

Electronic Supplementary Information

Brønsted Acid Promoted Benzylic C-H Bond Functionalization of Azaarenes: Nucleophilic Addition to Aldehydes

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1. General information

Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). Nuclear magnetic resonance (NMR) spectra were recorded on Varian MERCURY plus spectrometer (¹H 500 MHz, ¹³C 125 MHz) or a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for ¹H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ¹³C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl₃: δ 77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

Reagents: Substituted 2-methylquinolines was synthesized starting from *para*-substituted anilines and crotonaldehyde according to the method reported by Minamikawa, J.-i. *et. al.*¹. Liquid aromatic aldehydes, 2,6-lutidine, 2-picoline and 4-picoline were used after distillation. Solid aromatic aldehydes, ethyl glyoxylate (50 % in toluene) and organic solvents were used directly.

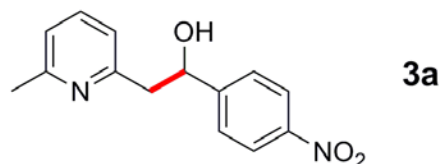
2. General experimental procedures for benzylic C-H functionalization of azaarenes

Method A: An oven-dried reaction vessel was charged with 2,6-lutidine (**1a**, 85.8 mg, 0.8 mmol, 4 equiv.), 1,2-dichloroethane (DCE, 0.2 mL), *p*-nitro-benzaldehyde (**2a**, 30.2 mg, 0.2 mmol) and acetic acid (12 μ L, 0.2 mmol, 1 equiv.) under argon. The vessel was sealed and heated at 100 °C (oil bath temperature) for 36 h. After the resulting mixture was cooled to room temperature, aqueous Na₂CO₃ solution (5%, 10 ml) was added and the mixture was extracted with dichloromethane (3 \times 10 ml), and washed with brine (2 \times 10 ml). The organic layer was dried with anhydrous Na₂SO₄, and concentrated under vacuum. The residue was chromatographed on a silica gel column eluted with a mixture of petroleum ether and ethyl acetate (1:1) to give pure products **3a** (49.6 mg, 96 % yield).

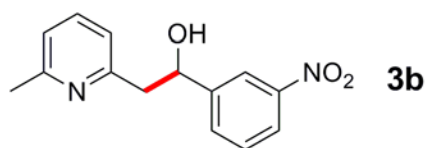
Method B: An oven-dried reaction vessel was charged with 2-methylquinoline (**1b**, 57.3 mg, 0.4 mmol, 2 equiv.), 1,4-dioxane (0.2 mL), H₂O (20 μ L), *p*-nitro-benzaldehyde (**2a**, 30.2 mg, 0.2 mmol) and acetic acid (12 μ L, 0.2 mmol, 1 equiv.) under argon. The vessel was sealed and heated at 80 °C (oil bath temperature) for 5 h. After the resulting mixture was cooled to room temperature, aqueous Na₂CO₃ solution (5%, 10 ml) was added and the mixture was extracted with dichloromethane (3 \times 10 ml), and washed with brine (2 \times 10 ml). The organic layer was dried with anhydrous Na₂SO₄, and concentrated under vacuum. The residue was chromatographed on a silica gel column eluted with a mixture of petroleum ether and ethyl acetate (1:1) to give pure products **3h** (52.1 mg, 95 % yield).

2. Characterization data of product 3a-3t

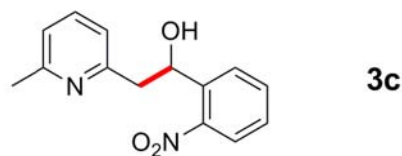
¹ Matsugi, M.; Fujio Tabusa, F.; Minamikawa, J.-i. *Tetrahedron Lett.* **2000**, *41*, 8523-8525.



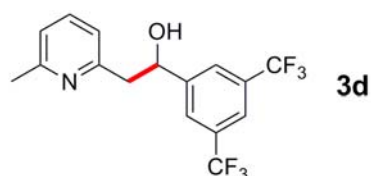
3a: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 8.20 (dt, $J=2.5, 9.0$ Hz, 2H), 7.60 (dt, $J=2.5, 9.0$ Hz, 2H), 7.52 (t, $J=8.0$ Hz, 1H), 7.07 (d, $J=8.0$ Hz, 1H), 6.90 (d, $J=8.0$ Hz, 1H), 5.25 (dd, $J=2.5, 8.5$ Hz, 1H), 3.12 (dd, $J=3.0, 15.0$ Hz, 1H), 3.04 (dd, $J=9.0, 15.0$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 158.4, 157.7, 151.1, 147.3, 137.6, 126.8, 123.8, 121.9, 120.9, 72.8, 44.7, 24.6; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{N}_2$, 259.1077; found : 259.1064.



3b: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 8.30 (t, $J=1.5$ Hz, 1H), 8.11 (dd, $J=1.0, 8.0$ Hz, 1H), 7.78 (d, $J=6.5$ Hz, 1H), 7.54 (d, $J=8.0$ Hz, 1H), 7.50 (d, $J=8.0$ Hz, 1H), 7.07 (d, $J=7.0$ Hz, 1H), 6.91 (d, $J=8.0$ Hz, 1H), 5.24 (dd, $J=3.0, 9.0$ Hz, 1H), 3.03-3.14 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 158.5, 157.7, 148.5, 146.7, 137.6, 132.2, 129.4, 122.4, 121.9, 121.2, 120.8, 72.7, 44.8, 24.6; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{N}_2$, 259.1077; found : 259.1065.

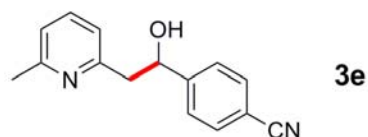


3c: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.99 (dd, $J=1.5, 8.0$ Hz, 1H), 7.96 (dd, $J=1.5, 8.0$ Hz, 1H), 7.62-7.66 (m, 1H), 7.54 (t, $J=8.0$ Hz, 1H), 7.40-7.43 (m, 1H), 7.07 (d, $J=8.0$ Hz, 1H), 6.98 (d, $J=8.0$ Hz, 1H), 5.62 (dd, $J=2.0, 9.0$ Hz, 1H), 3.30 (dd, $J=2.0, 15.0$ Hz, 1H), 3.00 (dd, $J=9.0, 15.0$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 159.0, 157.6, 147.8, 139.9, 137.7, 133.7, 128.8, 128.1, 124.4, 121.8, 120.9, 69.4, 44.4, 24.6; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{N}_2$, 259.1077; found : 259.1068.

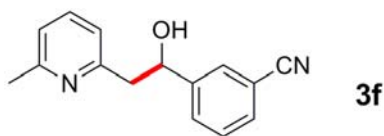


3d: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.90 (s, 2H), 7.77 (s, 1H), 7.54 (t, $J=8.0$ Hz, 1H), 7.08 (d, $J=8.0$ Hz, 1H), 6.92 (d, $J=8.0$ Hz, 1H), 5.26 (dd, $J=2.5, 9.0$ Hz, 1H), 3.12 (dd, $J=3.0, 15.0$ Hz, 1H),

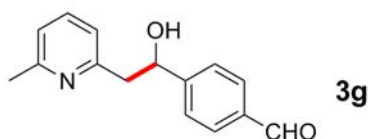
3.05 (dd, $J=9.0, 15.0$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 158.3, 157.8, 147.1, 137.7, 131.7 (q, $J=33.0$ Hz), 126.4 (q, $J=2.6$ Hz), 123.7 (d, $J=271.1$ Hz), 122.0, 121.3 (q, $J=3.9$ Hz), 120.9, 72.5, 44.8, 24.5; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{ONF}_6$, 350.0974; found: 350.0957.



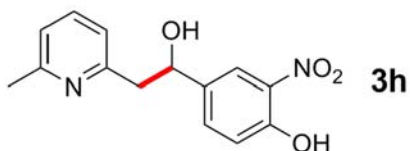
3e: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.63 (dt, $J=2.0, 8.5$ Hz, 2H), 7.50-7.55 (m, 3H), 7.06 (d, $J=8.0$ Hz, 1H), 6.89 (d, $J=8.0$ Hz, 1H), 5.19 (dd, $J=3.0, 9.0$ Hz, 1H), 3.01-3.10 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 158.6, 157.7, 149.8, 137.6, 132.4, 126.7, 121.8, 120.8, 119.2, 111.1, 72.90, 44.8, 24.6; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{ON}_2$, 239.1179; found : 239.1168.



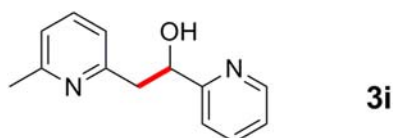
3f: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.74 (s, 1H), 7.67 (d, $J=8.0$ Hz, 1H), 7.53 (m, 2H), 7.45 (t, $J=8.4$ Hz, 1H), 7.07 (d, $J=7.2$ Hz, 1H), 6.90 (d, $J=8.0$ Hz, 1H), 5.17 (dd, $J=2.8, 8.0$ Hz, 1H), 3.11-3.00 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 158.4, 157.6, 145.9, 137.5, 130.9, 130.4, 129.7, 129.1, 121.7, 120.8, 119.0, 112.4, 72.5, 44.9, 24.4; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{ON}_2$, 239.1179; found : 239.1165.



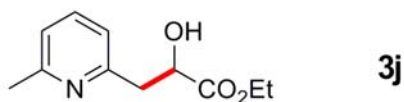
3g: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 10.00 (s, 1H), 7.86 (d, $J=8.5$ Hz, 2H), 7.60 (d, $J=8.5$ Hz, 2H), 7.51 (t, $J=8.0$ Hz, 1H), 7.06 (d, $J=8.0$ Hz, 1H), 6.90 (d, $J=7.5$ Hz, 1H), 5.22 (dd, $J=3.5, 9.0$ Hz, 1H), 3.03-3.12 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 192.3, 158.8, 157.7, 151.4, 137.6, 135.7, 130.1, 126.6, 121.7, 120.8, 73.2, 44.8, 24.6; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}$, 242.1176, found : 242.1166.



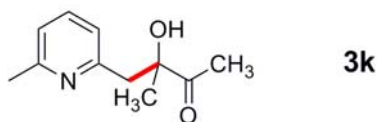
3h: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 10.53 (s, 1H), 8.17 (s, 1H), 7.67 (d, $J=6.8$ Hz, 1H), 7.52 (t, $J=8.4$ Hz, 1H), 7.14 (d, $J=8.8$ Hz, 1H), 7.06 (d, $J=7.2$ Hz, 1H), 6.91 (d, $J=7.6$ Hz, 1H), 5.13 (dd, $J=2.8, 7.2$ Hz, 1H), 3.09-3.00 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 158.5, 157.7, 154.3, 137.5, 137.1, 135.4, 133.5, 122.3, 121.7, 120.8, 119.9, 72.1, 44.8, 24.4; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{O}_4\text{N}_2$, 275.1032; found : 275.1021.



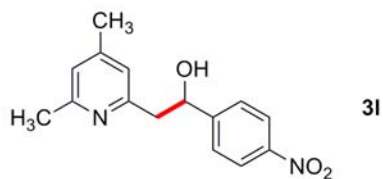
3i: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 8.55 (d, $J=3.2$, 1H), 7.68 (t, $J=7.6$ Hz, 1H), 7.56 (d, $J=7.6$ Hz, 1H), 7.49 (d, $J=8.8$ Hz, 1H), 7.17 (s, 1H), 7.03 (d, $J=8.4$ Hz, 1H), 6.96 (d, $J=8.0$ Hz, 1H), 5.20 (dd, $J=2.4, 8.8$ Hz, 1H), 3.34 (dd, $J=2.4, 14.8$ Hz, 1H), 3.08 (dd, $J=8.8, 14.4$ Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 163.0, 159.0, 157.4, 148.5, 137.2, 136.7, 122.1, 121.3, 120.9, 120.4, 73.9, 44.1, 24.4; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$, 215.1184; found : 215.1168.



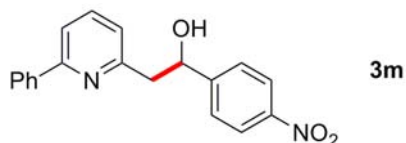
3j: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.50 (t, $J=7.5$ Hz, 1H), 7.02 (d, $J=8.0$ Hz, 1H), 6.97 (d, $J=8.0$ Hz, 1H), 4.62 (dd, $J=3.5, 7.0$ Hz, 1H), 4.19 (d, $J=2.0$ Hz, 2H), 3.26 (dd, $J=3.5, 15.0$ Hz, 1H), 3.14 (dd, $J=7.0, 10.0$ Hz, 1H), 2.50 (s, 3H), 1.22 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 173.9, 157.8, 137.3, 121.7, 120.6, 120.9, 70.9, 61.4, 40.3, 24.5, 14.4; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{16}\text{O}_3\text{N}$, 210.1125; found: 210.1119.



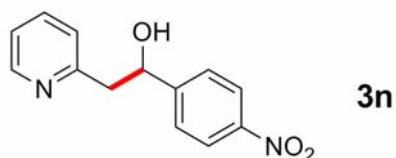
3k: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.51 (t, $J=6.8$, 1H), 6.99 (d, $J=7.6$ Hz, 1H), 6.95 (d, $J=7.6$ Hz, 1H), 3.33 (d, $J=3.6$ Hz, 1H), 2.96 (d, $J=15.2$ Hz, 1H), 2.48 (s, 3H), 2.26 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 215.0, 158.0, 157.1, 137.4, 121.4, 121.36, 80.0, 44.5, 25.8, 25.5, 24.2; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}$, 194.1181; found: 194.1172.



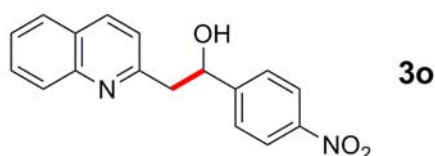
3l: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 8.20 (d, $J=8.8$, 2H), 7.59 (d, $J=8.8$ Hz, 2H), 6.89 (s, 1H), 6.73 (s, 1H), 5.22 (dd, $J=2.0$, 8.8 Hz, 1H), 3.08-2.95 (m, 2H), 2.52 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 158.1, 157.3, 152.2, 148.8, 147.2, 126.7, 123.6, 122.6, 121.7, 72.7, 44.5, 24.2, 21.0; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}_2$, 273.1239; found: 273.1231.



3m: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 8.21 (d, $J=8.4$, 2H), 7.96 (d, $J=7.2$ Hz, 2H), 7.72 (t, $J=7.6$ Hz, 1H), 7.66 (d, $J=8.8$ Hz, 1H), 7.62 (d, $J=8.0$ Hz, 2H), 7.53-7.46 (m, 3H), 7.05 (d, $J=7.2$ Hz, 1H), 6.76 (s, 1H), 5.37 (d, $J=6.0$ Hz, 1H), 3.26-3.14 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 158.9, 156.8, 151.7, 147.4, 138.7, 138.2, 129.6, 129.1, 127.0, 126.8, 123.7, 122.3, 119.2, 72.6, 44.9; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{O}_3\text{N}_2$, 321.1239; found: 321.1232.



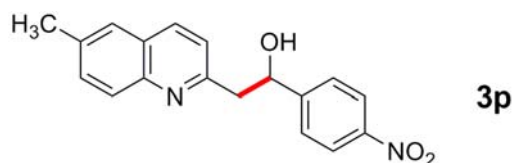
3n: known compound, CAS: 20151-01-3; the following NMR data were the same as literature report². ^1H NMR (400 MHz, CDCl_3 , TMS) δ 8.54 (s, 1H), 8.20 (d, $J=8.0$ Hz, 2H), 7.65 (s, 1H), 7.60 (d, $J=7.2$ Hz, 2H), 7.23 (s, 1H), 7.10 (d, $J=6.4$ Hz, 1H), 6.42 (s, 1H), 5.29 (d, $J=7.6$ Hz, 1H), 3.19-3.07 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3 , TMS) δ 159.0, 151.6, 148.7, 147.3, 137.3, 126.7, 123.9, 123.7, 122.2, 72.5, 44.9.



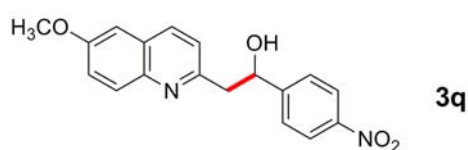
3o: known compound, CAS: 38101-97-2; the following NMR data were the same as literature

² Houminer, Y.; Williams, D. L. *J. Org. Chem.* **1983**, *48*, 2622-2625.

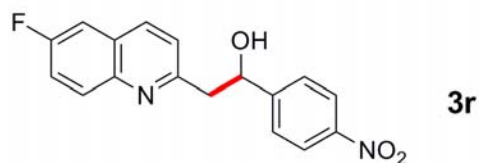
report³. ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.22 (d, *J*=8.8Hz, 2H), 8.13 (d, *J*=8.0Hz, 1H), 8.06 (d, *J*=8.4 Hz, 1H), 7.82 (d, *J*=7.6 Hz, 1H), 7.76 (t, *J*=7.2 Hz, 1H), 7.65 (d, *J*=8.8 Hz, 2H), 7.56 (t, *J*=7.2 Hz, 1H), 7.22 (d, *J*=8.8 Hz, 1H), 6.72 (s, 1H), 5.45 (d, *J*=5.6 Hz, 1H), 3.38-3.25 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 159.6, 151.9, 148.0, 146.6, 136.2, 129.6, 129.0, 128.9, 127.6, 126.8, 126.1, 123.6, 121.9, 45.8, 45.2.



