Electronic Supplementary Information

C(sp^3)-C(sp^3) bond formation via Copper/Brønsted acid Co-catalyzed C(sp^3)–H bond Oxidative Cross-Dehydrogenative-Coupling (CDC) of Azaarenes

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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). Elemental analyses were performed at the Analytical Laboratory of the Xiangtan University. Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for ^{1}H 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 ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: 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: Unless stated otherwise, substituted 2-methylquinolines was synthesized starting from *para*-substituted anilines and crotonaldehyde according to the method reported by Minamikawa, J.-i. *et. al.* [1]. Substituted N-phenyltetrahydroisoquinoline was synthesized starting from tetrahydroisoquinoline and iodobenzene catalyzed CuI.[2]

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

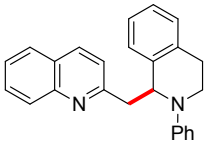
[2] (a) Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 6968-6969. (b) X.-Z. Shu, X.-F. Xia, Y.-F. Yang, K.-G. Ji, X.-Y. Liu, Y.-M. Liang, *J. Org. Chem.* **2009**, *74*, 7464-7469.

2. General experimental procedures for the benzylic CDC of azaarenes

A general experimental procedure is described as following:

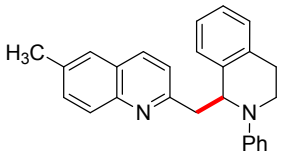
An oven-dried reaction vessel was charged with 2-methylquinoline (**1a**) (57.2 mg, 0.4 mmol), DCE (0.5 mL), PivOH (5.1 mg, 0.05 mmol, 25 mol%), $Cu(OTf)_2$ (3.6 mg, 0.01 mmol, 5 mol %) and N-phenyltetrahydroisoquinoline (**1b**) (41.8 mg, 0.2 mmol) under O_2 (1 atm). The vessel was sealed and heated at 60 °C (oil bath temperature) for 36 h. The resulting mixture was cooled to room temperature, transferred to silica gel column directly and eluted with hexanes and ethyl acetate (9:1) to give products **3a** (63.0 mg, 90 % yield).

3. Characterization data of products 3a-3q



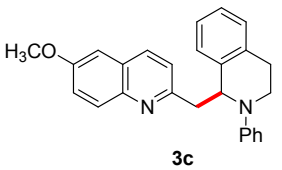
3a

3a: white solid; m.p. 118-120 °C; IR (KBr) ν 1593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.13 (d, *J*=8.0 Hz, 1H), 7.94 (d, *J*=9.2 Hz, 1H), 7.73 (m, 2H), 7.49 (t, *J*=7.2 Hz, 1H), 7.14 (m, 4H), 7.06 (d, *J*=8.0 Hz, 1H), 7.01 (m, 1H), 6.92 (d, *J*=8.4 Hz, 2H), 6.86 (d, *J*=8.4 Hz, 1H), 6.66 (t, *J*=6.8 Hz, 1H), 5.45 (t, *J*=6.0 Hz, 1H), 3.78 (m, 1H), 3.67 (m, 2H), 3.34 (m, 1H), 3.11 (m, 1H), 2.90 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$, TMS) δ159.8, 149.3, 148.0, 138.2, 135.8, 134.8, 129.3, 129.2, 129.0, 128.6, 127.6, 127.4, 126.9, 126.6, 125.8, 125.7, 122.8, 117.4, 114.0, 60.0, 45.4, 41.7, 27.2 ; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}N_2$, 351.1856; found: 351.1849.



3b

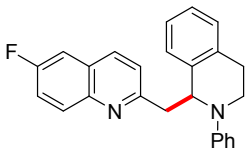
3b: white solid; m. p. 122-124 °C; IR (KBr) ν 1594 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.02 (d, *J*=7.2 Hz, 1H), 7.85 (d, *J*=8.0 Hz, 1H), 7.53 (m, 2H), 7.15 (s, 4H), 7.00 (m, 2H), 6.92 (d, *J*=8.4 Hz, 2H), 6.85 (d, *J*=6.4 Hz, 1H), 6.66 (t, *J*=6.8 Hz, 1H), 5.43 (t, *J*=5.6 Hz, 1H), 3.78 (m, 1H), 3.65 (m, 2H), 3.31 (m, 1H), 3.11 (m, 1H), 2.91 (d, *J*=15.6 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ158.9, 149.4, 146.7, 138.4, 135.7, 135.3, 134.9, 131.6, 129.2, 128.8, 128.6, 127.5, 127.0, 126.7, 126.5, 125.8, 122.8, 117.4, 114.1, 60.1, 45.5, 41.8, 27.3, 21.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}N_2$, 365.2012; found: 365.2009.



3c

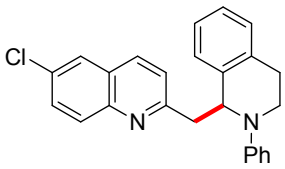
3c: white solid; m. p. 51-53 °C; IR (KBr) ν 1595 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.02 (d, *J*=9.2 Hz, 1H), 7.84 (d, *J*=8.4 Hz, 1H), 7.36 (m, 1H), 7.14 (m, 4H), 7.00 (m, 3H), 6.91 (d, *J*=8.0 Hz, 2H), 6.85 (d, *J*=8.0 Hz, 1H), 6.66 (t, *J*=7.2 Hz, 1H), 5.41 (t, *J*=7.2 Hz, 1H), 3.92 (s, 3H), 3.78 (m, 1H), 3.65 (m, 2H), 3.29 (m, 1H), 3.11 (m, 1H), 2.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ157.4, 157.3, 149.4, 144.2, 138.8, 135.0, 134.7, 130.5, 129.2,

128.6, 127.8, 127.5, 126.7, 125.8, 123.1, 122.0, 117.4, 114.0, 105.2, 60.3, 55.6, 45.3, 41.8, 27.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}N_2O$, 381.1948; found: 381.1955.



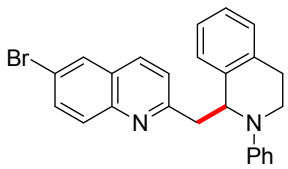
3d

3d: white solid; m. p. 133-135 °C; IR (KBr) ν 1594 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.11 (m, 1H), 7.88 (d, *J*=8.8 Hz, 1H), 7.47 (m, 1H), 7.36 (m, 1H), 7.14 (m, 4H), 7.06 (d, *J*=8.4 Hz, 1H), 7.01 (m, 1H), 6.90 (d, *J*=8.0 Hz, 2H), 6.85 (d, *J*=7.6 Hz, 1H), 6.66 (t, *J*=7.6 Hz, 1H), 5.42 (t, *J*=6.4 Hz, 1H), 3.77 (m, 1H), 3.66 (m, 2H), 3.31 (m, 1H), 3.10 (m, 1H), 2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ161.4, 159.3, (d, *J*=2.8 Hz), 159.0, 149.4, 145.2, 138.2, 135.3 (d, *J*=5.2 Hz), 131.6 (d, *J*=9.0 Hz), 129.2, 128.7, 127.5, 127.4 (d, *J*=3.0 Hz), 126.8, 125.9, 123.6, 119.6 (d, *J*=25.6 Hz), 117.5, 114.1, 110.7 (d, *J*=21.5 Hz), 60.0, 45.5, 41.8, 27.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_2F$, 369.1761; found: 369.1756.



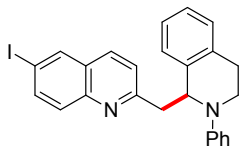
3e

3e: white solid; m. p.134-136 °C; IR (KBr) ν 1593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.05 (d, *J*=8.8 Hz, 1H), 7.84 (d, *J*=8.4 Hz, 1H), 7.73 (d, *J*=1.6 Hz, 1H), 7.64 (dd, *J*=2.4, 9.6 Hz, 1H), 7.14 (m, 4H), 7.06 (d, *J*=8.0 Hz, 1H), 7.01 (m, 1H), 6.90 (d, *J*=8.4 Hz, 2H), 6.84 (d, *J*=8.0 Hz, 1H), 6.66 (t, *J*=7.6 Hz, 1H), 5.42 (t, *J*=7.2 Hz, 1H), 3.75 (m, 1H), 3.64 (m, 2H), 3.31 (m, 1H), 3.10 (m, 1H), 2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ160.4, 149.4, 146.5, 138.2, 135.0, 134.9, 131.6, 130.8, 130.3, 129.3, 128.7, 127.6, 127.4, 126.8, 126.3, 125.9, 123.8, 117.6, 114.1, 60.0, 45.6, 41.9, 27.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_2Cl$, 385.1465; found: 385.1466.



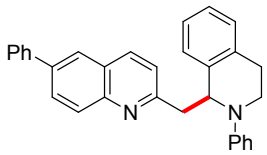
3f

3f: white solid; m. p. 132-134 °C; IR (KBr) ν 1593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ7.98 (d, *J*=8.4 Hz, 1H), 7.90 (s, 1H), 7.83 (d, *J*=8.8 Hz, 1H), 7.77 (d, *J*=9.2 Hz, 1H), 7.14 (m, 4H), 7.05 (d, *J*=8.8 Hz, 1H), 7.01 (m, 1H), 6.90 (d, *J*=8.4 Hz, 2H), 6.83 (d, *J*=8.0 Hz, 1H), 6.66 (t, *J*=6.4 Hz, 1H), 5.42 (t, *J*=6.8 Hz, 1H), 3.76 (m, 1H), 3.64 (m, 2H), 3.30 (m, 1H), 3.11 (m, 1H), 2.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ160.5, 149.3, 146.7, 138.2, 135.0, 134.9, 132.8, 131.0, 129.7, 129.3, 128.7, 128.1, 127.4, 126.8, 125.9, 123.7, 119.7, 117.6, 114.1, 60.0, 45.6, 41.8, 27.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_2Br$, 429.0961; found: 429.0959.



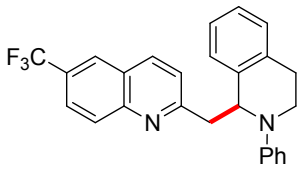
3g

3g: white solid; m. p. 121-123 °C; IR (KBr) ν 1593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.14 (s, 1H), 7.94 (d, *J*=9.2 Hz, 1H), 7.83 (m, 2H), 7.14 (m, 4H), 7.05 (d, *J*=8.0 Hz, 1H), 7.01 (m, 1H), 6.90 (d, *J*=8.4 Hz, 2H), 6.83 (d, *J*=7.6 Hz, 1H), 6.66 (t, *J*=7.6 Hz, 1H), 5.42 (t, *J*=6.4 Hz, 1H), 3.76 (m, 1H), 3.65 (m, 2H), 3.30 (m, 1H), 3.12 (m, 1H), 2.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ160.7, 149.4, 147.1, 138.2, 138.1, 136.4, 135.0, 134.6, 131.0, 129.3, 128.8, 128.7, 127.4, 126.8, 125.9, 123.5, 117.7, 114.3, 91.2, 60.0, 45.6, 42.0, 27.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_2I$, 477.0822; found: 477.0823.



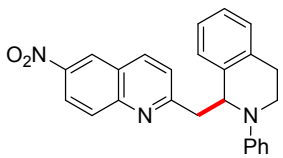
3h

3h: white solid; m. p. 159-161 °C; IR (KBr) ν 1592 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.19 (d, *J*=8.8 Hz, 1H), 7.98 (m, 3H), 7.72 (d, *J*=7.6 Hz, 2H), 7.49 (t, *J*=8.0 Hz, 2H), 7.39 (t, *J*=7.2 Hz, 1H), 7.12 (m, 4H), 7.08 (d, *J*=8.4 Hz, 1H), 7.02 (m, 1H), 6.94 (d, *J*=7.6 Hz, 2H), 6.88 (d, *J*=8.0 Hz, 1H), 6.67 (t, *J*=6.8 Hz, 1H), 5.46 (t, *J*=6.8 Hz, 1H), 3.79 (m, 1H), 3.68 (m, 2H), 3.34 (m, 1H), 3.11 (m, 1H), 2.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ160.0, 149.4, 147.6, 140.0, 138.7, 138.3, 136.1, 135.0, 129.6, 129.3, 129.2, 129.1, 128.7, 127.7, 127.6, 127.5, 127.2, 126.8, 125.9, 125.4, 123.3, 117.5, 114.2, 60.1, 45.6, 41.9, 27.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{27}N_2$, 427.2169; found: 427.2166.



3i

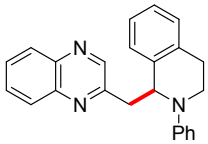
3i: yellow solid; m. p. 93-95 °C; IR (KBr) ν 1597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.23 (d, *J*=9.2 Hz, 1H), 8.02 (m, 2H), 7.88 (d, *J*=8.8 Hz, 1H), 7.14 (m, 5H), 7.00 (m, 1H), 6.90 (m, 3H), 6.67 (t, *J*=6.4 Hz, 1H), 5.46 (t, *J*=6.8 Hz, 1H), 3.72 (m, 3H), 3.35 (m, 1H), 3.11 (m, 1H), 2.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ162.6, 149.4, 149.2, 138.2, 136.5, 135.0, 130.4, 129.3, 128.8, 127.4, 126.9, 126.0, 125.7, 125.64, 125.58, 125.1 (q, *J*=3.0 Hz), 124.1, 117.8, 114.4, 60.0, 45.8, 42.0, 27.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{22}N_2F_3$, 419.1730; found: 419.1727.



3j

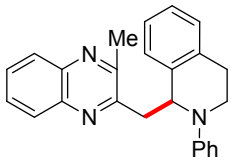
3j: yellow solid; m. p. 157-159 °C; IR (KBr) ν 1595, 1530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.71 (s, 1H),

8.47 (d, *J*=8.8 Hz, 1H), 8.23 (d, *J*=9.2 Hz, 1H), 8.09 (d, *J*=8.4 Hz, 1H), 7.16 (m, 5H), 7.02 (m, 1H), 6.88 (m, 3H), 6.66 (t, *J*=7.6 Hz, 1H), 5.47 (t, *J*=5.6 Hz, 1H), 3.75 (m, 1H), 3.69 (m, 2H), 3.38 (m, 1H), 3.11 (m, 1H), 2.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 164.4, 138.0, 137.4, 135.0, 131.0, 129.3, 128.9, 127.3, 127.2, 127.0, 126.0, 125.9, 125.7, 124.8, 124.5, 123.0, 118.0, 117.9, 114.5, 60.0, 46.0, 42.0, 27.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_3O_2$, 396.1706; found: 396.1704.



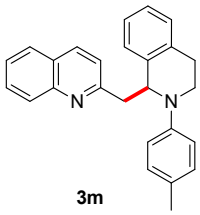
3k

3k: white solid; m. p. 122-124 °C; IR (KBr) ν 1596cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ8.43 (s, 1H), 8.11 (d, *J*=7.2 Hz, 1H), 8.03 (d, *J*=8.0 Hz, 1H), 7.74 (m,2H), 7.15 (m, 4H), 7.04 (m, 1H), 6.90 (m, 3H), 6.70 (t, *J*=6.8 Hz, 1H), 5.41 (t, *J*=7.6 Hz, 1H), 3.79 (m, 1H), 3.68 (m, 2H), 3.37 (m, 1H), 3.10 (m, 1H), 2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ154.9, 149.3, 146.6, 137.7, 135.0, 130.0, 129.4, 129.3, 129.2, 129.1, 129.0, 127.2, 127.1, 126.2, 118.1, 114.6, 60.0, 43.0, 42.1, 27.2; HRMS (ESI) m/z: $[M-H]^+$ calcd for $C_{24}H_{20}N_3$, 350.1652; found: 350.1648.



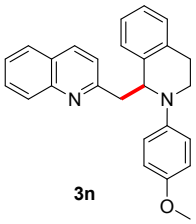
3l

3l: white solid; m. p. 136-138 °C; IR (KBr) ν 1594 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ8.12 (d, *J*=8.0 Hz, 1H), 7.95 (d, *J*=7.6 Hz, 1H), 7.70 (m,2H), 7.18 (m, 4H), 7.01 (d, *J*=8.4 Hz, 2H), 6.95 (t, *J*=7.6 Hz, 1H), 6.70 (t, *J*=6.4 Hz, 2H), 5.57 (t, *J*=6.4 Hz, 1H), 3.80 (m, 1H), 3.64 (m, 2H), 3.35 (m, 1H), 3.08 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ154.5, 153.7, 149.0, 141.3, 141.0, 138.0, 135.0, 129.3, 129.2, 129.0, 128.8, 128.6, 128.4, 127.1, 127.0, 126.2, 117.6, 113.7, 59.6, 42.5, 41.5, 27.9, 22.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}N_3$, 366.1965; found: 366.1961.



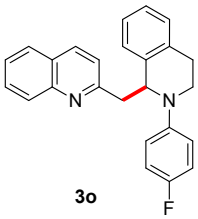
3m

3m: white solid; m. p. 106-108 °C; IR (KBr) ν 1597 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ8.11 (d, *J*=8.4 Hz, 1H), 7.94 (d, *J*=8.0 Hz, 1H), 7.72 (m, 2H), 7.49 (t, *J*=7.2 Hz, 1H), 7.10 (m, 3H), 7.00 (m, 1H), 6.94 (d, *J*=9.2 Hz, 2H), 6.89 (d, *J*=8.0 Hz, 1H), 6.82 (d, *J*=8.8 Hz, 2H), 5.38 (t, *J*=7.2 Hz, 1H), 3.75 (m, 1H), 3.65 (m, 2H), 3.33 (m, 1H), 3.09 (m, 1H), 2.86 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ160.2, 148.1, 147.5, 138.4, 135.9, 135.0, 129.7, 129.3, 129.2, 128.8, 127.6, 127.5, 127.0, 126.9, 126.6, 125.9, 125.8, 122.9, 114.9, 60.4, 45.5, 41.8, 27.1, 20.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}N_2$, 365.2012; found: 365.2009.



