Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Cascade imination, Buchwald-Hartwig cross coupling and cycloaddition reaction: synthesis of pyrido[2,3-*d*]pyrimidines

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General Information

Melting points were measured with a Buchi B-540 melting point apparatus and are uncorrected. IR spectra were recorded on Elmer FT-IR-2000 spectrometer on a thin film using chloroform. NMR spectra were recorded on Avance DPX 300 MHz FT-NMR spectrometer or Bruker Avance III 500 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on Trace DSQ GCMS instrument. All the commercially available regents were used as received. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Merck). Column chromatography was performed on silica gel (100-200 mesh, Merck). All MW reactions were carried out in a Synthos 3000 (Anton Paar) microwave reactor.

Microwave Instrumentation

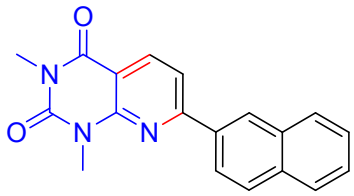
All microwave reactions were carried out in a Synthos 3000 (Anton Paar) microwave reactor. The multitude microwave has a twin magnetron (2.45 GHz) with maximum output power of 1400 W. The output power can be controlled in unpulsed control mode over whole power which is adjustable in 1 W increment. A Motorola 68xxx series microprocessor system control is used to measure power, pressure, time and temperature during the reaction. The temperature and pressure were monitored throughout the reaction by an infrared detector. The temperature can be measured from 0 to 280 ^{o}C with uncertainty ± 1%. The temperature during the MW reaction was monitored by an externally calibrated IR sensor. The pressure can be measured from 0 to 86 bar with uncertainty ± 0.2 bar. The MW power is initially set at 700 W and the reaction is run. However, during the course of the reaction, once the set temperature and pressure limit is reached, the reactor automatically adjusts the power by lowering it.

General procedure for the synthesis of *β*-bromovinyl aldehydes 1a-j: The *β*-bromovinyl aldehydes were synthesized by following known procedure.[1] Anhydrous DMF (24.0 mmol) was added dropwise to an ice cold solution of PBr_3 (12.0 mmol) under N_2 atmosphere. The reaction mixture was stirred for 15 minutes at 0 ^{o}C and then a solution of the acetophenone derivative/cyclic ketone (3.0 mmol) was added into the reaction mixture using a dropping funnel. The reaction mixture was allowed to attain room temperature and then refluxed for 5 hours. After completion of the reaction, the reaction mixture was poured into water and extracted with ethyl acetate (3 x 50 mL). The ethyl acetate layer was washed with water, brine and dried over anhydrous Na_2SO_4. The crude product obtained after removal of the solvent was purified by column chromatography over silica gel using EtOAc/Hexane as the eluent to obtain **1a-j**.

The *ortho*-bromobenzaldehydes **1k-m** were procured from Sigma-Aldrich.

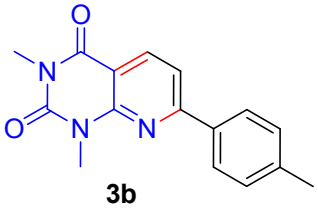
General procedure for the synthesis of compounds 3a-o: A mixture of *β*-bromovinyl/aryl aldehyde (**1a**, 1.0 mmol), 6-amino-1,3-dialkyluracil (**2a**, 1.0 mmol), $Pd(OAc)_2$ (2.5 mol %), xantphos (5.0 mol %) and K_2CO_3 (1 mmol) was irradiated in a closed vessel in a Synthos 3000 microwave reactor at 700 Watt (120 ^oC and 14 bar) for 5 minutes. After completion of the reaction, the reaction mixture was treated with water (40 mL) and then extracted with ethylacetate (30 x 3 mL). The organic portion was washed with water, dried over anhydrous sodium sulfate and the solvent was removed in vacuo to obtain a crude product which on silica gel column chromatographic purification using EtOAc/hexane as the eluent afforded compounds **3a-o**.

Spectral and Analytical data:



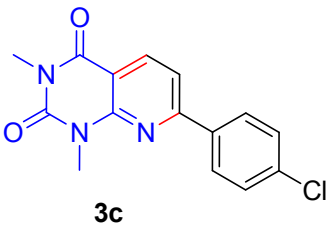
3a

1,3-Dimethyl-7-(naphthalen-3-yl)pyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione (3a): Yellow solid; m.p. 208-209 °C (lit. m.p. 210-211 °C)[2]. IR ($CHCl_3$, cm^{-1}): 2925, 1705, 1659, 1557, 1423, 1372, 1289, 1018, 791. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.51 (s, 3H), 3.88 (s, 3H), 7.56 (d, *J* = 5.4 Hz, 2H), 7.81 (d, *J* = 4.8 Hz, 1H), 7.80-8.01 (m, 3H), 8.24 (d, *J* = 7.1 Hz, 1H), 8.52 (d, *J* = 7.9 Hz, 1H), 8.59 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 28.4, 29.4, 108.9, 115.3, 122.2, 124.3, 126.6, 127.4, 127.6, 127.7, 128.6, 128.9, 132.8, 133.1, 138.2, 150.6, 151.6, 161.0, 161.3. MS (EI, *m/z*): 317.3 [M^+]. Anal. calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.77; H, 4.61; N, 13.17.



3b

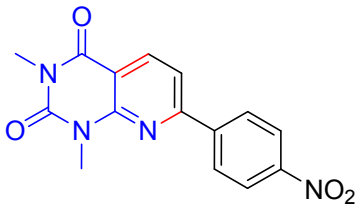
1,3-Dimethyl-7-p-tolylpyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione (3b): Yellow solid; m.p. 180-182 °C (lit. m.p. 183 °C)[3]. IR ($CHCl_3$, cm^{-1}): 2924, 1707, 1661, 1597, 1424, 1370, 1099, 789. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.44 (s, 3H), 3.51 (s, 3H), 3.83 (s, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 8.47 (d, *J* = 8.5 Hz, 1H).[3,4] ^{13}C NMR ($CDCl_3$, 75 MHz): 21.4, 28.3, 29.3, 108.6, 114.7, 127.3, 129.6, 134.6, 138.1, 141.1, 150.6, 151.6, 161.1, 161.3.[3,4] MS (EI, *m/z*): 281.3 [M^+]. Anal. calcd. for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.37; N, 14.94. Found: C, 68.12; H, 5.46; N, 14.78.



3c

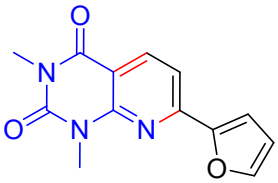
7-(4-Chlorophenyl)-1,3-dimethylpyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione (3c): Yellow solid; m.p. 142-145 °C (lit. m.p. 139-140 °C)[4]. IR ($CHCl_3$, cm^{-1}): 2924, 1705, 1661, 1600, 1566, 1424, 1090, 750. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.51 (s, 3H), 3.82 (s, 3H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.51 (d, *J* = 8.0 Hz, 1H).[4] ^{13}C NMR ($CDCl_3$, 75 MHz): 28.5, 29.5, 109.3, 114.9, 128.8, 129.2, 135.9, 136.9, 138.6, 159.9, 161.3.[4] MS (EI, *m/z*): 301.7 [M^+]. Anal. calcd. for $C_{15}H_{12}ClN_3O_2$: C, 59.71; H, 4.01; N, 13.93. Found: C, 59.58; H, 3.92; N, 13.77.

1,3-Dimethyl-7-(4-nitrophenyl)pyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione (3d): Yellow solid; m.p. 161-163 °C (lit.



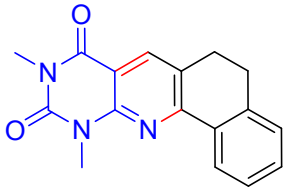
3d

m.p. 283-285 °C)[4]. IR ($CHCl_3$, cm^{-1}): 2918, 1710, 1662, 1562, 1466, 1345, 1219, 1018, 772. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.30 (s, 3H), 3.72 (s, 3H), 6.92 (d, *J* = 4.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 8.24 (d, *J* = 8.3 Hz, 2H), 8.61 (d, *J* = 4.8 Hz, 1H).[4] ^{13}C NMR ($CDCl_3$, 75 MHz): 28.5, 29.7, 121.0, 123.2, 128.7, 145.9, 147.6, 151.1, 151.8, 152.8, 160.5.[4] MS (EI, *m/z*): 312.2 [M^+]. Anal. calcd. for $C_{15}H_{12}N_4O_4$: C, 57.69; H, 3.87; N, 17.94. Found: C, 57.81; H, 3.64; N, 18.09.



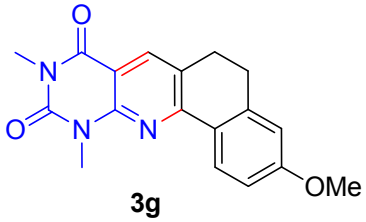
3e

7-(Furan-2-yl)-1,3-dimethylpyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione (3e): Brown solid; m.p. 136-140 °C. IR ($CHCl_3$, cm^{-1}): 2921, 1706, 1658, 1602, 1476, 1366, 1295, 1018, 750. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.49 (s, 3H), 3.76 (s, 3H), 6.60 (d, *J* = 5.0 Hz, 1H), 7.57 (d, *J* = 4.8 Hz, 1H), 7.62 (s, 1H), 8.45 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 28.3, 29.2, 108.5, 112.2, 112.6, 113.3, 138.2, 144.9, 150.7, 151.5, 152.6, 161.1. MS (EI, *m/z*): 257.2 [M^+]. Anal. calcd. for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.74; H, 4.62; N, 16.21.



3f

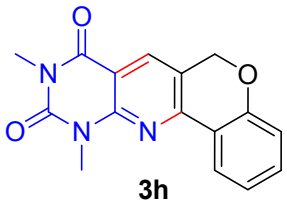
9,11-Dimethyl-5,6-dihydrobenzo[h]pyrimido[4,5-b]quinoline-8,10(9H,11H)-dione (3f): Yellow solid; m.p. 253-255 °C (lit. m.p. 252-253 °C)[5]. IR ($CHCl_3$, cm^{-1}): 2946, 1706, 1654, 1599, 1444, 1370, 1219, 1018, 773. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.00-3.04 (m, 4H), 3.51 (s, 3H), 3.83 (s, 3H), 7.29 (d, *J* = 3.8 Hz, 1H), 7.38-7.40 (m, 2H), 8.26 (s, 1H), 8.34-8.39 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 27.1, 27.9, 28.4, 29.4, 108.9, 126.2, 127.2, 127.3, 128.2, 130.9, 133.3, 136.4, 139.5, 149.7, 151.7, 156.7, 161.5.[6] MS (EI, *m/z*): 293.3 [M^+]. Anal. calcd. for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.78; H, 5.01; N, 14.15.



3g

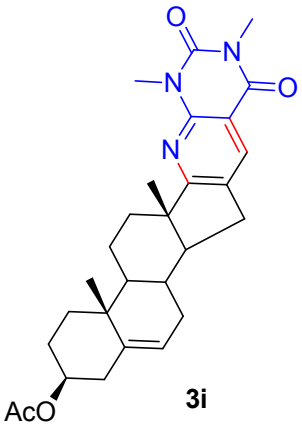
3-Methoxy-9,11-dimethyl-5,6-dihydrobenzo[h]pyrimido[4,5-b]quinoline-8,10(9H,11H)-dione (3g): Yellow solid; m.p. 216-219 °C. IR ($CHCl_3$, cm^{-1}): 2926, 1701, 1657, 1598, 1411, 1368, 1277, 1044, 790. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.92-3.03 (m, 4H), 3.50 (s, 3H), 3.81 (s, 3H), 3.89 (s, 3H), 6.79 (s, 1H), 6.92 (d, *J* = 6.0 Hz, 1H), 8.20 (s, 1H), 8.30 (d, *J* = 8.5

Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 27.1, 28.3, 29.4, 29.7, 55.4, 108.1, 113.1, 126.2, 126.3, 128.1, 135.9, 141.6, 149.7, 151.7, 156.8, 161.6, 161.9. MS (EI, *m/z*): 323.3 [M^+]. Anal. calcd. for $C_{18}H_{17}N_3O_3$: C, 66.86; H, 5.30; N, 13.00. Found: C, 66.59; H, 5.48; N, 13.31.



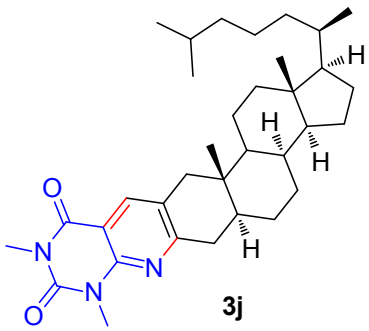
3h

1,3-Dimethylpyrimido[4,5-b][1,8]naphthyridine-2,4(1H,3H)-dione (3h): Yellow solid; m.p. 269 °C (lit. m.p. 274-275 °C)[5]. IR ($CHCl_3$, cm^{-1}): 2924, 1715, 1670, 1618, 1500, 1437, 1181, 1119, 721. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.50 (s, 3H), 3.81 (s, 3H), 5.29 (s, 2H), 7.00 (d, J = 7.5 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 8.18 (s, 1H), 8.24 (d, J = 7.7 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): 28.7, 29.7, 112.1, 131.7, 133.1, 138.6, 141.6, 151.2, 160.6. MS (EI, *m/z*): 295.2 [M^+]. Anal. calcd. for $C_{16}H_{13}N_3O_3$: C, 65.08; H, 4.44; N, 14.23. Found: C, 65.36; H, 4.67; N, 14.41.



3i

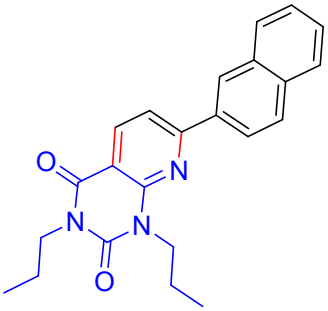
3β-Acetoxy-1',3'-dimethyl-5-en-androst[16,17-g]pyrido[2',3'-d]pyrimidine-2,4(1H,3H)-dione (3i): White solid; m.p. 146-148 °C. IR ($CHCl_3$, cm^{-1}): 2924, 2853, 1732, 1709, 1663, 1612, 1462, 1243, 1032, 771. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.78 (s, 3H), 0.93 (s, 3H), 0.75-2.80 (m, 20H), 3.41 (s, 3H), 3.67 (s, 3H), 4.52-4.59 (m, 1H), 5.36 (s, 1H), 8.14 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.2, 17.1, 21.4, 22.7, 27.7, 28.4, 29.4, 29.7, 30.8, 31.9, 33.2, 36.9, 38.1, 46.3, 50.5, 55.7, 73.7, 108.1, 121.9, 131.6, 132.7, 140.1, 148.6, 150.4, 161.9, 170.5, 179.2. MS (EI, *m/z*): 477.6 [M^+]. Anal. calcd. for $C_{28}H_{35}N_3O_4$: C, 70.42; H, 7.39; N, 8.80. Found: C, 70.73; H, 7.48; N, 8.87.



3j

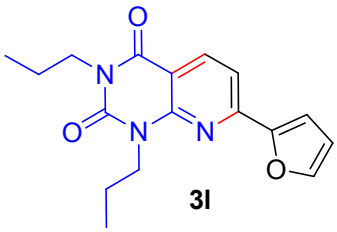
1',3'-Dimethyl-cholest[2,3-g]pyrido[2',3'-d]pyrimidine-2,4(1H,3H)-dione (3j): White solid; m.p. 164-167 °C. IR ($CHCl_3$, cm^{-1}): 2929, 2867, 1709, 1663, 1612, 1467, 1382, 1019, 752. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.69 (s, 3H), 0.88 (s, 3H), 0.70-2.87 (m, 39H), 3.45 (s, 3H), 3.69 (s, 3H), 8.10 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 18.7, 22.6, 22.8, 23.8, 28.0, 28.2, 35.6, 35.8, 36.2, 39.5, 39.9, 42.5, 53.5, 56.3, 56.4, 107.7, 127.2, 128.3, 138.0, 153.7, 161.6, 162.3. MS (EI, *m/z*):

533.7 [M^+]. Anal. calcd. for $C_{34}H_{51}N_3O_2$: C, 76.50; H, 9.63; N, 7.87. Found: C, 76.75; H, 9.59; N, 7.75.



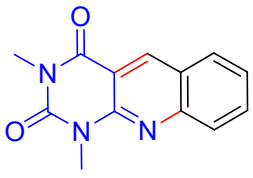
3k

7-(Naphthalen-3-yl)-1,3-dipropylpyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione (3k): Yellow solid; m.p. 142-145 °C. IR ($CHCl_3$, cm^{-1}): 2928, 1704, 1661, 1560, 1421, 1373, 1288, 1019, 789. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.00 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.0 Hz, 3H), 1.70-1.79 (m, 2H), 1.85-1.94 (m, 2H), 4.07 (t, J = 7.5 Hz, 2H), 4.46 (t, J = 7.5 Hz, 2H), 7.56 (d, J = 5.9 Hz, 2H), 7.79 (d, J = 7.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.5 Hz, 2H), 8.22 (d, J = 7.2 Hz, 1H), 8.51 (d, J = 6.9 Hz, 1H), 8.57 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 11.3, 21.1, 43.3, 44.1, 109.0, 115.1, 124.2, 126.6, 127.5, 127.7, 128.6, 128.9, 133.1, 134.3, 134.8, 138.3, 150.5, 151.1, 160.9, 161.2. MS (EI, *m/z*): 373.4 [M^+]. Anal. calcd. for $C_{23}H_{23}N_3O_2$: C, 73.97; H, 6.21; N, 11.25. Found: C, 74.12; H, 6.24; N, 11.49.



