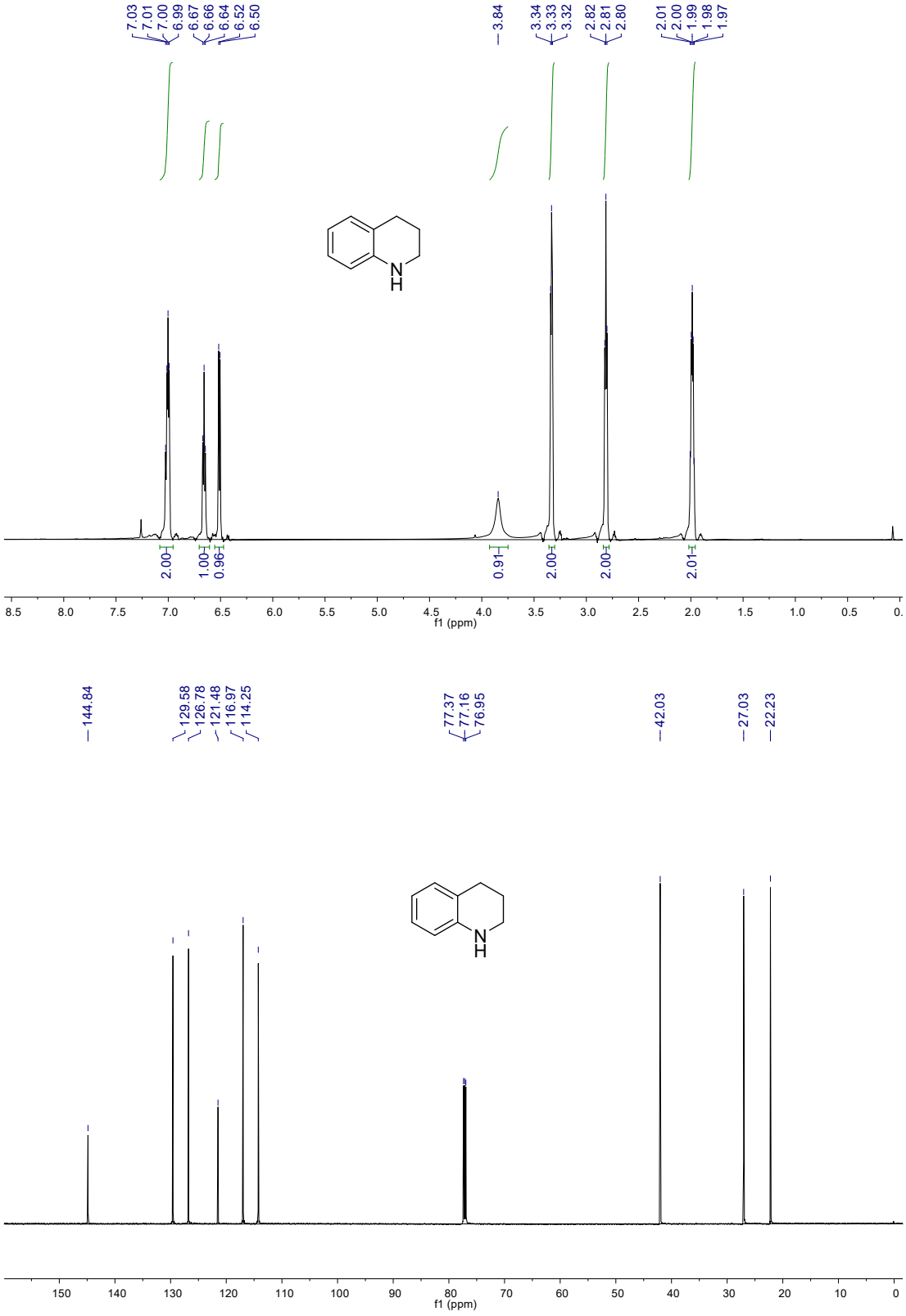
^{1}H and ^{13}C NMR Spectra of **3o**



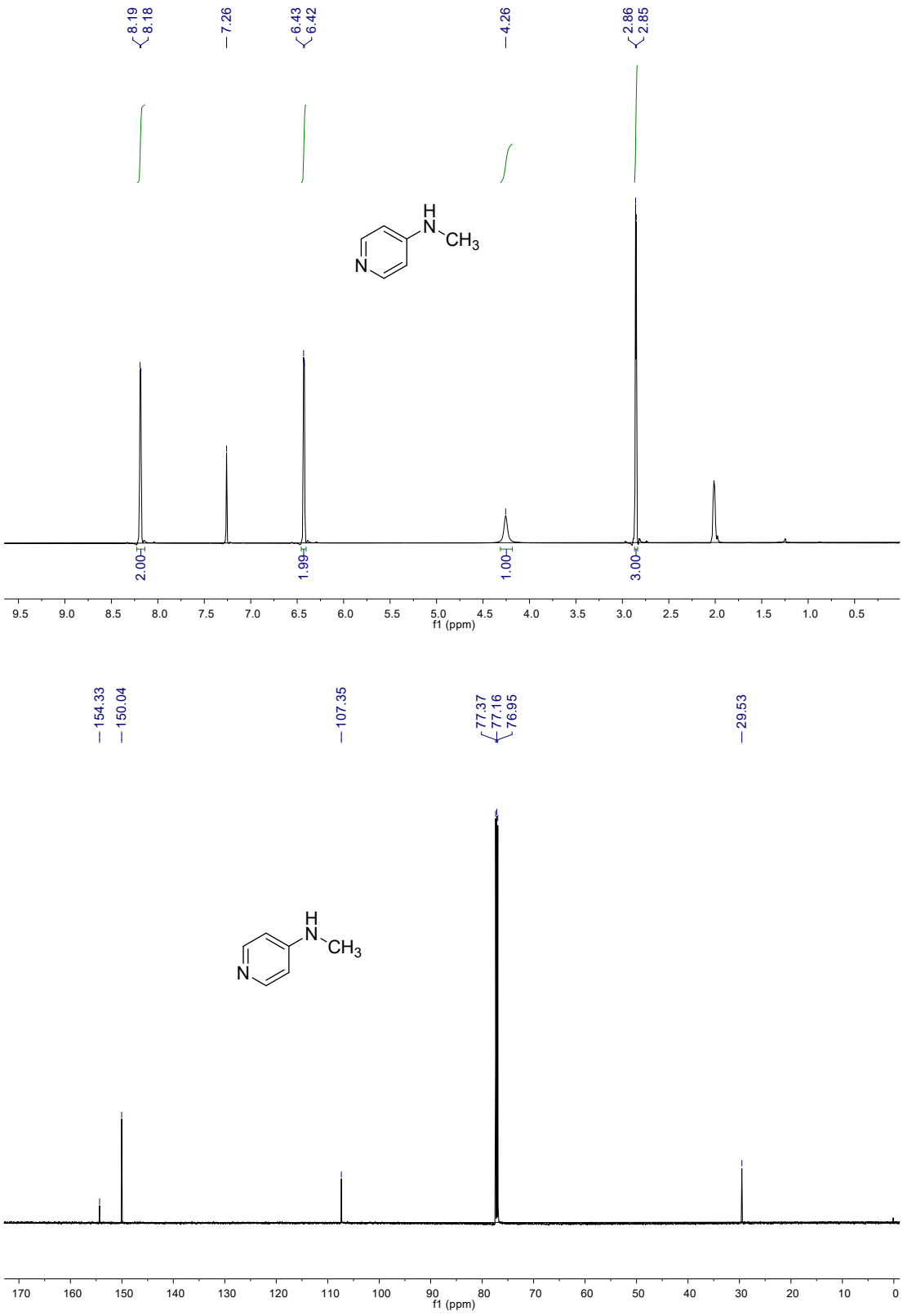
