Supporting information

Asymmetric Synthesis of Chiral Primary Amines by Transfer Hydrogenation of *N*-(*tert*-Butanesulfinyl)ketimines

David Guijarro[*], *Óscar Pablo and Miguel Yus*[*]

Departamento de Química Orgánica, Facultad de Ciencias and Instituto de Síntesis Orgánica (ISO), Universidad de Alicante, Apdo. 99, 03080 Alicante (Spain).

dguijarro@ua.es; yus@ua.es

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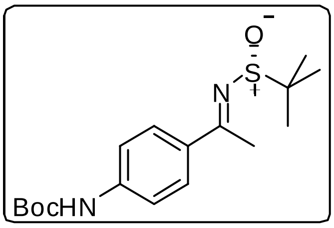
1. General information

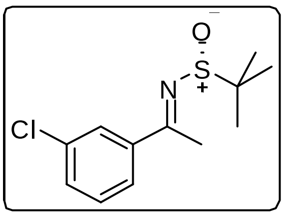
All glassware was dried in an oven at 100 ºC and cooled to room temperature under argon before use. All reactions were carried out under an argon atmosphere. All starting materials needed for the synthesis of imines **1** and *ent*-**1**, $[RuCl_2(p\text{-cymene})]_2$, (1*S*,2*R*)-1-amino-2-indanol (**3**), (1*R*,2*S*)-1-amino-2-indanol (*ent*-**3**) and *t*-BuOK were commercially available and were used as received. Commercially available 4 Å molecular sieves were dried in a Kugelrohr distillation apparatus at 120 ºC under vacuum for 5h before use. Commercially available anhydrous isopropanol was used as solvent in all the transfer hydrogenation reactions. Column chromatography was performed with silica gel 60 of 230–400 mesh. Thin layer chromatography (TLC) was performed on precoated silica gel plates; detection was done by UV_{254} light and staining with phosphomolybdic acid (solution of 1 g of phosphomolybdic acid in 24 mL of absolute ethanol); R_f values are given under these conditions. When mentioned, an R_f value measured on deactivated silica gel means that the TLC plate was eluted with a mixture of 5% triethylamine in hexane and dried before applying the sample. Melting points (mp) are uncorrected. Unless otherwise stated, NMR samples were prepared using $CDCl_3$ as solvent. The internal references used for NMR spectra were tetramethylsilane (TMS) for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR; chemical shifts are given in δ (ppm) and coupling constants (*J*) in Hz. Mass spectra (EI) were obtained at 70 eV. The HRMS (EI) were performed by the Technical Services of the University of Alicante. HPLC analyses were performed at 25 ºC.

2. Synthesis of imines 1 and *ent*-1

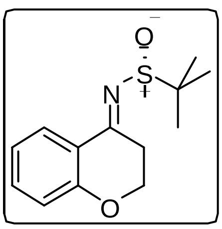
N-(*tert*-butanesulfinyl)imines **1** and *ent*-**1** were prepared by reaction of (*R*)-*tert*-butanesulfinamide (for **1**) or (*S*)-*tert*-butanesulfinamide (for *ent*-**1**) with the corresponding ketones, according to a literature procedure.[1] Imines **1a**,[2] **1b**,[2] **1c**,[3] **1d**,[4] **1e**,[5] **1g**,[2] **1i**,[6] **1j**,[2] **1k**,[6] **1l**,[1] **1m**,[7] **1n**,[7] **1o**,[2] **1q**,[8] and *ent*-**1a**[6] were identified by comparison of their ^{1}H NMR spectra with the previously reported data. The corresponding physical, spectroscopic and analytical data for imines **1f**, **1h**, **1p** and *ent*-**1r** follow.



***tert*-Butyl (*R*)-4-[1-(*tert*-butanesulfinylimino)ethyl]phenyl carbamate (1f).** Yellow solid; mp not determined (decomposes); R_f 0.63 (hexane/ethyl acetate: 1/1); $[\alpha]_D^{20}$ +38.0 (*c* 1.3, CH_2Cl_2); IR (KBr) 3240, 3052, 1718, 1594, 1265, 1155 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.31 (9H, s), 1.52 (9H, s), 2.72 (3H, s), 7.05 (1H, br s), 7.45, 7.85 (2H each, 2 d, *J* = 8.6 Hz each); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.6, 22.4, 28.2, 57.1, 81.0, 117.5, 128.5, 132.8, 142.0, 152.3, 175.8; *m/z* (DIP) 282 (M^+ - C_4H_8, 18%), 281 (34), 231 (63), 228 (33), 226 (42), 219 (43), 193 (26), 162 (46), 134 (21), 131 (71), 119 (98), 70 (23), 69 (100), 44 (22); HRMS: M^+ - C_4H_8 found 282.1036, $C_{13}H_{18}N_2O_3S$ requires 282.1038.

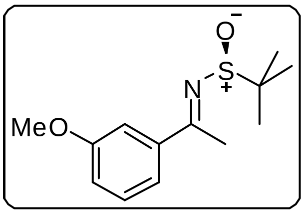


(*R*)-*N*-[1-(3-Chlorophenyl)ethylidene]-2-methylpropane-2-sulfinamide (1h).[9] Yellow oil; R_f 0.56 (hexane/ethyl acetate: 1/1); $[\alpha]_D^{20}$ +12.0 (*c* 1.0, CH_2Cl_2); IR (neat) 3070, 1605, 1564, 1071 cm^{-1}; ^{1}H-RMN (300 MHz, $CDCl_3$) δ 1.33 (9H, s), 2.76 (3H, s), 7.37 (1H, t, *J* = 7.8 Hz), 7.46, 7.75 (1H each, 2 d, *J* = 7.8 Hz each), 7.85 (1H, s); ^{13}C-RMN (75 MHz, $CDCl_3$) δ 19.7, 22.5, 57.7, 125.3, 127.3, 129.7, 131.5, 134.6, 140.4, 174.7; *m/z* (DIP) 257 (M^+, <1%), 201 (25), 157 (52), 139 (21), 109 (33), 71 (20), 70 (20), 57 (75), 43 (100), 41 (25).



(*R*)-*N*-(Chroman-4-ylidene)-2-methylpropane-2-sulfinamide (1p). Red oil; R_f 0.54 (hexane/ethyl acetate: 1/1); $[\alpha]_D^{20}$ -71.0 (*c* 1.3, $CHCl_3$); IR (neat) 3069, 1591, 1079 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.33 (9H, s), 3.27 (1H, ddd, *J* = 17.4, 7.3, 4.2 Hz), 3.51 (1H, ddd, *J* = 17.4, 8.6, 4.8 Hz), 4.29-4.40 (2H, m), 6.92

(1H, dd, J = 8.4, 1.1 Hz), 6.98 (1H, dt, J = 7.6, 1.1 Hz), 7.33 (1H, dt, J = 8.4, 1.7 Hz), 8.00 (1H, dd, J = 7.6, 1.7 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 22.6, 30.7, 57.9, 65.5, 118.0, 121.1, 121.3, 126.9, 134.2, 159.2, 169.6; *m/z* (DIP) 251 (M^+, <1%), 195 (94), 147 (100), 119 (36), 57 (22); HRMS: M^+ found 251.0969, $C_{13}H_{17}NO_2S$ requires 251.0980.



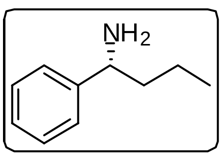
(*S*)-*N*-[1-(3-Methoxyphenyl)ethylidene]-2-methylpropane-2-sulfinamide (*ent*-1r). White solid; mp 65-66 ºC; R_f 0.48 (hexane/ethyl acetate: 1/1); $[\alpha]_D^{20}$ -6.0 (c 1.8, CH_2Cl_2); IR (KBr) 3069, 1608, 1575, 1287, 1068 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.32 (9H, s), 2.76 (3H, s), 3.84 (3H, s), 7.04 (1H, d, J = 8.3 Hz), 7.34 (1H, t, J = 8.3 Hz), 7.36-7.47 (2H, m); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.8, 22.4, 55.3, 57.4, 112.4, 117.3, 119.7, 129.4, 140.1, 159.5, 176.1; *m/z* (DIP) 253 (M^+, <1%), 197 (15), 149 (23), 148 (13), 70 (18), 57 (15), 43 (100); HRMS: M^+ found 253.1112, $C_{13}H_{19}NO_2S$ requires 253.1137.

3. General procedure for the asymmetric transfer hydrogenation of imines 1

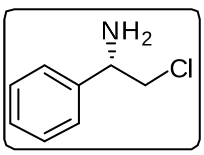
A mixture of $[RuCl_2(p\text{-cymene})]_2$ (28 mg, 0.045 mmol), the ligand **3** (14 mg, 0.09 mmol), 4 Å molecular sieves (0.5 g) and anhydrous *i*-PrOH (2 mL) was heated up to 90 ºC (oil bath temperature) for 20 min. During this heating period, the initially orange reaction mixture turned into a dark red colour. The reaction was then cooled to 40 ºC and a solution of the imine **1** (0.9 mmol) in *i*-PrOH (9 mL) and *t*-BuOK (2.25 mL of a 0.1 M solution in *i*-PrOH, 0.225 mmol) were successively added. After completion of the reaction (monitored by TLC), the reaction mixture was passed through a small column of silica gel, the column was washed with ethyl acetate and the combined organic phases were evaporated to give a residue that was directly submitted to the desulfinylation step.

4. General procedure for the removal of the sulfinyl group. Isolation of amines 2a-2e, 2g-2q and *ent*-2

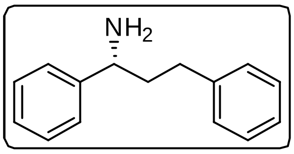
The crude mixture of the transfer hydrogenation reaction was dissolved in a 1.5 M solution of HCl in methanol (4 mL; prepared by dropwise addition of $SOCl_2$ to methanol at 0 ºC) and stirred overnight at room temperature. Then, the solvent was evaporated, a 2 M aqueous HCl solution (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The organic layers were discarded. The aqueous layer was basified with a buffer solution of NH_3 (1 M) / NH_4Cl (1 M) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried (Na_2SO_4). After filtration and evaporation of the solvent, pure amines **2a-2e**, **2g-2q** and *ent*-**2** were obtained in the yields indicated in Table 2. Amines **2a**, *ent*-**2a** and **2b**, which are commercially available, were identified by comparison of their spectroscopic data (^{1}H and ^{13}C NMR) with authentic samples. The corresponding physical and spectroscopic data for amines **2c-2e, 2g-2q** and *ent*-**2r** follow.



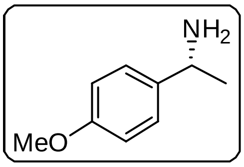
(*R*)-1-Phenylbutan-1-amine (2c).[10] Yellow oil; R_f 0.62 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +26.0 (c 1.1, EtOH, 99% ee) {literature[11] $[\alpha]_D^{20}$ for *ent*-**2c** = -2.3 (c 1.0, EtOH, 11% ee)}; IR (neat) 3362, 3288, 3060, 1600, 1452 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 7.3 Hz), 1.15-1.43 (2H, m), 1.58-1.72 (4H, m), 3.88 (1H, t, J = 6.9 Hz), 7.19-7.36 (5H, m); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0, 19.7, 41.8, 56.0, 126.3, 126.8, 128.4, 146.7; *m/z* 149 (M^+, 4%), 132 (40), 117 (75), 115 (43), 106 (100), 103 (73), 91 (28), 77 (45), 51 (27).



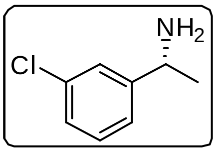
(*S*)-2-Chloro-1-phenylethanamine (2d).[12] Brown oil; R_f 0.38 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +26.0 (c 0.8, EtOH, 99% ee) {literature[12] $[\alpha]_D^{20}$ +9.1 (c 1.0, EtOH, 32% ee)}; IR (neat) 3383, 3269, 3030, 1587, 1455, 1121 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.83 (2H, br s), 3.55 (1H, dd, J = 10.7, 9.0 Hz), 3.71 (1H, dd, J = 10.7, 3.8 Hz), 4.24 (1H, dd, J = 9.0, 3.8 Hz), 7.26-7.41 (5H, m); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 51.7, 57.2, 126.6, 128.0, 128.6, 141.8; *m/z* 155 (M^+, <1%), 106 (100), 104 (15), 79 (27), 77 (21).



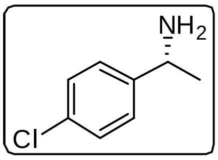
(*R*)-1,3-Diphenylpropan-1-amine (2e).[13] White solid; mp 54 ºC; R_f 0.55 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +6.0 (c 0.5, $CHCl_3$, 98% ee) {literature[13] $[\alpha]_D^{25}$ +9.1 (c 0.5, $CHCl_3$, 97% ee)}; IR (KBr) 3362, 3296, 3026, 1602, 1494, 1453 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.62 (2H, br s), 2.01 (2H, m), 2.50-2.70 (2H, m), 3.91 (1H, t, J = 6.9 Hz), 7.13-7.21 (3H, m), 7.23-7.36 (7H, m); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 32.8, 41.0, 55.7, 125.8, 126.4, 127.0, 128.3, 128.5, 141.9, 146.2; *m/z* 211 (M^+, <1%), 106 (100), 91 (10), 79 (12).



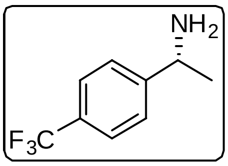
(*R*)-1-(4-Methoxyphenyl)ethanamine (2g).[14] Colorless oil; R_f 0.17 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +23.5 (c 0.9, $CHCl_3$, 95% ee) {literature[14] $[\alpha]_D^{20}$ for *ent*-**2g** = -23.0 (c 0.88, $CHCl_3$, 90% ee)}; IR (neat) 3359, 3285, 1610, 1513, 1248 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.36 (3H, d, J = 6.6 Hz), 1.87 (2H, br s), 3.79 (3H, s), 4.07 (1H, q, J = 6.6 Hz), 6.87, 7.26 (2H each, 2 d, J = 8.6 Hz each); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 25.6, 50.7, 55.3, 113.8, 126.7, 139.7, 158.4; *m/z* 151 (M^+, 6%), 136 (100), 109 (15).



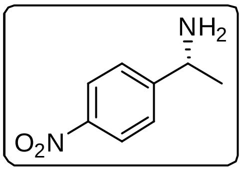
(*R*)-1-(3-Chlorophenyl)ethanamine (2h).[15] Colorless oil; R_f 0.36 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +27.5 (c 1.2, $CHCl_3$, >99% ee) {literature[15] $[\alpha]_D^{21}$ for *ent*-**2h** -12.6 (neat, 80% ee)}; IR (neat) 3368, 3286, 3060, 1596, 1571, 1431, 1079 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.36 (3H, d, J = 6.6 Hz), 1.59 (2H, br s), 4.09 (1H, q, J = 6.6 Hz), 7.16-7.27 (3H, m), 7.35 (1H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 25.6, 50.9, 123.9, 125.9, 126.9, 129.7, 134.2, 149.8; *m/z* 155 (M^+, 2%), 142 (31), 140 (100), 138 (13), 77 (22), 75 (11).



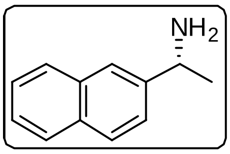
(*R*)-1-(4-Chlorophenyl)ethanamine (2i).[16] Colorless oil; R_f 0.33 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +31.0 (c 1.2, $CHCl_3$, >99% ee) {literature[16] $[\alpha]_D^{20}$ +18.9 (c 1.0, $CHCl_3$, 92% ee)}; IR (neat) 3365, 3285, 3046, 1590, 1491, 1093 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.35 (3H, d, J = 6.7 Hz), 1.56 (2H, br s), 4.10 (1H, q, J = 6.7 Hz), 7.24-7.31 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.7, 50.6, 127.1, 128.5, 132.2, 146.1; *m/z* 155 (M^+, 3%), 142 (25), 140 (100), 139 (14), 138 (31), 137 (11), 77 (23), 75 (18), 51 (10).



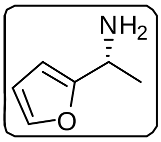
(*R*)-1-[4-(Trifluoromethyl)phenyl]ethanamine (2j).[17] Colorless oil; R_f 0.31 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +20.0 (c 1.0, MeOH, 99% ee) {literature[18] $[\alpha]_D^{24}$ for *ent*-**2j** = -13.0 (c 1.95, MeOH, 60% ee)}; IR (neat) 3360, 3231, 3070, 1619, 1462, 1326, 1124 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.40 (3H, d, J = 6.6 Hz), 1.67 (2H, br s), 4.19 (1H, q, J = 6.6 Hz), 7.47, 7.59 (2H each, 2 d, J = 8.2 Hz each); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 25.7, 51.0, 122.4, 125.4, 126.1, 129.1, 151.6 (ArC); *m/z* 189 (M^+, <1%), 187 (27), 174 (100), 172 (90), 145 (33), 105 (28), 77 (22).



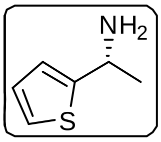
(*R*)-1-(4-Nitrophenyl)ethanamine (2k).[14] Yellow oil; R_f 0.20 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +10.5 (c 1.0, $CHCl_3$, 97% ee) {literature[14] $[\alpha]_D^{24}$ for *ent*-**2k** = -16.0 (c 0.76, $CHCl_3$, 96% ee)}; IR (neat) 3370, 3215, 3075, 1597, 1516, 1346 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.40 (3H, d, J = 6.7 Hz), 1.64 (2H, br s), 4.26 (1H, q, J = 6.7 Hz), 7.54, 8.17 (2H each, 2 d, J = 8.8 Hz each); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 25.7, 50.8, 123.6, 126.6, 146.7, 155.1; *m/z* 166 (M^+, <1%), 151 (100), 105 (30), 104 (13).



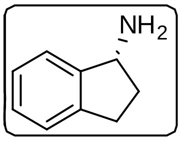
(*R*)-1-(2-Naphthyl)ethanamine (2l).[19] White solid; mp 74-75 ºC; R_f 0.40 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +23.0 (*c* 2.0, EtOH, 98% ee) {literature[19] $[\alpha]_D^{25}$ +19.9 (*c* 2.5, EtOH, 94% ee)}; IR (KBr) 3361, 3290, 3054, 1599, 1573, 1468 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.47 (3H, d, *J* = 6.6 Hz), 1.65 (2H, br s), 4.28 (1H, q, *J* = 6.6 Hz), 7.40-7.52 (3H, m), 7.77 (1H, s), 7.79-7.84 (3H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.6, 51.4, 123.7, 124.5, 125.5, 126.0, 127.6, 127.7, 128.2, 132.6, 133.5, 145.1; *m/z* 171 (M^+, 18%), 157 (14), 156 (100), 129 (45), 128 (29), 127 (19).



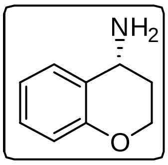
(*R*)-1-(2-Furyl)ethanamine (2m).[20] Yellow oil; R_f 0.35 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +25.5 (*c* 1.1, EtOH, 99% ee) {literature[20] $[\alpha]_D^{20}$ +22.7 (*c* 1.0, EtOH, 92% ee)}; IR (neat) 3368, 3290, 3113, 1600, 1149 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.42 (3H, d, *J* = 6.7 Hz), 1.62 (2H, br s), 4.07 (1H, q, *J* = 6.7 Hz), 6.09 (1H, d, *J* = 3.2 Hz), 6.29 (1H, dd, *J* = 3.2, 1.4 Hz), 7.31-7.34 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.0, 45.0, 103.2, 109.9, 141.1, 160.2; *m/z* 111 (M^+, 29%), 110 (11), 109 (29), 96 (100), 95 (14), 94 (47), 82 (19), 80 (18), 69 (28), 65 (18), 54 (18).



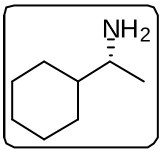
(*R*)-1-(2-Thienyl)ethanamine (2n).[21] Colorless oil; R_f 0.50 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +18.5 (*c* 1.0, MeOH, 97% ee) {literature[21] $[\alpha]_D^{20}$ for *ent*-**2n** -13.0 (*c* 5.0, MeOH)}; IR (neat) 3363, 3290, 3102, 3070, 1592, 1444, 1371, 1308 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.48 (3H, d, *J* = 6.6 Hz), 1.65 (2H, br s), 4.37 (1H, q, *J* = 6.6 Hz), 6.88-6.96 (2H, m), 7.17 (1H, dd, *J* = 5.0, 0.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.3, 47.3, 122.0, 123.3, 126.5, 152.8; *m/z* 127 (M^+, 22%), 126 (15), 112 (100), 111 (17), 110 (56), 109 (18), 85 (41), 84 (11), 66 (11), 58 (12).



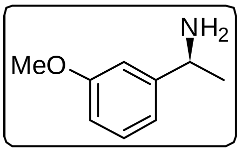
(*R*)-2,3-Dihydro-1*H*-inden-1-amine (2o).[22] Brown oil; R_f 0.58 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ -22.0 (*c* 1.2, $CHCl_3$, 93% ee) {literature[22] $[\alpha]_D^{23}$ for *ent*-**2o** +20.0 (*c* 1.0, $CHCl_3$, 96% ee)}; IR (neat) 3368, 3284, 1477, 1216 cm^{-1}; ^{1}H-RMN (300 MHz, $CDCl_3$) δ 1.57-1.80 (1H, m), 1.77 (2H, br s), 2.42-2.54, 2.72-2.86, 2.88-3.00 (1H each, 3 m), 4.34 (1H, t, *J* = 7.3 Hz), 7.13-7.36 (5H, m); ^{13}C-RMN (75 MHz, $CDCl_3$) δ 30.0, 37.3, 57.2, 123.2, 124.6, 126.4, 127.1, 143.0, 147.4; *m/z* 133 (M^+, 9%), 132 (100), 118 (35), 117 (87), 116 (75), 115 (90).



(*R*)-Chroman-4-amine (2p).[23] Orange oil; R_f 0.36 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ +13.5 (*c* 1.6, $CHCl_3$, 98% ee); $[\alpha]_D^{20}$ for *N*-acetyl **2p**[24] +58.0 (*c* 0.5, $CHCl_3$, 98% ee) {literature[23] $[\alpha]_D^{23}$ for *N*-acetyl *ent*-**2p** = -55.2 (*c* 0.36, $CHCl_3$, 87% ee)}; IR (neat) 3360, 3291, 3063, 1581, 1488, 1226 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.62 (2H, br s), 1.77-1.87, 2.09-2.19 (1H each, 2 m), 4.02 (1H, t, *J* = 5.3 Hz), 4.14-4.33 (2H, m), 6.81 (1H, d, *J* = 7.7 Hz), 6.90, 7.14 (1H each, 2 t, *J* = 7.7 Hz each), 7.29 (1H, d, *J* = 7.7 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 32.1, 44.9, 62.7, 116.8, 120.3, 126.6, 128.3, 128.7, 154.2; *m/z* 149 (M^+, 20%), 148 (19), 132 (66), 131 (67), 121 (100), 93 (28), 77 (23), 66 (21), 51 (16).



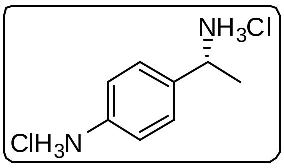
(*R*)-1-Cyclohexylethanamine (2q).[25] Colorless oil; R_f 0.16 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ -1.1 (*c* 2.0, $CHCl_3$, 69% ee) {literature[25] $[\alpha]_D^{24}$ for *ent*-**2q** +2.1 (*c* 1.1, $CHCl_3$, >99% ee)}; IR (neat) 3362, 3287, 1603, 1449, 1372 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.88-1.04 (2H, m), 1.03 (3H, d, *J* = 8.4 Hz), 1.07-1.27 (4H, m), 1.30 (2H, br s), 1.59-1.83 (5H, m), 2.66 (1H, quintet, *J* = 6.3 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.7, 26.2, 26.3, 26.5, 28.7, 28.9, 45.3, 51.4; *m/z* 127 (M^+, 10%), 126 (22), 112 (67), 95 (80), 82 (32), 81 (37), 79 (29), 77 (25), 70 (34), 69 (20), 68 (25), 67 (100), 65 (21), 56 (50), 55 (99), 54 (59), 53 (54), 51 (22).



(*S*)-1-(3-Methoxyphenyl)ethanamine (*ent*-2r).[26] Colorless oil; R_f 0.26 (ethyl acetate, deactivated silica gel); $[\alpha]_D^{20}$ -25.8 (*c* 2.1, $CHCl_3$, >99% ee) {literature[26] $[\alpha]_D^{25}$ -26.8 (*c* 1.15, $CHCl_3$, 85% ee)}; IR (neat) 3361, 3292, 3048, 1600, 1486, 1260, 1042 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.37 (3H, d, *J* = 6.6 Hz), 1.83 (2H, br s), 3.79 (3H, s), 4.07 (1H, q, *J* = 6.6 Hz), 6.77 (1H, d, *J* = 8.3 Hz), 6.87-6.93 (2H, m), 7.23 (1H, t, *J* = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.4, 51.1, 54.9, 111.1, 111.8, 117.8, 129.2, 149.4, 159.5; *m/z* 151 (M^+, 9%), 136 (100), 109 (17).

5. Synthesis of amine 2f · 2HCl

A 2 M solution of HCl in Et_2O (10 mL, 20 mmol) was added to the crude mixture of the asymmetric transfer hydrogenation of imine **1f** and the mixture was stirred overnight. After filtration, the white solid was washed with Et_2O (3 × 10 mL) and dried, affording a 97% yield of the **2f** dihydrochloride.



(*R*)-1-(4-Aminophenyl)ethanamine dihydrochloride (2f · 2HCl).[27] Brownish solid; $[\alpha]_D^{20}$ +6.0 (*c* 0.6, MeOH, 98% ee); IR (KBr) 3500-2500, 1600, 1518, 1385, 1225 cm^{-1}; ^{1}H-RMN (300 MHz, CD_3OD) δ 1.62 (3H, d, *J* = 6.8 Hz), 4.56 (1H, q, *J* = 6.8 Hz), 7.51, 7.67 (2H each, 2 d, *J* = 8.5 Hz each); ^{13}C-RMN (75 MHz, CD_3OD) δ 20.6, 51.7, 124.9, 129.8, 133.1, 140.5.

6. Determination of the enantiomeric excesses of amines 2 and *ent*-2

Benzoyl chloride (64 μL, 0.55 mmol; for the benzoylation of amine **2f**, 128 μL, 1.1 mmol were used) was added to a solution of amine **2** or *ent*-**2** (0.5 mmol) and triethylamine (90 μL, 0.65 mmol; for the benzoylation of amine **2f**, 360 μL, 2.6 mmol were used) in $CHCl_3$ (10 mL) at 0 ºC. After stirring for 4 h at room temperature, the organic phase was washed with a 2 M aqueous HCl solution (3 × 5 mL) and the aqueous layers were discarded. The organic phase was washed with brine (2 × 5 mL) and then dried (Na_2SO_4). After filtration and evaporation of the solvent, the expected benzamides were purified by column chromatography (silica gel, hexane/ethyl acetate). These benzamides were analyzed by HPLC on a ChiralCel OD-H column using a 254 nm UV detector, 10% *i*-PrOH in hexane as eluent and a flow rate of 0.5 mL/min. The major enantiomer was the one with lower retention time in all cases, except for amines *ent*-**2a** and *ent*-**2r**. The racemic amines were prepared by reaction of the corresponding ketones with a solution of NH_3 in EtOH following a literature procedure,[17] and were benzoylated as described above. The retention times of the two enantiomers of all the benzamides are collected in Table 1.

TABLE 1. HPLC retention times of the two enantiomers of the *N*-benzoyl amines

Amine	Retention time of *N*-benzoyl **2** (min)	Retention time of *N*-benzoyl *ent*-**2** (min)
2a	32	49
2b	18	30
2c	17	29
2d	33	64
2e	59	78
2f	29[a]	35[a]
2g	33	49

2h	25	44
2i	24	40
2j	24	41
2k	78	103
2l	33	96
2m	18	23
2n	22	34
2o	27	44
2p	26	34
2q	13	20
2r	32	72

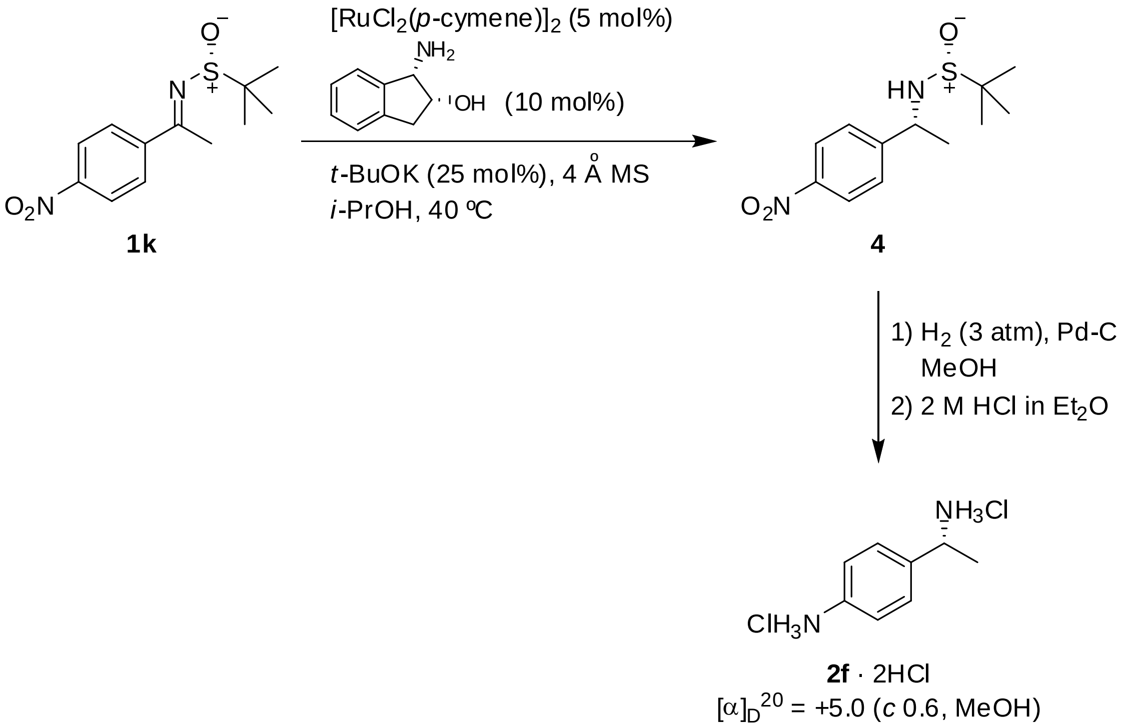
[a] Both amino groups of amine **2f** were benzoylated. The retention times correspond to the dibenzamide enantiomers.

The enantiomeric excesses obtained are collected in Table 2 of the article. The absolute configuration of the major enantiomer of amines **2a**-**2e**, **2g**-**2q** and *ent*-**2** was determined by comparison of the sign of their specific rotation with the data reported in the literature. The absolute configuration of amine **2f** was determined as described below.

7. Determination of the absolute configuration of amine 2f

The (*R*) absolute configuration of the major enantiomer of amine **2f** was tentatively assigned according to the order of elution of its two benzoylated enantiomers in the HPLC analysis by analogy to the rest of the benzamides. Since the specific rotation of either amine **2f** or its hydrochloride had not been reported, we decided to prepare this amine by another route in order to confirm its absolute configuration. We had observed that the asymmetric transfer hydrogenation of imine **1k** led to sulfinamide **4** with (*R*) absolute configuration (Scheme 1). The crude mixture of this reaction (459 mg, 1.7 mmol) dissolved in MeOH (10 mL) was treated with hydrogen gas (3 atm) in the presence of Pd-C (30 mg) at room temperature during 6 h in order to reduce the nitro group to an amino group. After filtration to remove the Pd-C, solvent was evaporated and the resulting residue was directly submitted to the desulfinylation reaction with a solution of HCl in Et_2O as described above, giving amine **2f** dihydrochloride. The specific rotation of this product was $[\alpha]_D^{20}$ = +5.0 (*c* 0.6, MeOH), which matches with the value measured for the product obtained in the reaction of entry 6 in Table 2 of the article (see section 5 above), thus confirming the (*R*) absolute configuration of the latter.

SCHEME 1. Another route to prepare amine 2f



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(24) *N*-Acetyl **2p** was prepared by dropwise addition of Ac_2O (16 mg, 0.15 mmol) to a solution of amine **2p** (20 mg, 0.13 mmol) and triethylamine (24 µl, 0.17 mmol) in $CHCl_3$ (5 mL). After stirring for 2.5 h at room temperature, the organic phase was washed with a 2 M aqueous HCl solution (3 × 5 mL) and the aqueous layers were discarded. The organic phase was washed with brine (2 × 5 mL) and then dried (Na_2SO_4). Filtration and evaporation of the solvent afforded the expected acetamide.

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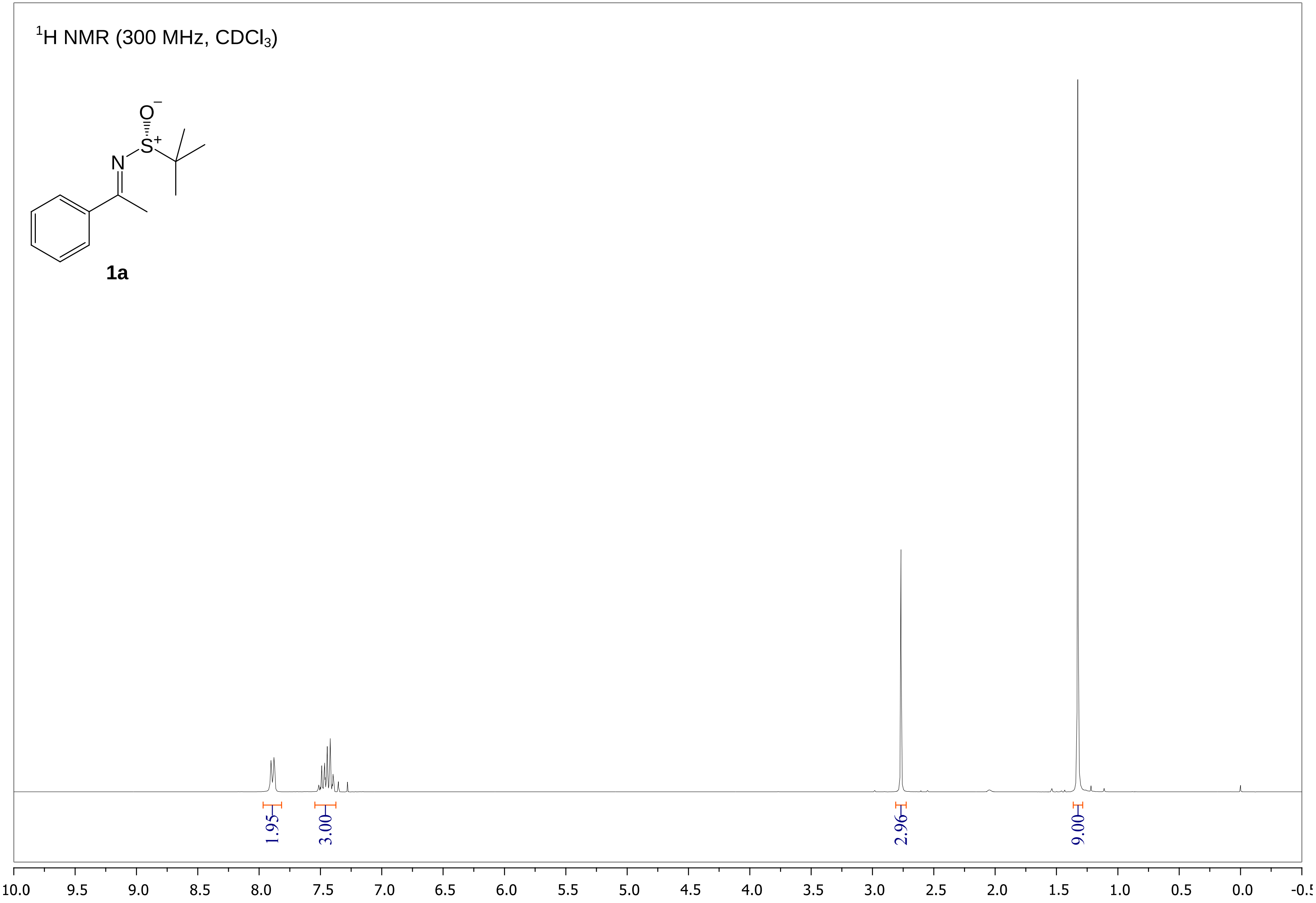
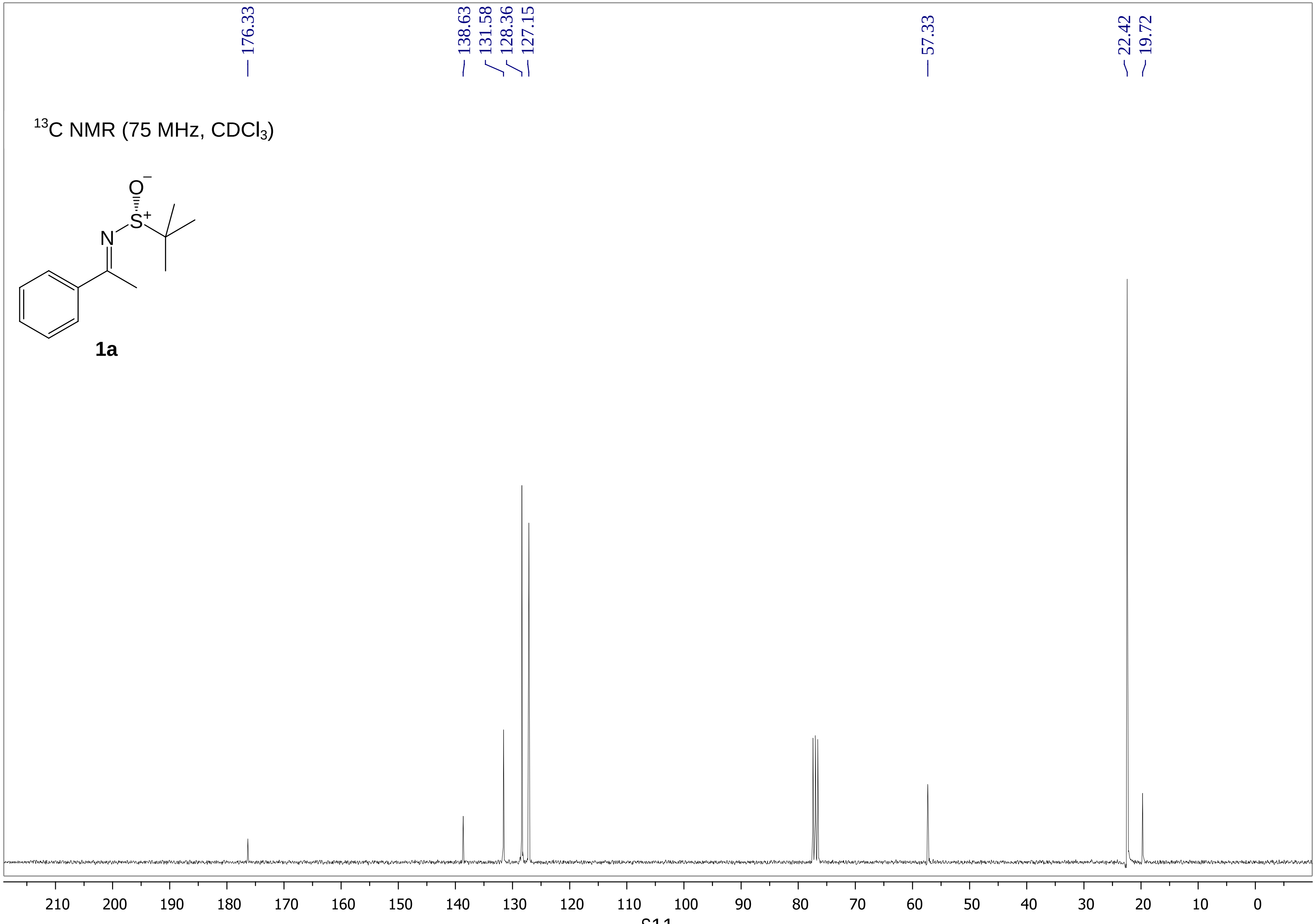
9. NMR spectra