3l

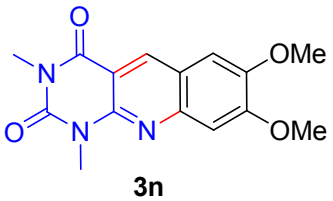
7-(Furan-2-yl)-1,3-dipropylpyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione (3l): Yellow solid; m.p. 114-116 °C. IR ($CHCl_3$, cm^{-1}): 2927, 1705, 1659, 1599, 1473, 1369, 1299, 1017, 759. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.99 (t, J = 7.5 Hz, 3H), 1.03 (t, J = 7.5 Hz, 3H), 1.69-1.77 (m, 2H), 1.78-1.85 (m, 2H), 4.04 (t, J = 6.0 Hz, 2H), 4.35 (t, J = 6.0 Hz, 2H), 6.60 (d, J = 3.5 Hz, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.56 (d, J = 4.8 Hz, 1H), 7.61 (s, 1H), 8.45 (d, J = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 11.3, 21.0, 43.2, 44.0, 108.7, 112.0, 112.5, 113.1, 138.3, 144.9, 150.5, 151.0, 152.4, 152.8, 160.9. MS (EI, *m/z*): 313.3 [M^+]. Anal. calcd. for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.34; H, 6.10; N, 13.50.



3m

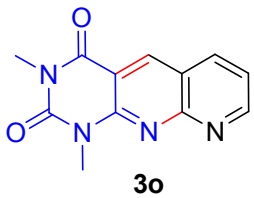
1,3-Dimethylpyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (3m): Yellow solid; m.p. 210-212 °C (lit. m.p. 212 °C)[7]. IR ($CHCl_3$, cm^{-1}): 2921, 1708, 1659, 1621, 1608, 1470, 1292, 1018, 790. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.54 (s, 3H), 3.84 (s, 3H), 7.50-7.55 (m, 1H), 7.80-7.85 (m, 1H), 7.93-8.02 (m, 2H), 9.02 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 28.5, 29.7, 110.9, 124.7, 125.8, 128.1, 129.3, 133.2, 140.1, 149.9, 161.4.

MS (EI, *m/z*): 241.2 [M^+]. Anal. calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.44; H, 4.67; N, 17.71.



3n

7,8-Dimethoxy-1,3-dimethylpyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (3n): Yellow solid; m.p. 248-250 °C. IR ($CHCl_3$, cm^{-1}): 2923, 1703, 1657, 1611, 1502, 1422, 1254, 1007, 747. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.52 (s, 3H), 3.81 (s, 3H), 3.96 (s, 3H), 4.01 (s, 3H), 7.14 (s, 1H), 7.31 (s, 1H), 8.81 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 29.5, 29.7, 56.2, 56.4, 105.9, 108.7, 113.7, 120.3, 136.1, 137.2, 147.8, 149.5, 153.2, 155.8, 161.7. MS (EI, *m/z*): 301.3 [M^+]. Anal. calcd. for $C_{15}H_{15}N_3O_4$: C, 59.79; H, 5.02; N, 13.95. Found: C, 59.46; H, 4.87; N, 13.74.



3o

1,3-Dimethylpyrimido[4,5-b][1,8]naphthyridine-2,4(1H,3H)-dione (3o): Yellow solid; m.p. 183-186 °C. IR ($CHCl_3$, cm^{-1}): 2924, 1715, 1670, 1618, 1500, 1437, 1181, 1119, 721. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.55 (s, 3H), 3.90 (s, 3H), 7.71 (d, J = 7.2 Hz, 1H), 8.33-8.38 (m, 1H), 9.08 (s, 1H), 9.19 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 28.7, 29.7, 112.1, 131.7, 133.1, 138.6, 141.6, 151.2, 160.6. MS (EI, *m/z*): 242.2 [M^+]. Anal. calcd. for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.38; H, 3.97; N, 22.91.

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6. Q. Jairo, I. Braulio, I. Henry, A. Rodrigo, O. Antonio, S. Adolfo and N. Manuel. *J. Heterocycl. Chem.*, 2001, **38**, 339.
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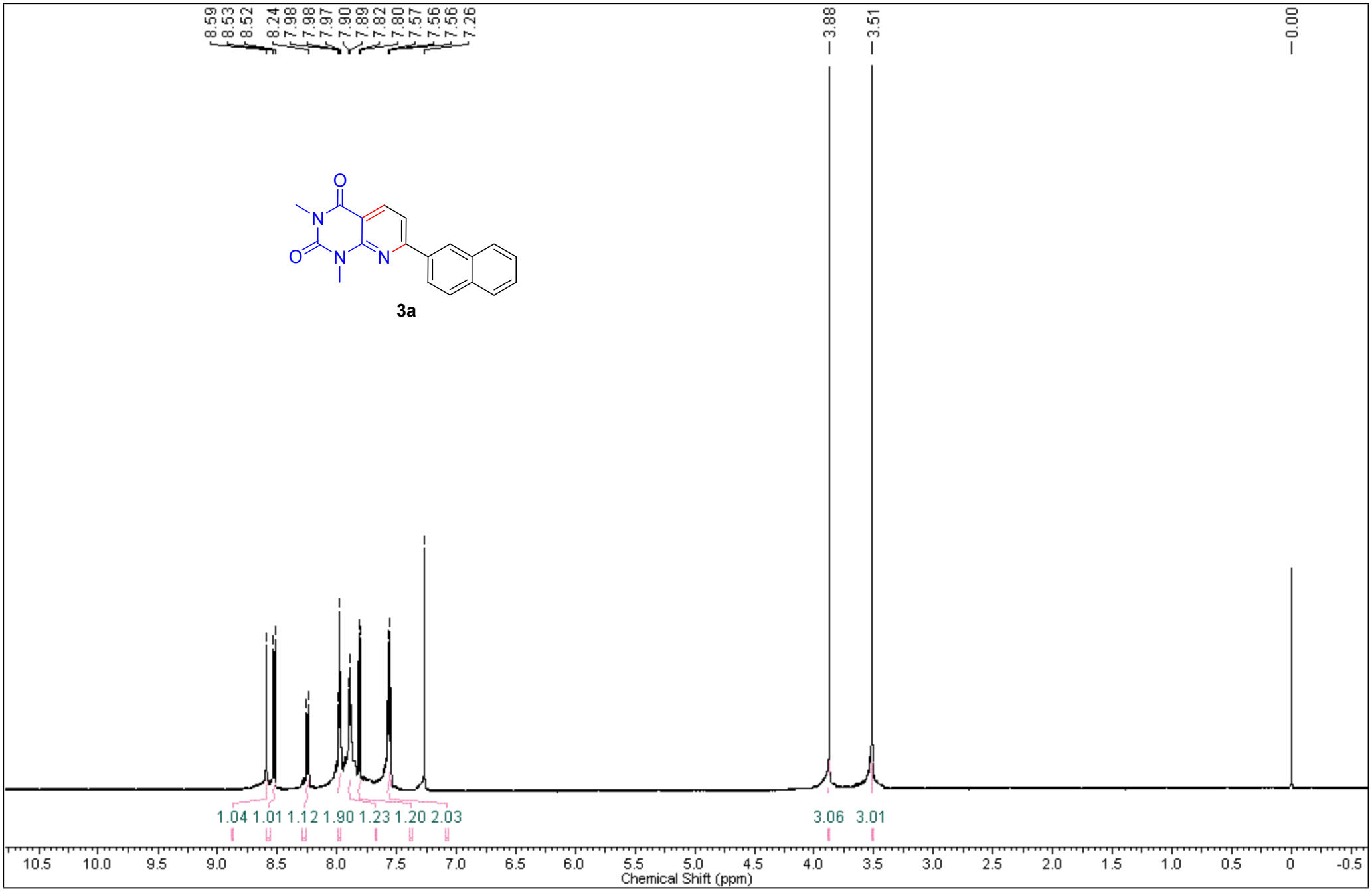
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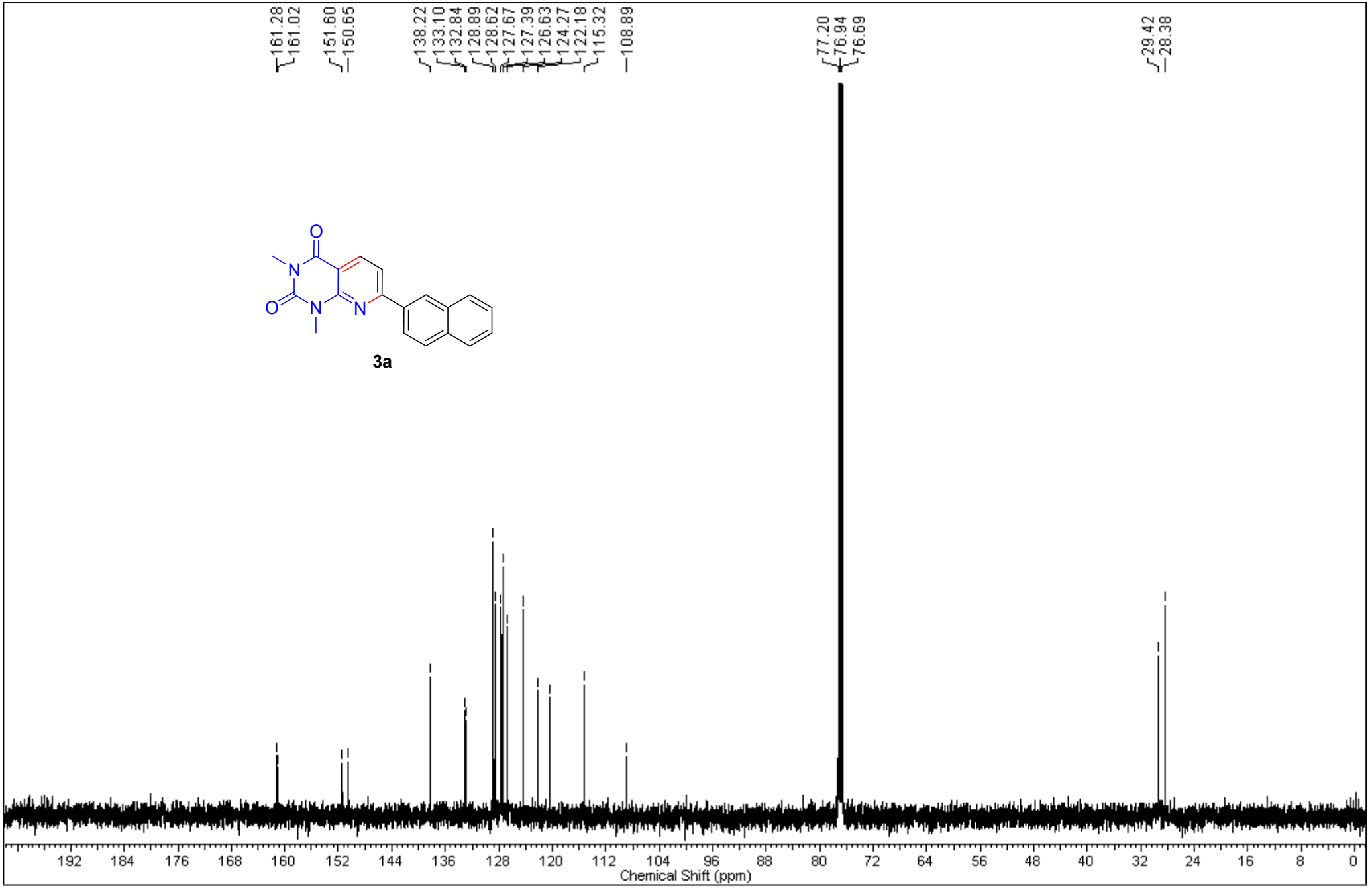
7.56
7.56
7.26
3.88
3.51
0.00
O
N
O
N
N
3a
1.04 1.01 1.12 1.90 1.23 1.20 2.03
3.06 3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)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122.18
115.32
108.89
77.20
76.94
76.69
29.42
28.38
O
N
O
N
N
3a
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160
152
144
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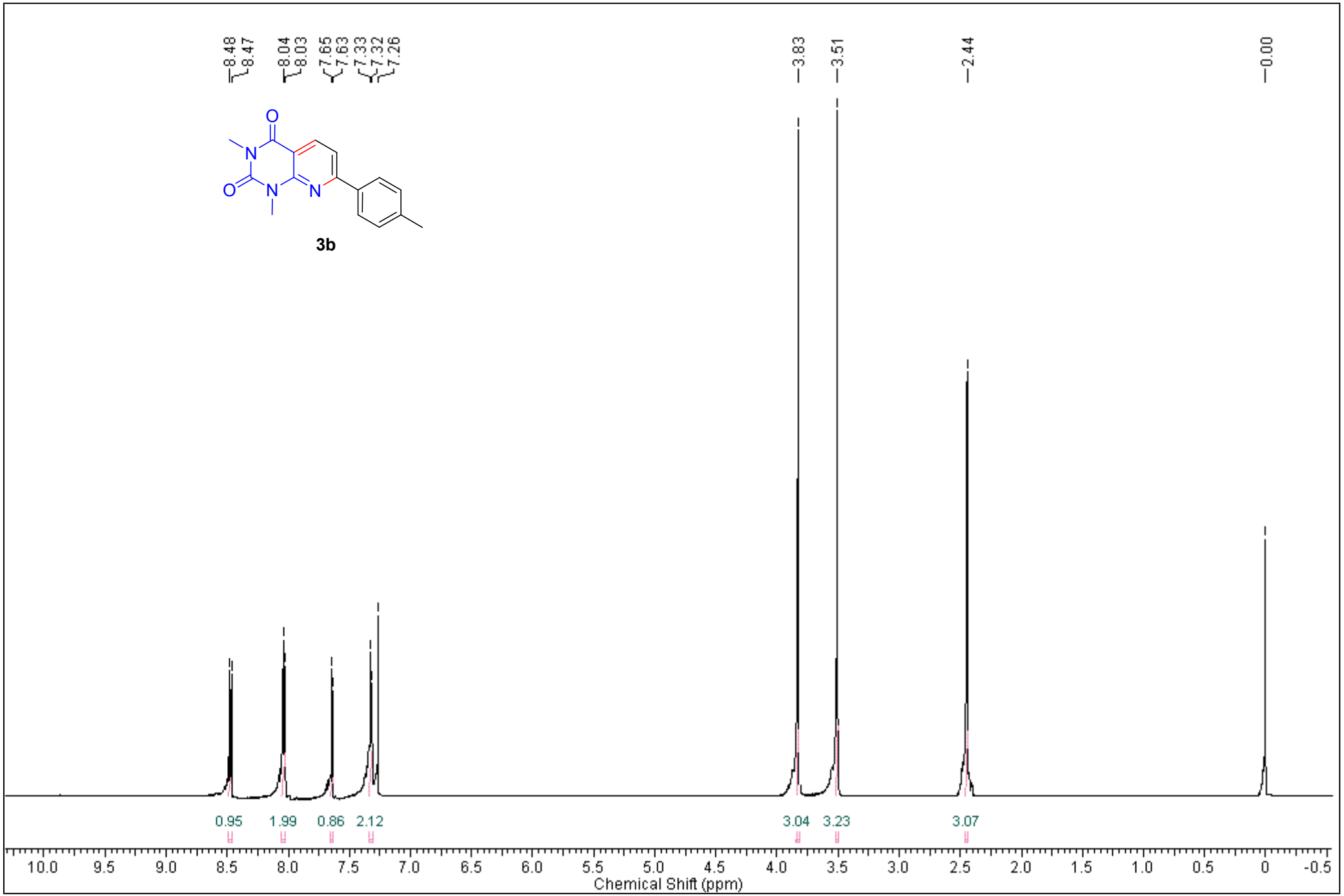
Chemical Shift (ppm)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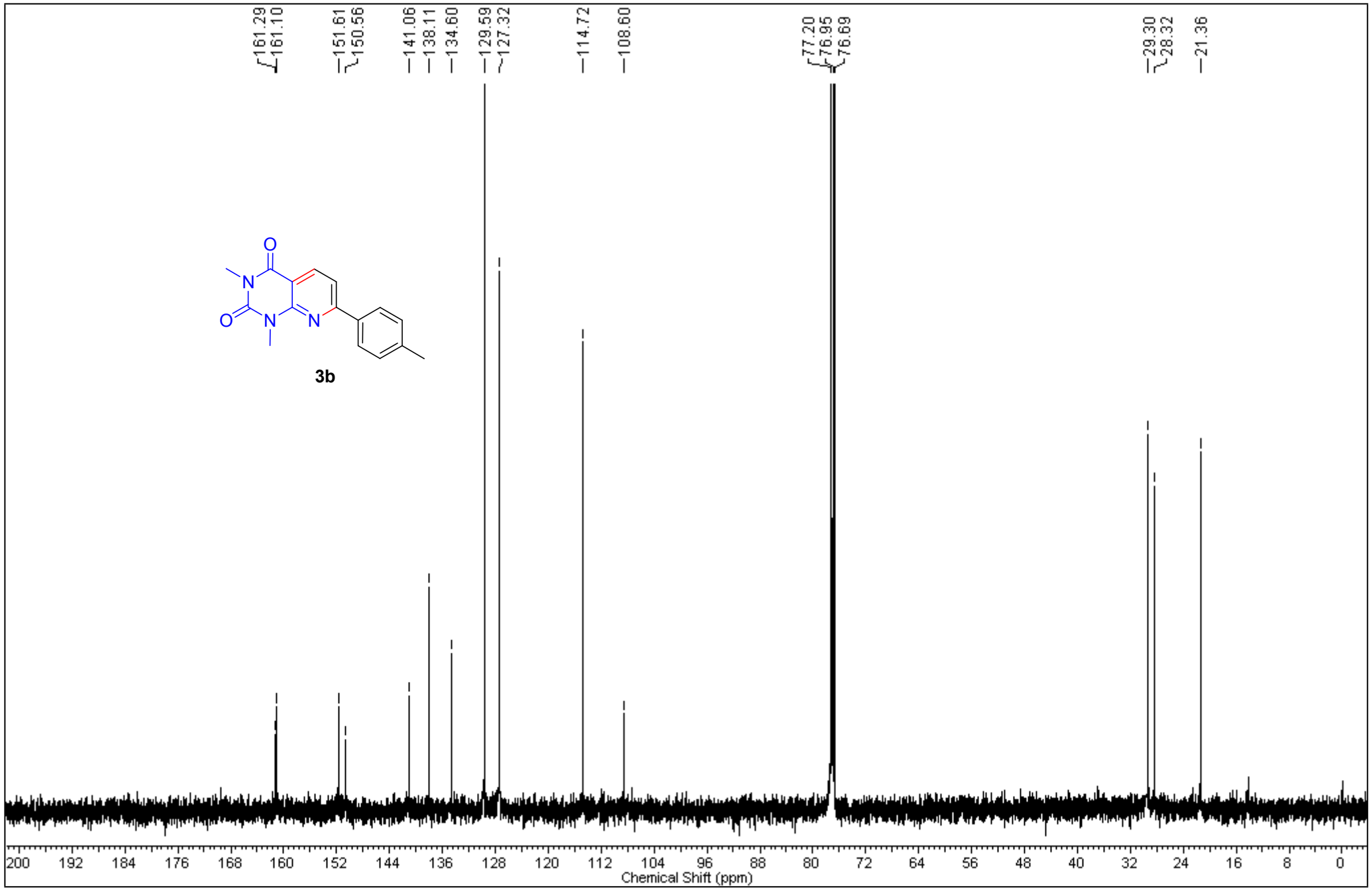
Chemical Shift (ppm)

