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Supporting Information

Iron(III)-Catalyzed Dehydrogenative Cross-Coupling Reaction of Indoles with Benzylamines to Prepare 3-Aminoindole Derivatives

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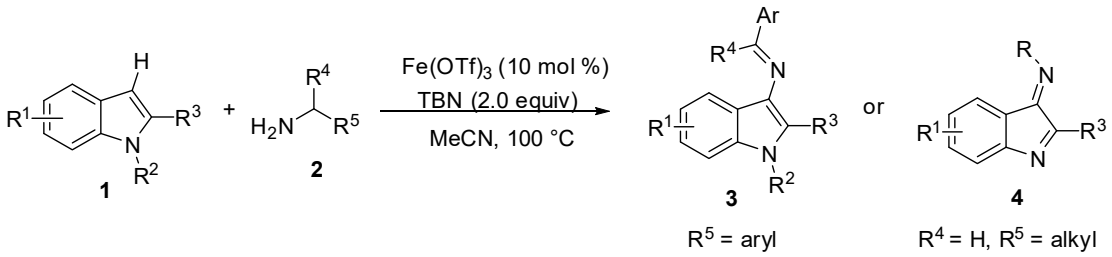
Contents

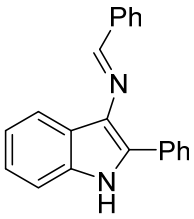
1. General experimental information

^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 MHz or 600 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on an LTQ FT spectrometer, and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Chromatography was performed using with 300-400 mesh silica gel (SiO_2). Unless otherwise noted, all reactions were performed under air atmosphere. All reagents and solvents were obtained from commercial sources and where appropriate, purified prior to use. Benzylamines **2a-2v** was purchased from Sigma-Aldrich.

2. General procedure for the synthesis of compounds 3 and 4

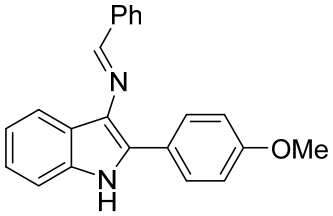


General procedure A: In a dry Teflon-sealed reaction flask equipped with a magnetic stir bar was charged with the corresponding indoles **1** (0.3 mmol), amine **2** (0.6 mmol, 2.0 equiv.), $Fe(OTf)_3$ (0.015 g, 10 mol%), and TBN (0.062 g, 0.6 mmol, 2.0 equiv.). Then, MeCN (3.0 mL) was added. The mixture was stirred at 100 °C for 10-18 h (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/10, ethyl acetate/petroleum ether) to afford 3-aminoindoles **3** or indolenine imine **4**.



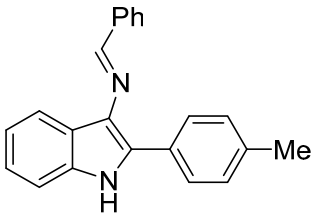
3aa

***(E)*-N-Benzylidene-2-phenyl-1H-indol-3-amine (3aa)**, a yellow solid, 0.075 g, 85% yield. Mp: 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.18 (brs, 1H), 7.91 (d, J = 2.0 Hz, 3H), 7.86 (d, J = 6.8 Hz, 2H), 7.41 (d, J = 7.6 Hz, 5H), 7.31 (t, J = 7.6 Hz, 2H), 7.20–7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 137.7, 135.4, 131.9, 131.6, 130.1, 128.6, 128.5, 127.9, 127.8, 127.5, 125.8, 123.0, 121.9, 120.9, 119.7, 111.5; IR (thin film) 3573, 3394, 3056, 1641, 1597, 1573, 1535, 938, 742 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2$ $[M+H]^+$: 297.1386, found: 297.1376.



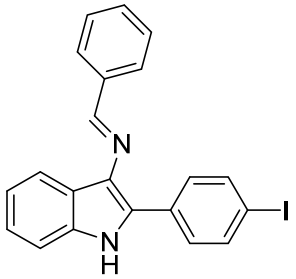
3ba

***(E)*-N-Benzylidene-2-(4-methoxyphenyl)-1H-indol-3-amine (3ba)**, a yellow solid, 0.067 g, 68% yield. Mp: 155–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.18 (brs, 1H), 7.93 (d, J = 6.8 Hz, 3H), 7.86 (d, J = 8.4 Hz, 2H), 7.47–7.41 (m, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.23–7.16 (m, 2H), 7.00 (d, J = 7.6 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 155.6, 137.9, 135.3, 132.4, 130.0, 129.3, 128.6, 127.8, 124.8, 124.4, 122.6, 122.1, 120.8, 119.6, 114.1, 111.3, 55.3; IR (thin film) 3573, 3475, 2959, 2924, 1604, 1536, 1307, 740 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2O[M+H]^+$: 327.1492, found: 327.1482.



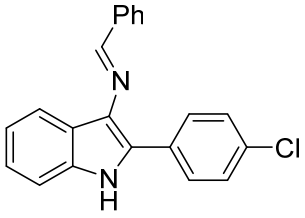
3ca

***(E)*-N-benzylidene-2-(p-tolyl)-1H-indol-3-amine (3ca)**, a yellow oil, 0.086 g, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.14 (brs, 1H), 7.91 (d, J = 6.8 Hz, 3H), 7.76 (d, J = 8.4 Hz, 2H), 7.44–7.39 (m, 3H), 7.28 (d, J = 6.8 Hz, 1H), 7.22–7.16 (m, 4H), 6.99 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 137.9, 137.5, 135.4, 132.4, 130.0, 129.3, 128.8, 128.6 127.9, 127.8, 125.4, 122.8, 122.0, 120.8, 119.7, 114.3, 21.2; IR (thin film) 3433, 3144, 2964, 1605, 1600, 1438, 1354, 737 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found: 311.1541.



3da

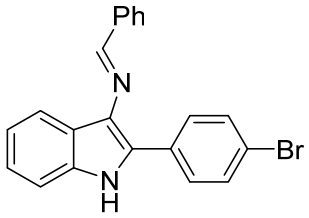
***(E)*-N-(2-(4-iodophenyl)-1H-indol-3-yl)-1-phenylmethanimine (3da)**, a yellow solid, 0.078 g, 62% yield. Mp: 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.23 (s, 1H), 7.94 (d, J = 7.6 Hz, 3H), 7.81 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H),7.50–7.44 (m, 3H), 7.41 (d, J = 7.6 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 137.7, 137.6, 135.6, 131.2, 130.7, 130.4, 129.5, 128.7, 128.0, 126.5, 123.5, 121.9, 121.2, 119.9, 111.6, 93.3; IR (thin film) 3440, 3049, 1599, 1570, 1478, 1430, 817, 738 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{15}IN_2$ $[M+H]^+$: 423.0353, found: 423.0352.



3ea

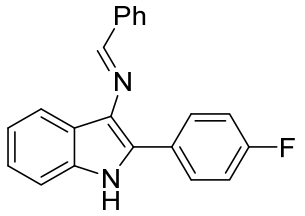
***(E)*-N-Benzylidene-2-(4-chlorophenyl)-1H-indol-3-amine (3ea)**, a yellow oil, 0.087 g, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.15 (brs, 1H), 7.89–7.86 (m, 3H), 7.76 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 6.8 Hz, 3H), 7.35 (d, J = 8.4 Hz, 2H),

7.27 (d, J = 7.6 Hz, 1H), 7.22–7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 137.6, 135.5, 133.4, 130.8, 130.3, 130.1, 129.0, 128.8 128.6, 127.9, 126.1, 123.3, 121.8, 121.1, 119.8, 111.6; IR (thin film) 3574, 3412, 3053, 1651, 1610, 1569, 1529, 830, 738 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}ClN_2$ $[M+H]^+$: 331.0997, found: 331.0994.



3fa

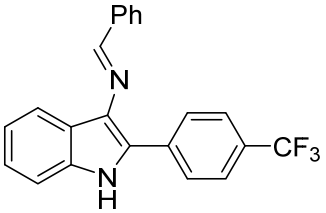
***(E)*-N-Benzylidene-2-(4-bromophenyl)-1H-indol-3-amine (3fa)**, a yellow solid, 0.100 g, 89% yield. Mp: 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.18 (brs, 1H), 7.90–7.88 (m, 3H), 7.73 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.48–7.43 (m, 3H), 7.32 (d, J = 7.6 Hz, 1H), 7.24–7.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 137.6, 135.5, 131.6, 130.7, 130.6, 130.4, 129.3, 128.7 128.0, 126.3, 123.3, 121.8, 121.7, 121.1, 119.8, 111.6; IR (thin film) 3573, 3438, 3010, 1651, 1572, 1526, 1006, 737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$: 375.0491, found: 375.0519.



3ga

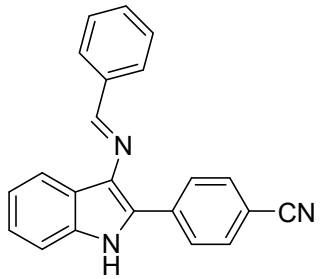
***(E)*-N-Benzylidene-2-(4-fluorophenyl)-1H-indol-3-amine (3ga)**, a yellow solid, 0.076 g, 81% yield. Mp: 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.18 (brs, 1H), 7.95–7.88 (m, 5H), 7.49–7.44 (m, 3H), 7.39 (d, J = 8.0 Hz, 1H), 7.27–7.20 (m, 2H), 7.18 (t, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6 (d, J = 247.2 Hz), 156.5, 137.7, 135.4, 131.3, 130.3, 129.7, 129.6, 128.7, 127.9, 125.7, 123.1, 121.9, 121.1, 119.8, 115.7 (d, J = 21.2 Hz), 111.5; IR (thin film) 3573, 3420, 3046, 1656, 1605, 1537, 1500, 836, 742 cm^{-1}; HRMS (ESI) m/z calcd for

$C_{21}H_{16}FN_2[M+H]^+$: 315.1292, found: 315.1291.



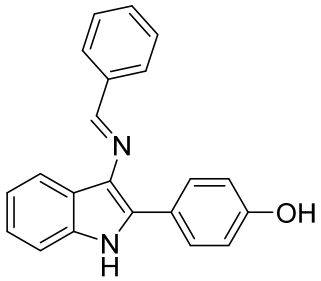
3ha

***(E)*-N-Benzylidene-2-(4-(trifluoromethyl)phenyl)-1H-indol-3-amine (3ha)**, a yellow solid, 0.079 g, 72% yield. Mp: 172–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.27 (brs, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.92–7.88 (m, 3H), 7.66 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 6.0 Hz, 3H), 7.35 (d, J = 8.0 Hz, 1H), 7.27–7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 137.4, 135.8, 135.1, 130.6, 129.8, 129.1 (q, J = 30.8 Hz), 128.8, 128.1, 127.7, 127.4, 125.6 (q, J = 269.8 Hz), 125.5 (q, J = 4.6 Hz), 123.8, 122.9, 121.7, 120.0, 111.7; IR (thin film) 3574, 3436, 3055, 1674, 1603, 1573, 849, 739 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{16}F_3N_2$ $[M+H]^+$: 365.1260, found: 365.1290.



