Supporting Information
For

A Mild and Facile Synthesis of Polyfunctionalized Pyridines: Merging Three-Component Cyclization and Aerobic Oxidation by Amine/Metal Catalysts

Chunyin Zhu*, Benwei Bi, Ya Ding, Te Zhang, and Qiu-Yun Chen

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China
* E-mail: zhucycn@gmail.com

List of contents

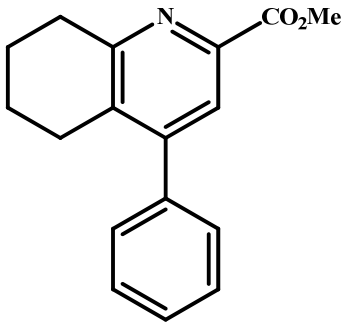
General Information

Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H (400MHz) and ^{13}C NMR (100MHz) data were recorded on Bruker AVANCEII400MHz spectrometer using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

General procedures for reactions

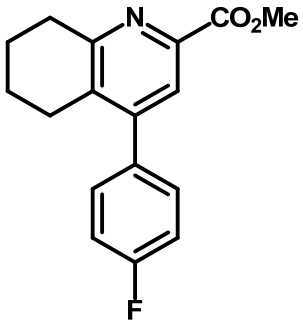
To a solution of β, γ-unsaturated α-ketoester (0.5 mmol) in 1.5 mL methanol was added ketone or aldehyde (0.6 mmol), ceric ammonium nitrate (0.05mmol), pyrrolidine (0.1 mmol) and ammonium acetate (0.6 mmol). The reaction mixture was stirred at room temperature under air atmosphere (open flask). The reaction was monitored by thin layer chromatography (TLC). When the reaction was completed, it was diluted with water and extracted with ethyl acetate 3 times. Removal of solvent followed by column chromatography afforded desired products.

Compound characterizations



Methyl 4-phenyl-5,6,7,8-tetrahydroquinoline-2-carboxylate **3aa**

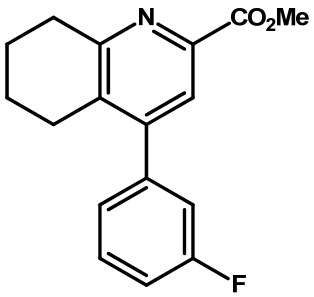
Petroleum ether/ethyl acetate = 2:1, 76% yield (215 mg),white solid, Mp 119-120 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.77 (s, 1H), 7.35-7.41 (m, 3H), 7.23-7.26 (m, 2H), 3.93 (s, 3H), 3.05 (t, *J* = 6.4 Hz, 2H), 2.64 (t, *J* = 6.4 Hz, 2H), 1.84-1.90 (m, 2H), 1.64-1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 158.3, 150.2, 144.6, 138.3, 134.1, 128.3, 127.9, 123.4, 52.6, 33.1, 27.6, 22.5, 22.4. MS (ESI, *m/z*) 268.3 (M + H^+), 290.3 (M + Na^+). IR (film) *v*/cm^{-1} 2947(s), 1711(vs), 1583(m), 1454(m), 1248(vs), 1130(s), 702(s). Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.31; H, 6.34; N, 5.32.



Methyl 4-(4-fluorophenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ba**

Petroleum ether/ethyl acetate = 2:1, 75% yield (270 mg),white solid, Mp 103-104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.75 (s, 1H), 7.22-7.24 (m, 2H), 7.08

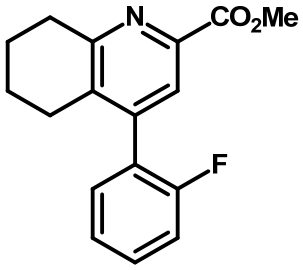
(t, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 1.84-1.90 (m, 2H), 1.67-1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.5 (d, *J* = 247.3 Hz), 158.6, 149.4, 144.8, 134.3(4) (d, *J* = 2.4 Hz), 134.2(8), 130.2 (d, *J* = 7.9 Hz), 123.5, 115.5 (d, *J* = 21.2 Hz), 52.8, 33.2, 27.8, 22.6, 22.5. MS (ESI, *m/z*) 286.3 (M + H^+), 308.3 (M + Na^+).IR (film) *v*/cm^{-1} 2948(s), 1731(vs), 1609(m), 1508(s), 1254(vs), 1130(m), 846(s). Anal. calcd for $C_{17}H_{16}FNO_2$: C, 71.56; H, 5.65; N, 4.91. Found: C, 71.64; H, 5.43; N, 4.99.



Methyl 4-(3-fluorophenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ca**

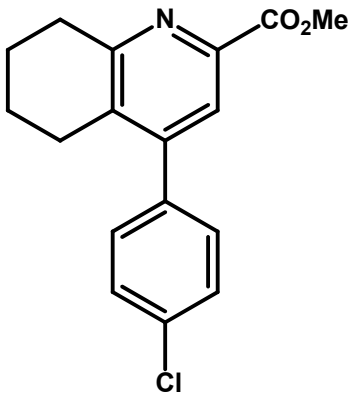
Petroleum ether/ethyl acetate = 2:1, 68% yield (164 mg),white solid, Mp 76-77 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.83 (s, 1H), 7.42-7.47 (m,1H), 7.02-7.16(m ,3H), 4.01 (s, 3H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.71 (t, *J* = 6.4 Hz, 2H), 1.94-1.97 (m, 2H), 1.77-1.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.5 (d, *J* = 245.2 Hz), 158.7, 149.1 (d, *J* = 2.6 Hz), 144.8, 140.5 (d, *J* = 6.8 Hz), 134.1, 130.1 (d, *J* = 8.1 Hz), 124.2 (d, *J* = 2.8 Hz), 123.3, 115.6 (d, *J* = 21.8 Hz), 115.1 (d, *J* = 20.7 Hz), 52.8, 33.2, 27.7, 22.6, 22.5. MS (ESI, *m/z*) 286.2 (M + H^+), 308.2 (M + Na^+). IR (film) *v*/cm^{-1} 2961(vs), 1723(vs), 1445(s), 1264(s), 1117(m), 788(s). Anal. calcd for $C_{17}H_{16}FNO_2$: C, 71.56; H, 5.65; N,

4.91. Found: C, 71.43; H, 5.57; N, 5.11.



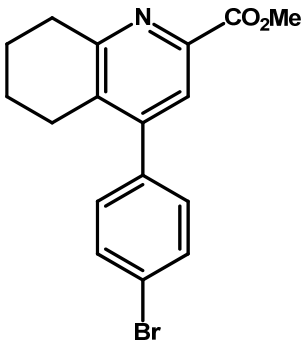
Methyl 4-(2-fluorophenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3da**

Petroleum ether/ethyl acetate = 2:1, 66% yield (144 mg),white solid, Mp 75-76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.85 (s, 1H), 7.41-7.46 (m,1H), 7.16-7.26 (m , 3H) , 4.00 (s, 3H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.56-2.70 (m, 2H) 1.92-1.96 (m, 2H), 1.70-1.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 158.9 (d, *J* = 246.0 Hz), 158.3, 144.7 (d, *J* = 14.5 Hz), 135.4, 130.5 (d, *J* = 2.8 Hz), 130.3 (d, *J* = 7.9 Hz), 125.8 (d, *J* = 15.8 Hz), 124.3 (d, *J* = 3.0 Hz), 123.9, 115.7 (d, *J* = 22.2 Hz), 52.7, 33.1, 26.8 (d, *J* = 2.9 Hz), 22.6, 22.2. MS (ESI, *m/z*) 286.2 (M + H^+), 308.2 (M + Na^+). IR (film) *ν*/cm^{-1} 2934(vs), 1706(vs), 1584(m), 1264(s), 762(s), 615(w). Anal. calcd for $C_{17}H_{16}FNO_2$: C, 71.56; H, 5.65; N, 4.91. Found: C, 71.48; H, 5.33; N, 4.76.



Methyl 4-(4-chlorophenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ea**

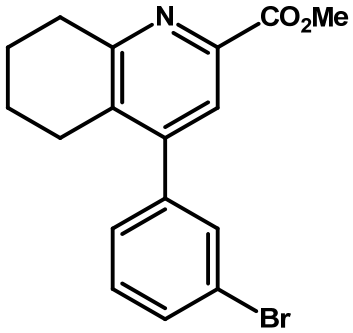
Petroleum ether/ethyl acetate = 5:1, 85% yield (235 mg),white solid, Mp 128-129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.74 (s, 1H), 7.36-7.38 (m, 2H), 7.17-7.20 (m, 2H), 3.93 (s, 3H), 3.05 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 1.85-1.88 (m, 2H), 1.68-1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 158.6, 149.1, 144.8, 136.8, 134.3, 134.1, 129.8, 128.7, 123.3, 52.8, 33.2, 27.7, 22.6, 22.5. MS (ESI, *m/z*) 302.2 (M + H^+), 324.2 (M + Na^+).IR (film) *ν*/cm^{-1} 2931(s), 1716(vs), 1609(m), 1500(s), 1446(s), 1354(s), 1246(vs), 1124(s), 839(s). Anal. calcd for $C_{17}H_{16}ClNO_2$: C, 67.66; H, 5.34; N, 4.64. Found: C, 67.87; H, 5.44; N, 4.85.



Methyl 4-(4-bromophenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3fa**

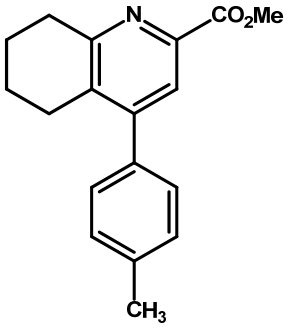
Petroleum ether/ethyl acetate = 2:1, 69% yield (168 mg),white solid, Mp 163-164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.74 (s, 1H), 7.51-7.55 (m,2H), 7.11-7.14 (m,2H), 3.93 (s, 3H), 3.05 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 1.85-1.89 (m, 2H), 1.68-1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 158.7, 149.2, 144.9, 137.3, 134.1, 131.7, 130.1, 123.3, 122.5, 52.8, 33.2, 27.7, 22.6, 22.5. MS (ESI, *m/z*) 346.2 (M + H^+), 368.2 (M + Na^+). IR (film) *ν*/cm^{-1}

2955(m), 1709(vs), 1585(m), 1455(m), 1239(vs), 1130(s), 823(s). Anal. calcd for $C_{17}H_{16}BrNO_2$: C, 58.97; H, 4.66; N, 4.05. Found: C, 59.12; H, 4.54; N, 4.23.



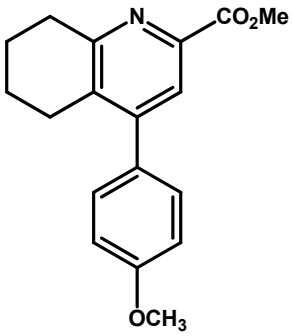
Methyl 4-(3-bromophenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ga**

Petroleum ether/ethyl acetate = 2:1, 72% yield (150 mg),white solid, Mp 1086-107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.73 (s, 1H), 7.47-7.50 (m,1H), 7.40 (t, *J* = 1.6 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.16-7.18 (m,1H), 3.93 (s, 3H), 3.05 (t, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 6.4 Hz, 2H), 1.85-1.88 (m, 2H), 1.68-1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 158.5, 148.6, 144.7, 140.3, 133.9, 131.2, 131.0, 129.9, 126.9, 123.1, 122.3, 52.7, 33.0, 27.5, 22.5, 22.3. MS (ESI, *m/z*) 346.1 (M + H^+), 368.1 (M + Na^+). IR (film) *ν*/cm^{-1} 3055(m), 2948(s), 1731(vs), 1577(s), 1423(vs), 1355(s), 1231(vs), 1130(s), 1008(m), 793(s). Anal. calcd for $C_{17}H_{16}BrNO_2$: C, 58.97; H, 4.66; N, 4.05. Found: C, 58.88; H, 4.73; N, 3.92.



Methyl 4-(p-tolyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ha**

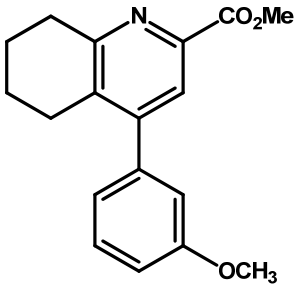
Petroleum ether/ethyl acetate = 2:1, 66% yield (280 mg),white solid, Mp 107-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.76 (s, 1H), 7.19-7.21 (m, 2H), 7.13-7.15 (m, 2H), 3.93 (s, 3H), 3.05 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.4 Hz, 2H), 2.36 (s, 3H), 1.85-1.88 (m, 2H), 1.67-1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 158.3, 150.4, 144.7, 137.9, 135.5, 134.3, 129.0, 128.3, 123.6, 52.7, 33.2, 27.8, 22.7, 22.6, 21.2. MS (ESI, *m/z*) 282.2 ($M + H^+$),304.2 ($M + Na^+$).IR (film) *v*/cm^{-1} 2940(vs), 1709(vs), 1594(s), 1517(s), 1446(vs), 1246(vs), 1124(vs), 808(vs). Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.74; H, 6.76; N, 5.11.



Methyl 4-(4-methoxyphenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ia**

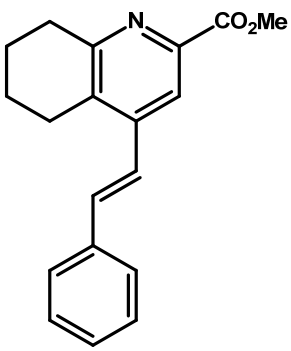
Petroleum ether/ethyl acetate = 2:1, 66% yield (336 mg),white solid, Mp 99-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.76 (s, 1H), 7.17(5)-7.18(0) (m, 2H),

6.90-6.92 (m, 2H), 3.92 (s, 3H), 3.80 (s, 3H), 3.04 (t, *J* = 6.4 Hz, 2H), 2.66 (t, *J* = 6.4 Hz, 2H), 1.84-1.87 (m, 2H), 1.66-1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 159.4, 158.3, 150.0, 144.6, 134.4, 130.6, 129.7, 123.7, 113.8, 55.2, 52.7, 33.2, 27.9, 22.7, 22.6. MS (ESI, *m/z*) 298.2 (M + H^+),320.2 (M + Na^+). IR (film) *v*/cm^{-1} 2940(s), 1716(vs), 1615(s), 1508(vs), 1239(vs), 1130(s), 1031(s), 831(m). Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.68; H, 6.58; N, 4.67.



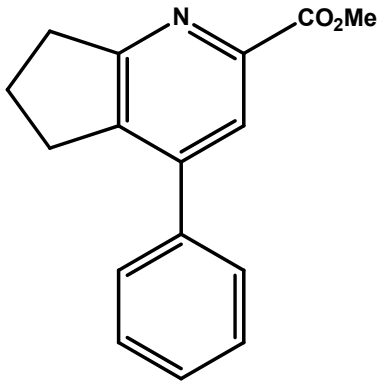
Methyl 4-(3-methoxyphenyl)-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ja**

Petroleum ether/ethyl acetate = 2:1, 75% yield (188 mg),white solid, Mp 58-59 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.84 (s, 1H), 7.37 (t, *J* = 8.0 Hz, 1H),6.94-6.97 (m,1H), 6.86-6.89 (m,1H),6.82-6.83 (m,1H),3.99 (s, 3H), 3.85 (s, 3H), 3.11 (t, *J* = 6.4 Hz, 2H), 2.71 (t, *J* = 6.4 Hz, 2H), 1.92-1.94 (m, 2H), 1.74-1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 159.5, 158.5, 150.3, 144.7, 139.9, 134.3, 129.6, 123.5, 120.8, 114.2, 113.5, 55.3, 52.8, 33.3, 27.8, 22.7, 22.6. MS (ESI, *m/z*) 298.2 (M + H^+), 320.2 (M + Na^+). IR (film) *v*/cm^{-1} 3055(w), 2944(s), 1731(vs), 1584(s), 1255(s), 1038(s), 788(m). Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.92; H, 6.36; N, 4.87.



(E)-Methyl 4-styryl-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ka**

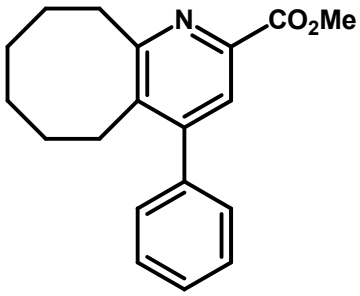
Petroleum ether/ethyl acetate = 2:1, 71% yield (217 mg),white solid, Mp 123-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.11 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.19-7.36 (m, 5H), 3.95 (s, 3H), 2.82-3.02 (m, 4H), 1.57-1.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 158.5, 144.7, 144.6, 136.3, 134.7, 133.3, 128.8, 128.7, 127.0, 122.7, 118.7, 52.8, 33.4, 26.2, 22.4(1), 22.3(6). MS (ESI, *m/z*) 294.3 ($M + H^+$), 316.3 ($M + Na^+$). IR (film) *v*/cm^{-1} 2940(s), 1709(vs), 1585(m), 1455(s), 1224(vs), 970(m), 761(m). Anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.54; H, 6.45; N, 4.89.



Methyl 4-phenyl-6,7-dihydro-5H-cyclopenta[b]pyridine-2-carboxylate **3ab**

Petroleum ether/ethyl acetate = 2:1, 86% yield (125 mg),white solid, Mp 108-109 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.97 (s, 1H), 7.38-7.47 (m, 5H), 3.96

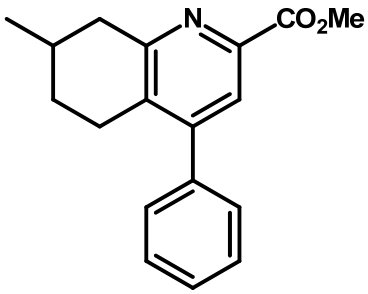
(s, 3H), 3.12 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.07-2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.2, 146.4, 145.8, 138.8, 137.6, 128.6, 128.1, 122.8, 52.7, 34.5, 31.0, 23.5. MS (ESI, *m/z*) 254.2 (M + H^+), 276.2 (M + Na^+). IR (film) *v*/cm^{-1} 2948(s), 1731(vs), 1585(s), 1361(m), 1239(vs), 993(m), 769(s). Anal. calcd for $C_{16}H_{15}NO_2$: C, 75.87; H,5.97; N, 5.53. Found: C, 75.69; H, 6.11; N, 5.65.



Methyl 4-phenyl-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-2-carboxylate

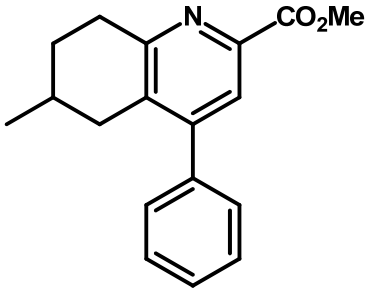
3ac

Petroleum ether/ethyl acetate = 2:1, 75% yield (180 mg),white solid, Mp 62-63 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.84 (s, 1H), 7.43-7.47 (m,3H), 7.28-7.30 (m,2H), 4.00 (s, 3H), 3.17 (t, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 6.4 Hz, 2H), 1.89-1.92 (m, 2H), 1.45-1.54 (m, 2H), 1.35-1.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 150.5, 137.7, 128.3, 128.2, 127.8, 124.5, 52.7, 35.4, 31.0, 30.9, 27.4, 26.4, 25.6. MS (ESI, *m/z*) 296.2 (M + H^+), 318.2 (M + Na^+). IR (film) *v*/cm^{-1} 2935(m), 1713(vs), 1437(w), 1247(s), 701(m). Anal. calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.45; H, 6.96; N, 4.57.



Methyl 7-methyl-4-phenyl-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ad**

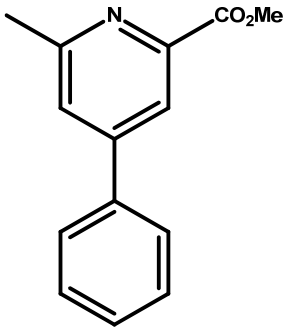
Petroleum ether/ethyl acetate = 2:1, 72% yield (205 mg),yellow solid, Mp 65-66 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.85 (s, 1H), 7.41-7.47 (m, 3H), 7.30-7.32 (m, 2H), 4.00 (s, 3H), 3.26 (q, *J* = 4.4 Hz, 1H), 2.65-2.76 (m, 2H), 1.86-2.05 (m, 2H), 1.27-1.33 (m, 2H), 1.12 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 158.2, 150.2, 144.8, 138.4, 133.6, 128.3, 128.2, 128.0, 123.5, 52.7, 41.7, 30.6, 28.9, 27.2, 21.5. MS (ESI, *m/z*) 282.2 ($M + H^+$), 304.2 ($M + Na^+$). IR (film) *v*/cm^{-1} 3446(m), 2944(vs), 2216(s), 1740(vs), 1445(m), 1134(m), 926(m). Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 77.01; H, 7.02; N, 4.87.



Methyl 6-methyl-4-phenyl-5,6,7,8-tetrahydroquinoline-2-carboxylate **3ae**

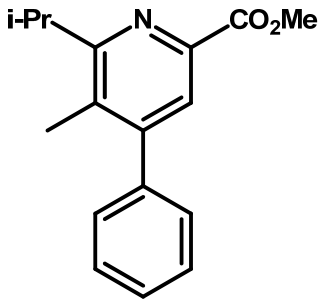
Petroleum ether/ethyl acetate = 2:1, 74% yield (211 mg),yellow solid, Mp 56-57 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.84 (s, 1H), 7.43-7.49 (m, 3H), 7.29-7.32 (m, 2H), 3.99 (s, 3H), 3.20-3.27 (m, 1H), 3.04-3.13 (m, 1H),

2.71-2.76 (m, 1H), 2.32-2.39 (m, 1H), 2.00-2.05 (m, 1H), 1.77-1.84 (m, 1H), 1.53-1.60(m, 1H), 1.01 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 158.2, 150.3, 144.7, 138.4, 133.8, 128.4(2), 128.4(0), 128.1, 123.6, 52.8, 36.1, 32.9, 30.9, 28.9, 21.5. MS (ESI, *m/z*) 282.2 (M + H^+), 304.2 (M + Na^+). IR (film) ν/cm^{-1} 3420(w), 2961(s), 1723(vs), 1454(m), 1238(vs), 779(m), 692(m). Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.69; H, 7.08; N, 5.21.



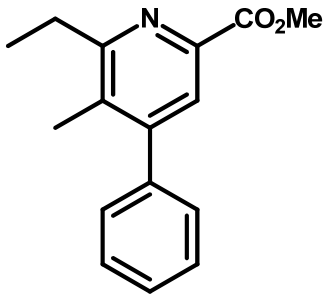
Methyl 6-methyl-4-phenylpicolinate **3af**

Petroleum ether/ethyl acetate = 2:1, 84% yield (169 mg), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.15 (d, J = 1.2 Hz, 1H), 7.61-7.63 (m, 2H), 7.50 (d, J = 1.2 Hz, 1H), 7.40-7.46 (m, 3H), 3.97 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 159.4, 149.7, 148.0, 137.3, 129.3, 129.1, 127.0, 124.4, 120.6, 52.9, 24.7. MS (ESI, *m/z*) 228.1 (M + H^+), 250.1 (M + Na^+). IR (film) ν/cm^{-1} 2940(vs), 1724(vs), 1438(s), 1085(s), 1015(m), 769(vs), 692(s). calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.25; H, 5.47; N, 6.43.



Methyl 6-isopropyl-5-methyl-4-phenylpicolinate **3ag**

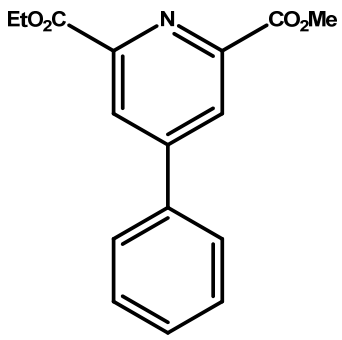
Petroleum ether/ethyl acetate = 2:1, 85% yield (313 mg), yellow solid, Mp 44-45 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.22 (d, *J* = 1.6 Hz, 1H), 7.69-7.71 (m, 2H), 7.47-7.54 (m, 3H), 4.03 (s, 3H), 2.17-2.25 (m, 1H), 1.58 (s, 3H), 0.97 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.7, 149.4, 148.3, 137.6, 129.3, 129.2, 127.1, 124.5, 120.8, 53.0, 47.5, 29.2, 22.4. MS (ESI, *m/z*) 270.2 (M + H^+). IR (film) *v*/cm^{-1} 2963(vs), 1716(vs), 1594(s), 1446(s), 1254(s), 769(m), 684(m). Anal. calcd for $C_{17}H_{19}NO_2$: C, 75.81; H,7.11; N, 5.20. Found: C, 75.77; H, 6.86; N, 5.33.



Methyl 6-ethyl-5-methyl-4-phenylpicolinate **3ah**

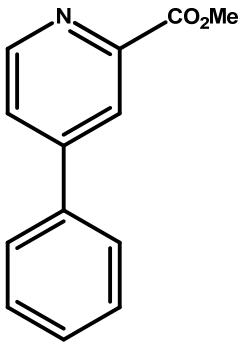
Petroleum ether/ethyl acetate = 5:1, 65% yield (305 mg), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.88 (s, 1H), 7.43-7.49 (m, 3H), 7.31-7.33 (m, 2H), 4.00 (s, 3H), 3.02 (q, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.36 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.0, 150.7, 144.5, 139.1, 132.4, 128.6, 128.4,

128.0, 124.0, 52.7, 29.5, 16.0, 13.1. MS (ESI, *m/z*) 256.2 (M + H^+), 278.2 (M + Na^+). IR (film) *v*/cm^{-1} 2963(vs), 2239(w), 1747(vs), 1594(m), 1231(m), 778(s). Anal. calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.10; H, 6.63; N, 5.61.



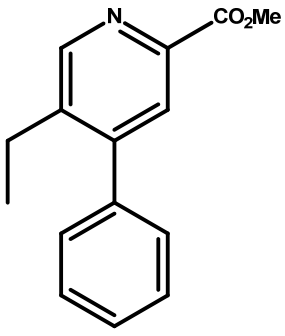
2-ethyl 6-methyl 4-phenylpyridine-2,6-dicarboxylate **3ai**

Petroleum ether/ethyl acetate = 2:1, 74% yield (184 mg), white solid, Mp 42-43 ℃. ^1H NMR (400 MHz, $CDCl_3$)δ 8.48-8.50 (m, 2H), 7.70-7.73 (m, 2H), 7.46-7.50 (m, 3H), 4.48 (q, *J* = 6.8 Hz, 2H), 4.01 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.8, 151.1, 149.2, 148.9, 136.2, 130.1, 129.4, 127.2, 125.6(4), 125.5(7), 62.5, 53.2, 14.3. MS (ESI, *m/z*) 286.1 (M + H^+). IR (film) *v*/cm^{-1} 2987(s), 2239 (m), 1716(vs), 1438(s), 1245(s), 1032(s), 908(s). Anal. calcd for $C_{16}H_{15}NO_4$: C, 67.36; H,5.30; N, 4.91. Found: C, 67.49; H, 5.54; N, 5.12.



Methyl 4-phenylpicolinate **3aj**

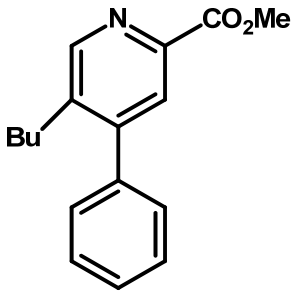
Petroleum ether/ethyl acetate = 2:1, 62% yield (347 mg), brown oil. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.80-8.81 (m, 1H), 8.41 (d, *J* = 1.6 Hz, 1H) 7.50-7.73 (m, 6H), 4.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 150.1, 149.5, 148.3, 136.9, 129.5, 129.1, 126.9, 124.5, 122.9, 52.8. MS (ESI, *m/z*) 214.1 (M + H^+), 236.1 (M + Na^+). IR (film) *v*/cm^{-1} 3064(w), 3032(w), 2948(m), 2239(w), 1739(vs), 1608(s), 1438(s), 1316(s), 961(m), 754(s). Anal. calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.10; H, 5.45; N, 6.30.



Methyl 5-ethyl-4-phenylpicolinate **3ak**

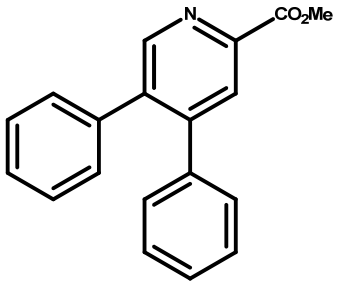
Petroleum ether/ethyl acetate = 2:1, 88% yield (446 mg), brown oil. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.67 (s, 1H), 8.00 (s, 1H), 7.44-7.50 (m, 3H), 7.32-7.34 (m, 2H), 4.01 (s, 3H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 150.5, 149.8, 145.3, 140.7, 138.0, 128.4, 128.3,

128.2, 125.9, 52.7, 23.6, 15.1. MS (ESI, *m/z*) 242.2 (M + H^+), 264.2 (M + Na^+).IR (film) *v*/cm^{-1} 3425(w), 2963(s), 1724(vs), 1594(m), 1431(s), 1246(vs), 1124(s), 707(s). Anal. calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.39; H, 5.99; N, 6.02.



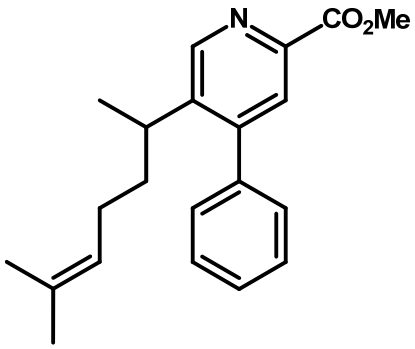
Methyl 5-butyl-4-phenylpicolinate **3al**

Petroleum ether/ethyl acetate = 2:1, 81% yield (317 mg), brown oil. ^1H NMR (400 MHz, $CDCl_3$)δ 8.65 (s, 1H), 8.01 (s, 1H), 7.45-7.50 (m, 3H), 7.30-7.34 (m, 2H),4.02 (s, 3H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.43-1.49 (m, 2H), 1.22-1.29 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 150.7, 149.8, 145.0, 139.3, 137.9, 128.2, 128.1, 127.9, 125.6, 52.3, 32.6, 29.7, 21.9, 13.3. MS (ESI, *m/z*) 270.2 (M + H^+), 292.2 (M + Na^+). IR (film) *v*/cm^{-1} 2961(vs), 1731(vs), 1454(m), 1108(m), 969(w), 701(w). Anal. calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.70; H, 6.86; N, 5.44.



