

Electronic Supplementary Information

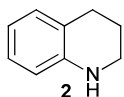
An efficient one pot transfer hydrogenation and N-alkylation of quinolines with alcohols mediated by Pd/C/Zn.

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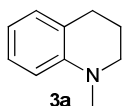
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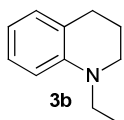
1. Evidences of known compounds.



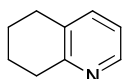
1,2,3,4-Tetrahydroquinoline. Yellow oil. *R_f* 0.50 (hexane–ethyl acetate, 1 : 1). IR (neat) 3196, 3134, 2916, 2849, 1679, 1589, 1486, 1384, 1281, 819, 742 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 6.96 (2H, m), 6.62 (1H, ddd, $J = 7.4, 7.4, 1.2$ Hz), 6.5 (1H, d, $J = 8.4$ Hz), 3.81 (1H, br, NH), 3.31 (2H, t, $J = 5.5$ Hz), 2.77 (2H, t, $J = 6.4$ Hz), 1.95 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ 142.6, 127.3, 124.5, 119.2, 114.7, 112.0, 39.8, 24.8, 20.0. Lit.¹



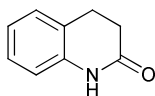
1-Methyl-1,2,3,4-tetrahydroquinoline. Yellow oil. *R_f* 0.78 (hexane–ethyl acetate, 1 : 1). IR (neat) 2926, 2856, 1602, 1506, 1223, 1058, 723 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 7.13 (1H, dd, $J = 7.5, 7.5$ Hz), 7.00 (1H, d, $J = 7.1$ Hz), 6.66 (2H, m), 3.28 (2H, t, $J = 5.6$ Hz), 2.94 (3H, s), 2.81 (2H, t, $J = 6.4$ Hz), 2.04 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ 146.2, 128.6, 126.5, 122.2, 115.5, 110.3, 50.5, 38.4, 27.1, 21.7. Lit.²



1-Ethyl-1,2,3,4-tetrahydroquinoline. Yellow oil. *R_f* 0.80 (hexane–ethyl acetate, 1 : 1). IR (neat) 2921, 2841, 1607, 1499, 1371, 1248, 1086, 758 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 7.04 (1H, dd, $J = 7.6, 7.6$ Hz), 6.93 (1H, d, $J = 7.6$ Hz), 6.57 (2H, m, $J = 7.6$ Hz), 3.34 (2H, q, $J = 7.2$ Hz), 3.26 (2H, t, $J = 6.2$ Hz), 2.75 (2H, t, $J = 6.2$ Hz), 1.96 (m, 2H), 1.13 (2H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 142.9, 127.0, 124.9, 120.3, 113.3, 108.4, 46.3, 43.2, 26.1, 20.2, 10.7. Lit.¹

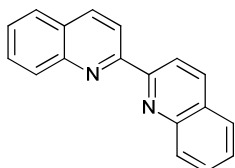


5,6,7,8-Tetrahydroquinoline. Yellow oil. *R_f* 0.63 (hexane–ethyl acetate, 1 : 1). IR (neat) 2921, 2847, 1602, 1453, 740, 696 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 8.33 (1H, d, $J = 4.1$ Hz), 7.33 (1H, d, $J = 7.3$ Hz), 7.01 (1H, d, $J = 7.3, 4.1$ Hz), 2.92 (3H, t, $J = 6.2$ Hz), 2.76 (2H, t, $J = 6.3$ Hz), 7.33 (1H, d, $J = 7.3$ Hz), 1.85 (4H, m). HRMS found for $[\text{M}+\text{H}]^+$ 134.0970; $\text{C}_9\text{H}_{12}\text{N}$ requires 134.0970. Lit.³

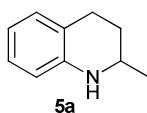


3,4-Dihydroquinolin-2(1H)-one. Yellow oil. *R_f* 0.49 (hexane–ethyl acetate, 1 : 1). IR (neat) 3185, 3080, 2906, 1699, 1587, 1379, 1196, 824, 742 cm^{-1} . ^1H NMR (CDCl_3 , 300

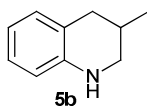
MHz): δ 7.92 (1H, br, NH), 7.18 (2H, m), 6.99 (2H, ddd, $J = 7.5, 7.5, 1.1$ Hz), 6.74 (1H, dd, $J = 7.7, 1.4$ Hz), 2.98 (2H, t, $J = 7.1$ Hz), 2.64 (2H, t, $J = 7.3$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 171.6, 137.8, 128.3, 126.9, 124.0, 123.5, 116.0, 31.2, 25.6. Lit.⁴



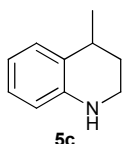
2, 2'-Biquinoline. Yellow solid, mp: 193-196 °C. R_f 0.80 (hexane–ethyl acetate, 1 : 1). IR (neat) 2911, 2847, 1671, 1597, 1492, 1384, 1276, 740 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 8.86 (2H, d, $J = 8.6$ Hz), 8.34 (2H, d, $J = 8.6$ Hz), 8.24 (2H, d, $J = 8.6$ Hz), 7.90 (2H, d, $J = 8.4$ Hz), 7.76 (2H, ddd, $J = 8.4, 6.9, 1.5$ Hz), 7.58 (2H, ddd, $J = 8.1, 6.9, 1.2$ Hz). Lit.⁵



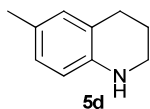
2-Methyl-1,2,3,4-tetrahydroquinoline. Yellow oil. R_f 0.89 (hexane–ethyl acetate, 1 : 1). IR (neat) 3394, 2968, 2924, 2849, 1605, 1587, 1490, 1309, 728 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 6.96 (2H, m), 6.60 (1H, ddd, $J = 7.4, 7.4, 1.1$ Hz), 6.47 (1H, dd, $J = 8.1, 1.2$ Hz), 3.69 (1H, br), 3.40 (1H, m), 2.79 (2H, m), 1.93 (1H, m), 1.59 (1H, m), 1.20 (3H, d, $J = 6.3$ Hz). HRMS found for $[\text{M}+\text{H}]^+$ 148.1128; $\text{C}_{10}\text{H}_{14}\text{N}$ requires 148.1126. Lit.⁶



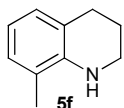
3-Methyl-1,2,3,4-tetrahydroquinoline. Yellow oil. R_f 0.67 (hexane–ethyl acetate, 1 : 1). IR (neat) 3512, 2982, 2926, 2852, 1598, 1230, 1052, 736 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 6.98 (2H, m), 6.63 (1H, ddd, $J = 7.4, 7.4, 1.2$ Hz), 6.50 (1H, d, $J = 7.9$ Hz), 3.66 (1H, br), 3.28 (1H, m), 2.91 (1H, t, $J = 9.7$ Hz), 2.80 (1H, m), 2.45 (1H, m), 2.07 (1H, m), 1.07 (3H, d, $J = 6.6$ Hz). HRMS found for $[\text{M}+\text{H}]^+$ 148.1128; $\text{C}_{10}\text{H}_{14}\text{N}$ requires 148.1126. Lit.⁶



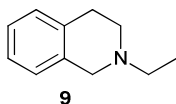
4-Methyl-1,2,3,4-tetrahydroquinoline. Yellow oil. R_f 0.74 (hexane–ethyl acetate, 1 : 1). IR (neat) 3676, 2991, 2916, 2842, 1610, 1078, 1079, 756, 673 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.08 (1H, dd, $J = 7.6$ Hz), 6.99 (1H, ddd, $J = 7.7, 7.5, 1.5$ Hz), 6.66 (1H, ddd, $J = 7.4, 7.4, 1.2$ Hz), 6.50 (1H, dd, $J = 8.0, 1.2$ Hz), 3.59 (1H, br, NH), 3.32 (2H, m), 2.94 (1H, m), 2.01 (1H, m), 1.70 (1H, m), 1.32 (3H, d, $J = 7.0$ Hz). HRMS found for $[\text{M}+\text{H}]^+$ 148.1128; $\text{C}_{10}\text{H}_{14}\text{N}$ requires 148.1126. Lit.⁷



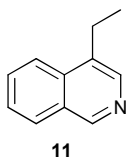
6-Methyl-1,2,3,4-tetrahydroquinoline. Yellow oil. *R_f* 0.57 (hexane–ethyl acetate, 1 : 1). IR (neat) 3420, 2911, 2845, 1656, 1599, 1502, 1359, 1302, 1069, 804 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 6.78 (2H, m), 6.43 (1H, d, $J = 8.6$ Hz), 3.28 (2H, t, $J = 5.5$ Hz), 3.15 (1H, br, NH), 2.74 (2H, t, $J = 6.4$ Hz), 2.21 (3H, s), 1.94 (2H, m). HRMS found for $[\text{M}+\text{H}]^+$ 148.1129; $\text{C}_{10}\text{H}_{14}\text{N}$ requires 148.1126. Lit.⁷



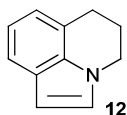
8-Methyl-1,2,3,4-tetrahydroquinoline. Yellow oil. *R_f* 0.70 (hexane–ethyl acetate, 1 : 1). IR (neat) 3421, 2916, 2847, 1597, 1504, 1463, 1299, 1236, 1104, 1042, 758, 727 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 6.94 (2H, m), 6.64 (1H, dd, $J = 7.4$ Hz), 3.56 (1H, br, NH), 3.43 (2H, t, $J = 5.5$ Hz), 2.86 (2H, t, $J = 6.4$ Hz), 2.15 (3H, s), 2.01 (2H, m). HRMS found for $[\text{M}+\text{H}]^+$ 148.1128; $\text{C}_{10}\text{H}_{14}\text{N}$ requires 148.1126. Lit.⁷



2-Ethyl-1,2,3,4-tetrahydroisoquinoline. Yellow oil. *R_f* 0.62 (hexane–ethyl acetate, 1 : 1). IR (neat) 2921, 2852, 1589, 1379, 1276, 1189, 1150, 735 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.10 (3H, m), 7.02 (1H, m), 3.63 (2H, s), 2.92 (2H, t, $J = 5.9$ Hz), 2.74 (2H, t, $J = 5.9$ Hz), 2.59 (2H, q, $J = 7.2$ Hz), 1.19 (3H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 132.2, 127.6, 126.2, 125.8, 124.8, 54.5, 51.2, 50.9, 28.0, 12.2. Lit.⁸

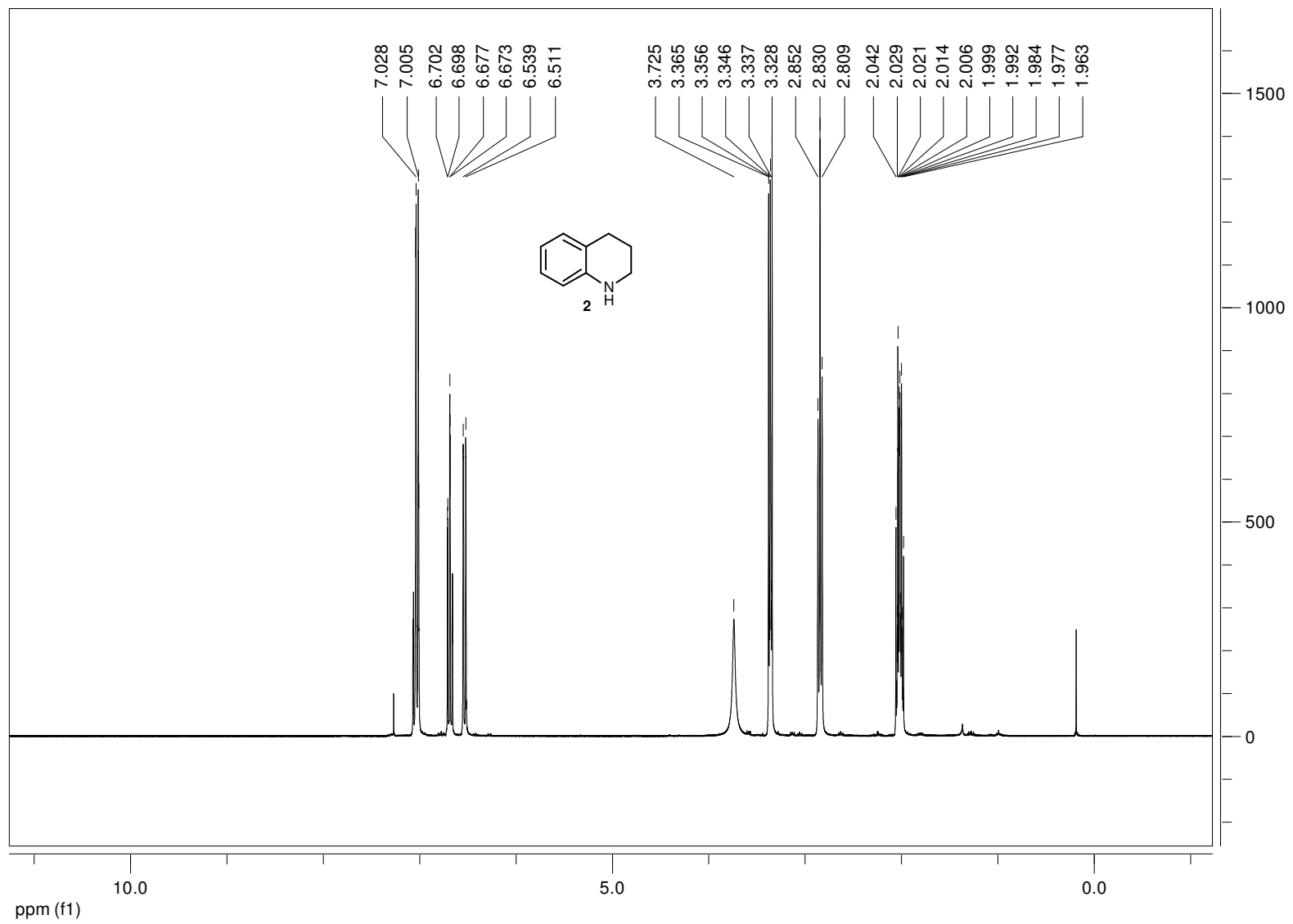


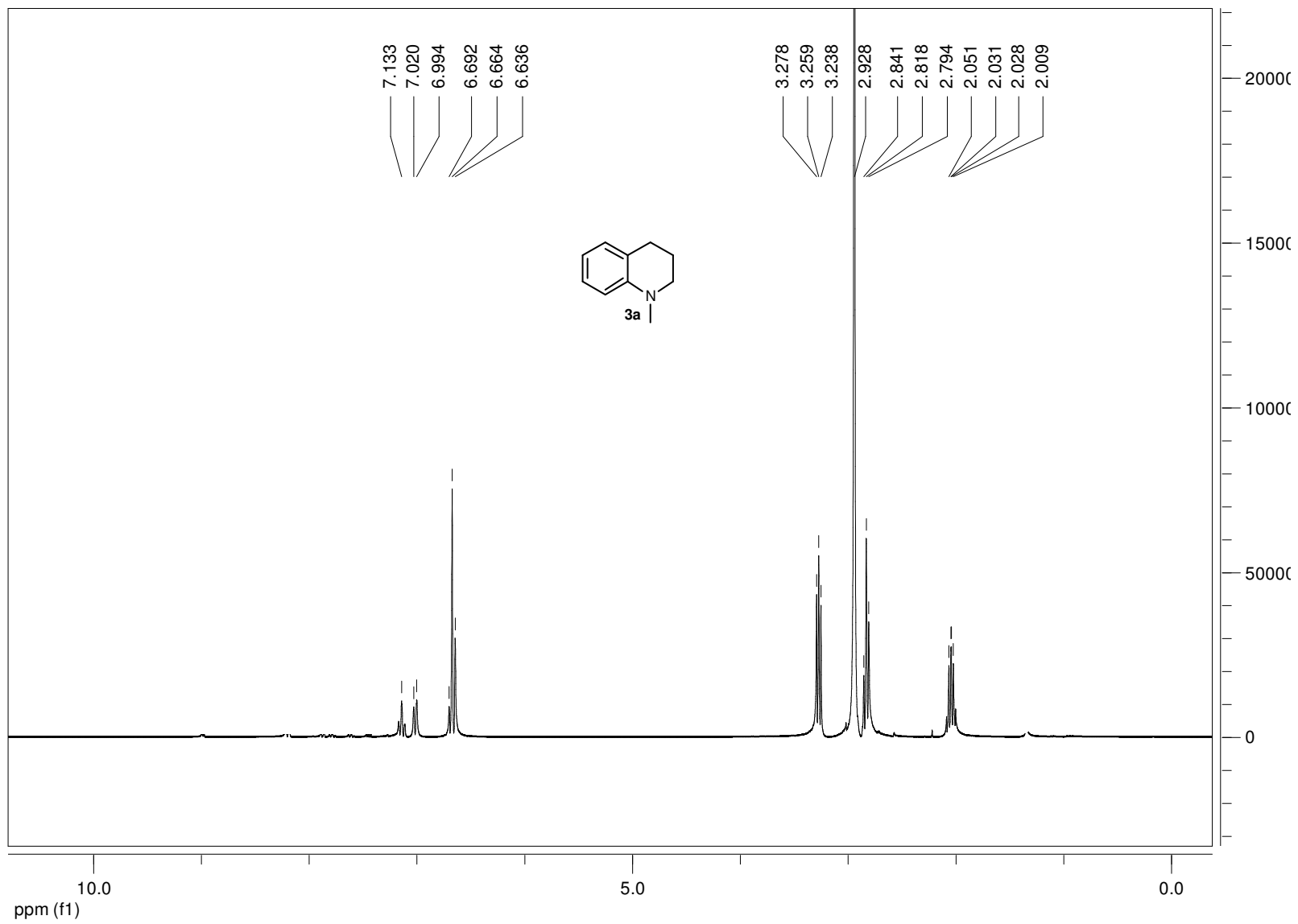
4-Ethylisoquinoline. Yellow oil. *R_f* 0.71 (hexane–ethyl acetate, 1 : 1). IR (neat) 3100, 1582, 1439, 1232, 727 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.11 (s, 1H), 8.38 (s, 1H), 8.00 (1H, d, $J = 8.2$ Hz), 7.98 (1H, d, $J = 8.2$ Hz), 7.71 (1H, ddd, $J = 8.2, 8.2, 1.3$ Hz, 1H), 7.59 (1H, dd, $J = 8.2, 8.2$ Hz), 3.06 (2H, q, $J = 7.5$ Hz), 1.38 (3H, t, $J = 7.5$ Hz). MS (E.I.): m/z (%) 157 (80.3); 142 (100); 128 (10.6); 115 (34.8); 89 (6.0). Lit.⁹

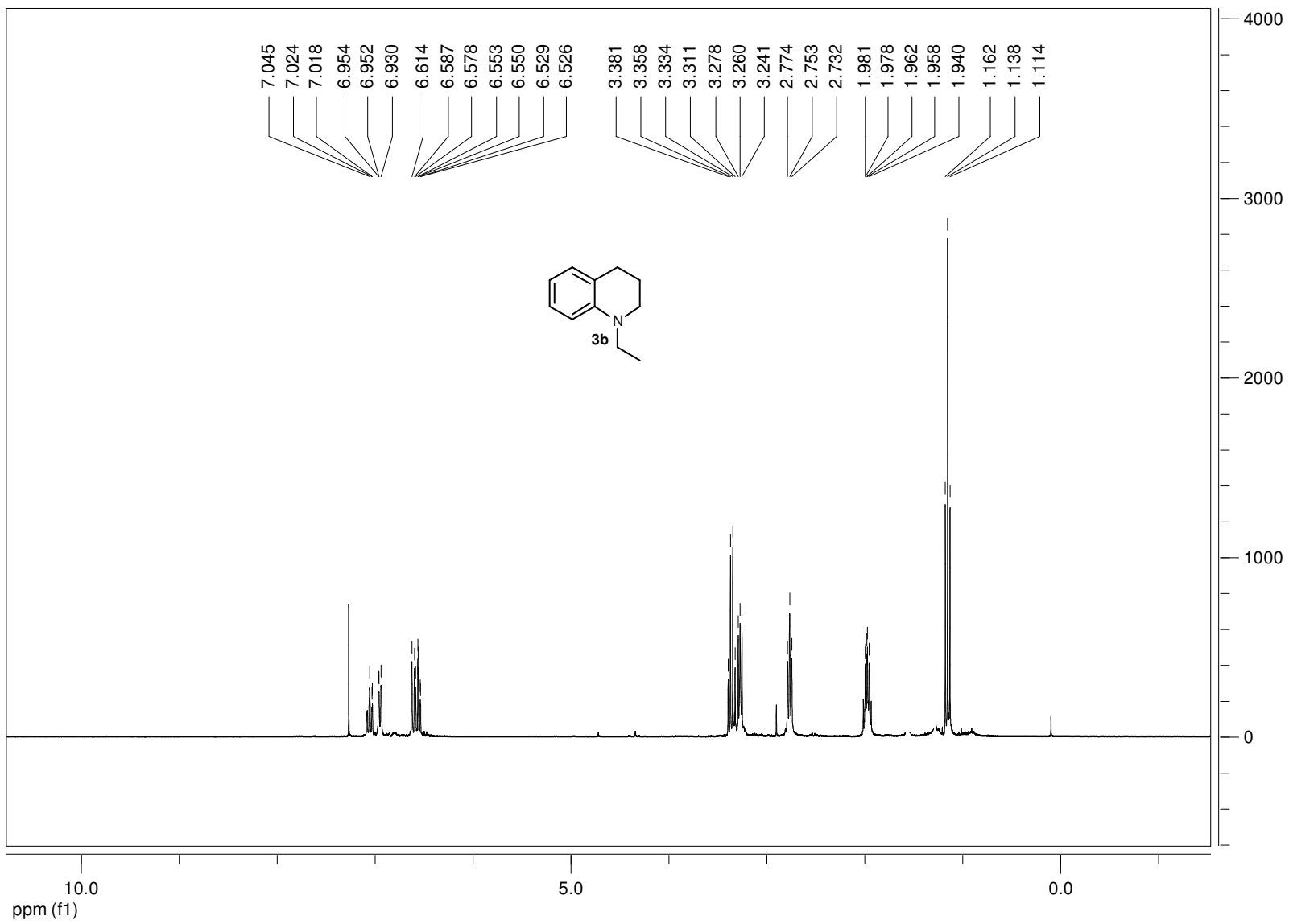


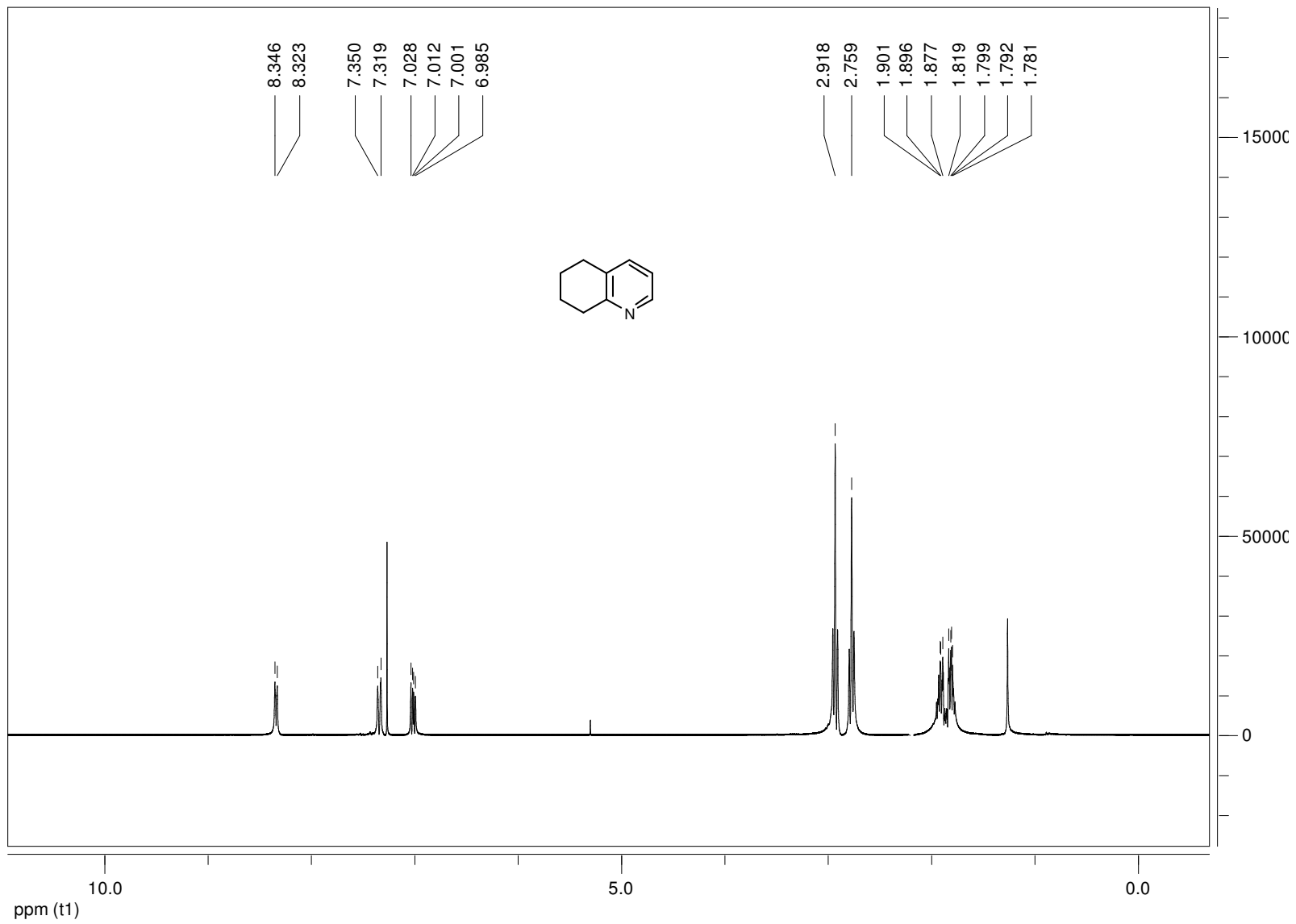
5,6-Dihydro-4H-pyrrolo[3,2,1-ij]quinoline. Yellow oil. *R_f* 0.87 (hexane–ethyl acetate, 1 : 1). IR (neat) 2921, 2849, 1461, 1381, 1261, 1071, 801, 724 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.37 (1H, dd, $J = 7.9, 0.8$ Hz), 7.00 (1H, d, $J = 3.0$ Hz), 6.94 (1H, dd, $J = 7.1, 7.1$ Hz), 6.84 (1H, dd, $J = 7.0, 0.9$ Hz), 6.37 (1H, d, $J = 3.0$ Hz), 4.09 (2H, t, $J = 5.7$ Hz), 2.93 (2H, t, $J = 6.1$ Hz), 2.17 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ 134.2, 126.0, 125.9, 121.7, 119.6, 118.3, 118.1, 100.4, 44.2, 24.8, 23.0. Lit.¹⁰