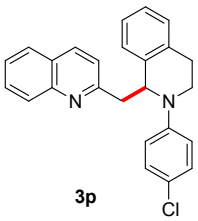
3n

3n: white solid; m. p. 106-108 °C; IR (KBr) ν 1598 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.09 (d, *J*=8.0 Hz, 1H), 7.95 (d, *J*=8.4 Hz, 1H), 7.72 (m, 2H), 7.49 (t, *J*=7.6 Hz, 1H), 7.13 (m, 3H), 7.01 (s, 1H), 6.88 (m, 3H), 6.71 (d, *J*=7.6 Hz, 2H), 5.30 (t, *J*=6.4 Hz, 1H), 3.73 (m, 1H), 3.68 (s, 3H), 3.59 (m, 2H), 3.32 (m, 1H), 3.09 (m, 1H), 2.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ160.3, 152.6, 148.1, 144.3, 138.4, 135.8, 134.8, 129.4, 129.1, 128.9, 127.6, 127.5, 127.0, 126.6, 125.9, 125.8, 122.9, 117.3, 114.6, 60.9, 55.8, 45.4, 42.4, 27.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}N_2O$, 381.1948; found: 381.1955.



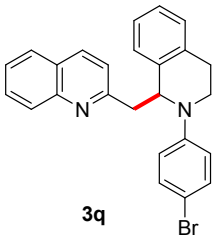
3o

3o: white solid; m. p. 156-158 °C; IR (KBr) ν 1597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.10 (d, *J*=8.0 Hz, 1H), 7.95 (d, *J*=8.0 Hz, 1H), 7.73 (m, 2H), 7.49 (t, *J*=7.2 Hz, 1H), 7.15 (m, 2H), 7.04 (m, 2H), 6.89 (d, *J*=6.8 Hz, 1H), 6.83 (m, 4H), 5.35 (t, *J*=6.4 Hz, 1H), 3.75 (m, 1H), 3.59 (m, 2H), 3.31 (m, 1H), 3.08 (m, 1H), 2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ159.9, 157.2, 154.8, 148.1, 146.2, 138.2, 135.9, 134.7, 129.4, 129.1, 128.8, 127.6, 127.4, 127.0, 126.8, 125.9, (d, *J*=5.4 Hz), 122.8, 116.0, (d, *J*=7.4 Hz), 115.5, (d, *J*=21.8 Hz), 60.6, 45.6, 42.3, 27.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_2F$, 369.1761; found: 369.1756.



3p

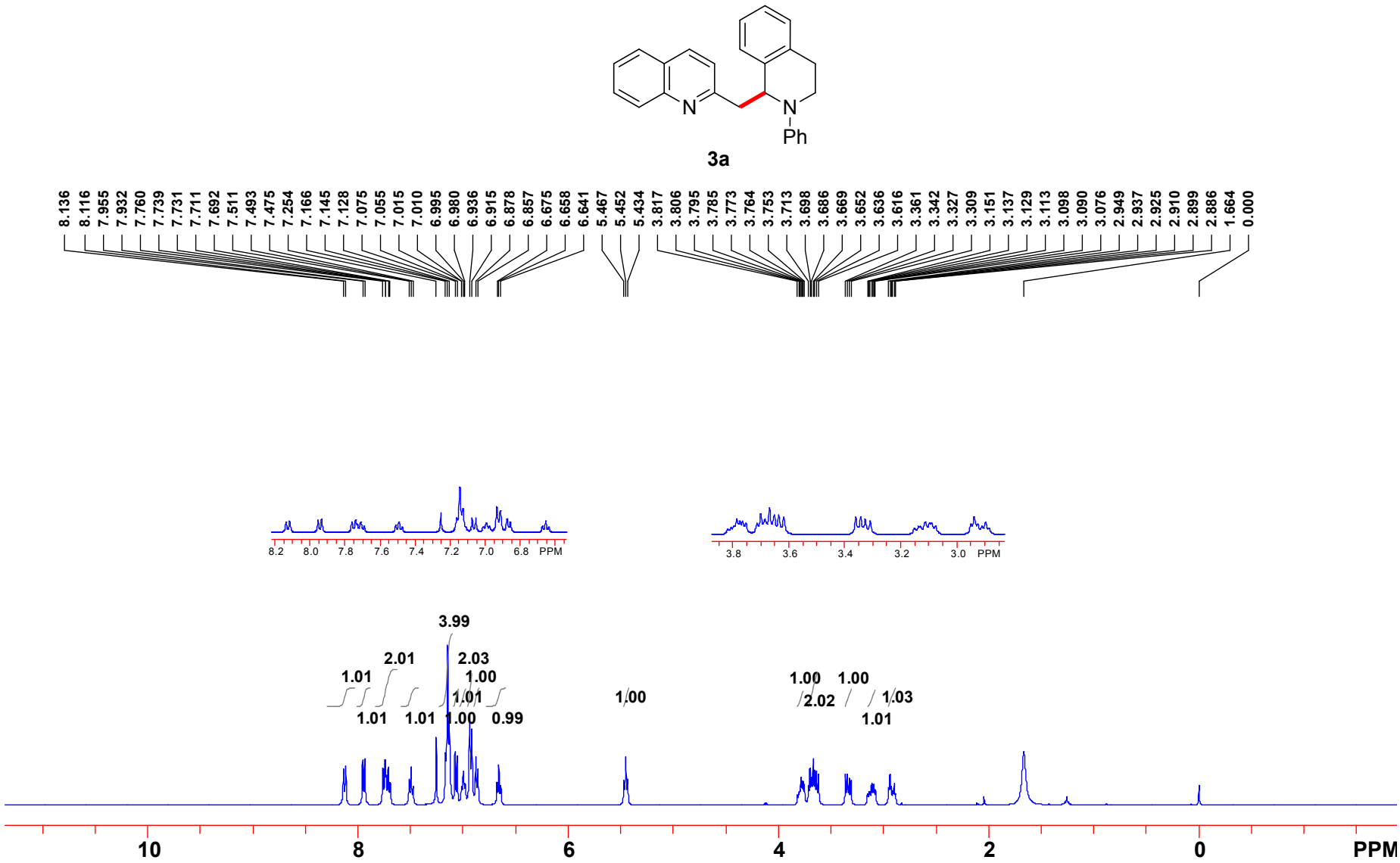
3p: white solid; m. p. 157-159 °C; IR (KBr) ν 1593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.12 (d, *J*=8.4 Hz, 1H), 7.95 (d, *J*=8.0 Hz, 1H), 7.74 (m, 2H), 7.50 (t, *J*=7.6 Hz, 1H), 7.14 (m, 2H), 7.04 (m, 4H), 6.86 (m, 3H), 5.41 (t, *J*=6.4 Hz, 1H), 3.75 (m, 1H), 3.61 (m, 2H), 3.32 (m, 1H), 3.09 (m, 1H), 2.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ159.7, 148.0, 138.1, 136.0, 134.7, 129.6, 129.1, 129.0, 128.7, 127.7, 127.4, 127.3, 127.0, 126.9, 126.1, 126.0, 122.8, 115.2, 60.2, 45.6, 42.0, 27.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_2Cl$, 385.1465; found: 385.1466.



3q

3q: white solid; m. p. 156-158 °C; IR (KBr) ν 1595 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ8.11 (d, *J*=8.4 Hz, 1H), 7.95 (d, *J*=9.2 Hz, 1H), 7.74 (m, 2H), 7.50 (t, *J*=8.0 Hz, 1H), 7.14 (m, 4H), 7.02 (d, *J*=8.4 Hz, 2H), 6.87 (d, *J*=8.0 Hz, 1H), 6.80 (d, *J*=9.2 Hz, 2H), 5.41 (t, *J*=6.4 Hz, 1H), 3.75 (m, 1H), 3.61 (m, 2H), 3.31 (m, 1H), 3.09 (m, 1H), 2.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ159.6, 148.4, 138.0, 136.0, 134.7, 131.9, 129.6, 129.1, 128.7, 127.7, 127.6, 127.4, 127.0, 126.9, 126.1, 126.0, 122.8, 115.6, 109.2, 60.1, 45.6, 42.0, 27.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}N_2Br$, 429.0961; found: 429.0959.

4. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3q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3.8 3.6 3.4 3.2 3.0 PPM
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2.03
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1.03
1.01
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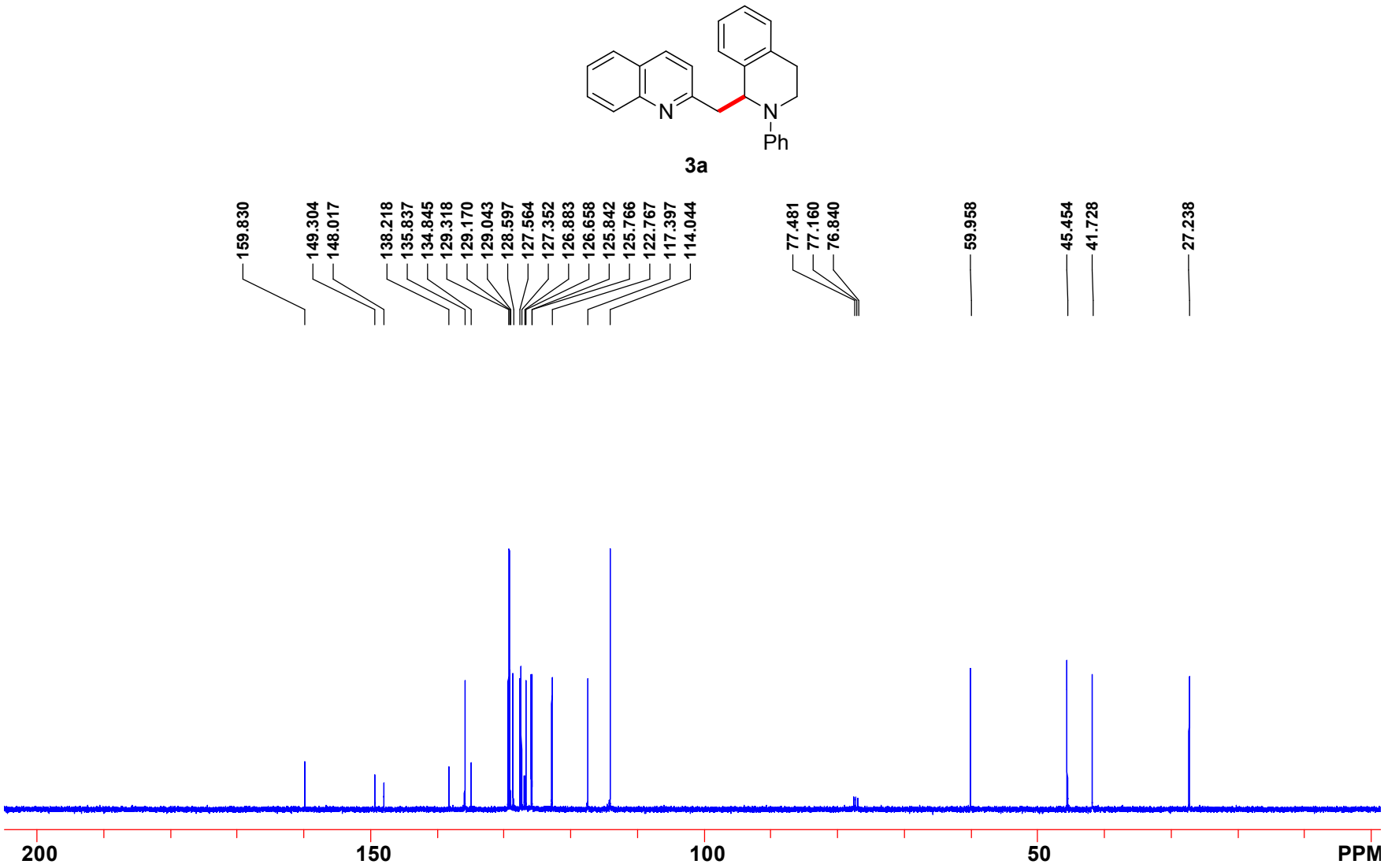
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122.767
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50
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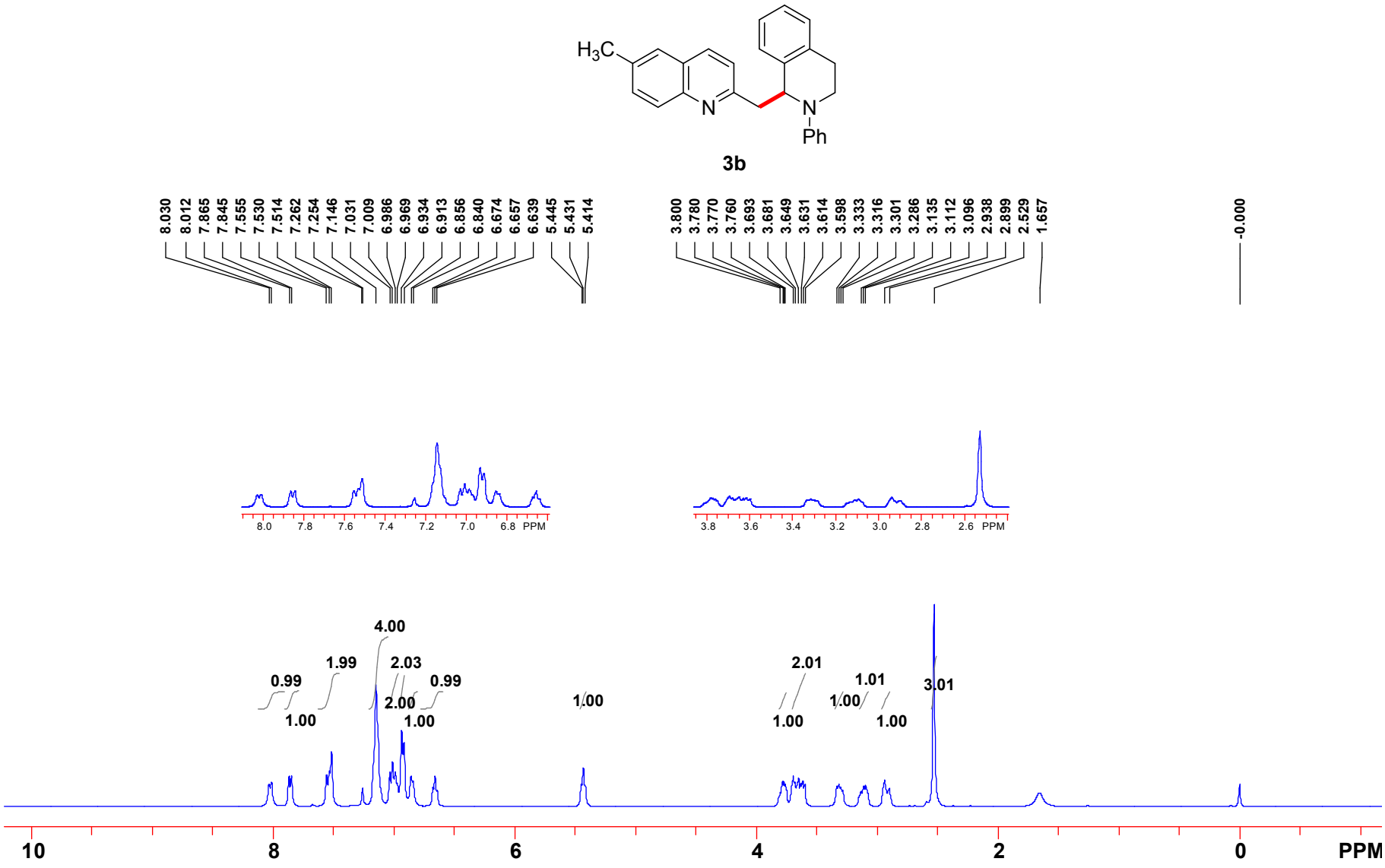
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6.674
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3.631
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3.333
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3.286
3.135
3.112
3.096
2.938
2.899
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1.657
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1.99
4.00
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1.01
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3.01
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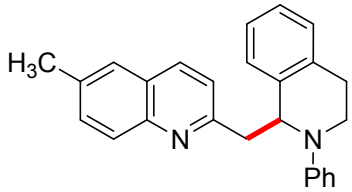
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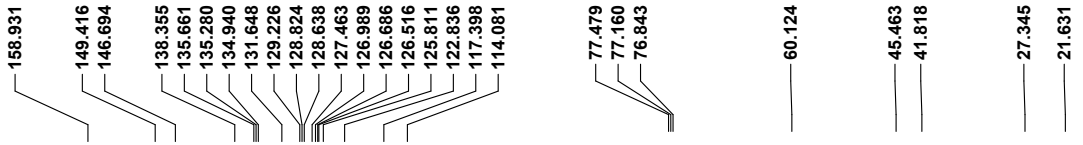
Ph