Methyl 4,5-diphenylpicolinate **3am**

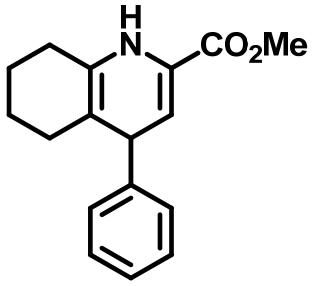
Petroleum ether/ethyl acetate = 2:1, 83% yield (269 mg), brown oil. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.70 (s, 1H), 8.15 (s, 1H), 7.10-7.25 (m, 10H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 151.0, 146.8, 146.6, 138.8, 137.6, 136.6, 129.6, 129.1, 128.9, 128.7, 128.3(2), 128.3(0), 128.1, 127.8, 126.2, 52.8. MS (ESI, *m/z*) 290.1 (M + H$^+$). IR (film) *ν*/cm^{-1} 3055(s), 2940(s), 1955(w), 1878(w), 1739(s), 1115(w), 701(m). Anal. calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 79.12; H, 5.45; N, 4.69.



Methyl 5-(6-methylhept-5-en-2-yl)-4-phenylpicolinate **3an**

Petroleum ether/ethyl acetate = 2:1, 92% yield (453 mg), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.74 (s, 1H), 7.99 (s, 1H), 7.45-7.51 (m, 3H), 7.28-7.30 (m, 2H), 4.88 (t, *J* = 6.8 Hz, 1H), 4.03 (s, 3H), 3.02 (q, *J* = 7.2 Hz, 1H), 1.77-1.83 (m, 2H), 1.63-1.74 (m, 2H), 1.60 (s, 3H), 1.46 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 149.8, 148.6, 144.6, 144.1, 137.9, 131.7, 128.3, 128.2, 127.9, 125.7, 123.3, 52.4, 37.5, 32.5, 25.6, 25.3, 21.7, 17.3. MS (ESI, *m/z*) 324.3 (M + H$^+$), 346.3 (M + Na$^+$).IR (film) *ν*/cm^{-1} 2935(vs), 2233(m), 1740(vs), 1573(m), 1428(s), 1307(w), 1247(w), 1125(m), 909(w), 709(m). Anal.

calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 78.16; H, 7.87; N, 4.19.



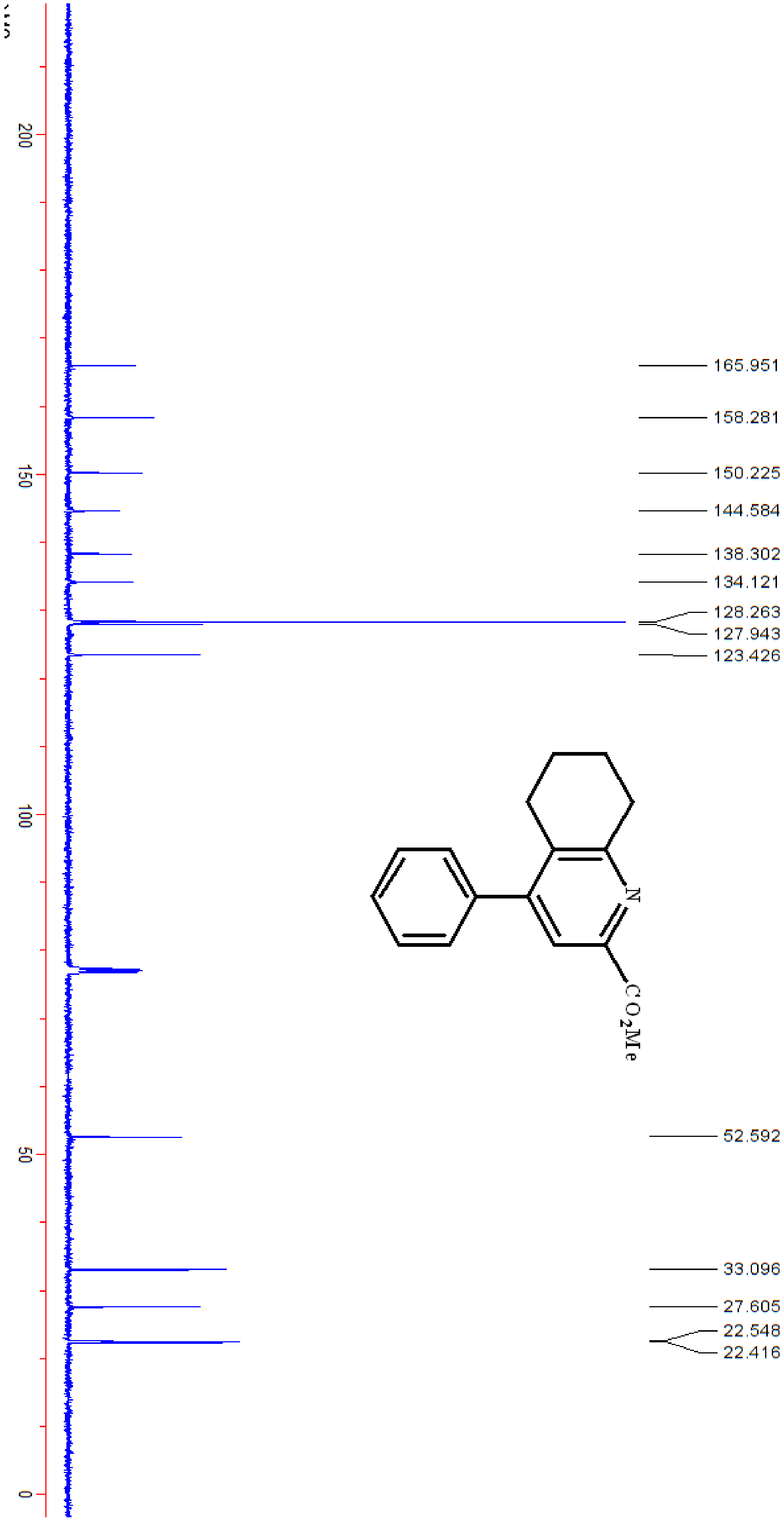
Methyl 4-phenyl-1,4,5,6,7,8-hexahydroquinoline-2-carboxylate **4aa**

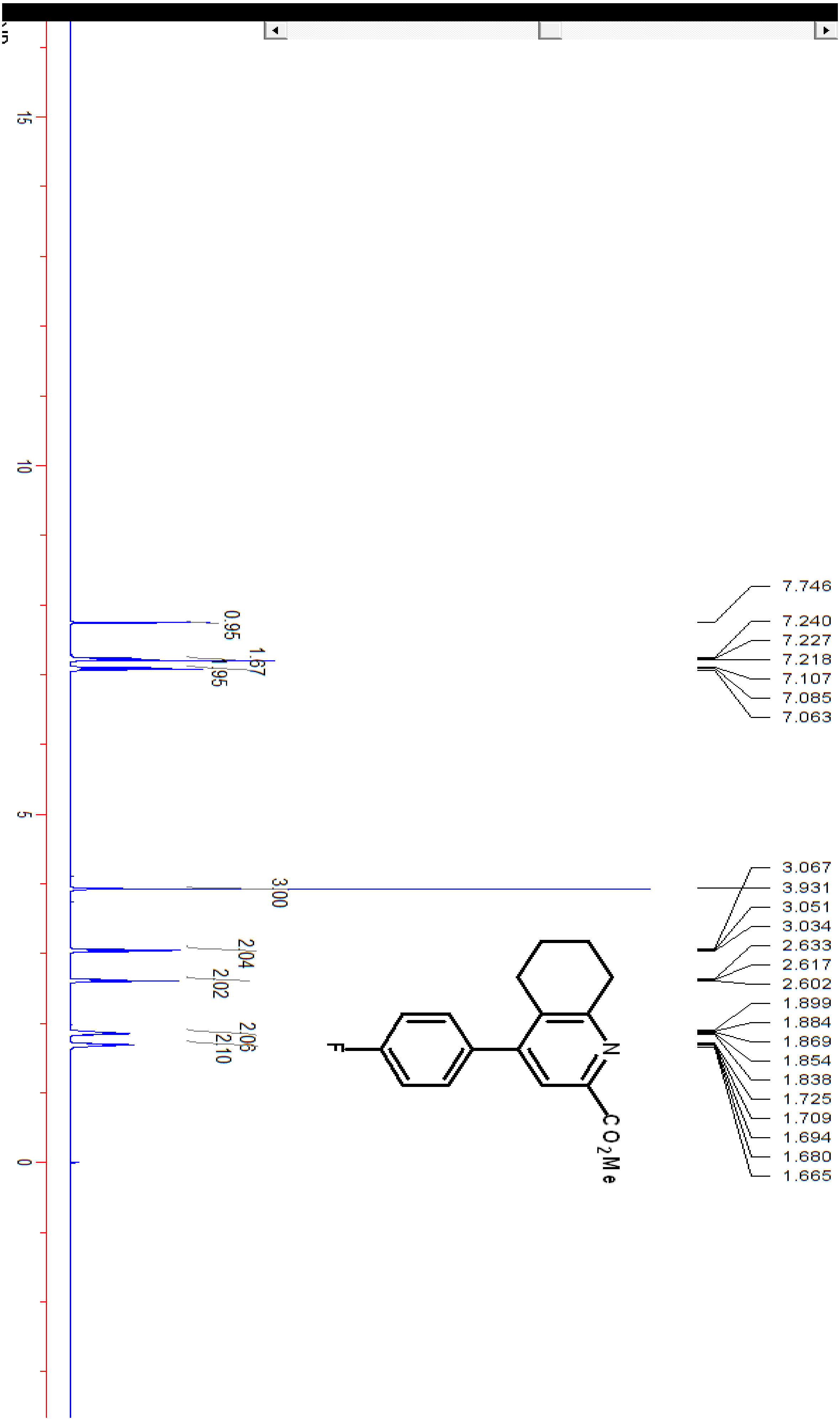
Petroleum ether/ethyl acetate =5:1, 95% yield (213 mg),yellow solid, Mp 40-41 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.19-7.31 (m, 5H), 5.60-5.61 (m, 1H), 5.63 (s, 1H), 4.07 (d, J = 5.2 Hz, 1H), 3.75 (s, 3H), 2.08-2.12 (m, 2H), 1.83-1.89 (m, 2H), 1.68-1.75 (m, 2H), 1.57-1.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 146.3, 129.3, 128.2(3), 128.1(5), 127.7, 126.1, 108.9, 104.1, 51.8, 46.1, 26.8, 24.8, 22.9, 22.3. MS (ESI, m/z) 270.2 ($M + H^+$), 292.2 ($M + Na^+$).IR (film) v/cm^{-1} 2938(vs), 1695(vs), 1439(m), 1259(s), 760(w), 696(s). Anal. calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.67; H, 6.92; N, 5.04.

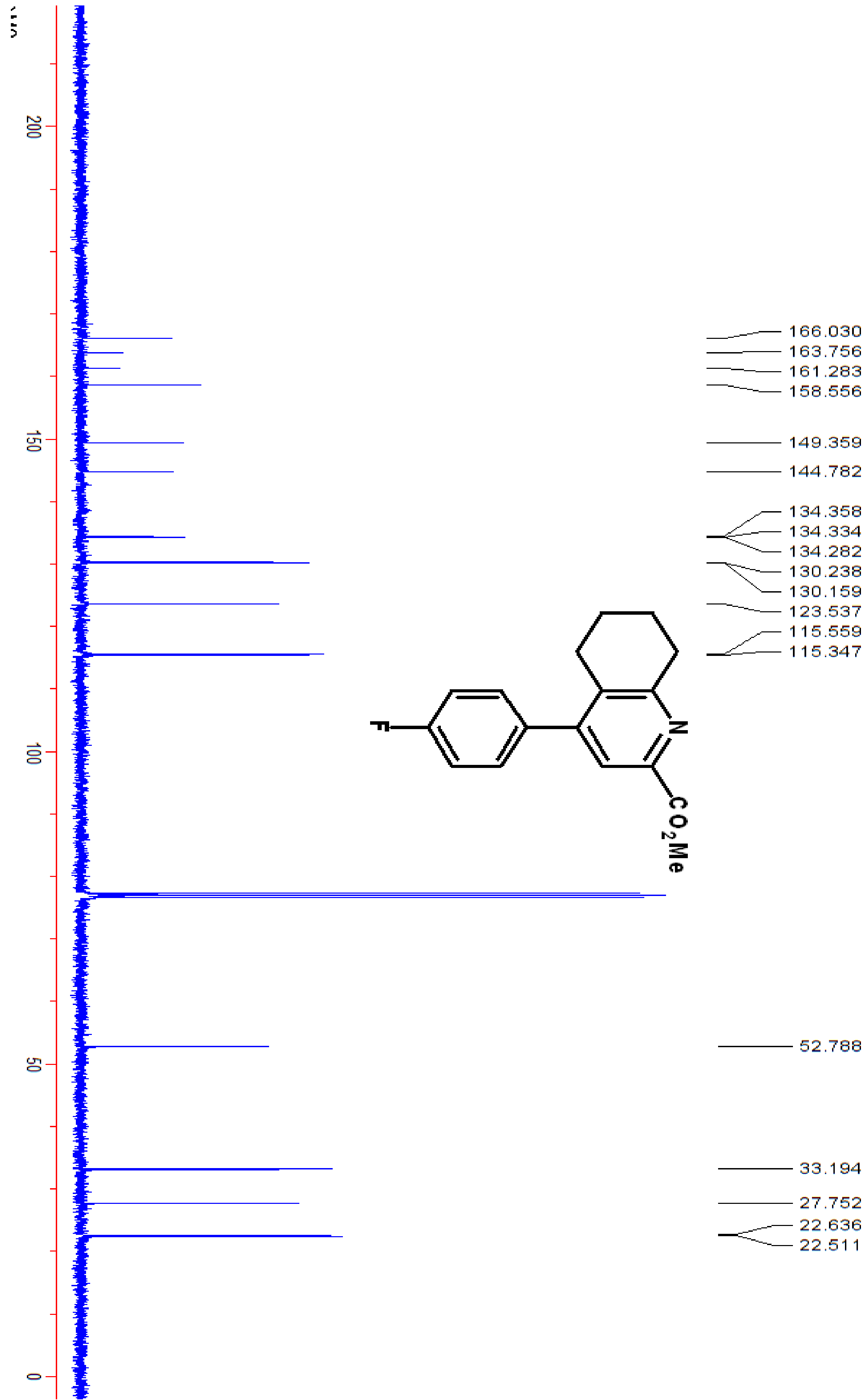
Reference:

1. (a) Cao, C. L.; Sun, X. L.; Kang, Y. B.; Tang, Y. *Org. Lett.* **2007**, *9*, 4151. (b) Palacios, F.; Vicario, J.; Aparicio, D. *Eur. J. Org. Chem.* **2006**, 2843.

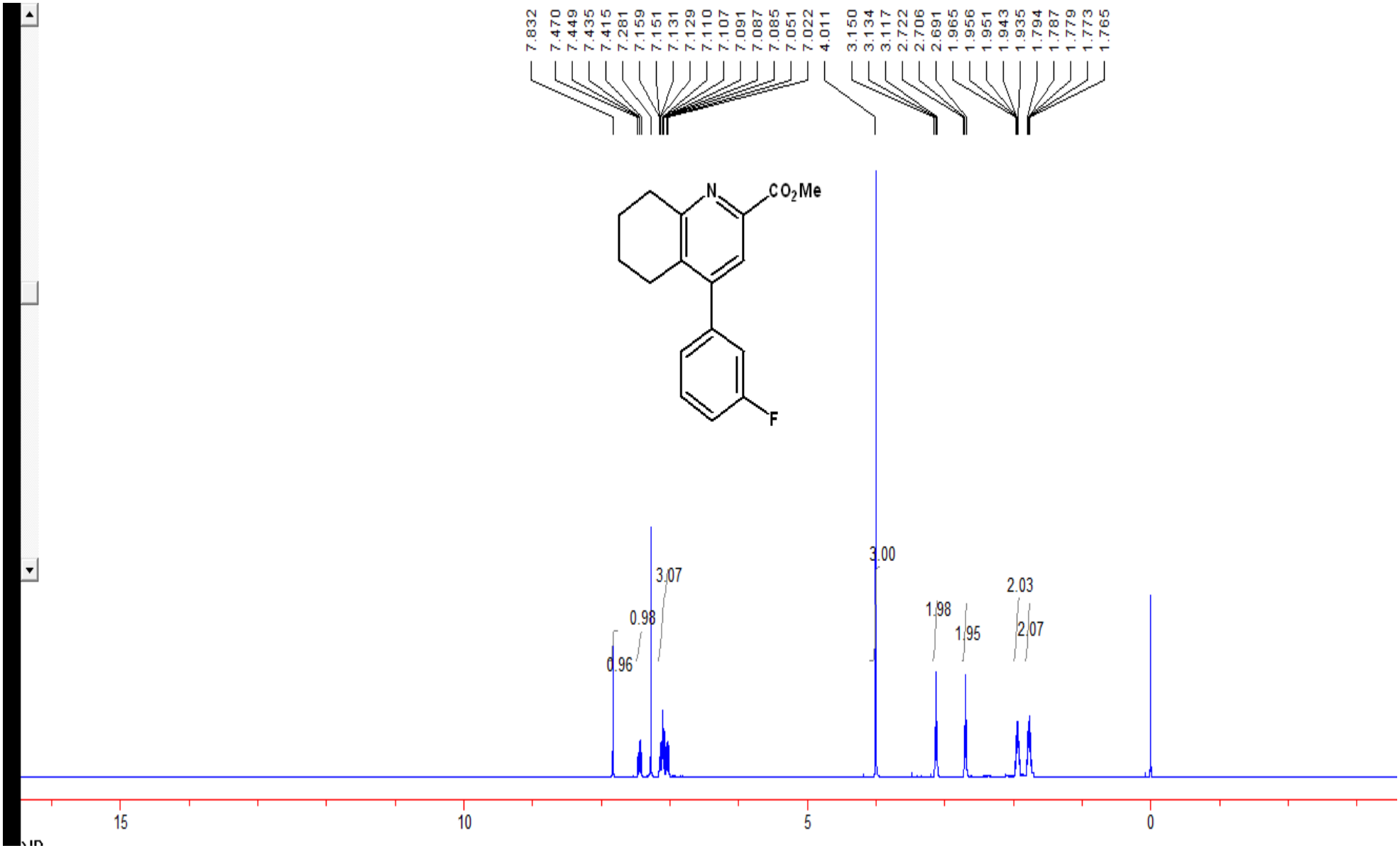
Spectroscopic Data for Products

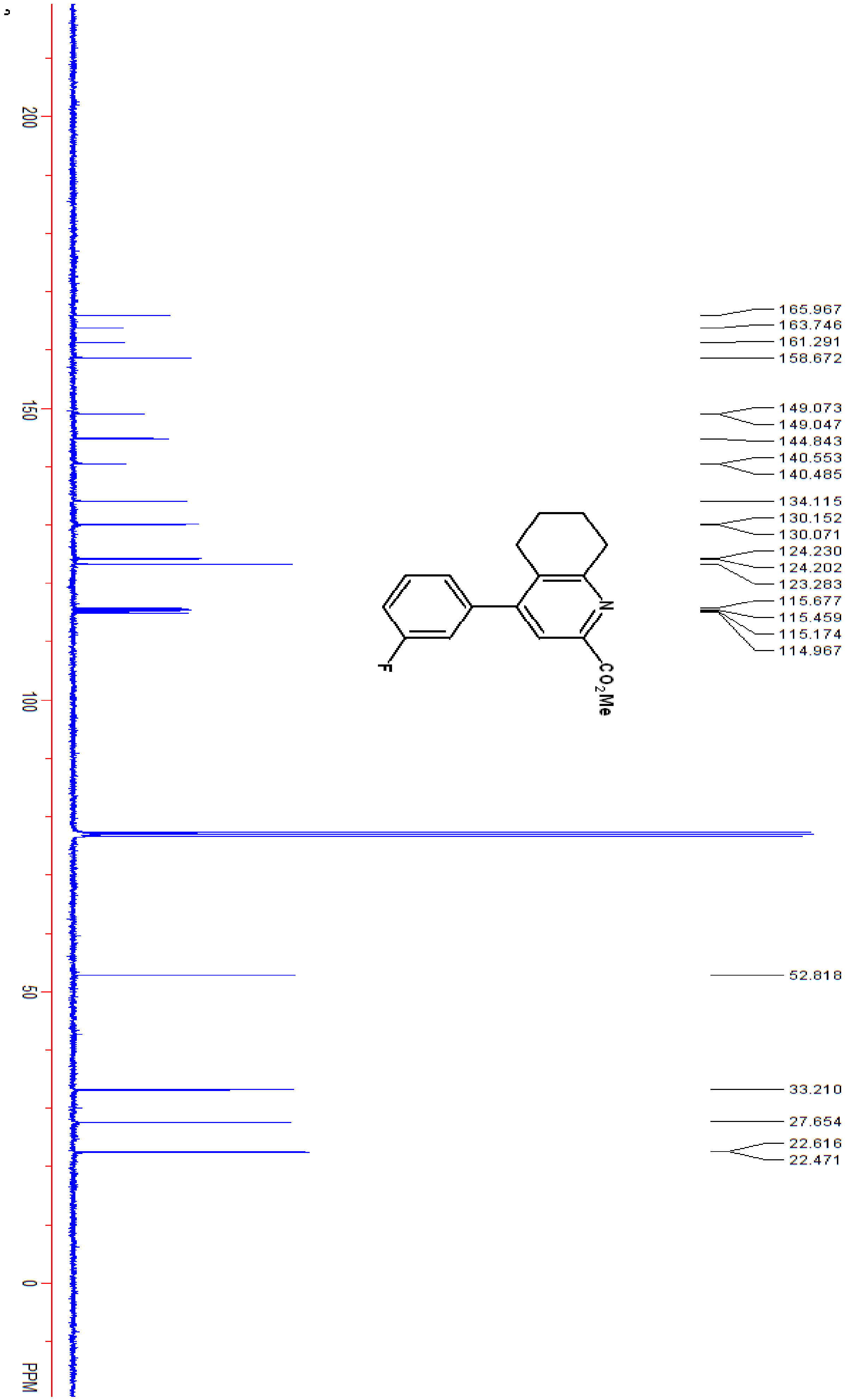

165.951
158.281
150.225
144.584
138.302
134.121
128.263
127.943
123.426
52.592
33.096
27.605
22.548
22.416
200
150
100
50
0
N
CO2Me


7.746
7.240
7.227
7.218
7.107
7.085
7.063
3.067
3.931
3.051
3.034
2.633
2.617
2.602
1.899
1.884
1.869
1.854
1.838
1.725
1.709
1.694
1.680
1.665
0.95
1.67
1.95
3.00
2.04
2.02
2.06
2.10
15
10
5
0
N
F
CO_2Me

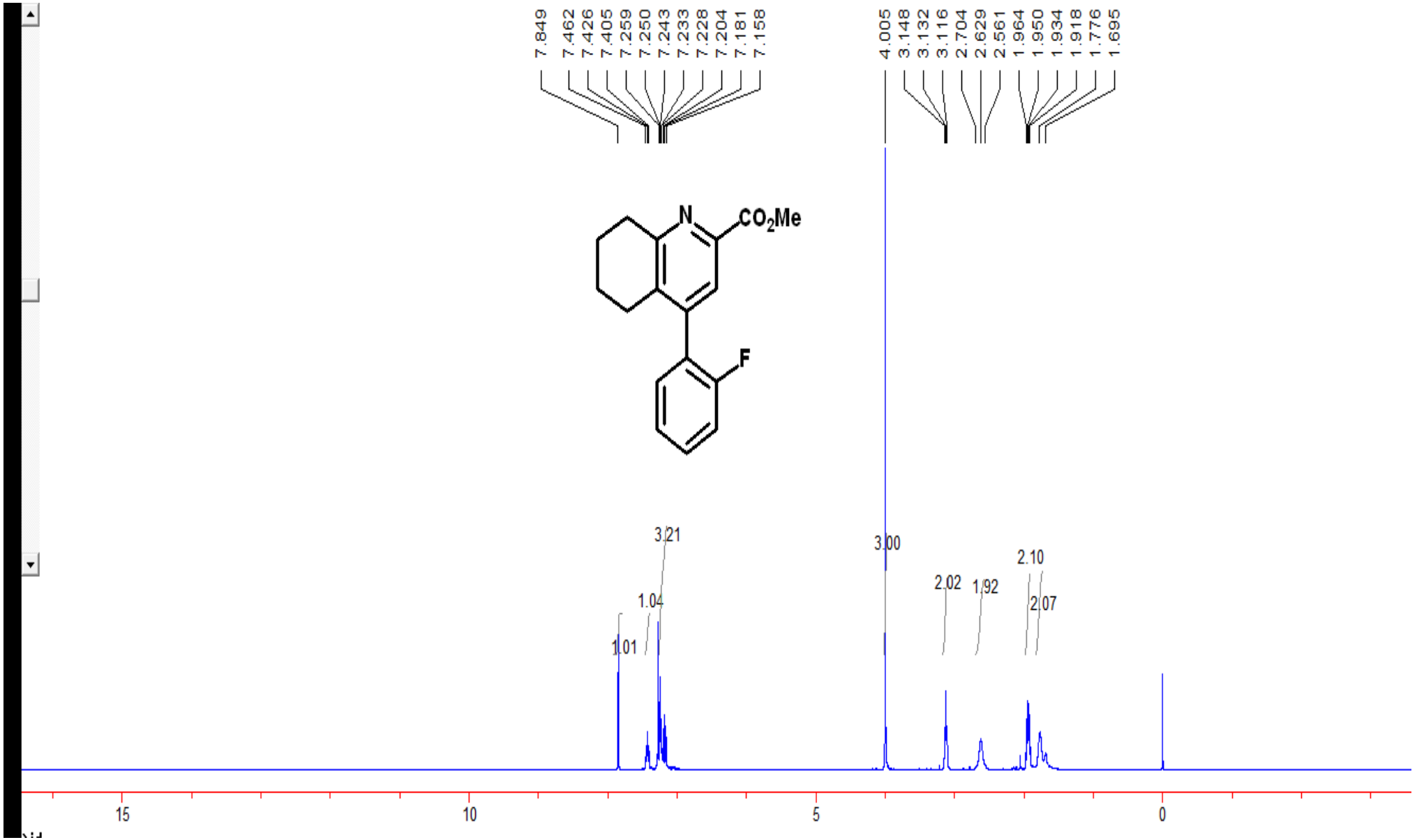


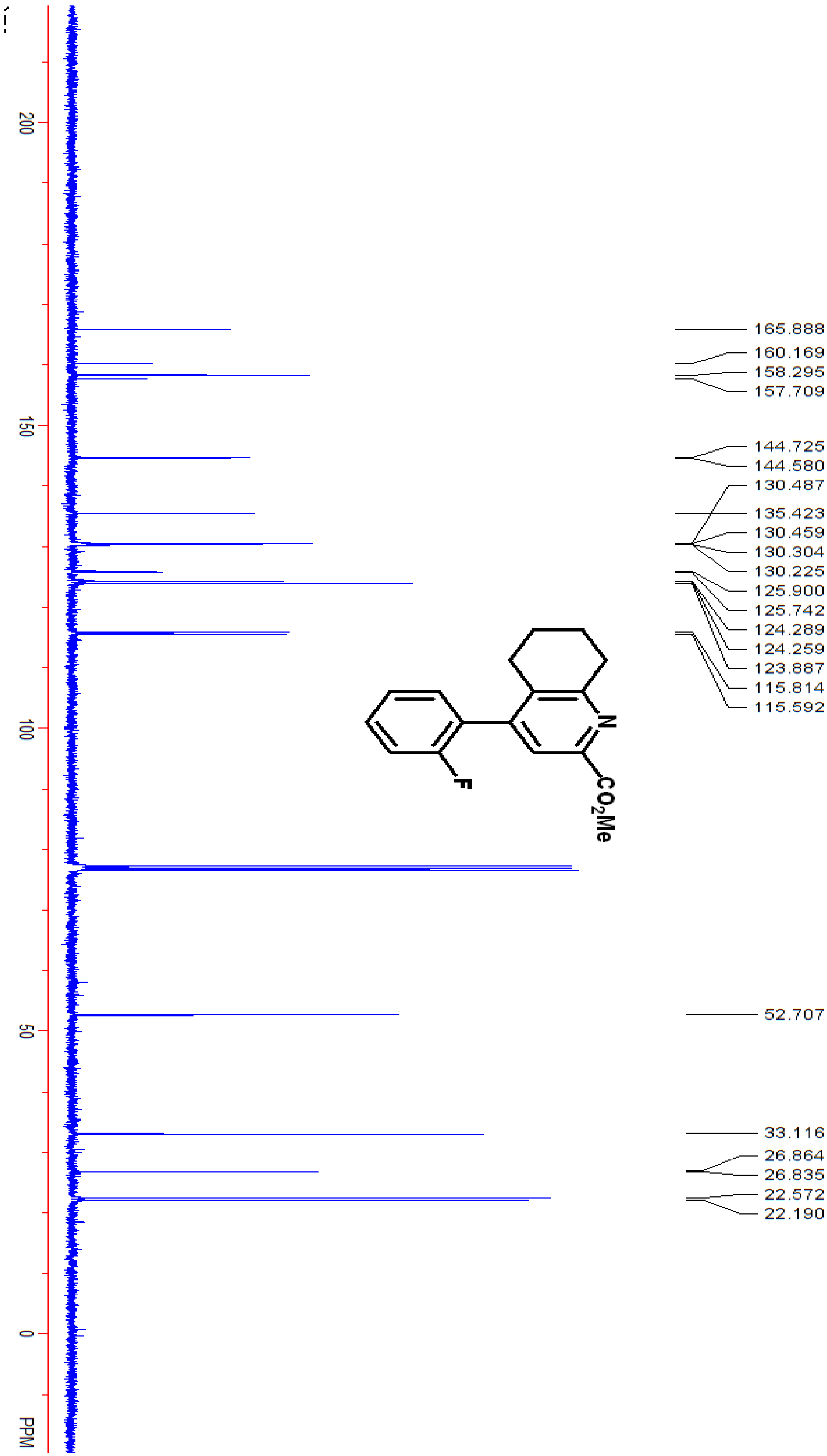
166.030
163.756
161.283
158.556
149.359
144.782
134.358
134.334
134.282
130.238
130.159
123.537
115.559
115.347
52.788
33.194
27.752
22.636
22.511
F
N
CO2Me
200
150
100
50
0