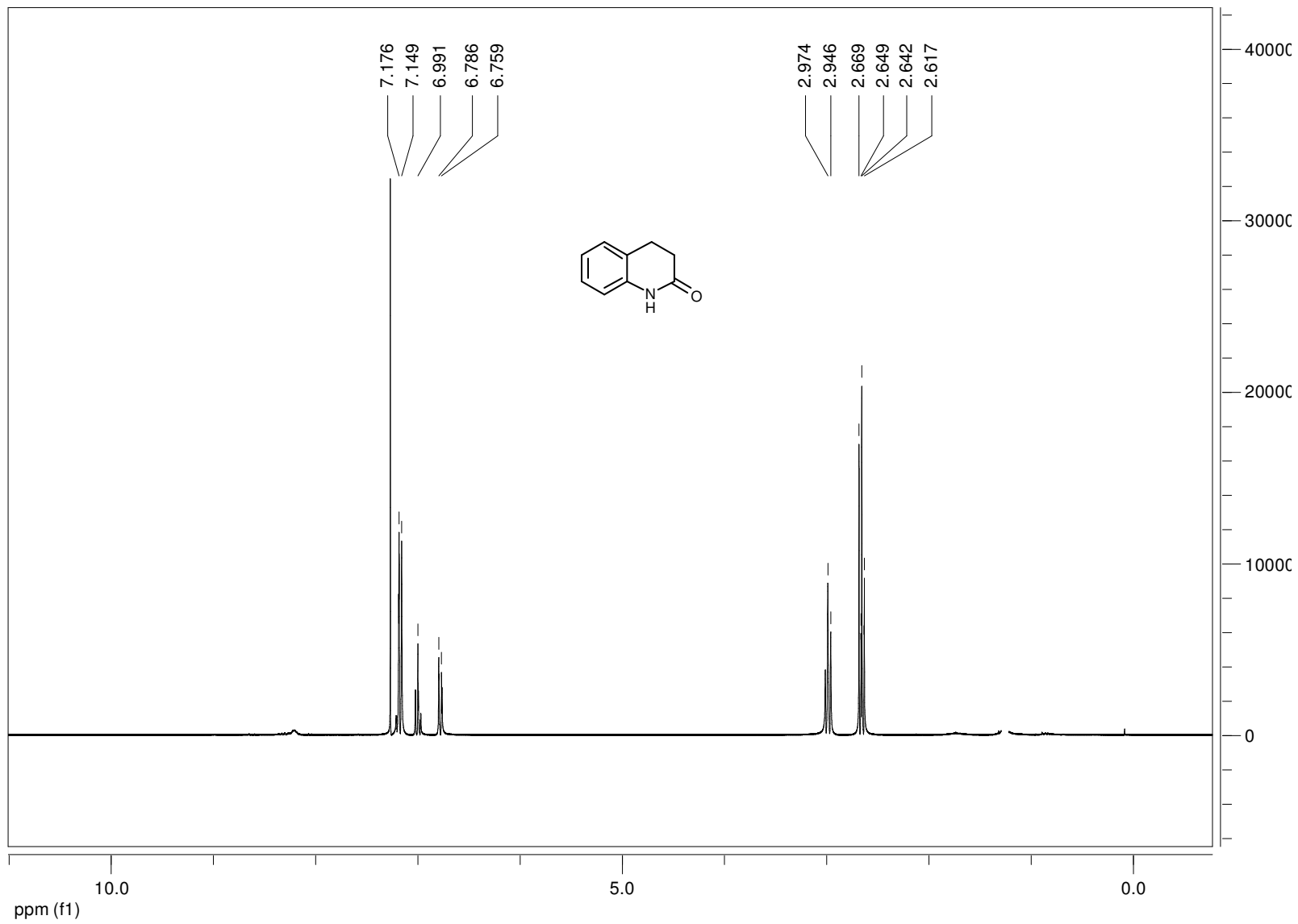
2. Spectra of known compounds.

