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SUPPORTING INFORMATION

Hβ zeolite mediated sustainable solvent free synthesis of indole-2-carboxylic esters

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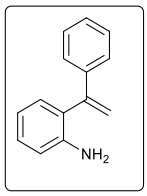
1. General Information

1b-1l and **1n** were synthesized using previous method[1], remaining all the chemicals were procured from Sigma-Aldrich and used without any further purification. The zeolite β catalyst in ammonia form with a Si/Al ratio of 19 was purchased from Alfa-Aesar. All the samples were systematically characterized using various spectroscopic techniques. ^{1}H NMR spectra were acquired using Bruker VX NMR FT-300, 400 or 500 MHz spectrometers, while ^{13}C NMR spectra were obtained using Bruker VX NMR FT-101 and 125 MHz spectrometers in $CDCl_3$. The chemical shifts (δ) were reported in *ppm* units downfield from TMS as an internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (J) were reported in hertz (Hz), and the following multiplicities were recorded: s (singlet), brs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), and m (multiplet). The Shimadzu GC-2014 gas chromatograph was used to perform the gas chromatography analysis. It is equipped with an FID detector and a capillary column (EB-5, 30 m in length, 0.25 mm in inner diameter and with a 0.25 mm film). TLC inspections were carried out on Silica Gel 60 F_{254} plates. Column chromatography was performed using silica gel (100-200 mesh). The XRD patterns of the samples were obtained using a regular Regaku miniflux X-ray Diffractometer with Ni-filtered CuKα radiation at 2θ = 2°-80°. The scanning rate was set at 2° min^{-1}, and the beam voltage and current were 30 kV and 15 mA, respectively.

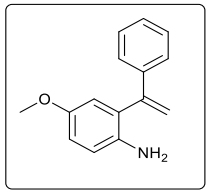
2. Spectroscopic data

2-(1-Phenylvinyl) aniline (1b)[2]



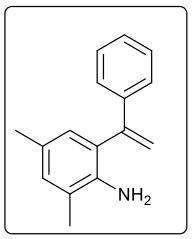
Yellow oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.68-7.65 (m, 2H), 7.58-7.54 (m, 3H), 7.44-7.40 (m, 2H), 7.08-7.04 (m, 1H), 6.88 (d, *J* = 6.6 Hz, 1H), 6.06 (d, *J* = 1.6 Hz, 1H), 5.63 (d, *J* = 1.4 Hz, 1H), 3.73 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 147.48, 144.33, 139.97, 131.11, 129.10, 128.90, 128.40, 126.98, 118.53, 116.39, 115.87.

4-Methoxy-2-(1-phenylvinyl) aniline (1c)[2]



Yellow oil, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.39-7.36 (m, 2H), 7.34-7.27 (m, 3H), 6.77 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.72 (d, *J* = 2.9 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 5.80 (d, *J* = 1.4 Hz, 1H), 5.35 (d, *J* = 1.4 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 152.56, 147.21, 139.48, 137.69, 128.65, 128.19, 126.68, 116.96, 116.17, 114.68, 55.80.

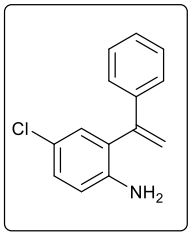
2,4-Dimethyl-6-(1-phenylvinyl)aniline (1f)



Yellow oil, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.29-7.23 (m, 2H), 7.22-7.13 (m, 3H), 6.79 (s, 1H), 6.71 (s, 1H), 5.69 (d, *J* = 2.7 Hz, 1H), 5.22 (d, *J* = 2.9 Hz, 1H), 3.15 (s, 2H),

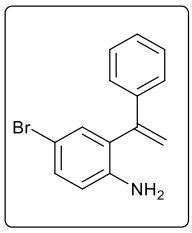
2.14 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 147.38, 139.71, 139.38, 130.49, 128.81, 128.36, 127.84, 127.03, 126.68, 126.49, 122.35, 115.72, 20.25, 17.53.

4-Chloro-2-(1-phenylvinyl)aniline (1g)[3]



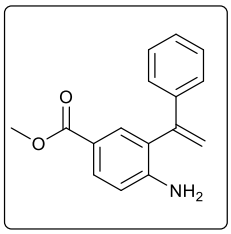
Yellow oil, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.28-7.19 (m, 5H), 7.06-6.96 (m, 2H), 6.50 (t, 1H), 5.71 (d, *J* = 1.3 Hz, 1H), 5.25 (d, *J* = 1.3 Hz, 1H), 3.21 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 146.07, 142.56, 138.86, 130.22, 128.65, 128.56, 128.49, 128.31, 126.52, 122.79, 116.74, 116.64.

Bromo-2-(1-phenylvinyl)aniline (1h)[3]



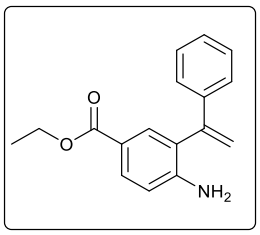
Yellow oil, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.38-7.28 (m, 5H), 7.26-7.20 (m, 2H), 6.56 (d, *J* = 9.0 Hz, 1H), 5.80 (s, 1H), 5.35 (s, 1H), 3.54 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 147.00, 146.63, 139.61, 130.42, 129.02, 128.58, 128.13, 127.23, 126.55, 116.65, 116.27, 109.92.

Methyl 4-amino-3-(1-(cyclohexa-2,4-dien-1-yl)vinyl)benzoate (1j)[3]



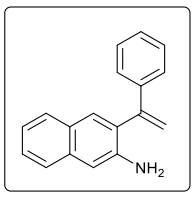
Yellow oil, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.88-7.82 (m, 2H), 7.39-7.29 (m, 5H), 6.66 (d, *J* = 8.9 Hz, 1H), 5.84 (d, *J* = 1.1 Hz, 1H), 5.39 (d, *J* = 1.2 Hz, 1H), 3.98 (br s, 2H), 3.86 (br s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 162.52, 143.73, 141.47, 134.24, 128.04, 126.14, 123.97, 123.62, 121.82, 121.34, 114.79, 112.21, 109.73, 46.93.

Ethyl 4-amino-3-(1-(cyclohexa-2,4-dien-1-yl)vinyl)benzoate (1k)[3]



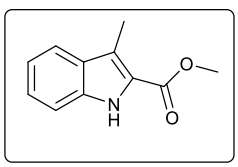
Yellow oil, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) = 7.89-7.83 (m, 2H), 7.39-7.35 (m, 2H), 7.34-7.30 (m, 3H), 6.66 (d, *J* = 8.8 Hz, 1H), 5.84 (d, *J* = 1.3 Hz, 1H), 5.40 (d, *J* = 1.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.97 (br s, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 166.82, 148.39, 146.26, 138.96, 132.72, 130.86, 128.72, 128.36, 126.55, 126.09, 119.92, 116.94, 114.44, 60.41, 14.48.

3-(1-Phenylvinyl)naphthalen-2-amine (1n)[3]



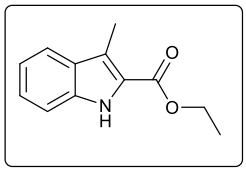
Yellow oil, 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.82-7.66 (m, 2H), 7.43-7.38 (m, 2H), 7.37-7.31 (m, 2H), 7.29-7.22 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 1H), 5.90 (d, *J* = 1.5 Hz, 1H), 5.40 (d, *J* = 1.5 Hz, 1H), 3.98 (br s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 146.22, 138.77, 137.98, 132.78, 127.71, 127.45, 127.38, 127.01, 125.71, 124.69, 124.01, 122.51, 120.44, 120.04, 117.08, 115.55.

Methyl 3-methyl-1*H*-indole-2-carboxylate (Table 1, 3a)[4]



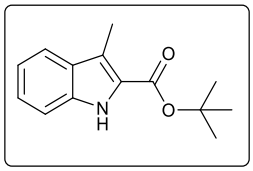
White solid, 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.83 (br s, 1H), 7.68 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.41-7.30 (m, 2H), 7.20-7.11 (m, 1H), 3.97 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 162.19, 134.98, 127.43, 124.56, 122.16, 119.74, 119.26, 118.85, 110.65, 50.65, 8.89.

Ethyl 3-methyl-1*H*-indole-2-carboxylate (Table 1, 3b)[5]



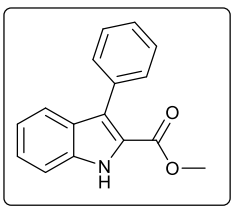
White solid, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.64 (br s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.38-7.30 (m, 2H), 7.16-7.12 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 162.62, 135.80, 128.60, 125.59, 120.79, 119.92, 111.59, 60.68, 14.49, 9.93.

***tert*-Butyl 3-methyl-1*H*-indole-2-carboxylate (Table 1, 3c)**



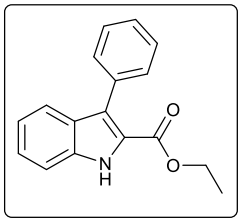
White solid, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.60 (br s, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.37-7.28 (m, 2H), 7.15-7.10 (m, 1H), 2.58 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.03, 135.51, 128.69, 125.29, 124.69, 120.68, 119.77, 119.23, 111.51, 81.60, 28.47, 9.96. HRMS (ESI): m/z calcd for $C_{14}H_{17}NO_2$ $[M+H-^{t}butyl]^{+}$ 176.0712 found 176.0716.

Methyl 3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3d)[4]



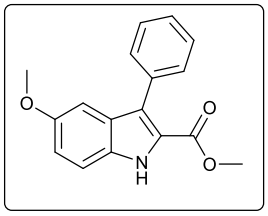
White solid, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.15 (br s, 1H), 7.6 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.57-7.54 (m, 2H), 7.47-7.42 (m, 3H), 7.40-7.33 (m, 2H), 7.16-7.13 (m, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.54, 135.86, 133.47, 130.59, 127.92, 127.30, 125.93, 124.44, 122.44, 121.82, 120.95, 111.79, 51.85.

Ethyl 3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3e)[4]



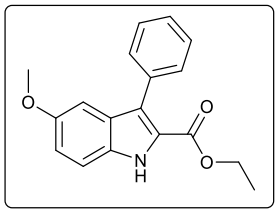
White solid, 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.12 (br s, 1H), 7.63 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.57-7.54 (m, 2H), 7.46 -7.43 (m, 3H), 7.39-7.33 (m, 2H), 7.16 -7.13 (m, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.07, 135.74, 133.54, 130.68, 127.97, 127.76, 127.22, 125.80, 124.27, 122.82, 121.78, 120.87, 111.72, 60.91, 14.07.

Methyl 5-methoxy-3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3f)[4]



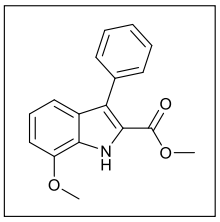
White solid, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.10 (br s, 1H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.53-7.45 (m, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 9.5 Hz, 1H), 7.08-7.00 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.25, 155.04, 133.63, 131.06, 130.45, 127.97, 127.20, 123.94, 122.93, 117.68, 112.67, 101.55, 55.76, 51.74.

Ethyl 5-methoxy-3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3g)[6]



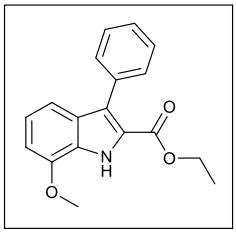
White solid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.90 (br s, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.42-7.32 (m, 2H), 7.06-6.98 (m, 2H), 4.28 (q, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.86, 155.00, 133.74, 131.00, 130.56, 127.84, 127.14, 117.54, 112.65, 101.54, 60.80, 55.76, 14.08.

Methyl 7-methoxy-3-phenyl-1H-indole-2-carboxylate (Table 1, 3h)[7]



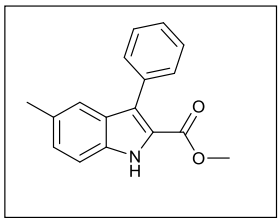
White solid, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.15 (s, 1H), 7.61-7.51 (m, 2H), 7.50-7.42 (m, 2H), 7.41-7.33 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 4.00 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 162.17, 146.40, 133.56, 130.54, 129.03, 127.85, 127.22, 124.71, 122.13, 121.33, 113.94, 104.55, 55.52, 51.75.

Ethyl 7-methoxy-3-phenyl-1H-indole-2-carboxylate (Table 1, 3i)[8]



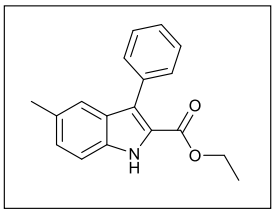
White solid, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.18 (br s, 1H), 7.62-7.50 (m, 2H), 7.49-7.30 (m, 3H), 7.20 (s, 1H), 7.05 (t, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) = 161.80, 146.41, 133.69, 130.67, 129.11, 127.75, 127.17, 127.00, 124.54, 122.56, 121.28, 113.93, 104.49, 60.84, 55.51, 14.12.

Methyl 5-methyl-3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3j)[7]



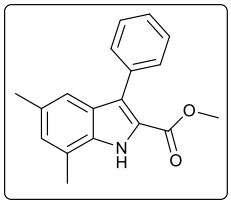
White solid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.95 (br s, 1H), 7.57-7.52 (m, 2H), 7.50-7.44 (m, 2H), 7.42-7.36 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.19 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.81 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 162.47, 134.19, 133.62, 130.57, 130.38, 128.13, 127.88, 127.19, 123.94, 122.47, 120.92, 111.41, 51.75, 21.48.

Ethyl 5-methyl-3-phenyl-1H-indole-2-carboxylate (Table 1, 3k)[6]



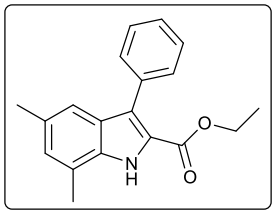
White solid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.96 (brs, 1H), 7.55 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.49-7.41 (m, 2H), 7.41-7.30 (m, 3H), 7.18 (dd, *J* = 8.5, 1.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 162.15, 134.19, 133.76, 130.69, 130.29, 128.17, 127.76, 127.13, 123.77, 122.88, 120.89, 111.44, 60.85, 21.50, 14.08.

Methyl 5,7-dimethyl-3-phenyl-1H-indole-2-carboxylate (Table 1, 3l)



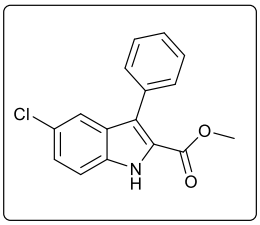
White solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.80 (br s, 1H), 7.54 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.46 (td, *J* = 6.9, 1.8 Hz, 2H), 7.42-7.33 (m, 1H), 7.24 (s, 1H), 7.01 (s, 1H), 3.81 (s, 3H), 2.52 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 162.60, 133.99, 133.82, 130.70, 130.55, 128.20, 127.85, 127.77, 127.15, 124.40, 122.27, 120.71, 118.49, 51.75, 21.43, 16.55. HRMS (ESI): m/z calcd for $C_{18}H_{17}NO_2$ $[M+H]^+$ 280.1337 found 280.1340.

Ethyl 5,7-dimethyl-3-phenyl-1H-indole-2-carboxylate (Table 1, 3m)



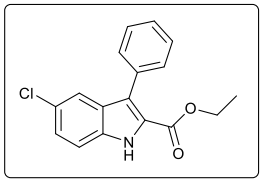
White solid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.82 (br s, 1H), 7.53 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.48- 7.41 (m, 2H), 7.40-7.33 (m, 1H), 7.23 (s, 1H), 7.00 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 2.37 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.29, 133.95, 130.67, 128.09, 127.83, 127.70, 127.08, 124.21, 122.70, 120.70, 118.47, 60.83, 21.43, 16.58, 14.06. HRMS (ESI): m/z calcd for $C_{19}H_{19}NO_2$ $[M+H]^+$ 294.1494 found 294.1499.

Methyl 5-chloro-3-phenyl-1H-indole-2-carboxylate (Table 1, 3n)[7]



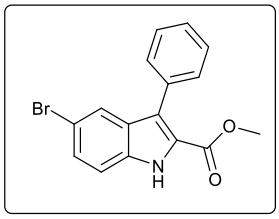
Brown solid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.08 (br s, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.54-7.43 (m, 4H), 7.43-7.34 (m, 2H), 7.31 (dd, *J* = 8.8, 1.9 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.15, 133.99, 132.75, 130.42, 128.89, 128.06, 127.57, 126.77, 126.46, 123.83, 123.58, 121.04, 112.90, 51.98.

Ethyl 5-chloro-3-phenyl-1H-indole-2-carboxylate (Table 1, 3o)



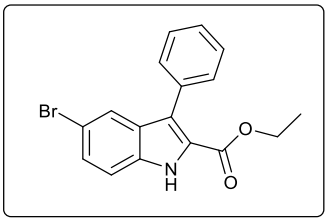
Brown solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.20 (br s, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.54-7.50 (m, 2H), 7.49-7.43 (m, 2H), 7.42-7.35 (m, 2H), 7.30 (dd, *J* = 8.7, 2.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.76, 133.92, 132.83, 130.50, 128.89, 127.88, 127.46, 126.65, 126.28, 123.95, 123.63, 120.96, 112.86, 61.11, 13.99. HRMS (ESI): m/z calcd for $C_{17}H_{14}ClNO_2$ $[M+H]^+$ 300.0791 found 300.0798.

Methyl 5-bromo-3-phenyl-1H-indole-2-carboxylate (Table 1, 3p)[4]



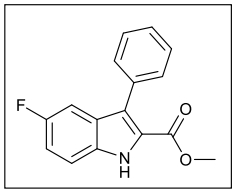
Brown solid, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.20 (br s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.53-7.38 (m, 6H), 7.32 (d, *J* = 8.9 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.22, 134.32, 132.76, 130.44, 129.50, 128.89, 128.06, 127.57, 124.16, 123.68, 123.41, 114.21, 113.36, 52.00.

Ethyl 5-bromo-3-phenyl-1H-indole-2-carboxylate (Table 1, 3q)[6]



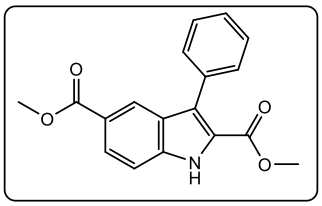
White solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.20 (br s, 1H), 7.74 (s, 1H), 7.51 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.48-7.36 (m, 4H), 7.32 (d, *J* = 8.7 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.78, 134.21, 132.83, 130.55, 129.58, 128.80, 127.93, 127.52, 124.16, 123.82, 123.55, 114.16, 113.28, 61.17, 14.03.

Methyl 5-fluoro-3-phenyl-1H-indole-2-carboxylate (Table 1, 3r)[7]



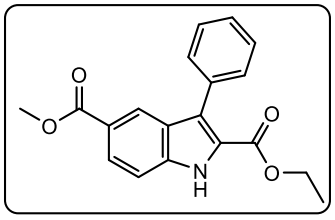
White solid, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.00 (br s, 1H), 7.57-7.50 (m, 2H), 7.50-7.43 (m, 2H), 7.43-7.35 (m, 2H), 7.28 (d, *J* = 2.5 Hz, 1H), 7.13 (td, *J* = 9.0, 2.5 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 162.15, 132.99, 132.29, 130.36, 128.02, 127.47, 123.91, 115.29, 114.93, 112.78, 112.66, 106.26, 105.94, 51.93.

Dimethyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3s)



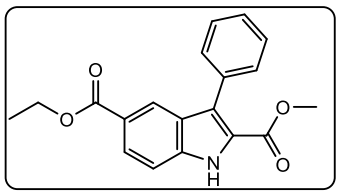
White solid, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 9.14 (br s, 1H), 8.40-8.36 (m, 1H), 8.06 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.57-7.41 (m, 6H), 3.90 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 167.48, 161.94, 137.88, 132.50, 130.46, 128.02, 127.61, 126.82, 125.62, 125.05, 123.65, 123.20, 111.45, 51.93. HRMS (ESI): m/z calcd for $C_{18}H_{15}NO_4$ $[M+H]^+$ 310.1079 found 310.1064.

2-Ethyl 5-methyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3t)



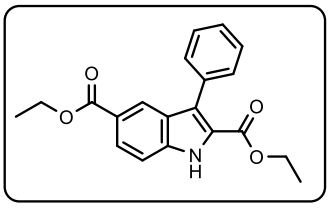
White solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 9.20 (br s, 1H), 8.35-8.29 (m, 1H), 7.99 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.49 (dt, *J* = 8.3, 1.5 Hz, 2H), 7.45-7.33 (m, 4H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) = 167.52, 161.59, 137.86, 132.63, 130.56, 127.88, 127.55, 126.71, 125.46, 125.02, 124.06, 123.13, 111.45, 61.12, 51.92, 13.96. HRMS (ESI): m/z calcd for $C_{19}H_{17}NO_4$ $[M+H]^+$ 324.1235 found 324.1233.

5-Ethyl 2-methyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3u)



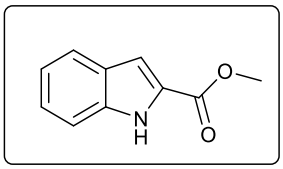
White solid, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 9.11 (br s, 1H), 8.40-8.35 (m, 1H), 8.06 (dd, *J* = 8.9, 1.6 Hz, 1H), 7.58-7.53 (m, 2H), 7.53-7.40 (m, 4H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 167.10, 162.05, 137.94, 132.61, 130.54, 128.08, 127.66, 126.87, 125.05, 123.64, 111.4, 60.84, 52.01, 14.44. HRMS (ESI): m/z calcd for $C_{19}H_{17}NO_4$ $[M+H]^+$ 324.1235 found 324.1234.

Diethyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3v)



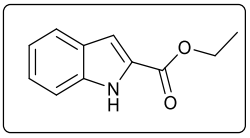
White solid, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) = 9.15 (br s, 1H), 8.41-8.36 (m, 1H), 8.06 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.56 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.51-7.39 (m, 4H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) = 167.13, 161.66, 137.89, 132.72, 130.65, 127.94, 127.60, 126.77, 125.53, 125.01, 124.09, 123.57, 111.43, 61.17, 60.83, 14.44, 14.04. HRMS (ESI): m/z calcd for $C_{20}H_{19}NO_4$ $[M+H]^+$ 338.1392 found 338.1404.

Methyl 1H-indole-2-carboxylate (Table 1, 3y)[9]



White solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.07 (br s, 1H), 7.69 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.42 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.32 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.24-7.21 (m, 1H), 7.19-7.12 (m, 1H), 3.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 162.51, 136.88, 127.45, 127.08, 125.41, 122.61, 120.81, 111.88, 108.79, 52.01.

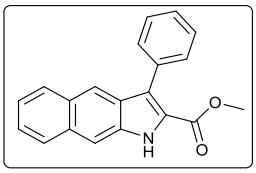
Ethyl 1H-indole-2-carboxylate (Table 1, 3z)[10]



White solid, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.15 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.35-7.28 (m, 1H), 7.23 (s, 1H), 7.17-7.09 (m, 1H), 4.42 (qd, *J* =

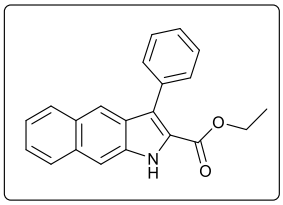
7.2, 1.9 Hz, 2H), 1.42 (td, *J* = 7.2, 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.09, 136.83, 127.47, 125.30, 122.57, 120.74, 111.85, 108.62, 61.02, 14.38.

Methyl 3-phenyl-1H-benzo[f]indole-2-carboxylate (Table 1, 3za)



White solid, 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.97 (br s, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.64-7.55 (m, 4H), 7.55-7.45 (m, 4H), 7.44-7.37 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (PPM) = 162.57, 133.52, 132.30, 131.82, 130.66, 128.92, 127.93, 127.34, 126.09, 125.92, 124.01, 122.24, 121.56, 121.04, 120.59, 120.26, 51.85. HRMS (ESI): m/z calcd for $C_{20}H_{15}NO_2$ $[M+H]^+$ 302.1181 found 302.1186.

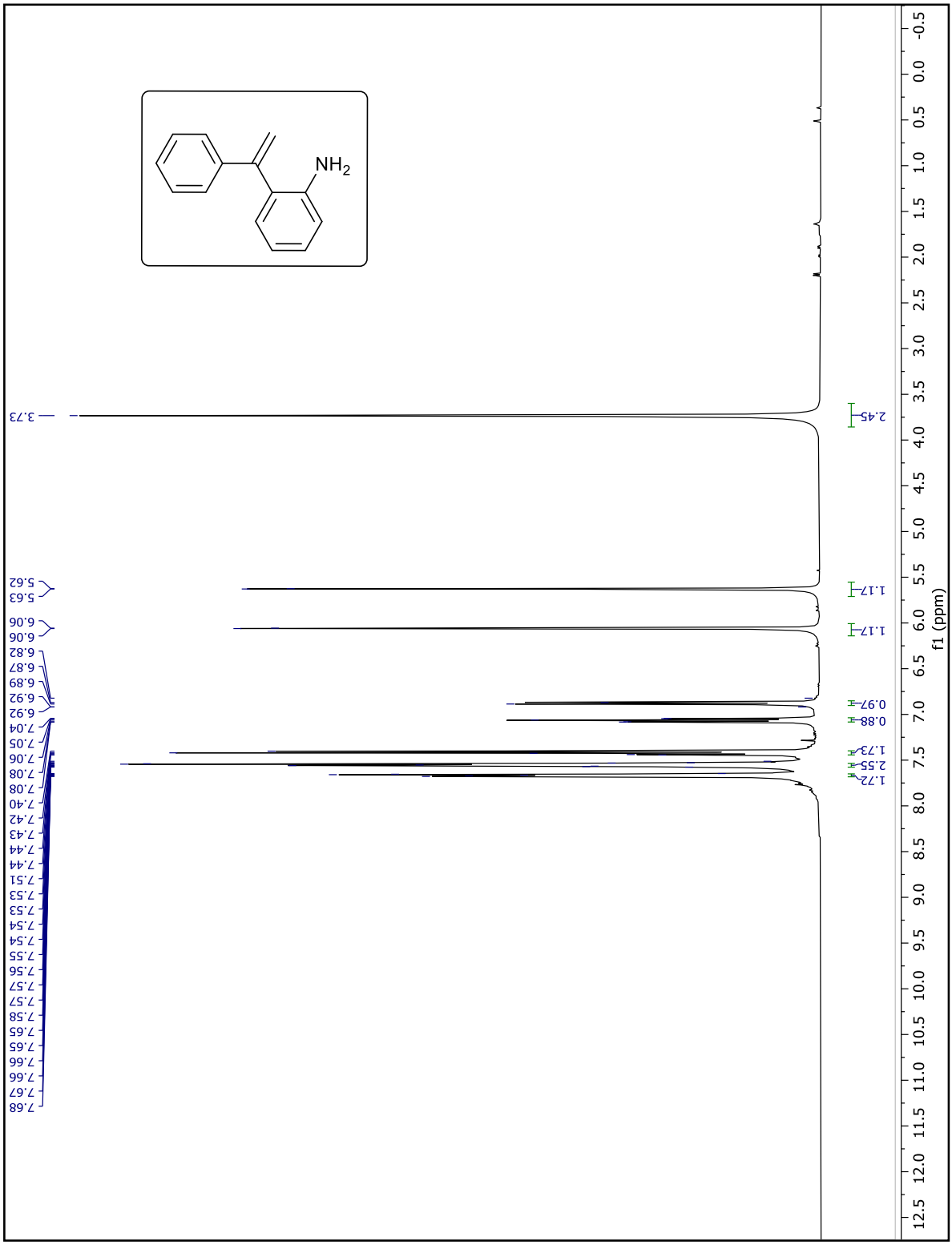
Ethyl 3-phenyl-1H-benzo[f]indole-2-carboxylate (Table 1, 3zb)

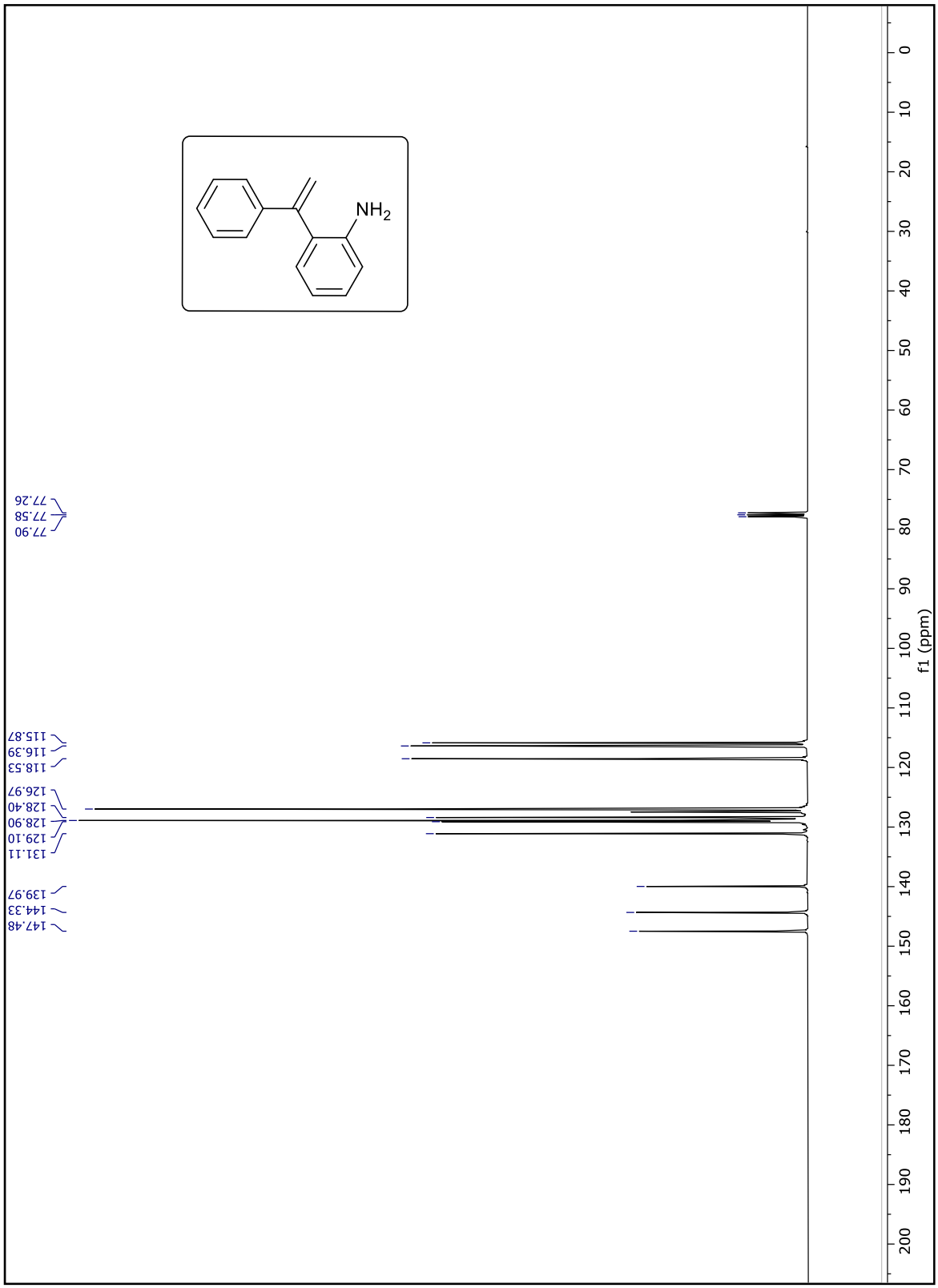


White solid, 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.77 (br s, 1H), 8.18 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.96-7.89 (m, 1H), 7.67-7.55 (m, 4H), 7.55-7.36 (m, 5H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 162.31, 133.69, 132.27, 131.80, 130.79, 128.90, 127.78, 127.27, 126.01, 125.83, 124.05, 122.16, 121.64, 121.50, 120.70, 120.28, 60.97, 14.12. HRMS (ESI): m/z calcd for $C_{21}H_{17}NO_2$ $[M+H]^+$ 316.1337 found 316.1345.