176.33
138.63
131.58
128.36
127.15
57.33
22.42
19.72
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1a
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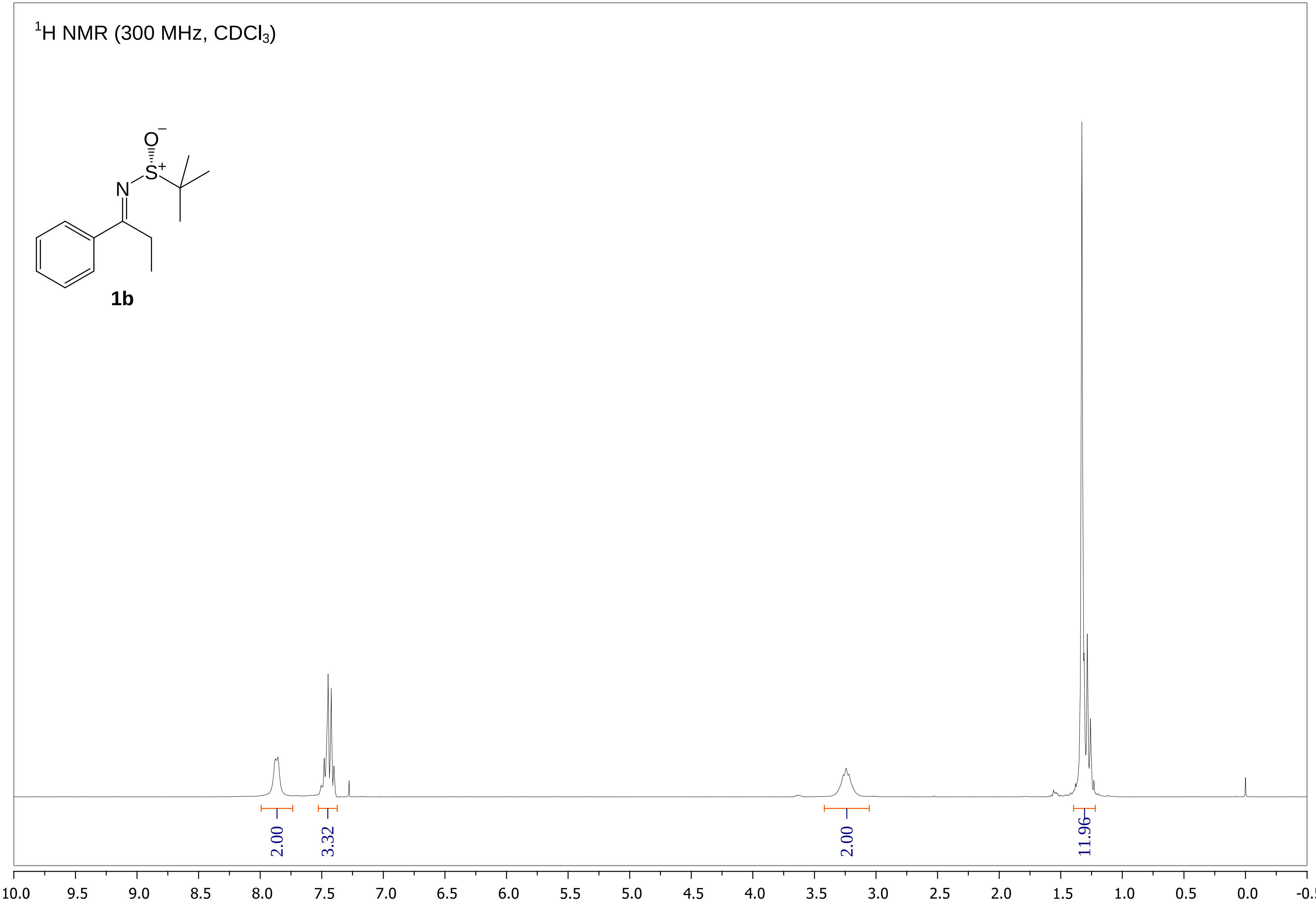
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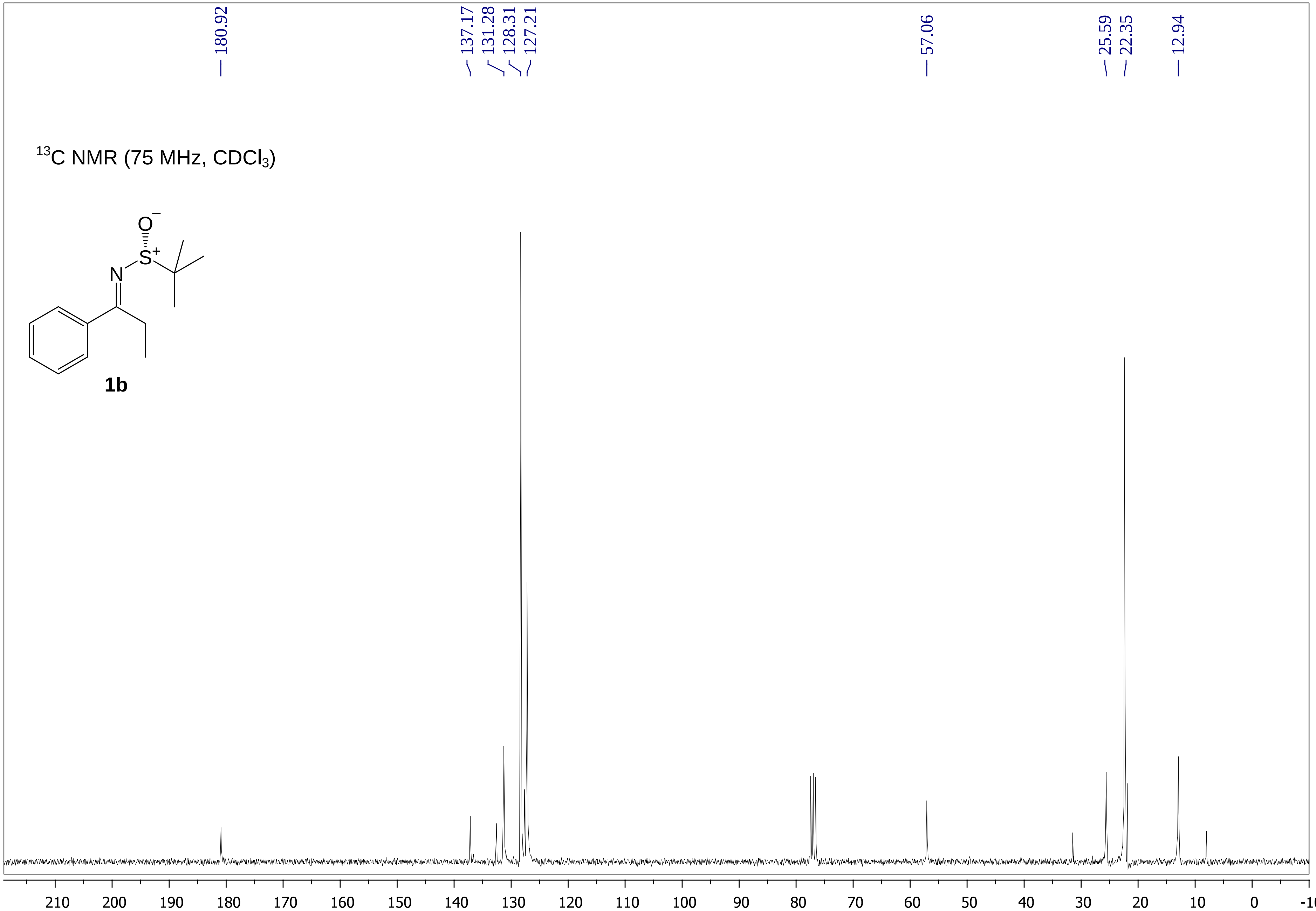
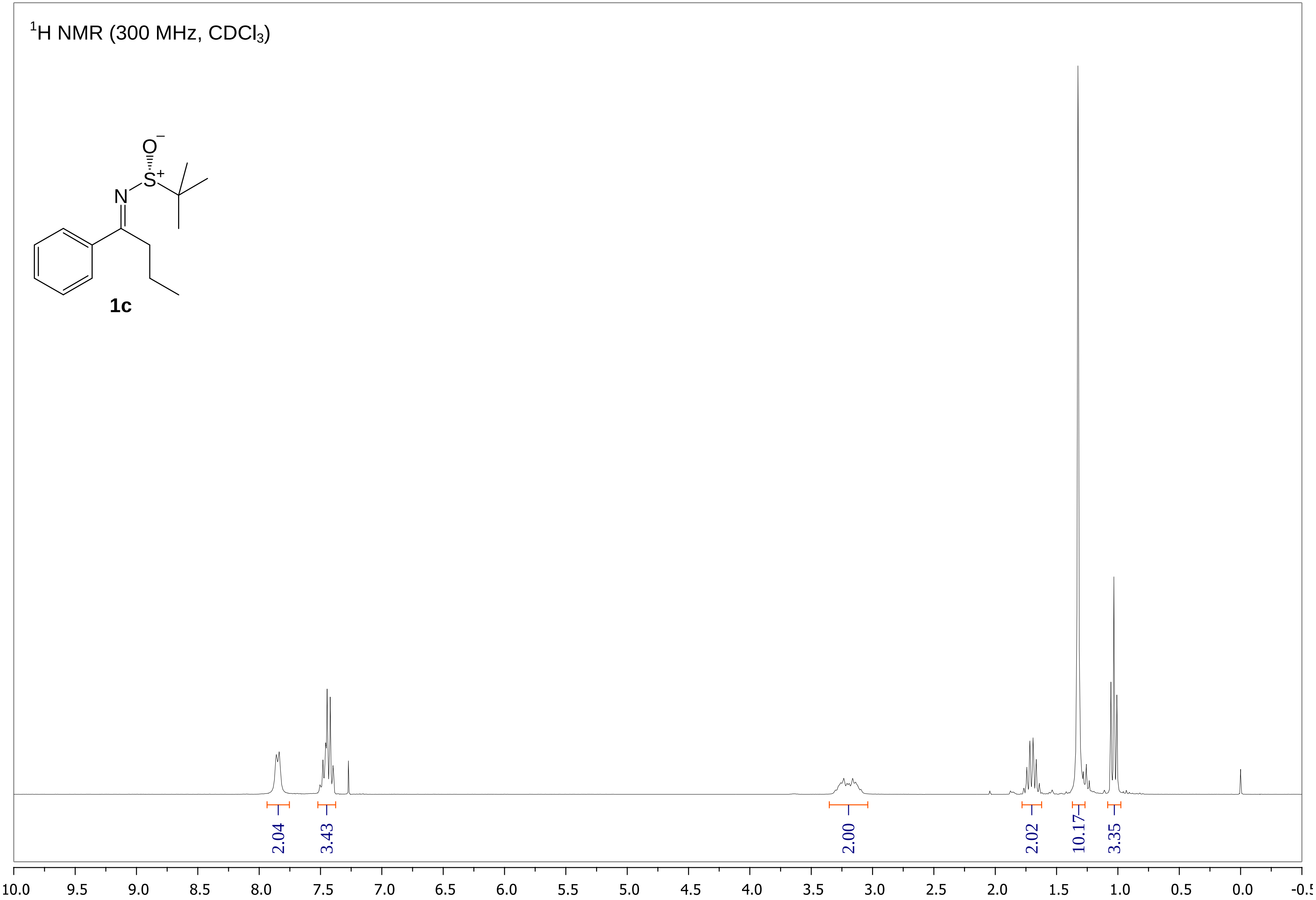
3.32
2.00
11.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


180.92
137.17
131.28
128.31
127.21
57.06
25.59
22.35
12.94
^{13}C NMR (75 MHz, $CDCl_3$)
O
S
N
1b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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O
S+
N
1c
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3.43
2.00
2.02
10.17
3.35
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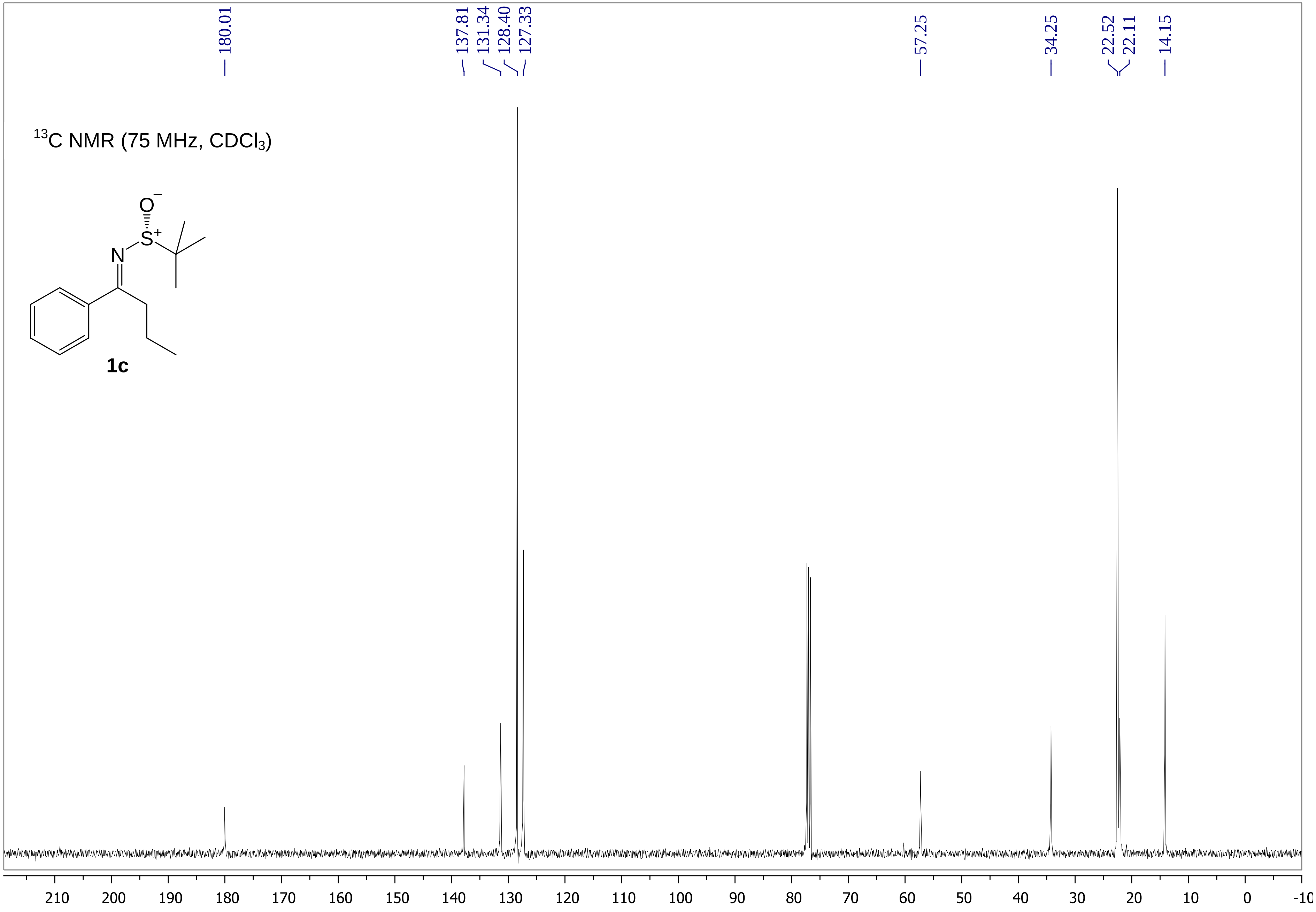
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137.81
131.34
128.40
127.33
57.25
34.25
22.52
22.11
14.15
^{13}C NMR (75 MHz, $CDCl_3$)
O
S
N
1c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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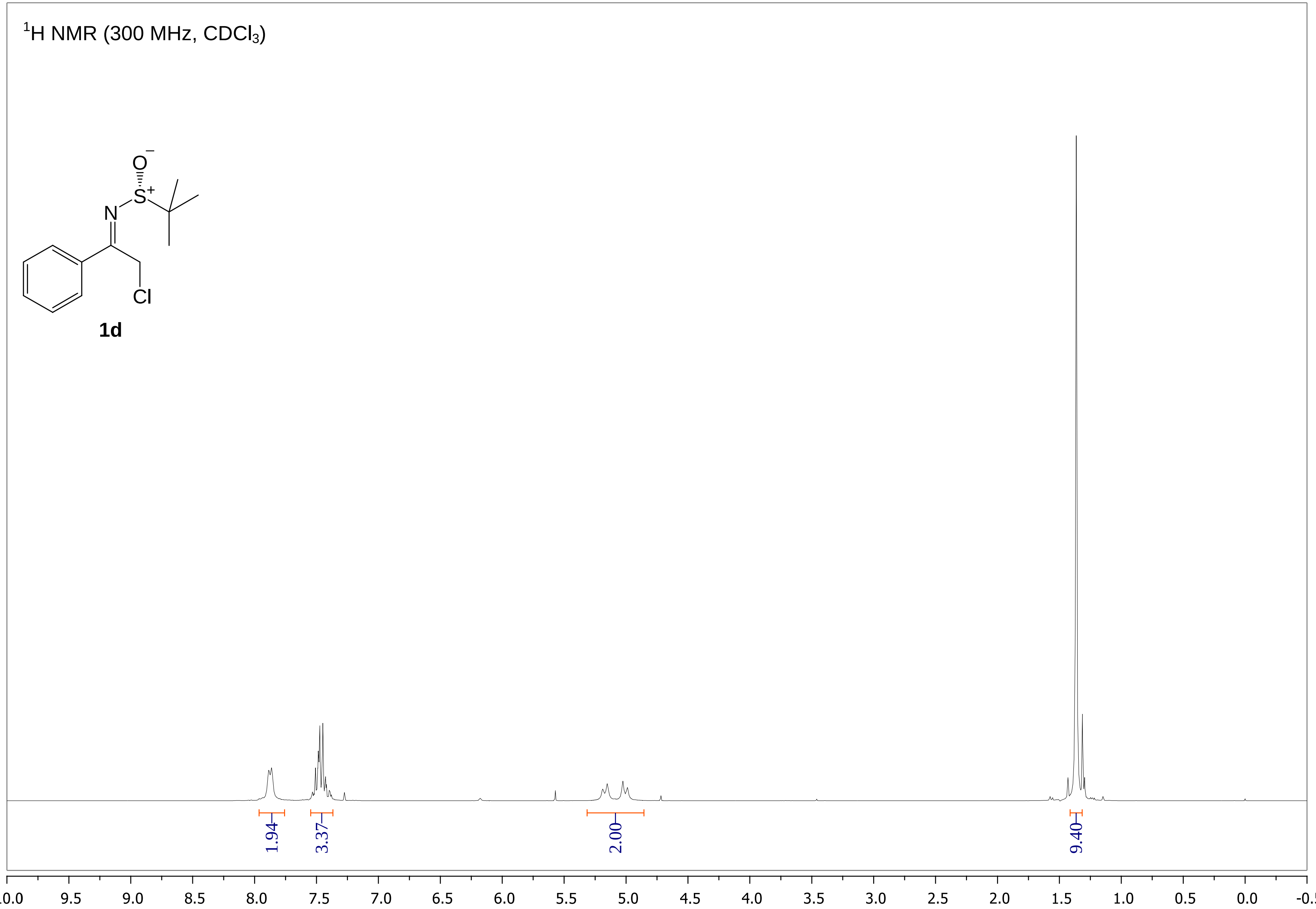

1H NMR (300 MHz, CDCl3)
O
N
S+
Cl
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3.37
2.00
9.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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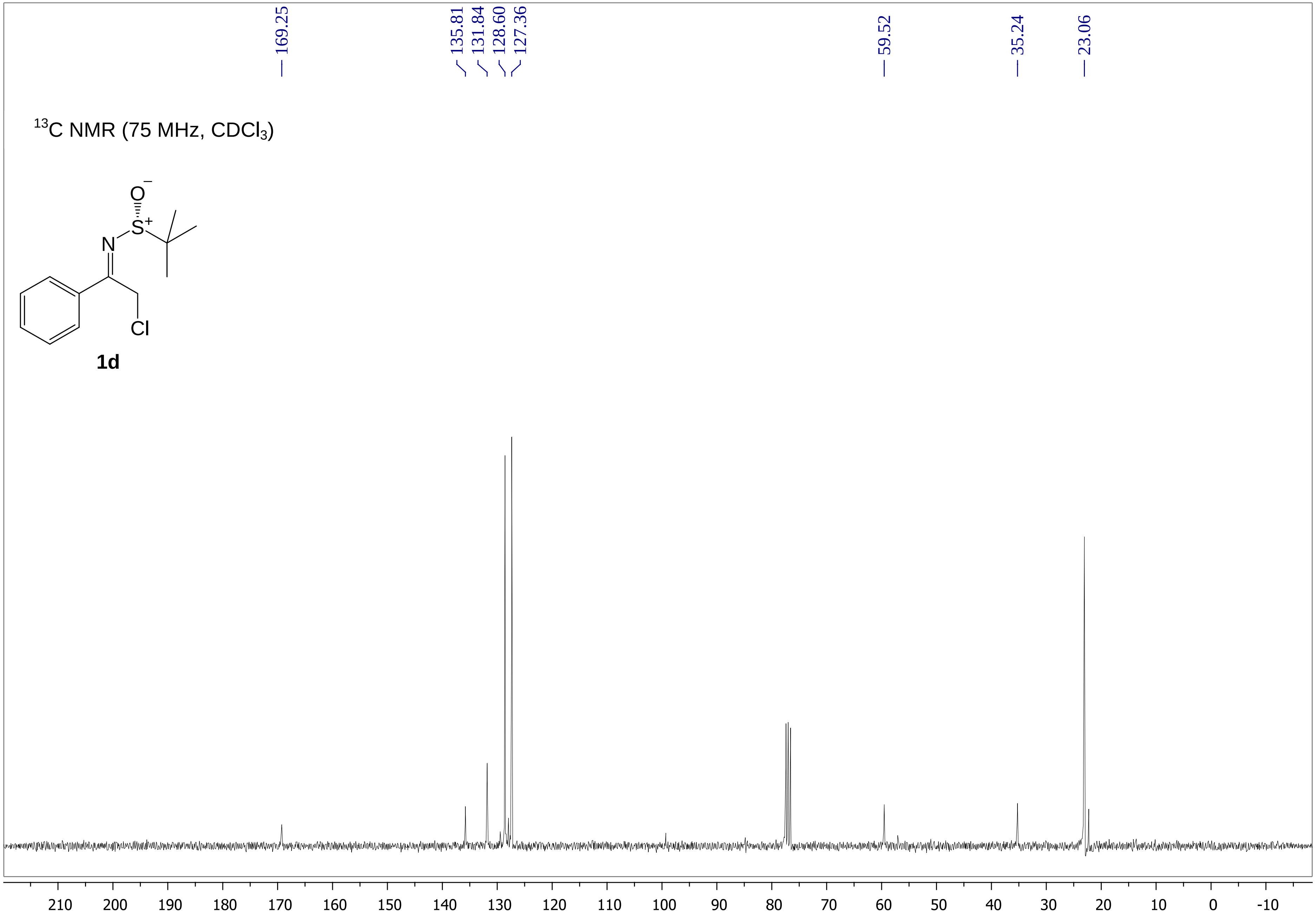
3.0
2.5
2.0
1.5
1.0
0.5
0.0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135.81
131.84
128.60
127.36
59.52
35.24
23.06
13C NMR (75 MHz, CDCl3)
O
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Cl
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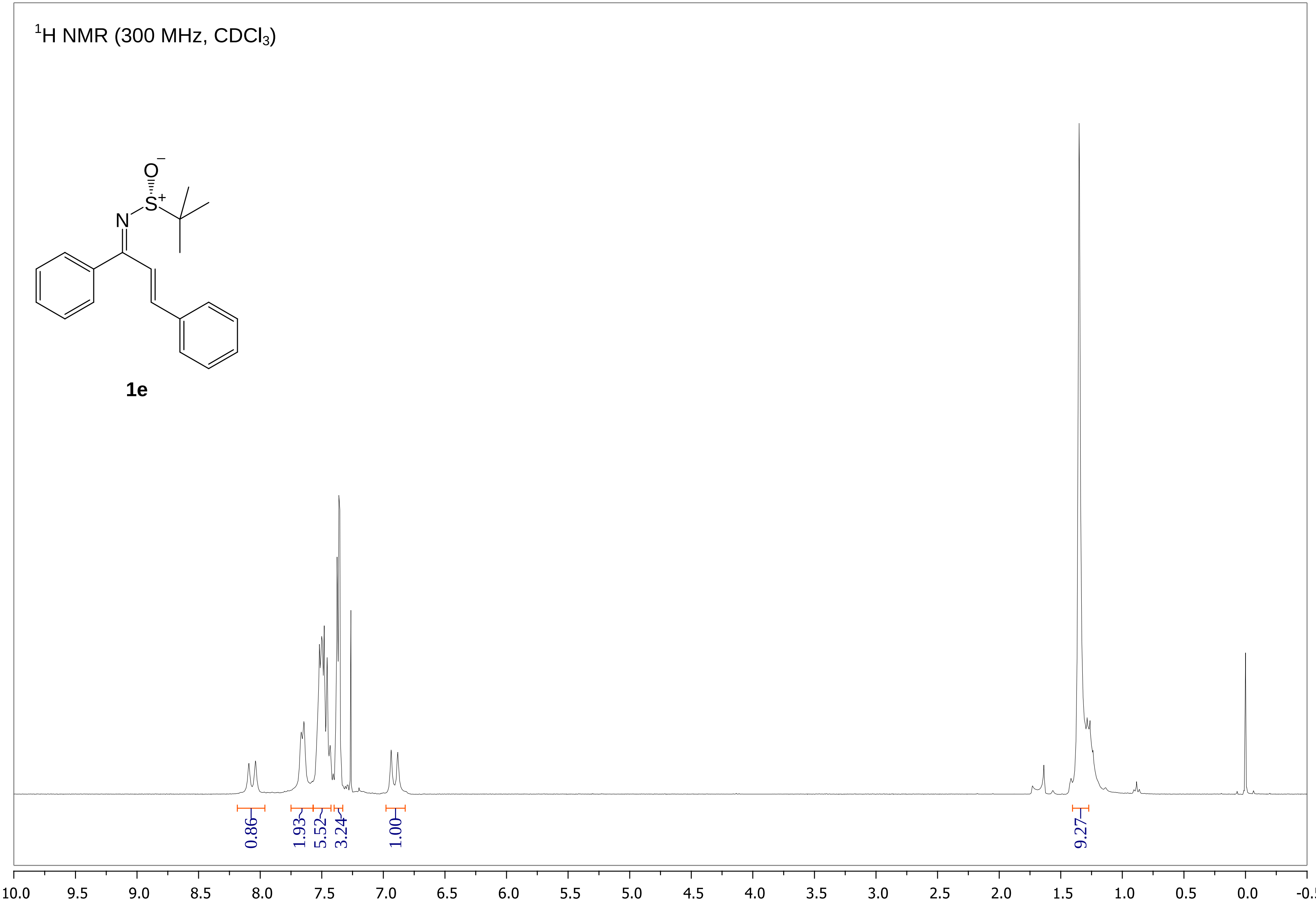

^{1}H NMR (300 MHz, $CDCl_3$)
O
S
N
1e
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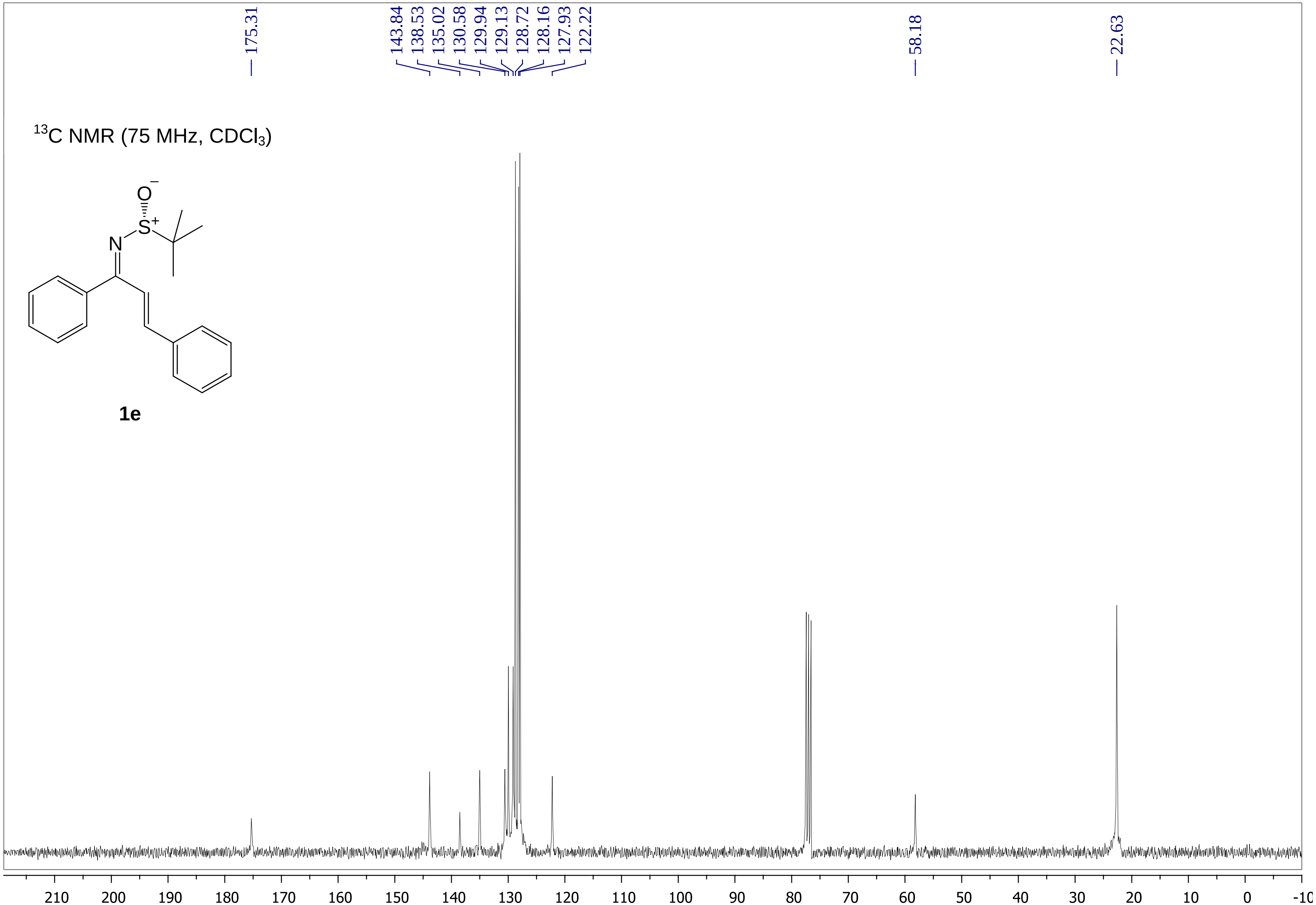
1.93
5.52
3.24
1.00
9.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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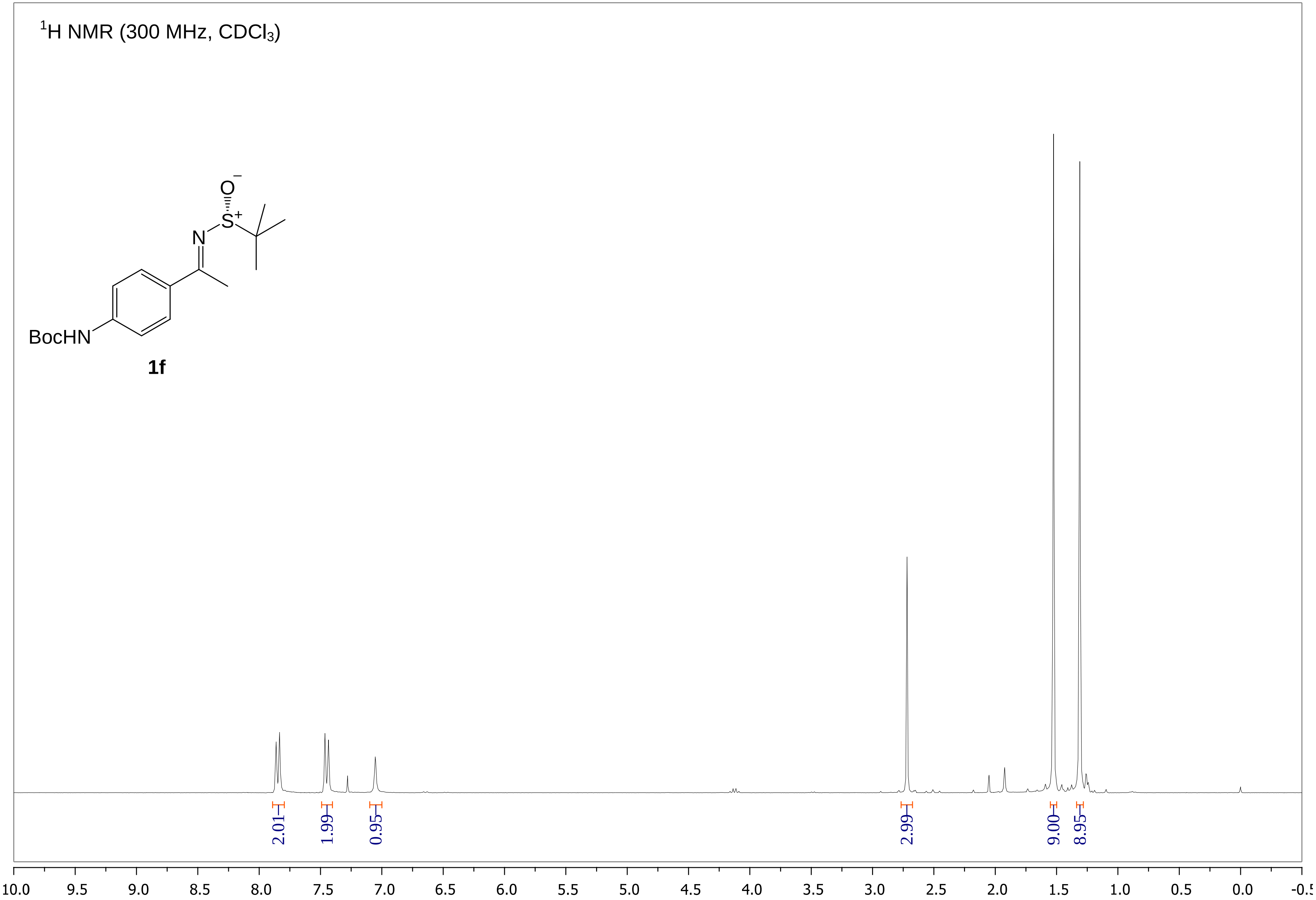
138.53
135.02
130.58
129.94
129.13
128.72
128.16
127.93
122.22
58.18
22.63
13C NMR (75 MHz, CDCl3)
O
S
N
1e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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S+
N
BocHN
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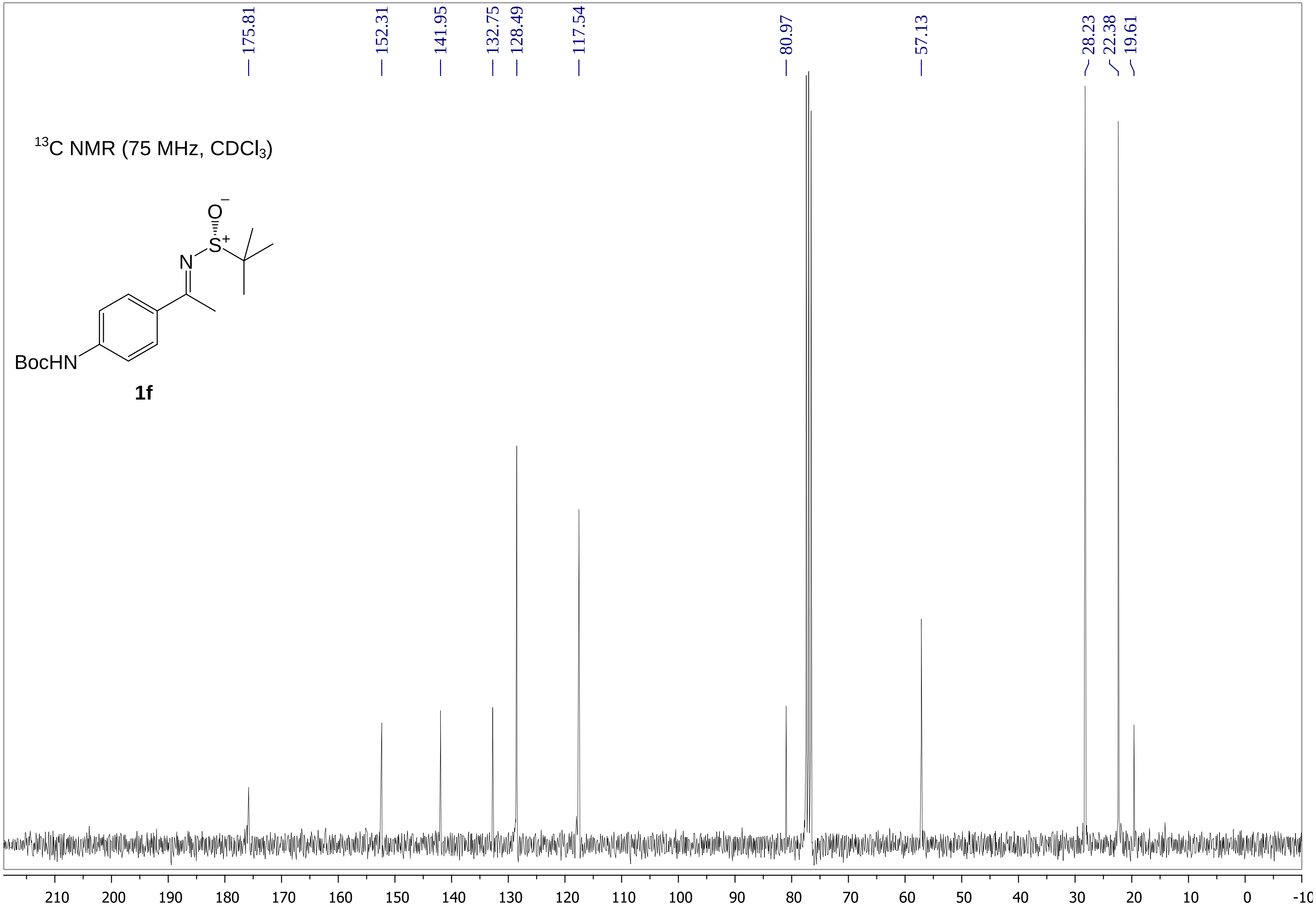
1.99
0.95
2.99
9.00
8.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



