Aza- Annulation of Enynyl Azides: A New Approach to substituted Pyridines

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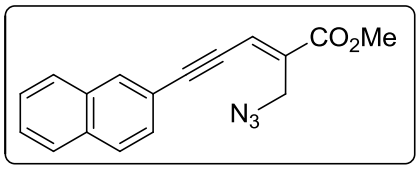
General. Reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light and anisaldehyde or potassium permanganate or β-naphthol for visualization. Column chromatography was performed on silica gel (60–120 mesh) using n-hexane and ethyl acetate as eluent. Evaporation of solvents was conducted under reduced pressure at temperatures less than 45 °C. FTIR spectra were recorded on KBr thin film. ^{1}H NMR (300 MHz and 500 MHz) and ^{13}C NMR (75 MHz and 125 MHz) spectra were recorded in $CDCl_3$ solvent. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz) respectively. Chemical shifts are reported relative to residual solvent as an internal standard for ^{1}H and ^{13}C ($CDCl_3$: δ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). Mass spectra were obtained on VG 70–70H or LC/MSD trap SL spectrometer operating at 70 eV using direct inlet system.

Experimental section

Substituted azides **1a-1n** have been prepared using the literature procedure,[1] and known compounds data compared with the reported data. Characterization data for new compounds is given below.

General procedure for the preparation of MBH -azides (1a-1n): To a stirred solution of corresponding MBH-acetate (1 equiv.) in 10 mL of aqueous methanol (MeOH/water: 9/1) was added sodium azide (1.5 equiv.) at room temperature and stirred for given time. After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc: hexanes) to afford the corresponding product.

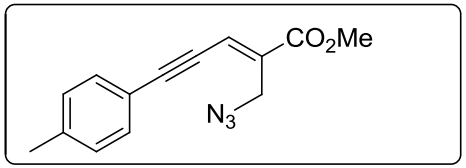
(*E*)-Methyl 2-(azidomethyl)-5-(naphthalen-2-yl)pent-2-en-4-ynoate (1b):



Following the general procedure, methyl 3-acetoxy-2-methylene-5-(naphthalen-2-yl)pent-4-ynoate (1g, 3.24 mmol) was allowed to react with sodium azide (0.32 g, 4.87 mmol) for 2 h. After the work-up, the residue was purified by column chromatography on silica gel (4% EtOAc in petroleum ether) to afford the azide **1b** (0.83 g, 88% yield) as yellow solid. R_f = 0.5 (petroleum ether: EtOAc = 9:1); M.P.: 53 - 55 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 8.5 Hz, 1H), 7.89 (dd, J = 14.2, 8.2 Hz, 2H), 7.75 (dd, J = 7.2, 1.1 Hz,

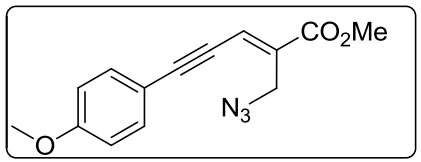
1H), 7.62 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.55 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.27 (s, 1H), 4.41 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.99, 135.67, 133.18, 133.11, 131.65, 130.43, 128.51, 127.43, 126.78, 125.76, 125.25, 124.72, 119.49, 102.59, 89.23, 52.56, 48.09; IR (KBr): ν_{max} = 2189, 2077, 2103, 1710, 1239, 1101, 803, 775 cm^{-1}; MS (ESI): *m/z* 314 $(M+Na)^+$; HRMS (ESI): *m/z* calcd for $C_{17}H_{13}NaN_3O_2$ $(M+Na)^+$: 314.0908, found: 314.0908.

(*E*)-Methyl 2-(azidomethyl)-5-(3-(*p*-toyl)pent-2-en-4-ynoate (1d):



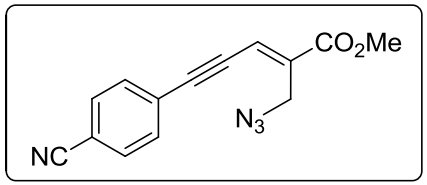
Following the general procedure, methyl 3-acetoxy-2-methylene-5-(p-tolyl)pent-4-ynoate (1 g, 3.67 mmol) was allowed to react with sodium azide (0.36 g, 5.51 mmol) for 5 h. After the work-up, the residue was purified by column chromatography on silica gel (4% EtOAc in petroleum ether) to afford the azide **1d** (0.8 g, 85% yield) as yellow solid. R_f = 0.6 (petroleum ether: EtOAc = 9:1); M.P.: 43 - 45 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.11 (s, 1H), 4.30 (s, 2H), 3.85 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.98, 140.21, 135.21, 131.91, 129.30, 125.75, 124.88, 118.70, 104.69, 84.09, 52.45, 48.12; IR (KBr): ν_{max} = 2950, 2192, 2100, 1716, 1109, 1250, 763 cm^{-1}; MS (ESI): *m/z* 278 $(M+Na)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_aN_3O_2$ $(M+Na)^+$: 278.0900, found: 278.0895.

(*E*)-Methyl 2-(azidomethyl)-5-(4-methoxyphenyl)pent-2-en-4-ynoate (1e):



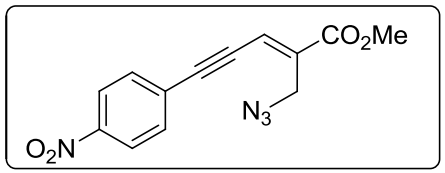
Following the general procedure, methyl 3-acetoxy-5-(4-methoxyphenyl)-2-methylenepent-4-ynoate (1 g, 3.47 mmol) was allowed to react with sodium azide (0.39 g, 5.20 mmol) for 3 h. After the workup, the residue was purified by column chromatography on silica gel (5% EtOAc in petroleum ether) to afford the azide **1e** (0.81 g, 86 % yield) as brown yellow solid. R_f = 0.6 (petroleum ether: EtOAc = 9:1). M.P: 52 - 54 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.11 (s, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.04, 160.76, 134.57, 133.71, 125.06, 114.20, 113.78, 104.93, 83.88, 55.32, 52.40, 48.11; IR (KBr): ν_{max} = 2948, 2189, 2102, 1714, 1595, 1251, 833 cm^{-1}; MS (ESI): *m/z* 294 $(M+Na)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_aN_3O_3$ $(M+Na)^+$: 294.0849, found: 294.0859.

(*E*)-Methyl 2-(azidomethyl)-5-(4-cyanophenyl)pent-2-en-4-ynoate (1g):



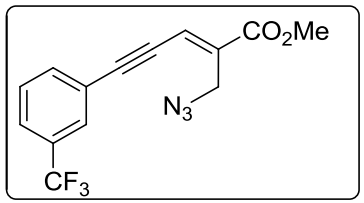
Following the general procedure, methyl 3-acetoxy-5-(4-cyanophenyl)-2-methylenepent-4-ynoate (1g, 3.53 mmol) was allowed to react with sodium azide (0.34 g, 5.30 mmol) for 2 h. After the workup, the residue was purified by column chromatography on silica gel (4% EtOAc in petroleum ether) to afford the azide **1g** (0.76 g, 80 % yield) as brown yellow solid, R_f = 0.6 (petroleum ether: EtOAc = 4:1). M.P: 75 - 77 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.67 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.09 (s, 1H), 4.29 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 165.46, 137.56, 132.31, 132.13, 126.41, 123.21, 118.02, 112.68, 101.09, 87.80, 52.63, 48.09; IR (KBr): ν_{max} = 2924, 2093, 2125, 1717, 1614, 1286, 1253, 842,553. MS (ESI): *m/z* 267 $(M+H)^+$ Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 62.99; H, 3.91; N, 21.07.

(*E*)-Methyl 2-(azidomethyl)-5-(4-nitrophenyl)pent-2-en-4-ynoate (1h):



Following the general procedure, methyl 3-acetoxy-2-methylene-5-(4-nitrophenyl)pent-4-ynoate (1g, 3.30 mmol) was allowed to react with sodium azide (0.321 g, 4.95 mmol) for 3 h. After the work-up, the residue was purified by column chromatography on silica gel (4 % EtOAc in petroleum ether) to afford the azide **1h** (0.61 g, 71 % yield) as brown yellow solid. R_f = 0.6 (petroleum ether : EtOAc = 4:1) M.P: 75 - 77 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, J = 8.9 Hz, 2H), 7.66 (d, J = 8.9 Hz, 2H), 7.10 (s, 1H), 4.31 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.46, 147.70, 137.87, 132.66, 128.30, 123.67, 123.11, 100.73, 88.50, 52.72, 48.16; IR (KBr): v_{max} = 2093, 2125, 1718, 1614, 1528, 1346, 856 cm^{-1}; MS (ESI): *m/z* 287 $(M+H)^+$; Anal. Calcd for $C_{13}H_{10}N_4O_4$: C, 54.55; H, 3.52; N, 19.57. Found: C, 54.09; H, 3.38; N, 19.9.

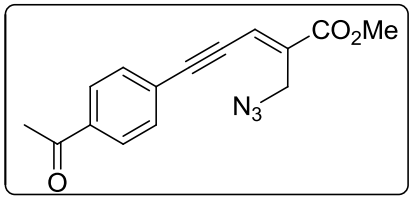
(*E*)-Methyl 2-(azidomethyl)-5-(3-(trifluoromethyl)phenyl)pent-2-en-4-ynoate (1i):



Following the general procedure, methyl 3-acetoxy-2-methylene-5-(3-(trifluoromethyl)phenyl)pent-4-ynoate (1 g, 3.06 mmol) was allowed to react with sodium azide (0.3 g, 4.60 mmol) for 2 h. After the work-up, the residue was purified by column chromatography on silica gel (3% EtOAc in petroleum ether) to afford the azide **1i** (0.65 g, 69% yield) as white solid. R_f = 0.6 (petroleum ether :

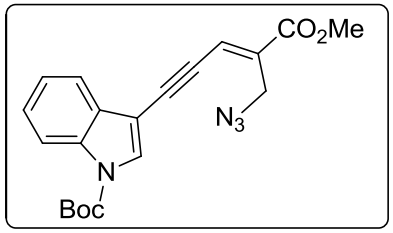
EtOAc = 9:1). M.P: 138 - 140 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.66 (t, J = 7.5 Hz, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.10 (s, 1H), 4.31 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.68, 136.96, 134.98, 131.48, 131.05, 129.15, 128.63, 126.15, 123.73, 122.74, 101.78, 85.54, 52.64, 48.18; IR (KBr): ν_{max} = 2925, 2854, 2095, 1718, 1121, 770, 692 cm^{-1}; MS (ESI): *m/z* 310 $(M+H)^+$; Anal. Calcd for $C_{14}H_{10}F_3N_3O_2$: C, 54.37; H, 3.26; N, 13.59. Found: C, 54.95; H, 3.96; N, 11.7.

(*E*)-Methyl 5-(4-acetylphenyl)-2-(azidomethyl)pent-2-en-4-ynoate (1j):



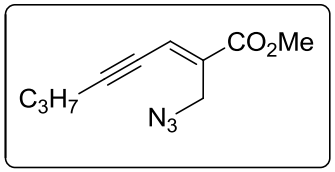
Following the general procedure, methyl 3-acetoxy-5-(4-acetylphenyl)-2-methylenepent-4-ynoate (1 g, 3.33 mmol) was allowed to react with sodium azide (0.325 g, 5.00 mmol) for 4 h. After the workup, the residue was purified by column chromatography on silica gel (5 % EtOAc in petroleum ether) to afford the azide **1j** (0.78 g, 82% yield) as white solid. R_f = 0.5 (petroleum ether: EtOAc = 9:1). M.P: 70-72 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.11 (s, 1H), 4.31 (s, 2H), 3.87 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.07, 165.64, 137.17, 136.87, 132.04, 128.29, 126.32, 123.79, 102.47, 86.96, 52.60, 48.12, 26.64; IR (KBr): ν_{max} = 2953, 2113, 2082, 1716, 1708, 1611, 1257, 1110, 844, 763 cm^{-1}; MS (ESI): *m/z* 284 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}N_3O_3$ $(M+H)^+$: 284.1029, found: 284.1025.

(*E*)-*tert*-Butyl-3-(4-(azidomethyl)-5-methoxy-5-oxopent-3-en-1-yn-1-yl)-1*H*-indole-1-carboxylate (1k):



Following the general procedure, *tert*-butyl-3-(3-acetoxy-4-(methoxycarbonyl)pent-4-en-1-yn-1-yl)-1*H*-indole-1-carboxylate (1g, 2.51 mmol) was allowed to react with sodium azide (0.245 g, 3.77 mmol) for 2 h. After the work-up, the residue was purified by column chromatography on silica gel (6% EtOAc in petroleum ether) to afford the azide **1k** (0.70 g, 73% yield) as brown solid. R_f = 0.5 (petroleum ether: EtOAc = 9:1); M.P: 82 - 84 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, J = 7.8 Hz, 1H), 7.89 (s, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.45 – 7.30 (m, 2H), 7.19 (s, 1H), 4.37 (s, 2H), 3.87 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.87, 148.70, 134.70, 134.62, 130.54, 129.80, 125.51, 124.73, 123.61, 119.85, 115.37, 102.19, 97.09, 88.44, 84.84, 52.46, 48.16, 28.03; IR (KBr): v_{max} = 2123, 2091, 1736, 1708, 1228, 1155, 760 cm^{-1}; MS (ESI): *m/z* 381 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}N_4O_4$ $(M+H)^+$: 381.1557, found: 381.1559.

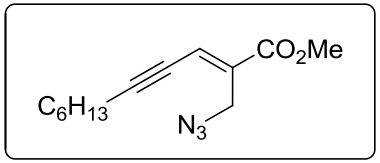
(*E*)-Methyl 2-(azidomethyl)oct-2-en-4-ynoate (1l):



Following the general procedure, methyl 3-acetoxy-2-methyleneoct-4-ynoate (1 g, 4.46 mmol) was allowed to react with sodium azide (0.435 g, 6.69 mmol) for 1 h. After the work-up, the residue was purified by column chromatography on silica gel (3 % EtOAc in petroleum ether) to afford the azide **1l (**0.75 g, 80% yield) as pale yellow liquid, R_f = 0.4 (petroleum ether : EtOAc = 9:1); ^{1}H NMR

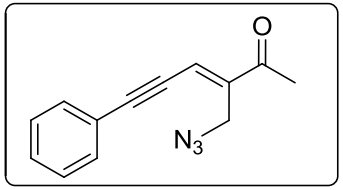
(300 MHz, $CDCl_3$): δ 6.90 (s, 1H), 4.20 (s, 2H), 3.82 (s, 3H), 2.42 (t, J = 6.9 Hz, 2H), 1.69-1.55 (m, 2H), 1.02 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.05, 135.05, 125.68, 106.94, 76.35, 52.28, 47.85, 21.89, 21.43, 13.41; IR (KBr): ν_{max} = 2965, 2937, 2215, 2098, 1718, 1268, 1108, 763 cm^{-1}; MS (ESI): *m/z* 230 $(M+Na)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}N_3O_2$ $(M+H)^+$: 208.1084, found: 208.1080.

(*E*)-Methyl 2-(azidomethyl)undec-2-en-4-ynoate (1m):



Following the general procedure, methyl 3-acetoxy-2-methyleneundec-4-ynoate (1 g, 3.75 mmol) was allowed to react with sodium azide (0.366 g, 5.63 mmol) for 3 h. After work-up, the residue was purified by column chromatography on silica gel (3 % EtOAc in petroleum ether) to afford the azide **1m** (0.81 g, 87% yield) as pale yellow liquid. R_f = 0.4 (petroleum ether : EtOAc = 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.89 (t, J = 2.3 Hz, 1H), 4.20 (s, 2H), 3.82 (s, 3H), 2.44 (td, J = 7.0, 2.3 Hz, 2H), 1.67 – 1.28 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.07, 135.04, 125.72, 107.19, 76.26, 52.28, 47.87, 31.18, 28.49, 28.13, 22.44, 19.95, 13.94; IR (KBr): ν_{max} = 2928, 2857, 2211, 2099, 1718, 1267, 1106, 763 cm^{-1}; MS (ESI): *m/z* 272 $(M+Na)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{19}NaN_3O_2$ $(M+Na)^+$: 272.1369, found: 272.1364.

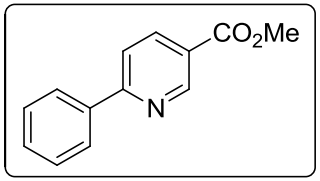
(*E*)-3-(Azidomethyl)-6-phenylhex-3-en-5-yn-2-one (1n):



Following the general procedure, 4-methylene-5-oxo-1-phenylhex-1-yn-3-yl acetate (1 g, 4.13 mmol) was allowed to react with sodium azide (0.402 g, 6.19 mmol). After 2 h, the residue was purified by column chromatography on silica gel (8% EtOAc in petroleum ether) to afford the corresponding azide **1n** (0.80 g, 86% yield) as brown solid. R_f = 0.5 petroleum ether : EtOAc = 4:1); M.P: 47-49 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (dd, J = 7.4, 1.8 Hz, 2H), 7.39 (q, J = 5.4 Hz, 3H), 6.97 (s, 1H), 4.29 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.89, 143.80, 132.02, 129.91, 128.63, 124.51, 121.77, 106.04, 84.64, 47.03, 25.56; IR (KBr): ν_{max} = 2926, 2095, 1741, 1656, 1255, 758, 689 cm^{-1}; MS (ESI): *m/z* 248 $(M+Na)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}N_3O$ $(M)^+$: 225.0896, found: 225.0893.

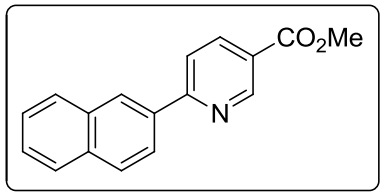
General procedure for the preparation of substituted Pyridines (2a-2n): To a stirred solution of alkynyl azide **1a-1n** (1 equiv.) in 1,2-dichloroethane (3.0 mL) was added $AgSbF_6$ (0.3 equiv.) and TFA (2 equiv.) at 80 ^oC. After completion of the reaction (Table 1), the mixture was quenched by saturated $NaHCO_3$ and stirred for 30 min. The mixture was extracted with CH_2Cl_2, organic layer was washed with H_2O, brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc: hexanes) to afford the corresponding product.

Methyl 6-phenylnicotinate (2a):



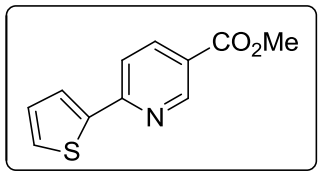
Following the general procedure, azide **1a** (100 mg, 0.41 mmol) was allowed to react with $AgSbF_6$ (42 mg, 0.12 mmol) and TFA (61 μL, 0.82 mmol) for 10 h. After the workup, the residue was purified by column chromatography on silica gel (10% EtOAc in petroleum ether) to afford the pyridine **2a**. (73 mg, 82% yield) as yellow solid; R_f = 0.6 (petroleum ether : EtOAc = 7:3). Spectral data of **2a** was compared with the reported data.[2]

Methyl 6-(napthalen-2-yl)nicotinate (2b):



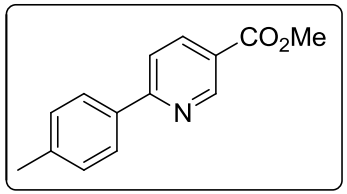
Following the general procedure, azide **1b** (100 mg, 0.34 mmol) was allowed to react with $AgSbF_6$ (35 mg, 0.10 mmol) and TFA (51.0 μL, 0.68 mmol) for 22 h. After the workup, the residue was purified by column chromatography on silica gel (12% EtOAc in petroleum ether) to afford the pyridine **2b** (71 mg, 79% yield) as yellow solid. R_f = 0.6 (petroleum ether : EtOAc = 7:3); M.P: 82 - 84 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.40 (s, 1H), 8.45 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 1.2 Hz, 1H), 7.94 (t, J = 8.1 Hz, 2H), 7.76-7.45 (m, 5H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.73, 162.96, 150.82, 137.59, 137.25, 133.86, 130.76, 129.65, 128.42, 127.96, 126.80, 126.03, 125.27, 125.21, 124.68, 124.25, 52.52; IR (KBr): v_{max} = 2924, 1722, 1596, 1314, 1130, 781 cm^{-1}; MS (ESI): *m/z* 264 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{17}H_{14}NO_2$ $(M+H)^+$: 264.1019, found: 264.1022.

Methyl 6-(thiophen-2-yl)nicotinate (2c):



Following the general procedure, azide **1c** (100 mg, 0.40 mmol) was allowed to react with $AgSbF_6$ (41 mg, 0.12 mmol) and TFA (60.1 μL, 0.80 mmol) for 8 h. After the workup, the residue was purified by column chromatography on silica gel (10% EtOAc in petroleum ether) to afford the pyridine **2c** (69 mg, 78% yield) as yellow solid. R_f = 0.5 (petroleum ether: EtOAc = 4:1); M.P: 110-112 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.15 (dd, J = 2.1, 0.7 Hz, 1H), 8.28 (dd, J = 8.3, 2.2 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.49 (dd, J = 5.0, 1.0 Hz, 1H), 7.15 (dd, J = 5.0, 3.7 Hz, 1H), 3.96 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$): δ 165.66, 155.89, 151.05, 143.93, 137.77, 129.48, 128.38, 126.35, 123.80, 118.02, 52.33; IR (KBr): ν_{max} = 2923, 2852, 1714, 1297, 1122, 778, 772 cm^{-1}; MS (ESI): *m/z* 220 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{11}H_{10}NO_2S$ $(M+H)^+$: 220.0426, found: 220.0426.

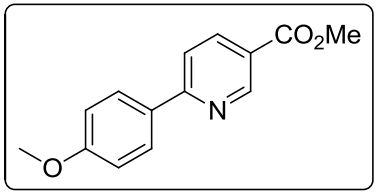
Methyl 6-(*p*-tolyl)nicotinate (2d):



Following the general procedure, compound **1d** (100 mg, 0.39 mmol) was allowed to react with $AgSbF_6$ (40 mg, 0.12 mmol) and TFA (58.2 μL, 0.78 mmol) for 10 h. After the workup, the residue was purified by column chromatography on silica gel (13% EtOAc in

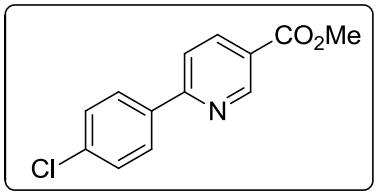
petroleum ether) to afford the pyridine **2d** (72 mg, 81% yield) as pale yellow solid. R_f = 0.5 (petroleum ether : EtOAc = 4:1). Spectral data of **2d** was compared with the reported data.[3]

Methyl 6-(4-methoxyphenyl)nicotinate (2e):



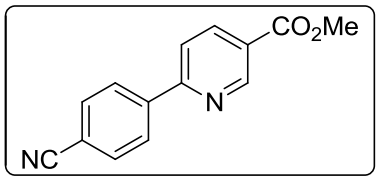
Following the general procedure, compound **1e** (100 mg, 0.36 mmol) was allowed to react with $AgSbF_6$ (37 mg, 0.11 mmol) and TFA (54.8 μL, 0.73 mmol) for 8 h. After the workup, the residue was purified by column chromatography on silica gel (12% EtOAc in petroleum ether) to afford the pyridine **2e** (78 mg, 86% yield) as yellow solid. R_f = 0.5 (petroleum ether : EtOAc = 4:1). Spectral data of **2e** was compared with the reported data.[2]

Methyl 6-(4-chlorophenyl)nicotinate (2f):



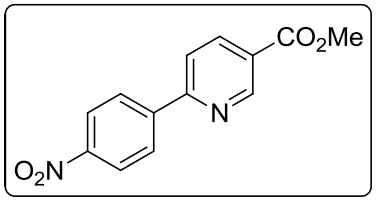
Following the general procedure, azide **1f** (100 mg, 0.36 mmol) was allowed to react with $AgSbF_6$ (38 mg, 0.11 mmol) and TFA (54.0 μL, 0.72 mmol) for 10 h. After the workup, the residue was purified by column chromatography on silica gel (15% EtOAc in petroleum ether) to afford the pyridine **2f** (60 mg, 66% yield) as pale yellow solid. R_f = 0.4 (petroleum ether: EtOAc = 4:1). Spectral data of **2f** was compared with the reported data.[4]

Methyl 6-(4-cyanophenyl)nicotinate (2g):



Following the general procedure, azide **1g** (100 mg, 0.37 mmol) was allowed to react with $AgSbF_6$ (39 mg, 0.11 mmol) and TFA (55.8 μL, 0.75 mmol) for 14 h. After the workup, the residue was purified by column chromatography on silica gel (10% EtOAc in petroleum ether) to afford the corresponding pyridine **2g** (54 mg, (60 % yield) as brown solid. R_f = 0.4 (petroleum ether: EtOAc = 4:1); M.P: 118 - 120 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.31 (d, J = 1.5 Hz, 1H), 8.41 (dd, J = 8.3, 2.1 Hz, 1H), 8.19 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 4.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.45, 158.57, 151.19, 142.29, 138.22, 132.66, 127.89, 125.37, 120.30, 118.52, 113.47, 52.52; IR (KBr): ν_{max} = 2923, 2100, 1720, 1292, 1118 cm^{-1}; MS (ESI): *m/z* 239 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{11}N_2O_2$ $(M+H)^+$: 239.0815, found: 239.0813.

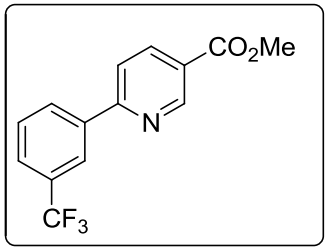
Methyl 6-(4-nitrophenyl)nicotinate (2h):



Following the general procedure, (*E*)-methyl 2-(azidomethyl)-5-(4-nitrophenyl)pent-2-en-4-ynoate (**1h,** 100 mg, 0.35 mmol) was allowed to react with $AgSbF_6$ (36 mg, 0.10 mmol) and TFA (51.8 μL, 0.69 mmol) for 18 h. After the workup, the residue was purified by column chromatography on silica gel (12% EtOAc in petroleum ether) to afford **2h** (56 mg, 62% yield) as white solid. R_f = 0.4

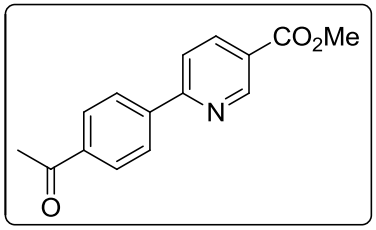
(petroleum ether: EtOAc = 4:1); M.P: 225 - 227 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.48 – 8.30 (m, 3H), 8.25 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.1 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.51, 158.18, 156.72, 151.20, 143.92, 138.29, 128.20, 125.65, 124.09, 120.60, 52.59; IR (KBr): ν_{max} = 2924, 1717, 1340, 1295, 1124, 749 cm^{-1}; MS (ESI): *m/z* 259 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}N_2O_4$ $(M+H)^+$: 259.0713, found: 259.0711.

Methyl 6-(3-(trifluoromethyl)phenyl)nicotinate (2i):



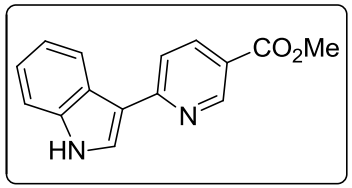
Following the general procedure, azide **1i** (100 mg, 0.32 mmol) was allowed to react with $AgSbF_6$ (33 mg, 0.09 mmol) and TFA (24 μL, 0.64 mmol) for 16 h. After the workup, the residue was purified by column chromatography on silica gel (10 % EtOAc in petroleum ether) to afford the pyridine **2i** (63 mg, 69% yield) as yellow solid. R_f = 0.6 (petroleum ether: EtOAc = 4:1); M.P: 95-97 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.31 (s, 1H), 8.46 – 8.32 (m, 2H), 8.25 (d, J = 7.7 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.78 – 7.57 (m, 2H), 3.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.61, 159.19, 151.09, 139.00, 138.15, 130.46, 129.40, 126.50, 126.45, 124.92, 124.26, 124.21, 119.92, 52.46; IR (KBr): ν_{max} = 2925, 1721, 1339, 1117, 782 cm^{-1}; MS (ESI): *m/z* 282 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{11}F_3NO_2$ $(M+H)^+$: 282.0736, found: 282.0748.

Methyl 6-(4-acetyphenyl)nicotinate (2j):



Following the general procedure, azide **1j** (100 mg, 0.35 mmol) was allowed to react with $AgSbF_6$ (36 mg, 0.10 mmol) and TFA (52.4 μL, 0.70 mmol) for 18 h. After the work up, the residue was purified by column chromatography on silica gel (10% EtOAc in petroleum ether) to afford pyridine **2j** (68 mg, 75 % yield) as yellow solid. R_f = 0.5 (petroleum ether: EtOAc = 4:1); M.P:150-152 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.31 (s, 1H), 8.39 (dd, J = 8.3, 2.0 Hz, 1H), 8.17 (d, J = 8.3 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.3 Hz, 1H), 3.99 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.68, 165.60, 159.46, 151.04, 142.30, 138.05, 137.81, 128.84, 127.50, 124.89, 120.37, 52.45, 26.77; IR (KBr): ν_{max} = 2922, 1719, 1679, 1302, 1267, 779 cm^{-1}; MS (ESI): *m/z* 256 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}NO_3$ $(M+H)^+$: 256.0968, found: 256.0966.

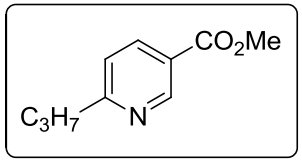
Methyl 6-(1*H*-indol-3-yl)nicotinate (2k):



Following the general procedure, compound **1k** (90 mg, 0.23 mmol) was allowed to react with $AgSbF_6$ (24 mg, 0.07 mmol) and TFA (35.1 μL, 0.47 mmol) for 18 h. After the workup, the residue was purified by column chromatography on silica gel (35% EtOAc in petroleum ether) to afford the pyridine **2k** (48 mg, 80% yield) as yellow solid. R_f = 0.4 (petroleum ether: EtOAc = 1:1); M.P: 218-220;

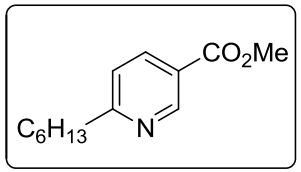
^{1}H NMR (300 MHz, DMSO-d_6): δ 12.18 (s, 1H), 9.02 (s, 1H), 8.52 (d, J = 2.3 Hz, 1H), 8.37 (t, J = 7.3 Hz, 2H), 8.16 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 6.9 Hz, 1H), 7.31 – 7.15 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.54, 156.55, 147.56, 139.03, 137.18, 129.94, 129.81, 124.63, 122.59, 121.27, 121.16, 120.19, 112.45, 112.05, 52.33; IR (KBr): ν_{max} = 2922, 2645, 1726, 1598, 1437, 1290, 745 cm^{-1}; MS (ESI): *m/z* 253 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{13}N_2O_2$ $(M+H)^+$ 253.09683: found: 253.0971.

Methyl 6-propylnicotinate (2l):



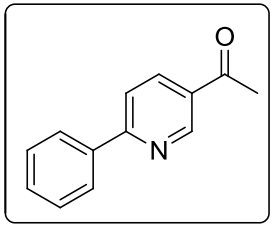
Following the general procedure, azide **1l** (100 mg, 0.48 mmol) was allowed to react with $AgSbF_6$ (48 mg, 0.14 mmol) and TFA (71.6 µL, 0.96 mmol) for 20 h. After the workup, the residue was purified by column chromatography on silica gel (13% EtOAc in petroleum ether) to afford the pyridine **2l** (73 mg, 84% yield) as pale yellow liquid. R_f = 0.4 (petroleum ether: EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.13 (d, J = 1.5 Hz, 1H), 8.19 (dd, J = 8.1, 2.2 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 3.94 (s, 3H), 2.86 – 2.80 (m, 2H), 1.85 – 1.72 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.86, 165.88, 150.38, 137.22, 123.37, 122.31, 52.12, 40.35, 22.76, 13.68; IR (KBr): ν_{max} = 2959, 1727,1598, 1287, 1118, 768 cm^{-1}; MS (ESI): *m/z* 180 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}NO_2$ $(M+H)^+$: 180.1019, found: 180.1018.

Methyl 6-hexylnicotinate (2m):



Following the general procedure, azide **1m** (100 mg, 0.40 mmol) was allowed to react with $AgSbF_6$ (41 mg, 0.12 mmol) and TFA (59.6 μL, 0.80 mmol) for 26 h. After the workup, the residue was purified by column chromatography on silica gel (15% EtOAc in petroleum ether) to afford the corresponding pyridine **2m** (76 mg, 86% yield) as pale yellow liquid. R_f = 0.5 (petroleum ether: EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (d, J = 2.0 Hz, 1H), 8.19 (dd, J = 8.1, 2.2 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 3.94 (s, 3H), 2.90 – 2.79 (m, 2H), 1.75 (dd, J = 14.5, 7.7 Hz, 2H), 1.39 – 1.27 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.24, 166.00, 150.51, 137.28, 123.39, 122.30, 52.22, 38.59, 31.62, 29.61, 29.00, 22.52, 14.03; IR (KBr): ν_{max} = 2927, 2856, 1727,1598, 1288, 1118, 769 cm^{-1}; MS (ESI): *m/z* 222 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{20}NO_2$ $(M+H)^+$: 222.1488, found: 222.1484.

1-(6-Phenylpyridin-3-yl)ethanone (2n):

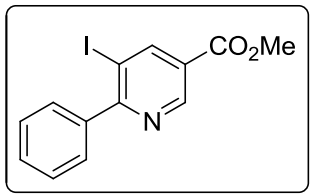


Following the general procedure, azide **1n** (160 mg, 0.71 mmol) was allowed to react with $AgSbF_6$ (73 mg, 0.21 mmol) and TFA (105.6 μL, 1.42 mmol) for 2 h. After the workup, the residue was purified by column chromatography on silica gel (8% EtOAc in

petroleum ether) to afford the pyridine **2n** (128 mg, 91% yield) as yellow solid. R_f = 0.6 (petroleum ether: EtOAc = 4:1). Spectral data of **2n** was compared with the literature data.[5]

General procedure for the preparation of substituted Iodo-pyridines (3a-3g and 3h): To a solution of azide (1 equiv.) **1a-1n** in CH_2Cl_2 and $NaHCO_3$ (1 equiv.) was added at 0 ^oC followed by the addition of iodine (5 equiv.), the solution was stirred at room temperature for given time (Scheme 1). After completion of the reaction, the mixture was quenched with $Na_2S_2O_3$ solution and extracted with EtOAc, organic layer was washed with H_2O, brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc: hexanes) to afford the corresponding product. In the case of **1a**, **1f**, **1g**, **1l** and **1n** the formation of **4a** to **4e** were observed either as a minor or as an exclusive product.

Methyl 5-iodo-6-phenylnicotinate (3a):

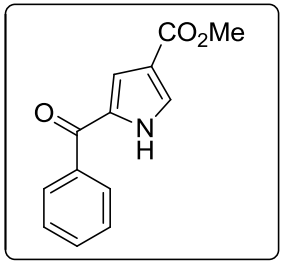


Following the general procedure, azide **1a** (100 mg, 0.41 mmol) was allowed to react with $NaHCO_3$ (34 mg, 0.41 mmol) and iodine (524 mg, 2.07 mmol) for 22 h. After the workup, the residue was purified by column chromatography on silica gel (10 % EtOAc in petroleum ether) to afford the iodo pyridine **3a** (85 mg, 60% yield) along with acyl pyrrole **4a** (21 mg, 21 % yield).

3a: Brown solid; R_f = 0.5 (petroleum ether: EtOAc = 4:1); M.P: 134-136 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.19 (d, J = 1.5 Hz, 1H), 8.85 (d, J = 1.6 Hz, 1H), 7.63 (d, J = 3.5 Hz, 2H), 7.47 (d, J = 3.2 Hz, 3H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.01,

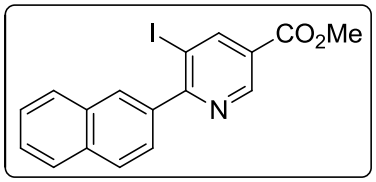
164.29, 149.43, 148.58, 141.05, 129.26, 129.13, 128.02, 125.30, 93.12, 52.64; IR (KBr): ν_{max} = 2925, 2853, 1730, 1277, 1122 cm^{-1}; MS (ESI): *m/z* 340 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}INO_2$ $(M+H)^+$: 339.9819, found: 339.9829.

Methyl 5-benzoyl-1*H*-pyrrole-3-carboxylate (4a):



Brown solid; R_f = 0.3 (petroleum ether: EtOAc = 4:1); M.P: 120 - 122 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 10.87 (s, 1H), 7.93 (d, J = 7.2 Hz, 2H), 7.76 (s, 1H), 7.66 – 7.43 (m, 3H), 7.33 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.46, 164.49, 137.42, 132.57, 131.47, 129.37, 129.11, 128.57, 119.93, 118.28, 51.52; IR (KBr): ν_{max} = 3264, 2925, 2854, 1728, 1631, 1289, 1217 cm^{-1}. MS (ESI): *m/z* 230 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{12}NO_3$ $(M+H)^+$: 230.0806, found: 230.0811.

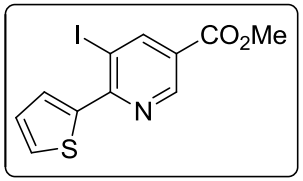
Methyl 5-iodo-6-(naphthalen-2-yl)nicotinate (3b):



Following the general procedure, azide **1b** (100 mg, 0.34 mmol) was allowed to react with $NaHCO_3$ (29 mg, 0.34 mmol) and iodine (433 mg, 1.72 mmol) for 22 h. After the workup, the residue was purified by column chromatography on silica gel (8% EtOAc in petroleum ether) to afford the corresponding iodo pyridine **3b** (117 mg, 88% yield) as yellow solid. R_f = 0.6 (petroleum ether: EtOAc

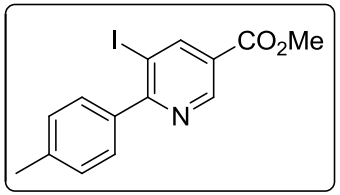
= 4:1); M.P: 172-174 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.29 (d, J = 1.8 Hz, 1H), 8.91 (d, J = 1.8 Hz, 1H), 8.08 – 7.92 (m, 2H), 7.65-7.30 (m, 5H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.94, 164.38, 149.51, 147.86, 139.42, 133.57, 130.52, 129.40, 128.50, 126.67, 126.20, 125.88, 125.11, 125.06, 96.38, 52.77; IR (KBr): ν_{max} = 2924, 1724, 1271, 1113, 776 cm^{-1}; MS (ESI): *m/z* 390 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{17}H_{13}INO_2$ $(M+H)^+$: 389.9985, found: 389.9999.

Methyl 5-iodo-6-(thiophen-2-yl)nicotinate (3c):



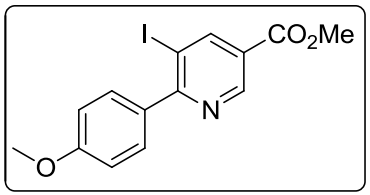
Following the general procedure, azide **1c** (100 mg, 0.40 mmol) was allowed to react with $NaHCO_3$ (34 mg, 0.40 mmol) and iodine (512 mg, 2.02 mmol) for 23 h. After the workup, the residue was purified by column chromatography on silica gel (10% EtOAc in petroleum ether) to afford the iodo pyridine **3c** (122 mg, 87% yield) as white solid. R_f = 0.6 (petroleum ether: EtOAc = 4:1); M.P: 102-104 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (d, J = 1.8 Hz, 1H), 8.83 (d, J = 1.8 Hz, 1H), 8.29 (d, J = 3.7 Hz, 1H), 7.56 (d, J = 5.0 Hz, 1H), 7.22 – 7.08 (m, 1H), 3.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.17, 156.71, 150.15, 149.00, 143.75, 130.56, 130.35, 127.60, 124.09, 88.79, 52.57; IR (KBr): ν_{max} = 2925, 2854, 1702, 1432, 1294, 1123, 724 cm^{-1}; MS (ESI): *m/z* 346 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{11}H_9INO_2S$ $(M+H)^+$: 345.9385, found: 345.9393.

Methyl 5-iodo-6-(*p*-tolyl)nicotinate (3d):



Following the general procedure, **1d** (100 mg, 0.39 mmol) was allowed to react with $NaHCO_3$ (32 mg, 0.39 mmol) and iodine (495 mg, 1.96 mmol) for 16 h. After the workup, the residue was purified by column chromatography on silica gel (12% EtOAc in petroleum ether) to afford the iodo pyridine **3d** (98 mg, 71 % yield) as pale yellow solid. R_f = 0.5 (petroleum ether: EtOAc = 4:1); M.P: 70-72 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.17 (d, J = 1.7 Hz, 1H), 8.83 (d, J = 1.7 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 3.98 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.05, 164.44, 149.49, 148.67, 139.46, 138.24, 129.19, 128.77, 125.12, 93.12, 52.68, 21.48; IR (KBr): ν_{max} = 2923, 1724, 1426, 1289, 771 cm^{-1}; MS (ESI): *m/z* 354 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}INO_2$ $(M+H)^+$: 353.9979, found: 353.9985.

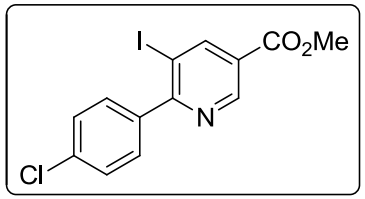
Methyl 5-iodo-6-(4-methoxyphenyl)nicotinate (3e):



Following the general procedure, (*E*)-methyl 2-(azidomethyl)-5-(4-methoxyphenyl)pent-2-en-4-ynoate (**1e** , 100 mg, 0.37 mmol) was allowed to react with $NaHCO_3$ (31 mg, 0.37 mmol) and iodine (467 mg, 1.84 mmol) for 3 h. After the workup, the residue was purified by column chromatography on silica gel (10 % EtOAc in petroleum ether) to afford the iodo pyridine **3e** (126 mg, 92% yield) as white solid. R_f = 0.6 (petroleum ether: EtOAc = 4:1); M.P: 80-82 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, J = 1.9 Hz, 1H), 8.82

(d, J = 1.9 Hz, 1H), 7.66 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.97 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.46, 164.41, 160.44, 149.43, 148.76, 133.38, 130.88, 128.76, 124.83, 114.27, 113.36, 92.86, 55.35, 52.61; IR (KBr): ν_{max} = 2952, 2837, 1715, 1294, 1255, 1173 cm^{-1}; MS (ESI): *m/z* 370 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}INO_3$ $(M+H)^+$: 369.9928, found: 369.9934.

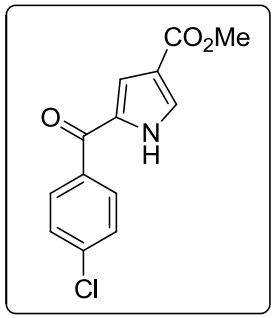
Methyl 6-(4-chorophenyl)-5-iodonicotinate (3f):



Following the general procedure, **1f** (100 mg, 0.36 mmol) was allowed to react with $NaHCO_3$ (31 mg, 0.36 mmol) and iodine (460 mg, 1.81 mmol) for 20 h. After the workup, the residue was purified by column chromatography on silica gel (8% EtOAc in petroleum ether) to afford the iodo pyridine **3f** (27 mg, 20% yield) along with acyl pyrrole **4b (**50 mg, 52% yield).

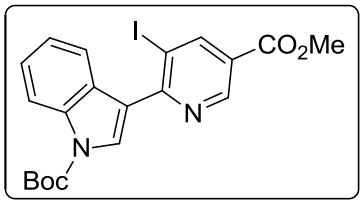
3f: White solid; R_f = 0.6 (petroleum ether: EtOAc = 4:1); M.P: 106-108 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.18 (d, J = 1.8 Hz, 1H), 8.84 (d, J = 1.8 Hz, 1H), 7.61 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 3.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.23, 163.81, 149.56, 148.80, 139.41, 135.54, 130.73, 128.36, 125.59, 92.90, 52.75; IR (KBr): ν_{max} = 2923, 2857, 1726, 1457, 1280 cm^{-1}; MS (ESI): *m/z* 373$(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{10}ClINO_2$ $(M+H)^+$: 373.9439, found: 373.9438.

Methyl 5-(4-chlorobenzoyl)-1*H*-pyrrole-3-carboxylate (4b):



4b: Yellow solid; R_f = 0.3 (petroleum ether: EtOAc = 4:1); M.P: 130-132 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 1.7 Hz, 1H), 7.50 (d, J = 8.5 Hz, 2H), 7.28 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.80, 164.26, 139.02, 135.62, 131.15, 130.42, 129.09, 128.93, 119.43, 118.58, 51.55; IR (KBr): ν_{max} = 3263, 2925, 1727, 1623, 1289, 757cm^{-1}; MS (ESI): *m/z* 264 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}ClNO_3$ $(M+H)^+$: 264.0422, found: 264.0420.

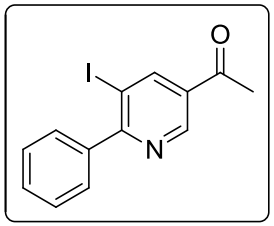
***tert*-Butyl-3-(3-iodo-5-(methoxycarbonyl)pyridin-2-yl)-1*H*-indole-1-carboxylate (3g):**



Following the general procedure, azide **1k** (100 mg, 0.26 mmol) was allowed to react with $NaHCO_3$ (22 mg, 0.26 mmol) and iodine (332 mg, 1.31 mmol) for 20 h. After the workup, the residue was purified by column chromatography on silica gel (13% EtOAc in petroleum ether) to afford the iodo pyridine **3g** (114 mg, 90% yield) as yellow solid. R_f = 0.5 (petroleum ether: EtOAc = 4:1); M.P: 106-108 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.24 (d, J = 1.9 Hz, 1H), 8.88 (d, J = 1.9 Hz, 1H), 8.33 (s, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.1 Hz, 1H), 7.30 (t, J = 7.0 Hz, 1H), 3.99 (s, 3H), 1.70 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ

164.43, 159.24, 149.39, 148.91, 135.14, 128.73, 128.03, 124.99, 124.67, 123.35, 121.61, 120.91, 115.26, 93.62, 84.52, 52.71, 28.21; IR (KBr): ν_{max} = 2979, 1732, 1370, 1279, 1152, 750 cm^{-1}; MS (ESI): *m/z* 479 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{20}IN_2O_4$ $(M+H)^+$: 479.0462, found: 479.0449.

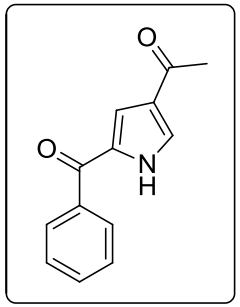
1-(5-Iodo-6-phenylpyridin-3-yl)ethanone (3h):



Following the general procedure, azide **1n** (100 mg, 0.44 mmol) was allowed to react with $NaHCO_3$ (37 mg, 0.44 mmol) and iodine (562 mg, 2.22 mmol) for 12 h. After the workup, the residue was purified by column chromatography on silica gel (10% EtOAc in petroleum ether) to afford the iodo pyridine **3h** (82 mg, 57% yield) along with the acyl pyrrole **4e** (20 mg, 21 % yield).

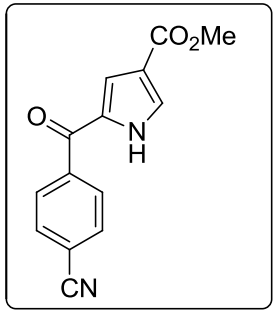
3h: Yellow solid; R_f = 0.5 (petroleum ether: EtOAc = 4:1); M.P: 93-95 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.77 (s, 1H), 7.63 (d, *J* = 3.9 Hz, 2H), 7.48 (d, *J* = 3.6 Hz, 3H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.22, 165.08, 148.49, 147.31, 141.03, 131.52, 129.42, 129.18, 128.12, 94.01, 26.89; IR (KBr): ν_{max} = 2921, 1679, 1571, 1264, 743 cm^{-1}; MS (ESI): *m/z* 324 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}INO$ $(M+H)^+$: 323.9879, found: 323.9871.

1-(5-Benzoyl-1*H*-pyrrol-3-yl)ethanone (4e):



4e: Yellow solid; R_f = 0.4 (petroleum ether: EtOAc = 4:1); M.P: 90-92 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.72 (s, 1H), 7.93 (d, J = 7.1 Hz, 2H), 7.75 (s, 1H), 7.62 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.31 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.31, 185.54, 137.27, 132.60, 131.77, 129.01, 128.56, 127.70, 118.36, 27.32; IR (KBr): ν_{max} = 3257, 1718, 1628, 1548, 1376, 1286 cm^{-1}; MS (ESI): *m/z* 214 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NO_2$ $(M+H)^+$: 214.0862, found: 214.0858.