3b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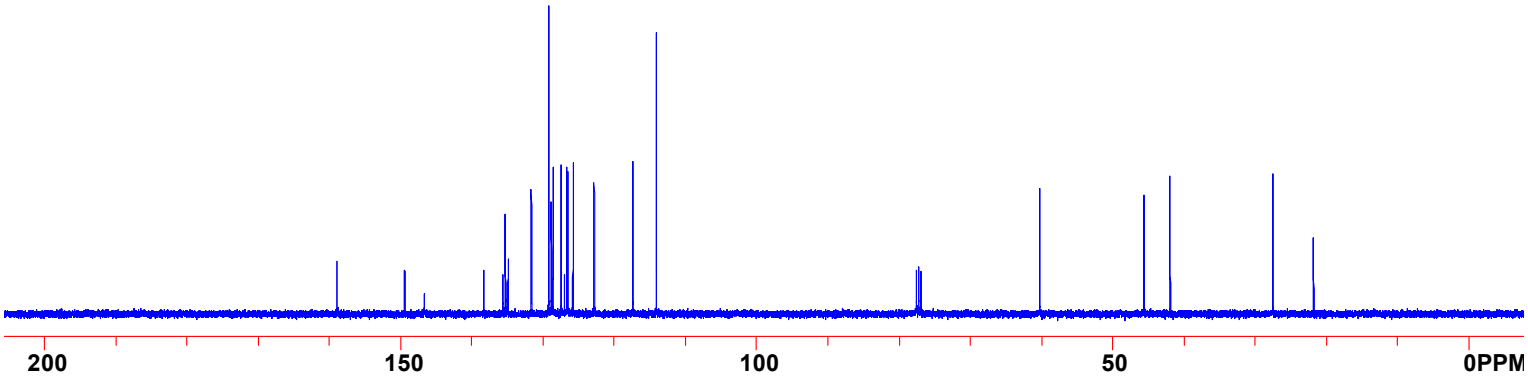
21.631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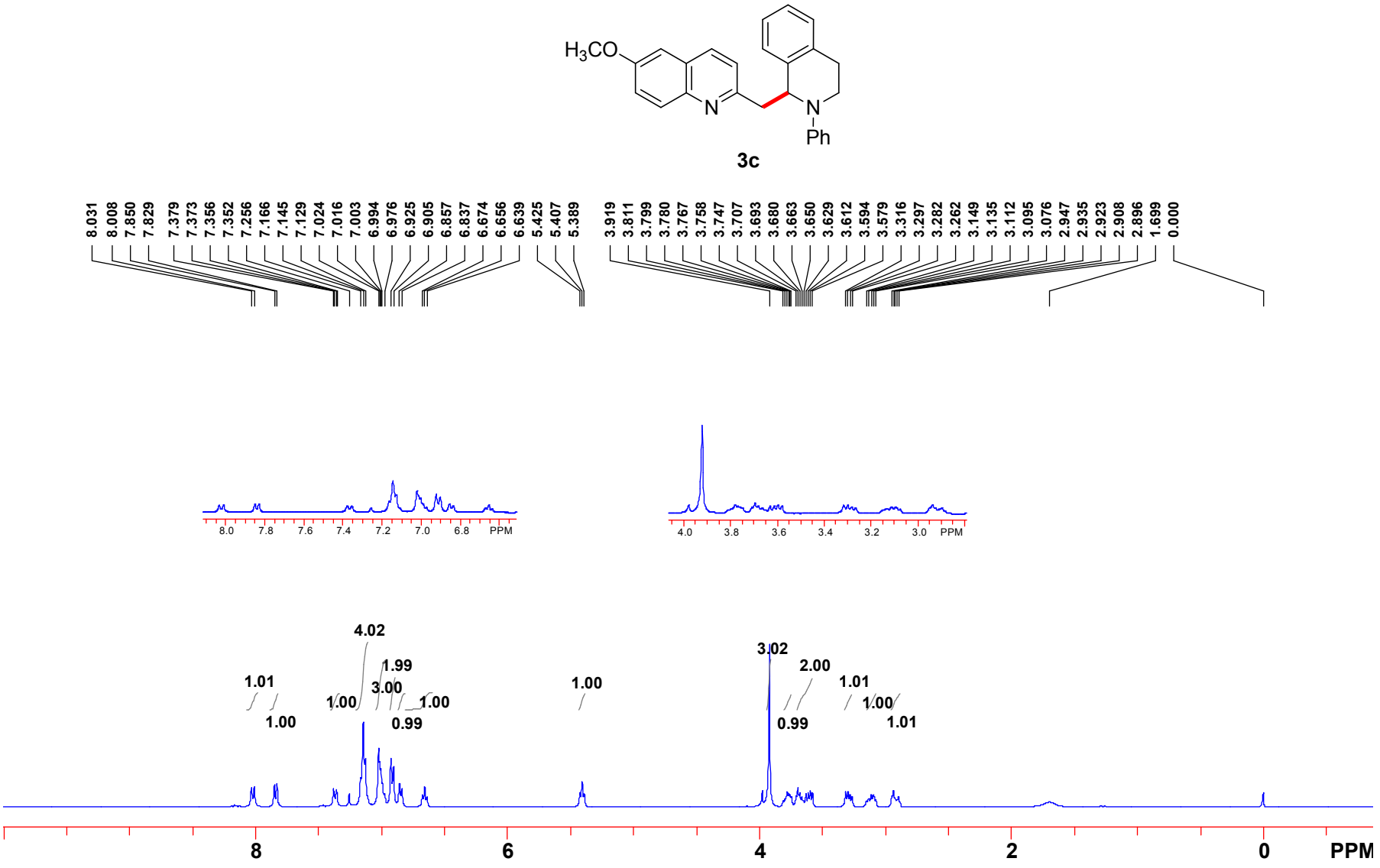
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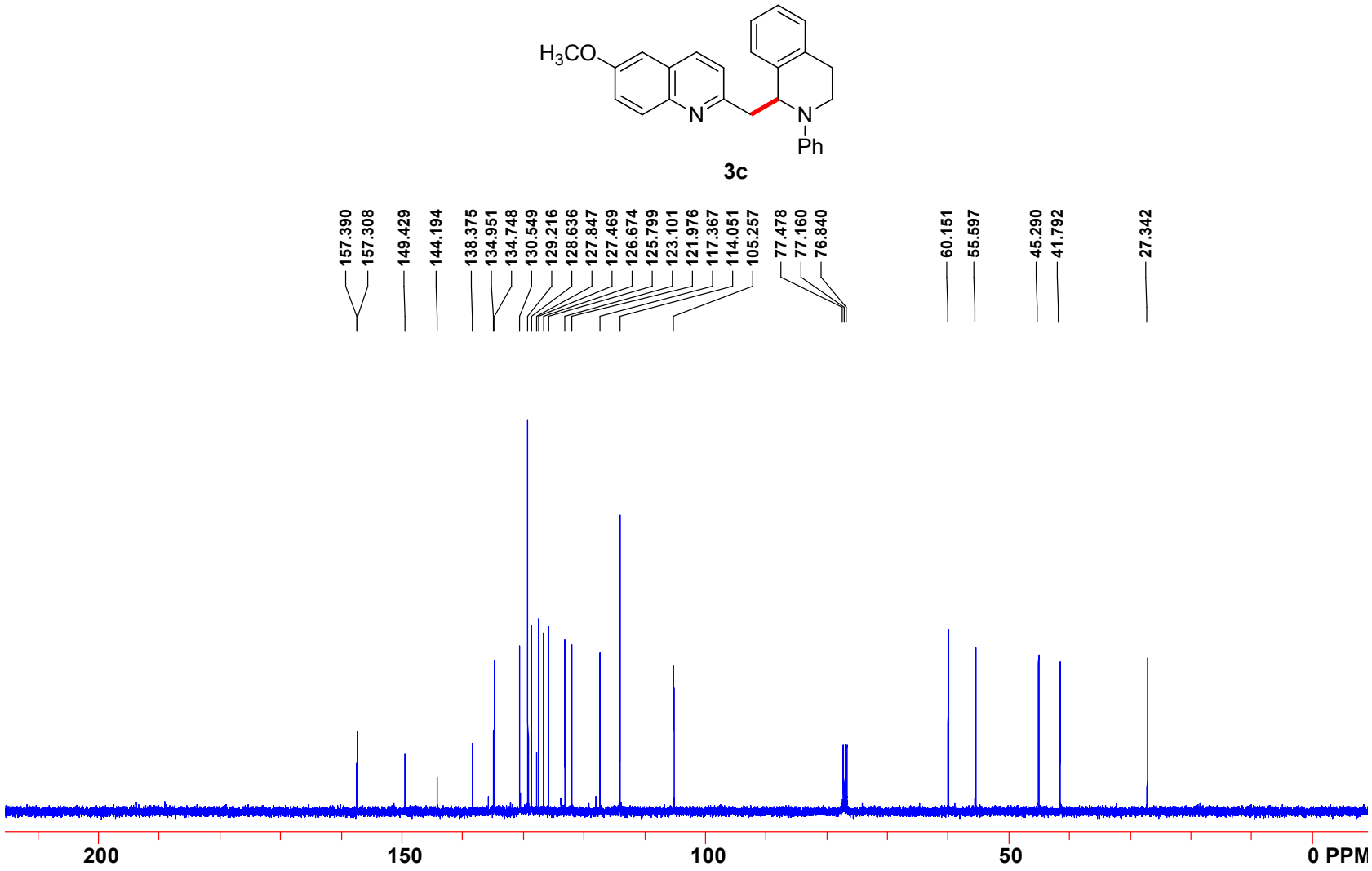
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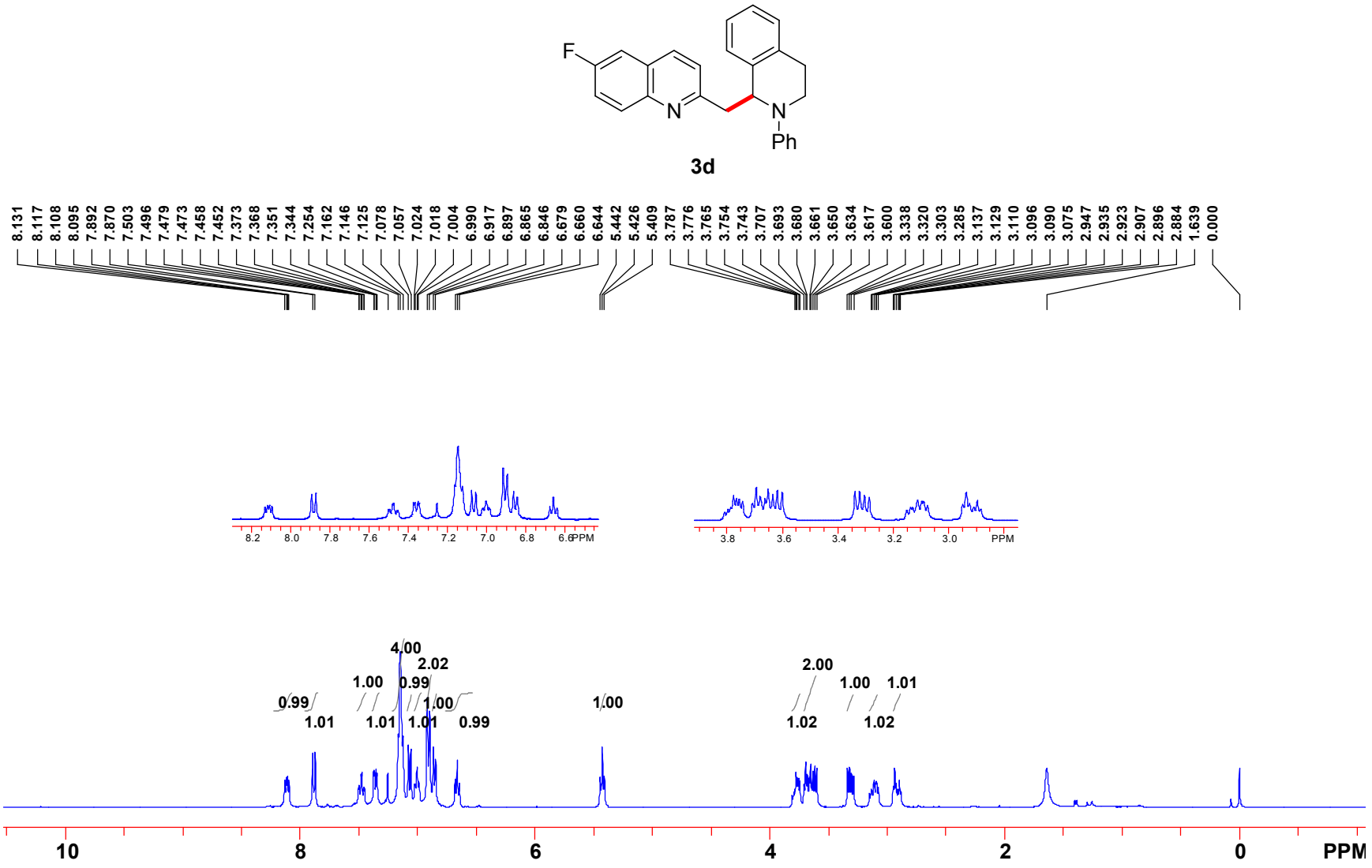
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3.8 3.6 3.4 3.2 3.0 PPM
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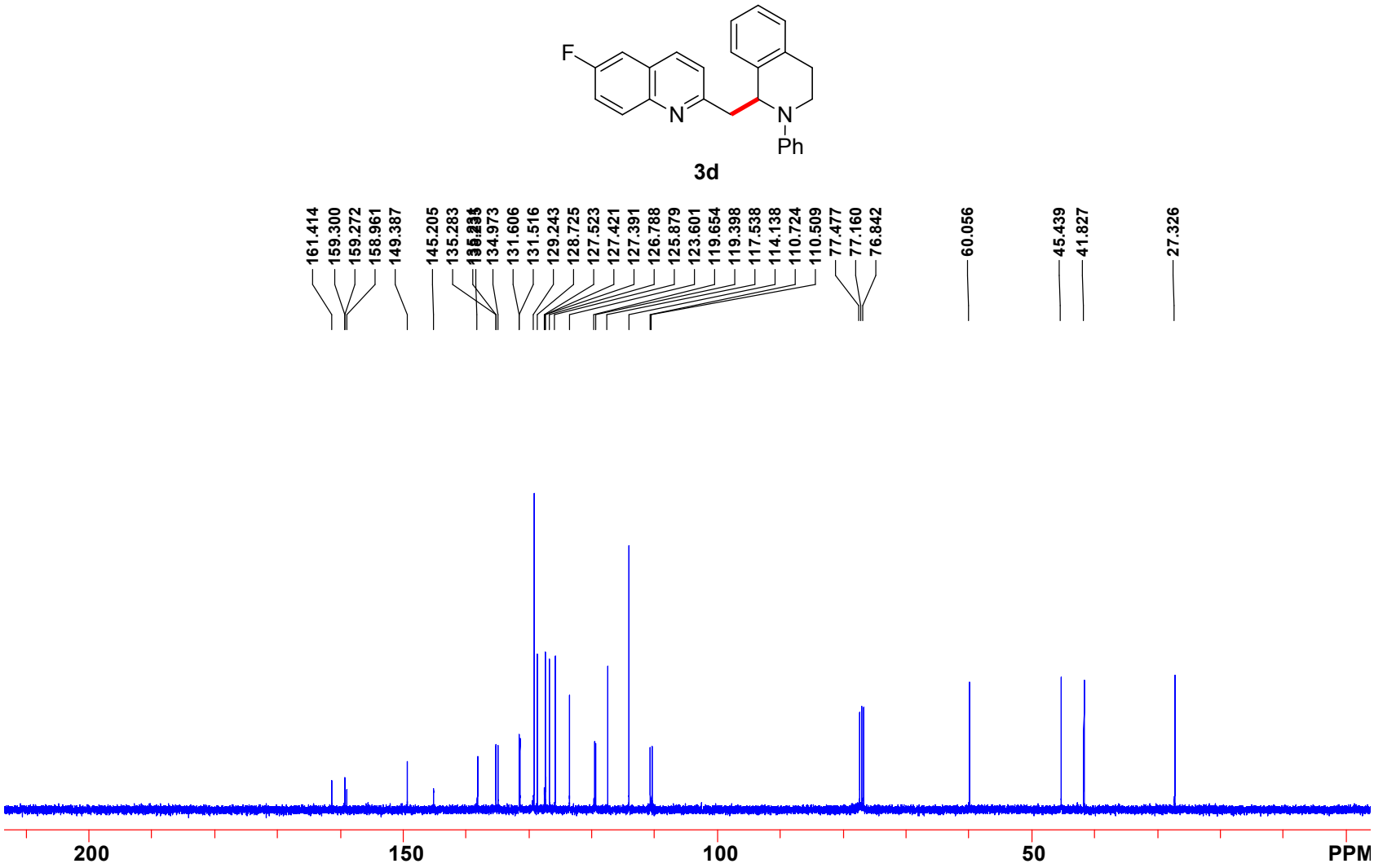
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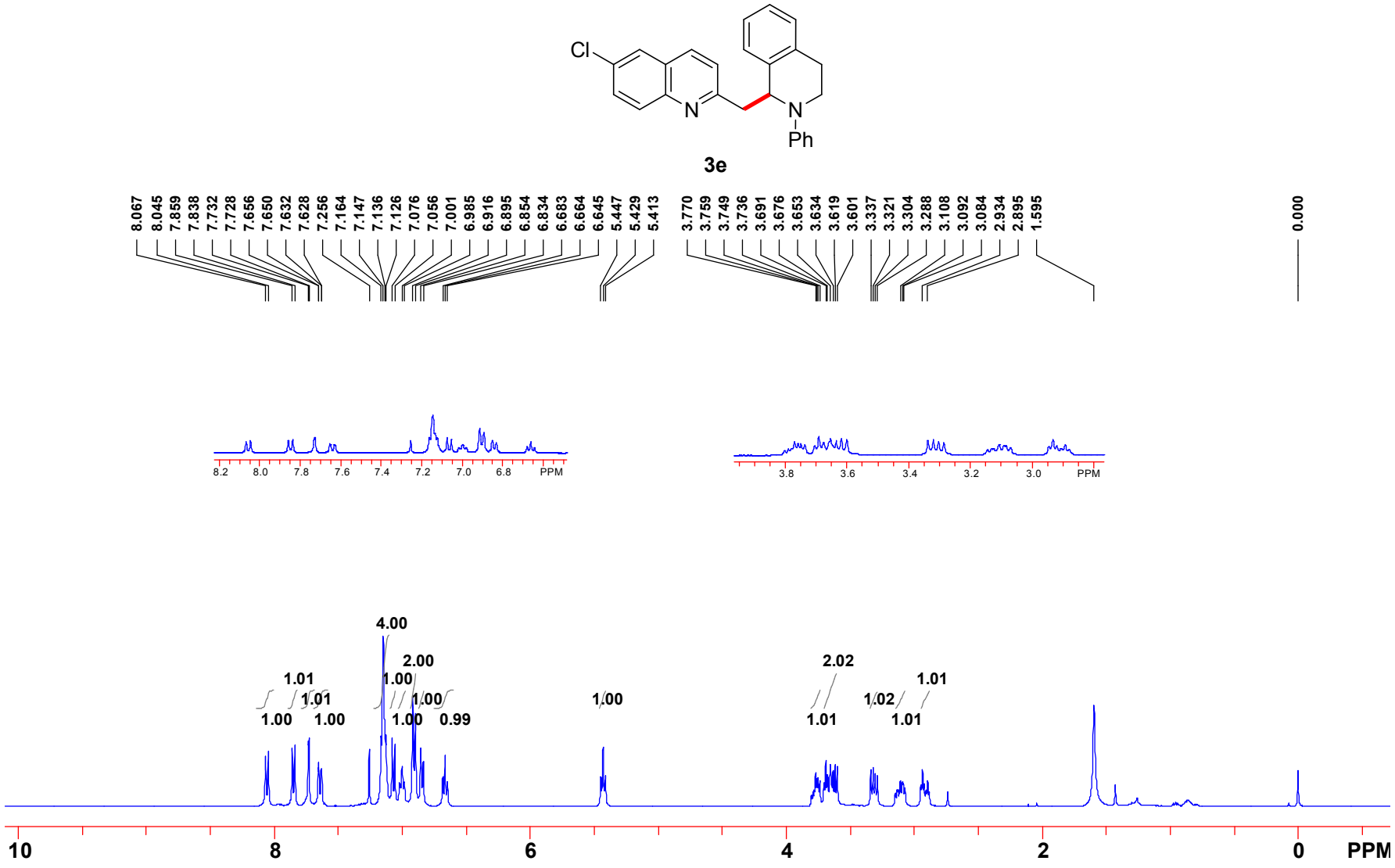
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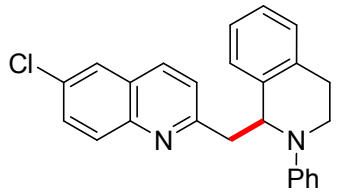
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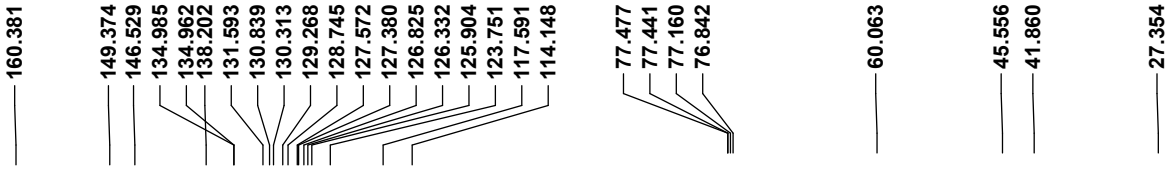
Ph