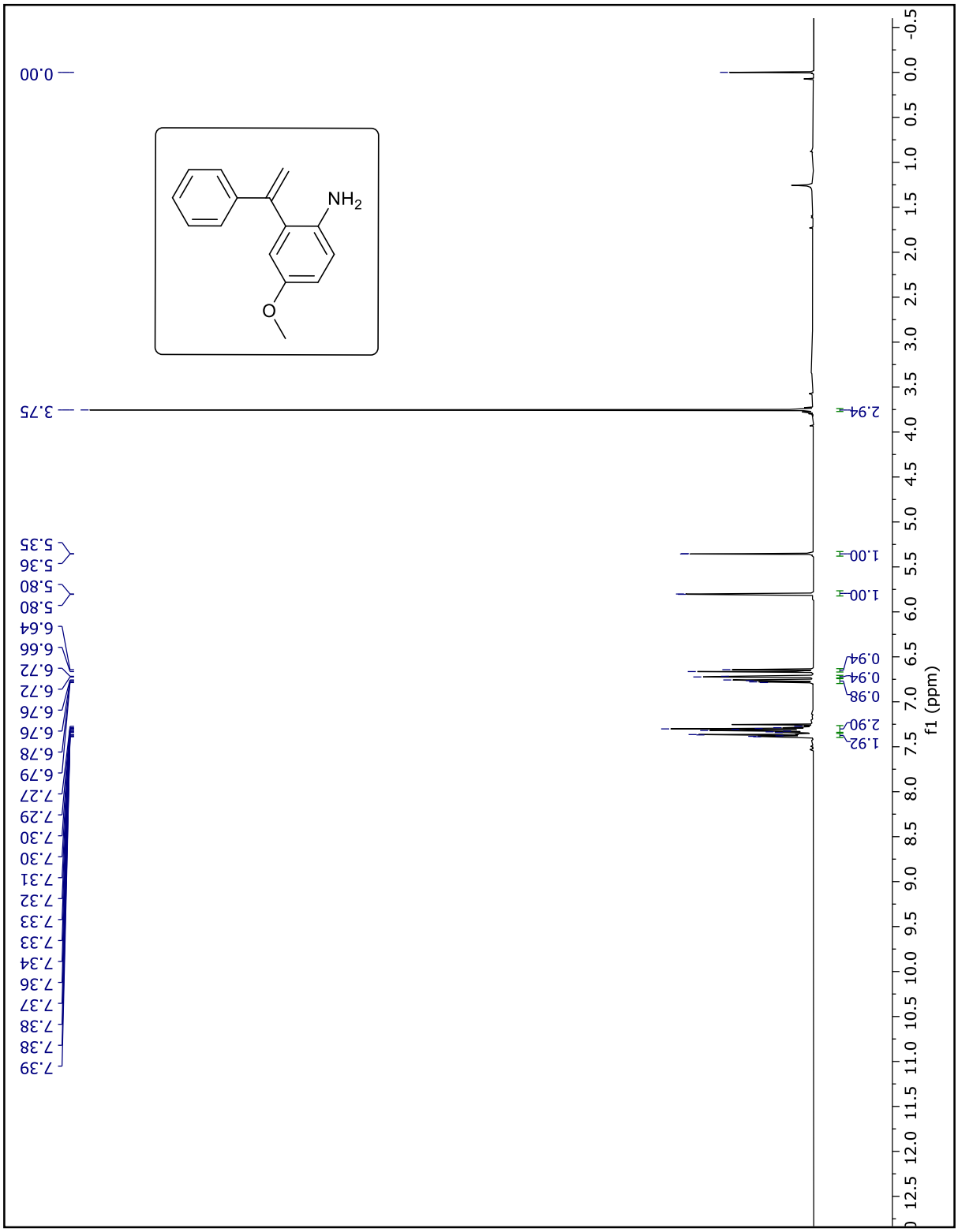
3. Copies of ^{1}H and ^{13}C NMR spectra of compounds:

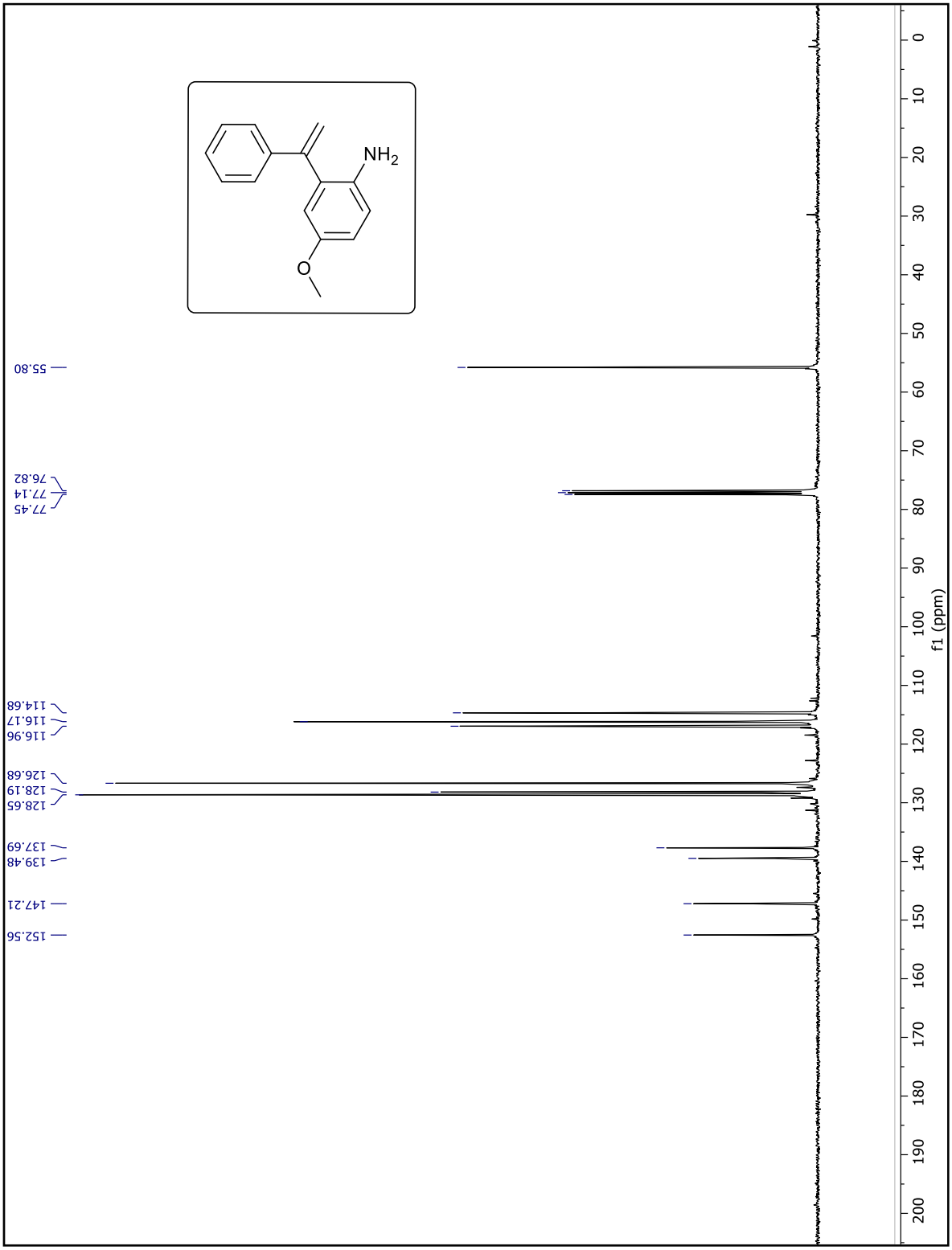
2-(1-Phenylvinyl)aniline (1b)



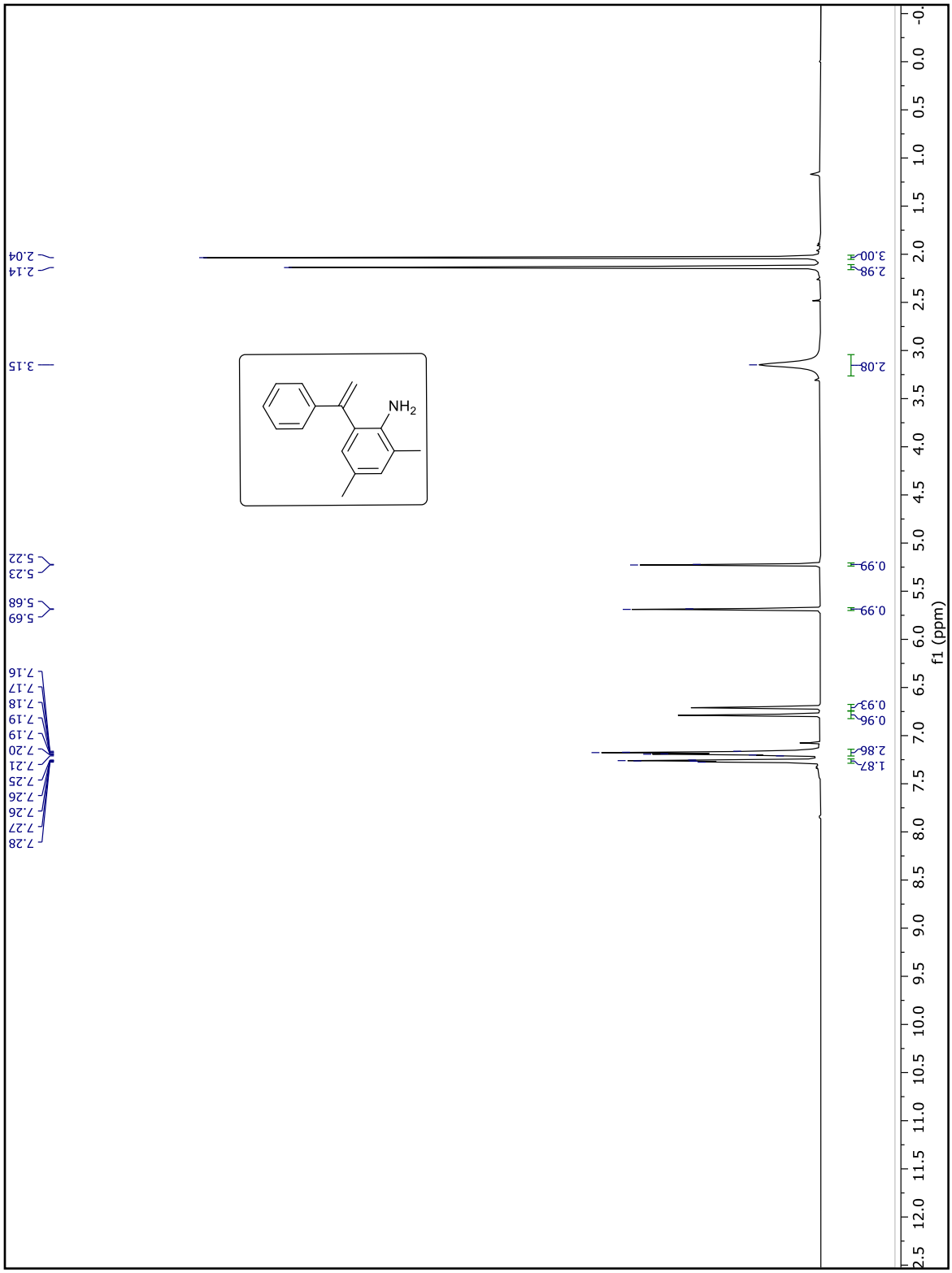

NH2
77.26
77.58
77.90
115.87
116.39
118.53
126.97
128.40
128.90
129.10
131.11
139.97
144.33
147.48
f1 (ppm)

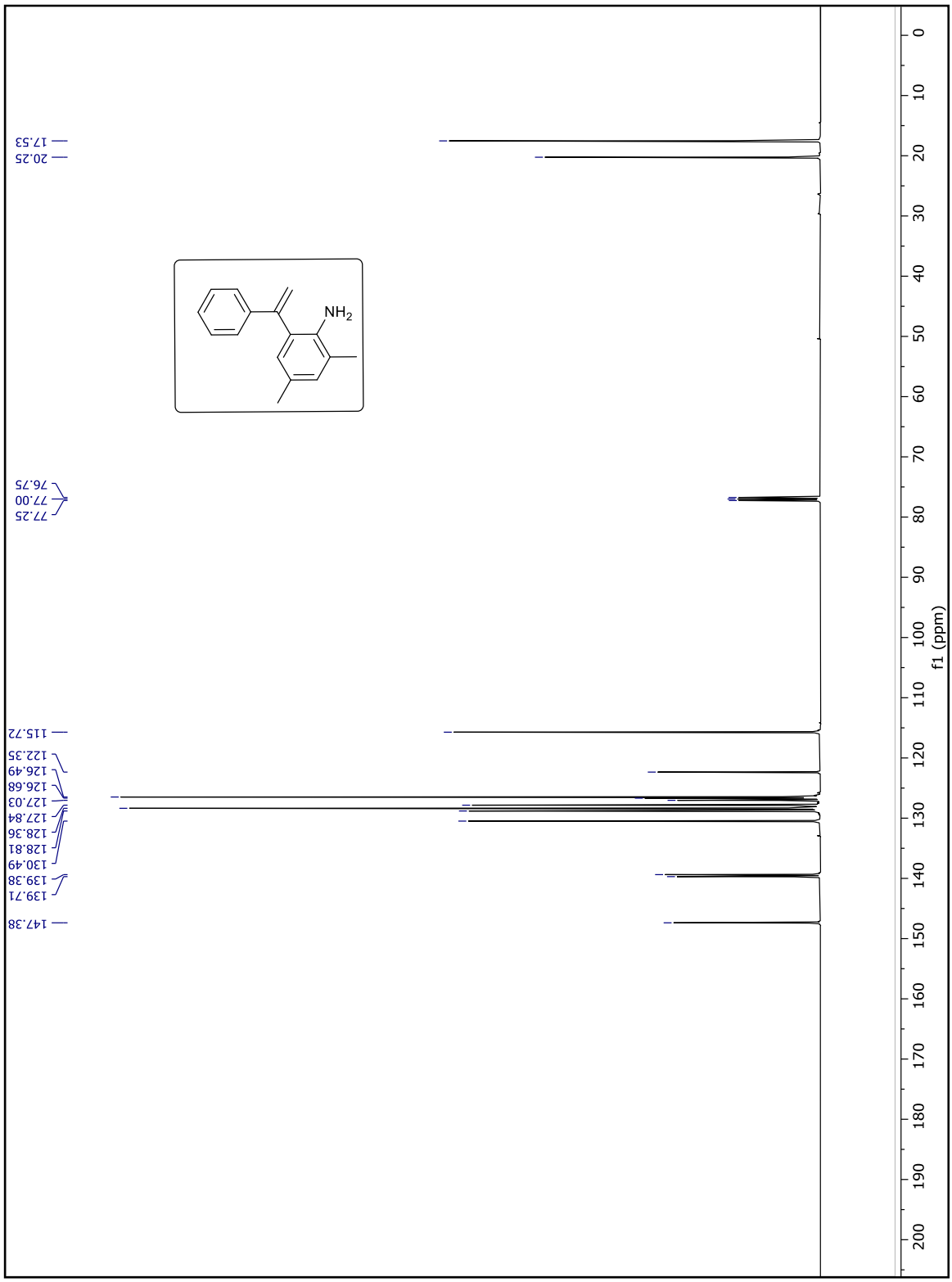
4-Methoxy-2-(1-phenylvinyl)aniline (1c)



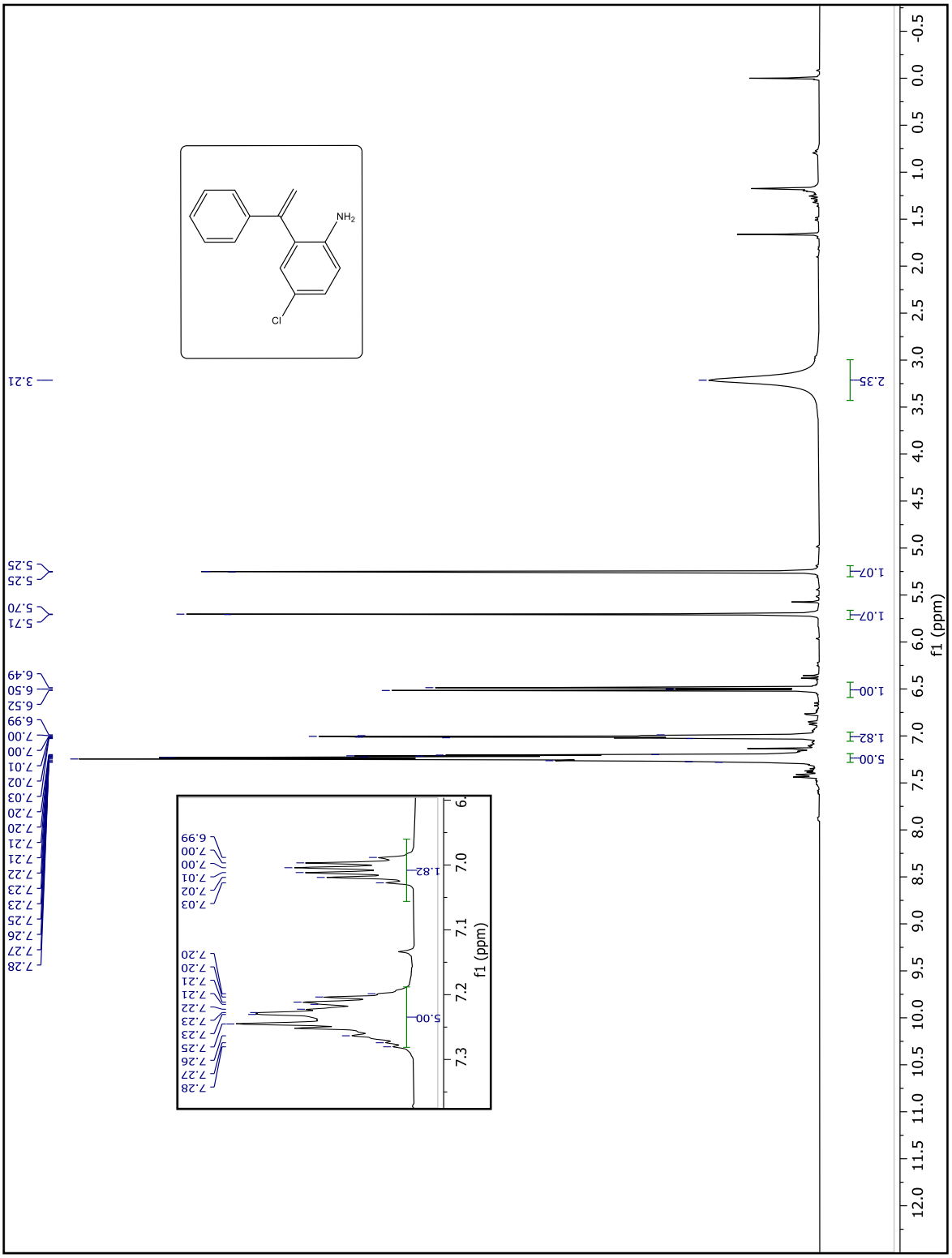

NH2
O
55.80
76.82
77.14
77.45
114.68
116.17
116.96
126.68
128.19
128.65
137.69
139.48
147.21
152.56
f1 (ppm)

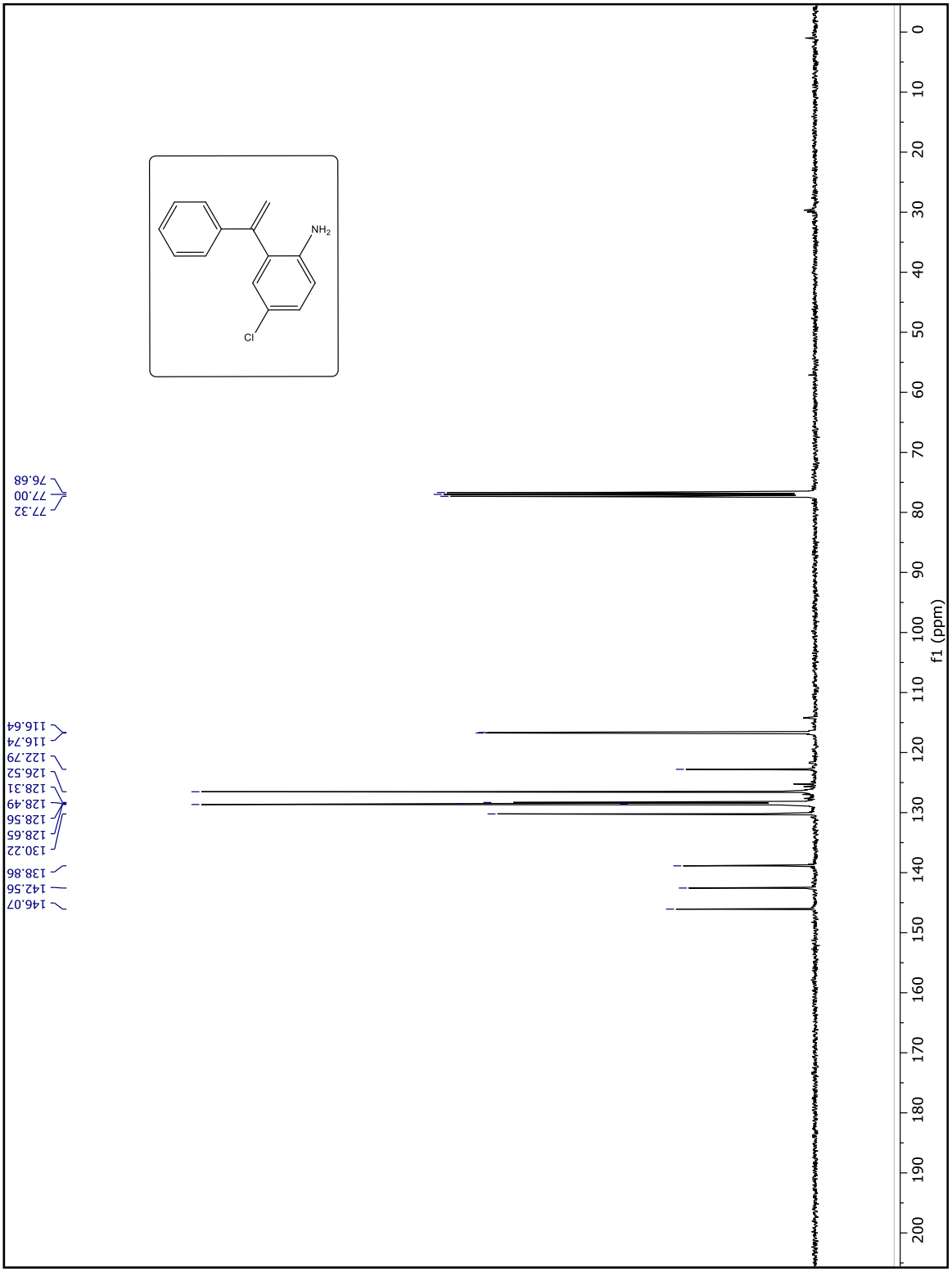
2,4-Dimethyl-6-(1-phenylvinyl)aniline (1f)



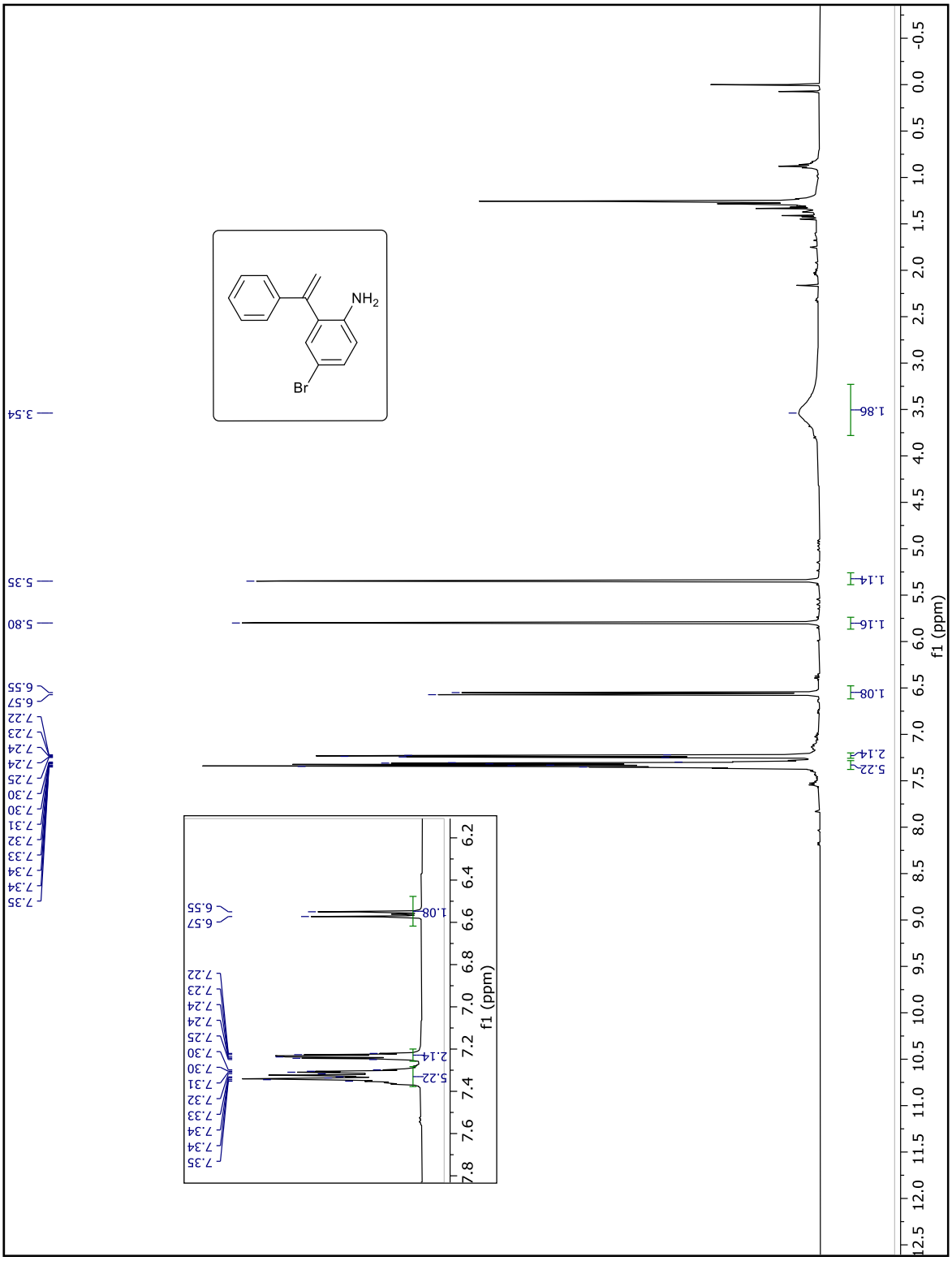

NH2
17.53
20.25
76.75
77.00
77.25
115.72
122.35
126.49
126.68
127.03
127.84
128.36
128.81
130.49
139.38
139.71
147.38
f1 (ppm)

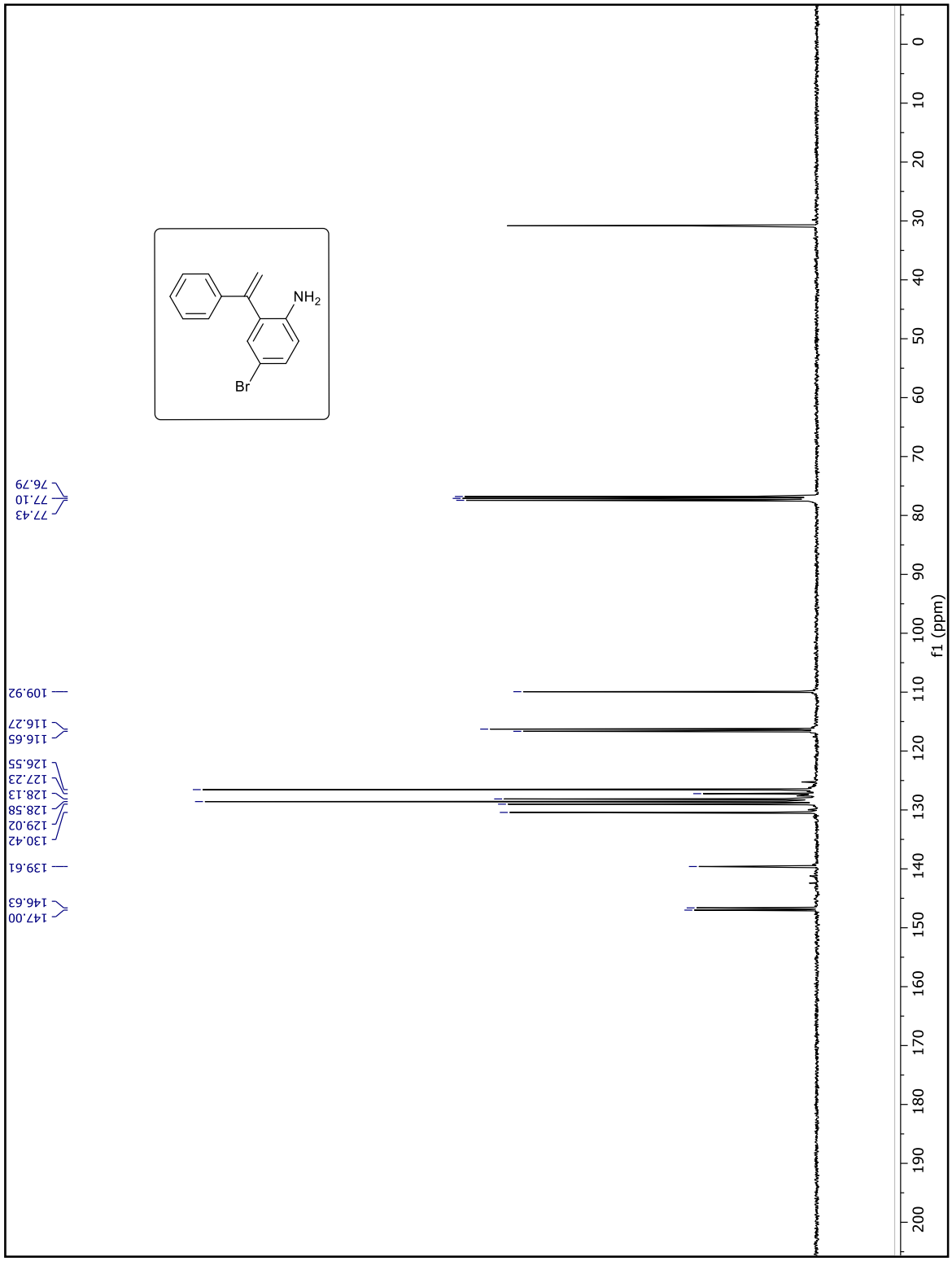
4-Chloro-2-(1-phenylvinyl)aniline (1g)



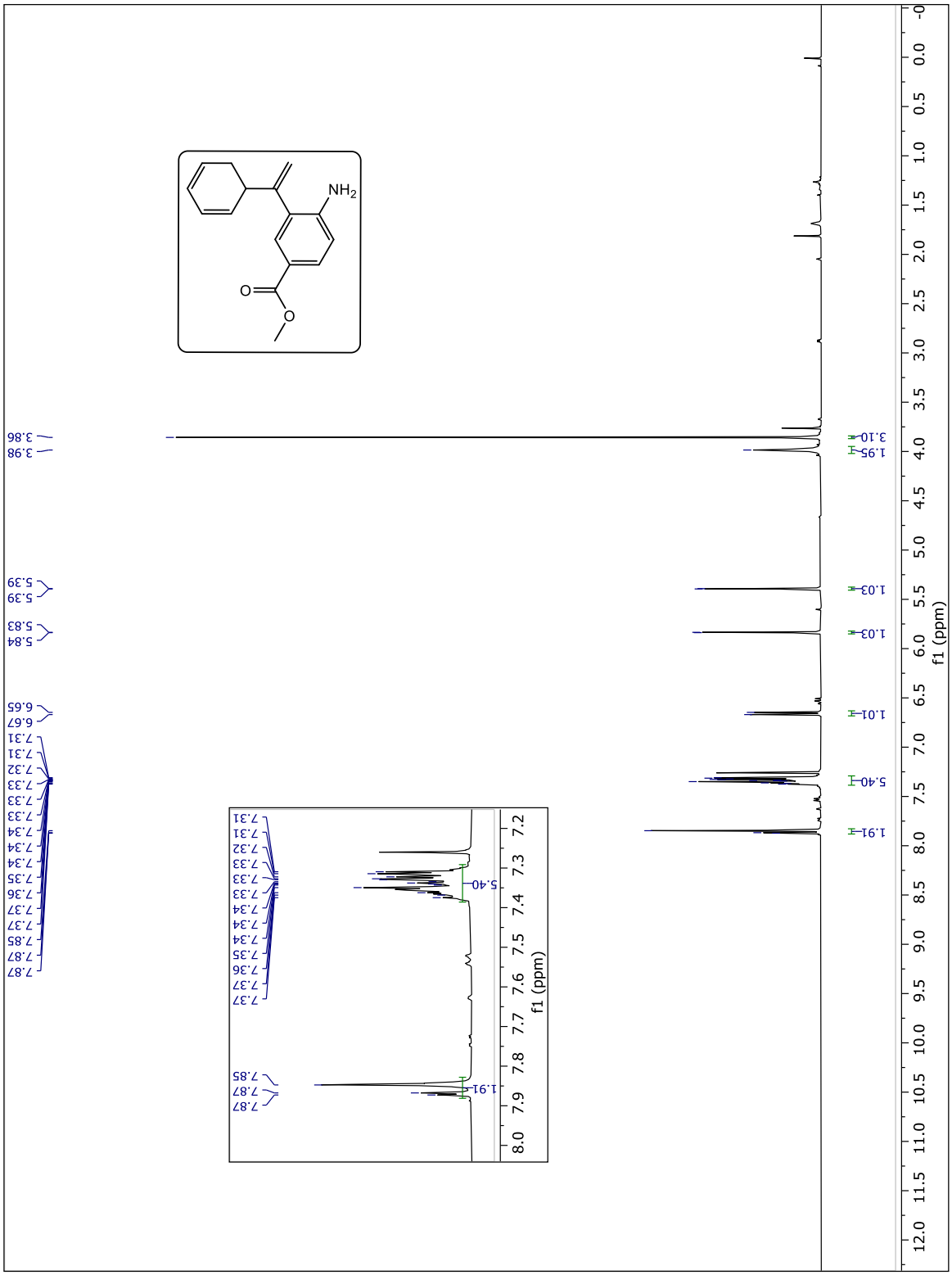

NH2
Cl
76.68
77.00
77.32
116.64
116.74
122.79
126.52
128.31
128.49
128.56
128.65
130.22
138.86
142.56
146.07
f1 (ppm)

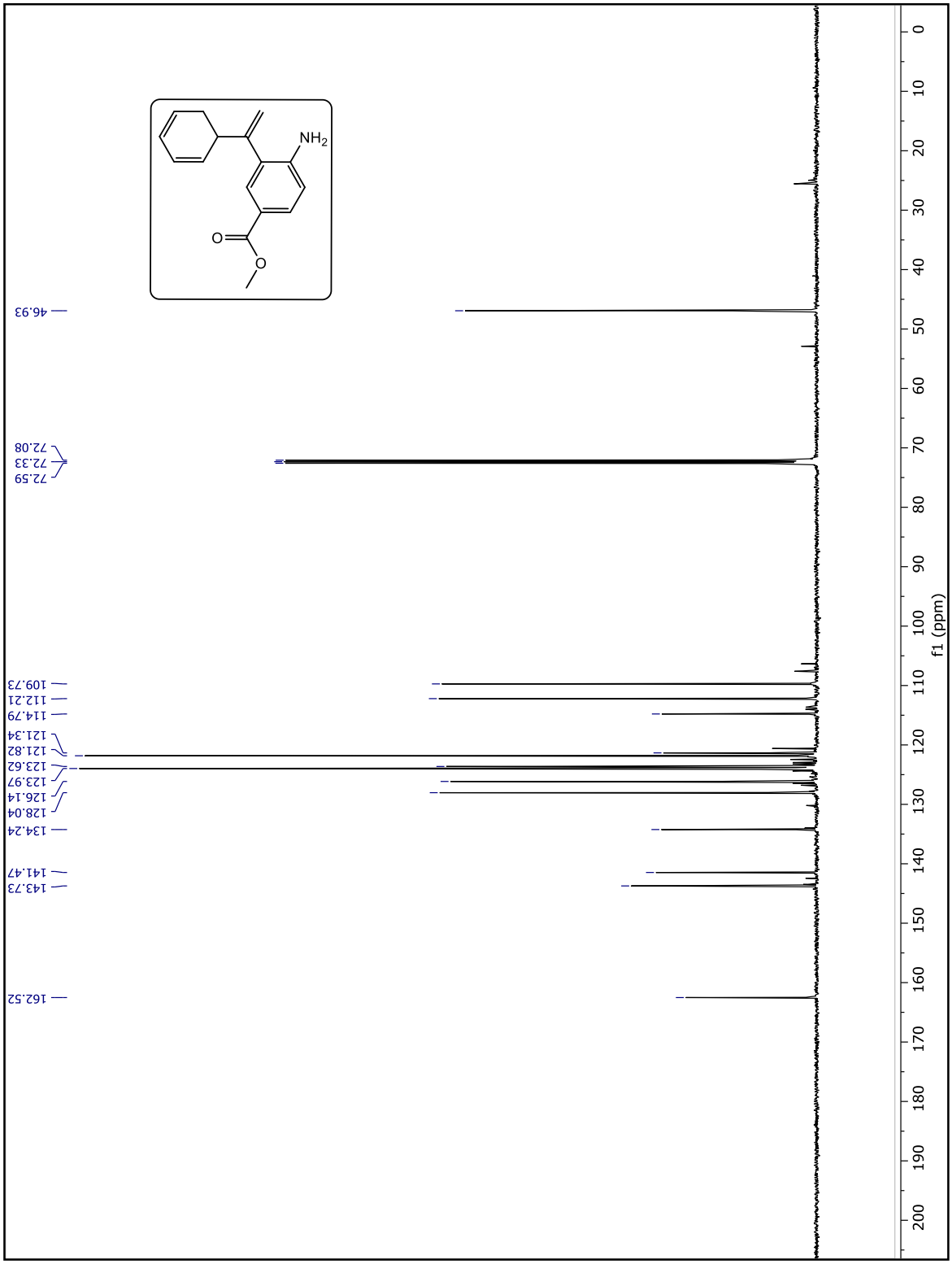
4-Bromo-2-(1-phenylvinyl)aniline (1h)



