Thiourea as an efficient organocatalyst for the transfer hydrogenation of 2-substituted quinoline derivatives

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Supplementary Information

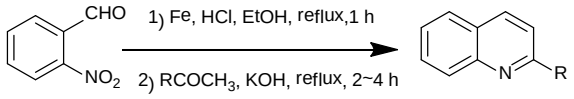
Content

General Information

Materials. Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. Solvents for chromatography were of technical grade and were distilled prior to use. Solvents used in the reactions were reagent grade. For thin-layer chromatography (TLC), silica gel plates coated glass plates (Haiyang) were used and chromatograms were visualized by irradiation with UV light. Column chromatography was performed using silica gel (200-300 mesh) from Macherey-Nagel. Solvent mixtures are understood as volume/volume.

Instrumentation. All NMR experiments were performed on a Bruker Avance 400 MHz or 500 MHz NMR spectrometer equipped with a 5 mm BBO probe at 295 K. The data were collected and processed by TOPSPIN software (Bruker) running on a PC with Microsoft Windows 7. Proton and ^{13}C chemical shifts were referred to the solvent signal ($CDCl_3$) at 7.26 and 77 ppm, respectively. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, cm = complex multiplet) and coupling constant in Hertz (Hz). Infrared (IR) spectra were reported in terms of frequency of absorbtion (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak). GC analyses were carried out with a SHIMADZU GC-2010 Plus gas chromatograph equipped with a Agilent J&W scientific fused silica GC column (30 m × 0.250 mm, 0.25 micron HP-5 stationary phase: (5%-Phenyl)-methylpolysiloxane) using nitrogen as carrier gas; T-program standard 60-250 °C (15 °C/min heating rate), injector and transfer line 250 °C.

General Procedure for Synthesis of 2-substituted quinoline derivatives



$R^{1\text{-}11}$: Table 2, Entry 1-11

2-substituted quinoline derivatives were prepared according to known protocols[1] and their NMR data were in agreement with those in the literature.

General Procedure for 2-substituted tetrahydroquinoline derivatives

An oven-dried flask was fitted with magnetic stirring bar and charged with 2-substituted quinoline (0.20 mmol), thiourea **T1** (3 mol%), Hantzsch dihydropyridine (3.0 equiv.) and toluene (1 mL). The resulting mixture was stirred at 60°C for 18-48 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane/EtOAc (20:1) as eluent to yield the corresponding 1,2,3,4-tetrahydroquinolines. All the products are known products and their NMR data are identical to those in the literature[2]. Their NMR and IR data are given below.

Physical data

2-Phenyl-1,2,3,4-tetrahydroquinoline(Table 2, entry 1)

A colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.45-7.28 (m, 5 H), 7.08-6.98 (m, 2 H), 6.67 (t, J = 7.3 Hz, 1 H,), 6.56 (d, J = 7.8 Hz, 1 H), 4.45 (dd, J = 3.2, 9.3 Hz, 1 H), 4.06 (br s, 1 H), 2.94 (ddd, J = 16.1, 10.7, 5.4 Hz, 1 H), 2.76 (dt, J = 16.4, 4.7 Hz, 1 H), 2.19-2.09 (m, 1 H), 2.08-1.96 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 144.8, 144.7, 129.3, 128.6, 127.4, 126.9, 126.5, 120.9, 117.2, 114.0, 56.3, 31.0, 26.4; **IR** (KBr): 3350, 2945, 2920, 1474, 1303, 1249, 760, 701 cm^{-1}.

2-(4-Methylphenyl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 2)

A colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.36-7.29 (m, 2 H), 7.24-7.16 (m, 2 H),7.09-6.99 (m, 2 H), 6.69 (t, J=7.4 Hz, 1 H), 6.56 (d, J = 7.7 Hz, 1 H), 4.43 (dd, J = 9.5, 3.2 Hz, 1 H), 4.03 (br s, 1 H), 2.97 (ddd, J = 16.4, 10.9, 5.5 Hz, 1 H), 2.77 (dt, J = 16.3, 4.7 Hz, 1 H), 2.39 (s, 3 H) , 2.18-2.09 (m, 1 H), 2.07-1.95 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 144.8, 141.8, 137.0, 129.2, 129.2, 126.8, 126.4, 120.8, 117.0, 113.9, 56.0, 31.0, 26.5, 21.0; **IR** (KBr): 3358, 2929, 2854, 1605, 1587, 1298, 1088, 833, 755 cm^{-1}.

2-(2,4-Dimethylphenyl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 3)

A colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45-7.36 (m, 1 H), 7.10-6.95 (m, 4 H), 6.66 (t, J=7.3 Hz, 1 H), 6.54 (d, J = 8.3 Hz, 1 H), 4.64 (dd, J = 9.2, 3.0 Hz, 1 H), 3.93 (br s, 1 H), 2.94 (ddd, J = 16.3, 11.1, 5.4 Hz, 1 H), 2.77 (dt, J = 16.3, 4.0 Hz, 1 H), 2.36 (s, 3 H), 2.33 (s, 3 H), 2.15-2.05 (m, 1 H), 1.99-1.85 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 145.1, 139.6, 136.6, 134.6, 131.3, 129.3, 127.1, 126.8, 126.0,

120.8, 117.0, 114.0, 52.0, 29.3, 26.6, 20.9, 19.0; **IR** (KBr): 3352, 2918, 2856, 1607, 1583, 1302, 1097, 831, 752 cm^{-1}.

2-(4-Isopropylphenyl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 4)

A colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.36-7.28 (m, 2 H), 7.25-7.17 (m, 2 H), 7.05-6.95 (m, 2 H), 6.64 (t, J=7.4 Hz, 1 H), 6.53 (d, J = 8.2 Hz, 1 H), 4.41 (dd, J = 9.5, 3.2 Hz, 1 H), 4.05 (br s, 1 H), 2.93 (ddd, J = 16.3, 9.7, 5.5 Hz, 1 H), 2.77 (dt, J = 16.4, 4.6 Hz, 1 H), 2.16-2.06 (m, 1 H), 2.05-1.93 (m, 1 H) , 1.26 (d, J = 7.0 Hz, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 148.0, 144.8, 142.2, 129.0, 126.8, 126.6, 126.5, 120.8, 117.1, 113.9, 56.2, 33.8, 30.9, 26.5, 24.1; **IR** (KBr): 3388, 2939, 2854, 1605, 1587, 1433, 1298, 1166, 1068, 833, 750 cm^{-1}.

2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 5)

A colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.35-7.28 (m, 2 H), 7.04-6.97 (m, 2 H), 6.93-6.86 (m, 2 H), 6.65 (t, J = 7.3 Hz, 1 H), 6.53 (d, J = 8.0 Hz, 1 H), 4.39 (dd, J = 9.6, 3.1 Hz, 1 H), 3.99 (br s, 1 H), 3.82 (s, 3 H), 2.93 (ddd, J = 16.4, 11.0, 5.4 Hz, 1 H), 2.74 (dt, J = 16.3, 4.5 Hz, 1 H), 2.13-2.04 (m, 1 H), 2.02-1.92 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 159.0, 144.8, 136.9, 129.3, 127.6, 126.8, 120.9, 117.1, 113.9, 113.9, 55.7, 55.3, 31.1, 26.6; **IR** (KBr): 3365, 2923, 2838, 1603, 1516, 1485, 1251, 1032, 832, 746 cm^{-1}.