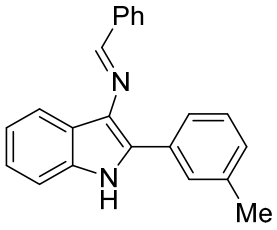
3ia

***(E)*-4-(3-(benzylideneamino)-1H-indol-2-yl)benzonitrile (3ia)**, a yellow solid, 0.075 g, 78% yield. Mp: 187–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.33 (s, 1H), 8.08 (d, J = 8.4 Hz, 2H), 7.96-7.91 (m, 3H), 7.75 (d, J = 8.4 Hz, 2H),7.52–7.50 (m, 3H), 7.45 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.6 Hz 2H), 7.24 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 137.2, 136.1, 136.0, 132.3, 130.9, 128.9, 128.8, 128.4, 128.2, 127.8, 124.3, 121.6, 121.4, 120.1, 119.0, 111.8, 110.2. IR (thin film) 3437, 2918, 2320, 2228, 1638, 1602, 1492, 841, 737 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{15}N_3$ $[M+H]^+$: 322.1339, found: 322.1338.



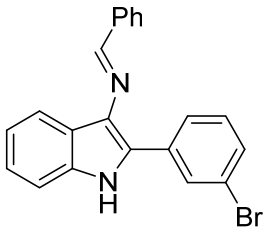
3ja

***(E)*-4-(3-(benzylideneamino)-1H-indol-2-yl)phenol (3ja)**, a green solid, 0.059 g, 63% yield. Mp: 211–212 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.21 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 4H), 7.49-7.43 (m, 3H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.23–7.17 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 2H). 13C NMR (100 MHz, $CDCl_3$): δ 155.9, 155.4, 137.8, 135.3, 132.4, 130.1, 129.5, 128.6, 127.8, 124.8, 124.5, 122.7, 122.1, 120.9, 119.6, 115.6, 111.3. IR (thin film) 3465, 3405, 2063, 1637, 1439, 1261, 732, 686 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{16}N_2O$ $[M+H]^+$: 313.1335, found: 313.1333.



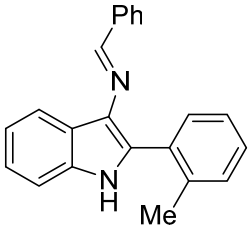
3ka

***(E)*-N-Benzylidene-2-(m-tolyl)-1H-indol-3-amine (3ka)**, a yellow oil, 0.083 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.08 (s, 1H), 8.18 (brs, 1H), 7.92 (d, *J* = 6.4 Hz, 3H), 7.72 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.46–7.40 (m, 3H), 7.33–7.30 (m, 2H), 7.32 (dd, *J* = 6.8 Hz, 14.4 Hz, 2H), 7.15–7.11 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.2, 138.0, 137.9, 135.4, 132.1, 131.6, 130.1, 128.7, 128.6, 128.4, 128.3, 128.0, 125.8, 125.1, 122.9, 122.0, 120.8, 119.7, 111.5, 21.6; IR (thin film) 3574, 3412, 3050, 2921, 1651, 1603, 1573, 1451, 1370, 739 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found: 311.1543.



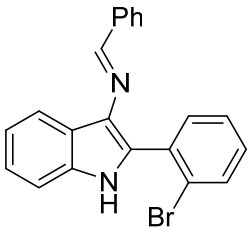
3la

***(E)*-N-Benzylidene-2-(3-bromophenyl)-1H-indol-3-amine (3la)**, a yellow oil, 0.106 g, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.22 (brs, 1H), 8.12 (s, 1H), 7.93–7.88 (m, 3H), 7.78 (d, J = 7.6 Hz, 1H), 7.48–7.42 (m, 3H), 7.40 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.26–7.15 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 137.6, 135.6, 133.7, 130.7, 130.4, 130.2, 130.1, 129.9, 128.7 128.1, 126.6, 126.1, 123.5, 122.6, 121.7, 121.1, 119.9, 111.6; IR (thin film) 3574, 3433, 3016, 1650, 1620, 1594, 736, 687 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$: 375.0491, found: 375.0514.



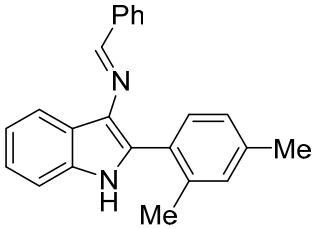
3ma

***(E)*-N-Benzylidene-2-(o-tolyl)-1H-indol-3-amine (3ma)**, a yellow oil, 0.073 g, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.05 (brs, 1H), 7.98–7.96 (m, 1H), 7.76 (d, J = 4.0 Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.38–7.28 (m, 6H), 7.22 (t, J = 4.0 Hz, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 137.7, 137.6, 135.2, 132.6, 131.7, 130.9, 130.5, 130.0, 128.5, 128.4, 127.7, 126.0, 125.6, 122.6, 122.1, 120.7, 119.7, 111.3, 20.7; IR (thin film) 3404, 3057, 2963, 1608, 1573, 1451, 1369, 1329, 740 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found: 311.1545.



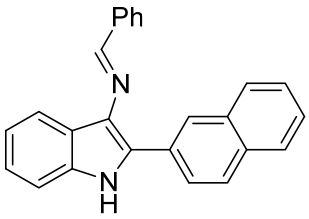
3na

***(E)*-N-Benzylidene-2-(2-bromophenyl)-1H-indol-3-amine (3na)**, a yellow solid, 0.067 g, 60% yield. Mp: 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H), 8.49 (brs, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 5.6 Hz, 2H), 7.70–7.65 (m, 2H), 7.38–7.31 (m, 5H), 7.28–7.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 137.7, 134.9, 134.3, 133.4, 132.4, 130.8, 130.2, 129.5, 128.6, 127.9, 127.0, 126.7, 123.2, 122.6, 121.3, 120.8, 119.9, 111.6; IR (thin film) 3573, 3265, 3050, 1610, 1575, 924, 767, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$: 375.0491, found: 375.0471.



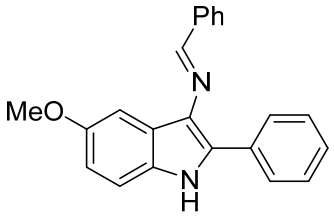
3oa

***(E)*-N-Benzylidene-2-(2,4-dimethylphenyl)-1H-indol-3-amine (3oa)**, a yellow solid, 0.087 g, 89% yield. Mp: 119–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.03 (brs, 1H), 7.99 (d, J = 6.4 Hz, 1H), 7.79 (d, J = 5.6 Hz, 2H) 7.38–7.33 (m, 5H), 7.22 (d, J = 4.0 Hz, 2H), 7.12 (s, 1H), 7.08 (d, J = 7.6 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 155.4, 138.3, 137.8, 137.4, 135.2, 132.8, 131.4, 130.8, 129.9, 128.8, 128.5, 127.7, 126.4, 125.9, 122.5, 122.2, 120.7, 119.7, 111.2, 21.2, 20.7; IR (thin film) 3178, 3055, 2963, 2918, 1652, 1614, 1428, 1370, 808 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2$ $[M+H]^+$: 325.1699, found: 325.1700.



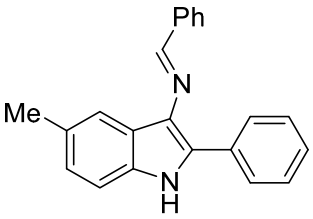
3pa

***(E)*-N-Benzylidene-2-(naphthalen-2-yl)-1H-indol-3-amine (3pa)**, a yellow oil, 0.091 g, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.21 (brs, 1H), 8.20 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.92–7.87 (m, 3H), 7.79–7.75 (m, 3H), 7.43–7.39 (m, 5H), 7.26 (d, J = 6.8 Hz, 1H), 7.20–7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 137.8, 135.6, 133.4, 132.5, 131.9, 130.2, 129.2, 128.7, 128.2, 128.0, 127.9, 127.8, 127.6, 126.8, 126.3, 126.1, 125.8, 123.1, 122.0, 120.9, 119.8, 111.5; IR (thin film) 3574, 3425, 3053, 1621, 1573, 1016, 856, 743 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{19}N_2$ $[M+H]^+$: 347.1543, found: 347.1571.



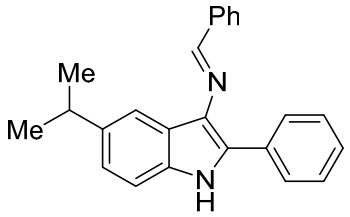
3qa

***(E)*-N-Benzylidene-5-methoxy-2-phenyl-1H-indol-3-amine (3qa)**, a yellow oil, 0.067 g, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.17 (brs, 1H), 7.93–7.89 (m, 4H), 7.47–7.43 (m, 5H), 7.38 (s, 1H), 7.34–7.31 (m, 1H), 7.29–7.24 (m, 1H), 6.91–6.89 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 155.0, 137.7, 132.6, 131.8, 130.7, 130.1, 128.6, 128.5, 127.9, 127.8, 127.5, 125.8, 122.3, 112.4, 112.1, 102.5, 56.1; IR (thin film) 3575, 3413, 2927, 1616, 1528, 1481, 1210, 690 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{18}KN_2O$ $[M+K]^+$: 365.1051, found: 365.1071.



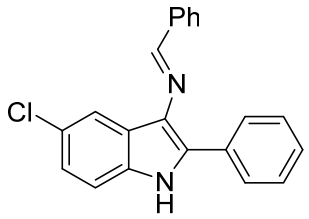
3ra

***(E)*-N-Benzylidene-5-methyl-2-phenyl-1H-indol-3-amine (3ra)**, a yellow oil, 0.086 g, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.10 (brs, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H) , 7.69 (s, 1H) 7.47–7.41 (m, 5H), 7.32 (t, J = 7.2 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 137.8, 133.8, 132.1, 131.9, 130.2, 130.0, 128.6, 128.5, 127.9, 127.8, 127.4, 125.6, 124.6, 122.2, 119.5, 111.2, 21.4; IR (thin film) 3574, 3379, 3056, 2917, 1591, 1573, 1449, 1309, 769 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found: 311.1569.



