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Supporting Information

A heavy metal- and oxidant-free one-pot pyridine synthesis based on a Lewis acid-catalyzed four-component reaction

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Experimental Section

General methods

All melting points reported in this work were measured in open capillaries. Flash chromatography was performed on silica gel (230-400 mesh). The ^{1}H and ^{13}C NMR spectra were measured at 250 and 63 MHz, respectively, using a Bruker 250 MHz (Avance) instrument in $CDCl_3$ using residual non-deuterated solvent as internal standard. Chemical shifts are reported as δ values (ppm). All one- and two-dimensional NMR spectra were obtained using standard Bruker software throughout. IR spectra were recorded on a Perkin-Elmer FT-IR Paragon1000 spectrometer FT-IR instrument in film form, prepared by evaporation of a few drops of sample solution over a sodium chloride window. Elemental analyses were obtained by the CAI de Microanálisis, Universidad Complutense, using a Leco CHN 932 Elemental Analyzer.

Synthesis of pyridine derivatives. General procedure

To a stirred solution of 2-furylmethylamine (1 equiv, 3 mmol) and the suitable 1,3-dicarbonyl compound **1** (1 equiv, 3 mmol) in ethanol (3 mL) was added $InCl_3$ (10% mol) and stirring was continued for 30 min at room temperature. Then the reaction mixture was cooled to 5 ^{o}C. The suitable unsaturated aldehyde **3** (1.2 equiv, 3.6 mmol) was then added and stirring was continued under the same conditions for 2 hrs. After completion of the reaction (checked by NMR), the solvent was evaporated under reduced pressure under 25 ^{o}C. The crude was then subjected to microwave irradiation for 30 min with a power level of 200 W and a temperature of 100 ^{o}C. After completion of the reaction (checked by TLC), the resulting pyridine derivatives **4** & **9** were purified by neutral alumina column chromatography using petroleum ether-ethyl acetate mixture (12:1 to 5:1, v/v) as eluent to give pure compounds (**4a-4l** & **9a – 9i**). Characterization data for all final compounds follow.

Ethyl 2-methylpyridine-3-carboxylate (4a)[1]

Isolated as an oil (95%). ν_{max} (NaCl) 2983, 1724, 1585, 1441, 1278, 1254, 1084 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 1.8, 4.8 Hz, 1H), 8.20 (dd, *J* = 1.8, 7.9 Hz, 1H), 7.22 (dd, *J* = 4.8, 7.9 Hz, 1H), 4.39 (q, *J* = 7.3 Hz, 2H), 2.85 (s, 3H), 1.41 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 167.0, 160.2, 152.1, 138.8, 126.1, 121.3, 61.7, 25.5, 14.7. Anal. Calcd for $C_9H_{11}NO_2$: C 65.44, H 6.71, N 8.48. Found: C 65.18, H 6.81, N 8.29.

Ethyl 4-ethyl-2,5-dimethylpyridine-3-carboxylate (4b)

Isolated as an oil (85%); υ_{max} (NaCl) 2977, 1727, 1459, 1385, 1158 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 8.28 (s, 1H), 4.43 (q, *J* = 7.5 Hz, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 2.49 (s, 3H), 2.29 (s, 3H), 1.41 (t, *J* = 7.5 Hz, 3H), 1.17 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 169.2, 152.3, 150.5, 148.0, 129.2, 128.6, 61.3, 23.9, 22.4, 15.6, 14.1, 13.7. Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found C, 69.38; H, 8.37; N, 6.97.

Ethyl 2-methyl-4-phenylpyridine-3-carboxylate (4c)

Isolated as an oil (88%); υ_{max} (NaCl) 2926, 2360, 1578, 1446, 1264 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.2 Hz, 1H), 7.52 – 7.34 (m, 5H), 7.19 (dd, *J* = 5.2, 0.4 Hz, 1H), 4.15 (q, *J* = 7.5 Hz, 2H), 2.67 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 168.6, 155.5, 149.6, 147.9, 138.4, 128.5, 128.4, 127.8, 121.5, 61.3, 22.8, 13.6. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found 74.43; H, 6.35; N, 5.76.

[1] Kao, B.-C.; Doshi, H.; Reyes-Rivera, H.; Titus, D. D.; Yin, M. L.; Dalton, D. R. *J. Heterocycl. Chem*. **1991**, *28*, 1315.

Ethyl 2-(3-butenyl)pyridine-3-carboxylate (4d)

Isolated as an oil (86%); υ_{max} (NaCl) 2981, 1725, 1584, 1569, 1441, 1277, 1253 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.67 (dd, *J* = 1.9, 4.8 Hz, 1H), 8.18 (dd, *J* = 1.9, 7.9 Hz, 1H), 7.23 (dd, *J* = 4.8, 7.9 Hz, 1H), 5.89-6.00 (m, 1H), 4.96-5.12 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.25-3.31 (m, 2H), 2.47-2.56 (m, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 162.8, 152.2, 138.9, 138.4, 126.3, 121.3, 115.3, 61.8, 36.8, 34.3, 14.7. Anal. Calcd. for $C_{12}H_{15}NO_2$: C 70.22, H 7.37, N 6.82. Found: C 69.93, H 7.44, N 6.72.

Ethyl 2-{[3-(ethoxycarbonyl)-5-methyl-2-pyridyl]methylthio}acetate (4e)

Isolated as an oil (75%); υ_{max} (NaCl) 2925, 2854, 1725, 1452, 1155 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.08 (s, 1H), 4.46 – 4.37 (m, 4H), 4.18 (q, *J* = 7.5 Hz, 2H), 3.32 (s, 2H), 2.39 (s, 3H), 1.44 (t, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.4, 166.2, 156.6, 151.9, 139.5, 131.7, 124.7, 61.6, 61.3, 37.0, 33.5, 17.9, 14.2, 14.1. Anal. Calcd. for $C_{14}H_{19}NO_4S$: C, 56.55; H, 6.44; N, 4.71. Found C, 56.42; H, 6.49; N, 4.85

***tert*-Butyl 2-but-3-enyl-5-methylpyridine-3-carboxylate (4f)**

Isolated as an oil (82%) ; υ_{max} (NaCl) 2927, 1719, 1454, 1302, 1252, 909 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 2.1 Hz, 1H), 5.99 – 5.86 (m, 1H), 5.12 – 4.97 (m, 2H), 3.23 - 3.17 (m, 2H), 2.53 - 2.44 (m, 2H), 2.36 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 166.5, 158.6, 151.7, 138.5, 138.1, 130.3, 127.1, 114.7, 82.1, 35.8, 34.0, 28.2, 17.8. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found C, 72.68; H, 8.76; N, 5.81.

***tert*-Butyl 2-but-3-enyl-4-methylpyridine-3-carboxylate (4g)**

Isolated as an oil (85%) υ_{max} (NaCl) 2926, 1722, 1449, 1126 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 5.1 Hz, 1H), 5.98 – 5.85 (m, 1H), 5.13 – 4.99 (m, 2H), 2.94 – 2.87 (m, 2H), 2.57 – 2.48 (m, 2H), 2.36 (s, 3H), 1.64 (s, 9H). ^{13}C NMR

(63 MHz, $CDCl_3$) δ 167.9, 157.2, 149.1, 144.0, 137.9, 130.9, 122.8, 114.9, 82.7, 35.5, 33.8, 28.1, 19.1. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found C, 72.97; H, 8.78; N, 5.50.

***tert*-Butyl 2-but-3-enyl-4-ethyl-5-methylpyridine-3-carboxylate (4h)**

Isolated as an oil (79%); υ_{max} (NaCl) 2925, 1726, 1448 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 8.31 (s, 1H), 5.93 (m, 1H), 5.09 (ddd, *J* = 17.1, 3.4, 1.6 Hz, 1H), 5.03 – 4.96 (m, 1H), 2.91 – 2.76 (m, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.57 – 2.43 (m, 2H), 2.30 (s, 3H), 1.64 (s, 9H), 1.21 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 168.5, 154.9, 150.3, 147.5, 138.0, 130.3, 128.8, 114.7, 82.6, 35.3, 33.8, 28.1, 23.8, 15.6, 13.7. Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found C, 73.97; H, 9.37; N, 5.27.

***tert*-Butyl 2-but-3-enyl-4-phenylpyridine-3-carboxylate (4i)**

Isolated as an oil (86%) υ_{max} (NaCl) 2925, 1723, 1450, 1069 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.1 Hz, 1H), 7.47 – 7.41 (m, 5H), 7.16 (d, *J* = 5.1 Hz, 1H), 6.06 – 5.83 (m, 1H), 5.12 (ddd, *J* = 17.1, 3.4, 1.6 Hz, 1H), 5.05 – 5.00 (m, 1H), 3.05 – 2.95 (m, 2H), 2.62 – 2.53 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 167.5, 158.0, 149.2, 147.7, 138.5, 137.9, 129.8, 128.4, 128.4, 128.3, 121.8, 114.9, 82.6, 35.5, 33.8, 27.7. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found C, 77.87; H, 7.60; N, 4.63.

Ethyl 2-[(3*E*,5*E*)hepta-3,5-dienyl]pyridine-3-carboxylate (4j)

Isolated as an oil (81%); υ_{max} (NaCl) 3010, 1724, 1471, 1165 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.14 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.03 – 5.87 (m, 2H), 5.63 – 5.43 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.20 – 3.14 (m, 2H), 2.42 (dd, *J* = 15.4, 7.1 Hz, 2H), 1.65 (d, *J* = 6.5 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 166.7, 162.4, 151.7, 138.4, 131.6, 130.8, 127.2, 125.8, 120.9, 61.4, 36.9, 32.8, 18.0, 14.2. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found C, 73.62; H, 7.75; N, 5.87.

Methyl 2-[(3*E*,5*E*)hepta-3,5-dienyl]-4-methylpyridine-3-carboxylate (4k)

Isolated as an oil (86%); υ_{max} (NaCl) 2924, 1730, 1441 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.1 Hz, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 6.09 – 5.99 (m, 2H), 5.67 – 5.57 (m, 2H), 3.96 (s, 3H), 2.89 – 2.82 (m, 2H), 2.55 – 2.46 (m, 2H), 2.34 (s, 3H), 1.75 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 169.1, 157.9, 149.6, 144.8, 131.5, 130.9, 130.6, 129.3, 127.4, 122.7, 52.3, 36.3, 32.6, 19.5, 18.0. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found C, 73.22; H, 7.65; N, 5.86

Methyl 2-((3*E*,5*E*)hepta-3,5-dienyl)-5-methylpyridine-3-carboxylate (4l)

Isolated as an oil (82%); υ_{max} (NaCl) 2925, 1726, 1560, 1205, 989 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.50 – 8.49 (m, 1H), 7.98 (dd, *J* = 2.3, 0.6 Hz, 1H), 6.12 – 5.98 (m, 2H), 5.71 – 5.55 (m, 2H), 3.94 (s, 3H), 3.24 – 3.18 (m, 2H), 2.48 (dd, *J* = 15.3, 7.1 Hz, 2H), 2.37 (s, 3H), 1.74 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 167.2, 159.5, 152.4, 138.8, 131.6, 131.0, 130.8, 130.3, 127.1, 124.8, 52.3, 36.4, 32.8, 18.0, 17.8. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found C, 73.23; H, 7.60; N, 5.89.

Ethyl 3-methyl-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7a)

Isolated as an oil (76%); υ_{max} (NaCl) 2928, 1726, 1455, 1251, 1150 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.25 (s, 1H), 4.43 (q, *J* = 7.5 Hz, 2H), 2.81 – 2.68 (m, 4H), 2.51 (s, 3H), 1.84 – 1.79 (m, 4H), 1.41 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 168.9, 151.4, 150.3, 143.2, 130.1, 128.8, 61.3, 26.2, 26.2, 22.3, 22.1, 22.1, 14.2. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found 70.98; H, 7.97; N, 6.16.

***Tert*-Butyl 3-but-3-enyl-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7b)**

Isolated as an oil (93%); υ_{max} (NaCl) 2929, 2857, 1565, 1455, 1254, 1041, 911 cm^{-1}. ^{1}H NMR δ (250 MHz, $CDCl_3$) δ 8.27 (s, 1H), 6.00 – 5.84 (m, 1H), 5.09 (ddd, *J* = 17.1, 3.5, 1.6 Hz, 1H), 5.04 – 4.97 (m, 1H), 2.87 – 2.80 (m, 2H), 2.78 – 2.71 (m, 4H), 2.59 – 2.37

(m, 2H), 1.85 – 1.80 (m, 4H), 1.63 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 168.1, 153.8, 150.0, 142.7, 138.0, 130.4, 130.0, 114.7, 82.5, 35.2, 33.9, 28.1, 26.3, 26.0, 22.2, 22.1. Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found C, 75.31; H, 8.62; N, 4.97.

Methyl 3-((3*E*,5*E*)hepta-3,5-dienyl)-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7c)

Isolated as an oil (90%); υ_{max} (NaCl) 2930, 1729, 1440, 1248 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.30 (s, 1H), 6.12 – 5.98 (m, 2H), 5.67 – 5-57 (m, 2H), 3.94 (s, 3H), 2.81 – 2.70 (m, 6H), 2.48 (dd, *J* = 15.6, 7.0 Hz, 2H), 1.84 – 1.79 (m, 4H), 1.75 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 169.4, 154.5, 150.6, 143.3, 131.5, 130.8, 130.7, 130.3, 128.6, 127.2, 52.2, 36.0, 32.7, 26.3, 26.2, 22.1, 22.1, 18.0. Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found C, 75.93; H, 8.01; N, 4.76.

Ethyl 2-{[4-(ethoxycarbonyl)-3-5,6,7,8-tetrahydroisoquinolyl]methylthio}acetate (7d)

Isolated as an oil (78%); υ_{max} (NaCl) 2925, 1728, 1450 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.30 (s, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.02 (s, 2H), 3.31 (s, 2H), 2.78 (bs, 4H), 1.84 – 1.77 (m, 4H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.3, 168.1, 152.0, 150.6, 144.5, 131.8, 128.5, 61.6, 61.3, 36.2, 33.3, 29.7, 26.5, 26.4, 22.1, 21.9, 14.1. Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.51; H, 6.87; N, 4.15. Found C, 60.26; H, 6.96; N, 3.98.

3,7,7-Trimethyl-7,8-dihydroquinolin-5(6*H*)-one (7e)

Isolated as an oil (76%); υ_{max} (NaCl) 2955, 1690, 1276,cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 2.0 Hz, 1H), 3.02 (s, 2H), 2.56 (s, 2H), 2.40 (s, 3H), 1.13 (s, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 198.4, 159.4, 154.5, 134.5, 131.7, 126.5, 52.1, 46.0, 33.0, 28.2, 18.0. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found C, 76.29; H, 7.82; N, 7.53.

1-Ethyl-2-methyl-5,6-dihydrobenzo[*f*]quinolone (7f)

Isolated as an oil (90%); υ_{max} (NaCl) 2928, 1582, 1425, 1385, 1013, 749 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.66 – 7.63 (m, 1H), 7.37 – 7.28 (m, 3H), 3.00 – 2.91 (m, 4H), 2.87 – 2.82 (m, 2H), 2.40 (s, 3H), 1.41 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 157.9, 148.0, 147.5, 139.8, 133.5, 130.8, 129.2, 127.9, 127.7, 127.4, 126.0, 33.2, 29.5, 23.3, 16.5, 13.8. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found C, 86.22; H, 7.81; N, 6.04.

1-Phenyl-5,6-dihydrobenzo[*f*]quinoline (7g)

Isolated as an oil (78%); υ_{max} (NaCl) 3056, 2925, 1586, 1447, 1074, 840 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.1 Hz, 1H), 7.42 – 7.27 (m, 7H), 7.18 (d, *J* = 5.1 Hz, 1H), 6.87 – 6.81 (m, 2H), 3.14 – 3.08 (m, 2H), 3.04 – 2.98 (m, 2H).^{13}C NMR (63 MHz, $CDCl_3$) δ 160.4, 147.0, 146.7, 140.6, 138.9, 132.3, 129.6, 128.8, 128.8, 128.1, 127.9, 127.6, 127.4, 125.5, 124.6, 32.9, 29.1. Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found C, 88.49; H, 5.71; N, 5.59.

2,3,4,7,8,9,10-Hexahydrophenanthridin-1(2*H*)-one (7h)

Isolated as an oil (74%); υ_{max} (NaCl) 2928, 1684, 1591, 1435cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.98 (s, 1H), 3.09 (t, *J* = 6.2 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H), 2.82 (t, *J* = 6.2 Hz, 2H), 2.68 (dd, *J* = 7.5, 5.0 Hz, 2H), 2.24 - 2.14 (m, 2H), 1.99 – 1.80 (m, 4H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 198.4, 162.6, 160.5, 135.3, 131.1, 125.9, 38.6, 33.1, 32.2, 28.3, 22.8, 22.5, 22.1. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found C, 77.42; H, 7.69; N, 6.91.

1,2,3,4,7,8-Hexahydrobenzo[*a*]phenanthridine (7i)

Isolated as an oil (88%); υ_{max} (NaCl) 2930, 1642, 1438, 1053 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.68 – 7.65 (m, 1H), 7.35 – 7.23 (m, 3H), 3.07 – 2.95 (m, 4H), 2.90 – 2.83 (m, 4H), 1.96 – 1.86 (m, 2H), 1.81 – 1.73 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$)

δ 156.6, 148.0, 143.0, 139.8, 133.2, 131.3, 128.7, 128.5, 127.7, 127.3, 125.7, 32.9, 29.9, 29.4, 26.4, 23.1, 22.2. Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found C, 86.58; H, 7.01; N, 6.17.

Ethyl 2-but-3-enyl-6-ethoxy-1-(2-furylmethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate

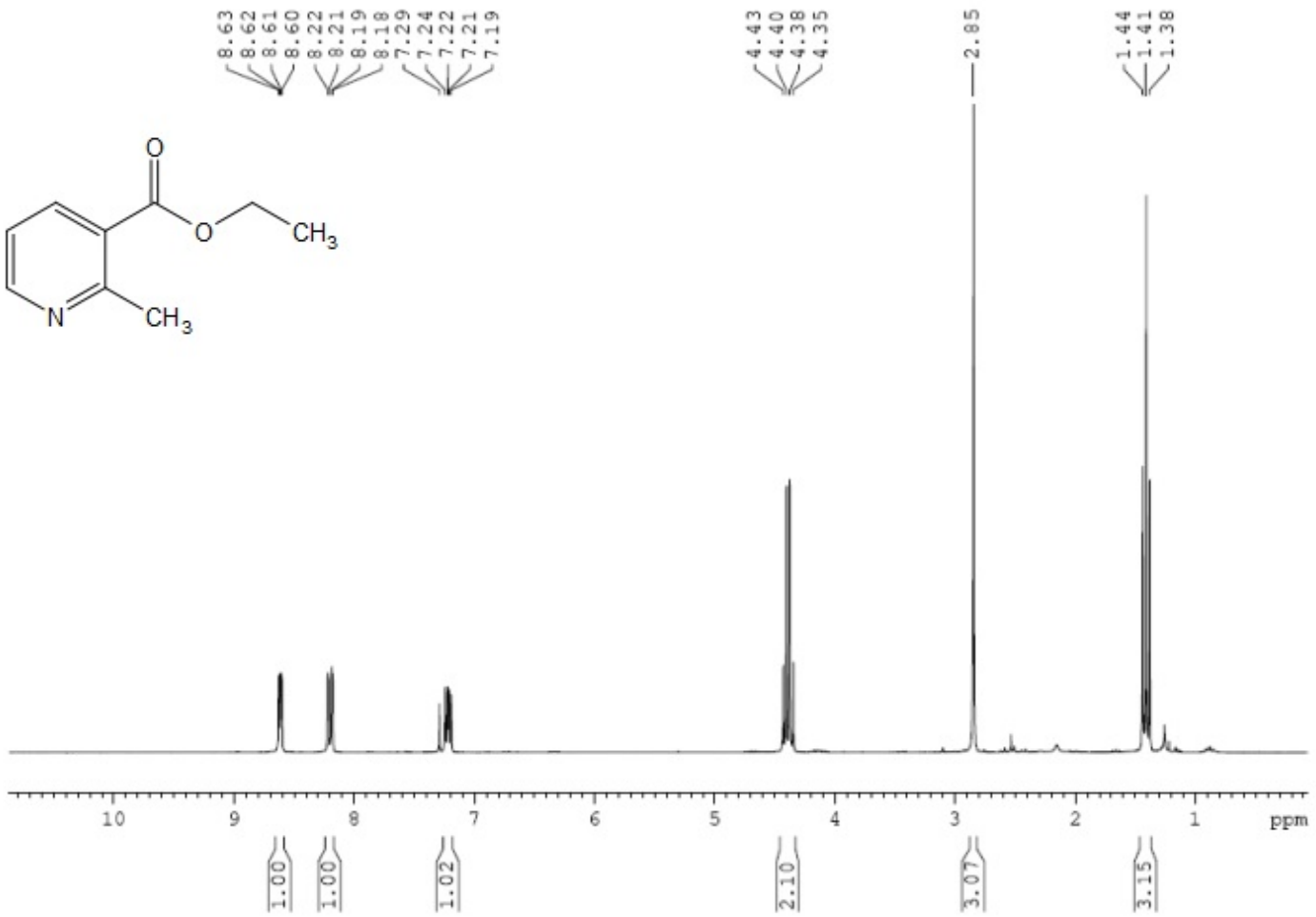
To a stirred solution of 2-furylmethylamine (1 equiv, 3 mmol) and ethyl 3-oxohept-6-enoate (1 equiv, 3 mmol) in ethanol (3 mL) was added $InCl_3$ (10% mol) and stirring was continued for 30 min at room temperature. Then the reaction mixture was cooled to 5 ^oC. Acrolein (1.2 equiv, 3.6 mmol) was then added and stirring was continued under the same conditions for 2 hrs. After completion of the reaction (checked by TLC and NMR), the solvent was evaporated under reduced pressure under 25 ^oC. The crude product obtained, which was isolated as an oil (90%), gave the following spectral data: υ_{max} (NaCl) 3067, 1721,1225, 1150 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 7.30 (d, J = 1.7 Hz, 1H), 6.26 (dd, J = 3.1, 1.7 Hz, 1H), 6.12 (d, J = 3.1 Hz, 1H), 5.95 – 5.75 (m, 1H), 5.06 – 4.91 (m, 2H), 4.61 – 4.49 (m, 2H), 4.29 (d, J = 16.9 Hz, 1H), 4.05 (d, J = 7.5 Hz, 1H), 3.44 (d, J = 7.5 Hz, 1H), 3.34 – 3.28 (m, 1H), 2.75 – 2.11 (m, 6H), 2.02 – 1.84 (m, 2H), 1.42 – 1.30 (m, 1H), 1.23 – 1.17 (m, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 168.0, 153.9, 151.7, 141.9, 137.6, 114.3, 110.0, 107.1, 98.4, 85.7, 61.8, 58.7, 45.9, 32.8, 29.4, 28.0, 25.0, 18.1, 15.1, 14.3.