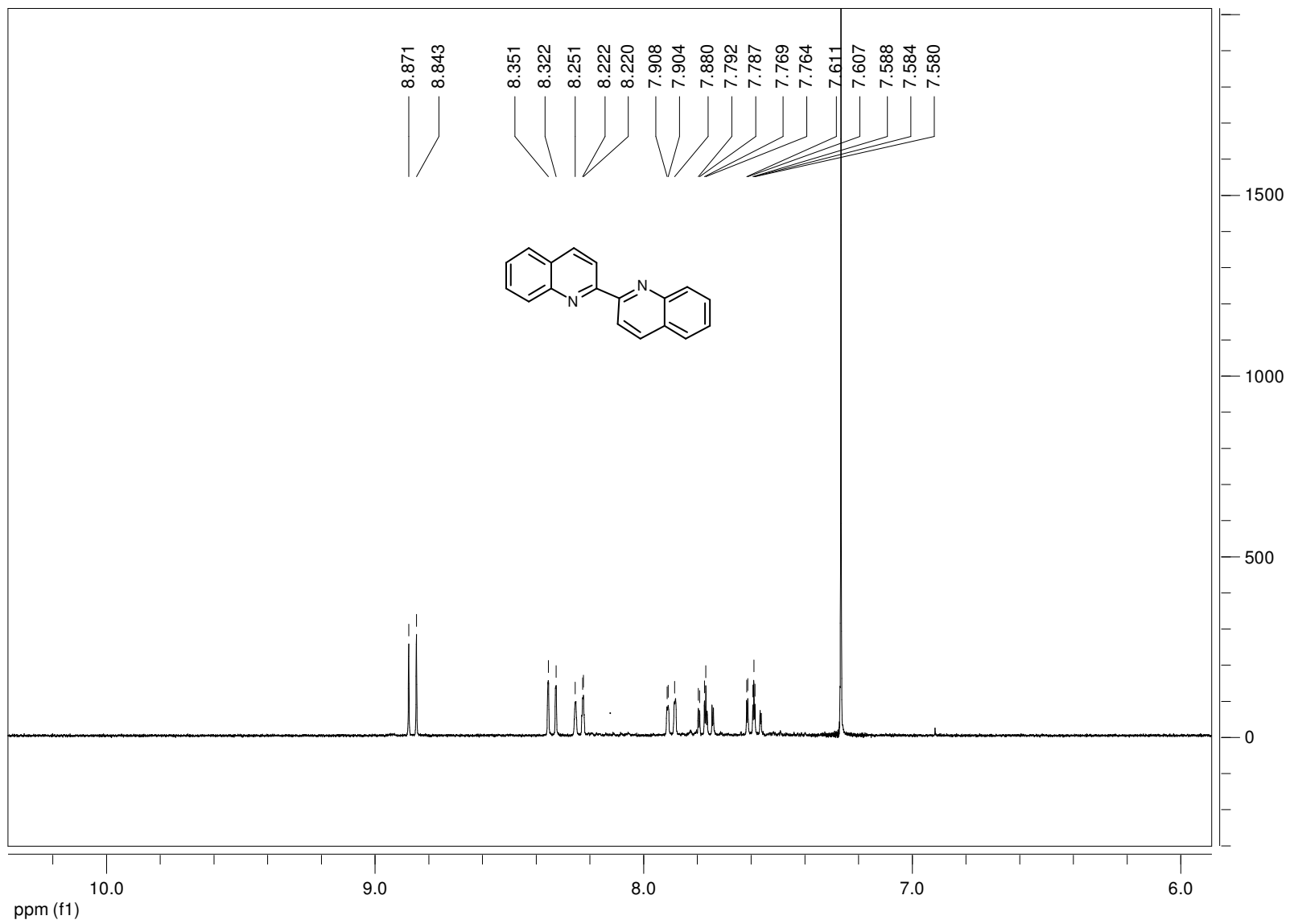


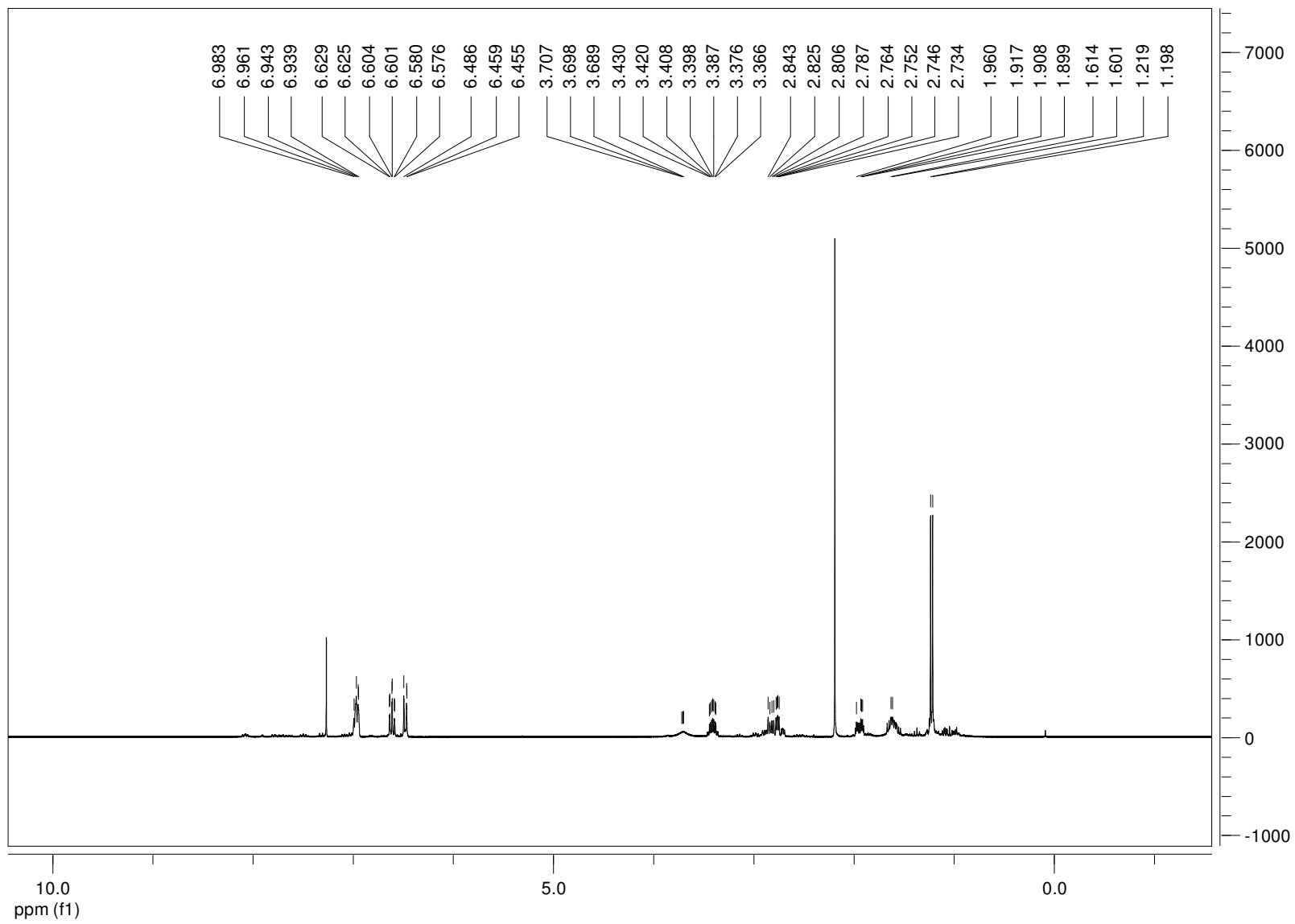


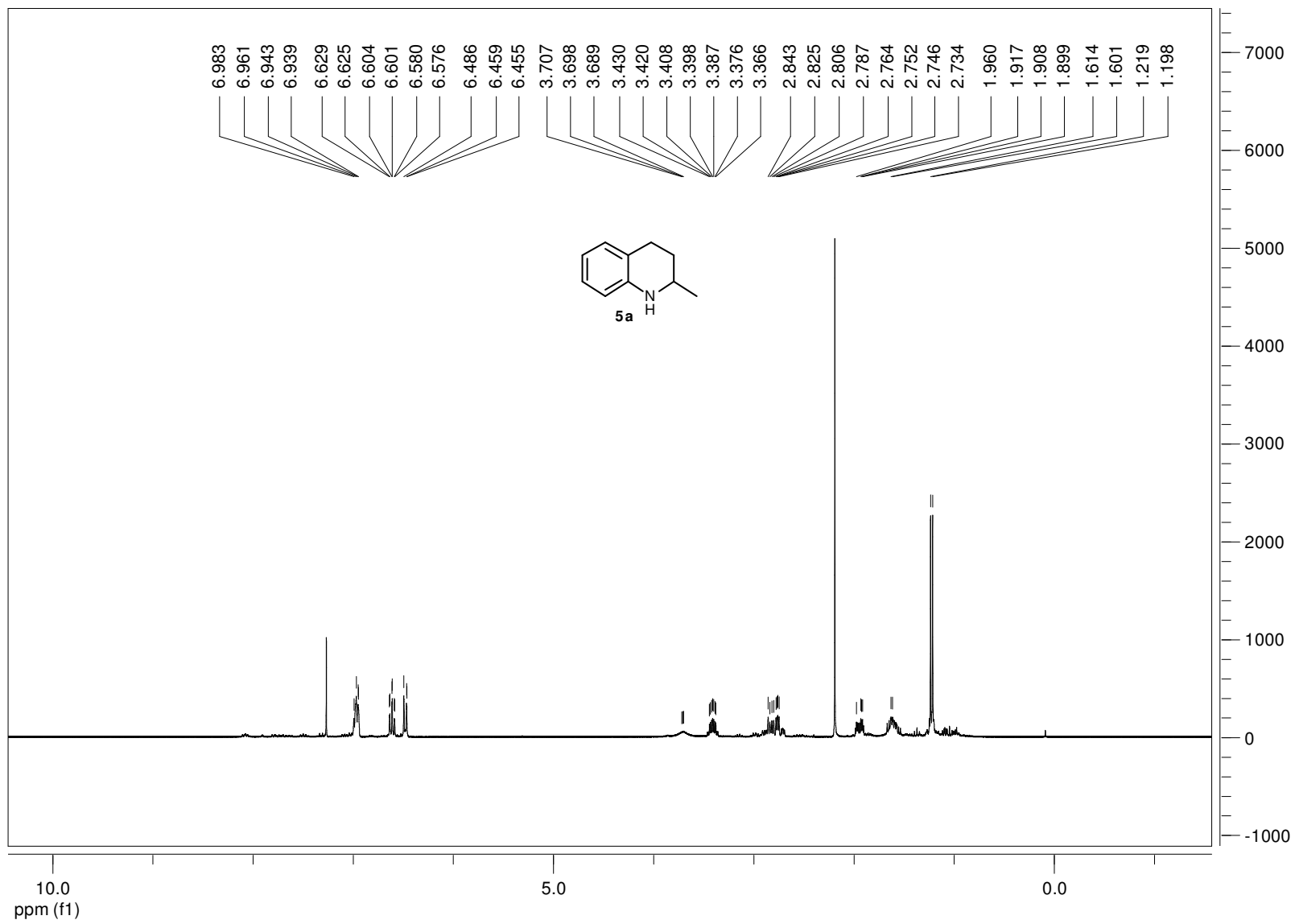


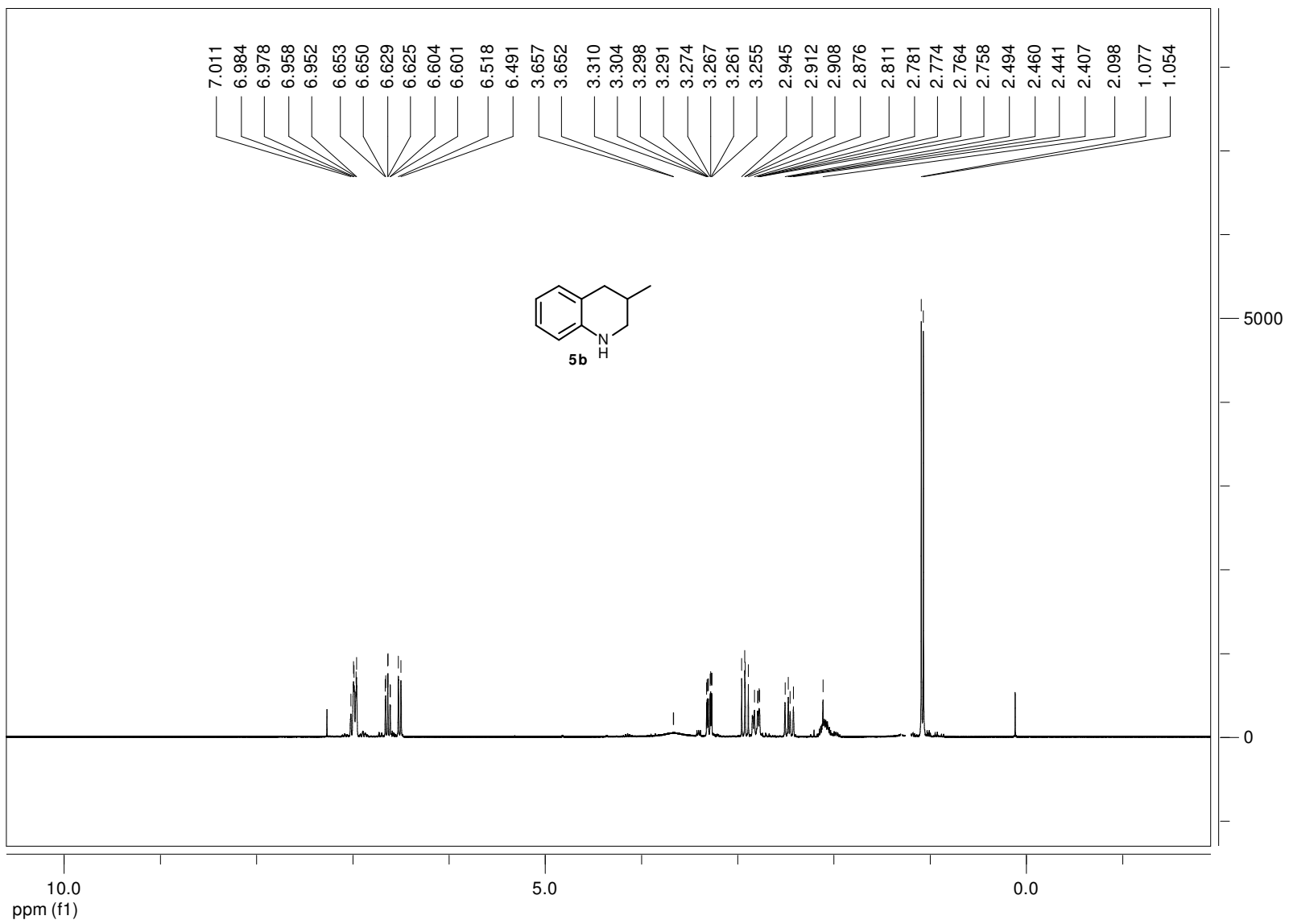


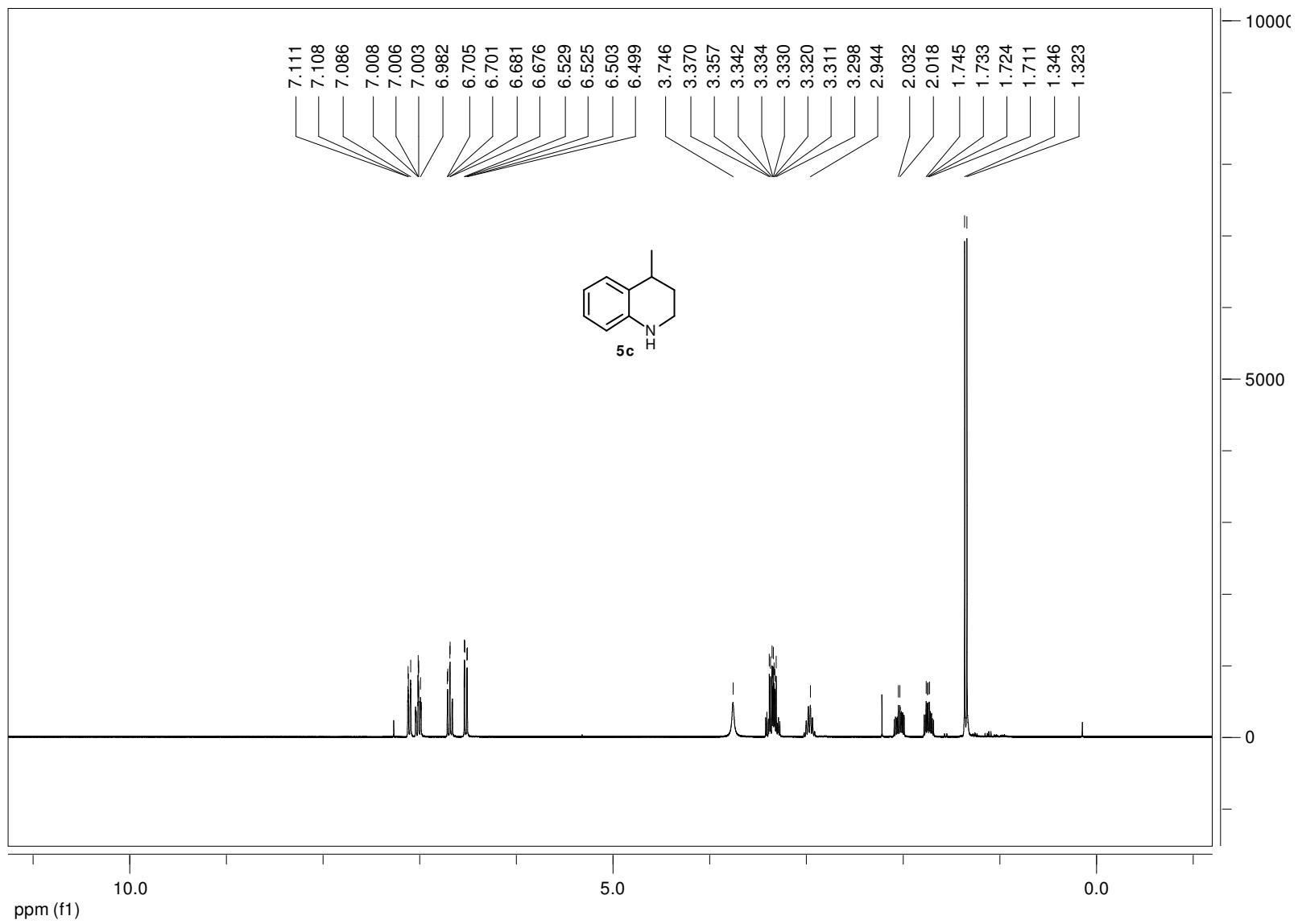


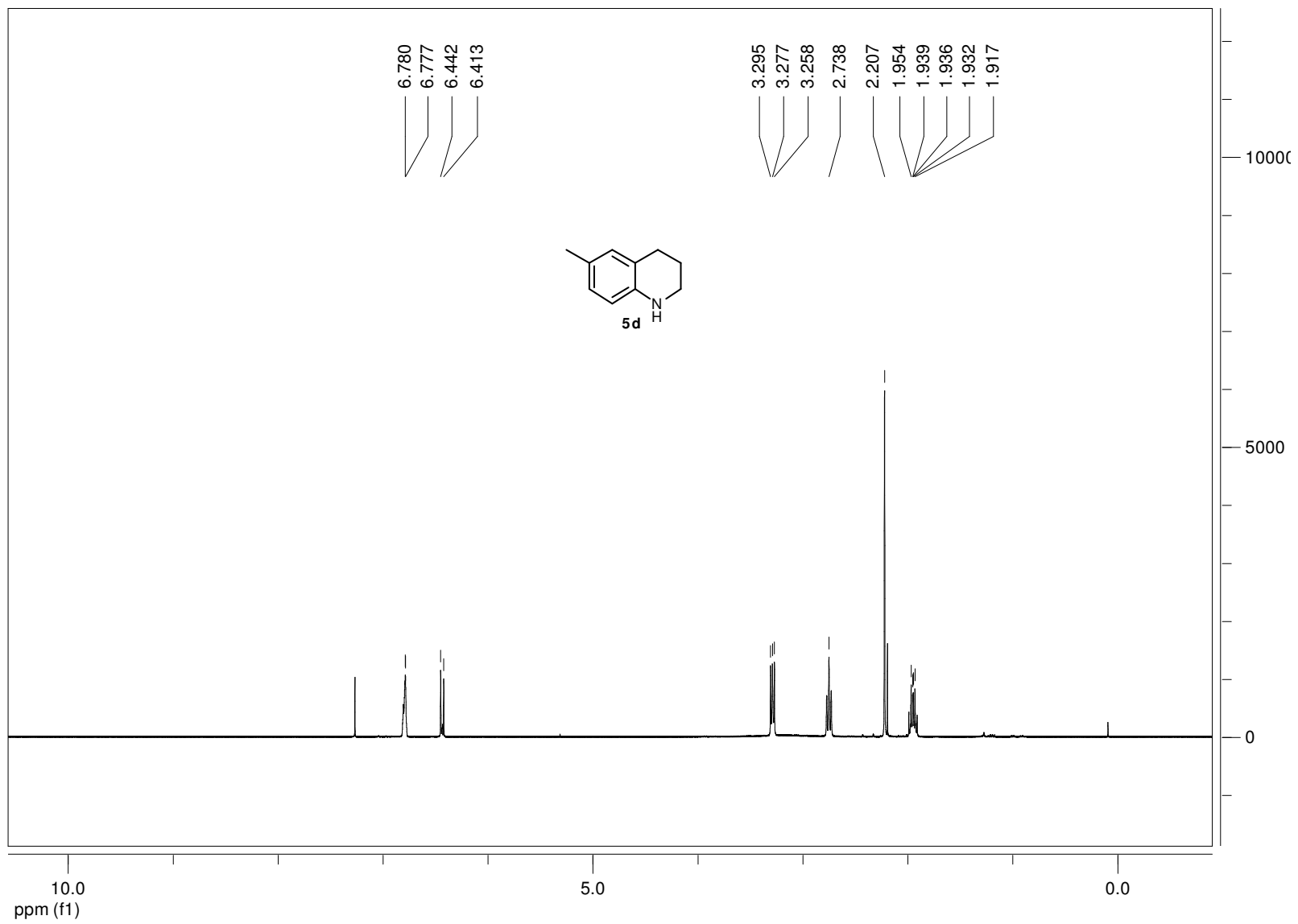


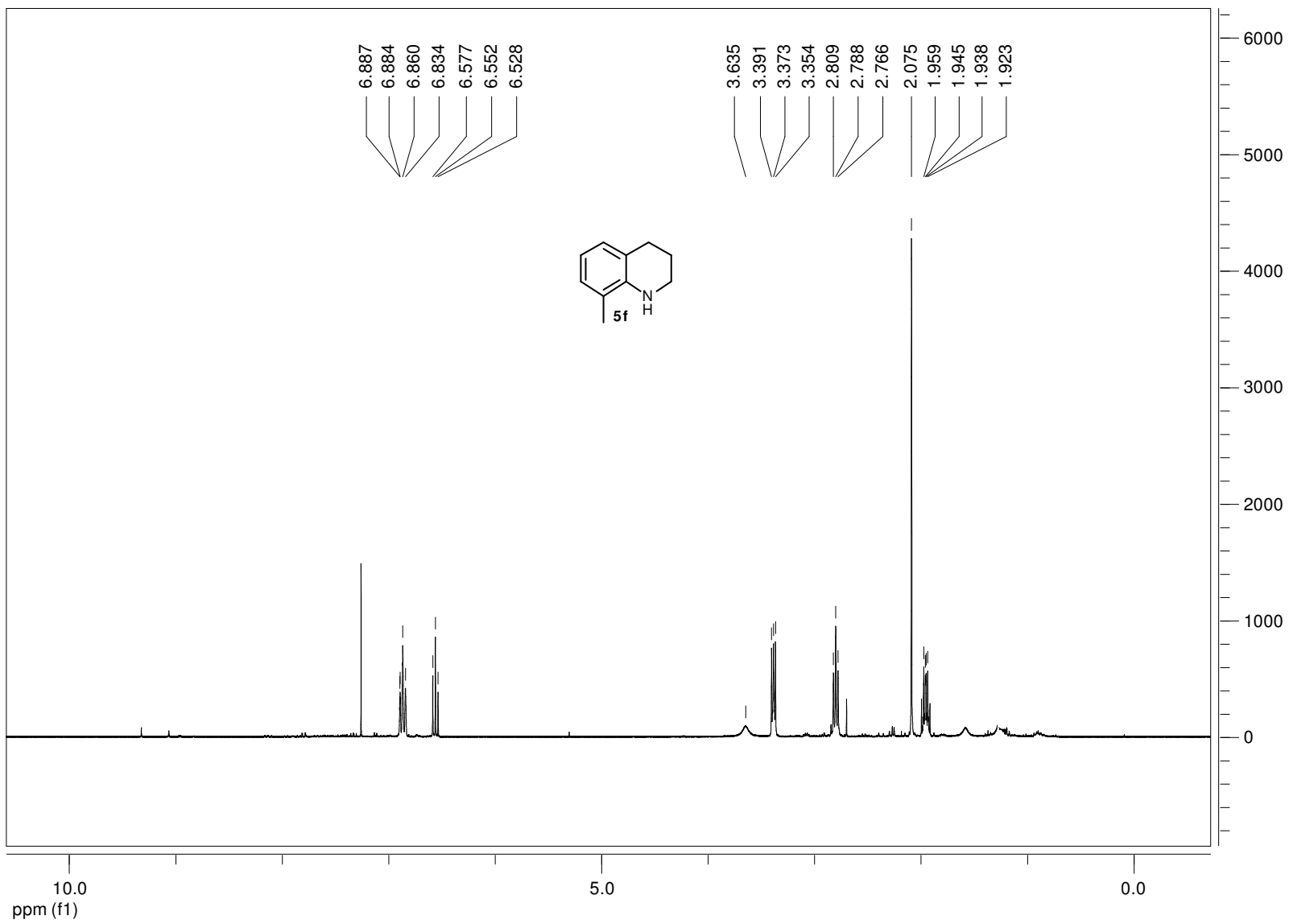


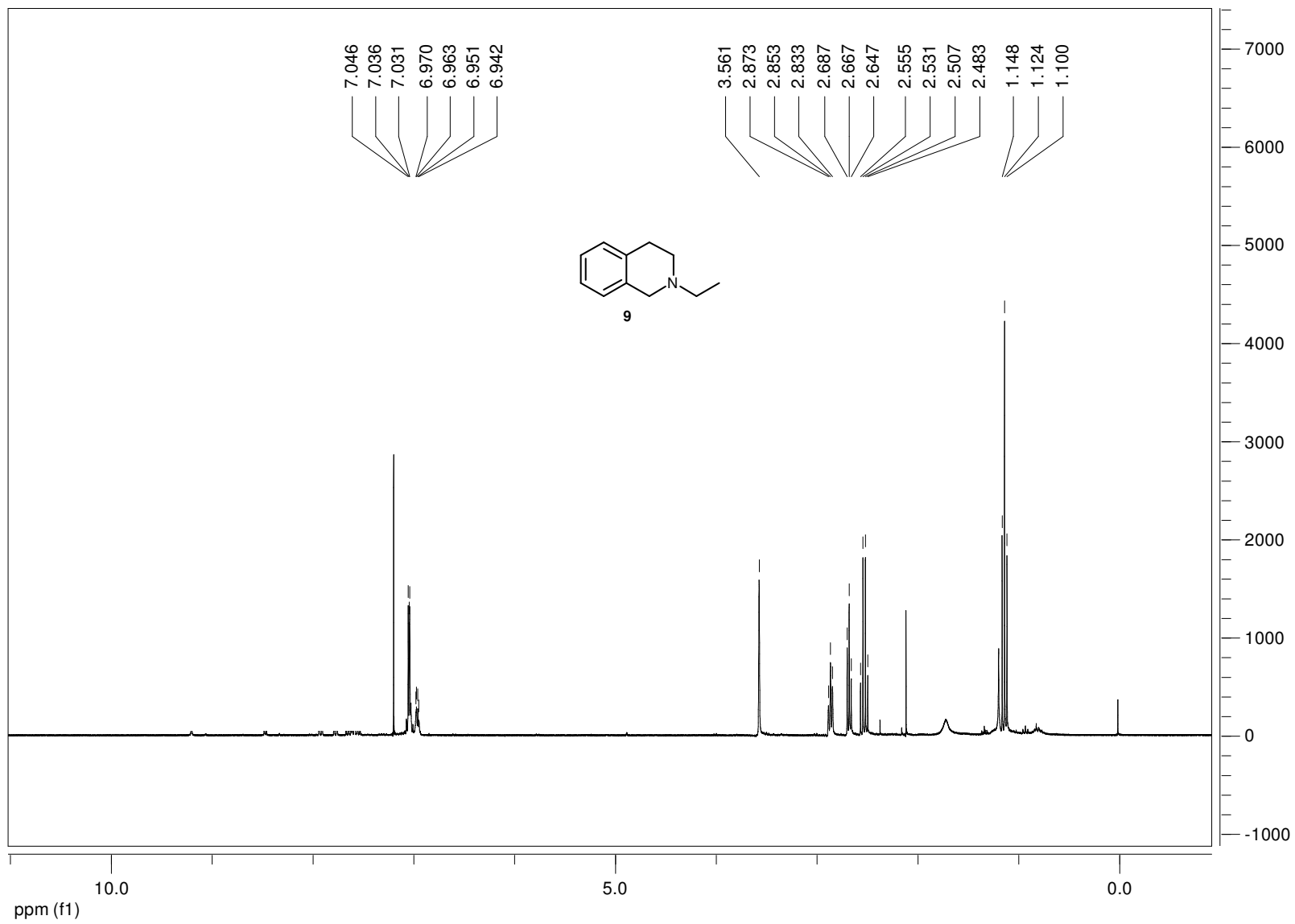


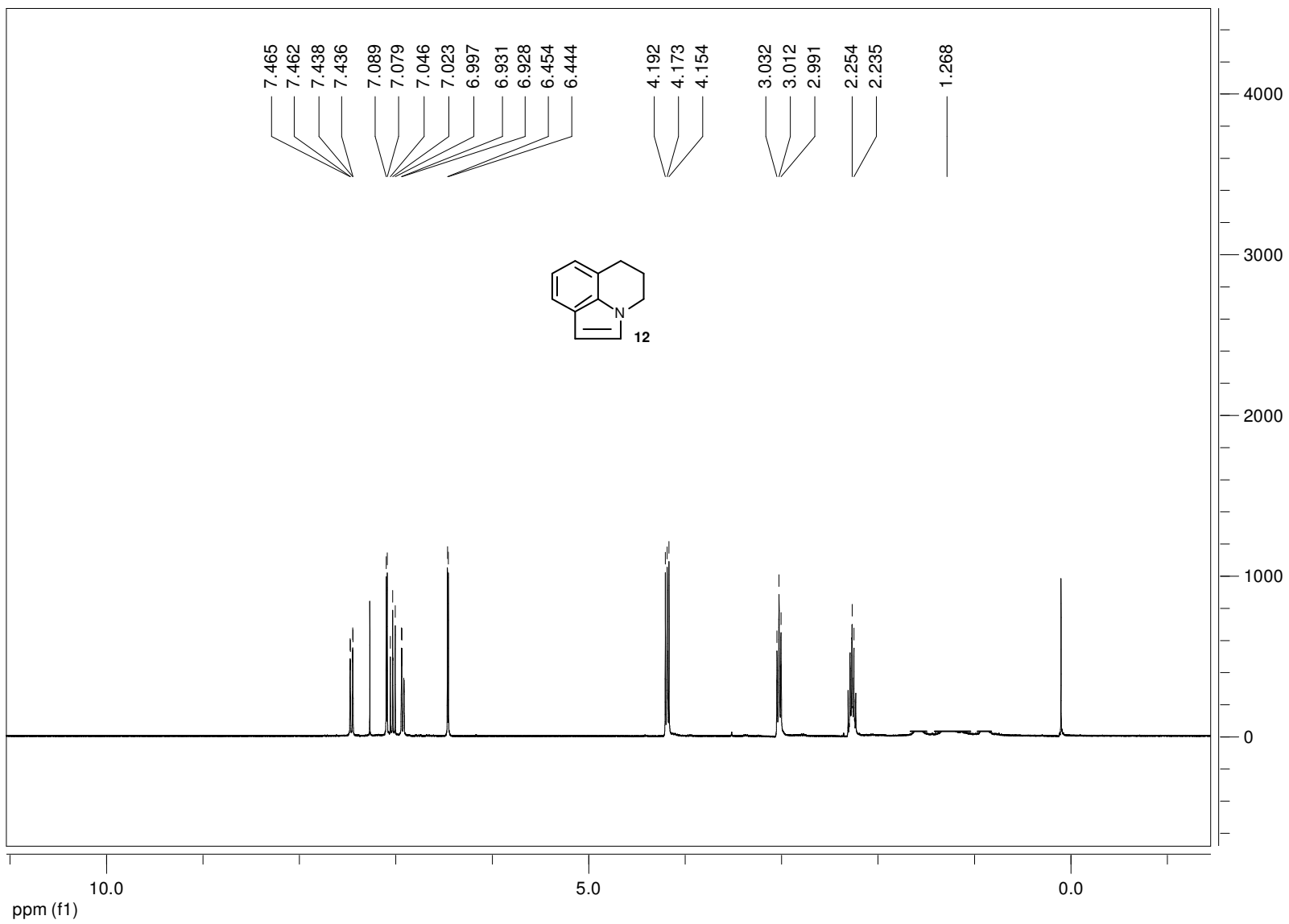






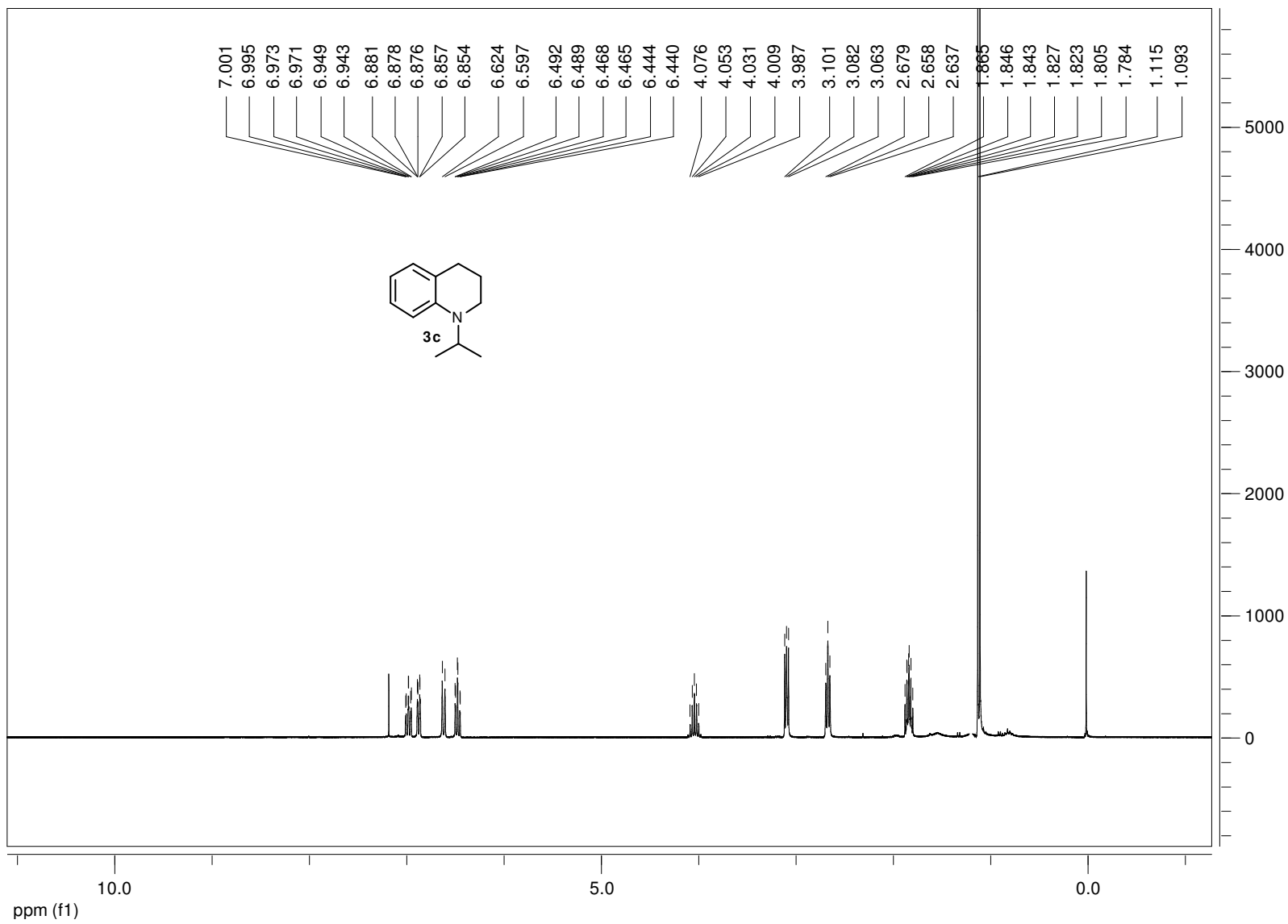




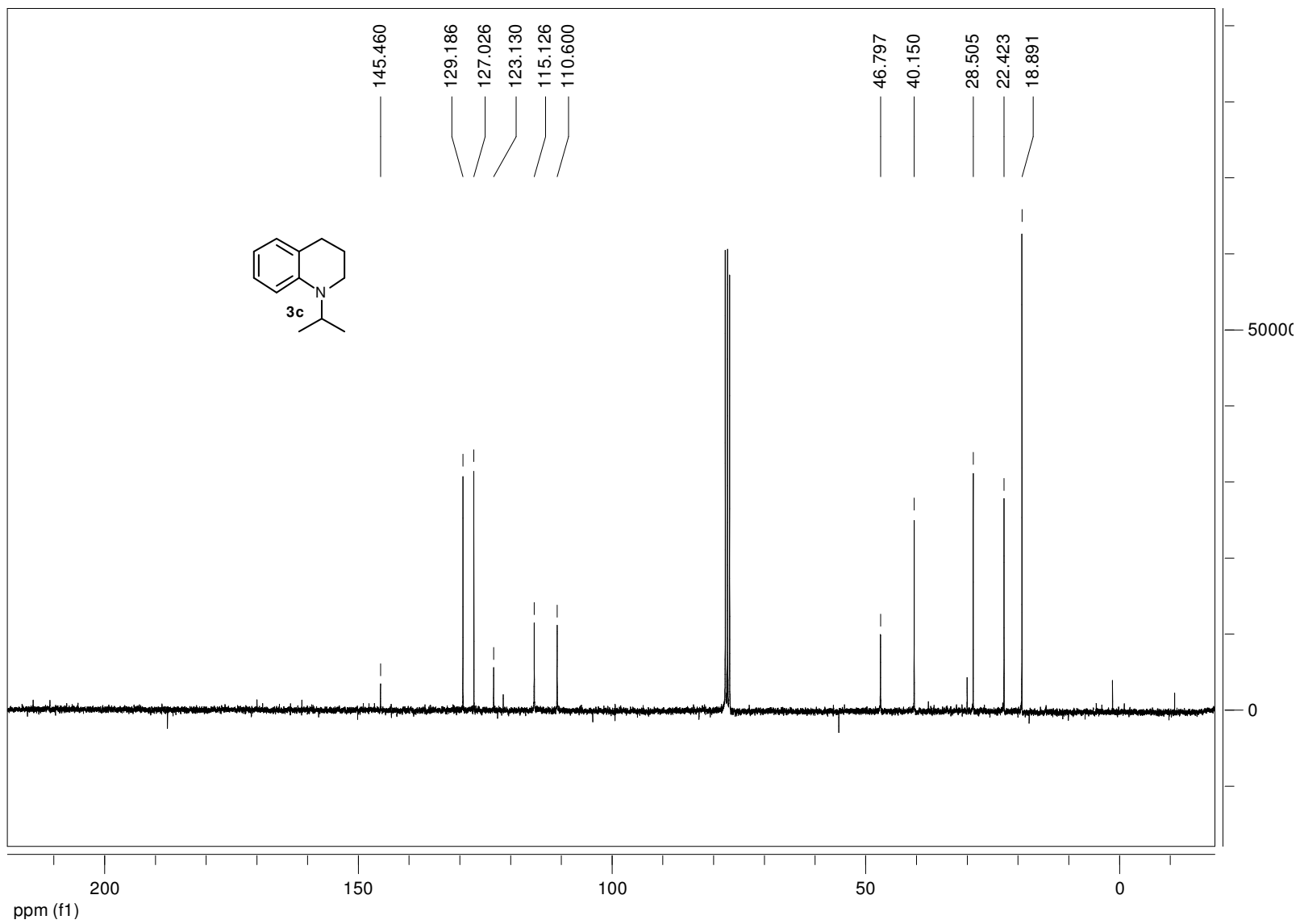


3. Spectra of new compounds.

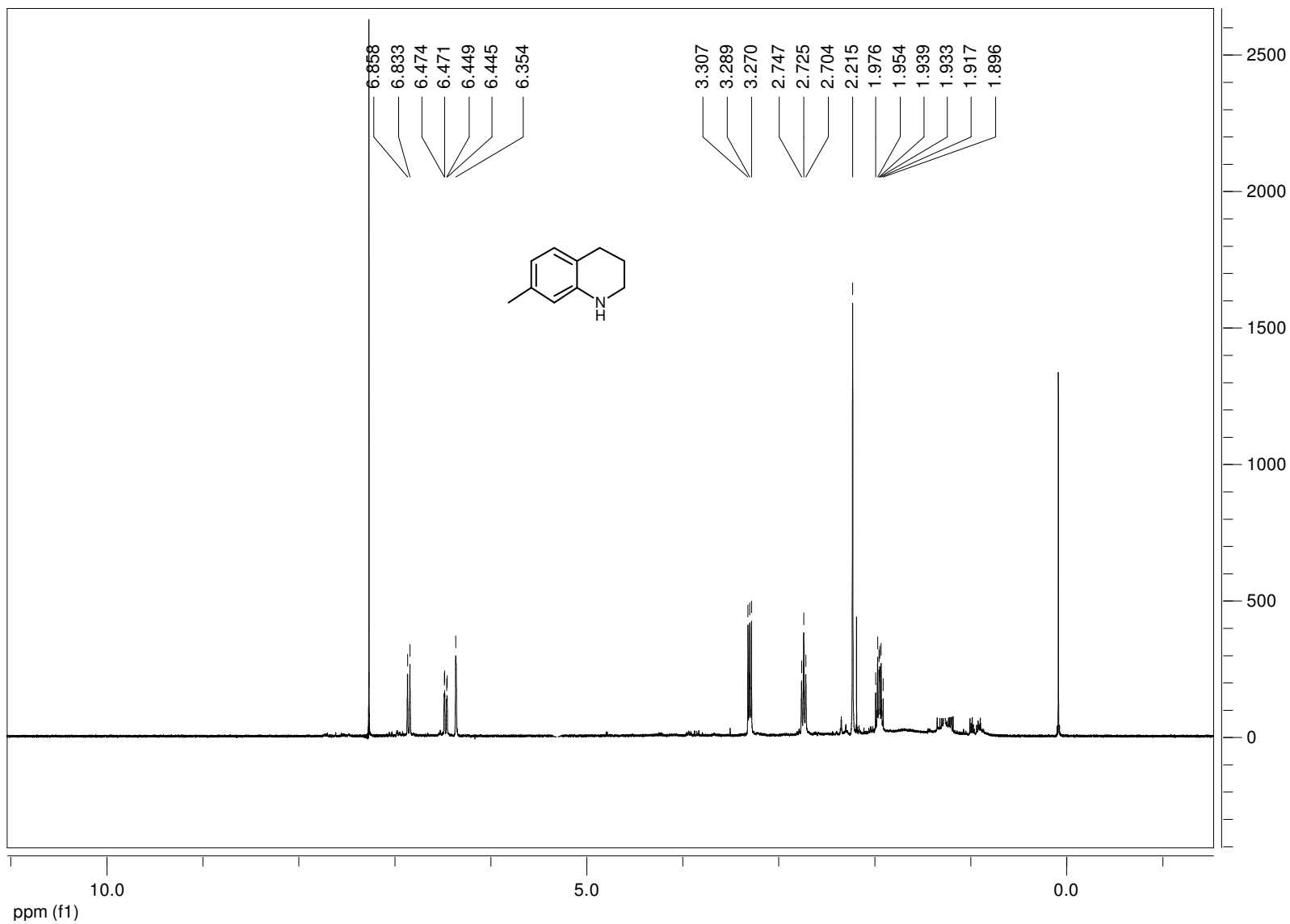
