1,2-Aminohalogenation of arynes with amines and organohalides

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Supporting information

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General information

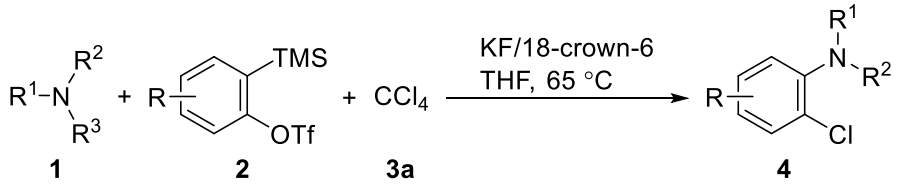
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. Infrared spectra were recorded on Thermo Scientific Nicolet iS10 spectrophotometer. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). ESI-mass data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. EI-mass data was acquired using a Thermo Q Exactive GC Orbitrap GC-MS/MS instrument equipped with an EI source and controlled by Xcalibur software. Melting points are uncorrected.

$Ph(CH_2)_3NMe_2$ (**1m**) and amines **1o-q** were prepared according to literature procedures.[1-3] The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Energy chemical, Bide Pharmatech Ltd., Accela ChemBio Co., J&K Scientific, Meryer, Acros, Alfa Aesar, and TCI.

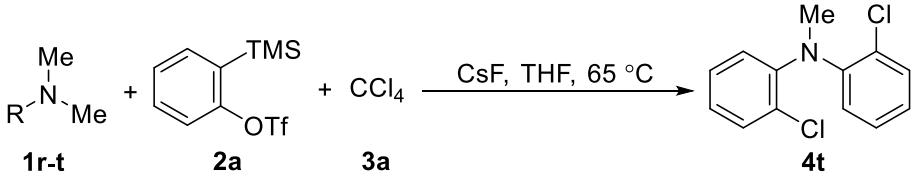
Unless otherwise noted, all the reactions were performed in oven-dried glassware with freshly distilled solvents.

Abbreviations: Bn = benzyl, DCE = 1, 2-dichloroethane, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, NBS = *N*-bromosuccinimide, NCS = *N*-chlorosuccinimide, NIS = *N*-iodosuccinimide, TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, THF = tetrahydrofuran, TMS = trimethylsilyl, Tf = trifluoromethanesulfonyl.

General procedure for the three-component reaction of amines, arynes, and carbon tetrachloride (Schemes 3 and 4)



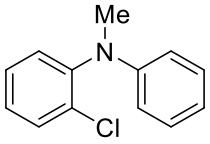
Sealed reaction tubes containing dry KF (34.9 mg, 0.60 mmol) and 18-crown-6 (159 mg, 0.60 mmol) were sequentially added tetrahydrofuran (0.20 mL), carbon tetrachloride (**3a**) (0.10 mL), amine **1** (0.20 mmol), and 2-(trimethylsilyl)aryl triflate **2** (0.30 mmol). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:4 to 0:1 v/v), to give compound **4**.



Sealed reaction tubes containing dry CsF (91.1 mg, 0.60 mmol) were sequentially added tetrahydrofuran (0.20 mL), carbon tetrachloride (**3a**) (0.10 mL), amine **1r-t** (0.20 mmol), and 2-(trimethylsilyl)phenyl triflate (**2a**) (89.5 mg, 0.30 mmol). The mixture was stirred at 65 °C for 12 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture

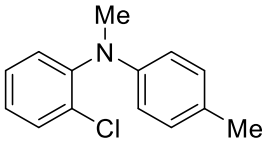
eluent of ethyl acetate and petroleum ether (1:40 v/v), to give compound **4t**.

Analytical data for the products (Schemes 3 and 4)



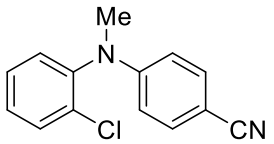
4a

2-Chloro-*N*-methyl-*N*-phenylaniline (**4a**). Yellow oil (41.3 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.29-7.24 (m, 2H), 7.21-7.15 (m, 3H), 6.75 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 8.0 Hz, 2H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 145.4, 133.7, 131.0, 130.3, 129.1, 128.3, 127.4, 117.9, 113.6, 39.1; IR (film, ν/cm^{-1}) 3069, 2983, 2924, 2820, 1592, 1478, 1420, 1213, 1144, 1050, 995, 921, 845, 758, 599; HRMS (ESI) calcd for $C_{13}H_{13}N^{35}Cl^{+}$ $(M + H)^{+}$ 218.0731, found 218.0735.



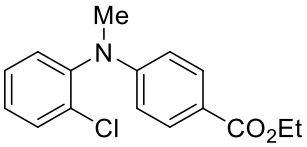
4b

2-Chloro-*N*-methyl-*N*-(*p*-tolyl)aniline (**4b**). Yellow oil (41.8 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 1H), 7.27-7.21 (m, 2H), 7.17-7.12 (m, 1H), 7.01-6.96 (m, 2H), 6.55-6.50 (m, 2H), 3.21 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 145.9, 133.4, 131.0, 129.8, 129.6, 128.2, 127.3, 127.0, 114.1, 39.3, 20.5; IR (film, ν/cm^{-1}) 3035, 2915, 1617, 1513, 1479, 1333, 1050, 903, 809, 731, 651; HRMS (ESI) calcd for $C_{14}H_{15}N^{35}Cl^{+}$ $(M + H)^{+}$ 232.0888, found 232.0881.



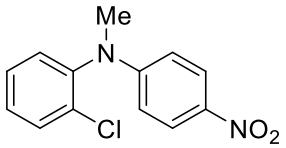
4c

4-((2-Chlorophenyl)(methyl)amino)benzonitrile (**4c**). Yellow oil (38.6 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.39-7.30 (m, 2H), 7.27 (dd, J = 7.6, 1.6 Hz, 1H), 6.52 (d, J = 8.8 Hz, 2H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 143.1, 133.6, 133.4, 131.2, 130.4, 128.9, 128.7, 120.4, 112.5, 99.2, 38.9; IR (film, ν/cm^{-1}) 3069, 2924, 2829, 2219, 1599, 1513, 1481, 1359, 1178, 1050, 904, 826, 731; HRMS (ESI) calcd for $C_{14}H_{12}N_2{}^{35}Cl^{+}$ $(M + H)^{+}$ 243.0684, found 243.0681.



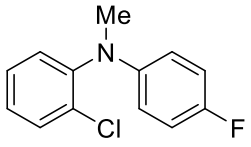
4d

Ethyl 4-((2-chlorophenyl)(methyl)amino)benzoate (**4d**). Yellow oil (35.7 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 2H), 7.49 (dd, J = 8.0, 1.2 Hz, 1H), 7.34-7.22 (m, 3H), 6.51 (d, J = 8.8 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 3.27 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 151.8, 143.8, 133.6, 131.1, 131.0, 130.4, 128.5, 128.4, 119.0, 111.8, 60.2, 38.9, 14.4; IR (film, ν/cm^{-1}) 3069, 2983, 2897, 1703, 1608, 1512, 1478, 1356, 1273, 1178, 1100, 1049, 833, 766, 732, 689; HRMS (ESI) calcd for $C_{16}H_{17}O_2N^{35}Cl^+$ $(M + H)^+$ 290.0942, found 290.0936.



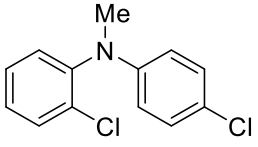
4e

2-Chloro-*N*-methyl-*N*-(4-nitrophenyl)aniline (**4e**). Pale green oil (44.7 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 9.2 Hz, 2H), 7.56 (dd, J = 7.6, 1.6 Hz, 1H), 7.40 (td, J = 7.6, 1.6 Hz, 1H), 7.35 (td, J = 7.6, 2.0 Hz, 1H), 7.30 (dd, J = 7.6, 2.0 Hz, 1H), 6.49 (d, J = 9.2 Hz, 2H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.9, 138.5, 133.5, 131.4, 130.3, 129.3, 128.9, 126.0, 111.6, 39.4; IR (film, ν/cm^{-1}) 3078, 2924, 2855, 1591, 1488, 1307, 1187, 1101, 1058, 911, 826, 735, 679; HRMS (ESI) calcd for $C_{13}H_{12}O_2N_2^{35}Cl^+$ $(M + H)^+$ 263.0582, found 263.0583.



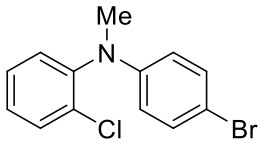
4f

2-Chloro-*N*-(4-fluorophenyl)-*N*-methylaniline (**4f**). Yellow oil (43.4 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 8.0, 1.6 Hz, 1H), 7.28-7.13 (m, 3H), 6.91-6.84 (m, 2H), 6.56-6.50 (m, 2H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3 (d, J = 235.0 Hz), 145.7, 145.3 (d, J = 1.8 Hz), 133.3, 131.1, 129.7, 128.3, 127.3, 115.5 (d, J = 22.1 Hz), 115.0 (d, J = 7.4 Hz), 39.6; IR (film, ν/cm^{-1}) 3061, 2915, 2811, 1505, 1479, 1333, 1230, 1050, 809, 756, 735; HRMS (ESI) calcd for $C_{13}H_{12}N^{35}ClF^+$ $(M + H)^+$ 236.0637, found 236.0635.



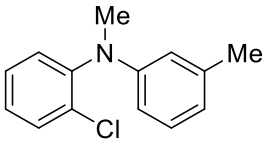
4g

2-Chloro-*N*-(4-chlorophenyl)-*N*-methylaniline (**4g**). Yellow oil (46.2 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.0, 1.6 Hz, 1H), 7.30-7.17 (m, 3H), 7.13-7.07 (m, 2H), 6.51-6.45 (m, 2H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 144.9, 133.6, 131.1, 130.2, 128.9, 128.4, 127.8, 122.7, 114.6, 39.2; IR (film, ν/cm^{-1}) 3061, 2945, 2889, 1591, 1488, 1340, 1247, 1050, 904, 817, 731, 679; HRMS (ESI) calcd for $C_{13}H_{12}N^{35}Cl_2^+$ $(M + H)^+$ 252.0341, found 252.0332.



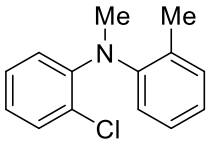
4h

N-(4-Bromophenyl)-2-chloro-*N*-methylaniline (**4h**). Colorless oil (54.1 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 8.0, 1.2 Hz, 1H), 7.33-7.20 (m, 5H), 6.47-6.42 (m, 2H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 144.8, 133.7, 131.8, 131.2, 130.2, 128.5, 127.9, 115.0, 109.9, 39.2; IR (film, ν/cm^{-1}) 3068, 2932, 2819, 1582, 1488, 1341, 1247, 1051, 809, 740, 679; HRMS (ESI) calcd for $C_{13}H_{12}N^{79}Br^{35}Cl^{+}$ $(M + H)^{+}$ 295.9836, found 295.9829.



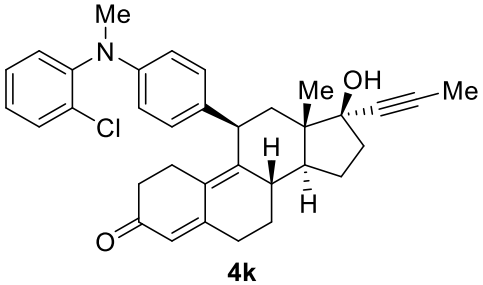
4i

2-Chloro-*N*-methyl-*N*-(*m*-tolyl)aniline (**4i**). Yellow oil (42.7 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 1H), 7.30-7.24 (m, 2H), 7.21-7.16 (m, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 7.6 Hz, 1H), 6.44-6.38 (m, 2H), 3.22 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 145.5, 138.8, 133.7, 131.0, 130.3, 128.9, 128.2, 127.4, 118.9, 114.3, 110.9, 39.1, 21.9; IR (film, ν/cm^{-1}) 3044, 2924, 1608, 1575, 1488, 1350, 1050, 758, 731, 689; HRMS (ESI) calcd for $C_{14}H_{15}N^{35}Cl^{+}$ $(M + H)^{+}$ 232.0888, found 232.0887.



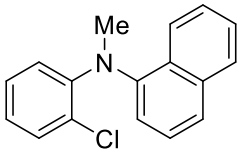
4j

2-Chloro-*N*-methyl-*N*-(*o*-tolyl)aniline (**4j**). Yellow oil (36.0 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.0, 1.6 Hz, 1H), 7.18-7.09 (m, 3H), 7.03-6.97 (m, 2H), 6.97-6.92 (m, 1H), 6.90 (dd, J = 8.0, 1.6 Hz, 1H), 3.15 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 148.4, 133.0, 131.5, 131.0, 129.3, 127.6, 126.7, 124.2, 124.0, 123.6, 121.4, 41.1, 18.6; IR (film, ν/cm^{-1}) 3061, 2958, 1582, 1479, 1316, 1235, 1050, 912, 758, 731, 672; HRMS (ESI) calcd for $C_{14}H_{15}N^{35}Cl^{+}$ $(M + H)^{+}$ 232.0888, found 232.0881.



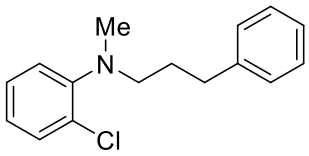
4k

(8*S*,11*R*,13*S*,14*S*,17*S*)-11-(4-((2-Chlorophenyl)(methyl)amino)phenyl)-17-hydroxy-13-methyl-17-(prop-1-yn-1-yl)-1,2,6,7,8,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one (**4k**). Pale green oil (70.1 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 1H), 7.27-7.23 (m, 2H), 7.19-7.14 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 8.4 Hz, 2H), 5.75 (s, 1H), 4.35 (br, 1H), 3.21 (s, 3H), 2.81-2.72 (m, 1H), 2.58-2.52 (m, 2H), 2.48-2.18 (m, 8H), 2.03-1.90 (m, 2H), 1.87 (s, 3H), 1.77-1.66 (m, 2H), 1.49-1.30 (m, 2H), 0.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 157.1, 146.9, 146.5, 145.5, 133.4, 133.2, 130.9, 129.9, 129.0, 128.1, 127.3, 127.1, 122.6, 113.8, 82.4, 82.3, 80.0, 49.8, 46.8, 39.6, 39.1, 39.0, 38.8, 36.8, 31.1, 27.3, 25.8, 23.3, 13.8, 3.9; IR (film, ν/cm^{-1}) 3422, 2941, 2880, 2245, 1651, 1505, 1488, 1341, 1238, 1041, 912, 731, 644; HRMS (ESI) calcd for $C_{34}H_{37}O_2N^{35}Cl^+$ $(M + H)^+$ 526.2507, found 526.2512.



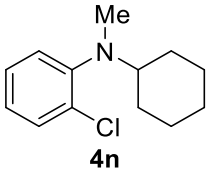
4l

N-(2-Chlorophenyl)-*N*-methylnaphthalen-1-amine (**4l**). Yellow oil (48.8 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.42-7.32 (m, 4H), 7.10-7.04 (m, 2H), 6.96-6.91 (m, 2H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 147.3, 135.0, 131.1, 129.3, 129.0, 128.3, 127.6, 125.9, 125.8, 125.7, 124.5, 124.3, 124.1, 123.8, 118.5, 42.0; IR (film, ν/cm^{-1}) 3052, 2958, 1565, 1480, 1393, 1308, 1101, 1041, 908, 771, 721; HRMS (ESI) calcd for $C_{17}H_{15}N^{35}Cl^+$ $(M + H)^+$ 268.0888, found 268.0893.



4m

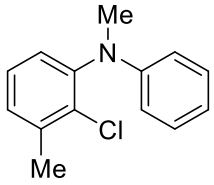
2-Chloro-*N*-methyl-*N*-(3-phenylpropyl)aniline (**4m**). Colorless oil (26.8 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.29-7.24 (m, 2H), 7.21-7.14 (m, 4H), 7.04 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.96-6.91 (m, 1H), 3.07-3.01 (m, 2H), 2.77 (s, 3H), 2.67-2.61 (m, 2H), 1.93-1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 142.2, 130.8, 129.2, 128.5, 128.4, 127.4, 125.9, 123.4, 121.5, 55.1, 41.2, 33.3, 29.1; IR (film, ν/cm^{-1}) 3061, 3018, 2932, 2855, 2803, 1591, 1479, 1452, 1290, 1041, 953, 749, 697; HRMS (ESI) calcd for $C_{16}H_{19}N^{35}Cl^+$ $(M + H)^+$ 260.1201, found 260.1193.



4n

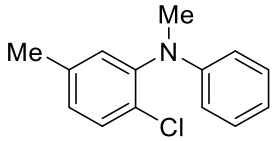
2-Chloro-*N*-cyclohexyl-*N*-methylaniline (**4n**). Yellow oil (34.8 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.06 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.93-6.88 (m, 1H), 3.14 (tt, *J* = 11.6, 3.2 Hz, 1H), 2.70 (s, 3H), 1.83-1.73 (m, 4H),

1.65-1.57 (m, 1H), 1.51-1.38 (m, 2H), 1.30-1.17 (m, 2H), 1.15-1.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 130.7, 129.4, 127.0, 123.0, 122.8, 61.6, 33.8, 29.2, 26.2, 26.1; IR (film, ν/cm^{-1}) 3069, 2925, 2853, 2794, 1592, 1481, 1454, 1299, 1101, 1050, 947, 759, 679; HRMS (ESI) calcd for $C_{13}H_{19}N^{35}Cl^+$ $(M + H)^+$ 224.1201, found 224.1204.

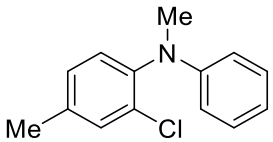


4o

2-Chloro-*N*,3-dimethyl-*N*-phenylaniline (**4o**). Colorless oil (42.2 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 4H), 7.14-7.09 (m, 1H), 6.74 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 3.22 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 145.5, 138.5, 134.2, 129.0, 128.9, 127.8, 127.4, 117.6, 113.2, 39.0, 20.9; IR (film, ν/cm^{-1}) 3061, 3031, 2924, 2811, 1599, 1572, 1496, 1341, 1273, 1050, 933, 741, 687; HRMS (ESI) calcd for $C_{14}H_{15}N^{35}Cl^+$ $(M + H)^+$ 232.0888, found 232.0890.

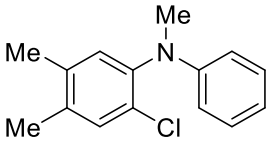


4p



4p'

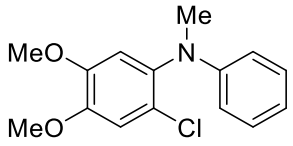
A 55:45 mixture of 2-chloro-*N*,5-dimethyl-*N*-phenylaniline (**4p**) and 2-chloro-*N*,4-dimethyl-*N*-phenylaniline (**4p'**) was obtained as a colorless oil (41.8 mg, 90% yield). Compound **4p** was distinguished from its regioisomer **4p'** by comparing the NMR proton-proton coupling constant for the proton next to the chlorine on the benzene ring. ^{1}H NMR (400 MHz, $CDCl_3$) for amine **4p**: δ 7.35 (d, J = 8.4 Hz, 1H), 7.22-7.13 (m, 2H), 7.11-7.06 (m, 1H), 7.01 (dd, J = 8.0, 1.6 Hz, 1H), 6.78-6.71 (m, 1H), 6.59 (t, J = 8.0 Hz, 2H), 3.23 (s, 3H), 2.30 (s, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) for amine **4p'**: δ 7.30 (s, 1H), 7.22-7.13 (m, 3H), 7.11-7.06 (m, 1H), 6.78-6.71 (m, 1H), 6.59 (t, J = 8.0 Hz, 2H), 3.22 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.8, 145.0, 142.7, 138.4, 137.8, 133.4, 131.4, 130.7, 130.6, 130.5, 130.0, 129.1, 129.0, 128.3, 117.7, 117.6, 113.5, 113.3, 39.1, 39.0, 20.9; IR (film, ν/cm^{-1}) 3037, 2924, 2810, 1591, 1496, 1340, 1135, 1048, 806, 740, 689; HRMS (ESI) calcd for $C_{14}H_{15}N^{35}Cl^+$ $(M + H)^+$ 232.0888, found 232.0885.



4q

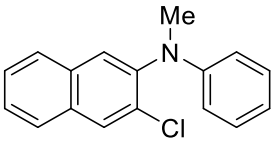
2-Chloro-*N*,4,5-trimethyl-*N*-phenylaniline (**4q**). Pale yellow oil (44.3 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.18-7.12 (m, 2H), 7.01 (s, 1H), 6.71 (t, J = 7.2 Hz, 1H), 6.59-6.54 (m, 2H), 3.18 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.6, 136.9, 136.4, 131.5, 131.1, 130.3, 129.0, 117.4, 113.2, 39.0, 19.3, 19.2; IR (film, ν/cm^{-1}) 3035, 2932, 2882,

2820, 1599, 1496, 1452, 1340, 1134, 981, 912, 731, 689, 637; HRMS (ESI) calcd for $C_{15}H_{17}N^{35}Cl^+$ $(M + H)^+$ 246.1044, found 246.1046.



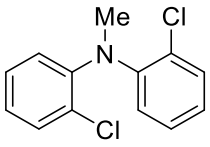
4r

2-Chloro-4,5-dimethoxy-*N*-methyl-*N*-phenylaniline (**4r**). Colorless oil (31.5 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 2H), 6.96 (s, 1H), 6.78-6.72 (m, 2H), 6.57 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 3.81 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 148.1, 137.5, 129.1, 124.9, 117.4, 113.0, 112.8, 112.7, 56.4, 56.3, 38.9; IR (film, ν/cm^{-1}) 3011, 2934, 2855, 1599, 1496, 1447, 1211, 1178, 1032, 844, 723, 693; HRMS (ESI) calcd for $C_{15}H_{17}O_2N^{35}Cl^+$ $(M + H)^+$ 278.0942, found 278.0945.



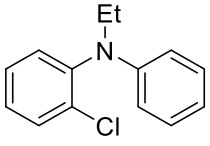
4s

3-Chloro-*N*-methyl-*N*-phenylnaphthalen-2-amine (**4s**). Pale yellow oil (45.5 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.78-7.71 (m, 3H), 7.51-7.43 (m, 2H), 7.22-7.17 (m, 2H), 6.78 (t, J = 7.2 Hz, 1H), 6.65 (dd, J = 8.8, 0.8 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 143.3, 133.1, 132.4, 132.3, 129.4, 129.1, 128.3, 127.5, 126.9, 126.8, 126.5, 118.1, 114.0, 39.8; IR (film, ν/cm^{-1}) 3052, 2924, 2811, 1591, 1496, 1454, 1356, 1127, 1006, 876, 741, 689, 609; HRMS (ESI) calcd for $C_{17}H_{15}N^{35}Cl^+$ $(M + H)^+$ 268.0888, found 268.0889.



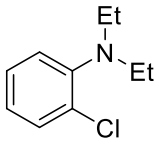
4t

2-Chloro-*N*-(2-chlorophenyl)-*N*-methylaniline (**4t**). Yellow oil (32.9 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 8.0, 1.6 Hz, 2H), 7.20 (td, J = 8.0, 1.6 Hz, 2H), 7.05-6.98 (m, 4H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 131.1, 129.5, 127.6, 124.5, 123.5, 41.0; IR (film, ν/cm^{-1}) 3069, 2966, 2924, 2855, 1591, 1471, 1316, 1238, 1084, 1050, 904, 758, 733; HRMS (ESI) calcd for $C_{13}H_{12}N^{35}Cl_2^+$ $(M + H)^+$ 252.0341, found 252.0344.



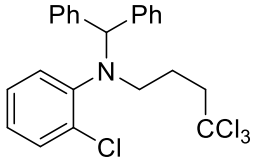
4u

2-Chloro-*N*-ethyl-*N*-phenylaniline (**4u**). Colorless oil (43.0 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 8.0, 0.8 Hz, 1H), 7.31-7.13 (m, 5H), 6.72 (td, J = 7.2, 0.8 Hz, 1H), 6.56 (dd, J = 8.0, 0.8 Hz, 2H), 3.68 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 143.7, 134.5, 131.8, 131.1, 129.1, 128.2, 127.6, 117.5, 113.5, 45.5, 12.8; IR (film, ν/cm^{-1}) 3061, 2975, 1599, 1496, 1368, 1264, 1050, 749, 689; HRMS (ESI) calcd for $C_{14}H_{15}N^{35}Cl^{+}$ $(M + H)^{+}$ 232.0888, found 232.0888.



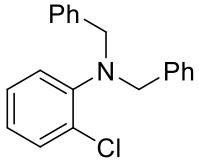
4v

2-Chloro-*N*,*N*-diethylaniline (**4v**). Colorless oil (30.2 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 8.0, 1.6 Hz, 1H), 7.19 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 7.08 (dd, J = 8.0, 1.6 Hz, 1H), 6.96 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 3.13 (q, J = 7.2 Hz, 4H), 1.03 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 131.0, 130.7, 127.0, 123.8, 123.7, 46.8, 12.3; IR (film, ν/cm^{-1}) 3061, 2968, 2924, 2855, 1592, 1479, 1462, 1375, 1256, 1050, 799, 759, 672; HRMS (ESI) calcd for $C_{10}H_{15}N^{35}Cl^{+}$ $(M + H)^{+}$ 184.0888, found 184.0890.



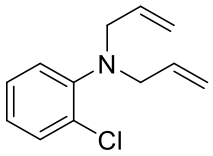
4w

N-Benzhydryl-2-chloro-*N*-(4,4,4-trichlorobutyl)aniline (**4w**). Colorless oil (58.4 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 5H), 7.30-7.25 (m, 4H), 7.23-7.18 (m, 2H), 7.04 (td, J = 7.6, 1.6 Hz, 1H), 6.96 (td, J = 7.6, 1.6 Hz, 1H), 6.82 (dd, J = 8.0, 1.6 Hz, 1H), 5.52 (s, 1H), 3.03 (t, J = 7.2 Hz, 2H), 2.65-2.58 (m, 2H), 1.86-1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 140.5, 132.6, 130.7, 128.7, 128.3, 127.3, 126.8, 126.7, 125.3, 100.0, 71.2, 52.9, 47.5, 23.5; IR (film, ν/cm^{-1}) 3354, 3069, 3035, 2932, 2856, 1591, 1479, 1444, 1256, 1050, 904, 741, 697, 623; HRMS (ESI) calcd for $C_{23}H_{22}N^{35}Cl_4^{+}$ $(M + H)^{+}$ 452.0501, found 452.0497.



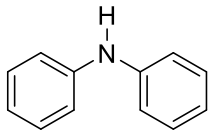
4x

N,*N*-Dibenzyl-2-chloroaniline (**4x**). Colorless oil (50.7 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 8.0, 1.6 Hz, 1H), 7.33-7.29 (m, 4H), 7.28-7.23 (m, 4H), 7.21-7.16 (m, 2H), 7.06-7.00 (m, 1H), 6.92-6.87 (m, 2H), 4.19 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 138.2, 130.7, 130.2, 128.6, 128.3, 127.1, 127.0, 124.0, 123.9, 56.2; IR (film, ν/cm^{-1}) 3065, 3025, 2931, 2846, 2806, 1591, 1479, 1455, 1368, 1204, 1032, 911, 733, 697; HRMS (ESI) calcd for $C_{20}H_{19}N^{35}Cl^{+}$ $(M + H)^{+}$ 308.1201, found 308.1201.



4y

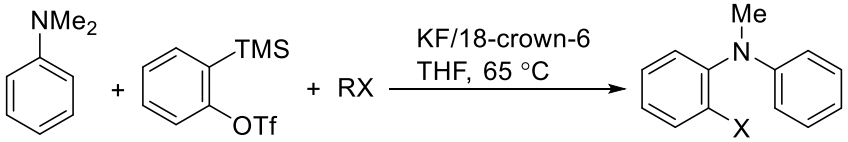
N,*N*-Diallyl-2-chloroaniline (**4y**). Colorless oil (31.6 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 8.0, 1.6 Hz, 1H), 7.19-7.13 (m, 1H), 7.03 (dd, J = 8.0, 1.6 Hz, 1H), 6.94 (td, J = 7.6, 1.6 Hz, 1H), 5.81 (ddt, J = 16.4, 10.0, 6.0 Hz, 2H), 5.22-5.10 (m, 4H), 3.72 (d, J = 6.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 134.9, 130.8, 129.7, 126.9, 123.6, 123.5, 117.7, 55.0; IR (film, ν/cm^{-1}) 3087, 2982, 2932, 2829, 1643, 1591, 1479, 1445, 1419, 1213, 1038, 995, 921, 756, 725, 686; HRMS (ESI) calcd for $C_{12}H_{15}N^{35}Cl^{+}$ $(M + H)^{+}$ 208.0888, found 208.0891.



5

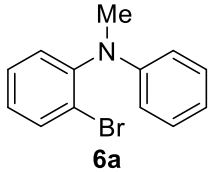
Diphenylamine (**5**). Pale yellow solid (27.8 mg, 82% yield); m.p. 49-50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 4H), 7.06 (dd, J = 8.4, 0.8 Hz, 4H), 6.92 (t, J = 7.2 Hz, 2H), 5.68 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 129.5, 121.1, 117.9. This result is consistent with previous literature.[4]

Reaction of various organohalides (Scheme 5)



1a **2a** **3b-j** **4a**, **6a**, or **7a**

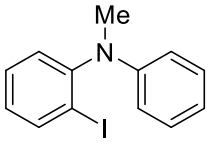
Sealed reaction tubes containing dry KF (34.9 mg, 0.60 mmol) and 18-crown-6 (159 mg, 0.60 mmol) were sequentially added tetrahydrofuran (0.20 mL), organohalide **3b-j** (0.60 mmol), amine **1a** (24.2 mg, 0.20 mmol), and 2-(trimethylsilyl)phenyl triflate (**2a**) (89.5 mg, 0.30 mmol). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:40 to 0:1 v/v), to give compound **4a**, **6a**, or **7a**.



6a

2-Bromo-*N*-methyl-*N*-phenylaniline (**6a**). Colorless oil (43.4 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.0, 1.6 Hz, 1H), 7.31 (td, J = 7.6, 1.6 Hz, 1H), 7.24 (dd, J = 8.0, 1.6 Hz, 1H), 7.21-7.15 (m, 2H), 7.11 (td, J = 8.0, 1.6 Hz, 1H), 6.75 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 8.8

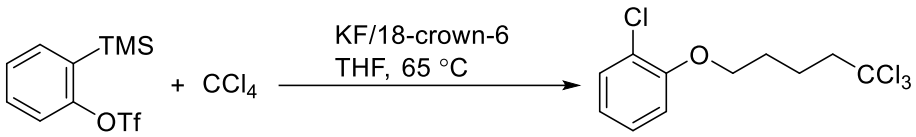
Hz, 2H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.0, 134.2, 130.5, 129.0, 127.9, 124.4, 117.8, 113.5, 39.1; IR (film, ν/cm^{-1}) 3061, 2906, 2811, 1599, 1582, 1496, 1341, 1032, 912, 723, 686, 651; HRMS (ESI) calcd for $C_{13}H_{13}N^{79}Br^+$ $(M + H)^+$ 262.0226, found 262.0226. This result is consistent with previous literature.[5]



7a

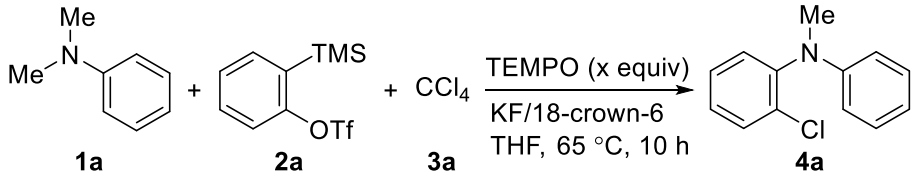
2-Iodo-*N*-methyl-*N*-phenylaniline (**7a**). Colorless oil (34.9 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.32-7.26 (m, 2H), 7.08-7.00 (m, 3H), 6.72-6.66 (m, 2H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 148.4, 137.9, 129.5, 123.0, 122.6, 120.6, 82.1, 40.3; IR (film, ν/cm^{-1}) 3042, 2924, 2811, 1575, 1480, 1341, 1256, 1129, 1066, 903, 809, 731, 797; HRMS (ESI) calcd for $C_{13}H_{13}NI^+$ $(M + H)^+$ 310.0087, found 310.0089.