3b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O
N
N
3b
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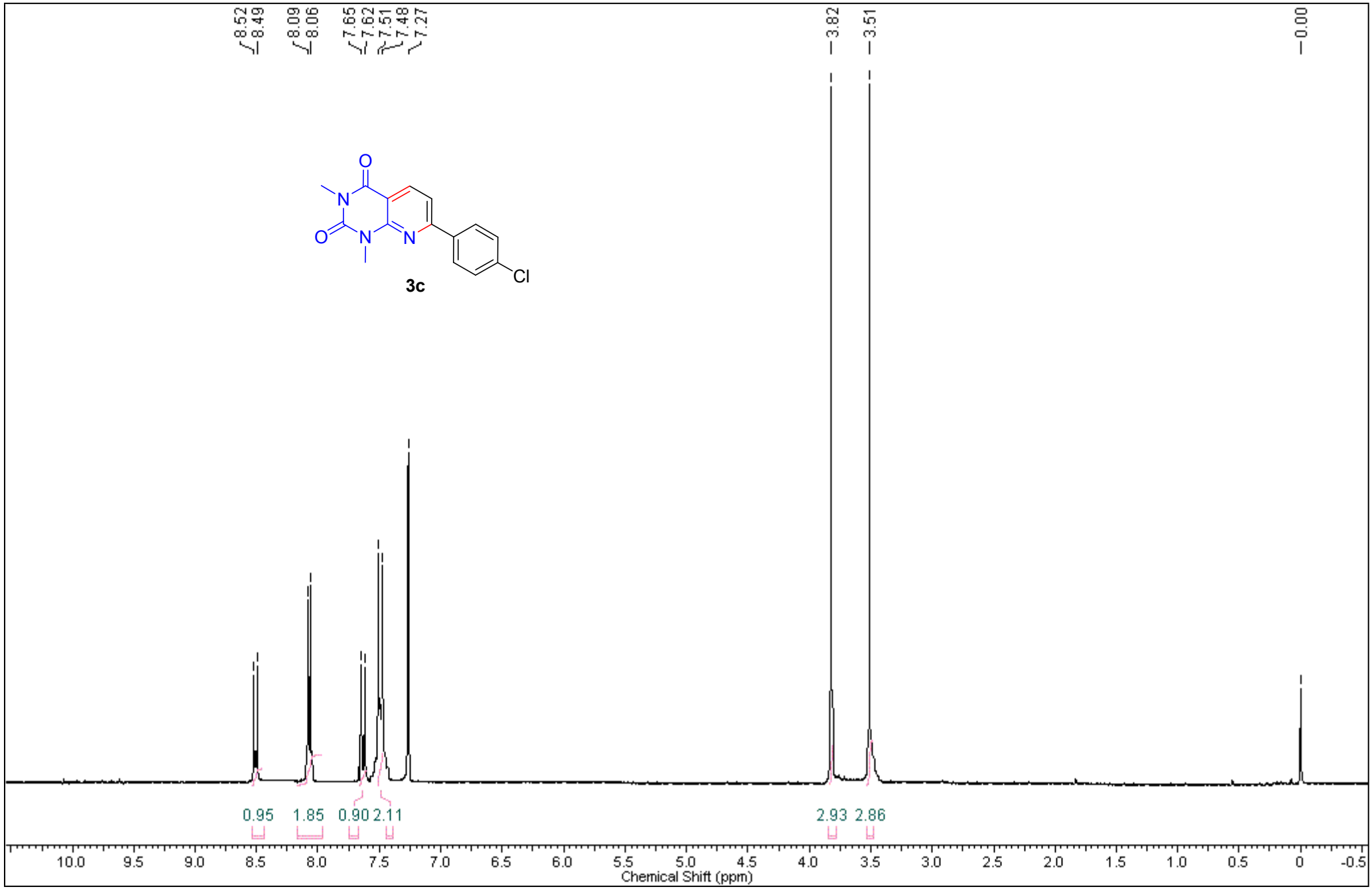
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Cl
3c
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2.93
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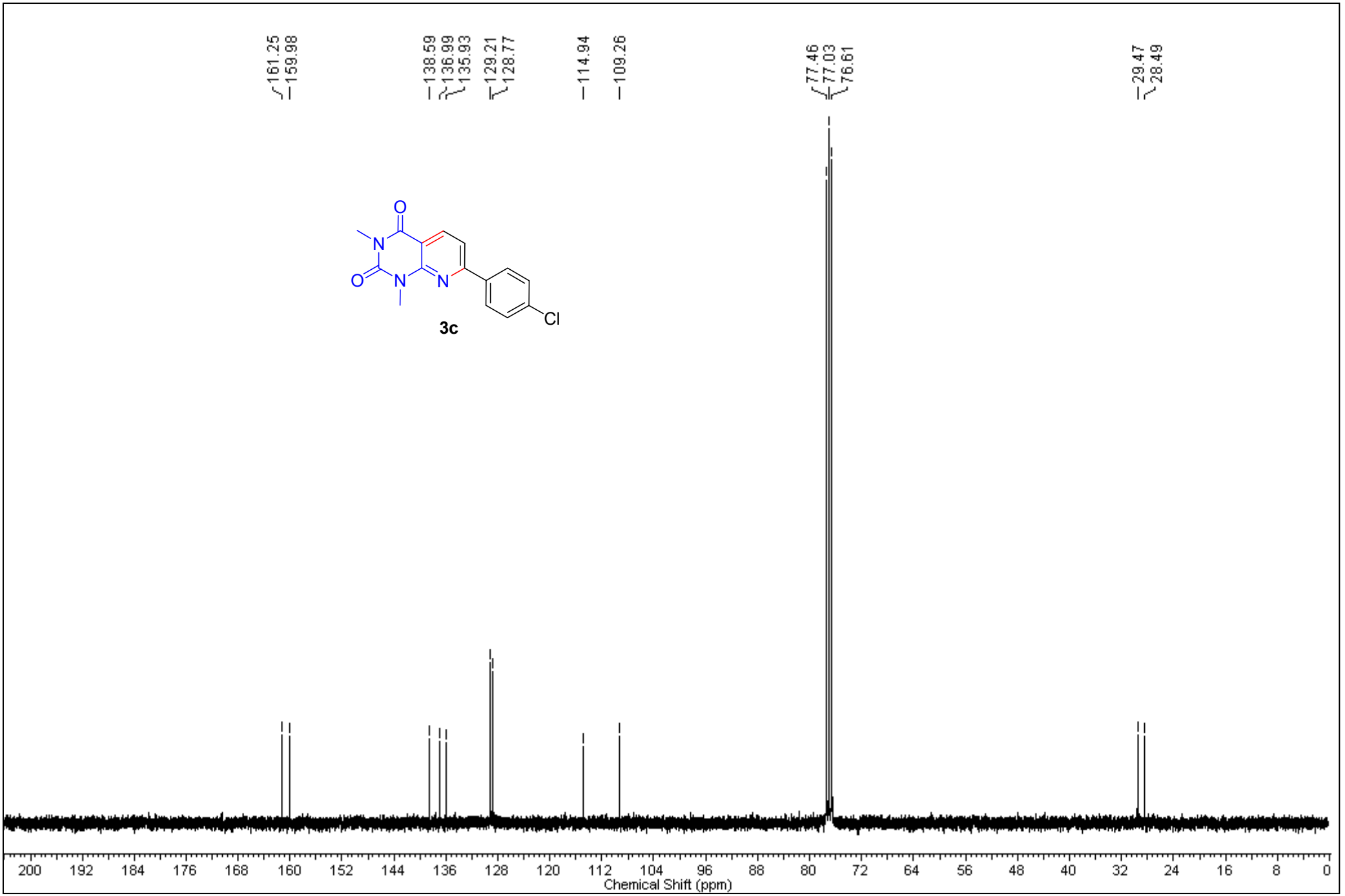
Chemical Shift (ppm)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O
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N
Cl
3c
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184
176
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152
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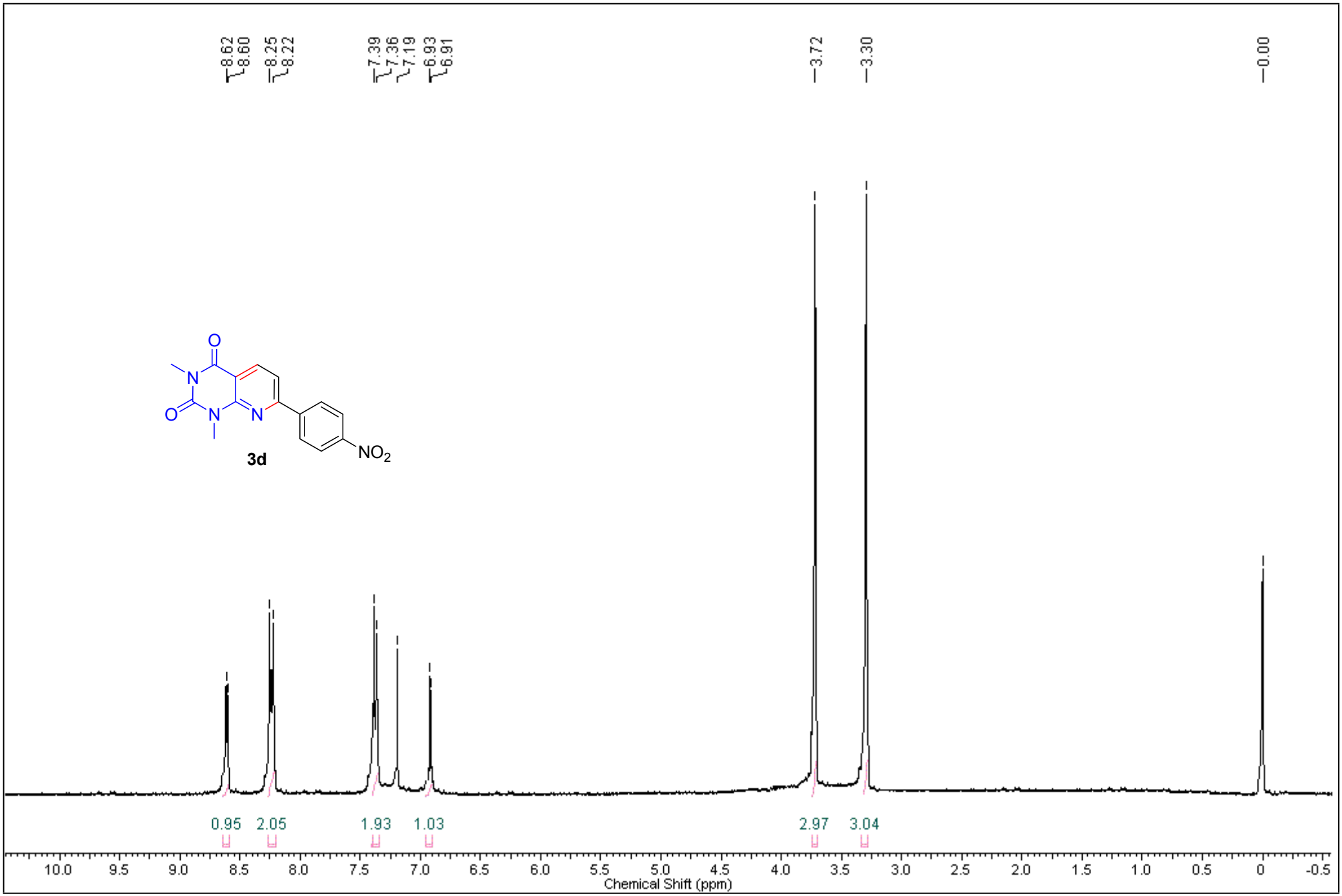
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N
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NO2
3d
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1.93