3e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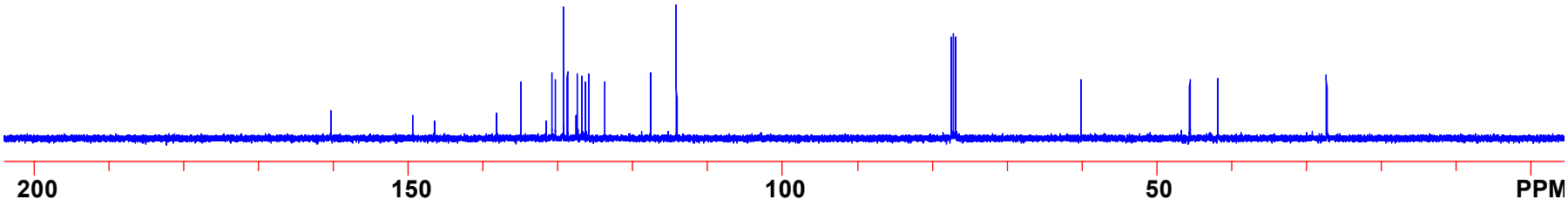
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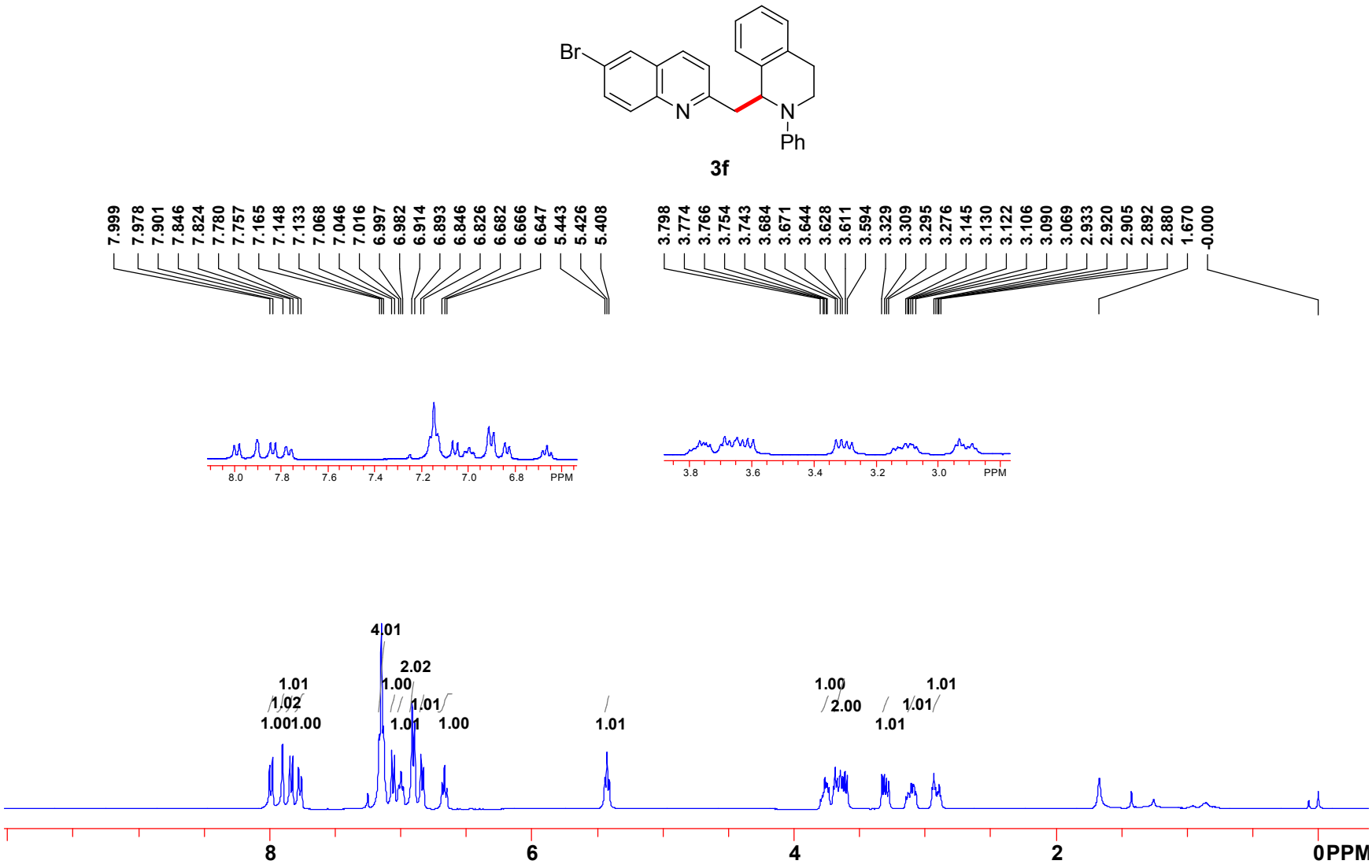
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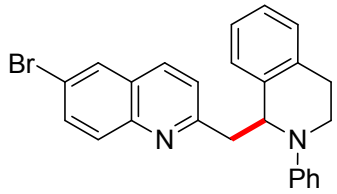
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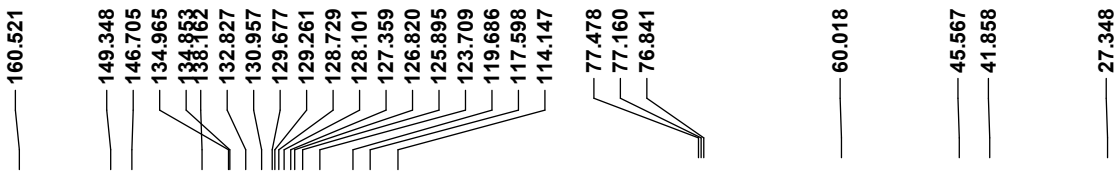
Ph