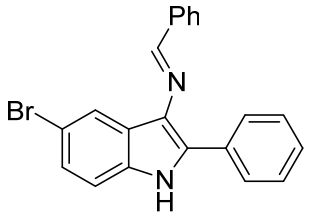
3sa

***(E)*-N-Benzylidene-5-isopropyl-2-phenyl-1H-indol-3-amine (3sa)**, a yellow oil, 0.098 g, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 1H), 8.14 (brs, 1H), 7.94 (d, J = 6.8 Hz, 2H), 7.86 (d, J = 7.6 Hz, 2H), 7.73 (brs, 1H), 7.46–7.38 (m, 5H), 7.30–7.27 (m, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 3.06–2.99 (m, 1H), 1.33 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 141.7, 137.8, 134.1, 132.1, 131.9, 130.1, 128.6, 128.5, 127.9, 127.9,127.4, 125.8, 122.1, 122.0, 116.8, 111.3, 34.4, 24.6.IR (thin film) 3575, 3413, 2927, 1616, 1528, 1481, 1370, 690 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2$ $[M+H]^+$: 339.1856, found: 339.1855.



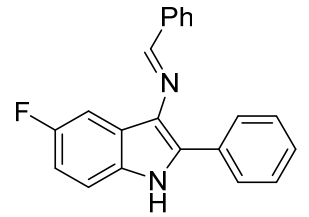
3ta

***(E)*-N-Benzylidene-5-chloro-2-phenyl-1H-indol-3-amine (3ta)**, a yellow oil, 0.088 g, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.28 (brs, 1H), 7.91 (d, *J* = 6.0 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 3H), 7.46–7.41 (m, 5H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.23–7.21 (m, 1H), 7.11 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 137.4, 133.7, 132.9, 131.3, 130.4, 128.7, 128.6, 128.1, 127.9, 127.8,126.5, 125.4, 123.2, 122.9, 119.1, 112.4. IR (thin film) 3573, 3433, 3305, 3065, 1641, 1603, 1572, 797, 683 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}ClN_2$ $[M+H]^+$: 331.0997, found: 331.1018.



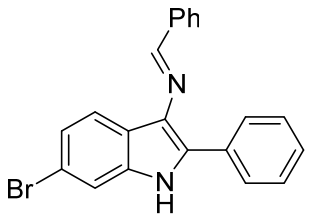
3ua

***(E)*-N-Benzylidene-5-bromo-2-phenyl-1H-indol-3-amine (3ua)**, a yellow oil, 0.094 g, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 1H), 8.21 (brs, 1H), 7.99 (s, 1H), 7.93 (d, *J* = 5.6 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.45–7.42 (m, 5H), 7.36–7.28 (m, 2H), 7.24 (t, *J* = 8.0 Hz,1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 137.4, 133.9, 132.6, 131.2, 130.4, 128.7, 128.6, 128.0, 127.9, 127.8, 125.7, 125.3, 123.5, 122.1, 114.0, 112.8. IR (thin film) 3573, 3265, 1610, 1575, 924, 767, 698 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$: 375.0491, found: 375.0511.



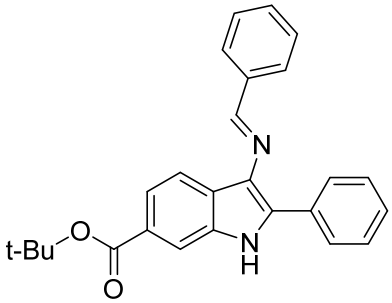
3va

***(E)*-N-(5-Fluoro-2-phenyl-1H-indol-3-yl)-1-phenylmethanimine (3va)**, a yellow oil, 0.071 g, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.23 (brs, 1H), 7.92–7.87 (m, 4H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.46–7.43 (m, 5H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.28–7.23 (m, 1H), 6.99–6.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (d, *J* = 234.0 Hz), 156.5, 137.5, 133.6, 131.8, 131.4, 130.3, 128.7, 128.6, 128.0, 127.9, 127.8, 125.9 (d, *J* = 4.0 Hz), 122.0 (d, *J* = 9.5 Hz), 112.1 (d, *J* = 9.5 Hz), 111.3 (d, *J* = 26.4 Hz), 105.1 (d, *J* = 24.0 Hz). IR (thin film) 3573, 3365, 1630, 1577, 928, 769, 688 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{14}FN_2$ $[M-H]^-$: 313.1141, found: 313.1158.



3wa

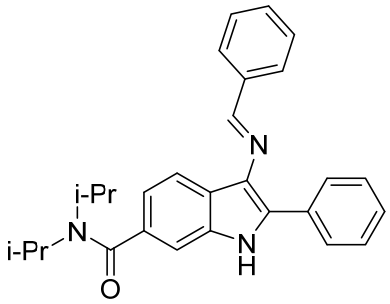
***(E)*-N-Benzylidene-6-bromo-2-phenyl-1H-indol-3-amine (3wa)**, a yellow oil, 0.102 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.24 (brs, 1H), 7.91 (d, *J* = 5.6 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.45–7.41 (m, 6H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.26 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 137.4, 136.1, 132.1, 131.2, 130.5, 128.7, 128.6, 128.0, 127.9, 127.8, 125.9, 124.1, 120.9, 120.8, 116.3, 114.4. IR (thin film) 3573, 3423, 3068, 1651, 1595, 1528, 796, 691 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$: 375.0491, found: 375.0503.



3xa

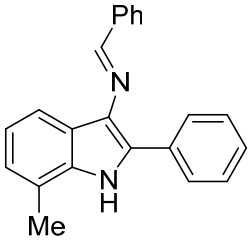
tert-Butyl *(E)*-3-(benzylideneamino)-2-phenyl-1H-indole-6-carboxylate (3xa), a yellow solid, 0.064 g, 54% yield. Mp: 166–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ

9.11 (s, 1H), 8.56 (s, 1H), 8.11 (s, 1H), 7.97-7.94 (m, 4H), 7.92 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H),7.52–7.46 (m, 5H), 7.40 (d, J = 7.6 Hz, 1H), 1.63 (s, 9H);^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 157.5, 137.5, 134.7, 134.4, 131.3, 130.5, 128.7, 128.2, 128.1, 126.4, 126.2, 124.9, 121.9, 118.9, 113.4, 80.7, 28.3; IR (thin film) 3437, 1710, 1638, 1452, 1224, 1096, 948, 745, 689, 642 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{24}N_2O_2$ $[M+H]^+$: 397.1911, found: 397.1908.



3ya

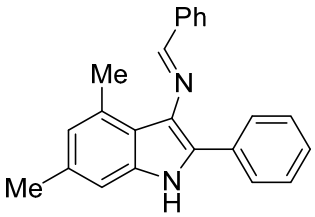
***(E)*-3-(Benzylideneamino)-N,N-diisopropyl-2-phenyl-1H-indole-6-carboxamide (3ya)**, a yellow solid, 0.080 g, 63% yield. Mp: 149–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.93 (s, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.86-7.84 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.43-7.39 (m, 6H),7.31–7.25 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.96-3.94 (m, 1H), 3.58-3.54 (m, 1H), 1.54-1.52 (m, 6H), 1.17-1.15 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 155.9, 137.8, 135.4, 133.8, 132.2, 131.9, 129.9, 128.5, 128.3, 128.2, 127.9, 127.3, 125.4, 121.7, 119.0, 117.3, 110.4, 20.8 (the carbon connected with N-atom of amide was not signal). IR (thin film) 3452, 2067, 1615, 1444, 1343, 1245, 762, 691 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{29}N_3O$ $[M+H]^+$: 424.2383, found: 424.2375.



3za

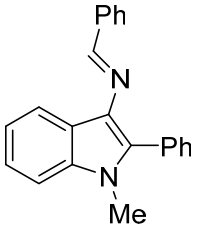
***(E)*-N-Benzylidene-7-methyl-2-phenyl-1H-indol-3-amine (3za)**, a yellow oil, 0.092 g, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.09 (brs, 1H), 7.95 (t, J =

6.8 Hz, 4H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.48–7.41 (m, 5H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.13–7.09 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 137.8, 134.9, 131.9, 131.7, 130.1, 128.6, 128.5, 128.0, 127.9, 127.5, 126.5, 123.7, 121.6, 121.1, 120.5, 117.6, 16.4. IR (thin film) 3573, 3433, 3008, 2963, 1660, 1607, 1599, 1448, 1323, 801 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found: 311.1549.



3aaa

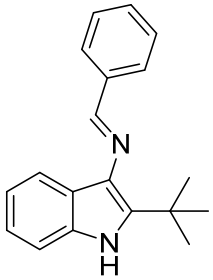
***(E)*-N-Benzylidene-4,6-dimethyl-2-phenyl-1H-indol-3-amine (3aaa)**, a yellow oil, 0.083 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.86 (brs, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 6.4 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.91 (s, 1H), 6.71 (s, 1H), 2.58 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 136.7, 135.8, 132.9, 132.5, 130.7, 129.9, 128.9, 128.7, 128.2, 127.1, 127.0, 126.8, 123.8, 123.6, 121.2, 108.6, 21.5, 20.3. IR (thin film) 3399, 3058, 2919, 1690, 1613, 1537, 1448, 1377, 692 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{19}N_2$ $[M-H]^-$: 323.1553, found: 323.1562.



3aab

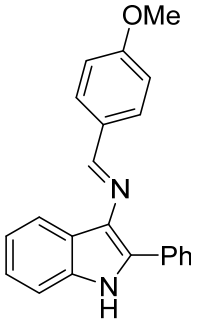
***(E)*-N-Benzylidene-1-methyl-2-phenyl-1H-indol-3-amine (3aab)**, a yellow oil, 0.056 g , 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.44–7.36 (m, 5H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.26–7.23 (m, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 138.1, 137.2, 136.8, 131.4, 130.7, 129.8, 128.5, 128.0, 127.9, 127.7, 125.5, 122.5, 121.0, 120.8, 119.8, 110.0, 31.4. IR (thin film) 3430,

2858, 2245,1651, 1607, 1528, 1446, 1304, 764 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found: 311.1533.