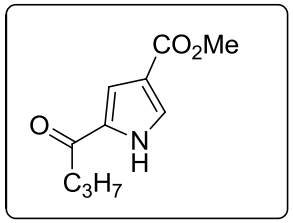
Methyl 5-(4-cyanobenzoyl)-1*H*-pyrrole-3-carboxylate (4c):



Following the general procedure, azide **1g** (100 mg, 0.37 mmol) was allowed to react with $NaHCO_3$ (32 mg, 0.37 mmol) and iodine (476 mg, 1.87 mmol) for 20 h. After the workup, the residue was purified by column chromatography on silica gel (15 % EtOAc in petroleum ether) to afford the acyl pyrrole **4c**. (75 mg, 79% yield) as yellow solid. R_f = 0.4 (petroleum ether: EtOAc = 4:1); M.P: 183-185 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 2.0 Hz, 1H), 7.27

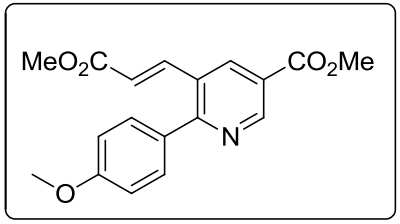
(s, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.31, 164.01, 140.84, 132.38, 130.76, 129.81, 129.35, 120.14, 118.81, 117.90, 115.79, 51.60; IR (KBr): ν_{max} = 3274, 2954, 228, 1717, 1626, 1295, 1231, 762 cm^{-1}; MS (ESI): *m/z* 277 $(M+Na)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{10}NaN_2O_3$ $(M+Na)^+$: 277.0584 , found: 277.0595.

Methyl 5-butyryl-1*H*-pyrrole-3-carboxylate (4d):



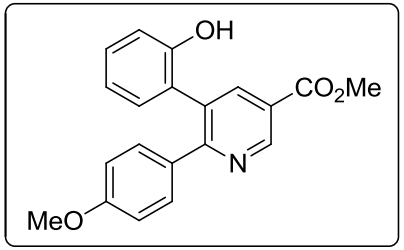
Following the general procedure, azide **1l** (93 mg, 0.45 mmol) was allowed to react with $NaHCO_3$ (37 mg, 0.45 mmol) and iodine (568 mg, 2.24 mmol) for 20 h. After the workup, the residue was purified by column chromatography on silica gel (15 % EtOAc in petroleum ether) to afford the acyl pyrrole **4d** (76 mg, 81% yield) as pale yellow liquid. R_f = 0.4 (petroleum ether: EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.73 (s, 1H), 7.59 (d, J = 1.9 Hz, 1H), 7.31 (d, J = 0.7 Hz, 1H), 3.85 (s, 3H), 2.77 (t, J = 7.4 Hz, 2H), 1.84 – 1.67 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.47, 164.34, 132.45, 127.90, 118.05, 116.17, 51.42, 39.89, 18.43, 13.89; IR (KBr): ν_{max} = 3270, 2925, 2854, 1715, 1654, 1209, 766 cm^{-1}; MS (ESI): *m/z* 196 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}NO_3$ $(M)^+$: 195.0872 , found: 195.0889.

(*E*)-Methyl 5-(3-methoxy-3-oxoprop-1-en-1-yl)-6-(4-methoxyphenyl)nicotinate (5a):



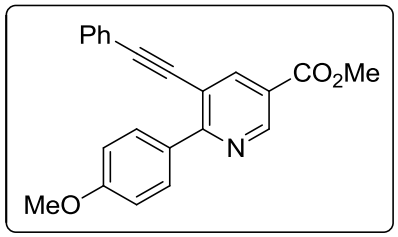
To a solution of methyl 5-iodo-6-(4-methoxyphenyl)nicotinate (**3e**, 100 mg, 0.27 mmol) , $Pd(OAc)_2$ (6 mg, 0.027 mmol, 10 mol %), Bu_4NBr (87 mg, 0.27 mmol), $NaHCO_3$ (57 mg, 0.67 mmol) and methy acrylate (25.6 mg, 0.29 mmol) in DMF (5 mL). The reaction mixture was heated at 80 ^oC for 2 h. After the completion of reaction quenched by aqueous NH_4Cl (10 mL) and reaction mixture was stirred for 30 min. The mixture was extracted with EtOAc (2 x 5 mL) organic layer was washed with H_2O (5 mL), brine (5 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude was purified by column chromatography on silica gel (15 % EtOAc in petroleum ether) to afford the product **5a** (77 mg, 86 % yield) as yellow solid. R_f = 0.5(petroleum ether: EtOAc = 4:1); M.P: 98-100 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.23 (d, J = 1.9 Hz, 1H), 8.52 (d, J = 1.9 Hz, 1H), 7.81 (d, J = 16.0 Hz, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 6.55 (d, J = 15.9 Hz, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.60, 165.44, 161.75, 160.91, 150.92, 142.05, 136.40, 131.58, 130.48, 127.84, 123.98, 121.20, 114.04, 55.41, 52.54, 51.90; IR (KBr): ν_{max} = 2925, 2848, 2364, 1716, 1248, 1174, 842, 794 cm^{-1}; MS (ESI): *m/z* 328 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}NO_5$ $(M+H)^+$: 328.1179, found: 328.1192.

Methyl 5-(2-hydroxyphenyl)-6-(4-methoxyphenyl)nicotinate (5b):



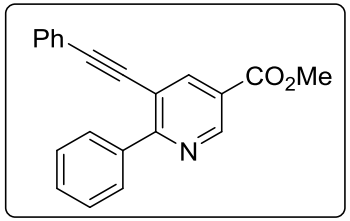
To a solution of **3e** 100 mg, 0.27 mmol), K_3PO_4 (229 mg, 1.08 mmol), $Pd(PPh_3)_4$ (31 mg, 0.02 mmol, 10 mol %), and (2-hydroxyphenyl)boronic acid (49 mg, 0.35 mmol) in DMF (5 mL) was degassed with N_2 for 20 min. The reaction mixture was heated at 80 ^oC for 6 h. After the completion of reaction, DMF was removed under vacuum, and the residue was dissolved in EtOAc (5 mL), filtered through celite and concentrated *in vacuo*. The crude was purified by column chromatography on silica gel (15 % EtOAc in petroleum ether) to afford the product **5b** (67 mg, 73% yield) as yellow solid. R_f = 0.5(petroleum ether: EtOAc = 4:1); M.P: 120-122 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.22 (d, J = 2.0 Hz, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.40 (d, J = 8.8 Hz, 2H), 7.22 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.76 (m, 3H), 3.96 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.73, 160.66, 160.25, 152.26, 149.82, 140.86, 131.27, 131.06, 130.94, 130.69, 129.75, 126.23, 123.75, 121.26, 116.41, 113.55, 55.19, 52.40; IR (KBr): ν_{max} = 3377, 2922, 1701, 1593, 1254, 1166, 755 cm^{-1}; MS (ESI): *m/z* 336 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{18}NO_4$ $(M+H)^+$: 336.1230, found: 336.1247.

Methyl 6-(4-methoxyphenyl)-5-(phenylethynyl)nicotinate (5c):



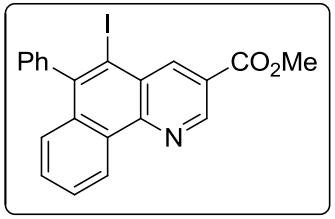
To a solution of **3e** (100 mg, 0.27 mmol) in trethylamine (3 mL) was added to a mixture of $Pd(Ph_3)_2Cl_2$ (19 mg, 0.027 mmol, 10 mol %) and copper(I)iodide (10 mg, 0.05 mmol, 20 mol %) in a flame dried flask. The mixture was degassed with N_2 for 15 min. Phenylacetylene (0.12 mL, 1.08 mmol) was added, and the mixture was stirred at room temperature overnight. After the completion of reaction, the mixture was diluted with Water (3 mL) and then the mixture was extracted with EtOAc (10 mL x 2). The combined organic layers were dried with anhydrous Na_2SO_4, filtered through celite, and concentrated *in vacuo*. The crude was purified by column chromatography on silica gel (18 % EtOAc in petroleum ether) to afford the product **5c** (87 mg, 93 % yield) as yellow solid. R_f = 0.4 (petroleum ether: EtOAc = 4:1); M.P: 100-102 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.16 (d, J = 2.1 Hz, 1H), 8.50 (d, J = 2.1 Hz, 1H), 8.13 (d, J = 8.8 Hz, 2H), 7.46 (dd, J = 6.6, 3.0 Hz, 2H), 7.37-7.34 (m, 3H), 7.03 (d, J = 8.8 Hz, 2H), 3.99 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.28, 161.92, 160.89, 150.84, 149.16, 142.03, 137.70, 131.44, 131.05, 128.84, 128.42, 123.06, 122.54, 118.87, 116.93, 114.22, 113.37, 95.13, 86.93, 55.34, 52.41; IR (KBr): ν_{max} = 2926, 1720, 1580, 1258, 1105, 751 cm^{-1}; MS (ESI): *m/z* 344 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{22}H_{18}NO_3$ $(M+H)^+$: 344.1281, found: 344.1292.

Methyl 6-phenyl-5-(phenylethynyl)nicotinate (5d):



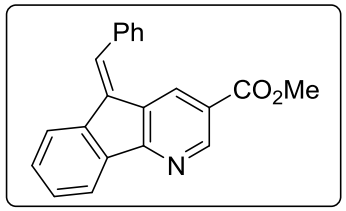
To a solution of **3a** (100 mg, 0.29 mmol) in trethylamine (5 mL) was added to a mixture of $Pd(Ph_3)_2Cl_2$ (21 mg, 0.02 mmol, 10 mol %) and copper(I)iodide (11 mg, 0.05 mmol, 20 mol %) in a flame dried flask. The mixture was degassed with N_2 for 15 min. Phenylacetylene (129 µL, 1.40 mmol) was added, and the mixture was stirred at room temperature overnight. After the completion of reaction, the mixture was diluted with Water (3 mL) and then the mixture was extracted with EtOAc (10 mL x 2). The combined organic layers were dried with anhydrous Na_2SO_4, filtered through celite, and concentrated *in vacuo*. The crude was purified by column chromatography on silica gel (10 % EtOAc in petroleum ether) to afford the product **5d** (78 mg, 85 % yield) as yellow solid. R_f = 0.6 (petroleum ether: EtOAc = 4:1); M.P: 110-115 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.20 (d, J = 1.6 Hz, 1H), 8.53 (d, J = 1.7 Hz, 1H), 8.15 – 8.00 (m, 2H), 7.53 – 7.31 (m, 8H), 4.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.16, 162.56, 149.14, 141.79, 138.43, 131.42, 129.62, 129.42, 128.87, 128.38, 127.94, 123.67, 122.40, 117.68, 95.35, 86.55, 52.47; IR (KBr): ν_{max} = 2926, 2205 1720, 1268, 1204, 745, 686 cm^{-1}; MS (ESI): *m/z* 314 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{21}H_{16}NO_2$ $(M+H)^+$: 314.1175, found: 314.1168.

Methyl 5-iodo-6-phenylbenzo[*h*]quinoline-3-carboxylate (6a):



To a solution methyl 6-phenyl-5-(phenylethynyl)nicotinate (**5d,** 30 mg, 0.095 mmol) in CH_2Cl_2 (3 mL) was slowly added solution of ICl in DCM (0.4 mL, 0.19 mmol) at 0 ^oC and the reaction mixture stirred for 48 h at room temperature. Upon completion, the reaction was diluted with CH_2Cl_2 (5 mL), washed with saturated aq. $Na_2S_2O_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (18 % EtOAc in petroleum ether) to afford the corresponding product **6a** (29 mg, 71% yield) as yellow solid. R_f = 0.4 (petroleum ether: EtOAc = 4:1); M.P: 170-175 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 9.50 (d, J = 2.0 Hz, 1H), 9.41 (dd, J = 8.3, 0.8 Hz, 1H), 9.30 (d, J = 2.0 Hz, 1H), 7.78 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.61 – 7.55 (m, 4H), 7.42 (d, J = 8.3 Hz, 1H), 7.32 – 7.29 (m, 2H), 4.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.68, 149.58, 148.76, 147.00, 144.18, 143.86, 134.73, 130.94, 129.79, 129.70, 128.63, 128.20, 128.03, 127.79, 127.03, 125.58, 125.04, 103.58, 52.63; IR (KBr): ν_{max} = 2921, 1721, 1318, 1269, 1251, 763 cm^{-1}; MS (ESI): *m/z* 440 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{21}H_{15}IO_2N$ $(M+H)^+$: 440.0142, found: 440.0126.

(*Z*)-Methyl-5-benzylidene-5*H*-indeno[1,2-*b*]pyridine-3-carboxylate (6b):



To a solution of **5d** (30 mg, 0.095 mmol), $Pd(OAc)_2$ (1 mg, 0.004 mmol), 1,1-bis(diphenylphosphino)ferrrocene (5 mg, 0.009 mmol) and toluene (0.3 mL) were added under N_2 atmosphere. The reaction mixture was stirred at room temperature for 5 min. Water (1.5µL, 0.09 mmol) was then added via microsyringe. The reaction mixture was heated at 100 ^oC and stirred at this temperature for 24 h. Upon completion of the reaction, resultant mixture was cooled to room temperature, diluted with CH_2Cl_2 (1 mL), and filtered through a celite plug. The filtrate was concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (15 % EtOAc in petroleum ether) to afford the azafluorene **6b** (21 mg, 68% yield) as yellow solid. R_f = 0.4 (petroleum ether: EtOAc = 4:1); M.P: 170-175 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.43 (s, 1H), 8.19 – 8.04 (m, 1H), 7.90 (s, 2H), 7.53 (td, J = 17.1, 8.2 Hz, 7H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.32, 163.22, 150.81, 141.01, 137.12, 135.62, 132.84, 132.12, 130.92, 130.05, 129.40, 128.99, 128.76, 123.30, 121.53, 120.32, 52.28; IR (KBr): ν_{max} = 2924, 2853, 1718, 1279, 697 cm^{-1}; MS (ESI): *m/z* 314 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{21}H_{16}NO_2$ $(M+H)^+$: 314.1175, found: 314.1166.

References:

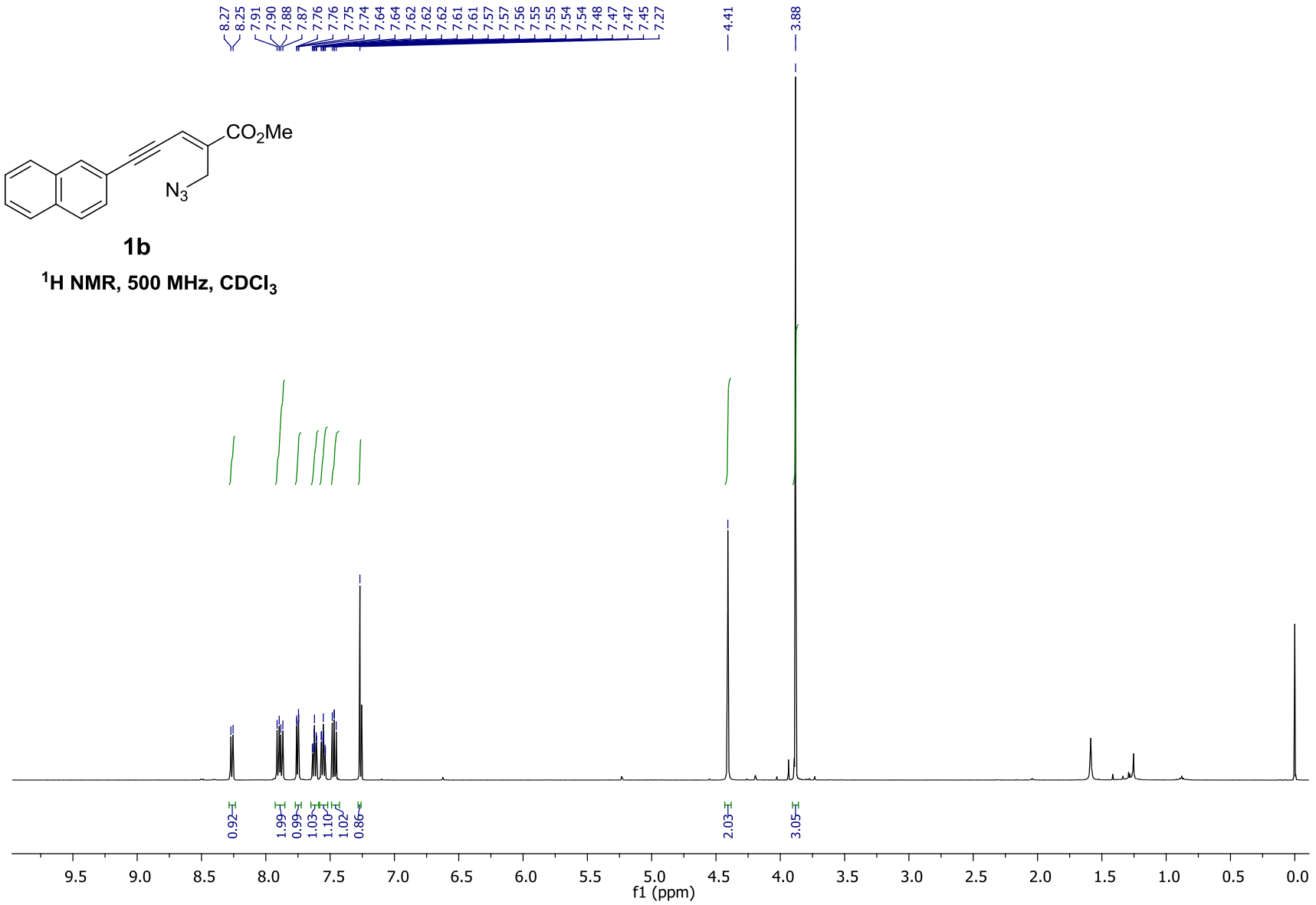
1) Park, S. P.; Ahn, S-H.; Lee, K -J. *Tetrahedron* **2010**, *66*, 3490.

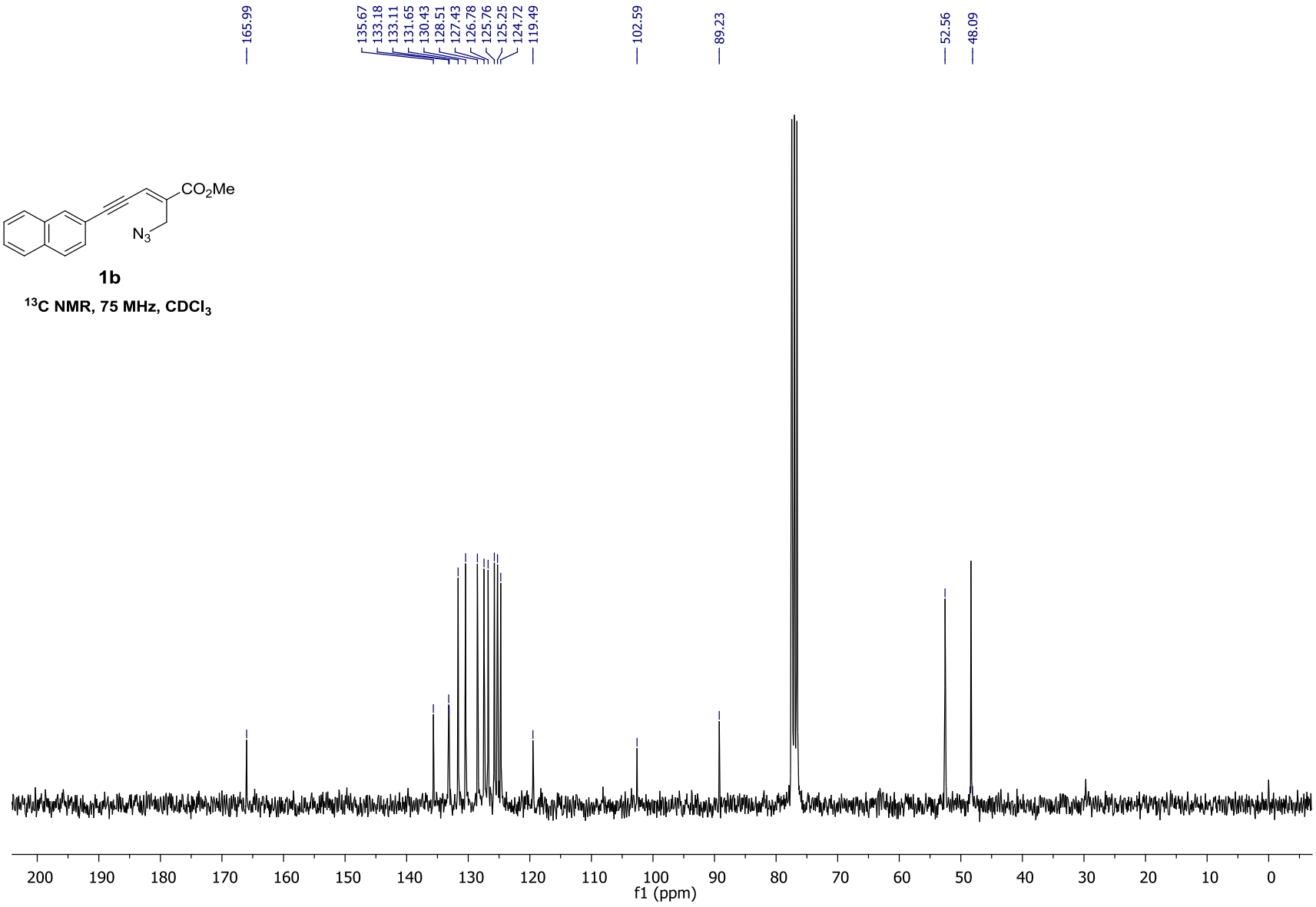
2) Gerber, R.; Frech, C. M. *Chem. Eur. J.* **2011**, *17*, 11893.

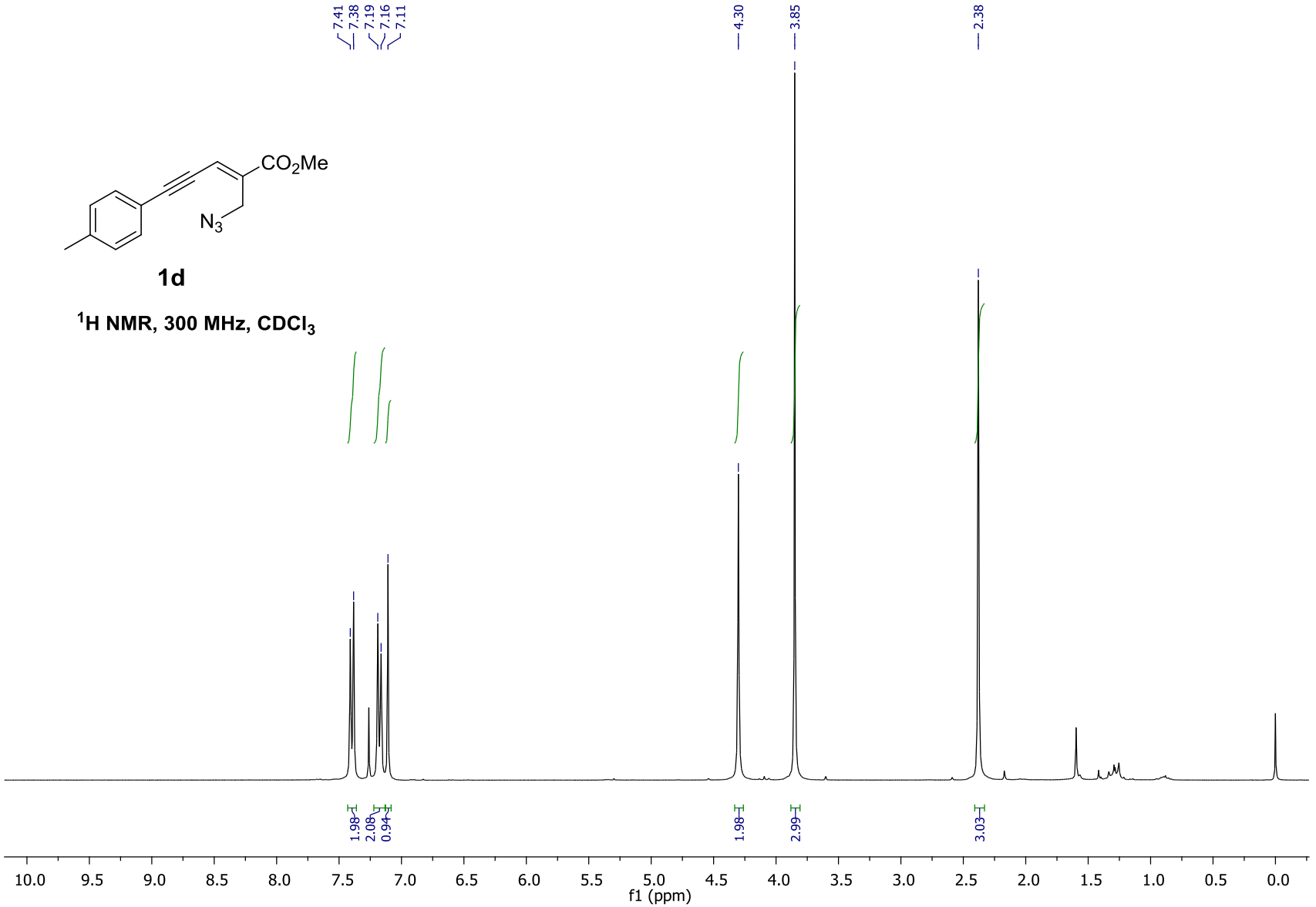
3) Inada, K.; Miyaura, N. *Tetrahedron* **2000**, *56*, 8661.

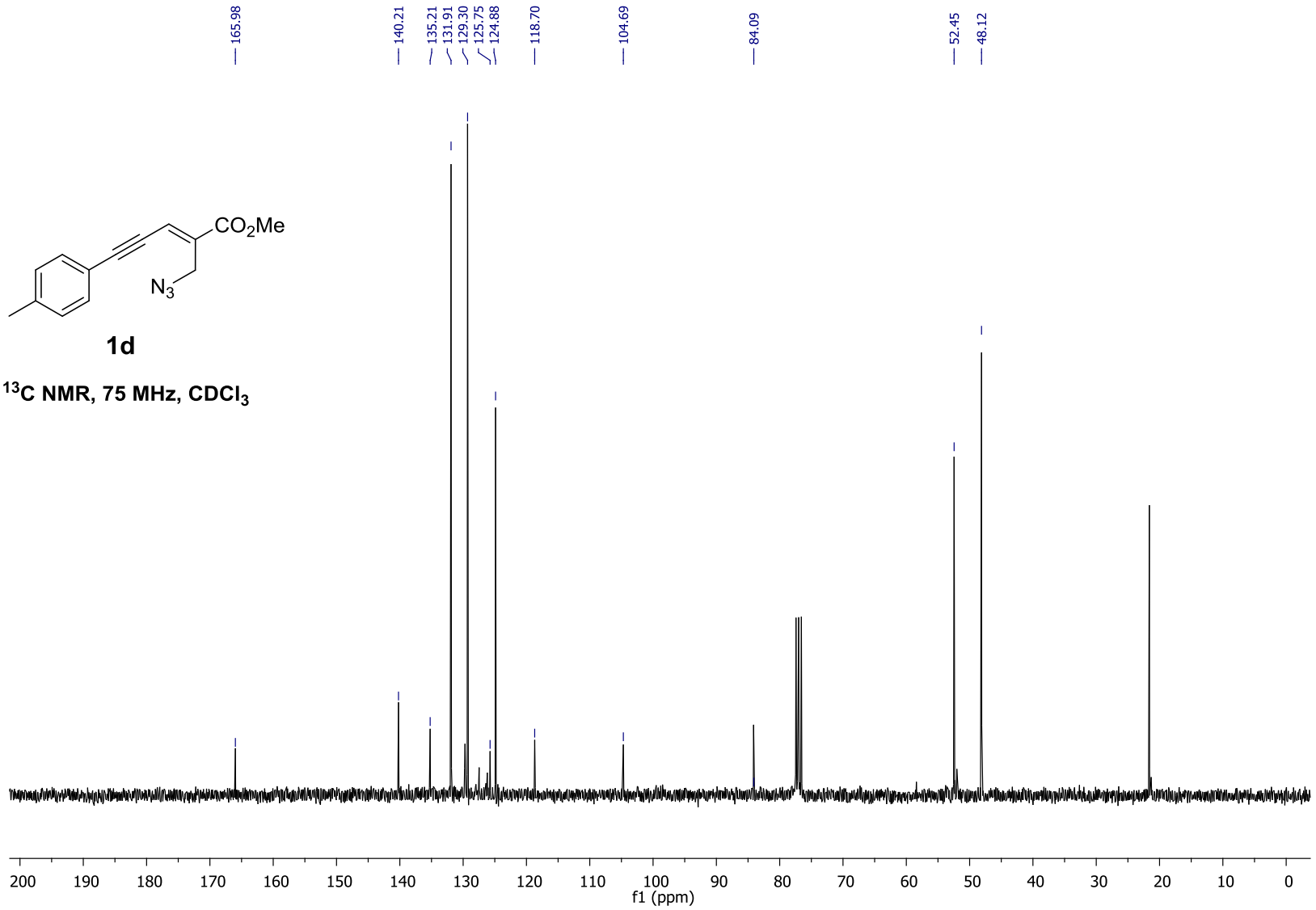
4) Shiao, M.-J.; Liu, K.-H.; Lin, P.-Y. *Heterocycles* **1993**, *36*, 507.

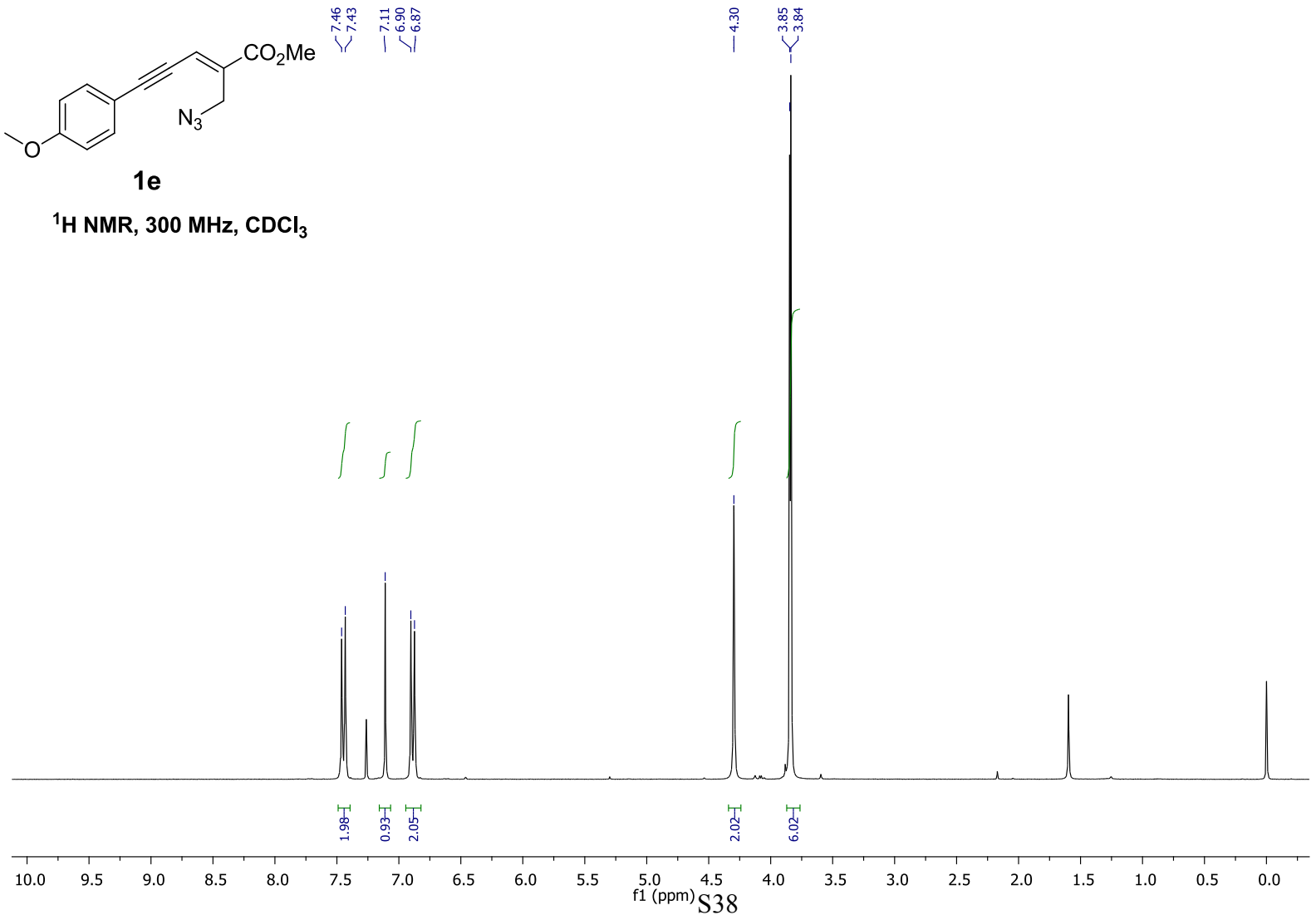
5) (a) El-Deeb, I. M.; Lee, S.H. *Bioorg. Med. Chem.* **2010**, *18*, 3860; (b) Comins, D. L.; Mantlo, N. B. *Tetrahedron Lett.* **1983**, *24*, 3683.


8.27
8.25
7.91
7.90
7.88
7.87
7.76
7.76
7.75
7.74
7.64
7.64
7.62
7.62
7.62
7.61
7.61
7.57
7.57
7.56
7.55
7.55
7.54
7.54
7.48
7.47
7.47
7.45
7.27
4.41
3.88
CO2Me
N3
1b
1H NMR, 500 MHz, CDCl3
0.92
1.99
0.99
1.03
1.10
1.02
0.86
2.03
3.05
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
f1 (ppm)


165.99
135.67
133.18
133.11
131.65
130.43
128.51
127.43
126.78
125.76
125.25
124.72
119.49
102.59
89.23
52.56
48.09
CO2Me
N3
1b
13C NMR, 75 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)

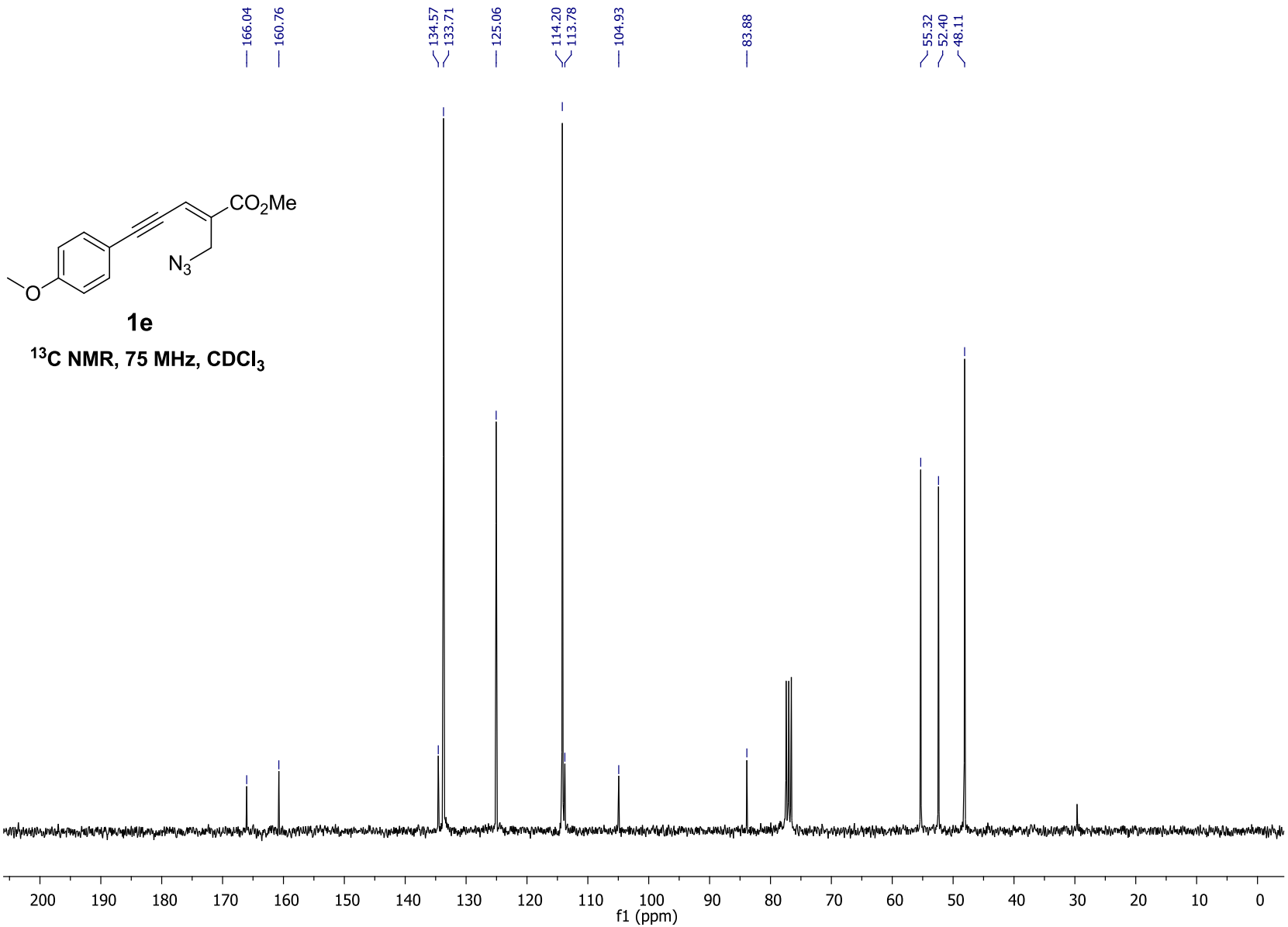

7.41
7.38
7.19
7.16
7.11
4.30
3.85
2.38
CO2Me
N3
1d
1H NMR, 300 MHz, CDCl3
1.98
2.06
0.94
1.98
2.99
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

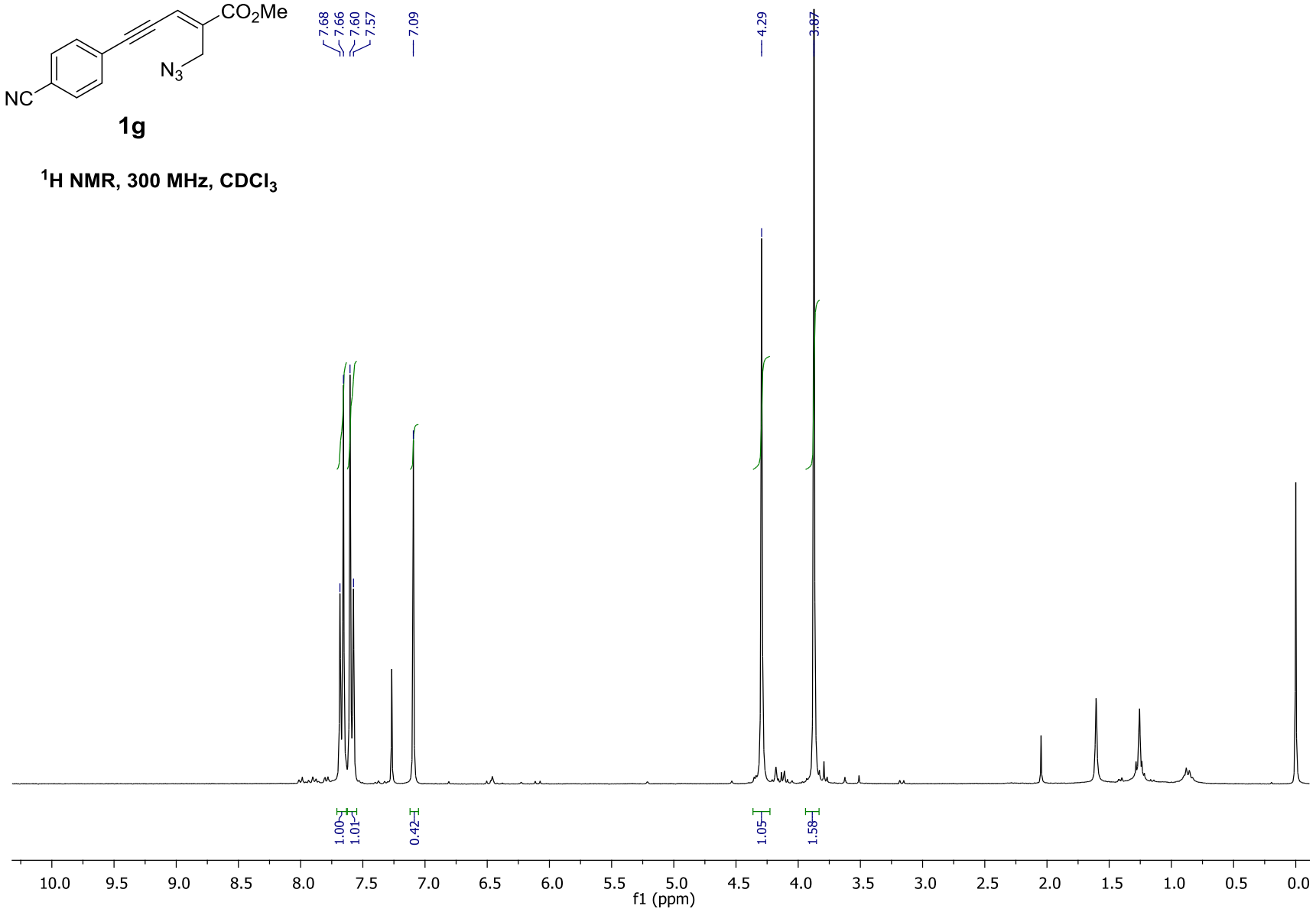

165.98
140.21
135.21
131.91
129.30
125.75
124.88
118.70
104.69
84.09
52.45
48.12
CO2Me
N3
1d
13C NMR, 75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



1e

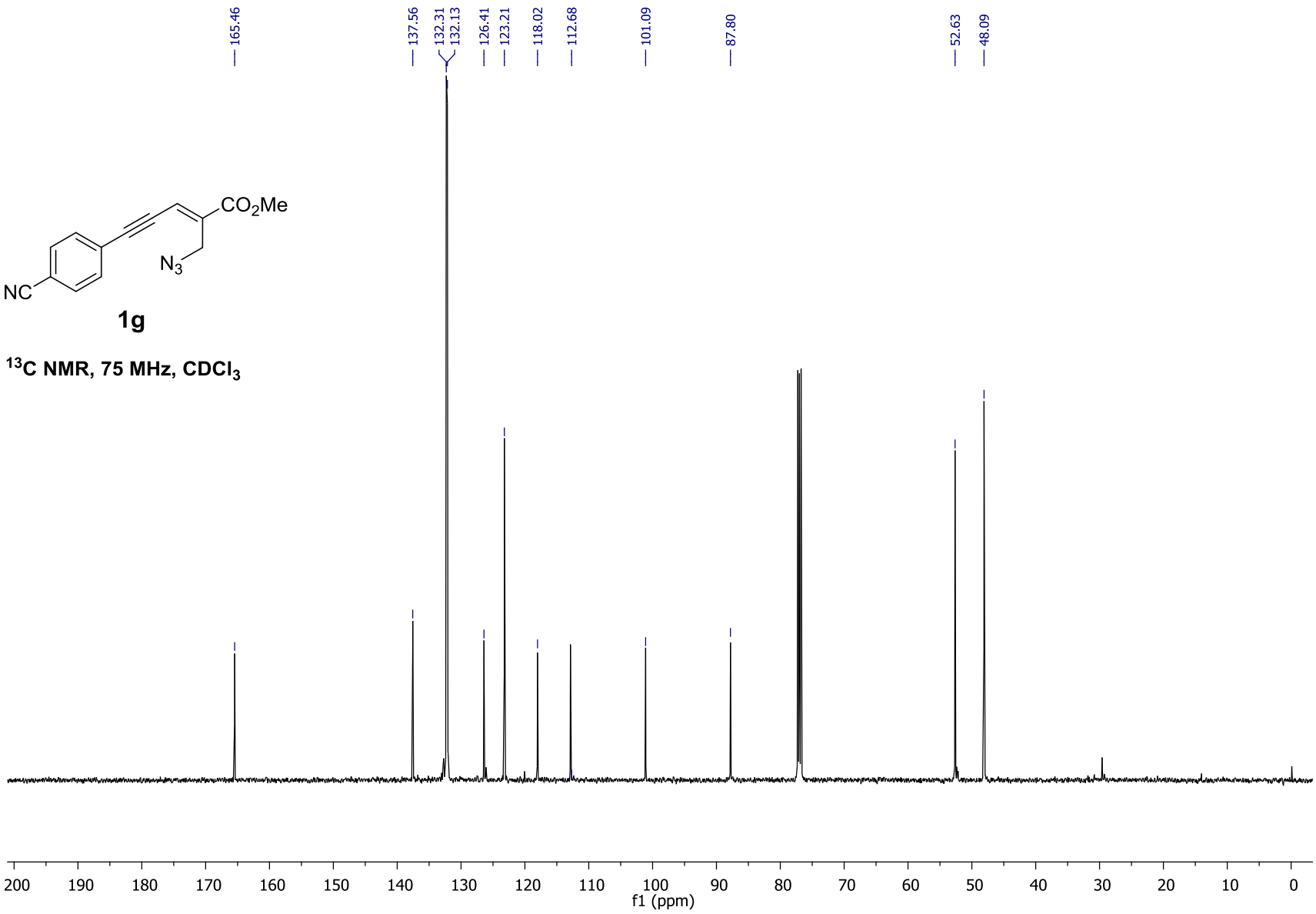
^{1}H NMR, 300 MHz, $CDCl_3$

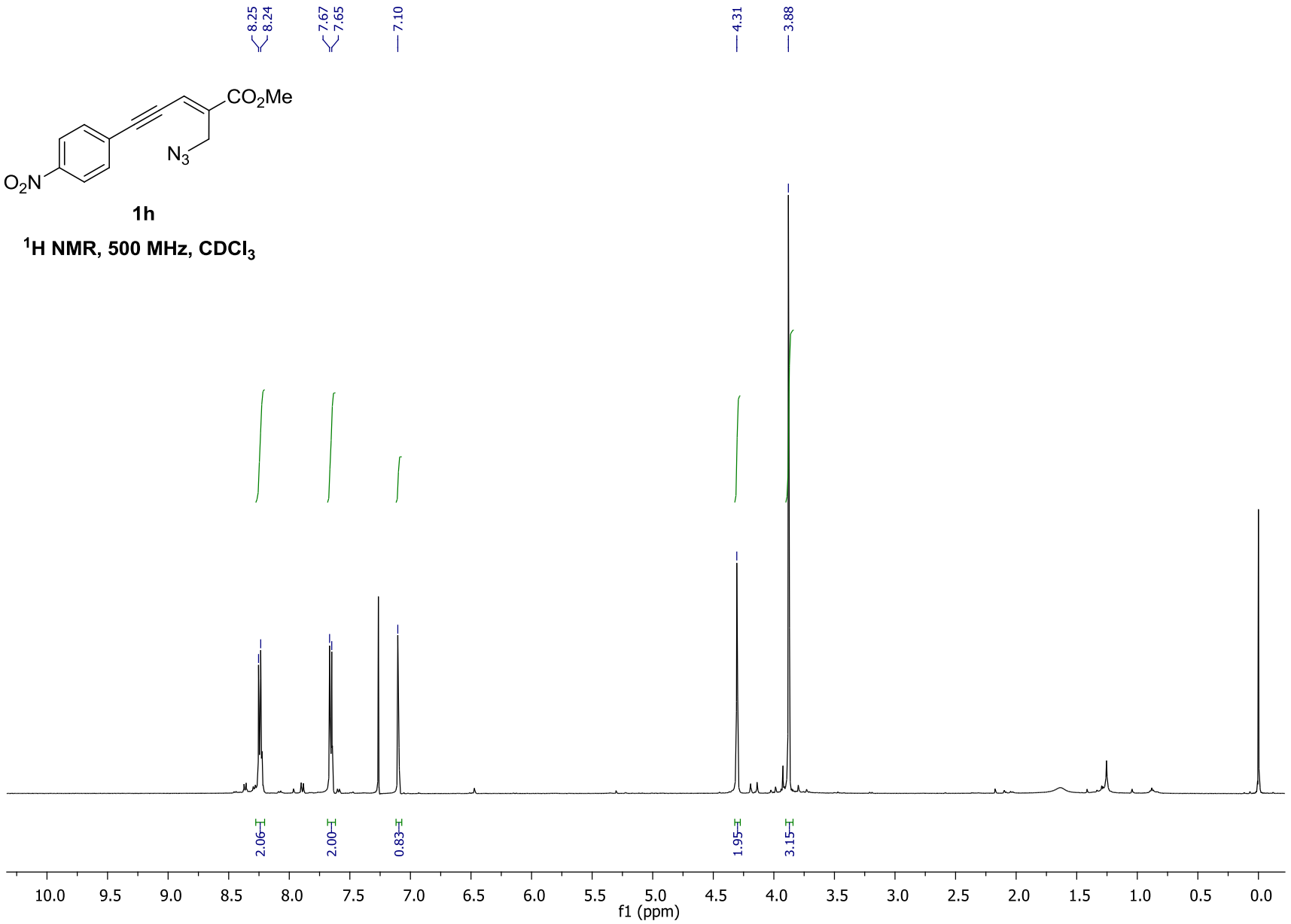

166.04
160.76
134.57
133.71
125.06
114.20
113.78
104.93
83.88
55.32
52.40
48.11
CO2Me
N3
O
1e
13C NMR, 75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

