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Supporting Information

for

Unnatural α-amino ethyl esters from diethyl malonate or ethyl β-bromo-α-hydroxyiminocarboxylate

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Characterization of all the compounds described, scans of ^{1}H and ^{13}C NMR spectra

Experimental

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, respectively. Shifts (δ) are given in ppm with respect to the TMS signal and cross-coupling constants (*J*) are given in Hertz. Column chromatography were performed either on Merck silica gel 60 (0.035 - 0.070 mm) or neutral alumina using a solvent pump and an automated collecting system driven by a UV detector set to 254 nm unless required otherwise. Sample deposition was carried out by absorption of the mixture to be purified on a small amount of the solid phase followed by its deposition of the top of the column. The low resolution mass spectra were obtained on an Agilent 1200 series LC/MSD system using an Agilent Jet-Stream atmospheric electrospray ionization system and the high resolution mass spectra (HRMS) were obtained using a Waters Micromass Q-TOF with an electrospray ion source.

General preparation of α-hydroxyimino esters 2a–aj: Step 1, Knoevenagel condensation of diethyl malonate and aldehydes, preparation of substituted diethyl 2-methylenemalonate **6**. Under an inert atmosphere, the corresponding aldehyde (0.047 mol), diethyl malonate (7.54 g, 0.047 mol), acetic acid (0.14 g, 0.002 mol), piperidine (0.2 g, 0.002 mol) and 4 Å molecular sieve (15 g) were heated in dry ethanol (20 mL, dried over 4 Å molecular sieves) without stirring at 60 °C for 10 hours. Unless stated below in particle cases, the ^{1}H NMR spectra of a crude sample pointed out the complete disappearance of the starting aldehyde. Step 2, reduction of the substituted diethyl 2-methylenemalonates **6**, preparation of the substituted malonates **3**. The suspension containing the 4 Å molecular sieve described above was filtered and the solid washed with dry ethanol. When relevant, 10% palladium over charcoal (1.27 g, 0.001 mol) was added to the resulting ethanol solution (160 mL total volume) and this was stirred overnight under a hydrogen atmosphere (1 atm). The resulting suspension was filtered, the filtrate concentrated to dryness to give fairly pure substituted malonates **3**. Alternatively, this hydrogenation was achieved by the addition, at 0 °C, of

sodium boron hydride (1.1 equiv) in small portions to the ethanolic solution and stirring overnight at 0 °C. This was followed by its (cautious) acidification with acetic acid, dilution in an excess of water extraction with ethyl acetate. The organic layer was then washed with water, brine, dried over magnesium sulfate and concentrated to dryness to yield the crude substituted malonates **3**. Step 3, preparation of α-hydroxyimino esters **2**. The crude substituted malonate (0.0422 mol) was dissolved in ethanol (60 mL, dried over 4 Å molecular sieve) and cooled to 0 °C. A 21% solution of sodium ethoxide in ethanol was added (18.4 mL, 0.0493 mol) followed by a slow addition of isoamyl nitrite (6.2 mL, 0.046 mol). This was stirred at 0 °C for two hours, made slightly acid by the addition of 1 N hydrochloric acid and diluted in water (200 mL). The solution was extracted with ethyl acetate, the organic layer was washed with water, brine, dried over magnesium sulfate and concentrated to dryness to yield the crude α-hydroxyimino esters **2** which were further purified as described below.

Ethyl 2-(hydroxyimino)-3-phenylpropanoate (2a): Obtained as a white solid (3.55 g, 60% from 3 g of benzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.76 (s, 1H, OH), 7.29 (m, 4H), 7.22 (m, 1H), 4.29 (q, 2H, *J* = 7.1 Hz), 3.99 (s, 2H), 1.32 (t, 3H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 163.2, 151.0, 135.7, 129.2, 128.5, 126.7, 61.9, 30.5, 26.9, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{13}NO_3Na$: 230.0793, found, 230.0800.

Ethyl 2-(hydroxyimino)-3-(o-tolyl)propanoate (2b): Obtained as a white solid (3.38 g, 61% from 3 g of 2-methylbenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 10.09 (s, 1H), 7.16 (m, 4H), 4.28 (q, 2H, *J* = 7.1 Hz), 4.00 (s, 2H), 2.41 (s, 3H), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.4, 151.2, 136.5, 133.9, 130.3, 128.6, 126.7, 126.0, 61.9, 27.9, 19.7, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NO_3Na$: 244.0950, found, 244.0942.

Ethyl 2-(hydroxyimino)-3-(m-tolyl)propanoate (2c): Obtained as an oil (3.71 g, 63% from 3.15 g of 3-methylbenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 6/1). ^{1}H NMR ($CDCl_3$): 9.59 (s, 1H), 7.16 (m, 3H), 7.05 (m, 1H), 4.31 (q, 2H, *J* = 7.1

Hz), 3.97 (s, 2H), 2.33 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.2, 151.1, 138.1, 135.6, 129.9, 128.4, 127.4, 126.2, 61.9, 30.4, 21.3, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NO_3Na$: 244.0950, found, 244.0954.

Ethyl 2-(hydroxyimino)-3-(p-tolyl)propanoate (2d): Obtained as a white solid (3.31 g, 60% from 3 g of 4-methylbenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 10.07 (s, 1H), 7.24 (m, 2H), 7.11 (m, 2H), 4.31 (q, 2H, *J* = 7.1 Hz), 3.97 (s, 2H), 2.35 (s, 3H), 1.35 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.3, 151.1, 136.2, 132.7, 129.2, 129.1, 61.9, 30.1, 21.0, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NO_3Na$: 244.0950, found, 244.0944.

Ethyl 2-(hydroxyimino)-3-(4-isopropylphenyl)propanoate (2e): Obtained as a solid (2.04 g, 48% from 2.5 g of 4-isopropylbenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.74 (s, 1H), 7.26 – 7.22 (m, 2H), 7.16 – 7.11 (m, 2H), 4.29 (q, 2H, *J* = 7.1 Hz), 3.95 (s, 2H), 2.87 (hept, 1H, *J* = 6.9 Hz), 1.32 (t, 3H, *J* = 7.1 Hz), 1.23 (d, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$): 163.3, 151.2, 147.2, 133.0, 129.1, 126.6, 61.8, 33.7, 30.1, 24.0, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{19}NO_3Na$, 272.1263, found, 272.1258.

Ethyl 3-cyclopentyl-2-(hydroxyimino)propanoate (2f): Obtained as a white solid (2.50 g, 35% from 3.49 g of cyclopentanecarbaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 85/15). ^{1}H NMR ($CDCl_3$): 9.51 (s, 1H), 4.32 (q, 2H, *J* = 7.0 Hz), 2.67 (d, 2H, *J* = 7.6 Hz), 2.20 (m, 1H), 1.70 (m, 4H), 1.53 (m, 2H), 1.36 (t, 3H, *J* = 7.0 Hz), 1.25 (m, 2H). ^{13}C NMR ($CDCl_3$): 163.8, 152.9, 61.6, 37.4, 32.5, 29.9, 24.7, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_{17}NO_3Na$: 222.1106, found, 222.1164.

Ethyl 3-cyclohexyl-2-(hydroxyimino)propanoate (2g): Obtained as a white solid (4.34 g, 50% from 4.50 g of cyclohexanecarbaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 9/1). ^{1}H NMR ($CDCl_3$): 9.85 (s, 1H), 4.31 (q, 2H, *J* = 7.2 Hz), 2.55 (d, 2H, *J* = 7.1 Hz), 1.70 (m, 6H), 1.36 (t, 3H, *J* = 7.0 Hz), 1.20 (m, 3H), 1.04 (m, 2H).

^{13}C NMR ($CDCl_3$): 163.8, 152.3, 61.6, 35.8, 33.3, 31.9, 26.2, 26.1, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{19}NO_3Na$: 236.1263, found, 236.1291.

Ethyl 2-(hydroxyimino)-3-(2-(trifluoromethyl)phenyl)propanoate (2h): Obtained as a white solid (4.65 g, 39% from 7.5 g of 2-(trifluoromethyl)benzaldehyde) after a recrystallization in n-heptane (plus charcoal decolourisation). ^{1}H NMR ($CDCl_3$): 9.66 (s, 1H), 7.68 (d(br), 1H, *J* = 7.5 Hz), 7.45 (m, 1H), 7.34 (m, 1H), 7.6 (d(br), 1H, *J* = 7.7 Hz), 4.29 (q, 2H, *J* = 7.2 Hz), 4.23 (s, 2H), 1.27 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 161.0, 150.5, 134.1, 131.9, 129.0, 128.5 (29 Hz), 126.6, 126.2 (6 Hz), 124.4 (273 Hz), 62.1, 27.3, 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{12}F_3NO_3Na$: 298.0667, found, 298.0660.

Ethyl 2-(hydroxyimino)-3-(3-(trifluoromethyl)phenyl)propanoate (2i): Obtained as a white solid (1.3 g, 41% from 2.01 g of 3-(trifluoromethyl)benzaldehyde)) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1 to 3/1). ^{1}H NMR ($CDCl_3$): 9.87 (s, 1H), 7.62 (s(br), 1H), 7.50 (m, 2H), 7.42 (m, 1H), 4.32 (q, 2H, *J* = 7.0 Hz), 4.05 (s, 2H), 1.35 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): 162.9, 150.2, 136.6, 132.6, 130.9 (32 Hz), 128.9, 126.1 (4 Hz), 124.1 (273 Hz), 123.6 (4 Hz), 62.1, 30.3, 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{12}F_3NO_3Na$: 298.0667, found, 298.0643.

Ethyl 2-(hydroxyimino)-3-(4-(trifluoromethyl)phenyl)propanoate (2j): Obtained as a white solid (4.61 g, 62% from 4.71 g of 4-(trifluoromethyl)benzaldehyde)) after a chromatography over silica gel (dichloromethane – ethanol 99/1). ^{1}H NMR ($CDCl_3$): 9.76 (s, 1H), 7.55 (m, 2H), 7.45 (m, 2H), 4.32 (q, 2H, *J* = 7.1 Hz), 4.05 (s, 2H), 1.35 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 150.2, 139.7, 129.5, 129.1 (32 Hz), 125.4 (4 Hz), 124.3 (272 Hz), 62.1, 30.4, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{13}F_3NO_3$: 276.0847, found, 276.0834.

Ethyl 3-(2-fluorophenyl)-2-(hydroxyimino)propanoate (2k): Obtained as a white solid (3.11 g, 57% from 3 g of 2-fluorobenzaldehyde), after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 10.20 (s, 1H), 7.22 (m, 2H), 7.05 (m, 2H), 4.30 (q, 2H, *J* = 7.1 Hz), 4.04 (s, 2H), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.1,

160.9 (247 Hz), 150.1, 130.6 (4 Hz), 128.3 (8 Hz), 124.0 (4 Hz), 122.8 (16 Hz), 115.3 (23 Hz), 62.0, 23.7 (4 Hz), 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_3Na$: 248.0699, found, 248.0704.

Ethyl 3-(3-fluorophenyl)-2-(hydroxyimino)propanoate (2l): Obtained as a white solid (9.46 g, 65% from 7.95 g of 3-fluorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^1H NMR ($CDCl_3$): 10.02 (s, 1H), 7.25 (m, 1H), 7.10 (m, 1H), 7.06 (m, 1H), 6.92 (m, 1H), 4.32 (q, 2H, *J* = 7.2 Hz), 3.99 (s, 2H), 3.74 (m, 1H), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 162.9 (245 Hz), 150.3, 138.0 (6 Hz), 129.8 (8 Hz), 124.8 (3 Hz), 116.2 (22 Hz), 113.6 (21 Hz), 62.0, 30.2, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_3Na$: 248.0699, found, 248.0699.

Ethyl 3-(4-fluorophenyl)-2-(hydroxyimino)propanoate (2m): Out of a 14.80 g crude batch, only a sample (0.51 g) was purified by a chromatography over silica gel (dichloromethane – ethanol 99/1 to 98/2) to give a white solid (0.41 g). ^1H NMR ($CDCl_3$): 9.88 (s, 1H), 7.30 (m, 2H), 6.97 (m, 2H), 4.31 (q, 2H, *J* = 7.2 Hz), 3.91 (s, 2H), 3.74 (m, 1H), 1.34 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.1, 161.7 (245 Hz), 150.8, 131.3 (3 Hz), 130.7 (8 Hz), 115.3 (21 Hz), 62.0, 29.7, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{13}FNO_3$: 226.0879, found, 226.0878.

Ethyl 3-(2,4-difluorophenyl)-2-(hydroxyimino)propanoate (2n): Obtained as a white solid (2.21 g, 50% from 2.57 g of 2,4-difluorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 6/1). ^1H NMR ($CDCl_3$): ^1H NMR ($CDCl_3$): 9.72 (s, 1H), 7.22 (m, 1H), 6.80 (m, 2H), 4.30 (q, 2H, *J* = 7.1 Hz), 3.98 (s, 2H), 1.33 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.1, 161.8 (12 and 248 Hz), 160.8 (12 and 249 Hz), 149.9, 131.2 (5 and 9 Hz), 118.5 (4 and 16 Hz), 111.1 (4 and 21 Hz), 103.7 (25 Hz), 62.1, 23.1 (4 Hz), 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}F_2NO_3Na$: 266.0605, found, 266.0601.

Ethyl 3-(2,6-difluorophenyl)-2-(hydroxyimino)propanoate (2o): Obtained as a white solid (4.66 g, 54% from 5.03 g of 2,6-difluorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^1H NMR ($CDCl_3$): 9.81 (s, 1H), 7.18 (m, 1H), 6.85 (m, 2H),

4.29 (q, 2H, *J* = 7.1 Hz), 4.01 (s, 2H), 1.30 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 162.7, 161.4 (249 and 8 Hz), 148.8, 128.1 (10 Hz), 112.2 (19 Hz), 111.0 (two signals), 61.9, 18.5 (4 Hz), 13.8. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}F_2NO_3Na$: 266.0605, found, 266.0613.

Ethyl 3-(2,3-difluorophenyl)-2-(hydroxyimino)propanoate (2p): Obtained as a white solid (4.36 g, 51% from 5 g of 2,3-difluorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 3.75/1.25). ^{1}H NMR ($CDCl_3$): 9.83 (s, 1H), 7.01 (m, 3H), 4.32 (q, 2H, *J* = 7.1 Hz), 4.06 (s, 2H), 1.33 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 162.8, 150.7 (248 and 13 Hz), 149.5, 149.0 (248 and 13 Hz), 125.2 (7 Hz), 125.1 (2 Hz), 123.8 (7 and 5 Hz), 115.6 (17 Hz), 62.1, 23.4 (4 and 3 Hz), 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}F_2NO_3Na$: 266.0604, found, 266.0603.

Ethyl 3-(2,5-difluorophenyl)-2-(hydroxyimino)propanoate (2q): Obtained as a white solid (4.83 g, 50% from 5.17 g of 2,5-difluorobenzaldehyde, 96% pure) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.66 (s, 1H), 6.95 (m, 3H), 4.32 (q, 2H, *J* = 7.1 Hz), 4.01 (s, 2H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 162.8, 158.6 (242 and 2 Hz), 156.8 (242 and 3 Hz), 149.6, 124.3 (19 and 8 Hz), 117.0 (25 and 4 Hz), 116.2 (25 and 9 Hz), 114.7 (24 and 8 Hz), 62.1, 23.7 (3 and 1 Hz), 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}F_2NO_3Na$: 266.0605, found, 266.0615.

Ethyl 3-(3,5-difluorophenyl)-2-(hydroxyimino)propanoate (2r): Obtained as a white solid (4.18 g, 46% from 5.35 g of 3,5-difluorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.91 (s, 1H), 6.88 (m, 2H), 6.68 (m, 1H), 4.34 (q, 2H, *J* = 7.1 Hz), 3.97 (s, 2H), 1.36 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.0 (248 and 13 Hz), 162.9, 149.7, 139.2 (10 Hz), 112.2 (two signals), 102.3 (25 Hz), 62.2, 30.2, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{12}F_2NO_3$: 244.0785, found, 244.0788.

Ethyl 2-(hydroxyimino)-3-(2,3,5-trifluorophenyl)propanoate (2s): Obtained as a white solid (3.02 g, 35% from 5.12 g of 2,3,5-trifluorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1) and a recrystallization in cyclohexane. ^{1}H NMR ($CDCl_3$): 10.02 (s(br), 1H), 6.78 (m, 2H), 4.33 (q, 2H, *J* = 7.2 Hz), 4.03 (s, 2H), 1.34 (t, 3H, *J*

= 7.2 Hz). ^{13}C NMR ($CDCl_3$): 162.7, 157.4 (244, 10 and 3 Hz), 150.3 (250, 28 and 13 Hz), 148.9, 145.6 (244, 12 and 3 Hz), 126.0 (14 and 9 Hz), 103.9 (27 and 21 Hz), 62.3, 13.9.

Ethyl 3-(2-chlorophenyl)-2-(hydroxyimino)propanoate (2t): As described in the text, the preparation of oxime **2t** had to be optimized. The condensation of diethylmalonate was run as described above but in dry isopropanol, the reduction was undertaken as described above but with tetramethyl ammonium borohydride instead of sodium boron hydride. Pure oxime **2t** was obtained as a white solid (5.98 g, 49% from 7.01 g of 2-chlorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.47 (s, 1H), 7.38 (m, 1H), 7.18 (m, 3H), 4.30 (q, 2H, *J* = 7.1 Hz), 4.13 (s, 2H), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.1, 150.5, 134.0, 133.5, 129.7, 129.5, 128.0, 126.8, 62.0, 28.5, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}ClNO_3Na$: 264.0403, found, 264.0401.

Ethyl-3-(3-chlorophenyl)-2-(hydroxyimino)propanoate (2u): The protocol described for the preparation of oxime **2t** was used to prepare compound **2u**, which was obtained as a light yellow solid (7.09 g, 59% from 7.01 g of 3-chlorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): 9.60 (s, 1H), 7.34 (m, 1H), 7.22 (m, 3H), 4.33 (q, 2H, *J* = 7.1 Hz), 3.97 (s, 2H), 1.36 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 150.4, 137.6, 134.3, 129.7, 129.4, 127.4, 126.9, 62.1, 30.1, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}ClNO_3Na$: 264.0403, found, 264.0406. Note: ^{1}H NMR data for diethyl 2-((3-chlorophenyl)(ethoxy)methyl)malonate (**7**) which were extracted from the ^{1}H NMR analysis of a (concentrated to dryness) 3 weeks-old ethanol solution of compound **6u**: ^{1}H NMR ($CDCl_3$): 7.40 (m, 1H), 7.34 (m, 1H), 7.29 (m, 2H), 4.88 (d, 1H, *J* = 10.2 Hz), 4.29 (m, 2H), 3.98 (m, 2H), 3.70 (d, 1H, *J* = 10.2 Hz), 3.37 (m, 2H), 1.32 (t, 3H, *J* = 7.3 Hz), 1.13 (t, 3H, *J* = 7.1 Hz), 1.05 (t, 3H, *J* = 6.9 Hz).

Ethyl-3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (2v): The protocol described for the preparation of oxime **2t** was used to prepare compound **2v**, which was obtained as a light yellow solid (8.4 g, 62% from 7.83 g of 4-chlorobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.70 (s, 1H), 7.27 (m, 4H),

4.31 (q, 2H, *J* = 7.1 Hz), 3.96 (s, 2H), 1.35 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 150.6, 134.1, 132.6, 130.6, 128.6, 62.0, 29.9, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{14}ClNO_2Na$, 264.0403, found, 264.0437. Spectroscopic data similar to the reported one [1].

Ethyl-3-(4-bromophenyl)-2-(hydroxyimino)propanoate (2w): Obtained as a white solid (1.43 g, 42% from 5.0 g of 4-bromobenzaldehyde), using sodium boron hydride at 4 °C overnight, after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.70 (s, 1H), 7.42 (m, 2H), 7.22 (m, 2H), 4.31 (q, 2H, *J* = 7.1 Hz), 3.96 (s, 2H), 1.32 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 150.5, 134.7, 131.6, 130.9, 120.6, 62.0, 29.9, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{13}BrNO_3$, 286.0079, found, 286.0056.

Ethyl 2-(hydroxyimino)-3-(2-methoxyphenyl)propanoate (2x): Obtained as a white solid (3.15 g, 60% from 3.0 g of 2-methoxybenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.65 (s, 1H), 7.22 (m, 1H), 7.14 (m, 1H), 6.88 (m, 2H), 4.29 (q, 2H, *J* = 7.1 Hz), 3.99 (s, 2H), 3.83 (s, 3H), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.5, 157.2, 151.6, 129.7, 127.8, 124.3, 120.5, 110.4, 61.7, 55.4, 25.7, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NO_4Na$: 260.0899, found, 260.0904.

Ethyl 2-(hydroxyimino)-3-(3-methoxyphenyl)propanoate (2y): Out of a 10.66 g batch, only a sample (0.43 g) was purified by a chromatography (dichloromethane – ethanol 98/2) to give a white solid (0.33 g). ^{1}H NMR ($CDCl_3$): 9.79 (s, 1H), 7.21 (t, 1H, *J* = 7.9 Hz), 6.93 (m, 1H), 6.91 (m, 1H), 6.77 (m, 1H), 4.30 (q, 2H, *J* = 7.1 Hz), 3.98 (s, 2H), 3.80 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.2, 159.7, 150.9, 137.2, 150.9, 137.2, 129.4, 121.5, 115.0, 112.1, 61.9, 55.1, 30.5, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NO_4Na$: 260.0849, found, 260.0898.

Ethyl 3-(2-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2z): Obtained as a white solid (10.78 g, 48% from 15.0 g of 2-(benzyloxy)benzaldehyde) after an initial recrystallization which gave 3.34 g of compound **2z** and a chromatography over silica gel of the filtrate (cyclohexane – ethyl acetate 4/1 to 7/3) followed by a recrystallization in

cyclohexane which gave an additional 7.44 g. Note: instead of 10 hours at 60 °C, for the condensation step, heating at 75 °C for 24 hours led to an almost complete disappearance of the starting aldehyde signal. ^{1}H NMR ($CDCl_3$) 9.14 (s(br), 1H), 7.46 (m, 2H), 7.39 (m, 2H), 7.32 (m, 1H) 6.90 (m, 2H), 5.11 (s, 2H), 4.15 (q, 2H, *J* = 7.2 Hz), 4.07 (s, 2H), 1.24 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.4, 156.4, 151.5, 137.1, 129.9, 128.5, 127.8, 127.7, 127.4, 124.7, 120.8, 111.8, 70.1, 61.6, 25.8, 13.9.

Ethyl 3-(3-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2aa): Obtained as a white solid (8.09 g, 37% from 15.0 g of 3-(benzyloxy)benzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1 to 7/3) and a recrystallization in cyclohexane. Note: instead of 10 hours at 60 °C, for the condensation step, heating at 75 °C for 24 hours led to an almost complete disappearance of the starting aldehyde signal. ^{1}H NMR ($CDCl_3$) 9.41 (s(br), 1H), 7.46 – 7.31 (m, 5H), 7.27 (m, 1H), 6.99 (m, 1H), 6.94 (m, 1H), 6.85 (m, 1H), 5.06 (s, 2H), 4.31 (q, 2H, *J* = 7.2 Hz), 3.99 (s, 2H), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.2, 159.0, 150.9, 137.2, 137.1, 129.5, 128.5, 127.9, 127.5, 121.9, 115.9, 113.0, 70.0, 61.9, 30.5, 14.0.

Ethyl 3-(4-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2ab): Obtained as a white solid (5.99 g, 40% from 10.03 g of 4-(benzyloxy)benzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1 to 1/2). Note: instead of 10 hours at 60 °C, for the condensation step, heating at 75 °C for 12 hours led to an almost complete disappearance of the starting aldehyde signal. ^{1}H NMR ($CDCl_3$) 8.63 (s(br), 1H), 7.46 – 7.32 (m, 5H), 7.27 (m, 2H), 6.92 (m, 2H), 5.07 (s, 2H), 4.31 (q, 2H, *J* = 7.2 Hz), 3.94 (s, 2H), 1.34 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.3, 157.6, 151.3, 137.3, 128.7, 128.5, 128.0, 127.9, 127.4, 114.9, 70.0, 61.9, 29.6, 14.0.

Ethyl 2-(hydroxyimino)-3-(pyridin-2-yl)propanoate (2ac): Obtained as a solid (4.94 g, 49% from 7.10 g of picolinaldehyde) after a chromatography over silica gel (dichloromethane – ethanol 97/3). 10.53 (s, 1H), 8.53 (m, 1H), 7.61 (dt, 1H, *J* = 1.8, 7.5 Hz), 7.29 (m, 1H), 7.17 (m, 1H), 4.29 (q, 2H, *J* = 7.1 Hz), 4.23 (s, 2H), 1.30 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$):

163.6, 156.6, 150.0, 149.0, 137.0, 123.5, 121.7, 61.8, 33.2, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{13}N_2O_3$: 209.0926, found, 209.0857.

Ethyl 2-(hydroxyimino)-3-(pyridin-3-yl)propanoate (2ad): Obtained as a tan solid (7.19 g, 43% from 8.47 g of nicotinaldehyde) after a chromatography over silica gel (dichloromethane – ethanol 97/3 to 96/4). ^{1}H NMR ($CDCl_3$): 12.79 (s, 1H), 8.65 (m, 1H), 8.46 (dd, 1H, *J* = 1.6, 4.9 Hz), 7.74 (m, 1H), 7.22 (m, 1H), 4.30 (q, 2H, *J* = 7.1 Hz), 4.01 (s, 2H), 1.32 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.7, 149.9, 149.6, 147.0, 137.6, 132.9, 123.7, 61.8, 28.1, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{13}N_2O_3$: 209.0926, found, 209.0921.

Ethyl 3-(furan-2-yl)-2-(hydroxyimino)propanoate (2ae): As mentioned in the text, in this specific case the reduction step with sodium borohydride was run in ethanol at -10 °C for 1h30 and compound **2ae** was obtained as a white solid (7.90 g, 47% from 8.07 g of furfural) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.72 (s, 1H), 7.31 (m, 1H), 6.30 (m, 1H), 6.13 (m, 1H), 4.33 (q, 2H, *J* = 7.1 Hz), 4.04 (s, 2H), 1.35 (t, 3H, *J* = 7.1 Hz), 1.25 (m, 2H). ^{13}C NMR ($CDCl_3$): 162.8, 148.7, 148.4, 141.5, 110.4, 107.0, 62.0, 23.5, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_9H_{12}NO_4$: 198.0766, found, 198.0775. ^{1}H NMR similar to the reported one [2].

Ethyl 2-(hydroxyimino)-3-(5-methylfuran-2-yl)propanoate (2af): Obtained as an off white solid (5.99 g, 33% from 10.11 g of 5-methylfuran-2-carbaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): 9.41 (s, 1H), 5.99 (m, 1H), 5.86 (m, 1H), 4.33 (q, 2H, *J* = 7.0 Hz), 3.98 (s, 2H), 2.25 (s, 3H), 1.35 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): 162.9, 151.1, 148.8, 146.7, 107.6, 106.3, 61.9, 26.9, 14.0, 13.5. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_{13}NO_4Na$: 234.0742, found, 234.0744. ^{1}H NMR similar to the reported one [3].

Ethyl 3-(4,5-dimethylfuran-2-yl)-2-(hydroxyimino)propanoate (2ag): As mentioned in the text, in this specific case the reduction step with sodium borohydride was run in THF (20 mL) and ethanol (20 mL) at -10 °C for 1h30 and compound **2ag** was obtained as a solid (0.84 g, 23% from 2.03 g of aldehyde **5ag**), after a chromatography over silica gel (cyclohexane –

ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.89 (s, 1H), 5.87 (s, 1H), 4.32 (q, 2H, *J* = 7.2 Hz), 3.94 (s, 2H), 2.15 (s, 3H), 1.88 (s, 3H), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 148.7, 146.3, 145.4, 114.6, 110.1, 61.9, 23.6, 14.0, 11.2, 9.8. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{15}NO_4Na$: 248.0899, found, 248.0896.

Ethyl 3-(5-ethylfuran-2-yl)-2-(hydroxyimino)propanoate (2ah): Obtained as a white solid (3.17 g, 34% from 5.14 g of 5-ethylfuran-2-carbaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.79 (s, 1H), 5.98 (m, 1H), 5.86 (m, 1H), 4.33 (q, 2H, *J* = 7.1 Hz), 3.99 (s, 2H), 2.60 (q, 2H, *J* = 7.4 Hz), 1.35 (t, 3H, *J* = 7.1 Hz), 1.20 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 156.8, 148.7, 146.6, 107.3, 104.6, 61.9, 23.7, 21.3, 14.0, 12.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{15}NO_4Na$: 248.0899, found, 248.0868.

Ethyl 2-(hydroxyimino)-3-(5-(trifluoromethyl)furan-2-yl)propanoate (2ai): Obtained as a white solid (0.62 g, 36% from 1.06 g of 5-trifluoromethylfuran-2-carbaldehyde), using sodium boron hydride at 0 °C, after two chromatography over silica gel (dichloromethane – ethanol 99/1) and (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.70 (s, 1H), 6.72 – 6.64 (m, 1H), 6.21 – 6.15 (m, 1H), 4.33 (q, 2H, *J* = 7.1 Hz), 4.05 (s, 2H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 162.7, 152.0, 147.6, 141.0 (q, *J* = 42.7 Hz), 119.2 (q, *J* = 266.7 Hz), 112.7 (q, *J* = 2.8 Hz), 108.18 (s), 62.4, 23.7, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{11}F_3NO_4$: 266.0640, found, 266.0584.

Ethyl 3-(5-ethylthiophen-2-yl)-2-(hydroxyimino)propanoate (2aj): Obtained as an oil (1.36 g, 29% from 2.69 g of 5-ethylthiophene-2-carbaldehyde), using sodium boron hydride at 0 °C, after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 10.06 (s, 1H), 6.75 (m, 1H), 6.59 (m, 1H), 4.34 (q, 2H, *J* = 7.2 Hz), 4.09 (s, 2H), 2.78 (m, 2H), 1.38 (t, 3H, *J* = 7.2 Hz), 1.28 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 150.1, 146.6, 133.9, 126.3, 122.8, 62.0, 24.8, 23.4, 15.8, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{15}NO_3SNa$: 264.0670, found, 264.0676.

Ethyl 2-(hydroxyimino)-3-(3-methylthiophen-2-yl)propanoate (2ak): Obtained as a yellow solid (1.38 g, 32% from 2.39 g of 3-methylthiophene-2-carbaldehyde), using sodium boron hydride at 0 °C, after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.88 (s, 1H), 7.06 (d, 1H, *J* = 5.1 Hz), 6.77 (d, 1H, *J* = 5.1 Hz), 4.33 (q, 2H, *J* = 7.2 Hz), 4.09 (s, 2H), 2.28 (s, 3H), 1.36 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 150.1, 135.0, 130.3, 129.7, 122.8, 62.0, 22.9, 14.0, 13.7. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_{13}NO_3SNa$: 250.0514, found, 250.0513.

Ethyl 3-(4,5-dimethylthiophen-2-yl)-2-(hydroxyimino)propanoate (2al): Obtained as an oil (0.69 g, 31% from 1.29 g of 4,5-dimethylthiophene-2-carbaldehyde; 90 % pure), using sodium boron hydride at 0 °C, after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.77 (s, 1H), 6.62 (s, 1H), 4.34 (q, 2H, *J* = 7.2 Hz), 4.03 (s, 2H), 2.28 (s, 3H), 2.06 (s, 3H), 1.37 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 150.1, 132.6, 131.7, 131.6, 129.6, 62.0, 24.6, 14.0, 13.4, 12.8. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{15}NSO_3Na$: 264.0670, found, 264.0656.

General method for the preparation of the α-amino esters by zinc-based reduction of the α-hydroxyimino esters: The considered substituted α-hydroxyimino ester (0.065 mol) was dissolved in ethanol (70 mL) and 37% hydrochloric acid (49 mL, 0.58 mol) and the solution was cooled to 0 °C. Powdered zinc (12.9 g, 0.19 mol, less than 10 μm size) was added in one portion. The mixture was stirred for 3 hours, diluted with water, made basic with 22% ammonia and extracted with ethyl acetate. The organic layer was washed with water, brine, dried over sodium carbonate and concentrated to dryness to yield the α-amino esters **1** which were in some cases further purified as described below. Note: these oily α-amino esters are not very stable, and unless the corresponding hydrochloric salt is made (by adding 4 N HCl in dioxane and concentration to dryness), many of them will slowly dimerize into the corresponding solid piperazine-2,5-diones even when stored at −20 °C.

Ethyl 2-amino-3-(*o*-tolyl)propanoate (1b): Obtained as an oil (2.69 g, 85% from 3.38 g of oxime). ^{1}H NMR ($CDCl_3$): 7.16 (m, 4H), 4.17 (q, 2H, *J* = 7.2 Hz), 3.71 (dd, 1H, *J* = 8.7, 5.6 Hz), 3.14 (dd, 1H, *J* = 13.8, 5.6 Hz), 2.84 (dd, 1H, *J* = 13.8, 8.7 Hz), 2.82 (s, 3H), 1.24 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 175.3, 136.5, 135.9, 130.5, 130.0, 126.8, 125.9, 60.9, 55.0, 38.9, 19.5, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{18}NO_2$: 208.1338, found, 208.1332.

Ethyl 2-amino-3-(*m*-tolyl)propanoate (1c): Obtained as an oil (3.07 g, 85% from 3.68 g of oxime). Analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(*p*-tolyl)propanoate (1d): Obtained as an oil (2.70 g, 87% from 3.31 g of oxime). ^{1}H NMR ($CDCl_3$): 7.11 (m, 4H), 4.19 (q, 2H, *J* = 7.1 Hz), 3.70 (dd, 1H, *J* = 7.9, 5.3 Hz), 3.07 (dd, 1H, *J* = 13.6, 5.3 Hz), 2.84 (dd, 1H, *J* = 13.6, 7.9 Hz), 2.34 (s, 3H), 1.28 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 175.1, 136.3, 134.2, 129.4, 129.2 (two signals), 129.1, 60.9, 55.9, 40.7, 21.0, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{18}NO_2$: 208.1338, found, 208.1333. Spectroscopic data similar to the reported one [5].

Ethyl 2-amino-3-(4-isopropylphenyl)propanoate hydrochloride (1e): Obtained from 2.02 g of the oxime as an oil which was immediately treated with a solution of hydrogen chloride in dioxane and concentrated to dryness to give the hydrochloride salt as a white powder (1.9 g, 91% pure). ^{1}H NMR (DMSO-d_6): 8.23 (s, 3H), 7.22 – 7.12 (m, 4H), 4.16 – 4.02 (m, 3H), 3.16 (dd, 1H, *J* = 13.9, 5.8 Hz), 3.01 (dd, 1H, *J* = 13.9, 7.8 Hz), 2.86 (hept, 1H, *J* = 6.9 Hz), 1.18 (d, 6H, *J* = 6.9 Hz), 1.06 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (DMSO-d_6): 169.3, 147.2, 132.2, 129.3, 126.3, 61.3, 53.4, 35.9, 33.0, 23.8, 13.7. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{22}NO_2$: 236.1651, found, 236.1651. ^{1}H NMR spectra not similar to the reported one [6].

Ethyl 2-amino-3-cyclopentylpropanoate (1f): Obtained as an oil (1.16 g, 85% from 1.46 g of oxime). ^{1}H NMR ($CDCl_3$): 4.17 (q, 2H, *J* = 7.2 Hz), 3.42 (dd, 1H, *J* = 5.8, 8.1 Hz), 1.93 (m, 1H), 1.80 (m, 2H), 1.75-1.48 (m, 8H), 1.27 (t, 3H, *J* = 7.2 Hz), 1.12 (m, 2H). ^{13}C NMR ($CDCl_3$): 174.5, 60.6, 54.1, 41.4, 36.7, 32.9, 32.3, 25.1, 24.9, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{20}NO_2$: 186.1494, found, 186.1491.

Ethyl 2-amino-3-cyclohexylpropanoate (1g): Obtained as an oil (2.35 g, 92% from 2.73 g of oxime). ^{1}H NMR ($CDCl_3$): 4.17 (m, 2H), 3.48 (dd, 1H, *J* = 5.8, 8.7 Hz), 1.72 (m, 5H), 1.61-137 (m, 5H), 1.28 (t, 3H, *J* = 7.3 Hz), 1.28-1.10 (m, 3H), 0.92 (m, 2H). ^{13}C NMR ($CDCl_3$): 174.7, 60.6, 52.2, 42.7, 34.1, 33.7, 32.6, 26.5, 26.2, 26.1, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{22}NO_2$: 200.1651, found, 200.1648. ^{1}H NMR spectra similar to the reported one [7].

Ethyl 2-amino-3-(2-(trifluoromethyl)phenyl)propanoate (1h): Obtained as an oil (7.22 g, 86% from 8.82 g of oxime). ^{1}H NMR ($CDCl_3$): 7.67 (m, 1H), 7.50 (m, 1H), 7.41 (m, 1H), 7.35 (m, 1H), 4.16 (q, 2H, *J* = 7.1 Hz), 3.75 (dd, 1H, *J* = 5.8, 8.7 Hz), 3.30 (dd, 1H, *J* = 5.8, 14.3 Hz), 2.97 (dd, 1H, *J* = 8.7, 14.3 Hz), 1.69 (s(br), 2H), 1.22 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.9, 136.4 (2 Hz), 131.8, 131.6, 129.1 (32 Hz), 126.8, 126.2 (5 Hz), 124.5 (274 Hz), 61.0, 55.6, 38.0, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{15}F_3NO_2$: 262.1055, found, 262.1065.

Ethyl 2-amino-3-(3-(trifluoromethyl)phenyl)propanoate (1i): Obtained as an oil (0.75 g, 78% from 1.01 g of oxime) . ^{1}H NMR ($CDCl_3$): 7.51 (m, 1H), 7.48 (m, 1H), 7.43 (m, 2H), 4.17 (q, 2H, *J* = 7.3 Hz), 3.74 (dd, 1H, *J* = 5.5, 7.5 Hz), 3.13 (dd, 1H, *J* = 5.5, 13.8 Hz), 2.96 (dd, 1H, *J* = 7.5, 13.8 Hz), 1.51 (s, 2H), 1.24 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 138.4, 132.8, 130.8 (32 Hz), 128.9, 126.0 (4 Hz), 124.2 (272 Hz), 123.6 (4 Hz), 61.1, 55.7, 40.9, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{15}F_3NO_2$: 262.1055, found, 262.1054.

Ethyl 2-amino-3-(4-(trifluoromethyl)phenyl)propanoate (1j): Obtained as an oil (1.23 g, 91% from 1.41 g of oxime). ^{1}H NMR ($CDCl_3$): 7.58 (d, 2H, *J* = 8.3 Hz), 7.35 (d, 2H, *J* = 8.3 Hz), 4.18 (q, 2H, *J* = 7.3 Hz), 3.74 (dd, 1H, *J* = 5.8, 7.8 Hz), 3.14 (dd, 1H, *J* = 5.8, 13.4 Hz), 2.96 (dd, 1H, *J* = 7.8, 13.4 Hz), 1.50 (s, 2H), 1.25 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 141.6, 129.6, 129.1 (32 Hz), 125.3 (4 Hz), 124.2 (270 Hz), 61.1, 55.6, 40.8, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{15}F_3NO_2$: 262.1055, found, 262.1129. ^{1}H NMR spectra similar to the reported one [6].

Ethyl 2-amino-3-(2-fluorophenyl)propanoate (1k): Obtained as an oil (2.57 g, 88% from 3.11 g of oxime). Analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(3-fluorophenyl)propanoate (1l): Obtained as an oil (4.89 g, 89% from 5.84 g of oxime). ^{1}H NMR ($CDCl_3$): 7.27 (m, 1H), 7.01-6.92 (m, 3H), 4.18 (q, 2H, *J* = 7.0 Hz), 3.72 (dd, 1H, *J* = 5.4, 7.9 Hz), 3.08 (dd, 1H, *J* = 5.4, 13.7 Hz), 2.88 (dd, 1H, *J* = 7.9, 13.7 Hz), 1.49 (s, 2H), 1.26 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): 174.8, 162.9 (246 Hz), 139.9 (7 Hz), 129.9 (8 Hz), 125.0 (3 Hz), 116.2 (21 Hz), 113.7 (20 Hz), 61.0, 55.7, 40.8, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{15}FNO_2$: 212.1087, found, 212.1088. ^{1}H NMR spectra similar to the reported one [5].

Ethyl 2-amino-3-(4-fluorophenyl)propanoate (1m): Obtained from 2.89 g of the crude oxime **2m** described above as an oil (2.21 g, 81% from 4-fluorobenzaldehyde) with analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(2,4-difluorophenyl)propanoate (1n): Obtained as an oil (1.11 g, 85% from 1.38 g of oxime). ^{1}H NMR ($CDCl_3$): 7.19 (m, 1H), 6.80 (m, 2H), 4.15 (q, 2H, *J* = 7.1 Hz), 3.70 (dd, 1H, *J* = 7.9, 5.9 Hz), 3.04 (dd, 1H, *J* = 13.7, 5.9 Hz), 2.89 (dd, 1H, *J* = 13.7, 7.9 Hz), 1.52 (s, 2H), 1.23 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.8, 162.0 (11 and 247 Hz), 161.3 (12 and 249 Hz), 132.1 (6 and 9 Hz), 120.3 (4 and 16 Hz), 111.1, (3 and 21 Hz), 103.7 (26 Hz), 61.0, 54.7, 34.1, 10.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{14}F_2NO_2$, 230.0993, found, 230.1006.

Ethyl 2-amino-3-(2,6-difluorophenyl)propanoate (1o): Obtained as an oil (3.46 g, 94% from 3.89 g of oxime). ^{1}H NMR ($CDCl_3$): 7.21 (m, 1H), 6.89 (m, 2H), 4.18 (q, 2H, *J* = 7.1 Hz), 3.75 (dd, 1H, *J* = 8.1, 6.2 Hz), 3.14 (dd, 1H, *J* = 13.7, 6.1 Hz), 2.97 (dd, 1H, *J* = 13.7, 8.1 Hz), 1.54 (s, 2H), 1.25 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.8, 161.8 (247 and 8 Hz), 128.4 (10 Hz), 113.5 (20 Hz), 111.1, 61.1, 54.2, 28.3, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{14}F_2NO_2$: 230.0993, found, 230.0995.

Ethyl 2-amino-3-(2,3-difluorophenyl)propanoate (1p): Obtained as an oil (3.36 g, 92% from 3.86 g of oxime). ^{1}H NMR ($CDCl_3$): 7.03 (m, 3H), 4.18 (q, 2H, *J* = 7.1 Hz), 3.76 (dd, 1H, *J* = 7.9, 5.9 Hz), 3.13 (ddd, 1H, *J* = 13.7, 5.9, 1.5 Hz), 2.97 (ddd, 1H, *J* = 13.7, 7.9, 1.3 Hz), 1.53 (s, 2H), 1.26 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 150.6 (248 and 13 Hz), 149.4

(247 and 13 Hz), 127.1 (13 Hz), 126.2 (3 Hz), 123.8 (7, 5 Hz), 115.8 (17 Hz), 61.1, 54.7, 34.5, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{14}F_2NO_2$: 230.0993, found, 230.1004.

Ethyl 2-amino-3-(2,5-difluorophenyl)propanoate (1q): Obtained as an oil (3.44 g, 95% from 3.85 g of oxime). ^{1}H NMR ($CDCl_3$): 6.96 (m, 3H), 4.19 (d, 2H, *J* = 7.1 Hz), 3.75 (dd, 1H, *J* = 7.9, 5.9 Hz), 3.08 (ddd, 1H, *J* = 13.7, 5.8, 1.2 Hz), 2.91 (ddd, 1H, *J* = 13.8, 7.9, 0.9 Hz), 1.52 (s, 2H), 1.26 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.0 (248 and 13 Hz), 162.9, 149.7, 139.2 (10 Hz), 112.2, 102.3 (25 Hz), 62.2, 30.2, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{14}F_2NO_2$: 230.0993, found, 230.1000.

Ethyl 2-amino-3-(3,5-difluorophenyl)propanoate (1r): Obtained as an oil (3.33 g, 84% from 4.18 g of oxime). ^{1}H NMR ($CDCl_3$): 6.73 (m, 3H), 4.20 (q, 2H, *J* = 7.1 Hz), 3.71 (s, 1H), 3.06 (dd, 1H, *J* = 13.6, 5.4 Hz), 2.87 (dd, 1H, *J* = 13.6, 7.7 Hz), 1.49 (s, 2H), 1.28 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.5, 163.0 (248 and 13 Hz), 141.4 (9 Hz), 112.1, 102.3 (25 Hz), 61.1, 55.5, 40.7, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{14}F_2NO_2$: 230.0993, found, 230.0995.

Ethyl 2-amino-3-(2,3,5-trifluorophenyl)propanoate (1s): Obtained as an oil (2.71 g, 94% from 3.04 g of oxime). ^{1}H NMR ($CDCl_3$): 6.86 – 6.75 (m, 2H), 4.18 (q, 2H, *J* = 7.1 Hz), 3.74 (dd, 1H, *J* = 5.9 and 7.8 Hz), 3.10 (ddd, 1H, *J* = 1.6, 5.9 and 13.7 Hz), 2.94 (ddd, 1H, *J* = 1.6, 7.8 and 13.7 Hz), 1.67 (s(br), 1H), 1.26 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.4, 157.4 (244, 10 and 3 Hz), 150.2 (251, 12 and 14 Hz), 145.9 (243, 13 and 4 Hz), 127.9 (9 and 15 Hz), 104.0 (21 and 27 Hz), 61.2, 54.5, 34.3, 14.0.

Ethyl 2-amino-3-(2-chlorophenyl)propanoate (1t): Obtained as an oil (4.18 g, 94% from 4.72 g of oxime). ^{1}H NMR ($CDCl_3$): 7.38 (m, 1H), 7.22 (m, 3H), 4.16 (m, 2H), 3.84 (dd, 1H, *J* = 8.5, 5.8 Hz), 3.24 (dd, 1H, *J* = 13.5, 5.8 Hz), 3.96 (dd, 1H, *J* = 13.5, 8.5 Hz), 1.23 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 175.0, 135.5, 134.4, 131.6, 129.6, 128.2, 126.7, 61.0, 54.4, 39.2, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{15}ClNO_2$: 228.0791, found, 228.0791.

Ethyl 2-amino-3-(3-chlorophenyl)propanoate (1u): Obtained as an oil (2.31 g, 92% from 2.66 g of oxime). ^{1}H NMR ($CDCl_3$): 7.23 (td, 3H, *J* = 4.3, 2.5 Hz), 7.14–7.08 (m, 1H), 4.18 (q,

2H, *J* = 7.1 Hz), 3.71 (dd, 1H, *J* = 7.8, 5.5 Hz), 3.06 (dd, 1H, *J* = 13.6, 5.5 Hz), 2.86 (dd, 1H, *J* = 13.6, 7.8 Hz), 1.57 (s, 2H), 1.26 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 139.5, 134.3, 129.7, 129.4, 127.5, 127.0, 61.0, 55.7, 40.7, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{15}ClNO_2$: 228.0791, found, 228.0726.

Ethyl 2-amino-3-(4-chlorophenyl)propanoate (1v): Obtained as an oil (1.48 g, 85% from 1.84 g of oxime). ^{1}H NMR ($CDCl_3$): 7.29 (m, 2H), 7.16 (m, 2H), 4.18 (q, 2H, *J* = 7.3 Hz), 3.69 (dd, 1H, *J* = 5.6, 7.5 Hz), 3.05 (dd, 1H, *J* = 5.6, 13.7 Hz), 2.84 (dd, 1H, *J* = 7.5, 13.7 Hz), 1.47 (s(l), 2H), 1.26 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.8, 135.9, 132.7, 130.6, 128.6, 61.0, 55.7, 40.5, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{15}ClNO_2$, 228.0791, found, 228.0806. Spectroscopic data similar to the reported one [5].

Ethyl 2-amino-3-(4-bromophenyl)propanoate (1w): Obtained as an oil (0.61 g, 86% from 0.74 g of oxime). ^{1}H NMR ($CDCl_3$): 7.44 (m, 2H), 7.10 (m, 2H), 4.18 (q, 2H, *J* = *7.3* Hz), 3.69 (dd, 1H, *J* = 5.3, 7.7 Hz), 3.04 (dd, 1H, *J* = 5.3, 13.7 Hz), 2.84 dd, 1H, *J* = 7.7, 13.7 Hz), 1.47 (s(l), 2H), 1.26 (t, 3H, *J* = *7.1* Hz). ^{13}C NMR ($CDCl_3$): 174.8, 136.4, 131.6, 131.0, 120.7, 61.0, 55.7, 40.5, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{15}BrNO_2$, 272.0286, found, 272.0296. Spectroscopic data similar to the reported one [5].

Ethyl 2-amino-3-(2-methoxyphenyl)propanoate (1x): Obtained as an oil (2.47 g, 83% from 3.15 g of oxime). Analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(3-methoxyphenyl)propanoate (1y): Obtained as an oil from 4.35 g of the crude compound **2y** described above (3.09 g, 75% from 3-methoxybenzaldehyde) with analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(2-(benzyloxy)phenyl)propanoate (1z): Obtained as an oil (7.84 g, 91% from 8.94 g of oxime) ^{1}H NMR ($CDCl_3$): 7.46-7.33 (m, 5H), 7.24 (m, 1H), 6.87 (m, 3H), 5.08 (s, 2H), 4.19 (q, 2H, *J* = 7.1 Hz), 3.73 (dd, 1H, *J* = 5.1, 7.9 Hz), 3.09 (dd, 1H, *J* = 5.1, 13.4 Hz), 2.85 (dd, 1H, *J* = 7.9, 13.4 Hz), 1.52 (s (br), 2H), 1.27 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.9, 159.0, 139.0, 137.0, 129.5, 128.5, 127.9, 127.4, 121.9, 116.0, 113.1, 69.9, 60.9, 55.8, 41.2, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{21}NO_3$: 300.1600, found, 300.1608.

Ethyl 2-amino-3-(3-(benzyloxy)phenyl)propanoate (1aa): Obtained as an oil (5.60 g, 92% from 6.33 g of oxime) ^{1}H NMR ($CDCl_3$): 7.48 (m, 2H), 7.41 (m, 2H), 7.34 (m, 1H), 7.25-7.18 (m, 2H), 6.94 (m, 2H), 5.13 (s, 2H), 4.12 (m, 2H), 3.88 (dd, 1H, *J* = 5.6, 8.5 Hz), 3.23 (dd, 1H, *J* = 5.6, 13.1 Hz), 2.88 (dd, 1H, *J* = 8.5, 13.1 Hz), 1.54 (s (br), 2H), 1.21 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 175.4, 156.8, 137.2, 131.3, 128.5, 128.1, 127.8, 127.0 (two signals), 126.4, 120.8, 111.8, 69.9, 60.7, 54.5, 36.8, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{21}NO_3$: 300.1600, found, 300.1611.

Ethyl 2-amino-3-(4-(benzyloxy)phenyl)propanoate (1ab): Obtained as an oil (11.08 g, 95% from 12.13 g of oxime) with analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(pyridin-2-yl)propanoate (1ac): Obtained as an oil (2.21 g, 56% from 4.28 g of oxime). ^{1}H NMR ($CDCl_3$): 8.55 (m, 1H), 7.61 (dt, 1H, *J* = 1.9, 7.6), 7.18 (m, 1H), 7.15 (m, 1H), 4.18 (q, 2H, *J* = 7.2 Hz), 3.98 (dd, 1H, *J* = 4.8, 8.2 Hz), 3.28 (dd, 1H, *J* = 4.8, 14.2 Hz), 3.04 (dd, 1H, *J* = 8.2, 14.2 Hz), 1.70 (s, 2H), 1.24 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 175.1, 158.1, 149.4, 136.3, 123.9, 121.6, 60.9, 54.5, 42.7, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{15}N_2O_2$: 195.1134, found, 195.1062.

Ethyl 2-amino-3-(pyridin-3-yl)propanoate (1ad): Obtained as an oil (4.07 g, 63% from 6.87 g of oxime). ^{1}H NMR ($CDCl_3$): 8.49 (m, 2H), 7.56 (m, 1H), 7.22 (ddd, 1H, *J* = 0.8, 4.8, 5.6 Hz), 4.16 (q, 2H, *J* = 7.2 Hz), 3.70 (dd, 1H, *J* = 5.5, 7.5 Hz), 3.05 (dd, 1H, *J* = 5.5, 13.5 Hz), 2.88 (dd, 1H, *J* = 7.5, 13.5 Hz), 1.46 (s, 2H), 1.23 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 174.6, 150.6, 148.2, 136.7, 132.9, 123.2, 61.1, 55.5, 38.2, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{15}N_2O_2$: 195.1134, found, 195.1131.

Ethyl 2-amino-3-(furan-2-yl)propanoate (1ae): Obtained as an oil (2.55 g, 89% from 3.08 g of oxime) with analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(5-methylfuran-2-yl)propanoate (1af): Obtained as an oil (1.46 g, 88% from 1.76 g of oxime) with analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(4,5-dimethylfuran-2-yl)propanoate (1ag): Obtained as an oil (0.79 g, 90% from 0.93 g of oxime). with analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(5-ethylfuran-2-yl)propanoate (1ah): Obtained as an oil (1.87 g, 94% from 2.11 g of oxime) with analytical data identical with the one we reported previously [4].

Ethyl 2-amino-3-(5-(trifluoromethyl)furan-2-yl)propanoate (1ai): Obtained as a 95% pure oil (0.53 g, 93% from 0.60 g of oxime). ^{1}H NMR ($CDCl_3$): 6.66 (dd, 1H, *J* = 3.3, 1.2 Hz), 6.20 – 6.15 (m, 1H), 4.20 – 4.10 (m, 2H), 3.79 – 3.73 (m, 1H), 3.08 (dd, 1H, *J* = 15.0, 5.4 Hz), 2.99 (dd, 1H, *J* = 15.0, 7.1 Hz), 1.60 (s(br), 2H), 1.22 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.2, 154.7, 141.0 (q, *J* = 42.6 Hz), 119.0 (q, *J* = 266.6 Hz), 112.4 (q, *J* = 2.8 Hz), 108.5, 61.3, 53.3, 33.4, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{13}F_3NO_3$, 252.0847, found, 252.0852.

Ethyl 2-amino-3-(5-ethylthiophen-2-yl)propanoate (1aj): Obtained as an oil (1.18 g, 92% from 1.36 g of oxime). ^{1}H NMR ($CDCl_3$): 6.66 (m, 1H), 6.61 (m, 1H), 4.21 (q, 2H, *J* = 5.1, 7.2 Hz), 3.68 (dd, 1H, *J* = 4.8, 7.3 Hz), 3.21 (dd, 1H, *J* = 4.8, 14.7 Hz), 3.04 (dd, 1H, *J* = 7.3, 14.7 Hz), 2.80 (m, 2H), 1.62 (s, 2H), 1.30 (t, 3H, *J* = 7.1 Hz), 1.29 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): 174.6, 146.7, 136.2, 126.1, 123.0, 61.0, 55.7, 35.4, 23.4, 15.8, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{18}NO_2S$: 228.1058, found, 228.1055.

Ethyl 2-amino-3-(3-methylthiophen-2-yl)propanoate (1ak): Obtained as an oil (1.10 g, 89% from 1.32 g of oxime). ^{1}H NMR ($CDCl_3$): 7.08 (d, 1H, *J* = 5.1 Hz), 6.80 (d, 1H, *J* = 5.1 Hz), 4.20 (m, 2H), 3.70 (dd, 1H, *J* = 5.1, 7.6 Hz), 3.23 (dd, 1H, *J* = 5.1, 14.7 Hz), 3.04 (dd, 1H, *J* = 7.6, 14.7 Hz), 2.20 (s, 3H), 1.59 (s, 2H), 1.28 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$): 174.6, 134.8, 132.5, 130.0, 122.6, 61.0, 55.8, 33.2, 14.1, 13.8. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{16}NO_2S$: 214.0902, found, 214.0901.

Ethyl 2-amino-3-(4,5-dimethylthiophen-2-yl)propanoate (1al): Obtained as an oil (0.46 g, 87%; 90% pure from 0.56 g of oxime). ^{1}H NMR ($CDCl_3$): 6.54 (s, 1H), 4.22 (d, 2H, *J* = 7.1 Hz), 3.66 (dd, 1H, *J* = 4.8, 7.4 Hz), 3.17 (dd, 1H, *J* = 4.8, 14.5 Hz), 3.03 (dd, 1H, *J* = 7.4, 14.5

Hz), 2.29 (s, 3H), 2.07 (s, 3H), 1.59 (s, 2H), 1.30 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.6, 133.9, 132.7, 131.7, 129.6, 61.0, 55.6, 35.1, 14.2, 13.4, 12.9. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{18}NO_2S$: 228.1058, found, 228.1053.

Ethyl 2-(hydroxyimino)-3-(tetrahydrofuran-2-yl)propanoate (9): This compound was obtained when using 10% Pd/C for the hydrogenation step described above for the general preparation of oximes **2** but letting it run 48 hours. Out a 12.8 g batch, only a sample (0.68 g) was purified by a chromatography (dichloromethane – ethanol 97/3) to give compound **9** an oil (0.56 g). ^{1}H NMR ($CDCl_3$): 9.74 (s, 1H), 4.32 (q, 2H, *J* = 7.2 Hz), 4.28 (m, 1H), 3.90 (m, 1H), 3.74 (m, 1H), 2.96 (dd, 1H, *J* = 5.5, 12.8 Hz), 2.80 (dd, 1H, *J* = 5.9, 12.8 Hz), 1.88 (m, 3H), 1.62 (m, 1H), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.6, 150.4, 67.7, 61.7, 58.4, 31.2, 30.6, 25.3, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_9H_{15}NO_4Na$: 224.0899, found, 224.0874.

Ethyl 2-amino-3-(tetrahydrofuran-2-yl)propanoate (10): This compound was obtained by following the general reduction protocol for the preparation of compounds **1** described above, as an oil (5.68 g, 35% from 8.28 g of furfural) as a mixture of two diasteroisomers in a 3/2 ratio. ^{1}H NMR ($CDCl_3$): Major isomer: 4.17 (q, 2H, *J* = 7.3), 4.01 (m, 1H), 3.85 (m, 1H), 3.72 (m, 1H), 3.62 (dd, 1H, *J* = 8.9, 3.5 Hz), 2.03 (m, 1H), 1.89 (m, 2H), 1.68 (ddd, 2H, *J* = 3.5, 8.9, 13.8 Hz), 1.68 (s, 2H), 1.51 (m, 1H), 1.27 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$): 176.1, 75.8, 67.6, 60.8, 52.5, 40.2, 31.7, 25.6, 14.2. Minor isomer: 4.17 (q, 2H, *J* = 7.2), 4.01 (m, 1H), 3.85 (m, 1H), 3.72 (m, 1H), 3.56 (dd, 1H, *J* = 7.3, 5.4), 2.03 (m, 1H), 1.89 (m, 2H), 1.80 (m, 2H), 1.61 (s, 2H), 1.49 (m, 1H), 1.27 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 175.6, 76.9, 67.7, 60.8, 53.3, 40.5, 31.7, 25.4, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_9H_{18}NO_3$: 188.1287, found, 188.1258.

Isolation of diethyl 2-(furan-2-ylmethyl)malonate (3ae): In this specific case, the following protocol was used: The ethanol solution obtained as described above and containing compound **6ae** was concentrated to dryness thoroughly. At 0 °C, under a calcium chloride-protected atmosphere, the resulting oil (5.86 g, 0.0246 mol) was dissolved in dry THF (100

mL) and sodium borohydride (0.65 g, 0.0172 mol) was added. This was stirred at 0 °C for 24 hours, diluted with water and ethyl acetate and made cautiously acidic with acetic acid. The resulting solution was extracted twice with ethyl acetate, the organic layer was washed with water, brine, dried over magnesium sulfate and concentrated to dryness. The residue was purified by column chromatography over silica gel (cyclohexane – dichloromethane 2/3 to 1/4) to yield compound **3ae** as an oil (2.91 g, 49%). ^{1}H NMR ($CDCl_3$): 7.31 (dd, 1H, *J* = 2.0, 0.9 Hz), 6.27 (dd, 1H, *J* = 3.2, 2.0 Hz), 6.08 (m, 1H), 4.21 (qd, 2H, *J* = 7.1, 1.5 Hz), 3.73 (t, 1H, *J* = 7.6 Hz), 3.06 (d, 2H, *J* = 7.6 Hz), 1.26 (t, 3H, *J* = 7.1 Hz).

Isolation of compounds 11 and 12: The crude mixtures resulting from the various trials to improve the reduction of **6ae** into **3ae** mentioned in the text and all containing ^{1}H NMR signals corresponding to compound **11** and **12** were gathered and purified by a chromatography over silica gel (cyclohexane – dichloromethane 2/1 to 0/1 to dichloromethane / ethanol 95/5) and the most polar fraction subjected to a second chromatography over silica gel (cyclohexane – ethyl acetate 4/1 to 1/2) to yield samples of compounds **11** (0.85 g, 9%) and **12** (0.21 g, 3%) as described below.

Ethyl 3-(furan-2-yl)-2-(hydroxymethyl)propanoate (11): ^{1}H NMR ($CDCl_3$): 7.33 (dd, 1H, *J* = 1.9, 0.9 Hz), 6.30 (dd, 1H, *J* = 3.2, 1.9 Hz), 6.09 (m, 1H), 4.20 (qd, 2H, *J* = 7.1, 2.1 Hz), 3.79 (m, 2H), 3.06 (m, 1H), 2.96 (m, 2H), 2.21 (t, 1H, *J* = 6.5 Hz), 1.28 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 174.1, 152.4, 141.5, 110.2, 106.7, 62.4, 60.9, 46.5, 26.8, 14.1. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_{14}O_4Na$: 221.0790, found, 221.0794.

2-(Furan-2-ylmethyl)propane-1,3-diol (12): ^{1}H NMR ($CDCl_3$): 7.33 (dd, 1H, *J* = 1.9, 0.9 Hz), 6.31 (dd, 1H, *J* = 3.2, 1.9 Hz), 6.07 (m, 1H), 3.82 (dd, 2H, *J* = 10.8, 4.2 Hz), 3.70 (dd, 2H, *J* = 10.8, 6.5 Hz), 2.73 (s, 1H), 2.71 (s, 1H), 2.34 (s, 2H), 2.15 (m, 1H). ^{13}C NMR ($CDCl_3$): 153.8, 141.3, 110.3, 106.3, 65.2, 41.7, 26.5. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_8H_{12}O_3Na$: 179.0684, found, 179.0685.

Preparation of compounds 14, 18 or 30: Step 1 Preparation of the brominated arylidenemalonate **13**, **17** or **29**. By using the Knoevenagel condensation described above,

these compounds were obtained respectively from 3-bromobenzaldehyde, 4-bromobenzaldehyde or 5-bromofuran-2-carbaldehyde and following a concentration to dryness, used directly. Step 2: cyclopropanation. The considered brominated alkylidenemalonate (14.8 mmol), cyclopropylboronic acid (1.66 g, 19.3 mmol) and caesium carbonate (18.84 g, 57.8 mmol) were dispersed in a 95/5 mixture of toluene and water (120 mL). This was degassed by passing a gentle stream of argon through the suspension, [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium complexed with dichloromethane (0.30 g, 0.36 mmol) was then added and this was heated to reflux under argon for 50 minutes. The resulting dark solution was diluted in ethyl acetate, washed with water, brine, dried over magnesium sulfate and concentrated to dryness. The residues were purified as described below.

Diethyl 2-(3-cyclopropylbenzylidene)malonate (14): This compound was obtained as an oil (4.68 g, 60% from 3-bromobenzaldehyde; 90 % pure) after a chromatography over silica gel (cyclohexane – ethyl acetate 95/5). ^{1}H NMR ($CDCl_3$): 7.72 (s, 1H), 7.27 (m, 2H), 7.17 (m, 1H), 7.11 (m, 1H), 4.36 (q, 2H, *J* = 7.1 Hz), 4.32 (q, 2H, *J* = 7.1 Hz), 1.90 (m, 1H), 1.35 (t, 3H, *J* = 7.1 Hz), 1.32 (t, 3H, *J* = 7.1 Hz), 0.99 (m, 2H), 0.69 (m, 2H). ^{13}C NMR ($CDCl_3$): 166.7, 164.2, 144.6, 142.3, 132.9, 128.6, 128.1, 126.8, 128.5, 126.2, 61.6, 61.5, 15.2, 14.1, 13.9, 9.2.

Diethyl 2-(4-cyclopropylbenzylidene)malonate (18): This compound was obtained as an oil (2.05 g, 47% from 4-bromobenzaldehyde) after a chromatography over silica gel (cyclohexane – ethyl acetate 95/5). ^{1}H NMR ($CDCl_3$): 7.70 (s, 1H), 7.37 (m, 2H), 7.08 (m, 2H), 4.36 (q, 2H, *J* = 7.1 Hz), 4.31 (q, 2H, *J* = 7.1 Hz), 1.91 (m, 1H), 1.33 (t, 6H, *J* = 7.1 Hz), 1.04 (m, 2H), 0.75 (m, 2H). ^{13}C NMR ($CDCl_3$): 166.9, 164.3, 147.6, 142.0, 130.0, 129.7, 125.9, 124.9, 61.6, 61.5, 15.6, 14.1, 13.9, 10.0 (two signals missing). HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{20}O_4Na$, 311.1259, found, 311.1258.

Diethyl 2-((5-cyclopropylfuran-2-yl)methylene)malonate (30): This compound was obtained as an oil (3.12 g, 75% from 5-bromofuran-2-carbaldehyde) after a chromatography

over silica gel (cyclohexane – ethyl acetate 8/1). ^{1}H NMR ($CDCl_3$): 7.32 (s, 1H), 6.65 (d, 1H, *J* = 3.4 Hz), 6.09 (d, 1H, *J* = 3.4 Hz), 4.37 (q, 2H, *J* = 7.1 Hz), 4.25 (q, 2H, *J* = 7.1 Hz), 1.89 (tt, 1H, *J* = 8.4, 5.0 Hz), 1.37 (t, 3H, *J* = 7.1 Hz), 1.30 (t, 3H, *J* = 7.1 Hz), 1.01 – 0.93 (m, 2H), 0.88 – 0.79 (m, 2H). ^{13}C NMR ($CDCl_3$): 166.8, 164.7, 162.5, 147.0, 127.4, 120.1, 119.9, 107.3, 61.5, 61.4, 14.3, 14.2, 9.7, 8.3, (one signal missing). HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{18}O_5Na$, 301.1052, found, 301.1034.

Preparations of oximes 21 or 25: The considered cyclopropyl-bearing arylidenemalonate **14** or **18** were reduced using two days-long catalytic hydrogenation with 10% palladium over charcoal as described above and the resulting compounds were then used directly to prepare the corresponding oximes as described above for the preparation of compounds **2** to give the target oximes as further described below.

Ethyl-2-(hydroxyimino)-3-(3-propylphenyl)propanoate (21): This compound was obtained as a white solid (1.40 g, 36%, un-optimized) after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.74 (bs, 1H), 7.19 (m, 3H), 7.05 (m, 1H), 4.31 (q, 2H, *J* = 7.2 Hz), 3.99 (s, 2H), 2.58 (m, 2H), 1.65 (m, 2H), 1.34 (t, 3H, *J* = 7.2 Hz), 0.96 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$): 163.3, 151.6, 143.0, 135.5, 129.3, 128.3, 126.8, 126.4, 61.9, 38.0, 30.5, 24.5, 14.0, 13.8. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{19}NO_3Na$, 272.1263, found, 272.1250.

Ethyl-2-(hydroxyimino)-3-(4-propylphenyl)propanoate (25): This compound was obtained as a white solid (2.64 g, 69%) after a chromatography over silica gel (cyclohexane – ethyl acetate 6/1). ^{1}H NMR ($CDCl_3$): 9.64 (s, 1H), 7.26 (m, 2H), 7.11 (m, 2H), 4.31 (q, 2H, *J* = 7.2 Hz), 3.98 (s, 2H), 2.57 (m, 2H), 1.64 (m, 2H), 1.34 (t, 3H, *J* = 7.2 Hz), 0.95 (t, 3H, *J* =7.3 Hz). ^{13}C NMR ($CDCl_3$): 163.3, 151.2, 141.0, 132.8, 129.0, 128.6, 61.8, 37.7, 30.1, 24.5, 14.0, 13.8. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{19}NO_3Na$, 272.1263, found, 272.1276.

Preparations of oximes 23, 27 or 32: The considered cyclopropyl-bearing arylidenemalonates **14**, **18** or **30** were reduced using sodium borohydride overnight at 4 °C as described above and the resulting malonates **16**, **20** or **31** were then used directly to

prepare the corresponding oxime as described above for the preparation of compounds **2** to give the target oximes which were purified and characterized as described below.

Ethyl 3-(3-cyclopropylphenyl)-2-(hydroxyimino)propanoate (23): This compound was obtained as a colourless oil (1.72 g, 50% from compound **14**) after a chromatography over silica gel (cyclohexane – ethyl acetate 6/1). ^{1}H NMR ($CDCl_3$): 9.99 (bs, 1H), 7.20 (m, 3H), 6.91 (m, 1H), 4.31 (q, 2H, *J* = 7.2 Hz), 3.97 (s, 2H), 2.58 (m, 2H), 1.88 (m, 1H), 1.34 (t, 3H, *J* = 7.2 Hz), 0.96 (m, 2H), 0.69 (m, 2H). ^{13}C NMR ($CDCl_3$): 163.3, 151.0, 144.2, 135.6, 128.4, 126.8, 126.2, 123.8, 61.9, 30.4, 15.3, 14.0, 9.1. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{17}NO_3Na$, 270.1106, found, 270.1112.

Ethyl 3-(4-cyclopropylphenyl)-2-(hydroxyimino)propanoate (27): This compound was obtained as a pale yellow solid (1.03 g, 88% from compound **18**) after a chromatography over silica gel (cyclohexane – ethyl acetate 6/1). ^{1}H NMR ($CDCl_3$): 9.31 (s, 1H), 7.22 (m, 2H), 6.99 (m, 2H), 4.29 (q, 2H, *J* = 7.2 Hz), 3.95 (s, 2H), 1.86 (m, 1H), 1.33 (t, 3H, *J* = 7.2 Hz), 0.93 (m, 2H), 0.67 (m, 2H). ^{13}C NMR ($CDCl_3$): 163.3, 151.2, 142.3, 132.6, 129.1, 125.8, 61.8, 30.0, 15.0, 14.0, 9.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{17}NO_3Na$, 270.1106, found, 270.1109.

Ethyl 3-(5-cyclopropylfuran-2-yl)-2-(hydroxyimino)propanoate (32): This compound was obtained as an orange solid (1.09 g, 44% from compound **30**) after a chromatography over silica gel (cyclohexane – ethyl acetate 4/1). ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): 9.42 (bs, 1H), 5.97 (m, 1H), 5.84 (d, 1H, *J* = 8.1 Hz), 4.33 (q, 2H, *J* = 7.1 Hz), 3.97 (s, 2H), 1.84 (m, 1H), 1.36 (t, 3H, *J* = 7.1 Hz), 0.84 (m, 2H), 0.73 (m, 2H). ^{13}C NMR ($CDCl_3$): 163.0, 156.5, 148.8, 146.3, 107.5, 104.2, 61.9, 23.7, 14.0, 8.7, 6.5. HRMS (*m/z*): HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NO_4Na$, 260.0899, found, 260.0892.

Preparation of compounds 22, 24, 26, 28 and 33: By using the general protocol described above for the reduction of compounds **2** into **1**, compounds **22**, **24**, **26**, **28** and **33** were isolated and characterized as described below.

Ethyl 2-amino-3-(3-propylphenyl)propanoate hydrochloride (22): Obtained as an oil which was immediately treated with a solution of hydrogen chloride in dioxane and concentrated to dryness to give the hydrochloride salt as a white powder (1.89 g 90%; still containing some ethanol). ^{1}H NMR (DMSO-d_6): 8.72 (bs, 3H), 7.24 (m, 1H), 7.08 (m, 3H), 4.18 (dd, 1H, *J* = 7.9, 5.6 Hz), 4.08 (q, 2H, *J* = 7.2 Hz), 3.21 (dd, 1H, *J* = 13.9, 5.6 Hz), 3.03 (dd, 1H, *J* = 13.9, 7.9 Hz), 2.53 (m, 2H), 1.58 (m, 2H), 1.08 (t, 3H, *J* = 7.2 Hz), 0.89 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (DMSO-d6): 169.4, 142.8, 135.0, 129.9, 128.9, 127.7, 127.2, 62.0, 53.7, 37.6, 36.5, 24.4, 14.2, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{22}NO_2$: 236.1651, found, 236.1637.

Ethyl 2-amino-3-(3-cyclopropylphenyl)propanoate (24): Obtained as an oil (1.66 g, 89%). ^{1}H NMR ($CDCl_3$): 7.19 (m, 1H), 6.95 (m, 3H), 4.19 (q, 2H, J = 7.0 Hz), 3.71 (dd, 1H, J = 5.2, 7.9 Hz), 3.05 (dd, 1H, J = 5.2, 13.5 Hz), 2.83 (dd, 1H, J = 7.9, 13.5 Hz), 1.88 (m, 1H), 1.53 (s, 2H), 1.28 (t, 3H, J = 7.0 Hz), 0.95 (m, 2H), 0.68 (m, 2H). ^{13}C NMR ($CDCl_3$): 175.0, 144.3, 137.2, 128.4, 126.8, 126.3, 124.0, 60.9, 55.8, 41.2, 15.3, 14.2, 9.2, 9.1. HRMS (m/z): $[M+H]^+$ calcd for $C_{14}H_{20}NO_2$: 234.1494, found, 234.1496.

Ethyl 2-amino-3-(4-propylphenyl)propanoate hydrochloride (26): Obtained as an oil which was immediately treated with a solution of hydrogen chloride in dioxane and concentrated to dryness to give the hydrochloride salt as a white powder (2.46 g, 85%; still containing some ethanol). ^{1}H NMR (DMSO-d_6): 8.59 (bs, 3H), 7.15 (s, 4H), 4.20 (dd, 1H, *J* = 7.5, 5.9 Hz), 4.10 (m, 2H), 3.16 (dd, 1H, *J* = 7.9, 5.9 Hz), 3.02 (dd, 1H, *J* = 14.2, 7.9 Hz), 2.54 (m, 2H), 1.58 (m, 2H), 1.09 (t, 3H, *J* = 7.2 Hz), 0.89 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (DMSO-d6): 169.5, 142.6, 132.3, 129.8, 129.0, 62.0, 53.7, 37.3, 36.2, 24.5, 14.2, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{22}NO_2$: 236.1651, found, 236.1659.

Ethyl 2-amino-3-(4-cyclopropylphenyl)propanoate (28): Obtained as an oil (0.71 g, 80%). ^{1}H NMR ($CDCl_3$): 7.09 (m, 2H), 7.01 (m, 2H), 4.18 (q, 2H, *J* = 7.0 Hz), 3.70 (dd, 1H, *J* = 5.2, 7.9 Hz), 3.06 (dd, 1H, *J* = 5.2, 13.7 Hz), 2.83 (dd, 1H, *J* = 7.9, 13.7 Hz), 1.87 (m, 1H), 1.54 (s, 2H), 1.28 (t, 3H, *J* = 7.0 Hz), 0.95 (m, 2H), 0.68 (m, 2H). ^{13}C NMR ($CDCl_3$): 175.0, 142.4,

134.2, 129.2, 125.9, 60.9, 55.9, 40.6, 15.0, 14.2, 9.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}NO_2$: 234.1494, found, 234.1490.

Ethyl 2-amino-3-(5-cyclopropylfuran-2-yl)propanoate (33): Obtained as an oil (0.70 g, 88%; 93% pure). ^{1}H NMR ($CDCl_3$): 5.99 (d, 1H, *J* = 3.1 Hz), 5.85 (d, 1H, *J* = 3.1 Hz), 4.20 (q, 2H, *J* = 7.2 Hz), 3.74 (dd, 1H, *J* = 7.1, 5.1 Hz), 3.03 (dd, 1H, *J* = 14.8, 5.1 Hz), 2.93 (dd, 1H, *J* = 14.8, 7.1 Hz), 1.84 (m, 1H), 1.36 (t, 3H, *J* = 7.2 Hz), 0.84 (m, 2H), 0.73 (m, 2H). ^{13}C NMR ($CDCl_3$): 174.7, 156.7, 149.0, 108.2, 104.0, 60.9, 53.7, 33.3, 14.1, 8.7, 6.4. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{17}NO_3$, 224.1287, found, 224.1282.

Diethyl 2-(1-(furan-2-yl)ethyl)malonate (34): The ethanol solution containing compound **6ae** and obtained as described above was concentrated to dryness thoroughly to give an oil (4.51 g, 0.0189 mol). This was dissolved under argon in dry THF (30 mL), cooled to 0 °C and a 3 M solution of methyl magnesium chloride in THF (16 mL, 0.0473 mol) was slowly added. This was stirred for 15 minutes at 0 °C, cautiously quenched with ethanol, diluted in water made acid with a 1 N solution of hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with water, brine, dried over magnesium sulfate, concentrated to dryness and the residue purified by a chromatography over silica gel (cyclohexane – dichloromethane 4/1) to yield compound **34** as a 95% pure oil (3.41 g, 70%). ^{1}H NMR ($CDCl_3$): 7.32 (t, 1H, *J* = 1.8, 0.9 Hz), 6.28 (dd, 1H, *J* = 3.2, 1.8 Hz), 6.10 – 6.03 (m, 1H), 4.22 (q, 2H, *J* = 7.1 Hz), 4.10 (m, 2H), 3.70 – 3.64 (m, 2H), 1.42 – 1.30 (m, 3H), 1.28 (t, 3H, *J* = 7.1 Hz), 1.18 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 168.1, 168.0, 156.1, 141.3, 110.0, 105.4, 61.4, 61.3, 57.0, 33.5, 17.0, 14.0, 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{18}O_5Na$, 277.1052, found, 277.1052. ^{1}H NMR data similar to the reported one [8].

Ethyl 2-(hydroxyimino)-3-phenylbutanoate (37): Step 1: preparation of diethyl 2-(1-phenylethyl)malonate (**36**): under a calcium chloride guard, diethyl malonate (5.32 g, 0.033 mol) was dissolved in dry DMF (50 mL, dried over 4 Å molecular sieves) and 60% sodium hydride in mineral oil (1.39 g, 0.0348 mol) was added portion-wise while maintaining the solution temperature at 20 °C with a water bath. This was stirred until the end of hydrogen

evolution and (1-chloroethyl)benzene 4.8 mL, 0.036 mol) was added. This was stirred for 7 days, diluted in water and ethyl acetate, the organic layer was washed 5 times with water, brine, dried over magnesium sulfate and concentrated to dryness under high vacuum to remove most of the unreacted diethyl malonate and (1-chloroethyl)benzene to give an oil (6.22 g) pure enough for the next step. Step 2: reaction with isoamylnitrite. Under an inert atmosphere, 4.68 g of the resulting oil was dissolved in dry ethanol (50 mL, dried over 4 Å molecular sieves) and cooled at 0 °C with ice. A solution of 21% sodium ethoxide in ethanol (7.7 mL, 0.0207 mol) was added followed by isoamylnitrite (2.6 mL, 0.0194 mol). This was allowed to warm to room temperature and stirred for 16 hours. The resulting solution was then treated as described above for the general preparation of α-hydroxyimino esters **2** and compound **37** was obtained as an oil (1.07 g, 14% from diethylmalonate) after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$, for once it is a separable but slowly equilibrating mixture of the two oxime isomers): 10.69 (s, 0.2H), 9.72 (s, 0.8H), 4.82 (q, 0.8H, *J* = 7.2 Hz), 4.21 (m, 2H), 4.02 (q, 0.2H, *J* = 7.2 Hz), 1.68 (d, 2.4H, *J* = 7.2 Hz), 1.54 (d, 0.6H, *J* = 7.2 Hz), 1.26 (t, 2.4H, *J* = 7.3 Hz), 1.15 (t, 0.6H, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$, major/minor: 162.6/163.3, 154.3/152.3, 140.6/141.2, 128.5/128.6, 127.6/127.7, 126.6/127.0, 61.5/61.6, 35.0/42.1, 15.5/18.7, 13.9/13.7. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{15}NO_3Na$, 244.0950, found, 244.0939.

Ethyl 2-amino-3-phenylbutanoate (38): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (0.76 g, 88%) containing a 1/2 mixture of two diasteroisomers. ^{1}H NMR ($CDCl_3$): 7.39-7.21 (m, 5H), 4.20 (q, 1.3H, *J* = 7.1 Hz), 4.20 (q, 0.7H, *J* = 7.1 Hz), 3.62 (d, 0.3H, *J* = 6.0 Hz), 3.56 (d, 0.7H, *J* = 7.2 Hz), 3.18 (m, 0.3H), 3.12 (m, 0.3H), 1.44 (s, 2H), 1.36 (d, 2H, *J* = 7.2 Hz), 1.34 (d, 1H, *J* = 6.0 Hz), 1.29 (t, 2H, *J* = 7.1 Hz), 1.16 (t, 1H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$) major diastereoisomer: 174.7, 142.2, 128.5, 127.9, 126.9, 60.8, 60.6, 44.4, 18.4, 14.2. minor diastereoisomer: 174.6, 143.0, 128.3, 127.7, 126.7, 60.7, 60.4, 43.5, 15.1, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{18}NO_2$, 208.1338, found, 208.1331.

Ethyl 2-(hydroxyimino)-3-methyl-3-phenylbutanoate (40): Under an inert atmosphere, ethyl 3-methyl-3-phenylbutanoate [9,10] (1.38 g, 6.68 mmol) was dissolved in dry THF (20 mL). This solution was cooled to −78 °C and a 2 N solution of lithium diisopropylamide in THF (3.5 mL, 7.02 mmol) was added. This was stirred for 5 minutes and isoamylnitrite (1 mL, 7.35 mmol) was added. The solution was allowed to warm to room temperature and stirred for 24 hours. This was diluted in water, made acid with 1 N hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with water, brine, dried over magnesium sulfate and concentrated to dryness. Under an inert atmosphere, this residue was diluted in dry ethanol (10 mL, dried over 4 Å molecular sieves), a 21% solution of sodium ethoxide in ethanol (1 mL) was added and this was heated to reflux for 7 hours. The resulting "transesterified" solution was diluted with water, made acidic with 1 N hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with water, brine, dried over magnesium sulfate and concentrated to dryness and purified by a chromatography over silica gel (cyclohexane – ethyl acetate 7/1 to 4/1) to yield the target oxime as an oil (0.24 g, 15%). ^{1}H NMR ($CDCl_3$): 8.57 (s, 1H), 7.35 (m, 4H), 7.21 (m, 1H), 4.11 (q, 2H, *J* = 7.1 Hz), 1.62 (s, 6H), 1.06 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 163.4, 158.6, 144.3, 128.2, 126.7, 126.4, 61.2, 42.9, 27.1, 13.7. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{17}NO_3Na$, 258.1106, found, 258.1087.

Ethyl 2-amino-3-methyl-3-phenylbutanoate (41): Compound **40** (0.23 g, 0.97 mmol) was dissolved in ethanol (5 mL); To this solution was added 37% hydrochloric acid (0.72 mL, 8.79 mmol) and powdered zinc (0.19 g, 2.93 mmol). This was stirred for 12 hours and another portion of 37% hydrochloric acid (0.72 mL, 8.79 mmol) followed by powdered zinc (0.19 g, 2.93 mmol) were added. Stirring at room temperature was resumed for 8 hours, the resulting solution was diluted in water, made basic with 33% ammonia, extracted with ethyl acetate, the organic layer was washed with water, brine, dried over sodium carbonate and concentrated to dryness to yield compound **41** as an oil (0.20 g, 92%). ^{1}H NMR ($CDCl_3$): 7.37 (m, 4H), 7.24 (m, 1H), 4.07 (q, 2H, *J* = 7.2 Hz), 3.65 (s, 1H), 1.43 (s, 6H), 1.15 (t, 3H, *J*

= 7.2 Hz). ^{13}C NMR ($CDCl_3$): 173.9, 146.3, 128.2, 126.4, 126.3, 64.0, 60.5, 41.9, 25.5, 23.3, 14.0. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{20}NO_2$, 222.1494, found, 222.1490.

Ethyl hydroxyphenylalaninate (42): Compound **2a** (0.1 g, 0.483 mmol) and trifluoromethane sulfonic acid (0.64 mL, 7.2 mmol) were dissolved in diethyl ether (10 mL). To this was added an initial 2 equivalents of triethylsilane (0.15 mL, 0.965 mmol) and following the monitoring of the reaction by LC/MS, additional equivalent of triethylsilane were added to reach a sum of 6 equivalents on day six. Following another day of stirring, water and 1 N hydrochloric acid were added to the resulting solution. This was stirred for 15 minutes made basic by adding 1 N sodium bicarbonate and extracted with ethyl acetate. The organic layer was washed with water, brine, concentrated to dryness and purified by a chromatography over silica gel (dichloromethane – ethanol 98/2, TLC detection using a $KMnO_4$ solution) to yield compound **42** as a film (0.07 g, 69%). ^{1}H NMR ($CDCl_3$): 7.34-7.21 (m, 5H), 5.87 (s, 1H), 4.21 (q, 2H, *J* = 7.2 Hz), 3.89 (dd, 1H, *J* = 5.9 and 8.5 Hz), 3.01 (dd, 1H, *J* = 6.0 et 14.1 Hz), 2.92 (dd, 1H, *J* = 8.2 et 14.0 Hz), 1.24 (t, 3H, *J* = 8.0). ^{13}C NMR ($CDCl_3$): 172.9, 136.6, 129.1, 128.6, 126.9, 66.2, 61.1, 35.5, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{16}NO_3$, 210.1130, found, 210.1136. ^{1}H NMR data similar to the reported one [11].

General protocol for the preparation of malonates 44a and 44b: Step 1: preparation of diethyl 2-(prop-2-yn-1-yl)malonate (**43**). Diethylmalonate (9.16 g, 0.057 mol), 80% propargyl bromide in toluene (6.36 mL, 0.057 mol) and potassium carbonate (8.7 g, 0.063 mol) were stirred in dry acetone (100 mL, dried over 4 Å molecular sieves) for 48 hours. The suspension was filtered and concentrated to dryness to give and oil still (15.52 g) containing about 55% of unreacted diethyl malonate. Since all our trials failed to purify this mixture, this was used directly. Step 2: In a calcium chloride-protected atmosphere, the crude diethyl 2-(prop-2-yn-1-yl)malonate described above (15.5 g), the relevant nitroalkane (0.078 mol) and phenylisocyanate (15.3 mL, 0.14 mol) were dissolved in dichloromethane (200 mL). To this solution were added 10 drops of triethylamine and this was stirred for 48 hours at 20 °C. The

resulting suspension was filtered, the filtrate concentrate to dryness and the residue further purified as described below.

Diethyl 2-((3-methylisoxazol-5-yl)methyl)malonate (44a): This compound was obtained as an oil (3.47 g, 23% from 1-nitroethane; still containing some aryl-bearing impurity) after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1) and extensive drying under vacuum at 80 °C to distil off some 3,4-dimethyl-1,2,5-oxadiazole 2-oxide. ^{1}H NMR ($CDCl_3$) 5.90 (s, 1H), 4.22 (m, 4H), 3.77 (t, 1H, *J* = 7.6 Hz), 3.33 (d, 2H, *J* = 7.6 Hz), 2.26 (s,3H), 1.27 (t, 6H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 168.9, 168.0, 159.8, 102.9, 61.9, 50.2, 25.9, 13.9, 11.3. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{17}NO_5Na$, 278.1004, found, 278.1003.

Diethyl 2-((3-ethylisoxazol-5-yl)methyl)malonate (44b): This compound was obtained as an oil (5.8 g, 33% from 1-nitropropane; still containing some aryl-bearing impurity) after a chromatography over silica gel (cyclohexane – ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$) 5.93 (s, 1H), 4.22 (m, 4H), 3.78 (t, 1H, *J* = 7.6 Hz), 3.34 (d, 2H, *J* = 7.6 Hz), 2.66 (q, 2H, *J* = 7.6 Hz), 1.27 (m, 9H). ^{13}C NMR ($CDCl_3$): 168.9, 168.0, 159.8, 102.9, 61.9, 50.2, 25.9, 13.9, 11.3. ^{13}C NMR ($CDCl_3$): 168.9, 168.0, 159.8, 102.9, 61.9, 50.2, 25.9, 13.9, 11.3. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{19}NO_5Na$, 292.1161, found, 292.1161.

Ethyl 2-(hydroxyimino)-3-(3-methylisoxazol-5-yl)propanoate (45a): This compound was obtained when following the general protocol for the transformation of compounds **3** into **2** as a solid (3.39 g, 50%) after a chromatography over silica gel (cyclohexane – ethyl acetate 9/1). ^{1}H NMR ($CDCl_3$): 10.17 (s(br), 1H), 5.92 (s, 1H), 4.34 (q, 2H, *J* = 7.2 Hz), 4.10 (s, 2H), 2.26 (s, 3H), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 166.2, 162.6, 160.0, 146.8, 103.1, 62.3, 22.5, 14.0, 11.3. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_9H_{12}N_2O_4Na$: 262.1055, found, 262.1147.

Ethyl 3-(3-ethylisoxazol-5-yl)-2-(hydroxyimino)propanoate (45b): This compound was obtained when following the general protocol for the transformation of compounds **3** into **2** as a solid (2.85 g, 58%). ^{1}H NMR ($CDCl_3$): 10.22 (s(br), 1H), 5.94 (s, 1H), 4.34 (q, 2H, *J* = 7.2 Hz), 4.10 (s, 2H), 2.65 (q, 2H, *J* = 7.6 Hz), 1.35 (t, 3H, *J* = 7.2 Hz), 1.24 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR ($CDCl_3$): 165.2, 165.4, 162.6, 146.8, 101.7, 60.3, 22.5, 19.5, 14.0, 12.5. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_{14}N_2O_4Na$: 249.0851, found, 249.0854.

Ethyl 2-amino-3-(3-methylisoxazol-5-yl)propanoate (46a): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (0.43 g, 35%). ^{1}H NMR ($CDCl_3$): 5.96 (s, 1H), 4.22 (qd, 2H, *J* = 7.2, 1.9 Hz), 3.84 (dd, 1H, *J* = 7.7, 5.0 Hz), 3.20 (dd, 1H, *J* = 15.0, 5.0 Hz), 3.05 (dd, 1H, *J* = 15.1, 7.7 Hz), 2.29 (s, 3H), 1.30 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): 173.9, 168.9, 159.9, 103.5, 61.4, 53.1, 32.1, 14.2, 11.4. HRMS (*m/z*): $[M+H]^+$ calcd for $C_9H_{15}N_2O_3$: 199.1083, found, 199.1085.

Ethyl 2-amino-3-(3-ethylisoxazol-5-yl)propanoate (46b): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (2.26 g, 84%).^{1}H NMR ($CDCl_3$): 5.98 (s, 1H), 4.22 (qd, 2H, *J* = 7.1, 2.3 Hz), 3.84 (dd, 1H, *J* = 7.7, 5.1 Hz), 3.21 (ddd, 1H, *J* = 15.0, 5.1, 0.7 Hz), 3.06 (ddd, 1H, *J* = 15.1, 7.7, 0.7 Hz), 2.68 (q, 2H, *J* = 7.6 Hz), 1.29 (t, 4H, *J* = 7.2 Hz), 1.27 (t, 2H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$): 173.9, 168.7, 165.2, 102.1, 61.4, 53.1, 32.2, 19.6, 14.2, 12.6. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{17}N_2O_3$: 213.1239, found, 213.1237.

Ethyl 3-bromo-2-(hydroxyimino)propanoate (47): Two preparations were used to synthesize compound **47**. The first one is very much the protocol described in a patent [12]: 75% pure ethyl bromopyruvate (5 mL, 0.0299 mol) was dissolved in water (10 mL) and chloroform (10 mL). To this was added hydroxylamine hydrochloride (2.52 g, 0.036 mol) and this was stirred in a closed vessel overnight. The resulting solution was diluted in dichloromethane, the organic layer was washed with water, brine, dried over magnesium sulfate, concentrated to dryness and recrystallized from *n*-heptane to yield compound **47** (still containing traces of ethyl 2-(hydroxyimino)propanoate; δ = 2.12 ppm) as white needles (5.43 g, 64%). Note: an improved yield (19.74 g, 77%) was obtained when following the same procedure but using 90% pure ethyl bromopyruvate. Alternatively, we used the following original protocol (very much inspired by a report [13] mentioning a one pot synthesis of ethyl 2-(hydroxyimino)acetate from glyoxylic acid): 3-bromo-2-oxopropanoic acid (5.85 g, 0.0316

mol), hydroxylamine hydrochloride (2.2 g, 0.0316 mol) and sodium bromide (6.5 g, 0.063 mol) were stirred overnight at 20 °C in dry ethanol (60 mL) and then heated to reflux for 30 minutes. This was dispersed in water and ethyl acetate, the organic layer was washed with water, brine, concentrated to dryness and the residue recrystallized from *n*-heptane to yield compound **47** (4.67 g, 70%) still containing some amount of its (oily) chlorinated homolog. ^{1}H NMR data similar to the reported one [12].

3-Ethyl-2-methylfuran (48ao): In a 500 mL flask fitted with a condenser and a dropping funnel, lithium aluminium hydride (0.91 g, 0.024 mol) was weighted. Under an argon atmosphere, dry ether (20 mL) was added and the suspension stirred. In another flask, dry aluminium trichloride (3.2 g, 0.024 mol) was dissolved in dry ether (25 mL); note: a slight heating can be observed. This solution was then added to the suspension described above (no or little heating occurred). To this suspension 1-(2-methylfuran-3-yl)ethan-1-one, prepared from acetylacetone and chloroacetaldehyde as described below for the preparation of 6,7-dihydrobenzofuran-4(5*H*)-one (2.97 g, 0.024 mol) dissolved in dry ether (50 mL) was added drop-wise, slowly enough to avoid too much reflux. The resulting solution was stirred for 2 hours, cautiously quenched with water, and cautiously diluted with a 3 N solution of sulfuric acid. This was diluted in water and ether, the organic layer was washed with water, brine, dried over magnesium sulfate and concentrated at atmospheric pressure to yield an oil containing compound **48ao** and some ether which was directly used for the cycloaddition reaction as described below.

4,5,6,7-Tetrahydrobenzofuran (48ap): Step 1, preparation of 6,7-dihydrobenzofuran-4(5*H*)-one [14]: under argon, cyclohexanedione (20.71 g, 0.18 mol) was dissolved in methanol (100 mL) and cooled to 0 °C. To this was added potassium hydroxide (12.2 g, 0.18 mol) and after stirring 30 minutes at 0 °C the 50% solution of chloroacetaldehyde in water (26.3 mL, 0.203 mol) was added. This was stirred overnight, the resulting solution made acidic with 1 N hydrochloric acid, extracted with ethyl acetate, the organic layer was washed with water, brine, dried over magnesium sulfate and concentrated to dryness to give the volatile 6,7-

dihydrobenzofuran-4(5*H*)-one (16.5 g) clean enough for the next step. Step 2, reduction with $AlLiH_4/AlCl_3$: from 6,7-dihydrobenzofuran-4(5*H*)-one (3.62 g, 0.026 mol) the procedure is identical to the one described above for the preparation of **48ao**. Note: but for the purification, this reduction protocol is pretty much identical to the one reported previously [15]. Again the oil containing **48ap** and some ether was used directly for the cycloaddition reaction as described below.

2-Ethyl-3-methylfuran (48aq): Step 1: preparation of ethyl 2-ethylfuran-3-carboxylate. By using the protocol described above for the synthesis of 6,7-dihydrobenzofuran-4(5H)-one, this volatile compound was obtained from ethyl 3-oxopentanoate (9.88 g, 0.068 mol) and chloroacetaldehyde after a chromatography over silica gel (cyclohexane – dichloromethane) as an oil still containing some cyclohexane (5.21 g). Step 2, reduction with $AlLiH_4/AlCl_3$: the procedure is identical to the one described above for the preparation of 3-ethyl-2-methylfuran (**48ao**) but for the differences that two equivalent of $AlCl_3$ and two equivalent of $AlLiH_4$ were used and that the reaction was left to stir for 50 hours before undertaking the work up procedure described above. This gave the volatile compound **48aq** as an oil still containing ether and cyclohexane which was used directly for the cycloaddition reaction as described below.

2-isopropyl-3-methylfuran (48ar): Step 1: preparation of ethyl 2-isopropylfuran-3-carboxylate. By using the protocol described above for the synthesis of 6,7-dihydrobenzofuran-4(5*H*)-one, this volatile compound was obtained from ethyl 4-methyl-3-oxopentanoate (6.92 g, 0.0437 mol) and chloroacetaldehyde after a chromatography over silica gel (cyclohexane – dichloromethane) as an oil still containing some cyclohexane (1.8 g). Step 2, reduction with $AlLiH_4/AlCl_3$: the procedure is identical to the one described above for the preparation of 3-ethyl-2-methylfuran (**48ao**) but for the differences that 2 equivalent of $AlCl_3$ and two equivalent of $AlLiH_4$ were used and that the reaction was left to stir for 50 hours before undertaking the work up procedure described above. This gave the volatile

compound **48ar** as an oil still containing ether and cyclohexane which was used directly for the cycloaddition reaction as described below.

Protocols for the synthesis of furan-bearing α-hydroxyimino esters by [2 + 4] cycloaddition Protocol b: The considered furan (0.013 mol), compound **47** (2.75 g, 0.013 mol) and sodium carbonate (1.5 g, 0.0144 mol) were dispersed in toluene (15 mL) before adding tetrabutylammonium bromide (0.042 g, 13 mmol). This was stirred for 1 hour, diluted in water and ethyl acetate, the organic layer was washed with water, brine, dried over magnesium sulfate, concentrated to dryness and further purified as described below. Protocol c: The considered furan (0.01 mol), compound **47** (2.10 g, 0.01 mol) and ammonium bicarbonate (0.86 g, 0.011 mol) were dispersed in ethyl acetate (10 mL) before adding water (2 mL). This was stirred for 1 hour, diluted in water and ethyl acetate, the organic layer was washed with water, brine, dried over magnesium sulfate, concentrated to dryness and further purified as described below. Protocol d: The considered furan (6.09 mmol), compound **47** (1.28 g, 6.09 mmol) and lithium carbonate (0.49 g, 6.69 mmol) were dispersed in ethyl acetate (10 mL) before adding water (2 mL). This was stirred for 1 hour, diluted in water and ethyl acetate made, the organic layer was washed with water, brine, dried over magnesium sulfate, concentrated to dryness and the residue further purified as described below. Protocol e: The considered furan (0.0117 mol), compound **47** (2.56 g, 0.0117 mol) and sodium carbonate (1.42 g, 0.0129 mol) were dispersed in ethyl acetate (6 mL) and water (3 mL). This was stirred for 1 hour, diluted in water and ethyl acetate, the organic layer was washed with water, brine, dried over magnesium sulfate, concentrated to dryness and further purified as described below.

Ethyl 2-(hydroxyimino)-3-(5-propylfuran-2-yl)propanoate (2am): This compound was obtained in the yield reported in Table 2, as a solid after a chromatography over silica gel (cyclohexane - ethyl acetate 5/1). ^{1}H NMR ($CDCl_3$): 9.15 (s(br), 1H), 5.98 (d, 1H, *J* = 3.0 Hz), 5.88 (m, 1H), 4.32 (q, 2H, *J* = 7.0 Hz), 3.99 (s, 2H), 2.55 (q, 2H, *J* = 7.7 Hz), 1.65 (m, 2H), 1.35 (t, 3H, *J* = 7.1 Hz), 0.95 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 155.5, 148.8,

146.8, 107.3, 105.5, 61.9, 30.0, 23.7, 21.3, 14.0, 13.7. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{17}NO_4Na$: 262.1055, found, 262.1047.

Ethyl 2-(hydroxyimino)-3-(5-pentylfuran-2-yl)propanoate (2an): This compound was obtained in the yield reported in Table 2, as a solid after a chromatography over silica gel (cyclohexane - ethyl acetate 5/1). ^1H NMR ($CDCl_3$): 8.33 (s(br), 1H), 5.98 (d, 1H, *J* = 3.0 Hz), 5.87 (m, 1H), 4.32 (q, 2H, *J* = 7.0 Hz), 3.99 (s, 2H), 2.57 (q, 2H, *J* = 7.7 Hz), 1.65 (m, 2H), 1.35 (t, 3H, *J* = 7.1 Hz), 1.32 (m, 4H), 0.91 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): 162.9, 155.7, 148.7, 146.5, 107.3, 105.3, 61.9, 31.3, 30.0, 27.6, 23.7, 22.3, 14.0, 13.9. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{121}NO_4Na$: 290.1368, found, 290.1366.

Ethyl 3-(4-ethyl-5-methylfuran-2-yl)-2-(hydroxyimino)propanoate (2ao): This compound was obtained in the yield reported in Table 2, as a solid after a chromatography over silica gel (cyclohexane - ethyl acetate 5/1). ^1H NMR ($CDCl_3$): 5.93 (s, 1H), 4.33 (q, 2H, *J* = 7.2 Hz), 3.95 (s, 2H), 2.29 (q, 2H, *J* = 7.4 Hz), 2.16 (s, 3H), 1.35 (t, 3H *J* = 7.2 Hz), 1.09 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 148.9, 145.5, 145.4, 121.4, 108.5, 61.9, 23.6, 18.0, 14.7, 14.0, 11.3. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{17}NO_4Na$: 262.1055, found, 262.1053.

Ethyl 2-(hydroxyimino)-3-(4,5,6,7-tetrahydrobenzofuran-2-yl)propanoate (2ap): This compound was obtained in the yield reported in Table 2, as a solid after a chromatography over silica gel (cyclohexane - ethyl acetate 5/1). ^1H NMR ($CDCl_3$): 5.91 (s, 1H), 4.33 (q, 2H, *J* = 7.2 Hz), 3.97 (s, 2H), 2.54 (m, 2H), 2.36 (m, 2H), 1.80 (m, 2H), 1.70 (m, 2H), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 149.7, 149.0, 146.0, 117.6, 107.8, 61.9, 23.7, 23.2, 23.1, 23.0, 22.0, 14.0. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{17}NO_4Na$: 274.1054, found, 274.1057.

Ethyl-3-(5-ethyl-4-methylfuran-2-yl)-2-(hydroxyimino)propanoate (2aq): This compound was obtained in the yield reported in Table 2, as a solid after a chromatography over silica gel (cyclohexane - ethyl acetate 5/1). ^1H NMR ($CDCl_3$): 8.56 (s(br), 1H), 5.86 (s, 1H), 4.33 (q, 2H, *J* = 7.2 Hz), 3.95 (s, 2H), 2.54 (q, 2H, *J* = 7.6 Hz), 1.89 (s, 3H), 1.35 (t, 3H *J* = 7.2 Hz), 1.16 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 151.5, 148.9, 145.3, 113.7, 110.0, 61.9,

23.6, 19.3, 14.0, 12.9, 9.7. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{17}NO_4Na$: 262.1055, found, 262.1053.

Ethyl 2-(hydroxyimino)-3-(5-isopropyl-4-methylfuran-2-yl)propanoate (2ar): This compound (90% pure) was obtained in the yield reported in Table 2, as a solid after a chromatography over silica gel (cyclohexane - ethyl acetate 5/1). ^1H NMR ($CDCl_3$): 5.83 (s, 1H), 4.32 (q, 2H, *J* = 7.2 Hz), 3.95 (s, 2H), 2.94 (sept, 1H), *J* = 7.0 Hz), 1.91 (s, 3H), 1.35 (t, 3H, *J* = 7.2 Hz), 1.20 (d, 6H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): 163.0, 154.5, 149.0, 145.0, 112.6, 110.0, 61.9, 26.2, 23.6, 21.3, 14.0, 9.7. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{19}NO_4Na$: 276.1212, found, 276.1213.

Ethyl 2-amino-3-(5-propylfuran-2-yl)propanoate (1am): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (0.93 g, 79%). ^1H NMR ($CDCl_3$): 6.00 (d, 1H, *J* = 3.0 Hz), 5.88 (dt, 1H, *J* = 3.0, 1.0 Hz), 4.20 (qd, 2H, *J* = 7.1, 2.6 Hz), 3.75 (dd, 1H, *J* = 7.1, 5.1 Hz), 3.05 (dd, 1H, *J* = 14.9, 5.1 Hz), 2.95 (dd, 1H, *J* = 14.9, 7.1 Hz), 2.55 (t, 3H, *J* = 7.4 Hz), 1.65 (m, 2H), 1.29 (t, 3H, *J* = 7.1 Hz), 0.96 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 155.7, 149.3, 108.1, 105.3, 60.9, 53.8, 33.7, 30.0, 21.3, 14.2, 13.7. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{20}NO_3$: 226.1443, found, 226.1449.

Ethyl 2-amino-3-(5-pentylfuran-2-yl)propanoate (1an): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (0.54 g, 90%). ^1H NMR ($CDCl_3$): 6.00 (d, 1H, *J* = 3.0 Hz), 5.88 (m, 1H), 4.20 (qd, 2H, *J* = 7.1, 2.6 Hz), 3.75 (dd, 1H, *J* = 7.1, 5.1 Hz), 3.07 (dd, 1H, *J* = 14.9, 5.1 Hz), 2.96 (dd, 1H, *J* = 14.9, 7.1 Hz), 2.56 (t, 3H, *J* = 7.4 Hz), 19.6 (s(br), 2H), 1.61 (m, 2H), 1.33 (m, 4H), 1.29 (t, 3H, *J* = 7.1 Hz), 0.91 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): 174.5, 156.0, 149.1, 108.2, 105.2, 61.0, 53.7, 33.5, 31.3, 28.0, 27.6, 22.4, 14.2, 13.9. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{24}NO_3$: 254.1756, found, 254.1756.

Ethyl 2-amino-3-(4-ethyl-5-methylfuran-2-yl)propanoate (1ao): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was

obtained as an oil (0.95 g, 82%). ^{1}H NMR ($CDCl_3$): 5.94 (s, 1H), 4.20 (m, 2H), 3.73 (dd, 1H, *J* = 4.9 and 7.4 Hz), 3.02 (dd, 1H, *J* = 4.9 and 14.7 Hz), 2.90 (dd, 1H, *J* = 7.4 and 14.7 Hz), 2.29 (q, 2H, *J* = 7.5), 2.16 (s, 3H), 1.83 (s (br), 2H), 1.27 (d, 3H *J* = 7.1 Hz), 1.05 (d, 3H *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 148.2, 145.7, 121.2, 109.2, 60.9, 53.8, 33.6, 18.0, 14.8, 14.2, 11.3. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{20}NO_3$: 226.1443, found, 226.1446.

Ethyl 2-amino-3-(4,5,6,7-tetrahydrobenzofuran-2-yl)propanoate (1ap): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (1.57 g, 82%). ^{1}H NMR ($CDCl_3$): 5.91 (s, 1H), 4.20 (m, 2H), 3.74 (dd, 1H, *J* = 5.0 and 7.4 Hz), 3.05 (dd, 1H, *J* = 5.0 and 14.8 Hz), 2.90 (dd, 1H, *J* = 7.4 and 14.8 Hz), 2.54 (m, 2H), 2.37 (m, 2H), 1.87 (s (br), 2H), 1.81 (m, 2H), 1.70 (m, 2H), 1.29 (d, 3H *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 150.0, 148.7, 117.4, 108.6, 61.1, 53.8, 33.7, 21.1 (two signals), 23.1, 22.0, 14.1. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{20}NO_3$: 238.1443, found, 238.1438.

Ethyl 2-amino-3-(5-ethyl-4-methylfuran-2-yl)propanoate (1aq): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (0.95 g, 82%). ^{1}H NMR ($CDCl_3$): 5.94 (s, 1H), 4.20 (m, 2H), 3.73 (dd, 1H, *J* = 4.9 and 7.4 Hz), 3.02 (dd, 1H, *J* = 4.9 and 14.7 Hz), 2.90 (dd, 1H, *J* = 7.4 and 14.7 Hz), 2.29 (q, 2H, *J* = 7.5), 2.16 (s, 3H), 1.83 (s (br), 2H), 1.27 (d, 3H *J* = 7.1 Hz), 1.05 (d, 3H *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$): 174.7, 148.2, 145.7, 121.2, 109.2, 60.9, 53.8, 33.6, 18.0, 14.8, 14.2, 11.3.

Ethyl 2-amino-3-(5-isopropyl-4-methylfuran-2-yl)propanoate (1ar): By using the general protocol described above for the reduction of compounds **2** into **1**, this compound was obtained as an oil (0.41 g, 86%; 90% pure). ^{1}H NMR ($CDCl_3$): 5.87 (s, 1H), 4.21 (m, 2H), 3.73 (dd, 1H, *J* = 5.1 and 6.8 Hz), 3.01 (dd, 1H, *J* = 5.1 and 14.8 Hz), 2.94 (sept, 1H, *J* = 7.0 Hz), 2.90 (dd, 1H, *J* = 6.8 and 14.8 Hz), 1.91 (s, 3H), 1.84 (s, 2H), 1.29 (q, 2H, *J* = 7.1), 1.20 (d, 6H *J* = 7.0 Hz).^{13}C NMR ($CDCl_3$): 174.6, 154.8, 147.6, 112.3, 111.1, 60.9, 53.6, 33.4,

26.1, 21.3, 21.2, 14.1, 9.7. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{22}NO_3$: 240.1600, found, 240.1602.

Ethyl 2-amino-3-(1,3-dioxolan-2-yl)propanoate (53): Step 1: the previously described [16] diethyl 2-((1,3-dioxolan-2-yl)methyl)malonate (**51**) (7.8 g, 0.317 mol) was dissolved in ethanol (40 mL) and potassium hydroxide (1.78 g, 0.0317 mol) dissolved in ethanol (60 mL) was added dropwise. The solution was stirred overnight at room temperature and then briefly heated to reflux. This was concentrated, dissolved in water which was made more basic with 22% ammonia. The aqueous phase was washed with dichloromethane, made acidic with 37% hydrochloric acid, extracted with ethyl acetate, the organic layer was washed with water, brine, dried over magnesium sulfate and concentrated to dryness to yield 90% pure 2-((1,3-dioxolan-2-yl)methyl)-3-ethoxy-3-oxopropanoic acid (**52**) (3.85 g, 55%). ^{1}H NMR ($CDCl_3$): 5.05 (t, 1H, *J* = 3.7 Hz), 4.24 (q, 2H, *J* = 7.1 Hz), 3.98 (m, 2H), 3.82 (m, 2H), 3.64 (t, 1H, *J* = 6.9 Hz), 2.40 (m, 2H), 1.30 (t, 3H, *J* = 7.1 Hz). Step 2: Under argon, this compound (3.85 g, 0.0176 mol) was dissolved in toluene (50 mL, dried over 4 Å molecular). Triethylamine (2.95 mL, 0.021 mol) was added and then diphenylphosphoryl azide (4.18 mL, 0.021 mol). This was stirred at 80 °C for 1.5 h, the toluene was removed under vacuum and the resulting oil repeatedly extracted with cyclohexane. Concentration to dryness of this extract led to an oil which was stirred at room temperature in 4% hydrochloric acid (50 mL) overnight. The resulting solution was diluted in more acid, washed with ethyl acetate, the aqueous phase was made basic with 22% ammonia, extracted with ethyl acetate, and this organic layer was washed with water, brine, dried over sodium carbonate and concentrated to dryness to yield the α-amino ester **53** as an oil (0.14 g, 16%). Alternatively, the same compound (0.44 g, 43%) was obtained from **53**, using the very mild reduction protocol described below for the preparation of α-amino ester **56**. ^{1}H NMR ($CDCl_3$): 5.03 (dd, 1H, *J* = 4.3, 5.0 Hz), 4.17 (q, 2H, *J* = 7.0 Hz), 3.96 (m, 2H), 3.85 (m, 2H), 3.66 (dd, 1H, *J* = 4.5, 8.3 Hz), 2.14 (ddd, 1H, *J* = 4.5, 5.0, 14.4 Hz), 1.93 (ddd, 1H, *J* = 4.3, 8.3, 14.4 Hz), 1.86 (s, 2H),

1.26 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): 175.3, 102.6, 64.9, 64.8, 61.0, 51.2, 38.3, 14.2. HRMS (*m/z*): $[M+H]^+$ calcd for $C_8H_{16}NO_4$, 190.1079, found, 190.1061.

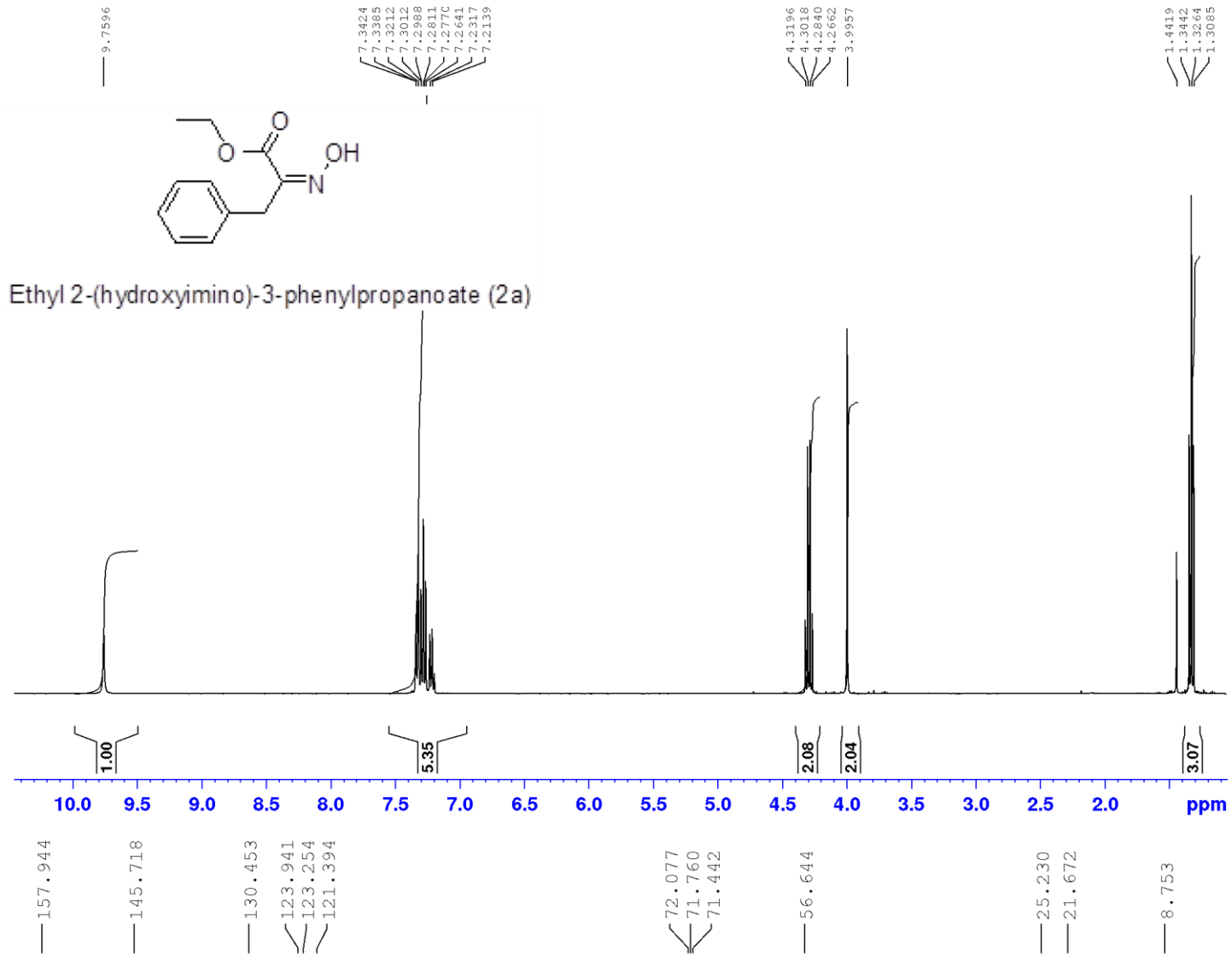
Ethyl 3-(1,3-dioxolan-2-yl)-2-(hydroxyimino)propanoate (54): This compound was obtained from compound **51** [16] as a solid (3.81 g, 28% from diethyl malonate) using the general preparation of oximes **2** from malonates described above after a chromatography over silica gel (cyclohexane – ethyl acetate 3/2) and a recrystallisation from cyclohexane (two crops). ^{1}H NMR (DMSO-d_6, not stable in $CDCl_3$): 12.34 (s (br), 1H), 5.11 (t, 1H, *J* = 5.5 Hz), 4.19 (q, 2H, *J* = 7.1 Hz), 3.87 (m, 2H), 3.75 (m, 2H), 2.83 (d, 2H, *J* = 5.2 Hz), 1.24 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (DMSO-d_6): 164.1, 147.3, 100.5, 64.5, 61.3, 30.1, 14.4. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_8H_{13}NO_5Na$, 226.0691, found, 226.0698.

Diethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)malonate (56): The following protocol is inspired from the reported procedure [17]. Under a calcium chloride-protected atmosphere, diethylmalonate (13.77 g, 0.0859 mol) was dissolved in dry DMF (110 mL, dried over 4 Å molecular sieves), This was cooled to 0 °C and 60% sodium hydride suspended in oil (3.33 g, 0.0832 mol) was added by portion. At the end of the hydrogen evolution, 2-(2-bromoethyl)-1,3-dioxolane (9.8 mL, 0.0834 mol) was added. The reaction wessel was brought back to room temperature and then heated at 80 °C for 4 hours. The resulting suspension was concentrated, the residue dissolved in a mixture of water and diethyether, the organic layer was washed with water four times, brine, dried over magnesium sulfate and concentrated to dryness. A distillation under a 5 mbar vaccum led to a fraction boiling at 148-150 °C which contained pure compound **56** (13.28 g, 59 %). ^{1}H NMR (DMSO-d_6) : 4.79 (t, 1H, *J* = 4.8 Hz), 4.12 (m, 2H), 3.87 (m, 2H), 3.76 (m, 2H), 3.51 (t, 1H, *J* = 7.6 Hz), 1.87 (m, 2H), 1.58 (m, 2H), 1.18 (t, 3H, *J* = 7.2 Hz).^{13}C NMR (DMSO-d_6): 169.3, 103.4, 64.7, 61.3, 51.2, 31.0, 23.3, 14.4. ^{1}H NMR data identical with the one reported previously [17].

Ethyl 4-(1,3-dioxolan-2-yl)-2-(hydroxyimino)butanoate (57): This compound was obtained from compound **56** (5.46 g) as a white powder (3.27 g, 71%) using the general preparation of oximes **2** from malonates described above and a chromatography over silica gel

(dichloromethane – ethanol 98/2). ^{1}H NMR (DMSO-d_6, not stable in $CDCl_3$): 12.14 (s (br), 1H), 4.79 (t, 1H, *J* = 4.4 Hz), 4.18 (q, 2H, *J* = 7.1 Hz), 3.85 (m, 2H), 3.75 (m, 2H), 2.53 (m, 2H), 1.73 (m, 2H), 1.23 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (DMSO-d_6): 164.2, 151.4, 103.4, 64.8, 61.1, 29.8, 19.4, 14.5. HRMS (*m/z*): $[M+Na]^+$ calcd for $C_9H_{15}NO_5Na$, 240.0848, found, 240.0845.