^{1}H and ^{13}C NMR Spectra of **3p**



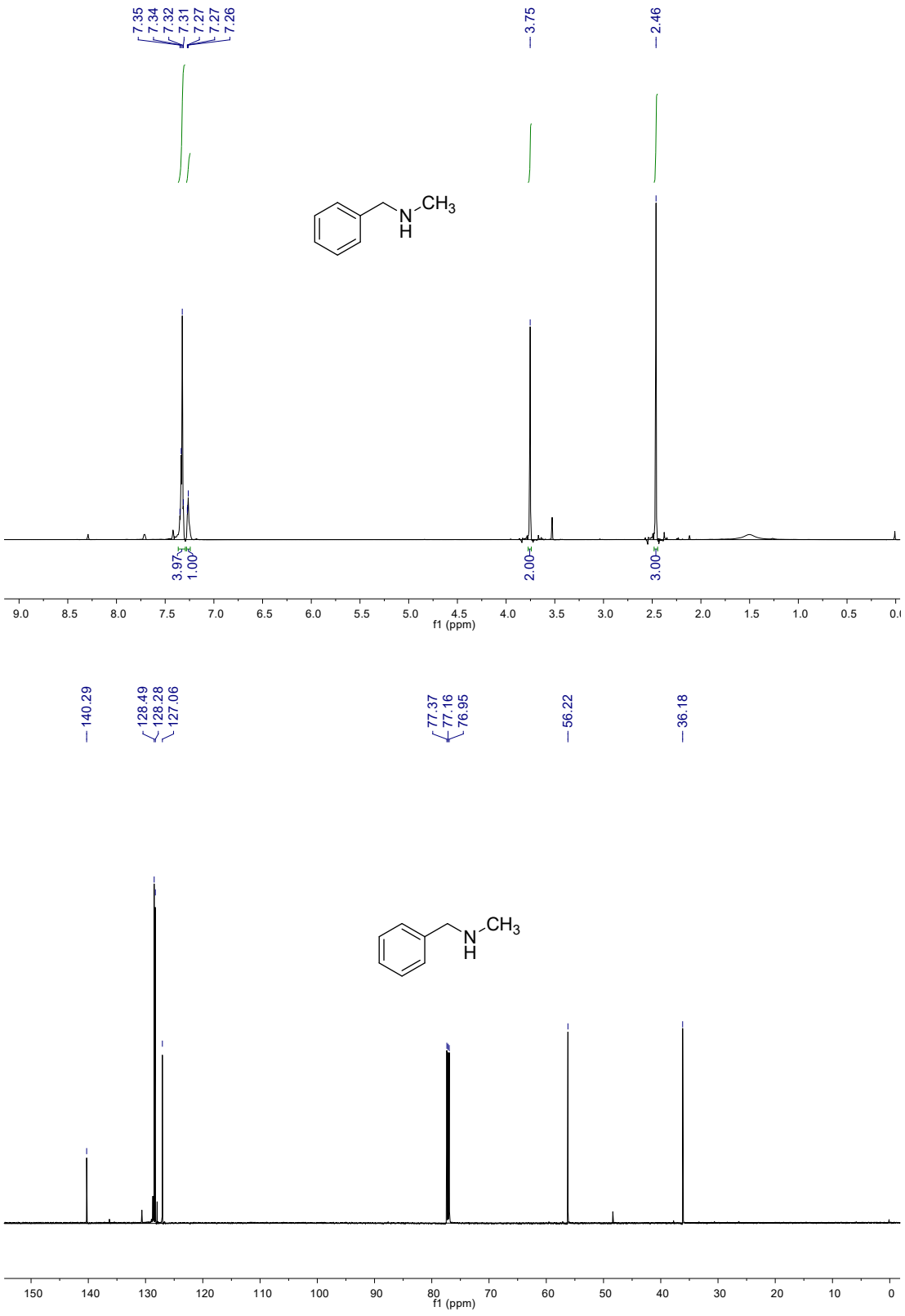
^{1}H and ^{13}C NMR