7.832
7.470
7.449
7.435
7.415
7.281
7.159
7.151
7.131
7.129
7.110
7.107
7.091
7.087
7.085
7.051
7.022
4.011
3.150
3.134
3.117
2.722
2.706
2.691
1.965
1.956
1.951
1.943
1.935
1.794
1.787
1.779
1.773
1.765
N
CO2Me
F
0.96
0.98
3.07
3.00
1.98
1.95
2.03
2.07
15
10
5
0

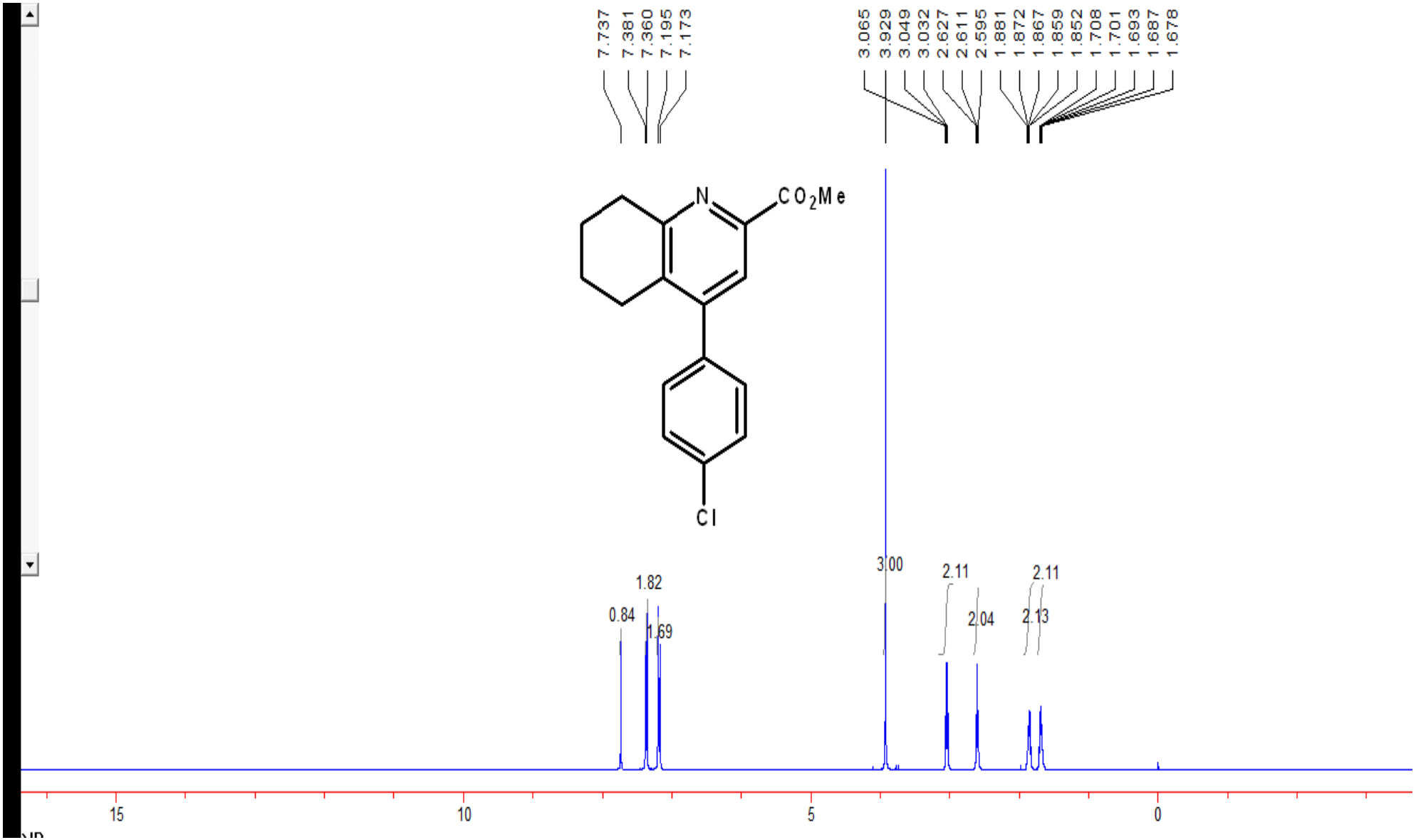


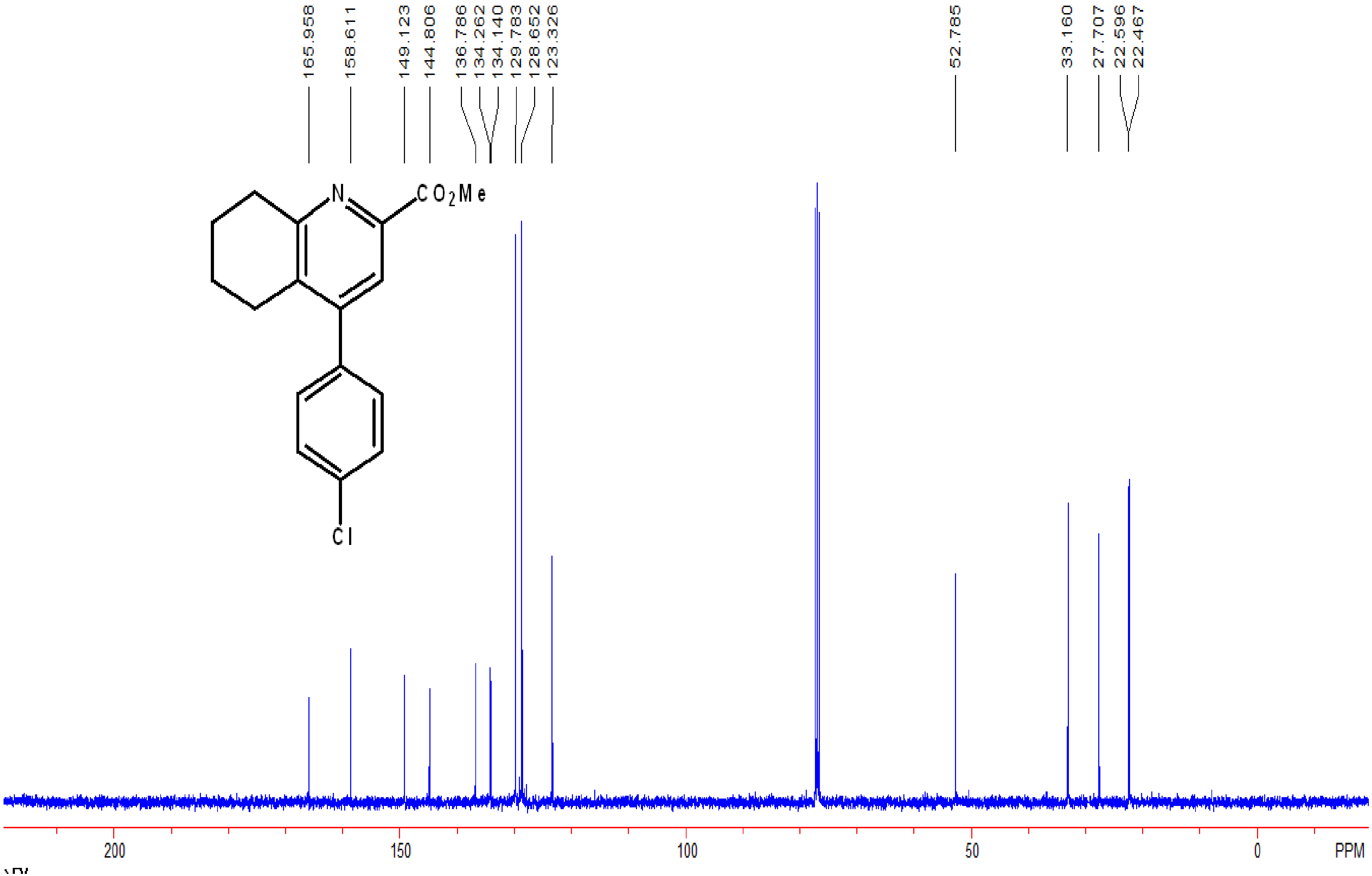
165.967
163.746
161.291
158.672
149.073
149.047
144.843
140.553
140.485
134.115
130.152
130.071
124.230
124.202
123.283
115.677
115.459
115.174
114.967
52.818
33.210
27.654
22.616
22.471
200
150
100
50
0
PPM
N
F
CO2Me

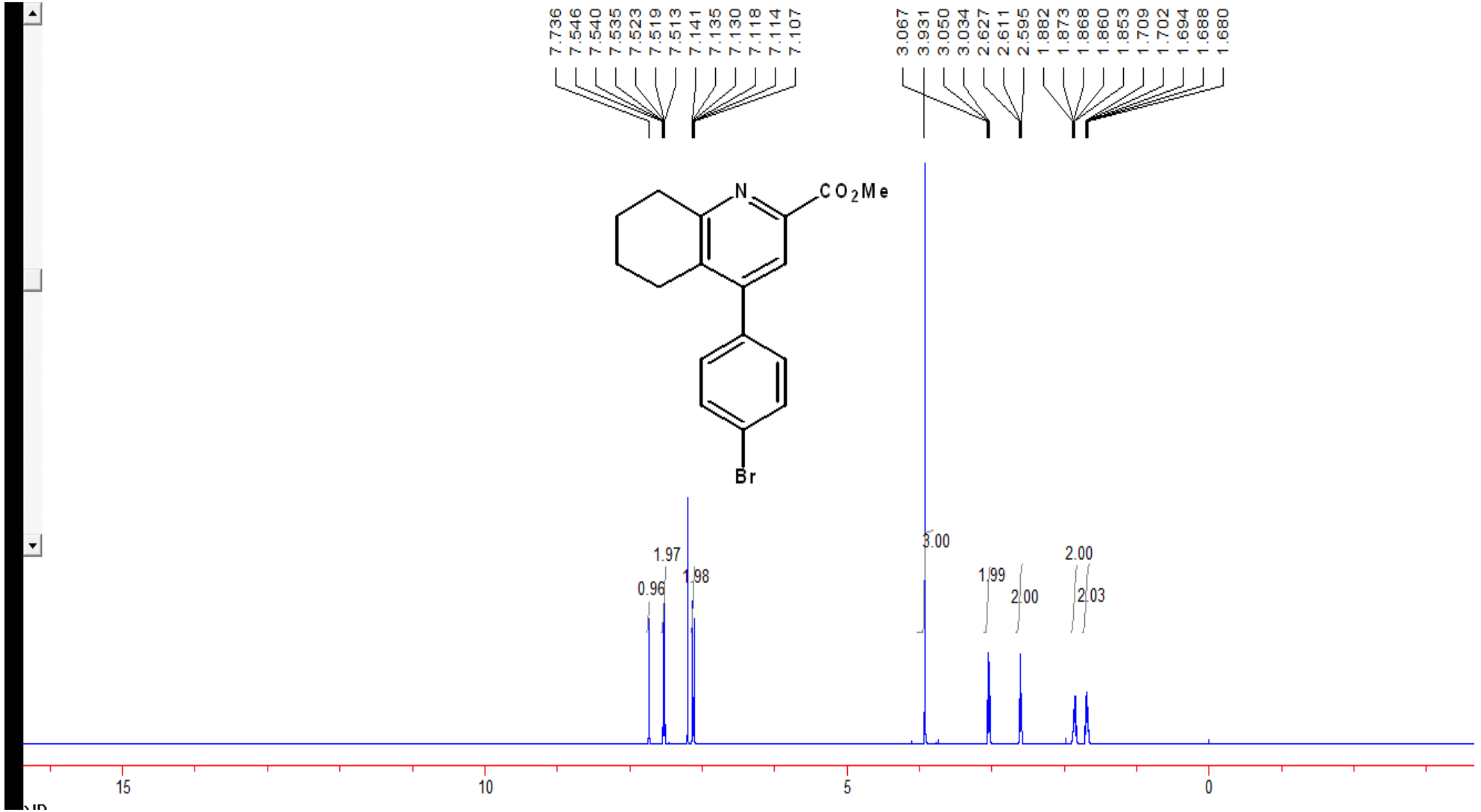

7.849
7.462
7.426
7.405
7.259
7.250
7.243
7.233
7.228
7.204
7.181
7.158
4.005
3.148
3.132
3.116
2.704
2.629
2.561
1.964
1.950
1.934
1.918
1.776
1.695
N
CO2Me
F
3.21
1.04
1.01
3.00
2.02
1.92
2.10
2.07
15
10
5
0

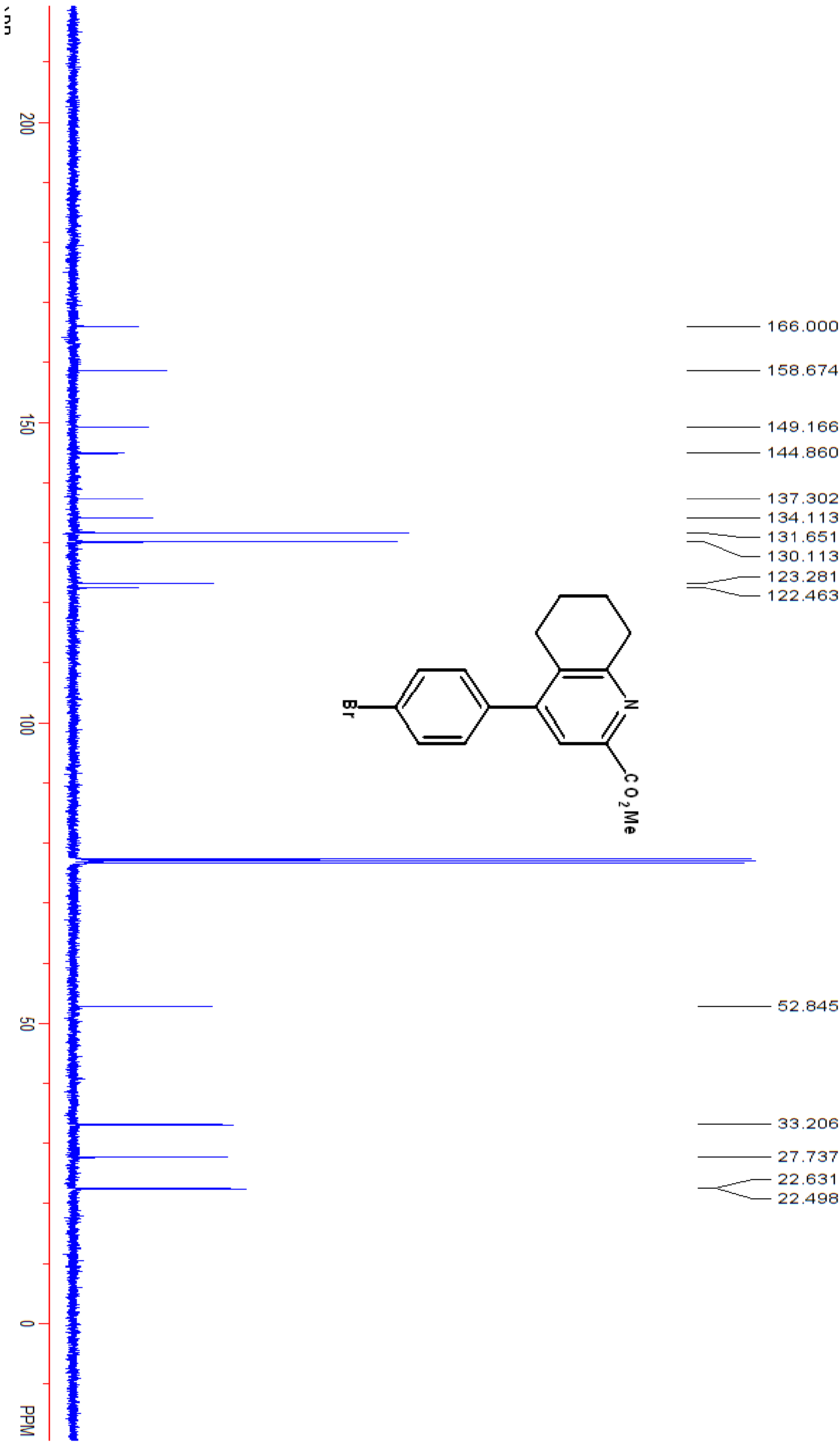


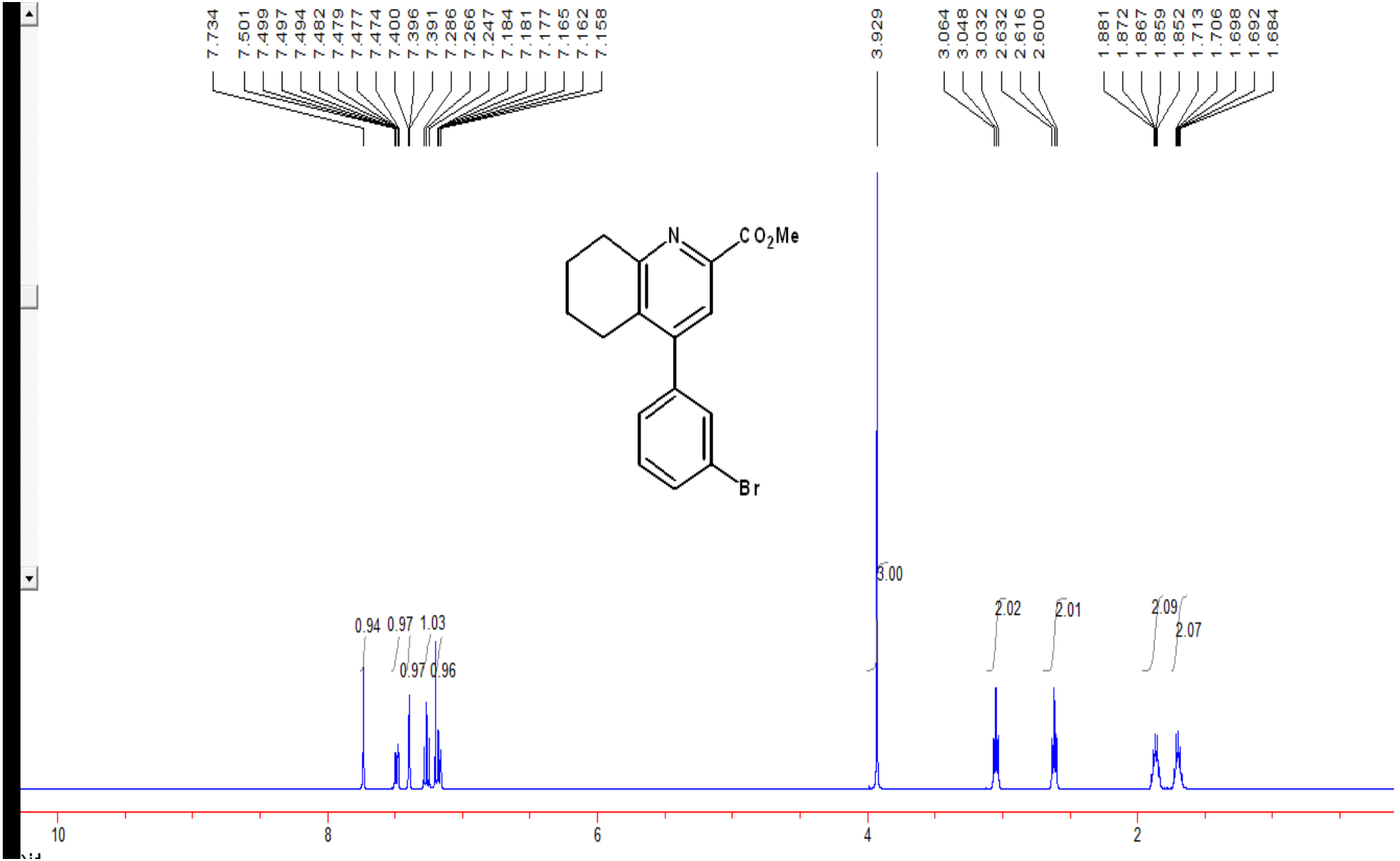
165.888
160.169
158.295
157.709
144.725
144.580
130.487
135.423
130.459
130.304
130.225
125.900
125.742
124.289
124.259
123.887
115.814
115.592
52.707
33.116
26.864
26.835
22.572
22.190
N
F
CO2Me
200
150
100
50
0
PPM

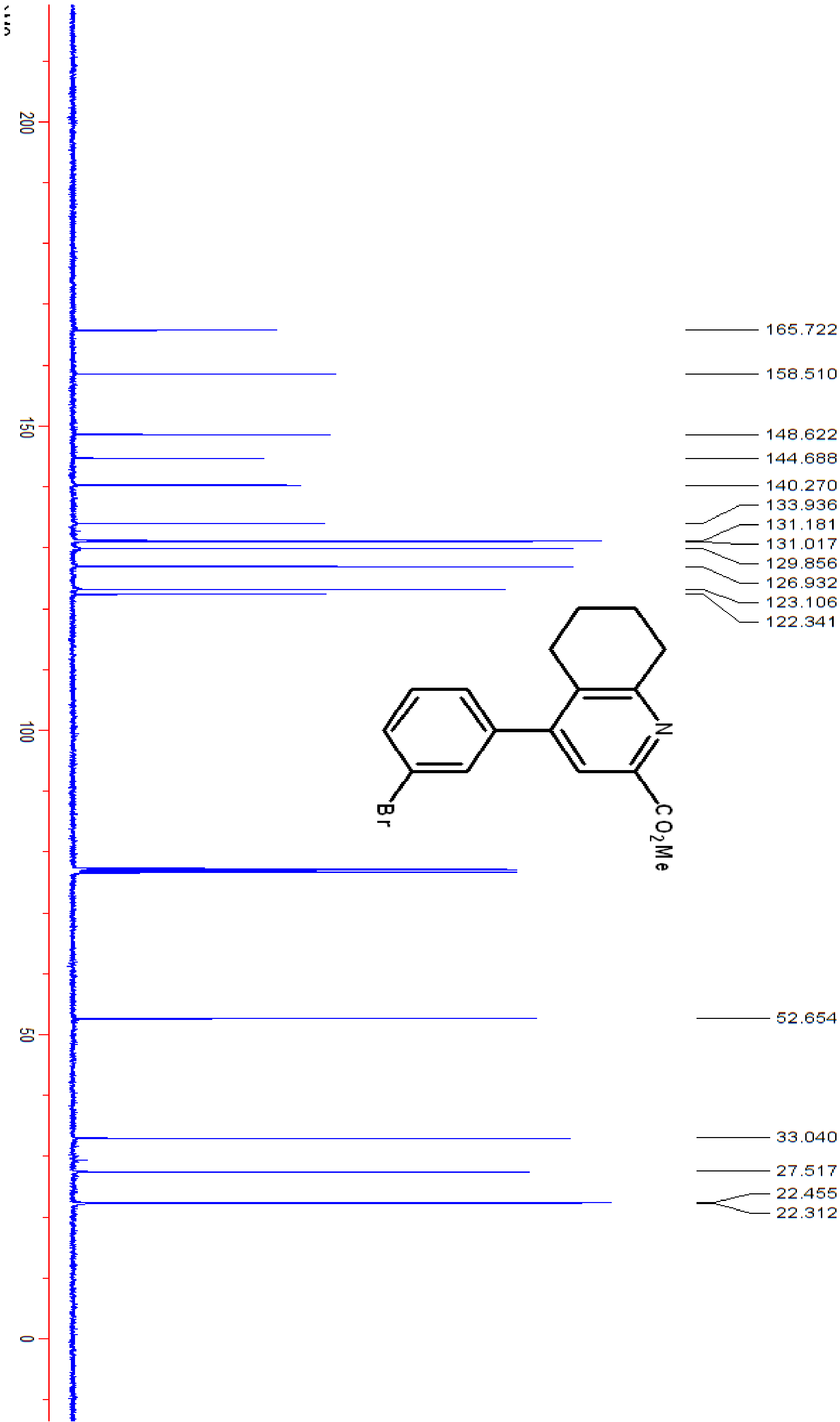

7.737
7.381
7.360
7.195
7.173
3.065
3.929
3.049
3.032
2.627
2.611
2.595
1.881
1.872
1.867
1.859
1.852
1.708
1.701
1.693
1.687
1.678
N
CO2Me
Cl
0.84
1.82
1.69
3.00
2.11
2.04
2.11
2.13
15
10
5
0

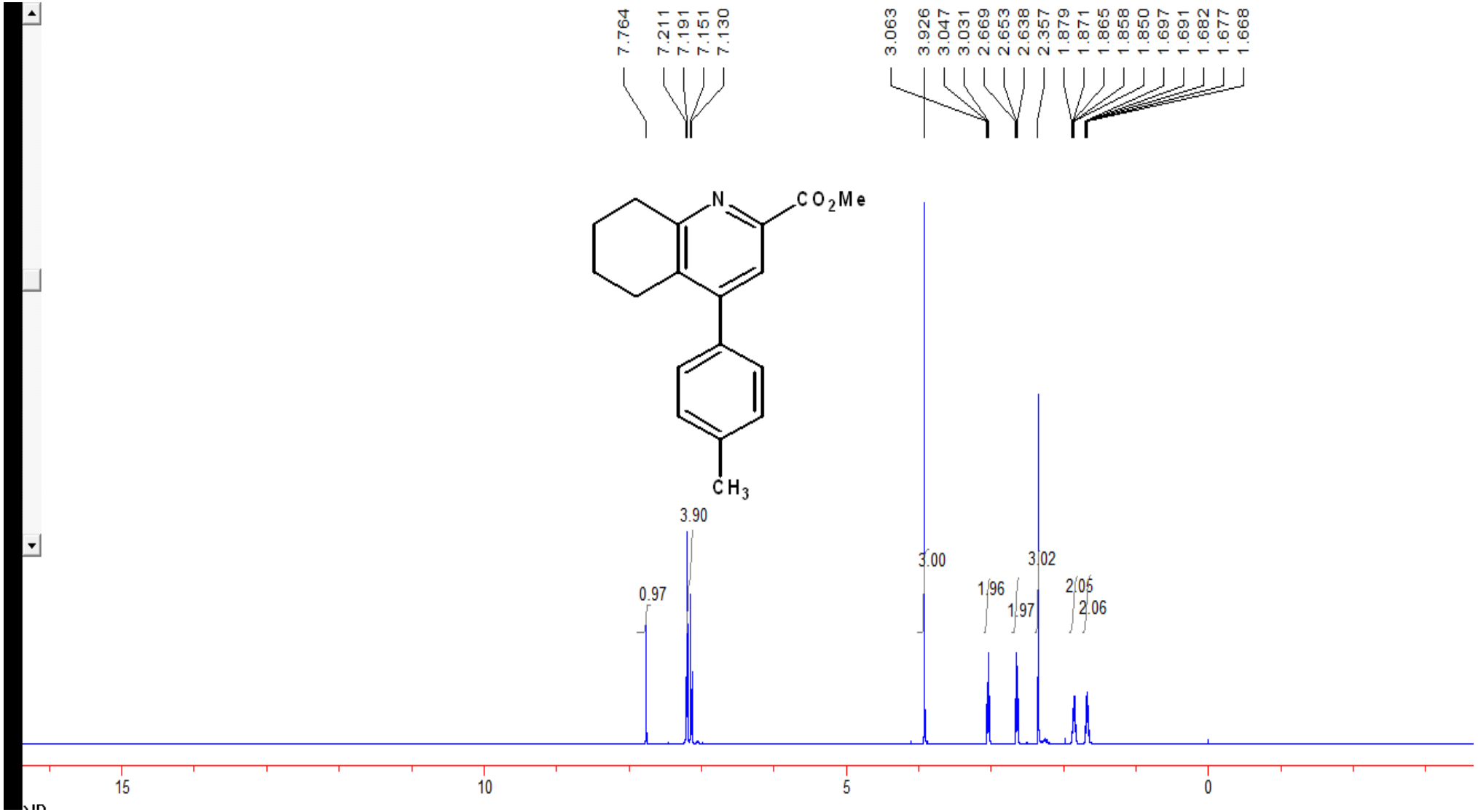

165.958
158.611
149.123
144.806
136.786
134.262
134.140
129.783
128.652
123.326
52.785
33.160
27.707
22.596
22.467
N
CO_2Me
Cl
200
150
100
50
0
PPM

