Supporting Information

Facile Synthesis of 3-Substituted Imidazo[1,2-*a*]pyridines Through Formimidamide Chemistry

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I: General Information:

All the reactions were performed in oven-dried glassware. Thin-layer chromatography (TLC) was performed using aluminum backed silica coated plates. TLC plates were visualized under Ultraviolet light. All the ^{1}H and ^{13}C NMRs were recorded on Bruker AVANCE III HD 400 MHz High-Performance Digital NMR spectrometer ^{1}H (400 MHz), ^{13}C (101 MHz) with complete proton decoupling for ^{13}C. Chemical shifts were analyzed on MestReNova software. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard ($CDCl_3$, ^{1}H: δ 7.26 ppm, ^{13}C: 77.16 ppm; DMSO, ^{1}H: δ 2.50 ppm, ^{13}C: δ 39.52 ppm). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd=doublet of doublet. High Resolution Mass Spectrometry (HRMS) were recorded on a Waters QTof-I spectrometer using electrospray ionization. Melting points were measured on a Standard Melting Point Apparatus and are uncorrected.

II. General procedure for the Synthesis of (Z)-1-benzyl-2-(((dimethylamino)methylene)amino)pyridin-1-ium bromides:

To the compound imine (**1**) (5g, 33.51mmol) in toluene (45ml) was added benzyl bromide (6.87g, 40.21mmol) and the contents were stirred at 110°C untill the starting material disappeared. The salt precipateated was filtered and washed with diethyl ether and dried under vaccum. Yellow colour solid, yield: 82%; ^{1}H NMR (400 MHz, Deuterium Oxide) δ 8.21 (d, J = 6.5 Hz, 1H), 8.06 (s, 1H), 7.94 (t, J = 8.0 Hz, 1H), 7.43 – 7.14 (m, 9H), 7.12 (t, J = 6.9 Hz, 1H), 5.48 (s, 2H), 3.12 (s, 3H), 3.02 (s, 4H); ^{13}C NMR (101 MHz, Deuterium Oxide) δ 158.24, 157.62, 144.28, 141.70, 135.02, 128.97, 128.48, 127.88, 117.29, 116.52, 57.01, 41.09, 35.17. **HRMS** (ES+) m/z calc. for [$C_{15}H_{18}N_3^+$+H^+]: 240.1495; found: 240.0837.

Note: All the pyridinium salts (**2a-2o, 5a-5d & 8a-8e**) were synthesized using the above procedure. In the case of salts that were semisolids and separate from toluene as a different layer, the toluene was carefully removed and the salt was dried under vaccum.

III. General procedure for the Synthesis of Imidazopyridines (3a-3o, 6a-6d & 9a-9e):

To the corresponding pyridinium salt (1g, 1eq) in dry THF (30ml) was added 60% NaH (2eq) and the contents were stirred at 65°C under nitrogen until the disappearance of starting material. The reaction mixture was then subjected to evaporation under reduced pressure and the residue was diluted with DCM (40ml). The organic layer was extracted with saturated NH_4Cl (20ml) followed by saturated NaCl solution and the organic layer was dried using Na_2SO_4 and evaporated under reduced pressure. The desired compound was obtained after performing column chromatography on silica gel using hexane : ethyl acetate as eluent.

3-phenylimidazo[1,2-a]pyridine (3a):

Pale brown solid; Melting point 90 – 93 ℃; Yield 44%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 8.56 (d, J = 7.0 Hz, 1H), 7.78 (s, 1H), 7.67 (d, J = 7.1 Hz, 3H), 7.56 (t, J = 7.7 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.31 (ddd, J = 9.0, 6.7, 1.3 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 169.91, 159.87, 141.49, 141.14, 136.91, 129.08, 128.19, 118.01, 112.70, 54.42. **HRMS** (ES+) m/z calc. for [$C_{13}H_{10}N_2$+H^+]: 195.0844; found: 195.0256.

3-(naphthalen-2-yl)imidazo[1,2-a]pyridine (3b):

Straw solid; Melting point 51 – 53 ℃; Yield 32.6%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 8.74 (d, J = 7.0 Hz, 1H), 8.25 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.07 – 7.95 (m, 2H), 7.92 (s, 1H), 7.81 (dd, J = 8.5, 1.9 Hz, 1H), 7.71 (d, J = 9.1 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.35 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 146.21, 133.75, 133.60, 132.74, 129.32, 128.55, 128.12, 127.14, 126.89, 126.83, 126.12, 126.06, 125.51, 125.23, 124.78, 118.09, 113.50. **HRMS** (ES+) m/z calc. for [$C_{17}H_{12}N_2$+H^+]: 245.1000; found: 245.0322.

3-(2-chlorophenyl)imidazo[1,2-a]pyridine (3c):

Light yellow Oil; Yield 40.6%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 8.00 (d, J = 6.9 Hz, 1H), 7.73 (s, 1H), 7.72 – 7.67 (m, 2H), 7.65 – 7.48 (m, 3H), 7.34 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 6.96 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 145.57, 133.99, 133.40, 131.29, 130.54, 128.29, 128.04, 125.29, 125.27, 122.69, 117.79, 113.04. **HRMS** (ES+) m/z calc. for [$C_{13}H_9ClN_2$+H^+]: 229.0454; found: 229.0067.

3-(2-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3d):

Off-white solid; Melting point 99 – 101 ℃; Yield 54.1%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 7.99 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 6.9 Hz, 1H), 7.87 (t, J = 7.3 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.62 (s, 1H), 7.32 (ddd, J = 9.0, 6.7, 1.2 Hz, 1H), 6.91 (t, J = 6.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 145.30, 134.06, 133.93 (d, *J* = 2.2 Hz), 133.54, 130.49, 129.88 (q, *J* = 29.0 Hz), 127.25 (q, *J* = 5.2 Hz), 125.59, 125.26, 124.73, 122.87, 120.90, 117.60, 113.23. **HRMS** (ES+) m/z calc. for [$C_{14}H_9F_3N_2$+H^+]: 263.0718; found: 262.9951.

3-(3-nitrophenyl)imidazo[1,2-a]pyridine (3e):

Yellow solid; Melting point 133 – 134 ℃; Yield 70.5%; **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.67 (d, J = 7.0 Hz, 1H), 8.44 (t, J = 2.0 Hz, 1H), 8.25 (ddd, J = 8.3, 2.3, 1.0 Hz, 1H), 8.15 (dd, J = 7.7, 0.8 Hz, 1H), 7.96 (s, 1H), 7.83 (t, J = 8.0 Hz, 1H), 7.71 (d, J = 9.1 Hz, 1H), 7.37 (ddd, J = 9.0, 6.7, 1.2 Hz, 1H), 7.03 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d^6) δ 148.94, 146.57, 134.36, 134.11, 131.28, 131.00, 125.83, 124.71, 123.52, 122.75, 122.20, 118.10, 113.80. **HRMS** (ES+) m/z calc. for [$C_{13}H_9N_3O_2$+H^+]: 240.0695; found: 239.9997.

3-(3-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3f):

Straw solid; Melting point 68 – 71 ℃; Yield 65.9%; **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.59 (d, J = 7.0 Hz, 1H), 8.06 – 7.96 (m, 2H), 7.91 (s, 1H), 7.79 (d, J = 5.2 Hz, 2H), 7.69 (d, J = 9.1 Hz, 1H), 7.35 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d^6) δ 146.40, 134.03, 131.69, 130.86, 130.74, 130.52, 130.42, 125.60, 124.86, 124.82, 124.63, 124.46, 124.42, 124.12, 118.05, 113.67. **^{13}C NMR** (101 MHz, DMSO-d^6) δ 146.40, 134.03, 131.69, 130.86, 130.52, 125.87, 125.60, 124.84 (q, J = 3.9 Hz), 124.63, 124.44 (q, J = 3.8 Hz), 124.12, 123.16, 118.05, 113.67.
HRMS (ES+) m/z calc. for [$C_{14}H_9F_3N_2$+H^+]: 263.0718; found: 262.9951.

3-(3-chlorophenyl)imidazo[1,2-a]pyridine (3g):

Light yellow Oil; Yield 45.2%; **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.59 (d, J = 7.0 Hz, 1H), 7.86 (s, 1H), 7.74 (t, J = 1.9 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.49 (ddd, J = 8.0, 2.2, 1.2 Hz, 1H), 7.34 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d^6) δ 146.32, 134.43, 133.83, 131.54, 131.49, 128.14, 127.48, 126.35, 125.46, 124.74, 124.13, 118.03, 113.58. **HRMS** (ES+) m/z calc. for [$C_{13}H_9ClN_2$+H^+]: 229.0454; found: 228.9779.

3-(3-fluorophenyl)imidazo[1,2-a]pyridine (3h):

Straw solid; Melting point 44 – 46 ℃; Yield 55.1%; **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.63 (d, J = 7.0 Hz, 1H), 7.85 (s, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.34 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.00 (t, J = 7.2 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d^6) δ 164.28, 161.85, 146.31, 133.78, 131.69 (dd, J = 12.8, 8.8 Hz), 125.42, 124.80, 124.35 (d, J = 2.6 Hz), 123.84 (d, J = 2.9 Hz), 118.03, 115.06 (d, J = 21.1 Hz), 114.54 (d, J = 22.6 Hz), 113.56. **HRMS** (ES+) m/z calc. for [$C_{13}H_9FN_2$+H^+]: 213.0750; found: 213.0141.

3-(4-bromophenyl)imidazo[1,2-a]pyridine (3i):

Off-white solid; Melting point 114 – 116 ℃ Yield 45.6%; **^{1}H NMR** (400 MHz, Methanol-d^4) δ 8.52 (d, J = 7.0 Hz, 1H), 7.75 (s, 1H), 7.73 (d, J = 3.0 Hz, 2H), 7.65 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.45 – 7.36 (m, 1H), 7.03 (t, J = 6.8 Hz, 1H); **^{13}C NMR** (101 MHz, Methanol-d^4) δ 146.04, 132.18, 131.16, 129.38, 127.78, 125.57, 124.90, 123.74, 121.87, 116.69, 113.20. **HRMS** (ES+) m/z calc. for [$C_{13}H_9BrN_2$+H^+]: 272.9949; found: 272.9240.

3-(4-fluorophenyl)imidazo[1,2-a]pyridine (3j):

Light yellow Oil; Yield 30.8%; **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.51 (d, J = 6.9 Hz, 1H), 7.76 (s, 1H), 7.72 (dd, J = 8.6, 5.5 Hz, 2H), 7.67 (d, J = 9.1 Hz, 1H), 7.40 (t, J = 8.8 Hz, 2H), 7.35 – 7.27 (m, 1H), 6.97 (t, J = 6.7 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d^6) δ 163.42, 160.98, 145.90, 133.02, 130.38 (d, J = 8.3 Hz), 125.85 (d, J = 3.0 Hz), 125.07, 124.45, 117.99, 116.71 (d, J = 21.6 Hz), 113.35. **HRMS** (ES+) m/z calc. for [$C_{13}H_9FN_2$+H^+]: 213.0750; found: 213.0140.

3-(3-chloro-4-fluorophenyl)imidazo[1,2-a]pyridine (3k):

Off-white solid; Melting point 128 – 130 ℃; Yield 68.6%; **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.55 (d, J = 7.0 Hz, 1H), 7.91 (dd, J = 7.1, 2.2 Hz, 1H), 7.82 (s, 1H), 7.74 – 7.64 (m, 2H), 7.59 (t, J = 8.9 Hz, 1H), 7.33 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 6.99 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d^6) δ 158.43, 155.97, 146.16, 133.73,

130.13, 128.83 (d, J = 7.4 Hz), 127.30 (d, J = 3.9 Hz), 125.42, 124.70, 123.38, 120.91 (d, J = 18.0 Hz), 118.01 (d, J = 10.9 Hz), 113.51. **HRMS** (ES+) m/z calc. for [$C_{13}H_8ClFN_2$+H^+]: 247.0360; found: 246.9800.

3-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3l):

Off-white solid; Melting point 150 – 152 ℃; Yield 58.1%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 8.68 (d, J = 7.0 Hz, 1H), 7.93 (t, J = 4.2 Hz, 3H), 7.89 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 9.1 Hz, 1H), 7.36 (ddd, J = 9.0, 6.7, 1.2 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 146.67, 134.38, 133.54, 128.16, 126.57 (q, J = 3.8 Hz), 126.04, 125.76, 124.85, 124.21, 123.34, 118.13, 113.75. **HRMS** (ES+) m/z calc. for [$C_{14}H_9F_3N_2$+H^+]: 263.0718; found: 263.0054.

3-(3,5-bis(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3m):

Off-white solid; Melting point 90 – 92 ℃; Yield 94.7%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 8.64 (d, J = 6.9 Hz, 1H), 8.35 (s, 2H), 8.13 (s, 1H), 8.04 (s, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.40 (t, J = 6.7 Hz, 1H), 7.06 (t, J = 6.7 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 146.73, 135.06, 131.84 (q), 128.36, 126.19, 125.06, 124.90, 122.91, 122.34, 121.50, 117.96, 113.92. **HRMS** (ES+) m/z calc. for [$C_{15}H_8F_6N_2$+H^+]: 331.0592; found: 330.9663.

3-(3,5-difluorophenyl)imidazo[1,2-a]pyridine (3n):

White solid; Melting point 114 – 115 ℃; Yield 86.3%; ^{1}H NMR (400 MHz, Methanol-*d*^{4}) δ 8.58 (d, J = 7.0 Hz, 1H), 7.79 (s, 1H), 7.66 (d, J = 9.1 Hz, 1H), 7.51 – 7.37 (m, 1H), 7.31 (d, J = 6.3 Hz, 2H), 7.14 – 6.94 (m, 2H); ^{13}C NMR (101 MHz, Methanol-*d*^{4}) δ 164.90 (d, J = 13.5 Hz), 162.43 (d, J = 13.5 Hz), 146.41, 132.07, 126.02, 123.99, 116.76, 113.50, 110.41 (d, J = 7.7 Hz), 110.21 (d, J = 7.7 Hz), 103.01 (t, J = 25.8 Hz). **HRMS** (ES+) m/z calc. for [$C_{13}H_8F_2N_2$+H^+]: 231.0656; found: 231.0055.

3-(2-chloro-6-fluorophenyl)imidazo[1,2-a]pyridine (3o):

Yellow solid; Melting point 96 – 99 ℃; Yield 43.6%; ^{1}H NMR (400 MHz, Methanol-*d*^{4}) δ 7.71 (d, J = 6.9 Hz, 1H), 7.67 (s, 2H), 7.65 (s, 1H), 7.40 (q, J = 9.5, 8.9 Hz, 4H), 7.17 (dd, J = 16.4, 8.1 Hz, 3H), 6.95 (t, J = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, Methanol-*d*^{4}) δ 155.21, 145.08, 136.37, 133.23, 130.69, 125.23, 124.89, 122.02, 121.12, 118.97, 116.77, 116.06, 112.22. **HRMS** (ES+) m/z calc. for [$C_{13}H_8ClFN_2$+H^+]: 247.0360; found: 247.0000.

6-chloro-3-phenylimidazo[1,2-a]pyridine (6a):

Straw solid; Melting point 51 – 54 ℃; Yield 41%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 8.60 (s, 1H), 7.84 (s, 1H), 7.76 – 7.67 (m, 3H), 7.57 (t, J = 7.6 Hz, 2H), 7.47 (t, J = 7.7 Hz, 1H), 7.36 (dd, J = 9.6, 1.9 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 146.11, 144.42, 141.09, 133.97, 129.83, 128.78, 128.16, 125.91, 122.33, 120.46, 118.88. **HRMS** (ES+) m/z calc. for [$C_{13}H_9ClN_2$+H^+]: 229.0454; found: 229.0259.

6-bromo-3-phenylimidazo[1,2-a]pyridine (6b):

Camel solid; Melting point 65 – 67 ℃; Yield 40.8%; **^{1}H NMR** (400 MHz, DMSO-*d*^{6}) δ 8.64 (s, 1H), 7.81 (s, 1H), 7.72 – 7.63 (m, 3H), 7.57 (t, J = 7.6 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.42 (dd, J = 9.5, 1.8 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d*^{6}) δ 144.45, 133.76, 129.83, 128.78, 128.73, 128.20, 127.98, 126.23, 124.27, 119.14, 107.47. **HRMS** (ES+) m/z calc. for [$C_{13}H_9BrN_2$+H^+]: 272.9949; found: 272.9345.

6-methyl-3-phenylimidazo[1,2-a]pyridine (6c):

Light yellow Oil; Yield 33.2%; ^{1}H NMR (400 MHz, Methanol-*d*^{4}) δ 8.24 (s, 1H), 7.65 – 7.49 (m, 6H), 7.46 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 10.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, Methanol-*d*^{4}) δ 144.80, 130.59, 129.00, 128.85, 128.37, 128.09, 127.84, 125.78, 123.10, 121.13, 115.94, 16.81. **HRMS** (ES+) m/z calc. for [$C_{14}H_{12}N_2$+H^+]: 209.1000; found: 209.0377.

3-phenyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine (6d):

Off-white solid; Melting point 121 – 123 ℃; Yield 26.5%; ^{1}H NMR (400 MHz, Methanol-d^4) δ 8.77 (s, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.73 – 7.45 (m, 6H); ^{13}C NMR (101 MHz, Methanol-d^4) δ 145.48, 132.61, 129.28, 128.89, 128.10, 127.72 (d, J = 5.8 Hz), 124.98, 122.95 (d, J = 5.9 Hz), 122.30, 120.77 (q, J = 2.4 Hz), 117.85, 117.05 (q, J = 34.0 Hz). **HRMS** (ES+) m/z calc. for [$C_{14}H_9F_3N_2$+H+]: 263.0718; found: 262.9951.

3-ethynylimidazo[1,2-a]pyridine (9a):

Pale brown solid; Melting point 76 – 79 ℃; Yield 24.2%; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.46 (d, J = 6.8 Hz, 1H), 7.96 (s, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.42 (t, J = 6.8 Hz, 1H), 7.12 (t, J = 6.8 Hz, 1H), 5.09 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d^6) δ 145.42, 138.87, 126.88, 125.96, 117.90, 114.27, 107.67, 91.68, 71.74. **HRMS** (ES+) m/z calc. for [$C_9H_6N_2$+H^+]: 143.0531; found: 143.0097.

3-vinylimidazo[1,2-a]pyridine (9b):

Red brown solid; Melting point 38 – 41 ℃; Yield 21.1%; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.63 (d, J = 6.9 Hz, 1H), 7.90 (s, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.09 (dd, J = 17.6, 11.5 Hz, 1H), 6.99 (t, J = 6.8 Hz, 1H), 5.84 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 11.6 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d^6) δ 145.69, 132.24, 125.09, 124.90, 124.16, 122.80, 117.80, 113.29, 113.21. **HRMS** (ES+) m/z calc. for [$C_9H_8N_2$+H^+]: 145.0687; found: 145.0249.

3-(prop-1-en-2-yl)imidazo[1,2-a]pyridine (9c):

Light yellow Oil; Yield 13.6%; ^{1}H NMR (400 MHz, Methanol-d4) δ 8.61 (d, J = 7.0 Hz, 1H), 7.62 (s, 1H), 7.59 (d, J = 9.1 Hz, 1H), 7.35 (t, J = 6.7Hz, 1H), 7.01 (t, J = 6.8 Hz, 1H), 5.44 (d, J = 10.8 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, Methanol-d^4) δ 146.14, 132.45, 131.18, 126.24, 125.41, 125.18, 116.58, 112.94, 112.27, 21.94. **HRMS** (ES+) m/z calc. for [$C_{10}H_{10}N_2$+H^+]: 159.0844; found: 159.0301.

(E)-3-(prop-1-en-1-yl)imidazo[1,2-a]pyridine (9d):

Brown solid; Melting point 59 – 61 ℃; Yield 48.2%; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.53 (d, J = 6.9 Hz, 1H), 7.75 (s, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.22 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 6.94 (td, J = 6.8, 1.3 Hz, 1H), 6.77 (dd, J = 15.9, 1.9 Hz, 1H), 6.31 (dq, J = 15.8, 6.7 Hz, 1H), 1.94 (dd, J = 6.8, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d^6) δ 145.03, 133.45, 130.80, 126.11, 124.75, 124.21, 117.71, 116.97, 112.85, 19.14. **HRMS** (ES+) m/z calc. for [$C_{10}H_{10}N_2$+H^+]: 159.0844; found: 159.0301.

(E)-3-(2,6-dimethylhepta-1,5-dien-1-yl)imidazo[1,2-a]pyridine (9e):

Light yellow Oil; Yield 24.2%; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.42 (d, J = 7.0 Hz, 1H), 7.61 (s, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.29 – 7.20 (m, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.45 (s, 1H), 5.17 (t, J = 6.7 Hz, 1H), 2.38 – 2.11 (m, 4H), 1.93 (s, 3H), 1.64 (d, J = 22.2 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d^6) δ 144.34, 140.34, 132.65, 131.67, 124.67, 124.48, 124.29, 122.80, 117.59, 112.65, 110.57, 40.53, 26.83, 25.97, 19.34, 18.10. **HRMS** (ES+) m/z calc. for [$C_{16}H_{20}N_2$+H^+]: 241.1626; found: 241.1004.

Procedure for one-pot synthesis of 3-phenylimidazo[1,2-*a*]pyridine (3a):

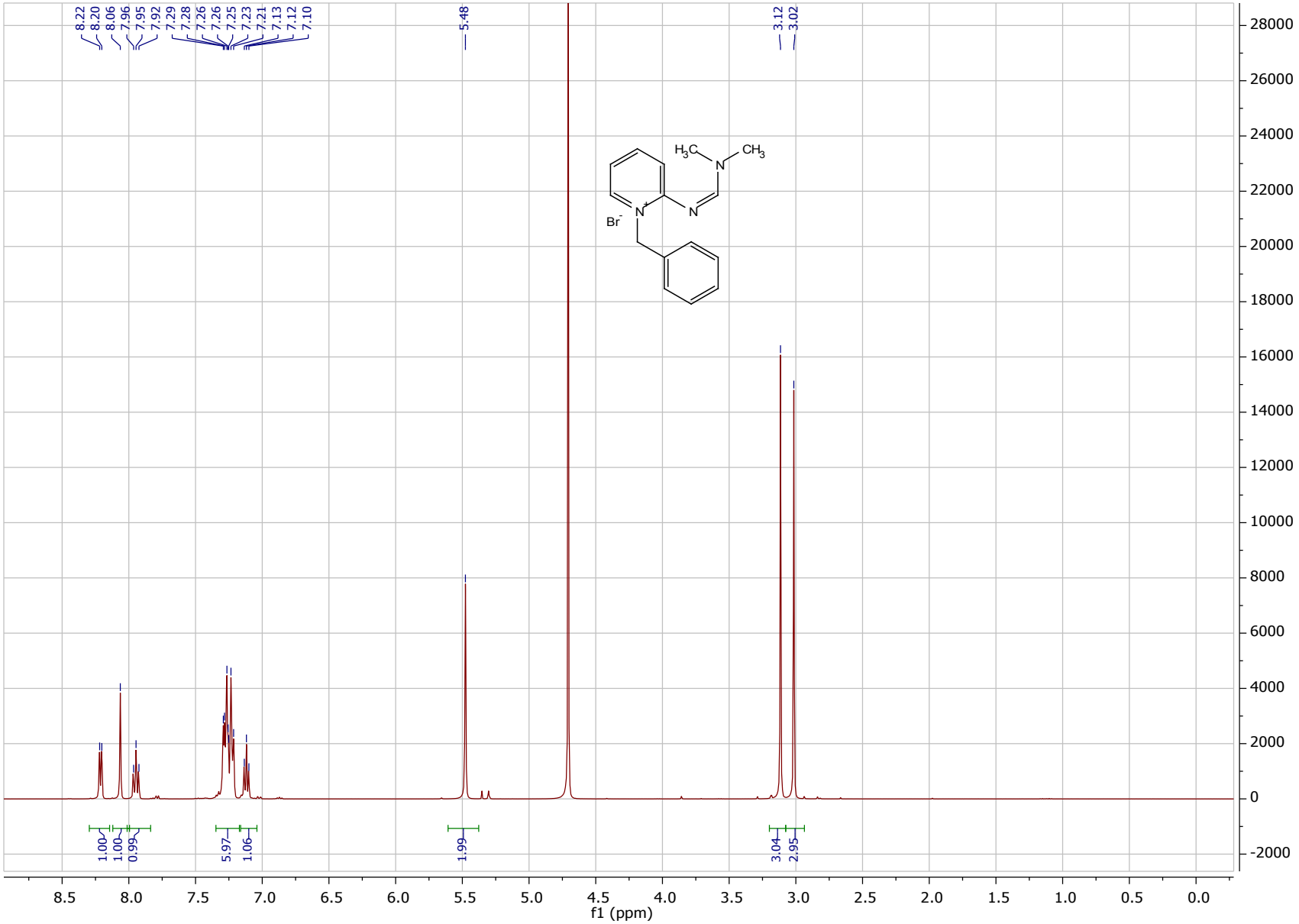
Aminopyridine (1g, 0.0106 mol), DMF DMA (1.58g, 0.133 mol) and benzyl bromide (1.82g, 0.0106mol) were added to a pressure tube and the contents were stirred at 120^{o}C on a hot plate until the disappearance of starting materials (typically ~1hr). Then while on heating 60% sodium hydride (0.51g, 0.021mol) was added portion wise over a period of 5 min and the stirring was continued for 15 min. The contents were then cooled, diluted with 30 ml DCM and then extracted with saturated NH_4Cl (20ml). The aqueous layer was again extracted with 2 more portions of DCM (15ml) and the organic layer was dried using Na_2SO_4 and evaporated under reduced pressure to afford

crude product. The crude product was purified on silica gel column using DCM : MeOH as eluent to yield compound **3a** as a yellow oil, Yield 58%.

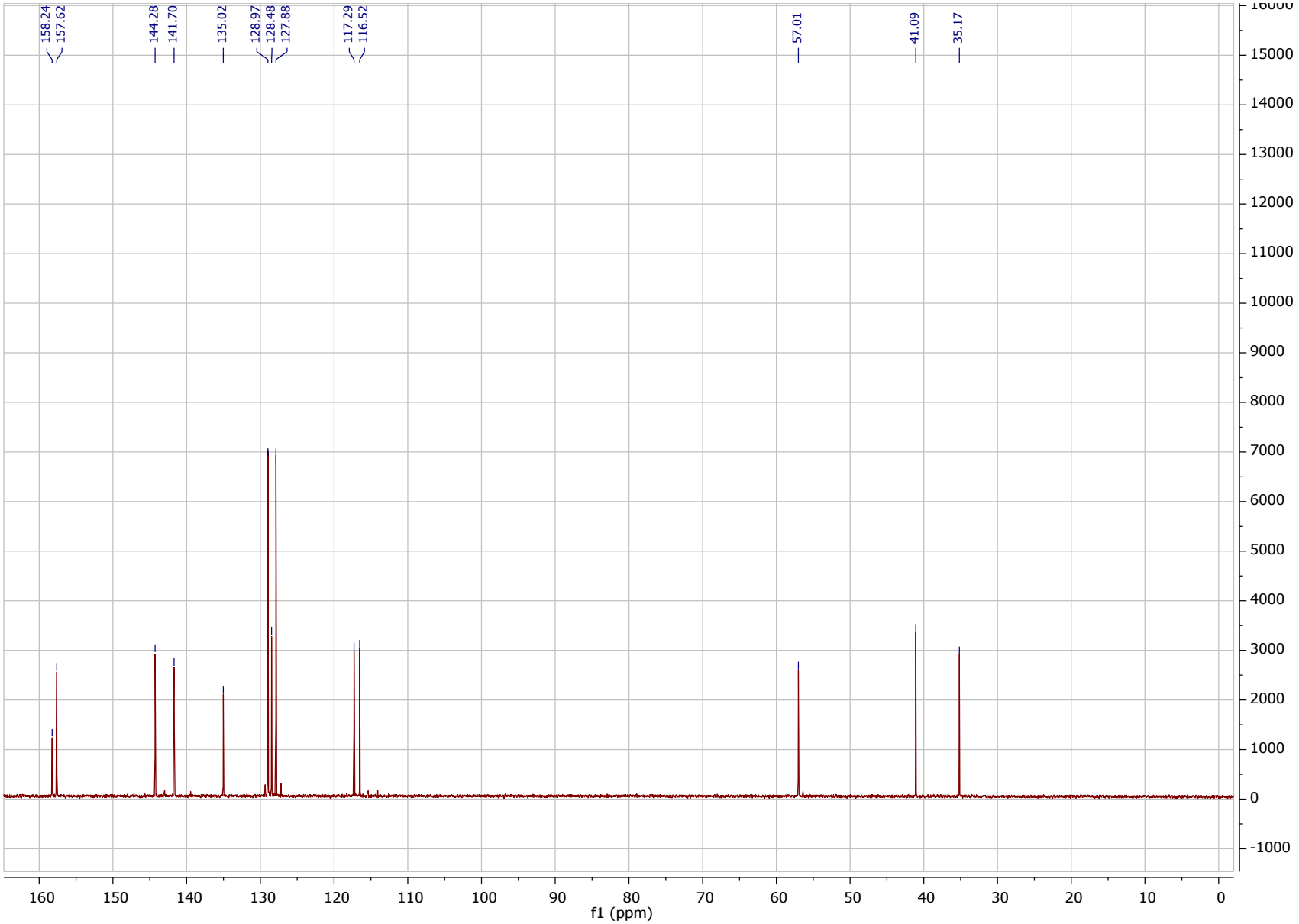
Procedure for synthesis of 1-benzylpyridin-2(1*H*)-imine (7):

(*Z*)-1-benzyl-2-(((dimethylamino)methylene)amino)pyridin-1-ium bromide (**2a**, 0.25g, 0.78mmol) was dissolved in water, to the above solution was added NaOH (0.94mmol, 38mg) and the contents were stirred at RT until the disappearance of the starting material (~45 min). The reaction mixture was extracted with DCM (10ml) twice then the organic layer was washed with brine, dried under Na_2SO_4. The resulting organic layer was reduced under pressure to afford crude product which was purified on silica gel column using DCM:MeOH as eluent to yield desired product in 41% yield; **^{1}H NMR** (400 MHz, DMSO-d^6) δ 8.93 (s, 1H), 8.23 (d, J = 5.5 Hz, 1H), 7.75 (t, J = 8.8 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.40 – 7.27 (m, 5H), 6.81 (t, J = 6.7 Hz, 1H), 5.50 (s, 2H); **^{13}C NMR** (101 MHz, DMSO-d^6) δ 169.91, 159.87, 141.49, 141.14, 136.91, 129.08, 128.19, 118.01, 112.70, 54.42. **HRMS** (ES+) m/z calc. for [$C_{12}H_{12}N_2$+H^+]: 185.1000; found: 185.0596.