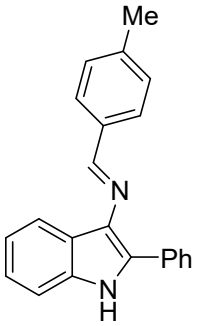
3aad

***(E)*-N-(2-(tert-Butyl)-1H-indol-3-yl)-1-phenylmethanimine (3aad)**, a red oil, 0.078 g, 95% yield; ; ^1H NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 1H), 8.04 (s, 1H), 7.91-7.88 (m, 3H), 7.47 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.16-7.14 (m, 2H), 1.59 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 142.9, 138.4, 133.4, 129.6, 128.6, 127.4, 123.7, 121.9, 121.5, 120.6, 119.3, 111.2, 33.2, 29.9. IR (thin film) 3451, 2951, 1637, 1454, 1429, 798, 743, 691 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}N_2$ $[M+H]^+$: 277.1699, found: 277.1696.



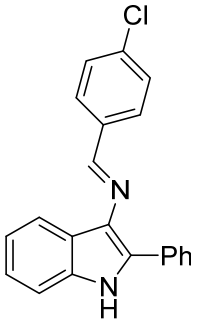
3ab

***(E)*-N-(4-Methoxybenzylidene)-2-phenyl-1H-indol-3-amine (3ab)**, a yellow oil, 0.093 g, 95% yield; ^1H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.20 (brs, 1H), 7.87–7.83 (m, 5H), 7.41 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.6 Hz, 2H), 7.20–7.12 (m, 2H), 6.96 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 156.5, 135.4, 131.8, 130.9, 130.7, 129.5, 128.5, 127.7, 127.3, 126.2, 122.8, 122.1, 120.6, 119.6, 114.1, 111.5, 55.3. IR (thin film) 3573, 3391, 2928, 1652, 1602, 1573, 1447, 1305, 1240, 732 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{19}N_2O[M+H]^+$: 327.1492, found: 327.1488.



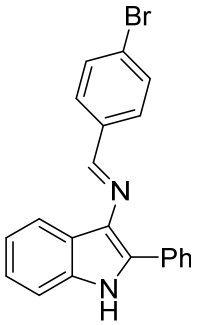
3ac

***(E)*-N-(4-Methylbenzylidene)-2-phenyl-1H-indol-3-amine (3ac)**, a yellow solid, 0.088 g, 95% yield. Mp: 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.19 (brs, 1H), 7.90–7.85 (m, 3H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.27–7.23 (m, 2H), 7.21–7.15 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 140.5, 135.5, 135.2, 131.8, 131.4, 129.4, 128.5, 128.0, 127.9, 127.4, 126.1, 122.9, 122.1, 120.7, 119.7, 111.5, 21.5. IR (thin film) 3573, 3435, 3049, 2921, 1639, 1596, 1490, 1446, 1370, 735 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found: 311.1537.



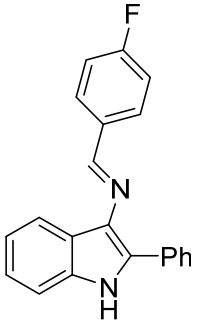
3ad

***(E)*-N-(4-Chlorobenzylidene)-2-phenyl-1H-indol-3-amine (3ad)**, a yellow solid, 0.083 g, 84% yield. Mp: 150–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.22 (brs, 1H), 7.91–7.86 (m, 3H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.46–7.39 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.24–7.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 136.3, 135.9, 135.9, 132.5, 131.6, 129.0, 128.9, 128.6, 128.0, 127.7, 125.5, 123.1, 121.9, 121.1, 119.8, 111.5. IR (thin film) 3573, 3408, 3052, 1639, 1607, 1576, 817, 743 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}ClN_2$ $[M+H]^+$: 331.0977, found: 331.0994.



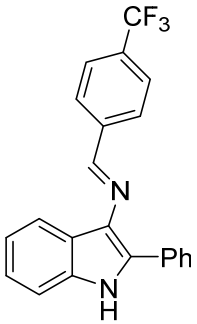
3ae

***(E)*-N-(4-Bromobenzylidene)-2-phenyl-1H-indol-3-amine (3ae)**, a yellow solid, 0.091 g, 81% yield. Mp: 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.17 (brs, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 16.0 Hz, 8.0 Hz, 2H), 7.21–7.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 136.7, 135.4, 132.6, 131.8, 131.6, 129.2, 128.6, 128.0, 127.7, 125.5, 124.4, 123.1, 121.8, 121.0, 119.8, 111.6. IR (thin film) 3573, 3409, 3062, 1639, 1607, 1528, 820, 736 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}BrN_2$ $[M+H]^+$: 375.0491, found: 375.0483.



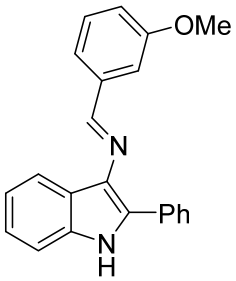
3af

***(E)*-N-(4-Fluorobenzylidene)-2-phenyl-1H-indol-3-amine (3af)**, a yellow solid, 0.076 g, 80% yield. Mp: 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.21 (brs, 1H), 7.90–7.86 (m, 5H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.34–7.31 (m, 2H), 7.24–7.17 (m, 2H), 7.15–7.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3 (d, *J* = 248.6 Hz), 155.0, 135.4, 134.1 (d, *J* = 2.2 Hz), 132.0 (d, *J* = 30.6 Hz), 129.7, 129.6, 128.6, 128.0, 127.6, 125.7, 123.1, 121.9, 120.9, 119.7, 115.8 (d, *J* = 21.9 Hz), 111.5. IR (thin film) 3573, 3438, 3049, 1639, 1598, 1527, 825, 736 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}FN_2$ $[M+H]^+$: 315.1292, found: 315.1291.



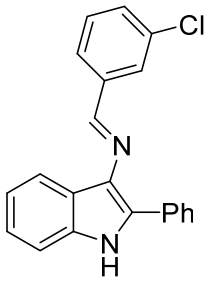
3ag

***(E)*-2-Phenyl-N-(4-(trifluoromethyl)benzylidene)-1H-indol-3-amine (3ag)**, a yellow solid, 0.097 g, 89% yield. Mp: 115–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.26 (brs, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.27–7.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 141.1, 135.5, 133.6, 131.7 (q, *J* = 32.1 Hz), 131.4, 131.1, 128.6, 128.2, 128.0, 127.9, 125.6 (q, *J* = 3.7 Hz), 125.2 (q, *J* = 247.9 Hz), 123.3, 121.7, 121.3, 119.9, 111.6. IR (thin film) 3575, 3393, 2924, 1617, 1535, 1478, 1323, 1064, 745 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{16}F_3N_2$ $[M+H]^+$: 365.1260, found: 365.1289.



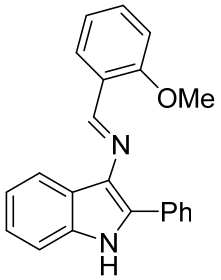
3ah

***(E)*-N-(3-Methoxybenzylidene)-2-phenyl-1H-indol-3-amine (3ah)**, a yellow solid, 0.078 g, 80% yield. Mp: 134–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.25 (brs, 1H), 7.91–7.85 (m, 3H), 7.55 (brs, 1H), 7.43–7.36 (m, 3H), 7.34–7.29 (m, 3H), 7.20–7.17 (m, 2H), 6.98 (d, *J* = 6.4 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 156.1, 139.3, 135.5, 132.1, 131.7, 129.6, 128.5, 128.0, 127.6, 125.7, 123.0, 122.0, 121.3, 120.9, 119.8, 116.9, 111.5, 111.3, 55.2. IR (thin film) 3573, 3402, 2922, 1644, 1607, 1572, 1424, 1375, 733 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{19}N_2O$ $[M+H]^+$: 327.1492, found: 327.1489.



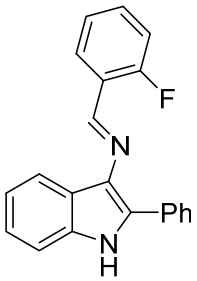
3ai

***(E)*-N-(3-Chlorobenzylidene)-2-phenyl-1H-indol-3-amine (3ai)**, a yellow solid, 0.083 g, 84% yield. Mp: 172–173°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.25 (brs, 1H), 7.92–7.88 (m, 4H), 7.75–7.74 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.37–7.34 (m, 4H), 7.26–7.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 139.7, 135.5, 134.8, 132.9, 131.5, 129.9, 129.8, 128.6, 128.1, 127.8, 127.5, 126.1, 125.4, 123.2, 121.9, 121.2, 119.8, 111.6. IR (thin film) 3574, 3443, 3055, 1648, 1594, 1560, 939, 740 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}ClN_2$ $[M+H]^+$: 331.0997, found: 331.1006.



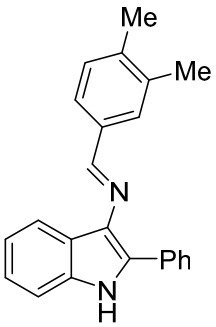
3aj

***(E)*-N-(2-Methoxybenzylidene)-2-phenyl-1H-indol-3-amine (3aj)**, a yellow solid, 0.081 g, 83% yield. Mp: 194–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 8.25 (s, 1H), 8.23 (s, 1H), 7.97–7.92 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40–7.30 (m, 3H), 7.24–7.17 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 152.9, 135.5, 131.9, 131.6, 131.4, 128.6, 127.9, 127.4, 127.0, 126.7, 126.3, 123.0, 122.1, 120.9, 120.0, 111.3, 111.1, 55.7. IR (thin film) 3573, 3428, 3052, 2962, 1639, 1590, 1447, 1370, 1243, 740 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{19}N_2O$ $[M+H]^+$: 327.1492, found: 327.1490.



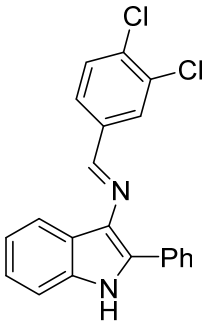
3ak

***(E)*-N-(2-Fluorobenzylidene)-2-phenyl-1H-indol-3-amine (3ak)**, a yellow solid, 0.072 g, 76% yield. Mp: 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (s, 1H), 8.24–8.18 (m, 2H), 7.96–7.94 (m, 1H), 7.89–7.87 (m, 2H), 7.46–7.42 (m, 2H), 7.37–7.31 (m, 3H), 7.23–7.18 (m, 3H), 7.13–7.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8 (d, J = 4.4 Hz), 135.5 (d, J = 247.2 Hz), 131.6, 131.4, 131.3, 128.6, 128.1, 127.7, 127.0, 126.0, 125.6 (d, J = 8.7 Hz), 124.4, 124.3, 123.2, 121.7, 121.2, 119.9, 115.8 (J = 21.2 Hz), 111.5. IR (thin film) 3573, 3434, 3053, 1639, 1559, 1520, 947, 735 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{16}FN_2$ $[M+H]^+$: 315.1292, found: 315.1290.