175.81
152.31
141.95
132.75
128.49
117.54
80.97
57.13
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22.38
19.61
13C NMR (75 MHz, CDCl3)
BocHN
1f
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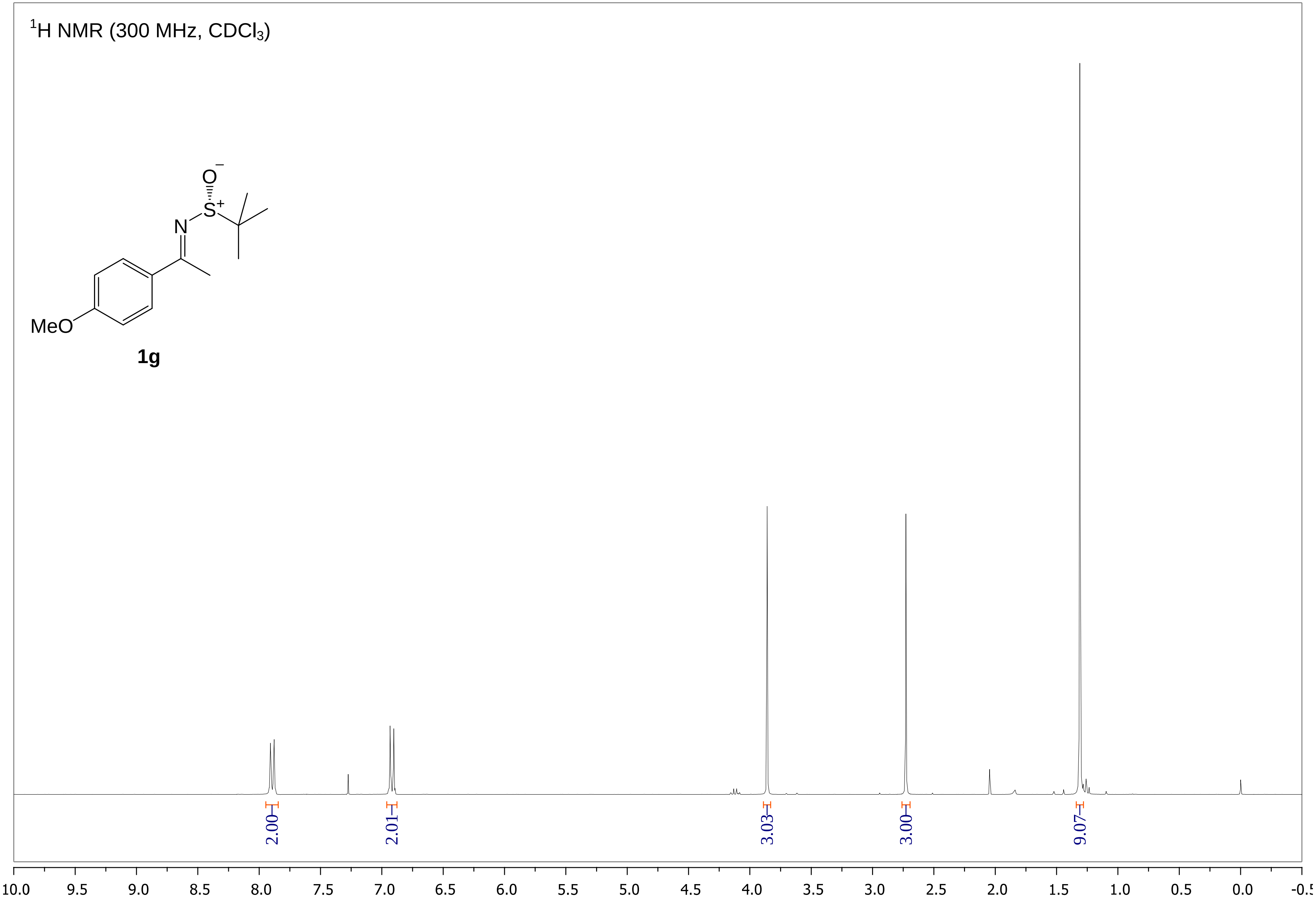
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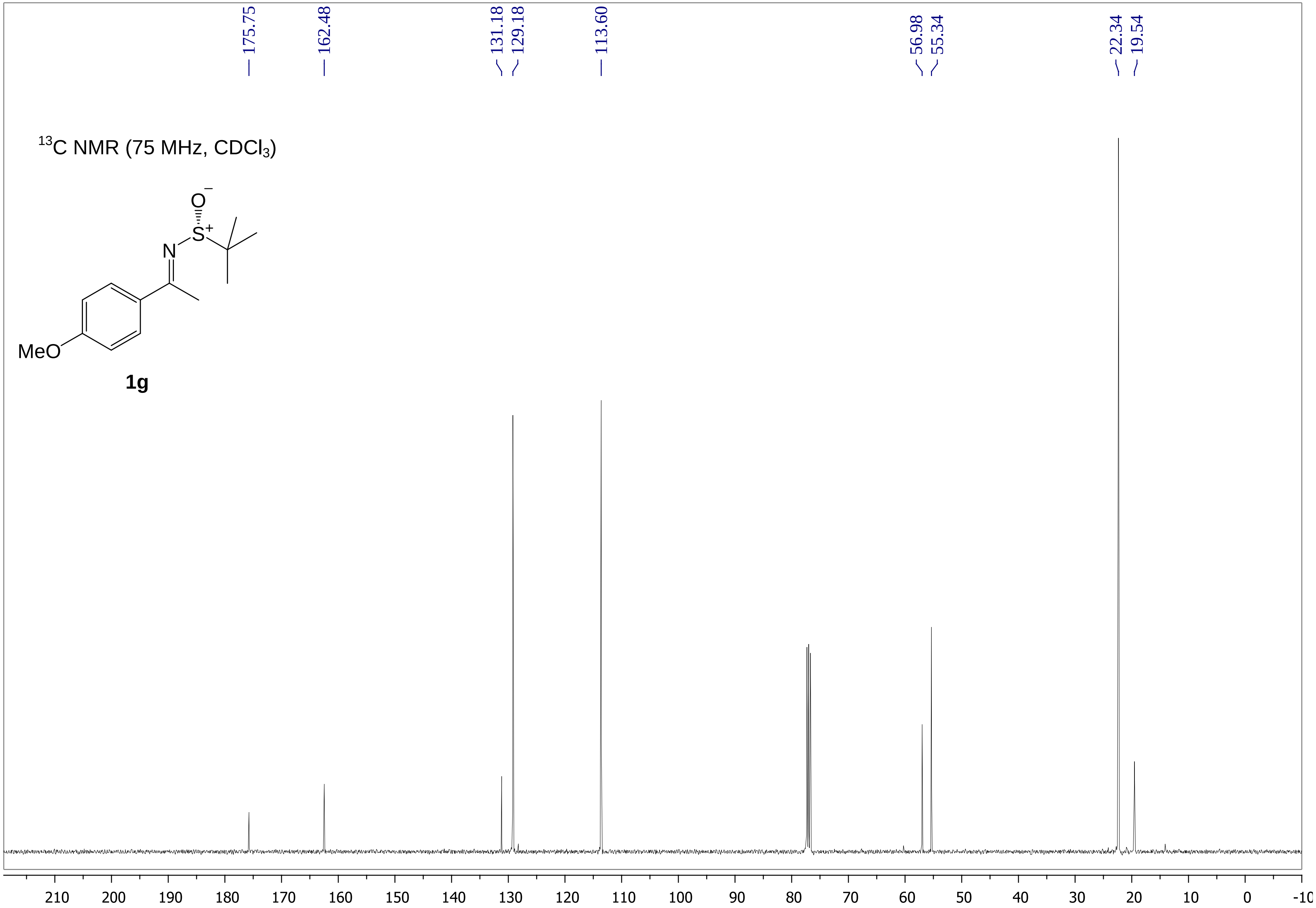
O
S
N
MeO
1g
2.00
2.01
3.03
3.00
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


175.75
162.48
131.18
129.18
113.60
56.98
55.34
22.34
19.54
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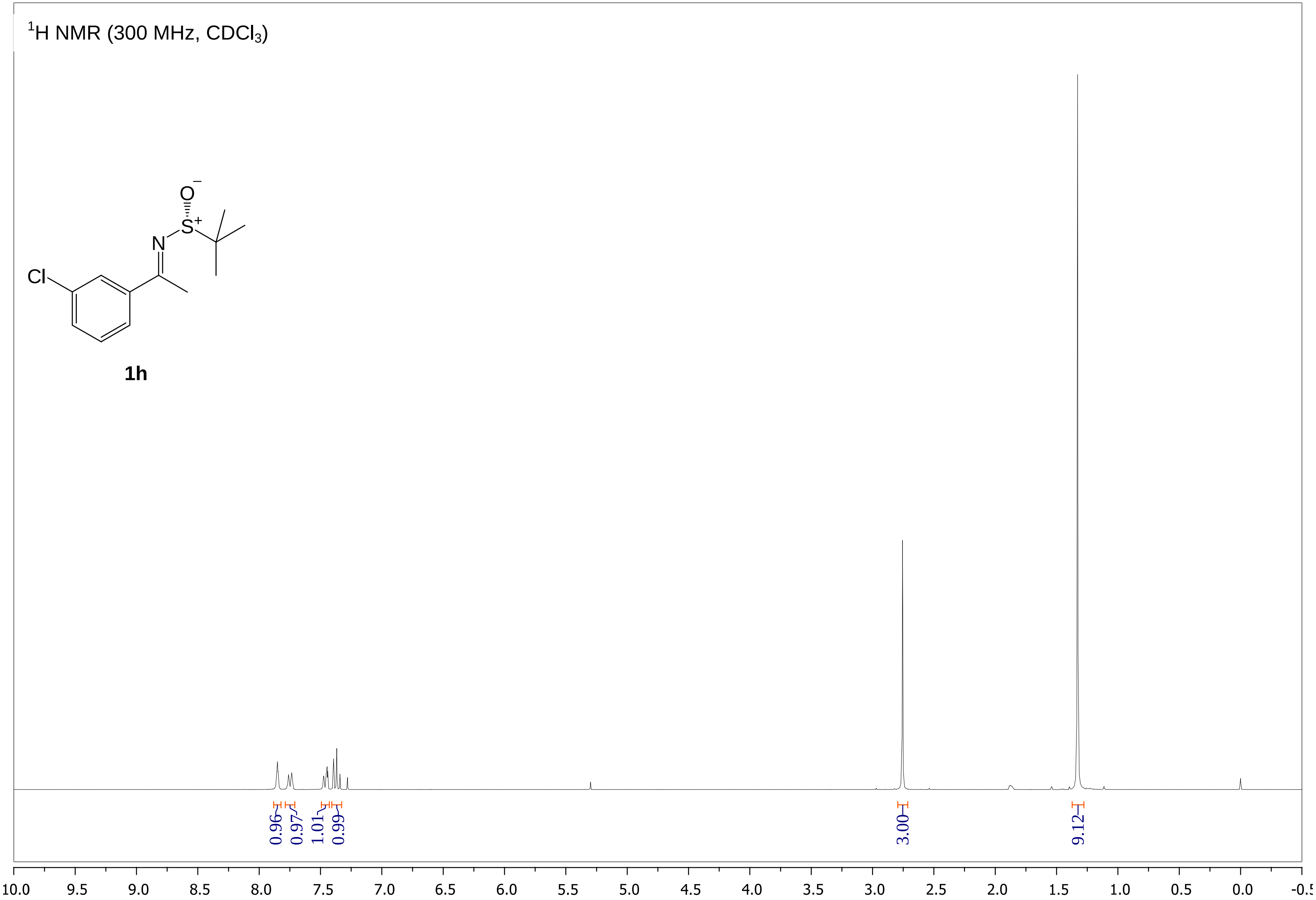
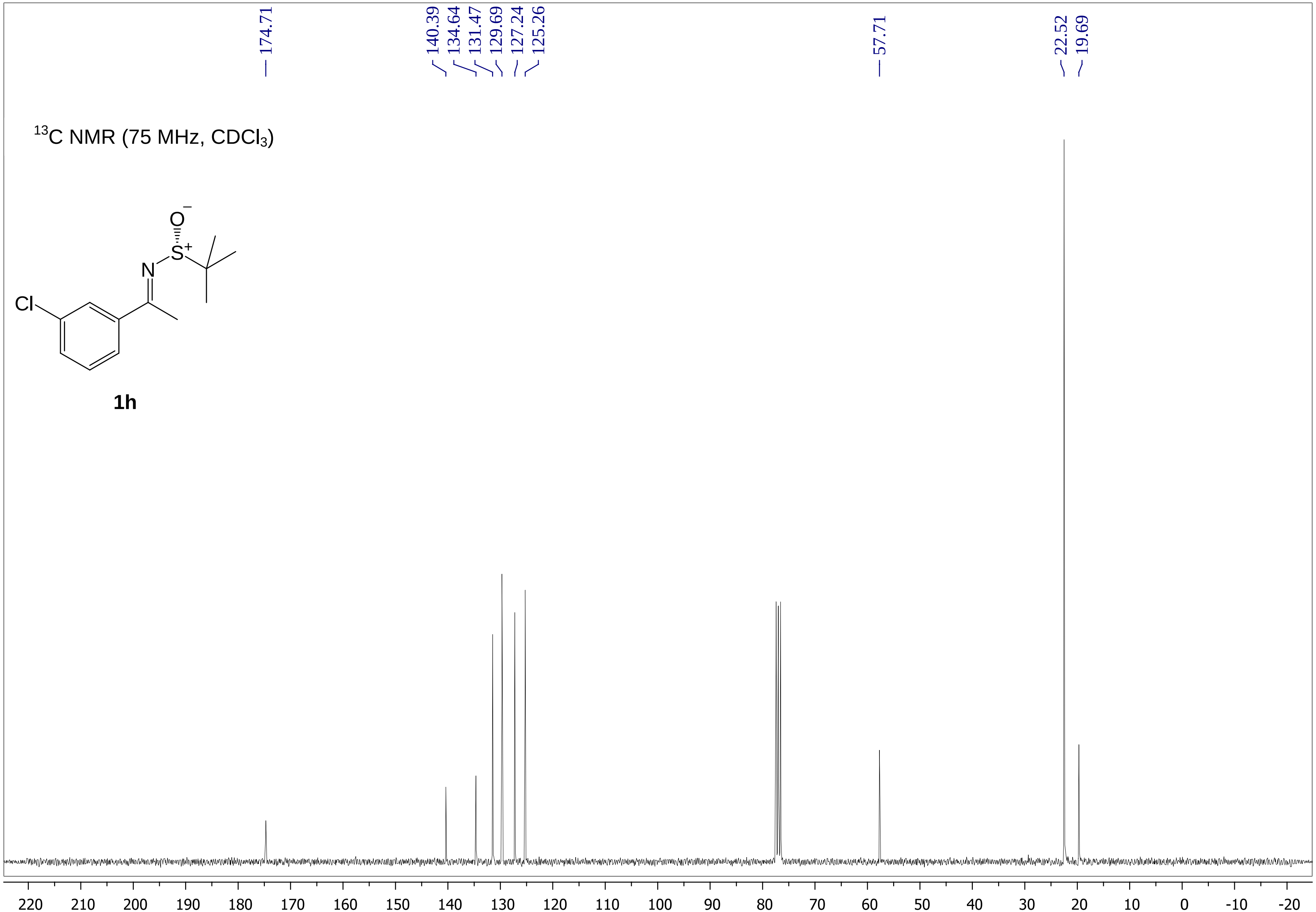
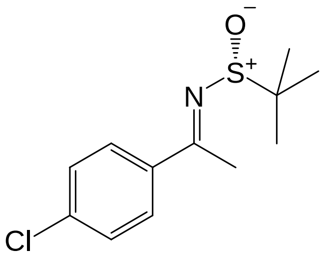
O
S
N
MeO
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



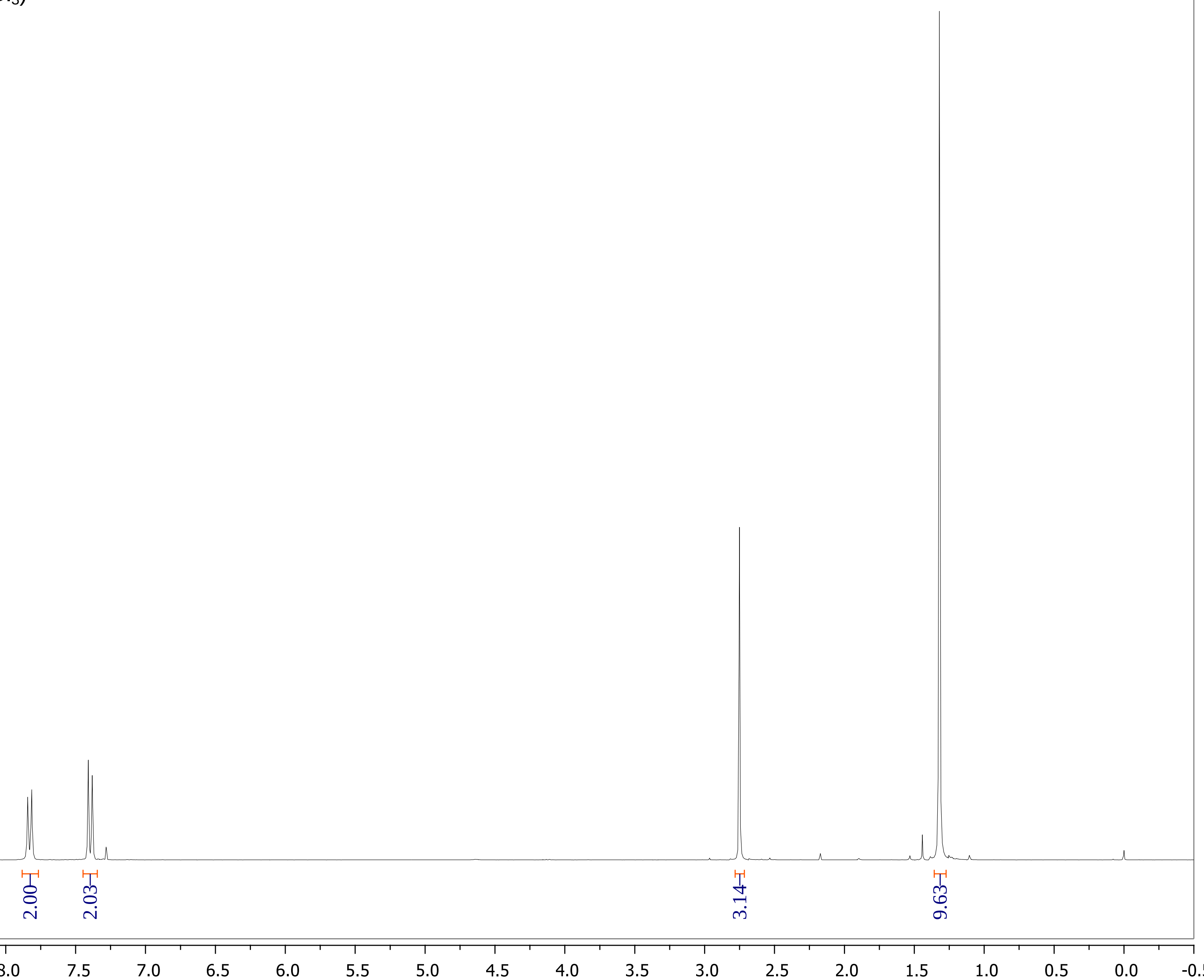
1H NMR (300 MHz, CDCl3)
O
S+
N
Cl
1h
0.96
0.97
1.01
0.99
3.00
9.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

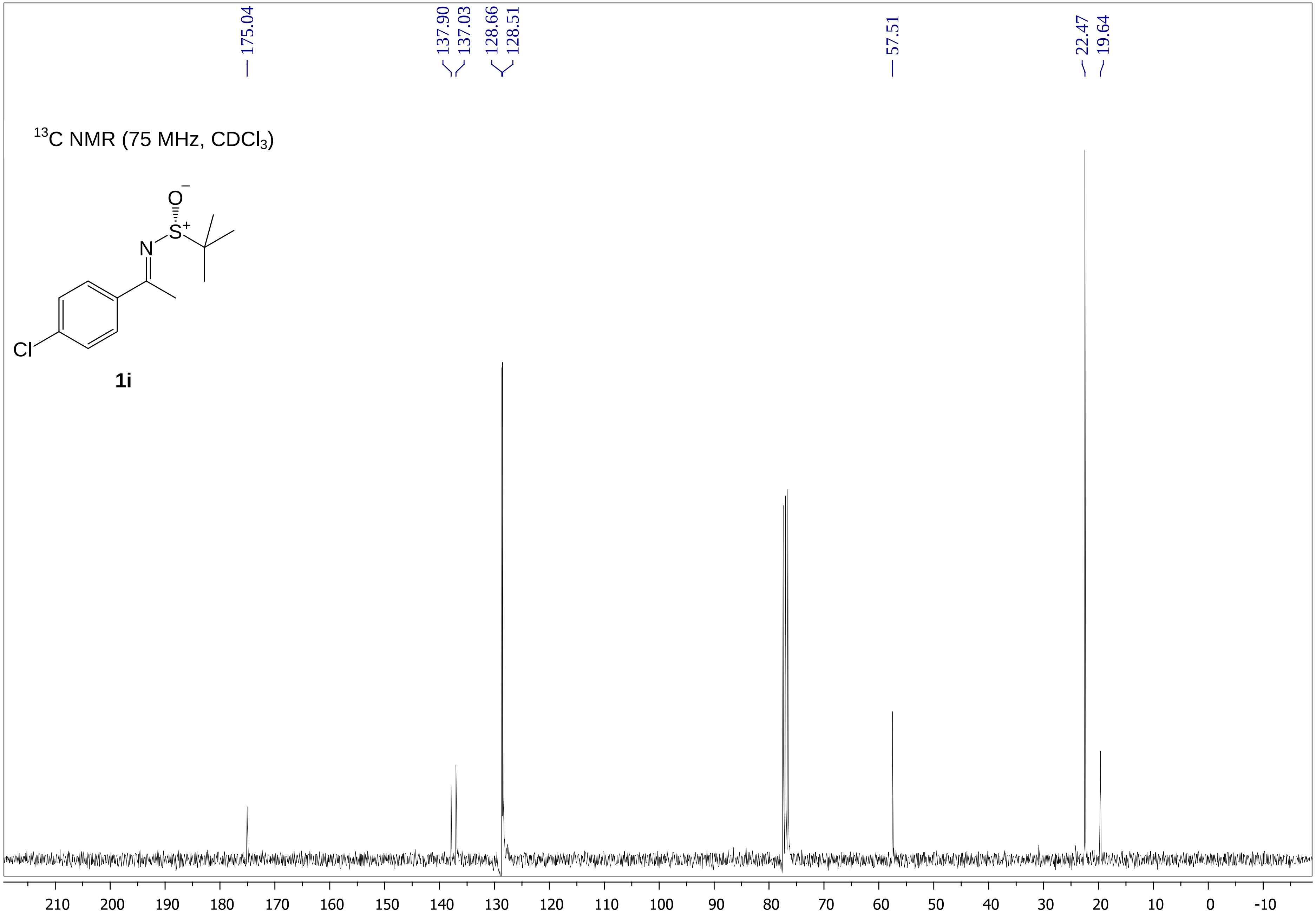

174.71
140.39
134.64
131.47
129.69
127.24
125.26
57.71
22.52
19.69
^{13}C NMR (75 MHz, $CDCl_3$)
O
S
N
Cl
1h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

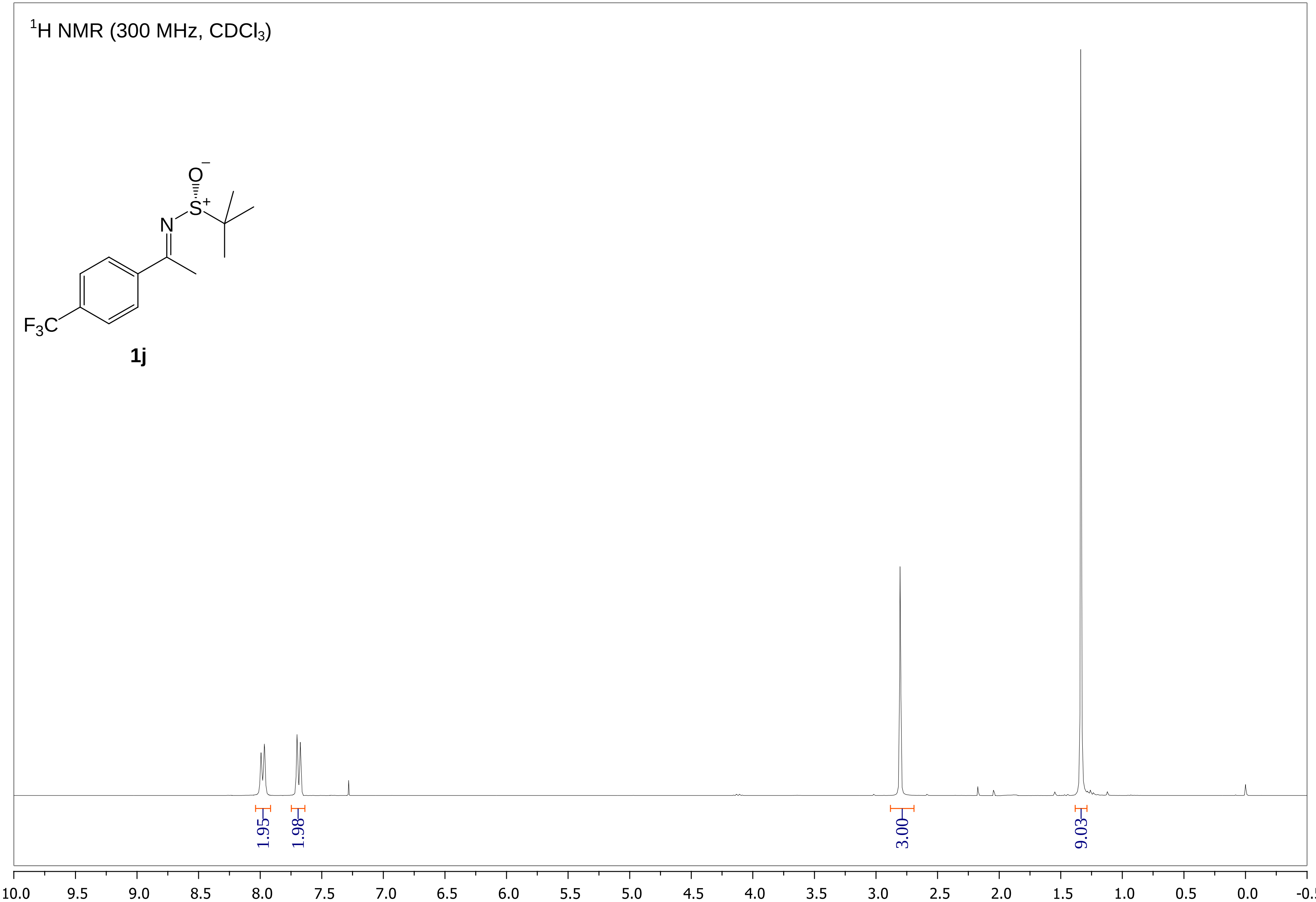
^1H NMR (300 MHz, $CDCl_3$)



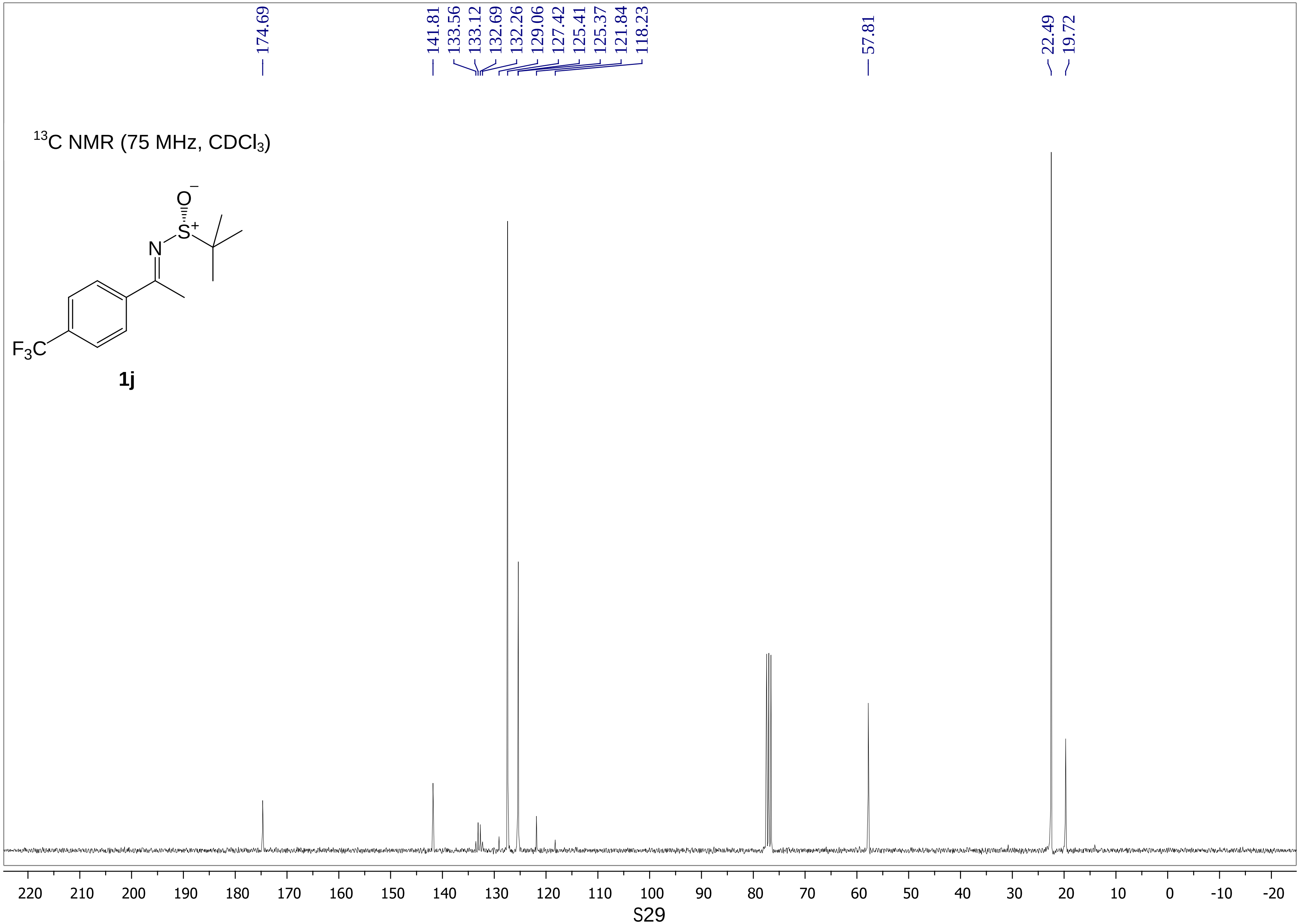
1i



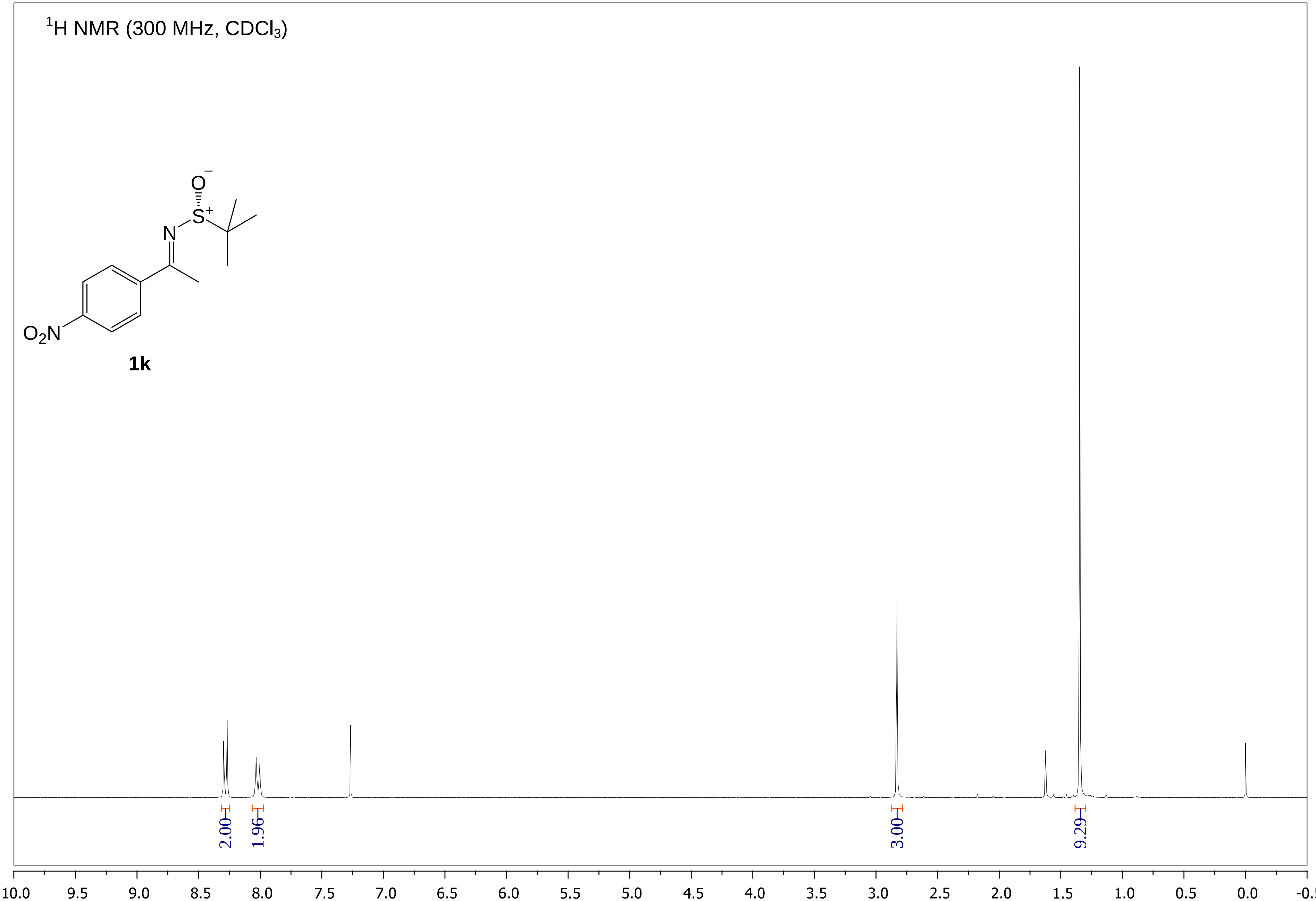

175.04
137.90
137.03
128.66
128.51
57.51
22.47
19.64
^{13}C NMR (75 MHz, $CDCl_3$)
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



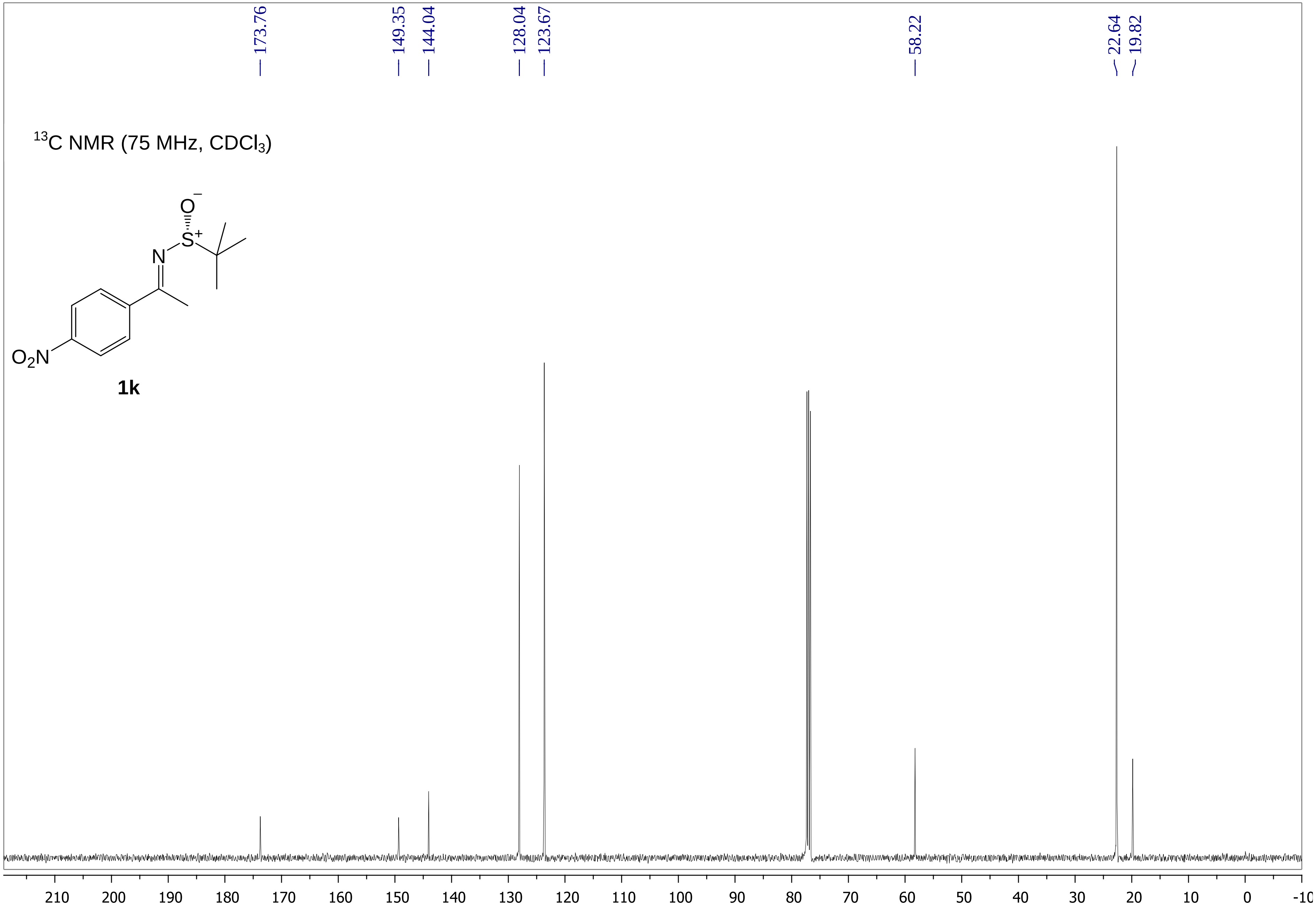
^{1}H NMR (300 MHz, $CDCl_3$)
O
S
N
F_3C
1j
1.95
1.98
3.00
9.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