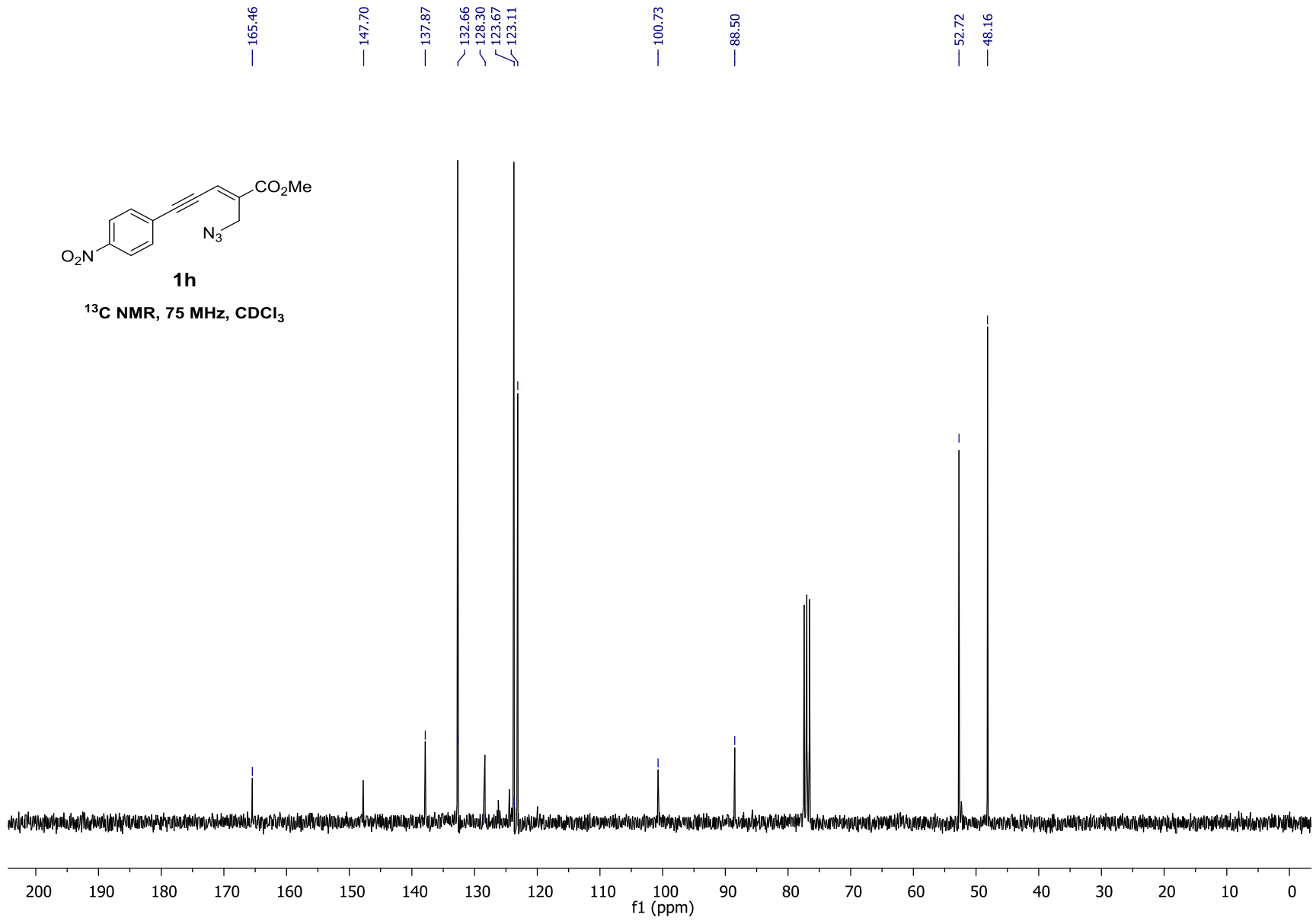


1g

^{1}H NMR, 300 MHz, $CDCl_3$


165.46
137.56
132.31
132.13
126.41
123.21
118.02
112.68
101.09
87.80
52.63
48.09
CO2Me
N3
NC
1g
13C NMR, 75 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)


8.25
8.24
7.67
7.65
7.10
4.31
3.88
CO2Me
N3
O2N
1h
1H NMR, 500 MHz, CDCl3
2.06
2.00
0.83
1.95
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
f1 (ppm)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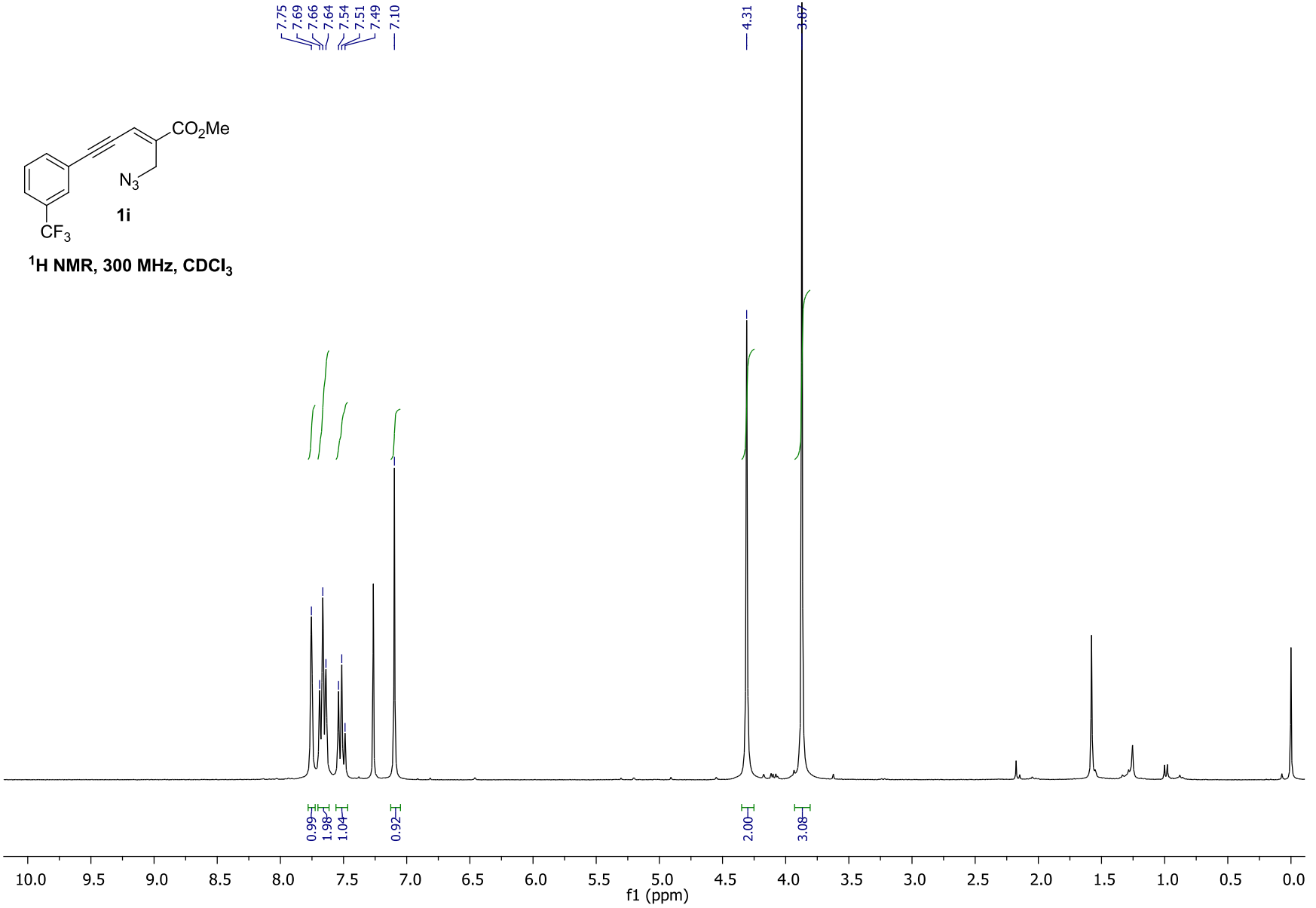
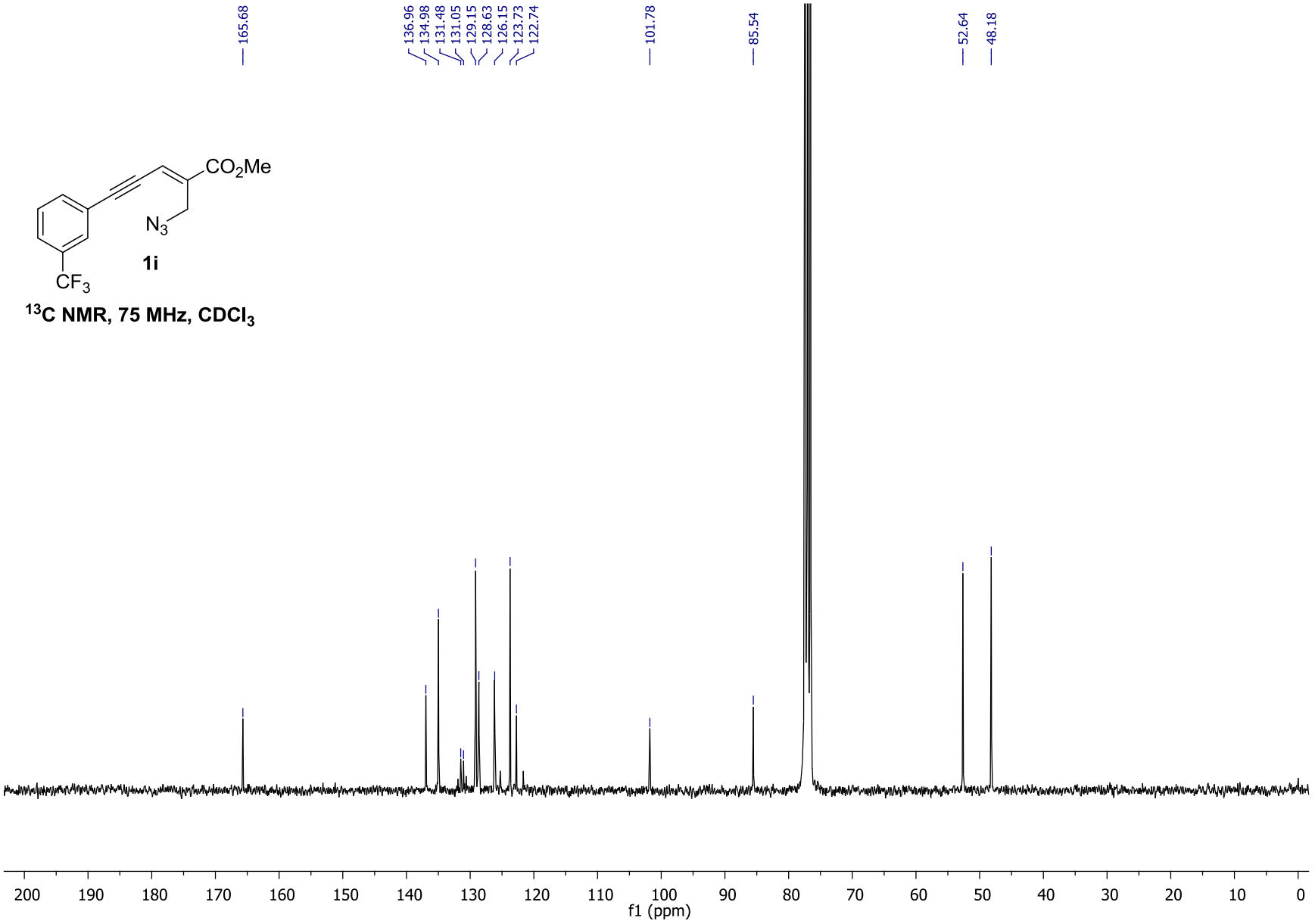
147.70
137.87
132.66
128.30
123.67
123.11
100.73
88.50
52.72
48.16
CO2Me
N3
O2N
1h
13C NMR, 75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.75
7.69
7.66
7.64
7.54
7.51
7.49
7.10
4.31
3.87
CO2Me
N3
CF3
1i
1H NMR, 300 MHz, CDCl3
0.99
1.98
1.04
0.92
2.00
3.08
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
f1 (ppm)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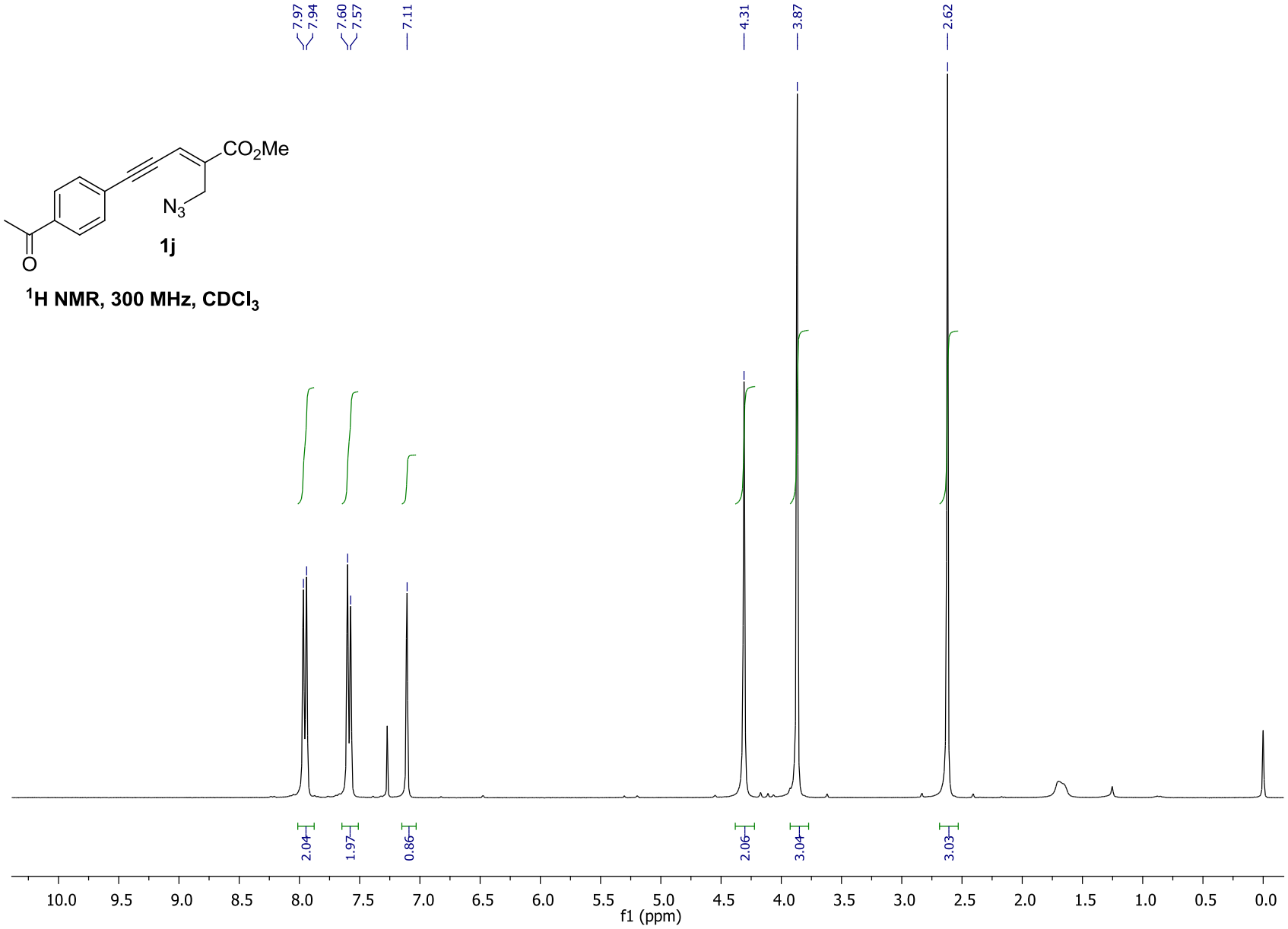
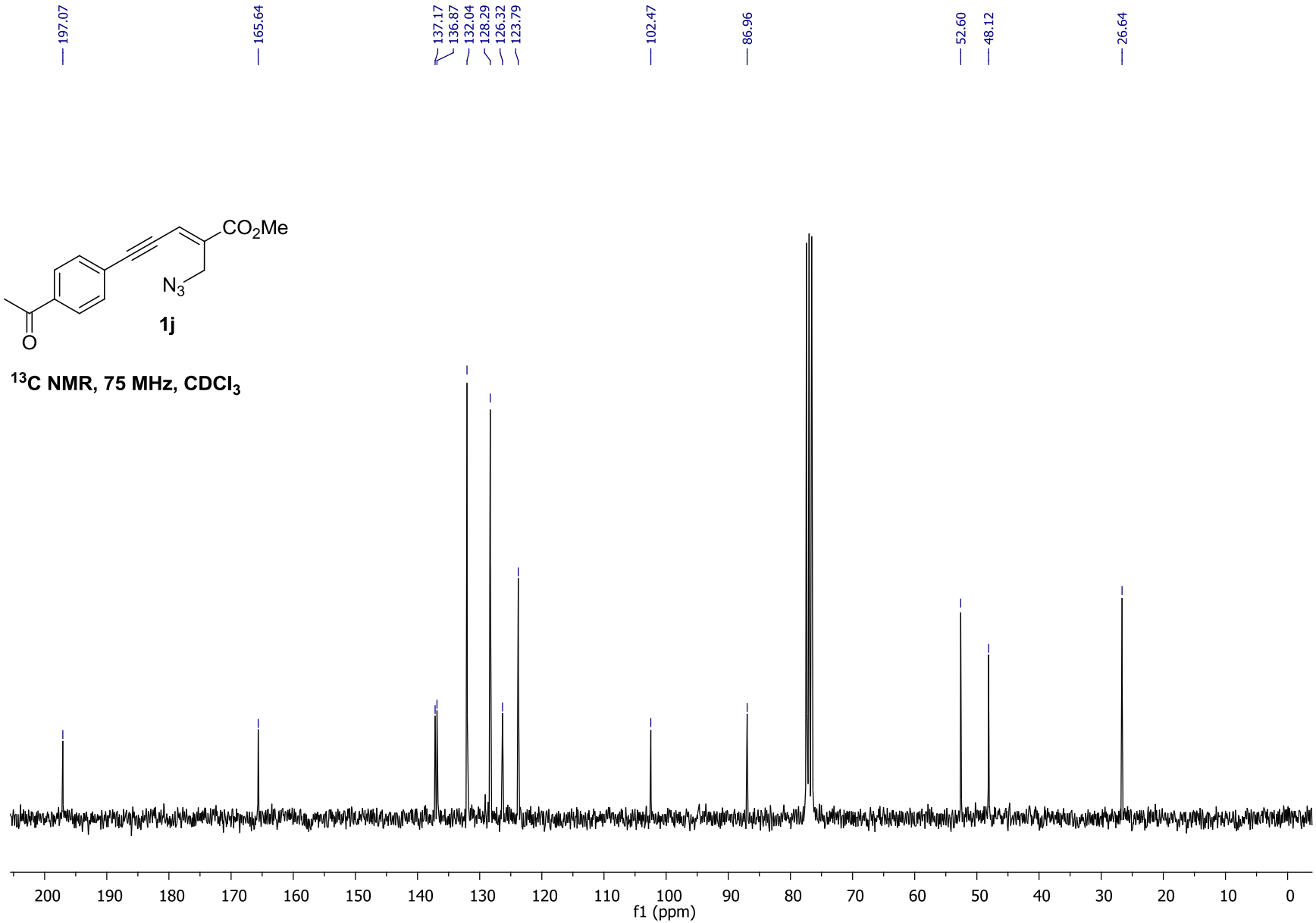
136.96
134.98
131.48
131.05
129.15
128.63
126.15
123.73
122.74
101.78
85.54
52.64
48.18
CO2Me
N3
CF3
1i
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.97
7.94
7.60
7.57
7.11
4.31
3.87
2.62
CO2Me
N3
O
1j
1H NMR, 300 MHz, CDCl3
2.04
1.97
0.86
2.06
3.04
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
f1 (ppm)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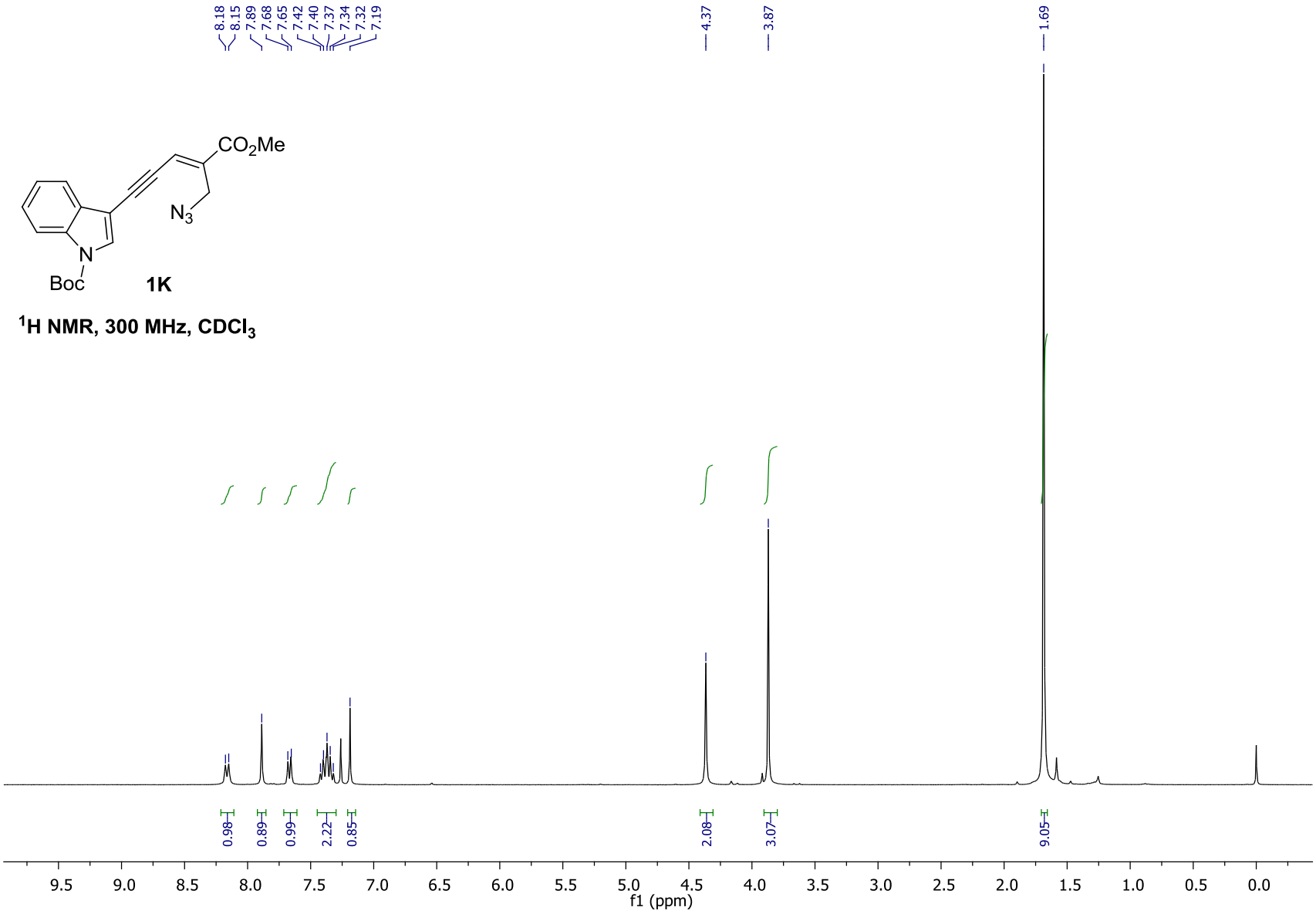
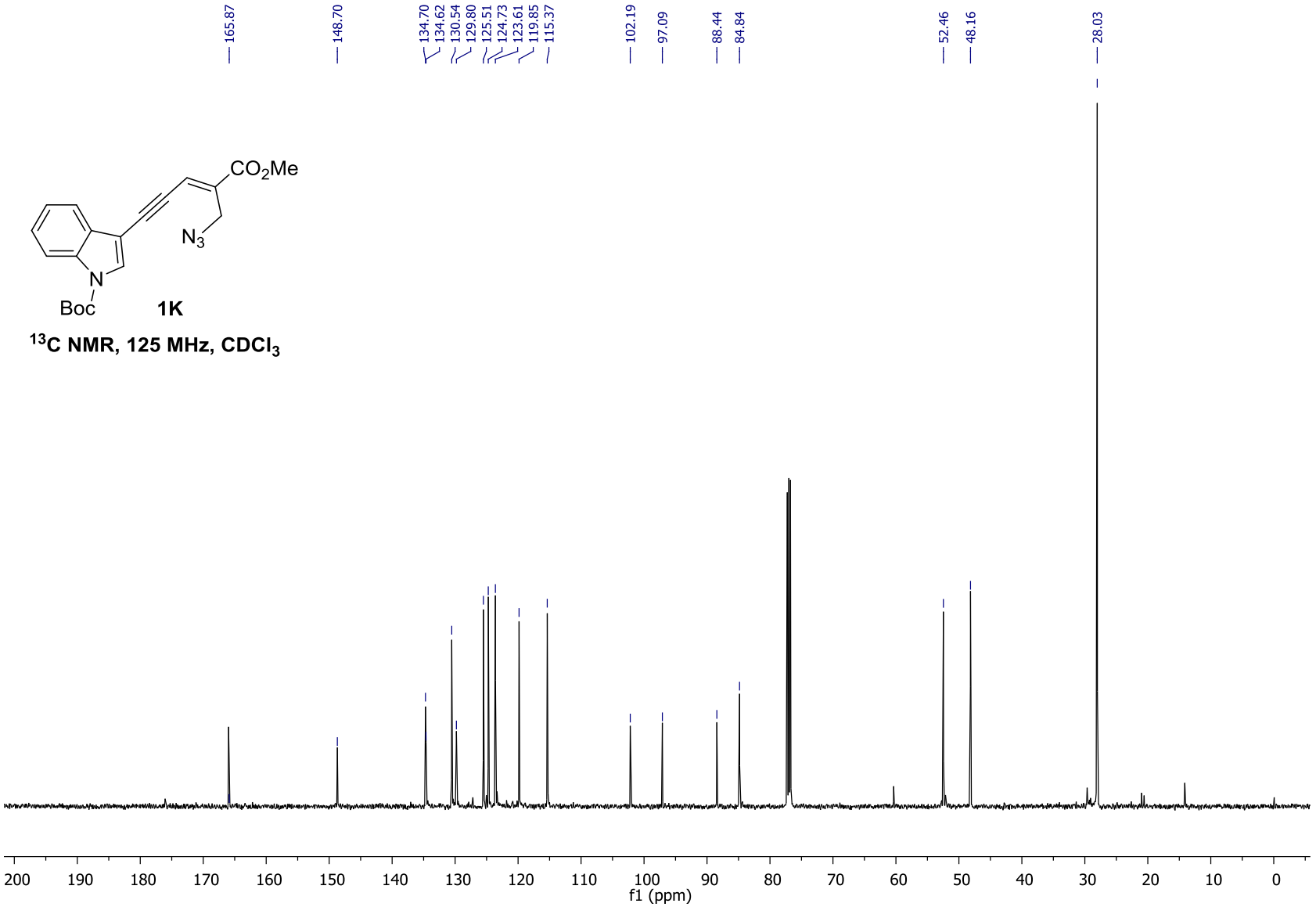
136.87
132.04
128.29
126.32
123.79
102.47
86.96
52.60
48.12
26.64
CO2Me
N3
O
1j
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1K

^{1}H NMR, 300 MHz, $CDCl_3$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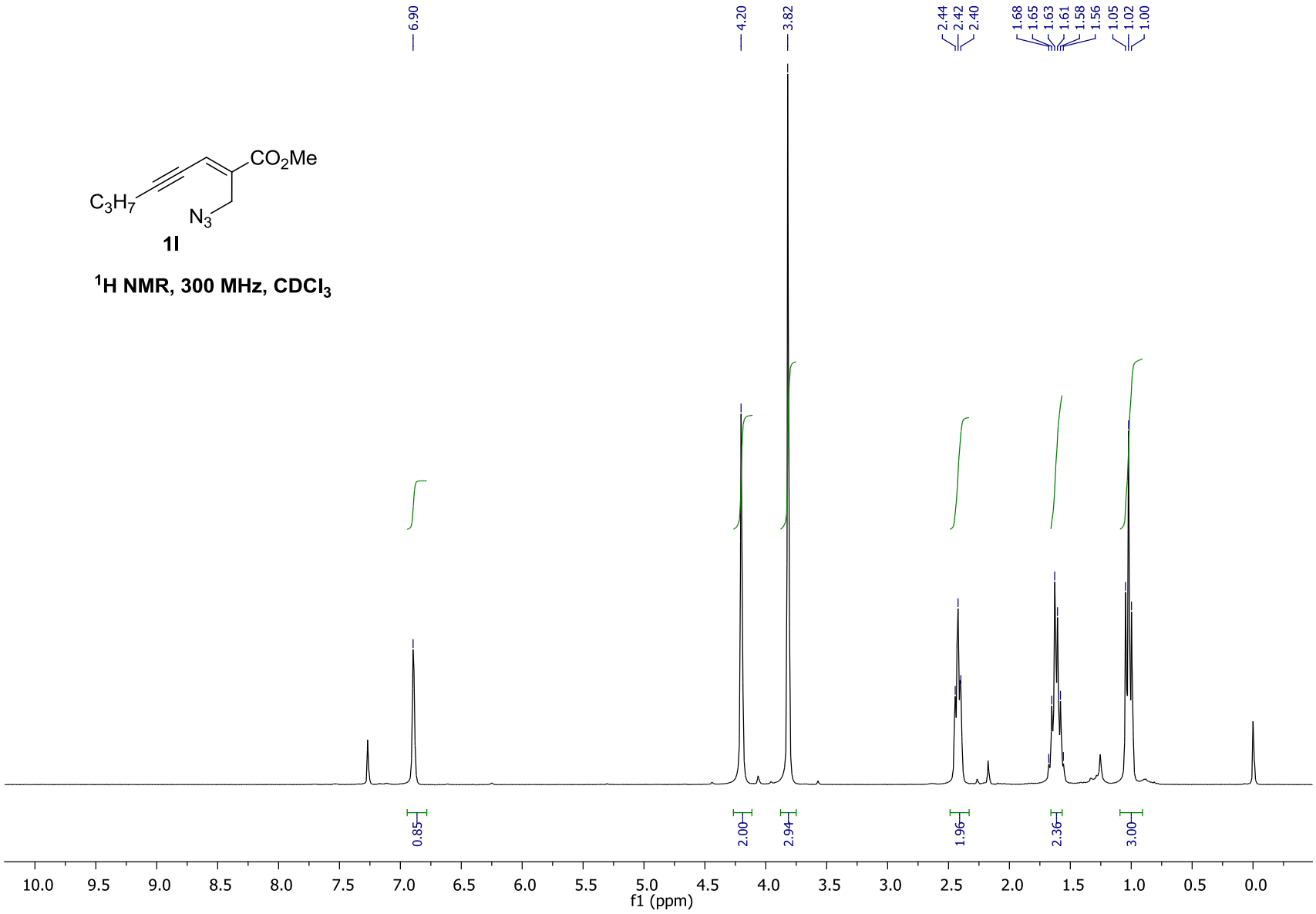
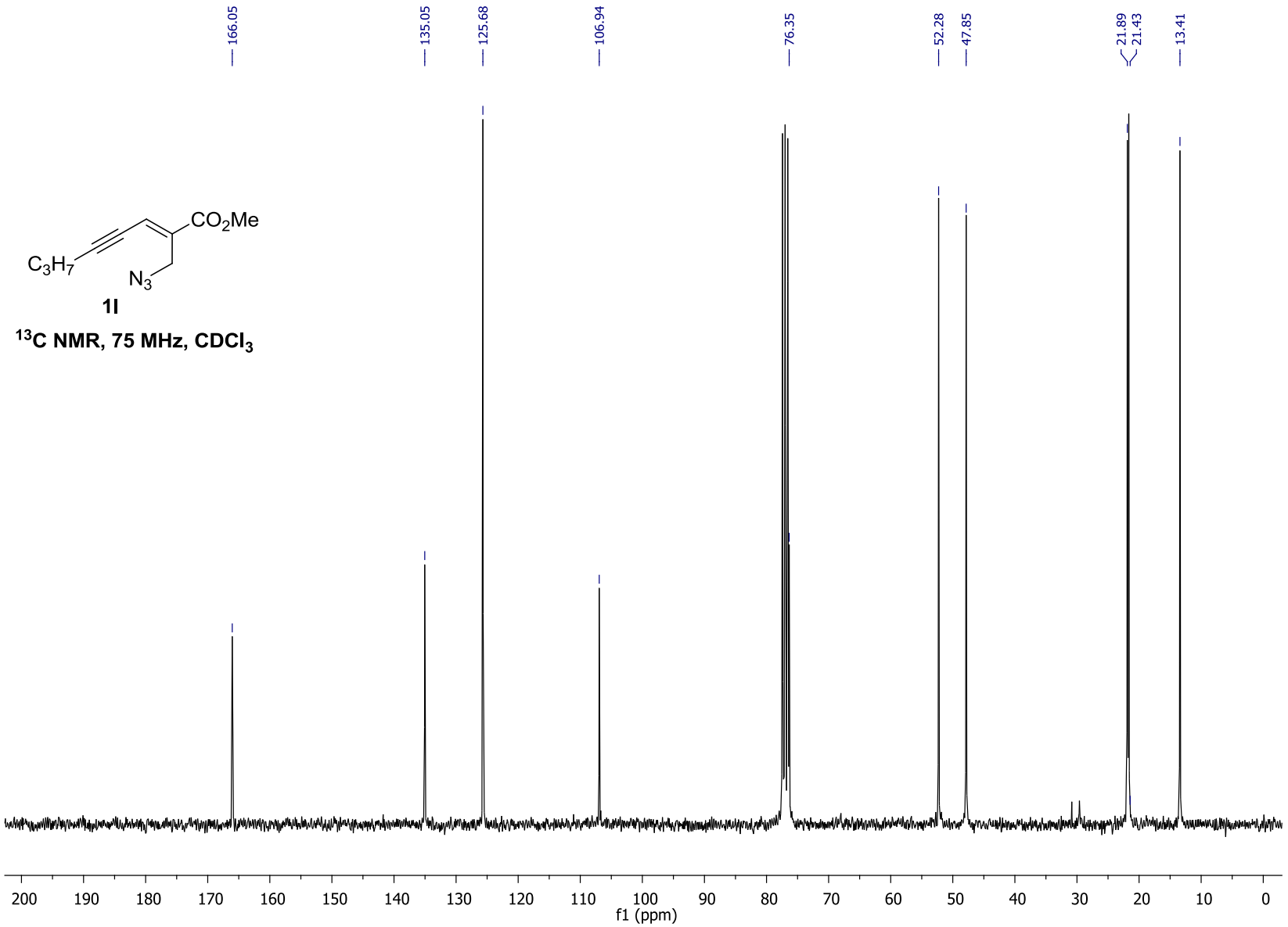
148.70
134.70
134.62
130.54
129.80
125.51
124.73
123.61
119.85
115.37
102.19
97.09
88.44
84.84
52.46
48.16
28.03
CO2Me
N3
N
Boc
1K
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.90
4.20
3.82
2.44
2.42
2.40
1.68
1.65
1.63
1.61
1.58
1.56
1.05
1.02
1.00
CO2Me
C3H7
N3
1l
1H NMR, 300 MHz, CDCl3
0.85
2.00
2.94
1.96
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
f1 (ppm)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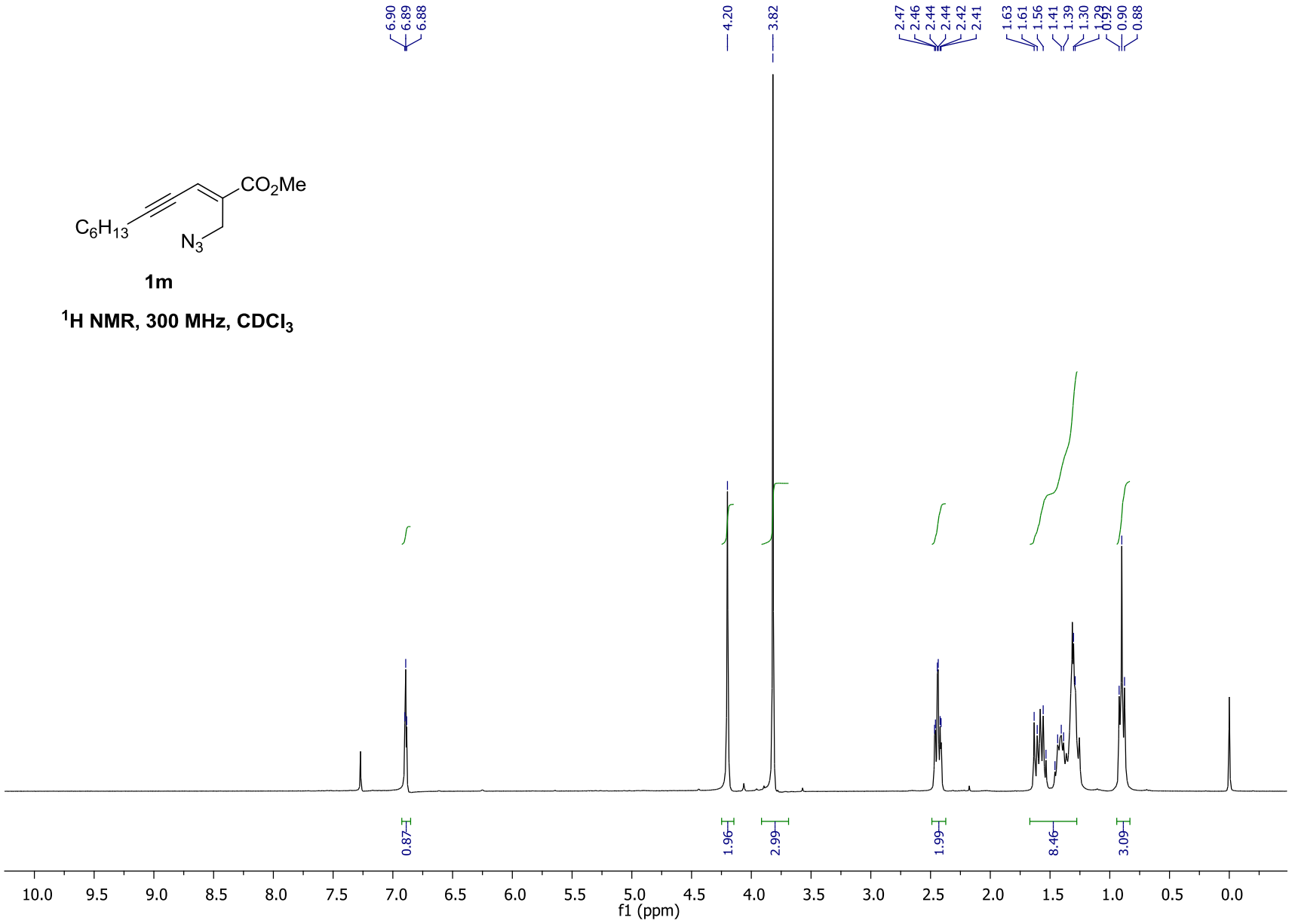
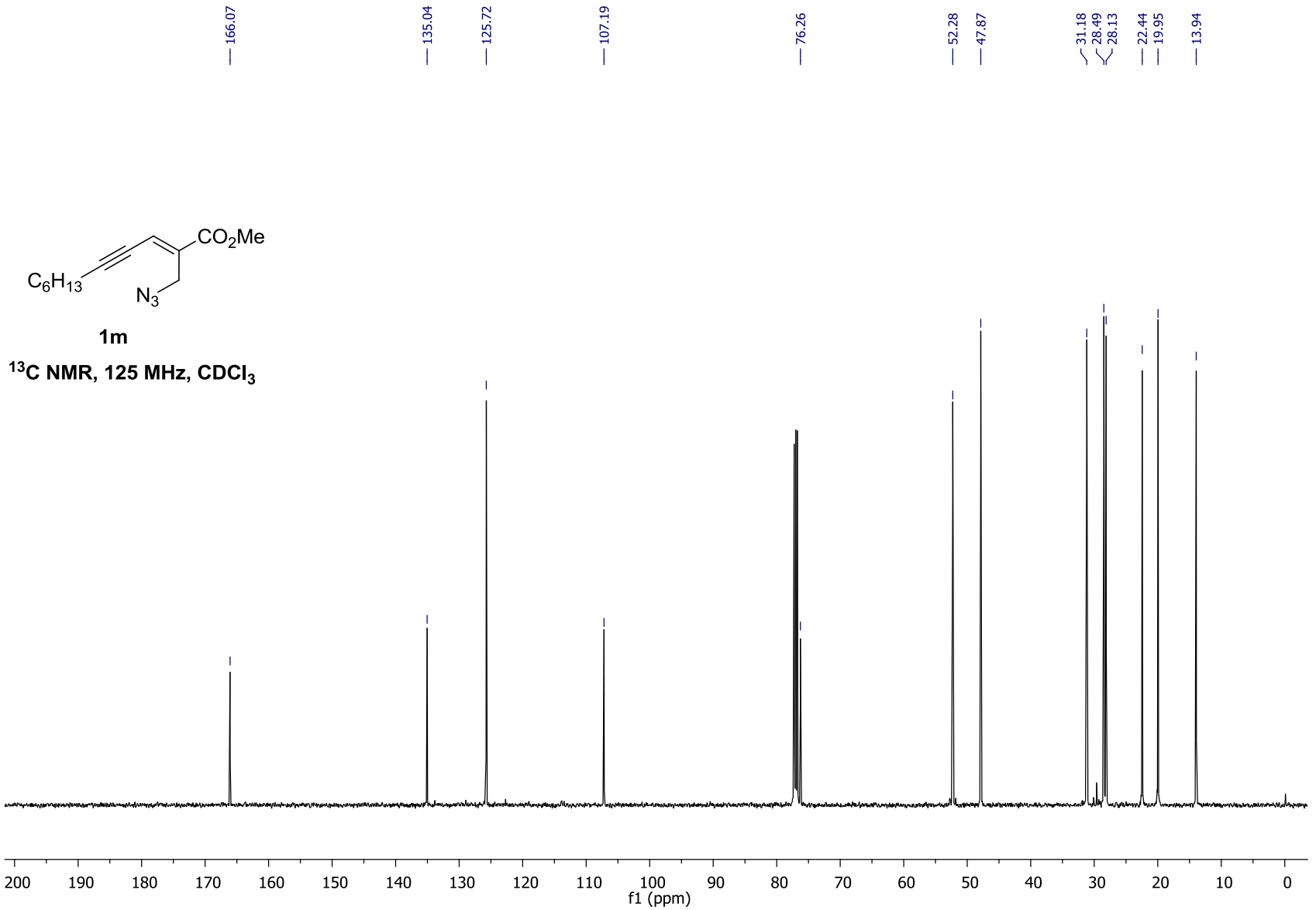
135.05
125.68
106.94
76.35
52.28
47.85
21.89
21.43
13.41
CO2Me
C3H7
N3
1l
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1m