3p: ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.21 (d, *J*=8.4 Hz, 2H), 8.02 (d, *J*=8.0 Hz, 1H), 7.95 (d, *J*=9.2 Hz, 1H), 7.64 (d, *J*=8.8 Hz, 2H), 7.57 (s, 2H), 7.16 (d, *J*=8.0 Hz, 1H), 6.79 (s, 1H), 5.42 (d, *J*=8.4 Hz, 1H), 3.35-3.22 (m, 2H), 2.55(s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 158.0, 157.1, 151.7, 147.4, 143.1, 136.1, 130.2, 128.1, 126.8, 123.7, 122.9, 122.3, 105.4, 72.4, 55.7, 45.2; HRMS (EI) *m/z* : [M]⁺ calcd for C₁₈H₁₆O₃N₂, 308.1161; found :308.1166.



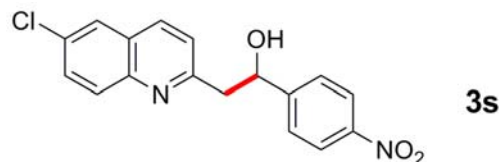
3q: ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.21 (d, *J*=8.8 Hz, 2H), 8.01 (d, *J*=8.4 Hz, 1H), 7.95 (d, *J*=9.2 Hz, 1H), 7.64 (d, *J*=8.0 Hz, 2H), 7.40 (dd, *J*=9.2, 2.4 Hz, 1H), 7.16 (d, *J*=8.0 Hz, 1H), 7.07 (d, *J*=2.0 Hz, 1H), 6.72 (s, 1H), 5.42 (d, *J*=6.8 Hz, 1H), 3.94 (s, 3H), 3.34-3.20 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 159.7, 152.0, 148.0, 146.6, 136.2, 132.4, 129.6, 129.0, 127.6, 126.8, 126.1, 123.5, 121.9, 72.4, 45.8, 45.2; HRMS (EI) *m/z* : [M]⁺ calcd for C₁₈H₁₆O₄N₂, 324.1110; found: 324.1115.



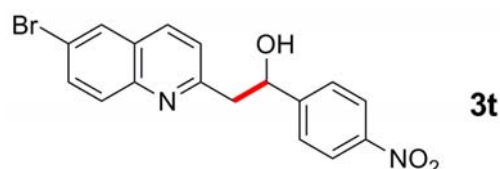
3r: ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.22 (d, *J*=8.8 Hz, 2H), 8.09 (d, *J*=4.0 Hz, 1H), 8.07 (s, 1H), 7.65 (d, *J*=8.4 Hz, 2H), 7.53 (d, *J*=2.8 Hz, 1H), 7.45 (dd, *J*=8.8, 2.4 Hz, 1H), 7.24 (d, *J*=8.8 Hz, 1H), 6.45 (s, 1H), 5.45 (d, *J*=8.4 Hz, 1H), 3.33-3.29 (m, 2H); ¹³C NMR (125 MHz, CDCl₃,

³ Franck, X.; Fournet, A.; Prina, E.; Mahieux, R.; Hocquemiller, R.; Figadere, B. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3635-3638.

TMS) δ 161.8, 159.1, 151.4, 144.1, 136.7 (d, $J=5.3$ Hz), 131.2 (d, $J=9.0$ Hz), 130.0, 127.6, 126.8, 123.8, 122.8, 120.4 (d, $J=157.0$ Hz), 111.0 (d, $J=114.0$ Hz), 72.2, 45.3; HRMS (EI) m/z : $[M]^+$ calcd for $C_{17}H_{13}FO_3N_2$, 312.0910; found: 312.0915.



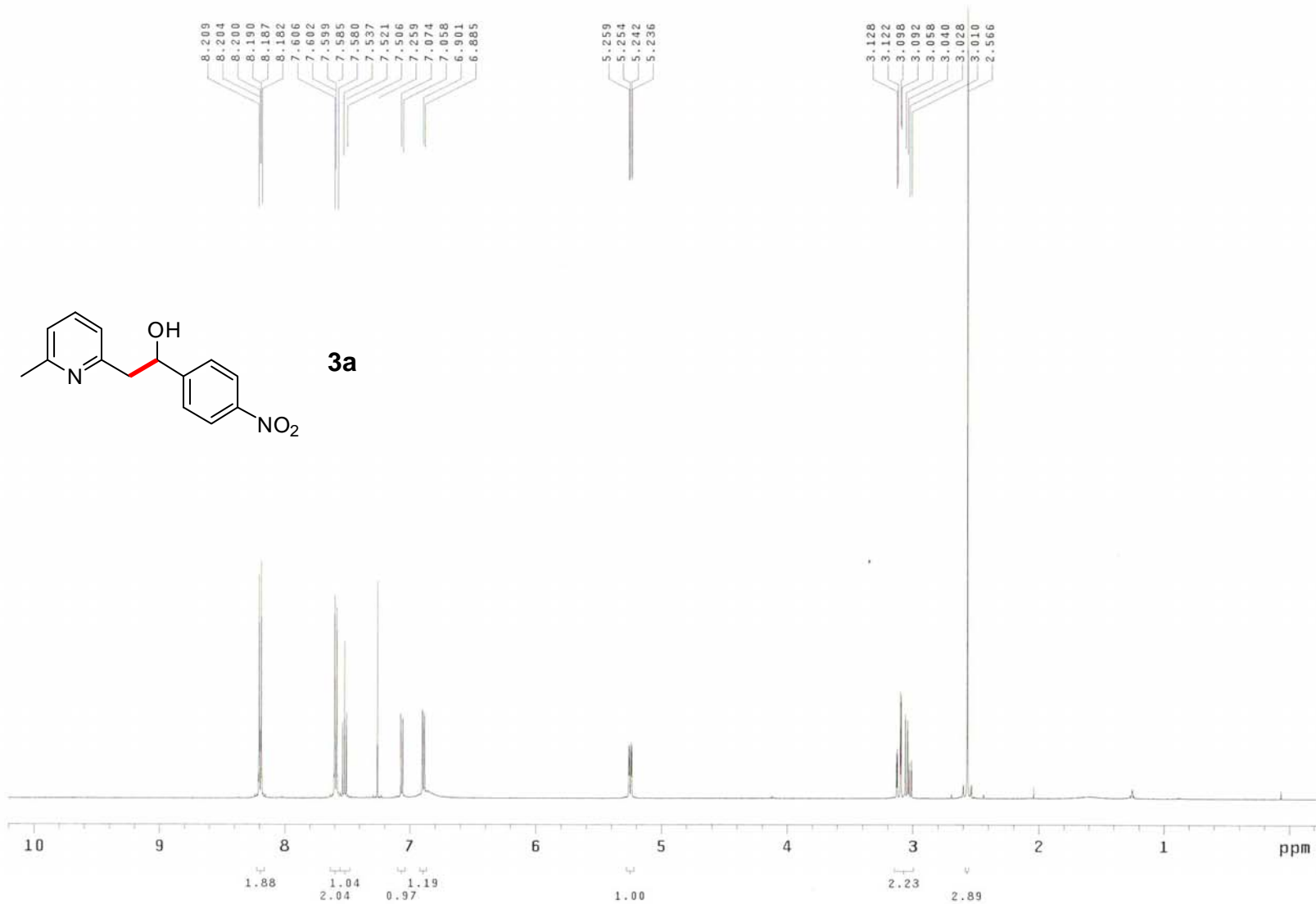
3s: 1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.22 (d, $J=8.4$ Hz, 2H), 8.05 (d, $J=8.4$ Hz, 1H), 8.00 (d, $J=8.4$, 1H), 7.81 (s, 1H), 7.69 (dd, $J=8.8$, 1.2 Hz, 1H), 7.64 (d, $J=8.8$ Hz, 2H), 7.25 (d, $J=10.8$ Hz, 1H), 6.35 (s, 1H), 5.45 (d, $J=6.8$ Hz, 1H), 3.37-3.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 160.1, 151.3, 147.4, 145.5, 136.3, 132.4, 131.1, 130.4, 127.7, 126.8, 126.5, 123.8, 123.0, 72.2, 45.6; HRMS (EI) m/z : $[M]^+$ calcd for $C_{17}H_{13}O_3N_2Cl$, 328.0615; found: 328.0619.



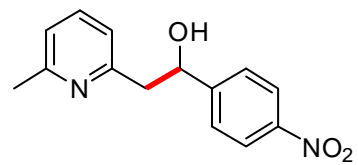
3t: 1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.22 (d, $J=8.4$ Hz, 2H), 8.04 (d, $J=8.4$ Hz, 1H), 7.99 (s, 1H), 7.94 (d, $J=9.2$ Hz, 1H), 7.82 (dd, $J=8.8$, 1.6 Hz, 1H), 7.64 (d, $J=8.4$ Hz, 2H), 7.25 (d, $J=8.8$ Hz, 1H), 6.37 (s, 1H), 5.45 (d, $J=8.4$ Hz, 1H), 3.37-3.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 160.2, 151.2, 147.3, 145.6, 136.2, 133.6, 130.4, 129.8, 128.1, 126.7, 123.8, 122.9, 120.5, 72.1, 45.5; HRMS (EI) m/z : $[M]^+$ calcd for $C_{17}H_{13}O_3N_2Br$, 374.0089; found: 374.0093.

4. Copies of 1H and ^{13}C NMR spectra of products 3a-3t

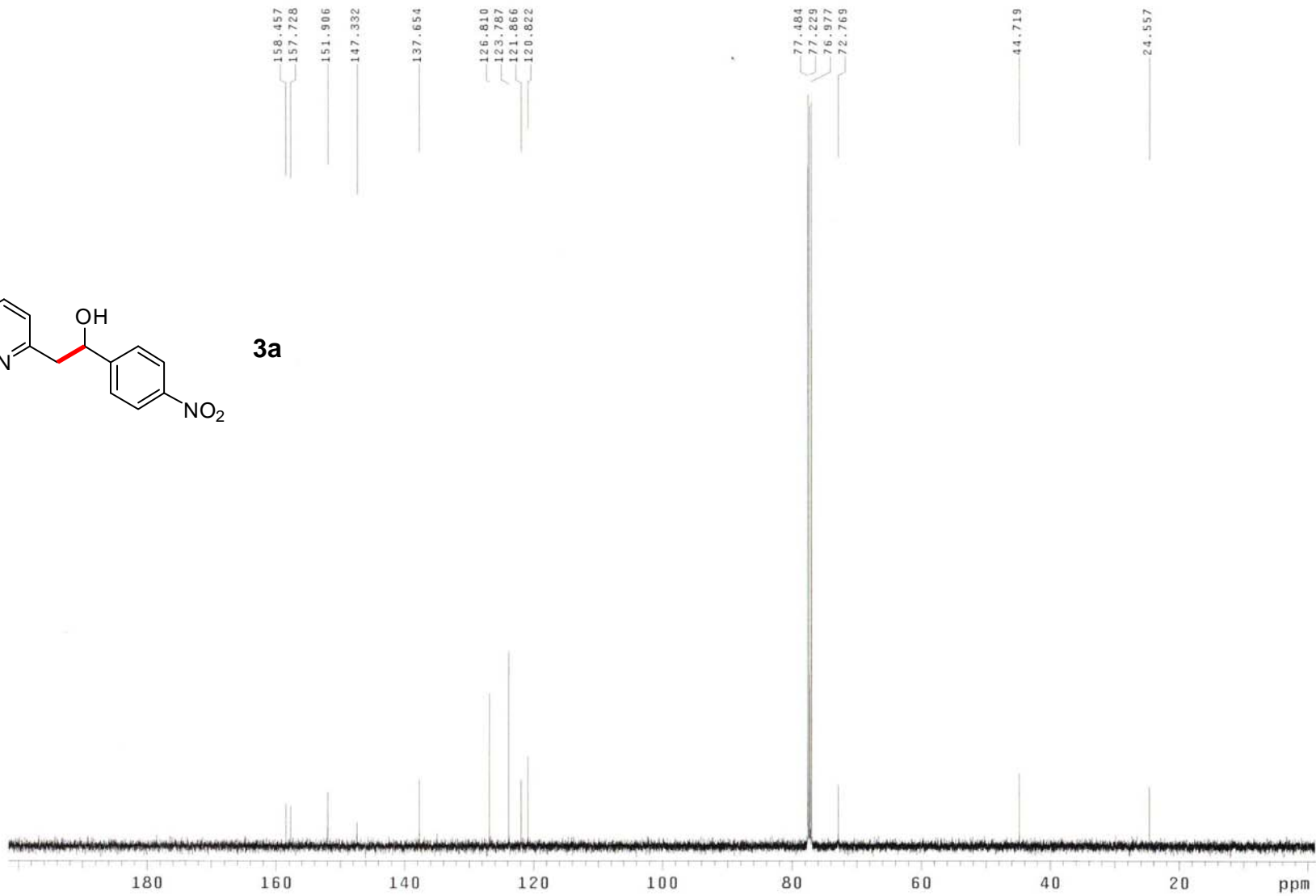
157 ppm



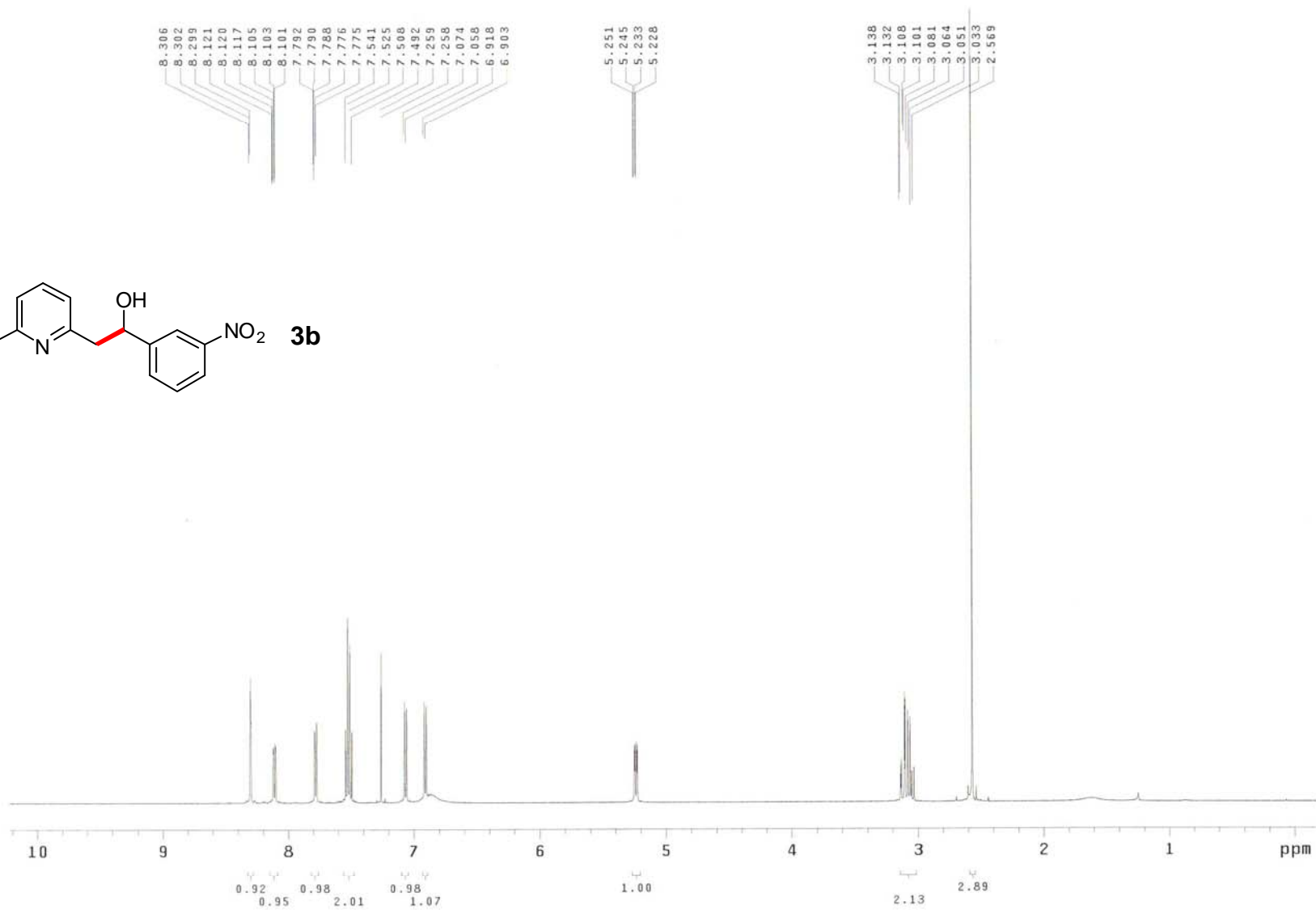
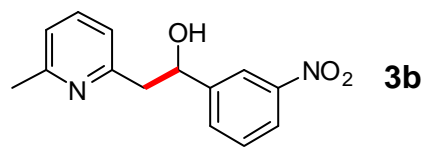
1697 ppm