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2.97
3.04
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9.5
9.0
8.5
8.0
7.5
7.0
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5.5
5.0
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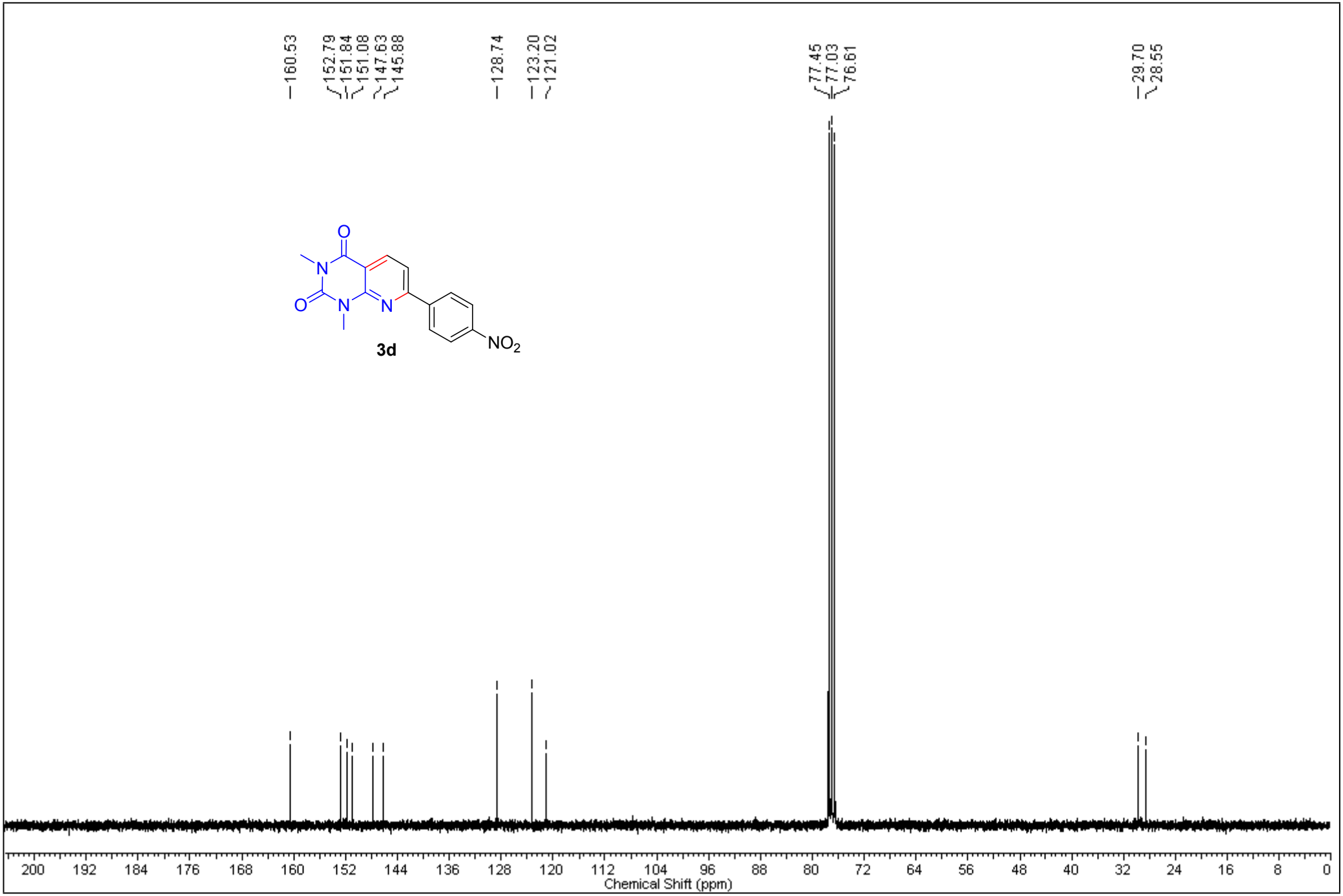
Chemical Shift (ppm)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N
N
NO2
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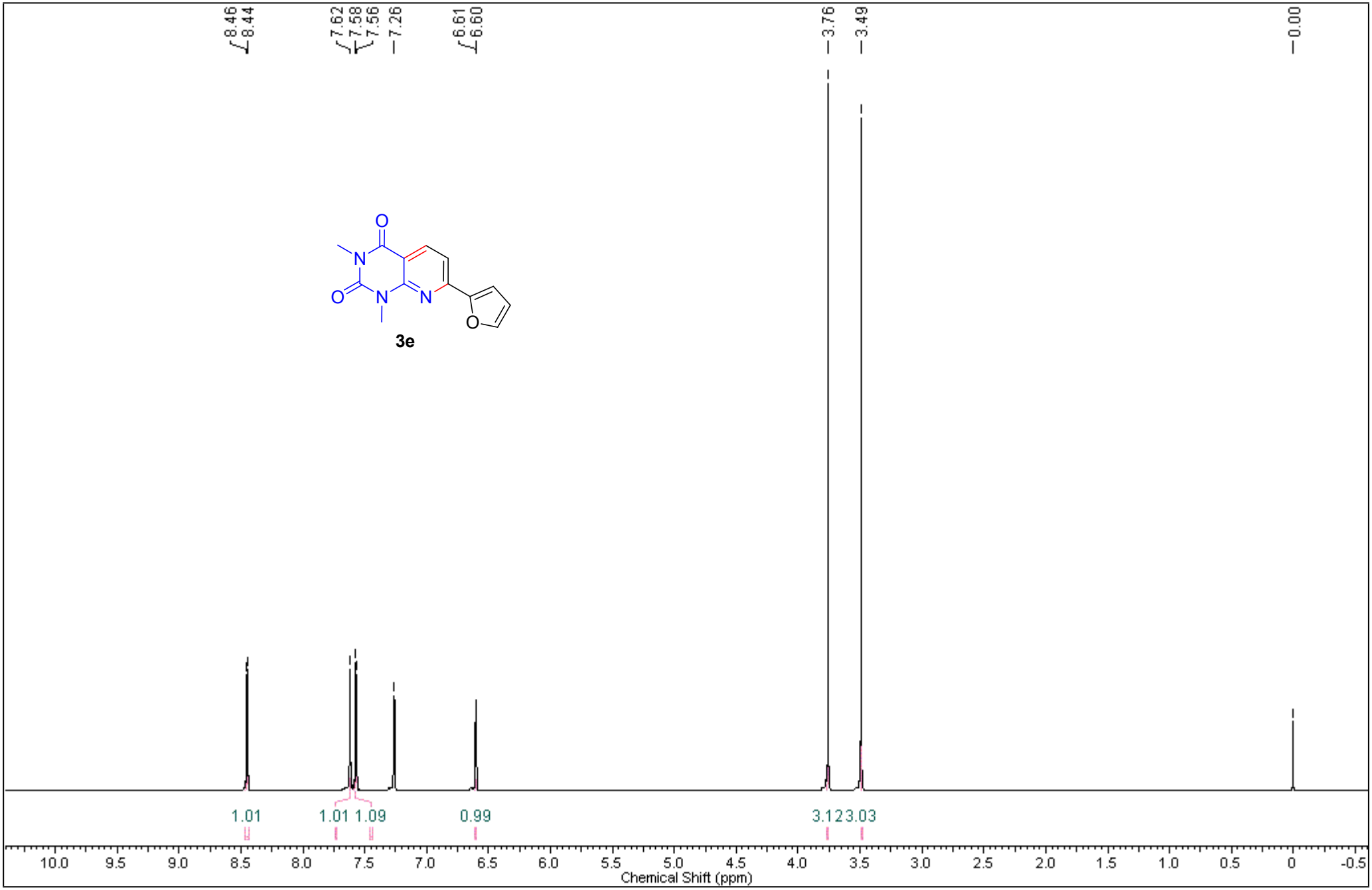
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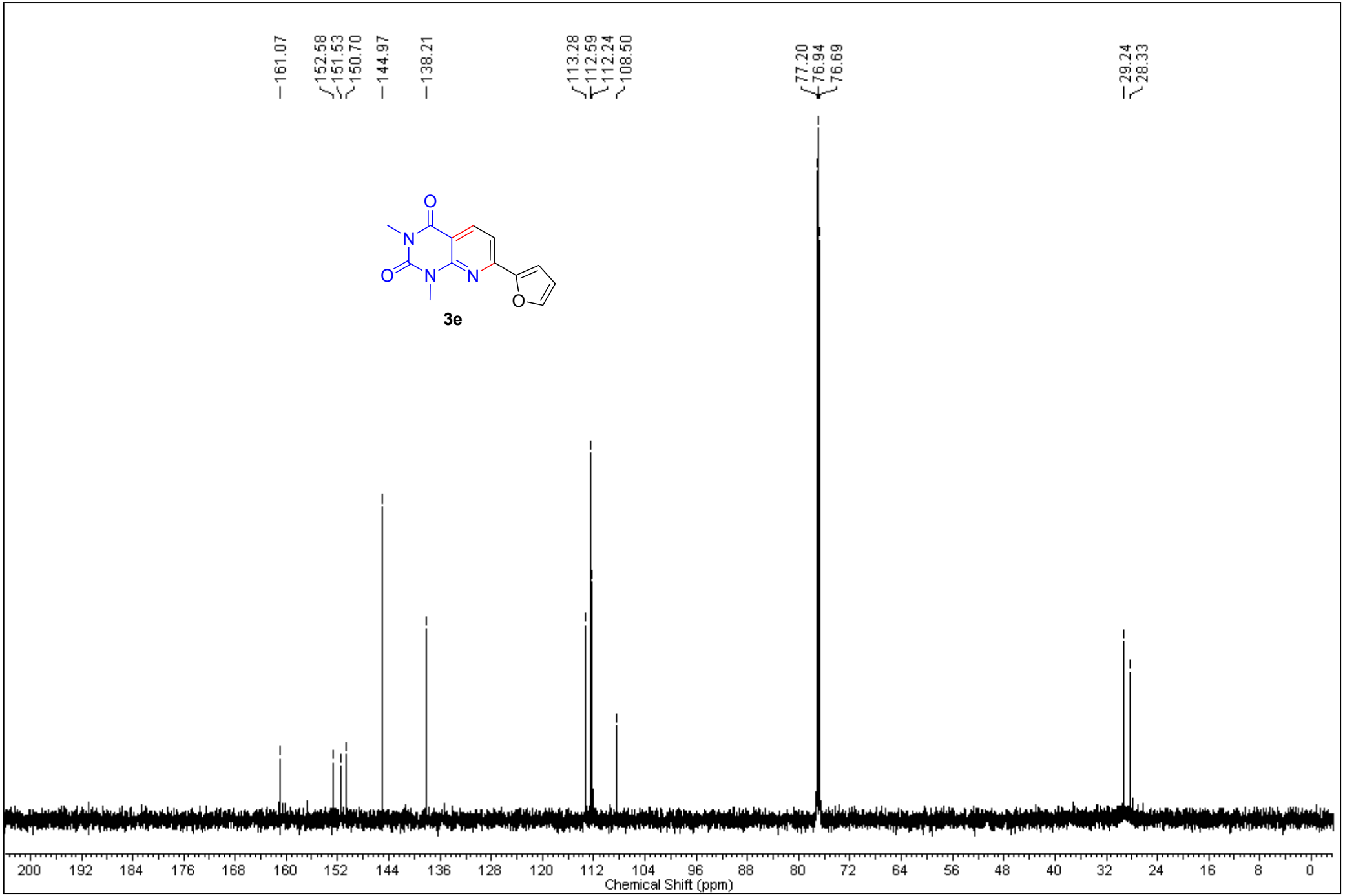
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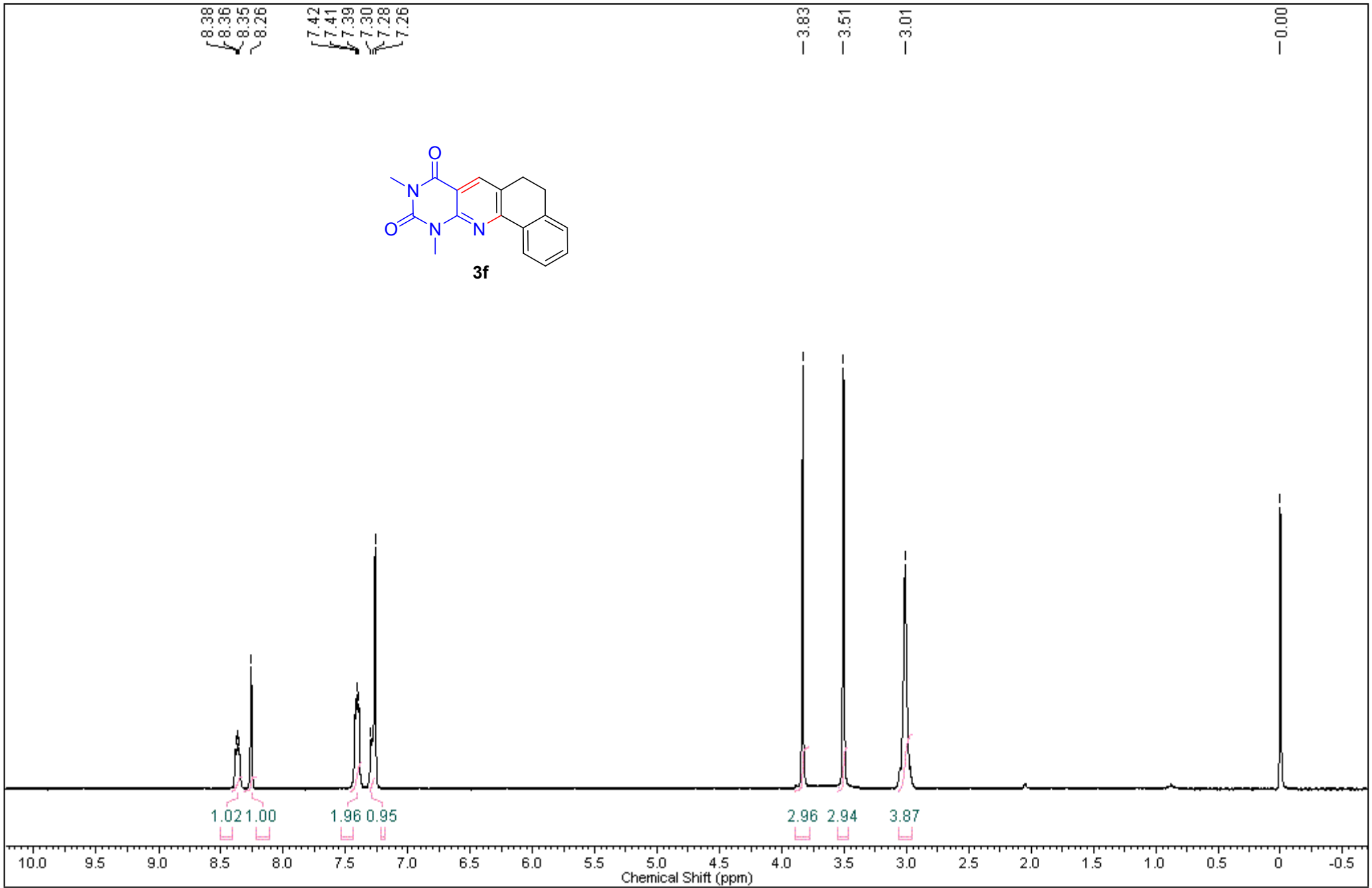
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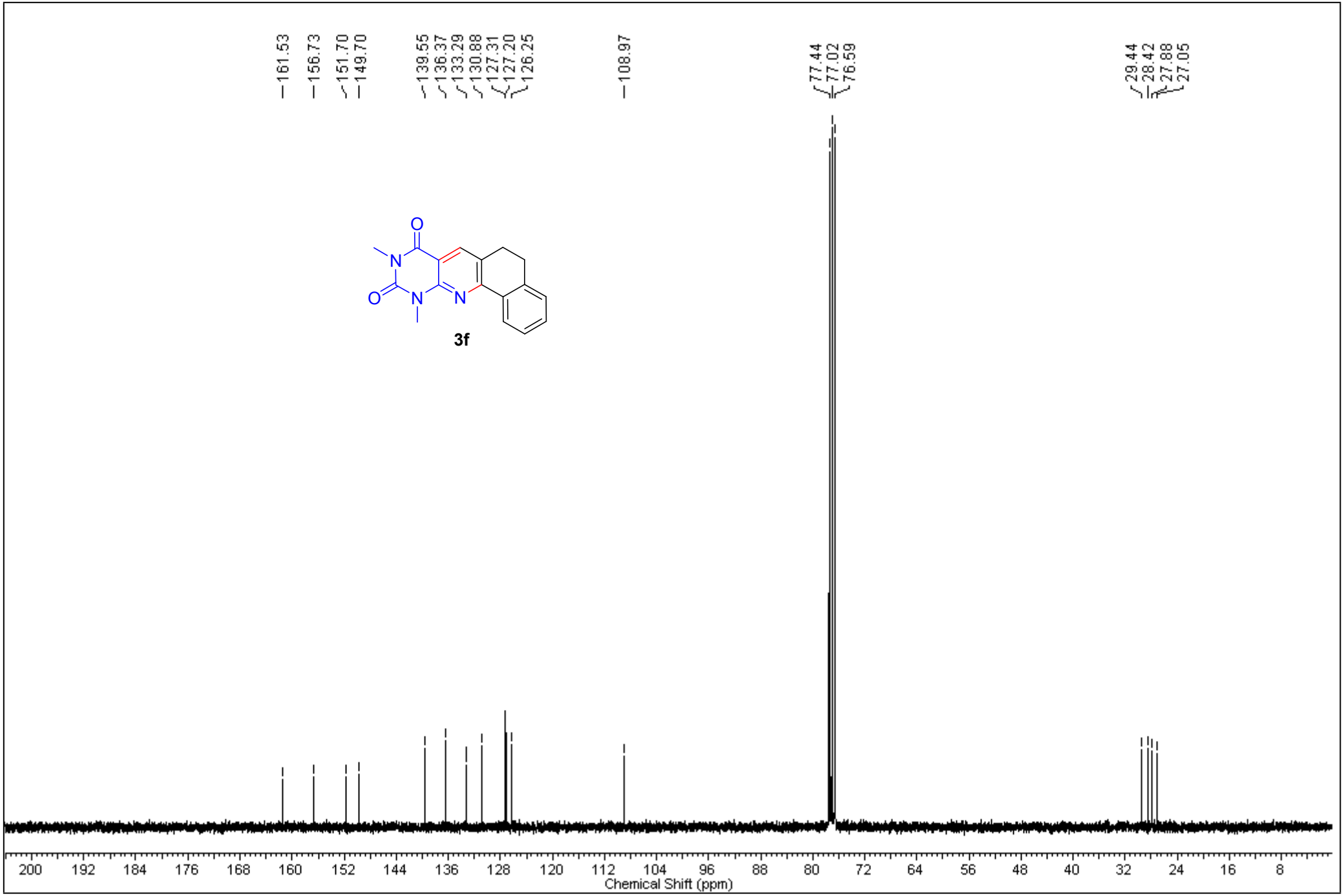
Chemical Shift (ppm)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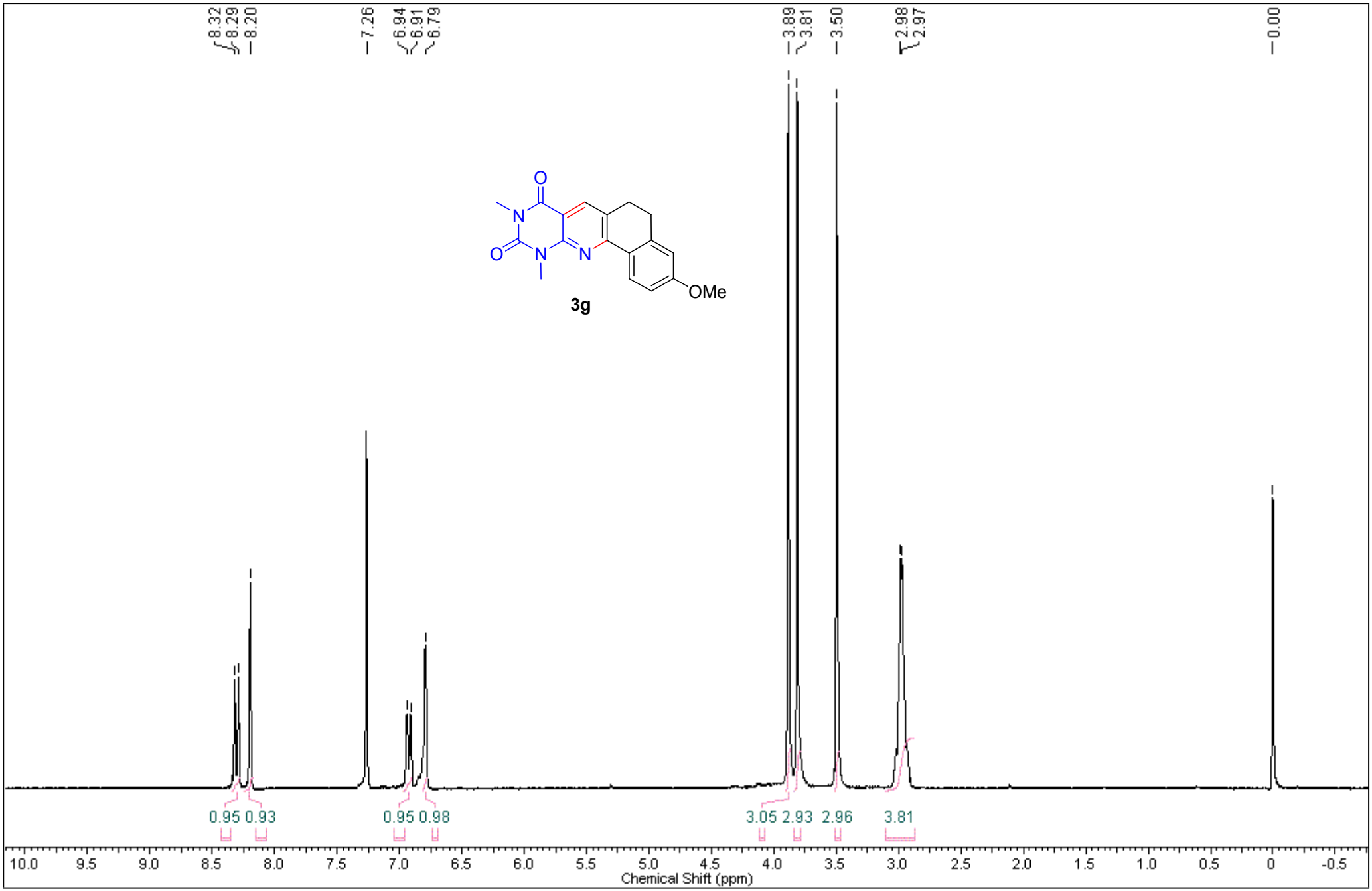