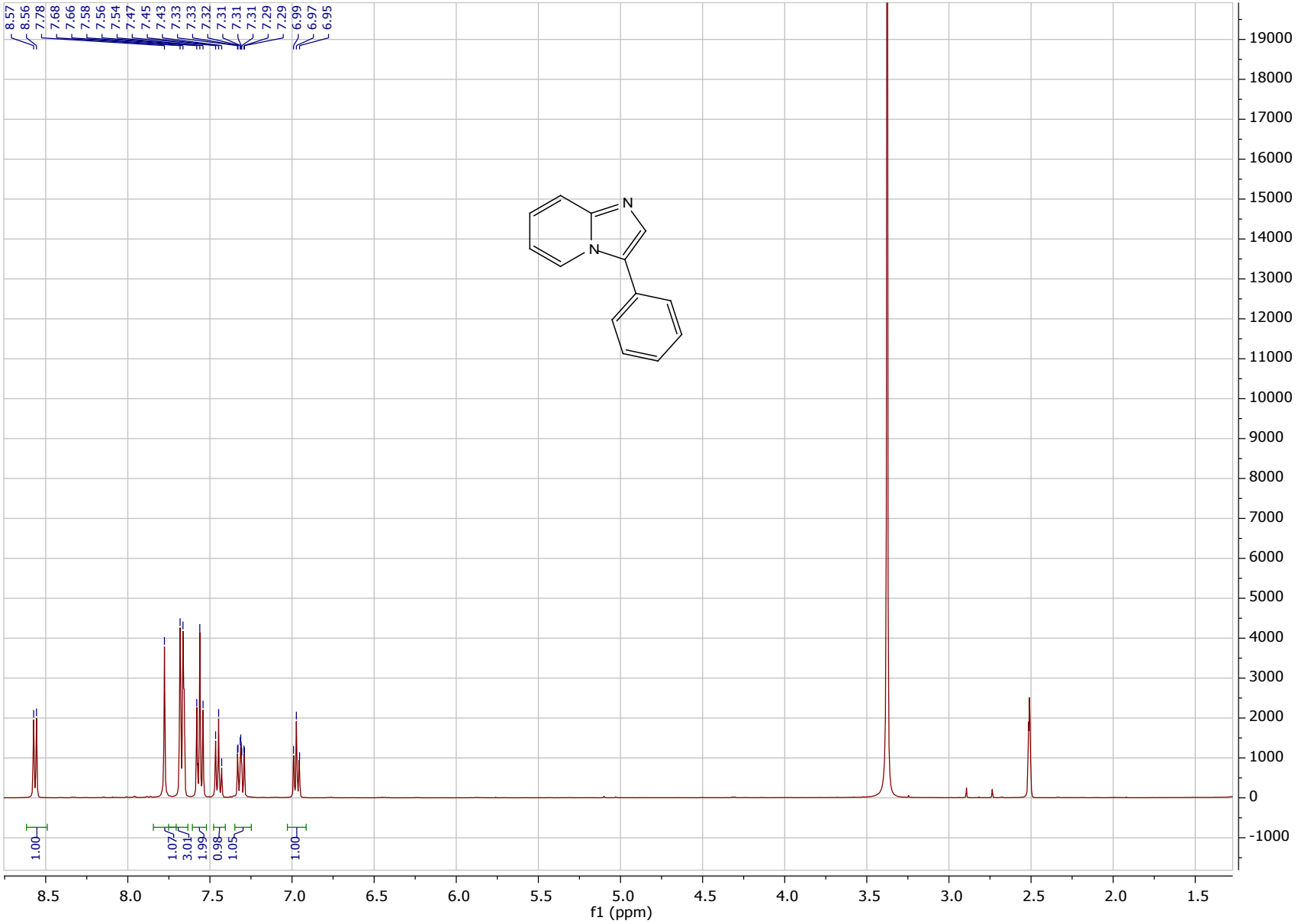
[1]H NMR of 1-benzyl-2-(((dimethylamino)methylene)amino)pyridin-1-ium bromide (2a):



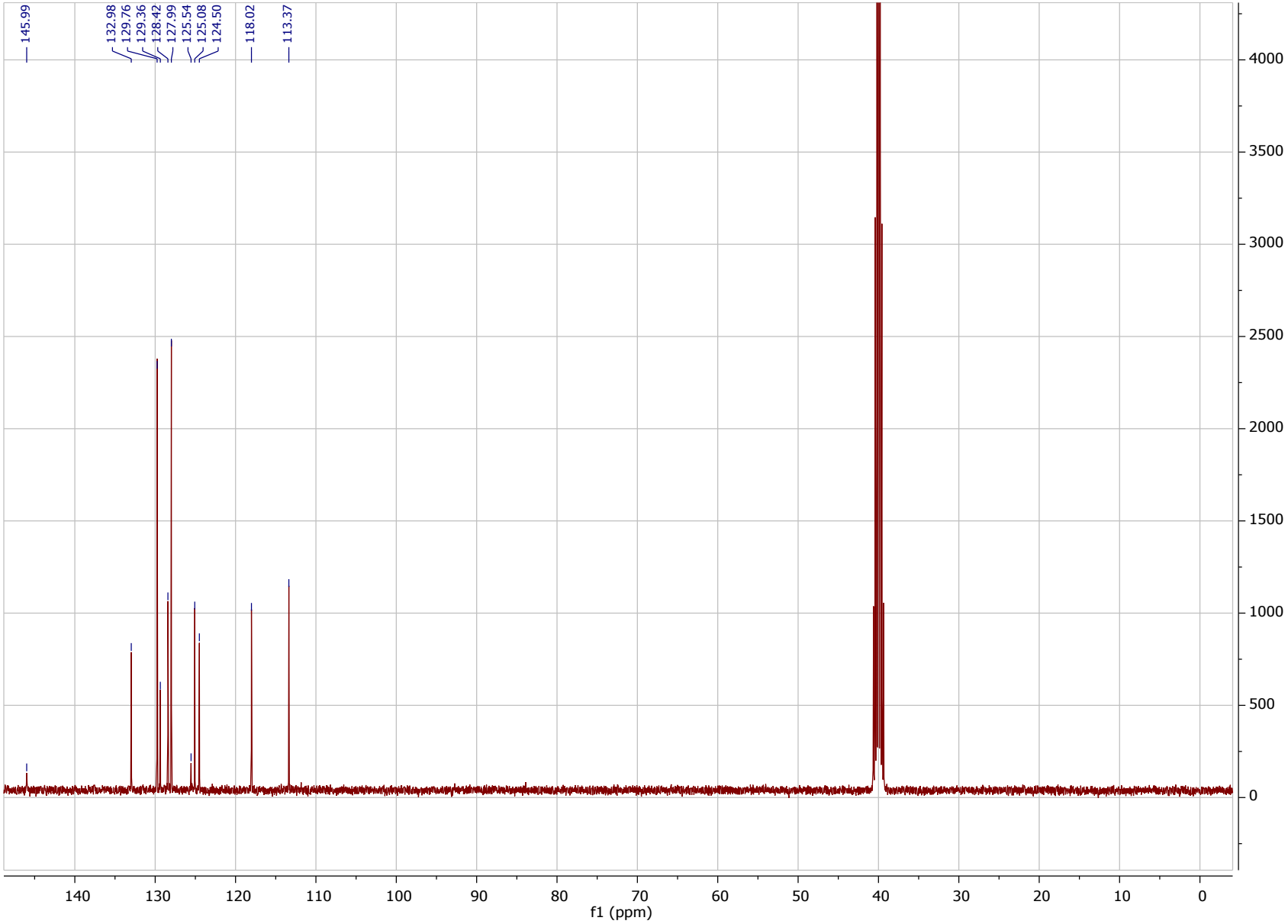
^{13}C NMR of (Z)-1-benzyl-2-(((dimethylamino)methylene)amino)pyridin-1-ium bromide (2a):



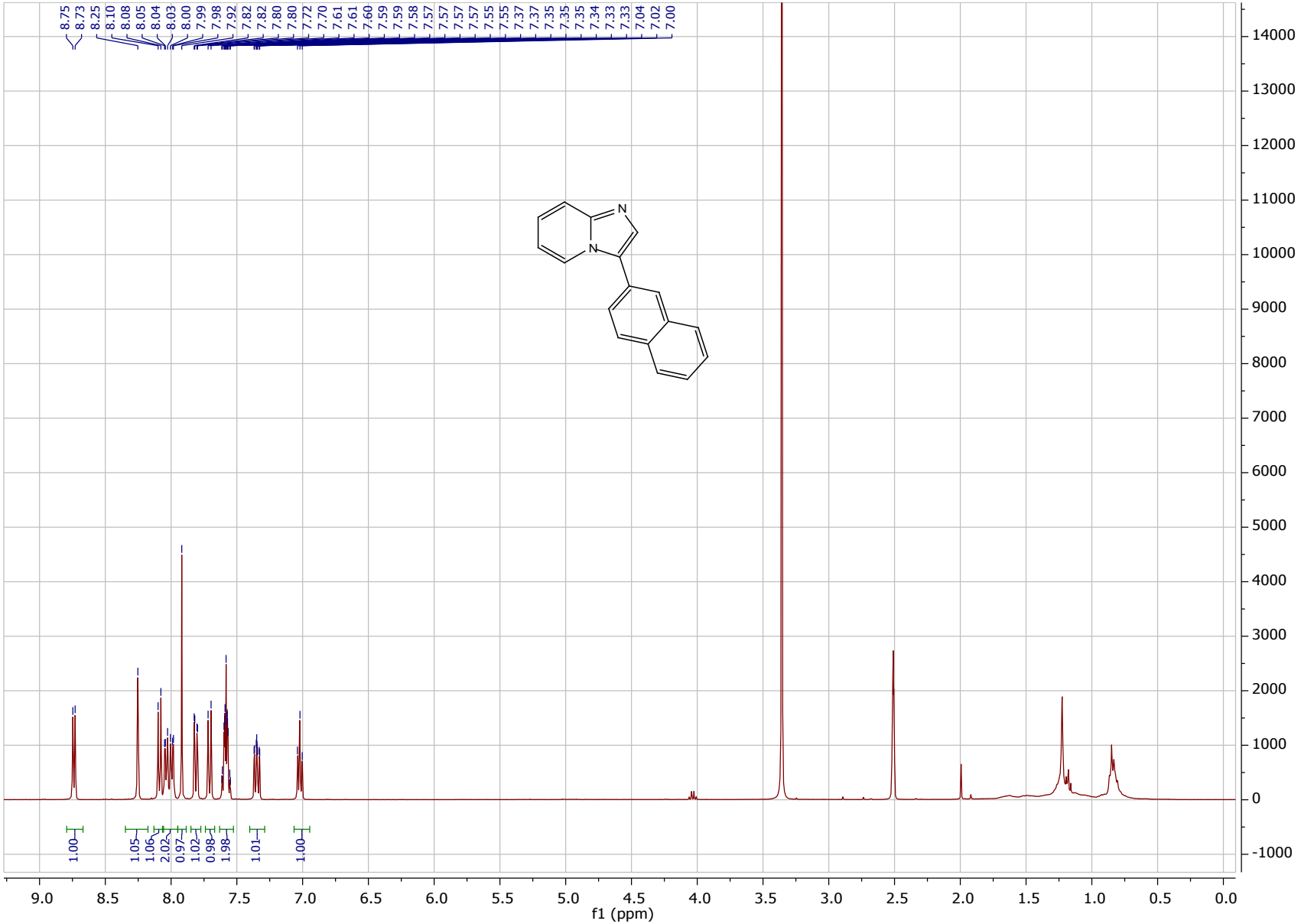
^{1}H NMR of 3-phenylimidazo[1,2-a]pyridine (3a):



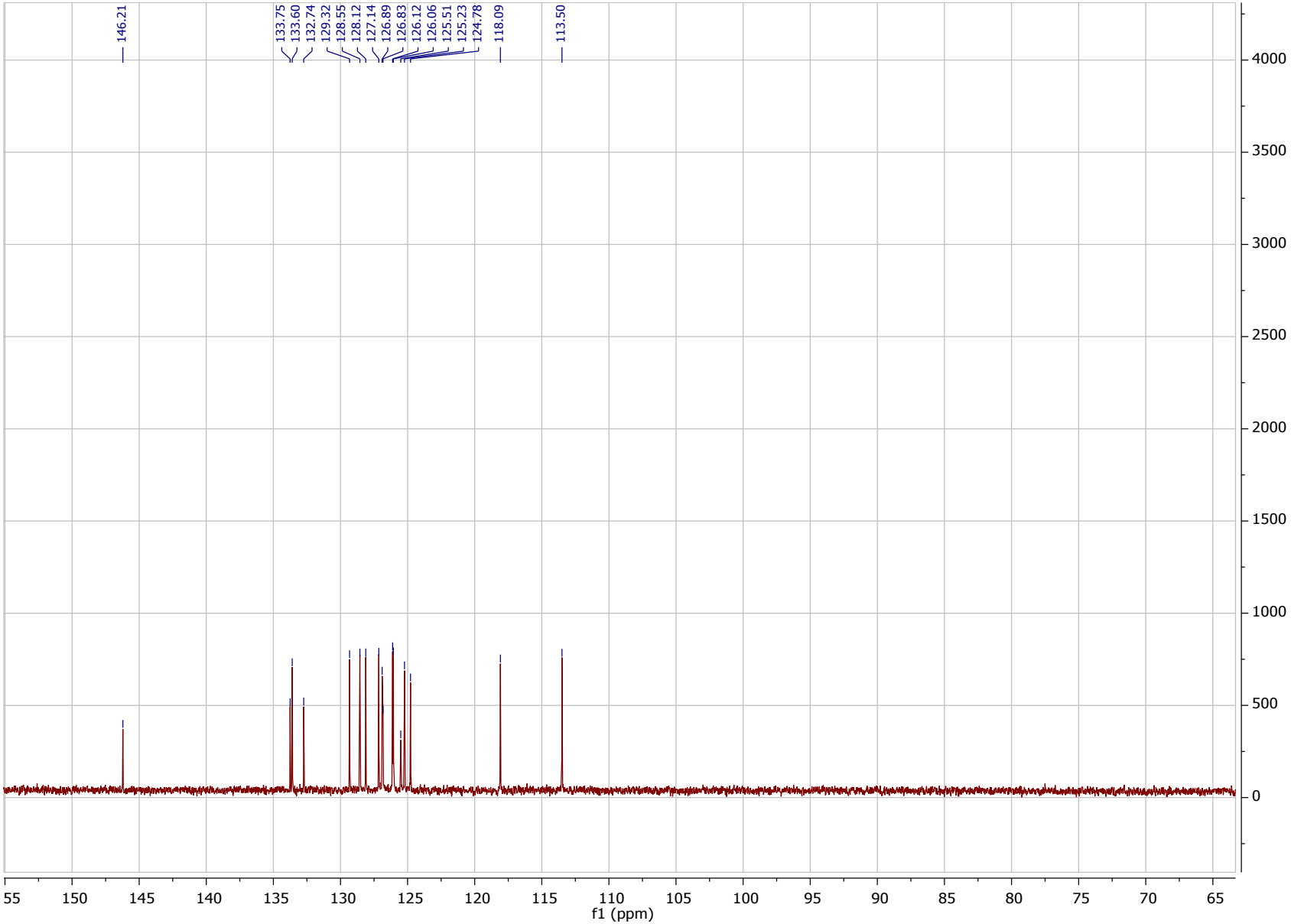
^{13}C NMR of 3-phenylimidazo[1,2-a]pyridine (3a):



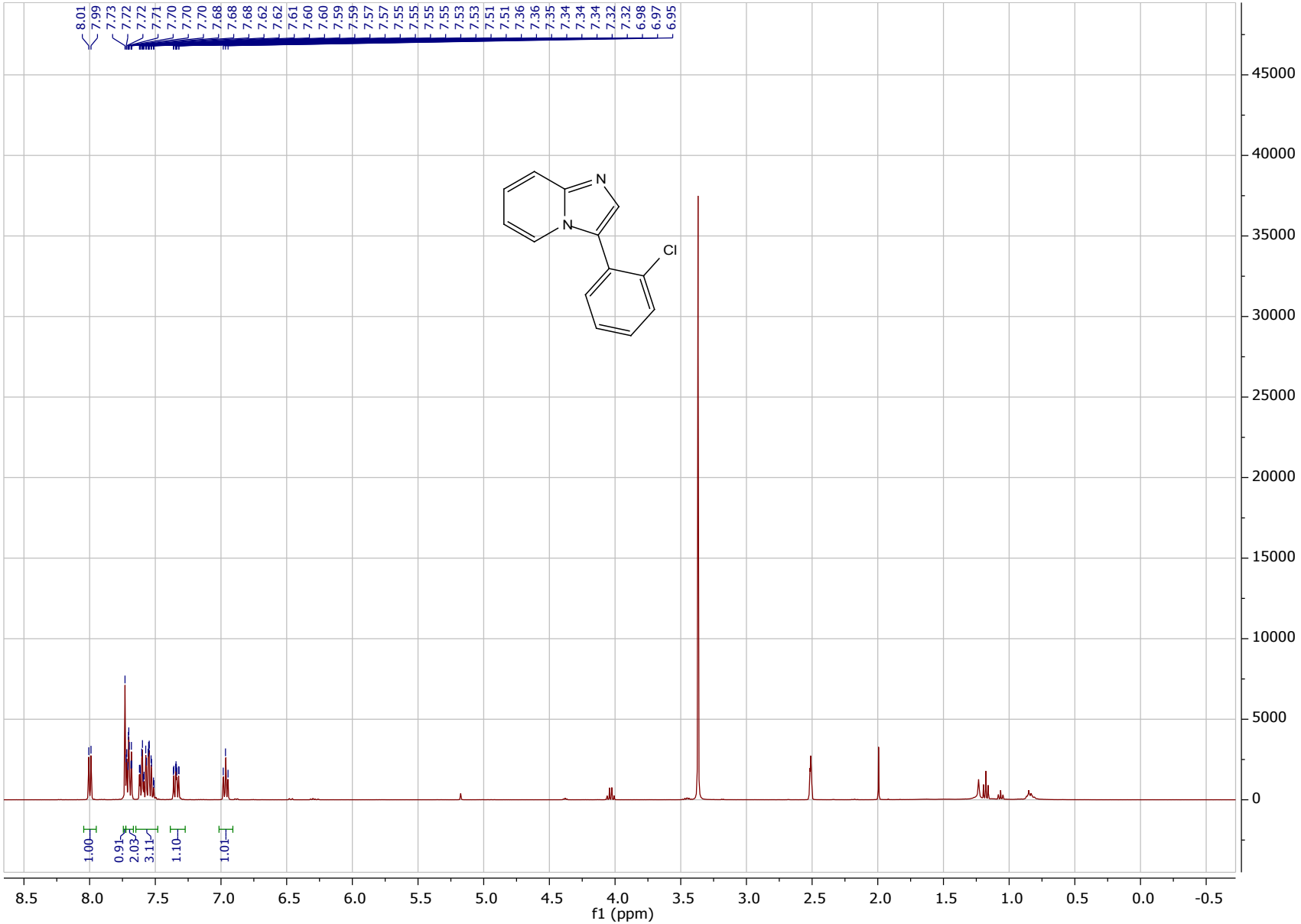
[1]H NMR of 3-(naphthalen-2-yl)imidazo[1,2-a]pyridine (3b):



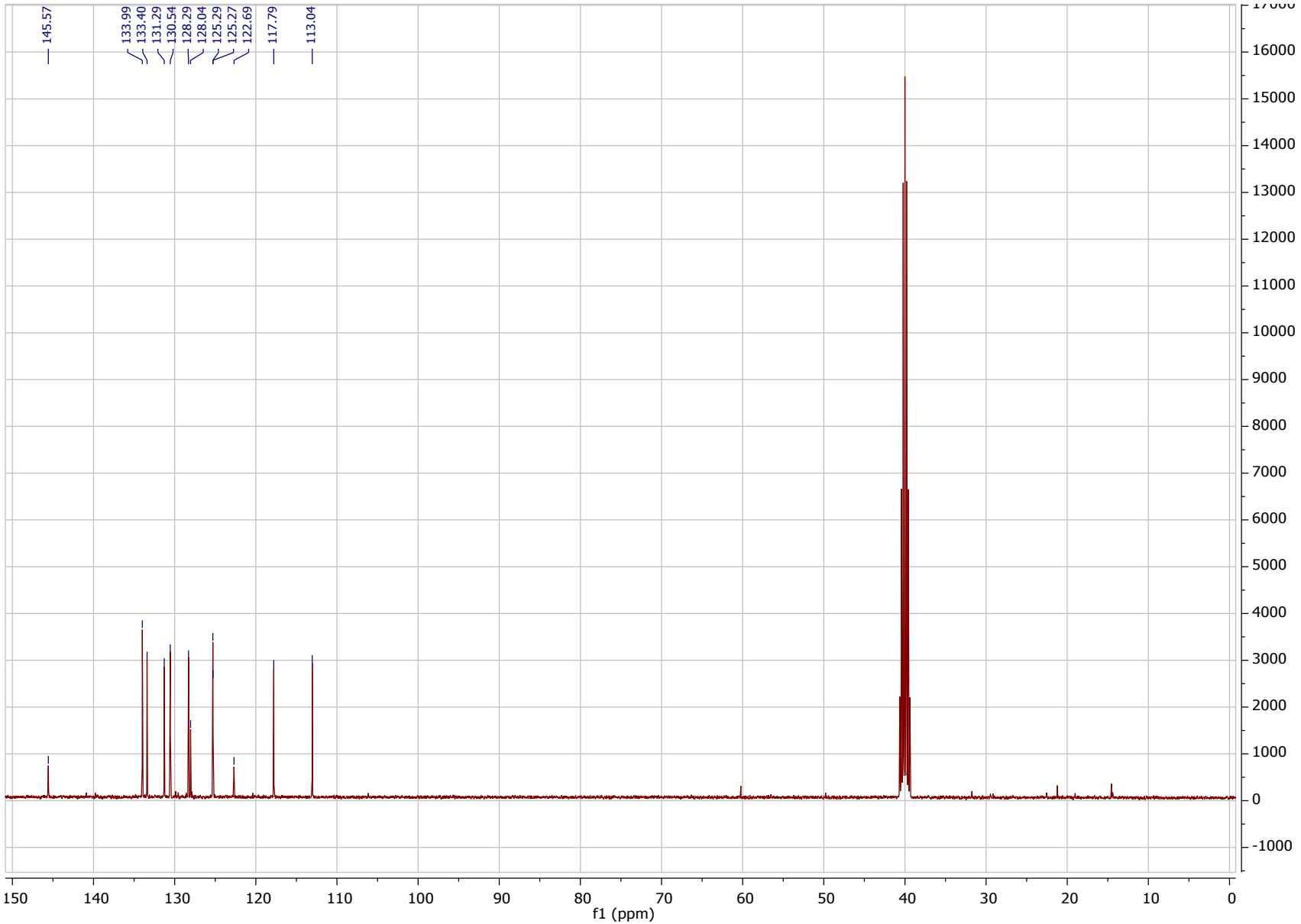
^{13}C NMR of 3-(naphthalen-2-yl)imidazo[1,2-a]pyridine (3b):



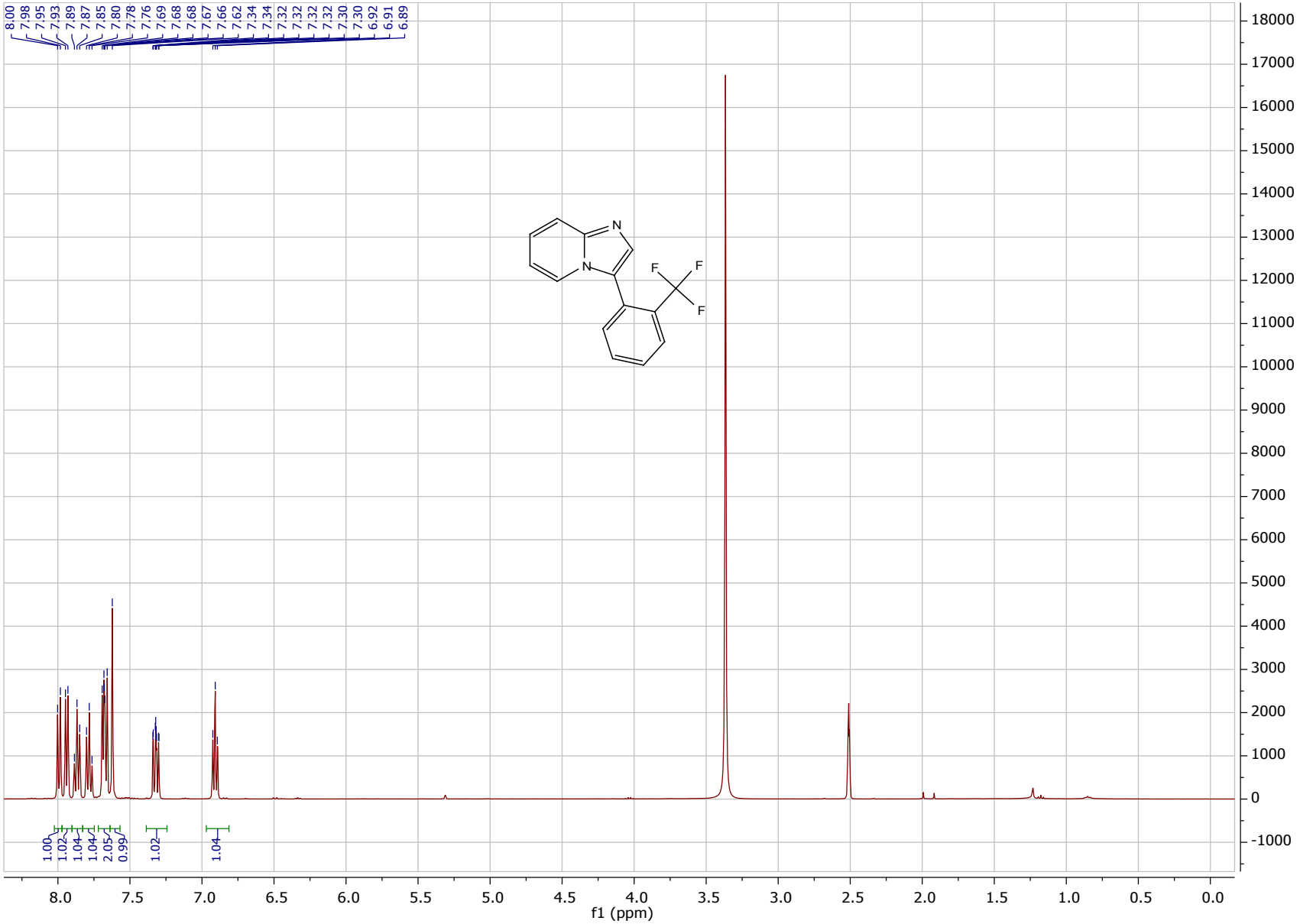
[1]H NMR of 3-(2-chlorophenyl)imidazo[1,2-a]pyridine (3c):