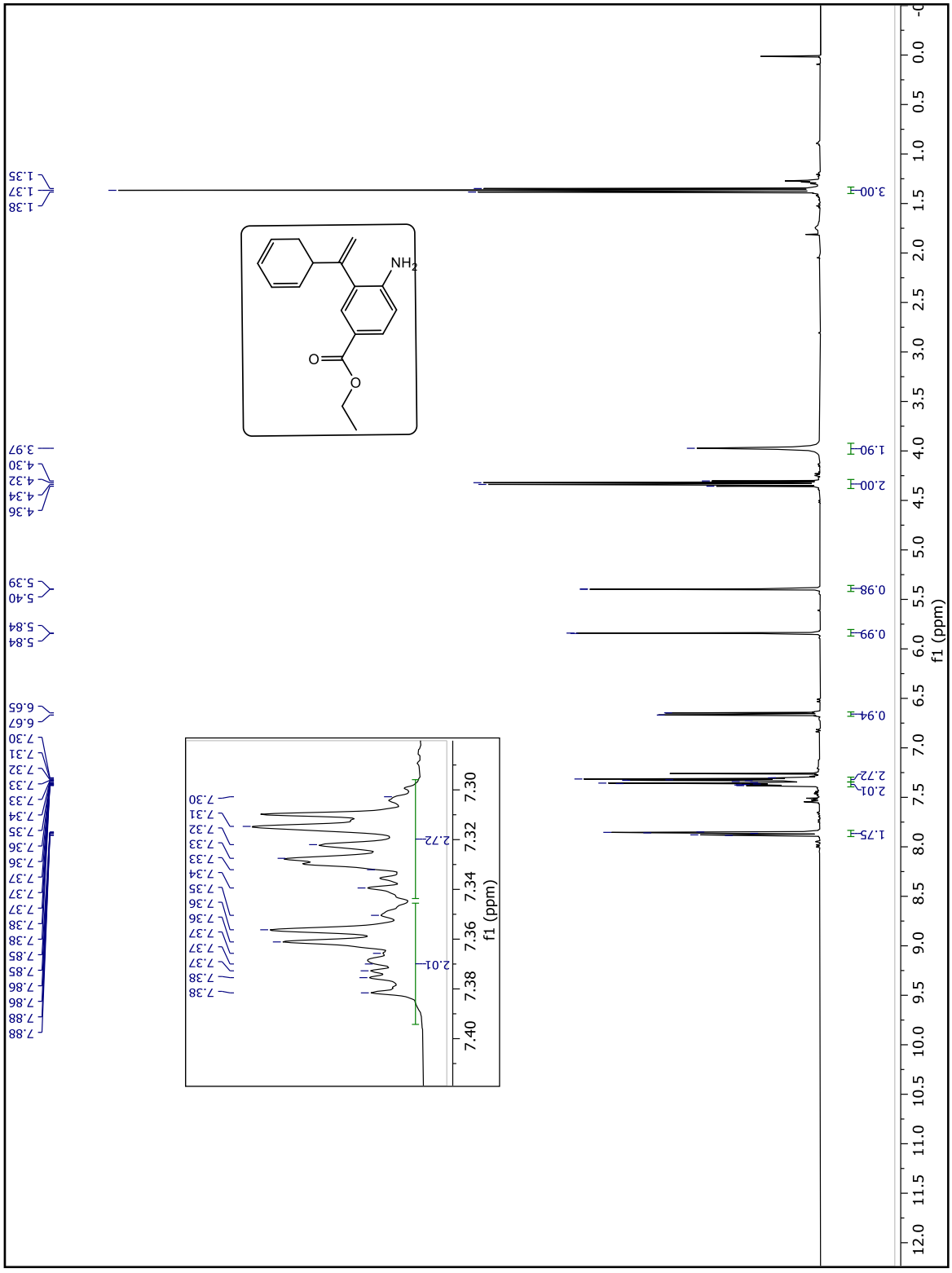

NH2
Br
147.00
146.63
139.61
130.42
129.02
128.58
128.13
127.23
126.55
116.65
116.27
109.92
77.43
77.10
76.79
f1 (ppm)

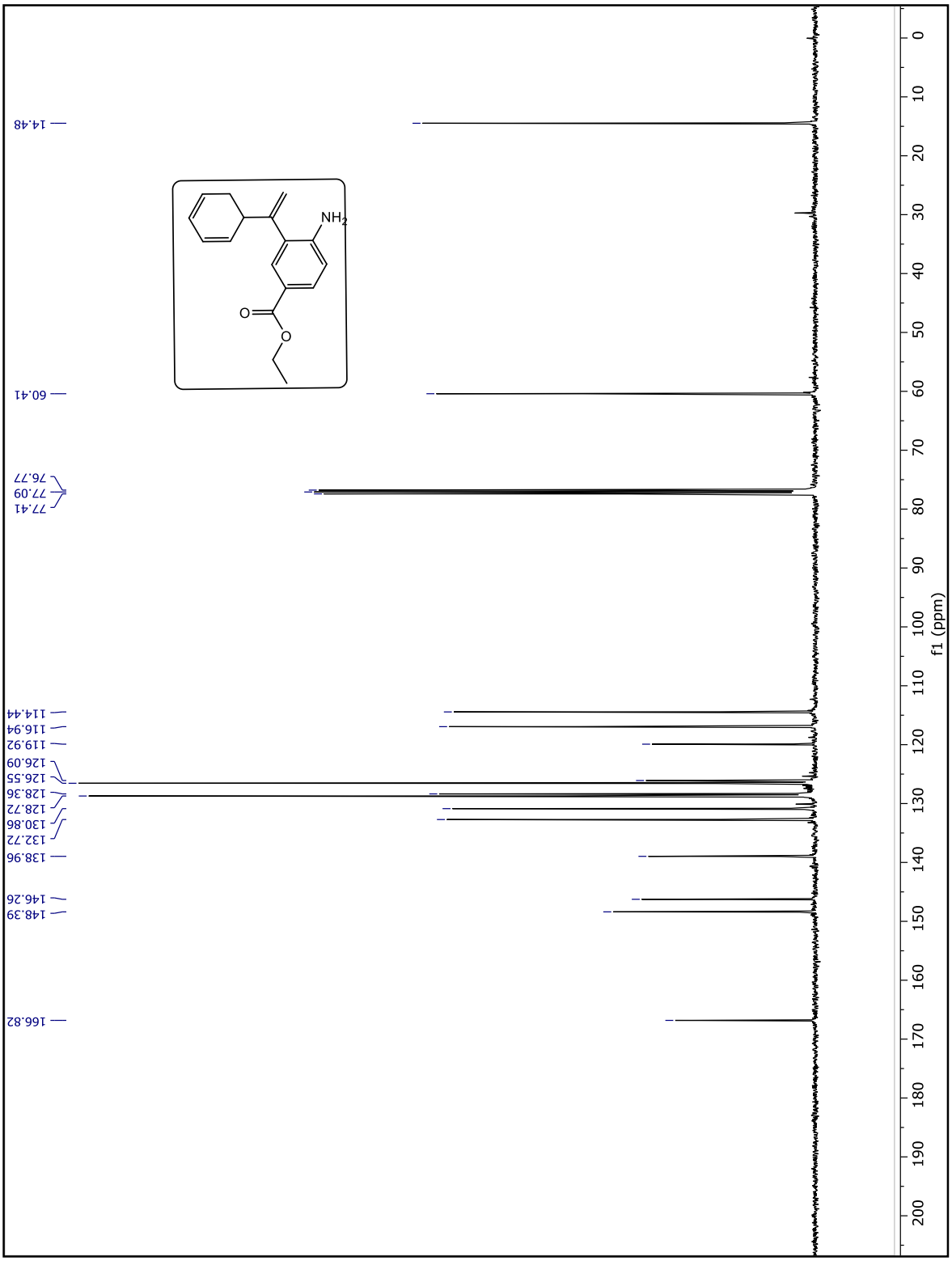
Methyl 4-amino-3-(1-(cyclohexa-2,4-dien-1-yl)vinyl)benzoate (1j)



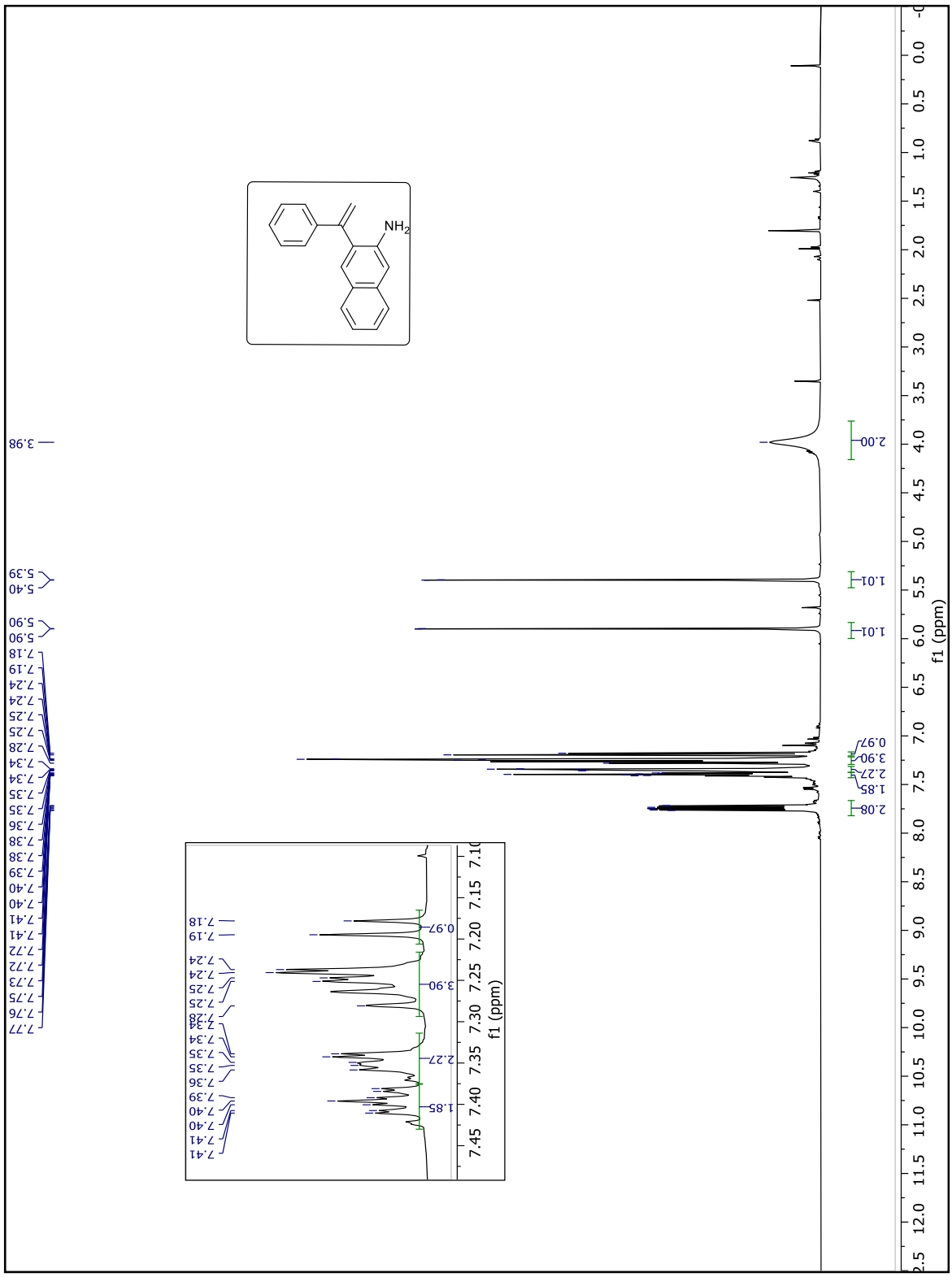

NH2
O
O
162.52
143.73
141.47
134.24
128.04
126.14
123.97
123.62
121.82
121.34
114.79
112.21
109.73
72.59
72.33
72.08
46.93
f1 (ppm)

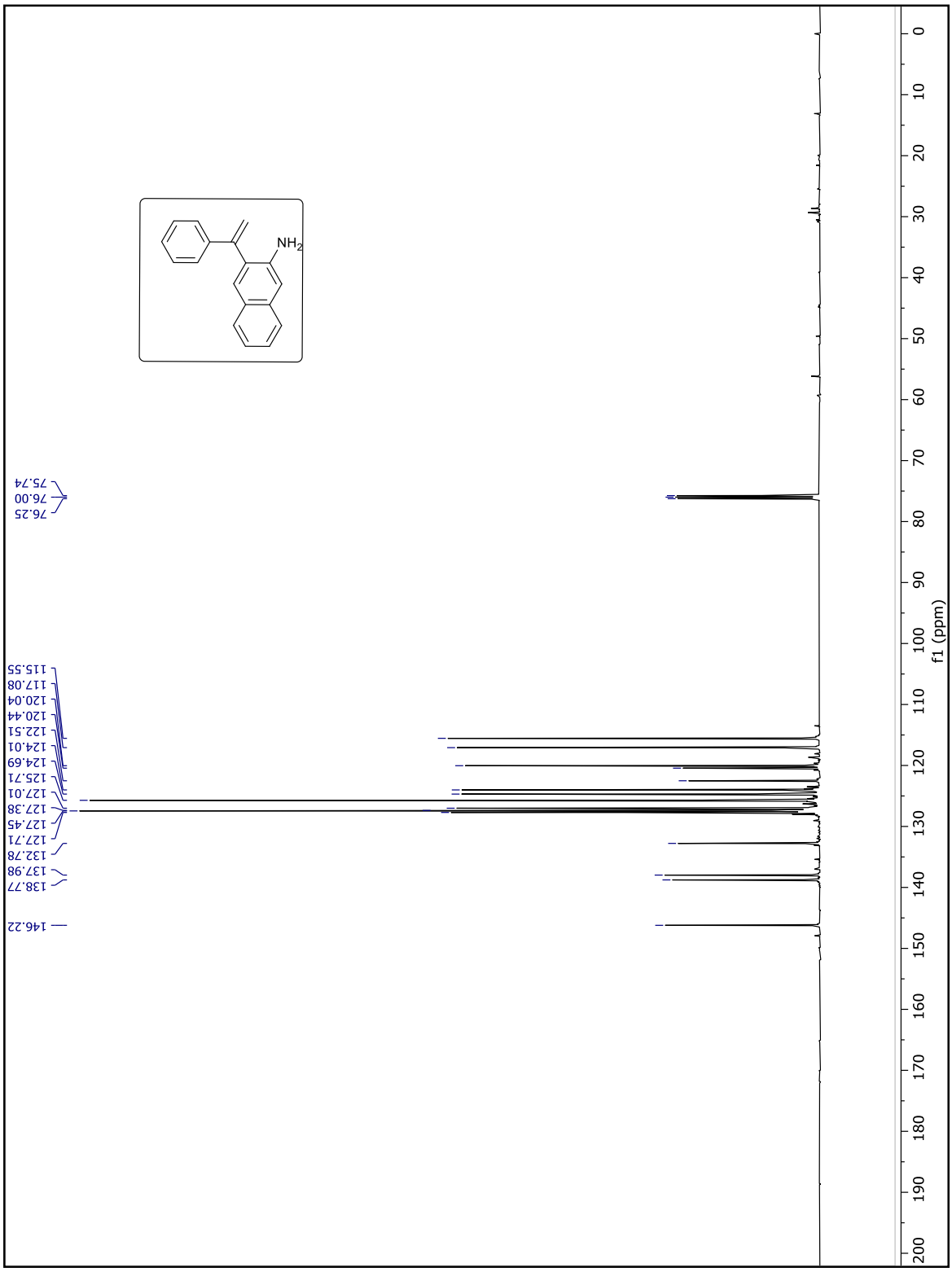
Ethyl 4-amino-3-(1-(cyclohexa-2,4-dien-1-yl)vinyl)benzoate (1k)



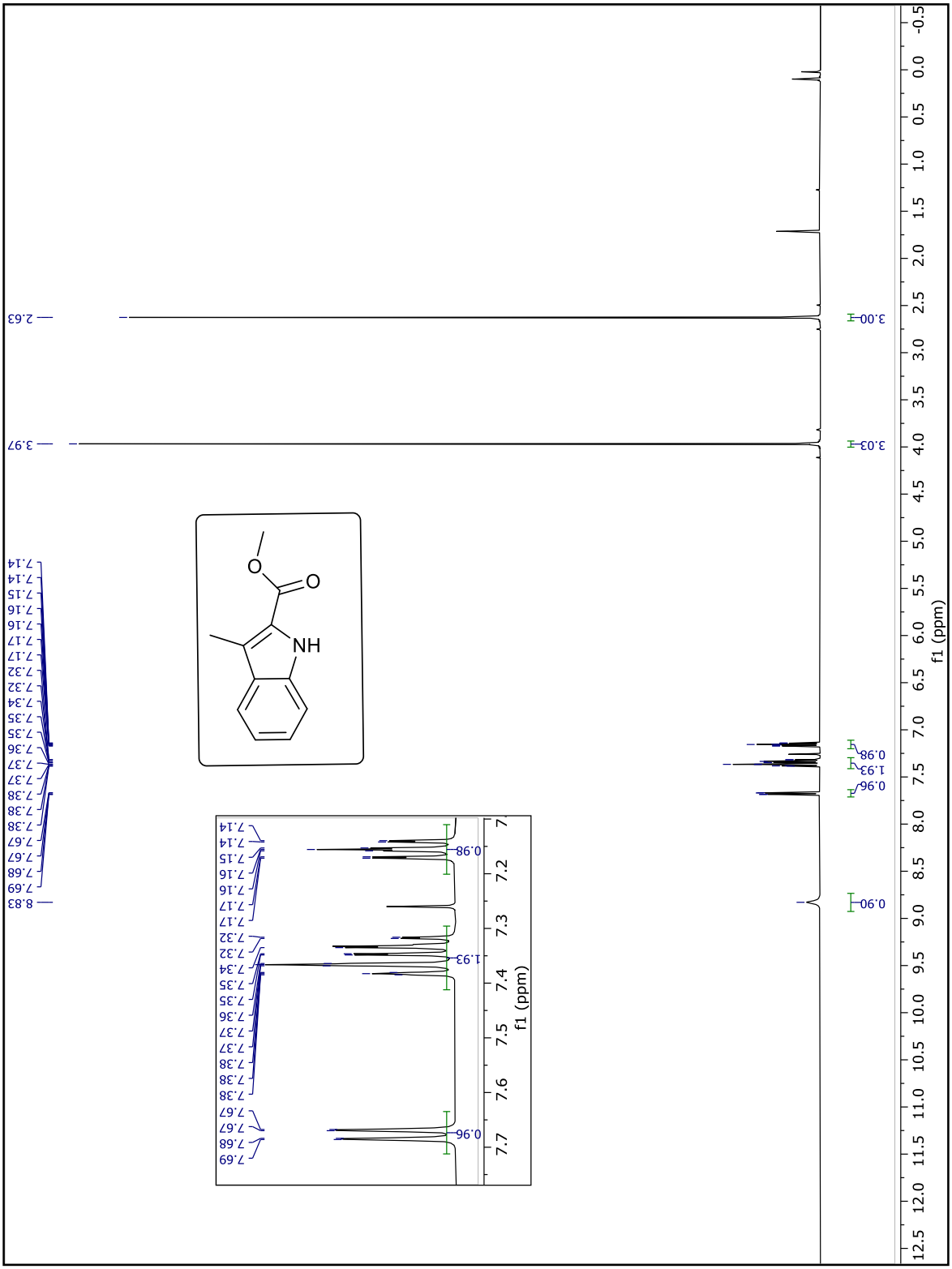

14.48
60.41
76.77
77.09
77.41
114.44
116.94
119.92
126.09
126.55
128.36
128.72
130.86
132.72
138.96
146.26
148.39
166.82
NH2
O
O
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

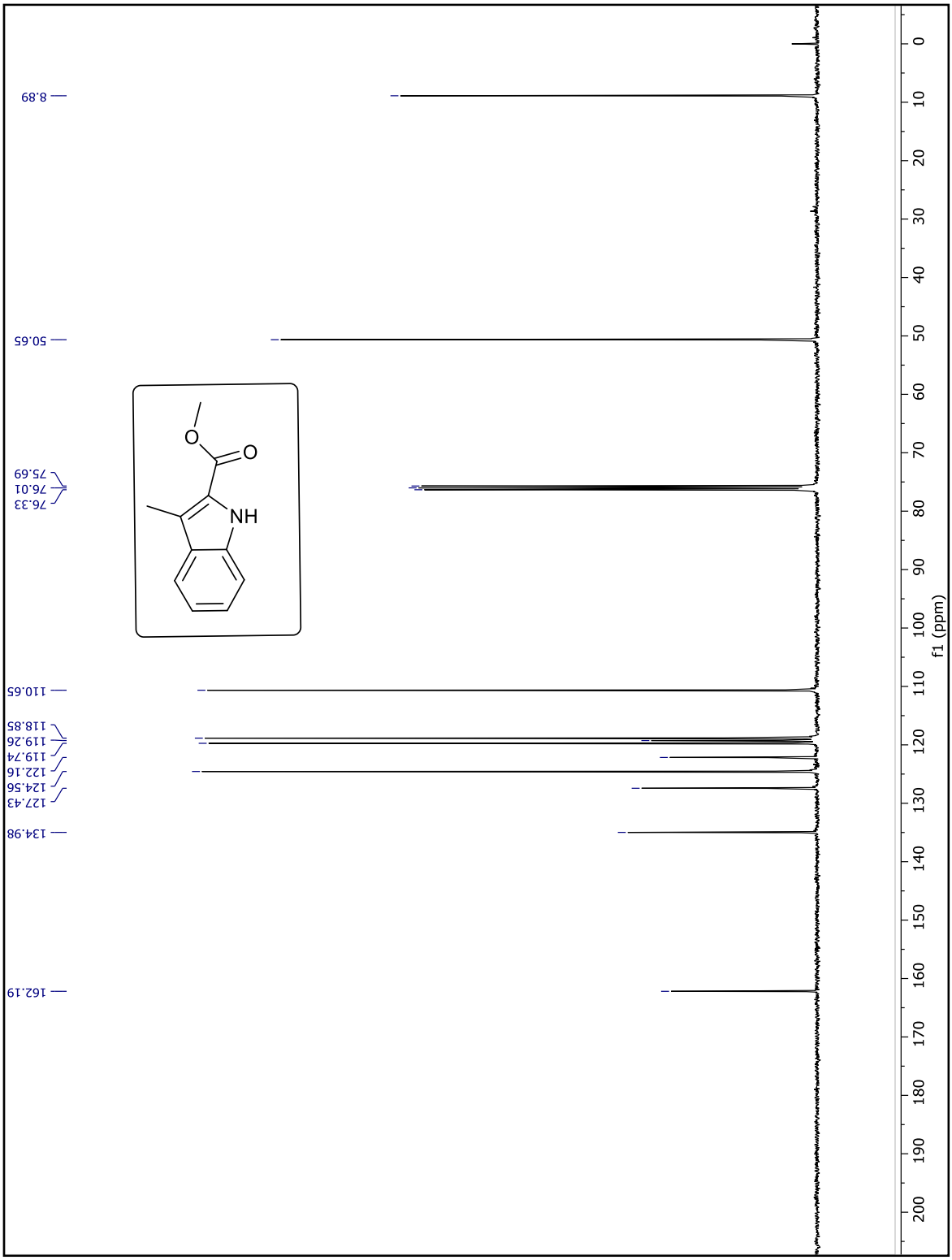
3-(1-Phenyl)vinylaphthalen-2-amine (1n)



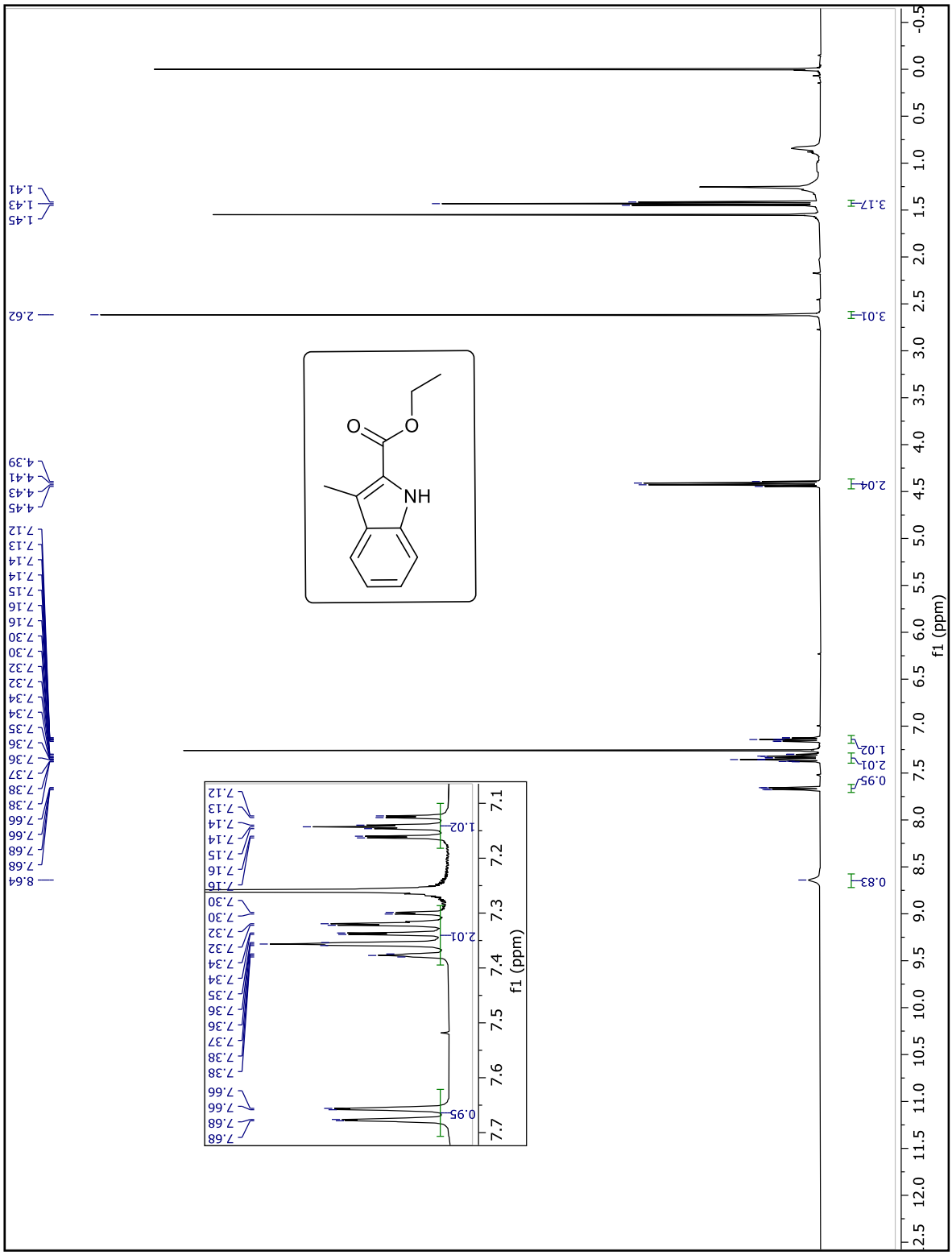

NH2
146.22
138.77
137.98
132.78
127.71
127.45
127.38
127.01
125.71
124.69
124.01
122.51
120.44
120.04
117.08
115.55
76.25
76.00
75.74
f1 (ppm)

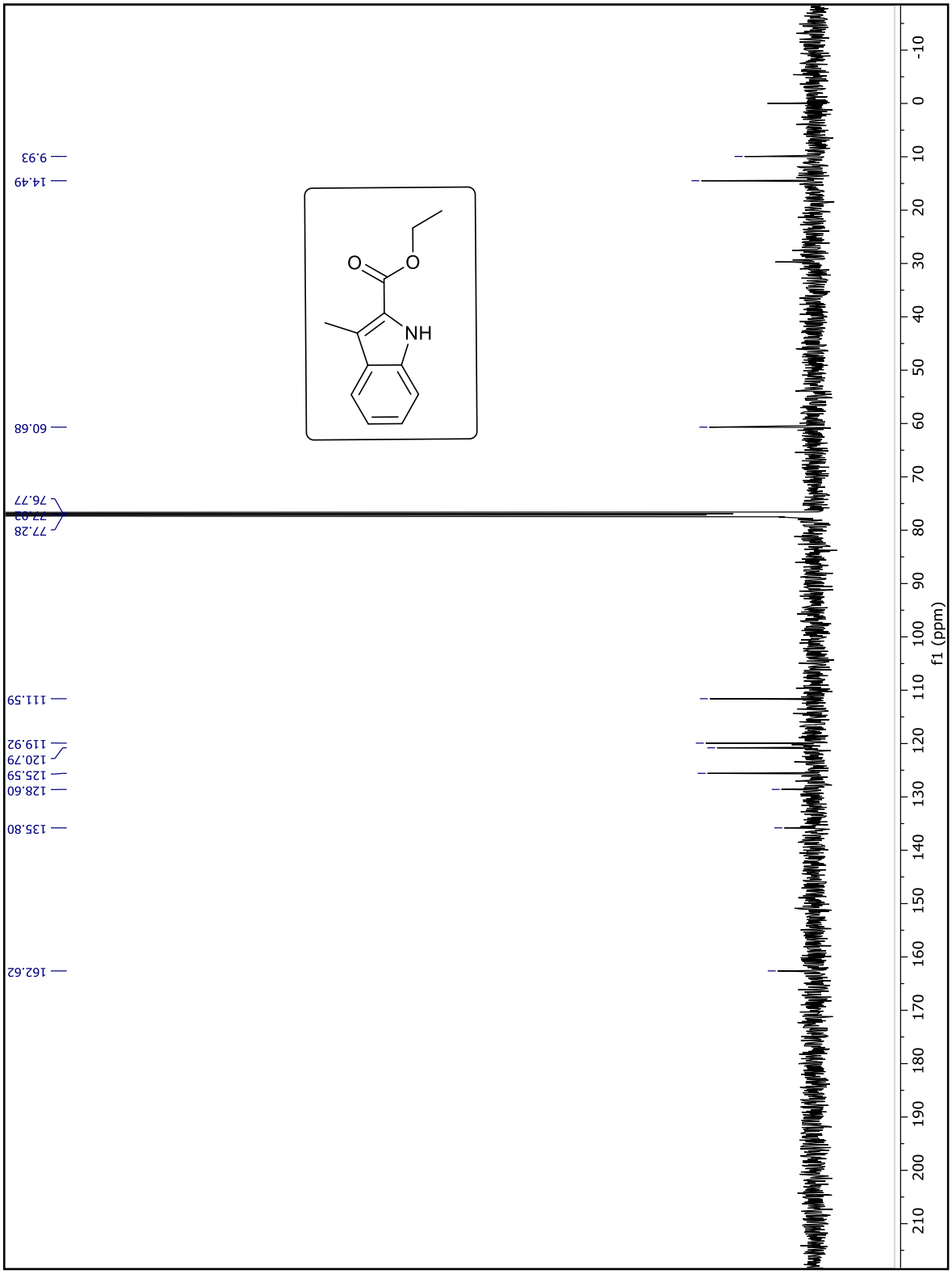
Methyl 3-methyl-1H-indole-2-carboxylate (Table 1, 3a)



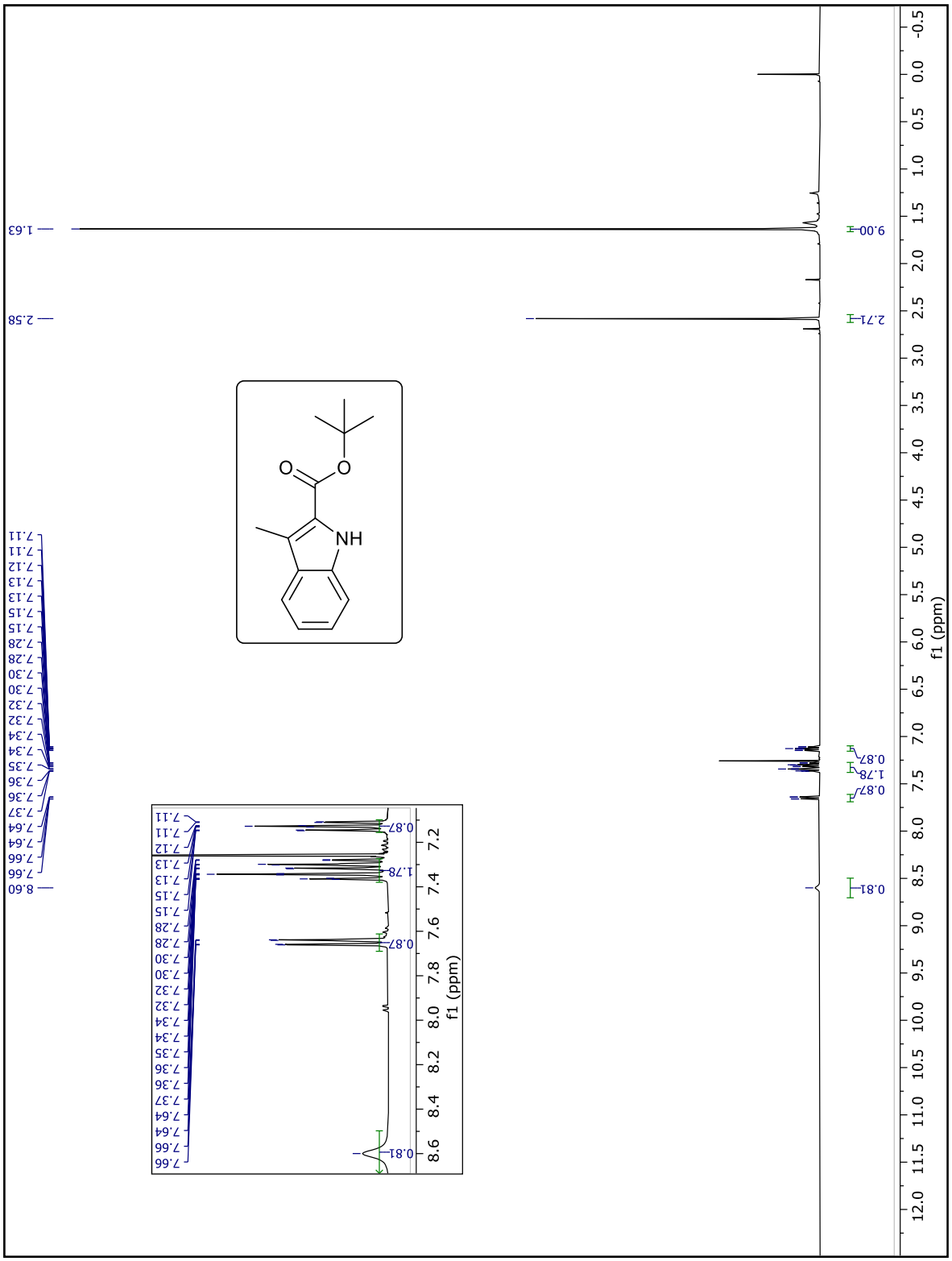

8.89
50.65
75.69
76.01
76.33
110.65
118.85
119.26
119.74
122.16
124.56
127.43
134.98
162.19
O
O
NH
f1 (ppm)

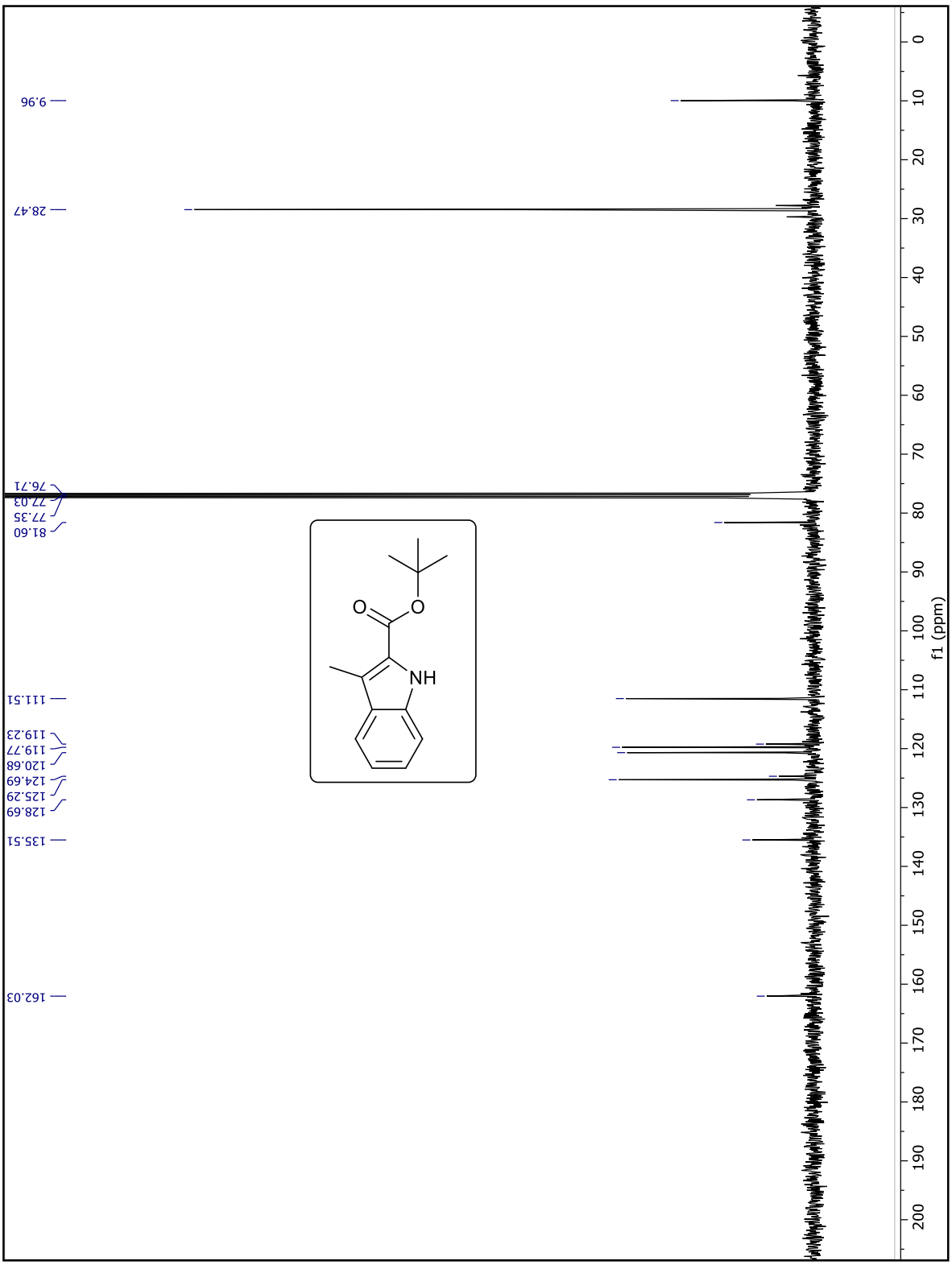
Ethyl 3-methyl-1*H*-indole-2-carboxylate (Table 1, 3b)