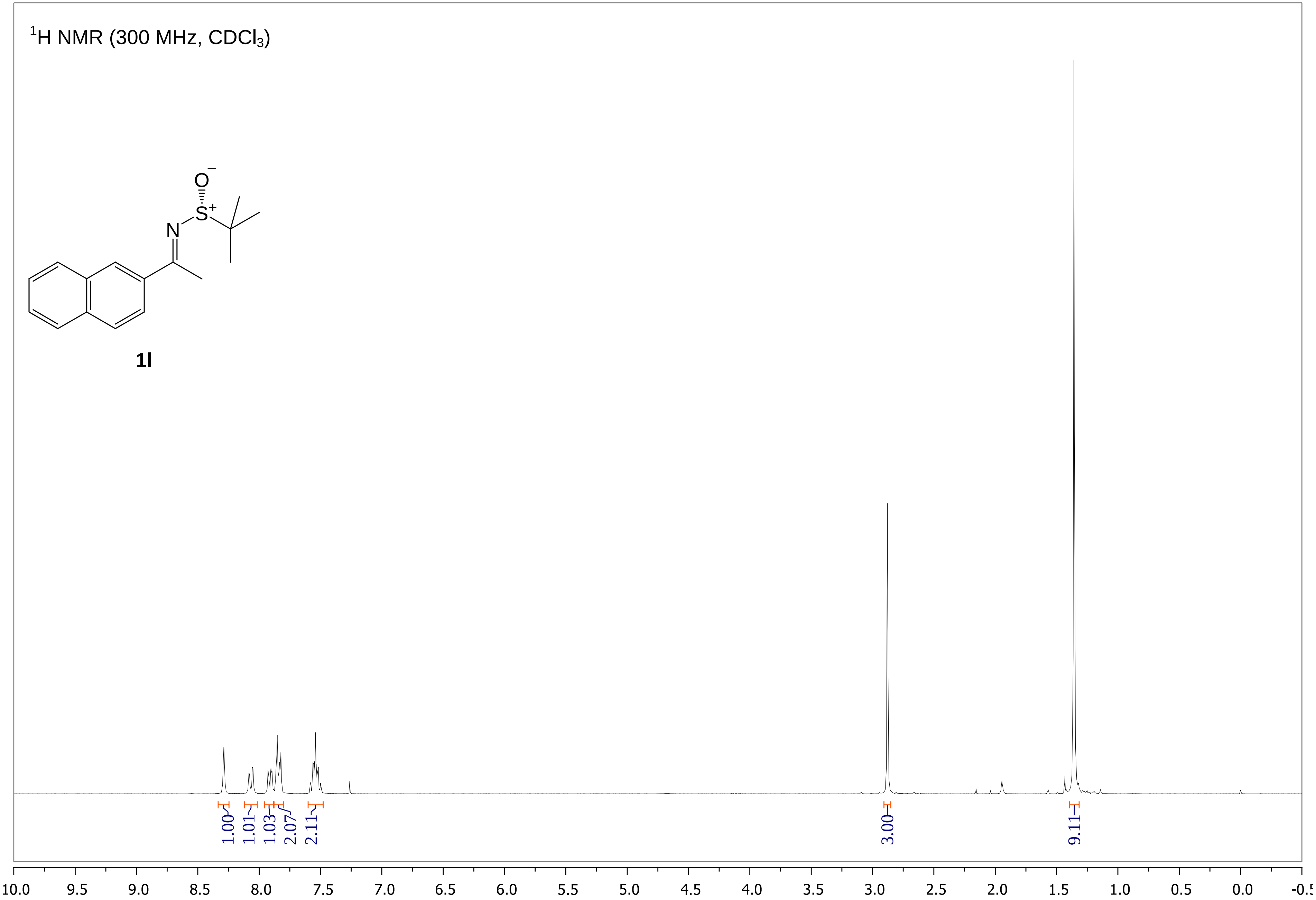


174.69
141.81
133.56
133.12
132.69
132.26
129.06
127.42
125.41
125.37
121.84
118.23
57.81
22.49
19.72
^{13}C NMR (75 MHz, CDCl$_3$)
O
S
N
F$_3$C
1j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

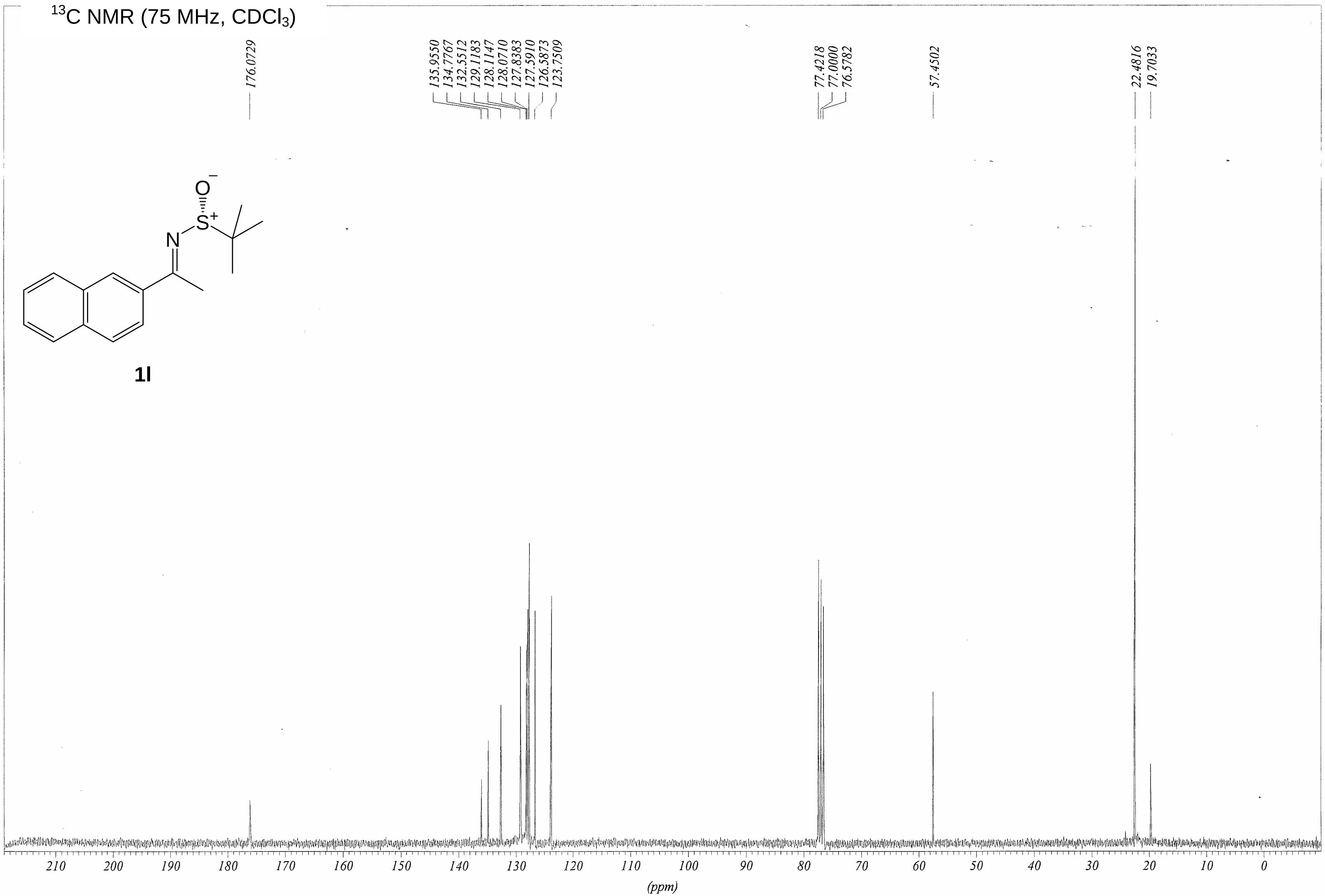


1H NMR (300 MHz, CDCl3)
O
S+
N
O2N
1k
2.00
1.96
3.00
9.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

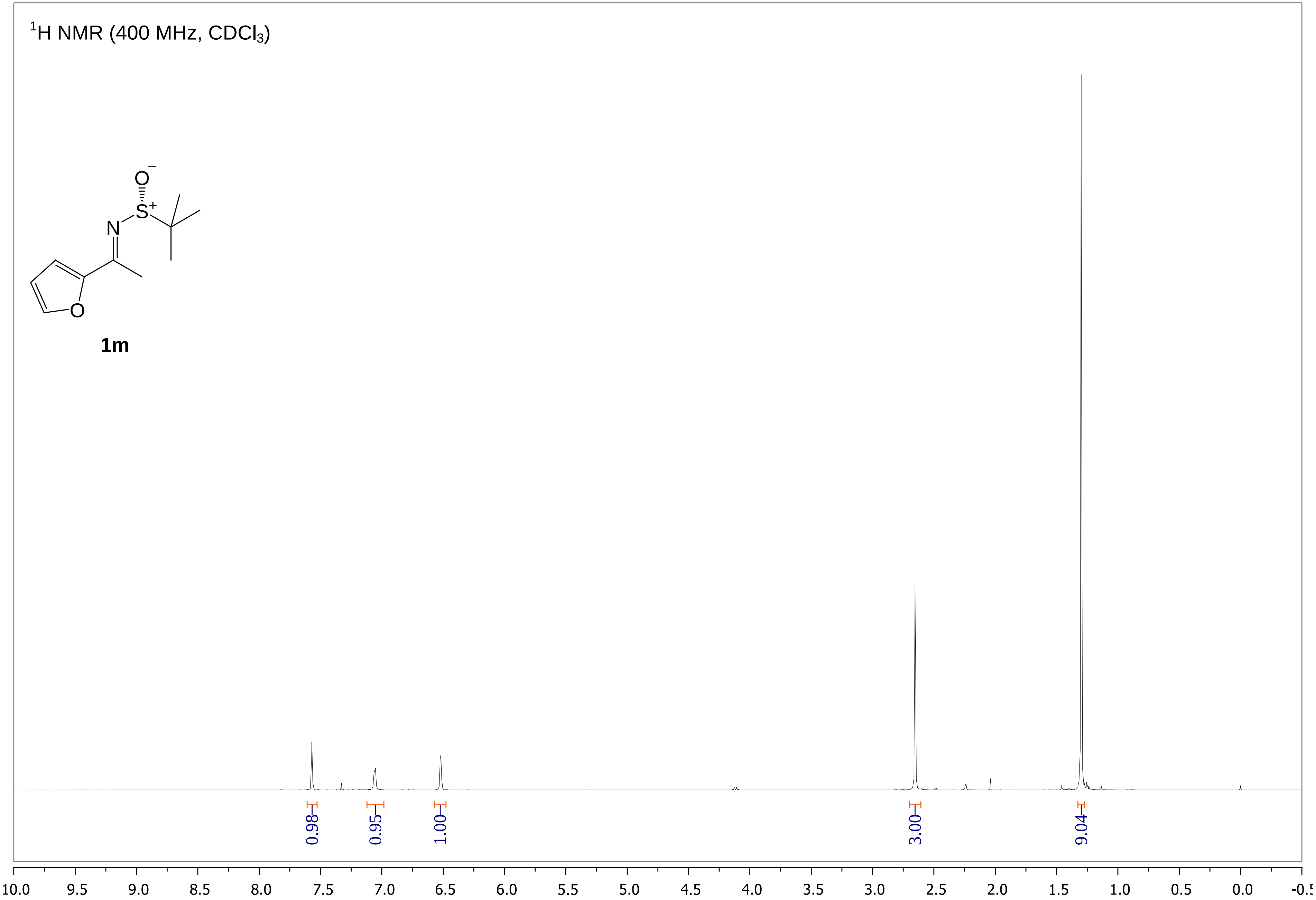

173.76
149.35
144.04
128.04
123.67
58.22
22.64
19.82
13C NMR (75 MHz, CDCl3)
O
S+
N
O2N
1k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


^{1}H NMR (300 MHz, $CDCl_3$)
1l
1.00
1.01
1.03
2.07
2.11
3.00
9.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

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



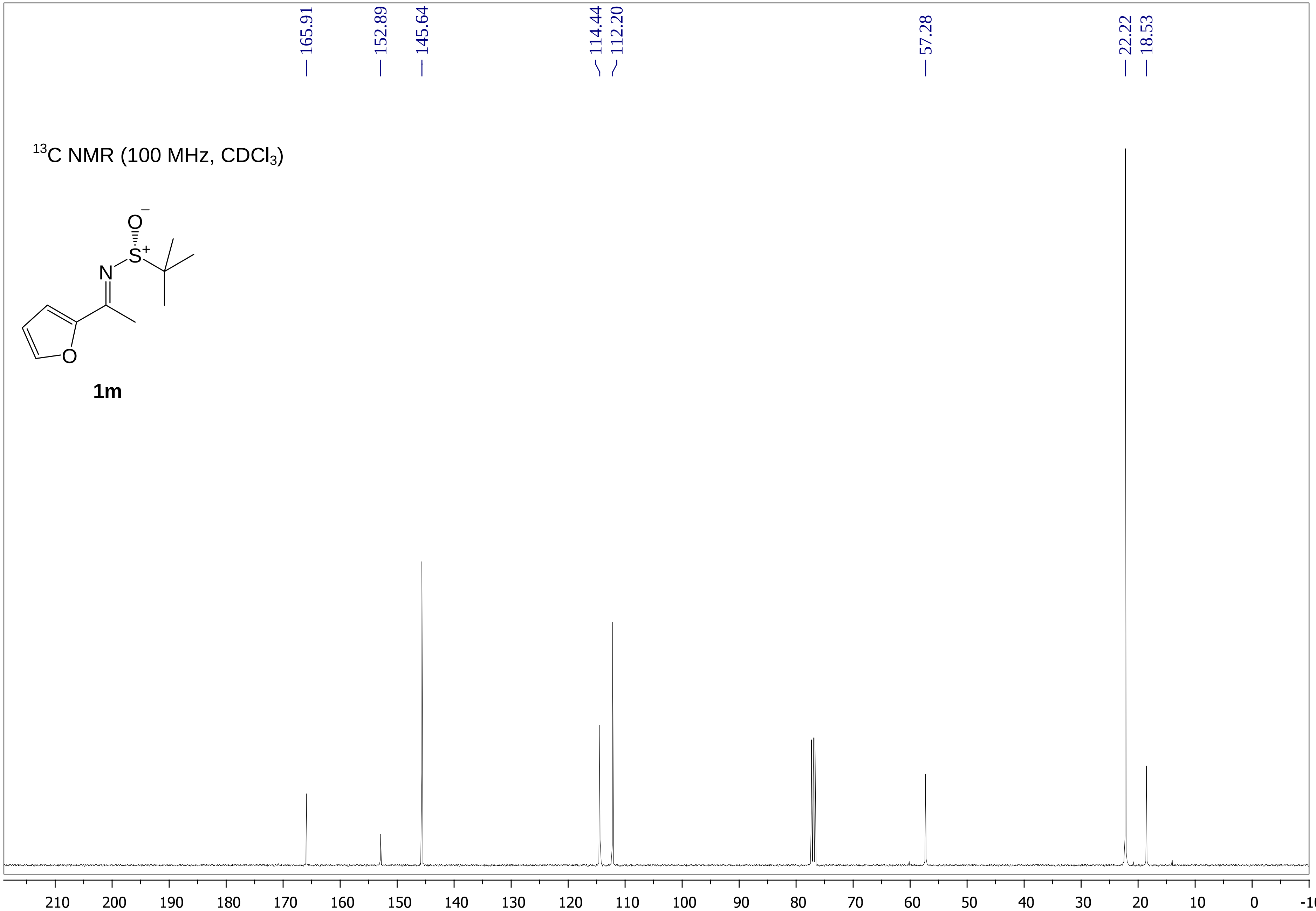
1l

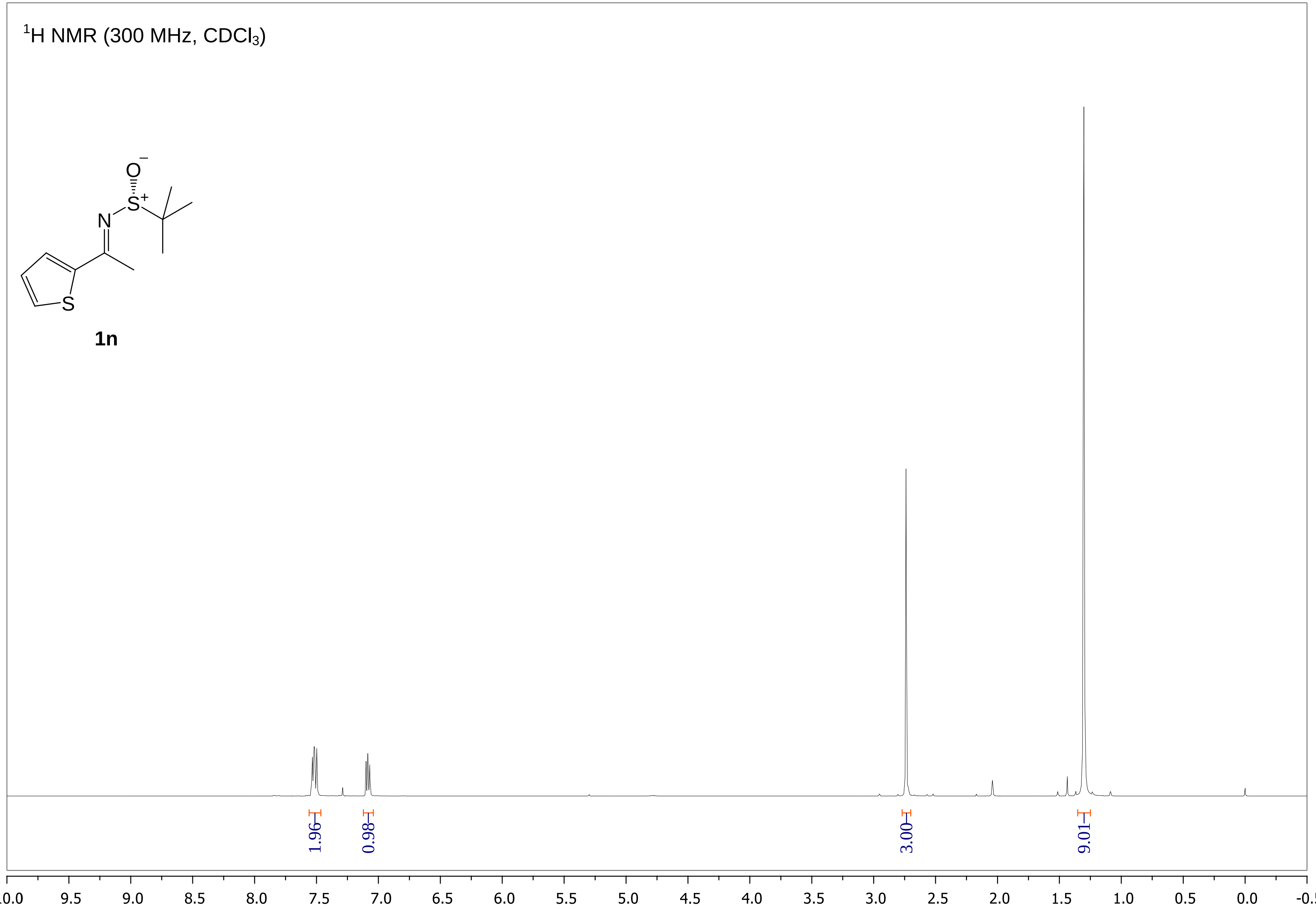


^{1}H NMR (400 MHz, CDCl$_3$)
O
S+
N
O
1m
0.98
0.95
1.00
3.00
9.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

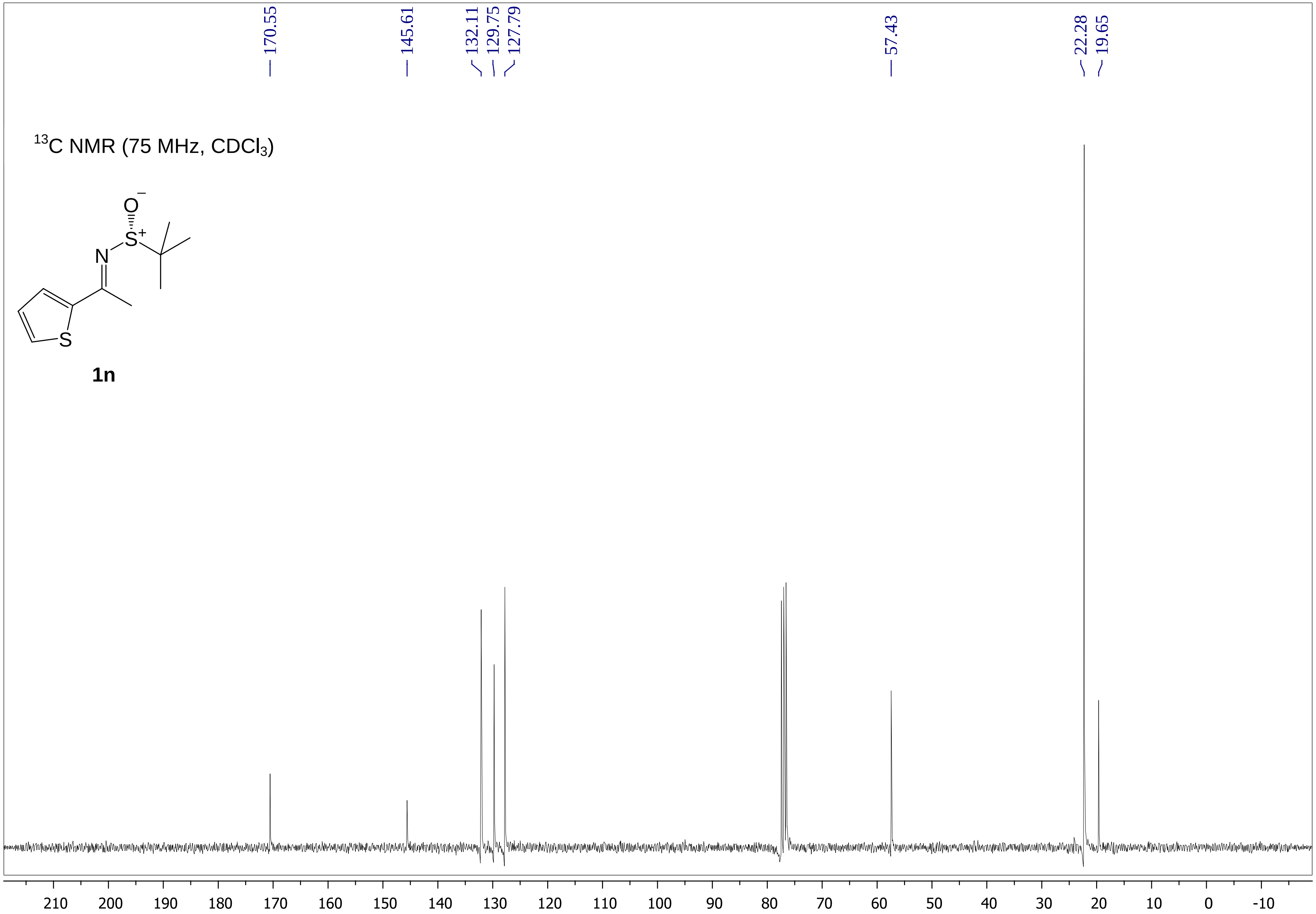
^{13}C NMR (100 MHz, $CDCl_3$)

1m

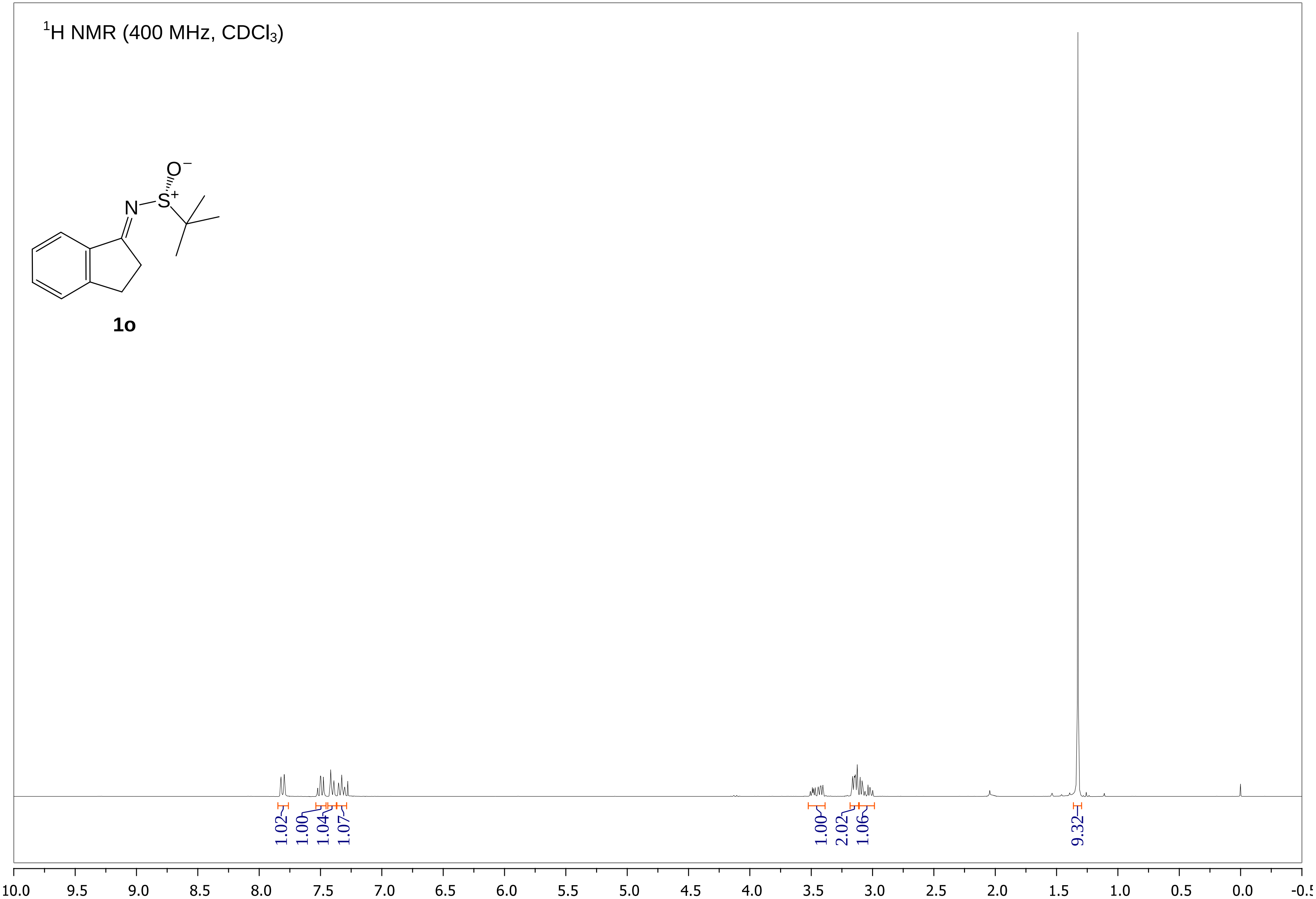


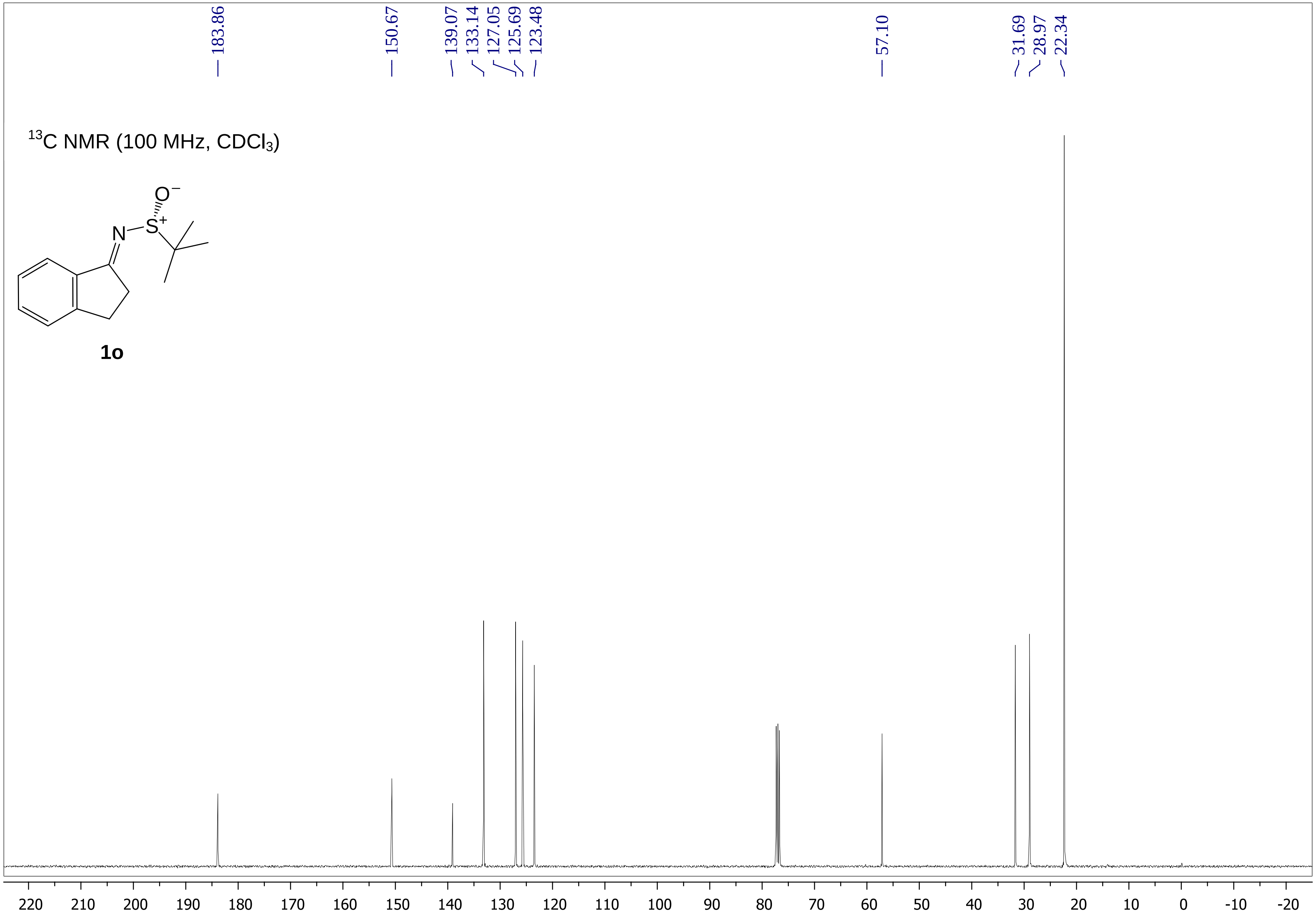


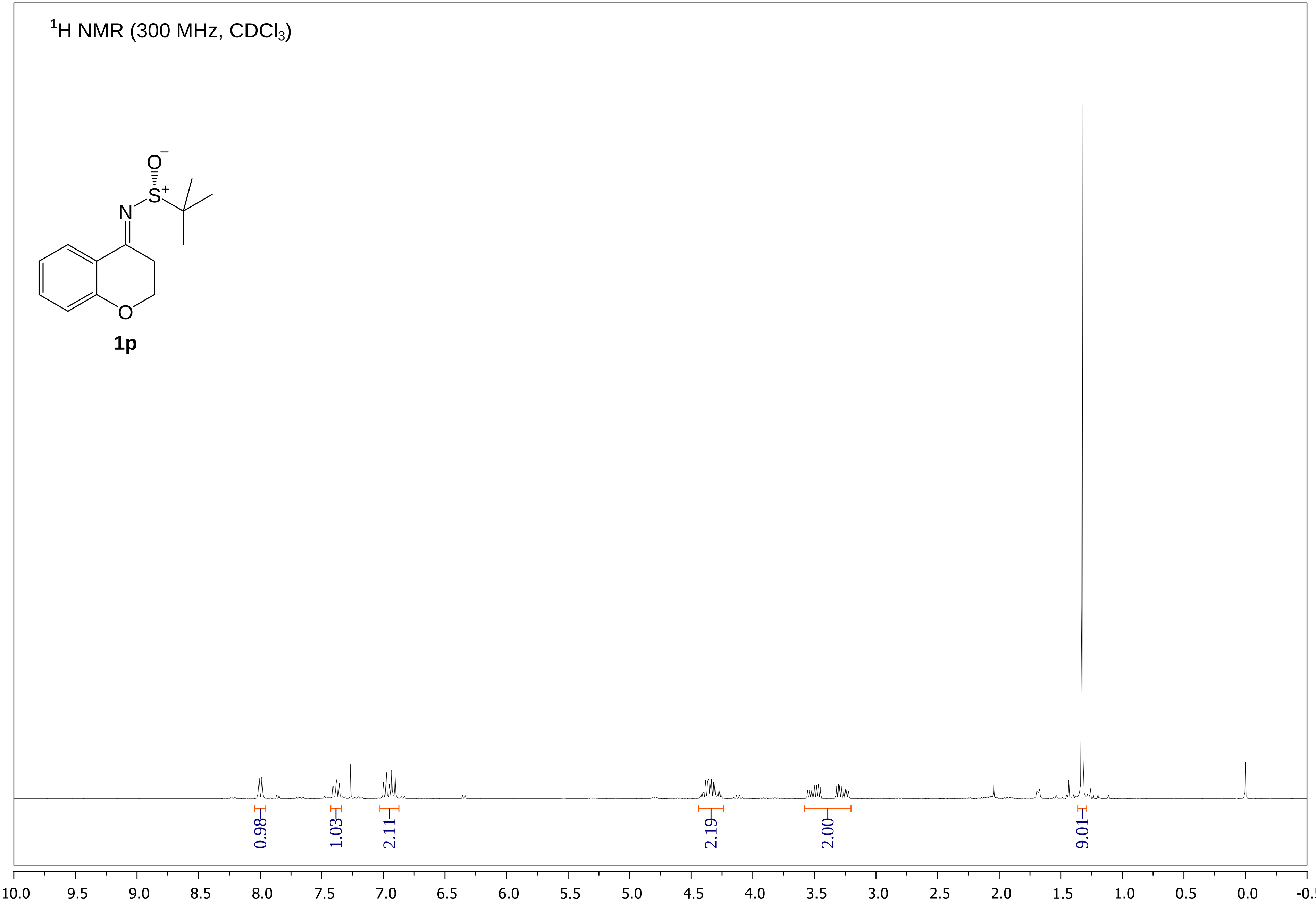
^{1}H NMR (300 MHz, CDCl$_3$)
1n
1.96
0.98
3.00
9.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



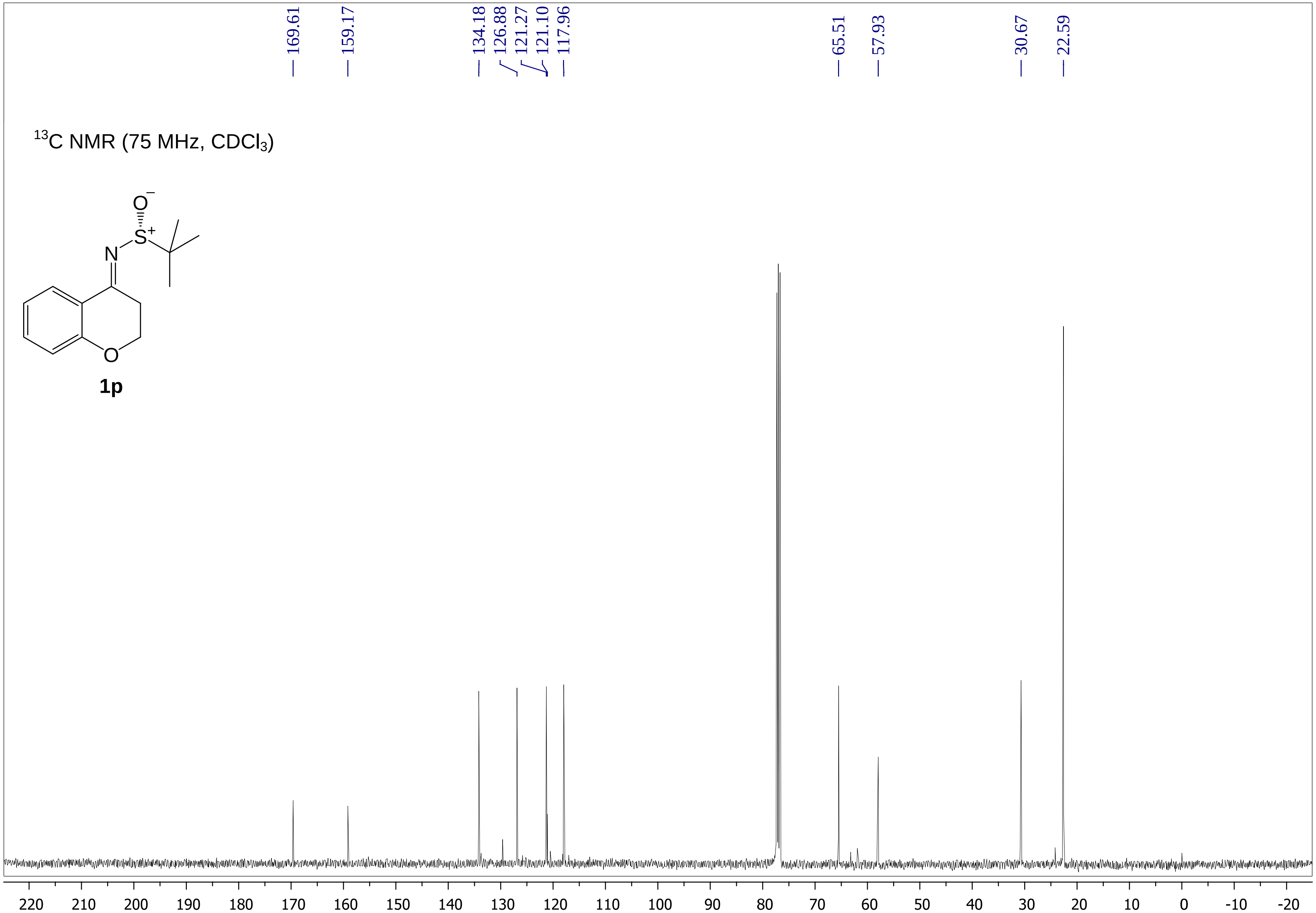
170.55
145.61
132.11
129.75
127.79
57.43
22.28
19.65
13C NMR (75 MHz, CDCl3)
O
S
N
S
1n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