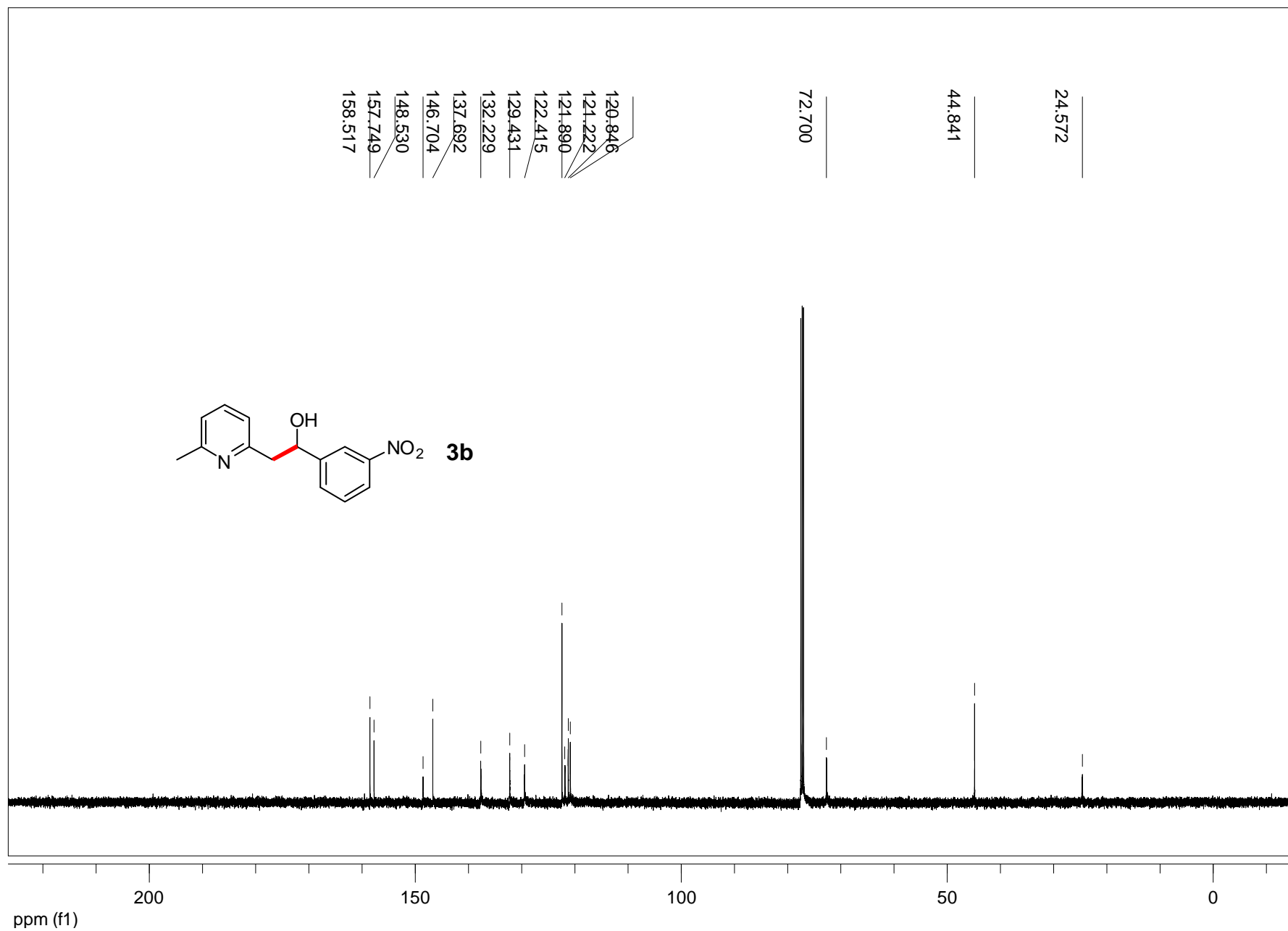


3a

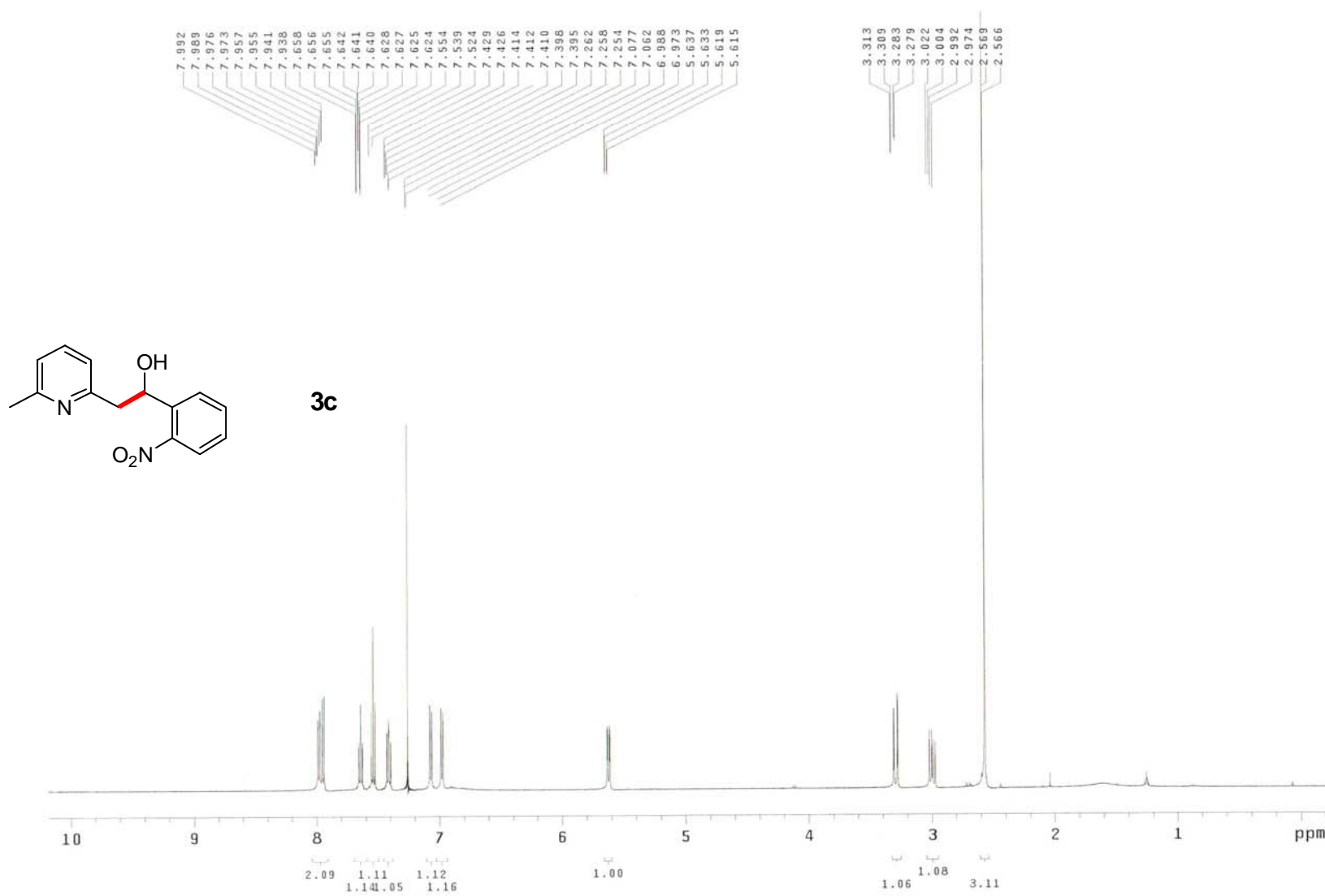


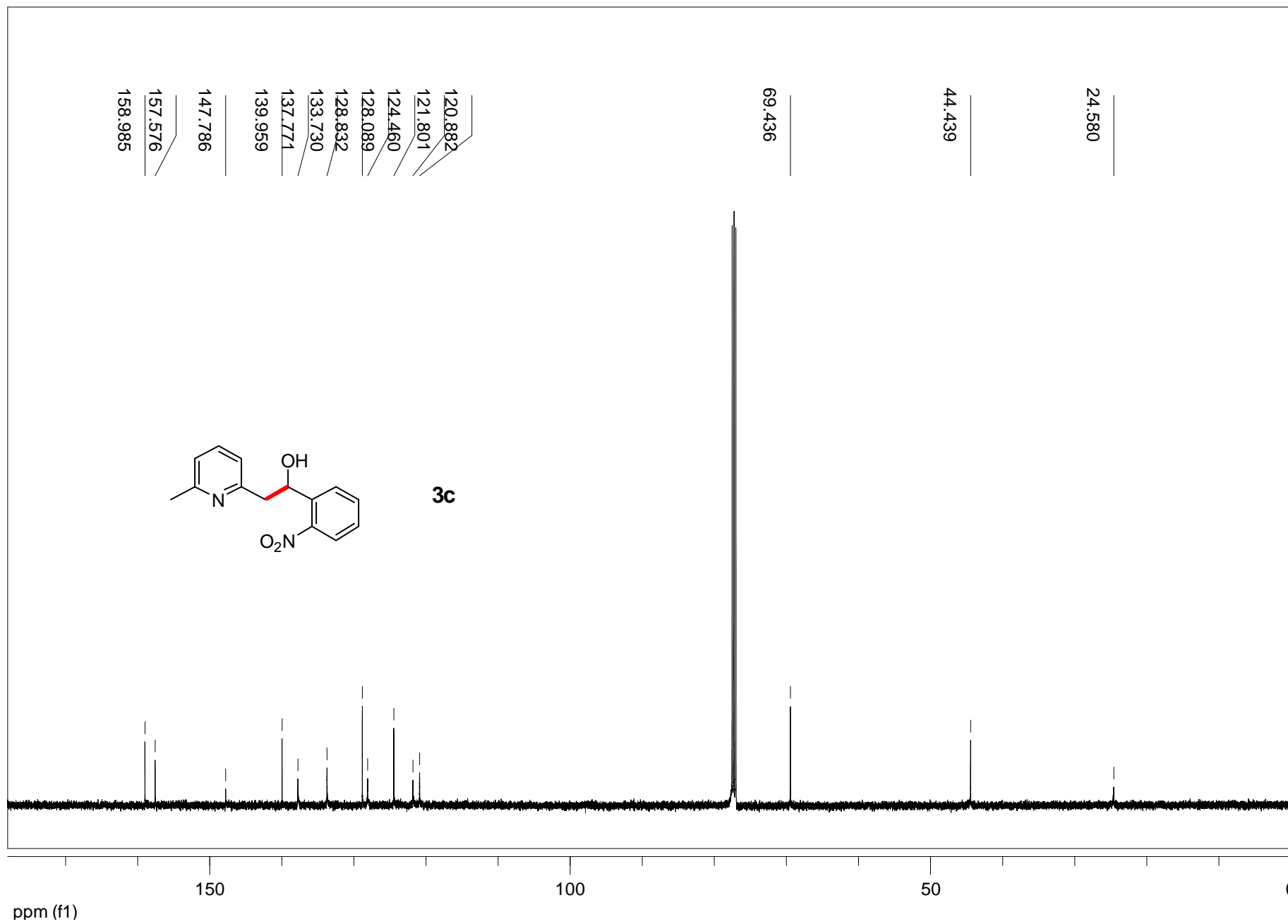
2034 ppm



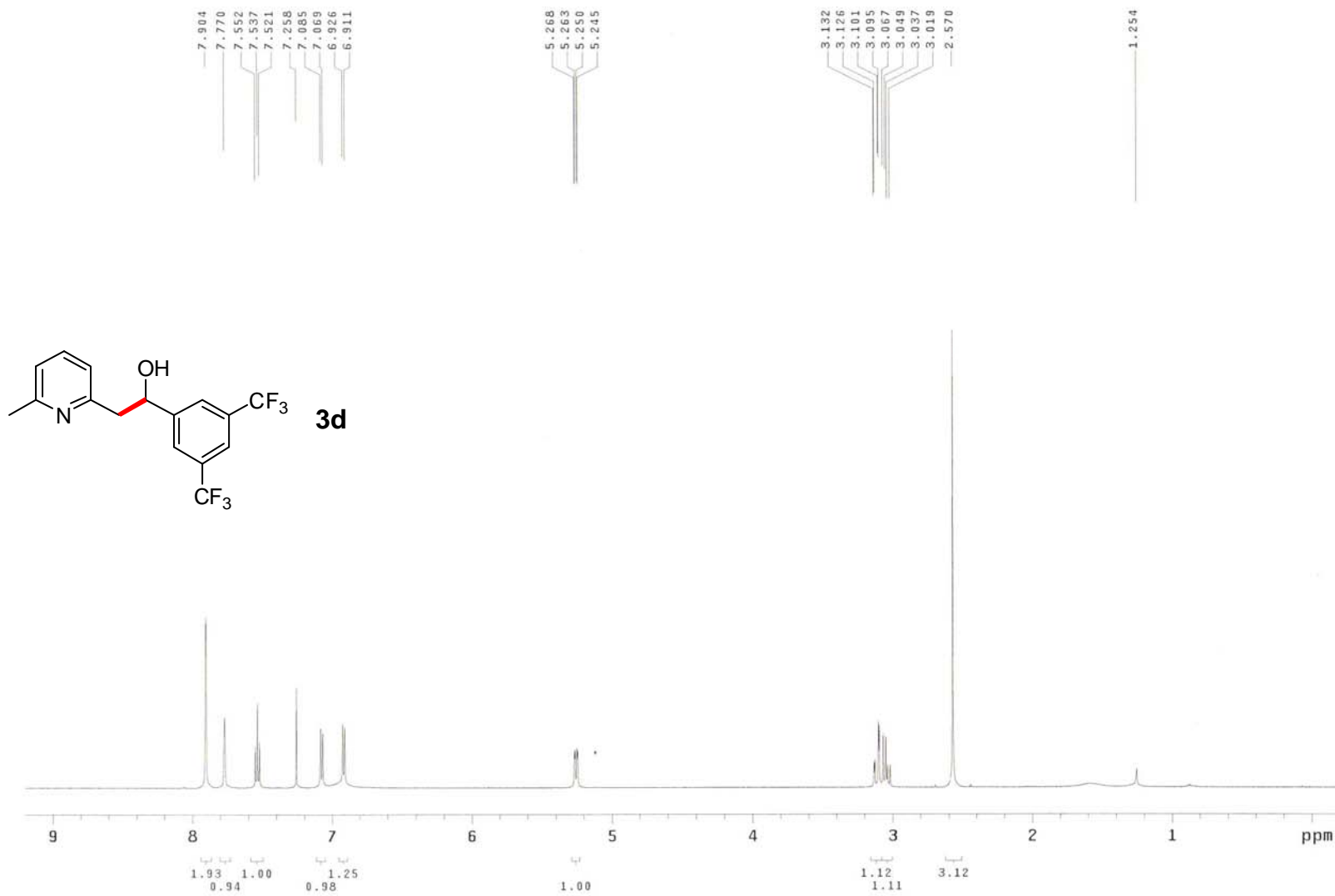


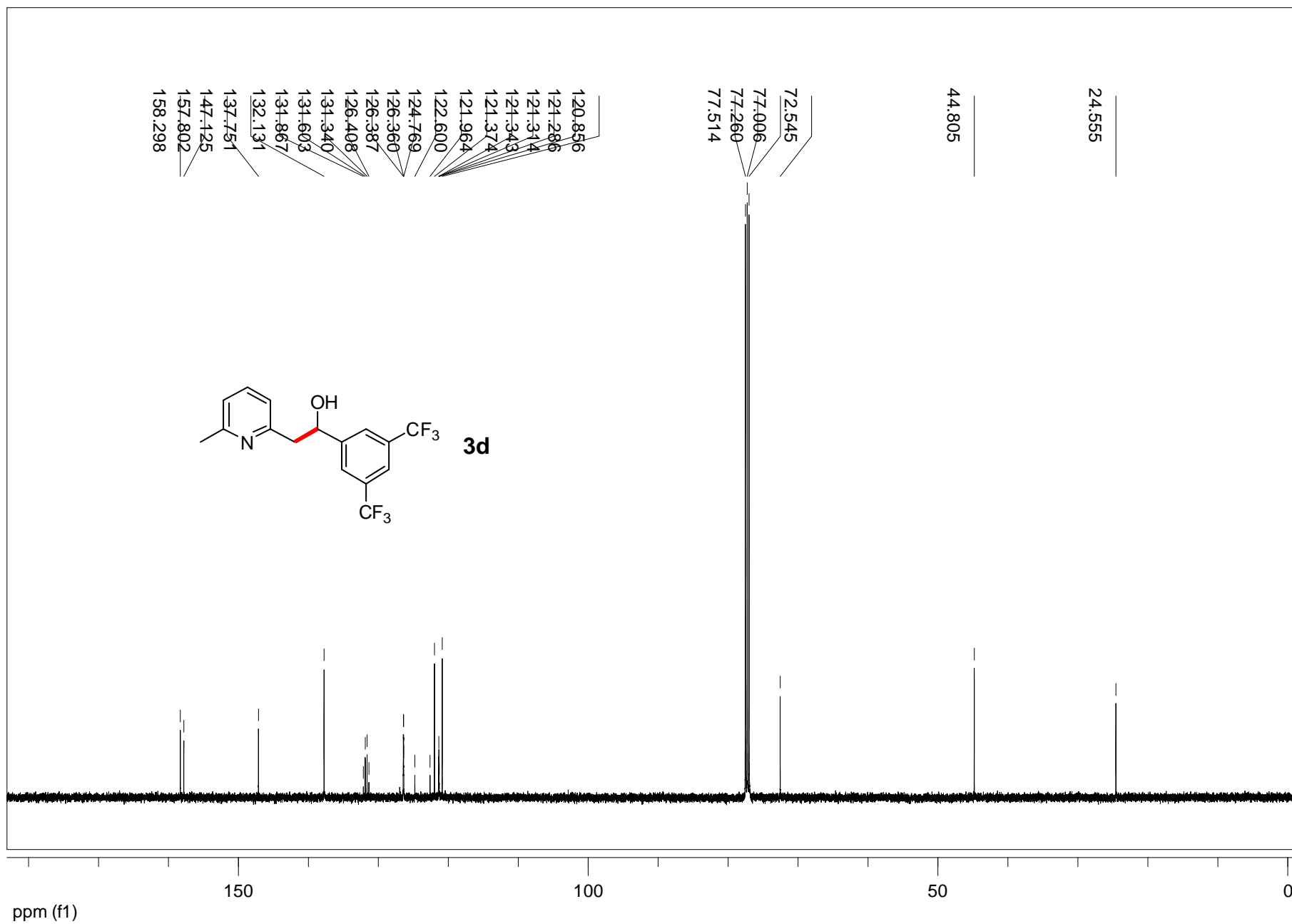
2033 3424



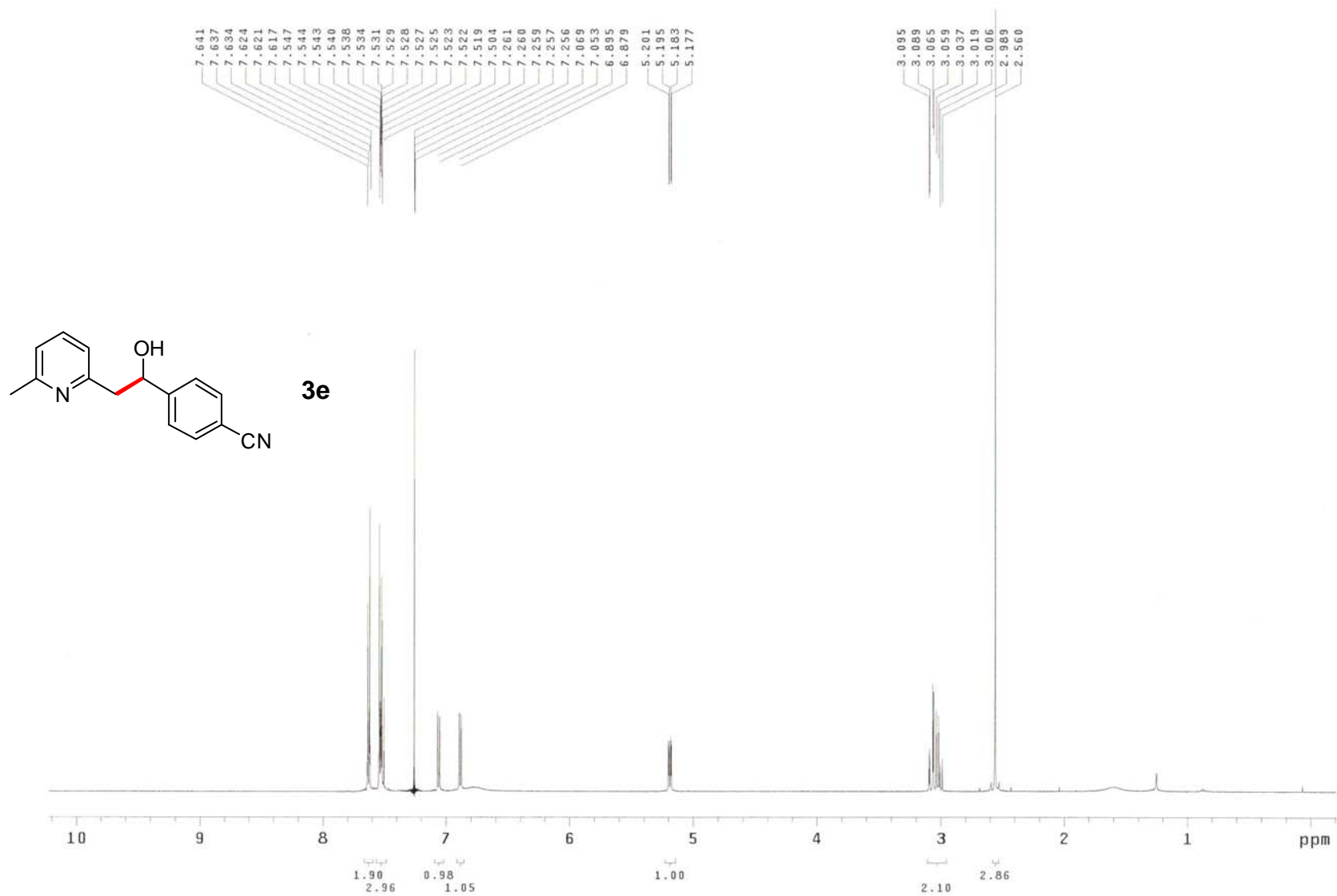