3f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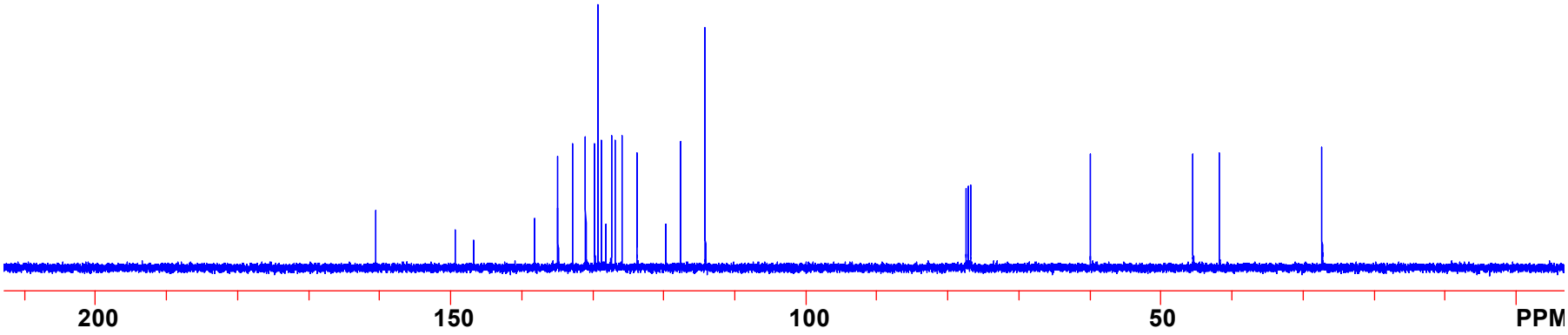
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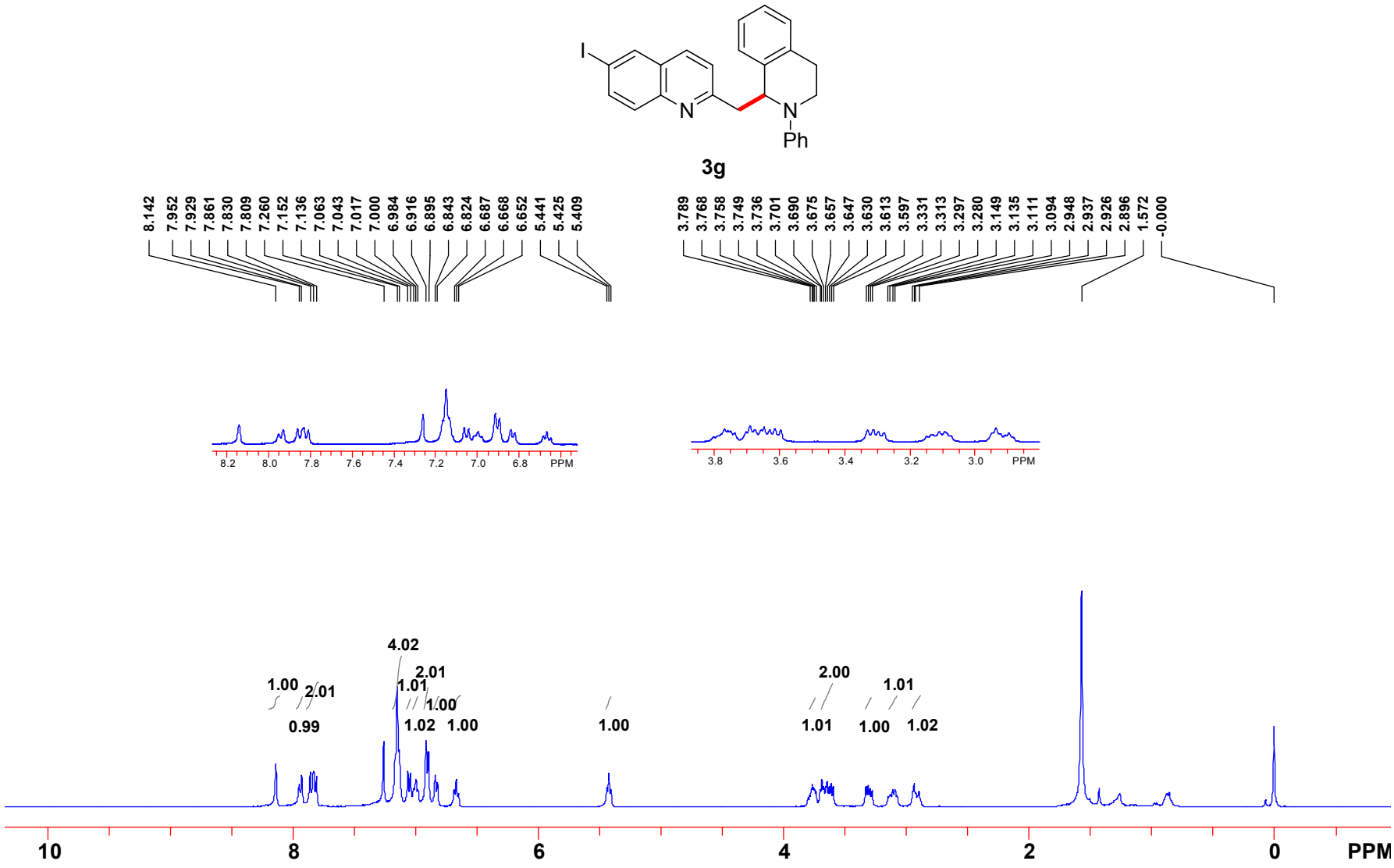
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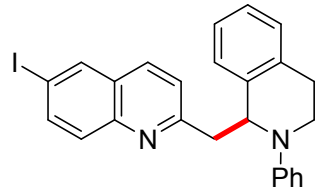
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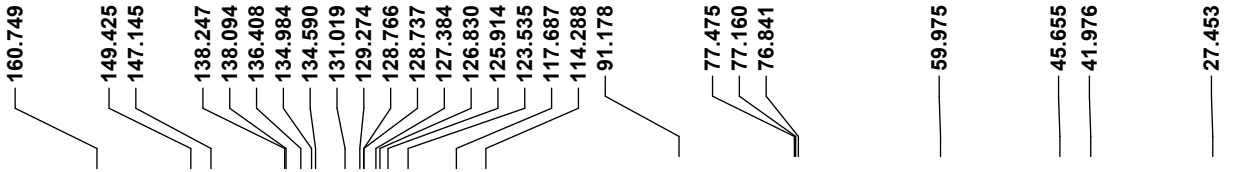
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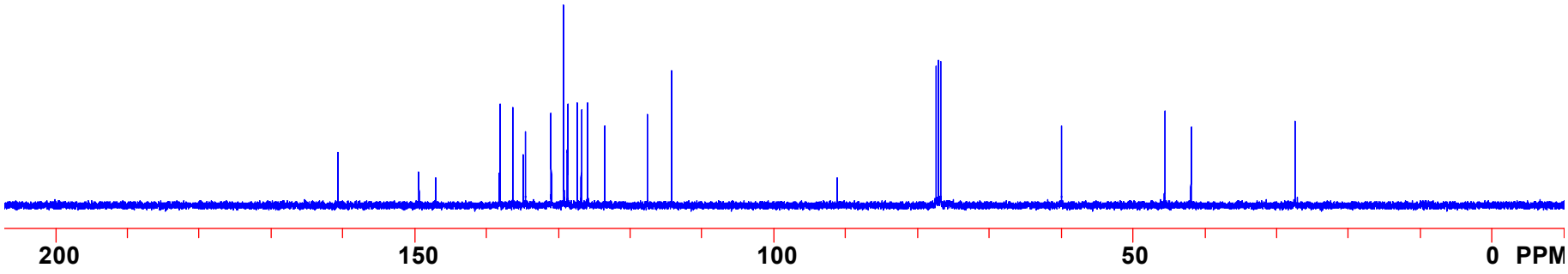
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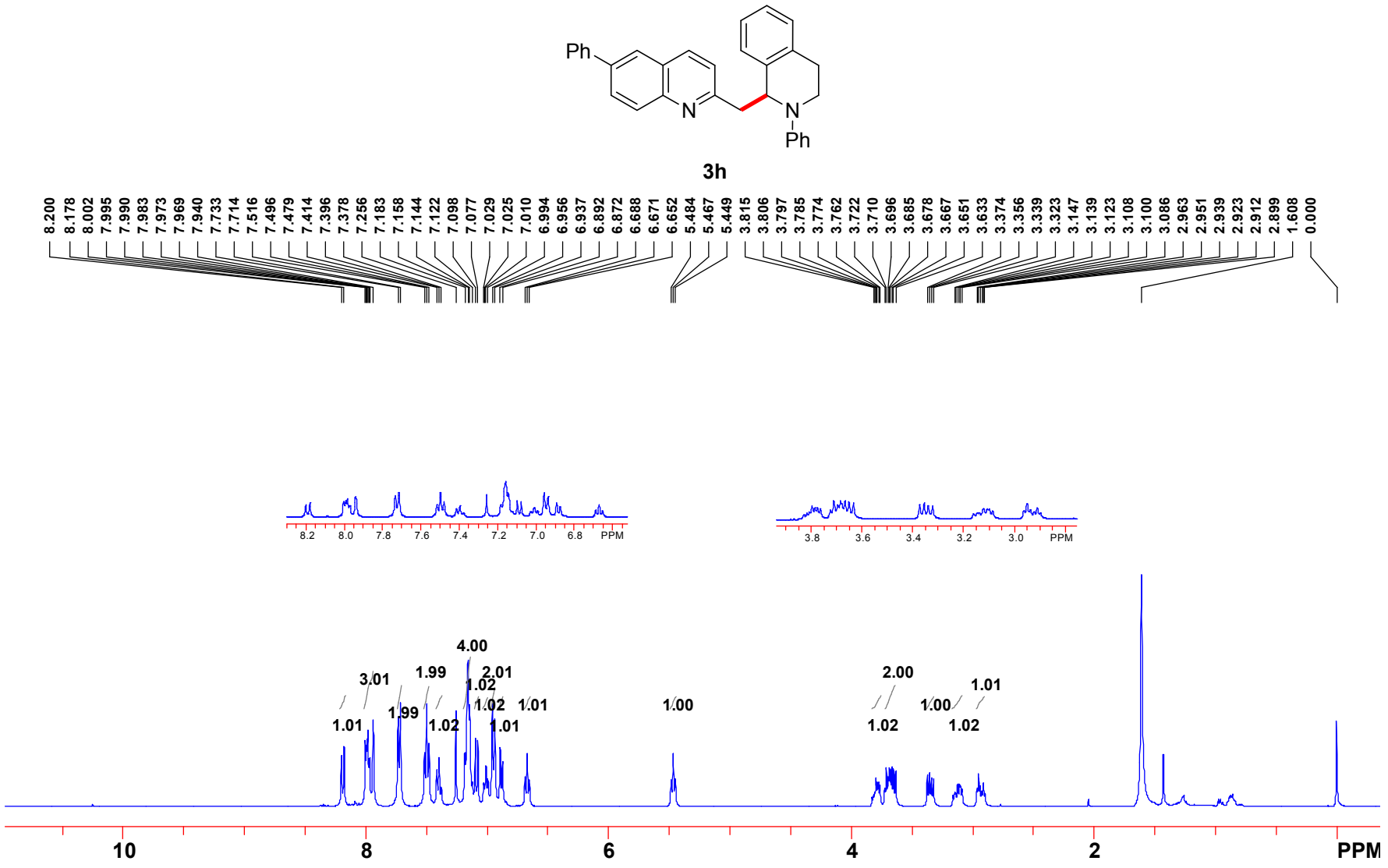
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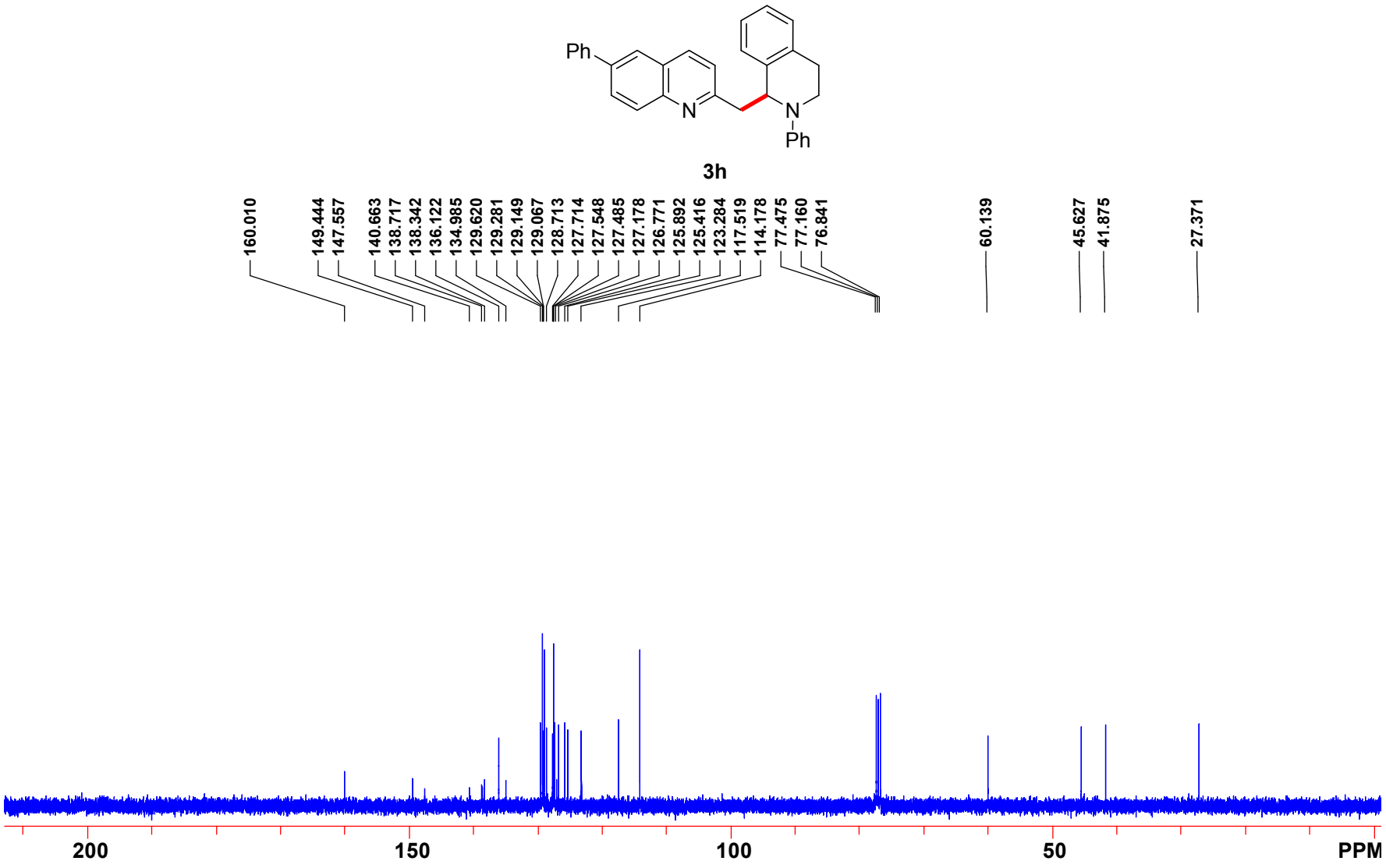