Ethyl 2-(3-butenyl)-1-(2-furylmethyl)-1,4-dihydropyridine-3-carboxylate

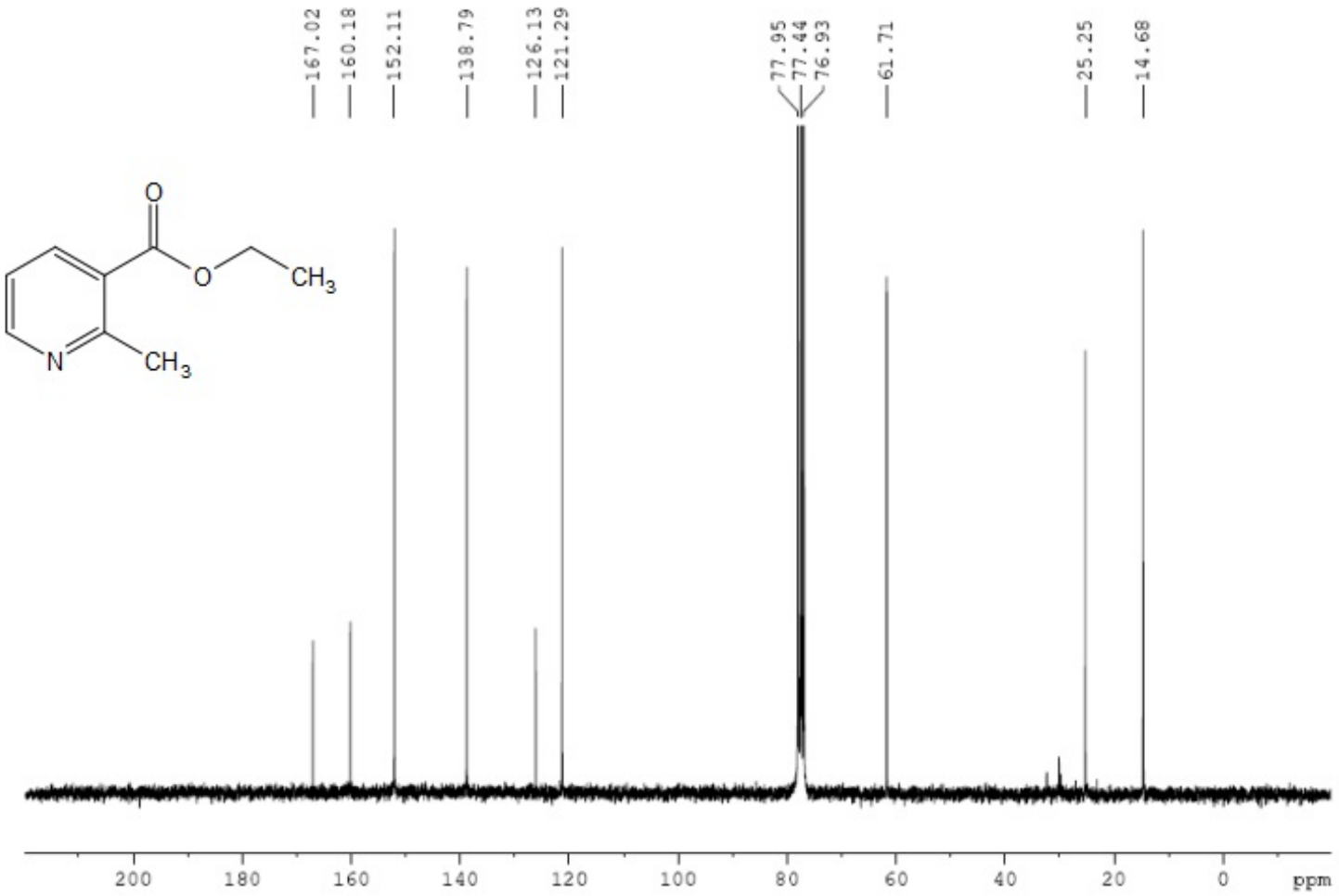
Compound **7** (1 equiv, 3 mmol) was dissolved in toluene (8 mL), and refluxed for 12 h. After completion of the reaction (checked by TLC), the solvent was removed. The crude product obtained, which was isolated as an oil (70%), gave the following spectral data: υ_{max} (NaCl) 3036, 1355, 1251 cm^{-1} ^1H NMR (250 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 1H), 6.35 – 6.33 (m, 1H), 6.28 – 6.22 (m, 1H), 6.00 – 5.85 (m, 1H), 5.79 (d, J = 7.8 Hz, 1H), 5.13 – 4.97 (m, 2H), 4.83 – 4.77 (m, 1H), 4.38 (s, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.15 (dd, J = 3.7, 1.4 Hz, 2H), 2.97 – 2.84 (m, 2H), 2.33 – 2.24 (m, 2H), 1.33 – 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 168.3, 153.1, 151.4, 142.3, 137.5, 130.4, 114.9, 110.3, 107.3, 104.4, 96.0, 59.3, 46.5, 32.8, 29.6, 27.5, 24.5, 14.4.

Spectra

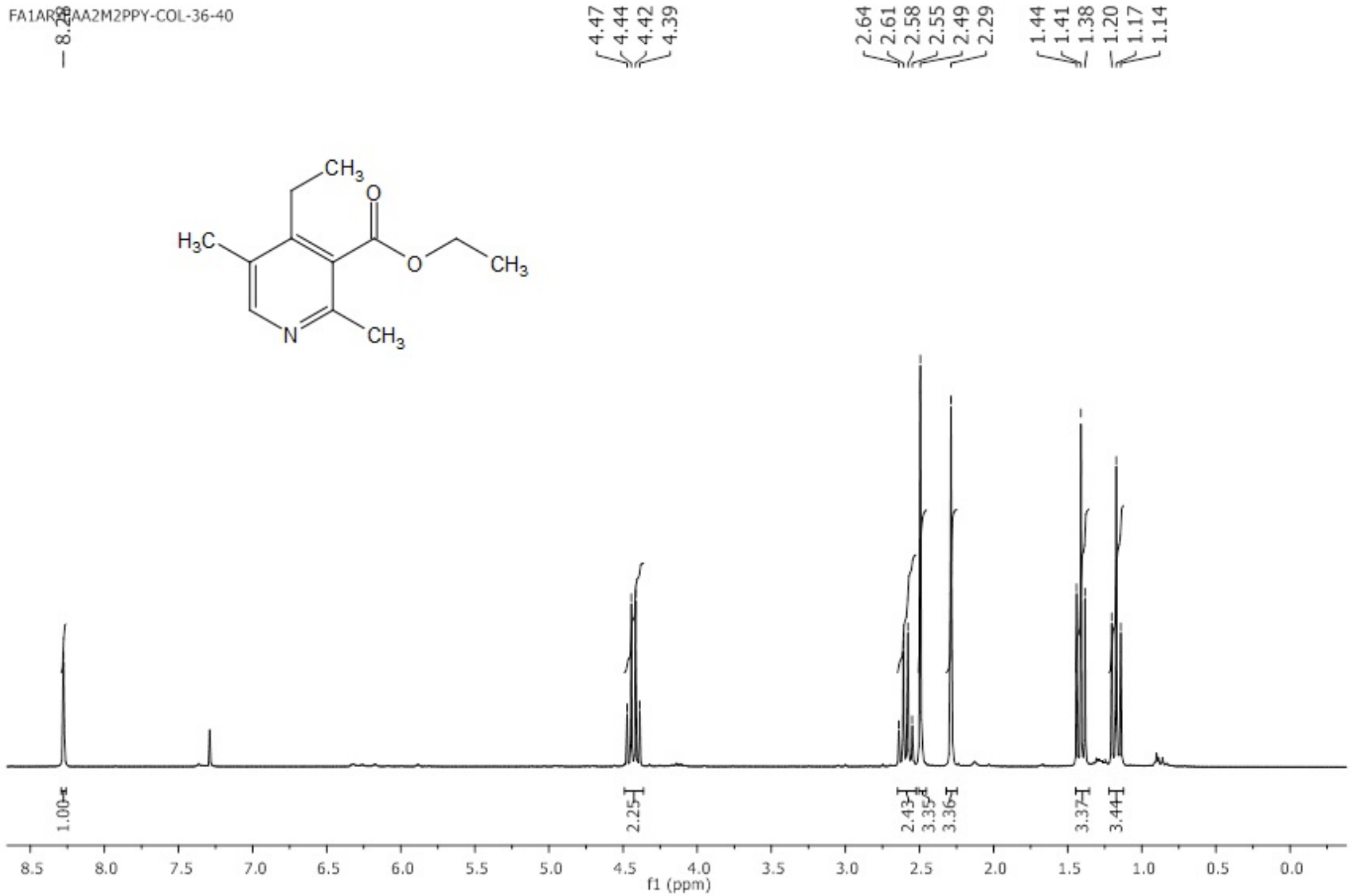
Ethyl 2-methylpyridine-3-carboxylate (4a)



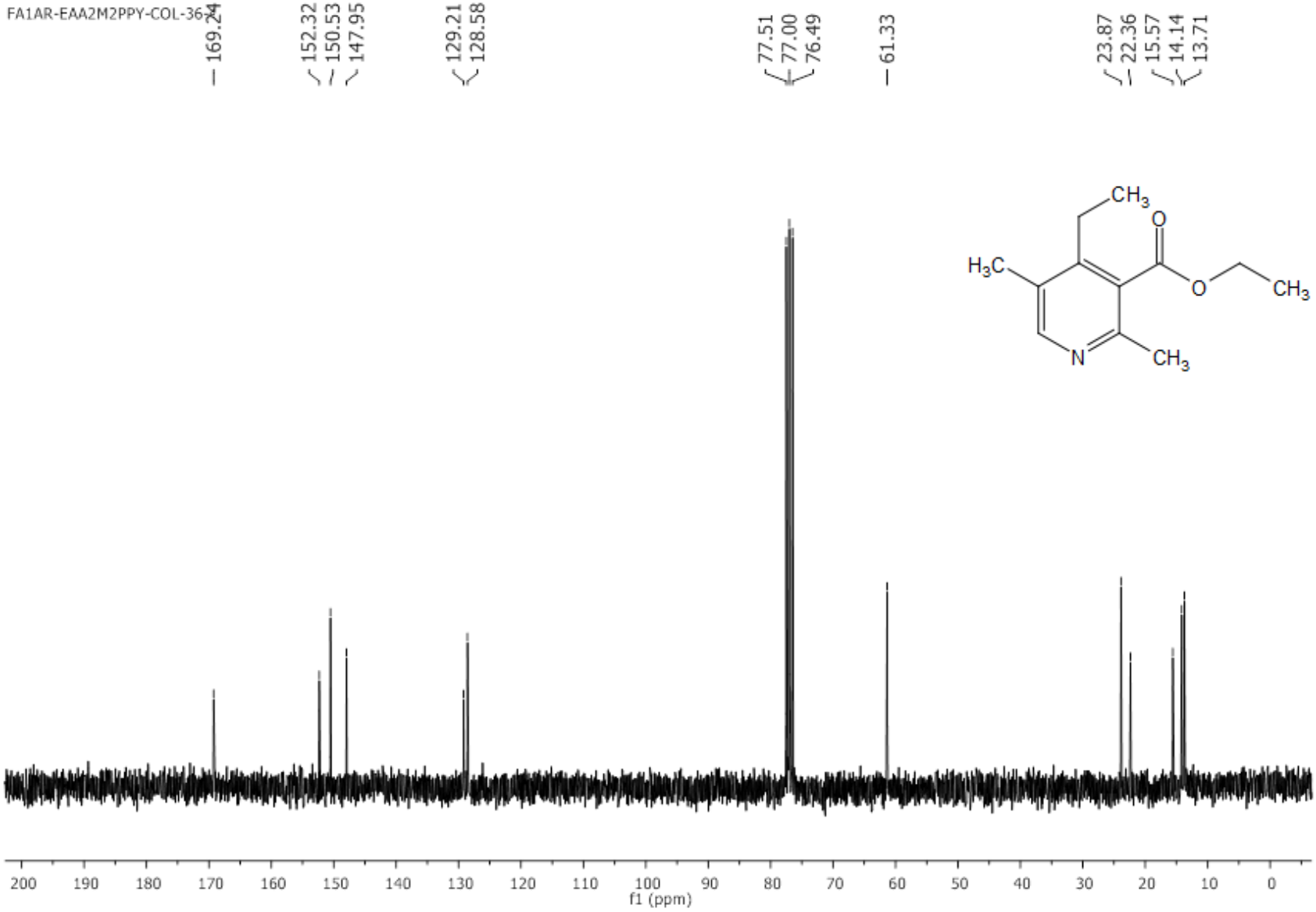
Ethyl 2-methylpyridine-3-carboxylate (4a)



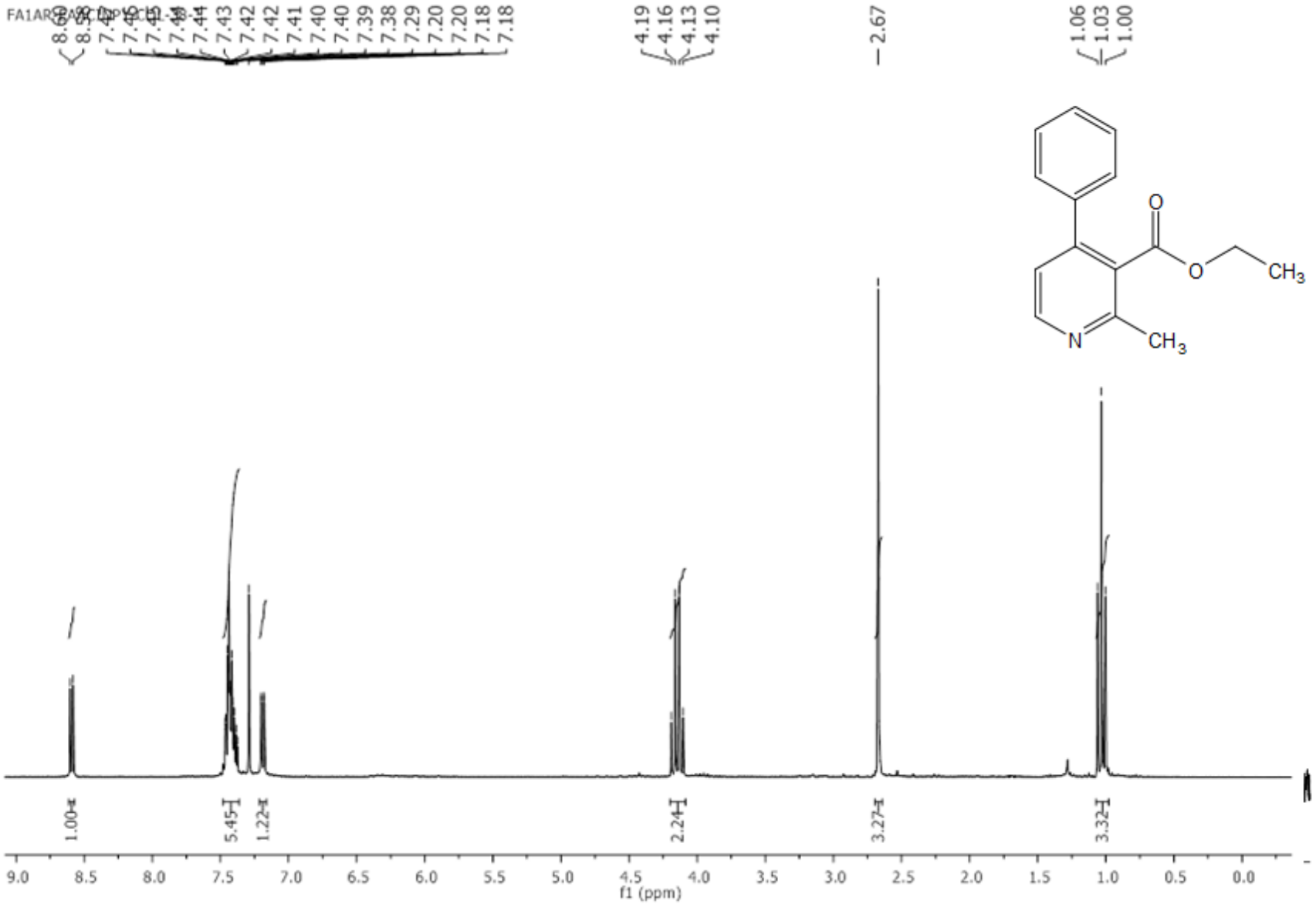
Ethyl 4-ethyl-2,5-dimethylpyridine-3-carboxylate (4b)



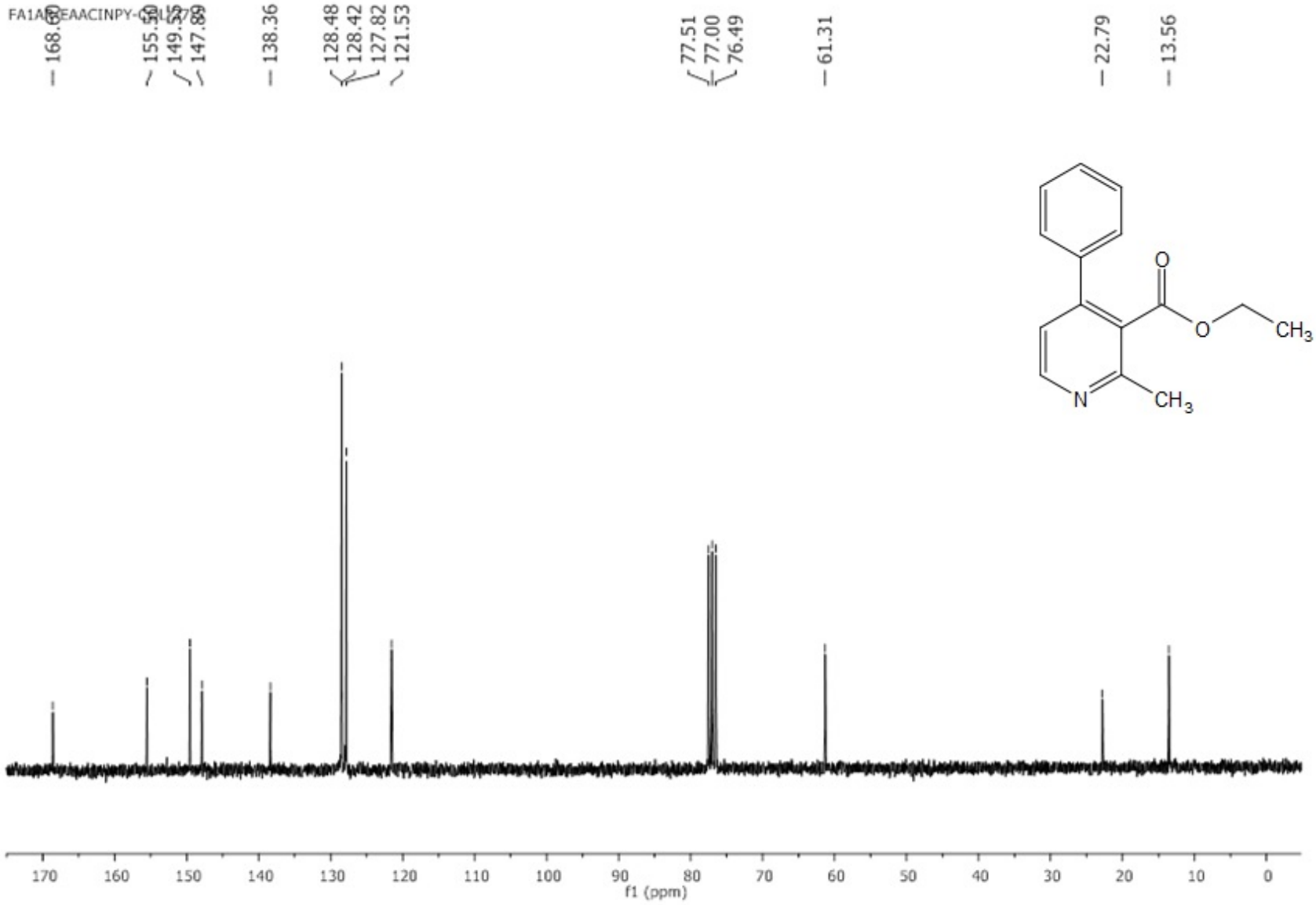
Ethyl 4-ethyl-2,5-dimethylpyridine-3-carboxylate (4b)



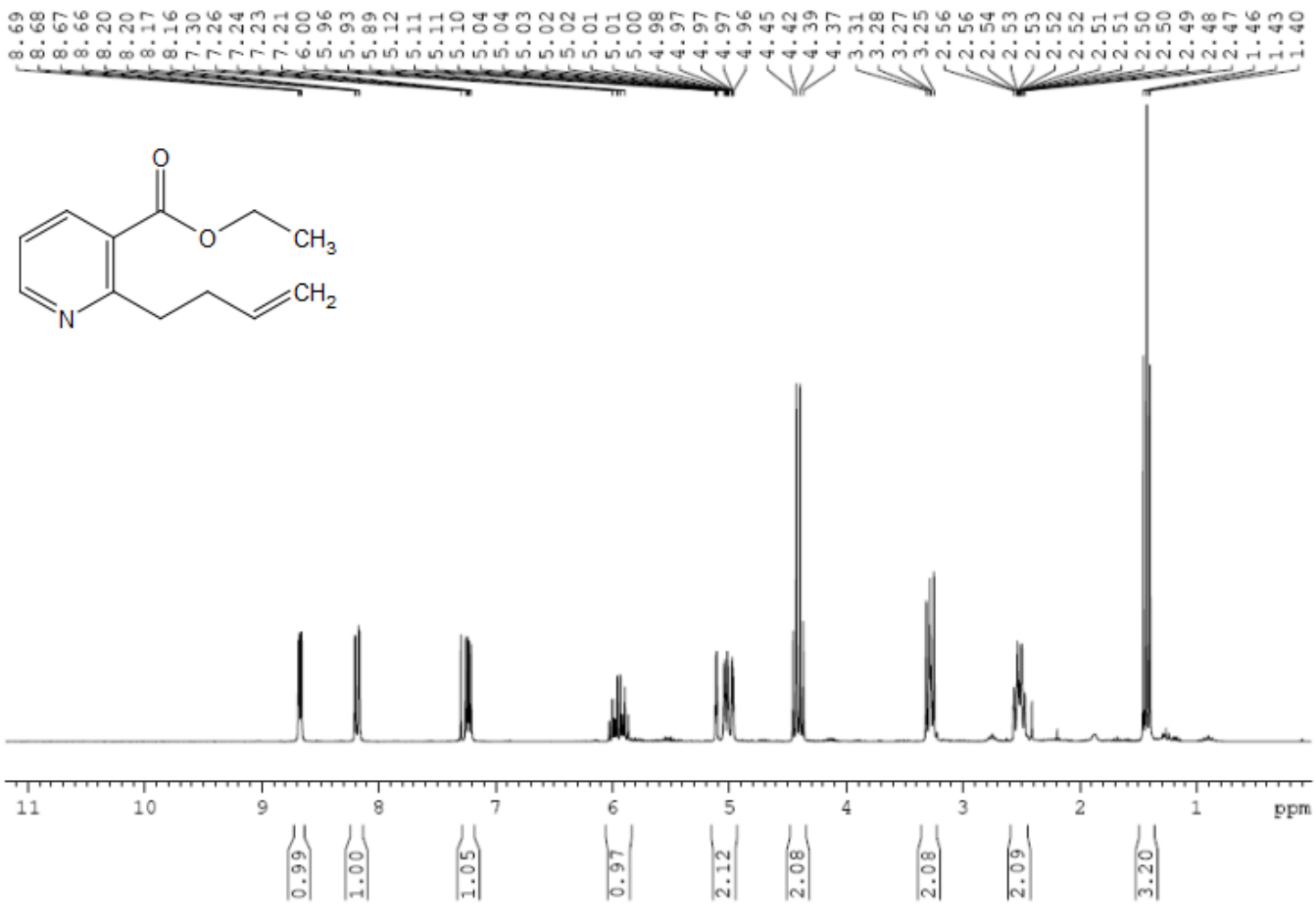
Ethyl 2-methyl-4-phenylpyridine-3-carboxylate (4c)