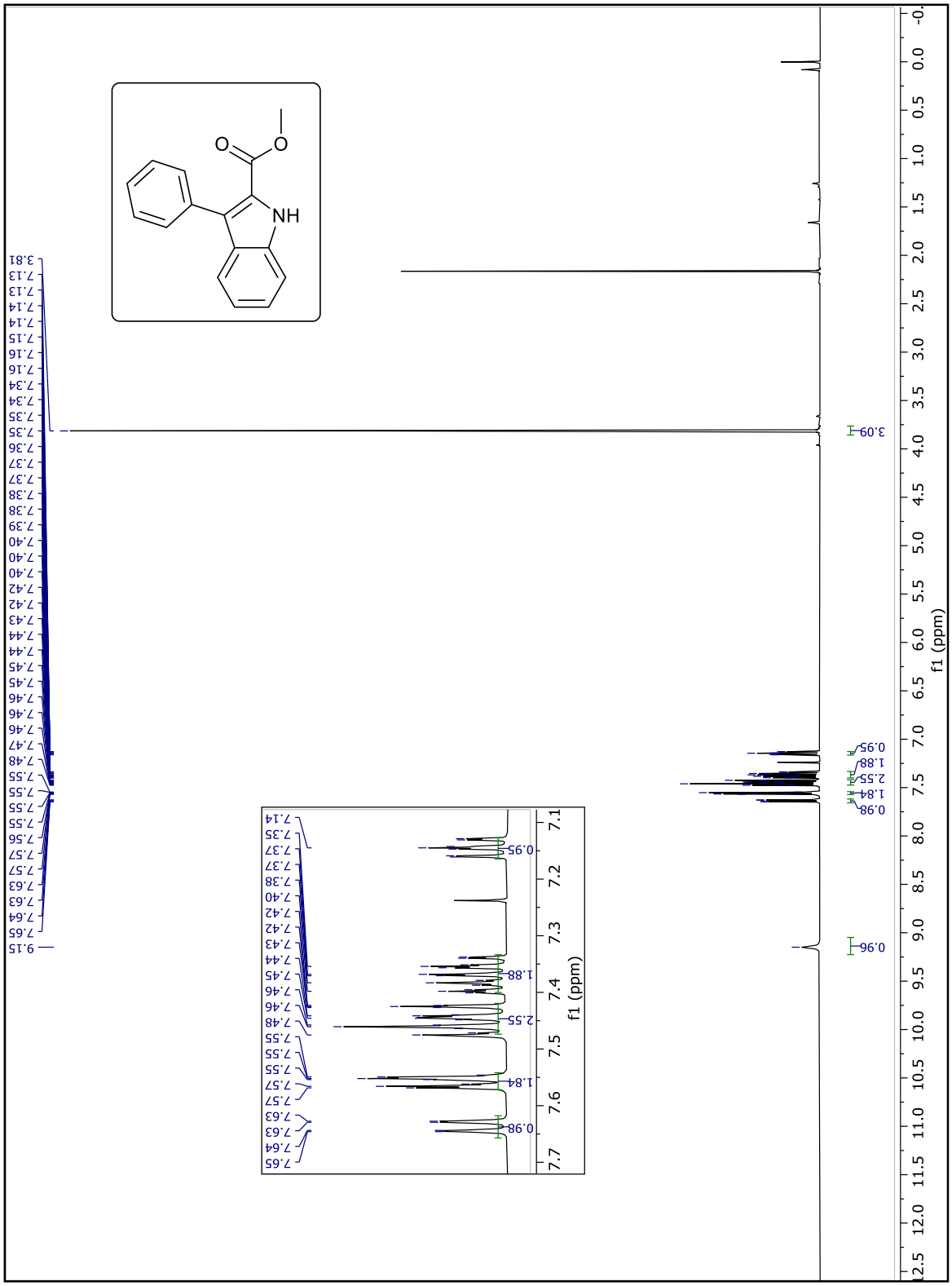

9.93
14.49
60.68
76.77
77.02
77.28
111.59
119.92
120.79
125.59
128.60
135.80
162.62
O
O
NH
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

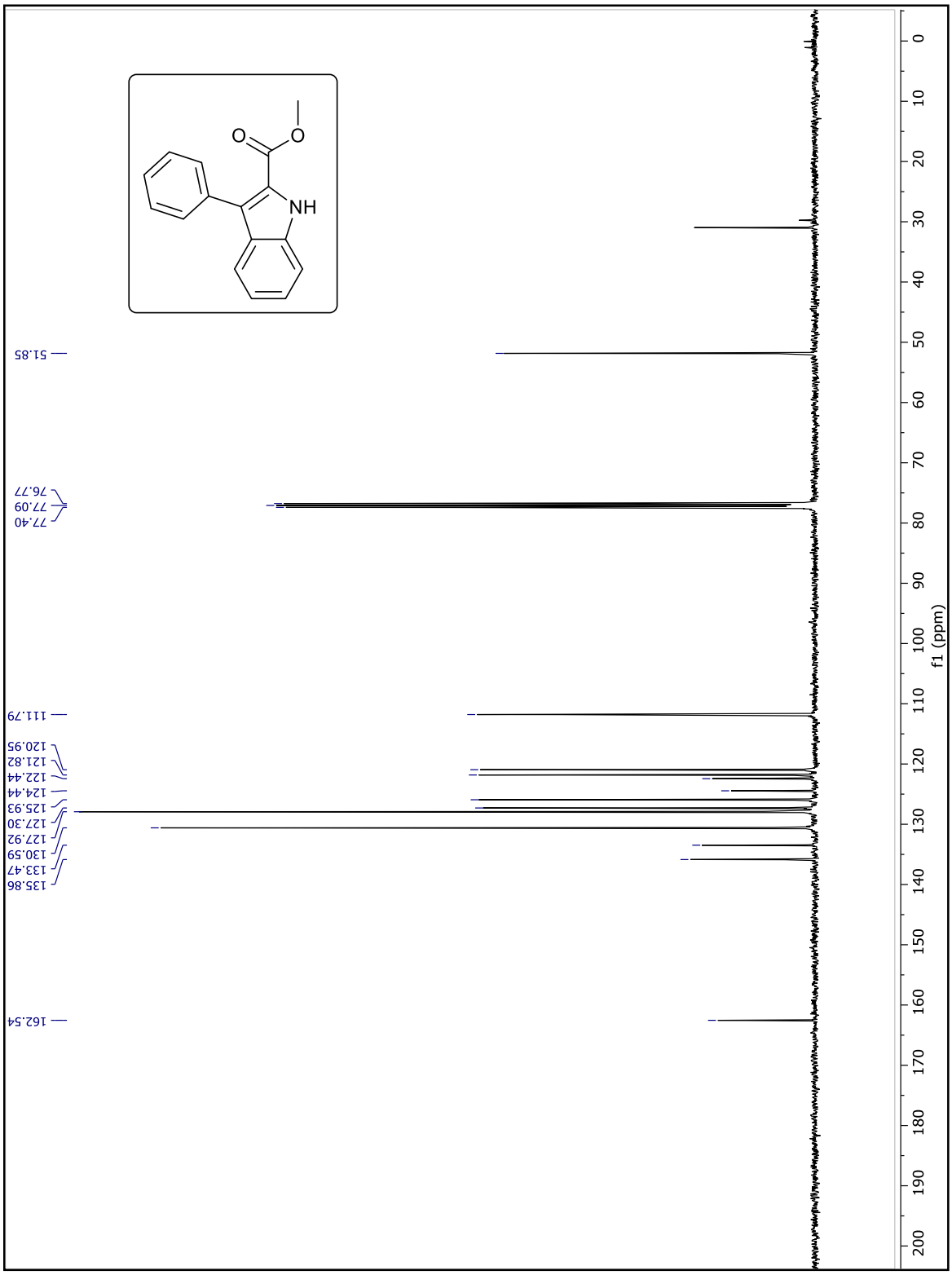
***tert*-Butyl 3-methyl-1*H*-indole-2-carboxylate (Table 1, 3c)**



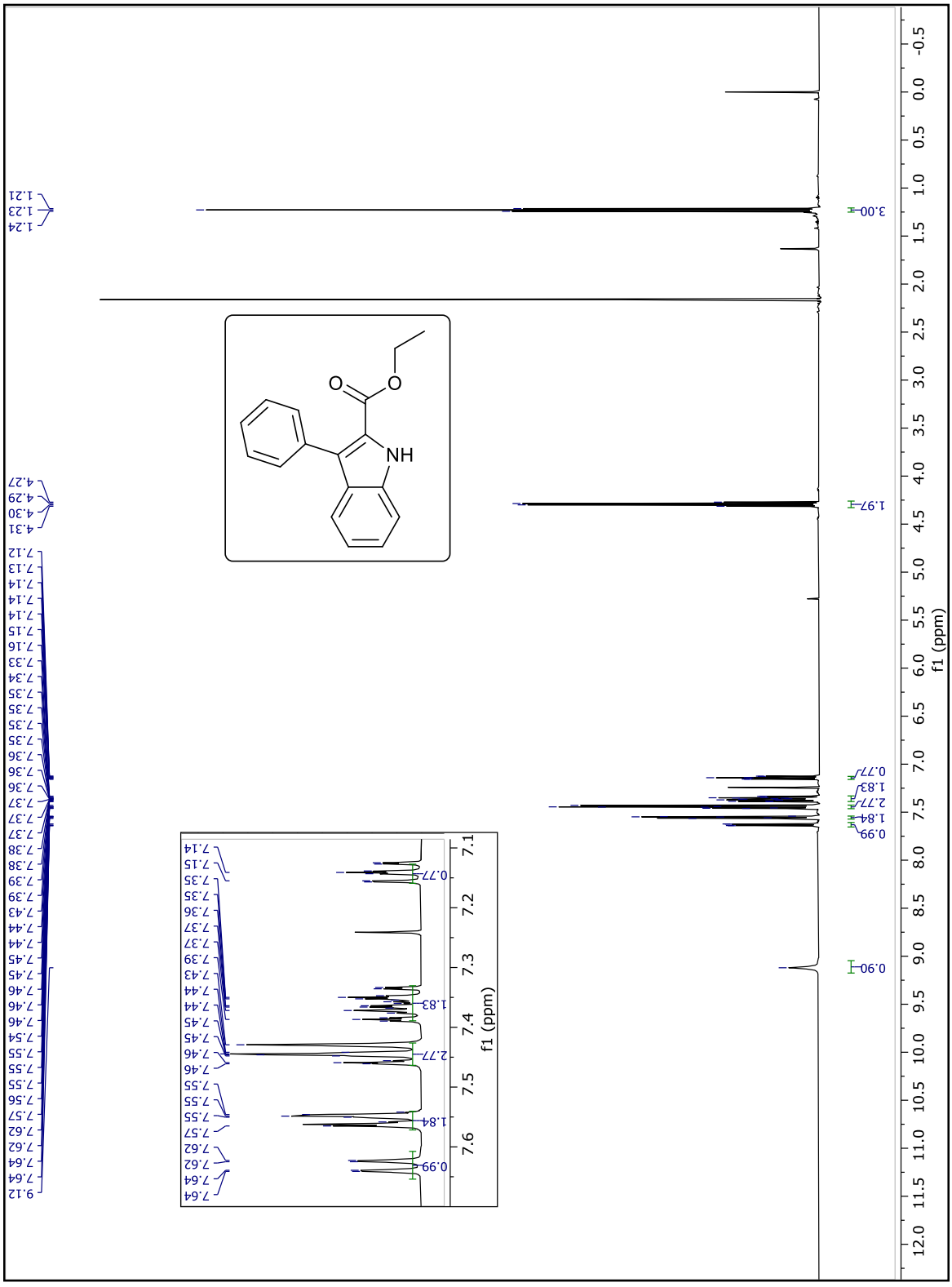

9.96
28.47
76.71
77.03
77.35
81.60
111.51
119.23
119.77
120.68
124.69
125.29
128.69
135.51
162.03
O
O
NH
f1 (ppm)

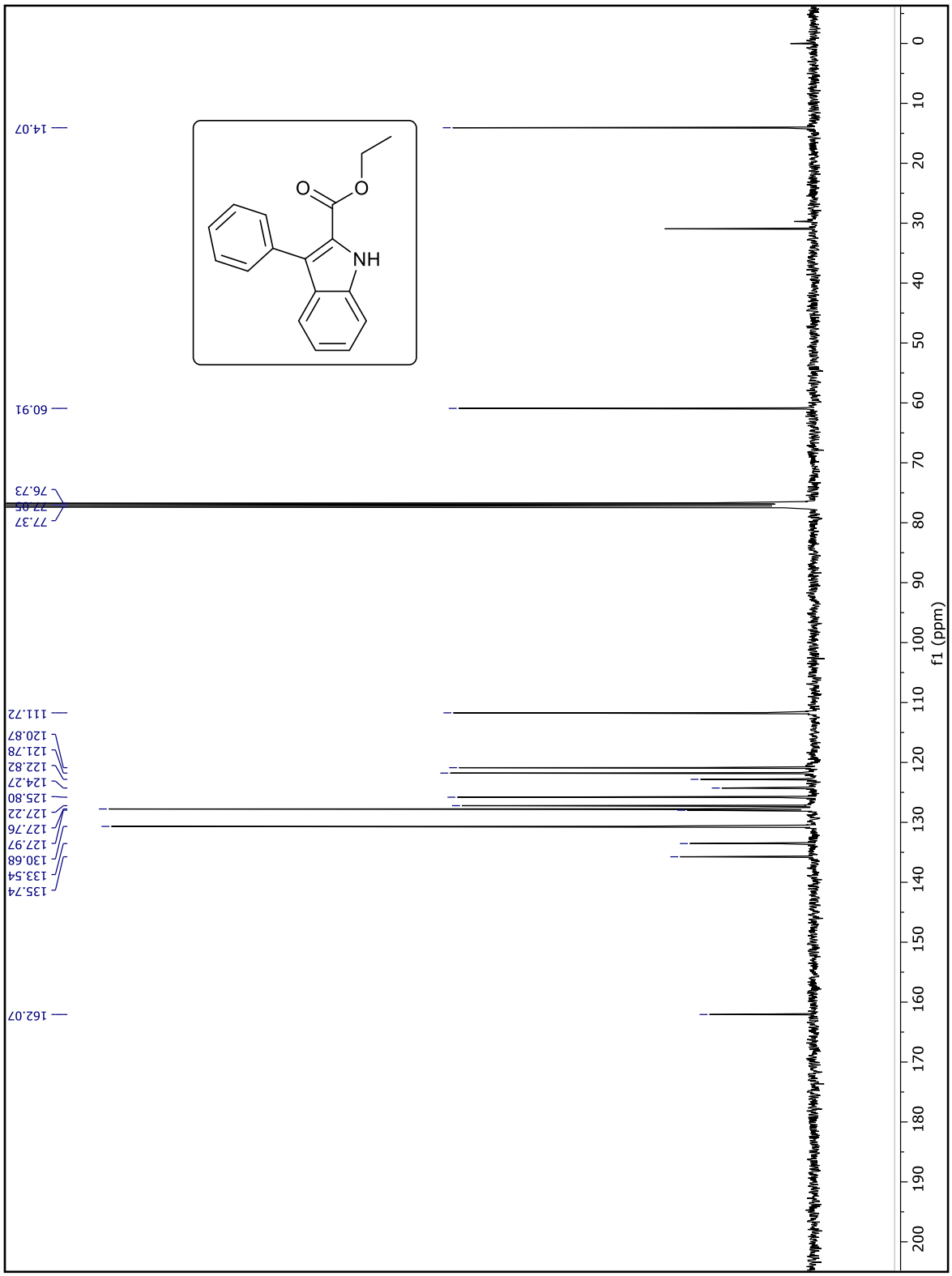
Methyl 3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3d)



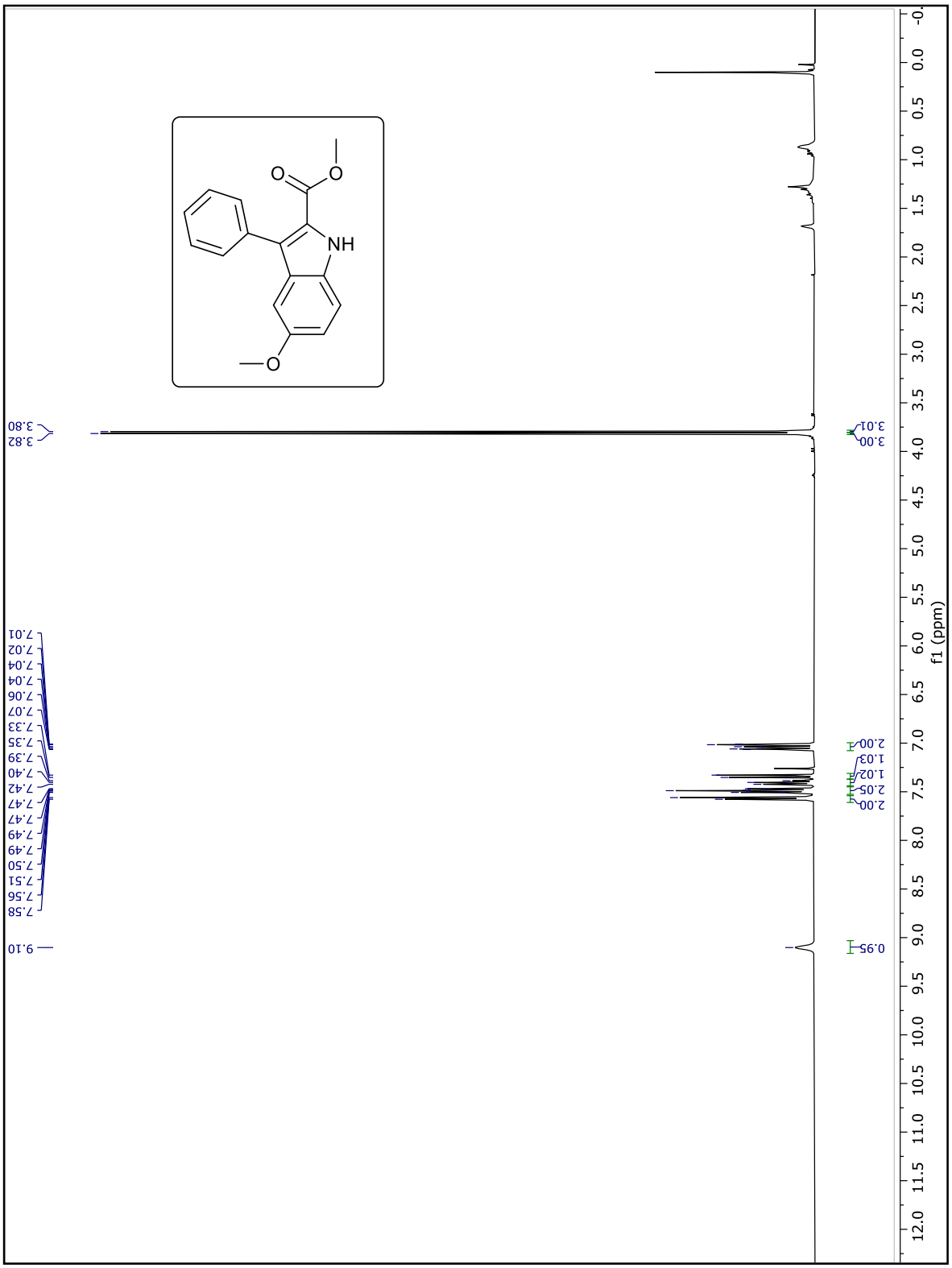

O
O
NH
51.85
76.77
77.09
77.40
111.79
120.95
121.82
122.44
124.44
125.93
127.30
127.92
130.59
133.47
135.86
162.54
f1 (ppm)

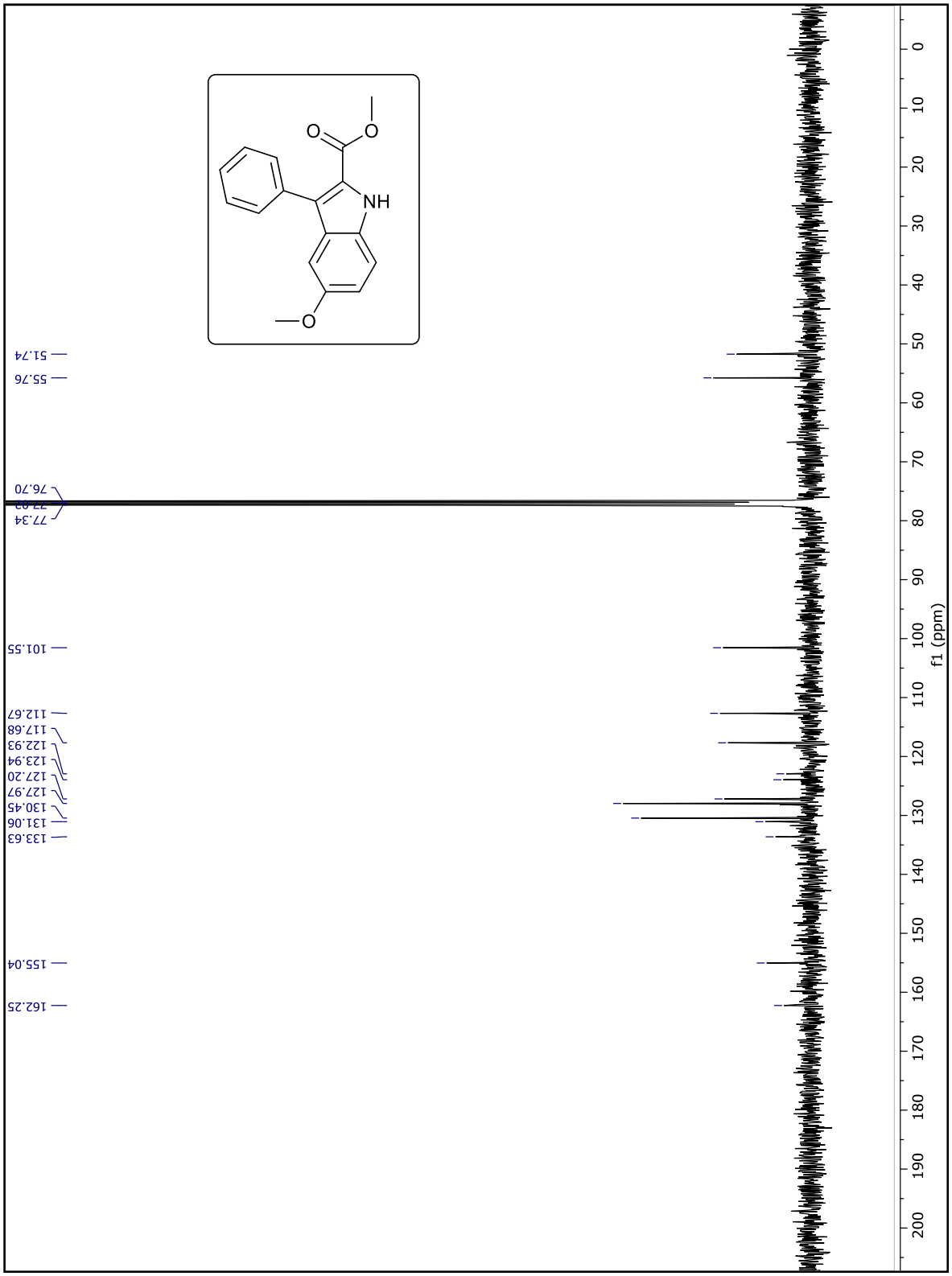
Ethyl 3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3e)



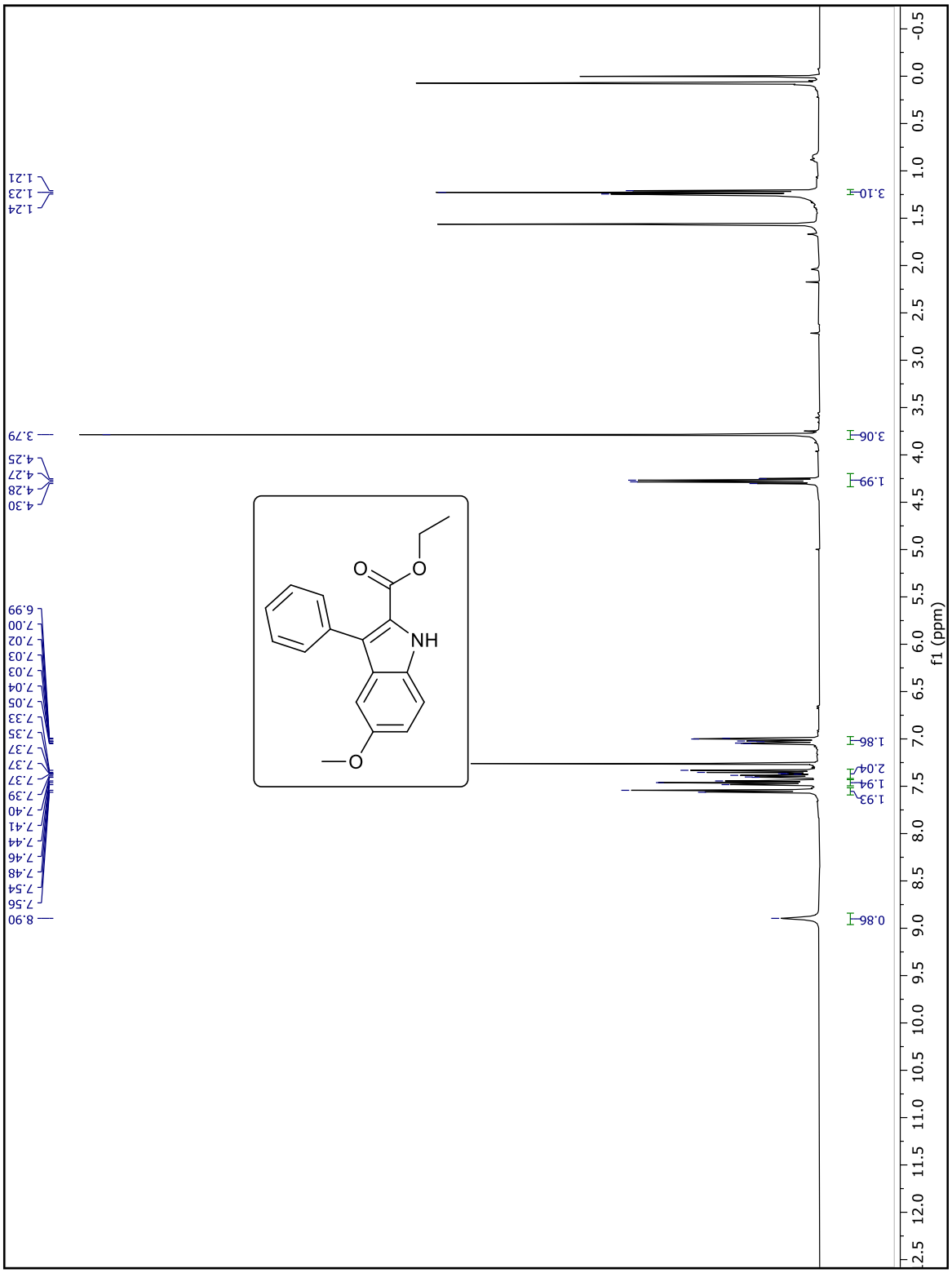

14.07
60.91
76.73
77.37
77.05
111.72
120.87
121.78
122.82
124.27
125.80
127.22
127.76
127.97
130.68
133.54
135.74
162.07
O
O
NH
f1 (ppm)

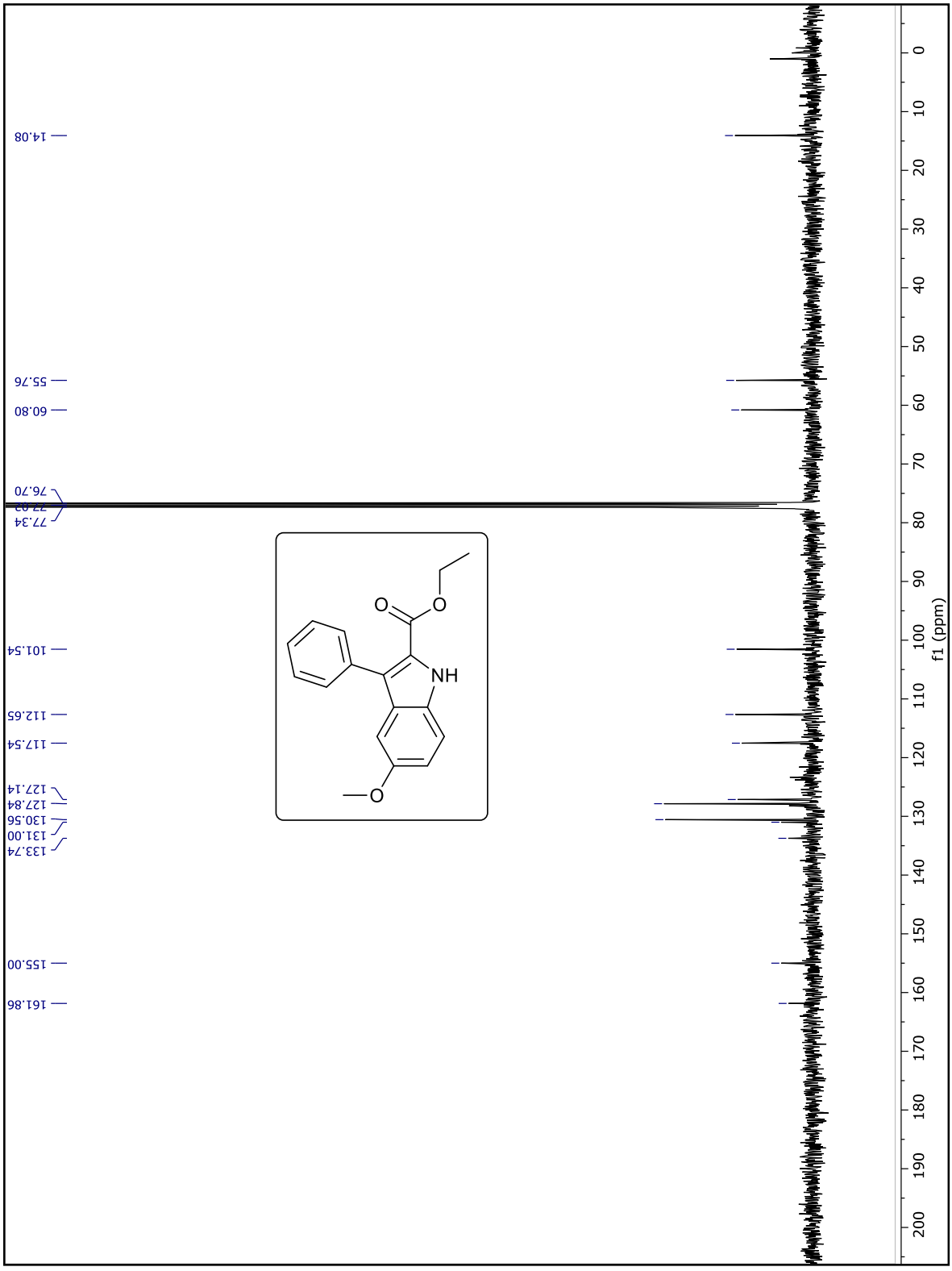
Methyl 5-methoxy-3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3f)



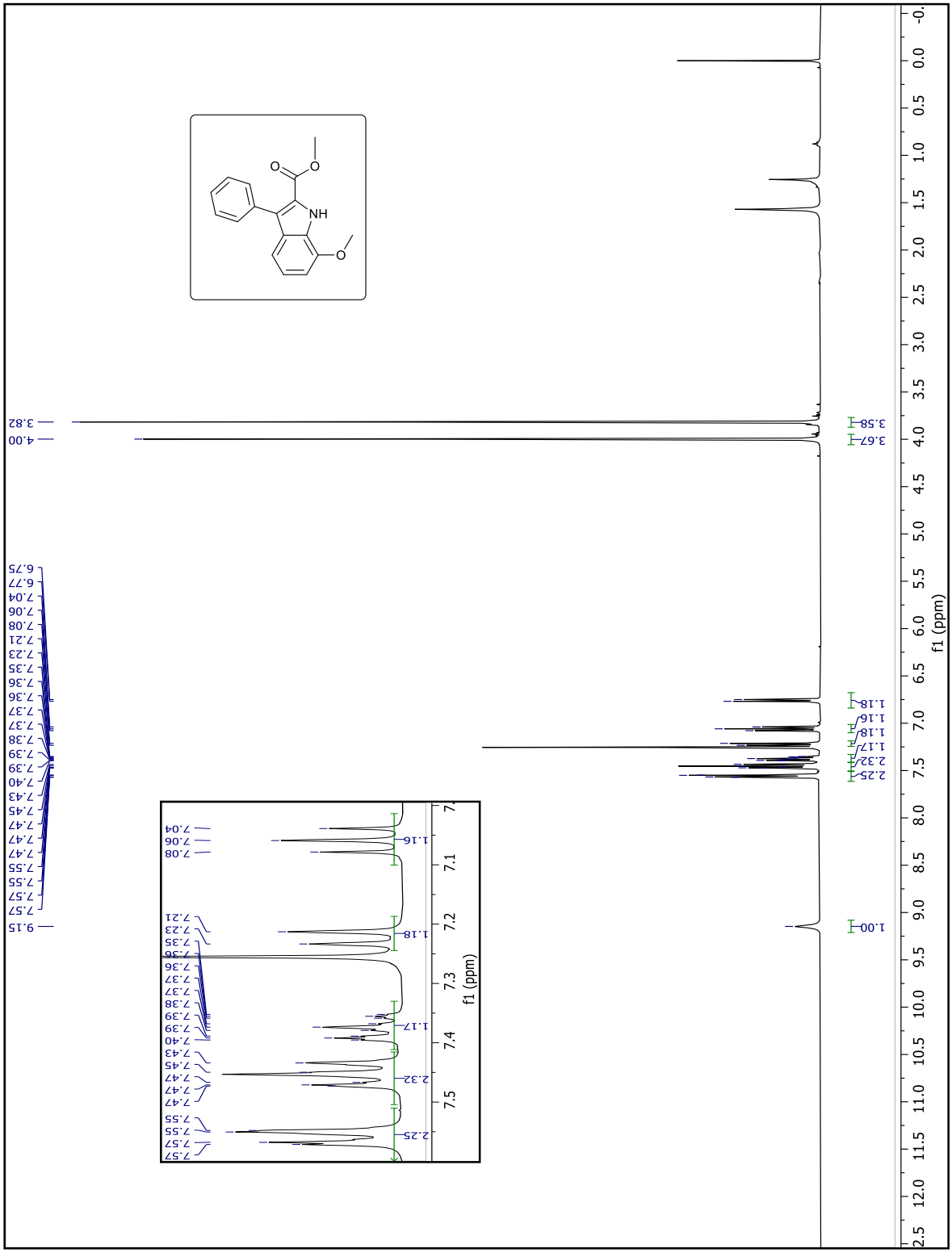

O
O
NH
O
51.74
55.76
76.70
77.03
77.34
101.55
112.67
117.68
122.93
123.94
127.20
127.97
130.45
131.06
133.63
155.04
162.25
f1 (ppm)