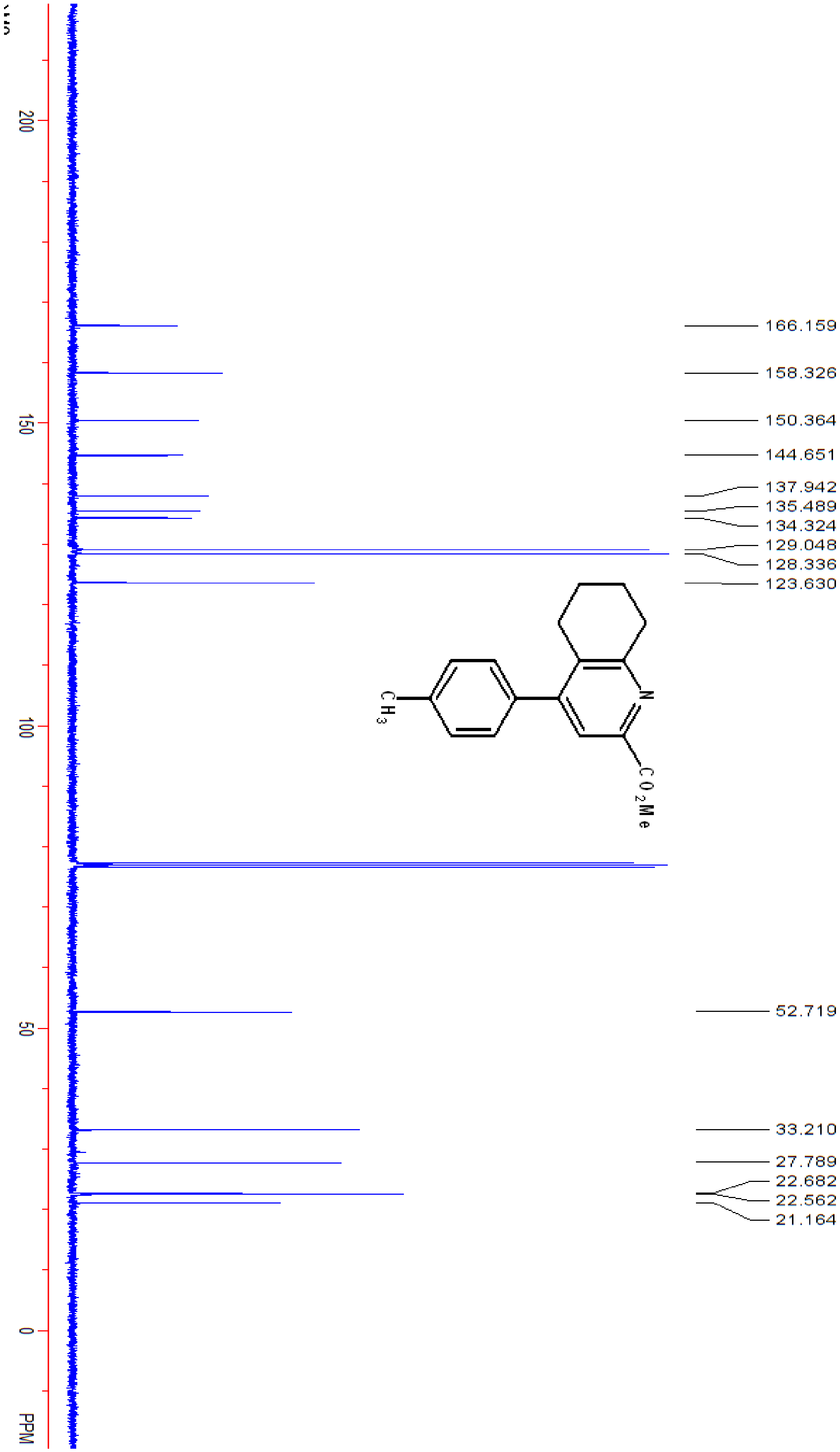

7.736
7.546
7.540
7.535
7.523
7.519
7.513
7.141
7.135
7.130
7.118
7.114
7.107
3.067
3.931
3.050
3.034
2.627
2.611
2.595
1.882
1.873
1.868
1.860
1.853
1.709
1.702
1.694
1.688
1.680
N
CO2Me
Br
0.96
1.97
1.98
3.00
1.99
2.00
2.00
2.03
15
10
5
0


166.000
158.674
149.166
144.860
137.302
134.113
131.651
130.113
123.281
122.463
52.845
33.206
27.737
22.631
22.498
200
150
100
50
0
PPM
Br
N
CO2Me

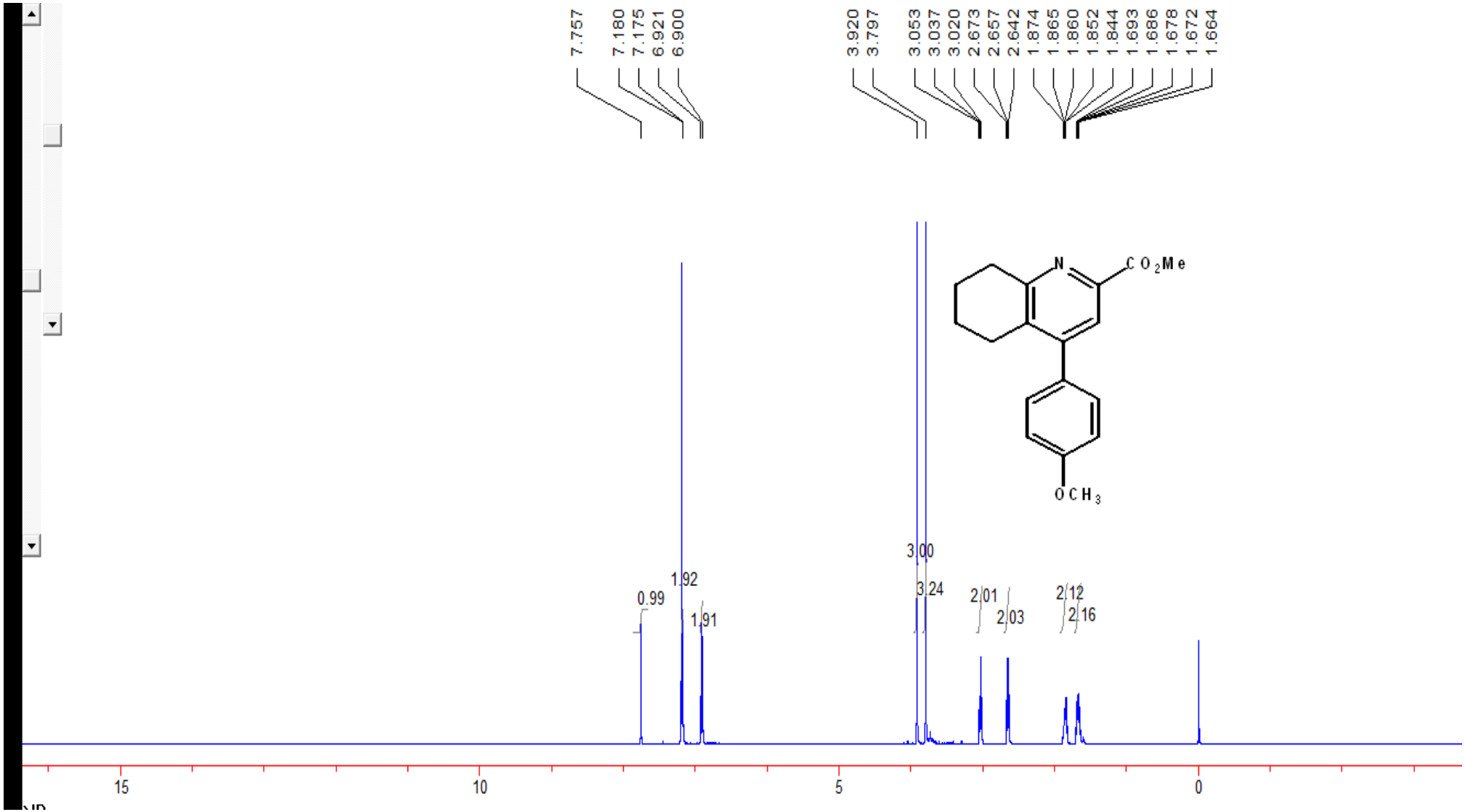

7.734
7.501
7.499
7.497
7.494
7.482
7.479
7.477
7.474
7.400
7.396
7.391
7.286
7.266
7.247
7.184
7.181
7.177
7.165
7.162
7.158
3.929
3.064
3.048
3.032
2.632
2.616
2.600
1.881
1.872
1.867
1.859
1.852
1.713
1.706
1.698
1.692
1.684
N
CO2Me
Br
0.94
0.97
1.03
0.97
0.96
3.00
2.02
2.01
2.09
2.07
10
8
6
4
2

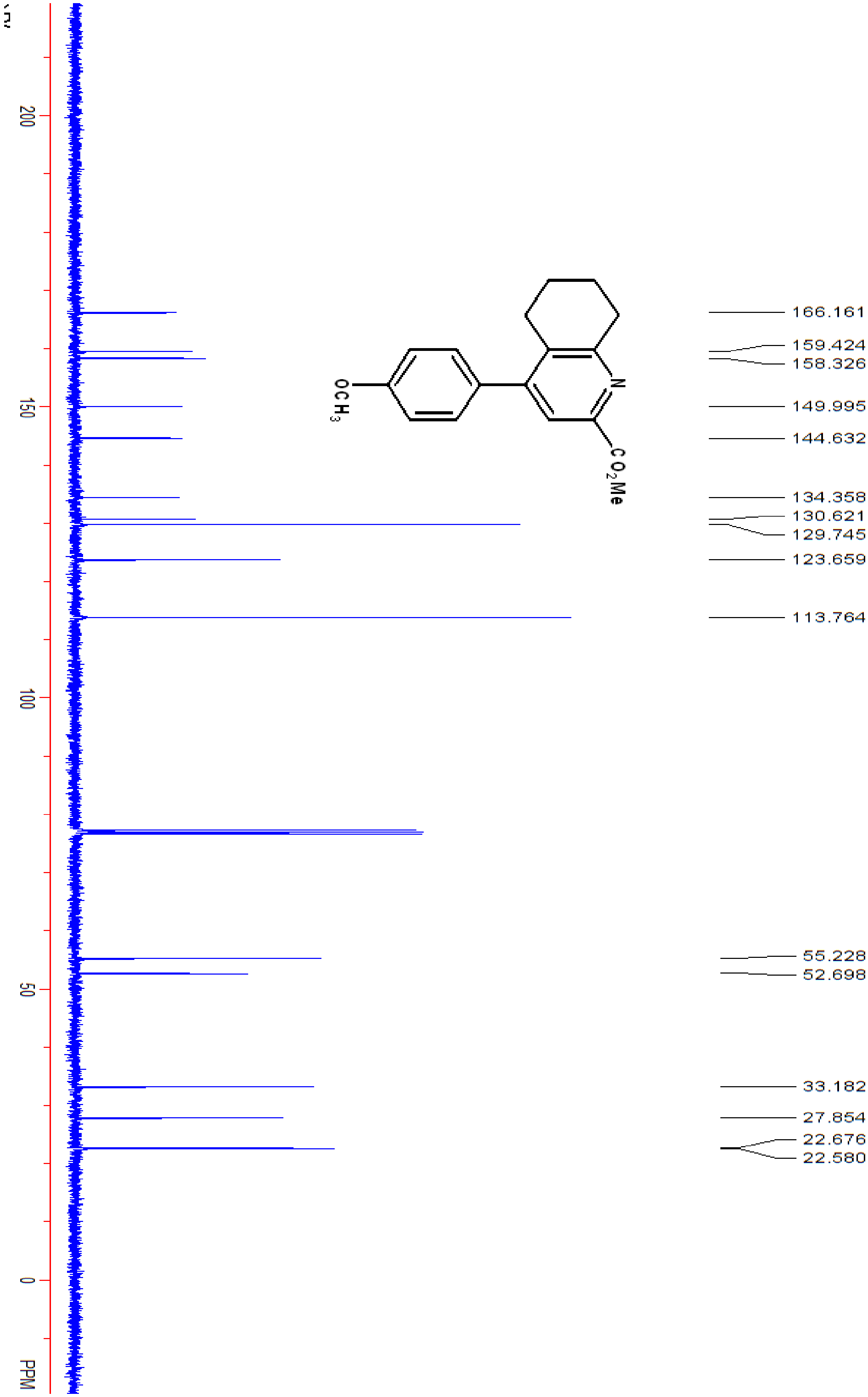

165.722
158.510
148.622
144.688
140.270
133.936
131.181
131.017
129.856
126.932
123.106
122.341
52.654
33.040
27.517
22.455
22.312
200
150
100
50
0
N
CO2Me
Br


7.764
7.211
7.191
7.151
7.130
3.063
3.926
3.047
3.031
2.669
2.653
2.638
2.357
1.879
1.871
1.865
1.858
1.850
1.697
1.691
1.682
1.677
1.668
N
CO2Me
CH3
3.90
0.97
3.00
1.96
1.97
3.02
2.05
2.06
15
10
5
0

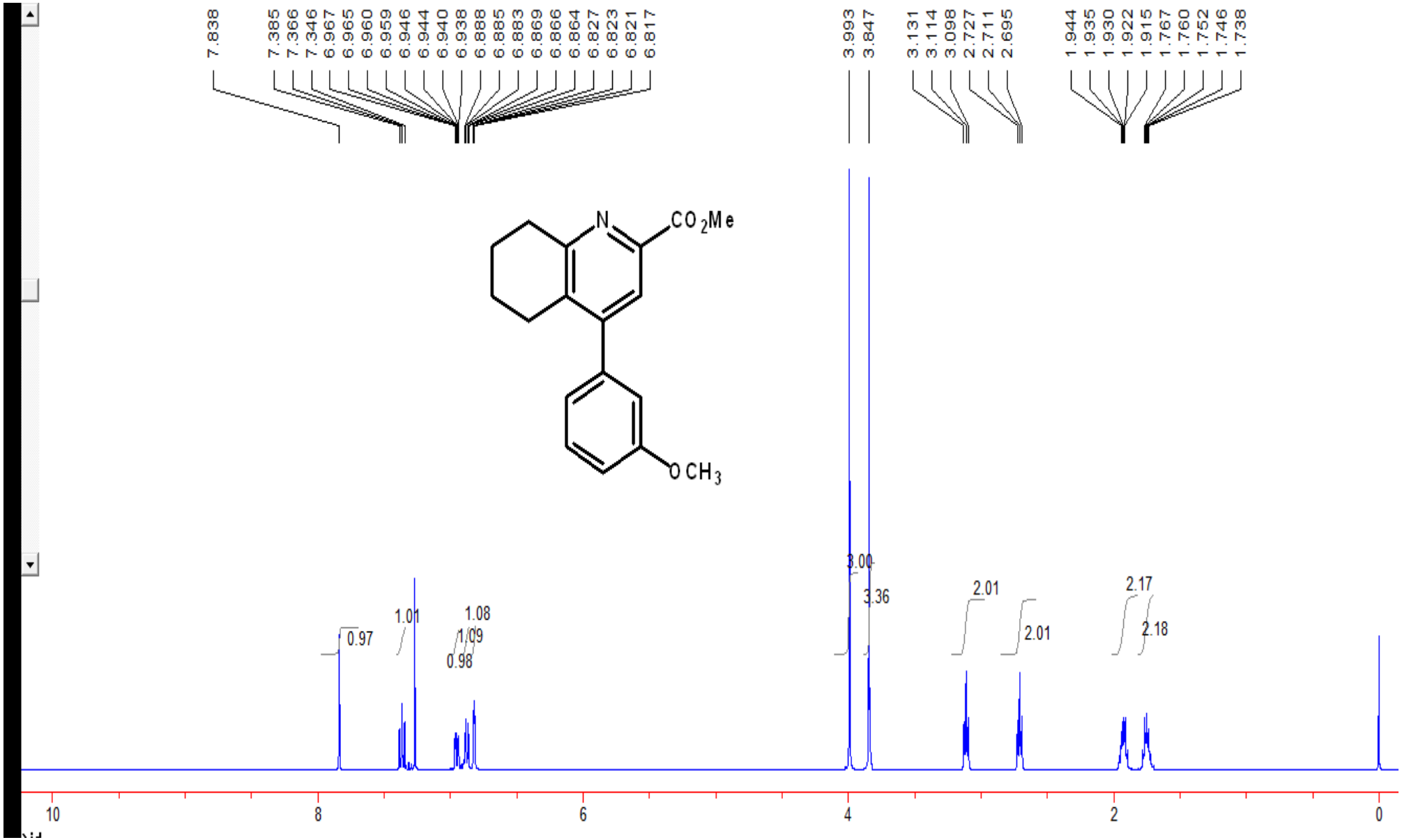


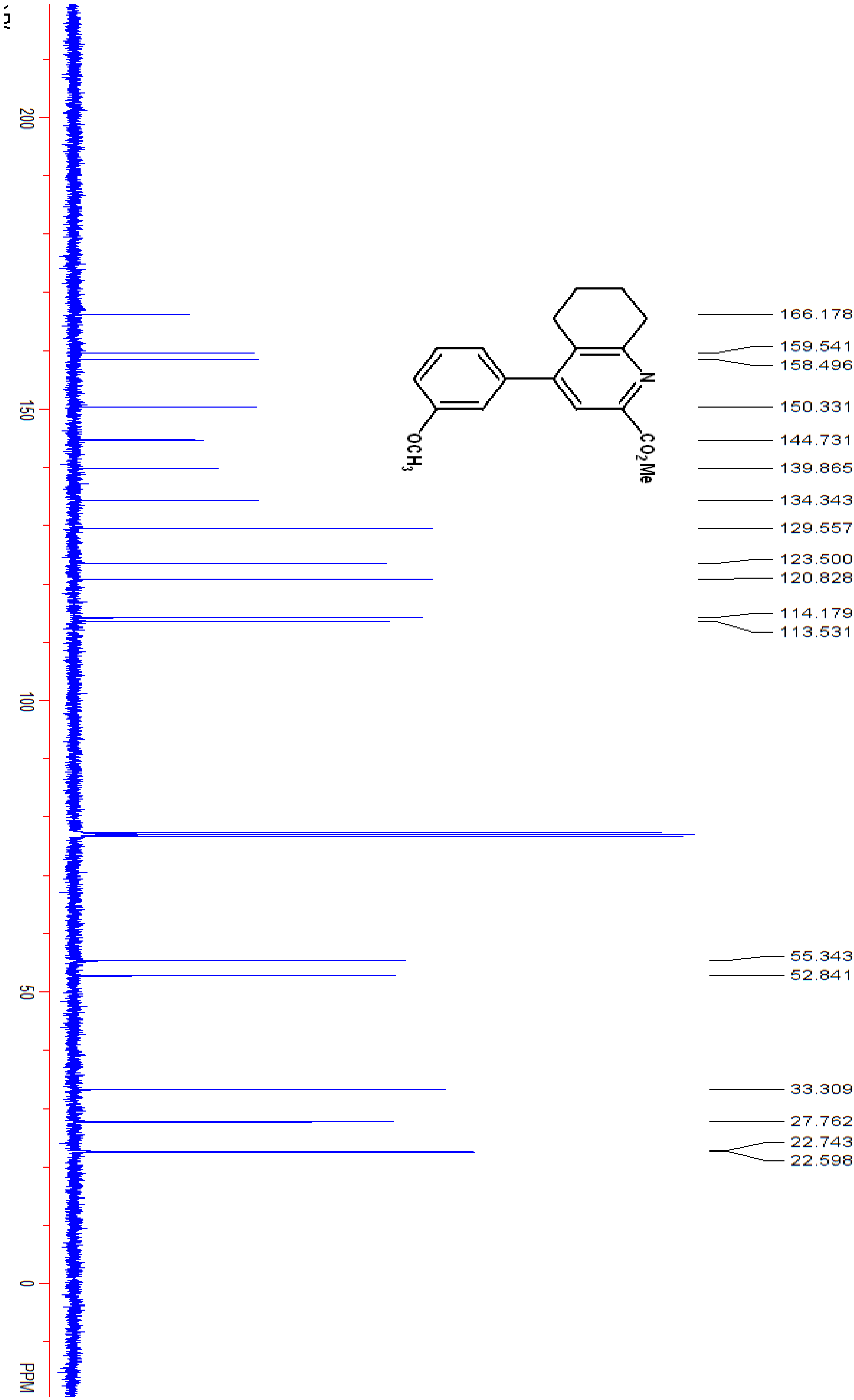
166.159
158.326
150.364
144.651
137.942
135.489
134.324
129.048
128.336
123.630
52.719
33.210
27.789
22.682
22.562
21.164
200
150
100
50
0
PPM
CH3
N
CO2Me


7.757
7.180
7.175
6.921
6.900
3.920
3.797
3.053
3.037
3.020
2.673
2.657
2.642
1.874
1.865
1.860
1.852
1.844
1.693
1.686
1.678
1.672
1.664
N
CO2Me
OCH3
0.99
1.92
1.91
3.00
3.24
2.01
2.03
2.12
2.16
15
10
5
0

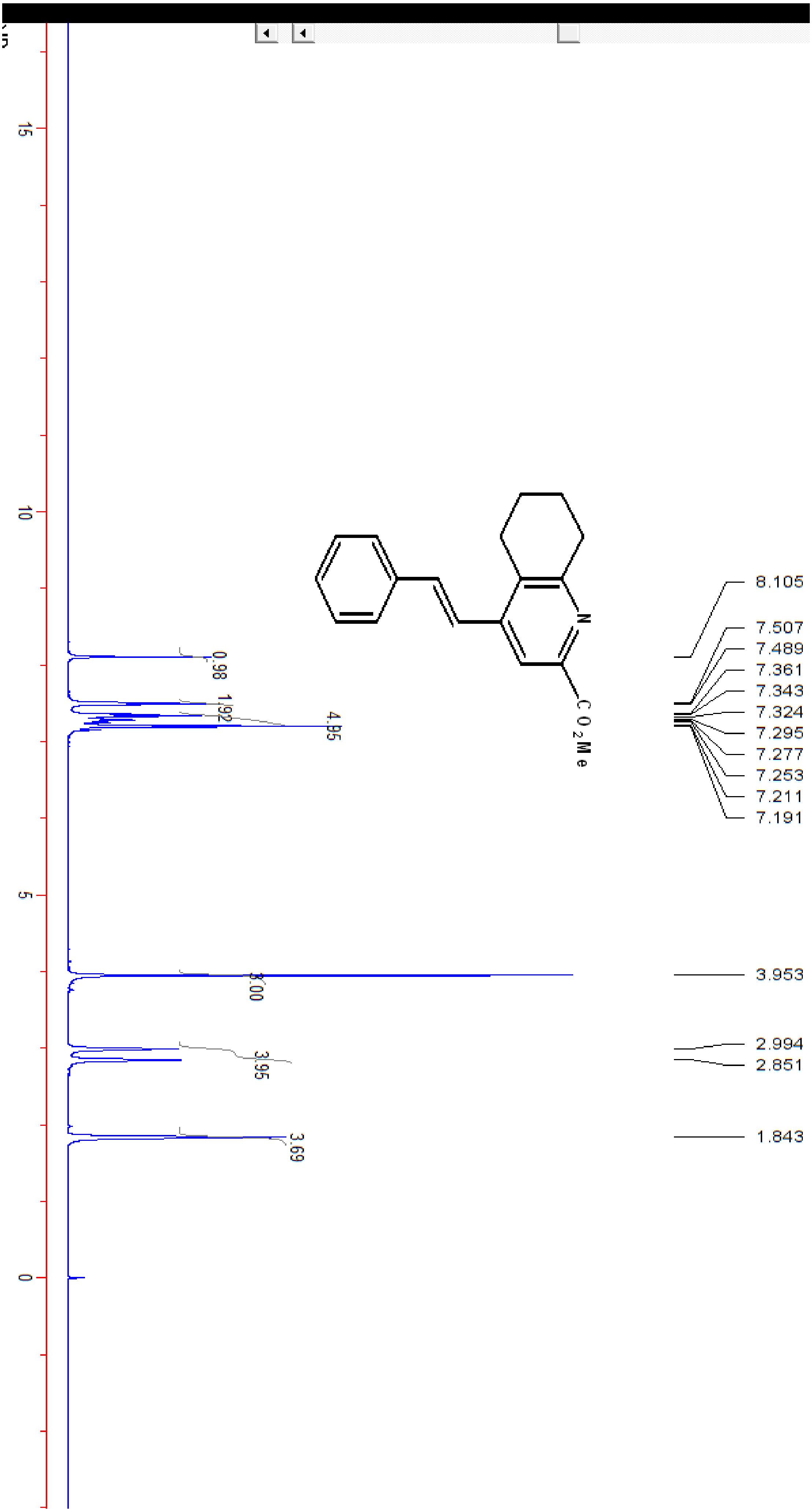


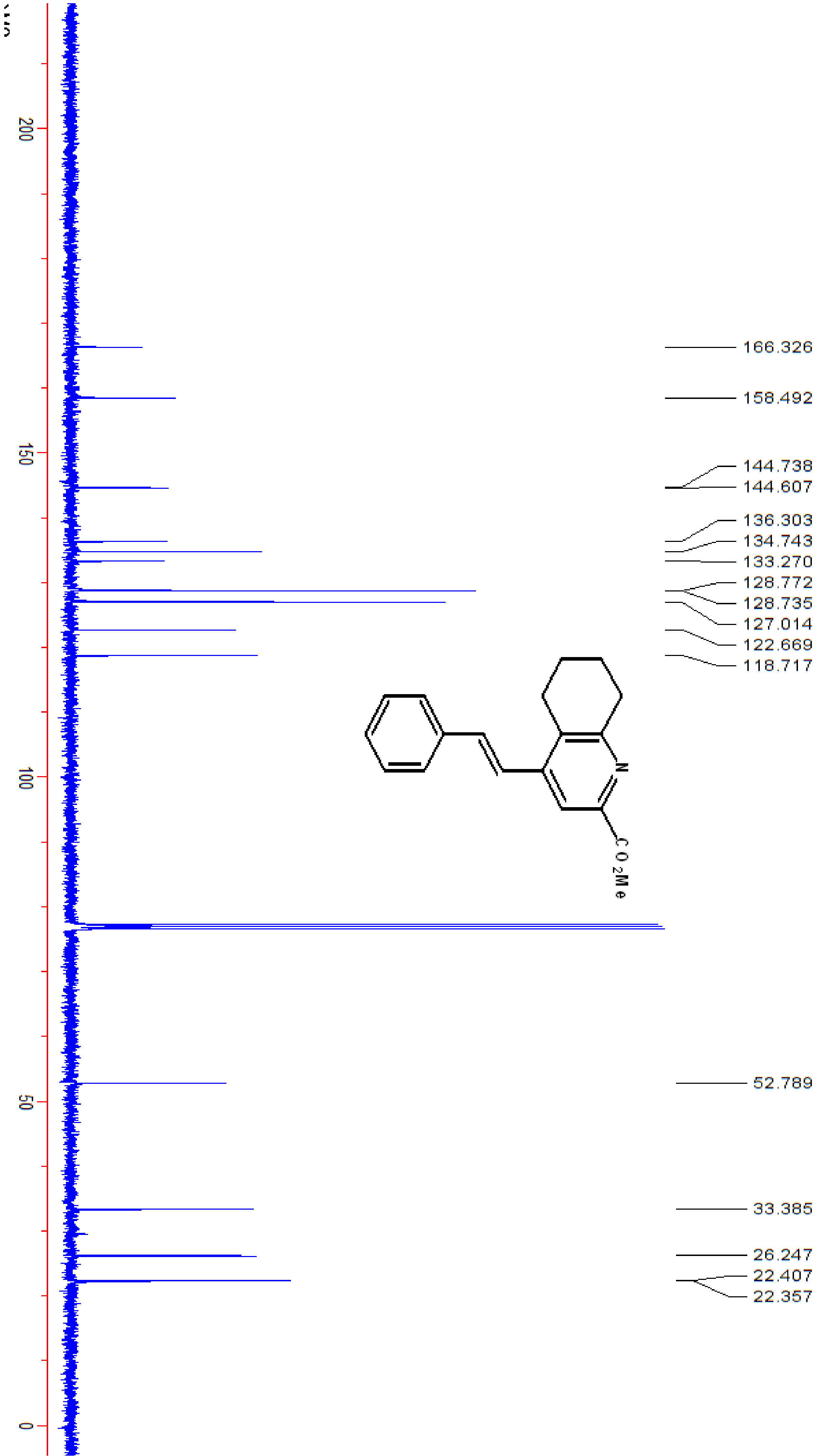
166.161
159.424
158.326
149.995
144.632
134.358
130.621
129.745
123.659
113.764
55.228
52.698
33.182
27.854
22.676
22.580
OCH3
N
CO2Me
200
150
100
50
0
PPM


7.838
7.385
7.366
7.346
6.967
6.965
6.960
6.959
6.946
6.944
6.940
6.938
6.888
6.885
6.883
6.869
6.866
6.864
6.827
6.823
6.821
6.817
3.993
3.847
3.131
3.114
3.098
2.727
2.711
2.695
1.944
1.935
1.930
1.922
1.915
1.767
1.760
1.752
1.746
1.738
N
CO2Me
OCH3
0.97
1.01
1.08
1.09
0.98
3.00
3.36
2.01
2.01
2.17
2.18
10
8
6
4
2
0