1H NMR (400 MHz, CDCl3)
1o
1.02
1.00
1.04
1.07
1.00
2.02
1.06
9.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

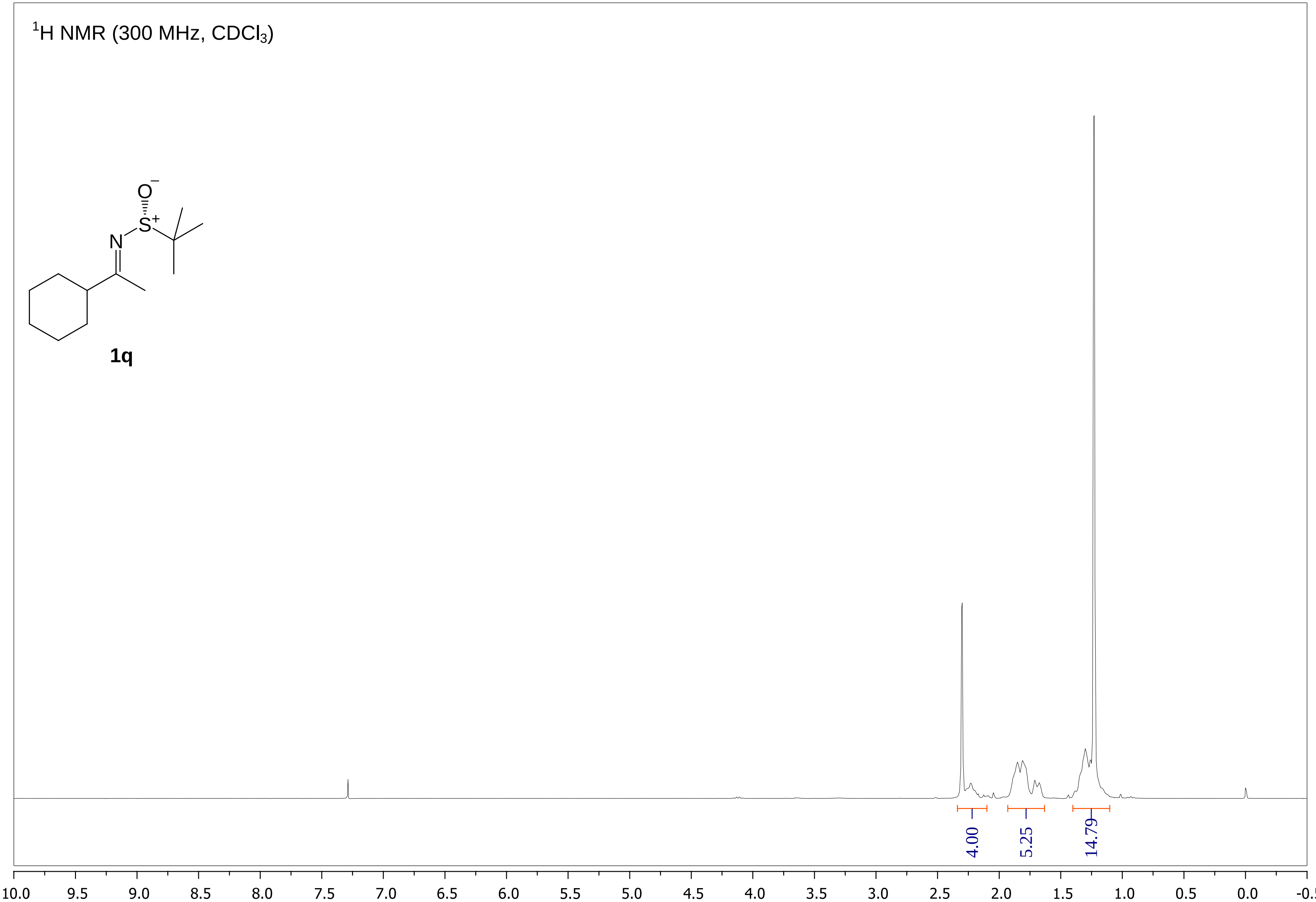

183.86
150.67
139.07
133.14
127.05
125.69
123.48
57.10
31.69
28.97
22.34
13C NMR (100 MHz, CDCl3)
O−
S+
N
1o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20



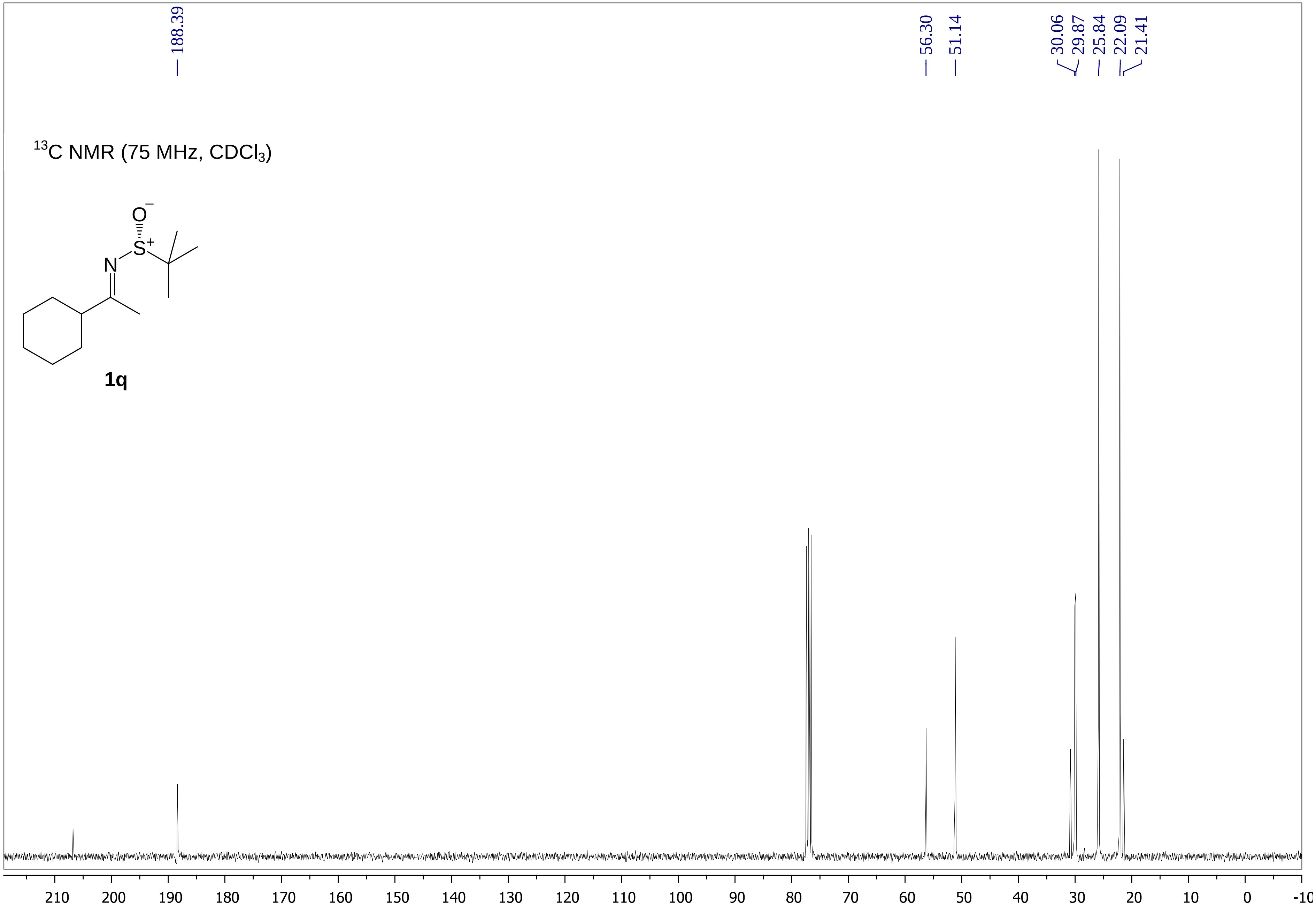
1H NMR (300 MHz, CDCl3)
1p
0.98
1.03
2.11
2.19
2.00
9.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

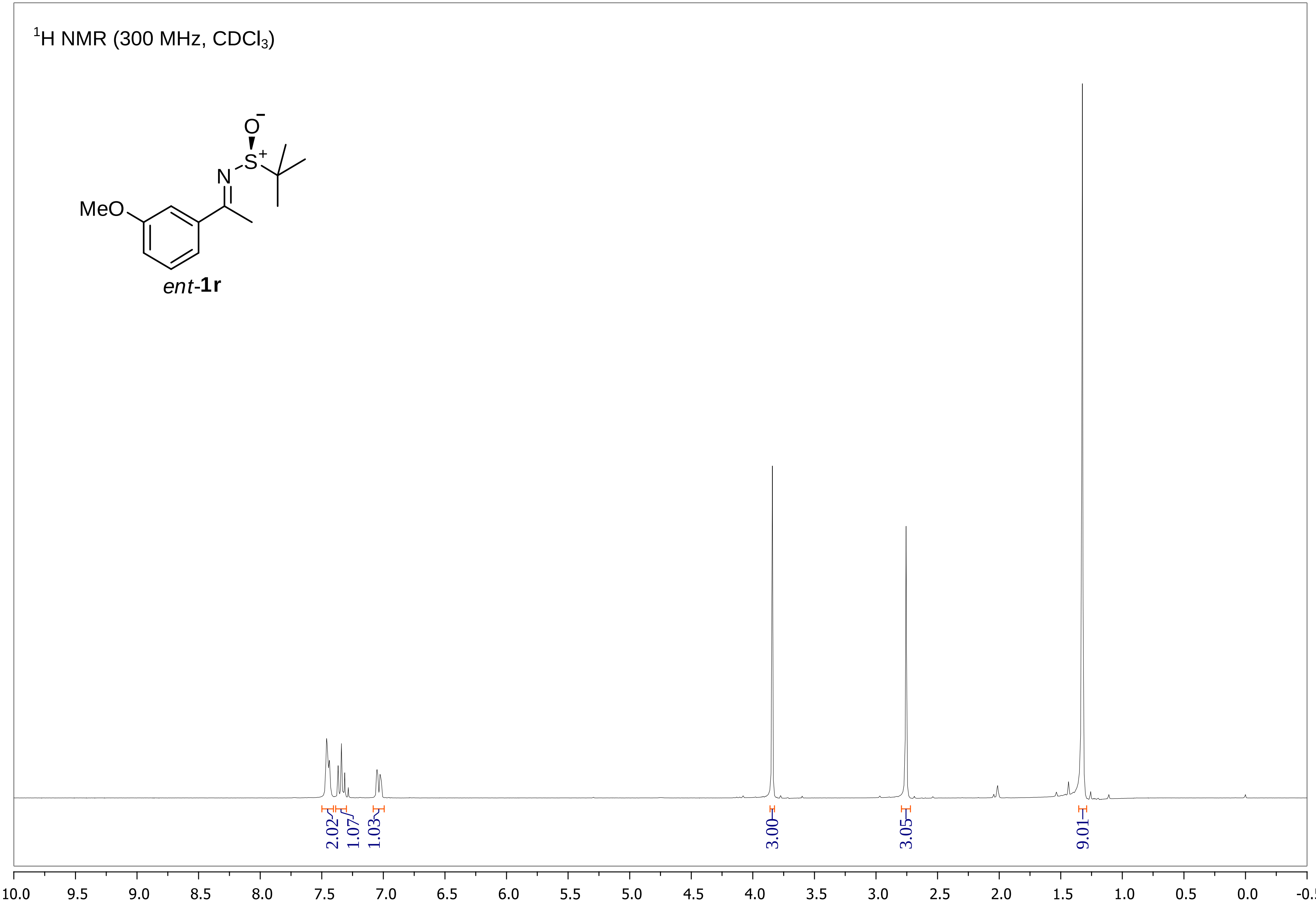


169.61
159.17
134.18
126.88
121.27
121.10
117.96
65.51
57.93
30.67
22.59
^{13}C NMR (75 MHz, $CDCl_3$)
1p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

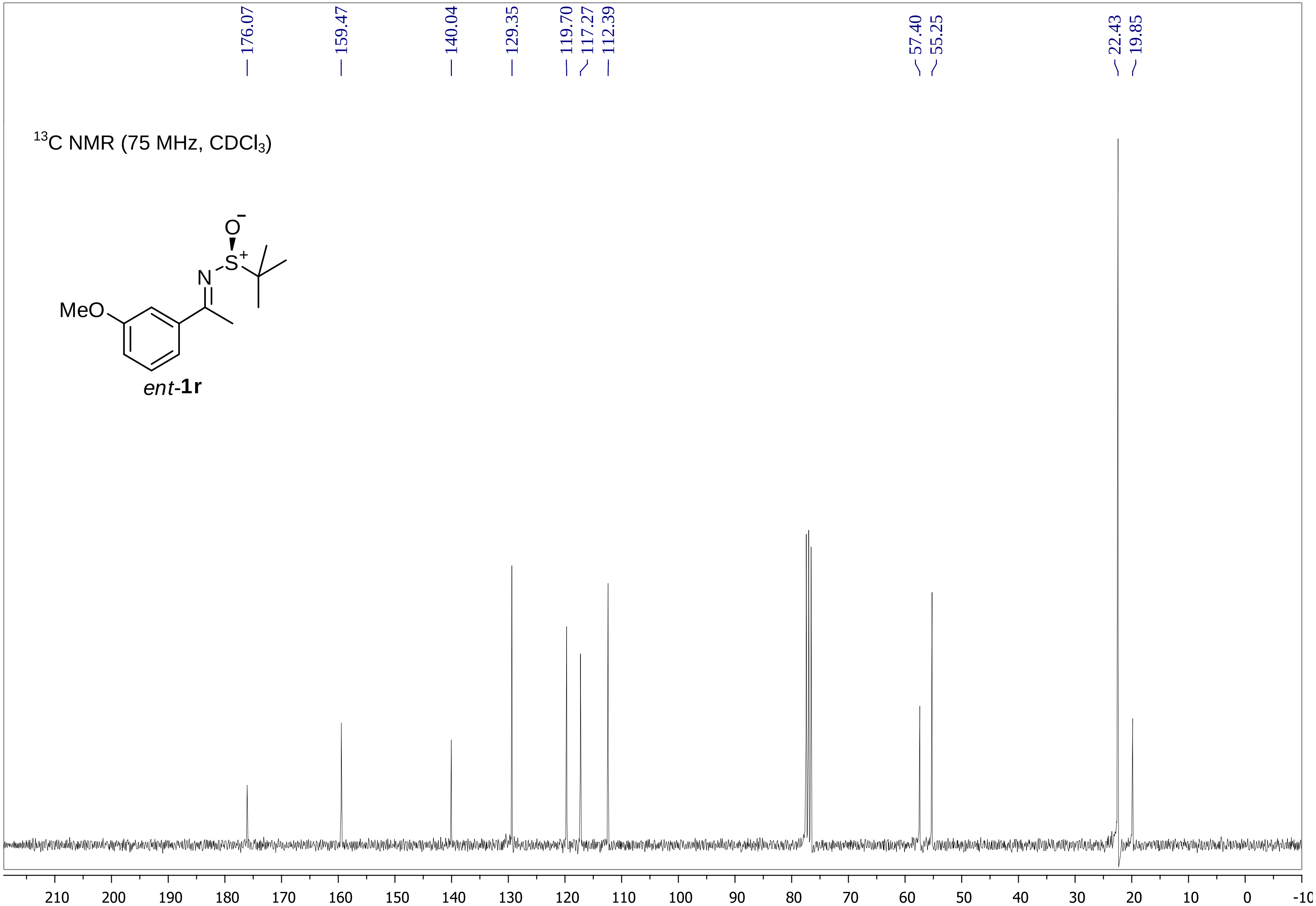


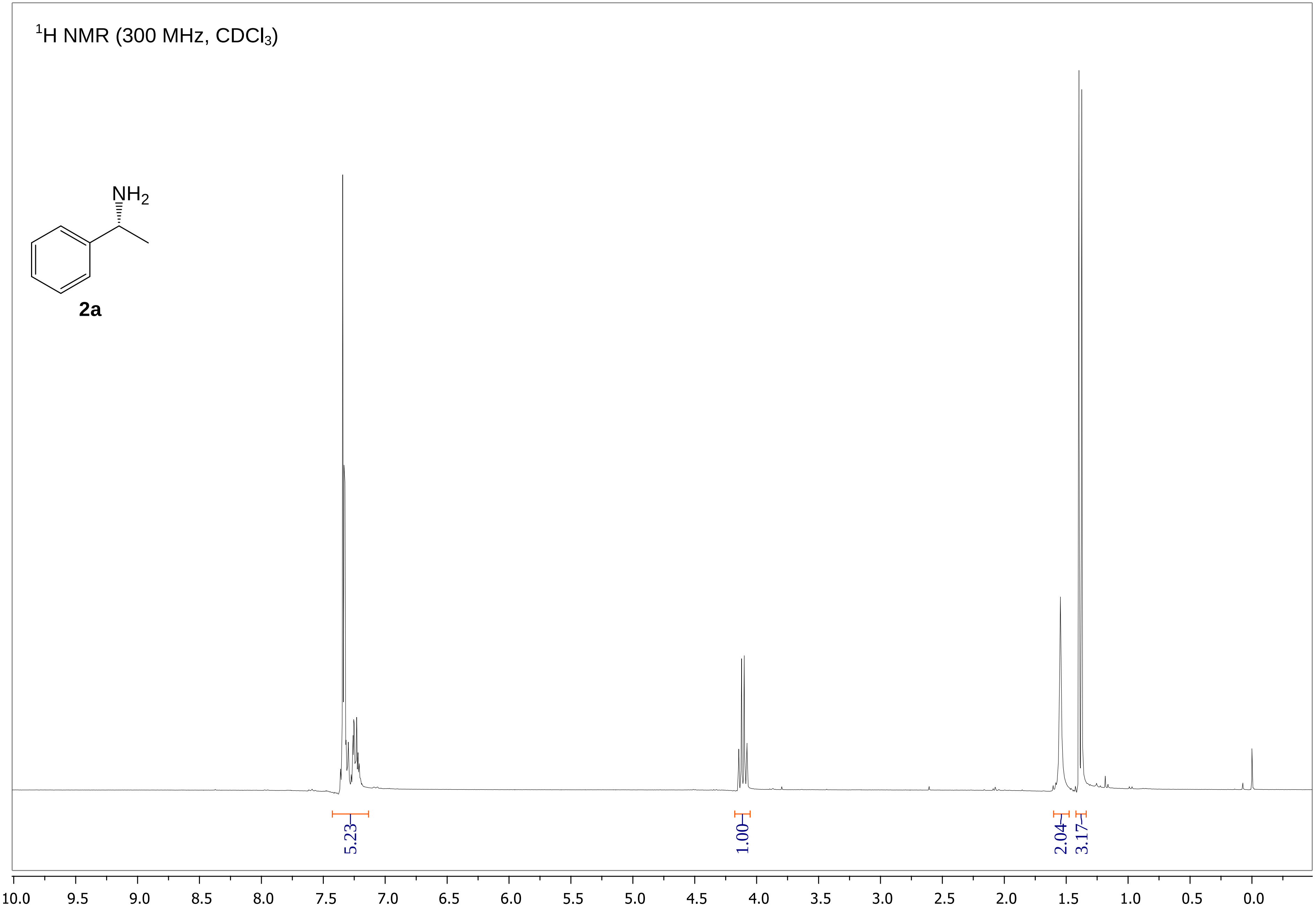
^{1}H NMR (300 MHz, $CDCl_3$)
O
S
N
1q
4.00
5.25
14.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

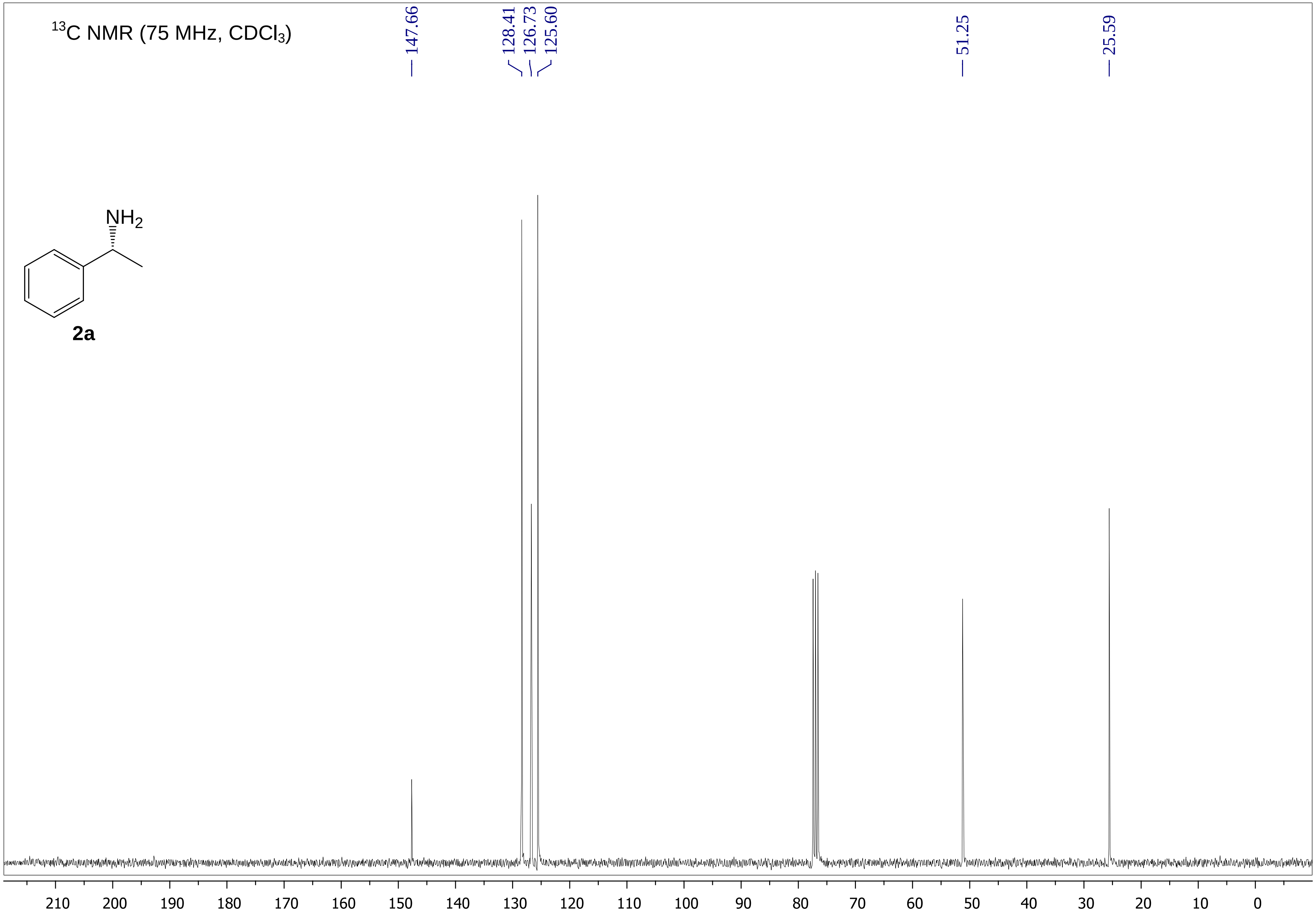

188.39
56.30
51.14
30.06
29.87
25.84
22.09
21.41
13C NMR (75 MHz, CDCl3)
1q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



^{1}H NMR (300 MHz, CDCl$_3$)
MeO
N
S
O
ent-1r
2.02
1.07
1.03
3.00
3.05
9.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

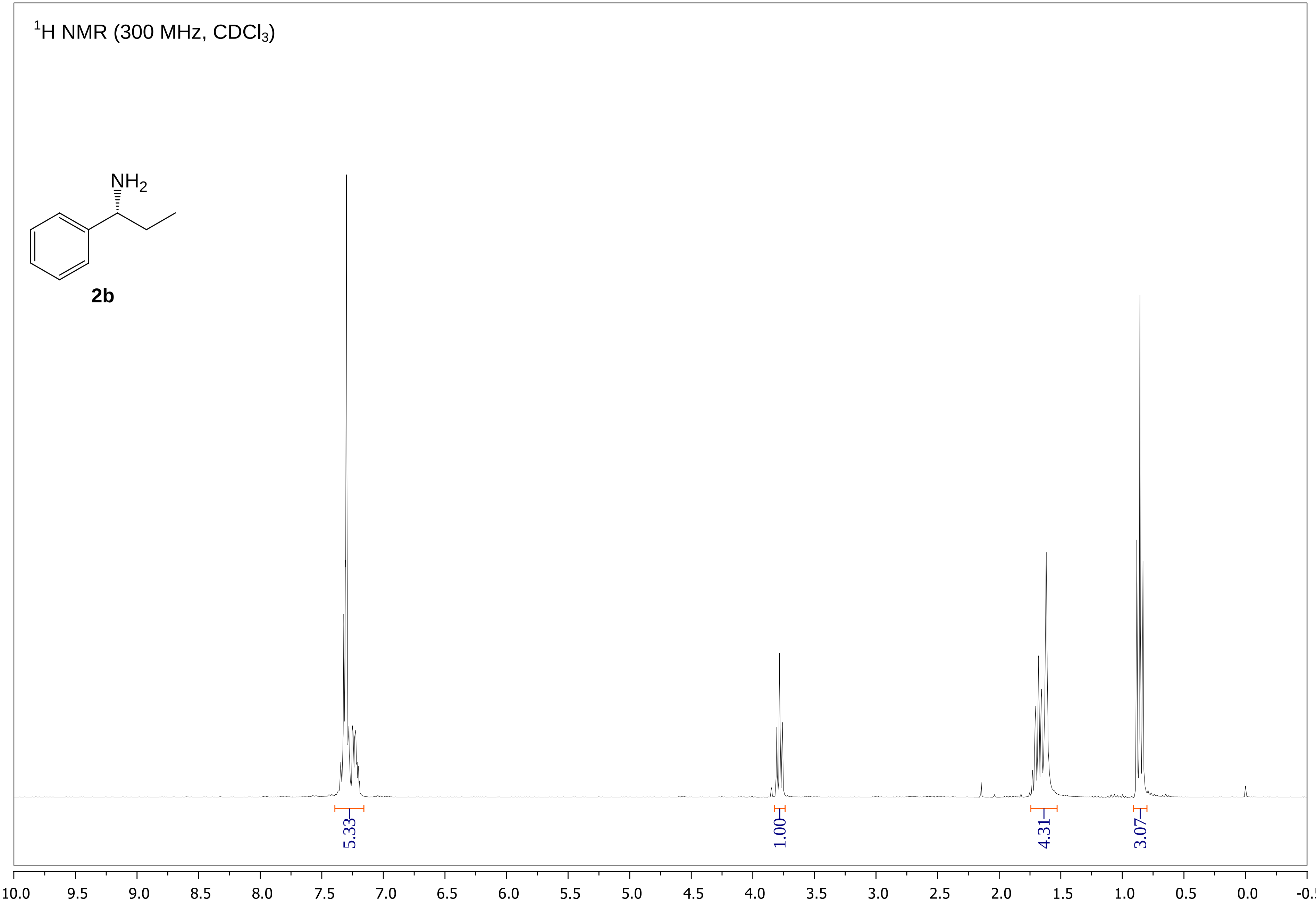

176.07
159.47
140.04
129.35
119.70
117.27
112.39
57.40
55.25
22.43
19.85
13C NMR (75 MHz, CDCl3)
MeO
N
S+
O−
ent-1r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


1H NMR (300 MHz, CDCl3)
NH2
2a
5.23
1.00
2.04
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

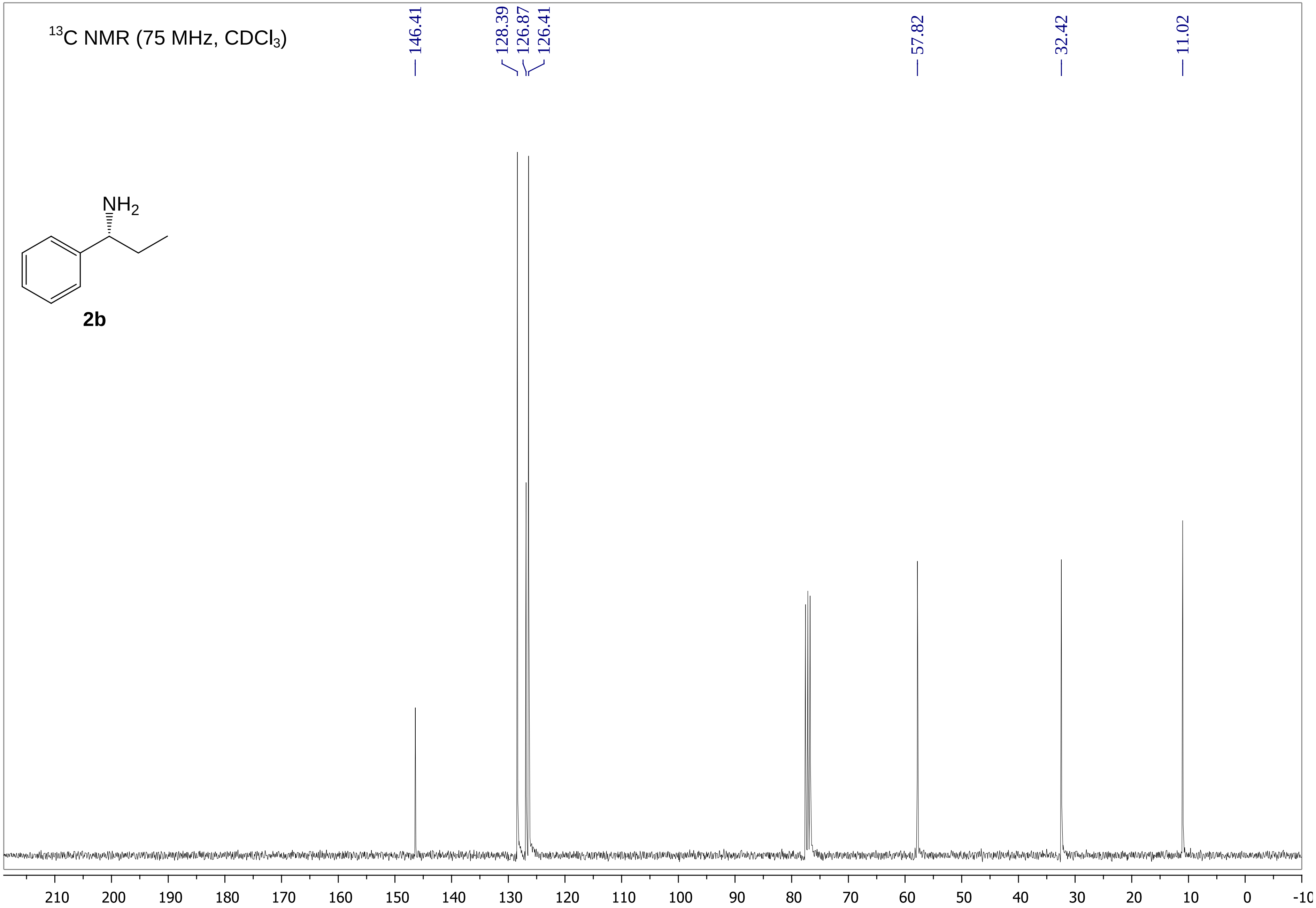


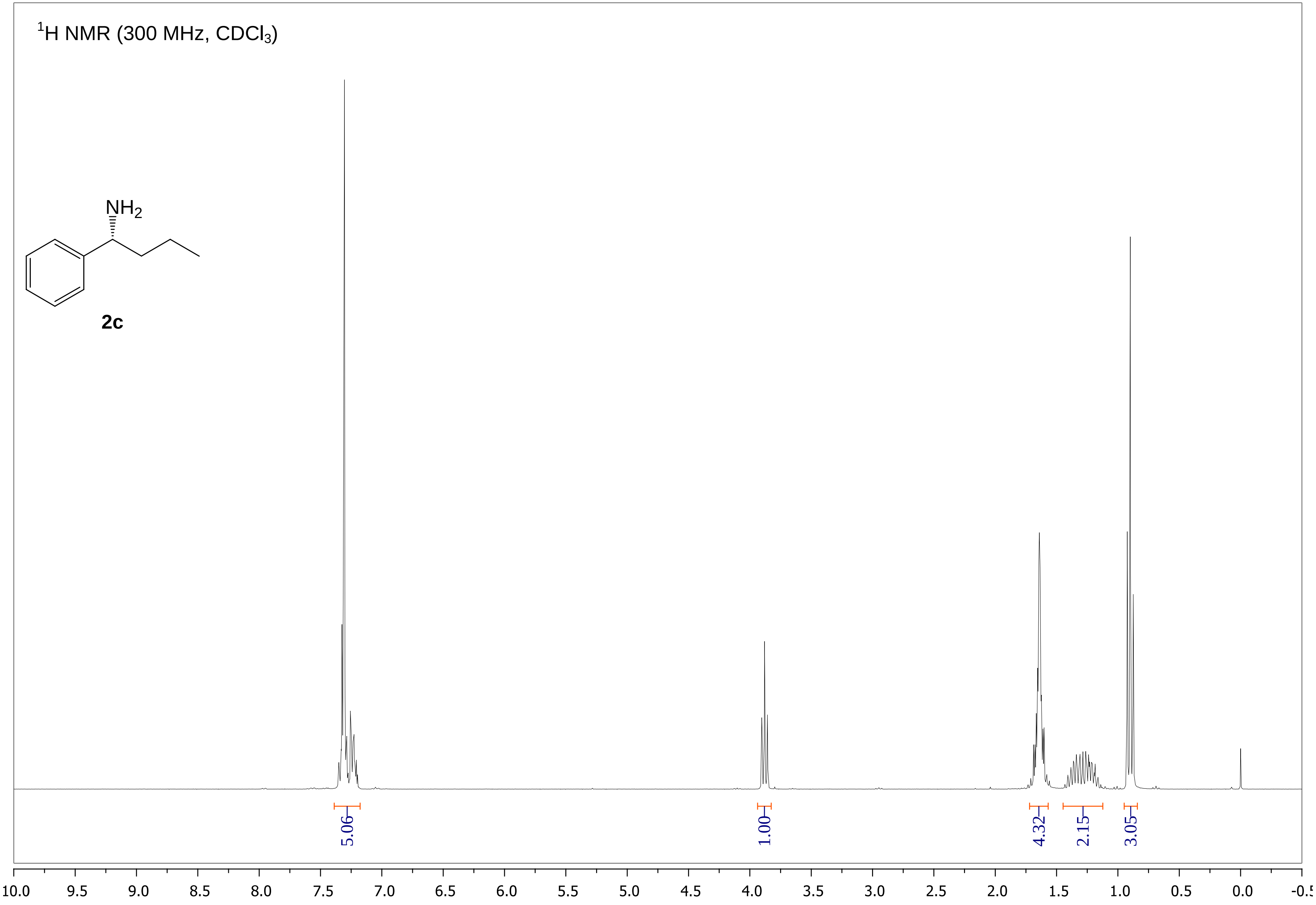
^{13}C NMR (75 MHz, $CDCl_3$)
147.66
128.41
126.73
125.60
51.25
25.59
NH_2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2a

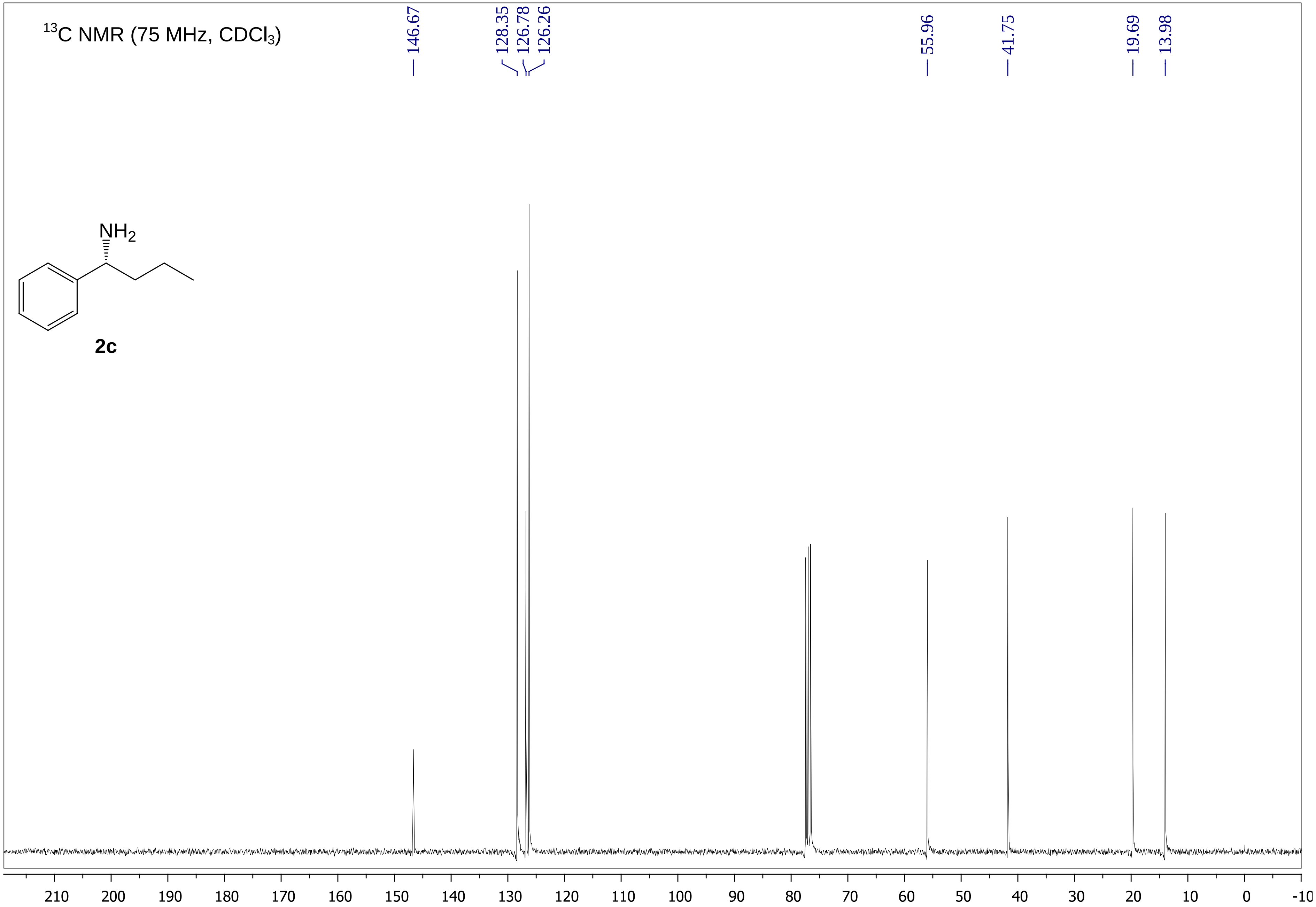


^{1}H NMR (300 MHz, $CDCl_3$)
NH_2
2b
5.33
1.00
4.31
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