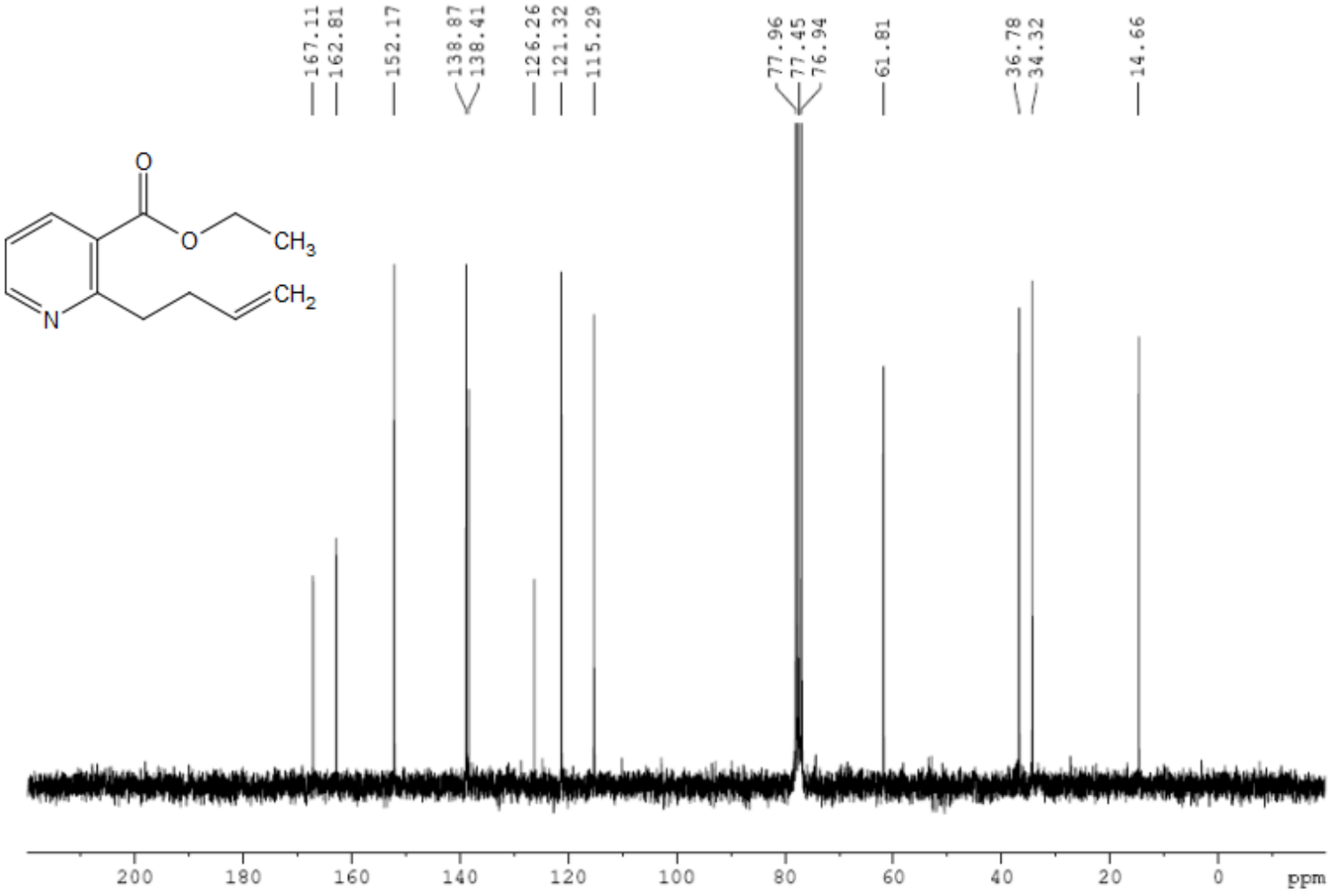
Ethyl 2-methyl-4-phenylpyridine-3-carboxylate (4c)



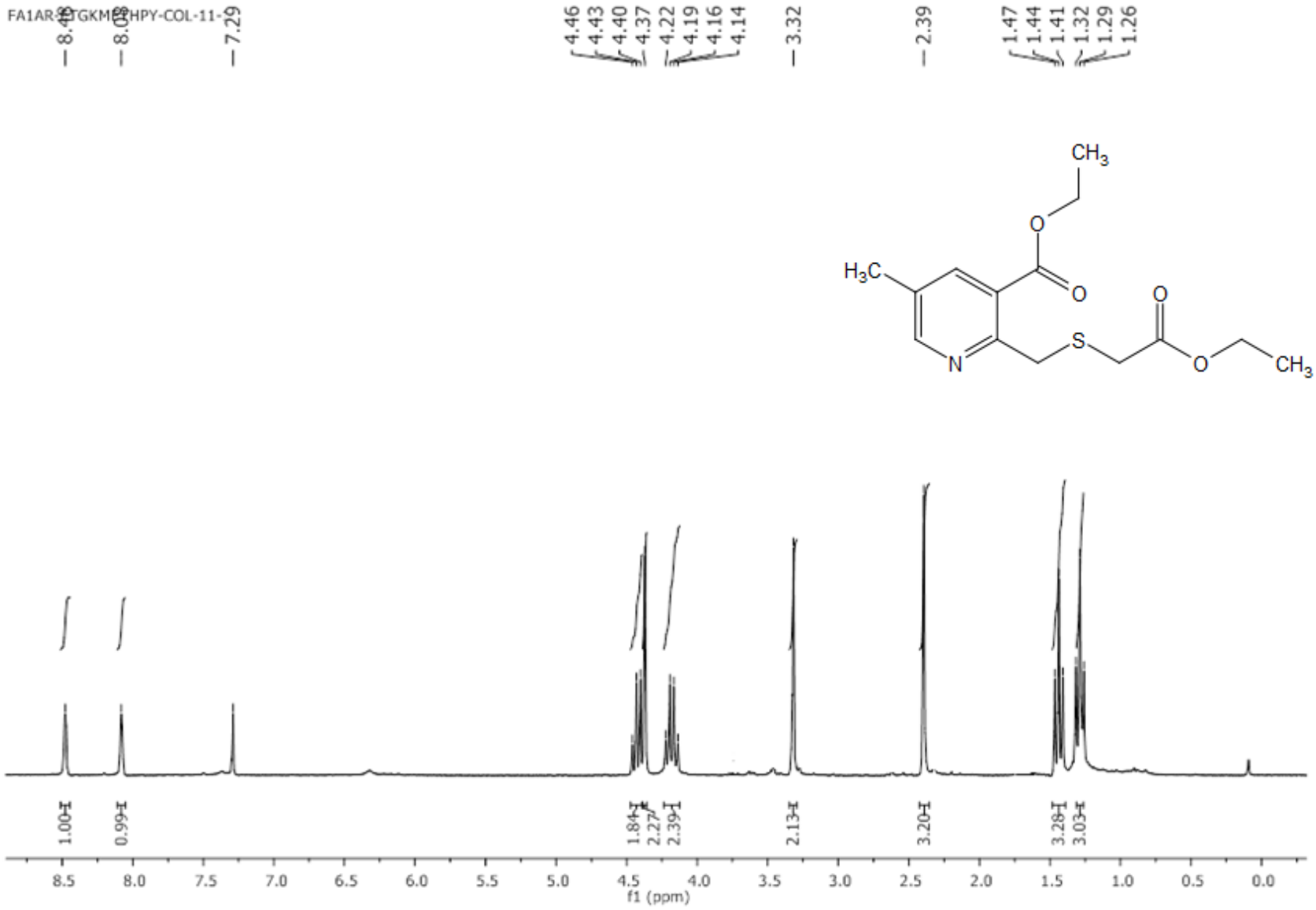
Ethyl 2-but-3-enylpyridine-3-carboxylate (4d)



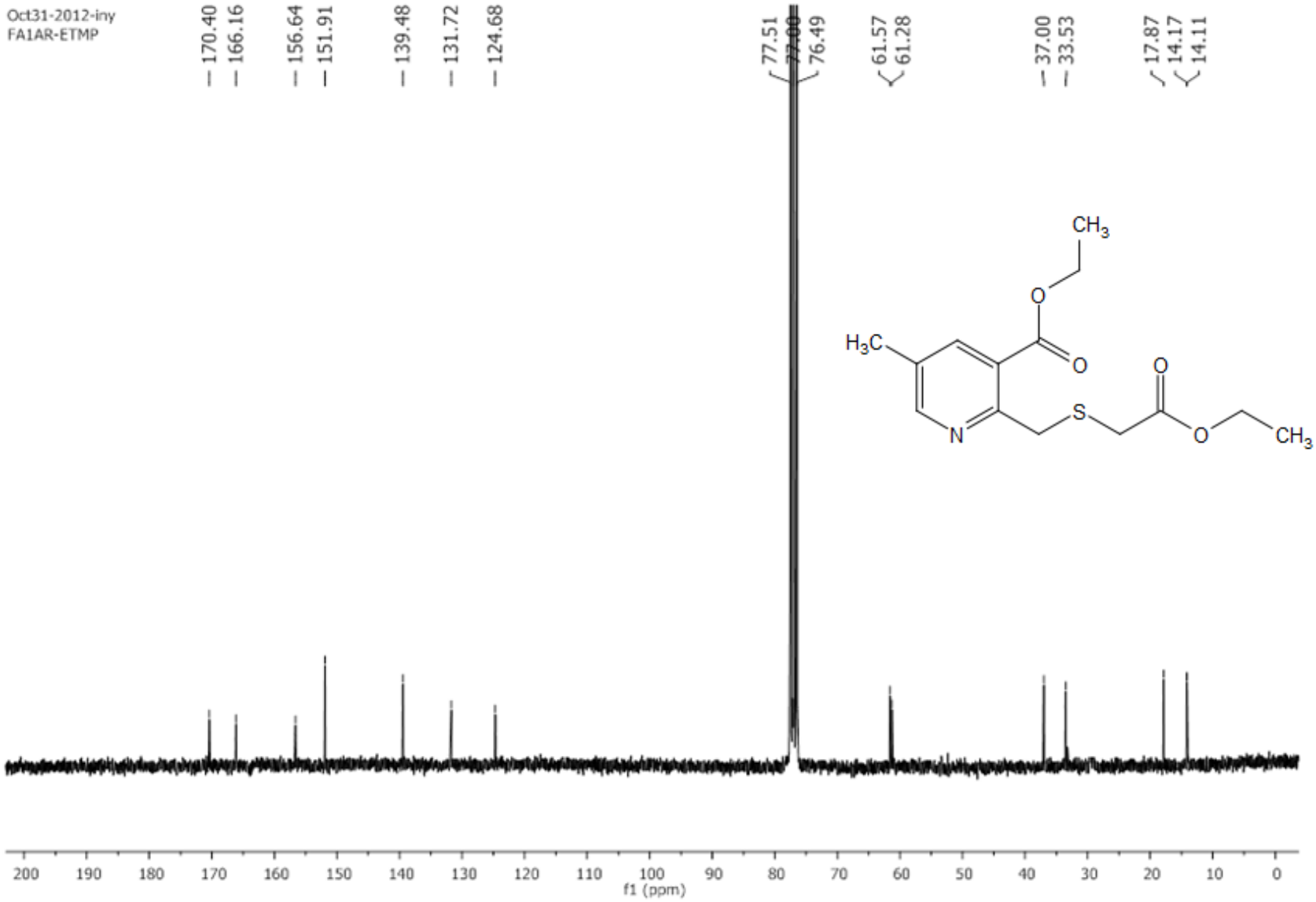
Ethyl 2-but-3-enylpyridine-3-carboxylate (4d)



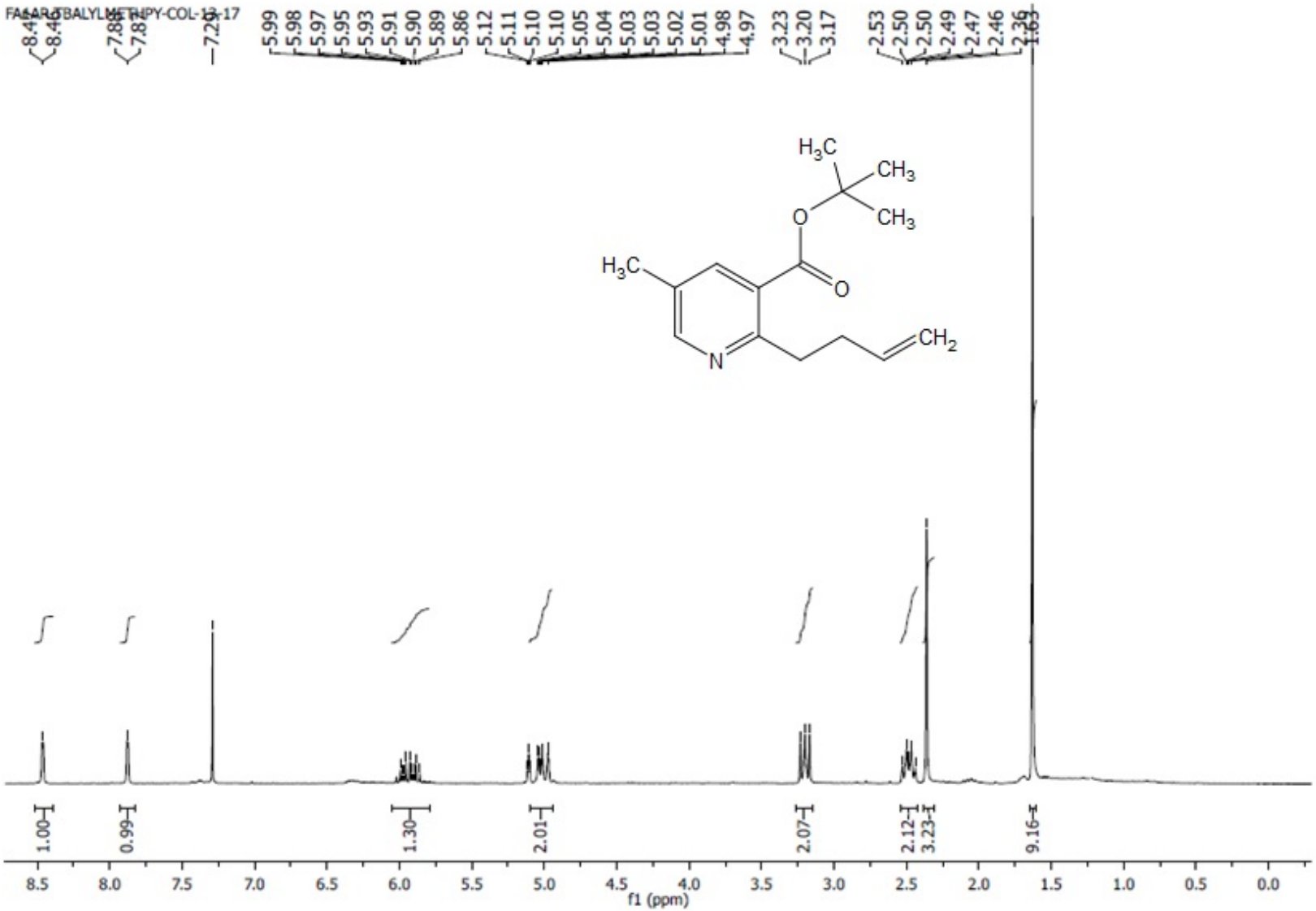
Ethyl 2-{[3-(ethoxycarbonyl)-5-methyl-2-pyridyl]methylthio}acetate (4e)



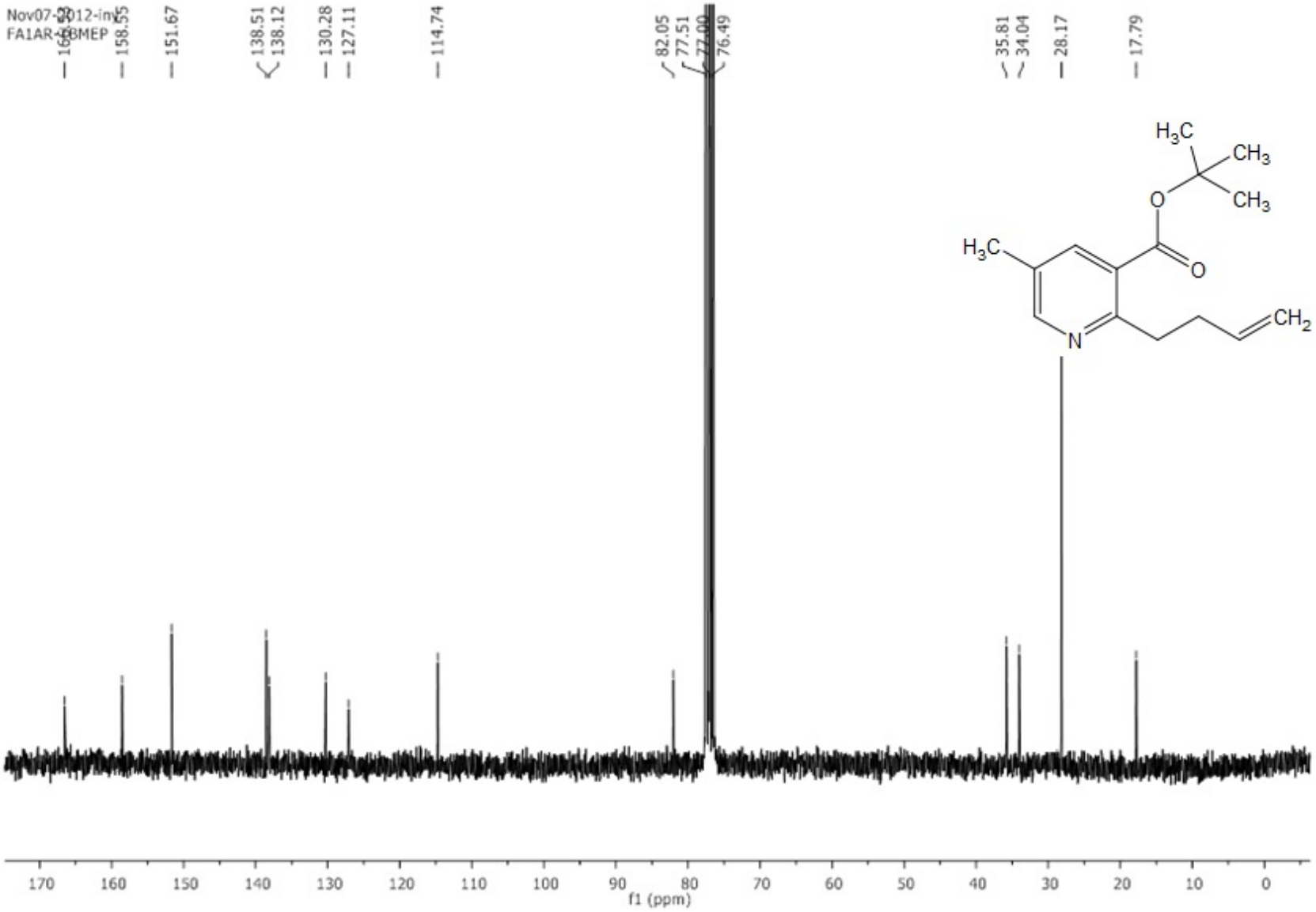
Ethyl 2-{[3-(ethoxycarbonyl)-5-methyl-2-pyridyl]methylthio}acetate (4e)



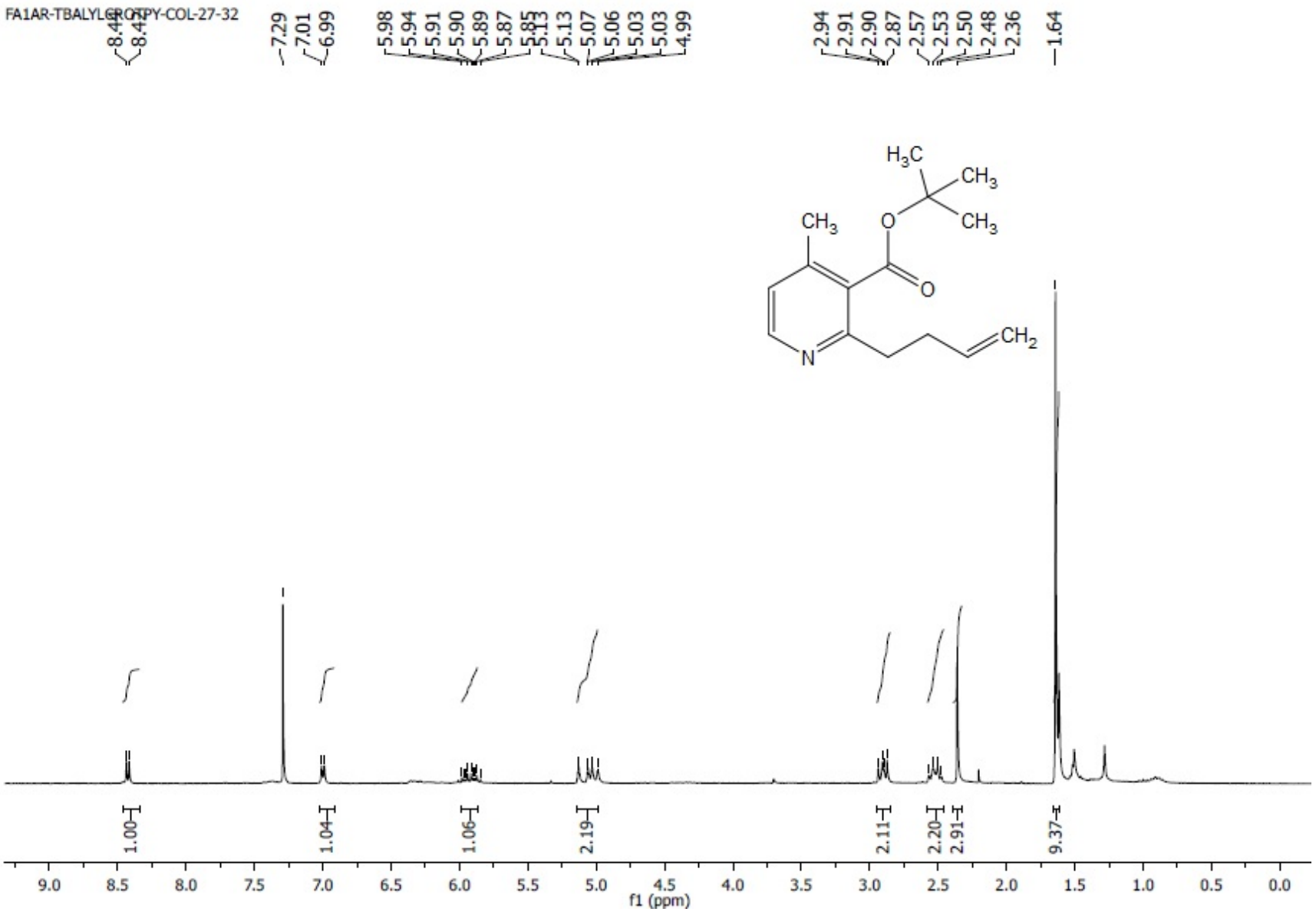
tert-Butyl 2-but-3-enyl-5-methylpyridine-3-carboxylate (4f)



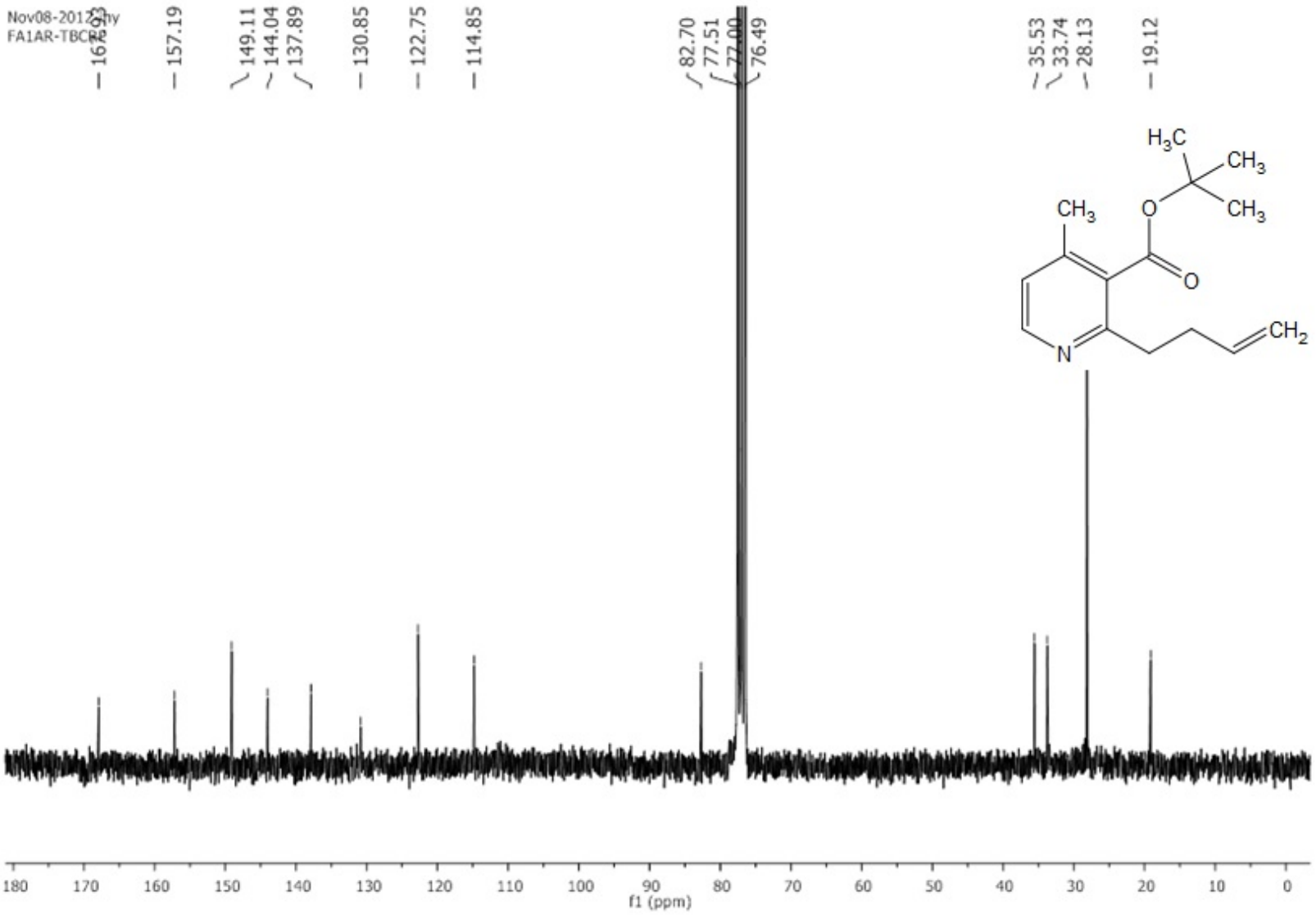
tert-Butyl 2-but-3-enyl-5-methylpyridine-3-carboxylate (4f)