Control experiments



2a **3a** **8**

Sealed reaction tube containing dry KF (34.9 mg, 0.60 mmol) and 18-crown-6 (159 mg, 0.60 mmol) were sequentially added tetrahydrofuran (0.20 mL), carbon tetrachloride (**3a**) (0.10 mL), and 2-(trimethylsilyl)phenyl triflate (**2a**) (89.5 mg, 0.30 mmol). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:20 v/v), to give 1-chloro-2-((5,5,5-trichloropentyl)oxy)benzene (**8**) as a colorless oil (33.7 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 8.0, 1.6 Hz, 1H), 7.19 (ddd, J = 8.4, 7.6, 1.6 Hz, 1H), 6.92-6.85 (m, 2H), 4.05 (t, J = 6.0 Hz, 2H), 2.83-2.78 (m, 2H), 2.06-1.89 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 130.4, 127.8, 123.1, 121.6, 113.5, 100.0, 68.6, 54.9, 28.0, 23.5; IR (film, ν/cm^{-1}) 3069, 2941, 2879, 1591, 1478, 1282, 1247, 1067, 912, 778, 731, 697; HRMS (EI) calcd for $C_{11}H_{12}O^{35}Cl_4^+$ (M^+) 299.9637, found 299.9636.



1a **2a** **3a** **4a**

x	yield (%)
0	95
2	81
10	37

Sealed reaction tube containing dry KF (34.9 mg, 0.60 mmol), 18-crown-6 (159 mg, 0.60 mmol), and TEMPO (62.4 mg, 0.40 mmol) were sequentially added tetrahydrofuran (0.20 mL), carbon

tetrachloride (**3a**) (0.10 mL), amine **1a** (24.2 mg, 0.20 mmol), and 2-(trimethylsilyl)phenyl triflate (**2a**) (89.5 mg, 0.30 mmol). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:40 v/v), to give compound **4a** (35.3 mg, 81% yield) as a yellow oil.

Instead, addition of 10 equiv. of TEMPO gave compound **4a** (16.1 mg, 37% yield).

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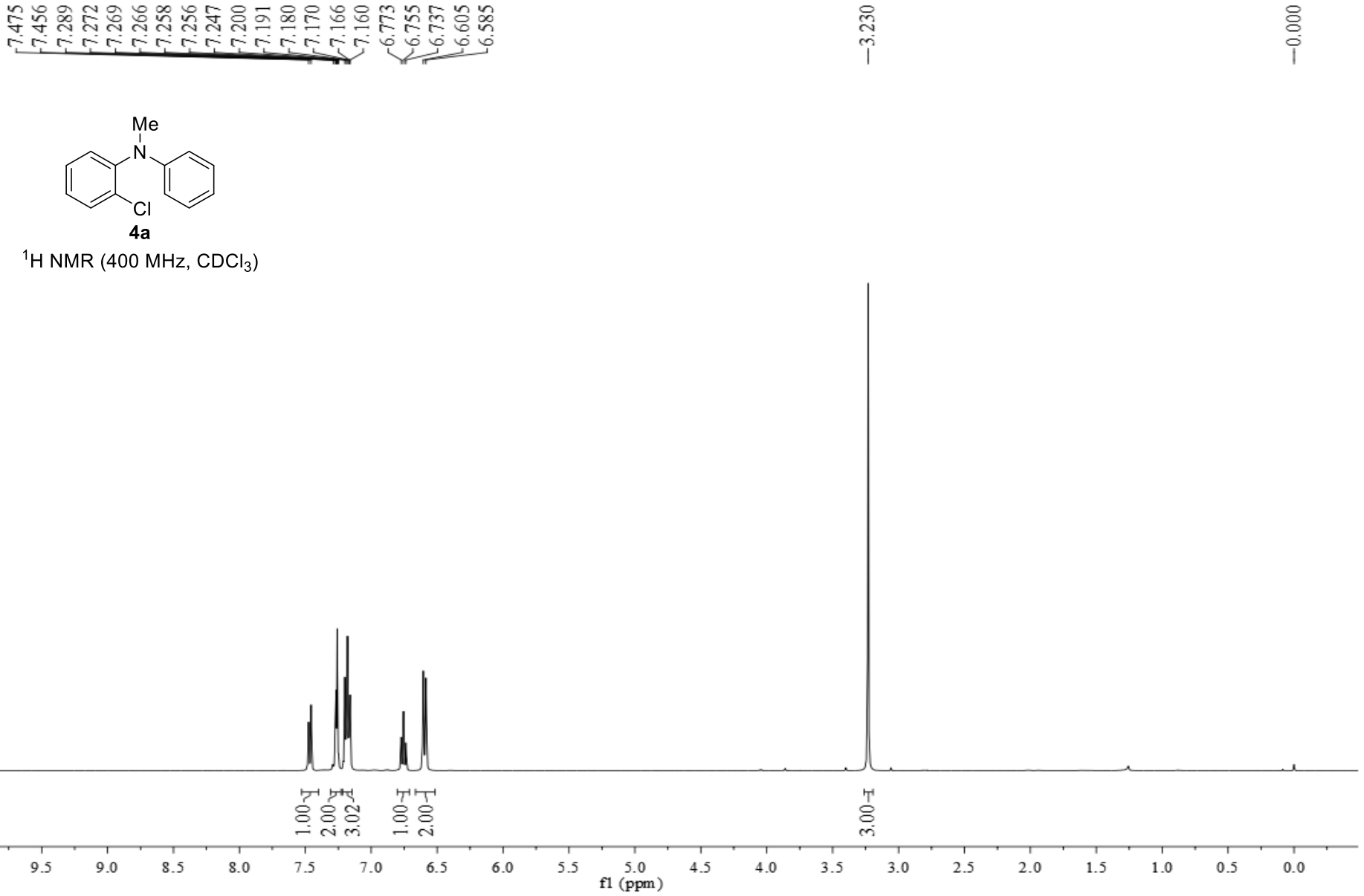
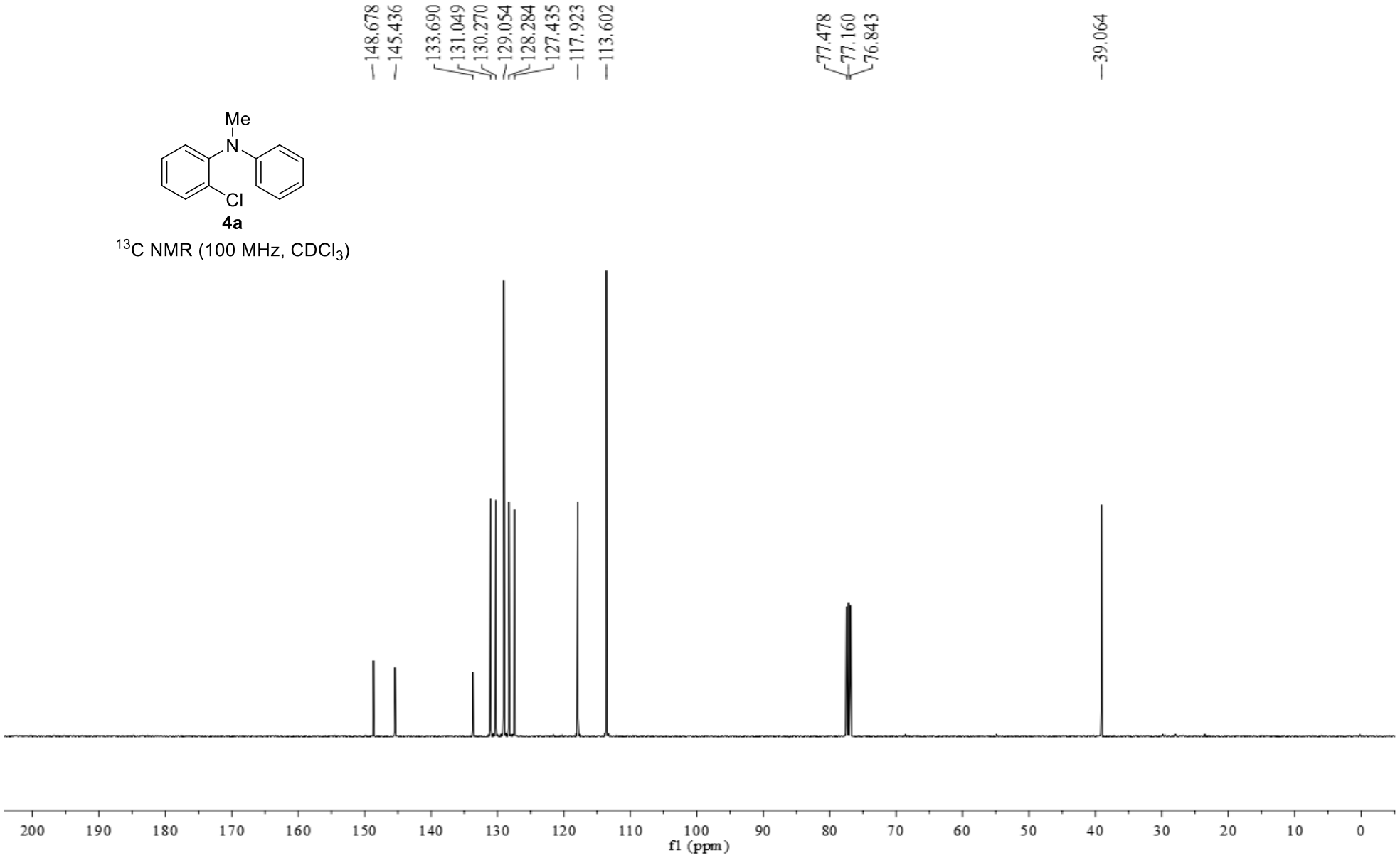


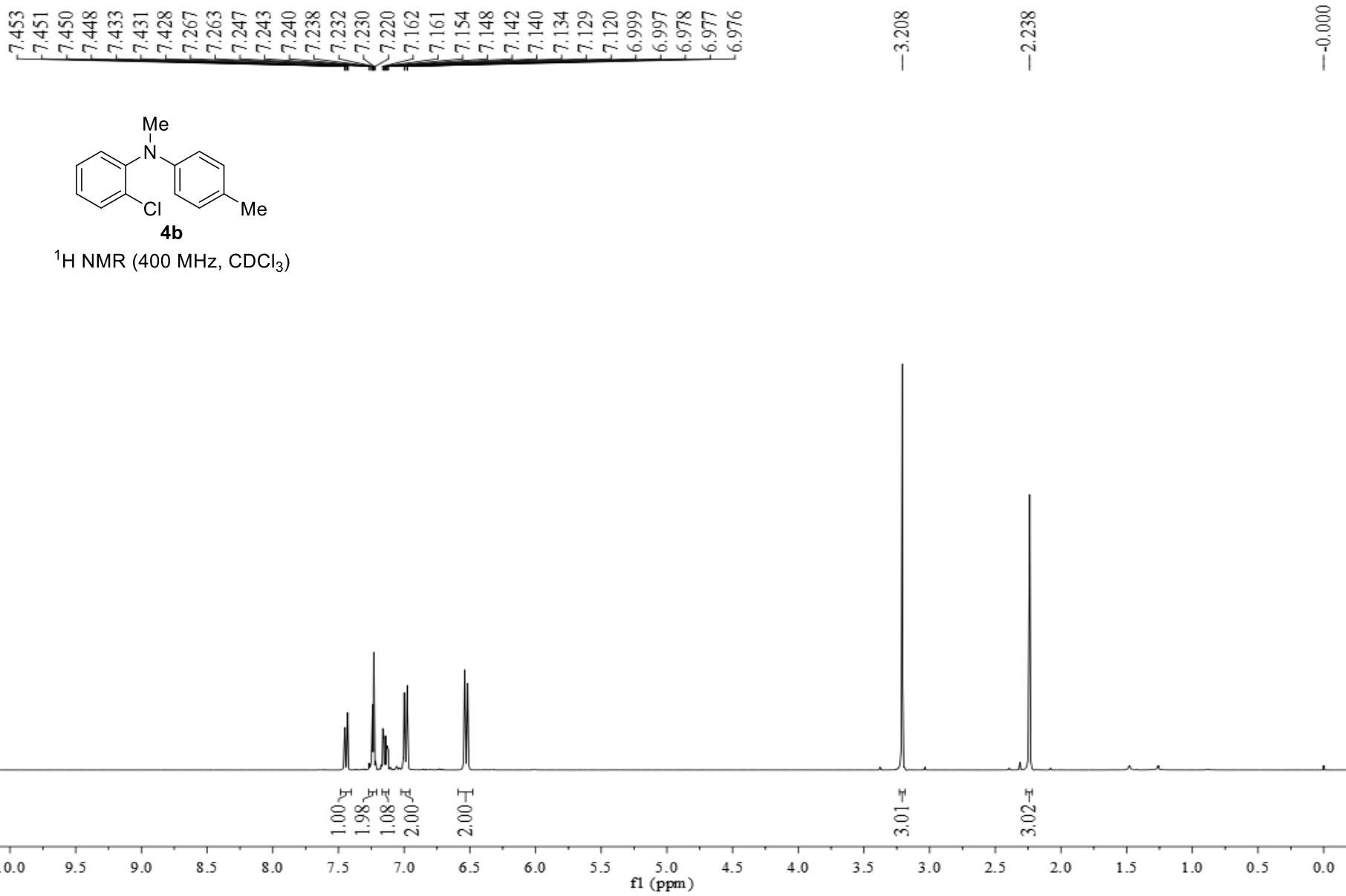
4a

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



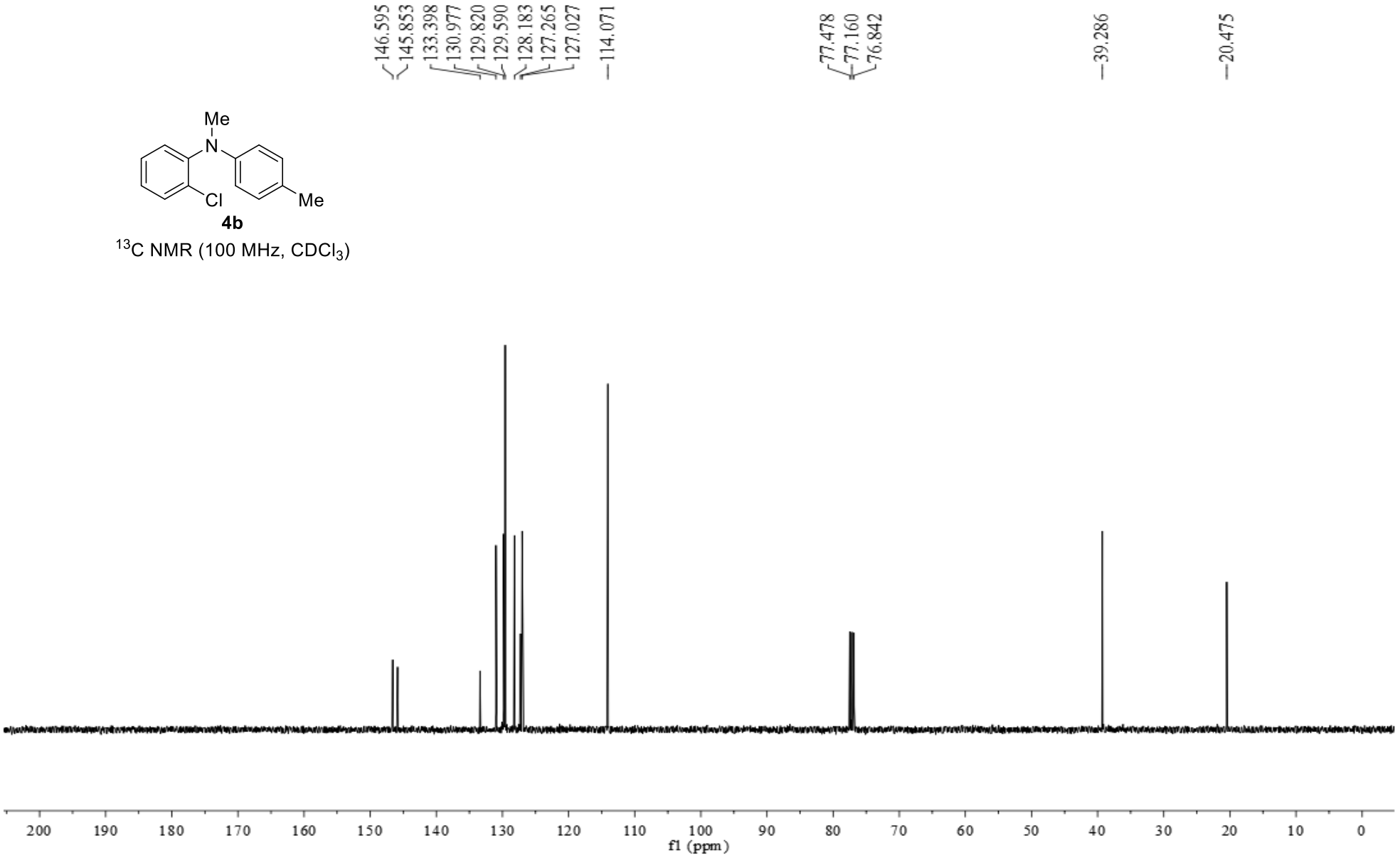
4a

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



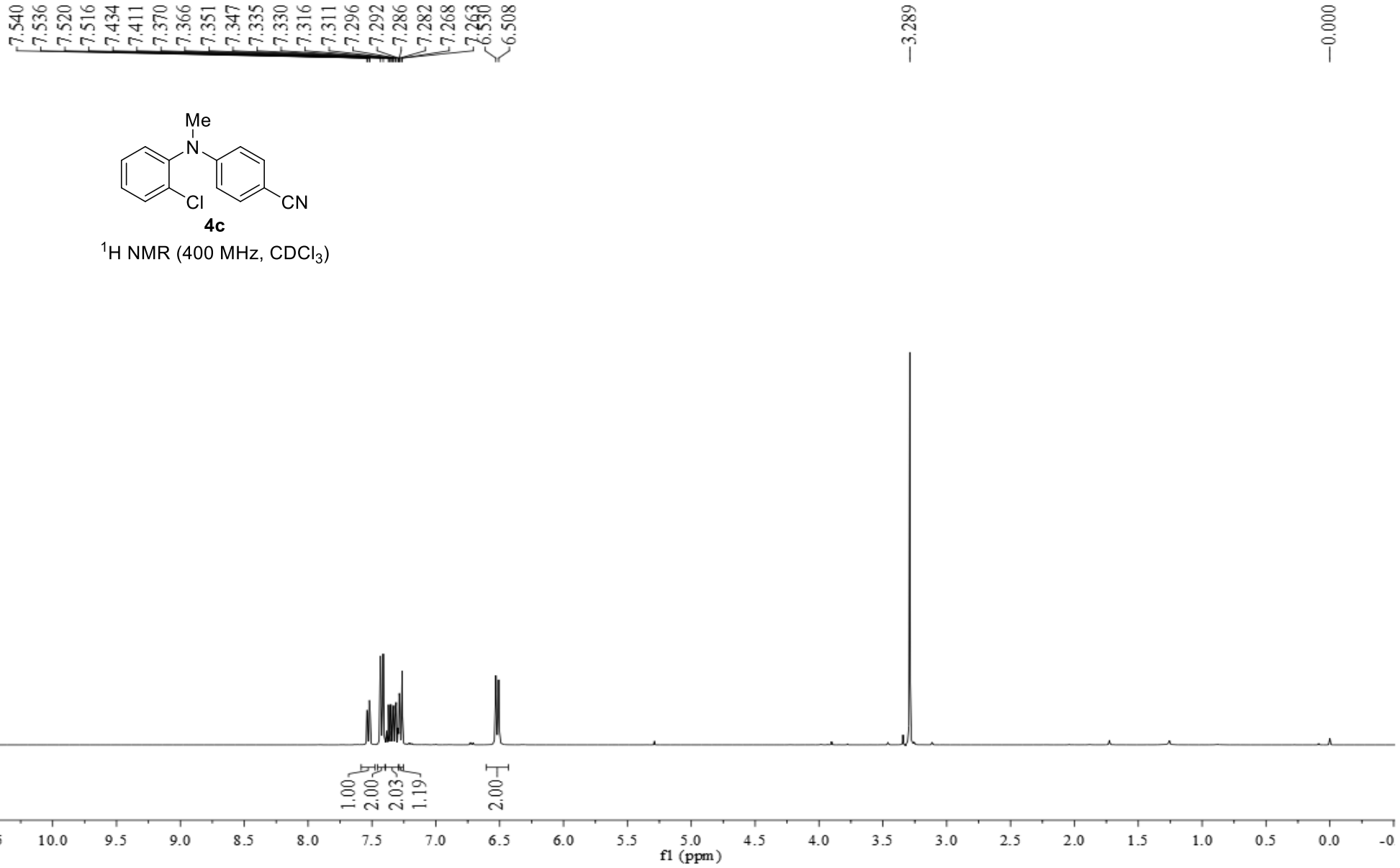
4b

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



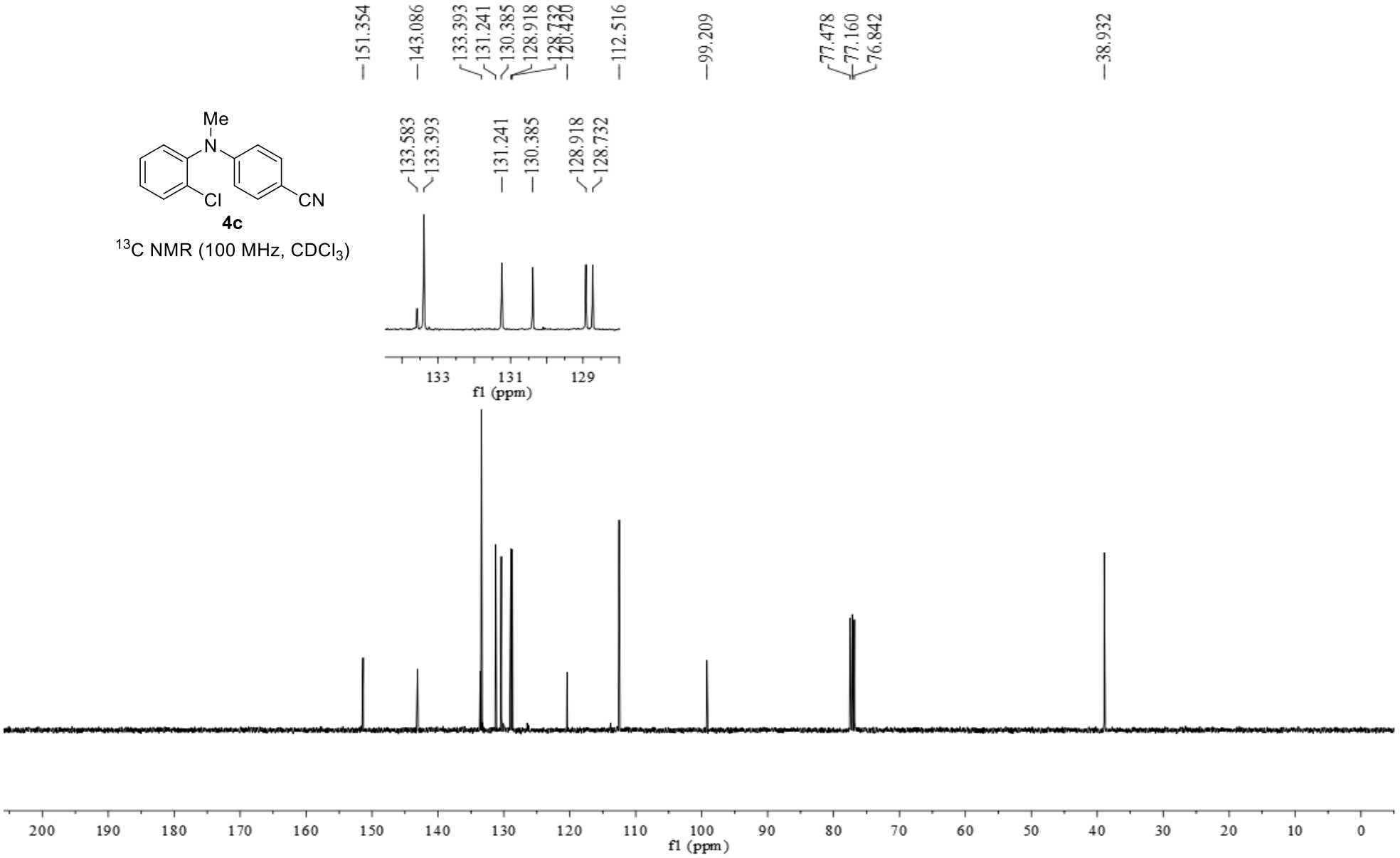
4b

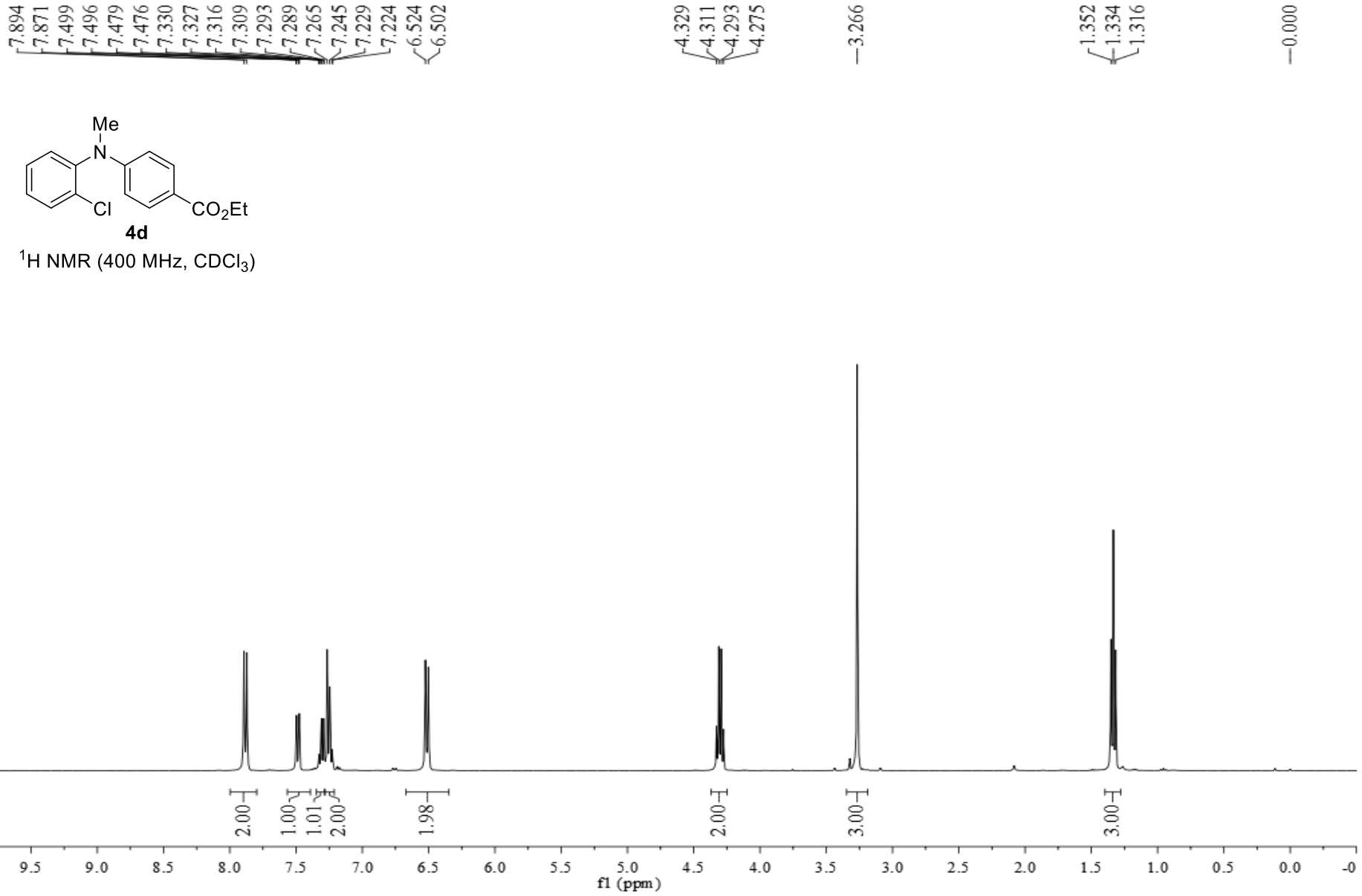
^{13}C NMR (100 MHz, $CDCl_3$)