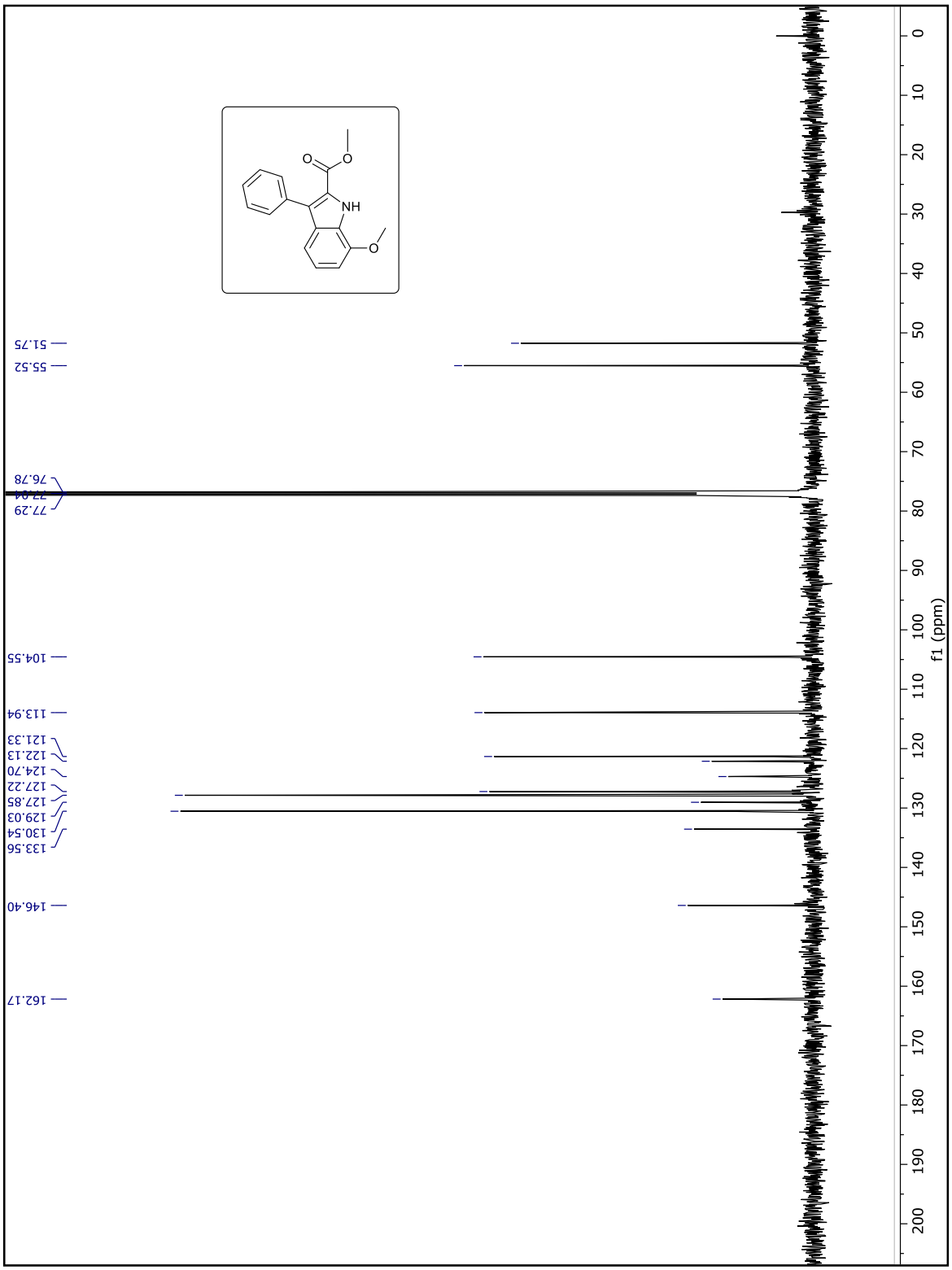
Ethyl 5-methoxy-3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3g)



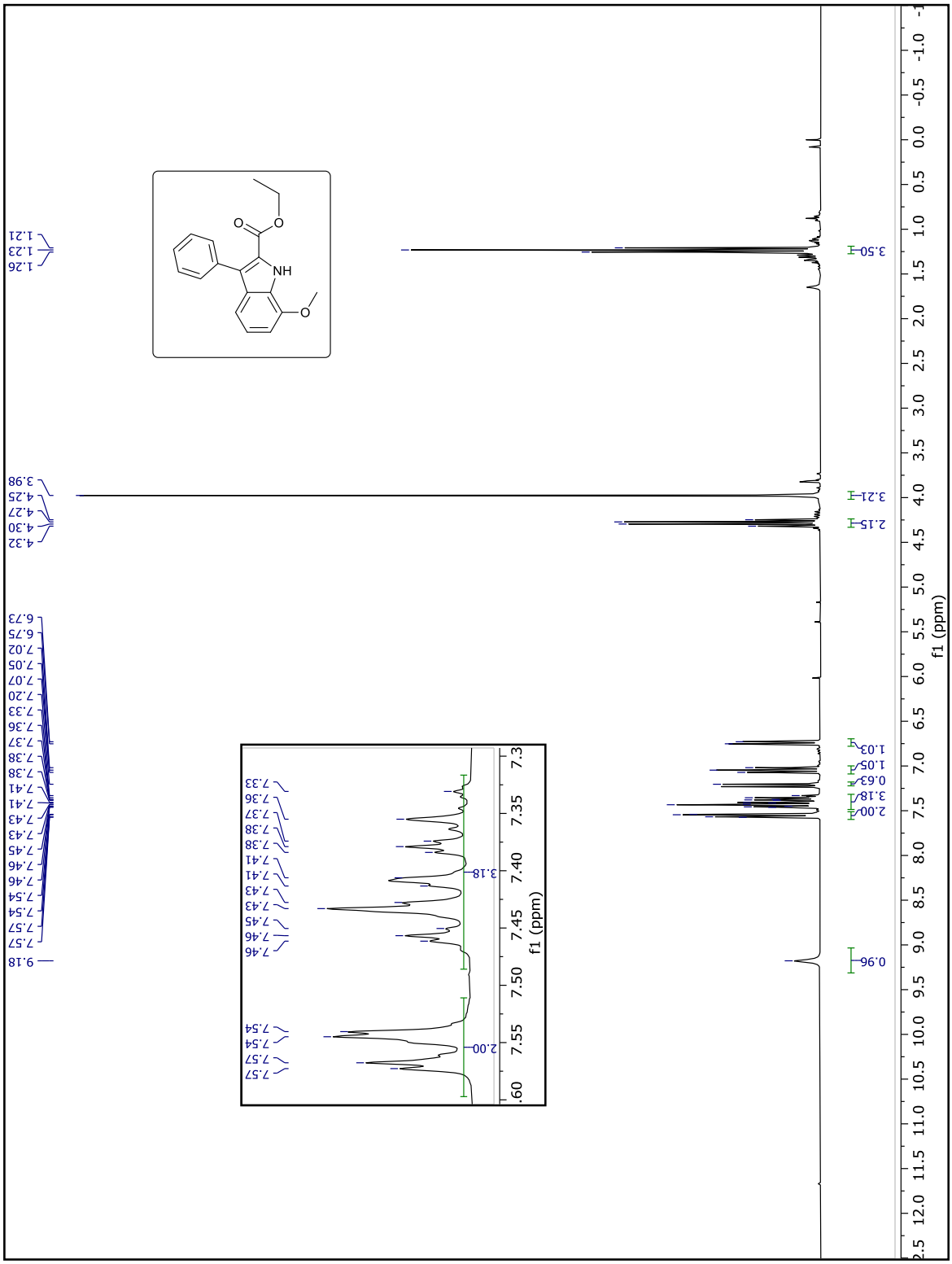

14.08
55.76
60.80
76.70
77.02
77.34
101.54
112.65
117.54
127.14
127.84
130.56
131.00
133.74
155.00
161.86
O
O
NH
O
f1 (ppm)

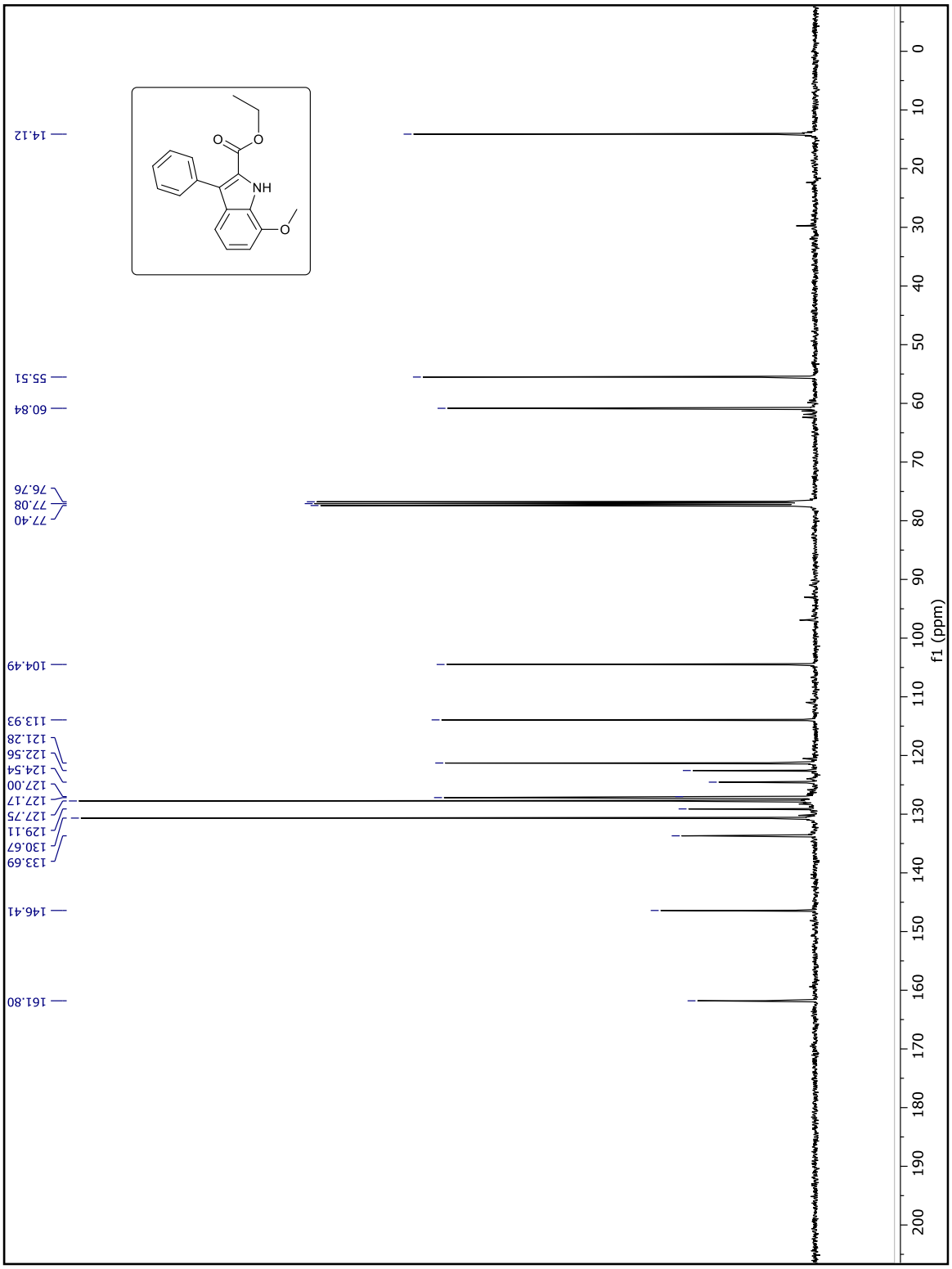
Methyl 7-methoxy-3-phenyl-1H-indole-2-carboxylate (Table 1, 3h)



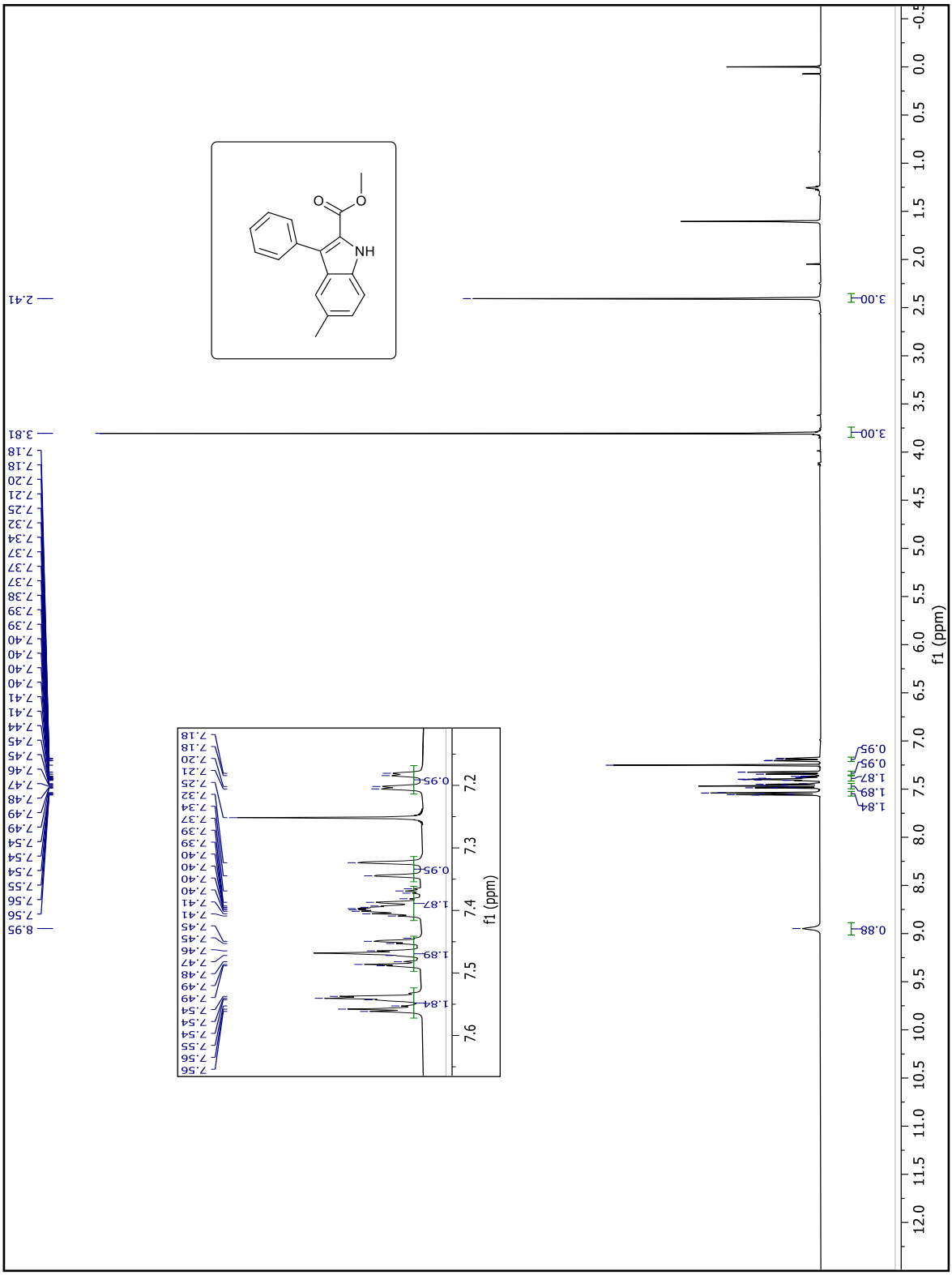

O
O
NH
O
51.75
55.52
76.78
77.04
77.29
104.55
113.94
121.33
122.13
124.70
127.22
127.85
129.03
130.54
133.56
146.40
162.17
f1 (ppm)

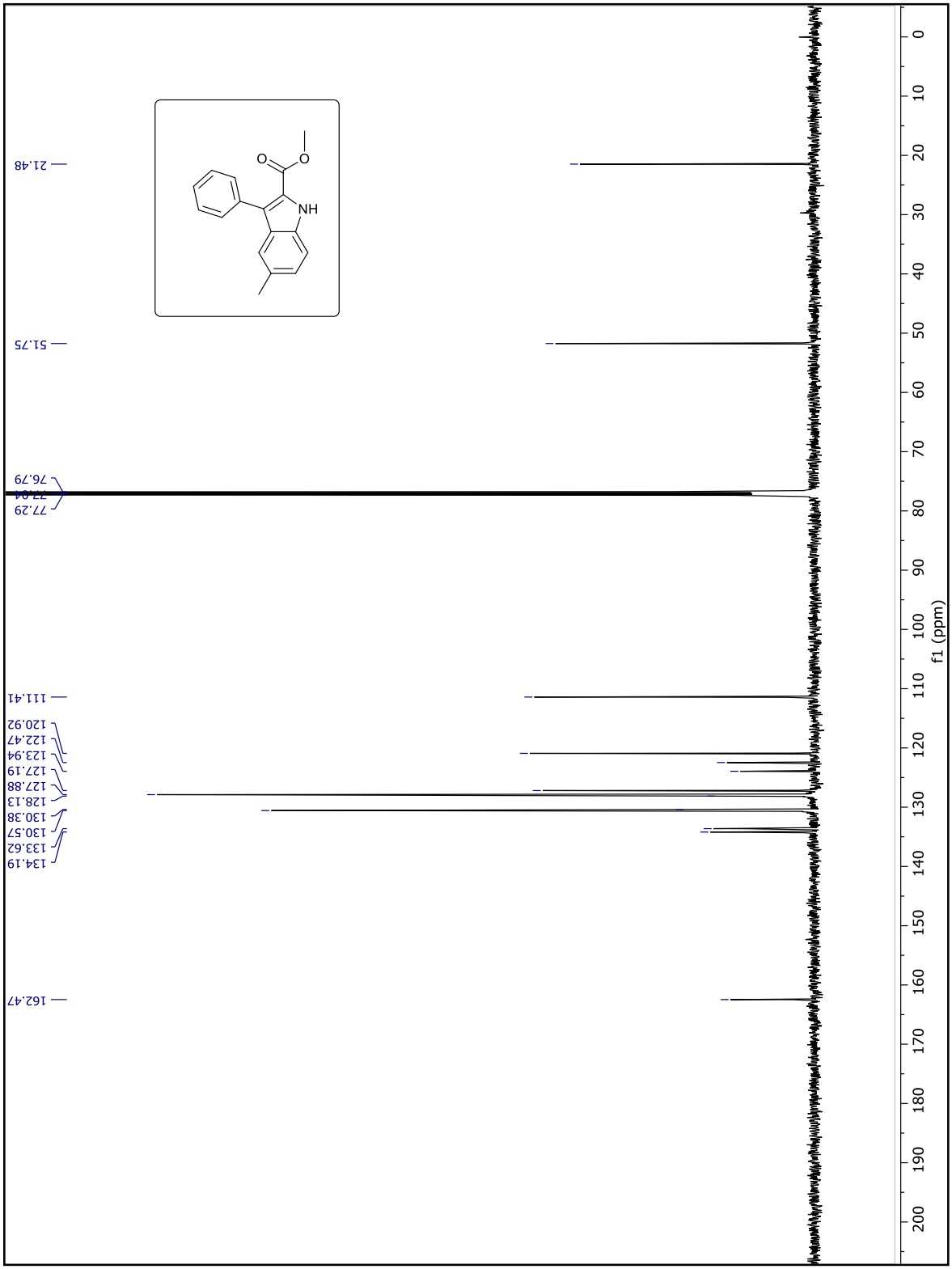
Ethyl 7-methoxy-3-phenyl-1H-indole-2-carboxylate (Table 1, 3i)



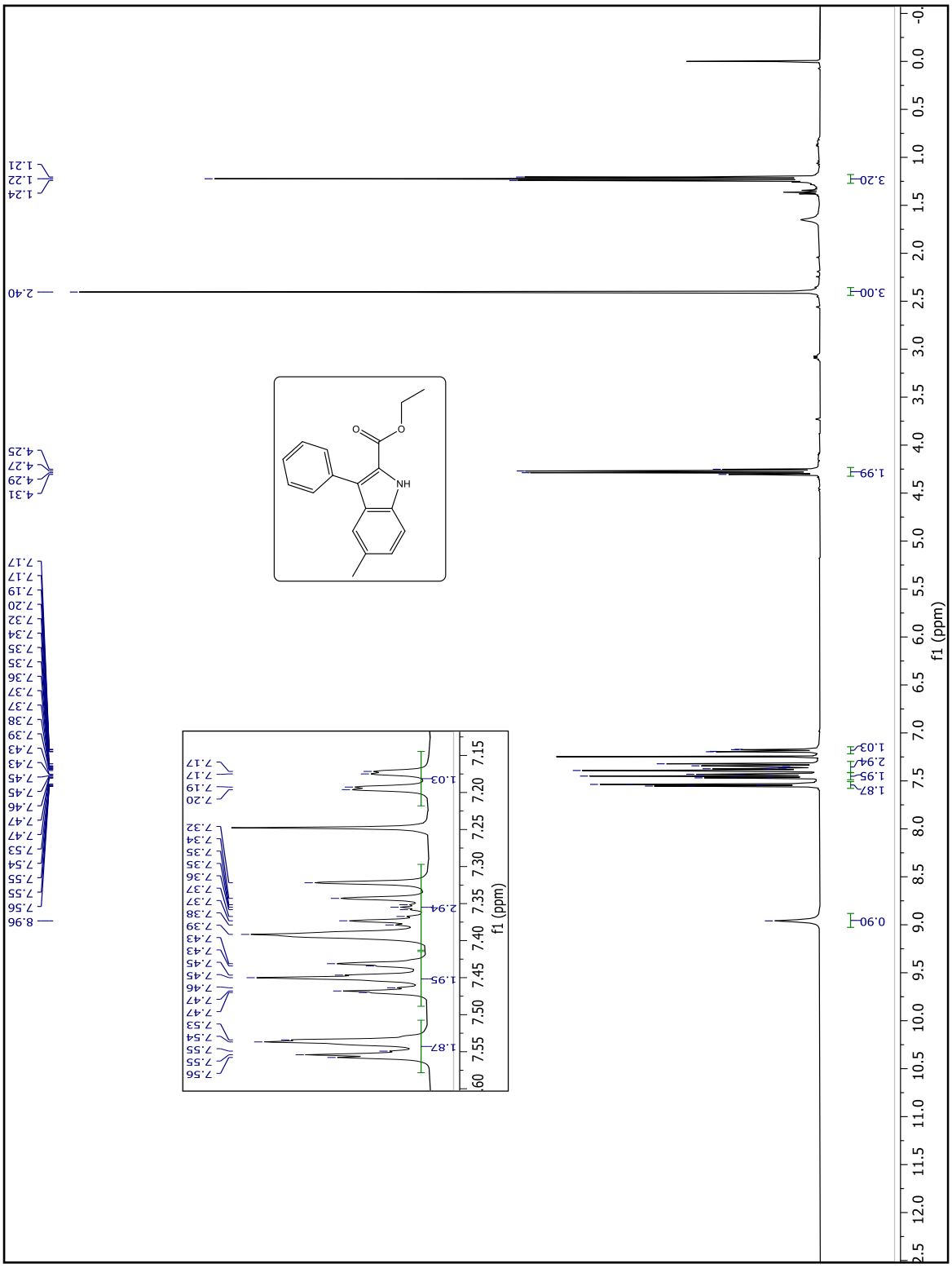

14.12
55.51
60.84
76.76
77.08
77.40
104.49
113.93
121.28
122.56
124.54
127.00
127.17
127.75
129.11
130.67
133.69
146.41
161.80
O
O
NH
O
f1 (ppm)

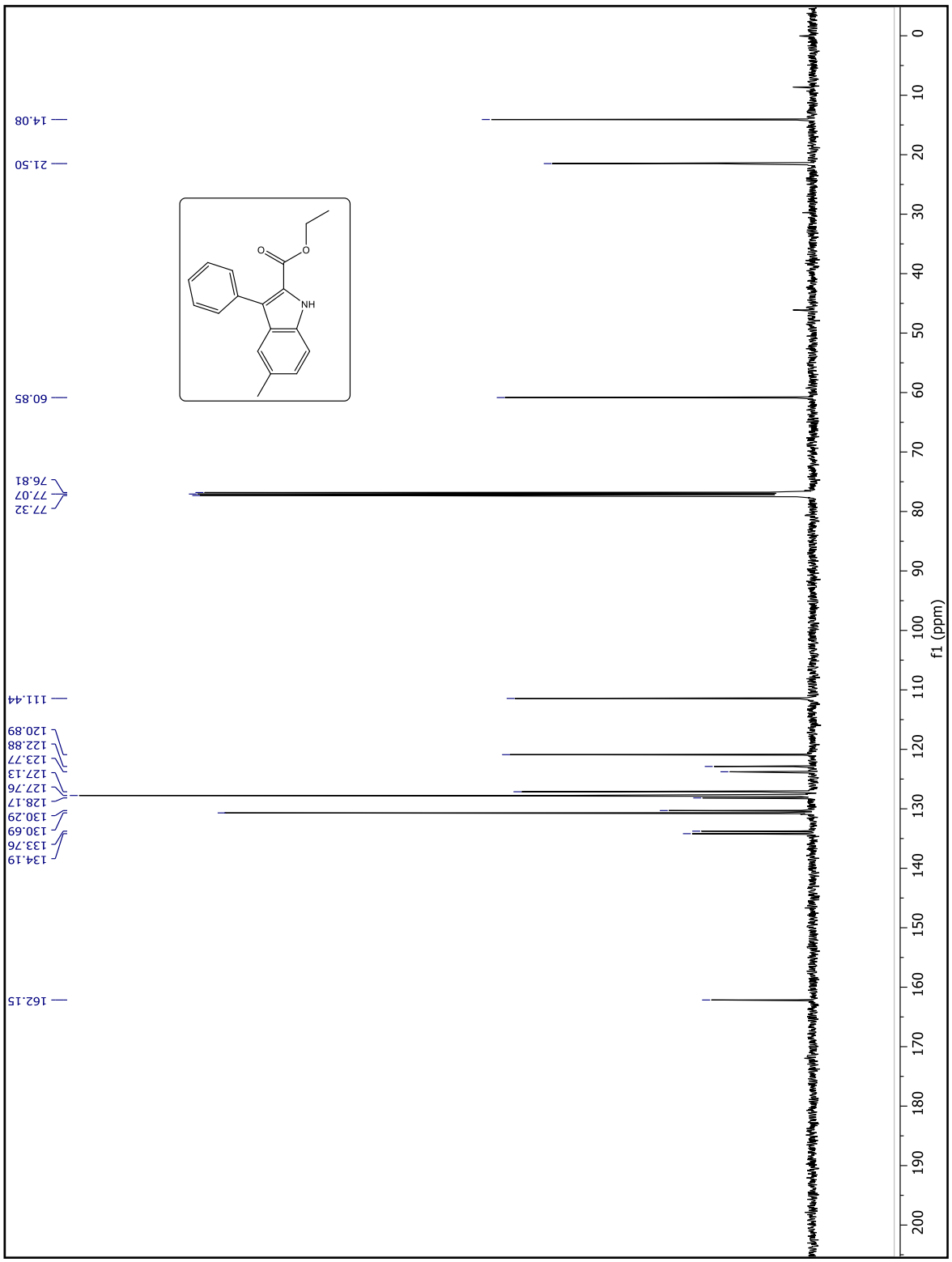
Methyl 5-methyl-3-phenyl-1*H*-indole-2-carboxylate (Table 1, 3j)



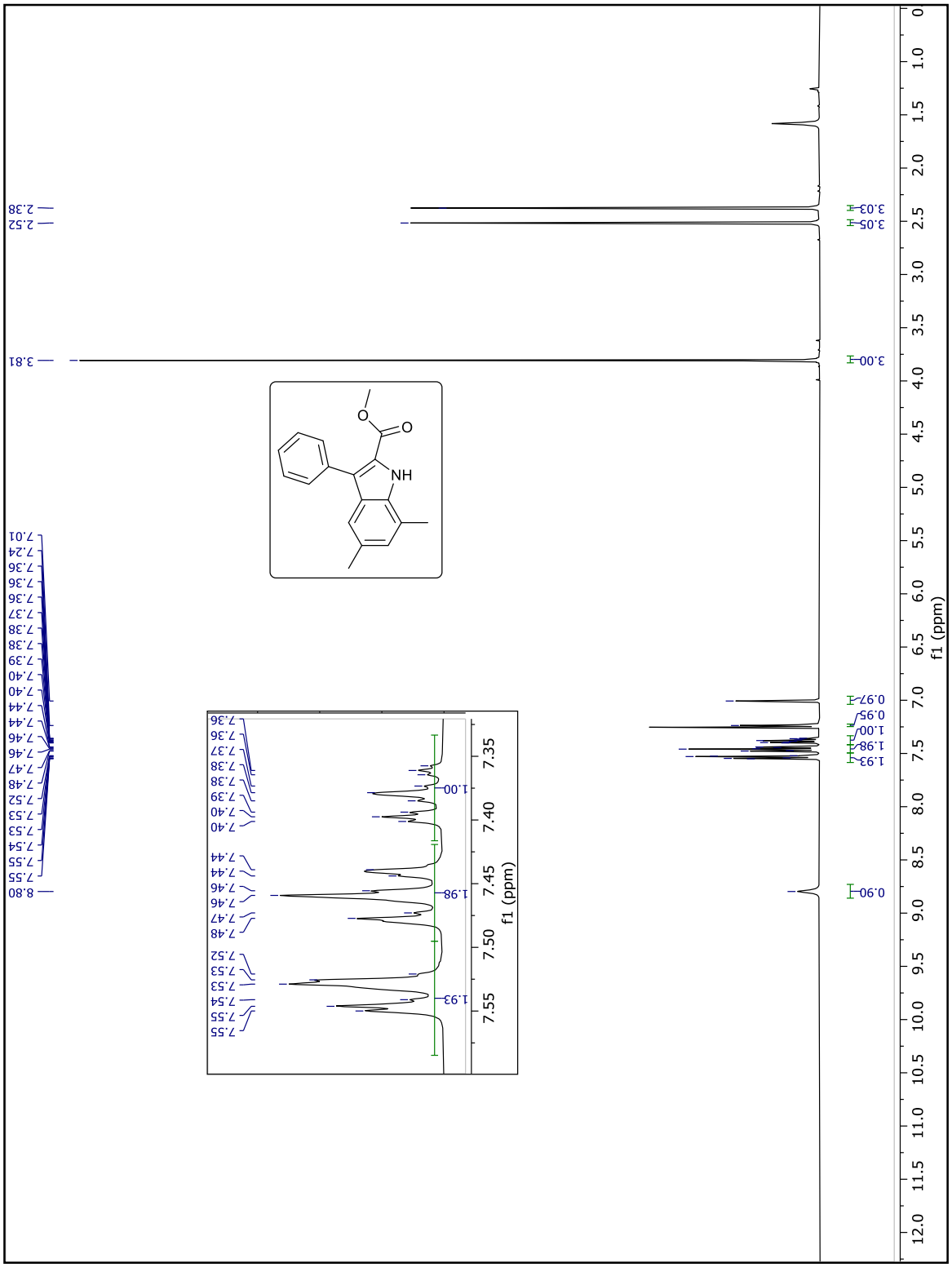

21.48
51.75
76.79
77.04
77.29
111.41
120.92
122.47
123.94
127.19
127.88
128.13
130.38
130.57
133.62
134.19
162.47
O
O
NH
f1 (ppm)

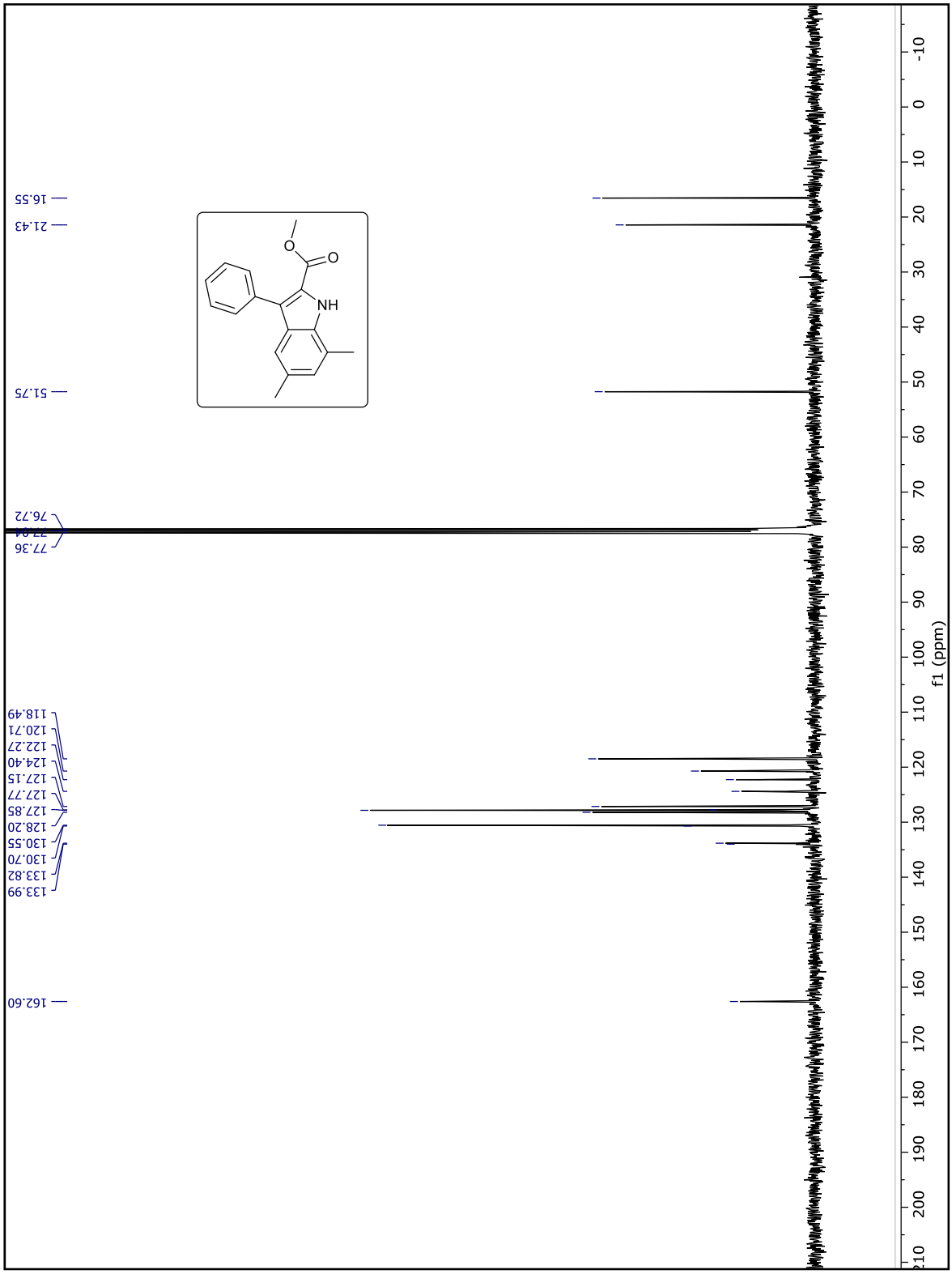
Ethyl 5-methyl-3-phenyl-1H-indole-2-carboxylate (Table 1, 3k)