^{1}H NMR, 300 MHz, $CDCl_3$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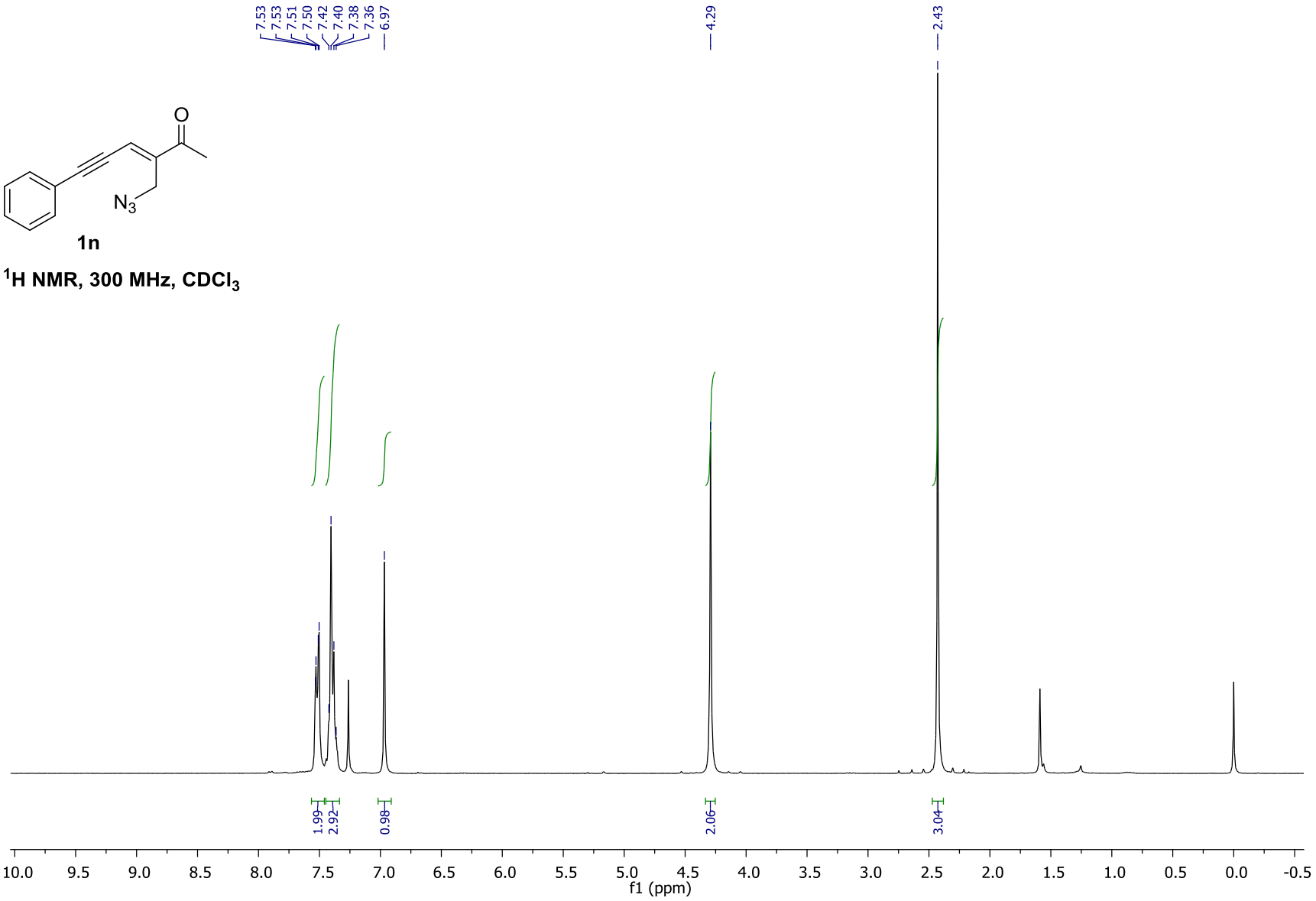
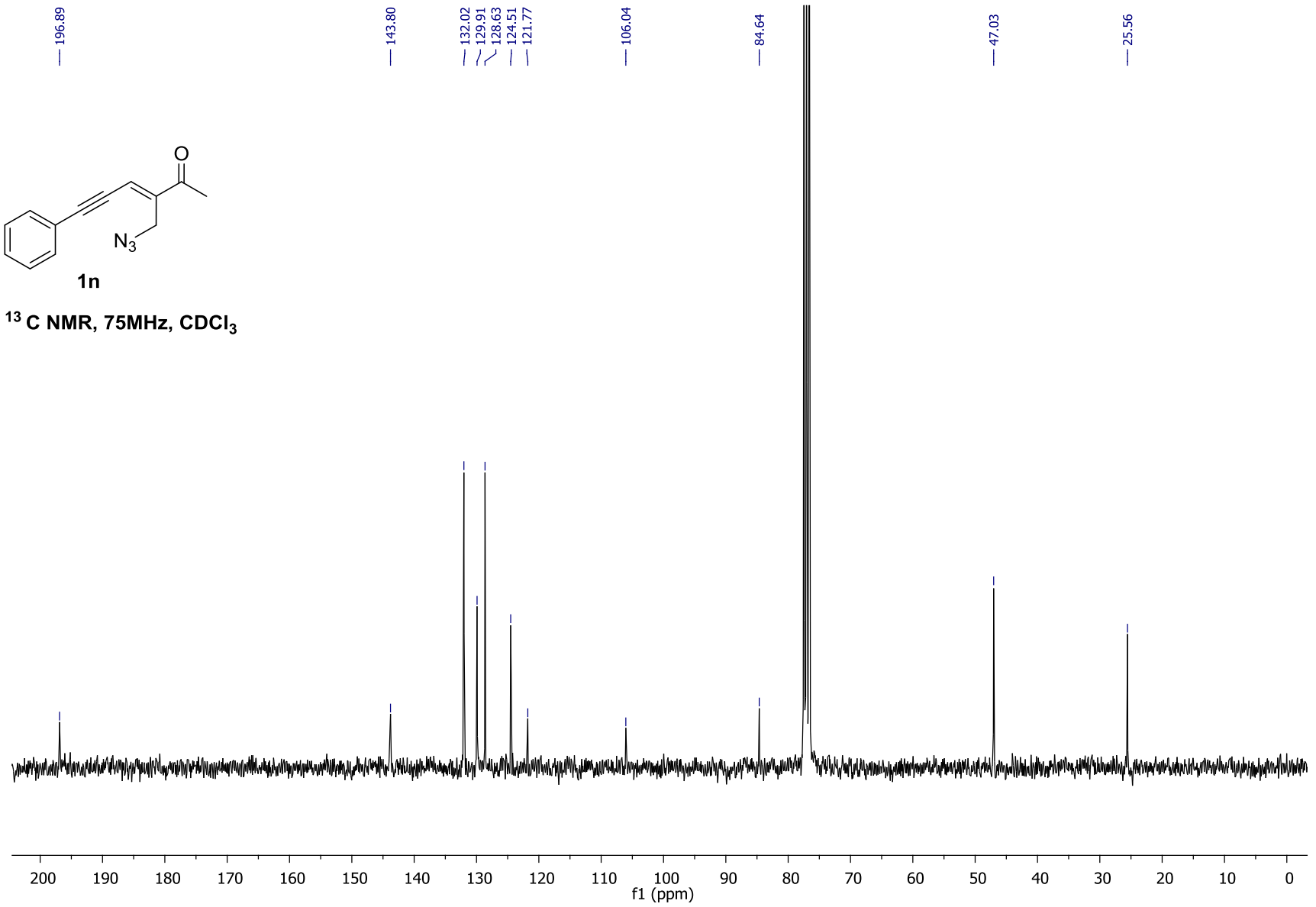
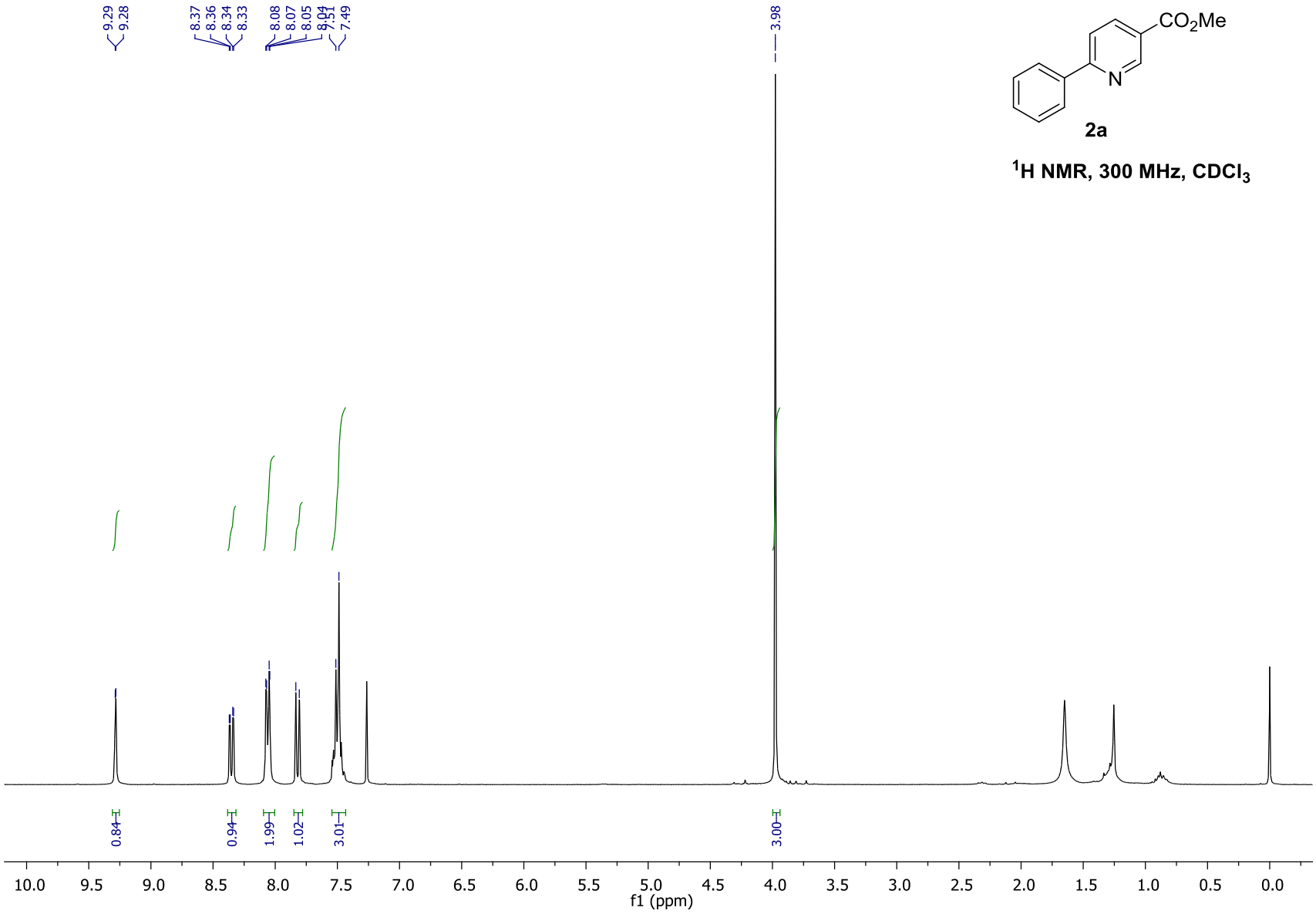
135.04
125.72
107.19
76.26
52.28
47.87
31.18
28.49
28.13
22.44
19.95
13.94
CO2Me
C6H13
N3
1m
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

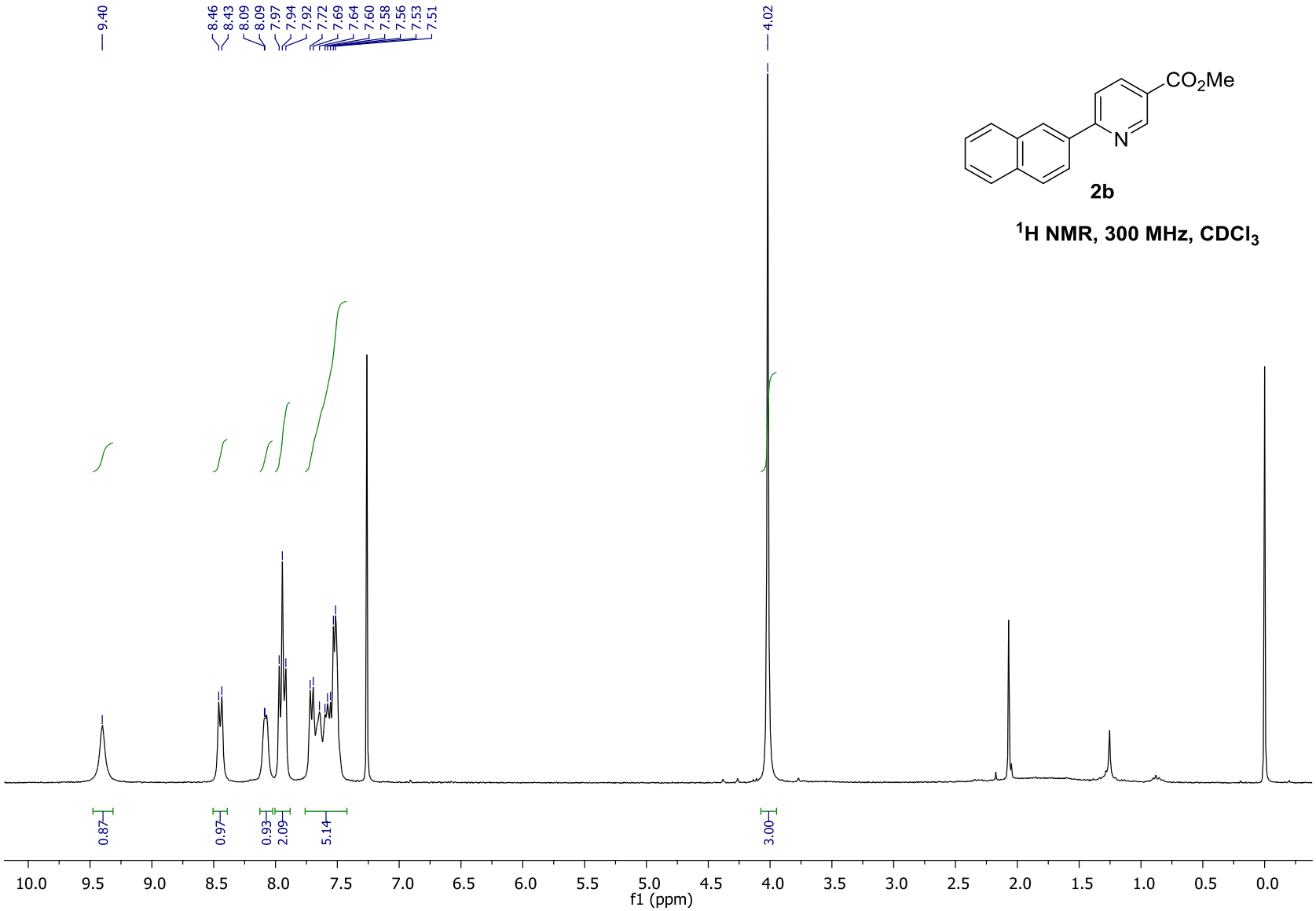

7.53
7.53
7.51
7.50
7.42
7.40
7.38
7.36
6.97
4.29
2.43
O
N3
1n
1H NMR, 300 MHz, CDCl3
1.99
2.92
0.98
2.06
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

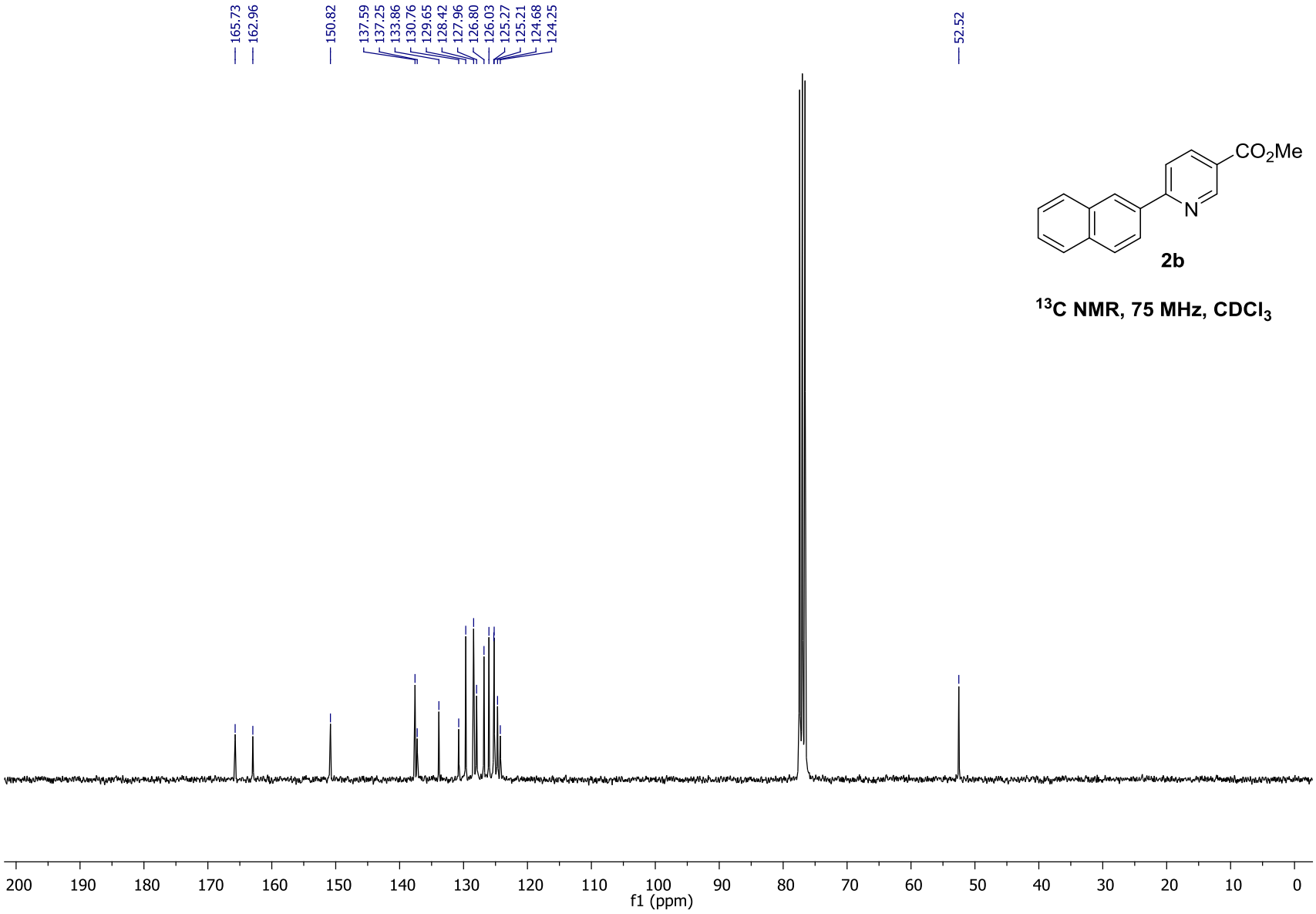


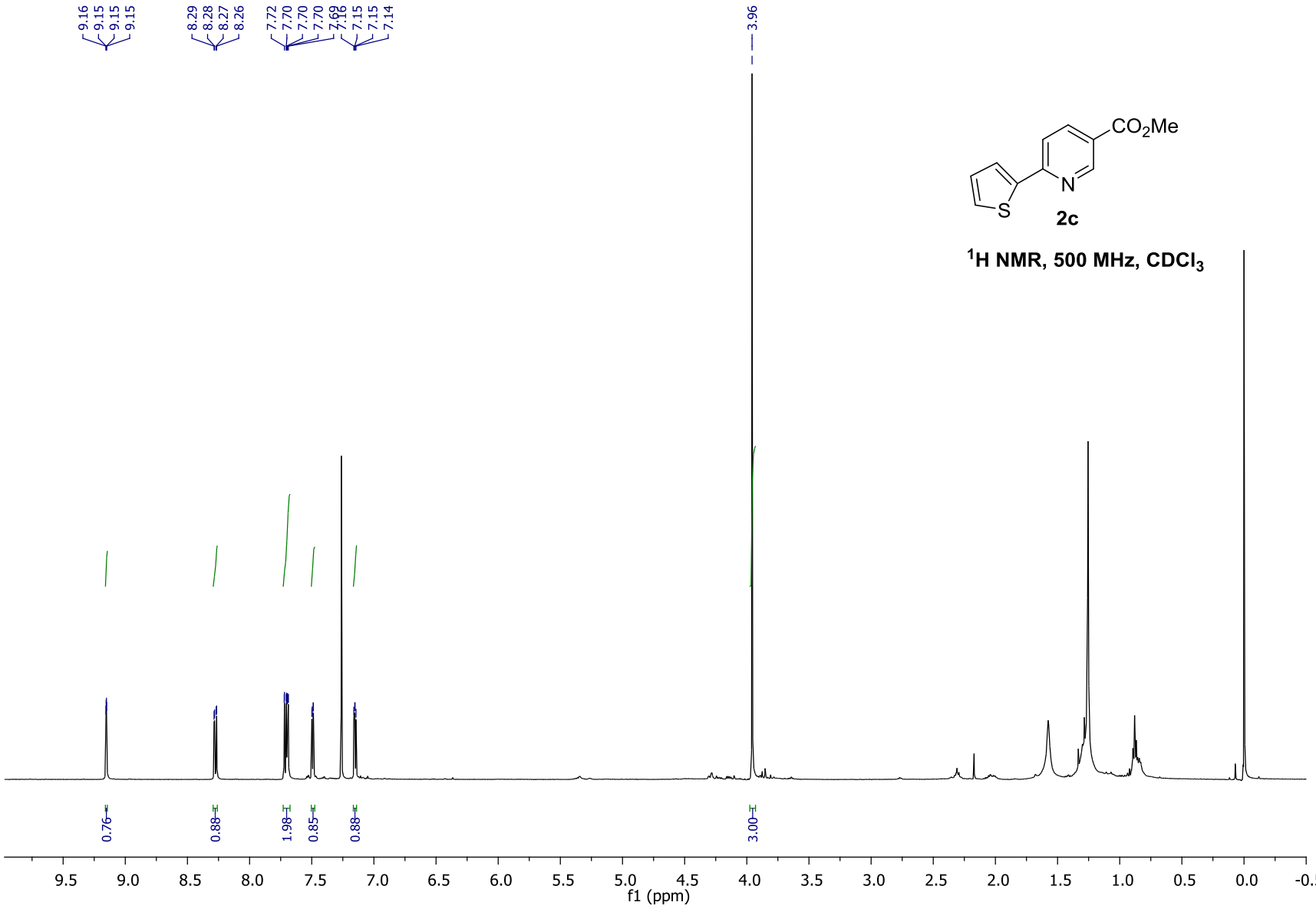
1n

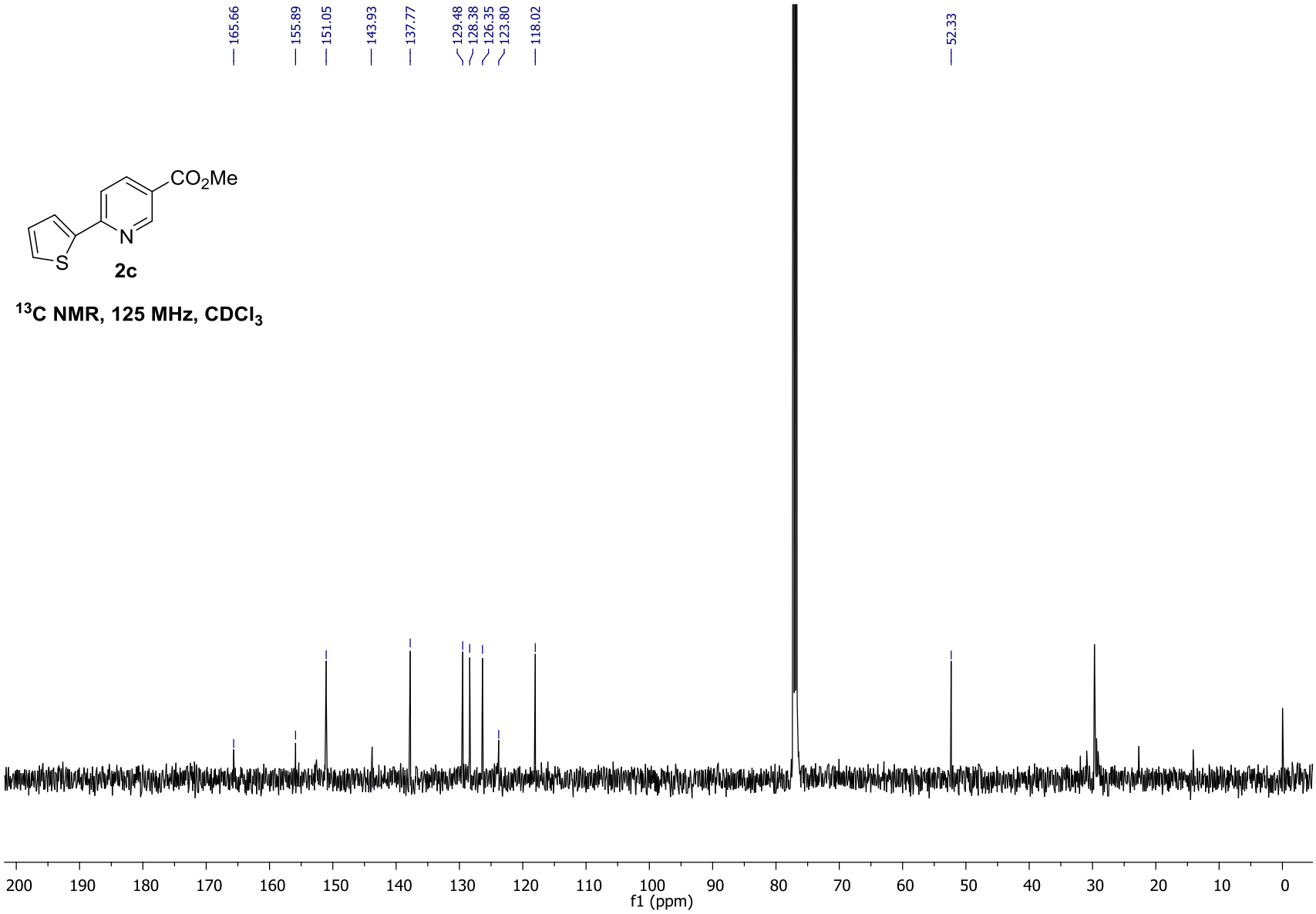
^{13}C NMR, 75MHz, $CDCl_3$

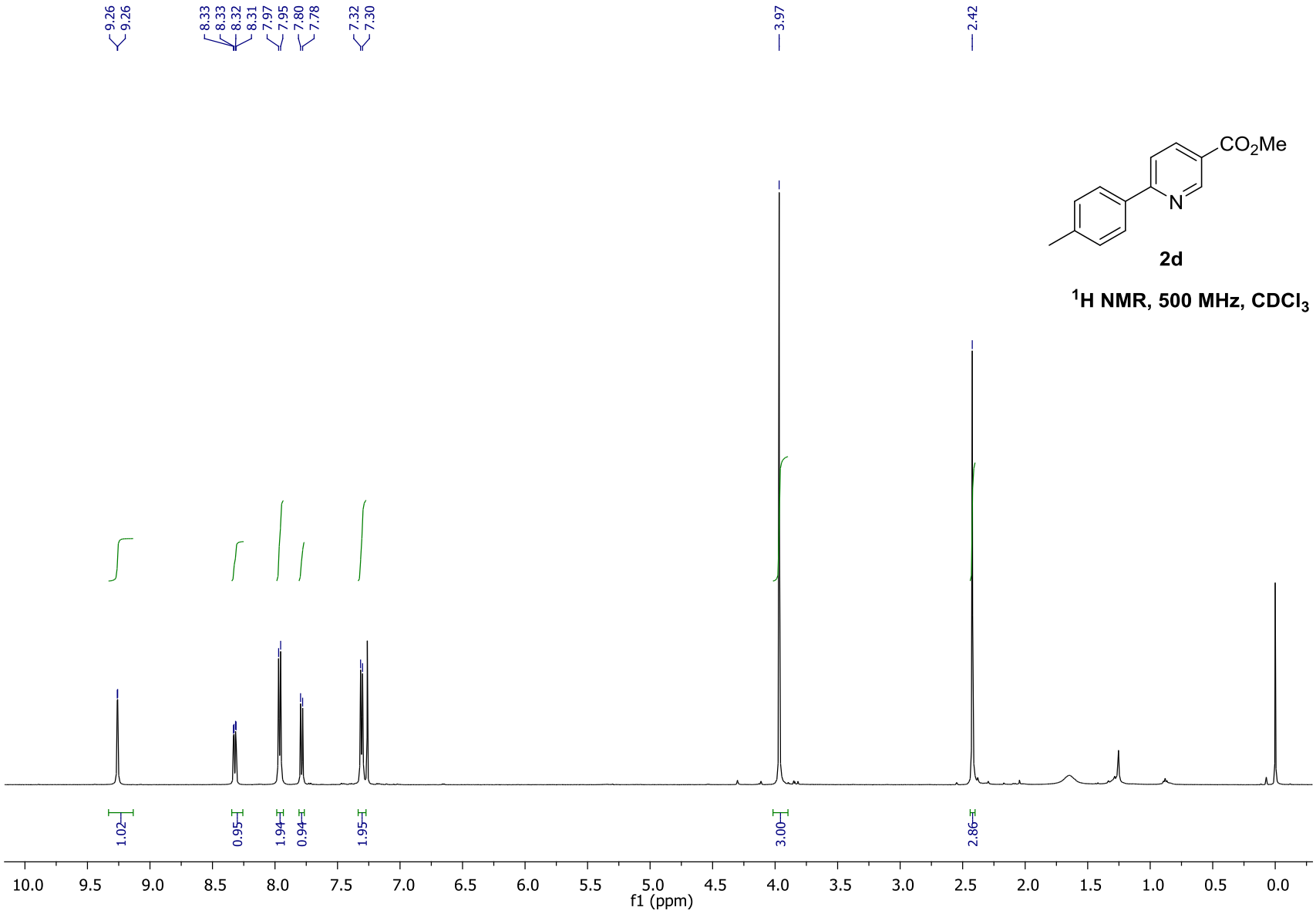

9.29
9.28
8.37
8.36
8.34
8.33
8.08
8.07
8.05
8.04
7.51
7.49
3.98
CO2Me
N
2a
1H NMR, 300 MHz, CDCl3
0.84
0.94
1.99
1.02
3.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


9.40
8.46
8.43
8.09
8.09
7.97
7.94
7.92
7.72
7.69
7.64
7.60
7.58
7.56
7.53
7.51
4.02
CO2Me
N
2b
1H NMR, 300 MHz, CDCl3
0.87
0.97
0.93
2.09
5.14
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
f1 (ppm)


165.73
162.96
150.82
137.59
137.25
133.86
130.76
129.65
128.42
127.96
126.80
126.03
125.27
125.21
124.68
124.25
52.52
CO2Me
N
2b
13C NMR, 75 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)


9.16
9.15
9.15
9.15
8.29
8.28
8.27
8.26
7.72
7.70
7.70
7.70
7.69
7.16
7.15
7.15
7.14
3.96
CO2Me
N
S
2c
1H NMR, 500 MHz, CDCl3
0.76
0.88
1.98
0.85
0.88
3.00
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
f1 (ppm)


165.66
155.89
151.05
143.93
137.77
129.48
128.38
126.35
123.80
118.02
52.33
CO2Me
N
S
2c
13C NMR, 125 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)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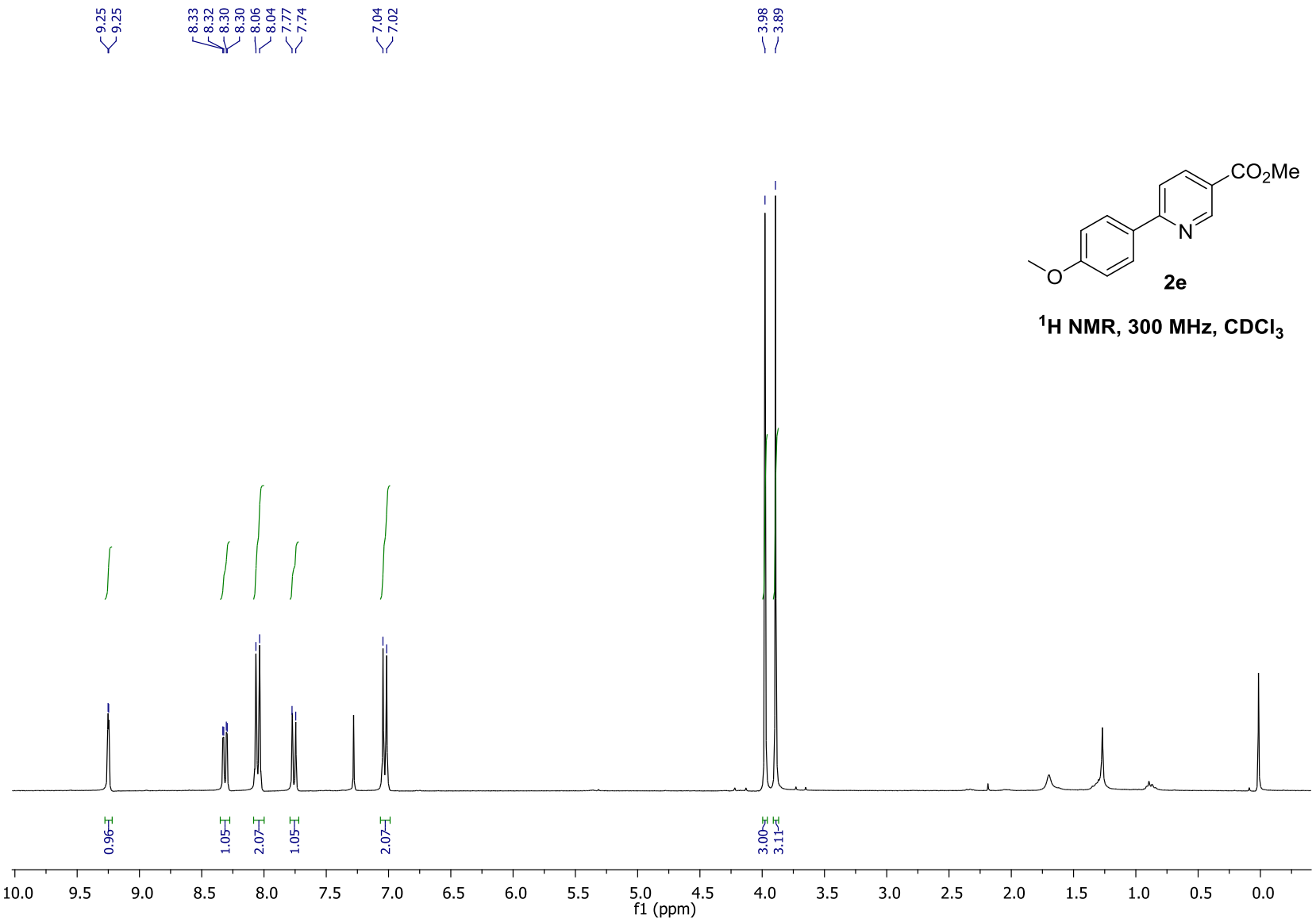
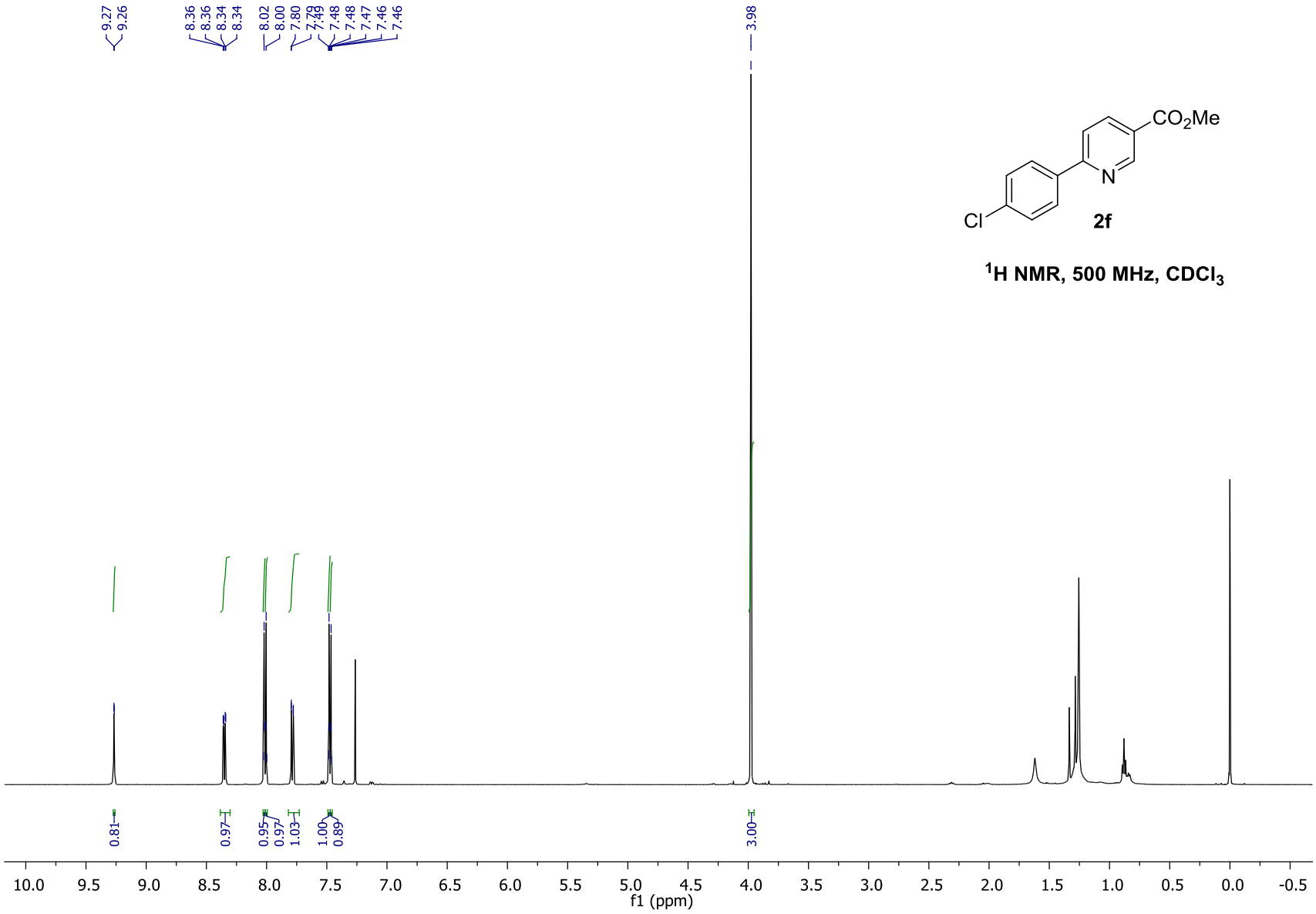
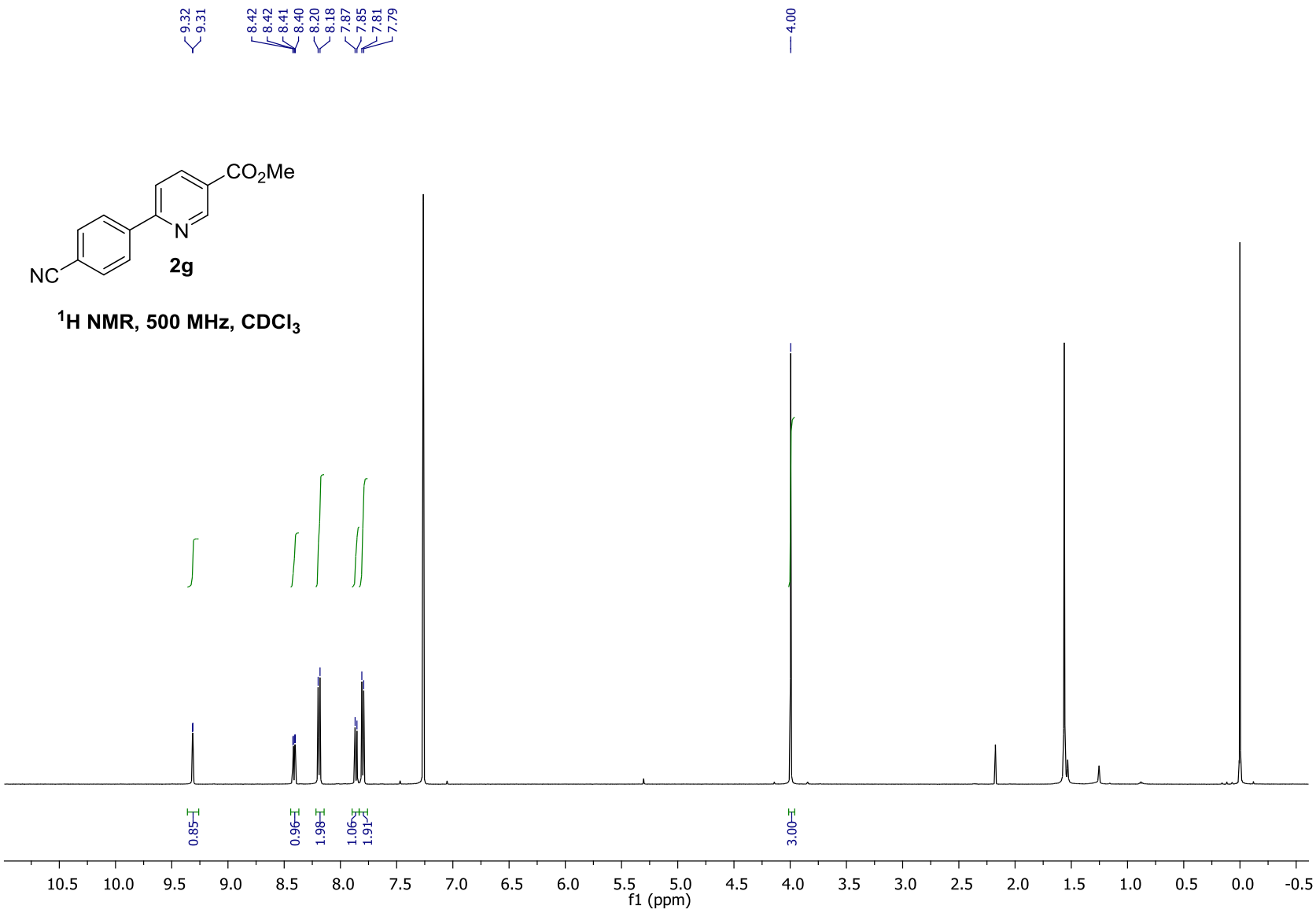
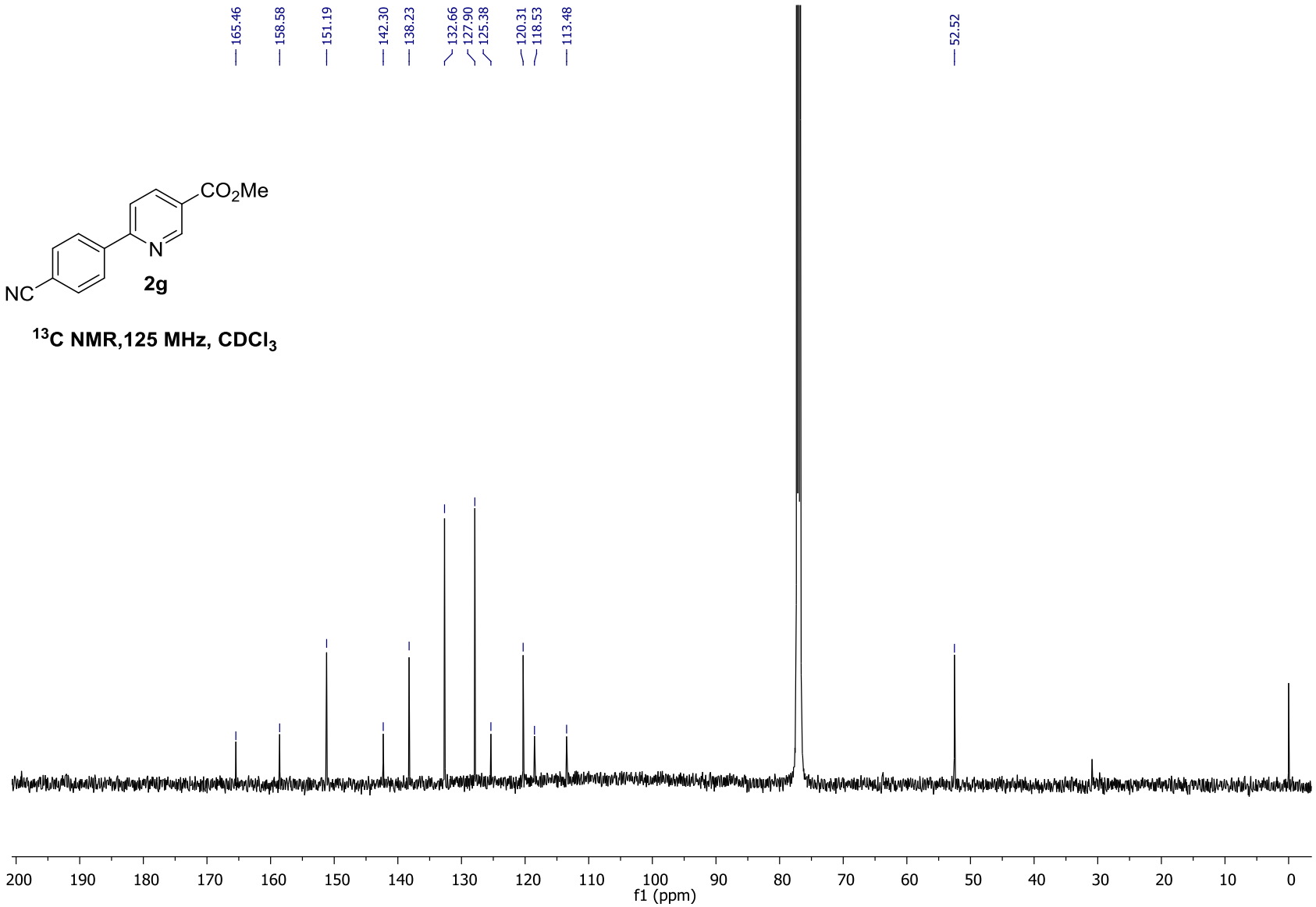
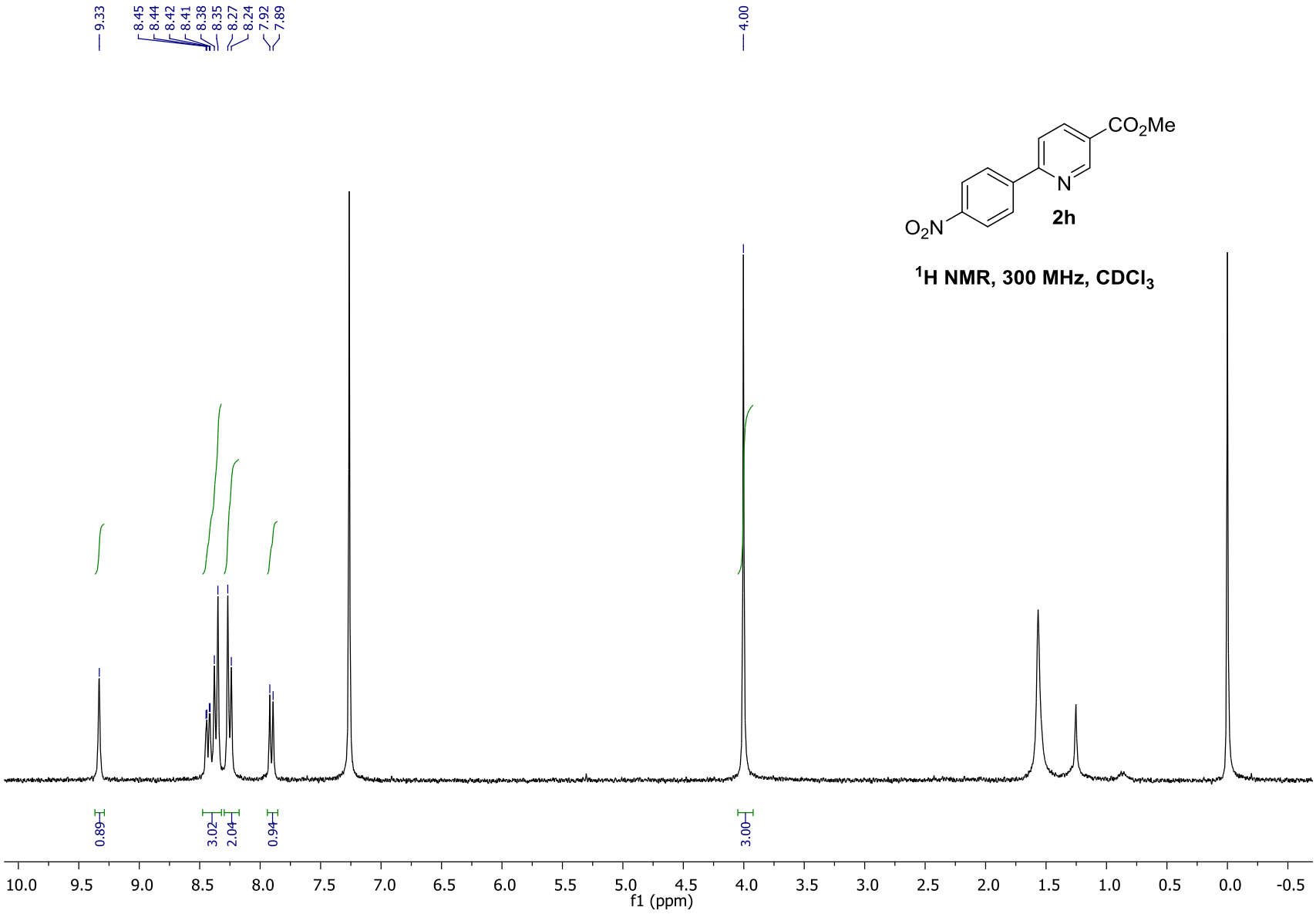
9.26
8.33
8.33
8.32
8.31
7.97
7.95
7.80
7.78
7.32
7.30
3.97
2.42
CO2Me
N
2d
1H NMR, 500 MHz, CDCl3
1.02
0.95
1.94
0.94
1.95
3.00
2.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

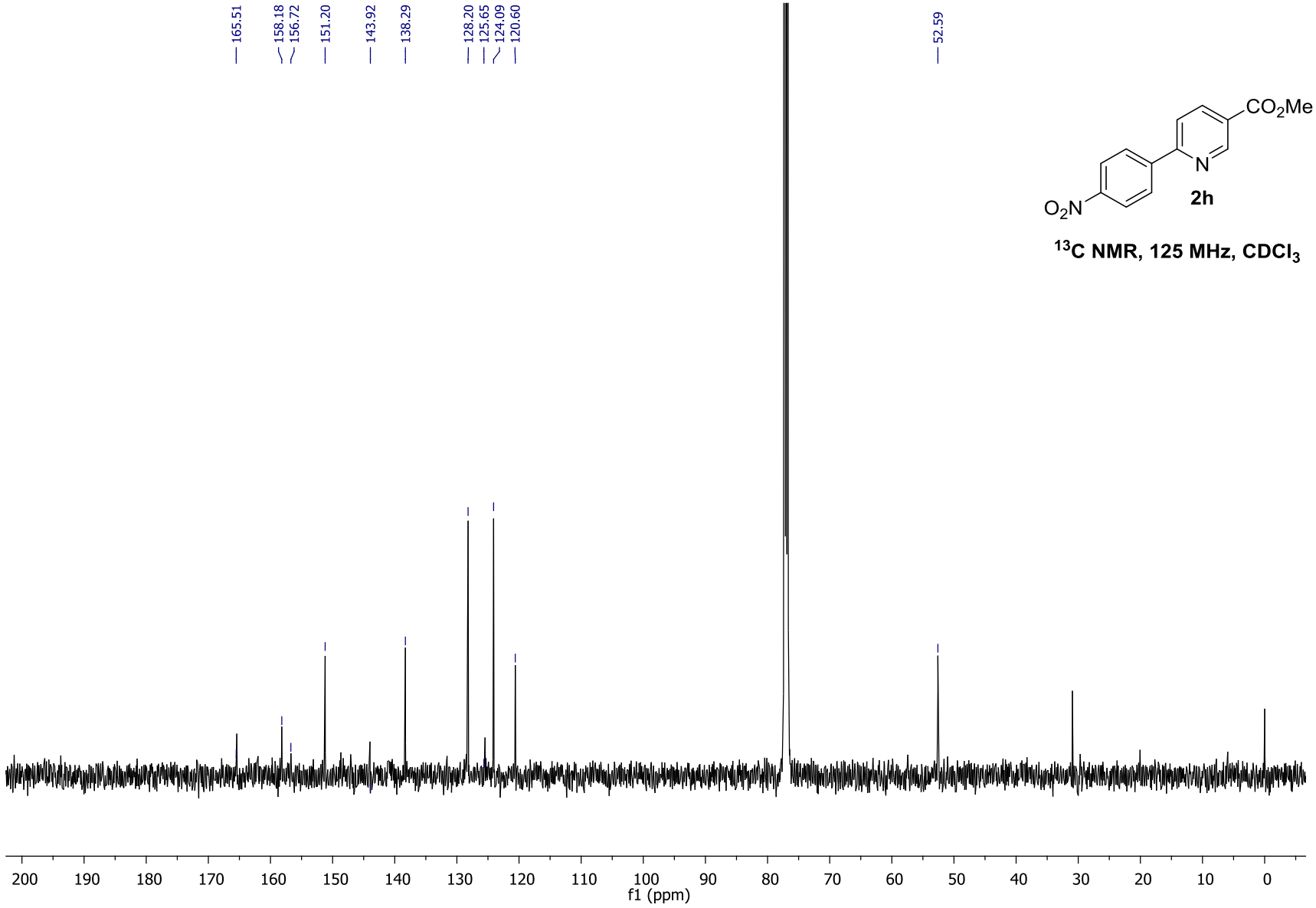

9.25
9.25
8.33
8.32
8.30
8.30
8.06
8.04
7.77
7.74
7.04
7.02
3.98
3.89
CO2Me
N
O
2e
1H NMR, 300 MHz, CDCl3
0.96
1.05
2.07
1.05
2.07
3.00
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