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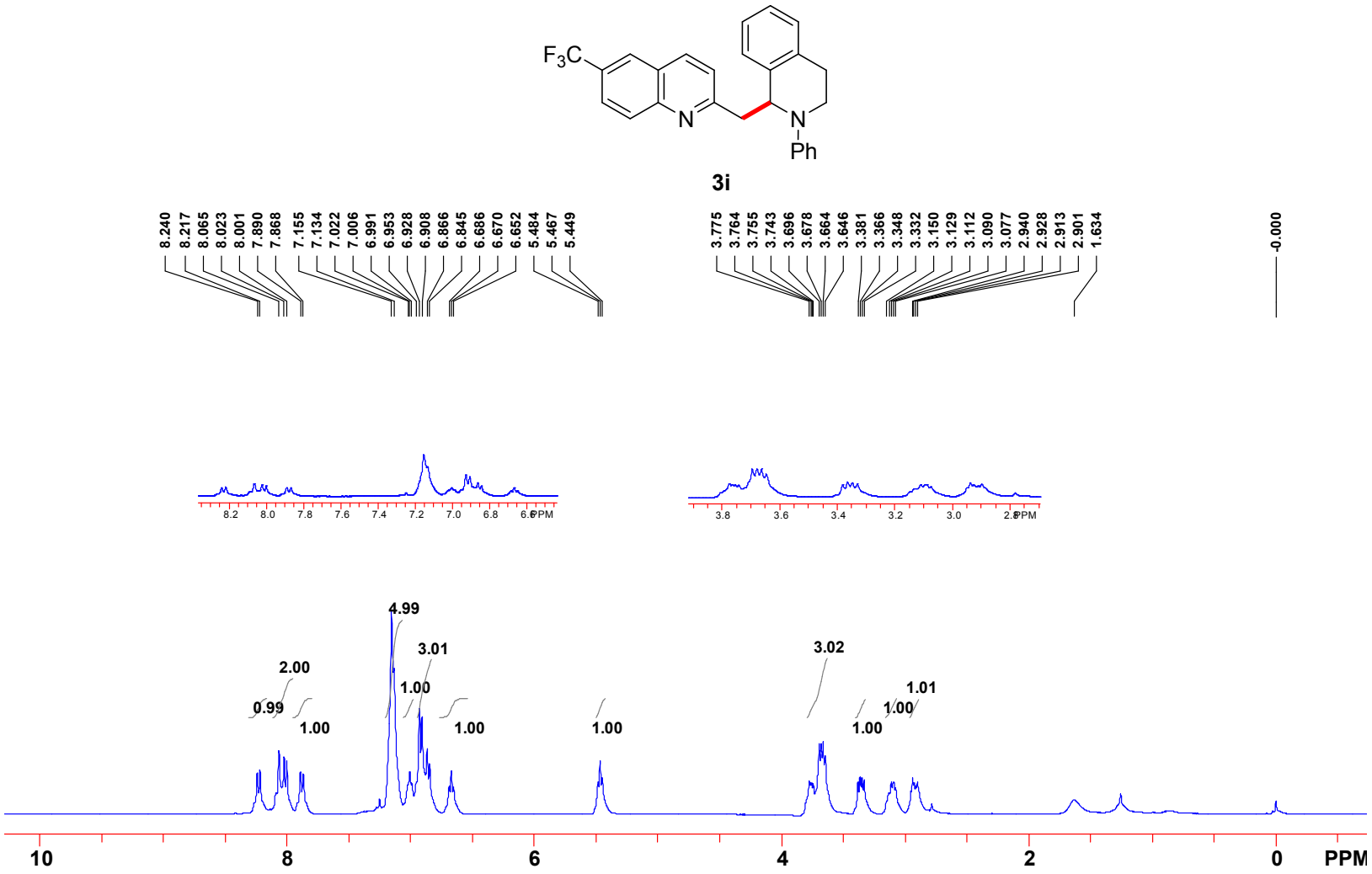
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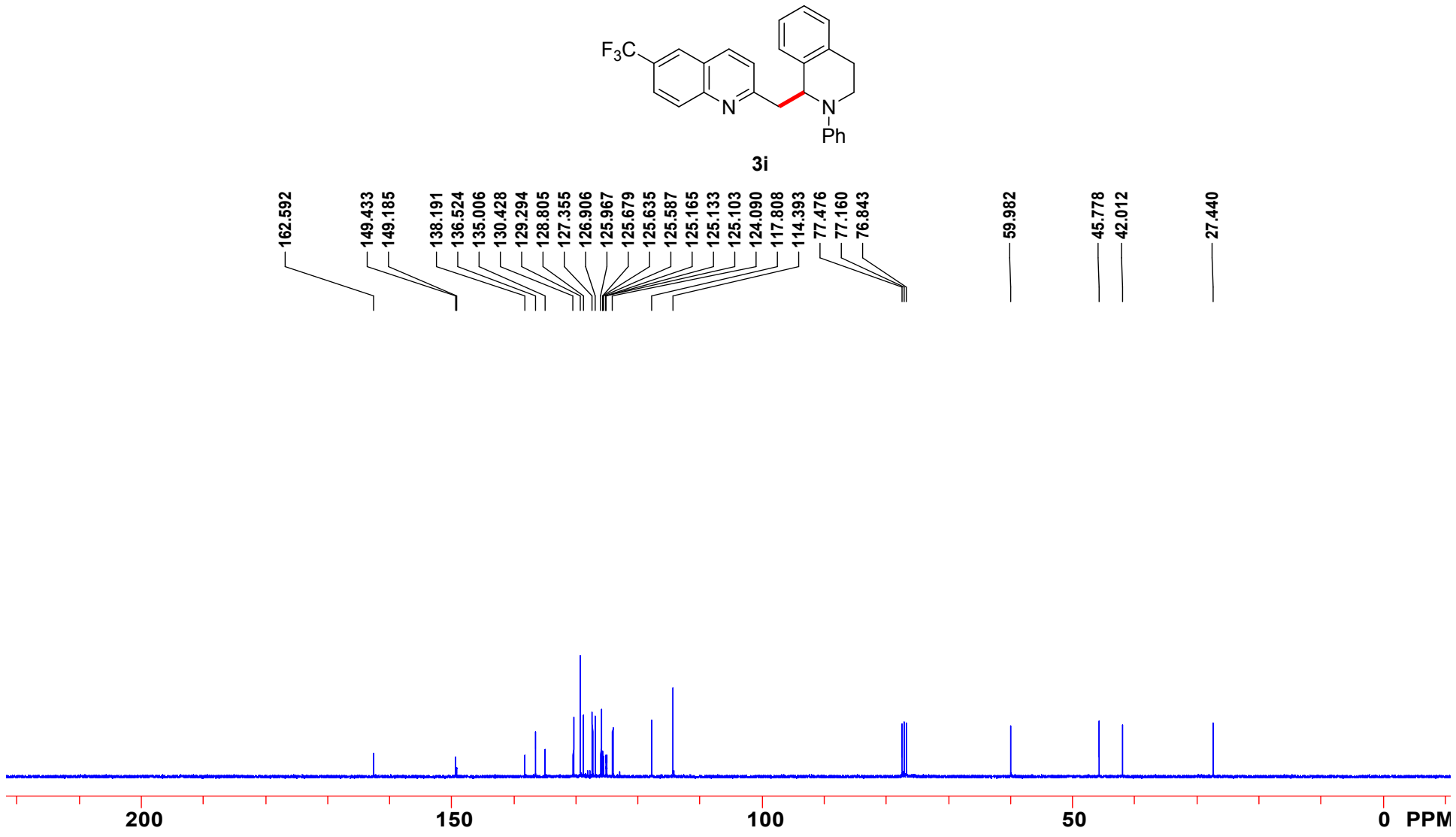
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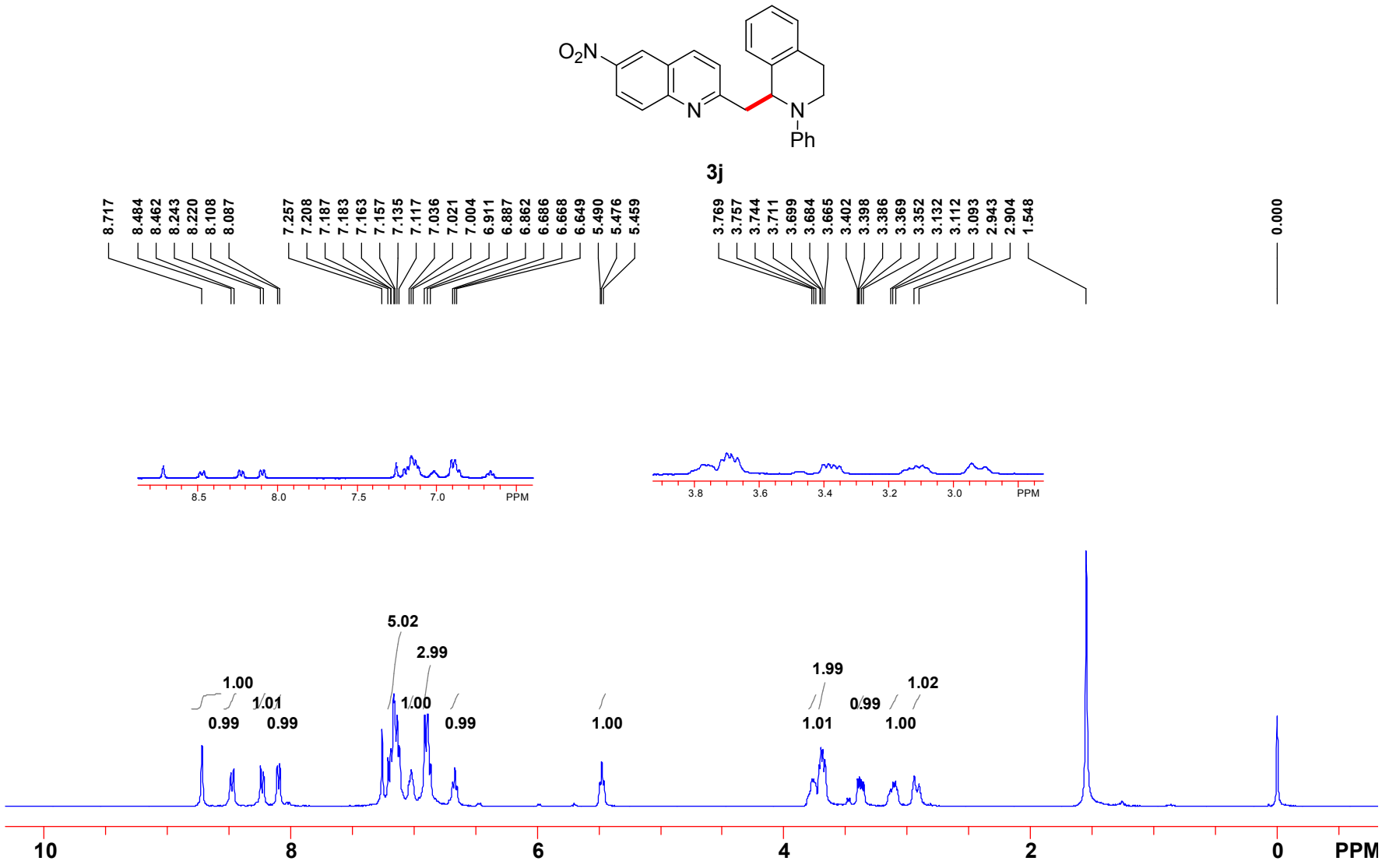
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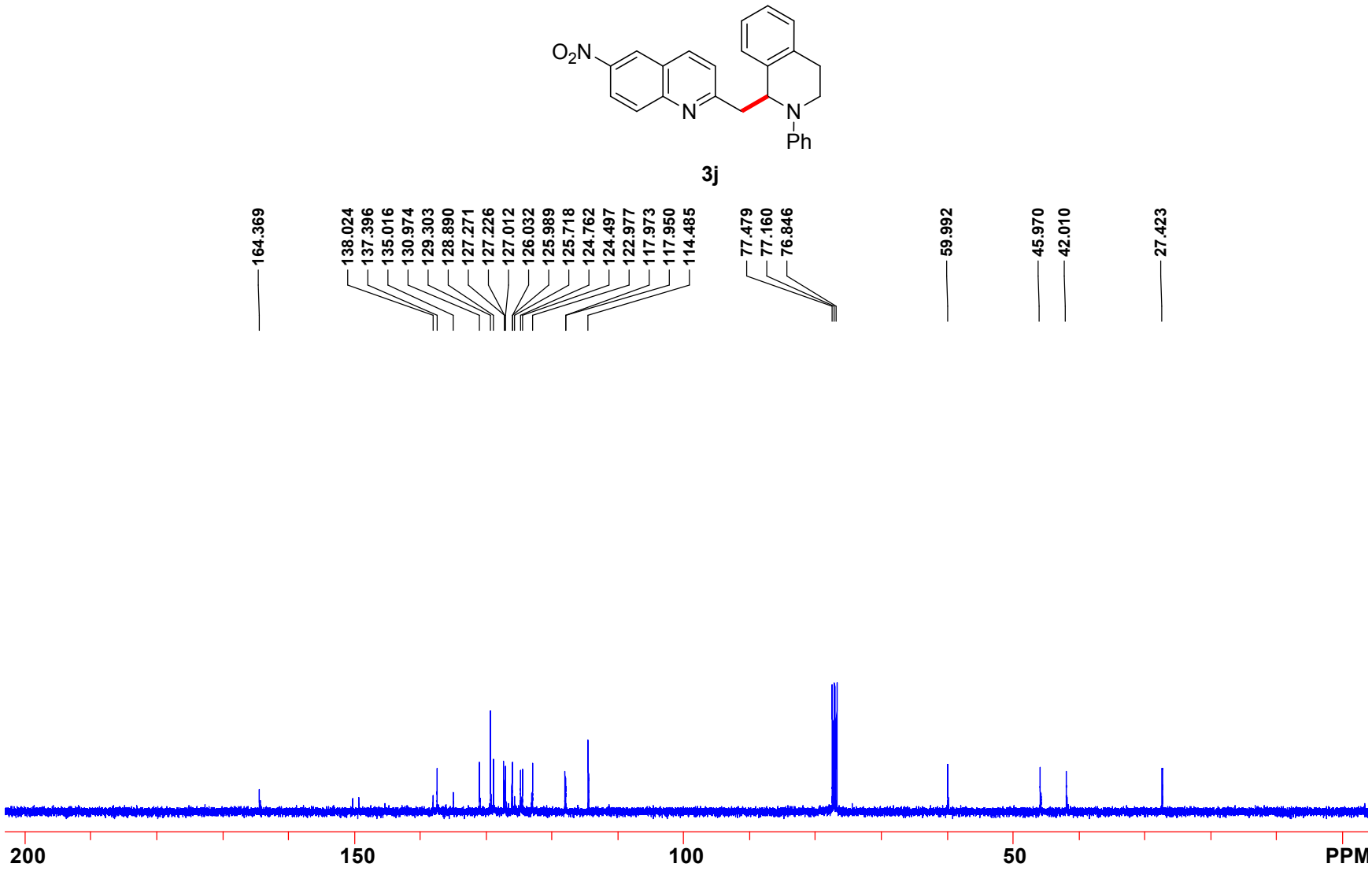
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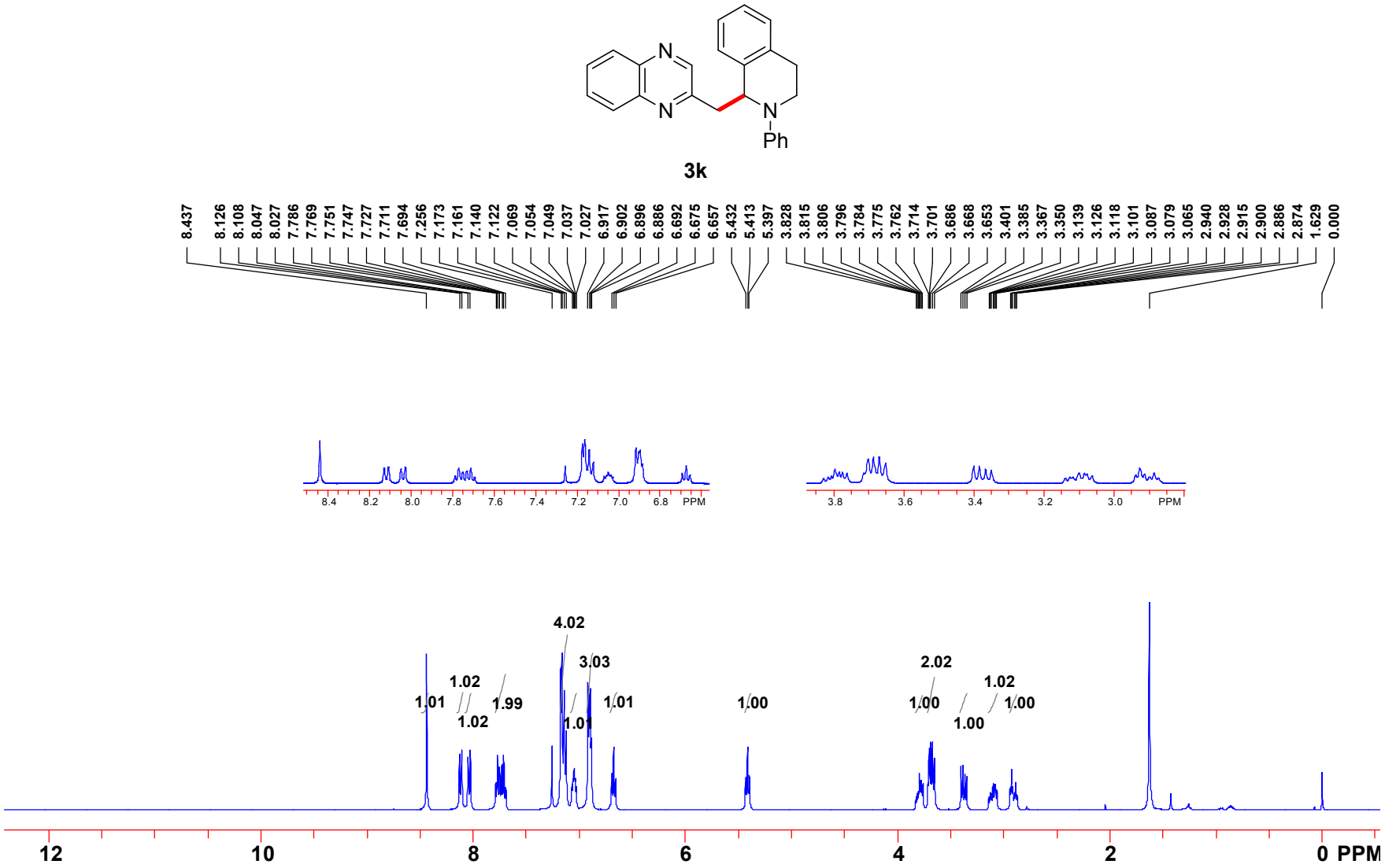
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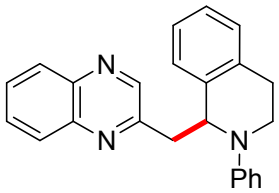
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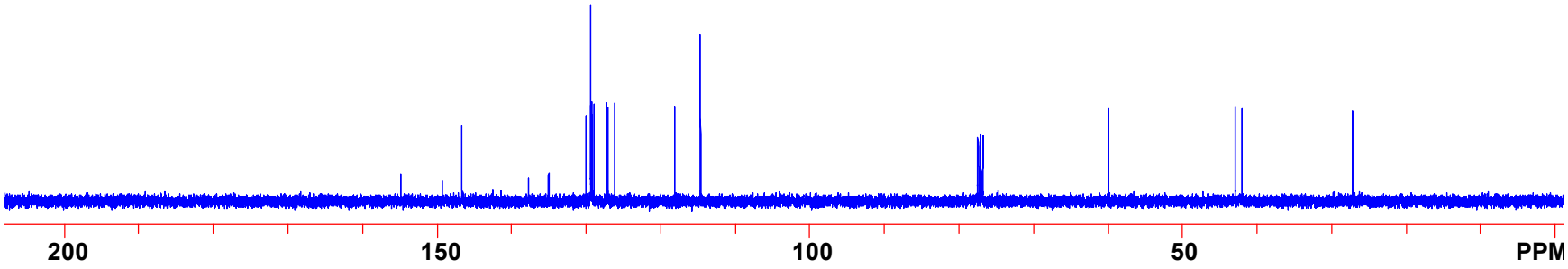