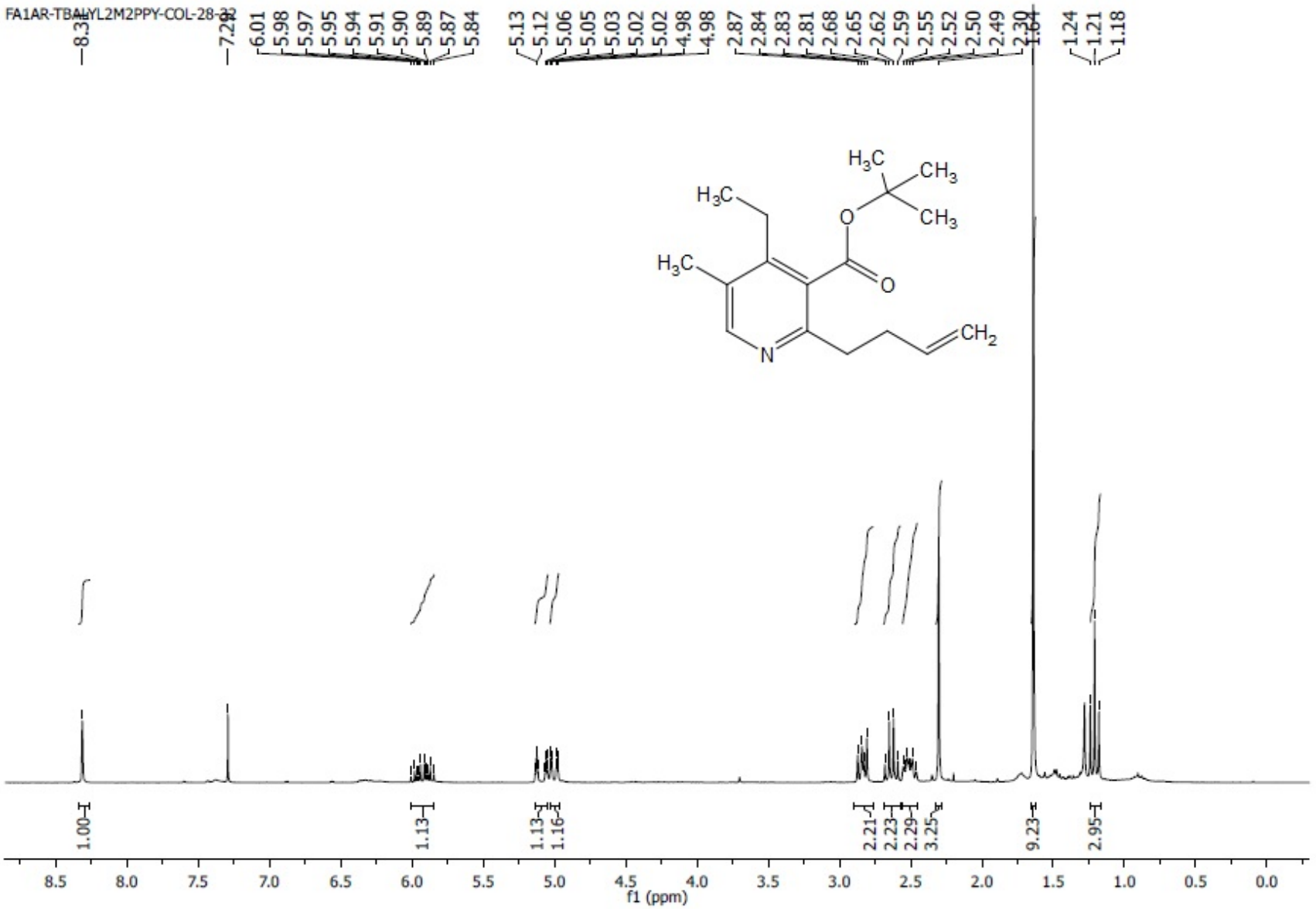
tert-Butyl 2-but-3-enyl-4-methylpyridine-3-carboxylate (4g)



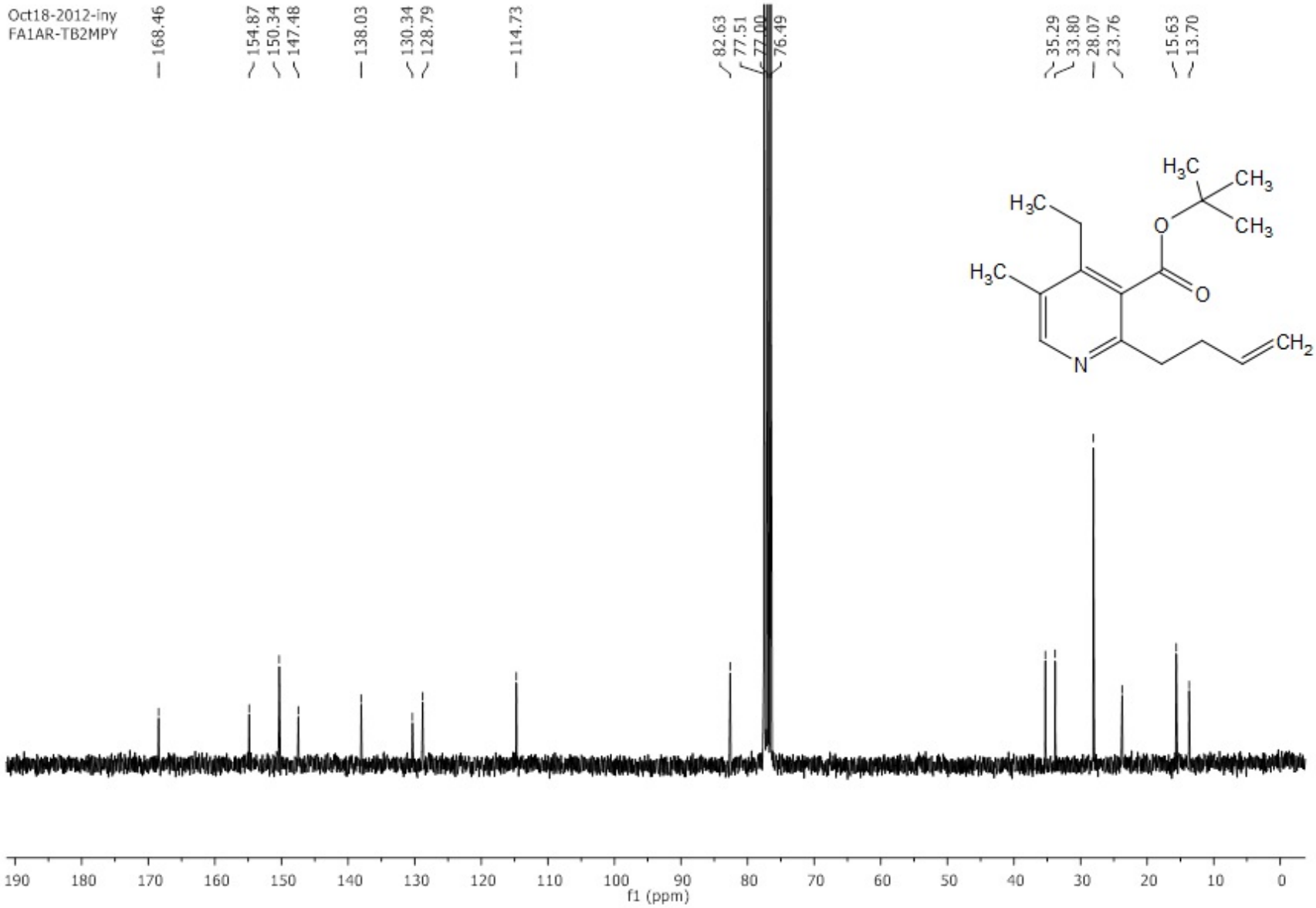
tert-Butyl 2-but-3-enyl-4-methylpyridine-3-carboxylate (4g)



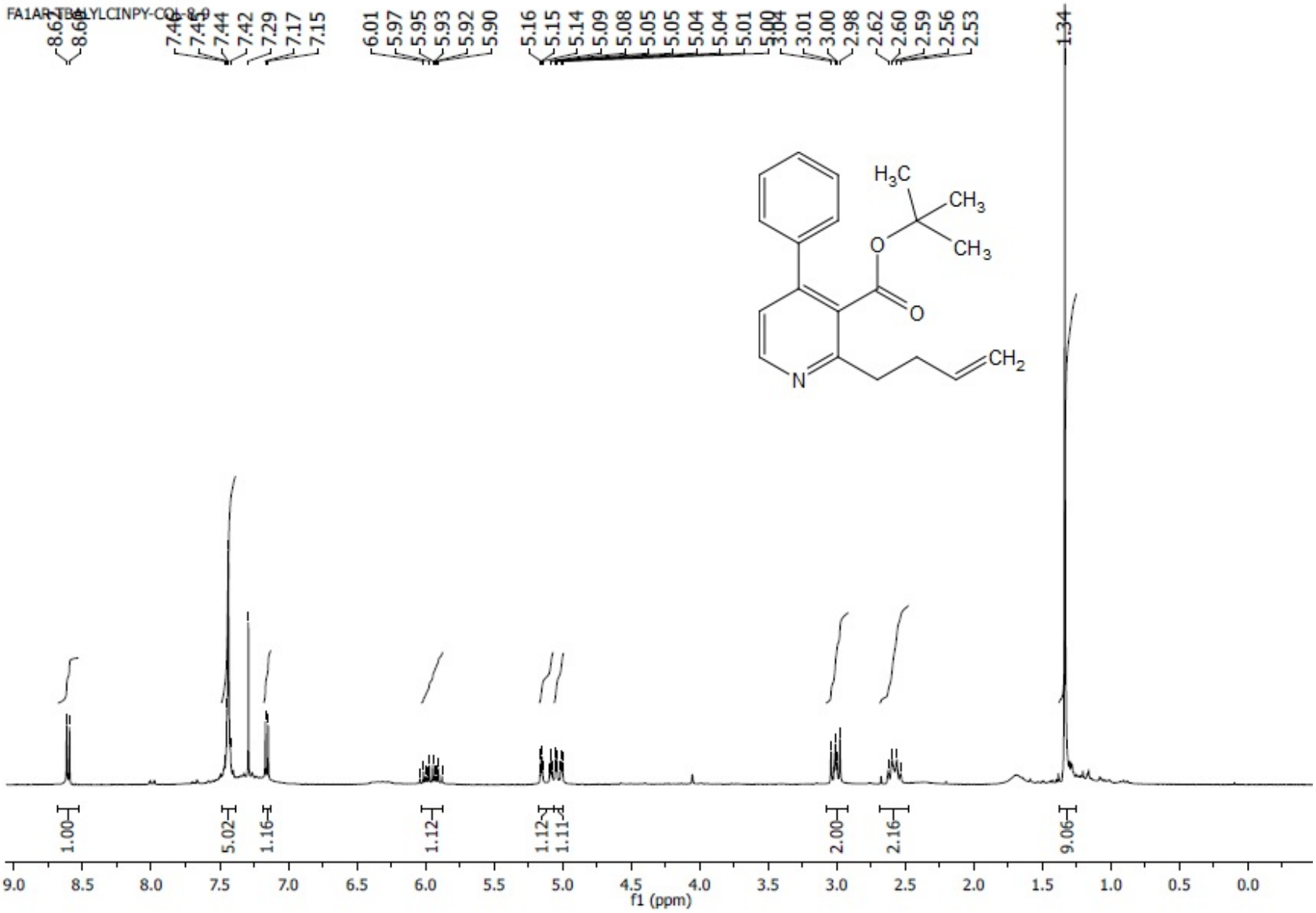
tert-Butyl 2-but-3-enyl-4-ethyl-5-methylpyridine-3-carboxylate (4h)



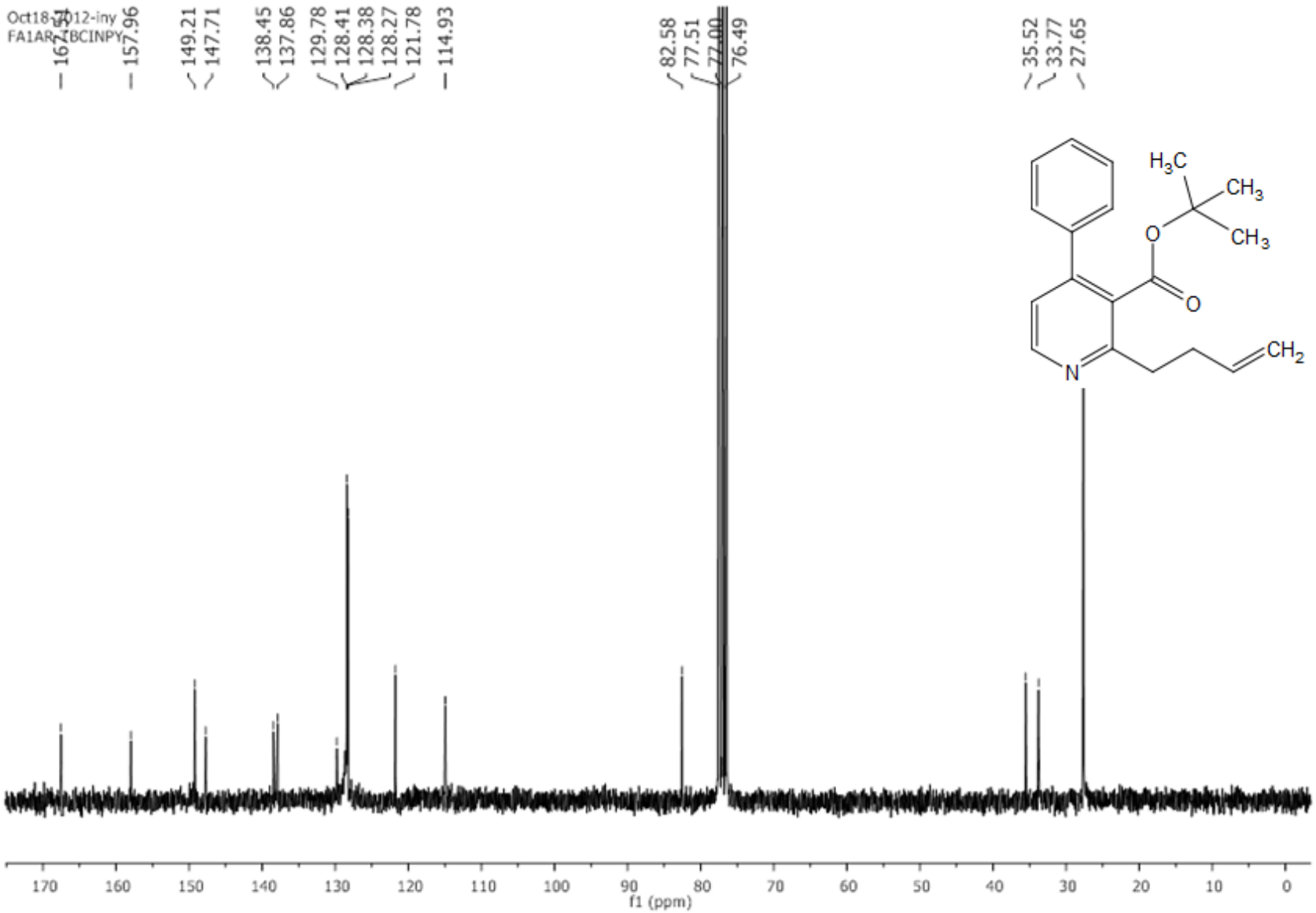
tert-Butyl 2-but-3-enyl-4-ethyl-5-methylpyridine-3-carboxylate (4h)



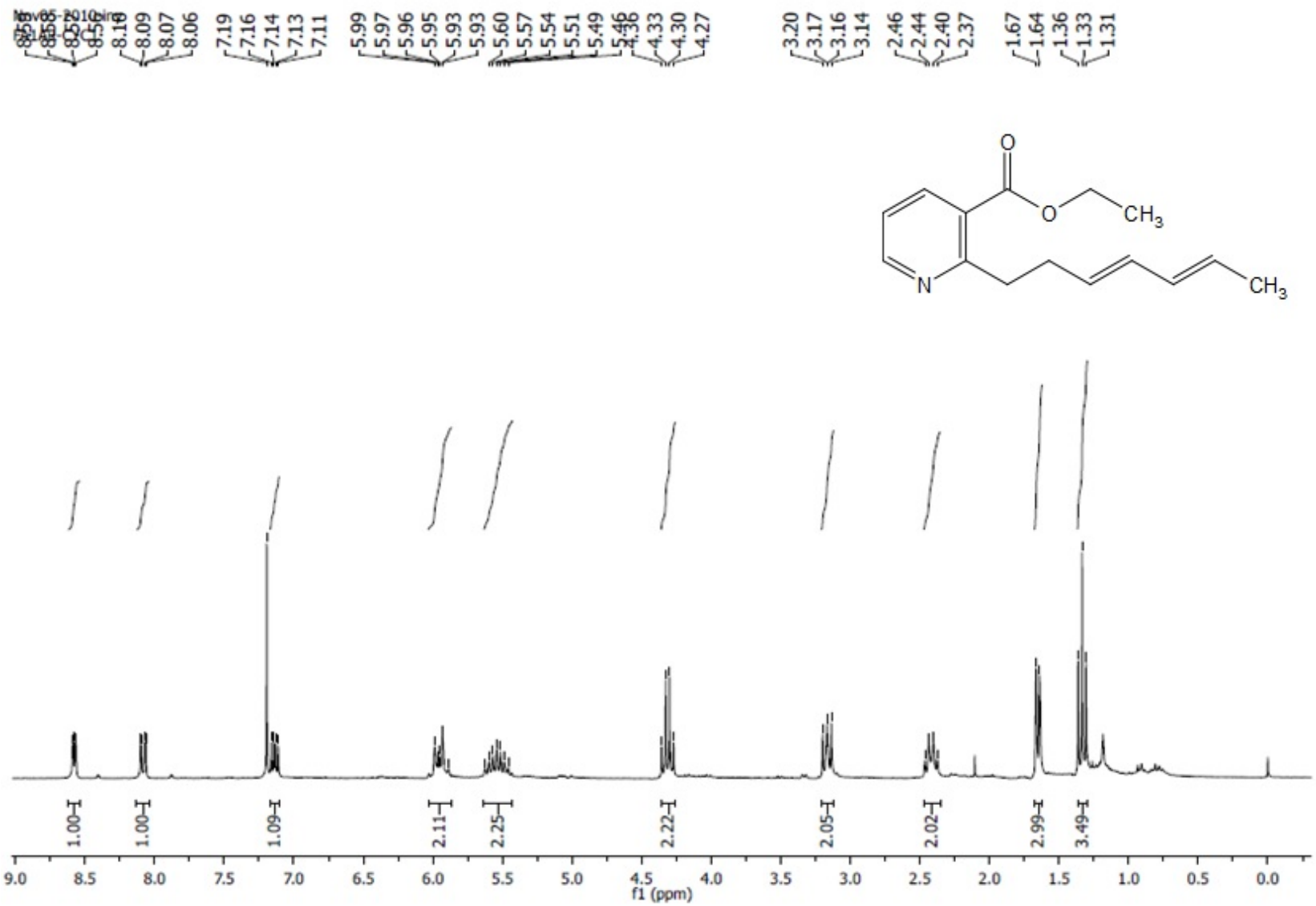
tert-Butyl 2-but-3-enyl-4-phenylpyridine-3-carboxylate (4i)



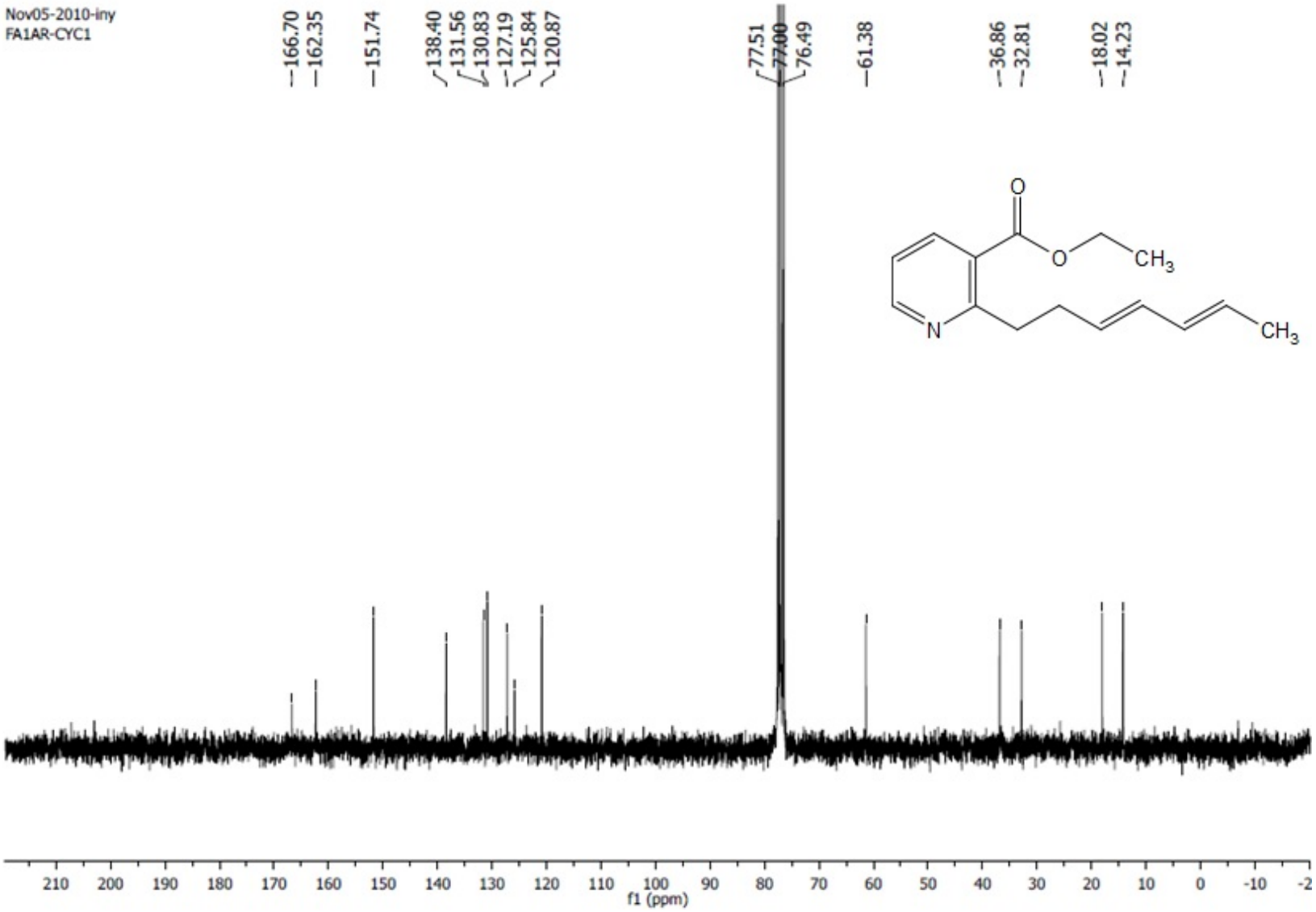
tert-Butyl 2-but-3-enyl-4-phenylpyridine-3-carboxylate (4i)