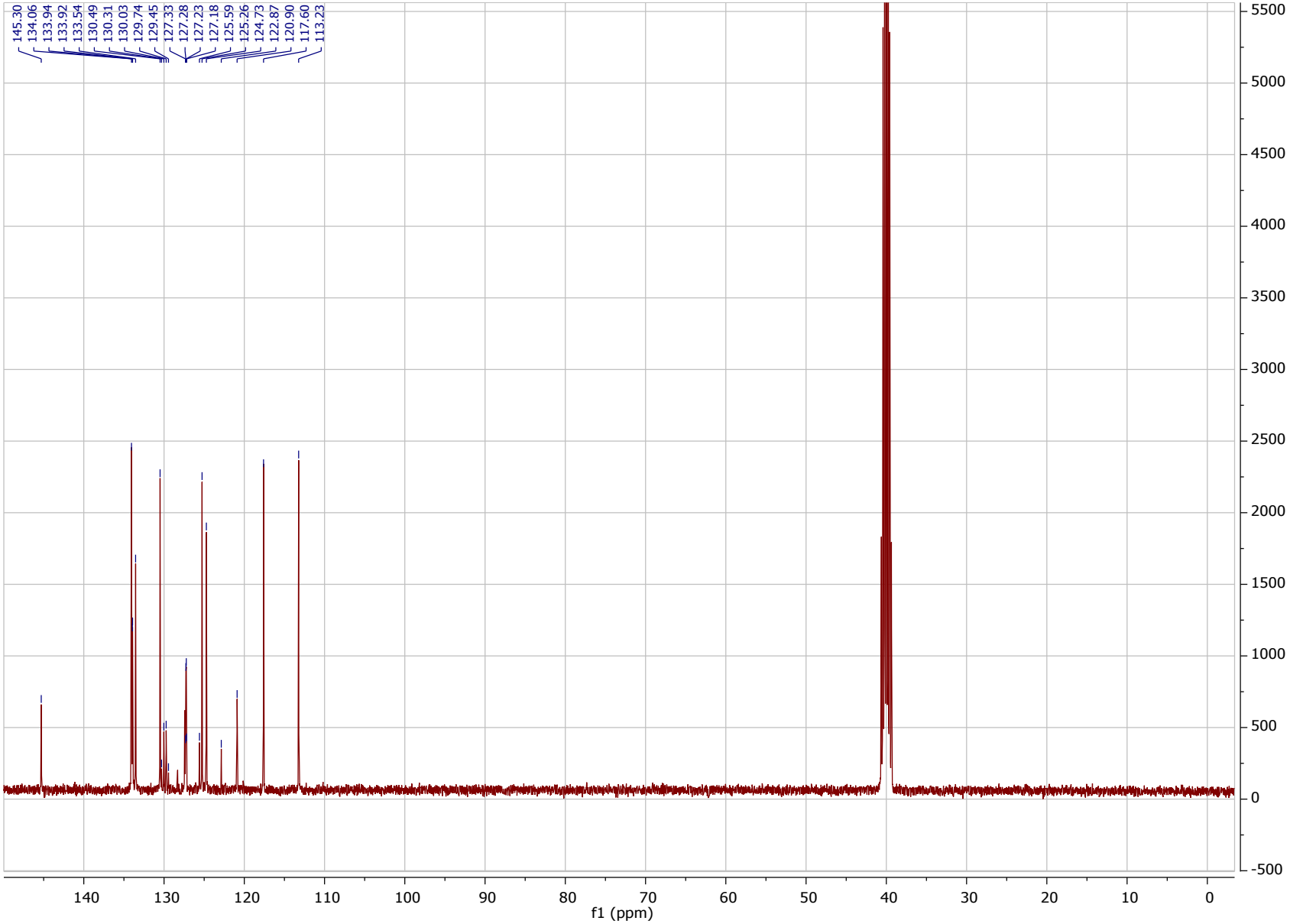
^{13}C NMR of 3-(2-chlorophenyl)imidazo[1,2-a]pyridine (3c):



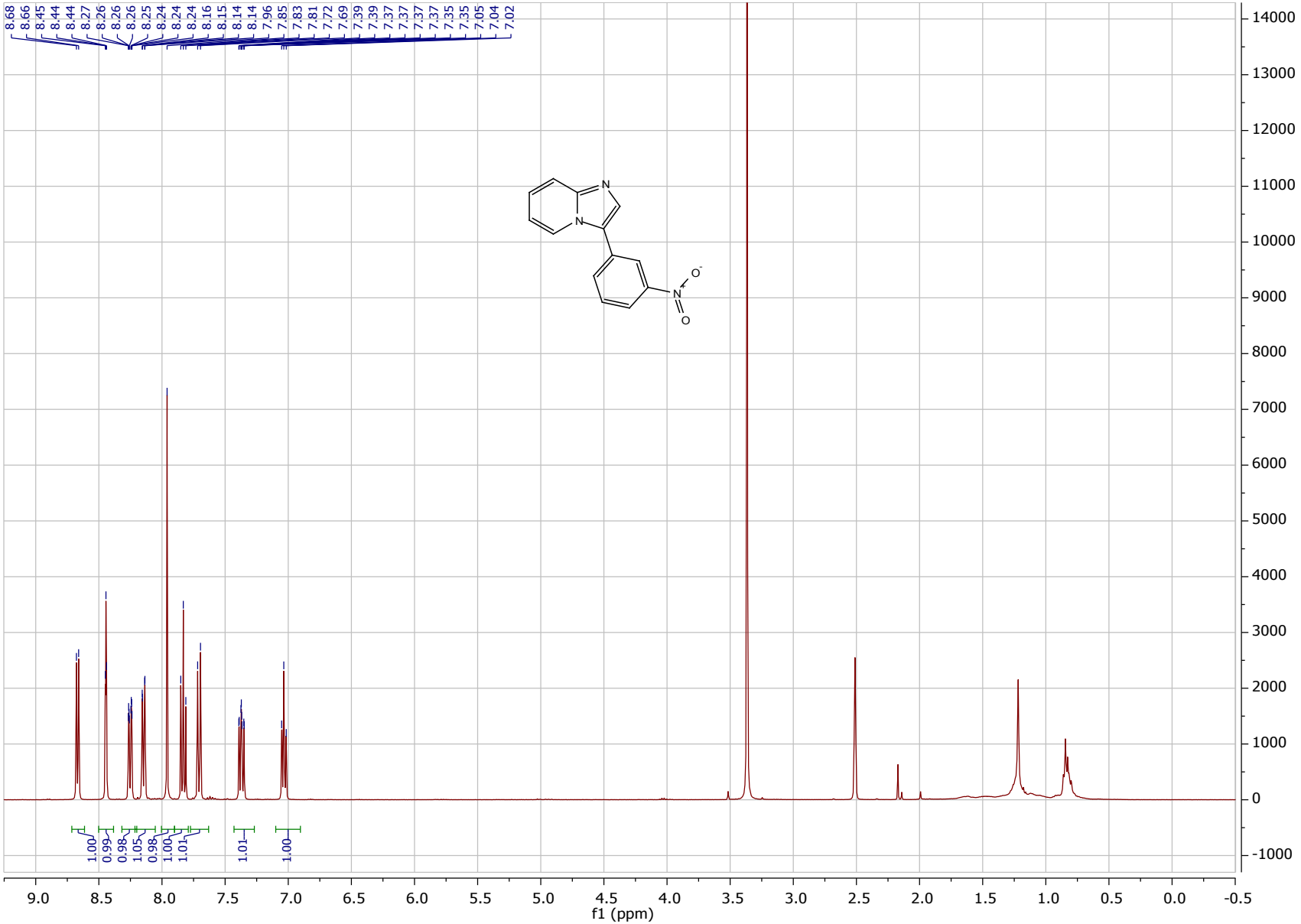
^{1}H NMR of 3-(2-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3d):



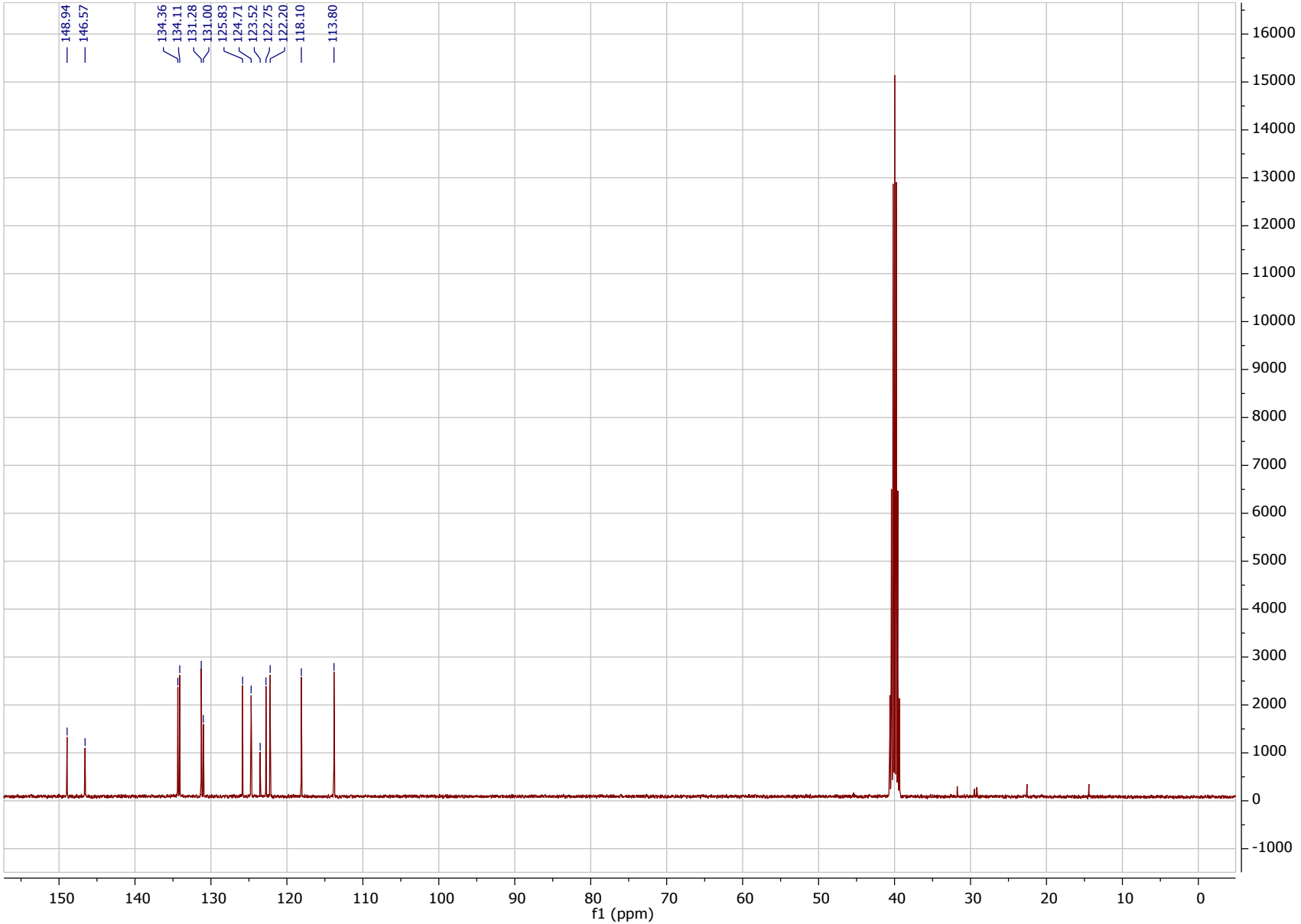
^{13}C NMR of 3-(2-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3d):



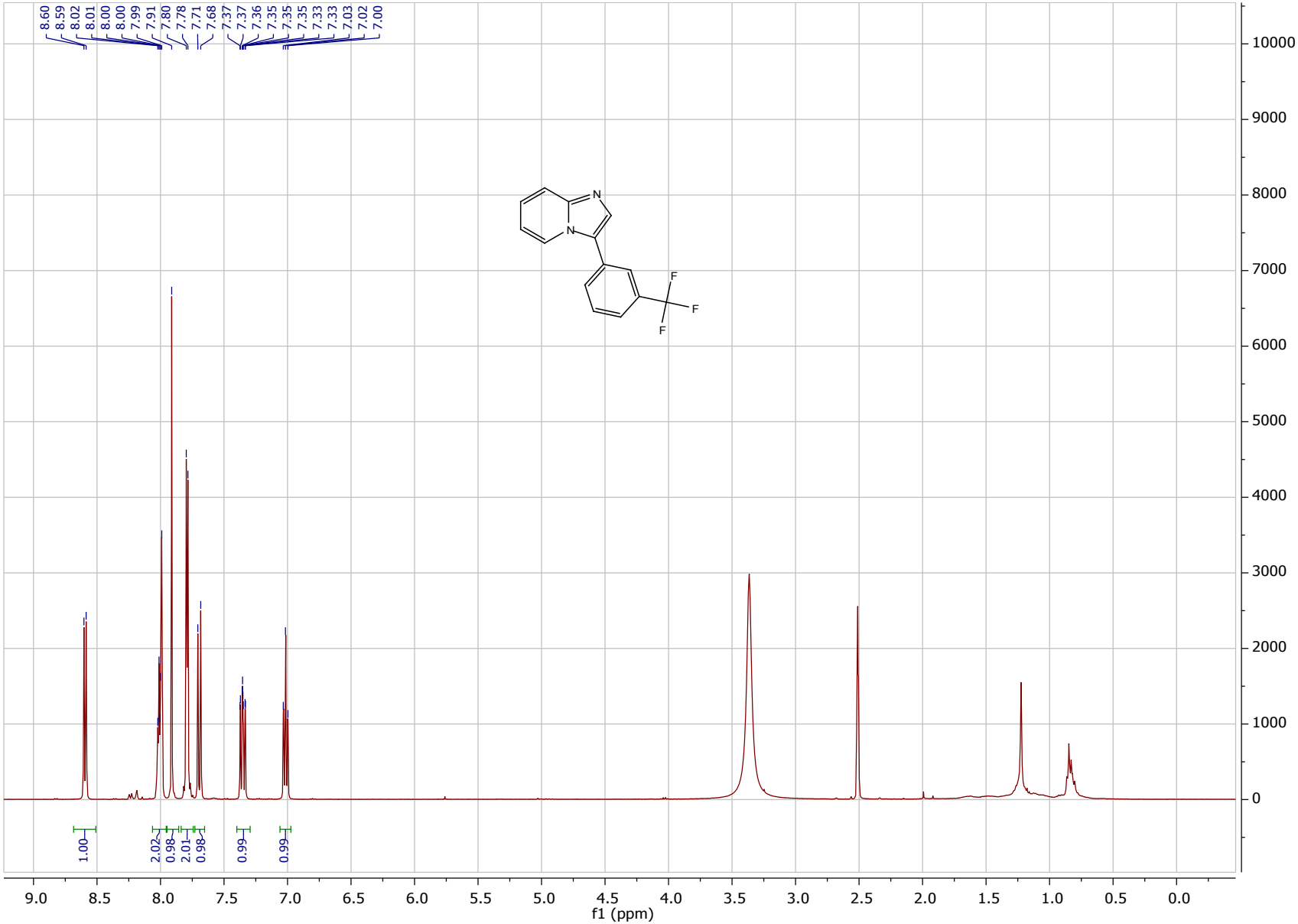
^{1}H NMR of 3-(3-nitrophenyl)imidazo[1,2-a]pyridine (3e):



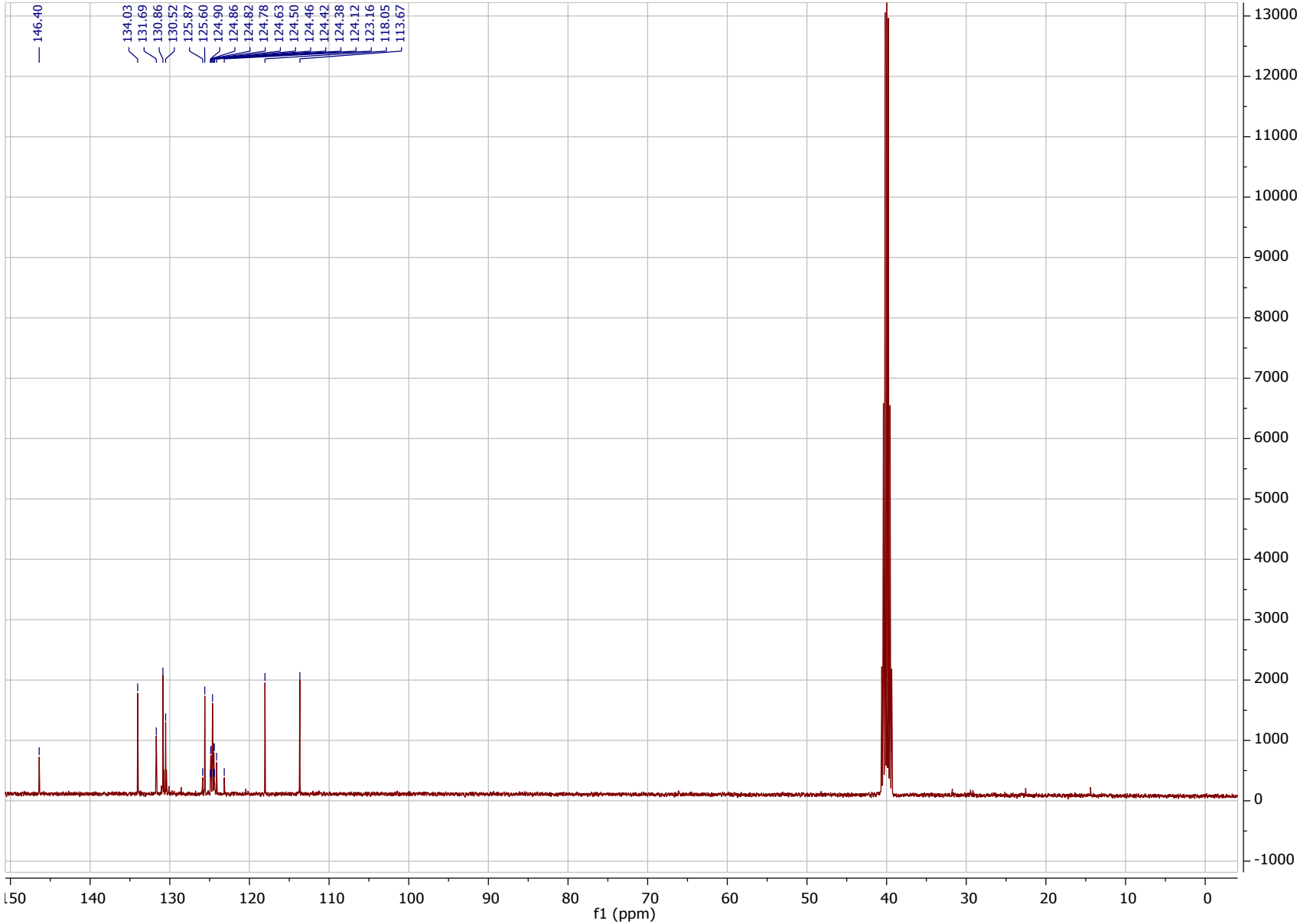
^{13}C NMR of 3-(3-nitrophenyl)imidazo[1,2-a]pyridine (3e):



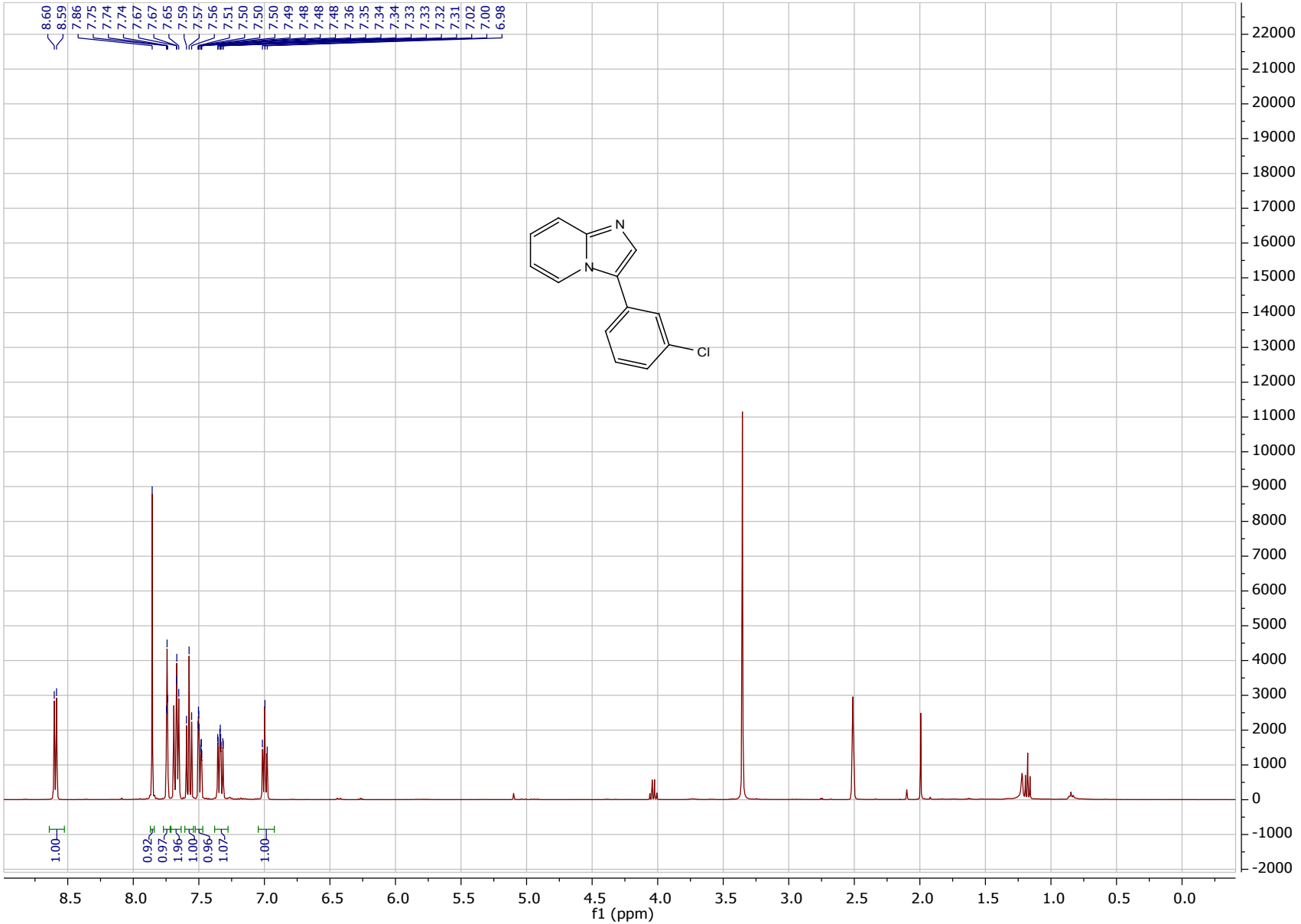
[1]H NMR of 3-(3-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3f):



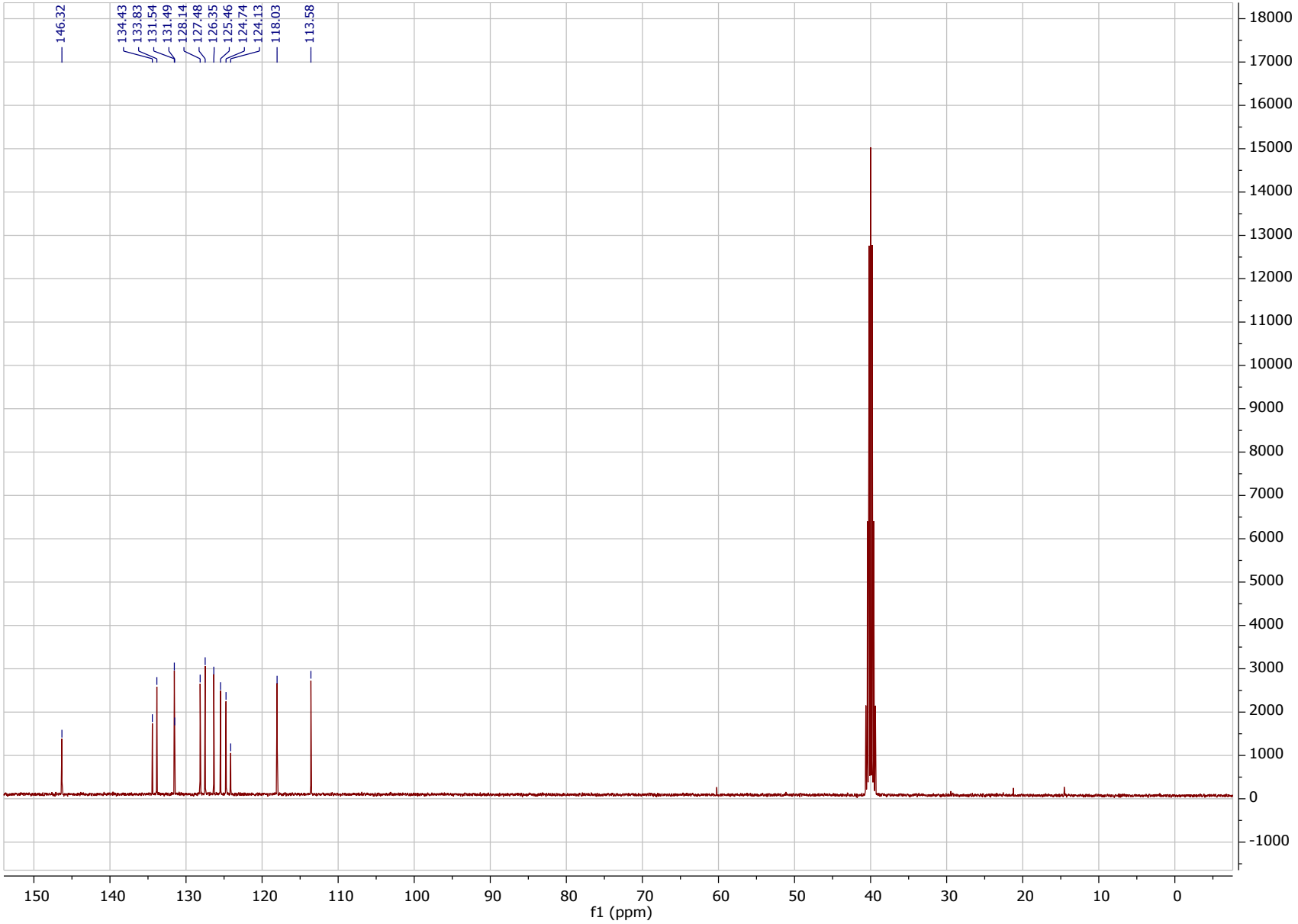
^{13}C NMR of 3-(3-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3f):



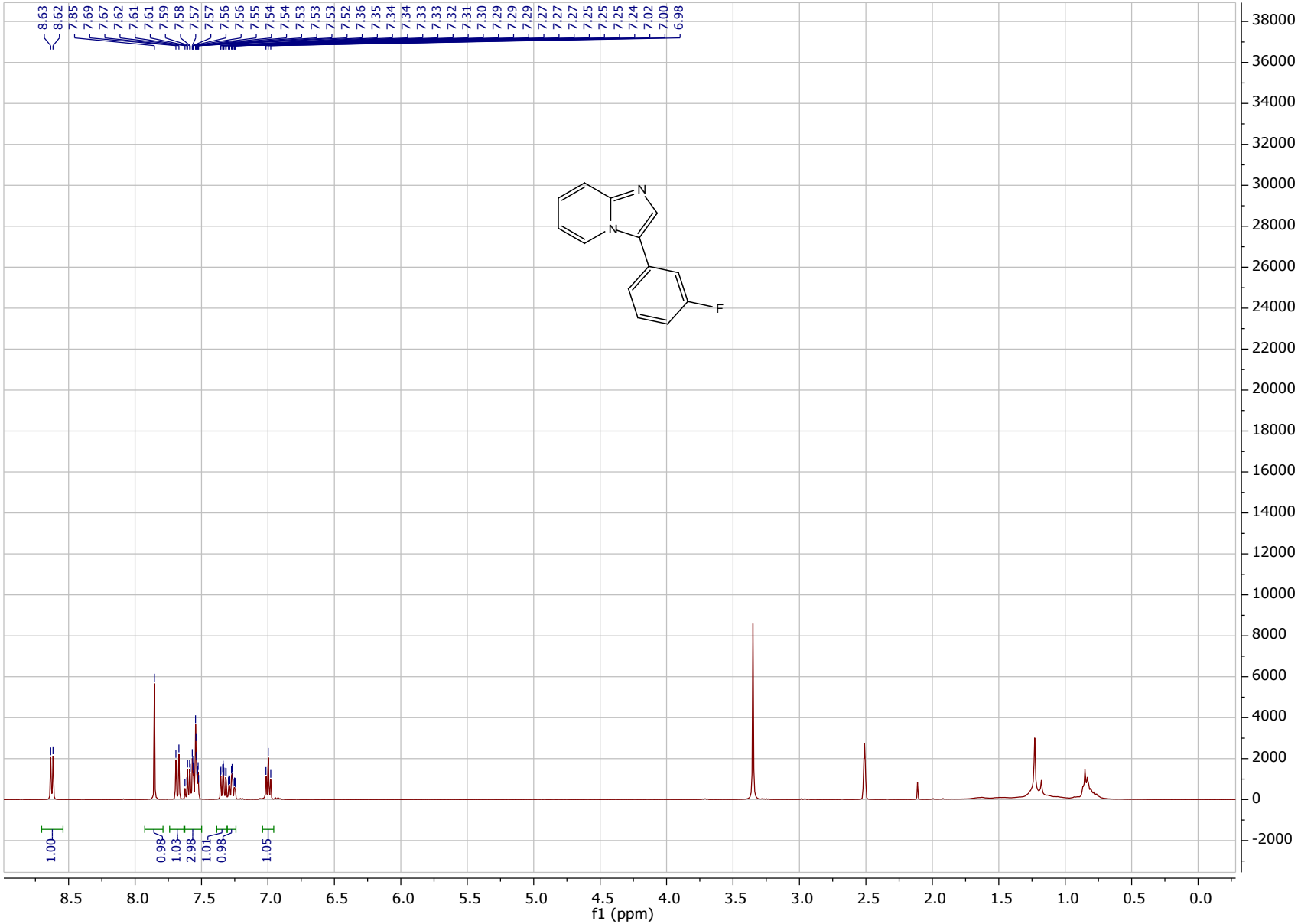
[1]H NMR of 3-(3-chlorophenyl)imidazo[1,2-a]pyridine (3g):