Compound **3c**



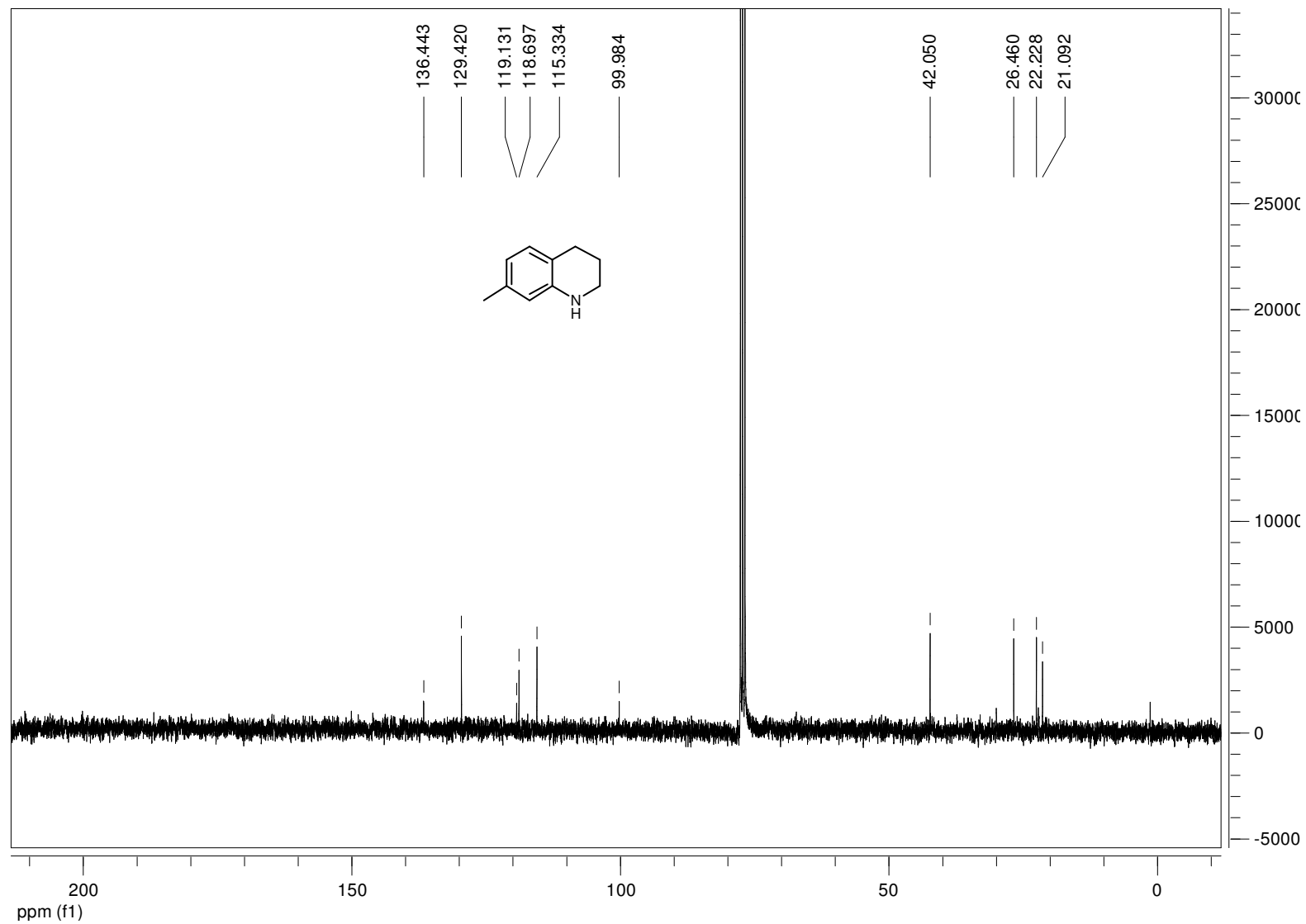
Compound **3c**



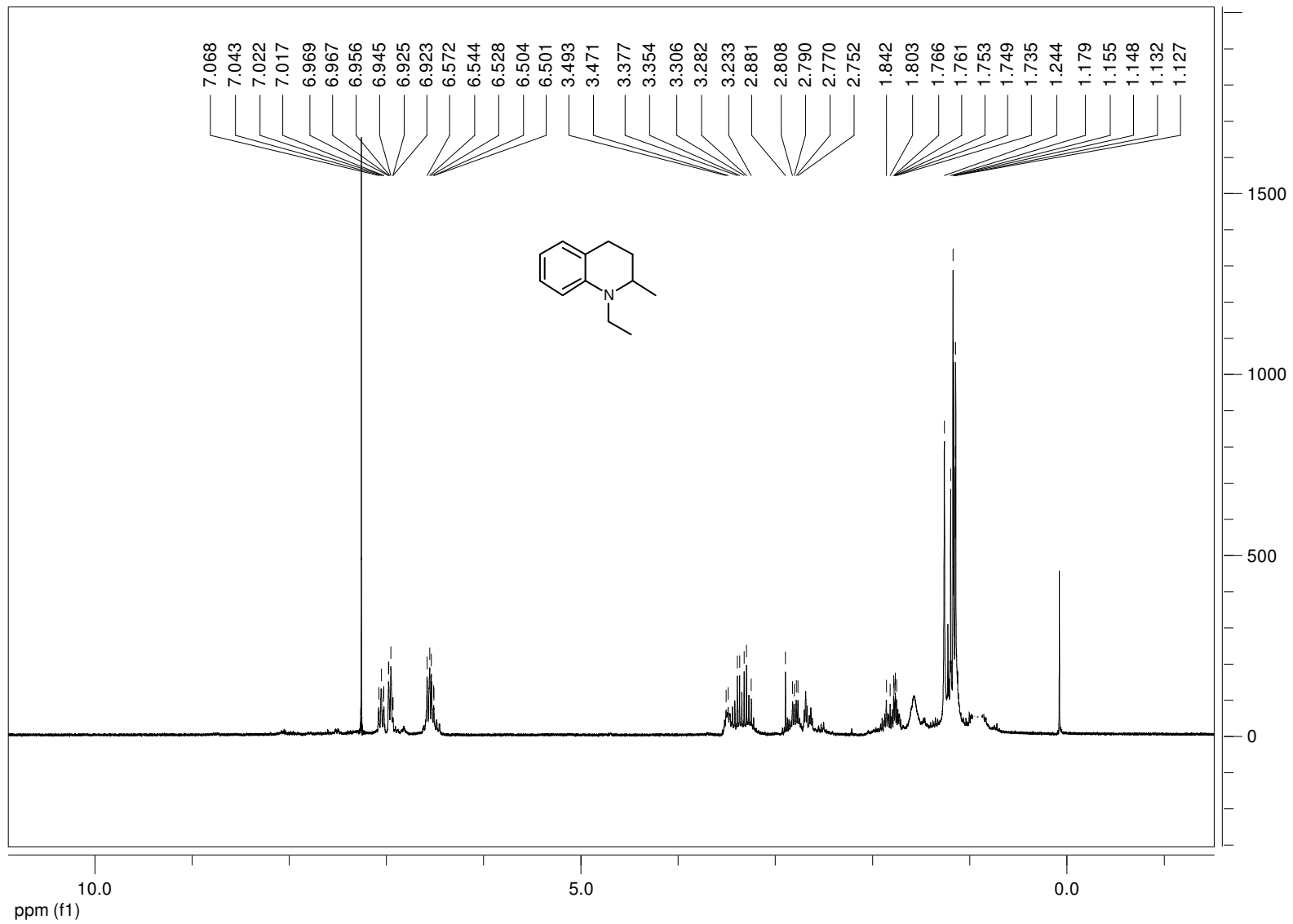
Compound **5e**



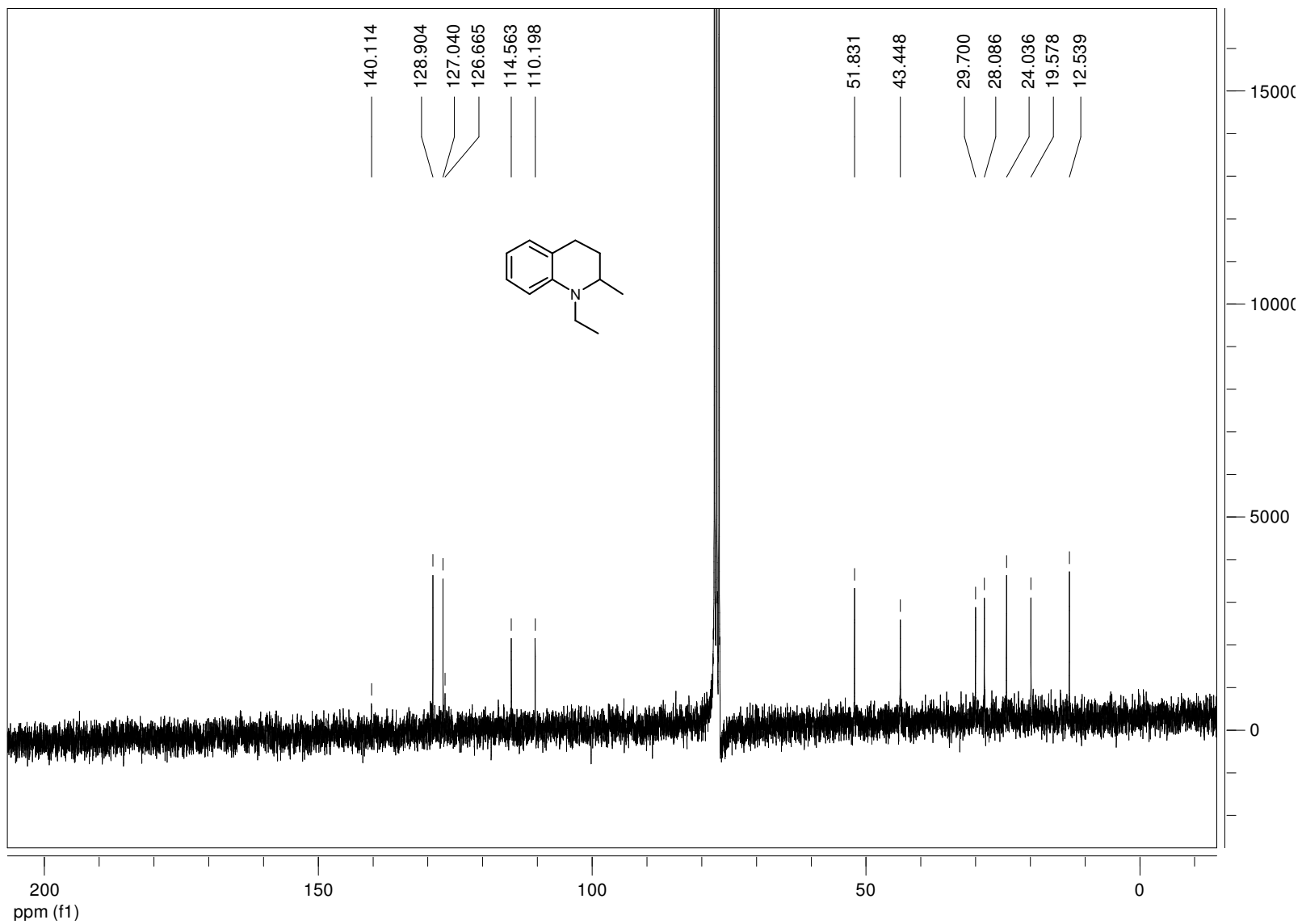
Compound **5e**



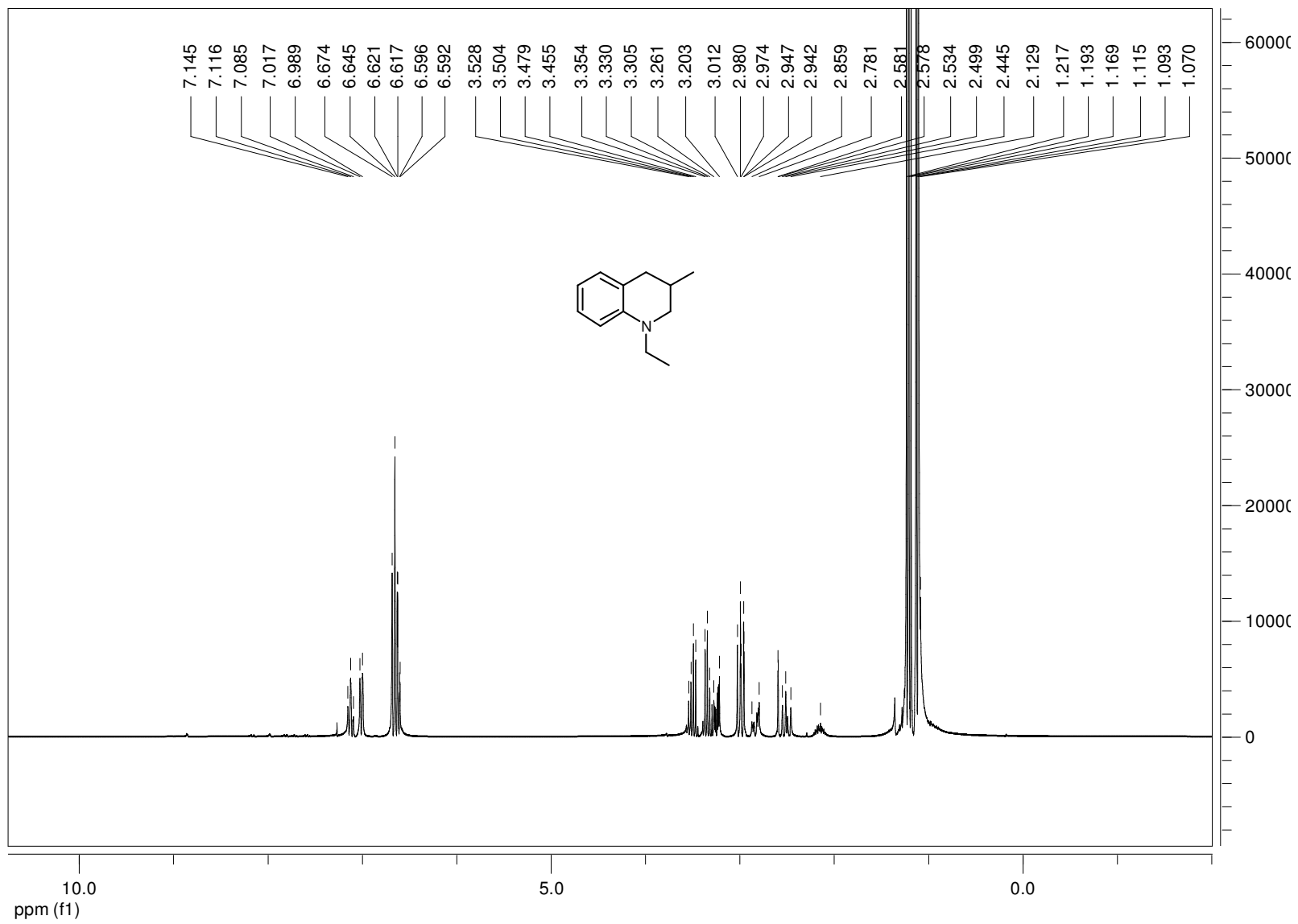
Compound **6a**



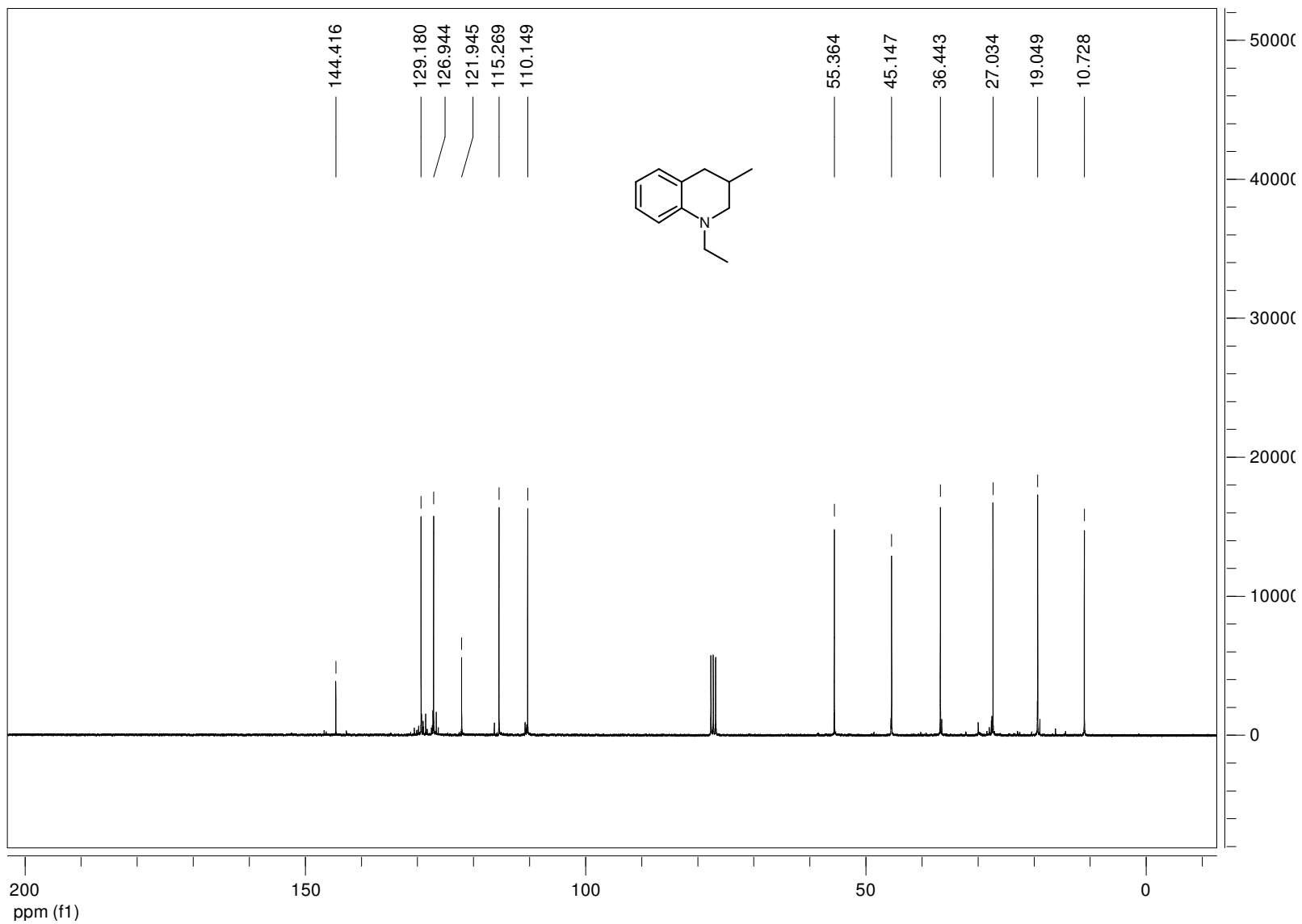
Compound **6a**



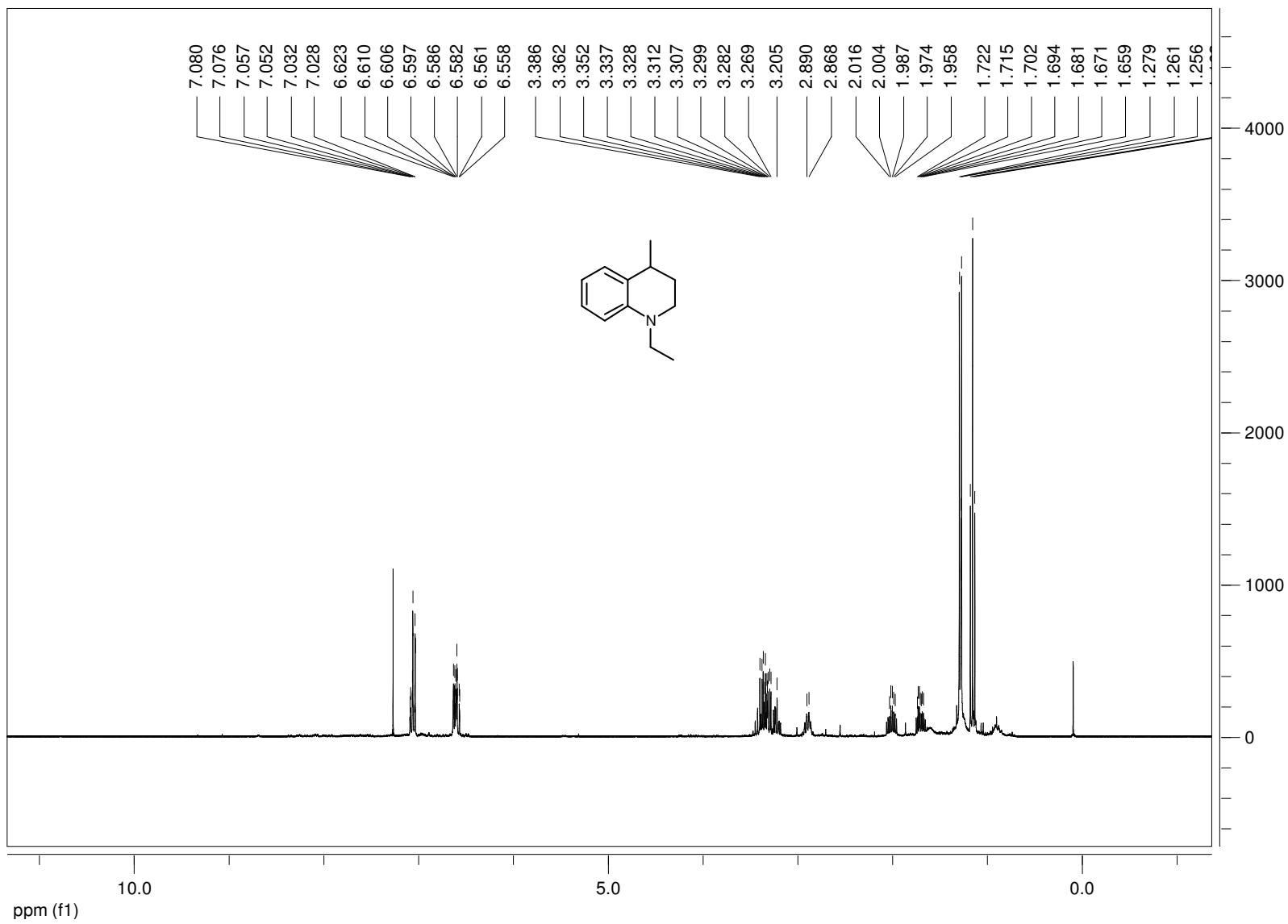
Compound **6b**



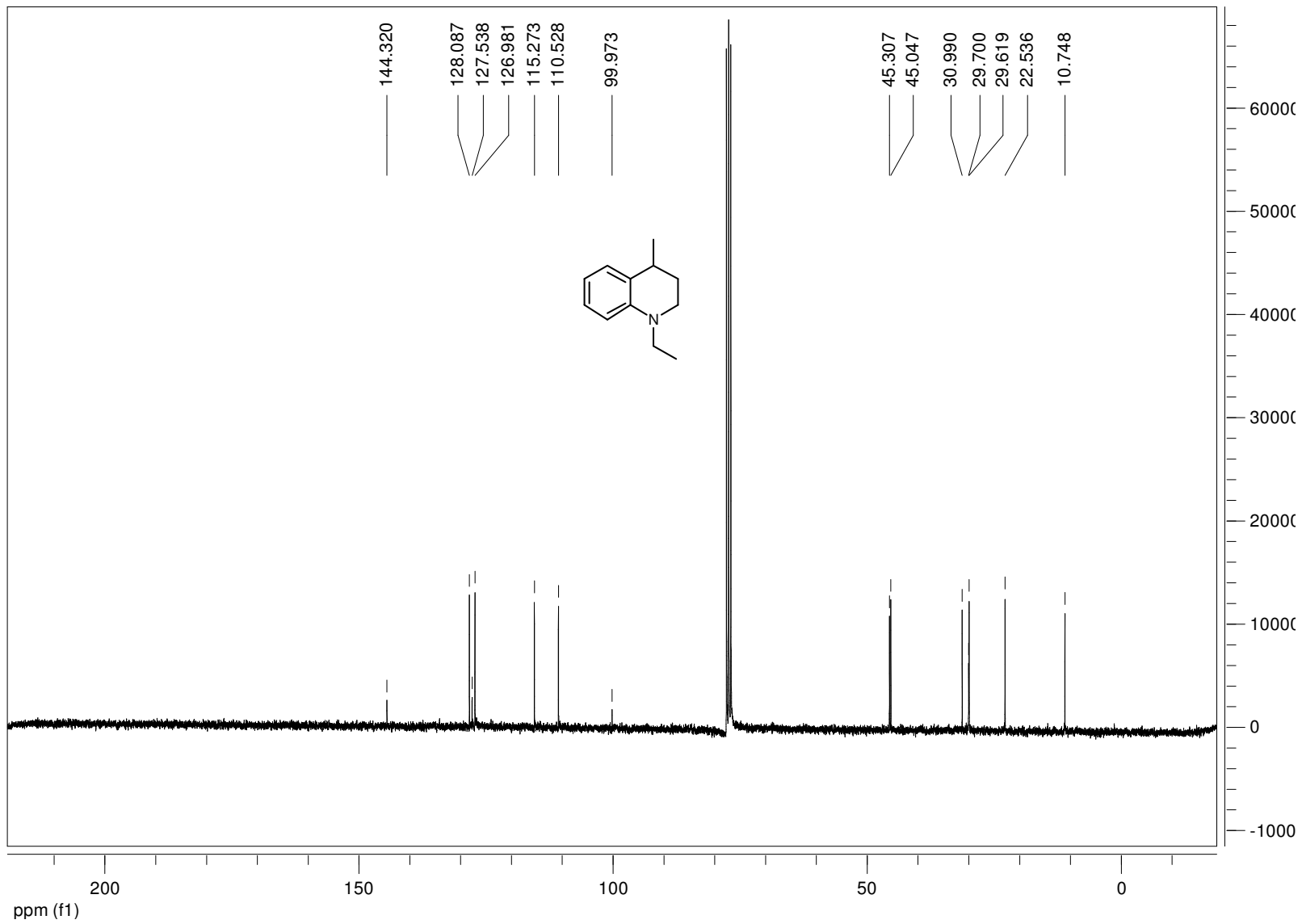
Compound **6b**



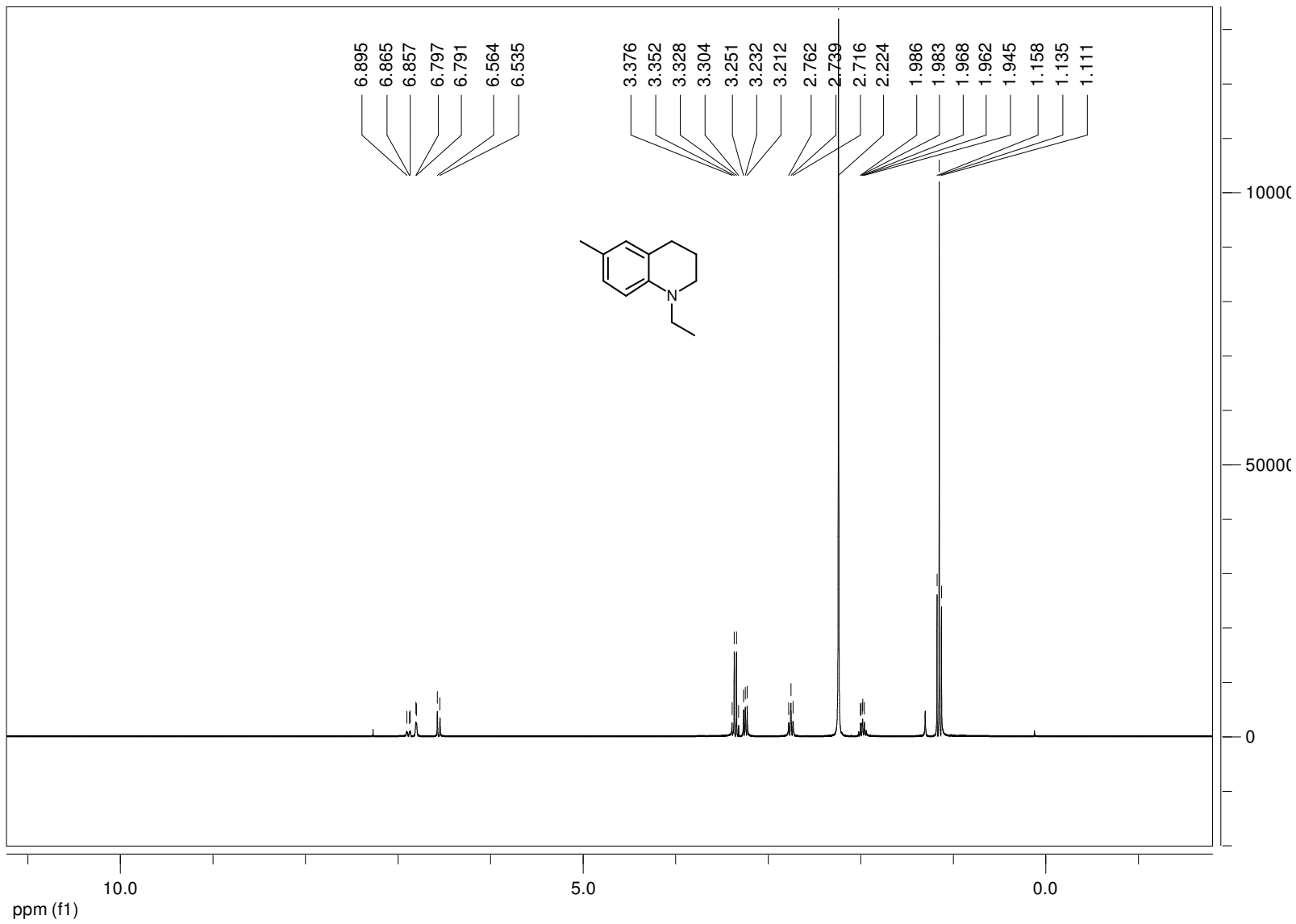
Compound **6c**



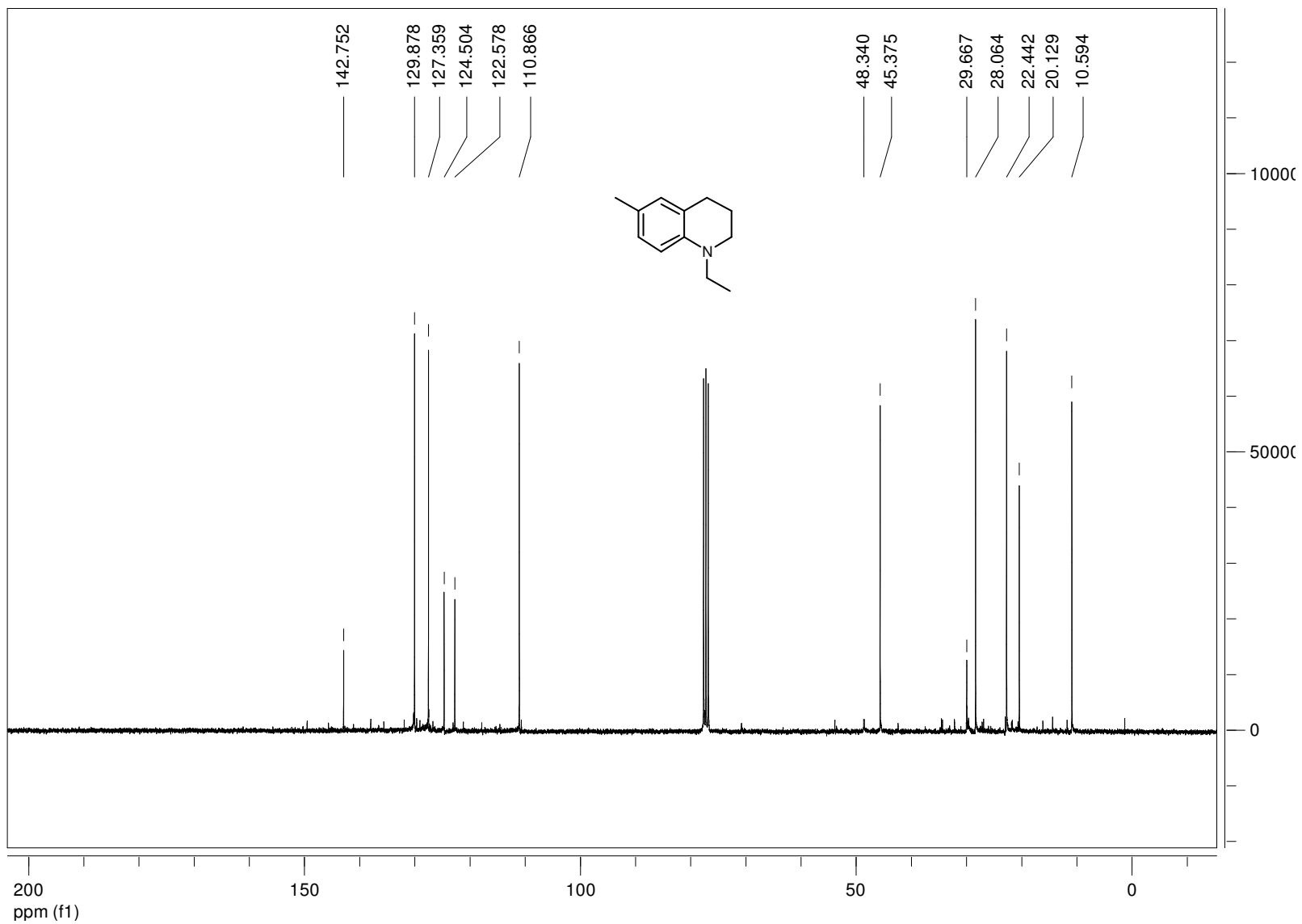
Compound **6c**