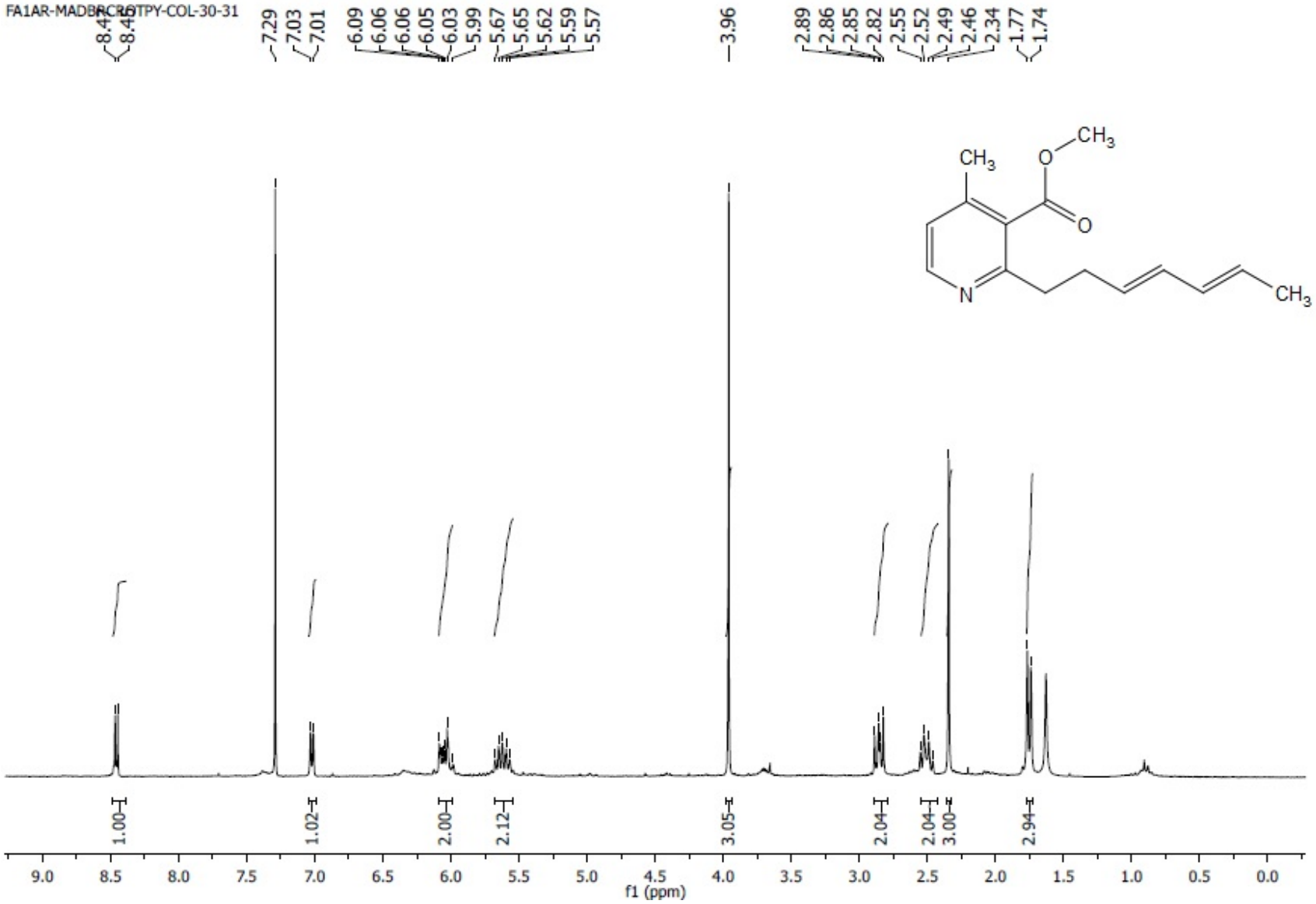
Ethyl 2-[(3*E*,5*E*)hepta-3,5-dienyl]pyridine-3-carboxylate (4j)



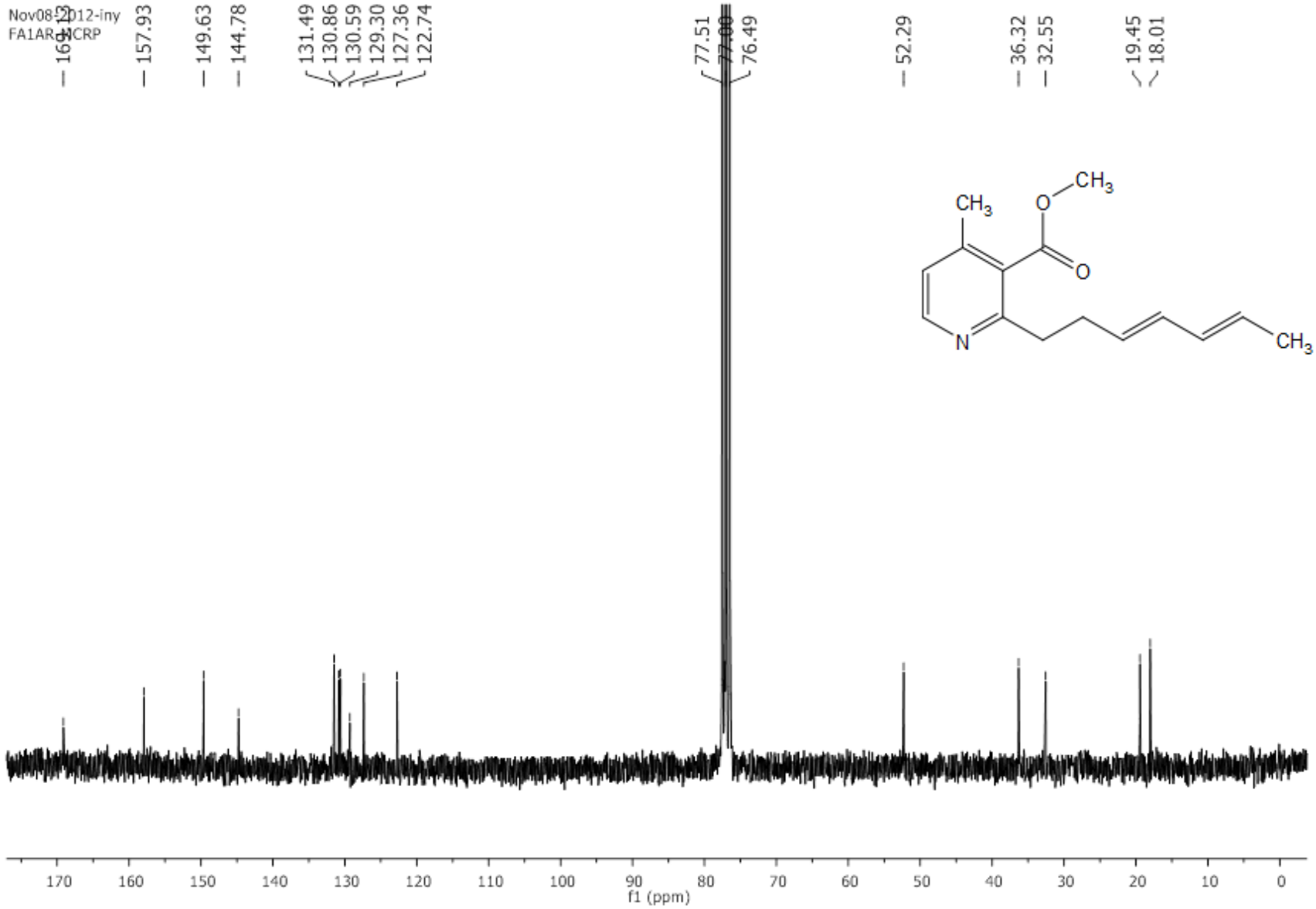
Ethyl 2-[(3*E*,5*E*)hepta-3,5-dienyl]pyridine-3-carboxylate (4j)



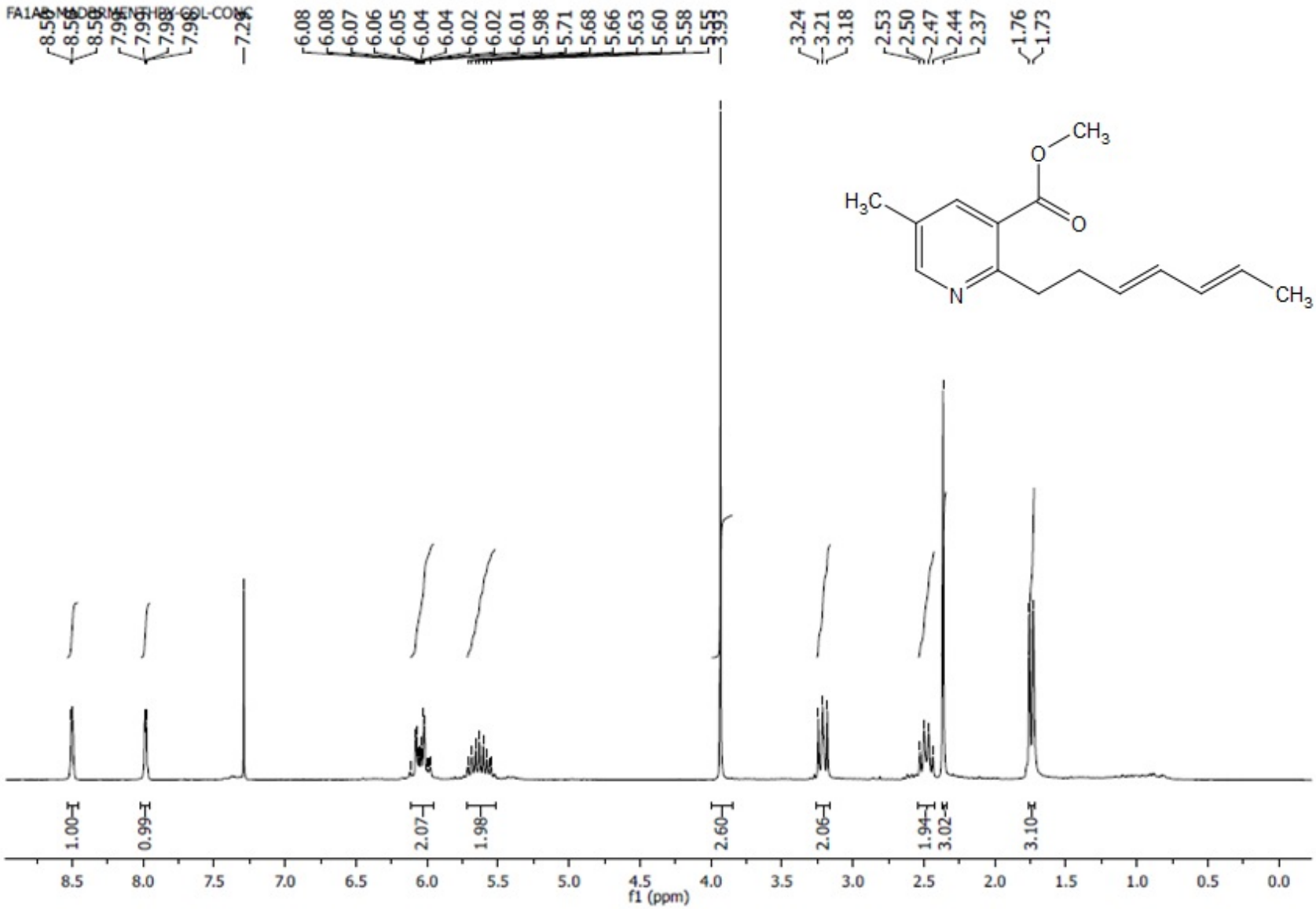
Methyl 2-[(3*E*,5*E*)hepta-3,5-dienyl]-4-methylpyridine-3-carboxylate (4k)



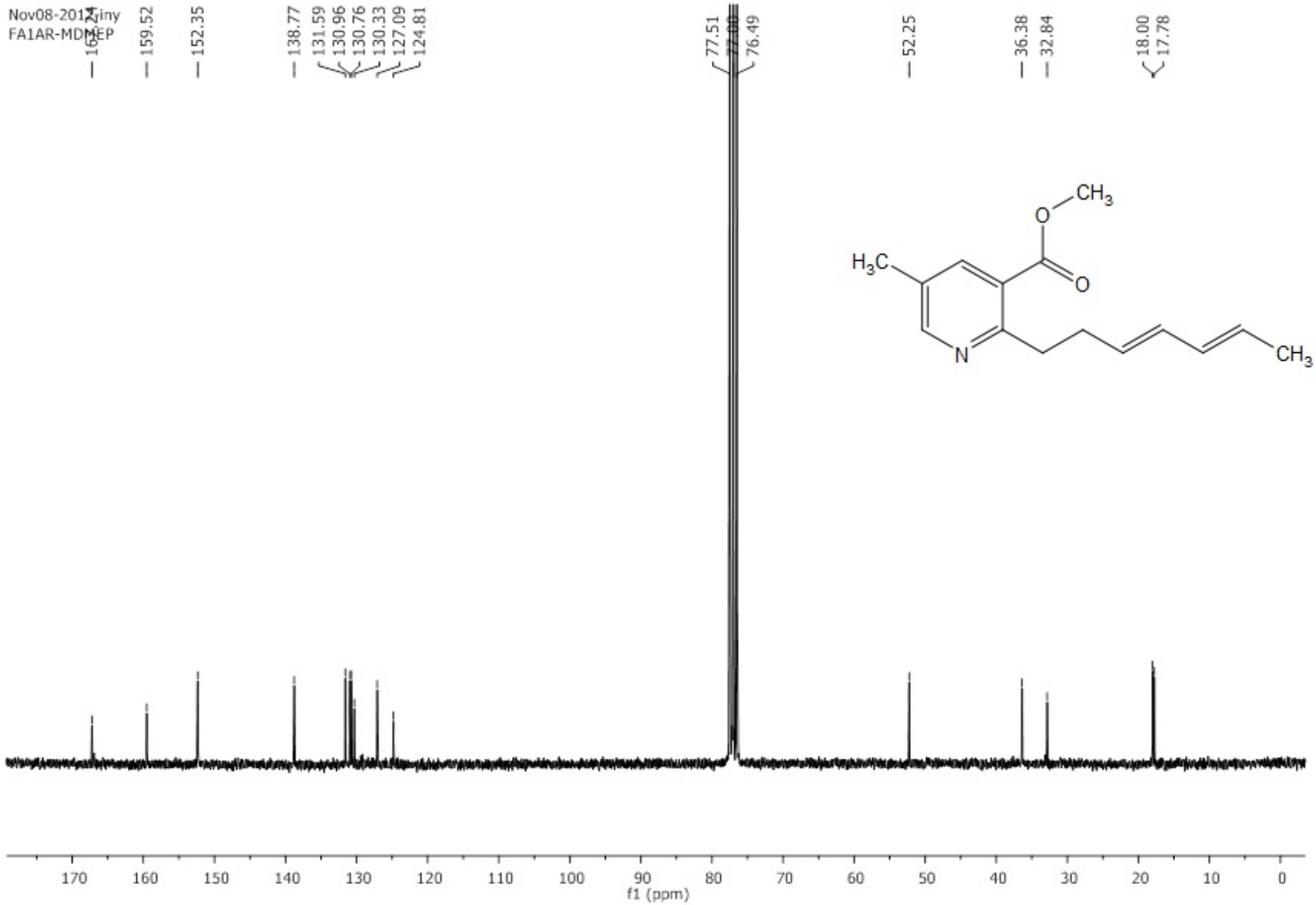
Methyl 2-[(3*E*,5*E*)hepta-3,5-dienyl]-4-methylpyridine-3-carboxylate (4k)



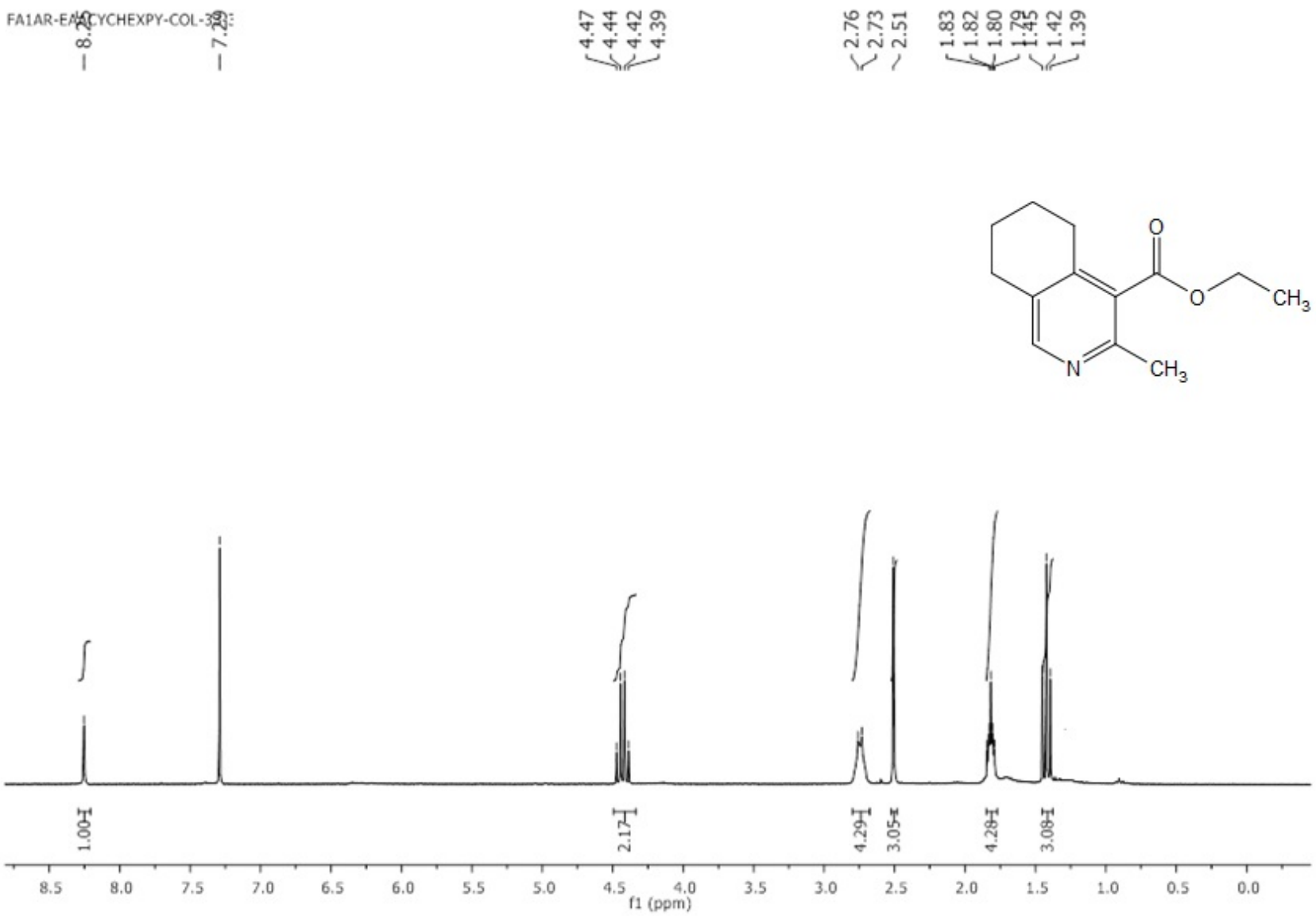
Methyl 2-((3E,5E)hepta-3,5-dienyl)-5-methylpyridine-3-carboxylate (4l)



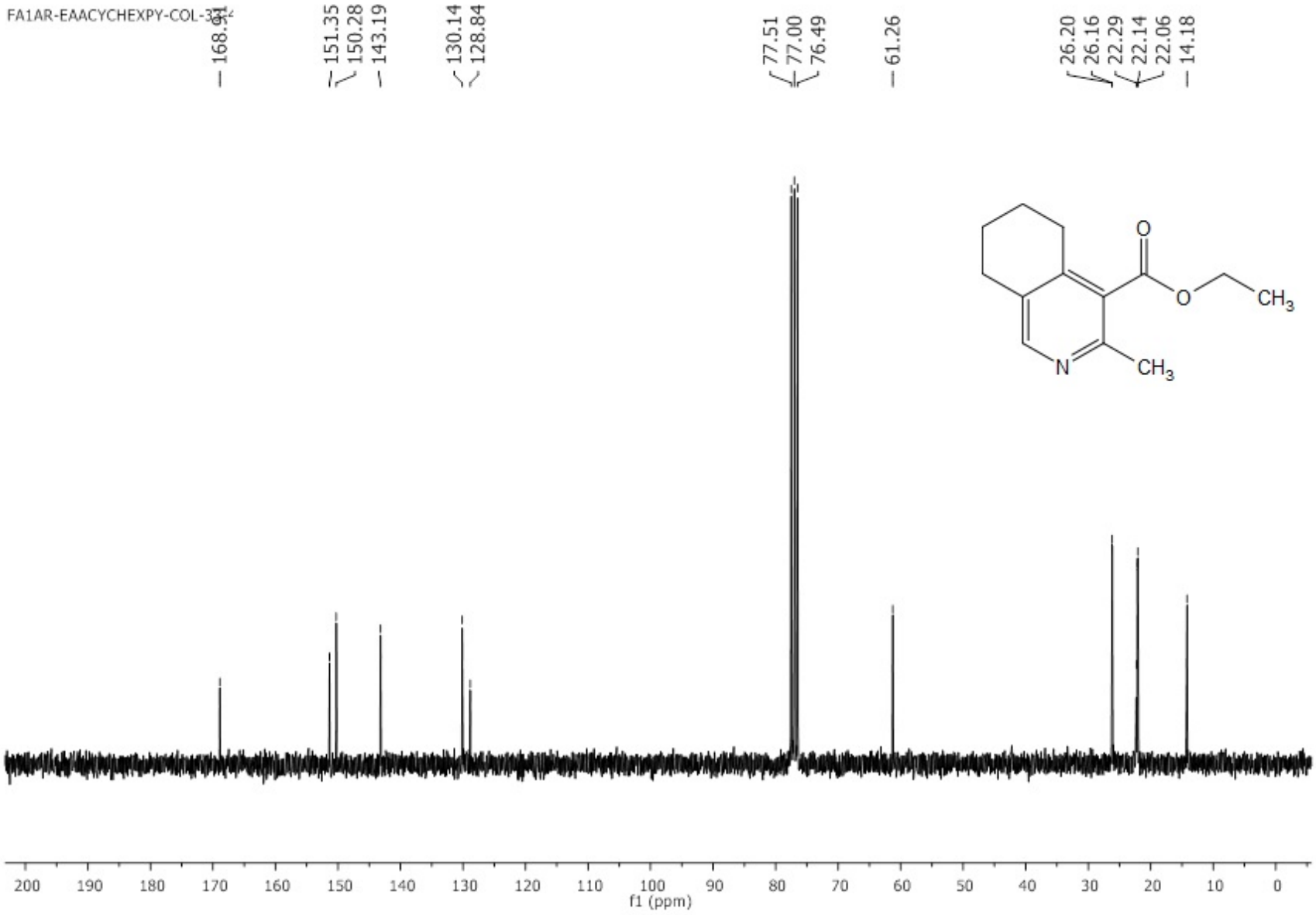
Methyl 2-((3E,5E)hepta-3,5-dienyl)-5-methylpyridine-3-carboxylate (4l)