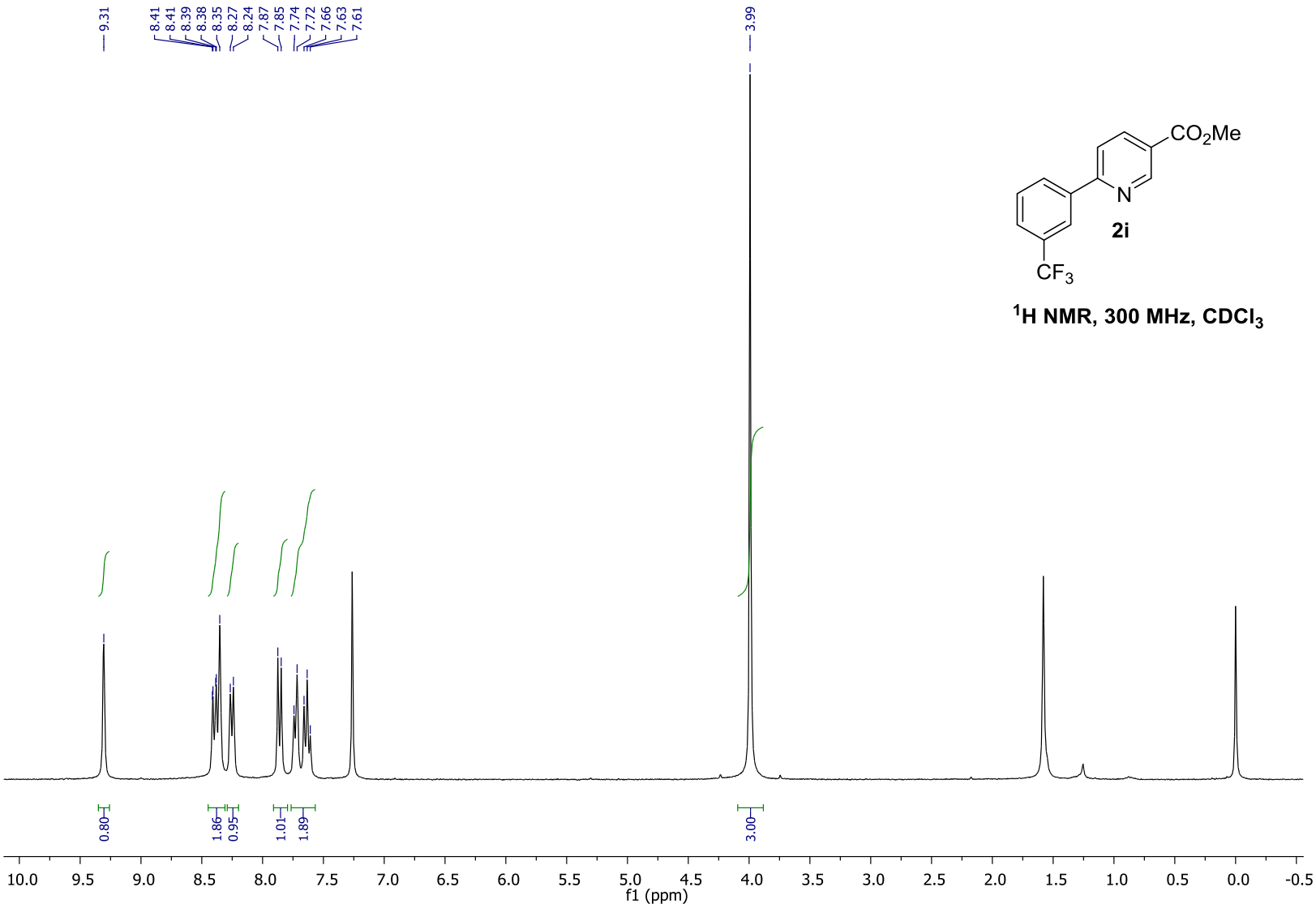

9.27
9.26
8.36
8.36
8.34
8.34
8.02
8.00
7.80
7.48
7.48
7.47
7.46
7.46
3.98
CO2Me
N
Cl
2f
1H NMR, 500 MHz, CDCl3
0.81
0.97
0.95
0.97
1.03
1.00
0.89
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

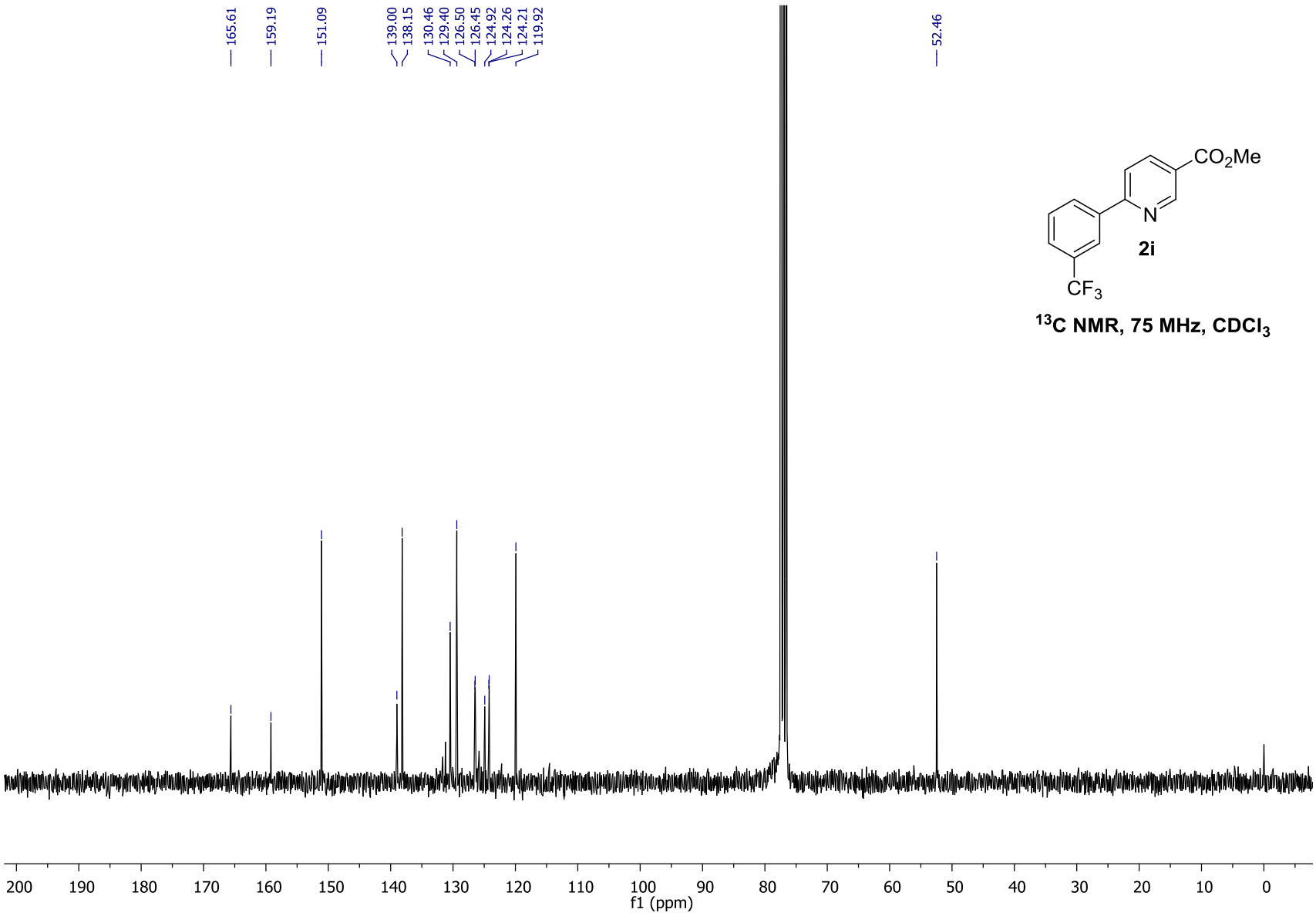

9.32
9.31
8.42
8.42
8.41
8.40
8.20
8.18
7.87
7.85
7.81
7.79
4.00
CO2Me
N
NC
2g
1H NMR, 500 MHz, CDCl3
0.85
0.96
1.98
1.06
1.91
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


165.46
158.58
151.19
142.30
138.23
132.66
127.90
125.38
120.31
118.53
113.48
52.52
CO2Me
N
NC
2g
13C NMR,125 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)


9.33
8.45
8.44
8.42
8.41
8.38
8.35
8.27
8.24
7.92
7.89
4.00
CO2Me
N
O2N
2h
1H NMR, 300 MHz, CDCl3
0.89
3.02
2.04
0.94
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
-0.5
f1 (ppm)


165.51
158.18
156.72
151.20
143.92
138.29
128.20
125.65
124.09
120.60
52.59
CO2Me
N
O2N
2h
13C NMR, 125 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)


9.31
8.41
8.41
8.39
8.38
8.35
8.27
8.24
7.87
7.85
7.74
7.72
7.66
7.63
7.61
3.99
CO2Me
N
2i
CF3
1H NMR, 300 MHz, CDCl3
0.80
1.86
0.95
1.01
1.89
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
-0.5
f1 (ppm)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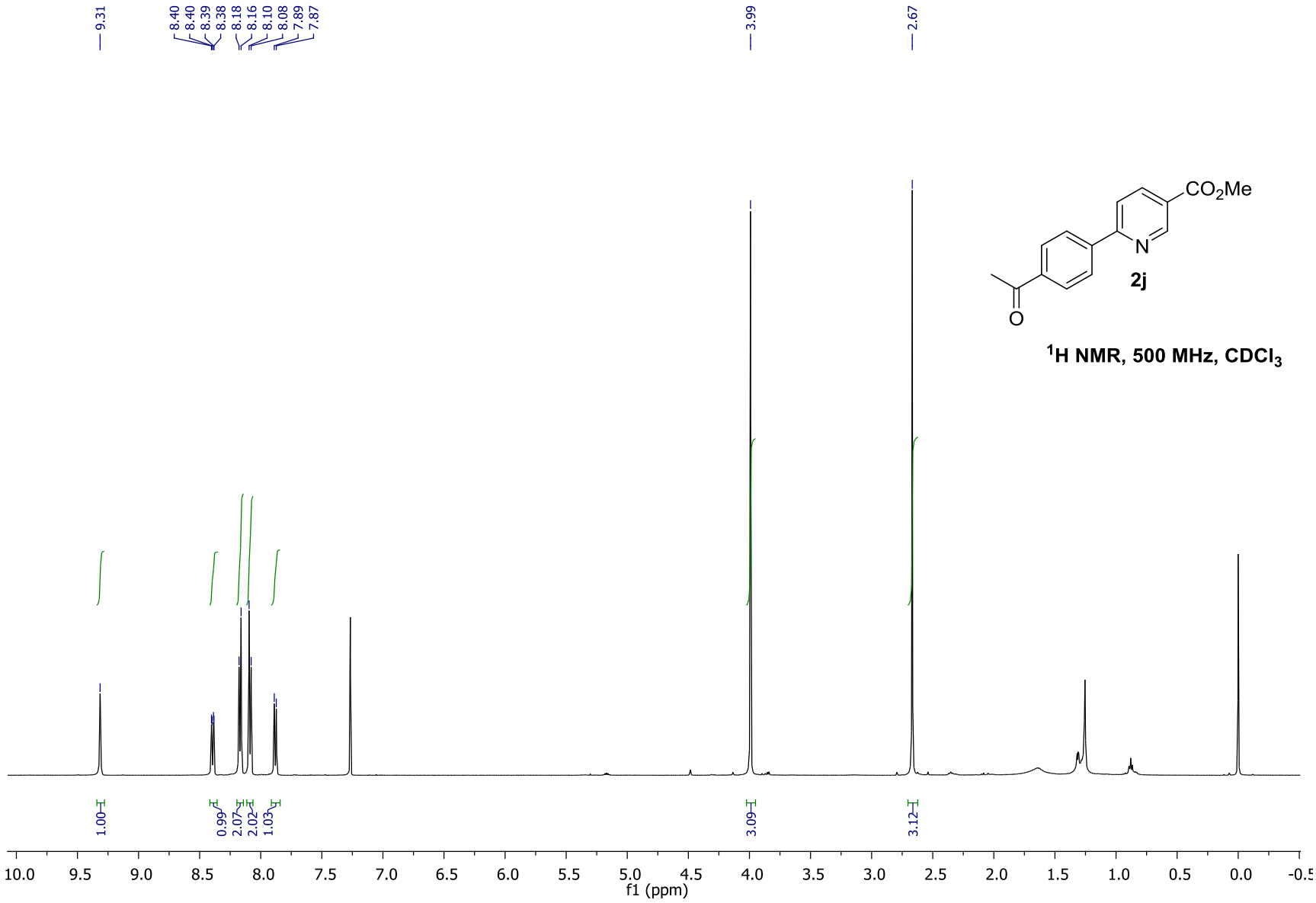
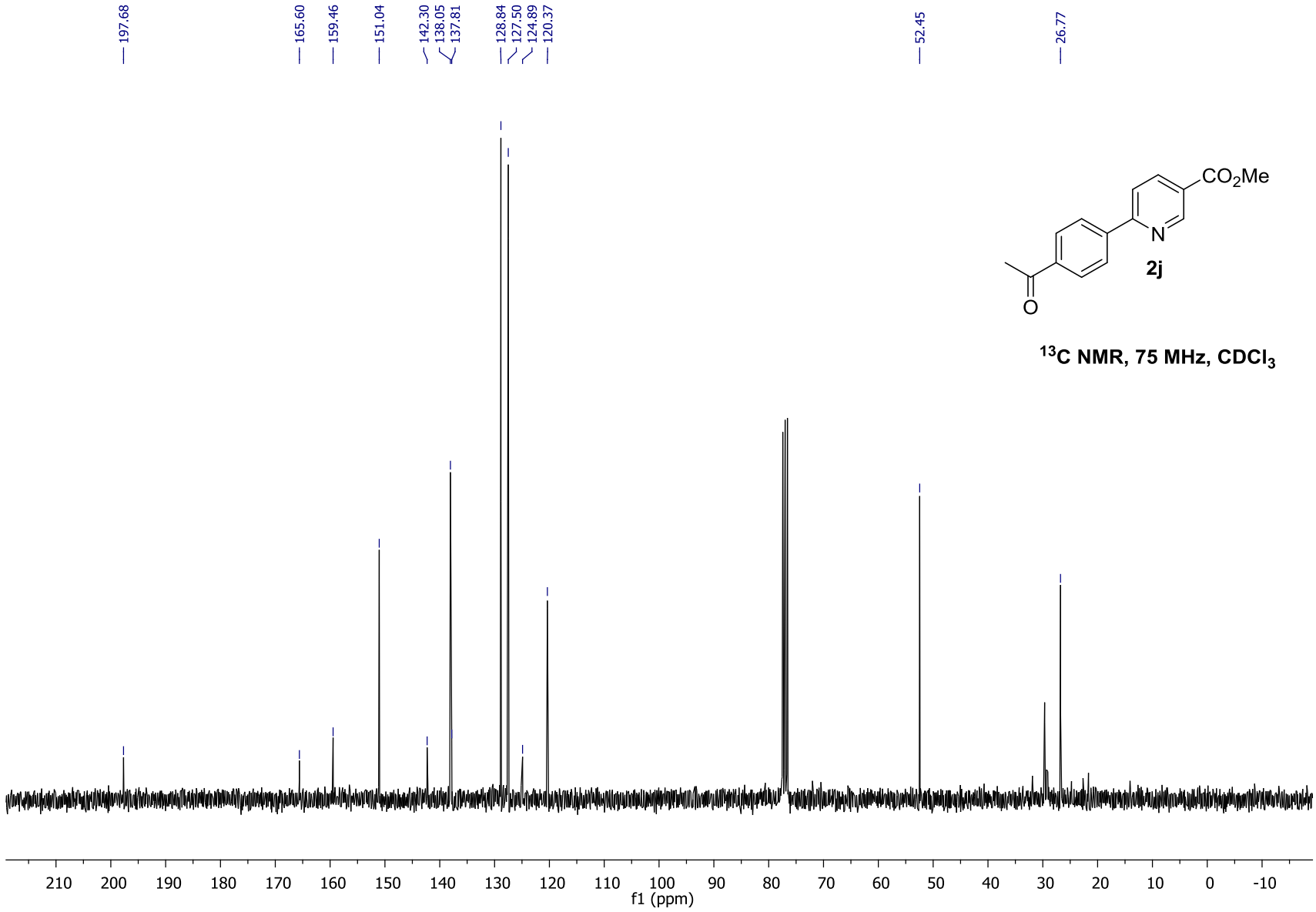
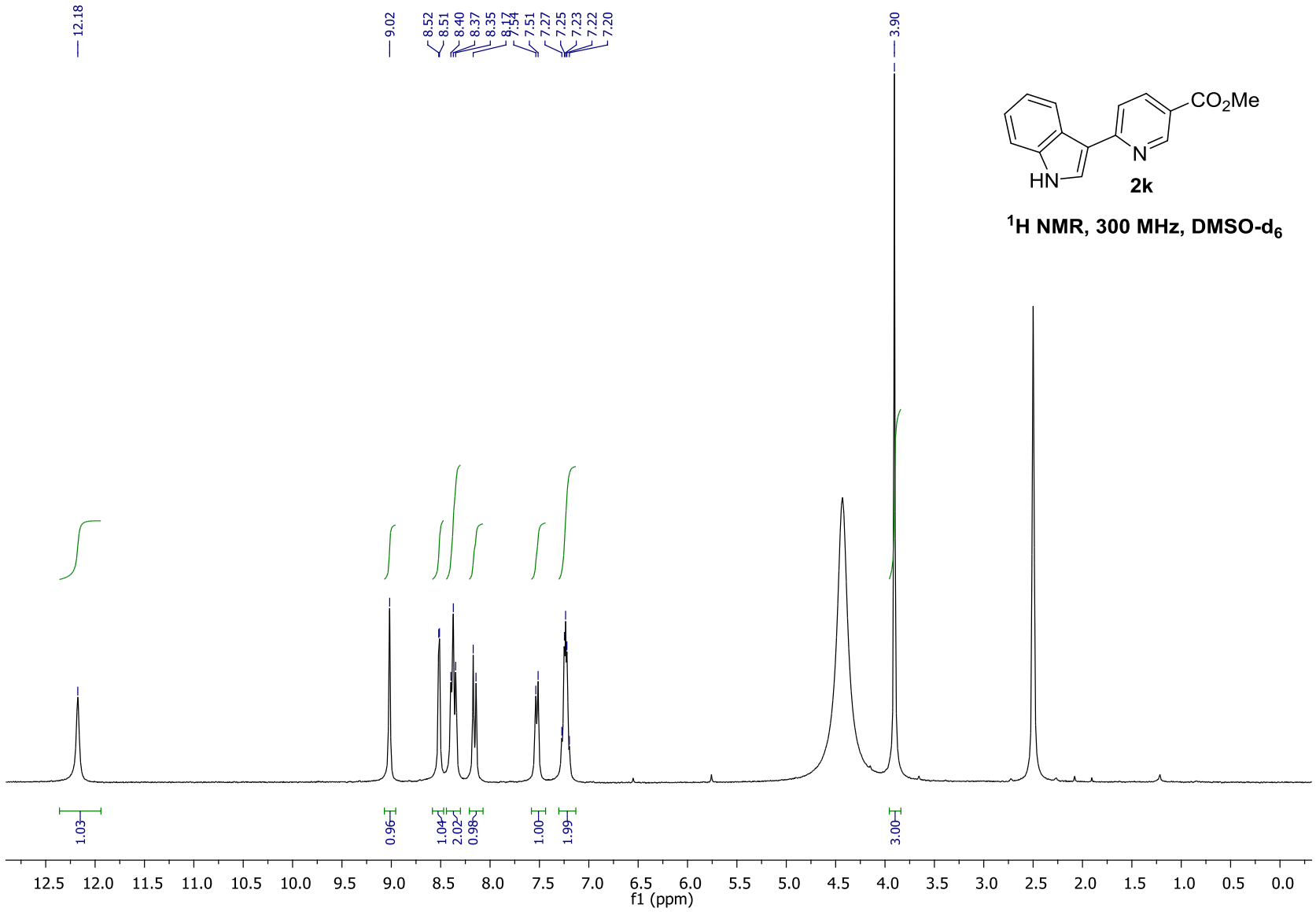
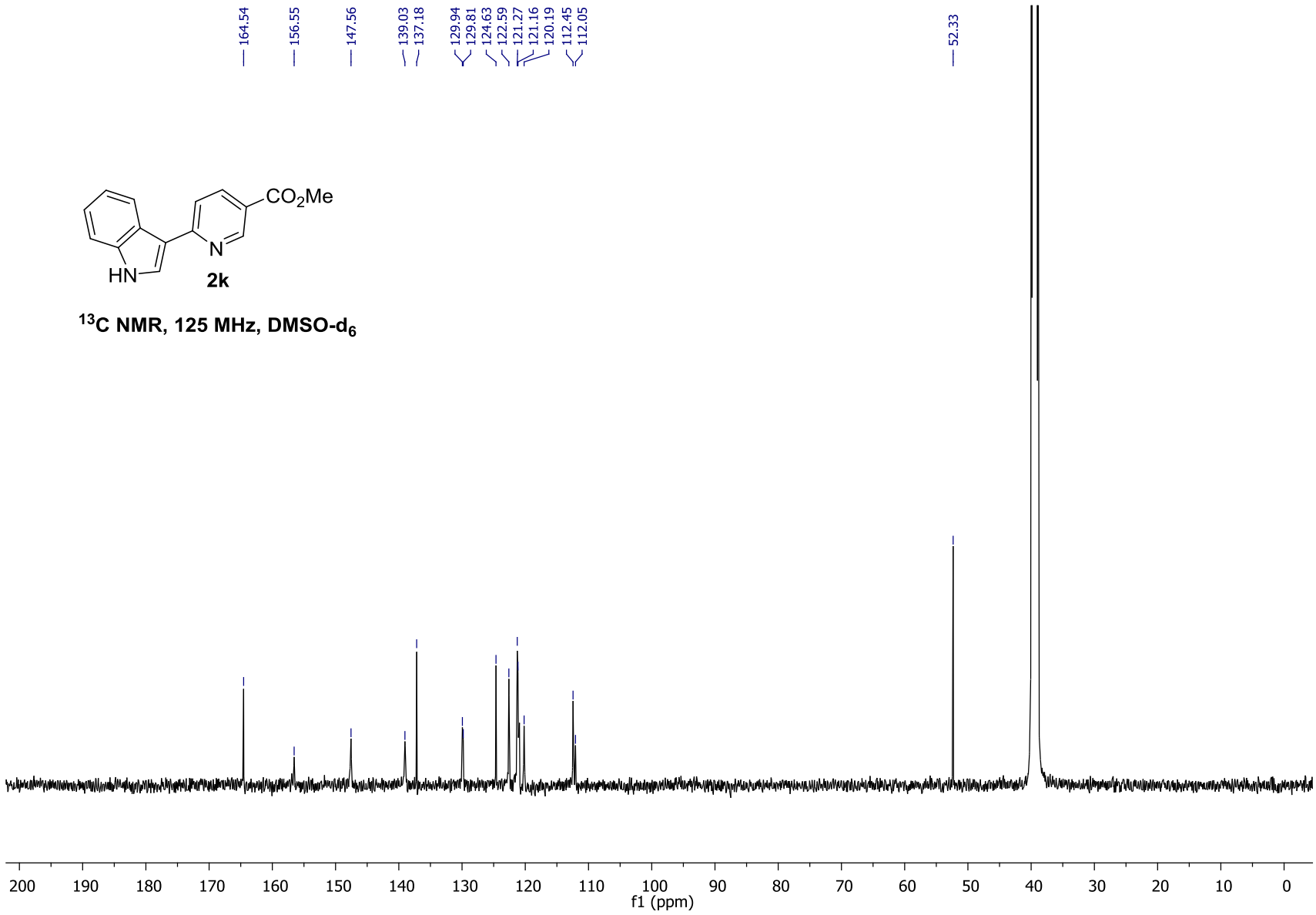
159.19
151.09
139.00
138.15
130.46
129.40
126.50
126.45
124.92
124.26
124.21
119.92
52.46
CO2Me
N
2i
CF3
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.31
8.40
8.40
8.39
8.38
8.18
8.16
8.10
8.08
7.89
7.87
3.99
2.67
CO2Me
N
O
2j
1H NMR, 500 MHz, CDCl3
1.00
0.99
2.07
2.02
1.03
3.09
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
f1 (ppm)


197.68
165.60
159.46
151.04
142.30
138.05
137.81
128.84
127.50
124.89
120.37
52.45
26.77
CO2Me
N
O
2j
13C NMR, 75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


12.18
9.02
8.52
8.51
8.40
8.37
8.35
8.17
8.14
7.51
7.27
7.25
7.23
7.22
7.20
3.90
CO2Me
N
HN
2k
1H NMR, 300 MHz, DMSO-d6
1.03
0.96
1.04
2.02
0.98
1.00
1.99
3.00
f1 (ppm)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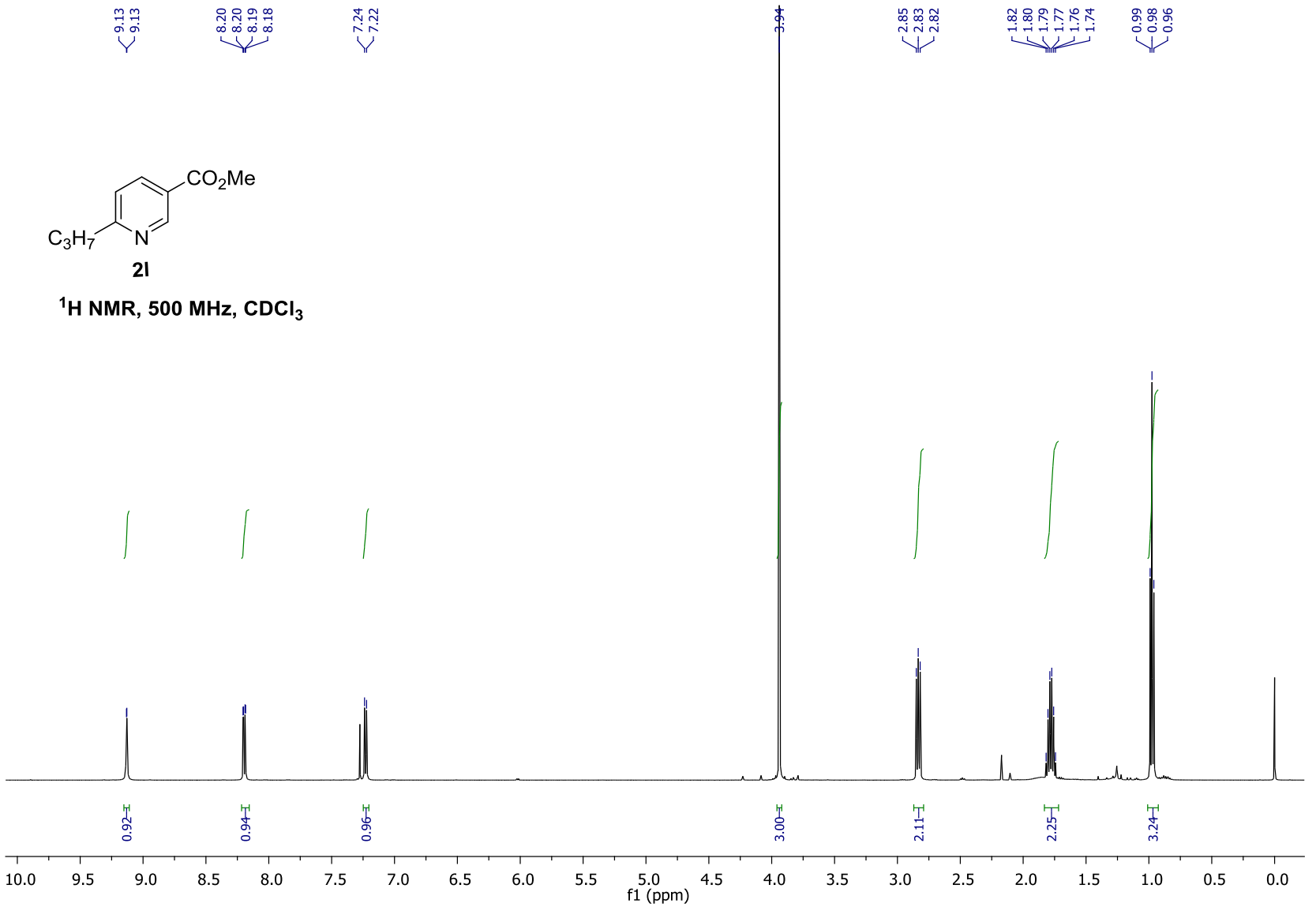
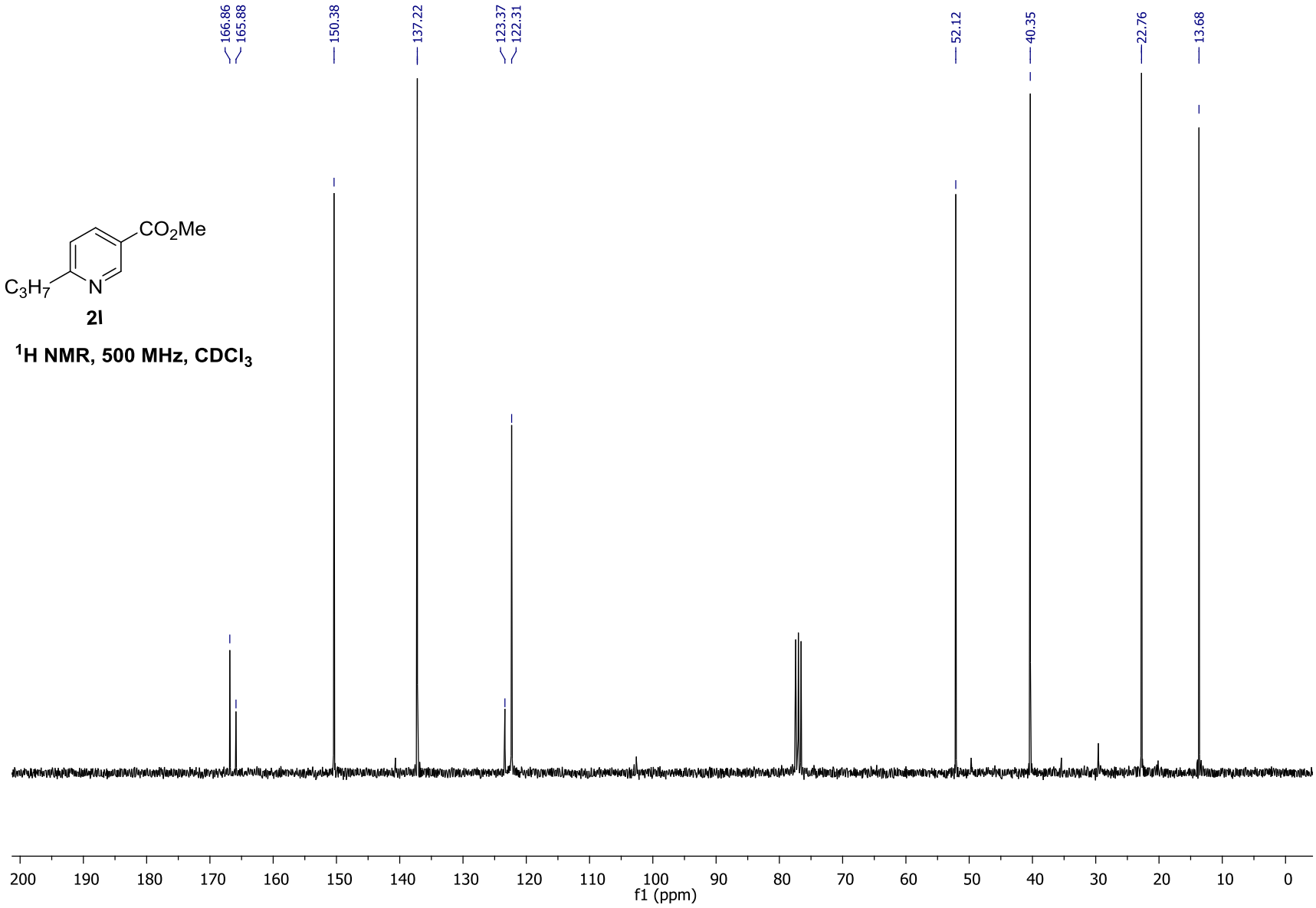
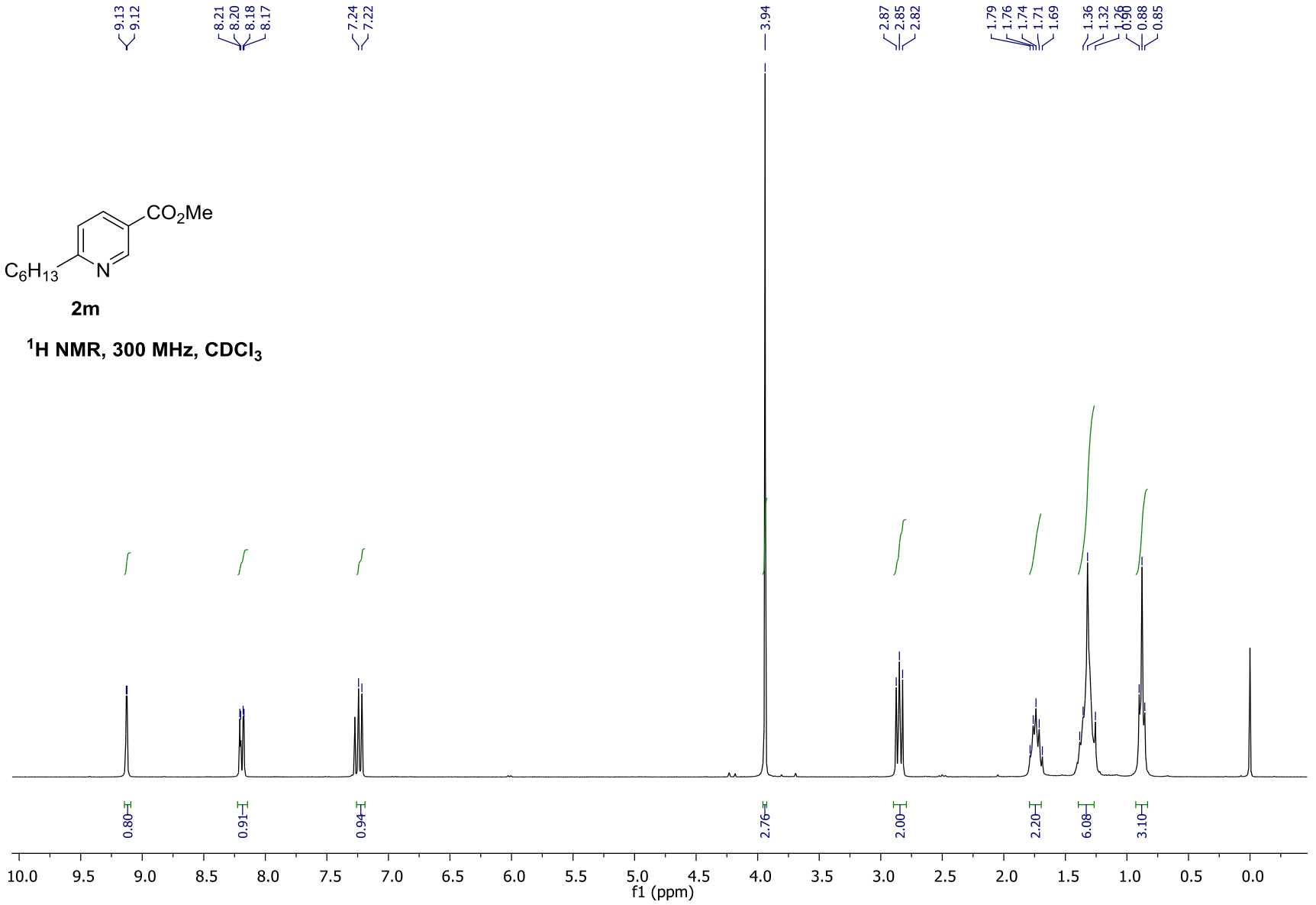
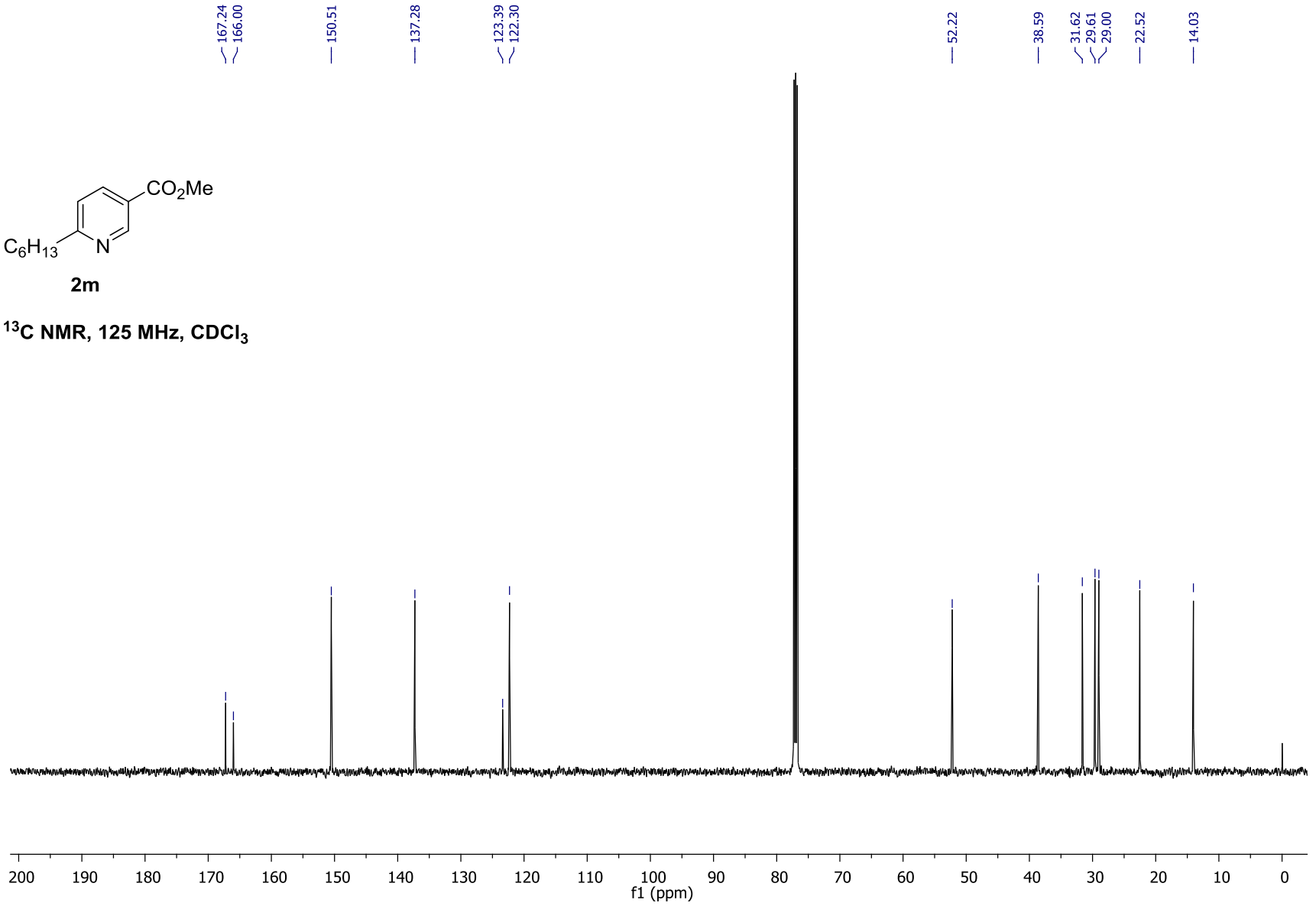
156.55
147.56
139.03
137.18
129.94
129.81
124.63
122.59
121.27
121.16
120.19
112.45
112.05
52.33
CO2Me
N
HN
2k
13C NMR, 125 MHz, DMSO-d6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.13
9.13
8.20
8.20
8.19
8.18
7.24
7.22
3.94
2.85
2.83
2.82
1.82
1.80
1.79
1.77
1.76
1.74
0.99
0.98
0.96
CO2Me
C3H7
N
2l
1H NMR, 500 MHz, CDCl3
0.92
0.94
0.96
3.00
2.11
2.25
3.24
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
f1 (ppm)

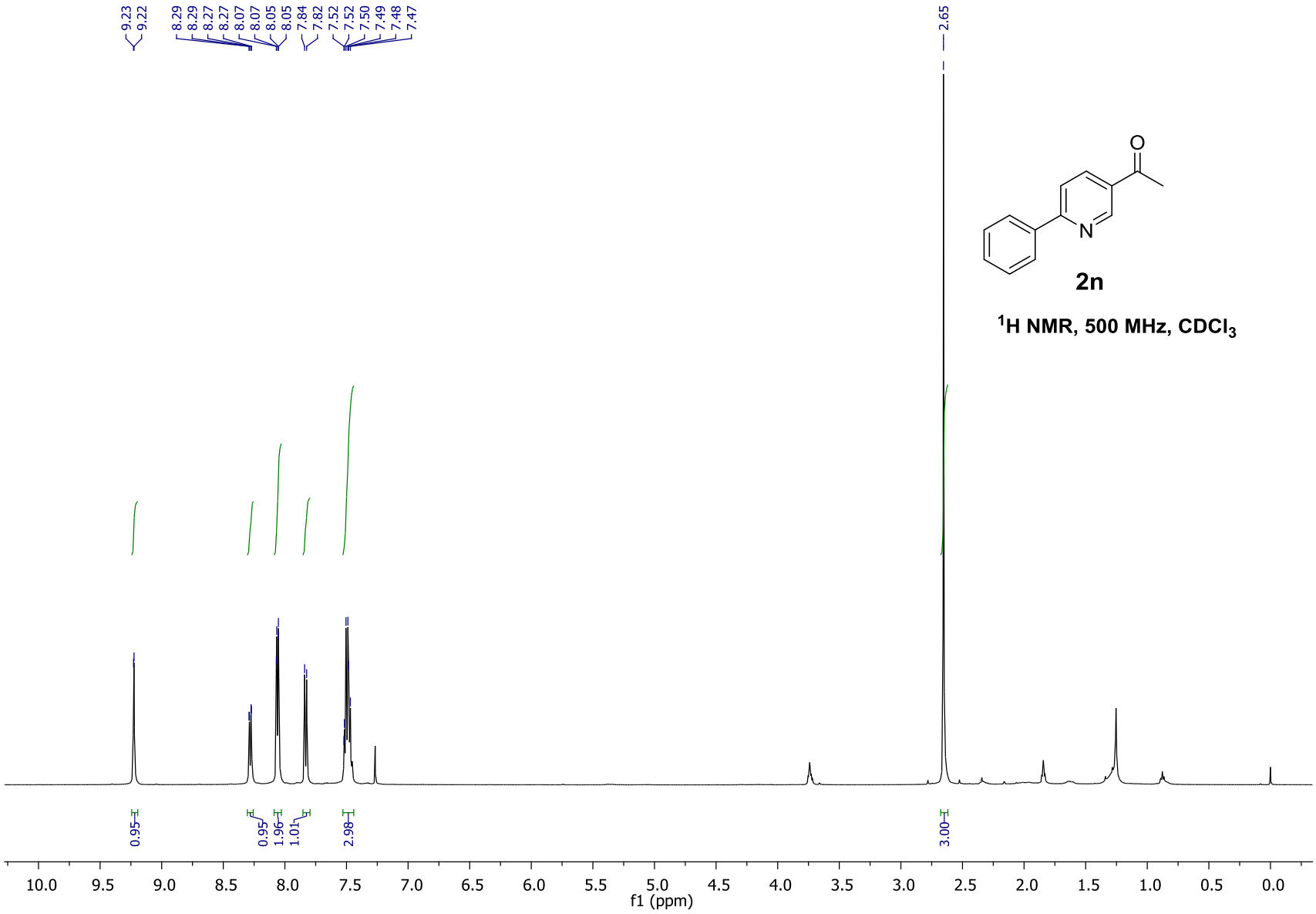

166.86
165.88
150.38
137.22
123.37
122.31
52.12
40.35
22.76
13.68
CO2Me
C3H7
N
2l
1H NMR, 500 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

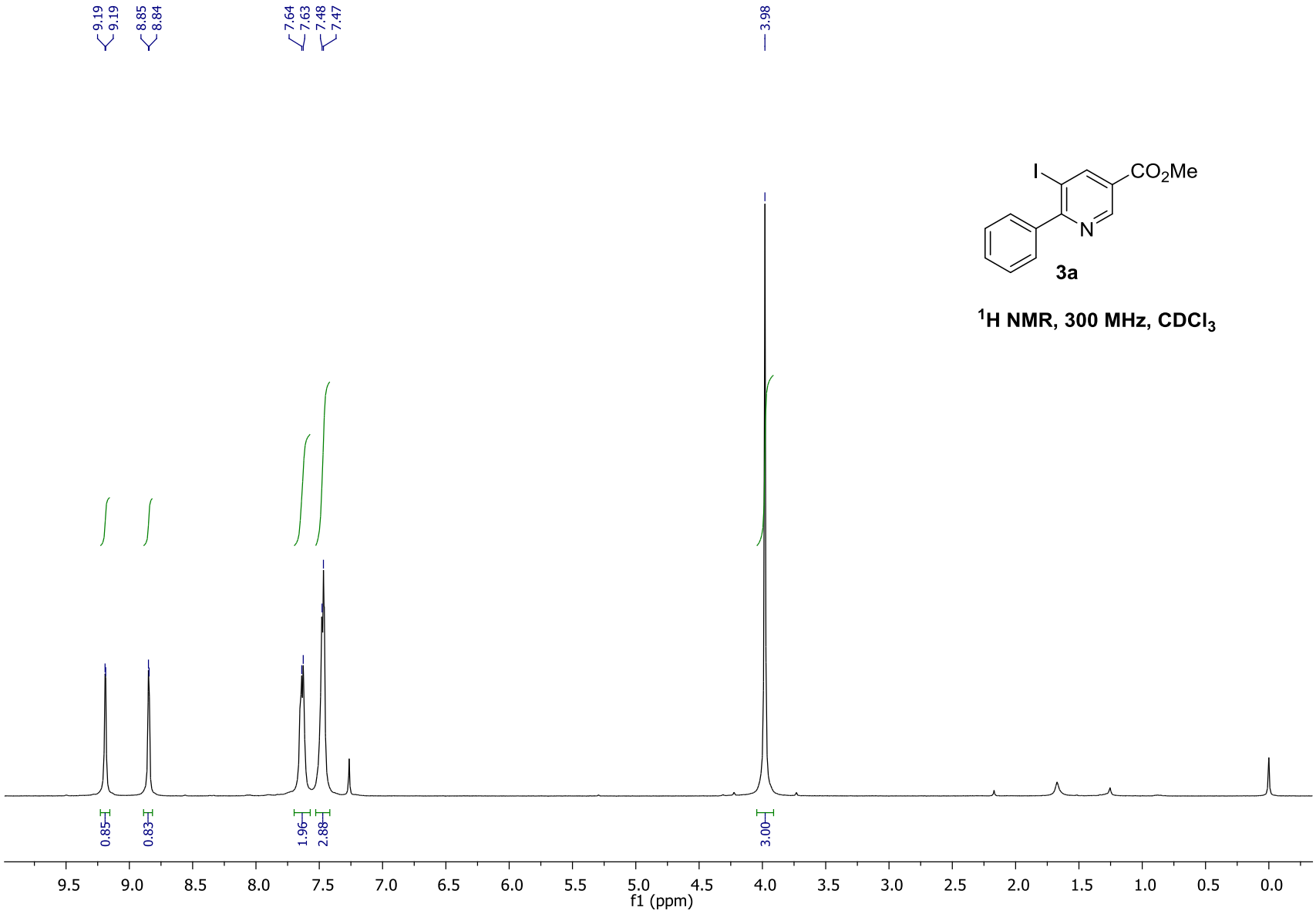

9.13
9.12
8.21
8.20
8.18
8.17
7.24
7.22
3.94
2.87
2.85
2.82
1.79
1.76
1.74
1.71
1.69
1.36
1.32
0.90
0.88
0.85
CO2Me
C6H13
N
2m
1H NMR, 300 MHz, CDCl3
0.80
0.91
0.94
2.76
2.00
2.20
6.08
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