2-(1,1'-biphenyl-4-yl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 6)

A colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63-7.54 (m, 4 H), 7.51-7.31 (m, 5 H), 7.07-6.97 (m, 2 H), 6.68 (t, J = 7.4 Hz, 1 H), 6.59 (d, J = 8.1 Hz, 1 H), 4.49 (dd, J = 9.3, 3.2 Hz, 1 H), 4.07 (br s, 1 H), 2.95 (ddd, J = 16.1, 10.5, 5.4 Hz, 1 H), 2.77 (dt, J = 16.4, 4.7 Hz, 1 H), 2.23-1.96 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 144.7, 143.9, 140.8, 140.5, 129.3, 128.8, 127.3, 127.3, 127.1, 127.0, 126.9, 120.9, 117.2, 114.0, 56.0, 31.0, 26.4; **IR** (KBr): 3362, 3028, 2925, 2852, 1604, 1579, 1483, 1309, 766, 746, 692 cm^{-1}.

2-(2-Fluorophenyl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 7)

A colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.52-7.43 (m, 1 H), 7.29-7.18 (m, 1 H), 7.17-6.96 (m, 4 H), 6.66 (t, J = 7.5 Hz, 1 H), 6.57 (d, J = 7.9 Hz, 1 H), 4.85 (dd, J = 8.2, 3.5 Hz, 1 H), 4.05 (br s, 1 H), 2.89 (ddd, J = 15.7, 9.3, 5.3 Hz, 1 H), 2.69 (dt, J = 16.3, 5.4 Hz, 1 H), 2.22-2.11 (m, 1 H), 2.08-1.94 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 161.8, 144.5, 131.6, 129.3, 128.7, 128.5, 127.9, 124.3, 120.9, 117.3,

115.4, 114.1, 48.8, 28.6, 25.7; **IR** (KBr): 3399, 2925, 2855, 1603, 1586, 1483, 1301, 750, 699 cm^{-1}.

2-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 8)

A colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 4 H), 7.07-6.96 (m, 2 H), 6.66 (t, J = 7.4 Hz, 1 H), 6.55 (d, J = 7.8 Hz, 1 H), 4.43 (dd, J = 9.1, 3.3 Hz, 1 H), 4.06 (br s, 1 H), 2.91 (ddd, J = 16.1, 10.3, 5.4 Hz, 1 H), 2.71 (dt, J = 16.4, 4.9 Hz, 1 H), 2.16-2.04 (m, 1 H), 2.02-1.88 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 144.2, 143.3, 133.0, 129.3, 128.7, 127.9, 126.9, 120.8, 117.4, 114.1, 55.6, 30.9, 26.1; **IR** (KBr): 3396, 2929, 1608, 1585, 1479, 1312, 785, 747, 696 cm^{-1}.

2-(4-Bromophenyl)-1,2,3,4-tetrahydroquinoline(Table 2, entry 9)

A colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.49-7.39 (m, 2 H), 7.30-7.21 (m, 2 H), 7.05-6.94 (m, 2 H), 6.65 (t, J = 7.0 Hz, 1 H), 6.53 (d, J = 7.9 Hz, 1 H), 4.40 (dd, J = 9.1, 3.2 Hz, 1 H), 4.00 (br s, 1 H), 2.89 (ddd, J = 16.3, 10.5, 5.5 Hz, 1 H), 2.70 (dt, J = 16.5, 4.8 Hz, 1 H), 2.14-2.03 (m, 1 H), 2.00-1.88 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 143.6, 141.0, 131.6, 129.2, 128.3, 126.9, 121.1, 121.0, 117.7, 114.3, 55.7, 30.8, 26.0; **IR** (KBr): 3387, 2925, 1606, 1585, 1475, 1311, 783, 748, 695 cm^{-1}.

2-Butyl-1,2,3,4-tetrahydroquinoline(Table 2, entry 10)

A colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.01-6.90 (m, 2 H), 6.60 (t, J = 7.4 Hz, 1 H), 6.48 (d, J = 7.7 Hz, 1 H), 3.81 (br s, 1H), 3.23 (tt, J = 9.3, 3.0 Hz, 1 H,), 2.81 (ddd, J = 16.3, 11.1, 5.5 Hz, 1 H), 2.73 (dt, J = 16.1, 4.5 Hz, 1 H), 2.01-1.91 (m, 1 H), 1.66-1.30 (m, 7 H), 0.93 (t, J = 7.1 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 144.9, 129.2, 126.7, 121.4, 116.9, 114.1, 51.6, 36.5, 28.1, 27.9, 26.6, 22.7, 14.1; **IR** (KBr): 3403, 2926, 2851, 1608, 1491, 1311, 740 cm^{-1}.

2-Isopropyl-1,2,3,4-tetrahydroquinoline(Table 2, entry 11)

A colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.04-6.89 (m, 2 H), 6.60 (t, J = 7.4 Hz, 1 H), 6.51 (d, J = 7.7 Hz, 1 H), 3.74 (br s, 1 H), 3.10-3.00 (m, 1 H), 2.88-2.69 (m, 2 H), 1.99-1.86 (m, 1 H), 1.80-1.59 (m, 2 H) , 1.00 (d, J = 10.4 Hz, 3 H), 0.99 (d, J = 10.4 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.3, 129.6, 127.0, 122.0, 117.2, 114.4, 57.7, 32.9, 27.1, 24.9, 19.0, 18.7; **IR** (KBr): 3399, 2920, 2844, 1608, 1486, 1384, 1311, 1273, 740, 699 cm^{-1}.