4c

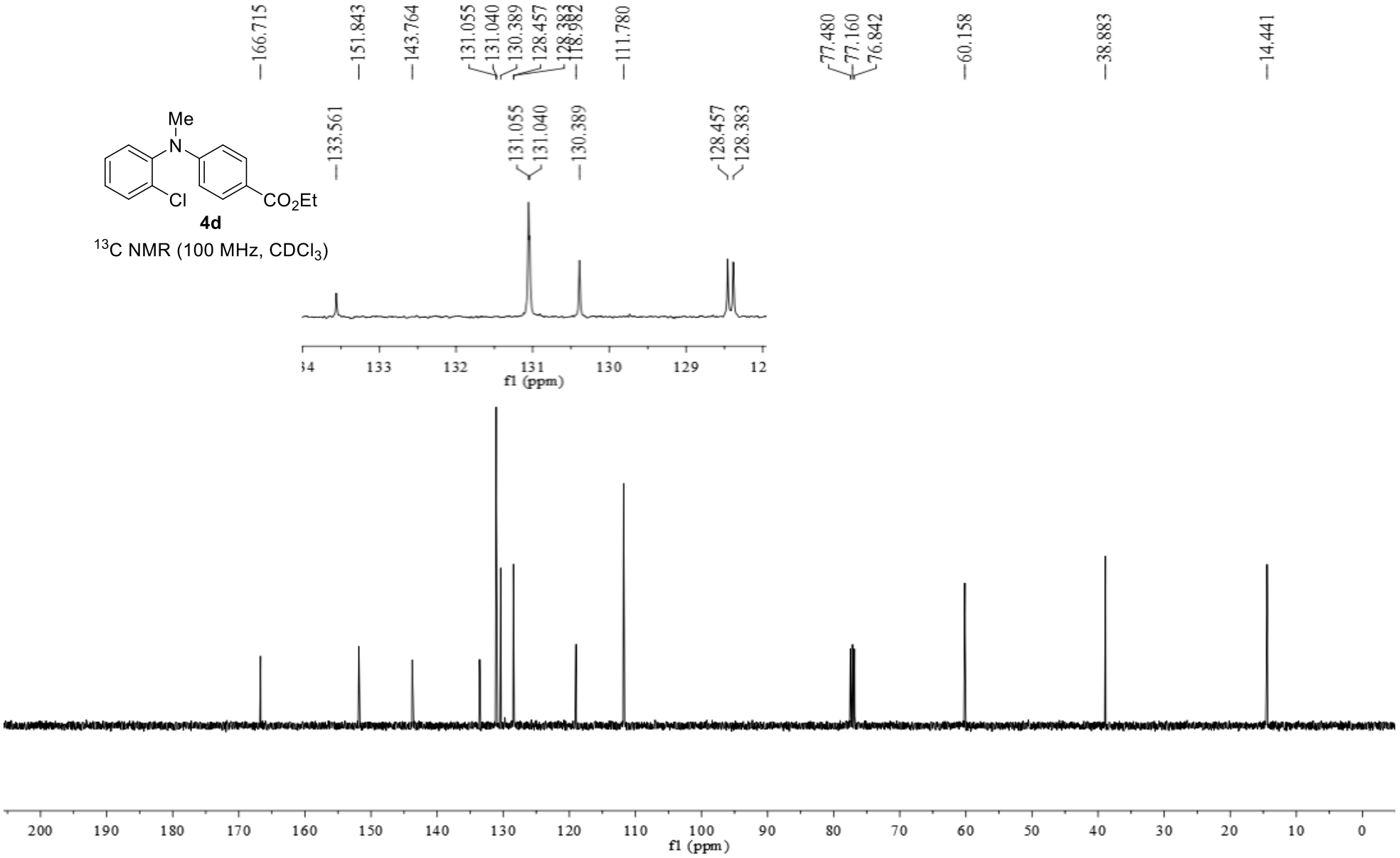
^{1}H NMR (400 MHz, $CDCl_3$)

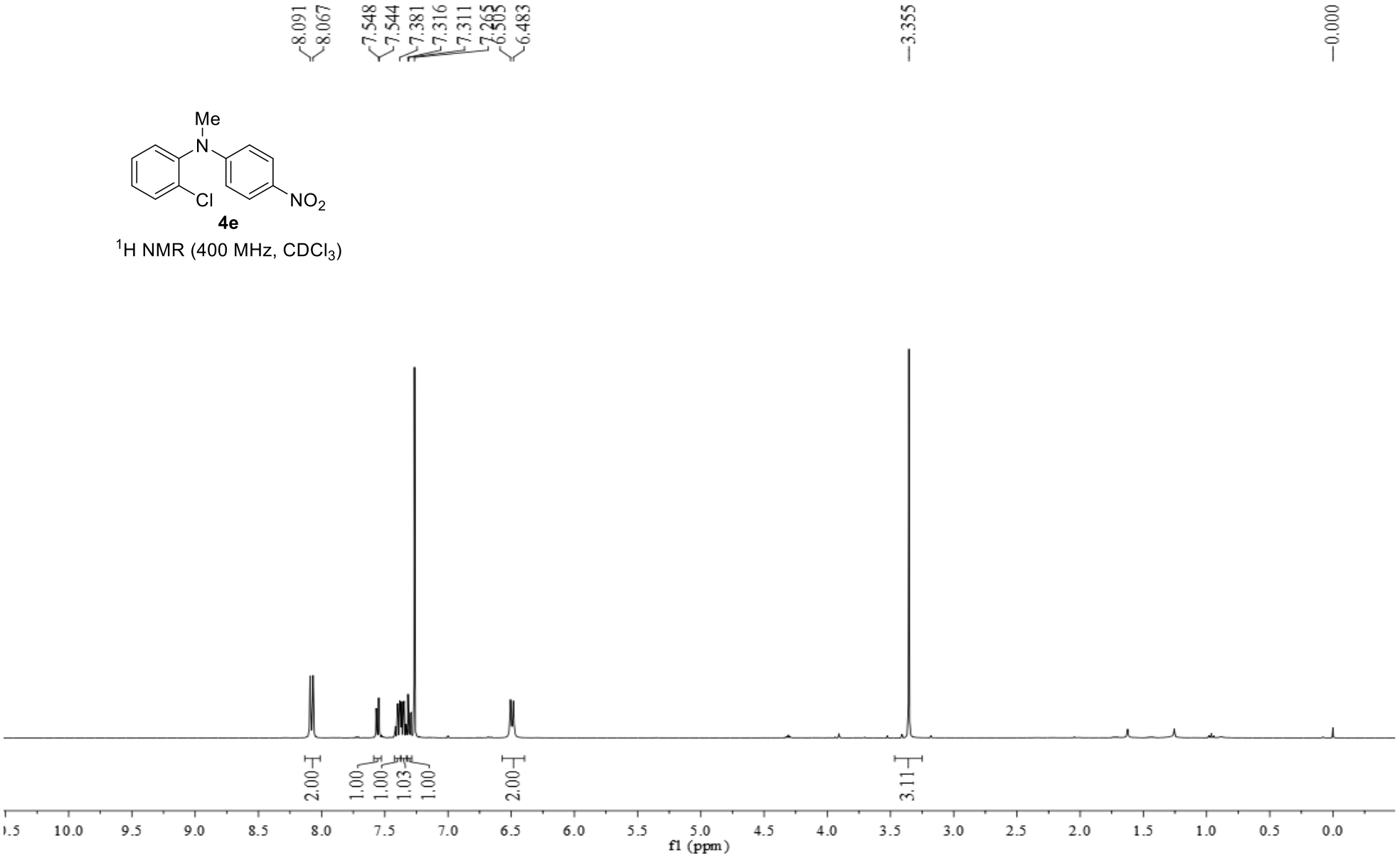

151.354
143.086
133.393
131.241
130.385
128.918
128.732
120.420
112.516
99.209
77.478
77.160
76.842
38.932
Me
N
Cl
CN
4c
13C NMR (100 MHz, CDCl3)
133.583
133.393
131.241
130.385
128.918
128.732
133
131
129
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4d

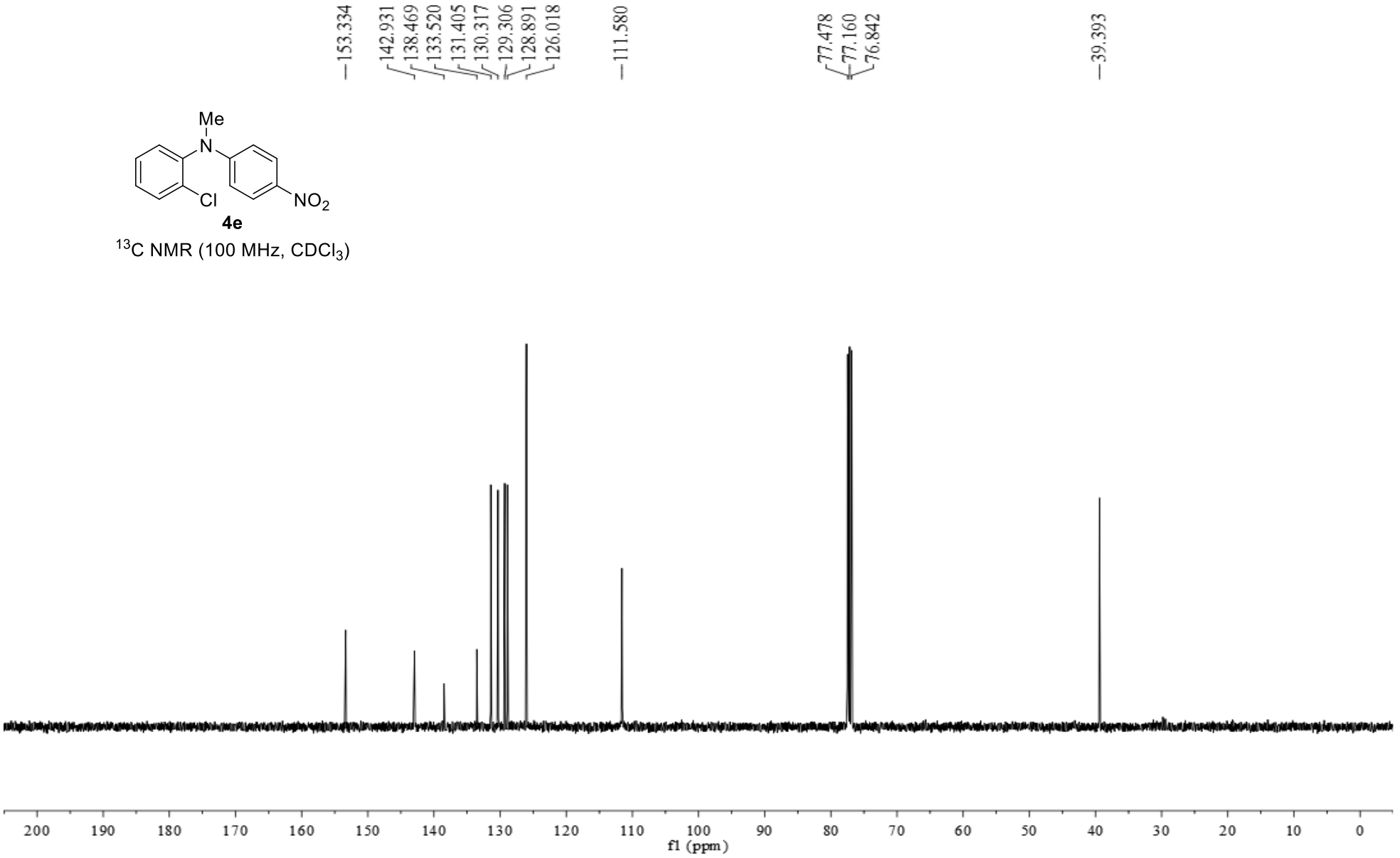
^{1}H NMR (400 MHz, $CDCl_3$)


166.715
151.843
143.764
131.055
131.040
130.389
128.457
128.383
118.982
111.780
77.480
77.160
76.842
60.158
38.883
14.441
Me
N
Cl
CO2Et
4d
13C NMR (100 MHz, CDCl3)
133.561
131.055
131.040
130.389
128.457
128.383
f1 (ppm)
f1 (ppm)



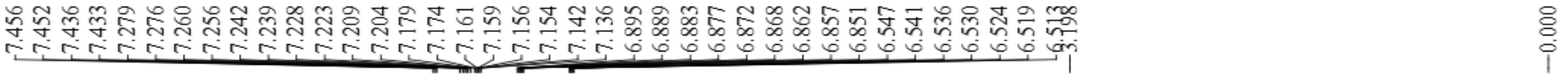
4e

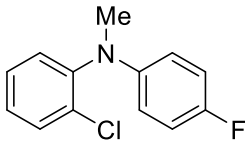
^{1}H NMR (400 MHz, $CDCl_3$)



4e

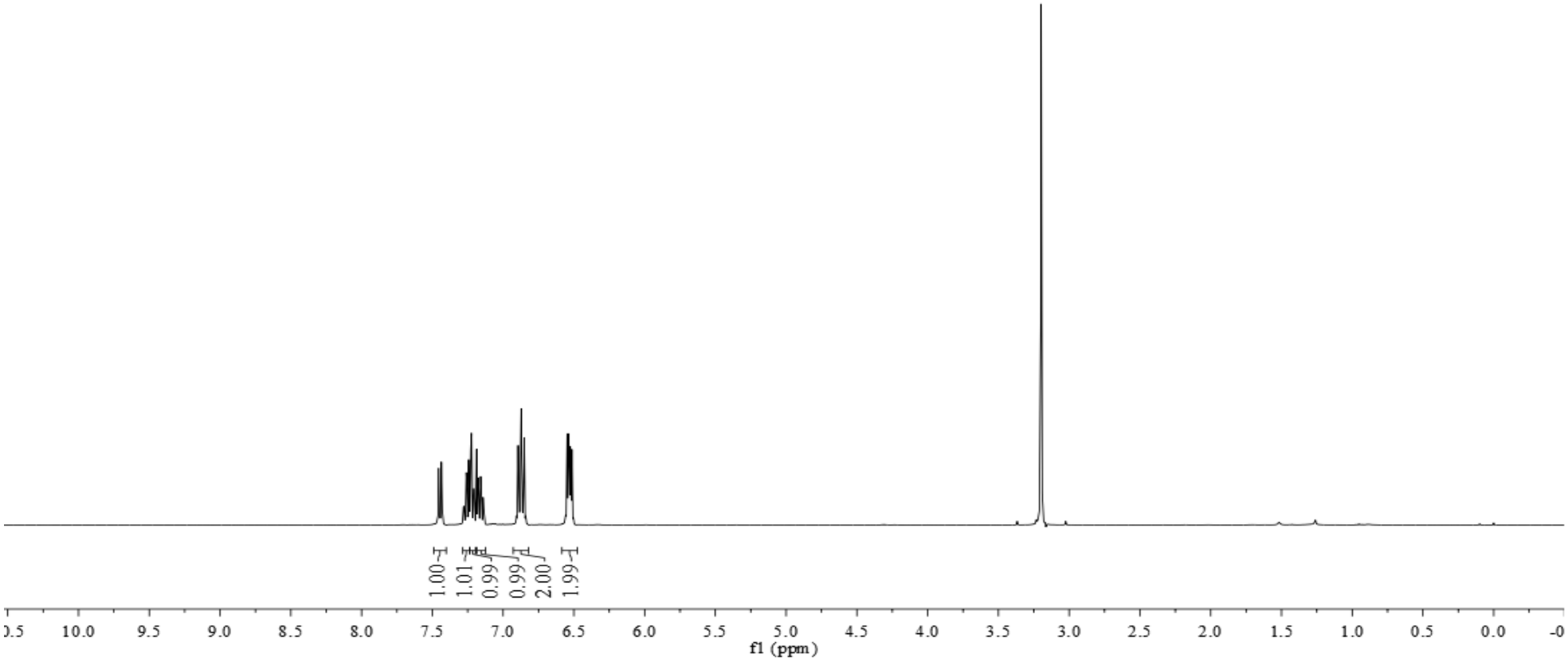
^{13}C NMR (100 MHz, $CDCl_3$)

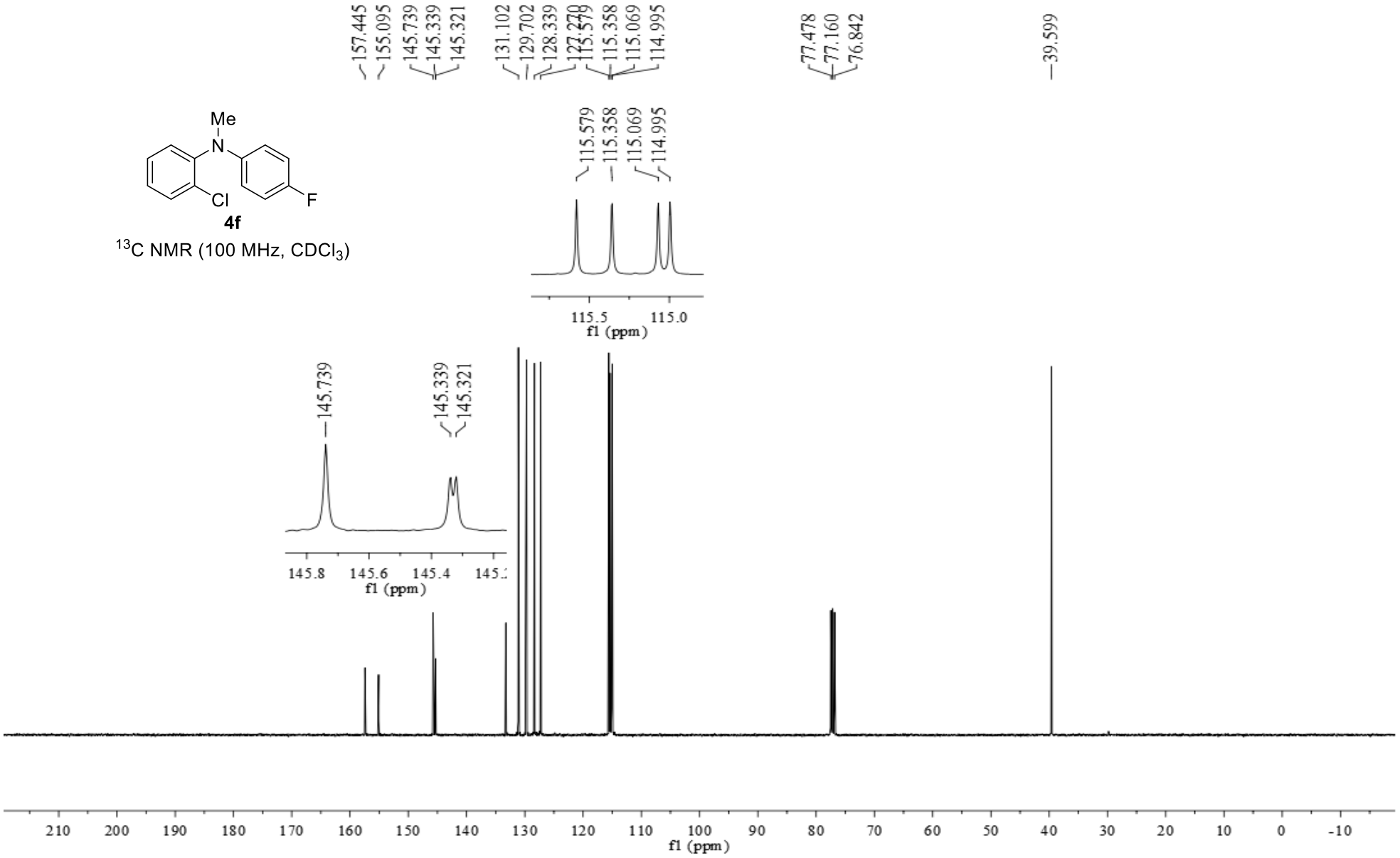


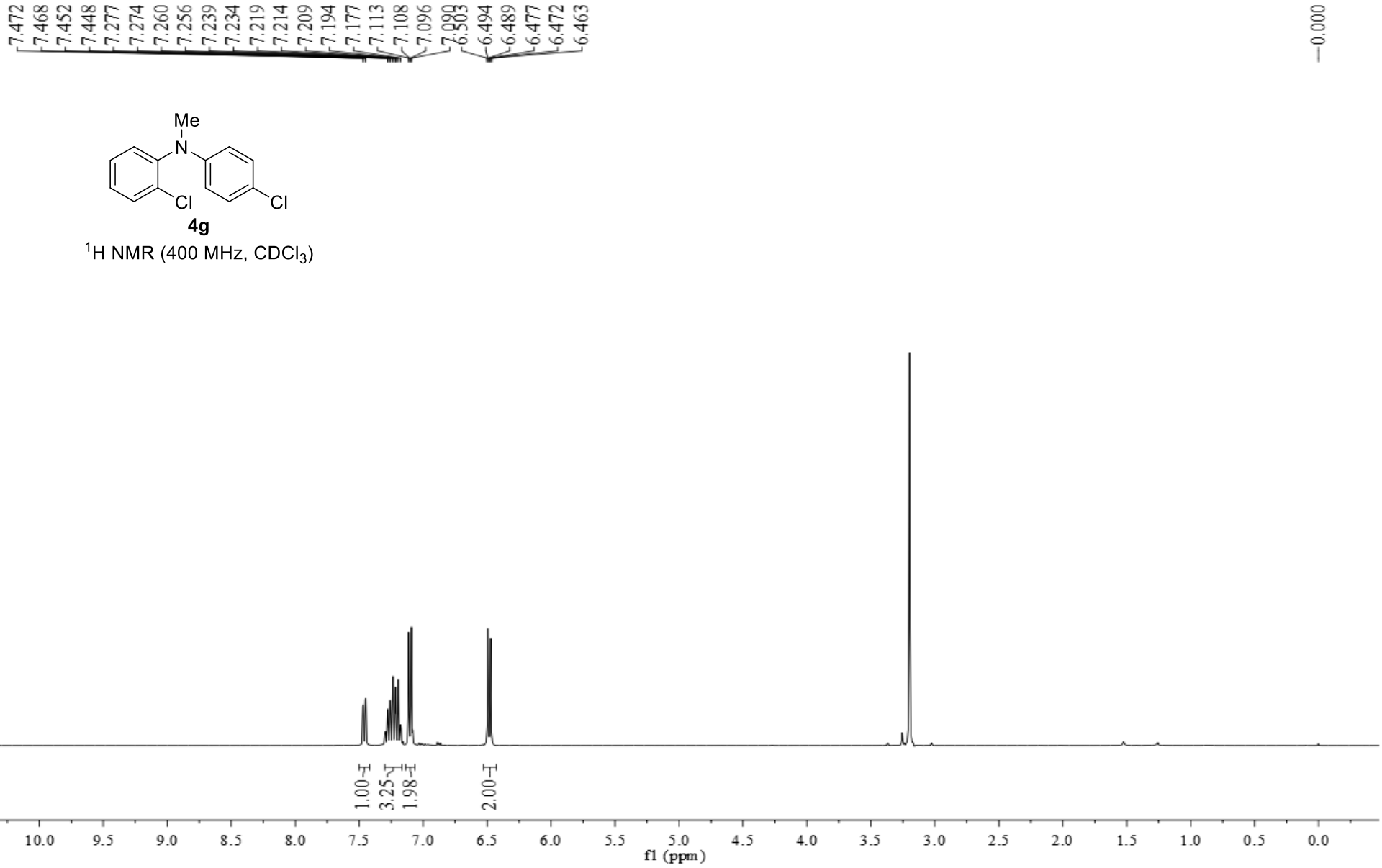


4f

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

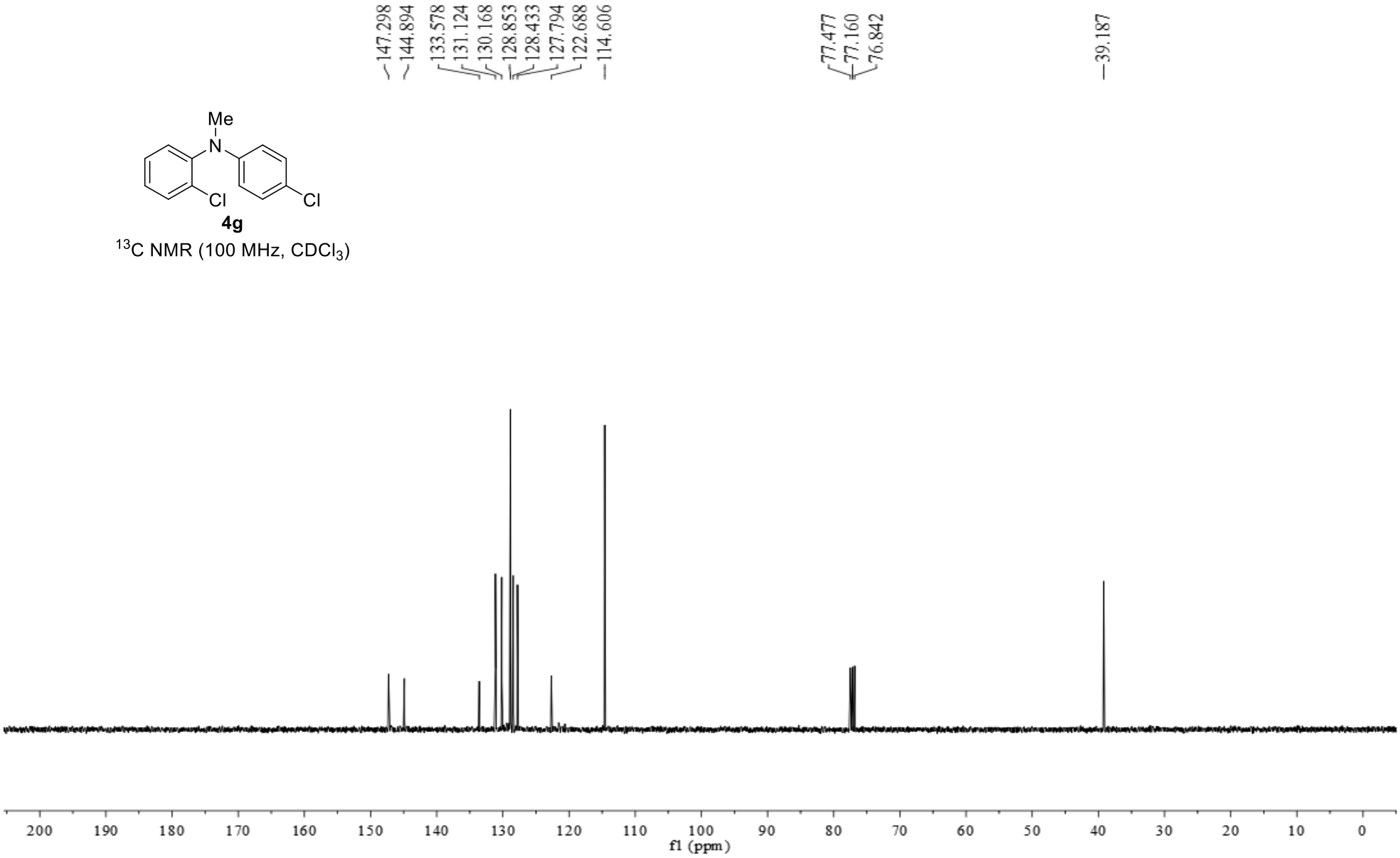



157.445
155.095
145.739
145.339
145.321
131.102
129.702
128.339
127.270
115.579
115.358
115.069
114.995
77.478
77.160
76.842
39.599
Me
N
Cl
F
4f
13C NMR (100 MHz, CDCl3)
115.579
115.358
115.069
114.995
115.5
115.0
f1 (ppm)
145.739
145.339
145.321
145.8
145.6
145.4
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