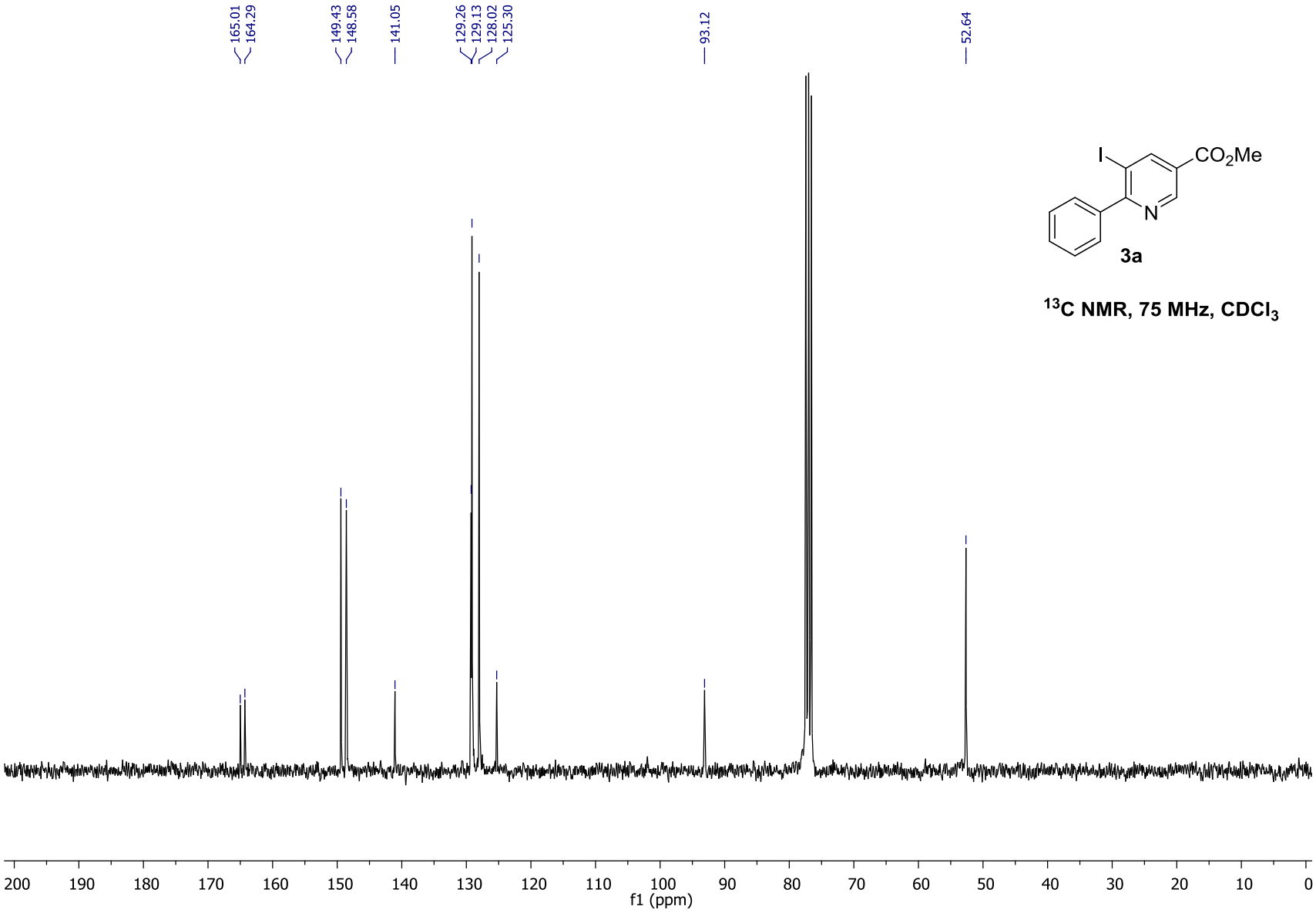


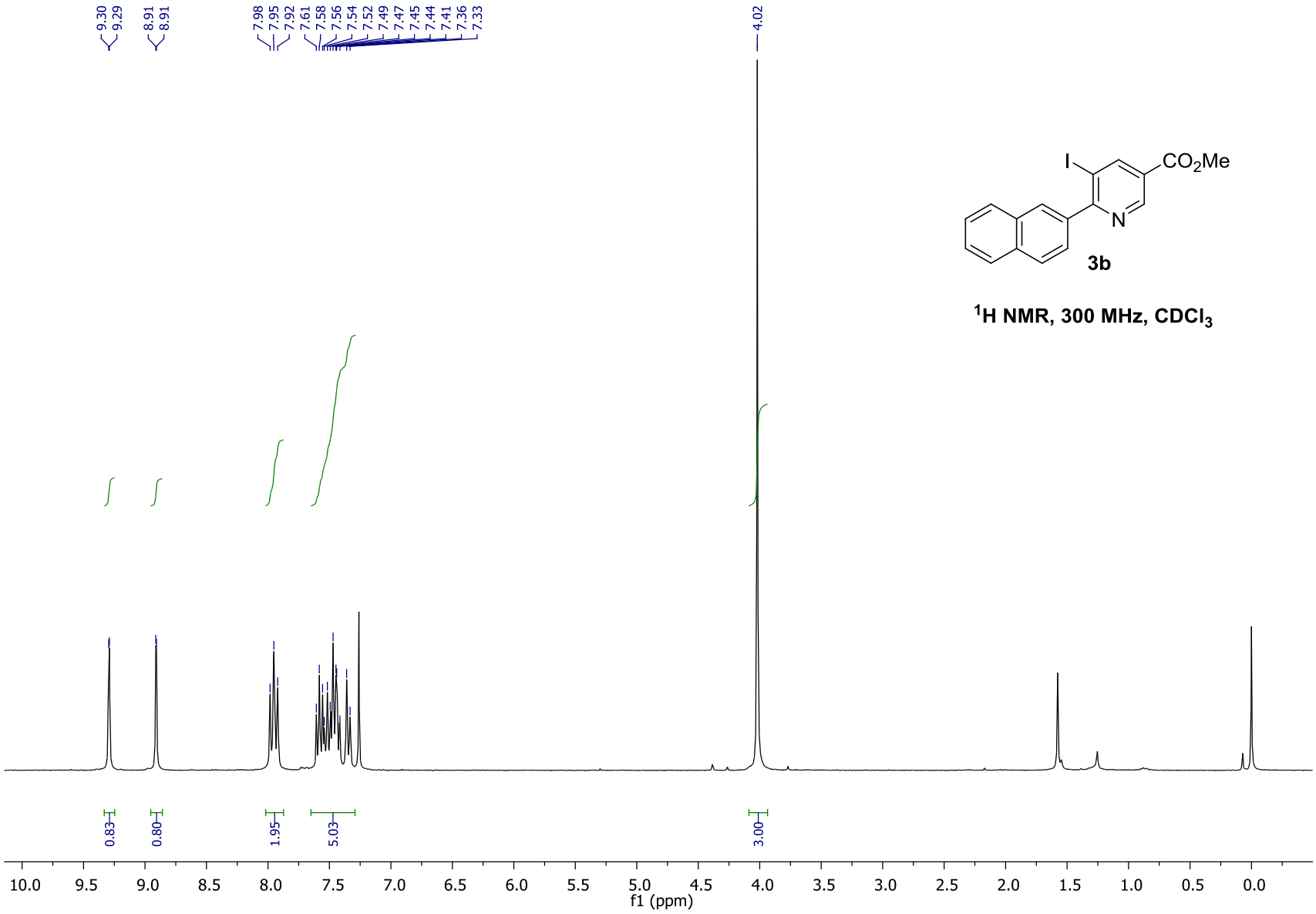
2m

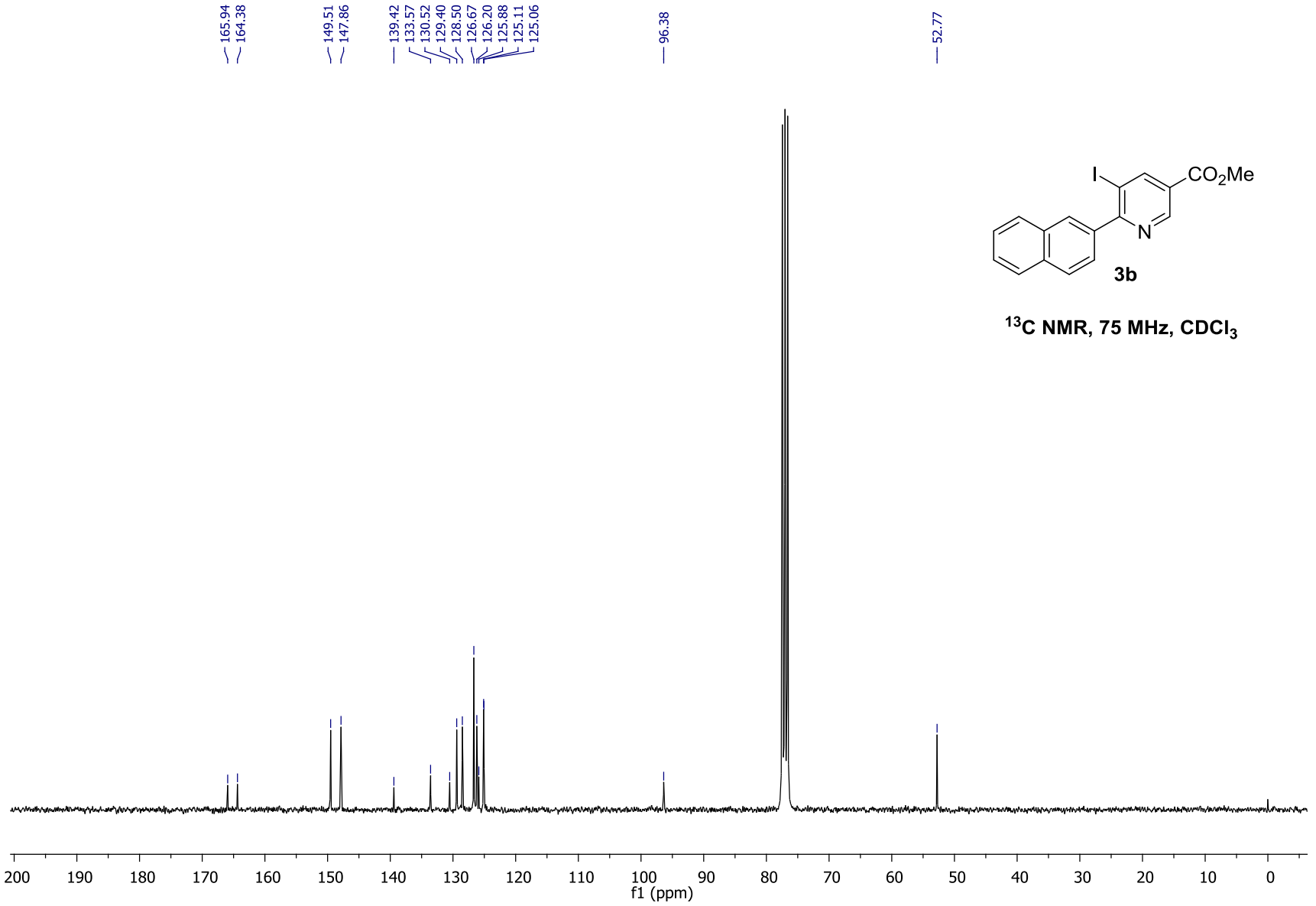
^{13}C NMR, 125 MHz, $CDCl_3$

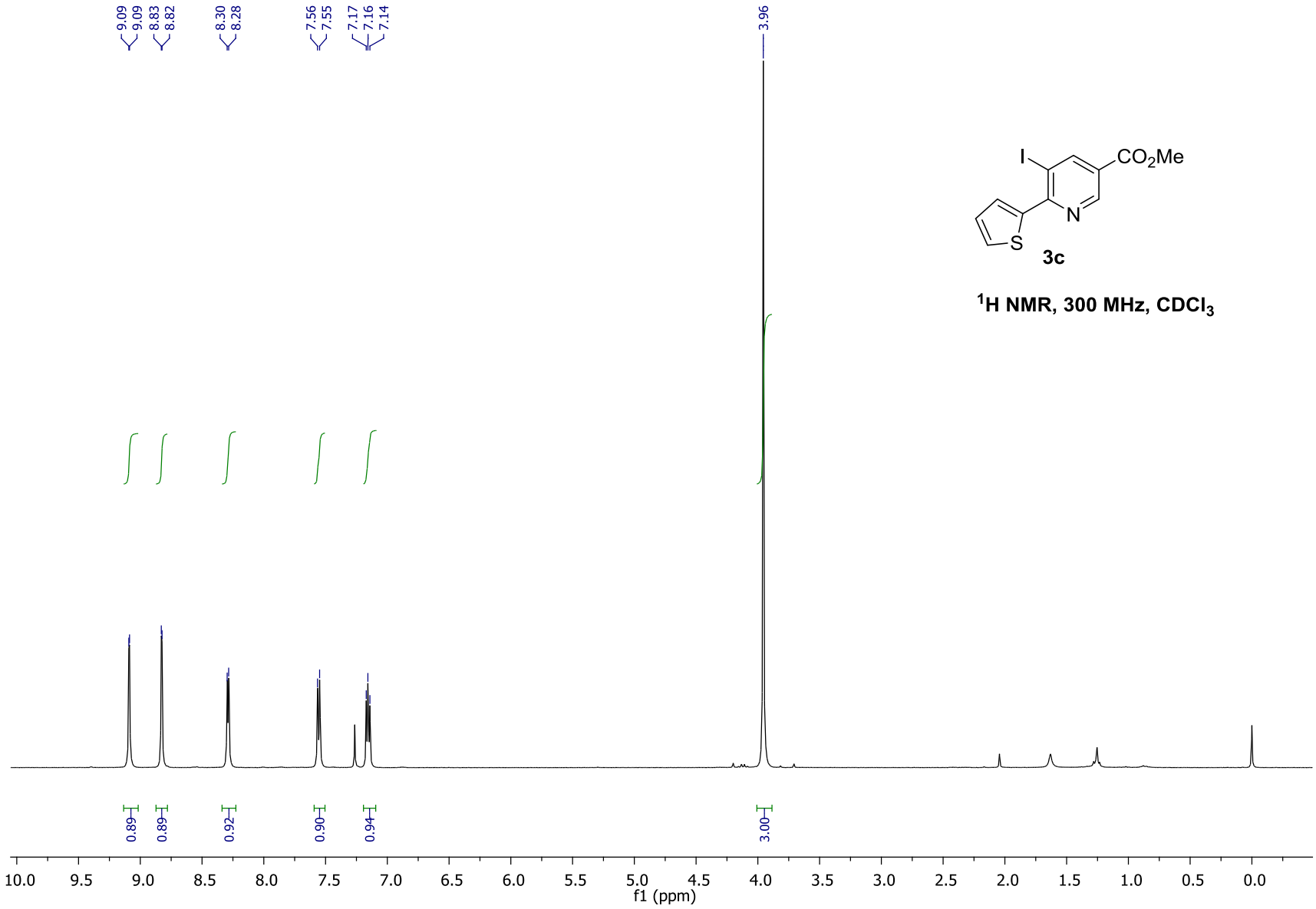

9.23
9.22
8.29
8.29
8.27
8.27
8.07
8.07
8.05
8.05
7.84
7.82
7.52
7.52
7.50
7.49
7.48
7.47
2.65
O
N
2n
^{1}H NMR, 500 MHz, CDCl$_3$
0.95
0.95
1.96
1.01
2.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

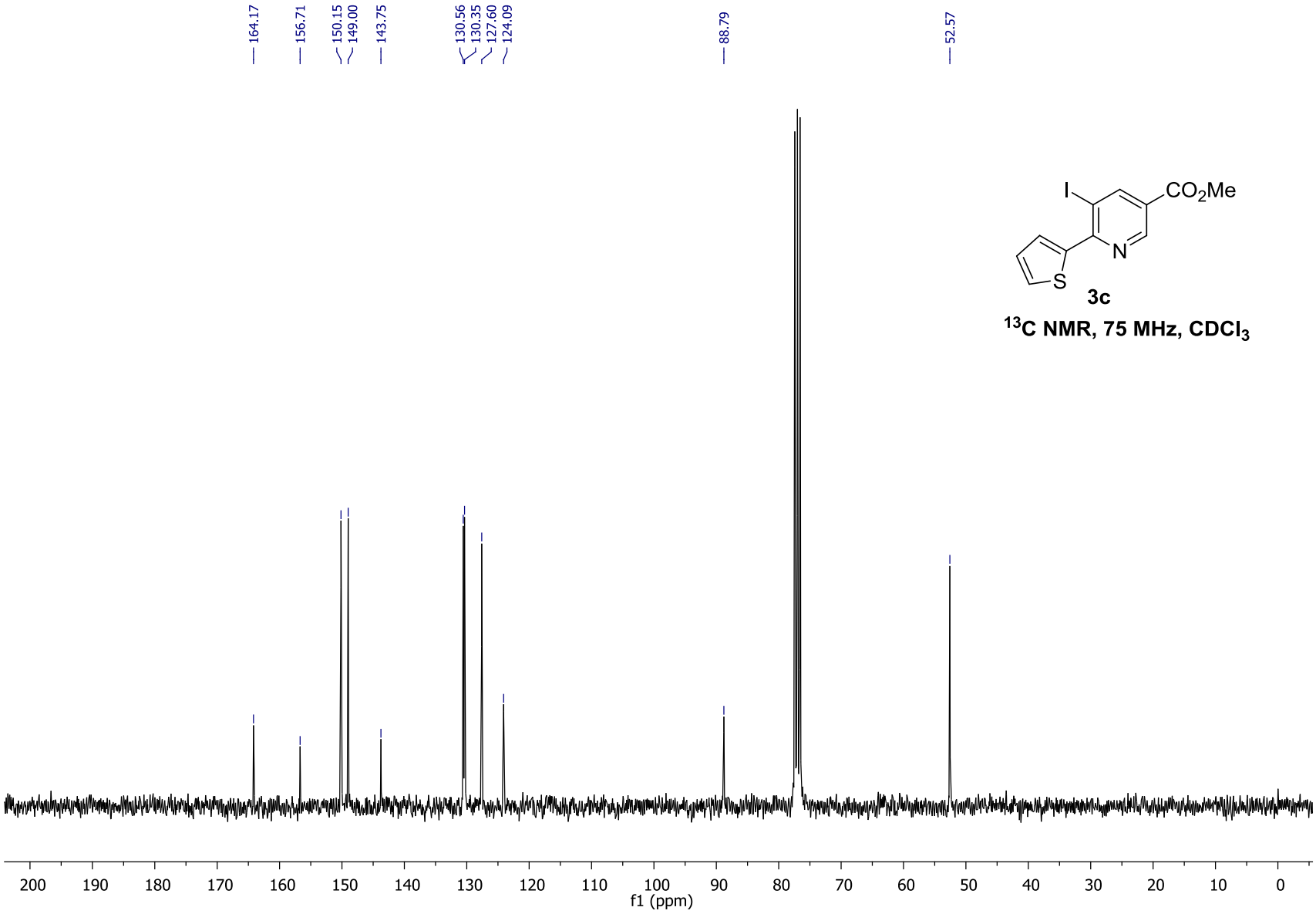

9.19
9.19
8.85
8.84
7.64
7.63
7.48
7.47
3.98
I
CO2Me
N
3a
1H NMR, 300 MHz, CDCl3
0.85
0.83
1.96
2.88
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

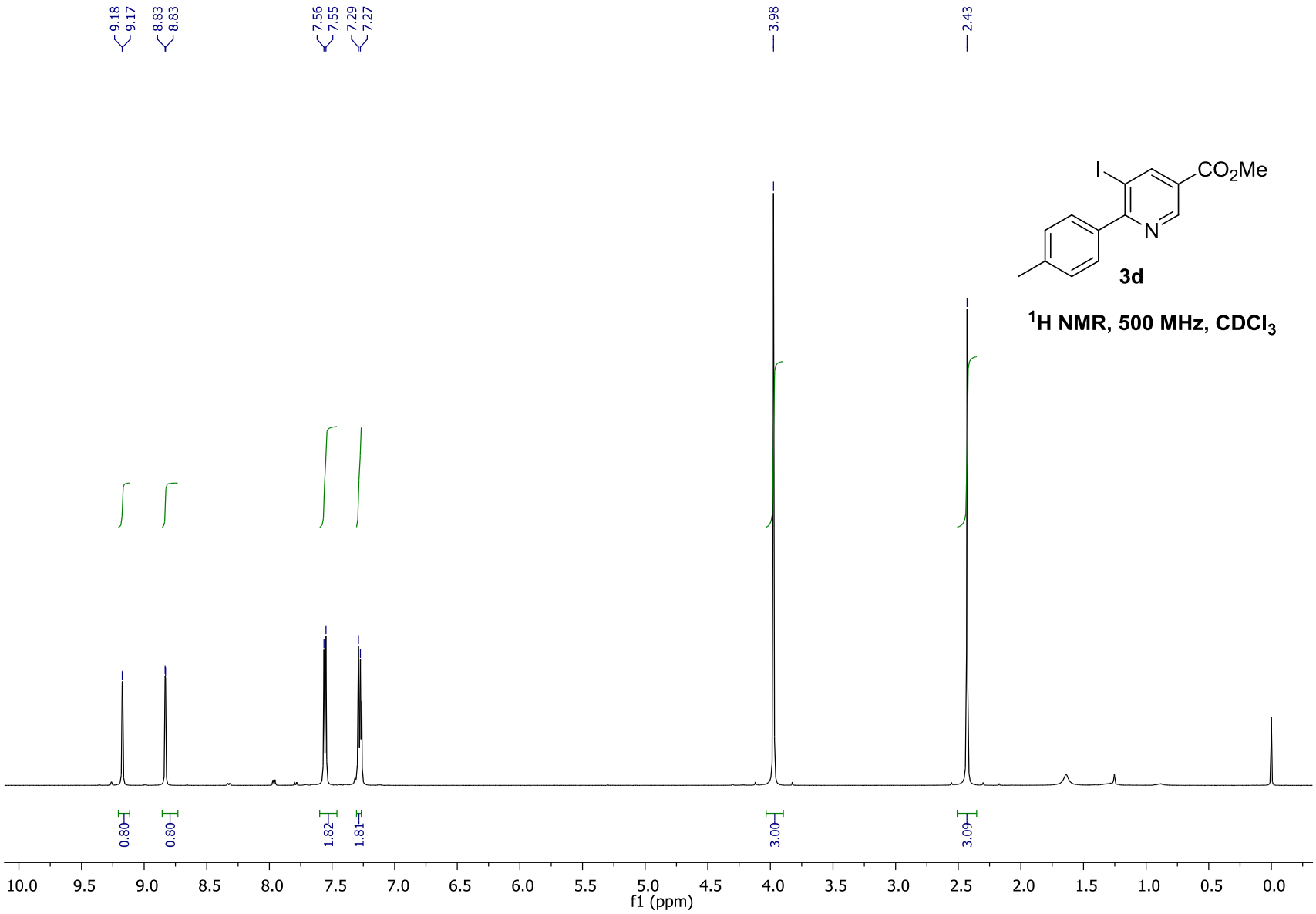

165.01
164.29
149.43
148.58
141.05
129.26
129.13
128.02
125.30
93.12
52.64
I
CO2Me
N
3a
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

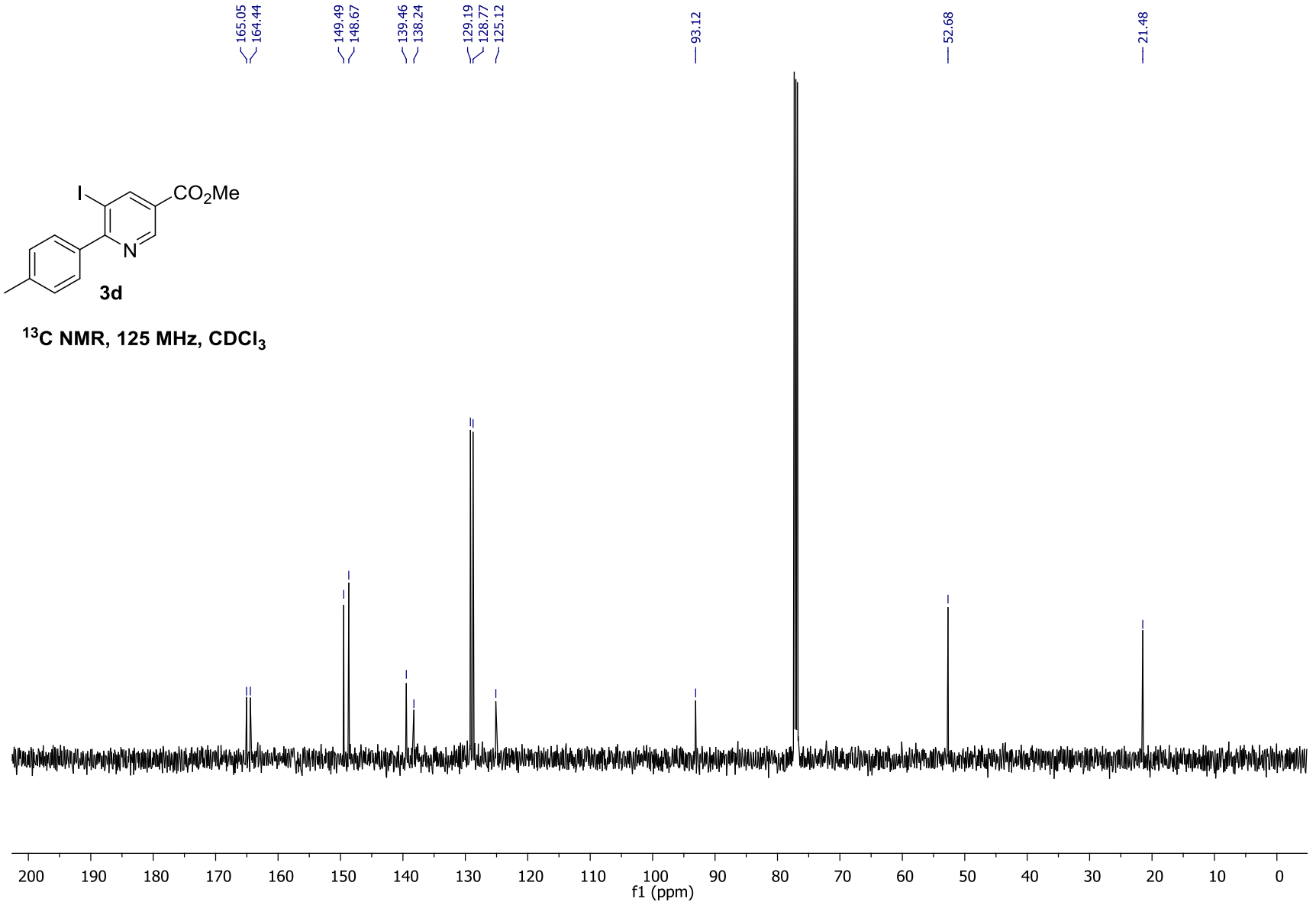

9.30
9.29
8.91
8.91
7.98
7.95
7.92
7.61
7.58
7.56
7.54
7.52
7.49
7.47
7.45
7.44
7.41
7.36
7.33
4.02
I
CO2Me
N
3b
1H NMR, 300 MHz, CDCl3
0.83
0.80
1.95
5.03
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

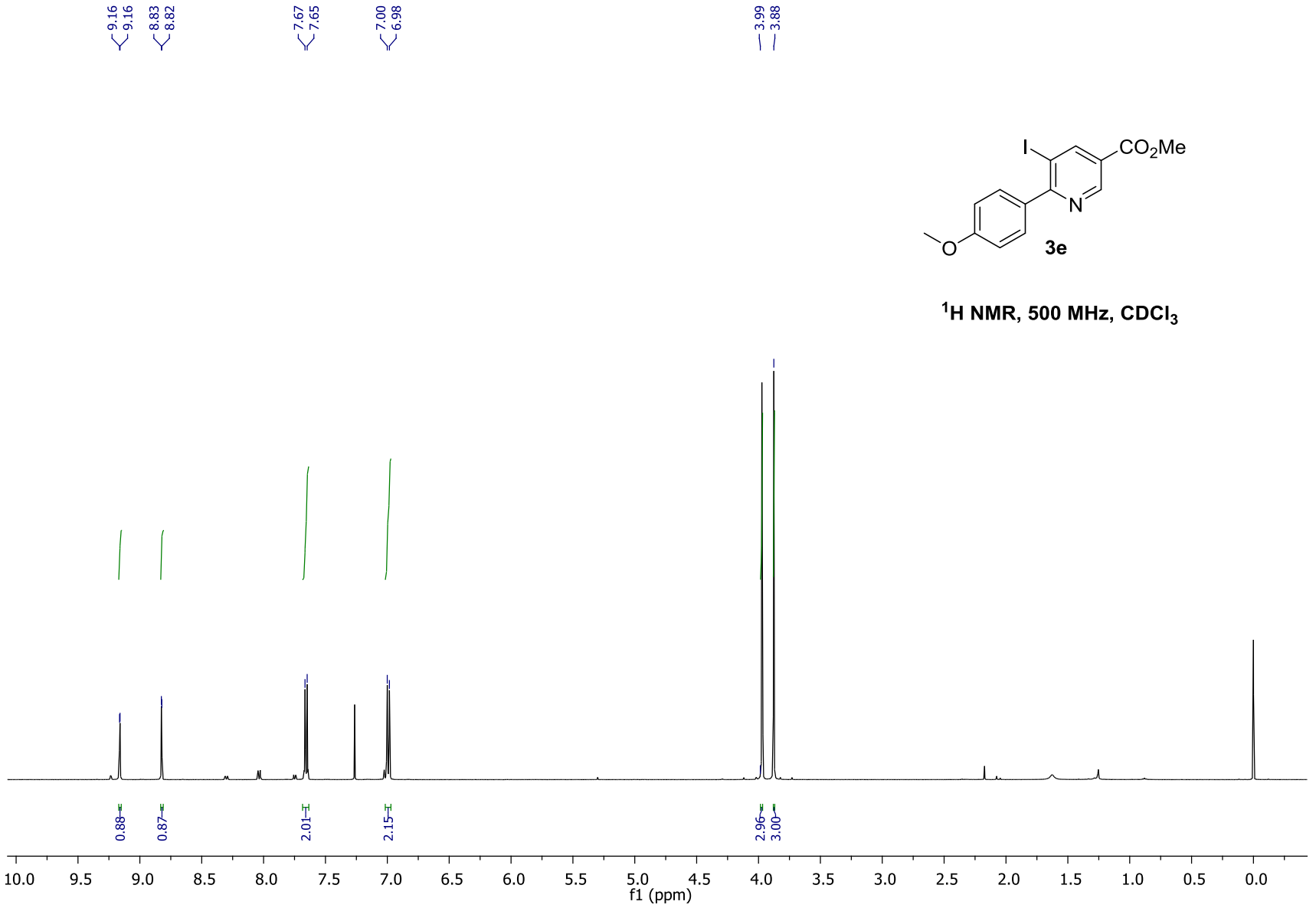

165.94
164.38
149.51
147.86
139.42
133.57
130.52
129.40
128.50
126.67
126.20
125.88
125.11
125.06
96.38
52.77
I
CO2Me
N
3b
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

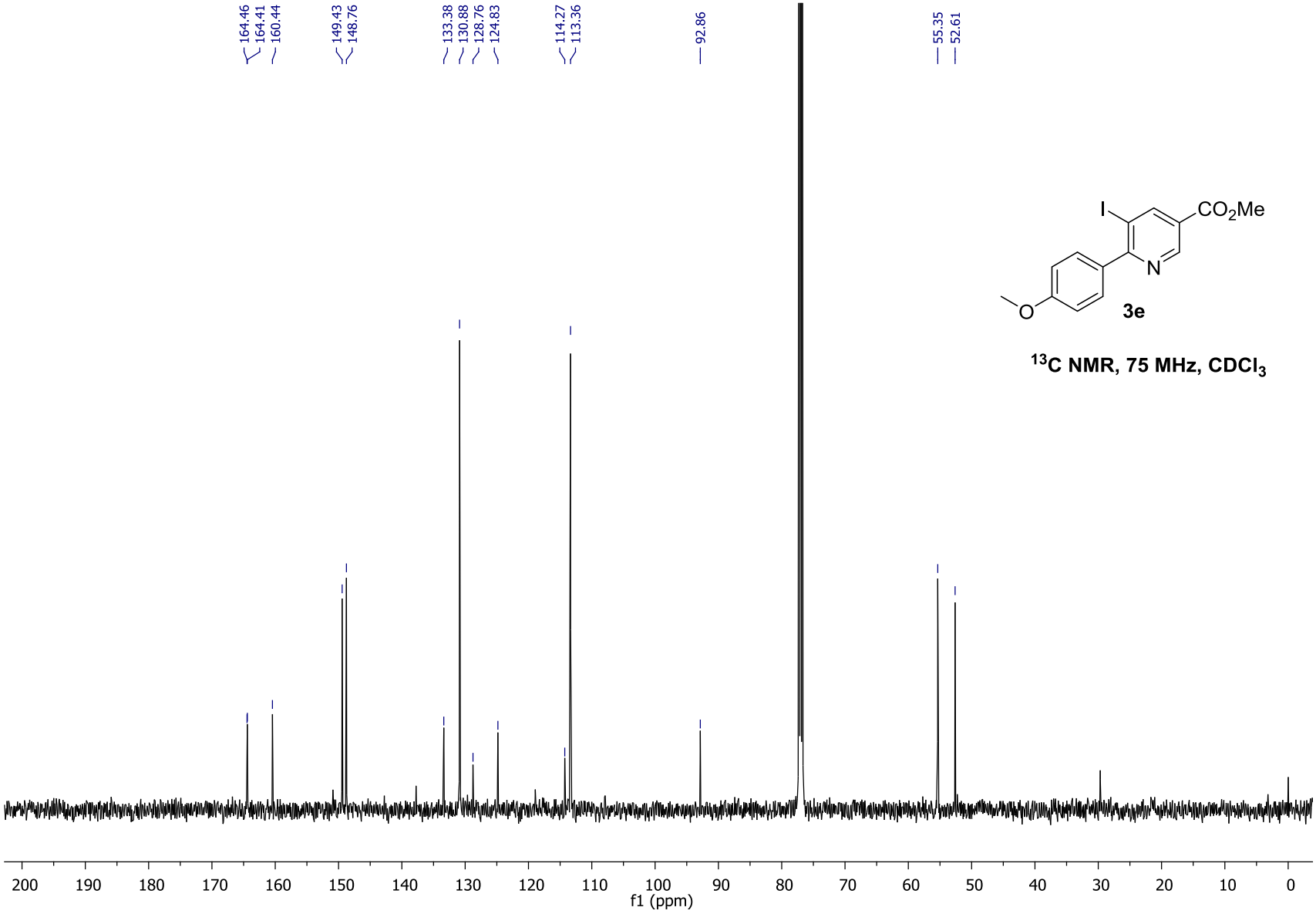

9.09
9.09
8.83
8.82
8.30
8.28
7.56
7.55
7.17
7.16
7.14
3.96
I
CO2Me
N
S
3c
1H NMR, 300 MHz, CDCl3
0.89
0.89
0.92
0.90
0.94
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

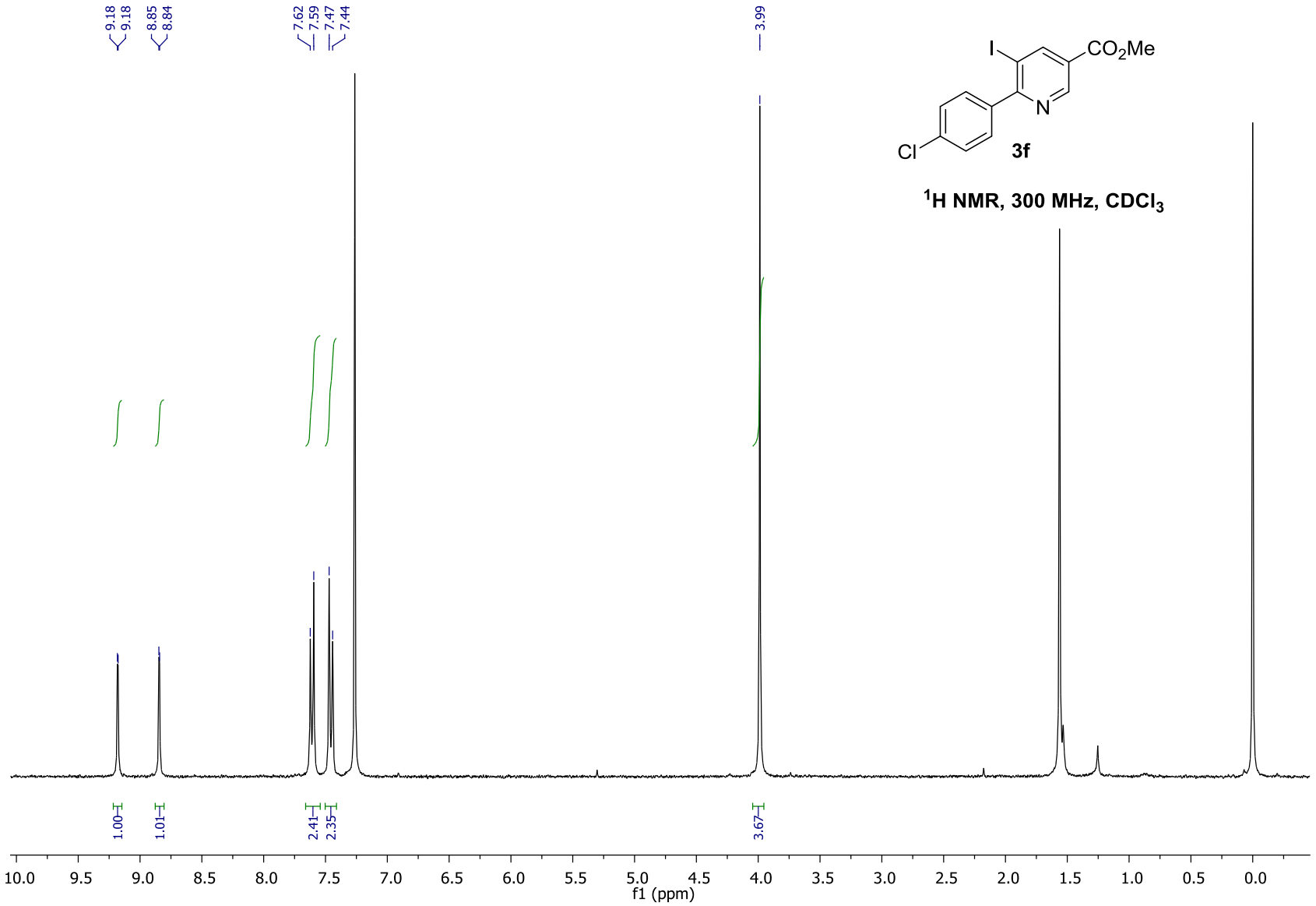

164.17
156.71
150.15
149.00
143.75
130.56
130.35
127.60
124.09
88.79
52.57
I
CO2Me
N
S
3c
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

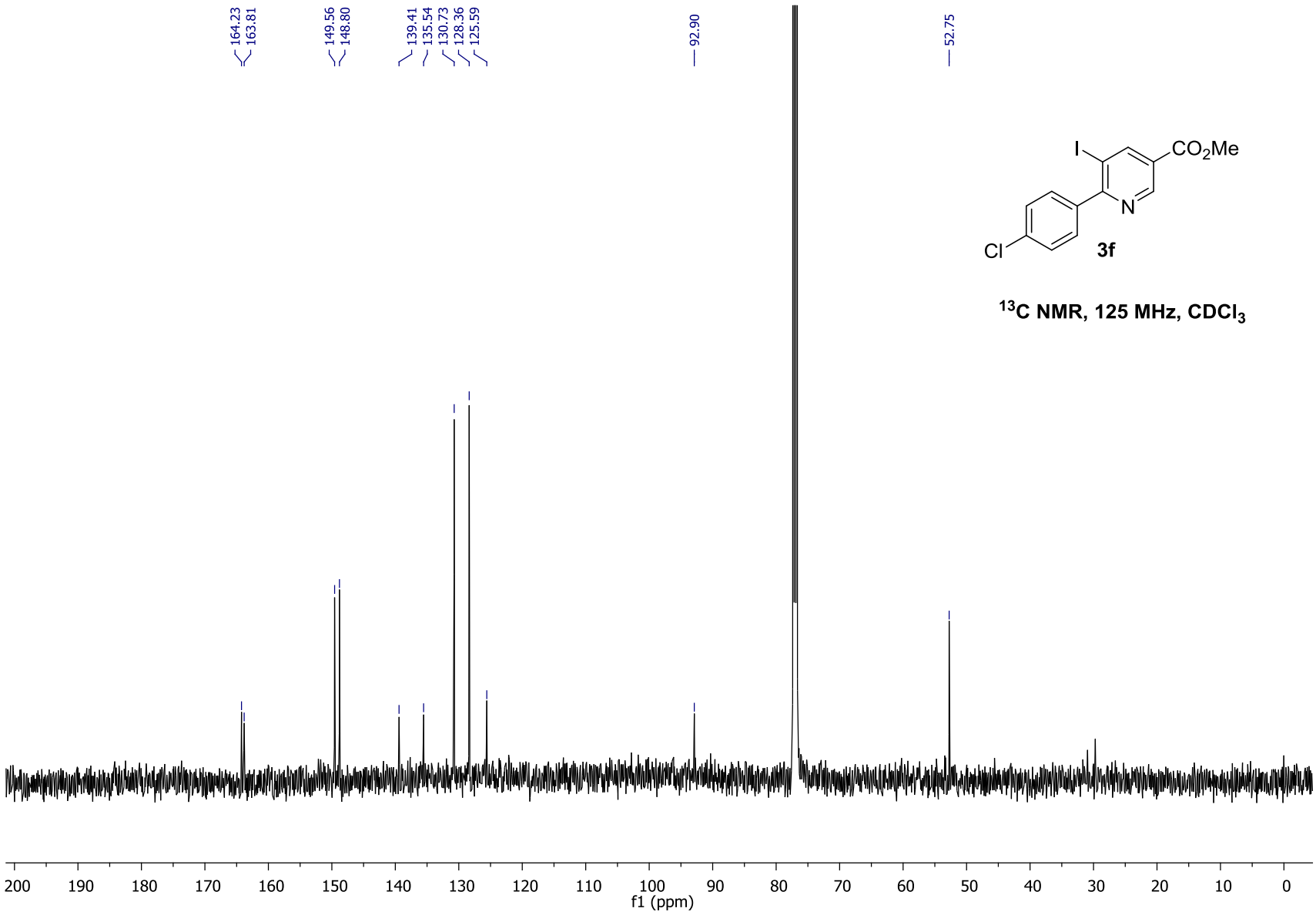

9.18
9.17
8.83
8.83
7.56
7.55
7.29
7.27
3.98
2.43
I
CO2Me
N
3d
1H NMR, 500 MHz, CDCl3
0.80
0.80
1.82
1.81
3.00
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

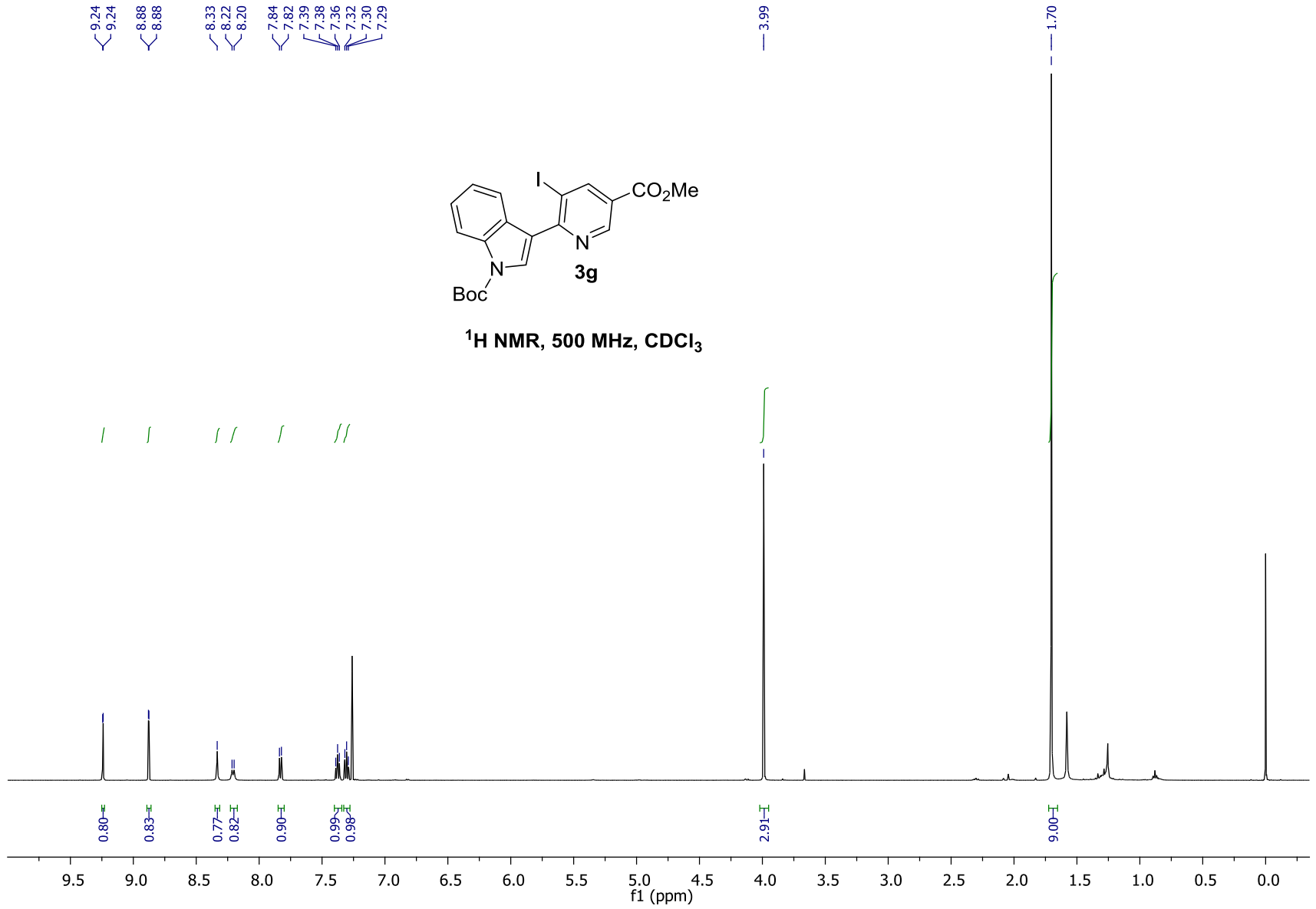

165.05
164.44
149.49
148.67
139.46
138.24
129.19
128.77
125.12
93.12
52.68
21.48
I
CO2Me
N
3d
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

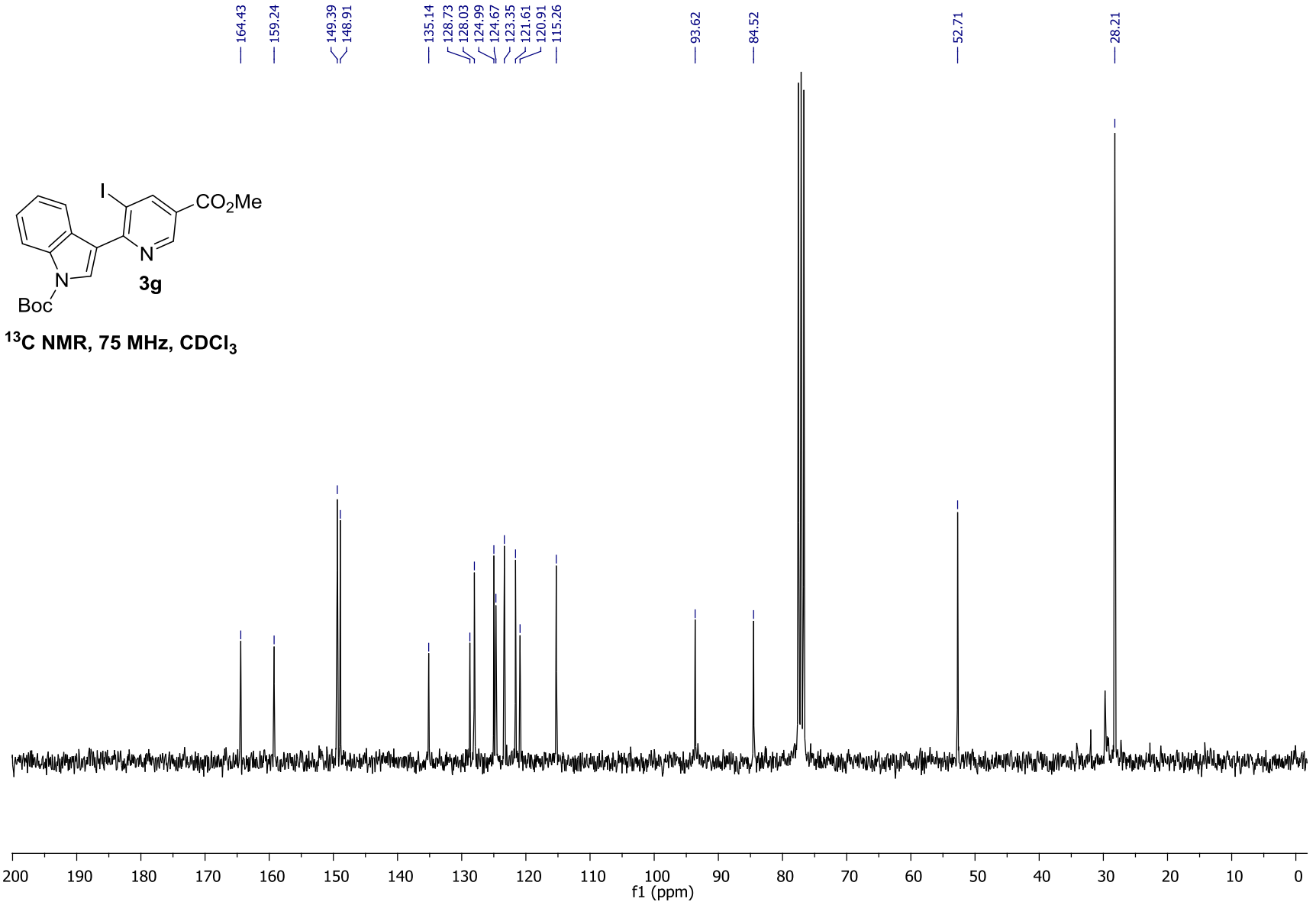

9.16
9.16
8.83
8.82
7.67
7.65
7.00
6.98
3.99
3.88
I
CO2Me
N
O
3e
1H NMR, 500 MHz, CDCl3
0.88
0.87
2.01
2.15
2.96
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.46
164.41
160.44
149.43
148.76
133.38
130.88
128.76
124.83
114.27
113.36
92.86
55.35
52.61
I
CO2Me
N
O
3e
13C NMR, 75 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)