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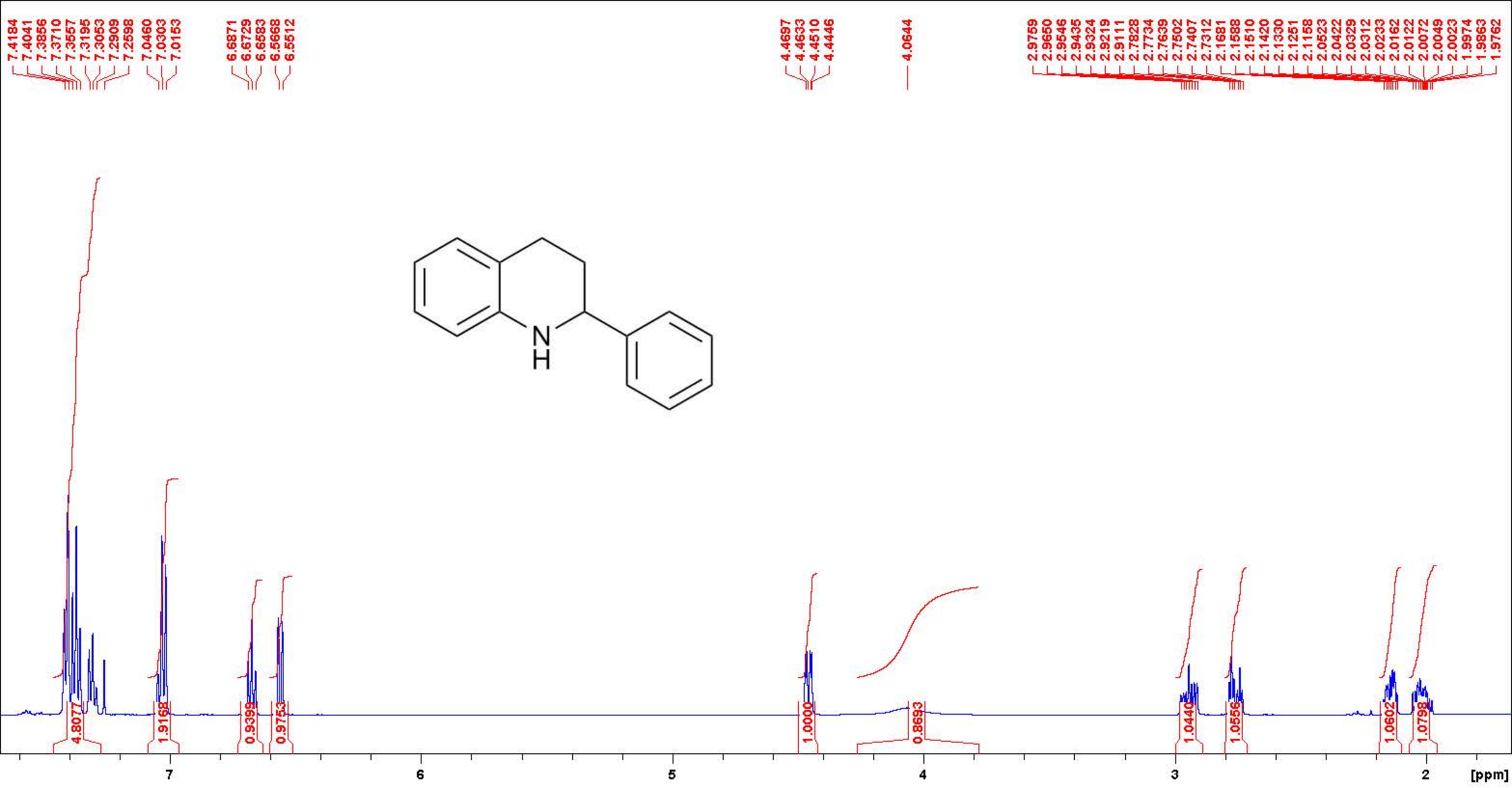
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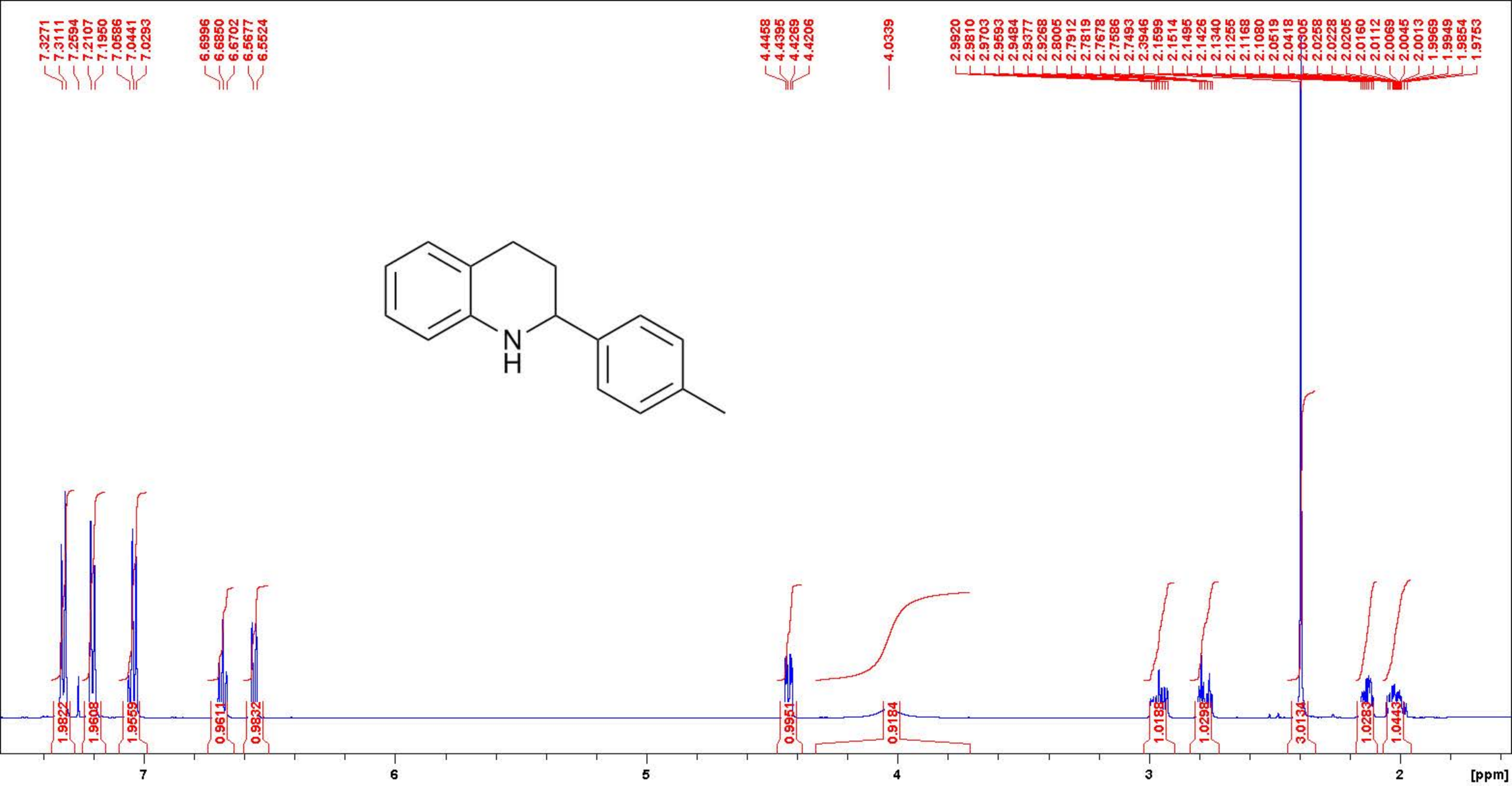