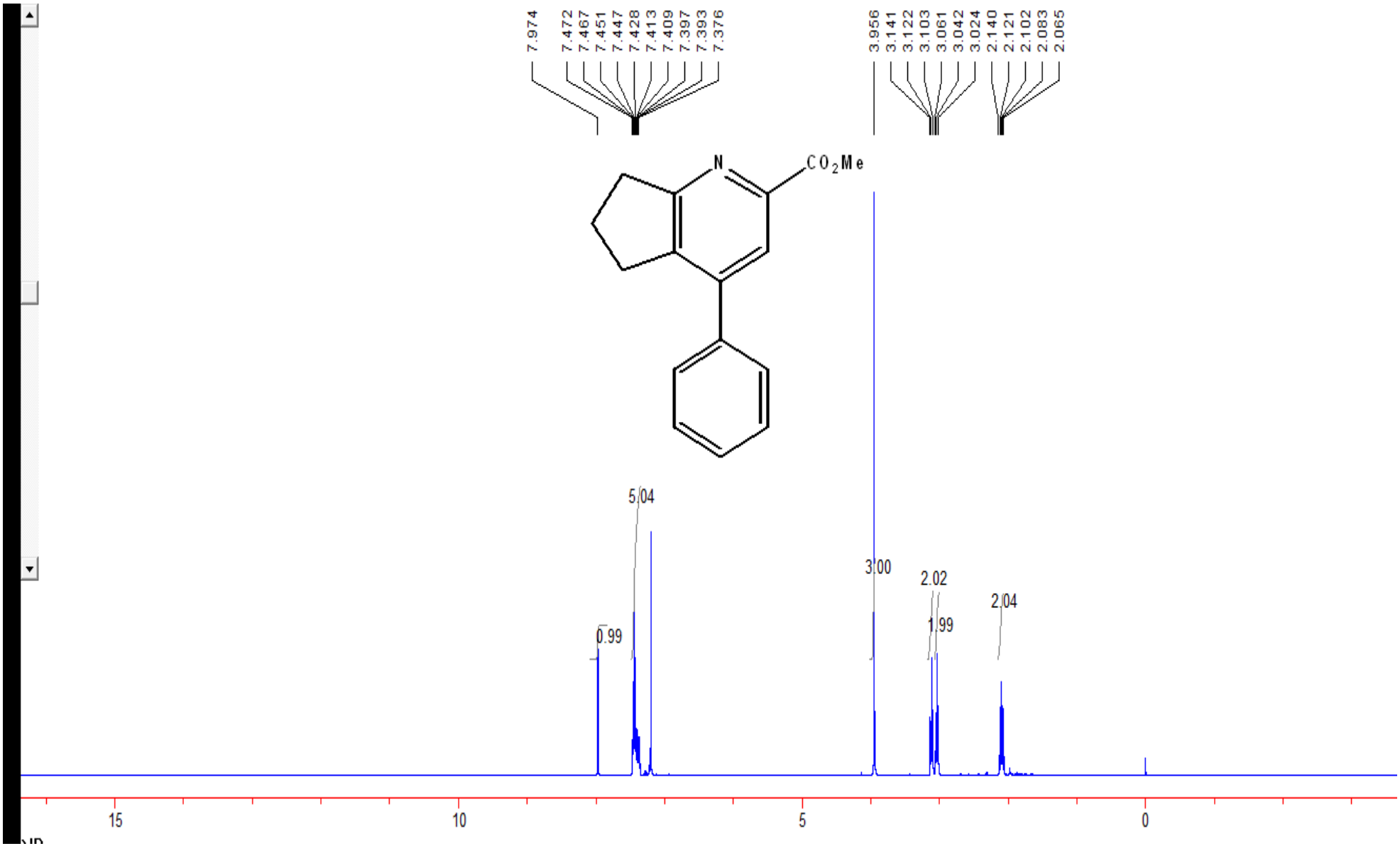


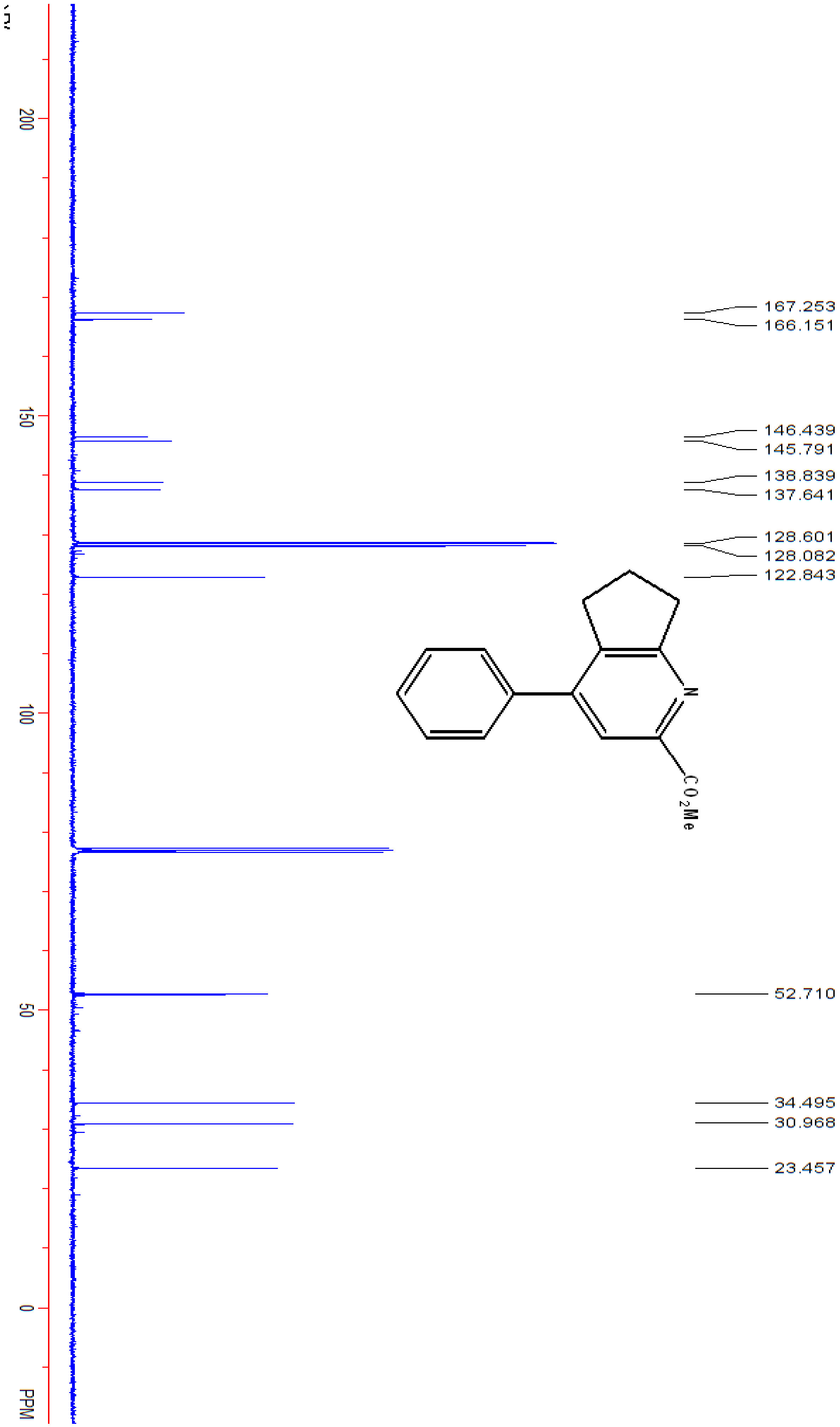
166.178
159.541
158.496
150.331
144.731
139.865
134.343
129.557
123.500
120.828
114.179
113.531
55.343
52.841
33.309
27.762
22.743
22.598
N
CO_2Me
OCH_3
200
150
100
50
0
PPM


8.105
7.507
7.489
7.361
7.343
7.324
7.295
7.277
7.253
7.211
7.191
3.953
2.994
2.851
1.843
N
CO2Me
0.98
1.92
4.95
3.00
3.95
3.69
15
10
5
0

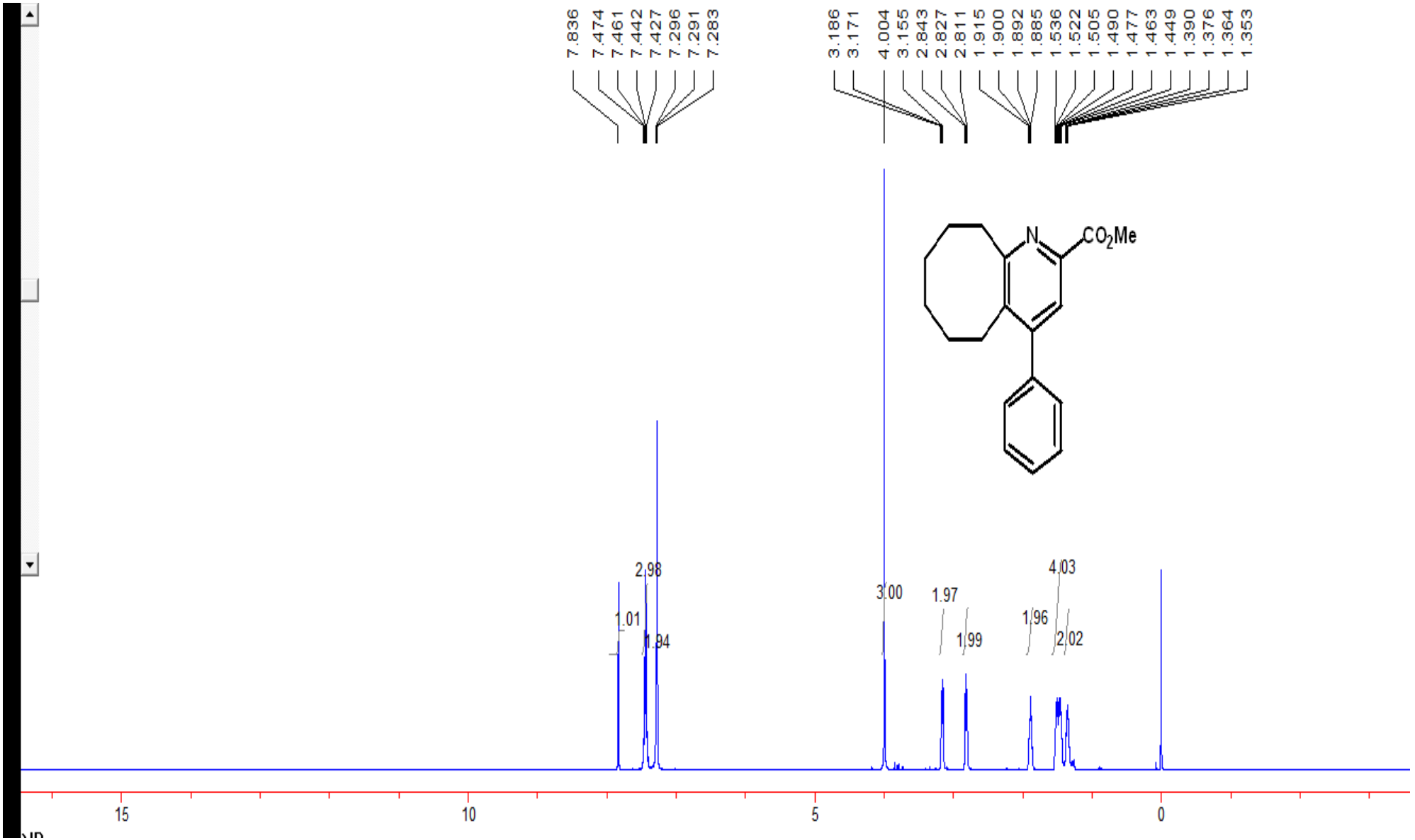


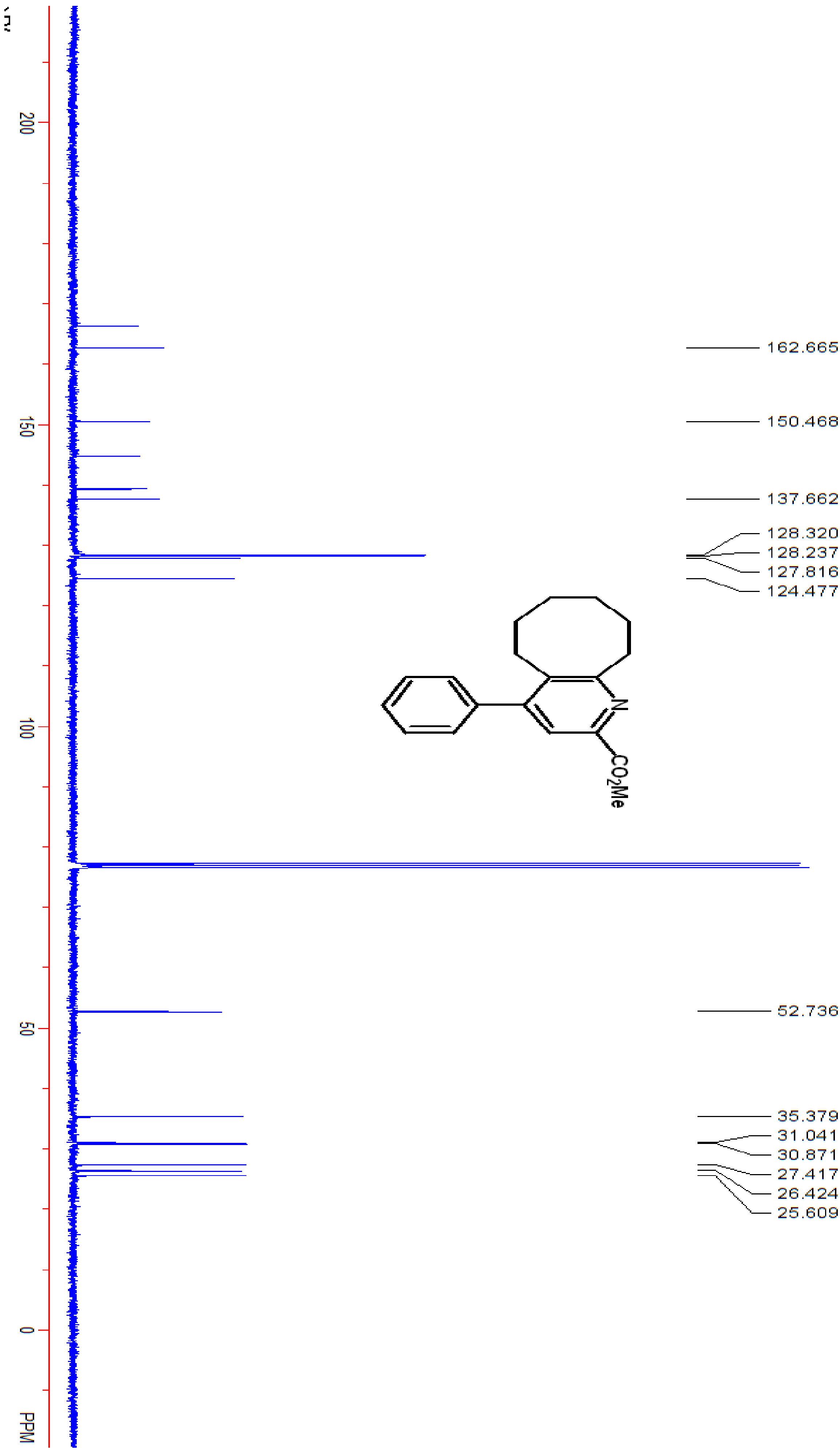
166.326
158.492
144.738
144.607
136.303
134.743
133.270
128.772
128.735
127.014
122.669
118.717
52.789
33.385
26.247
22.407
22.357
200
150
100
50
0
N
CO2Me

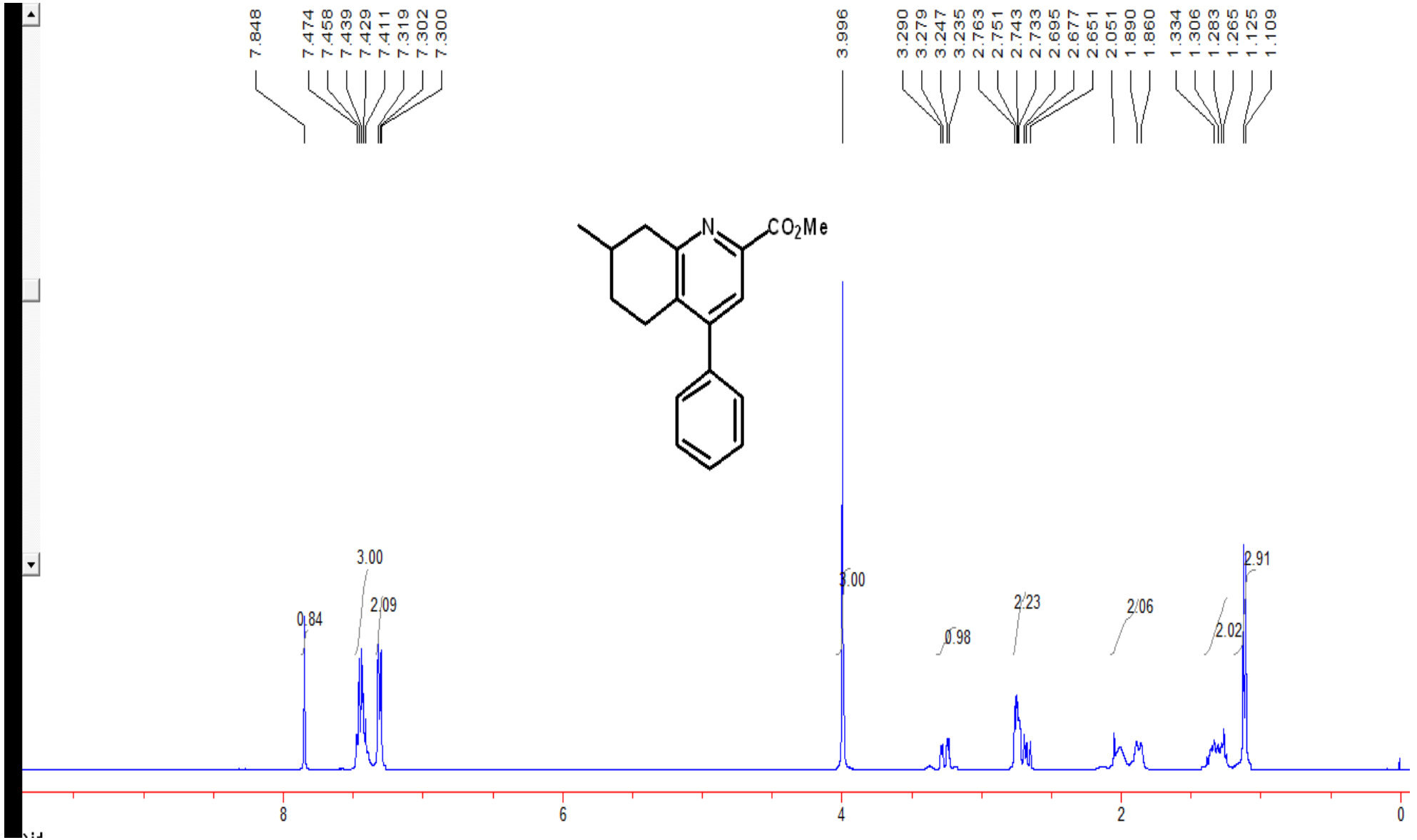

7.974
7.472
7.467
7.451
7.447
7.428
7.413
7.409
7.397
7.393
7.376
3.956
3.141
3.122
3.103
3.061
3.042
3.024
2.140
2.121
2.102
2.083
2.065
N
CO2Me
5.04
3.00
2.02
2.04
0.99
1.99
15
10
5
0

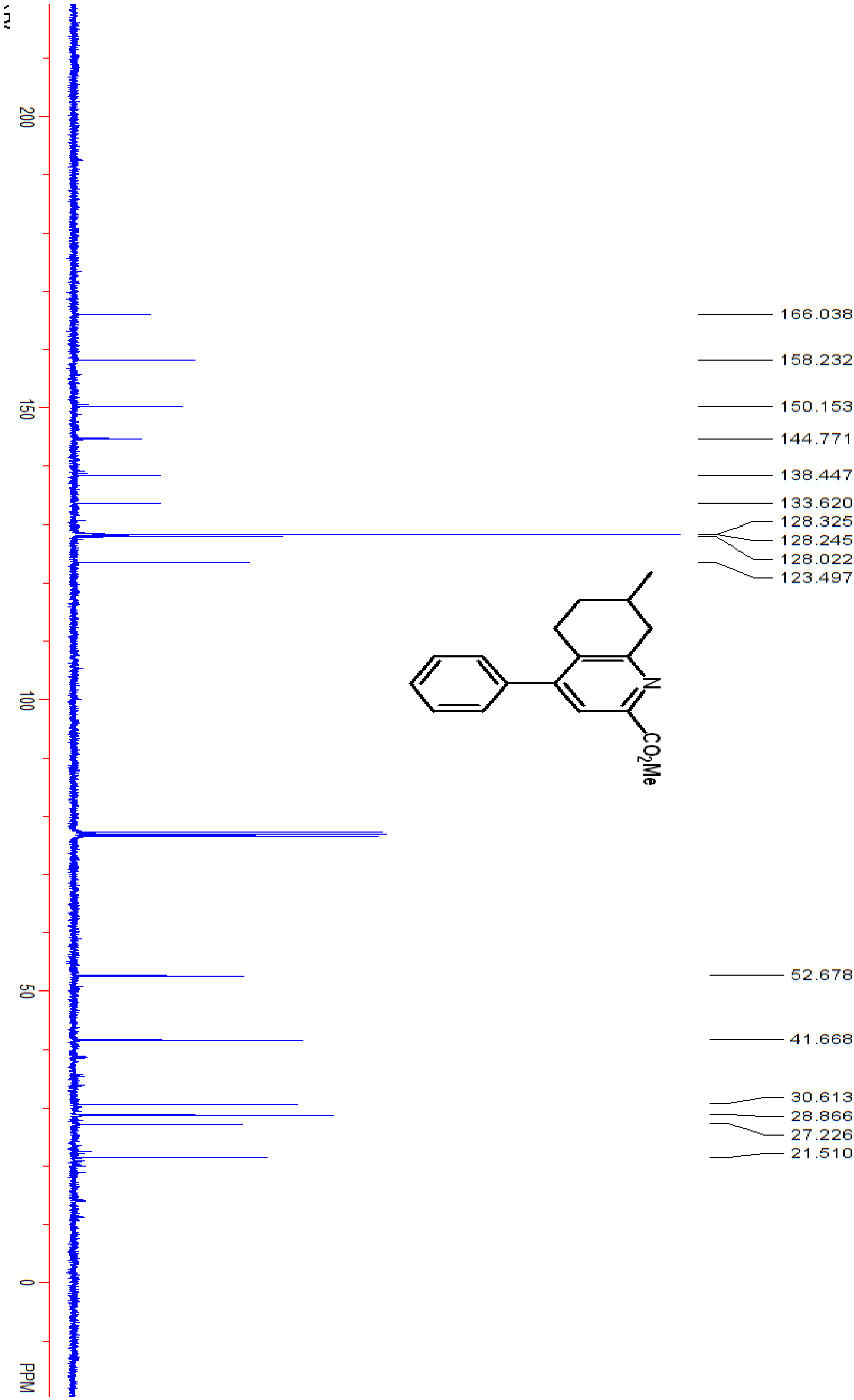


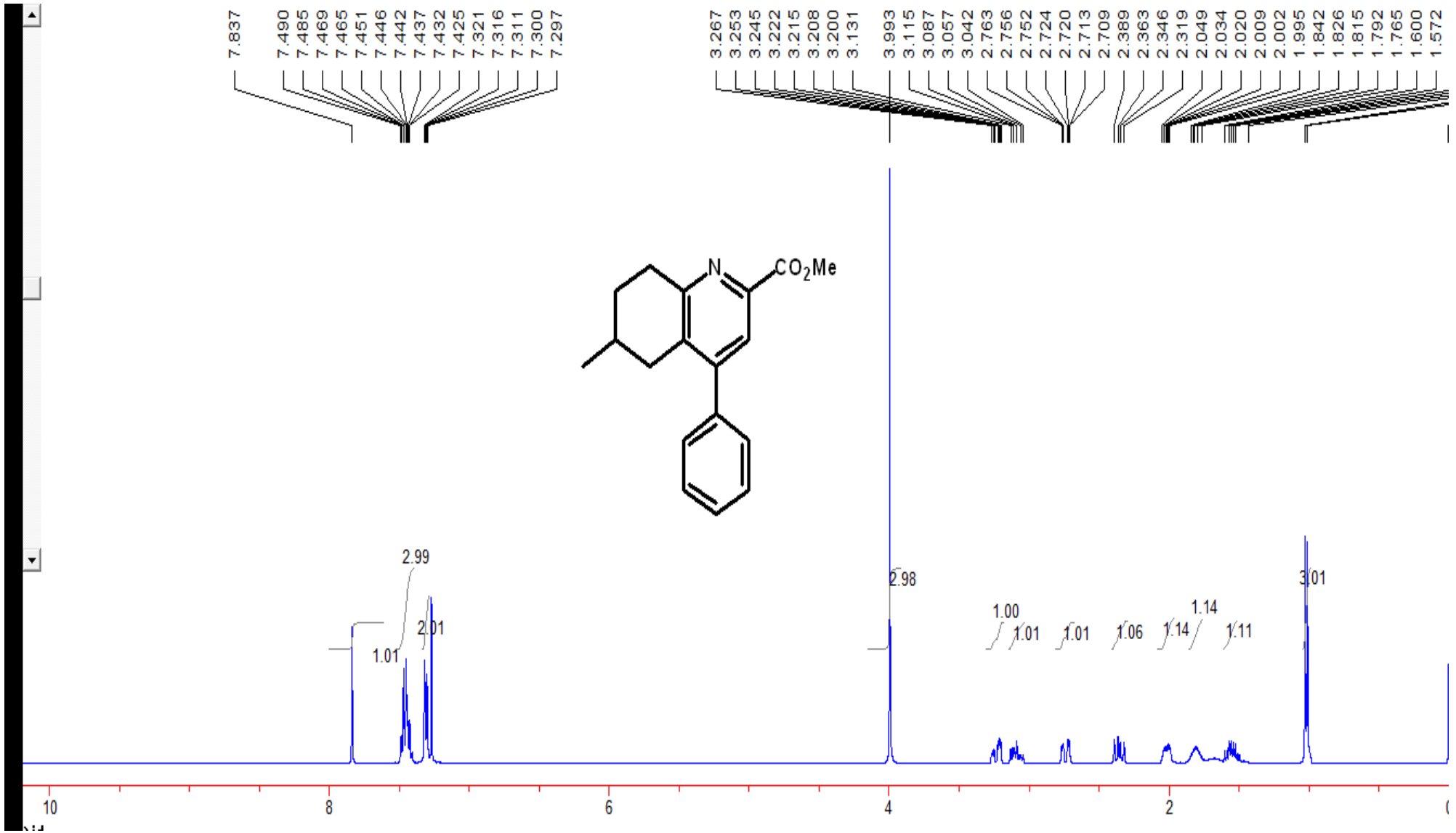
167.253
166.151
146.439
145.791
138.839
137.641
128.601
128.082
122.843
52.710
34.495
30.968
23.457
200
150
100
50
0
PPM
N
CO2Me

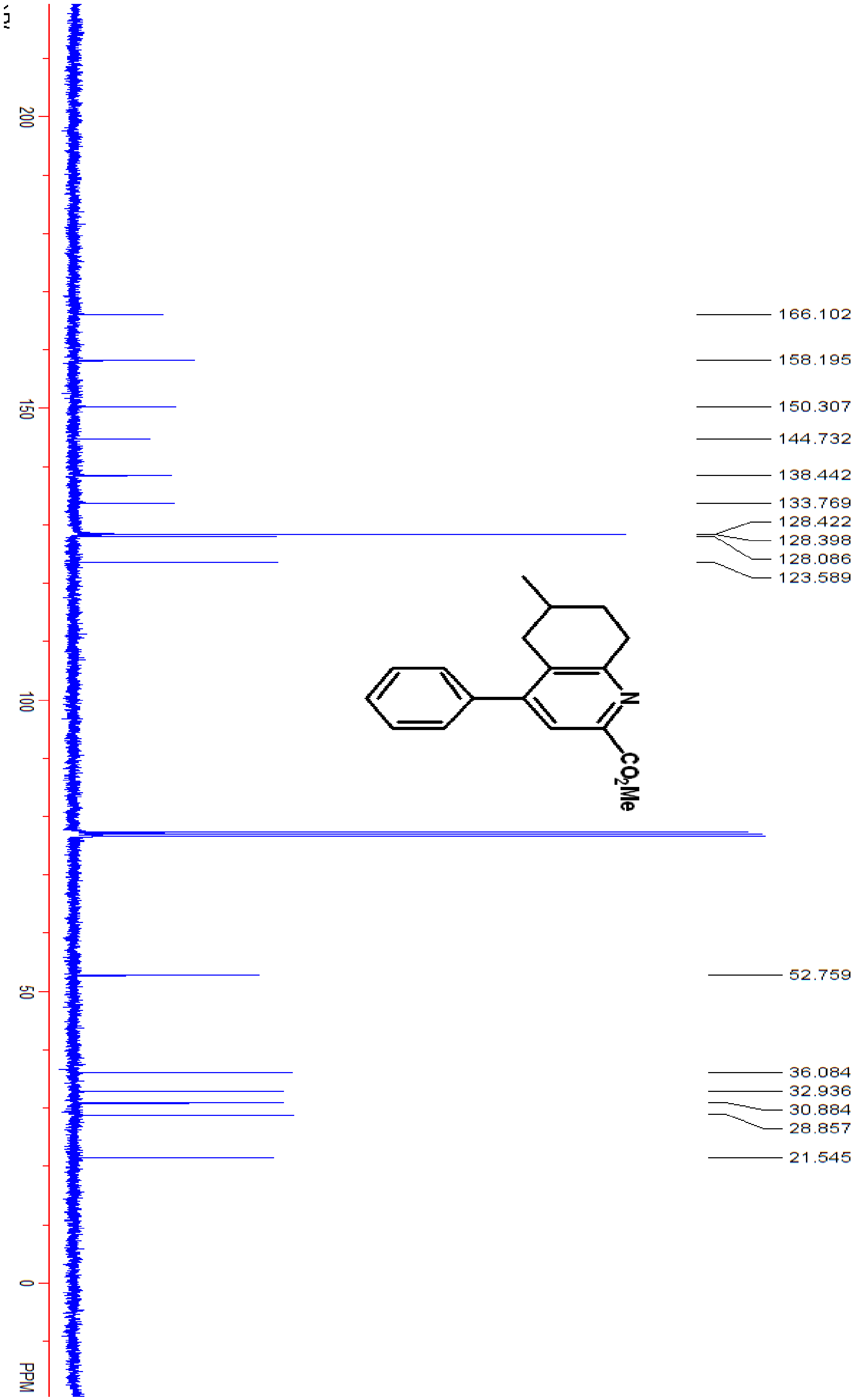

7.836
7.474
7.461
7.442
7.427
7.296
7.291
7.283
3.186
3.171
4.004
3.155
2.843
2.827
2.811
1.915
1.900
1.892
1.885
1.536
1.522
1.505
1.490
1.477
1.463
1.449
1.390
1.376
1.364
1.353
N
CO2Me
1.01
2.98
1.94
3.00
1.97
1.99
1.96
4.03
2.02
15
10
5
0