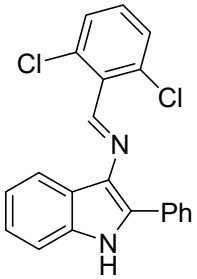
3al

***(E)*-N-(3,4-Dimethylbenzylidene)-2-phenyl-1H-indol-3-amine (3al)**, a yellow solid, 0.075 g, 78% yield. Mp: 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.24 (brs, 1H), 7.92 (d, J = 7.6 Hz, 3H), 7.73 (s, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.24–7.15 (m, 3H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 139.4, 136.9, 135.5, 135.4, 131.9, 131.1, 130.0, 129.1, 128.6, 127.8, 127.4, 126.3, 125.7, 123.0, 122.2, 120.7, 119.7, 111.4, 19.9, 19.8. IR (thin film) 3573, 3246, 3057, 2918, 1651, 1594, 1447, 1331, 731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2$ $[M+H]^+$: 325.1699, found: 325.1696.



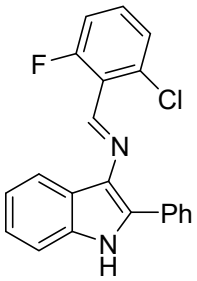
3am

***(E)*-N-(3,4-Dichlorobenzylidene)-2-phenyl-1H-indol-3-amine (3am)**, a yellow solid, 0.085 g, 78% yield. Mp: 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (s, 1H), 8.19 (brs, 1H), 7.87–7.80 (m, 4H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.44–7.41 (m, 3H), 7.35–7.27 (m, 2H), 7.22–7.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 137.9, 135.4, 133.6, 133.4, 132.9, 131.4, 130.5, 129.2, 128.6, 128.1, 127.9, 126.6, 125.0, 123.2, 121.7, 121.2, 119.8, 111.6. IR (thin film) 3573, 3433, 3053, 1650, 1601, 1592, 1550, 819, 740 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{15}Cl_2N_2$ $[M+H]^+$: 365.0607, found: 365.0604.



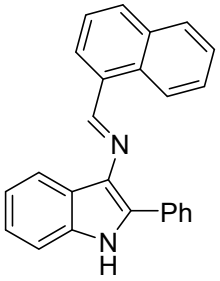
3an

***(E)*-N-(2,6-Dichlorobenzylidene)-2-phenyl-1H-indol-3-amine (3an)**, a yellow oil, 0.092 g, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.37 (brs, 1H), 8.05–8.03 (m, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.37–7.24 (m, 6H), 7.21–7.19 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 135.4, 134.8, 133.9, 133.4, 131.1, 129.7, 128.9, 128.4, 128.2, 127.9, 125.4, 123.1, 121.5, 121.4, 119.8, 111.5. IR (thin film) 3573, 3412, 3058, 1639, 1579, 1555, 738, 691 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{15}Cl_2N_2$ $[M+H]^+$: 365.0607, found: 365.0607.



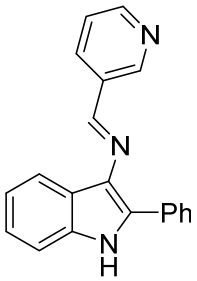
3ao

***(E)*-N-(2-Chloro-6-fluorobenzylidene)-2-phenyl-1H-indol-3-amine (3ao)**, a yellow solid, 0.082 g, 88% yield. Mp: 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (s, 1H), 8.34 (brs, 1H), 8.02 (d, *J* = 7.2 Hz, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39–7.32 (m, 2H), 7.25–7.22 (m, 4H), 7.16–7.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 258.2 Hz), 150.0 (d, *J* = 2.9 Hz), 135.5, 135.4, 135.3, 133.6, 131.3, 130.4 (d, *J* = 9.5 Hz), 128.6, 128.0, 126.1, 125.8 (d, *J* = 3.7 Hz), 124.1 (d, *J* = 11.6 Hz), 123.2, 121.5, 121.4, 119.9, 111.4 (d, *J* = 22.6 Hz), 111.5. IR (thin film) 3432, 3316, 1662, 1600, 900, 739, 691 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{15}ClFN_2$ $[M+H]^+$: 349.0902, found: 349.0902.



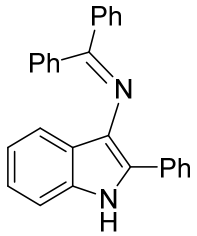
3ap

***(E)*-N-(Naphthalen-1-ylmethylene)-2-phenyl-1H-indol-3-amine (3ap)**, a yellow solid, 0.086 g, 83% yield. Mp: 196–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 9.09 (d, *J* = 6.4 Hz, 1H), 8.26 (s, 1H), 8.18 (d, *J* = 5.6 Hz, 1H), 8.03 (d, *J* = 6.0 Hz, 1H), 7.97 (d, *J* = 6.0 Hz, 2H), 7.92–7.90 (m, 2H), 7.59–7.52 (m, 3H), 7.47 (t, *J* = 6.0 Hz, 2H), 7.40 (d, *J* = 5.6 Hz, 1H), 7.35 (t, *J* = 6.0 Hz, 1H), 7.28–7.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 135.6, 134.0, 132.8, 132.0, 131.9, 131.4, 130.7, 128.7, 128.6, 128.2, 128.0, 127.7, 127.0, 126.8, 126.0, 125.5, 124.4, 123.1, 122.0, 121.1, 119.8, 111.6. IR (thin film) 3537, 3434, 3053, 1638, 1580, 1528, 774, 684 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{19}N_2$ $[M+H]^+$: 347.1543, found: 347.1571.



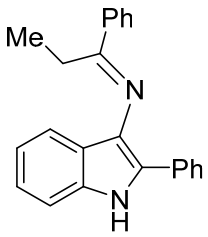
3aq

***(E)*-2-Phenyl-N-(pyridin-3-ylmethylene)-1H-indol-3-amine (3aq)**, a yellow solid, 0.046 g, 51% yield. Mp: 240–241 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.77 (s, 1H), 9.25 (s, 1H), 9.14 (s, 1H), 8.63 (d, J = 7.6 Hz, 1H), 8.34 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 7.4 Hz, 3H), 7.56–7.47 (m, 4H), 7.41 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.9, 150.9, 150.0, 136.2, 134.3, 134.2, 134.0, 132.2, 128.9, 128.8, 128.1, 124.7, 124.1, 123.3, 121.2, 121.1, 120.6, 112.5. IR (thin film) 3573, 3435, 3028, 1639, 1603, 1568, 801, 732 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{16}N_3$ $[M+H]^+$: 298.1339, found: 298.1335.



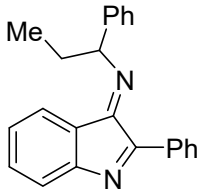
3ar

N-(Diphenylmethylene)-2-phenyl-1H-indol-3-amine (3ar), a yellow oil, 0.061 g, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (brs, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.50–7.47 (m, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.32–7.29 (m, 2H), 7.23–7.18 (m, 3H), 7.09–6.97 (m, 6H), 6.91 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 139.9, 137.2, 135.1, 132.3, 130.4, 129.4, 128.7, 128.6, 128.4, 128.0, 127.5, 127.3, 126.5, 126.1, 124.7, 122.7, 122.5, 119.4, 119.1, 110.6. IR (thin film) 3434, 3057, 1651, 1621, 1598, 802, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{21}N_2$ $[M+H]^+$: 373.1699, found: 373.1695.



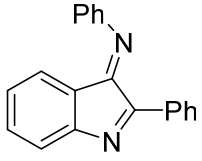
3as

***(E)*-1-Phenyl-N-(2-phenyl-1H-indol-3-yl)propan-1-imine (3as)**, a yellow oil, 0.050 g, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (brs, 1H), 8.10–8.05 (m, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.51–7.47 (m, 3H), 7.36–7.31 (m, 4H), 7.24–7.19 (m, 2H), 7.10–7.06 (m, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 0.88 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 138.3, 135.4, 132.3, 130.2, 128.7, 128.4, 127.7, 126.4, 126.3, 125.7, 123.0, 122.9, 122.8, 119.7, 118.7, 110.9, 24.5, 11.7. IR (thin film) 3475, 3057, 2992, 1651, 1621, 1598, 802, 758, 695 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{21}N_2$ $[M+H]^+$: 325.1700, found: 325.1695.



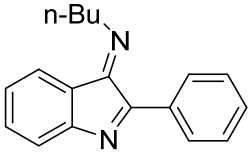
4as

(*E*)-2-Phenyl-N-(1-phenylpropyl)-3H-indol-3-imine (4as), a yellow oil, 0.013 g, 13% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44–8.42 (m, 2H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.49–7.45 (m, 5H), 7.44 –7.40 (m, 1H), 7.37–7.33 (m, 2H), 7.27–7.19 (m, 2H), 5.45 (t, *J* = 6.8 Hz, 1H), 2.13 (dd, *J* = 7.2 Hz, 14 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 163.1, 157.9, 143.2, 132.7, 132.5, 130.7, 130.4, 128.5, 128.1, 127.2, 127.0, 126.9, 126.2, 122.3, 121.7, 68.6, 32.7, 10.8. IR (thin film) 3474, 3042, 2980, 1650, 1623, 1594, 801, 757, 694 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{21}N_2$ $[M+H]^+$: 325.1700, found: 325.1696.



4at

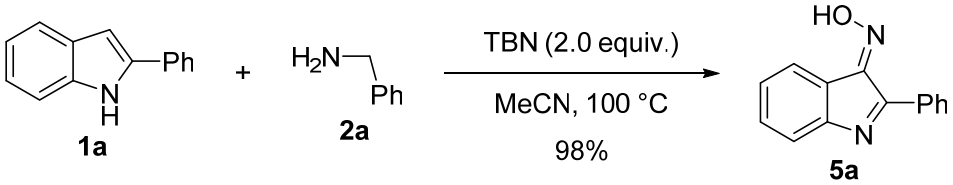
***(E)*-N,2-Diphenyl-3H-indol-3-imine (4at),** a yellow solid, 0.010 g, 12% yield. Mp: 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 6.4 Hz, 2H), 7.50–7.43 (m, 6H), 7.37–7.34 (m, 1H), 7.28–7.25 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 164.2, 157.8, 150.3, 133.2, 132.1, 131.0, 130.0, 129.3, 128.3, 126.8, 125.8, 125.2, 121.6, 121.5, 117.5. IR (thin film) 3057, 3043, 1642, 1625, 1596, 803, 753 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{15}N_2$ $[M+H]^+$: 283.1230, found: 283.1221.