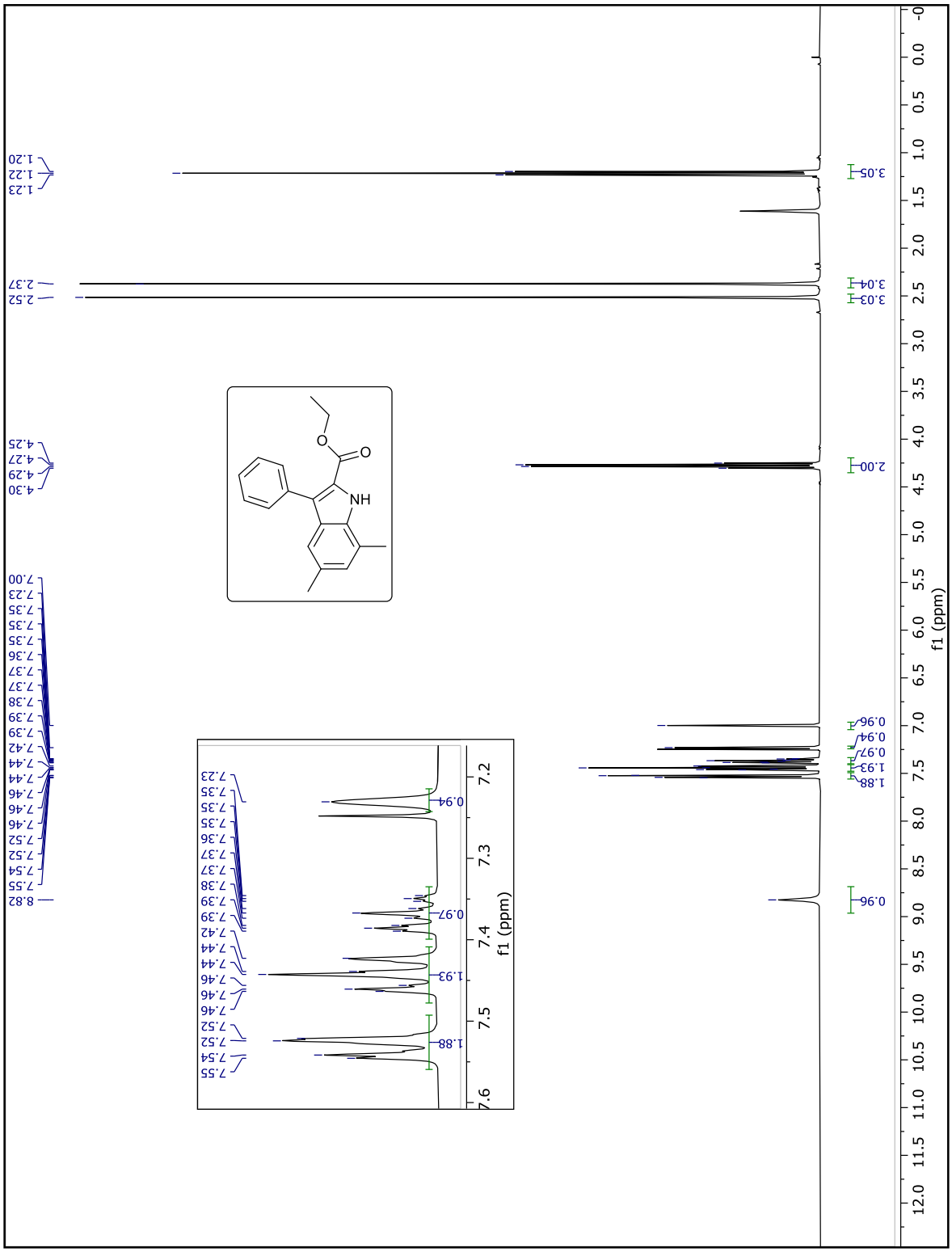

14.08
21.50
60.85
76.81
77.07
77.32
111.44
120.89
122.88
123.77
127.13
127.76
128.17
130.29
130.69
133.76
134.19
162.15
O
O
NH
f1 (ppm)

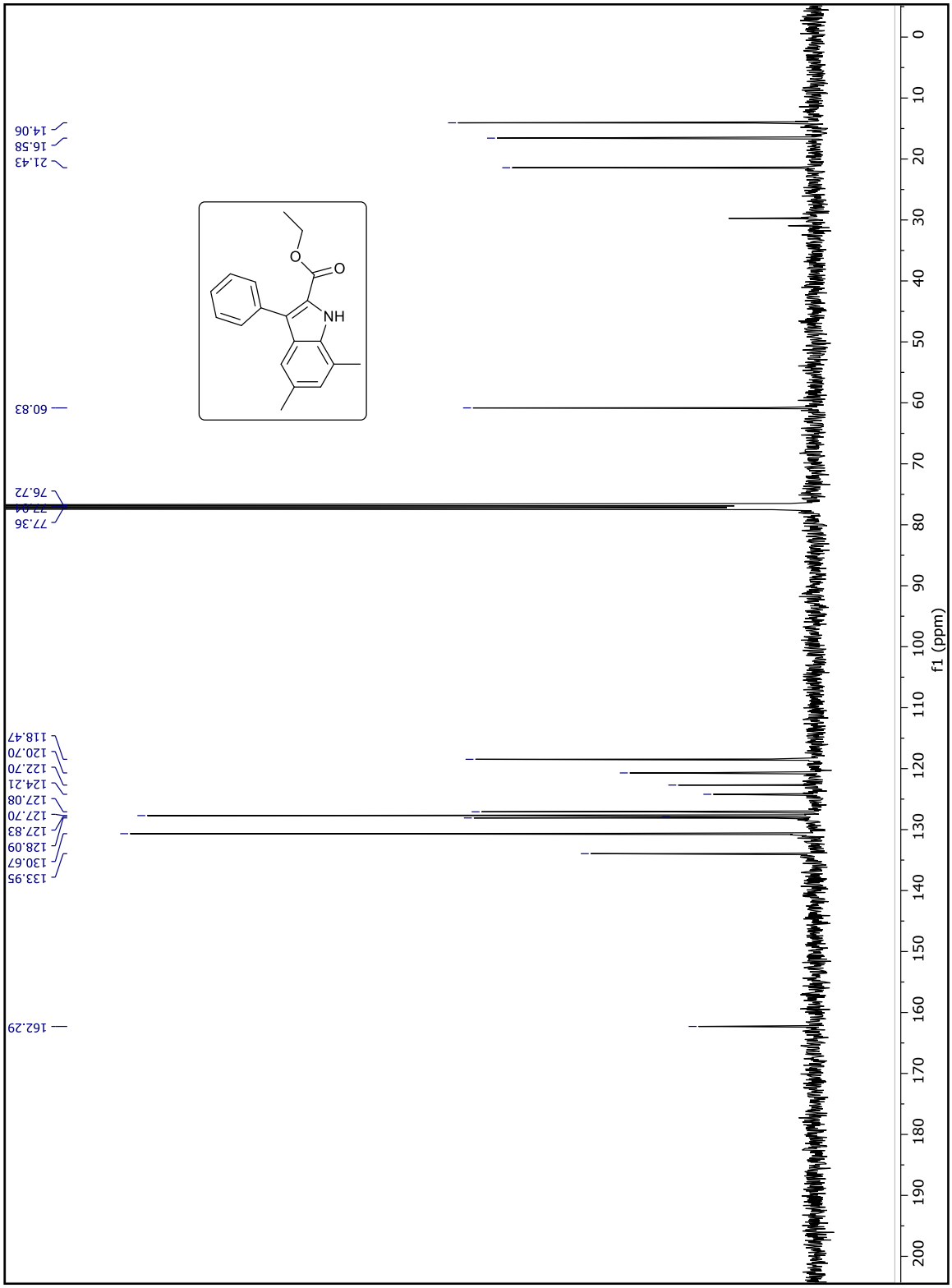
Methyl 5,7-dimethyl-3-phenyl-1H-indole-2-carboxylate (Table 1, 3l)



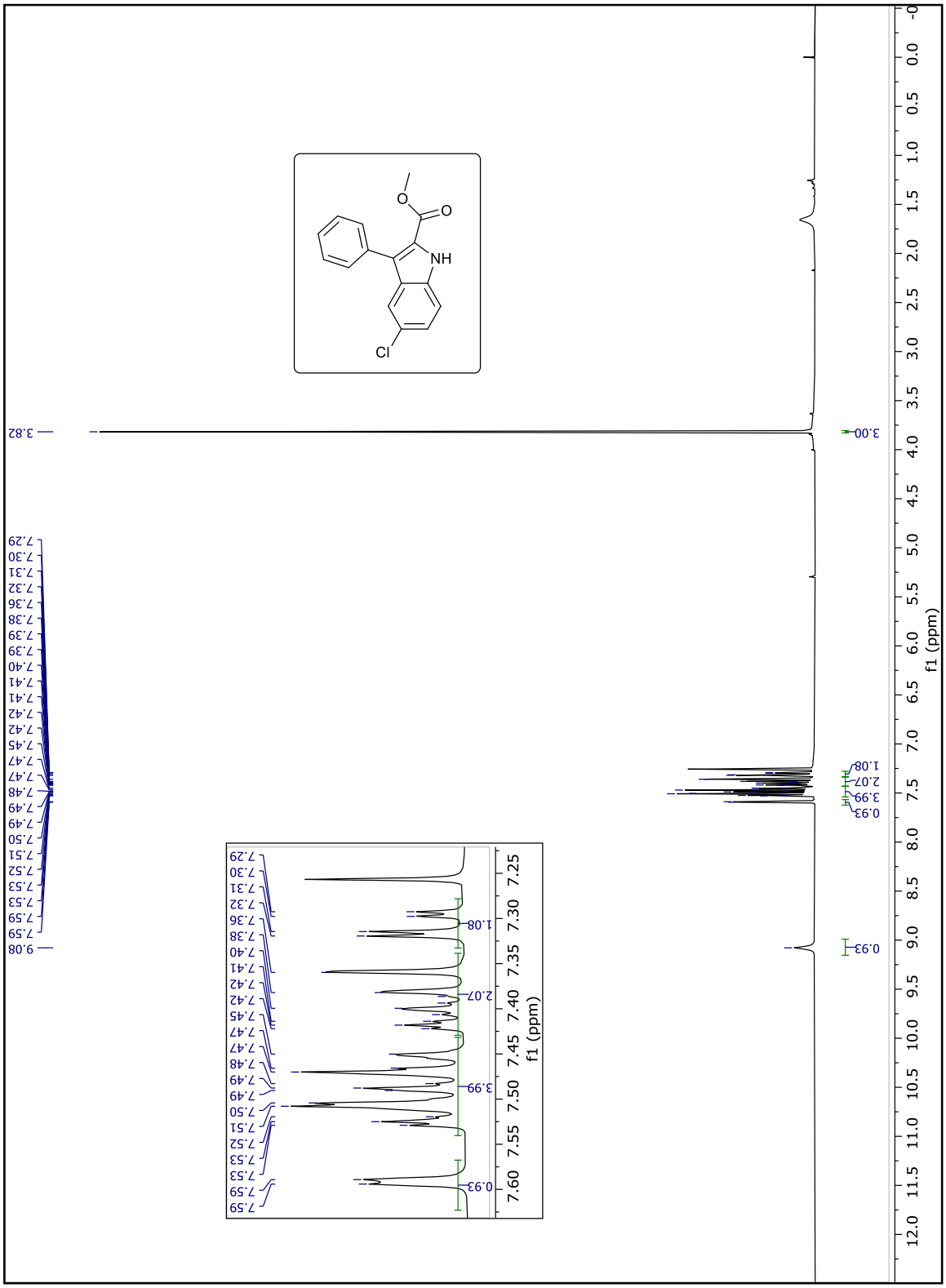

16.55
21.43
51.75
76.72
77.04
77.36
118.49
120.71
122.27
124.40
127.15
127.77
127.85
128.20
130.55
130.70
133.82
133.99
162.60
NH
O
O
f1 (ppm)

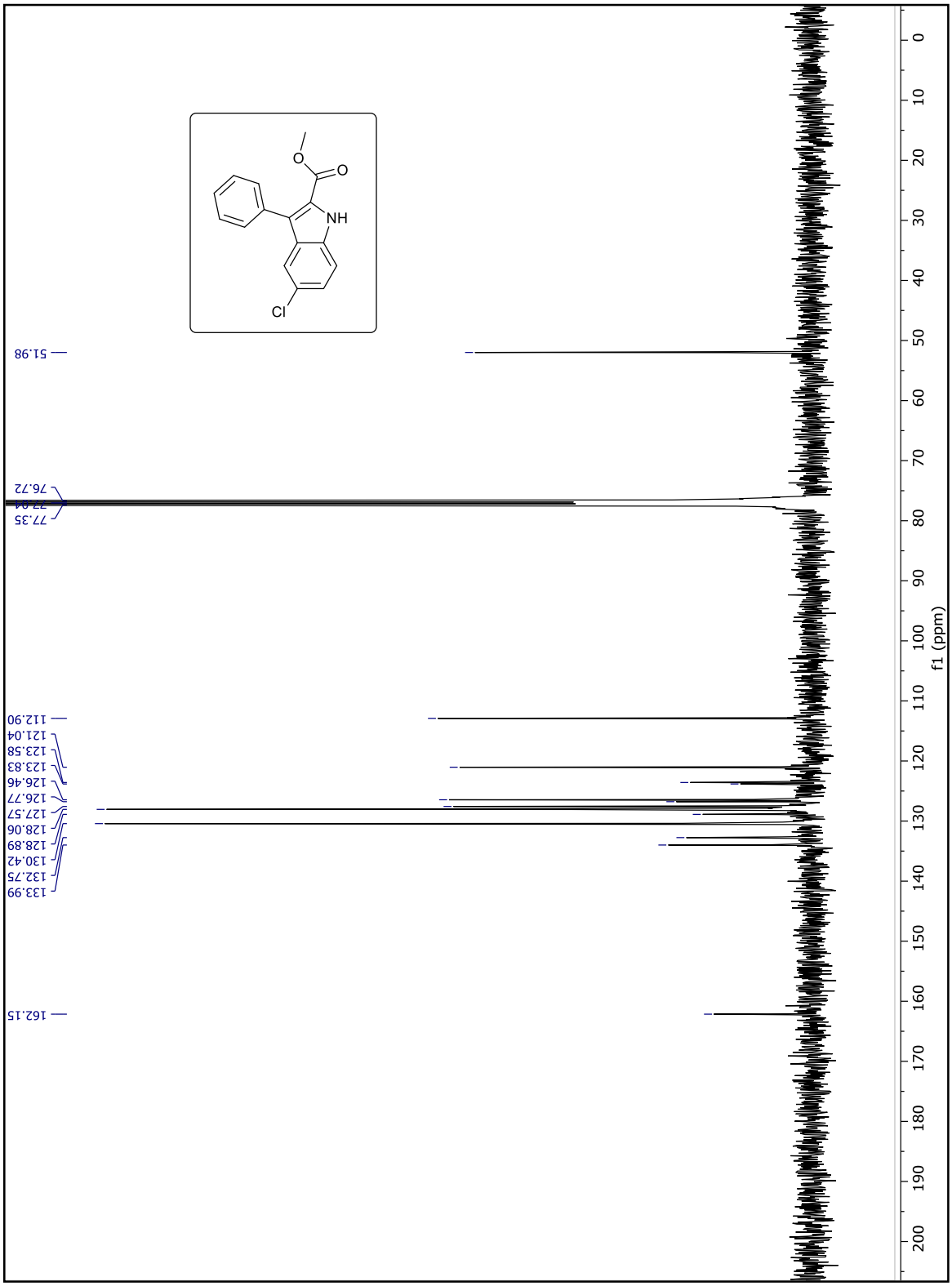
Ethyl 5,7-dimethyl-3-phenyl-1H-indole-2-carboxylate (Table 1, 3m)



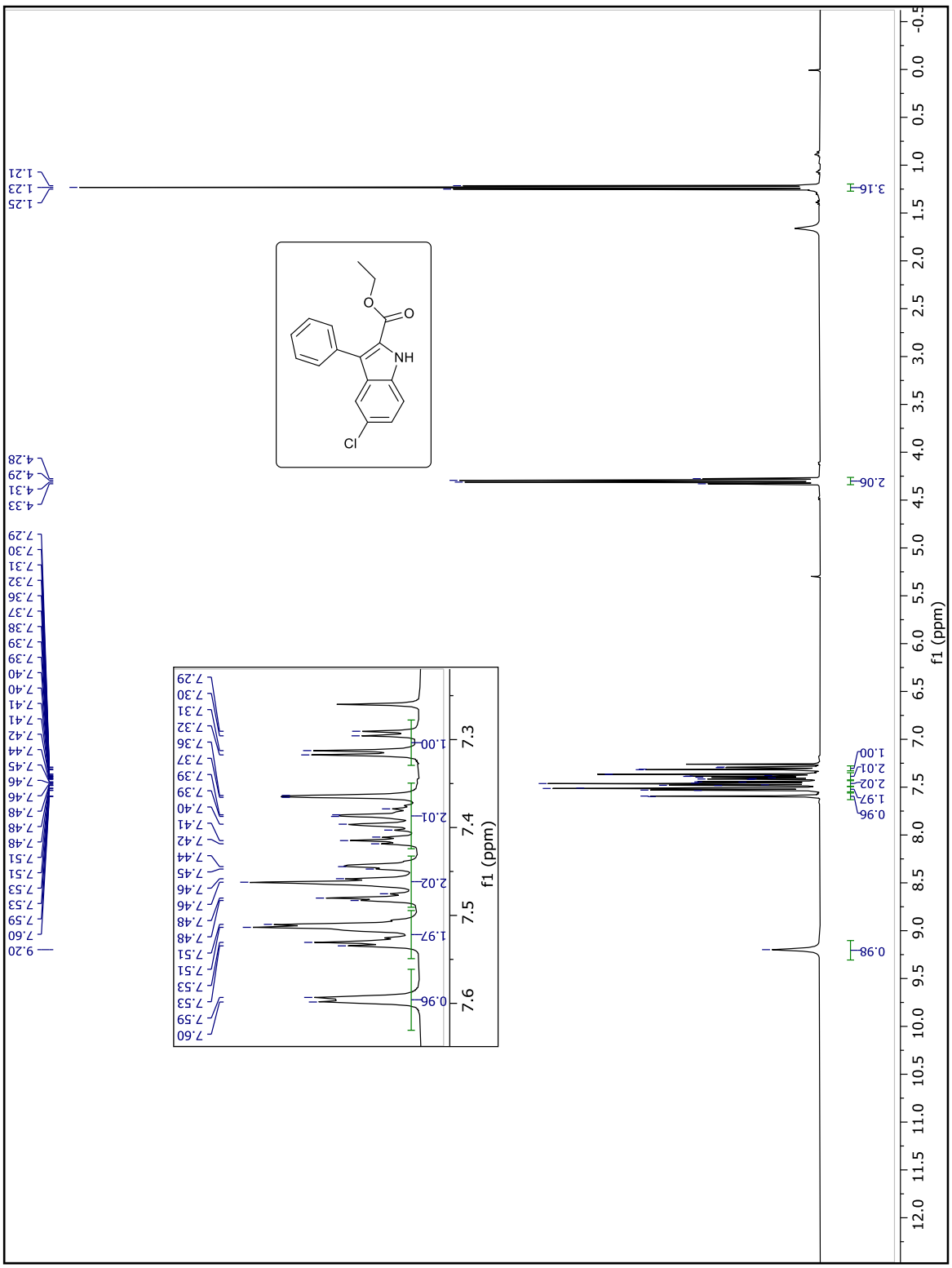

14.06
16.58
21.43
60.83
76.72
77.04
77.36
118.47
120.70
122.70
124.21
127.08
127.70
127.83
128.09
130.67
133.95
162.29
O
O
NH
f1 (ppm)

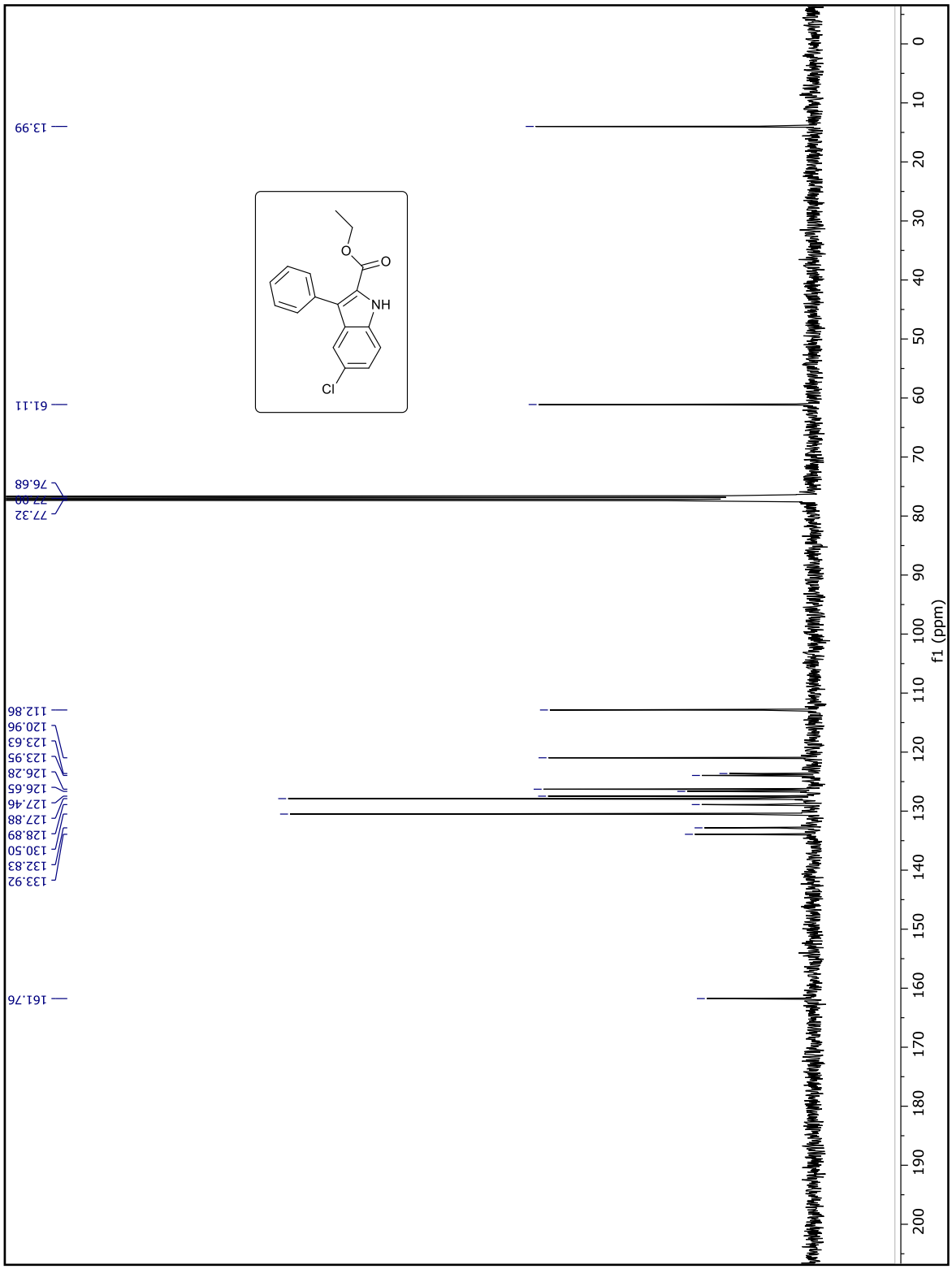
Methyl 5-chloro-3-phenyl-1H-indole-2-carboxylate (Table 1, 3n)



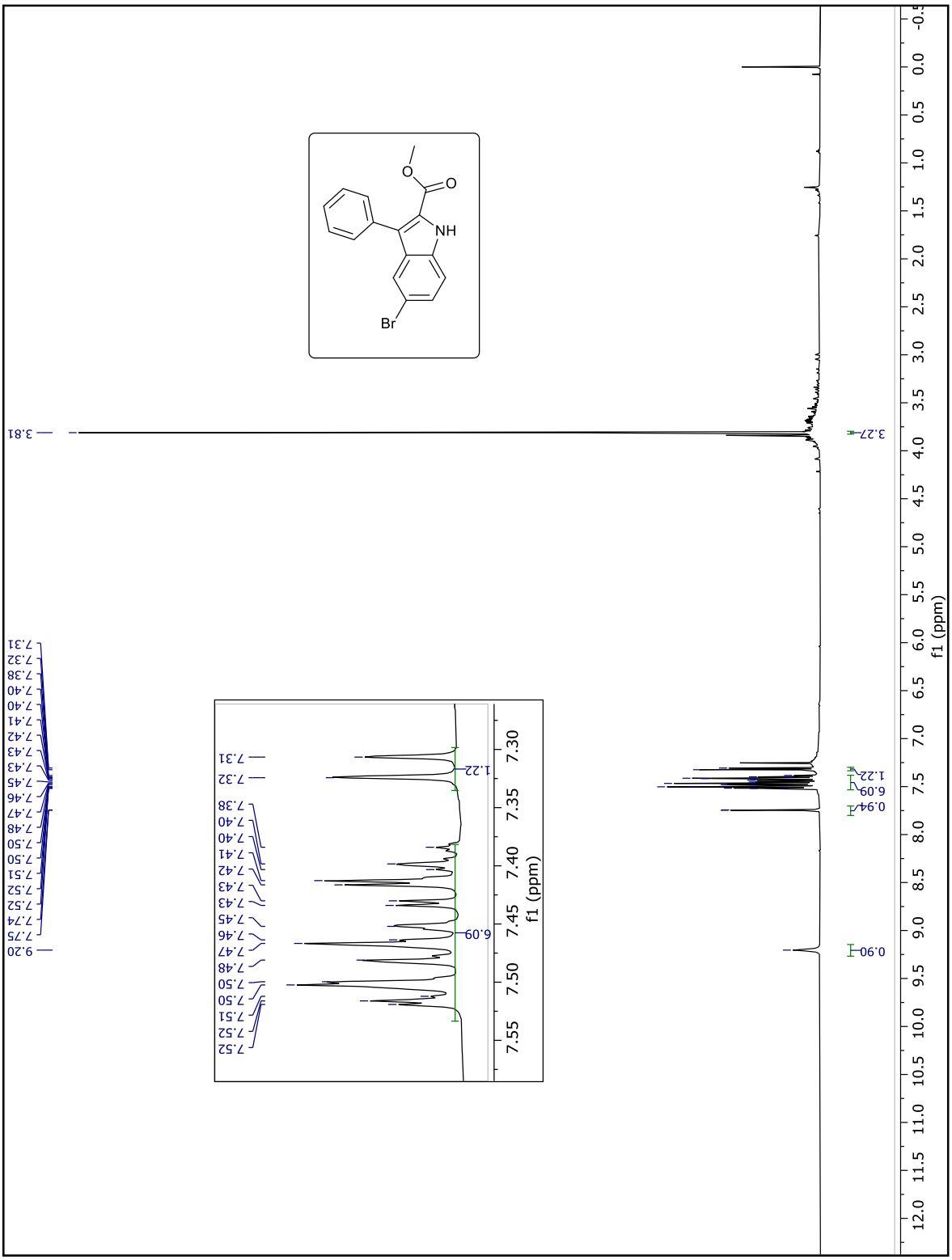

O
O
NH
Cl
51.98
76.72
77.04
77.35
112.90
121.04
123.58
123.83
126.46
126.77
127.57
128.06
128.89
130.42
132.75
133.99
162.15
f1 (ppm)

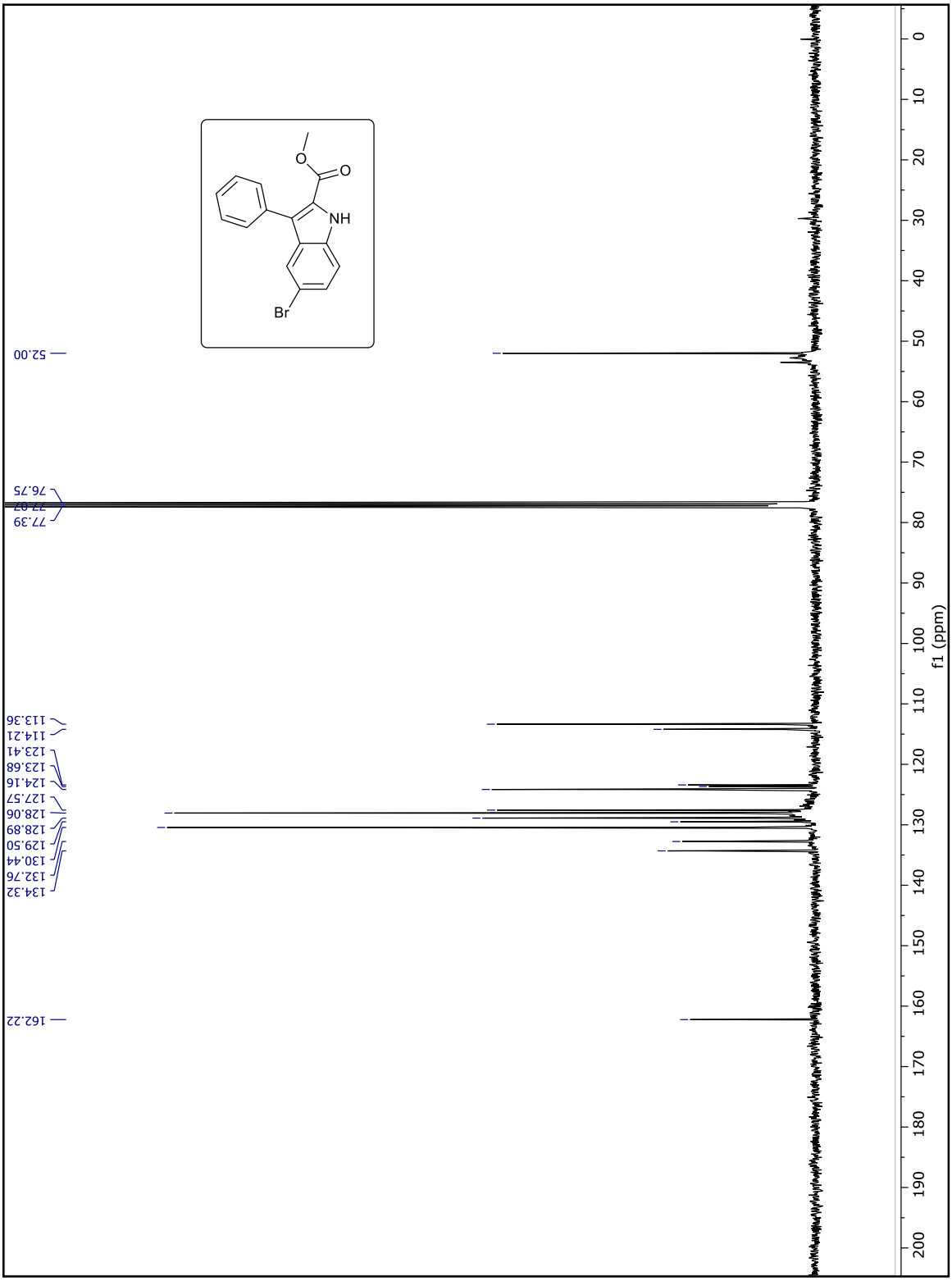
Ethyl 5-chloro-3-phenyl-1H-indole-2-carboxylate (Table 1, 3o)



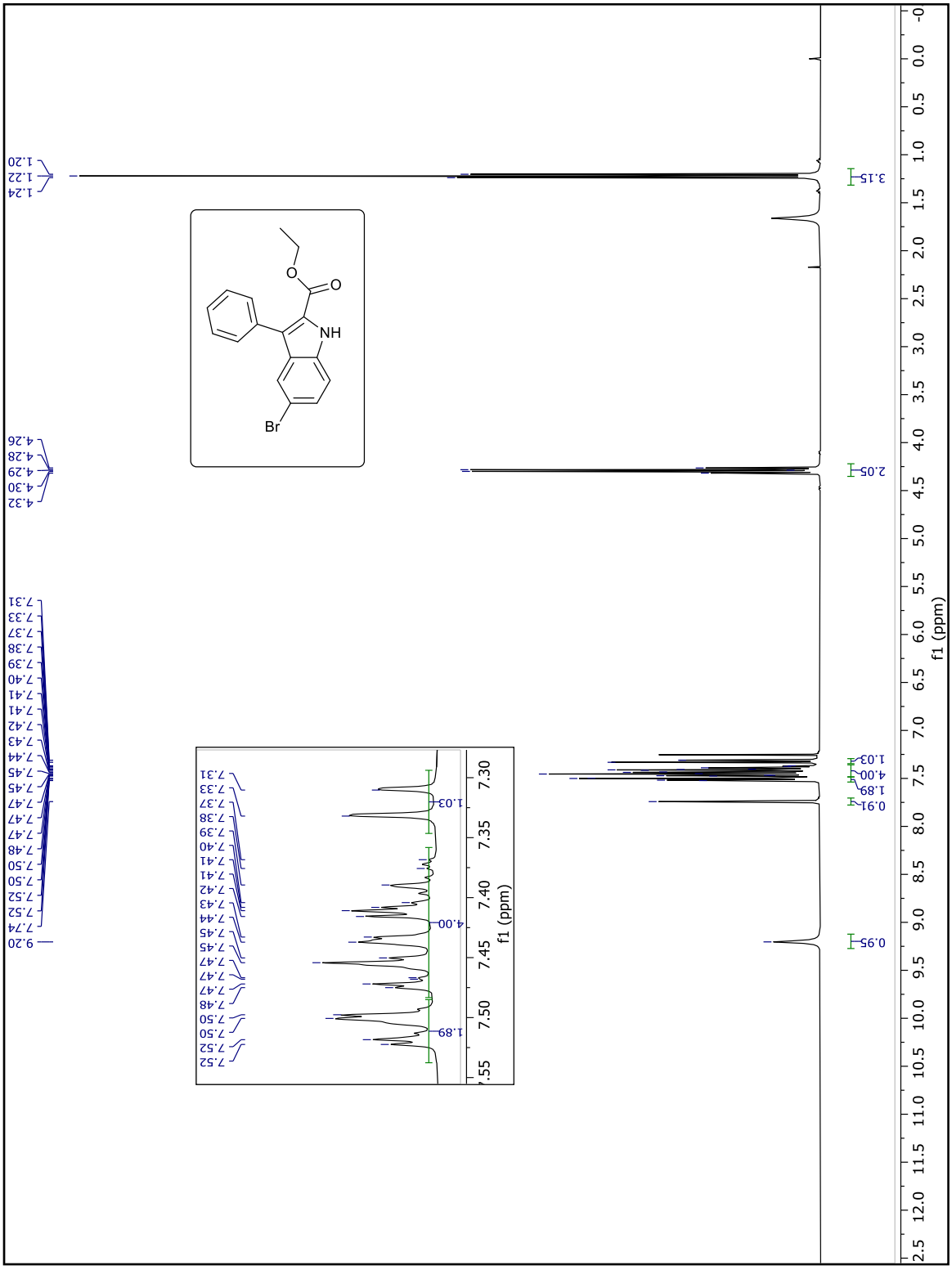

13.99
61.11
76.68
77.09
77.32
112.86
120.96
123.63
123.95
126.28
126.65
127.46
127.88
128.89
130.50
132.83
133.92
161.76
O
O
NH
Cl
f1 (ppm)