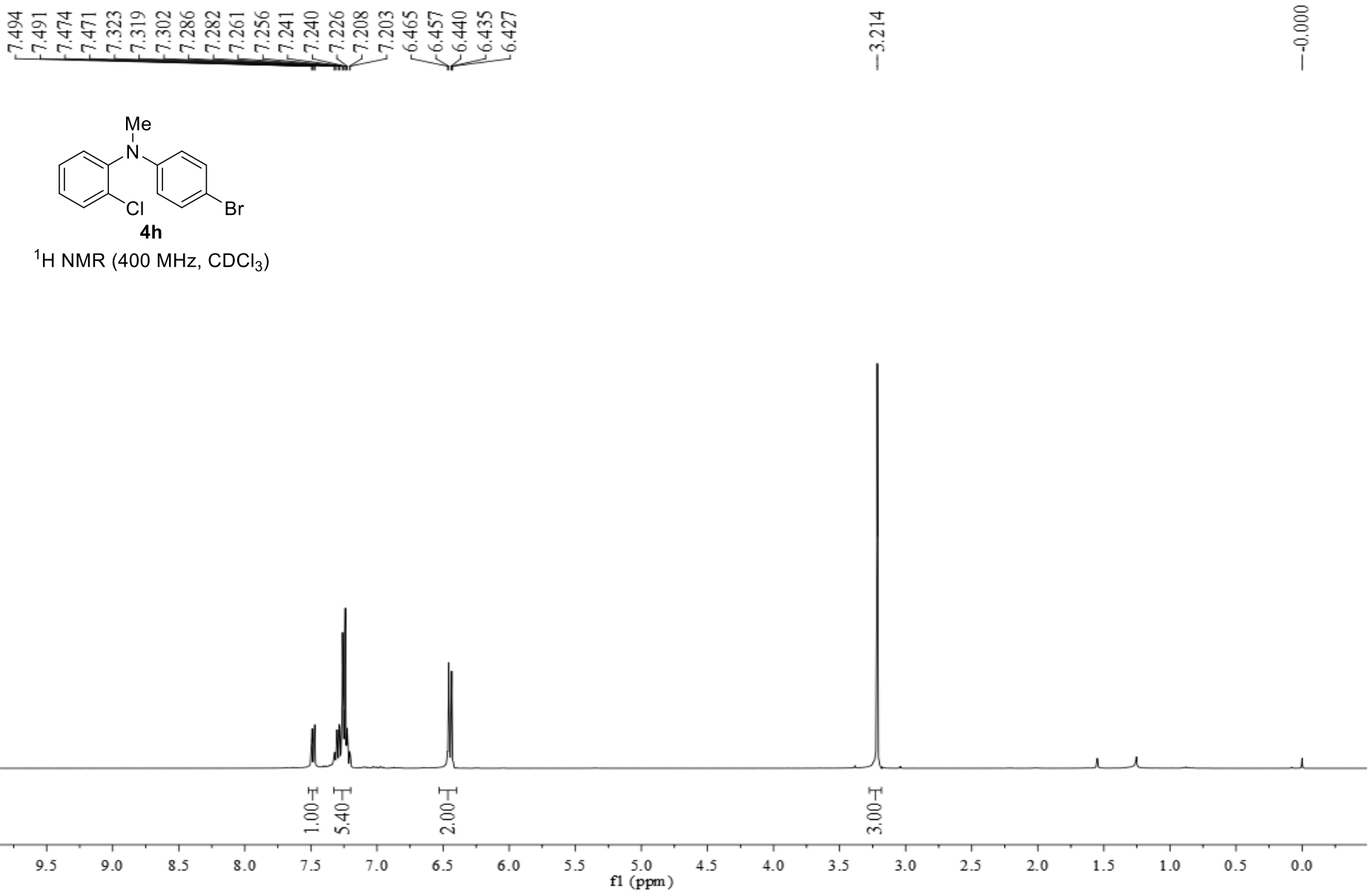
4g

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



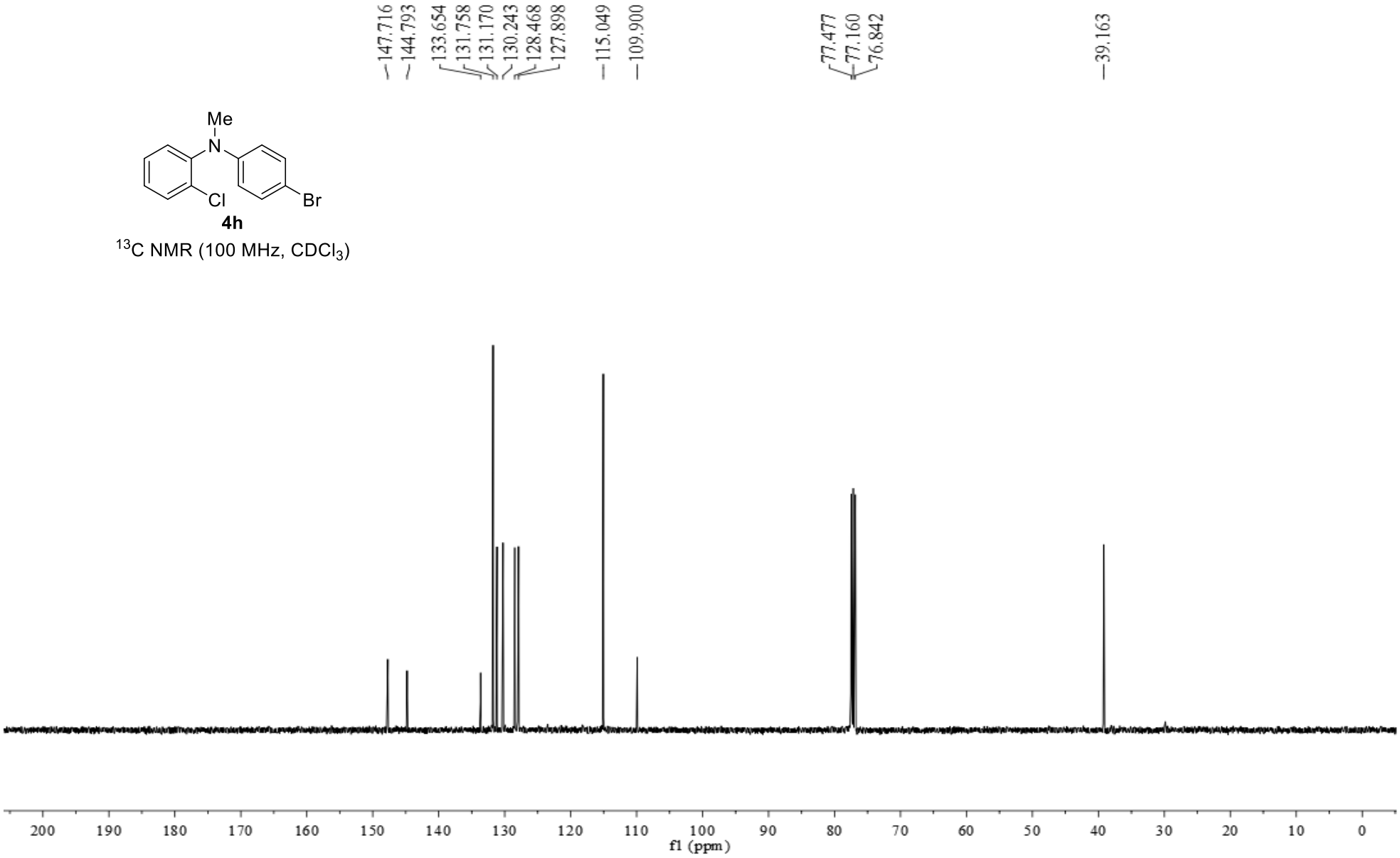
4g

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



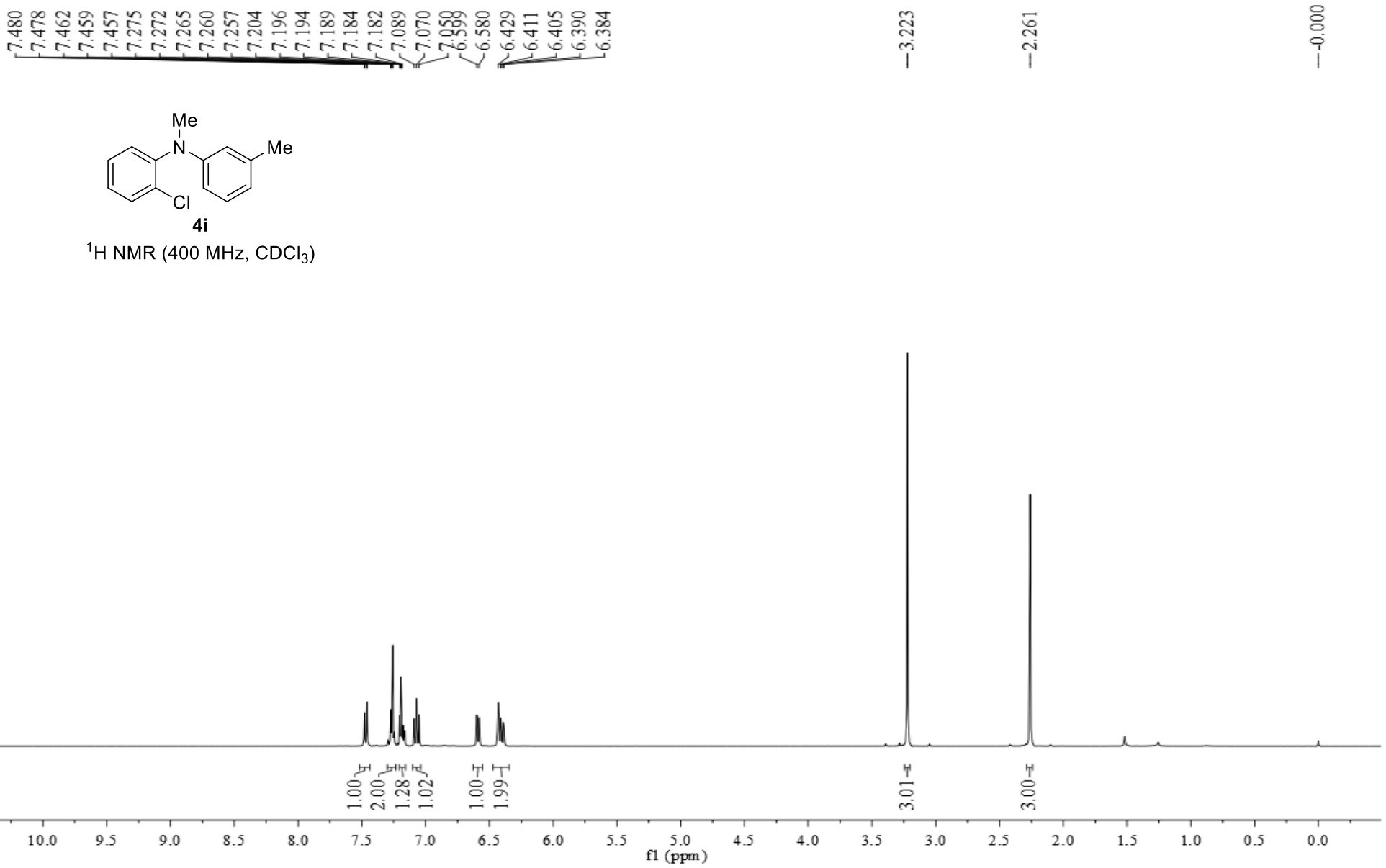
4h

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



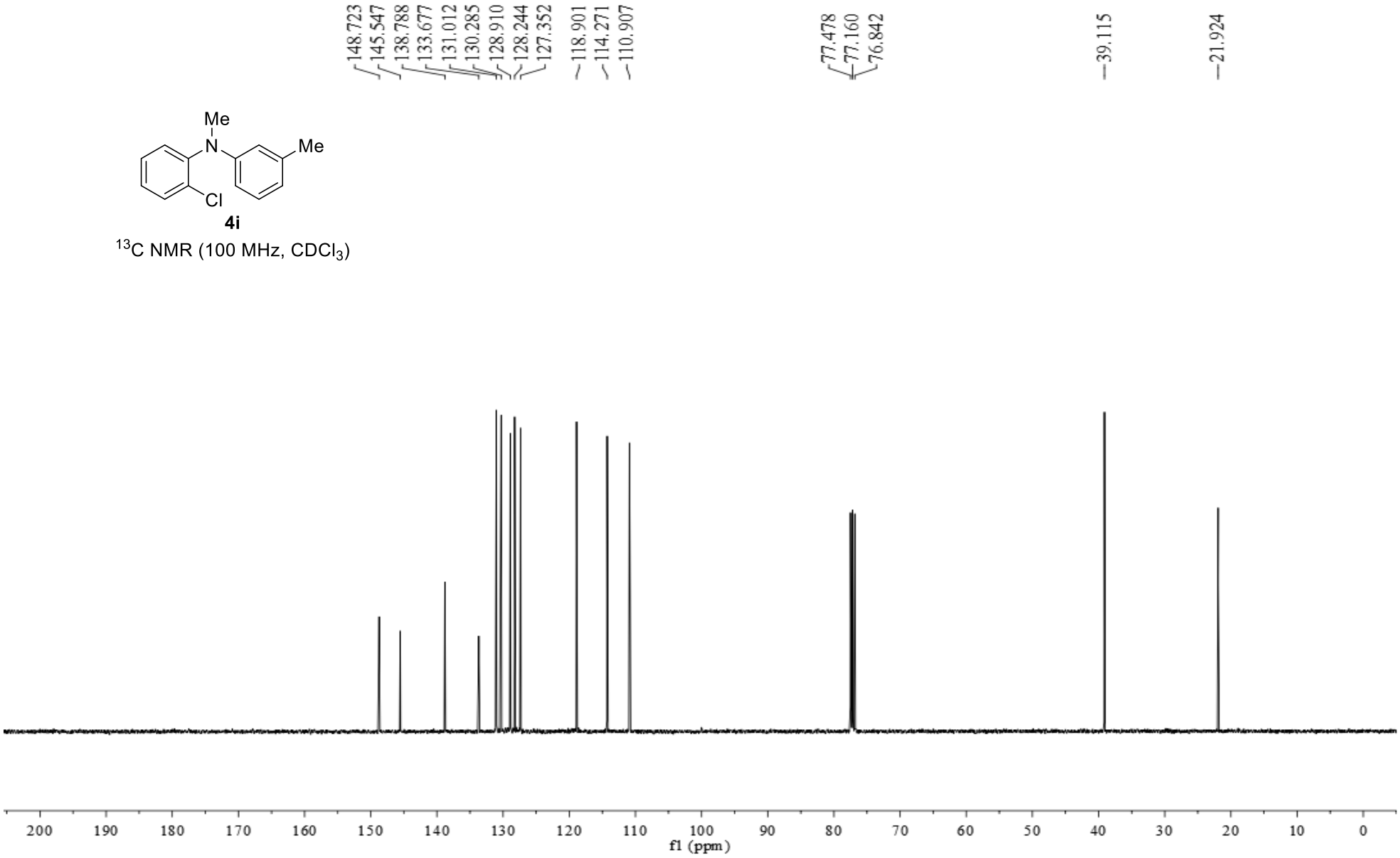
4h

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



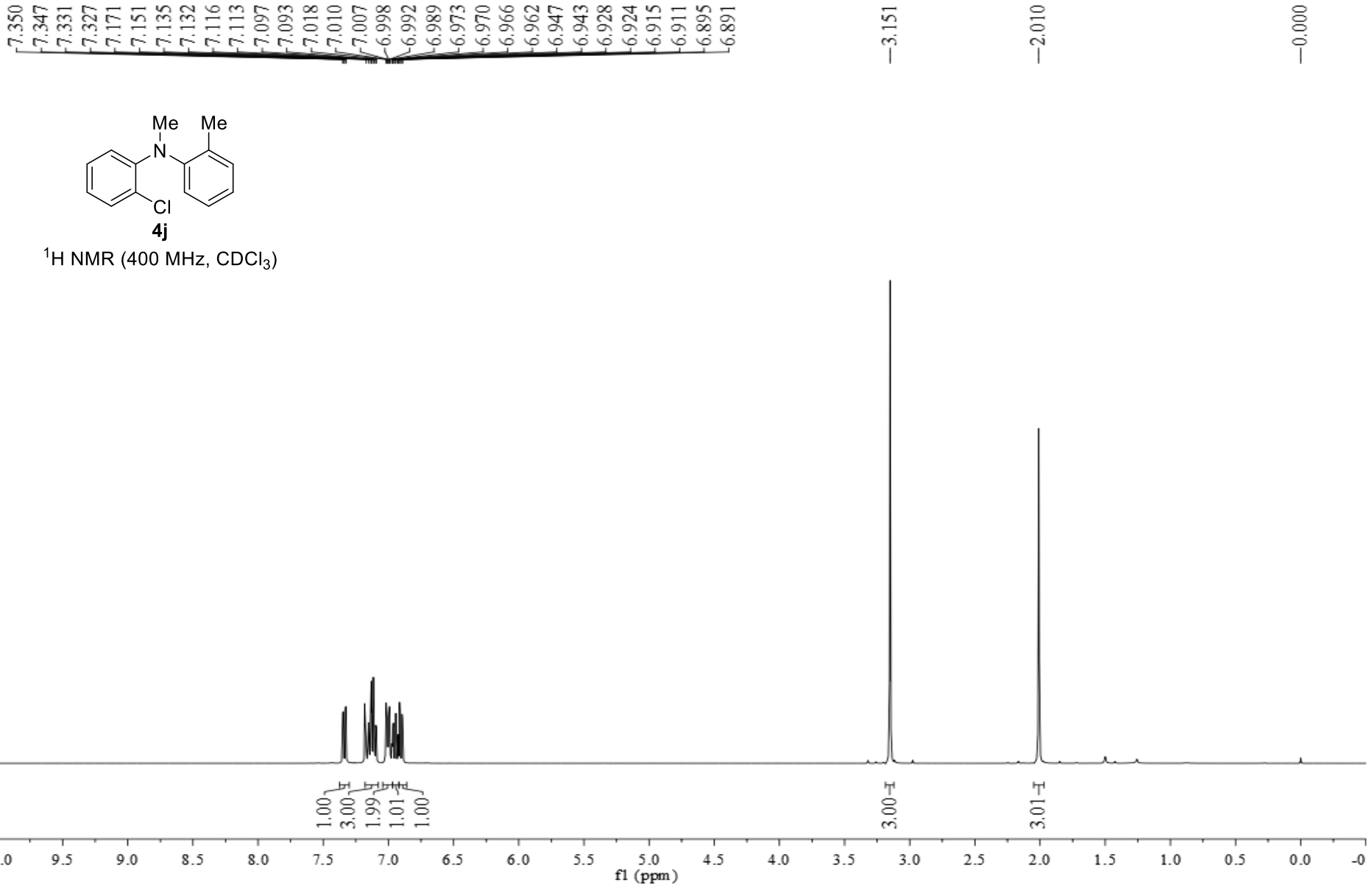
4i

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



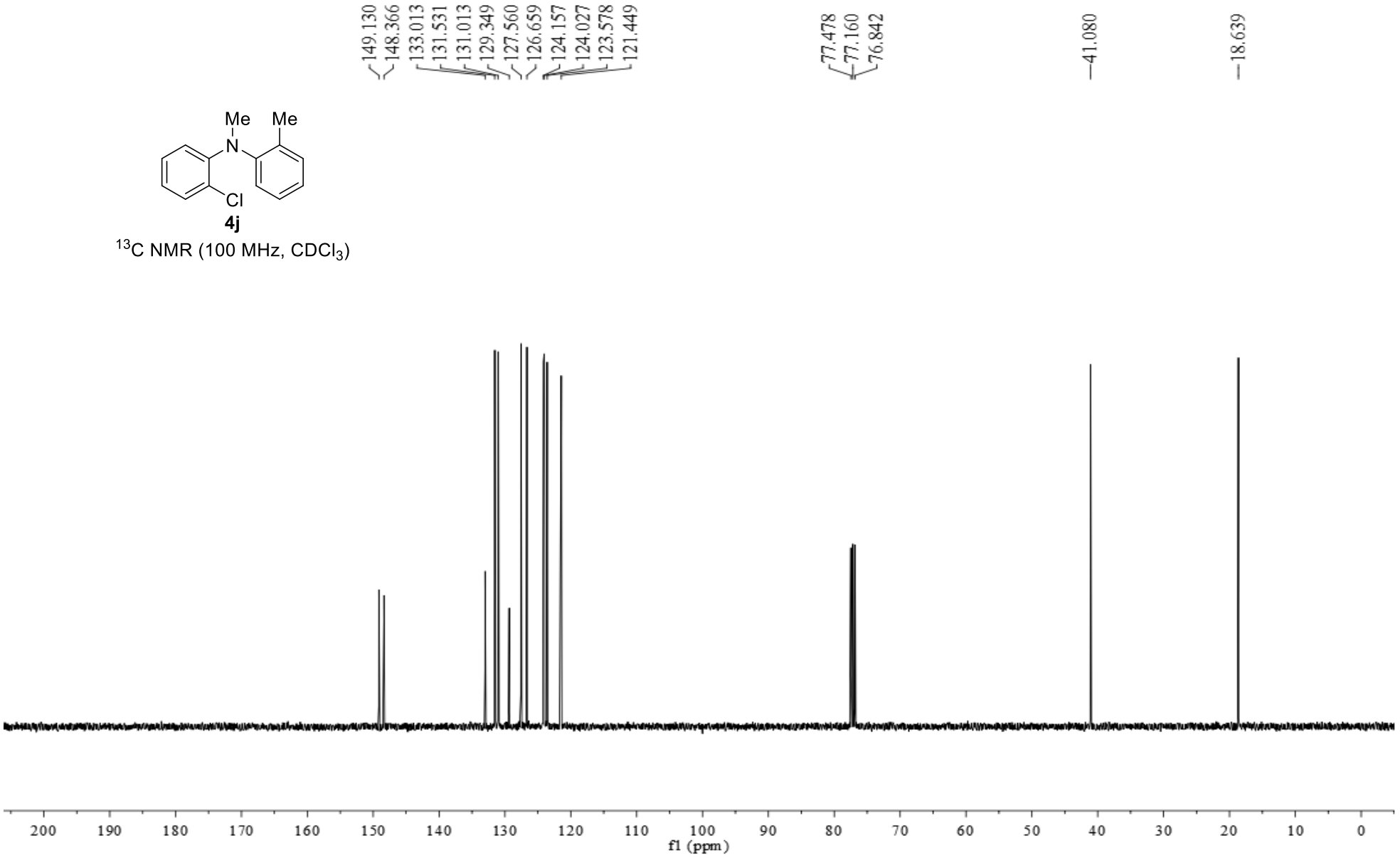
4i

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



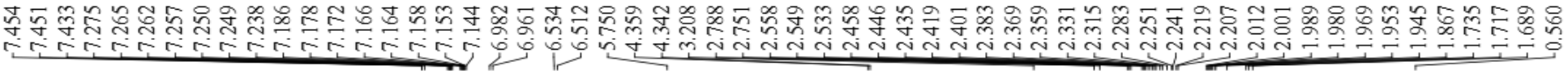
4j

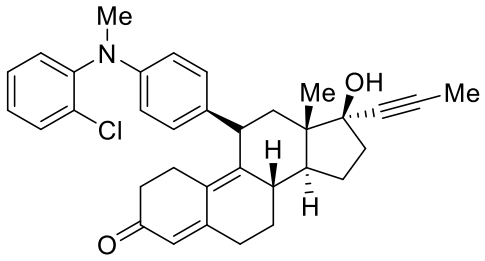
^{1}H NMR (400 MHz, $CDCl_3$)



4j

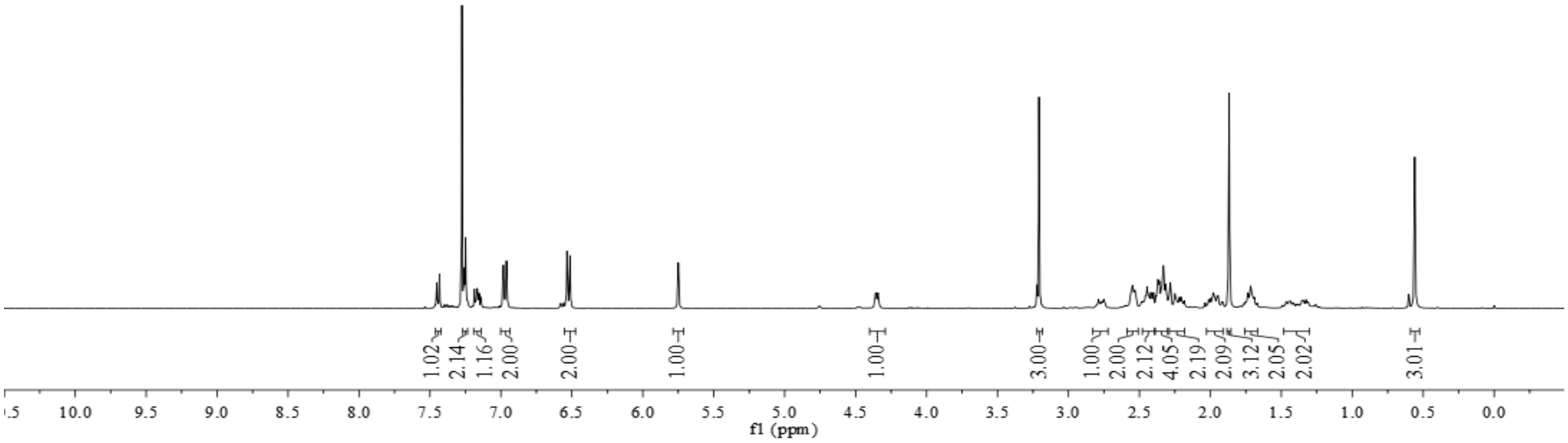
^{13}C NMR (100 MHz, $CDCl_3$)

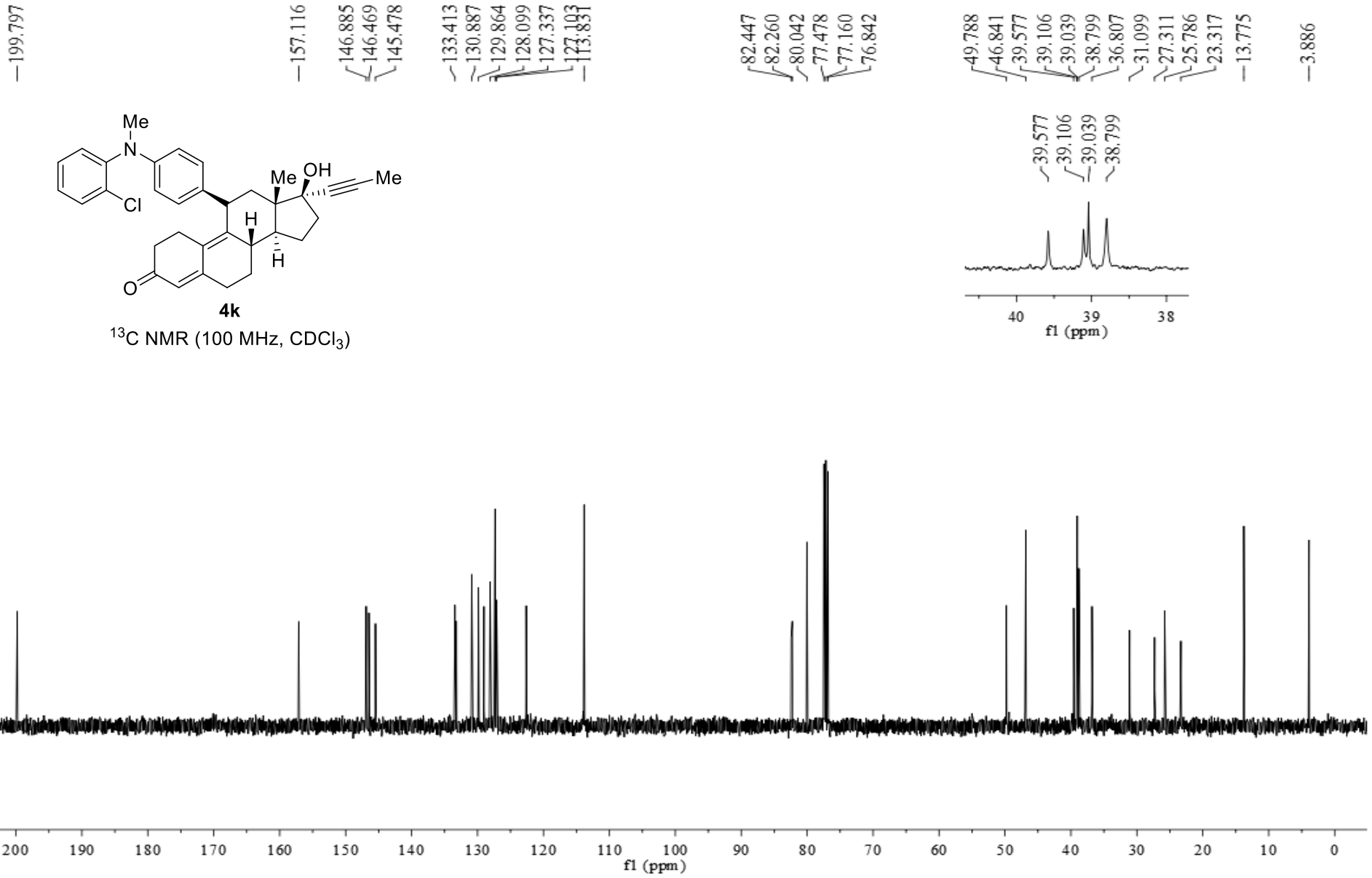




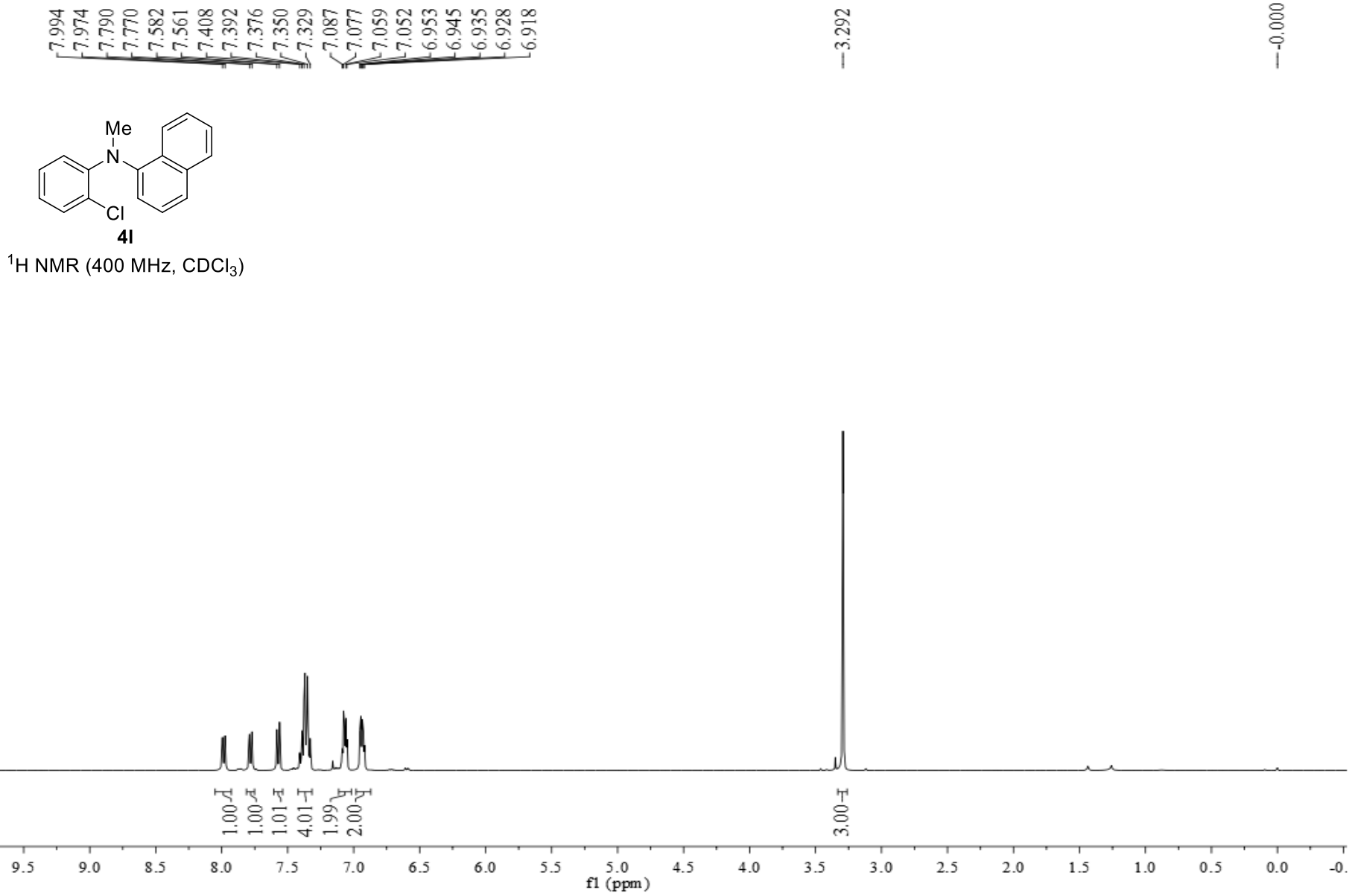
4k

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



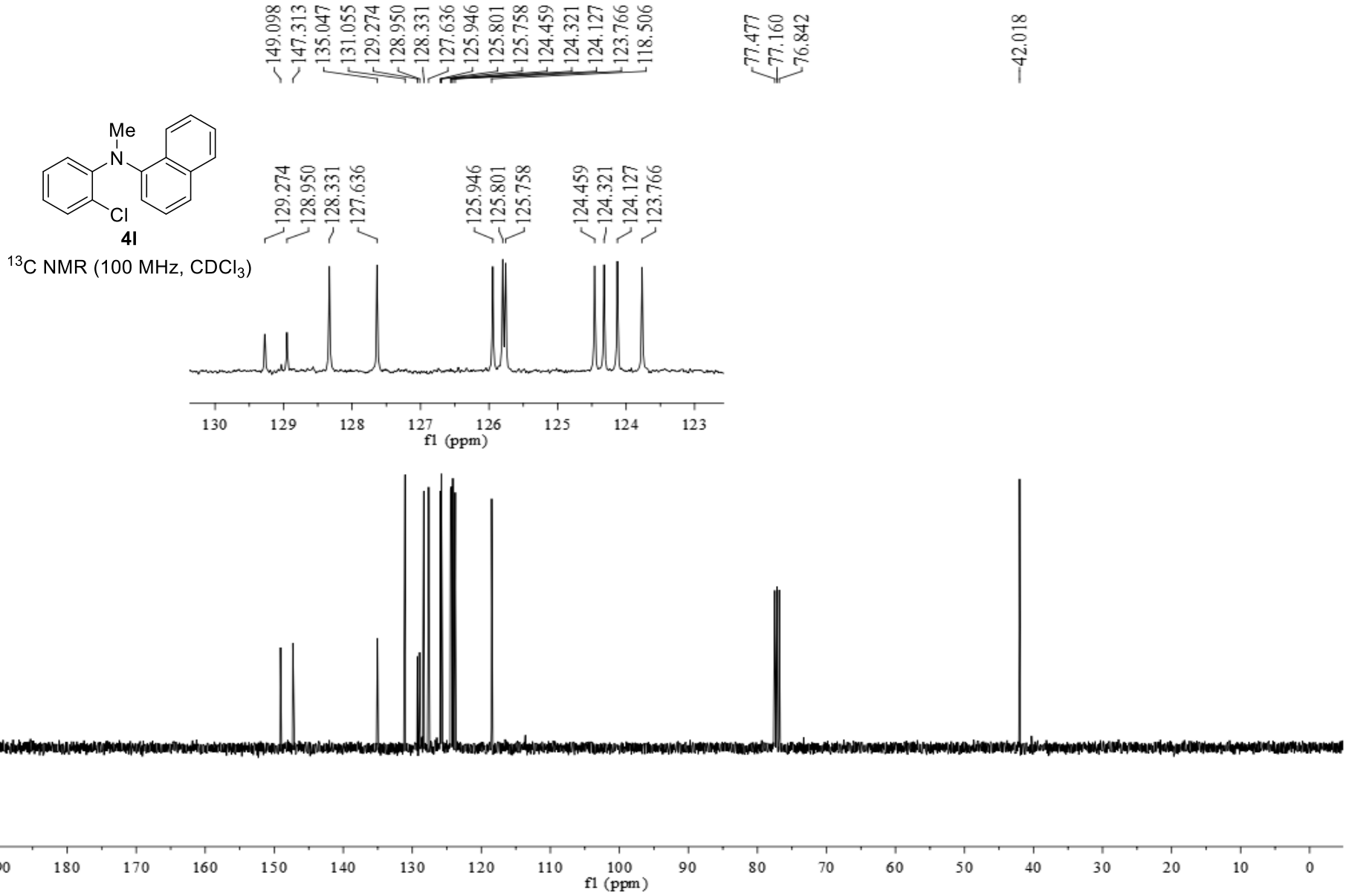


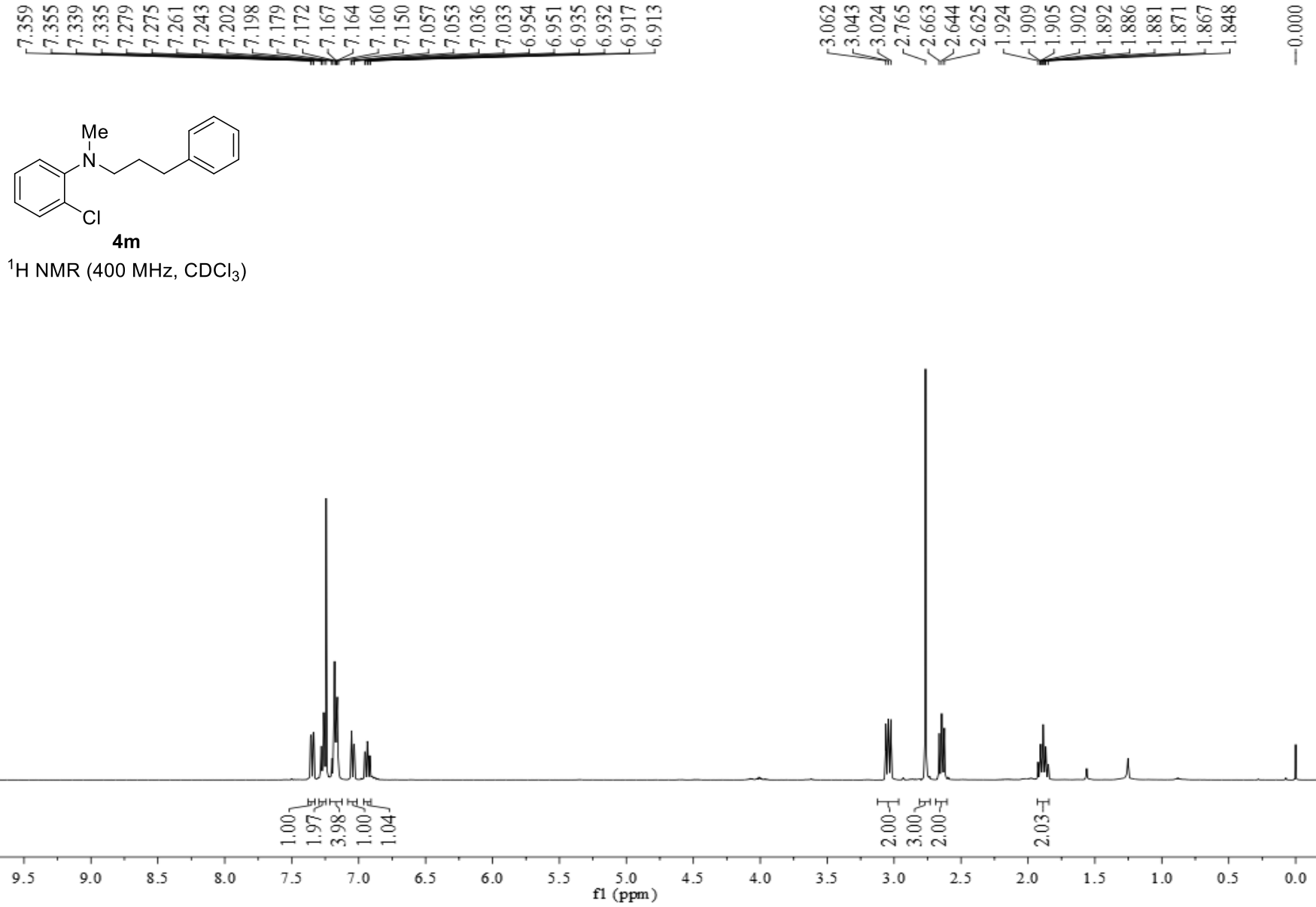
^{13}C NMR (100 MHz, $CDCl_3$)