Ethyl 2-amino-4-(1,3-dioxolan-2-yl)butanoate (58): Compound **57** (0.26 g, 1.19 mmol) and 10 % palladium over charcoal (0.12 g, 0.119 mmol) were dispersed in acetic acid (10 mL). This was charged with hydrogen (1 atm) and stirred for 24 hours. The resulting solution was filtered, concentrated to dryness, the residue was dispersed in water, made basic with 30% ammonia and this was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium carbonate and cocnetrated to dryness to give compound **58** as a volatile oil (0.16 g, 65 %). ^{1}H NMR (DMSO-d_6): 4.77 (t, 1H, *J* = 4.6 Hz), 4.08 (m, 2H), 3.86 (m, 2H), 3.75 (m, 2H), 3.29 (m, 1H), 1.76-1.45 (m, 6H), 1.19 (t, 3H, *J* = 7.06 Hz). ^{13}C NMR (DMSO-d_6): 176.1, 103.9, 64.7, 64.6, 60.4, 54.2, 30.1, 29.5, 14.6. HRMS (*m/z*): $[M+H]^+$ calcd for $C_9H_{18}NO_4$, 204.1236, found, 204.1235.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4.3196
4.3018
4.2840
4.2662
3.9957
1.4419
1.3442
1.3264
1.3085
O
O
OH
N
Ethyl 2-(hydroxyimino)-3-phenylpropanoate (2a)
1.00
5.35
2.08
2.04
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
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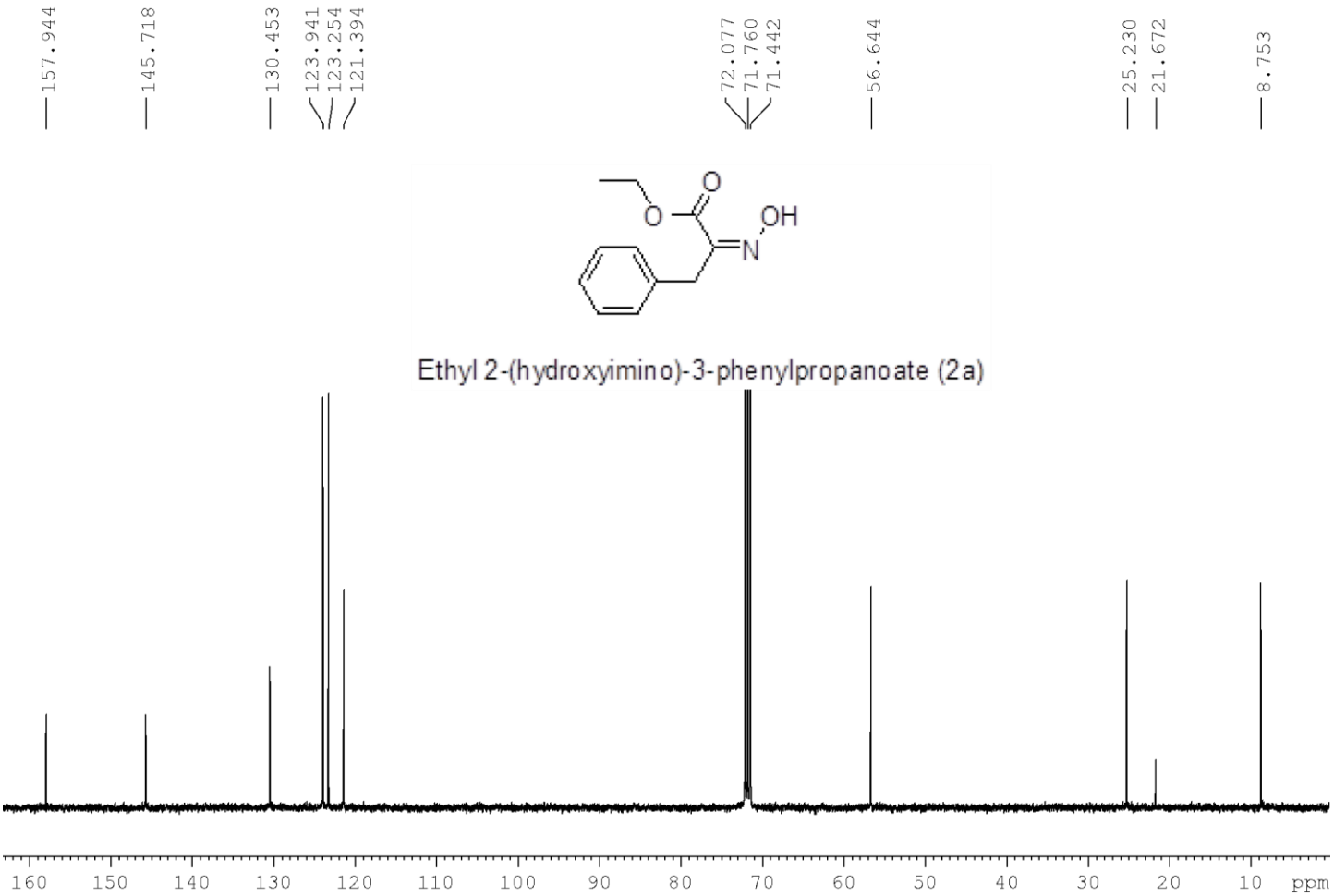
2.0
ppm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25.230
21.672
8.753
O
O
OH
N
Ethyl 2-(hydroxyimino)-3-phenylpropanoate (2a)
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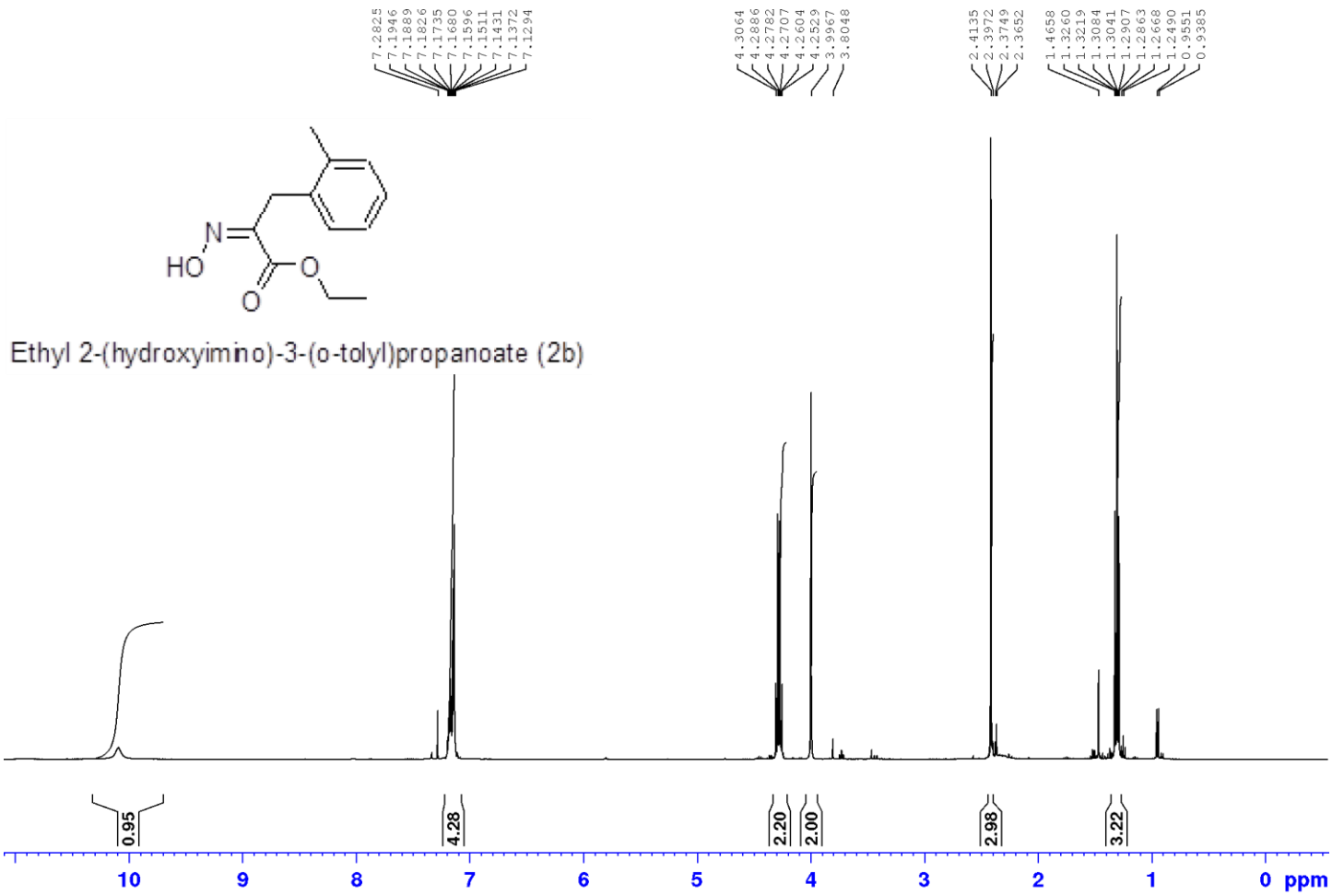
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.1431
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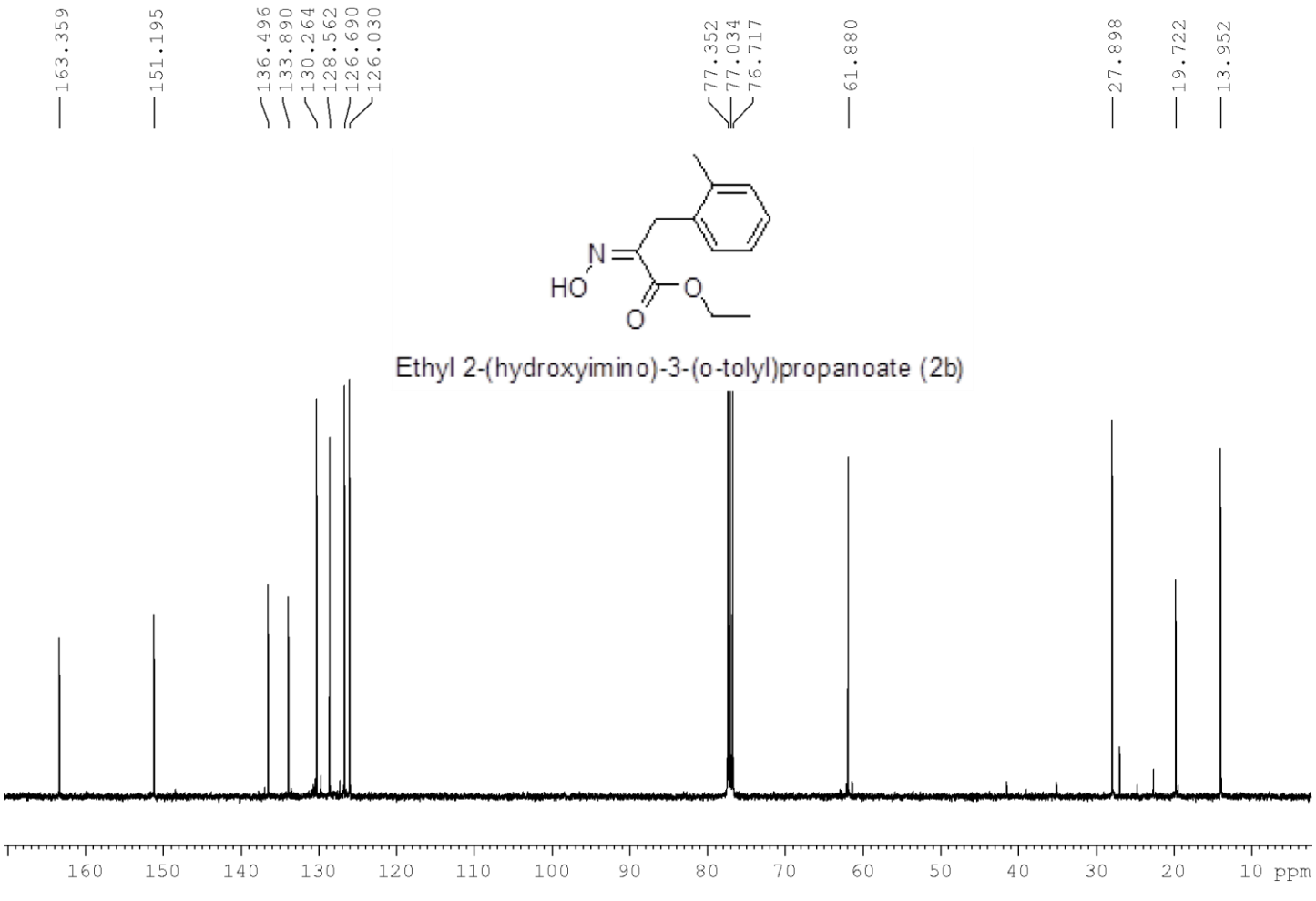
7.1294
4.3064
4.2886
4.2782
4.2707
4.2604
4.2529
3.9967
3.8048
2.4135
2.3972
2.3749
2.3652
1.4658
1.3260
1.3219
1.3084
1.3041
1.2907
1.2863
1.2668
1.2490
0.9551
0.9385
N
HO
O
O
Ethyl 2-(hydroxyimino)-3-(o-tolyl)propanoate (2b)
0.95
4.28
2.20
2.00
2.98
3.22
10
9
8
7
6
5
4
3
2
1
0 ppm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126.030
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77.034
76.717
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27.898
19.722
13.952
N
HO
O
O
Ethyl 2-(hydroxyimino)-3-(o-tolyl)propanoate (2b)
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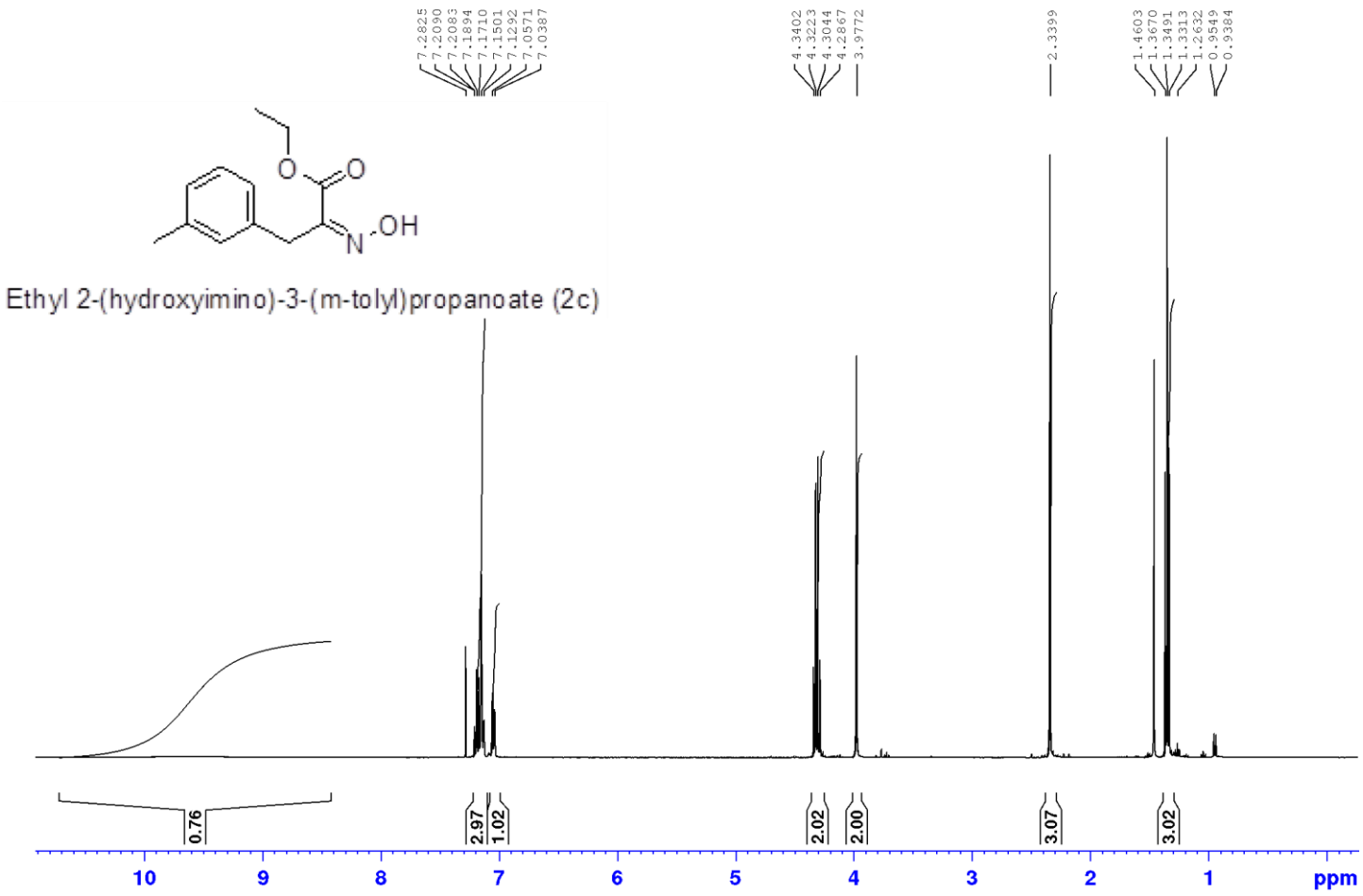
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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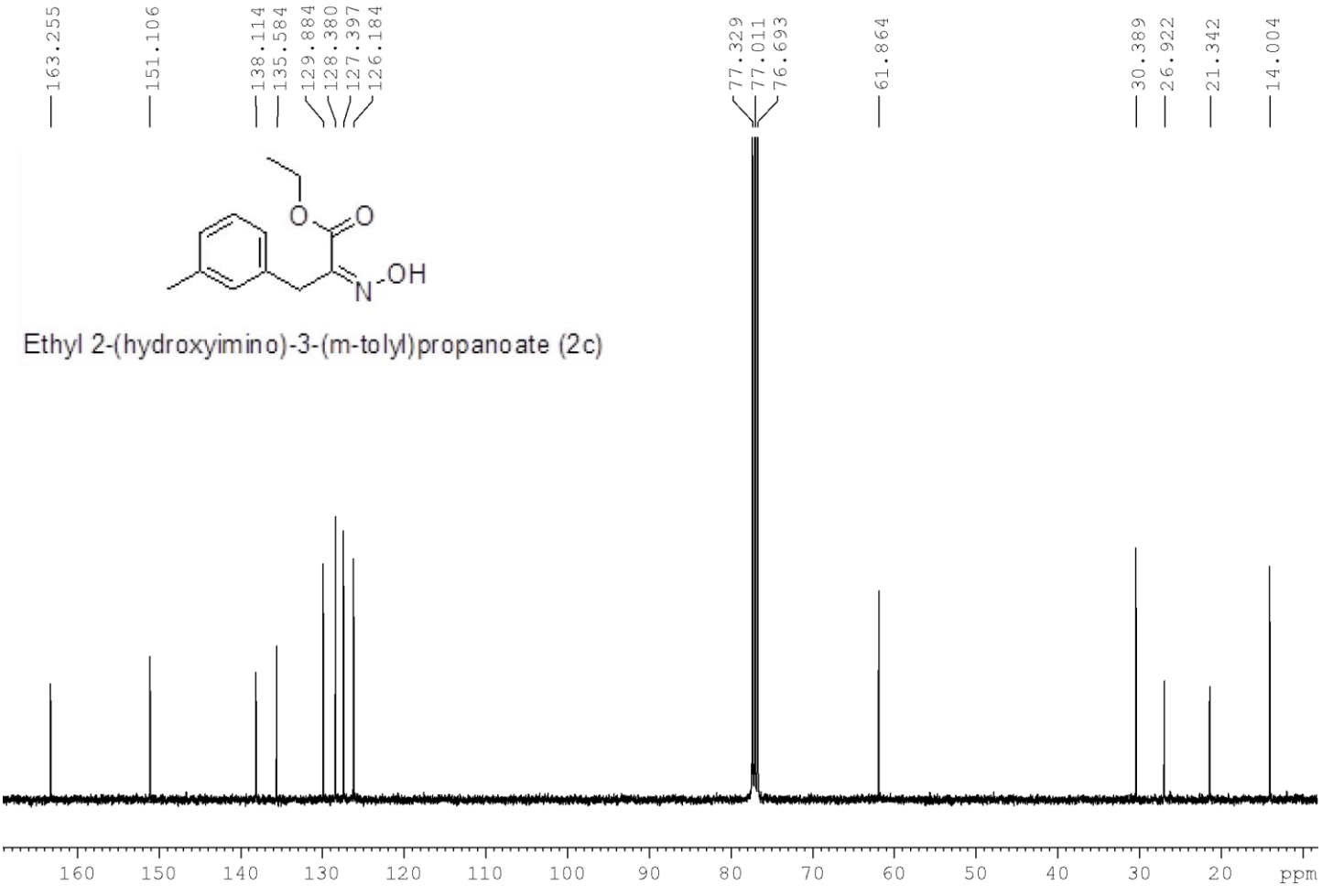
4.3044
4.2867
3.9772
2.3399
1.4603
1.3670
1.3491
1.3313
1.2632
0.9549
0.9384
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(m-tolyl)propanoate (2c)
0.76
2.97
1.02
2.02
2.00
3.07
3.02
10
9
8
7
6
5
4
3
2
1
ppm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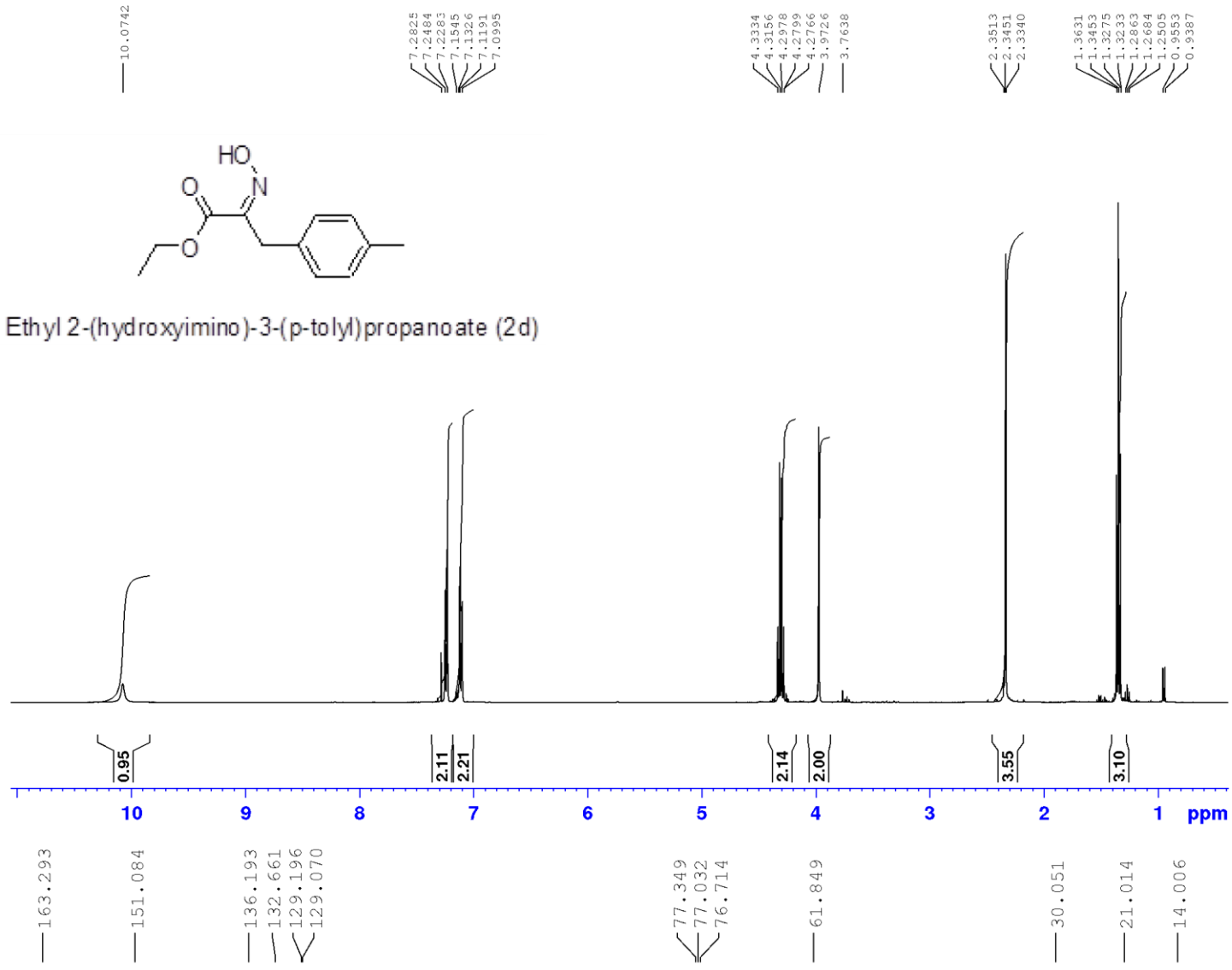
61.864
30.389
26.922
21.342
14.004
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(m-tolyl)propanoate (2c)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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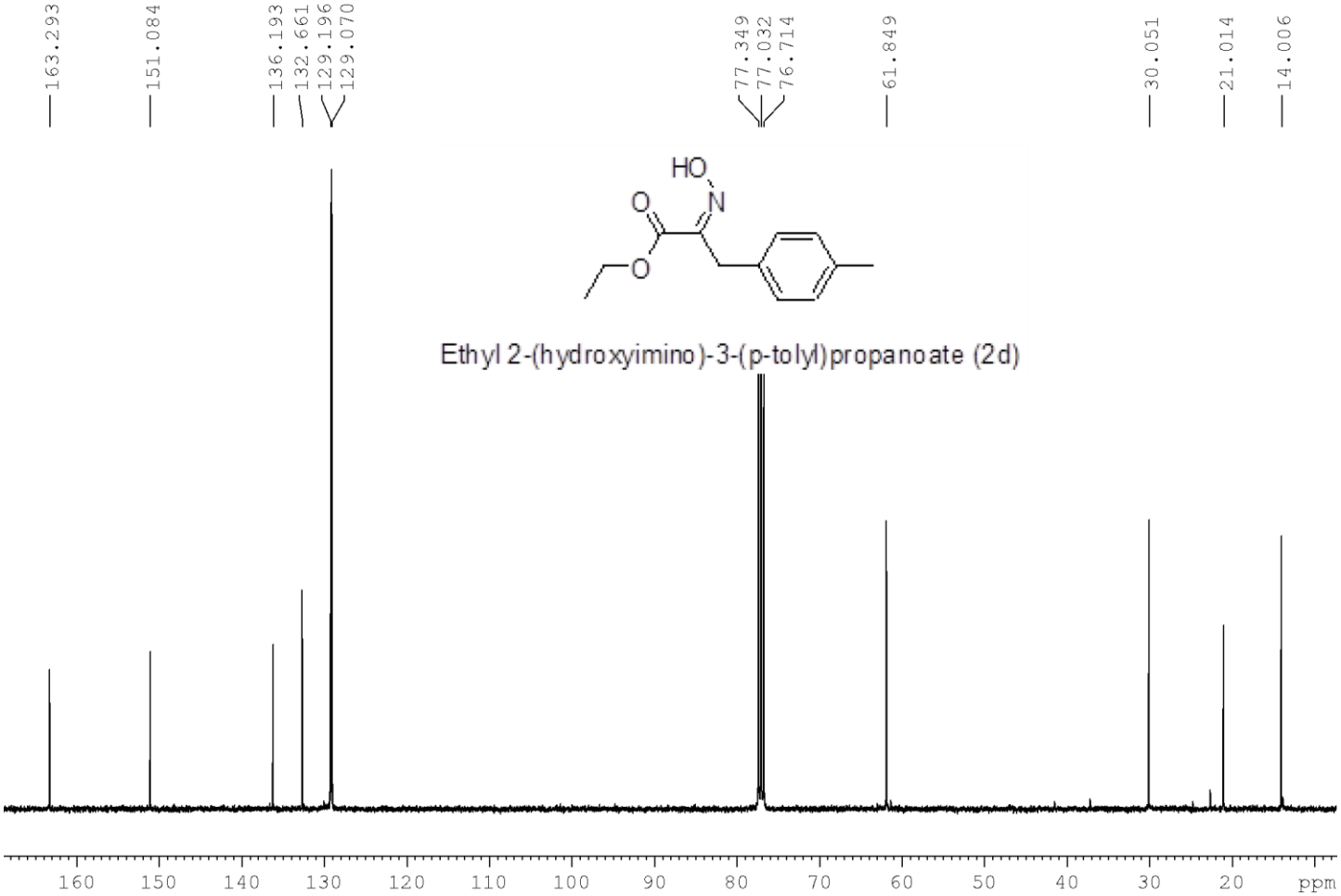
4.2978
4.2799
4.2766
3.9726
3.7638
2.3513
2.3451
2.3340
1.3631
1.3453
1.3275
1.3233
1.2863
1.2684
1.2505
0.9553
0.9387
HO
N
O
O
Ethyl 2-(hydroxyimino)-3-(p-tolyl)propanoate (2d)
0.95
2.11
2.21
2.14
2.00
3.55
3.10
10
9
8
7
6
5
4
3
2
1
ppm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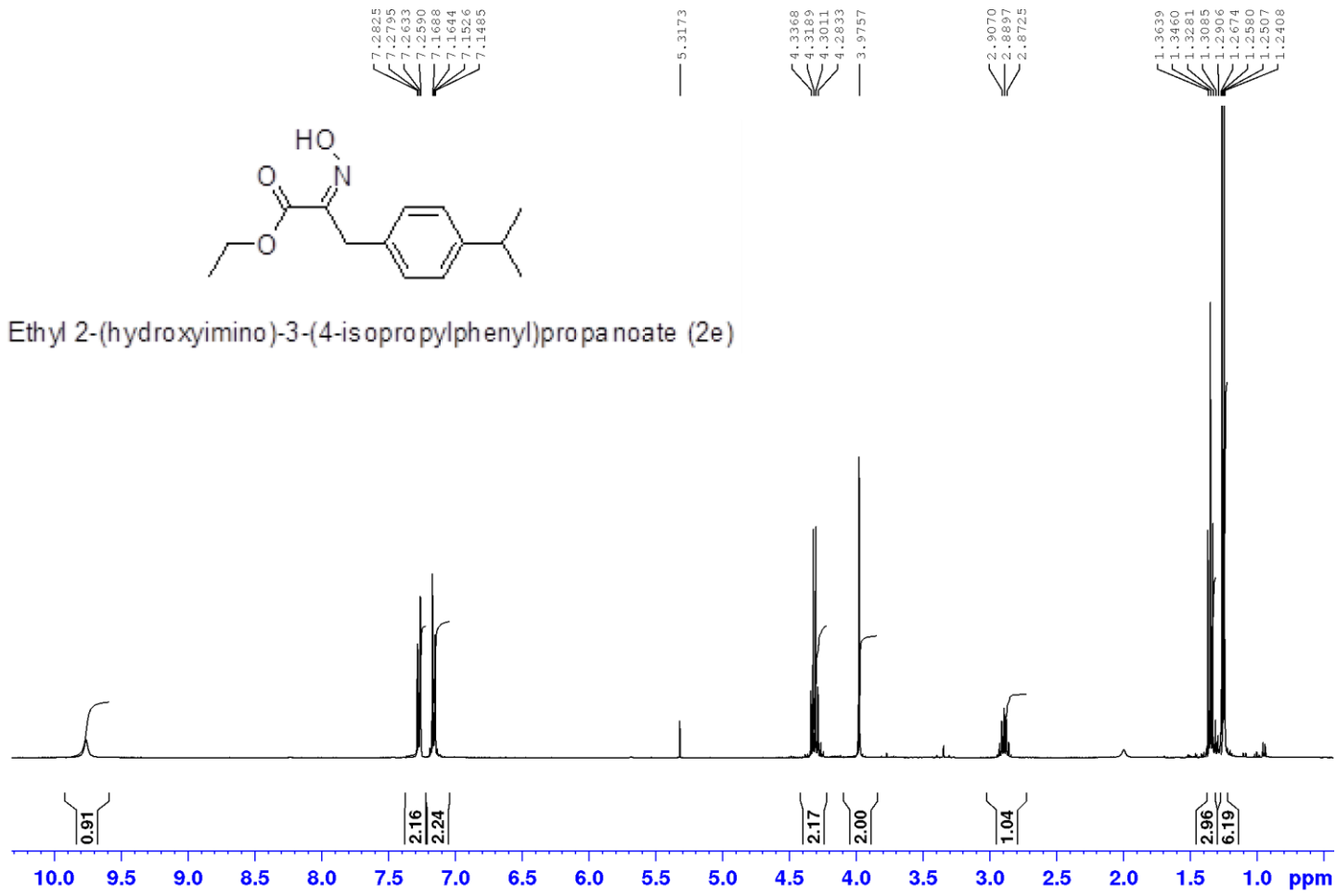
14.006
HO
N
O
O
Ethyl 2-(hydroxyimino)-3-(p-tolyl)propanoate (2d)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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4.2833
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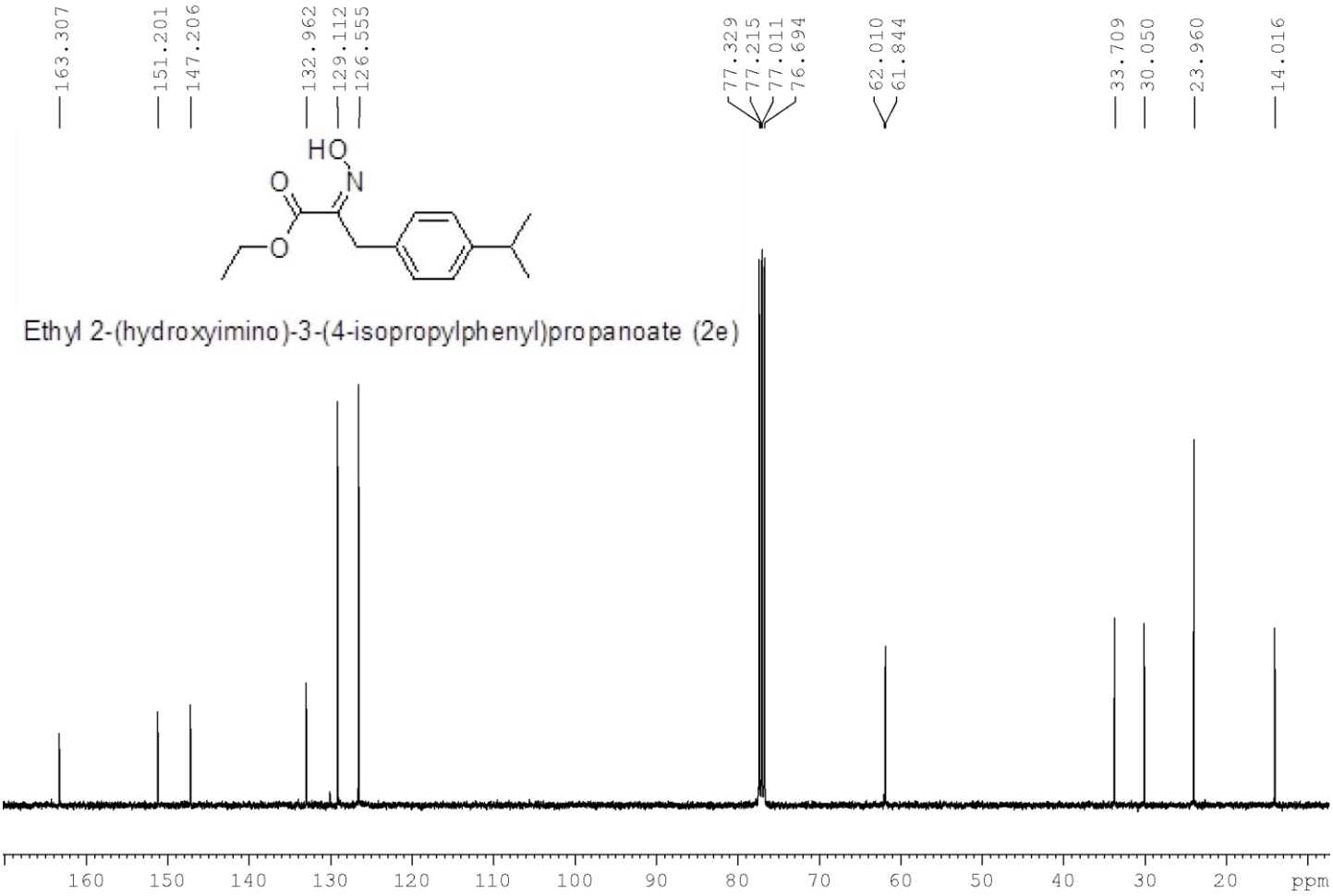
1.3460
1.3281
1.3085
1.2906
1.2674
1.2580
1.2507
1.2408
HO
N
O
O
Ethyl 2-(hydroxyimino)-3-(4-isopropylphenyl)propanoate (2e)
0.91
2.16
2.24
2.17
2.00
1.04
2.96
6.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm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33.709
30.050
23.960
14.016
HO
N
O
O
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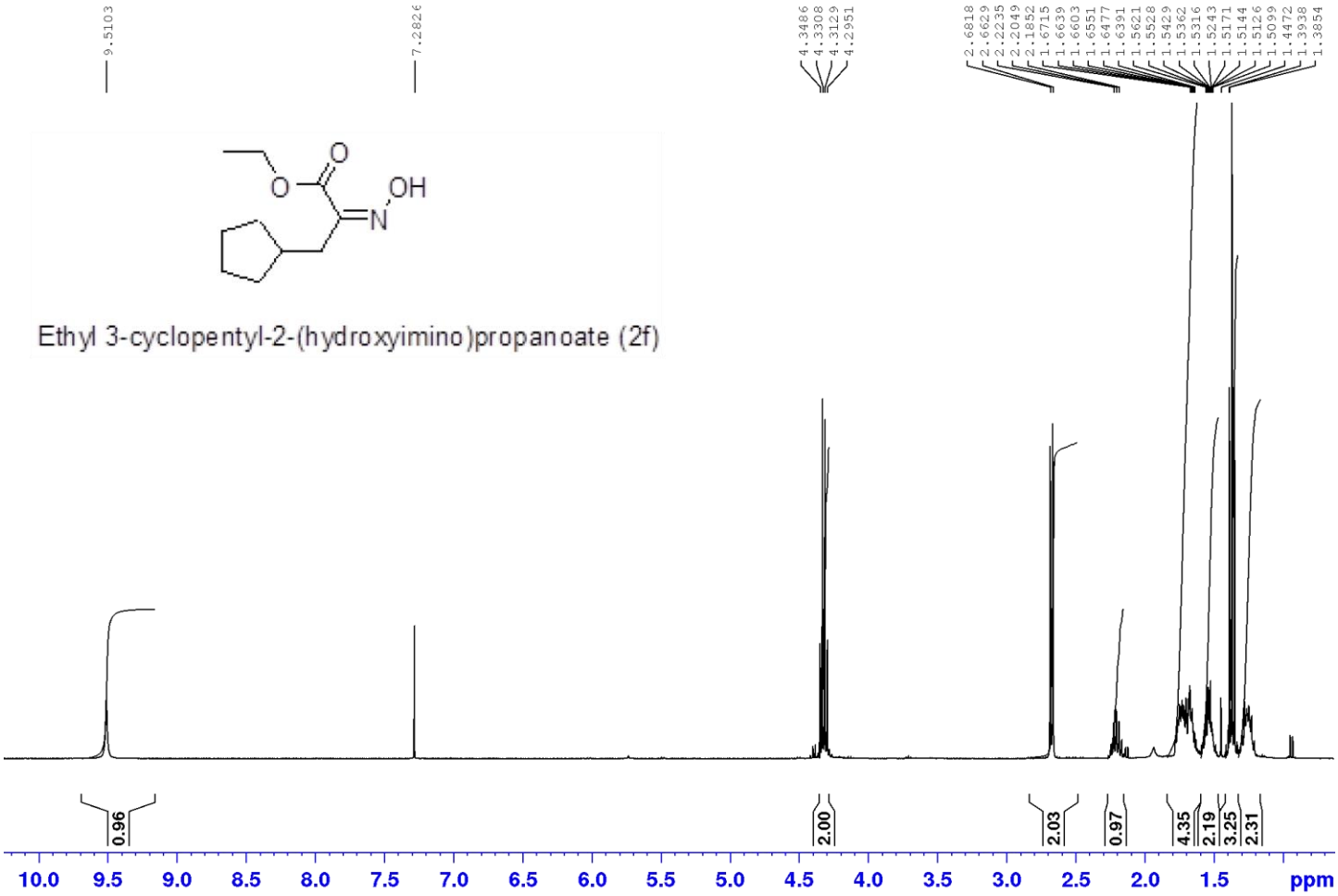
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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2.1852
1.6715
1.6639
1.6603
1.6551
1.6477
1.6391
1.5621
1.5528
1.5429
1.5362
1.5316
1.5243
1.5171
1.5144
1.5126
1.5099
1.4472
1.3938
1.3854
O
O
OH
N
Ethyl 3-cyclopentyl-2-(hydroxyimino)propanoate (2f)
0.96
2.00
2.03
0.97
4.35
2.19
3.25
2.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.5
3.0
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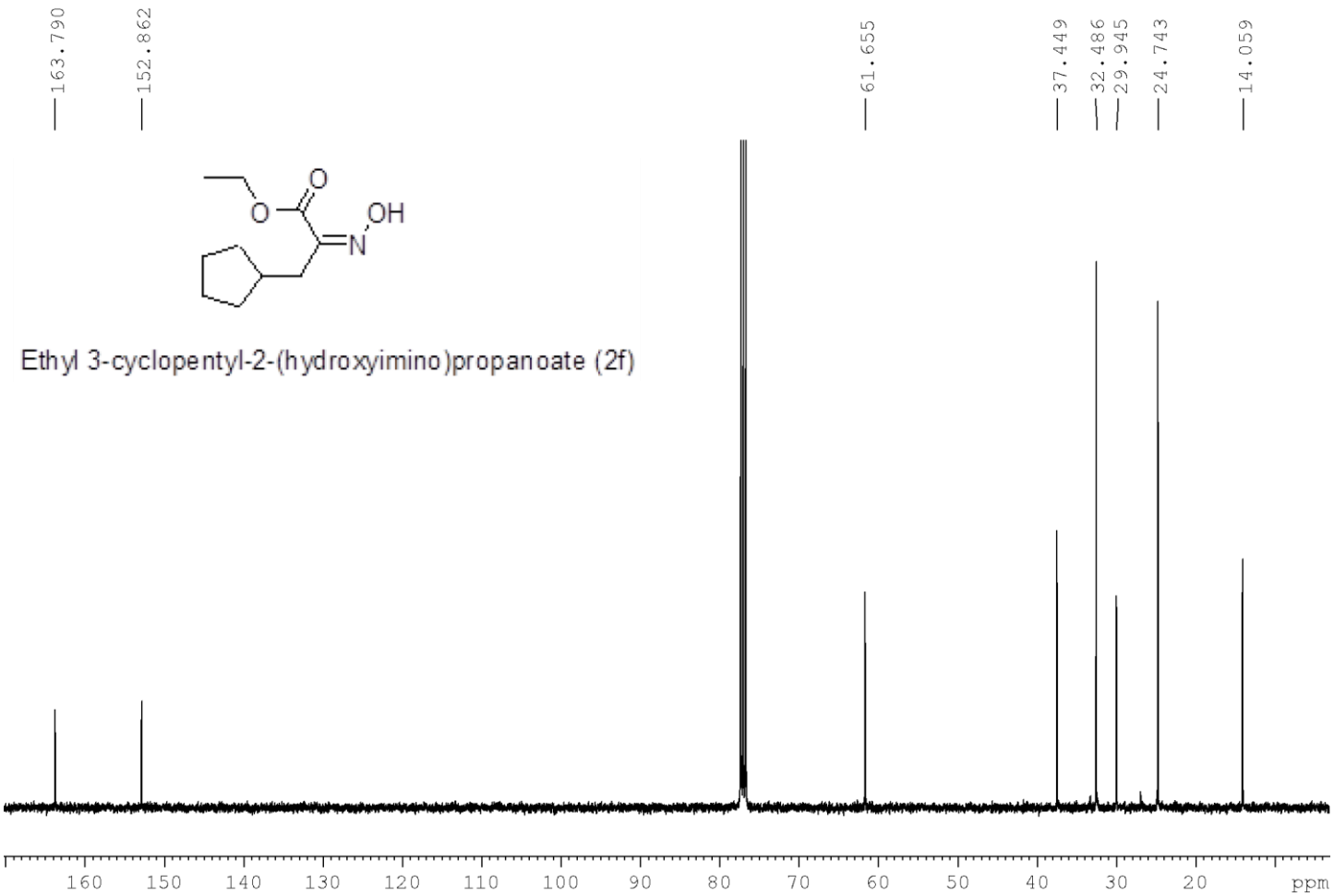
2.0
1.5
ppm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O
OH
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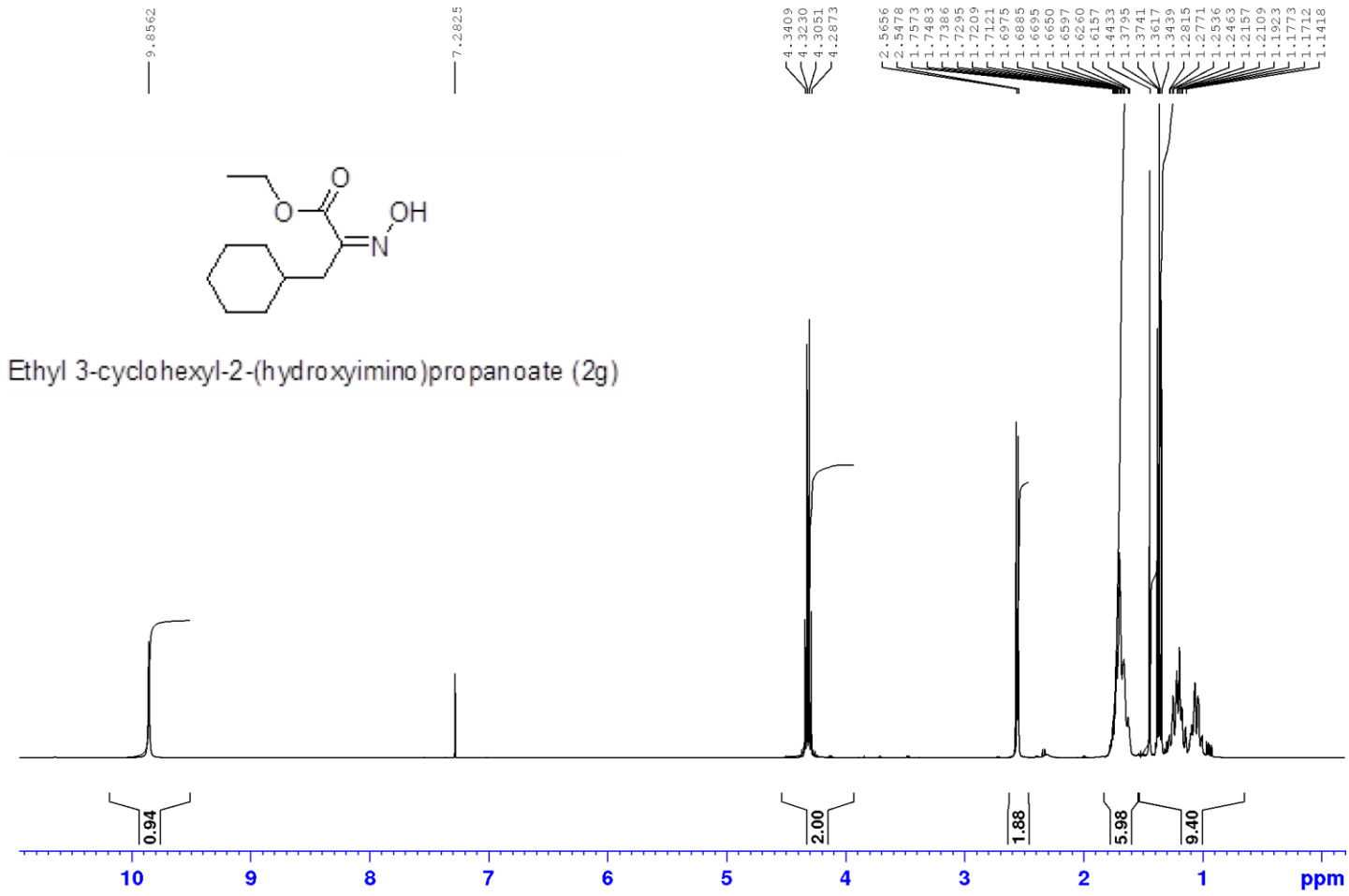
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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1.3617
1.3439
1.2815
1.2771
1.2536
1.2463
1.2157
1.2109
1.1923
1.1773
1.1712
1.1418
O
O
OH
N
Ethyl 3-cyclohexyl-2-(hydroxyimino)propanoate (2g)
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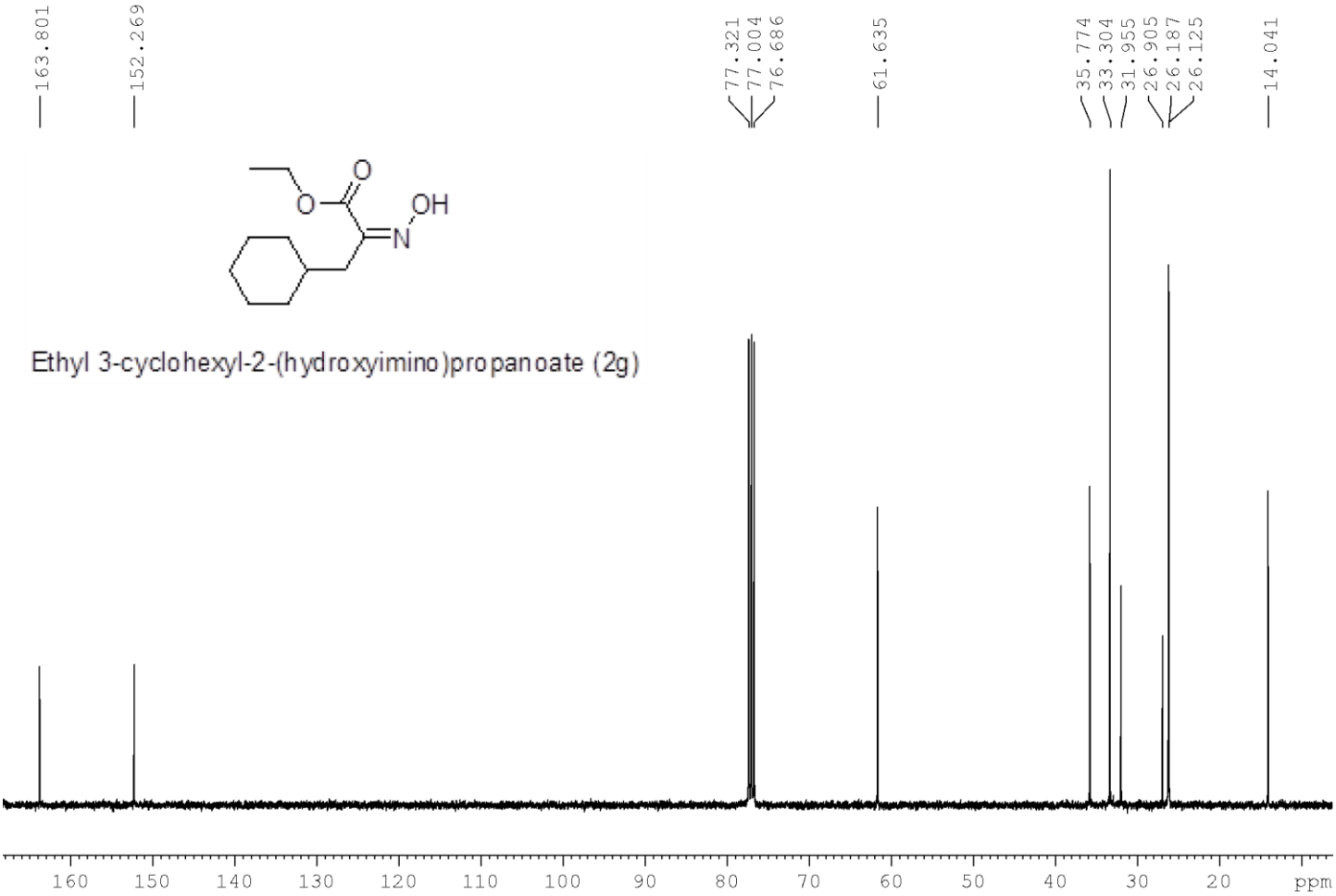
10
9
8
7
6
5
4
3
2
1
ppm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31.955
26.905
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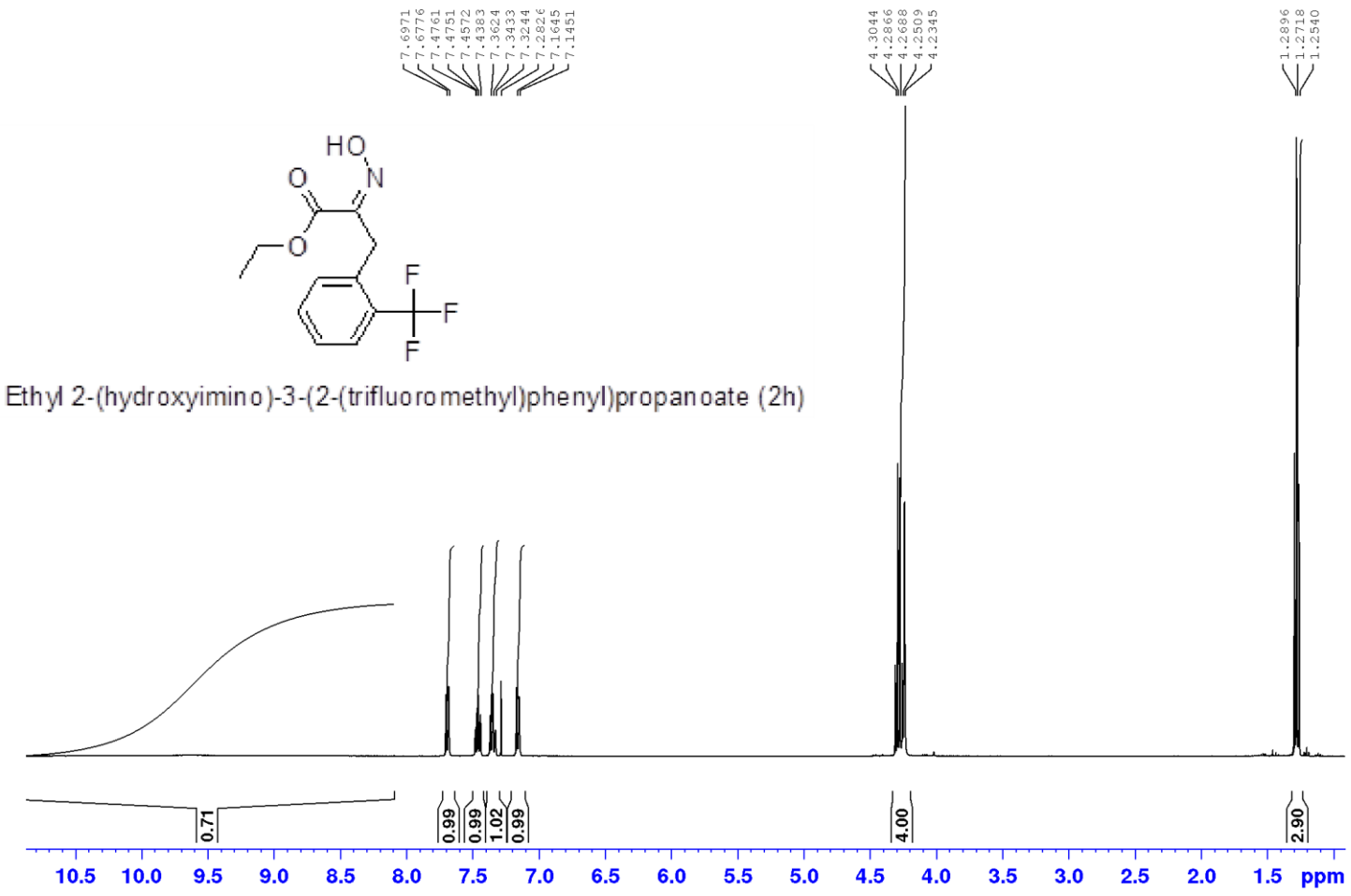
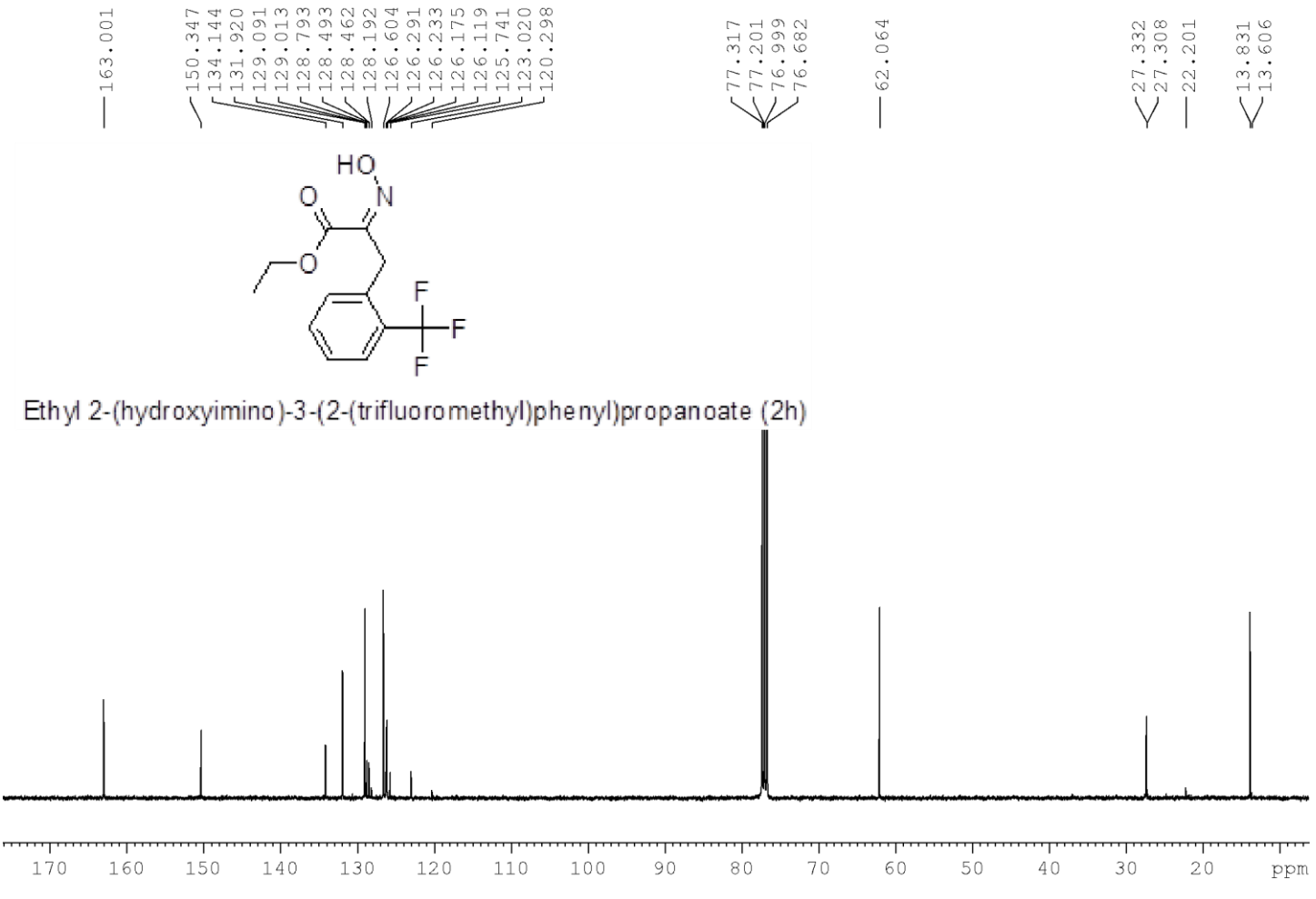
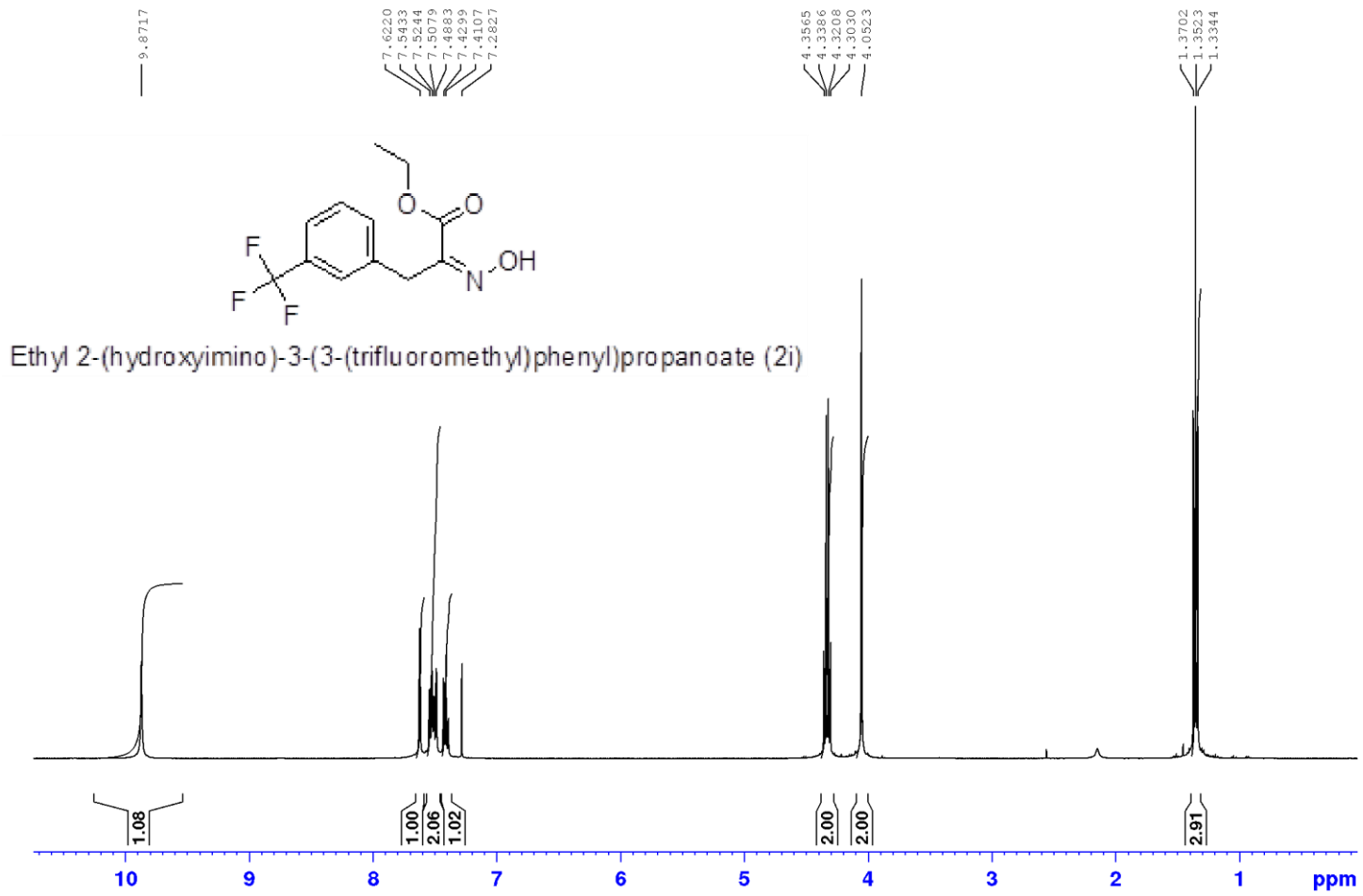
14.041
O
O
OH
N
Ethyl 3-cyclohexyl-2-(hydroxyimino)propanoate (2g)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



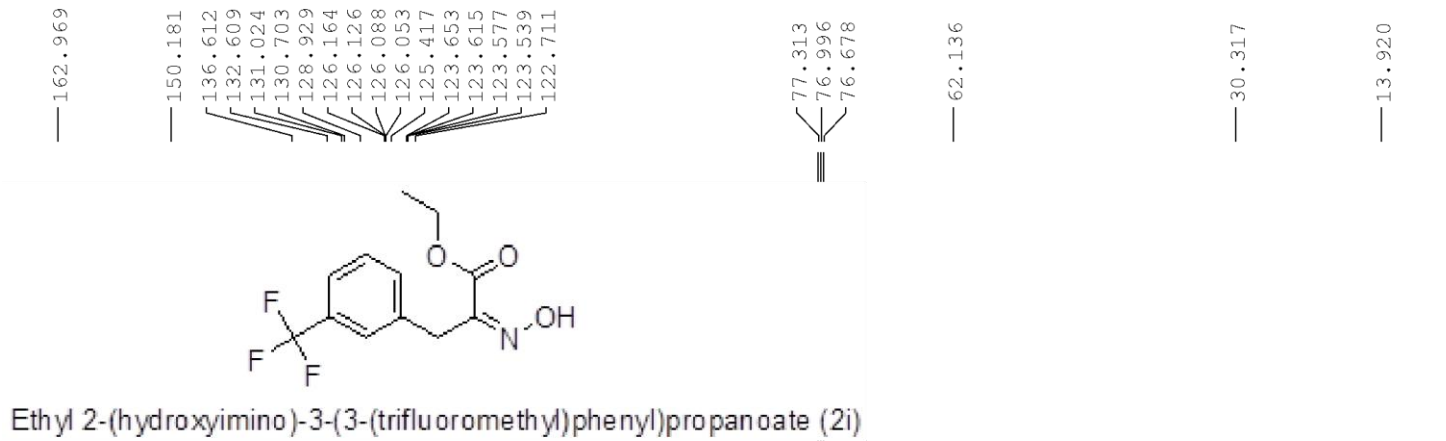
Ethyl 2-(hydroxyimino)-3-(2-(trifluoromethyl)phenyl)propanoate (2h)



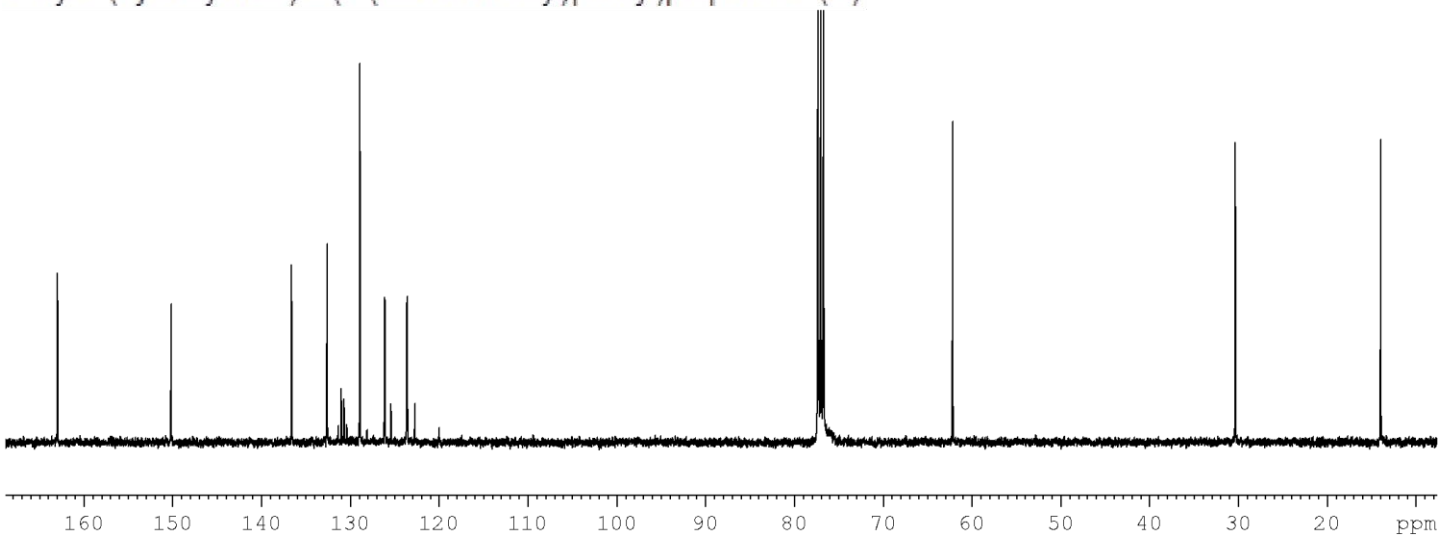
Ethyl 2-(hydroxyimino)-3-(2-(trifluoromethyl)phenyl)propanoate (2h)

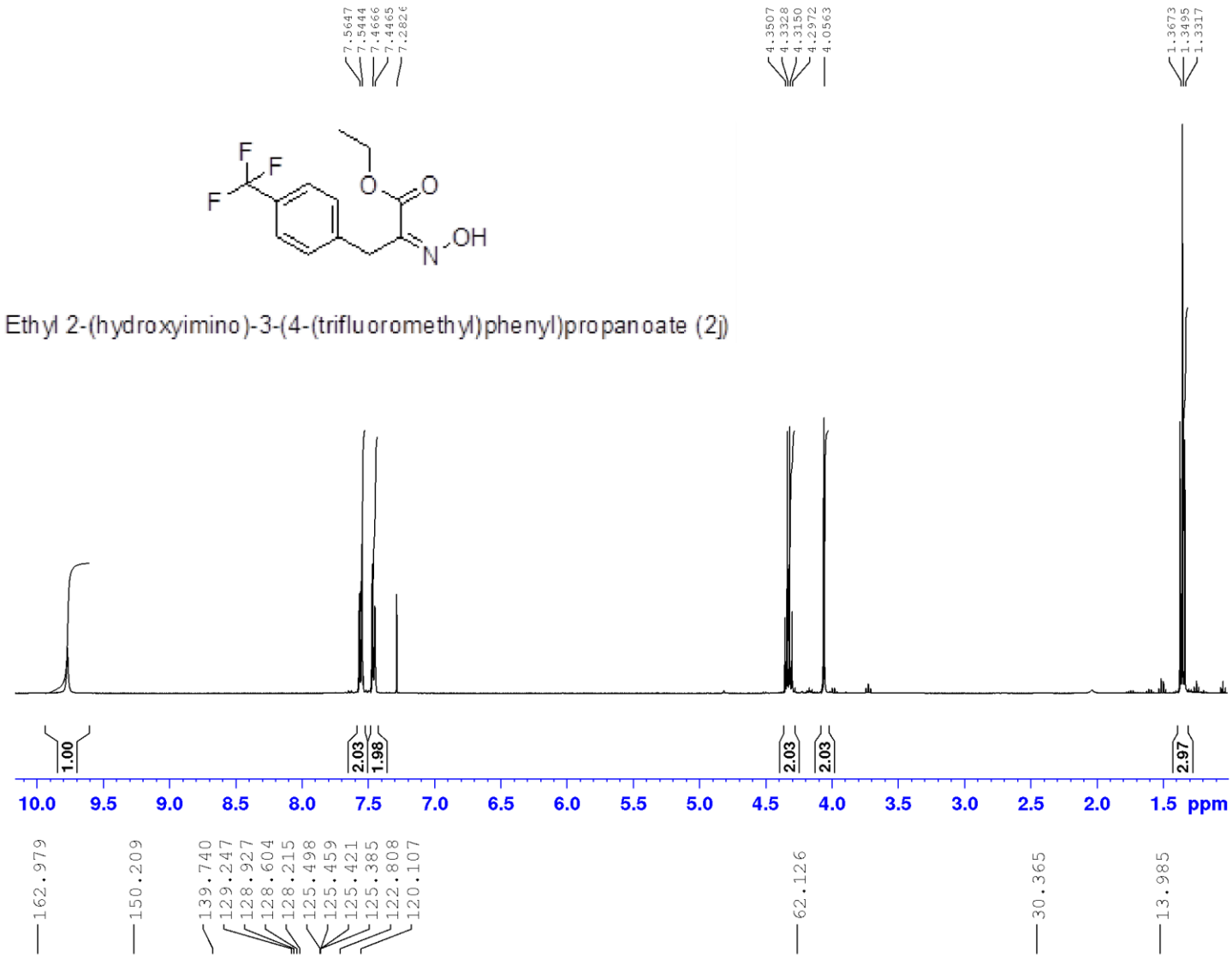


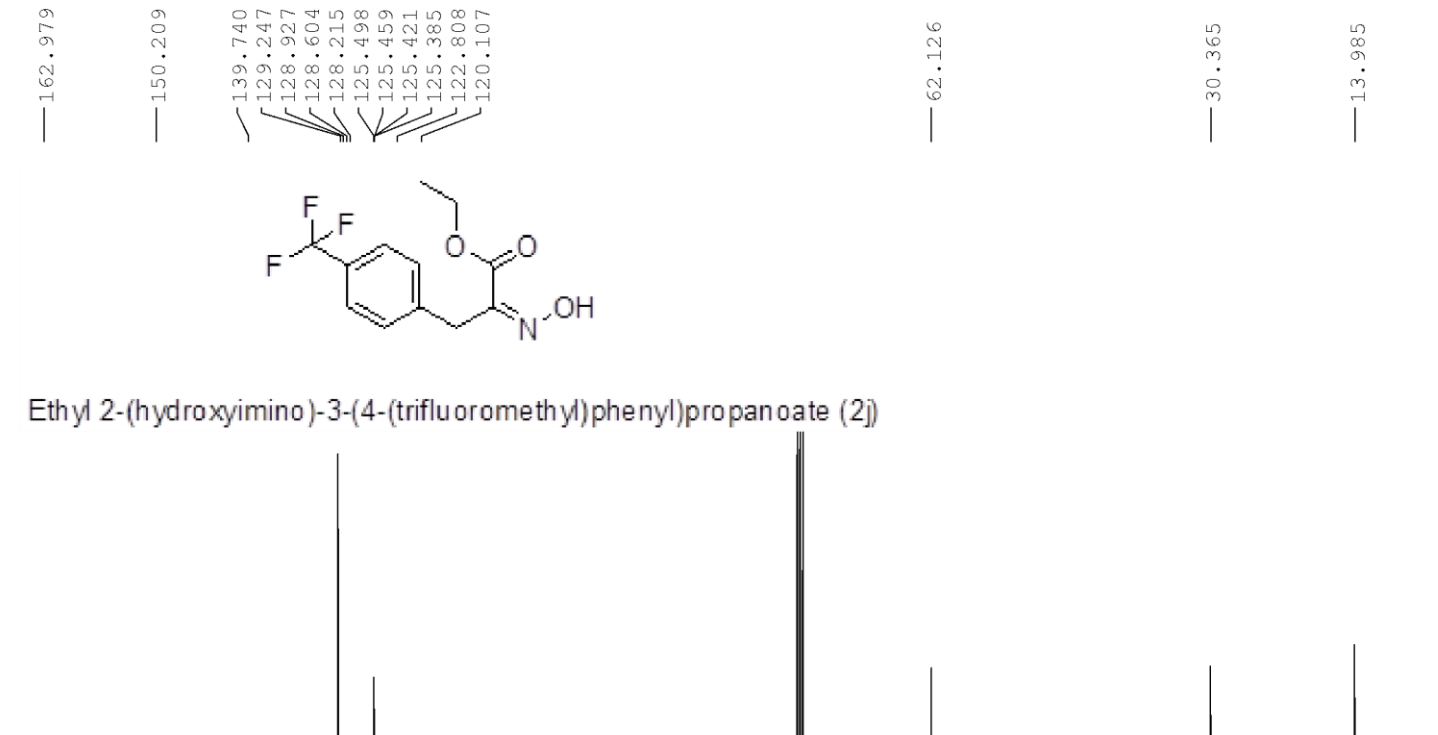
Ethyl 2-(hydroxyimino)-3-(3-(trifluoromethyl)phenyl)propanoate (2i)

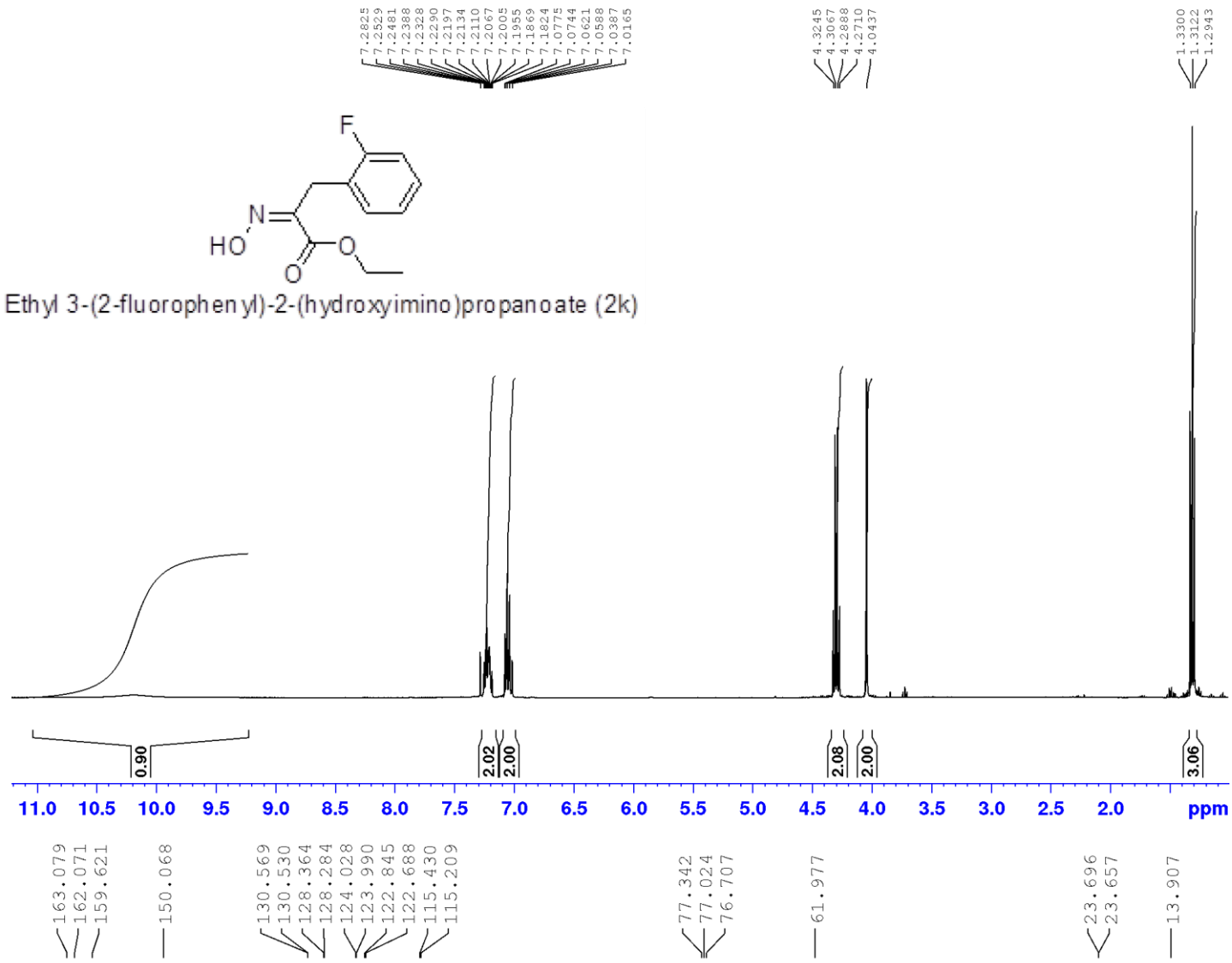


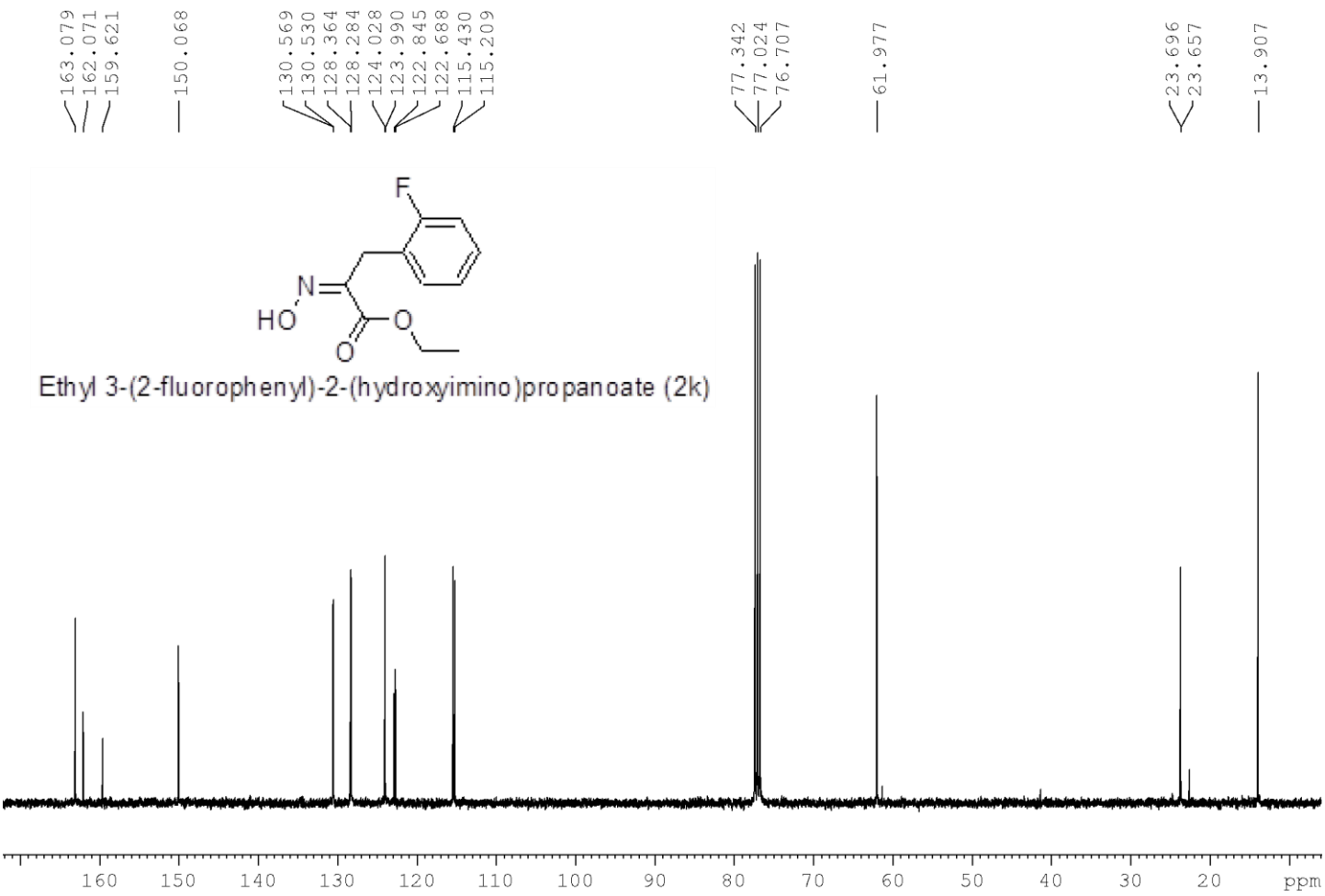
Ethyl 2-(hydroxyimino)-3-(3-(trifluoromethyl)phenyl)propanoate (2i)

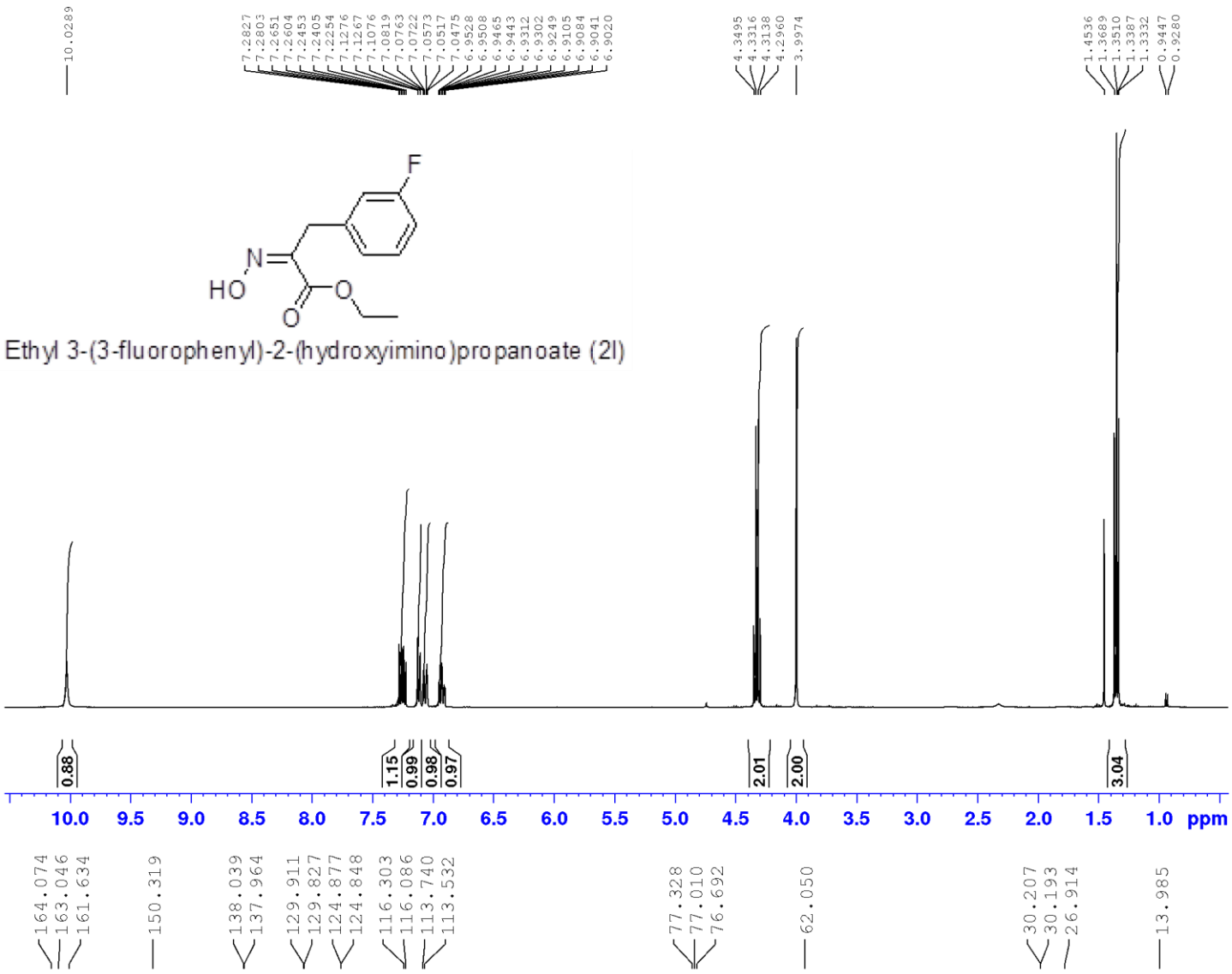


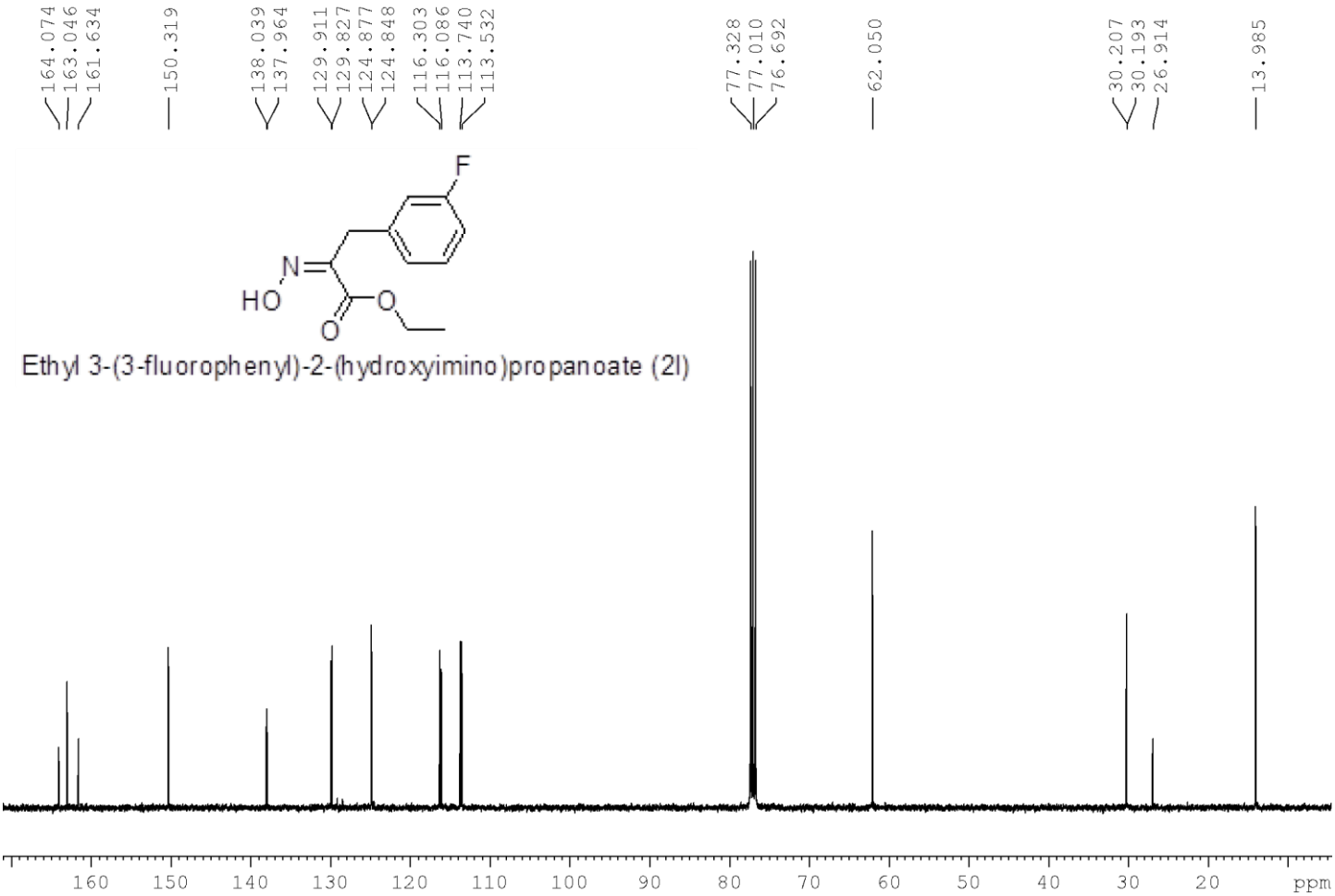

7.5647
7.5444
7.4666
7.4465
4.3507
4.3328
4.3150
4.2972
4.0563
1.3673
1.3495
1.3317
F
F
F
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(4-(trifluoromethyl)phenyl)propanoate (2j)
1.00
2.03
1.98
2.03
2.03
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

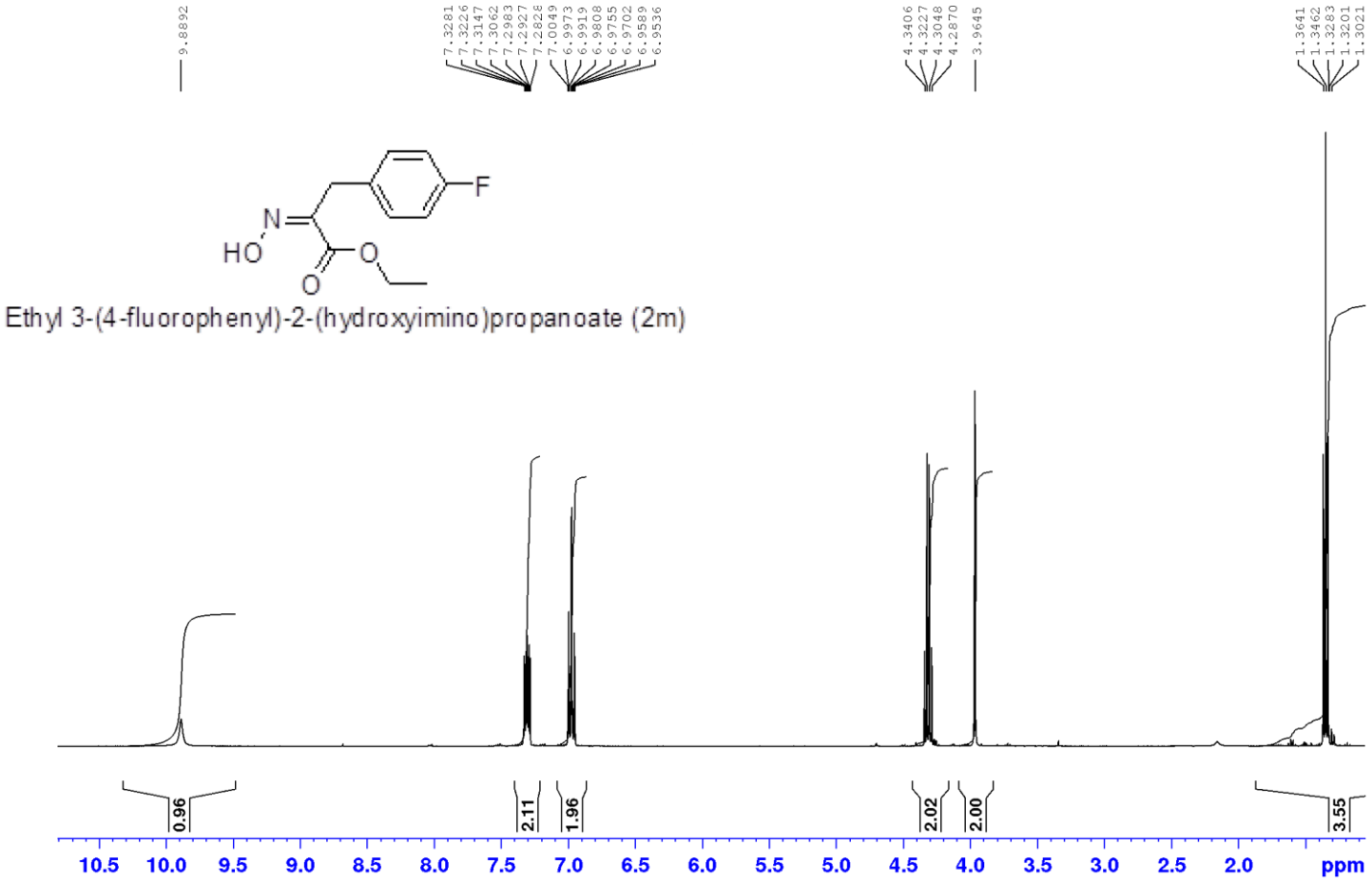

162.979
150.209
139.740
129.247
128.927
128.604
128.215
125.498
125.459
125.421
125.385
122.808
120.107
62.126
30.365
13.985
F
F
F
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(4-(trifluoromethyl)phenyl)propanoate (2j)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

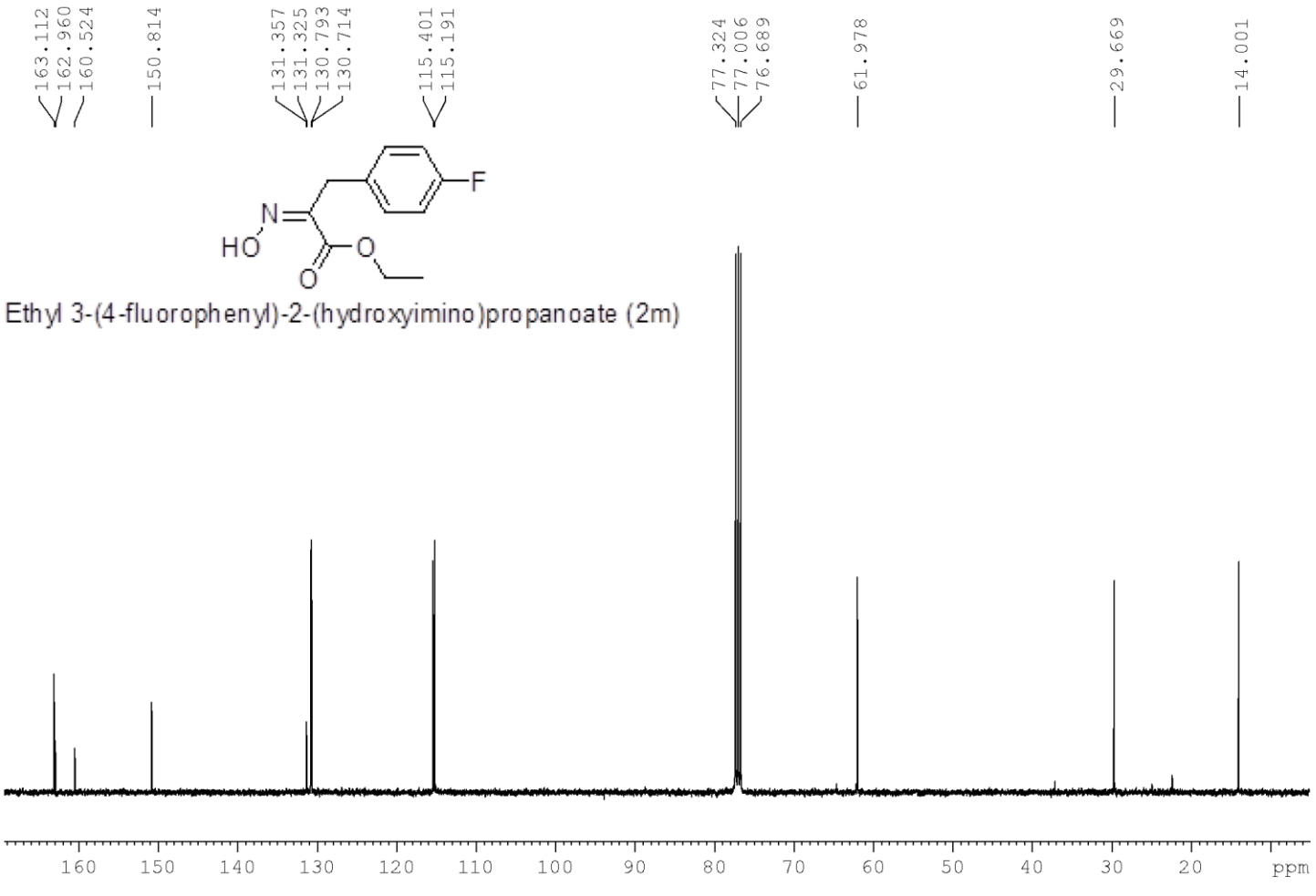

7.2825
7.2529
7.2481
7.2388
7.2328
7.2290
7.2197
7.2134
7.2110
7.2067
7.2005
7.1955
7.1869
7.1824
7.0775
7.0744
7.0621
7.0588
7.0387
7.0165
4.3245
4.3067
4.2888
4.2710
4.0437
1.3300
1.3122
1.2943
F
N
HO
O
O
Ethyl 3-(2-fluorophenyl)-2-(hydroxyimino)propanoate (2k)
0.90
2.02
2.00
2.08
2.00
3.06
11.0
10.5
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
ppm

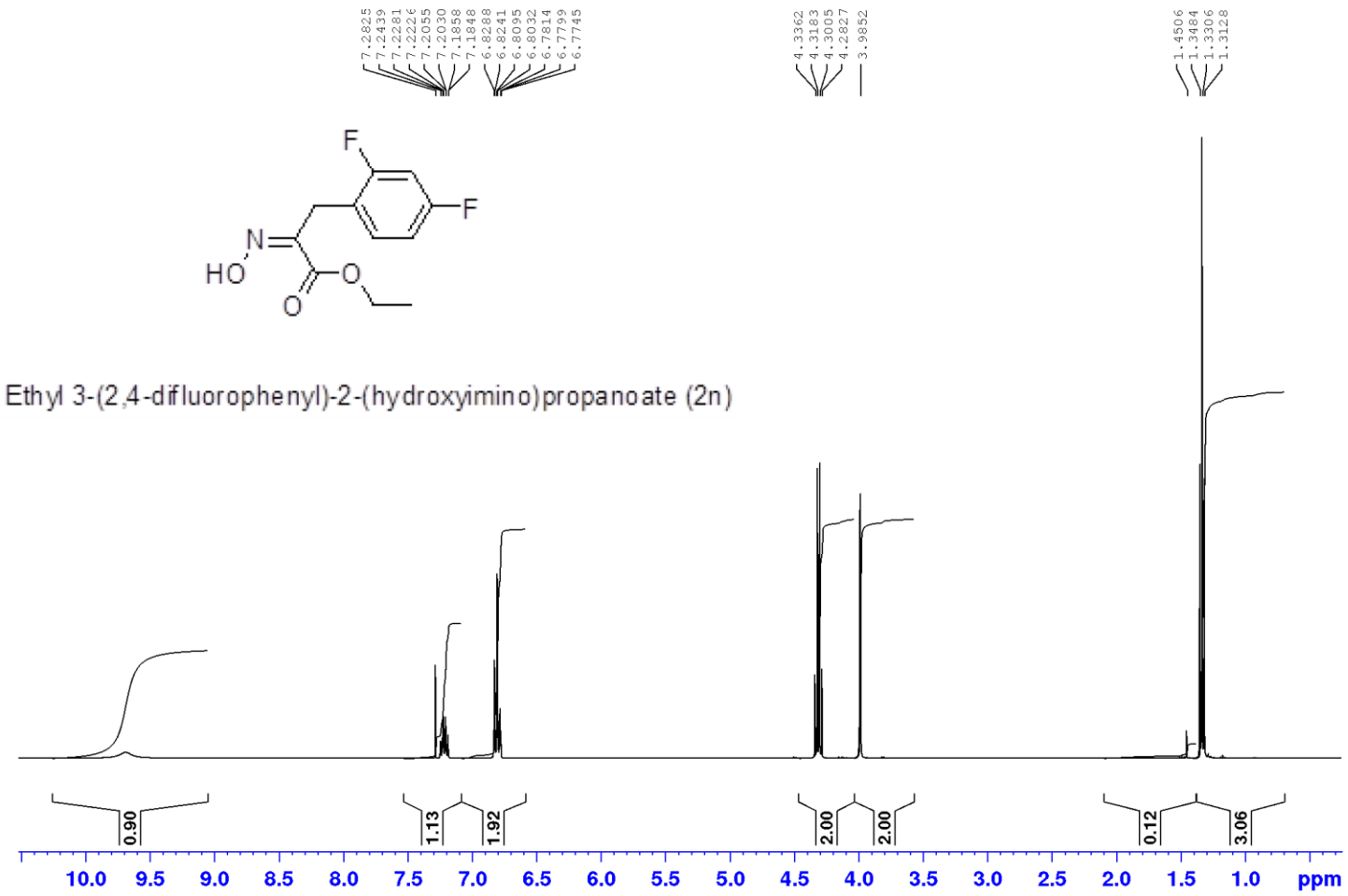

163.079
162.071
159.621
150.068
130.569
130.530
128.364
128.284
124.028
123.990
122.845
122.688
115.430
115.209
77.342
77.024
76.707
61.977
23.696
23.657
13.907
F
N
HO
O
O
Ethyl 3-(2-fluorophenyl)-2-(hydroxyimino)propanoate (2k)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

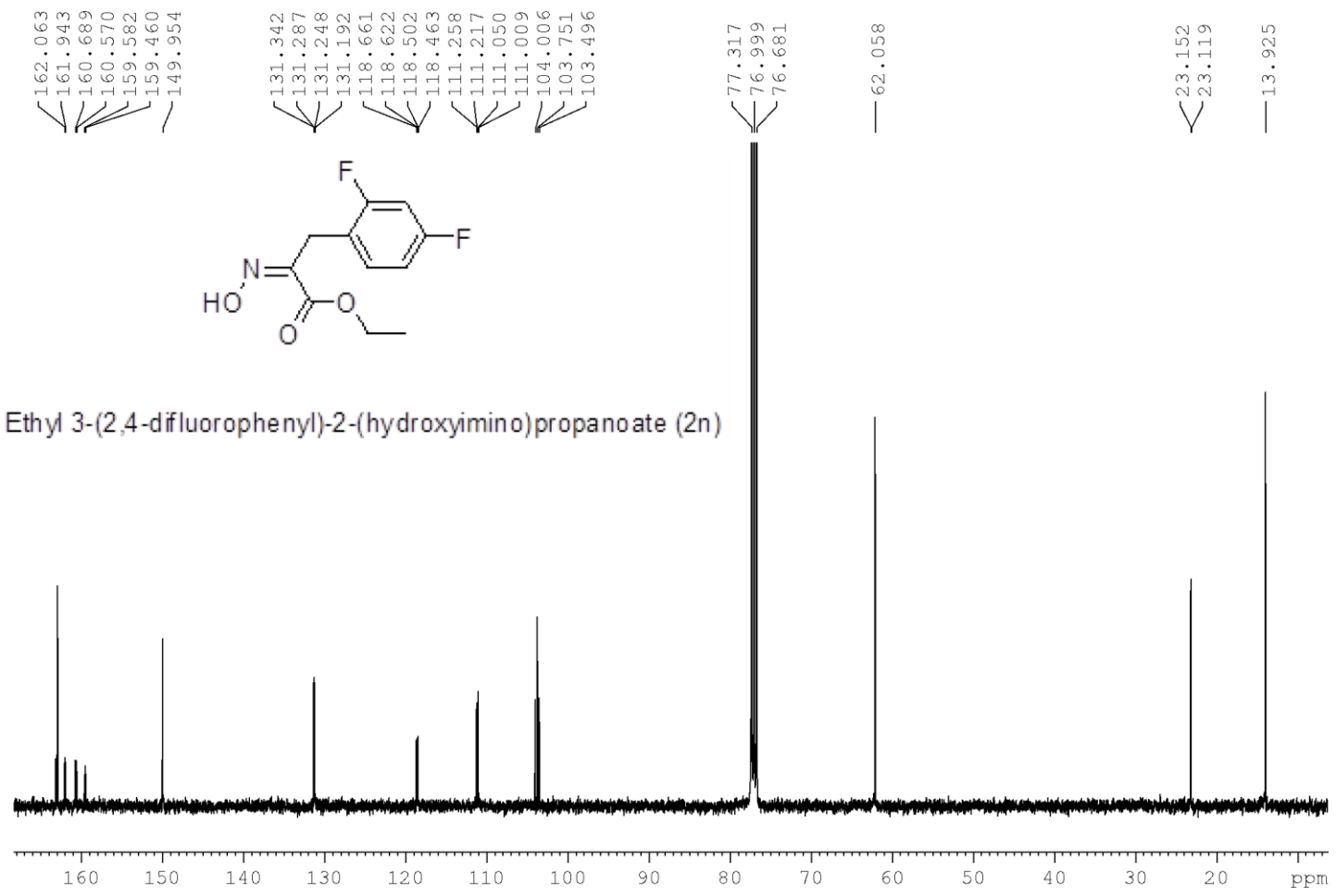

10.0289
7.2827
7.2803
7.2651
7.2604
7.2453
7.2405
7.2254
7.1276
7.1267
7.1076
7.0819
7.0763
7.0722
7.0573
7.0517
7.0475
6.9528
6.9508
6.9465
6.9443
6.9312
6.9302
6.9249
6.9105
6.9084
6.9041
6.9020
4.3495
4.3316
4.3138
4.2960
3.9974
1.4536
1.3689
1.3510
1.3387
1.3332
0.9447
0.9280
F
N
HO
O
O
Ethyl 3-(3-fluorophenyl)-2-(hydroxyimino)propanoate (2l)
0.88
1.15
0.99
0.98
0.97
2.01
2.00
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
ppm

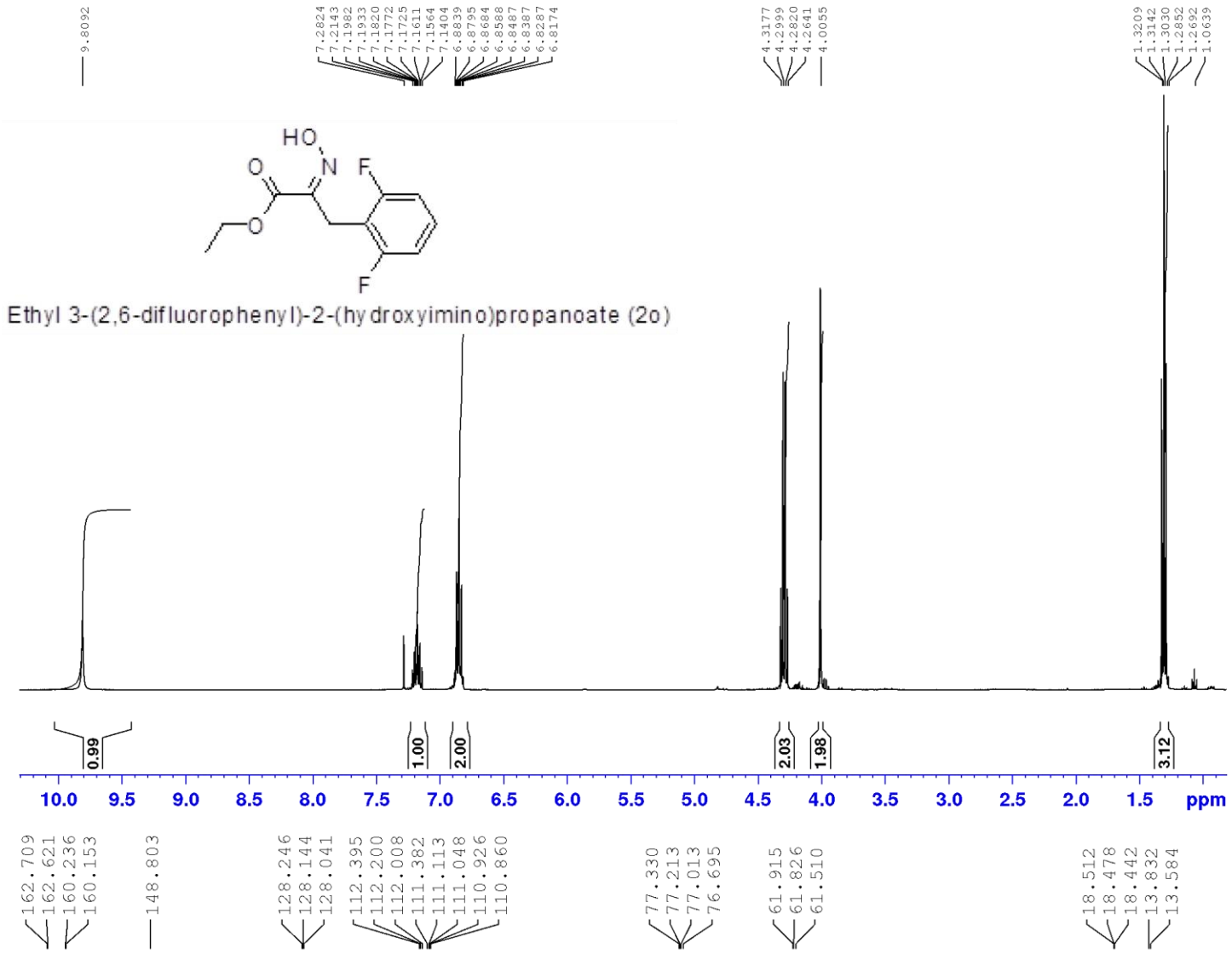

164.074
163.046
161.634
150.319
138.039
137.964
129.911
129.827
124.877
124.848
116.303
116.086
113.740
113.532
77.328
77.010
76.692
62.050
30.207
30.193
26.914
13.985
F
N
HO
O
O
Ethyl 3-(3-fluorophenyl)-2-(hydroxyimino)propanoate (2l)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

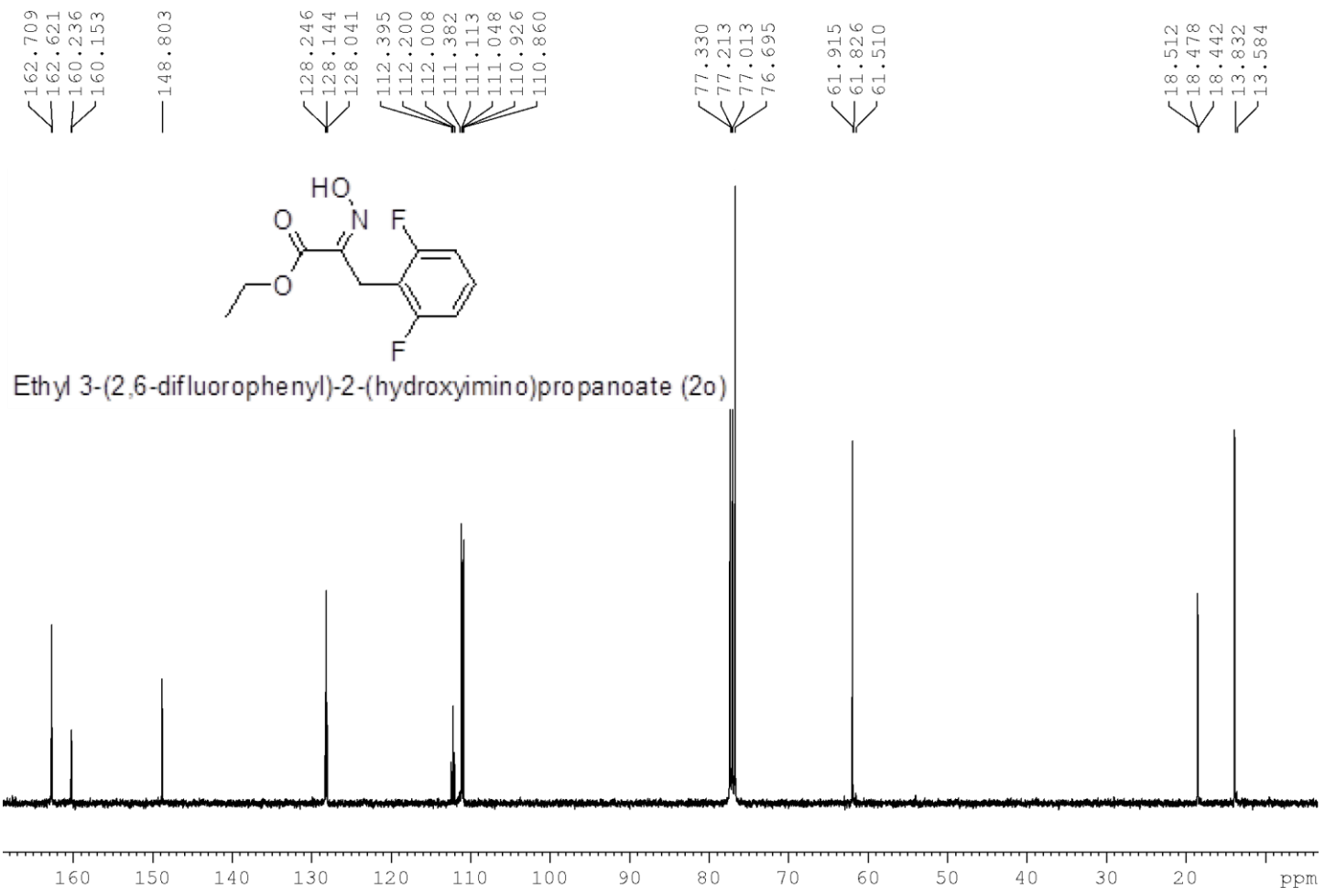

9.8892
7.3281
7.3226
7.3147
7.3062
7.2983
7.2927
7.2828
7.1049
6.9973
6.9919
6.9808
6.9755
6.9702
6.9589
6.9536
4.3406
4.3227
4.3048
4.2870
3.9645
1.3641
1.3462
1.3283
1.3201
1.3021
F
N
HO
O
O
Ethyl 3-(4-fluorophenyl)-2-(hydroxyimino)propanoate (2m)
0.96
2.11
1.96
2.02
2.00
3.55
10.5
10.0
9.5
9.0
8.5
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
ppm

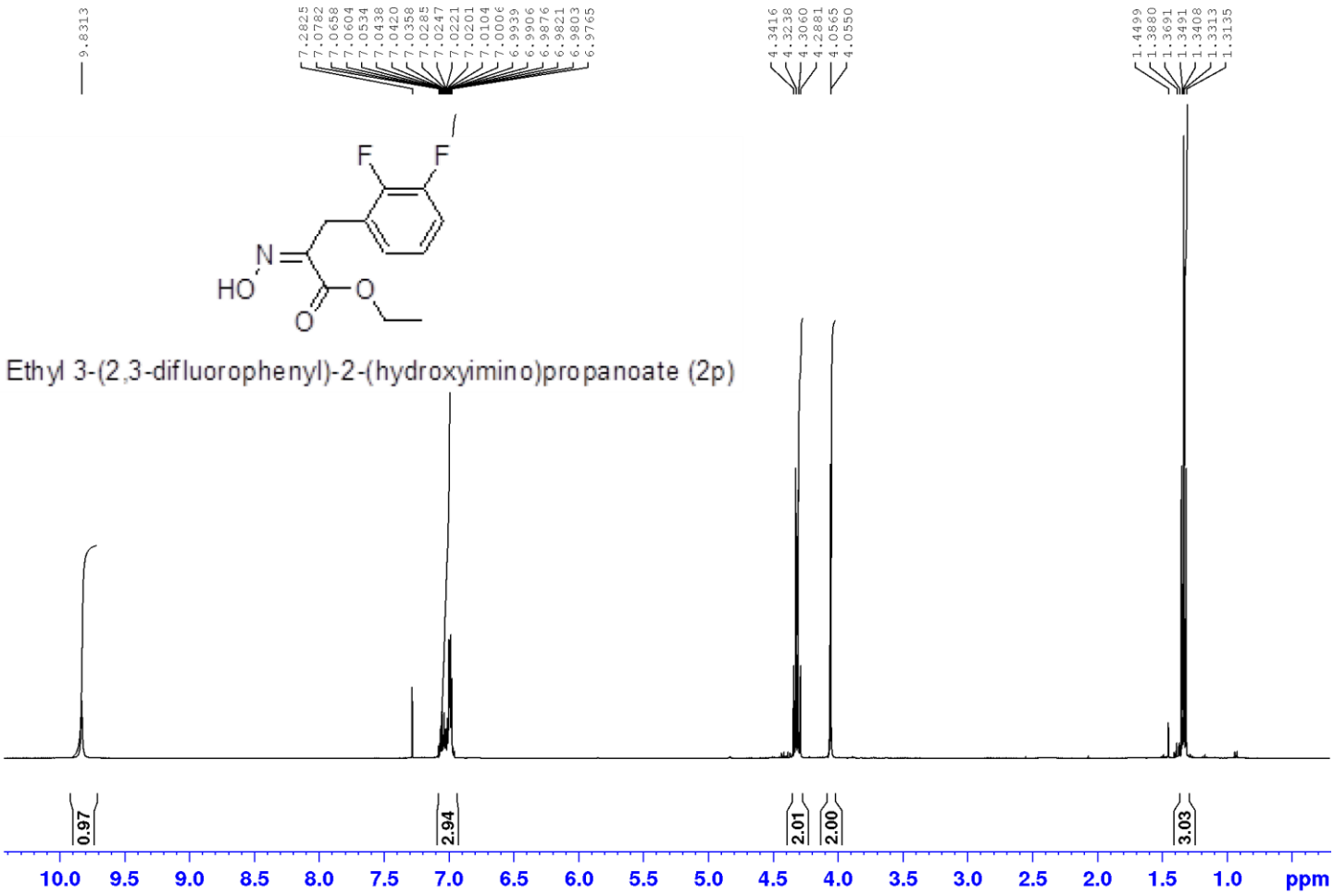

163.112
162.960
160.524
150.814
131.357
131.325
130.793
130.714
115.401
115.191
77.324
77.006
76.689
61.978
29.669
14.001
F
N
HO
O
O
Ethyl 3-(4-fluorophenyl)-2-(hydroxyimino)propanoate (2m)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.2825
7.2439
7.2281
7.2226
7.2055
7.2030
7.1858
7.1848
6.8288
6.8241
6.8095
6.8032
6.7814
6.7799
6.7745
4.3362
4.3183
4.3005
4.2827
3.9852
1.4506
1.3484
1.3306
1.3128
F
F
N
HO
O
O
Ethyl 3-(2,4-difluorophenyl)-2-(hydroxyimino)propanoate (2n)
0.90
1.13
1.92
2.00
2.00
0.12
3.06
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
ppm

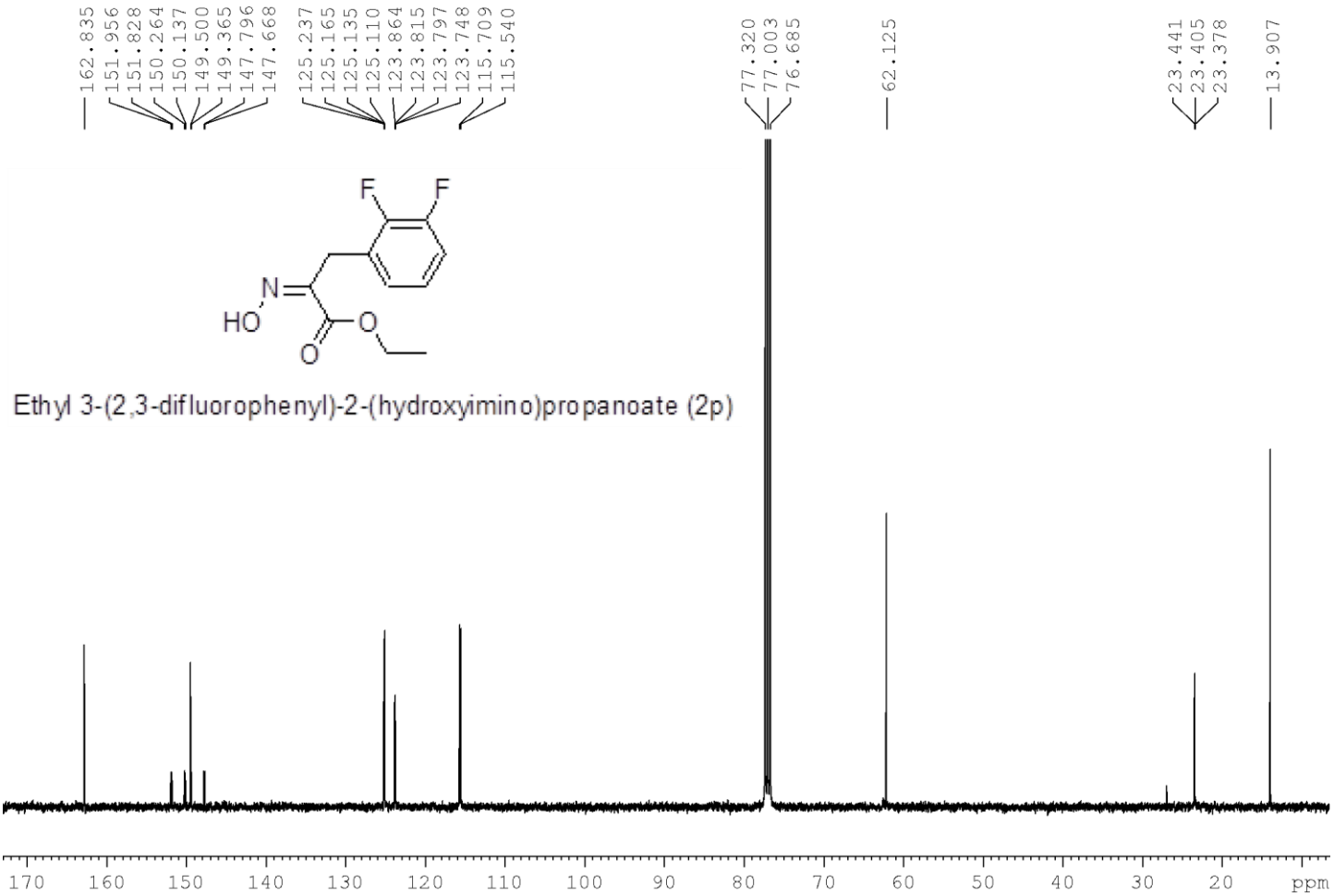

162.063
161.943
160.689
160.570
159.582
159.460
149.954
131.342
131.287
131.248
131.192
118.661
118.622
118.502
118.463
111.258
111.217
111.050
111.009
104.006
103.751
103.496
77.317
76.999
76.681
62.058
23.152
23.119
13.925
F
F
N
HO
O
O
Ethyl 3-(2,4-difluorophenyl)-2-(hydroxyimino)propanoate (2n)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


9.8092
7.2824
7.2143
7.1982
7.1933
7.1820
7.1772
7.1725
7.1611
7.1564
7.1404
6.8839
6.8795
6.8684
6.8588
6.8487
6.8387
6.8287
6.8174
4.3177
4.2999
4.2820
4.2641
4.0055
1.3209
1.3142
1.3030
1.2852
1.2692
1.0639
HO
N
O
O
F
F
Ethyl 3-(2,6-difluorophenyl)-2-(hydroxyimino)propanoate (2o)
0.99
1.00
2.00
2.03
1.98
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
ppm