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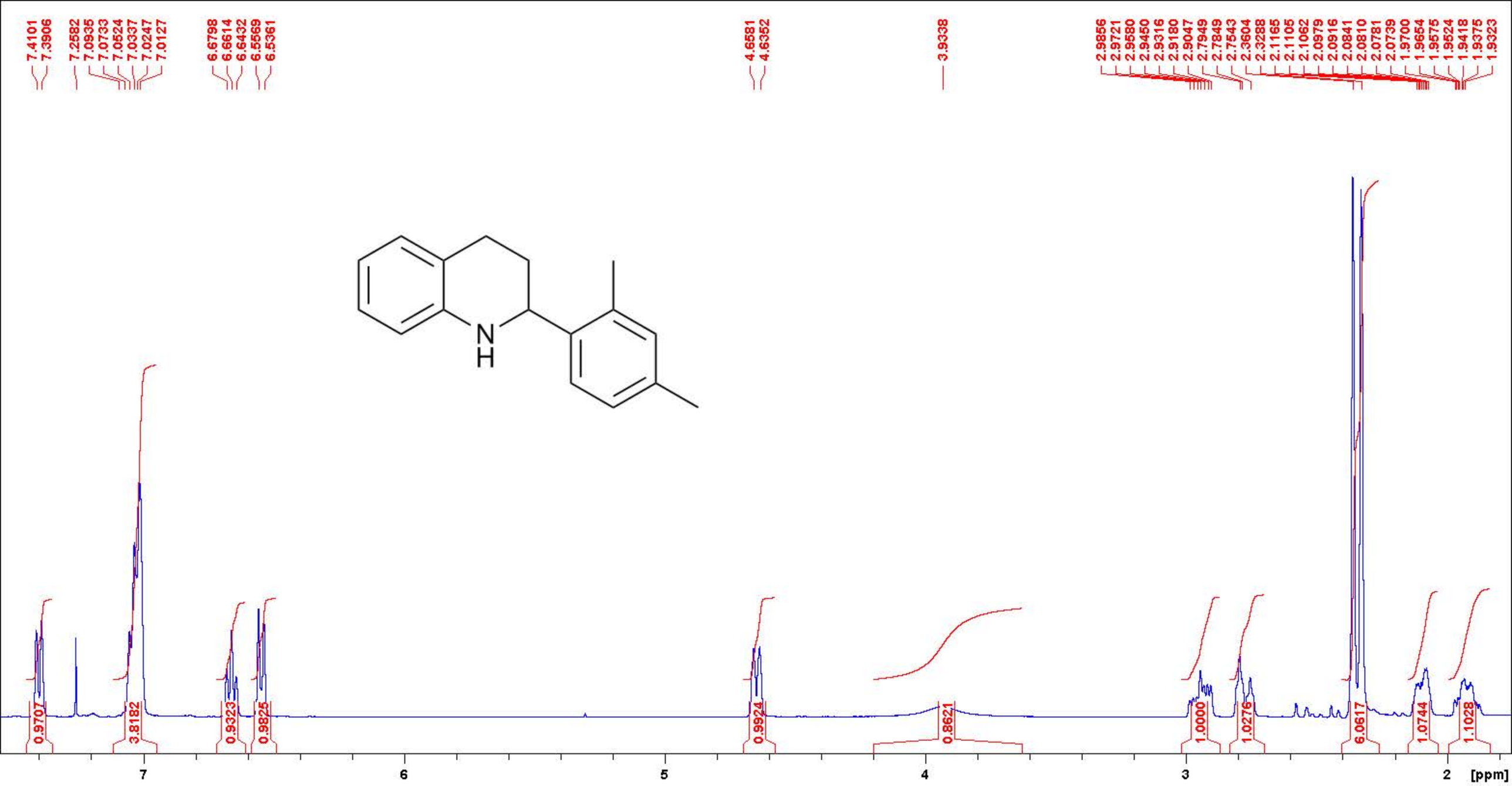
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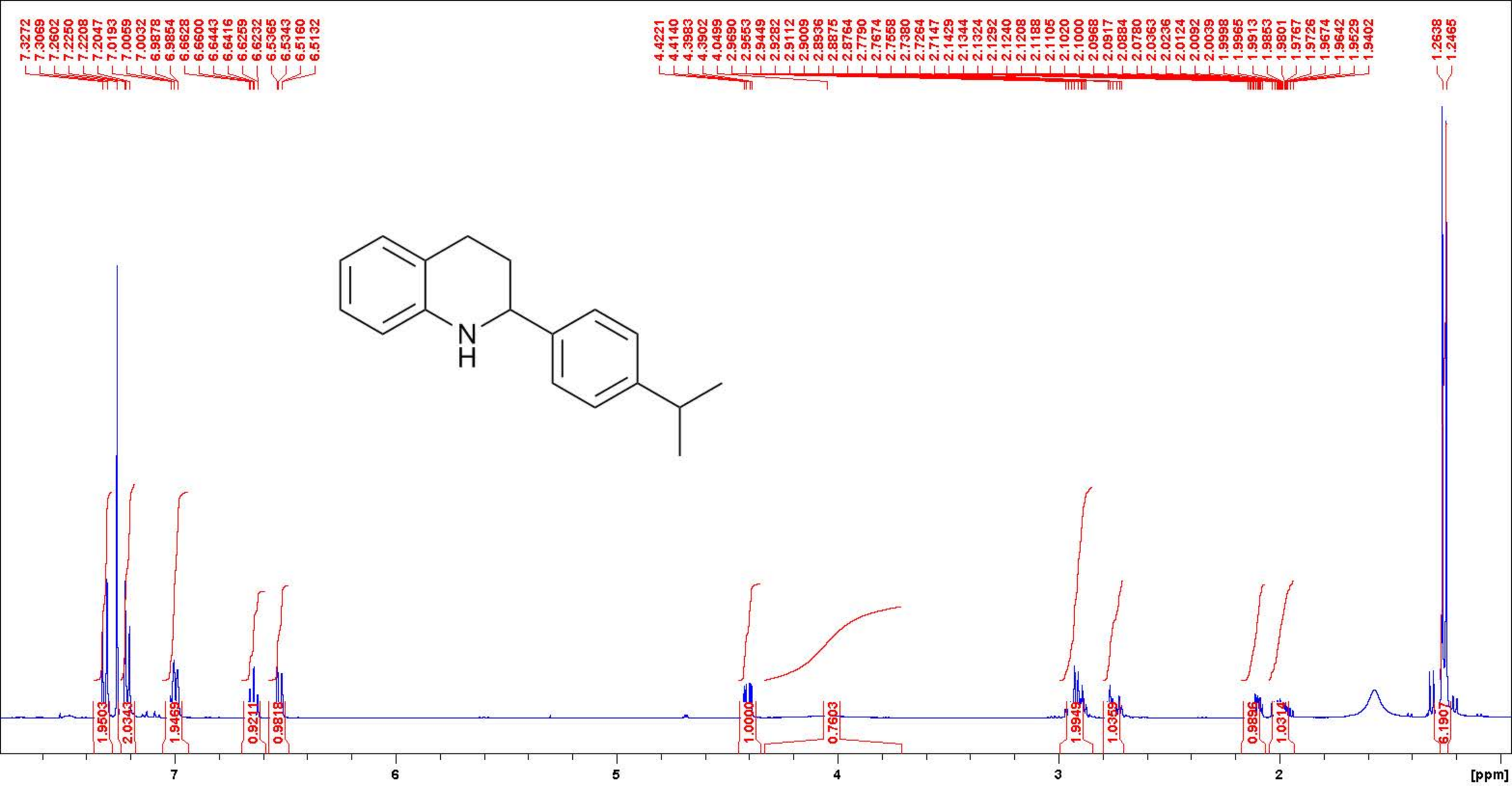