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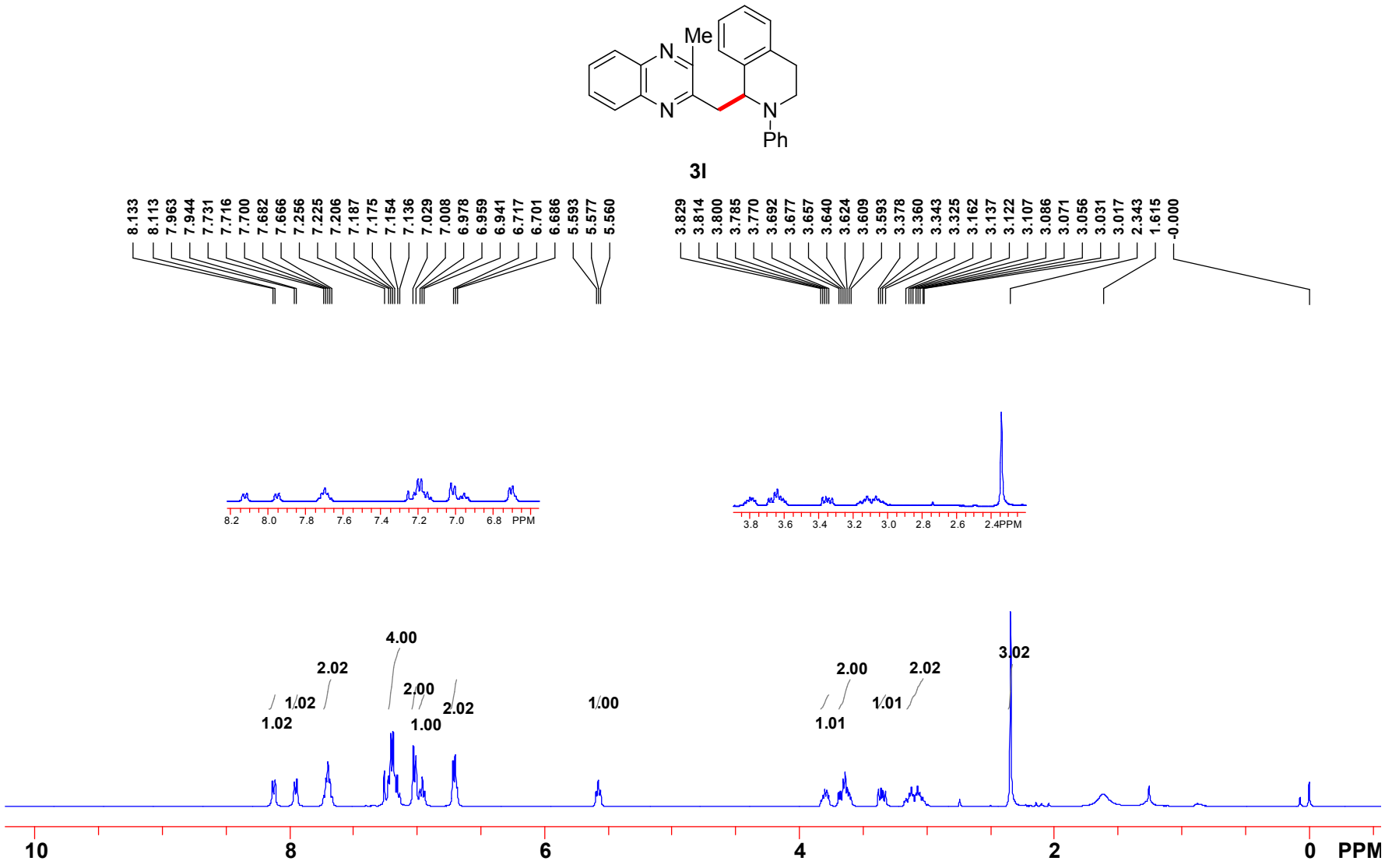
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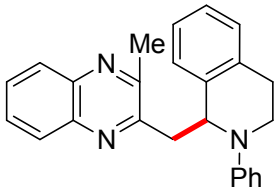
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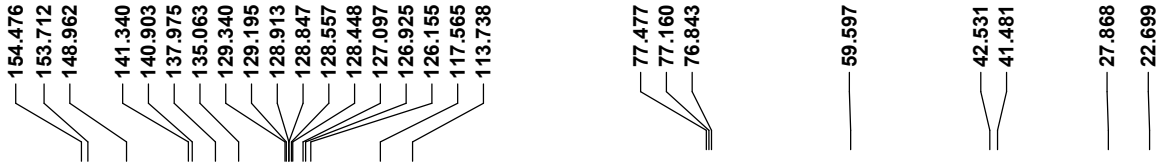
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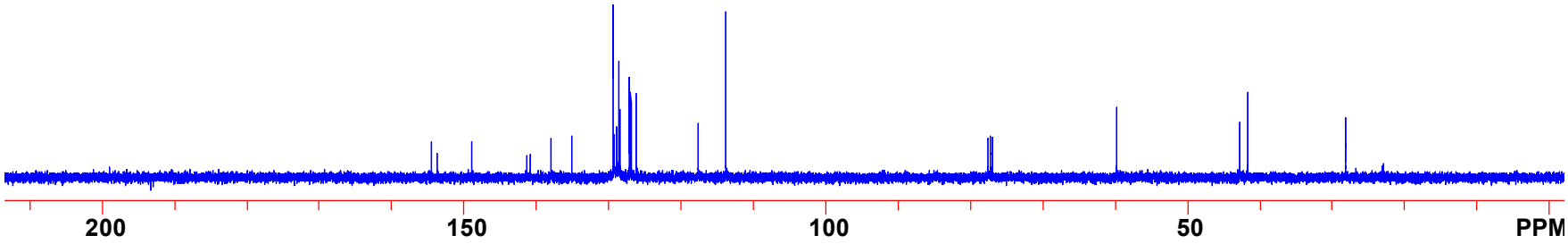
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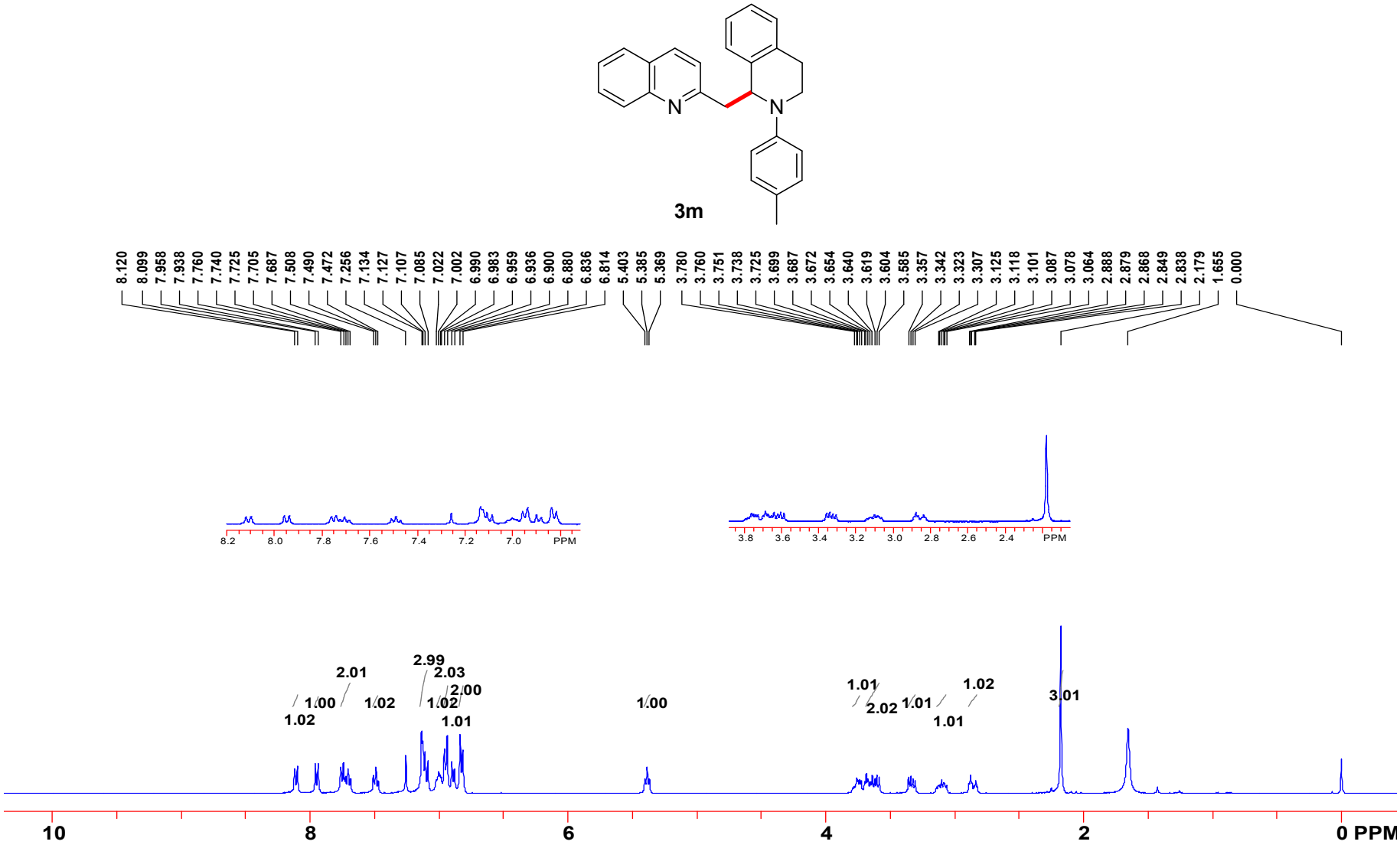
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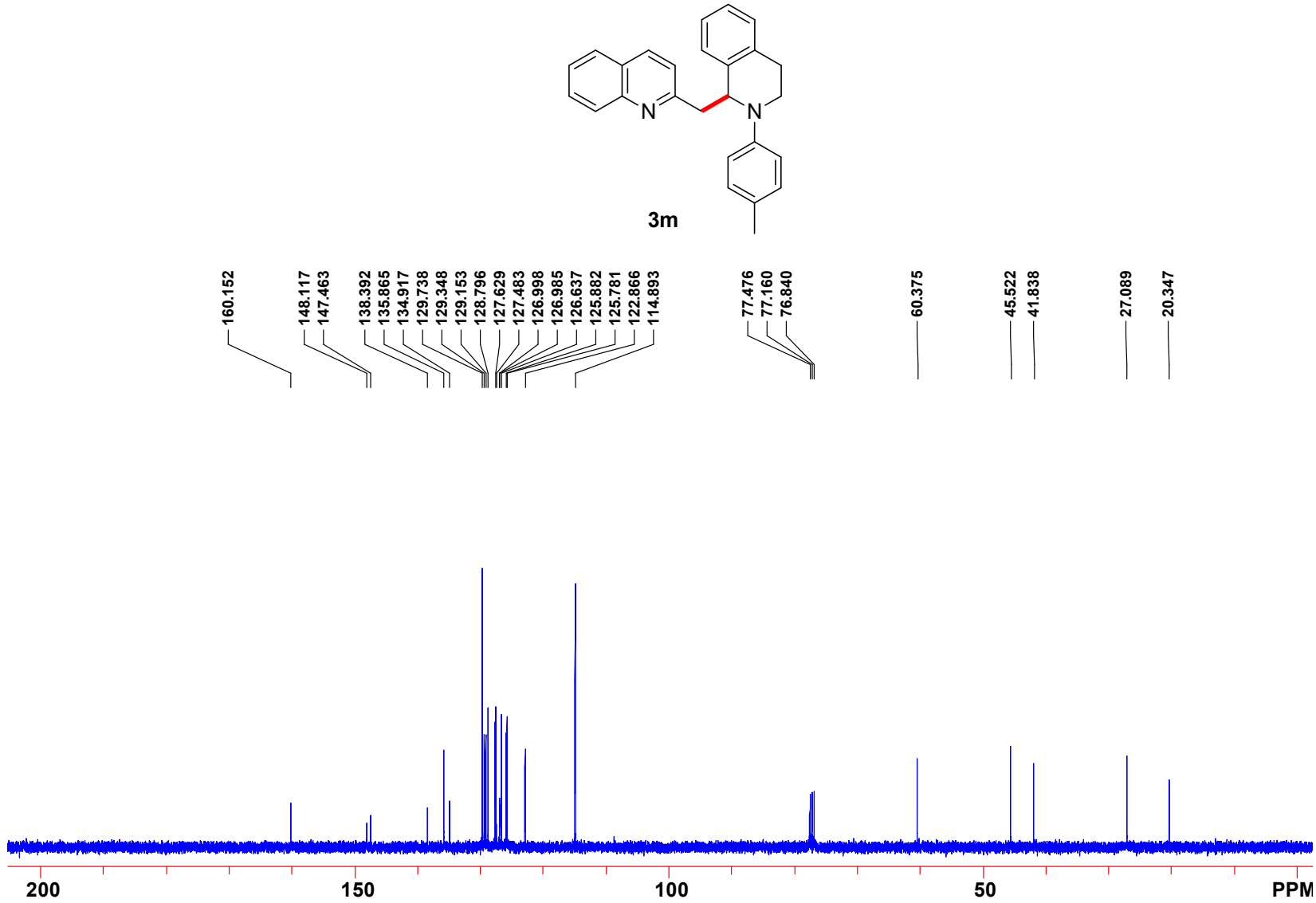
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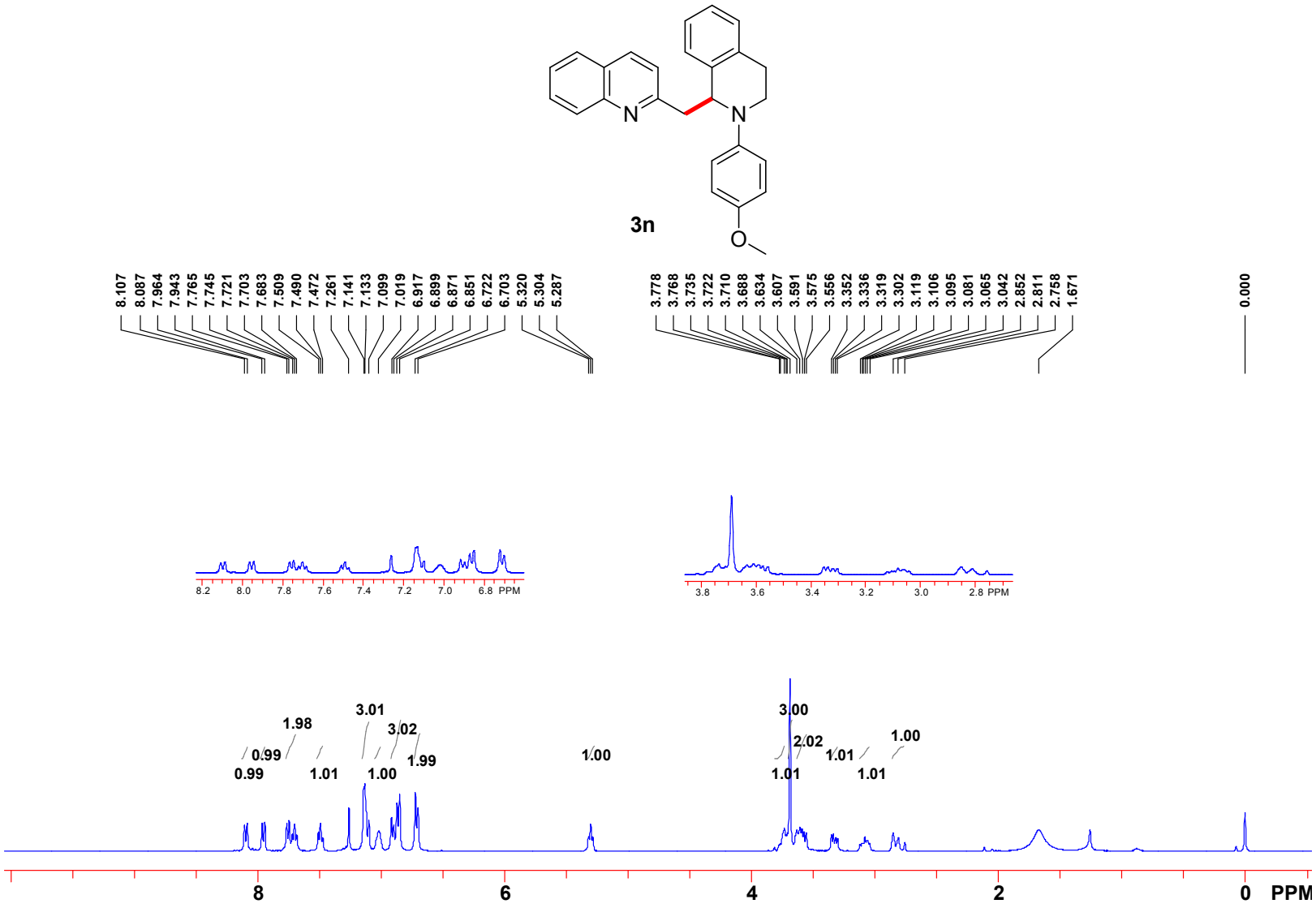