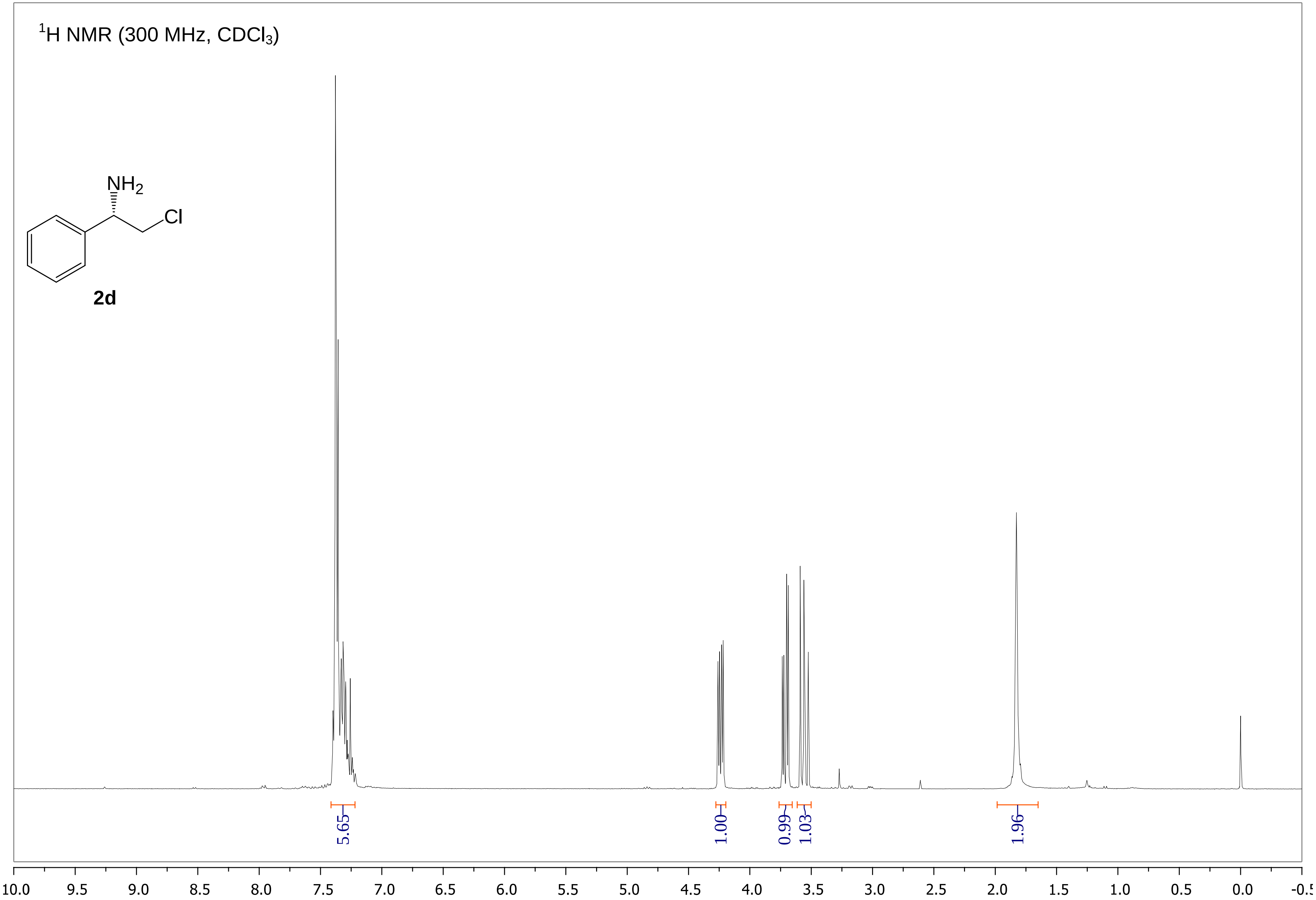

13C NMR (75 MHz, CDCl3)
146.41
128.39
126.87
126.41
57.82
32.42
11.02
NH2
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

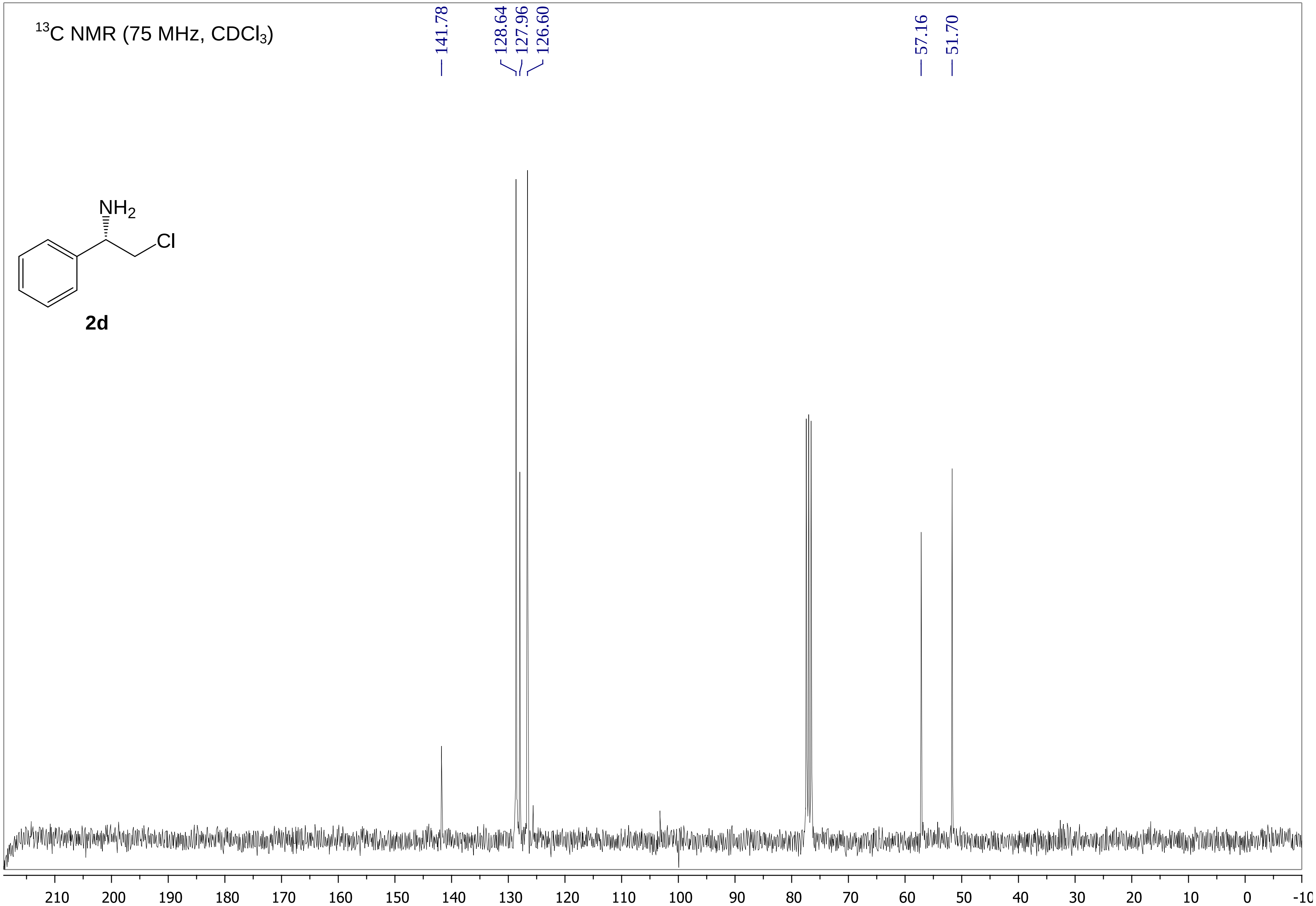


1H NMR (300 MHz, CDCl3)
NH2
2c
5.06
1.00
4.32
2.15
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

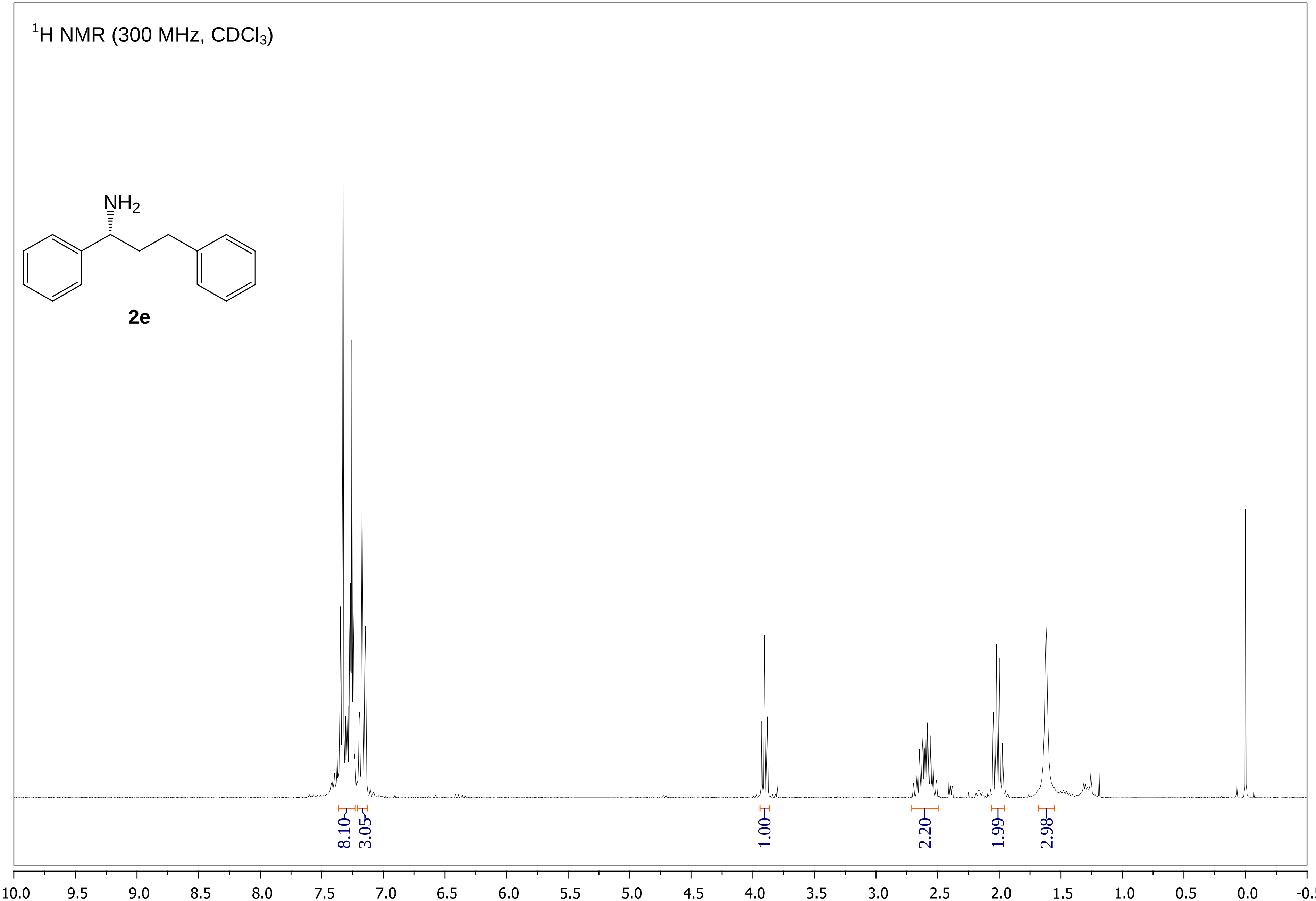


13C NMR (75 MHz, CDCl3)
146.67
128.35
126.78
126.26
55.96
41.75
19.69
13.98
NH2
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

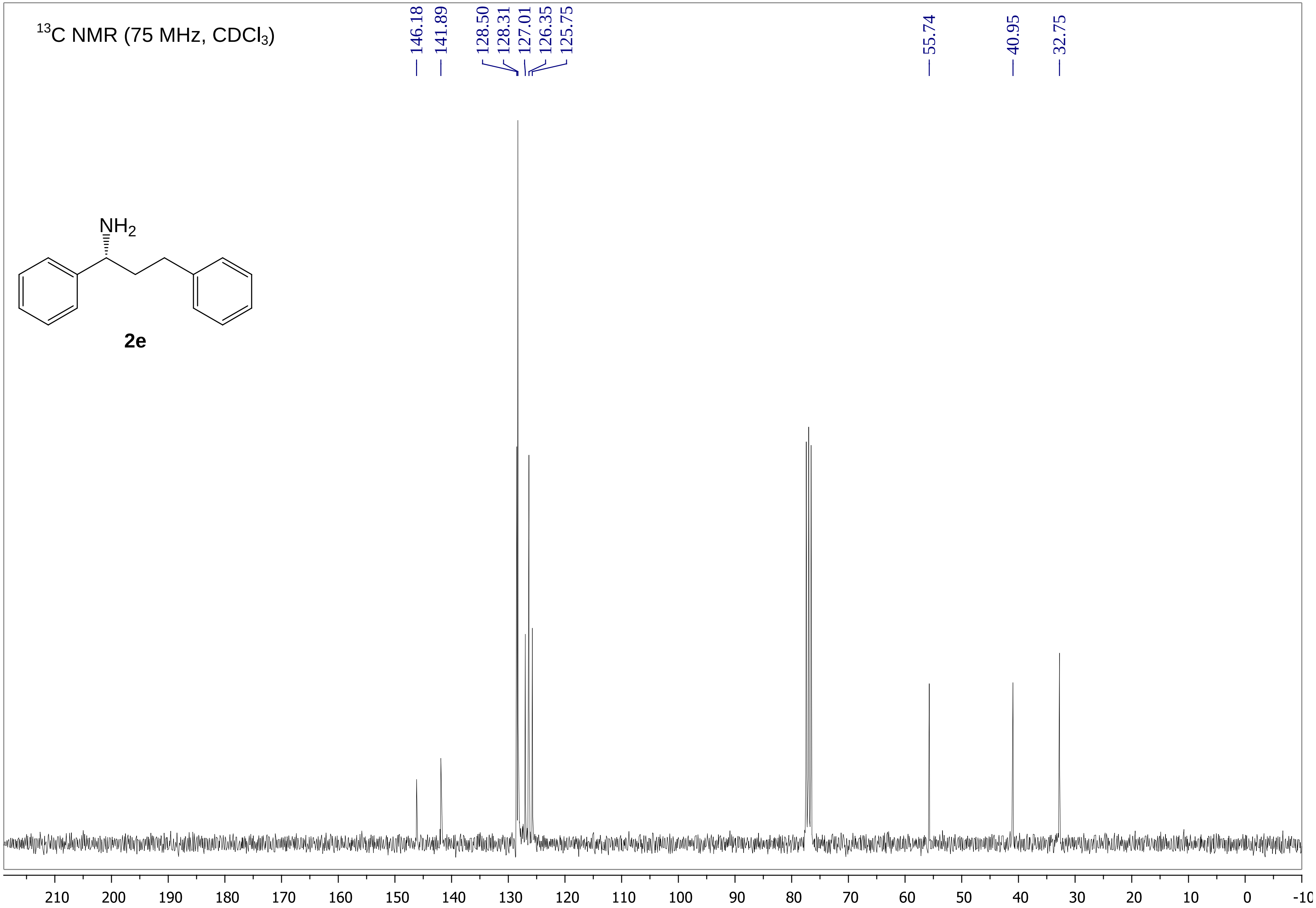

1H NMR (300 MHz, CDCl3)
NH2
Cl
2d
5.65
1.00
0.99
1.03
1.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



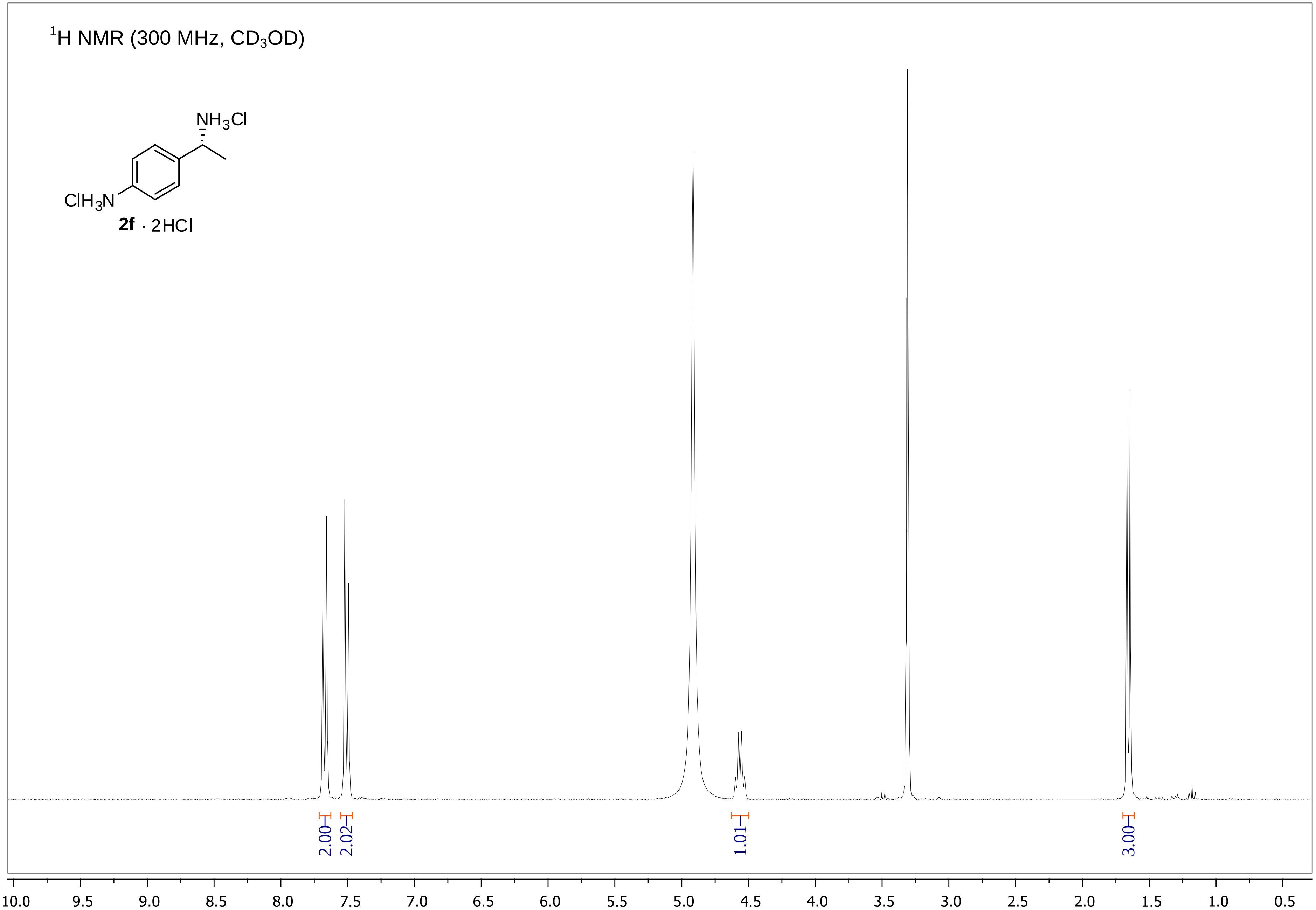
13C NMR (75 MHz, CDCl3)
141.78
128.64
127.96
126.60
57.16
51.70
NH2
Cl
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

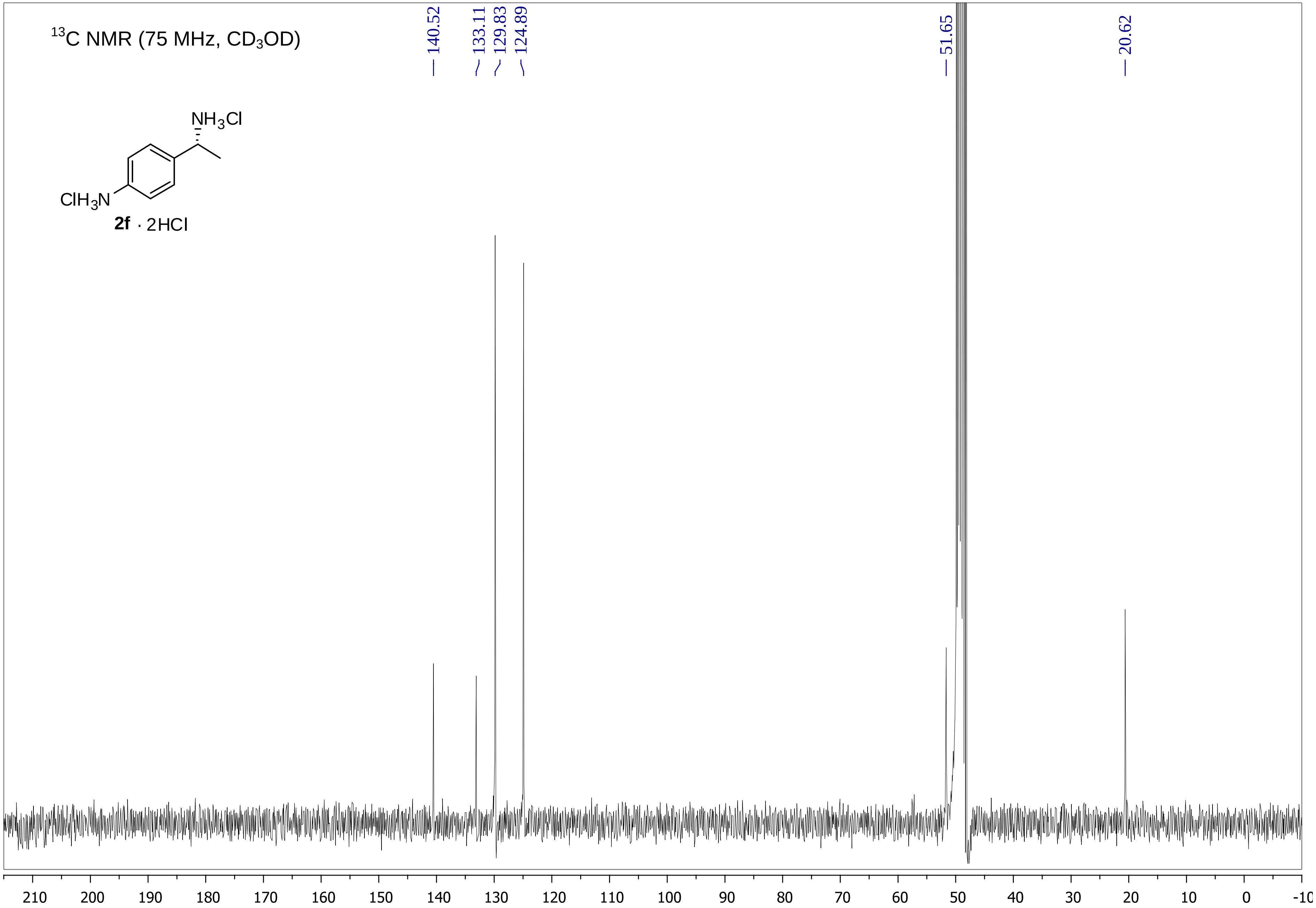


1H NMR (300 MHz, CDCl3)
NH2
2e
8.10
3.05
1.00
2.20
1.99
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

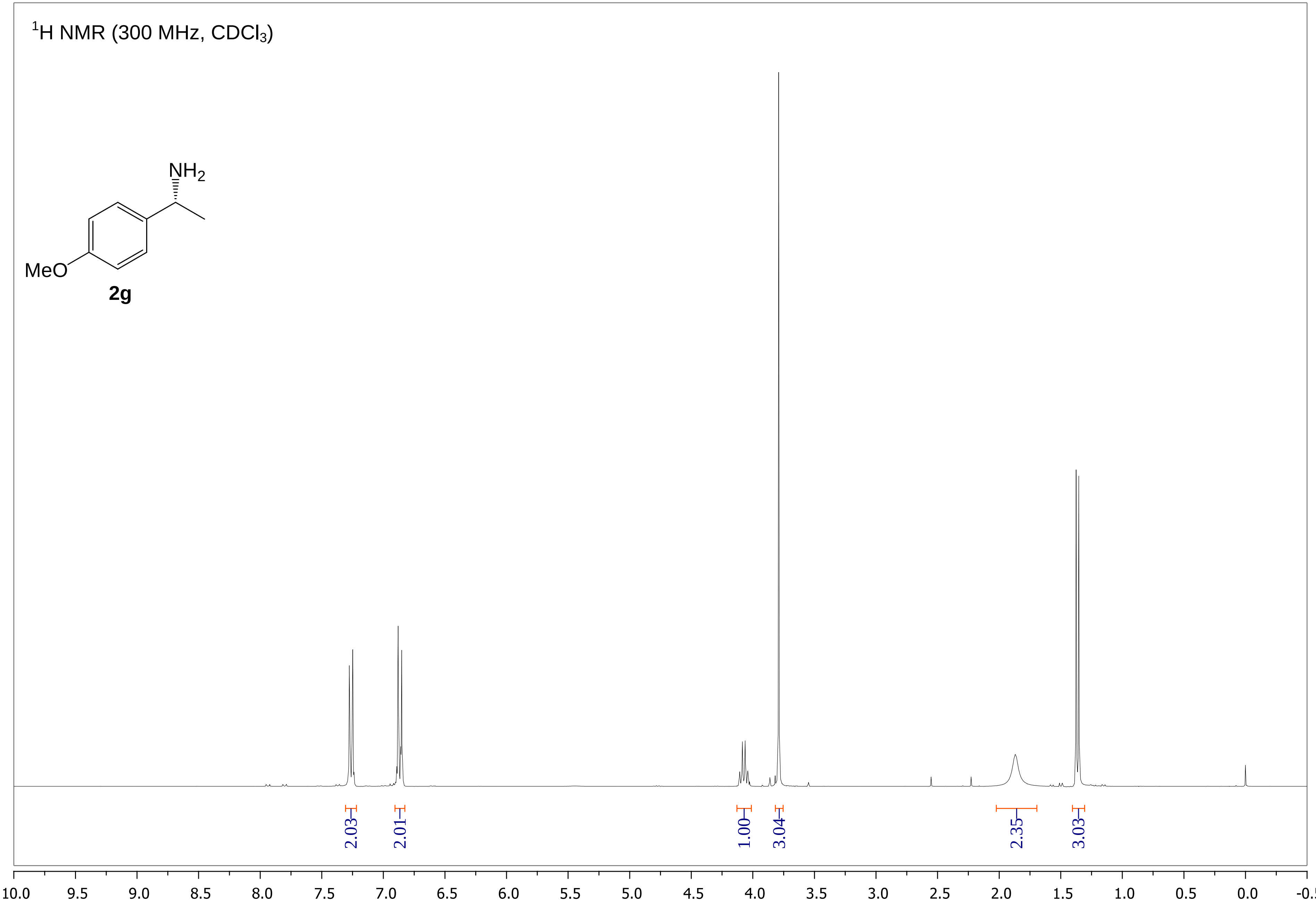


^{13}C NMR (75 MHz, $CDCl_3$)
NH_2
2e
146.18
141.89
128.50
128.31
127.01
126.35
125.75
55.74
40.95
32.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

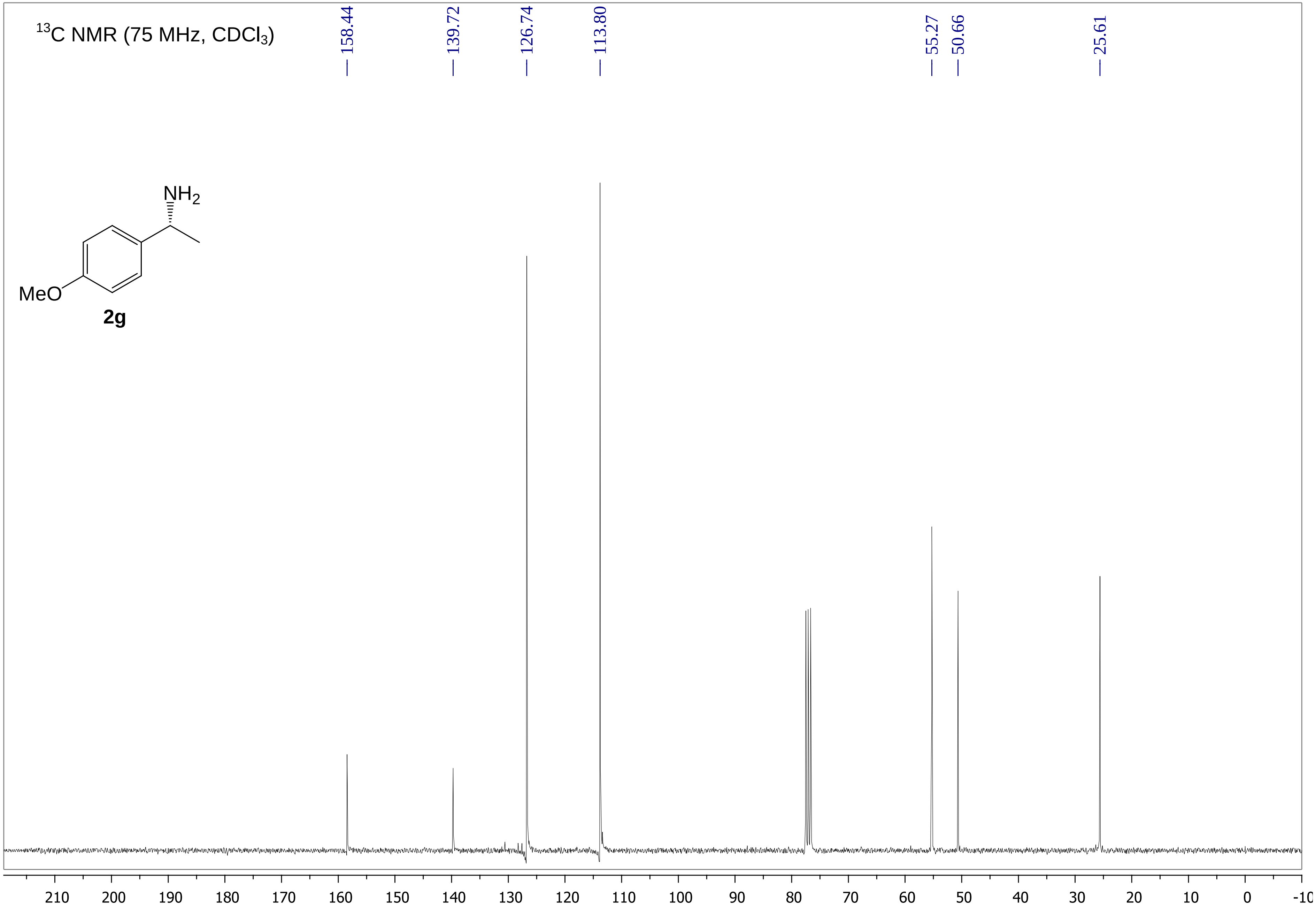

1H NMR (300 MHz, CD3OD)
NH3Cl
ClH3N
2f · 2HCl
2.00
2.02
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5



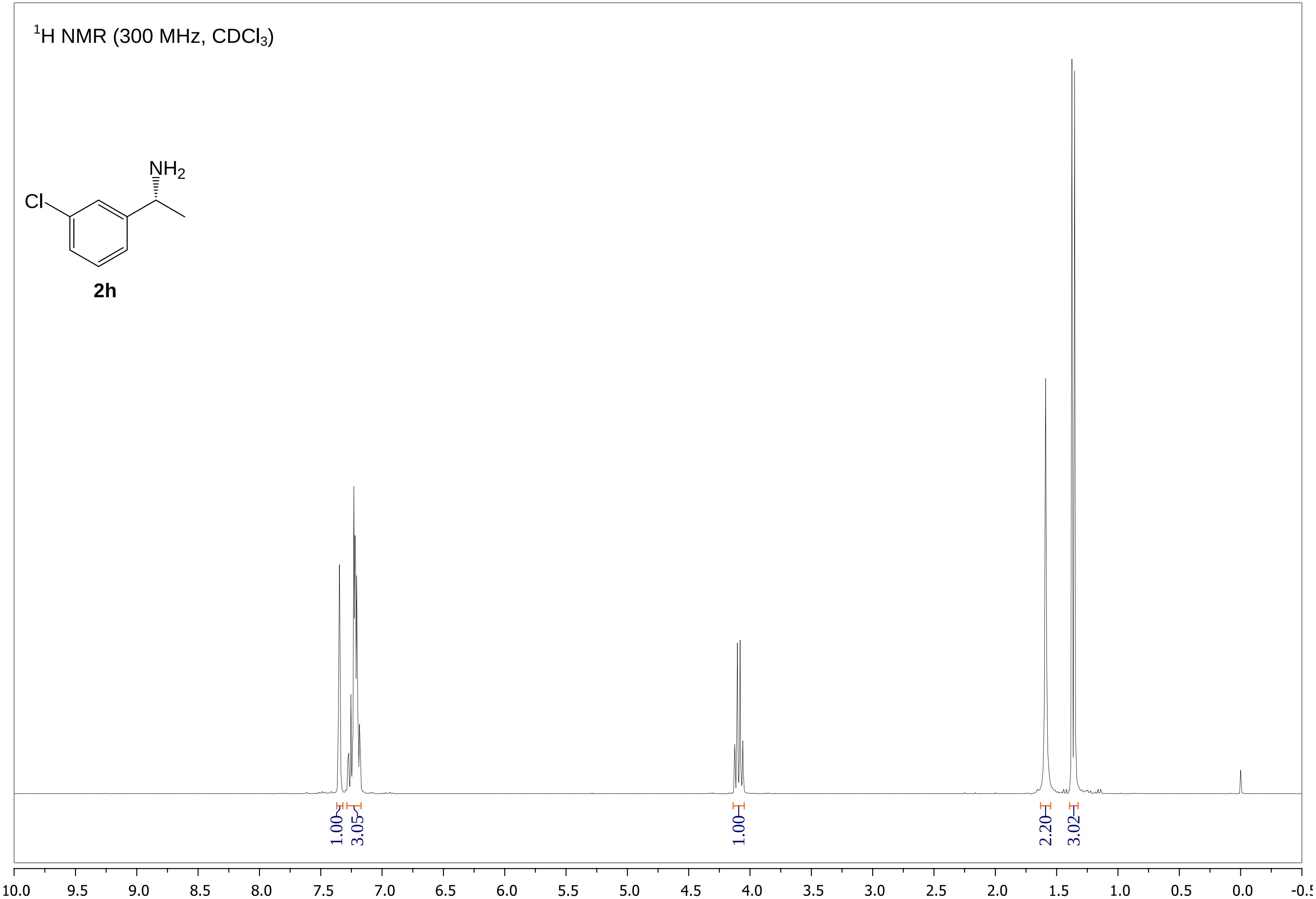
^{13}C NMR (75 MHz, CD_3OD)
140.52
133.11
129.83
124.89
51.65
20.62
NH_3Cl
ClH_3N
2f · 2HCl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



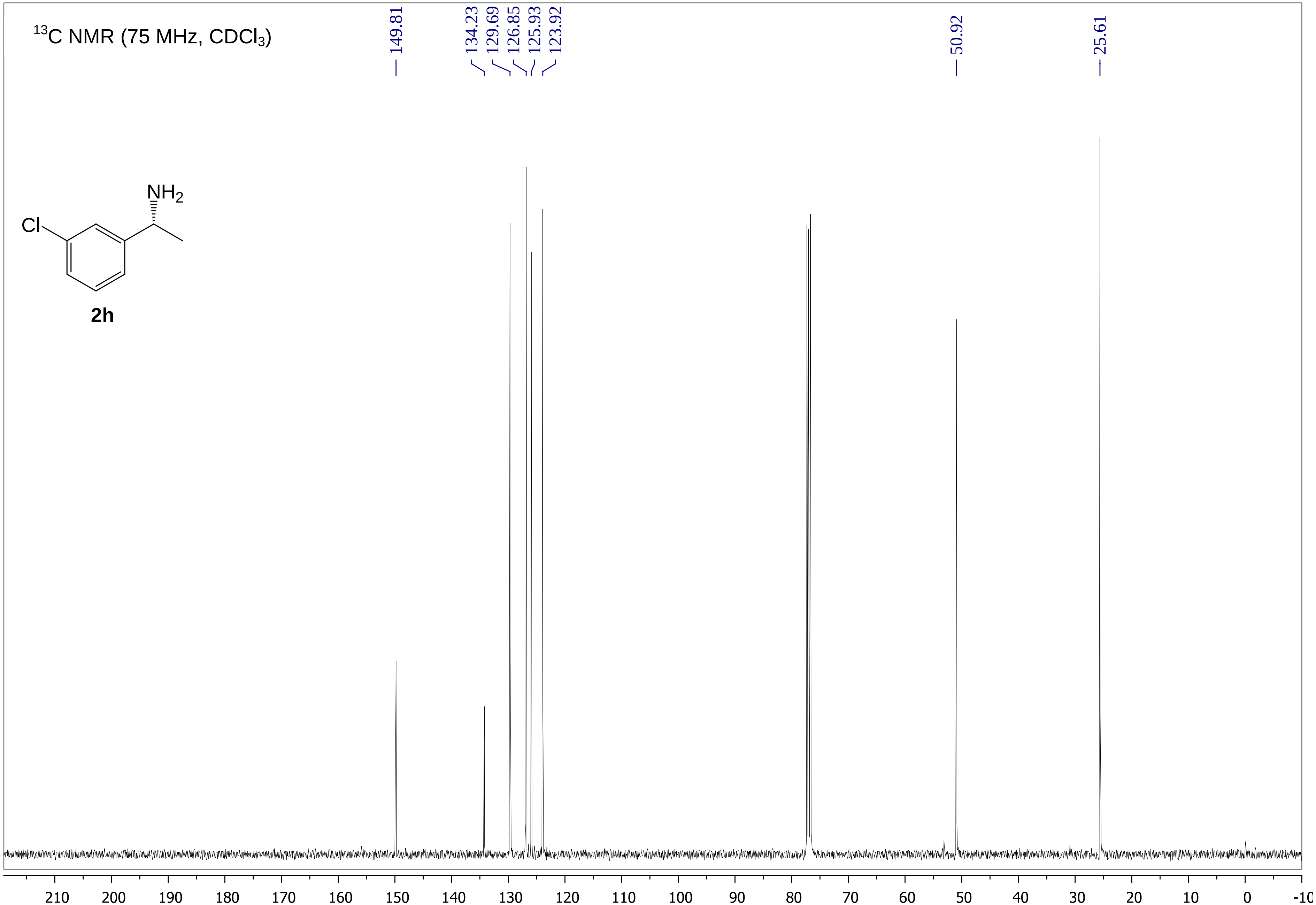
^{1}H NMR (300 MHz, CDCl$_3$)
NH$_2$
MeO
2g
2.03
2.01
1.00
3.04
2.35
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