4au

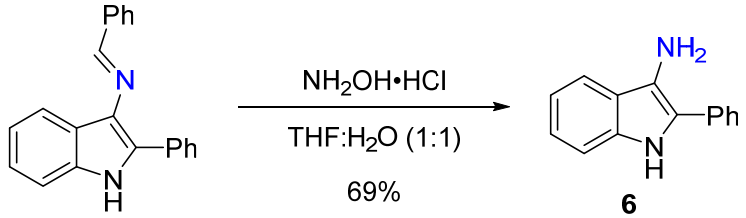
***(E)*-N-Butyl-2-phenyl-3H-indol-3-imine (4au)**, a yellow oil, 0.010 g, 12% yield; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.36 (d, *J* = 6.4 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.46-7.45 (m, 4H), 7.27-7.23 (m, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.01-1.92 (m, 2H), 1.61-1.55 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 157.5, 132.5, 132.4, 130.7, 130.2, 128.2, 127.0, 126.4, 122.5, 121.6 , 54.6, 33.1, 20.9, 14.0. IR (thin film) 3468,2958, 1529, 1489, 1260, 1028, 761, 691 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{18}N_2$ $[M+H]^+$: 263.1543, found: 263.1542.

3. Synthesis of compounds 5a, 6, 7 and 8



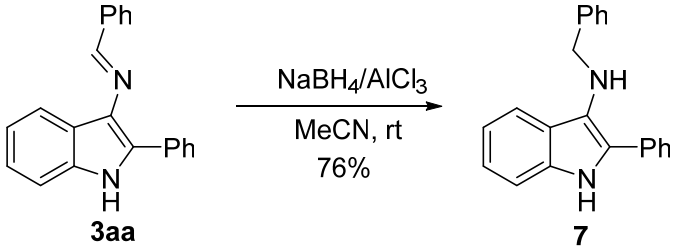
In a dried Teflon-sealed reaction flask equipped with a stir bar was charged with 2-phenylindoles **1a** (0.058 g, 0.3 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL). The reaction mixture was stirred at 100 °C for 0.5 h until **1a** was consumed completely (monitored by TLC). At this time, the reaction mixture was cooled to room temperature, filtered and washed with DCM. The corresponding oxime **5a** was obtained as a yellow solid (0.065 g, 98%).[1] Mp: 274–275 °C; ^{1}H NMR (400 MHz, DMSO-d_6): *δ* 14.27 (brs, 1H), 8.69 (d, *J* = 6.4 Hz, 2H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.00−7.89 (m, 5H), 7.77−7.73 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* 154.6,

154.5, 132.4, 131.6, 131.2, 130.3, 130.2, 130.1, 129.8, 128.8, 128.5, 127.6; IR (thin film) 3434, 3049, 1840, 1593, 1492, 1272, 1204, 1027, 753 cm^{-1}; HRMS (ESI) *m/z* calcd for C14H11N2O $[M+H]^+$: 223.0866, found: 223.0865.



3aa **6**

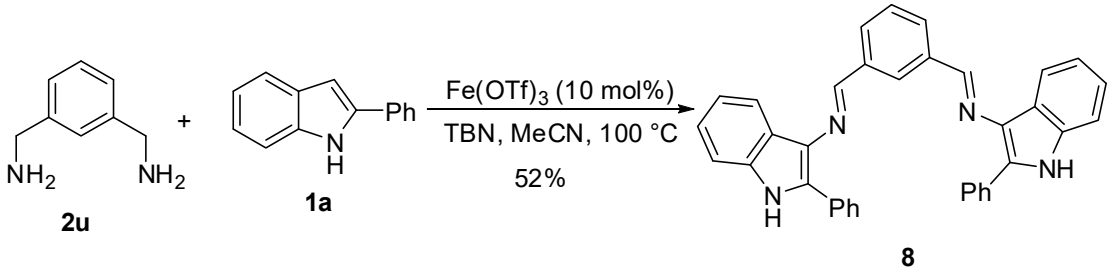
In a 25 mL reaction flask was charged with **3aa** (0.148 g, 0.5 mmol), $NH_2OH{\cdot}HCl$ (0.078 g, 1.5 equiv.), and THF: H_2O (1:1, 5 mL). The reaction mixture was stirred at room temperature 1.0 h until **3aa** was consumed completely (monitored by TLC). Then, water (10 mL) was added and the resulting mixture was extracted with ethylacetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na2SO4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (1/10 to 1/2, ethyl acetate/petroleum ether) to afford 3-aminoindole **6** as a purple solid (0.072 g, 69%).[2] Mp: 110–111 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.49 (s, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.2 Hz, 1H), 6.93 (t, J = 7.2 Hz, 1H), 4.48 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.9, 133.5, 128.6, 125.0, 124.9, 122.9, 122.8, 121.9, 118.8, 118.2, 117.3, 110.7; IR (thin film) 3400, 3051, 2845, 2830, 1610, 1375, 802, 694 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}N_2$ $[M+H]^+$: 209.1073, found: 209.1064.



3aa **7**

In a 25 mL reaction flask was charged with **3aa** (0.148 g, 0.5 mmol), MeCN (5 mL), $NaBH_4$ (0.078g, 1.5 equiv.) was added at 0 °C and stirred for 10 minutes, and then $AlCl_3$ (0.078g, 1.5 equiv.) was added. The reaction mixture was stirred at room

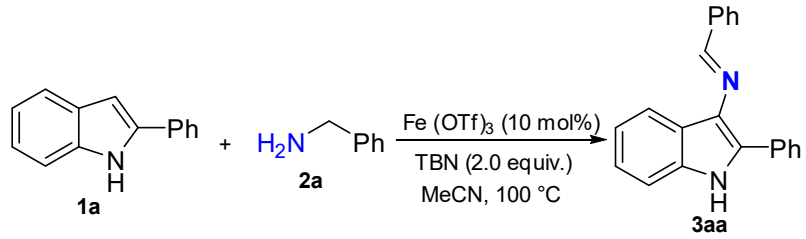
temperature for 2 hours until **3aa** was completely consumed (monitored by TLC). Then, water (10 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography (1/6 to 1/2, ethyl acetate/petroleum ether) to obtain 3-aminoindole **7** as a yellow oil (0.113 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33–7.16 (m, 8H), 7.11 (t, *J* = 7.6 Hz, 1H), 4.30 (s, 2H), 2.99 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 134.9, 132.5, 128.9, 128.4, 128.0, 127.1, 127.0, 126.6, 125.7, 124.6, 123.5, 122.5, 119.3, 118.3, 111.1, 53.9. IR (thin film) 3430, 3057, 2982, 1650, 1598, 954, 802, 695 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{27}H_{19}N_2$ $[M+H]^+$: 299.1548, found: 299.1554.



In a dried Teflon-sealed reaction flask equipped with a stir bar was charged with 2-arylindoles **1a** (0.232 g, 1.2 mmol, 8.0 equiv), **2u** (0.041 g, 0.3 mmol), $Fe(OTf)_3$ (0.015 g, 10 mol%), TBN (0.259 g, 2.4 mmol, 8.0 equiv), MeCN (6.0 mL). The reaction mixture was stirred at 100 °C for 15 h. At this time, the solvent was removed under reduced pressure. The residue was added with water (10 mL) and extracted by EtOAc (3 × 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was recrystallized with EtOH to afford the corresponding 3-aminoindole derivative **8** as a green solid (0.080 g, 52%). Mp: 200-201°C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.20 (s, 2H), 8.38 (s, 1H), 8.30 (brs, 2H), 8.06 (dd, *J* = 7.8 Hz, 1.8 Hz, 2H), 7.98–7.95 (m, 5H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 4H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.27–7.20 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.0, 138.2, 135.4, 132.2, 131.6, 129.0, 128.6, 128.2, 128.0, 127.9, 127.7, 125.8, 123.1, 122.0, 121.0,

119.9, 111.5. IR (thin film) 3573, 3394, 3056, 1641, 1619, 1573, 778, 748 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{36}H_{27}N_4$ $[M+H]^+$: 515.2230, found: 515.2219.

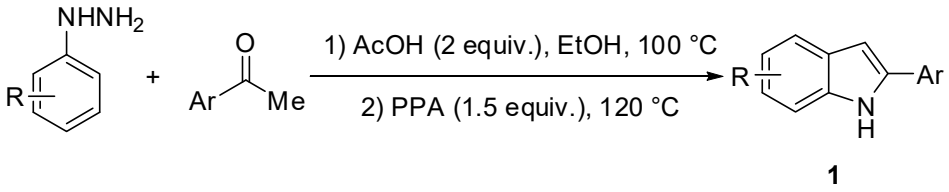
4. Gram scale preparation of 3aa



0.193 g, 1.0 mol	washing and recrystallization	0.211 g, 71% yield
1.930 g, 10.0 mol	washing and recrystallization	2.310 g, 78% yield

For an example (10 mmol of **1a**): In a dry 250 mL round-bottom flask equipped with a magnetic stir bar was charged with the corresponding indole **1a** (1.93 g, 10 mmol), **2a** (3.14 g, 20 mmol, 2.0 equiv.), $Fe(OTf)_3$ (0.502 g, 10 mol%), and TBN (2.06 g, 20 mmol, 2.0 equiv.). Then, MeCN (100 mL) was added. The mixture was stirred at 100 °C for 30 h (monitored by TLC). At this time, the solvent was removed under reduced pressure. The residue was added with water (50 mL) and extracted by EtOAc (3 × 50 mL). The combined organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was recrystallized with EtOH to afford 3-aminoindole **3aa** (2.310 g, 78%) as a yellow solid.