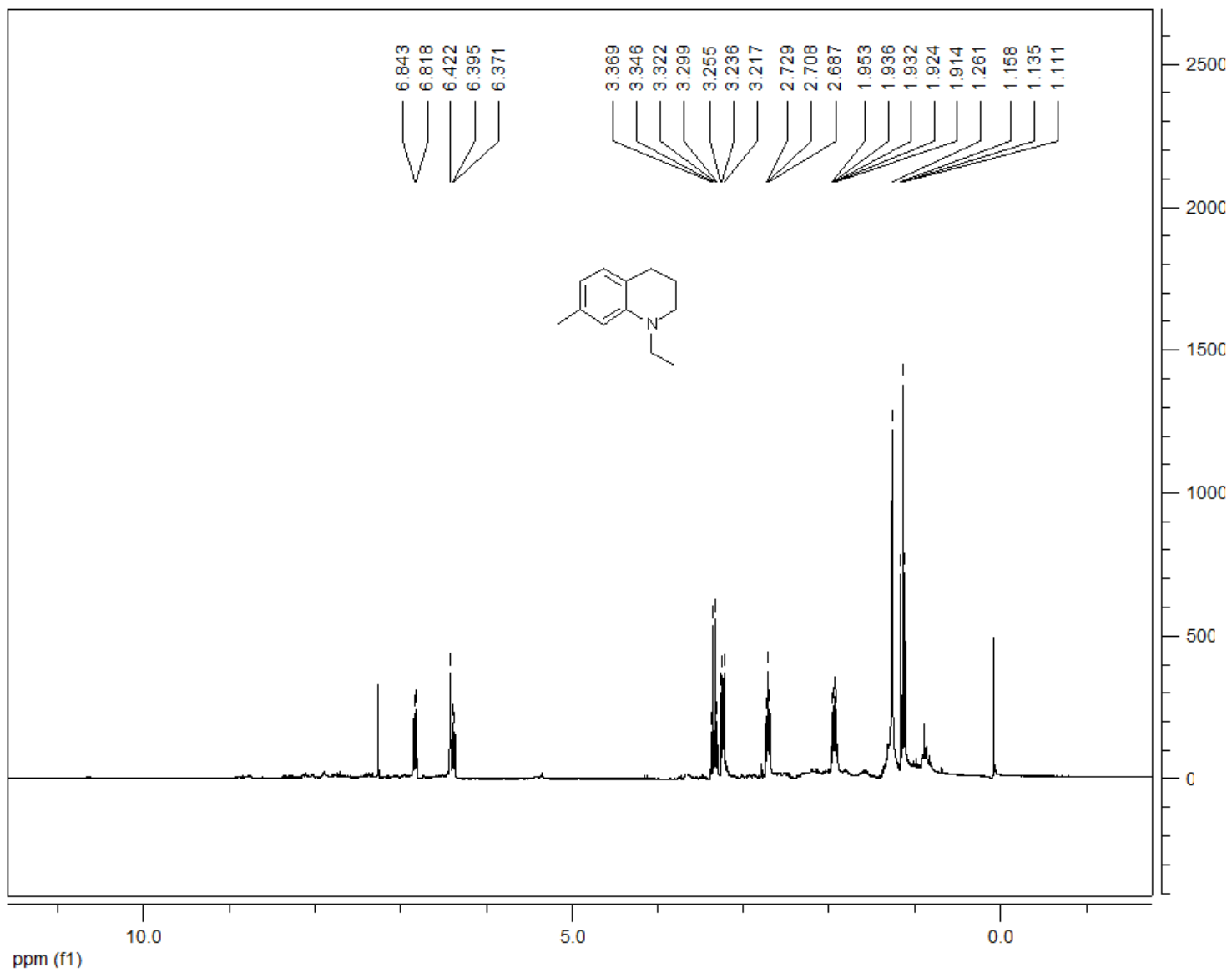
Compound **6d**



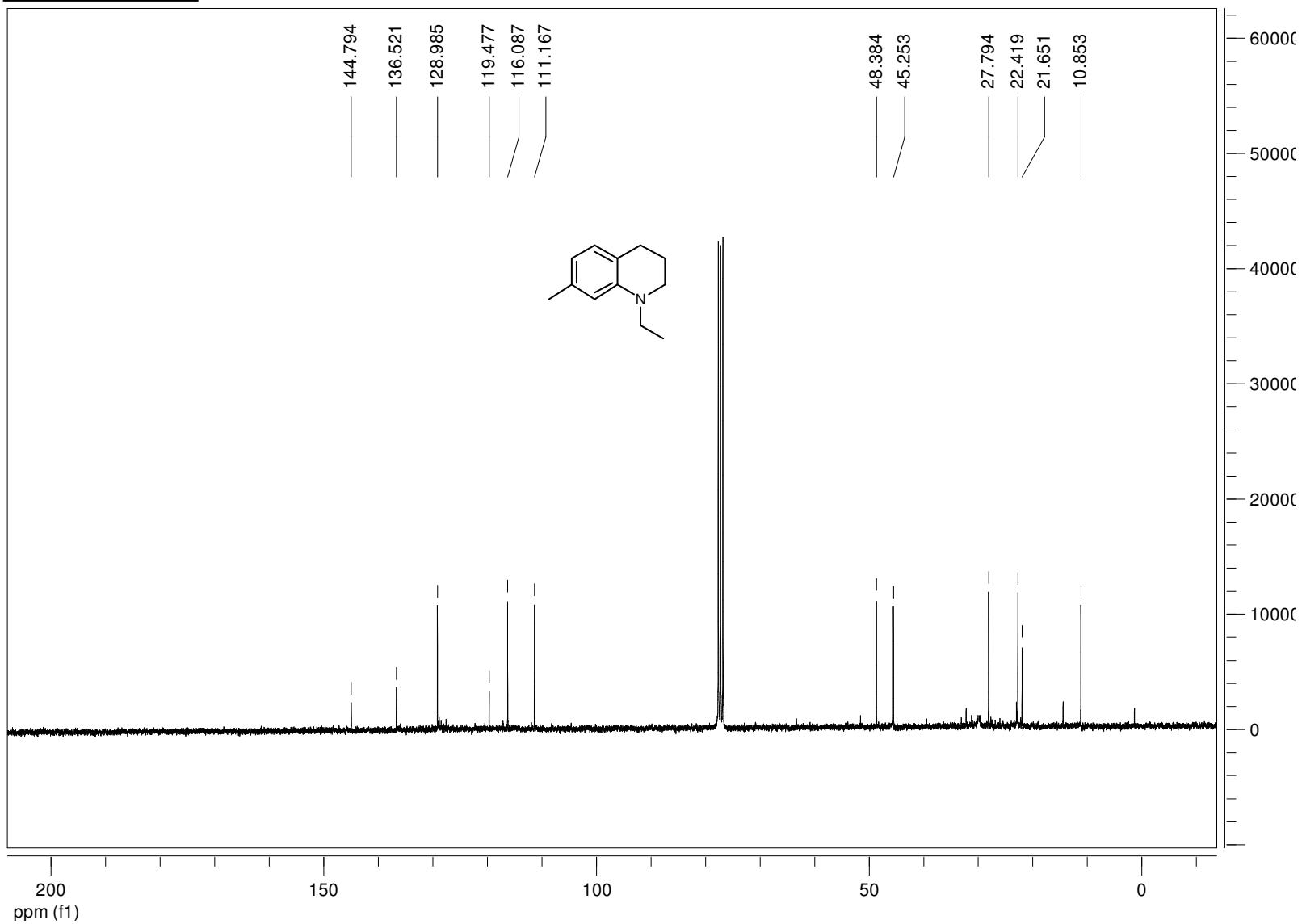
Compound **6d**



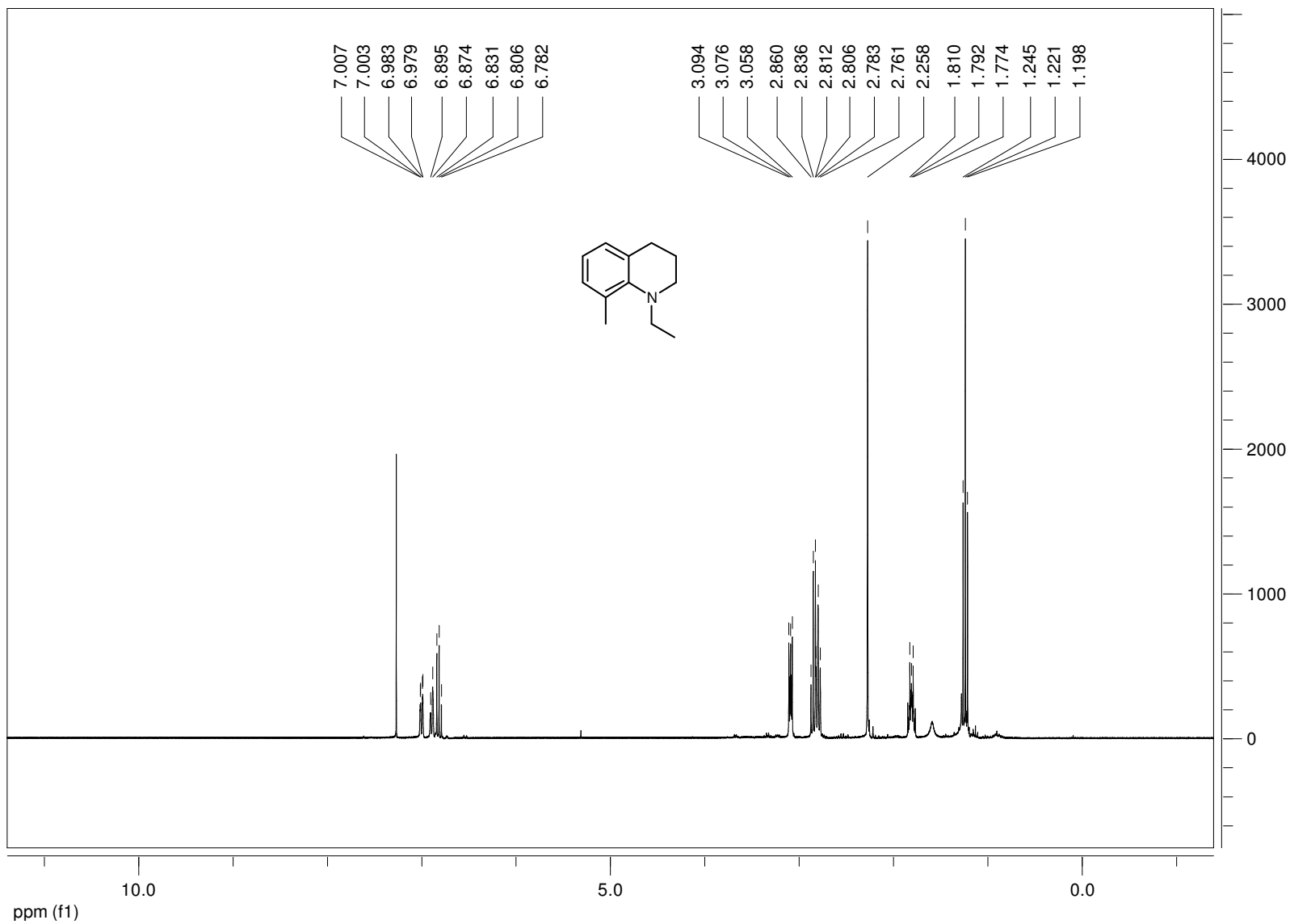
Compound **6e**



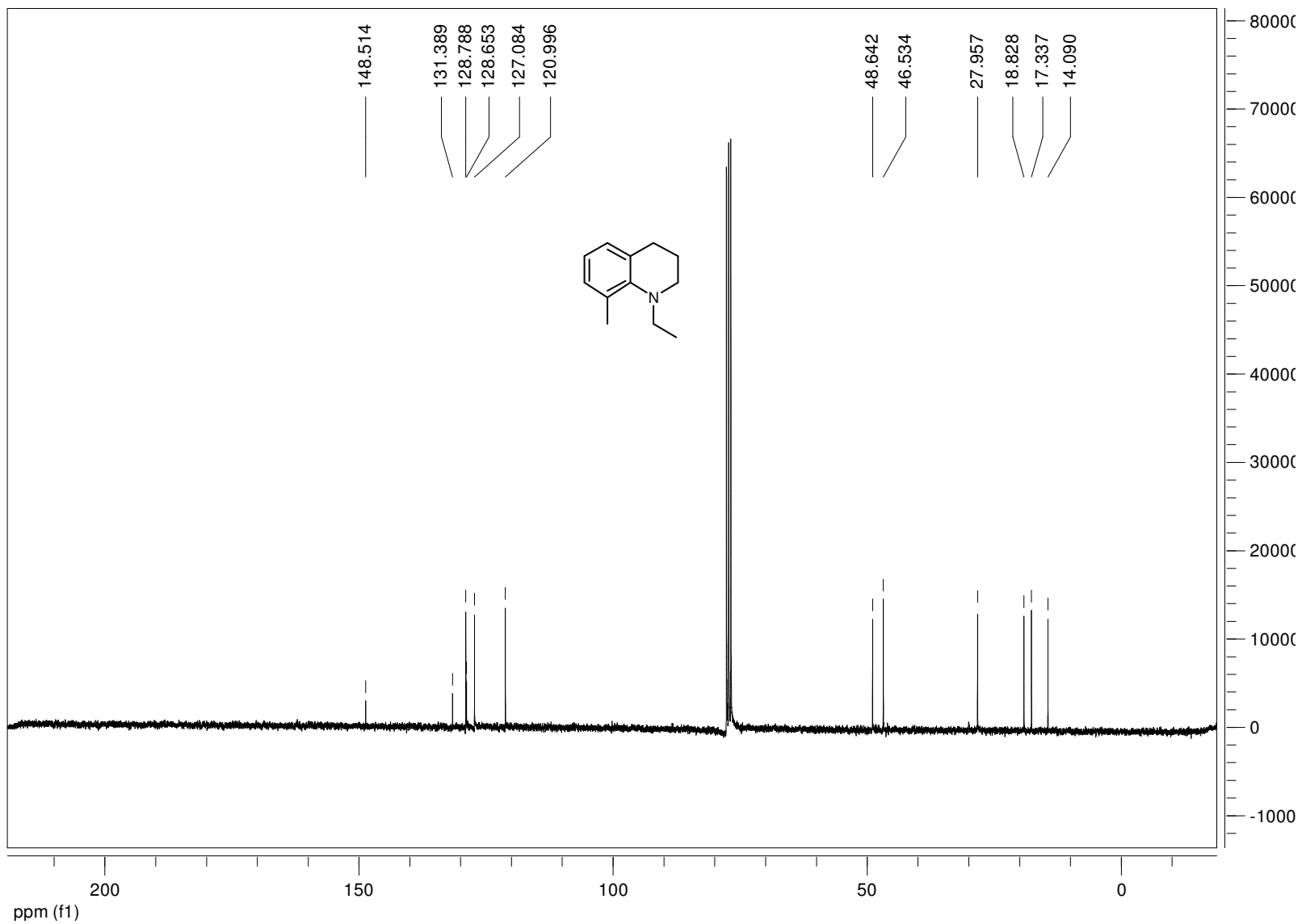
Compound **6e**



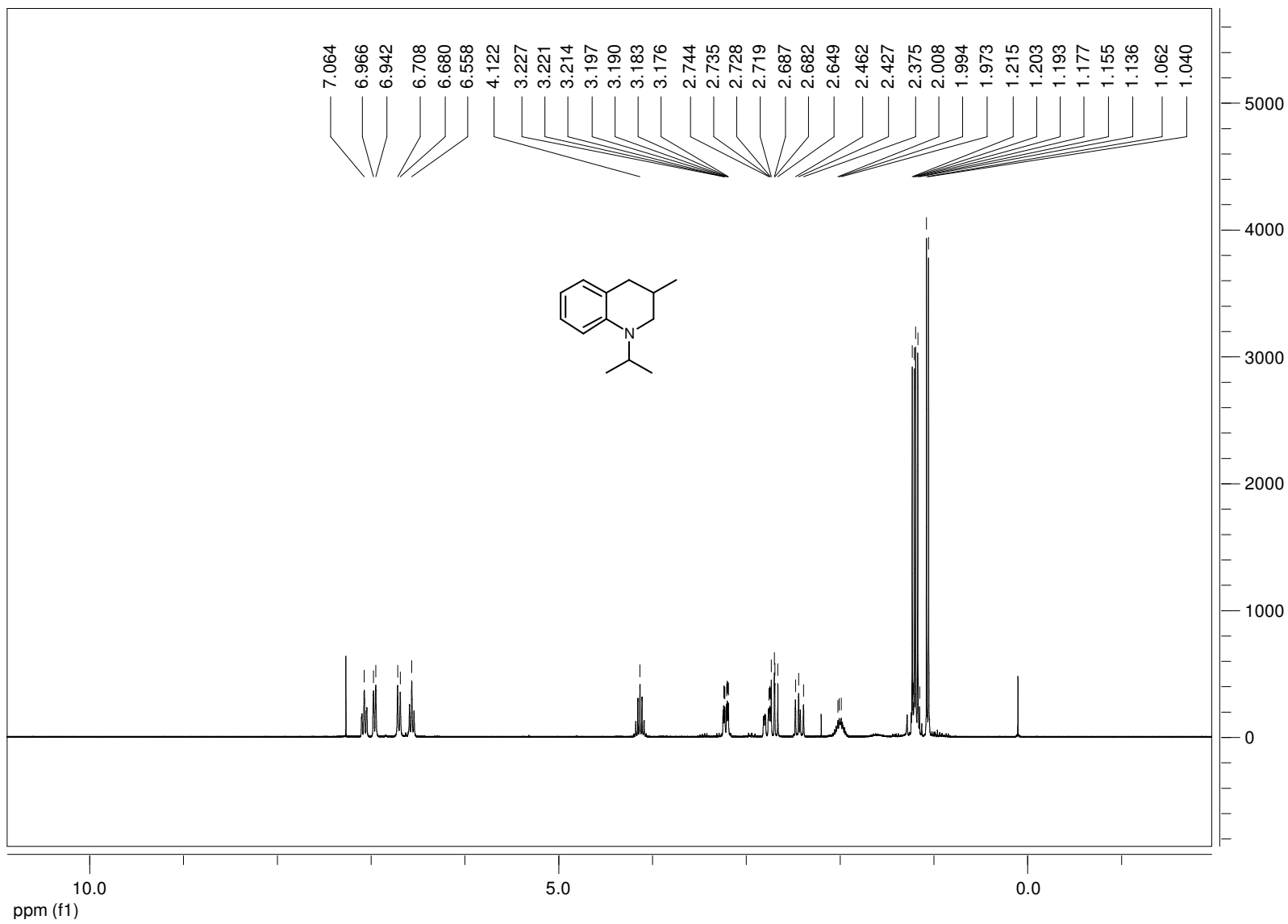
Compound **6f**



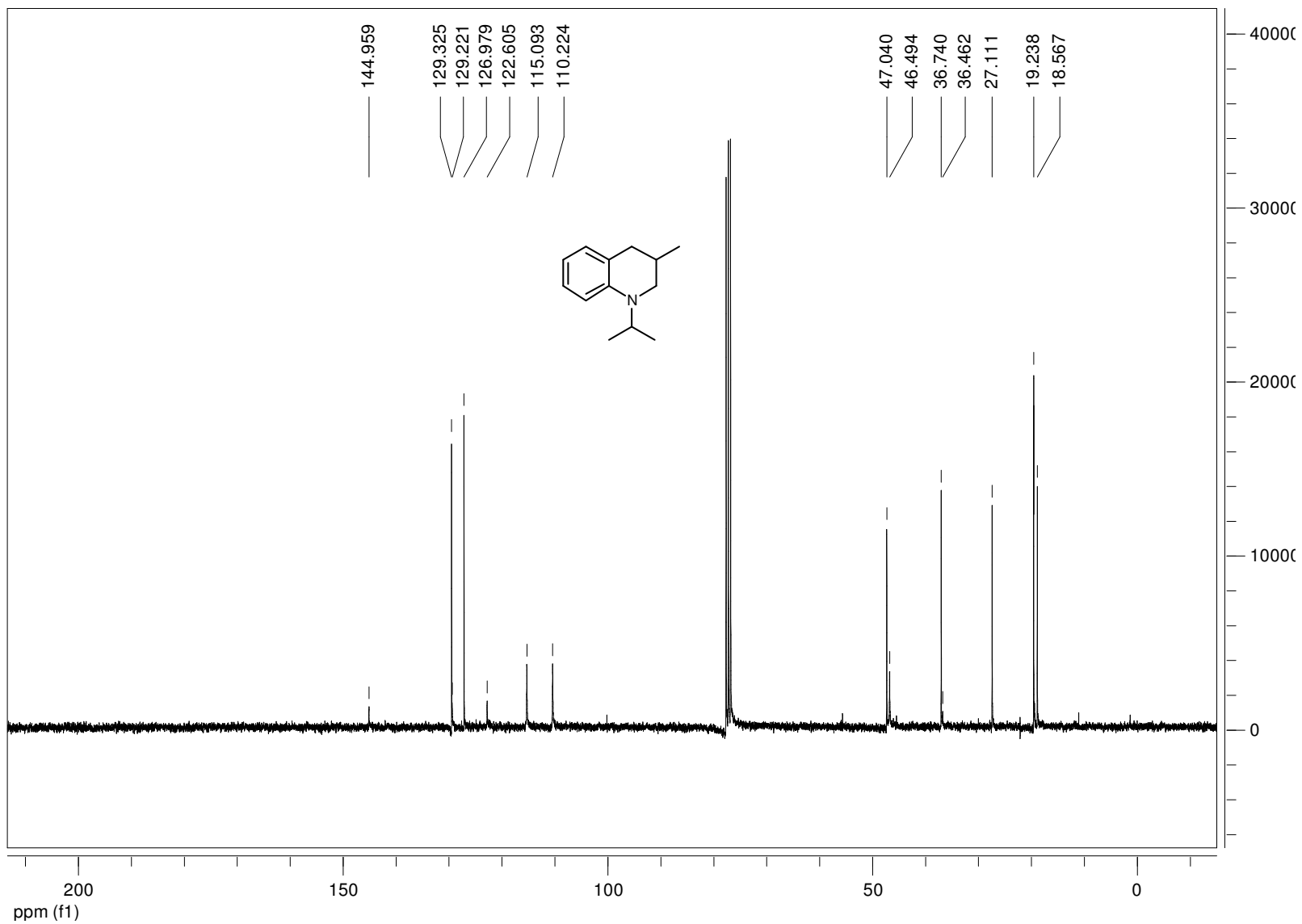
Compound **6f**



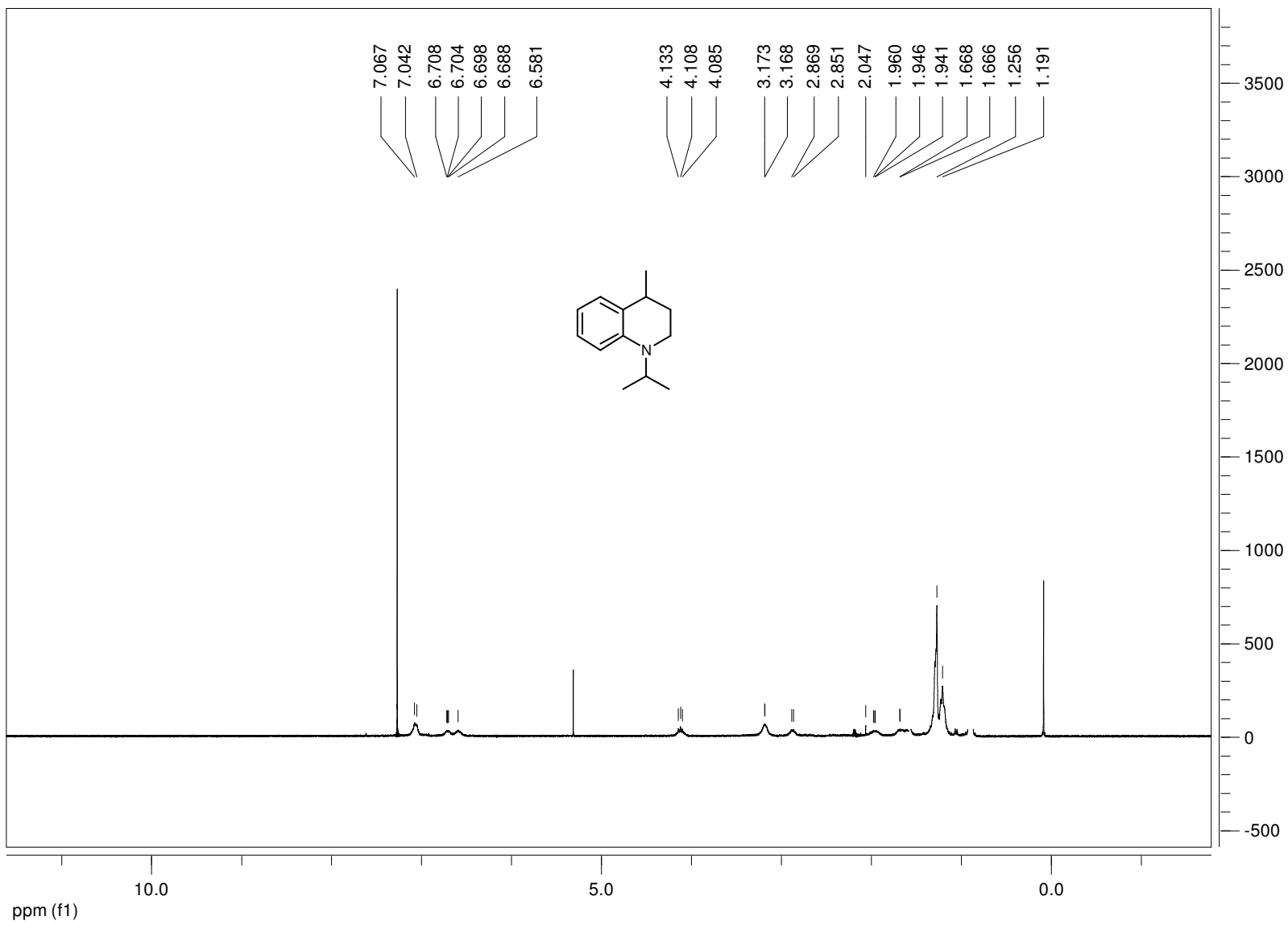
Compound **7b**



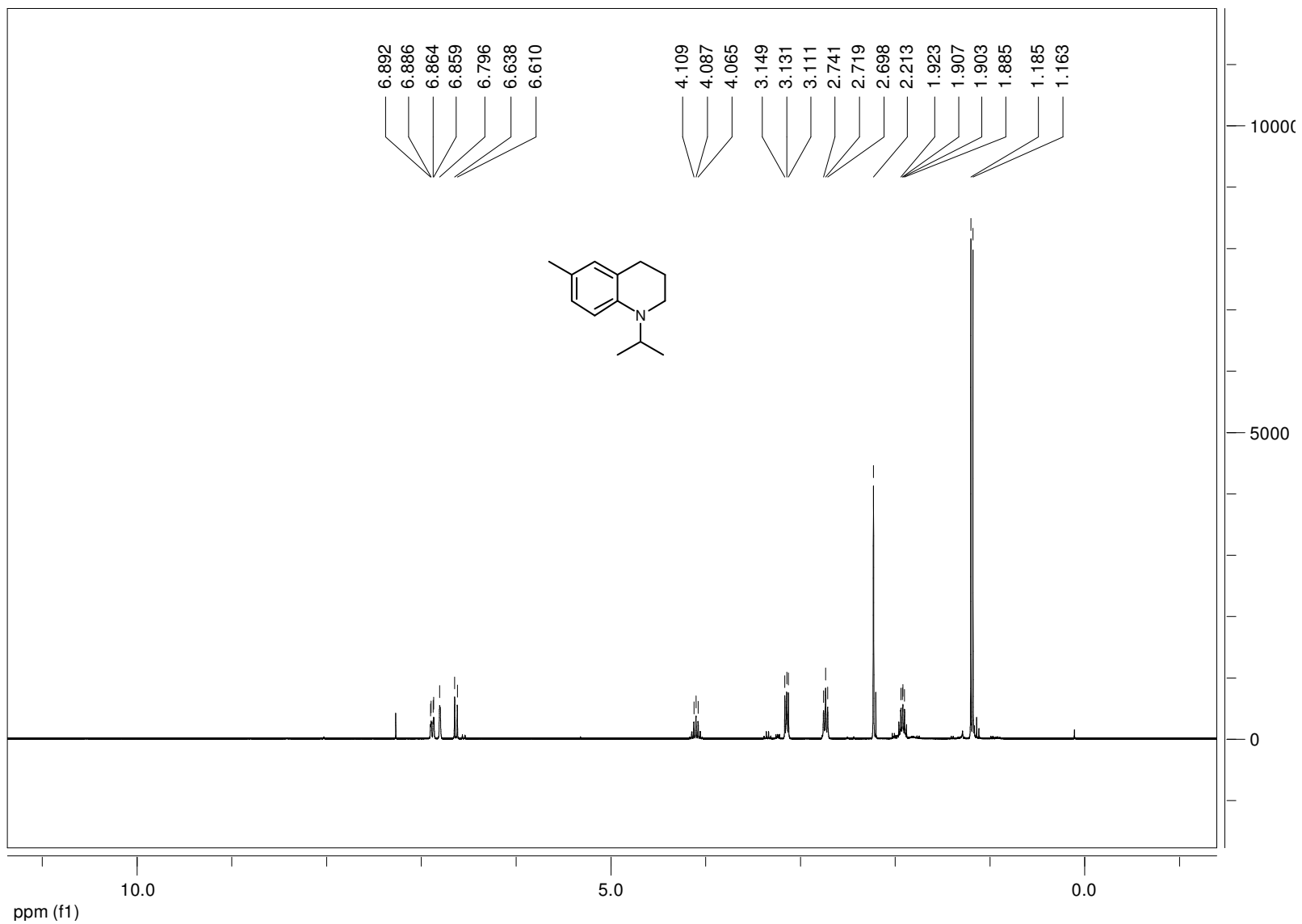
Compound **7b**



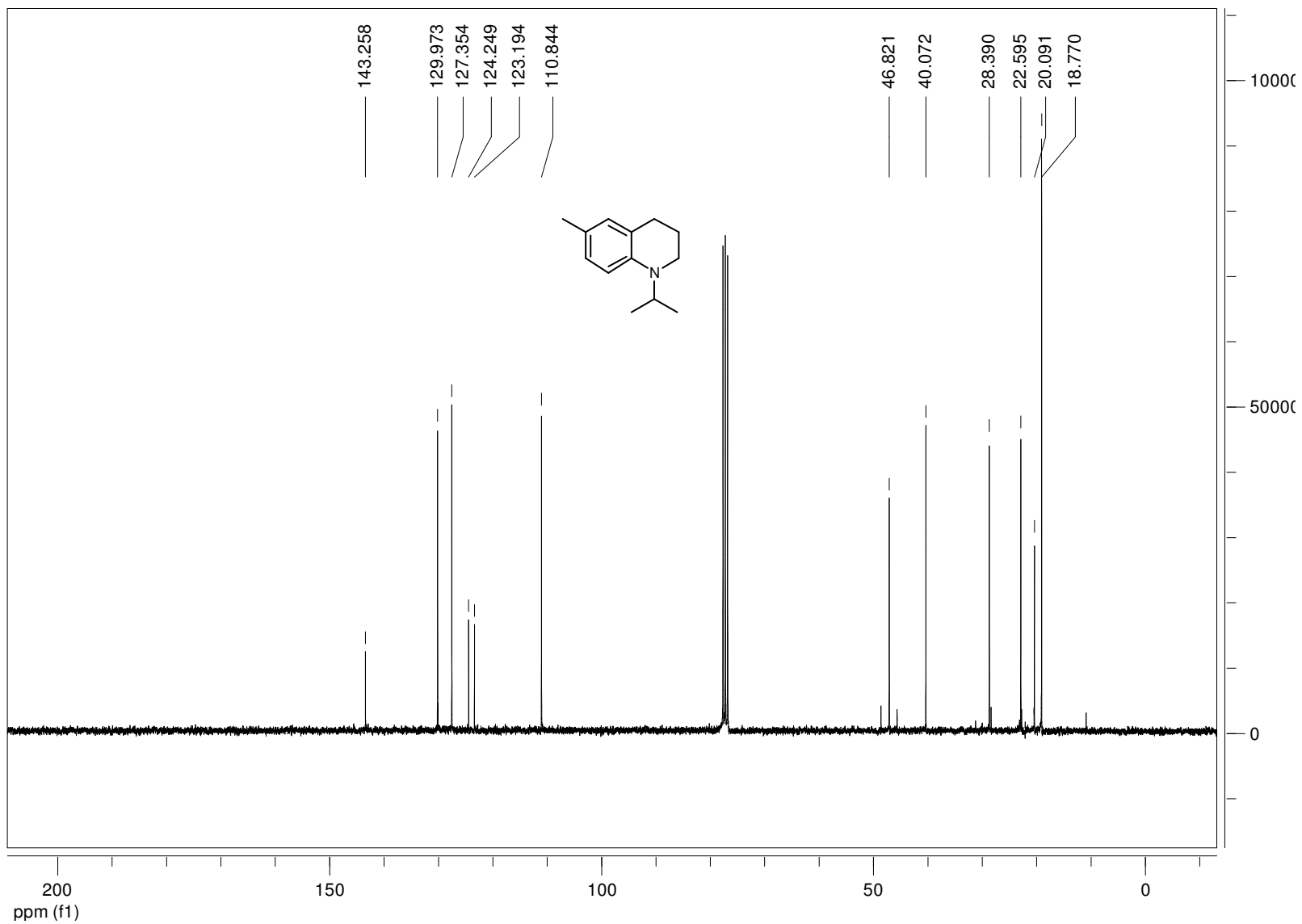
Compound **7c**