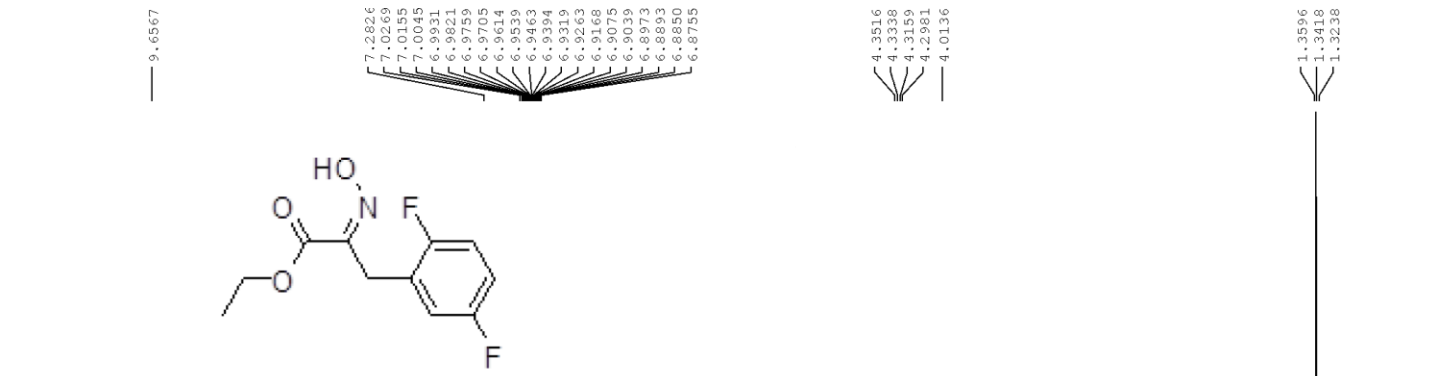

162.709
162.621
160.236
160.153
148.803
128.246
128.144
128.041
112.395
112.200
112.008
111.382
111.113
111.048
110.926
110.860
77.330
77.213
77.013
76.695
61.915
61.826
61.510
18.512
18.478
18.442
13.832
13.584
HO
N
O
O
F
F
Ethyl 3-(2,6-difluorophenyl)-2-(hydroxyimino)propanoate (2o)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



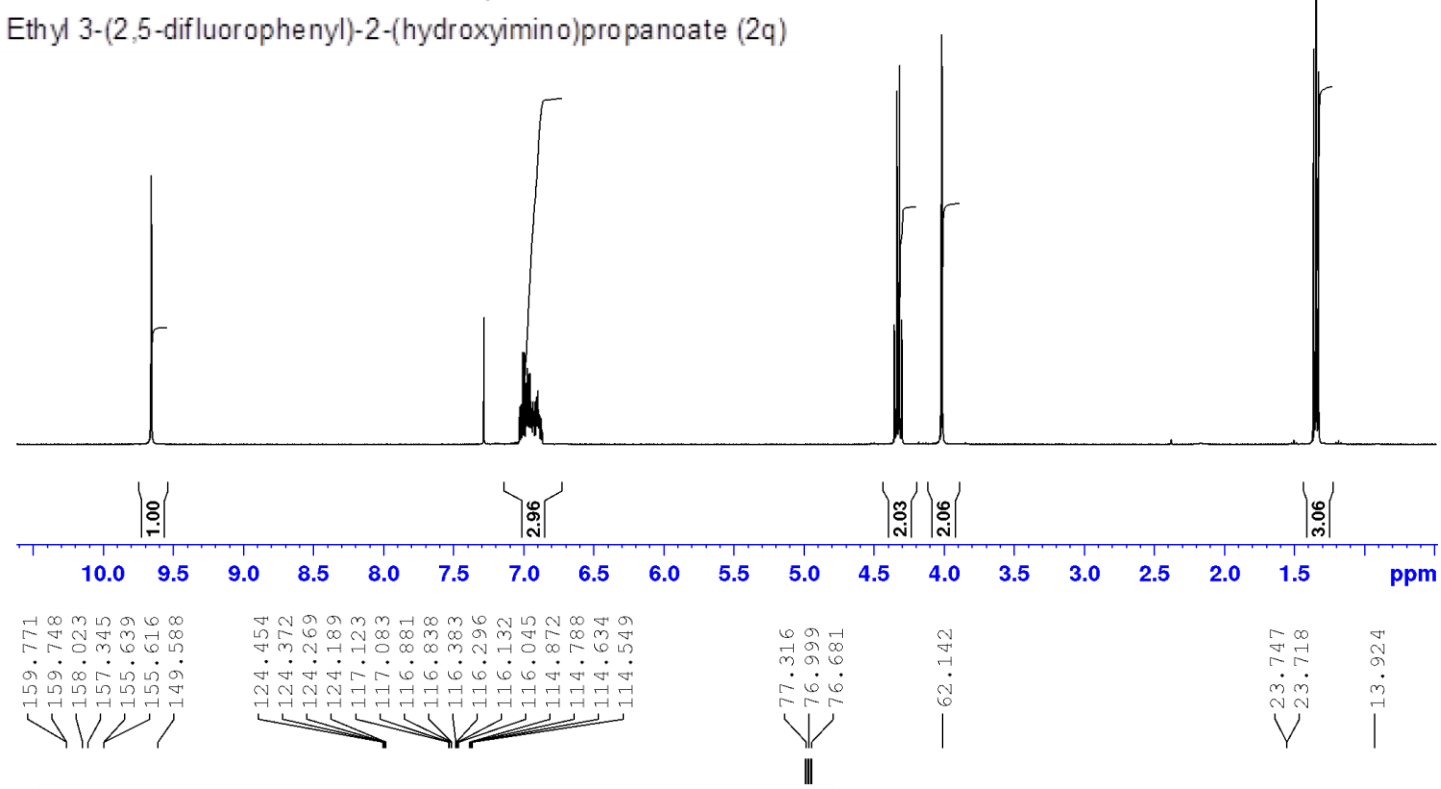
Ethyl 3-(2,3-difluorophenyl)-2-(hydroxyimino)propanoate (2p)

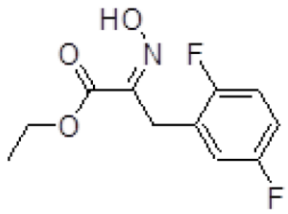


Ethyl 3-(2,3-difluorophenyl)-2-(hydroxyimino)propanoate (2p)

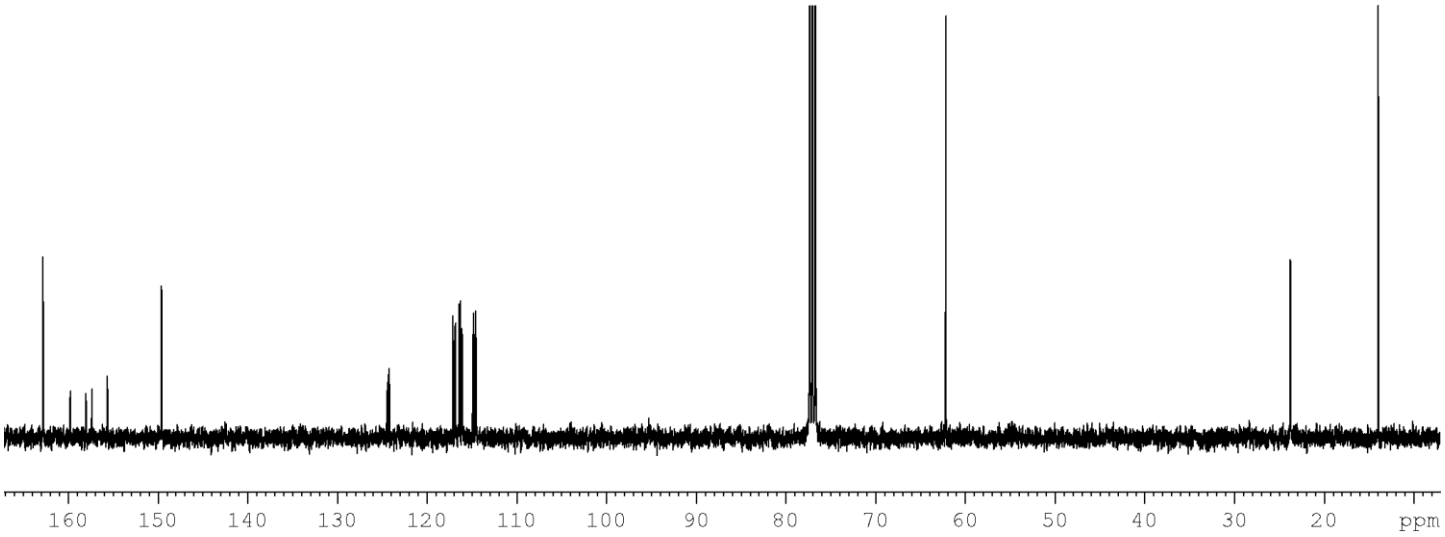


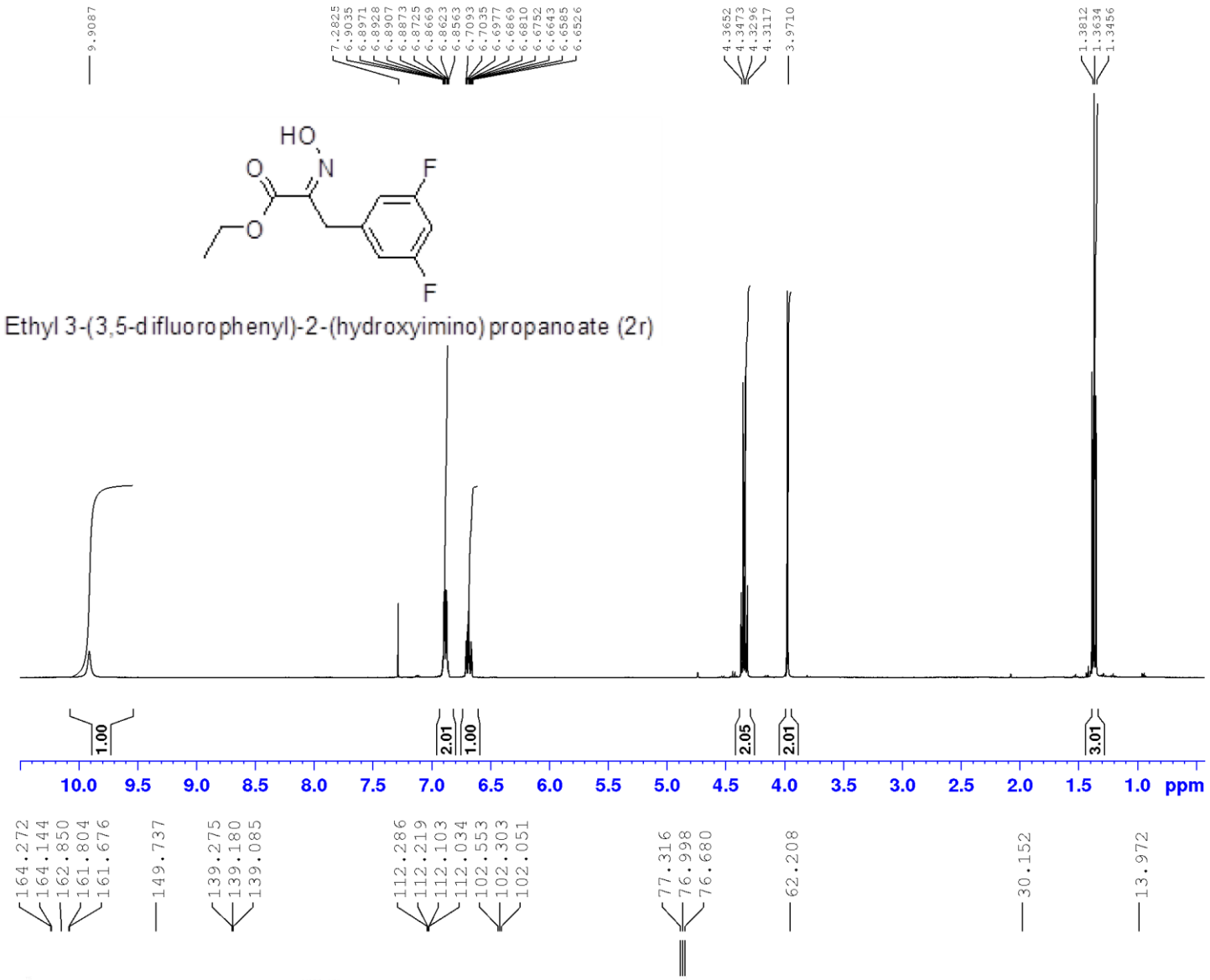
Ethyl 3-(2,5-difluorophenyl)-2-(hydroxyimino)propanoate (2q)

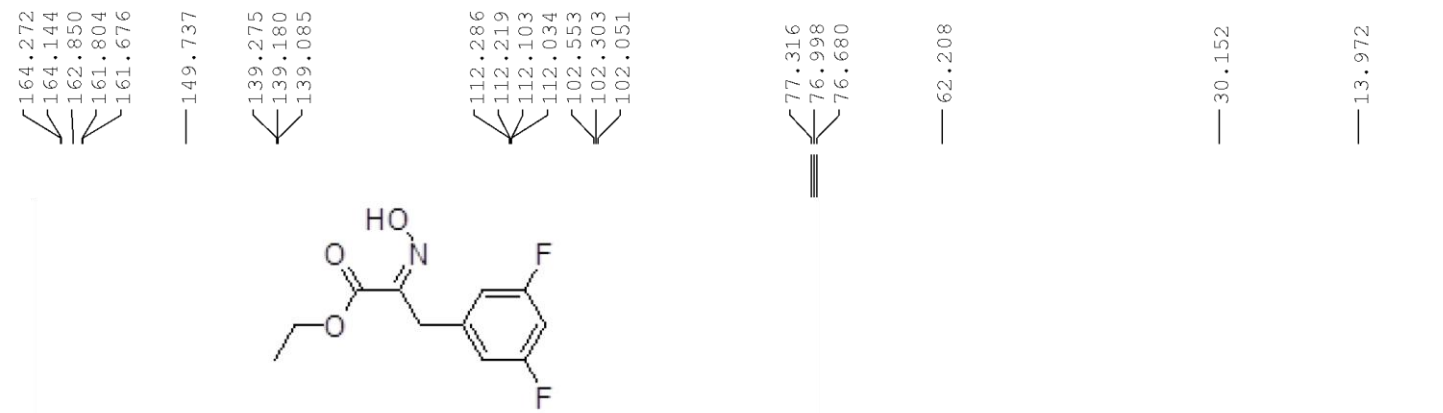




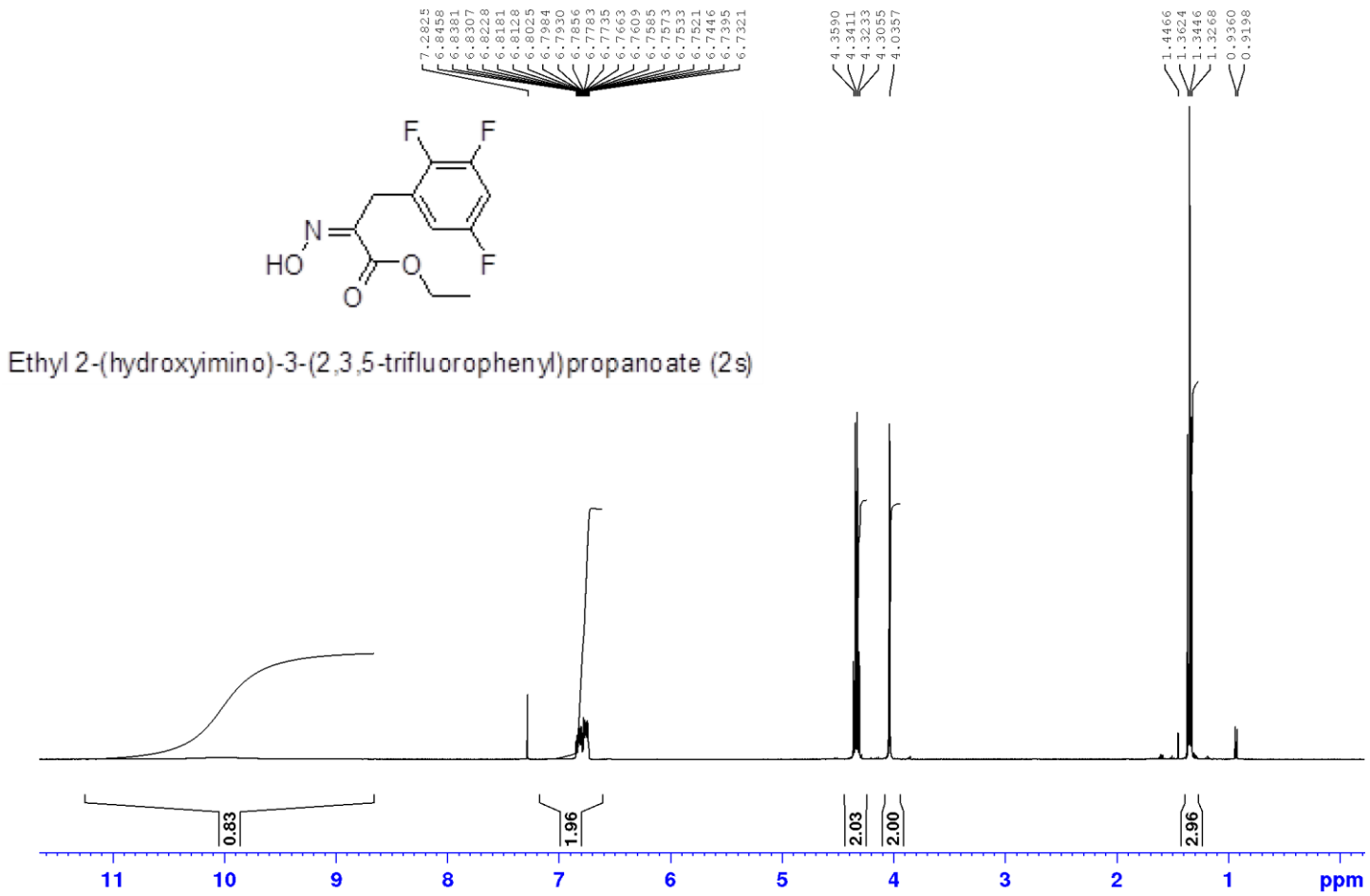
Ethyl 3-(2,5-difluorophenyl)-2-(hydroxyimino)propanoate (2q)

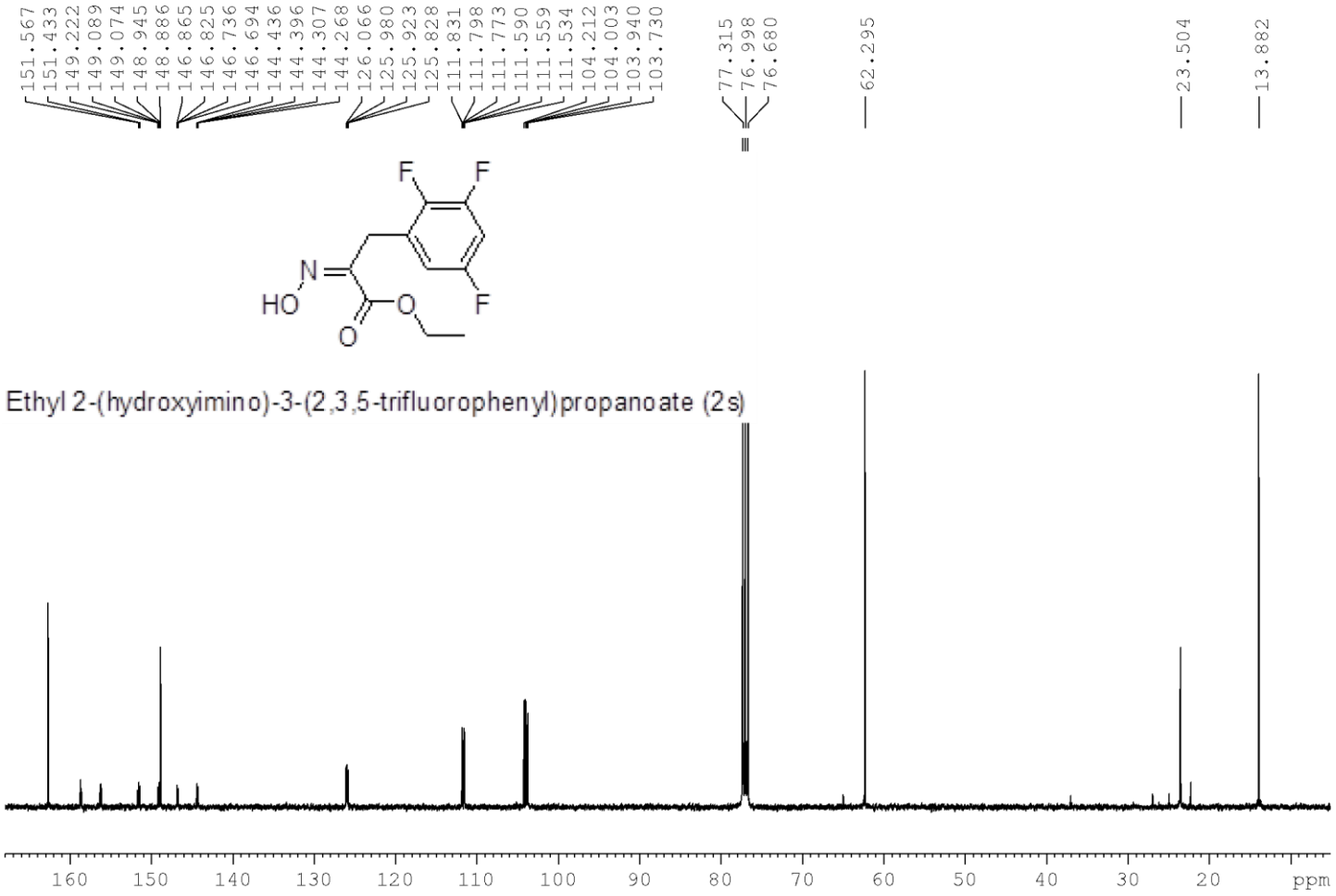


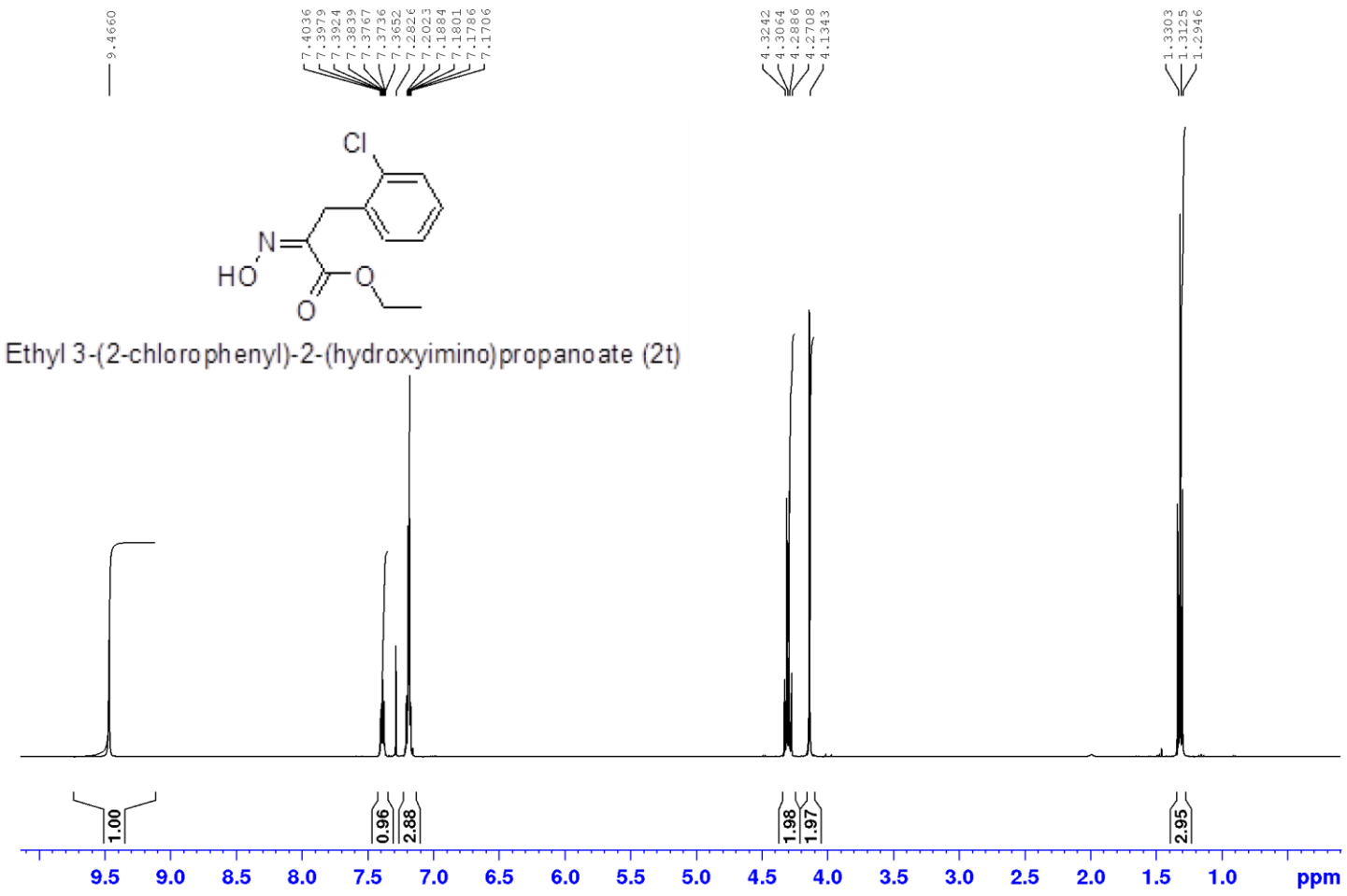

9.9087
7.2825
6.9035
6.8971
6.8928
6.8907
6.8873
6.8725
6.8669
6.8623
6.8563
6.7093
6.7035
6.6977
6.6869
6.6810
6.6752
6.6643
6.6585
6.6526
4.3652
4.3473
4.3296
4.3117
3.9710
1.3812
1.3634
1.3456
HO
N
O
O
F
F
Ethyl 3-(3,5-difluorophenyl)-2-(hydroxyimino)propanoate (2r)
1.00
2.01
1.00
2.05
2.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


164.272
164.144
162.850
161.804
161.676
149.737
139.275
139.180
139.085
112.286
112.219
112.103
112.034
102.553
102.303
102.051
77.316
76.998
76.680
62.208
30.152
13.972

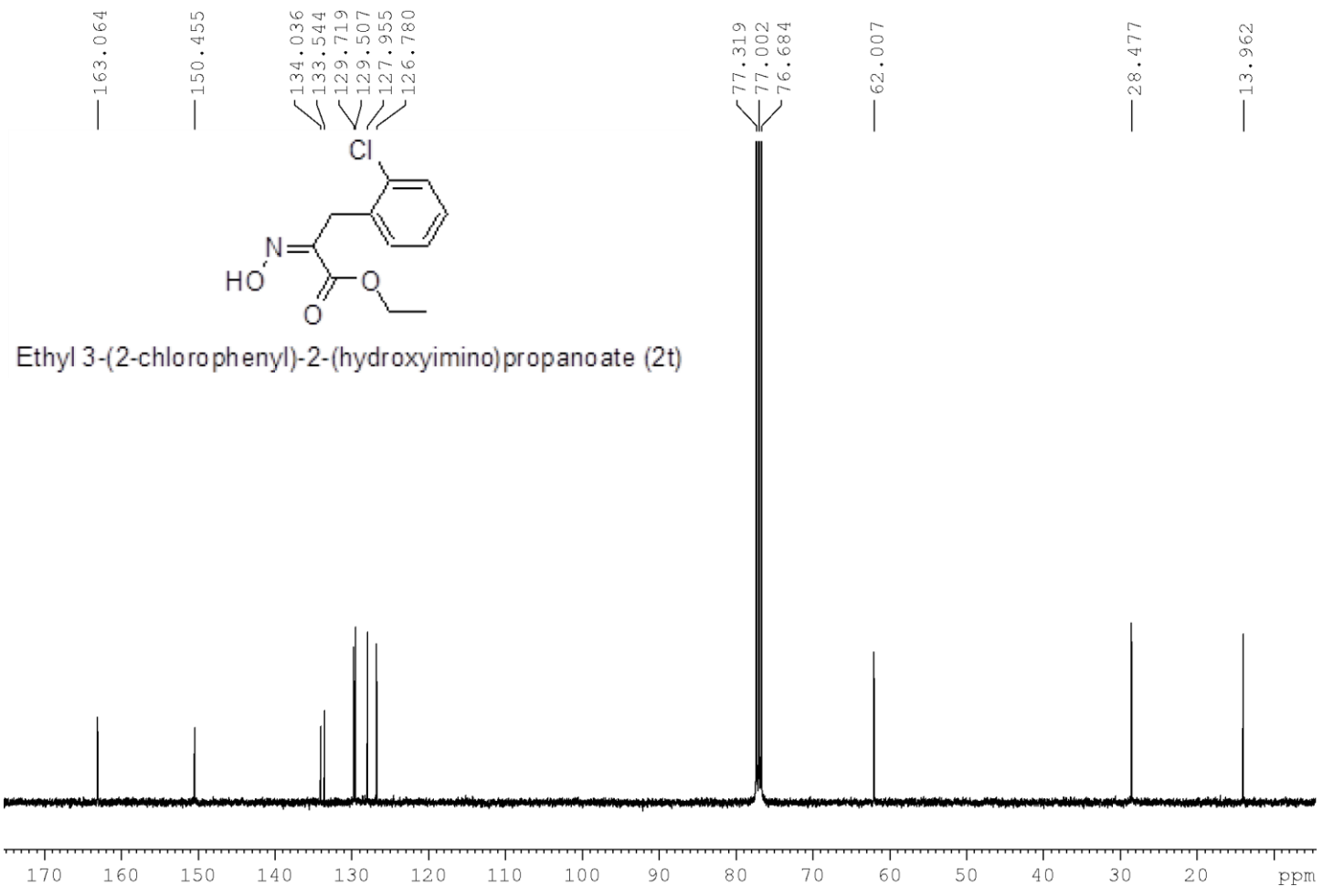
HO
N
O
O
F
F
Ethyl 3-(3,5-difluorophenyl)-2-(hydroxyimino)propanoate (2r)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.2825
6.8458
6.8381
6.8307
6.8228
6.8181
6.8128
6.8025
6.7984
6.7930
6.7856
6.7783
6.7735
6.7663
6.7609
6.7585
6.7573
6.7533
6.7521
6.7446
6.7395
6.7321
4.3590
4.3411
4.3233
4.3055
4.0357
1.4466
1.3624
1.3446
1.3268
0.9360
0.9198
F
F
F
N
HO
O
O
Ethyl 2-(hydroxyimino)-3-(2,3,5-trifluorophenyl)propanoate (2s)
0.83
1.96
2.03
2.00
2.96
11
10
9
8
7
6
5
4
3
2
1
ppm

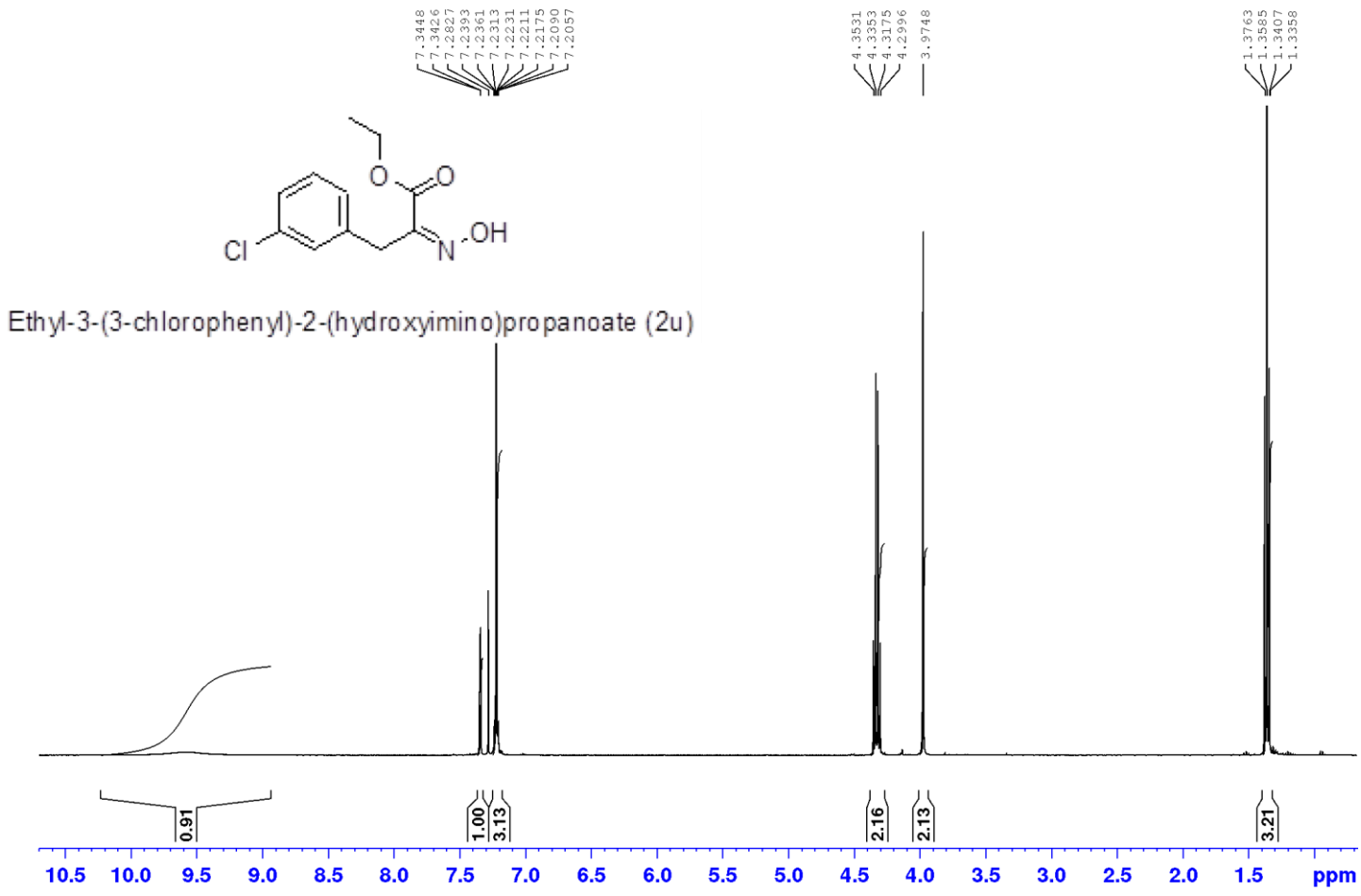

151.567
151.433
149.222
149.089
149.074
148.945
148.886
146.865
146.825
146.736
146.694
144.436
144.396
144.307
144.268
126.066
125.980
125.923
125.828
111.831
111.798
111.773
111.590
111.559
111.534
104.212
104.003
103.940
103.730
77.315
76.998
76.680
62.295
23.504
13.882
F
F
F
N
HO
O
O
Ethyl 2-(hydroxyimino)-3-(2,3,5-trifluorophenyl)propanoate (2s)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



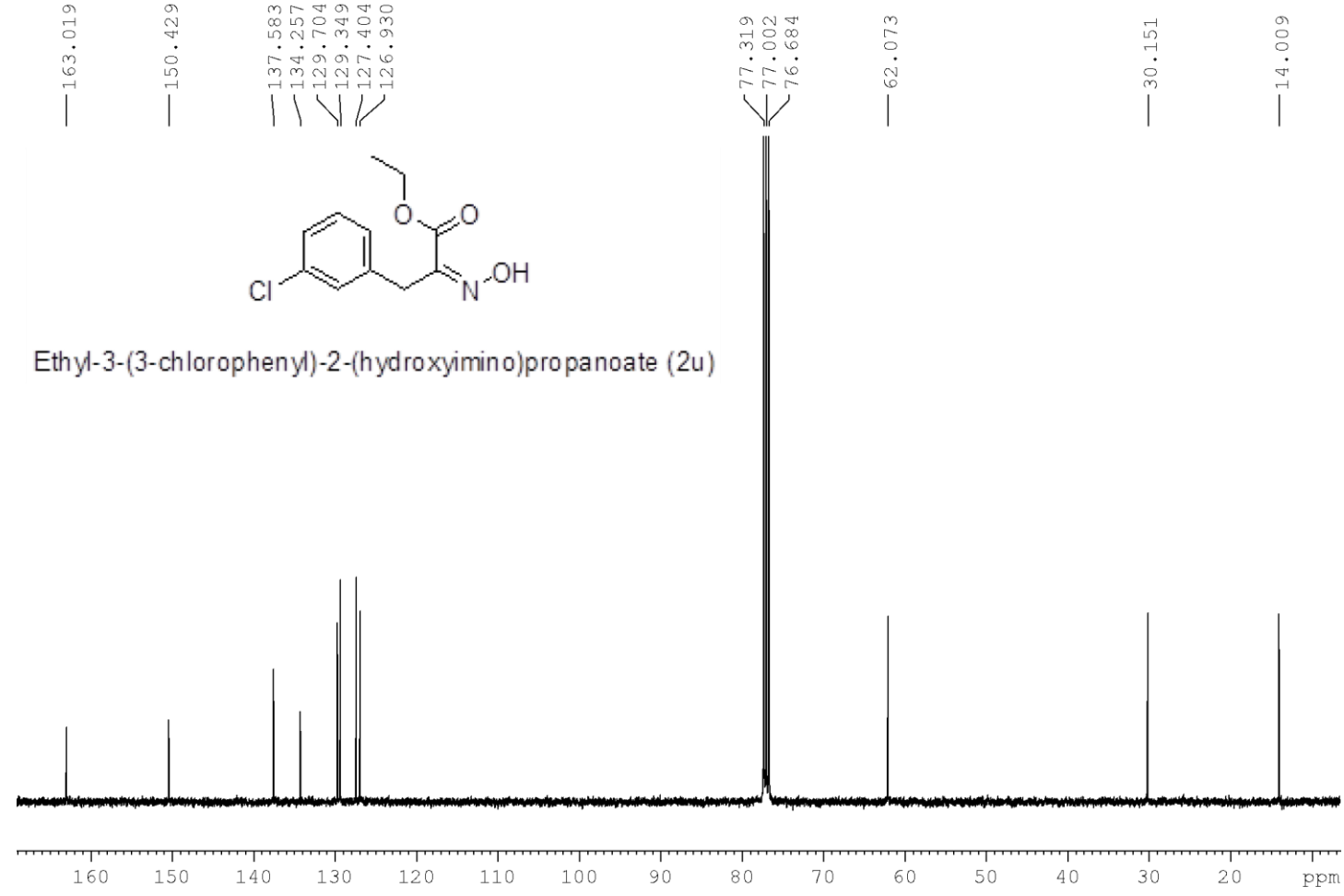
Ethyl 3-(2-chlorophenyl)-2-(hydroxyimino)propanoate (2t)



Ethyl 3-(2-chlorophenyl)-2-(hydroxyimino)propanoate (2t)

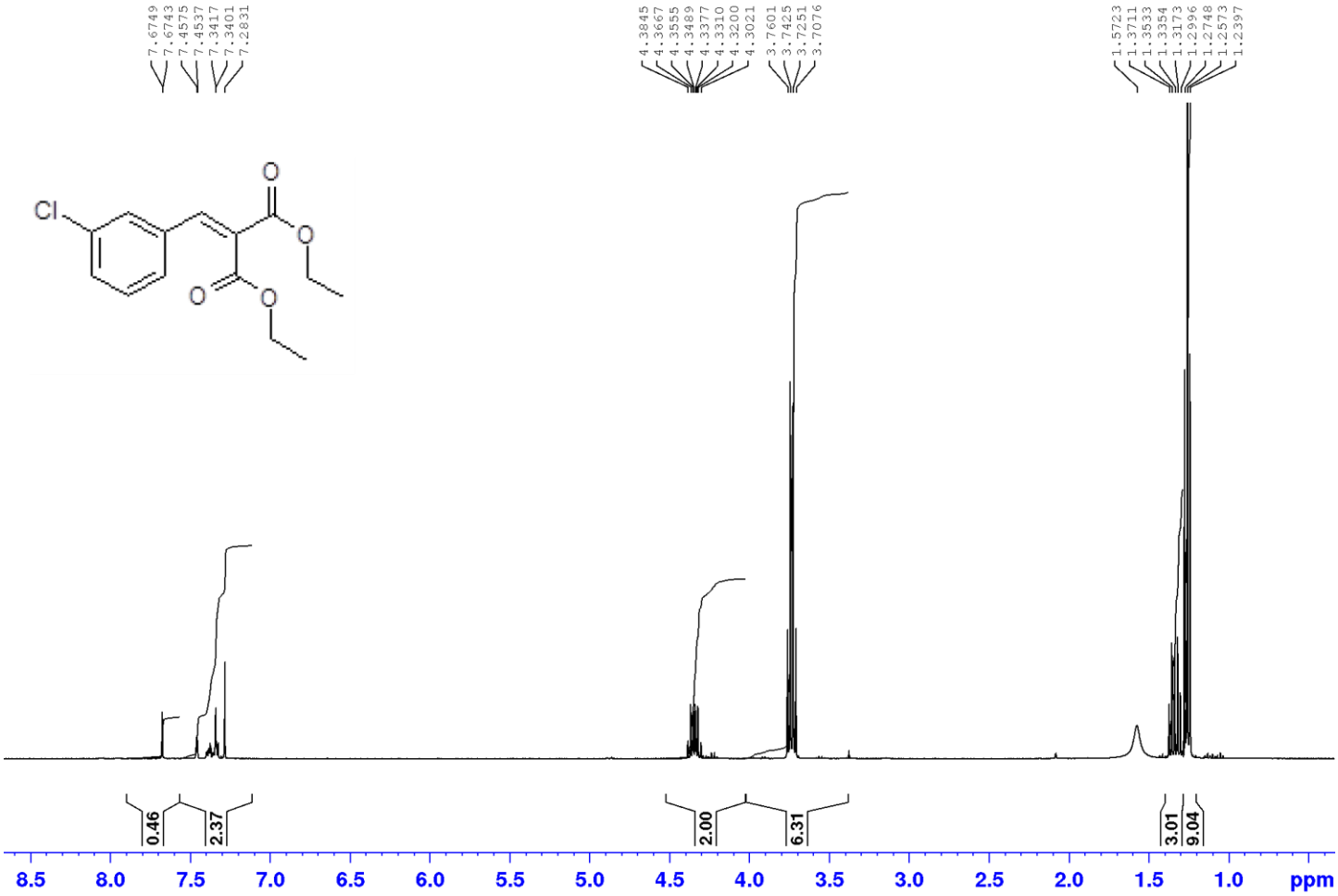


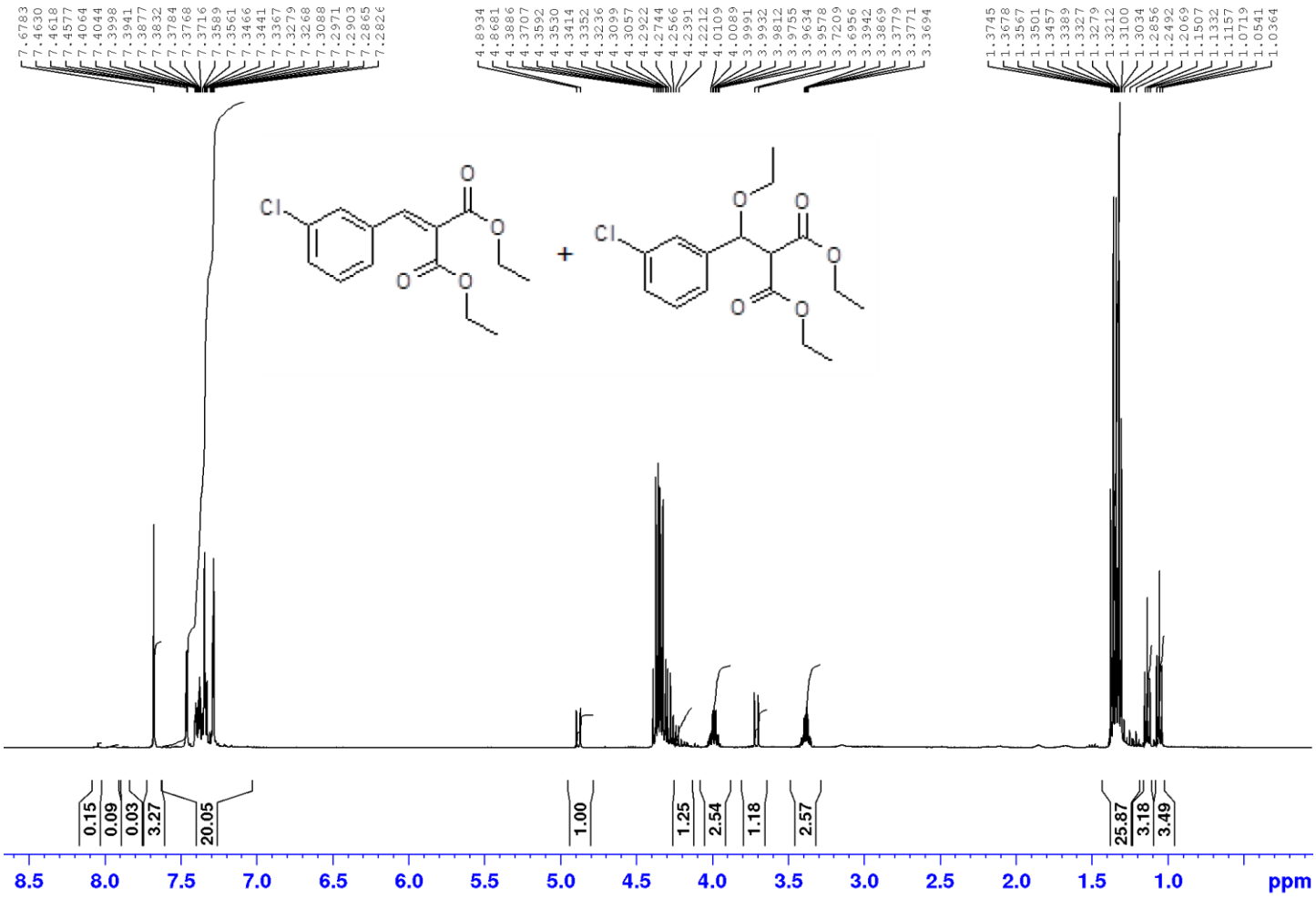
Ethyl-3-(3-chlorophenyl)-2-(hydroxyimino)propanoate (2u)

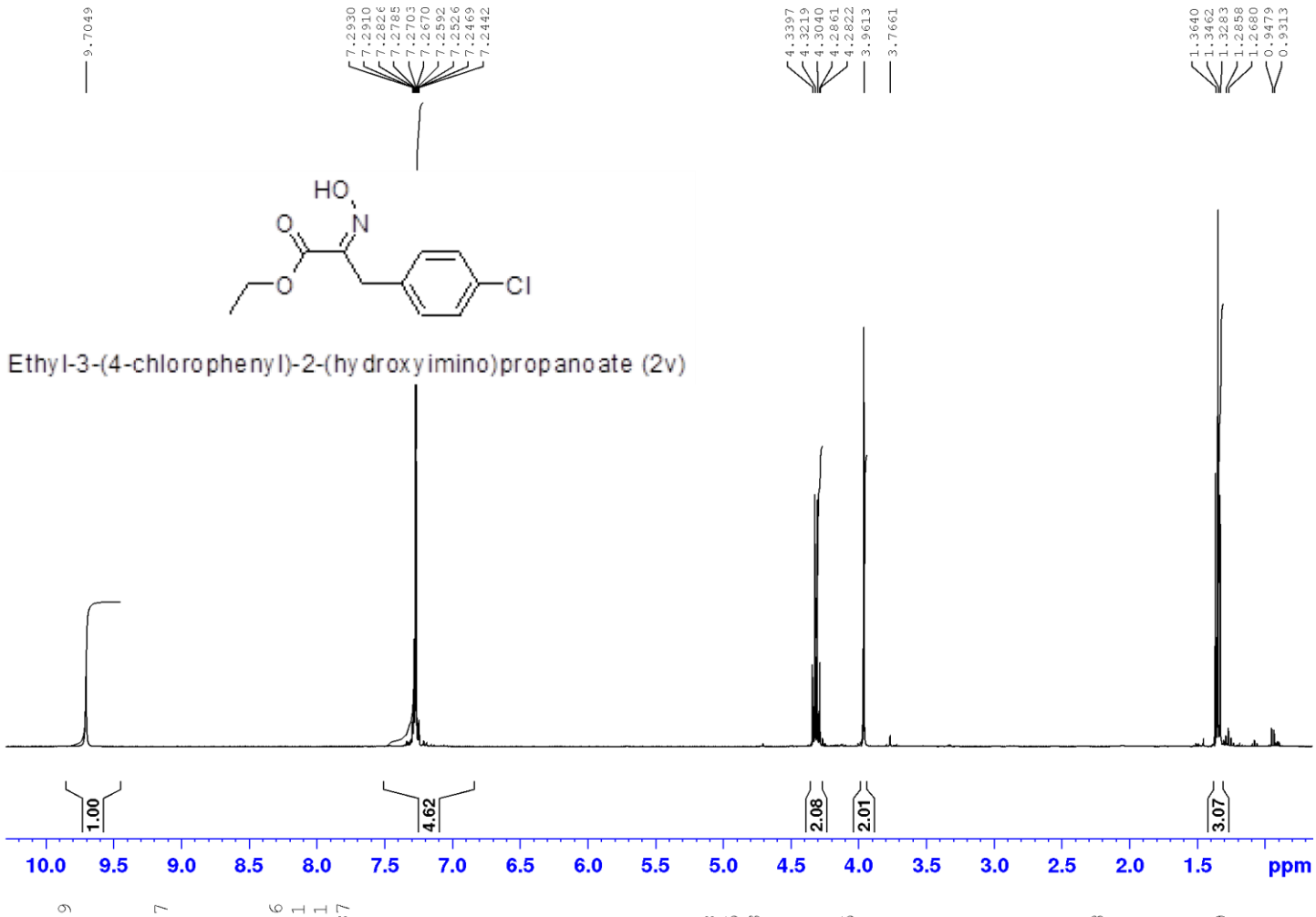


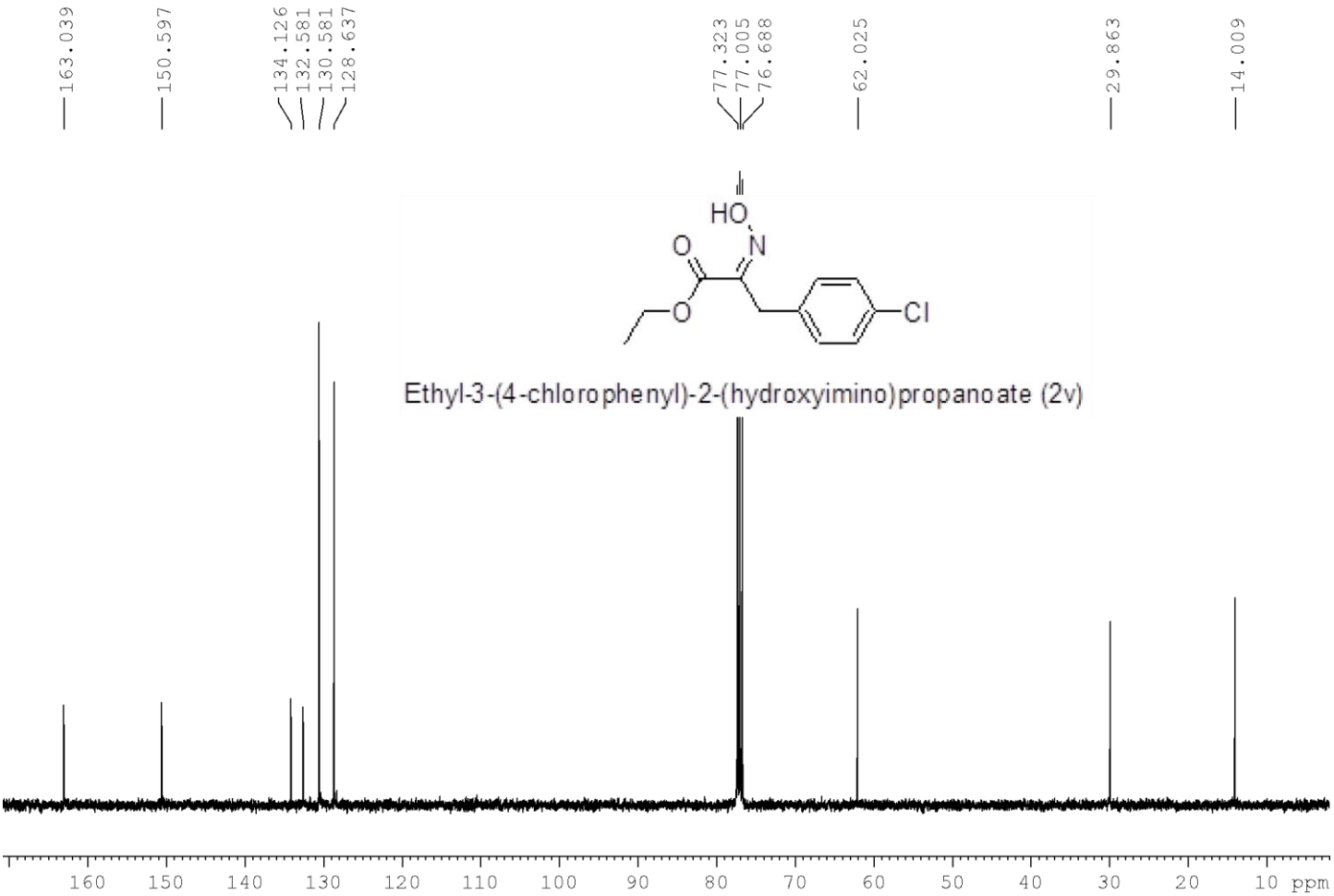
Ethyl-3-(3-chlorophenyl)-2-(hydroxyimino)propanoate (2u)

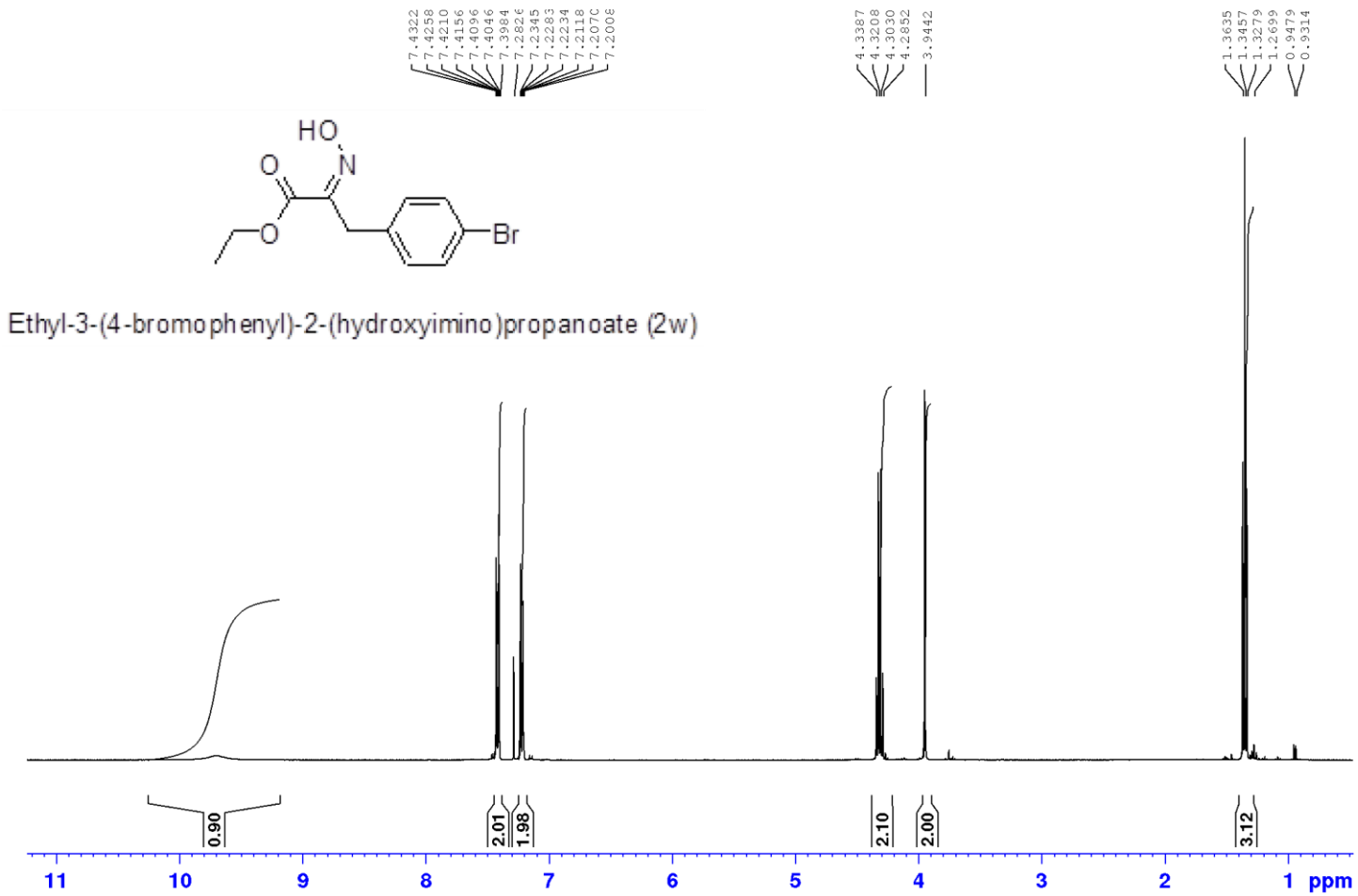
^{1}H NMR of a new and an old (15 days) sample of **6u** (with ethanol), the second one (concentrated to dryness) is also containing the ethanol adduct **7** :



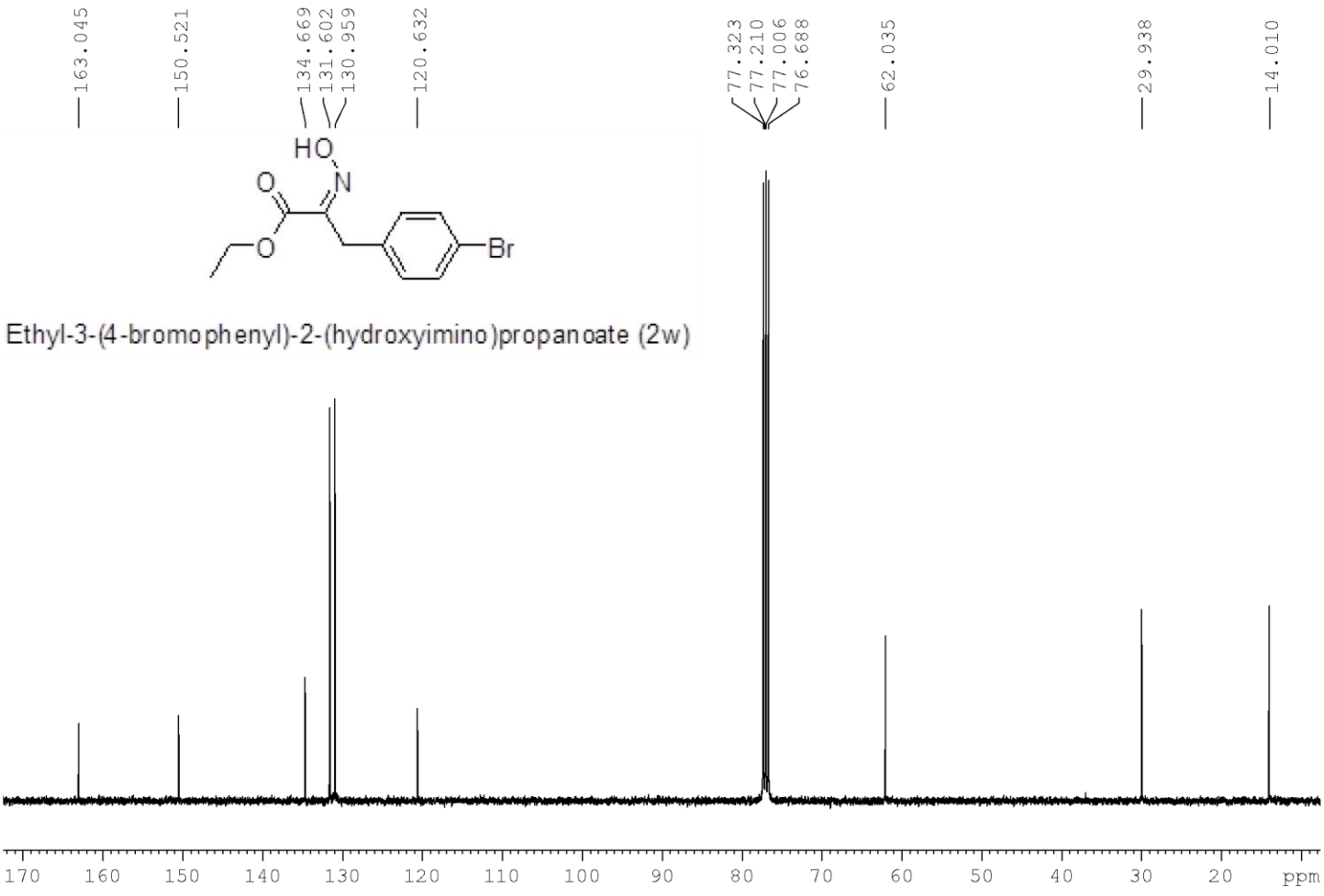

7.6783
7.4630
7.4618
7.4577
7.4064
7.4044
7.3998
7.3941
7.3877
7.3832
7.3784
7.3768
7.3716
7.3589
7.3561
7.3466
7.3441
7.3367
7.3279
7.3268
7.3088
7.2971
7.2903
7.2865
7.2826
4.8934
4.8681
4.3886
4.3707
4.3592
4.3530
4.3414
4.3352
4.3236
4.3099
4.3057
4.2922
4.2744
4.2566
4.2391
4.2212
4.0109
4.0089
3.9991
3.9932
3.9812
3.9755
3.9634
3.9578
3.7209
3.6956
3.3942
3.3869
3.3779
3.3771
3.3694
1.3745
1.3678
1.3567
1.3501
1.3457
1.3389
1.3327
1.3279
1.3212
1.3100
1.3034
1.2856
1.2492
1.2069
1.1507
1.1332
1.1157
1.0719
1.0541
1.0364
Cl
O
O
O
O
+
Cl
O
O
O
O
O
0.15
0.09
0.03
3.27
20.05
1.00
1.25
2.54
1.18
2.57
25.87
3.18
3.49
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
ppm


9.7049
7.2930
7.2910
7.2826
7.2785
7.2703
7.2670
7.2592
7.2526
7.2469
7.2442
4.3397
4.3219
4.3040
4.2861
4.2822
3.9613
3.7661
1.3640
1.3462
1.3283
1.2858
1.2680
0.9479
0.9313
HO
N
O
O
Cl
Ethyl-3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (2v)
1.00
4.62
2.08
2.01
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
ppm

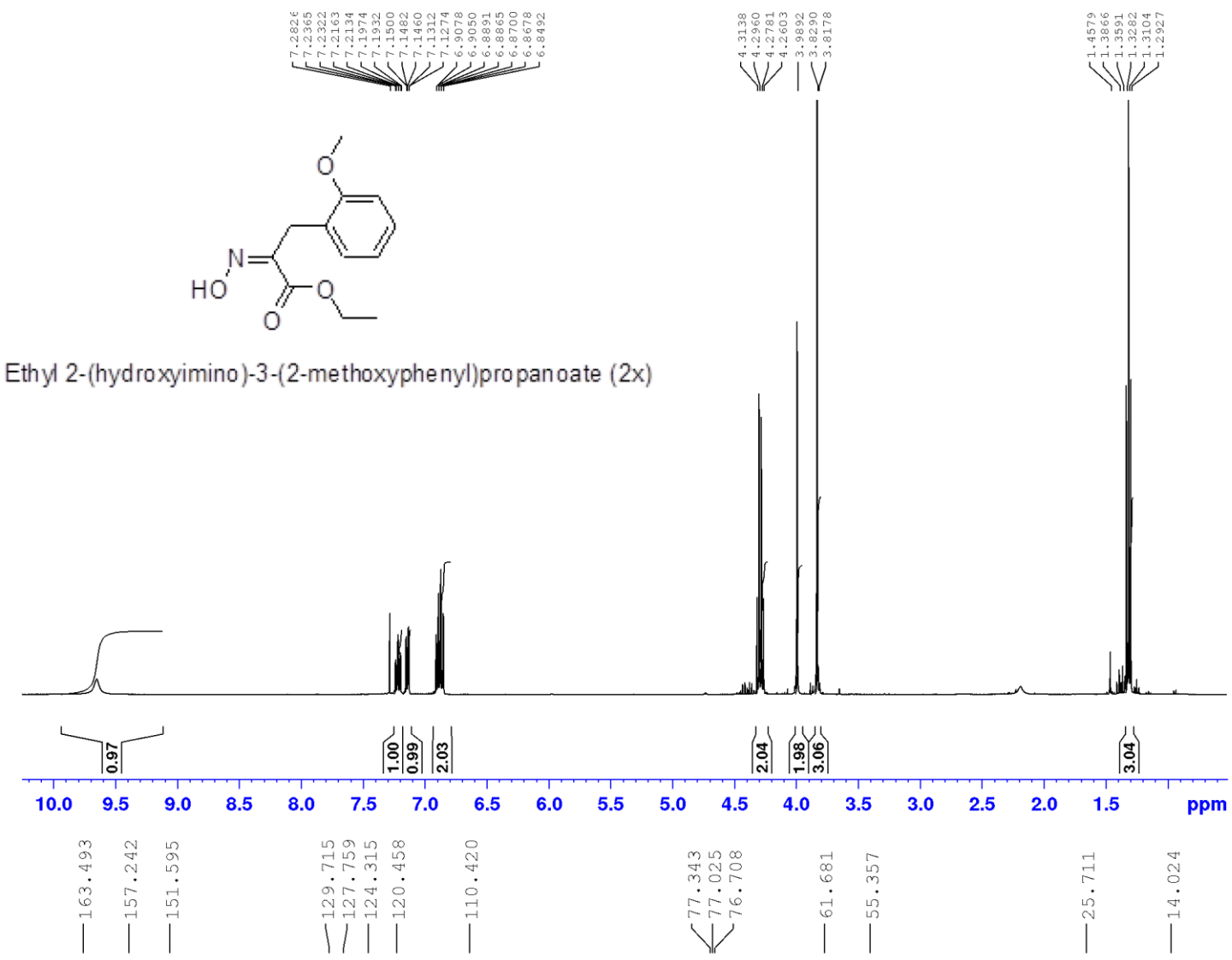

163.039
150.597
134.126
132.581
130.581
128.637
77.323
77.005
76.688
62.025
29.863
14.009
HO
N
O
O
Cl
Ethyl-3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (2v)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

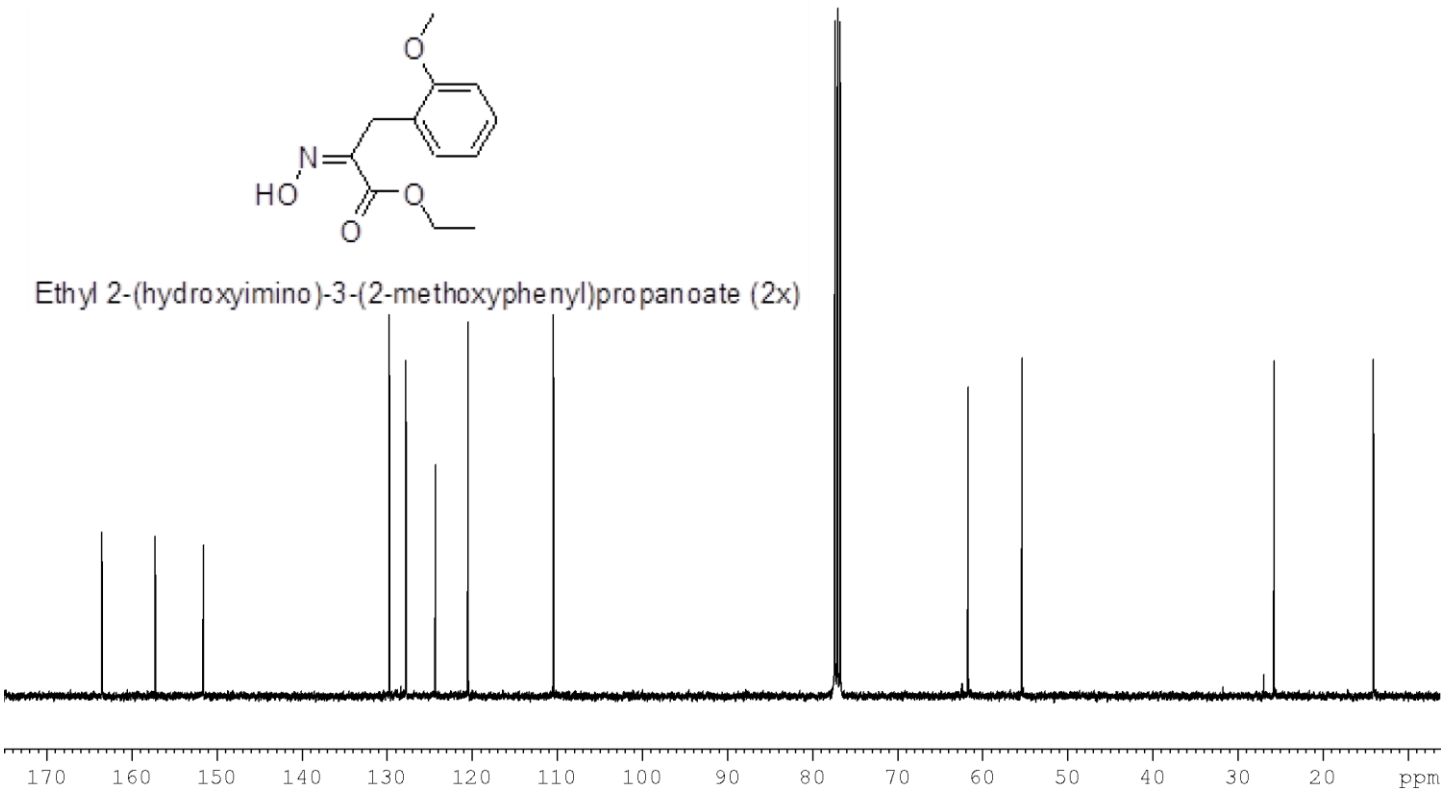


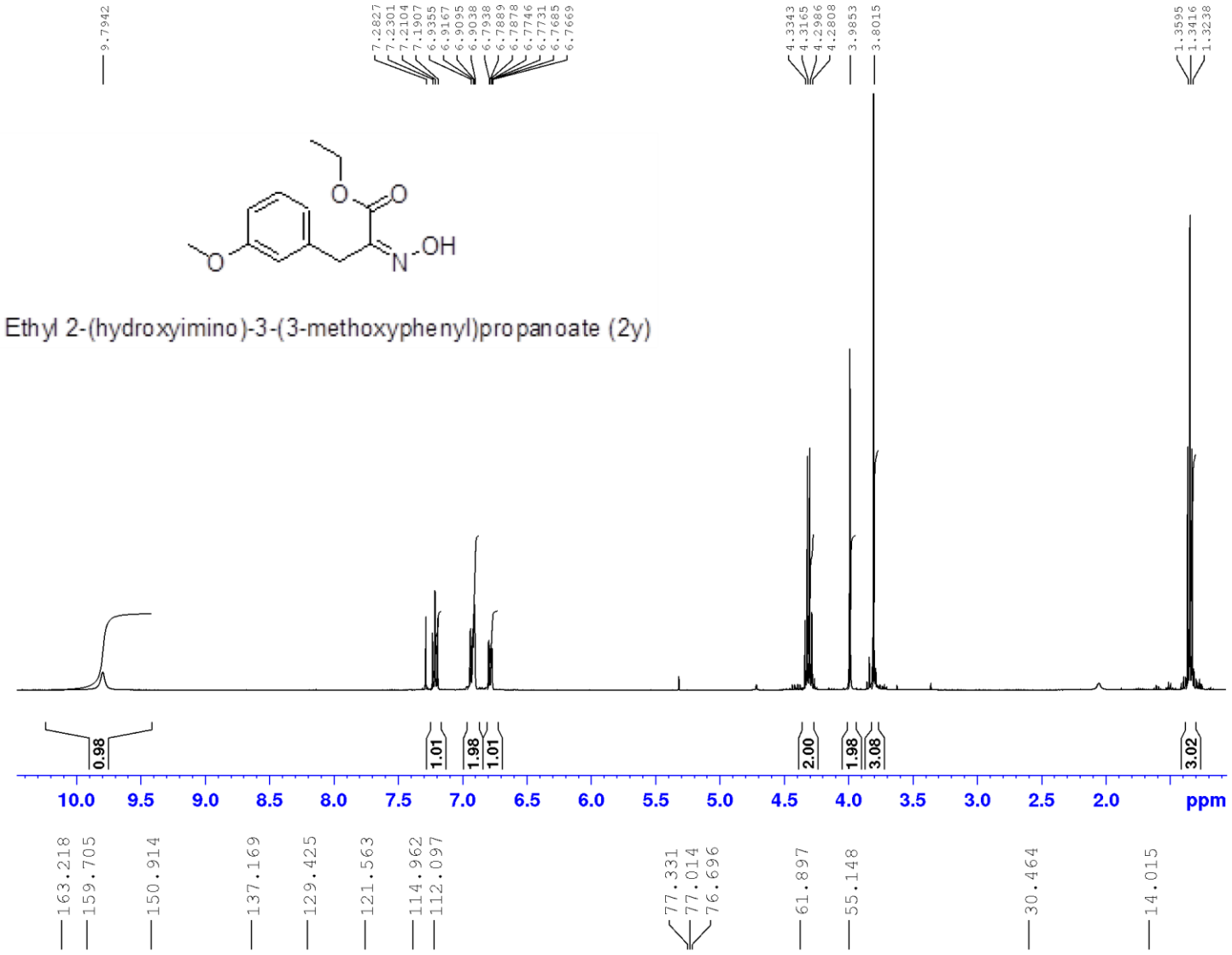
Ethyl-3-(4-bromophenyl)-2-(hydroxyimino)propanoate (2w)



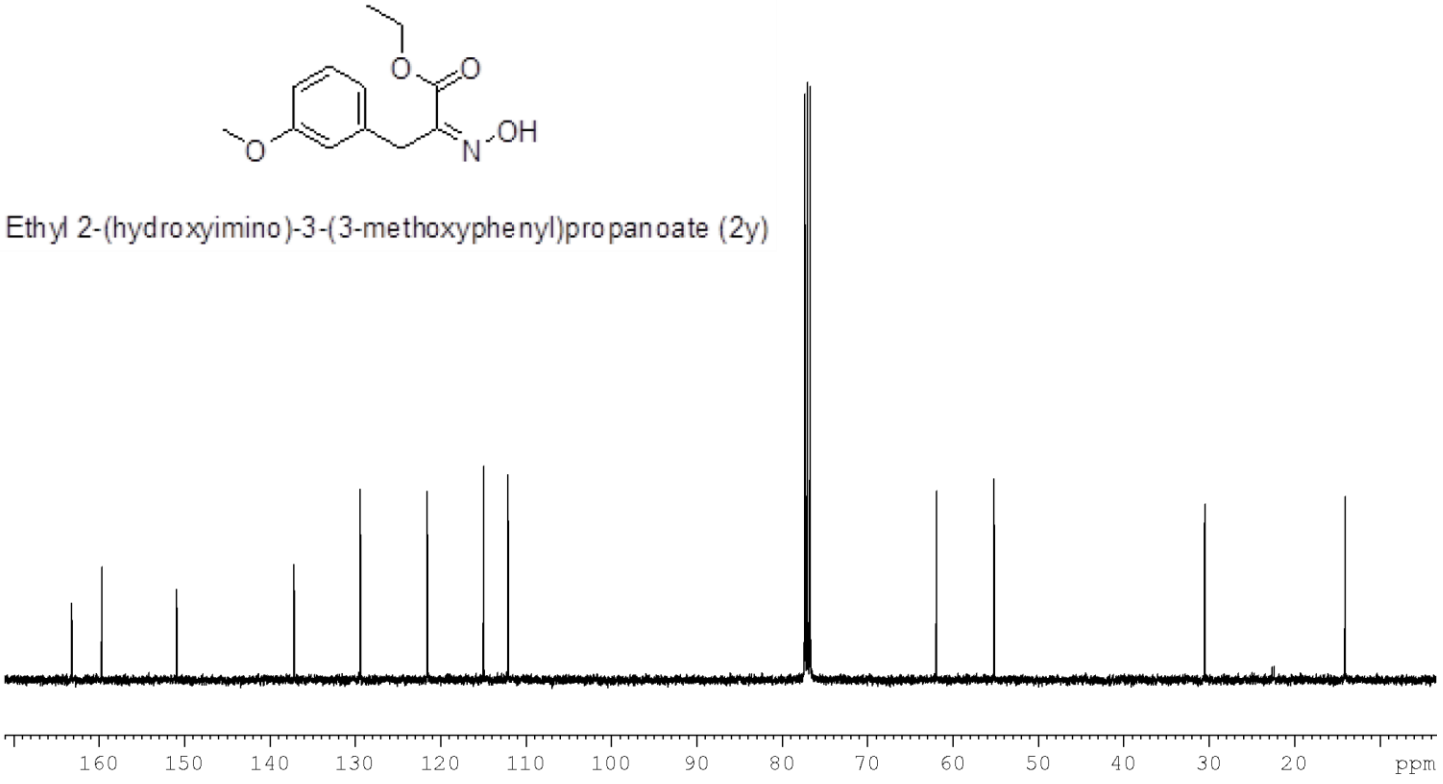
Ethyl-3-(4-bromophenyl)-2-(hydroxyimino)propanoate (2w)


Ethyl 2-(hydroxyimino)-3-(2-methoxyphenyl)propanoate (2x)
ppm

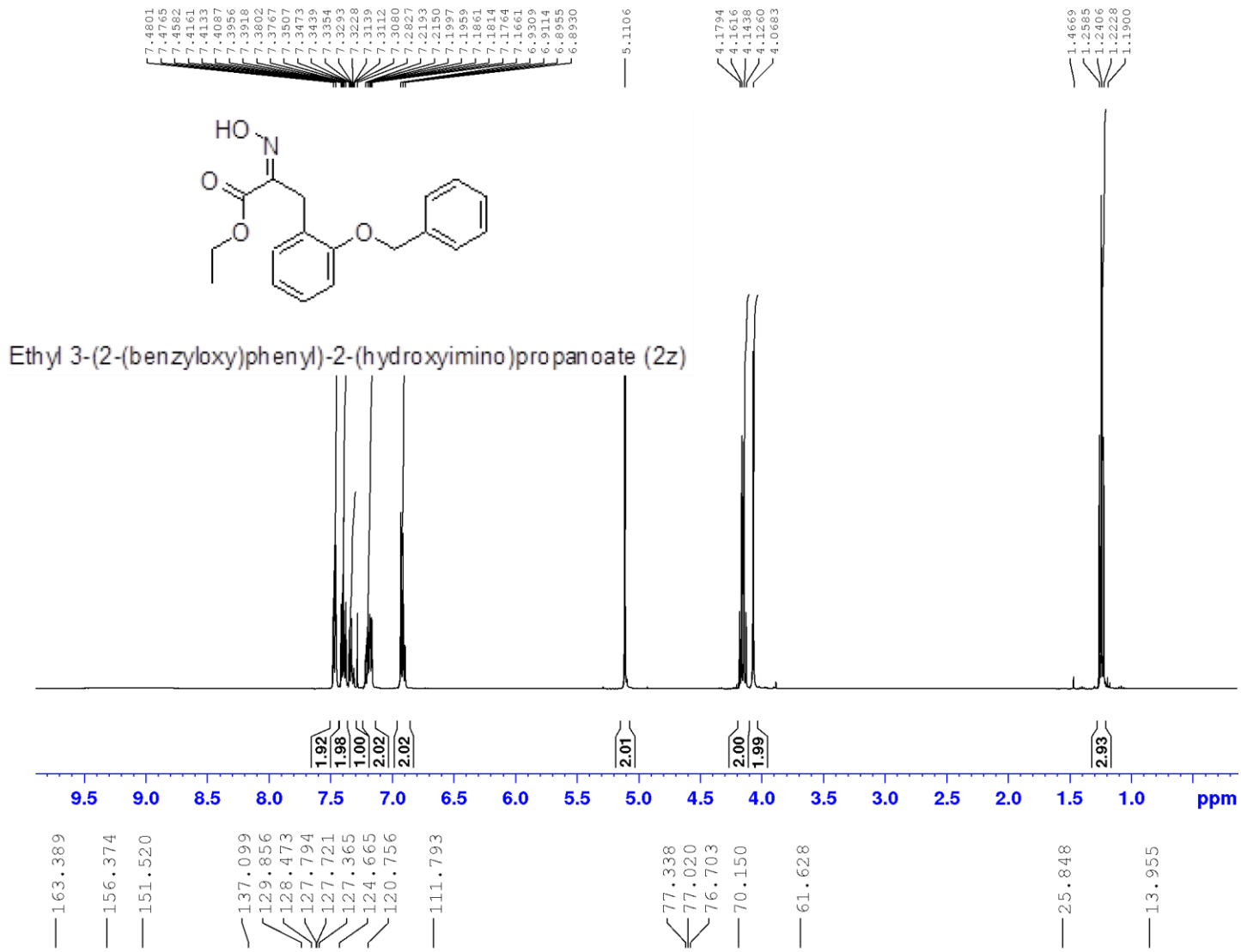

Ethyl 2-(hydroxyimino)-3-(2-methoxyphenyl)propanoate (2x)
ppm

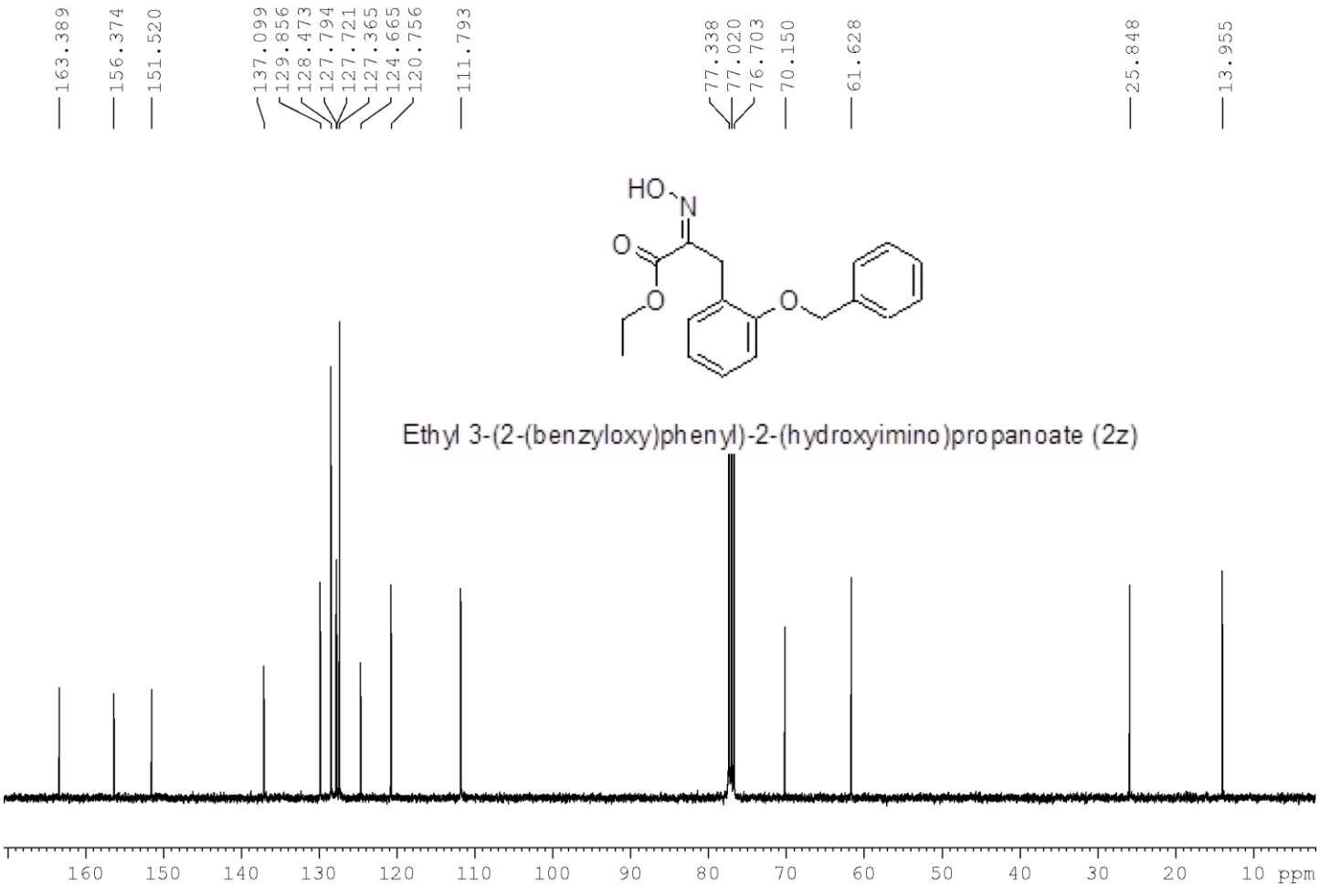


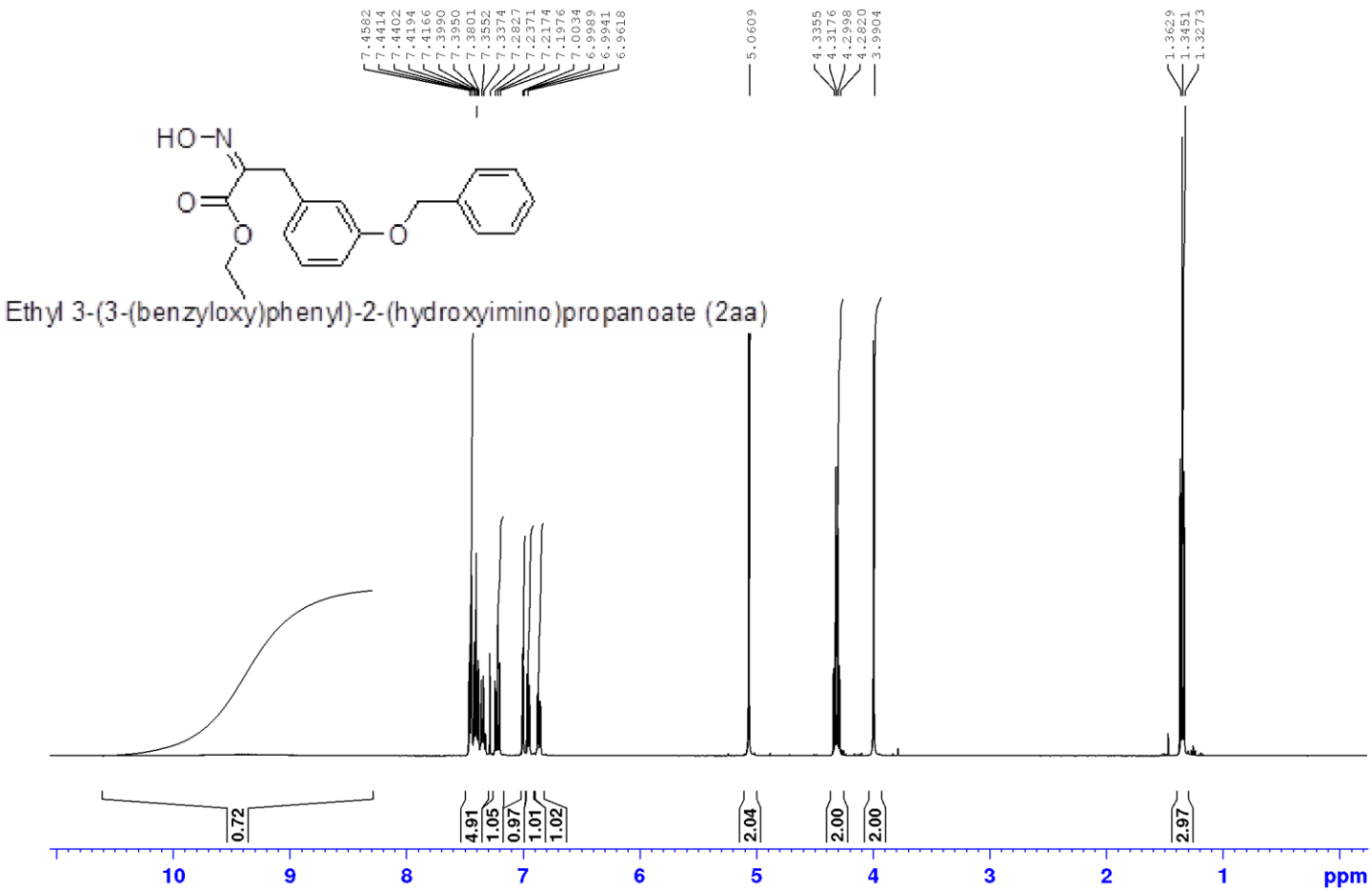
Ethyl 2-(hydroxyimino)-3-(3-methoxyphenyl)propanoate (2y)



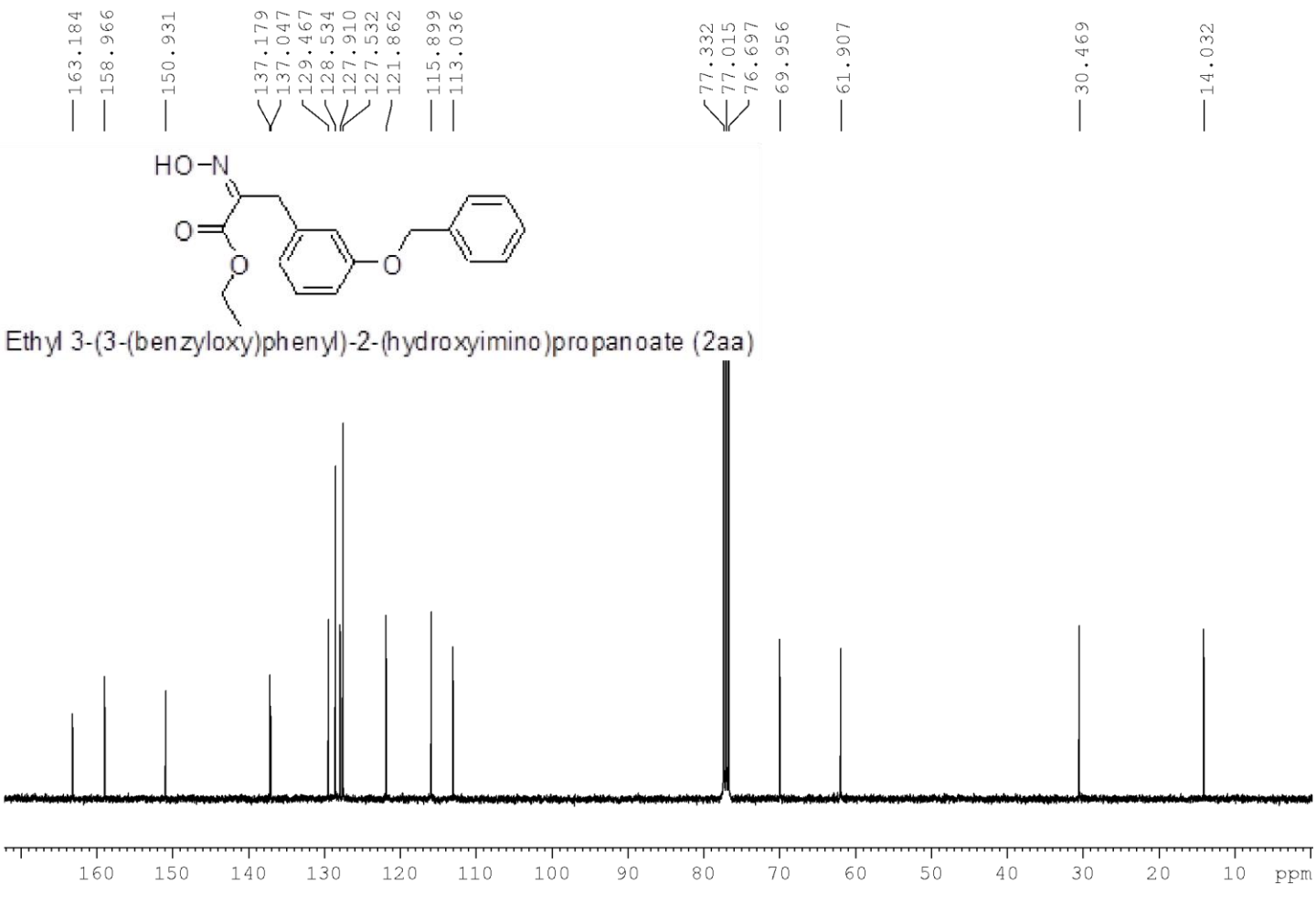
Ethyl 2-(hydroxyimino)-3-(3-methoxyphenyl)propanoate (2y)


7.4801
7.4765
7.4582
7.4161
7.4133
7.4087
7.3956
7.3918
7.3802
7.3767
7.3507
7.3473
7.3439
7.3354
7.3293
7.3228
7.3139
7.3112
7.3080
7.2827
7.2193
7.2150
7.1997
7.1959
7.1861
7.1814
7.1764
7.1661
6.9309
6.9114
6.8955
6.8930
5.1106
4.1794
4.1616
4.1438
4.1260
4.0683
1.4669
1.2585
1.2406
1.2228
1.1900
HO
N
O
O
O
Ethyl 3-(2-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2z)
1.92
1.98
1.00
2.02
2.02
2.01
2.00
1.99
2.93
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
ppm

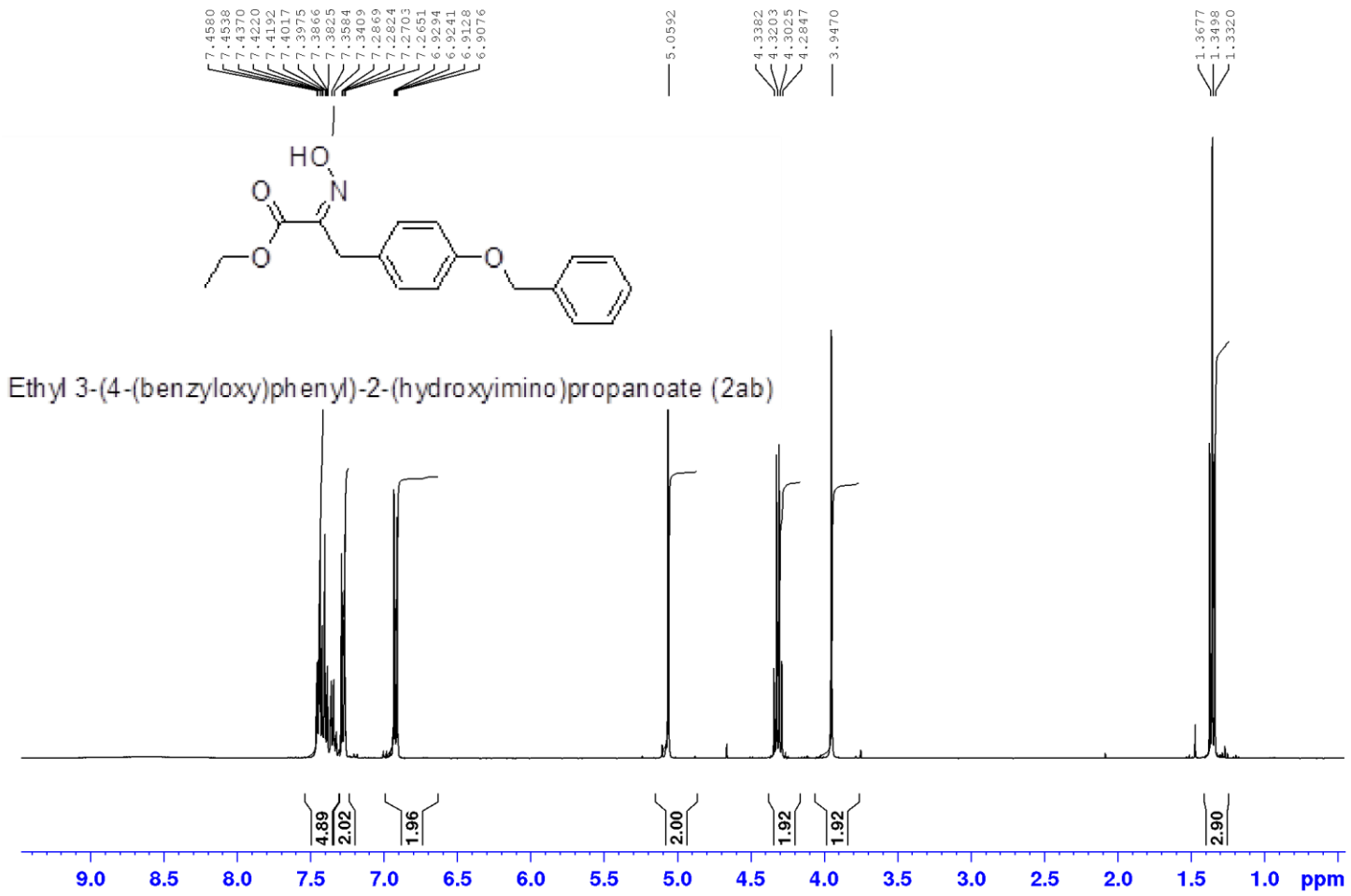

163.389
156.374
151.520
137.099
129.856
128.473
127.794
127.721
127.365
124.665
120.756
111.793
77.338
77.020
76.703
70.150
61.628
25.848
13.955
HO
N
O
O
O
Ethyl 3-(2-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2z)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

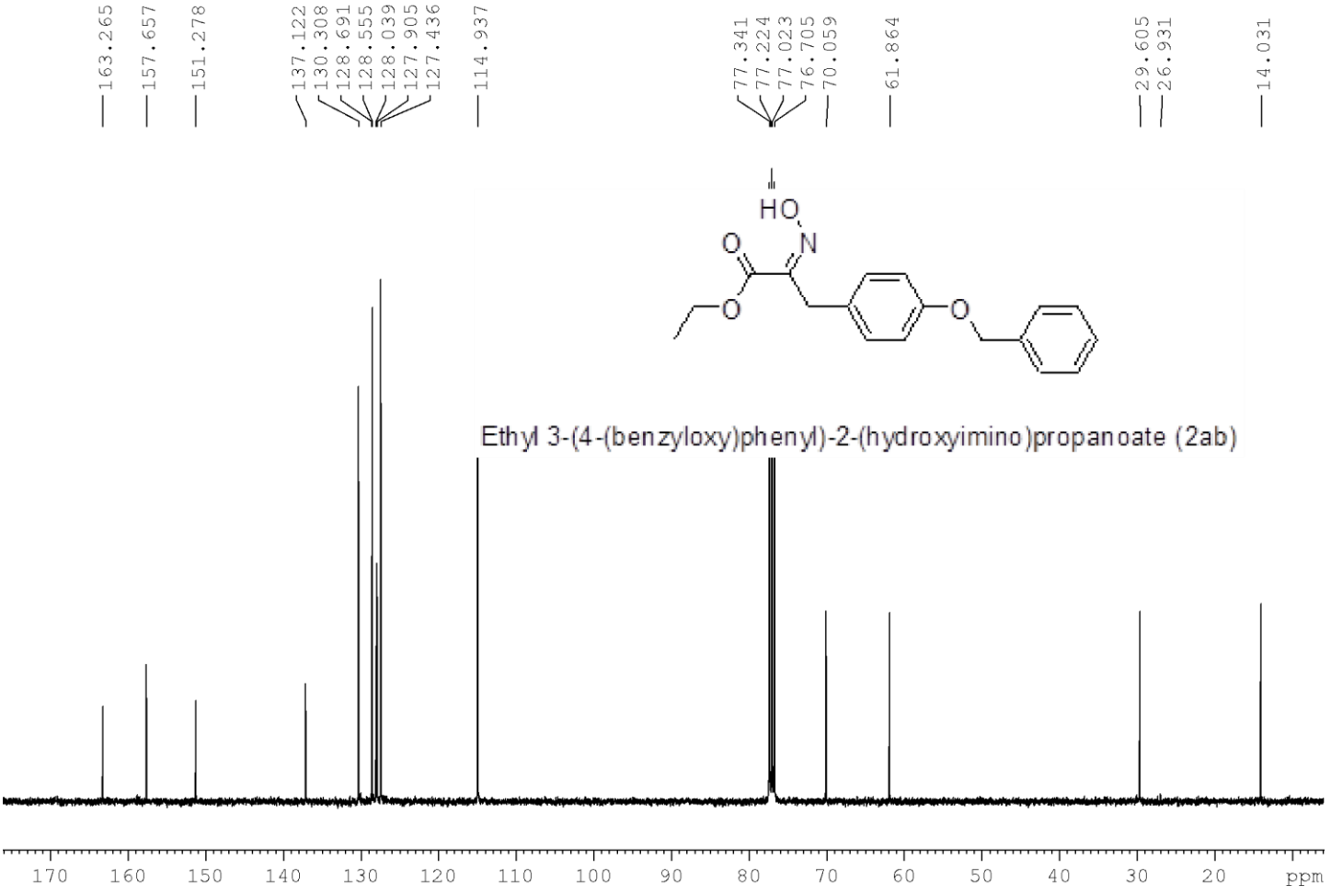


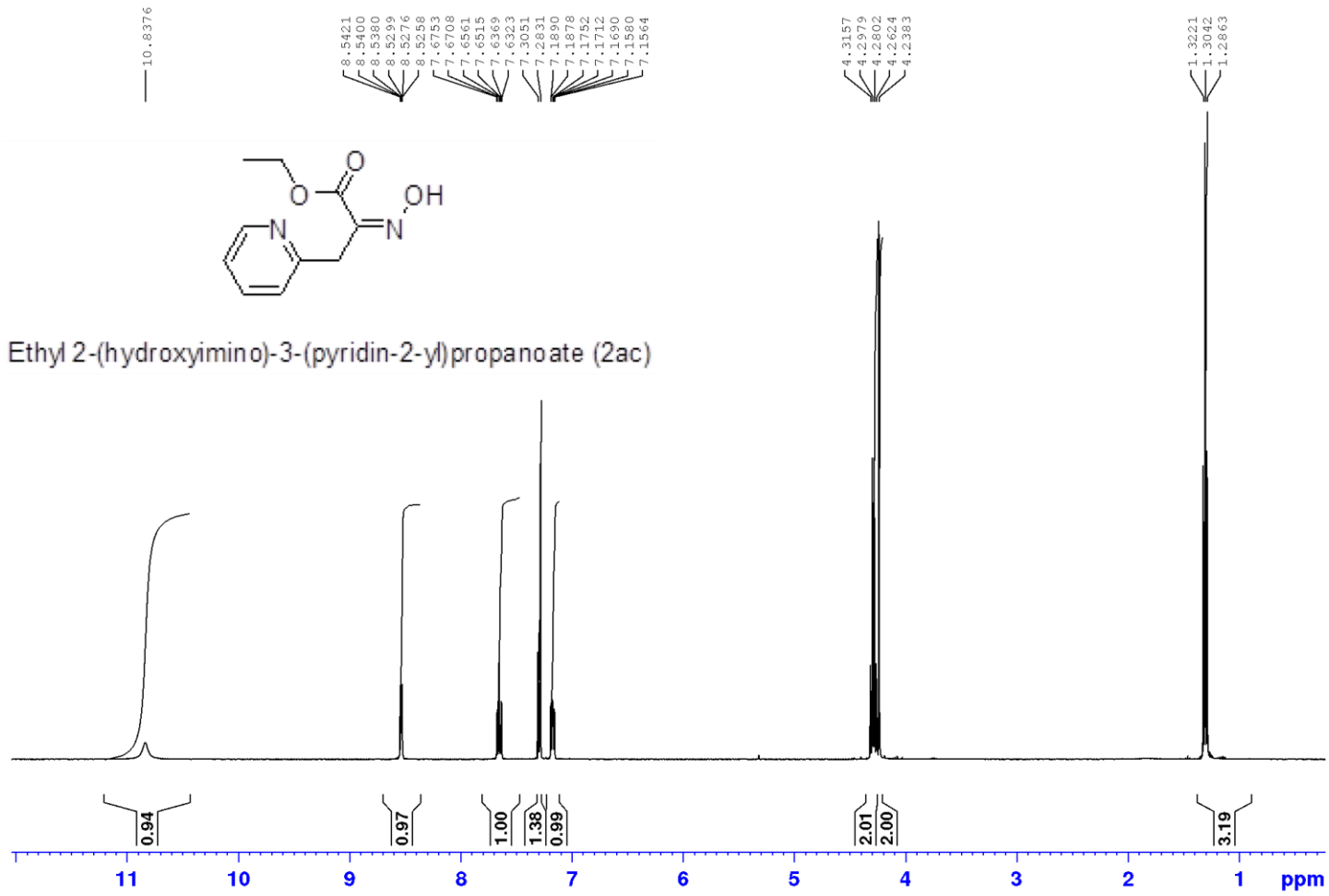
Ethyl 3-(3-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2aa)



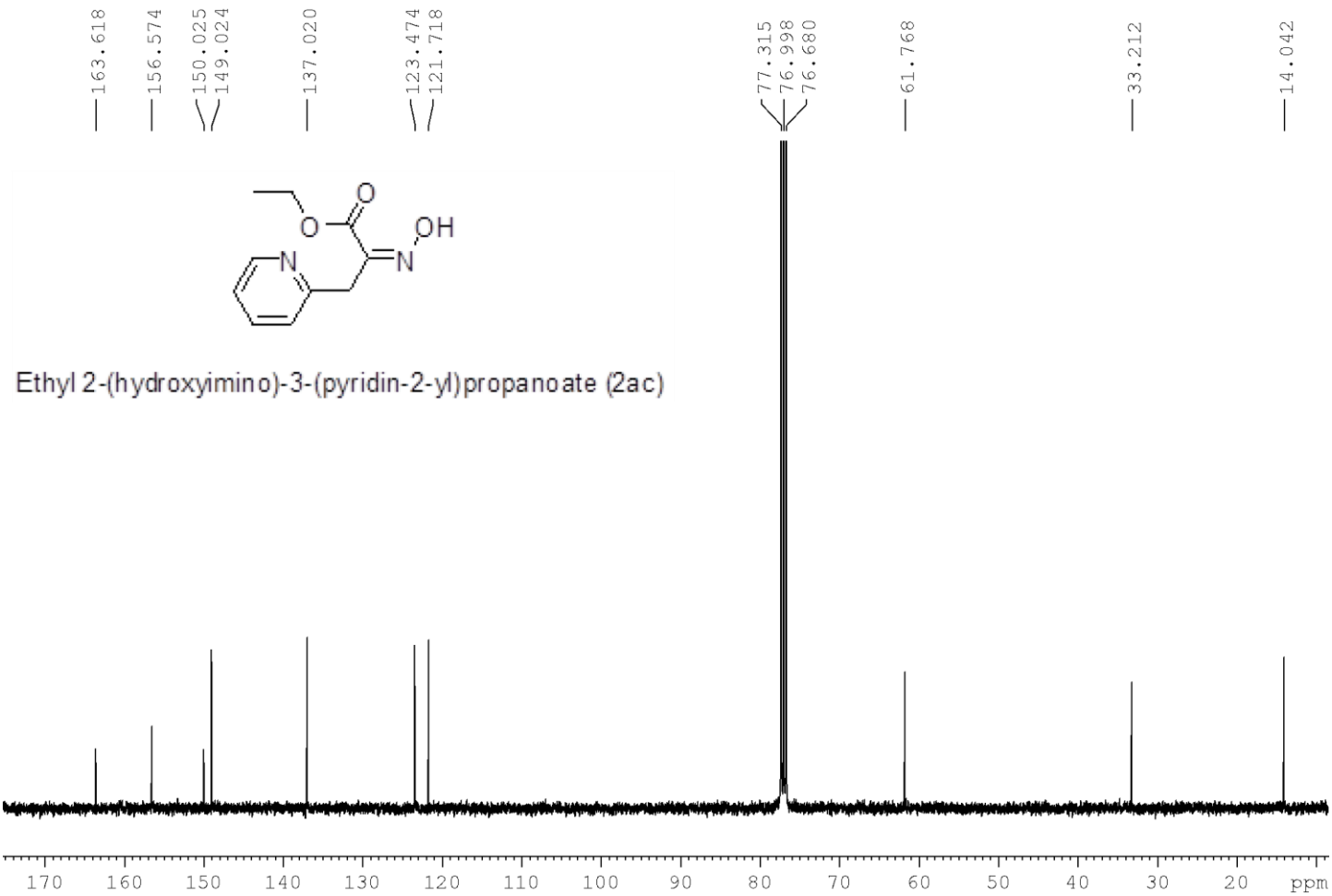
Ethyl 3-(3-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2aa)


7.4580
7.4538
7.4370
7.4220
7.4192
7.4017
7.3975
7.3866
7.3825
7.3584
7.3409
7.2869
7.2824
7.2703
7.2651
6.9294
6.9241
6.9128
6.9076
5.0592
4.3382
4.3203
4.3025
4.2847
3.9470
1.3677
1.3498
1.3320
HO
N
O
O
O
Ethyl 3-(4-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2ab)
4.89
2.02
1.96
2.00
1.92
1.92
2.90
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
ppm

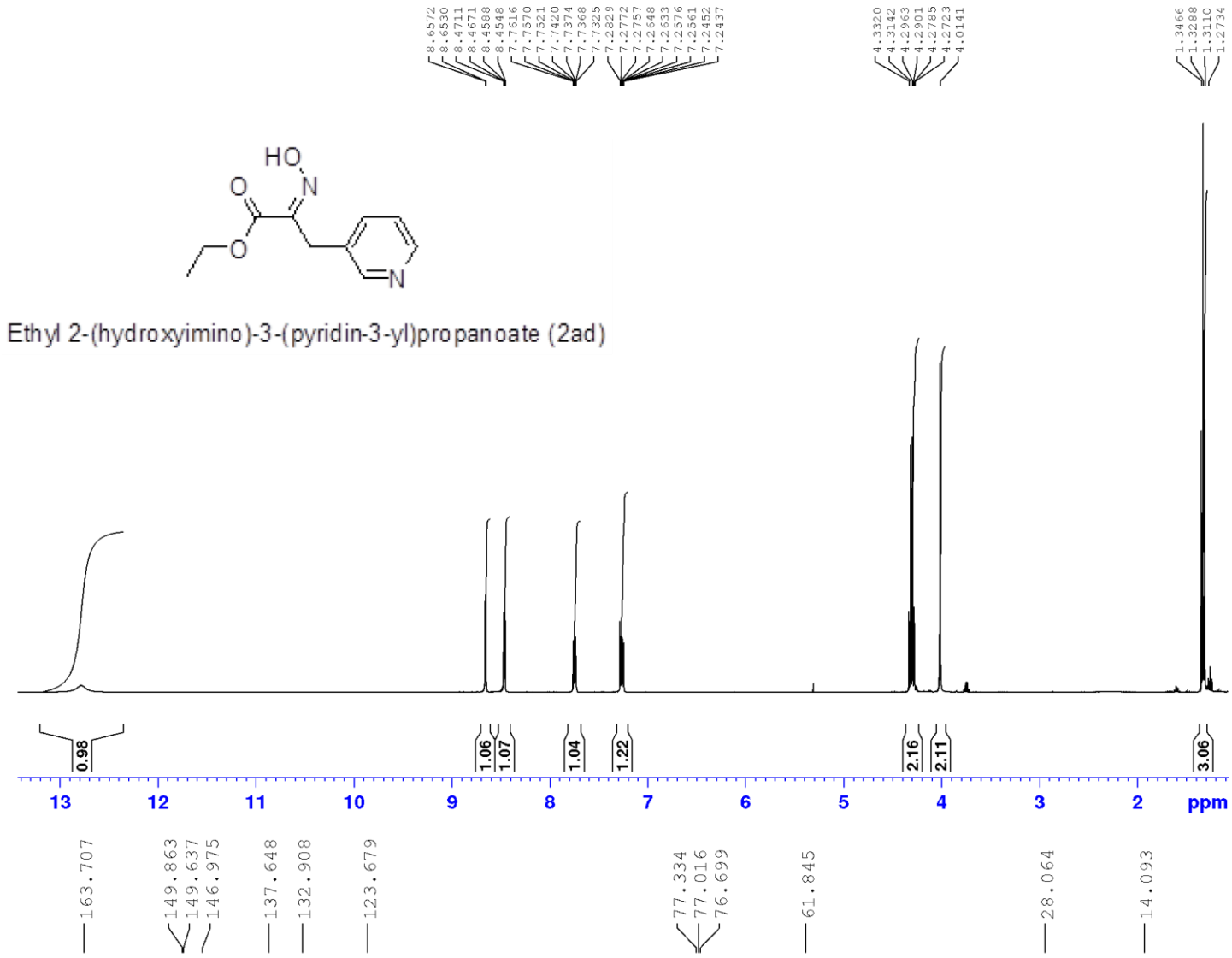

163.265
157.657
151.278
137.122
130.308
128.691
128.555
128.039
127.905
127.436
114.937
77.341
77.224
77.023
76.705
70.059
61.864
29.605
26.931
14.031
HO
N
O
O
O
Ethyl 3-(4-(benzyloxy)phenyl)-2-(hydroxyimino)propanoate (2ab)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

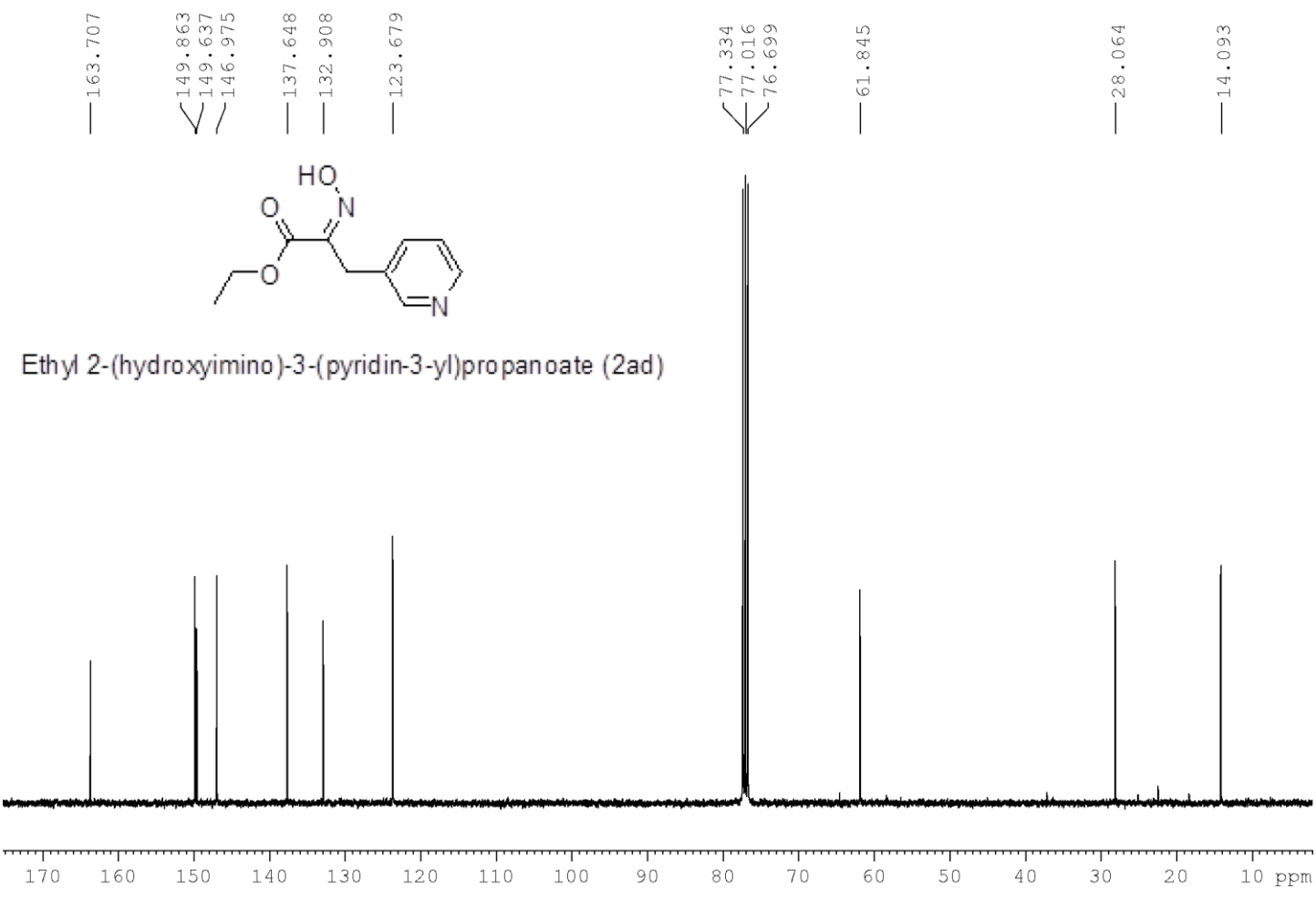


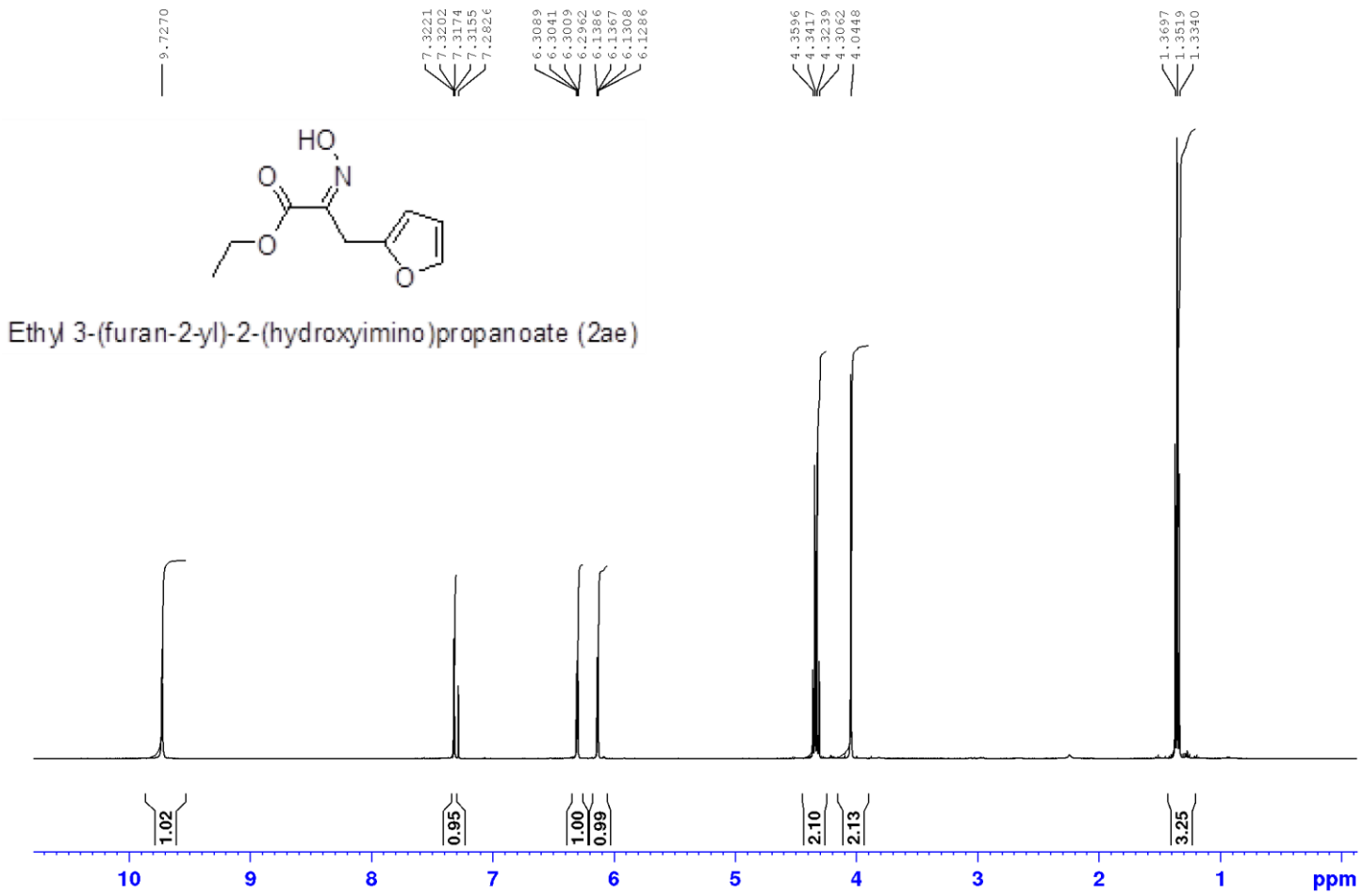
Ethyl 2-(hydroxyimino)-3-(pyridin-2-yl)propanoate (2ac)