5. General procedure for synthesis of 2-arylindoles 1

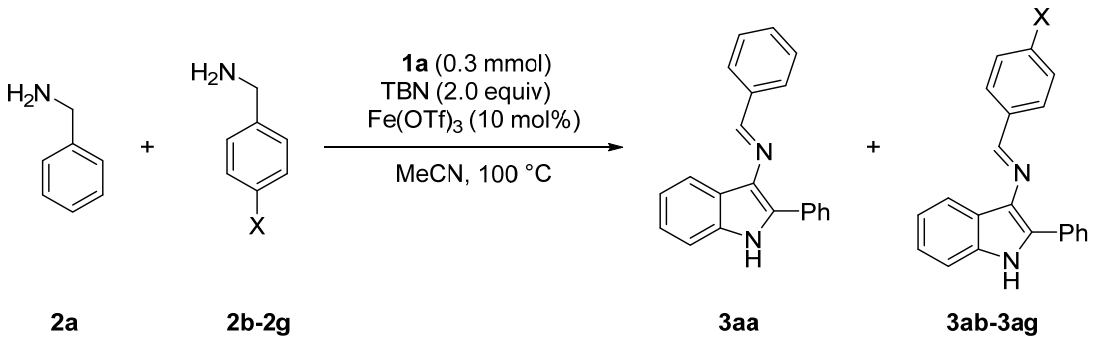


Procedure B: A mixture of acetophenone (10 mmol), phenylhydrazine (1.2 equiv), HOAc (20 mmol) and EtOH (6.0 mL) were taken in a 100 mL round bottom flask.Then, the reaction mixture was refluxed at 100 °C. When the reaction was completed (detected by TLC), it was cooled to room temperature. The EtOH was evaporated in vacuo, and then recrystallized with EtOAc and hexane. Next, freshly prepared phenylhydrazone (10 mmol) were taken in a 100 mL round bottom flask and 1.5 equiv. of polyphosphoric acid (PPA) was added at one time and the solution was

refluxed. After completion, the reaction mixture was cooled to room temperature, quenched with cold H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane as the eluent to afford the corresponding 2-arylindoles **1**.

Indoles (**1a-1m**)[3], (**1n-1v**)[4] , (**1w**, **1z**, **1aa-1ac**)[5], (**1j**, **1ad**)[6] and (**1x-1y**)[7] were prepared according to literature methods and their spectra data matched literature values.

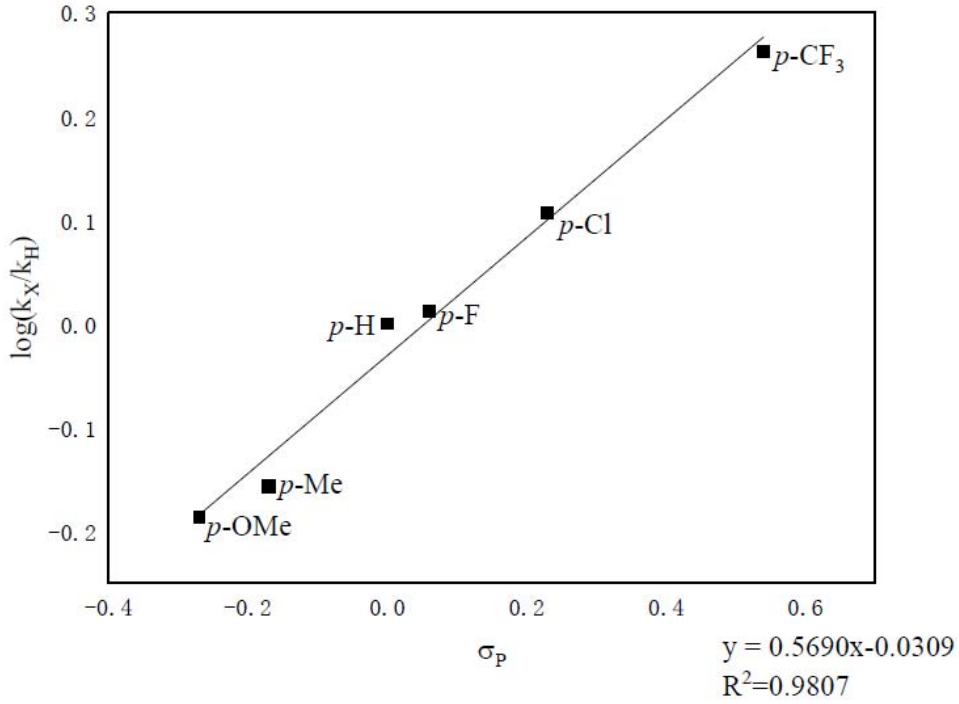
6. Description of Hammett study experiments

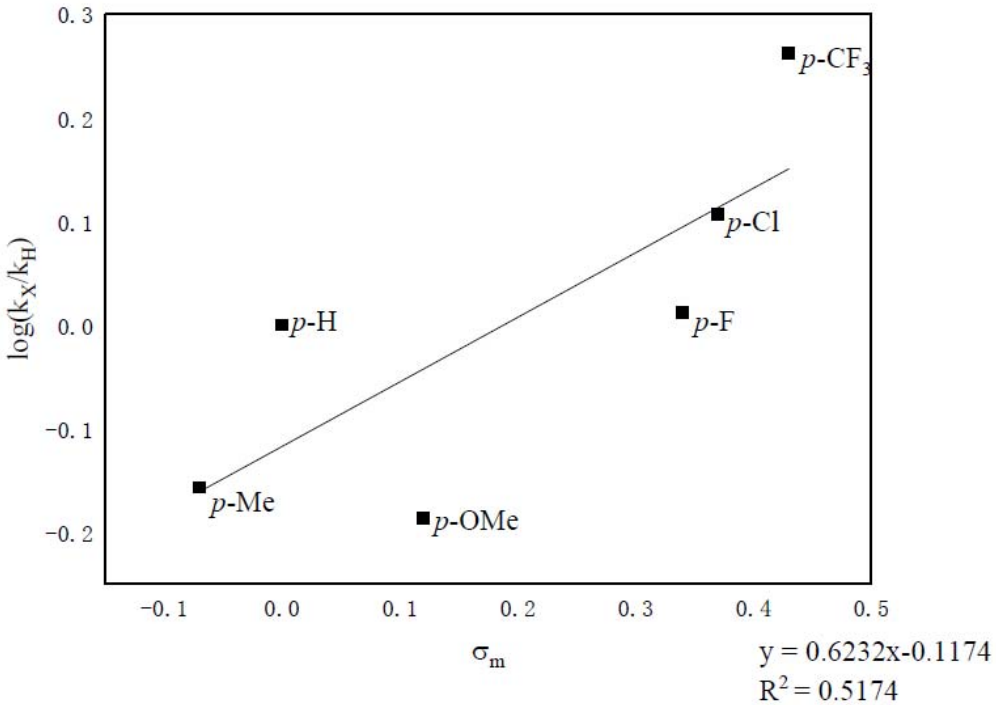


2a **2b-2g** **3aa** **3ab-3ag**

Competition experiments were set up using general procedure A, a 1:1 mixture of 1.0 equiv of **2a** and 1.0 equiv of **2b**, **2c**, **2d**, **2f**, or **2g**. The transformations were then monitored by ^{1}H NMR spectroscopy and run to 10% conversion. At this time, the ratio of the N-H of 3-aminoindole **3** resonances was recorded as in indication of the relative initial rates of the two substrates. The results were then plotted against Hammett parameters as illustrated in Figure.[8]

2	X	σ_p	σ_m	k_X/k_H	$\log(k_X/k_H)$
2b	*p*-OMe	-0.27	0.12	0.650	-0.187
2c	*p*-Me	-0.17	-0.07	0.697	-0.157
2a	*p*-H	0	0	1.00	0
2f	*p*-F	0.06	0.34	1.028	0.012
2d	*p*-Cl	0.23	0.37	1.28	0.107
2g	*p*-CF_3	0.54	0.43	1.83	0.262

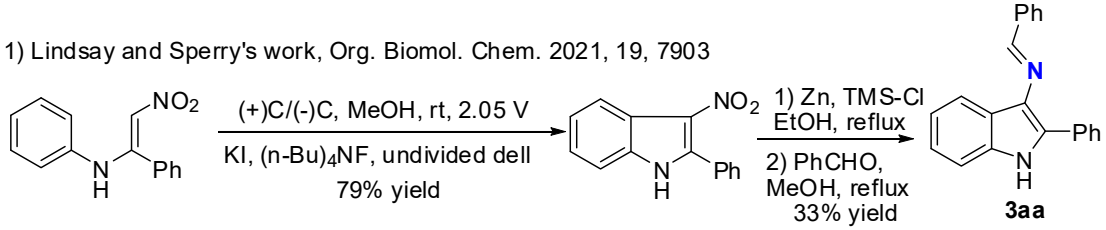

0.3
0.2
0.1
0.0
−0.1
−0.2
log(kX/kH)
p-CF3
p-Cl
p-H
p-F
p-Me
p-OMe
−0.4
−0.2
0.0
0.2
0.4
0.6
σP
y = 0.5690x-0.0309
R2=0.9807


0.3
0.2
0.1
0.0
−0.1
−0.2
log(kX/kH)
p-CF3
p-Cl
p-H
p-F
p-Me
p-OMe
−0.1
0.0
0.1
0.2
0.3
0.4
0.5
σm
y = 0.6232x-0.1174
R2 = 0.5174

7. Comparison of green metrics

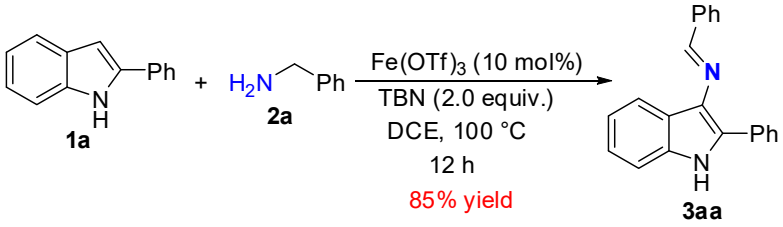
To show the green metrics, we compared two pathways to prepare 3-amino indole **3aa**.

1) Lindsay and Sperry's work, Org. Biomol. Chem. 2021, 19, 7903



26% yield in total

2) This work, one step



Entry	substrate **1**						**3aa**, Yield
Lindsay's work	0.15 mmol	KI (0.03 mmol)	$(n\text{-}Bu)_4NF$ (1.01 mmol)	Zn (1.56 mmol)	TMSCl (2.36 mmol)	PhCHO (0.98 mmol)	26%
This work	0.3 mmol	$BnNH_2$ (0.6 mmol)	$Fe(OTf)_3$ (0.03 mmol)	TBN (0.6 mmol)	-		85%

$$AE = \frac{\text{molecular mass of desired product}}{\text{molecular mass of all reactants}} \times 100\%$$

$$= \frac{296X0.15}{240X0.15 + 165X0.03 + 261X1.01 + 64X1.56 + 108X2.36+106X0.98} \times 100\% = 0.06\%$$

$$= \frac{296X0.3}{193X0.3+107X0.6+502X0.03+103X0.6} \times 100\% = \mathbf{45\%}$$

Therefore, compared with the existing procedure, the present reaction has 900-fold increase in atom economy for the preparation of **3aa**.