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3.81
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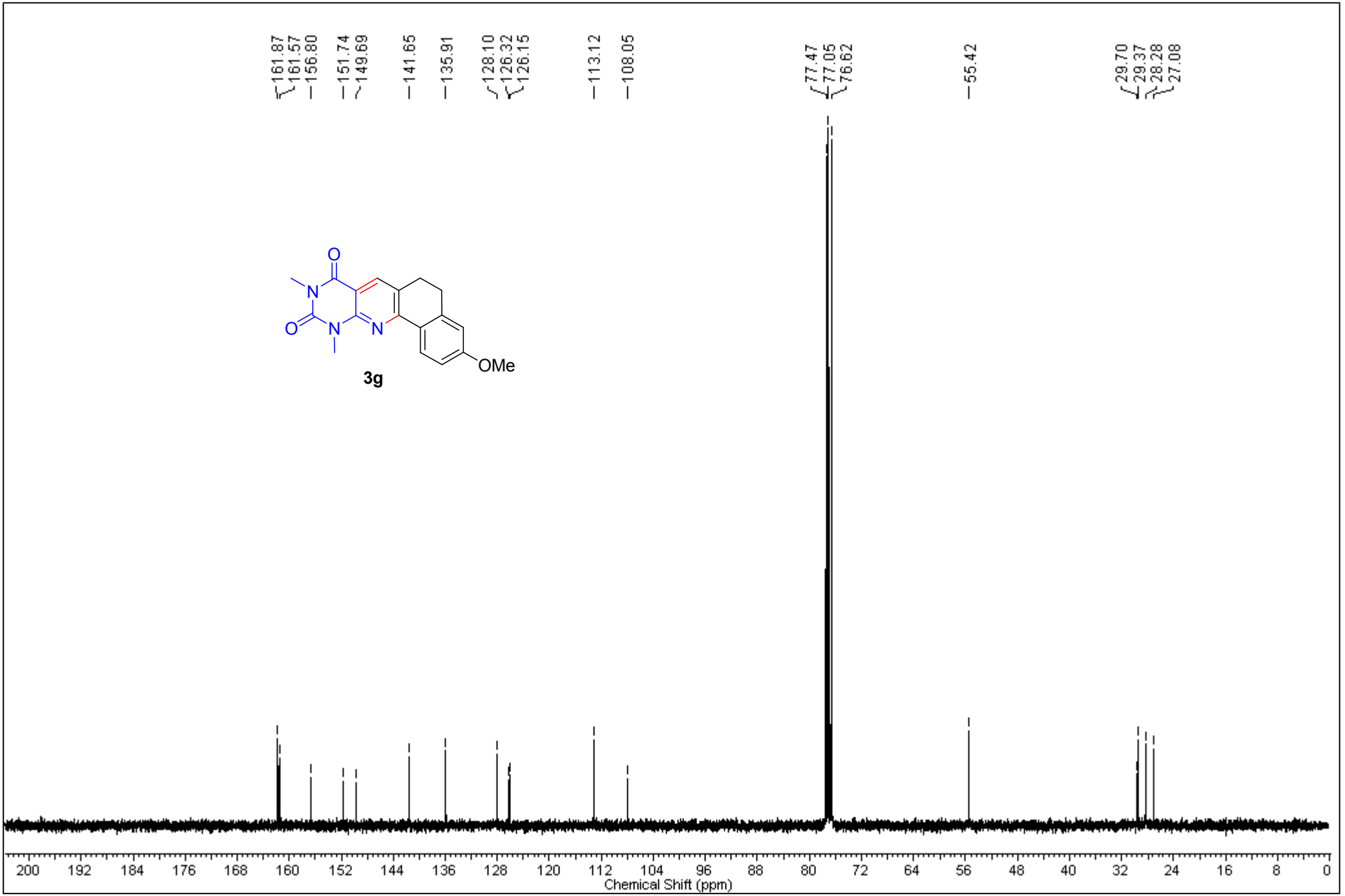
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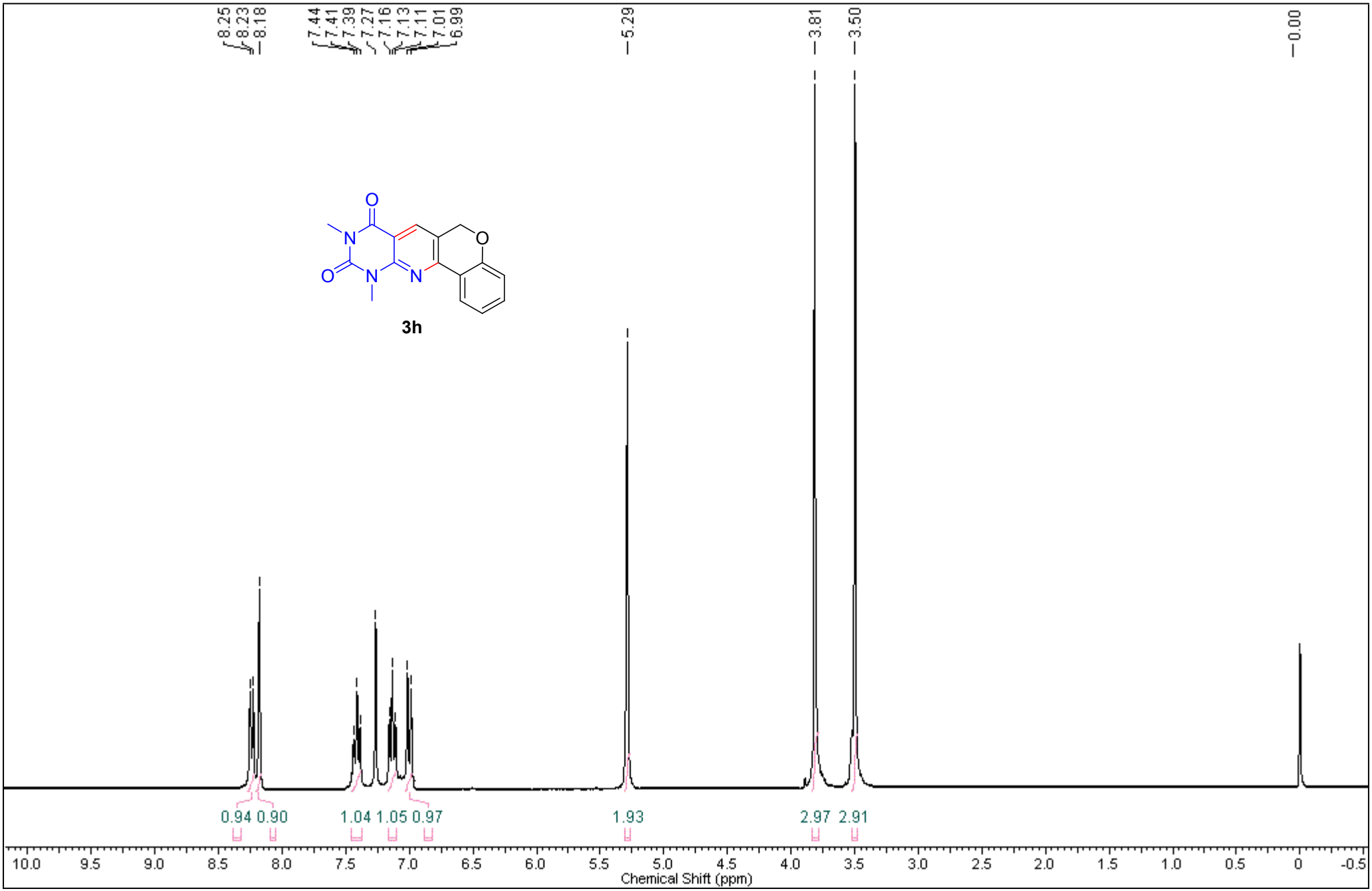
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2.97 2.91
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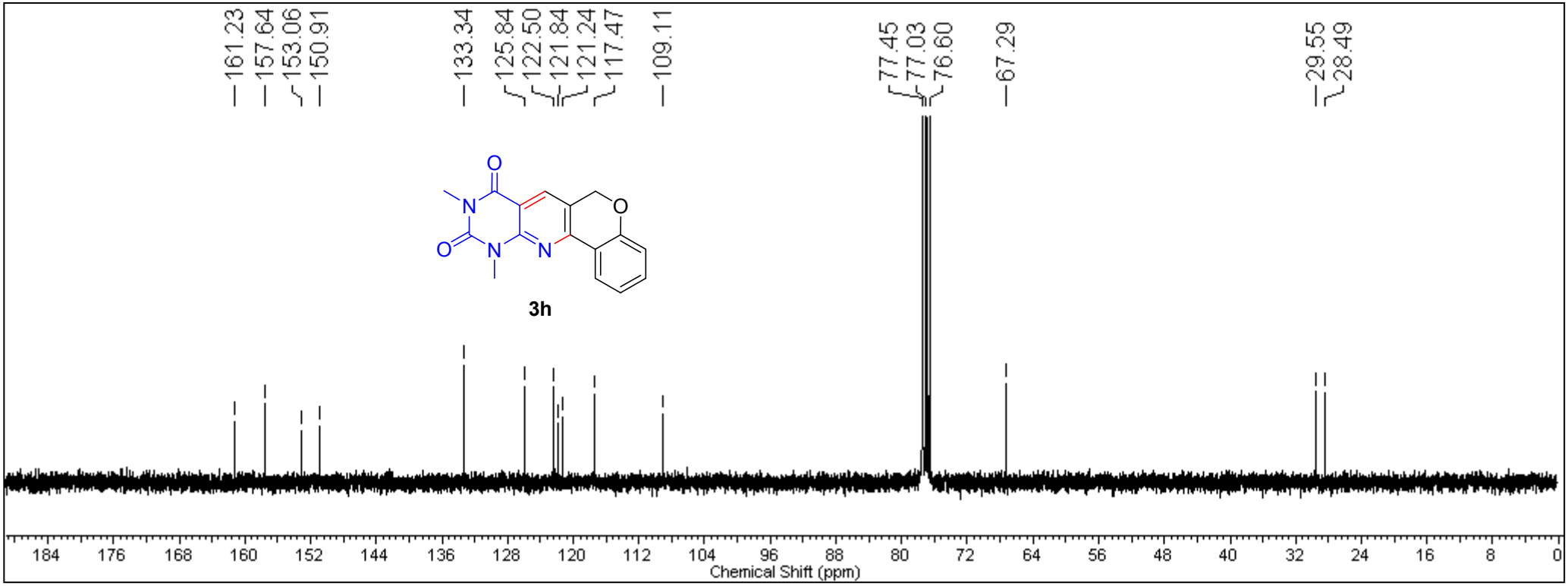
Chemical Shift (ppm)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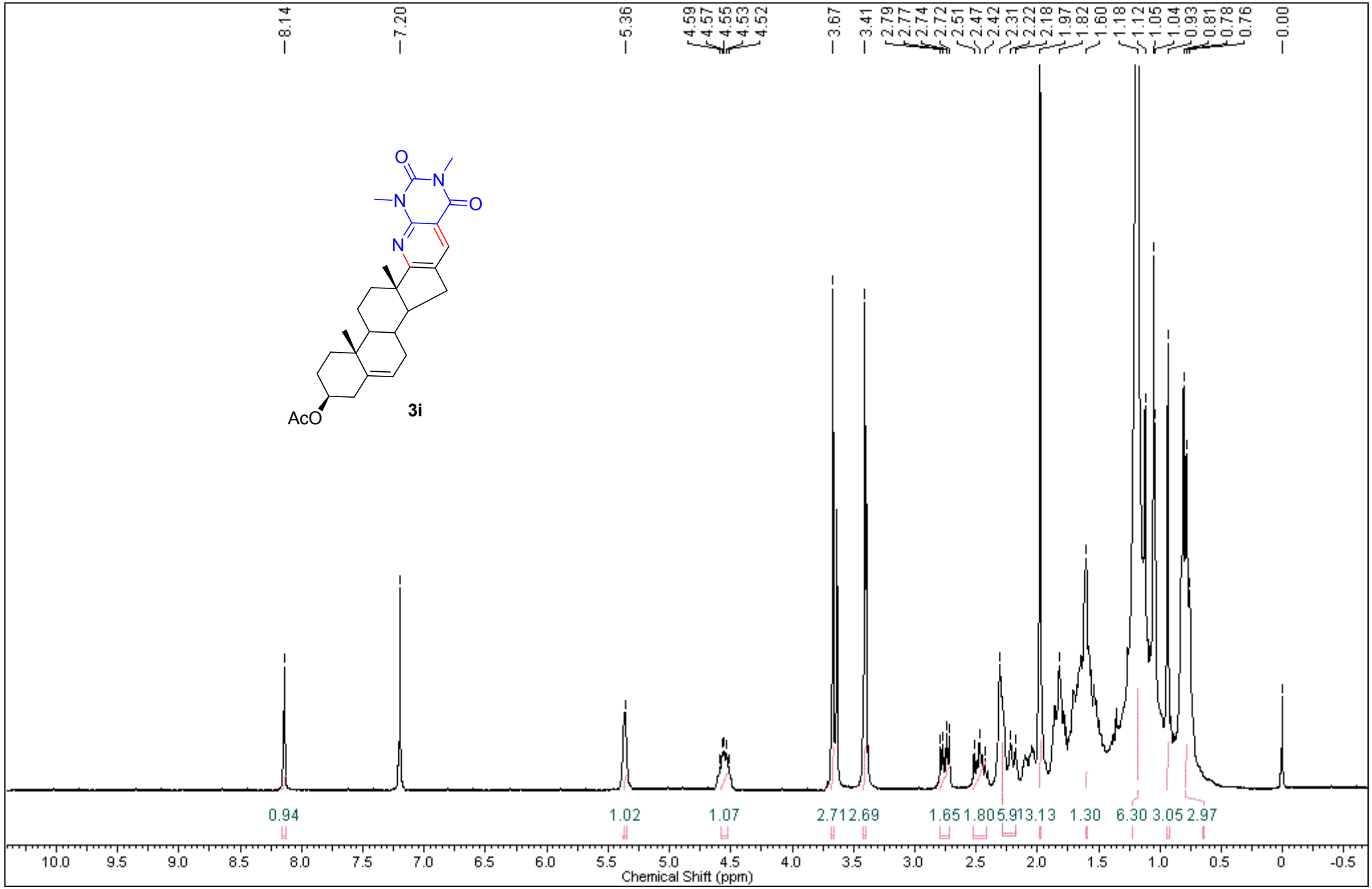
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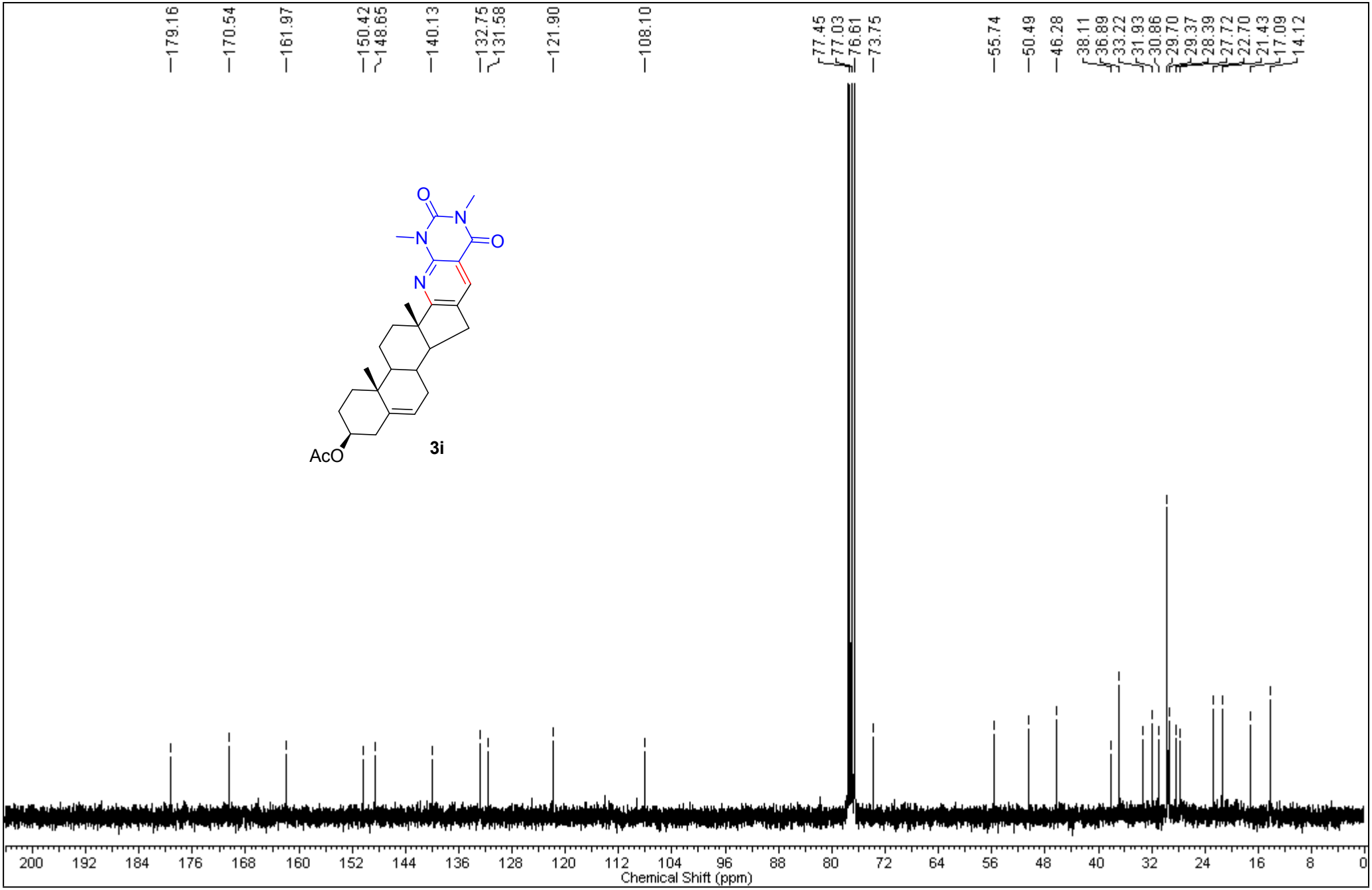
Chemical Shift (ppm)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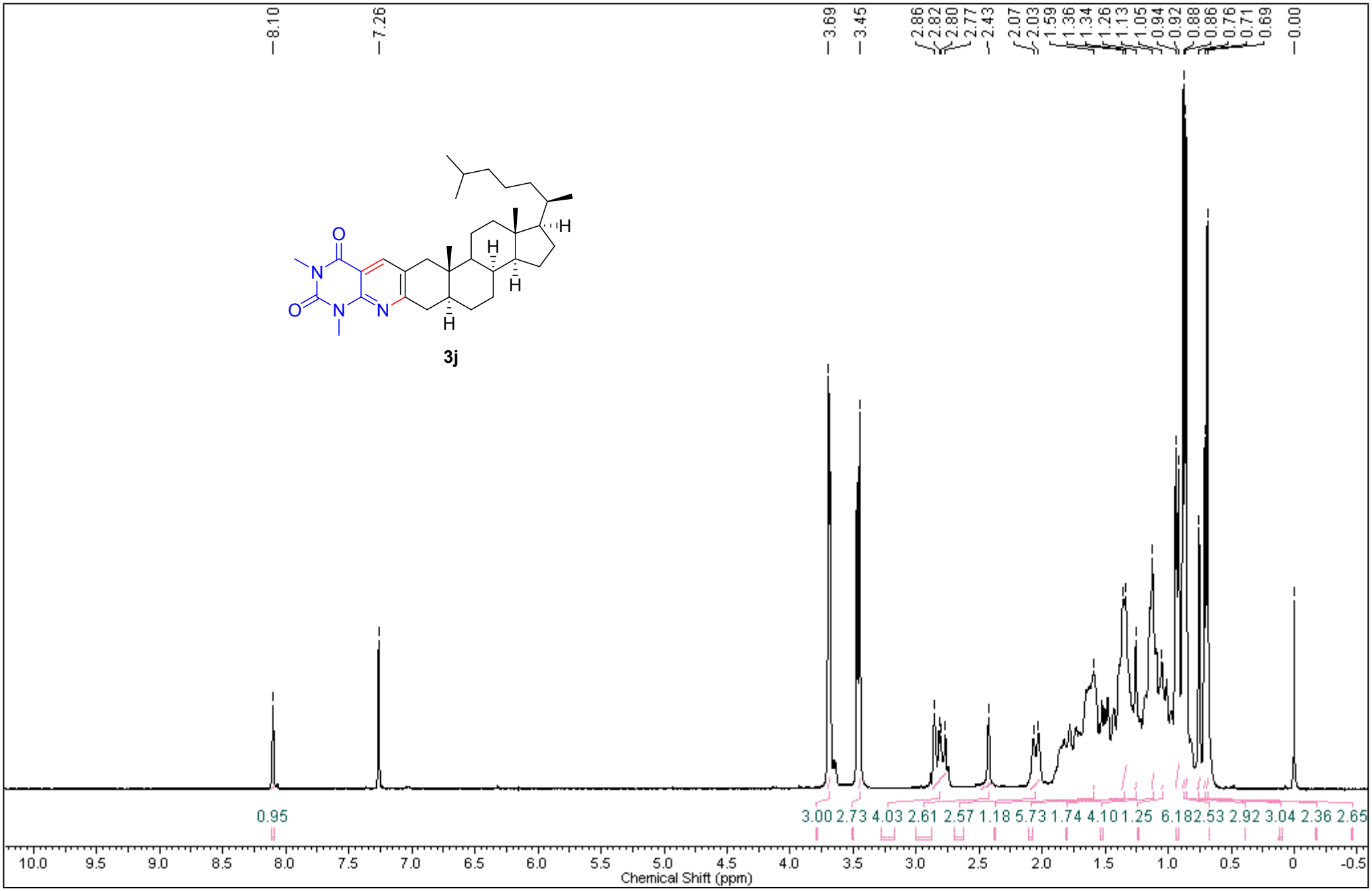
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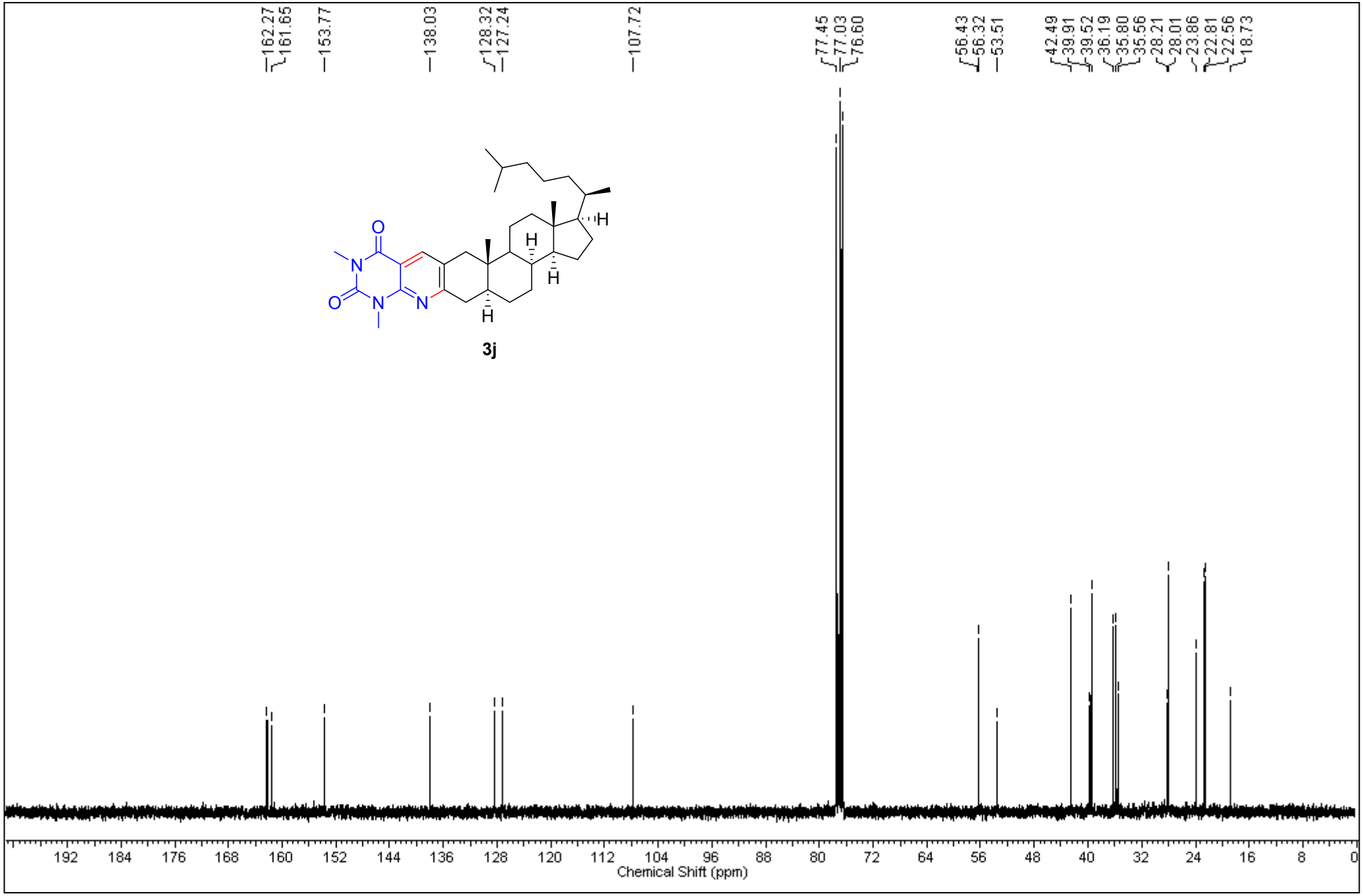
Chemical Shift (ppm)