4l

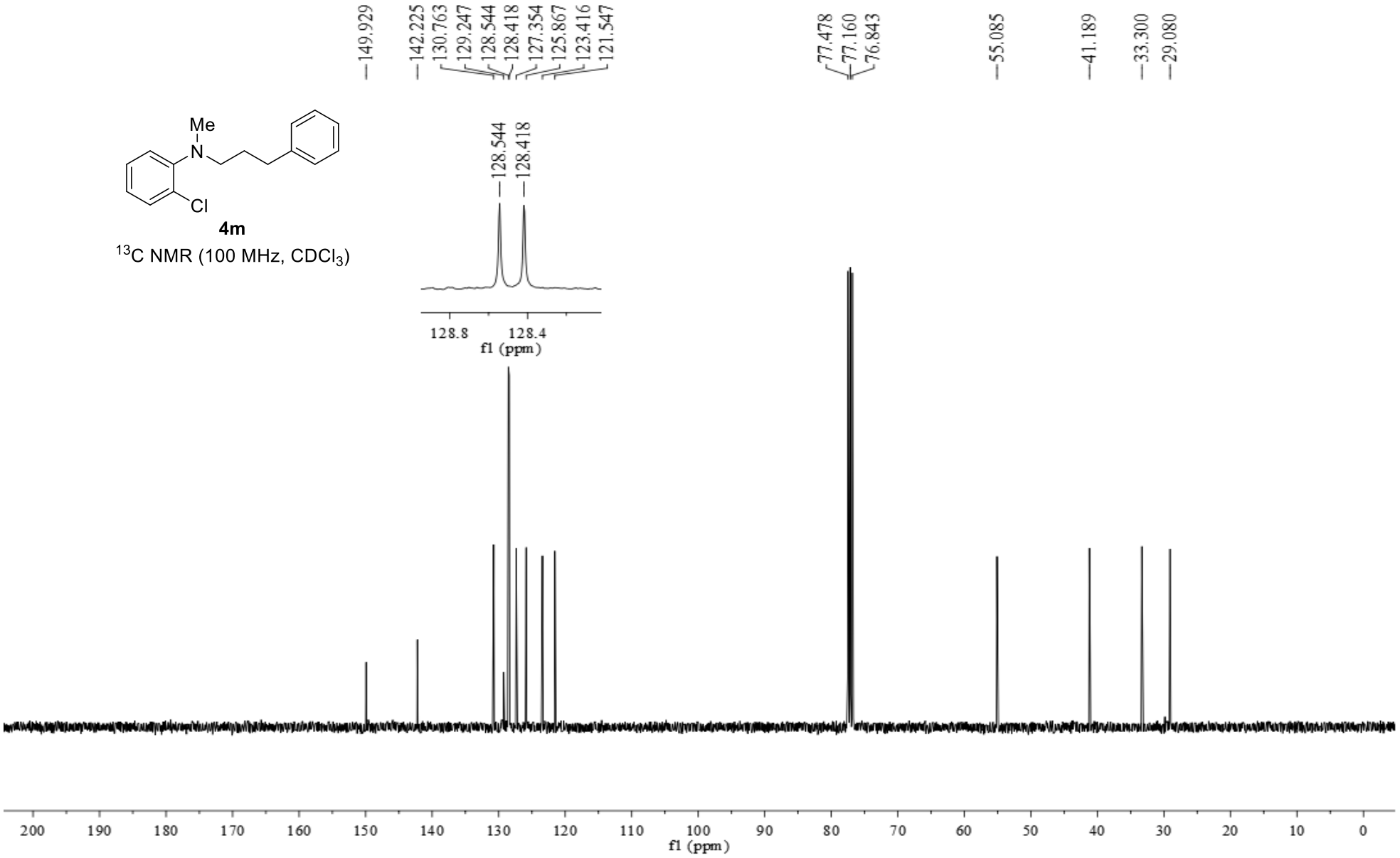
^{1}H NMR (400 MHz, $CDCl_3$)

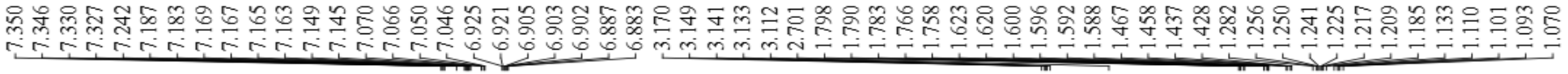

149.098
147.313
135.047
131.055
129.274
128.950
128.331
127.636
125.946
125.801
125.758
124.459
124.321
124.127
123.766
118.506
77.477
77.160
76.842
42.018
Me
N
Cl
4l
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)
f1 (ppm)

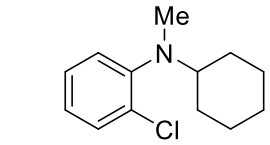


4m

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

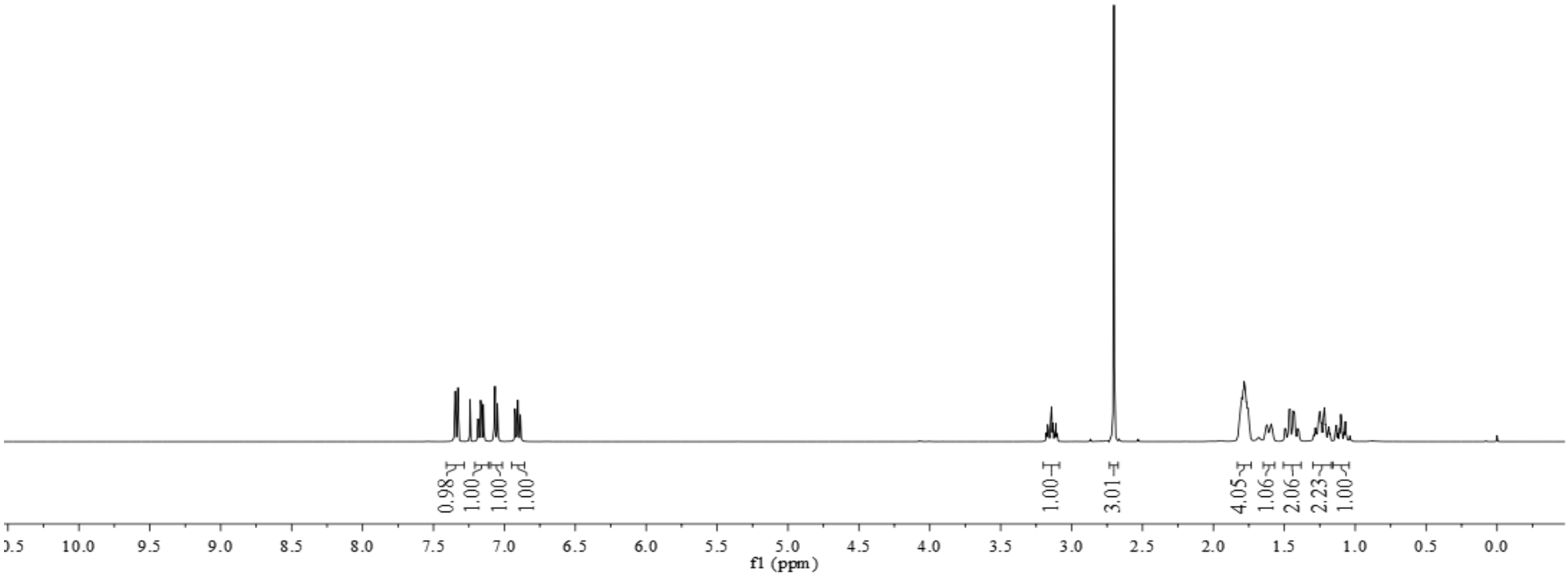

149.929
142.225
130.763
129.247
128.544
128.418
127.354
125.867
123.416
121.547
77.478
77.160
76.843
55.085
41.189
33.300
29.080
Me
N
Cl
4m
13C NMR (100 MHz, CDCl3)
128.544
128.418
128.8
128.4
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

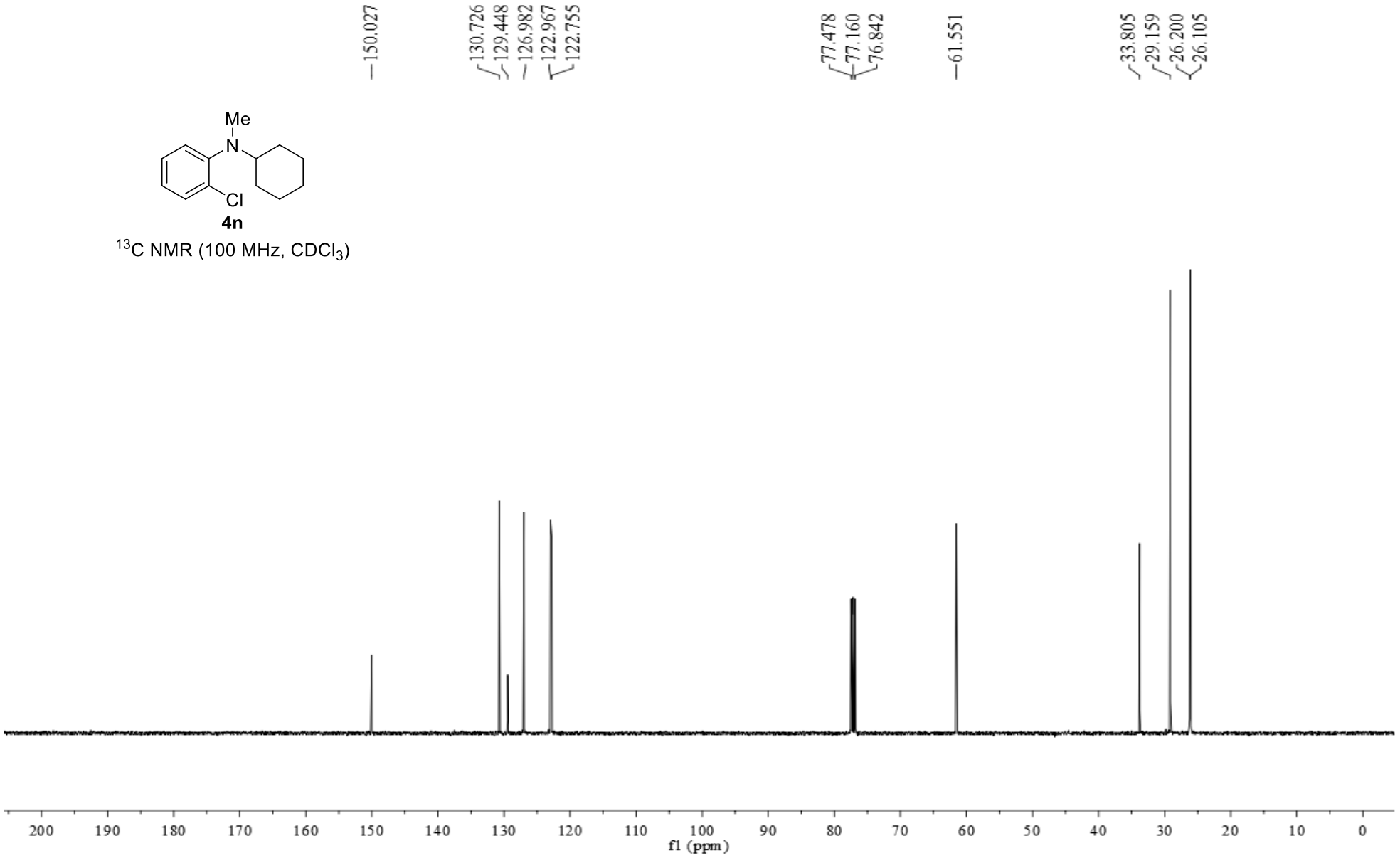


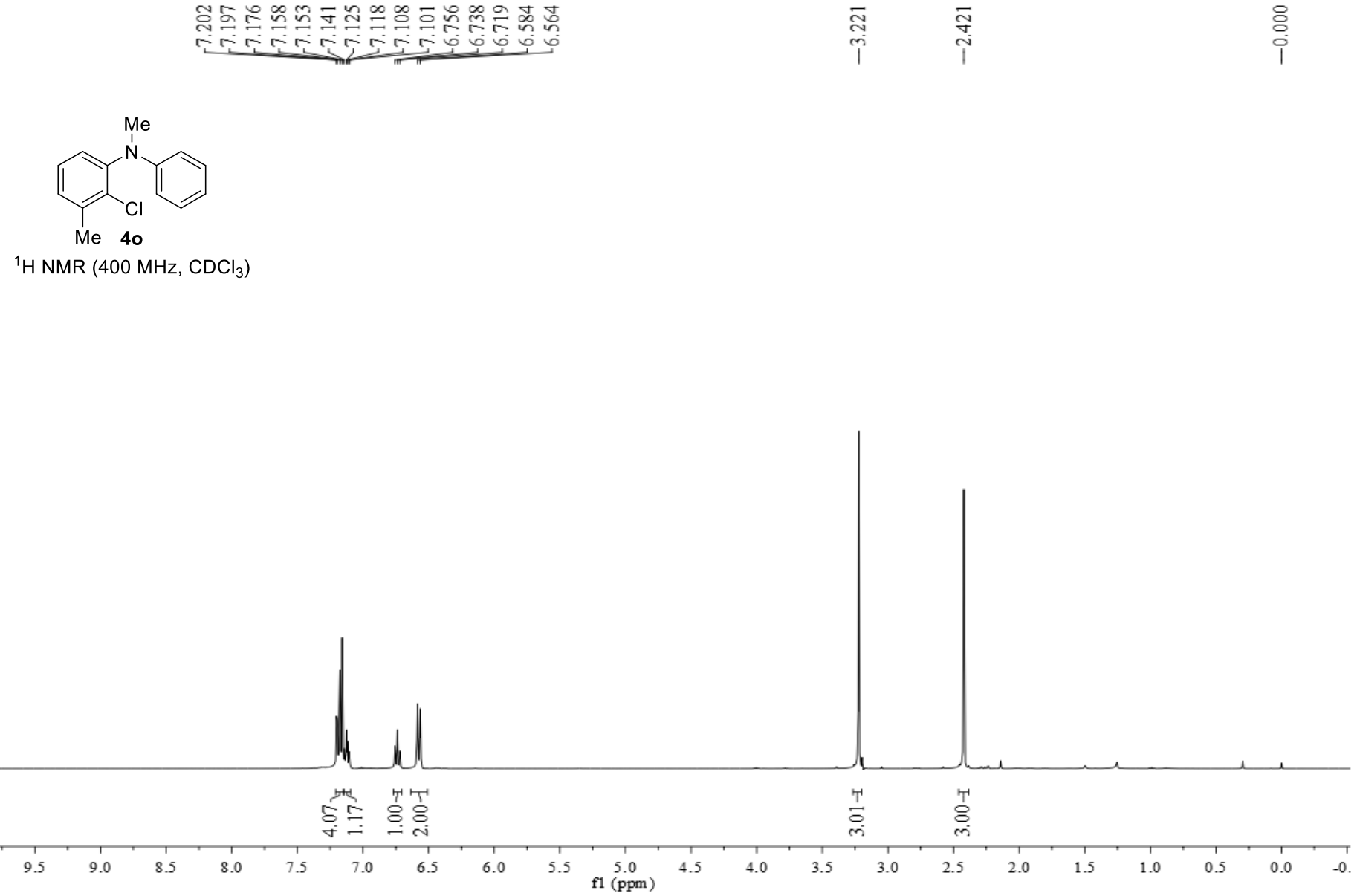


4n

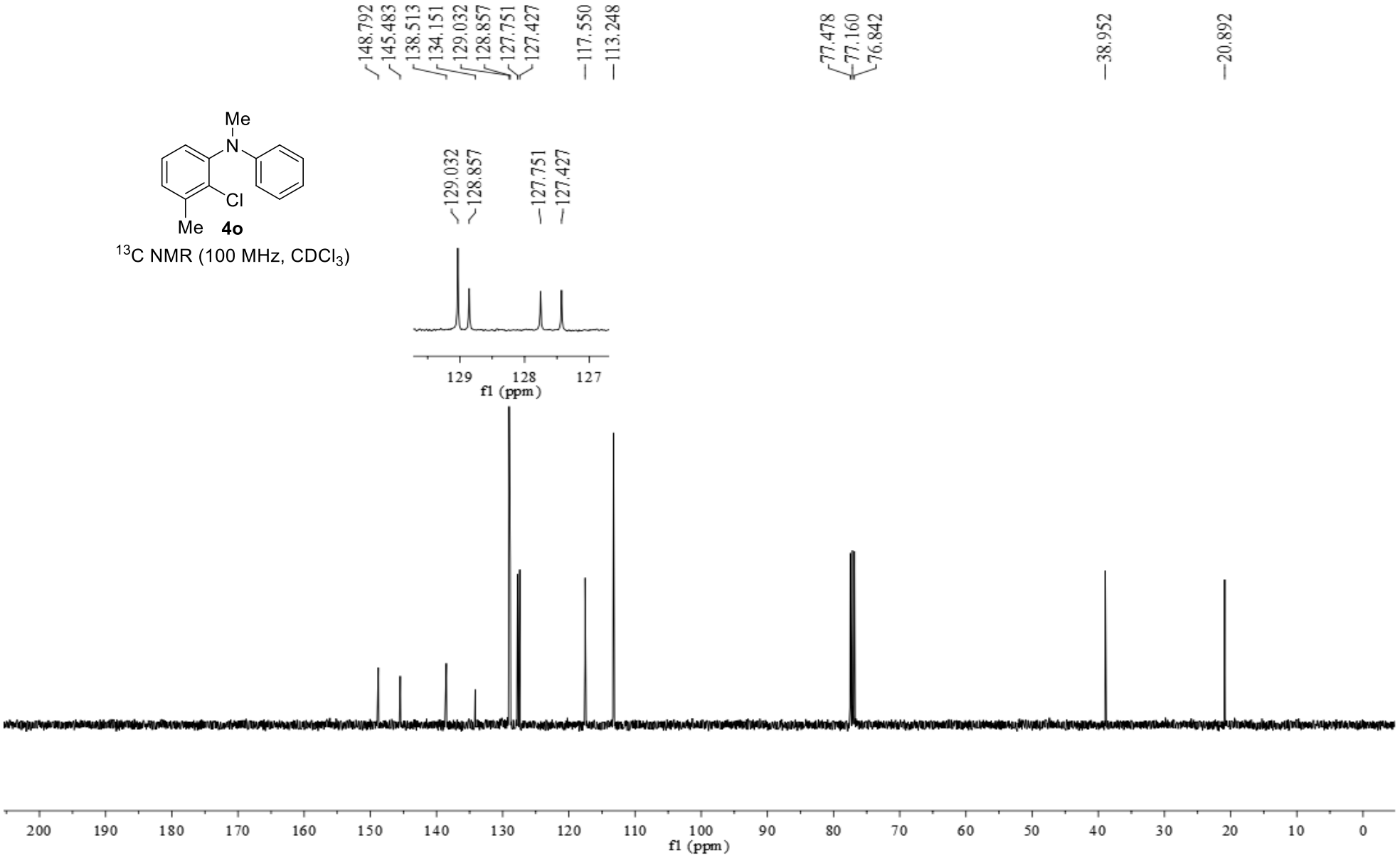
^{1}H NMR (400 MHz, $CDCl_3$)

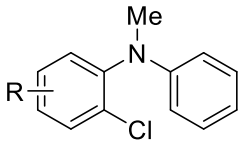



150.027
130.726
129.448
126.982
122.967
122.755
77.478
77.160
76.842
61.551
33.805
29.159
26.200
26.105
Me
N
Cl
4n
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



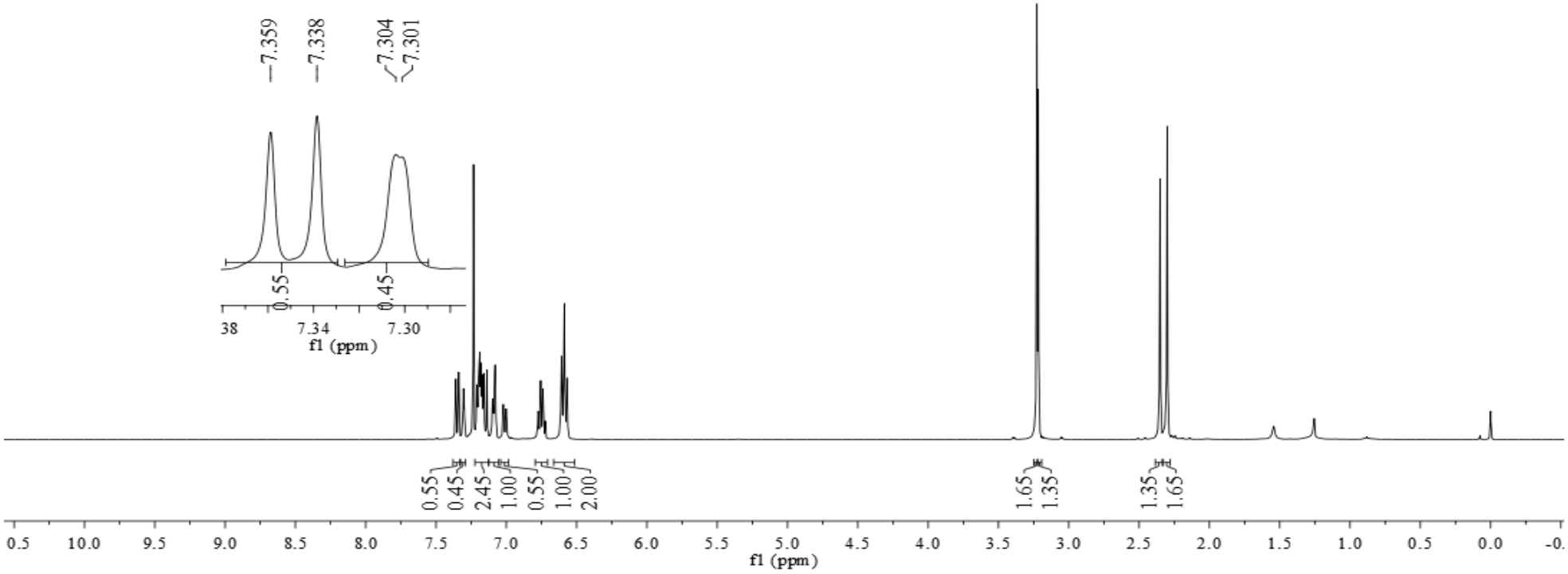
^{1}H NMR (400 MHz, $CDCl_3$)

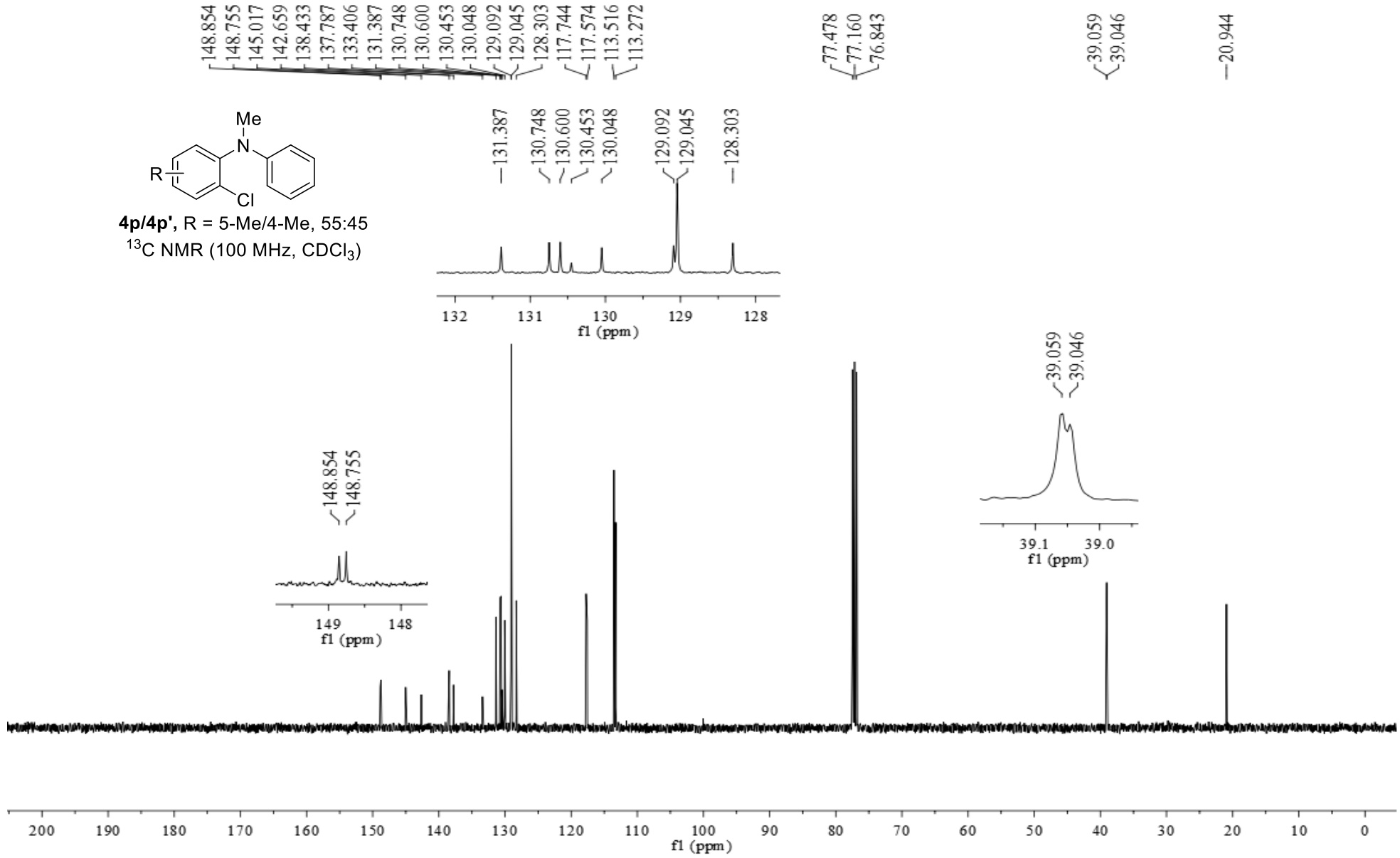

148.792
145.483
138.513
134.151
129.032
128.857
127.751
127.427
117.550
113.248
77.478
77.160
76.842
38.952
20.892
Me
N
Cl
Me
4o
^{13}C NMR (100 MHz, CDCl$_3$)
129.032
128.857
127.751
127.427
129
128
127
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