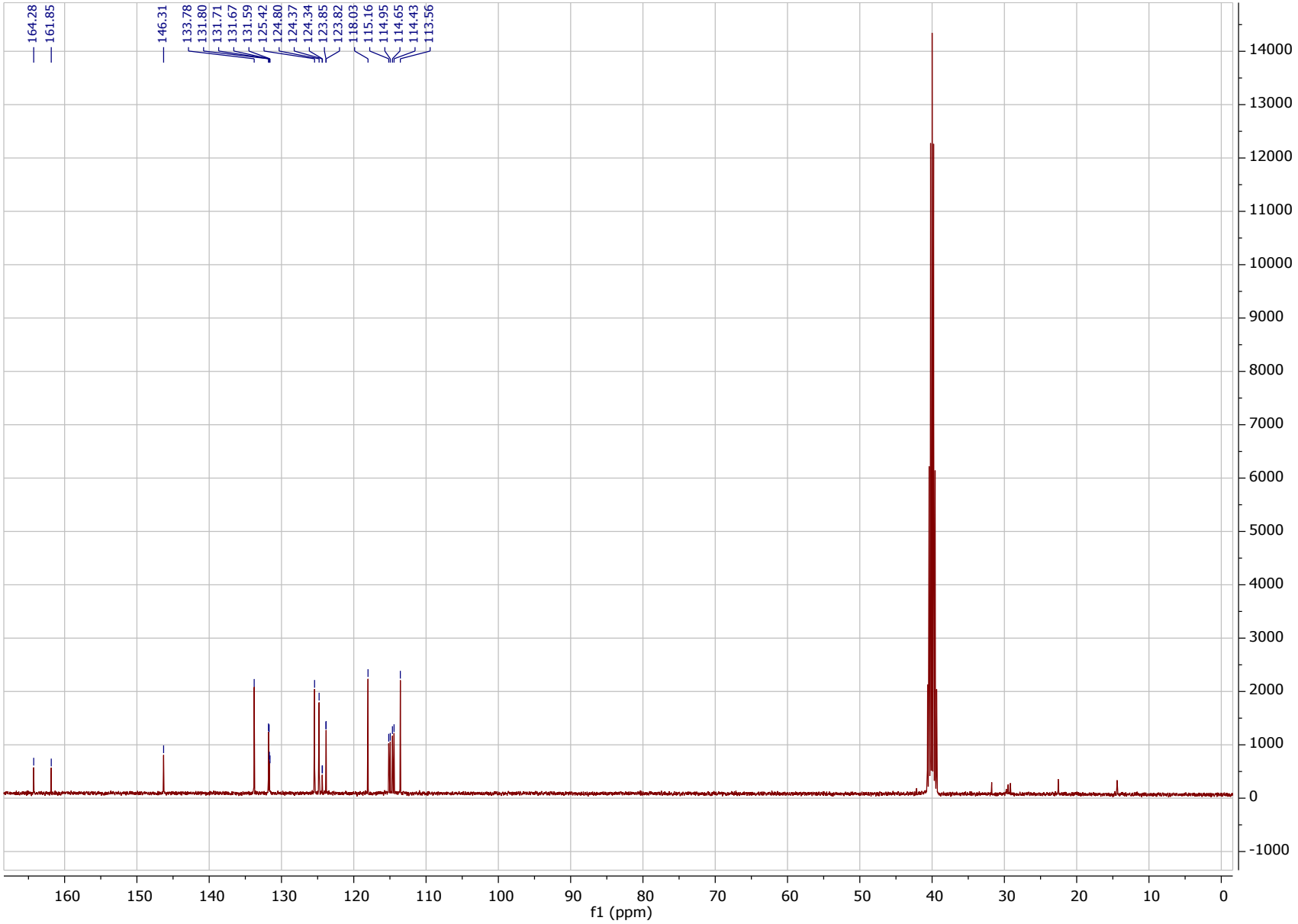
^{13}C NMR of 3-(3-chlorophenyl)imidazo[1,2-a]pyridine (3g):



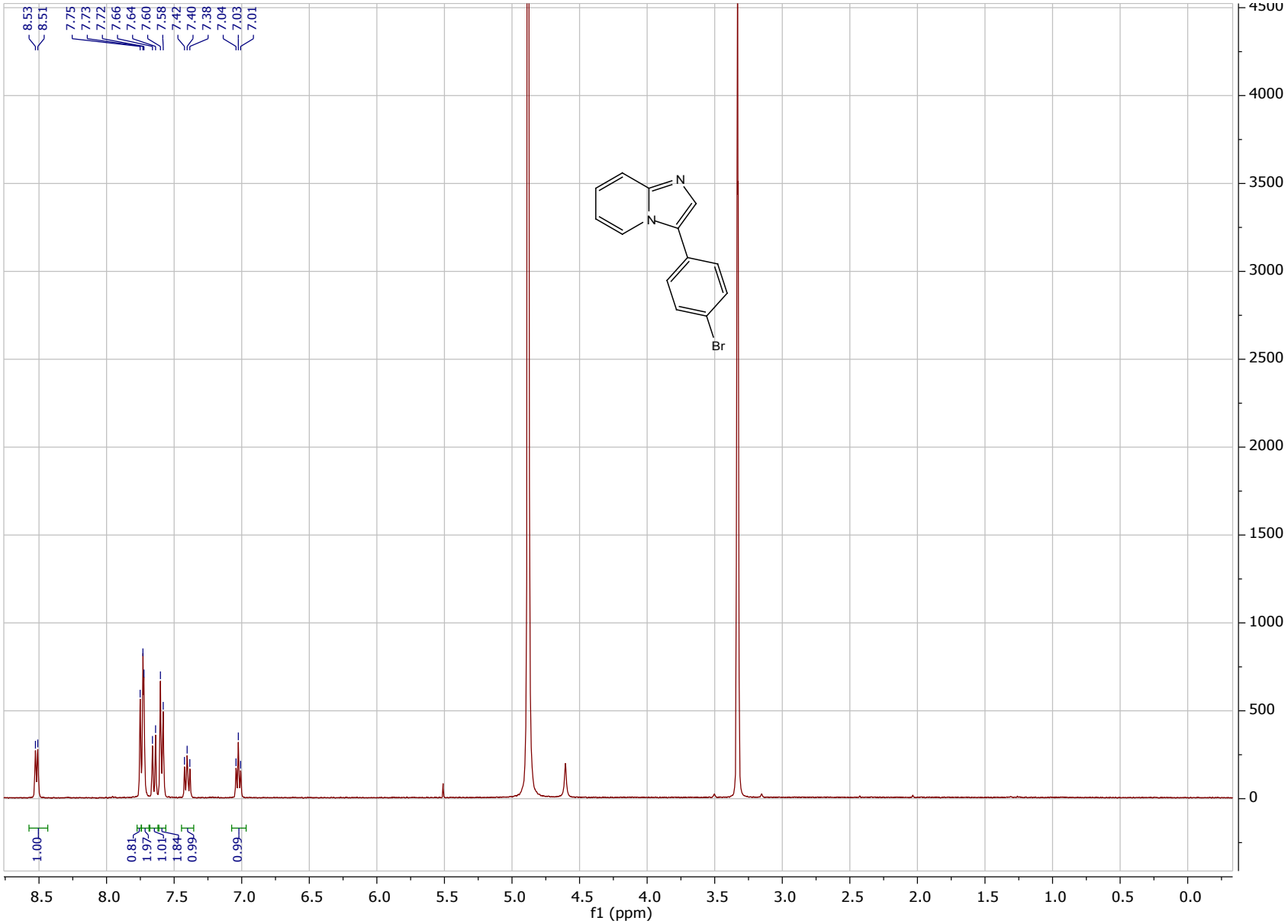
[1]H NMR of 3-(3-fluorophenyl)imidazo[1,2-a]pyridine (3h):



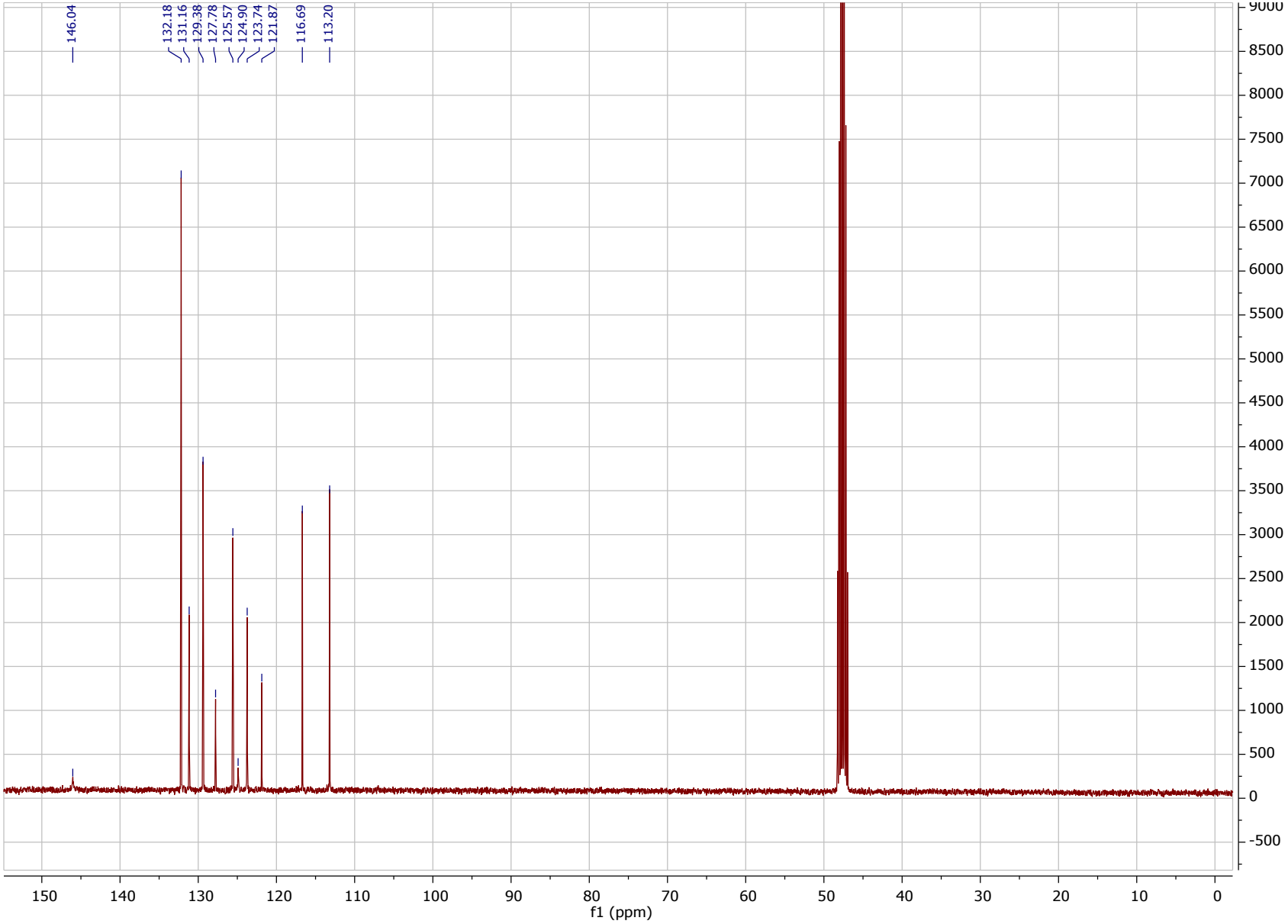
^{13}C NMR of 3-(3-fluorophenyl)imidazo[1,2-a]pyridine (3h):



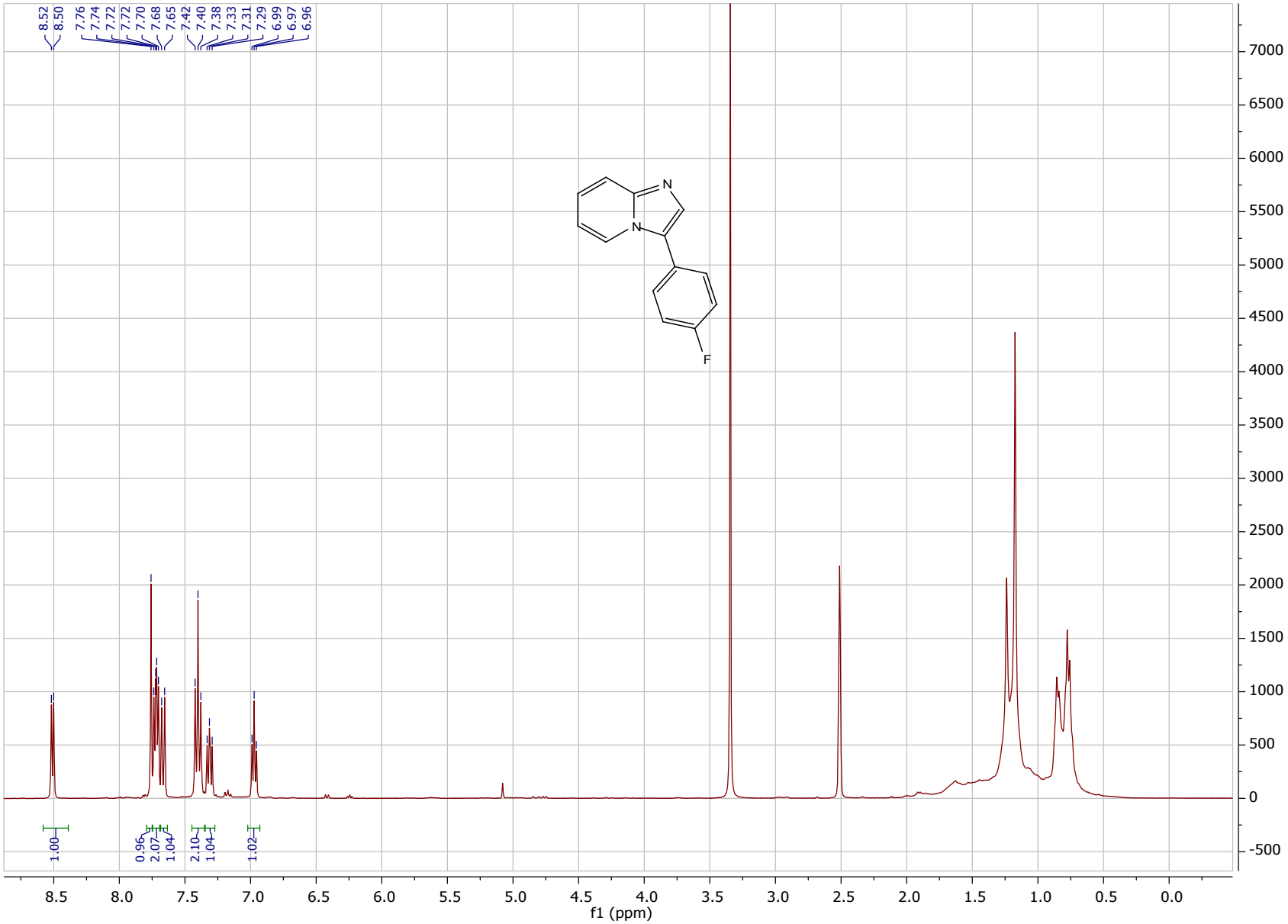
^{1}H NMR of 3-(4-bromophenyl)imidazo[1,2-a]pyridine (3i):



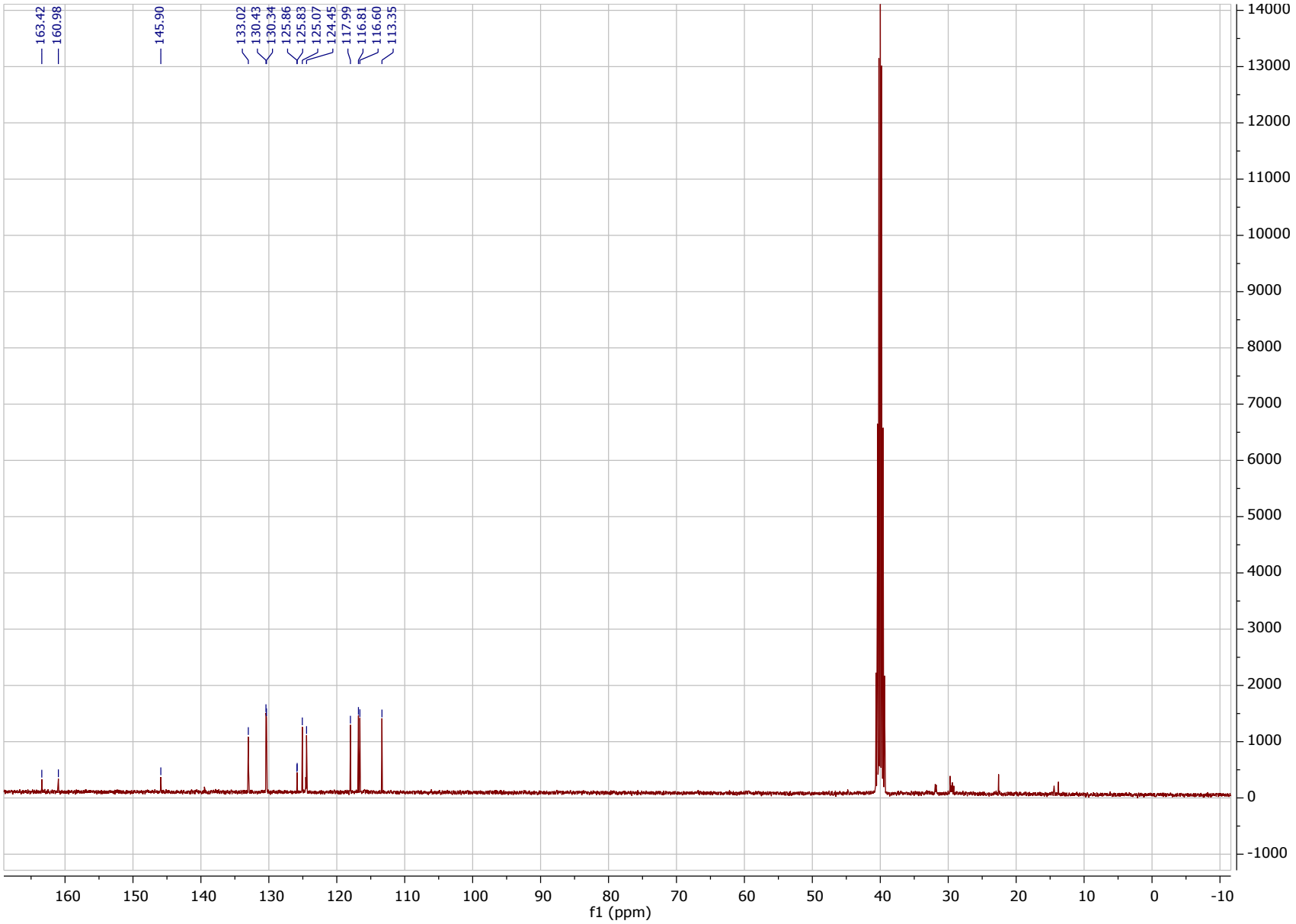
^{13}C NMR of 3-(4-bromophenyl)imidazo[1,2-a]pyridine (3i):



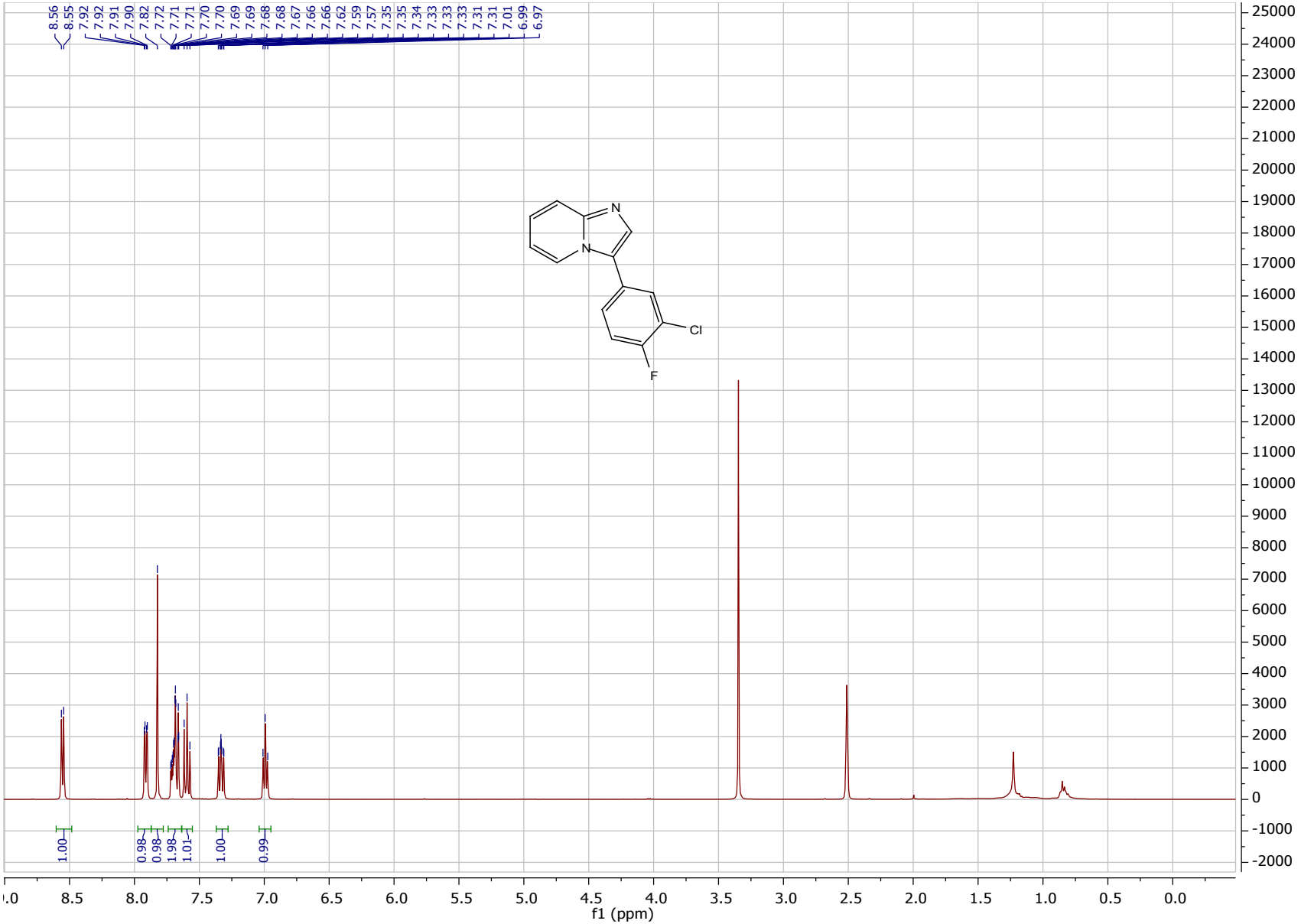
^{1}H NMR of 3-(4-fluorophenyl)imidazo[1,2-a]pyridine (3j):



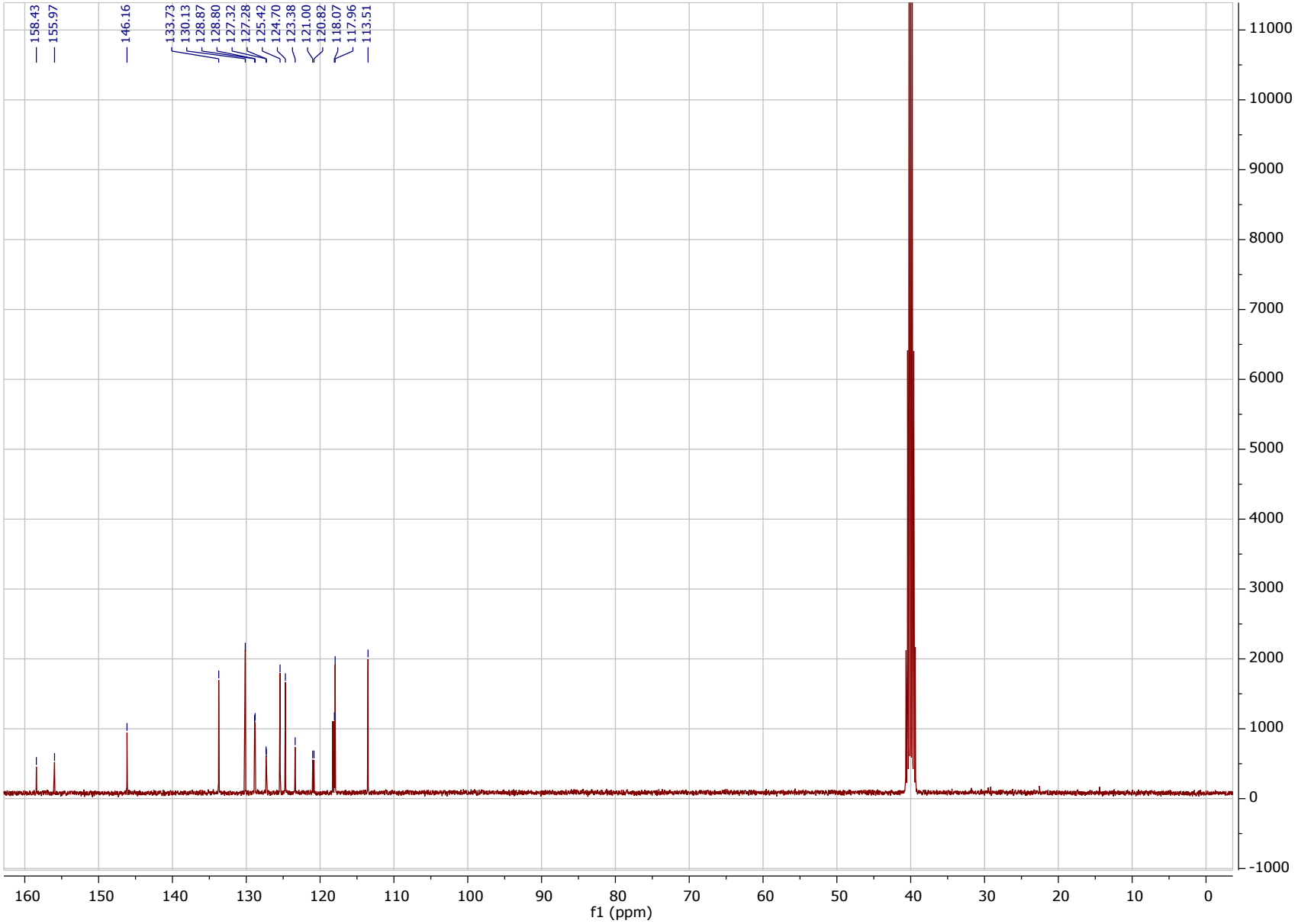
^{13}C NMR of 3-(4-fluorophenyl)imidazo[1,2-a]pyridine (3j):