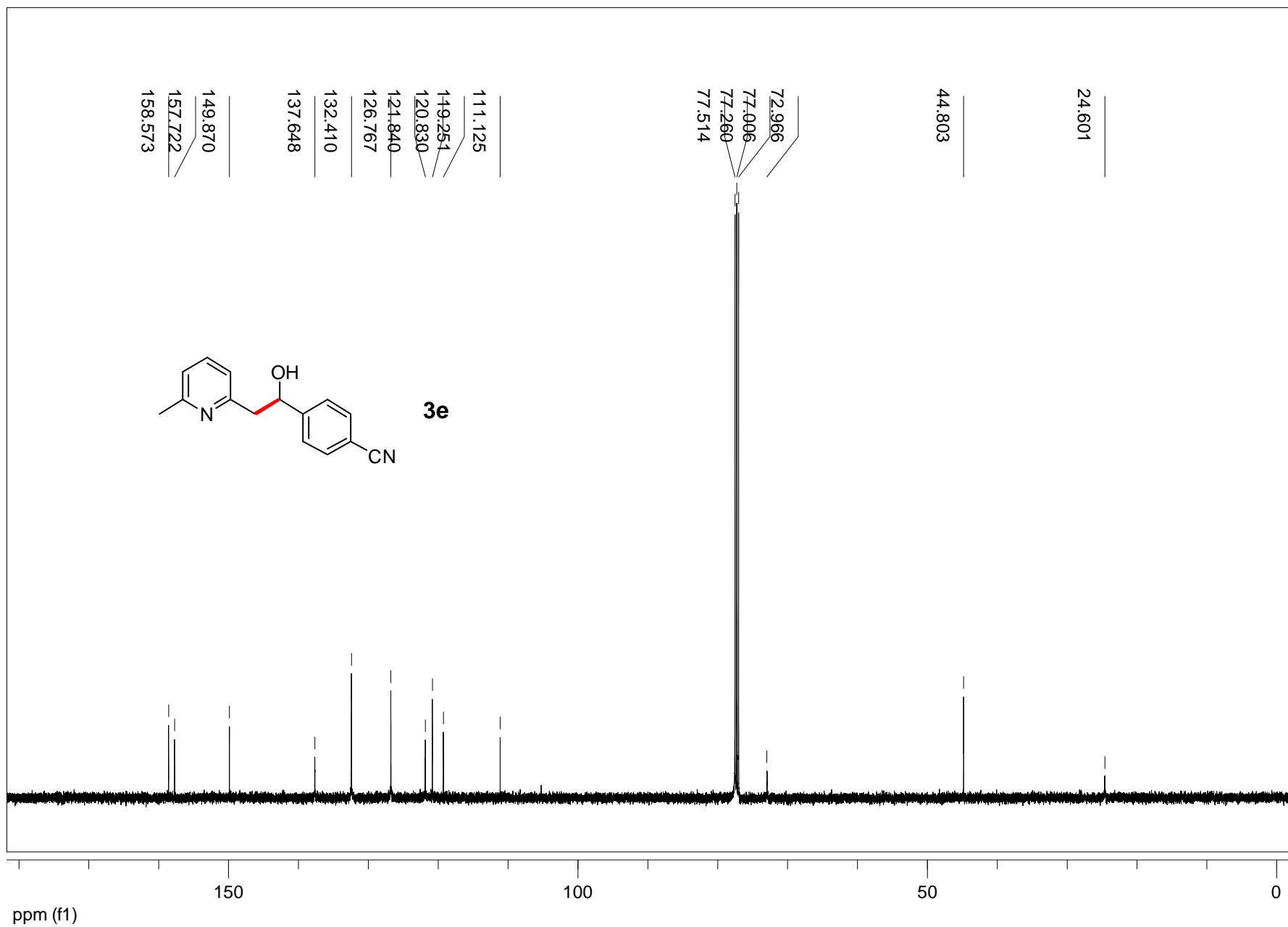
1569

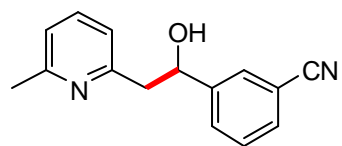




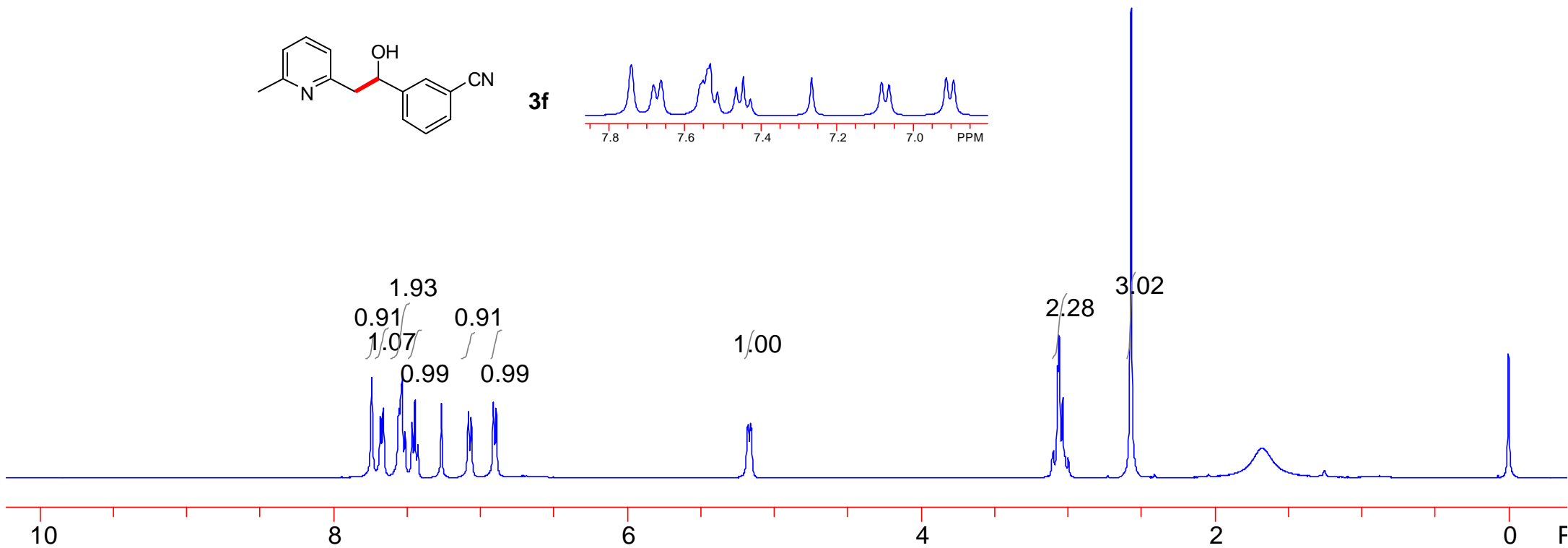
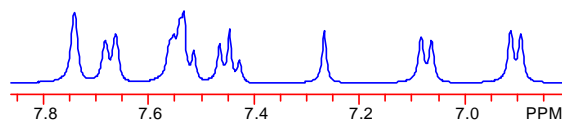
2058 500m

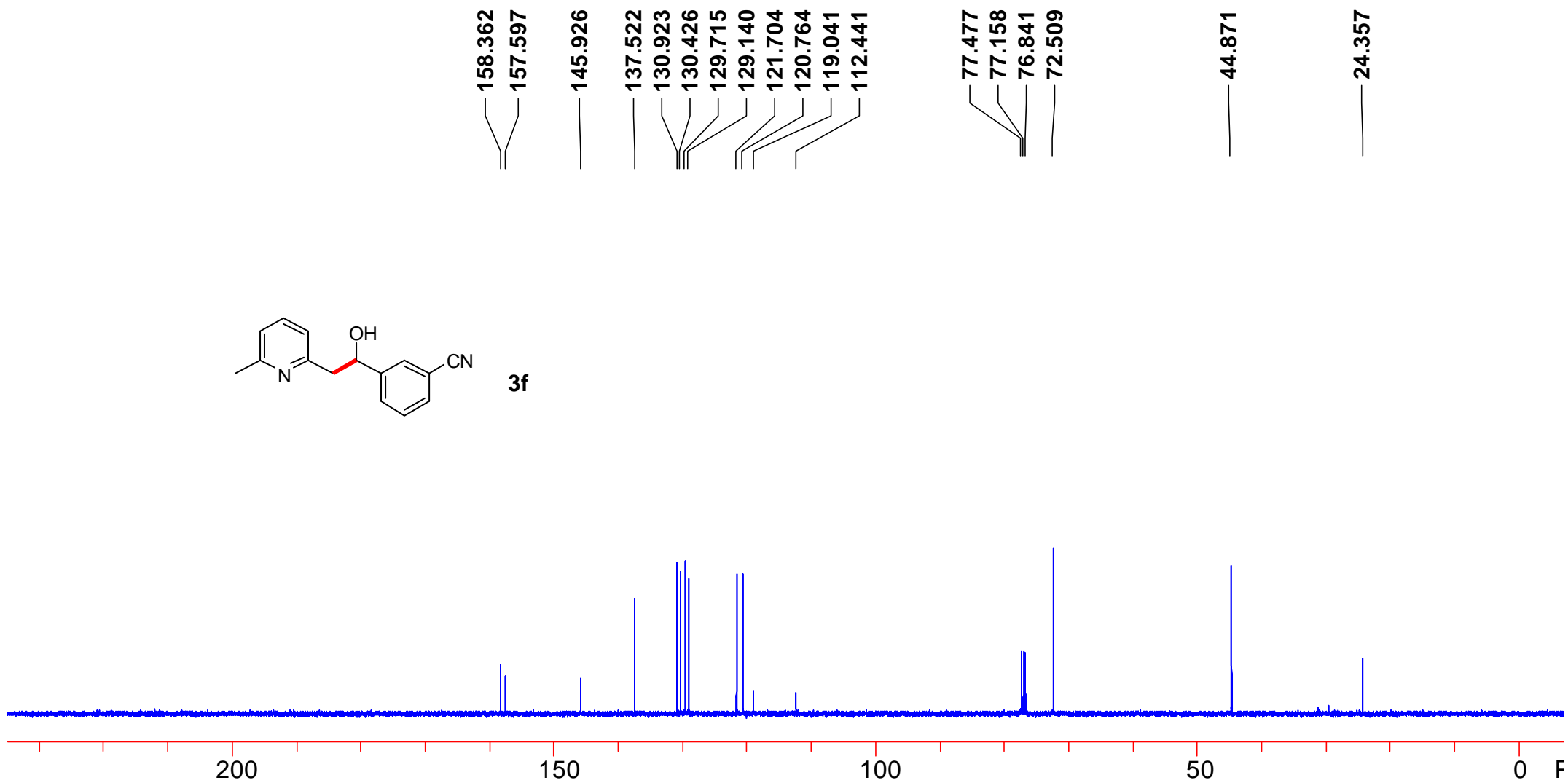
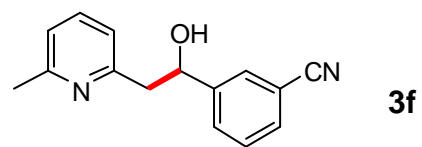