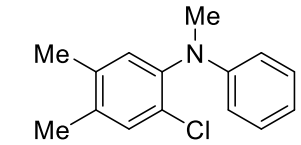


4p/4p', R = 5-Me/4-Me, 55:45

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

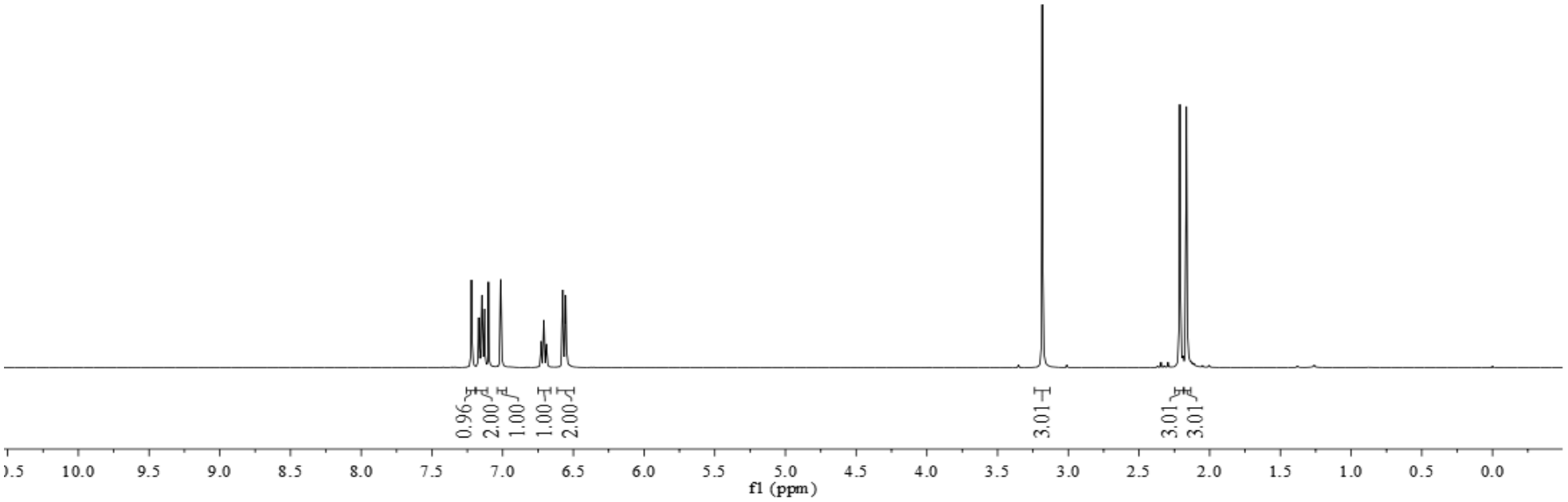


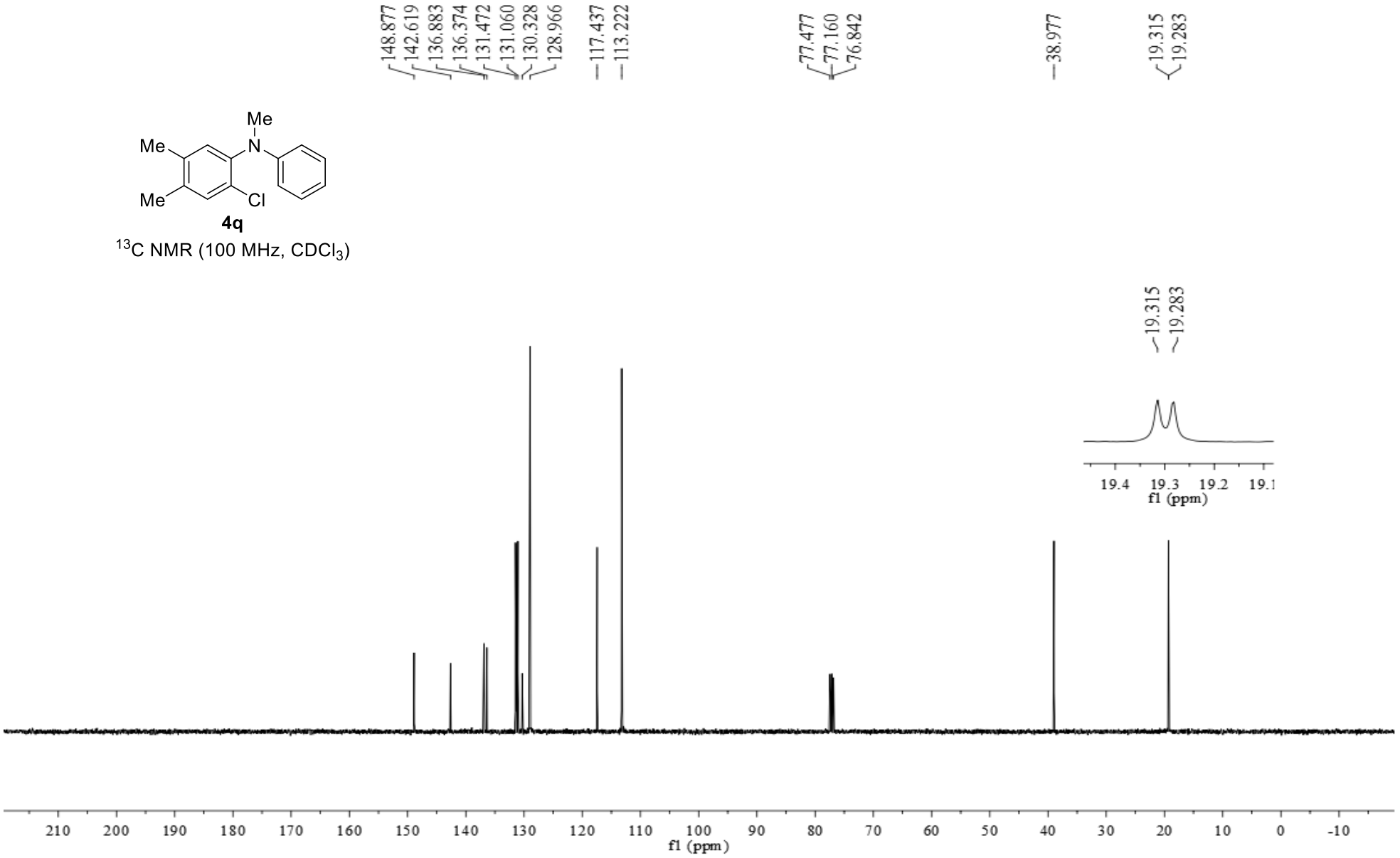

148.854
148.755
145.017
142.659
138.433
137.787
133.406
131.387
130.748
130.600
130.453
130.048
129.092
129.045
128.303
117.744
117.574
113.516
113.272
77.478
77.160
76.843
39.059
39.046
20.944
Me
N
R
Cl
4p/4p', R = 5-Me/4-Me, 55:45
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)

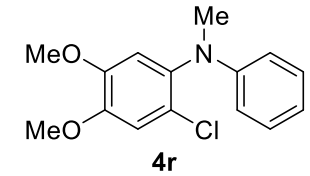


4q

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

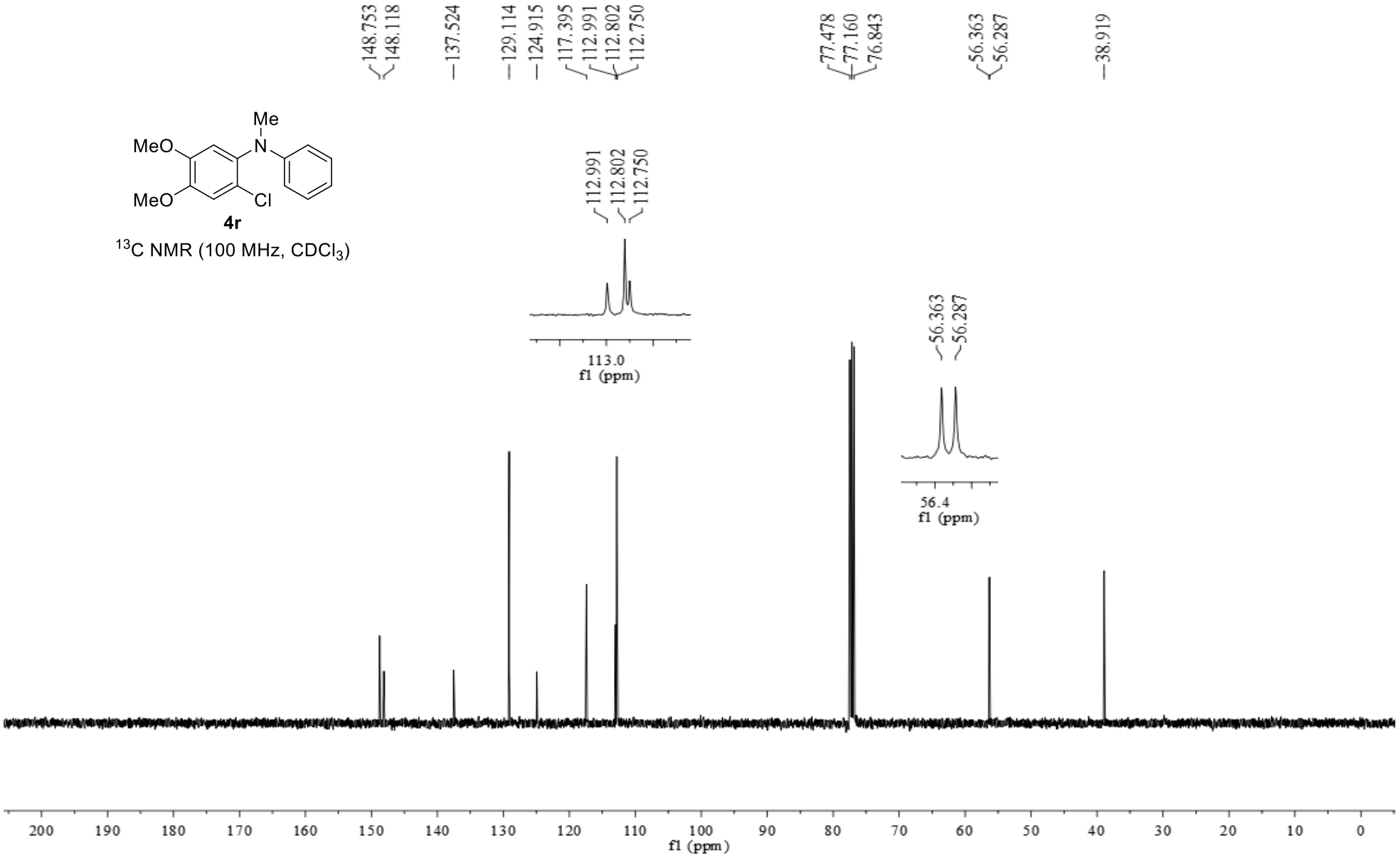


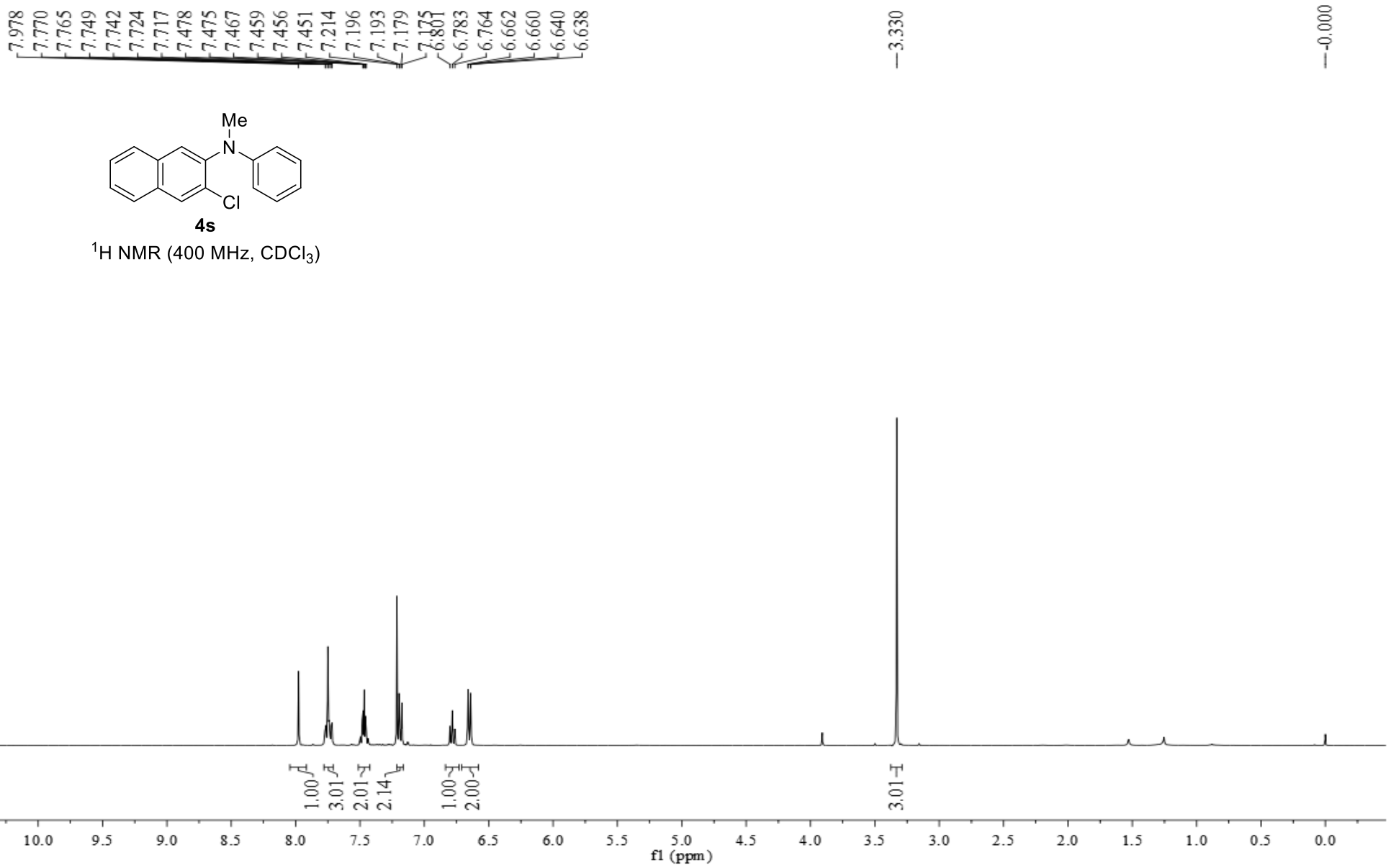

148.877
142.619
136.883
136.374
131.472
131.060
130.328
128.966
117.437
113.222
77.477
77.160
76.842
38.977
19.315
19.283
Me
N
Me
Me
Cl
4q
13C NMR (100 MHz, CDCl3)
19.315
19.283
19.4
19.3
19.2
19.1
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4r

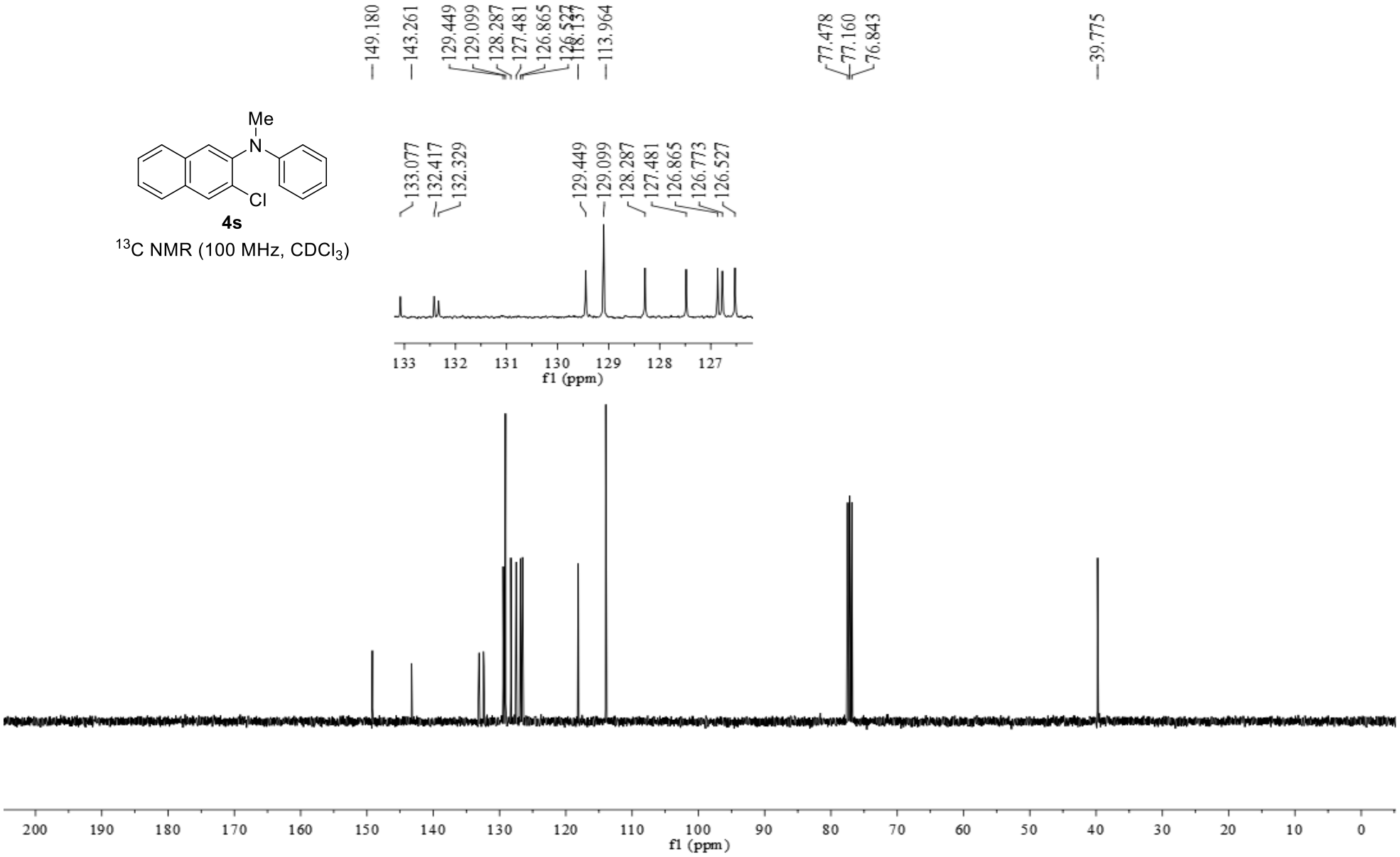
^{1}H NMR (400 MHz, $CDCl_3$)


148.753
148.118
137.524
129.114
124.915
117.395
112.991
112.802
112.750
77.478
77.160
76.843
56.363
56.287
38.919
Me
MeO
N
MeO
Cl
4r
13C NMR (100 MHz, CDCl3)
112.991
112.802
112.750
113.0
f1 (ppm)
56.363
56.287
56.4
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

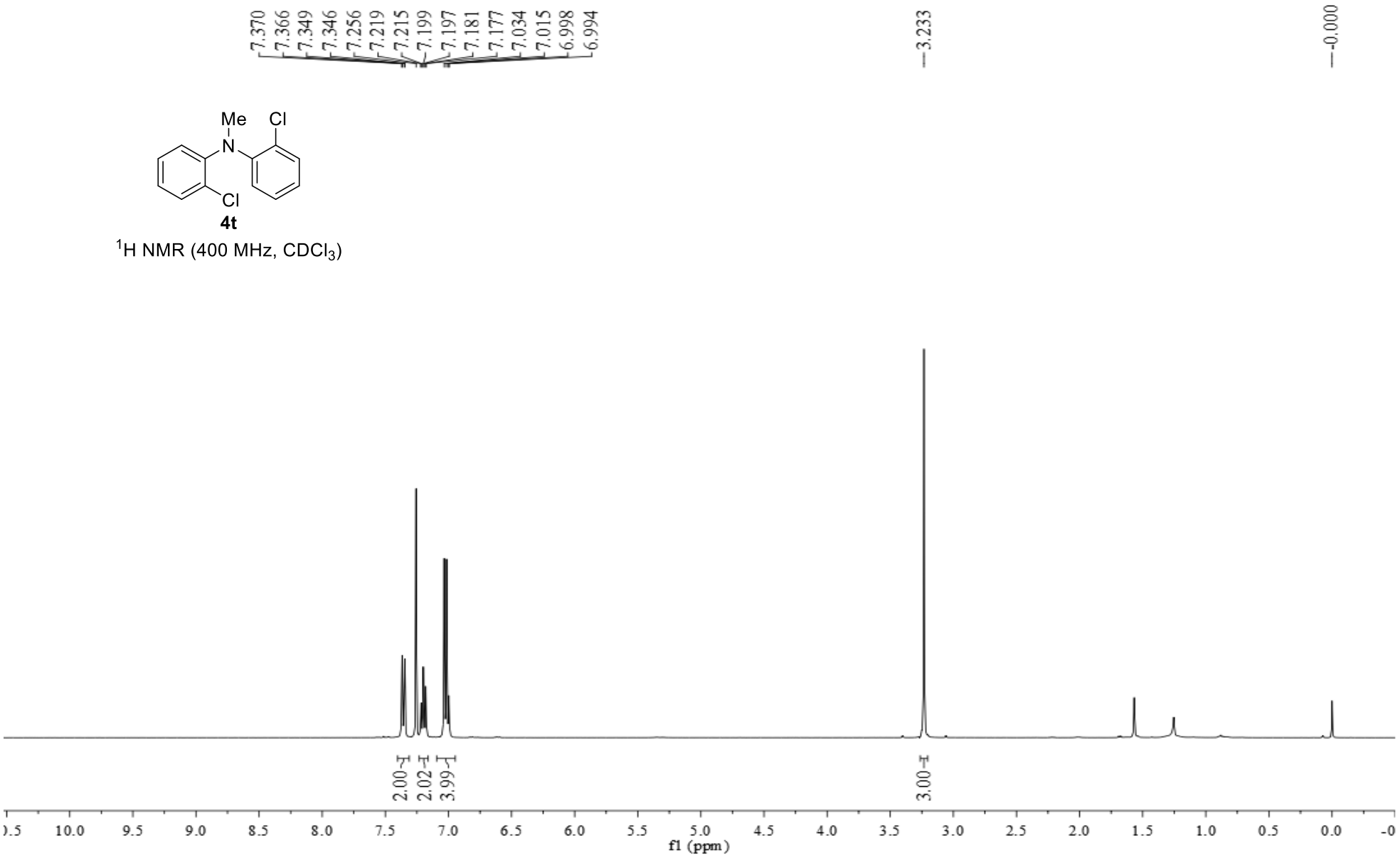


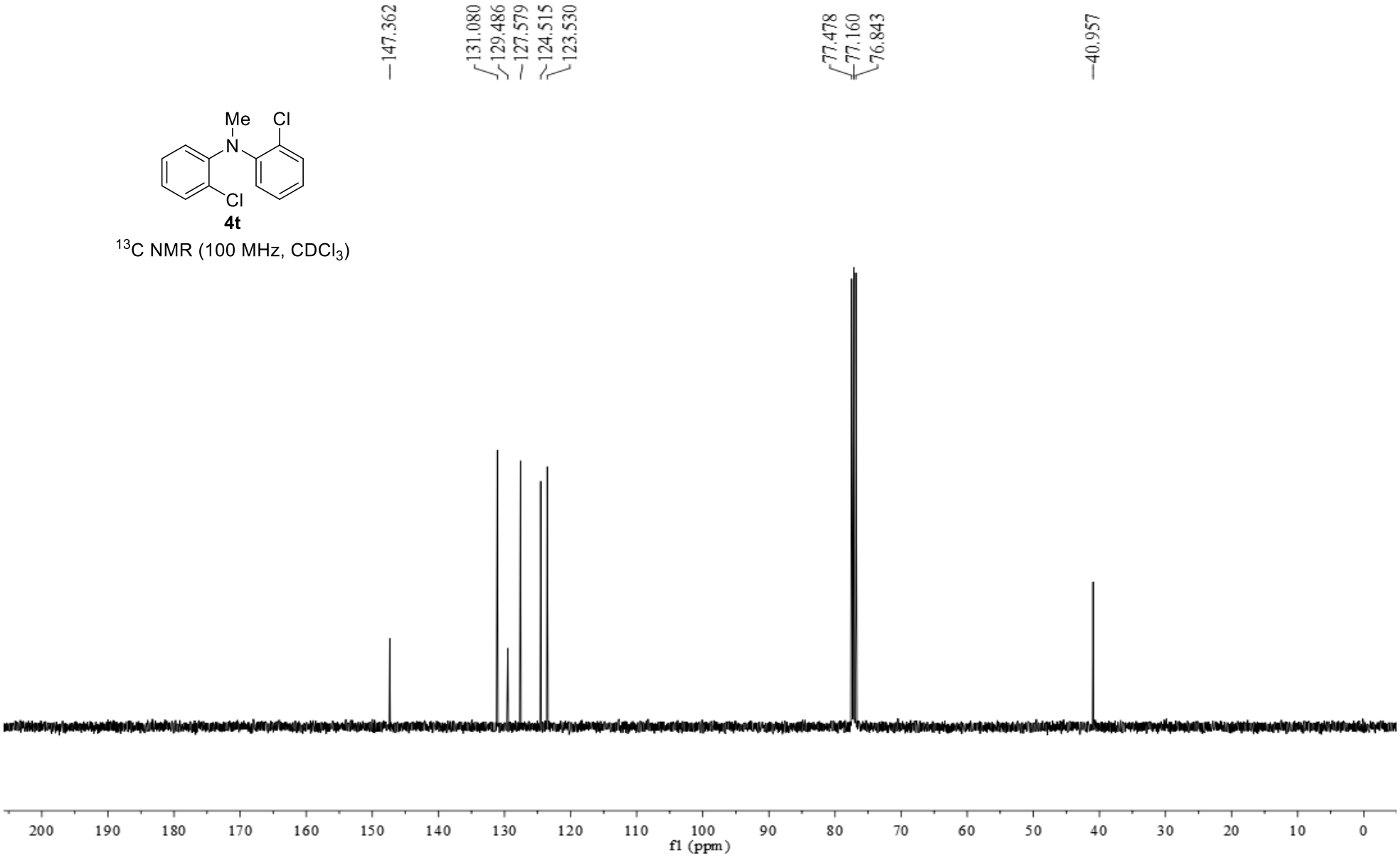
4s

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



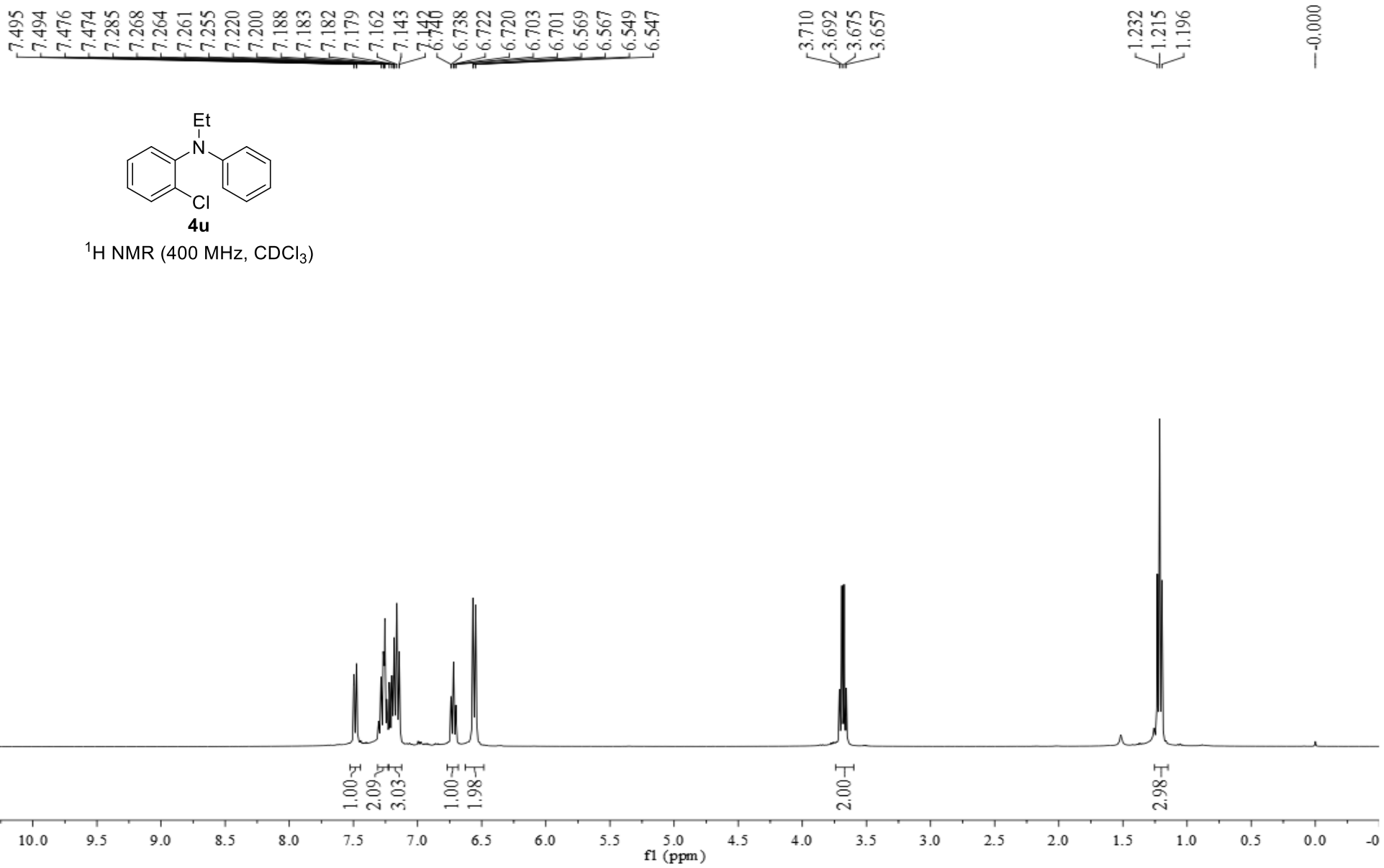
^{13}C NMR (100 MHz, $CDCl_3$)


7.370
7.366
7.349
7.346
7.256
7.219
7.215
7.199
7.197
7.181
7.177
7.034
7.015
6.998
6.994
3.233
0.000
Me
Cl
N
Cl
4t
1H NMR (400 MHz, CDCl3)
2.00
2.02
3.99
3.00
f1 (ppm)