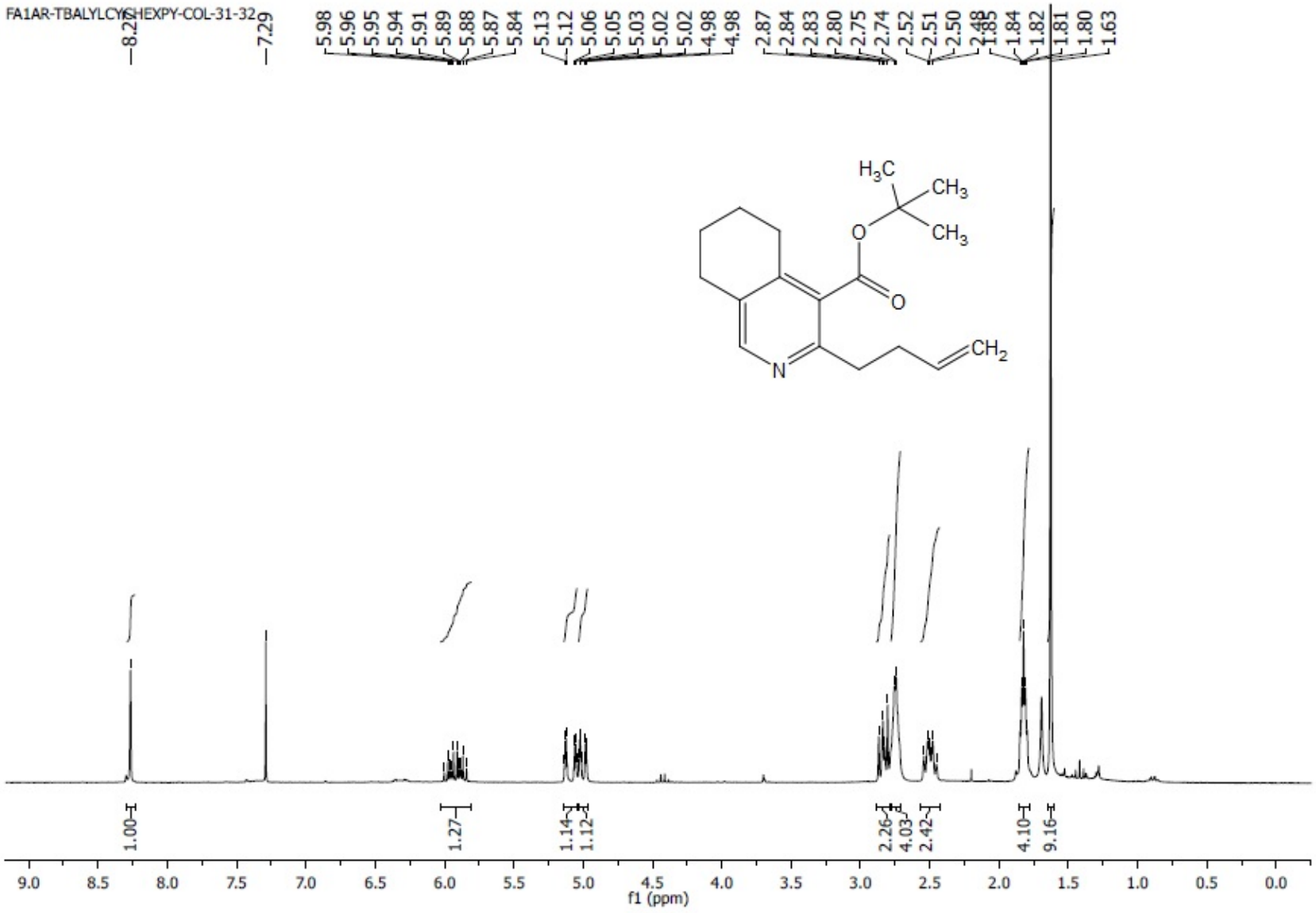
Ethyl 3-methyl-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7a)



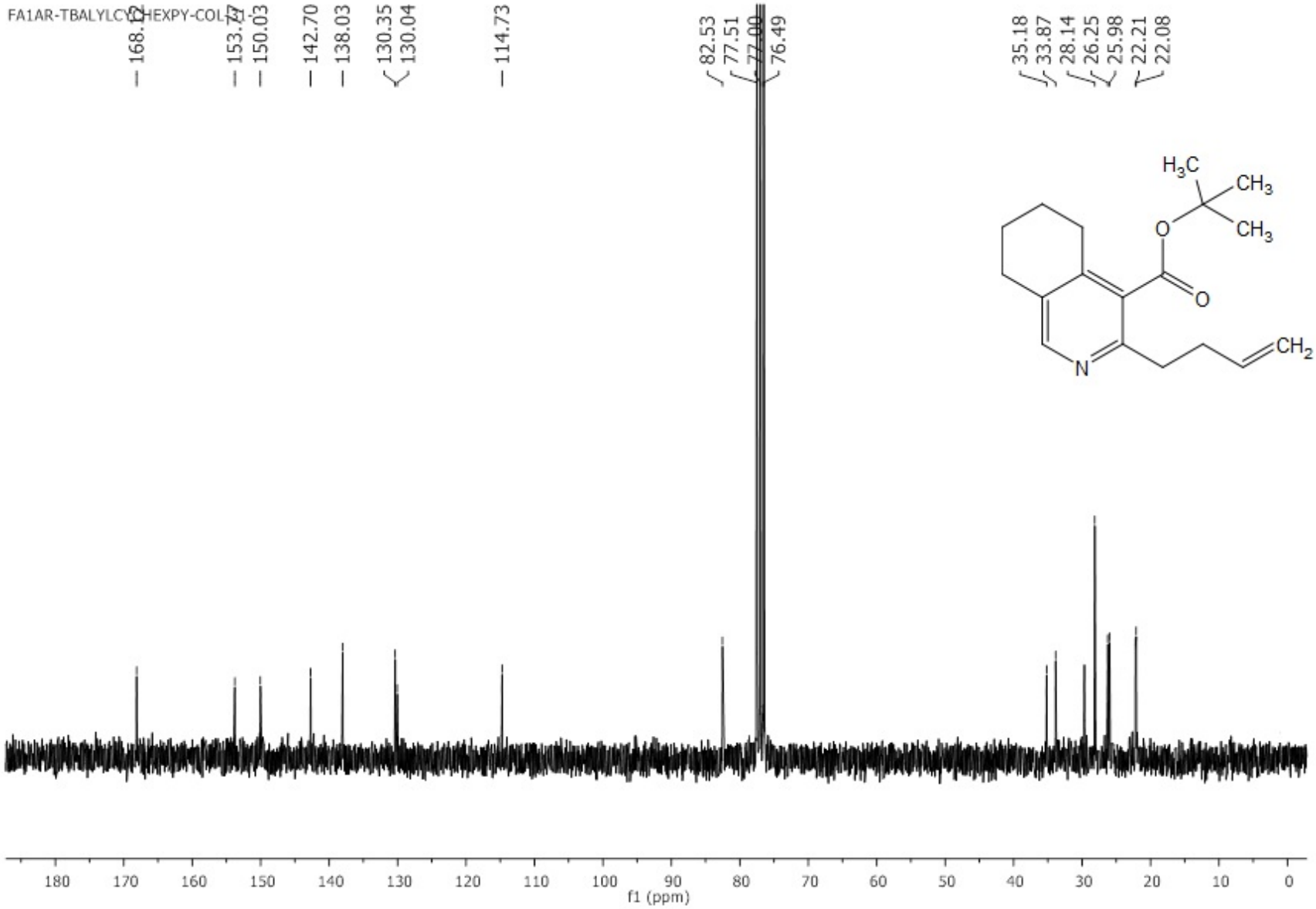
Ethyl 3-methyl-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7a)



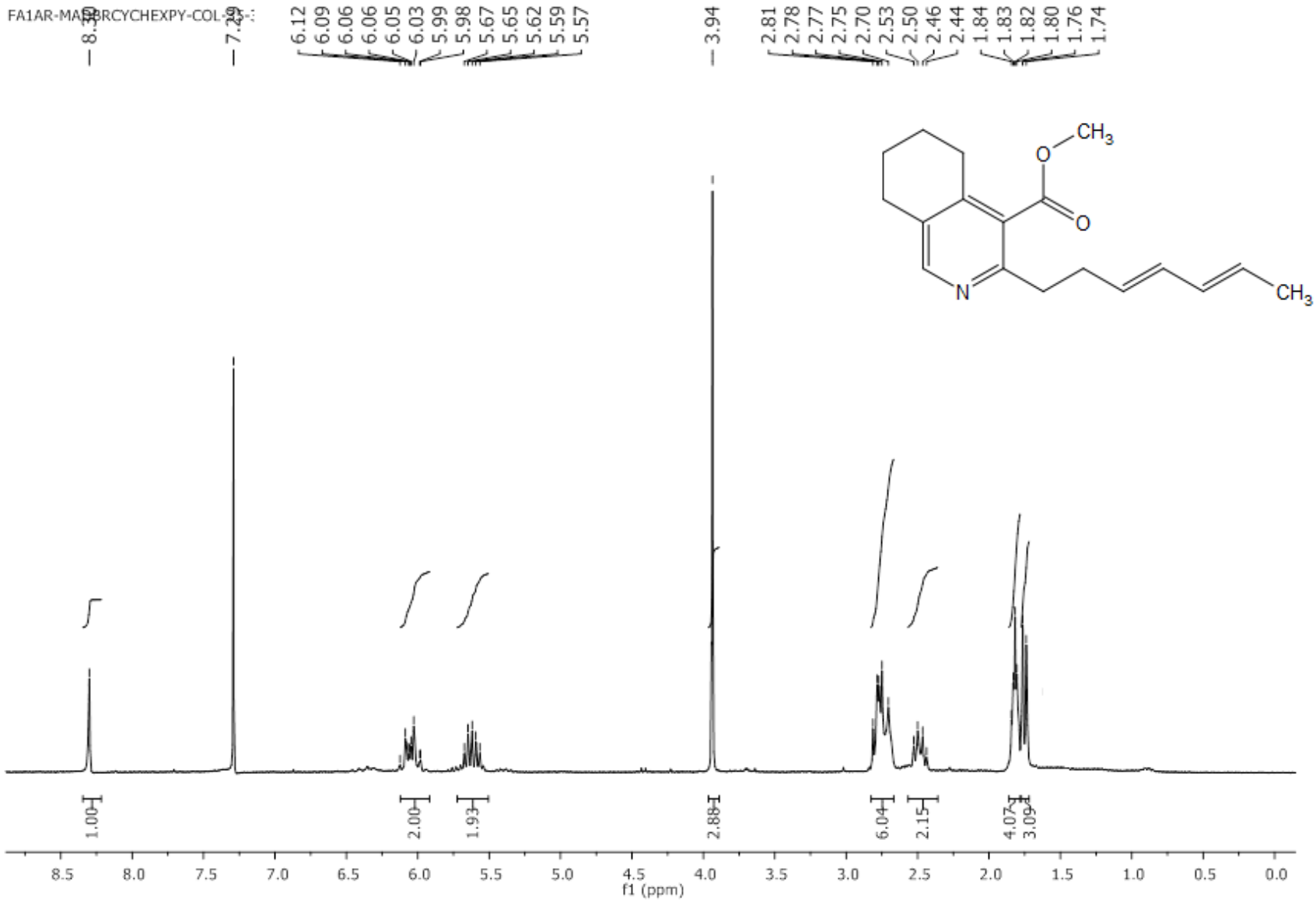
tert-Butyl 3-but-3-enyl-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7b)



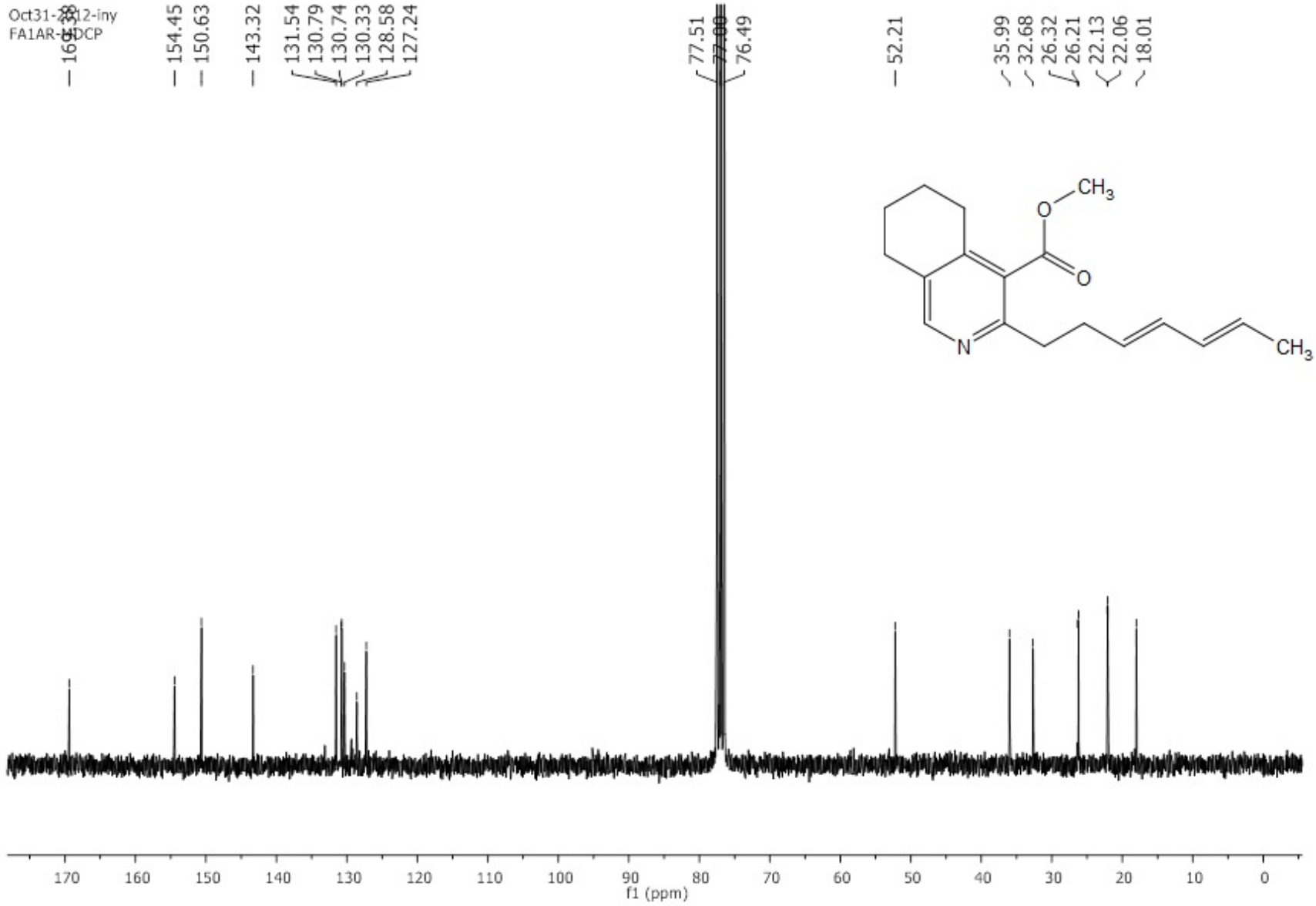
tert-Butyl 3-but-3-enyl-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7b)



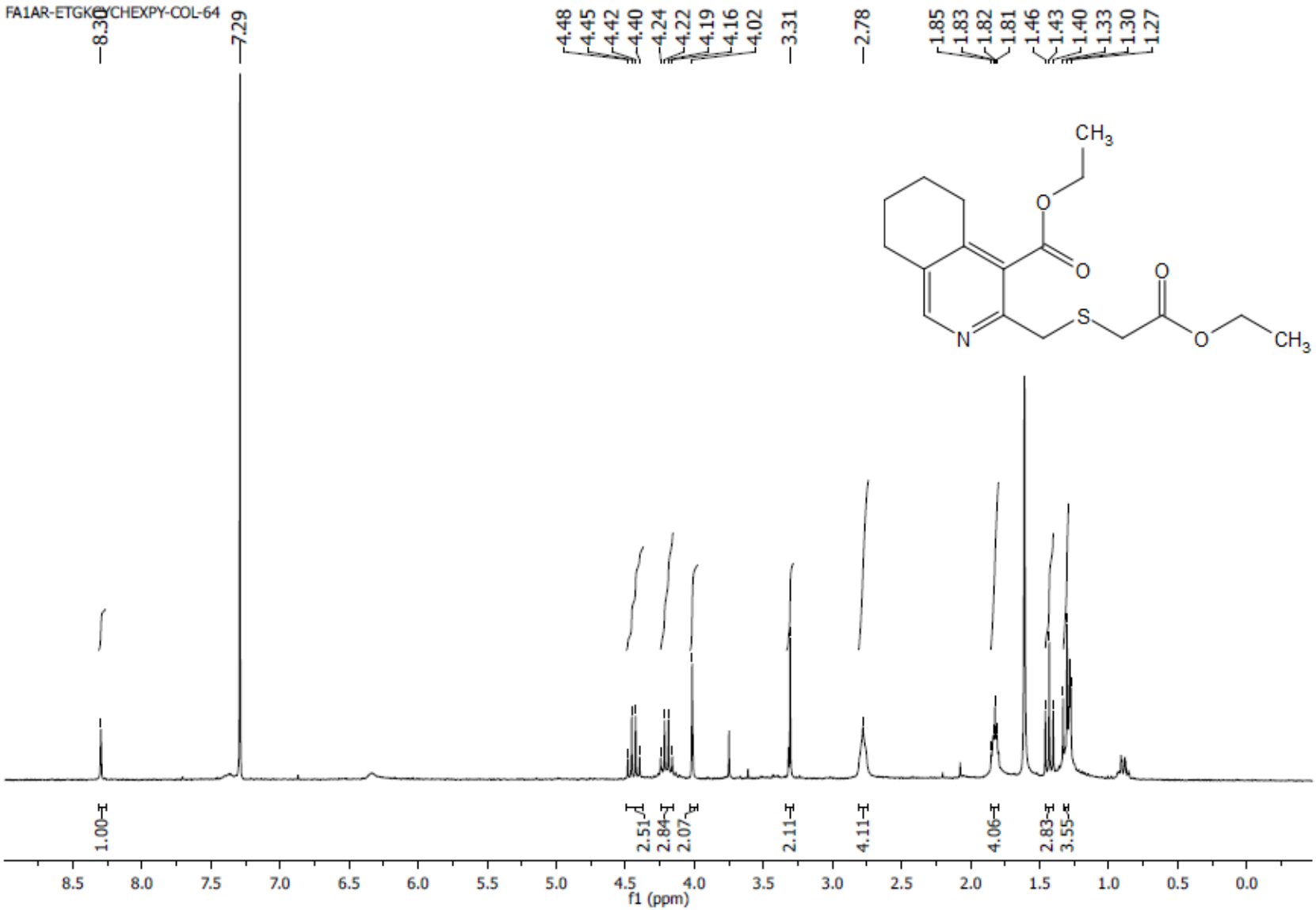
Methyl 3-((3E,5E)hepta-3,5-dienyl)-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7c)



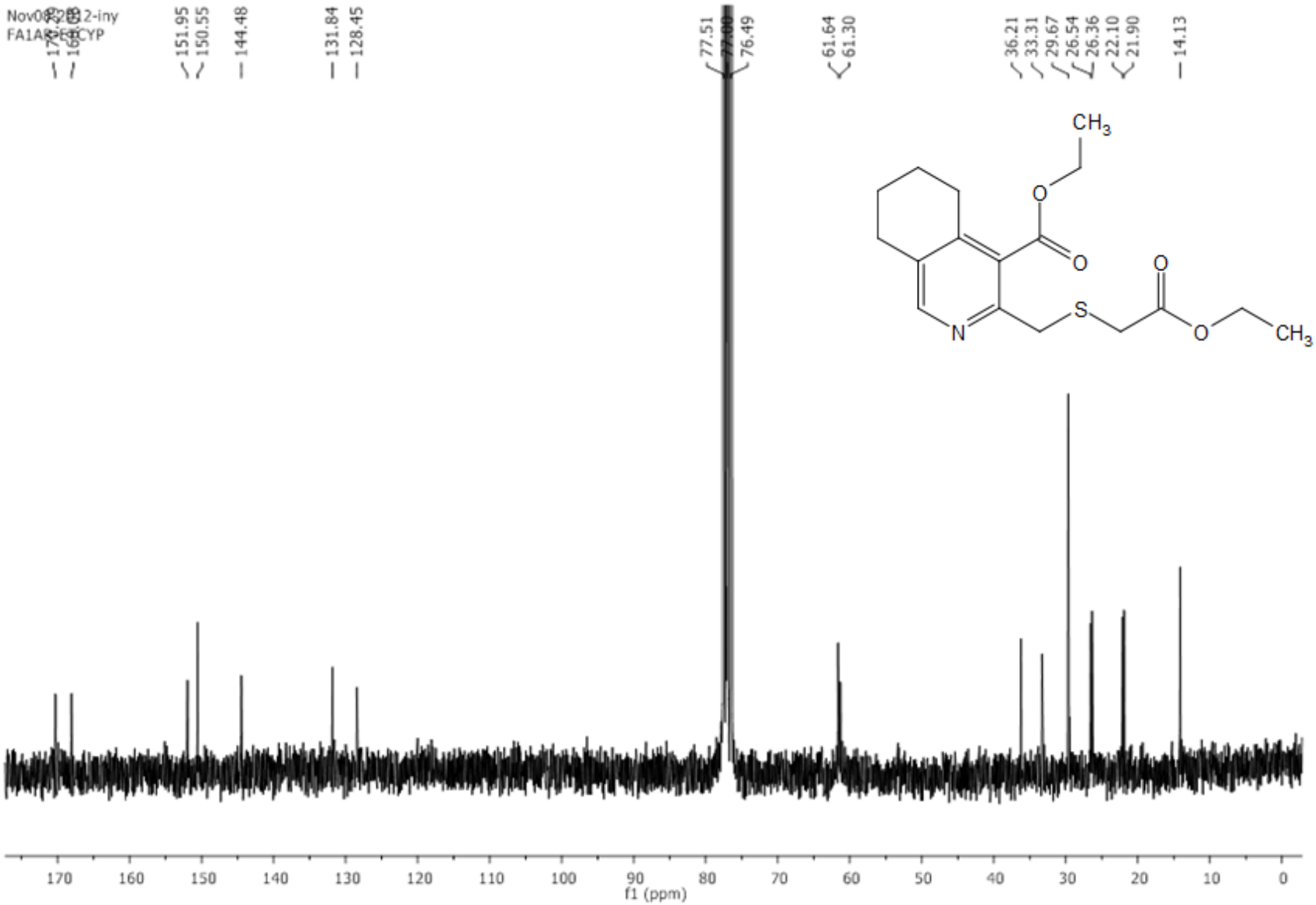
Methyl 3-((3E,5E)hepta-3,5-dienyl)-5,6,7,8-tetrahydroisoquinoline-4-carboxylate (7c)



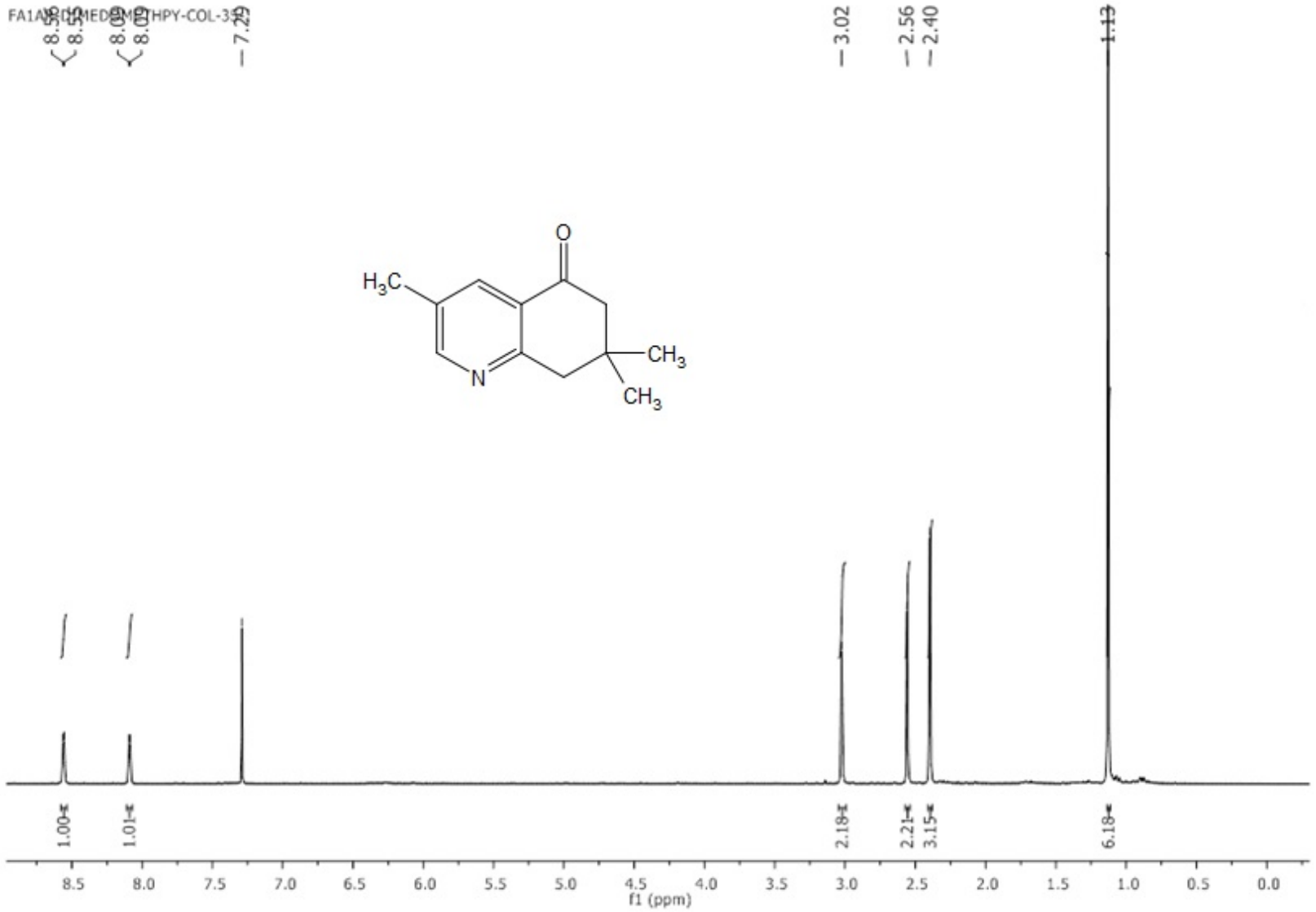
Ethyl 2-{[4-(ethoxycarbonyl)-3-5,6,7,8-tetrahydroisoquinolyl]methylthio}acetate (7d)