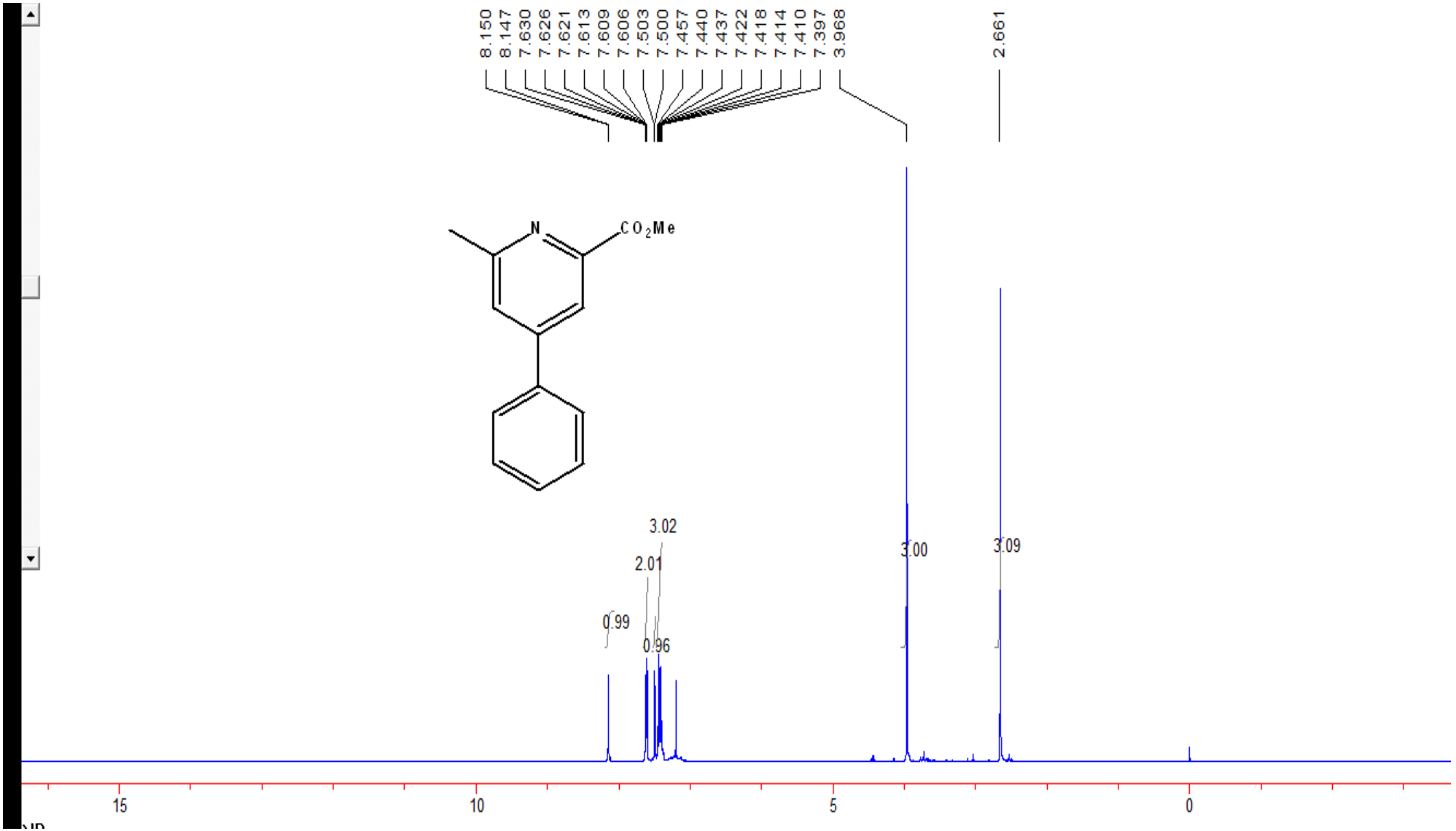

162.665
150.468
137.662
128.320
128.237
127.816
124.477
52.736
35.379
31.041
30.871
27.417
26.424
25.609
N
CO2Me
200
150
100
50
0
PPM

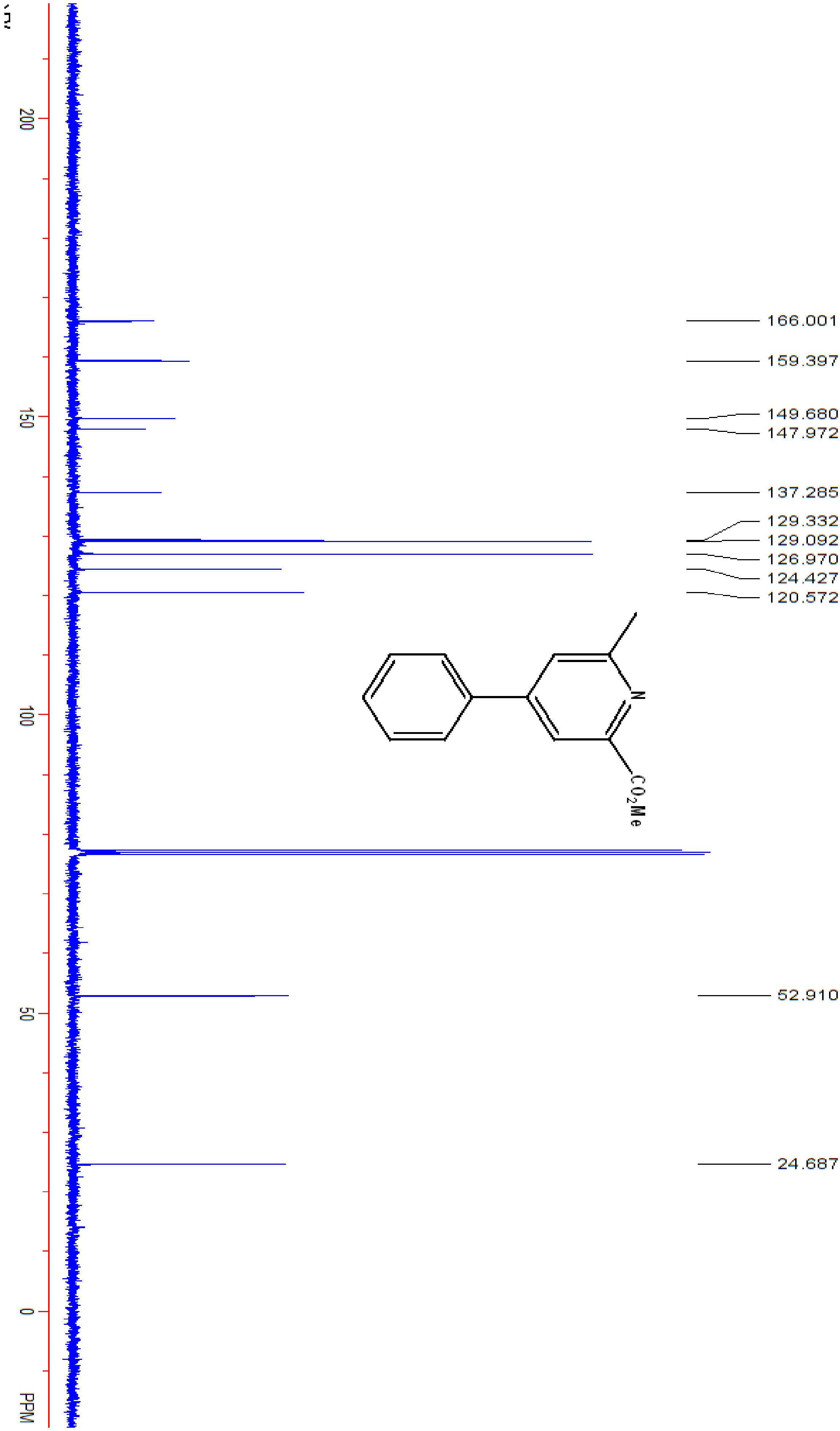

7.848
7.474
7.458
7.439
7.429
7.411
7.319
7.302
7.300
3.996
3.290
3.279
3.247
3.235
2.763
2.751
2.743
2.733
2.695
2.677
2.651
2.051
1.890
1.860
1.334
1.306
1.283
1.265
1.125
1.109
N
CO2Me
0.84
3.00
2.09
3.00
0.98
2.23
2.06
2.02
2.91
8
6
4
2
0


166.038
158.232
150.153
144.771
138.447
133.620
128.325
128.245
128.022
123.497
52.678
41.668
30.613
28.866
27.226
21.510
N
CO2Me
200
150
100
50
0
PPM

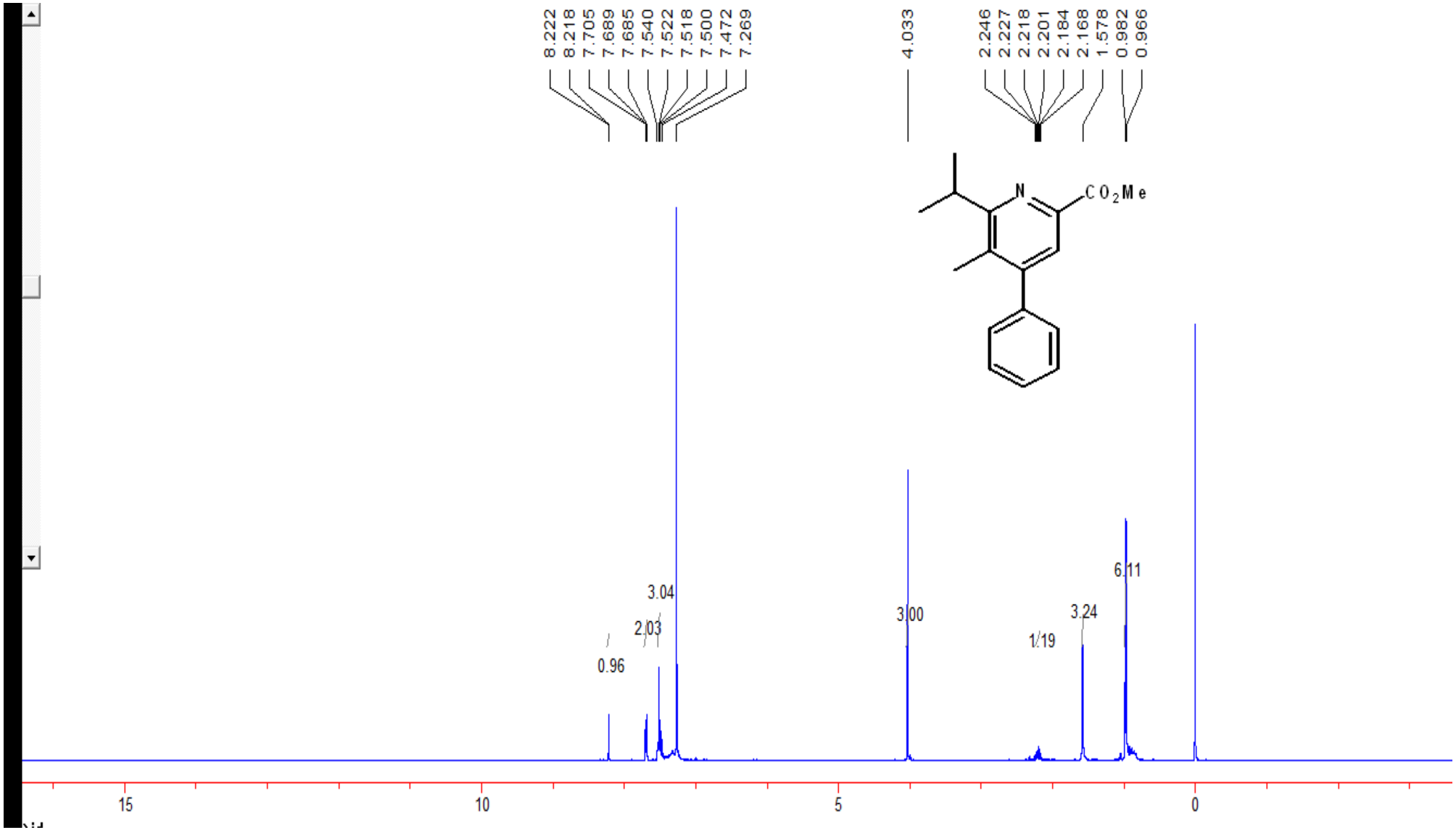

7.837
7.490
7.485
7.469
7.465
7.451
7.446
7.442
7.437
7.432
7.425
7.321
7.316
7.311
7.300
7.297
3.267
3.253
3.245
3.222
3.215
3.208
3.200
3.131
3.993
3.115
3.087
3.057
3.042
2.763
2.756
2.752
2.724
2.720
2.713
2.709
2.389
2.363
2.346
2.319
2.049
2.034
2.020
2.009
2.002
1.995
1.842
1.826
1.815
1.792
1.765
1.600
1.572
N
CO2Me
2.99
2.01
1.01
2.98
1.00
1.01
1.01
1.06
1.14
1.11
1.14
3.01
10
8
6
4
2

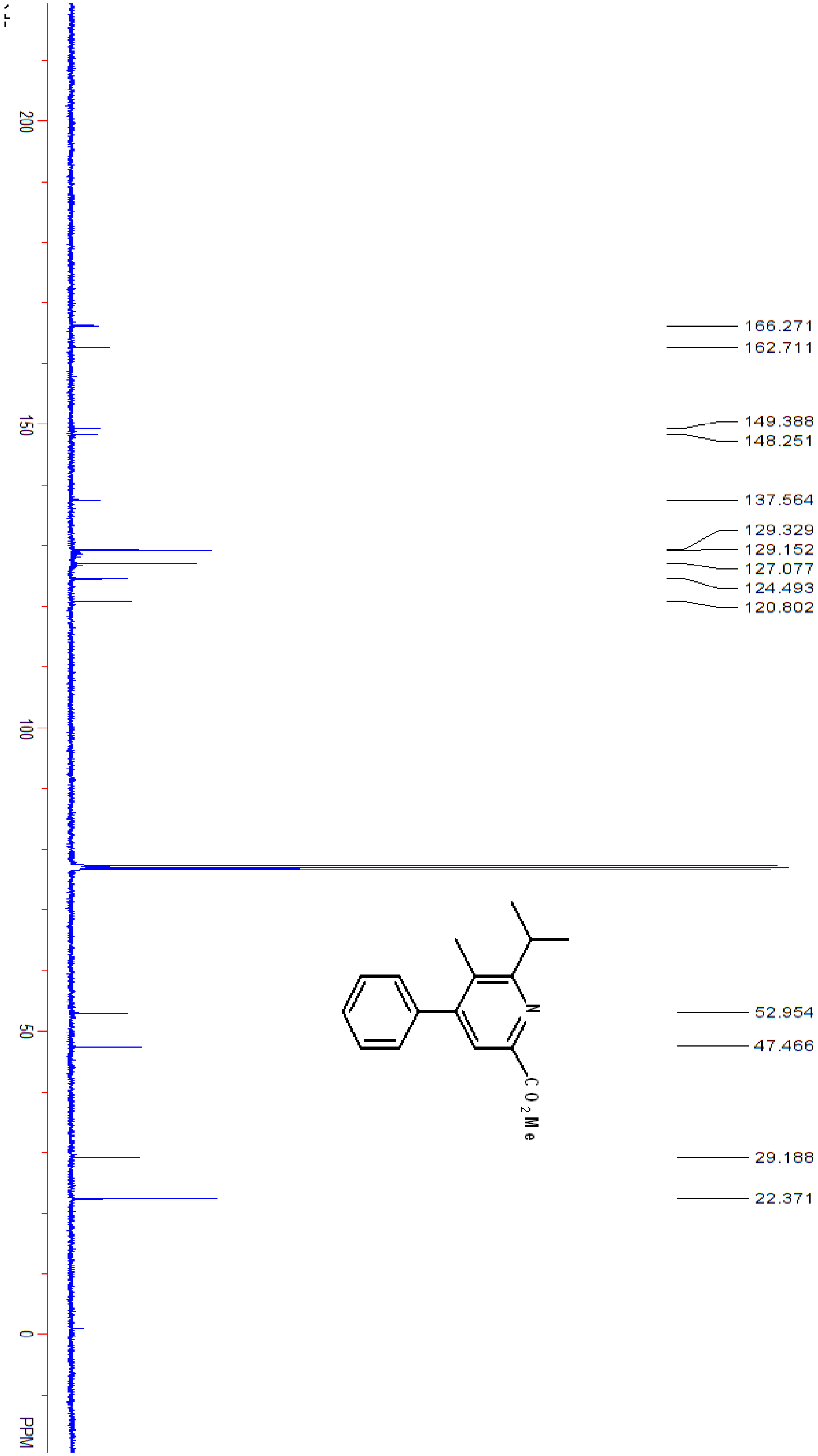

166.102
158.195
150.307
144.732
138.442
133.769
128.422
128.398
128.086
123.589
52.759
36.084
32.936
30.884
28.857
21.545
N
CO2Me
200
150
100
50
0
PPM


8.150
8.147
7.630
7.626
7.621
7.613
7.609
7.606
7.503
7.500
7.457
7.440
7.437
7.422
7.418
7.414
7.410
7.397
3.968
2.661
N
CO2Me
3.02
2.01
0.99
0.96
3.00
3.09
15
10
5
0

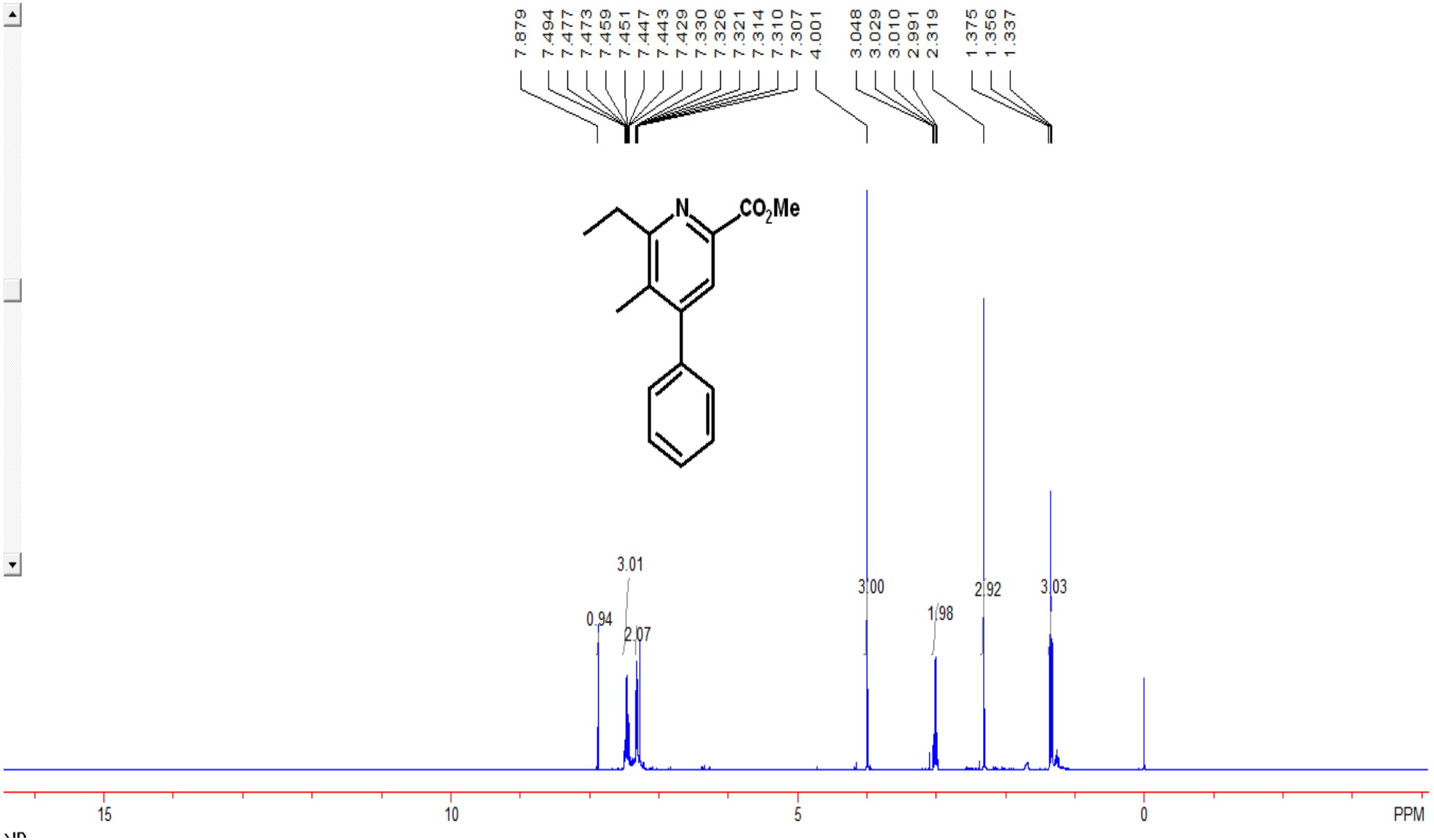


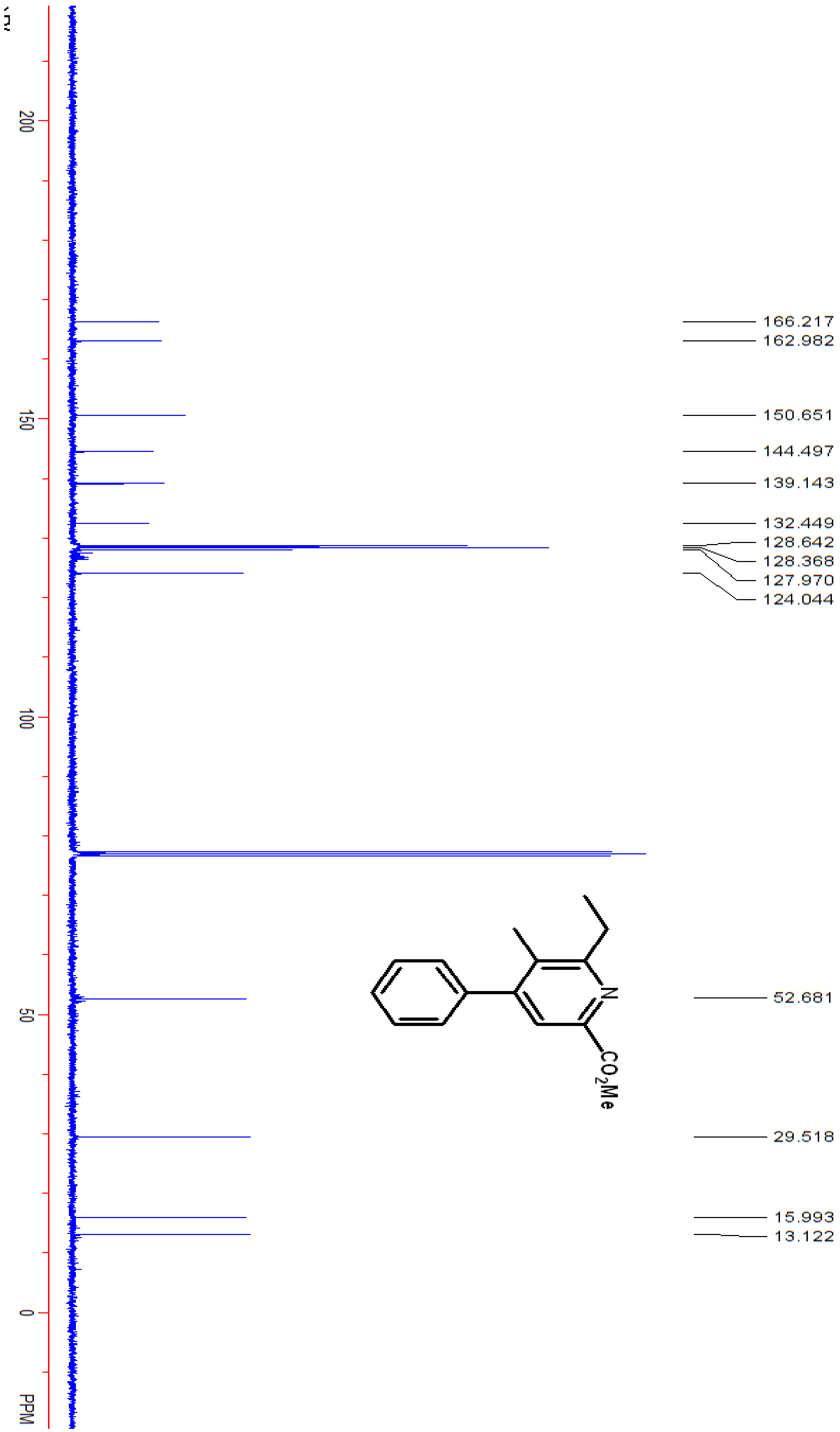
166.001
159.397
149.680
147.972
137.285
129.332
129.092
126.970
124.427
120.572
52.910
24.687
N
CO2Me
200
150
100
50
0
PPM


8.222
8.218
7.705
7.689
7.685
7.540
7.522
7.518
7.500
7.472
7.269
4.033
2.246
2.227
2.218
2.201
2.184
2.168
1.578
0.982
0.966
N
CO2Me
0.96
2.03
3.04
3.00
1.19
3.24
6.11
15
10
5
0

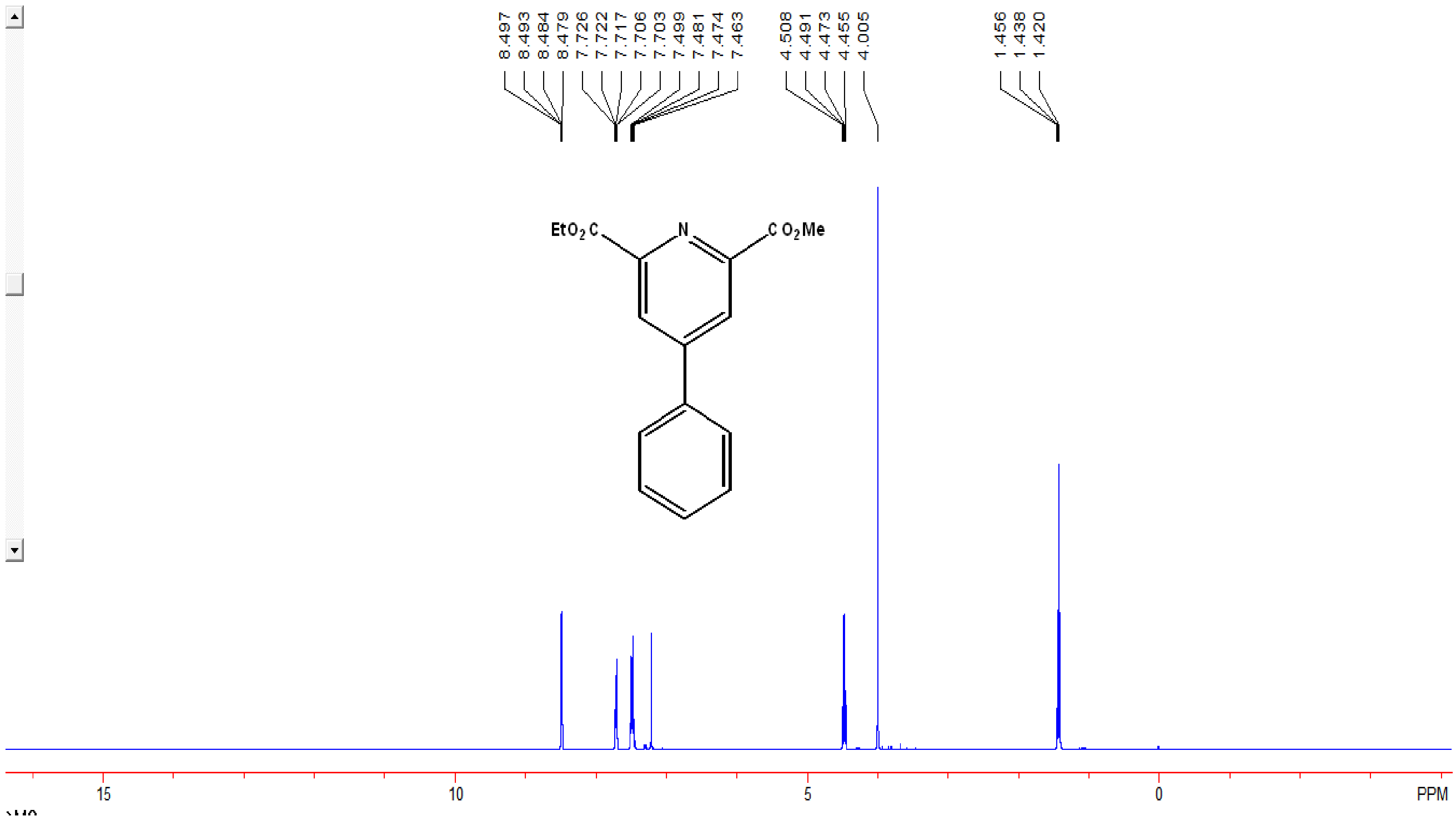


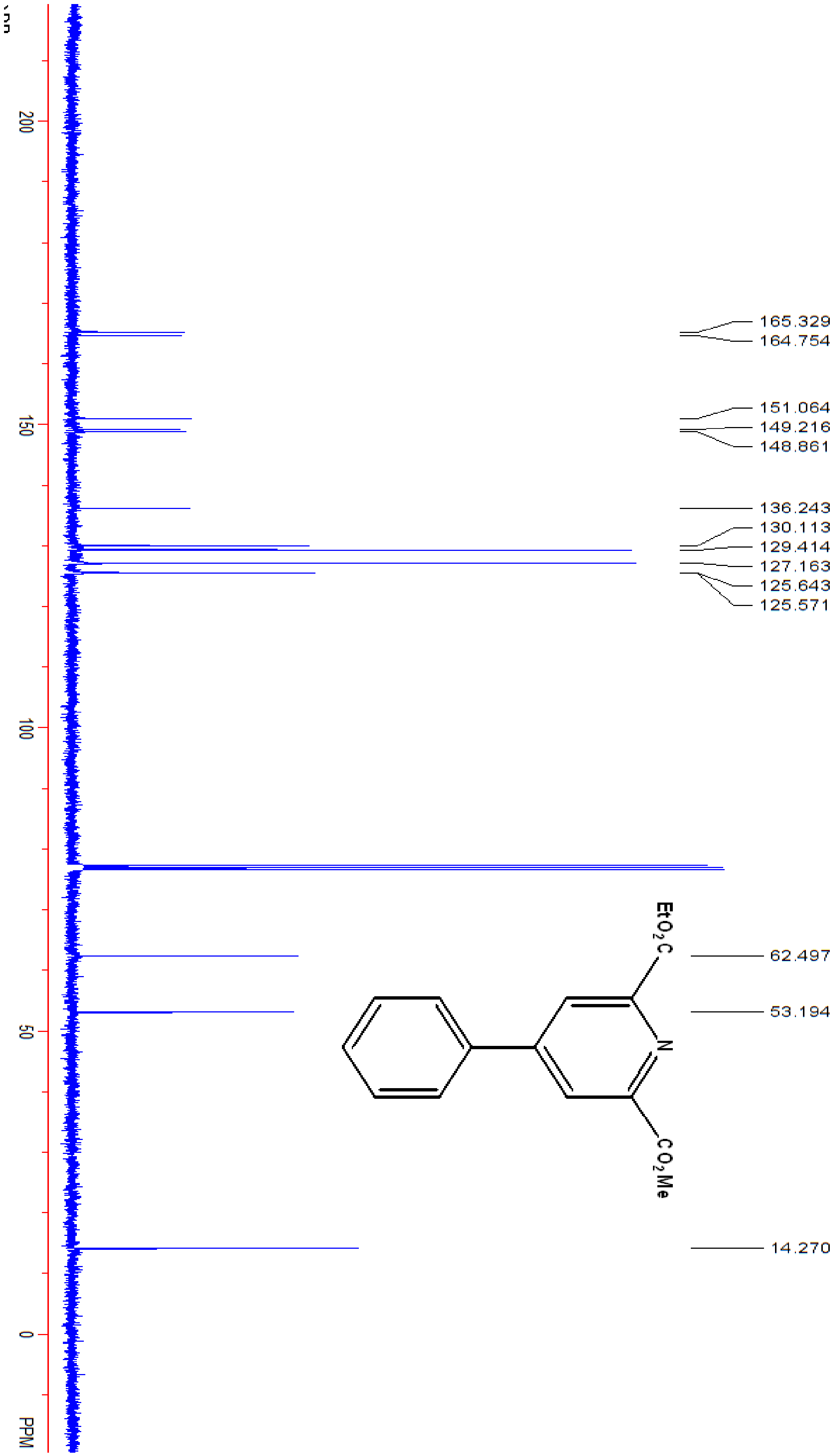
166.271
162.711
149.388
148.251
137.564
129.329
129.152
127.077
124.493
120.802
52.954
47.466
29.188
22.371
N
CO2Me
200
150
100
50
0
PPM