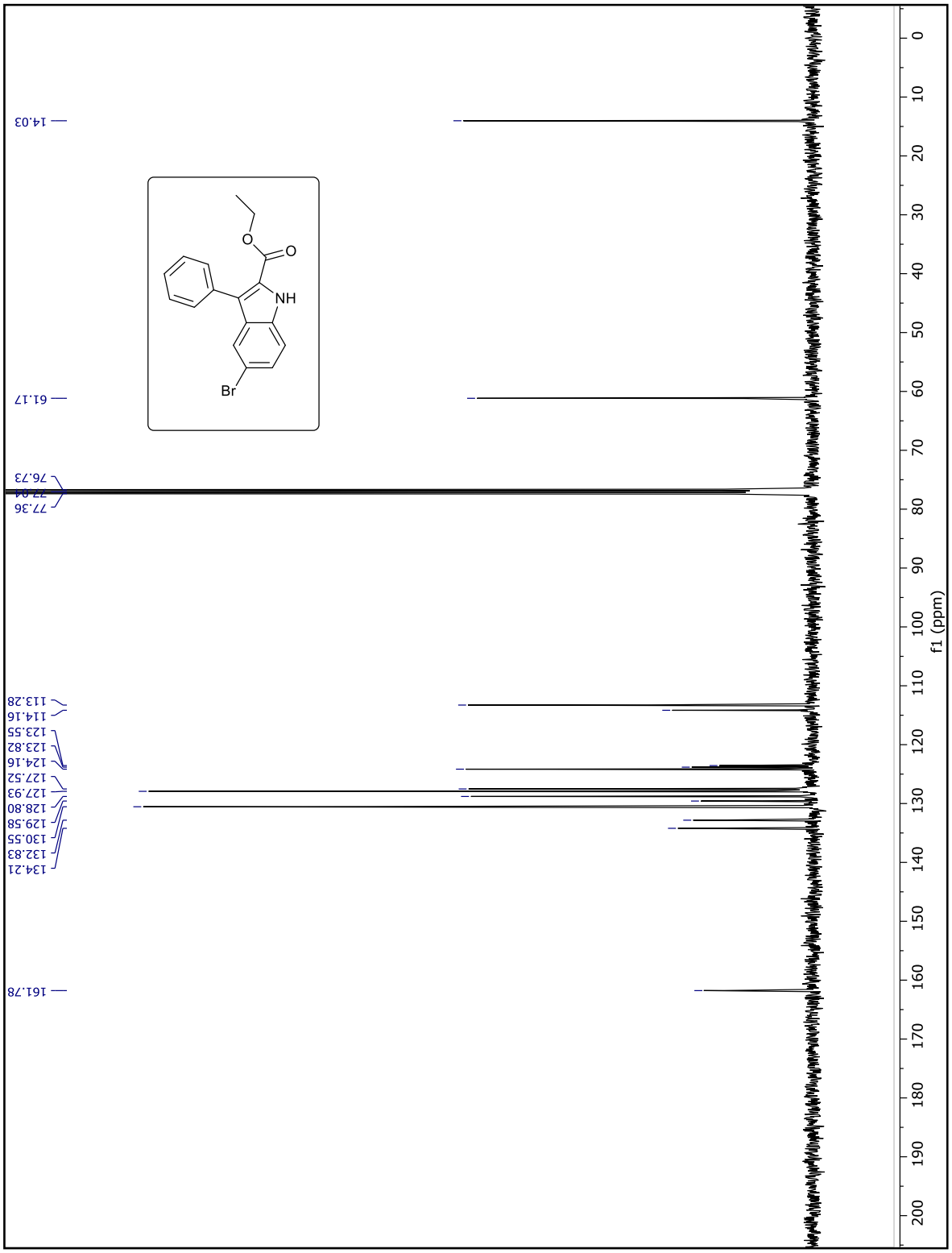
Methyl 5-bromo-3-phenyl-1H-indole-2-carboxylate (Table 1, 3p)



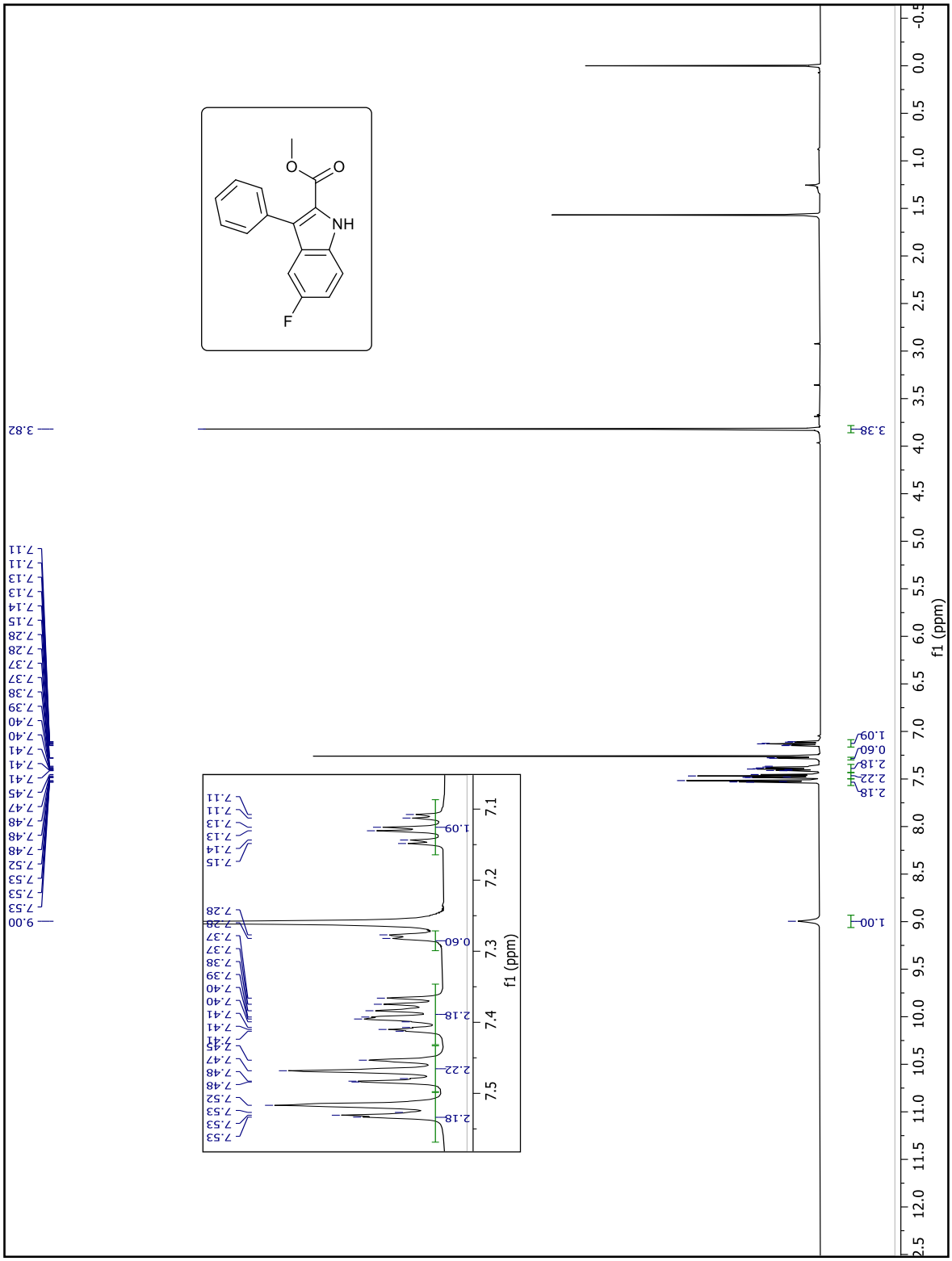

O
O
NH
Br
52.00
76.75
77.39
77.82
113.36
114.21
123.41
123.68
124.16
127.57
128.06
128.89
129.50
130.44
132.76
134.32
162.22
f1 (ppm)

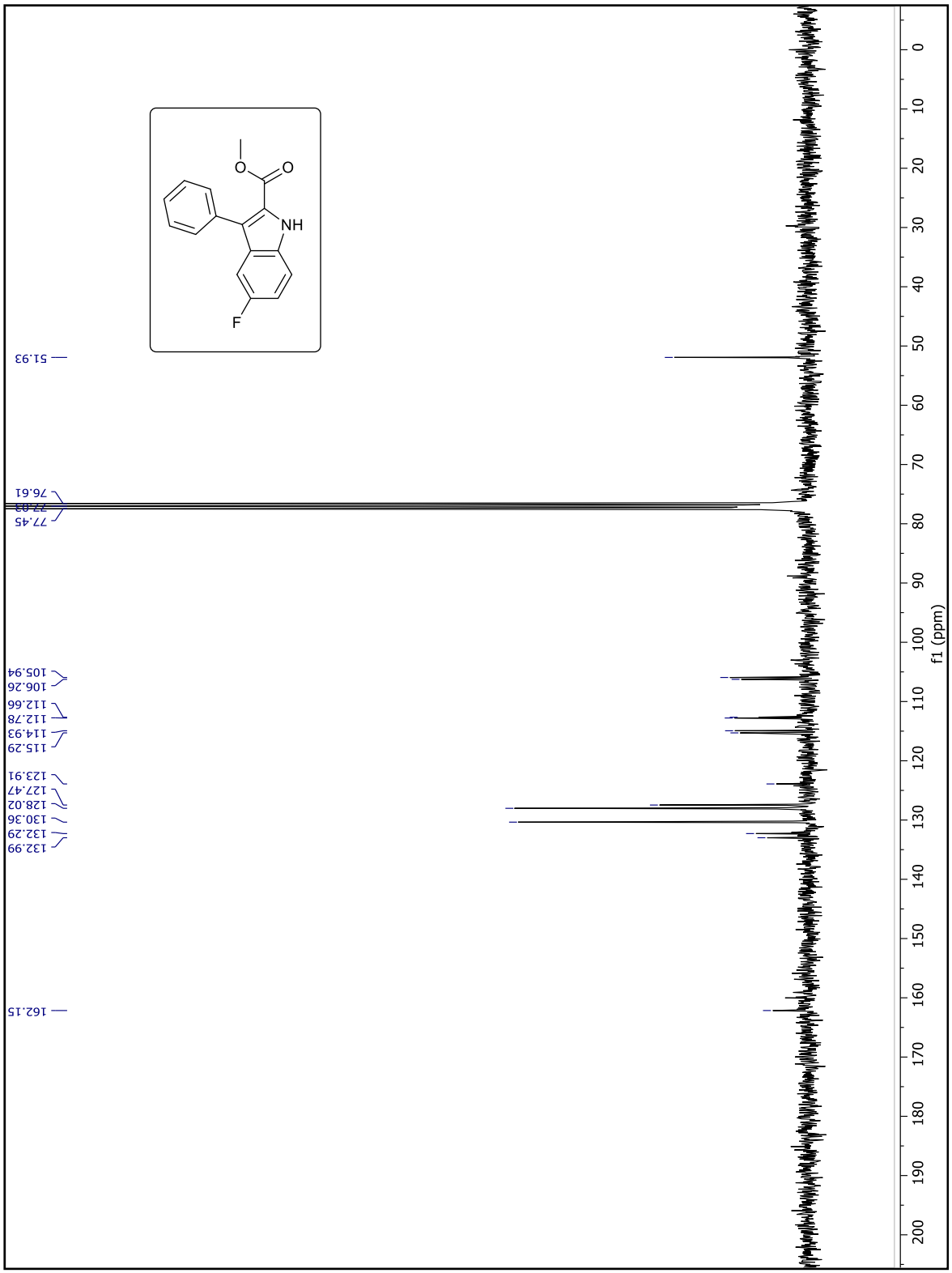
Ethyl 5-bromo-3-phenyl-1H-indole-2-carboxylate (Table 1, 3q)



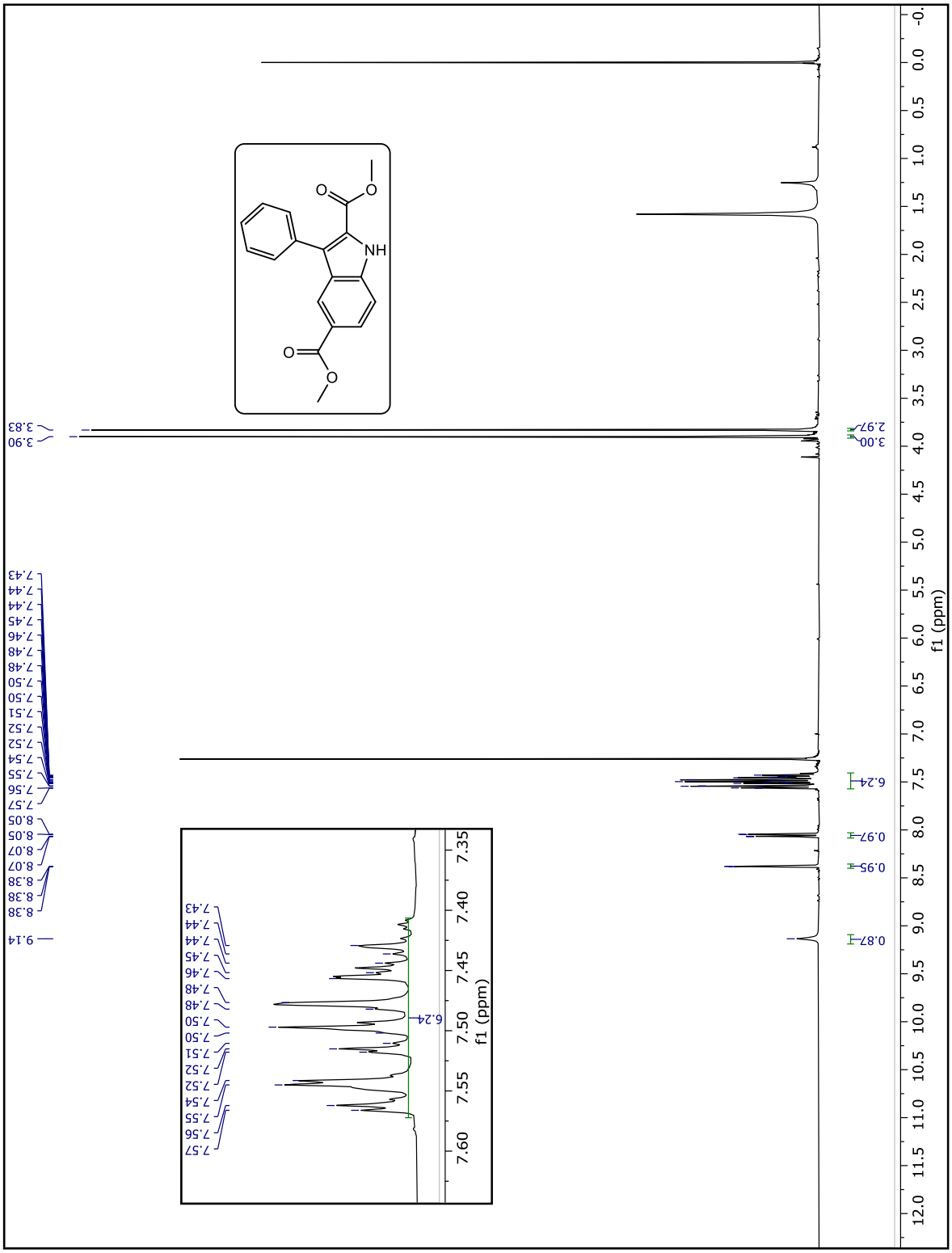

14.03
61.17
76.73
77.04
77.36
113.28
114.16
123.55
123.82
124.16
127.52
127.93
128.80
129.58
130.55
132.83
134.21
161.78
O
O
NH
Br
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

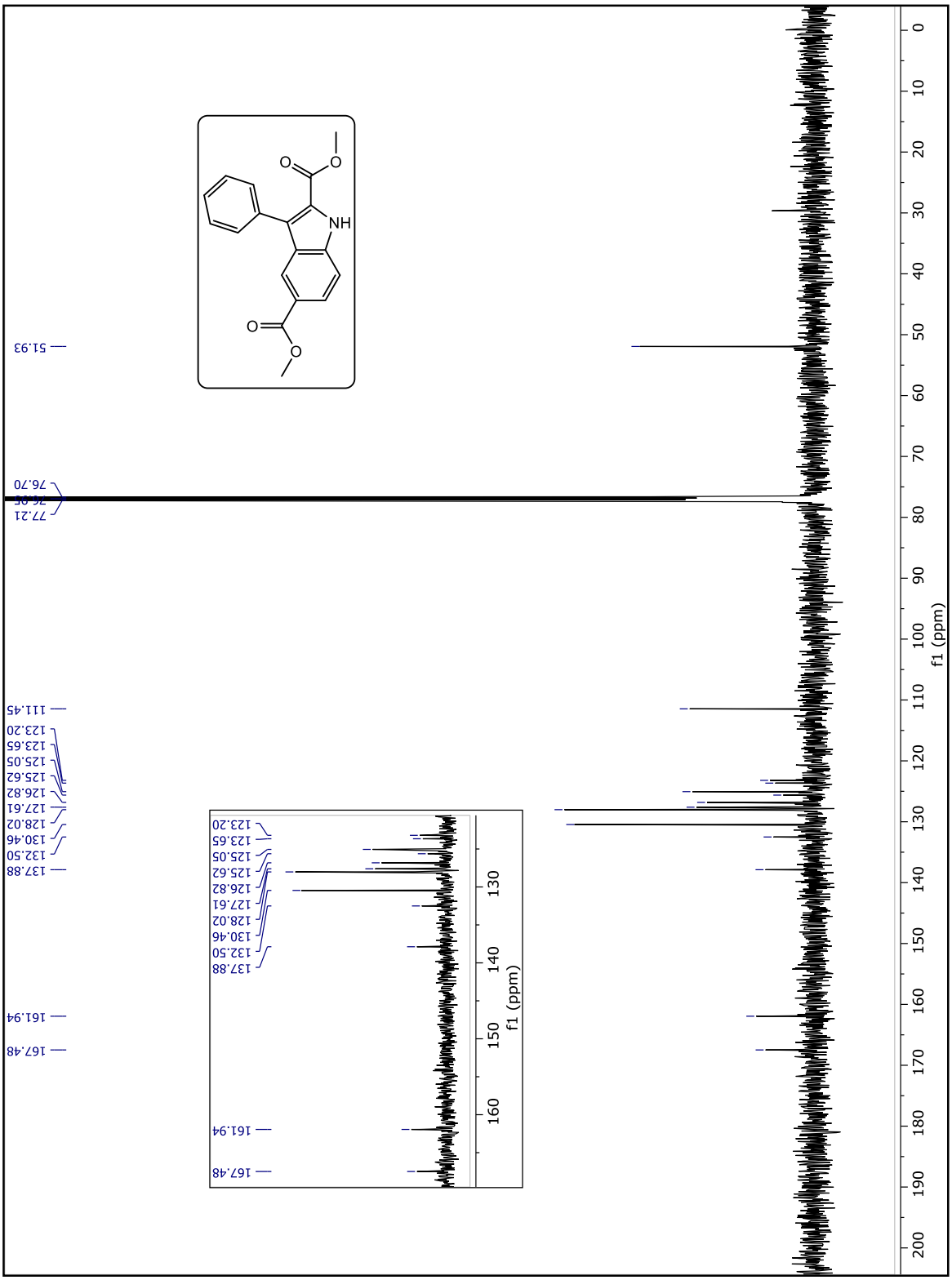
Methyl 5-fluoro-3-phenyl-1H-indole-2-carboxylate (Table 1, 3r)



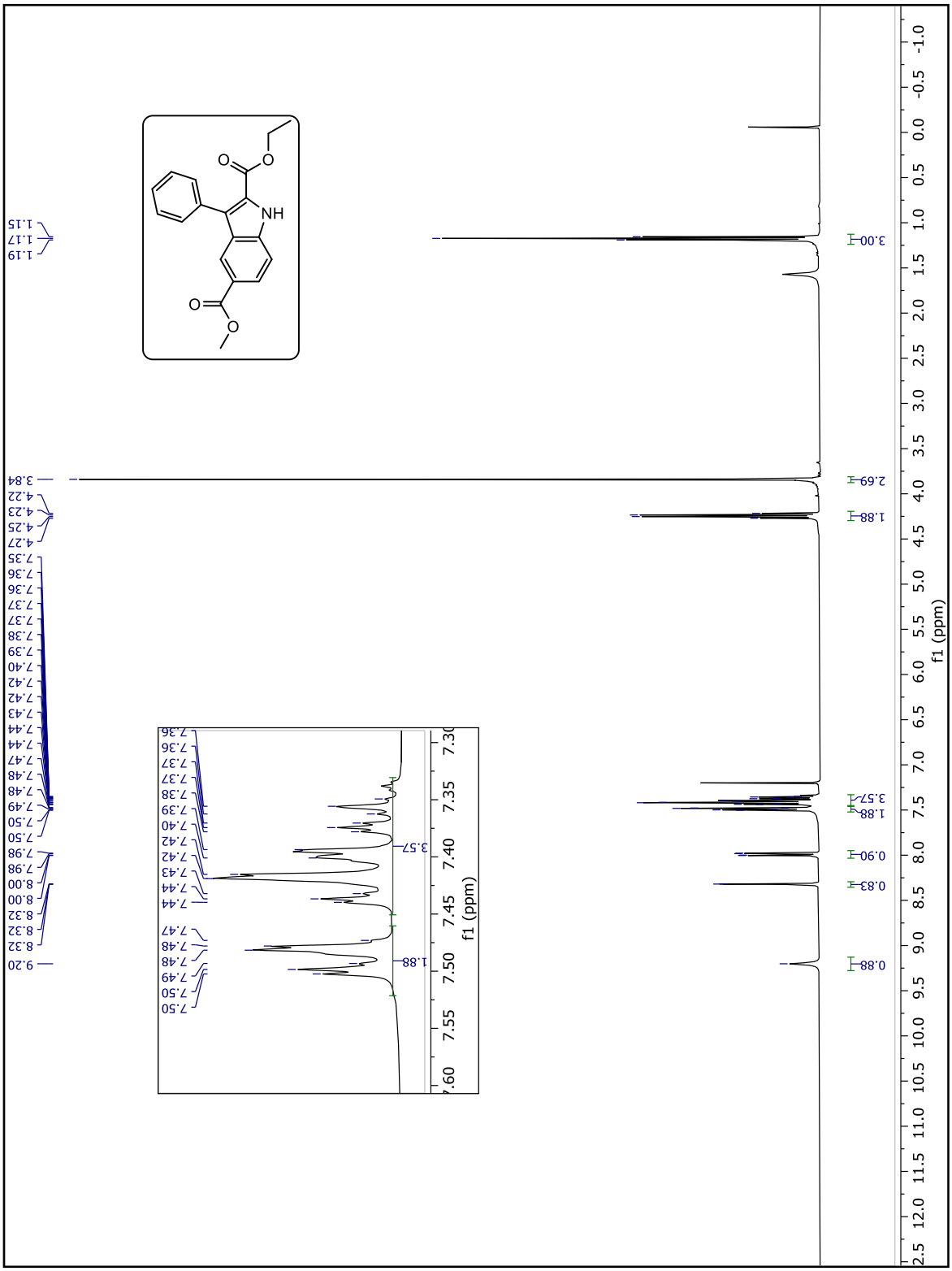

O
O
NH
F
51.93
76.61
77.45
105.94
106.26
112.66
112.78
114.93
115.29
123.91
127.47
128.02
130.36
132.29
132.99
162.15
f1 (ppm)

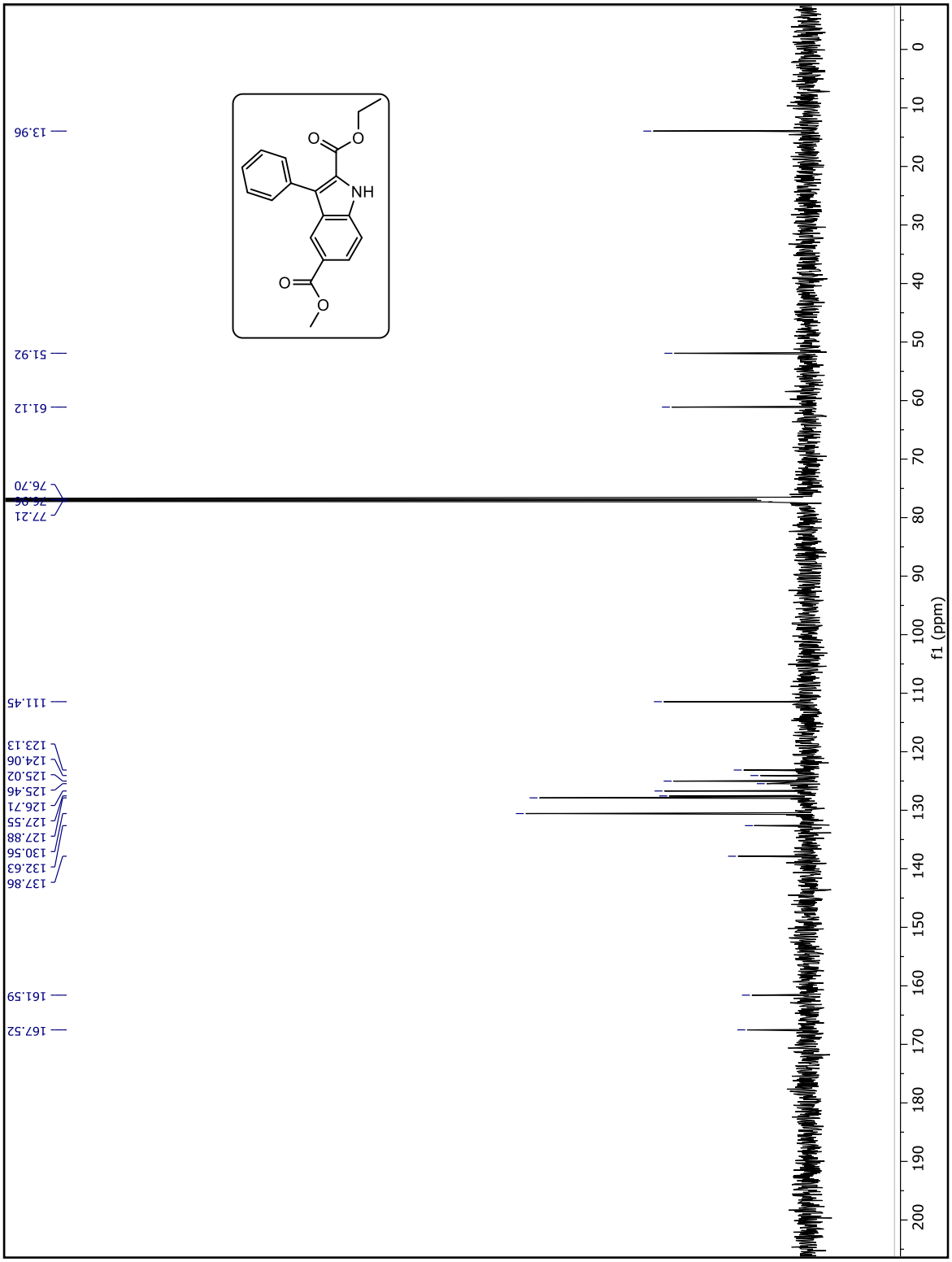
Dimethyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3s)



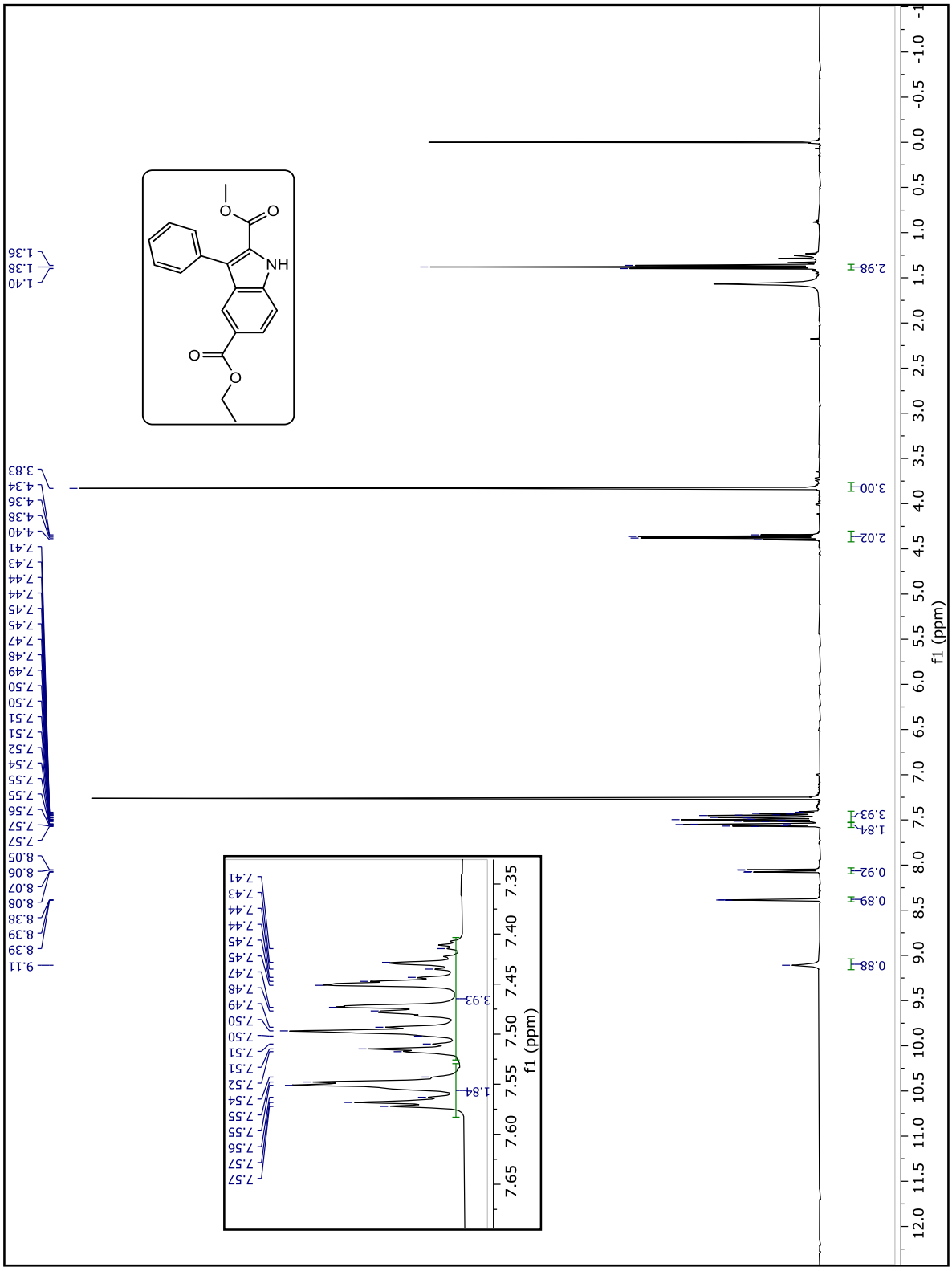

NH
O
O
O
O
51.93
76.70
77.05
77.21
111.45
123.20
123.65
125.05
125.62
126.82
127.61
128.02
130.46
132.50
137.88
161.94
167.48
f1 (ppm)

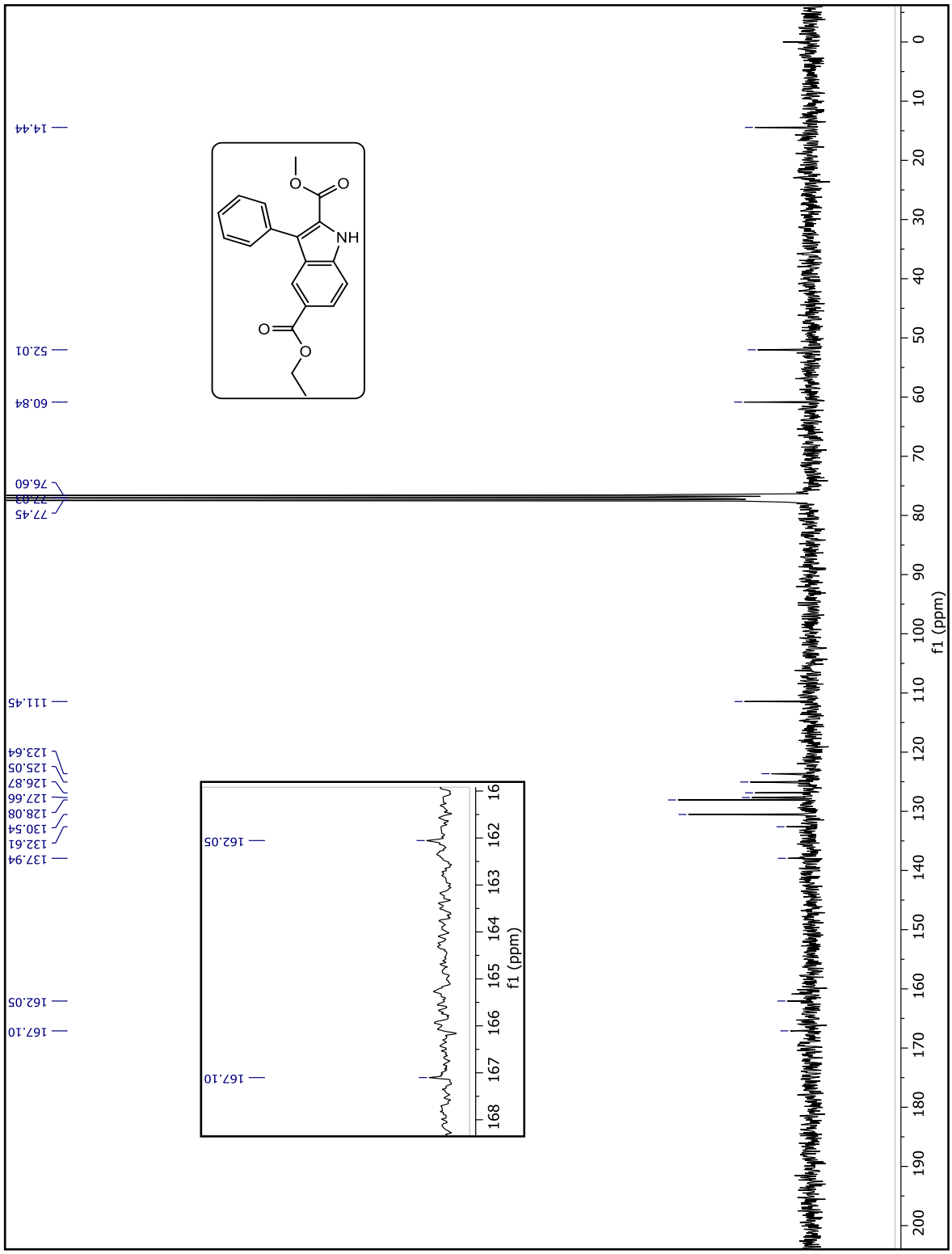
2-Ethyl 5-methyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3t)



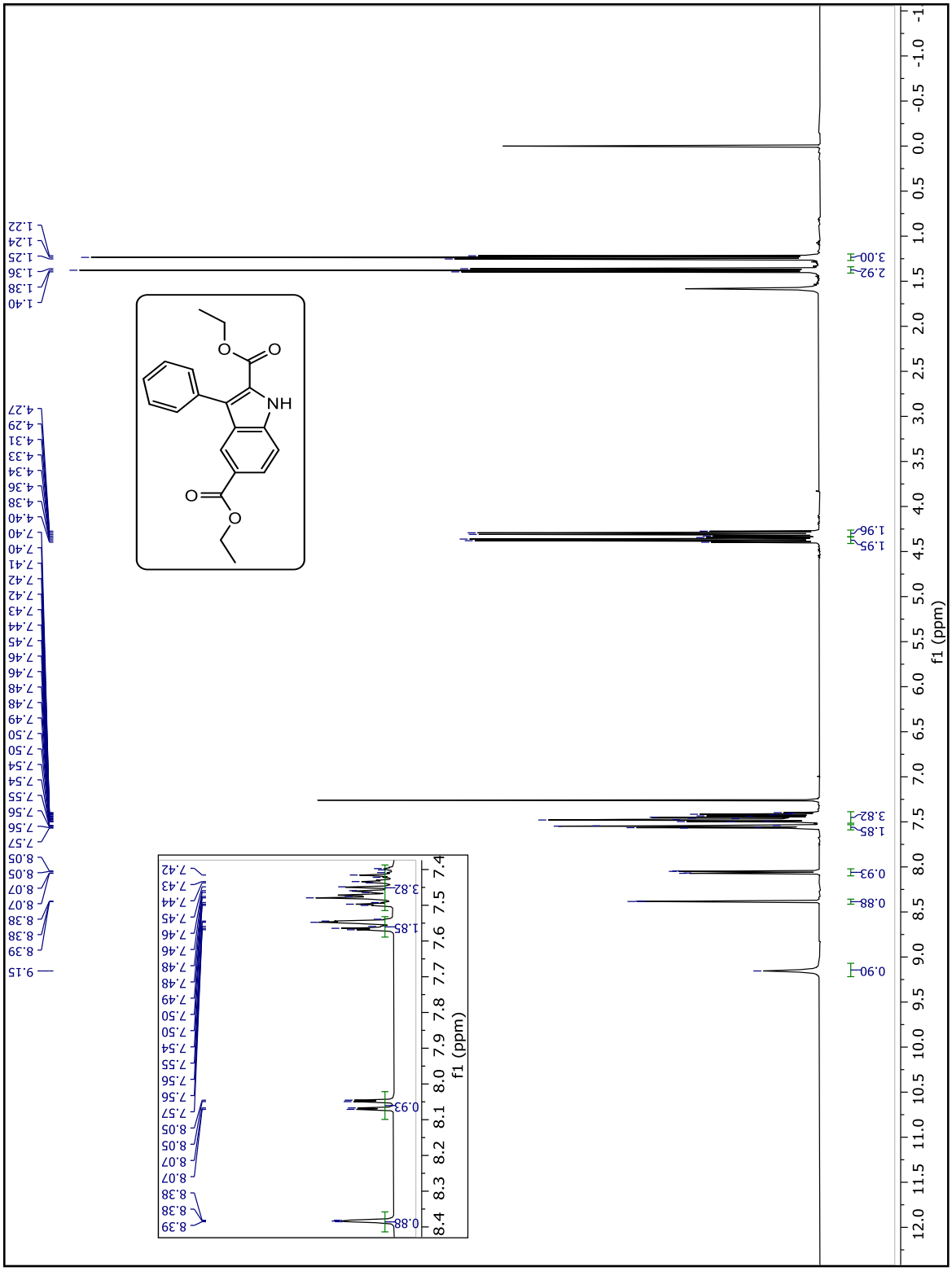

13.96
51.92
61.12
76.70
77.21
111.45
123.13
124.06
125.02
125.46
126.71
127.55
127.88
130.56
132.63
137.86
161.59
167.52
NH
O
O
O
O
f1 (ppm)