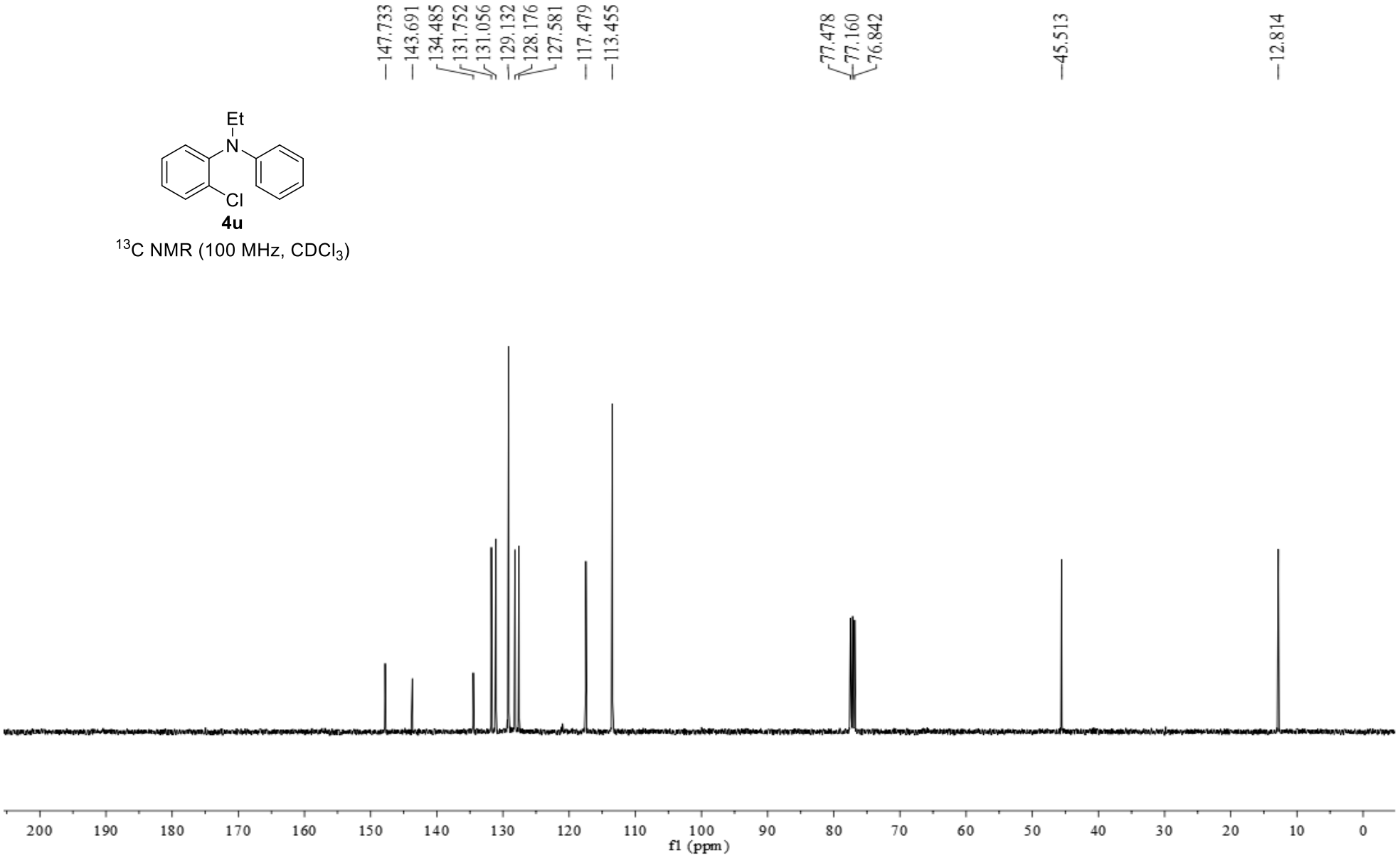
4t

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



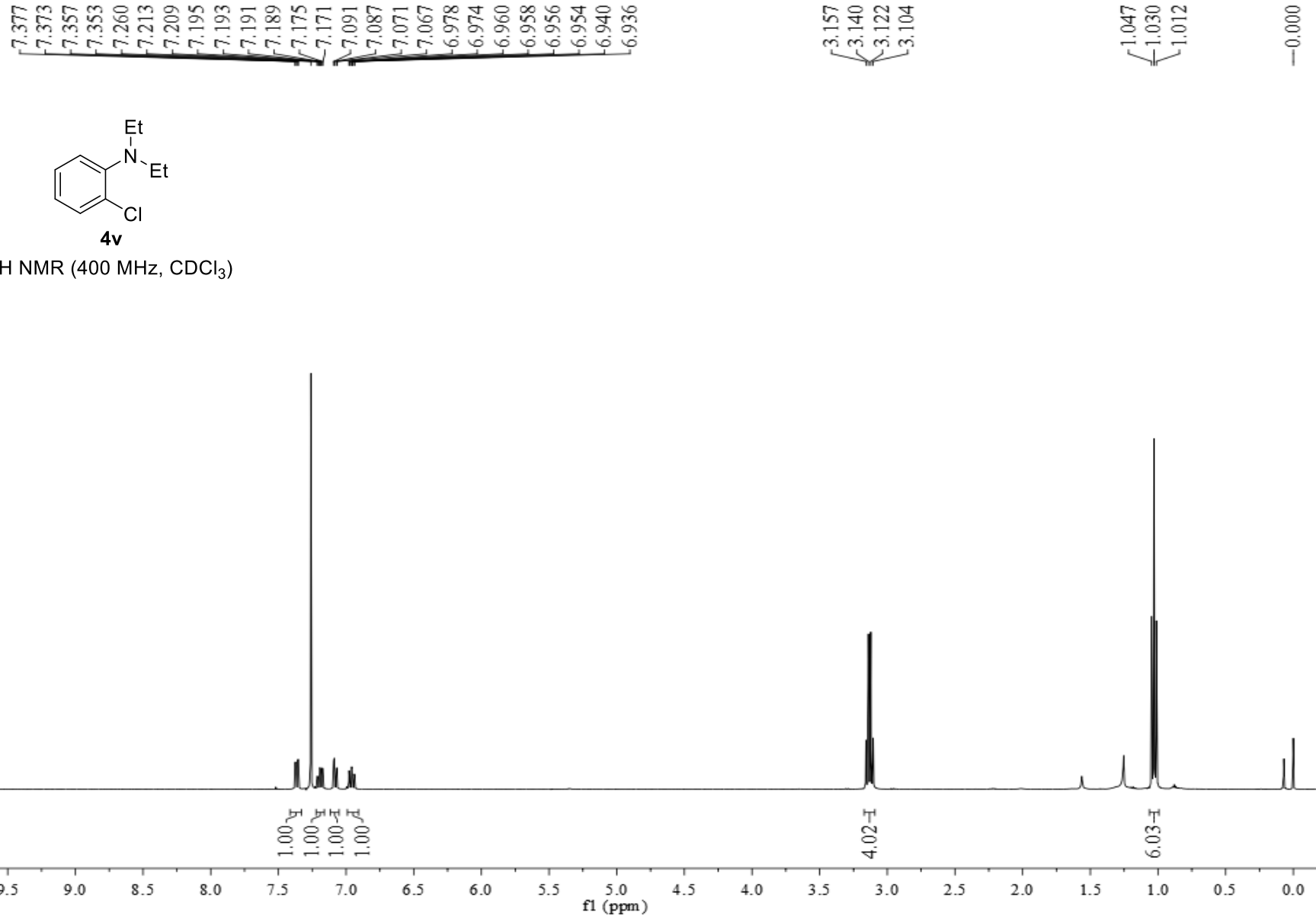
4u

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



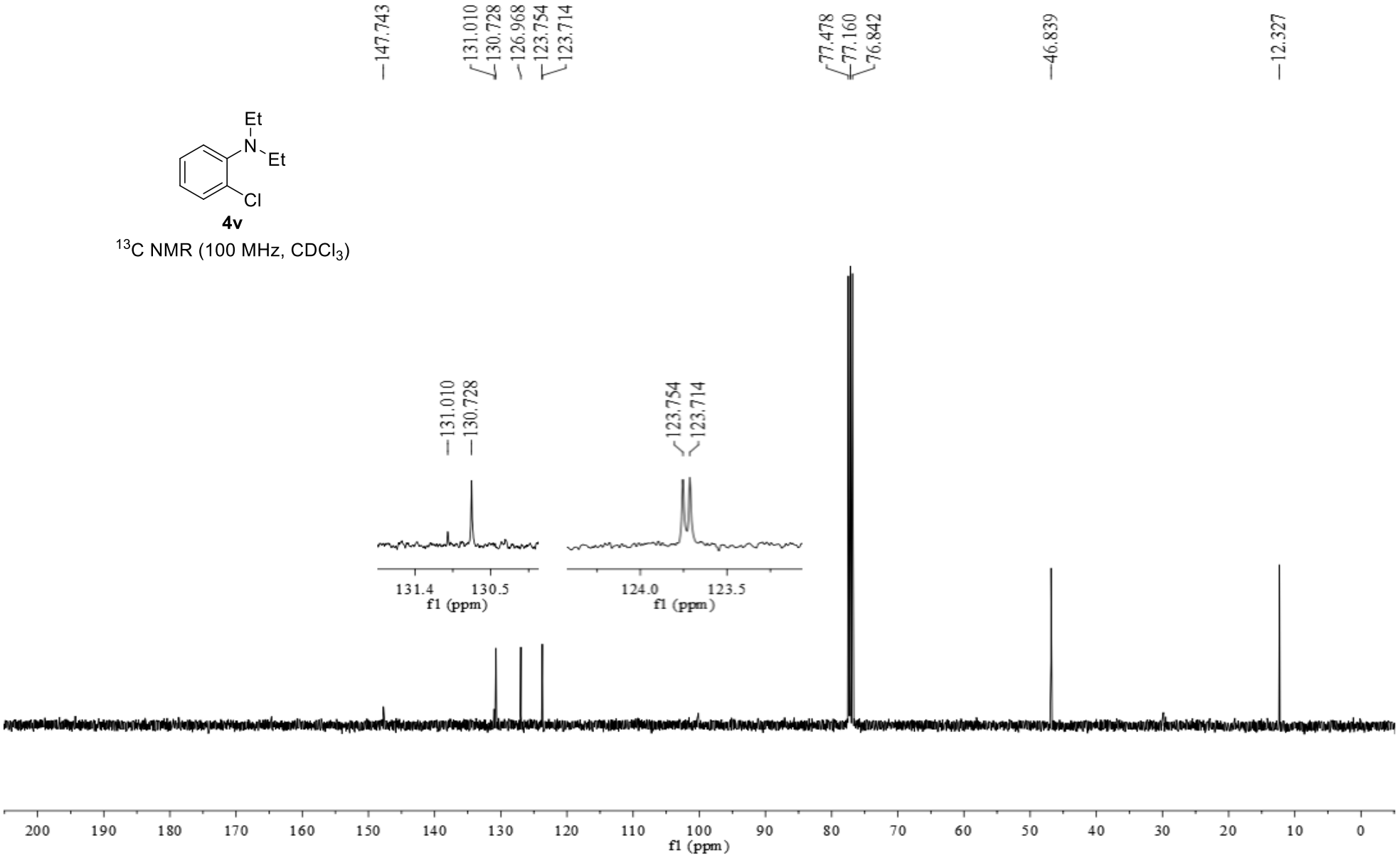
4u

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



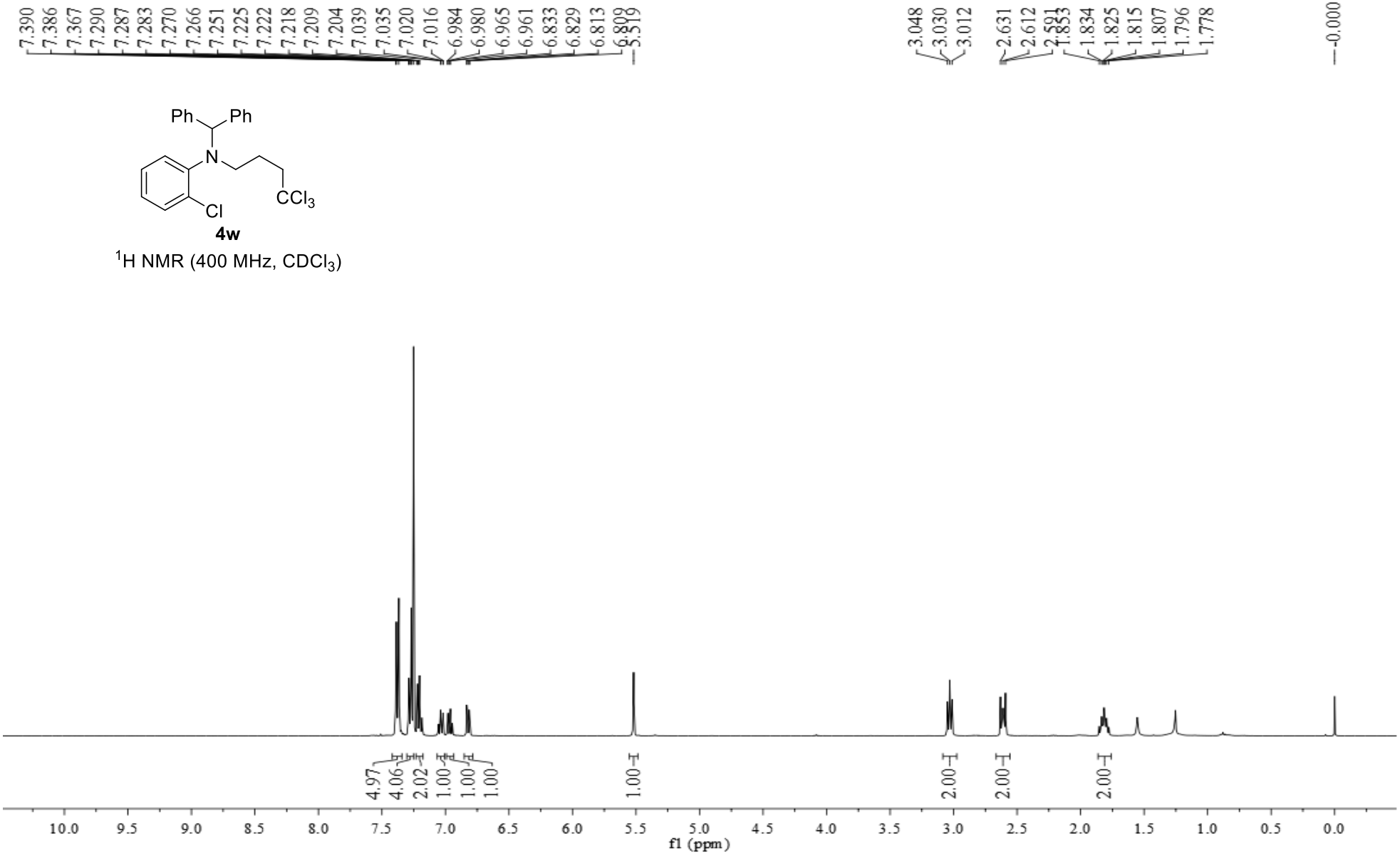
4v

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



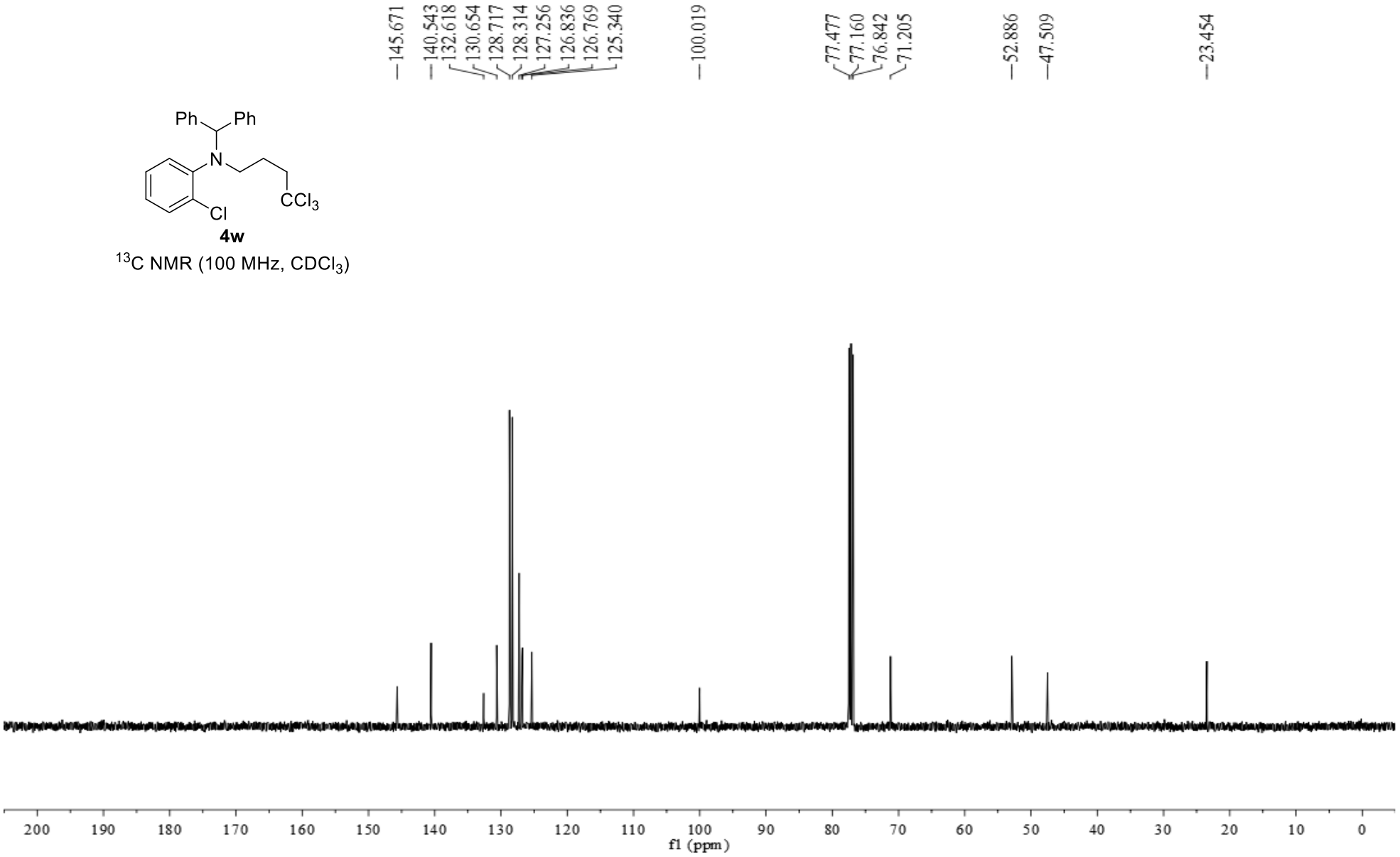
4v

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



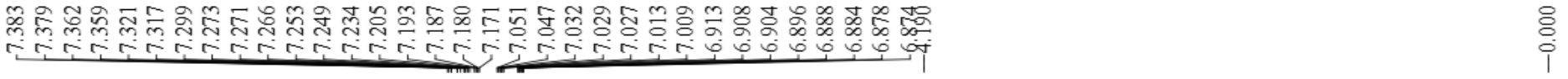
4w

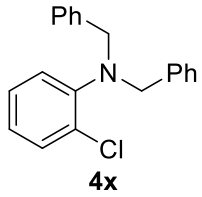
^{1}H NMR (400 MHz, $CDCl_3$)



4w

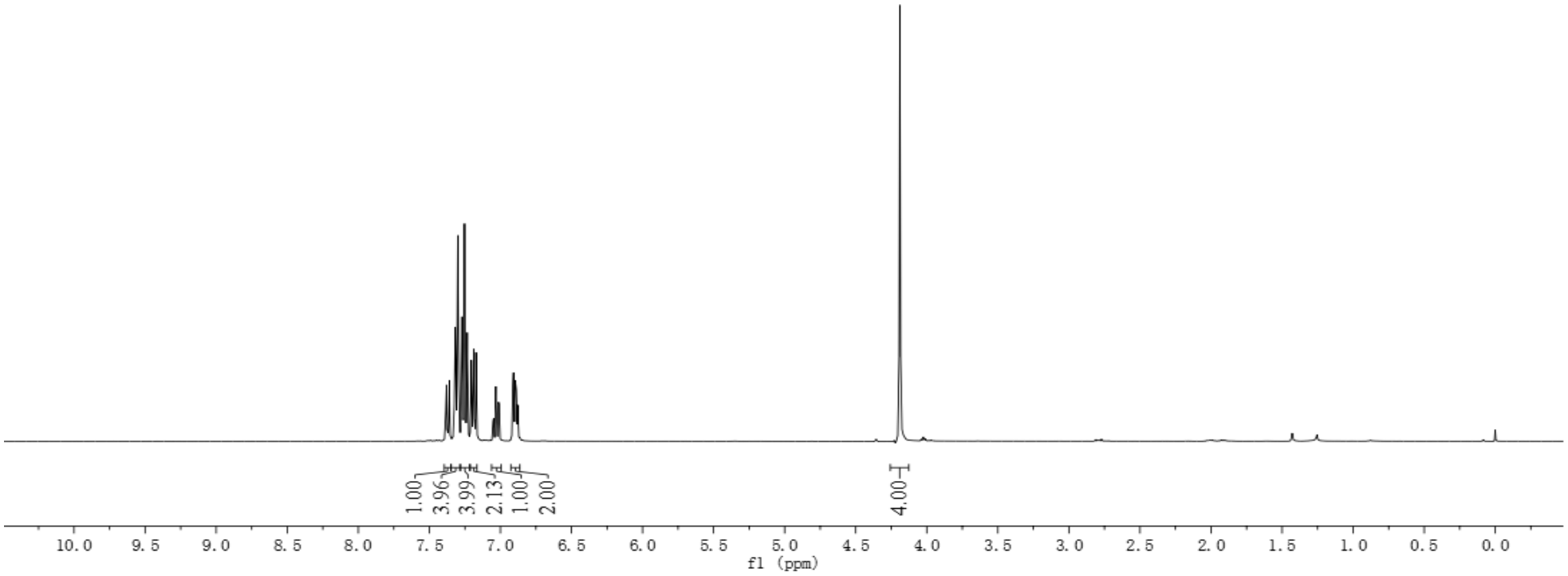
^{13}C NMR (100 MHz, $CDCl_3$)

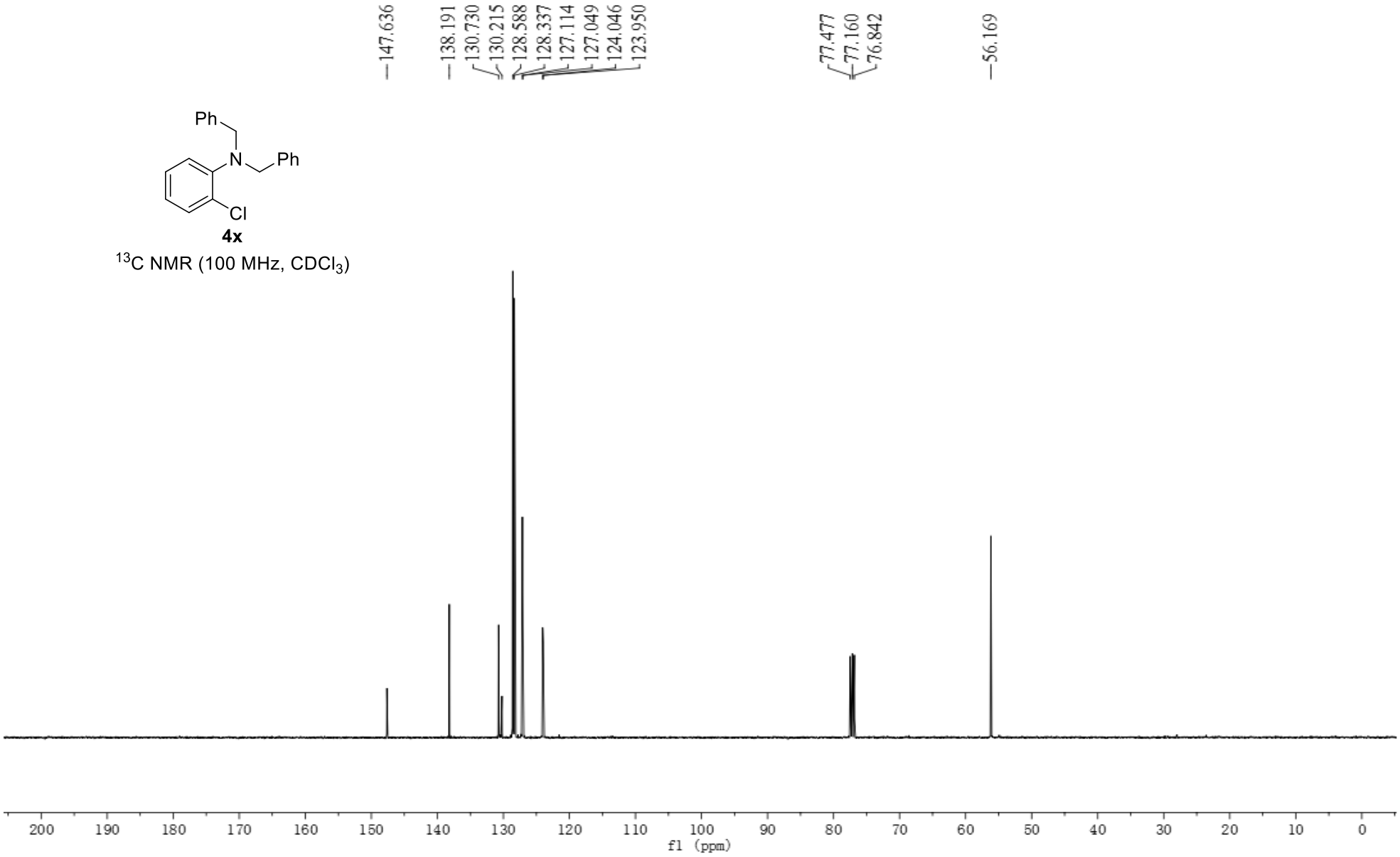




4x

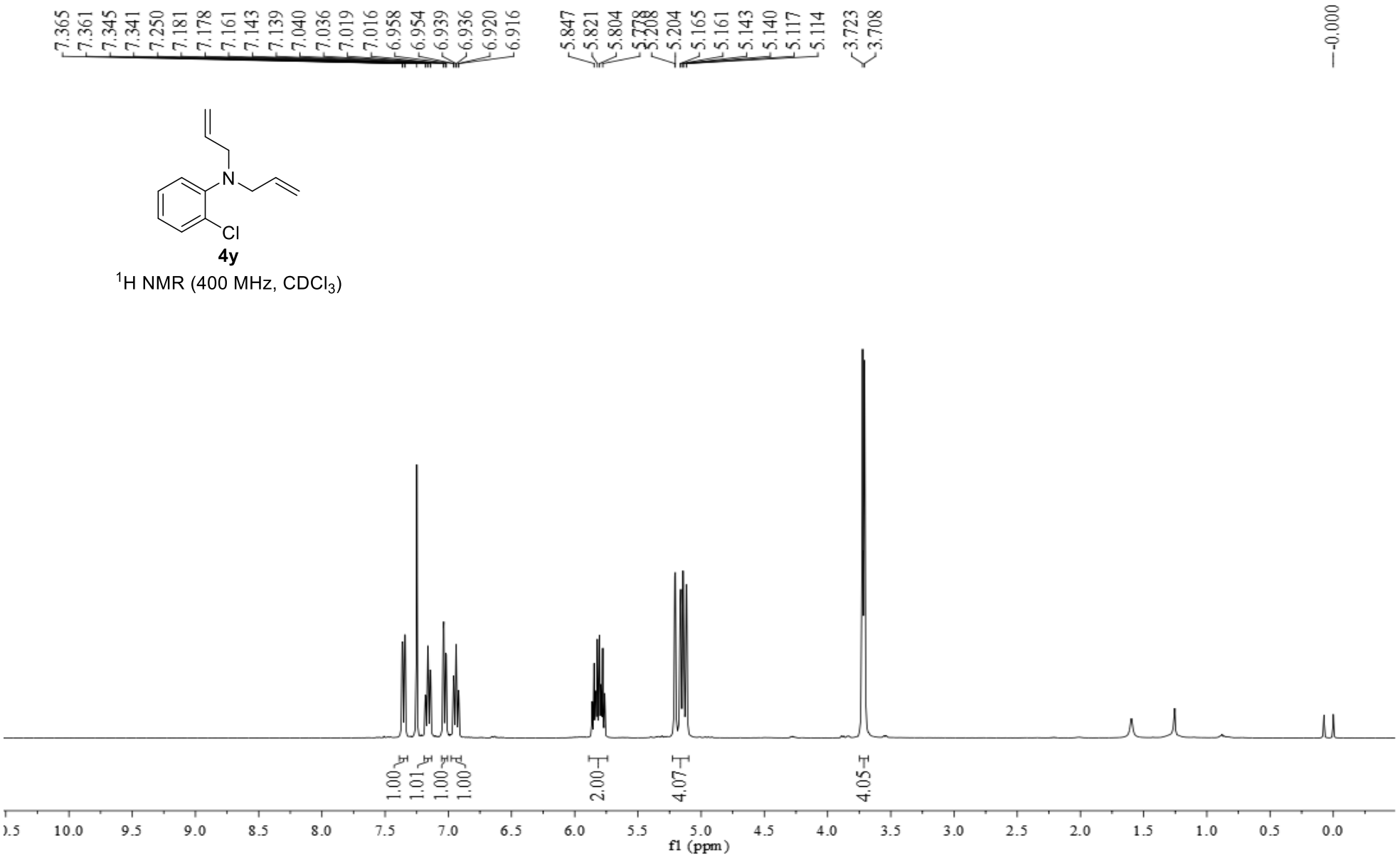
^{1}H NMR (400 MHz, $CDCl_3$)