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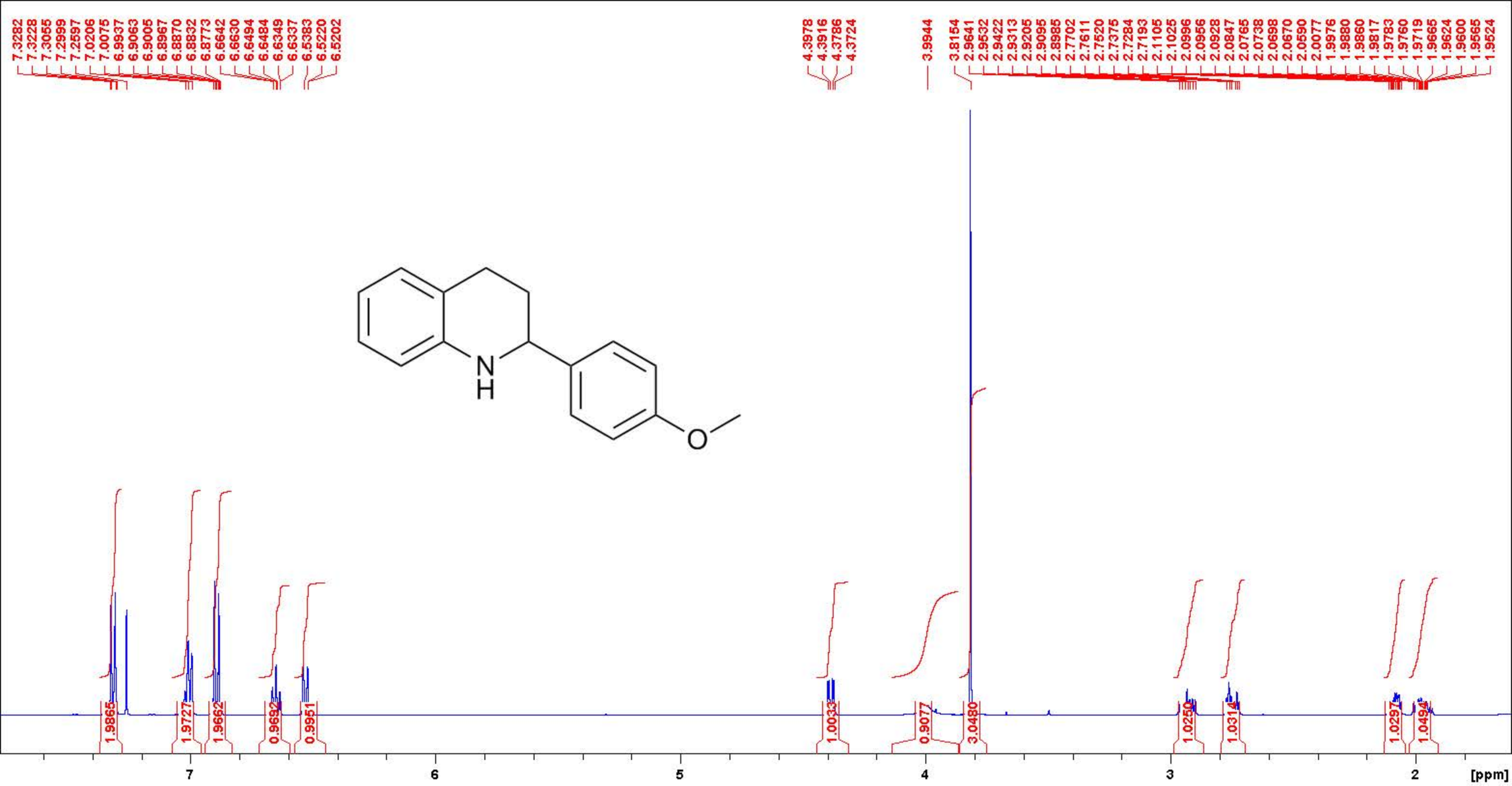
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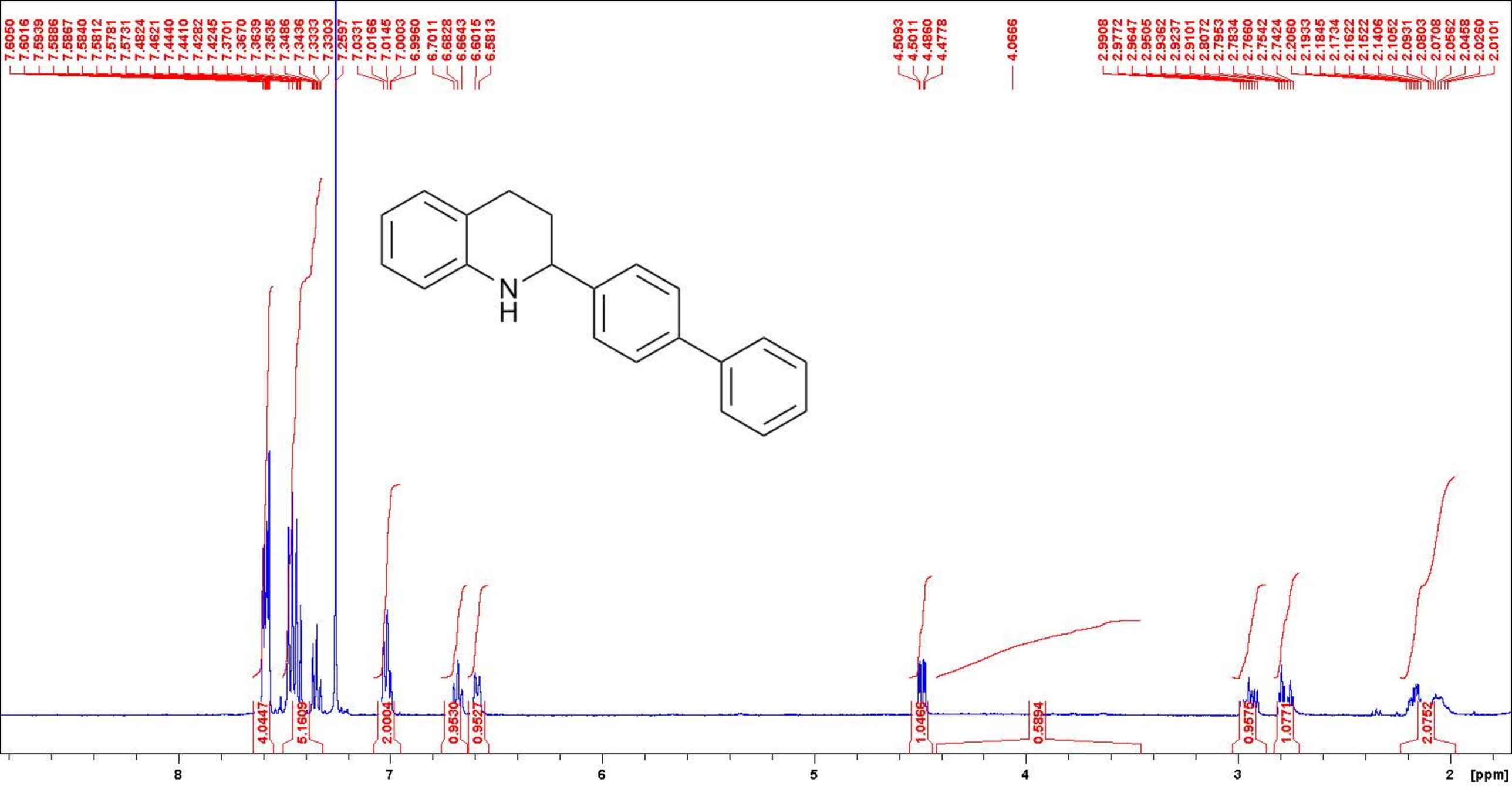