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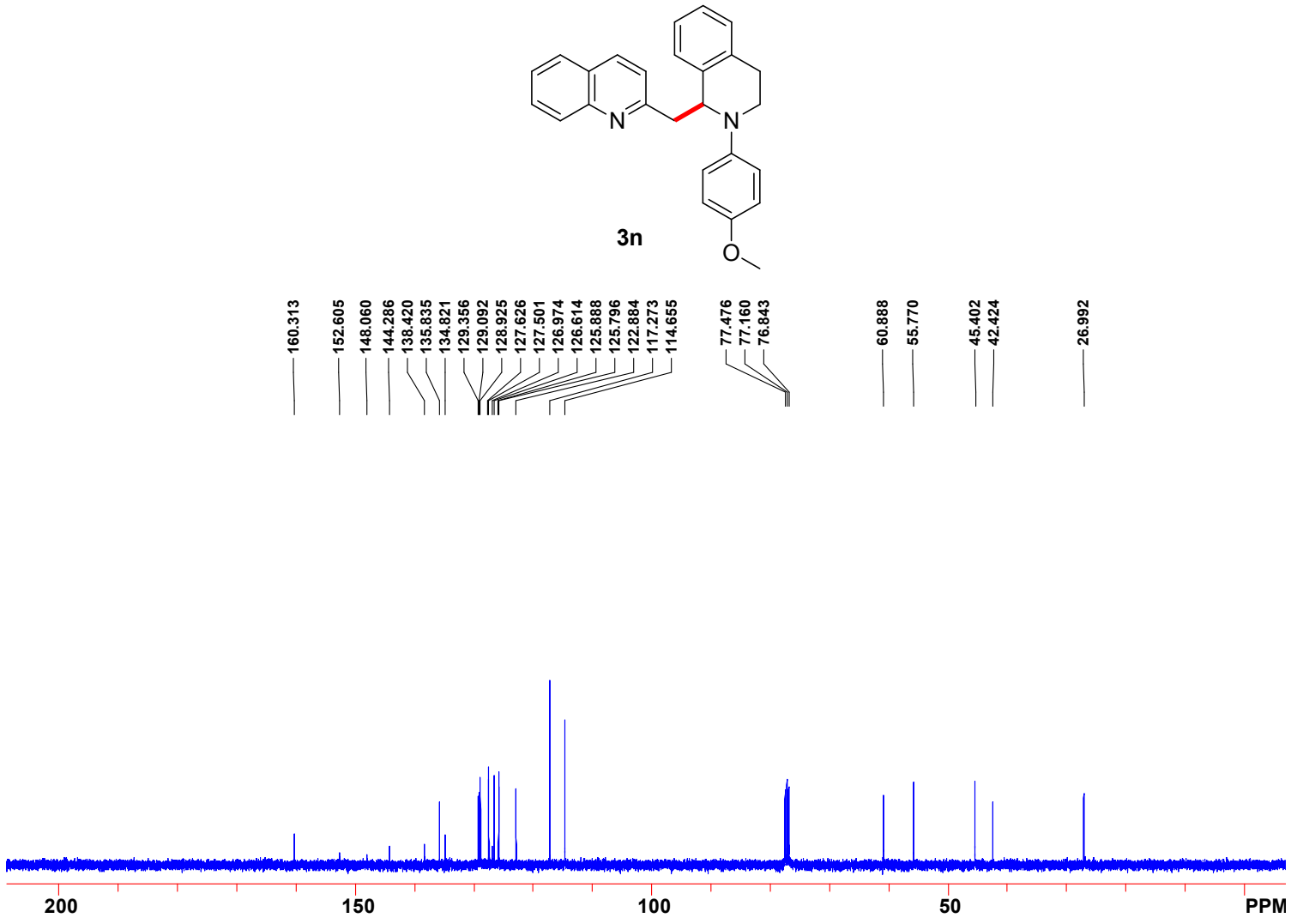
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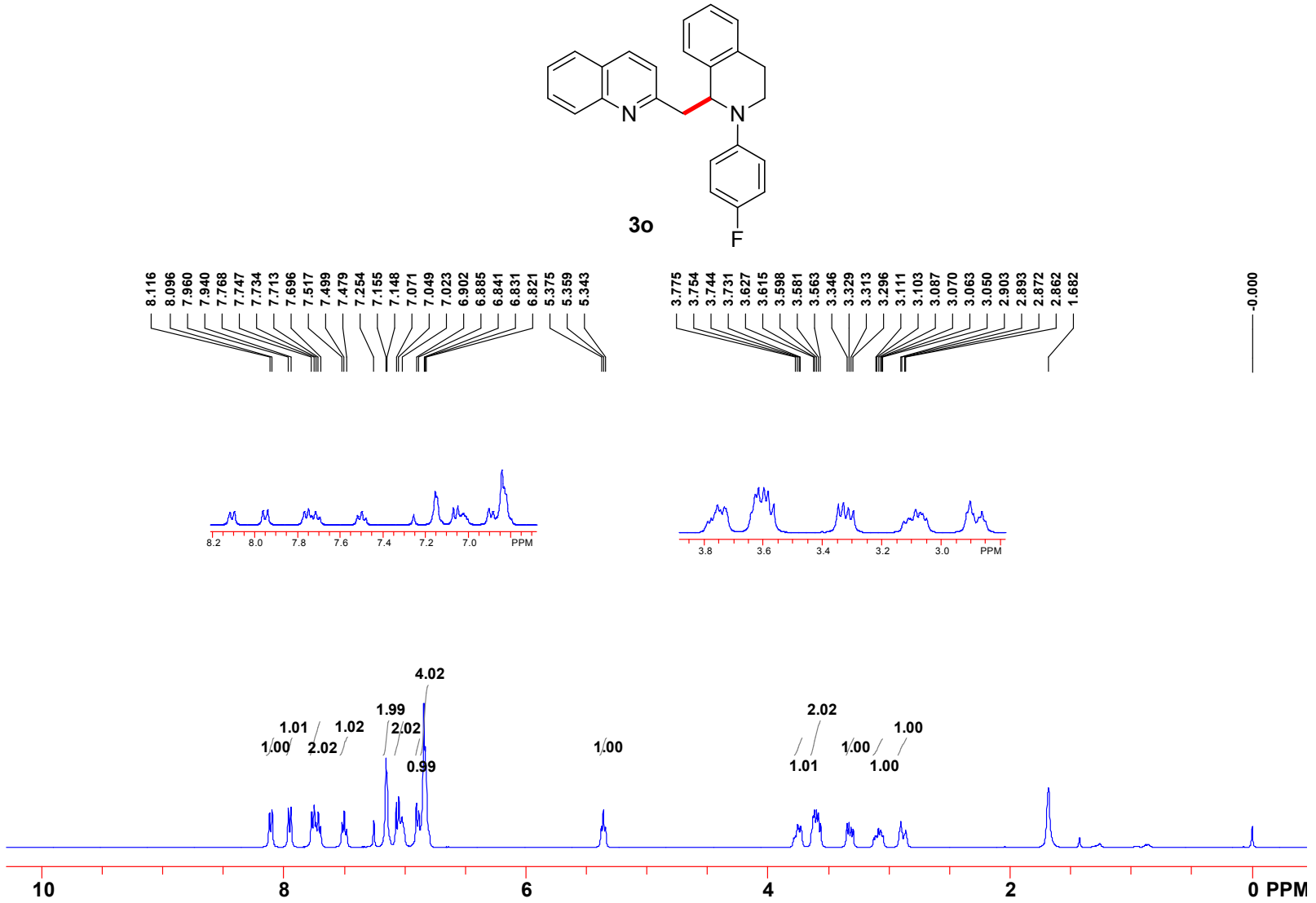
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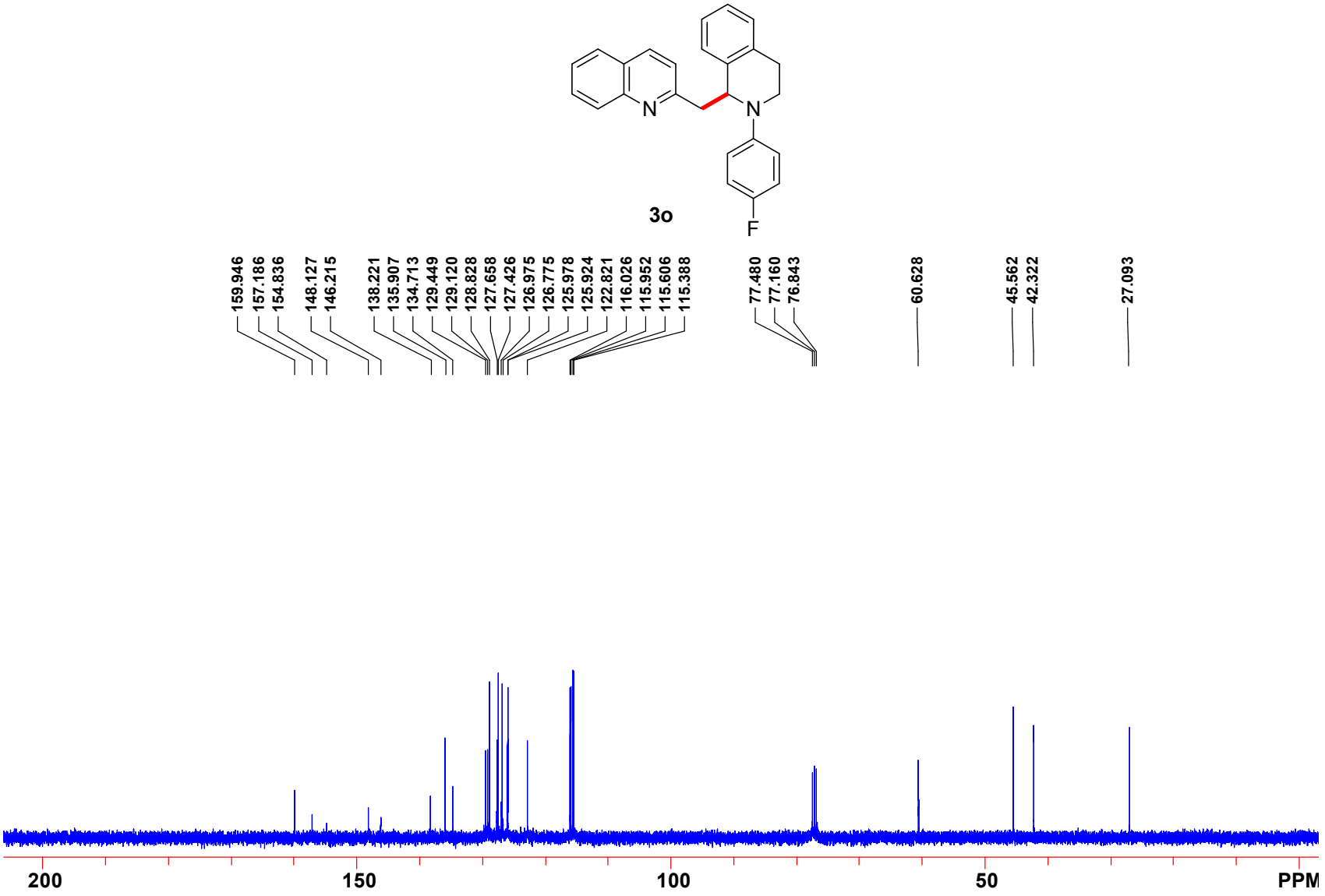
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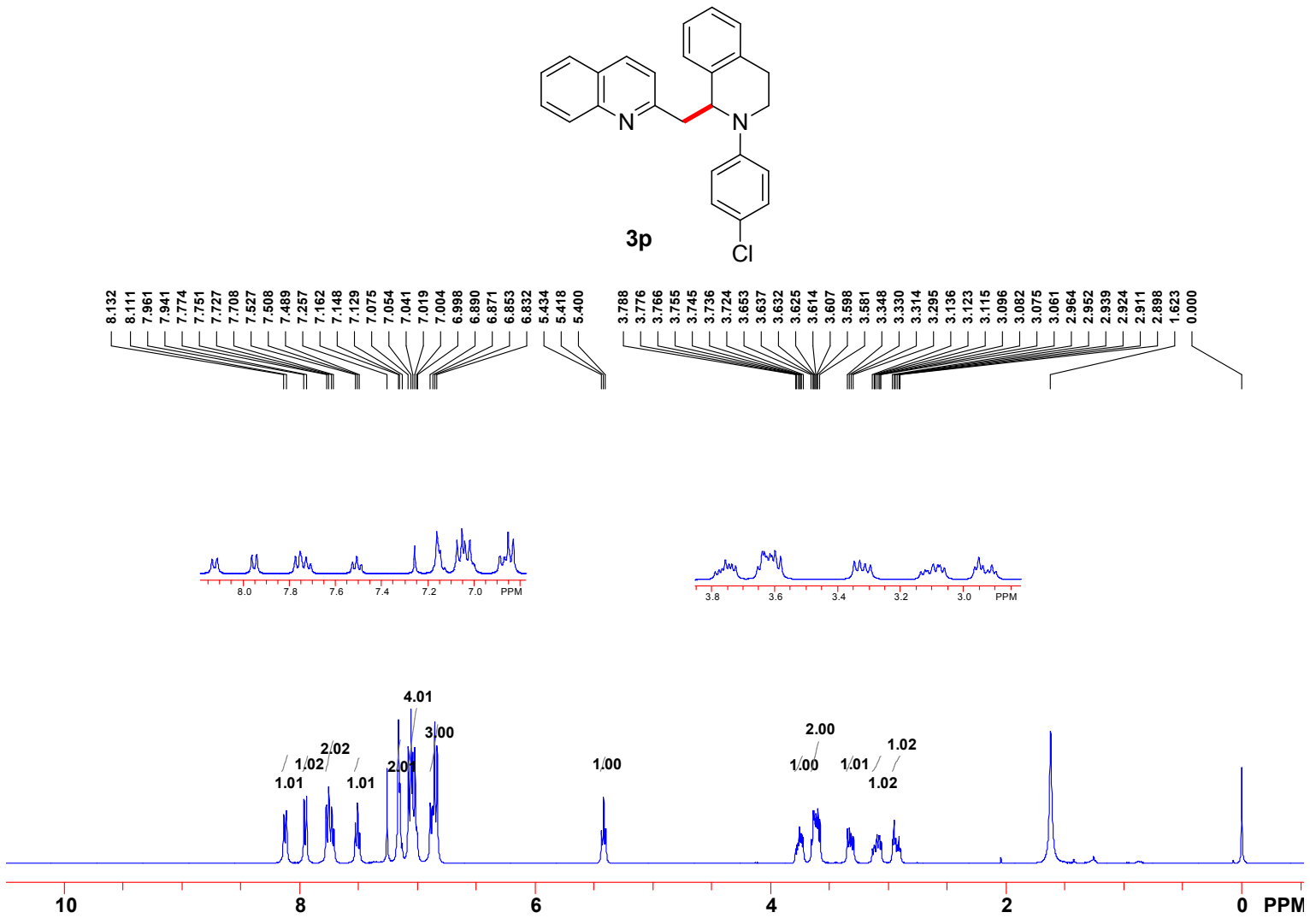
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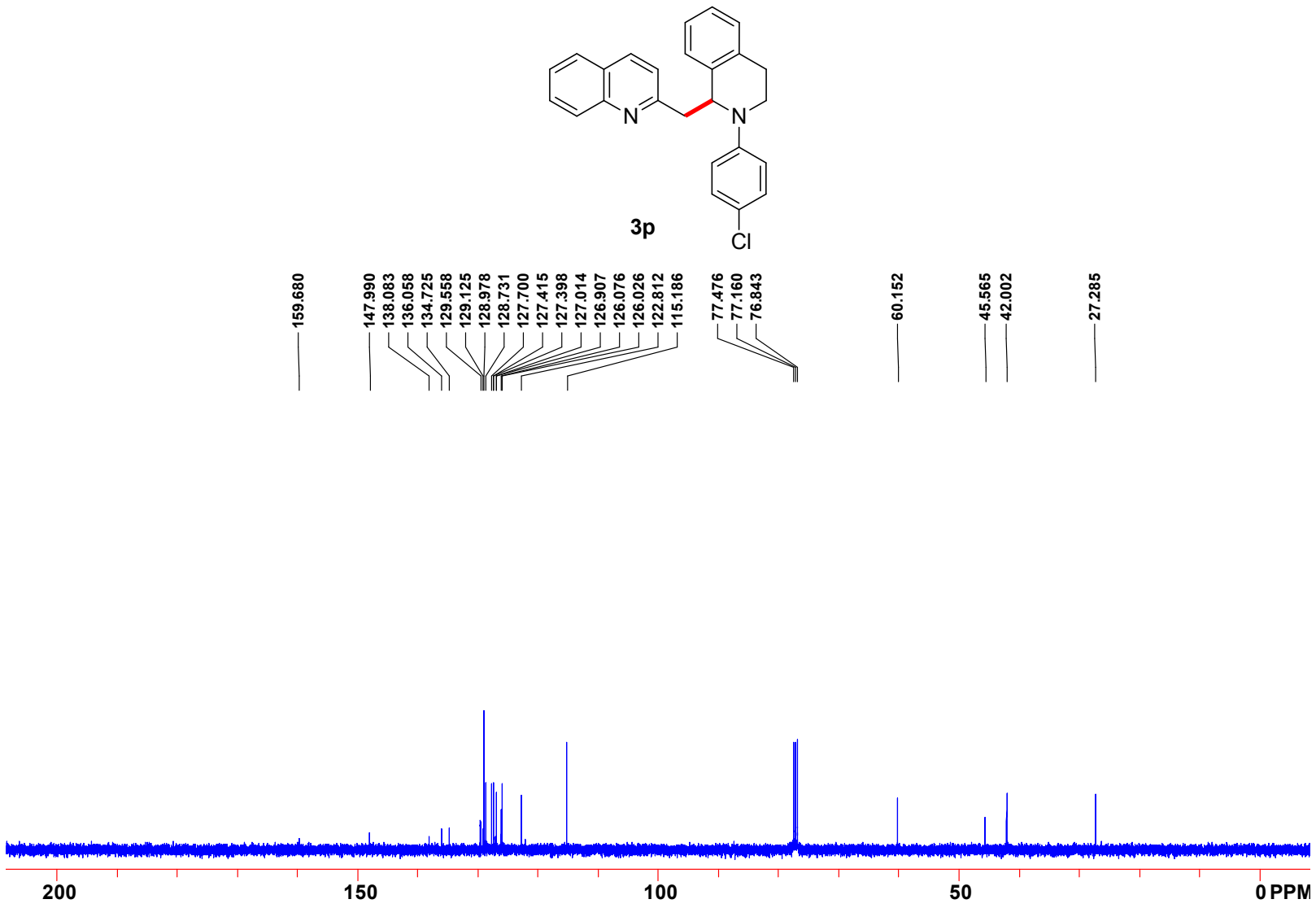
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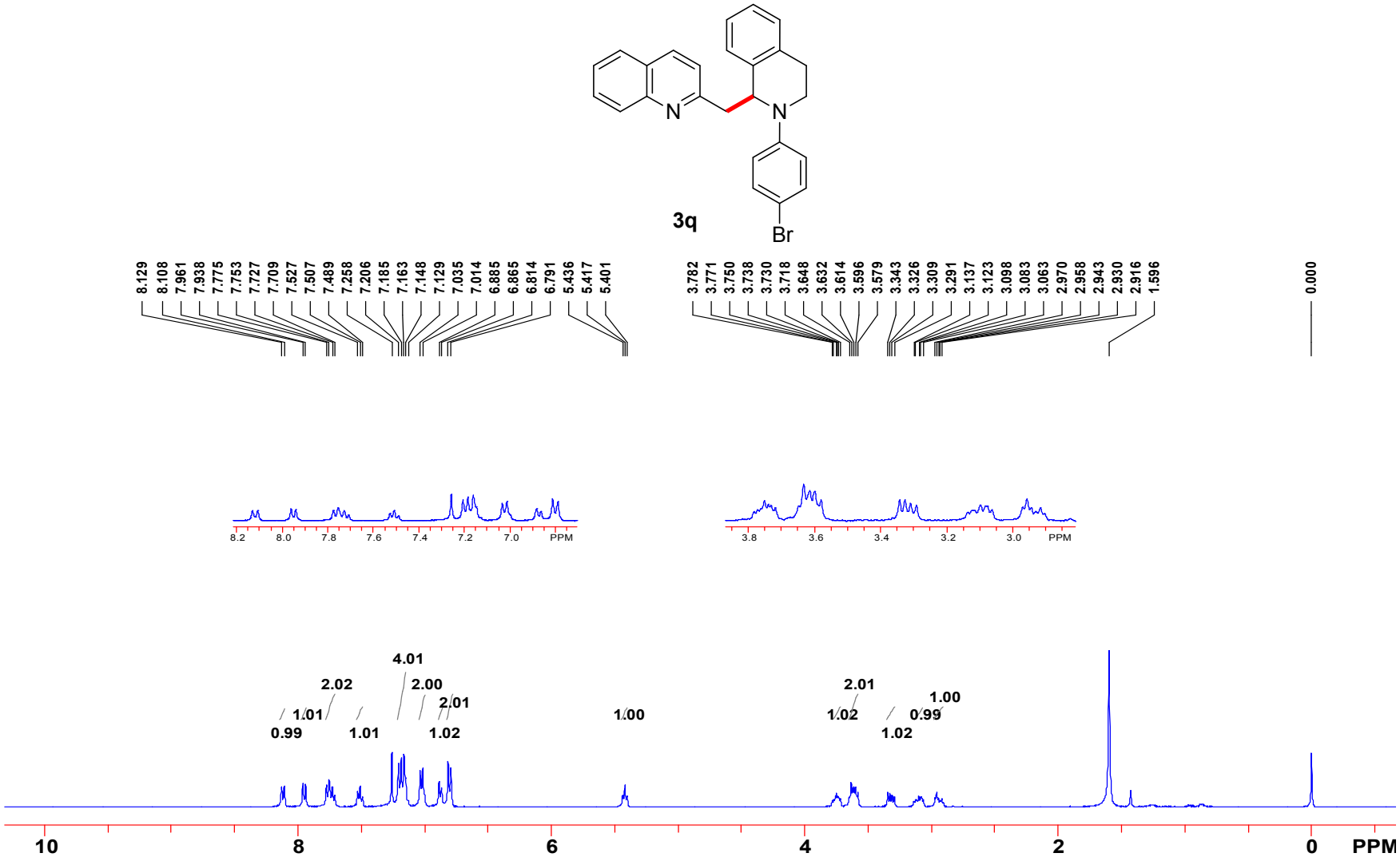
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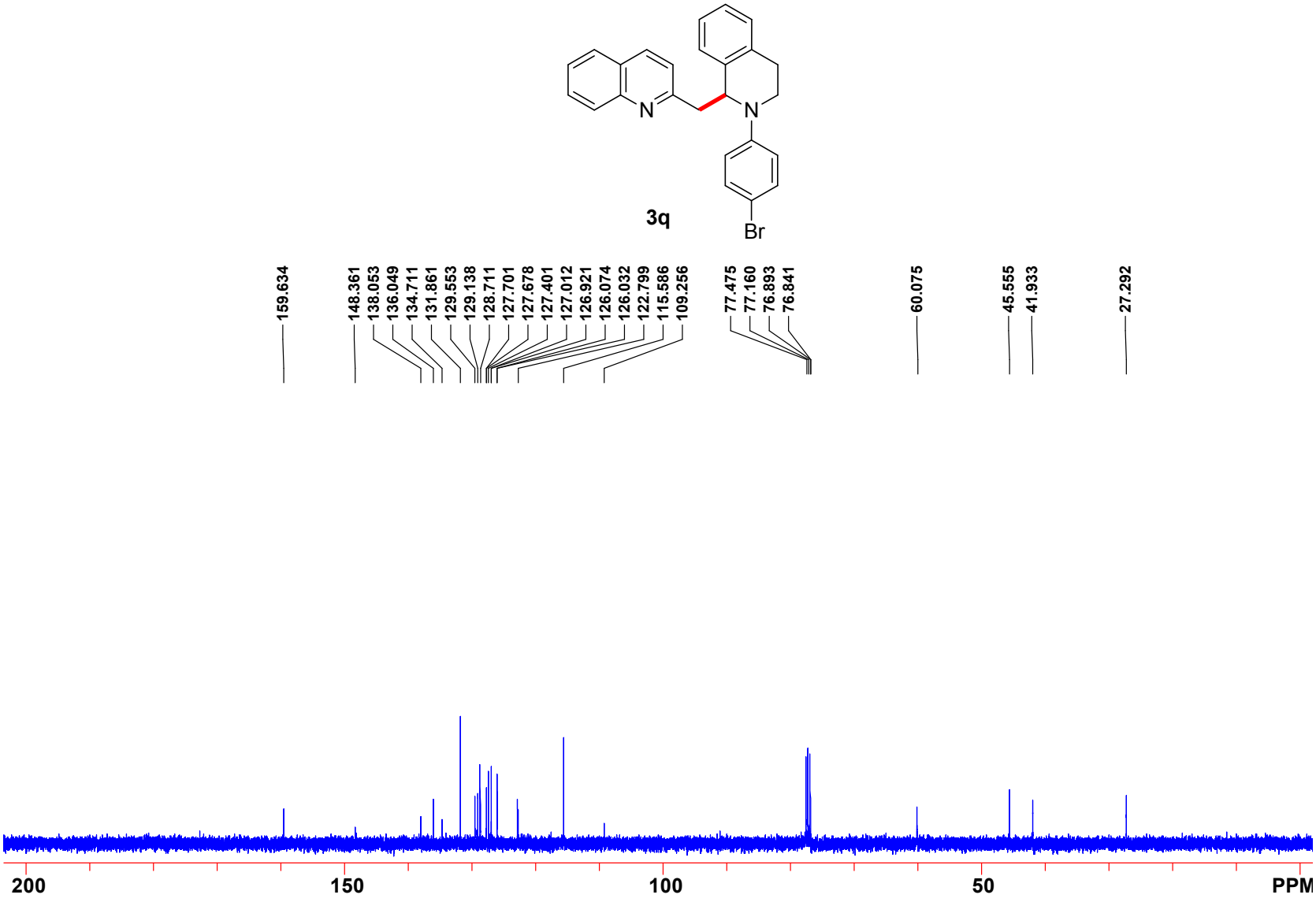
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