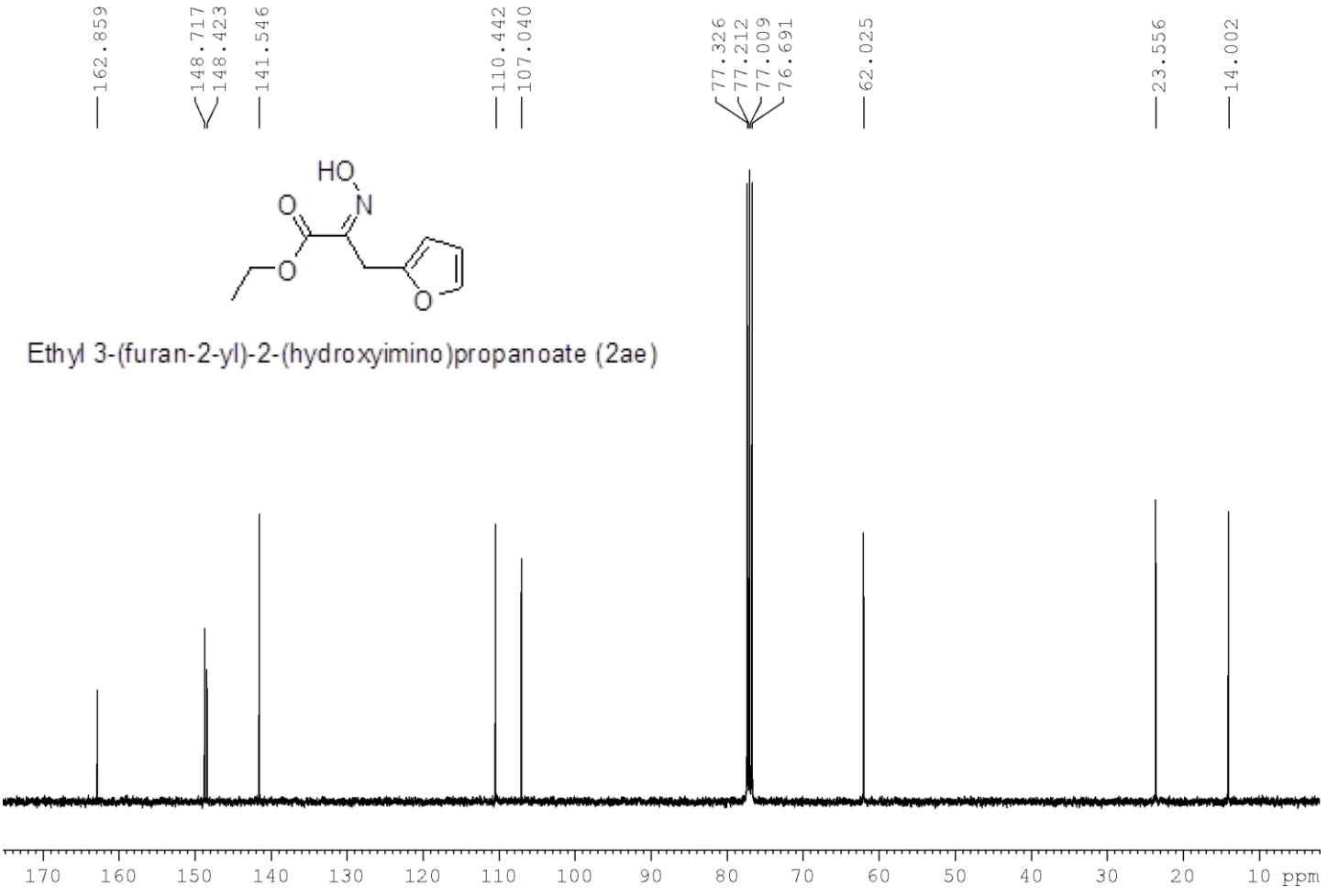


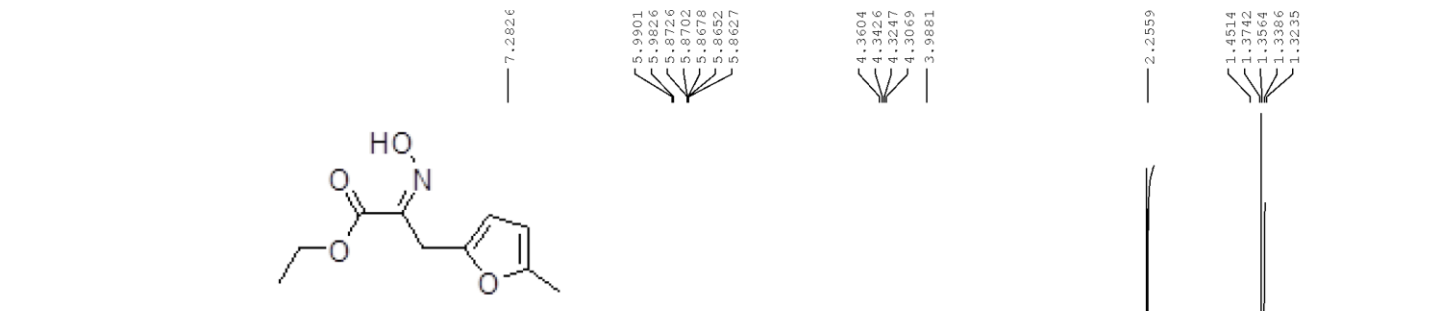
Ethyl 2-(hydroxyimino)-3-(pyridin-2-yl)propanoate (2ac)


8.6572
8.6530
8.4711
8.4671
8.4588
8.4548
7.7616
7.7570
7.7521
7.7420
7.7374
7.7368
7.7325
7.2829
7.2772
7.2757
7.2648
7.2633
7.2576
7.2561
7.2452
7.2437
4.3320
4.3142
4.2963
4.2901
4.2785
4.2723
4.0141
1.3466
1.3288
1.3110
1.2734
HO
N
O
O
N
Ethyl 2-(hydroxyimino)-3-(pyridin-3-yl)propanoate (2ad)
0.98
1.06
1.07
1.04
1.22
2.16
2.11
3.06
13
12
11
10
9
8
7
6
5
4
3
2
ppm

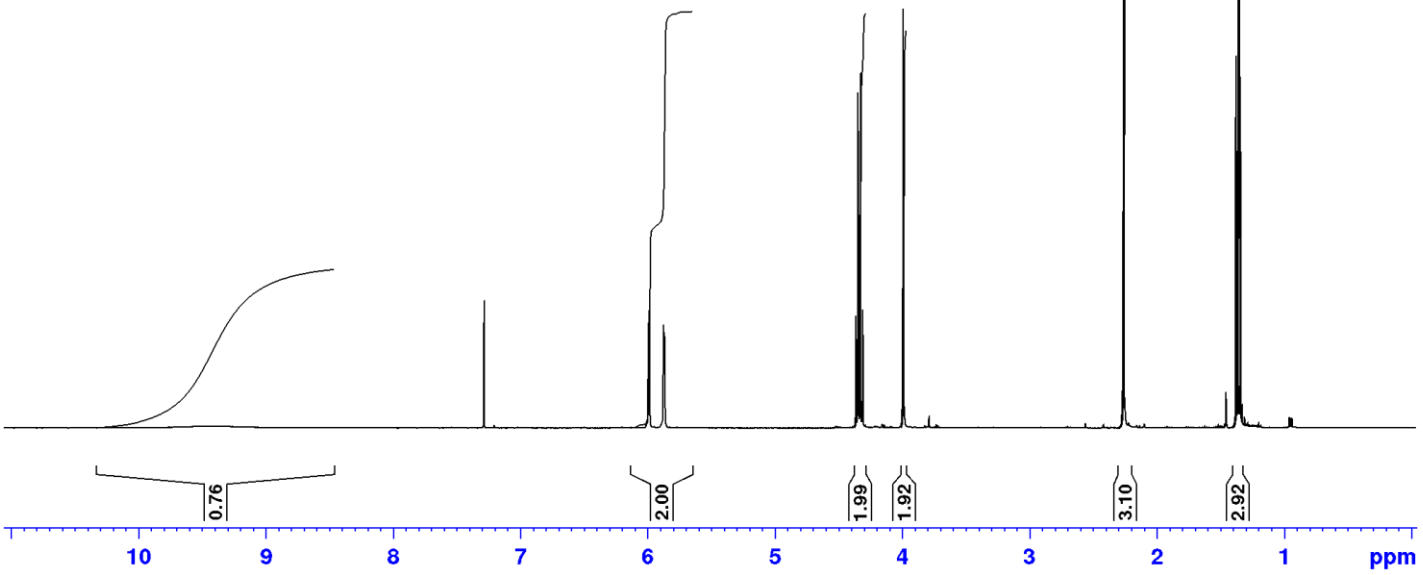

163.707
149.863
149.637
146.975
137.648
132.908
123.679
77.334
77.016
76.699
61.845
28.064
14.093
HO
N
O
O
N
Ethyl 2-(hydroxyimino)-3-(pyridin-3-yl)propanoate (2ad)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

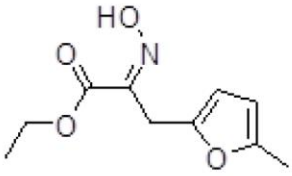

9.7270
7.3221
7.3202
7.3174
7.3155
7.2826
6.3089
6.3041
6.3009
6.2962
6.1386
6.1367
6.1308
6.1286
4.3596
4.3417
4.3239
4.3062
4.0448
1.3697
1.3519
1.3340
HO
N
O
O
O
Ethyl 3-(furan-2-yl)-2-(hydroxyimino)propanoate (2ae)
1.02
0.95
1.00
0.99
2.10
2.13
3.25
10
9
8
7
6
5
4
3
2
1
ppm


162.859
148.717
148.423
141.546
110.442
107.040
77.326
77.212
77.009
76.691
62.025
23.556
14.002
HO
N
O
O
O
Ethyl 3-(furan-2-yl)-2-(hydroxyimino)propanoate (2ae)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

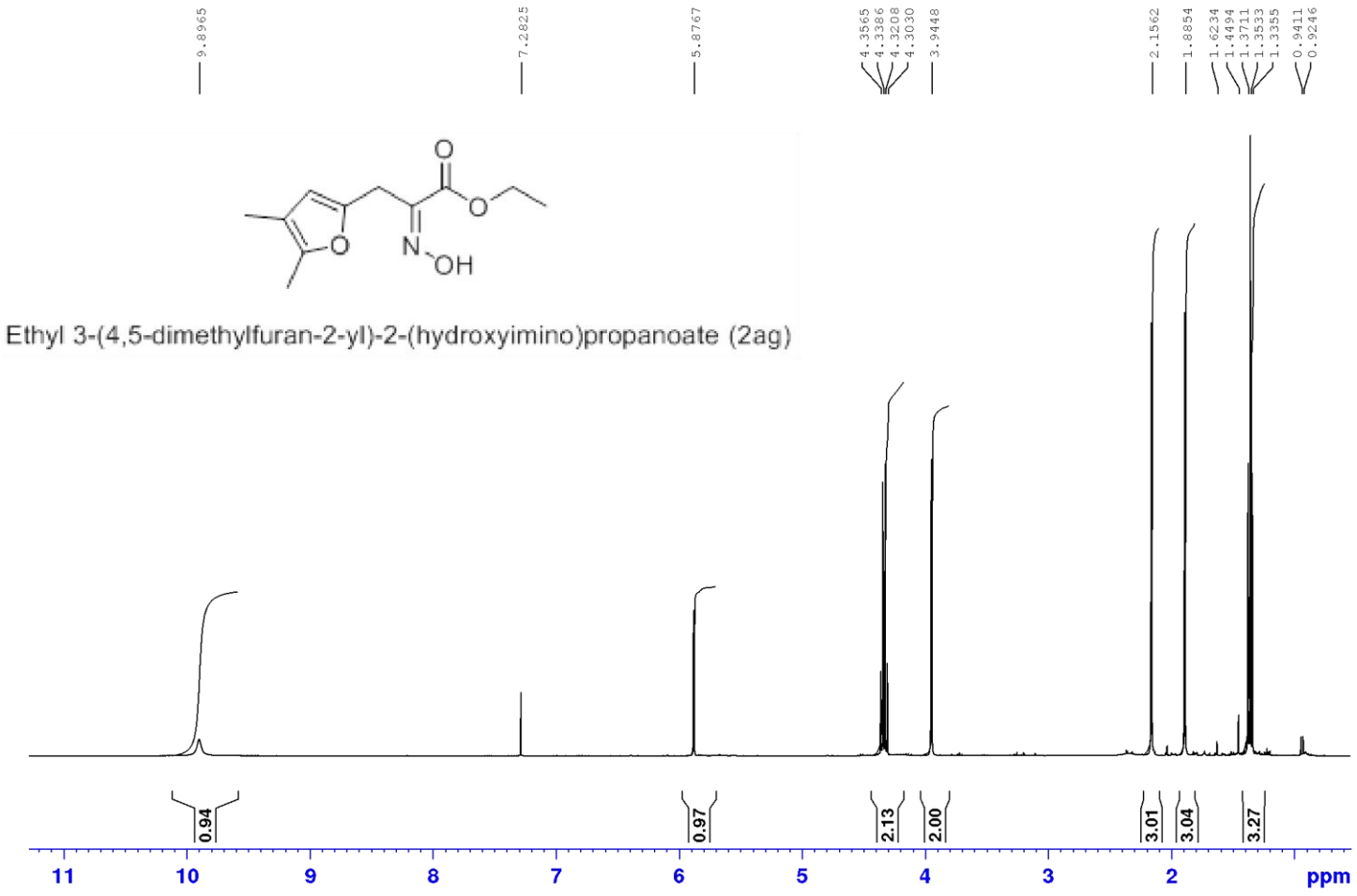


Ethyl 2-(hydroxyimino)-3-(5-methylfuran-2-yl)propanoate (2af)

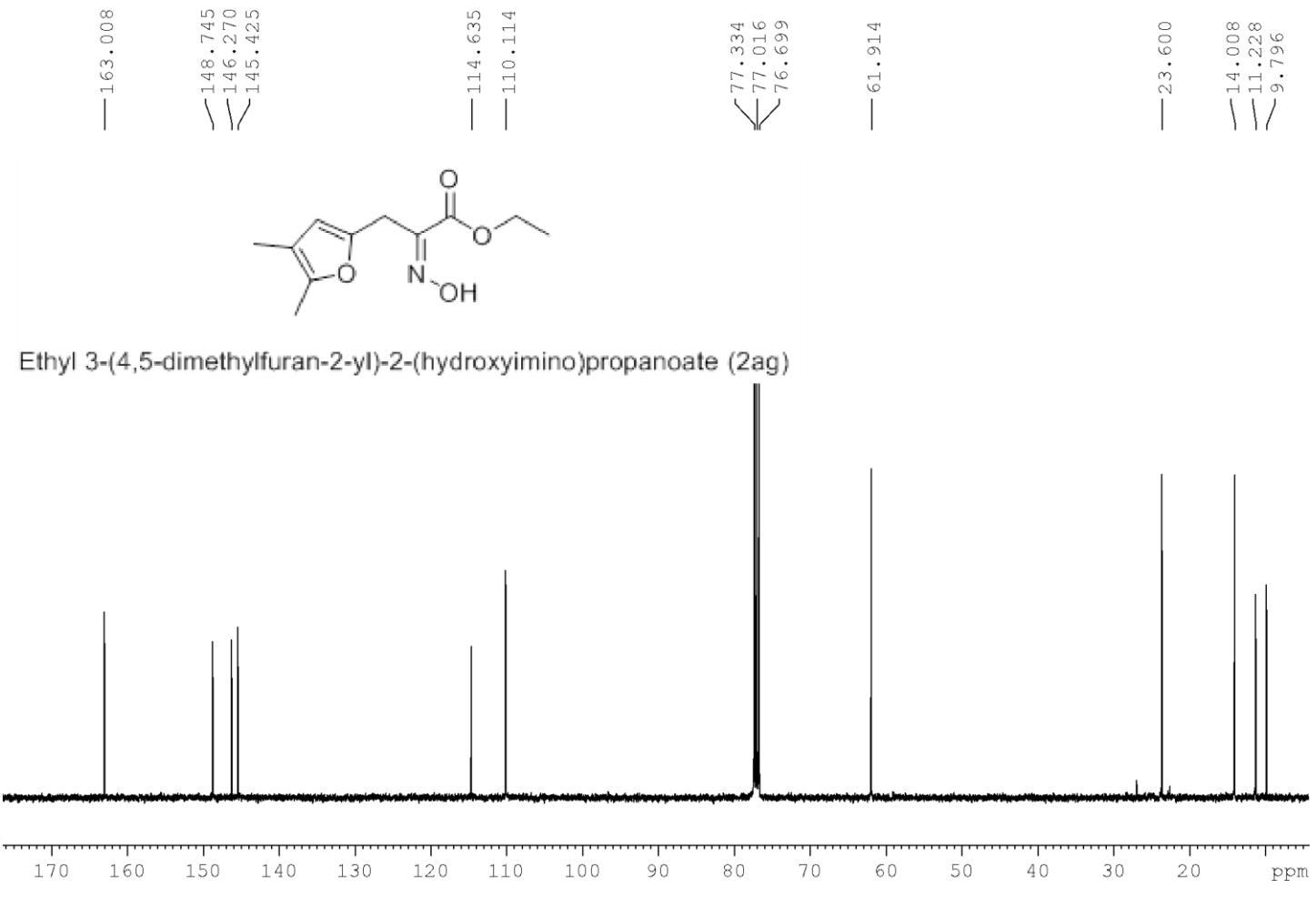




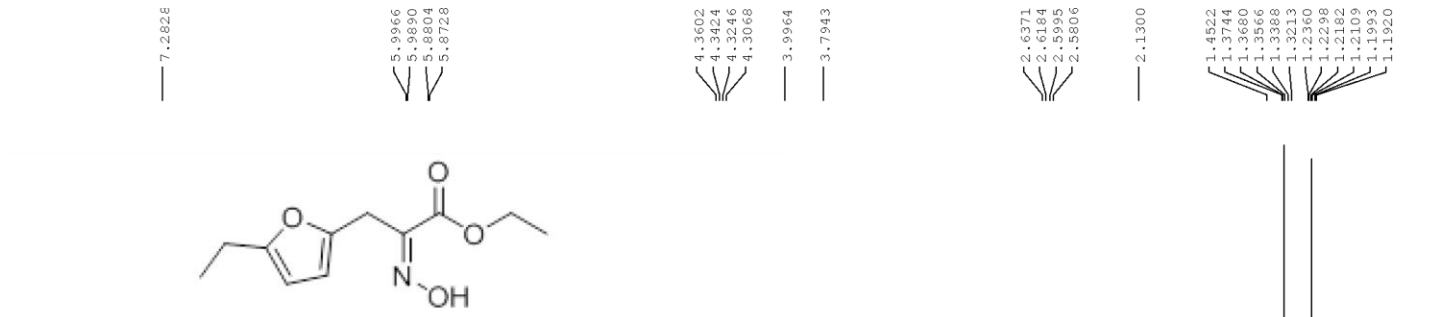
Ethyl 2-(hydroxyimino)-3-(5-methylfuran-2-yl)propanoate (2af)



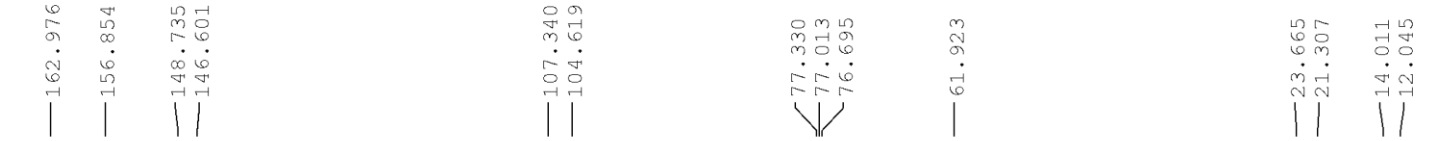
Ethyl 3-(4,5-dimethylfuran-2-yl)-2-(hydroxyimino)propanoate (2ag)

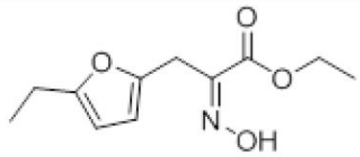


Ethyl 3-(4,5-dimethylfuran-2-yl)-2-(hydroxyimino)propanoate (2ag)

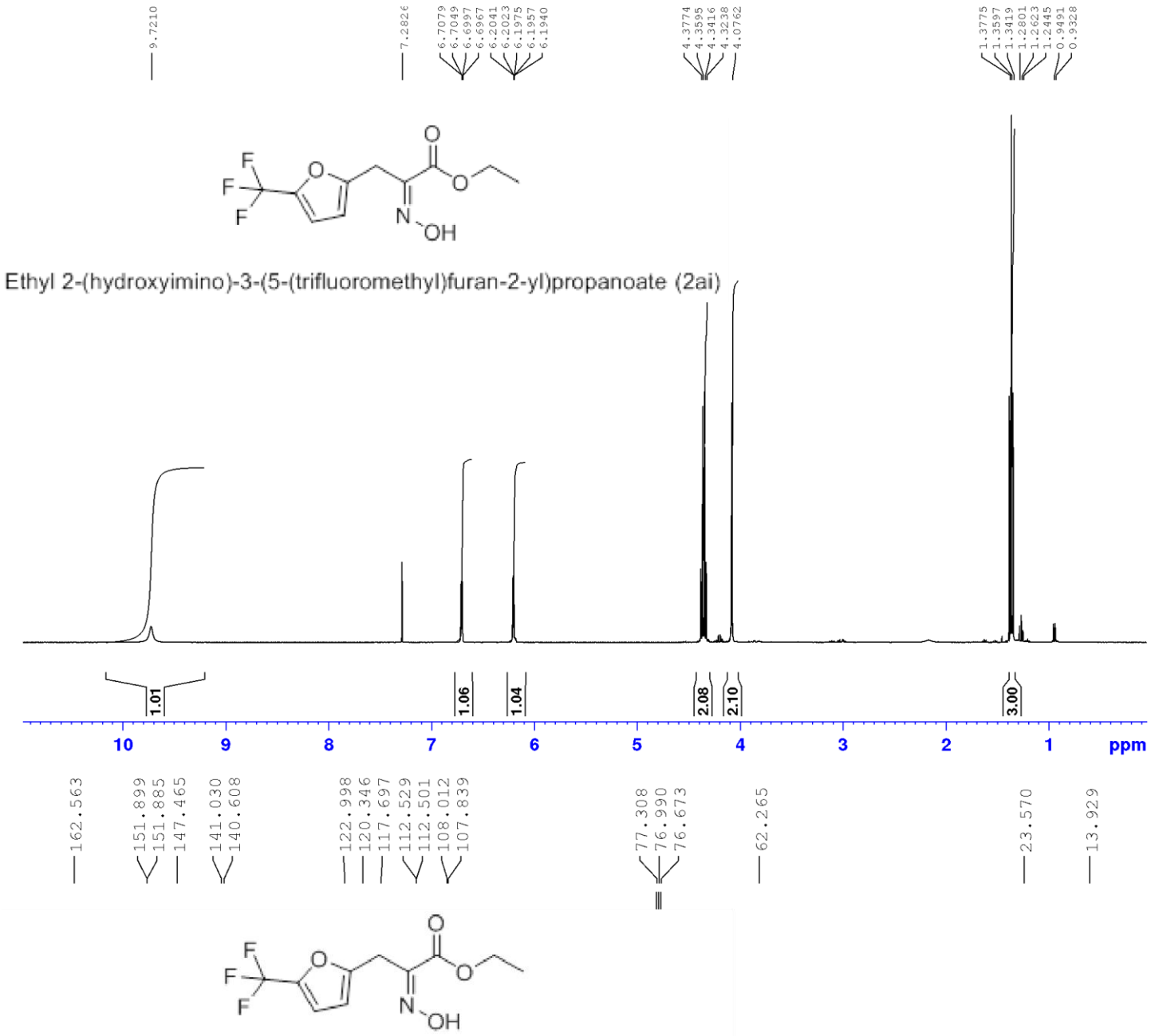


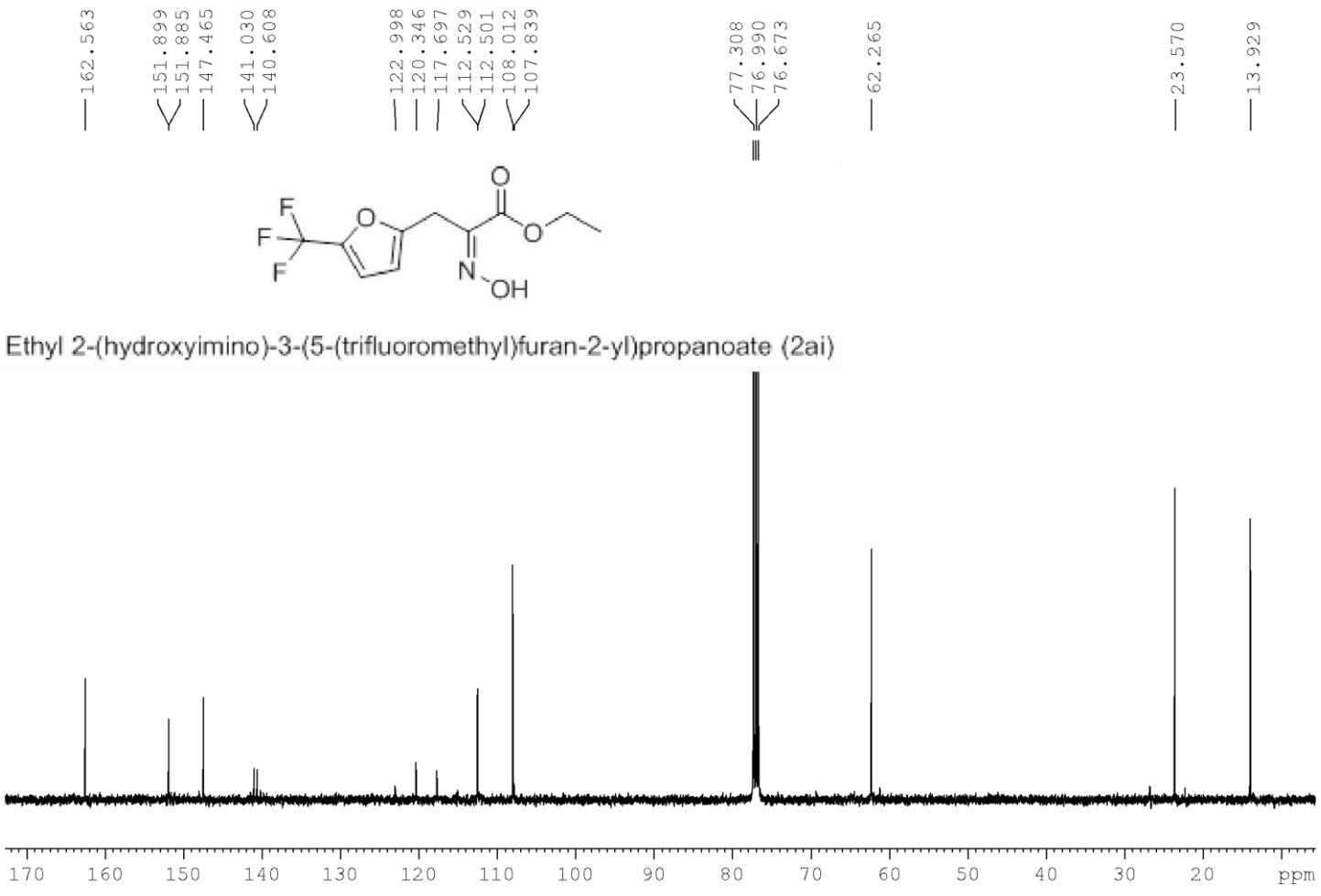
Ethyl 3-(5-ethylfuran-2-yl)-2-(hydroxyimino)propanoate (2ah)

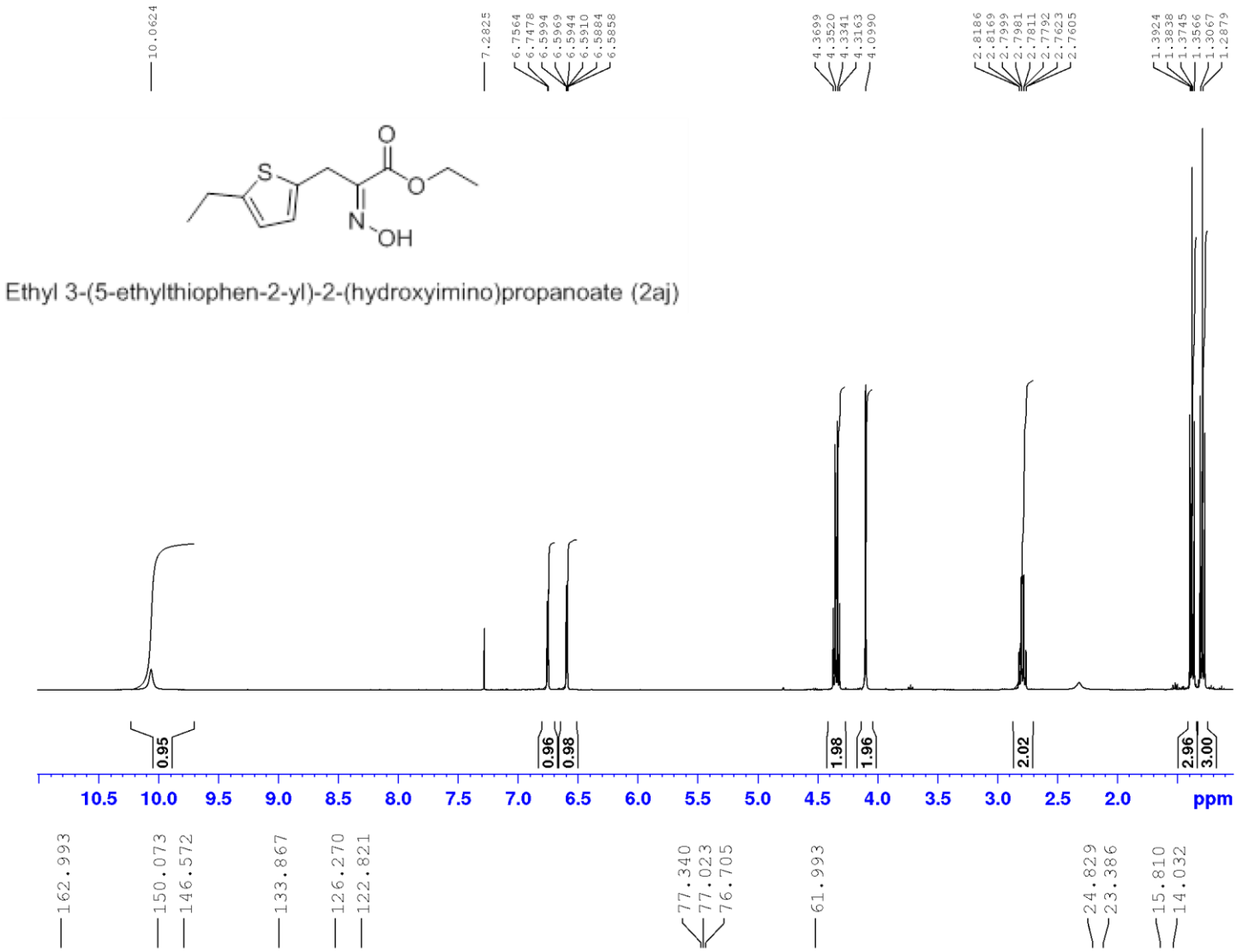




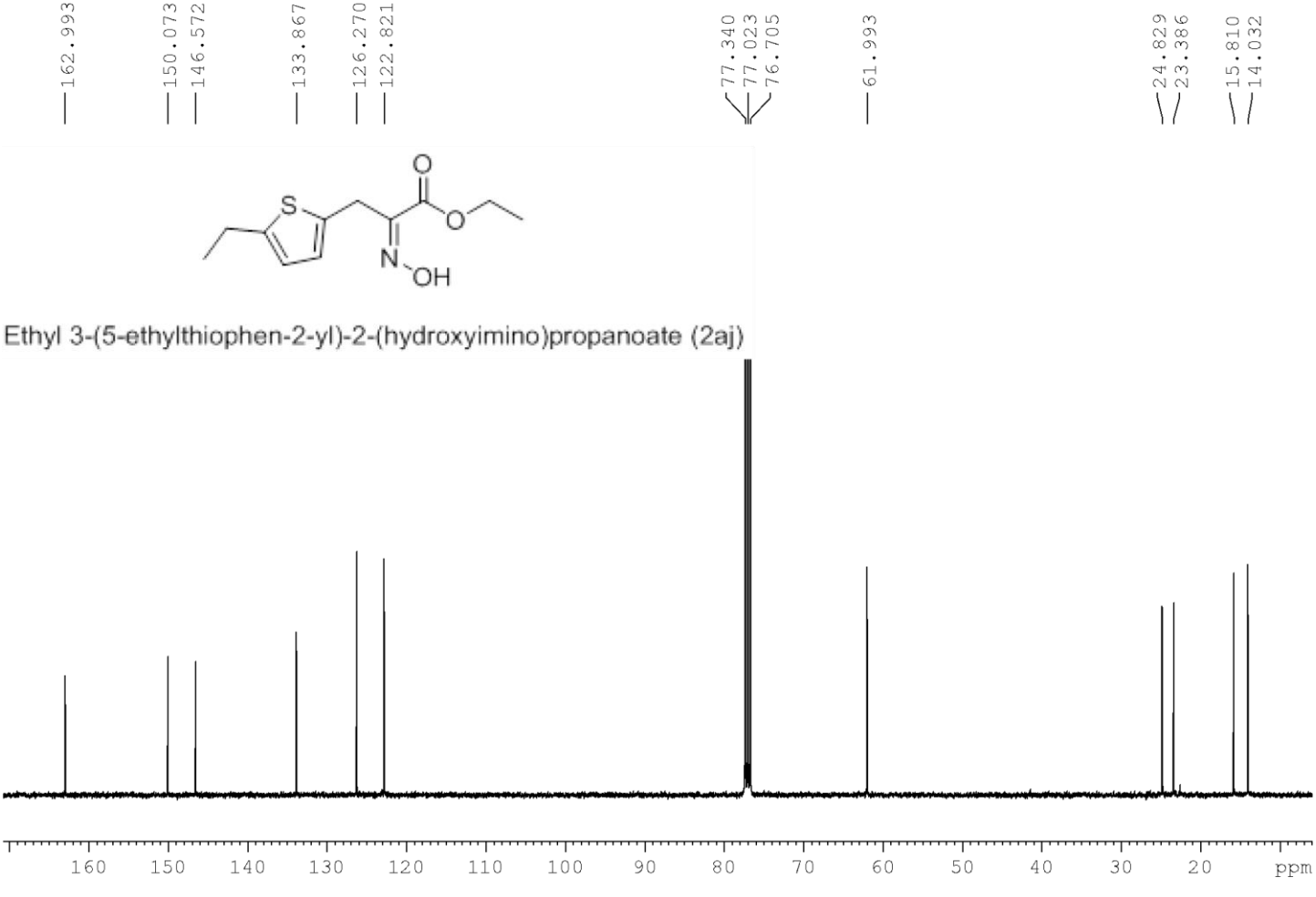
Ethyl 3-(5-ethylfuran-2-yl)-2-(hydroxyimino)propanoate (2ah)


9.7210
7.2826
6.7079
6.7049
6.6997
6.6967
6.2041
6.2023
6.1975
6.1957
6.1940
4.3774
4.3595
4.3416
4.3238
4.0762
1.3775
1.3597
1.3419
1.2801
1.2623
1.2445
0.9491
0.9328
F
F
F
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(5-(trifluoromethyl)furan-2-yl)propanoate (2ai)
1.01
1.06
1.04
2.08
2.10
3.00
10
9
8
7
6
5
4
3
2
1
ppm

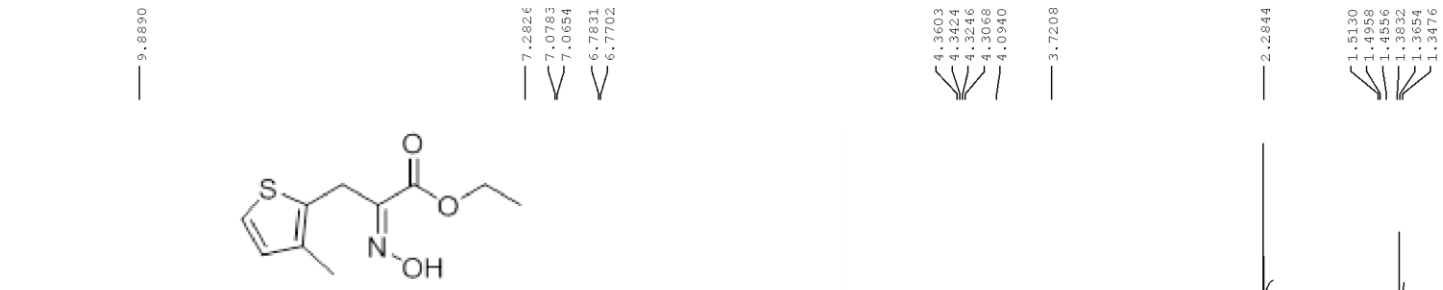

162.563
151.899
151.885
147.465
141.030
140.608
122.998
120.346
117.697
112.529
112.501
108.012
107.839
77.308
76.990
76.673
62.265
23.570
13.929
F
F
F
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(5-(trifluoromethyl)furan-2-yl)propanoate (2ai)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



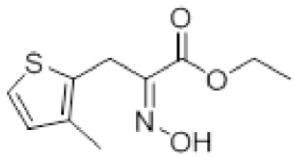
Ethyl 3-(5-ethylthiophen-2-yl)-2-(hydroxyimino)propanoate (2aj)



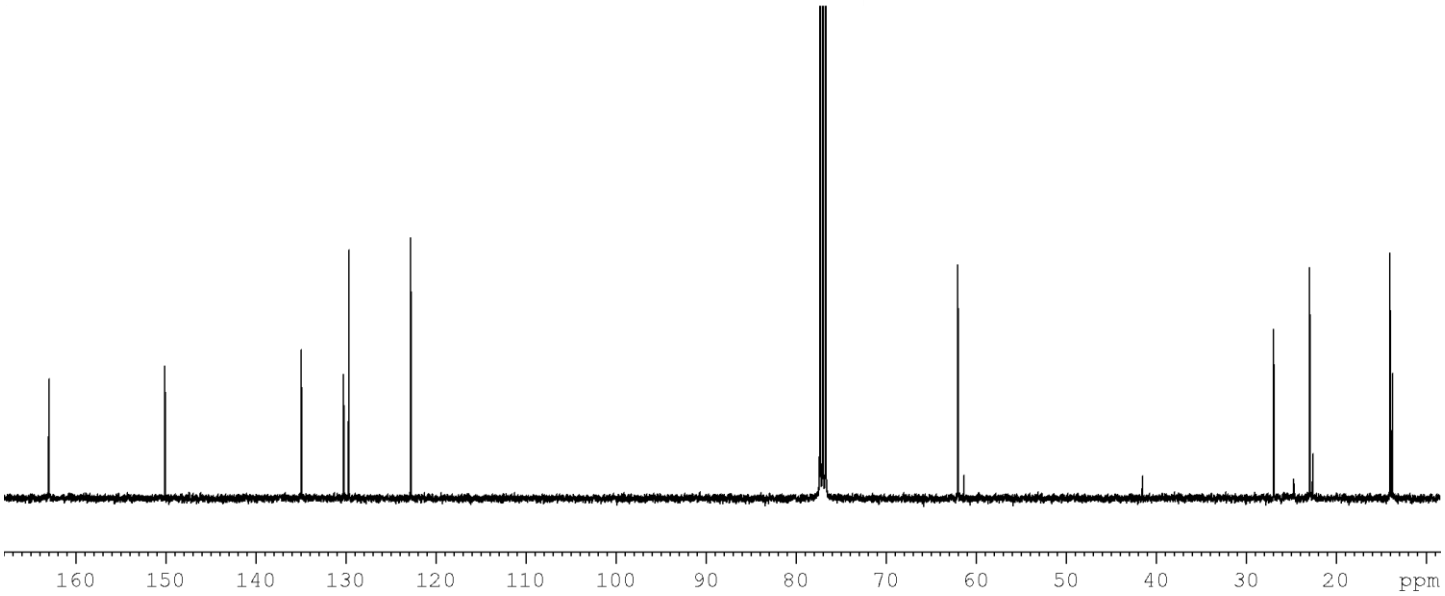
Ethyl 3-(5-ethylthiophen-2-yl)-2-(hydroxyimino)propanoate (2aj)

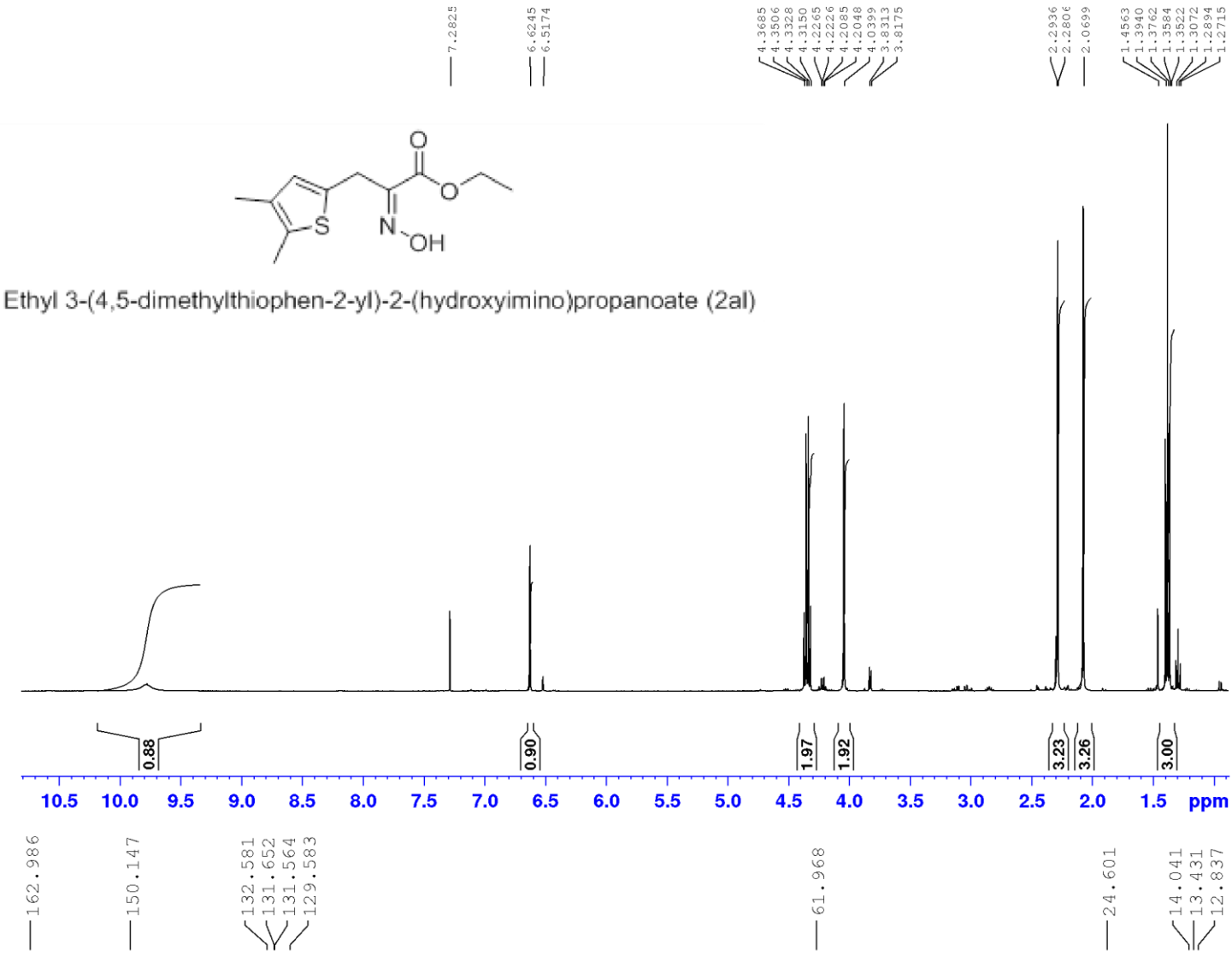


Ethyl 2-(hydroxyimino)-3-(3-methylthiophen-2-yl)propanoate (2ak)

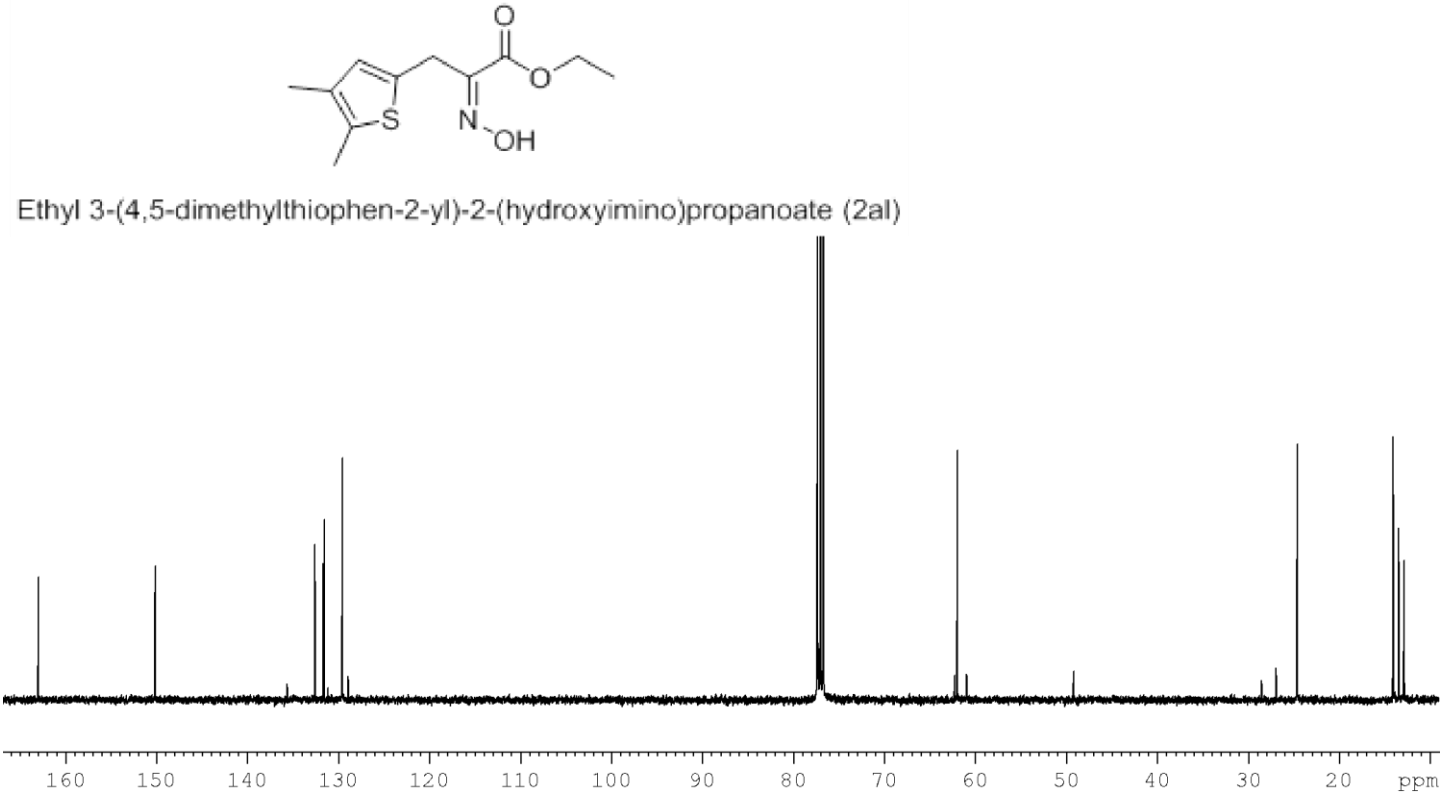


Ethyl 2-(hydroxyimino)-3-(3-methylthiophen-2-yl)propanoate (2ak)

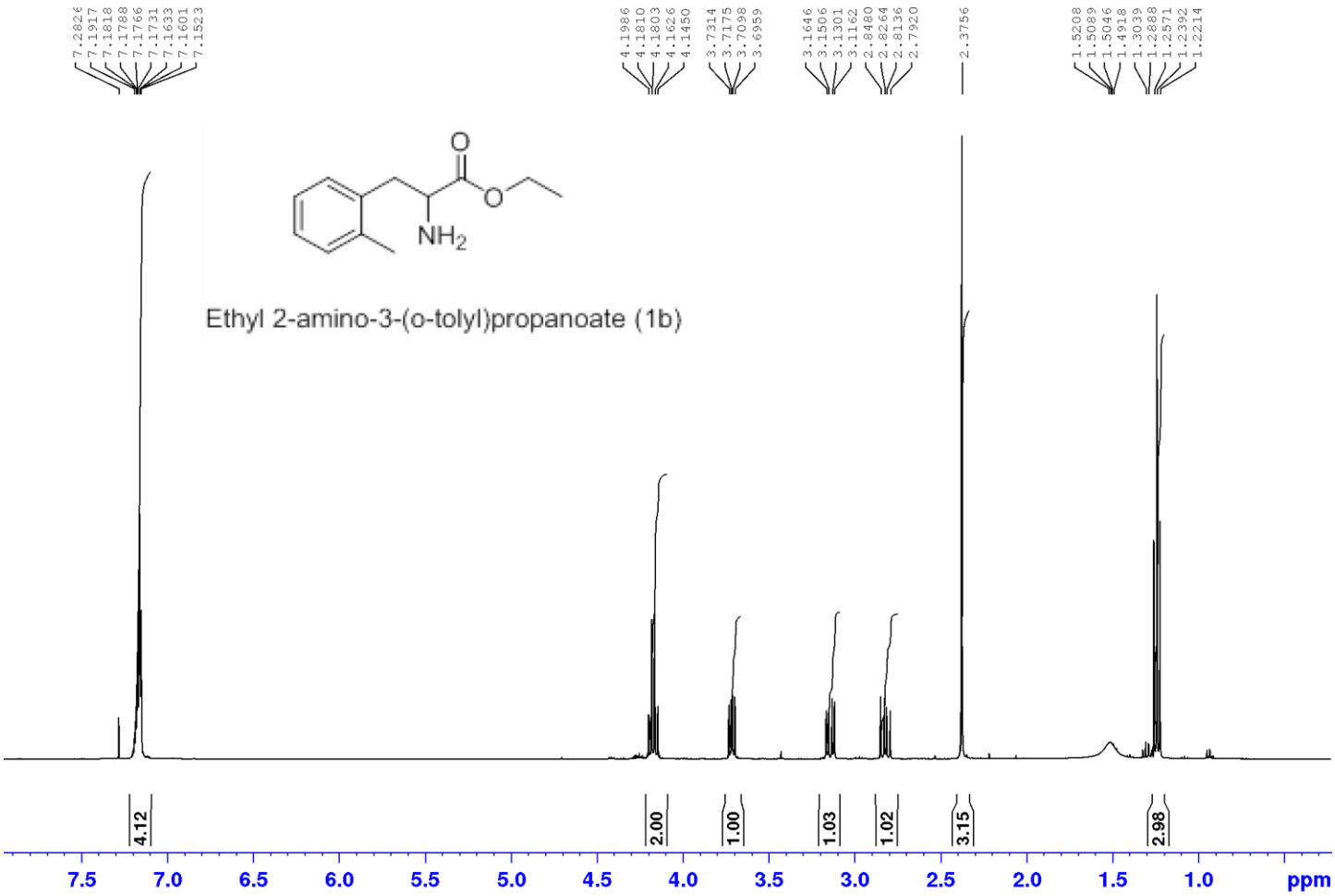


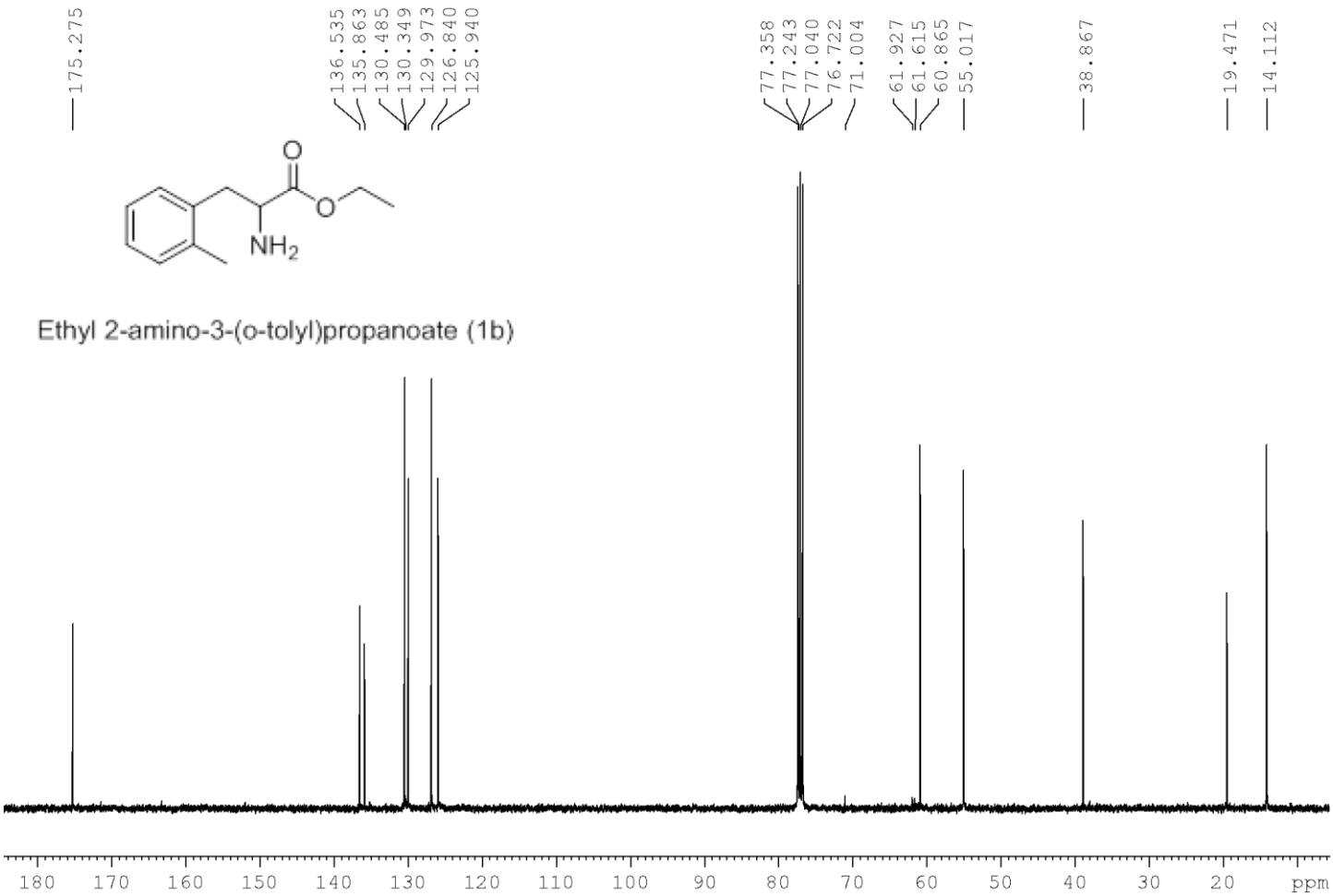


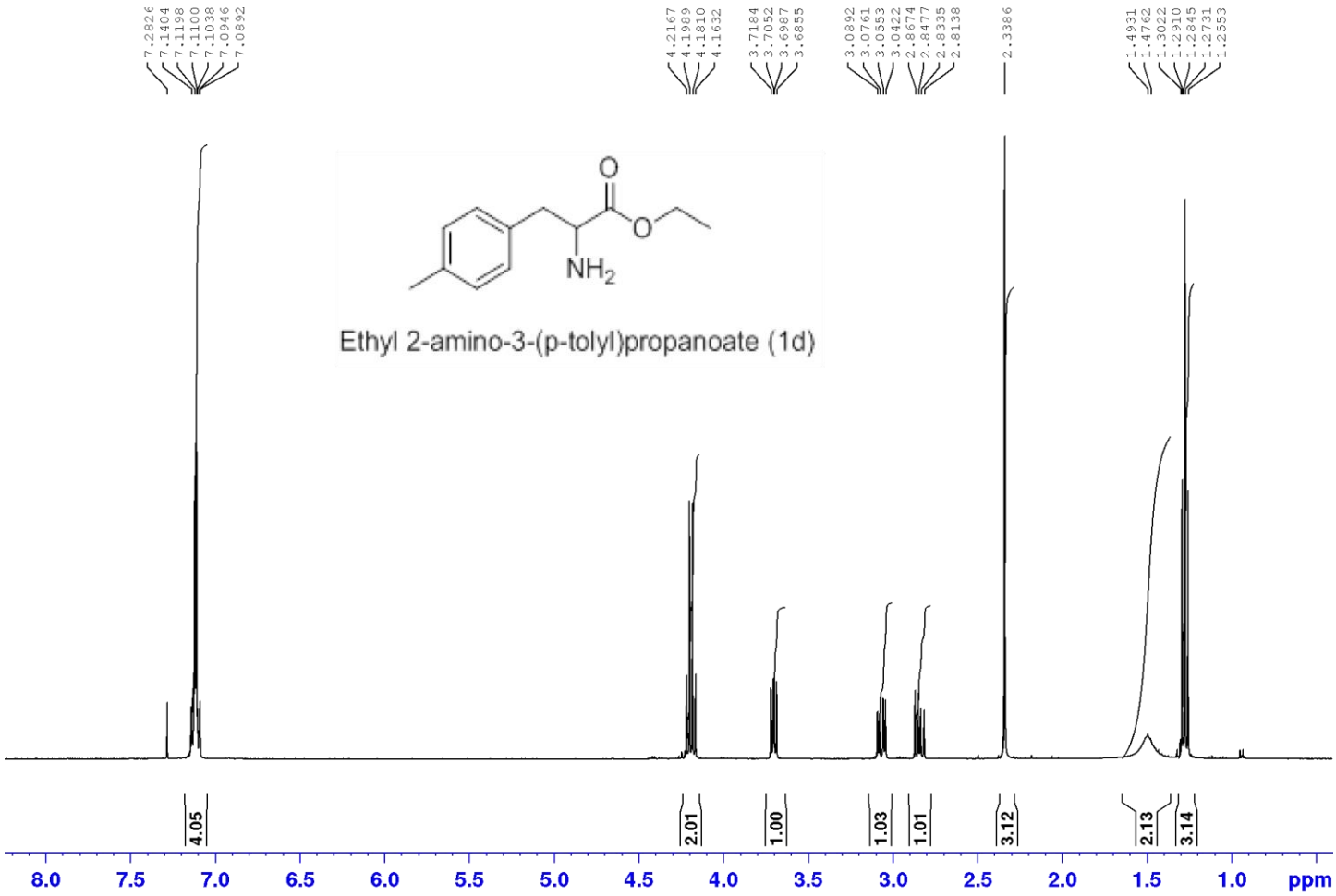
Ethyl 3-(4,5-dimethylthiophen-2-yl)-2-(hydroxyimino)propanoate (2al)

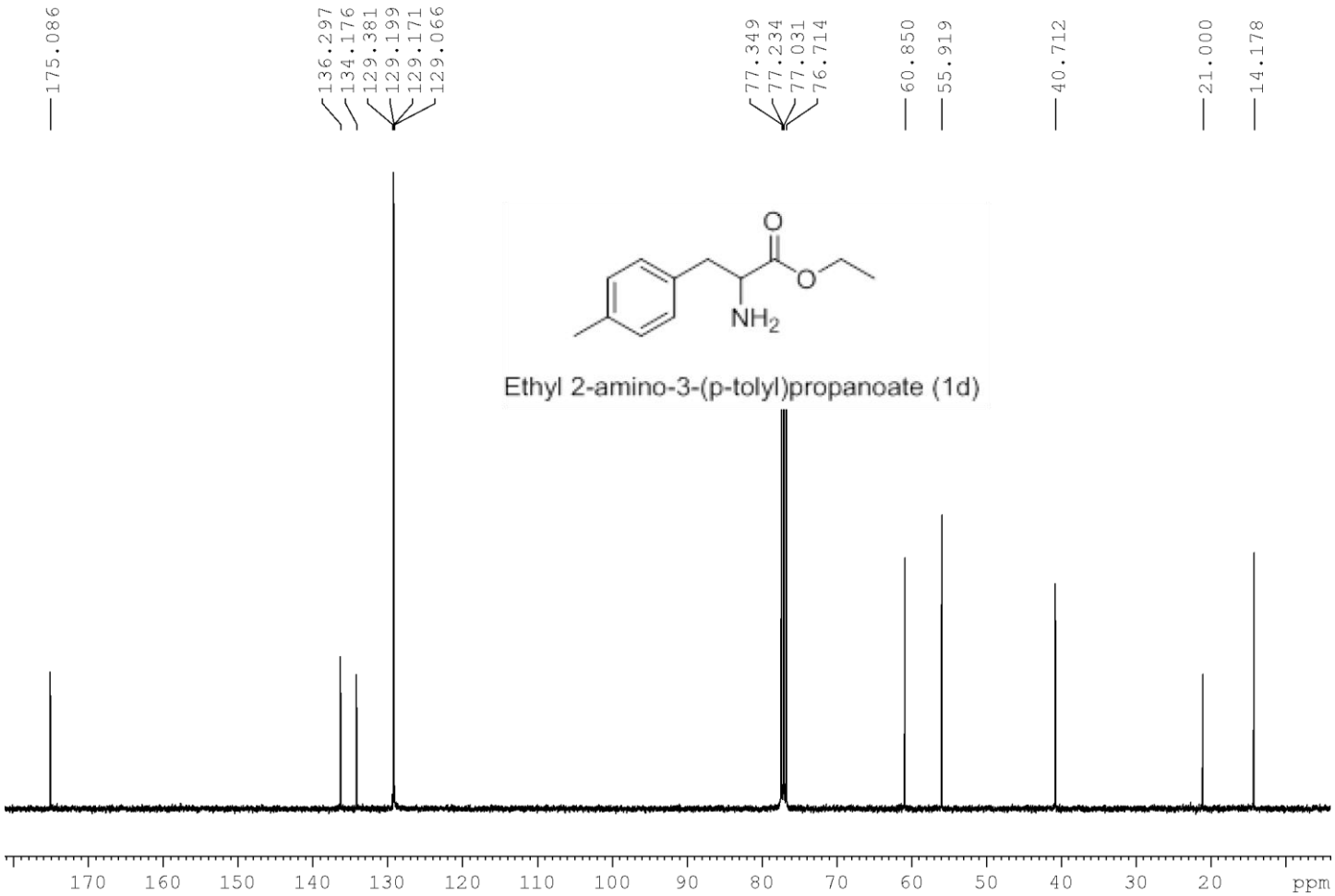


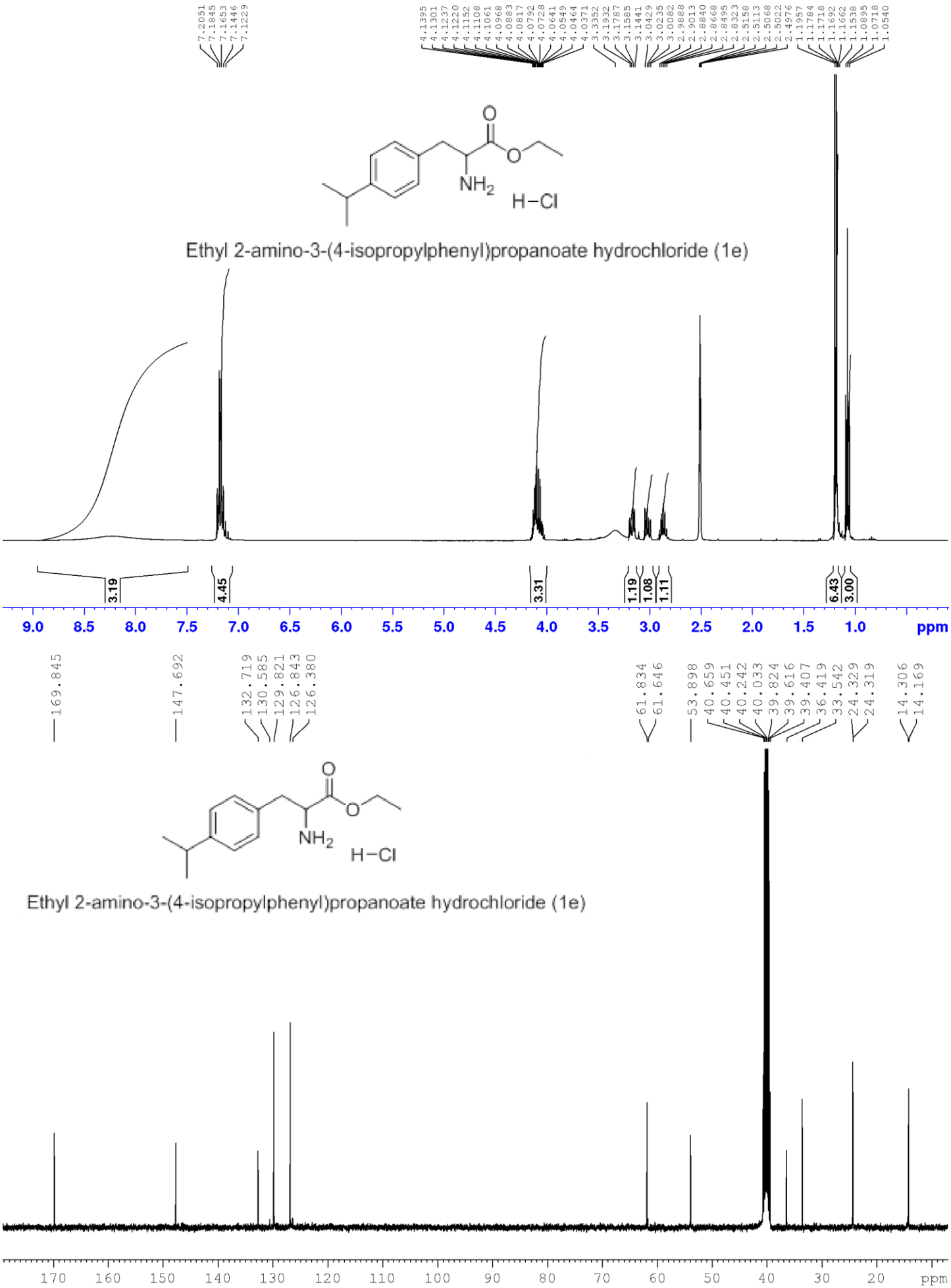
Ethyl 3-(4,5-dimethylthiophen-2-yl)-2-(hydroxyimino)propanoate (2al)

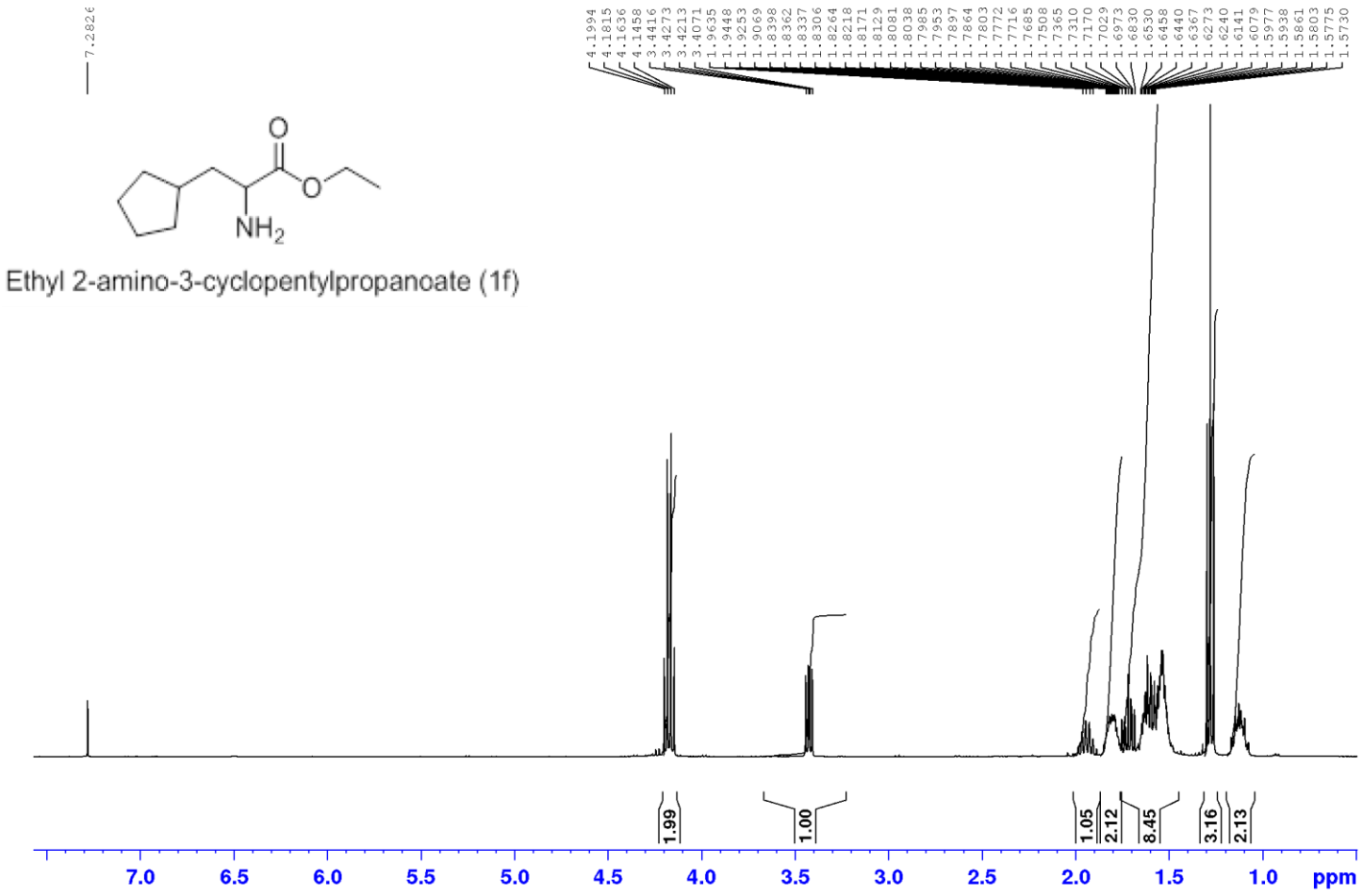

7.2826
7.1917
7.1818
7.1788
7.1766
7.1731
7.1633
7.1601
7.1523
4.1986
4.1810
4.1803
4.1626
4.1450
3.7314
3.7175
3.7098
3.6959
3.1646
3.1506
3.1301
3.1162
2.8480
2.8264
2.8136
2.7920
2.3756
1.5208
1.5089
1.5046
1.4918
1.3039
1.2888
1.2571
1.2392
1.2214
O
O
NH2
Ethyl 2-amino-3-(o-tolyl)propanoate (1b)
4.12
2.00
1.00
1.03
1.02
3.15
2.98
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
ppm

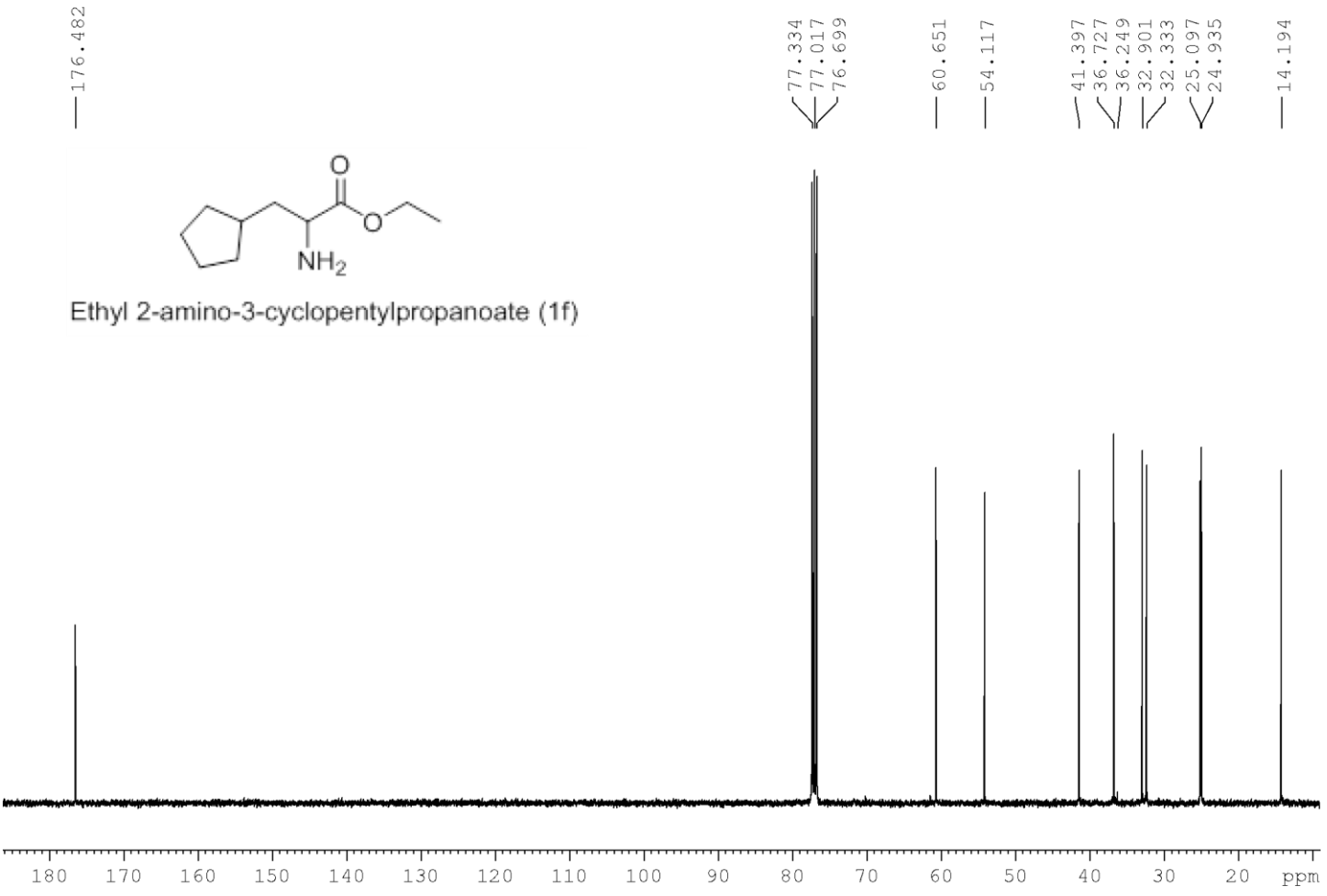

175.275
136.535
135.863
130.485
130.349
129.973
126.840
125.940
77.358
77.243
77.040
76.722
71.004
61.927
61.615
60.865
55.017
38.867
19.471
14.112
O
O
NH2
Ethyl 2-amino-3-(o-tolyl)propanoate (1b)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

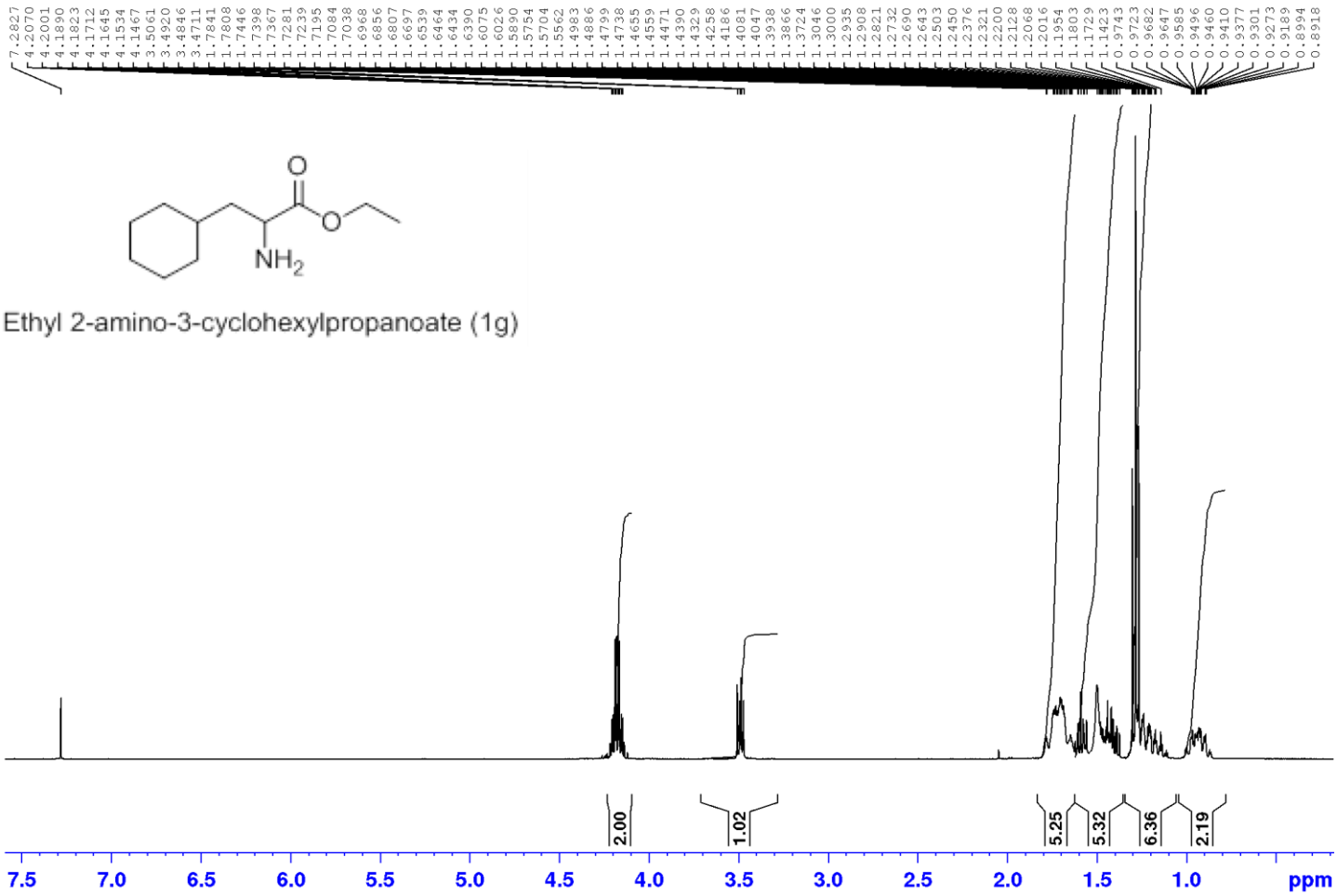

7.2826
7.1404
7.1198
7.1100
7.1038
7.0946
7.0892
4.2167
4.1989
4.1810
4.1632
3.7184
3.7052
3.6987
3.6855
3.0892
3.0761
3.0553
3.0422
2.8674
2.8477
2.8335
2.8138
2.3386
1.4931
1.4762
1.3022
1.2910
1.2845
1.2731
1.2553
O
O
NH2
Ethyl 2-amino-3-(p-tolyl)propanoate (1d)
4.05
2.01
1.00
1.03
1.01
3.12
2.13
3.14
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
ppm

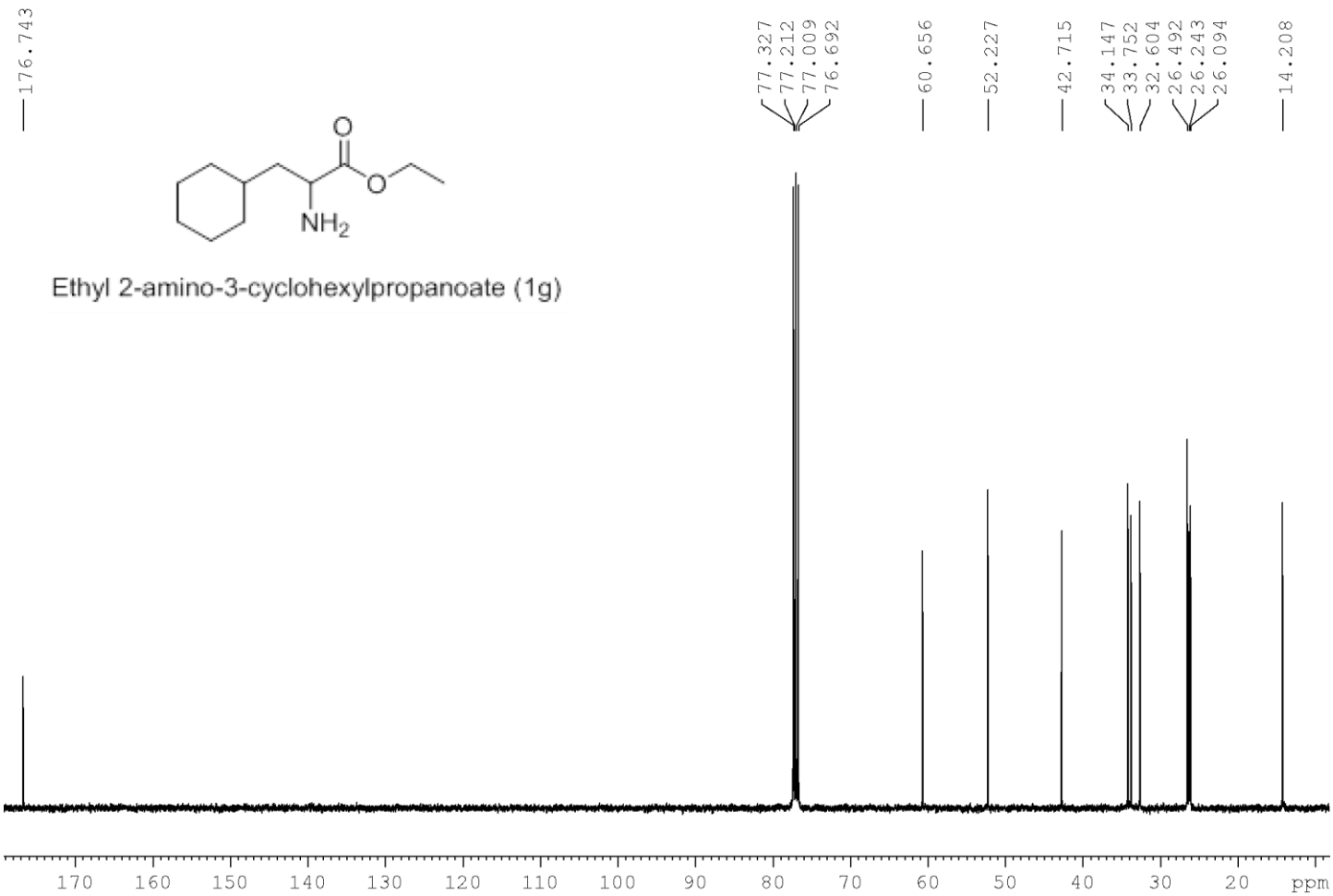

175.086
136.297
134.176
129.381
129.199
129.171
129.066
77.349
77.234
77.031
76.714
60.850
55.919
40.712
21.000
14.178
O
O
NH2
Ethyl 2-amino-3-(p-tolyl)propanoate (1d)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

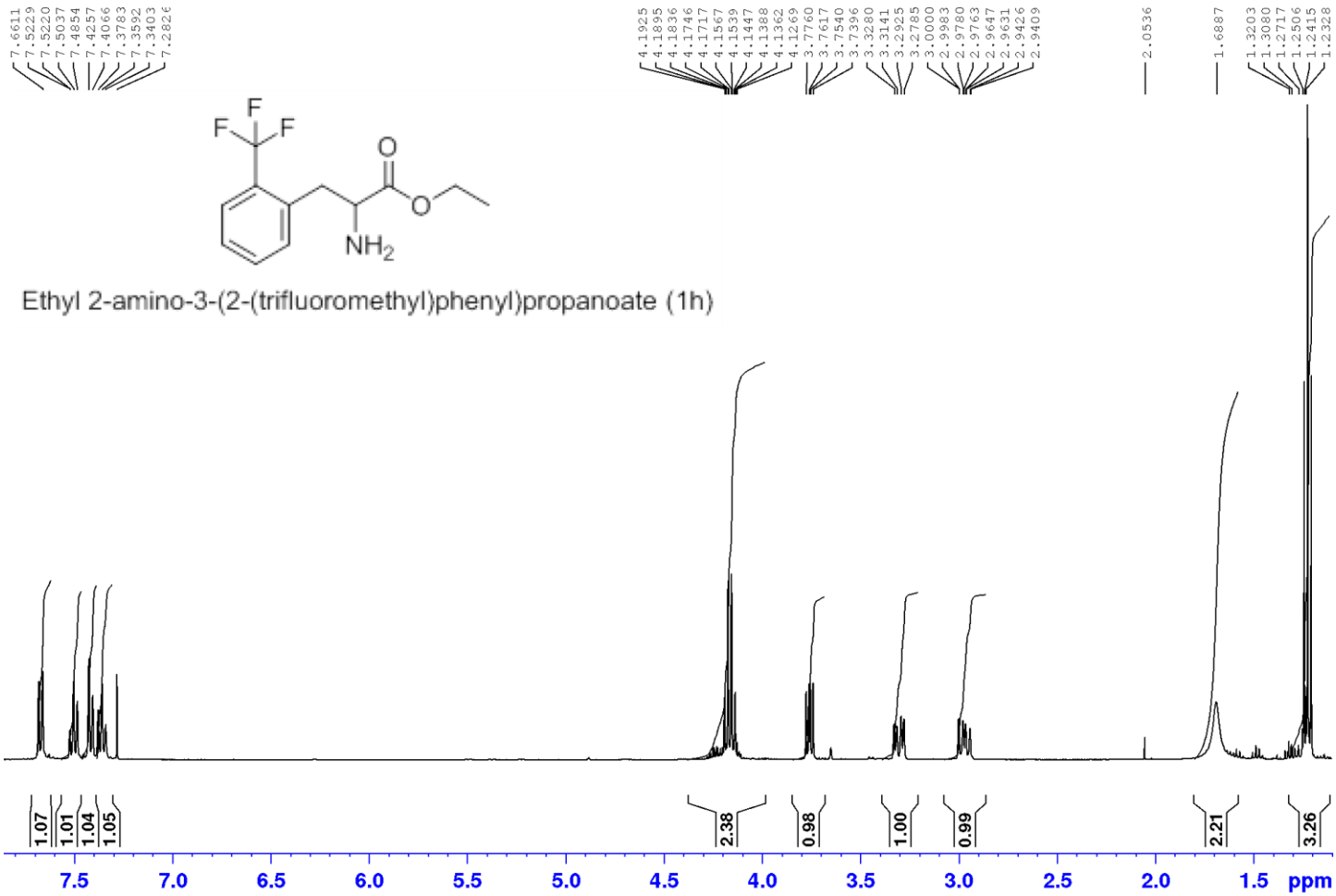

7.2051
7.1845
7.1653
7.1446
7.1229
4.1395
4.1301
4.1237
4.1220
4.1152
4.1108
4.1061
4.0968
4.0883
4.0817
4.0792
4.0728
4.0641
4.0549
4.0464
4.0371
3.3352
3.1932
3.1787
3.1585
3.1441
3.0429
3.0235
3.0082
2.9888
2.9013
2.8840
2.8668
2.8495
2.8323
2.5158
2.5113
2.5068
2.5022
2.4976
1.1957
1.1784
1.1718
1.1692
1.1662
1.1538
1.0895
1.0718
1.0540
O
O
NH2
H−Cl
Ethyl 2-amino-3-(4-isopropylphenyl)propanoate hydrochloride (1e)
3.19
4.45
3.31
1.19
1.08
1.11
6.43
3.00
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
ppm
169.845
147.692
132.719
130.585
129.821
126.843
126.380
61.834
61.646
53.898
40.659
40.451
40.242
40.033
39.824
39.616
39.407
36.419
33.542
24.329
24.319
14.306
14.169
O
O
NH2
H−Cl
Ethyl 2-amino-3-(4-isopropylphenyl)propanoate hydrochloride (1e)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

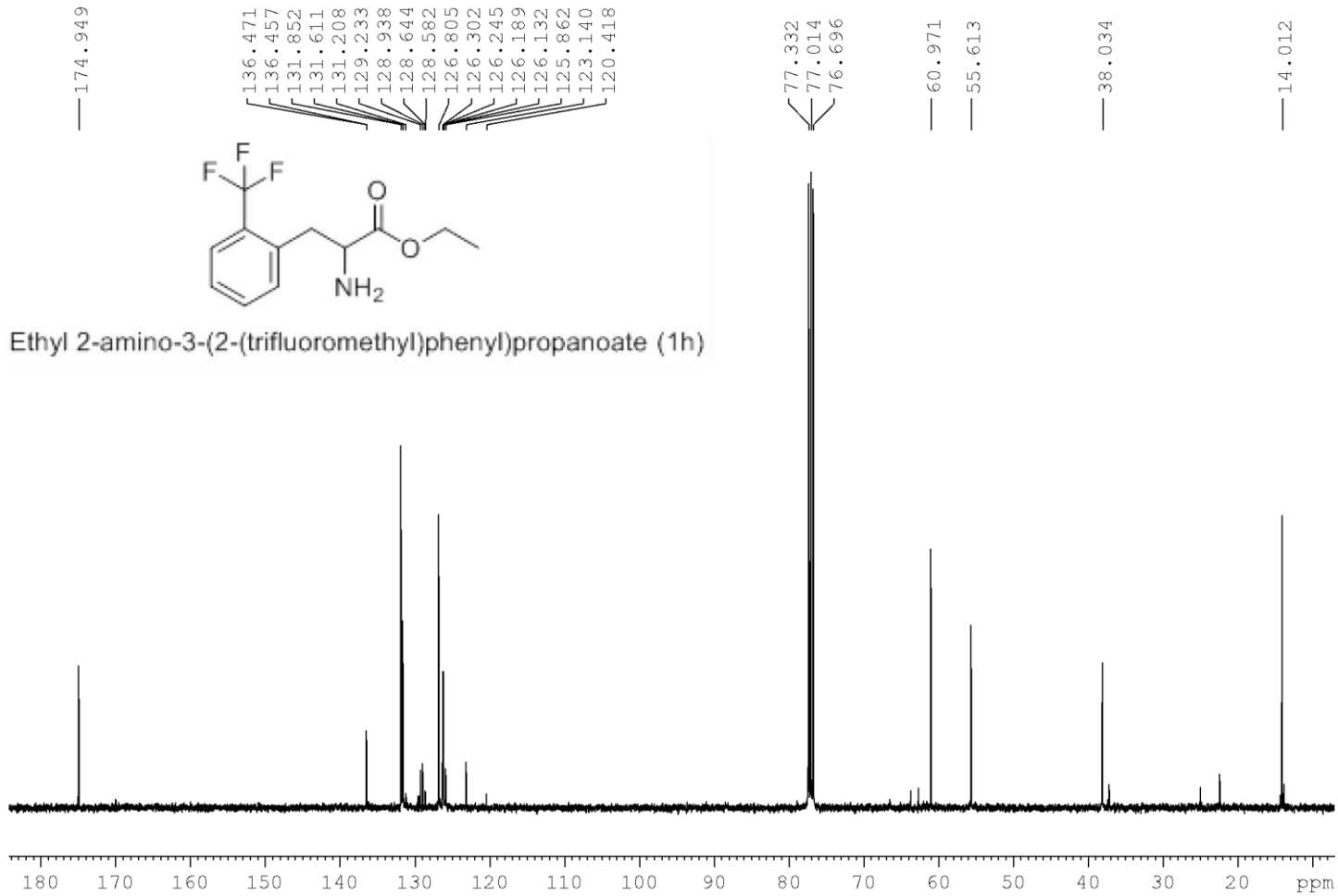

7.2826
4.1994
4.1815
4.1636
4.1458
3.4416
3.4273
3.4213
3.4071
1.9635
1.9448
1.9253
1.9069
1.8398
1.8362
1.8337
1.8306
1.8264
1.8218
1.8171
1.8129
1.8081
1.8038
1.7985
1.7953
1.7897
1.7864
1.7803
1.7772
1.7716
1.7685
1.7508
1.7365
1.7310
1.7170
1.7029
1.6973
1.6830
1.6530
1.6458
1.6440
1.6367
1.6273
1.6240
1.6141
1.6079
1.5977
1.5938
1.5861
1.5803
1.5775
1.5730
O
O
NH2
Ethyl 2-amino-3-cyclopentylpropanoate (1f)
1.99
1.00
1.05
2.12
8.45
3.16
2.13
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
ppm

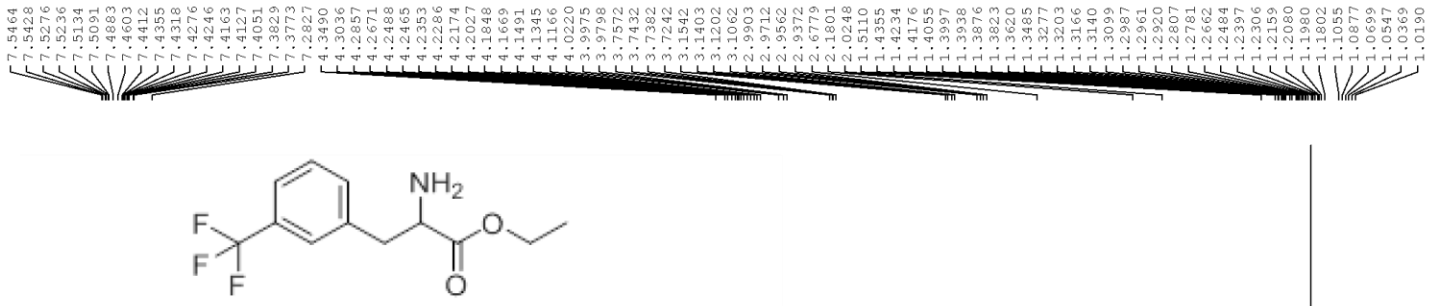

176.482
77.334
77.017
76.699
60.651
54.117
41.397
36.727
36.249
32.901
32.333
25.097
24.935
14.194
O
O
NH2
Ethyl 2-amino-3-cyclopentylpropanoate (1f)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.2827
4.2070
4.2001
4.1890
4.1823
4.1712
4.1645
4.1534
4.1467
3.5061
3.4920
3.4846
3.4711
1.7841
1.7808
1.7446
1.7398
1.7367
1.7281
1.7239
1.7195
1.7084
1.7038
1.6968
1.6856
1.6807
1.6697
1.6539
1.6464
1.6434
1.6390
1.6075
1.6026
1.5890
1.5754
1.5704
1.5562
1.4983
1.4886
1.4799
1.4738
1.4655
1.4559
1.4471
1.4390
1.4329
1.4258
1.4186
1.4081
1.4047
1.3938
1.3866
1.3724
1.3046
1.3000
1.2935
1.2908
1.2821
1.2732
1.2690
1.2643
1.2503
1.2450
1.2376
1.2321
1.2200
1.2128
1.2068
1.2016
1.1954
1.1803
1.1729
1.1423
0.9743
0.9723
0.9682
0.9647
0.9585
0.9496
0.9460
0.9410
0.9377
0.9301
0.9273
0.9189
0.8994
0.8918
O
O
NH2
Ethyl 2-amino-3-cyclohexylpropanoate (1g)
2.00
1.02
5.25
5.32
6.36
2.19
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
ppm

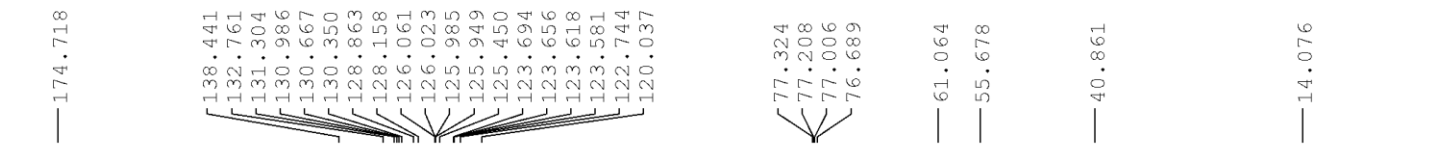

176.743
77.327
77.212
77.009
76.692
60.656
52.227
42.715
34.147
33.752
32.604
26.492
26.243
26.094
14.208
O
O
NH2
Ethyl 2-amino-3-cyclohexylpropanoate (1g)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

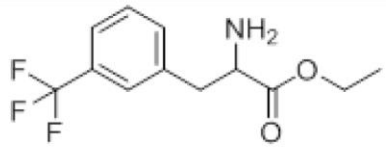

7.6611
7.5229
7.5220
7.5037
7.4854
7.4257
7.4066
7.3783
7.3592
7.3403
4.1925
4.1895
4.1836
4.1746
4.1717
4.1567
4.1539
4.1447
4.1388
4.1362
4.1269
3.7760
3.7617
3.7540
3.7396
3.3280
3.3141
3.2925
3.2785
3.0000
2.9983
2.9780
2.9763
2.9647
2.9631
2.9426
2.9409
2.0536
1.6887
1.3203
1.3080
1.2717
1.2506
1.2415
1.2328
F
F
F
O
O
NH2
Ethyl 2-amino-3-(2-(trifluoromethyl)phenyl)propanoate (1h)
1.07
1.01
1.04
1.05
2.38
0.98
1.00
0.99
2.21
3.26
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
ppm


174.949
136.471
136.457
131.852
131.611
131.208
129.233
128.938
128.644
128.582
126.805
126.302
126.245
126.189
126.132
125.862
123.140
120.418
77.332
77.014
76.696
60.971
55.613
38.034
14.012
F
F
F
O
O
NH2
Ethyl 2-amino-3-(2-(trifluoromethyl)phenyl)propanoate (1h)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

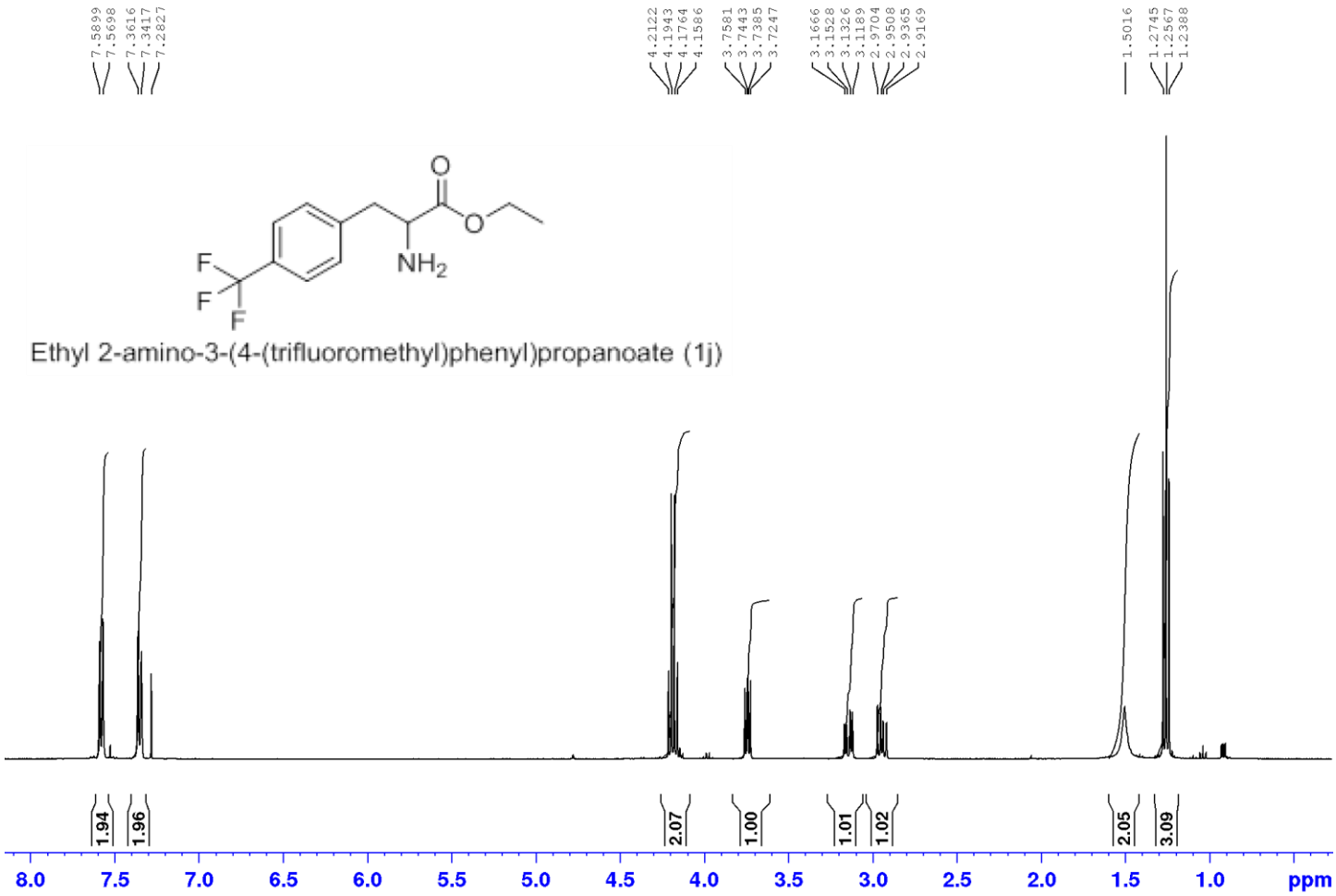


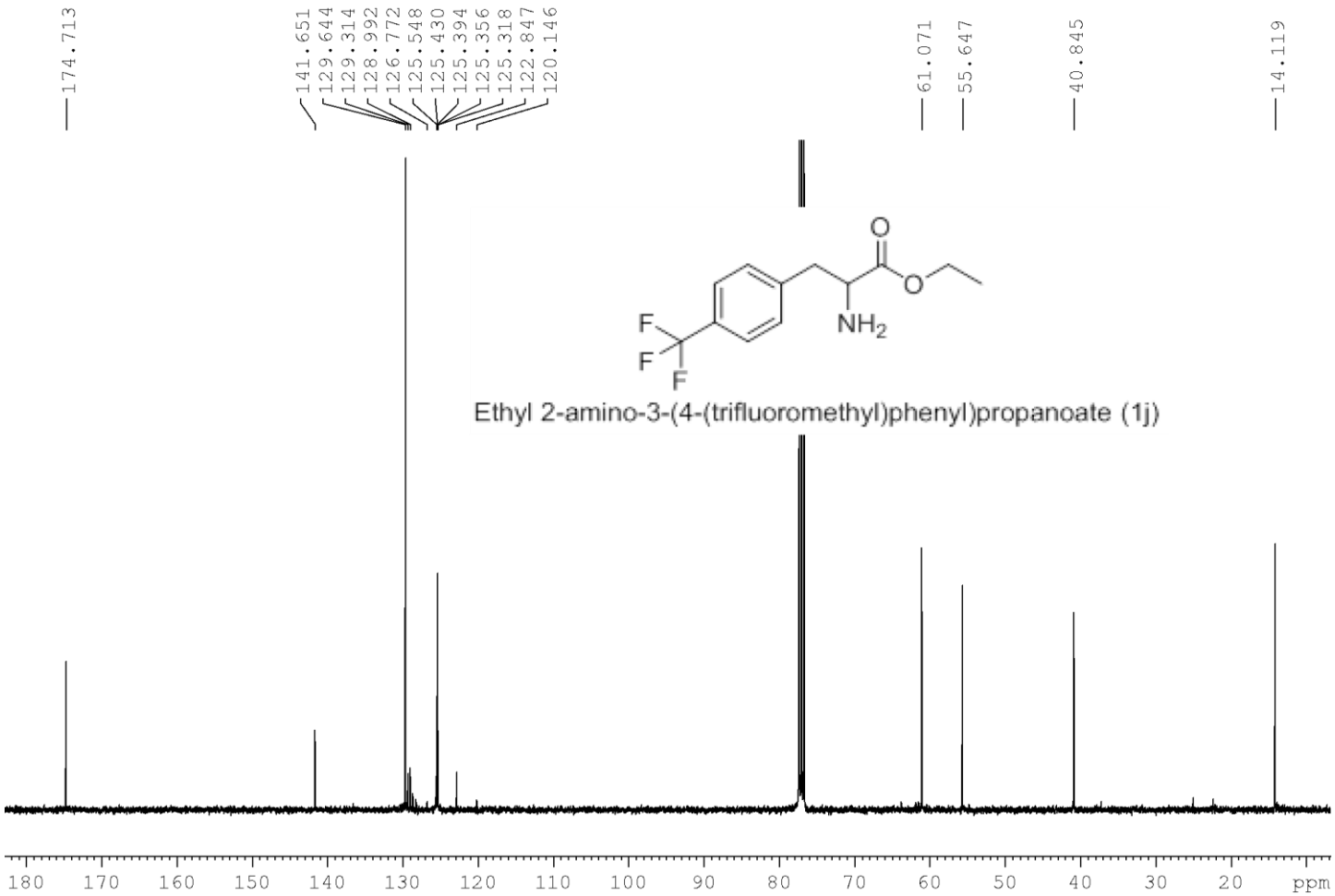
Ethyl 2-amino-3-(3-(trifluoromethyl)phenyl)propanoate (1i)

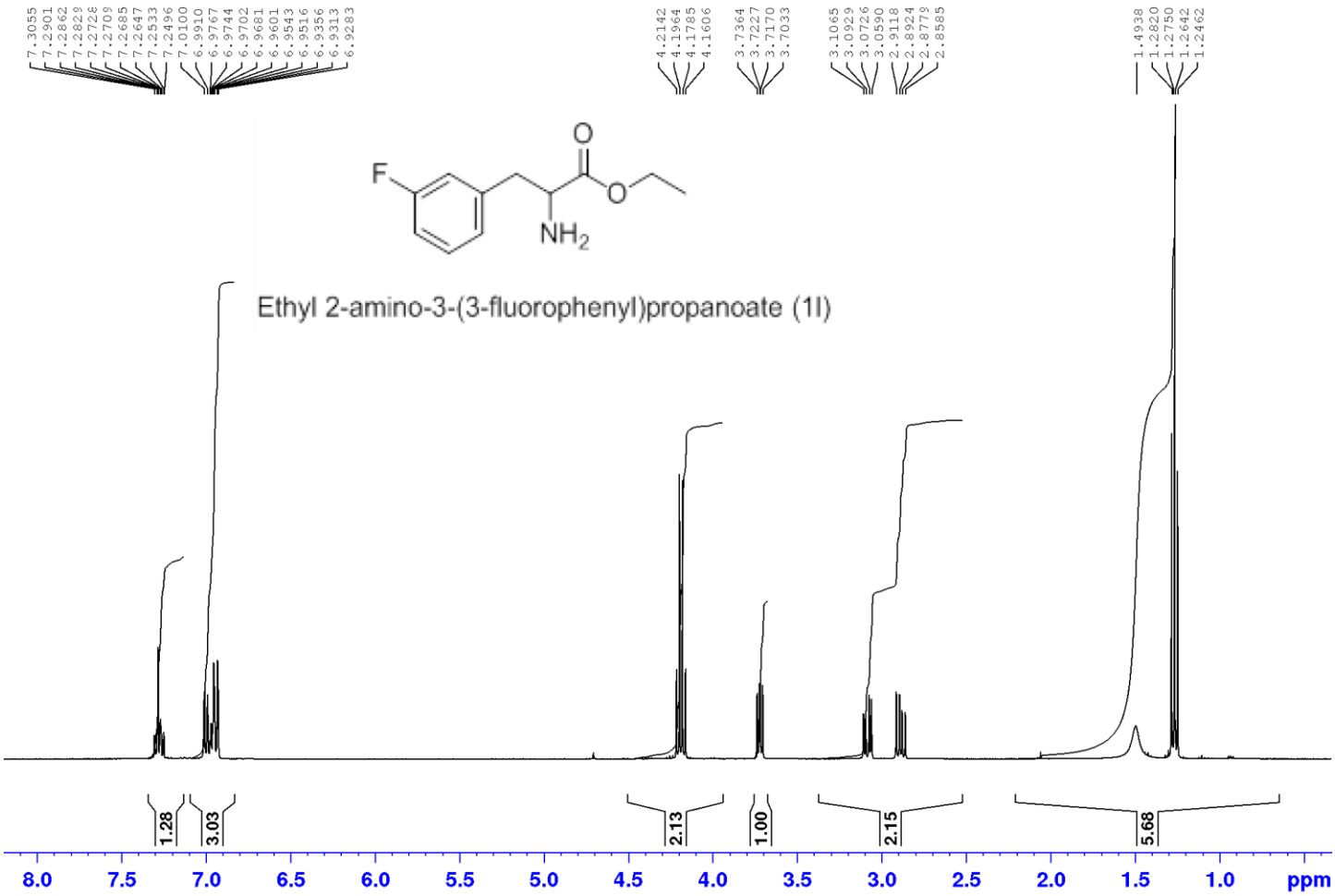




Ethyl 2-amino-3-(3-(trifluoromethyl)phenyl)propanoate (1i)


7.5899
7.5698
7.3616
7.3417
7.2827
4.2122
4.1943
4.1764
4.1586
3.7581
3.7443
3.7385
3.7247
3.1666
3.1528
3.1326
3.1189
2.9704
2.9508
2.9365
2.9169
1.5016
1.2745
1.2567
1.2388
O
O
NH2
F
F
F
Ethyl 2-amino-3-(4-(trifluoromethyl)phenyl)propanoate (1j)
1.94
1.96
2.07
1.00
1.01
1.02
2.05
3.09
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
ppm


174.713
141.651
129.644
129.314
128.992
126.772
125.548
125.430
125.394
125.356
125.318
122.847
120.146
61.071
55.647
40.845
14.119
O
O
NH2
F
F
F
Ethyl 2-amino-3-(4-(trifluoromethyl)phenyl)propanoate (1j)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.2862
7.2829
7.2728
7.2709
7.2685
7.2647
7.2533
7.2496
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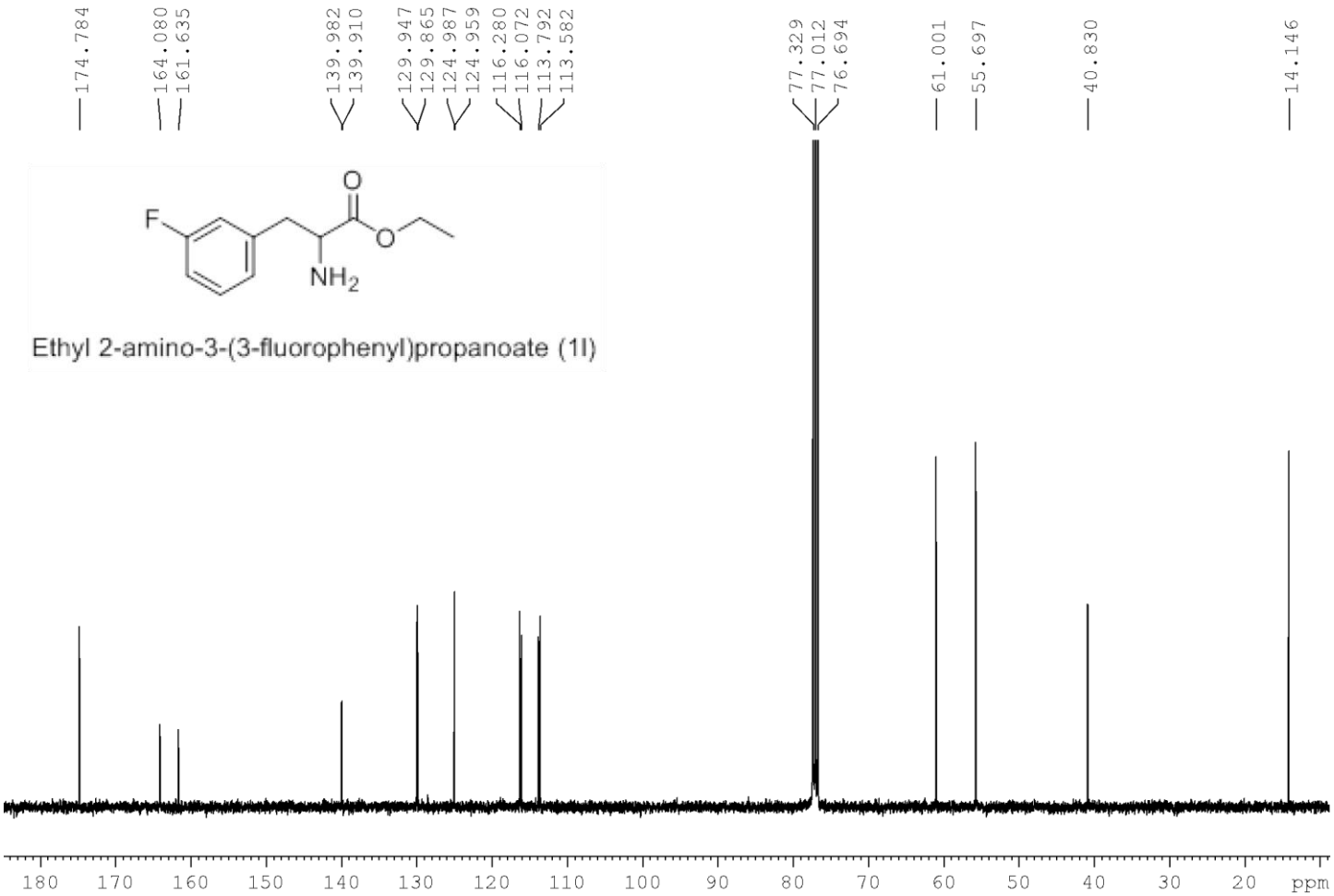
6.9910
6.9767
6.9744
6.9702
6.9681
6.9601
6.9543
6.9516
6.9356
6.9313
6.9283
4.2142
4.1964
4.1785
4.1606
3.7364
3.7227
3.7170
3.7033
3.1065
3.0929
3.0726
3.0590
2.9118
2.8924
2.8779
2.8585
1.4938
1.2820
1.2750
1.2642
1.2462
F
O
O
NH2
Ethyl 2-amino-3-(3-fluorophenyl)propanoate (1l)
1.28
3.03
2.13
1.00
2.15
5.68
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
ppm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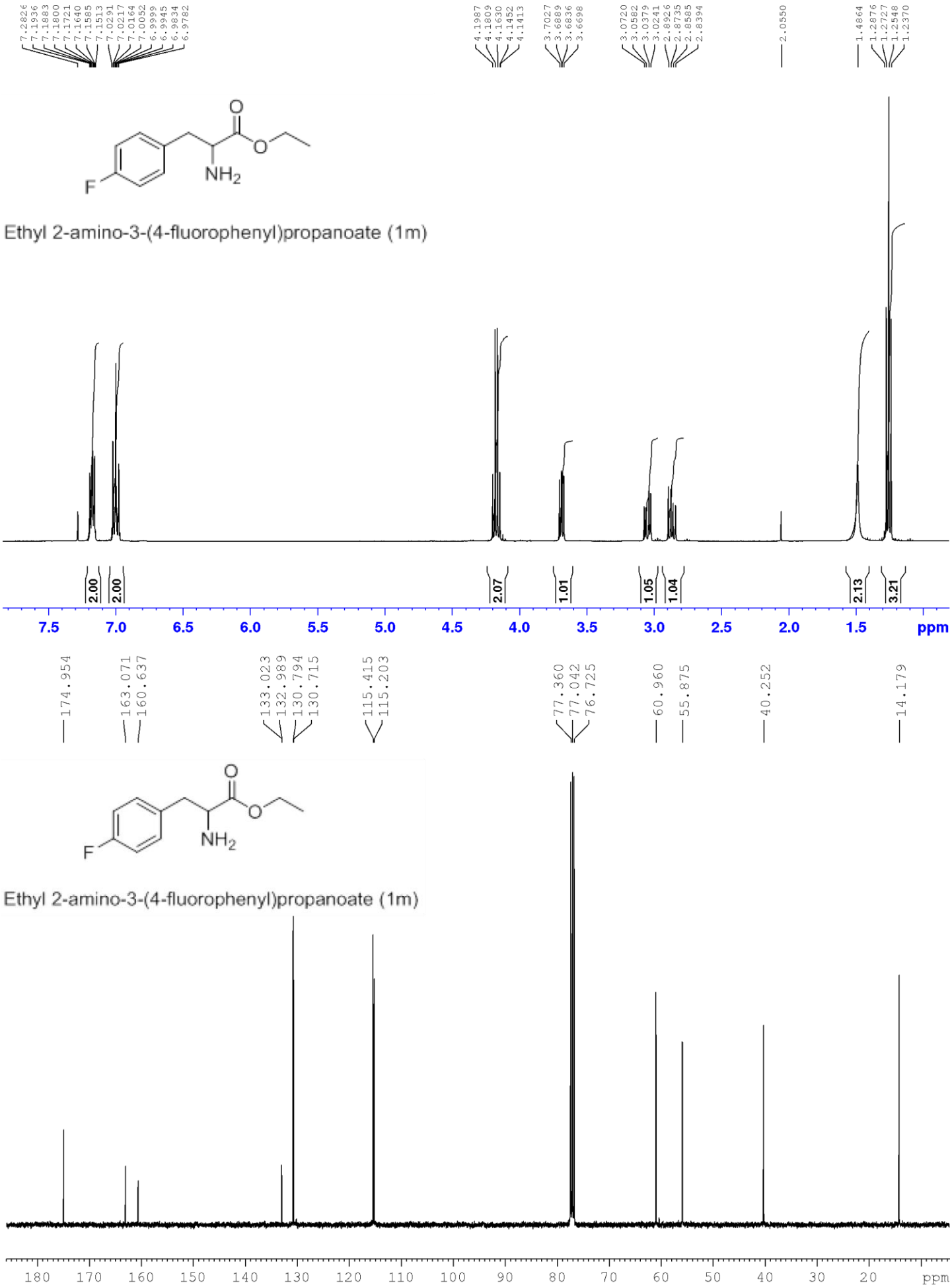
161.635
139.982
139.910
129.947
129.865
124.987
124.959
116.280
116.072
113.792
113.582
77.329
77.012
76.694
61.001
55.697
40.830
14.146
F
O
O
NH2
Ethyl 2-amino-3-(3-fluorophenyl)propanoate (1l)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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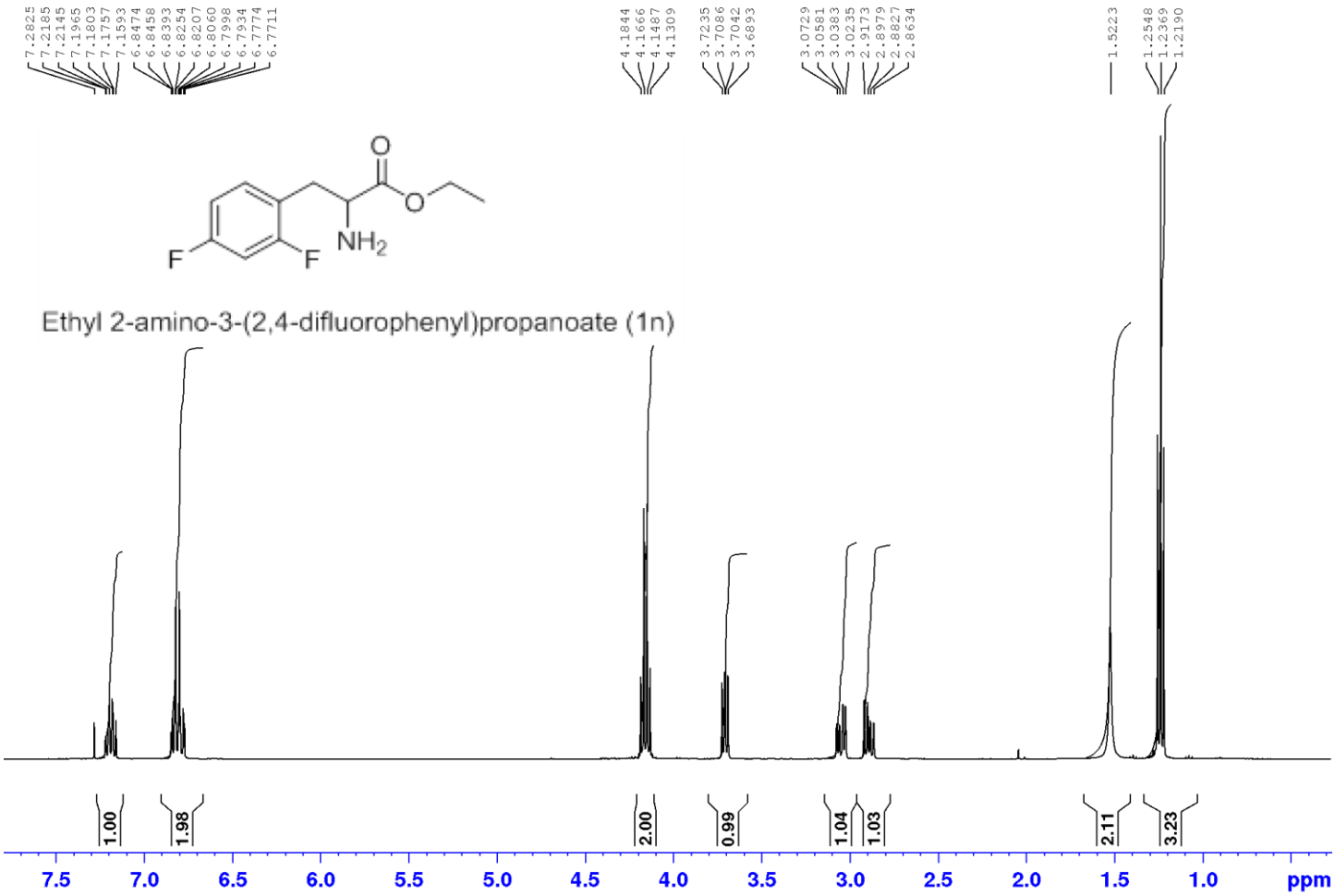
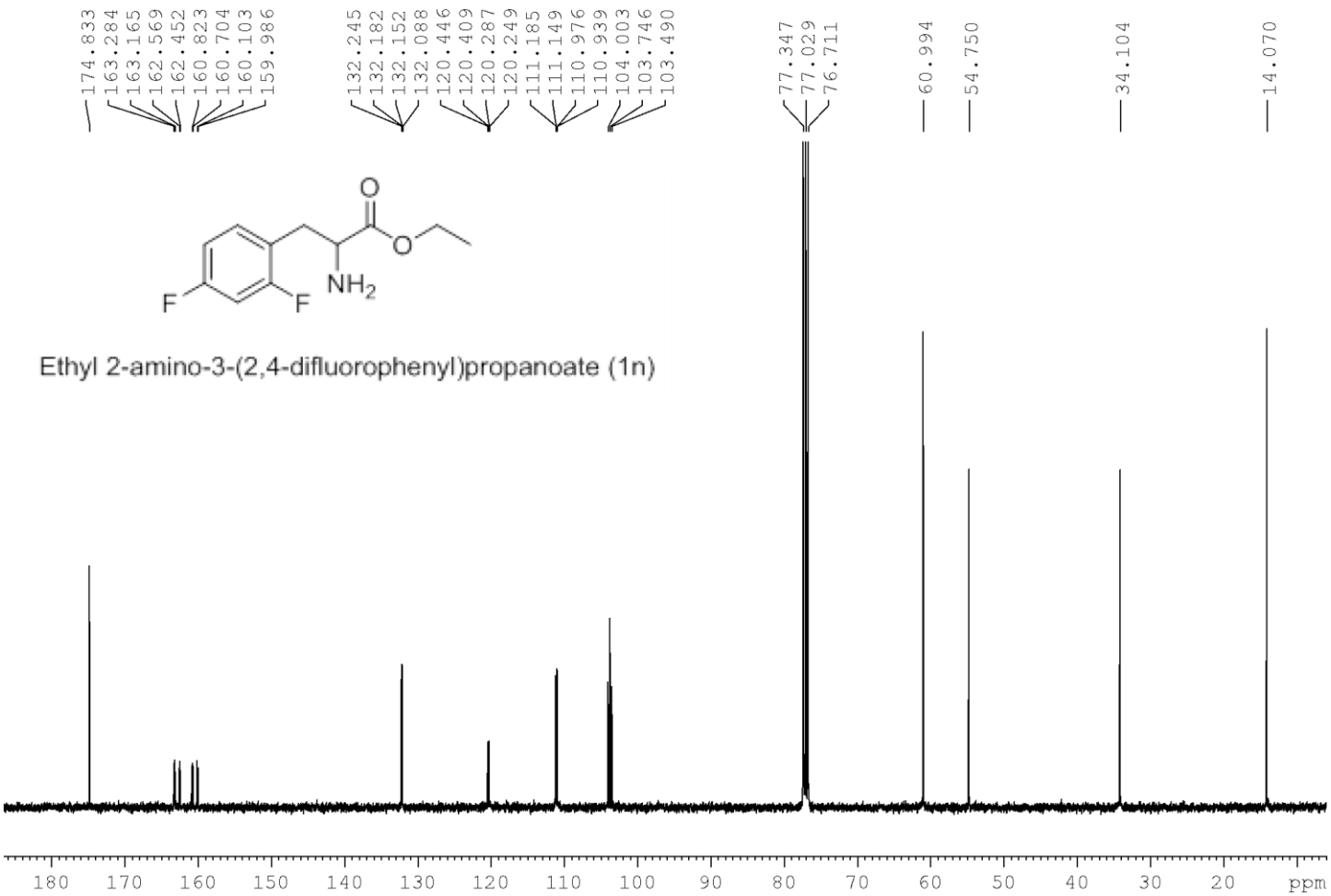
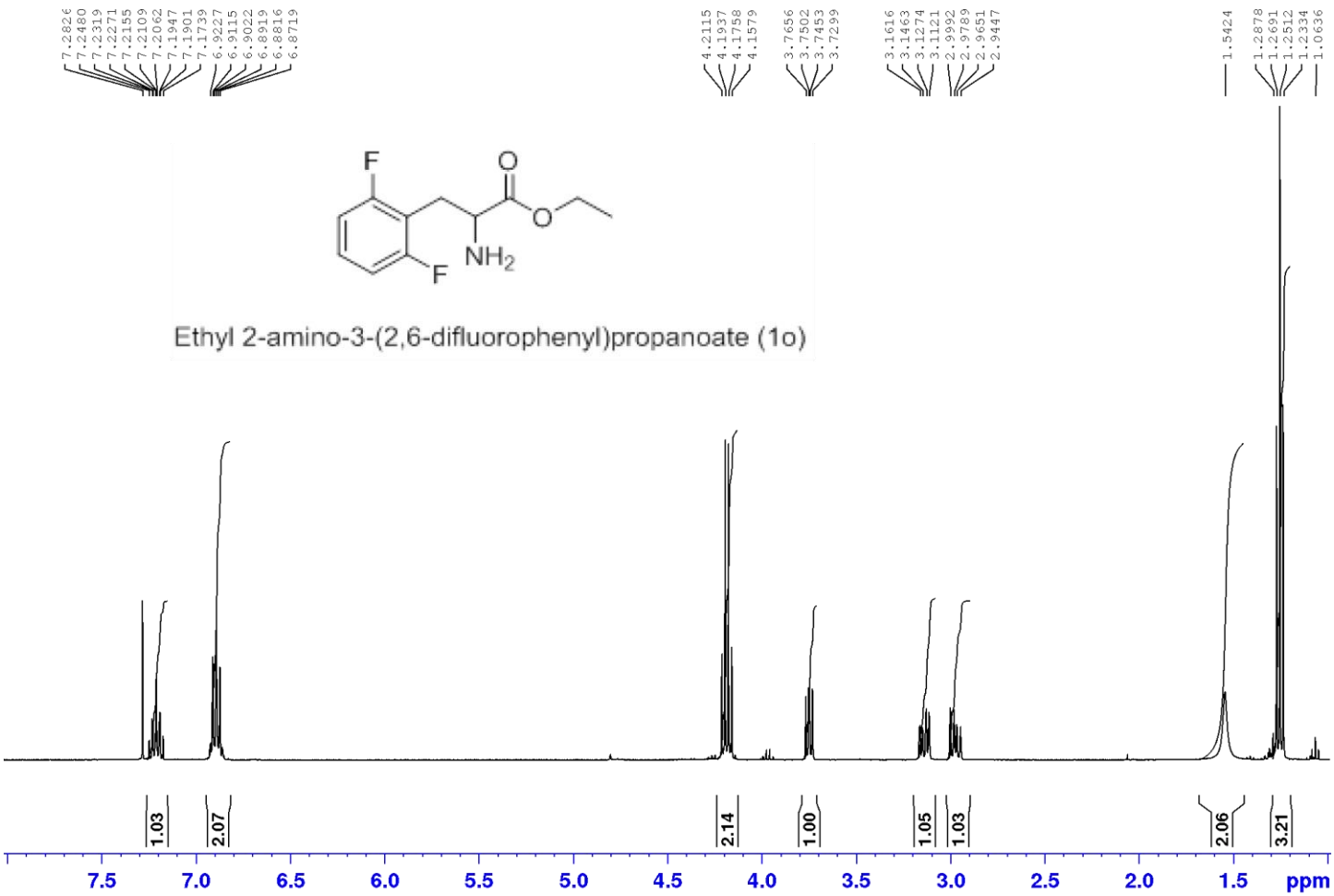
7.1883
7.1800
7.1721
7.1640
7.1585
7.1513
7.0291
7.0217
7.0164
7.0052
6.9999
6.9945
6.9834
6.9782
4.1987
4.1809
4.1630
4.1452
4.1413
3.7027
3.6889
3.6836
3.6698
3.0720
3.0582
3.0379
3.0241
2.8926
2.8735
2.8585
2.8394
2.0550
1.4864
1.2876
1.2727
1.2548
1.2370
O
O
NH2
F
Ethyl 2-amino-3-(4-fluorophenyl)propanoate (1m)
2.00
2.00
2.07
1.01
1.05
1.04
2.13
3.21
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
ppm