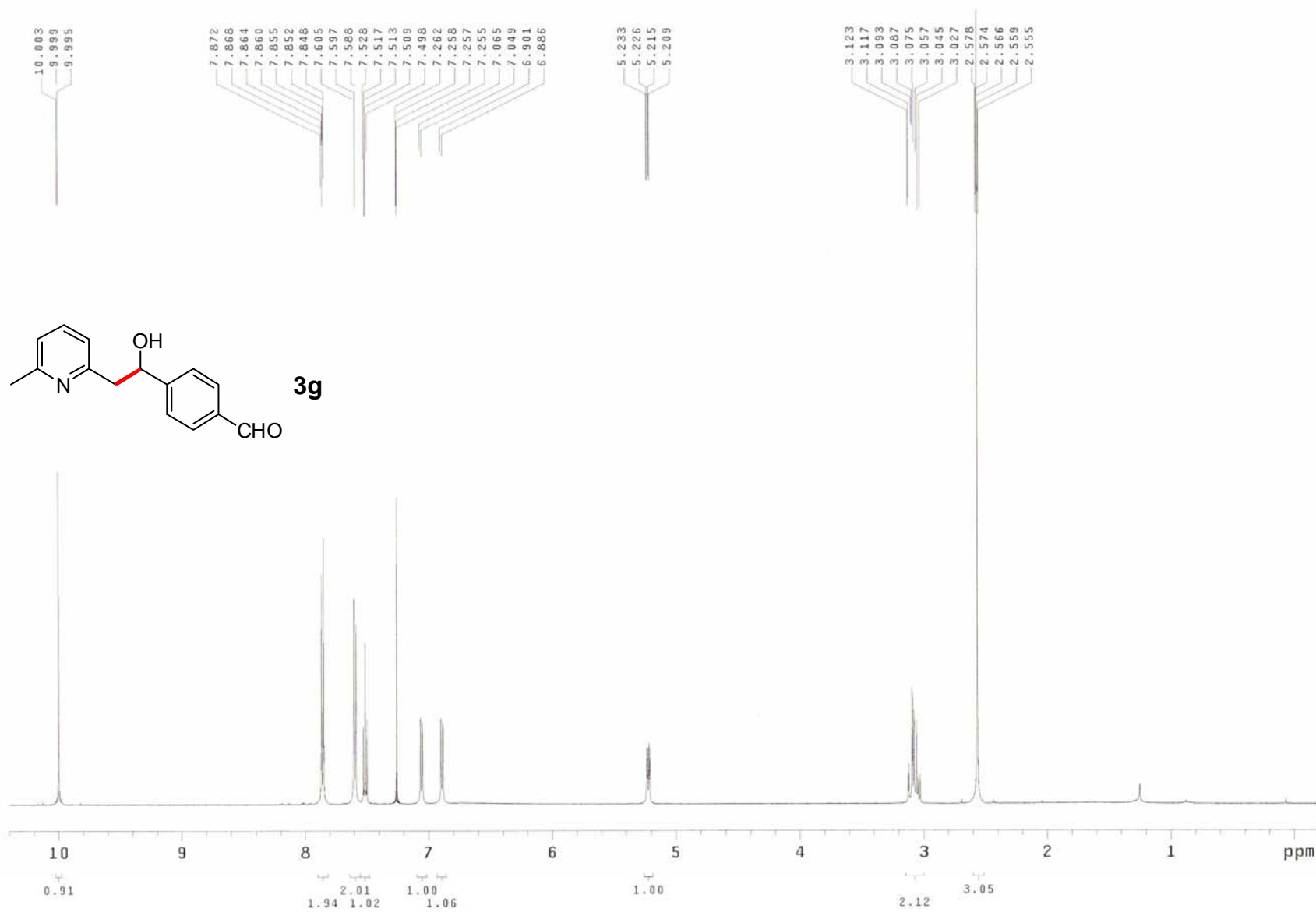


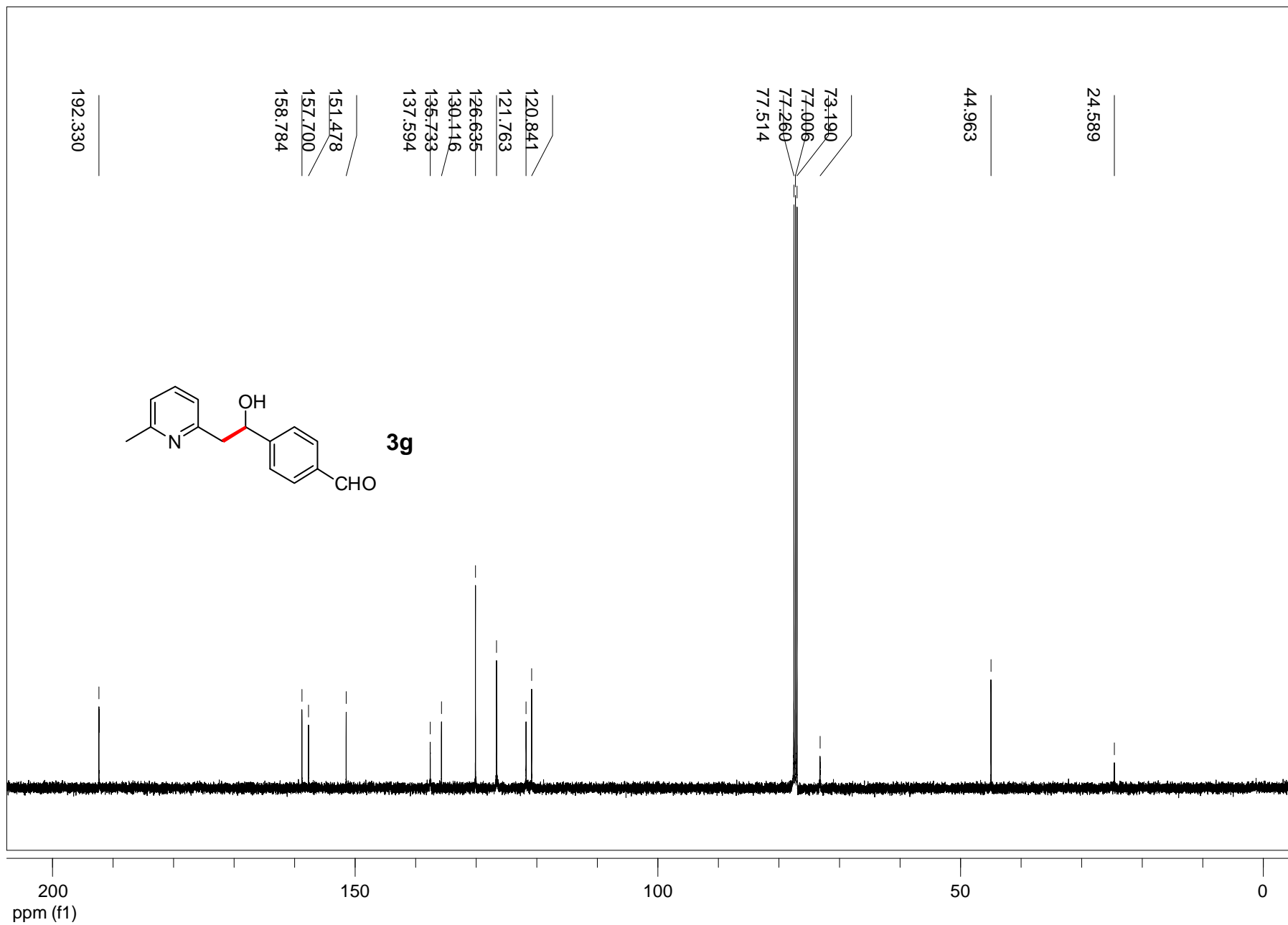
3f





2016 1000





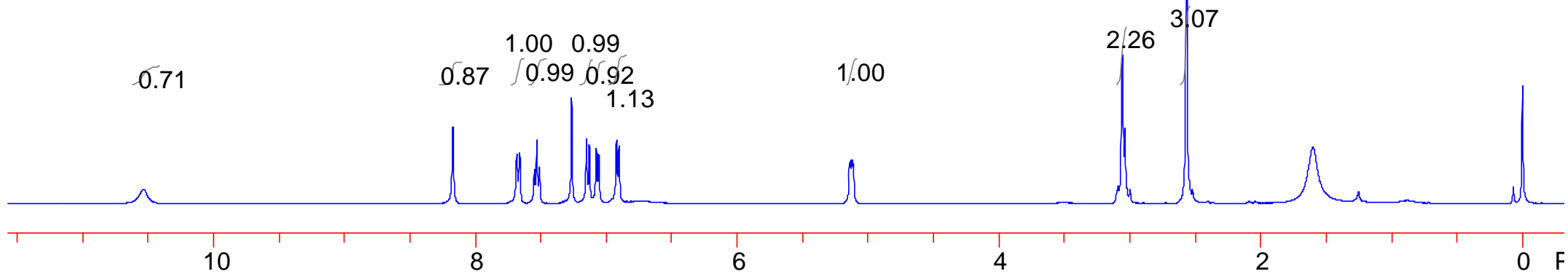
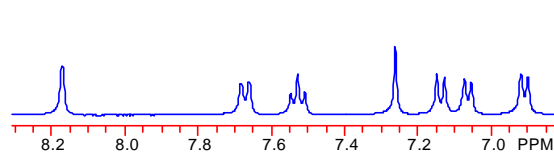
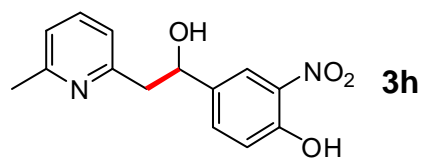
10.530

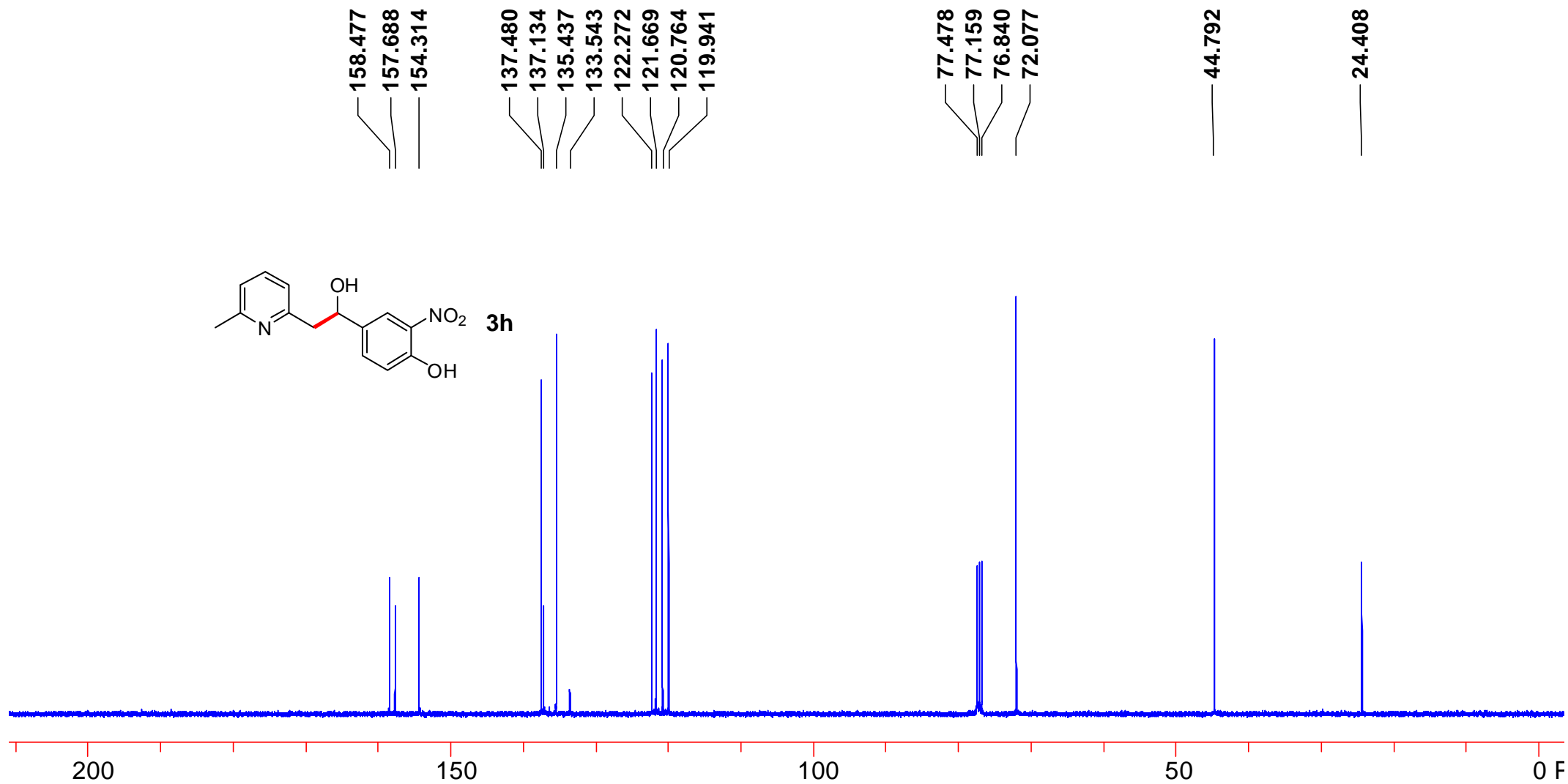
8.169
7.680
7.663
7.549
7.528
7.511
7.264
7.151
7.129
7.074
7.056
6.921
6.902
5.139
5.132
5.121
5.113

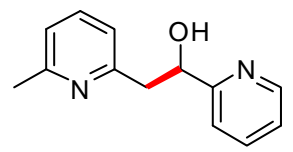
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3.055
3.037
3.037
2.999
2.567

1.601

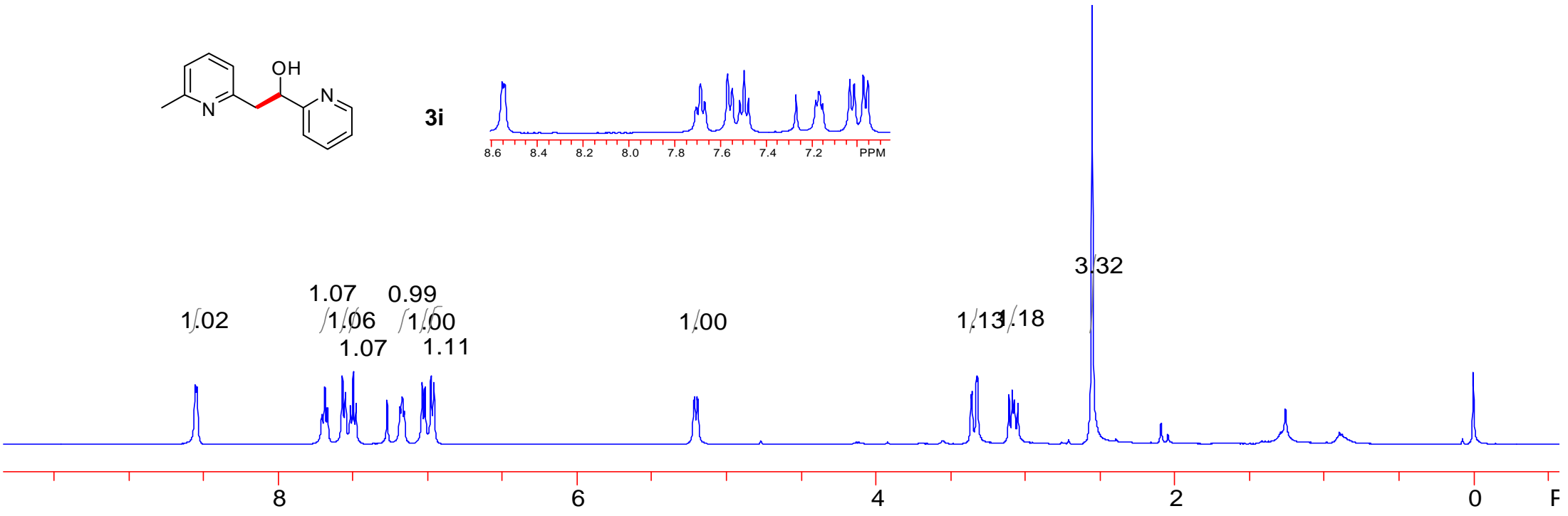
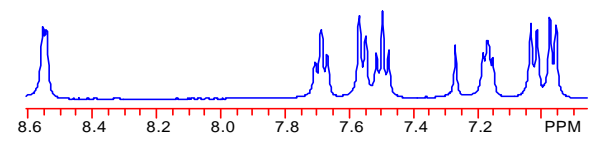
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0.000