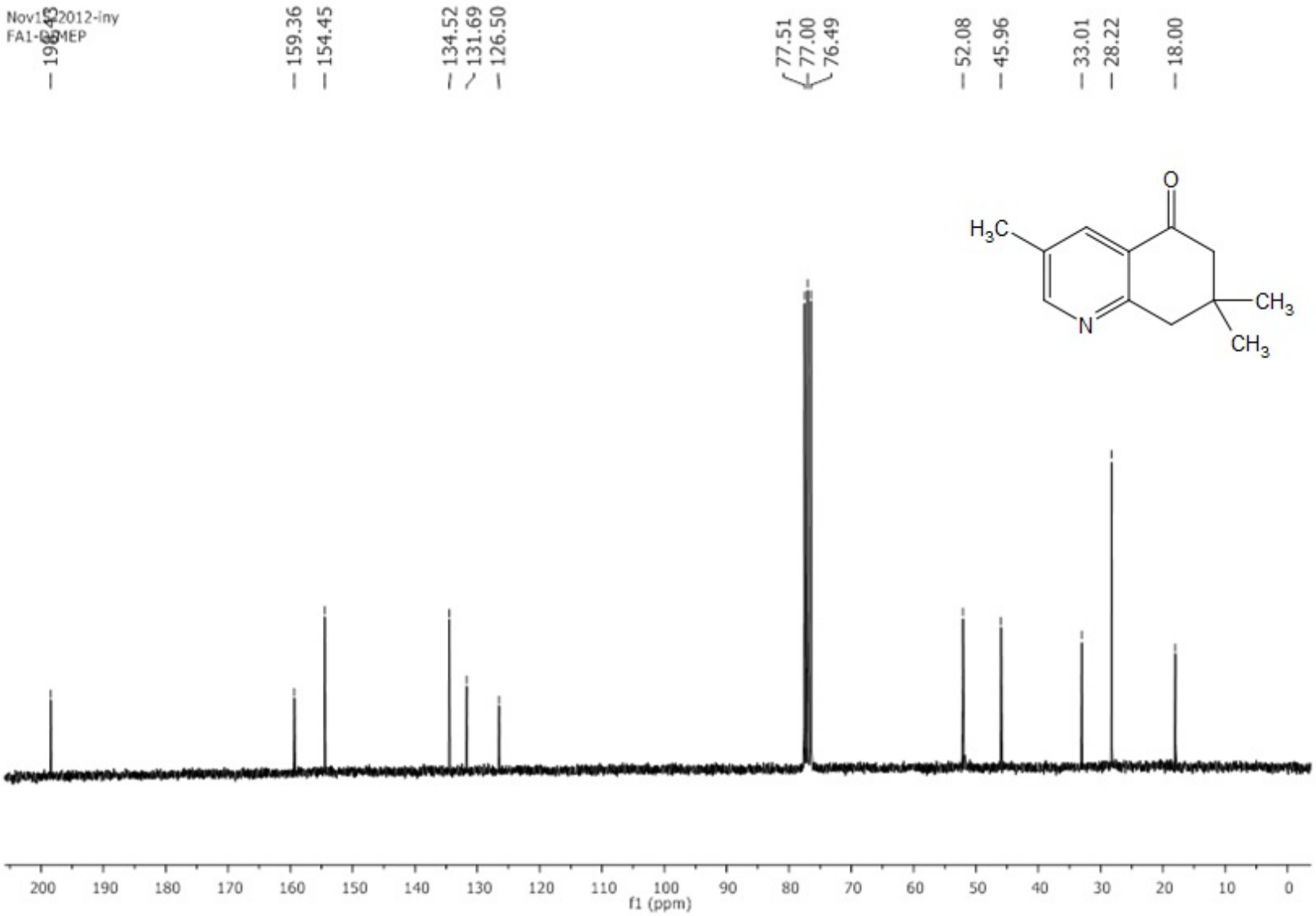
Ethyl 2-{[4-(ethoxycarbonyl)-3-5,6,7,8-tetrahydroisoquinolyl]methylthio}acetate (7d)



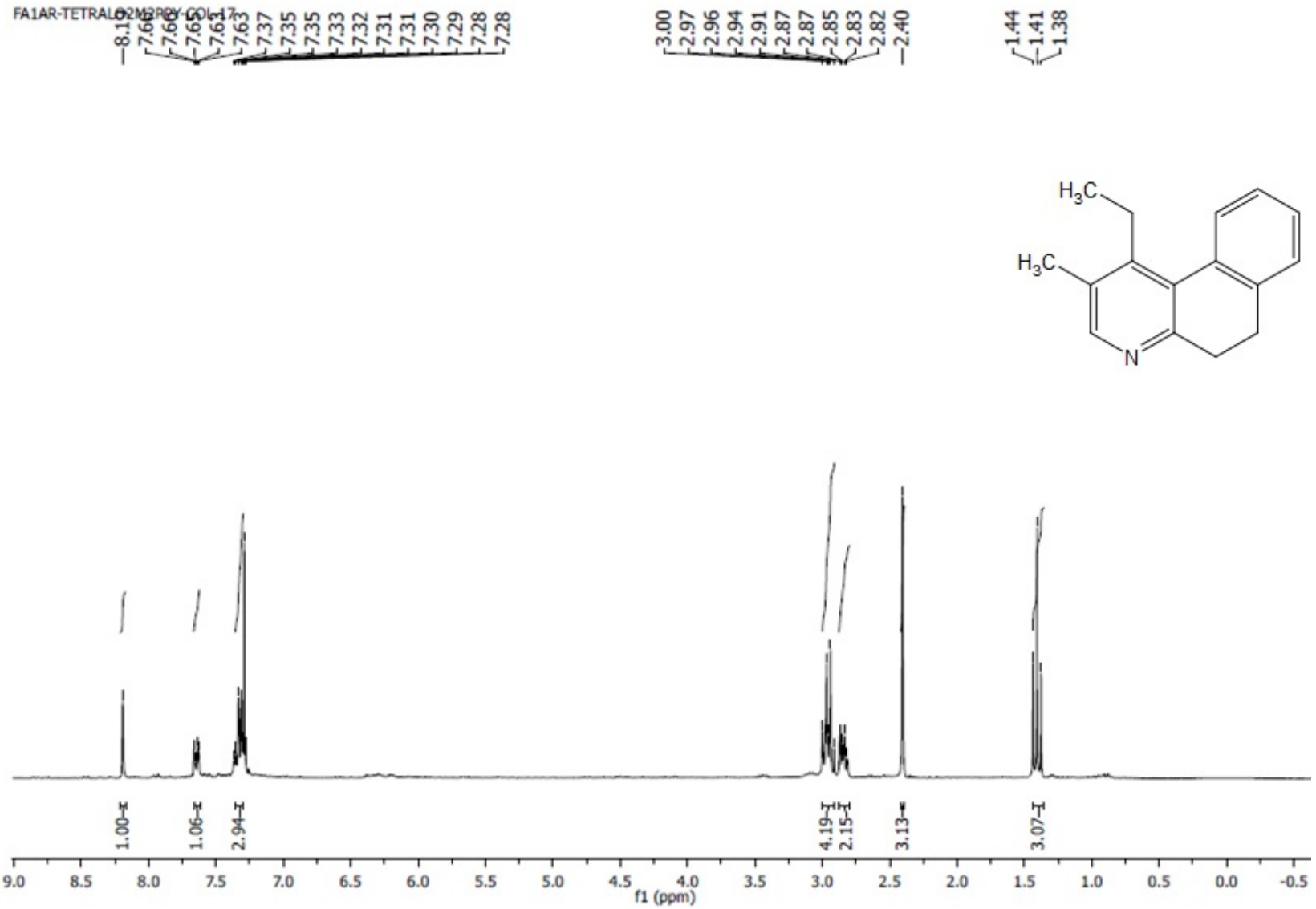
3,7,7-Trimethyl-7,8-dihydroquinolin-5(6*H*)-one (7e)



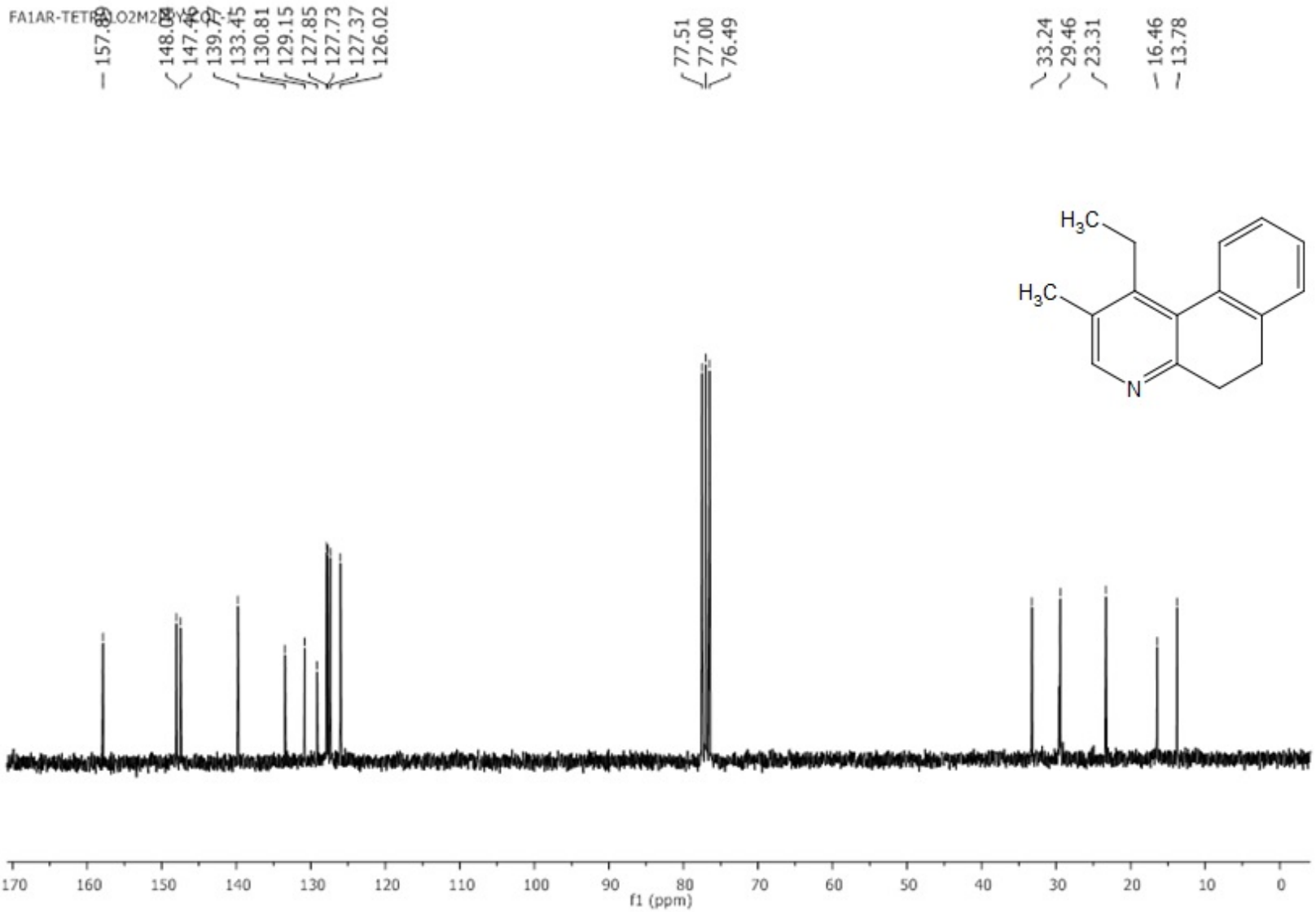
3,7,7-Trimethyl-7,8-dihydroquinolin-5(6*H*)-one (7e)



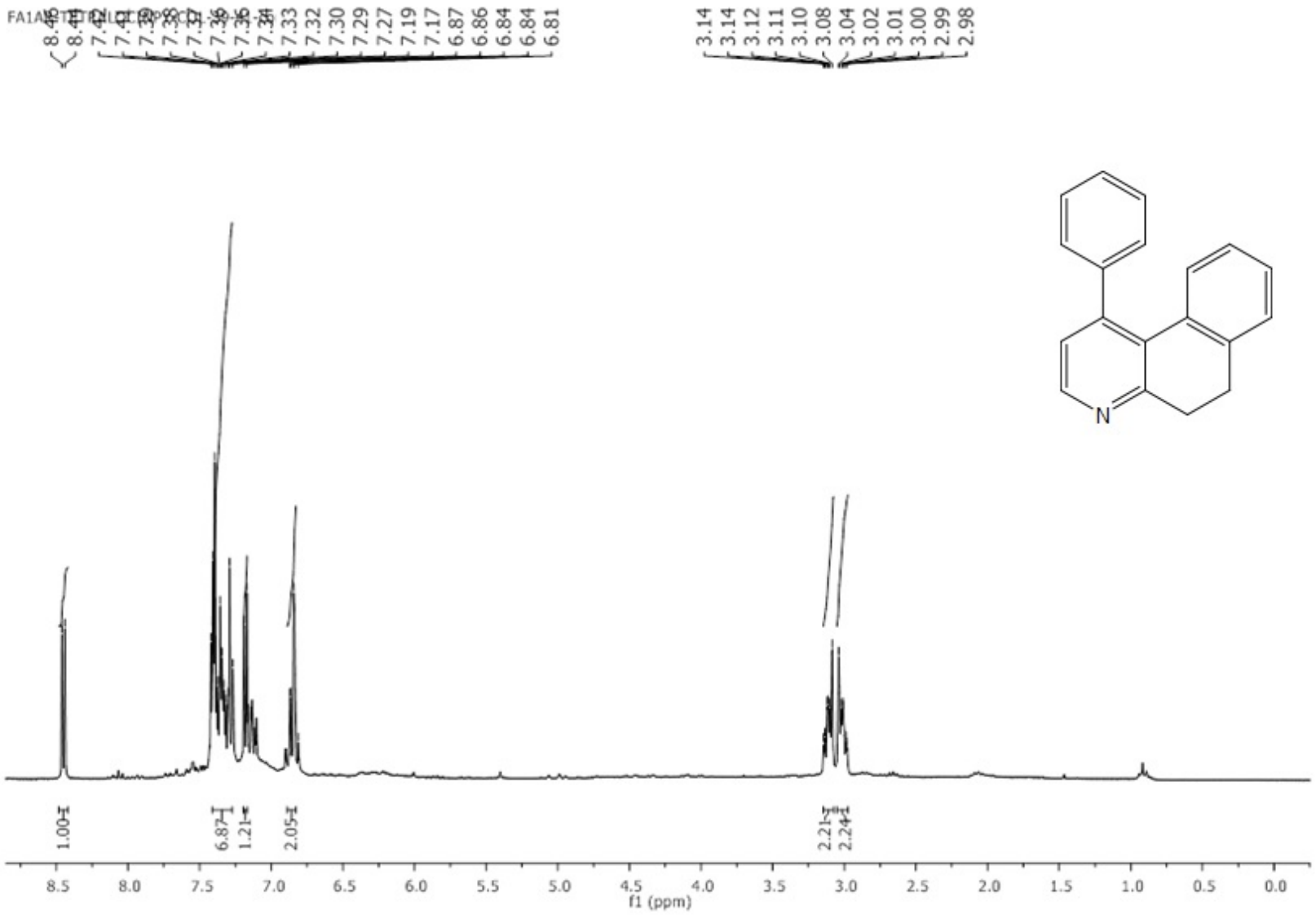
1-Ethyl-2-methyl-5,6-dihydrobenzo[*f*]quinoline (7f)



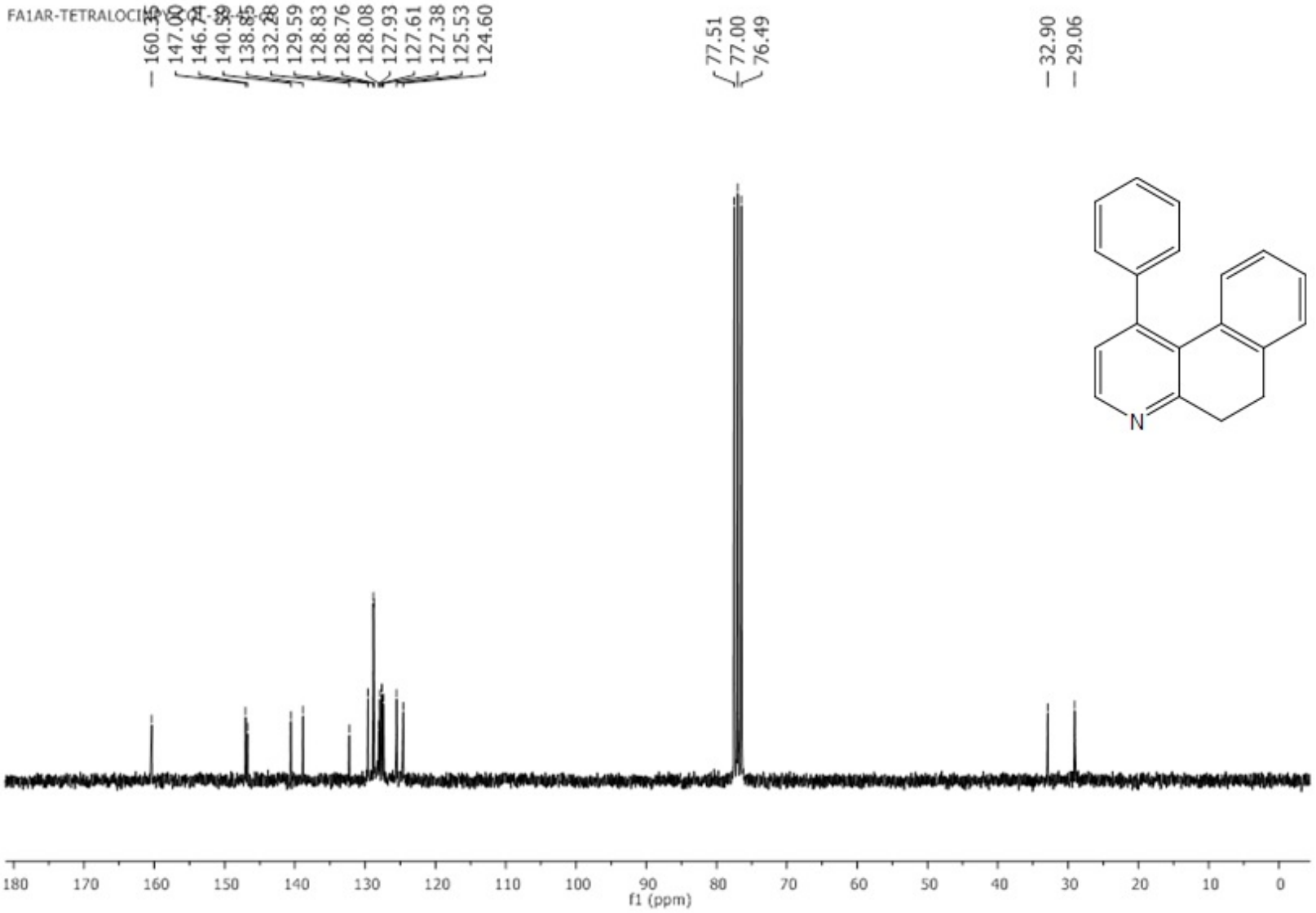
1-Ethyl-2-methyl-5,6-dihydrobenzo[*f*]quinoline (7f)



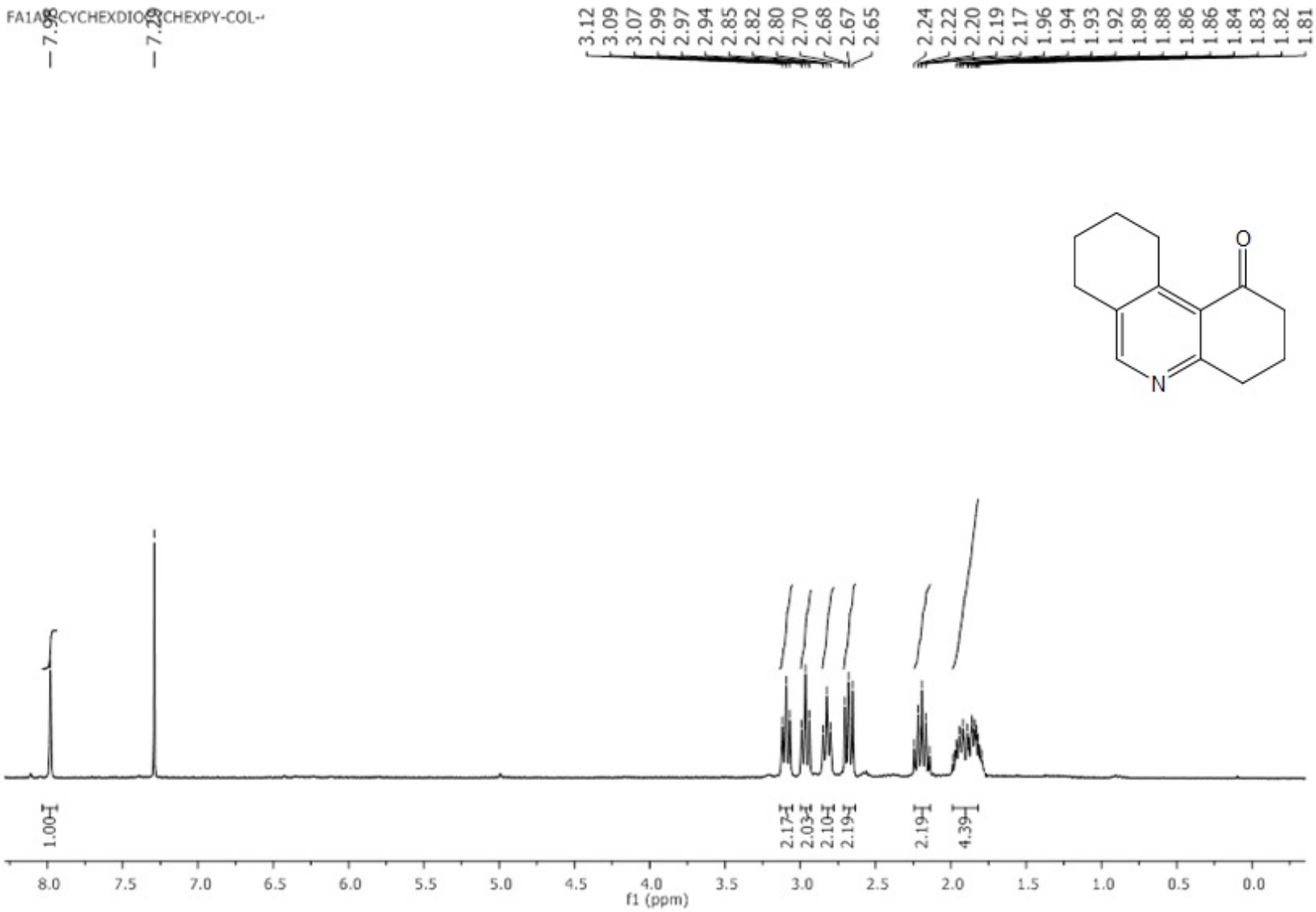
1-Phenyl-5,6-dihydrobenzo[*f*]quinolone (7g)