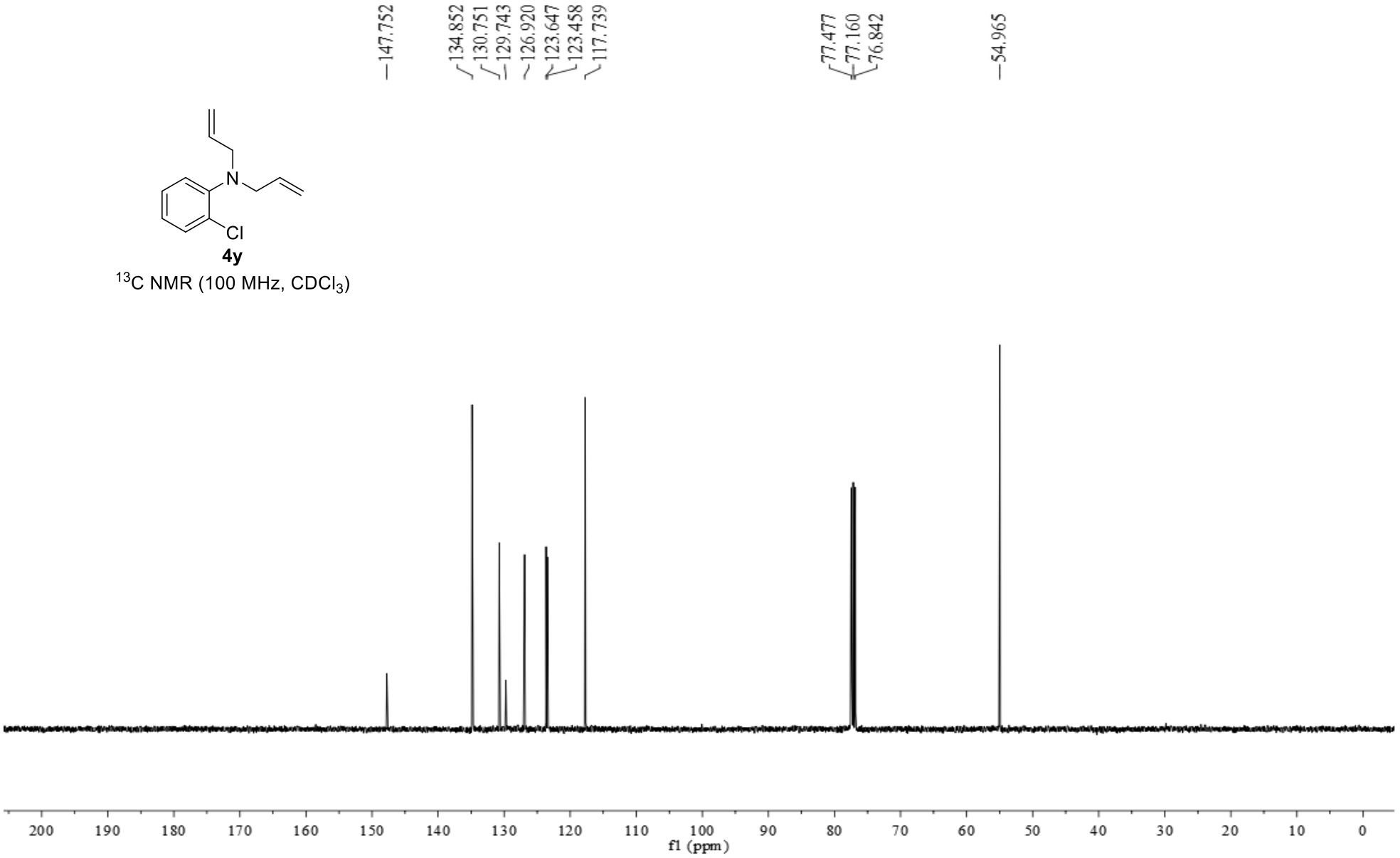
4x

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



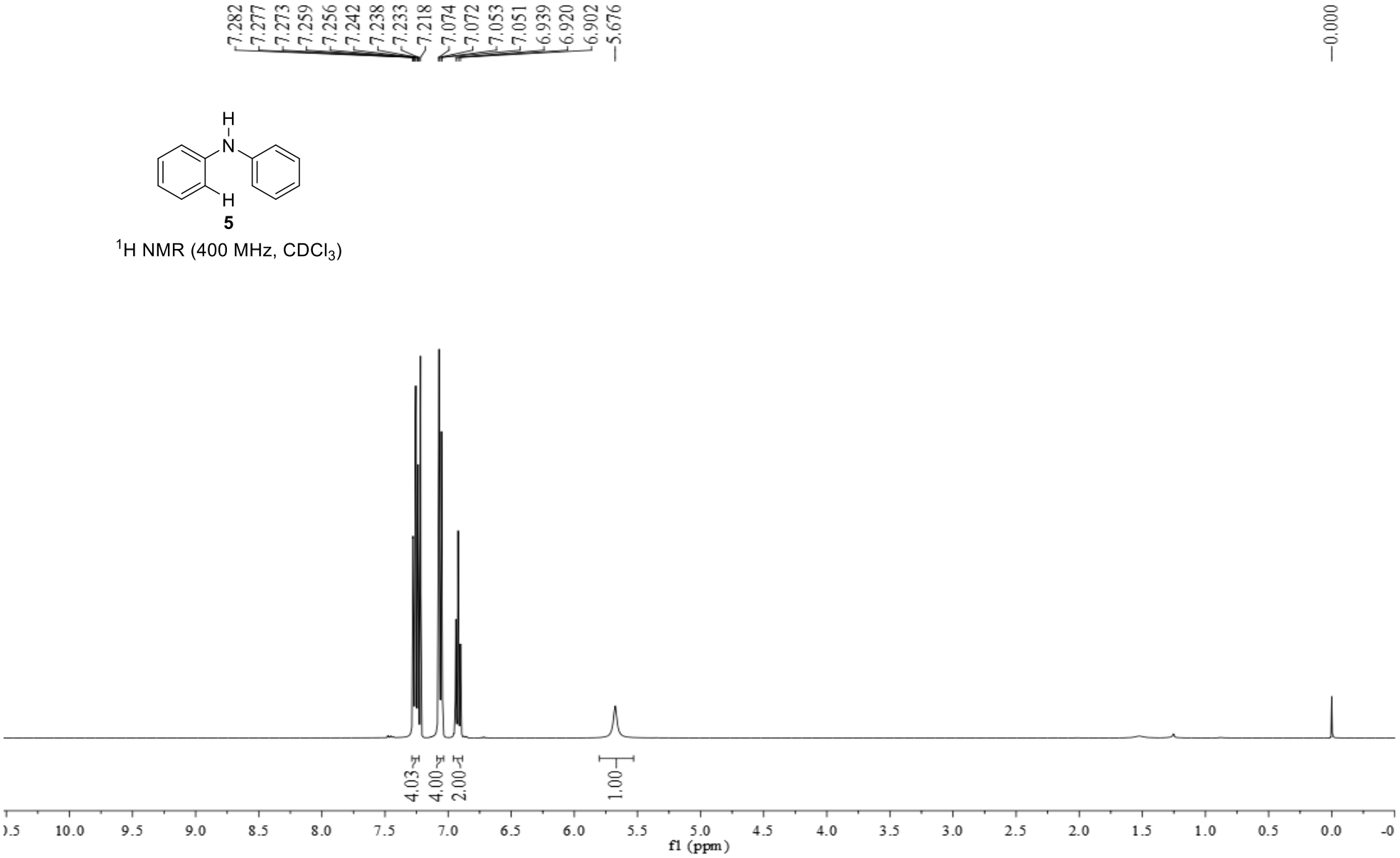
4y

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



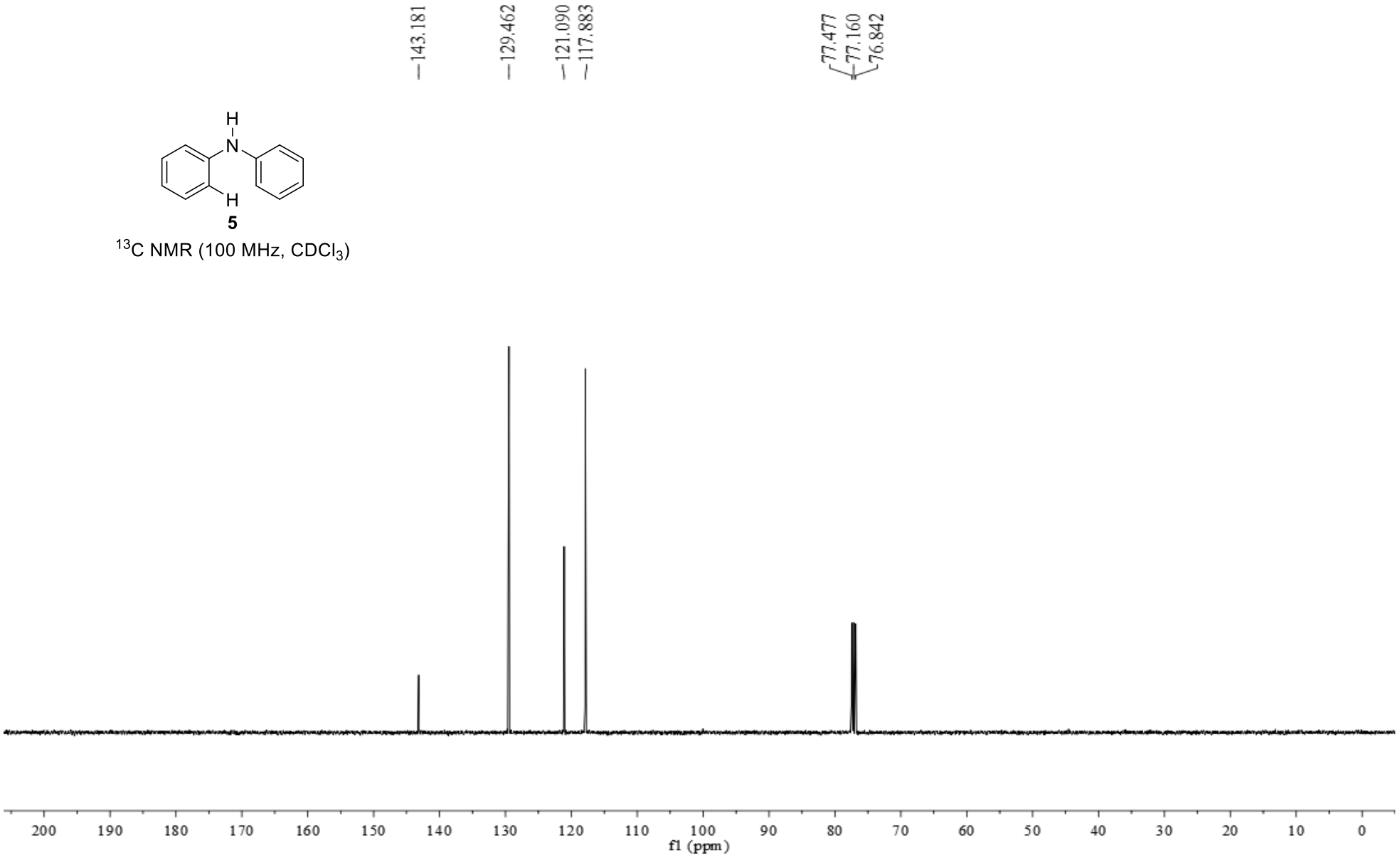
4y

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



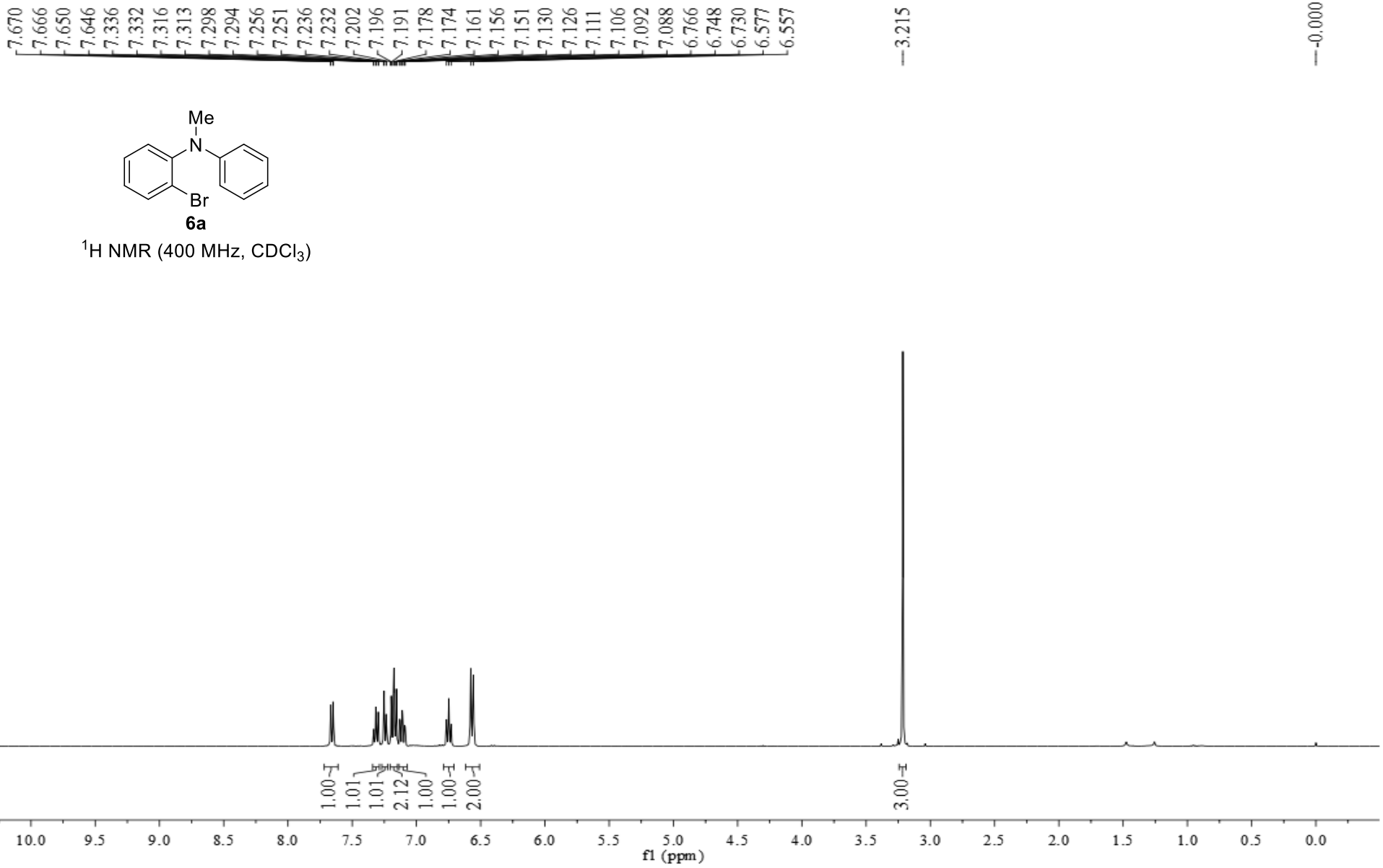
5

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



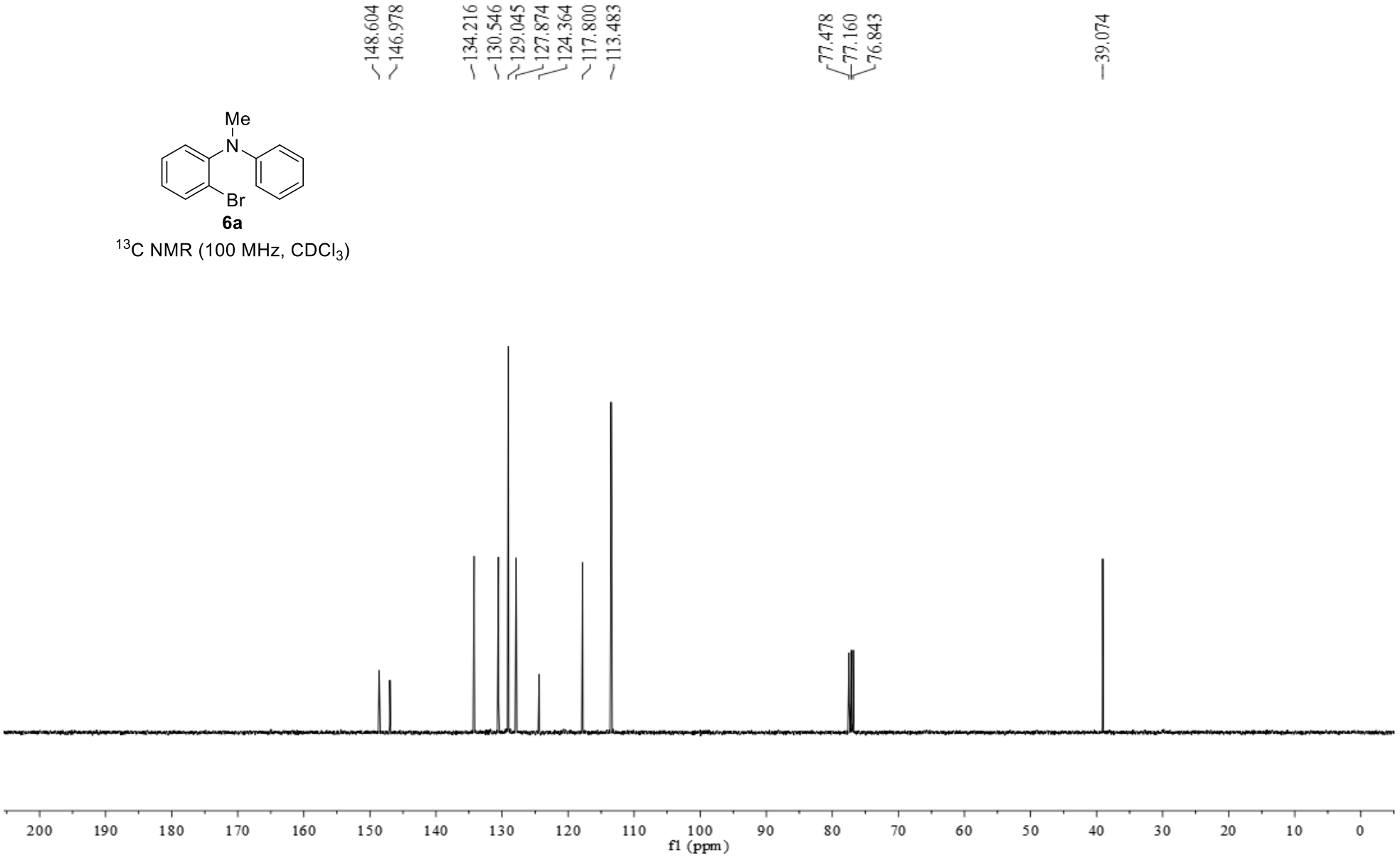
5

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



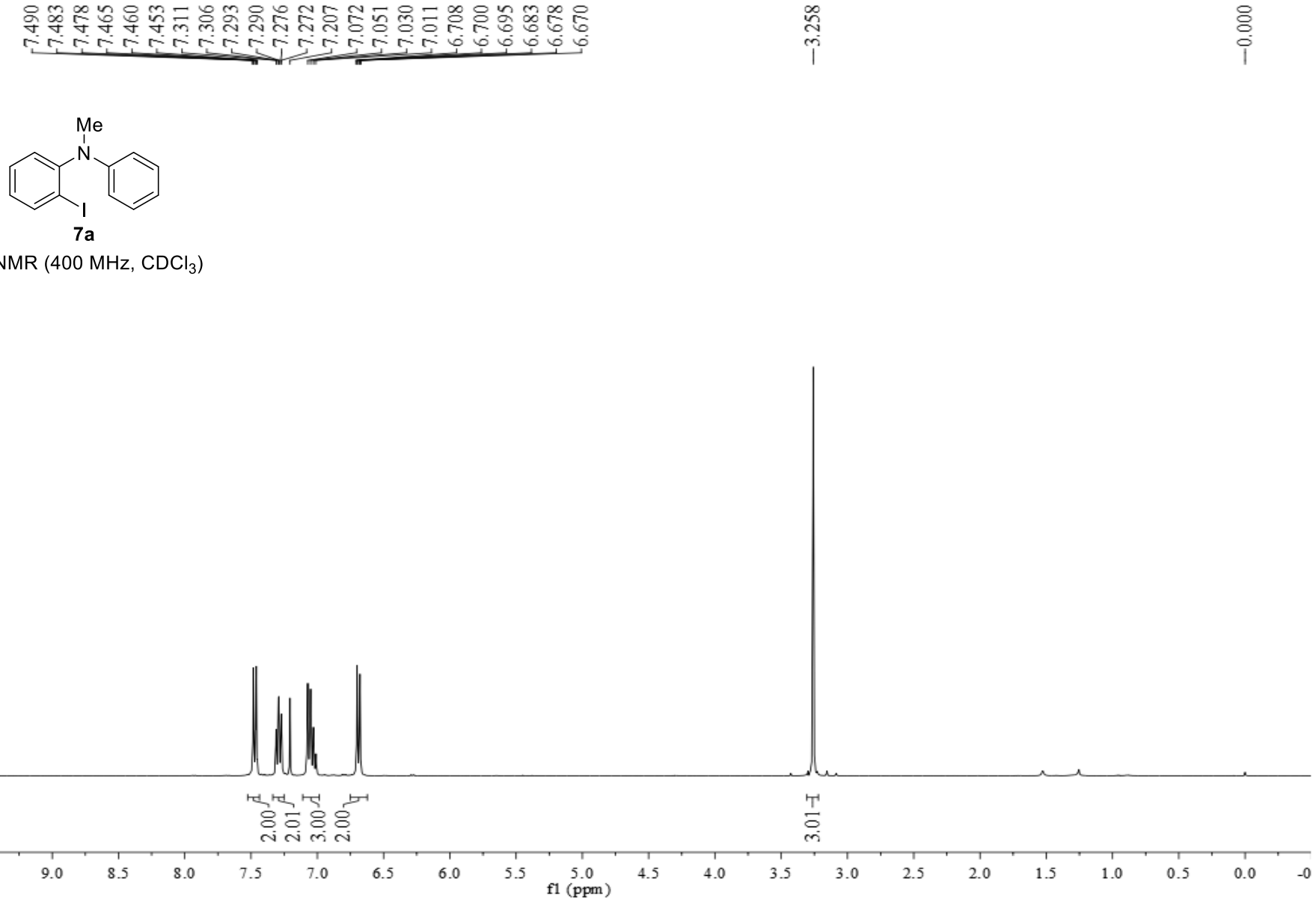
6a

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



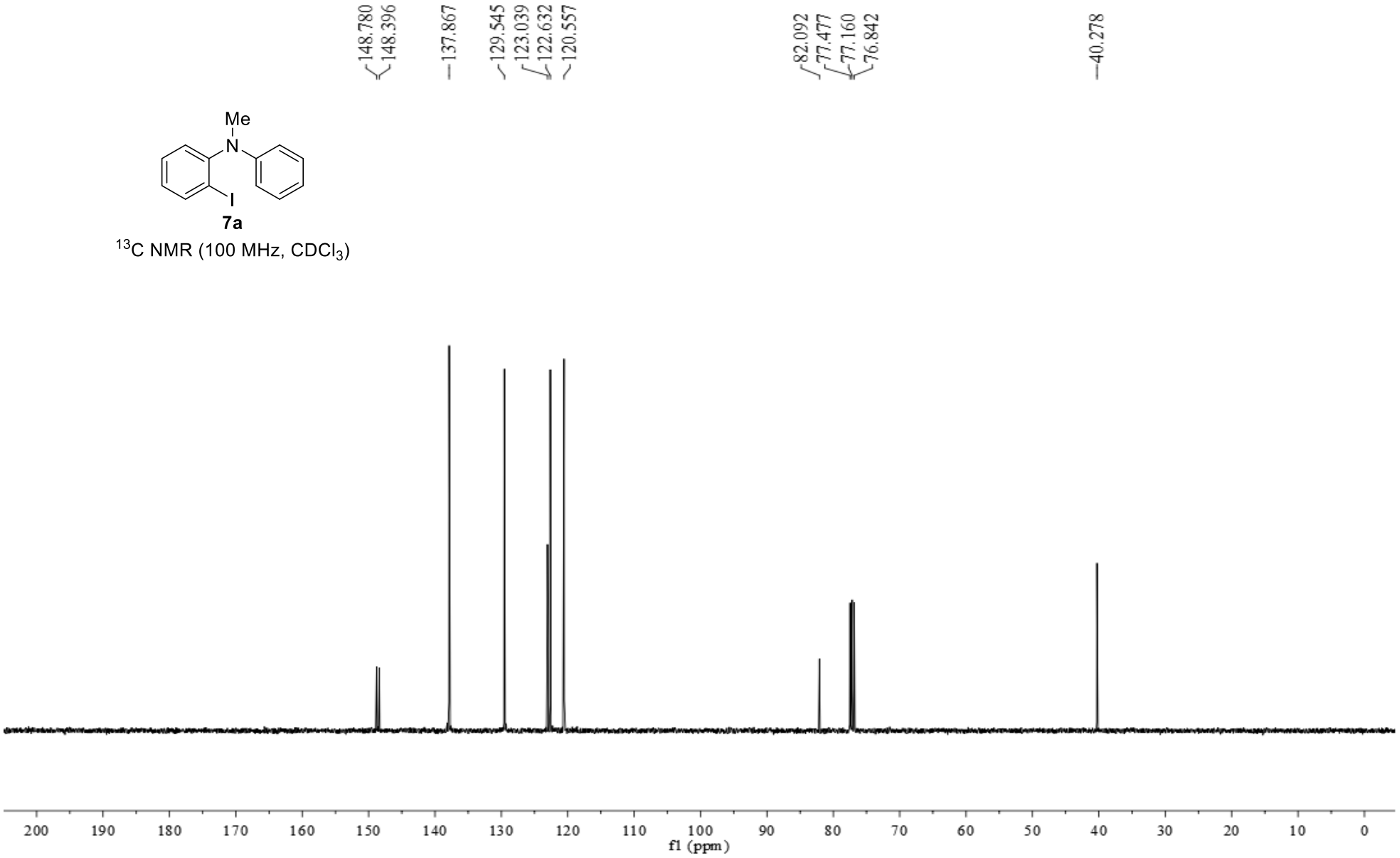
6a

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



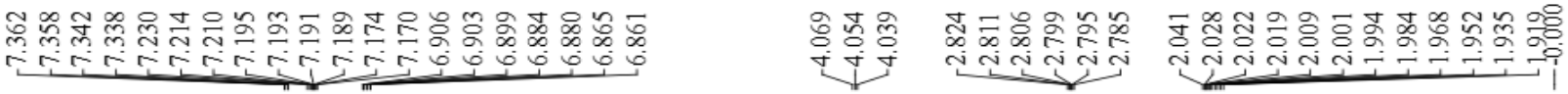
7a

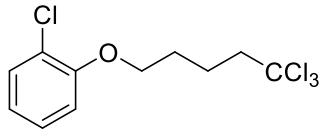
^{1}H NMR (400 MHz, $CDCl_3$)



7a

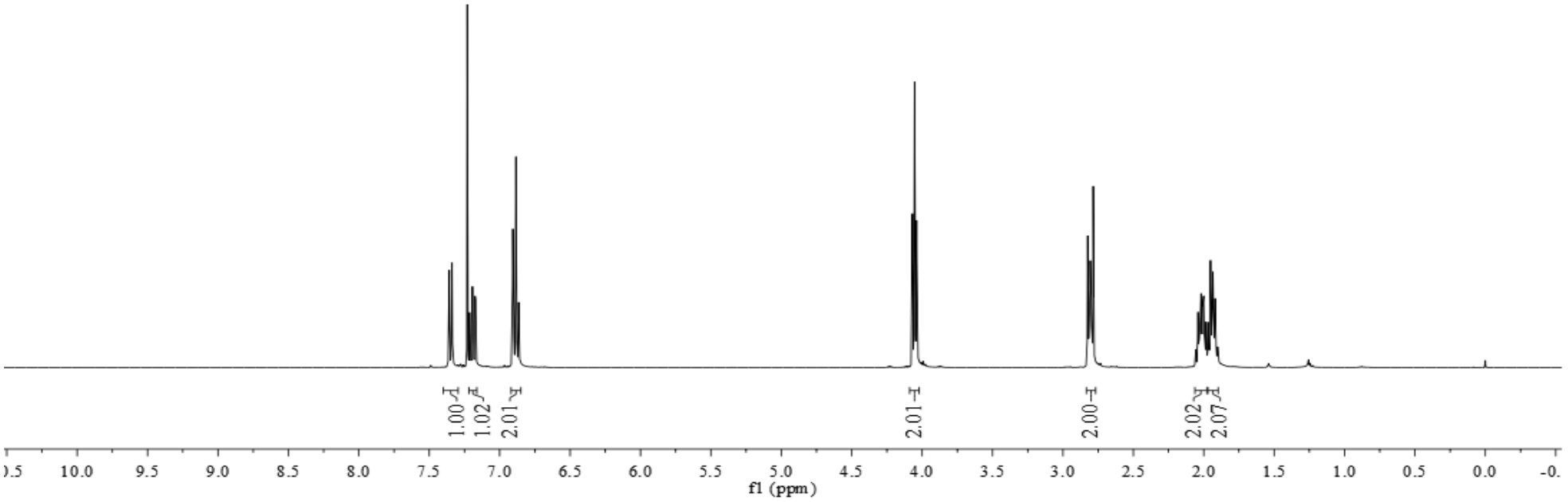
^{13}C NMR (100 MHz, $CDCl_3$)

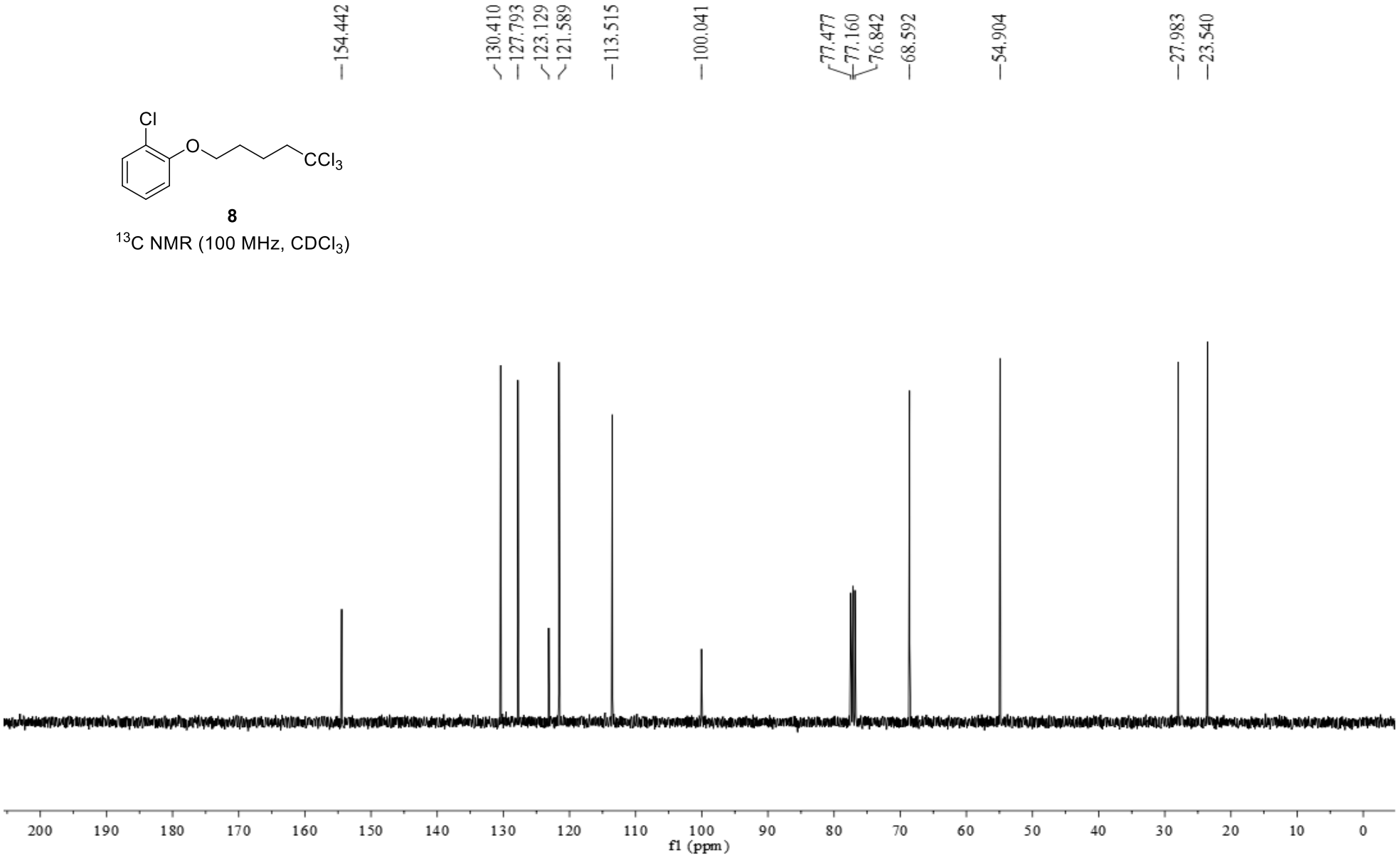




8

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





8

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