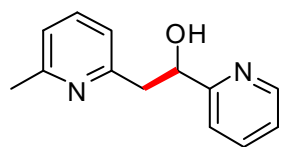






3i





3i

163.016

159.022

157.394

148.512

137.159

136.731

122.113

121.277

120.945

120.408

77.478

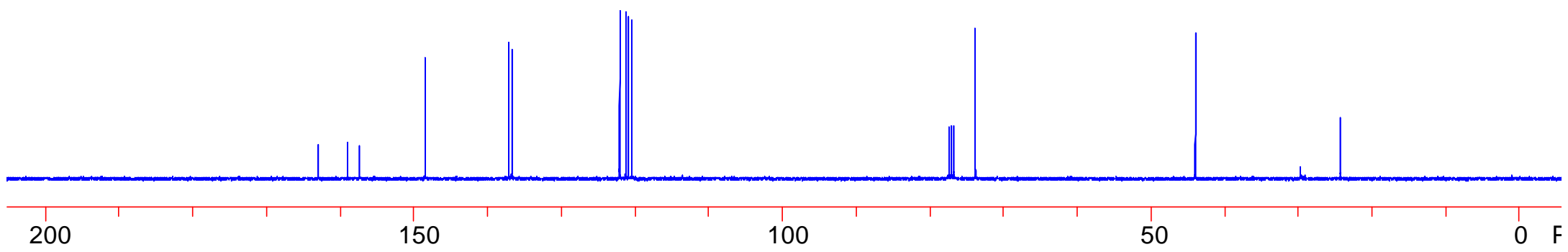
77.160

76.842

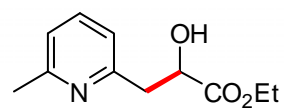
73.882

44.065

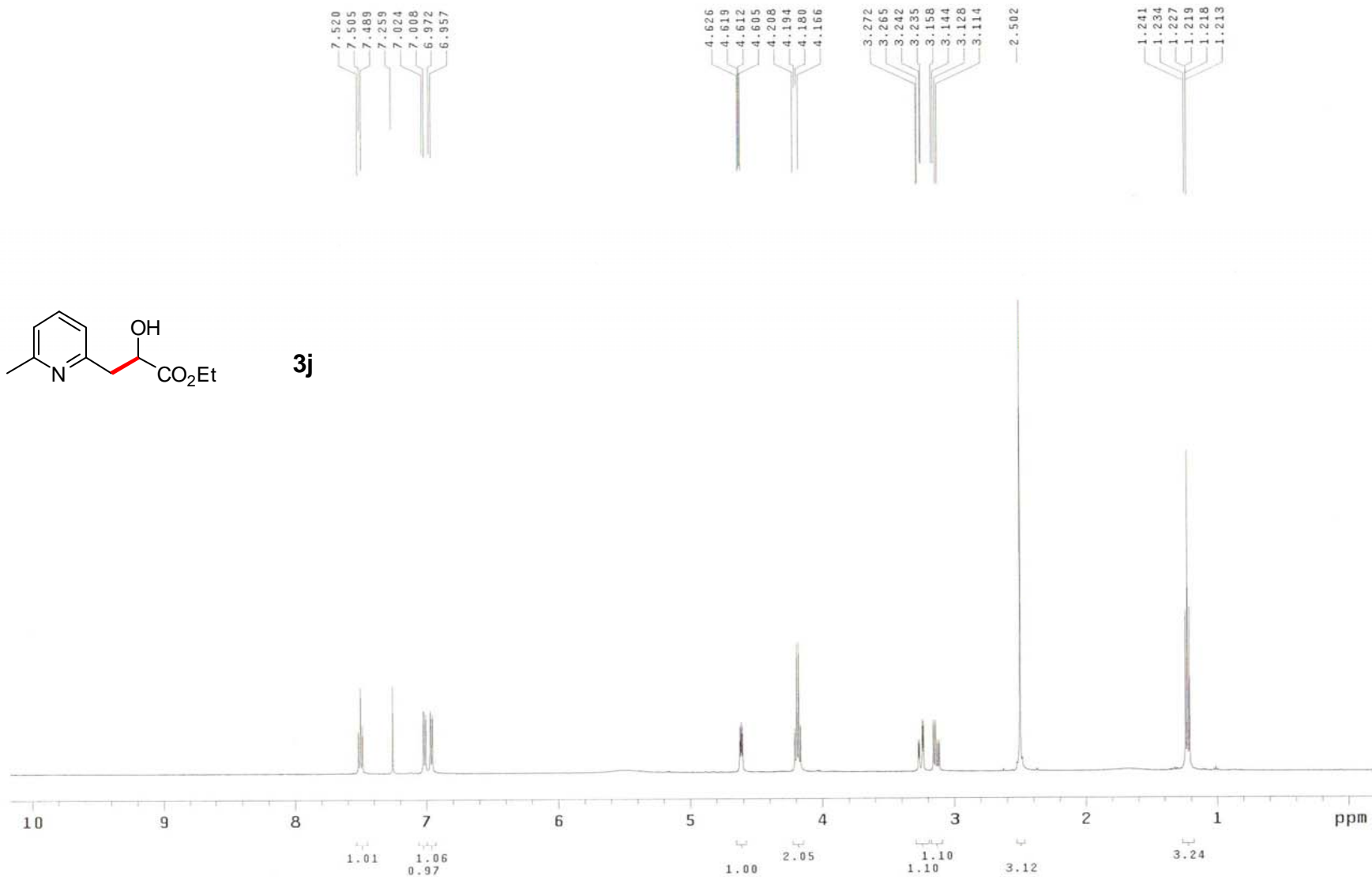
24.370

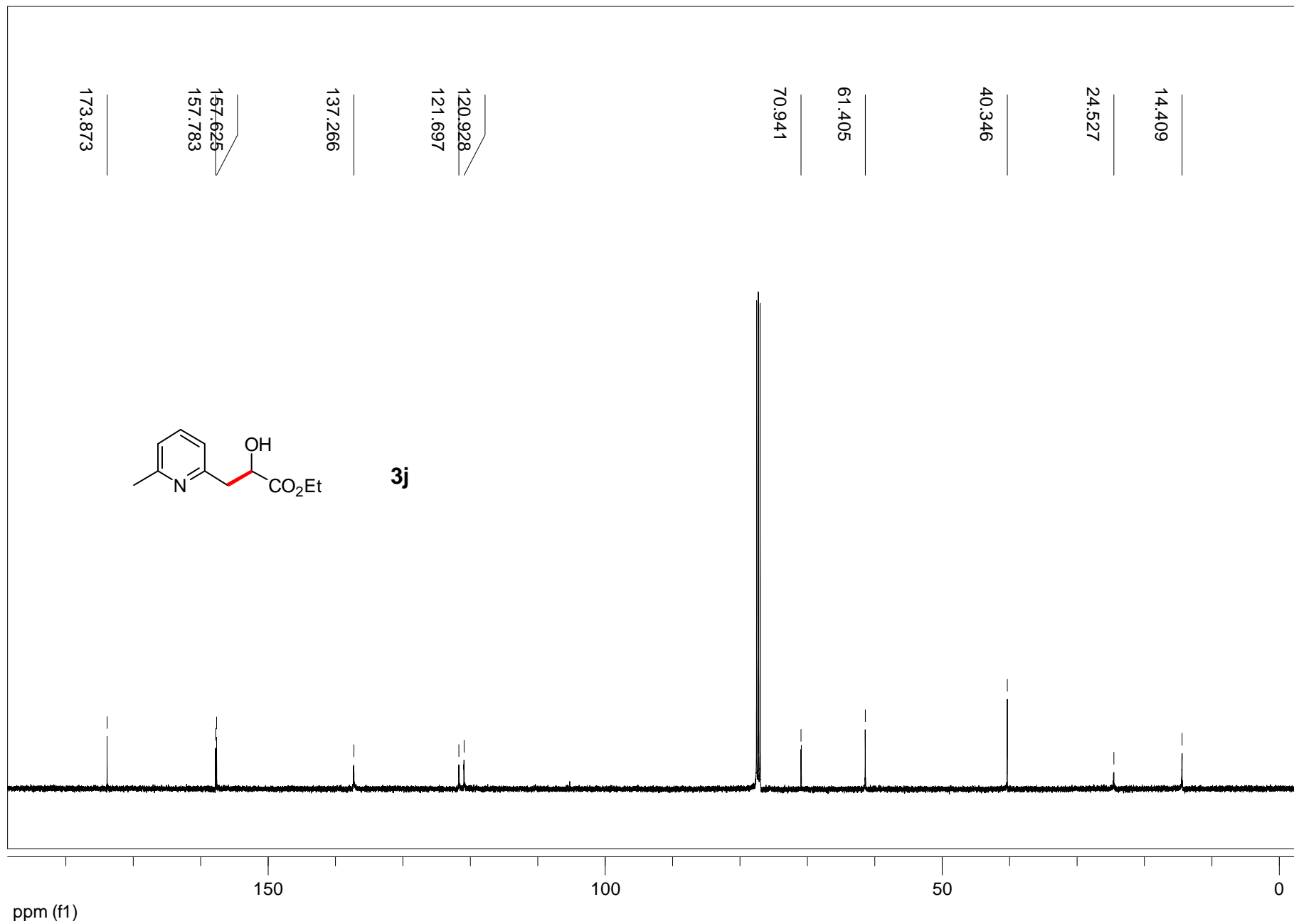


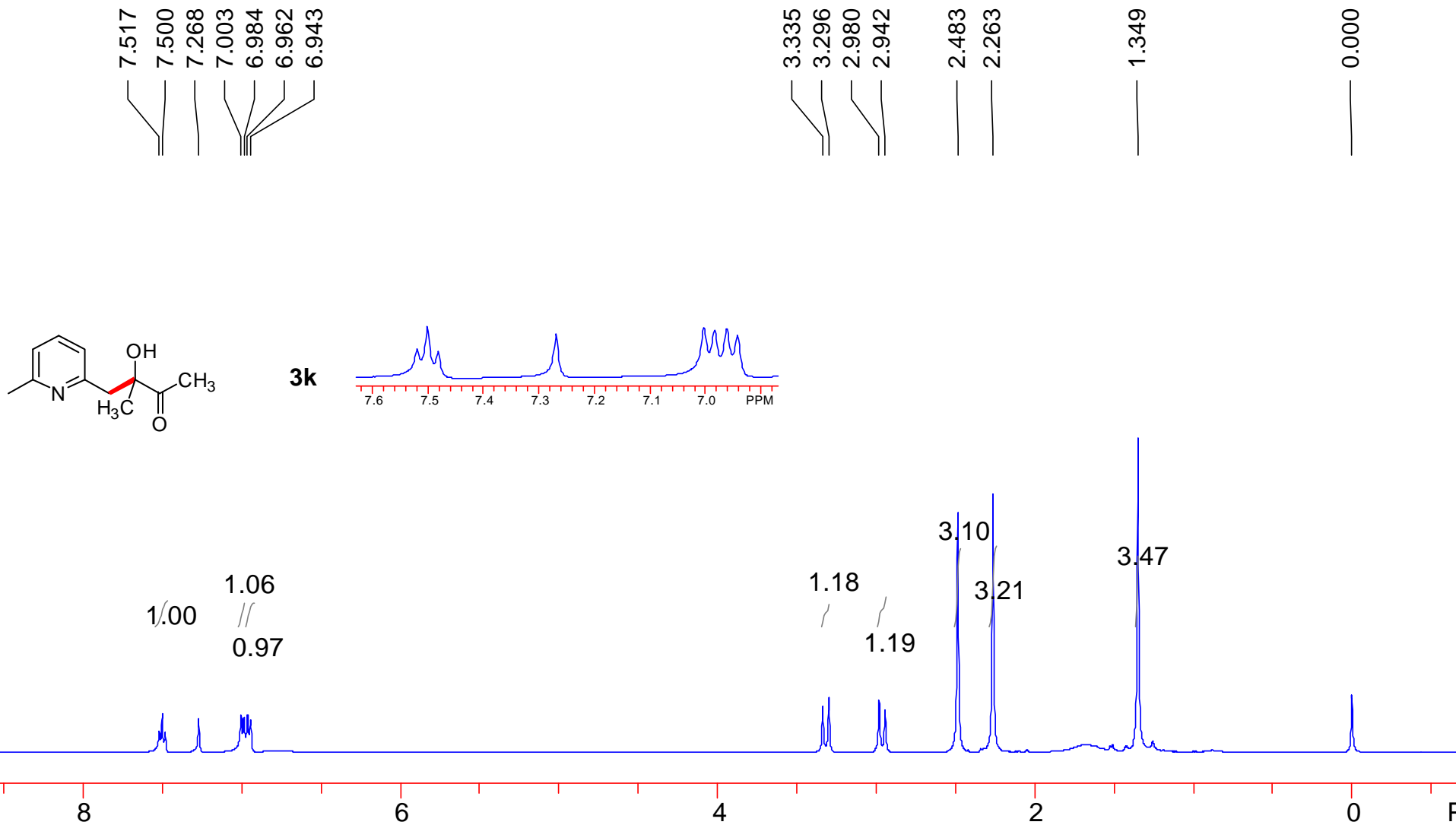
2056 130m



3j







215.059

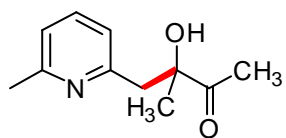
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137.400
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121.365

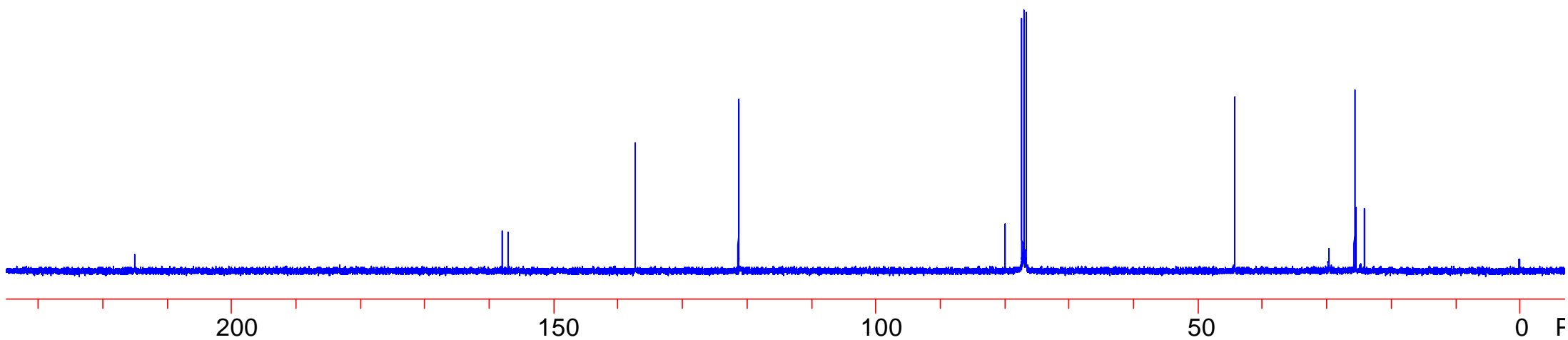
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77.478
77.364
77.349
77.160
77.093
77.075
76.841

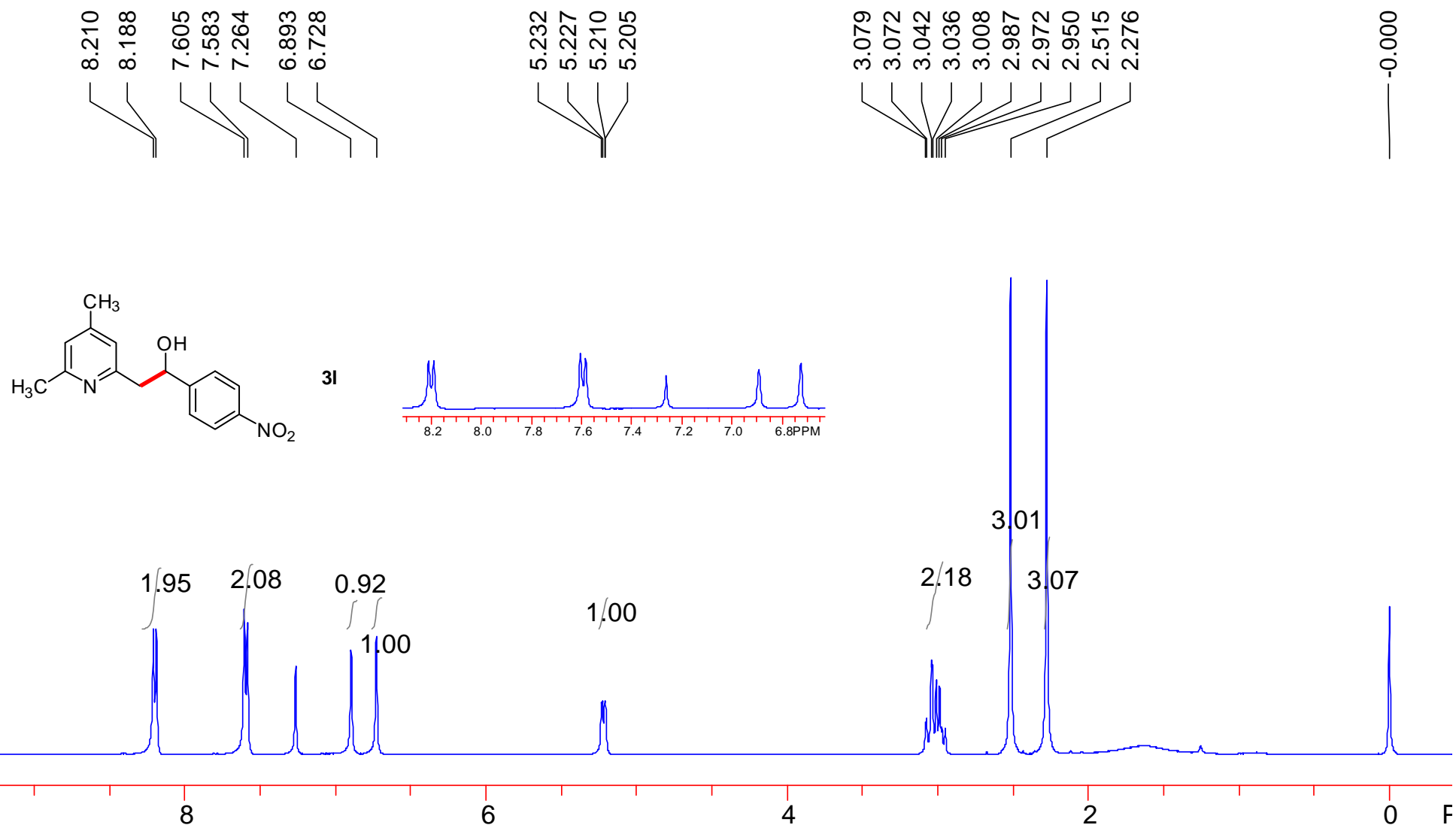
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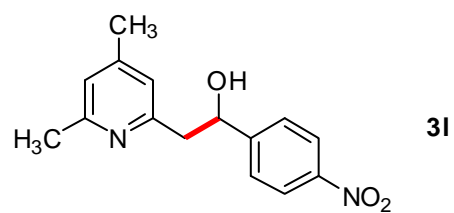
25.811
25.530
24.236



3k







158.082
157.263
152.004
148.773
147.242

126.711
123.600
122.651
121.713

77.478
77.158
76.842
72.708

44.549

24.150
20.965

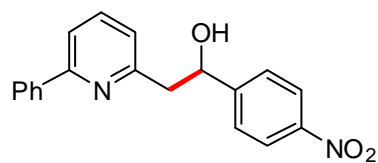
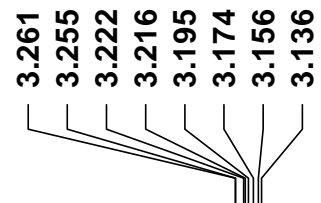
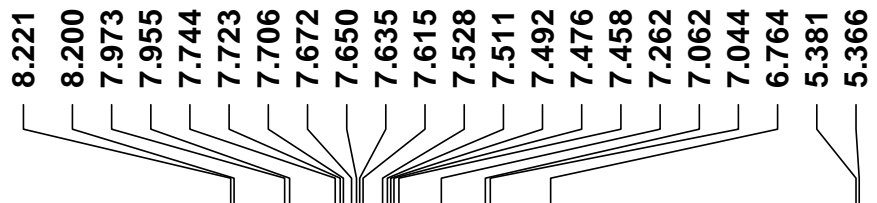
200

150

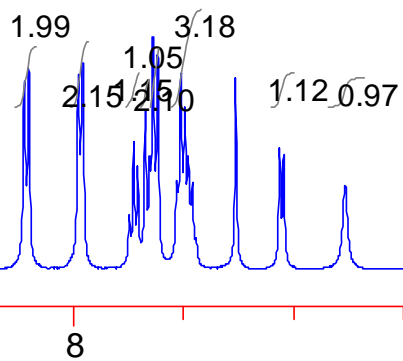
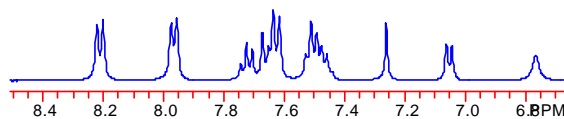
100