7.879
7.494
7.477
7.473
7.459
7.451
7.447
7.443
7.429
7.330
7.326
7.321
7.314
7.310
7.307
4.001
3.048
3.029
3.010
2.991
2.319
1.375
1.356
1.337
N
CO2Me
3.01
0.94
2.07
3.00
1.98
2.92
3.03
15
10
5
0
PPM

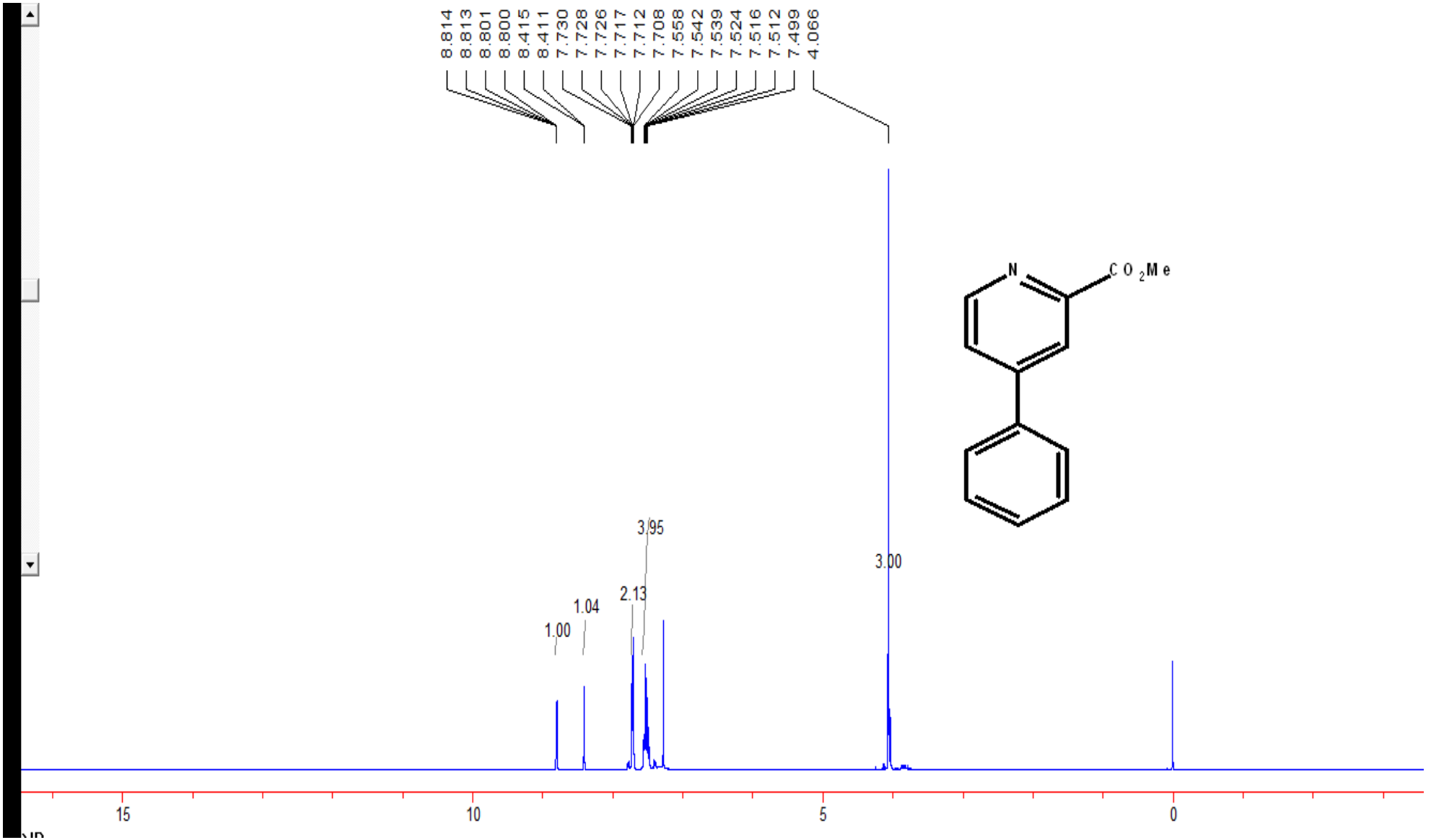


166.217
162.982
150.651
144.497
139.143
132.449
128.642
128.368
127.970
124.044
52.681
29.518
15.993
13.122
200
150
100
50
0
PPM
N
CO2Me

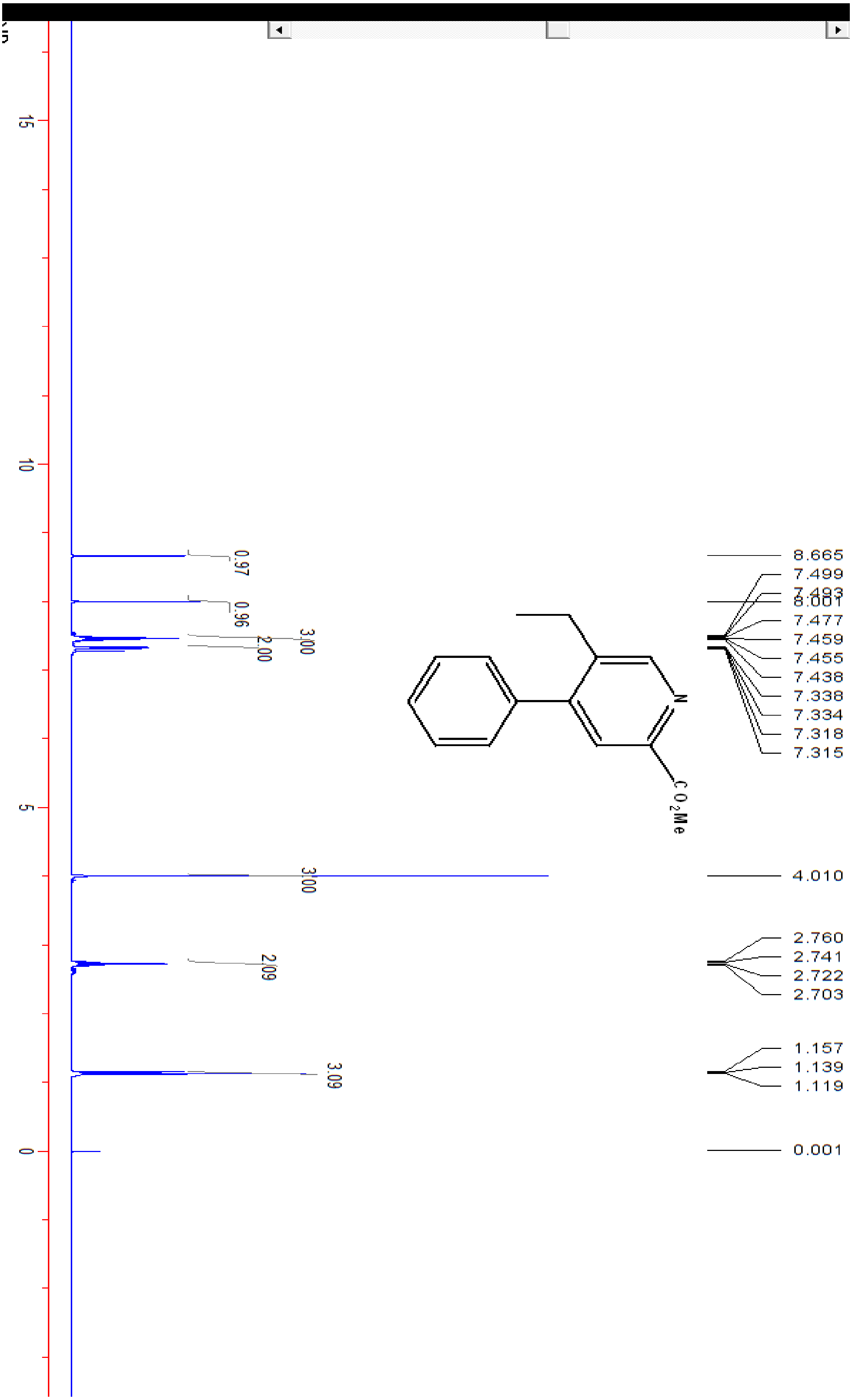

8.497
8.493
8.484
8.479
7.726
7.722
7.717
7.706
7.703
7.499
7.481
7.474
7.463
4.508
4.491
4.473
4.455
4.005
1.456
1.438
1.420
EtO2C
N
CO2Me
15
10
5
0
PPM



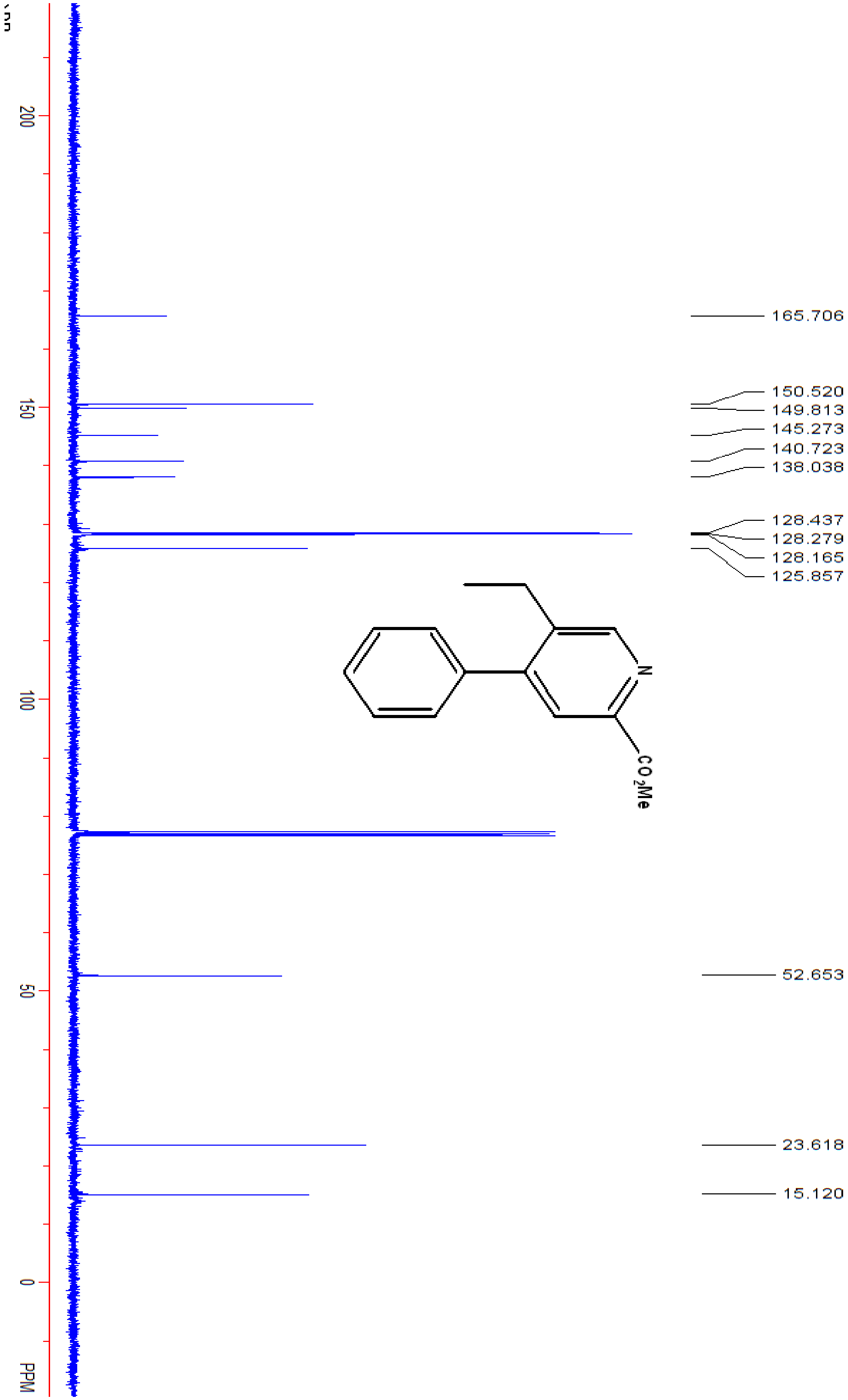
165.329
164.754
151.064
149.216
148.861
136.243
130.113
129.414
127.163
125.643
125.571
62.497
53.194
14.270
EtO2C
N
CO2Me
200
150
100
50
0
PPM


8.814
8.813
8.801
8.800
8.415
8.411
7.730
7.728
7.726
7.717
7.712
7.708
7.558
7.542
7.539
7.524
7.516
7.512
7.499
4.066
N
CO2Me
3.95
3.00
2.13
1.04
1.00
15
10
5
0

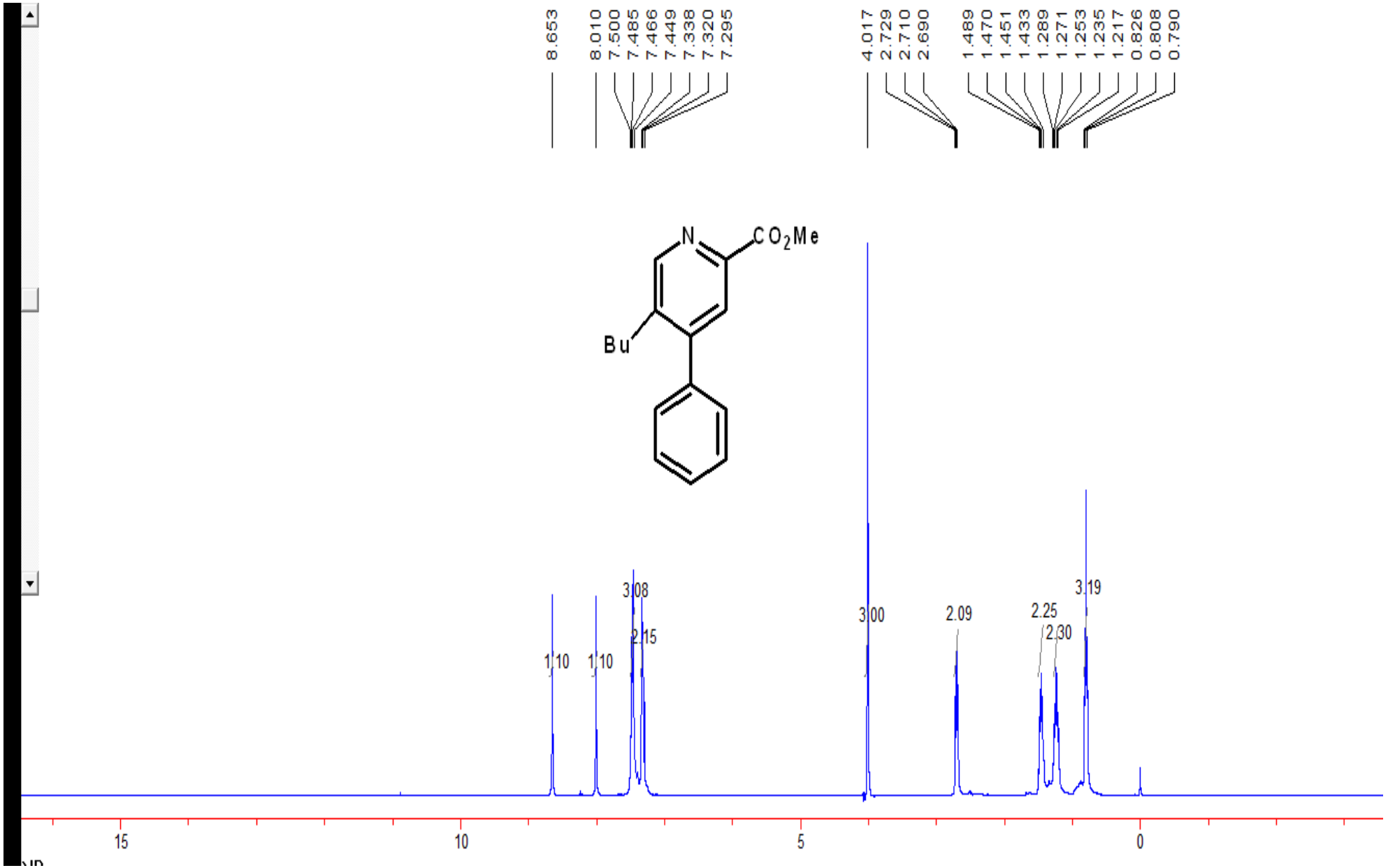

165.670
150.136
149.517
148.315
136.922
129.471
129.135
126.913
124.477
122.941
52.847
200
150
100
50
0
PPM
N
CO2Me

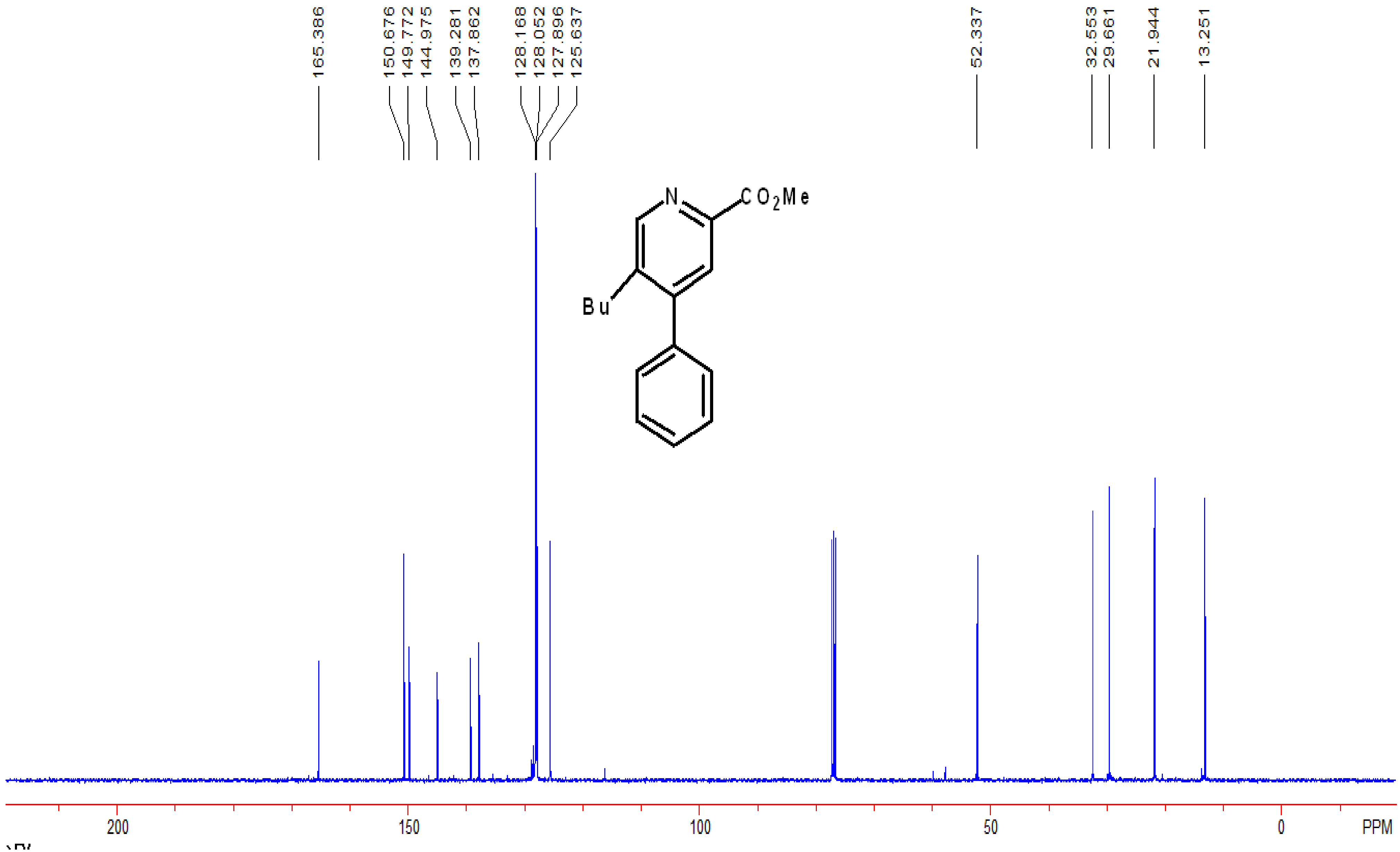


8.665
7.499
7.493
8.001
7.477
7.459
7.455
7.438
7.338
7.334
7.318
7.315
4.010
2.760
2.741
2.722
2.703
1.157
1.139
1.119
0.001
0.97
0.96
3.00
2.00
3.00
2.09
3.09
15
10
5
0
N
CO2Me

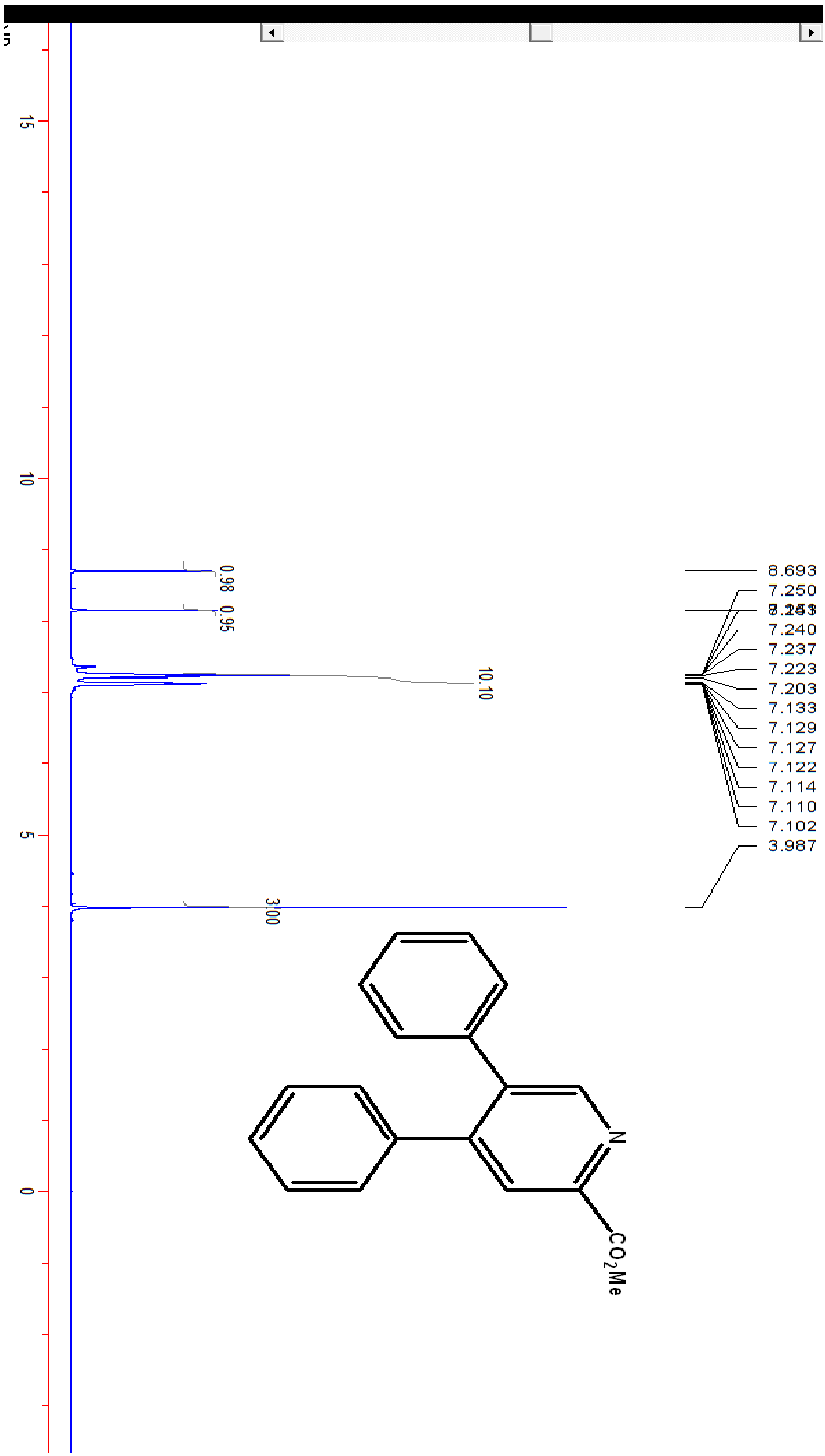


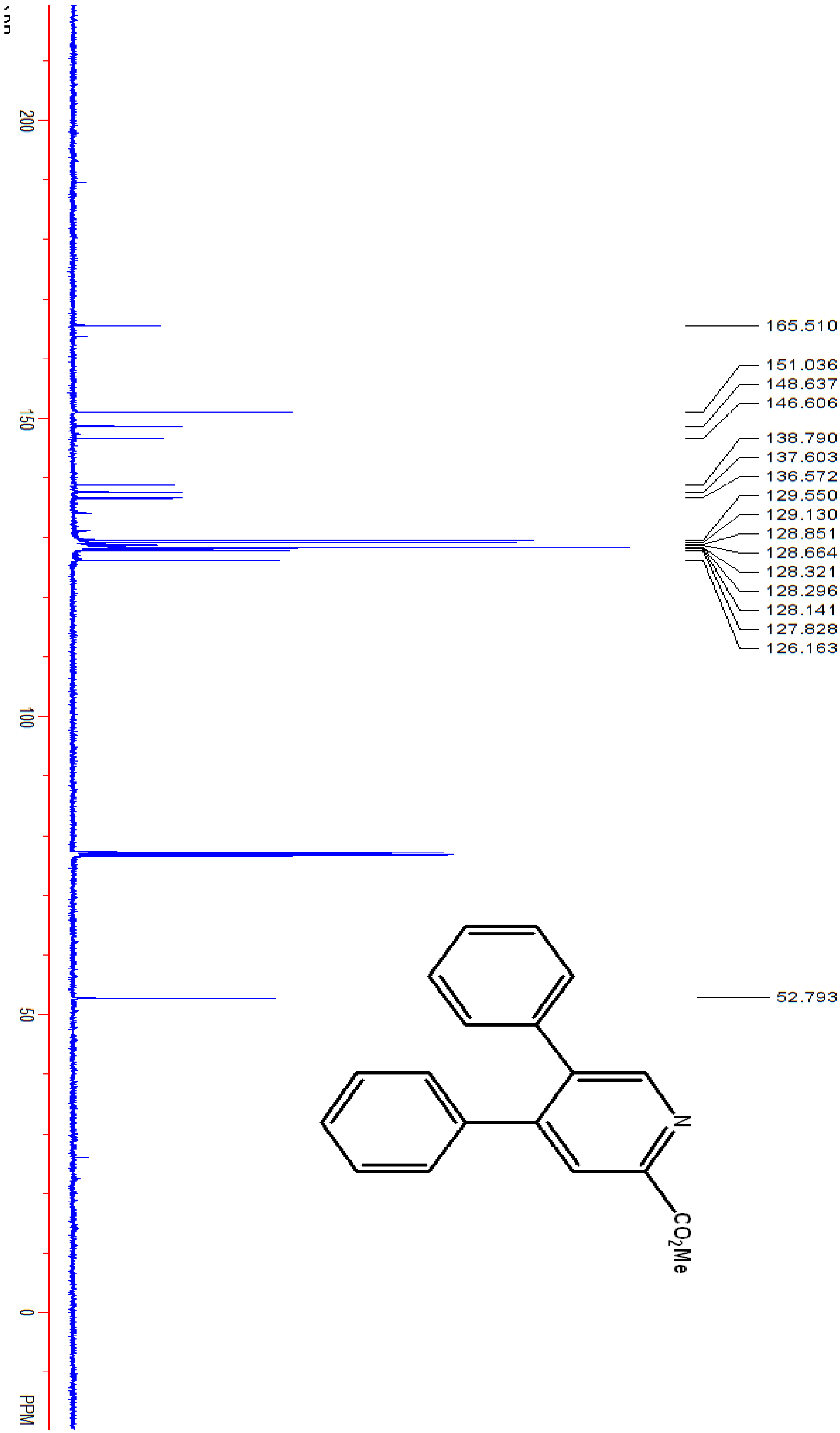
165.706
150.520
149.813
145.273
140.723
138.038
128.437
128.279
128.165
125.857
52.653
23.618
15.120
200
150
100
50
0
PPM
N
CO2Me


8.653
8.010
7.500
7.485
7.466
7.449
7.338
7.320
7.295
4.017
2.729
2.710
2.690
1.489
1.470
1.451
1.433
1.289
1.271
1.253
1.235
1.217
0.826
0.808
0.790
N
CO2Me
Bu
1.10
1.10
3.08
2.15
3.00
2.09
2.25
2.30
3.19
15
10
5
0