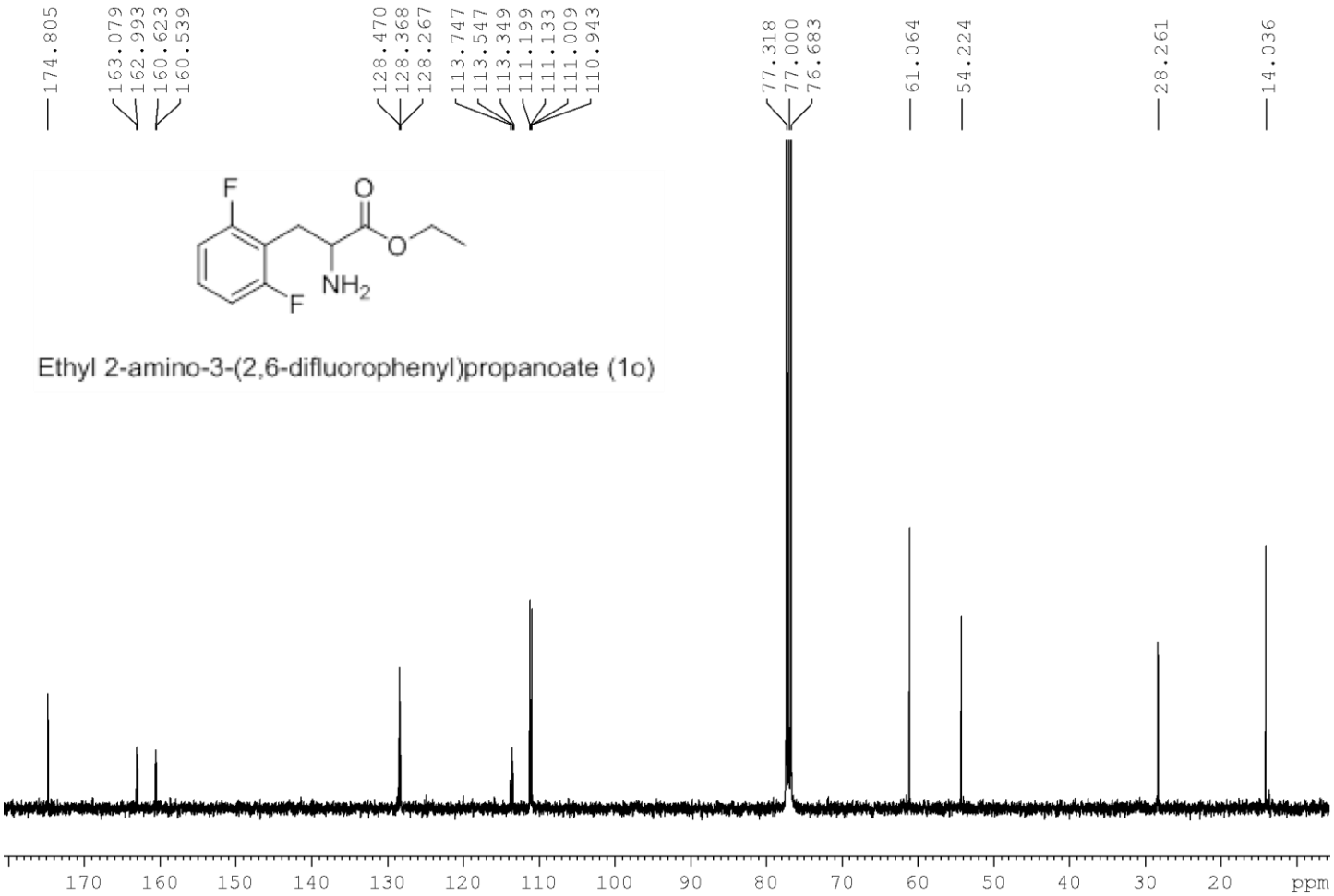
174.954
163.071
160.637
133.023
132.989
130.794
130.715
115.415
115.203
77.360
77.042
76.725
60.960
55.875
40.252
14.179
O
O
NH2
F
Ethyl 2-amino-3-(4-fluorophenyl)propanoate (1m)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.2825
7.2185
7.2145
7.1965
7.1803
7.1757
7.1593
6.8474
6.8458
6.8393
6.8254
6.8207
6.8060
6.7998
6.7934
6.7774
6.7711
4.1844
4.1666
4.1487
4.1309
3.7235
3.7086
3.7042
3.6893
3.0729
3.0581
3.0383
3.0235
2.9173
2.8979
2.8827
2.8634
1.5223
1.2548
1.2369
1.2190
O
O
NH2
F
F
Ethyl 2-amino-3-(2,4-difluorophenyl)propanoate (1n)
1.00
1.98
2.00
0.99
1.04
1.03
2.11
3.23
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
ppm

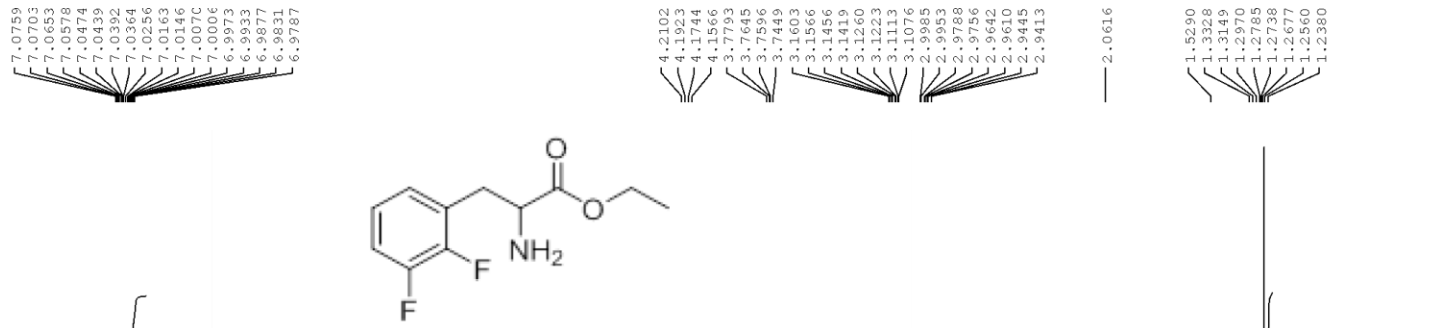

174.833
163.284
163.165
162.569
162.452
160.823
160.704
160.103
159.986
132.245
132.182
132.152
132.088
120.446
120.409
120.287
120.249
111.185
111.149
110.976
110.939
104.003
103.746
103.490
77.347
77.029
76.711
60.994
54.750
34.104
14.070
O
O
NH2
F
F
Ethyl 2-amino-3-(2,4-difluorophenyl)propanoate (1n)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



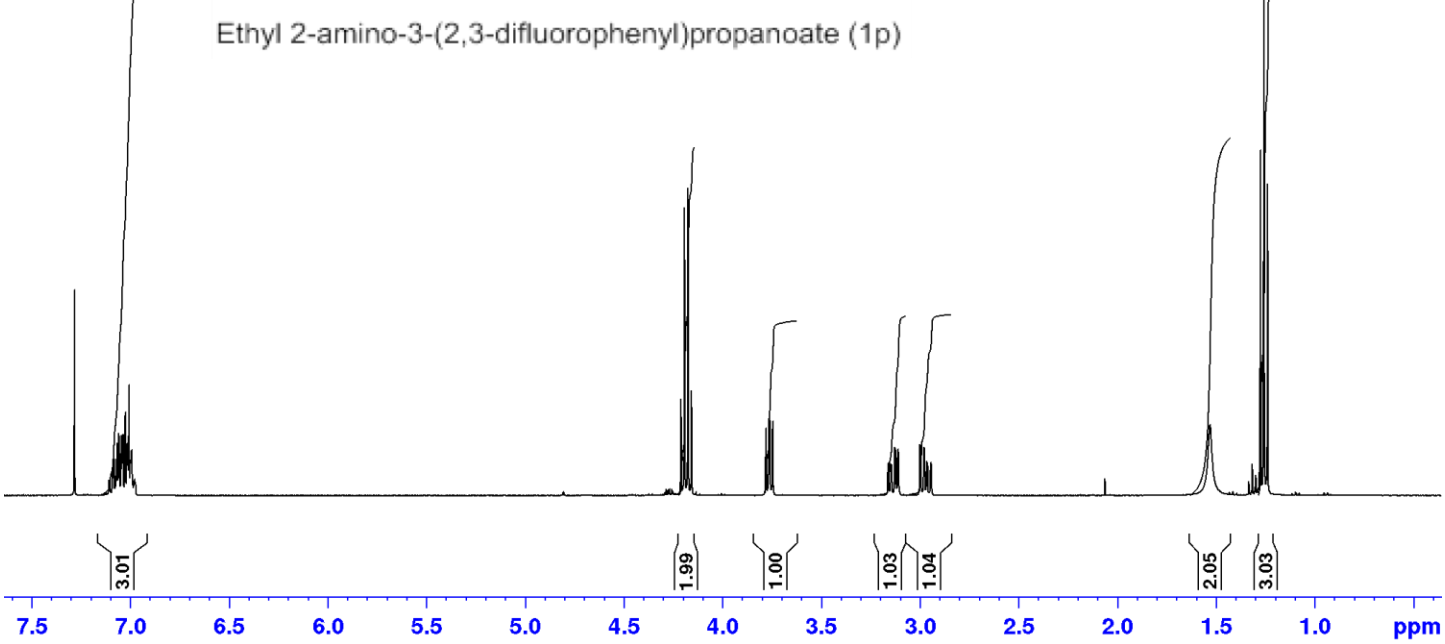
Ethyl 2-amino-3-(2,6-difluorophenyl)propanoate (1o)

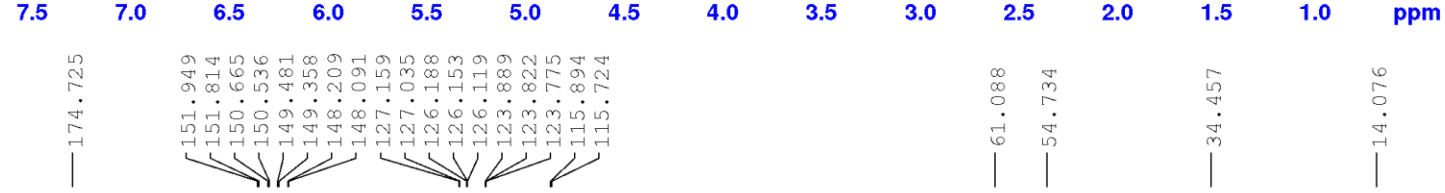


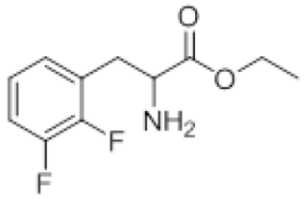
Ethyl 2-amino-3-(2,6-difluorophenyl)propanoate (1o)



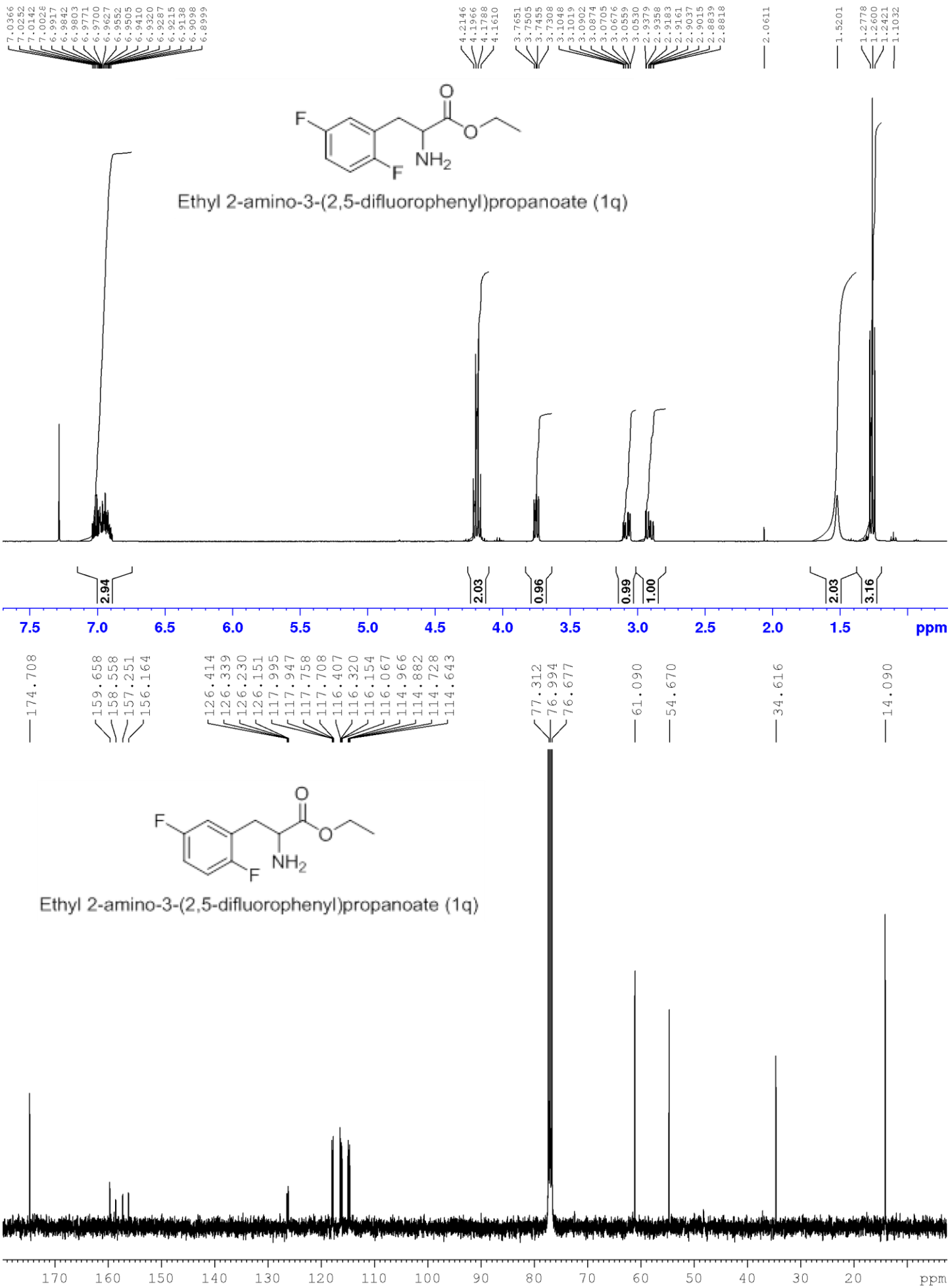
Ethyl 2-amino-3-(2,3-difluorophenyl)propanoate (1p)







Ethyl 2-amino-3-(2,3-difluorophenyl)propanoate (1p)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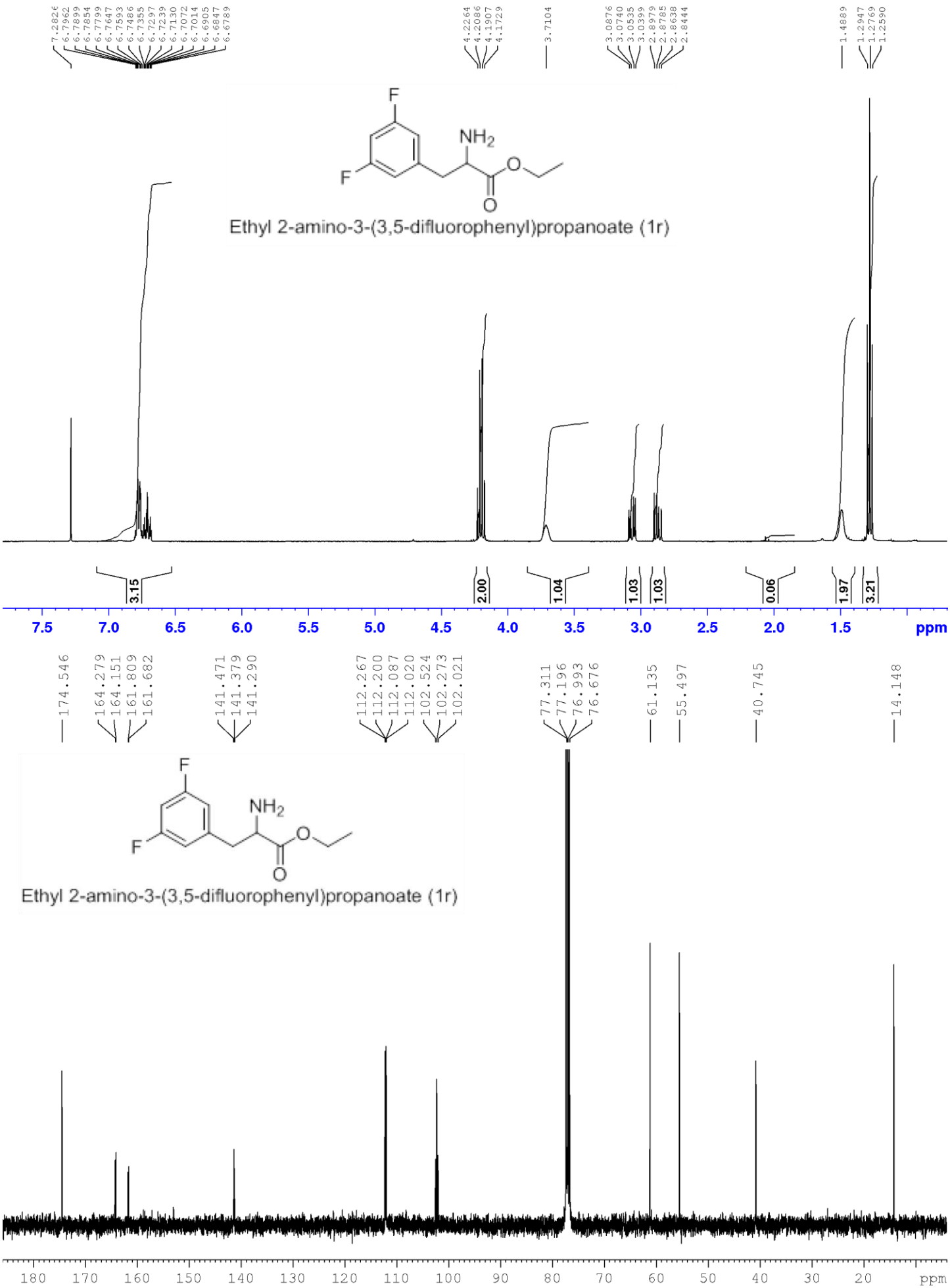
7.0142
7.0028
6.9917
6.9842
6.9803
6.9771
6.9700
6.9627
6.9552
6.9505
6.9410
6.9320
6.9287
6.9215
6.9138
6.9098
6.8999
4.2146
4.1966
4.1788
4.1610
3.7651
3.7505
3.7455
3.7308
3.1048
3.1019
3.0902
3.0874
3.0705
3.0676
3.0559
3.0530
2.9379
2.9358
2.9183
2.9161
2.9037
2.9015
2.8839
2.8818
2.0611
1.5201
1.2778
1.2600
1.2421
1.1032
F
O
O
NH2
F
Ethyl 2-amino-3-(2,5-difluorophenyl)propanoate (1q)
2.94
2.03
0.96
0.99
1.00
2.03
3.16
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
ppm
174.708
159.658
158.558
157.251
156.164
126.414
126.339
126.230
126.151
117.995
117.947
117.758
117.708
116.407
116.320
116.154
116.067
114.966
114.882
114.728
114.643
77.312
76.994
76.677
61.090
54.670
34.616
14.090
F
O
O
NH2
F
Ethyl 2-amino-3-(2,5-difluorophenyl)propanoate (1q)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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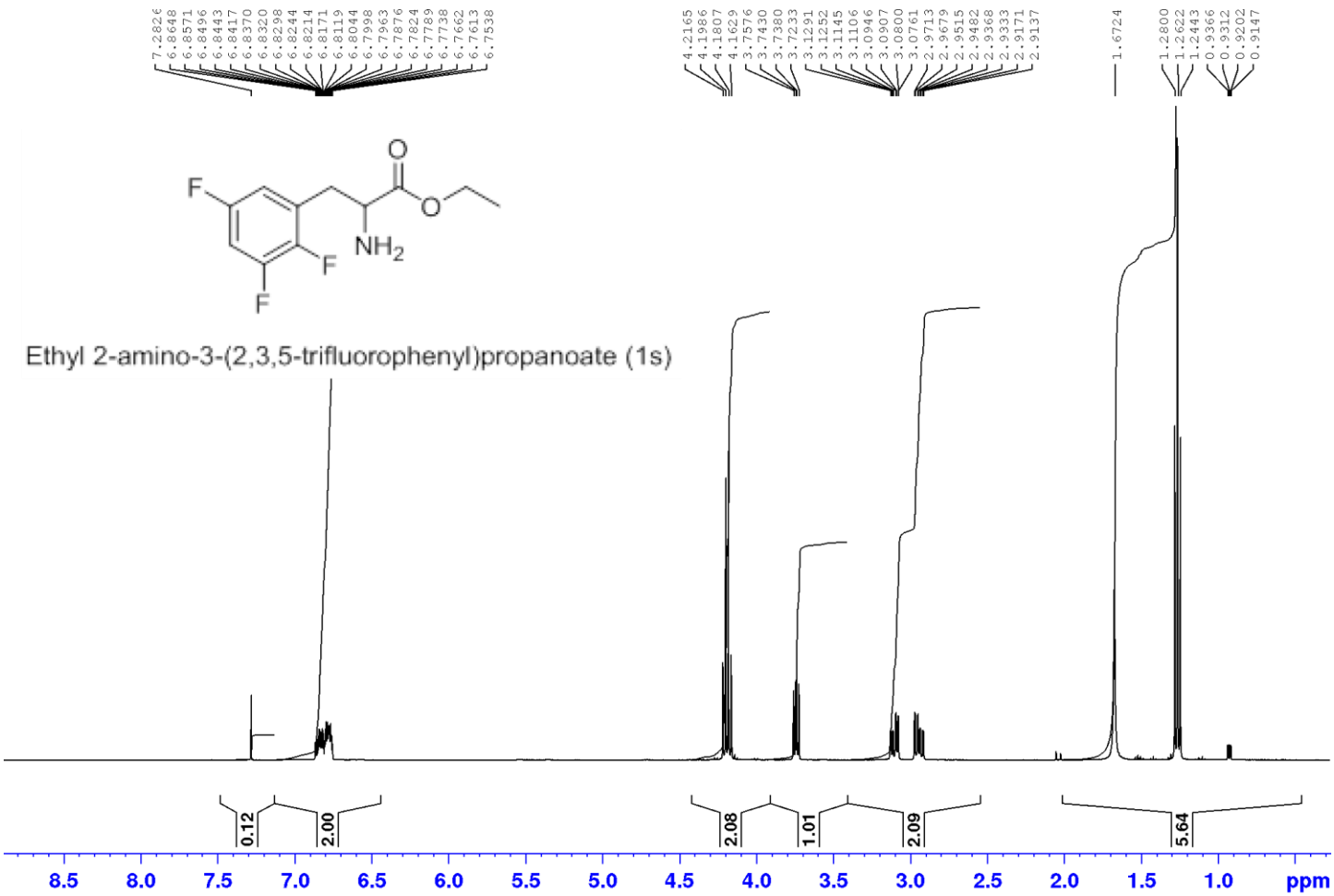
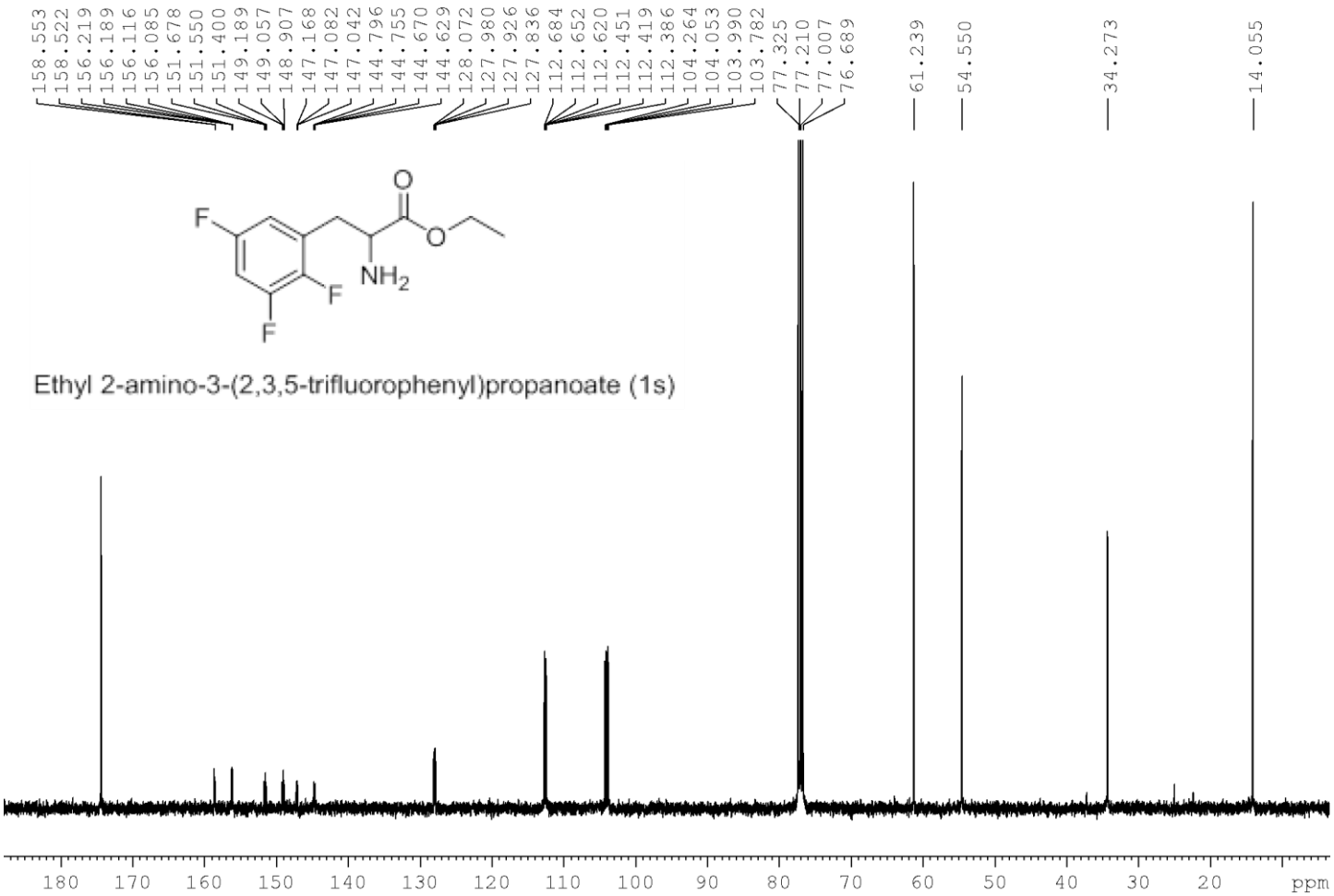
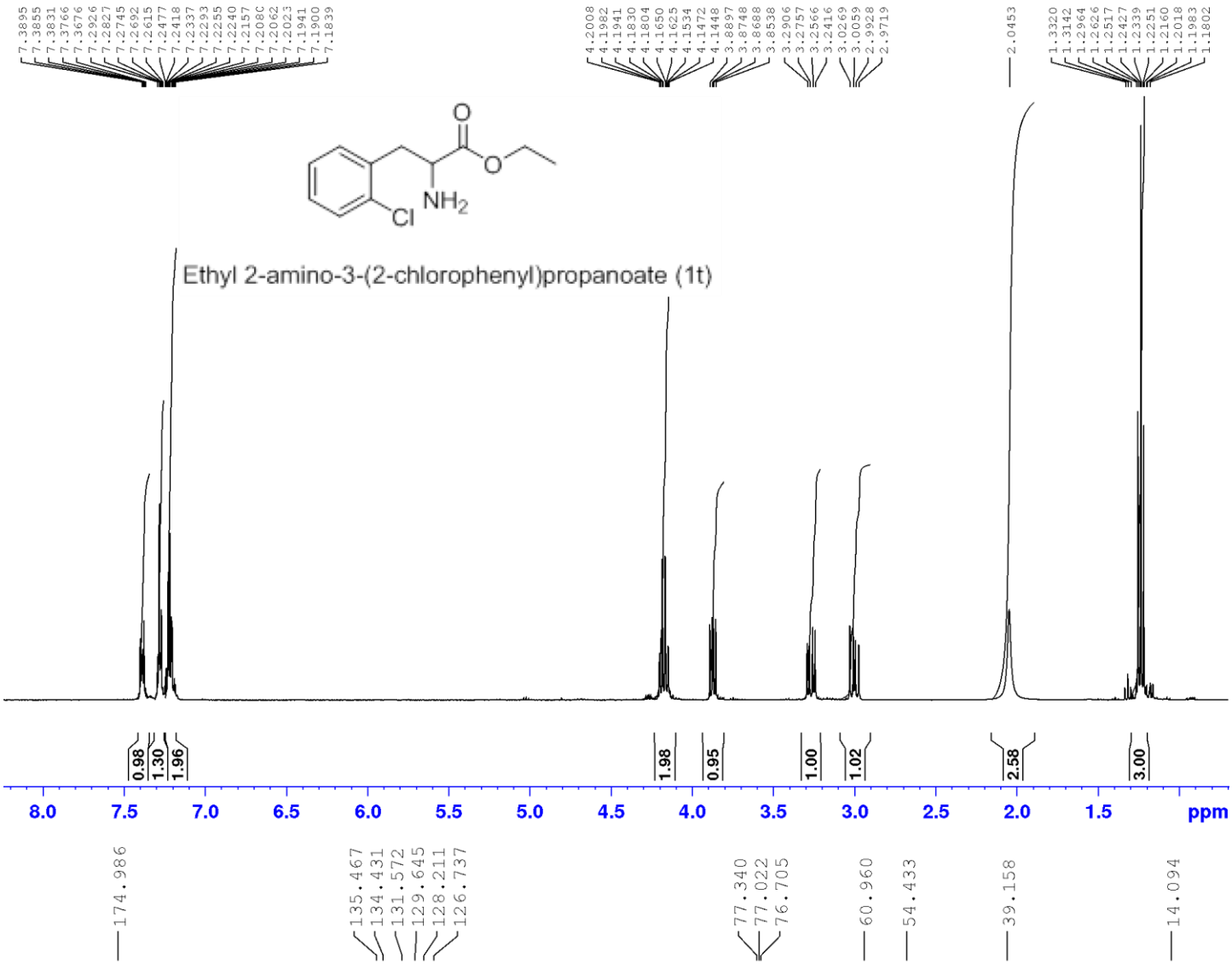
6.7962
6.7899
6.7854
6.7799
6.7647
6.7593
6.7486
6.7355
6.7297
6.7239
6.7130
6.7072
6.7014
6.6905
6.6847
6.6789
4.2264
4.2086
4.1907
4.1729
3.7104
3.0876
3.0740
3.0535
3.0399
2.8979
2.8785
2.8638
2.8444
1.4889
1.2947
1.2769
1.2590
F
NH2
F
O
O
Ethyl 2-amino-3-(3,5-difluorophenyl)propanoate (1r)
3.15
2.00
1.04
1.03
1.03
0.06
1.97
3.21
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
ppm
174.546
164.279
164.151
161.809
161.682
141.471
141.379
141.290
112.267
112.200
112.087
112.020
102.524
102.273
102.021
77.311
77.196
76.993
76.676
61.135
55.497
40.745
14.148
F
NH2
F
O
O
Ethyl 2-amino-3-(3,5-difluorophenyl)propanoate (1r)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

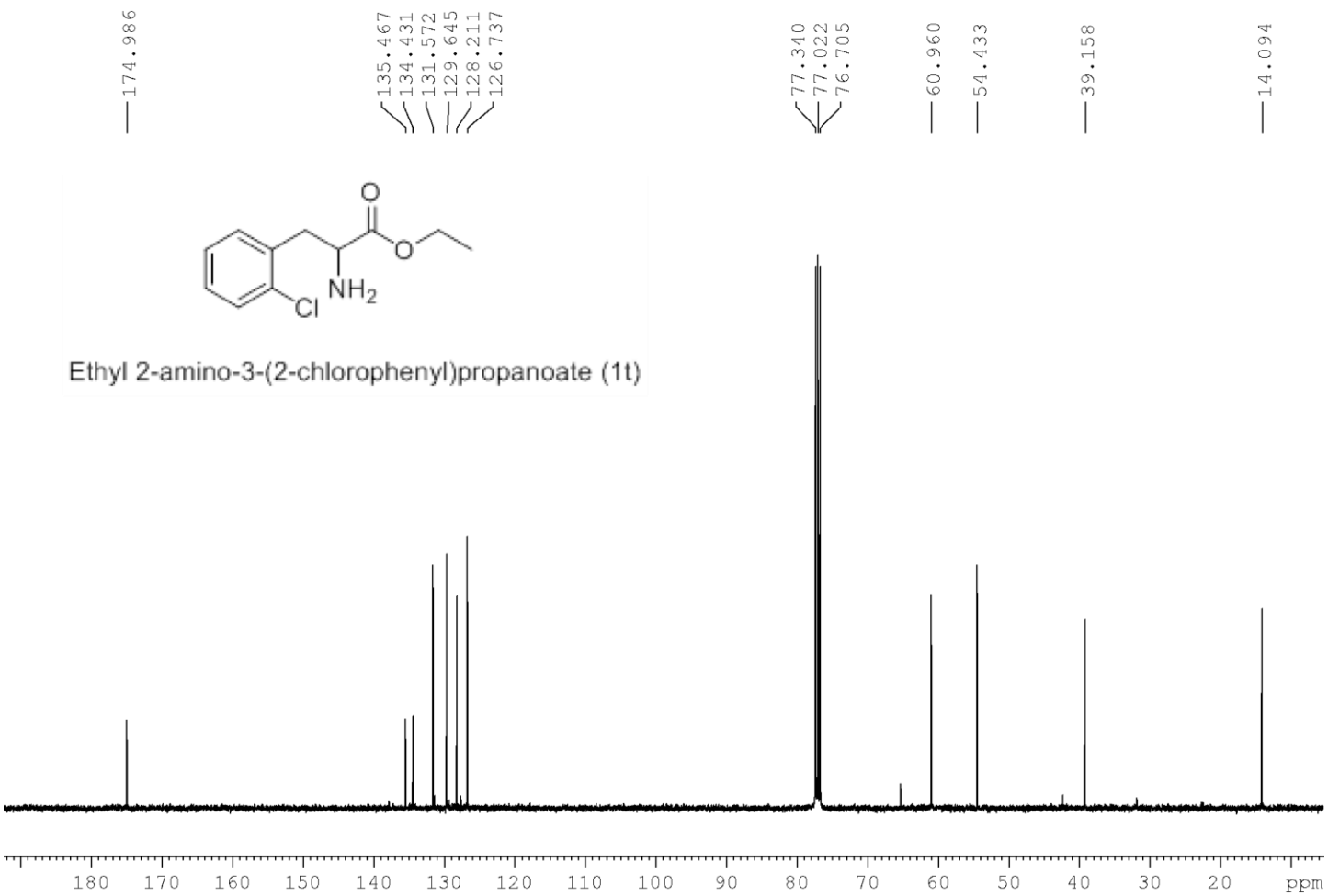


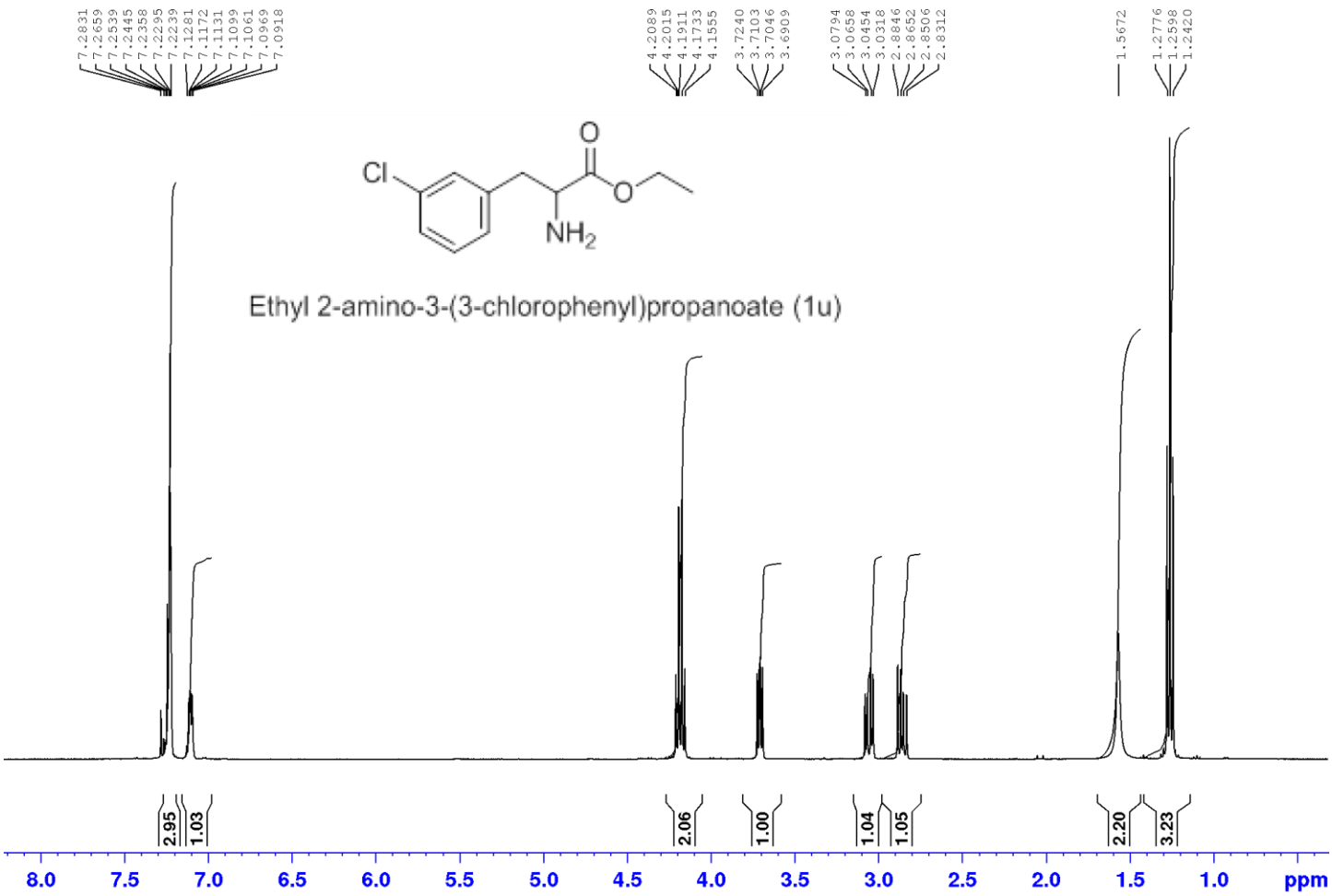
Ethyl 2-amino-3-(2,3,5-trifluorophenyl)propanoate (1s)



Ethyl 2-amino-3-(2,3,5-trifluorophenyl)propanoate (1s)


Ethyl 2-amino-3-(2-chlorophenyl)propanoate (1t)
ppm


Ethyl 2-amino-3-(2-chlorophenyl)propanoate (1t)
ppm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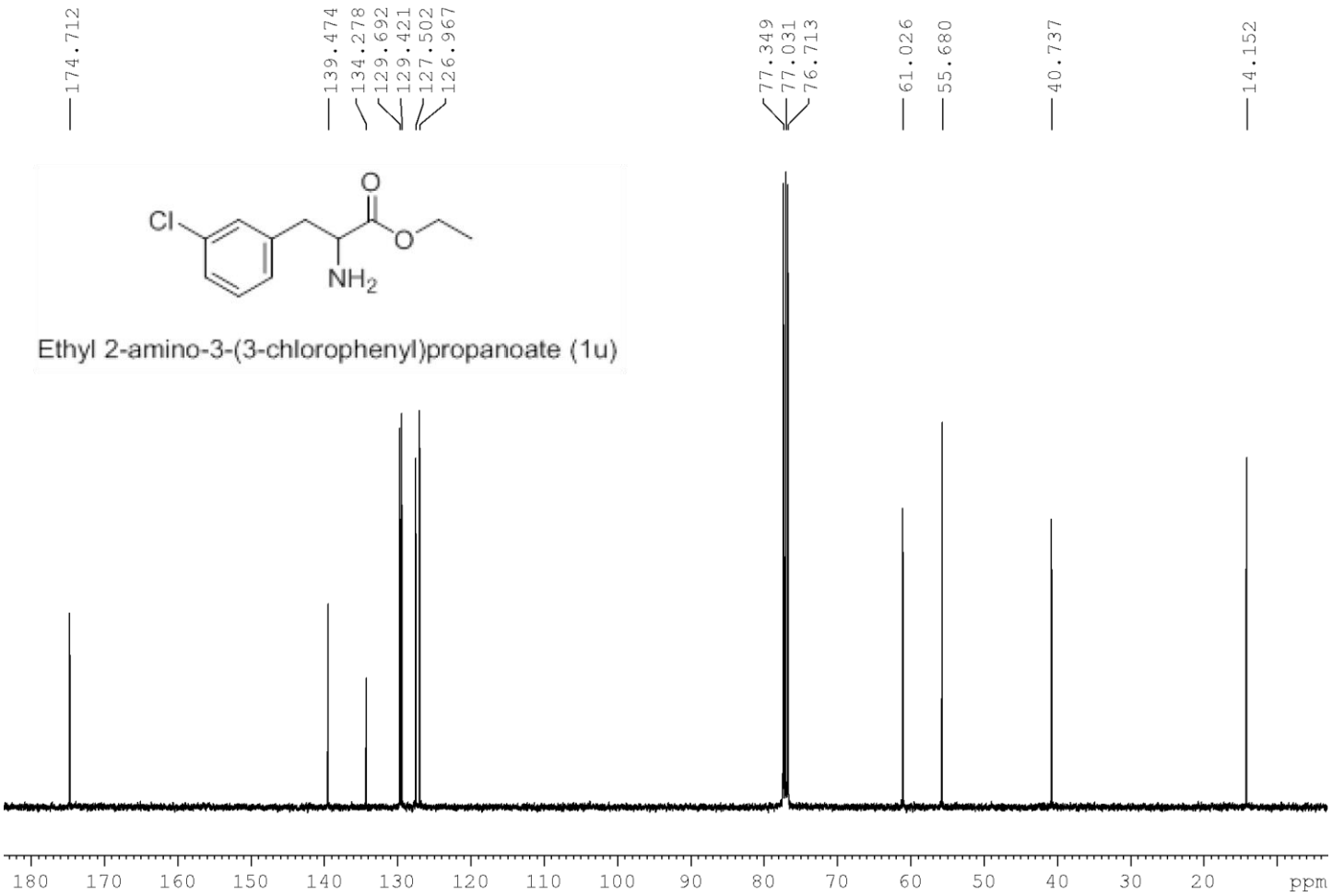
7.2445
7.2358
7.2295
7.2239
7.1281
7.1172
7.1131
7.1099
7.1061
7.0969
7.0918
4.2089
4.2015
4.1911
4.1733
4.1555
3.7240
3.7103
3.7046
3.6909
3.0794
3.0658
3.0454
3.0318
2.8846
2.8652
2.8506
2.8312
1.5672
1.2776
1.2598
1.2420
Cl
O
O
NH2
Ethyl 2-amino-3-(3-chlorophenyl)propanoate (1u)
2.95
1.03
2.06
1.00
1.04
1.05
2.20
3.23
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
ppm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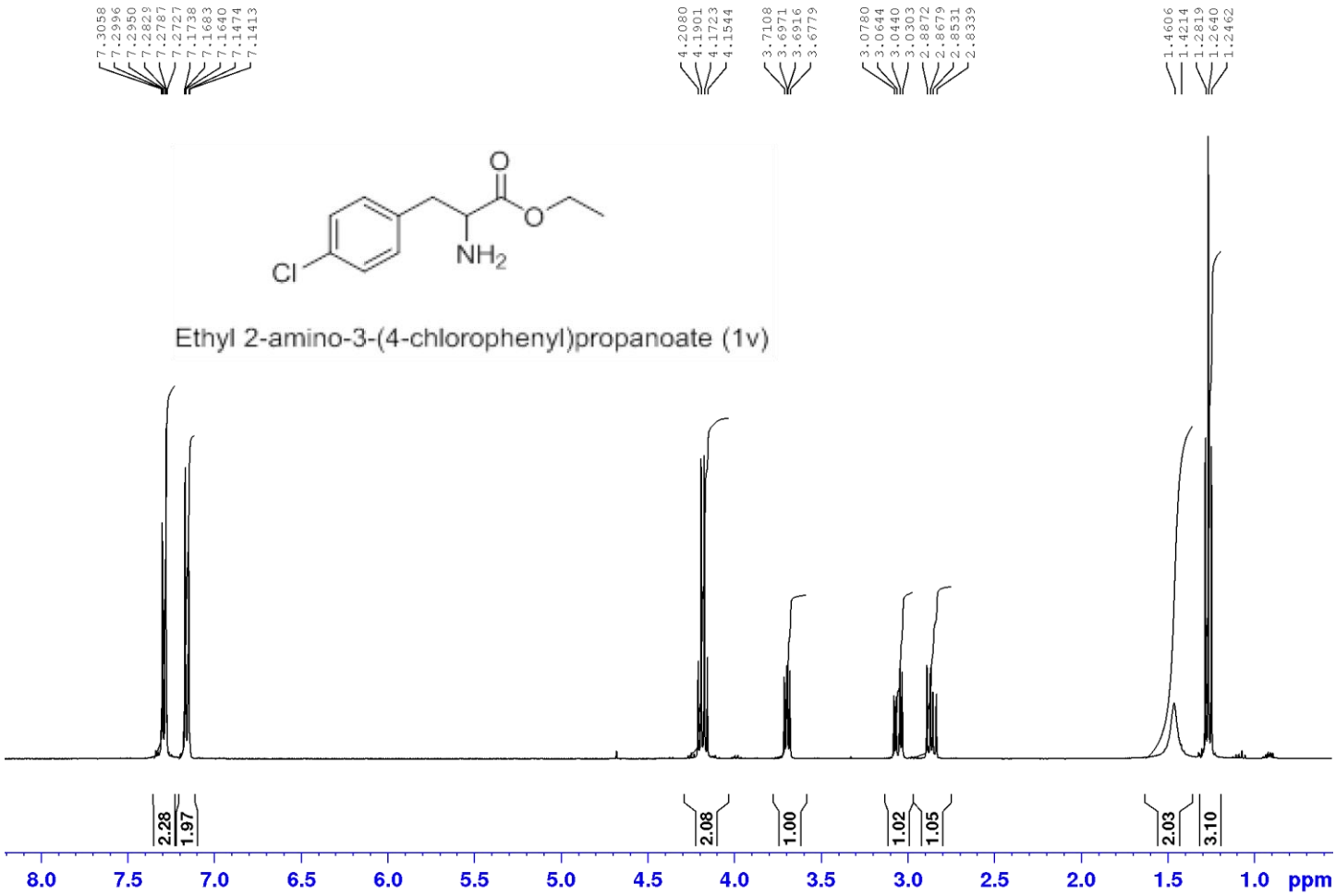
139.474
134.278
129.692
129.421
127.502
126.967
77.349
77.031
76.713
61.026
55.680
40.737
14.152
Cl
O
O
NH2
Ethyl 2-amino-3-(3-chlorophenyl)propanoate (1u)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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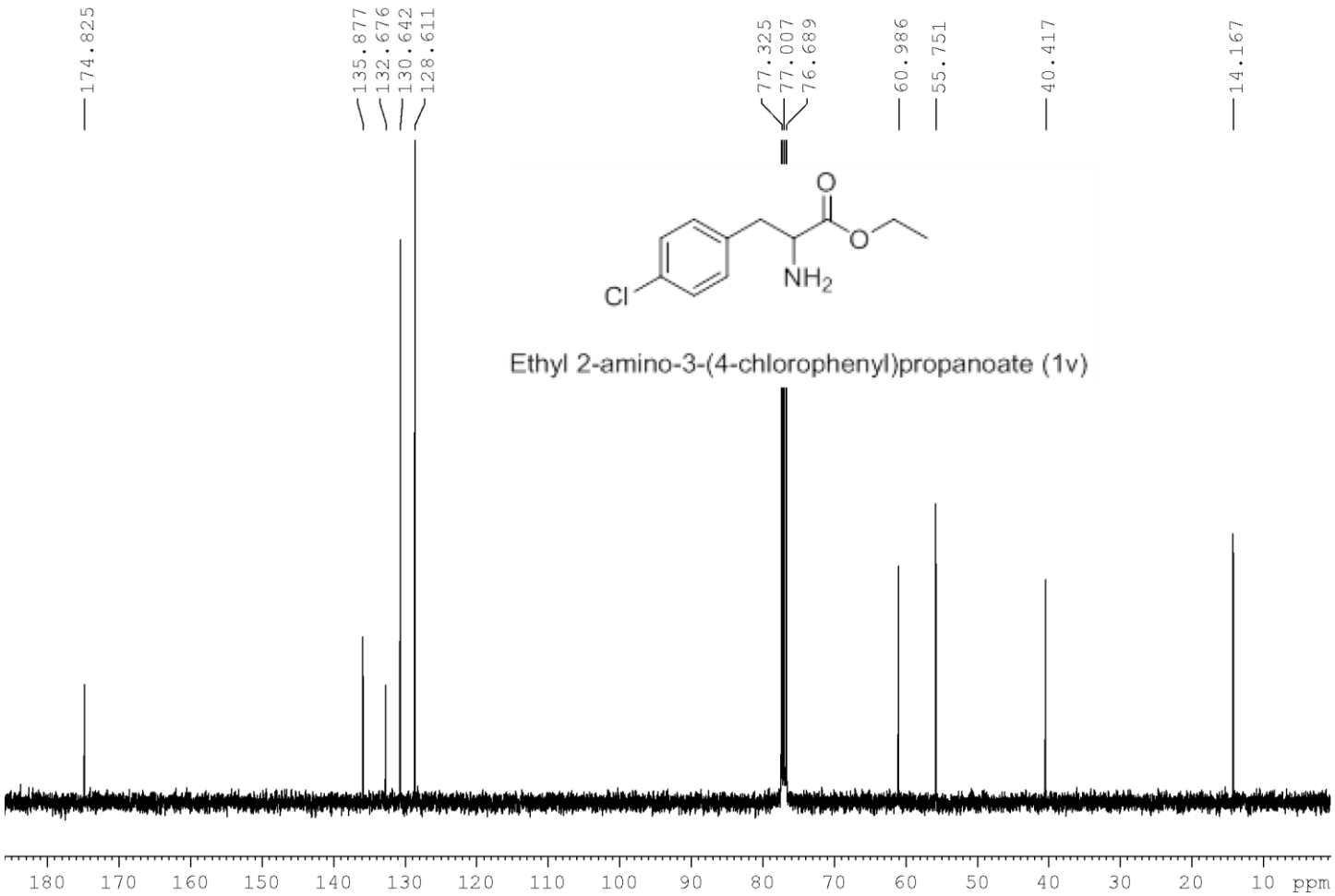
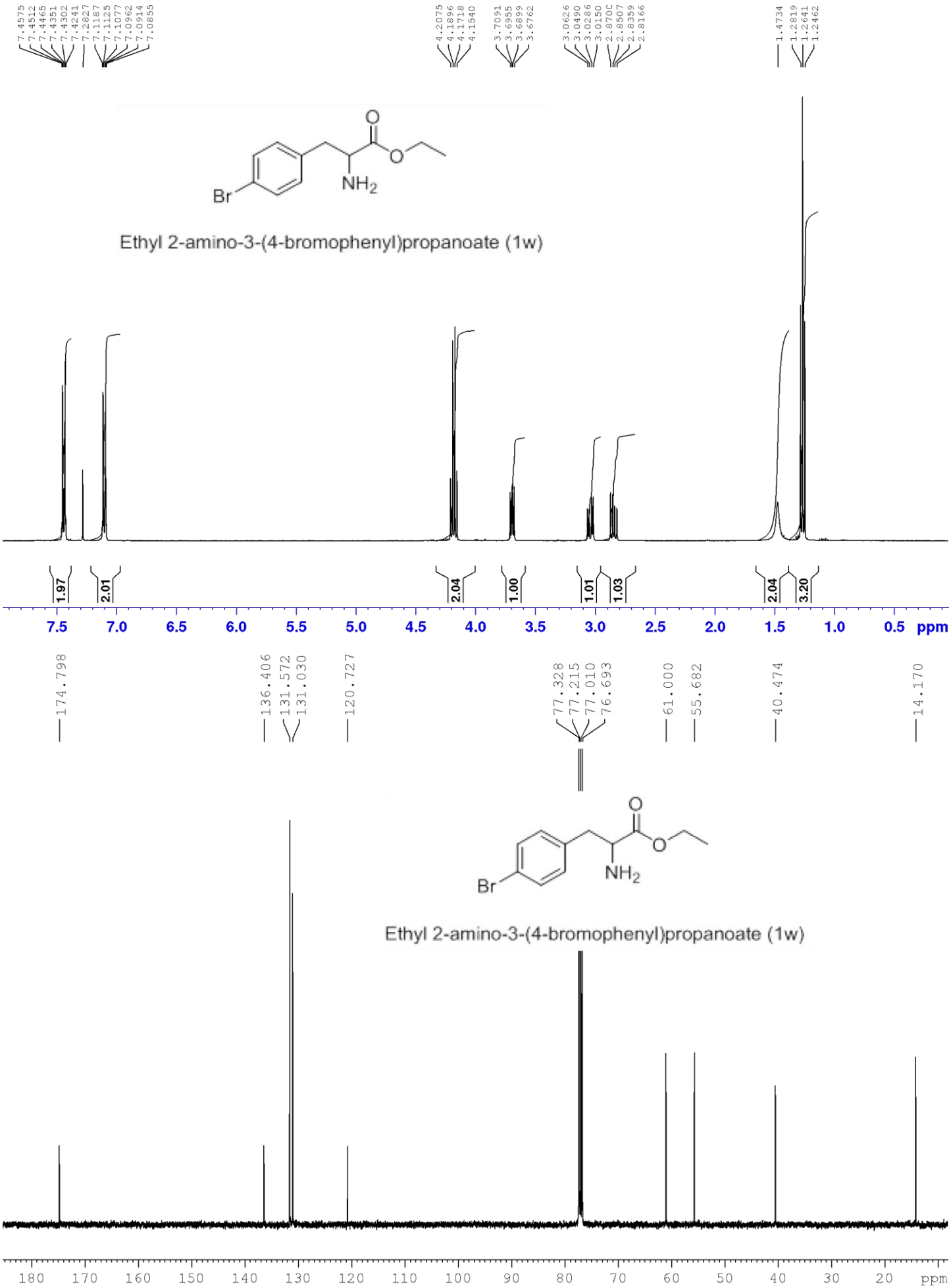
7.2950
7.2829
7.2787
7.2727
7.1738
7.1683
7.1640
7.1474
7.1413
4.2080
4.1901
4.1723
4.1544
3.7108
3.6971
3.6916
3.6779
3.0780
3.0644
3.0440
3.0303
2.8872
2.8679
2.8531
2.8339
1.4606
1.4214
1.2819
1.2640
1.2462
Cl
NH2
O
O
Ethyl 2-amino-3-(4-chlorophenyl)propanoate (1v)
2.28
1.97
2.08
1.00
1.02
1.05
2.03
3.10
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
ppm


174.825
135.877
132.676
130.642
128.611
77.325
77.007
76.689
60.986
55.751
40.417
14.167
Cl
NH2
O
O
Ethyl 2-amino-3-(4-chlorophenyl)propanoate (1v)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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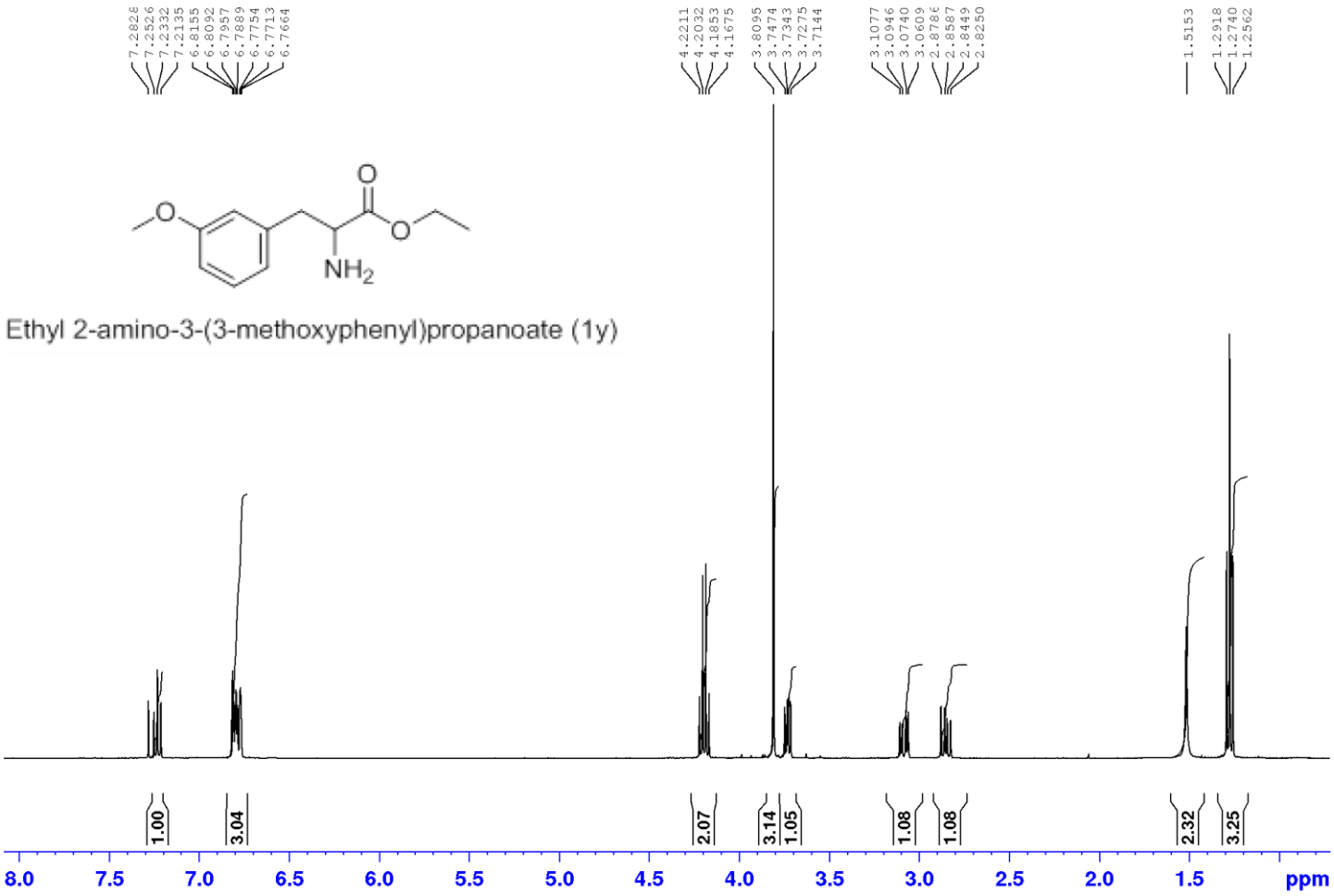
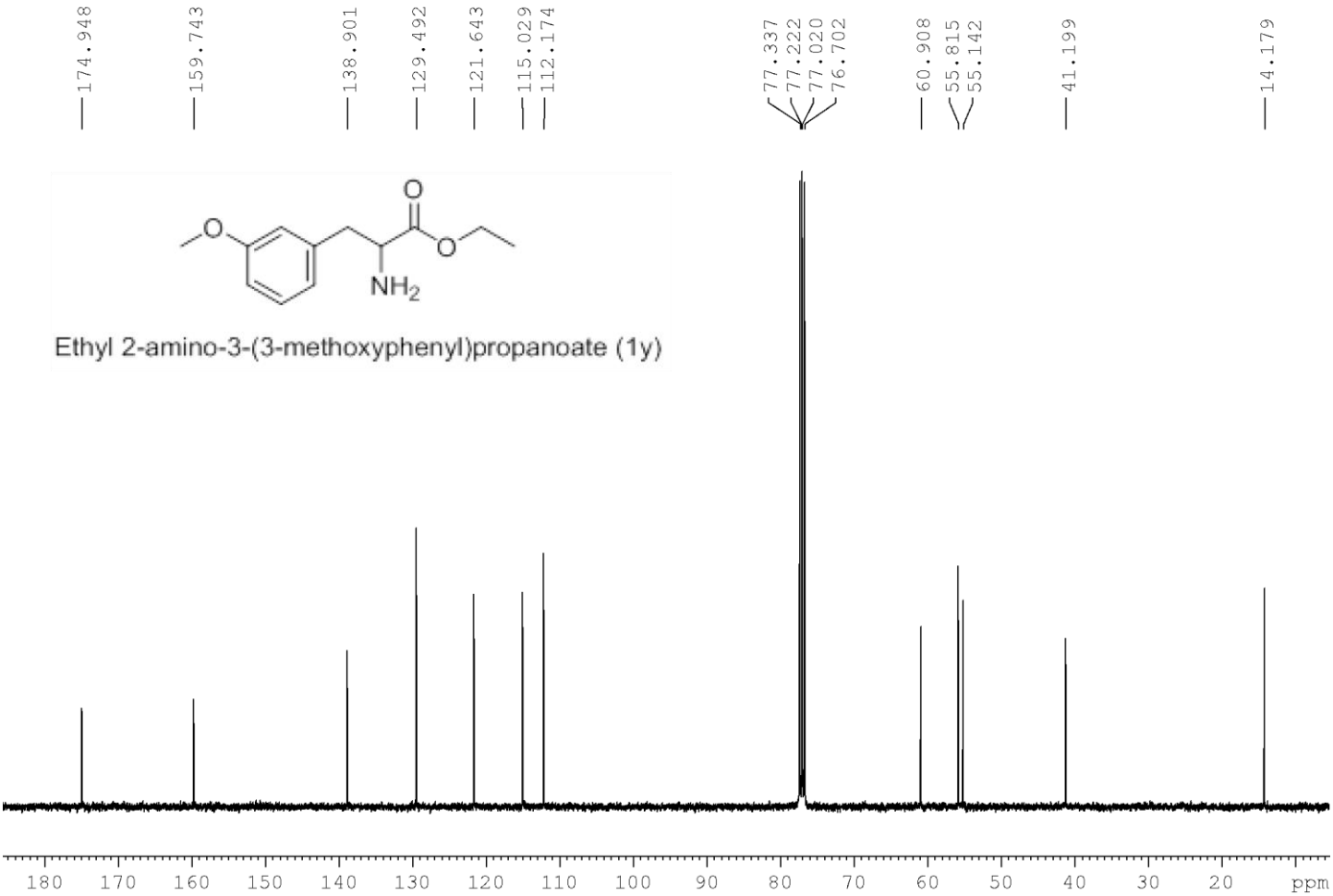
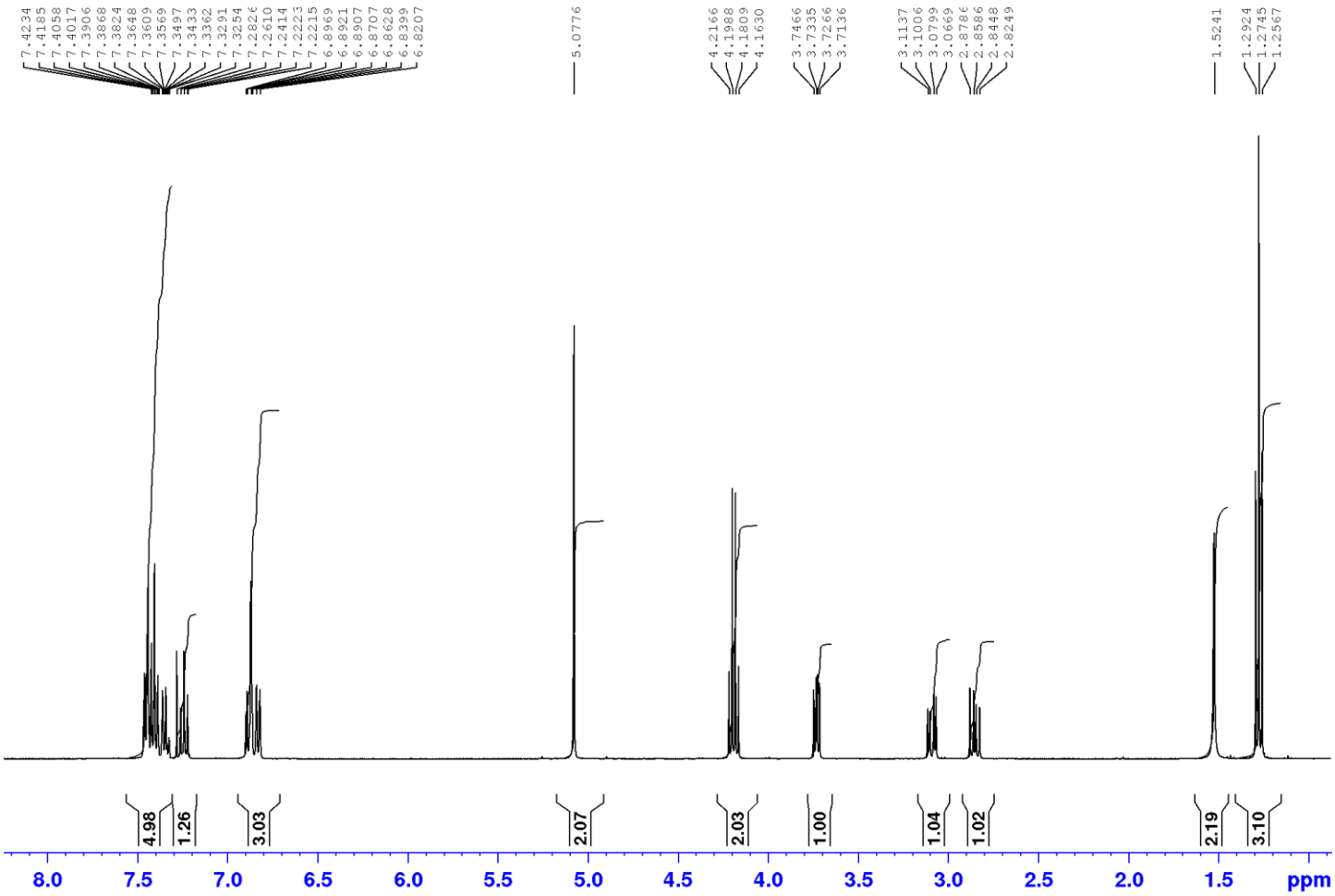
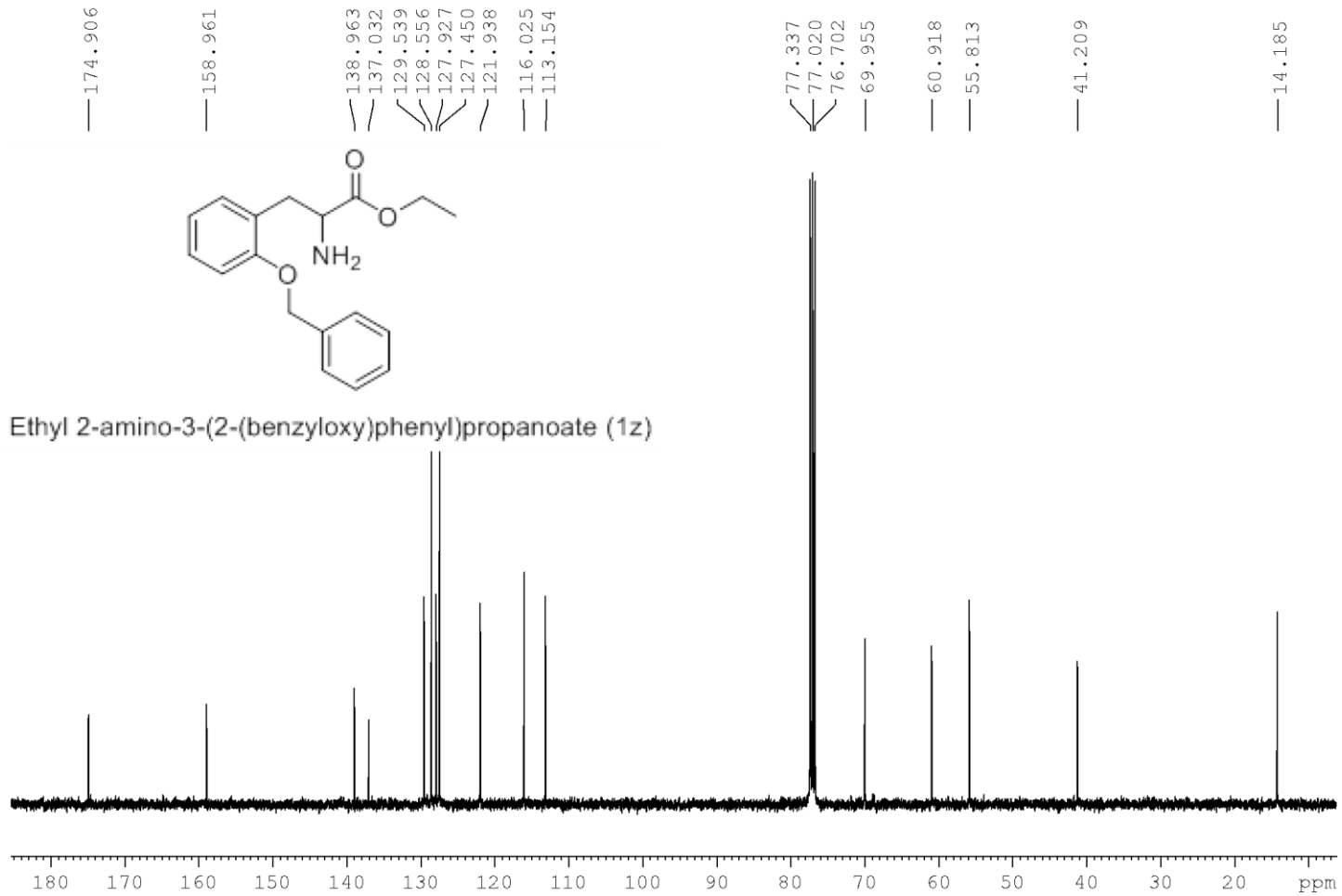
7.4465
7.4351
7.4302
7.4241
7.2827
7.1187
7.1125
7.1077
7.0962
7.0914
7.0855
4.2075
4.1896
4.1718
4.1540
3.7091
3.6955
3.6899
3.6762
3.0626
3.0490
3.0286
3.0150
2.8700
2.8507
2.8359
2.8166
1.4734
1.2819
1.2641
1.2462
Br
NH2
O
O
Ethyl 2-amino-3-(4-bromophenyl)propanoate (1w)
1.97
2.01
2.04
1.00
1.01
1.03
2.04
3.20
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
ppm
174.798
136.406
131.572
131.030
120.727
77.328
77.215
77.010
76.693
61.000
55.682
40.474
14.170
Br
NH2
O
O
Ethyl 2-amino-3-(4-bromophenyl)propanoate (1w)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

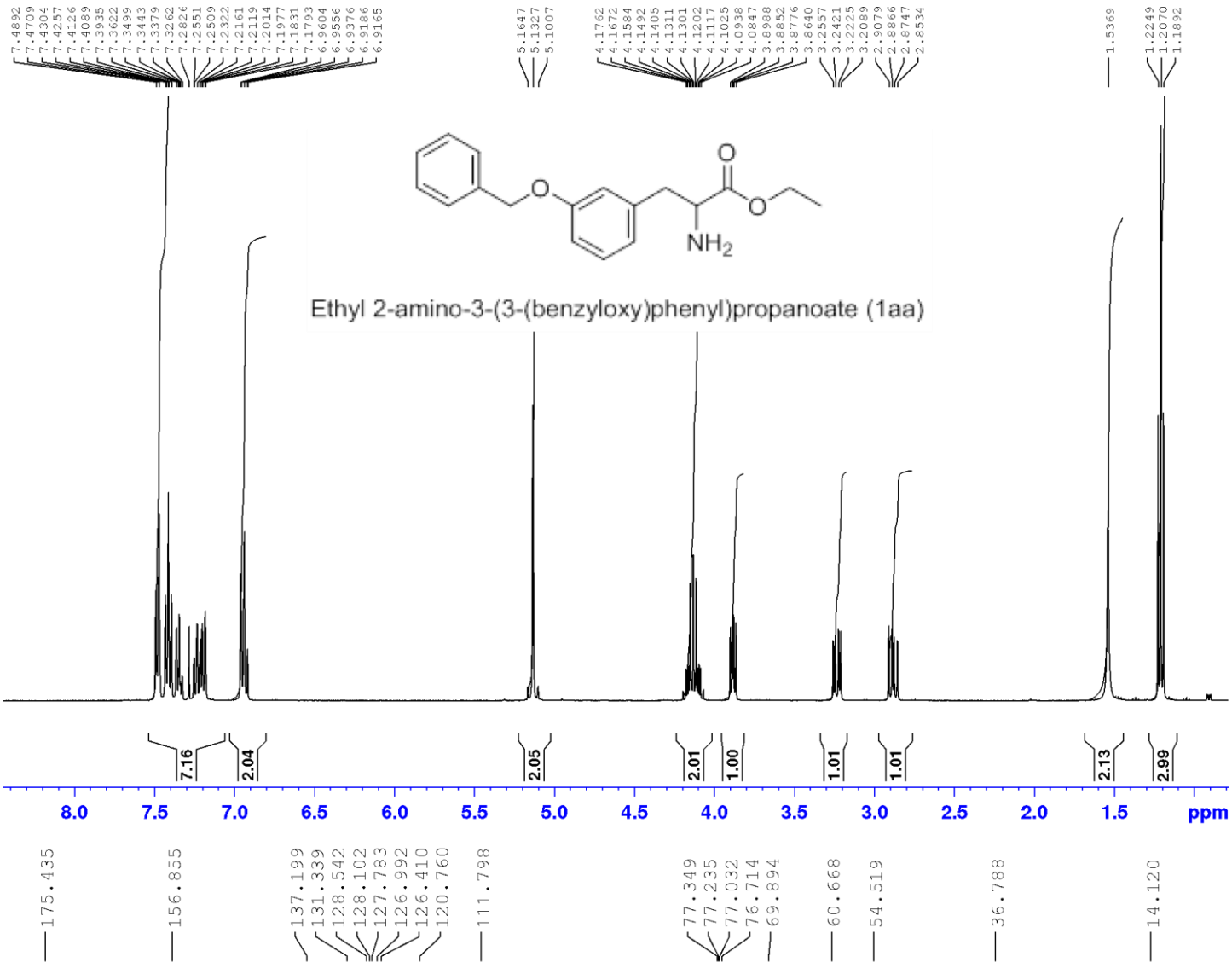

7.2828
7.2526
7.2332
7.2135
6.8155
6.8092
6.7957
6.7889
6.7754
6.7713
6.7664
4.2211
4.2032
4.1853
4.1675
3.8095
3.7474
3.7343
3.7275
3.7144
3.1077
3.0946
3.0740
3.0609
2.8786
2.8587
2.8449
2.8250
1.5153
1.2918
1.2740
1.2562
O
O
O
NH2
Ethyl 2-amino-3-(3-methoxyphenyl)propanoate (1y)
1.00
3.04
2.07
3.14
1.05
1.08
1.08
2.32
3.25
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
ppm

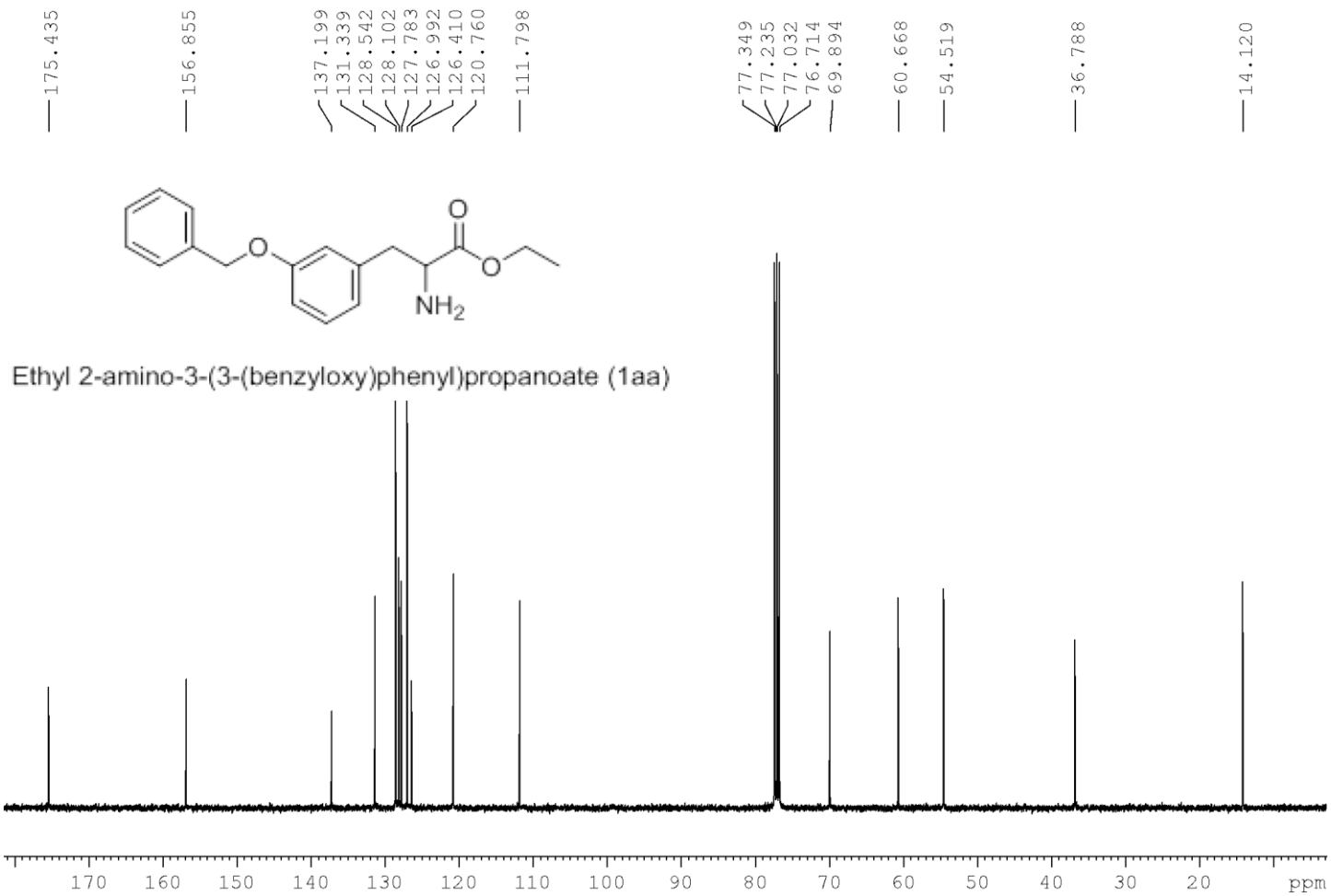

174.948
159.743
138.901
129.492
121.643
115.029
112.174
77.337
77.222
77.020
76.702
60.908
55.815
55.142
41.199
14.179
O
O
O
NH2
Ethyl 2-amino-3-(3-methoxyphenyl)propanoate (1y)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

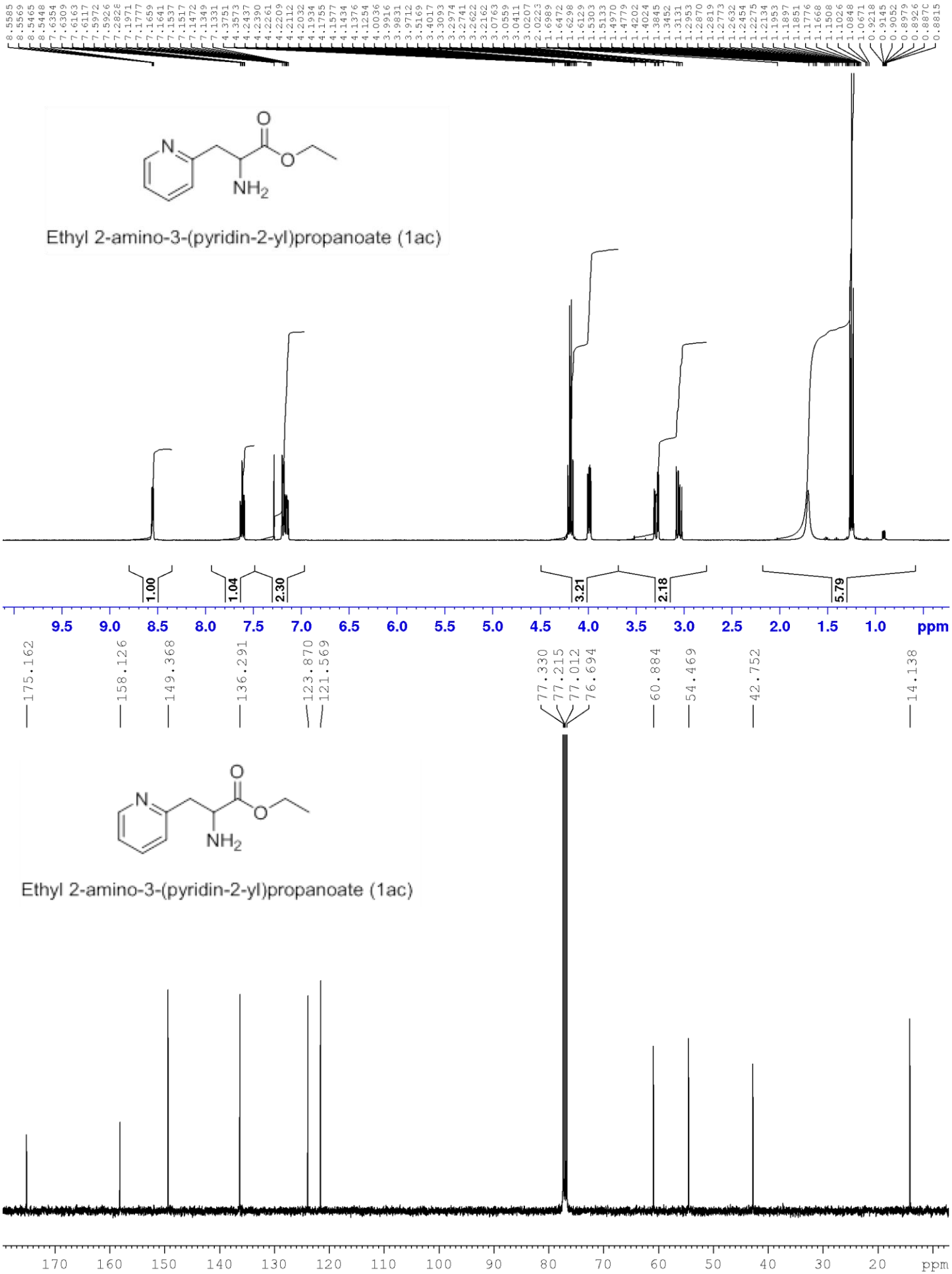


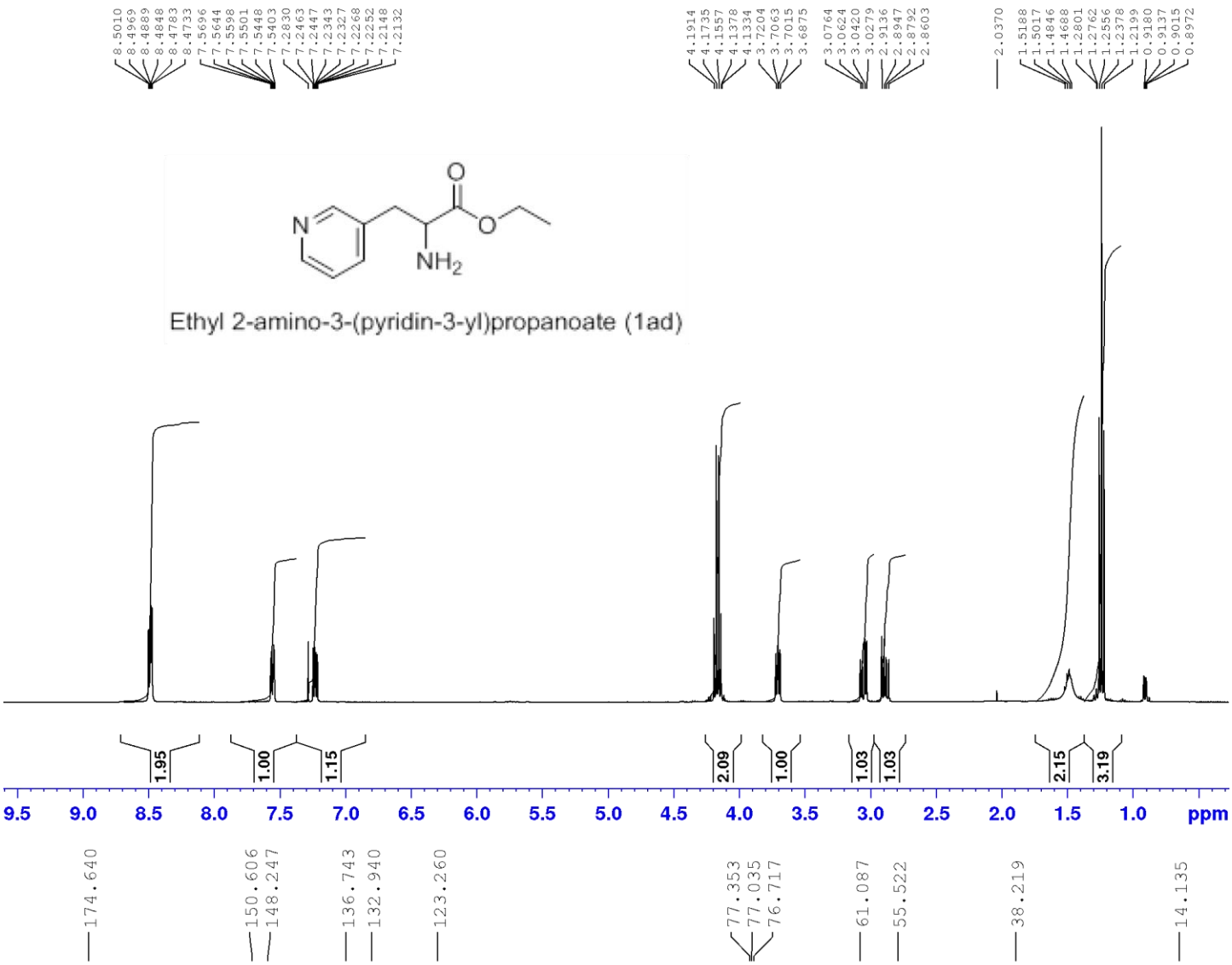


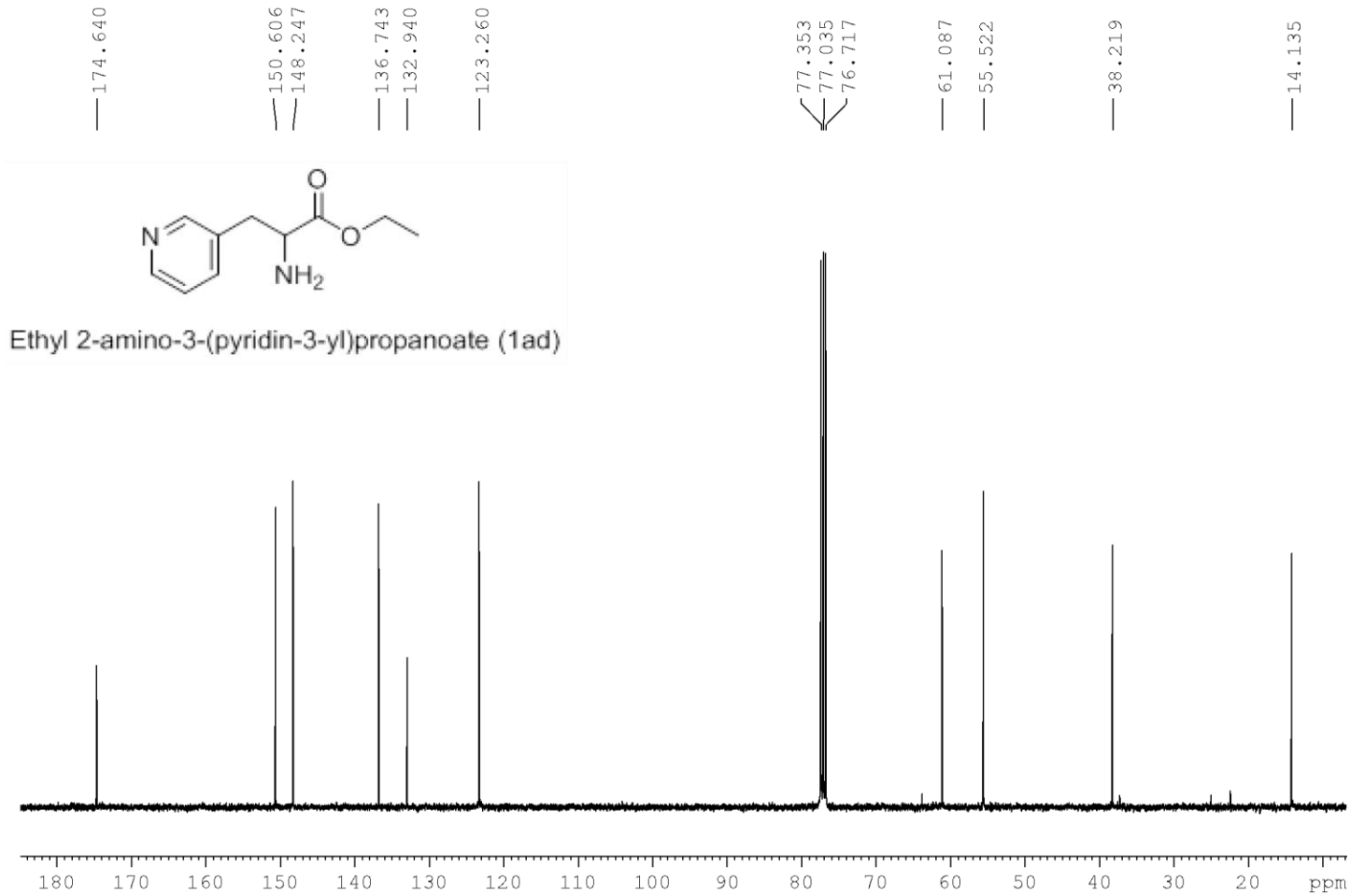
Ethyl 2-amino-3-(2-(benzyloxy)phenyl)propanoate (1z)

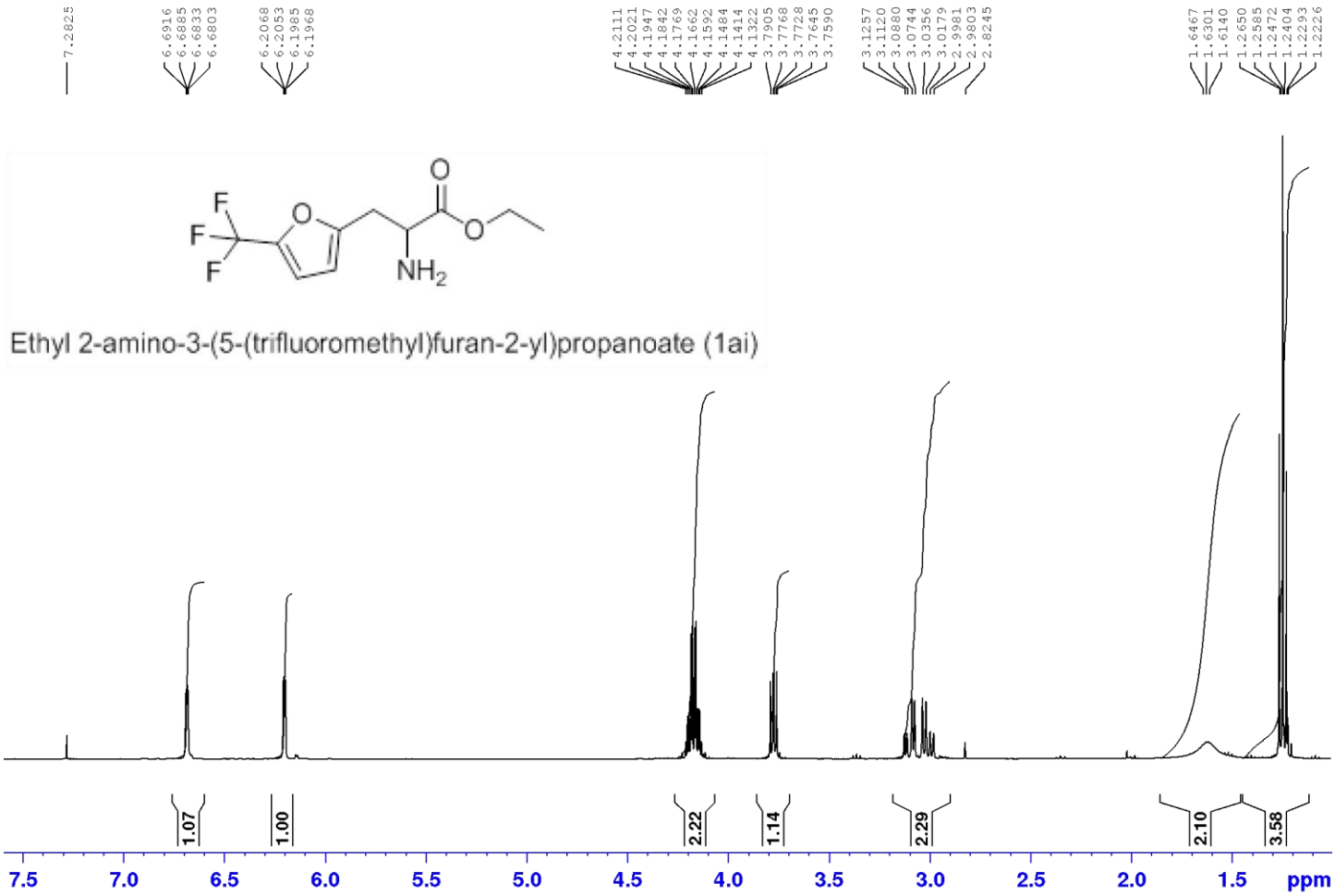

7.4892
7.4709
7.4304
7.4257
7.4126
7.4089
7.3935
7.3622
7.3499
7.3443
7.3379
7.3262
7.2826
7.2551
7.2509
7.2322
7.2161
7.2119
7.2014
7.1977
7.1831
7.1793
6.9604
6.9556
6.9376
6.9186
6.9165
5.1647
5.1327
5.1007
4.1762
4.1672
4.1584
4.1492
4.1405
4.1311
4.1301
4.1202
4.1117
4.1025
4.0938
4.0847
3.8988
3.8852
3.8776
3.8640
3.2557
3.2421
3.2225
3.2089
2.9079
2.8866
2.8747
2.8534
1.5369
1.2249
1.2070
1.1892
O
O
O
NH2
Ethyl 2-amino-3-(3-(benzyloxy)phenyl)propanoate (1aa)
7.16
2.04
2.05
2.01
1.00
1.01
1.01
2.13
2.99
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
ppm

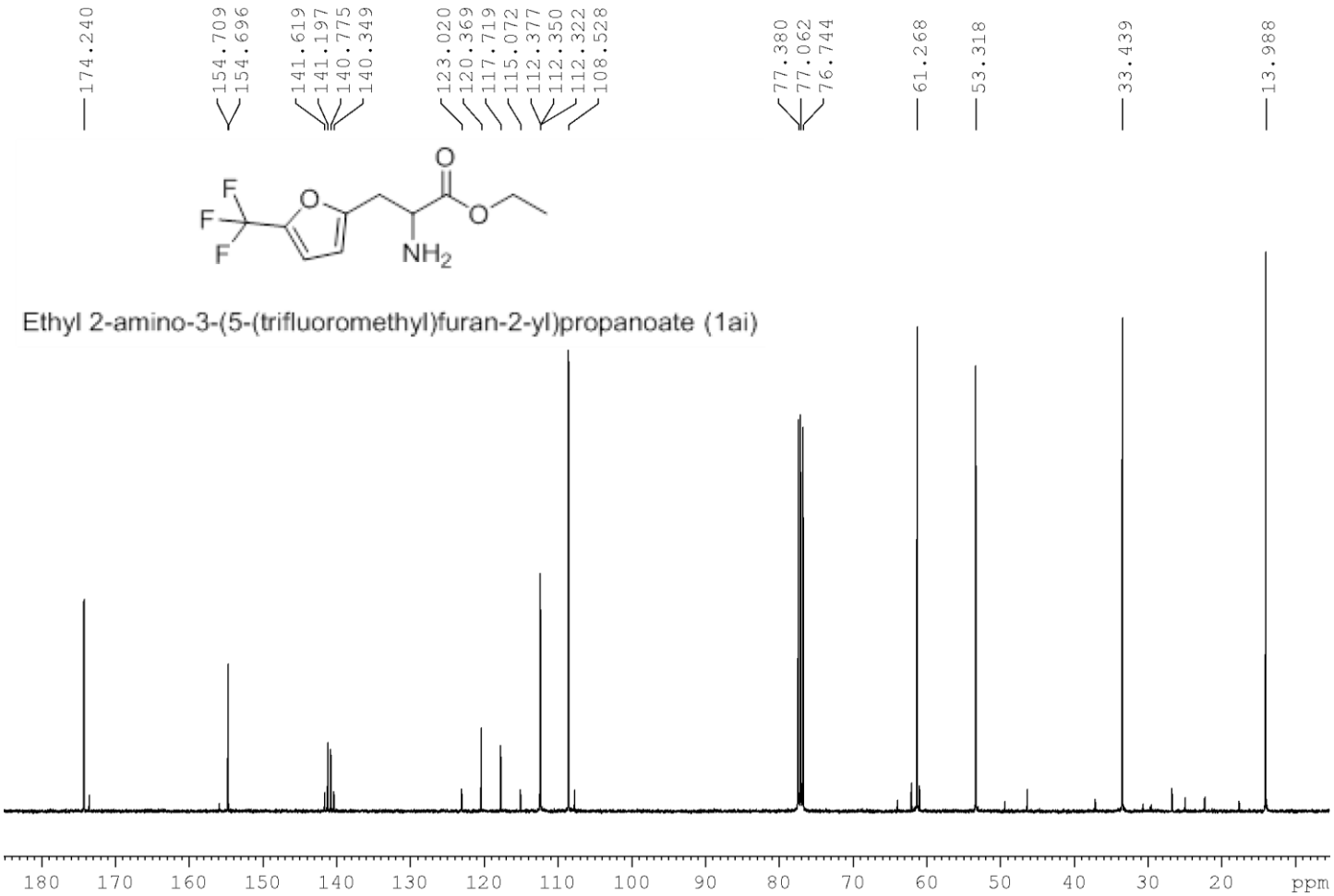

175.435
156.855
137.199
131.339
128.542
128.102
127.783
126.992
126.410
120.760
111.798
77.349
77.235
77.032
76.714
69.894
60.668
54.519
36.788
14.120
O
O
O
NH2
Ethyl 2-amino-3-(3-(benzyloxy)phenyl)propanoate (1aa)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

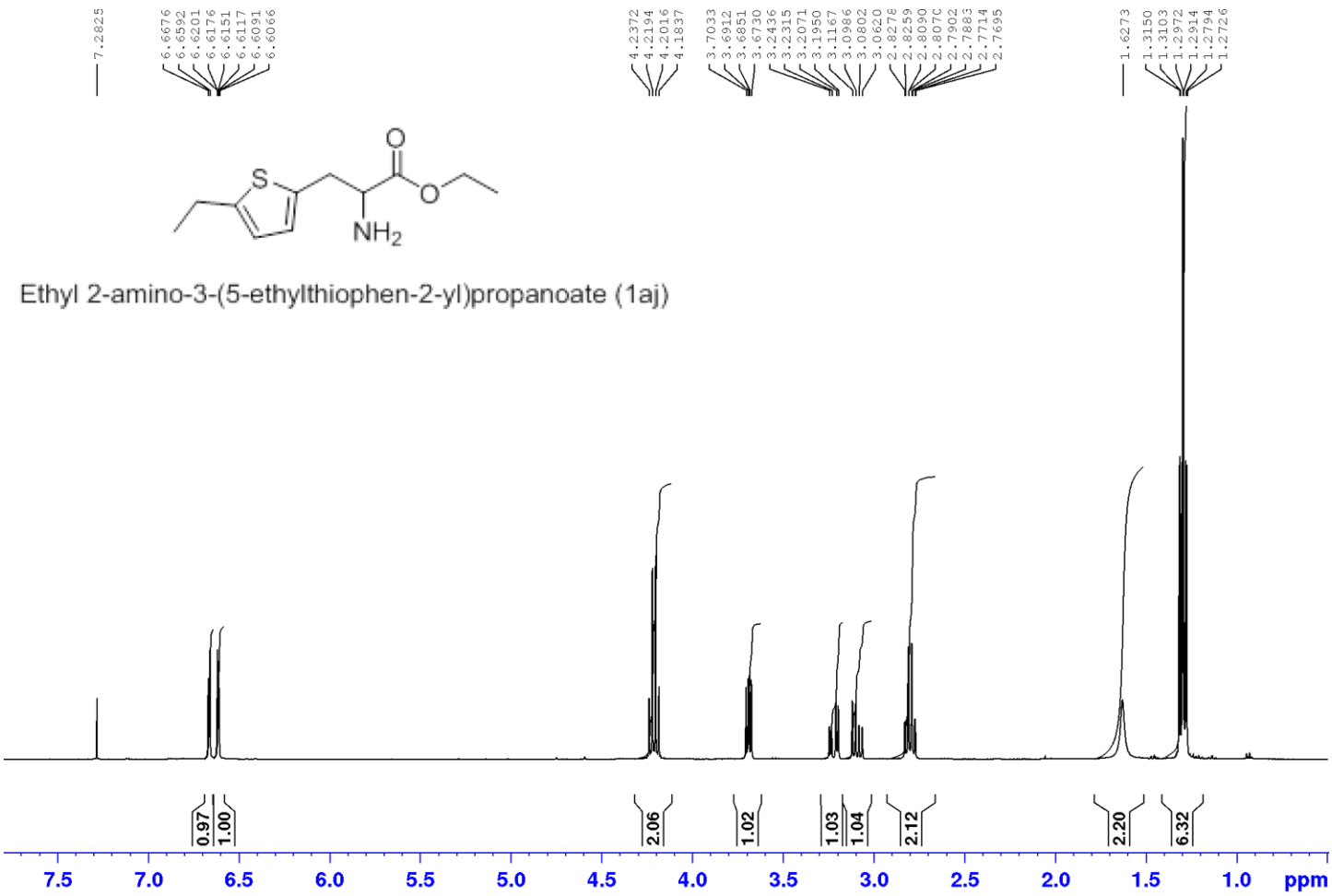

Ethyl 2-amino-3-(pyridin-2-yl)propanoate (1ac)
1.00
1.04
2.30
3.21
2.18
5.79
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
175.162
158.126
149.368
136.291
123.870
121.569
77.330
77.215
77.012
76.694
60.884
54.469
42.752
14.138
Ethyl 2-amino-3-(pyridin-2-yl)propanoate (1ac)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.5010
8.4969
8.4889
8.4848
8.4783
8.4733
7.5696
7.5644
7.5598
7.5501
7.5448
7.5403
7.2830
7.2463
7.2447
7.2343
7.2327
7.2268
7.2252
7.2148
7.2132
4.1914
4.1735
4.1557
4.1378
4.1334
3.7204
3.7063
3.7015
3.6875
3.0764
3.0624
3.0420
3.0279
2.9136
2.8947
2.8792
2.8603
2.0370
1.5188
1.5017
1.4846
1.4688
1.2801
1.2762
1.2556
1.2378
1.2199
0.9180
0.9137
0.9015
0.8972
O
N
O
NH2
Ethyl 2-amino-3-(pyridin-3-yl)propanoate (1ad)
1.95
1.00
1.15
2.09
1.00
1.03
1.03
2.15
3.19
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
ppm

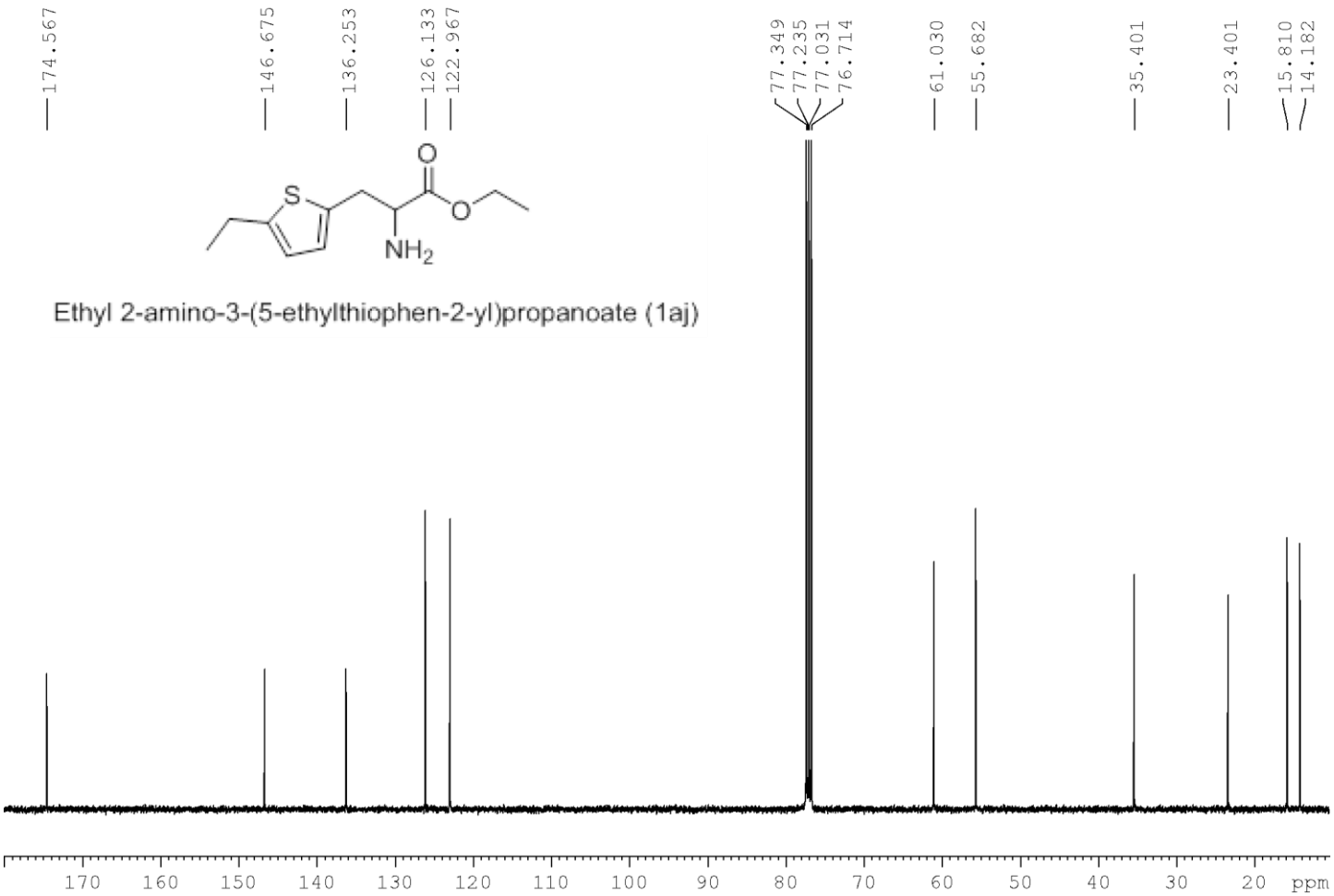

174.640
150.606
148.247
136.743
132.940
123.260
77.353
77.035
76.717
61.087
55.522
38.219
14.135
O
N
O
NH2
Ethyl 2-amino-3-(pyridin-3-yl)propanoate (1ad)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.2825
6.6916
6.6885
6.6833
6.6803
6.2068
6.2053
6.1985
6.1968
4.2111
4.2021
4.1947
4.1842
4.1769
4.1662
4.1592
4.1484
4.1414
4.1322
3.7905
3.7768
3.7728
3.7645
3.7590
3.1257
3.1120
3.0880
3.0744
3.0356
3.0179
2.9981
2.9803
2.8245
1.6467
1.6301
1.6140
1.2650
1.2585
1.2472
1.2404
1.2293
1.2226
F
F
F
O
O
O
NH2
Ethyl 2-amino-3-(5-(trifluoromethyl)furan-2-yl)propanoate (1ai)
1.07
1.00
2.22
1.14
2.29
2.10
3.58
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
ppm

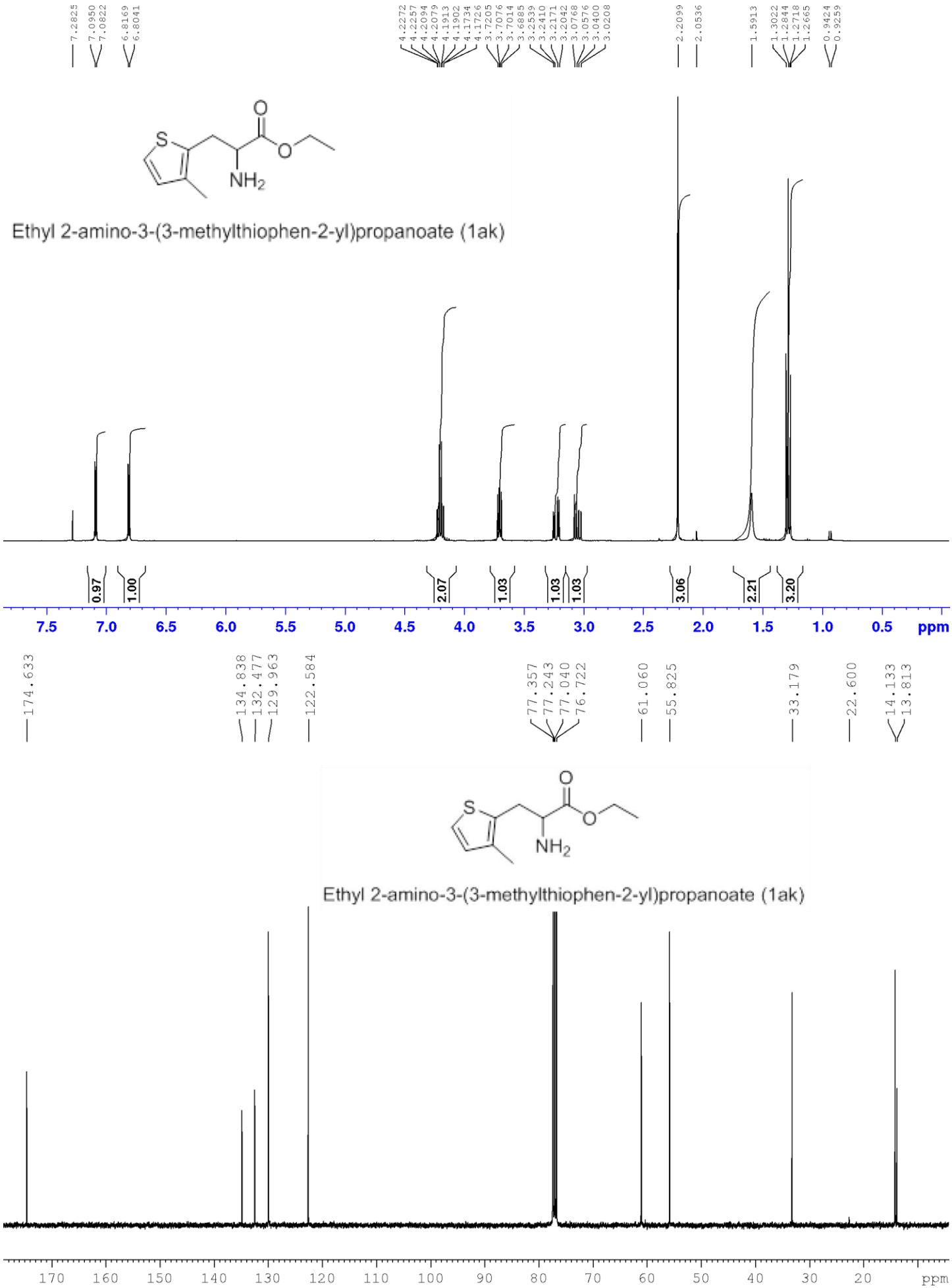

174.240
154.709
154.696
141.619
141.197
140.775
140.349
123.020
120.369
117.719
115.072
112.377
112.350
112.322
108.528
77.380
77.062
76.744
61.268
53.318
33.439
13.988
F
F
F
O
O
O
NH2
Ethyl 2-amino-3-(5-(trifluoromethyl)furan-2-yl)propanoate (1ai)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

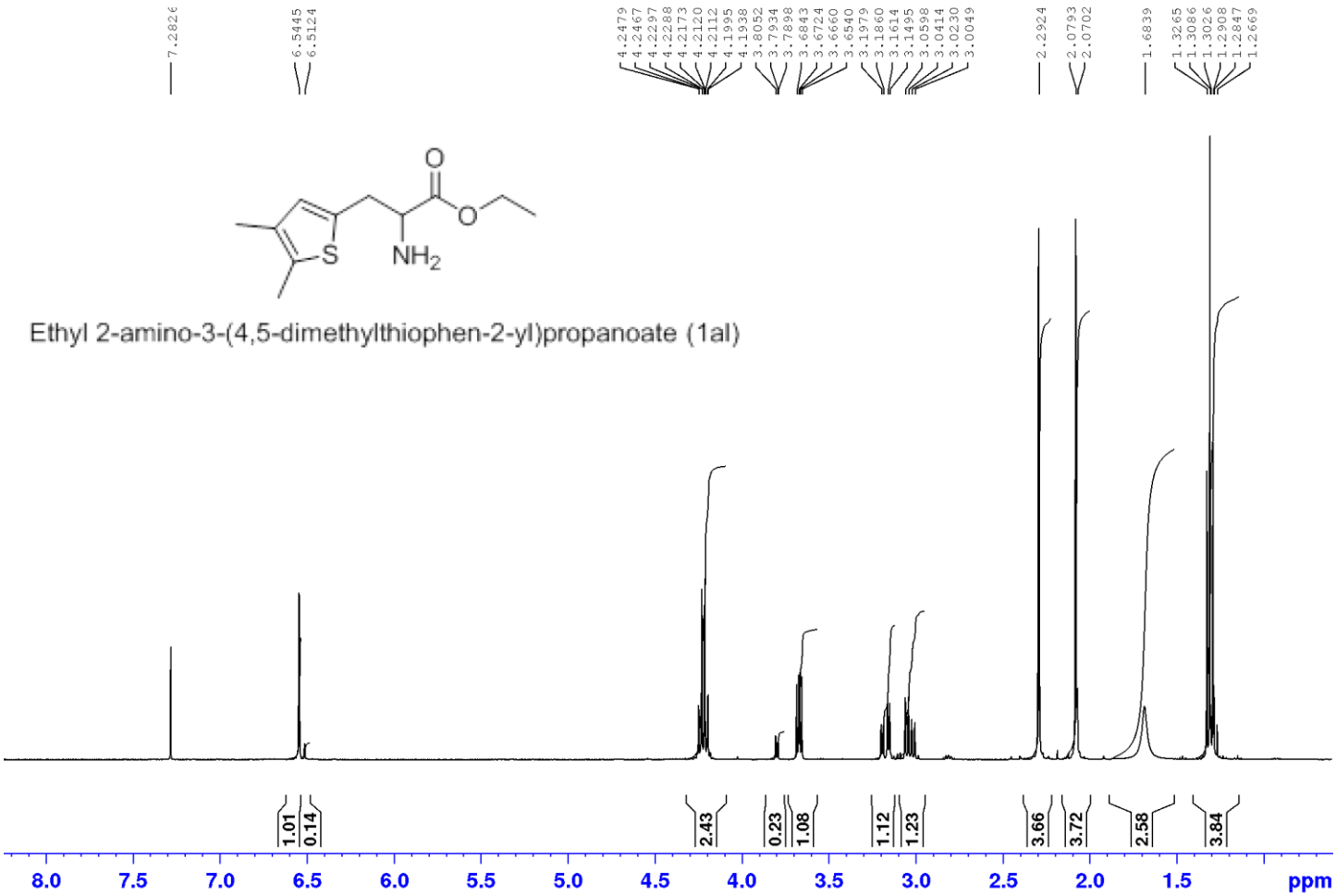


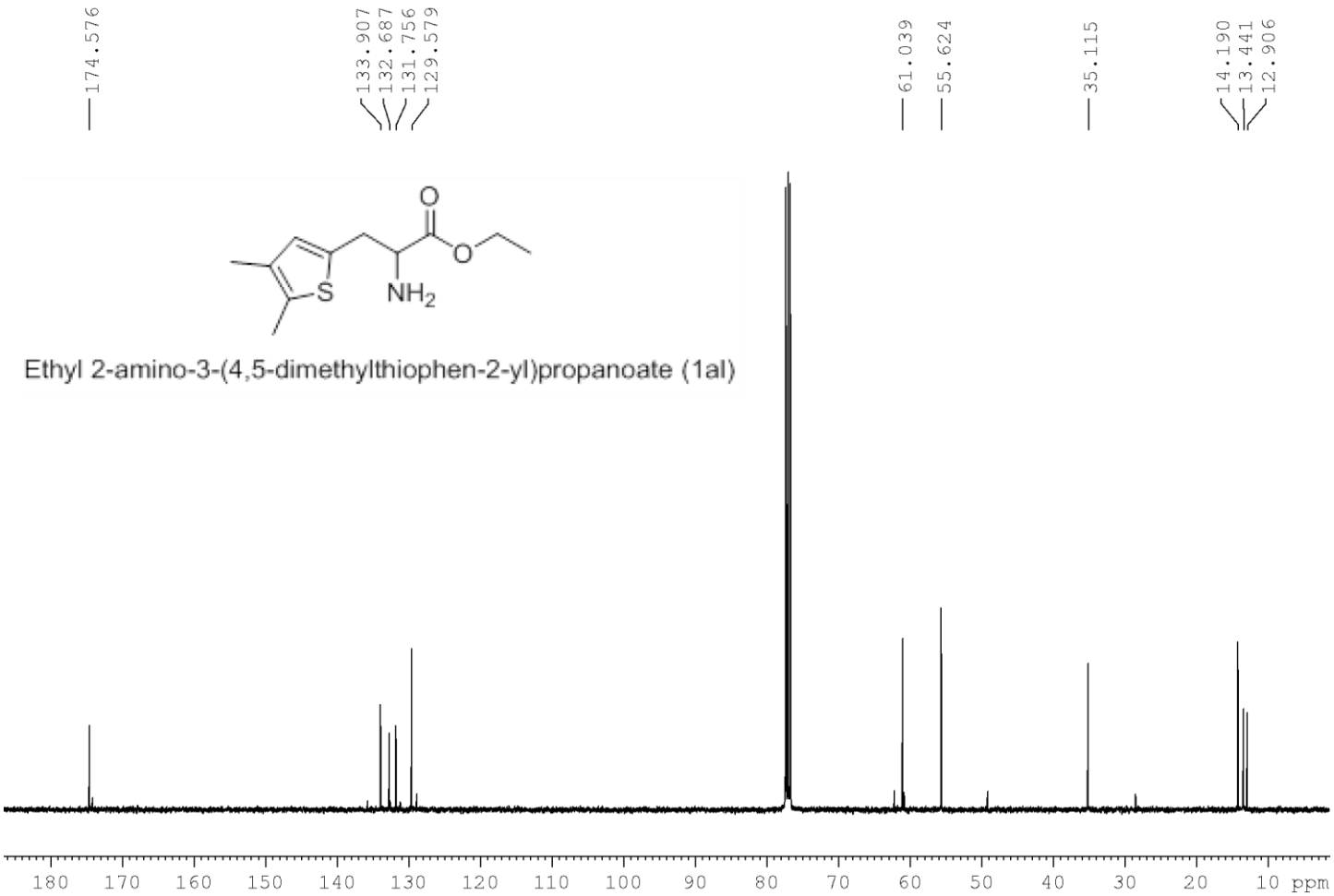
Ethyl 2-amino-3-(5-ethylthiophen-2-yl)propanoate (1aj)