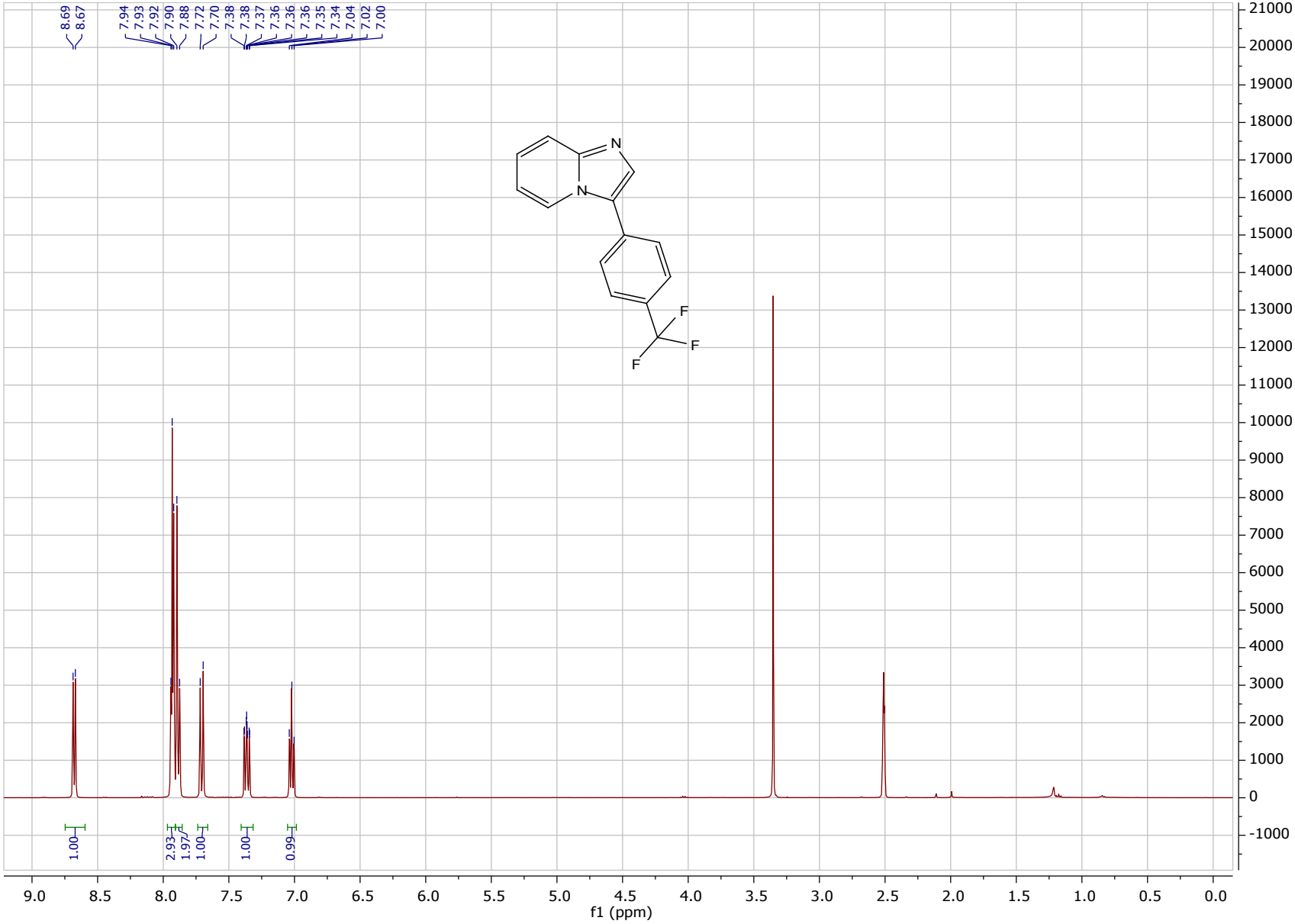
^{1}H NMR of 3-(3-chloro-4-fluorophenyl)imidazo[1,2-a]pyridine (3k):



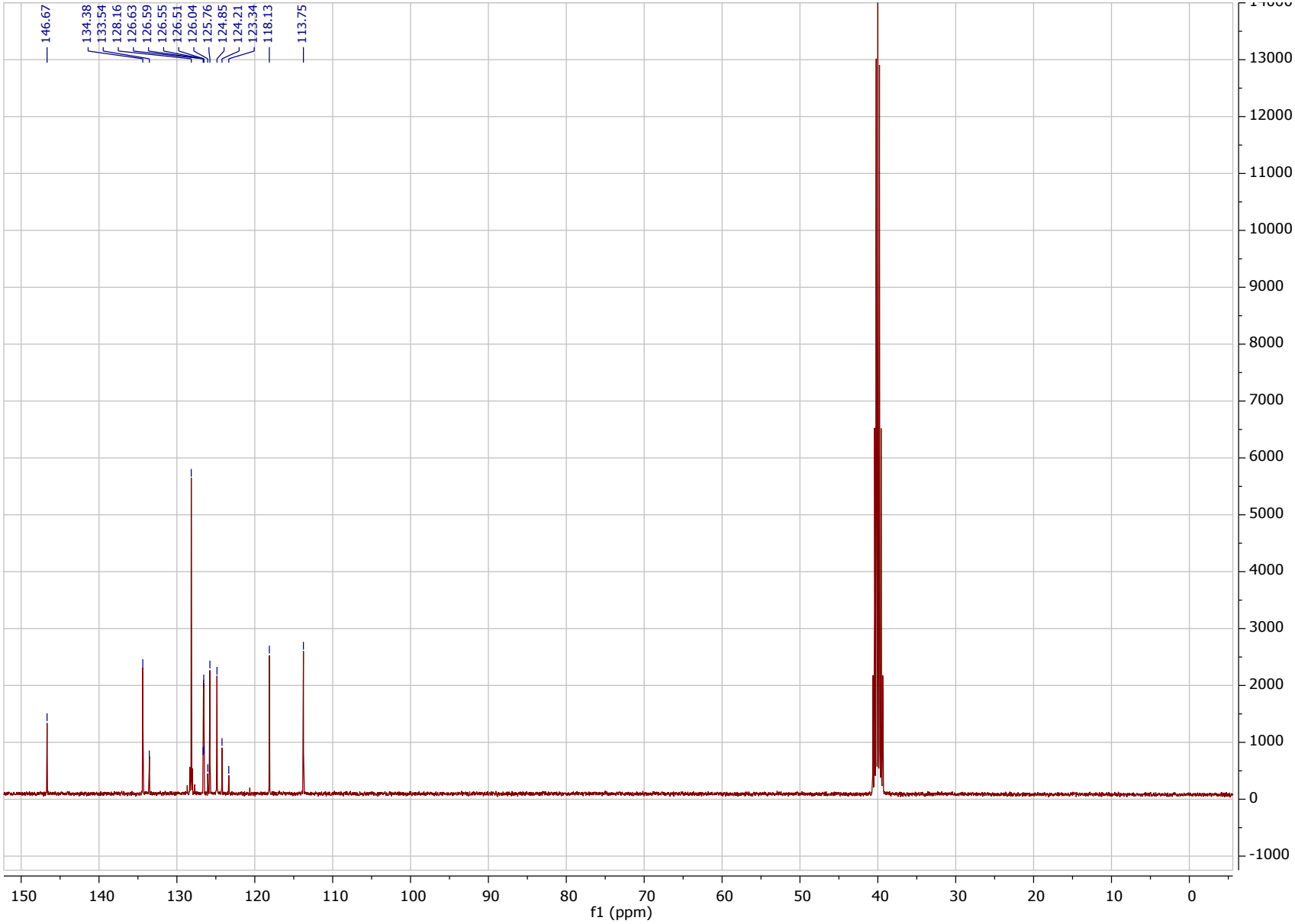
^{13}C NMR of 3-(3-chloro-4-fluorophenyl)imidazo[1,2-a]pyridine (3k):



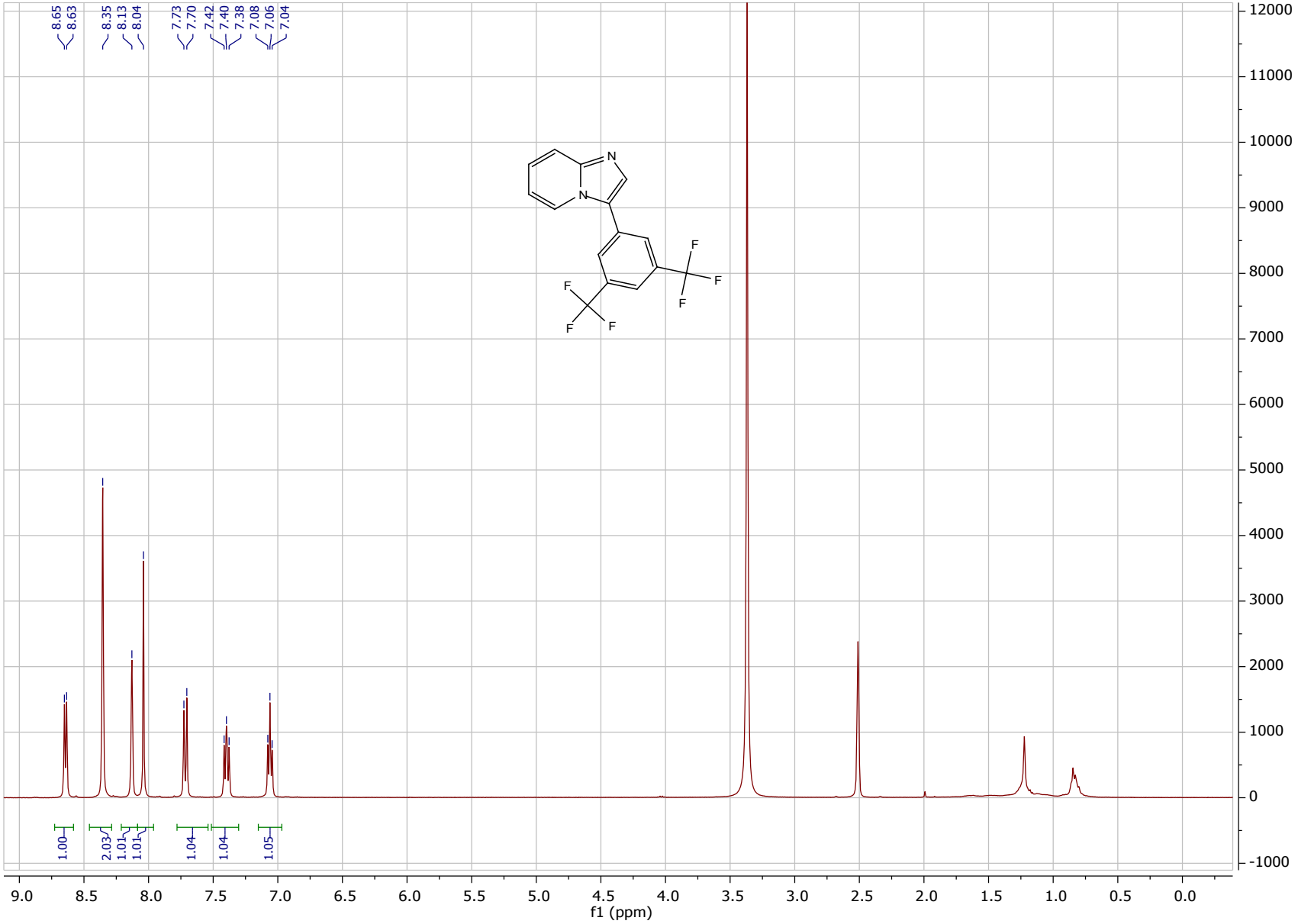
[1]H NMR of 3-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3l):



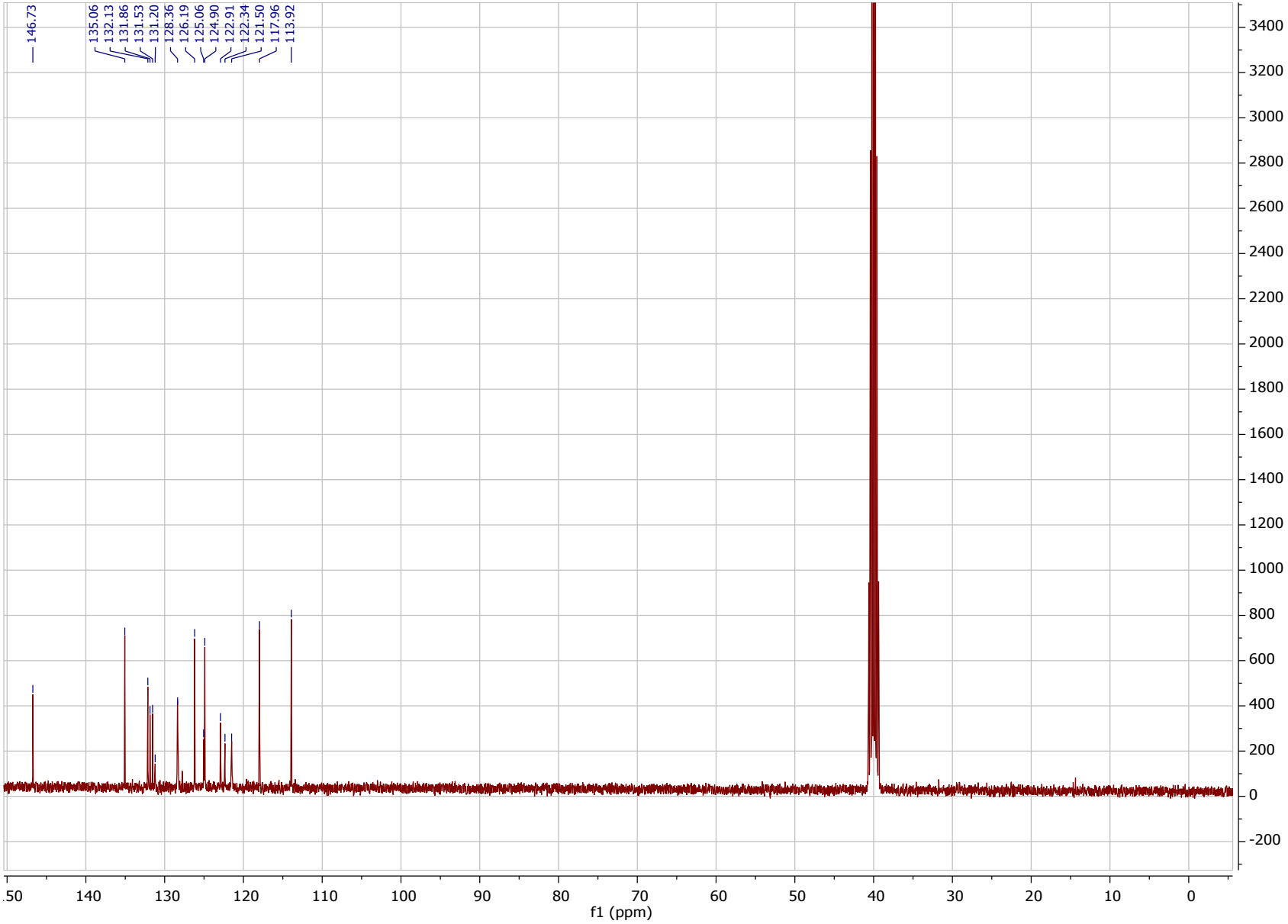
^{13}C NMR of 3-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3l):



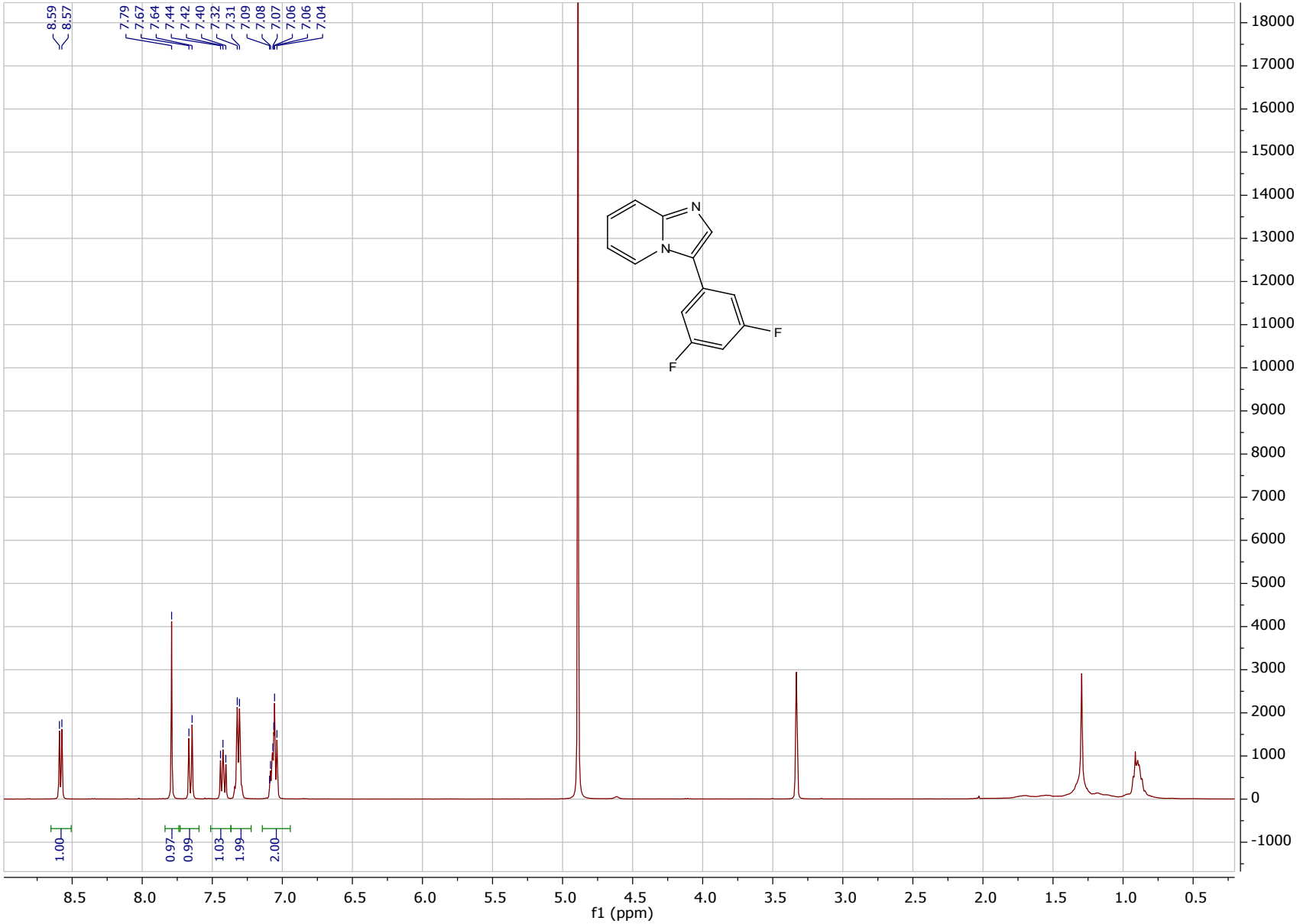
^{1}H NMR of 3-(3,5-bis(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3m):



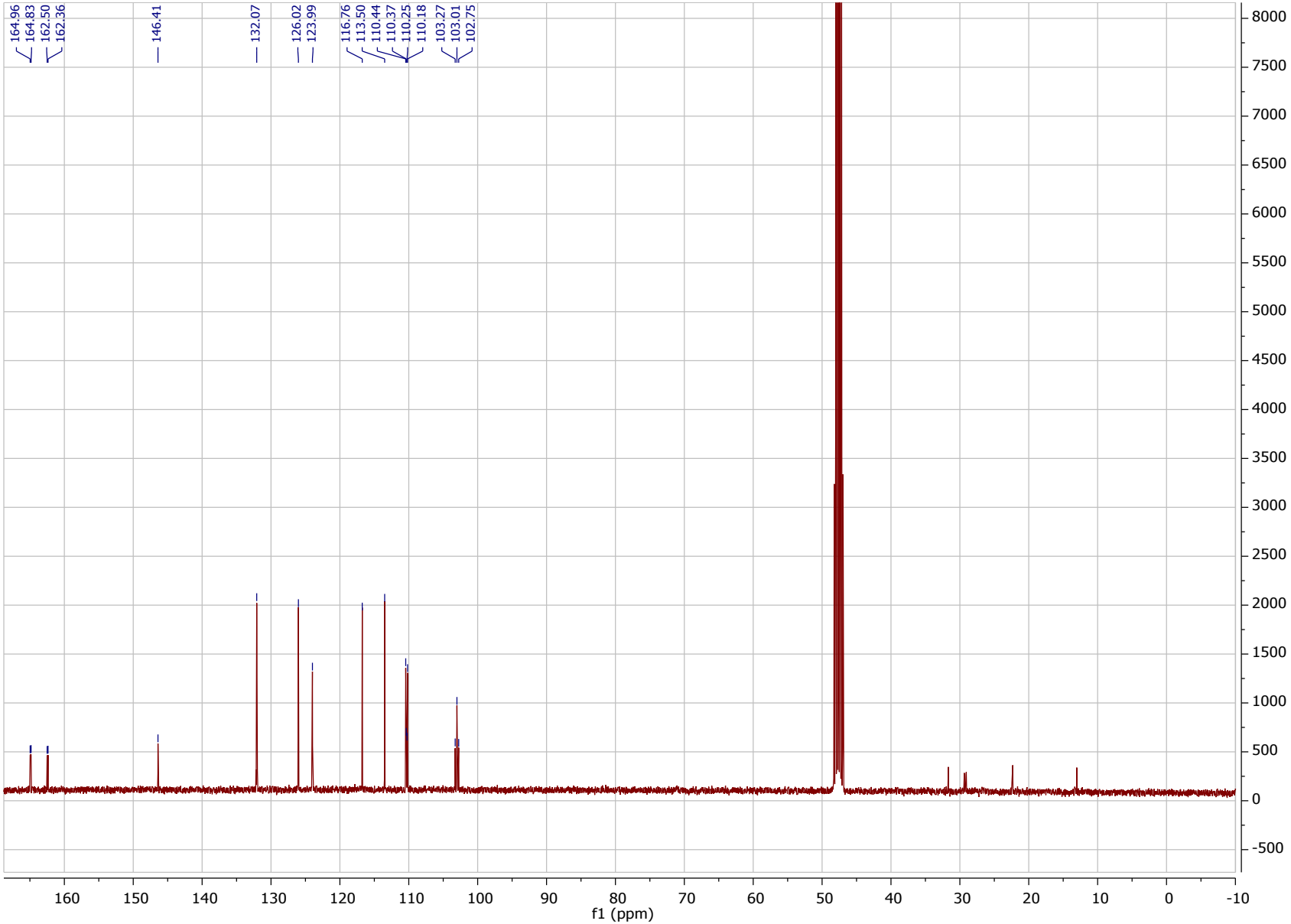
^{13}C NMR of 3-(3,5-bis(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3m):



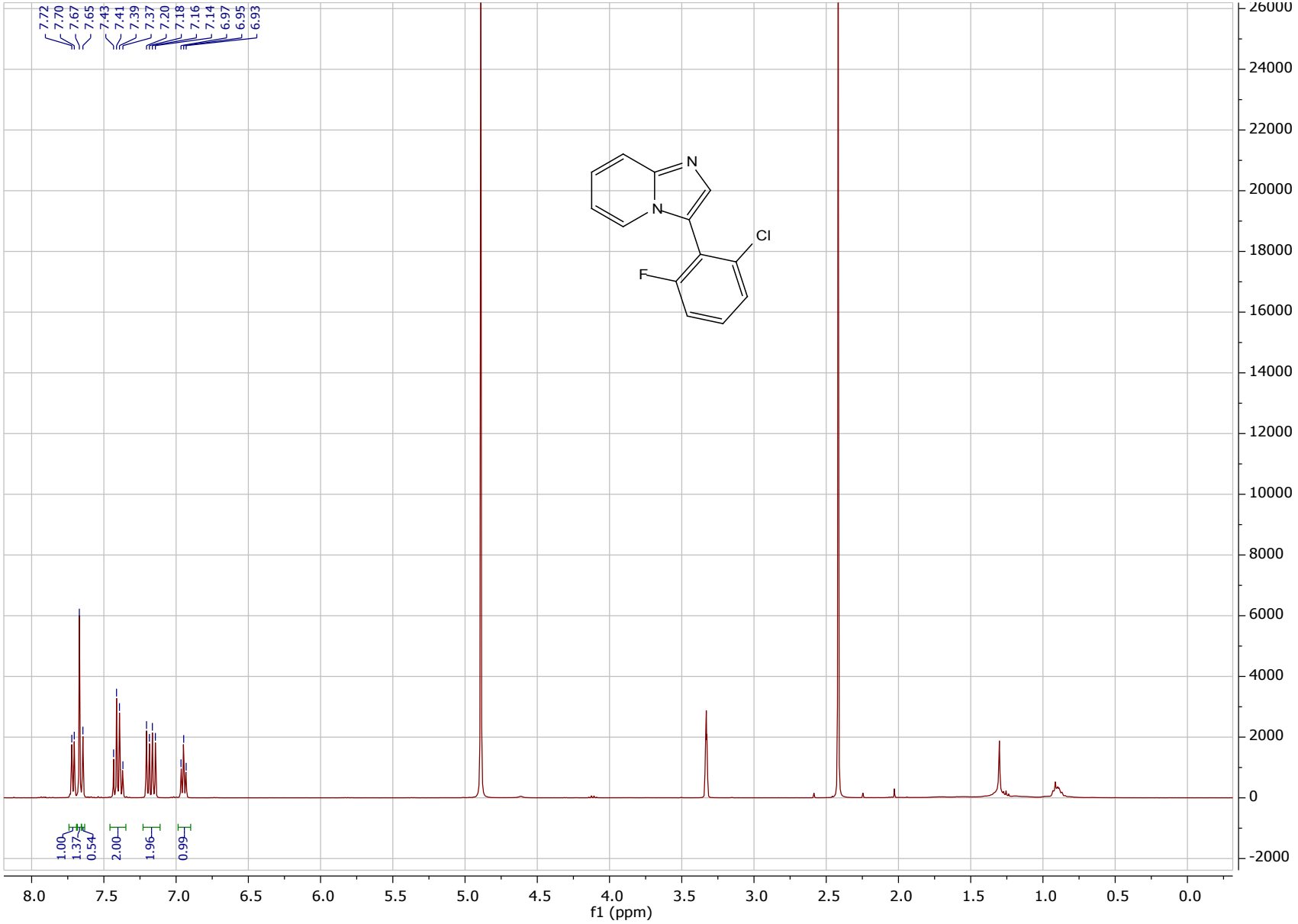
^{1}H NMR of 3-(3,5-difluorophenyl)imidazo[1,2-a]pyridine (3n):



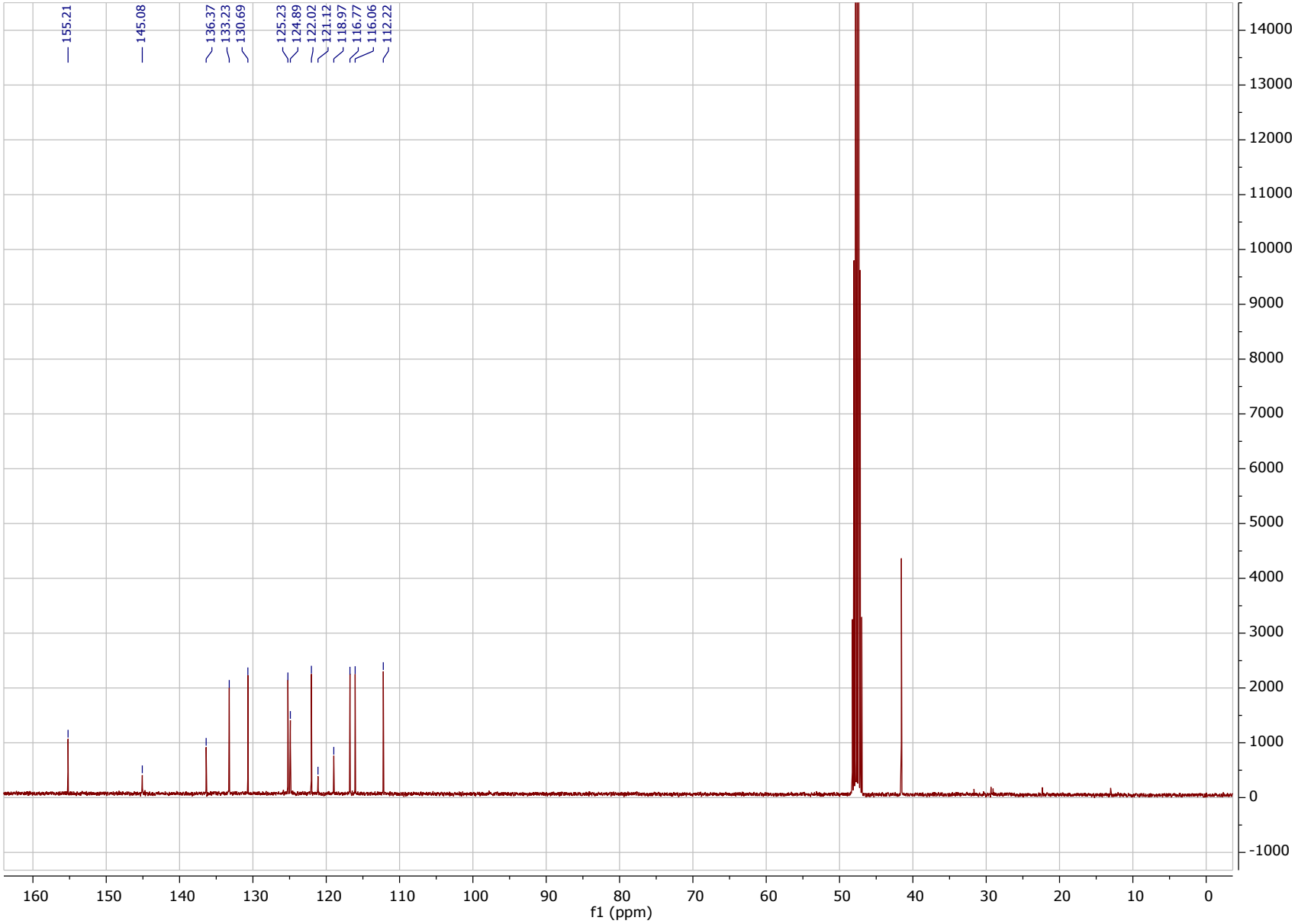
^{13}C NMR of 3-(3,5-difluorophenyl)imidazo[1,2-a]pyridine (3n):