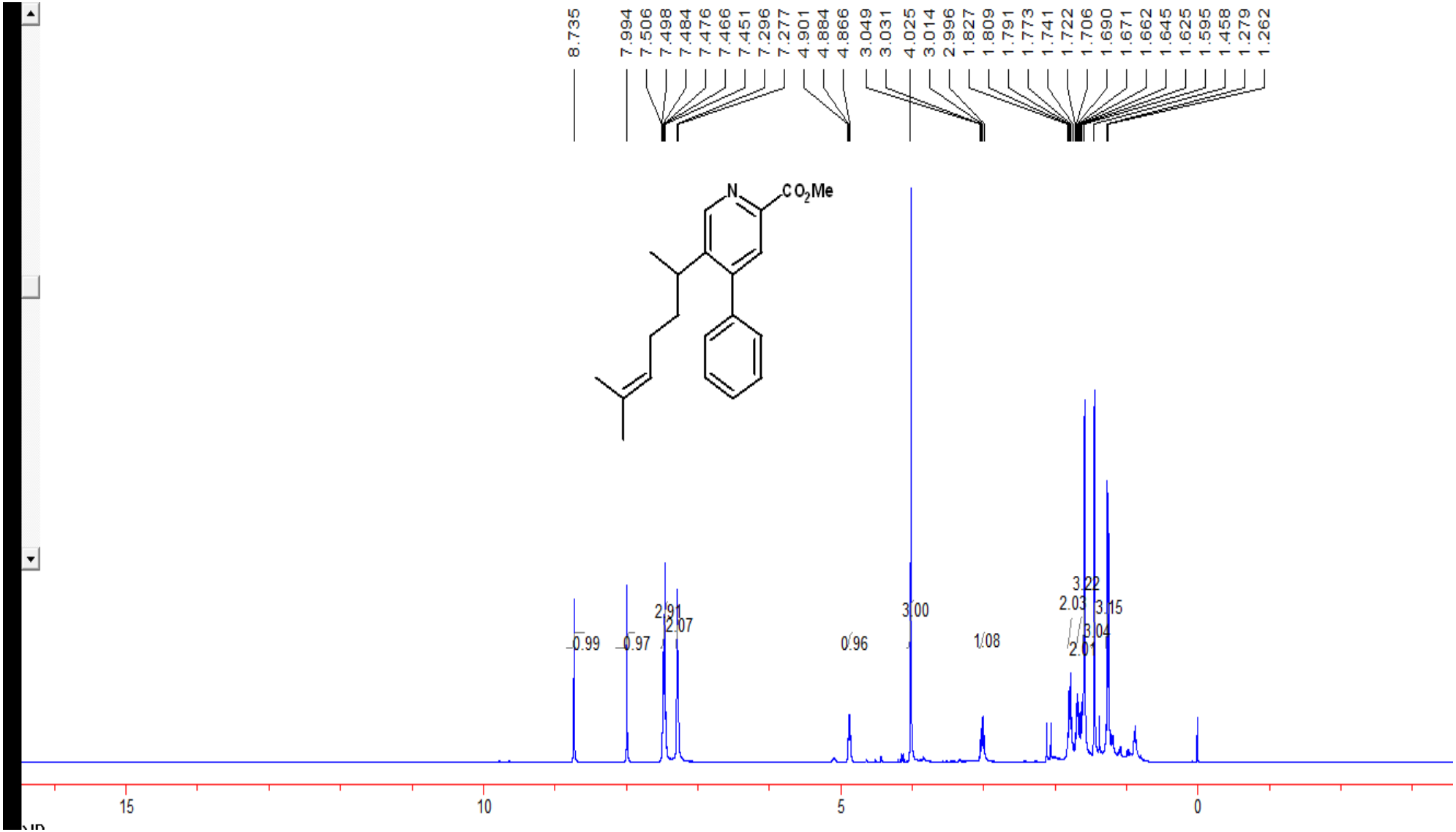


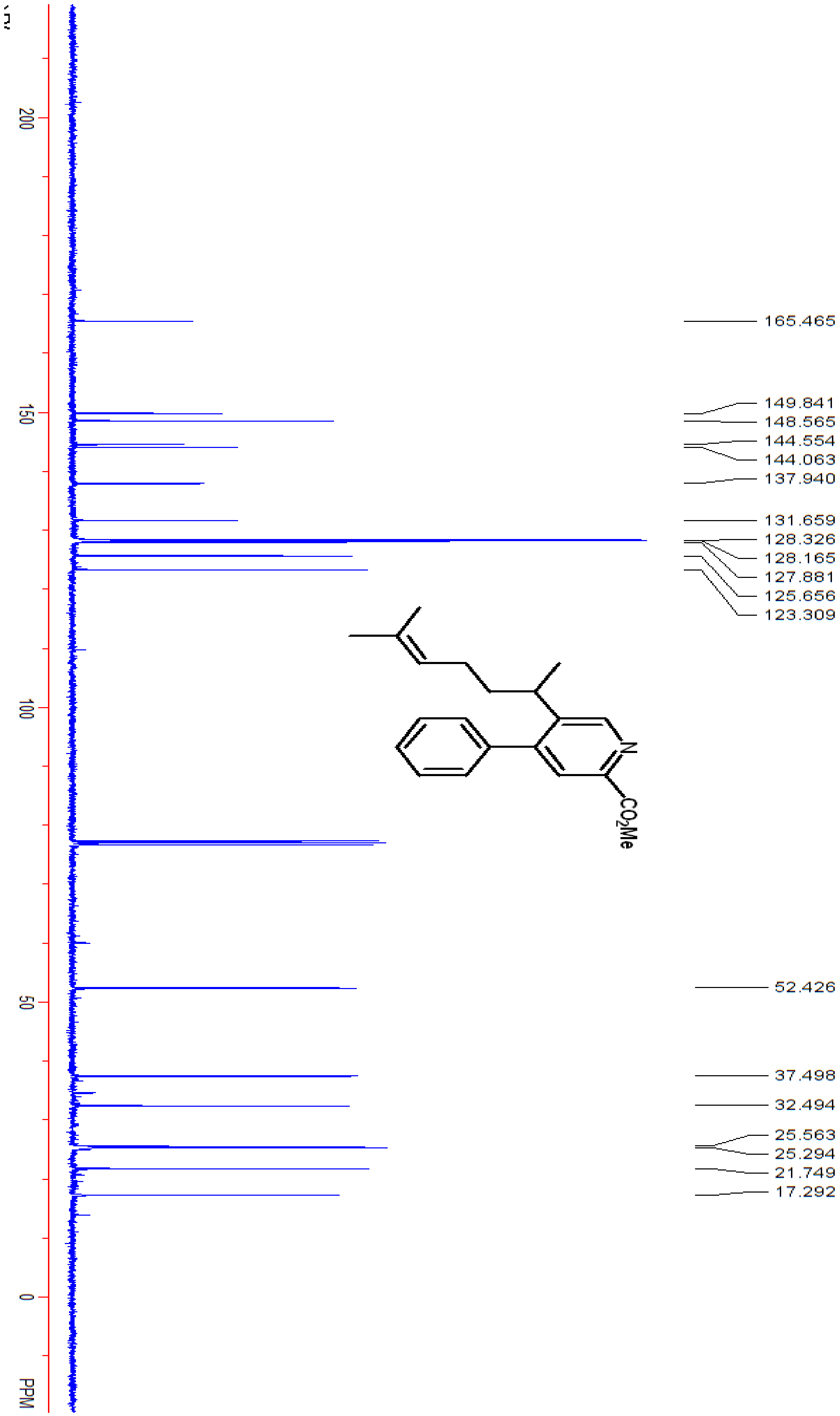
165.386
150.676
149.772
144.975
139.281
137.862
128.168
128.052
127.896
125.637
52.337
32.553
29.661
21.944
13.251
N
CO2Me
Bu
200
150
100
50
0
PPM


8.693
7.250
7.240
7.237
7.223
7.203
7.133
7.129
7.127
7.122
7.114
7.110
7.102
3.987
0.98
0.95
10.10
3.00
15
10
5
0
N
CO2Me

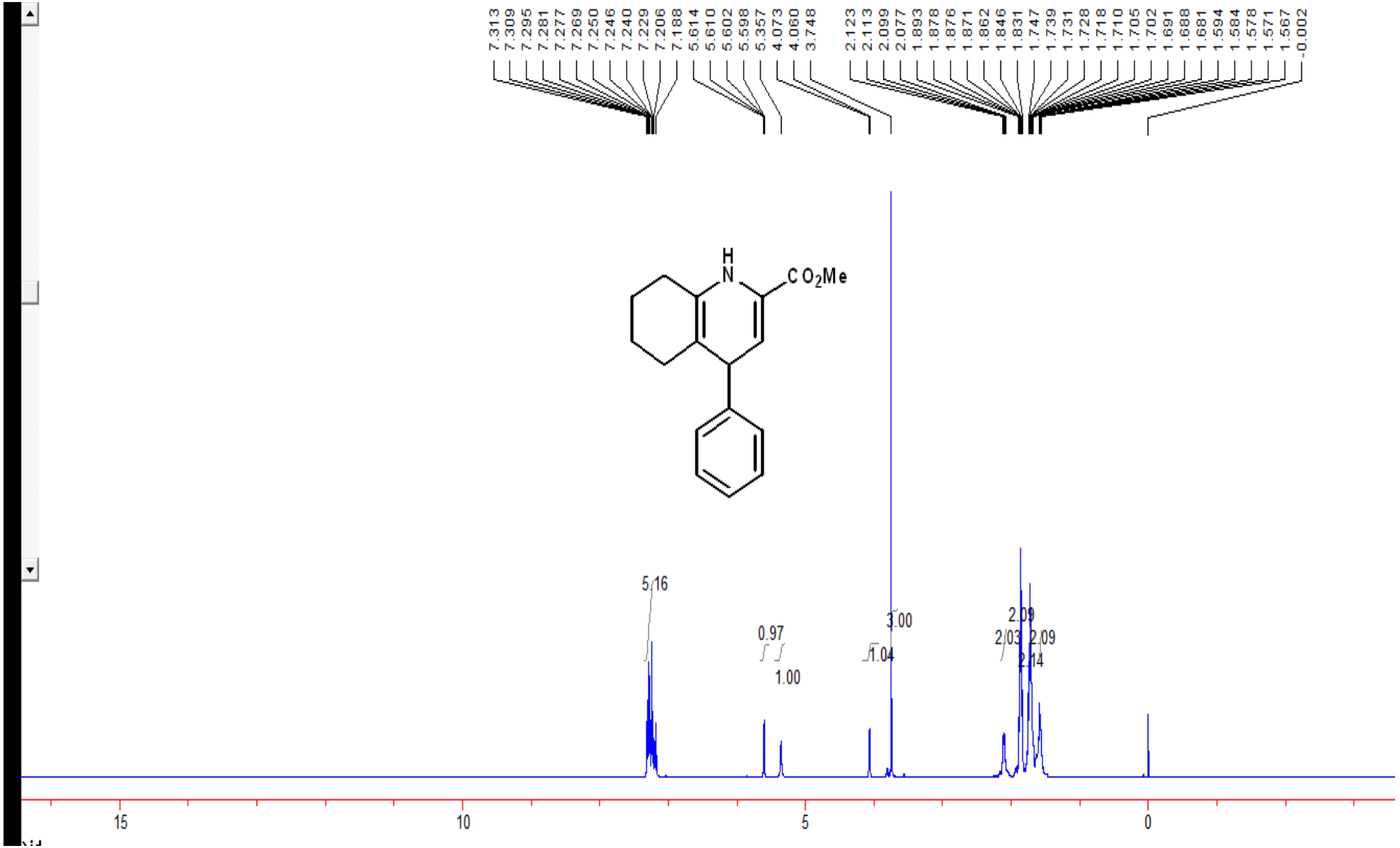


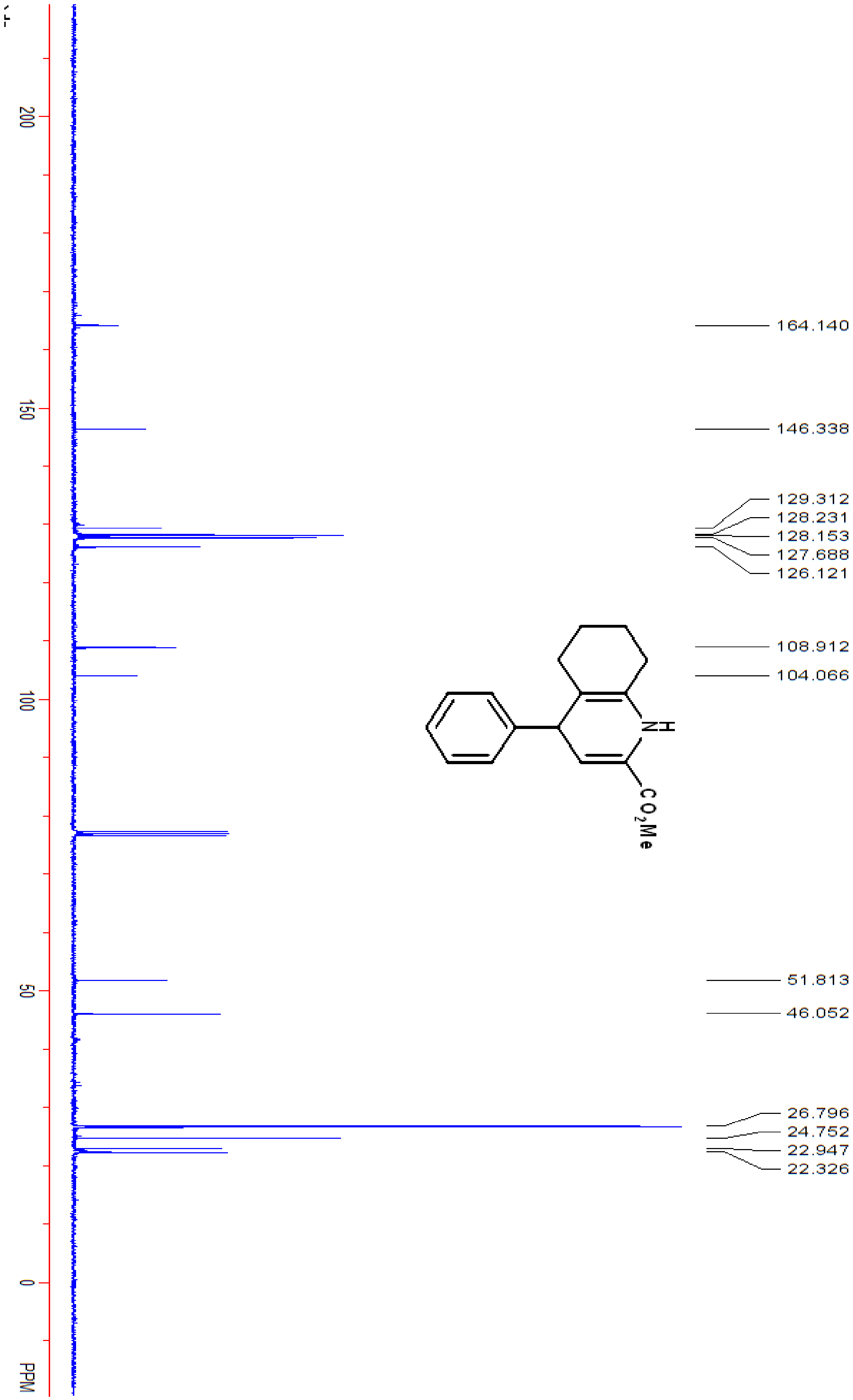
200
150
100
50
0
PPM
165.510
151.036
148.637
146.606
138.790
137.603
136.572
129.550
129.130
128.851
128.664
128.321
128.296
128.141
127.828
126.163
52.793
N
CO2Me


8.735
7.994
7.506
7.498
7.484
7.476
7.466
7.451
7.296
7.277
4.901
4.884
4.866
3.049
3.031
4.025
3.014
2.996
1.827
1.809
1.791
1.773
1.741
1.722
1.706
1.690
1.671
1.662
1.645
1.625
1.595
1.458
1.279
1.262
N
CO2Me
0.99
0.97
2.91
2.07
0.96
3.00
1.08
3.22
2.03
3.15
3.04
2.01
15
10
5
0



165.465
149.841
148.565
144.554
144.063
137.940
131.659
128.326
128.165
127.881
125.656
123.309
52.426
37.498
32.494
25.563
25.294
21.749
17.292
200
150
100
50
0
PPM
N
CO2Me


7.313
7.309
7.295
7.281
7.277
7.269
7.250
7.246
7.240
7.229
7.206
7.188
5.614
5.610
5.602
5.598
5.357
4.073
4.060
3.748
2.123
2.113
2.099
2.077
1.893
1.878
1.876
1.871
1.862
1.846
1.831
1.747
1.739
1.731
1.728
1.718
1.710
1.705
1.702
1.691
1.688
1.681
1.594
1.584
1.578
1.571
1.567
-0.002
H
N
CO2Me
5.16
0.97
1.00
1.04
3.00
2.09
2.03
2.09
2.14
15
10
5
0


164.140
146.338
129.312
128.231
128.153
127.688
126.121
108.912
104.066
51.813
46.052
26.796
24.752
22.947
22.326
NH
CO2Me
200
150
100
50
0
PPM

CIF for **3aa**:

```
data_s

_audit_creation_method                  SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common                   ?
_chemical_melting_point                 ?
_chemical_formula_moiety                ?
_chemical_formula_sum
 'C2.52 H2.52 N0.15 O0.30'
_chemical_formula_weight                39.60

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'   'C'    0.0033    0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'   'H'    0.0000    0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'   'N'    0.0061    0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'   'O'    0.0106    0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting                  ?
_symmetry_space_group_name_H-M          ?

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, y, -z+1/2'
 'x+1/2, y+1/2, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y, z-1/2'
 '-x+1/2, -y+1/2, -z'
 'x+1/2, -y+1/2, z-1/2'
```

```
_cell_length_a                    12.175(2)
_cell_length_b                    10.945(2)
_cell_length_c                    20.162(4)
_cell_angle_alpha                 90.00
_cell_angle_beta                  91.26(3)
_cell_angle_gamma                   90.00
_cell_volume                      2686.0(9)
_cell_formula_units_Z             54
_cell_measurement_temperature     293(2)
_cell_measurement_reflns_used     ?
_cell_measurement_theta_min       ?
_cell_measurement_theta_max       ?

_exptl_crystal_description        ?
_exptl_crystal_colour             ?
_exptl_crystal_size_max           ?
_exptl_crystal_size_mid           ?
_exptl_crystal_size_min           ?
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.322
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000                1136
_exptl_absorpt_coefficient_mu     0.087
_exptl_absorpt_correction_type    ?
_exptl_absorpt_correction_T_min   ?
_exptl_absorpt_correction_T_max   ?
_exptl_absorpt_process_details    ?

_exptl_special_details
;
  ?
;

_diffrn_ambient_temperature       293(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   ?
_diffrn_measurement_method          ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number            ?
_diffrn_standards_interval_count  ?
```

```
_diffrn_standards_interval_time      ?
_diffrn_standards_decay_%            ?
_diffrn_reflns_number                7633
_diffrn_reflns_av_R_equivalents      0.0239
_diffrn_reflns_av_sigmaI/netI        0.0274
_diffrn_reflns_limit_h_min           -11
_diffrn_reflns_limit_h_max           14
_diffrn_reflns_limit_k_min           -13
_diffrn_reflns_limit_k_max           12
_diffrn_reflns_limit_l_min           -23
_diffrn_reflns_limit_l_max           24
_diffrn_reflns_theta_min             3.19
_diffrn_reflns_theta_max             26.02
_reflns_number_total                 2551
_reflns_number_gt                    2235
_reflns_threshold_expression         >2sigma(I)

_computing_data_collection           ?
_computing_cell_refinement           ?
_computing_data_reduction            ?
_computing_structure_solution        'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement      'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics        ?
_computing_publication_material      ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0501P)^2^+1.0649P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
```

_refine_ls_hydrogen_treatment mixed
_refine_ls_extinction_method none
_refine_ls_extinction_coef ?
_refine_ls_number_reflns 2551
_refine_ls_number_parameters 182
_refine_ls_number_restraints 0
_refine_ls_R_factor_all 0.0464
_refine_ls_R_factor_gt 0.0386
_refine_ls_wR_factor_ref 0.0978
_refine_ls_wR_factor_gt 0.0931
_refine_ls_goodness_of_fit_ref 1.055
_refine_ls_restrained_S_all 1.055
_refine_ls_shift/su_max 0.000
_refine_ls_shift/su_mean 0.000

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group
O1 O 0.51739(8) 0.14519(8) 0.42079(5) 0.0298(3) Uani 1 1 d . . .
O2 O 0.37193(7) 0.21885(8) 0.47462(5) 0.0268(2) Uani 1 1 d . . .
N1 N 0.40883(8) 0.44536(10) 0.43373(5) 0.0211(3) Uani 1 1 d . . .
C4 C 0.58272(10) 0.50029(12) 0.34962(6) 0.0203(3) Uani 1 1 d . . .
C5 C 0.51148(10) 0.59268(12) 0.37049(6) 0.0202(3) Uani 1 1 d . . .
C6 C 0.56418(10) 0.38101(12) 0.37122(6) 0.0213(3) Uani 1 1 d . . .
H6 H 0.6092 0.3176 0.3576 0.026 Uiso 1 1 calc R . .
C7 C 0.47776(10) 0.35827(11) 0.41320(6) 0.0208(3) Uani 1 1 d . . .
C8 C 0.42514(10) 0.55983(12) 0.41253(6) 0.0203(3) Uani 1 1 d . . .
C9 C 0.67548(10) 0.52253(12) 0.30380(6) 0.0208(3) Uani 1 1 d . . .
C10 C 0.52137(11) 0.72306(12) 0.34665(7) 0.0254(3) Uani 1 1 d . . .
H10A H 0.5494 0.7232 0.3020 0.030 Uiso 1 1 calc R . .
H10B H 0.5736 0.7663 0.3751 0.030 Uiso 1 1 calc R . .
C11 C 0.68254(11) 0.45377(12) 0.24599(6) 0.0242(3) Uani 1 1 d . . .
H11 H 0.6281 0.3968 0.2356 0.029 Uiso 1 1 calc R . .

C12 C 0.45931(10) 0.22973(12) 0.43617(6) 0.0217(3) Uani 1 1 d . . .
C13 C 0.34754(12) 0.09552(13) 0.49651(7) 0.0301(3) Uani 1 1 d . . .
H13A H 0.3430 0.0421 0.4588 0.045 Uiso 1 1 calc R . .
H13B H 0.2787 0.0951 0.5188 0.045 Uiso 1 1 calc R . .
H13C H 0.4048 0.0678 0.5264 0.045 Uiso 1 1 calc R . .
C14 C 0.84551(11) 0.62152(12) 0.27625(7) 0.0282(3) Uani 1 1 d . . .
H14 H 0.9007 0.6774 0.2868 0.034 Uiso 1 1 calc R . .
C15 C 0.75793(10) 0.60761(12) 0.31827(7) 0.0243(3) Uani 1 1 d . . .
H15 H 0.7540 0.6552 0.3563 0.029 Uiso 1 1 calc R . .
C16 C 0.36360(11) 0.78275(12) 0.41591(6) 0.0249(3) Uani 1 1 d . . .
H16A H 0.2961 0.8297 0.4169 0.030 Uiso 1 1 calc R . .
H16B H 0.4151 0.8181 0.4479 0.030 Uiso 1 1 calc R . .
C17 C 0.85173(11) 0.55286(13) 0.21863(7) 0.0292(3) Uani 1 1 d . . .
H17 H 0.9104 0.5630 0.1904 0.035 Uiso 1 1 calc R . .
C18 C 0.34009(10) 0.65079(12) 0.43485(7) 0.0243(3) Uani 1 1 d . . .
H18A H 0.3349 0.6458 0.4827 0.029 Uiso 1 1 calc R . .
H18B H 0.2692 0.6276 0.4158 0.029 Uiso 1 1 calc R . .
C19 C 0.41133(11) 0.78978(13) 0.34687(7) 0.0278(3) Uani 1 1 d . . .
H19A H 0.4216 0.8746 0.3344 0.033 Uiso 1 1 calc R . .
H19B H 0.3610 0.7525 0.3149 0.033 Uiso 1 1 calc R . .
C20 C 0.76977(11) 0.46919(13) 0.20362(7) 0.0277(3) Uani 1 1 d . . .
H20 H 0.7731 0.4231 0.1650 0.033 Uiso 1 1 calc R . .

loop_
 _atom_site_aniso_label
 _atom_site_aniso_U_11
 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
O1 0.0333(5) 0.0233(5) 0.0333(5) 0.0047(4) 0.0109(4) 0.0061(4)
O2 0.0260(5) 0.0192(5) 0.0358(5) 0.0043(4) 0.0112(4) -0.0003(4)
N1 0.0209(5) 0.0207(6) 0.0216(5) 0.0005(4) 0.0016(4) -0.0001(4)
C4 0.0182(6) 0.0235(7) 0.0193(6) 0.0006(5) -0.0011(5) -0.0007(5)
C5 0.0202(6) 0.0216(7) 0.0187(6) 0.0004(5) -0.0010(5) -0.0003(5)
C6 0.0188(6) 0.0213(7) 0.0238(6) -0.0002(5) 0.0004(5) 0.0019(5)
C7 0.0195(6) 0.0221(7) 0.0206(6) 0.0006(5) -0.0007(5) 0.0006(5)
C8 0.0207(6) 0.0210(7) 0.0192(6) -0.0005(5) -0.0003(5) -0.0003(5)
C9 0.0194(6) 0.0198(7) 0.0232(6) 0.0045(5) 0.0017(5) 0.0026(5)
C10 0.0259(7) 0.0238(7) 0.0267(7) 0.0031(6) 0.0059(5) 0.0009(5)
C11 0.0218(6) 0.0243(7) 0.0266(7) 0.0011(6) 0.0011(5) 0.0008(5)
C12 0.0211(6) 0.0235(7) 0.0208(6) 0.0004(5) 0.0021(5) 0.0012(5)
C13 0.0309(7) 0.0195(7) 0.0404(8) 0.0072(6) 0.0102(6) -0.0020(6)

C14 0.0206(6) 0.0242(7) 0.0400(8) 0.0063(6) 0.0023(6) -0.0019(5)
C15 0.0225(6) 0.0231(7) 0.0273(7) 0.0006(6) 0.0007(5) 0.0005(5)
C16 0.0238(7) 0.0225(7) 0.0286(7) -0.0012(6) 0.0022(5) 0.0030(5)
C17 0.0223(6) 0.0334(8) 0.0322(7) 0.0121(6) 0.0082(5) 0.0046(6)
C18 0.0229(7) 0.0246(7) 0.0256(7) -0.0015(5) 0.0041(5) 0.0012(5)
C19 0.0303(7) 0.0226(7) 0.0305(7) 0.0051(6) 0.0037(6) 0.0040(6)
C20 0.0278(7) 0.0326(8) 0.0229(7) 0.0009(6) 0.0030(5) 0.0071(6)

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

loop_
_geom_bond_atom_site_label_1
_geom_bond_atom_site_label_2
_geom_bond_distance
_geom_bond_site_symmetry_2
_geom_bond_publ_flag
O1 C12 1.2091(15) . ?
O2 C12 1.3353(16) . ?
O2 C13 1.4528(16) . ?
N1 C8 1.3400(17) . ?
N1 C7 1.3415(17) . ?
C4 C6 1.3961(18) . ?
C4 C5 1.4028(18) . ?
C4 C9 1.4948(18) . ?
C5 C8 1.4113(18) . ?
C5 C10 1.5114(19) . ?
C6 C7 1.3872(18) . ?
C7 C12 1.4996(18) . ?
C8 C18 1.5120(18) . ?
C9 C11 1.3916(19) . ?
C9 C15 1.3953(18) . ?
C10 C19 1.5259(19) . ?
C11 C20 1.3878(19) . ?
C14 C15 1.3848(19) . ?
C14 C17 1.387(2) . ?
C16 C19 1.5221(19) . ?

```
C16 C18 1.5227(19) . ?
C17 C20 1.383(2) . ?

loop_
  _geom_angle_atom_site_label_1
  _geom_angle_atom_site_label_2
  _geom_angle_atom_site_label_3
  _geom_angle
  _geom_angle_site_symmetry_1
  _geom_angle_site_symmetry_3
  _geom_angle_publ_flag
C12 O2 C13 115.47(10) . . ?
C8 N1 C7 117.89(11) . . ?
C6 C4 C5 118.38(12) . . ?
C6 C4 C9 118.33(11) . . ?
C5 C4 C9 123.27(11) . . ?
C4 C5 C8 118.04(12) . . ?
C4 C5 C10 122.08(11) . . ?
C8 C5 C10 119.81(11) . . ?
C7 C6 C4 119.21(12) . . ?
N1 C7 C6 123.29(12) . . ?
N1 C7 C12 118.18(11) . . ?
C6 C7 C12 118.53(11) . . ?
N1 C8 C5 123.18(11) . . ?
N1 C8 C18 114.42(11) . . ?
C5 C8 C18 122.35(12) . . ?
C11 C9 C15 118.60(12) . . ?
C11 C9 C4 119.41(11) . . ?
C15 C9 C4 121.95(12) . . ?
C5 C10 C19 112.01(11) . . ?
C20 C11 C9 120.79(13) . . ?
O1 C12 O2 123.96(12) . . ?
O1 C12 C7 123.11(12) . . ?
O2 C12 C7 112.93(11) . . ?
C15 C14 C17 120.65(13) . . ?
C14 C15 C9 120.36(13) . . ?
C19 C16 C18 110.79(11) . . ?
C20 C17 C14 119.32(13) . . ?
C8 C18 C16 114.59(11) . . ?
C16 C19 C10 109.35(11) . . ?
C17 C20 C11 120.27(13) . . ?

_diffrn_measured_fraction_theta_max    0.966
_diffrn_reflns_theta_full              26.02
```

_diffrn_measured_fraction_theta_full 0.966
_refine_diff_density_max 0.167
_refine_diff_density_min -0.197
_refine_diff_density_rms 0.035