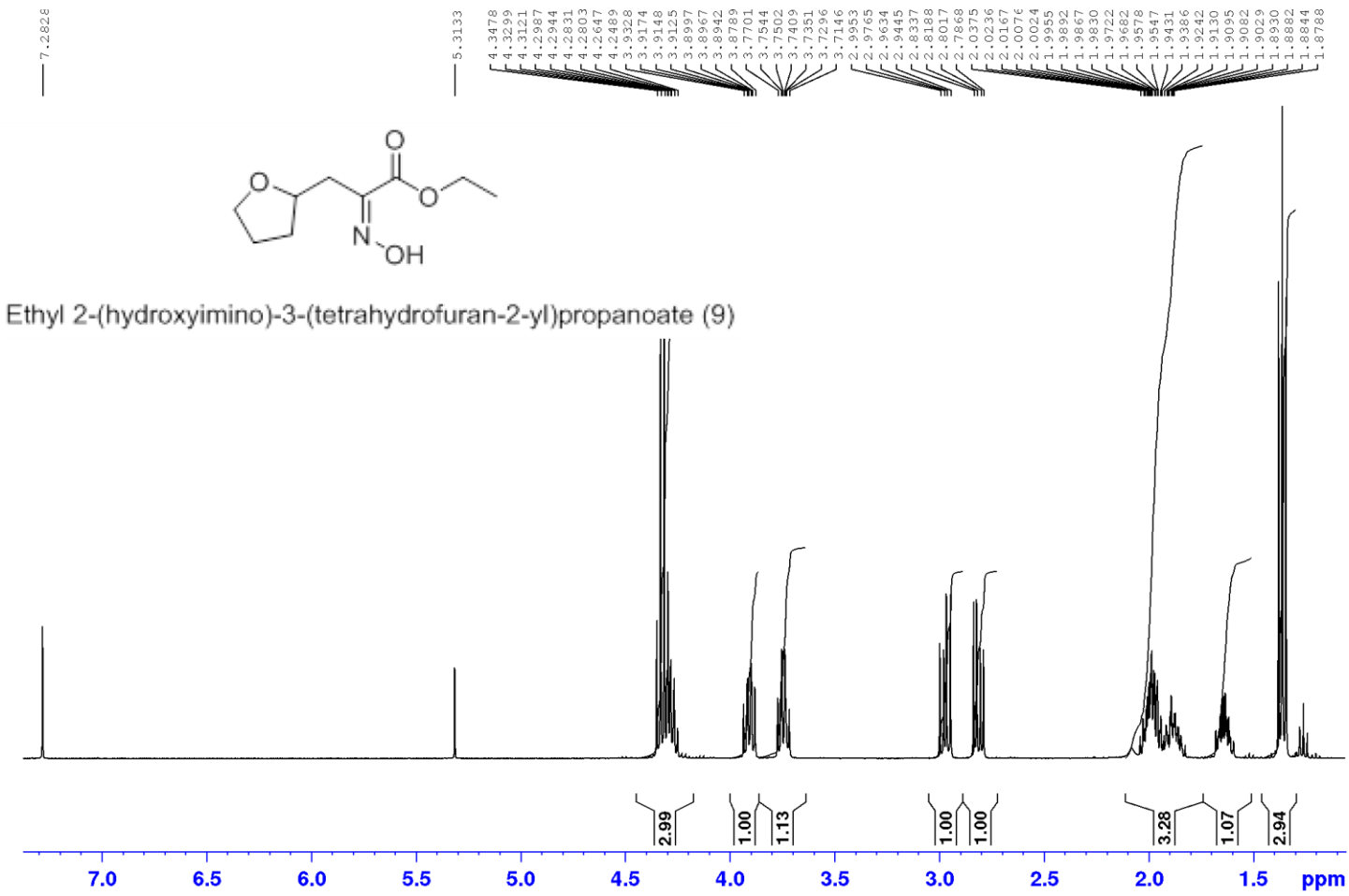


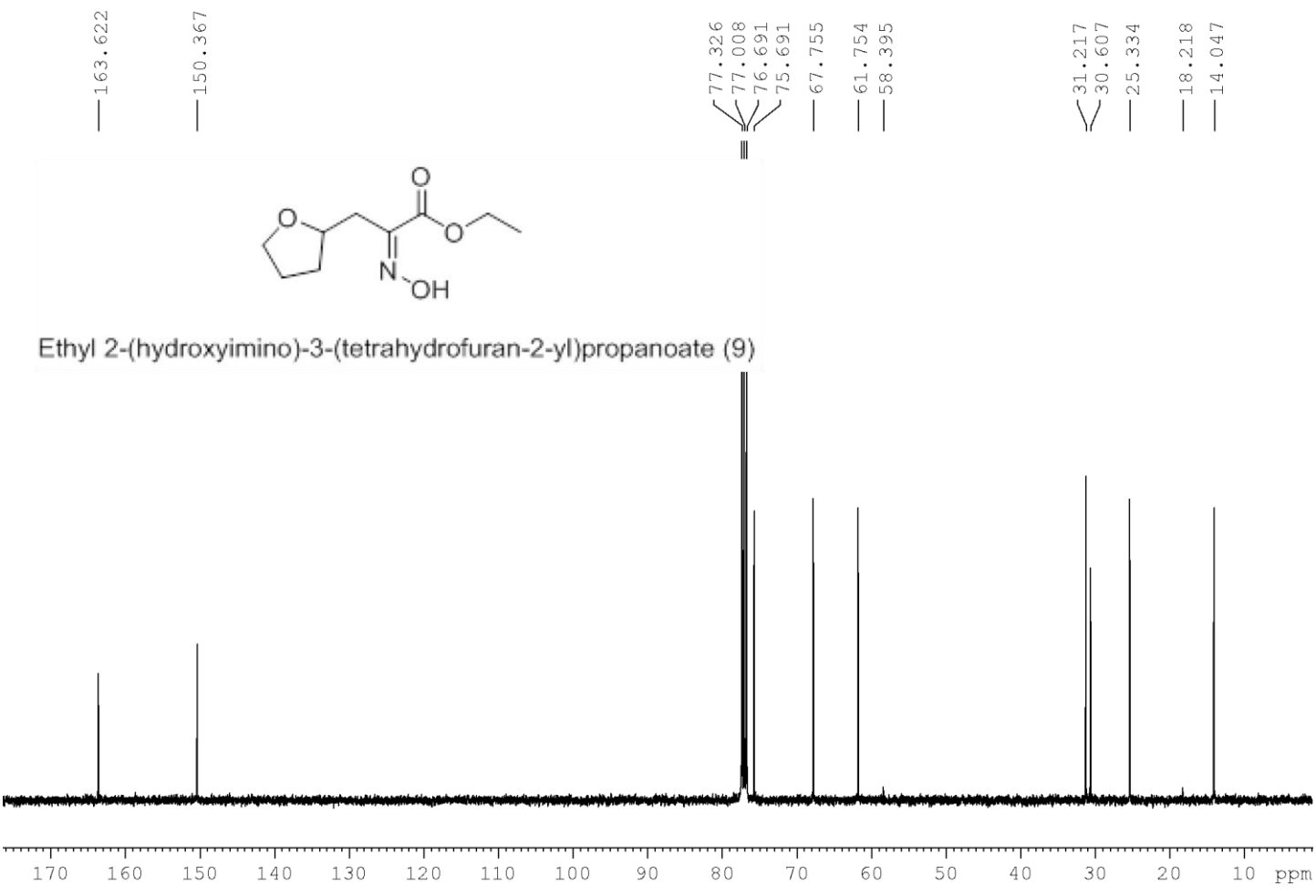
Ethyl 2-amino-3-(5-ethylthiophen-2-yl)propanoate (1aj)

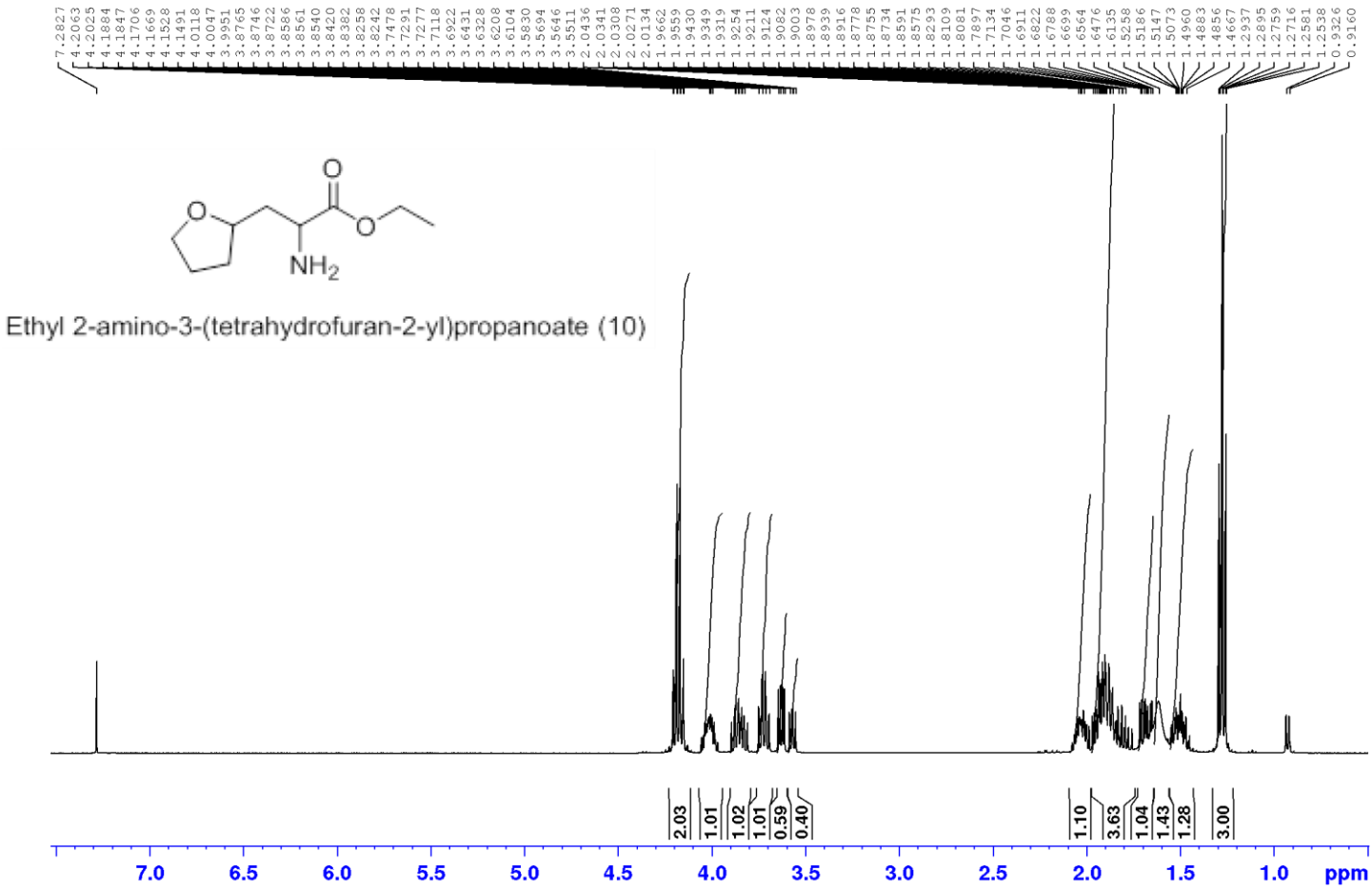

7.2825
7.0950
7.0822
6.8169
6.8041
4.2272
4.2257
4.2094
4.2079
4.1913
4.1902
4.1734
4.1726
3.7205
3.7076
3.7014
3.6885
3.2539
3.2410
3.2171
3.2042
3.0768
3.0576
3.0400
3.0208
2.2099
2.0536
1.5913
1.3022
1.2844
1.2718
1.2665
0.9424
0.9259
Ethyl 2-amino-3-(3-methylthiophen-2-yl)propanoate (1ak)
0.97
1.00
2.07
1.03
1.03
1.03
3.06
2.21
3.20
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
ppm
174.633
134.838
132.477
129.963
122.584
77.357
77.243
77.040
76.722
61.060
55.825
33.179
22.600
14.133
13.813
Ethyl 2-amino-3-(3-methylthiophen-2-yl)propanoate (1ak)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

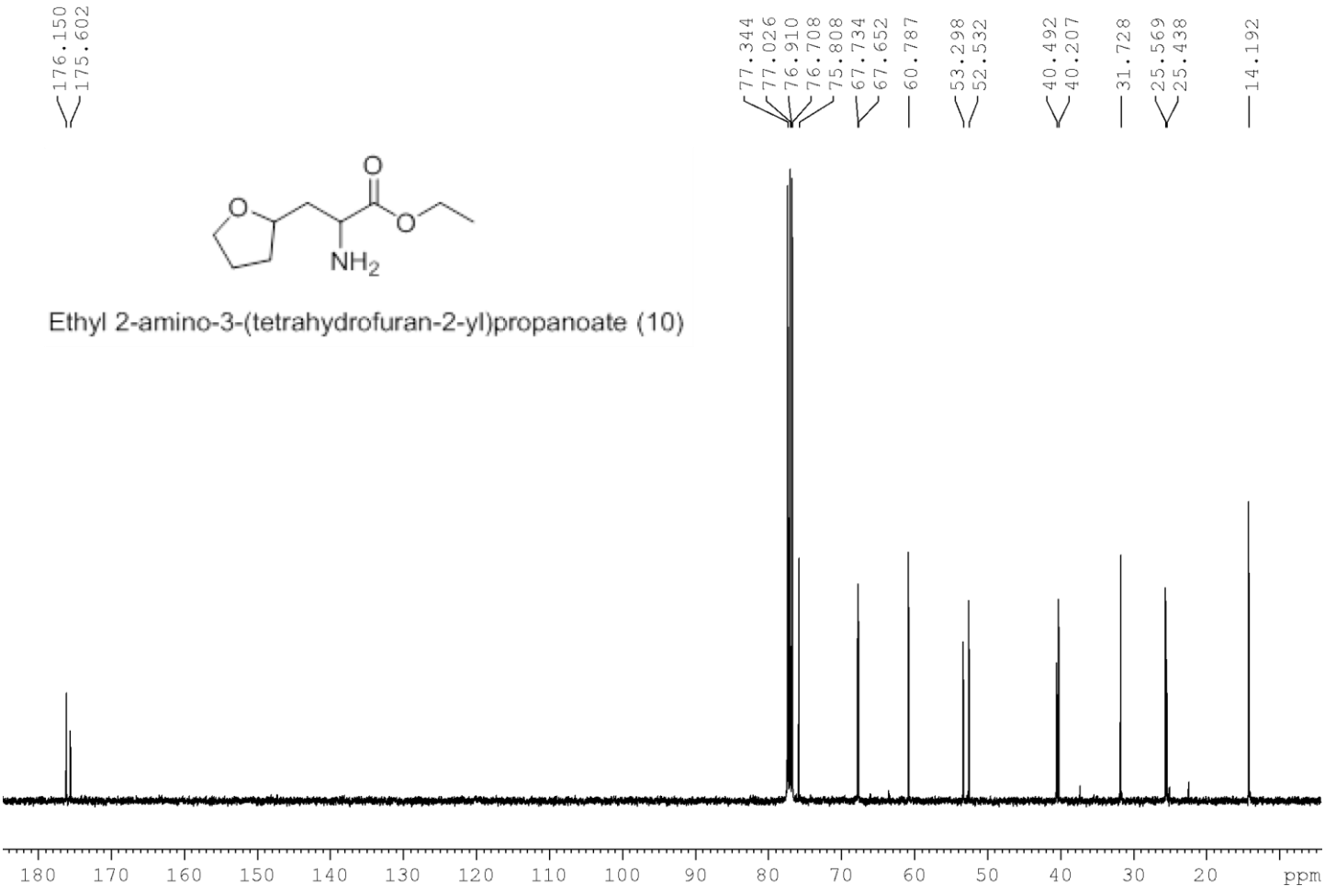

7.2826
6.5445
6.5124
4.2479
4.2467
4.2297
4.2288
4.2173
4.2120
4.2112
4.1995
4.1938
3.8052
3.7934
3.7898
3.6843
3.6724
3.6660
3.6540
3.1979
3.1860
3.1614
3.1495
3.0598
3.0414
3.0230
3.0049
2.2924
2.0793
2.0702
1.6839
1.3265
1.3086
1.3026
1.2908
1.2847
1.2669
O
O
S
NH2
Ethyl 2-amino-3-(4,5-dimethylthiophen-2-yl)propanoate (1al)
1.01
0.14
2.43
0.23
1.08
1.12
1.23
3.66
3.72
2.58
3.84
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
ppm

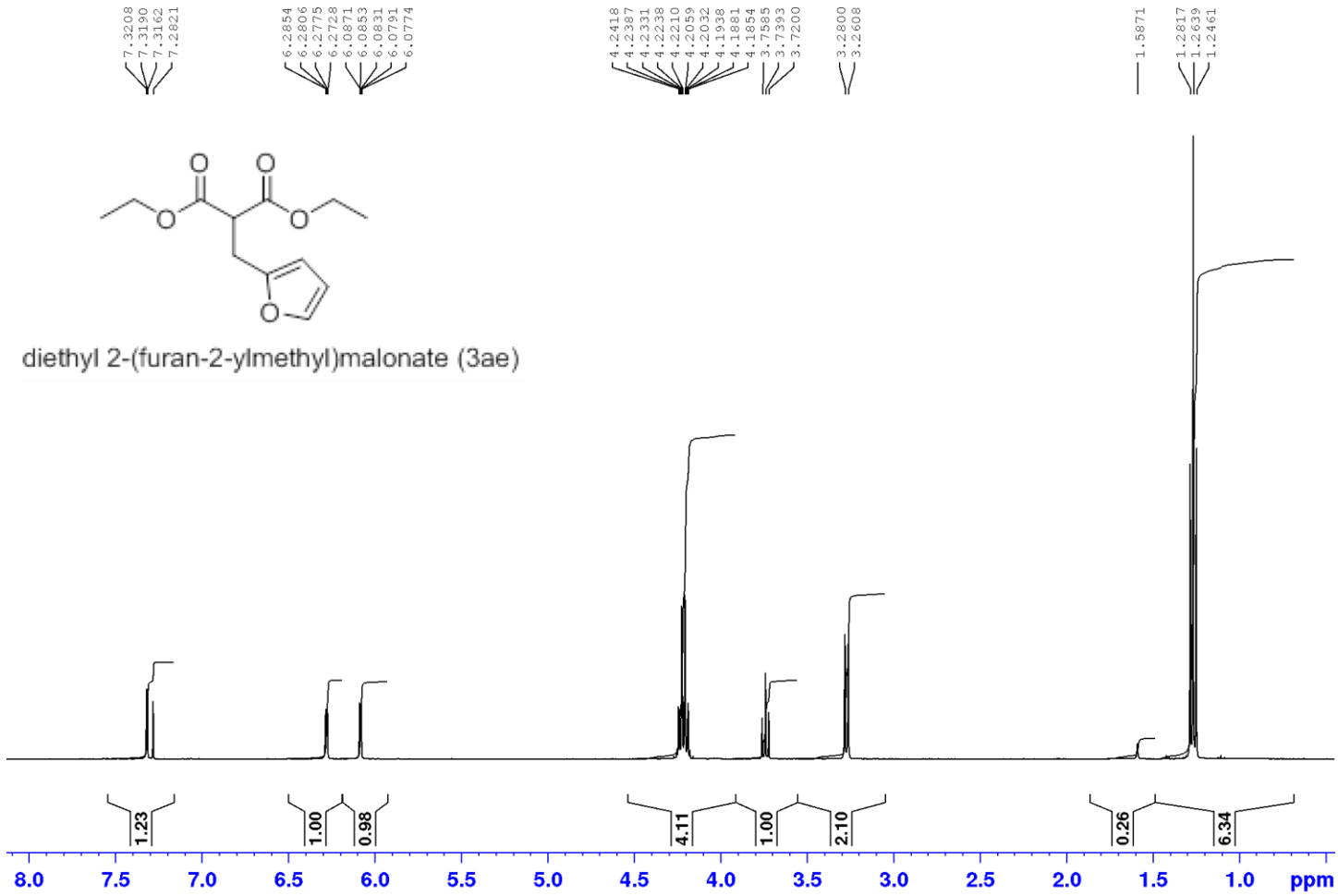

174.576
133.907
132.687
131.756
129.579
61.039
55.624
35.115
14.190
13.441
12.906
O
O
S
NH2
Ethyl 2-amino-3-(4,5-dimethylthiophen-2-yl)propanoate (1al)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

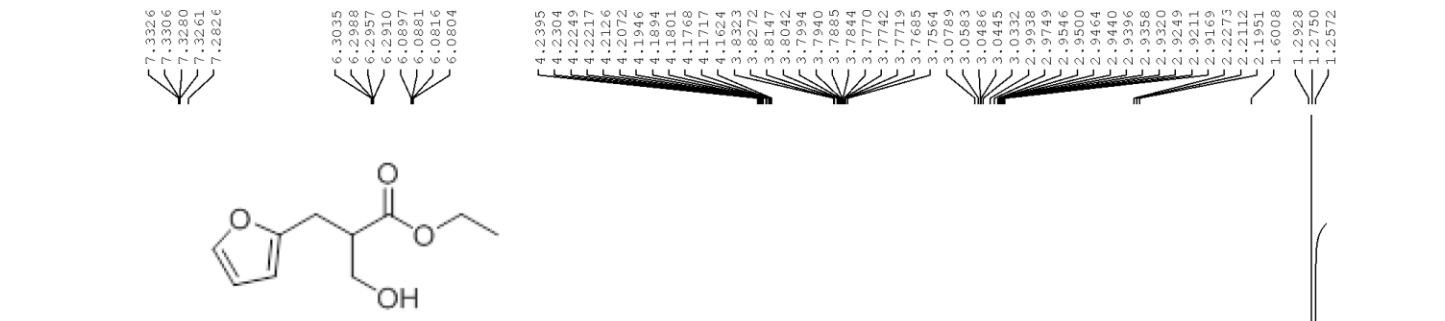

7.2828
5.3133
4.3478
4.3299
4.3121
4.2987
4.2944
4.2831
4.2803
4.2647
4.2489
3.9328
3.9174
3.9148
3.9125
3.8997
3.8967
3.8942
3.8789
3.7701
3.7544
3.7502
3.7409
3.7351
3.7296
3.7146
2.9953
2.9765
2.9634
2.9445
2.8337
2.8188
2.8017
2.7868
2.0375
2.0236
2.0167
2.0024
1.9955
1.9892
1.9867
1.9830
1.9722
1.9682
1.9578
1.9547
1.9431
1.9386
1.9242
1.9130
1.9095
1.9082
1.9029
1.8930
1.8882
1.8844
1.8788
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(tetrahydrofuran-2-yl)propanoate (9)
2.99
1.00
1.13
1.00
1.00
3.28
1.07
2.94
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


163.622
150.367
77.326
77.008
76.691
75.691
67.755
61.754
58.395
31.217
30.607
25.334
18.218
14.047
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(tetrahydrofuran-2-yl)propanoate (9)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

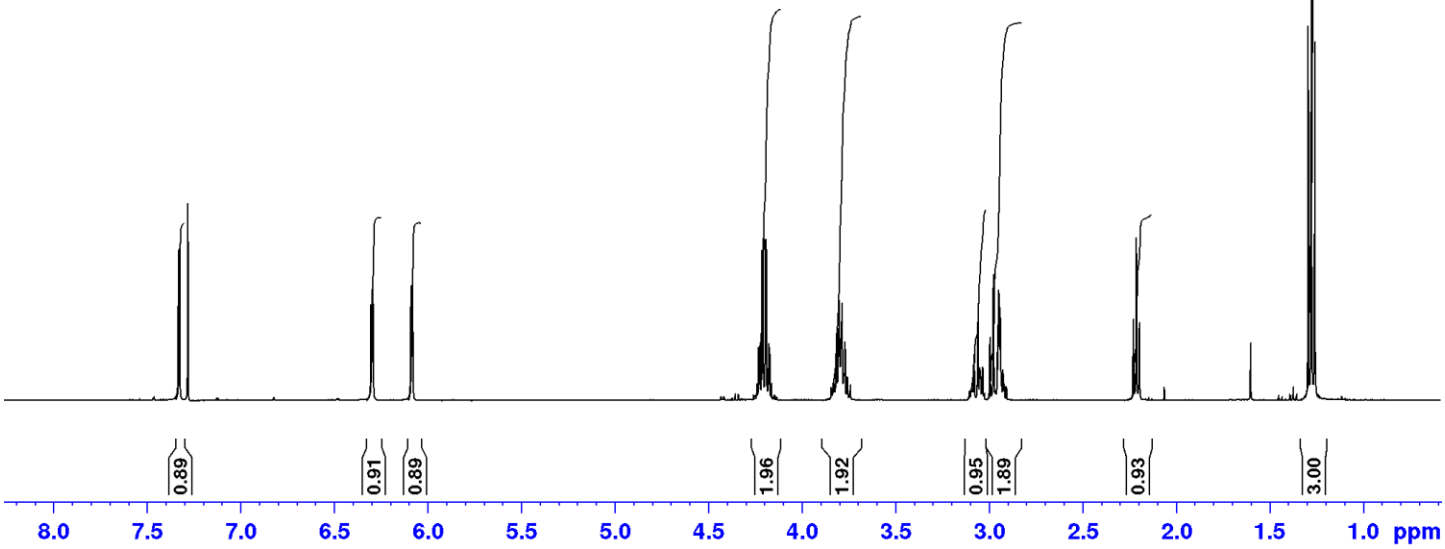

Ethyl 2-amino-3-(tetrahydrofuran-2-yl)propanoate (10)
2.03
1.01
1.02
1.01
0.59
0.40
1.10
3.63
1.04
1.43
1.28
3.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

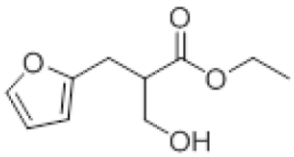

Ethyl 2-amino-3-(tetrahydrofuran-2-yl)propanoate (10)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.3208
7.3190
7.3162
7.2821
6.2854
6.2806
6.2775
6.2728
6.0871
6.0853
6.0831
6.0791
6.0774
4.2418
4.2387
4.2331
4.2238
4.2210
4.2059
4.2032
4.1938
4.1881
4.1854
3.7585
3.7393
3.7200
3.2800
3.2608
1.5871
1.2817
1.2639
1.2461
diethyl 2-(furan-2-ylmethyl)malonate (3ae)
1.23
1.00
0.98
4.11
1.00
2.10
0.26
6.34
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
ppm

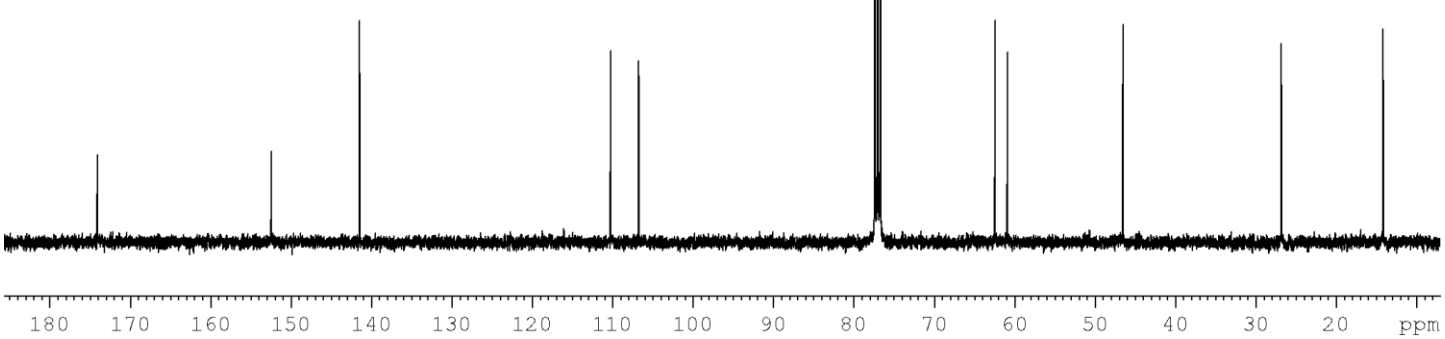


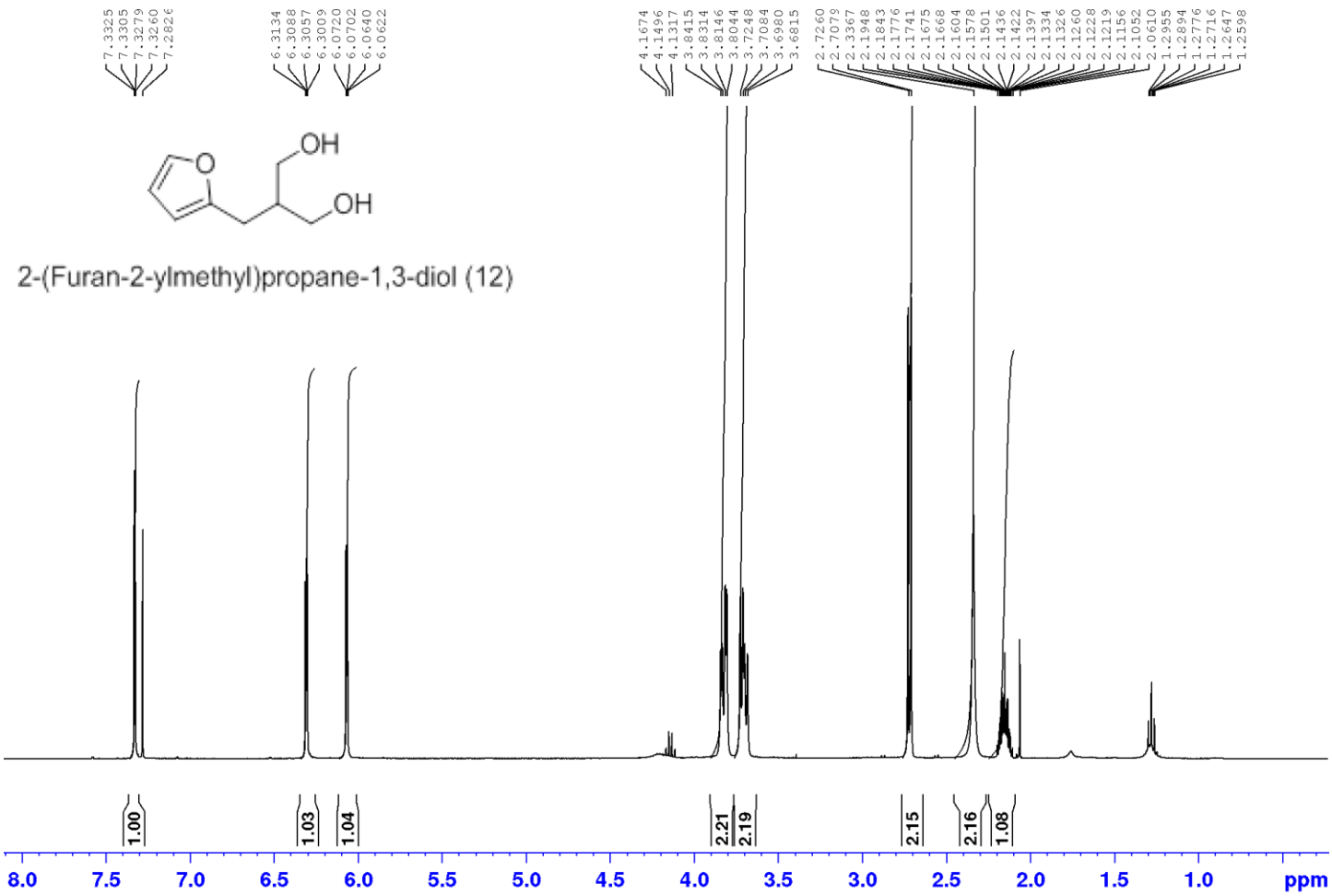
Ethyl 3-(furan-2-yl)-2-(hydroxymethyl)propanoate (11)

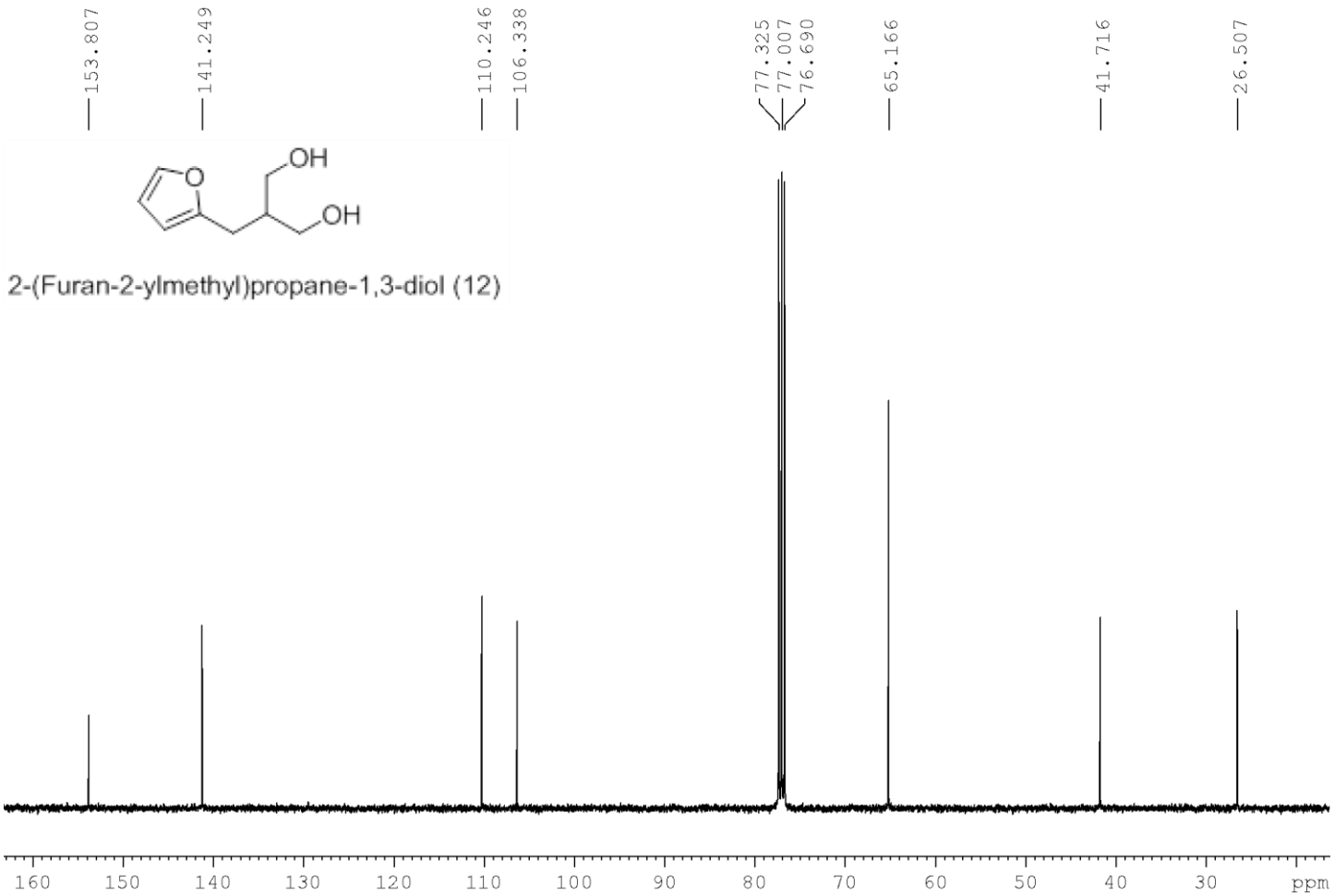


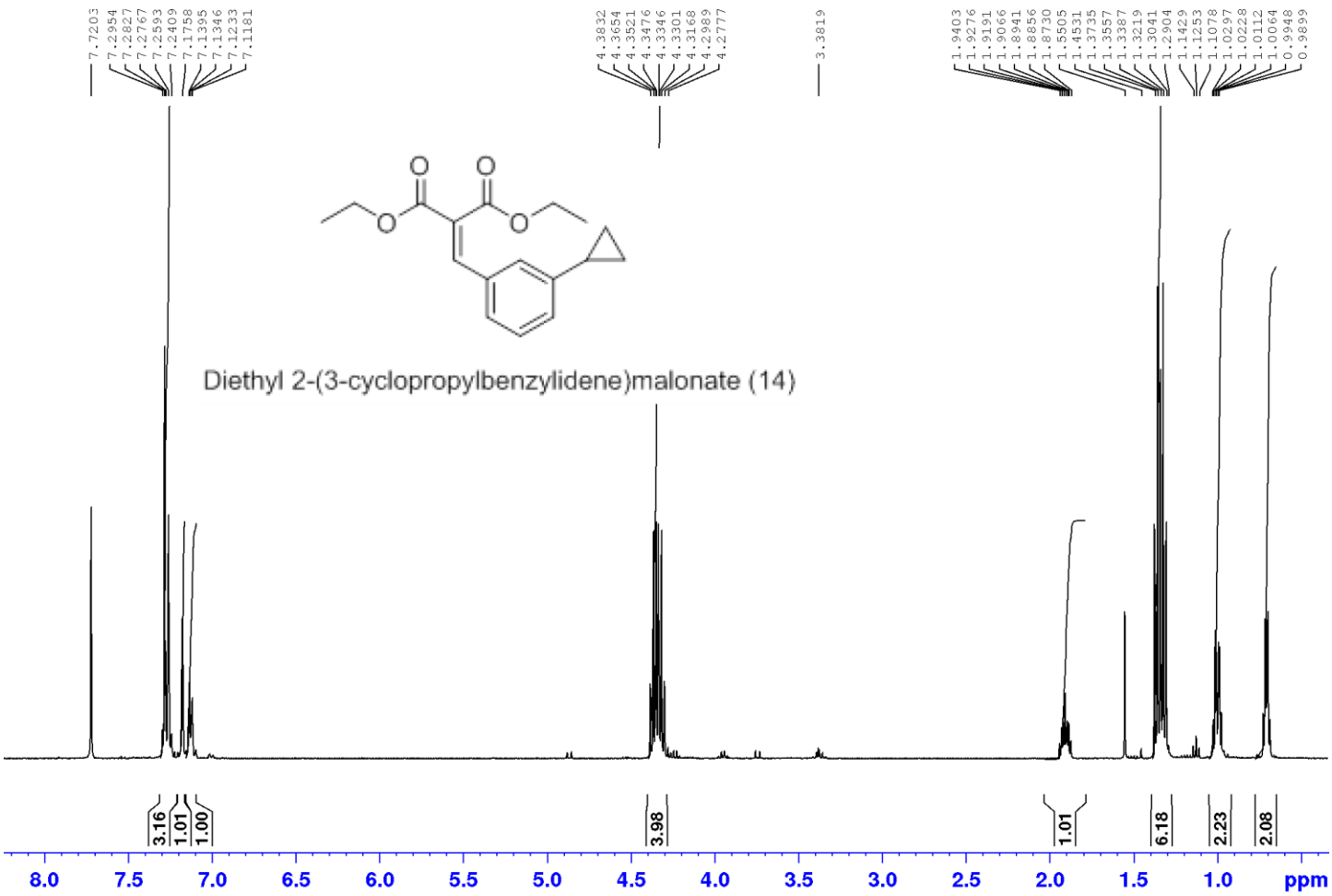


Ethyl 3-(furan-2-yl)-2-(hydroxymethyl)propanoate (11)

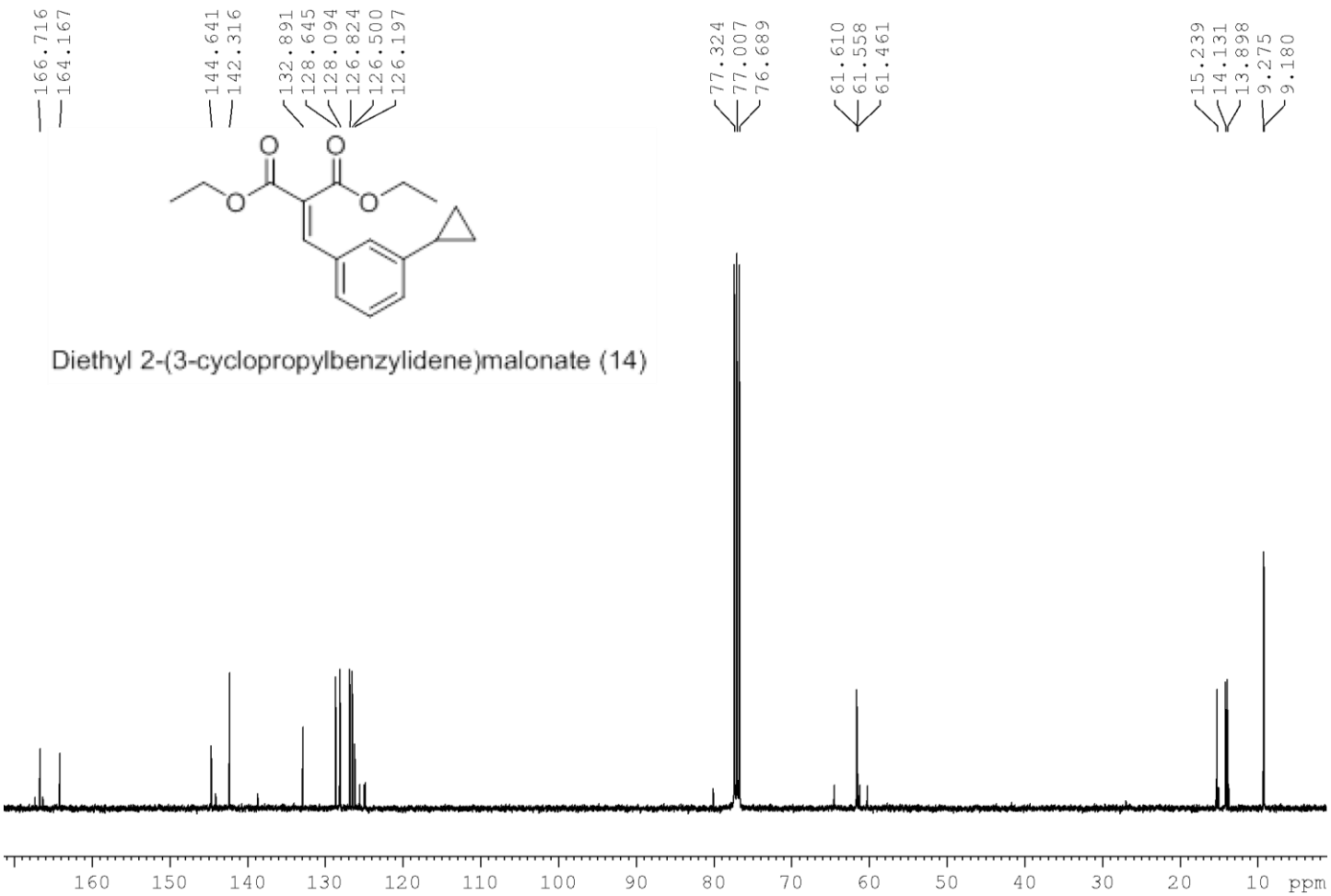



7.3325
7.3305
7.3279
7.3260
7.2826
6.3134
6.3088
6.3057
6.3009
6.0720
6.0702
6.0640
6.0622
4.1674
4.1496
4.1317
3.8415
3.8314
3.8146
3.8044
3.7248
3.7084
3.6980
3.6815
2.7260
2.7079
2.3367
2.1948
2.1843
2.1776
2.1741
2.1675
2.1668
2.1604
2.1578
2.1501
2.1436
2.1422
2.1397
2.1334
2.1326
2.1260
2.1228
2.1219
2.1156
2.1052
2.0610
1.2955
1.2894
1.2776
1.2716
1.2647
1.2598
OH
OH
O
2-(Furan-2-ylmethyl)propane-1,3-diol (12)
1.00
1.03
1.04
2.21
2.19
2.15
2.16
1.08
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
ppm

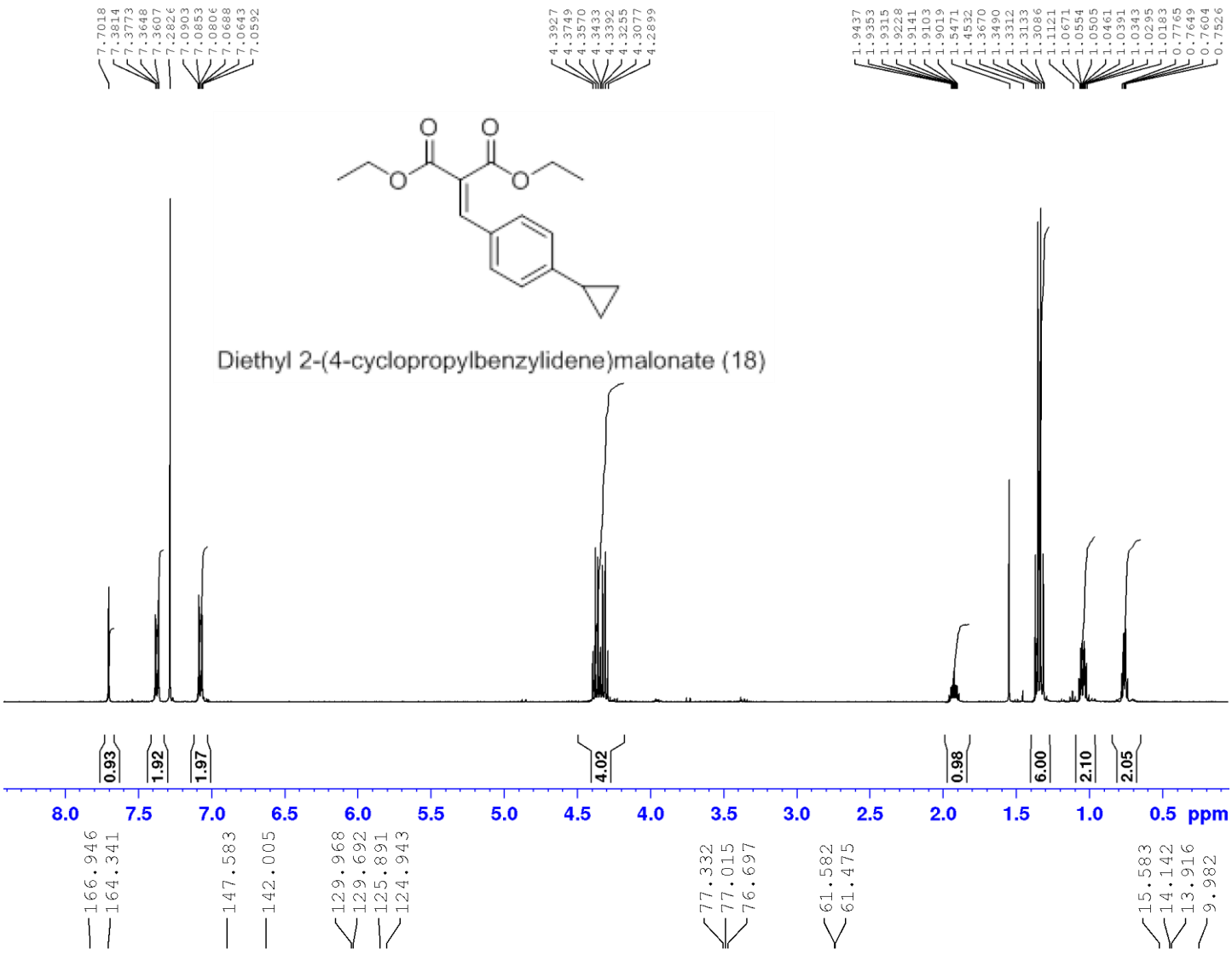

153.807
141.249
110.246
106.338
77.325
77.007
76.690
65.166
41.716
26.507
OH
OH
O
2-(Furan-2-ylmethyl)propane-1,3-diol (12)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

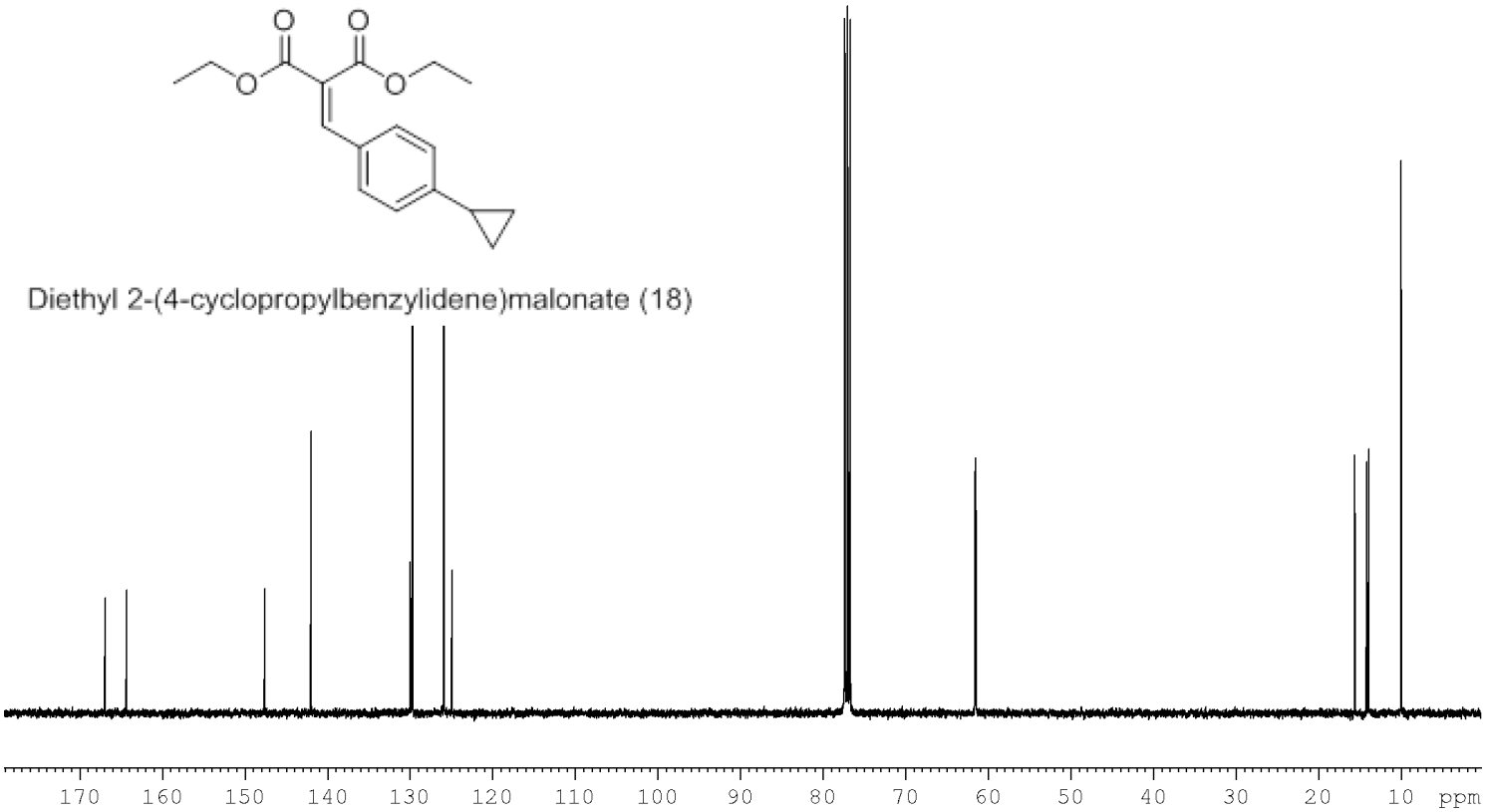


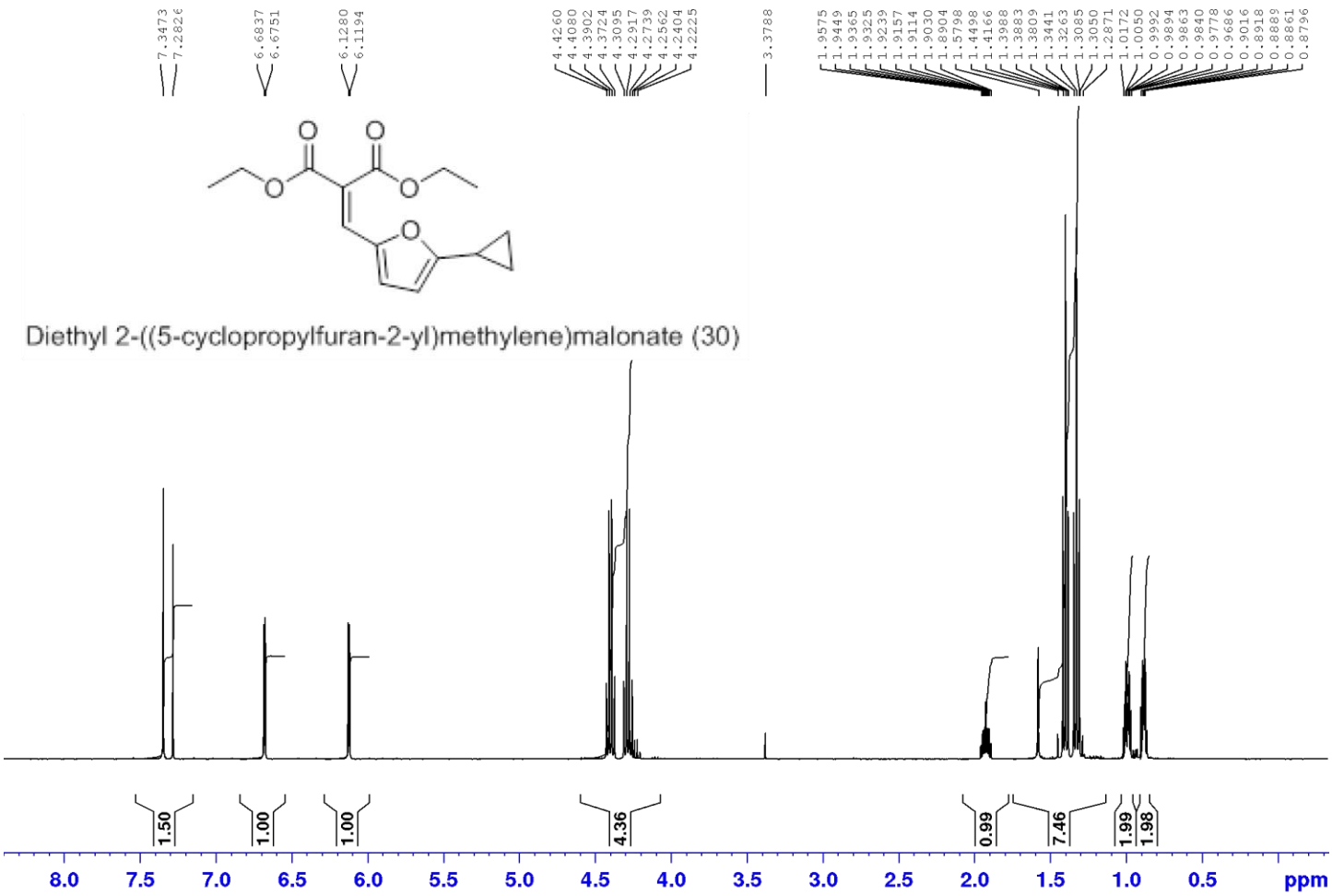
Diethyl 2-(3-cyclopropylbenzylidene)malonate (14)



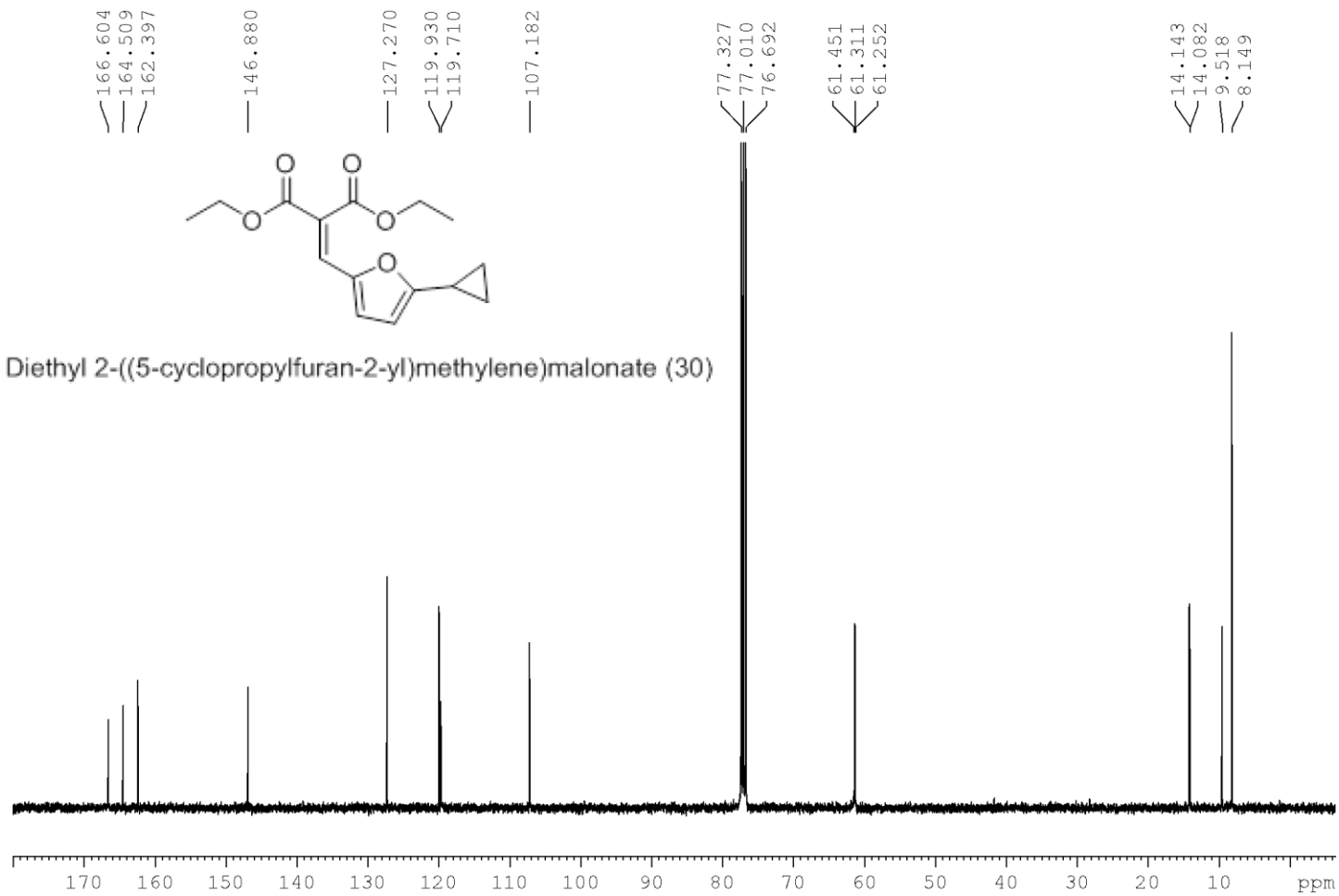
Diethyl 2-(3-cyclopropylbenzylidene)malonate (14)


Diethyl 2-(4-cyclopropylbenzylidene)malonate (18)
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 ppm

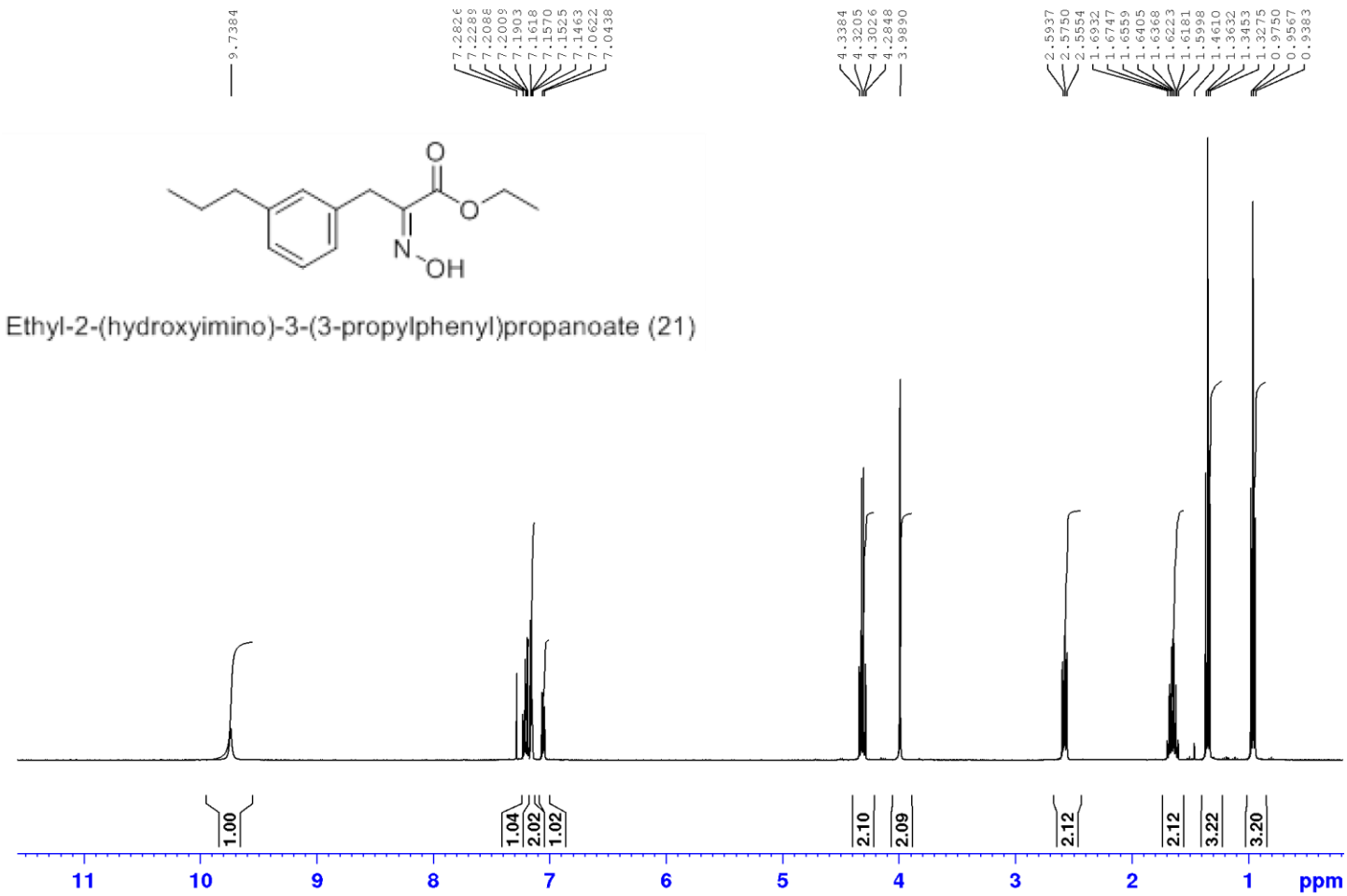

Diethyl 2-(4-cyclopropylbenzylidene)malonate (18)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

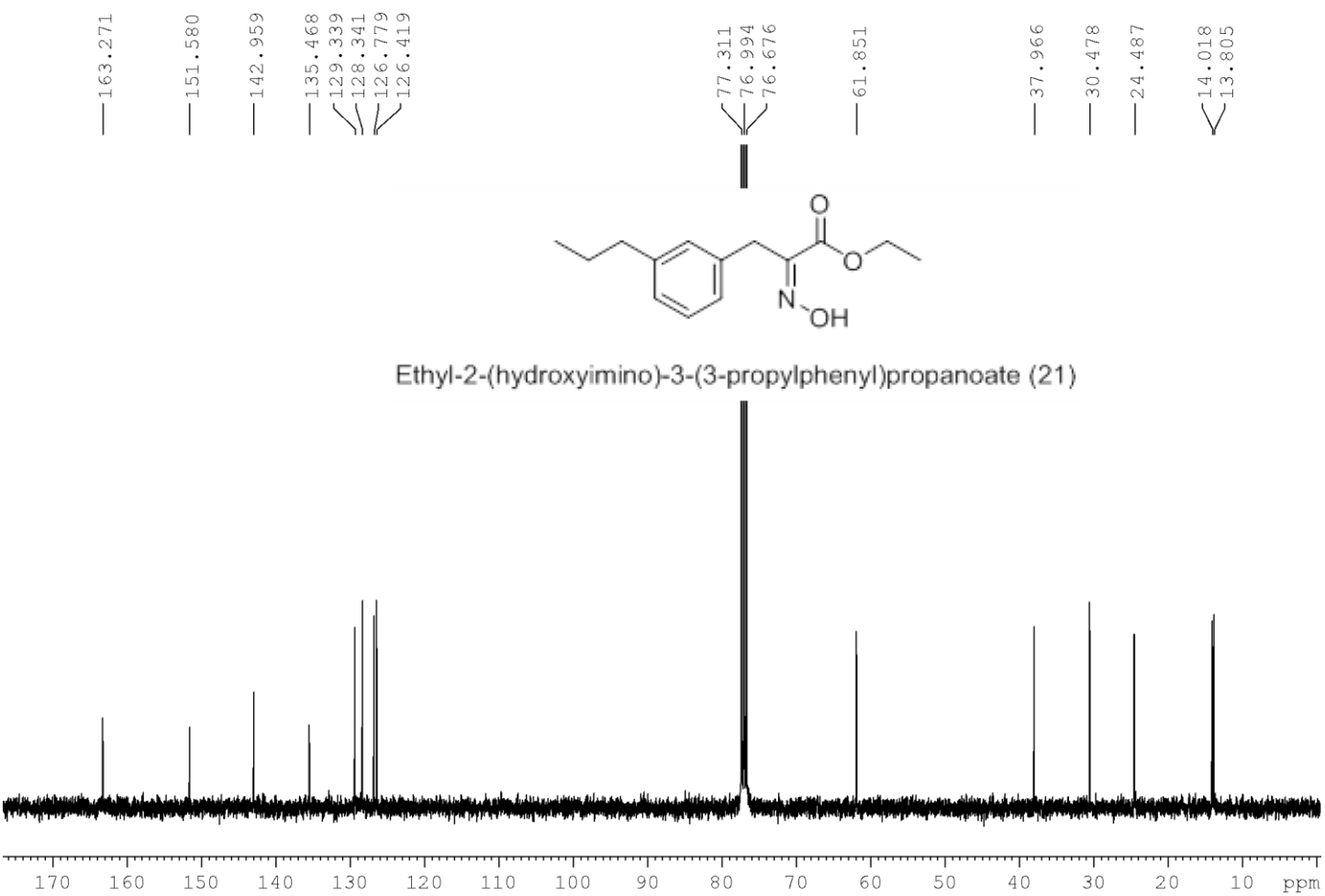


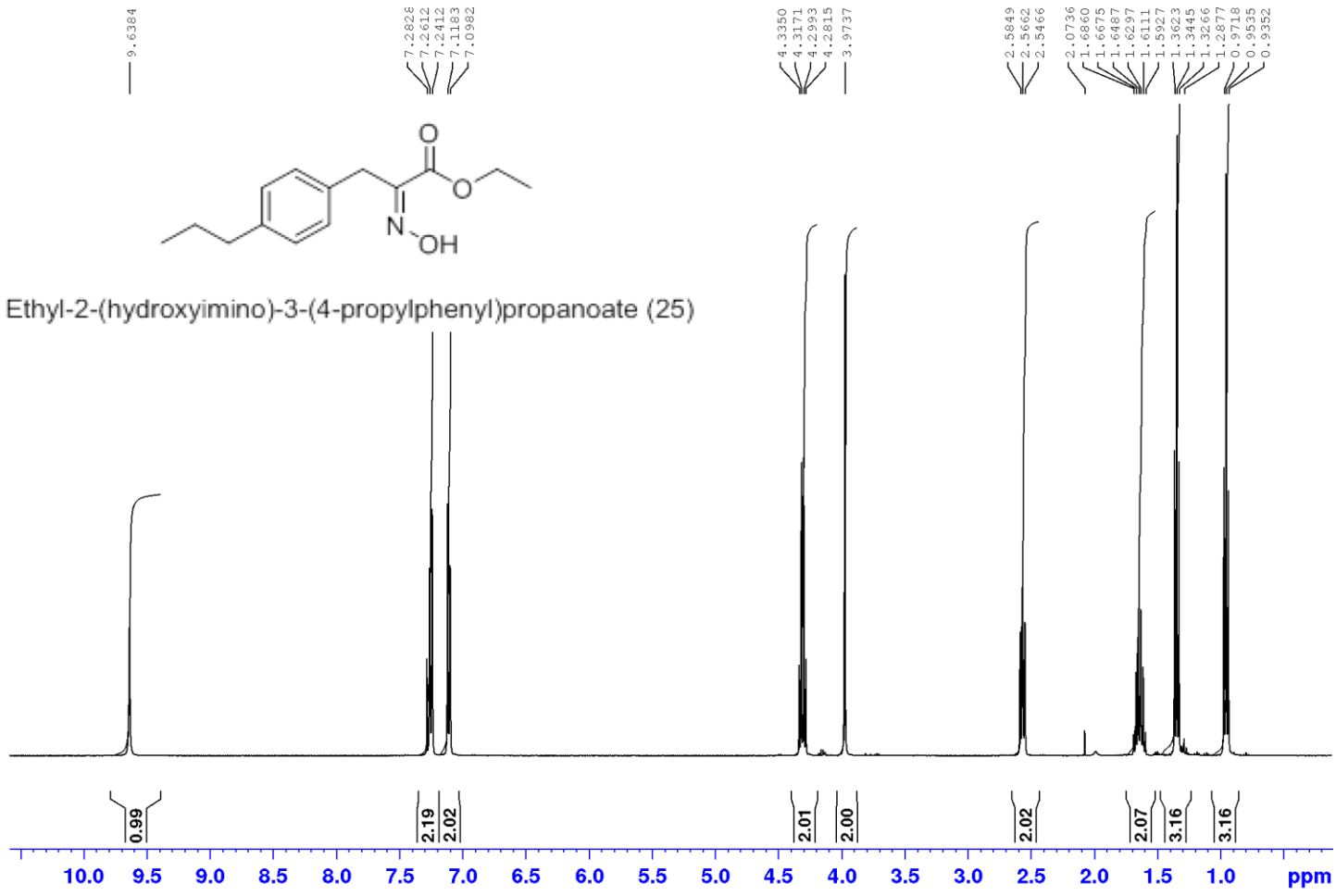
Diethyl 2-((5-cyclopropylfuran-2-yl)methylene)malonate (30)

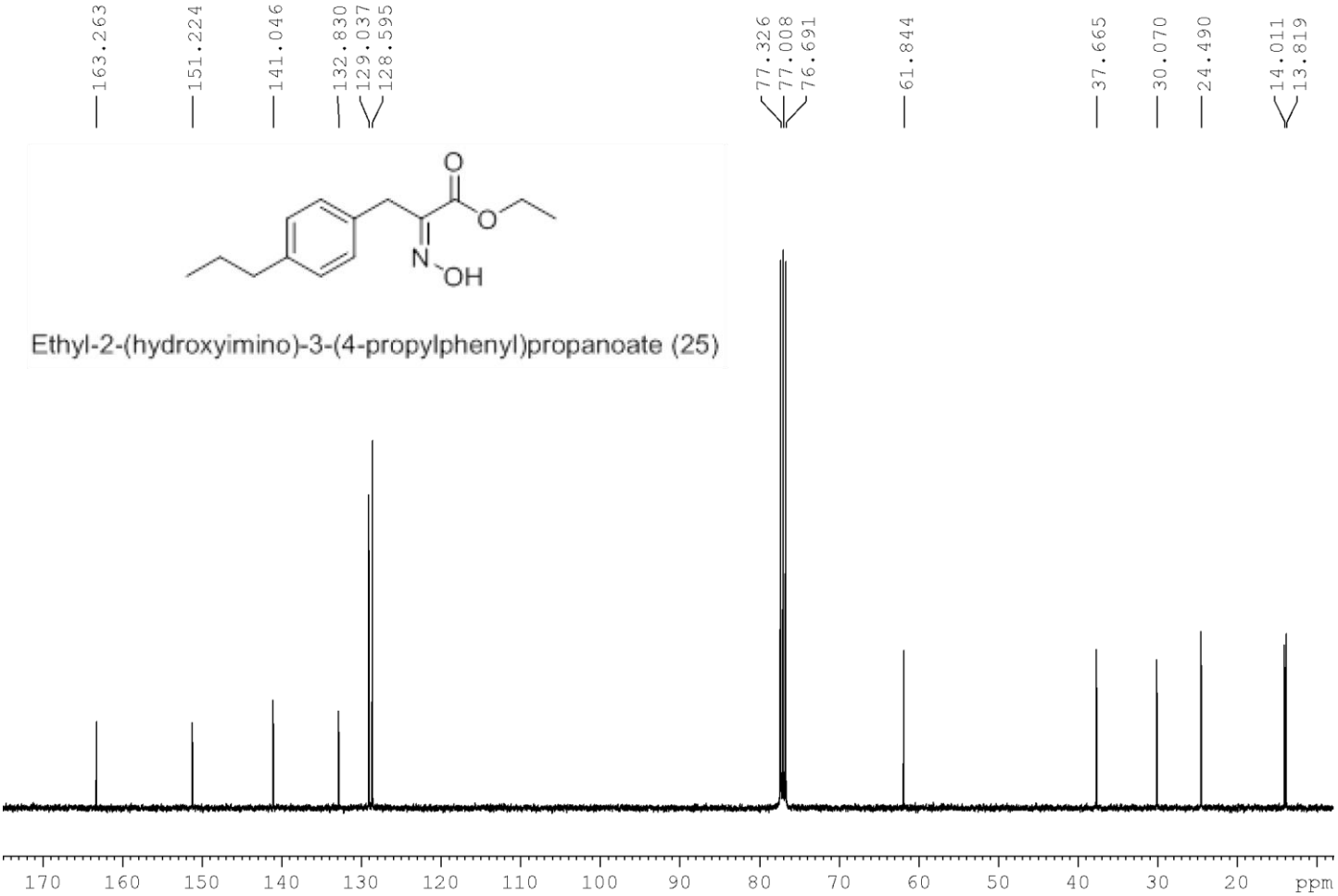


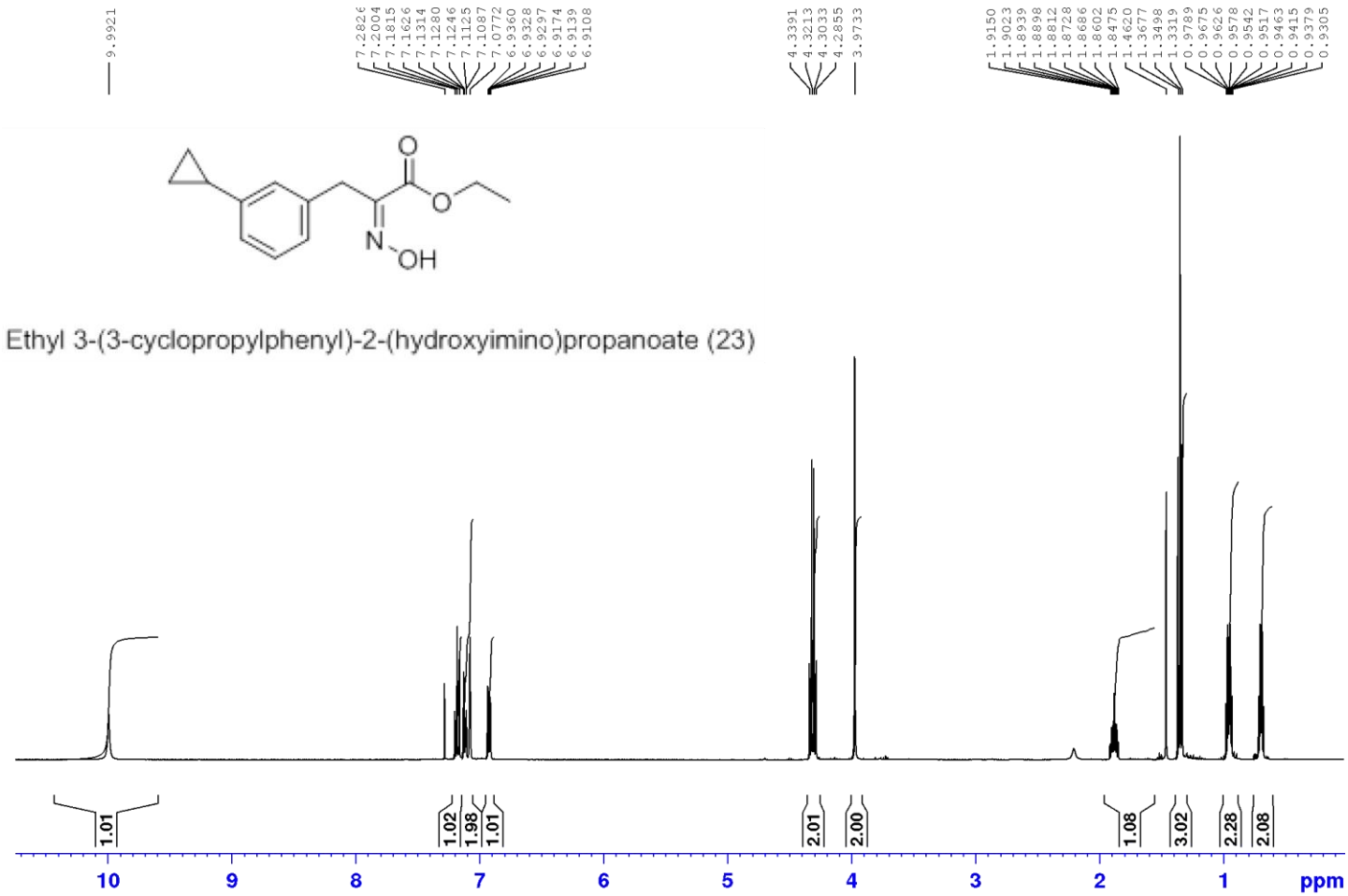
Diethyl 2-((5-cyclopropylfuran-2-yl)methylene)malonate (30)


9.7384
7.2826
7.2289
7.2088
7.2009
7.1903
7.1618
7.1570
7.1525
7.1463
7.0622
7.0438
4.3384
4.3205
4.3026
4.2848
3.9890
2.5937
2.5750
2.5554
1.6932
1.6747
1.6559
1.6405
1.6368
1.6223
1.6181
1.5998
1.4610
1.3632
1.3453
1.3275
0.9750
0.9567
0.9383
O
O
N
OH
Ethyl-2-(hydroxyimino)-3-(3-propylphenyl)propanoate (21)
1.00
1.04
2.02
1.02
2.10
2.09
2.12
2.12
3.22
3.20
11
10
9
8
7
6
5
4
3
2
1
ppm

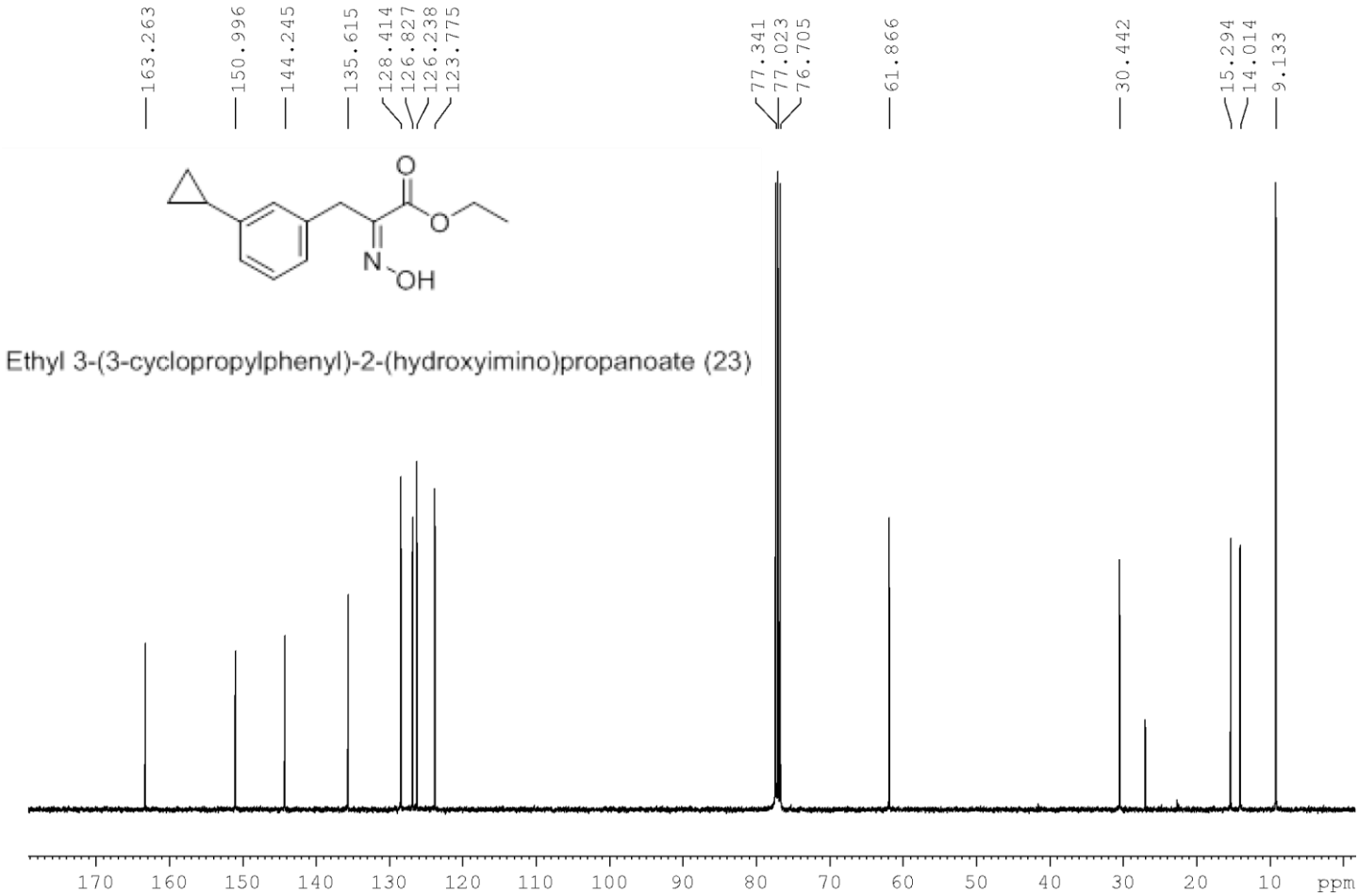

163.271
151.580
142.959
135.468
129.339
128.341
126.779
126.419
77.311
76.994
76.676
61.851
37.966
30.478
24.487
14.018
13.805
O
O
N
OH
Ethyl-2-(hydroxyimino)-3-(3-propylphenyl)propanoate (21)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.6384
7.2828
7.2612
7.2412
7.1183
7.0982
4.3350
4.3171
4.2993
4.2815
3.9737
2.5849
2.5662
2.5466
2.0736
1.6860
1.6675
1.6487
1.6297
1.6111
1.5927
1.3623
1.3445
1.3266
1.2877
0.9718
0.9535
0.9352
O
O
N
OH
Ethyl-2-(hydroxyimino)-3-(4-propylphenyl)propanoate (25)
0.99
2.19
2.02
2.01
2.00
2.02
2.07
3.16
3.16
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 ppm

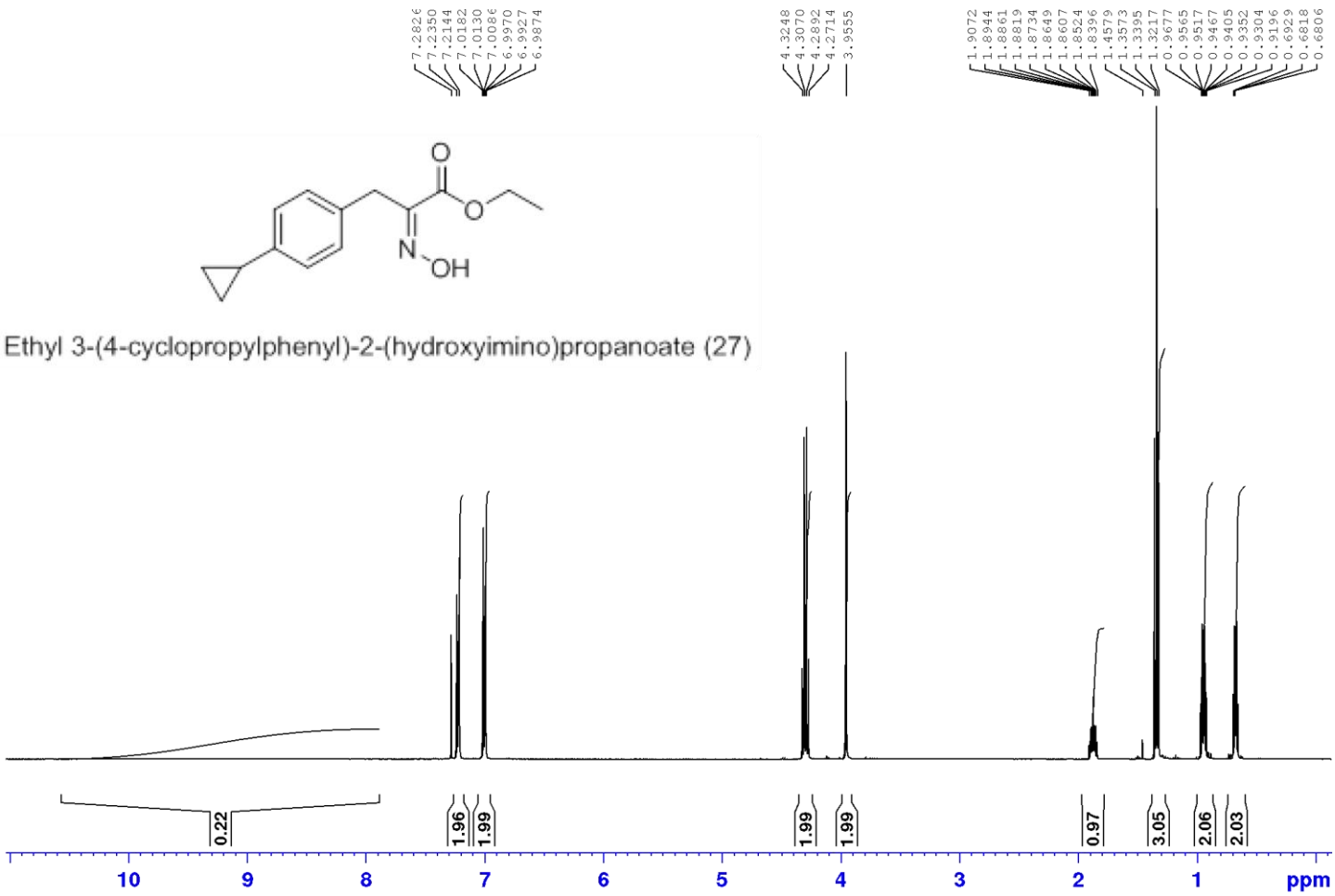

163.263
151.224
141.046
132.830
129.037
128.595
77.326
77.008
76.691
61.844
37.665
30.070
24.490
14.011
13.819
O
O
N
OH
Ethyl-2-(hydroxyimino)-3-(4-propylphenyl)propanoate (25)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

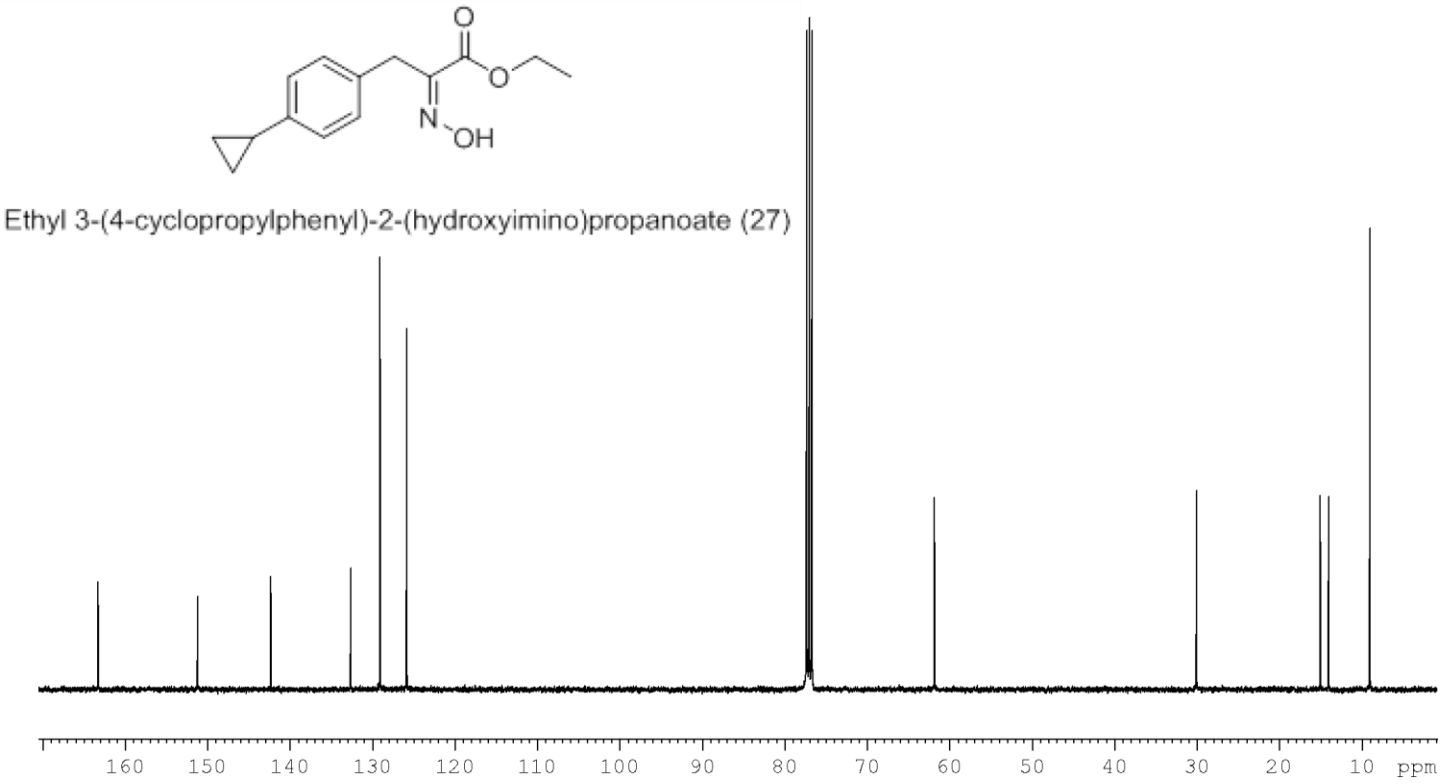


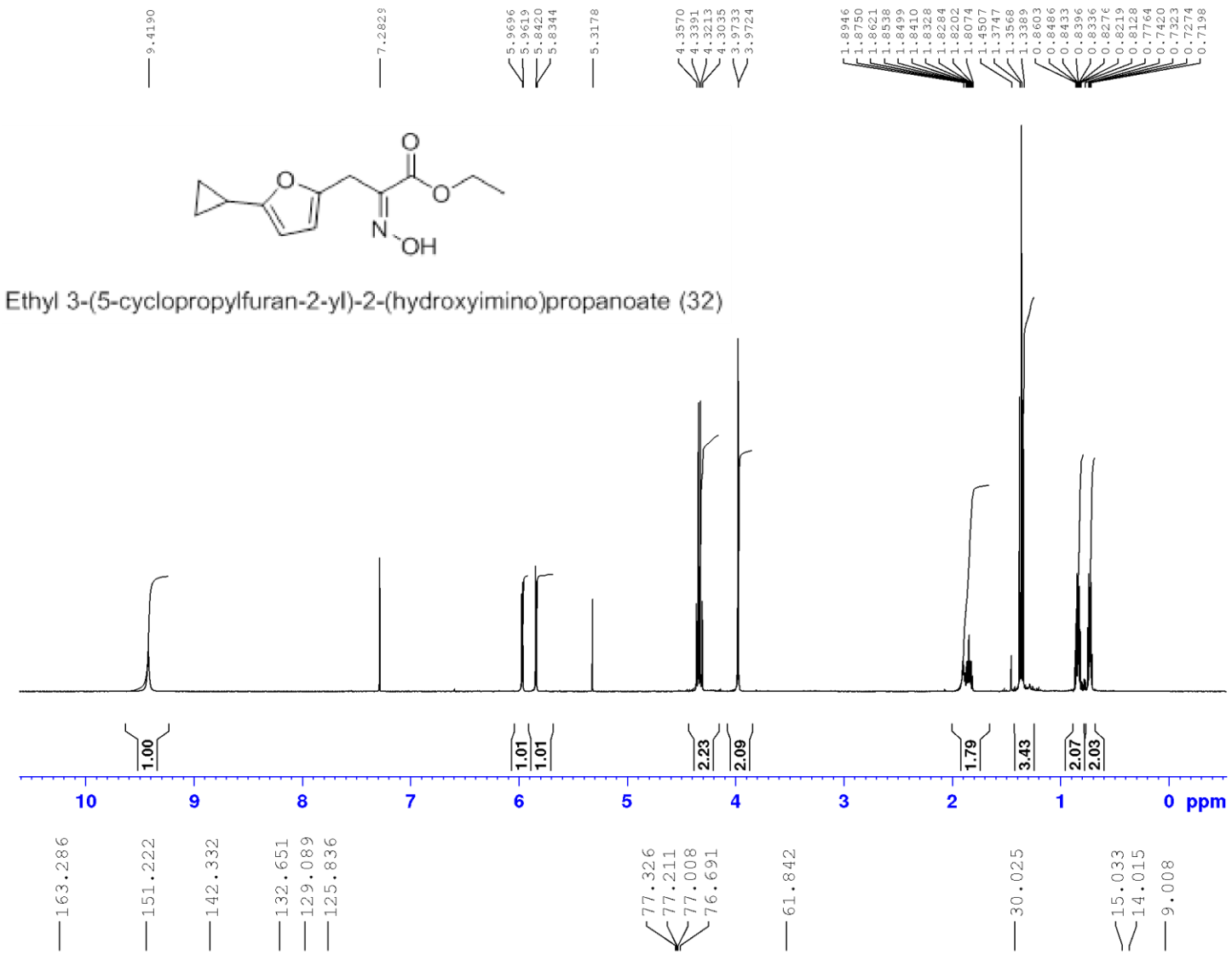
Ethyl 3-(3-cyclopropylphenyl)-2-(hydroxyimino)propanoate (23)

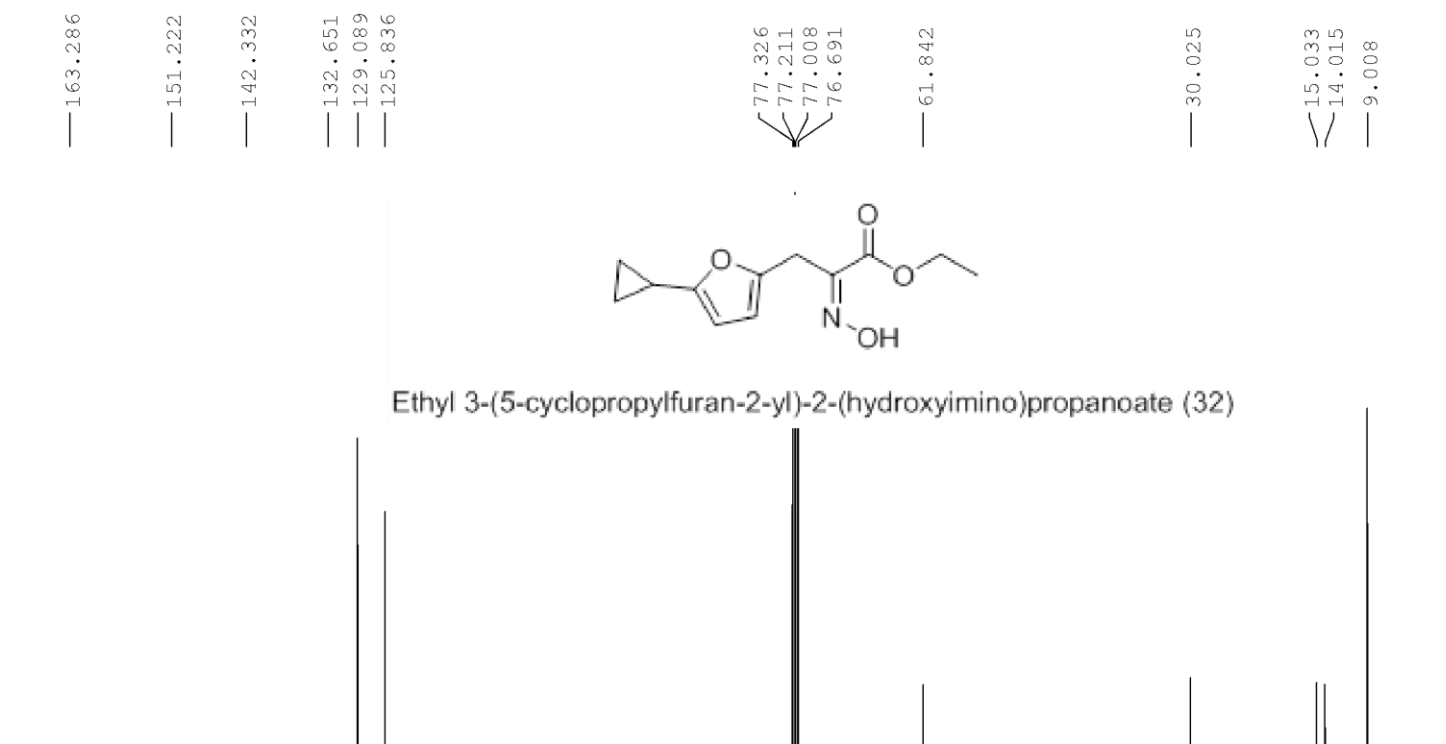


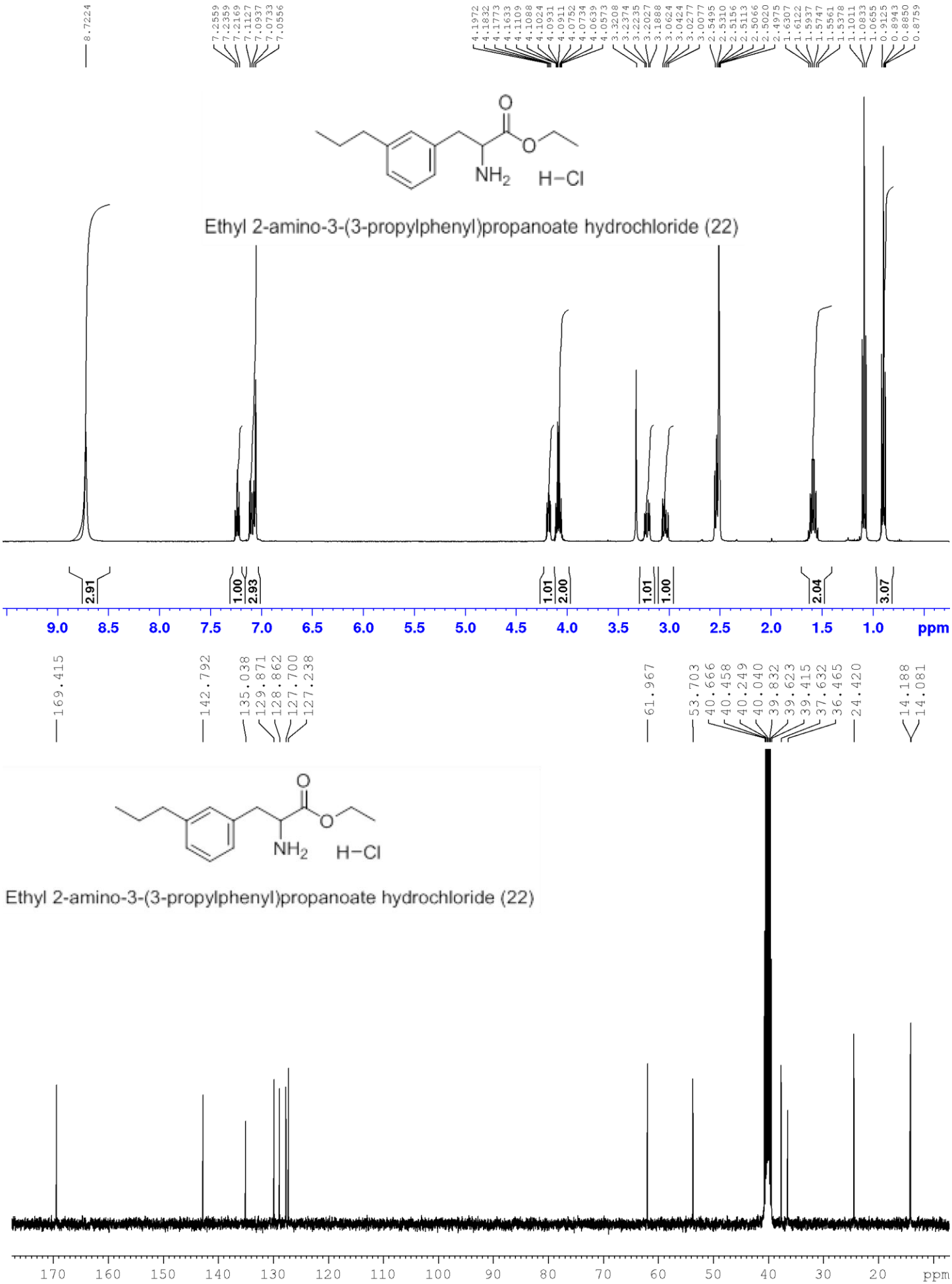
Ethyl 3-(3-cyclopropylphenyl)-2-(hydroxyimino)propanoate (23)

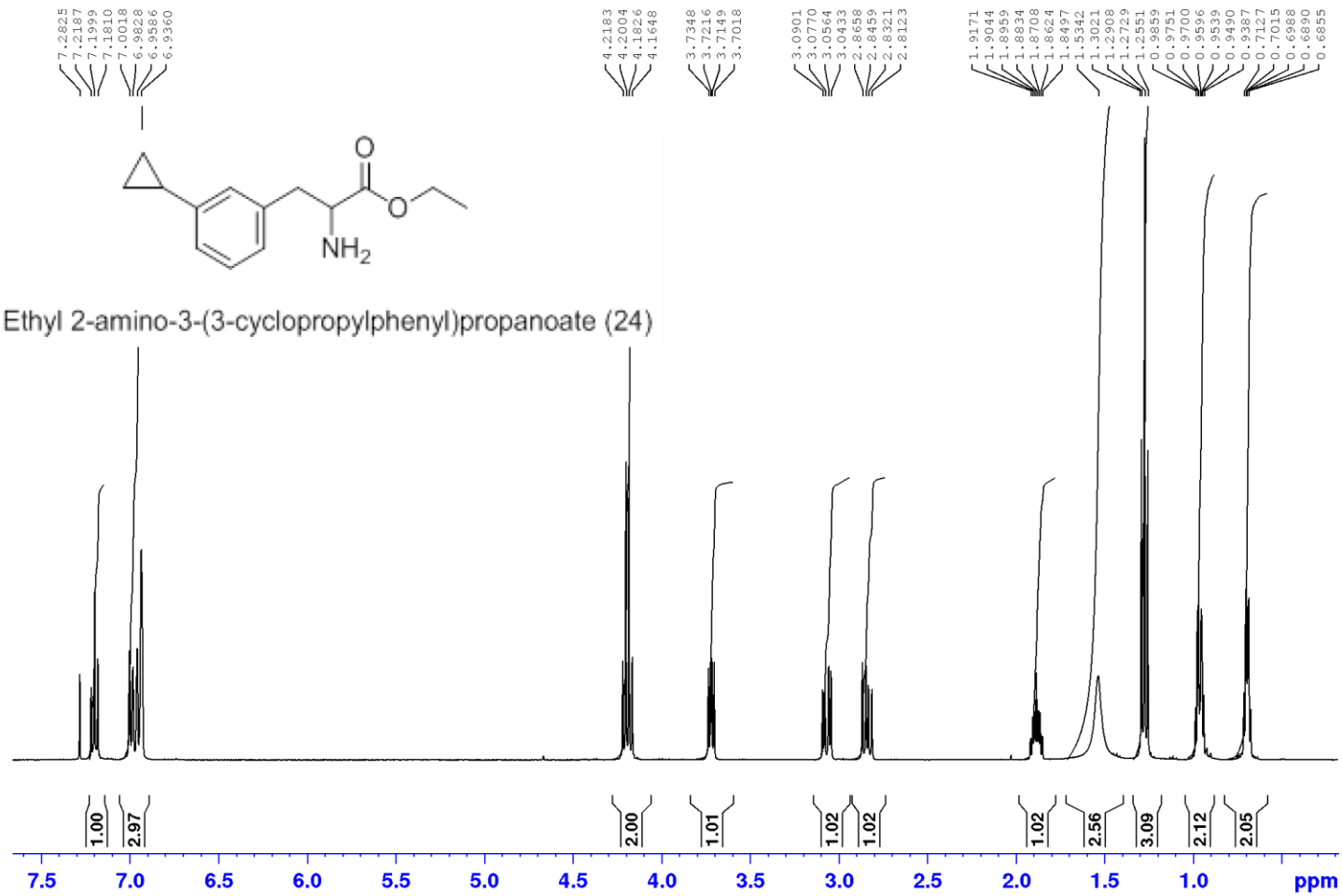

Ethyl 3-(4-cyclopropylphenyl)-2-(hydroxyimino)propanoate (27)
ppm


Ethyl 3-(4-cyclopropylphenyl)-2-(hydroxyimino)propanoate (27)
ppm

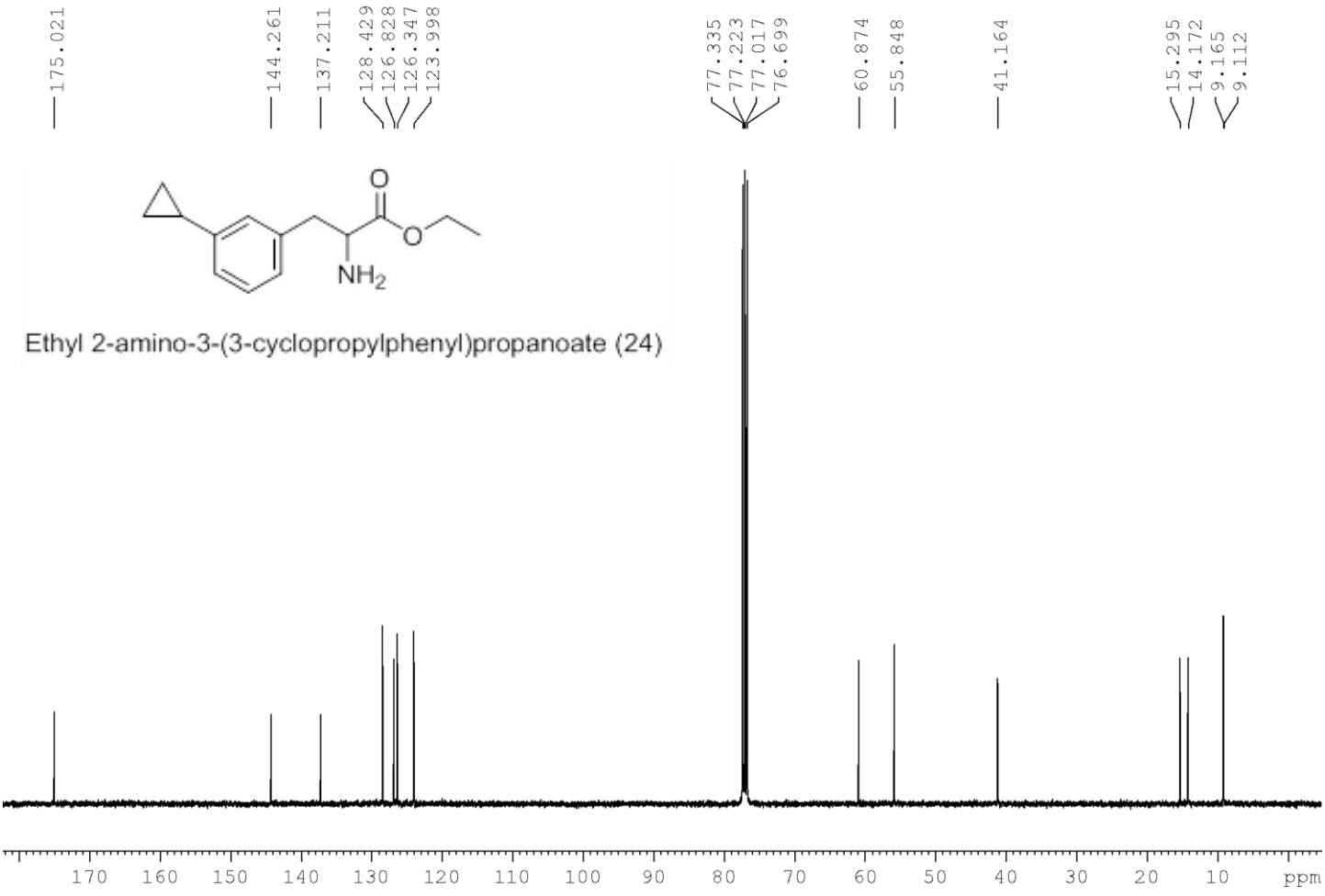

9.4190
7.2829
5.9696
5.9619
5.8420
5.8344
5.3178
4.3570
4.3391
4.3213
4.3035
3.9733
3.9724
1.8946
1.8750
1.8621
1.8538
1.8499
1.8410
1.8328
1.8284
1.8202
1.8074
1.4507
1.3747
1.3568
1.3389
0.8603
0.8486
0.8433
0.8396
0.8336
0.8276
0.8219
0.8128
0.7764
0.7420
0.7323
0.7274
0.7198
O
O
O
N
OH
Ethyl 3-(5-cyclopropylfuran-2-yl)-2-(hydroxyimino)propanoate (32)
1.00
1.01
1.01
2.23
2.09
1.79
3.43
2.07
2.03
10
9
8
7
6
5
4
3
2
1
0 ppm


163.286
151.222
142.332
132.651
129.089
125.836
77.326
77.211
77.008
76.691
61.842
30.025
15.033
14.015
9.008
O
O
O
N
OH
Ethyl 3-(5-cyclopropylfuran-2-yl)-2-(hydroxyimino)propanoate (32)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

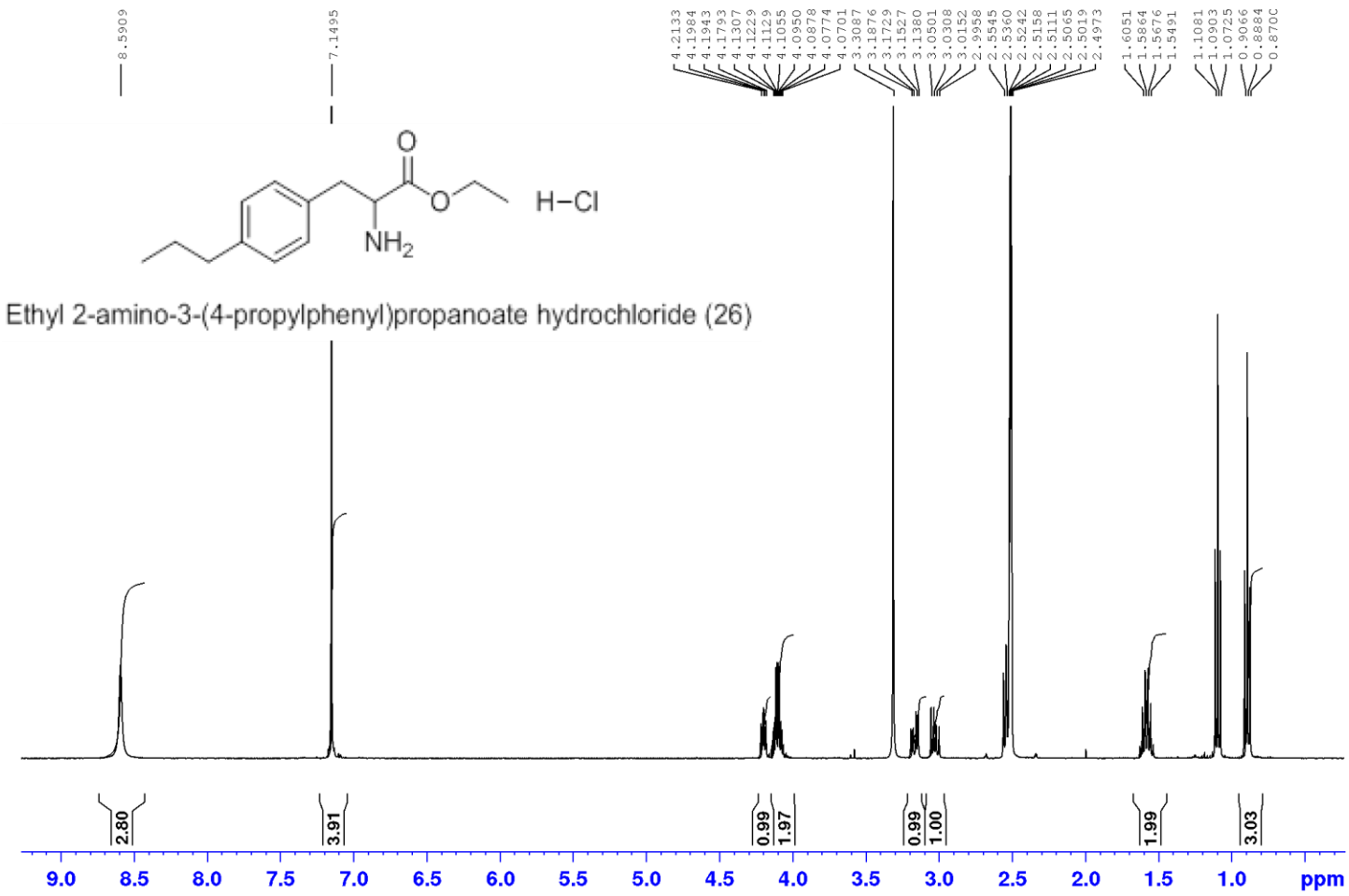

8.7224
7.2559
7.2359
7.2169
7.1127
7.0937
7.0733
7.0556
4.1972
4.1832
4.1773
4.1633
4.1109
4.1088
4.1024
4.0931
4.0911
4.0752
4.0734
4.0639
4.0573
3.3208
3.2374
3.2235
3.2027
3.1888
3.0624
3.0424
3.0277
3.0077
2.5495
2.5310
2.5156
2.5113
2.5066
2.5020
2.4975
1.6307
1.6122
1.5937
1.5747
1.5561
1.5378
1.1011
1.0833
1.0655
0.9125
0.8943
0.8850
0.8759
O
O
NH2
H−Cl
Ethyl 2-amino-3-(3-propylphenyl)propanoate hydrochloride (22)
2.91
1.00
2.93
1.01
2.00
1.01
1.00
2.04
3.07
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
ppm
169.415
142.792
135.038
129.871
128.862
127.700
127.238
61.967
53.703
40.666
40.458
40.249
40.040
39.832
39.623
39.415
37.632
36.465
24.420
14.188
14.081
O
O
NH2
H−Cl
Ethyl 2-amino-3-(3-propylphenyl)propanoate hydrochloride (22)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

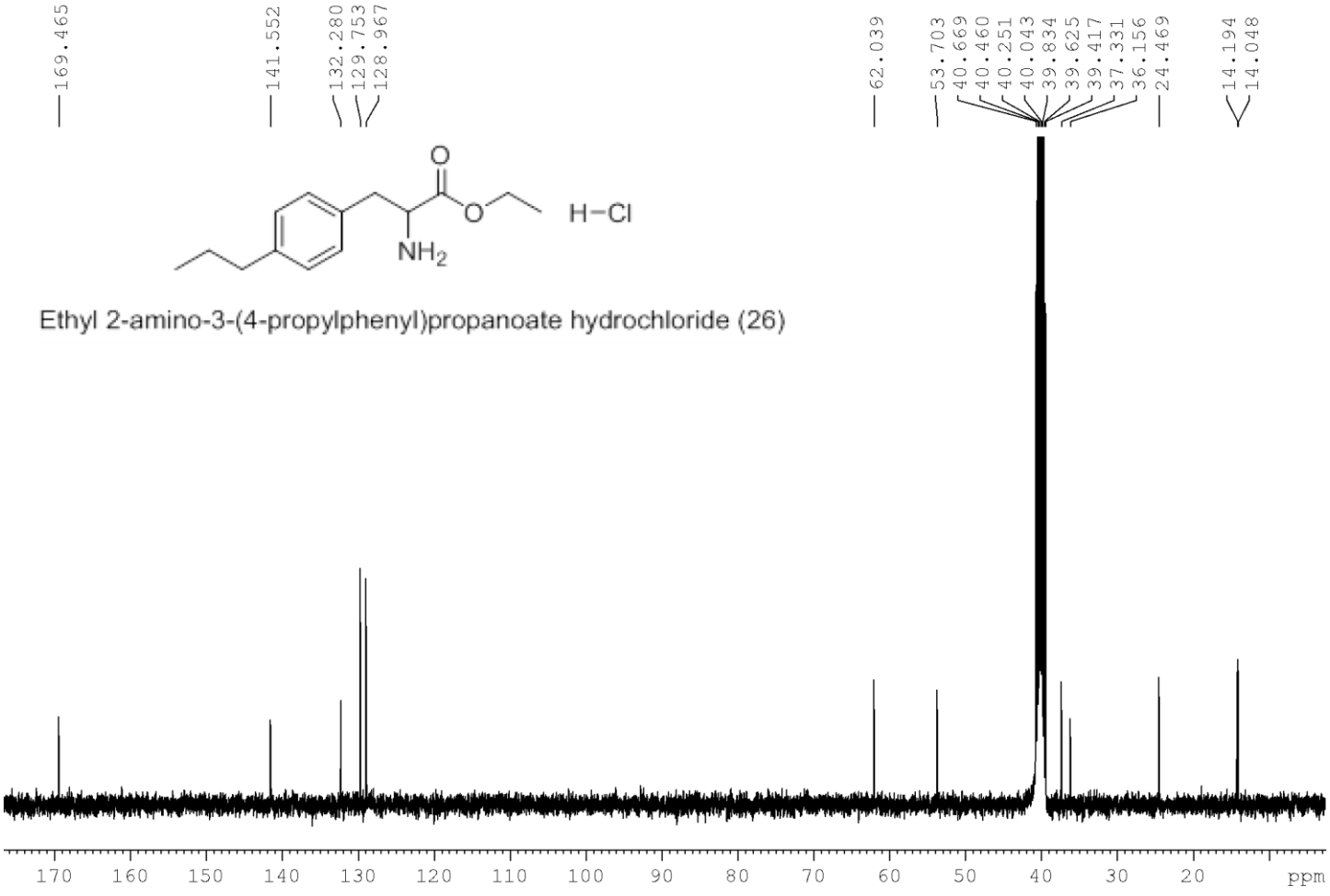


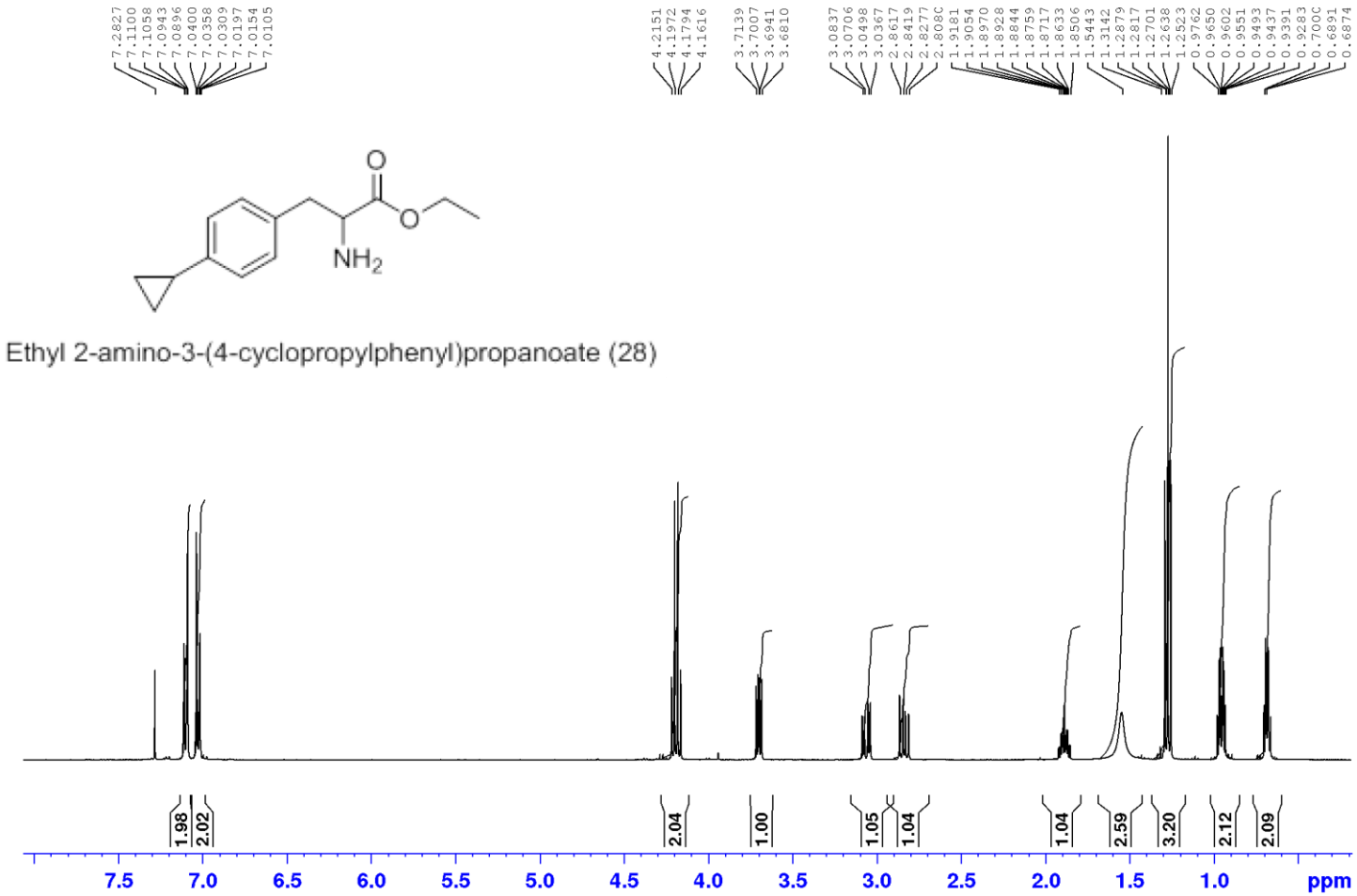
Ethyl 2-amino-3-(3-cyclopropylphenyl)propanoate (24)