Spectra of **3q**



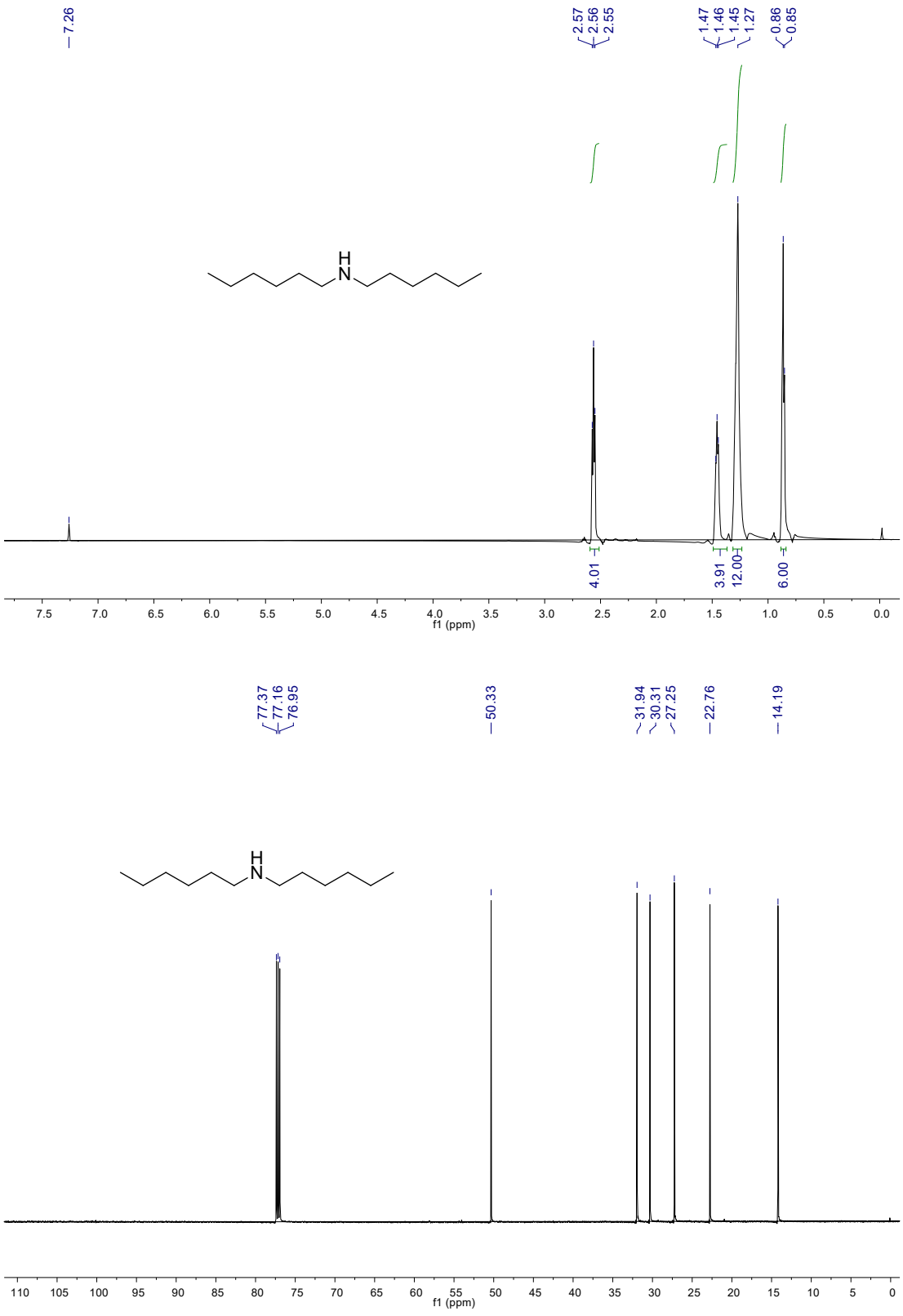
^{1}H and ^{13}C NMR Spectra of **3r**



^{1}H and ^{13}C NMR Spectra of **3s**



^{1}H and ^{13}C NMR Spectra of **3t**



^{1}H and ^{13}C NMR Spectra of **3u**