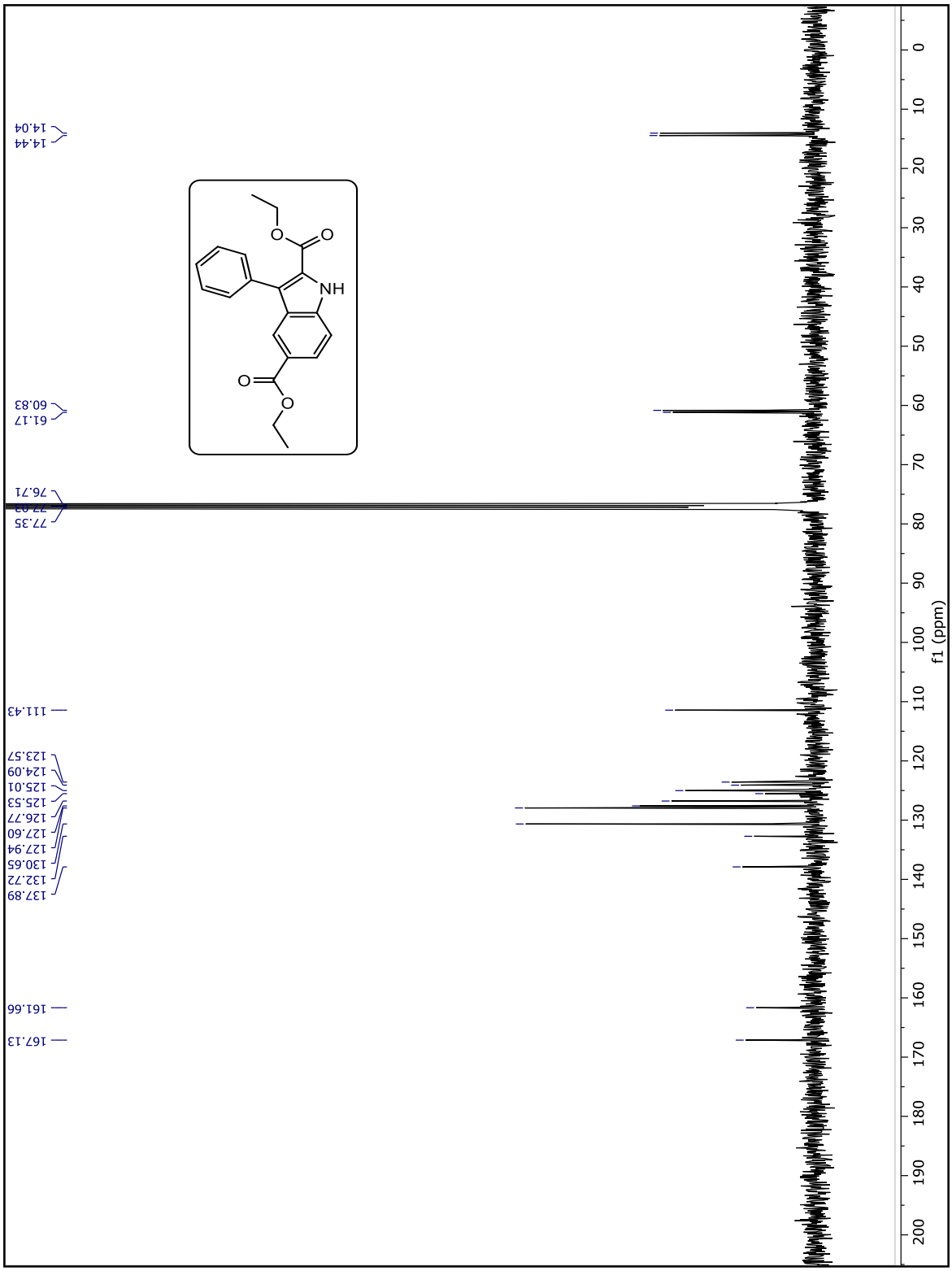
5-Ethyl 2-methyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3u)



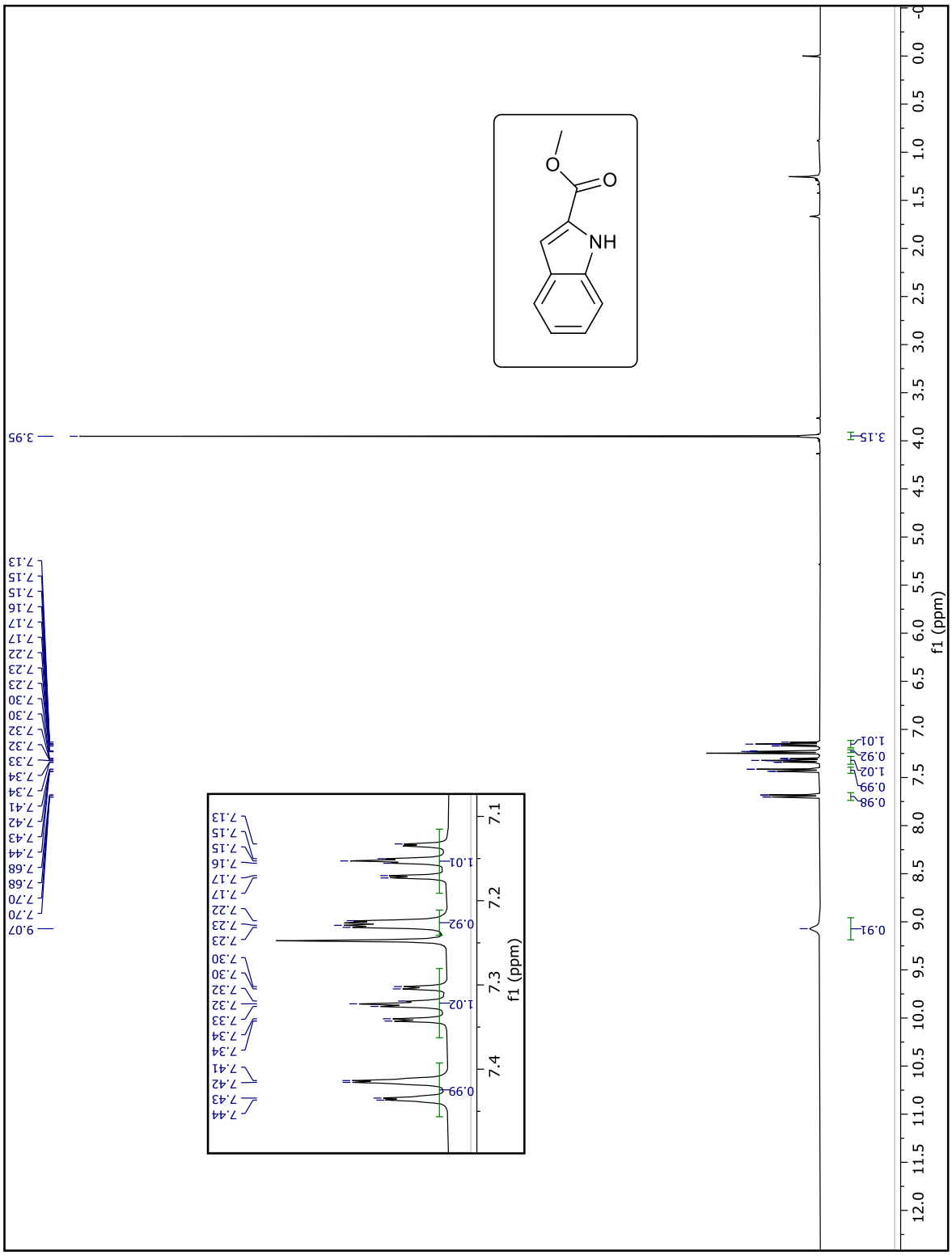

14.44
52.01
60.84
76.60
77.45
111.45
123.64
125.05
126.87
127.66
128.08
130.54
132.61
137.94
162.05
167.10
NH
f1 (ppm)

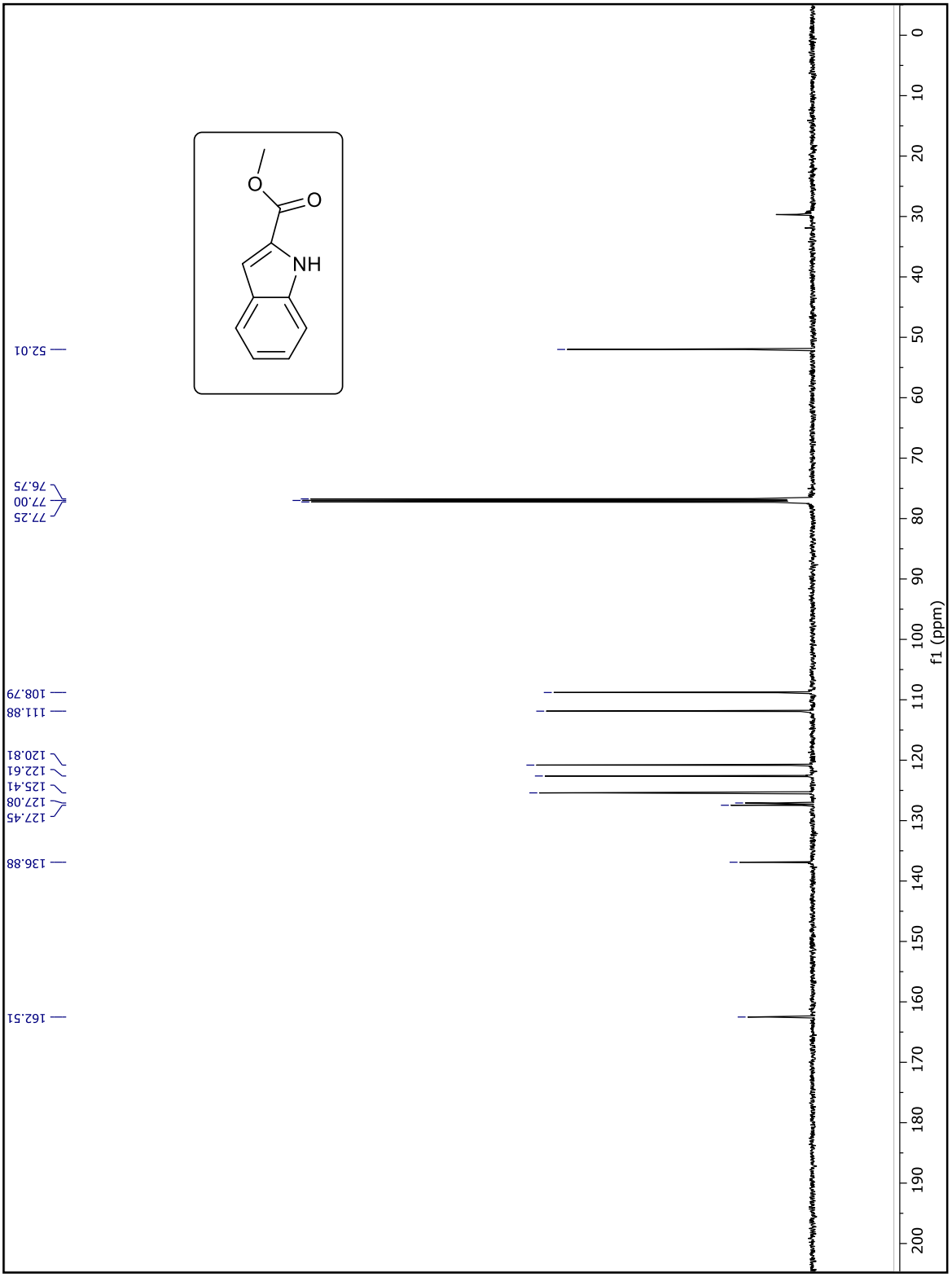
Diethyl 3-phenyl-1H-indole-2,5-dicarboxylate (Table 1, 3v)



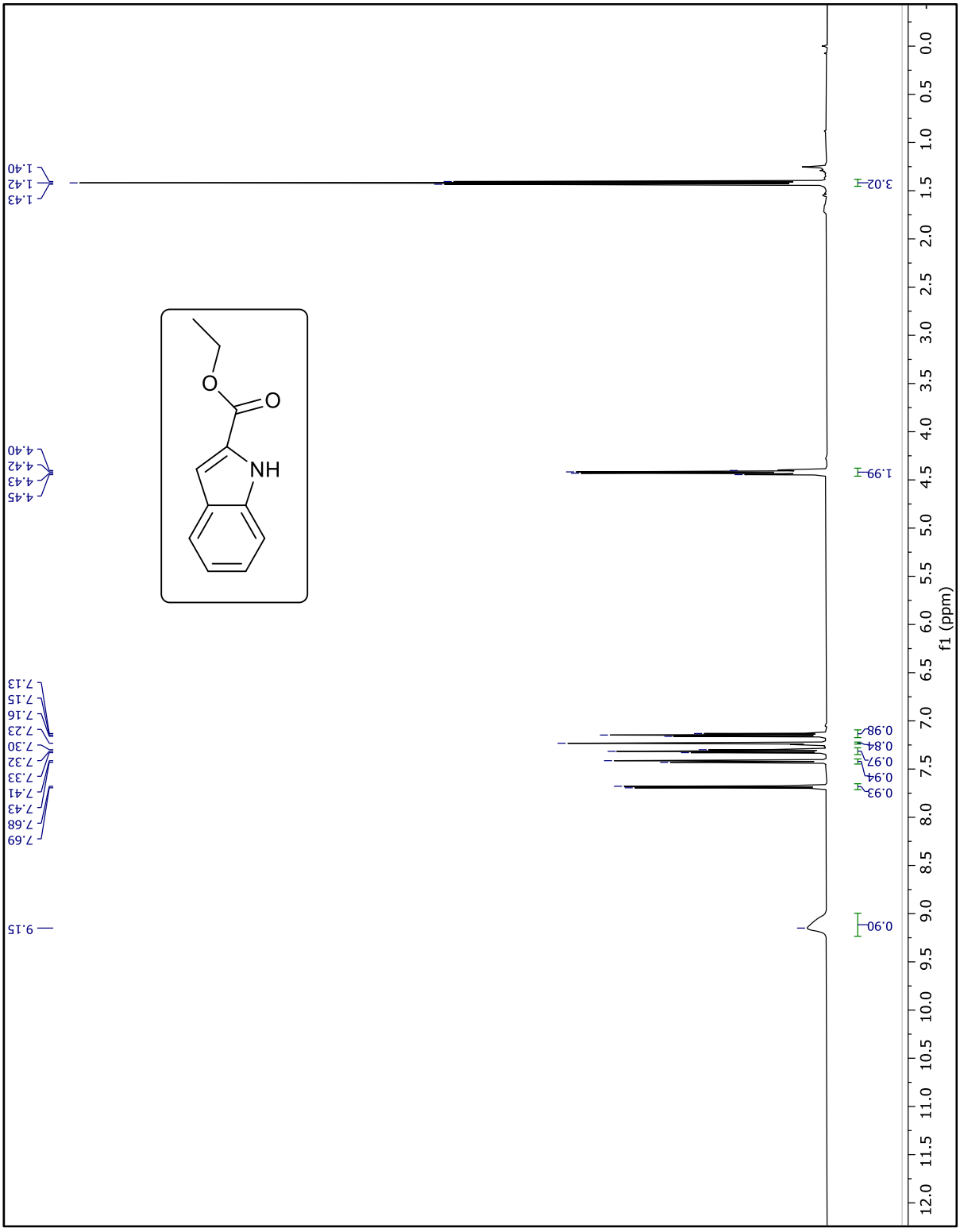

14.04
14.44
60.83
61.17
76.71
77.03
77.35
111.43
123.57
124.09
125.01
125.53
126.77
127.60
127.94
130.65
132.72
137.89
161.66
167.13
NH
O
O
O
O
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

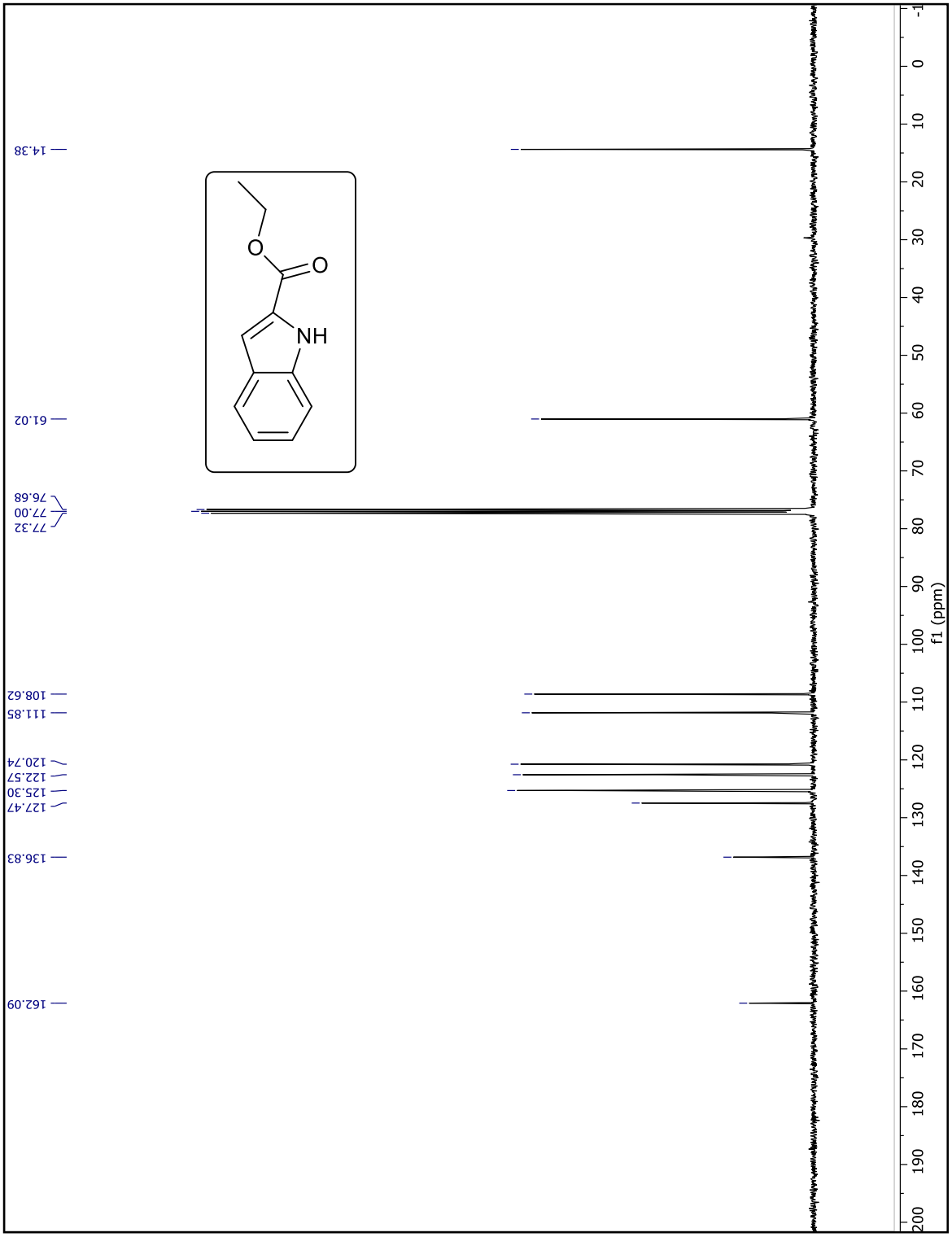
Methyl 1H-indole-2-carboxylate (Table 1, 3y)



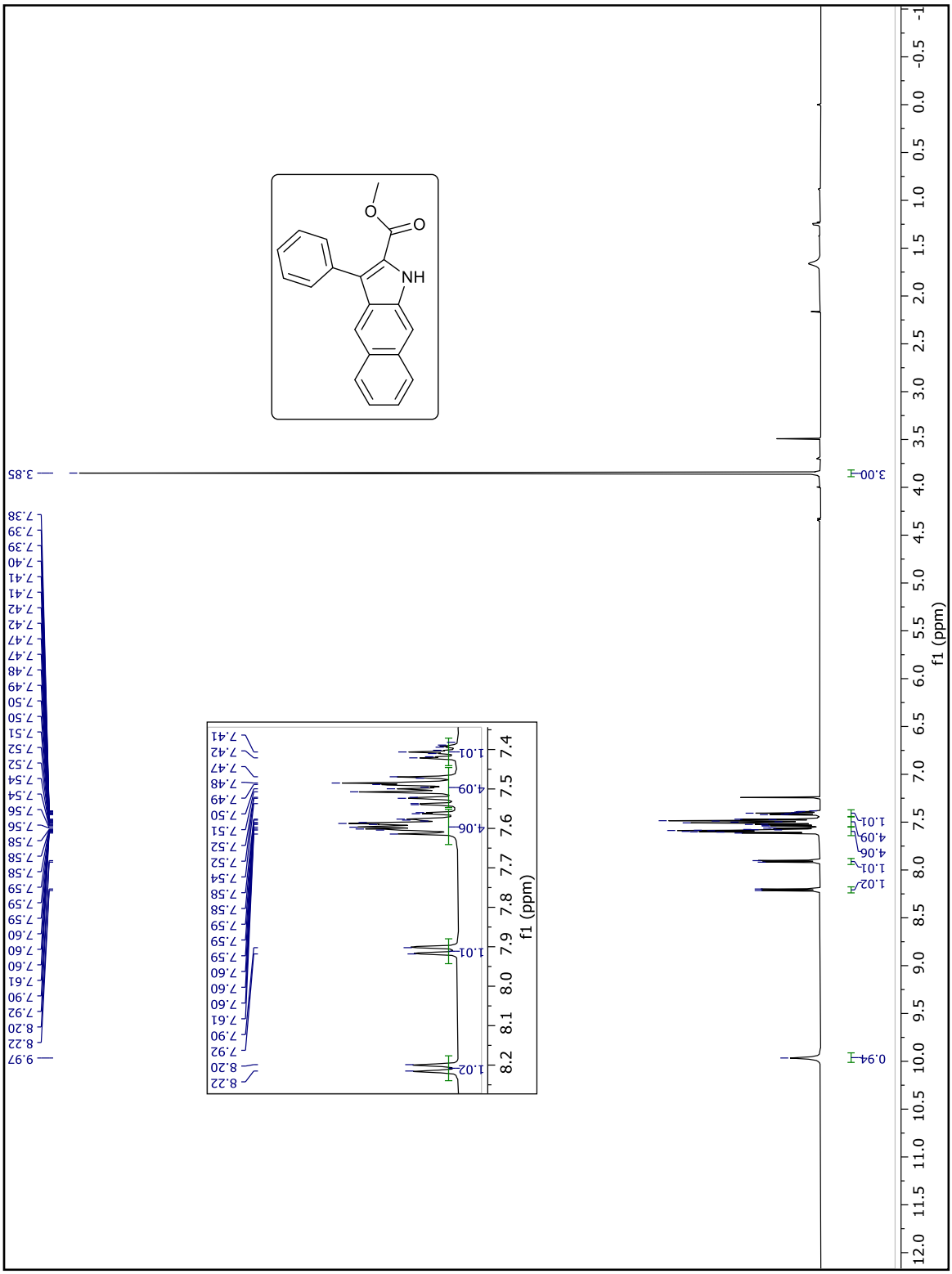

O
O
NH
52.01
76.75
77.00
77.25
108.79
111.88
120.81
122.61
125.41
127.08
127.45
136.88
162.51
f1 (ppm)

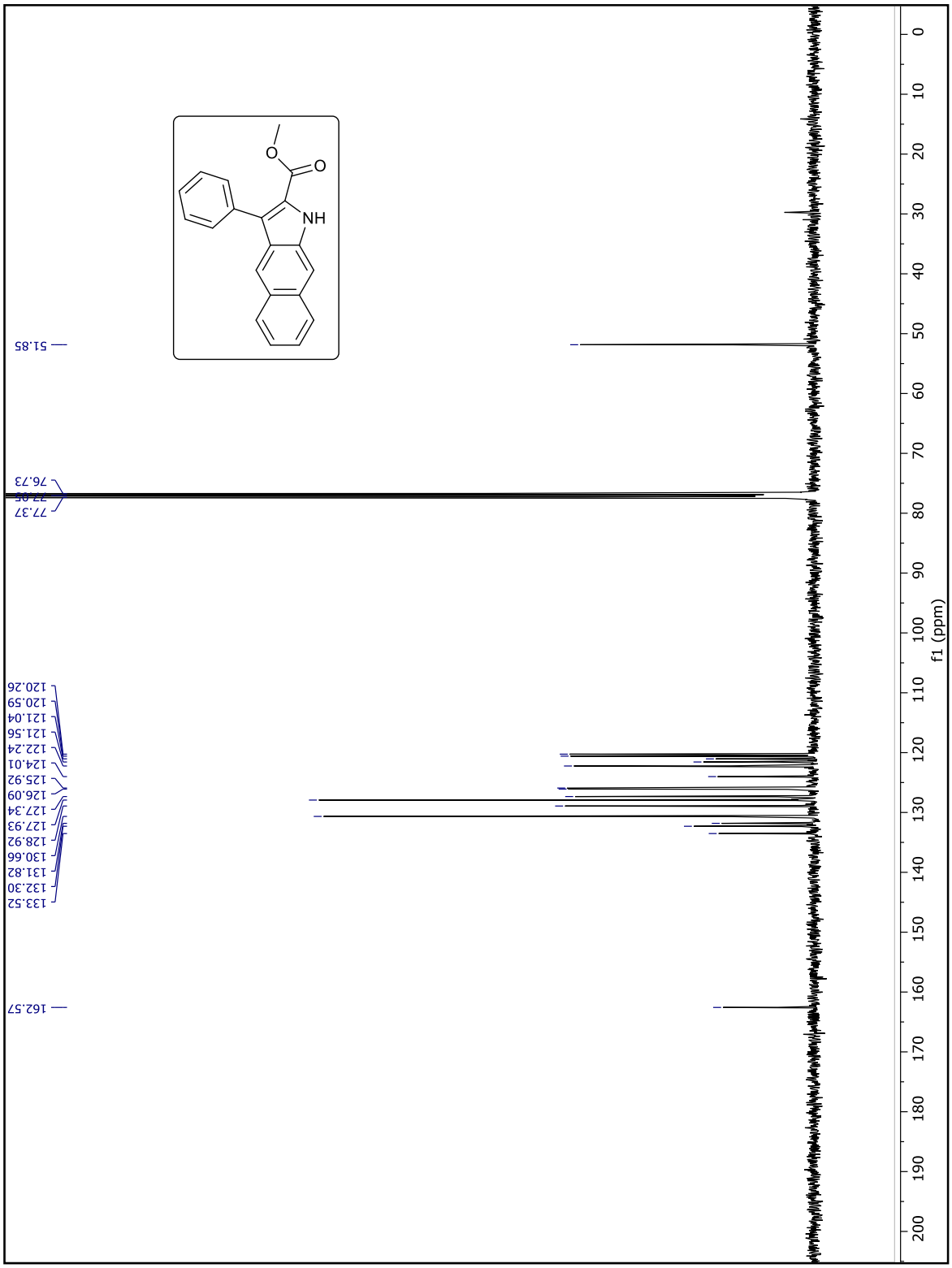
Ethyl 1H-indole-2-carboxylate (Table 1, 3z)



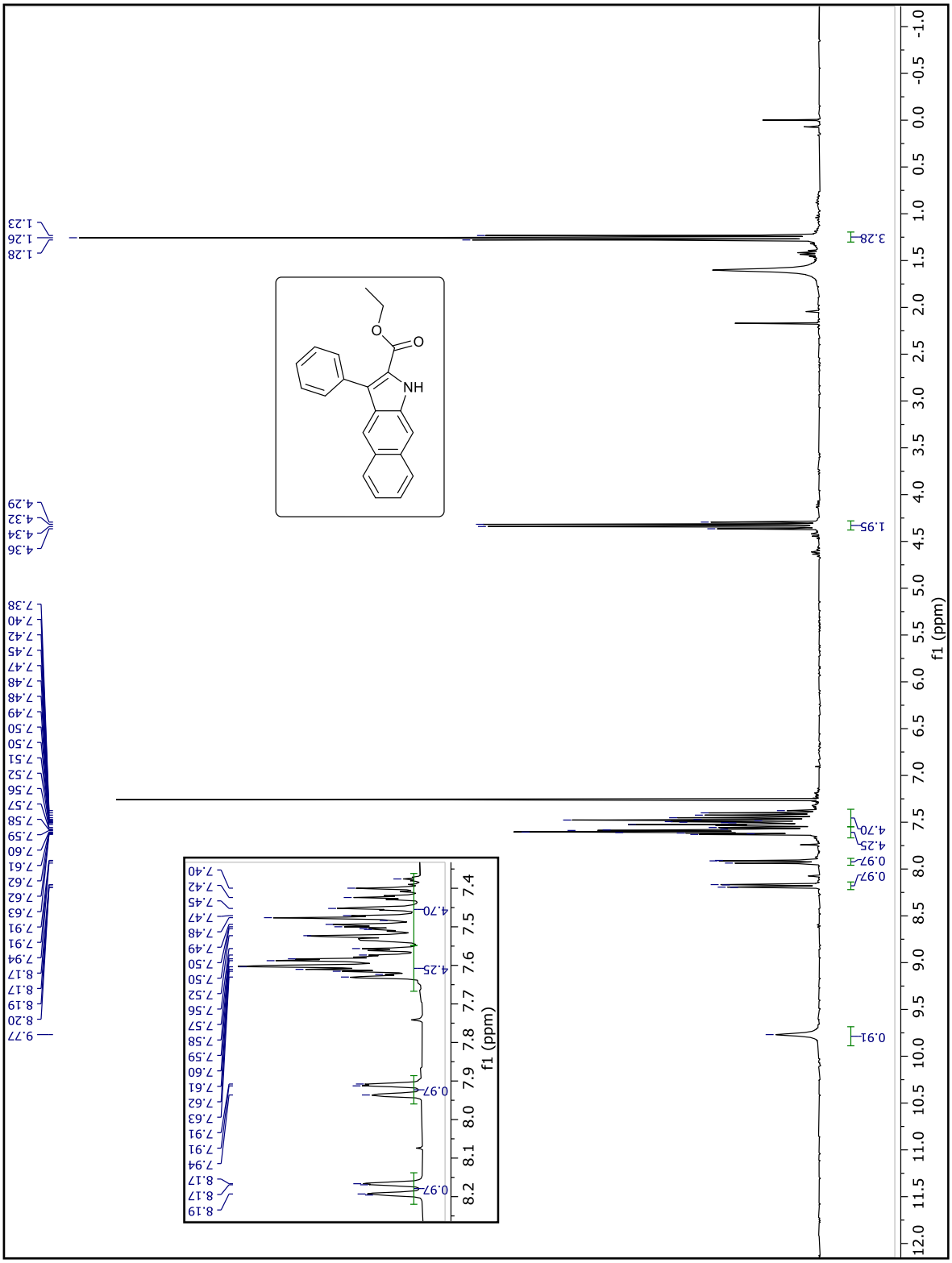

14.38
61.02
76.68
77.00
77.32
108.62
111.85
120.74
122.57
125.30
127.47
136.83
162.09
O
O
NH
f1 (ppm)

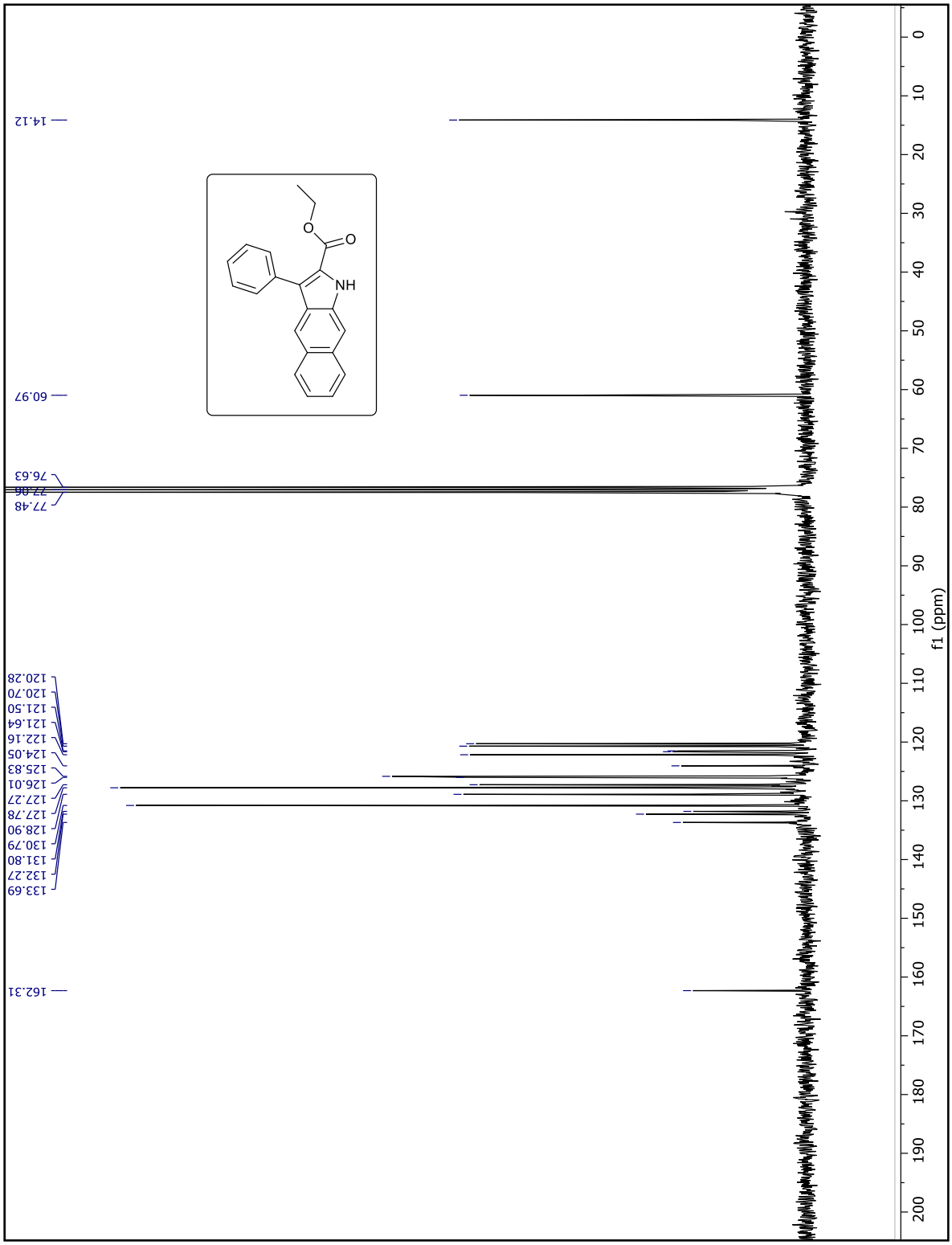
Methyl 3-phenyl-1H-benzo[f]indole-2-carboxylate (Table 1, 3za)




O
O
NH
51.85
76.73
77.05
77.37
120.26
120.59
121.04
121.56
122.24
124.01
125.92
126.09
127.34
127.93
128.92
130.66
131.82
132.30
133.52
162.57
f1 (ppm)

Ethyl 3-phenyl-1H-benzo[f]indole-2-carboxylate (Table 1, 3zb)




14.12
60.97
76.63
77.48
120.28
120.70
121.50
121.64
122.16
124.05
125.83
126.01
127.27
127.78
128.90
130.79
131.80
132.27
133.69
162.31
O
O
NH
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

4. References

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