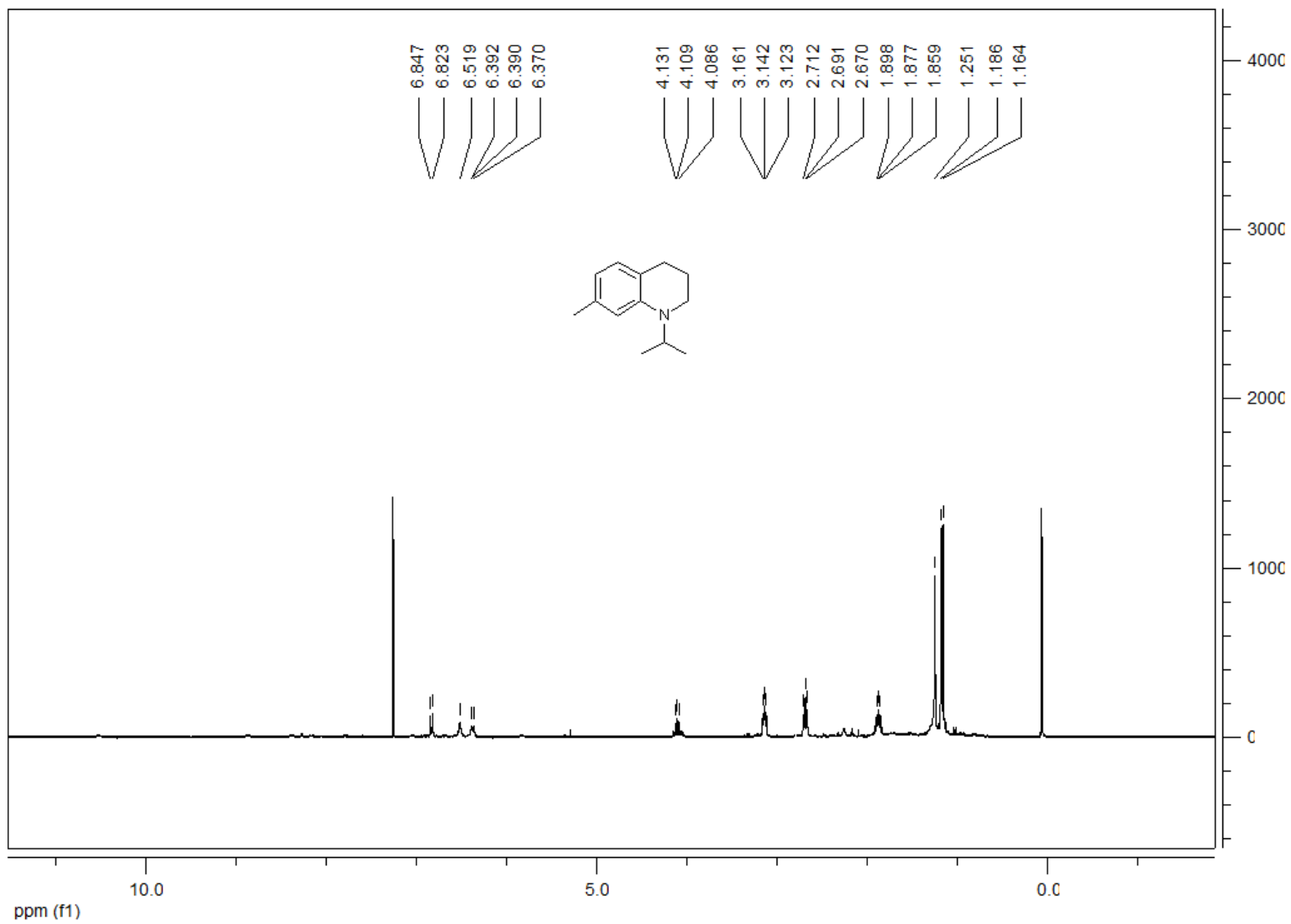
Compound **7d**

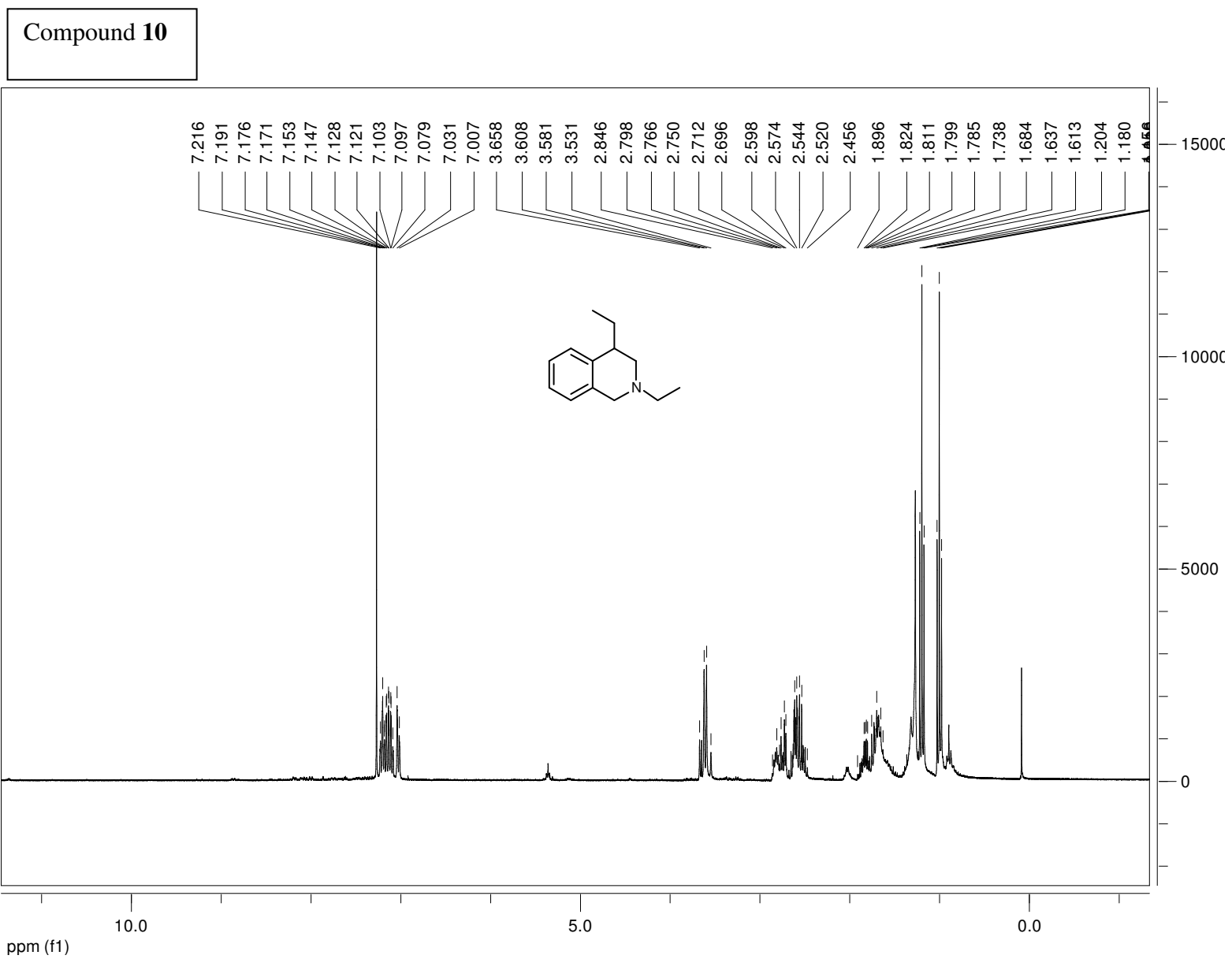


Compound **7d**

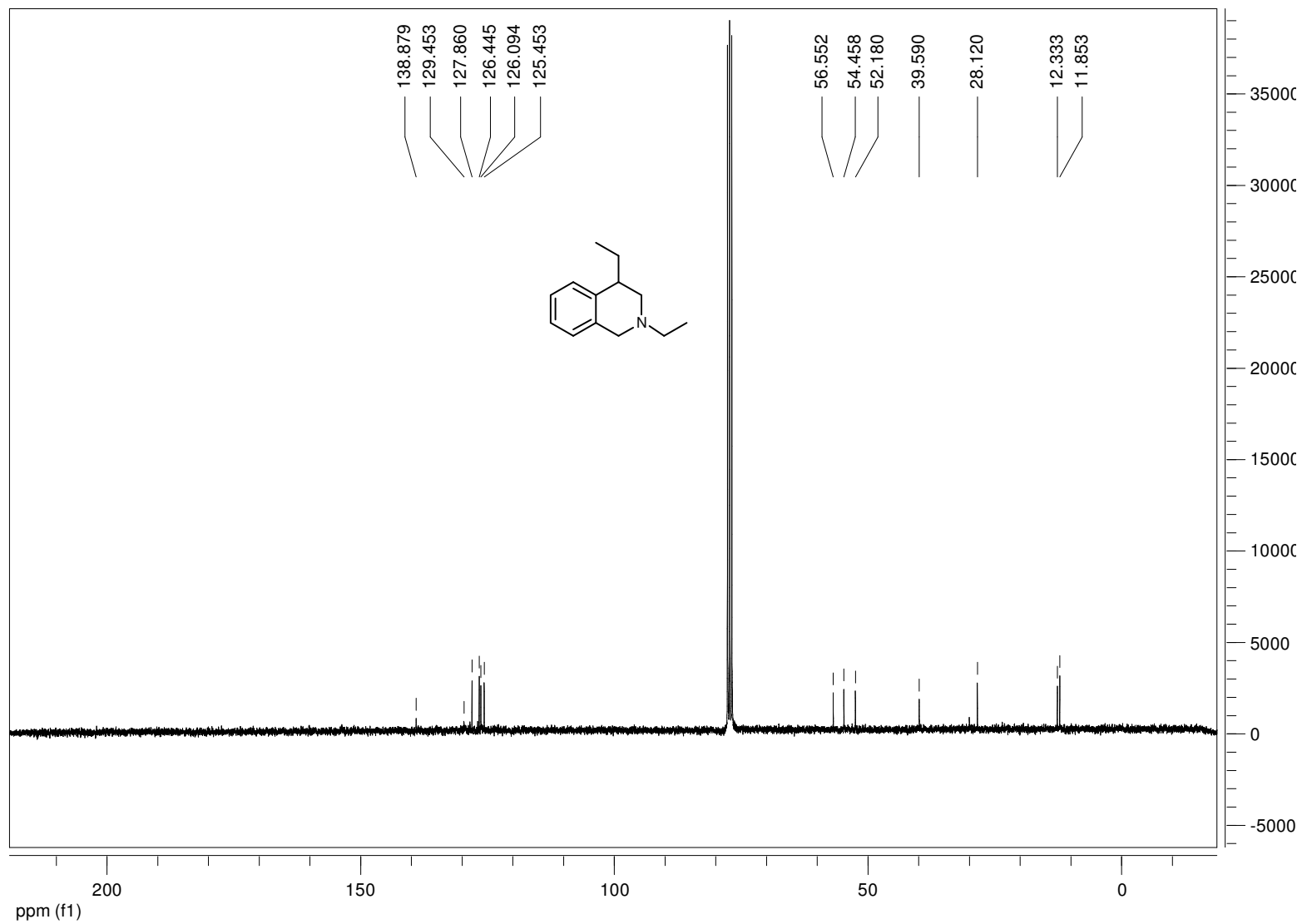


Compound 7e

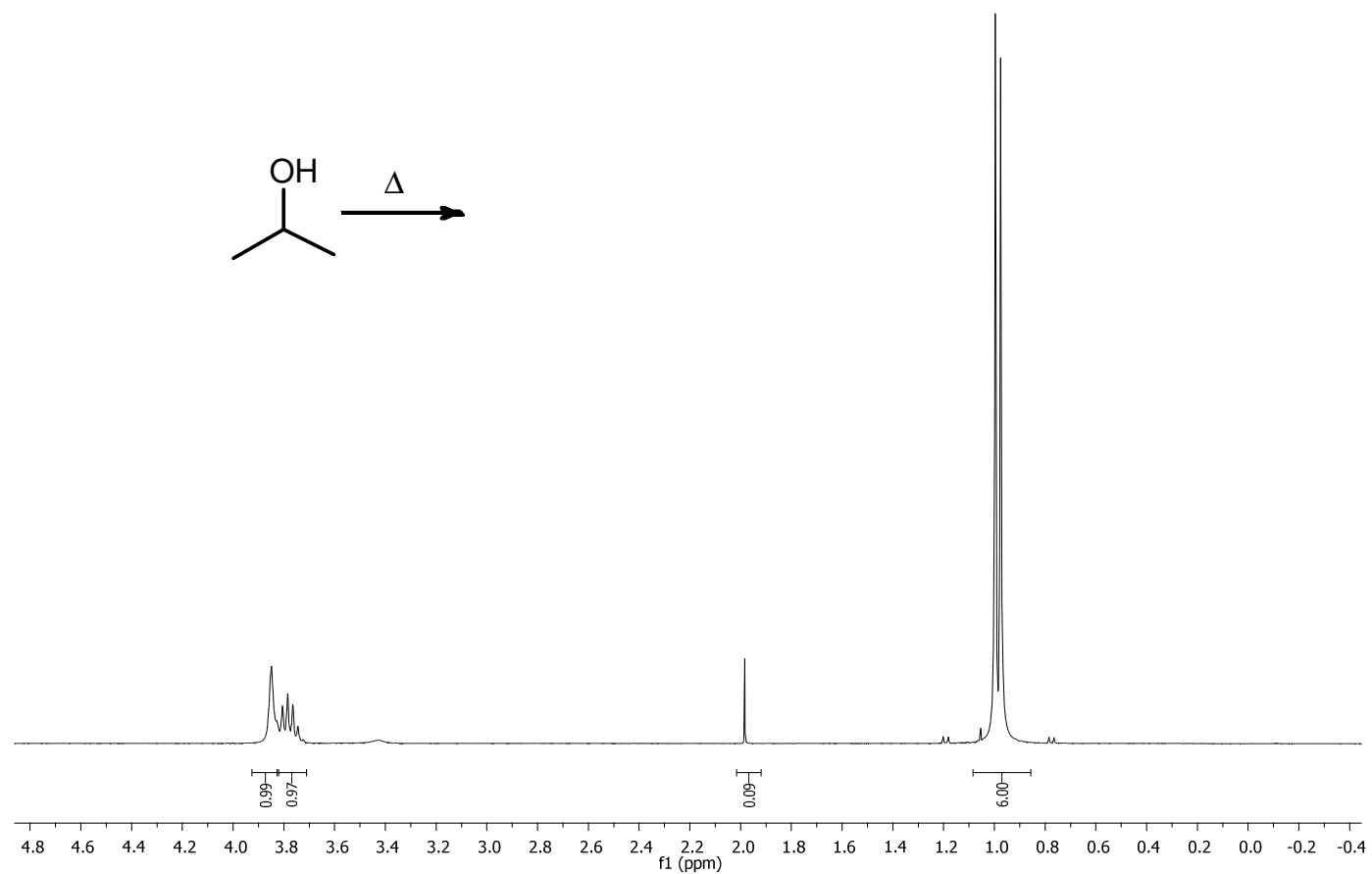




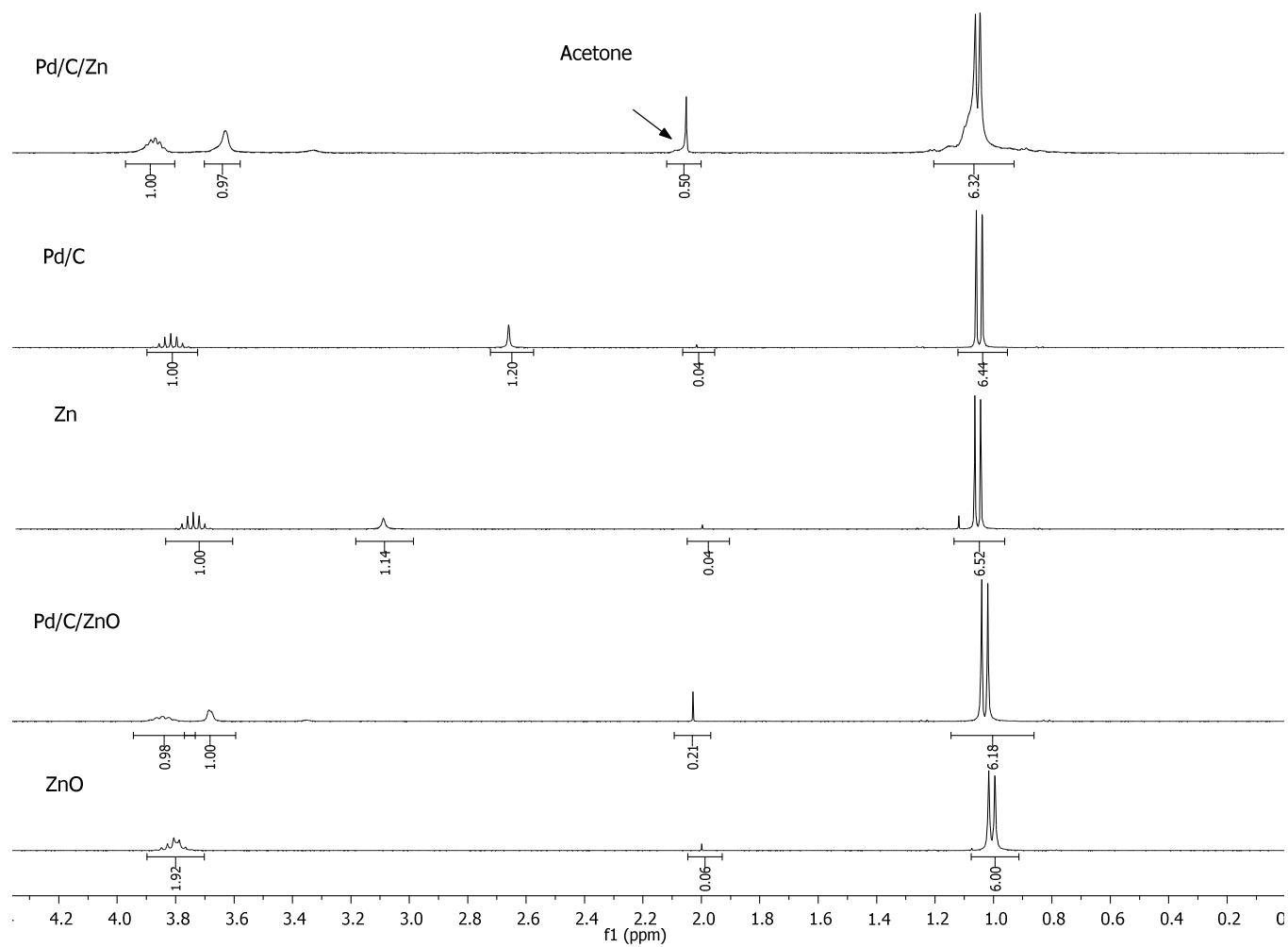
Compound **10**



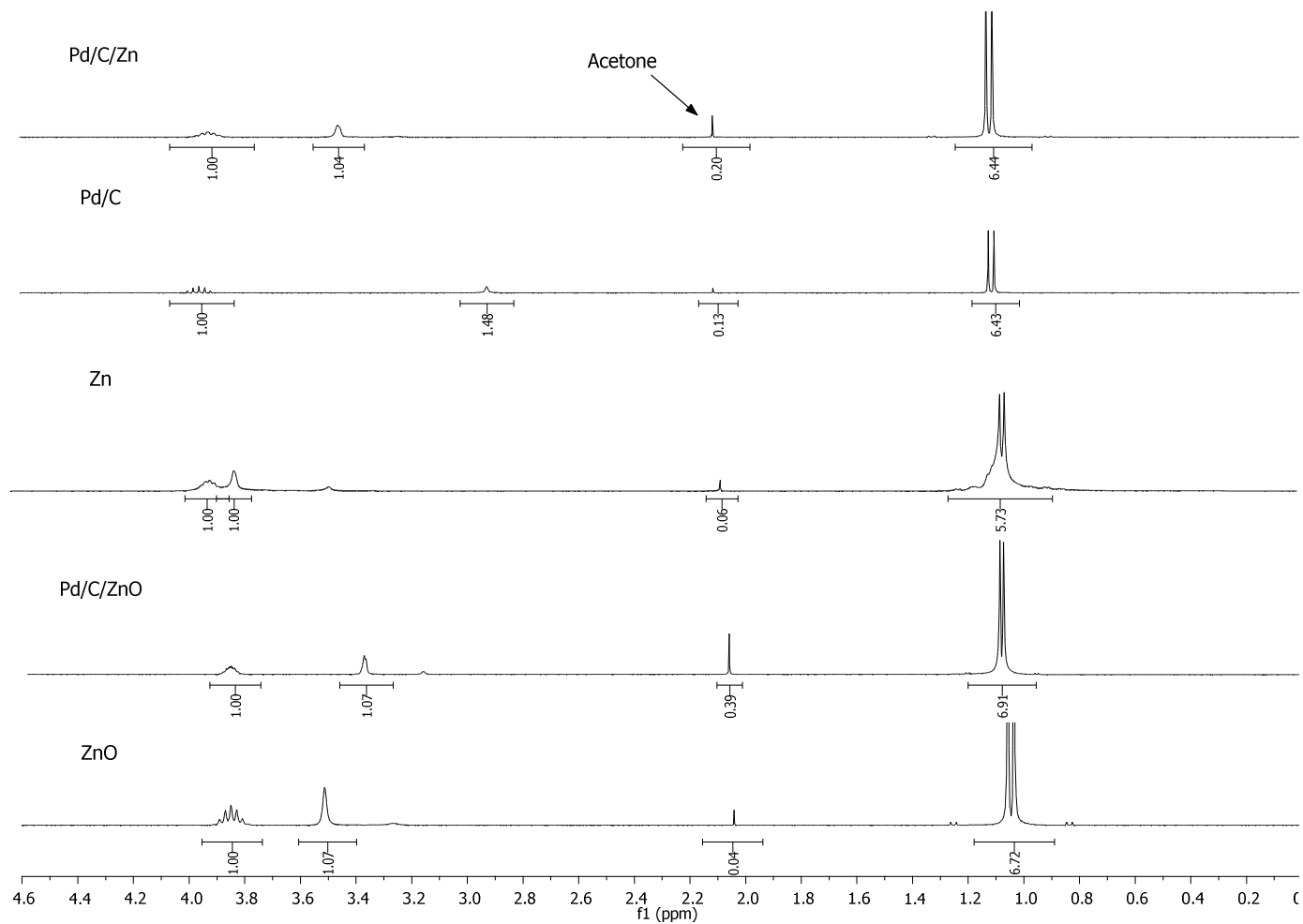
4. Spectra of acetone detection experience.



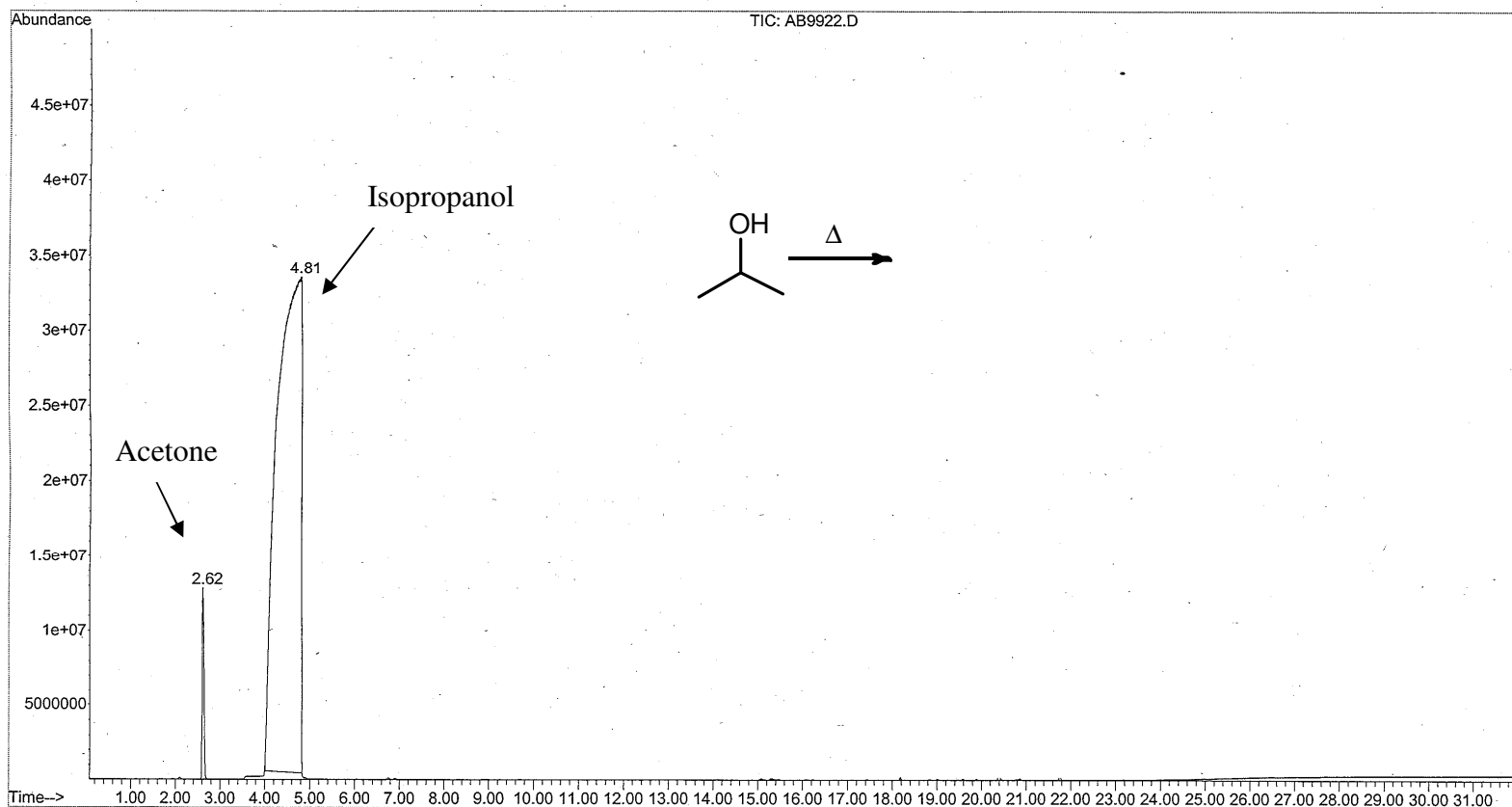
^1H NMR spectrum in CDCl_3 of the resulting mixture isopropanol/acetone after heating isopropanol at 150°C during 24°C