3j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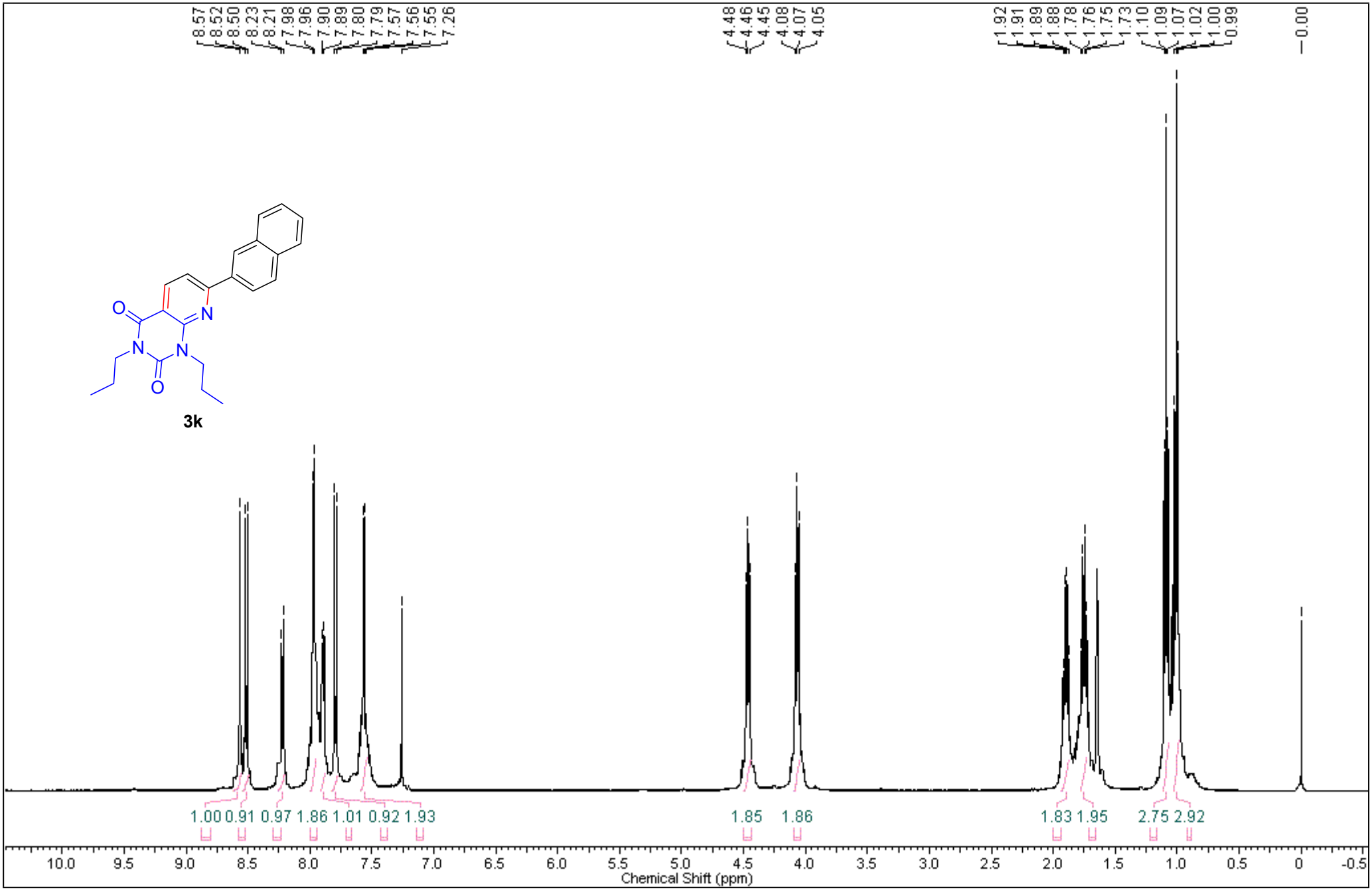
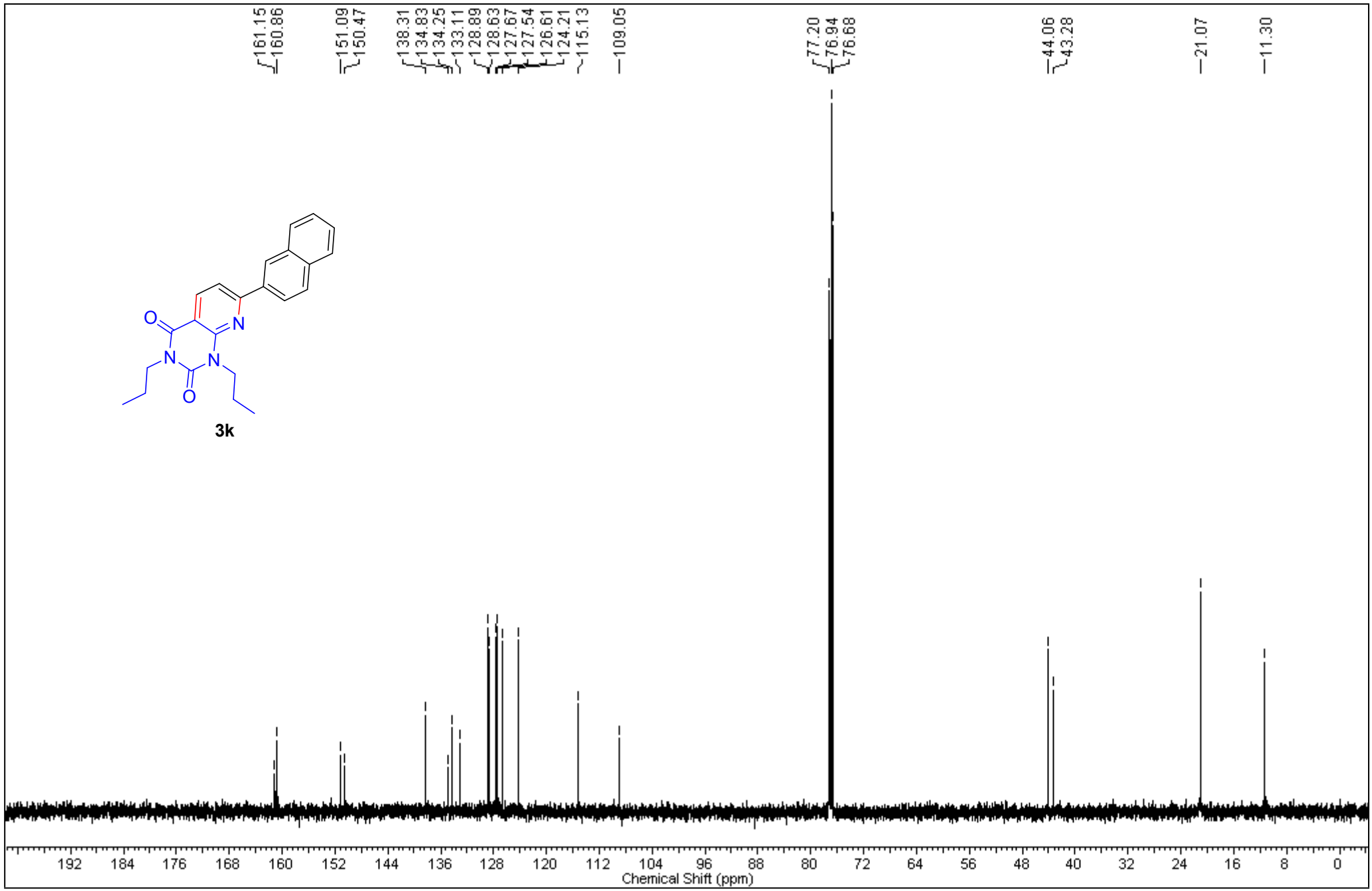
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