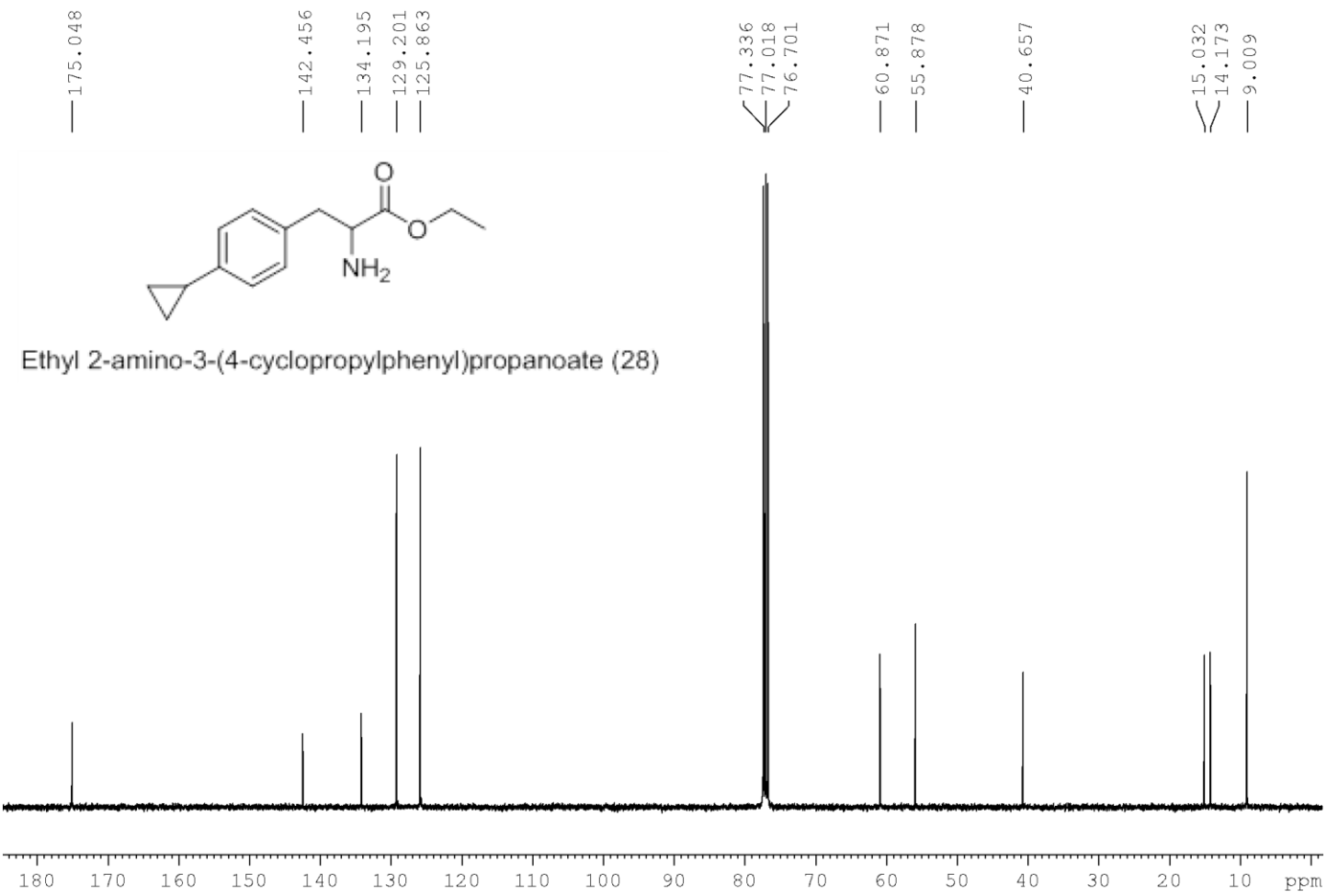


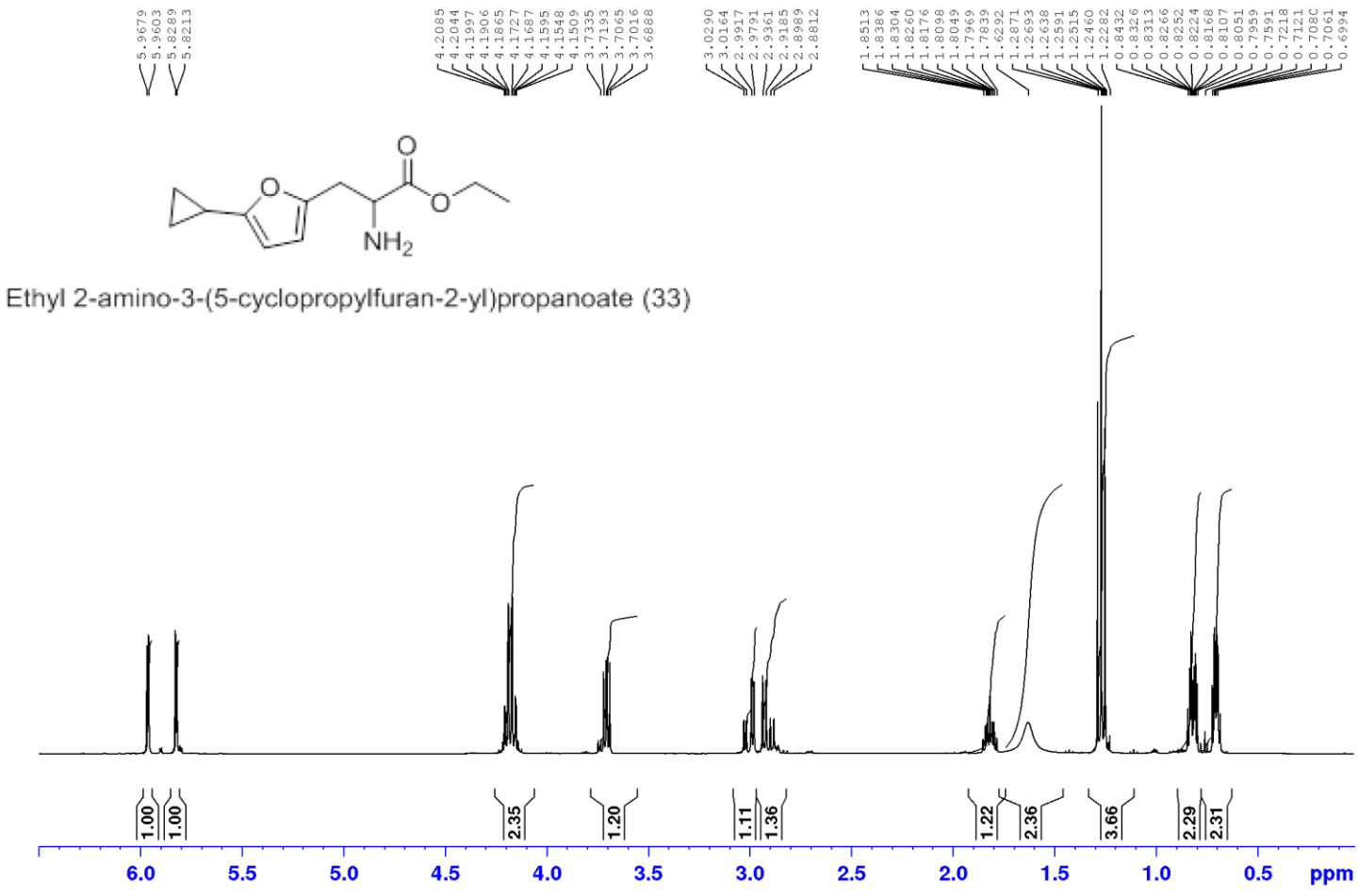
Ethyl 2-amino-3-(3-cyclopropylphenyl)propanoate (24)


8.5909
7.1495
4.2133
4.1984
4.1943
4.1793
4.1307
4.1229
4.1129
4.1055
4.0950
4.0878
4.0774
4.0701
3.3087
3.1876
3.1729
3.1527
3.1380
3.0501
3.0308
3.0152
2.9958
2.5545
2.5360
2.5242
2.5158
2.5111
2.5065
2.5019
2.4973
1.6051
1.5864
1.5676
1.5491
1.1081
1.0903
1.0725
0.9066
0.8884
0.8700
O
O
NH2
H−Cl
Ethyl 2-amino-3-(4-propylphenyl)propanoate hydrochloride (26)
2.80
3.91
0.99
1.97
0.99
1.00
1.99
3.03
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
ppm

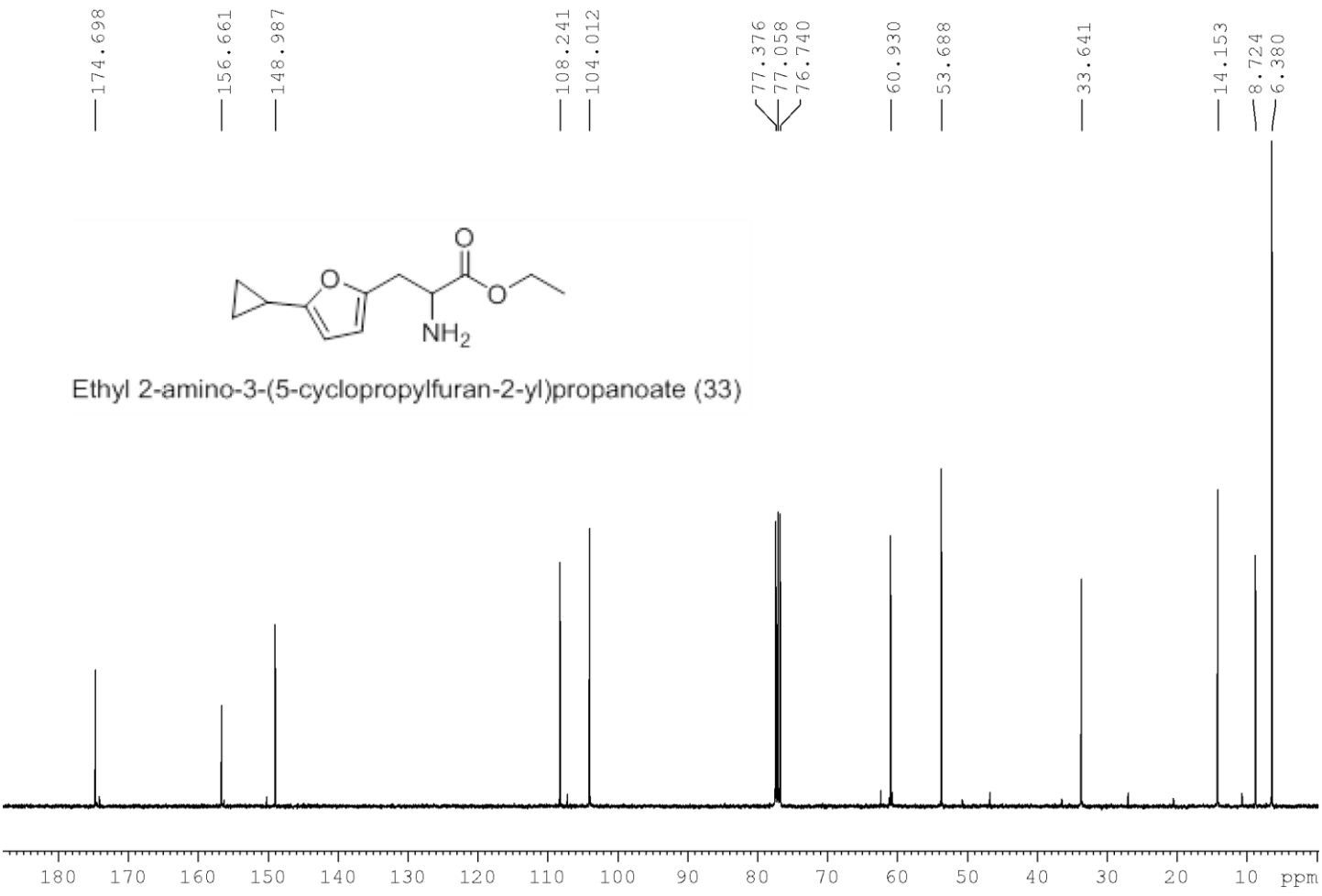

169.465
141.552
132.280
129.753
128.967
62.039
53.703
40.669
40.460
40.251
40.043
39.834
39.625
39.417
37.331
36.156
24.469
14.194
14.048
O
O
NH2
H−Cl
Ethyl 2-amino-3-(4-propylphenyl)propanoate hydrochloride (26)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


Ethyl 2-amino-3-(4-cyclopropylphenyl)propanoate (28)
ppm

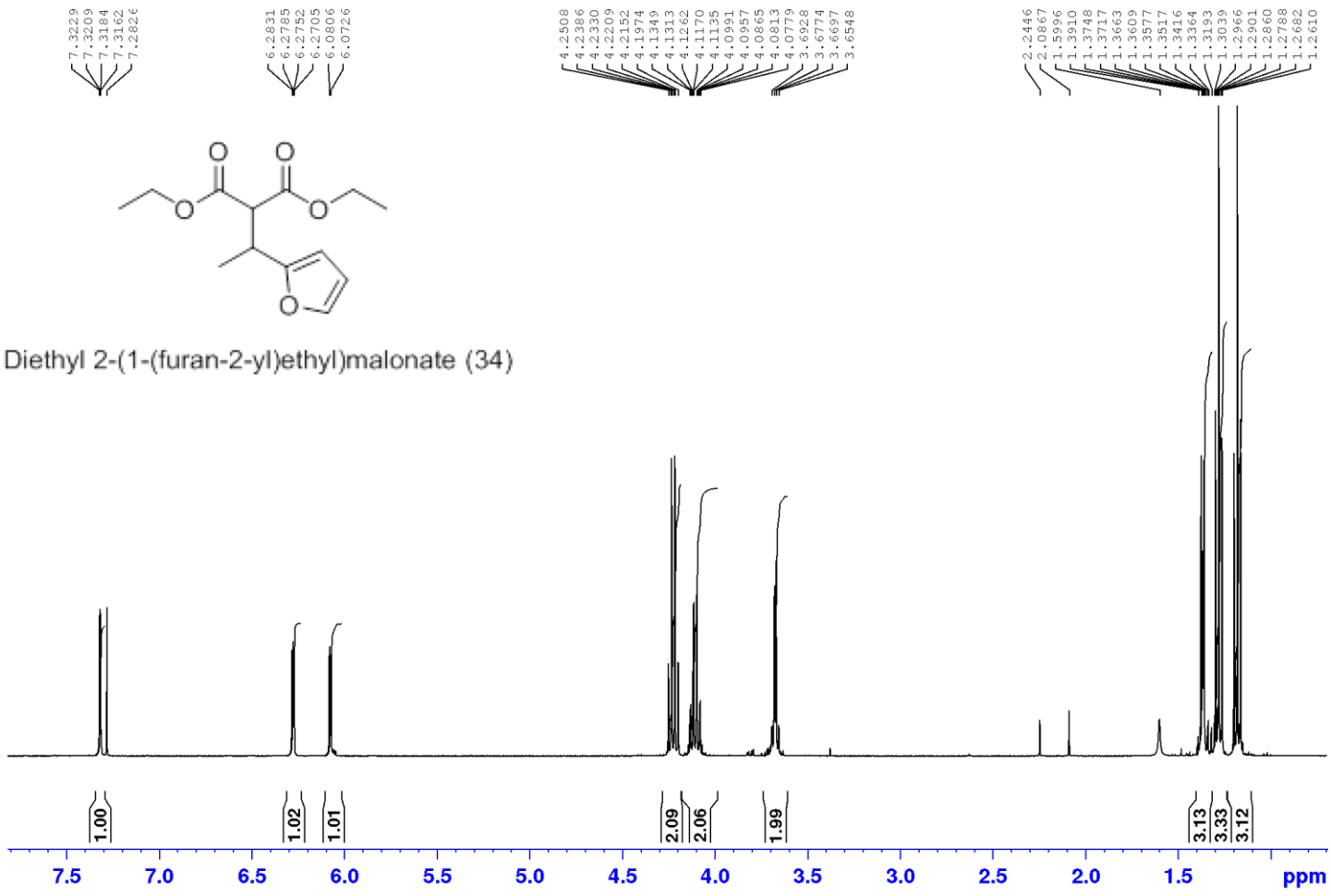

Ethyl 2-amino-3-(4-cyclopropylphenyl)propanoate (28)
ppm



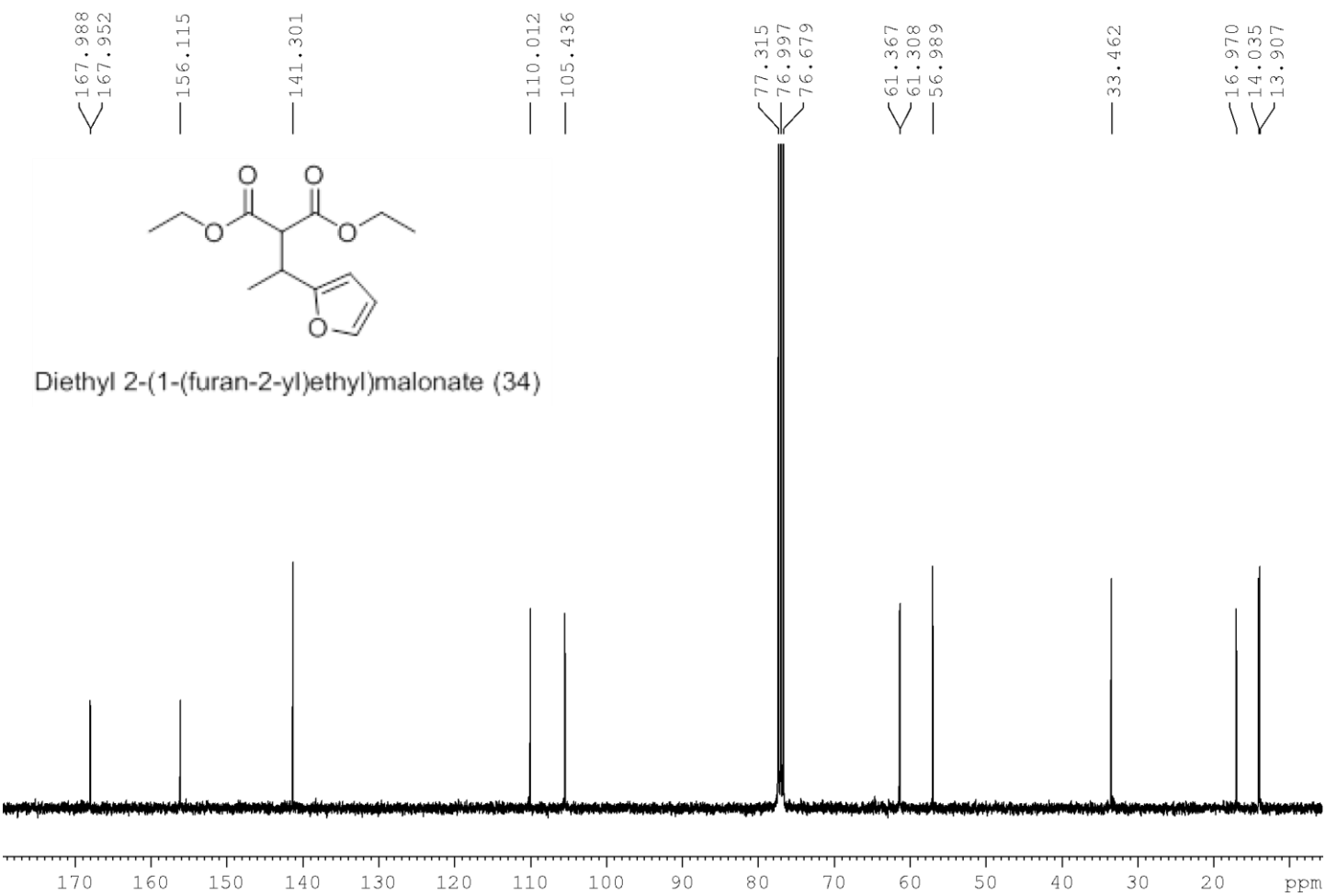
Ethyl 2-amino-3-(5-cyclopropylfuran-2-yl)propanoate (33)



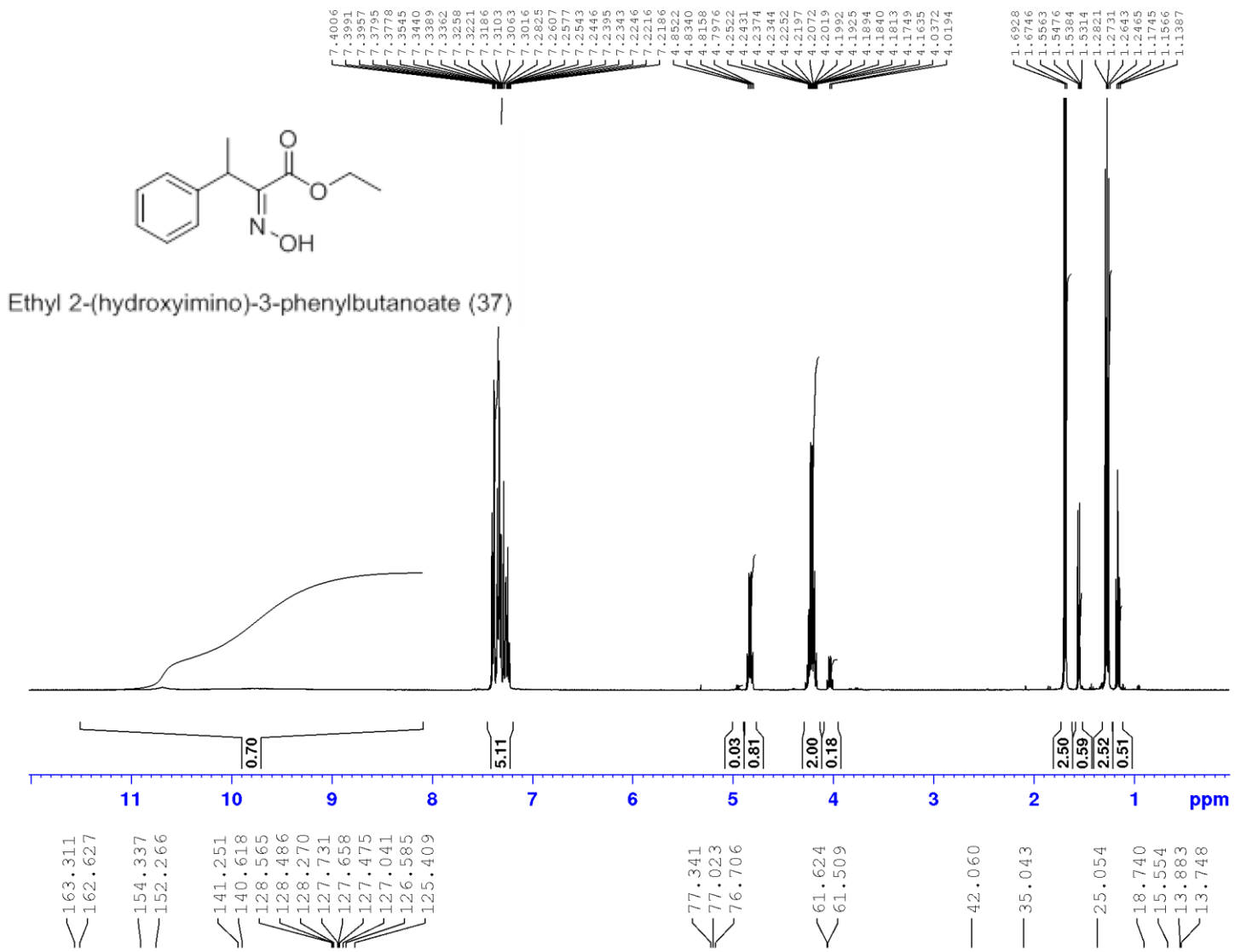
Ethyl 2-amino-3-(5-cyclopropylfuran-2-yl)propanoate (33)

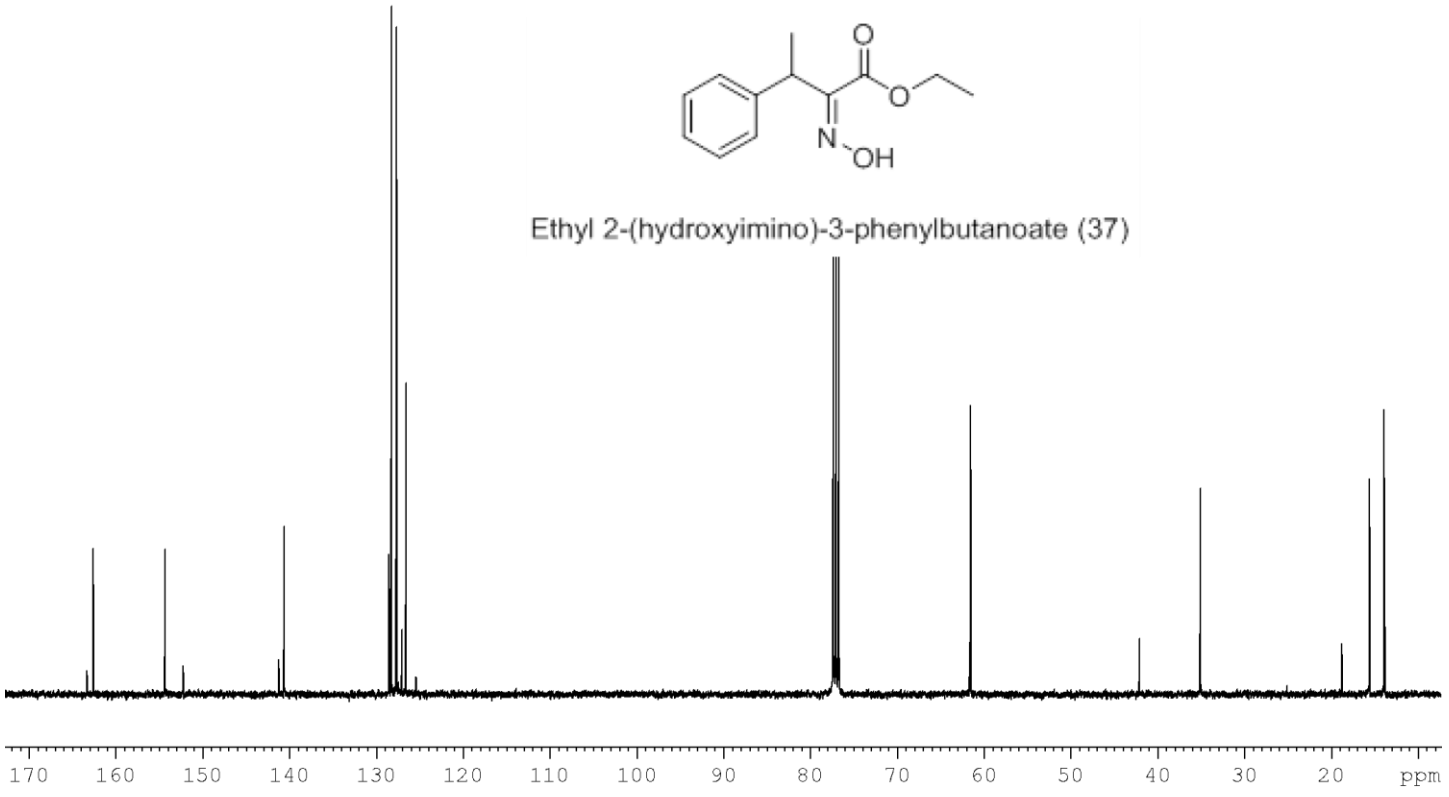


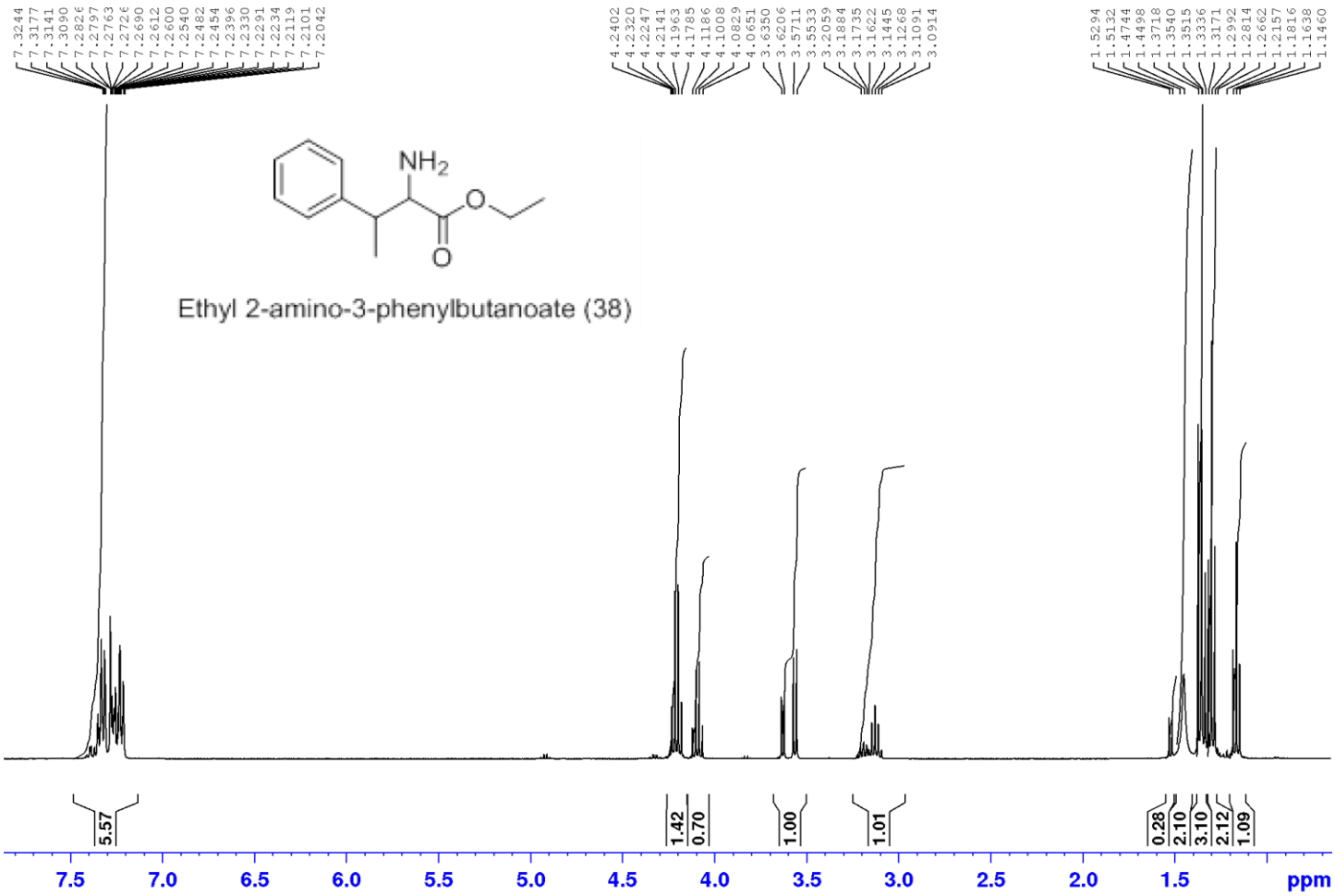
Diethyl 2-(1-(furan-2-yl)ethyl)malonate (34)

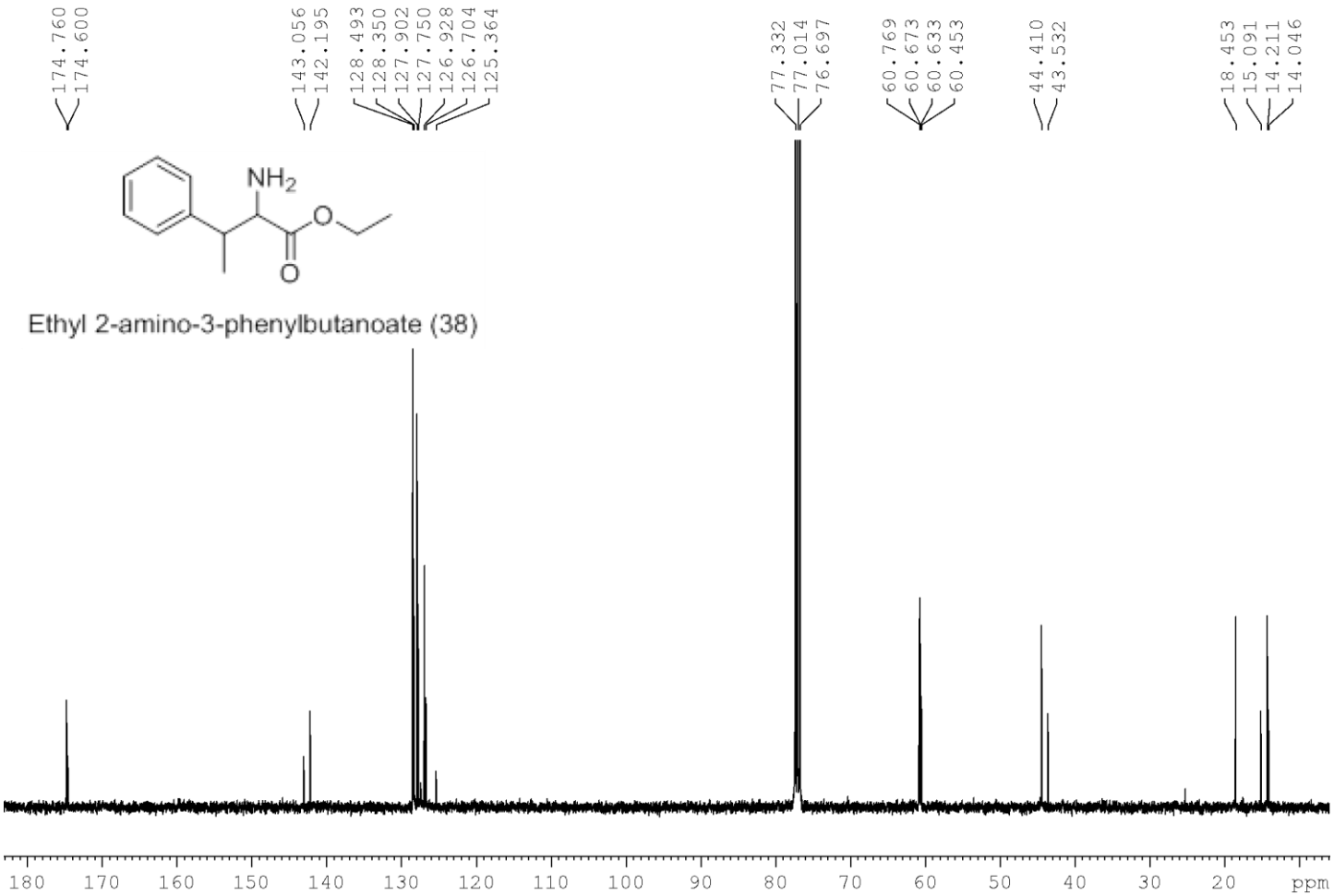


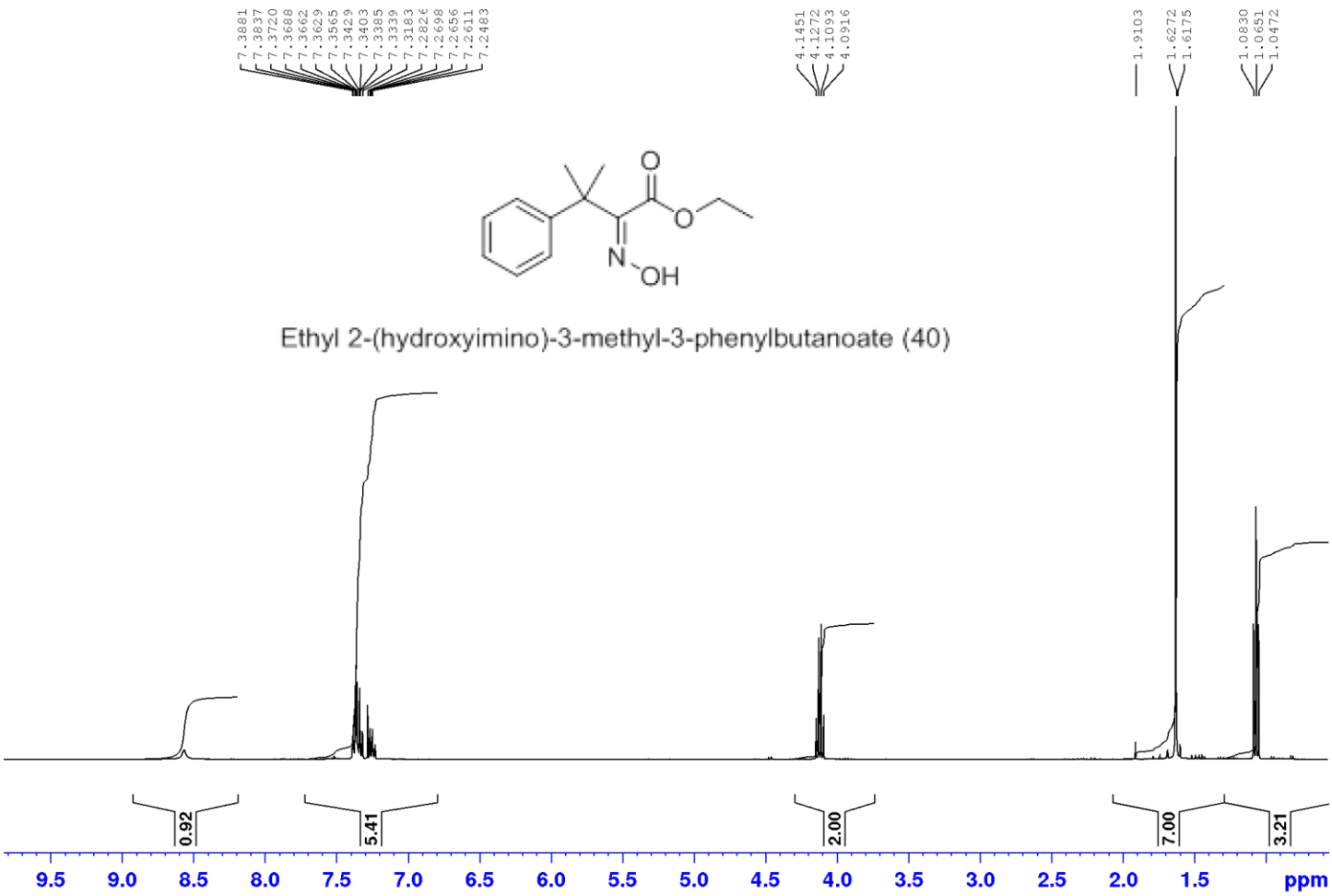
Diethyl 2-(1-(furan-2-yl)ethyl)malonate (34)


Ethyl 2-(hydroxyimino)-3-phenylbutanoate (37)
ppm

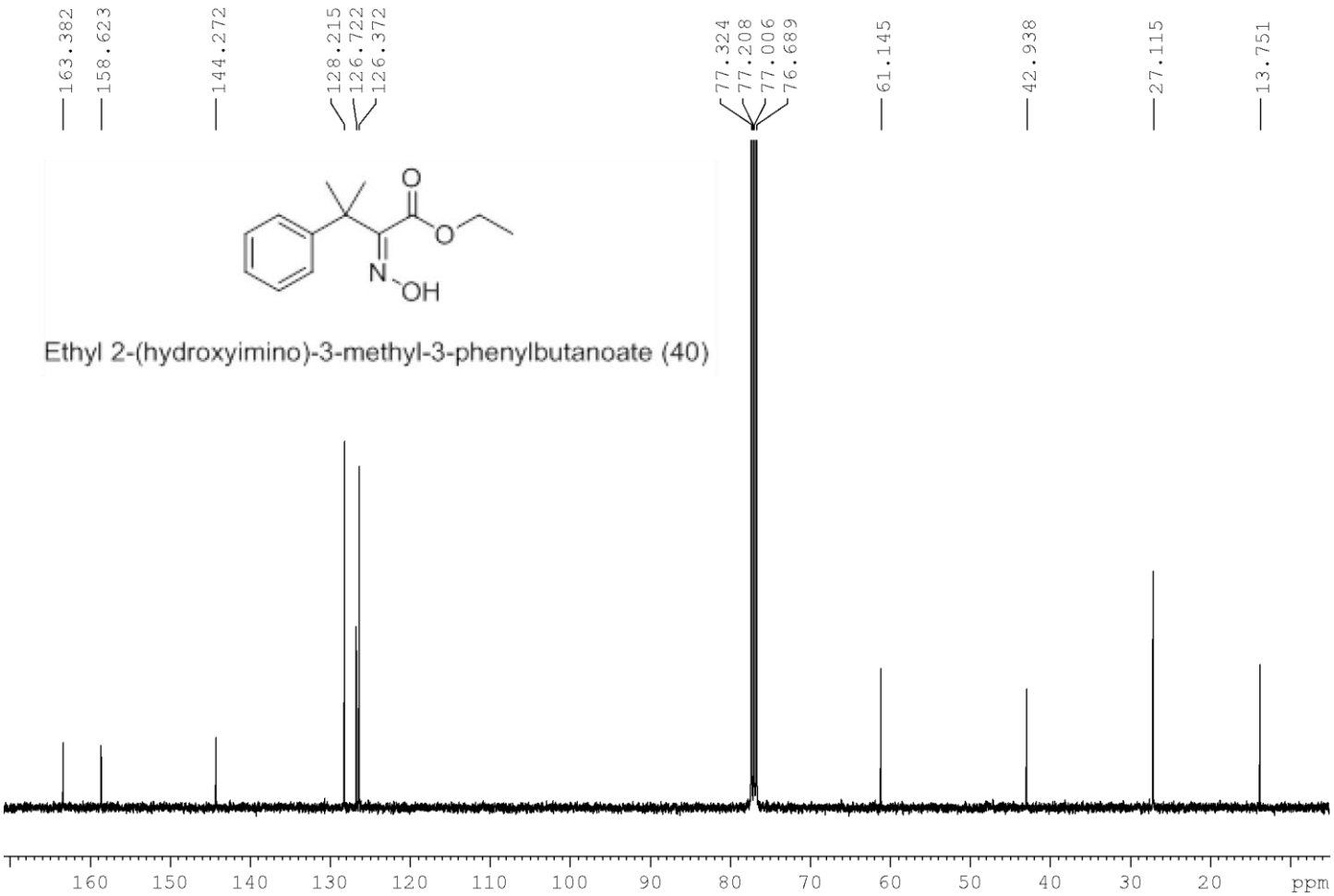

Ethyl 2-(hydroxyimino)-3-phenylbutanoate (37)
ppm


7.3244
7.3177
7.3141
7.3090
7.2826
7.2797
7.2763
7.2726
7.2690
7.2612
7.2600
7.2540
7.2482
7.2454
7.2396
7.2330
7.2291
7.2234
7.2119
7.2101
7.2042
4.2402
4.2320
4.2247
4.2141
4.1963
4.1785
4.1186
4.1008
4.0829
4.0651
3.6350
3.6206
3.5711
3.5533
3.2059
3.1884
3.1735
3.1622
3.1445
3.1268
3.1091
3.0914
1.5294
1.5132
1.4744
1.4498
1.3718
1.3540
1.3515
1.3336
1.3171
1.2992
1.2814
1.2662
1.2157
1.1816
1.1638
1.1460
NH2
O
O
Ethyl 2-amino-3-phenylbutanoate (38)
5.57
1.42
0.70
1.00
1.01
0.28
2.10
3.10
2.12
1.09
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
ppm

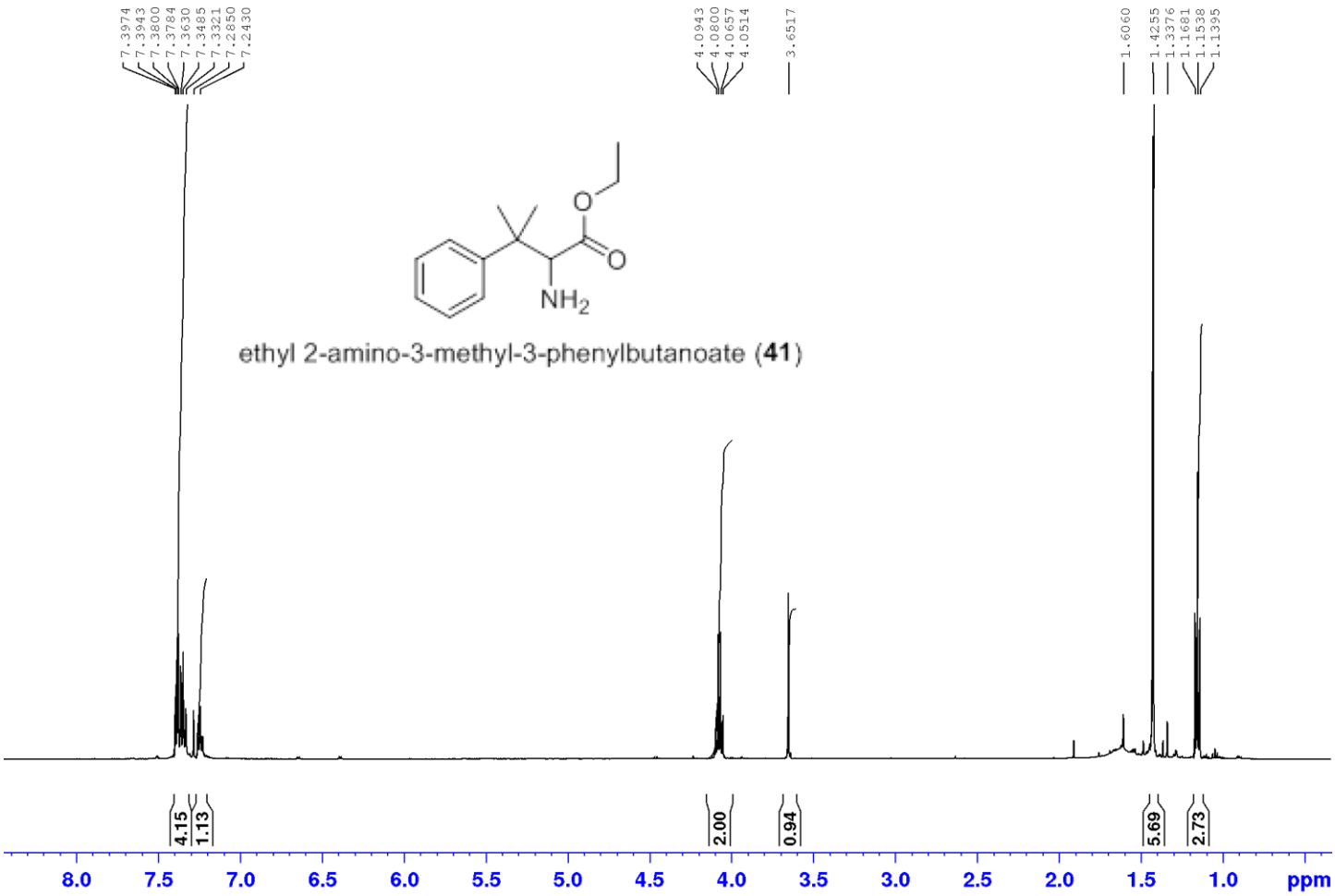

174.760
174.600
143.056
142.195
128.493
128.350
127.902
127.750
126.928
126.704
125.364
77.332
77.014
76.697
60.769
60.673
60.633
60.453
44.410
43.532
18.453
15.091
14.211
14.046
NH2
O
O
Ethyl 2-amino-3-phenylbutanoate (38)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



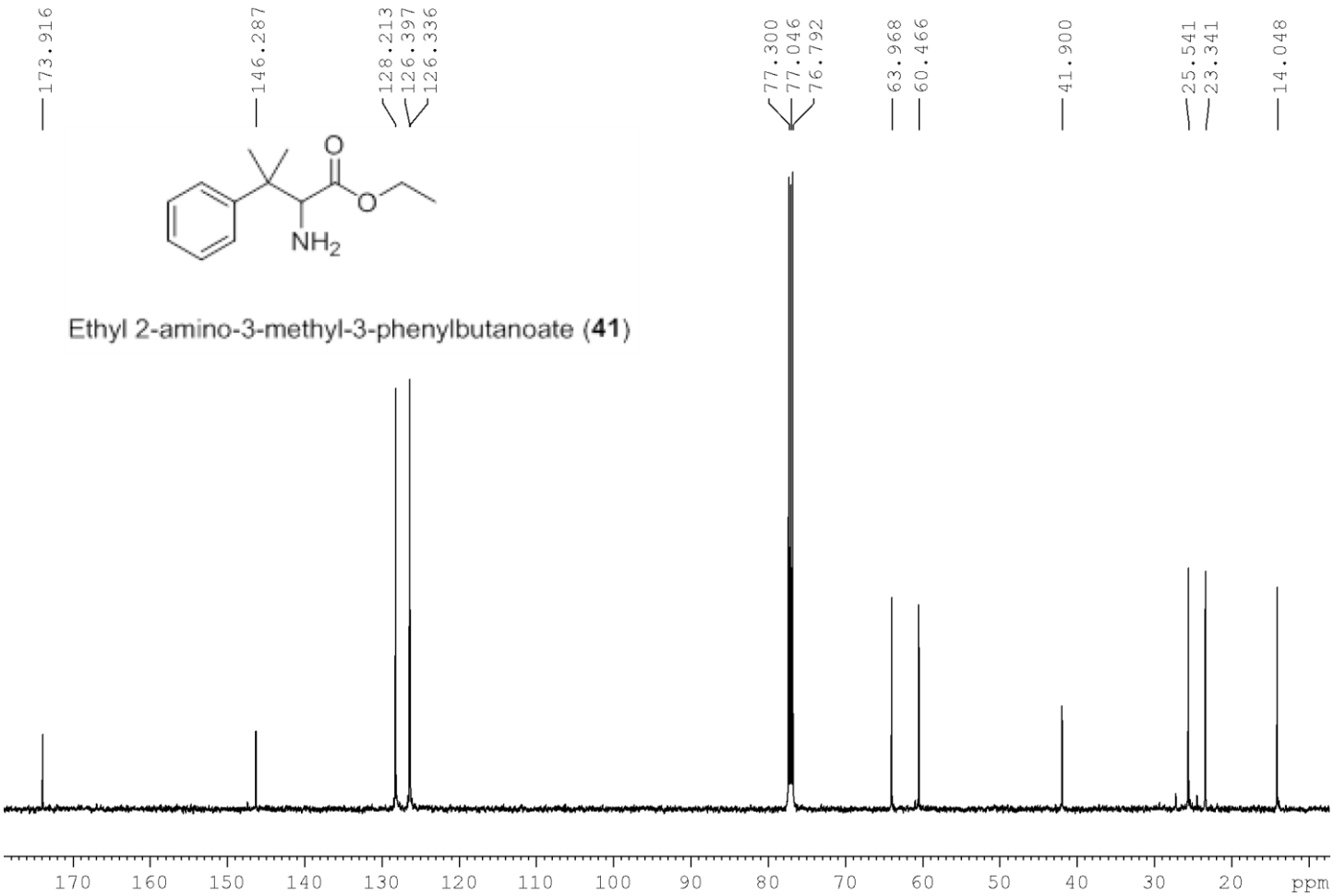
Ethyl 2-(hydroxyimino)-3-methyl-3-phenylbutanoate (40)



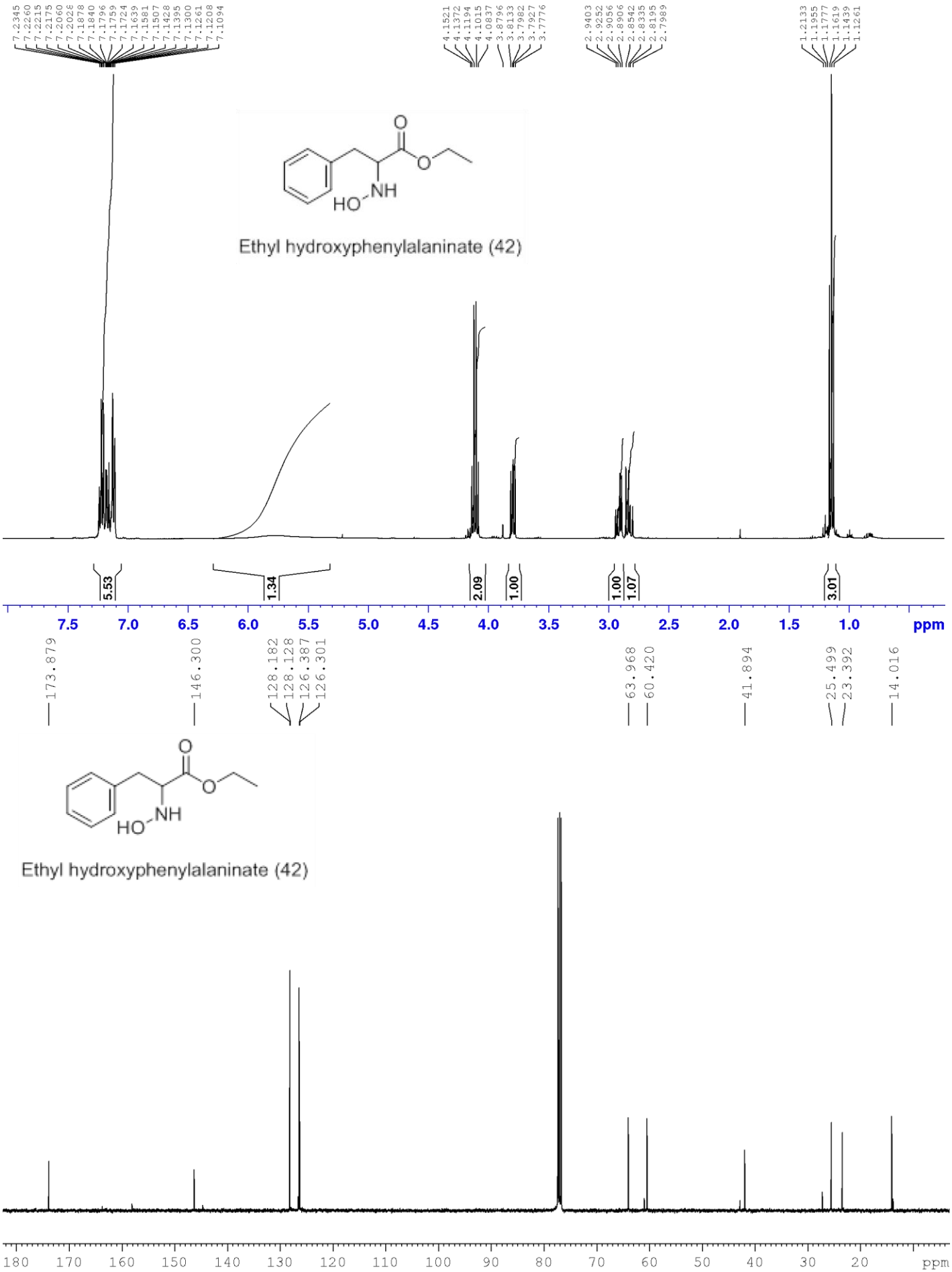
Ethyl 2-(hydroxyimino)-3-methyl-3-phenylbutanoate (40)

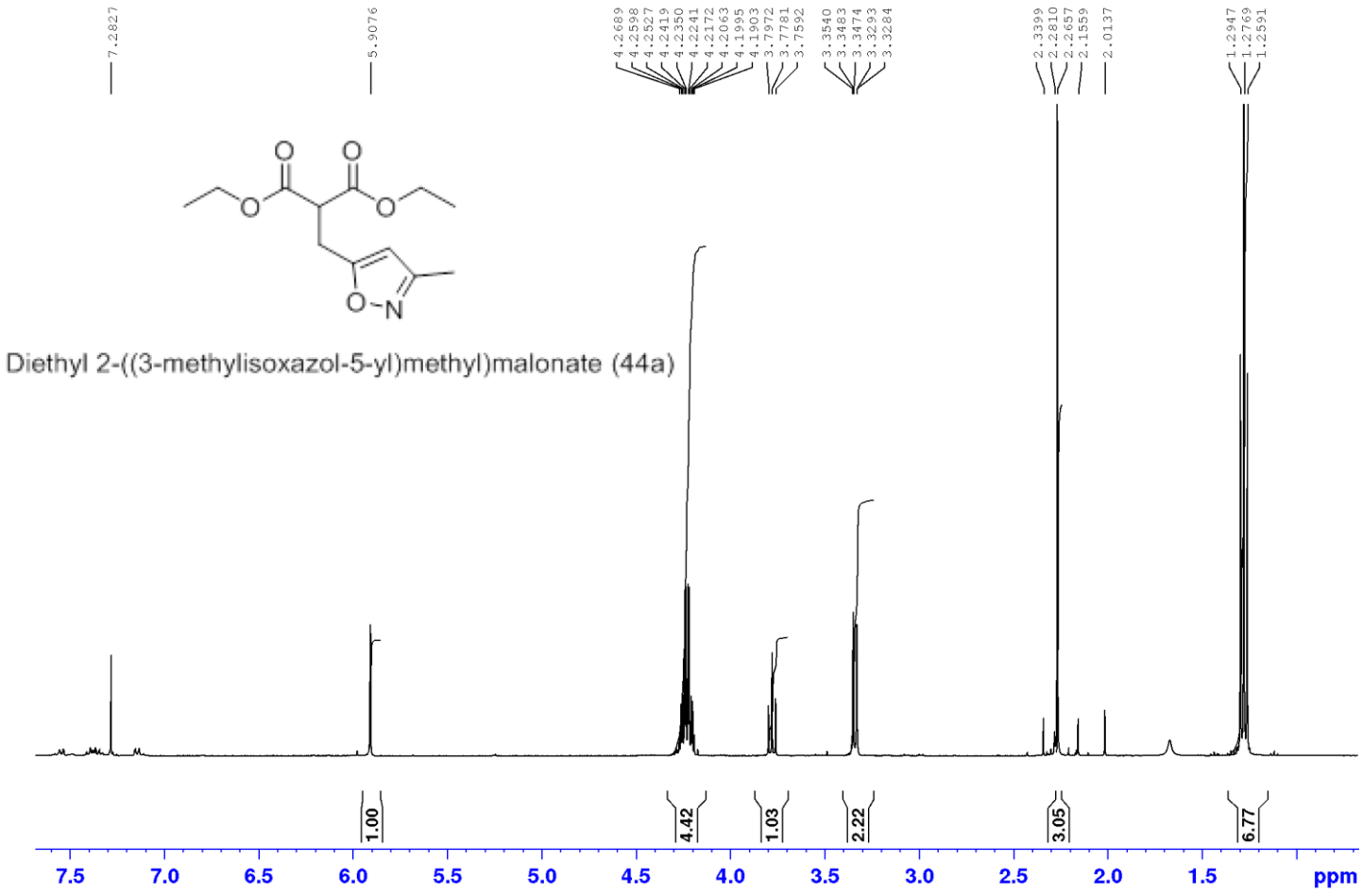


ethyl 2-amino-3-methyl-3-phenylbutanoate (**41**)

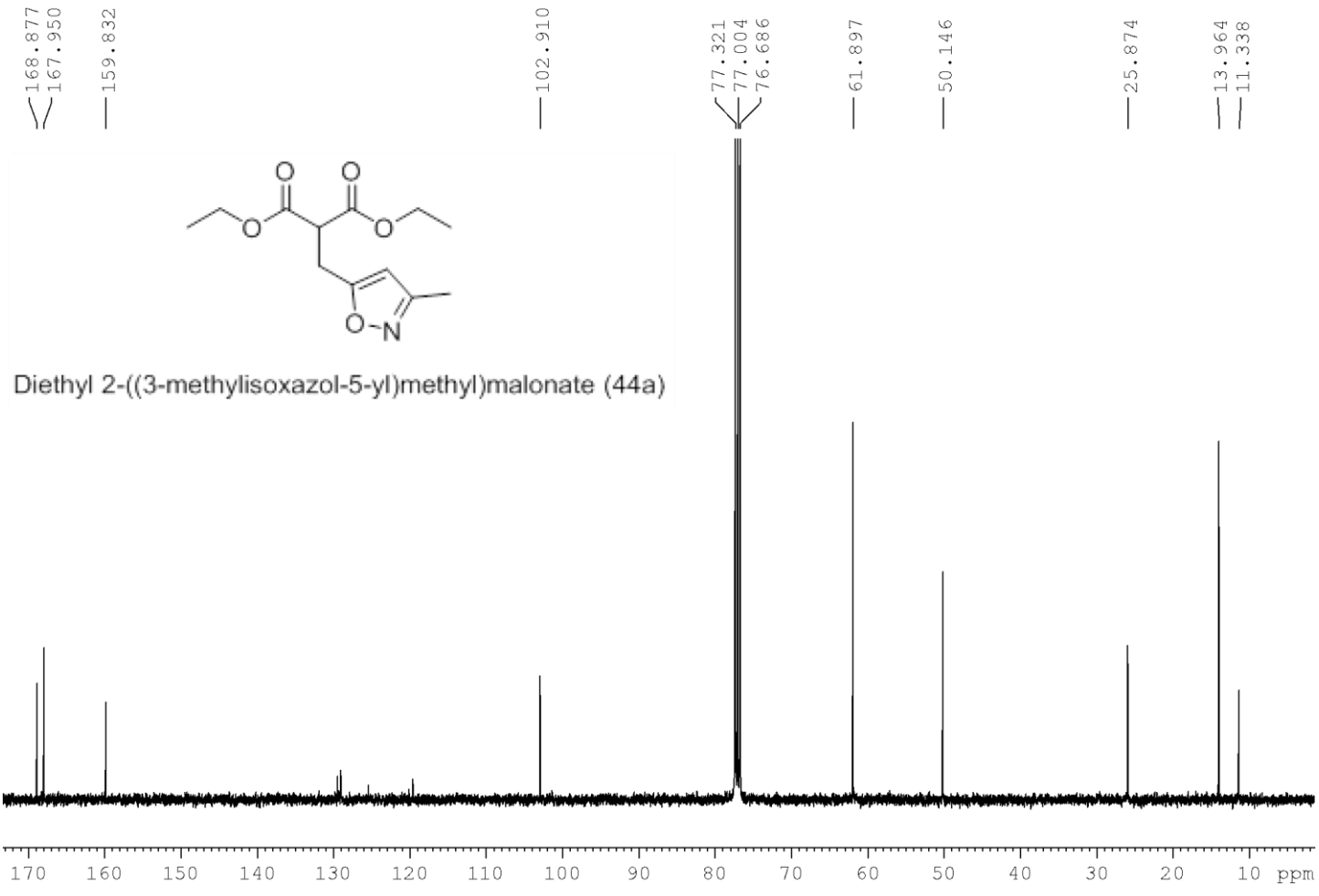


Ethyl 2-amino-3-methyl-3-phenylbutanoate (**41**)

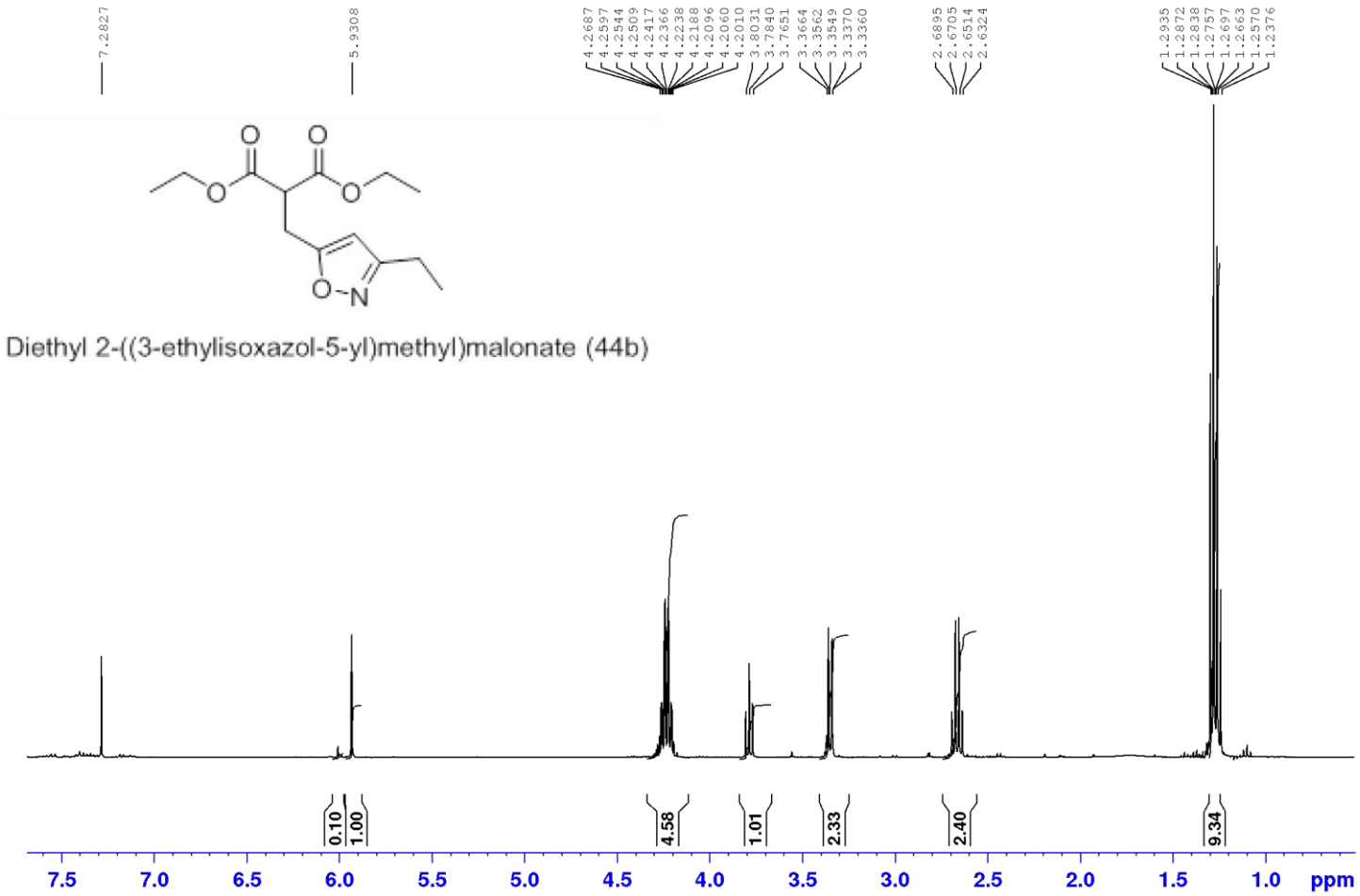

7.2345
7.2260
7.2215
7.2175
7.2060
7.2028
7.1878
7.1840
7.1796
7.1759
7.1724
7.1639
7.1581
7.1507
7.1428
7.1395
7.1300
7.1261
7.1208
7.1094
4.1521
4.1372
4.1194
4.1015
4.0837
3.8796
3.8133
3.7982
3.7927
3.7776
2.9403
2.9252
2.9056
2.8906
2.8542
2.8335
2.8195
2.7989
1.2133
1.1955
1.1777
1.1619
1.1439
1.1261
O
O
NH
HO
Ethyl hydroxyphenylalaninate (42)
5.53
1.34
2.09
1.00
1.00
1.07
3.01
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
ppm
173.879
146.300
128.182
128.128
126.387
126.301
63.968
60.420
41.894
25.499
23.392
14.016
O
O
NH
HO
Ethyl hydroxyphenylalaninate (42)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



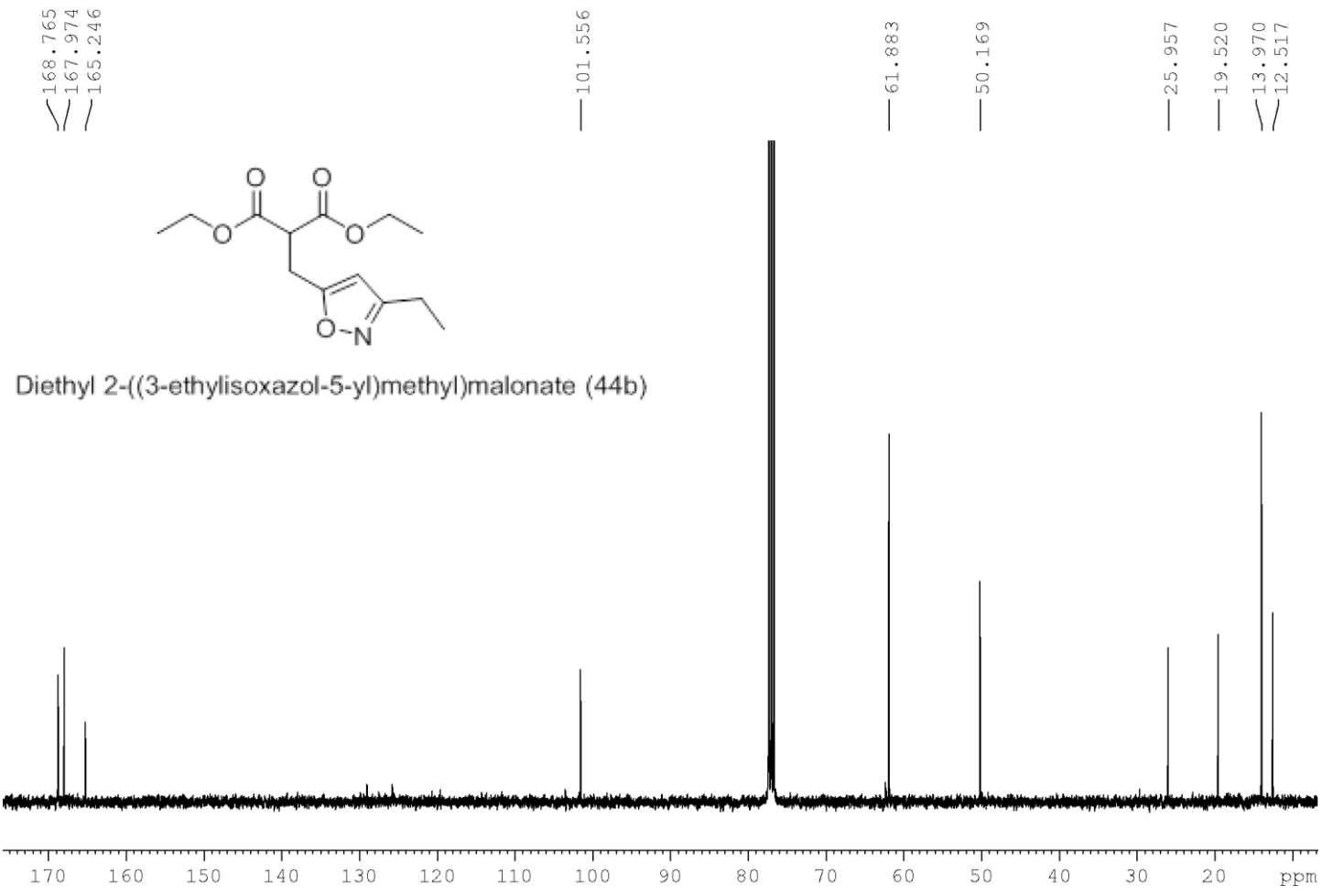
Diethyl 2-((3-methylisoxazol-5-yl)methyl)malonate (44a)



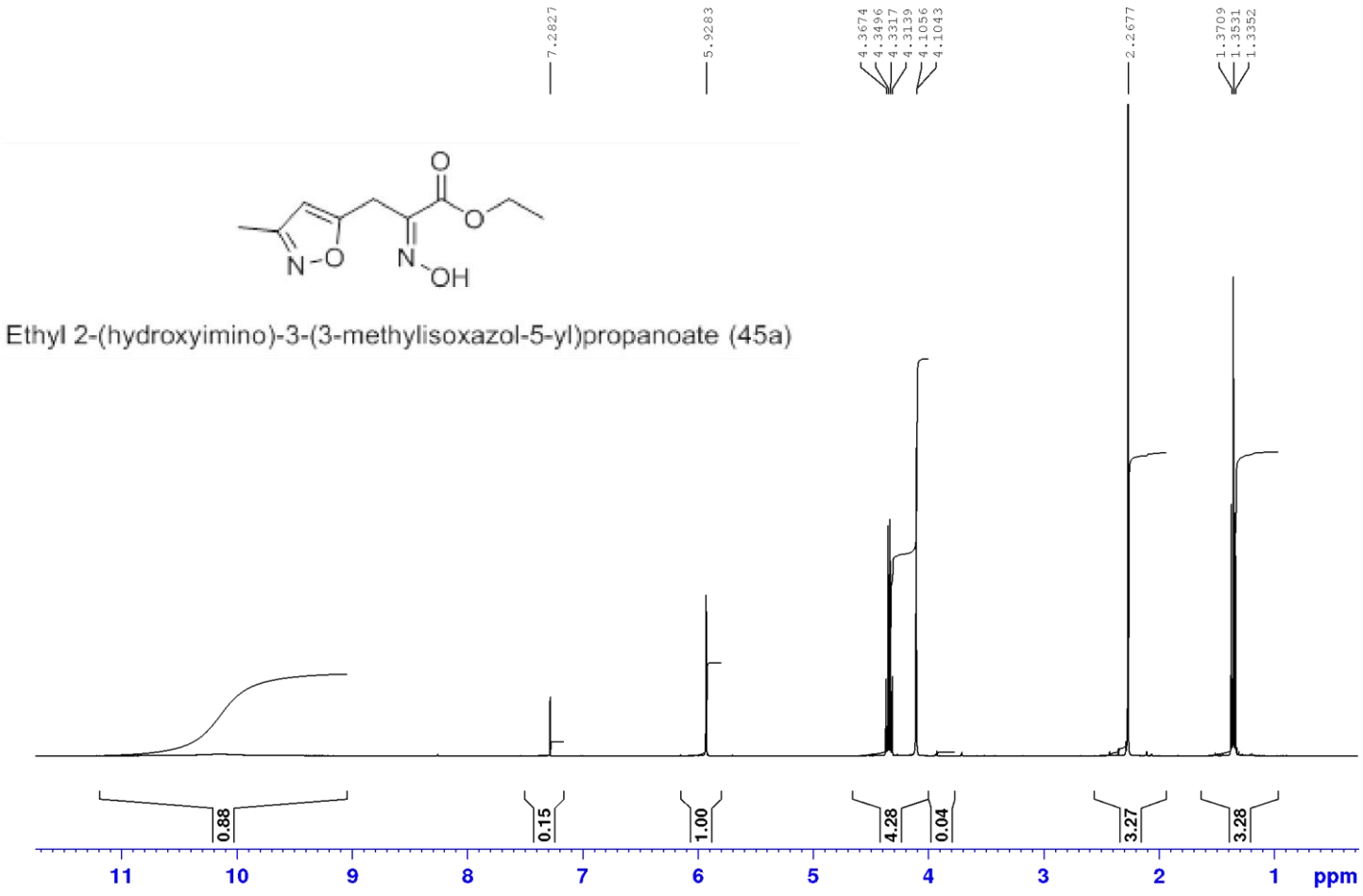
Diethyl 2-((3-methylisoxazol-5-yl)methyl)malonate (44a)



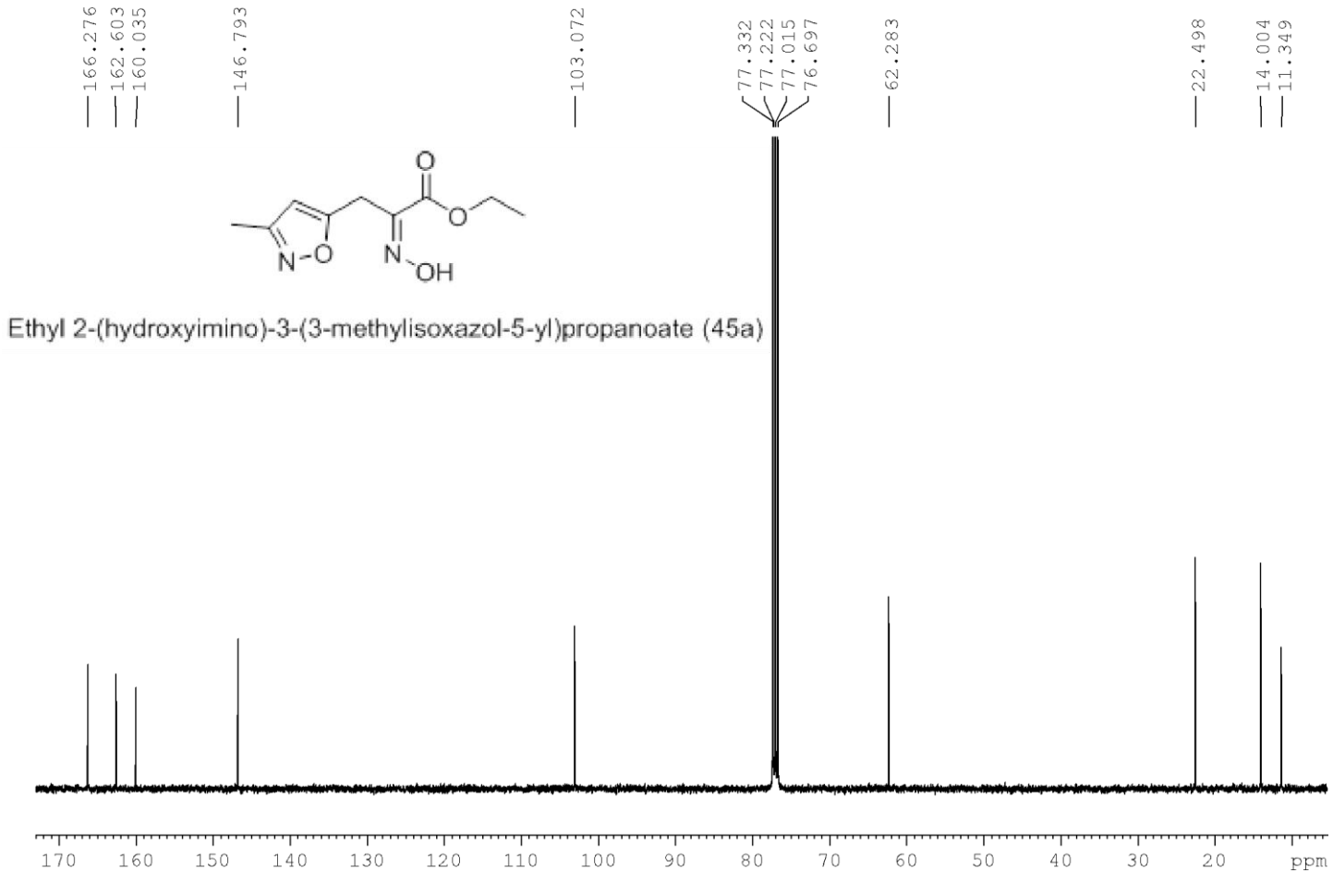
Diethyl 2-((3-ethylisoxazol-5-yl)methyl)malonate (44b)



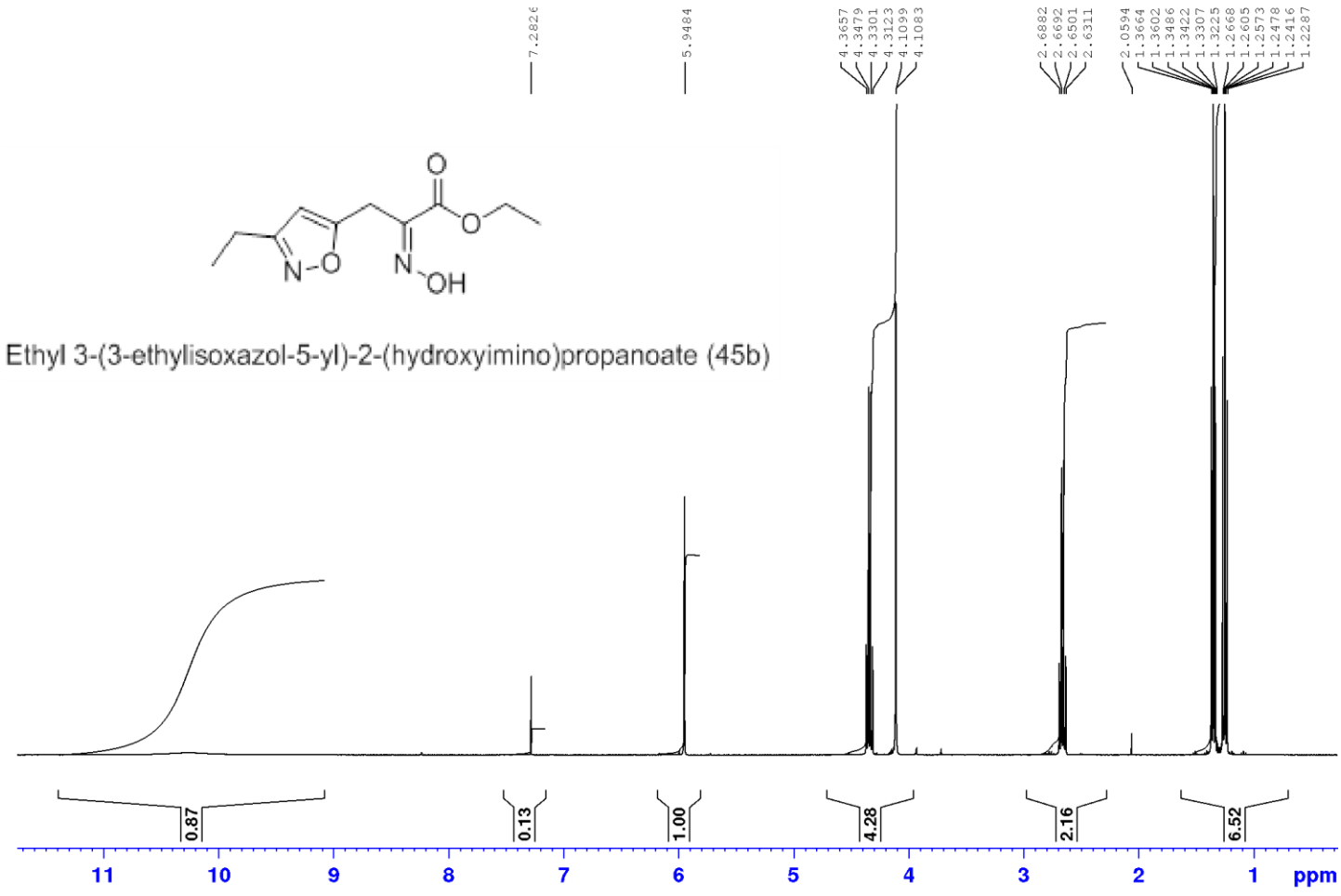
Diethyl 2-((3-ethylisoxazol-5-yl)methyl)malonate (44b)



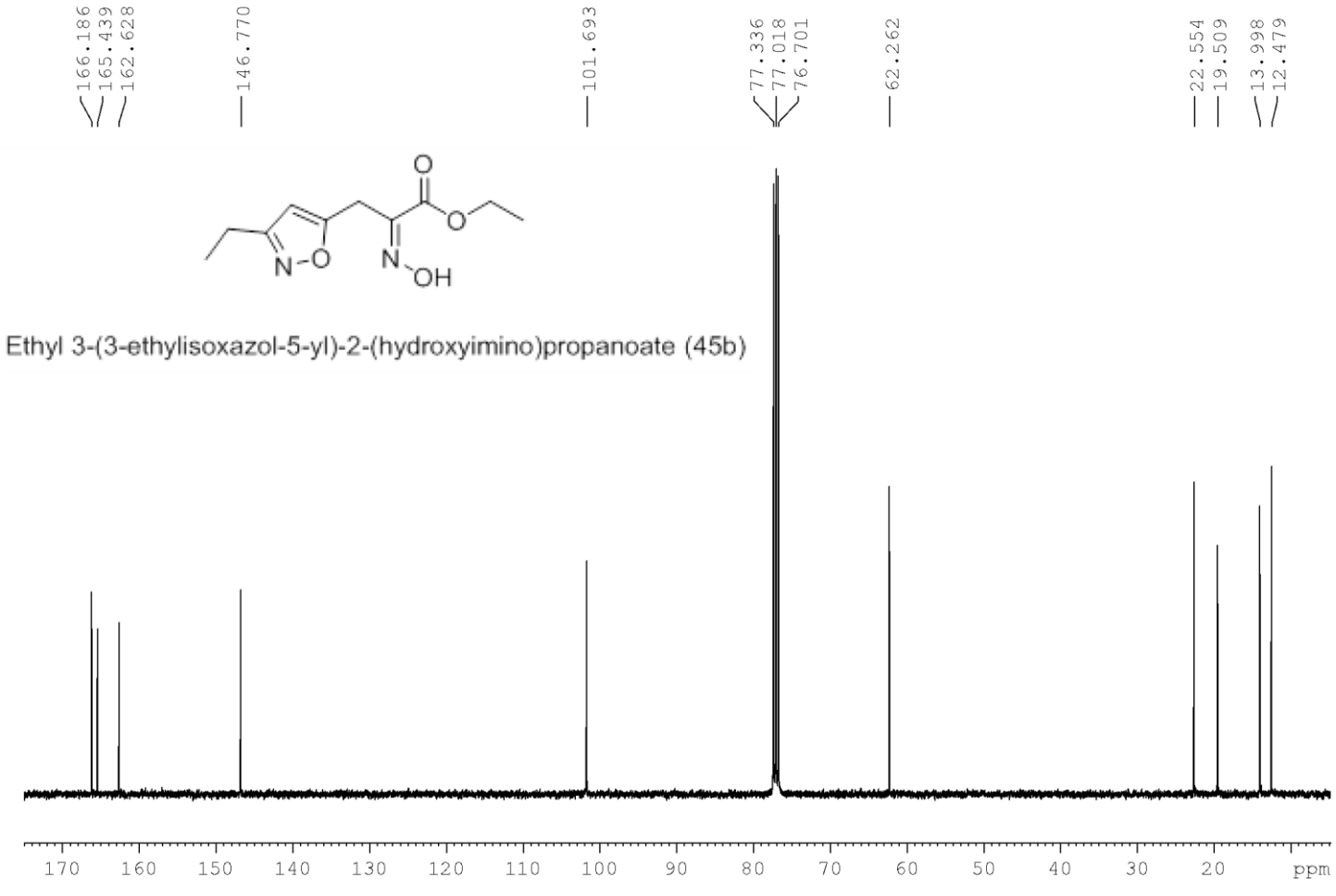
Ethyl 2-(hydroxyimino)-3-(3-methylisoxazol-5-yl)propanoate (45a)



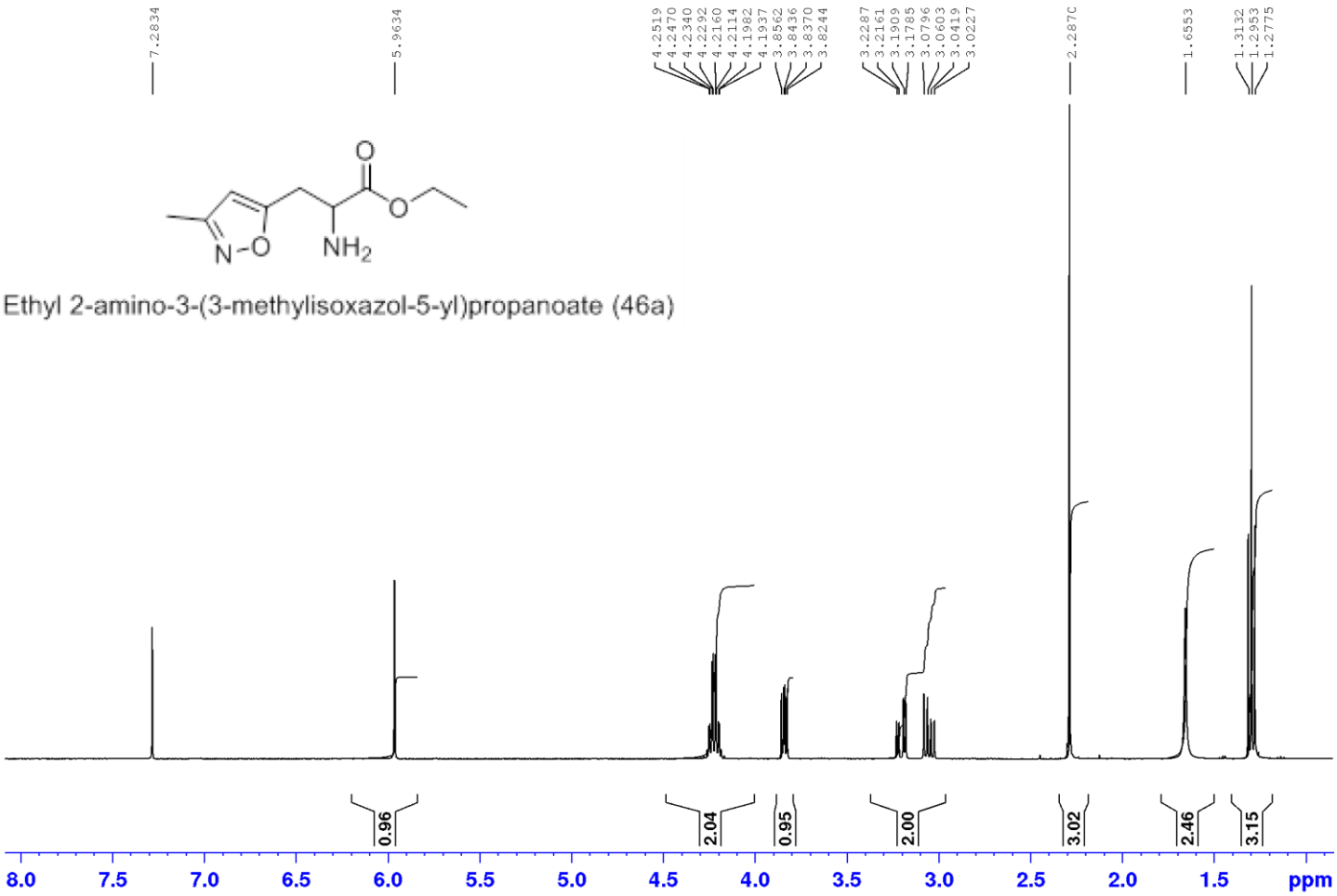
Ethyl 2-(hydroxyimino)-3-(3-methylisoxazol-5-yl)propanoate (45a)

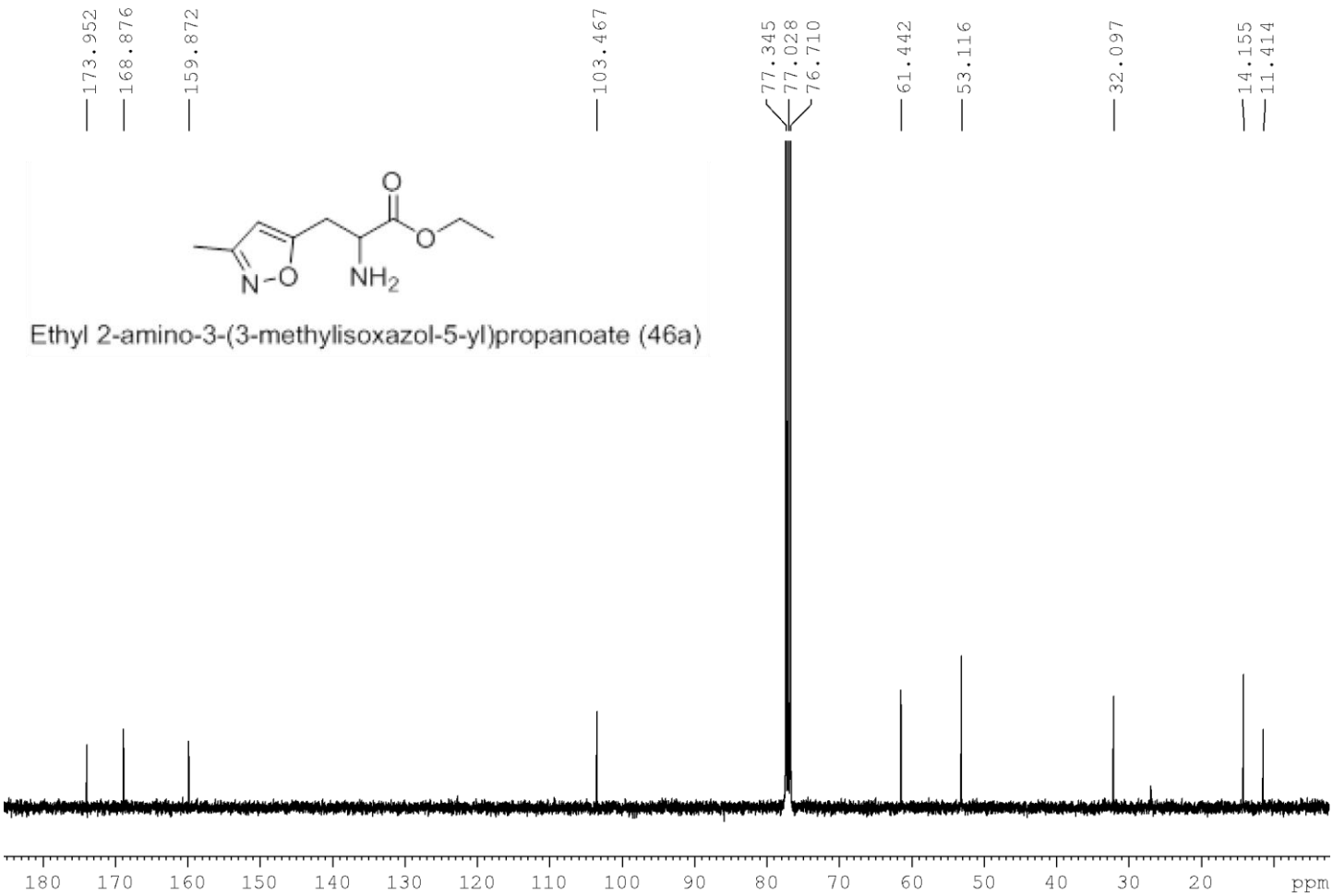


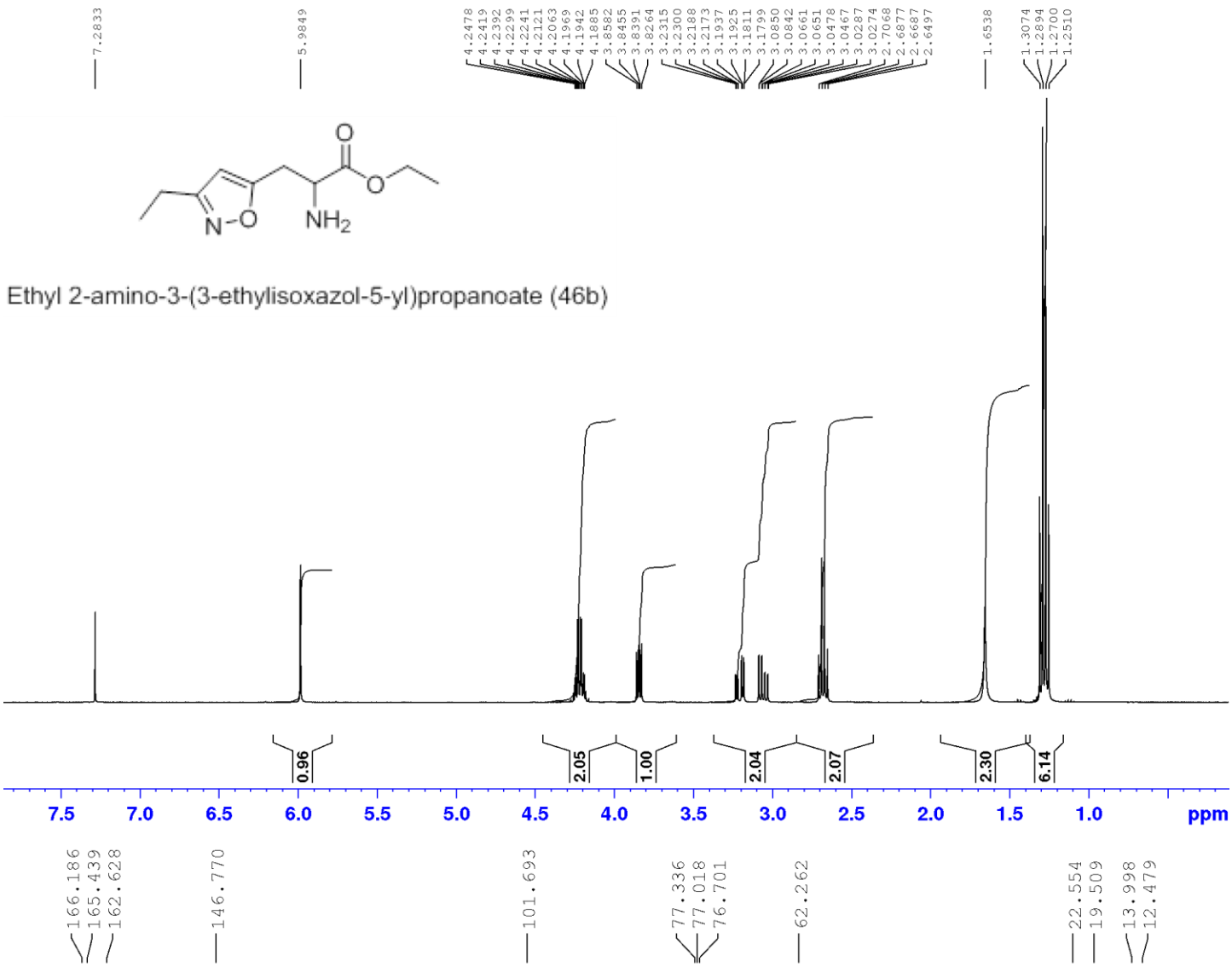
Ethyl 3-(3-ethylisoxazol-5-yl)-2-(hydroxyimino)propanoate (45b)

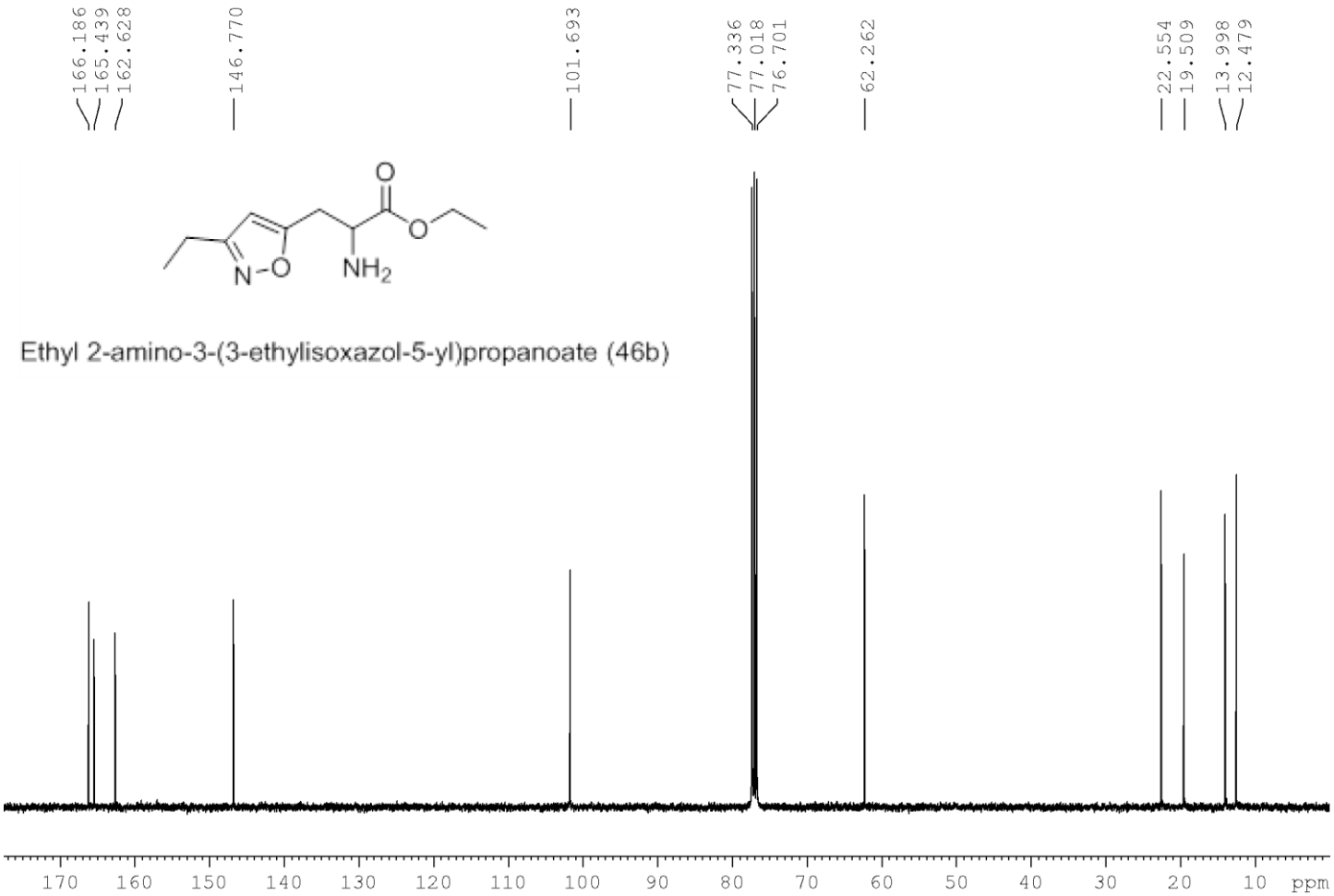


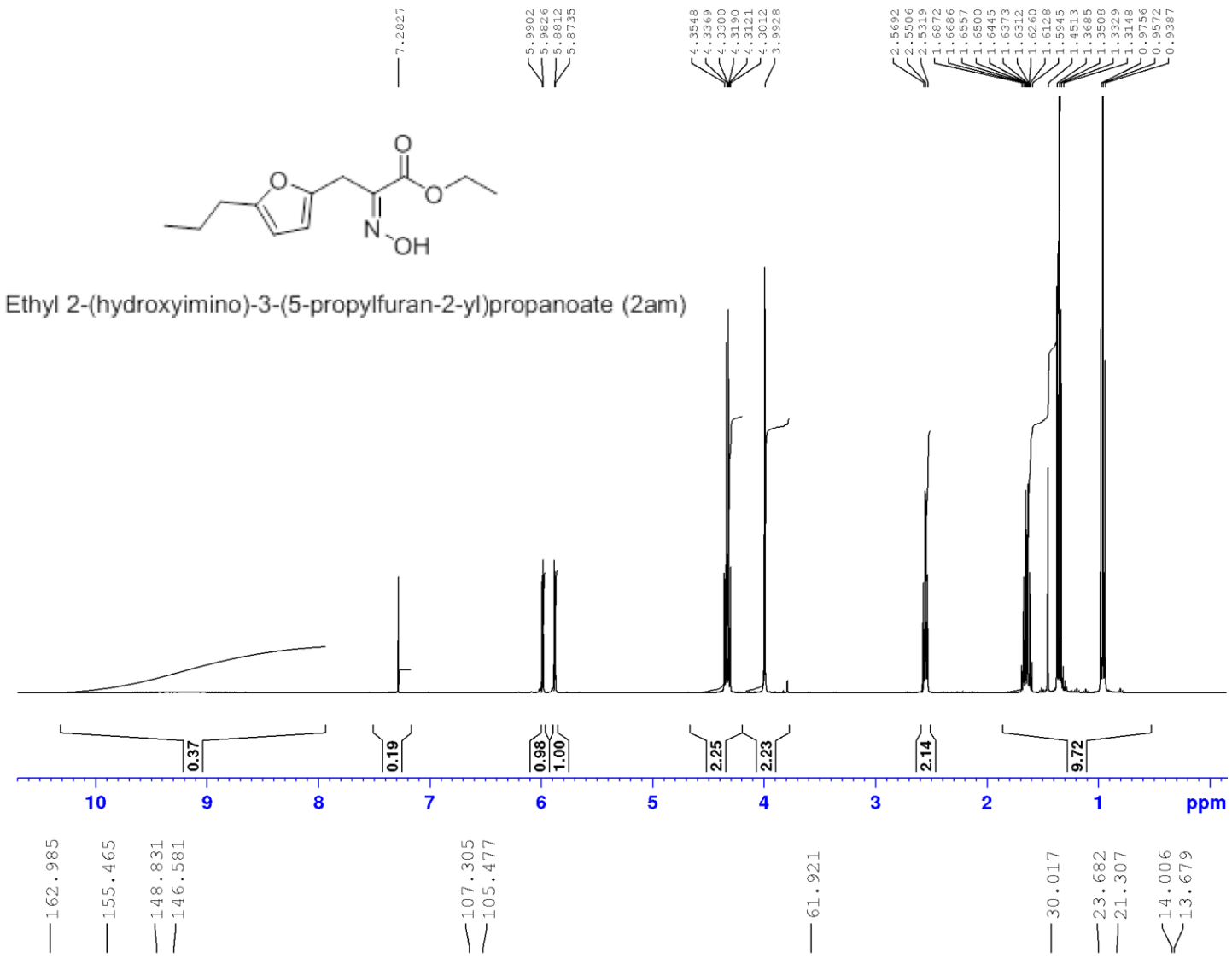
Ethyl 3-(3-ethylisoxazol-5-yl)-2-(hydroxyimino)propanoate (45b)

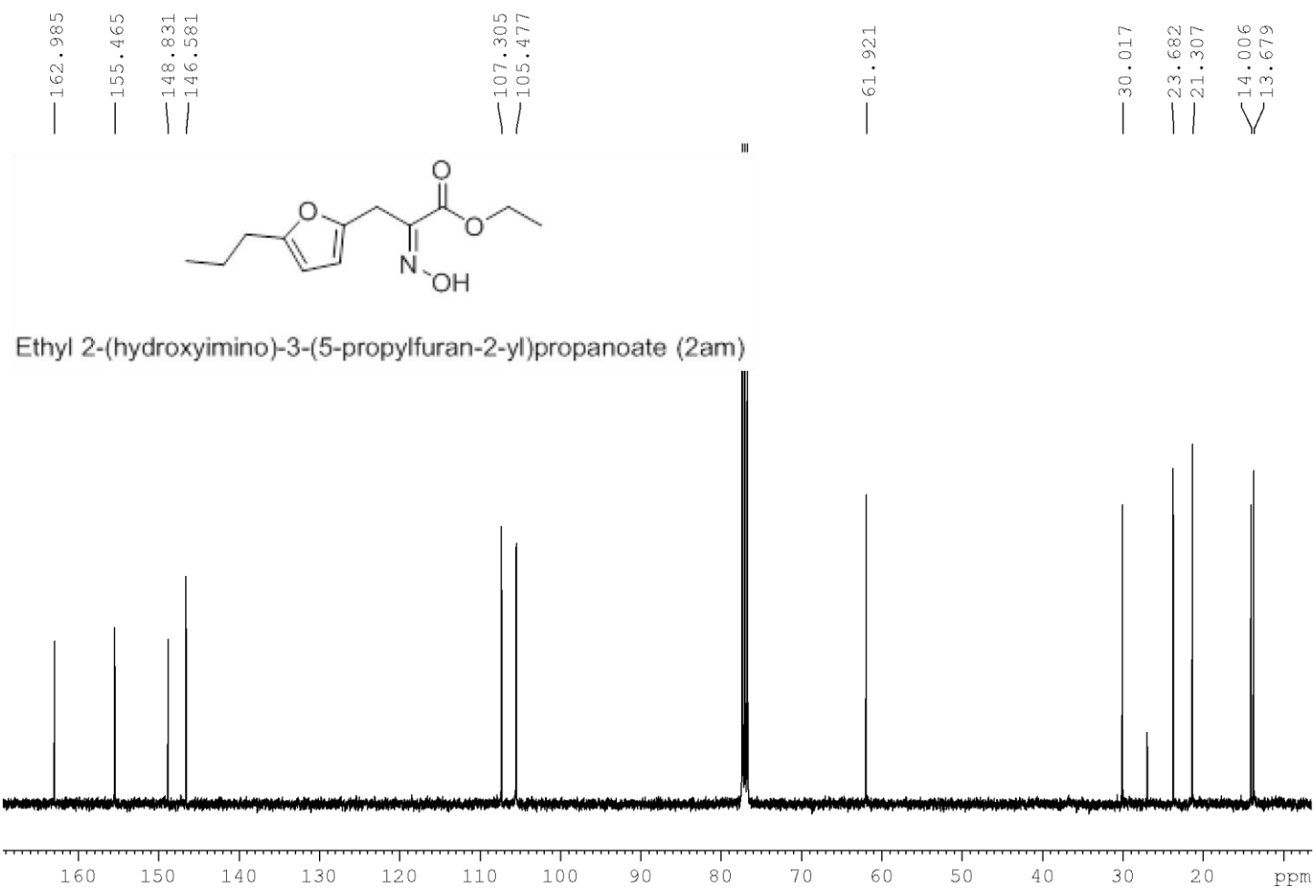

7.2834
5.9634
4.2519
4.2470
4.2340
4.2292
4.2160
4.2114
4.1982
4.1937
3.8562
3.8436
3.8370
3.8244
3.2287
3.2161
3.1909
3.1785
3.0796
3.0603
3.0419
3.0227
2.2870
1.6553
1.3132
1.2953
1.2775
O
O
N
O
NH2
Ethyl 2-amino-3-(3-methylisoxazol-5-yl)propanoate (46a)
0.96
2.04
0.95
2.00
3.02
2.46
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

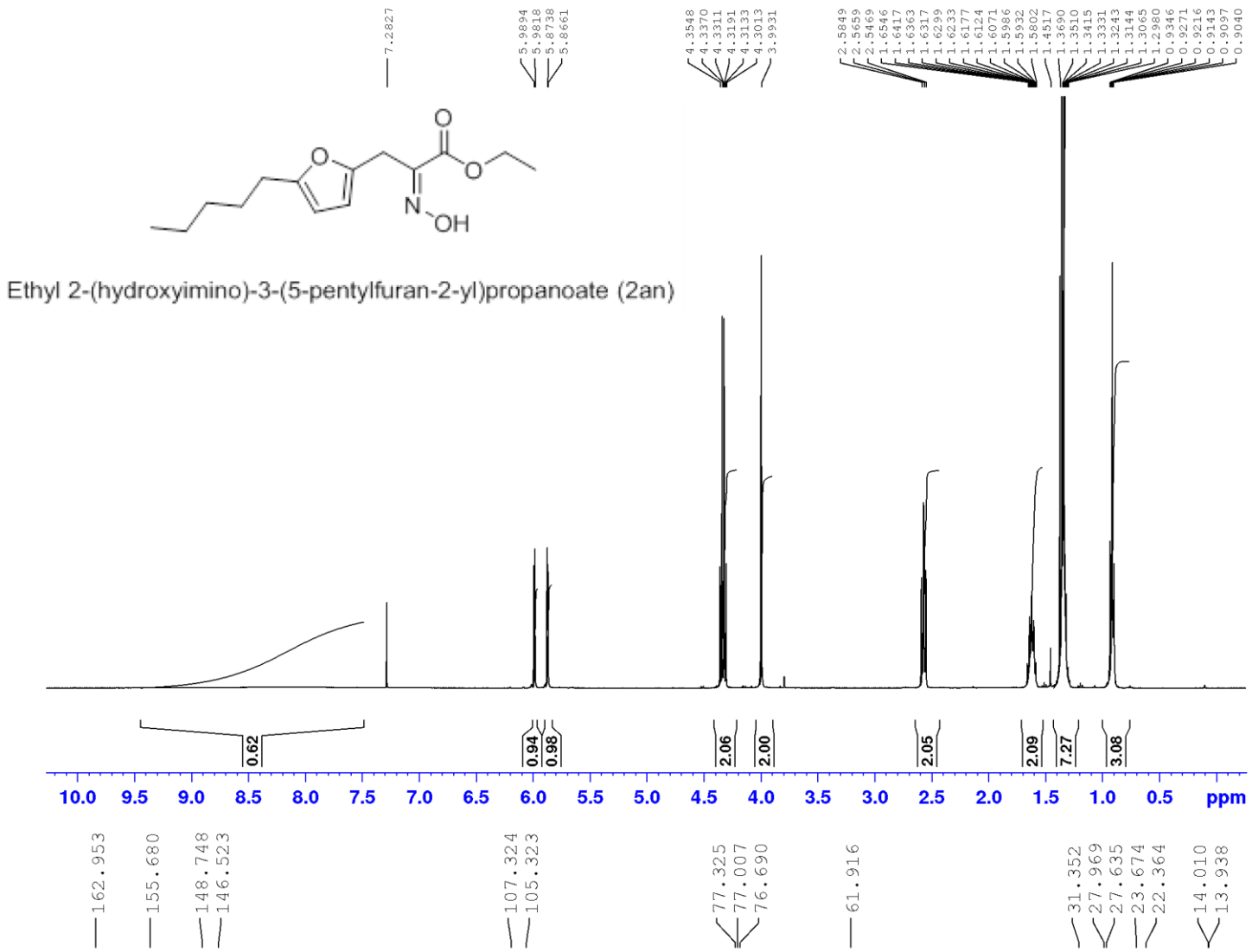

173.952
168.876
159.872
103.467
77.345
77.028
76.710
61.442
53.116
32.097
14.155
11.414
O
O
N
O
NH2
Ethyl 2-amino-3-(3-methylisoxazol-5-yl)propanoate (46a)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

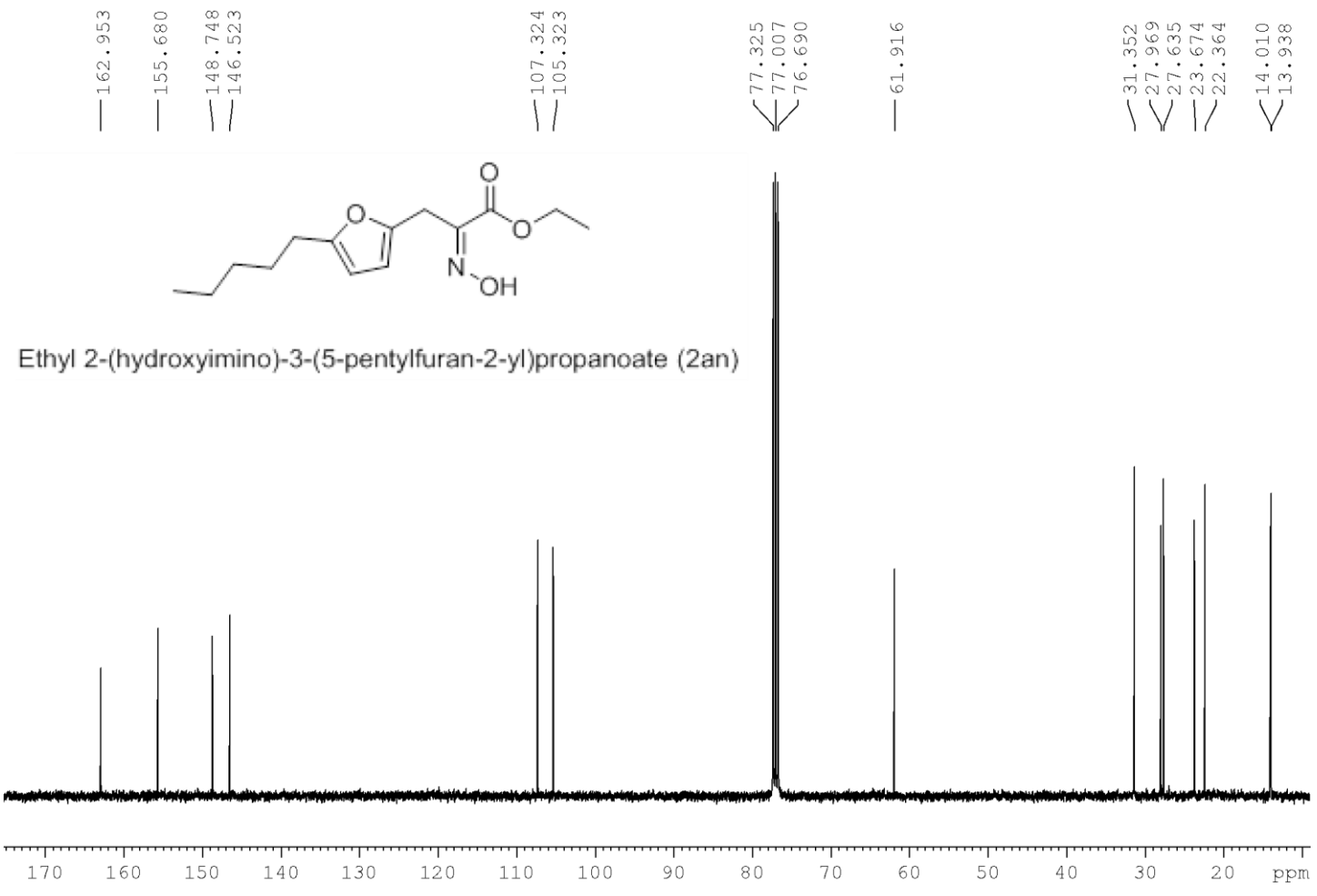

7.2833
5.9849
4.2478
4.2419
4.2392
4.2299
4.2241
4.2121
4.2063
4.1969
4.1942
4.1885
3.8582
3.8455
3.8391
3.8264
3.2315
3.2300
3.2188
3.2173
3.1937
3.1925
3.1811
3.1799
3.0650
3.0842
3.0661
3.0651
3.0478
3.0467
3.0287
3.0274
2.7068
2.6877
2.6687
2.6497
1.6538
1.3074
1.2894
1.2700
1.2510
O
O
N
O
NH2
Ethyl 2-amino-3-(3-ethylisoxazol-5-yl)propanoate (46b)
0.96
2.05
1.00
2.04
2.07
2.30
6.14
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
ppm