¹H NMR spectra in CDCl₃ of the resulting mixture isopropanol/acetone after heating isopropanol at 150°C during 24 h in the presence of 0.76 mmol of quinoline and the metals indicated for each case.

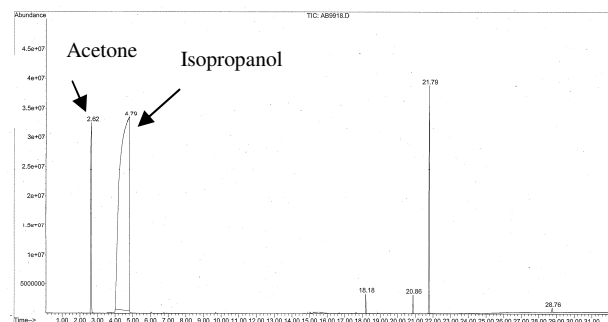


¹H NMR spectra in CDCl₃ of the resulting mixture isopropanol/acetone after heating isopropanol at 150°C during 24 h, in absence of quinoline, and the metals indicated for each case.

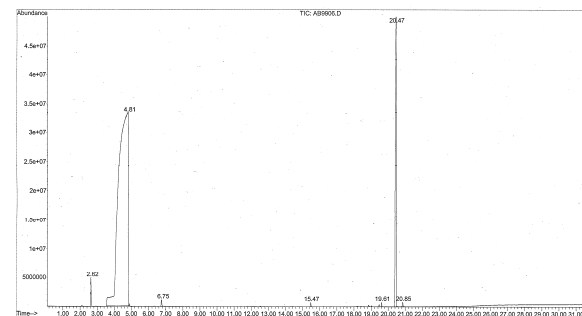


Gas chromatogram of the resulting mixture isopropanol/acetone after heating isopropanol at 150°C during 24 h.