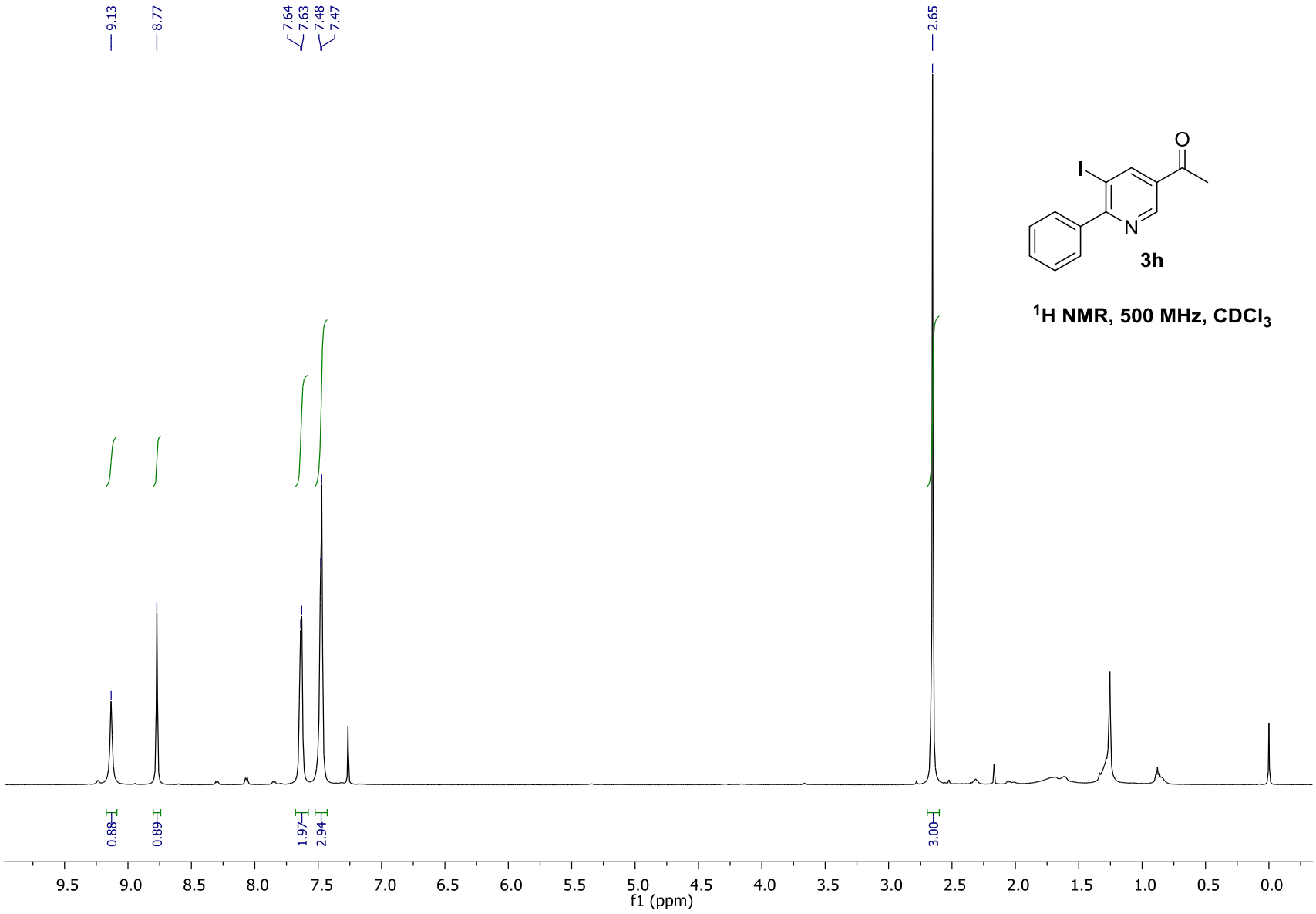

9.18
9.18
8.85
8.84
7.62
7.59
7.47
7.44
3.99
I
CO2Me
N
Cl
3f
1H NMR, 300 MHz, CDCl3
1.00
1.01
2.41
2.35
3.67
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

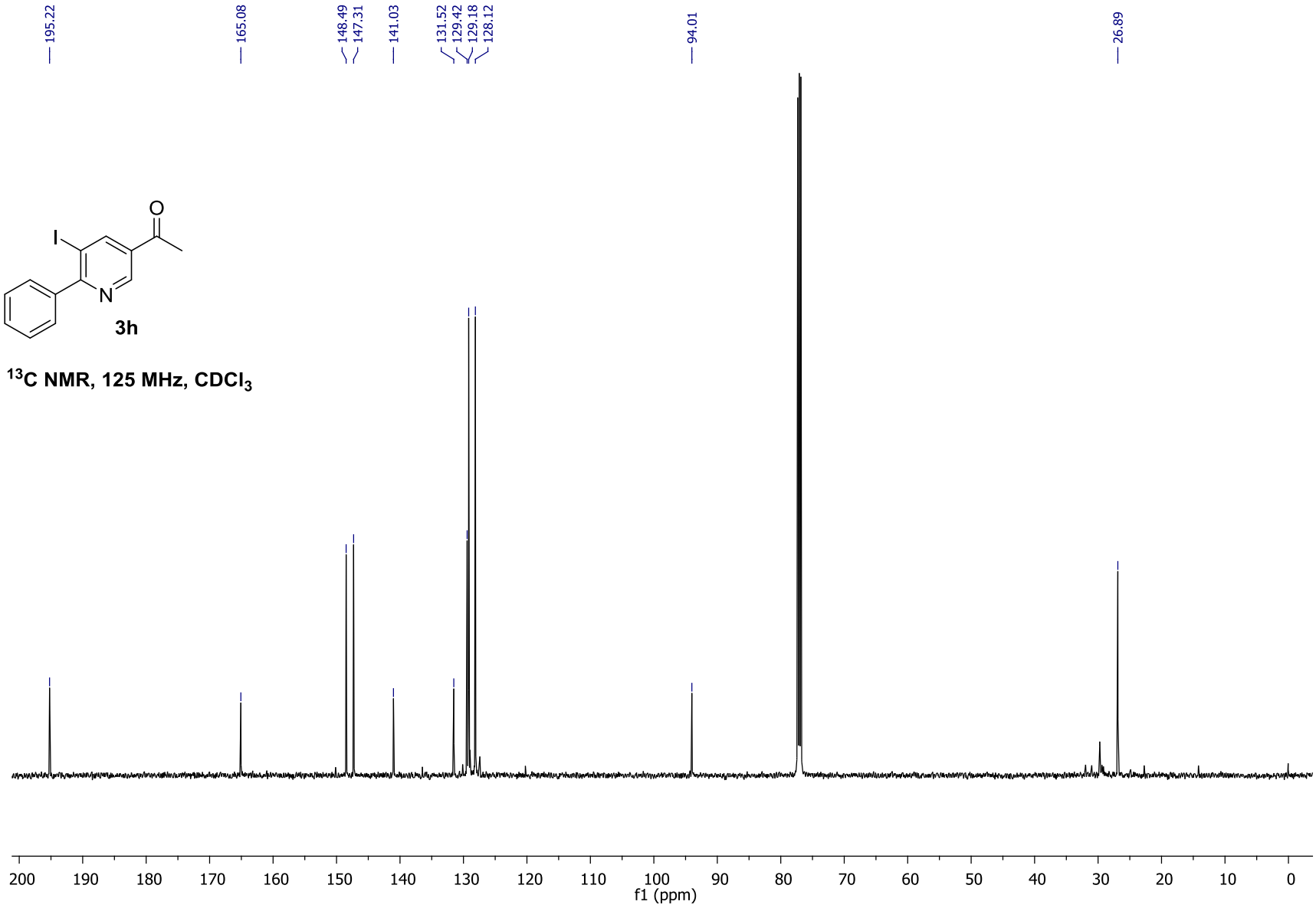

164.23
163.81
149.56
148.80
139.41
135.54
130.73
128.36
125.59
92.90
52.75
I
CO2Me
N
Cl
3f
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

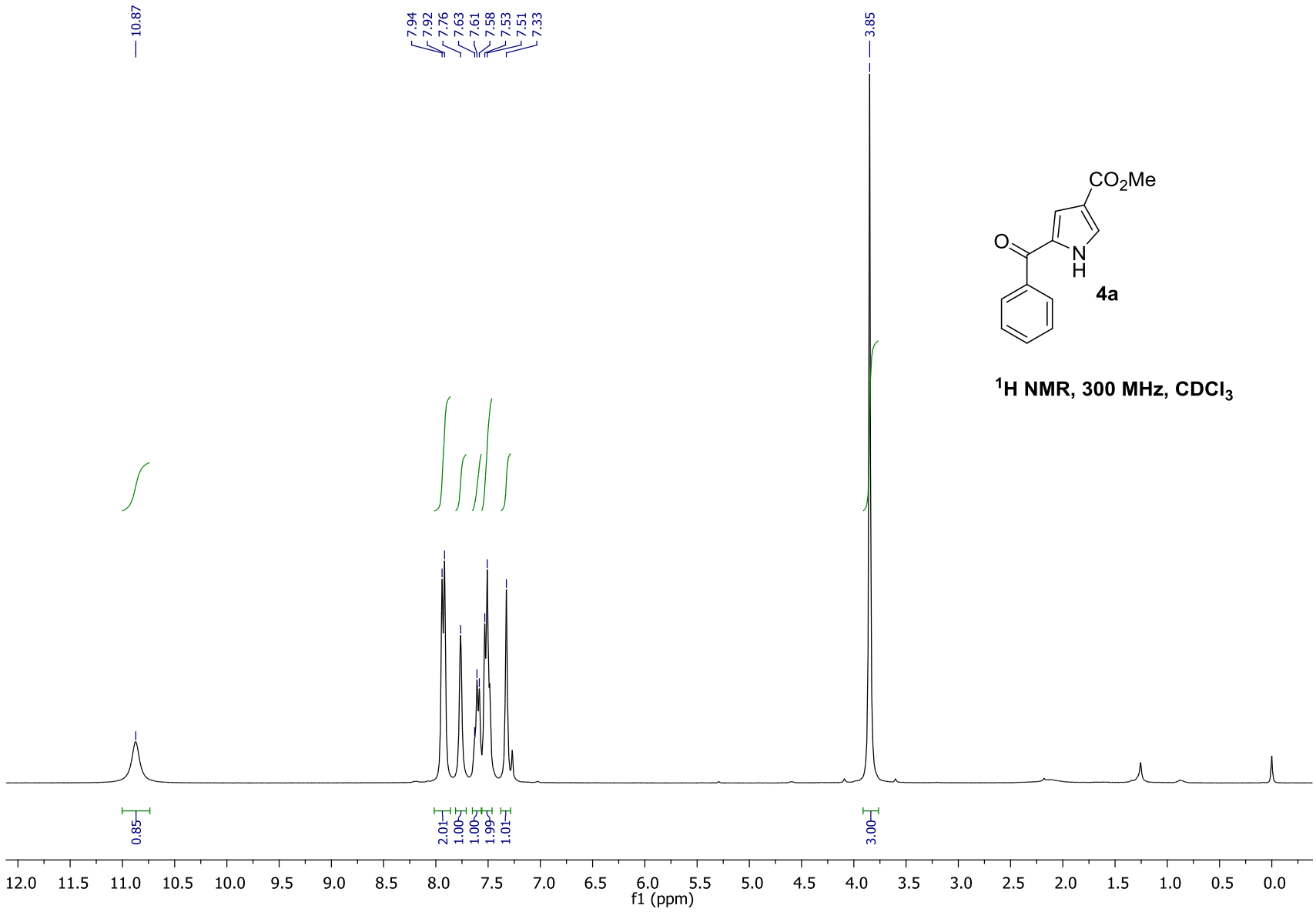

9.24
9.24
8.88
8.88
8.33
8.22
8.20
7.84
7.82
7.39
7.38
7.36
7.32
7.30
7.29
3.99
1.70
I
CO2Me
N
N
Boc
3g
1H NMR, 500 MHz, CDCl3
0.80
0.83
0.77
0.82
0.90
0.99
0.98
2.91
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

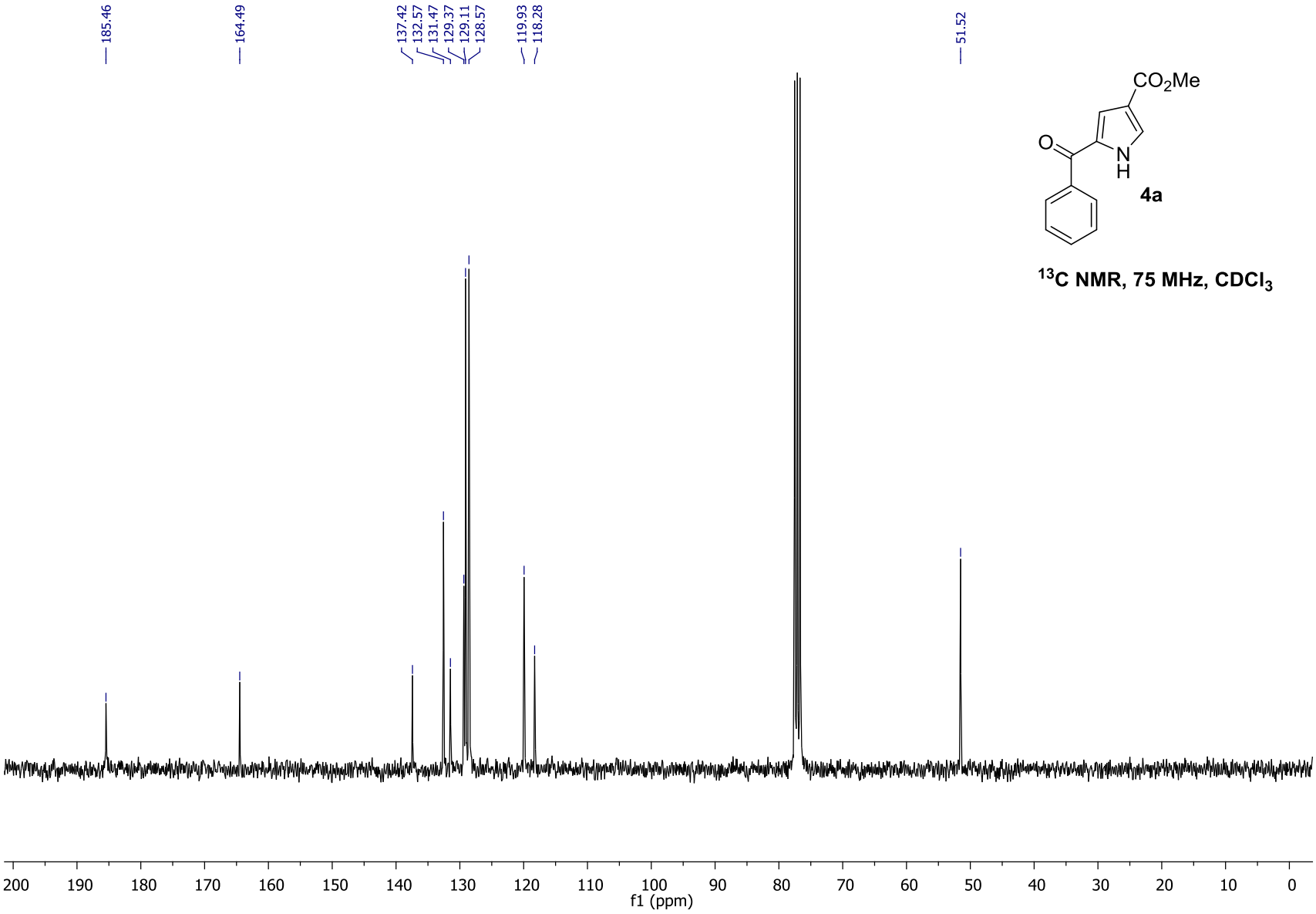


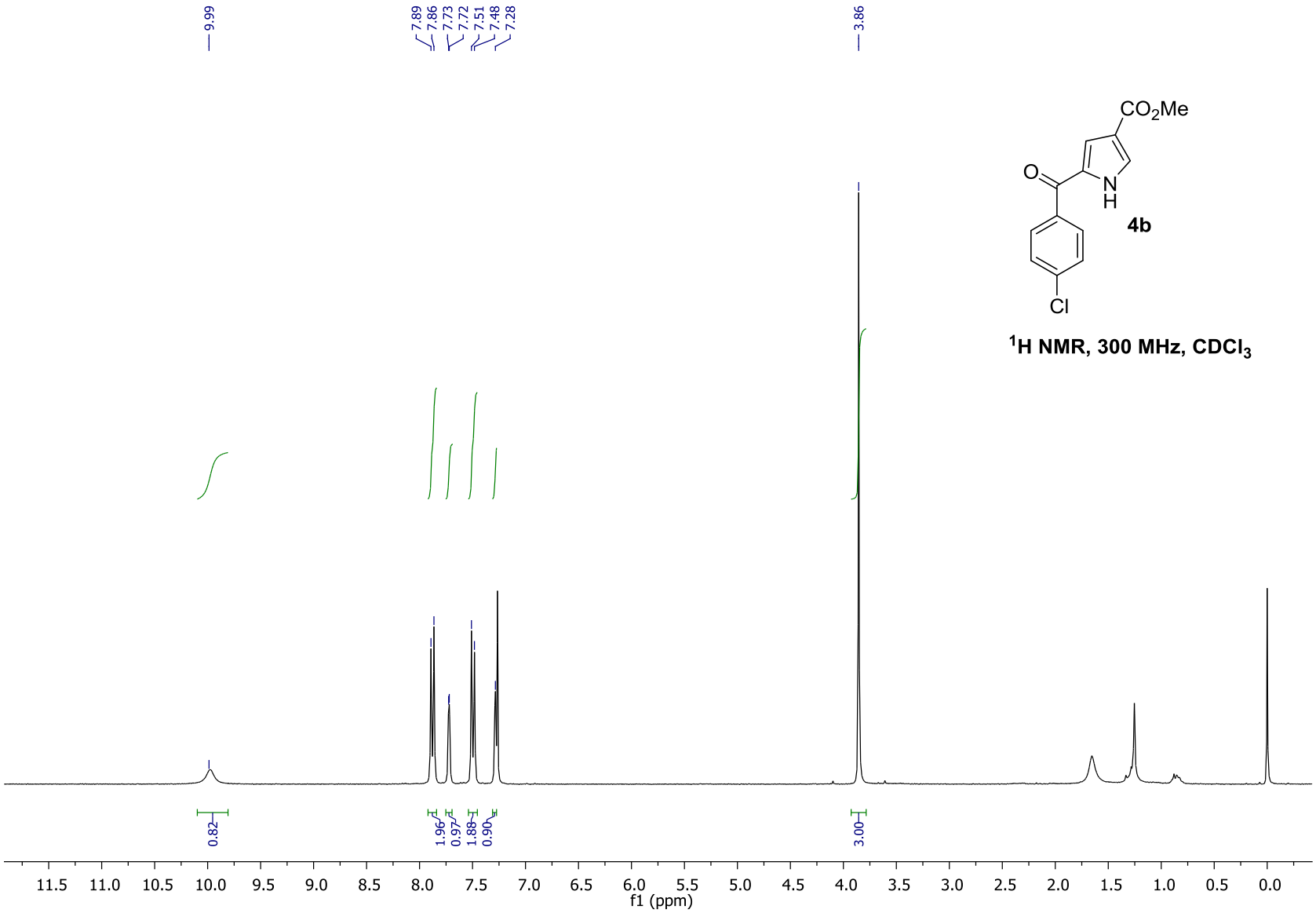
^{13}C NMR, 75 MHz, $CDCl_3$

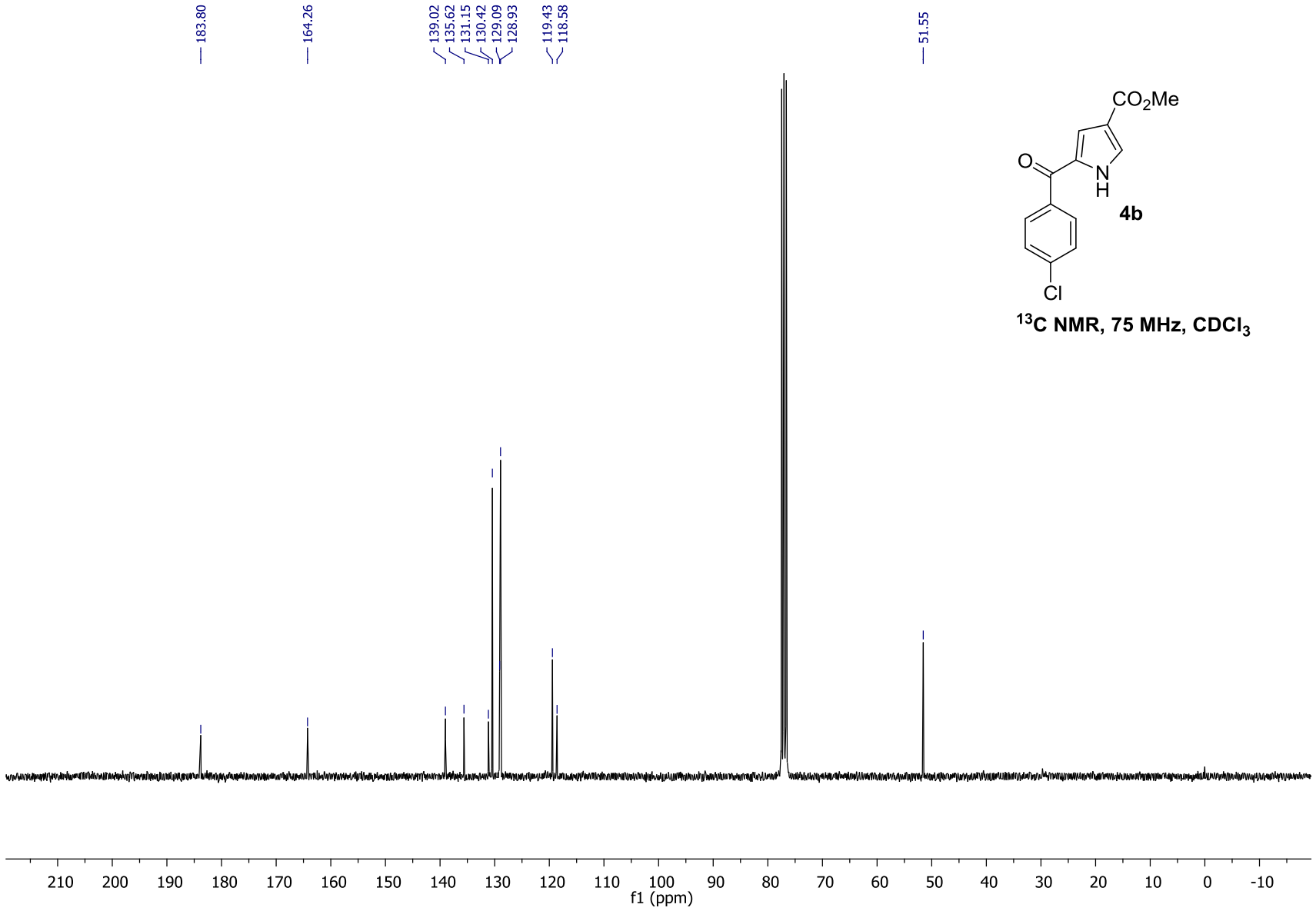

9.13
8.77
7.64
7.63
7.48
7.47
2.65
O
I
N
3h
^{1}H NMR, 500 MHz, CDCl$_3$
0.88
0.89
1.97
2.94
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

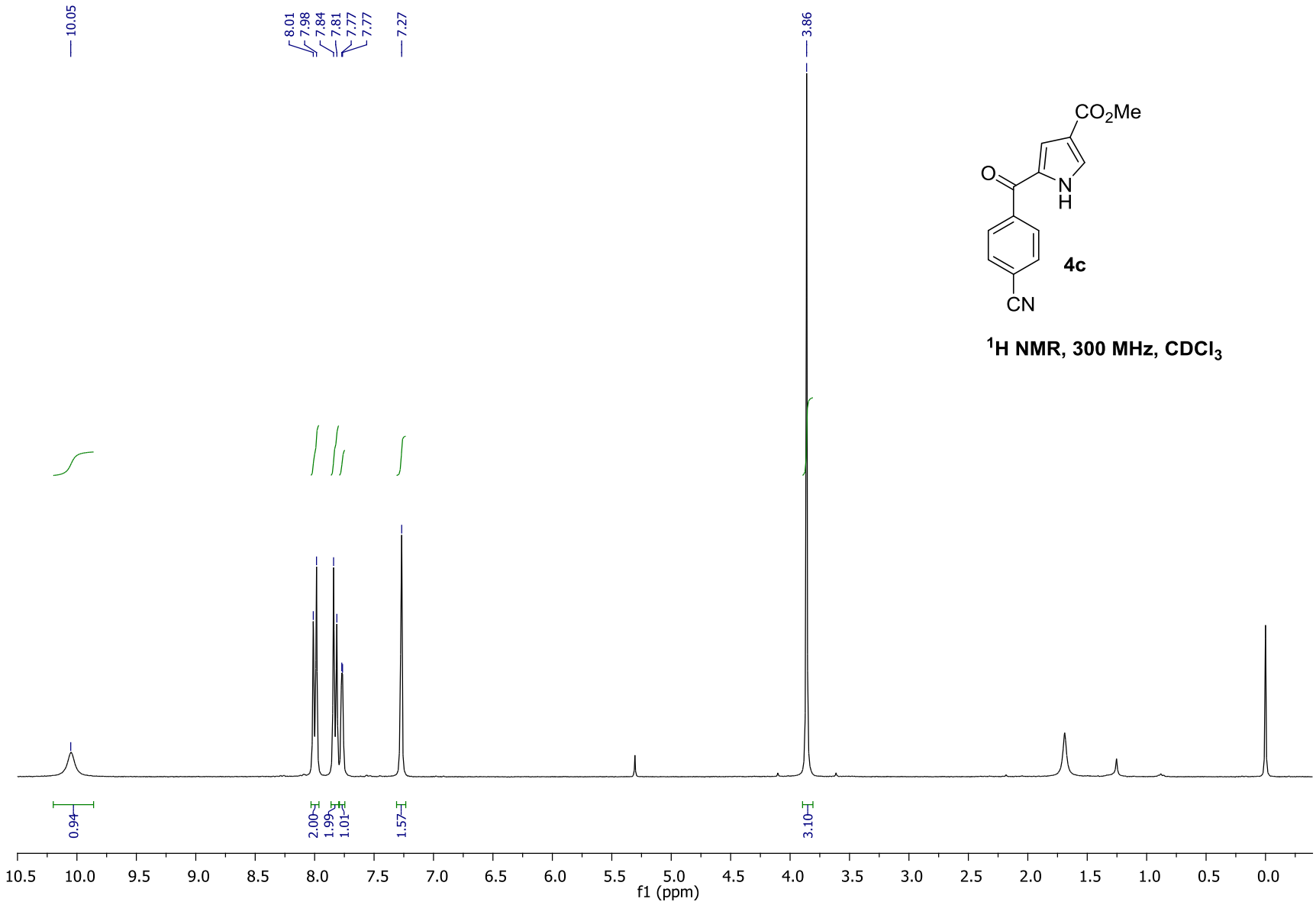

195.22
165.08
148.49
147.31
141.03
131.52
129.42
129.18
128.12
94.01
26.89
O
I
N
3h
^{13}C NMR, 125 MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

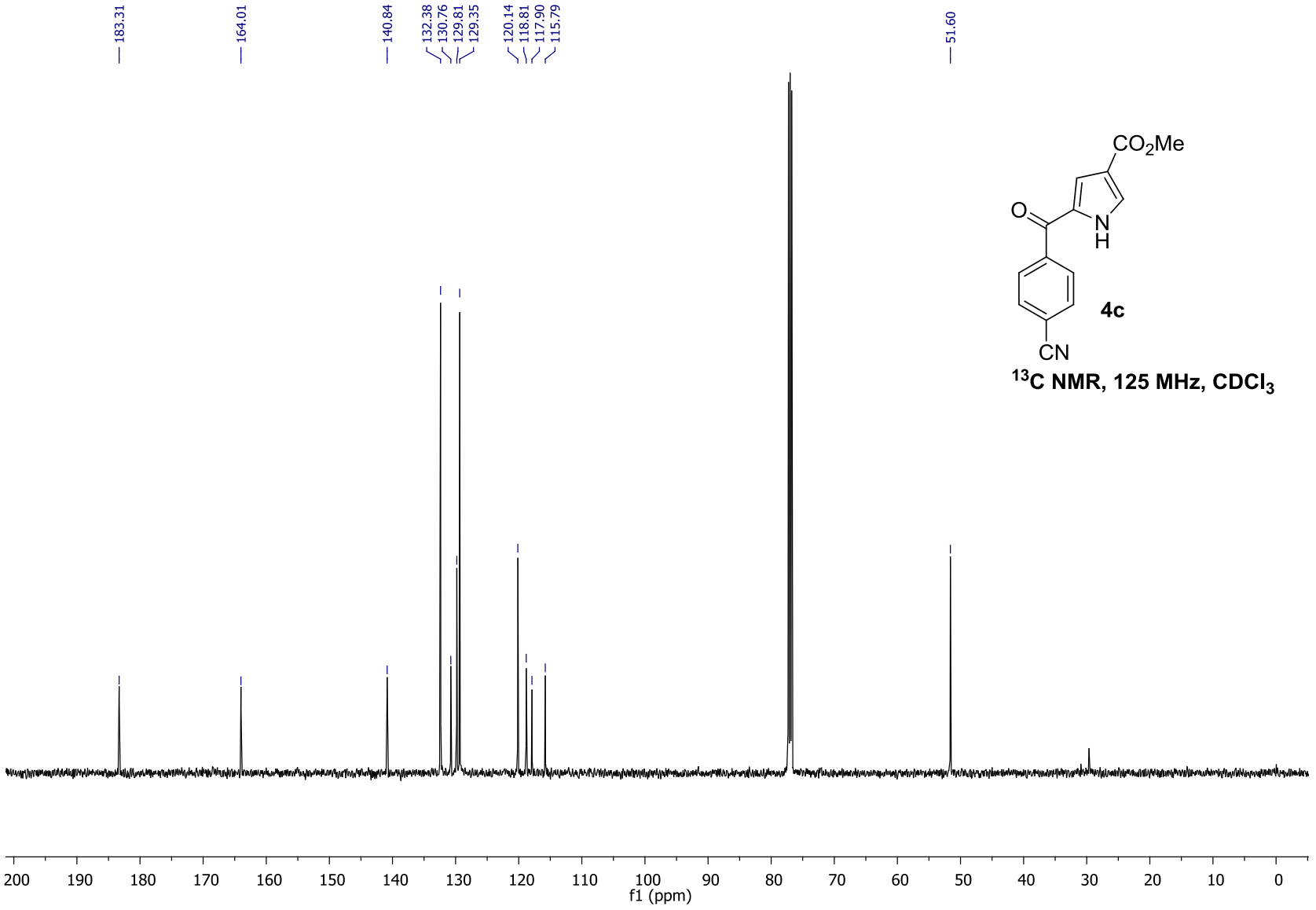

10.87
7.94
7.92
7.76
7.63
7.61
7.58
7.53
7.51
7.33
3.85
CO2Me
O
N
H
4a
1H NMR, 300 MHz, CDCl3
0.85
2.01
1.00
1.00
1.99
1.01
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

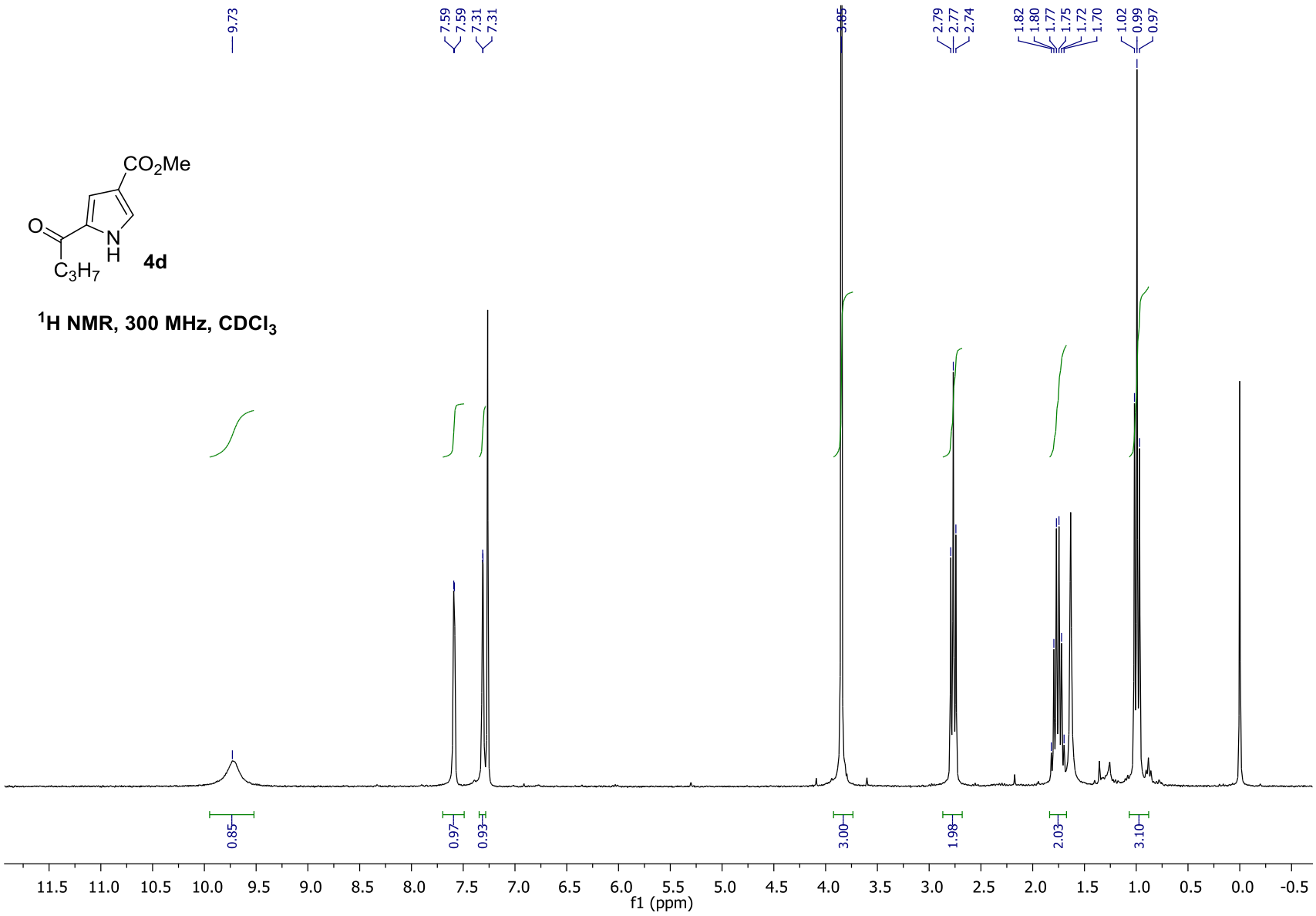

185.46
164.49
137.42
132.57
131.47
129.37
129.11
128.57
119.93
118.28
51.52
CO2Me
O
N
H
4a
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

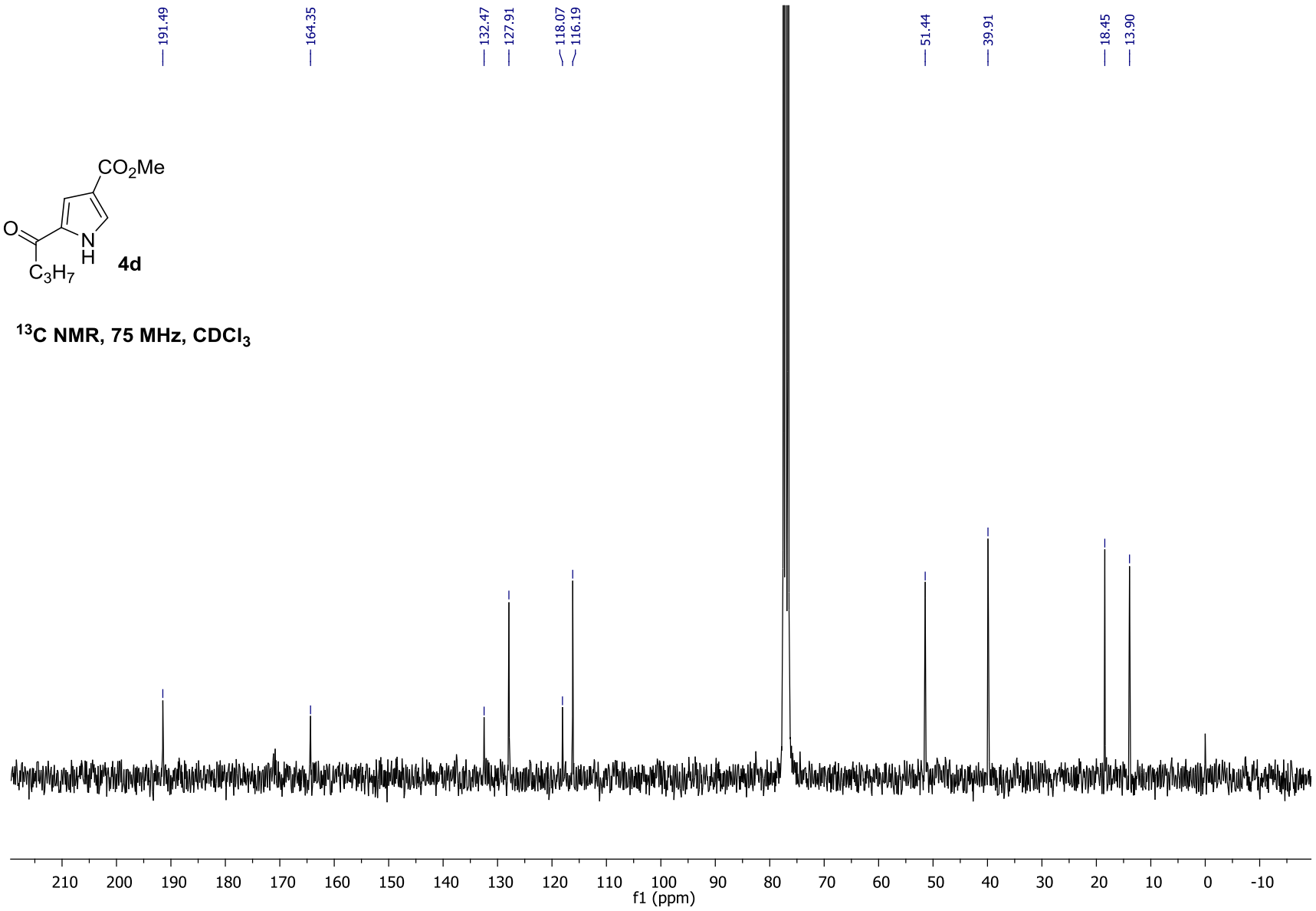

9.99
7.89
7.86
7.73
7.72
7.51
7.48
7.28
3.86
CO2Me
O
N
H
4b
Cl
1H NMR, 300 MHz, CDCl3
0.82
1.96
0.97
1.88
0.90
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


183.80
164.26
139.02
135.62
131.15
130.42
129.09
128.93
119.43
118.58
51.55
CO2Me
O
N
H
Cl
4b
13C NMR, 75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.05
8.01
7.98
7.84
7.81
7.77
7.77
7.27
3.86
CO2Me
O
N
H
CN
4c
1H NMR, 300 MHz, CDCl3
0.94
2.00
1.99
1.01
1.57
3.10
10.5 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
f1 (ppm)


183.31
164.01
140.84
132.38
130.76
129.81
129.35
120.14
118.81
117.90
115.79
51.60
CO2Me
O
N
H
CN
4c
13C NMR, 125 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)