50

0 F



3m



1.00

2.15

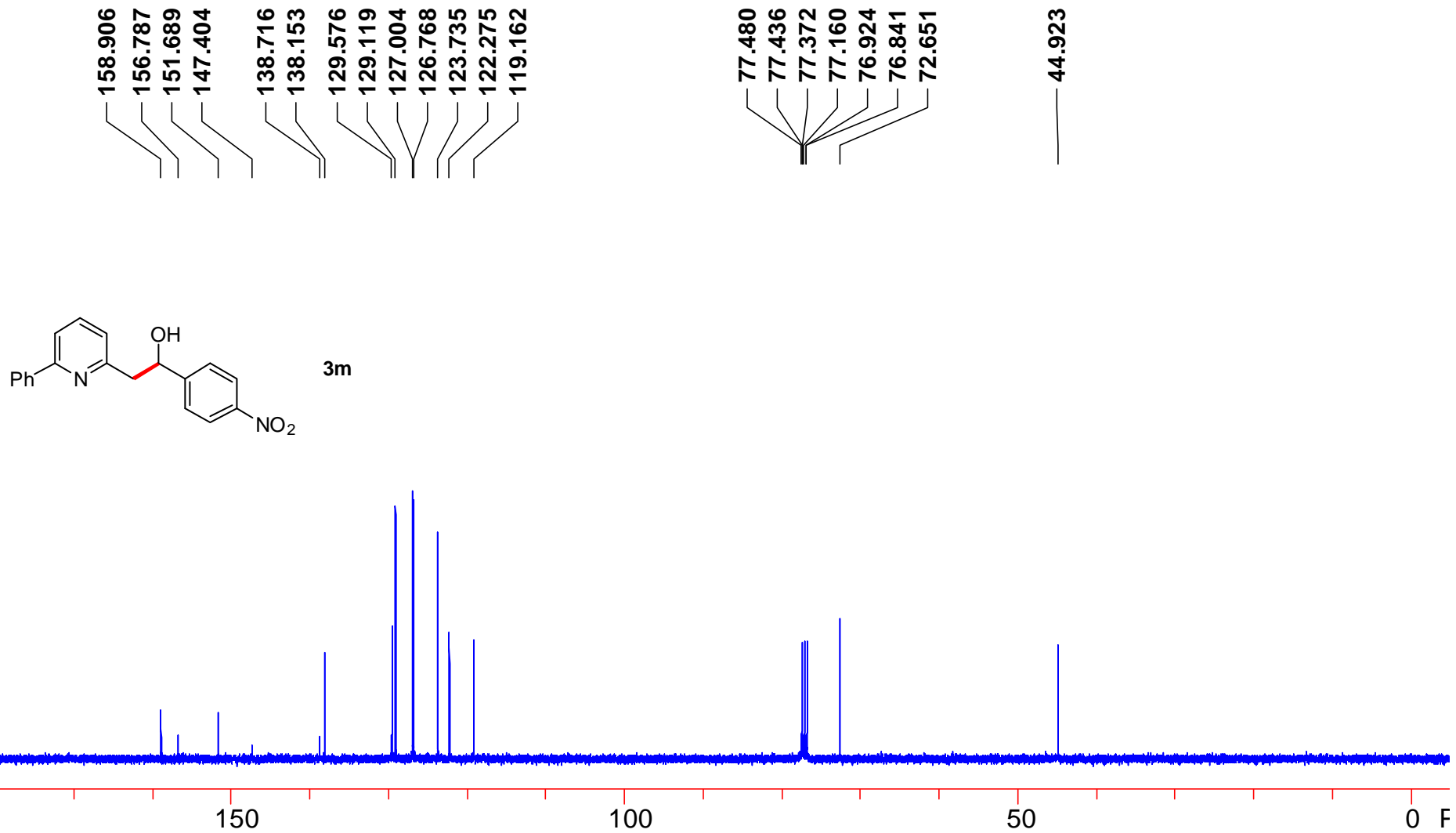
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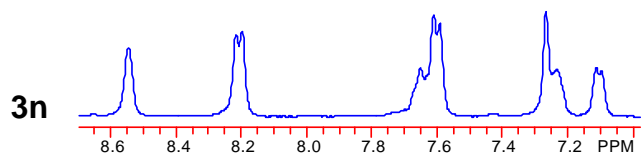
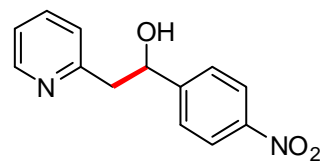
6

4

2

0 F





8.544

8.215

8.195

7.651

7.610

7.592

7.265

7.233

7.113

7.097

6.424

5.301

5.282

3.188

3.152

3.128

3.107

3.069

1.611

-0.000

1.14

2.07

2.14

1.08

0.91

1.09

0.80

1.00

2.21

8

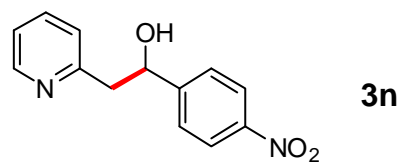
6

4

2

0

F



159.026

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77.160

76.841

72.616

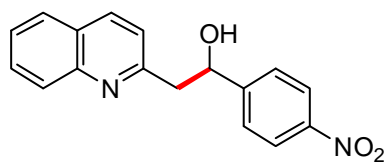
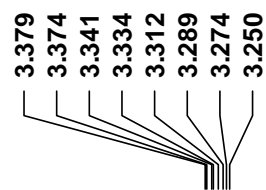
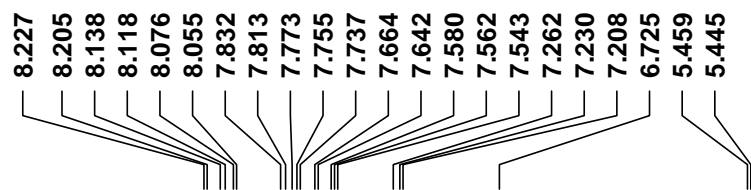
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150

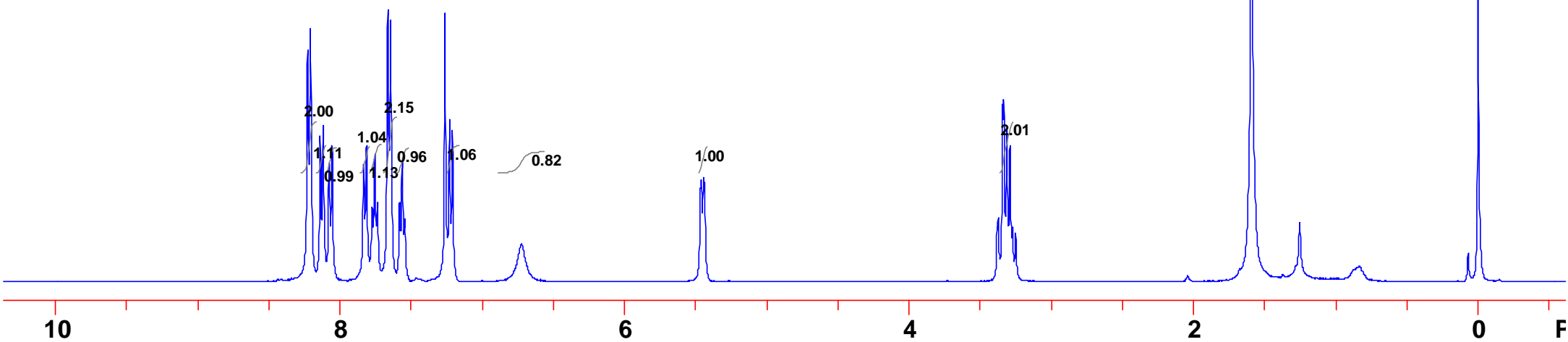
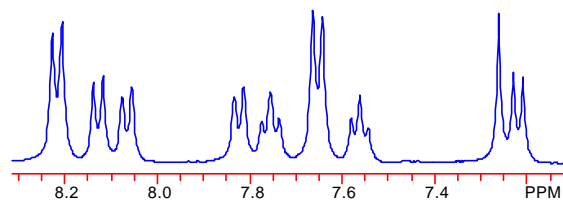
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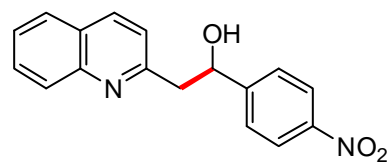
50

0F

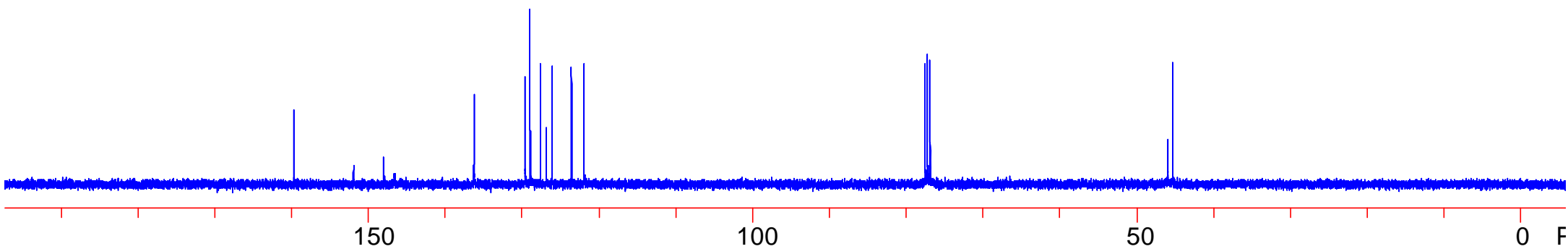
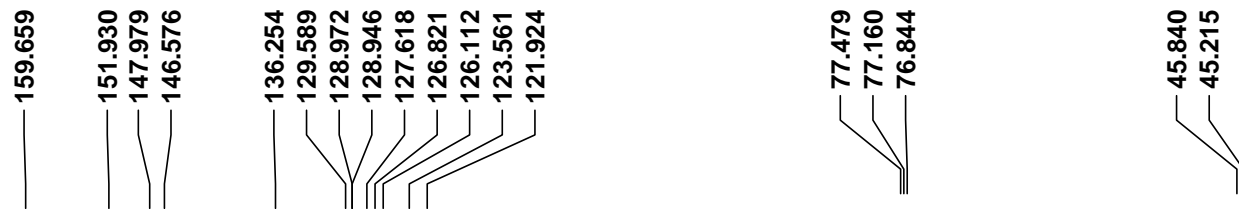


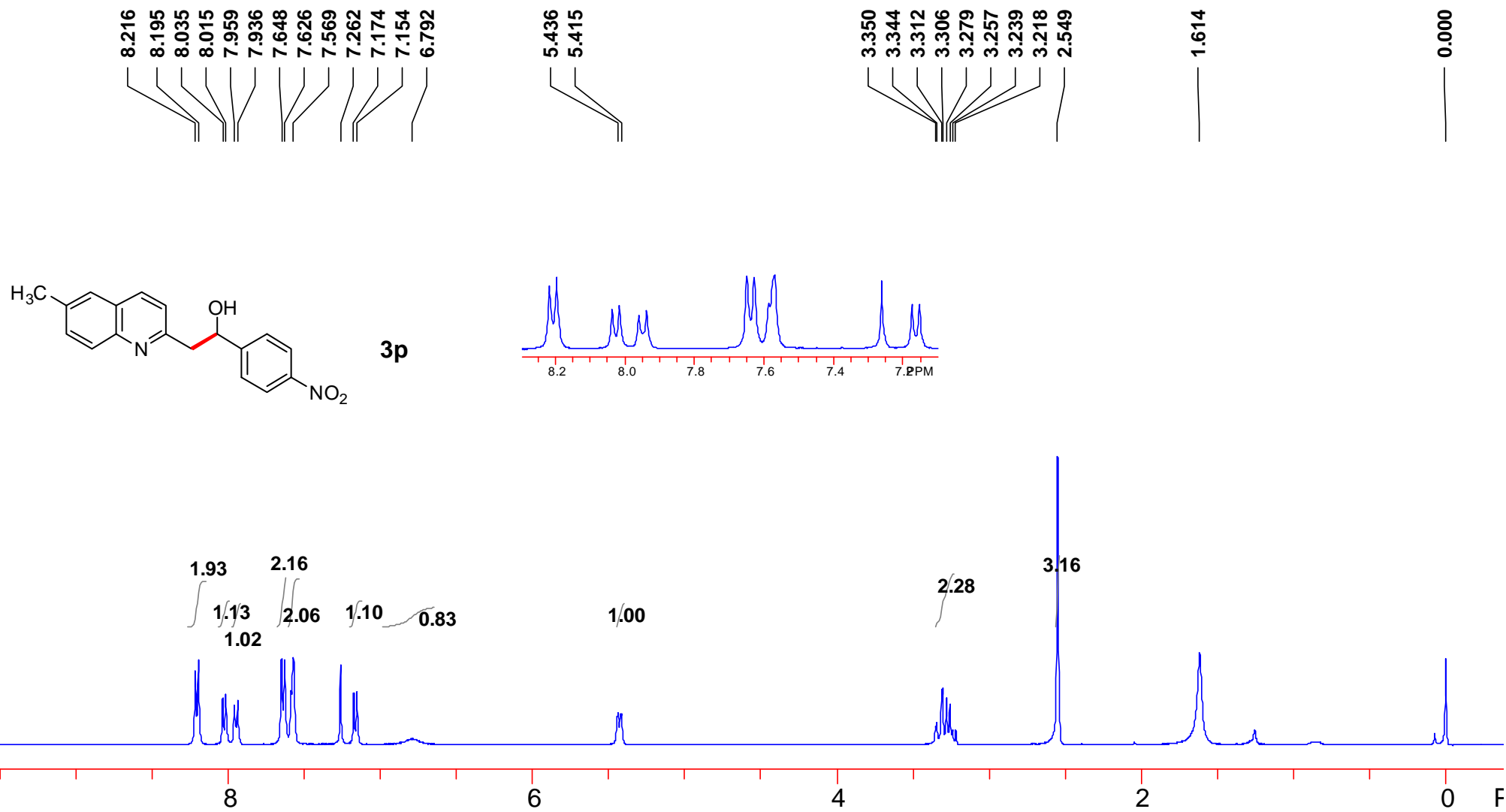
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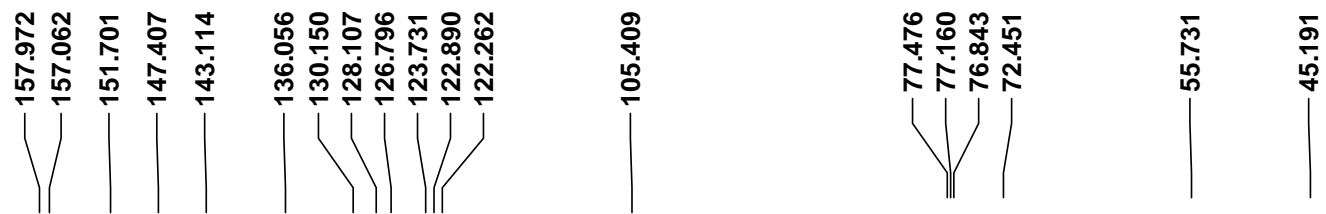
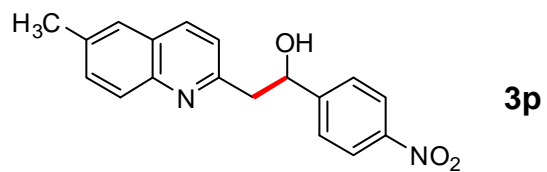


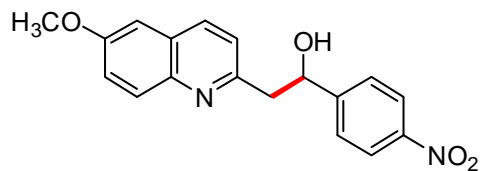


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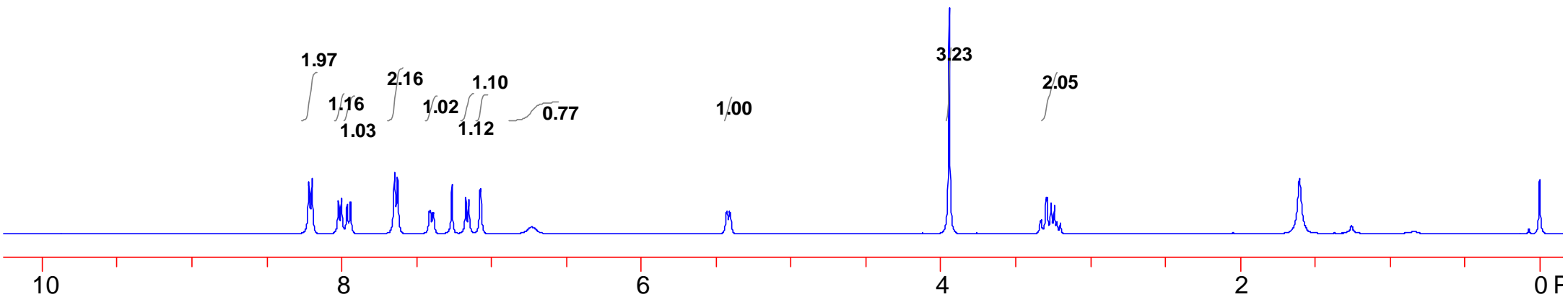
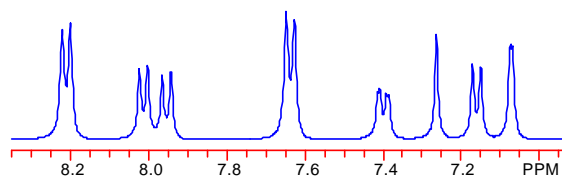