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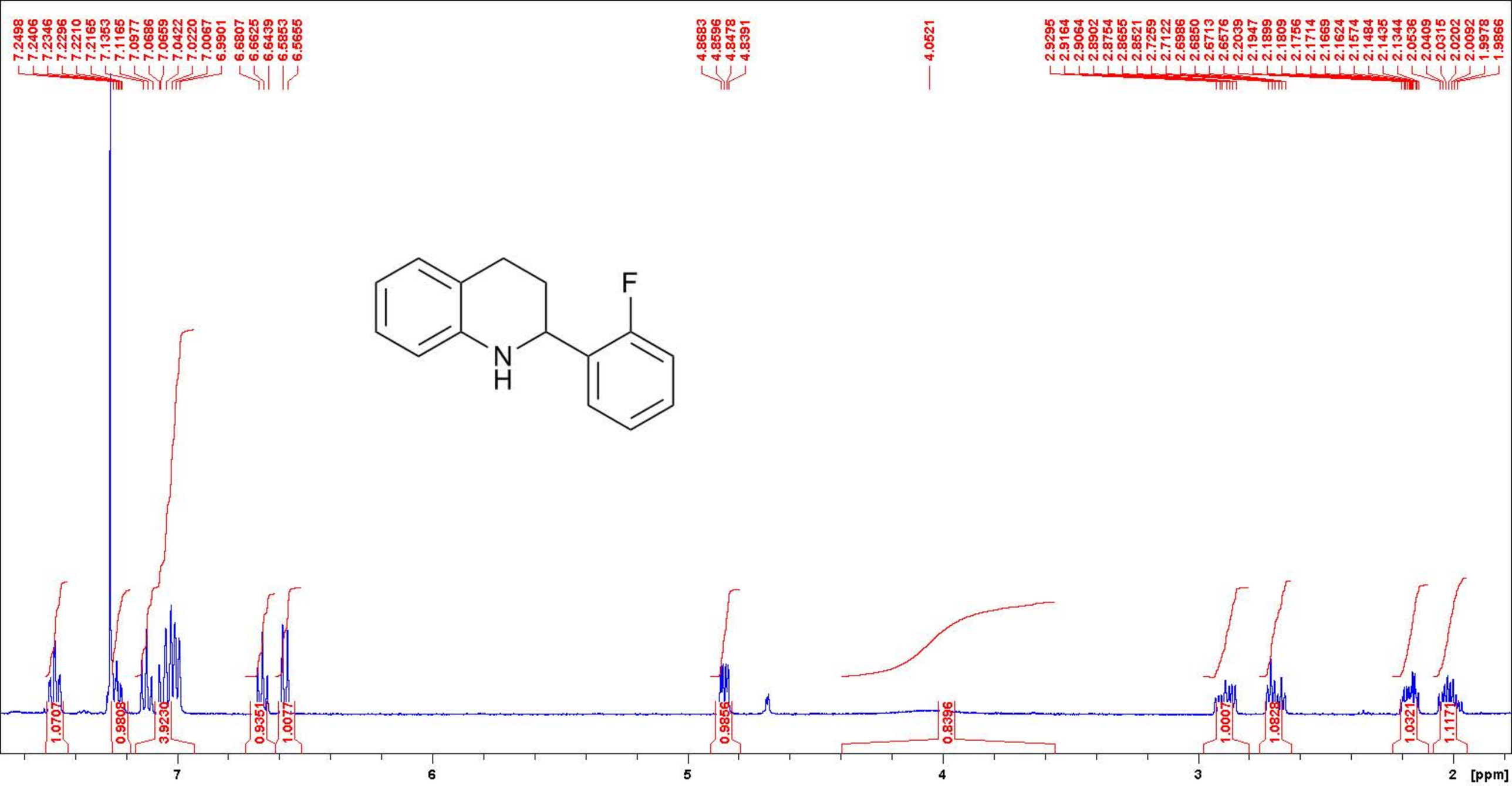
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