9.73
7.59
7.59
7.31
7.31
3.85
2.79
2.77
2.74
1.82
1.80
1.77
1.75
1.72
1.70
1.02
0.99
0.97
CO2Me
O
N
H
C3H7
4d
1H NMR, 300 MHz, CDCl3
0.85
0.97
0.93
3.00
1.98
2.03
3.10
11.5 11.0 10.5 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
f1 (ppm)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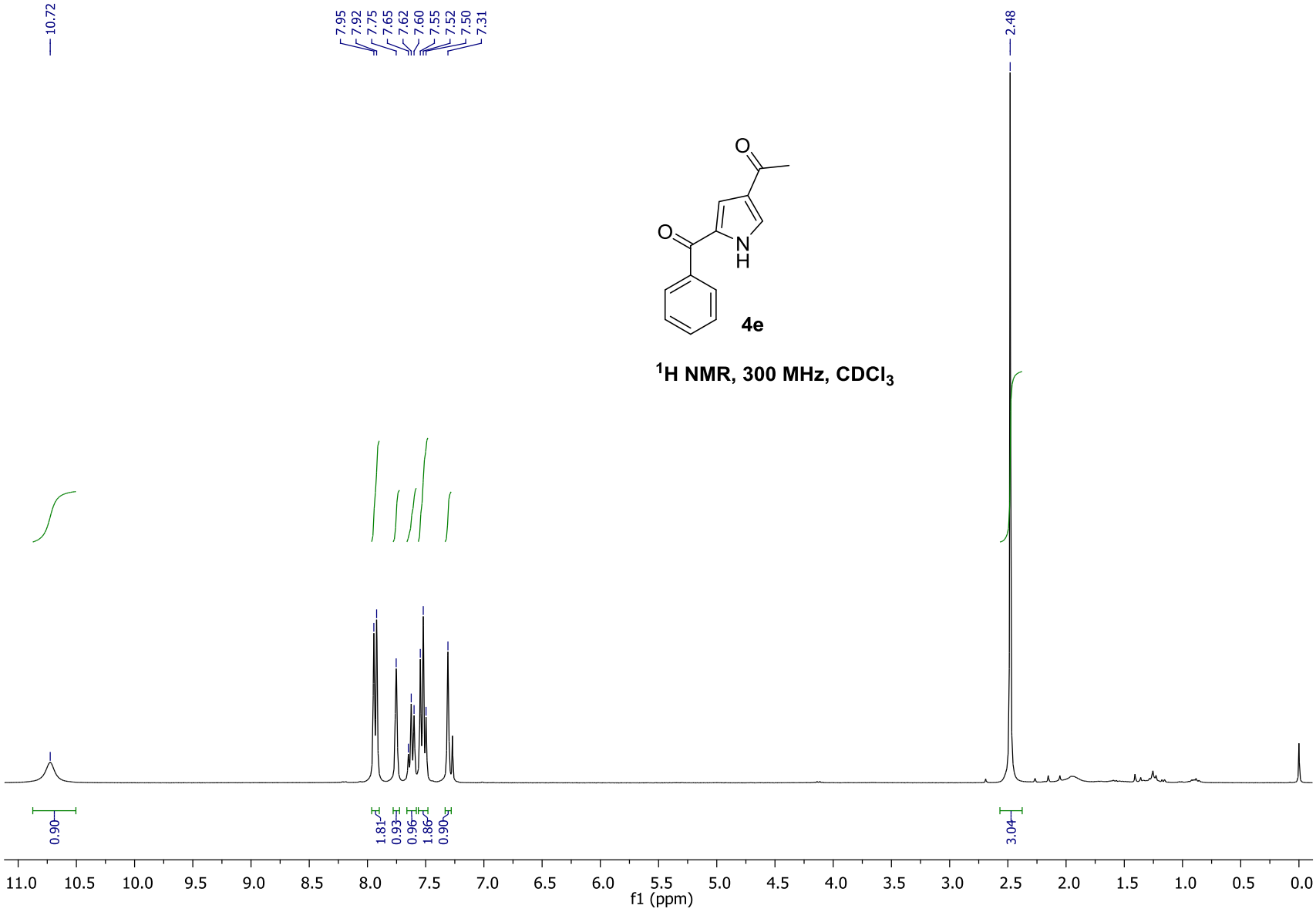
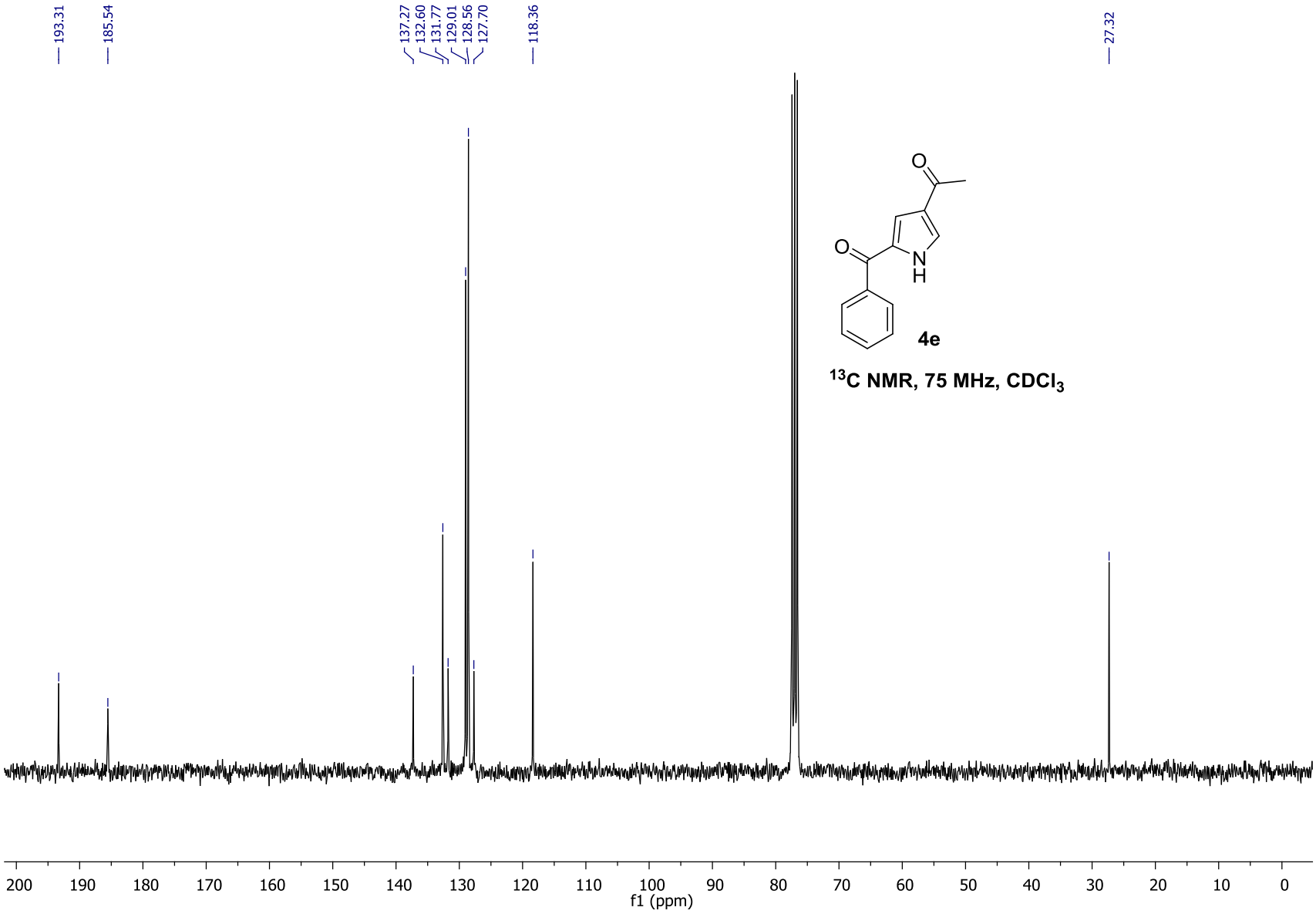
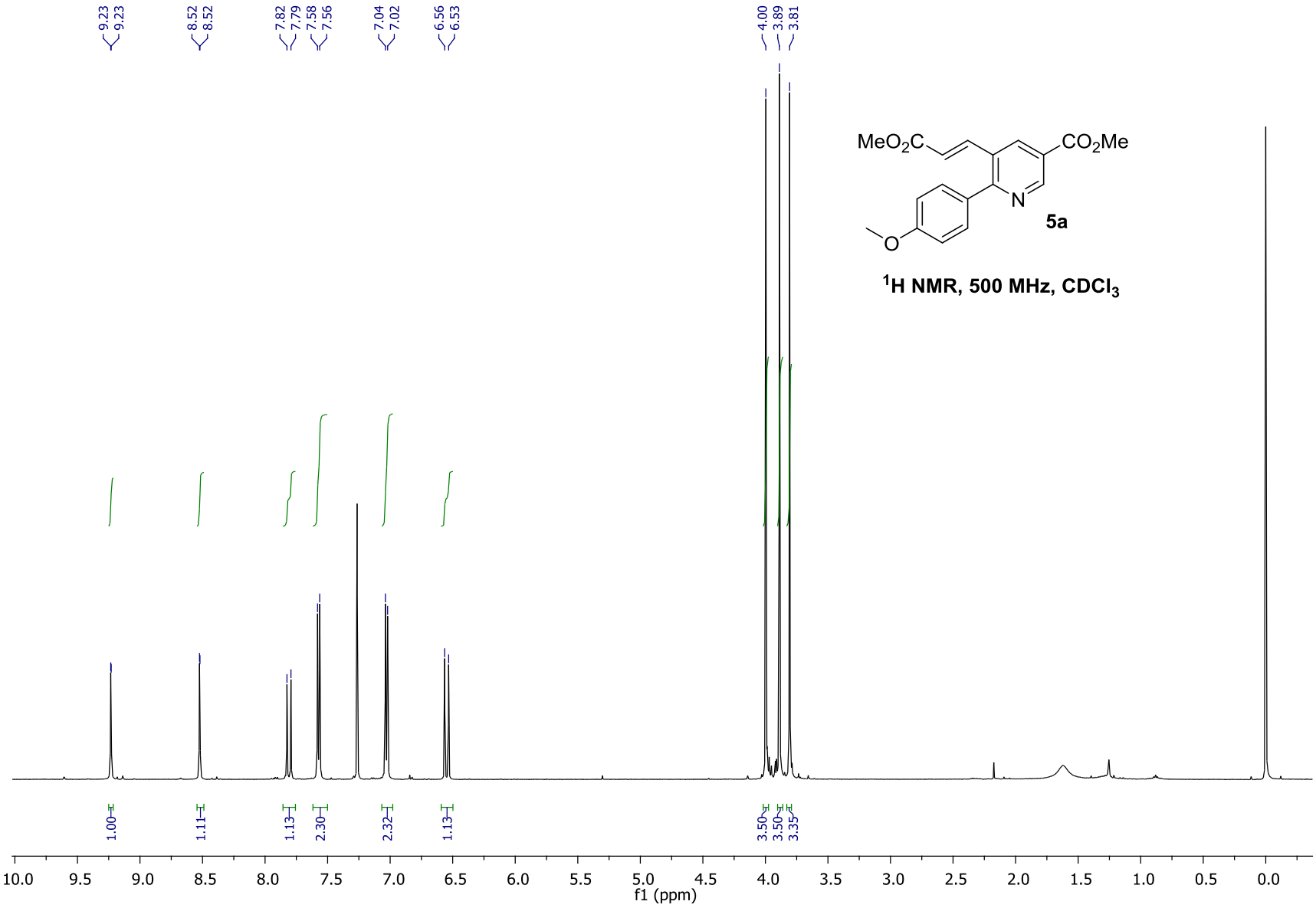
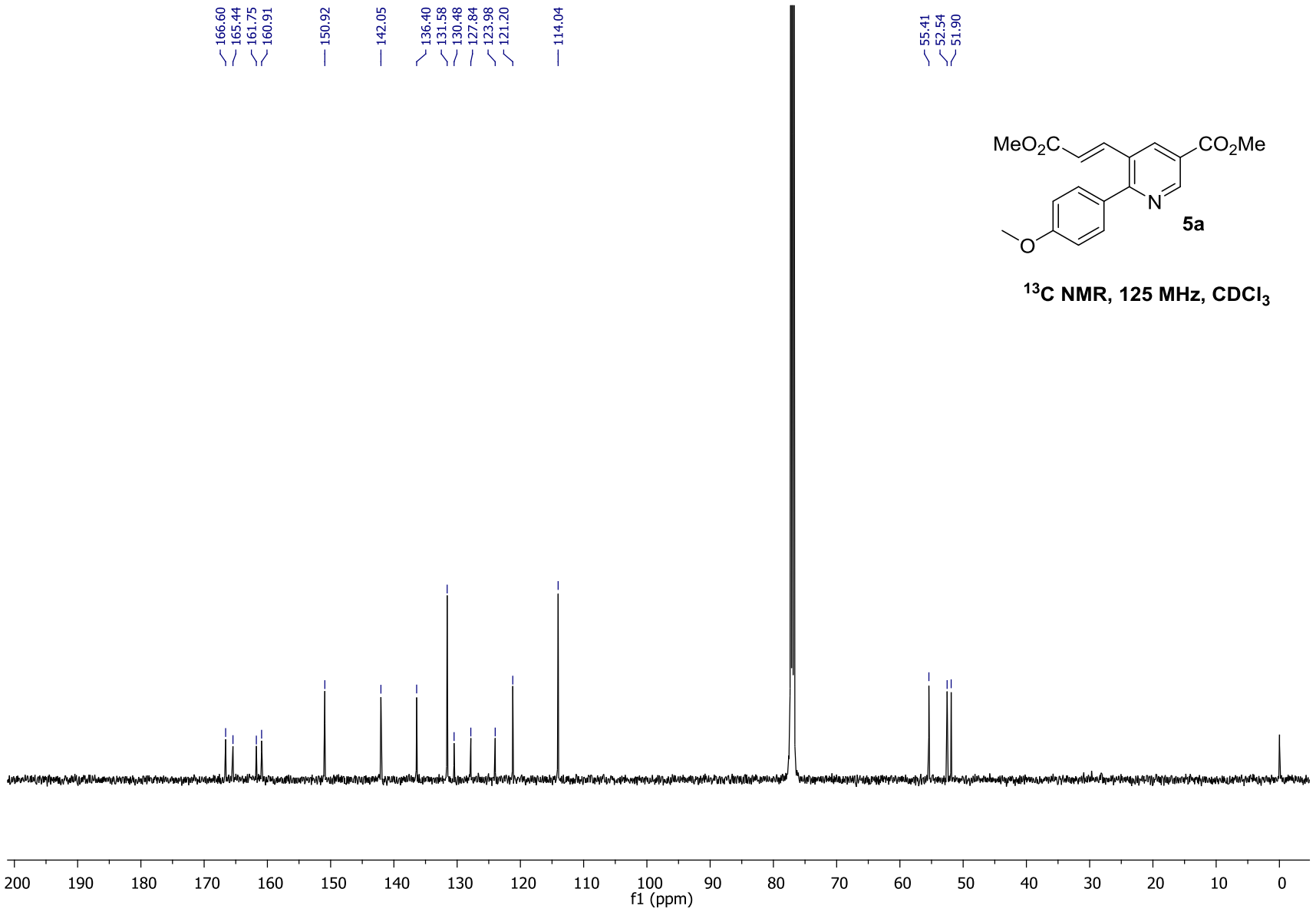
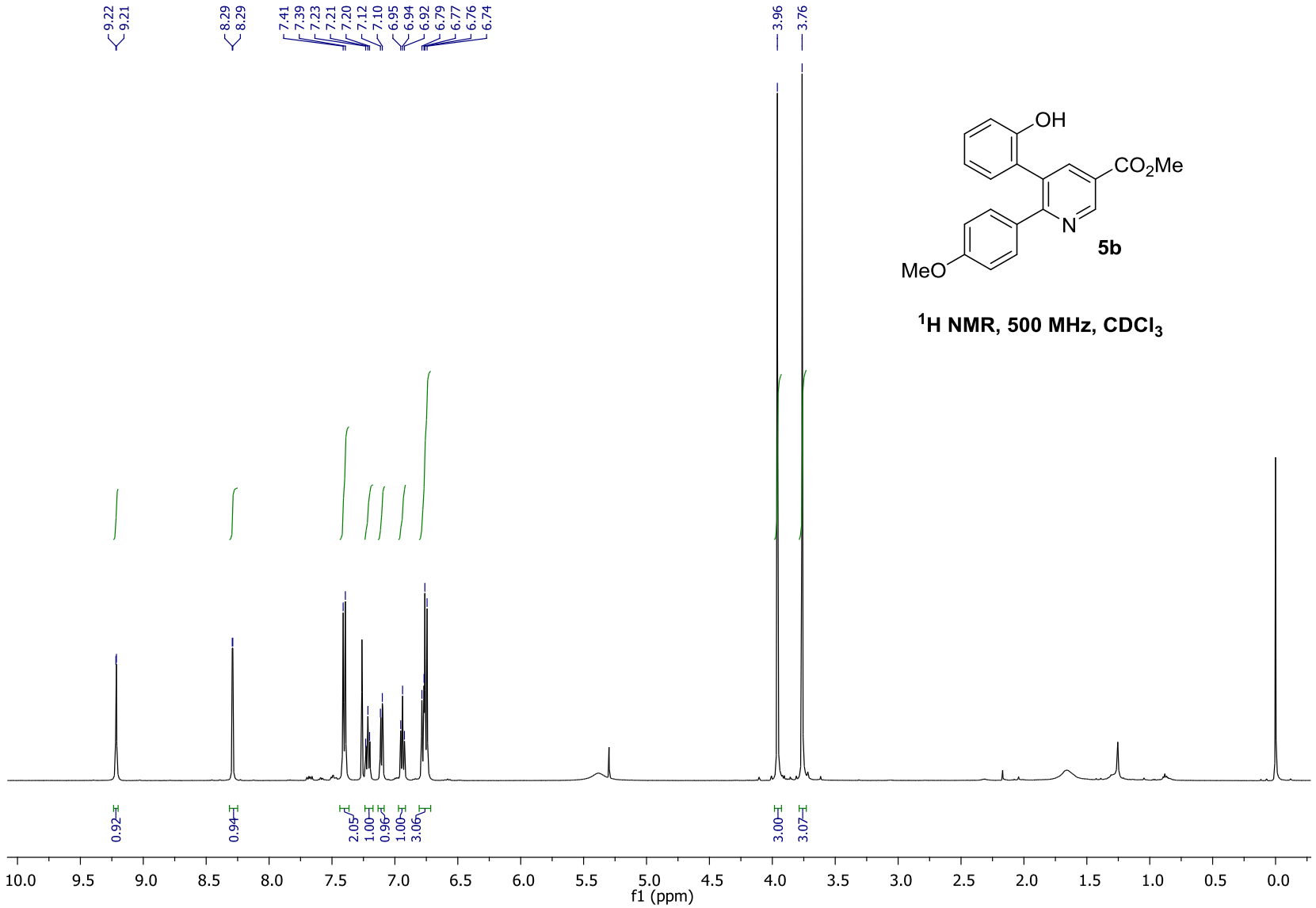
164.35
132.47
127.91
118.07
116.19
51.44
39.91
18.45
13.90
CO2Me
O
N
H
C3H7
4d
13C NMR, 75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

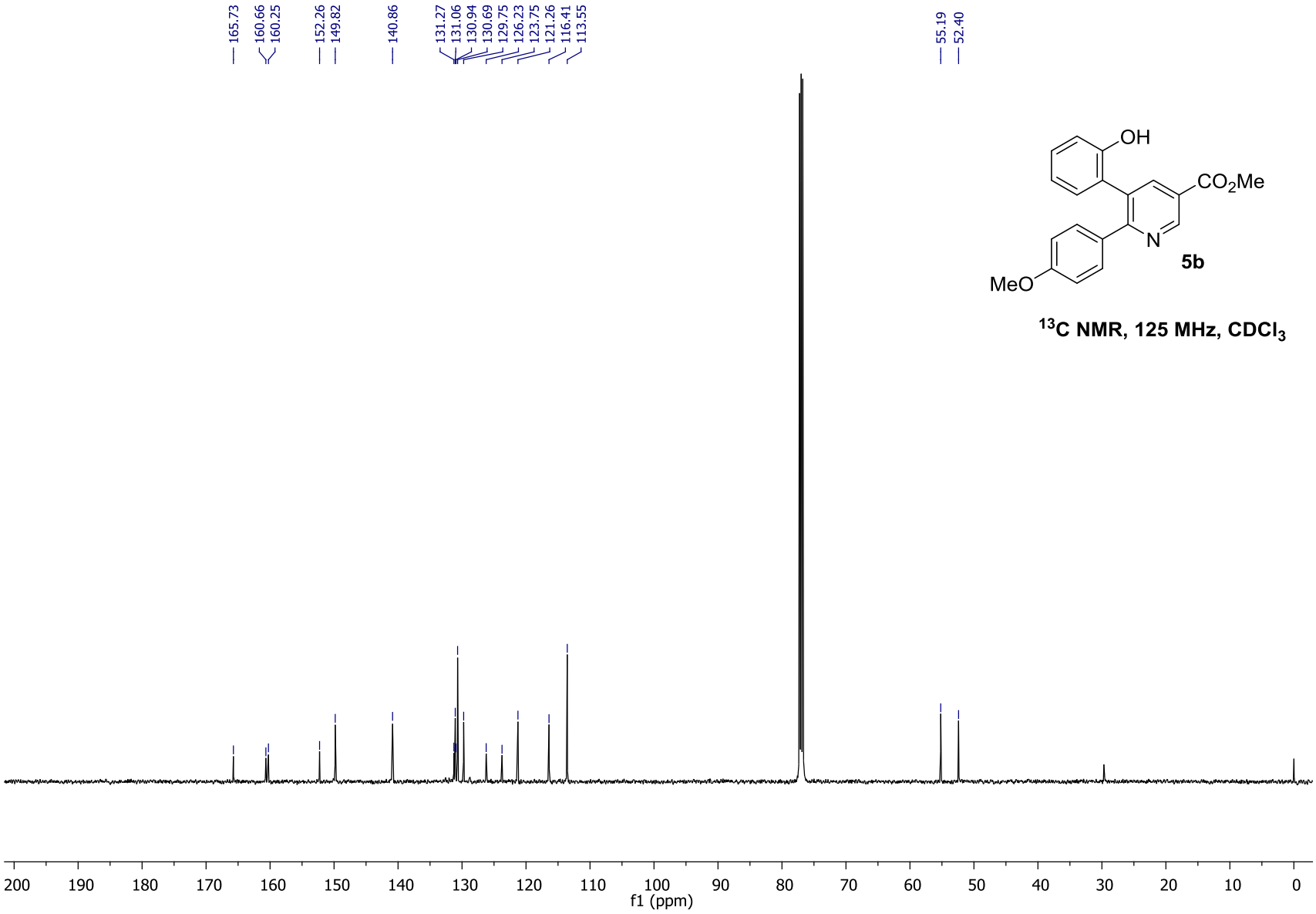

10.72
7.95
7.92
7.75
7.65
7.62
7.60
7.55
7.52
7.50
7.31
2.48
O
O
N
H
4e
^{1}H NMR, 300 MHz, CDCl$_3$
0.90
1.81
0.93
0.96
1.86
0.90
3.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

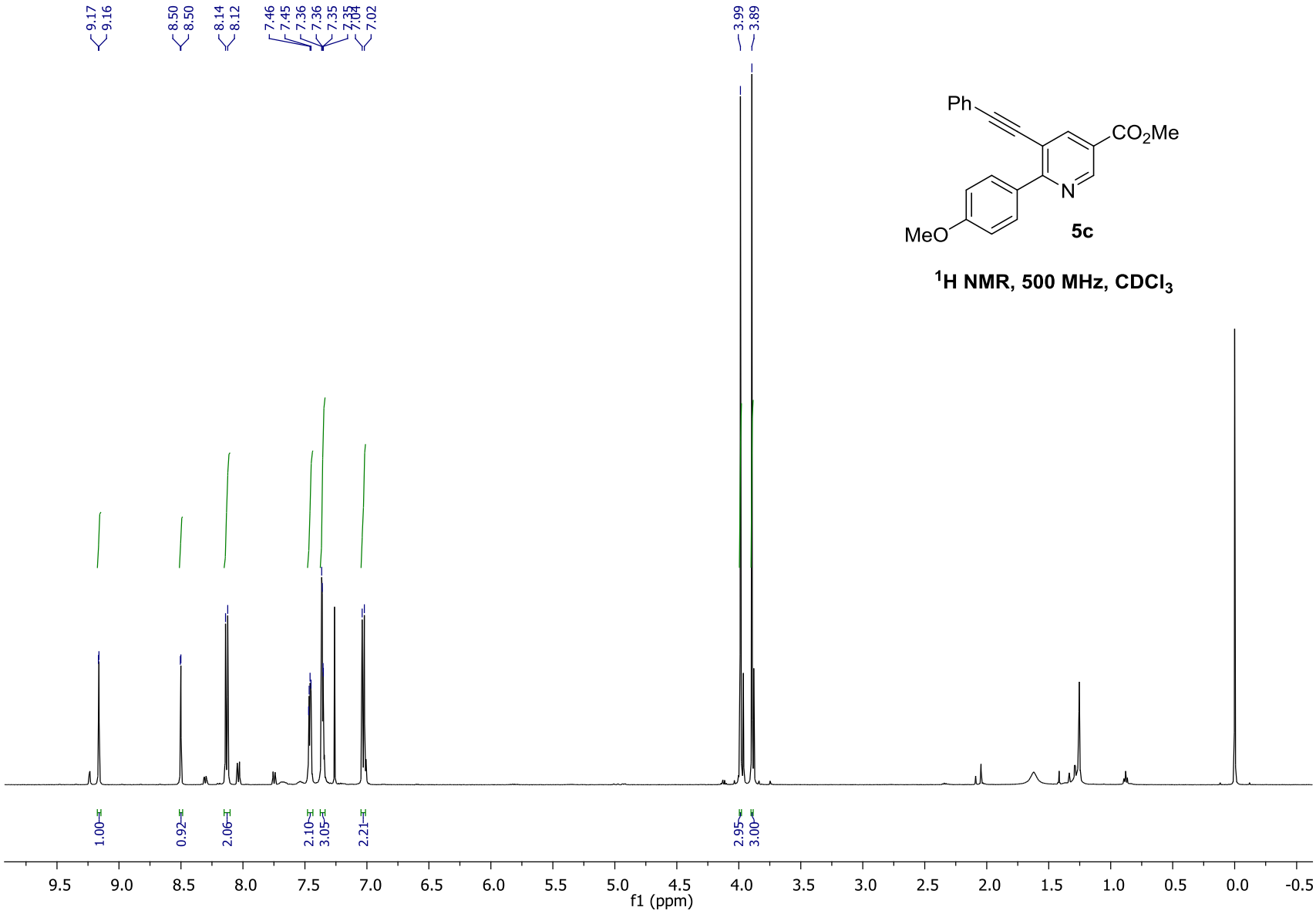

193.31
185.54
137.27
132.60
131.77
129.01
128.56
127.70
118.36
27.32
O
O
N
H
4e
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

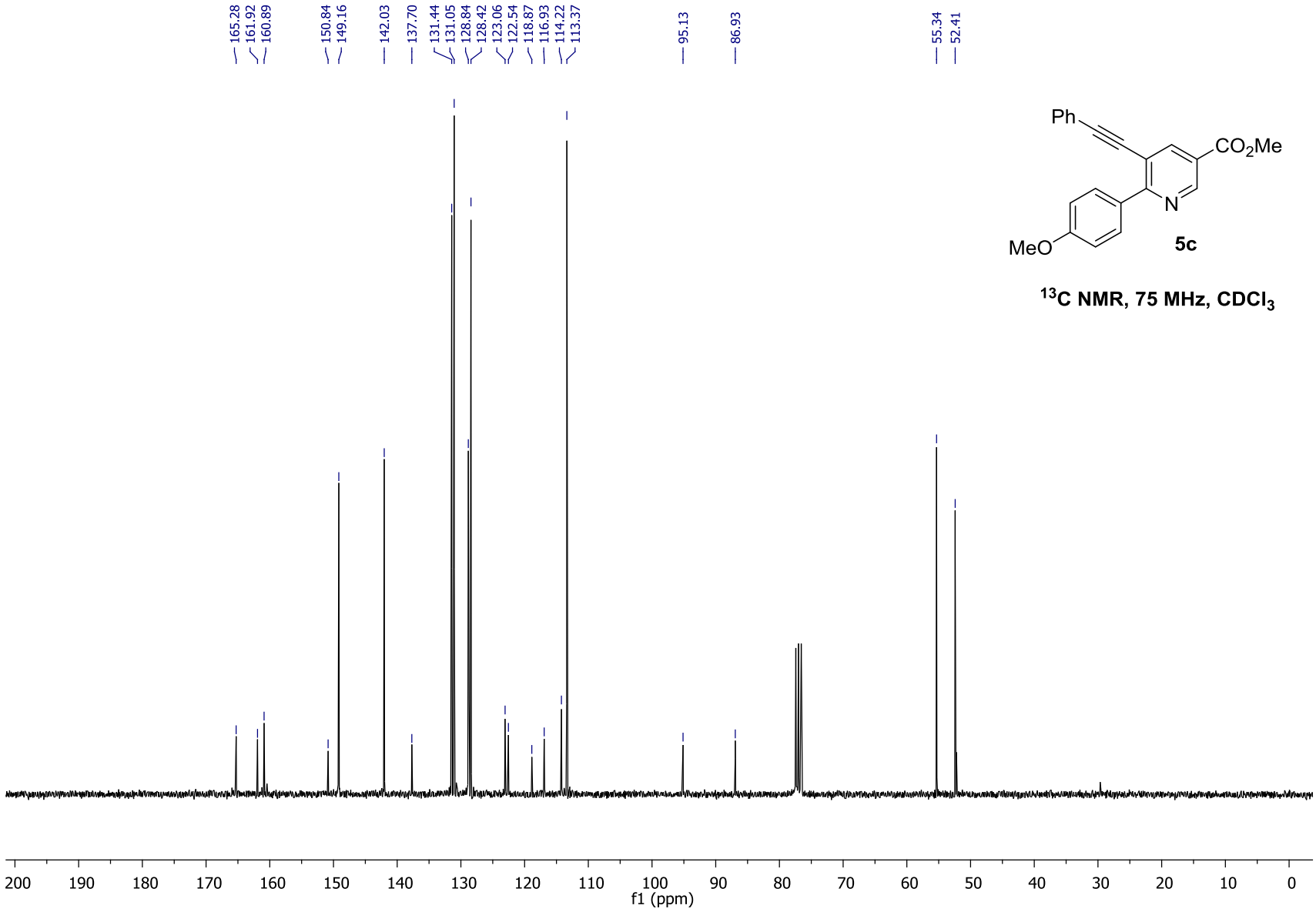

9.23
9.23
8.52
8.52
7.82
7.79
7.58
7.56
7.04
7.02
6.56
6.53
4.00
3.89
3.81
MeO2C
CO2Me
N
O
5a
1H NMR, 500 MHz, CDCl3
1.00
1.11
1.13
2.30
2.32
1.13
3.50
3.50
3.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

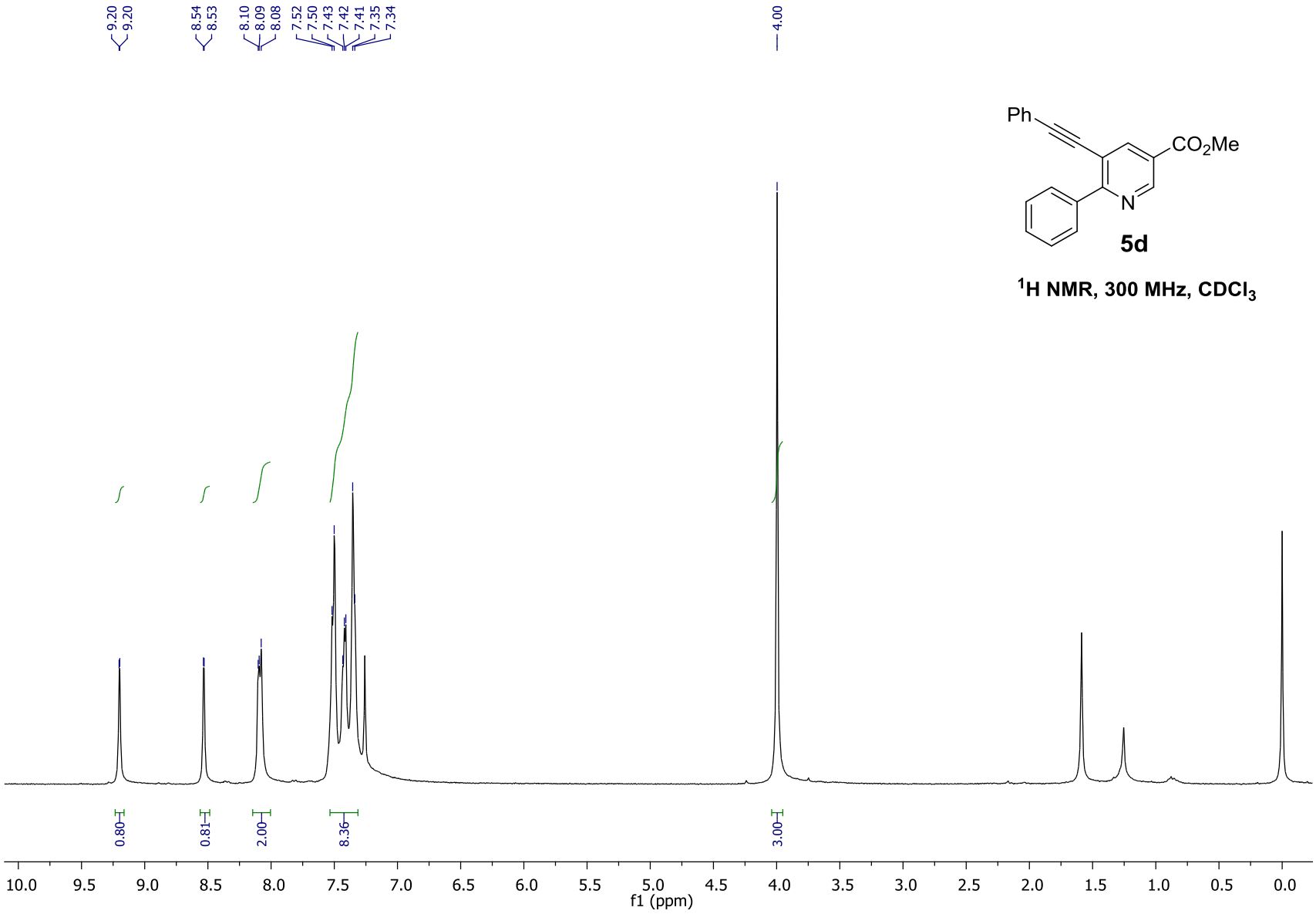

166.60
165.44
161.75
160.91
150.92
142.05
136.40
131.58
130.48
127.84
123.98
121.20
114.04
55.41
52.54
51.90
MeO2C
CO2Me
N
O
5a
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

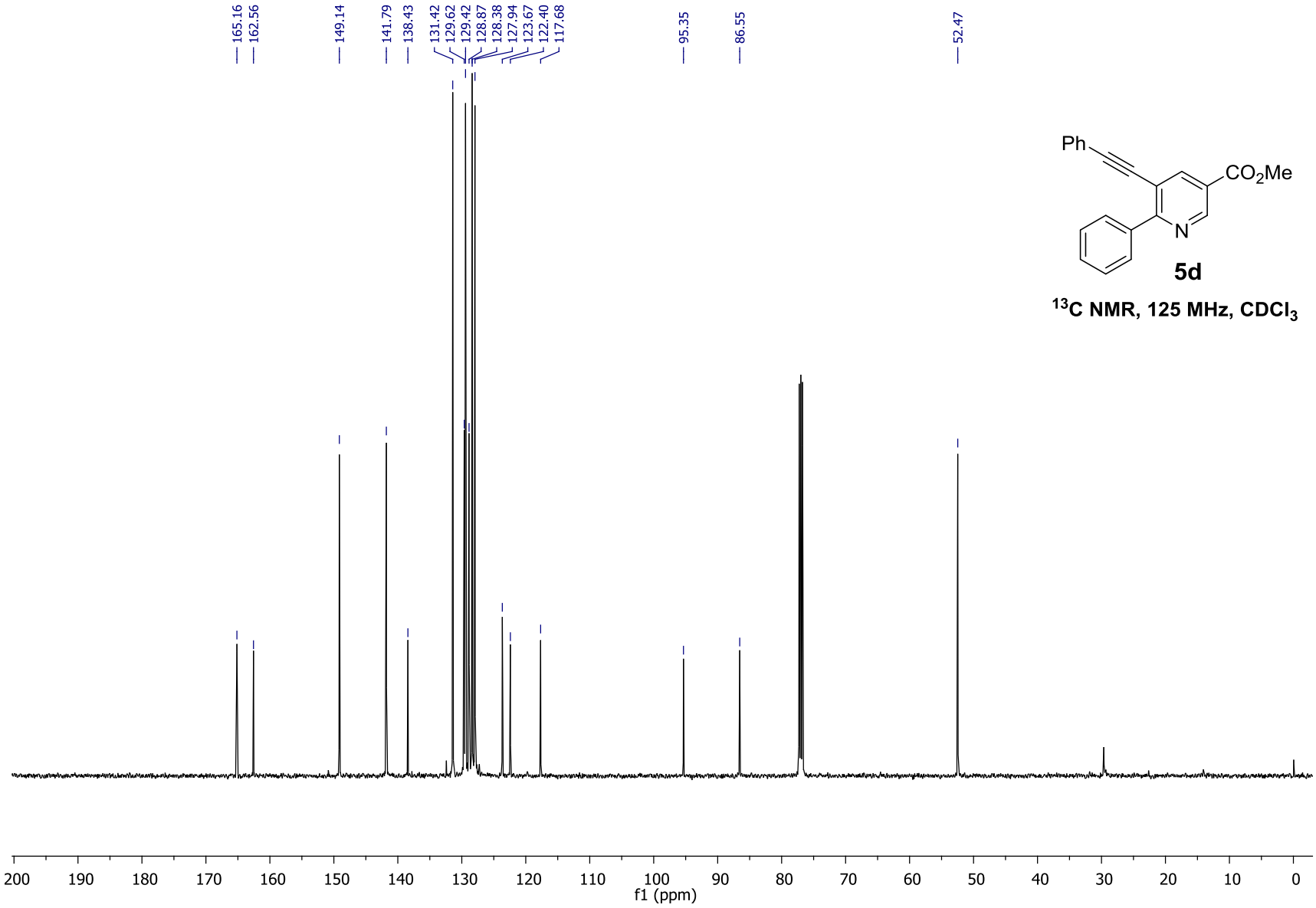

9.22
9.21
8.29
8.29
7.41
7.39
7.23
7.21
7.20
7.12
7.10
6.95
6.94
6.92
6.79
6.77
6.76
6.74
3.96
3.76
OH
CO2Me
N
MeO
5b
1H NMR, 500 MHz, CDCl3
0.92
0.94
2.05
1.00
0.96
1.00
3.06
3.00
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

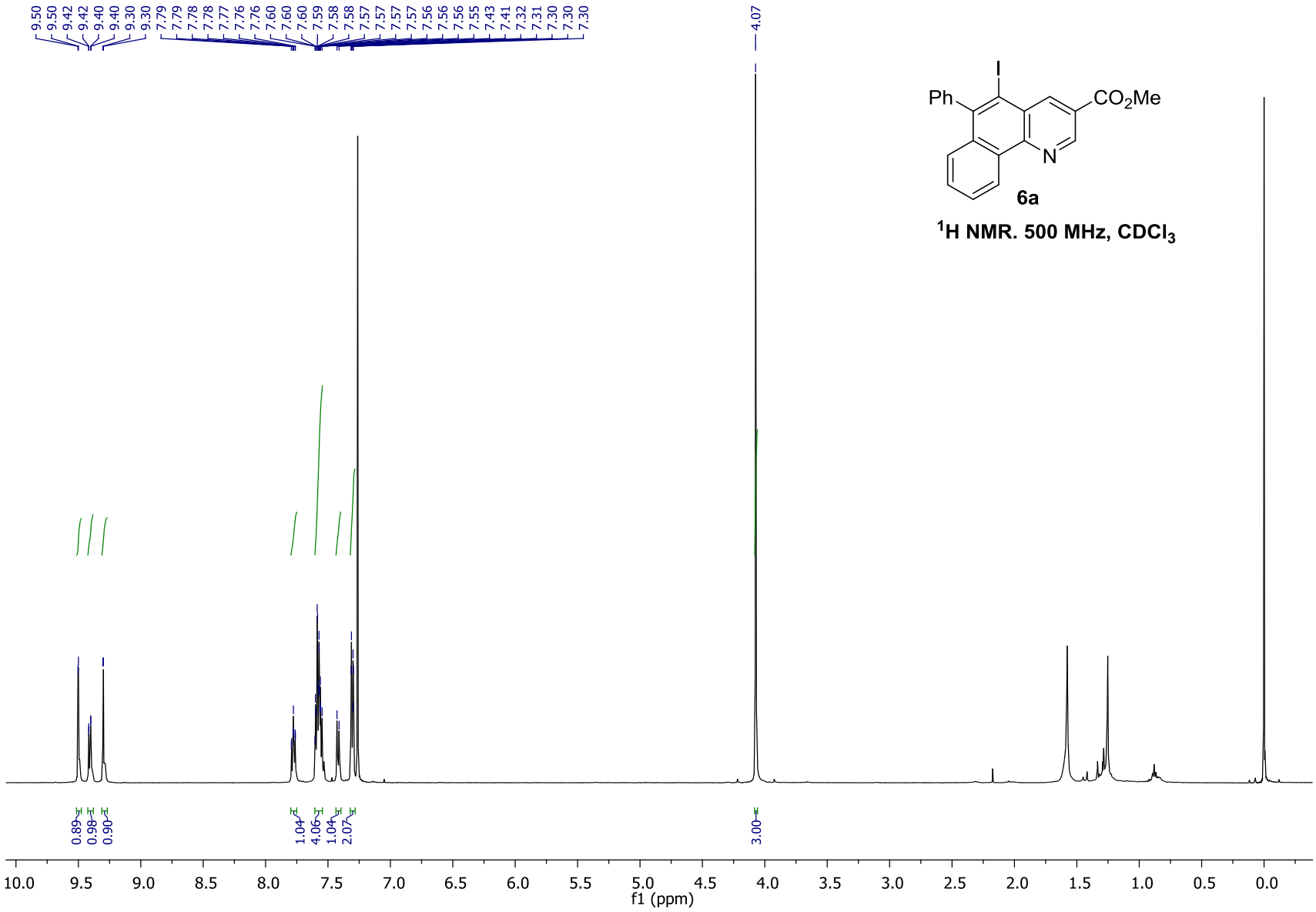

165.73
160.66
160.25
152.26
149.82
140.86
131.27
131.06
130.94
130.69
129.75
126.23
123.75
121.26
116.41
113.55
55.19
52.40
OH
CO2Me
N
MeO
5b
13C NMR, 125 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

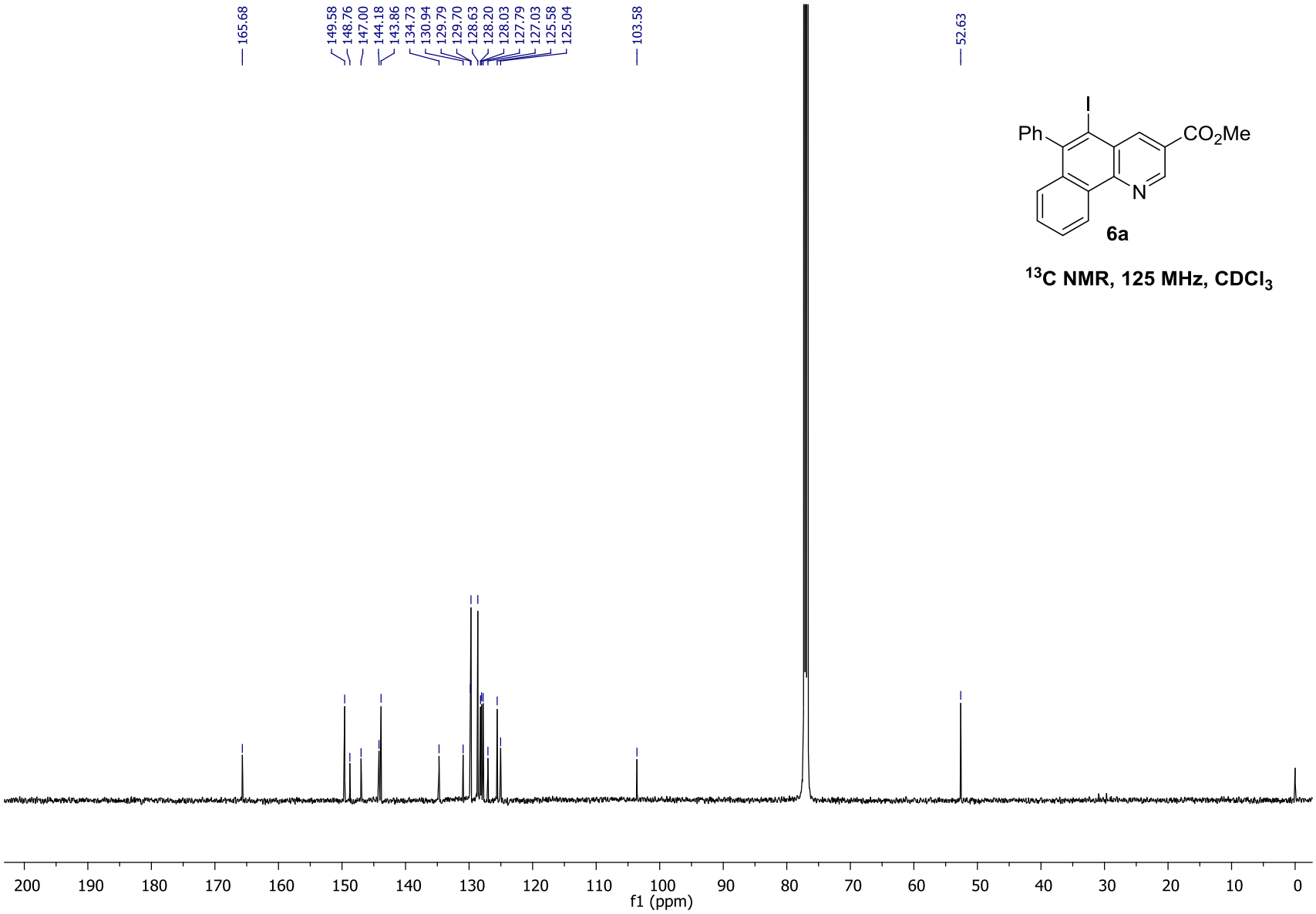

9.17
9.16
8.50
8.50
8.14
8.12
7.46
7.45
7.36
7.36
7.35
7.35
7.04
7.02
3.99
3.89
Ph
CO2Me
N
MeO
5c
1H NMR, 500 MHz, CDCl3
1.00
0.92
2.06
2.10
3.05
2.21
2.95
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

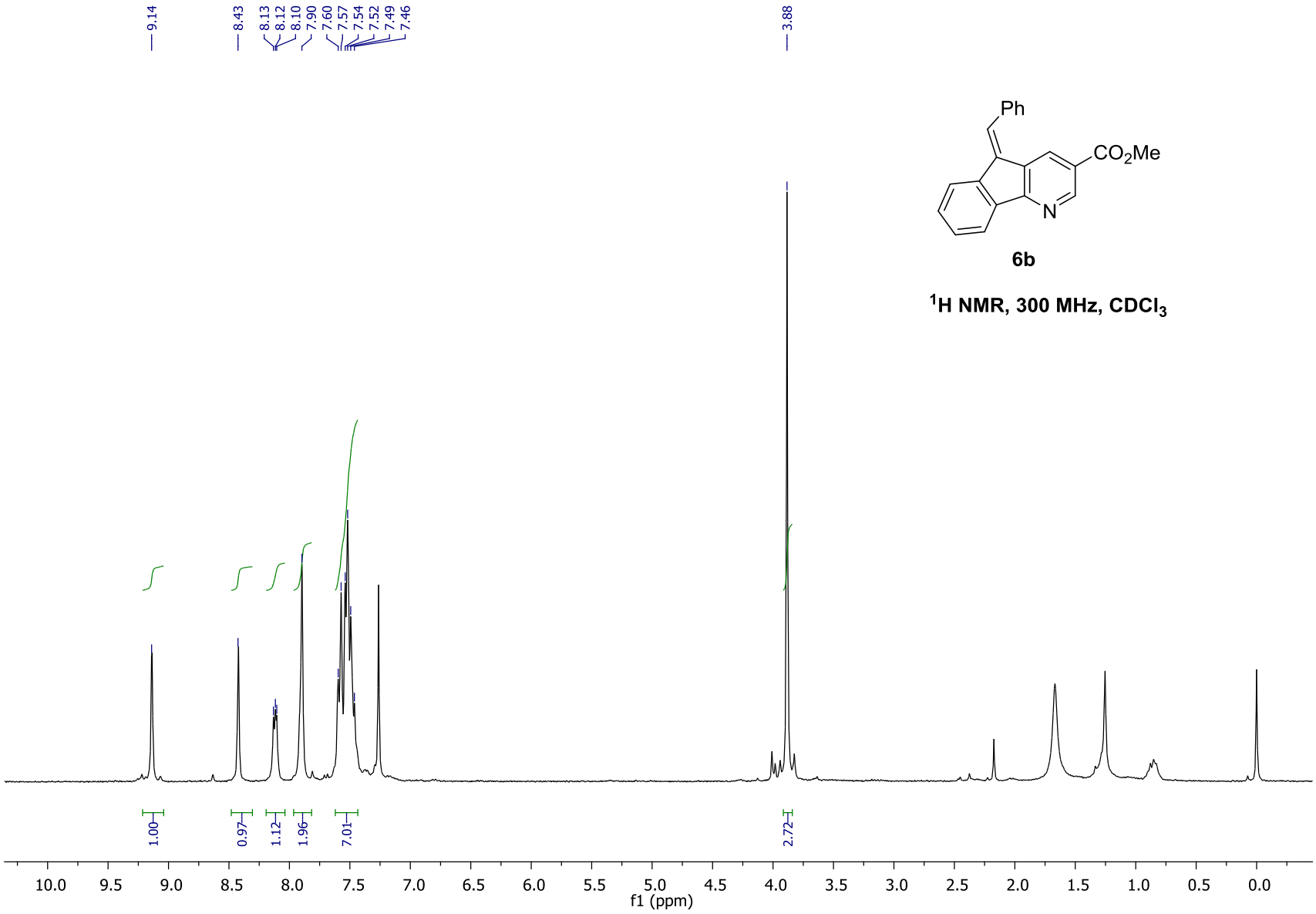

165.28
161.92
160.89
150.84
149.16
142.03
137.70
131.44
131.05
128.84
128.42
123.06
122.54
118.87
116.93
114.22
113.37
95.13
86.93
55.34
52.41
Ph
CO2Me
N
MeO
5c
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

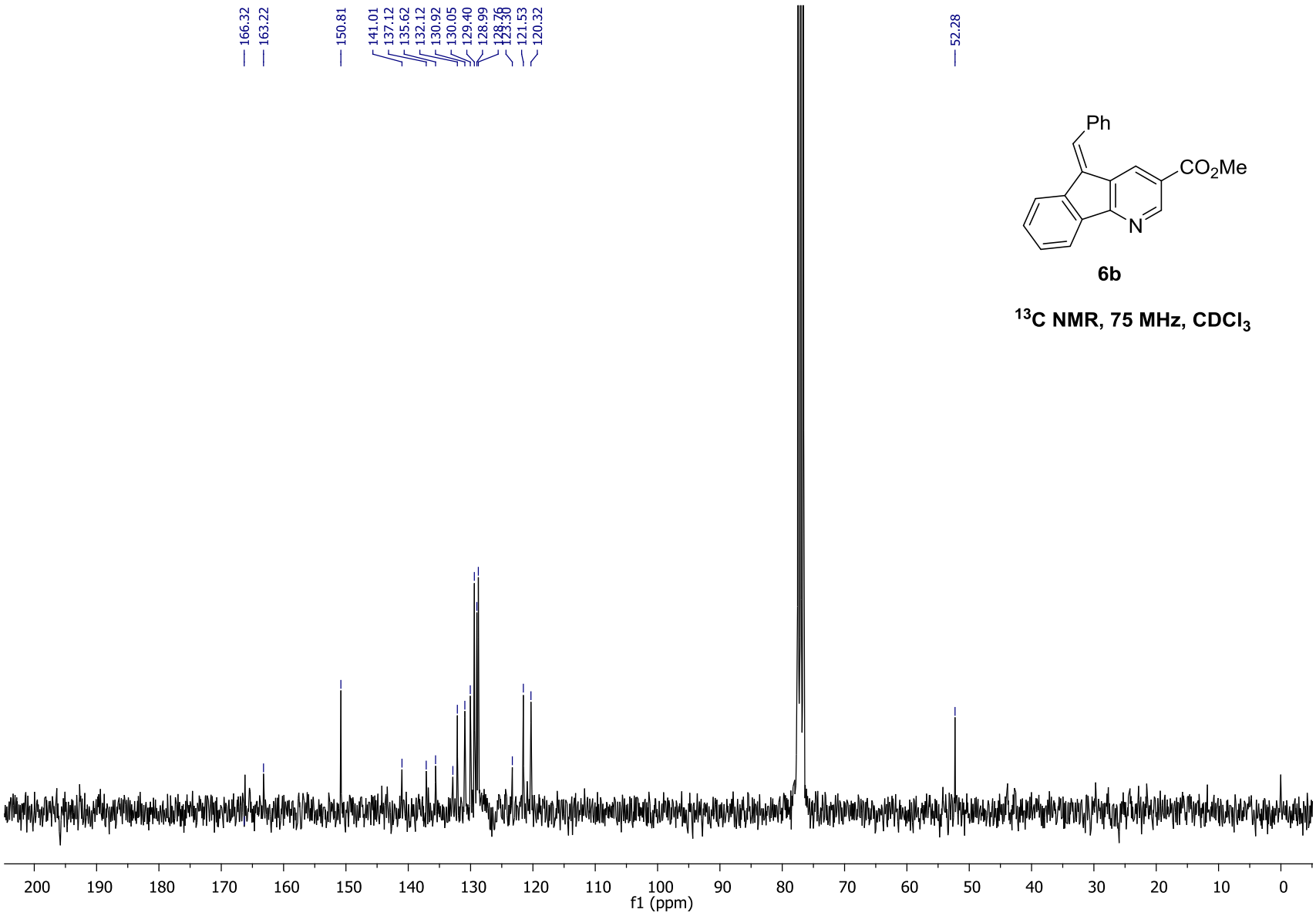

9.20
9.20
8.54
8.53
8.10
8.09
8.08
7.52
7.50
7.43
7.42
7.41
7.35
7.34
4.00
Ph
CO2Me
N
5d
1H NMR, 300 MHz, CDCl3
0.80
0.81
2.00
8.36
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.16
162.56
149.14
141.79
138.43
131.42
129.62
129.42
128.87
128.38
127.94
123.67
122.40
117.68
95.35
86.55
52.47
Ph
CO2Me
N
5d
13C NMR, 125 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)


9.50
9.50
9.42
9.42
9.40
9.40
9.30
9.30
7.79
7.79
7.78
7.78
7.77
7.76
7.76
7.60
7.60
7.60
7.59
7.58
7.58
7.57
7.57
7.57
7.57
7.56
7.56
7.56
7.55
7.43
7.41
7.32
7.31
7.30
7.30
7.30
4.07
I
Ph
CO2Me
N
6a
1H NMR. 500 MHz, CDCl3
0.89
0.98
0.90
1.04
4.06
1.04
2.07
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
f1 (ppm)


165.68
149.58
148.76
147.00
144.18
143.86
134.73
130.94
129.79
129.70
128.63
128.20
128.03
127.79
127.03
125.58
125.04
103.58
52.63
I
Ph
CO2Me
N
6a
13C NMR, 125 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)


9.14
8.43
8.13
8.12
8.10
7.90
7.60
7.57
7.54
7.52
7.49
7.46
3.88
Ph
CO2Me
N
6b
1H NMR, 300 MHz, CDCl3
1.00
0.97
1.12
1.96
7.01
2.72
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
f1 (ppm)


166.32
163.22
150.81
141.01
137.12
135.62
132.12
130.92
130.05
129.40
128.99
128.76
123.30
121.53
120.32
52.28
Ph
CO2Me
N
6b
13C NMR, 75 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)