3j


8.57
8.52
8.50
8.23
8.21
7.98
7.96
7.90
7.89
7.80
7.79
7.57
7.56
7.55
7.26
4.48
4.46
4.45
4.08
4.07
4.05
1.92
1.91
1.89
1.88
1.78
1.76
1.75
1.73
1.10
1.09
1.07
1.02
1.00
0.99
0.00
O
N
N
N
O
3k
1.00 0.91 0.97 1.86 1.01 0.92 1.93
1.85 1.86
1.83 1.95 2.75 2.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)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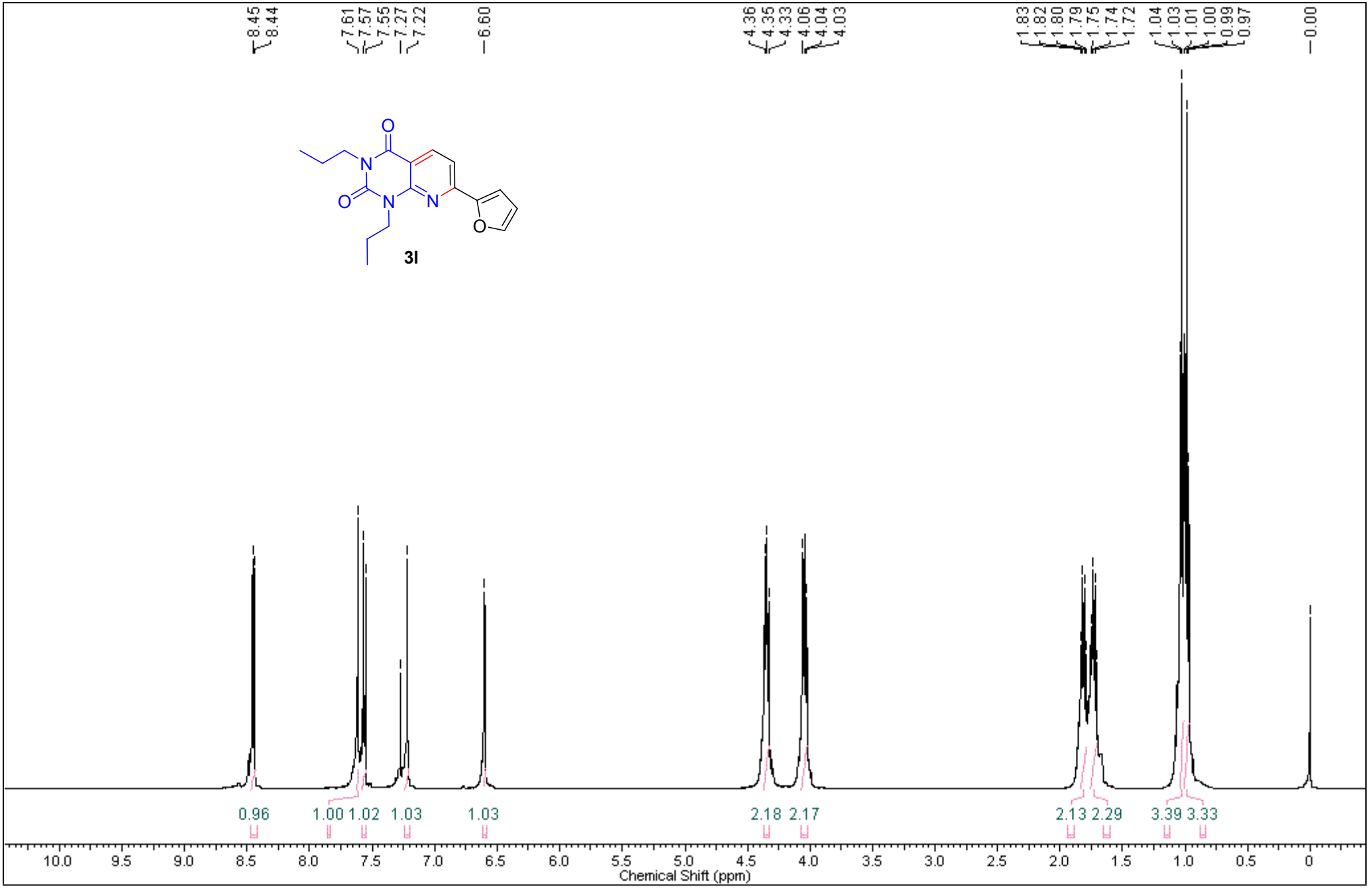
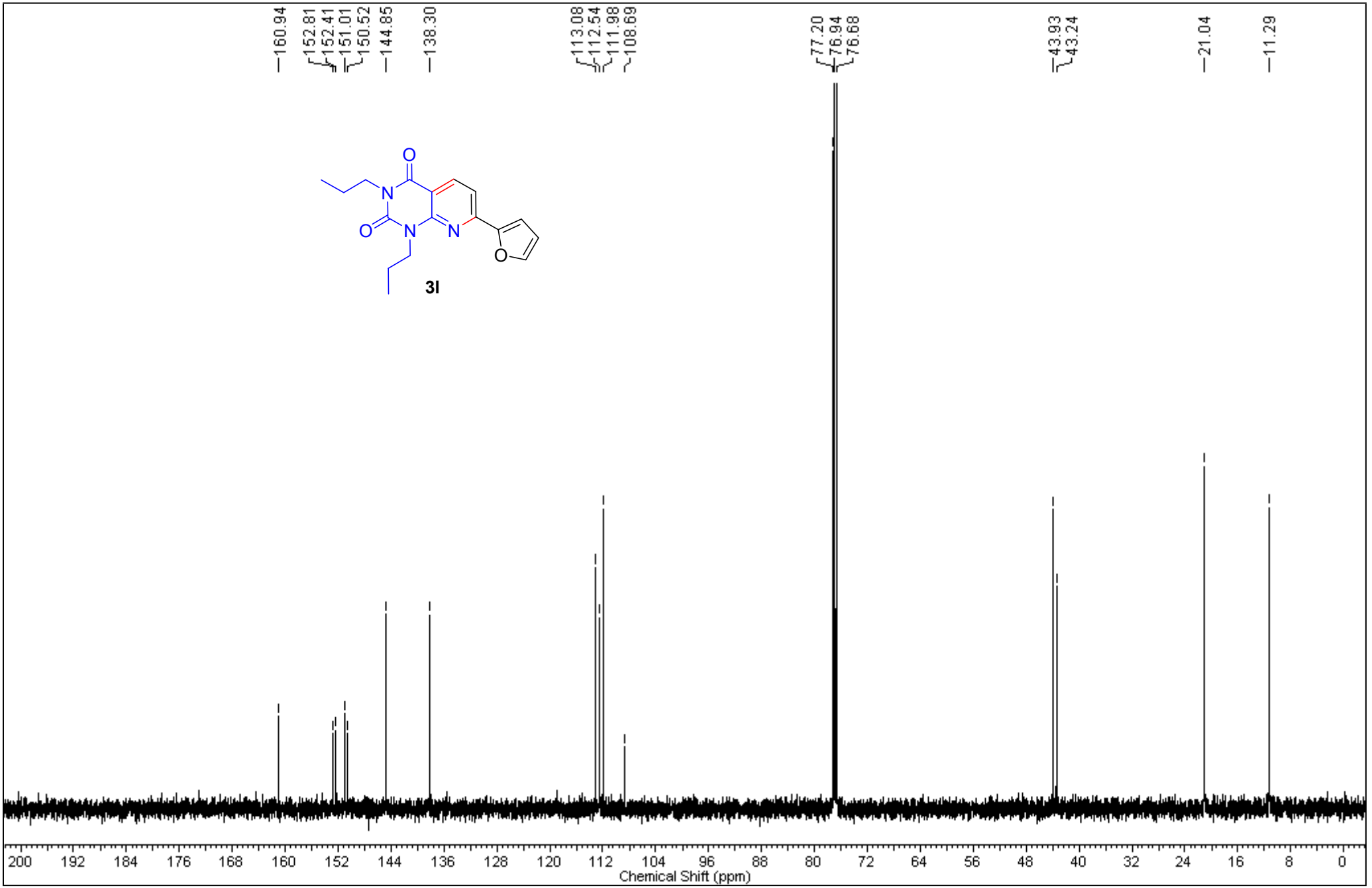
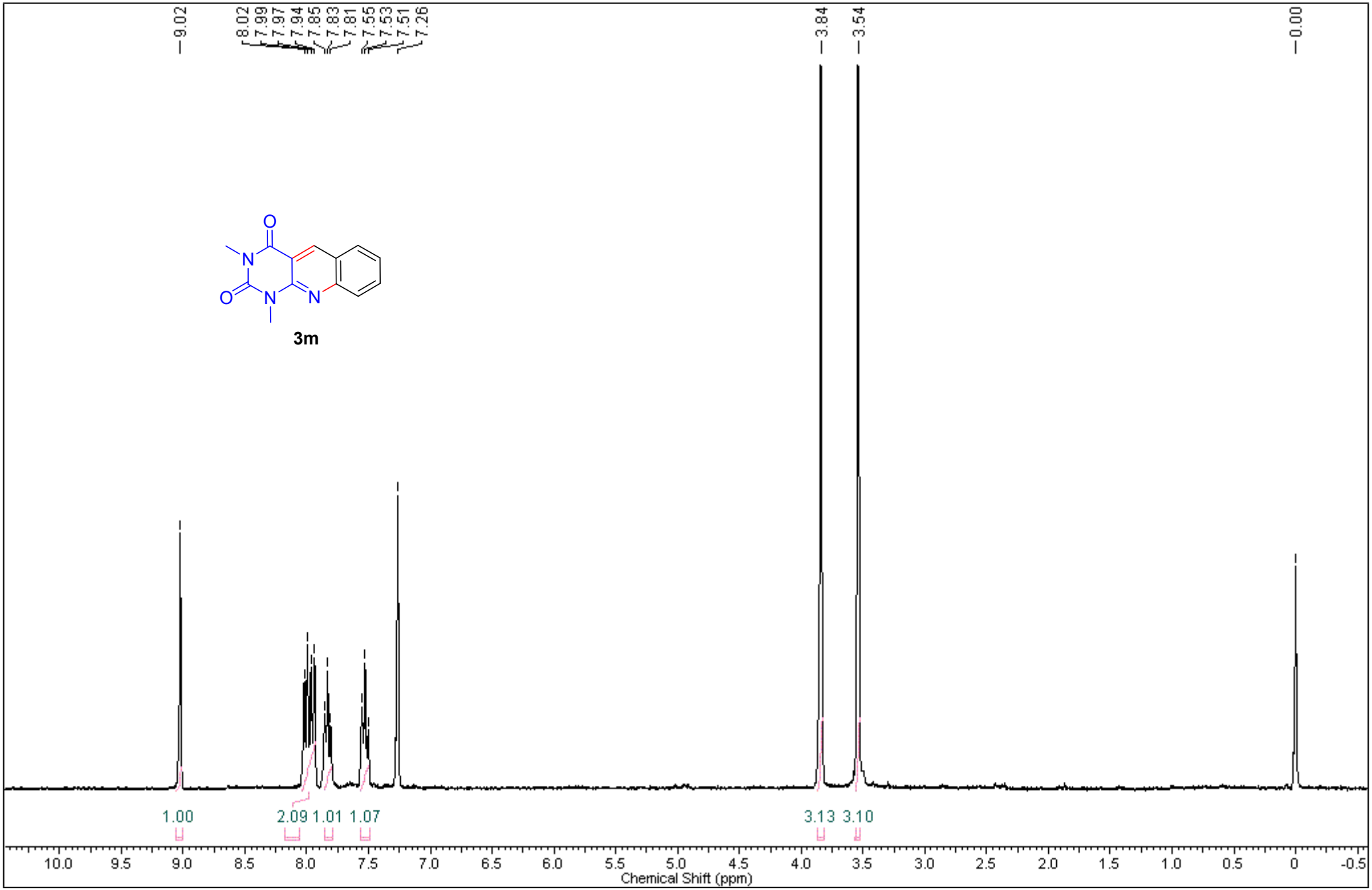
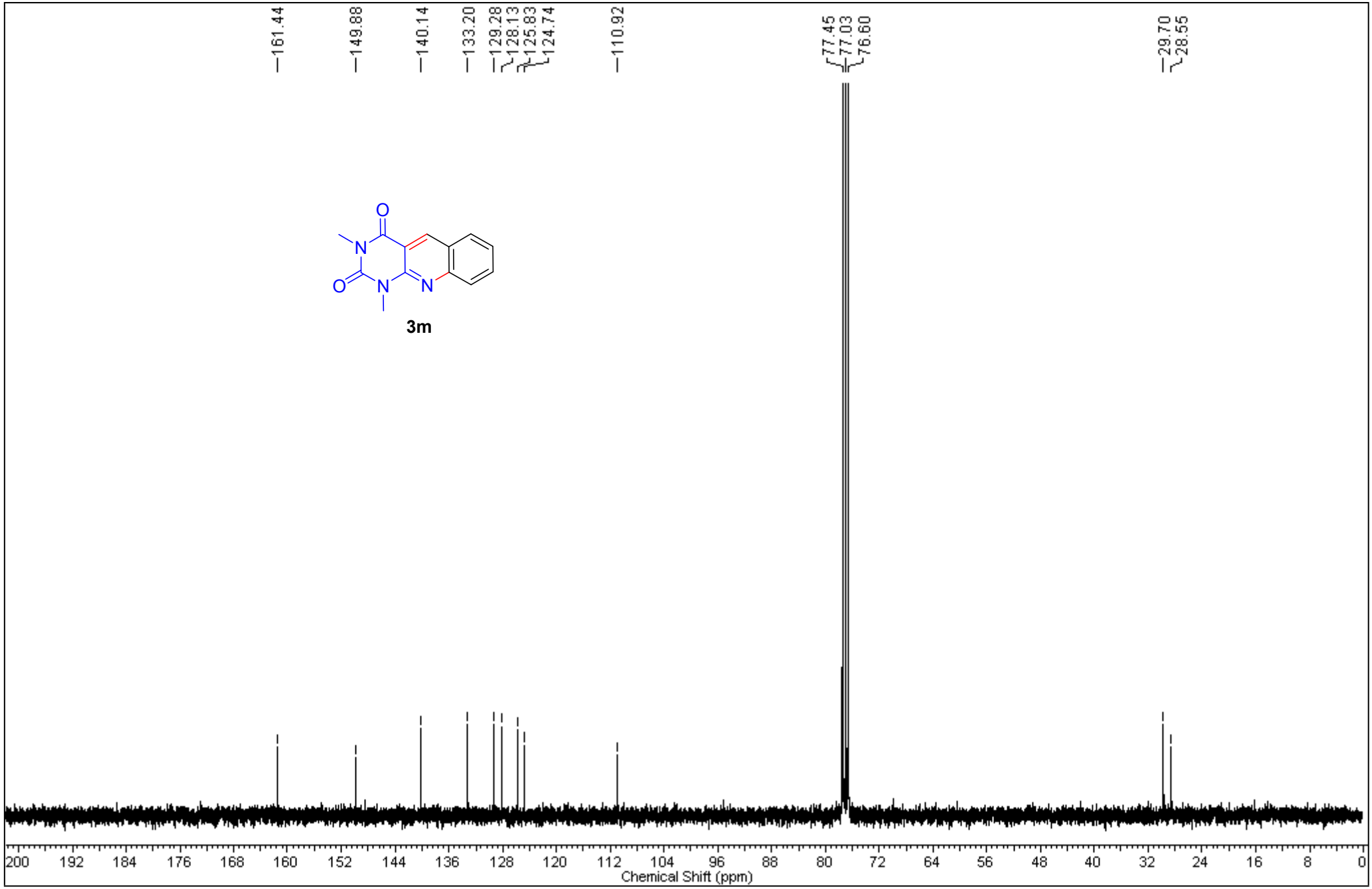
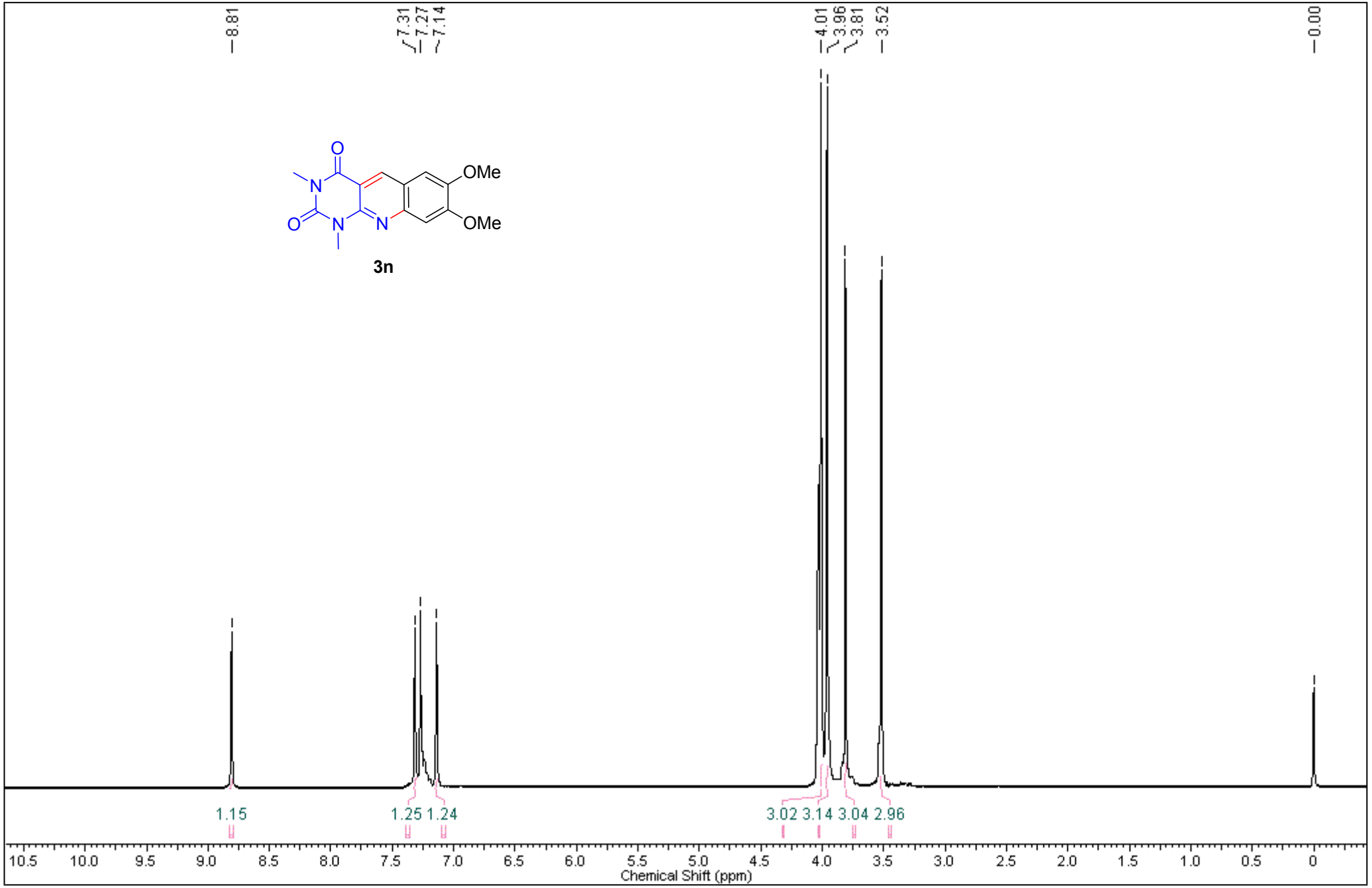
160.86
151.09
150.47
138.31
134.83
134.25
133.11
128.89
128.63
127.67
127.54
126.61
124.21
115.13
109.05
77.20
76.94
76.68
44.06
43.28
21.07
11.30
O
N
N
N
O
3k
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