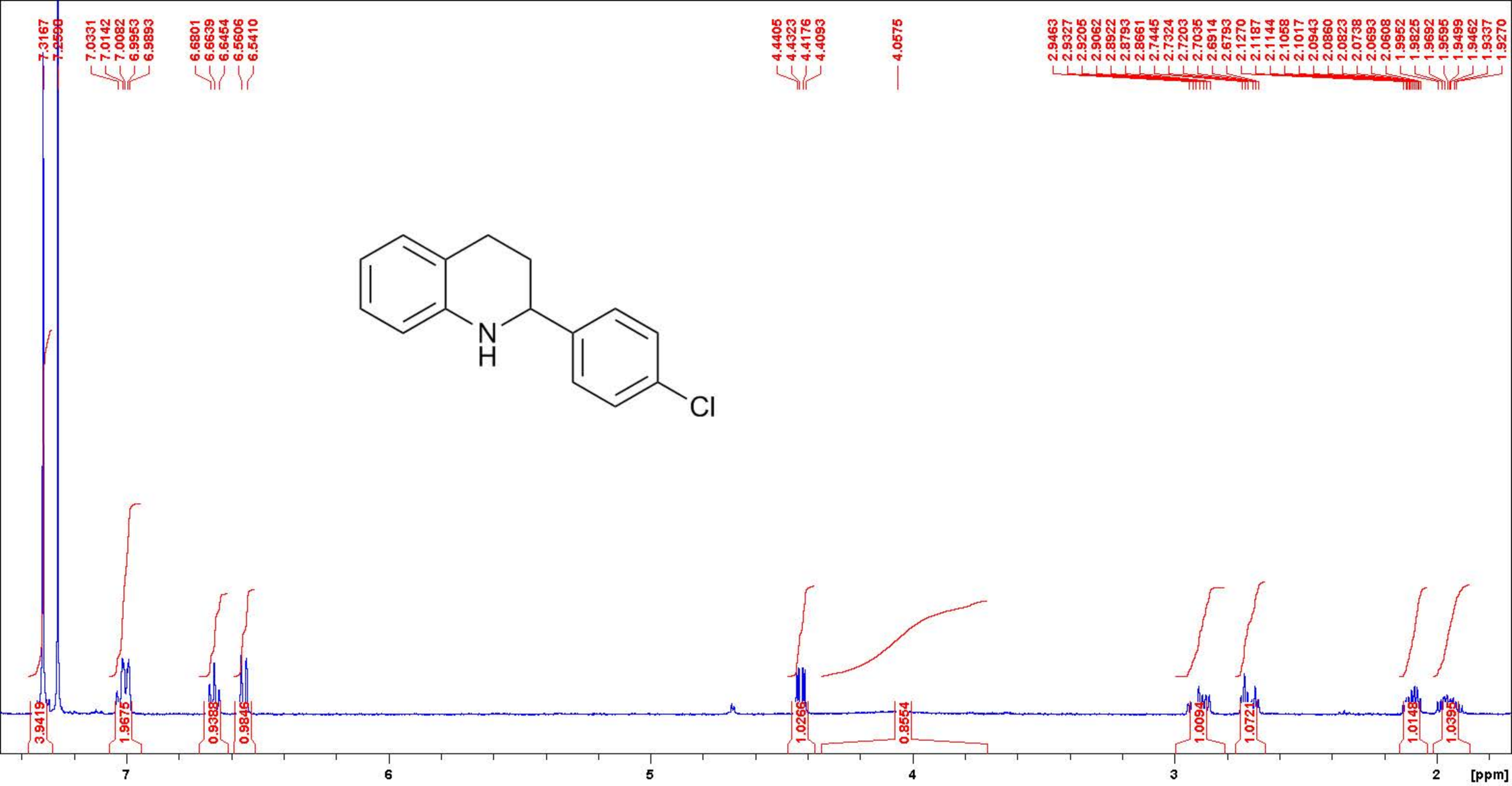
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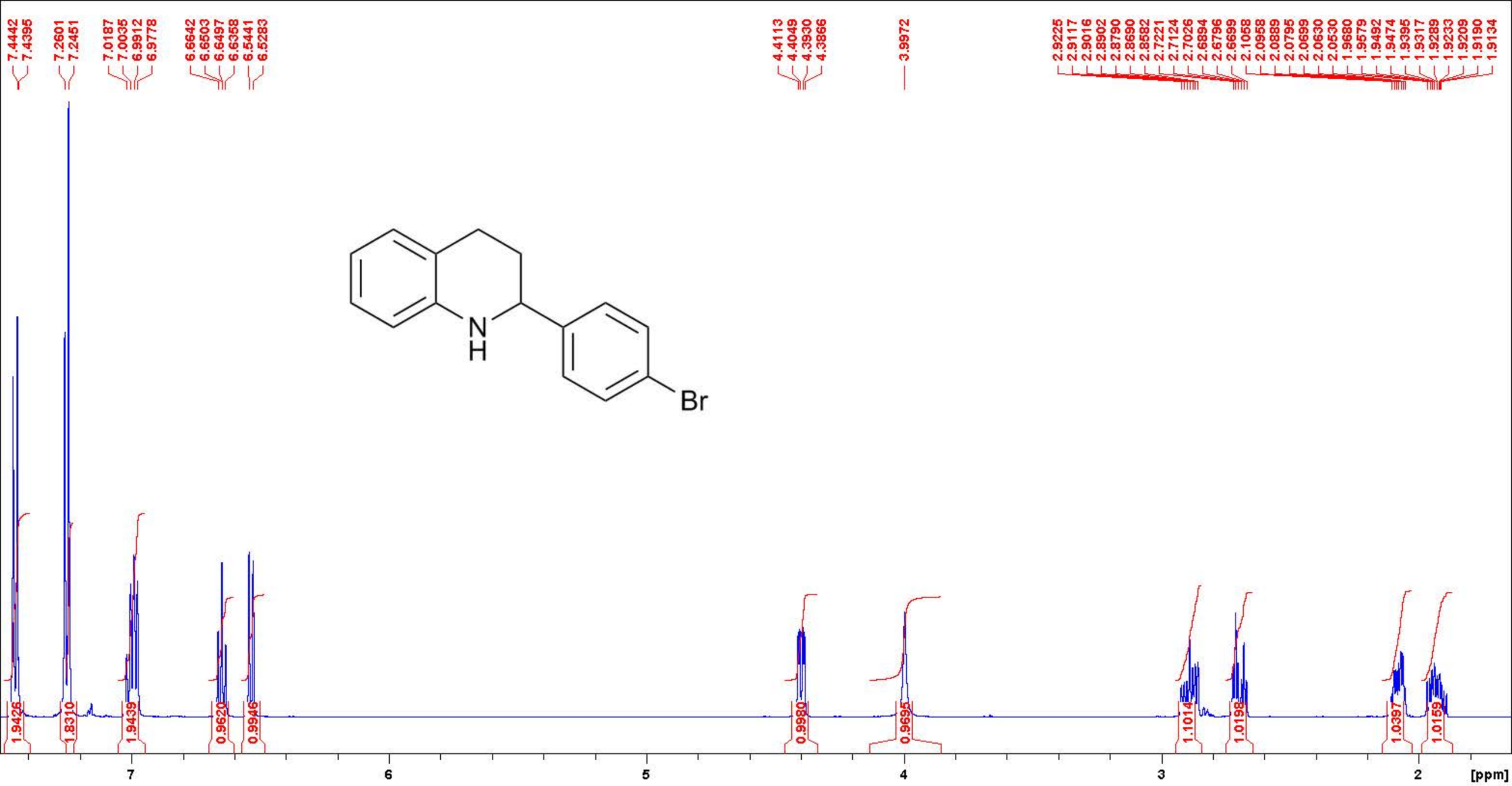
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