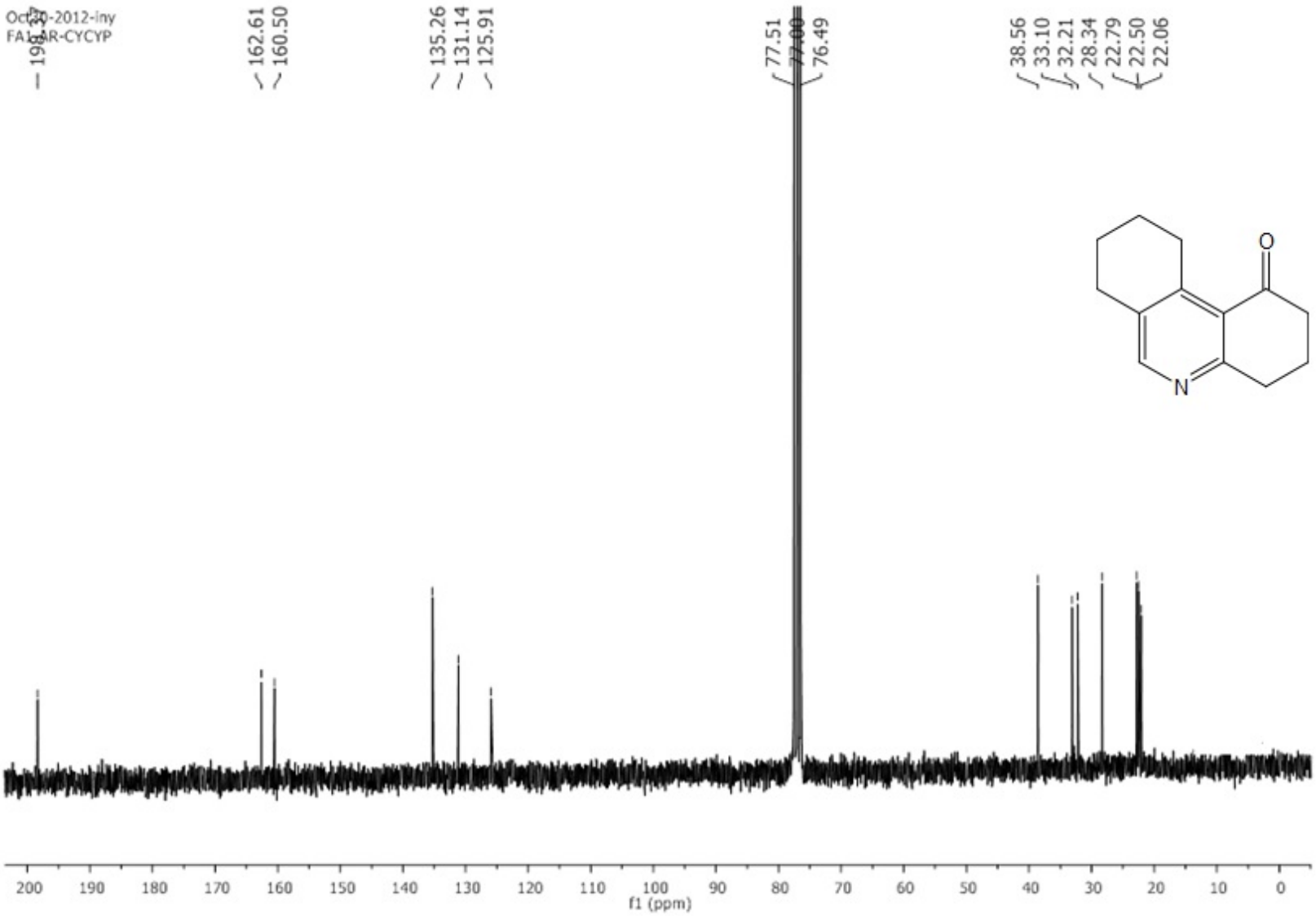
1-Phenyl-5,6-dihydrobenzo[*f*]quinolone (7g)



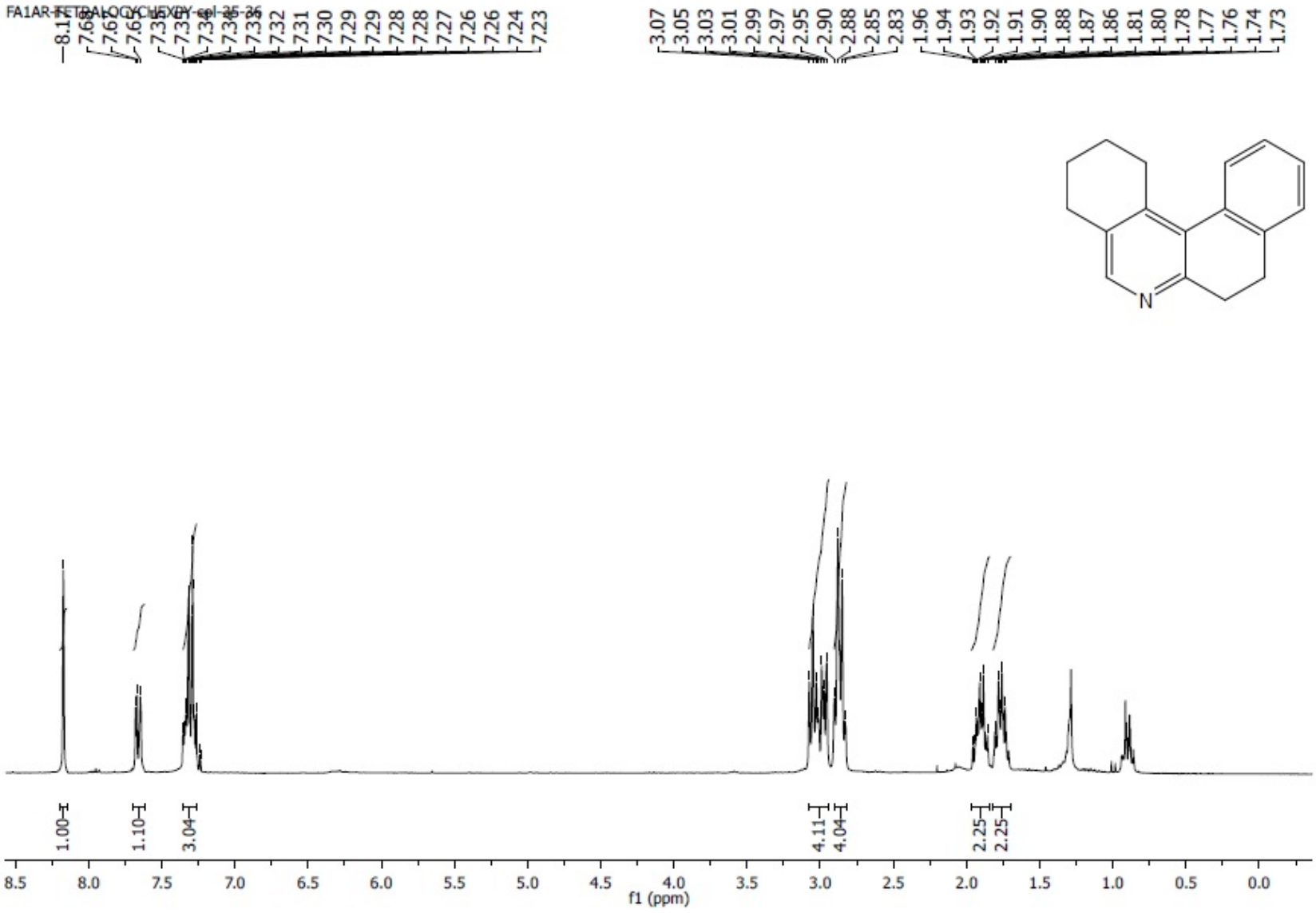
2,3,4,7,8,9,10-Heptahydrophenanthridin-1-one (7h)



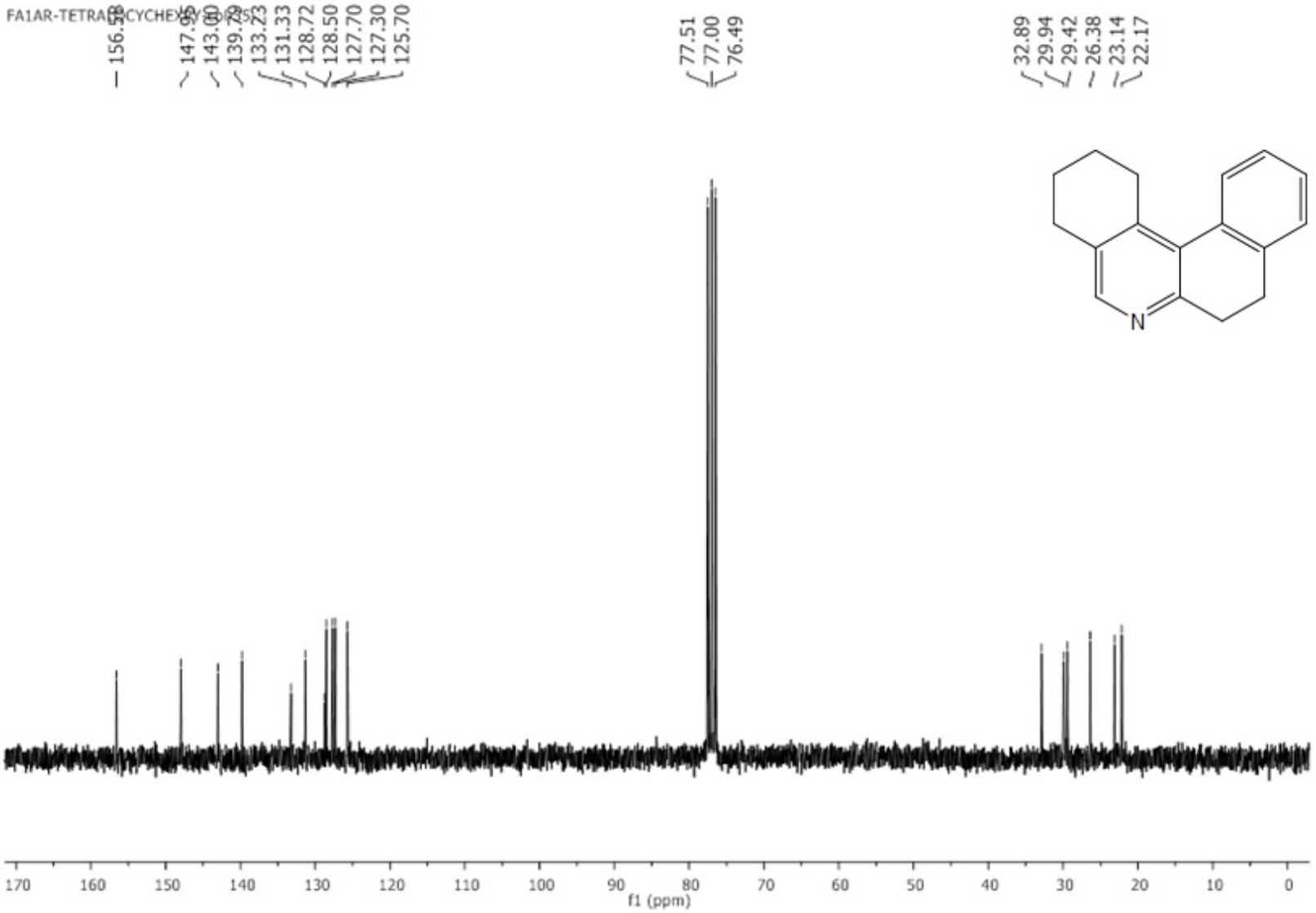
2,3,4,7,8,9,10-Heptahydrophenanthridin-1-one (7h)



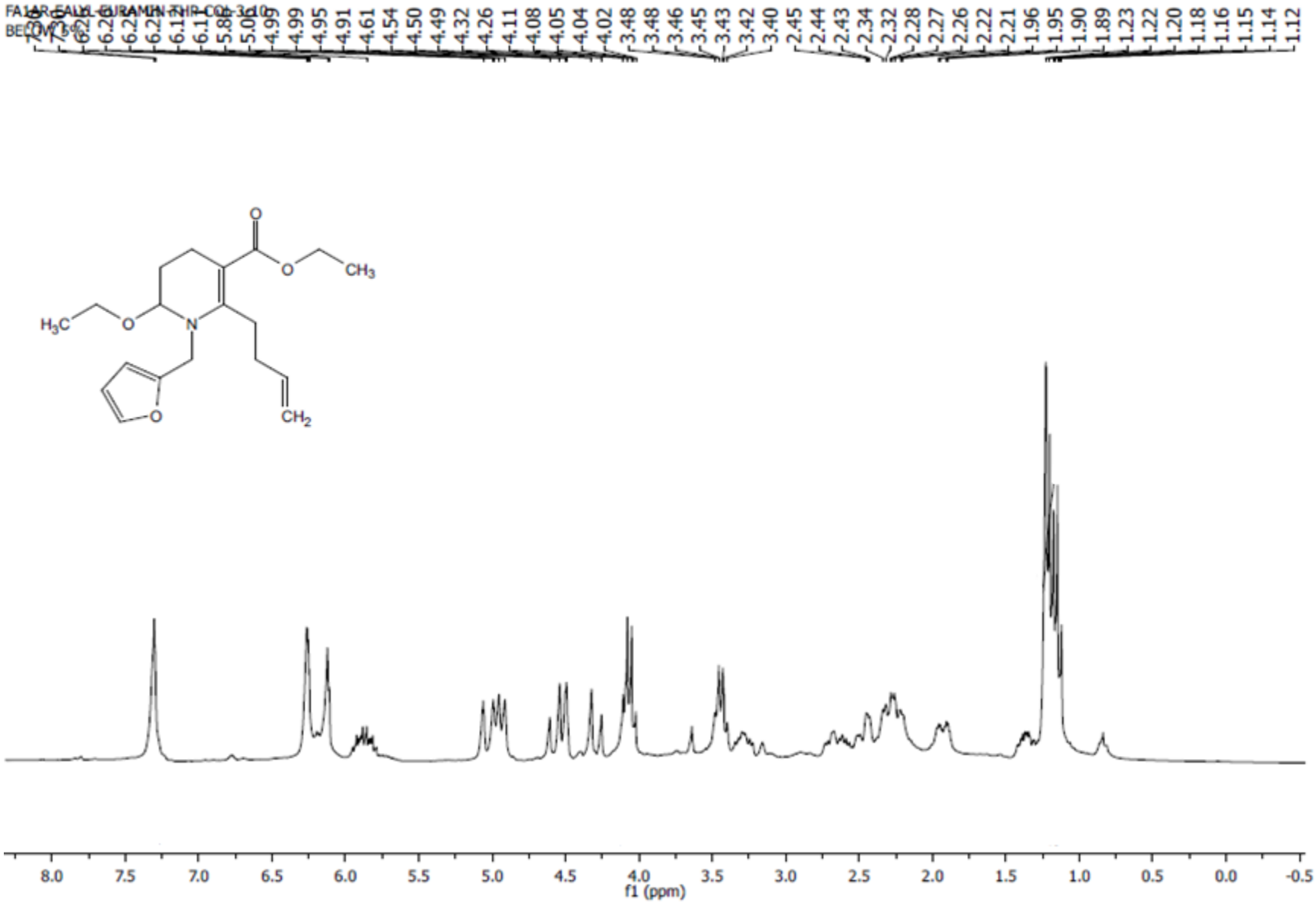
1,2,3,4,7,8-Hexahydrobenzo[*a*]phenanthridine (7i)



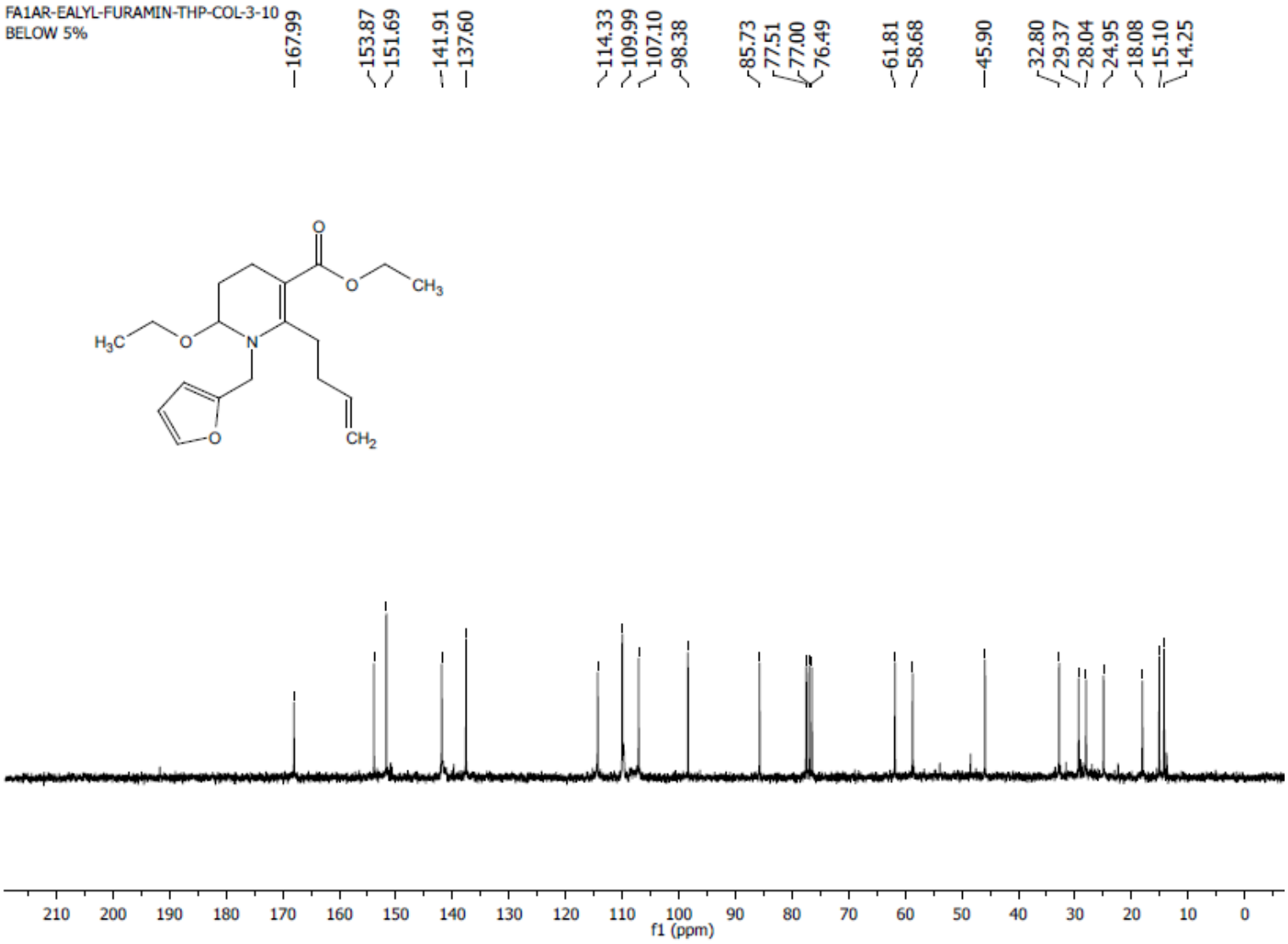
1,2,3,4,7,8-Hexahydrobenzo[*a*]phenanthridine (7i)



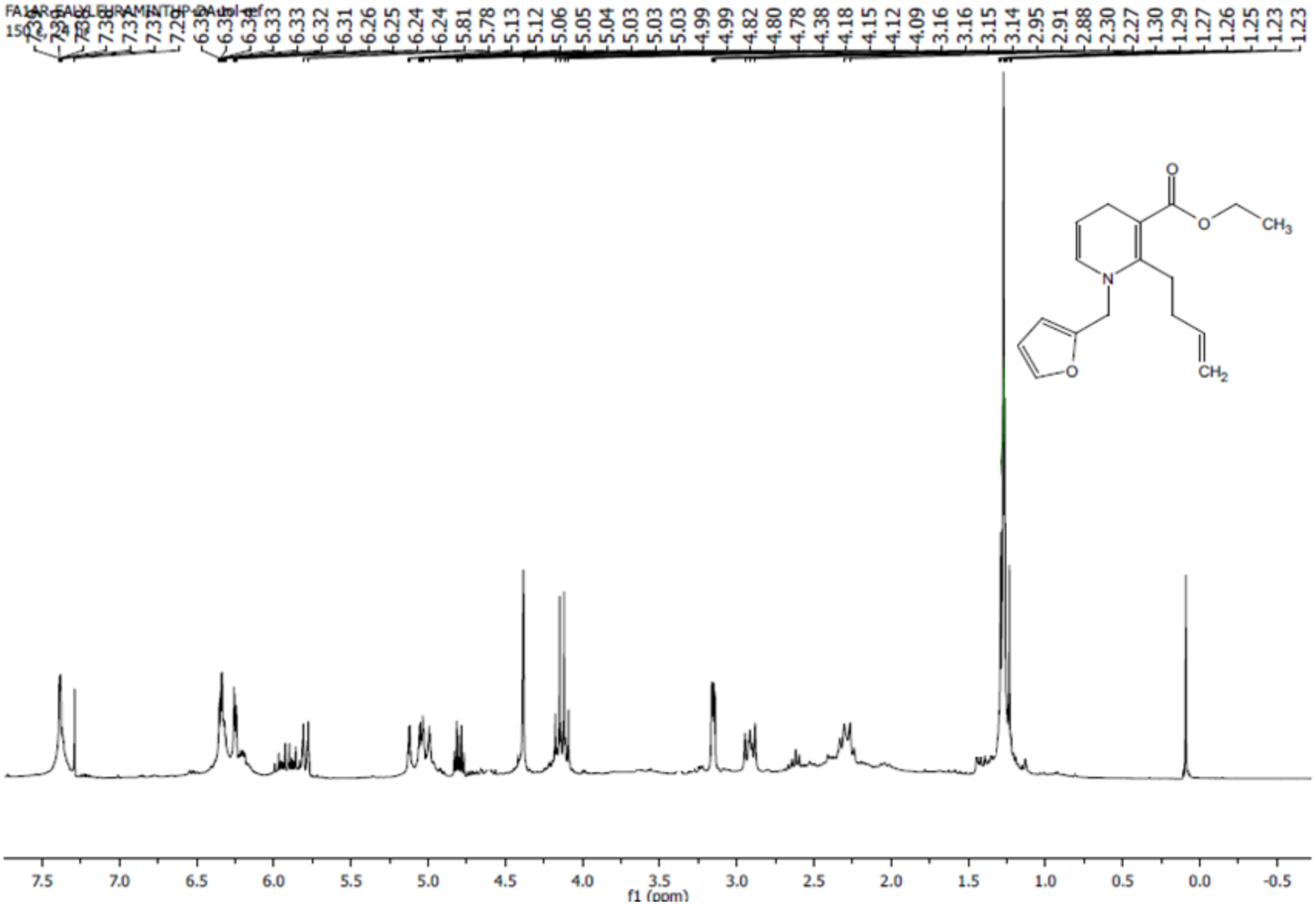
Ethyl 2-(3-butenyl)-6-ethoxy-1-(2-furylmethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate



Ethyl 2-(3-butenyl)-6-ethoxy-1-(2-furylmethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate



Ethyl 2-(3-butenyl)-1-(2-furylmethyl)-1,4-dihydropyridine-3-carboxylate



Ethyl 2-(3-butenyl)-1-(2-furylmethyl)-1,4-dihydropyridine-3-carboxylate