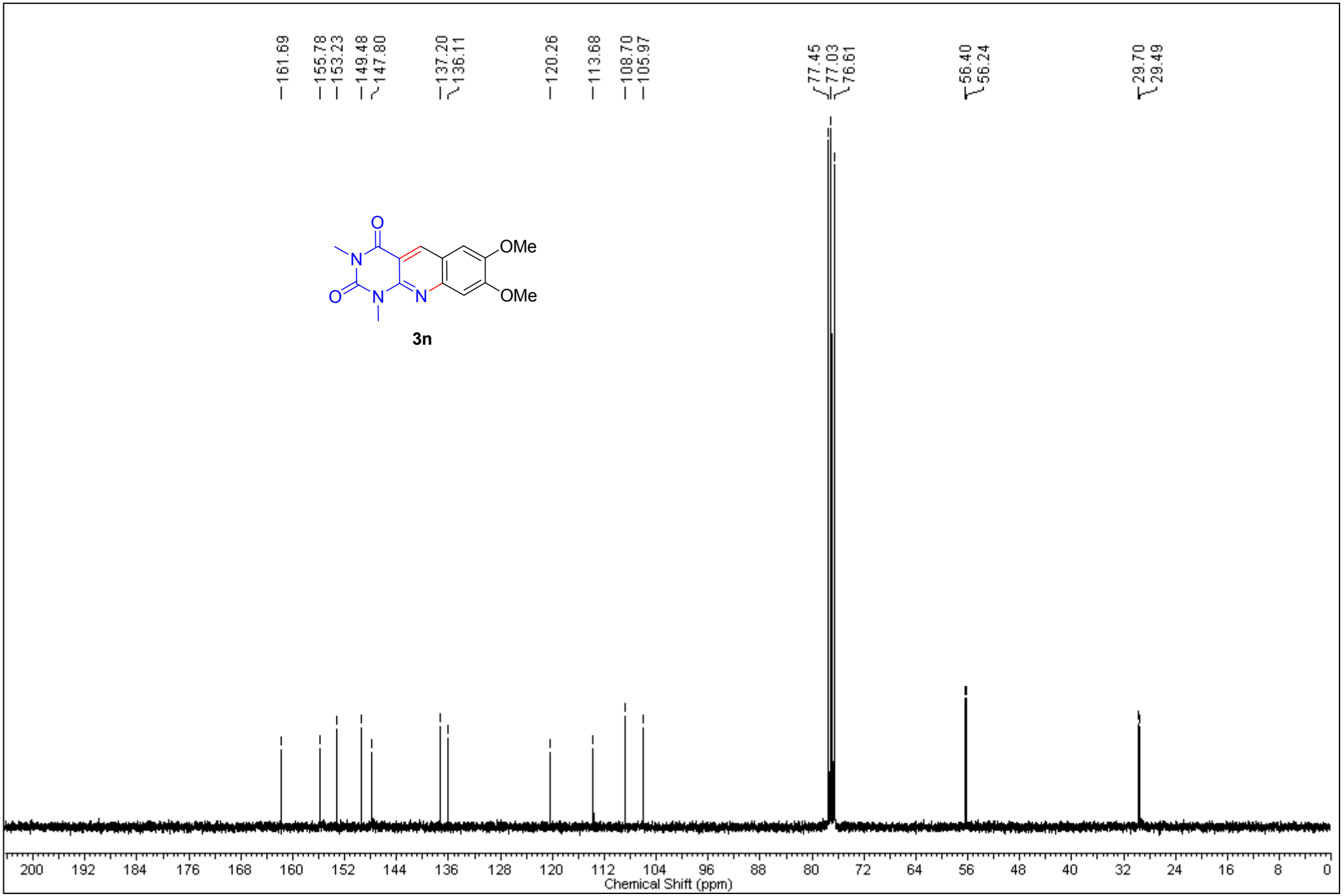

8.45
8.44
7.61
7.57
7.55
7.27
7.22
6.60
4.36
4.35
4.33
4.06
4.04
4.03
1.83
1.82
1.80
1.79
1.75
1.74
1.72
1.04
1.03
1.01
1.00
0.99
0.97
0.00
O
N
O
N
N
O
3l
0.96
1.00
1.02
1.03
1.03
2.18
2.17
2.13
2.29
3.39
3.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

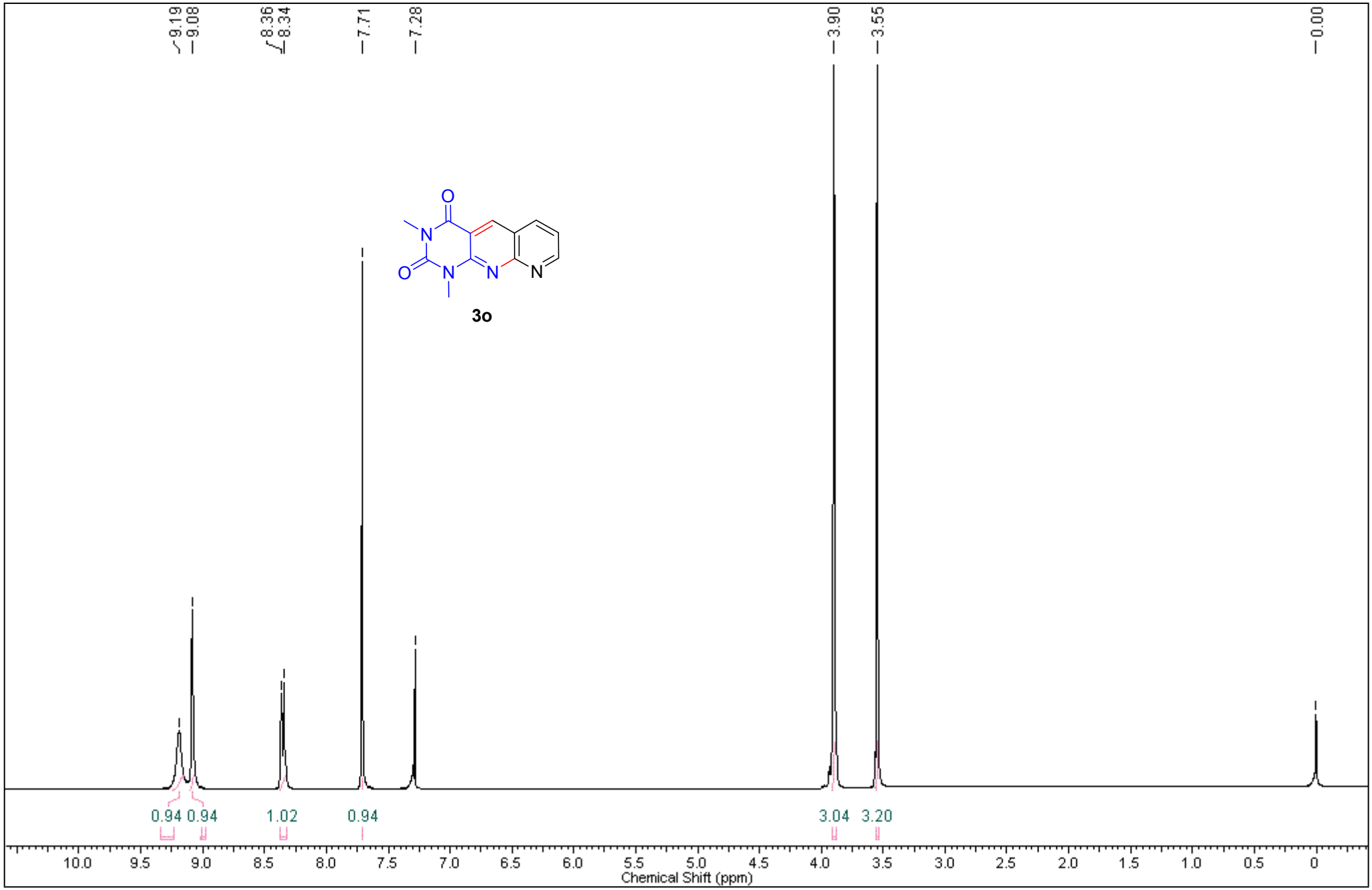

160.94
152.81
152.41
151.01
150.52
144.85
138.30
113.08
112.54
111.98
108.69
77.20
76.94
76.68
43.93
43.24
21.04
11.29
O
N
O
N
N
O
3l
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

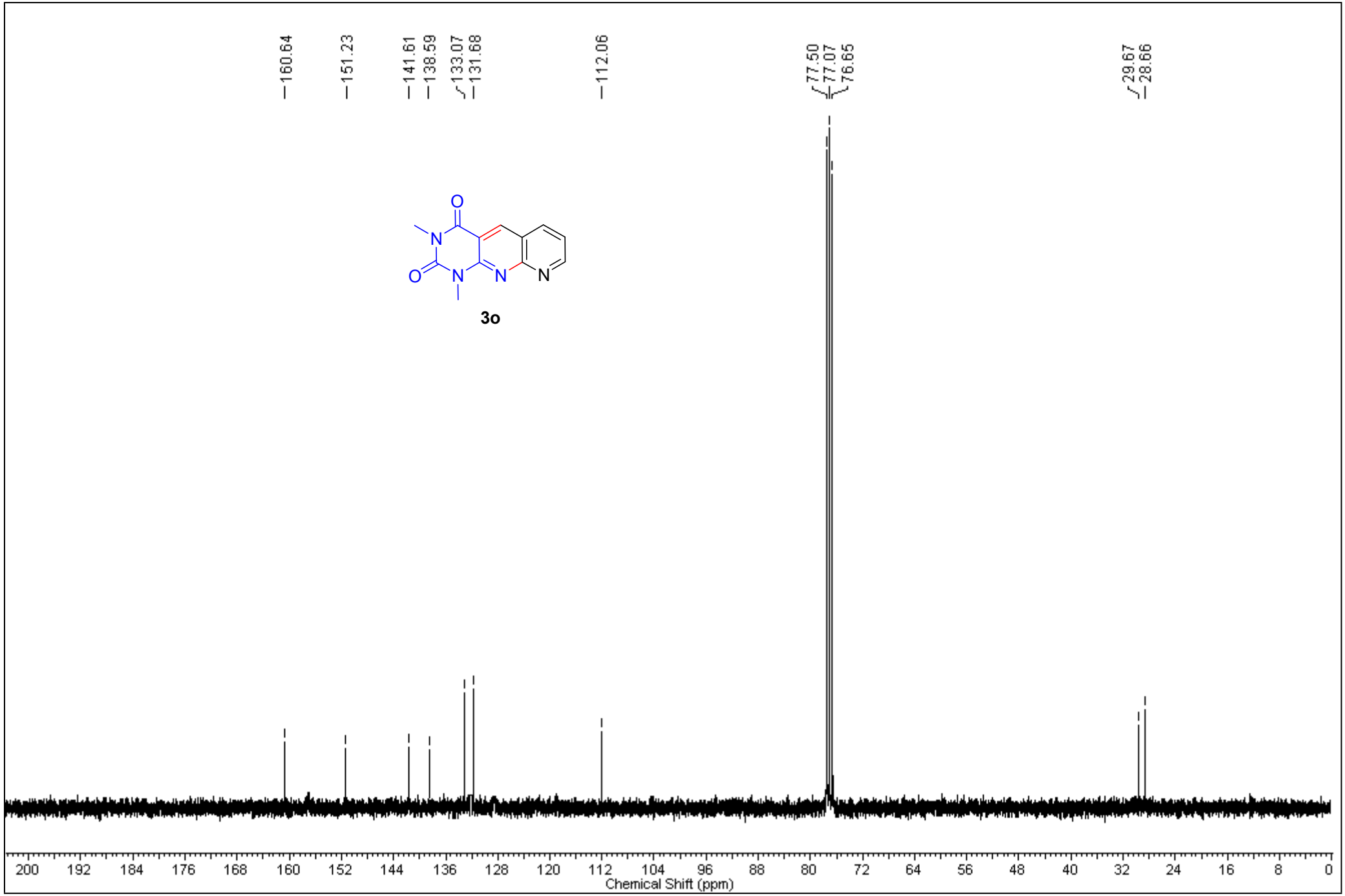

9.02
8.02
7.99
7.97
7.94
7.85
7.83
7.81
7.55
7.53
7.51
7.26
3.84
3.54
0.00
O
N
O
N
N
3m
1.00
2.09
1.01
1.07
3.13
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


161.44
149.88
140.14
133.20
129.28
128.13
125.83
124.74
110.92
77.45
77.03
76.60
29.70
28.55
O
N
O
N
N
3m
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


8.81
7.31
7.27
7.14
4.01
3.96
3.81
3.52
0.00
O
N
O
N
N
OMe
OMe
3n
1.15
1.25
1.24
3.02
3.14
3.04
2.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


161.69
155.78
153.23
149.48
147.80
137.20
136.11
120.26
113.68
108.70
105.97
77.45
77.03
76.61
56.40
56.24
29.70
29.49
O
N
O
N
N
OMe
OMe
3n
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


9.19
9.08
8.36
8.34
7.71
7.28
3.90
3.55
0.00
O
N
O
N
N
N
3o
0.94
0.94
1.02
0.94
3.04
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


160.64
151.23
141.61
138.59
133.07
131.68
112.06
77.50
77.07
76.65
29.67
28.66
O
N
O
N
N
N
3o
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)