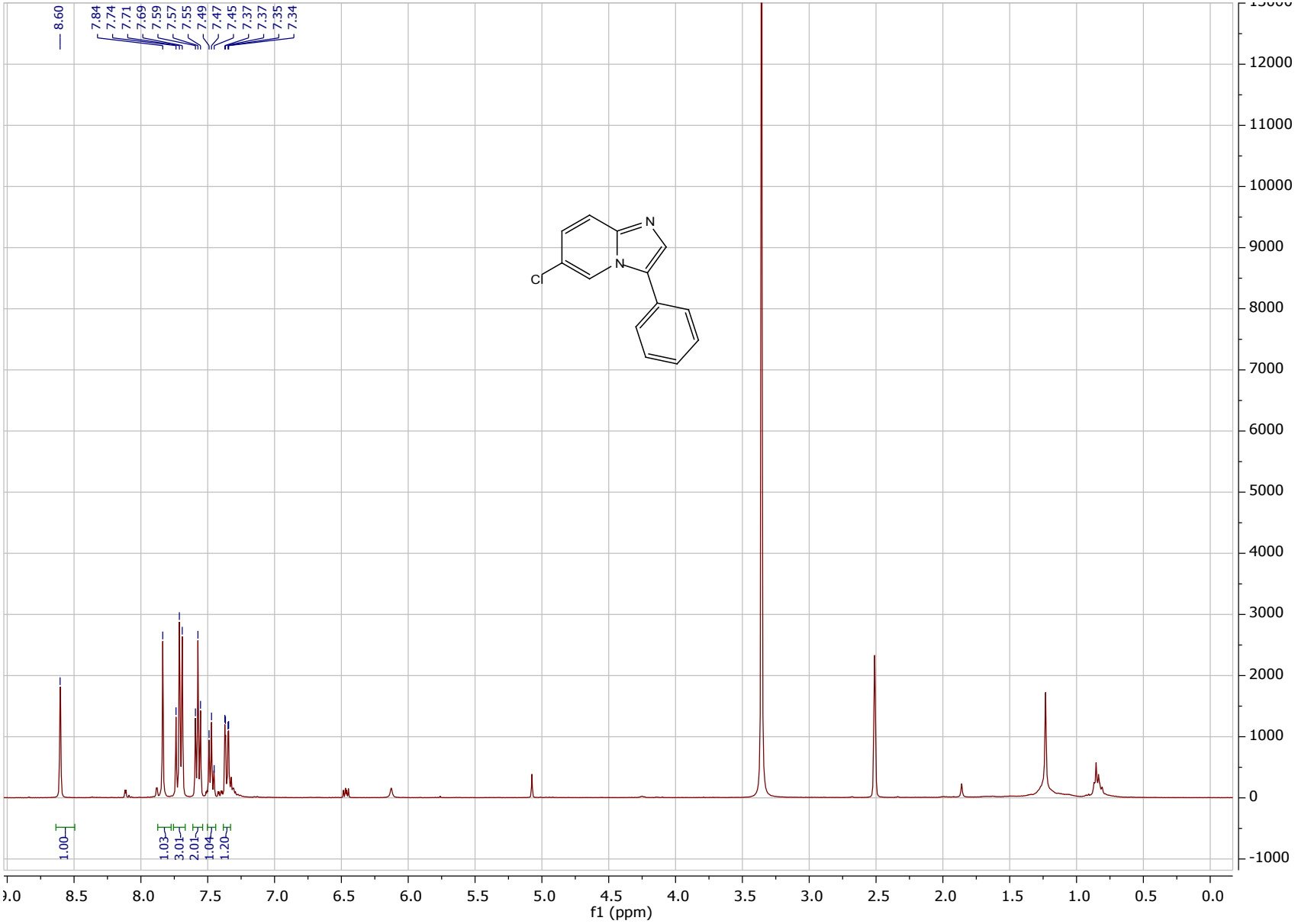
^{1}H NMR of 3-(2-chloro-6-fluorophenyl)imidazo[1,2-a]pyridine (3o):



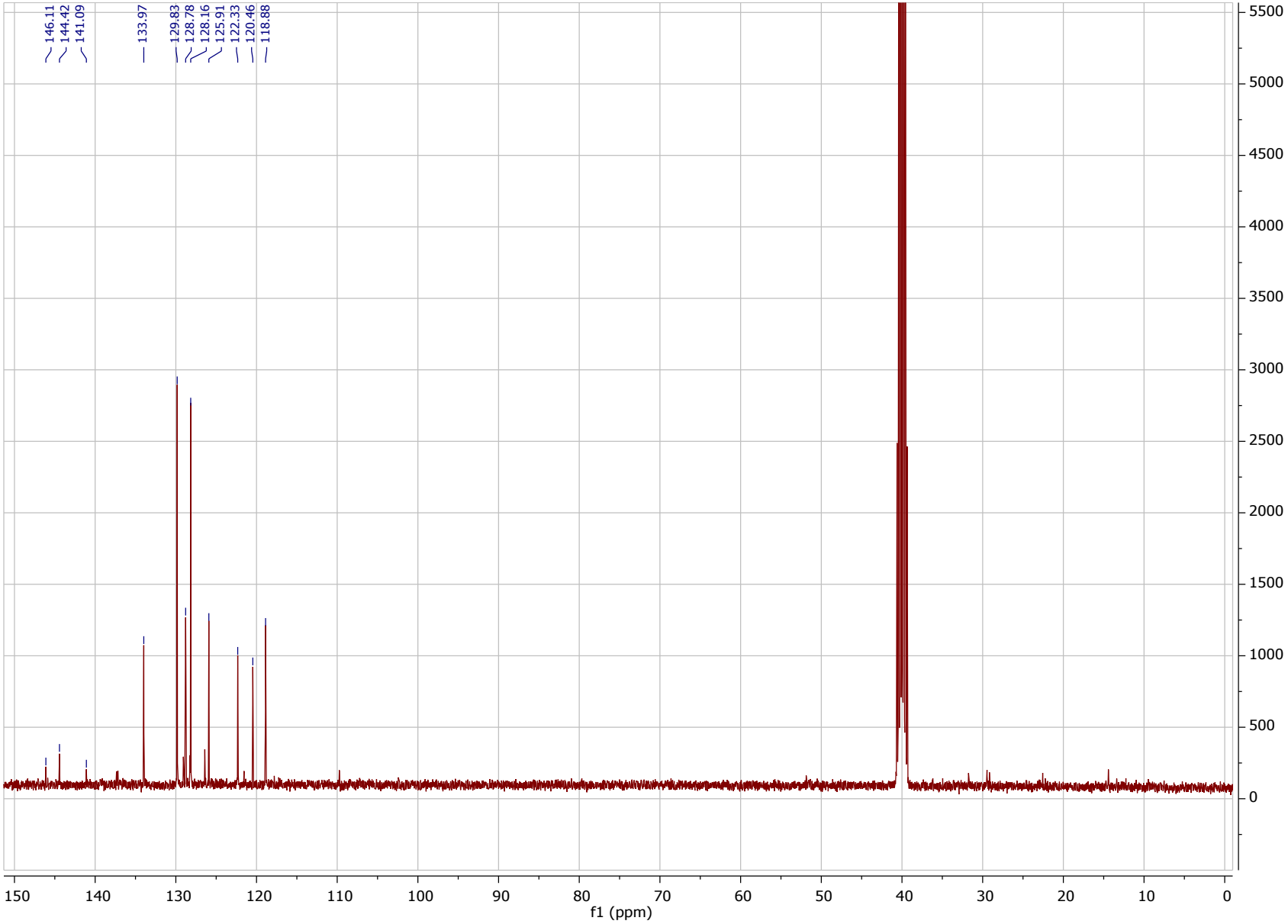
^{13}C NMR of 3-(2-chloro-6-fluorophenyl)imidazo[1,2-a]pyridine (3o):



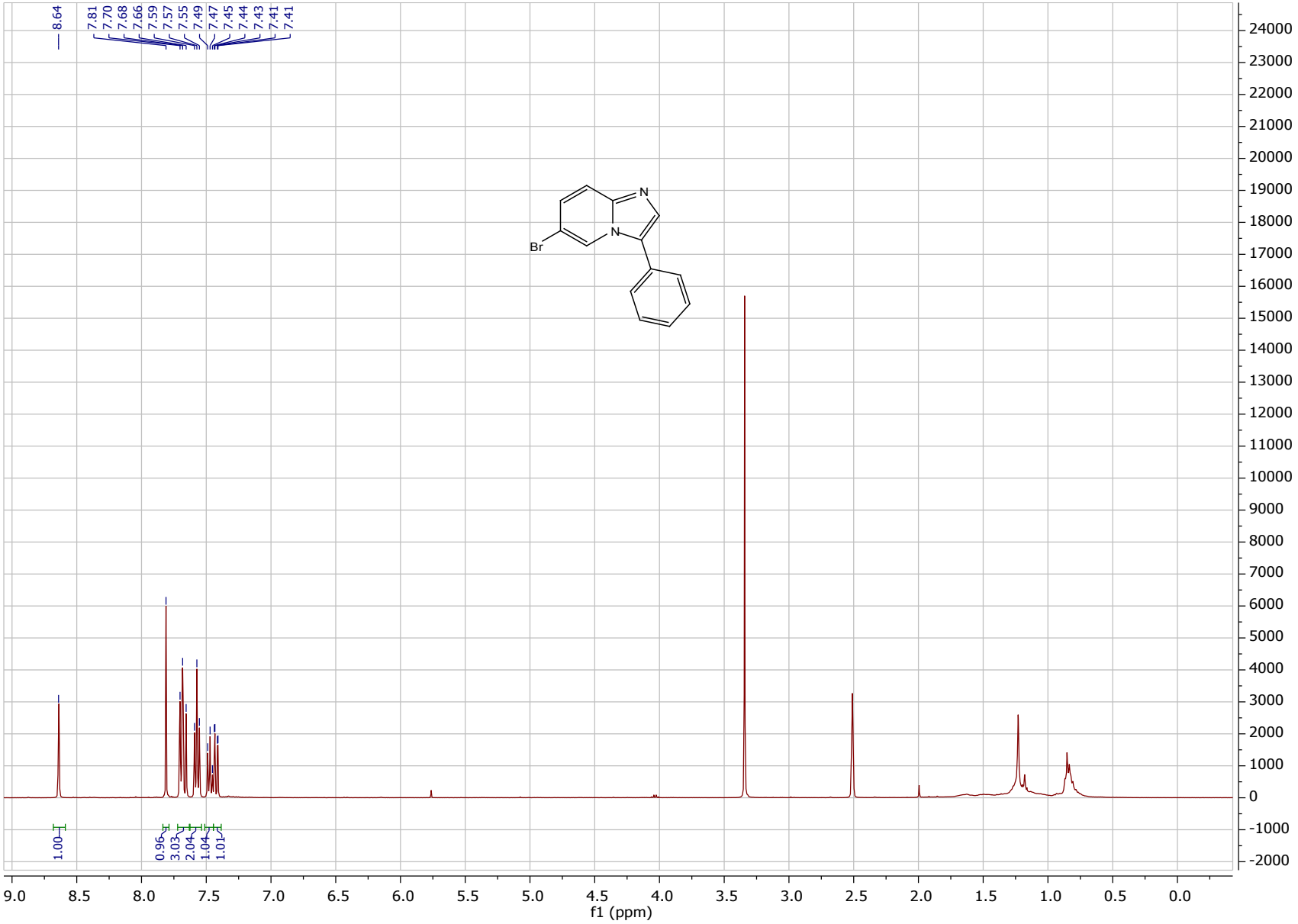
^{1}H NMR of 6-chloro-3-phenylimidazo[1,2-a]pyridine (6a):



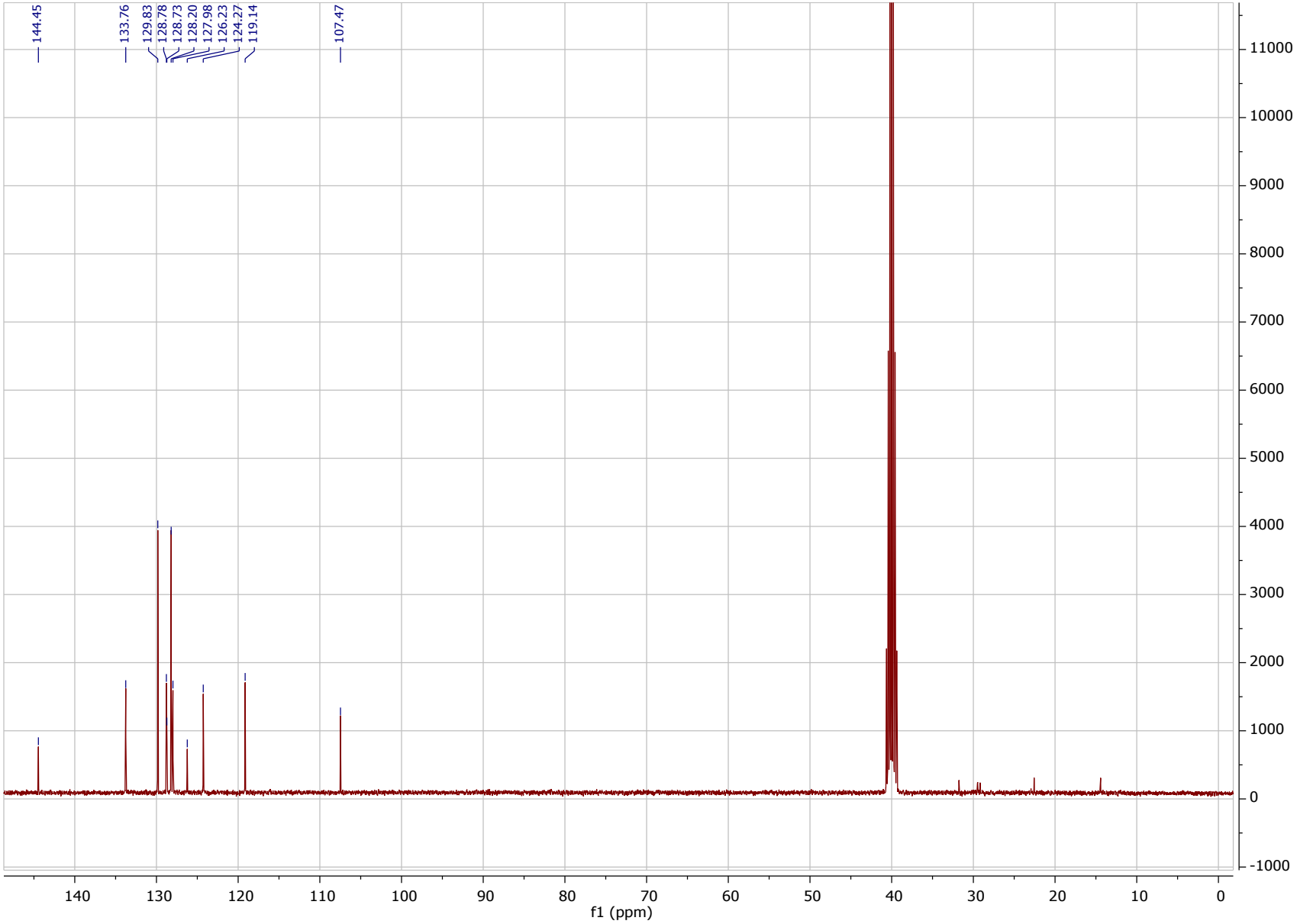
^{13}C NMR of 6-chloro-3-phenylimidazo[1,2-a]pyridine (6a):



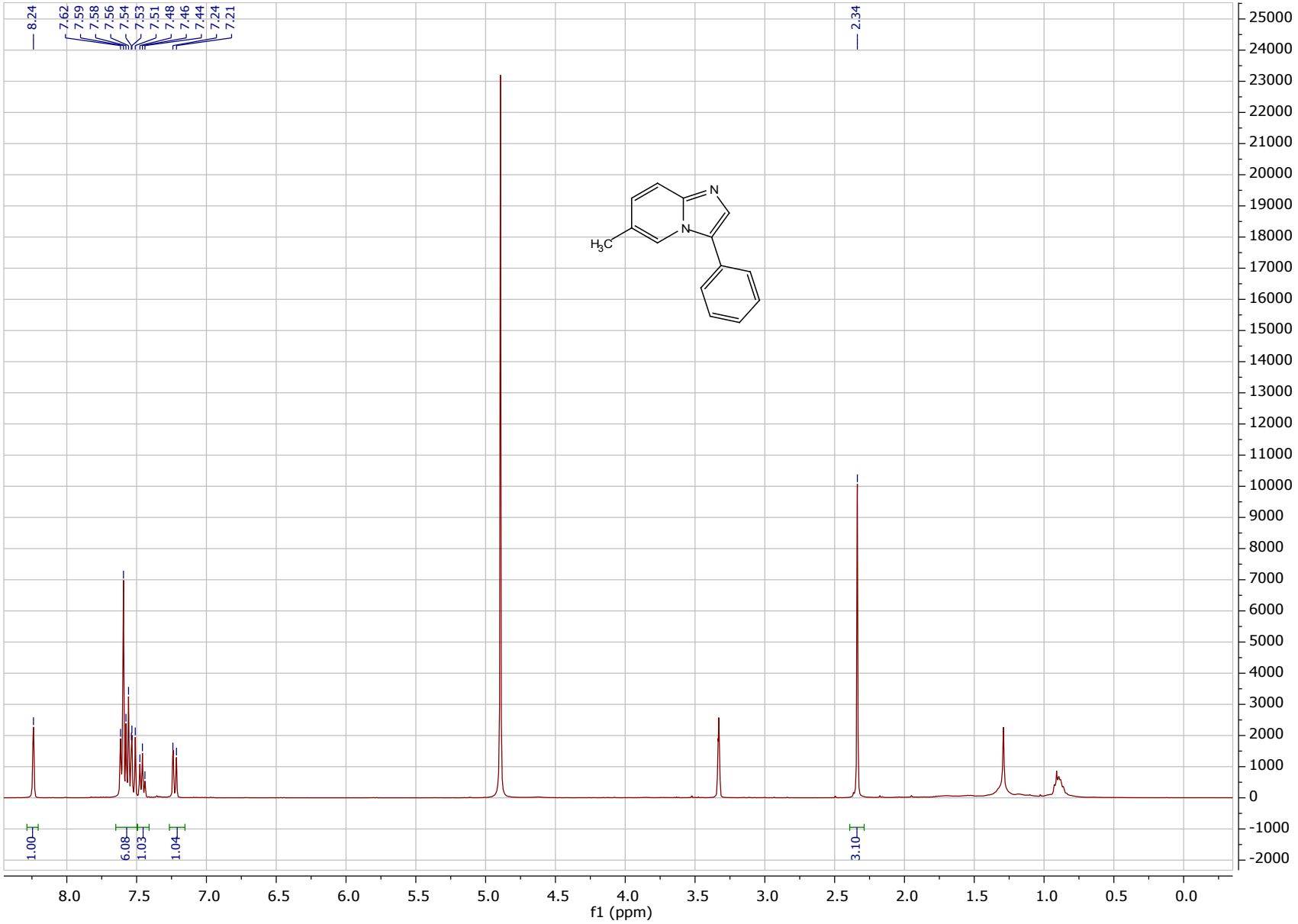
^{1}H NMR of 6-bromo-3-phenylimidazo[1,2-a]pyridine (6b):



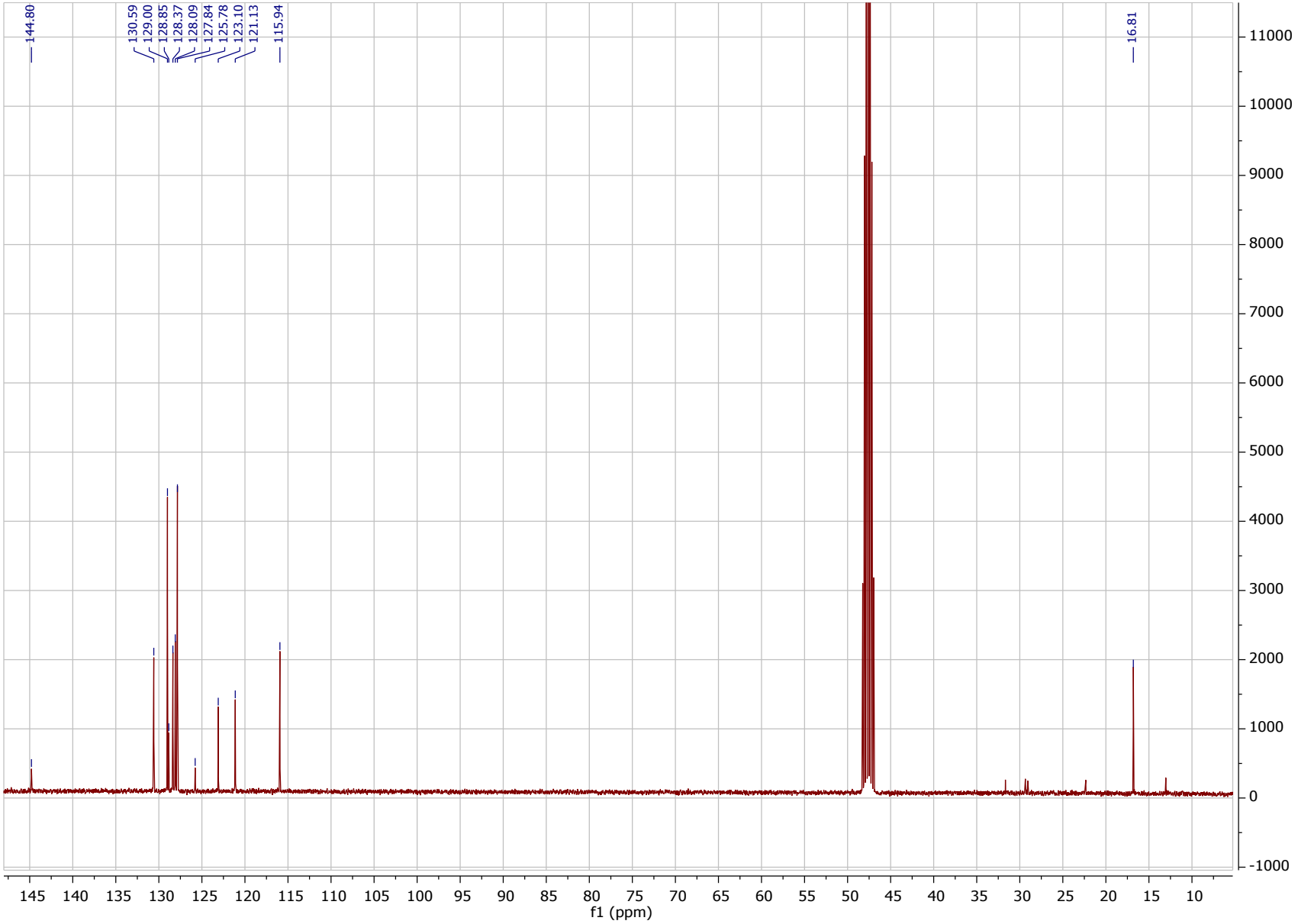
^{13}C NMR of 6-bromo-3-phenylimidazo[1,2-a]pyridine (6b):



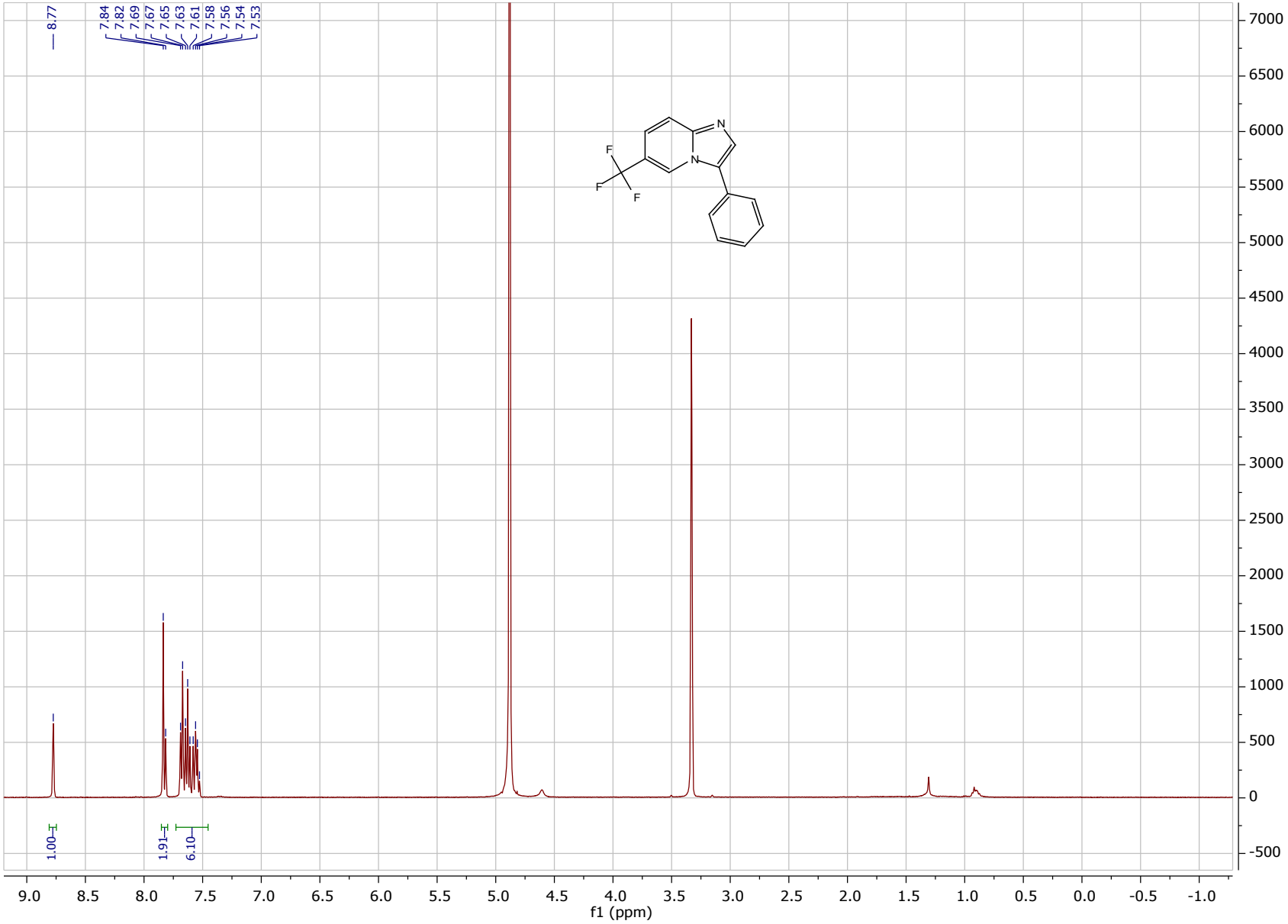
[1]H NMR of 6-methyl-3-phenylimidazo[1,2-a]pyridine (6c):