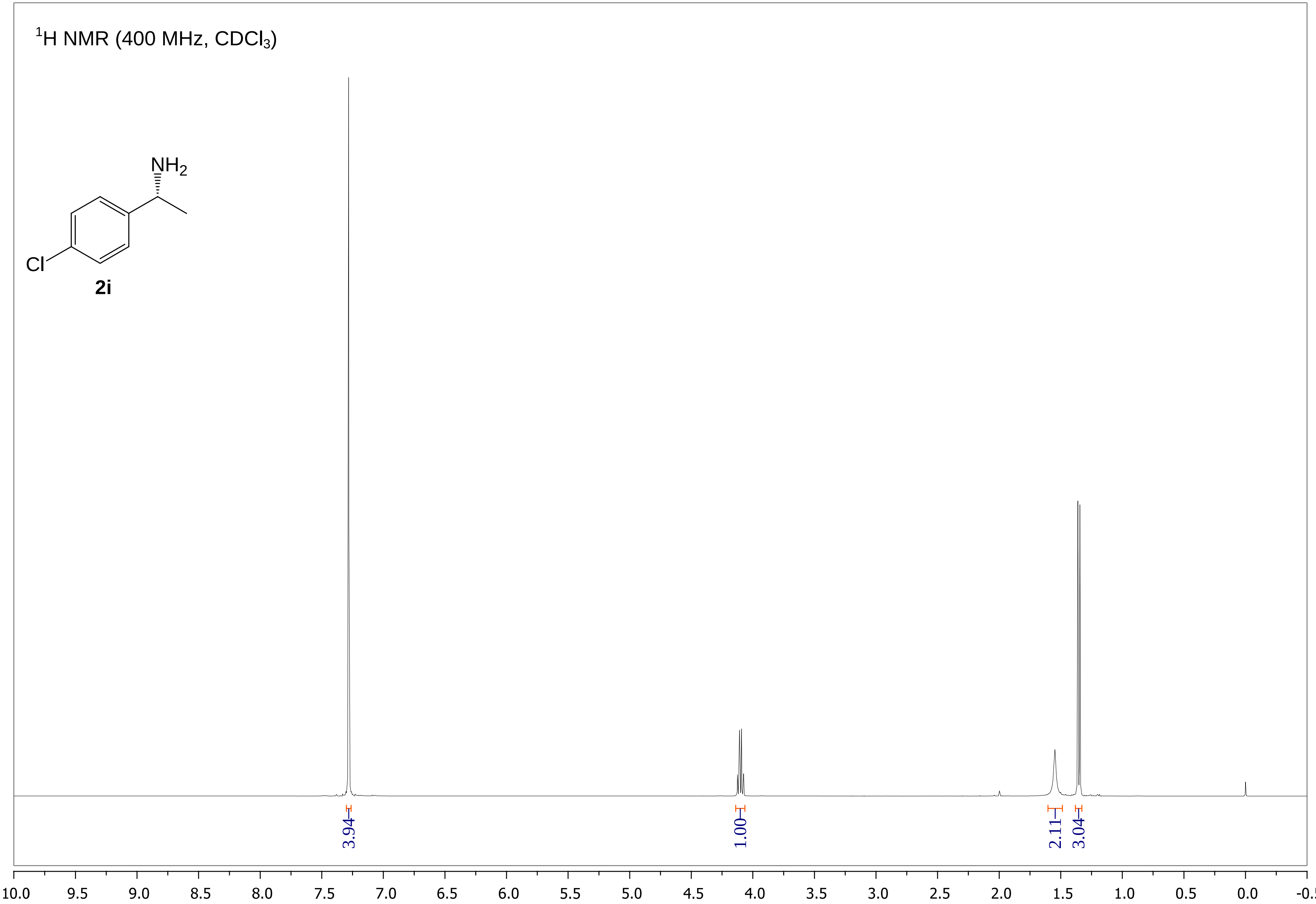
^{13}C NMR (75 MHz, CDCl$_3$)
158.44
139.72
126.74
113.80
55.27
50.66
25.61
NH2
MeO
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



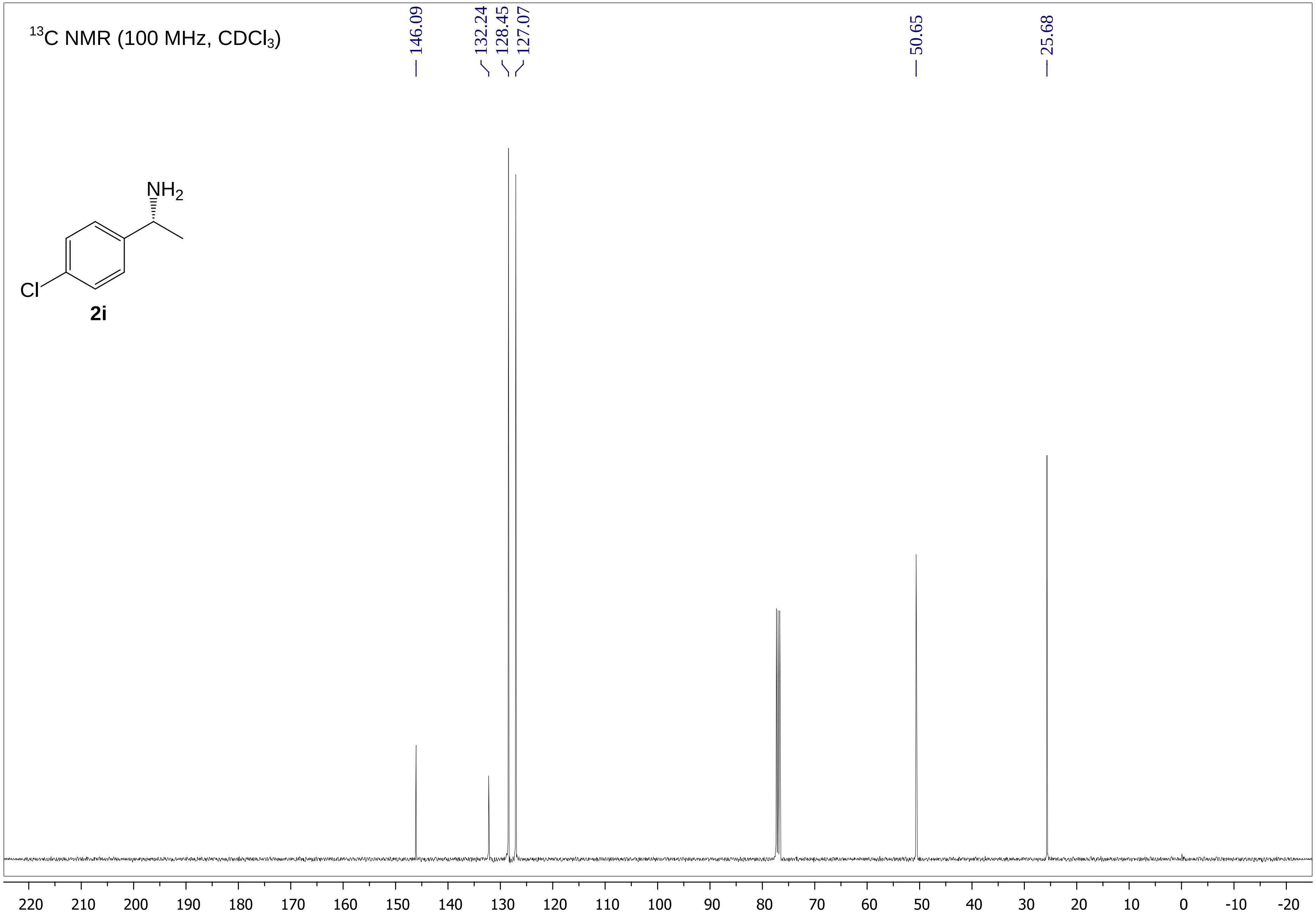
1H NMR (300 MHz, CDCl3)
NH2
Cl
2h
1.00
3.05
1.00
2.20
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



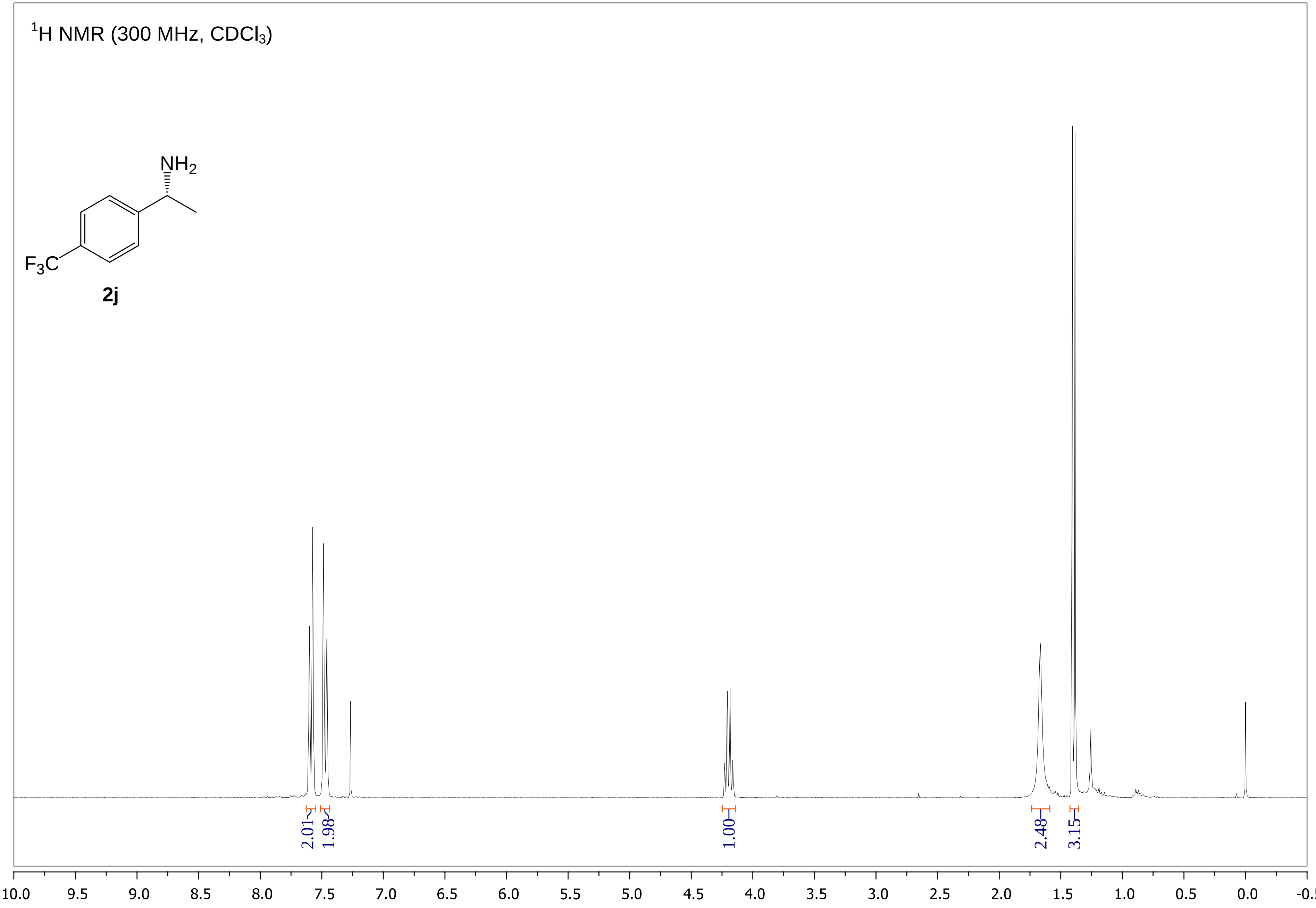
^{13}C NMR (75 MHz, $CDCl_3$)
149.81
134.23
129.69
126.85
125.93
123.92
50.92
25.61
NH_2
Cl
2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



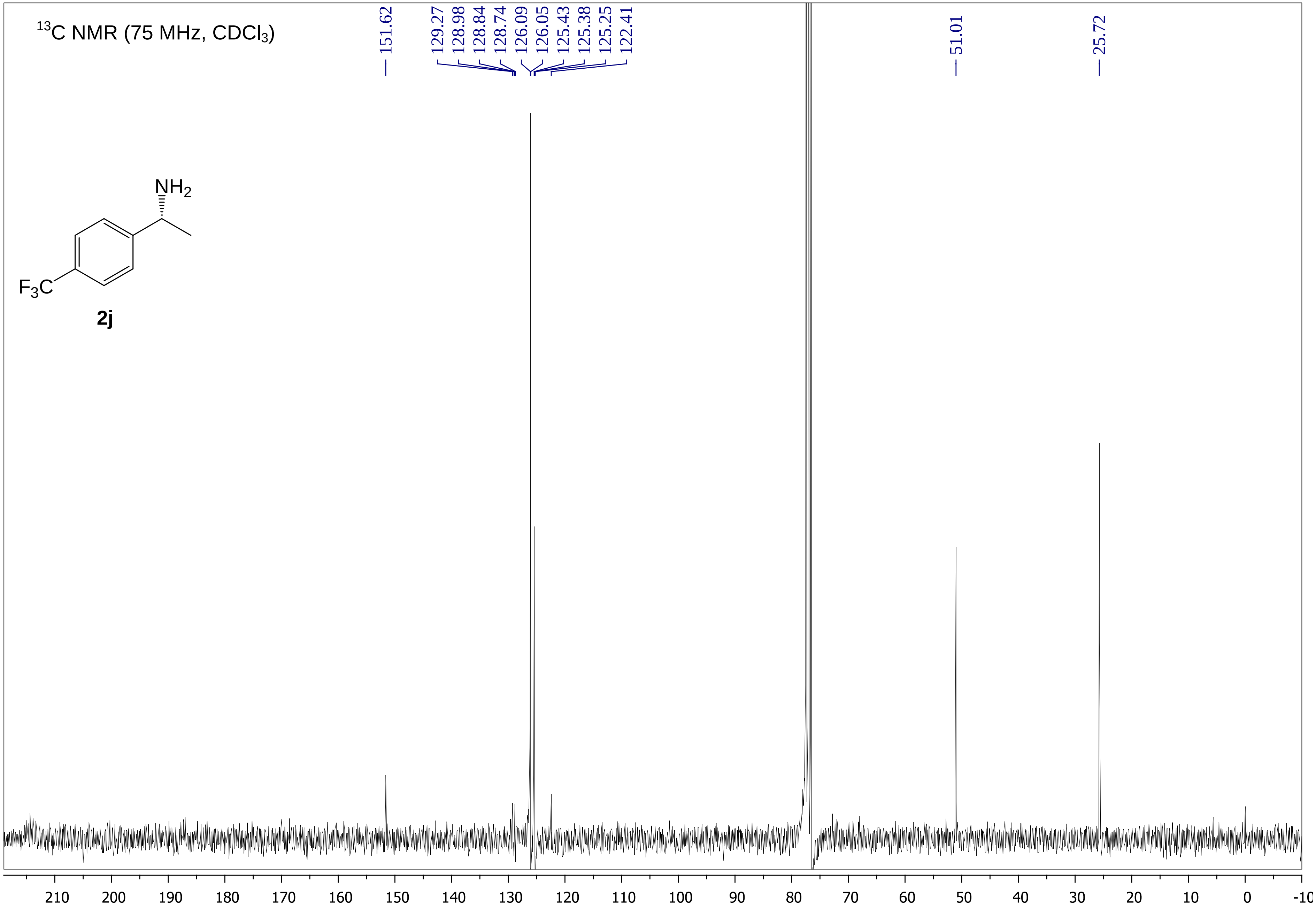
^{1}H NMR (400 MHz, CDCl$_3$)
NH$_2$
Cl
2i
3.94
1.00
2.11
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



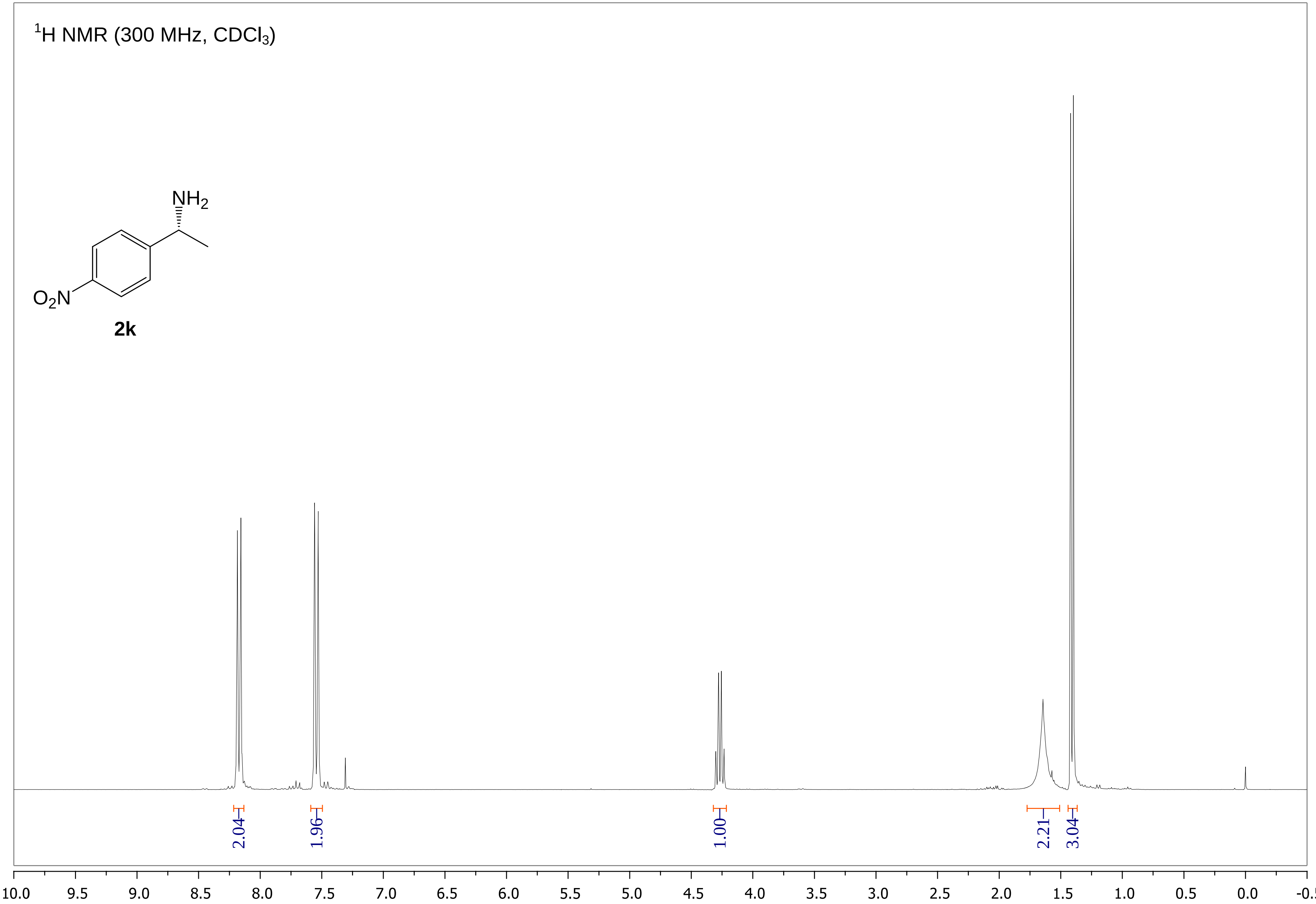
^{13}C NMR (100 MHz, $CDCl_3$)
146.09
132.24
128.45
127.07
50.65
25.68
NH_2
Cl
2i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20



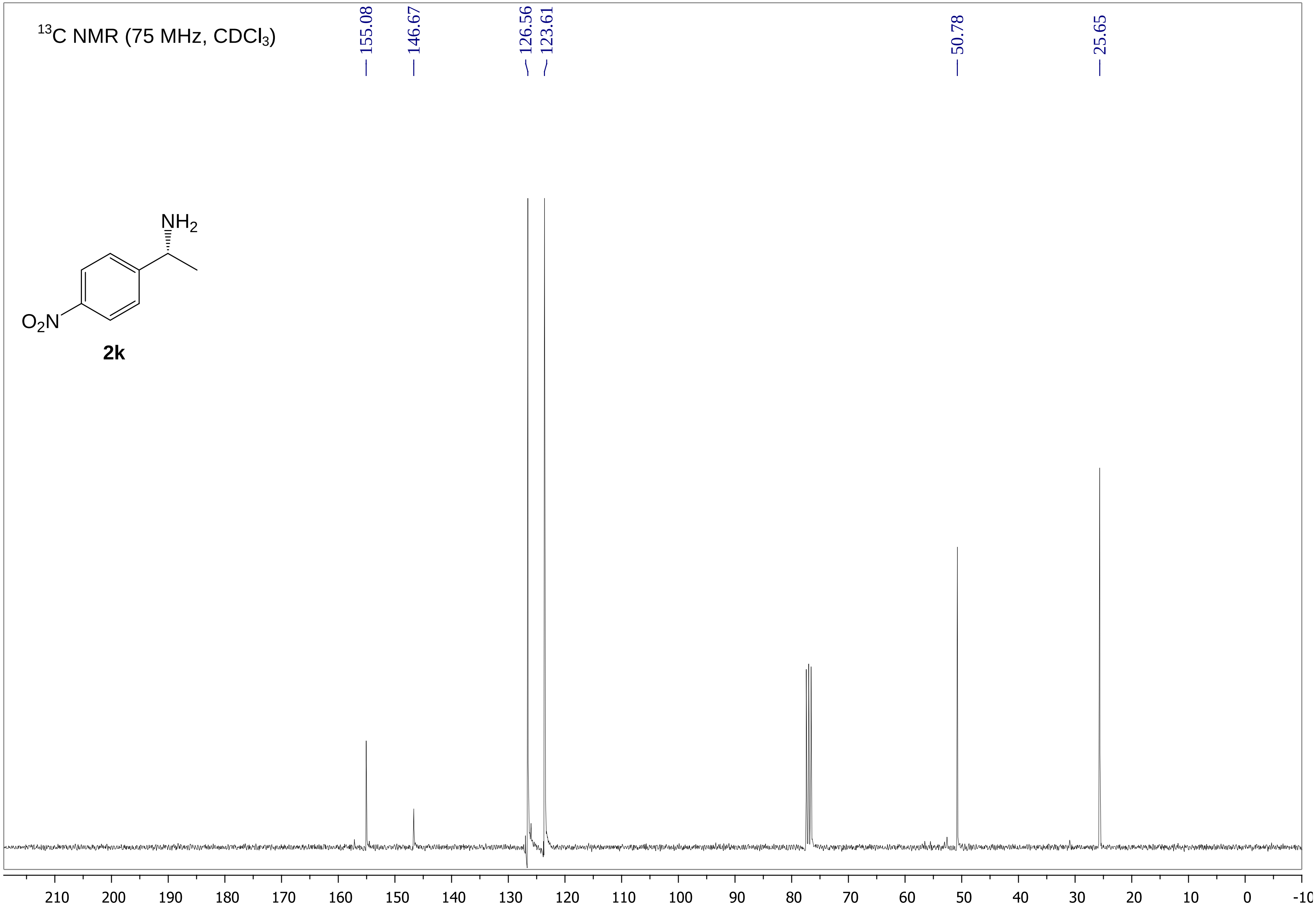
^{1}H NMR (300 MHz, CDCl$_3$)
NH$_2$
F$_3$C
2j
2.01
1.98
1.00
2.48
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



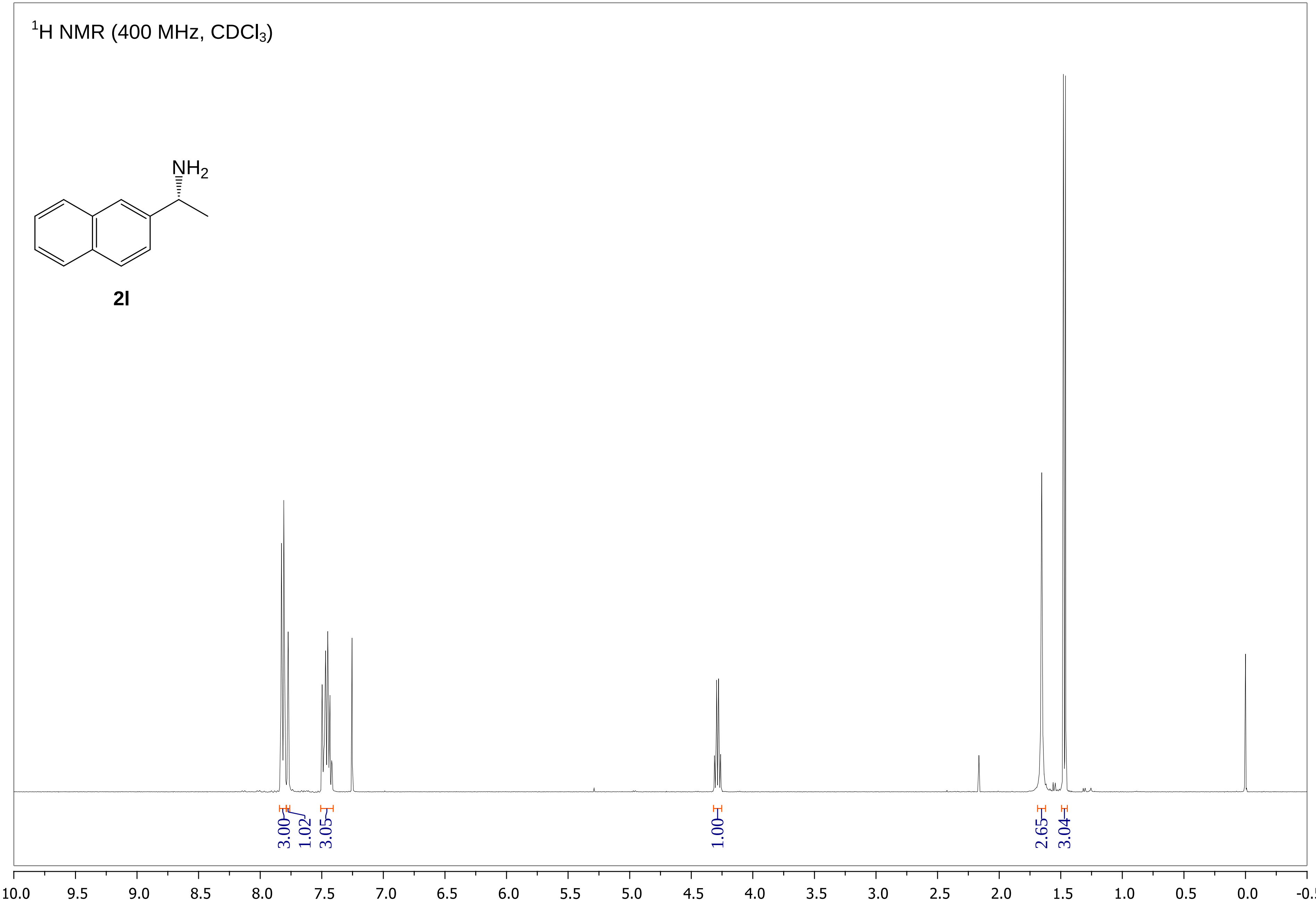
^{13}C NMR (75 MHz, $CDCl_3$)
151.62
129.27
128.98
128.84
128.74
126.09
126.05
125.43
125.38
125.25
122.41
51.01
25.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
NH_2
F_3C
2j



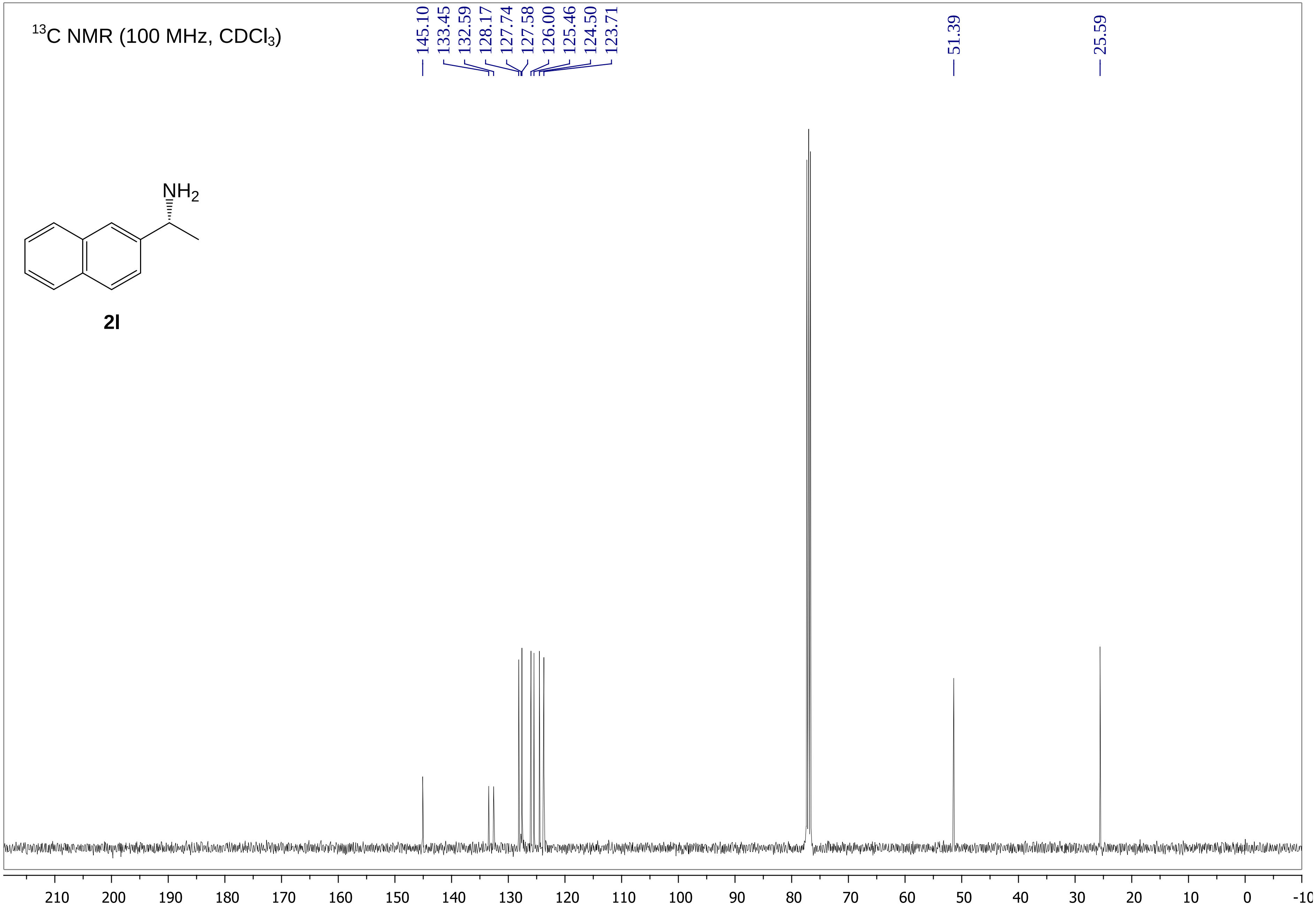
1H NMR (300 MHz, CDCl3)
NH2
O2N
2k
2.04
1.96
1.00
2.21
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



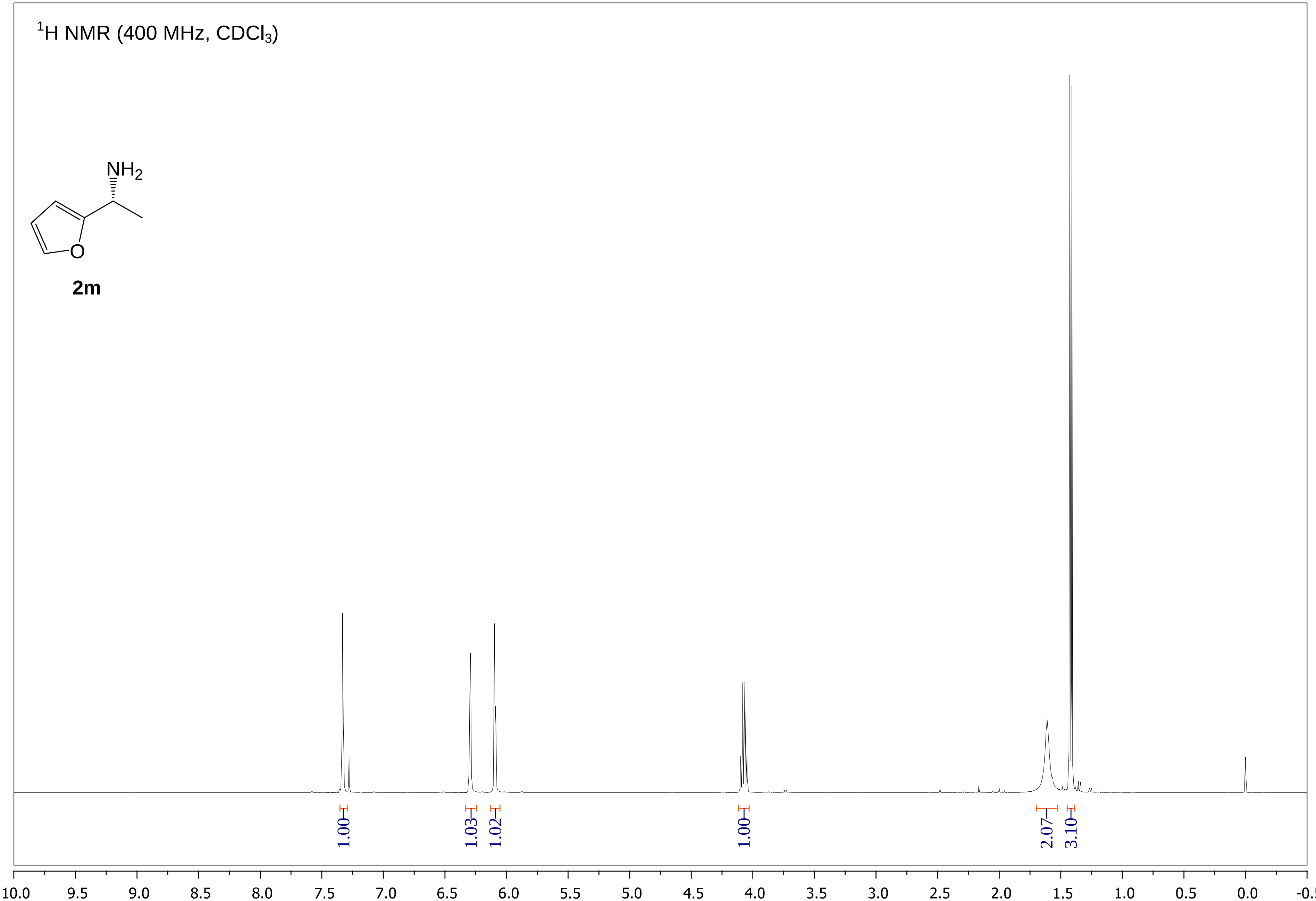
^{13}C NMR (75 MHz, $CDCl_3$)
155.08
146.67
126.56
123.61
50.78
25.65
NH_2
O_2N
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



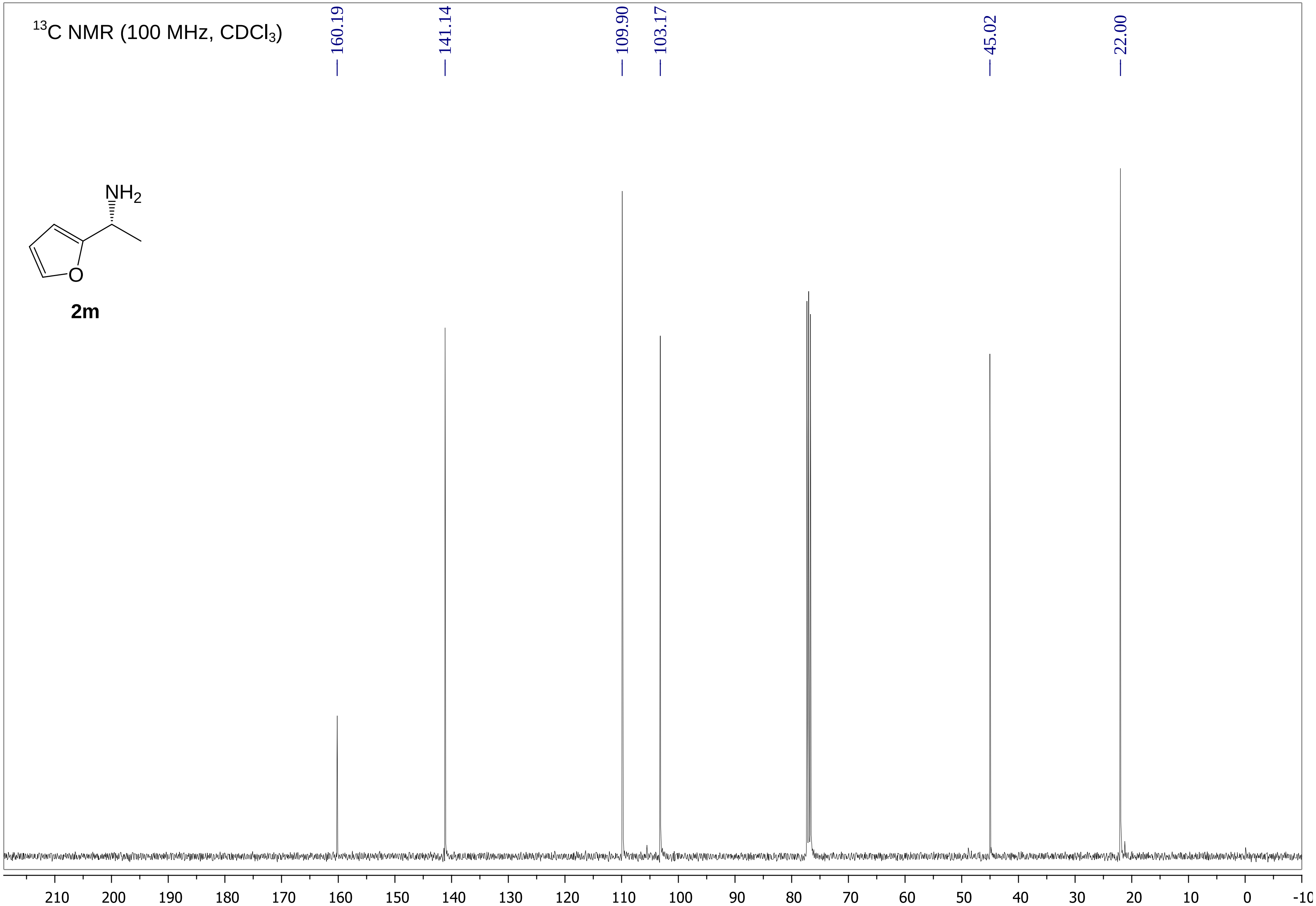
^{1}H NMR (400 MHz, $CDCl_3$)
NH_2
2l
3.00
1.02
3.05
1.00
2.65
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