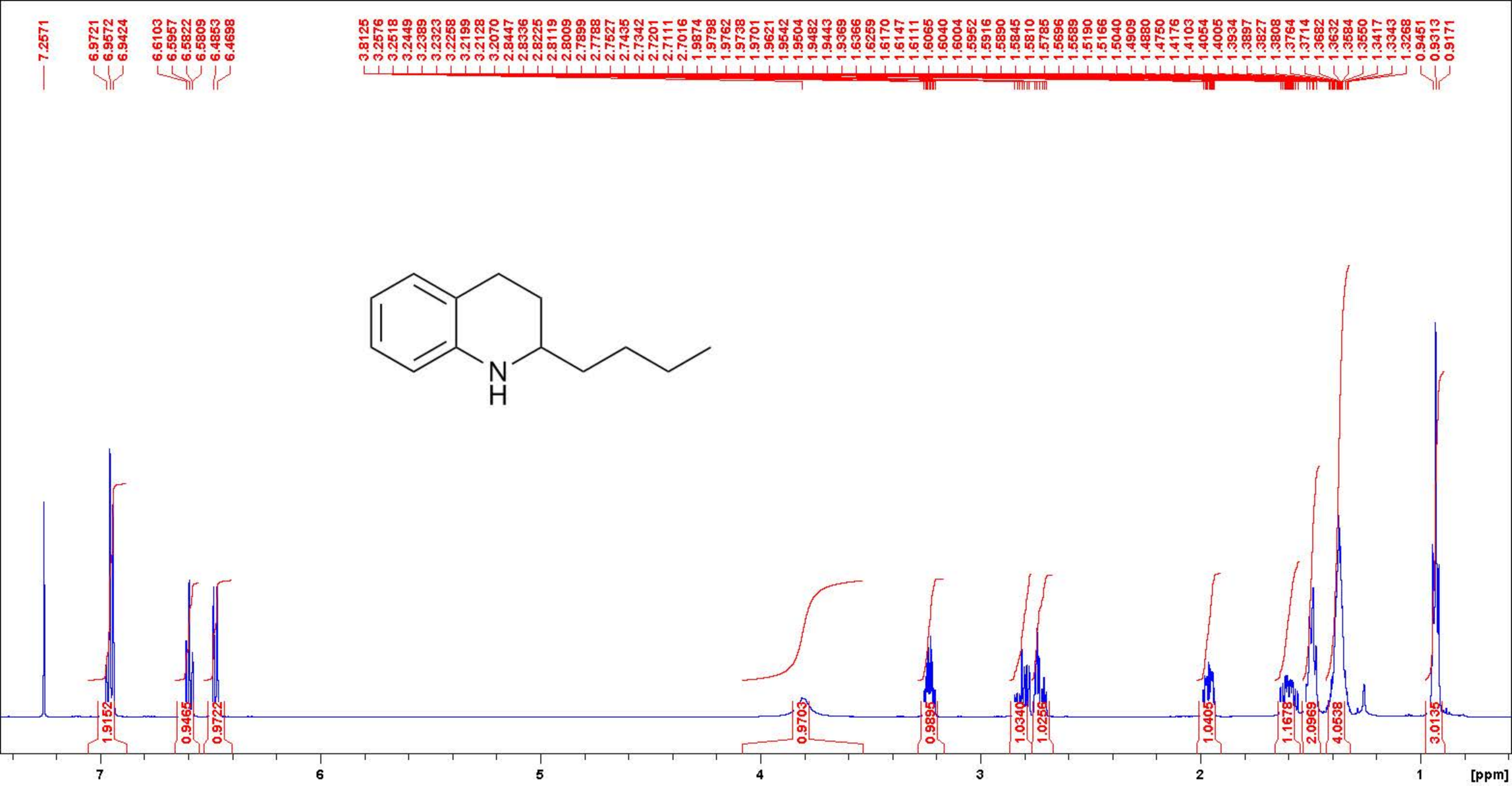
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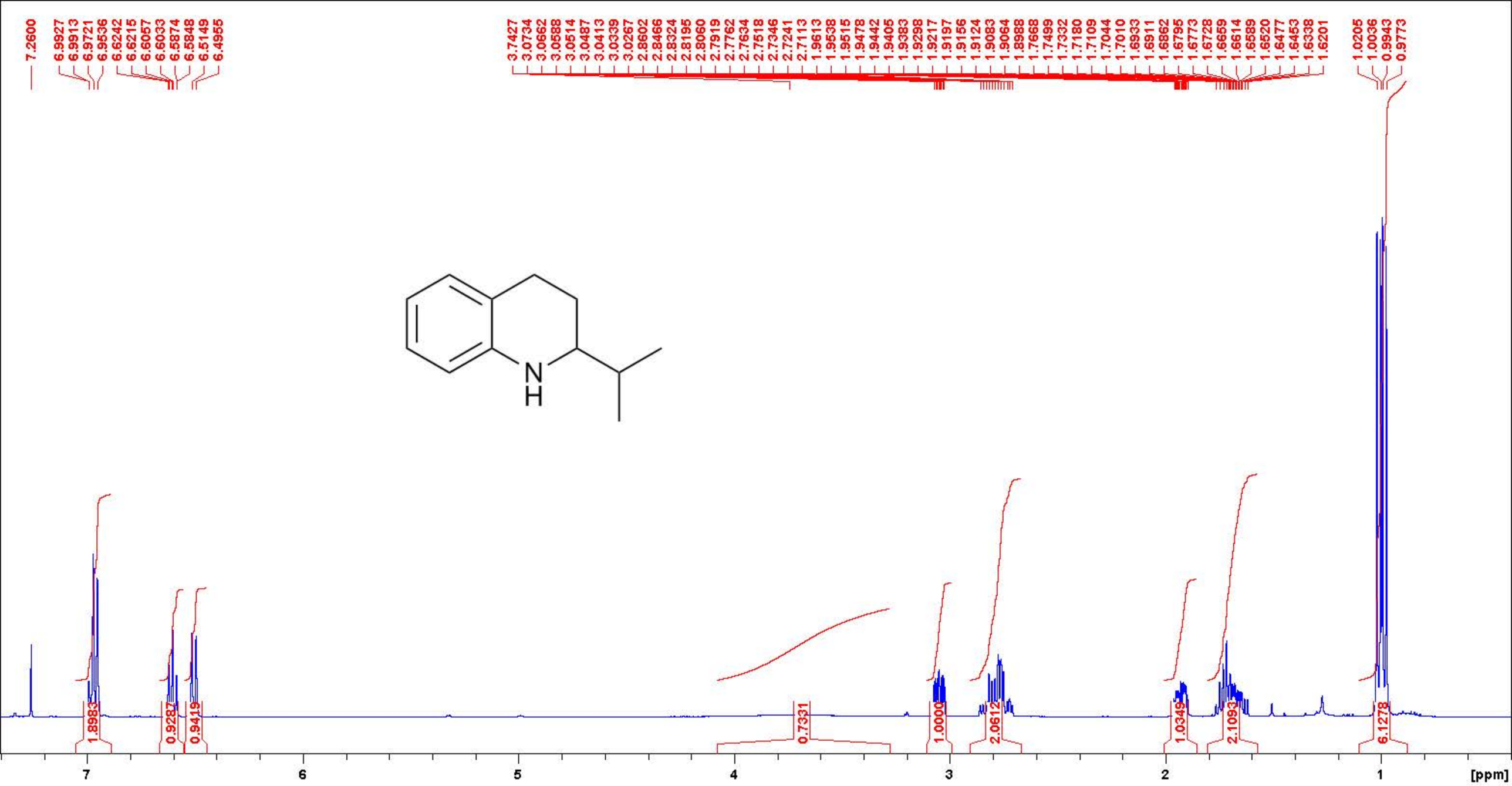
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