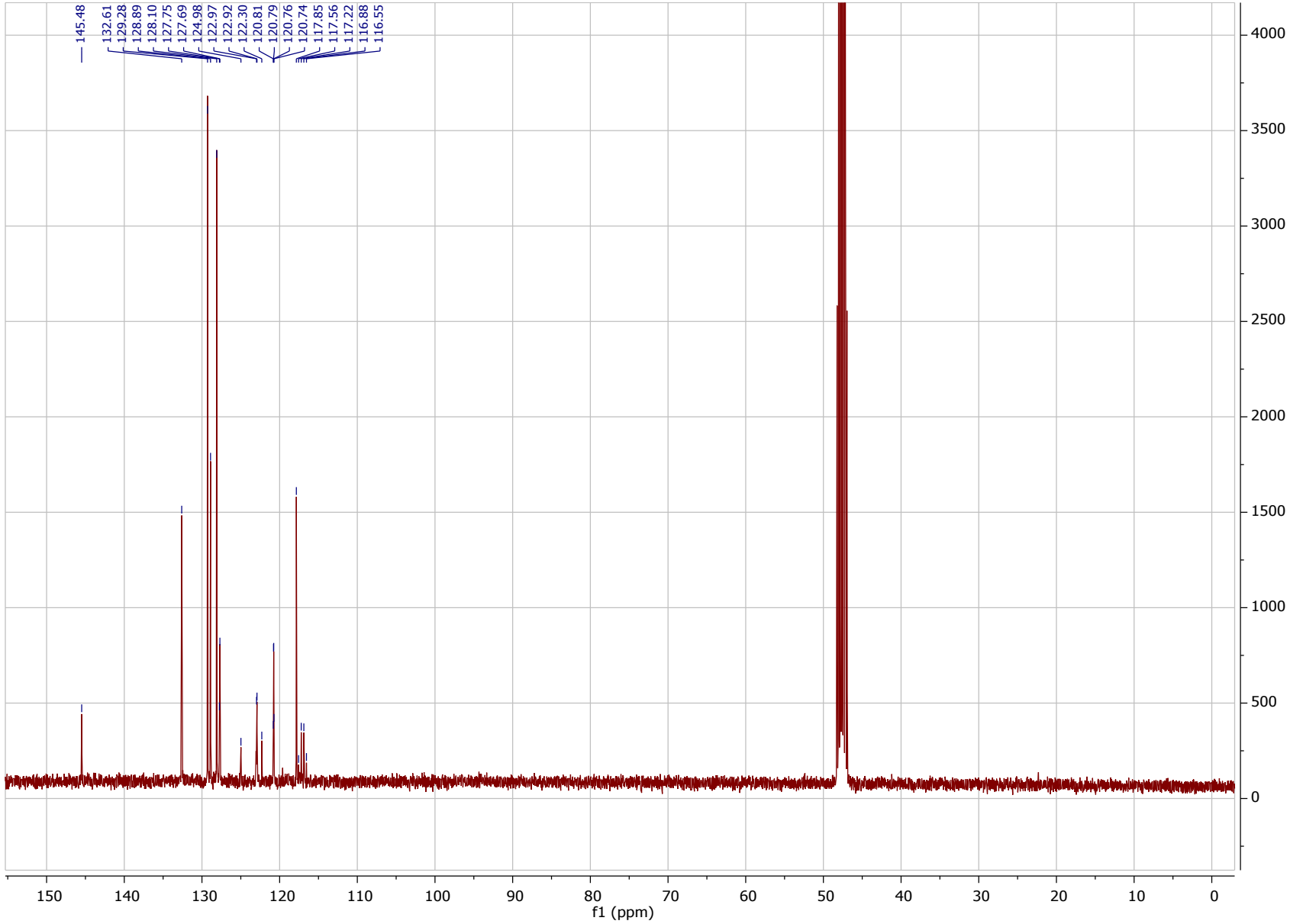
^{13}C NMR of 6-methyl-3-phenylimidazo[1,2-a]pyridine (6c):



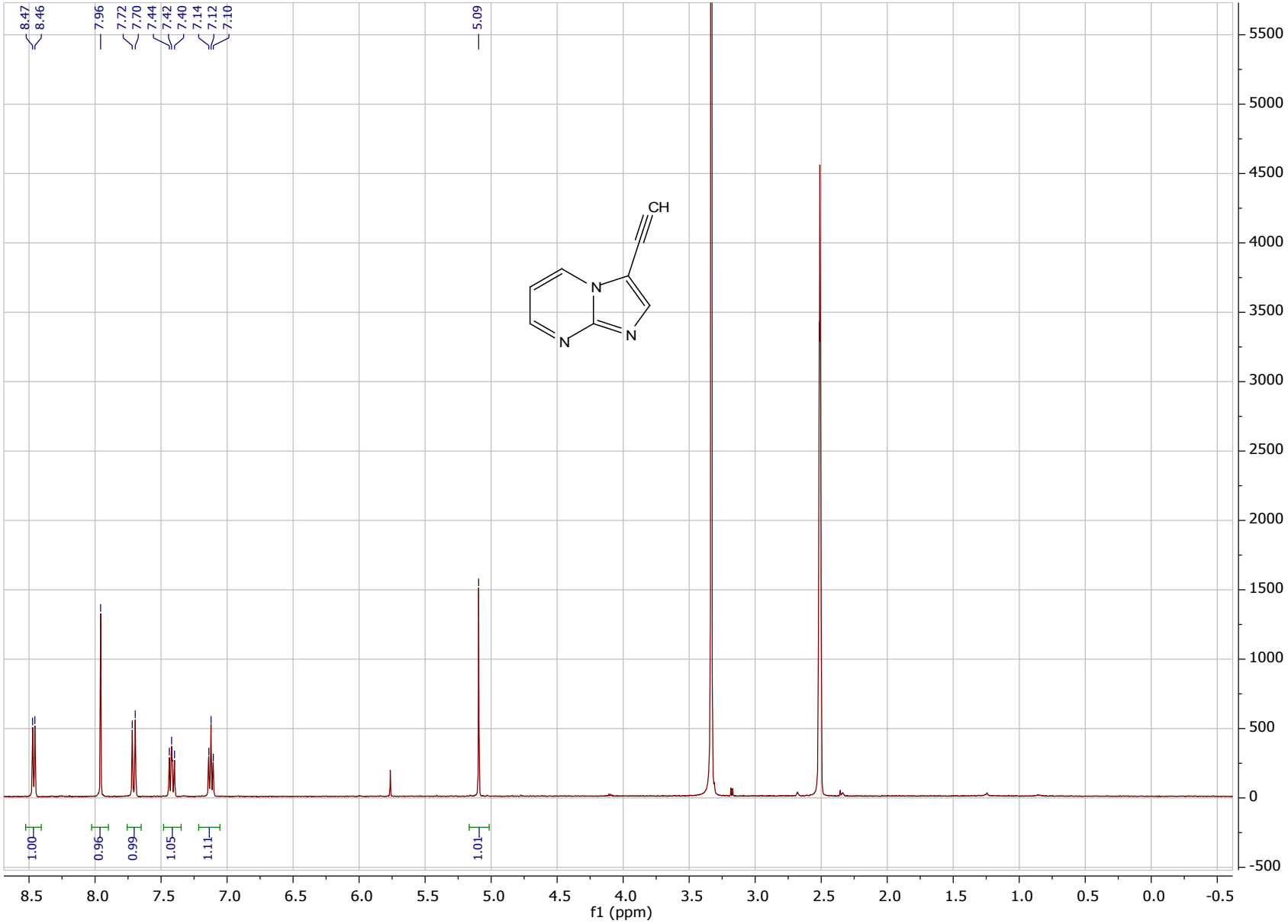
^{1}H NMR of 3-phenyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine (6d):



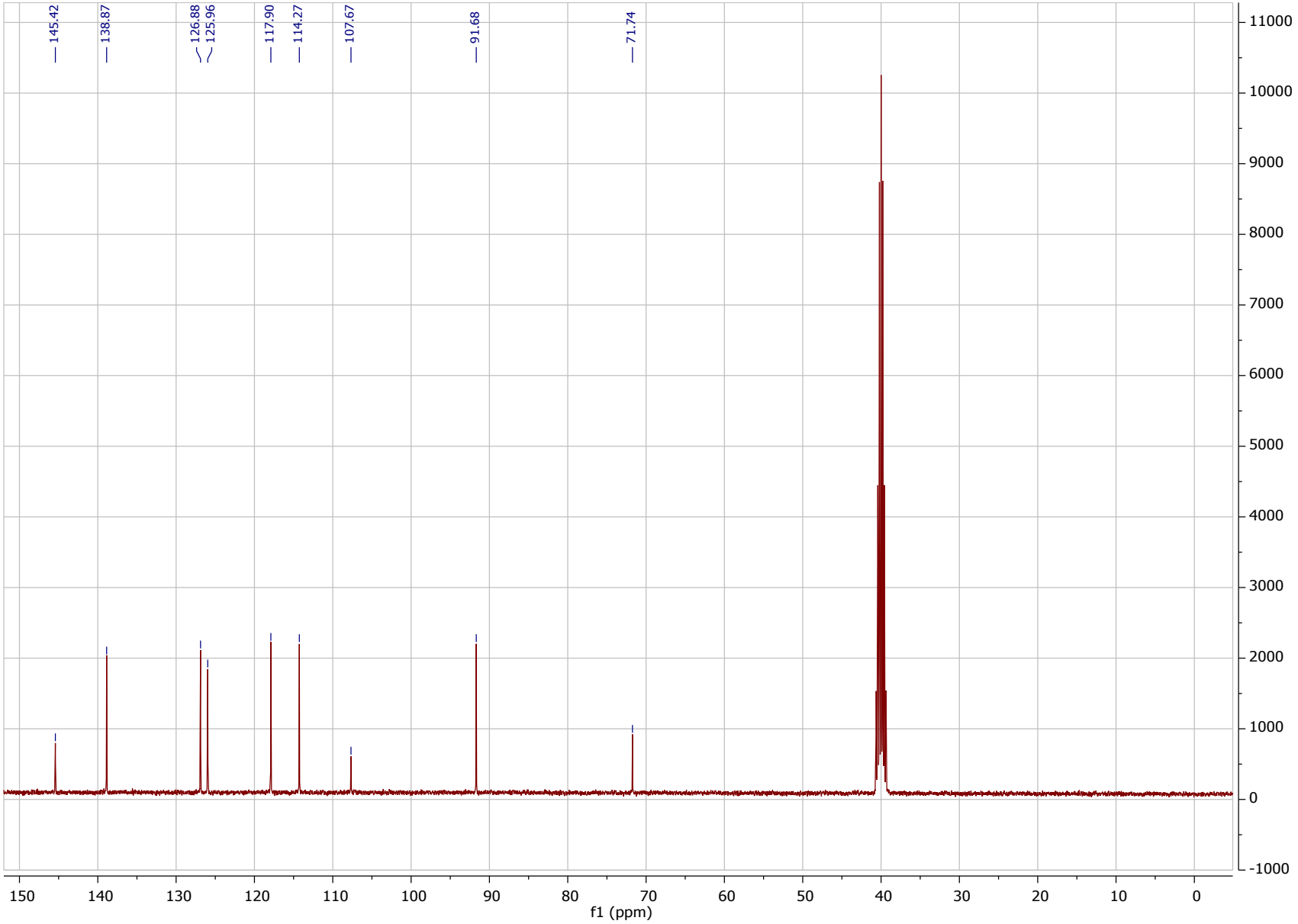
^{13}C NMR of 3-phenyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine (6d):



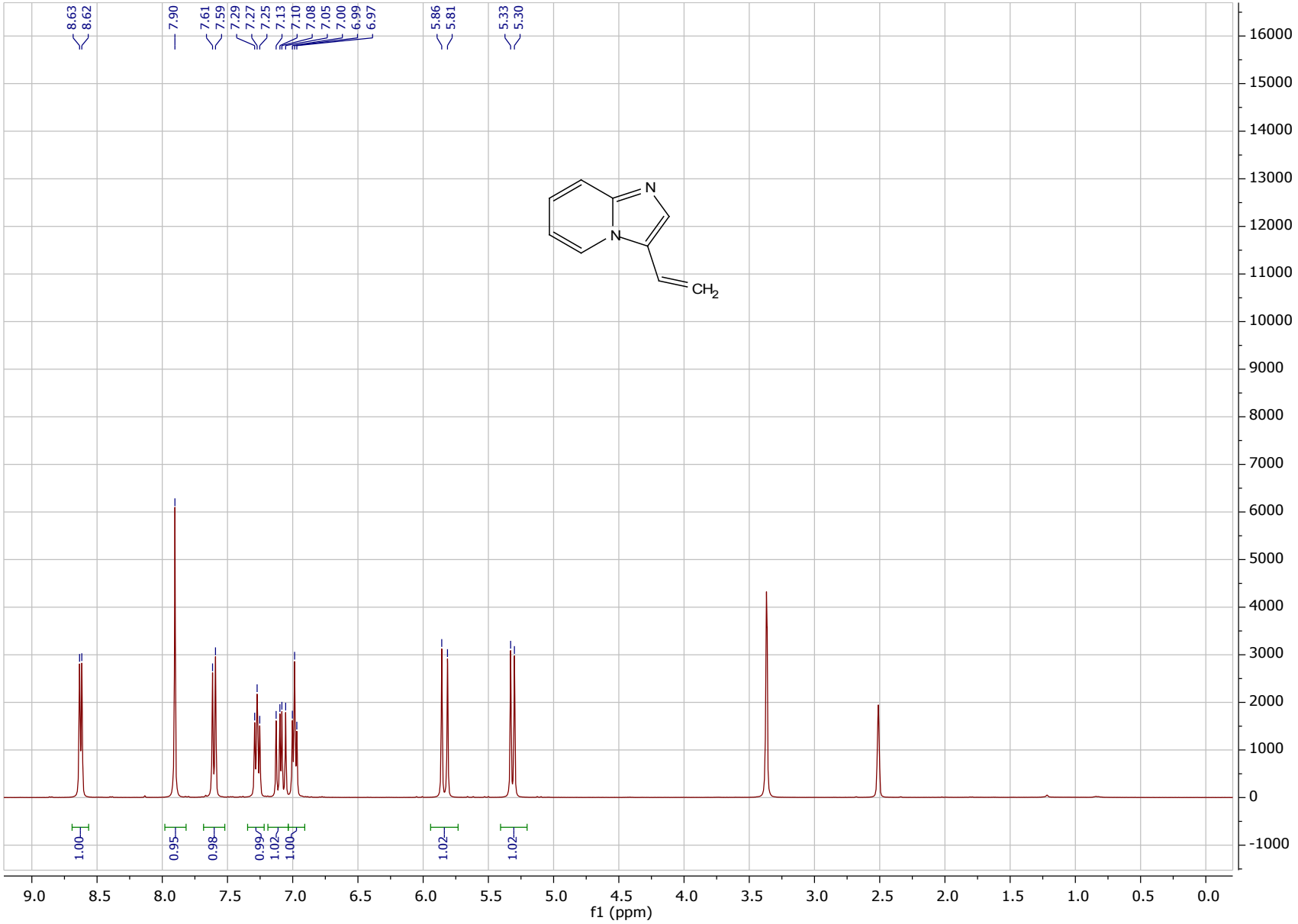
^{1}H NMR of 3-ethynylimidazo[1,2-a]pyridine (9a):



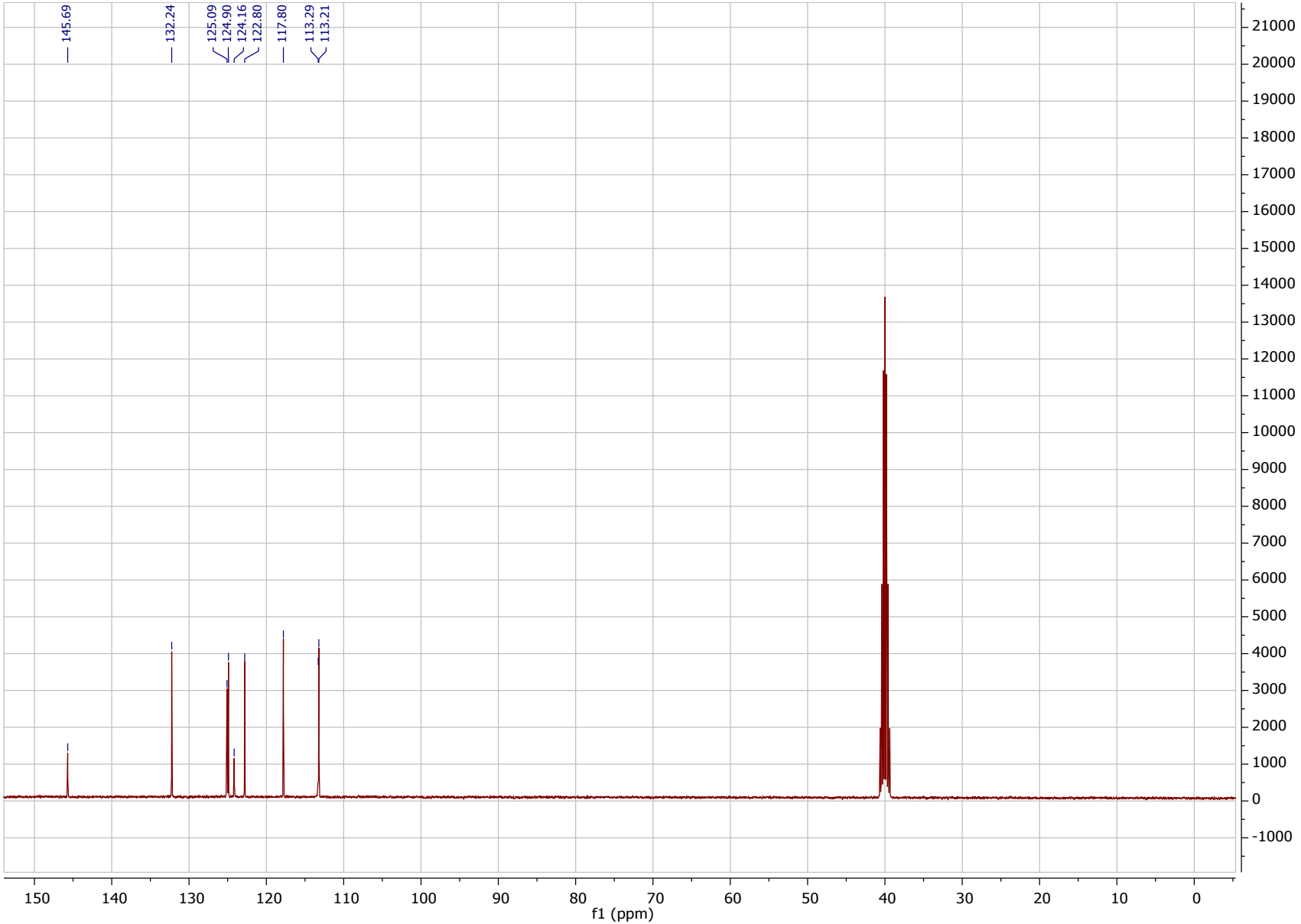
^{13}C NMR of 3-ethynylimidazo[1,2-a]pyridine (9a):



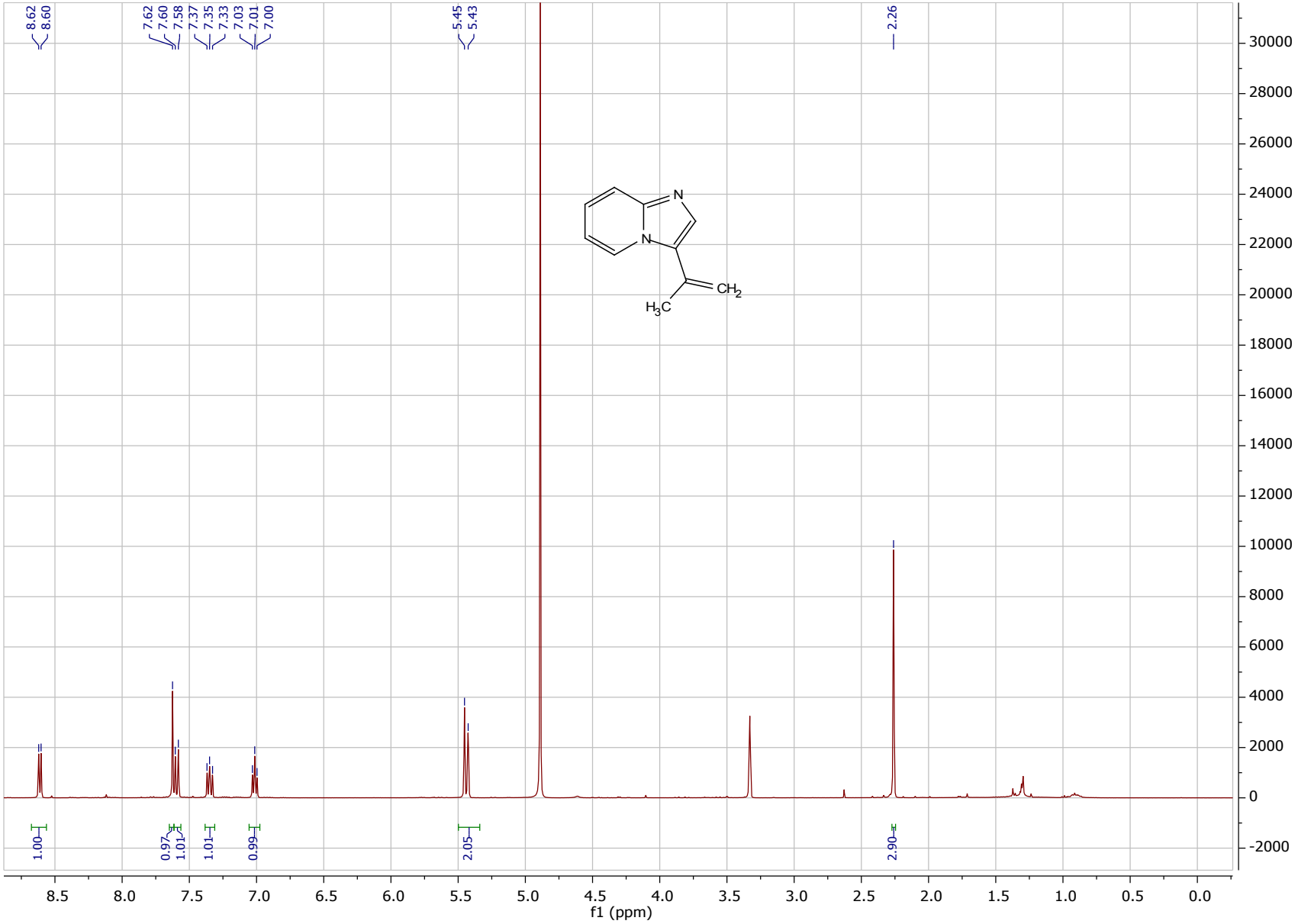
^{1}H NMR of 3-vinylimidazo[1,2-a]pyridine (9b):



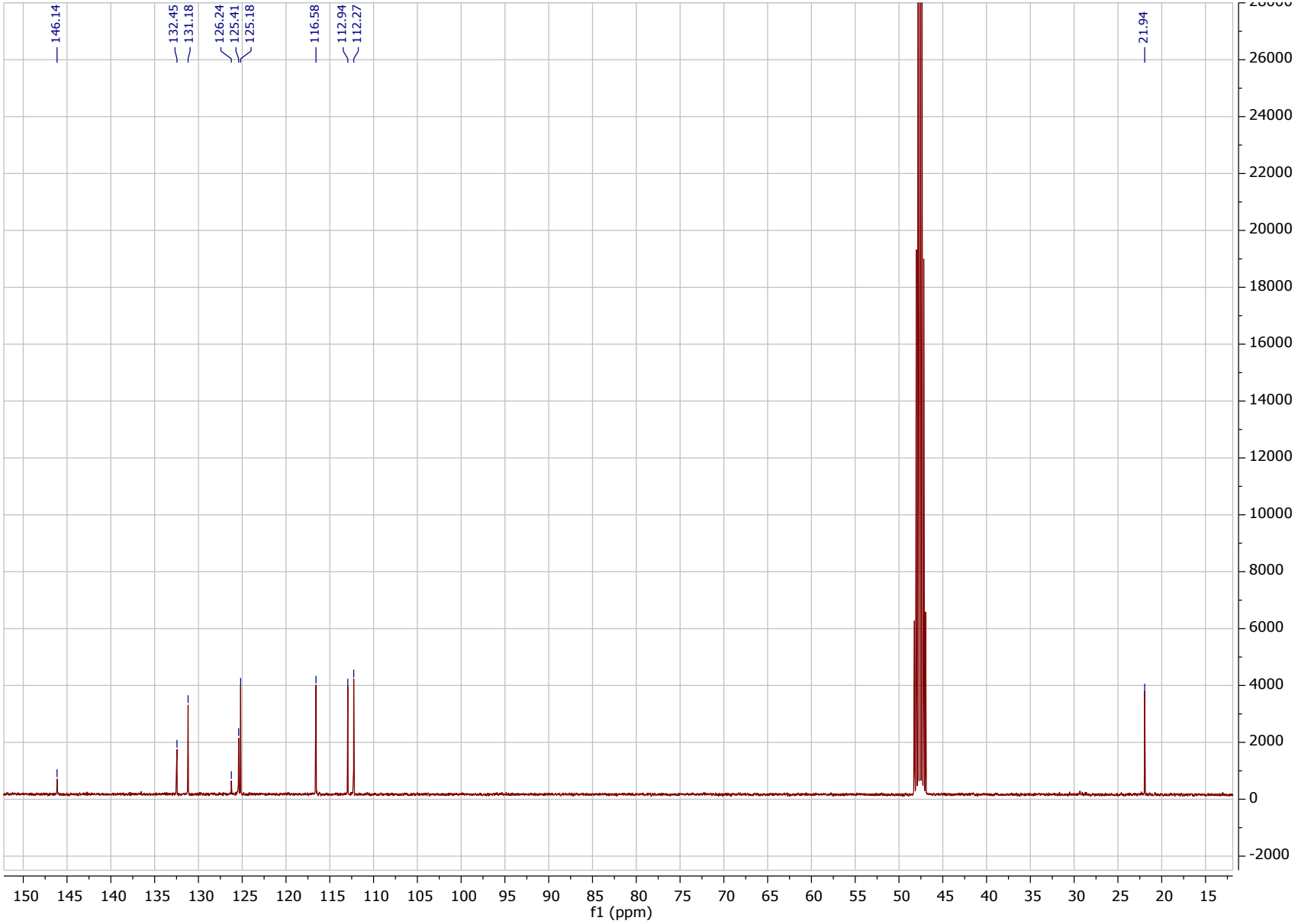
^{13}C NMR of 3-vinylimidazo[1,2-a]pyridine (9b):



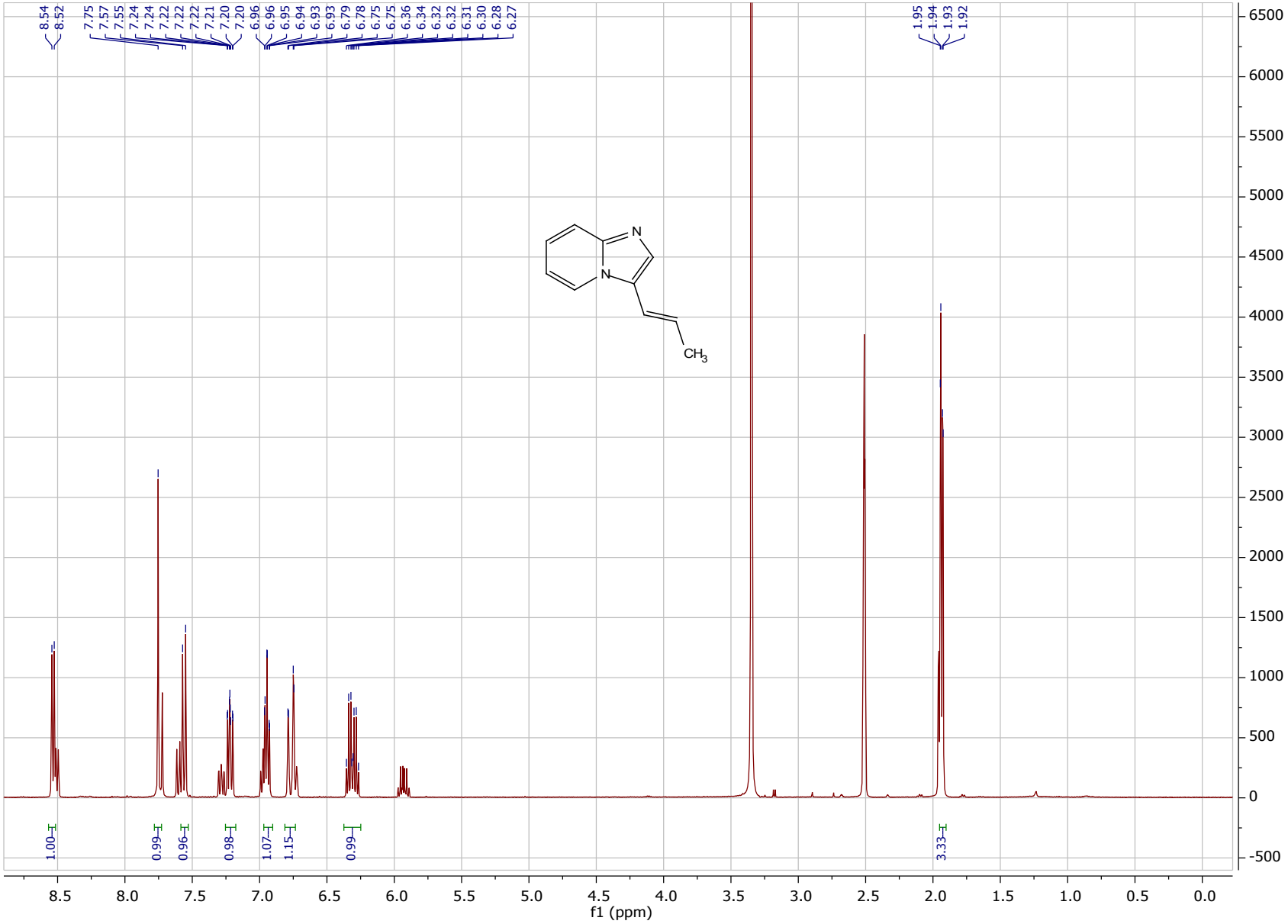
^{1}H NMR of 3-(prop-1-en-2-yl)imidazo[1,2-a]pyridine (9c):