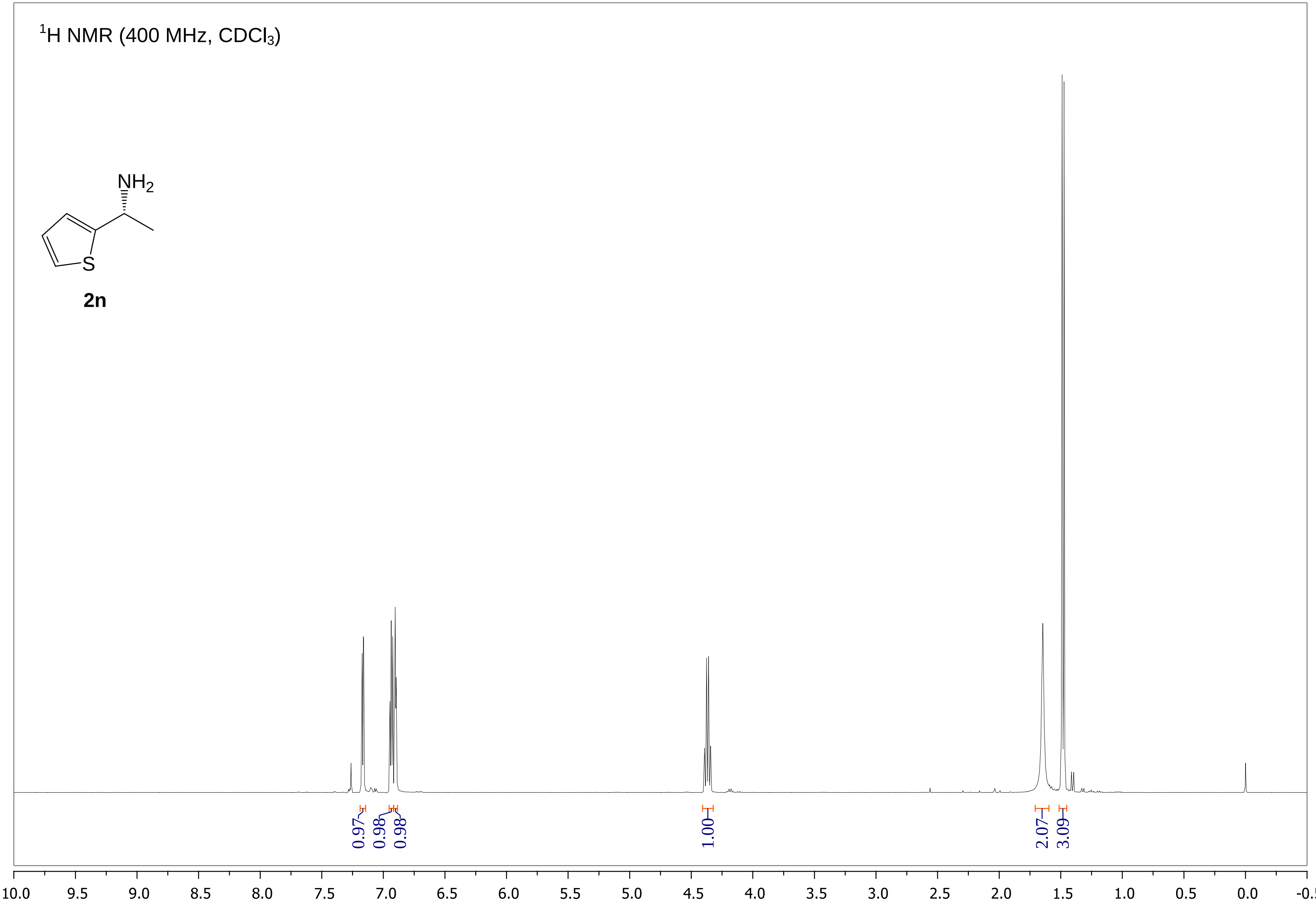
^{13}C NMR (100 MHz, CDCl$_3$)
145.10
133.45
132.59
128.17
127.74
127.58
126.00
125.46
124.50
123.71
51.39
25.59
NH$_2$
2l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

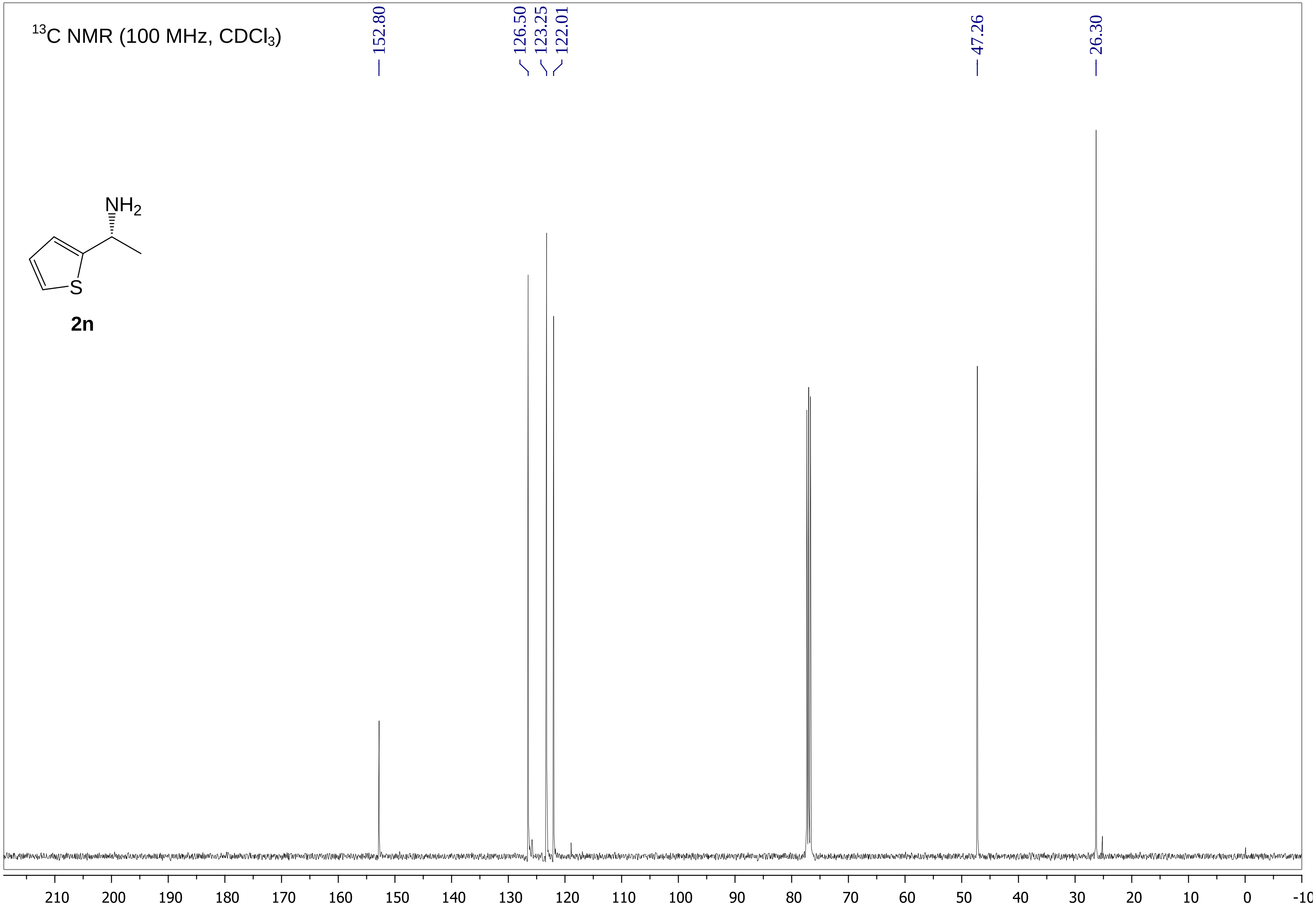


1H NMR (400 MHz, CDCl3)
NH2
O
2m
1.00
1.03
1.02
1.00
2.07
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

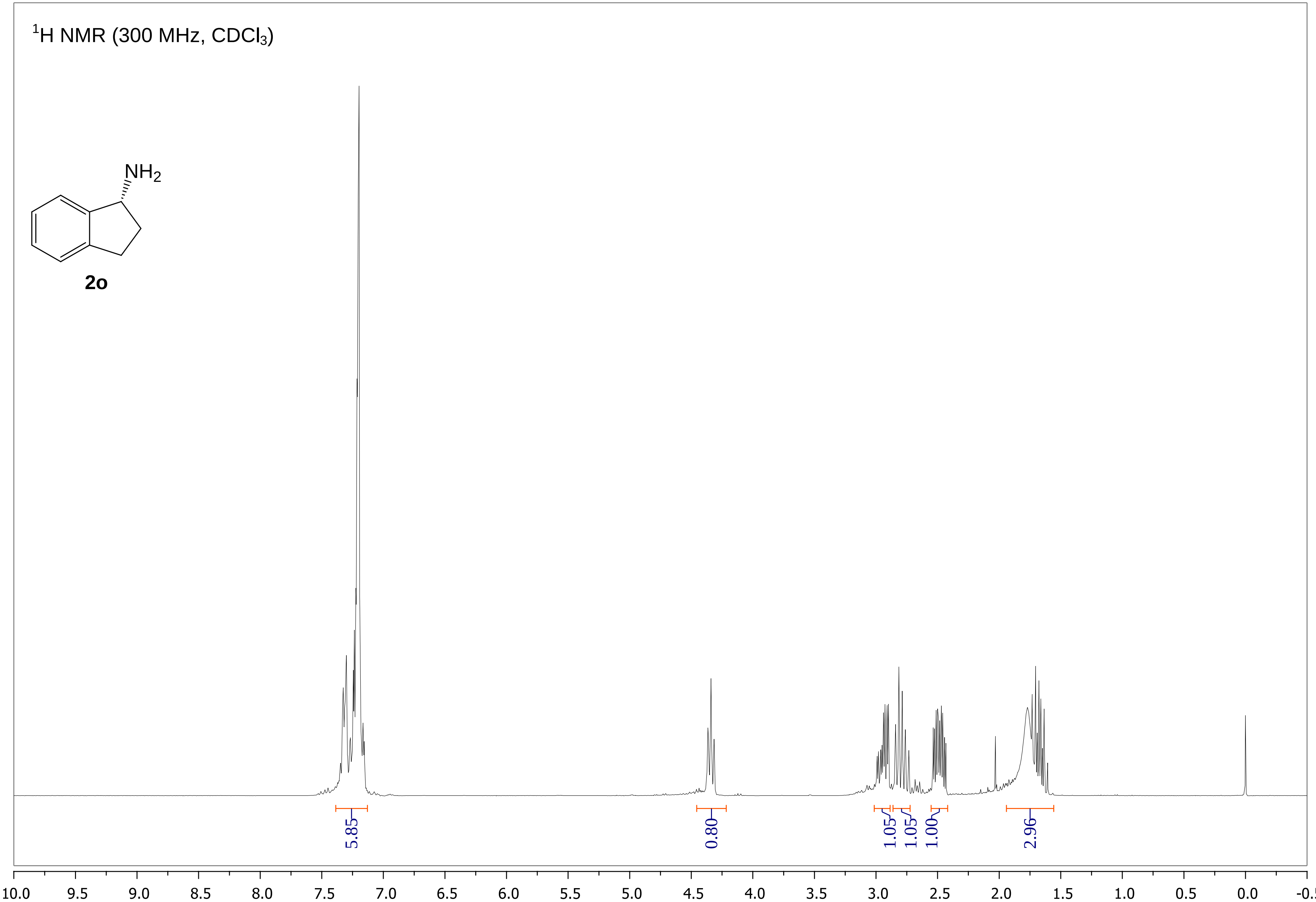


^{13}C NMR (100 MHz, $CDCl_3$)
160.19
141.14
109.90
103.17
45.02
22.00
NH_2
O
2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

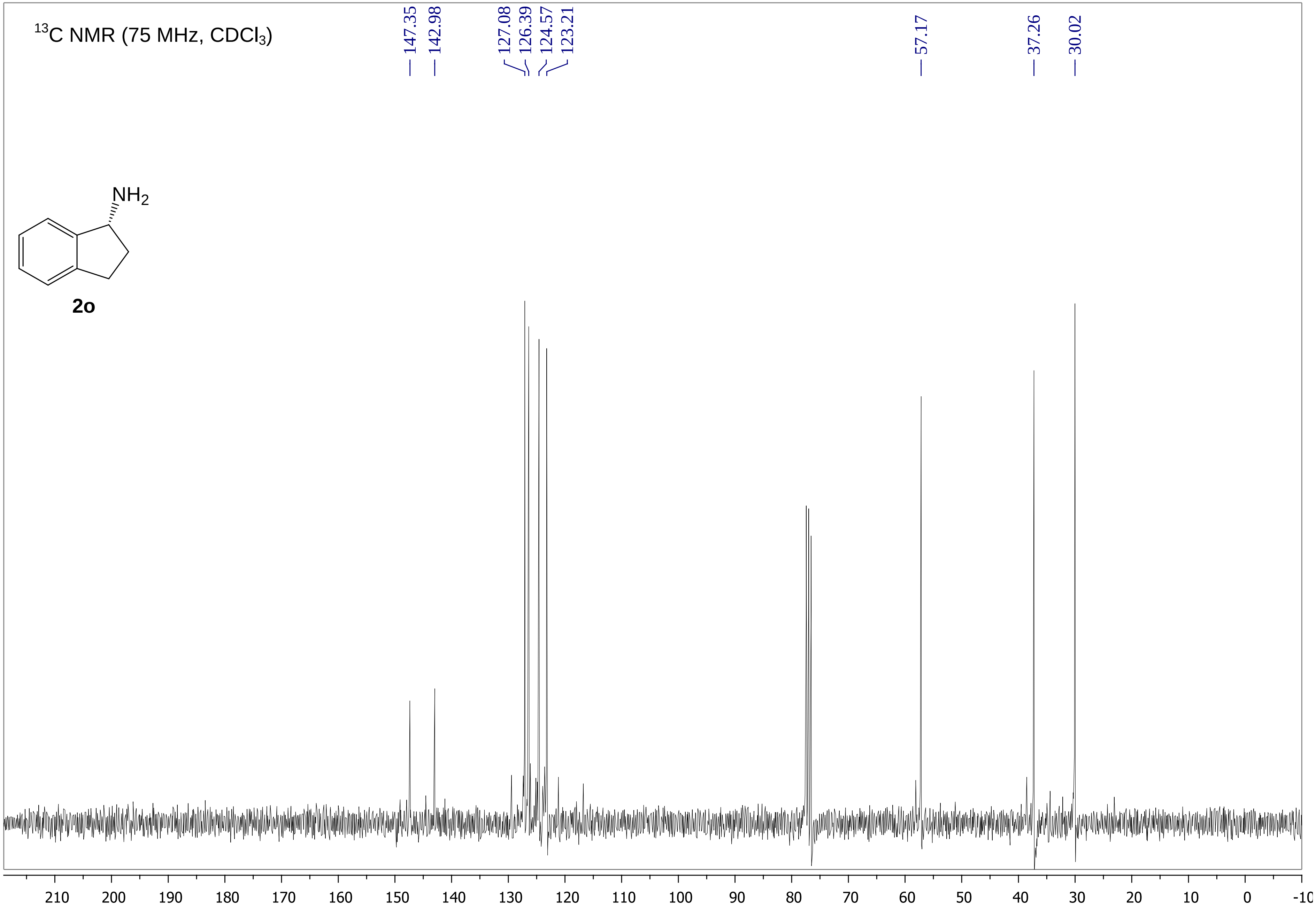

^{1}H NMR (400 MHz, $CDCl_3$)
NH2
S
2n
0.97
0.98
0.98
1.00
2.07
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



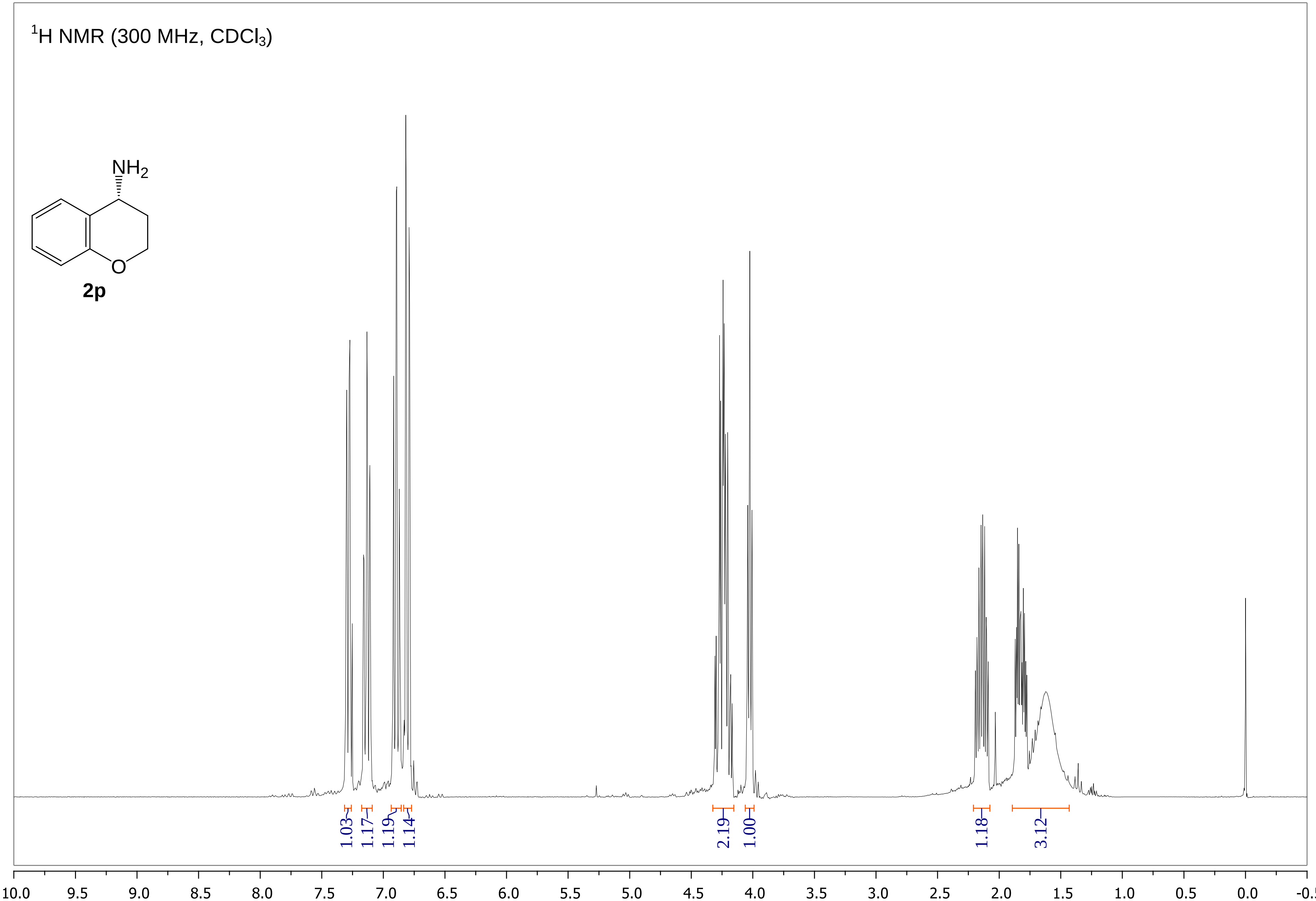
13C NMR (100 MHz, CDCl3)
152.80
126.50
123.25
122.01
47.26
26.30
NH2
S
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



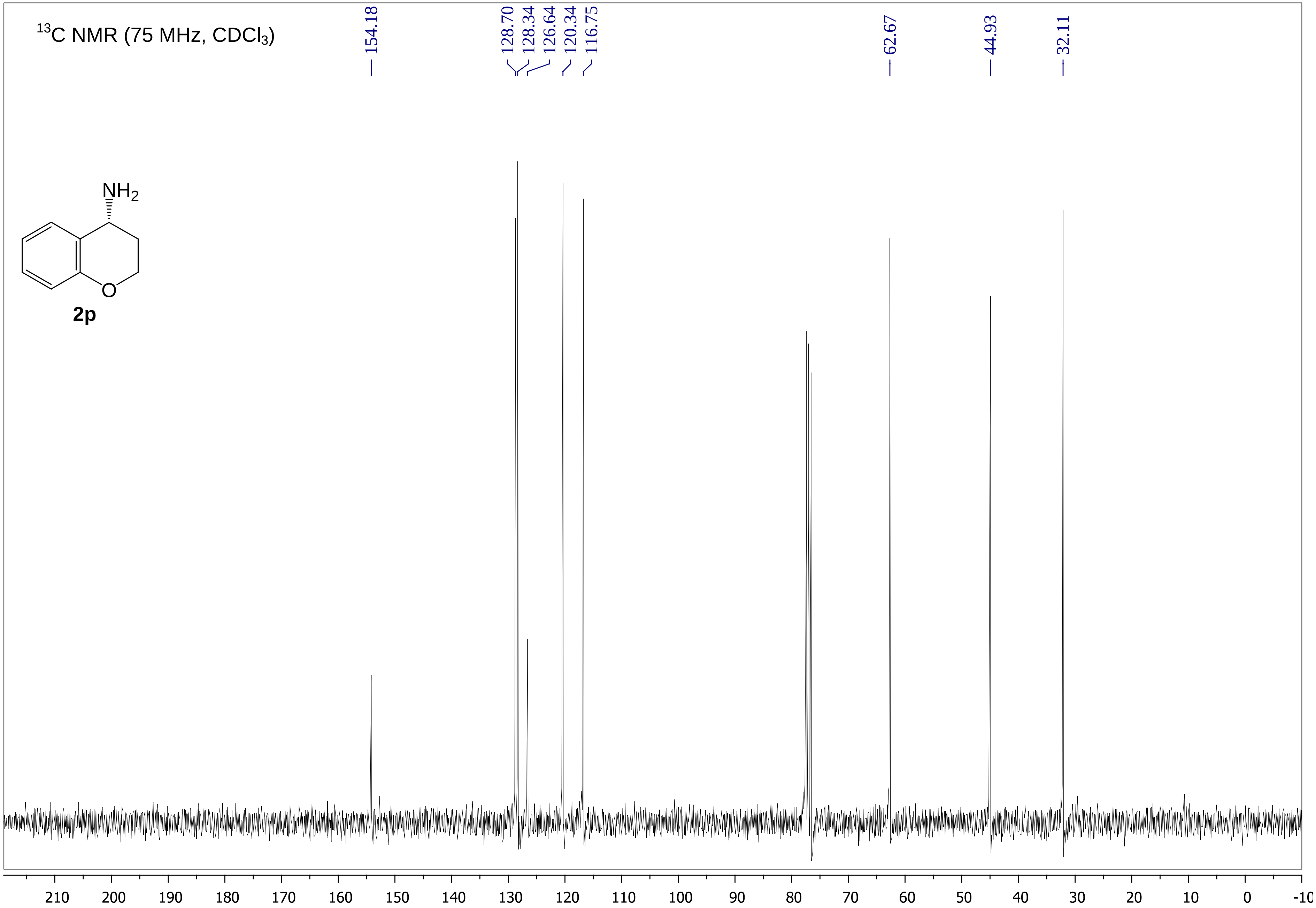
1H NMR (300 MHz, CDCl3)
NH2
2o
5.85
0.80
1.05
1.05
1.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



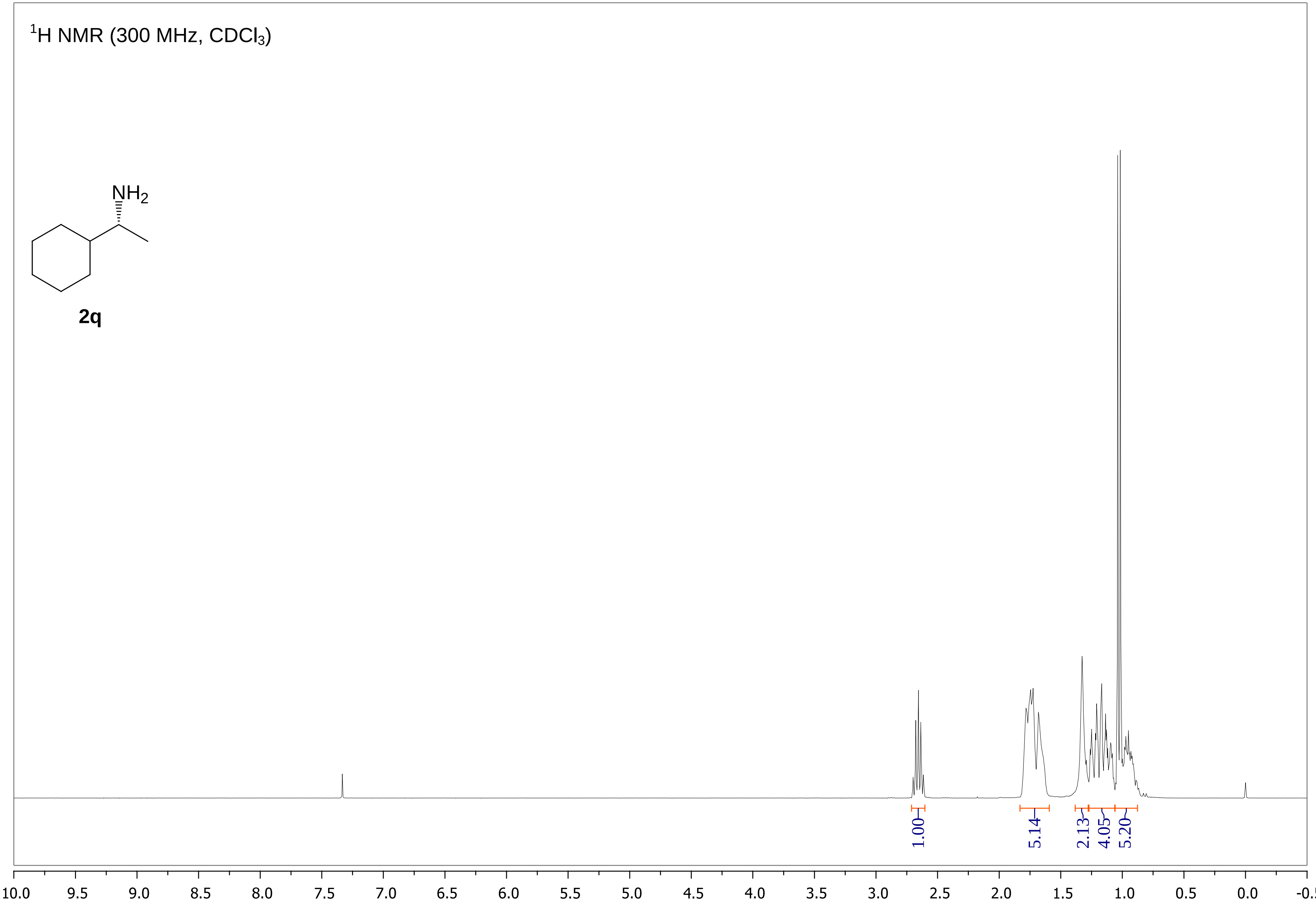
^{13}C NMR (75 MHz, CDCl$_3$)
147.35
142.98
127.08
126.39
124.57
123.21
57.17
37.26
30.02
NH2
2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



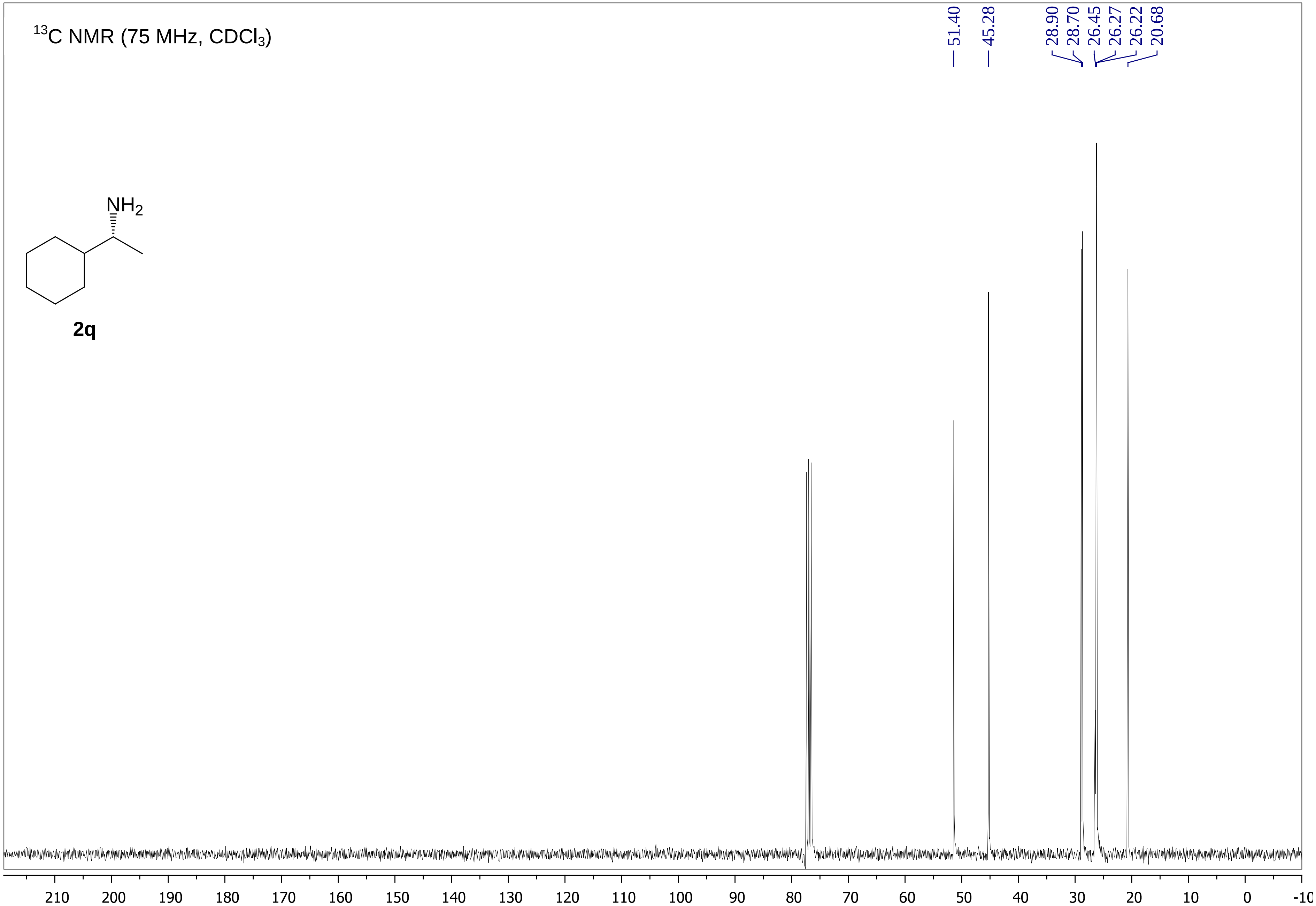
1H NMR (300 MHz, CDCl3)
NH2
O
2p
1.03
1.17
1.19
1.14
2.19
1.00
1.18
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



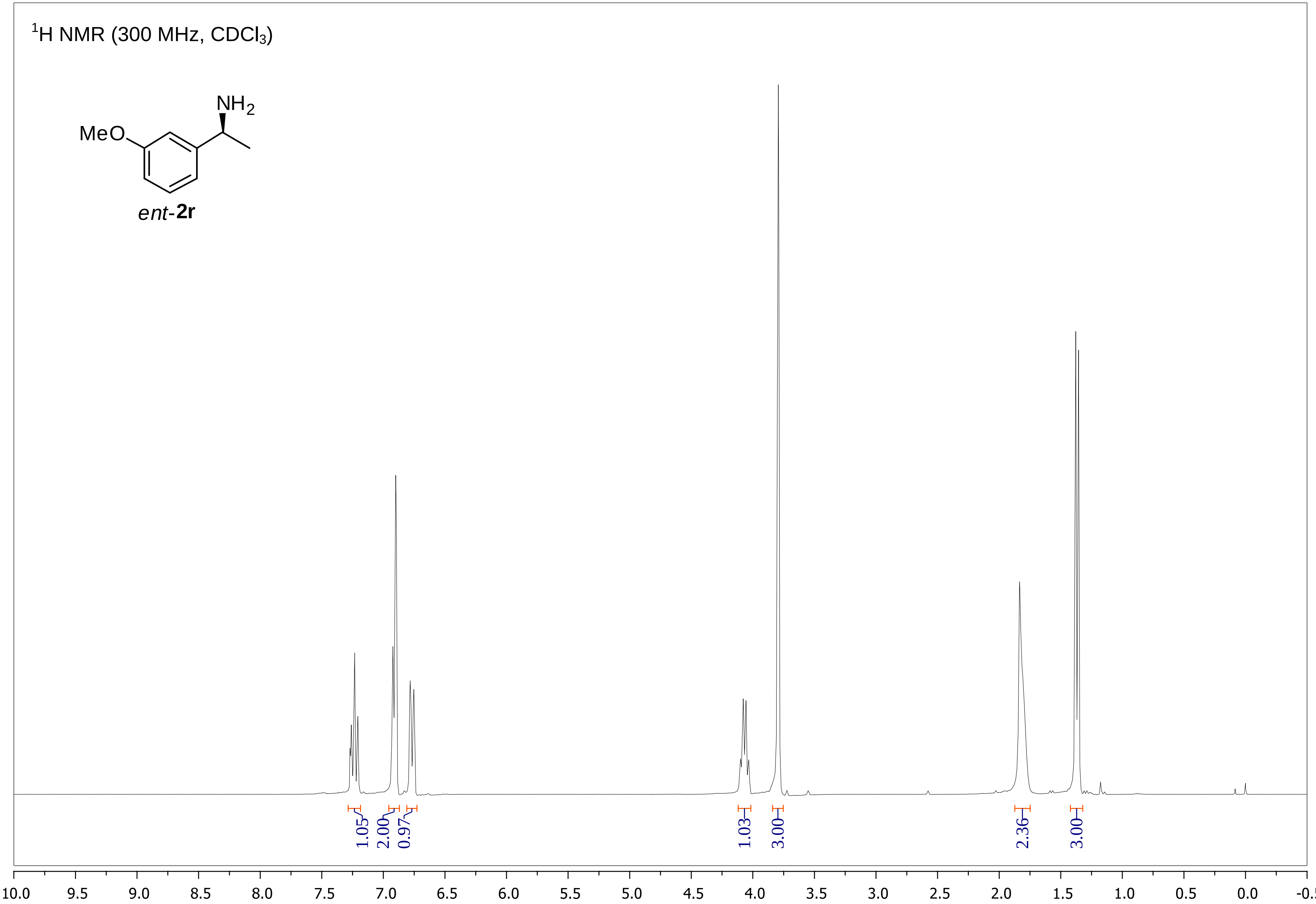
^{13}C NMR (75 MHz, $CDCl_3$)
154.18
128.70
128.34
126.64
120.34
116.75
62.67
44.93
32.11
NH_2
O
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



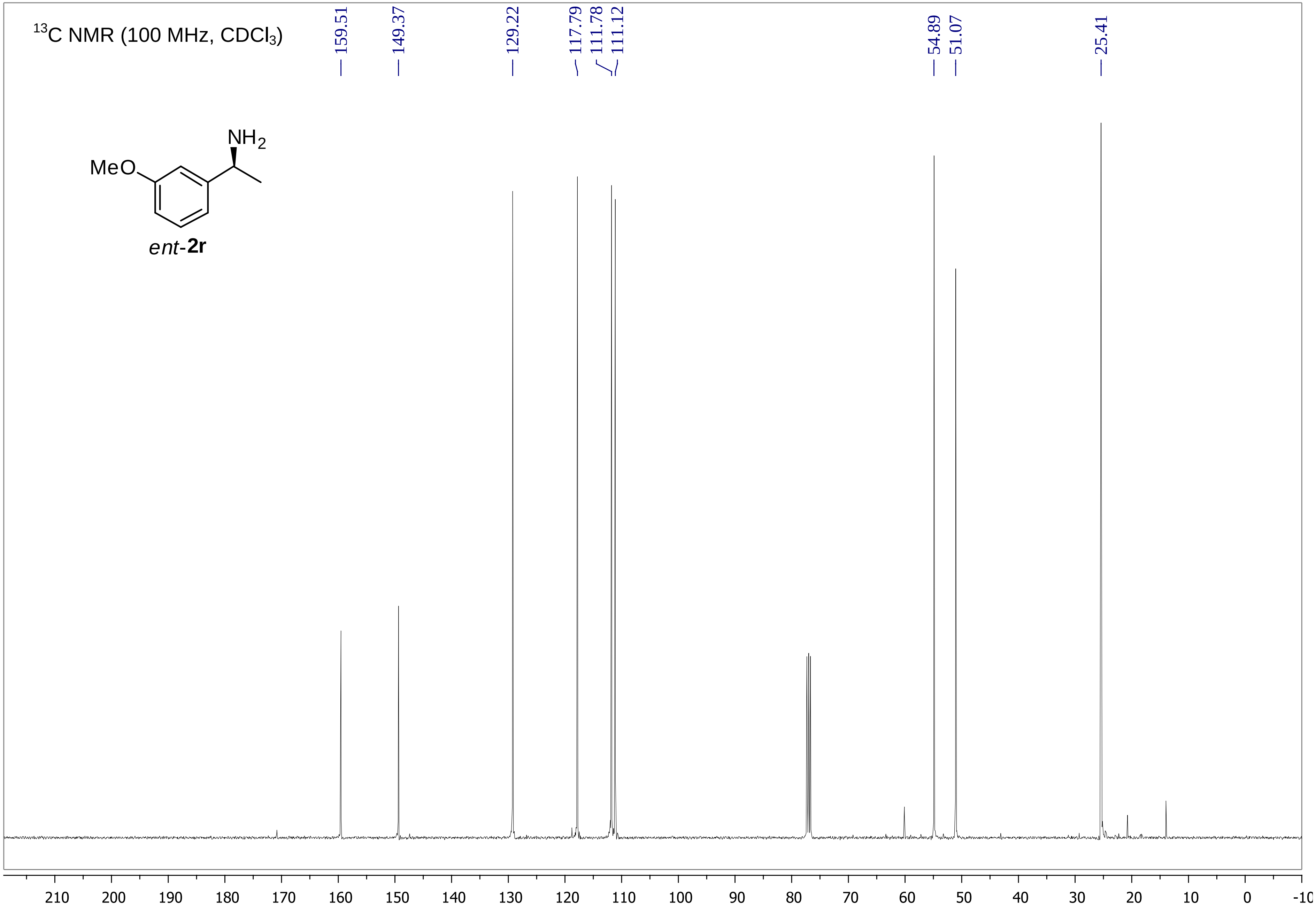
^{1}H NMR (300 MHz, $CDCl_3$)
NH_2
2q
1.00
5.14
2.13
4.05
5.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



13C NMR (75 MHz, CDCl3)
NH2
2q
51.40
45.28
28.90
28.70
26.45
26.27
26.22
20.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



^{1}H NMR (300 MHz, CDCl$_3$)
MeO
NH$_2$
ent-**2r**
1.05
2.00
0.97
1.03
3.00
2.36
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



^{13}C NMR (100 MHz, CDCl$_3$)
159.51
149.37
129.22
117.79
111.78
111.12
54.89
51.07
25.41
NH$_2$
MeO
ent-**2r**
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10