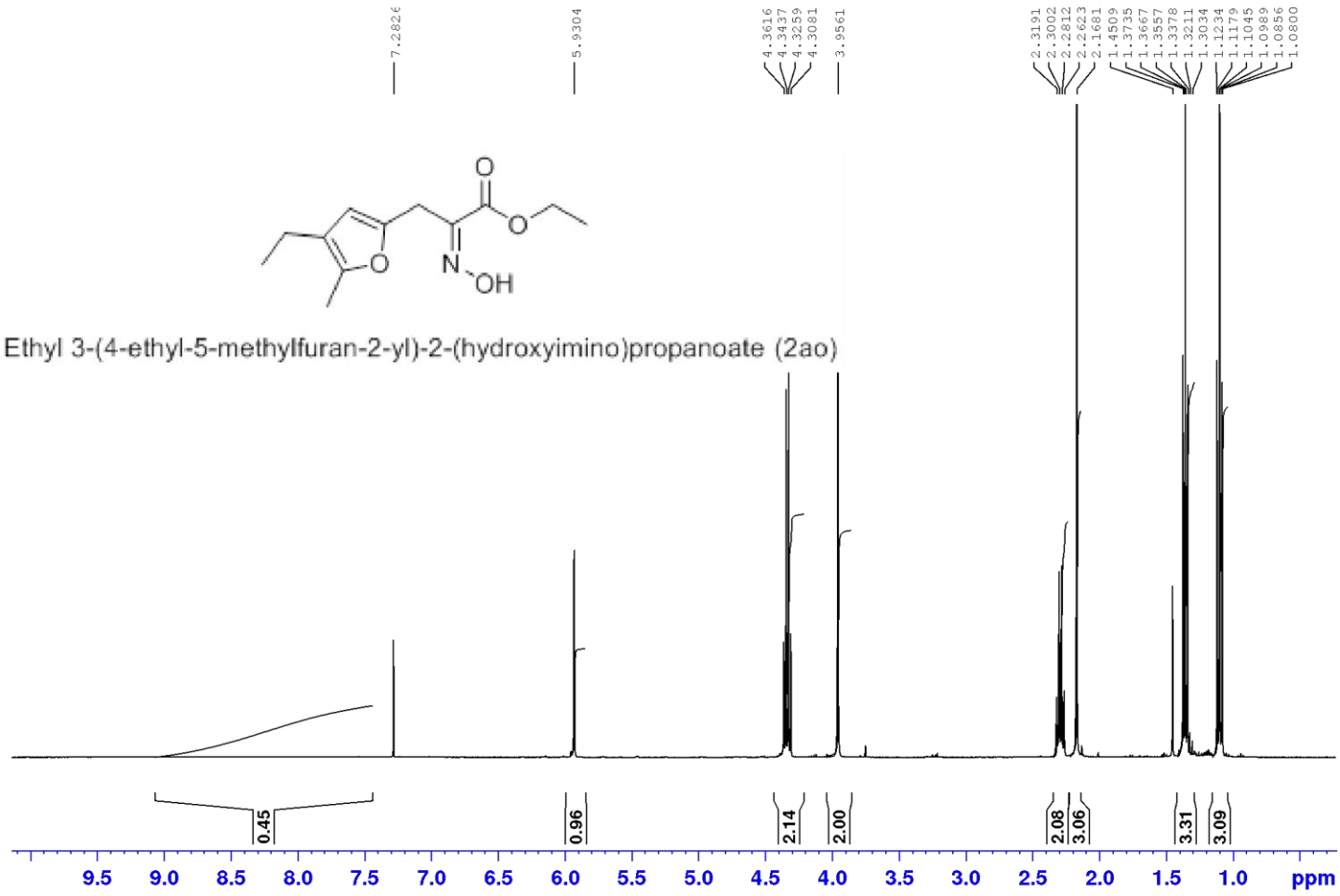

166.186
165.439
162.628
146.770
101.693
77.336
77.018
76.701
62.262
22.554
19.509
13.998
12.479
O
O
N
O
NH2
Ethyl 2-amino-3-(3-ethylisoxazol-5-yl)propanoate (46b)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.2827
5.9902
5.9826
5.8812
5.8735
4.3548
4.3369
4.3300
4.3190
4.3121
4.3012
3.9928
2.5692
2.5506
2.5319
1.6872
1.6686
1.6557
1.6500
1.6445
1.6373
1.6312
1.6260
1.6128
1.5945
1.4513
1.3685
1.3508
1.3329
1.3148
0.9756
0.9572
0.9387
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(5-propylfuran-2-yl)propanoate (2am)
0.37
0.19
0.98
1.00
2.25
2.23
2.14
9.72
10
9
8
7
6
5
4
3
2
1
ppm

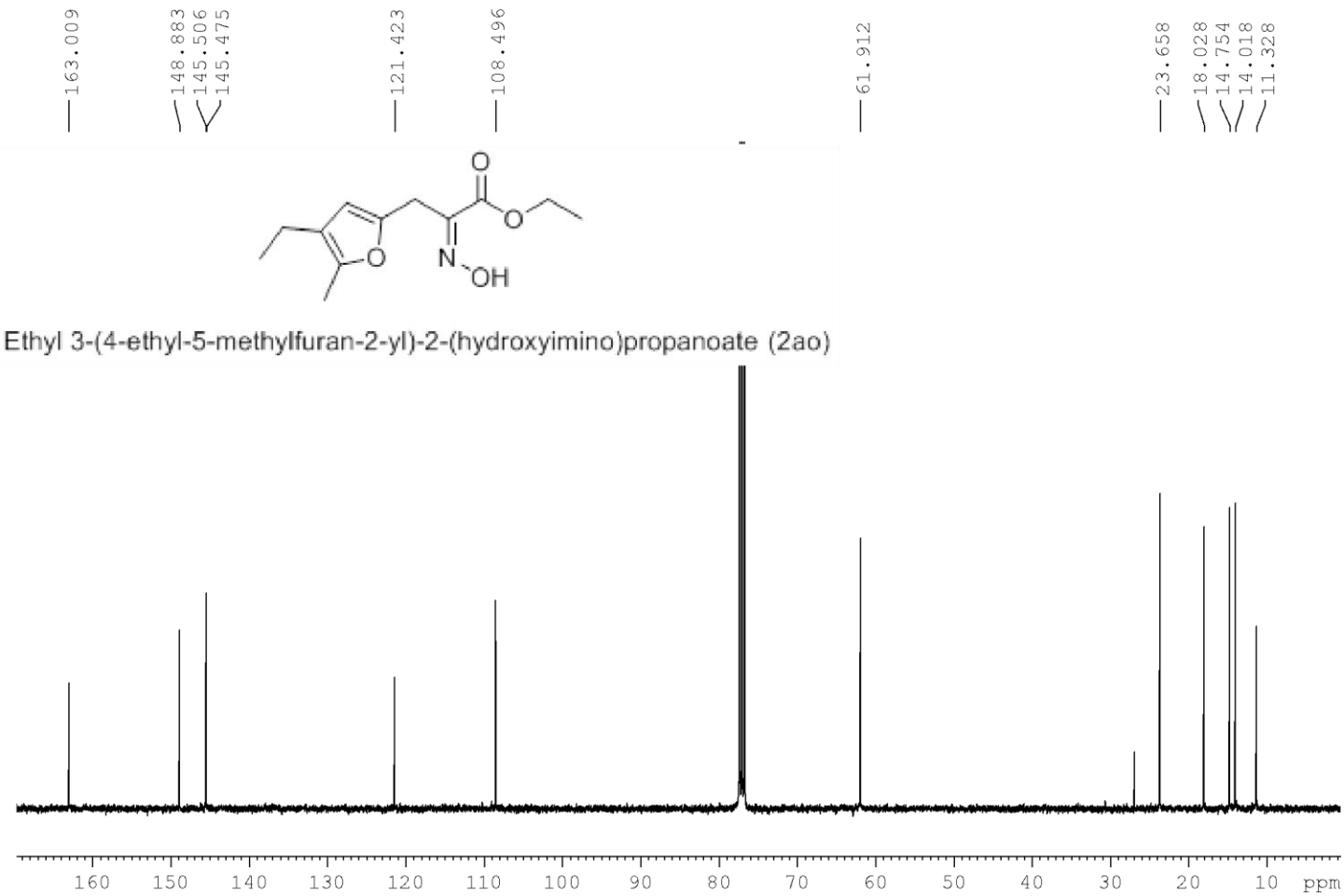

162.985
155.465
148.831
146.581
107.305
105.477
61.921
30.017
23.682
21.307
14.006
13.679
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(5-propylfuran-2-yl)propanoate (2am)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.2827
5.9894
5.9818
5.8738
5.8661
4.3548
4.3370
4.3311
4.3191
4.3133
4.3013
3.9931
2.5849
2.5659
2.5469
1.6546
1.6417
1.6363
1.6317
1.6299
1.6233
1.6177
1.6124
1.6071
1.5986
1.5932
1.5802
1.4517
1.3690
1.3510
1.3415
1.3331
1.3243
1.3144
1.3065
1.2980
0.9346
0.9271
0.9216
0.9143
0.9097
0.9040
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(5-pentylfuran-2-yl)propanoate (2an)
0.62
0.94
0.98
2.06
2.00
2.05
2.09
7.27
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 ppm

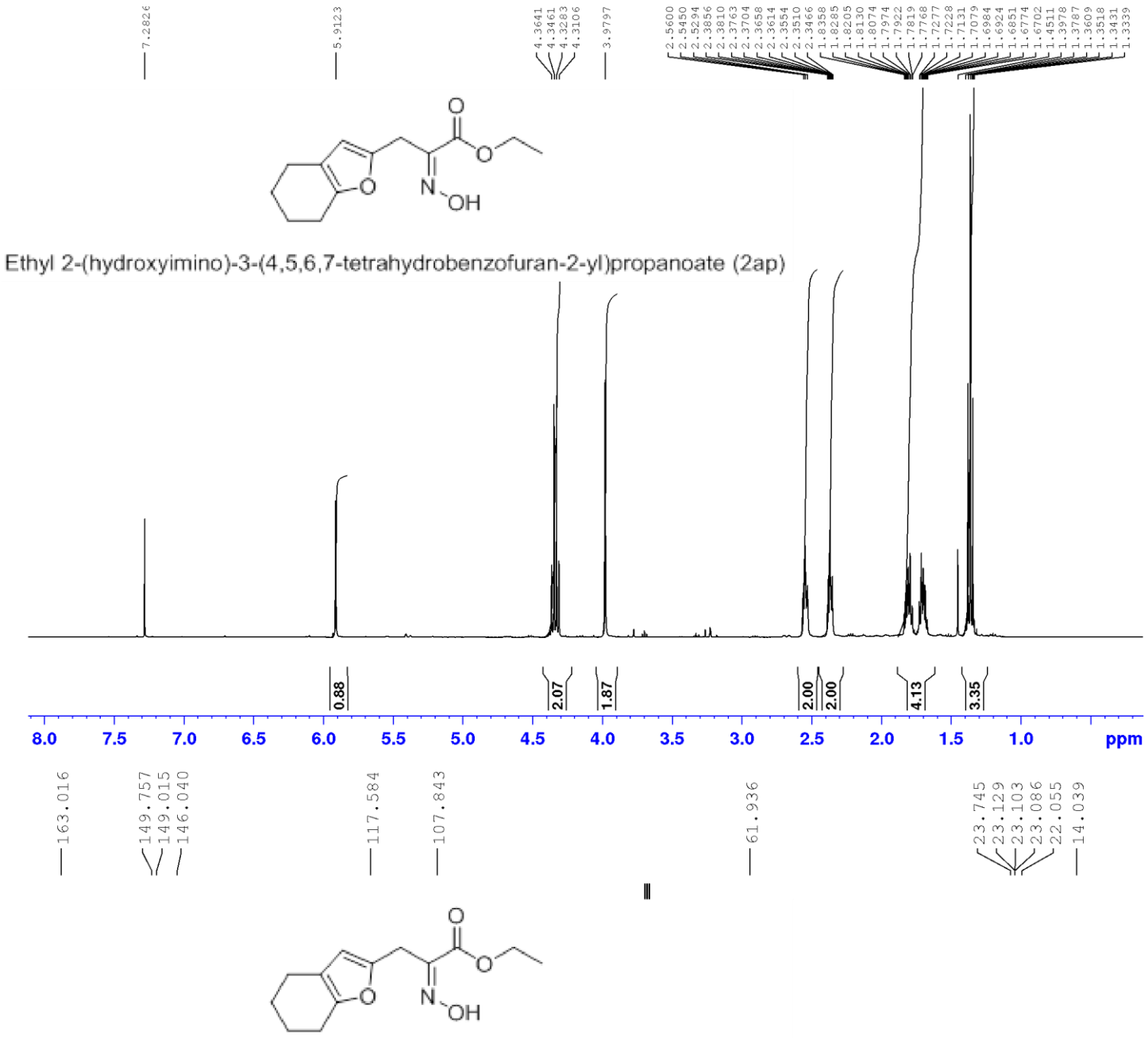

162.953
155.680
148.748
146.523
107.324
105.323
77.325
77.007
76.690
61.916
31.352
27.969
27.635
23.674
22.364
14.010
13.938
O
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(5-pentylfuran-2-yl)propanoate (2an)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

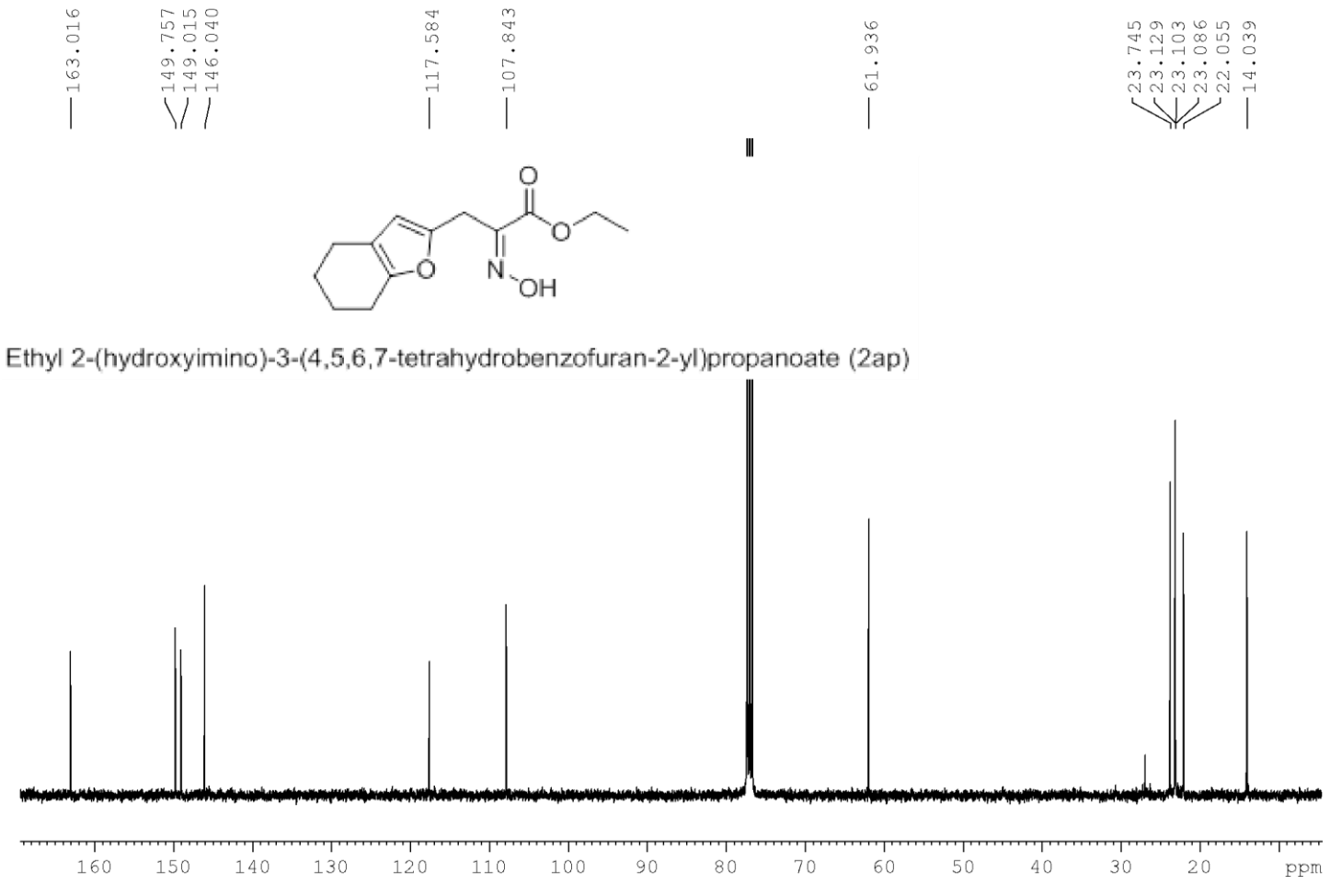


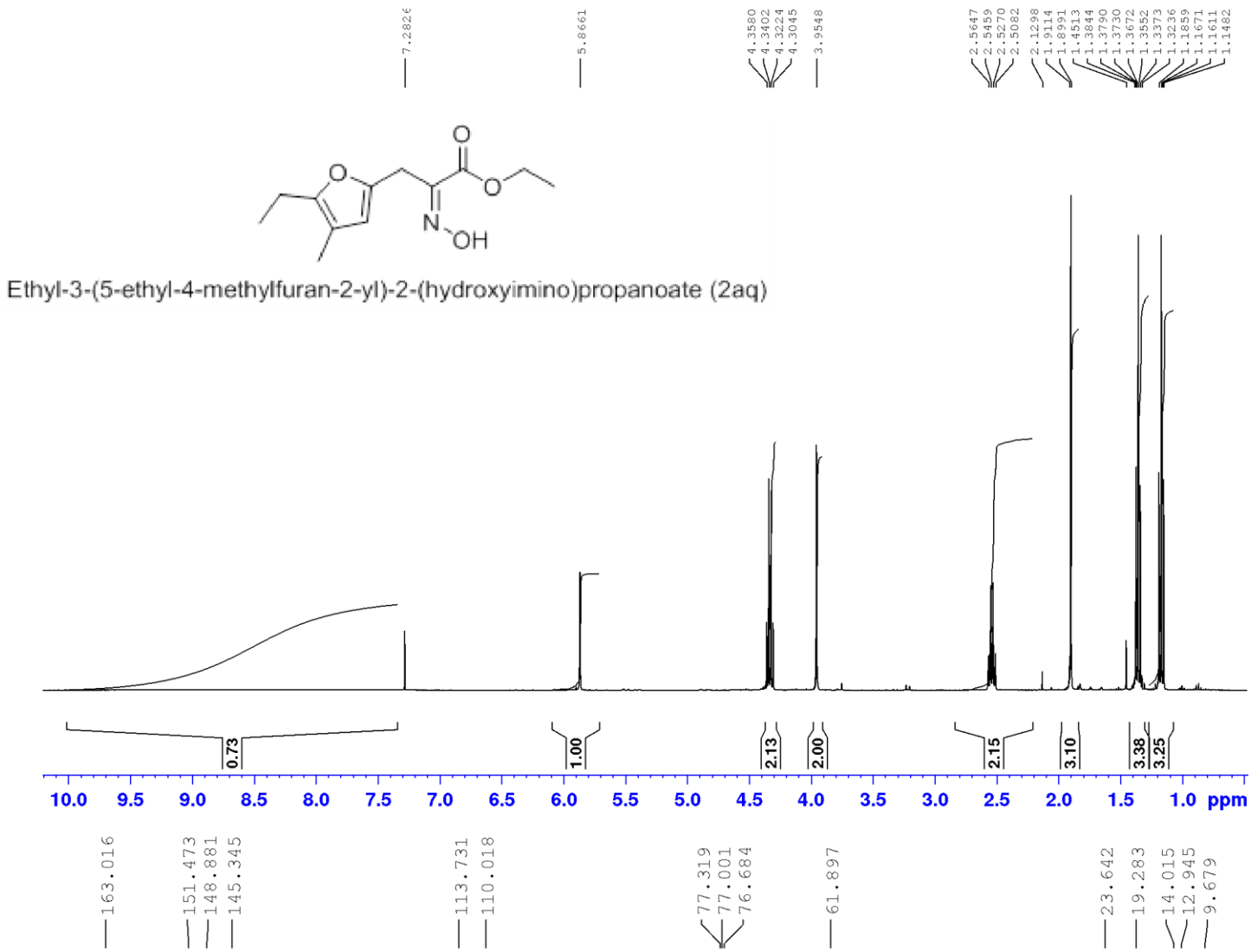
Ethyl 3-(4-ethyl-5-methylfuran-2-yl)-2-(hydroxyimino)propanoate (2ao)

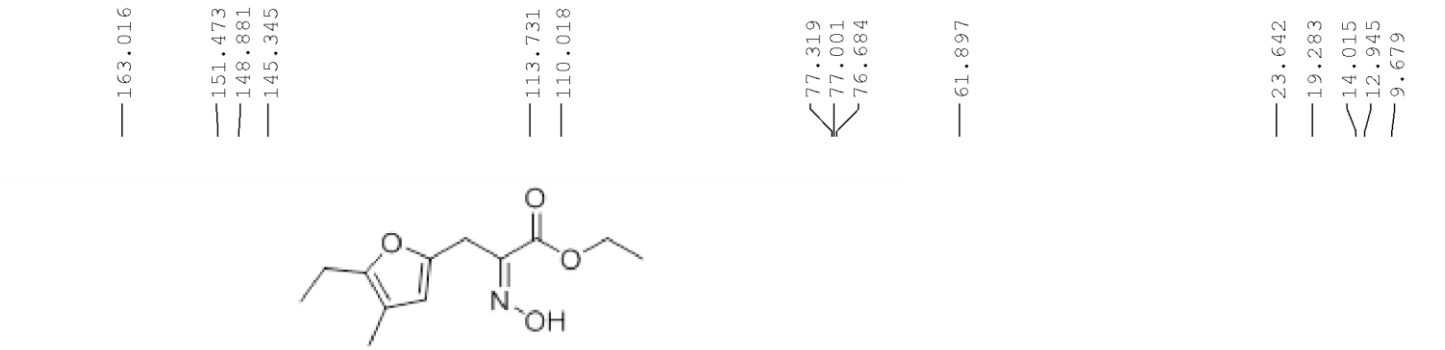


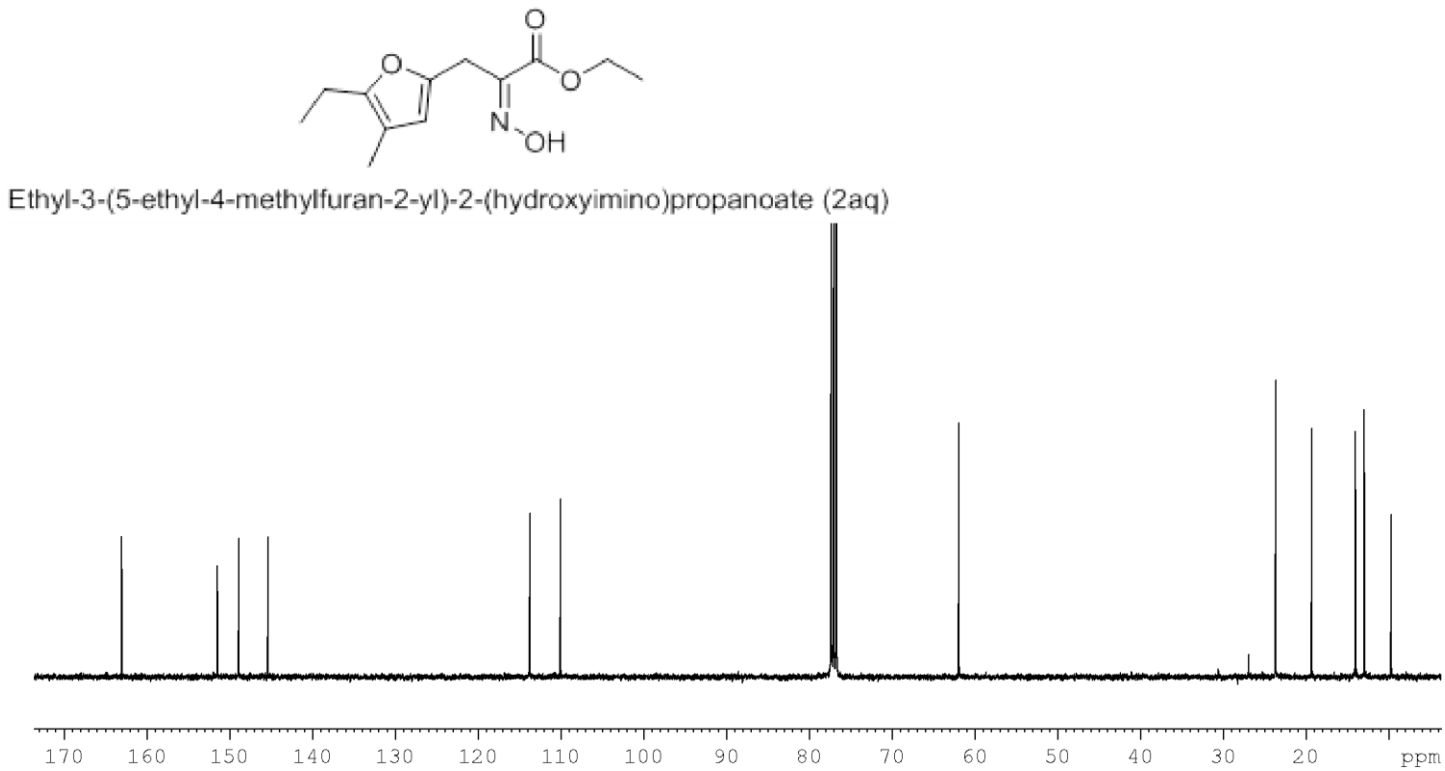
Ethyl 3-(4-ethyl-5-methylfuran-2-yl)-2-(hydroxyimino)propanoate (2ao)

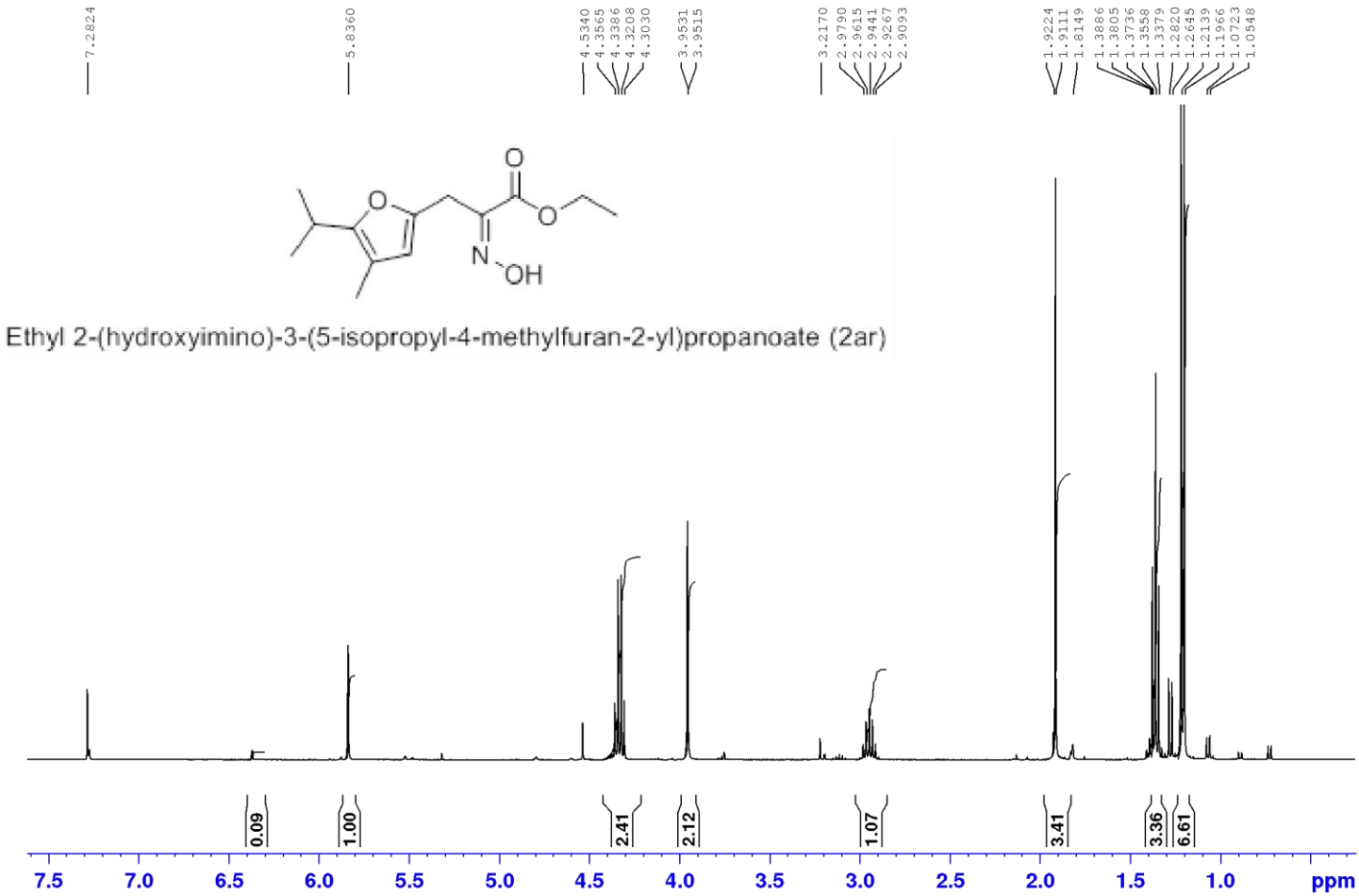

7.2826
5.9123
4.3641
4.3461
4.3283
4.3106
3.9797
2.5600
2.5450
2.5294
2.3856
2.3810
2.3763
2.3704
2.3658
2.3614
2.3554
2.3510
2.3466
1.8358
1.8285
1.8205
1.8130
1.8074
1.7974
1.7922
1.7819
1.7768
1.7277
1.7228
1.7131
1.7079
1.6984
1.6924
1.6851
1.6774
1.6702
1.4511
1.3978
1.3787
1.3609
1.3518
1.3431
1.3339
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(4,5,6,7-tetrahydrobenzofuran-2-yl)propanoate (2ap)
0.88
2.07
1.87
2.00
2.00
4.13
3.35
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
ppm


163.016
149.757
149.015
146.040
117.584
107.843
61.936
23.745
23.129
23.103
23.086
22.055
14.039
O
O
N
OH
Ethyl 2-(hydroxyimino)-3-(4,5,6,7-tetrahydrobenzofuran-2-yl)propanoate (2ap)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

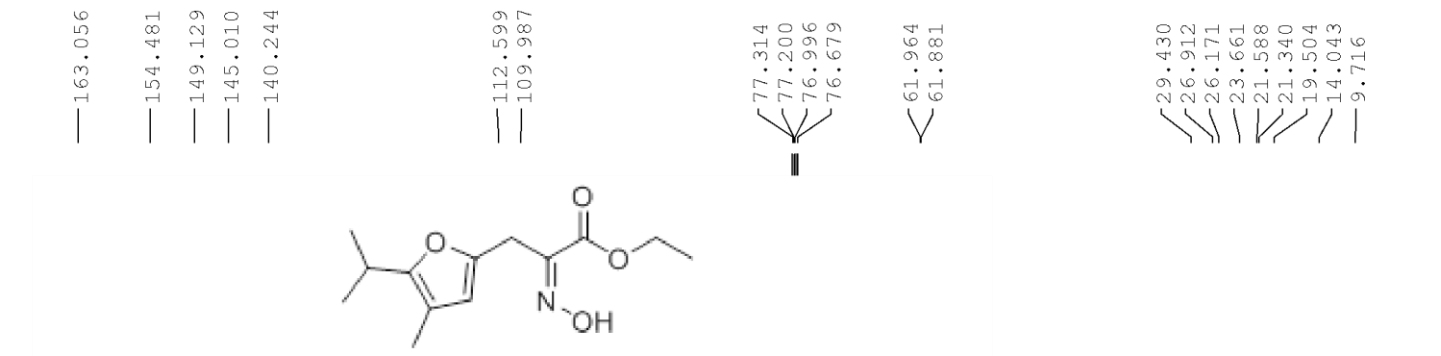

7.2826
5.8661
4.3580
4.3402
4.3224
4.3045
3.9548
2.5647
2.5459
2.5270
2.5082
2.1298
1.9114
1.8991
1.4513
1.3844
1.3790
1.3730
1.3672
1.3552
1.3373
1.3236
1.1859
1.1671
1.1611
1.1482
O
O
O
N
OH
Ethyl-3-(5-ethyl-4-methylfuran-2-yl)-2-(hydroxyimino)propanoate (2aq)
0.73
1.00
2.13
2.00
2.15
3.10
3.38
3.25
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 ppm


163.016
151.473
148.881
145.345
113.731
110.018
77.319
77.001
76.684
61.897
23.642
19.283
14.015
12.945
9.679

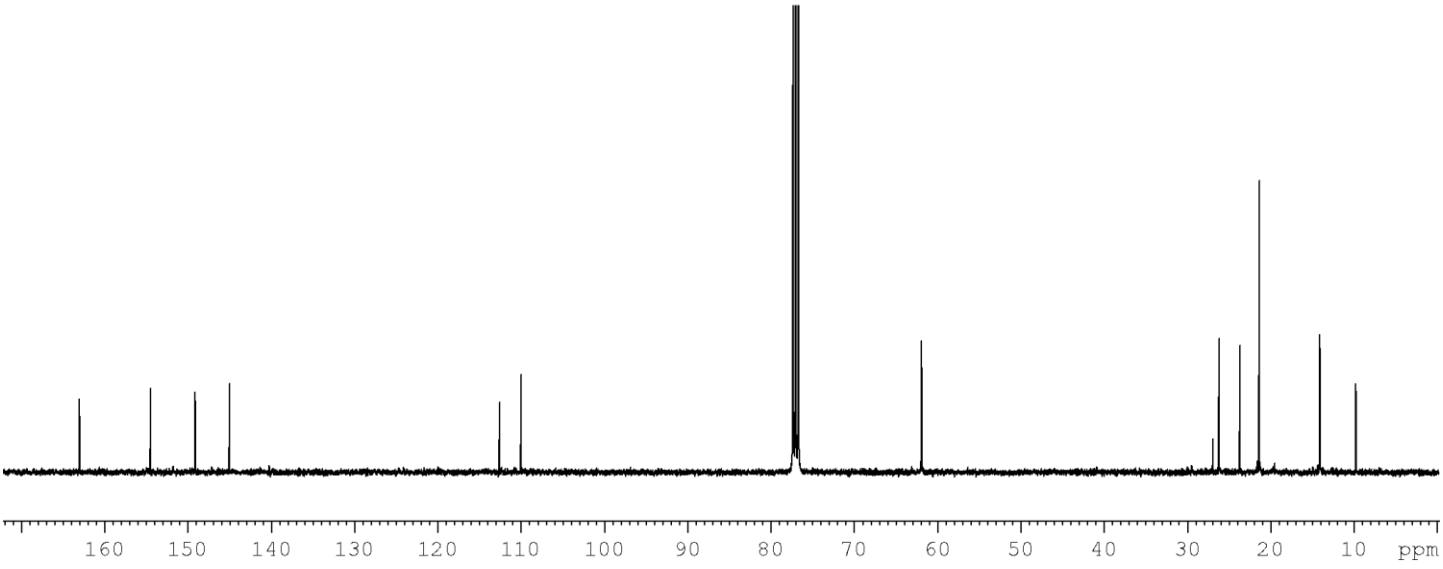

O
O
O
N
OH
Ethyl-3-(5-ethyl-4-methylfuran-2-yl)-2-(hydroxyimino)propanoate (2aq)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

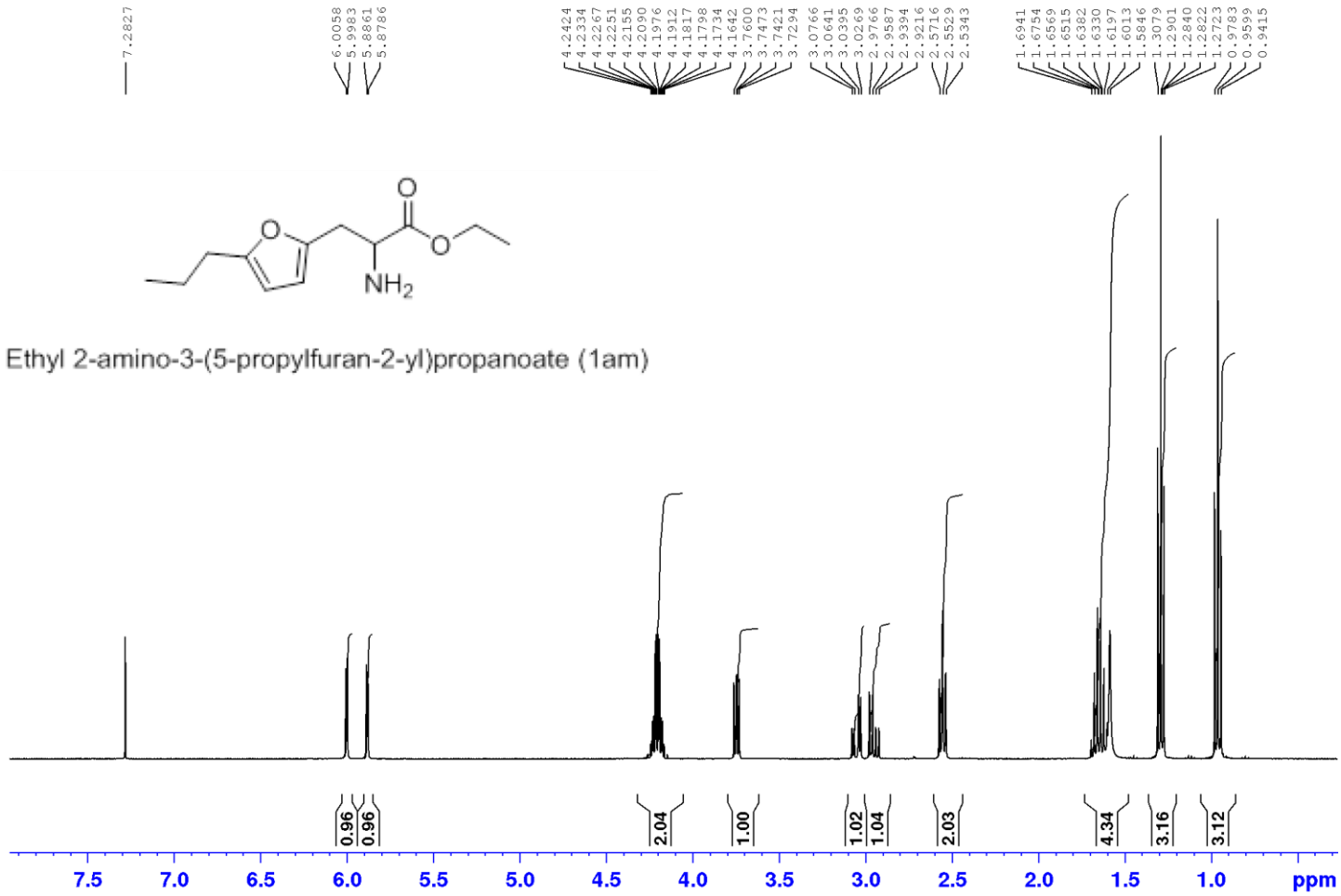


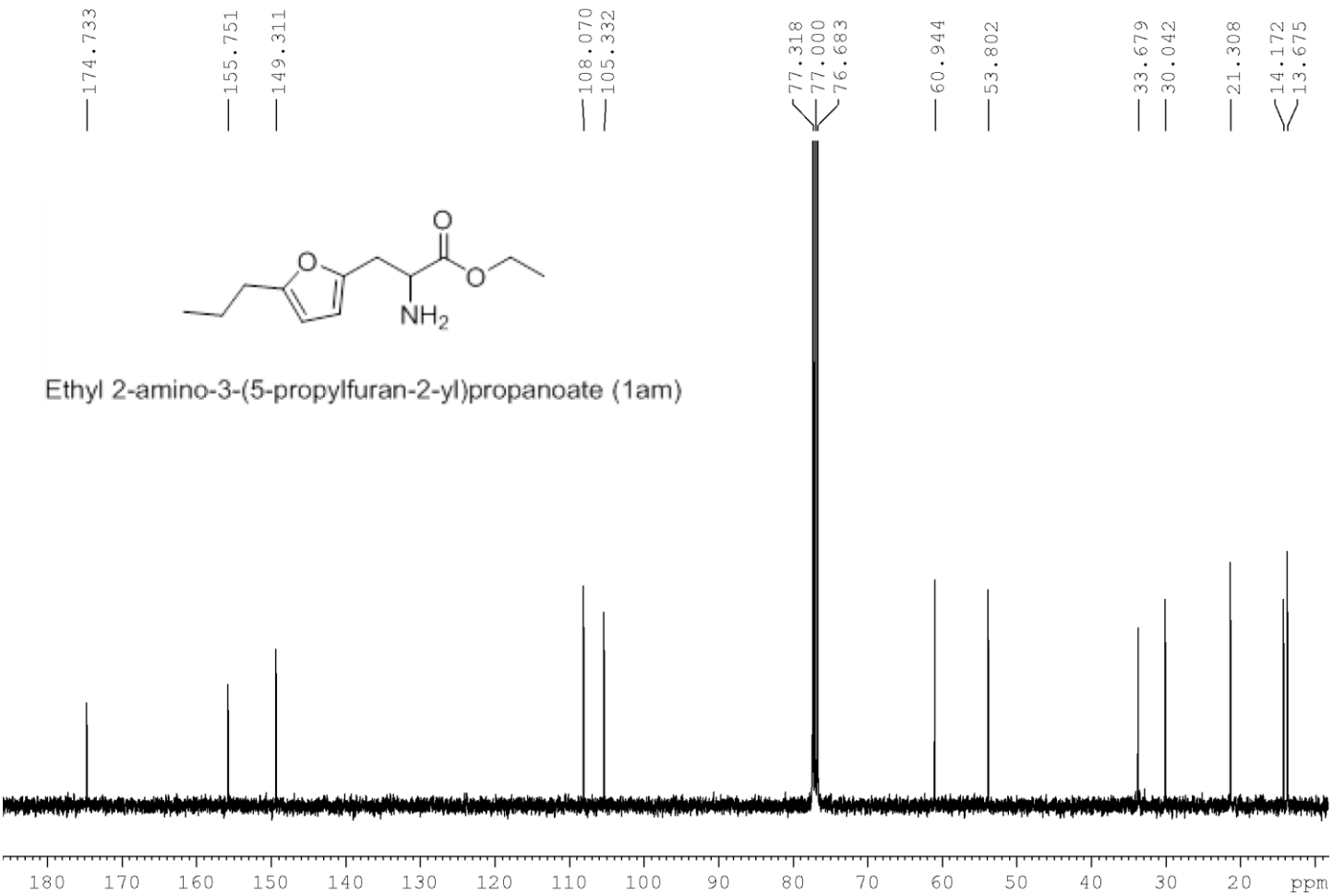
Ethyl 2-(hydroxyimino)-3-(5-isopropyl-4-methylfuran-2-yl)propanoate (2ar)

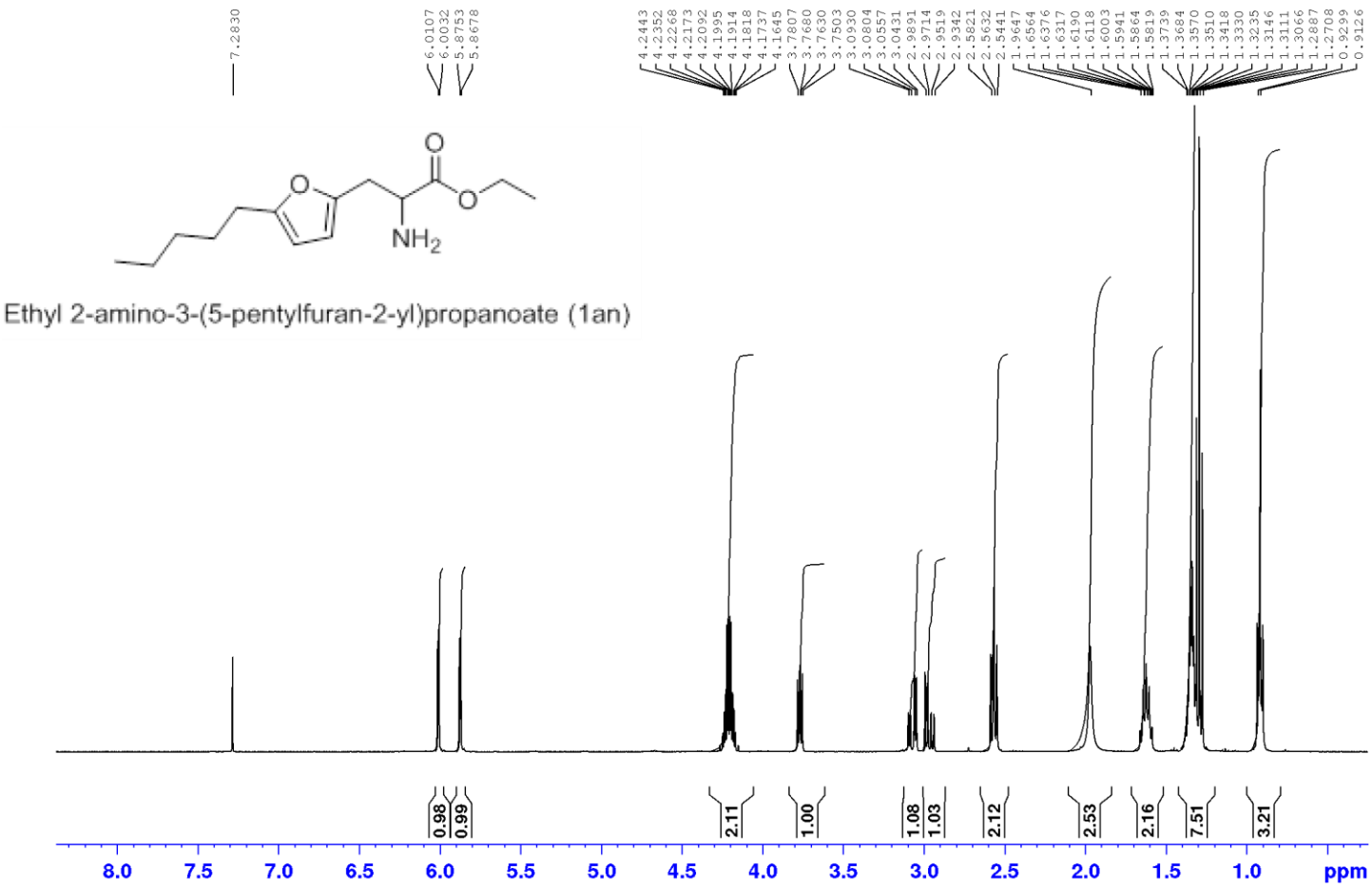


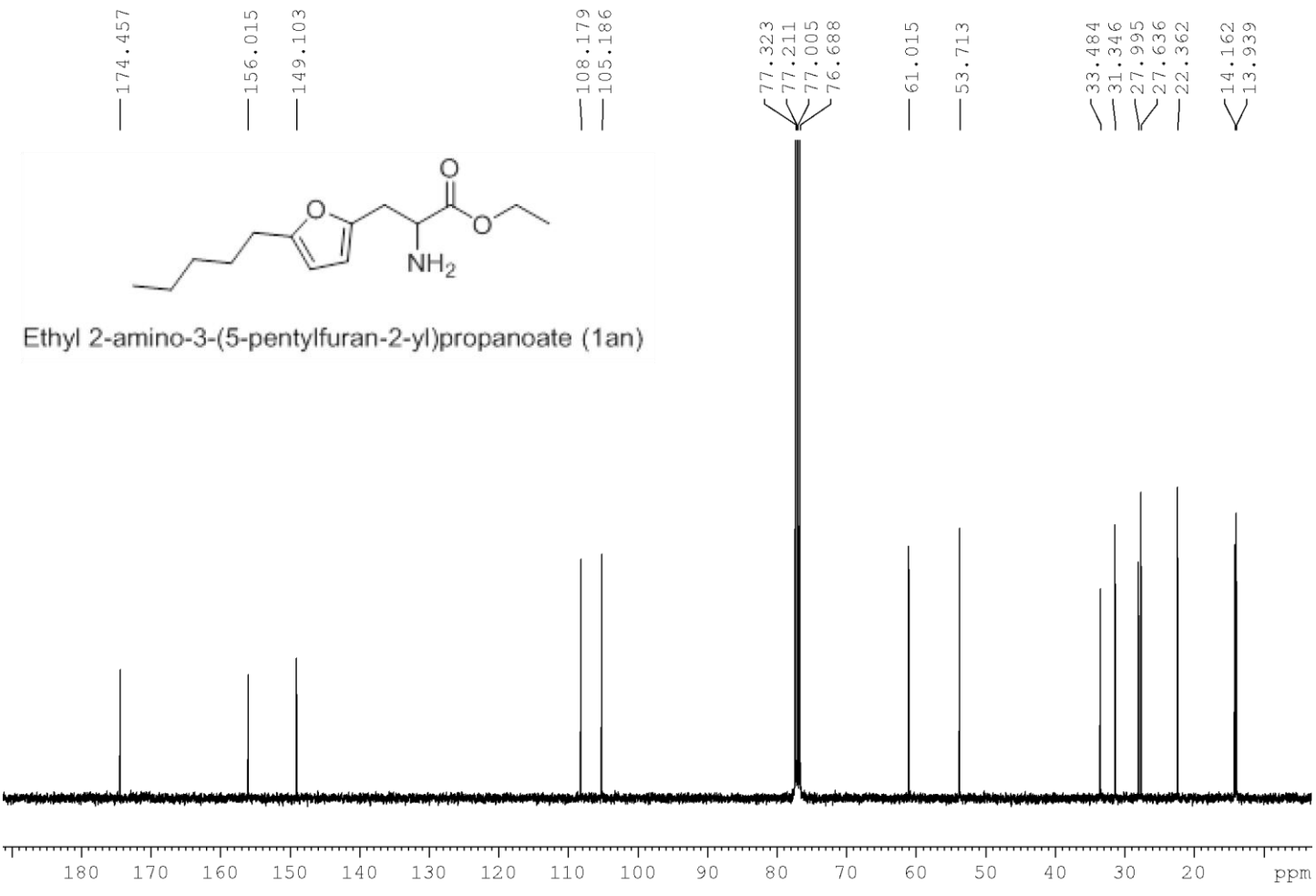
Ethyl 2-(hydroxyimino)-3-(5-isopropyl-4-methylfuran-2-yl)propanoate (2ar)

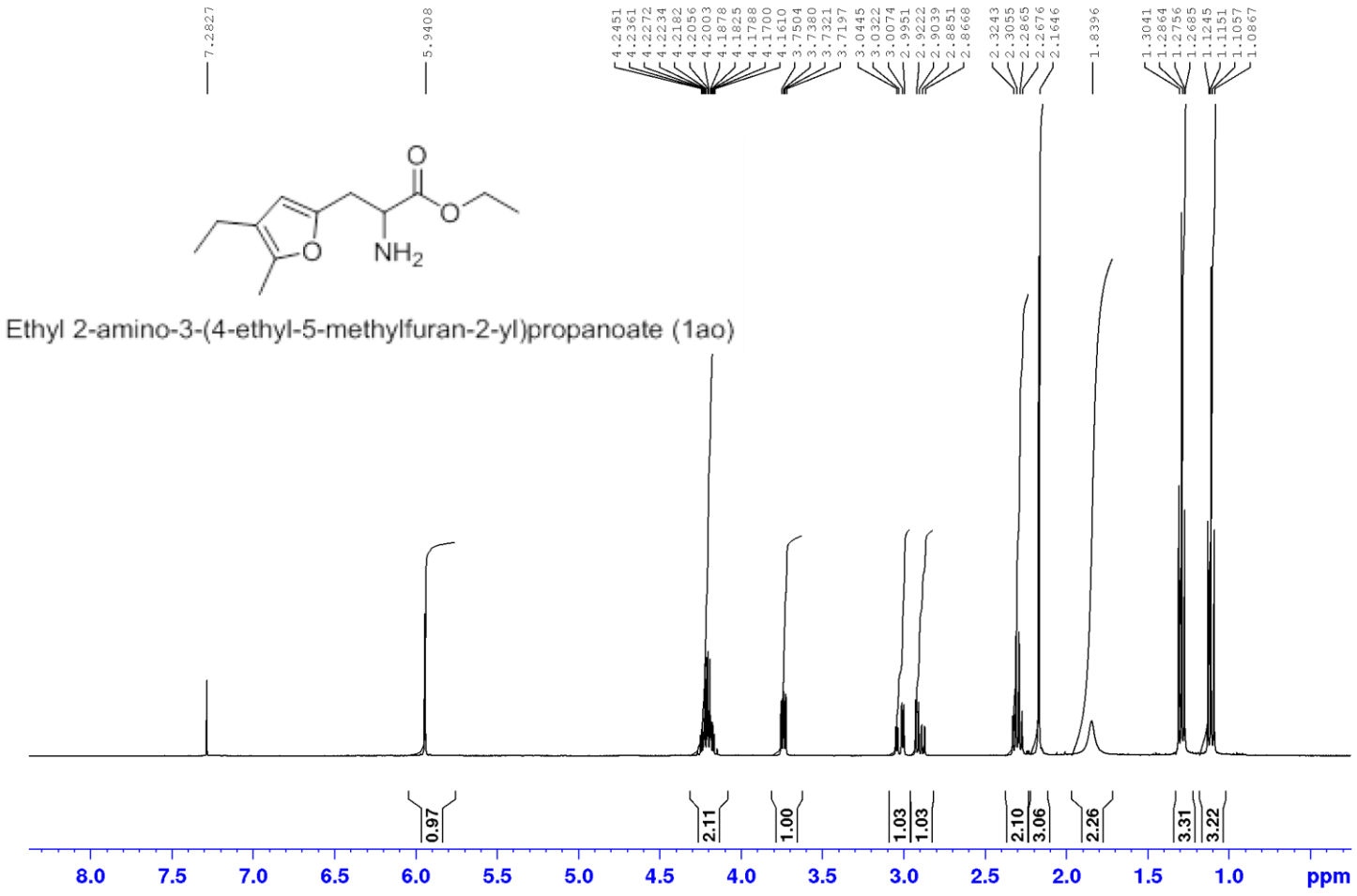



7.2827
6.0058
5.9983
5.8861
5.8786
4.2424
4.2334
4.2267
4.2251
4.2155
4.2090
4.1976
4.1912
4.1817
4.1798
4.1734
4.1642
3.7600
3.7473
3.7421
3.7294
3.0766
3.0641
3.0395
3.0269
2.9766
2.9587
2.9394
2.9216
2.5716
2.5529
2.5343
1.6941
1.6754
1.6569
1.6515
1.6382
1.6330
1.6197
1.6013
1.5846
1.3079
1.2901
1.2840
1.2822
1.2723
0.9783
0.9599
0.9415
O
O
O
NH2
Ethyl 2-amino-3-(5-propylfuran-2-yl)propanoate (1am)
0.96
0.96
2.04
1.00
1.02
1.04
2.03
4.34
3.16
3.12
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
ppm

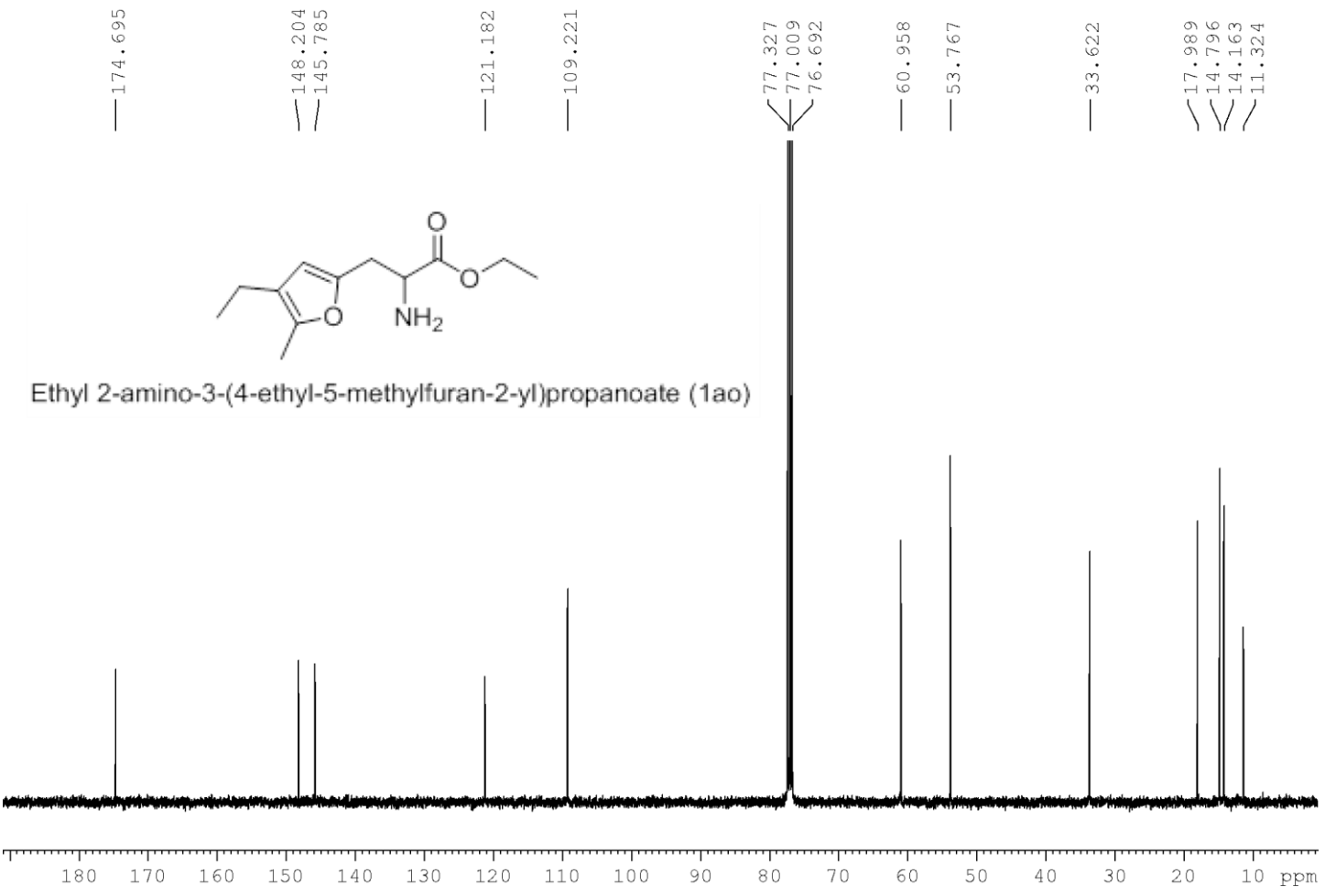

174.733
155.751
149.311
108.070
105.332
77.318
77.000
76.683
60.944
53.802
33.679
30.042
21.308
14.172
13.675
O
O
O
NH2
Ethyl 2-amino-3-(5-propylfuran-2-yl)propanoate (1am)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.2830
6.0107
6.0032
5.8753
5.8678
4.2443
4.2352
4.2268
4.2173
4.2092
4.1995
4.1914
4.1818
4.1737
4.1645
3.7807
3.7680
3.7630
3.7503
3.0930
3.0804
3.0557
3.0431
2.9891
2.9714
2.9519
2.9342
2.5821
2.5632
2.5441
1.9647
1.6564
1.6376
1.6317
1.6190
1.6118
1.6003
1.5941
1.5864
1.5819
1.3739
1.3684
1.3570
1.3510
1.3418
1.3330
1.3235
1.3146
1.3111
1.3066
1.2887
1.2708
0.9299
0.9126
O
O
O
NH2
Ethyl 2-amino-3-(5-pentylfuran-2-yl)propanoate (1an)
0.98
0.99
2.11
1.00
1.08
1.03
2.12
2.53
2.16
7.51
3.21
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
ppm

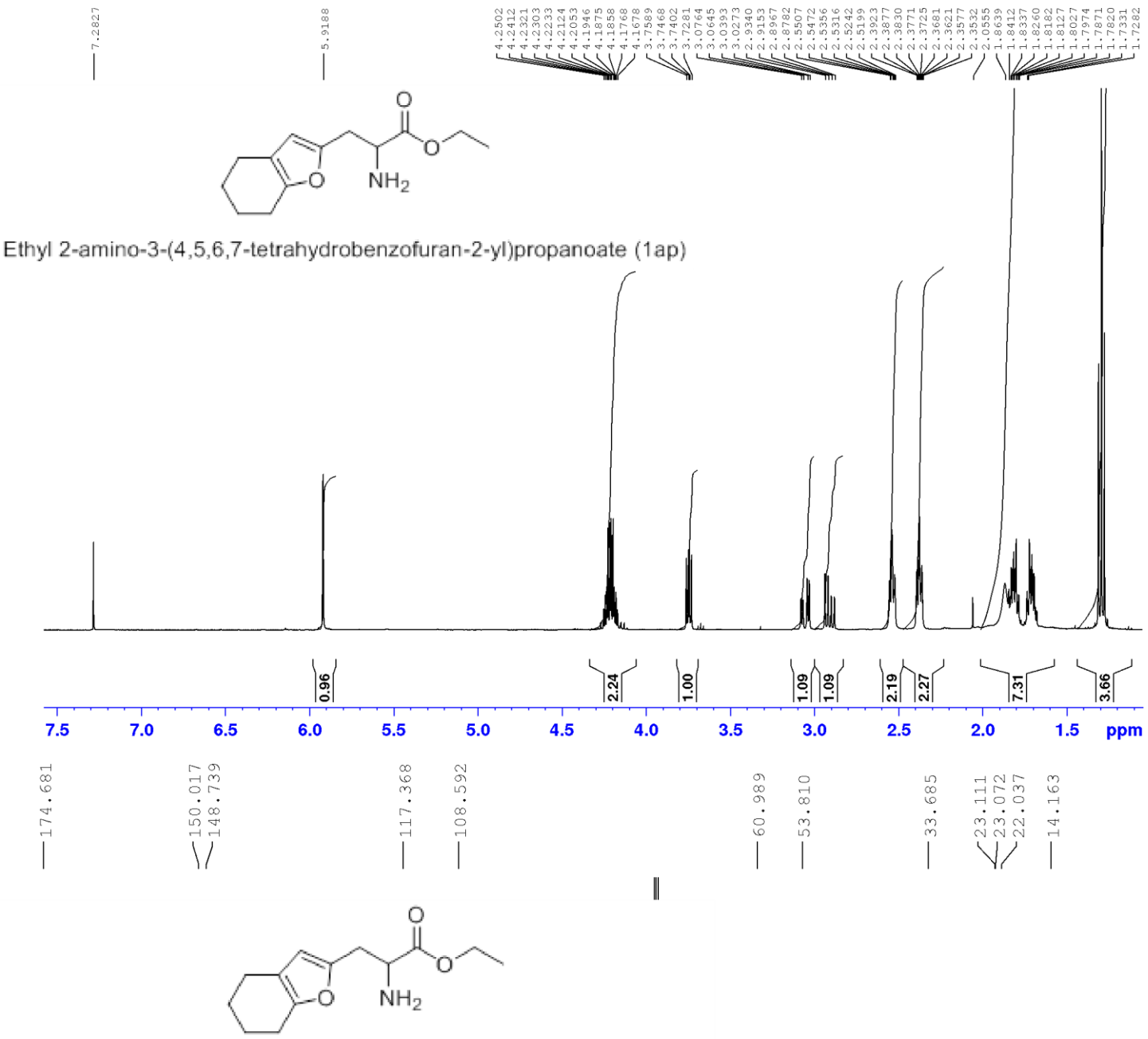

174.457
156.015
149.103
108.179
105.186
77.323
77.211
77.005
76.688
61.015
53.713
33.484
31.346
27.995
27.636
22.362
14.162
13.939
O
O
O
NH2
Ethyl 2-amino-3-(5-pentylfuran-2-yl)propanoate (1an)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



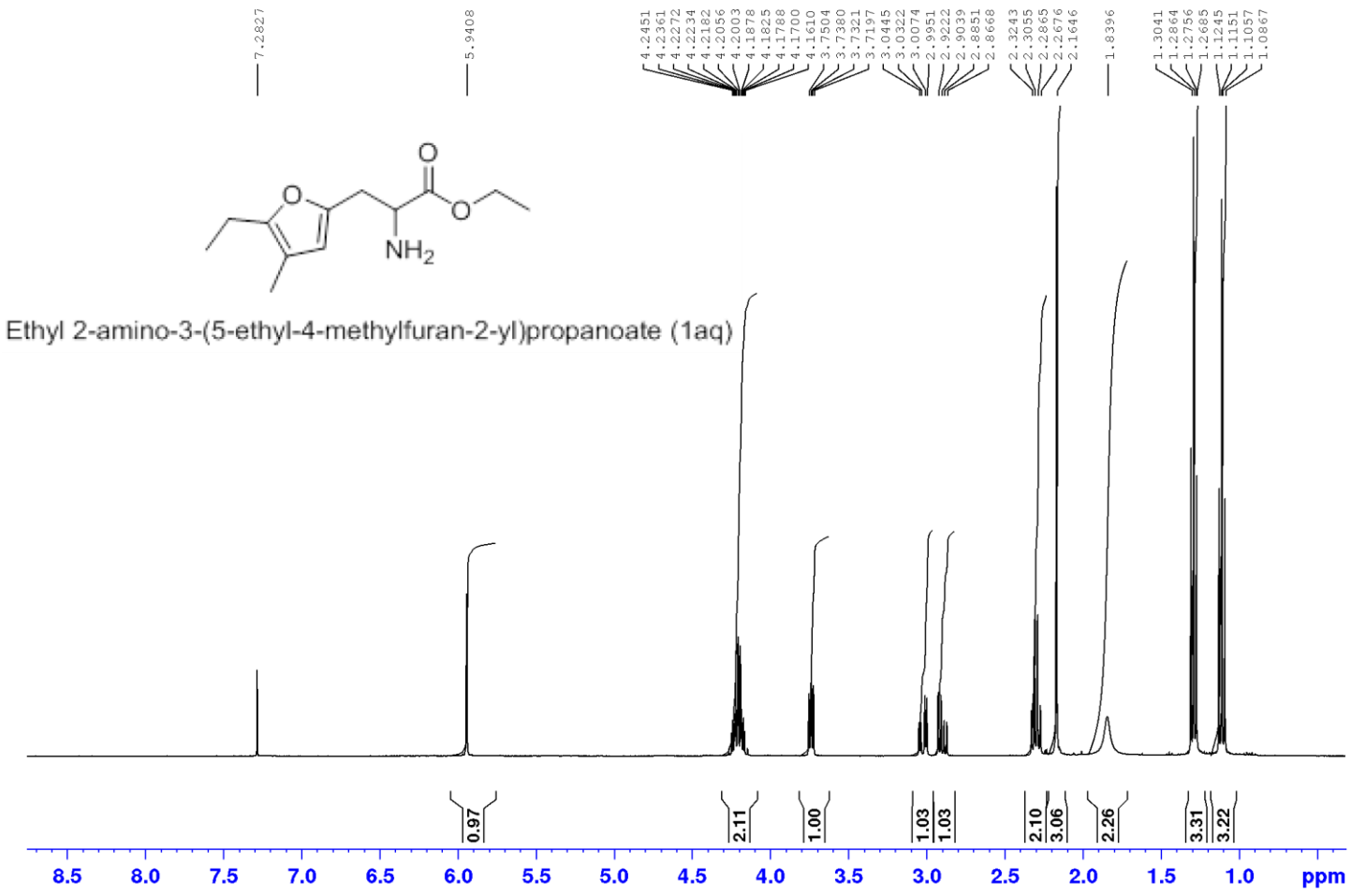
Ethyl 2-amino-3-(4-ethyl-5-methylfuran-2-yl)propanoate (1ao)



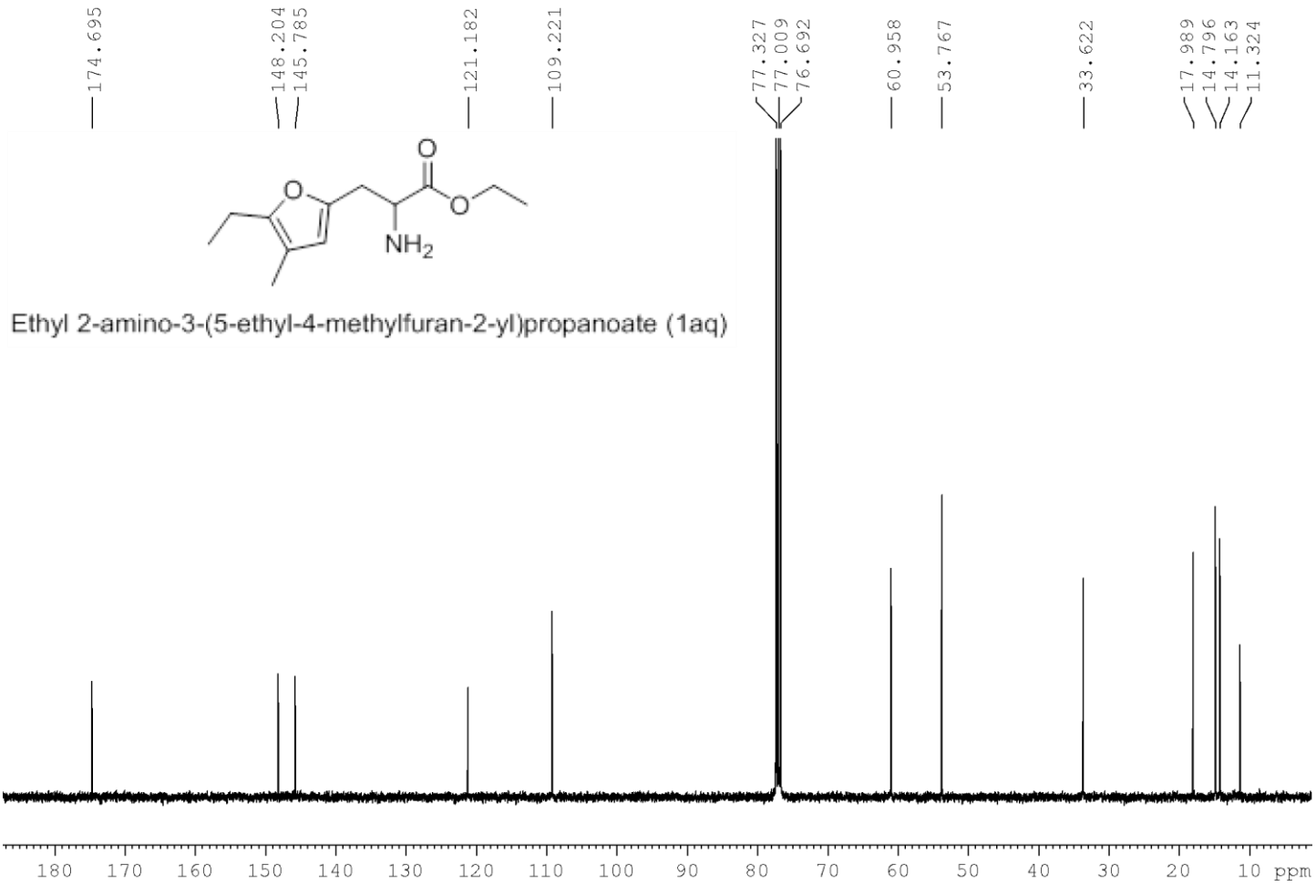
Ethyl 2-amino-3-(4-ethyl-5-methylfuran-2-yl)propanoate (1ao)


7.2827
5.9188
4.2502
4.2412
4.2321
4.2303
4.2233
4.2124
4.2053
4.1946
4.1875
4.1858
4.1768
4.1678
3.7589
3.7468
3.7402
3.7281
3.0764
3.0645
3.0393
3.0273
2.9340
2.9153
2.8967
2.8782
2.5507
2.5472
2.5356
2.5316
2.5242
2.5199
2.3923
2.3877
2.3830
2.3771
2.3725
2.3681
2.3621
2.3577
2.3532
2.0555
1.8639
1.8412
1.8337
1.8260
1.8182
1.8127
1.8027
1.7974
1.7871
1.7820
1.7331
1.7282
O
O
O
NH2
Ethyl 2-amino-3-(4,5,6,7-tetrahydrobenzofuran-2-yl)propanoate (1ap)
0.96
2.24
1.00
1.09
1.09
2.19
2.27
7.31
3.66
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
ppm

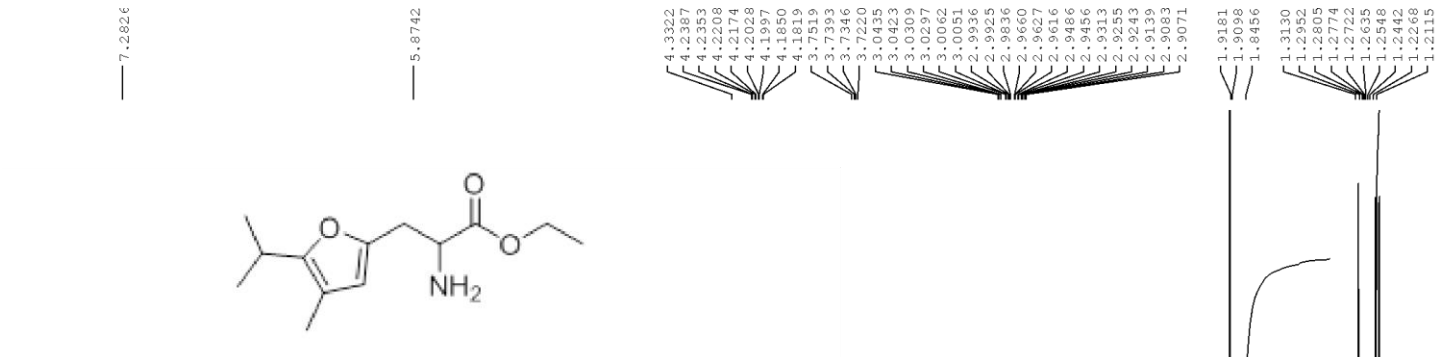
174.681
150.017
148.739
117.368
108.592
60.989
53.810
33.685
23.111
23.072
22.037
14.163
O
O
O
NH2
Ethyl 2-amino-3-(4,5,6,7-tetrahydrobenzofuran-2-yl)propanoate (1ap)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



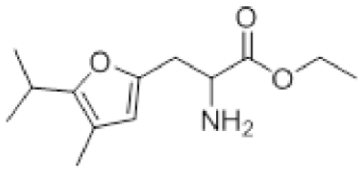
Ethyl 2-amino-3-(5-ethyl-4-methylfuran-2-yl)propanoate (1aq)



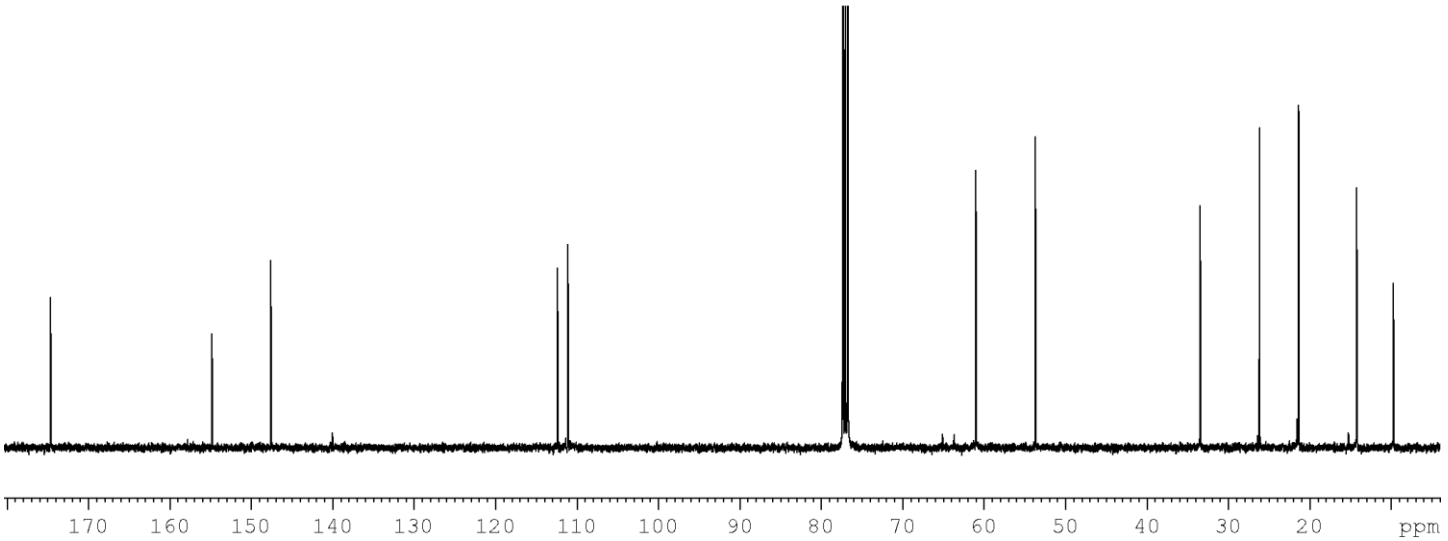
Ethyl 2-amino-3-(5-ethyl-4-methylfuran-2-yl)propanoate (1aq)

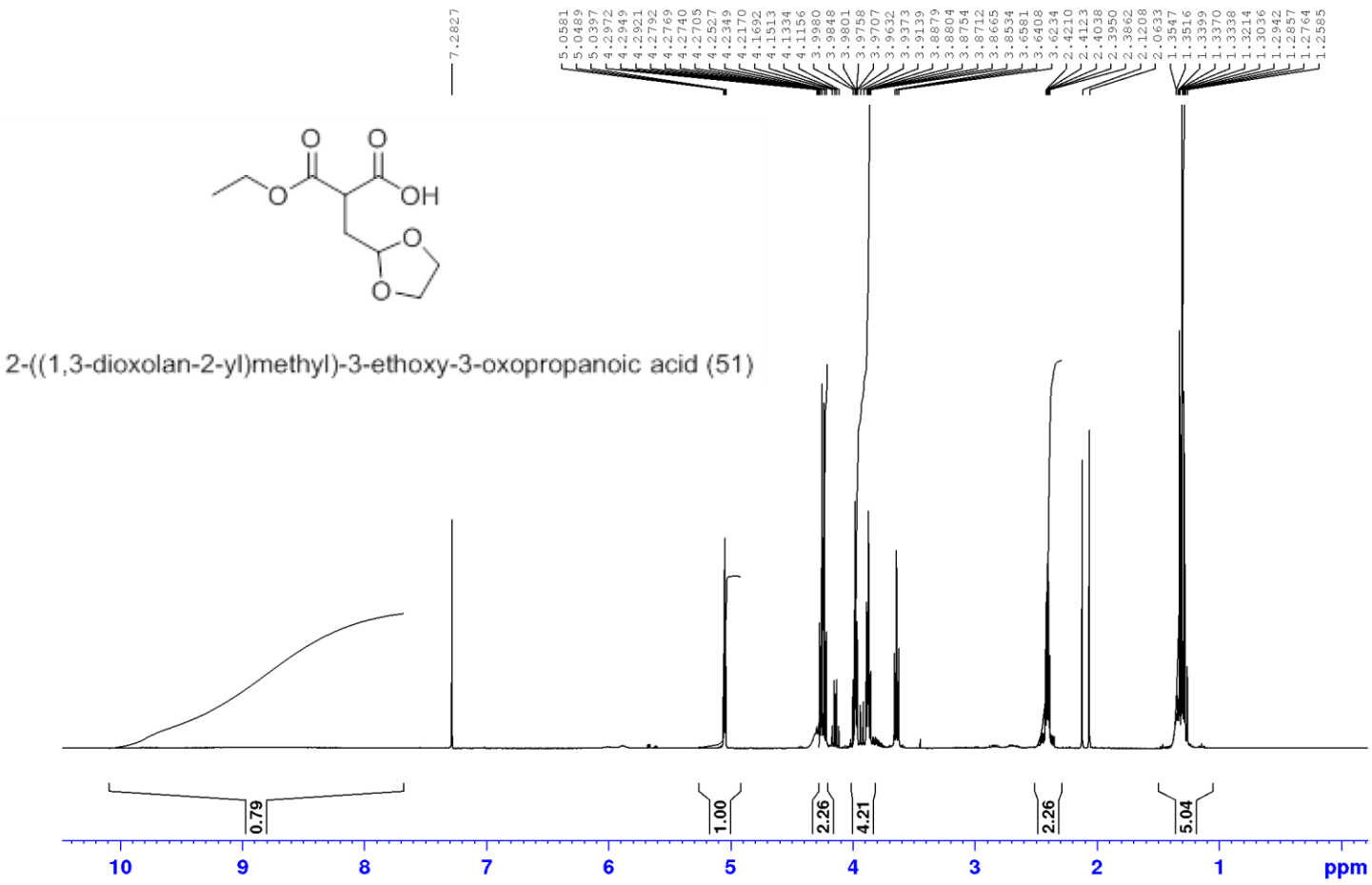


Ethyl 2-amino-3-(5-isopropyl-4-methylfuran-2-yl)propanoate (1ar)

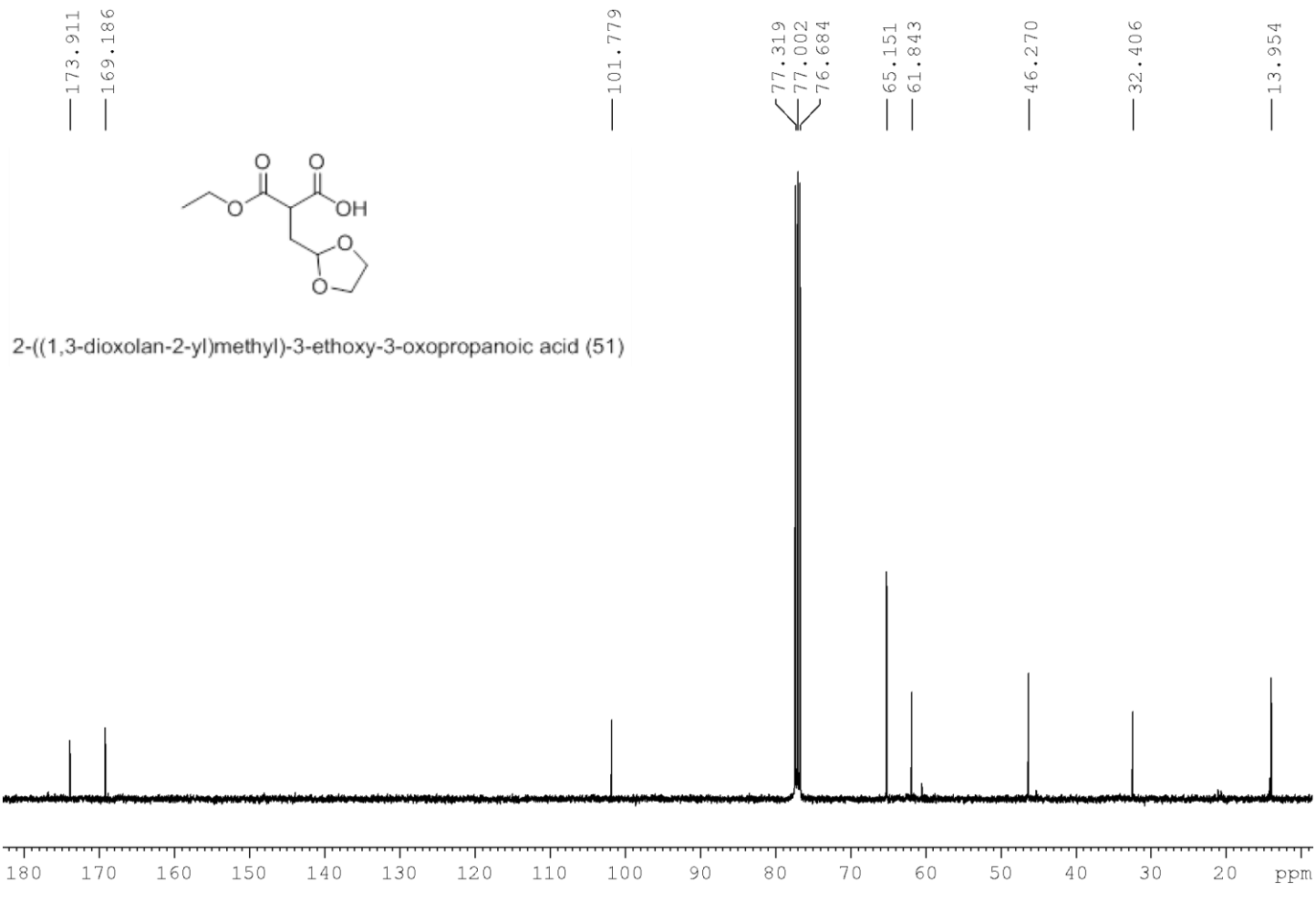


Ethyl 2-amino-3-(5-isopropyl-4-methylfuran-2-yl)propanoate (1ar)

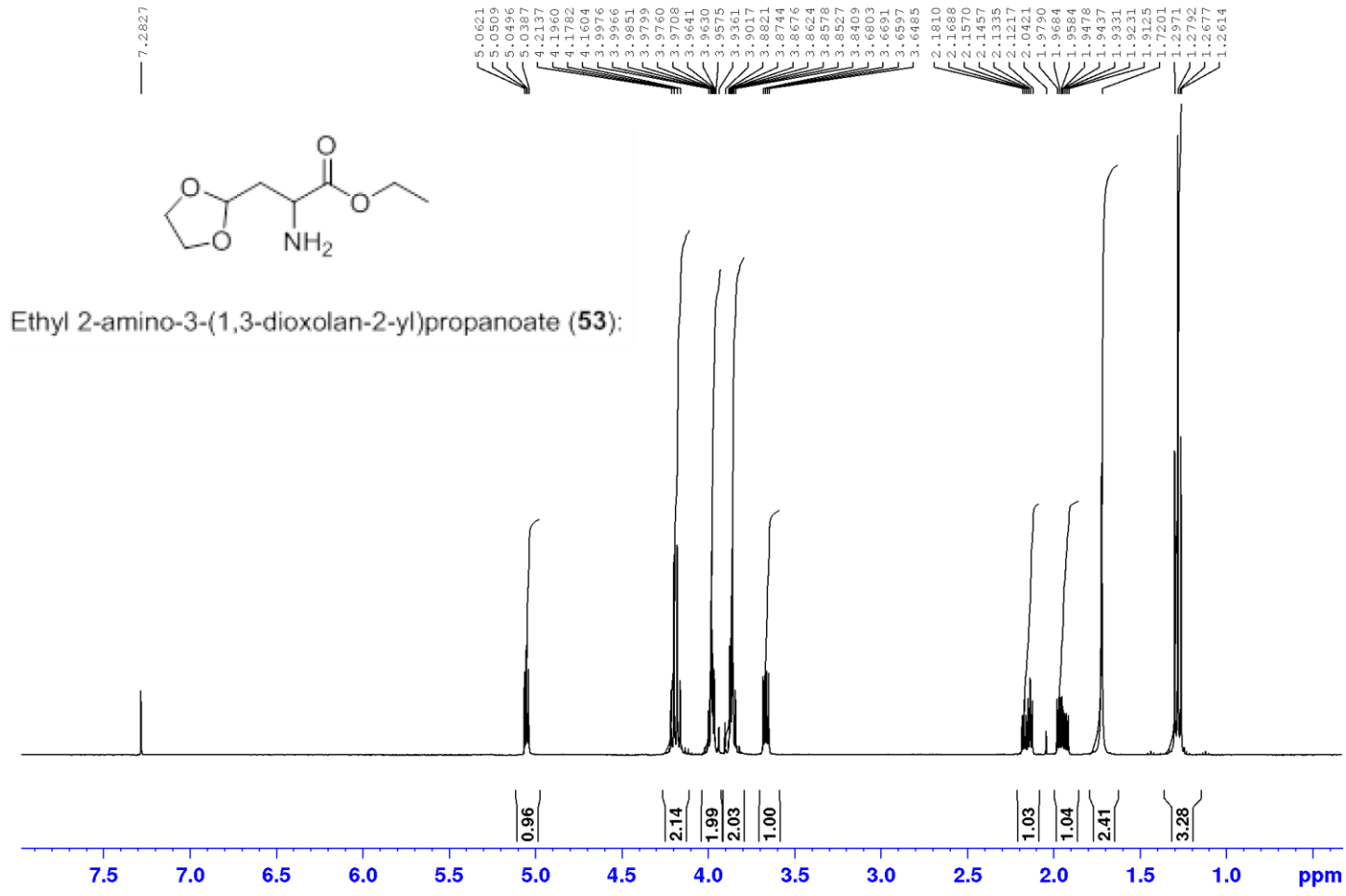




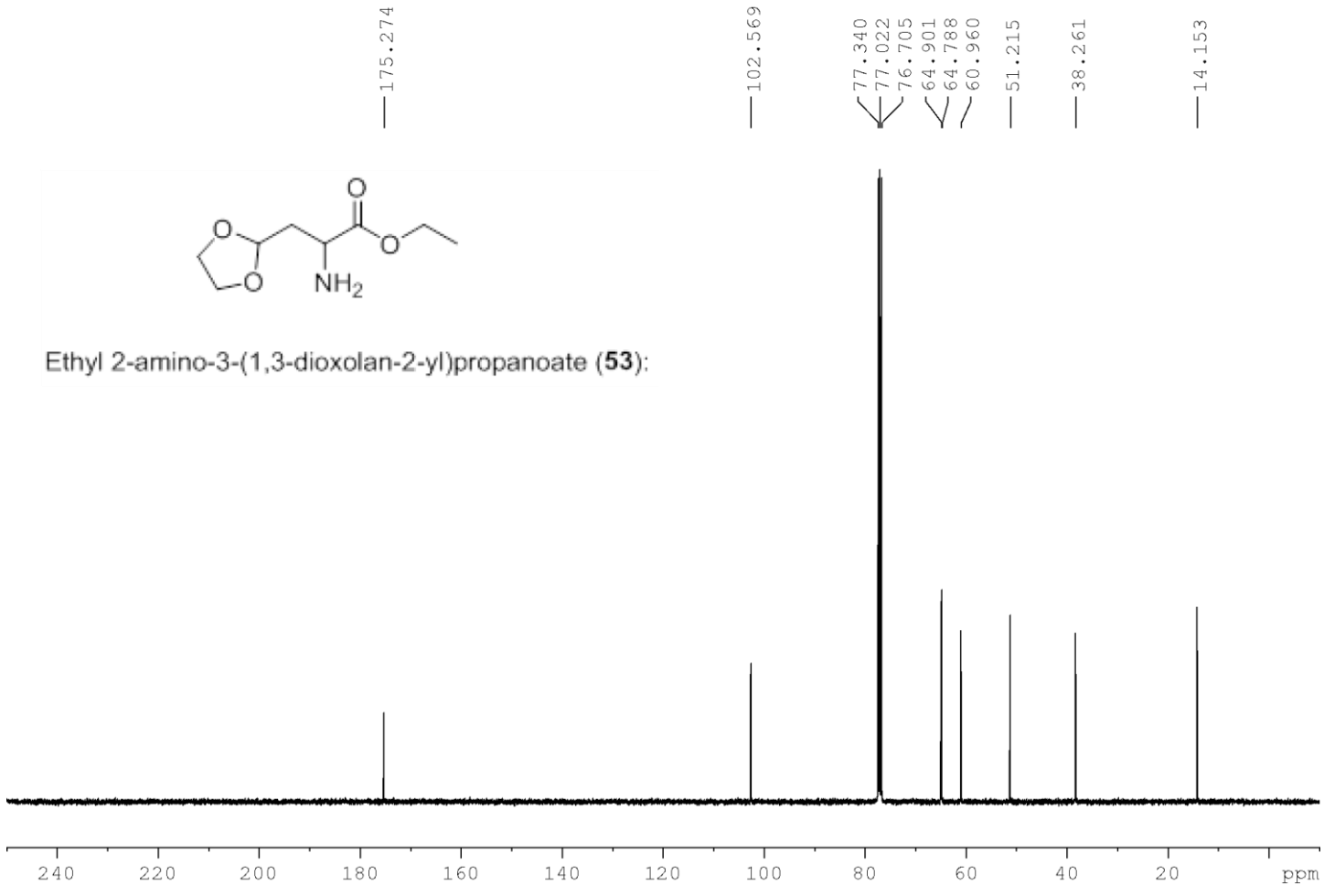
2-((1,3-dioxolan-2-yl)methyl)-3-ethoxy-3-oxopropanoic acid (51)



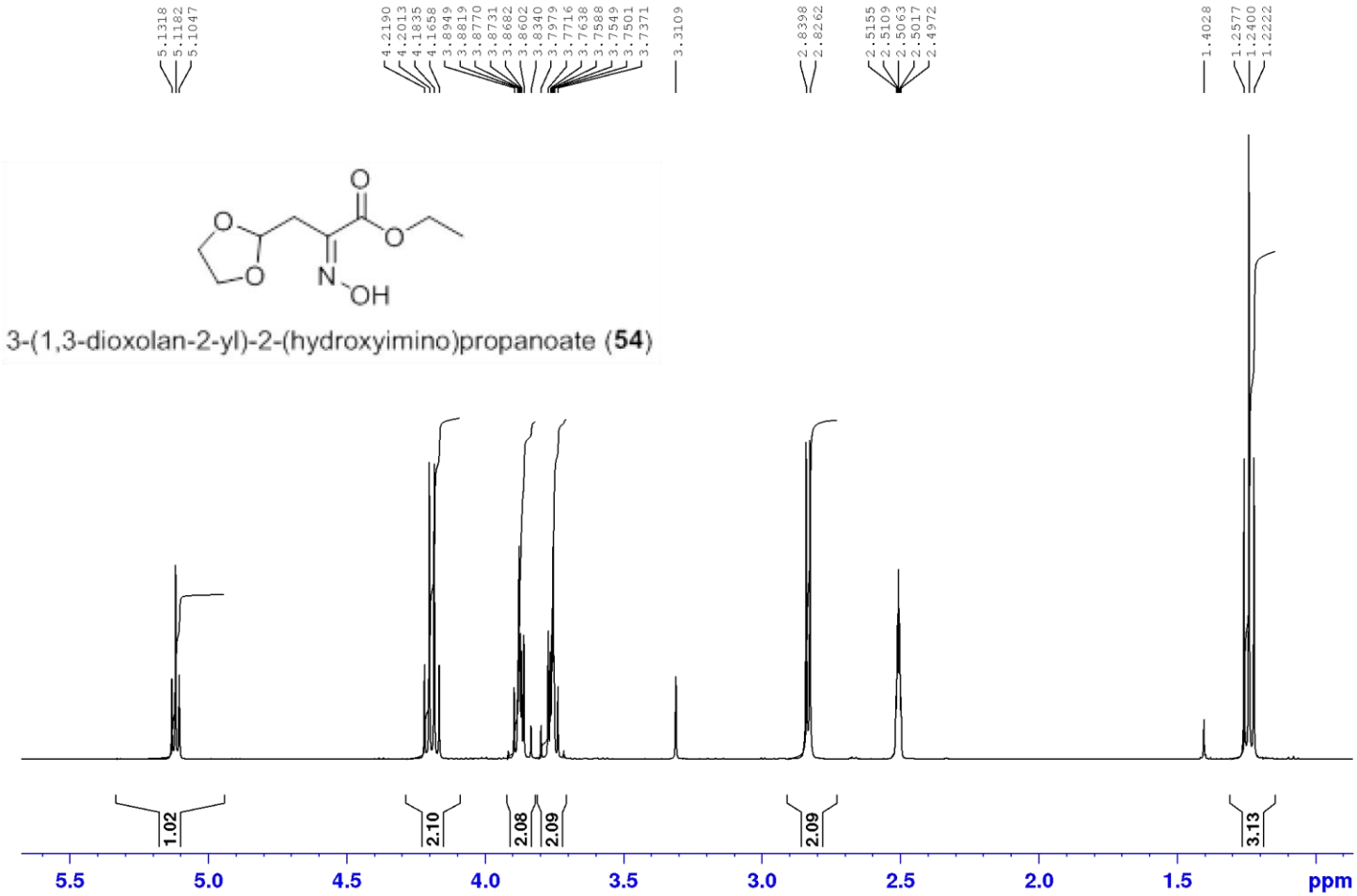
2-((1,3-dioxolan-2-yl)methyl)-3-ethoxy-3-oxopropanoic acid (51)

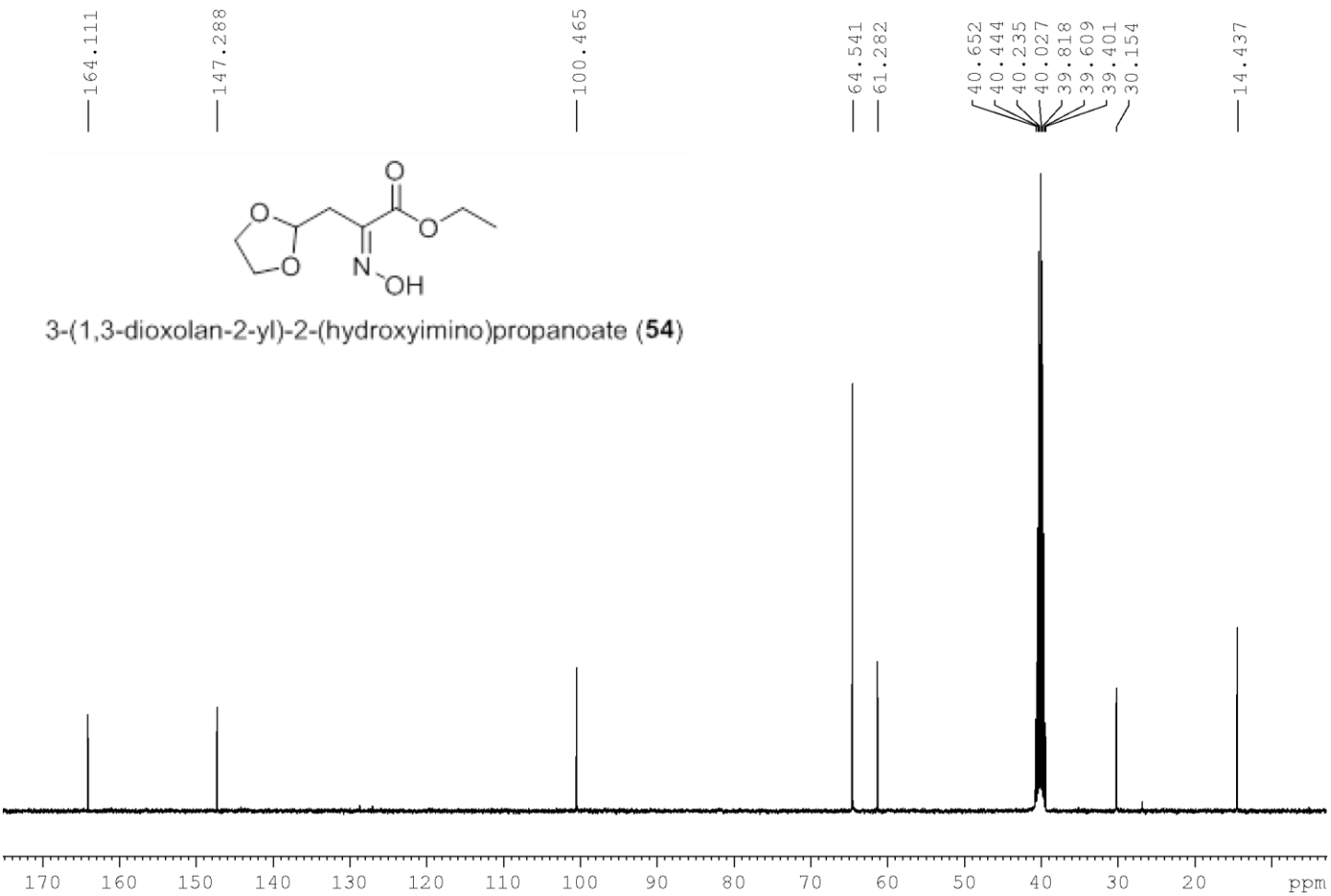


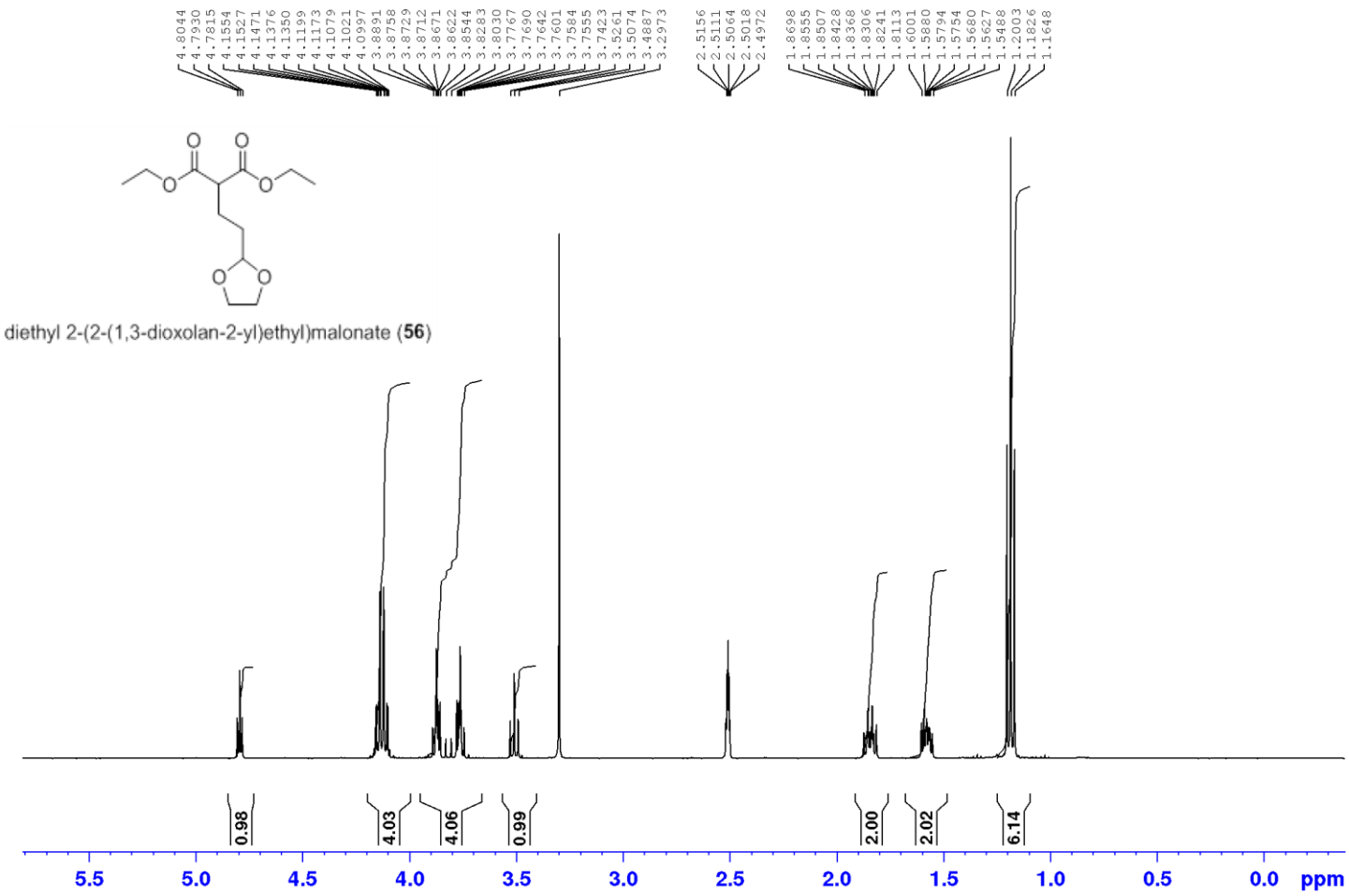
Ethyl 2-amino-3-(1,3-dioxolan-2-yl)propanoate (**53**):



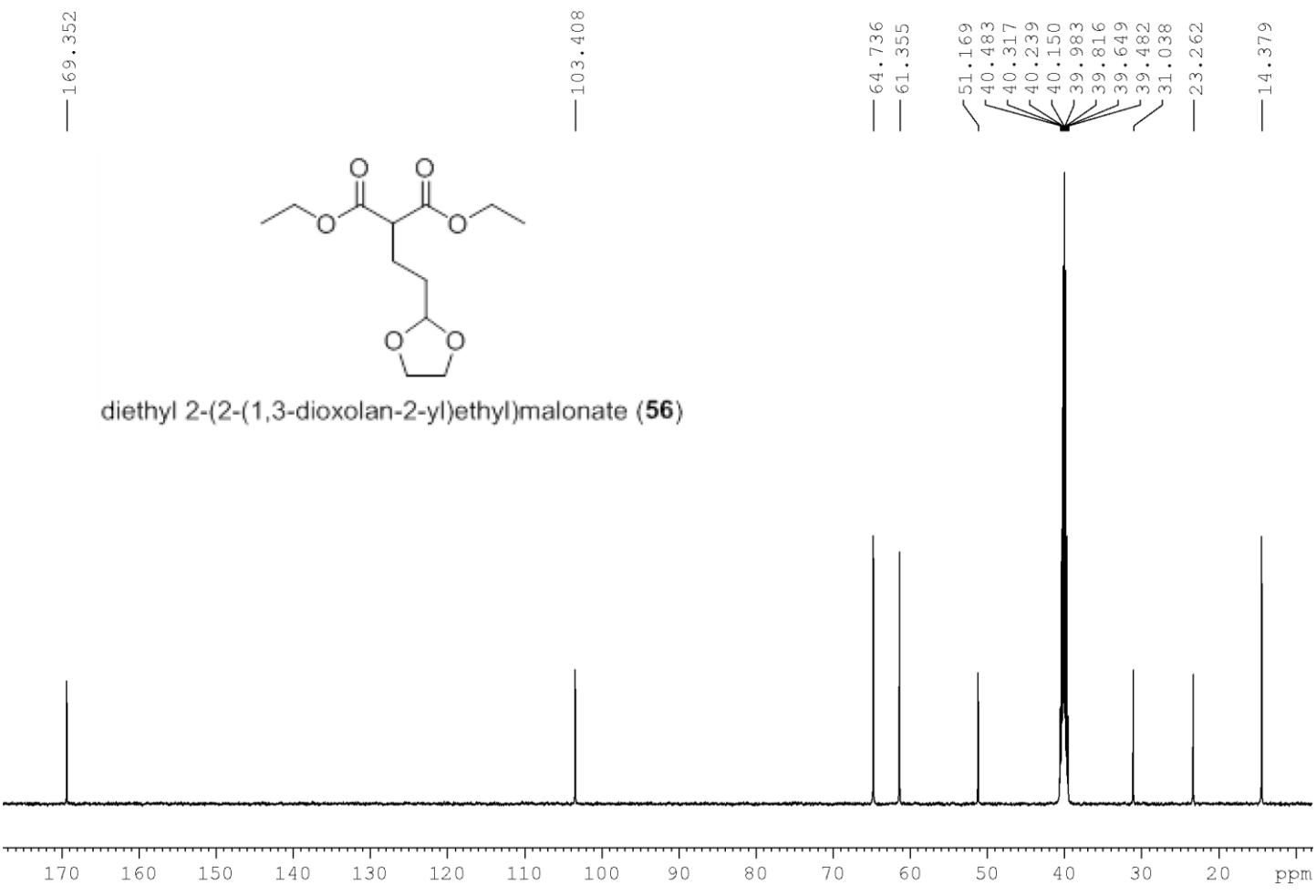
Ethyl 2-amino-3-(1,3-dioxolan-2-yl)propanoate (**53**):


5.1318
5.1182
5.1047
4.2190
4.2013
4.1835
4.1658
3.8949
3.8819
3.8770
3.8731
3.8682
3.8602
3.8340
3.7979
3.7716
3.7638
3.7588
3.7549
3.7501
3.7371
3.3109
2.8398
2.8262
2.5155
2.5109
2.5063
2.5017
2.4972
1.4028
1.2577
1.2400
1.2222
3-(1,3-dioxolan-2-yl)-2-(hydroxyimino)propanoate (54)
1.02
2.10
2.08
2.09
2.09
3.13
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

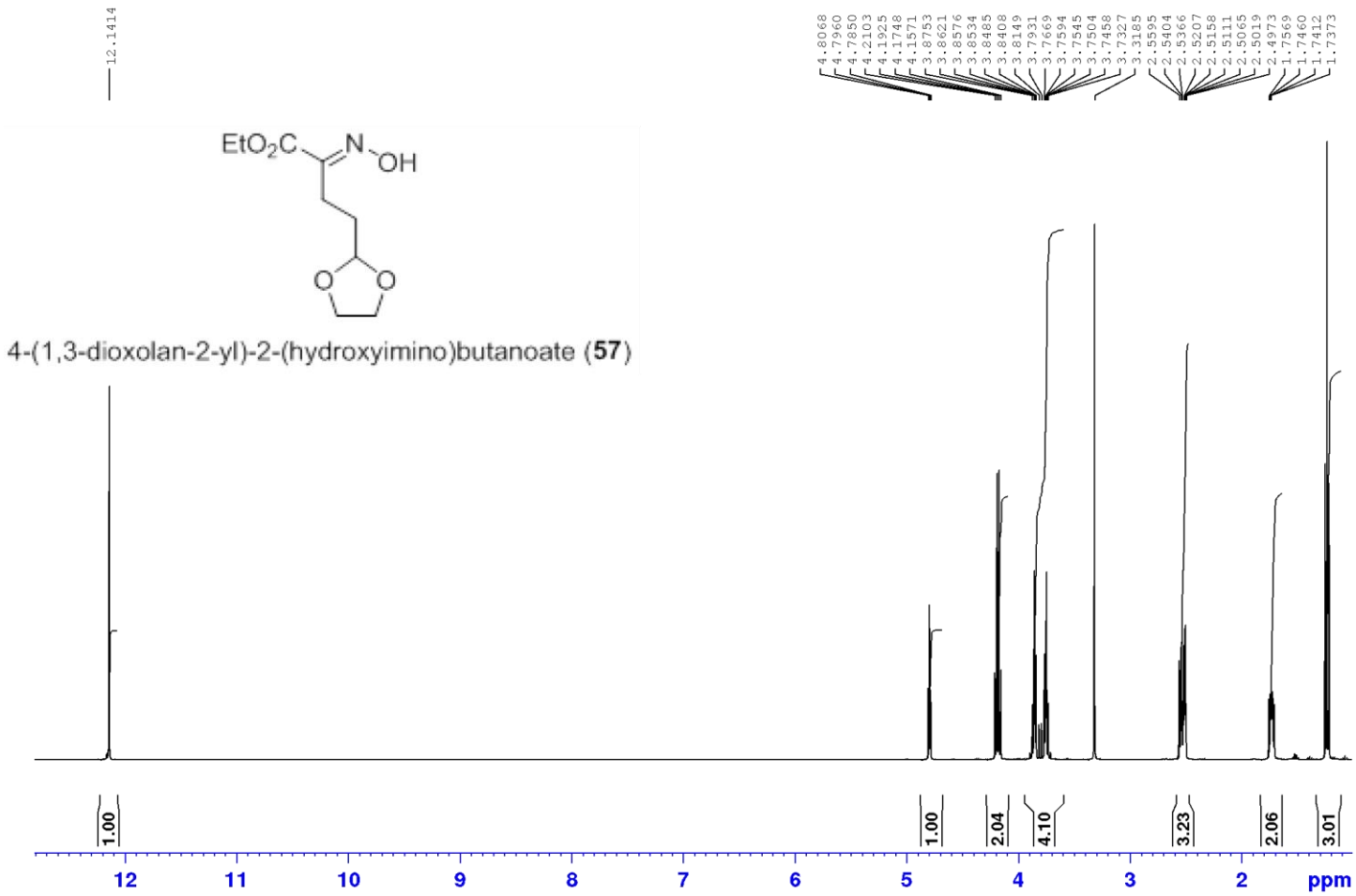

164.111
147.288
100.465
64.541
61.282
40.652
40.444
40.235
40.027
39.818
39.609
39.401
30.154
14.437
3-(1,3-dioxolan-2-yl)-2-(hydroxyimino)propanoate (54)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

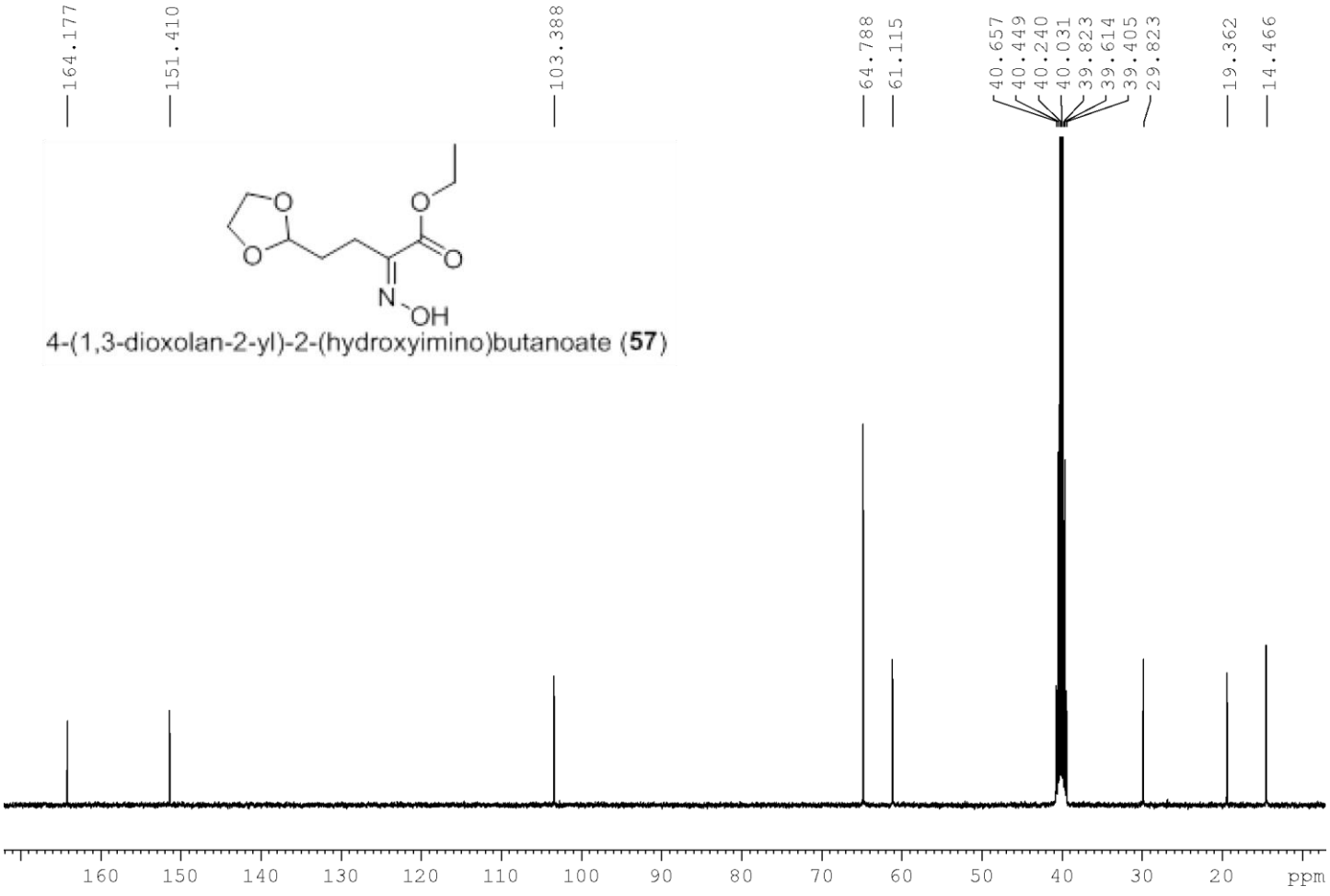


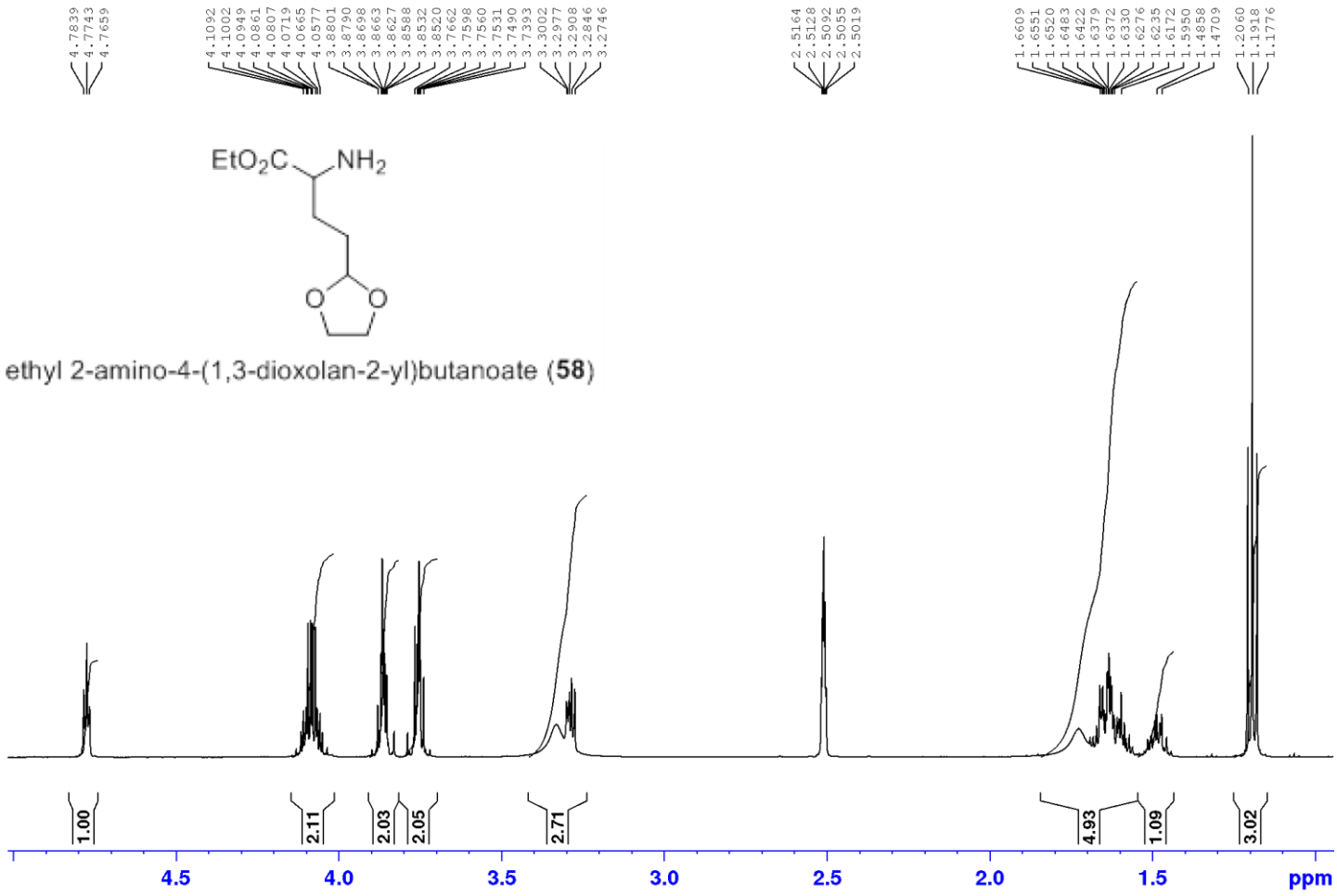
diethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)malonate (**56**)



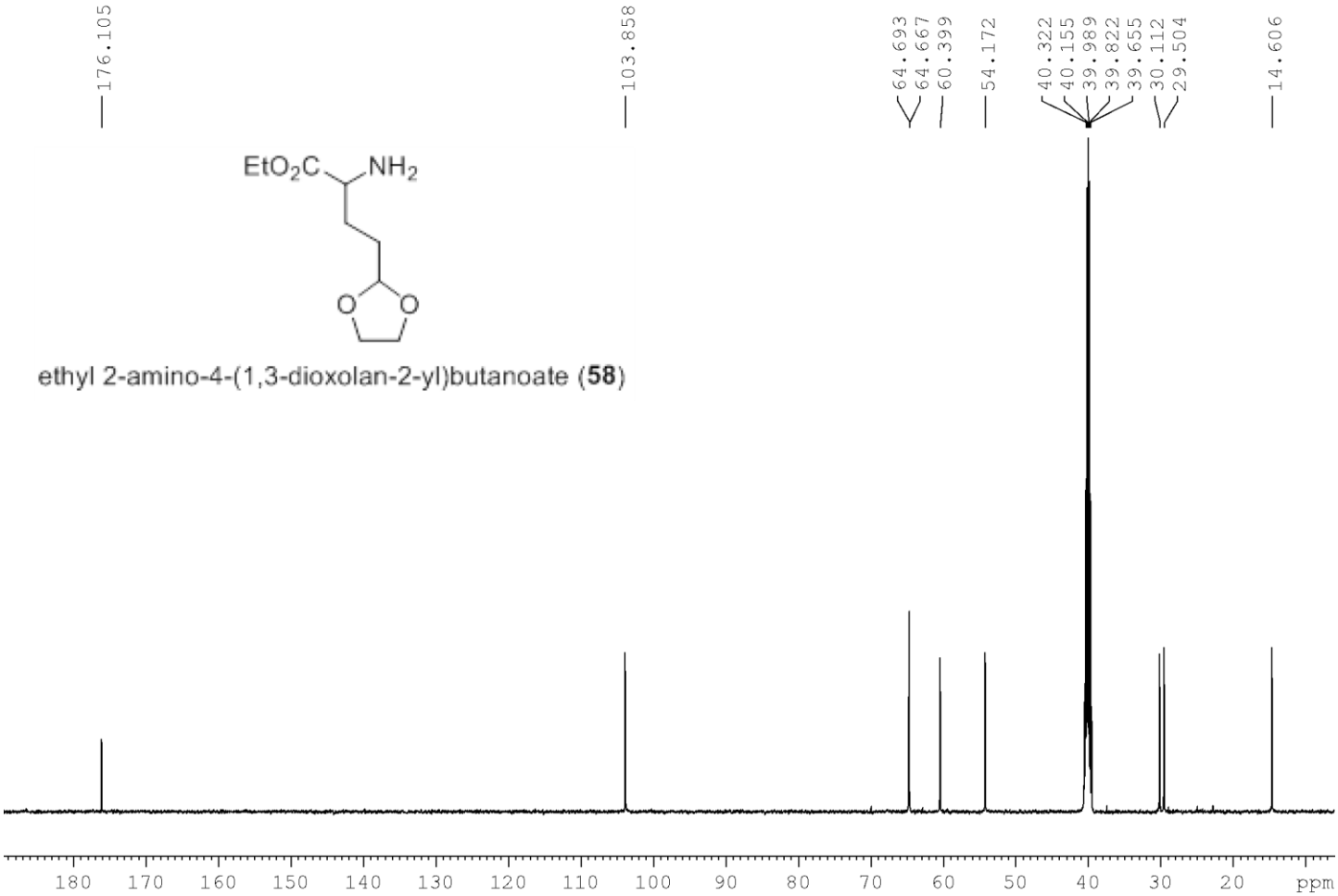
diethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)malonate (**56**)


12.1414
4.8068
4.7960
4.7850
4.2103
4.1925
4.1748
4.1571
3.8753
3.8621
3.8576
3.8534
3.8485
3.8408
3.8149
3.7931
3.7669
3.7594
3.7545
3.7504
3.7458
3.7327
3.3185
2.5595
2.5404
2.5366
2.5207
2.5158
2.5111
2.5065
2.5019
2.4973
1.7569
1.7460
1.7412
1.7373
EtO2C
N
OH
O
O
4-(1,3-dioxolan-2-yl)-2-(hydroxyimino)butanoate (57)
1.00
1.00
2.04
4.10
3.23
2.06
3.01
12
11
10
9
8
7
6
5
4
3
2
ppm


164.177
151.410
103.388
64.788
61.115
40.657
40.449
40.240
40.031
39.823
39.614
39.405
29.823
19.362
14.466
O
O
O
O
N
OH
4-(1,3-dioxolan-2-yl)-2-(hydroxyimino)butanoate (57)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



ethyl 2-amino-4-(1,3-dioxolan-2-yl)butanoate (**58**)



ethyl 2-amino-4-(1,3-dioxolan-2-yl)butanoate (**58**)

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