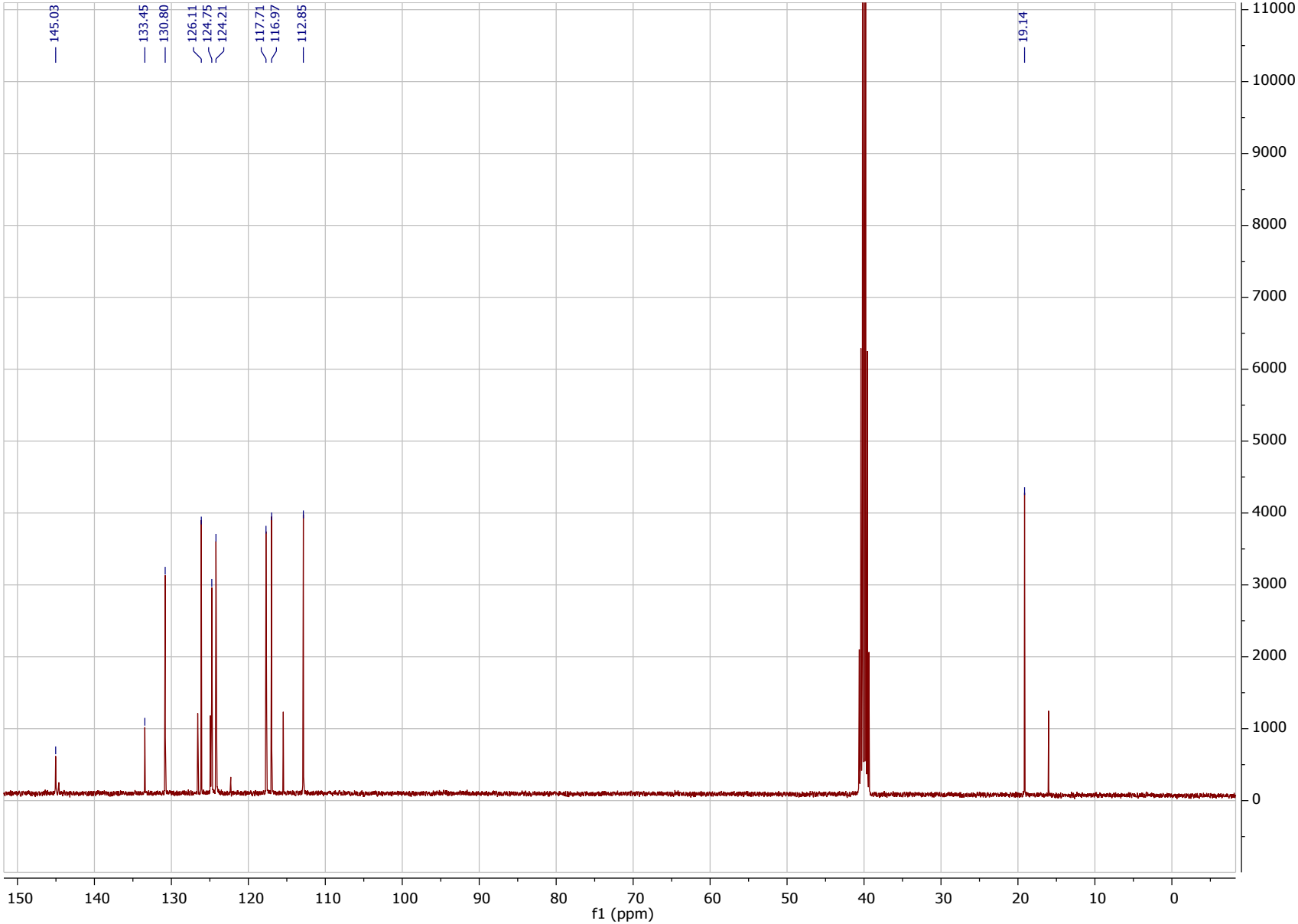
^{13}C NMR of 3-(prop-1-en-2-yl)imidazo[1,2-a]pyridine (9c):



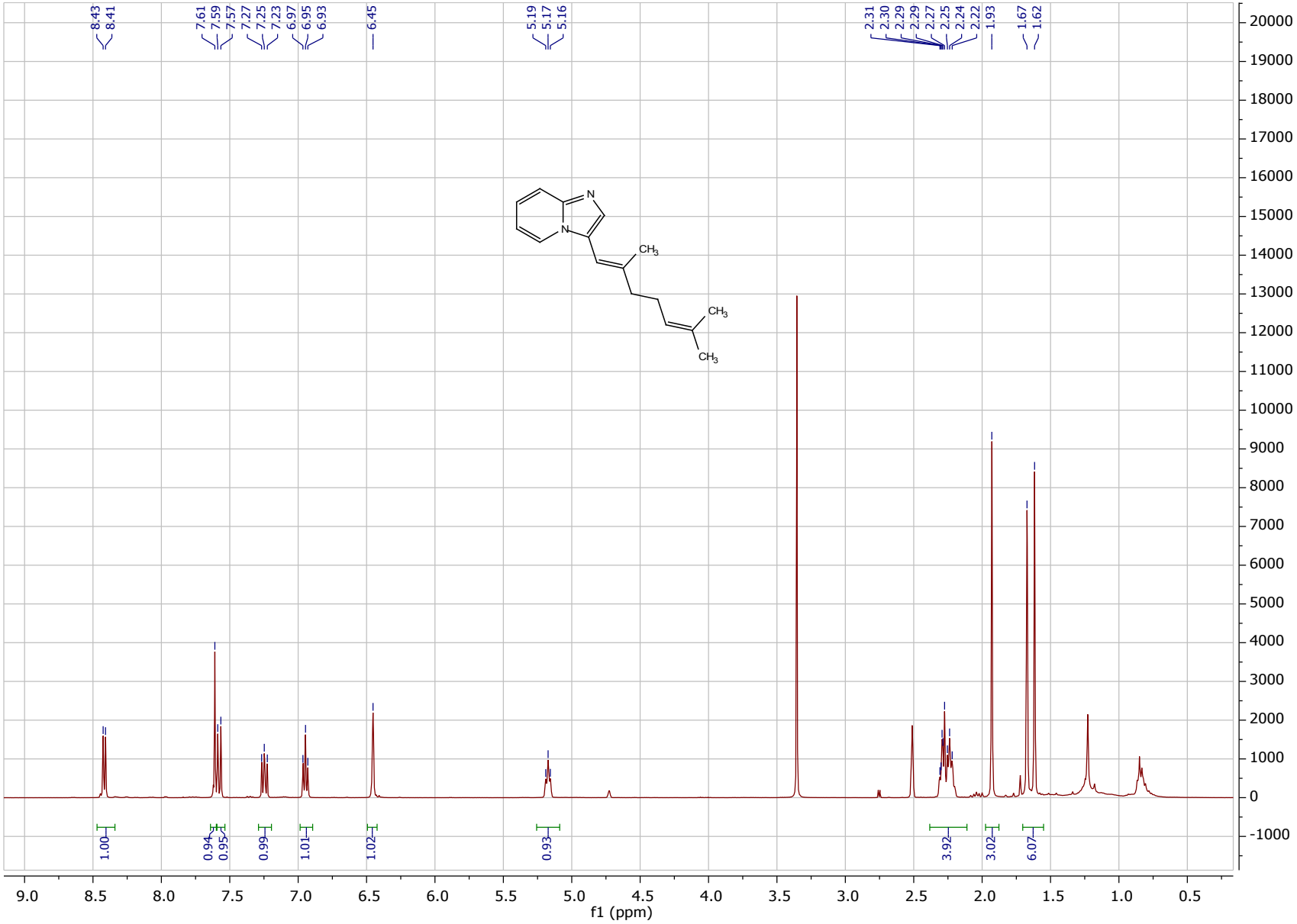
^{1}H NMR of (*E*)-3-(prop-1-en-1-yl)imidazo[1,2-a]pyridine (9d):



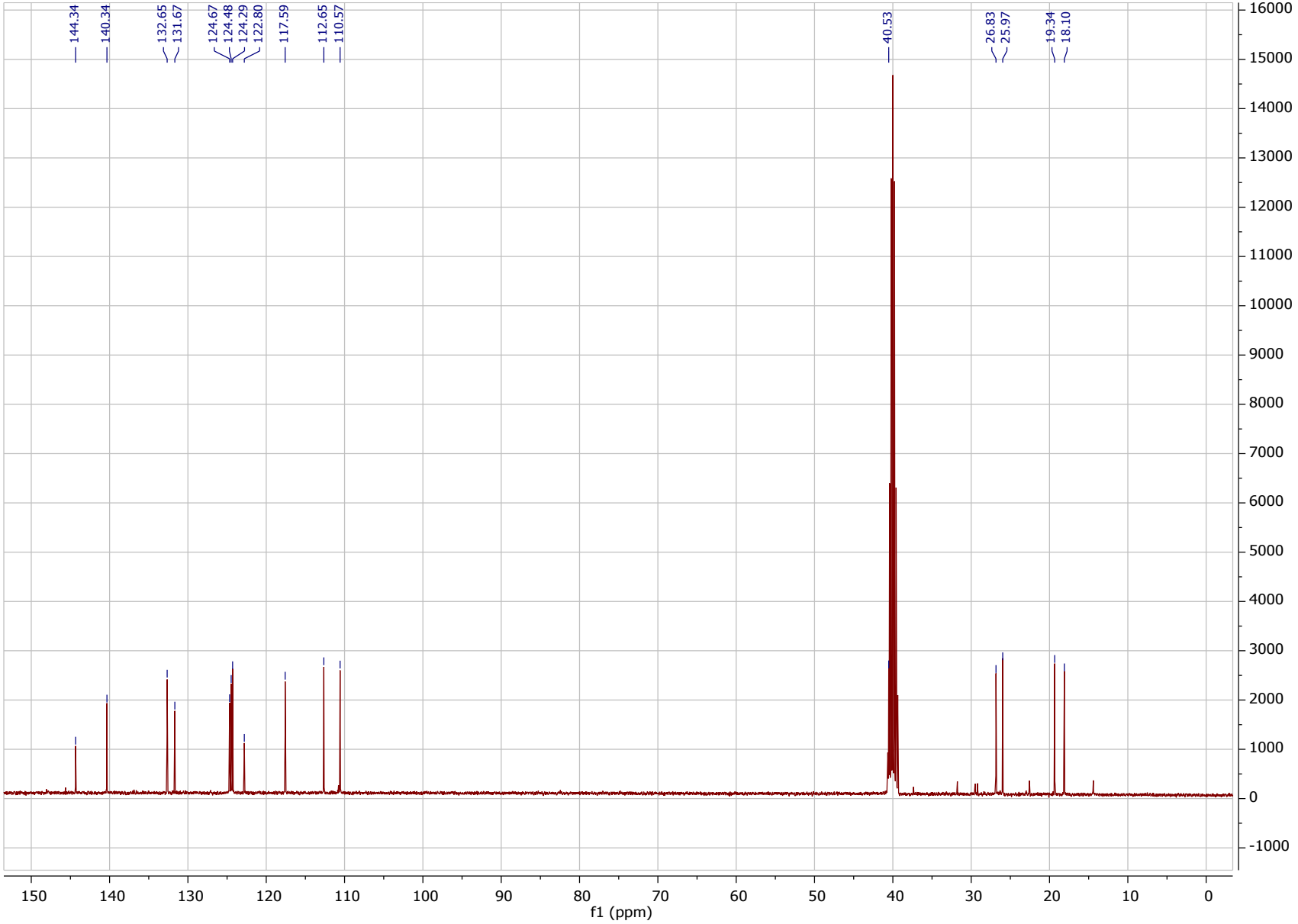
^{13}C NMR of (*E*)-3-(prop-1-en-1-yl)imidazo[1,2-a]pyridine (9d):



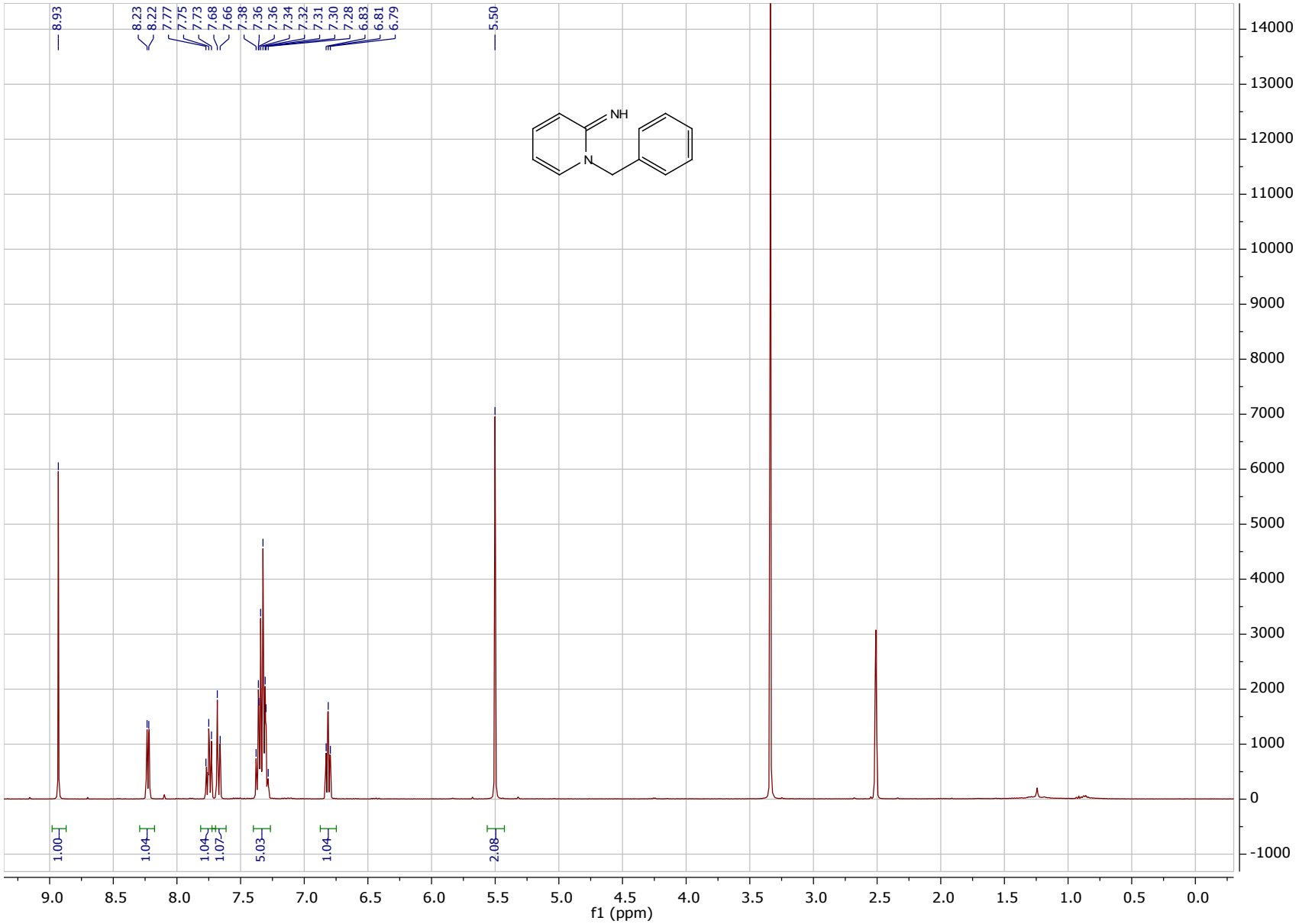
[1]H NMR of (E)-3-(2,6-dimethylhepta-1,5-dien-1-yl)imidazo[1,2-a]pyridine (9e):



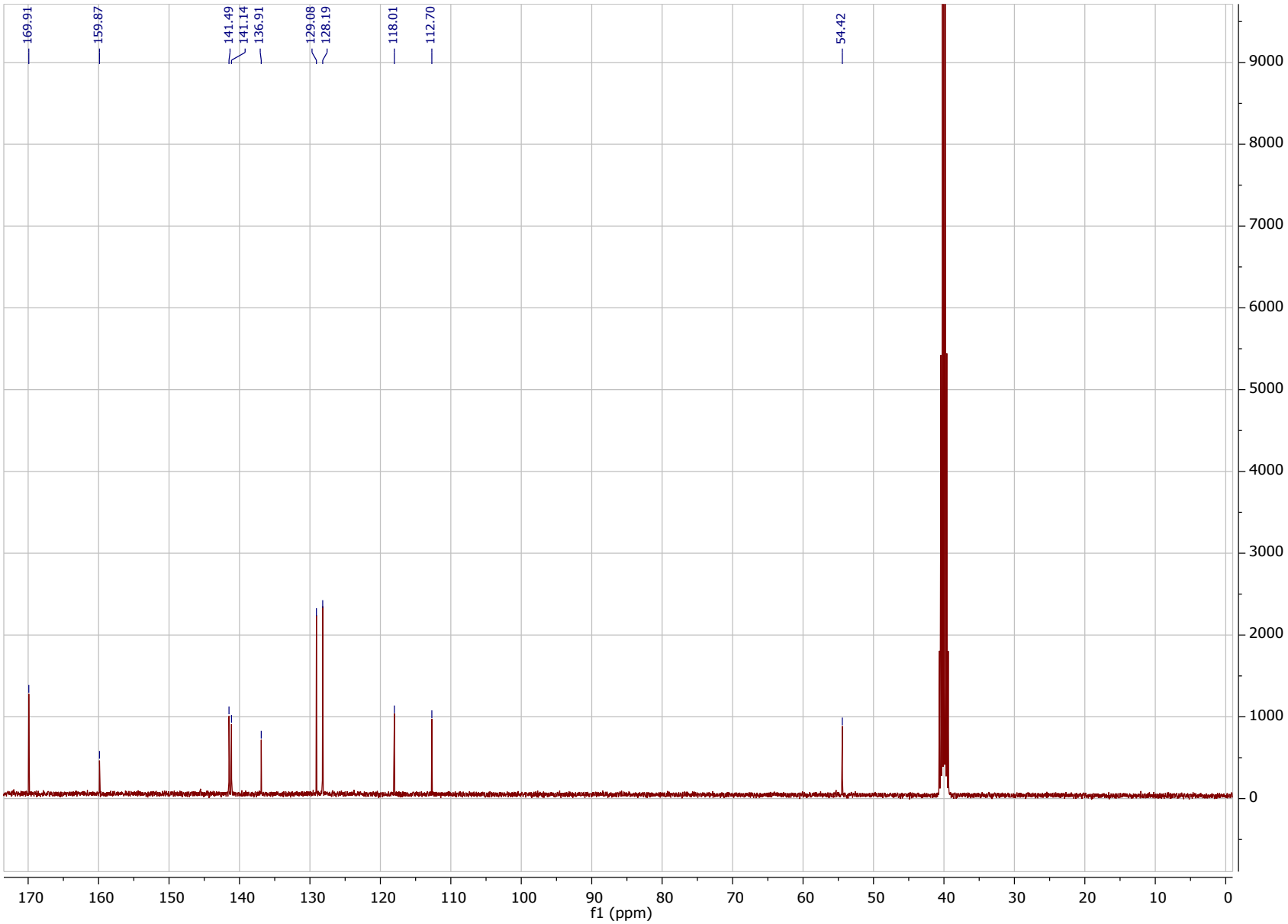
^{13}C NMR of (E)-3-(2,6-dimethylhepta-1,5-dien-1-yl)imidazo[1,2-a]pyridine (9e):



^{1}H NMR of 1-benzylpyridin-2(1*H*)-imine (7):



^{13}C NMR of 1-benzylpyridin-2(1*H*)-imine (7):



X-ray crystallography data for 1-benzyl-2-(((dimethylamino)methylene)amino)pyridin-1-ium bromide (2a):

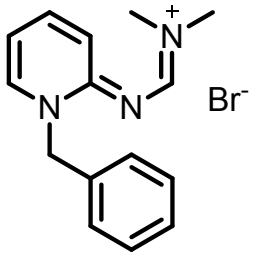
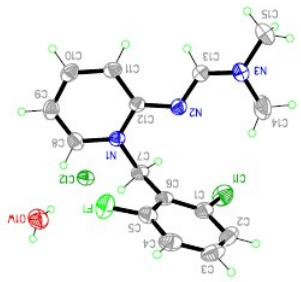


Table. Crystal data and structure refinement for Compound **2a**.

CCDC Identification code	1922120	
Empirical formula	C_{15} H_{20} Br N_3 O	
Formula weight	338.25	
Temperature	299(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 18.110(3) Å	α= 90°.
	b = 10.9556(18) Å	β= 109.622(5)°.
	c = 17.217(3) Å	γ = 90°.
Volume	3217.5(10) $Å^3$	
Z	8	
Density (calculated)	1.397 Mg/m^3	
Absorption coefficient	2.555 mm^{-1}	
F(000)	1392	
Crystal size	0.280 x 0.200 x 0.200 mm^3	
Crystal color / habit	colorless / block	
Theta range for data collection	3.030 to 25.462°.	

Index ranges	-21<=h<=21, -13<=k<=13, -20<=l<=20
Reflections collected	39434
Independent reflections	2977 [R(int) = 0.0718]
Completeness to theta = 25.242°	99.7 %
Absorption correction	multi-scan / sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2977 / 2 / 190
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0972
R indices (all data)	R1 = 0.0573, wR2 = 0.1101
Extinction coefficient	n/a
Largest diff. peak and hole	0.708 and -0.455 e.$Å^{-3}$

X-ray crystallography data for (E)-N-(((1-(2-chloro-6-fluorobenzyl)pyridin-2(1H)-ylidene)amino)methylene)-N-methylmethanaminium chloride (2o):



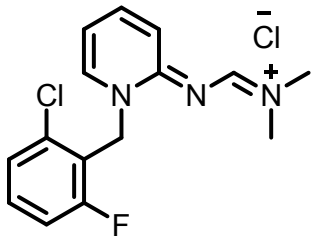
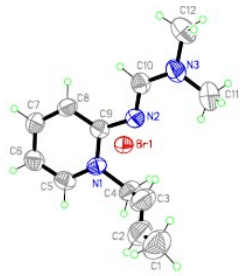


Table. Crystal data and structure refinement for compound **2o**.

CCDC Identification code	1920096	
Empirical formula	C_{15} H_{18} C_{l2} F N_3 O	
Formula weight	346.22	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4862(9) Å	α= 117.555(3)°.
	b = 10.3569(12) Å	β= 93.859(4)°.
	c = 10.6667(12) Å	γ = 95.336(4)°.
Volume	821.07(16) $Å^3$	
Z	2	
Density (calculated)	1.400 Mg/m^3	
Absorption coefficient	0.410 mm^{-1}	
F(000)	360	
Crystal size	0.320 x 0.200 x 0.140 mm^3	
Crystal color / habit	pale yellow / block	

Theta range for data collection	3.050 to 25.752°.
Index ranges	-10<=h<=10, -12<=k<=12, -13<=l<=13
Reflections collected	34369
Independent reflections	3136 [R(int) = 0.0343]
Completeness to theta = 25.242°	99.8 %
Absorption correction	multi-scan / sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3136 / 0 / 210
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.1006
R indices (all data)	R1 = 0.0446, wR2 = 0.1076
Extinction coefficient	0.050(5)
Largest diff. peak and hole	0.411 and -0.417 e.$Å^{-3}$

X-ray crystallography data for N-(((E)-(1-((E)-but-2-en-1-yl)pyridin-2(1H)-ylidene)amino)methylene)-N-methylmethanaminium (8d):



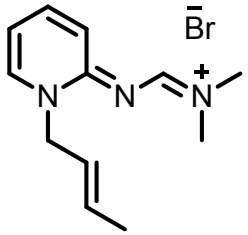


Table. Crystal data and structure refinement for compound **9d**.

CCDC Identification code	1910925	
Empirical formula	C_{12} H_{18} Br N_3	
Formula weight	284.20	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.2000(9) Å	α= 90°.
	b = 18.4716(17) Å	β= 96.769(3)°.
	c = 7.3285(7) Å	γ = 90°.
Volume	1371.1(2) $Å^3$	
Z	4	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	2.978 mm^{-1}	
F(000)	584	
Crystal size	0.350 x 0.150 x 0.120 mm^3	
Crystal color / habit	colorless / block	
Theta range for data collection	2.985 to 25.404°.	

Index ranges	-12<=h<=12, -22<=k<=22, -8<=l<=8
Reflections collected	49382
Independent reflections	2515 [R(int) = 0.0516]
Completeness to theta = 25.000°	99.8 %
Absorption correction	multi-scan / sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2515 / 0 / 149
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.1063
R indices (all data)	R1 = 0.0467, wR2 = 0.1102
Extinction coefficient	0.0147(14)
Largest diff. peak and hole	0.421 and -0.355 e.$Å^{-3}$

X-ray crystallography data for 3-(2-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3d):

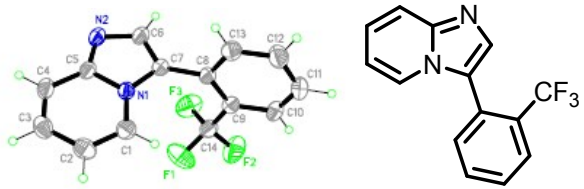


Table. Crystal data and structure refinement for **3d**.

CCDC Identification code	1920095	
Empirical formula	$C_{14}\ H_9\ F_3\ N_2$	
Formula weight	262.23	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.7552(7) Å	α= 90°.
	b = 9.5594(8) Å	β= 91.316(2)°.
	c = 12.4421(10) Å	γ = 90°.
Volume	1159.97(16) $Å^3$	
Z	4	
Density (calculated)	1.502 Mg/m^3	
Absorption coefficient	0.124 mm^{-1}	
F(000)	536	
Crystal size	0.340 x 0.300 x 0.280 mm^3	
Crystal color / habit	colorless / block	
Theta range for data collection	2.984 to 25.729°.	
Index ranges	-11<=h<=11, -11<=k<=11, -15<=l<=15	
Reflections collected	42264	

Independent reflections	2203 [R(int) = 0.0287]
Completeness to theta = 25.242°	99.8 %
Absorption correction	multi-scan / sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2203 / 0 / 173
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0553, wR2 = 0.1425
R indices (all data)	R1 = 0.0594, wR2 = 0.1469
Extinction coefficient	0.215(12)
Largest diff. peak and hole	0.425 and -0.286 e.$Å^{-3}$

X-ray crystallography data for 3-(4-bromophenyl)imidazo[1,2-a]pyridine (3i):

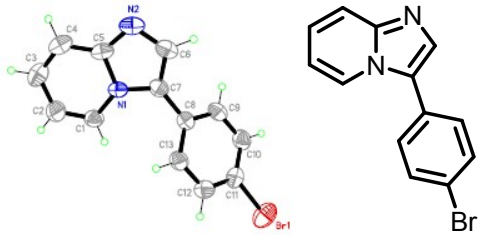


Table. Crystal data and structure refinement for **3i**.

CCDC Identification code	1920094	
Empirical formula	C_{13} H_9 Br N_2	
Formula weight	273.13	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 22.620(5) Å	α= 90°.
	b = 3.9660(8) Å	β= 90°.
	c = 12.201(3) Å	γ = 90°.
Volume	1094.6(4) $Å^3$	
Z	4	
Density (calculated)	1.657 Mg/m^3	
Absorption coefficient	3.725 mm^{-1}	
F(000)	544	
Crystal size	0.300 x 0.120 x 0.100 mm^3	
Crystal color /habit	colorless / block	
Theta range for data collection	3.339 to 25.303°.	

Index ranges	-27<=h<=27, -4<=k<=4, -14<=l<=14
Reflections collected	16352
Independent reflections	1992 [R(int) = 0.0362]
Completeness to theta = 25.242°	99.8 %
Absorption correction	multi-scan / sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1992 / 1 / 147
Goodness-of-fit on F^2	0.957
Final R indices [I>2sigma(I)]	R1 = 0.0266, wR2 = 0.0656
R indices (all data)	R1 = 0.0338, wR2 = 0.0693
Absolute structure parameter	0.187(16)
Extinction coefficient	0.0190(18)
Largest diff. peak and hole	0.338 and -0.433 e.$Å^{-3}$

X-ray crystallography data for (E)-3-(prop-1-en-1-yl)imidazo[1,2-a]pyridine (9d):

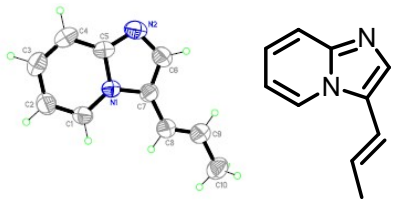


Table. Crystal data and structure refinement for **9d**.

CCDC Identification code	1910928	
Empirical formula	$C_{10}\ H_{10}\ N_2$	
Formula weight	158.20	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.4588(12) Å	α= 106.039(10)°.
	b = 8.1981(17) Å	β= 95.947(11)°.
	c = 8.3521(17) Å	γ = 92.951(10)°.
Volume	421.25(15) $Å^3$	
Z	2	
Density (calculated)	1.247 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	168	
Crystal size	0.220 x 0.200 x 0.120 mm^3	
Crystal color / habit	colorless / block	
Theta range for data collection	3.084 to 25.422°.	
Index ranges	-7<=h<=7, -9<=k<=9, -10<=l<=10	

Reflections collected	7413
Independent reflections	1538 [R(int) = 0.0342]
Completeness to theta = 25.000°	99.8 %
Absorption correction	multi-scan / sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1538 / 0 / 111
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1005
R indices (all data)	R1 = 0.0582, wR2 = 0.1109
Extinction coefficient	0.39(3)
Largest diff. peak and hole	0.148 and -0.173 e.$Å^{-3}$