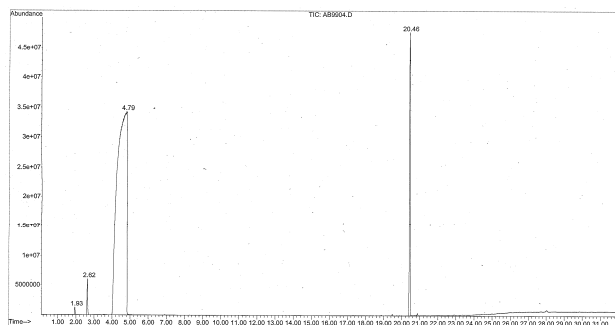
Pd/C/Zn



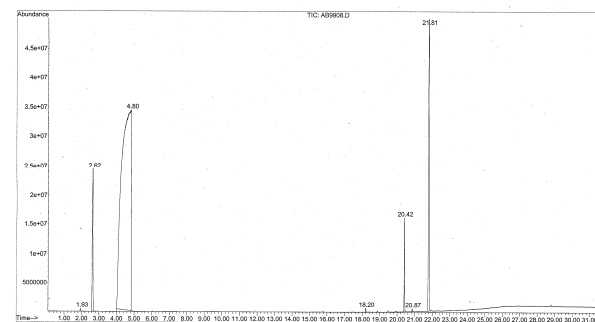
Zn



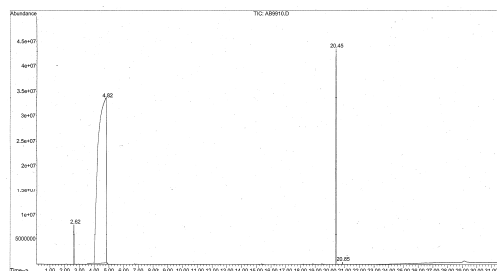
Pd/C



Pd/C/ZnO

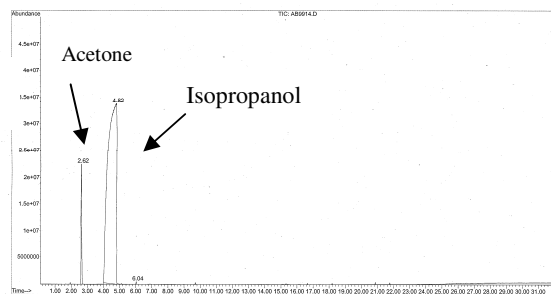


ZnO

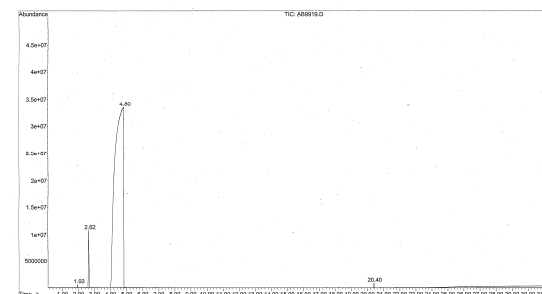


Gas chromatograms of the resulting reaction mixtures of after heating isopropanol at 150°C during 24 h in the presence of 0.76 mmol of quinoline and the metals indicated for each case.

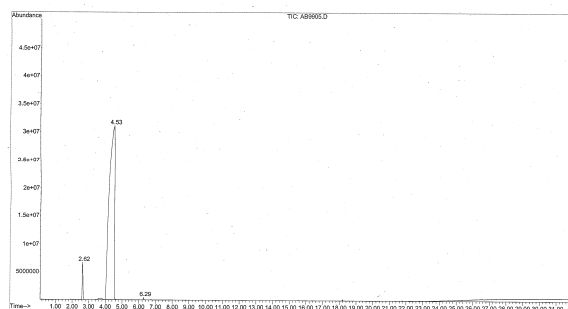
Pd/C/Zn



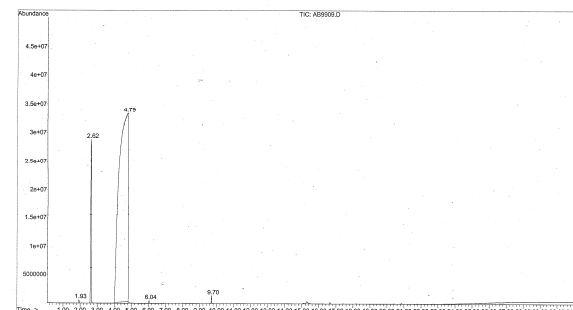
Zn



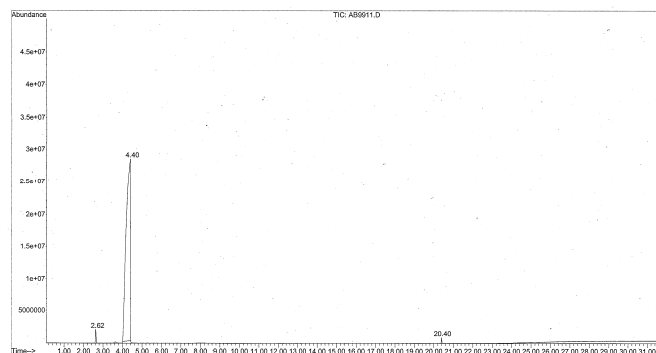
Pd/C



Pd/C/ZnO

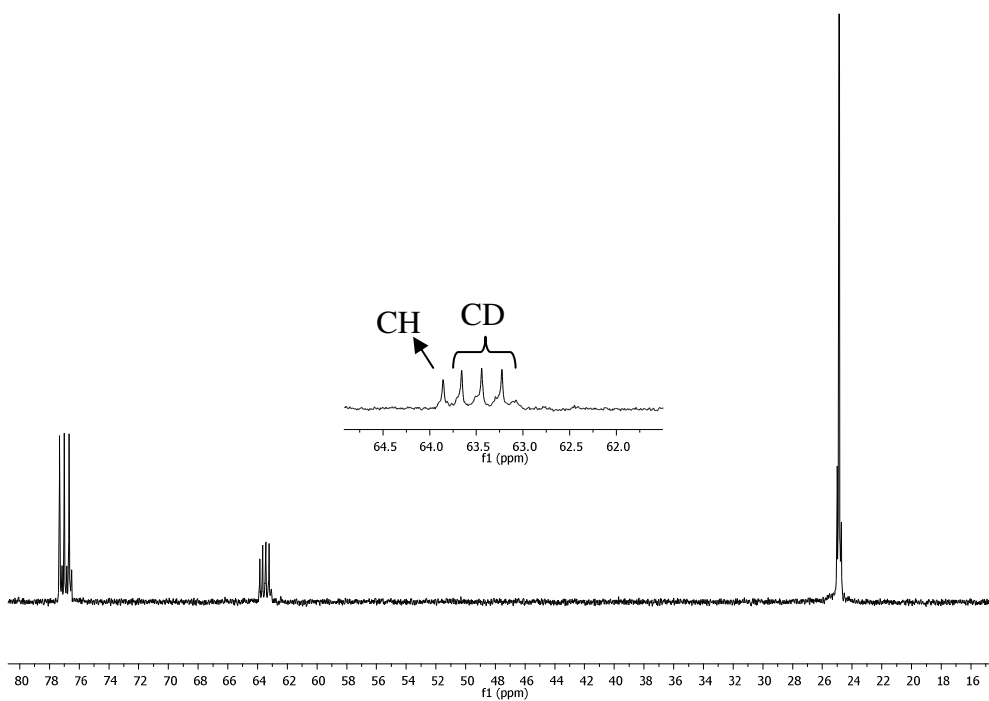
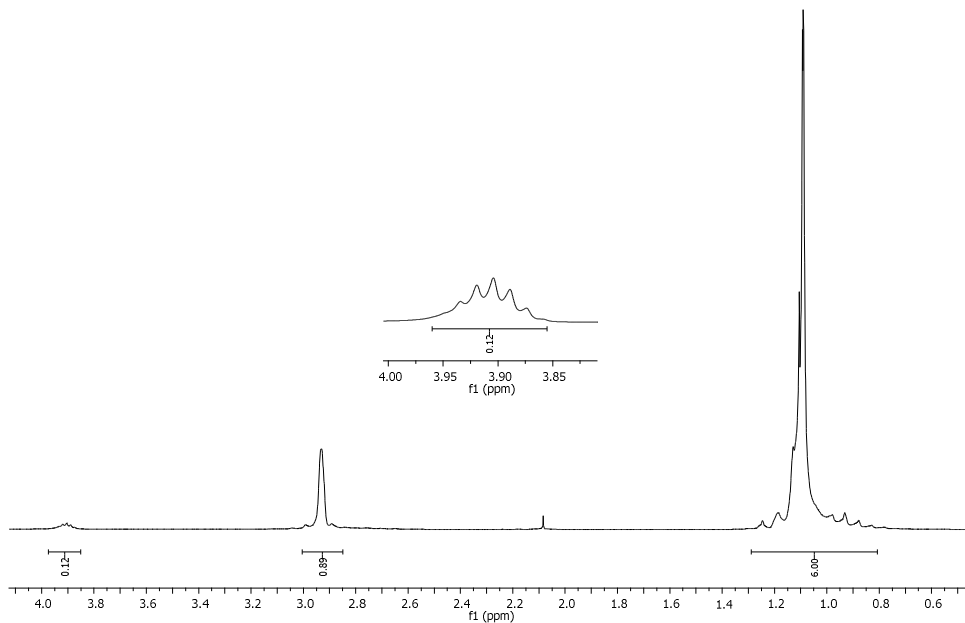
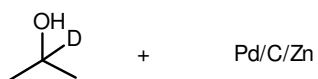


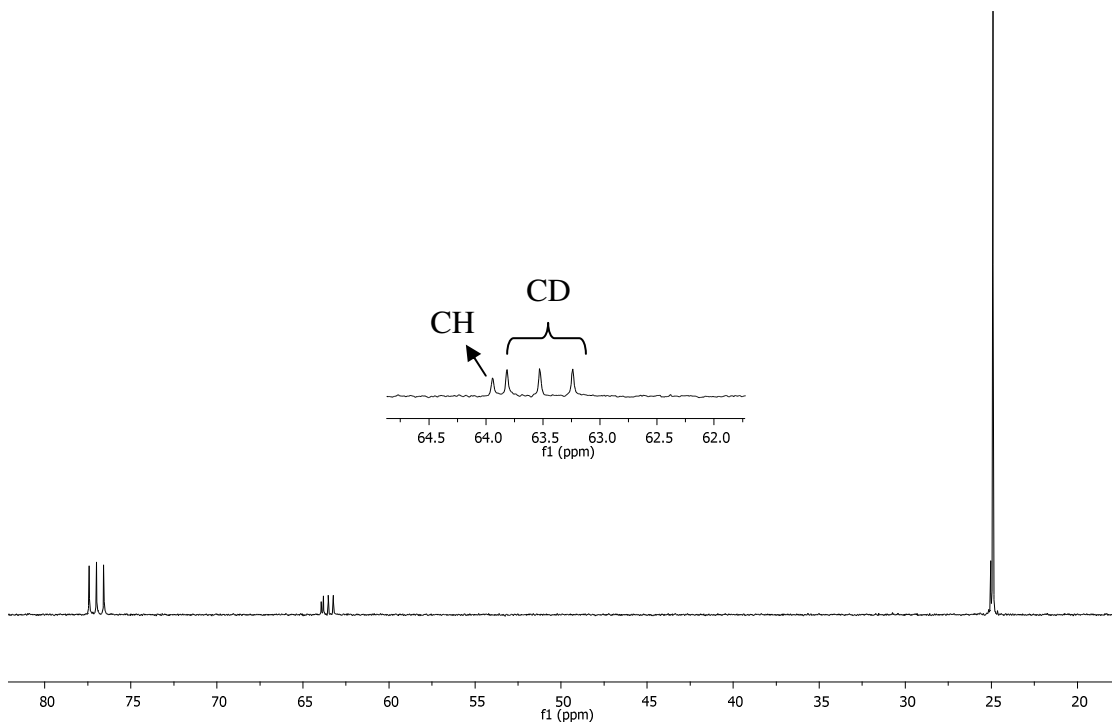
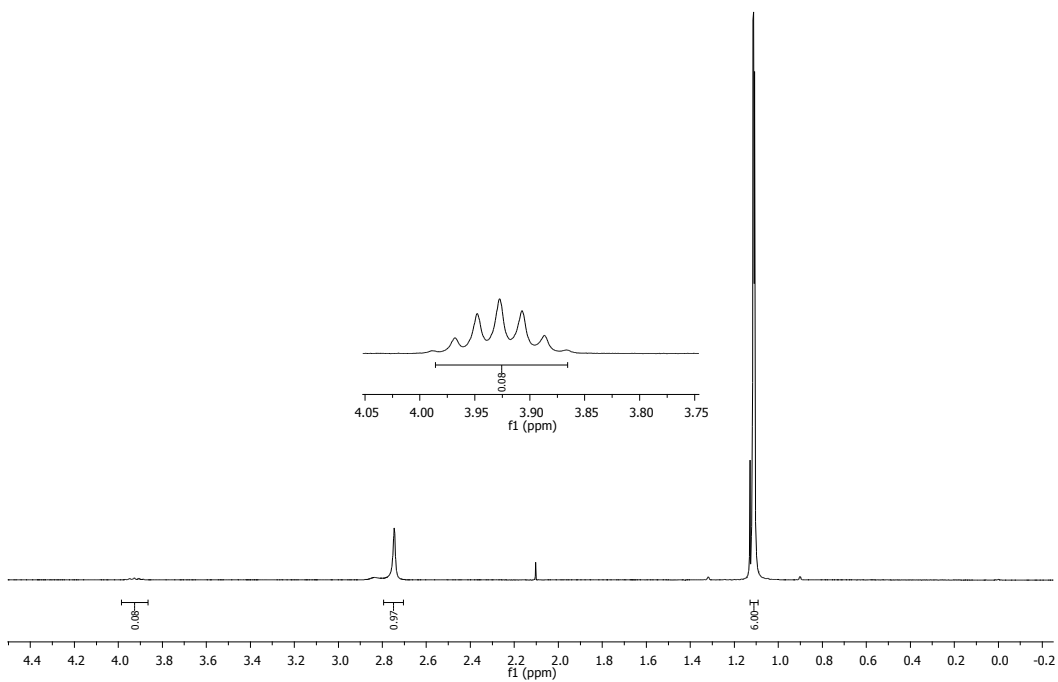
ZnO

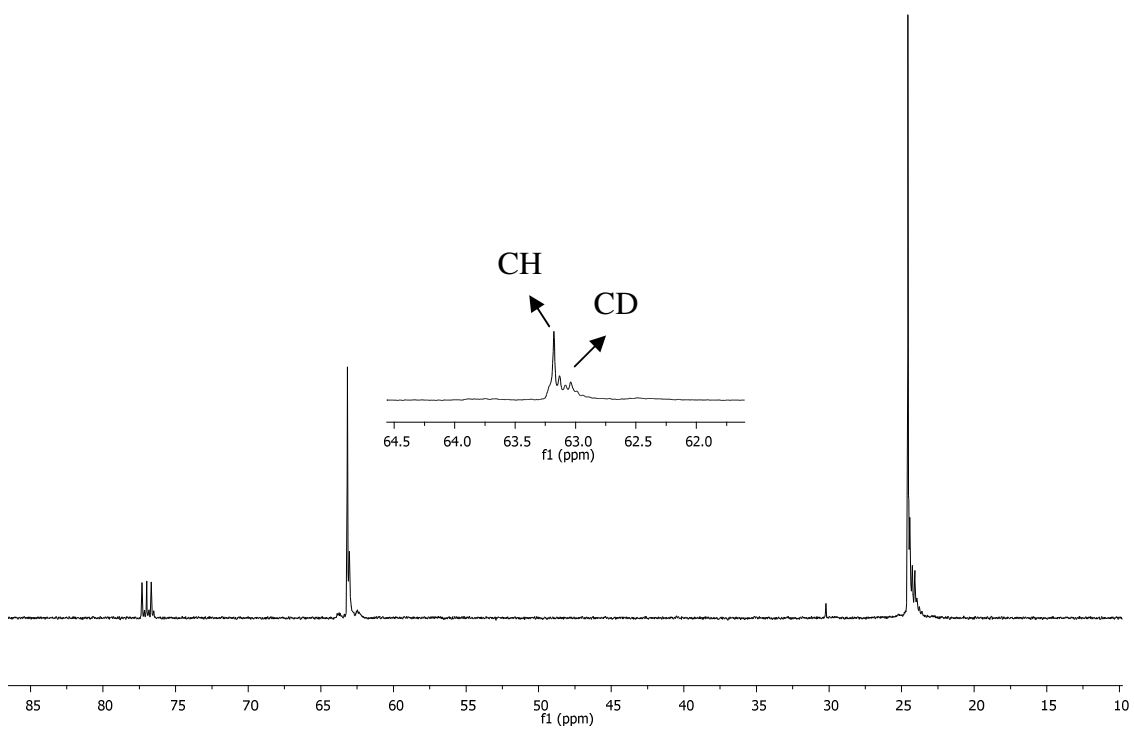
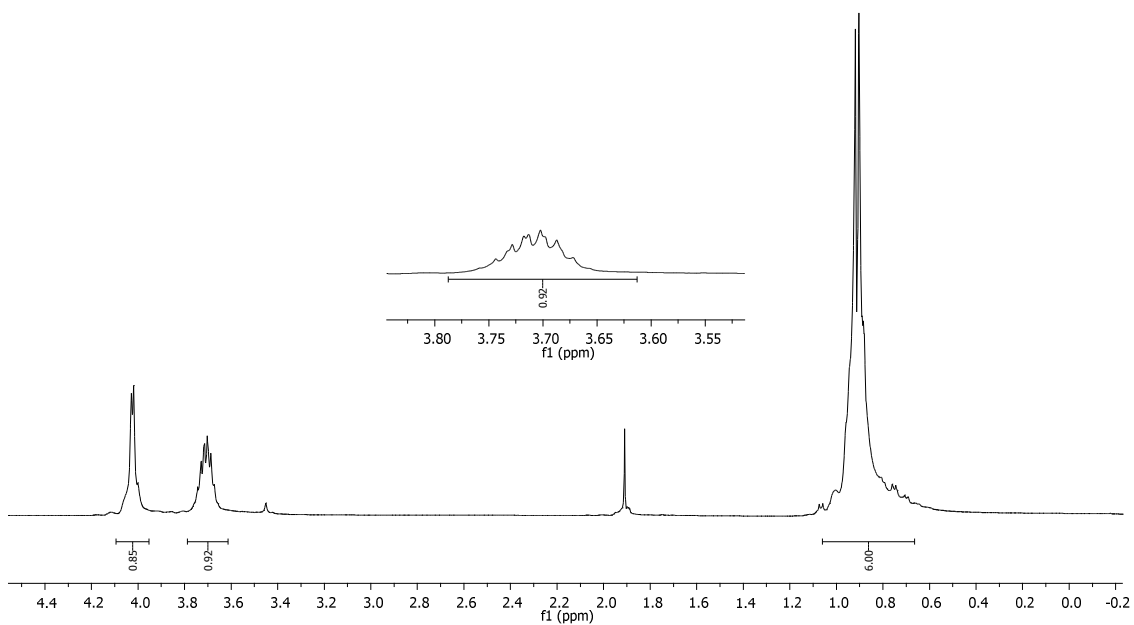
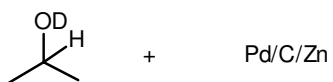


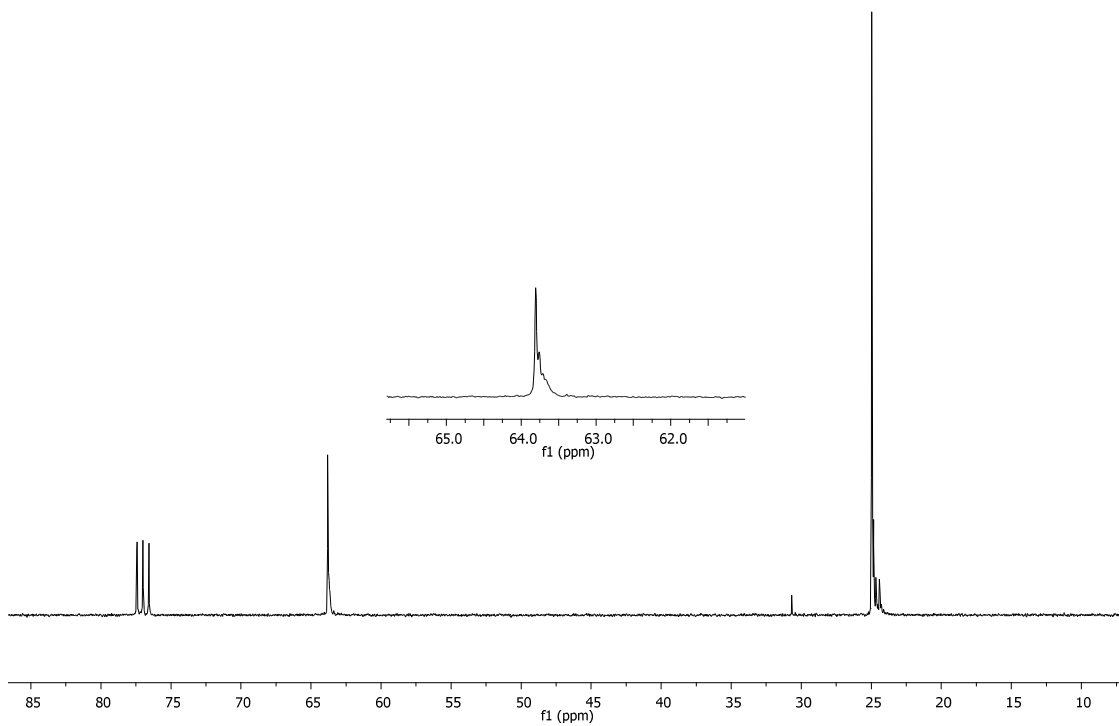
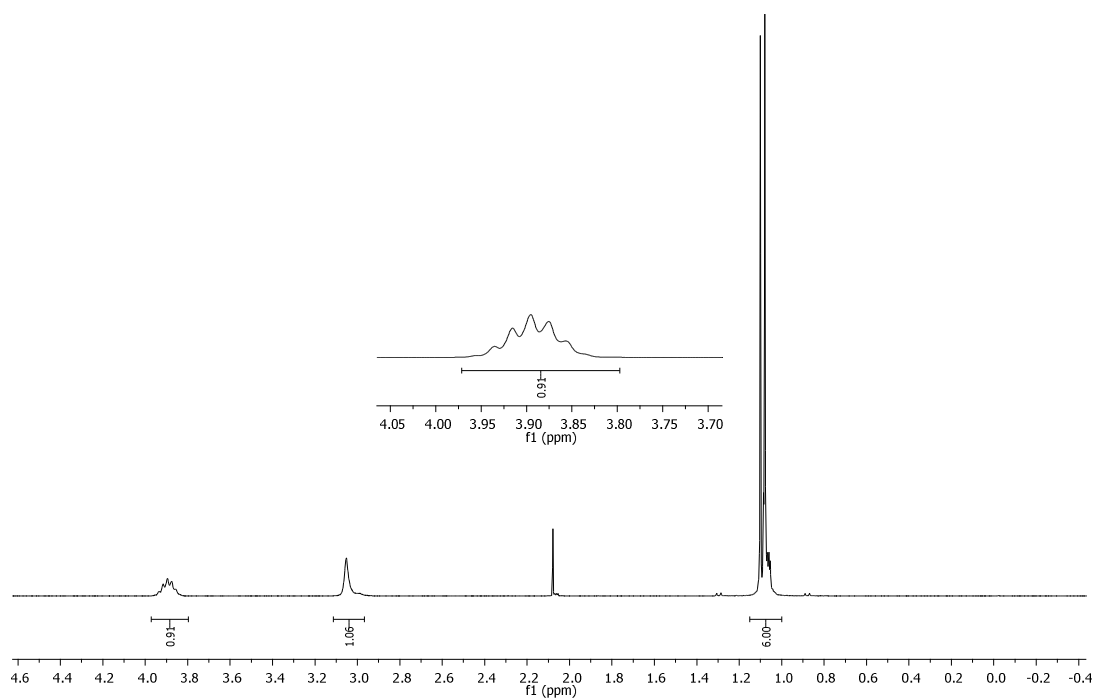
Gas chromatograms of the resulting mixtures isopropanol/acetone after heating isopropanol at 150°C during 24 h, in absence of quinoline, and the metals indicated for each case.

5. Spectra of 2-propanol-2-d₁ and 2-propan(ol-d) experiences.









6. References

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