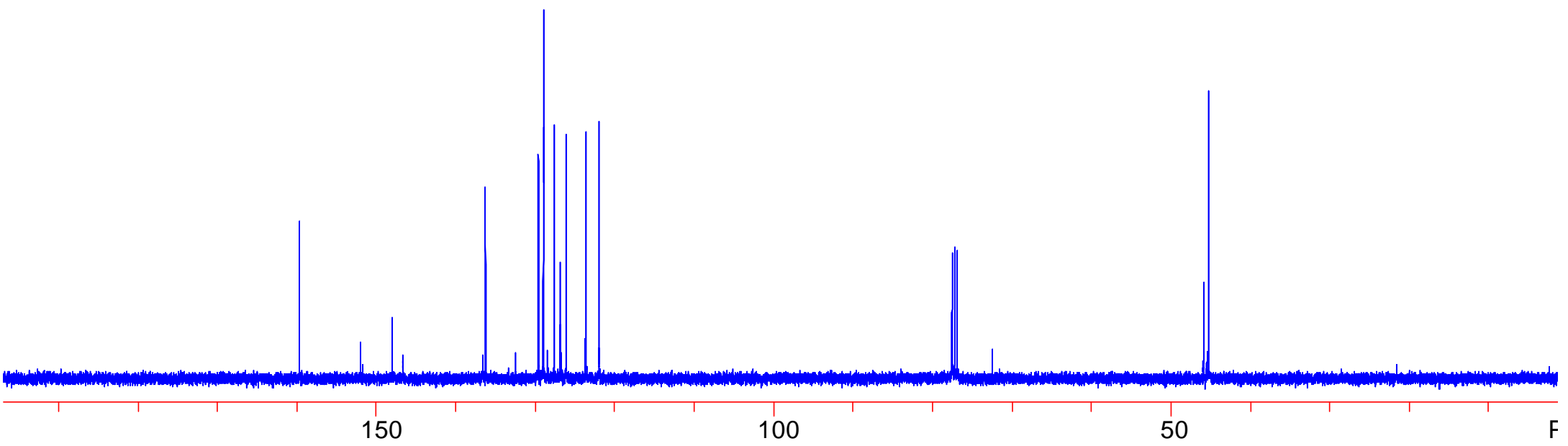
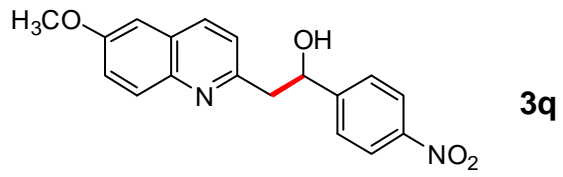
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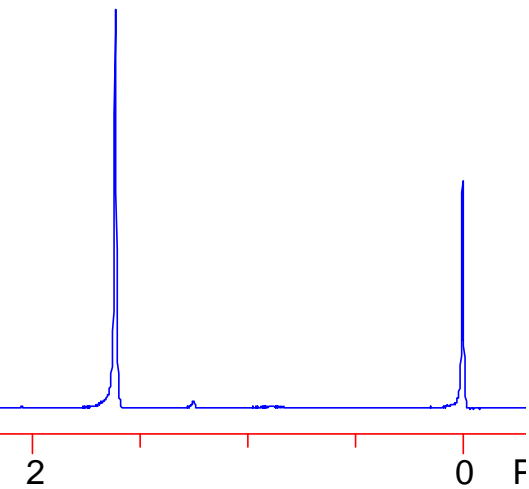
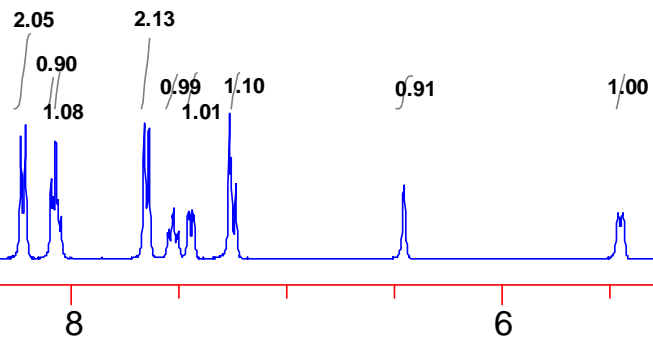
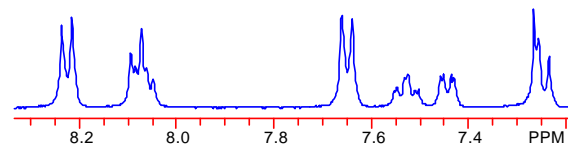
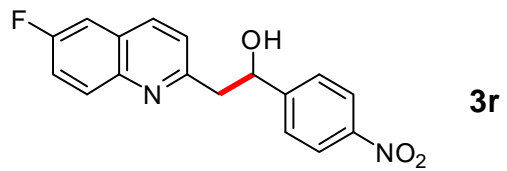
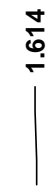
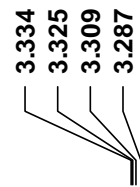
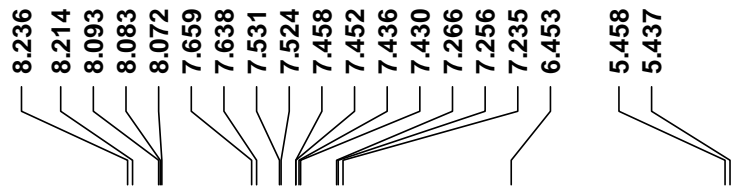


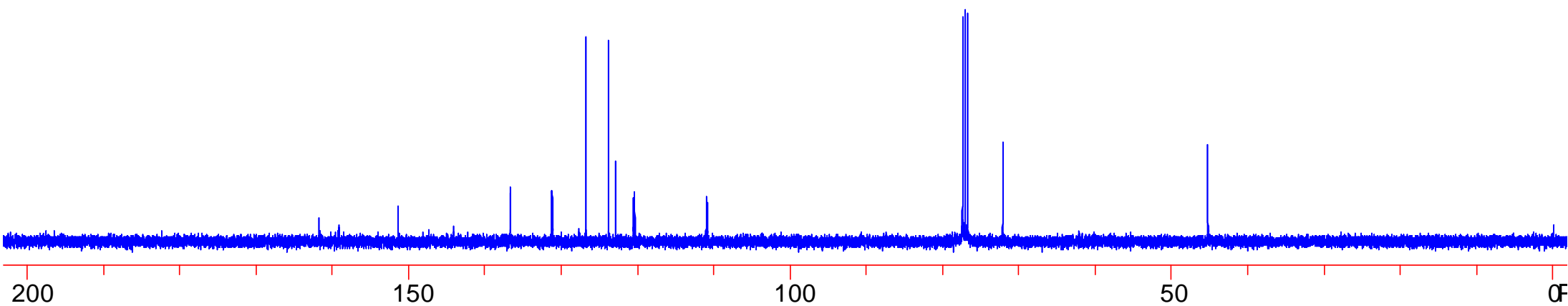
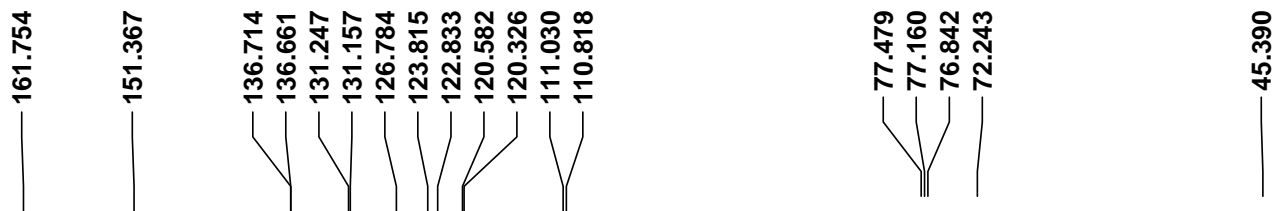
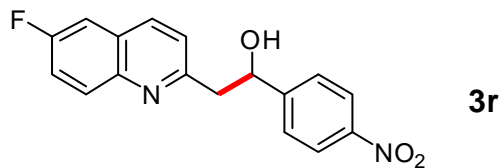
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123.538
121.925

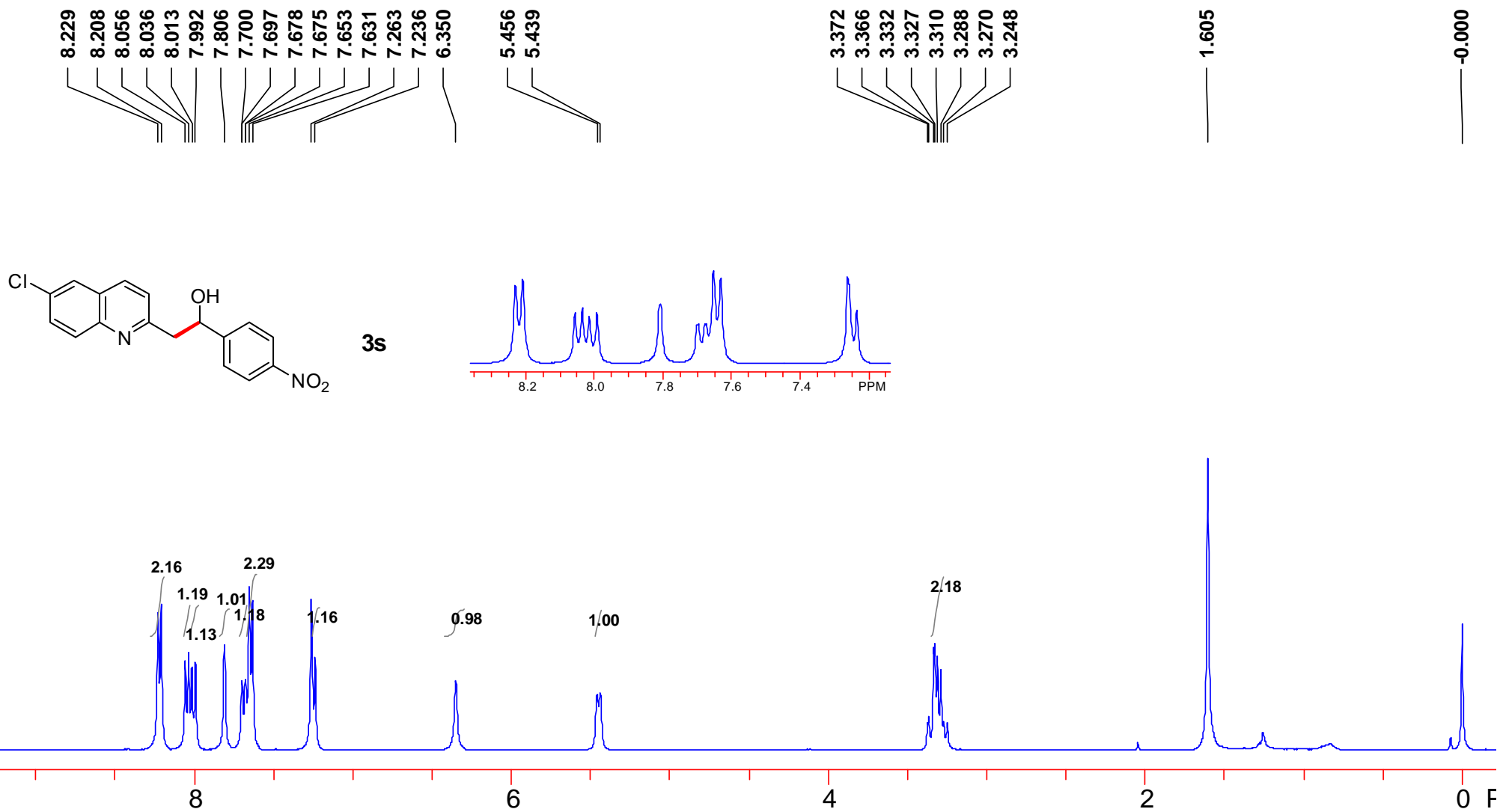
77.481
77.160
76.845
72.350

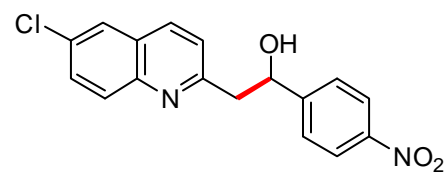
45.789
45.179









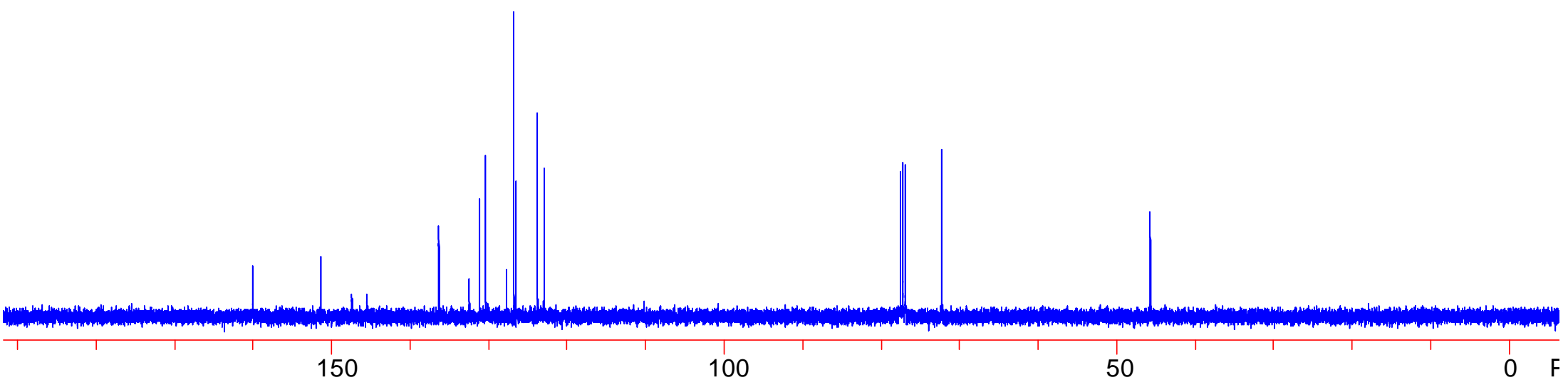


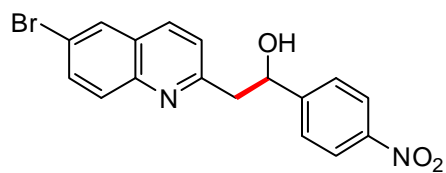
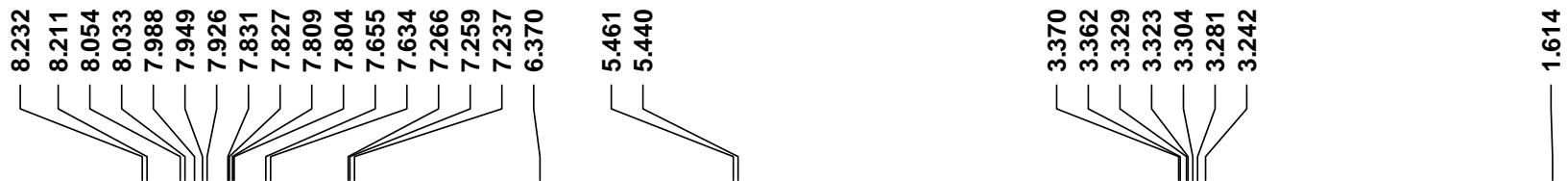
3s

160.076
151.317
147.403
145.484
136.328
132.440
131.132
130.357
127.661
126.768
126.500
123.776
122.966

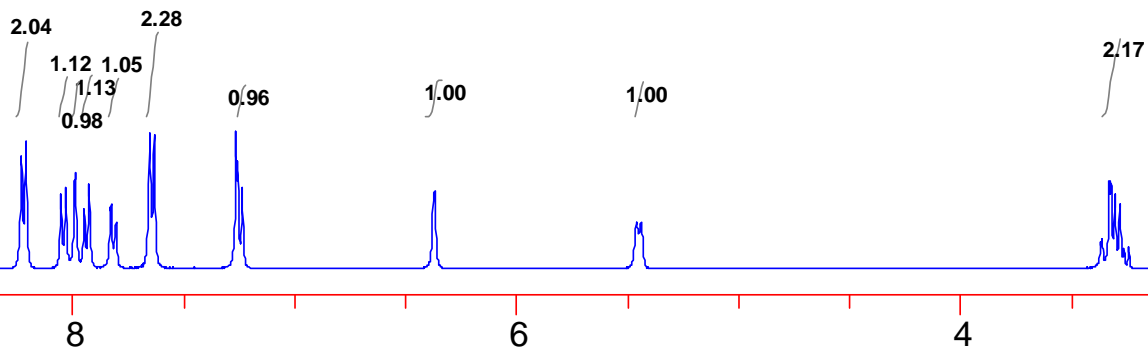
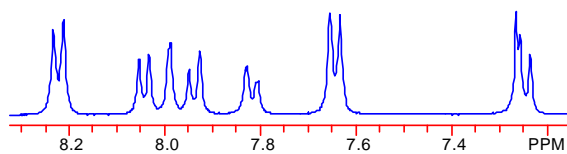
77.479
77.160
76.846
72.166

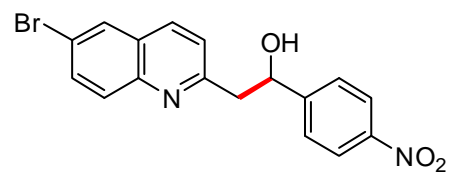
45.584





3t





160.236
151.280
147.354
145.642
136.277
133.695
130.456
129.870
128.164
126.767
123.810
122.942
120.501

77.478
77.160
76.843
72.136

45.554