Lindsay and sperry' s work

Parameter	Detail of parameters
1. Yield	26% in two steps
2. Cost of reactants to obtain	0.15 mmol of product nitroalkene KI nBu_4NF Zn TMSCl PhCHO
3. Safety	MeOH, EtOH
4. Technical setup	Common setup
5. Temperature/time	Heating 7 h +3 h + 1 h = 11 h
6. Workup and purification	Classical chromatography

This work

Parameter	Detail of parameters
1. Yield	85% in one step
2. Cost of reactants to obtain	0.3 mmol of product indole TBN $Fe(OTf)_3$ Benzylamine
3. Safety	DCE
4. Technical setup	Common setup
5. Temperature/time	heating, 12 h
6. Workup and purification	Simple extraction and recrystallization for 1 mmol or 10 mmol Classical chromatography (< 1.0 mmol)

8. References

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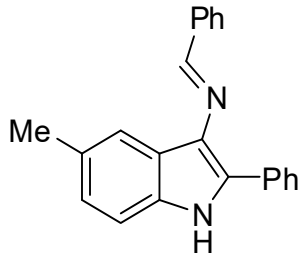
[7] X. H. Shan, H. X. Zheng, B. Yang, L. Tie, J. L. Fu, J. P. Qu and Y.-B. Kang, *Nat. Commun.* 2019, **10**, 908.

[8] C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* 1991, **91**, 165.

9. X-ray structures for compounds 3ra and 4at



3ra

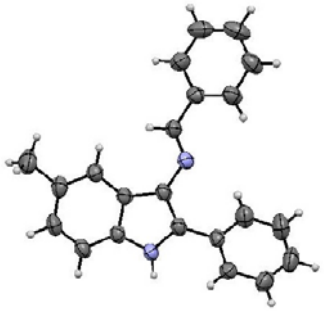
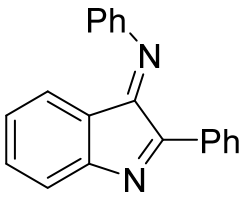


Figure S1: ORTEP diagram of **3ra** at 50% ellipsoid probability.



4at

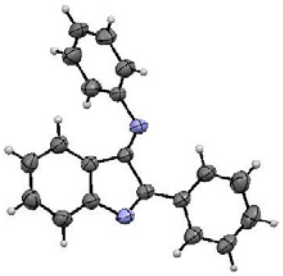
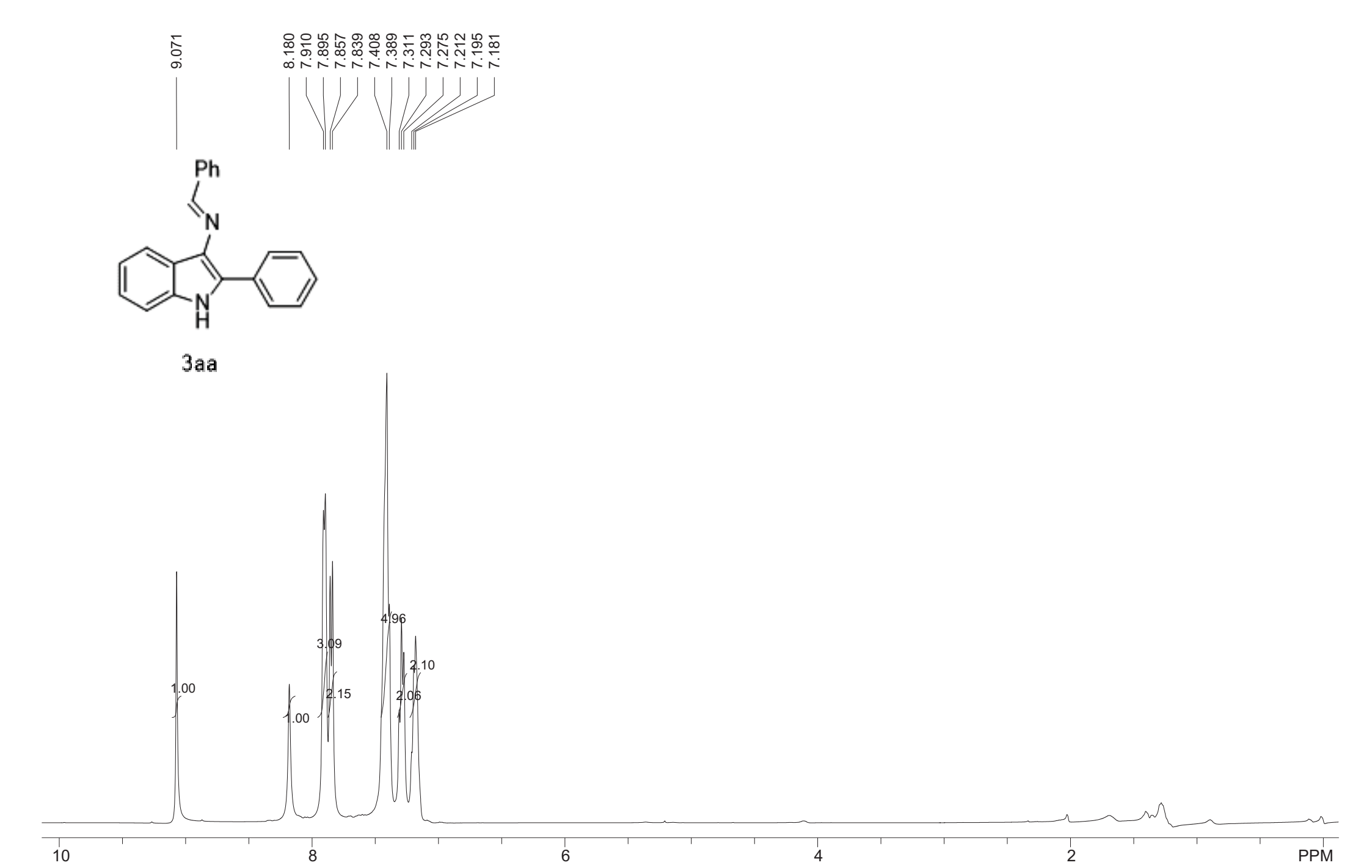


Figure S2: ORTEP diagram of **4at** at 50% ellipsoid probability.

10. NMR spectra for compounds 3, 4, 5a, 6, 7 and 8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7.389
7.311
7.293
7.275
7.212
7.195
7.181
Ph
N
N
H
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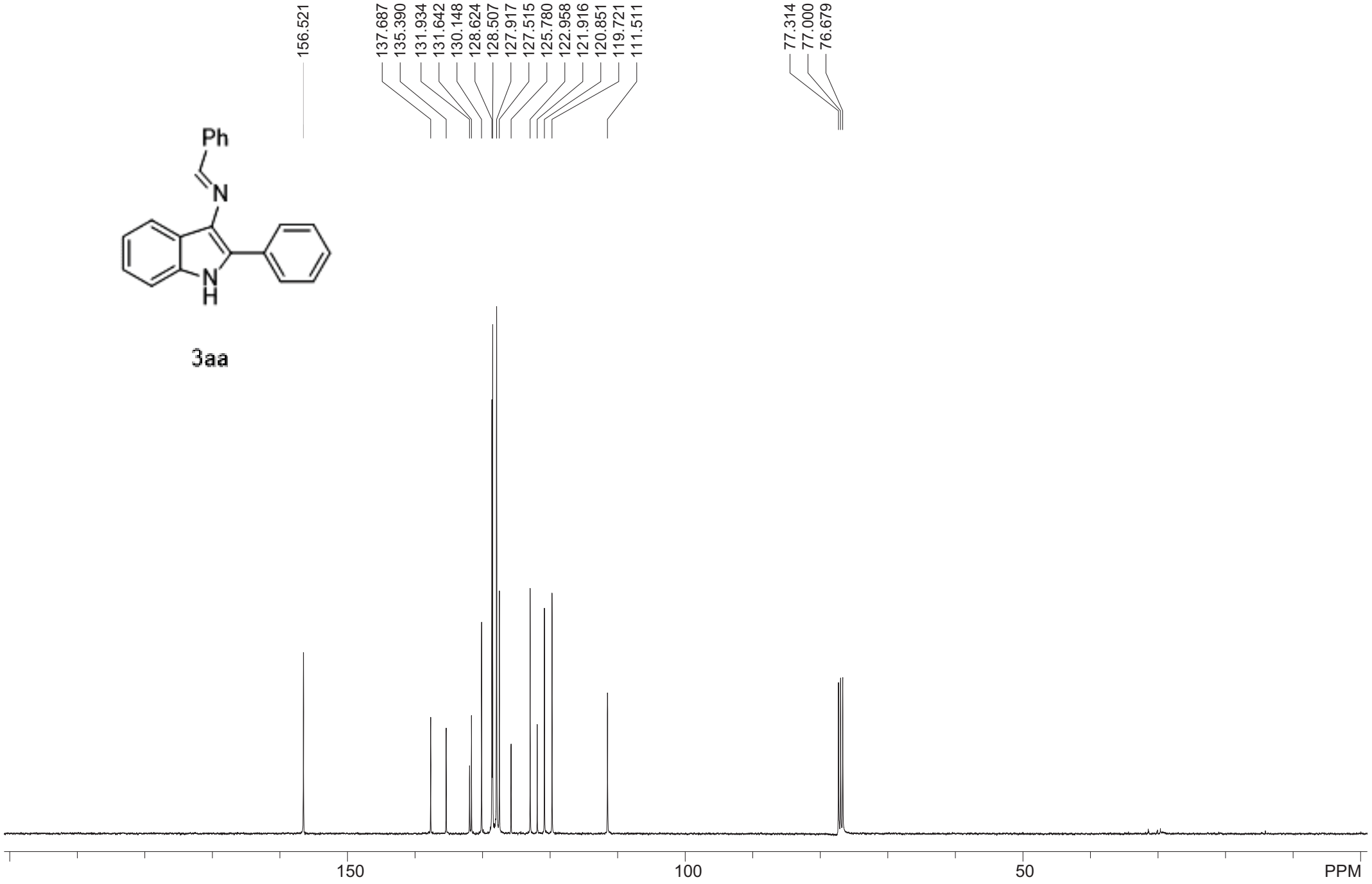
1.00
3.09
2.15
4.96
2.06
2.10
10
8
6
4
2
PPM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135.390
131.934
131.642
130.148
128.624
128.507
127.917
127.515
125.780
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121.916
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111.511
77.314
77.000
76.679
Ph
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N
H
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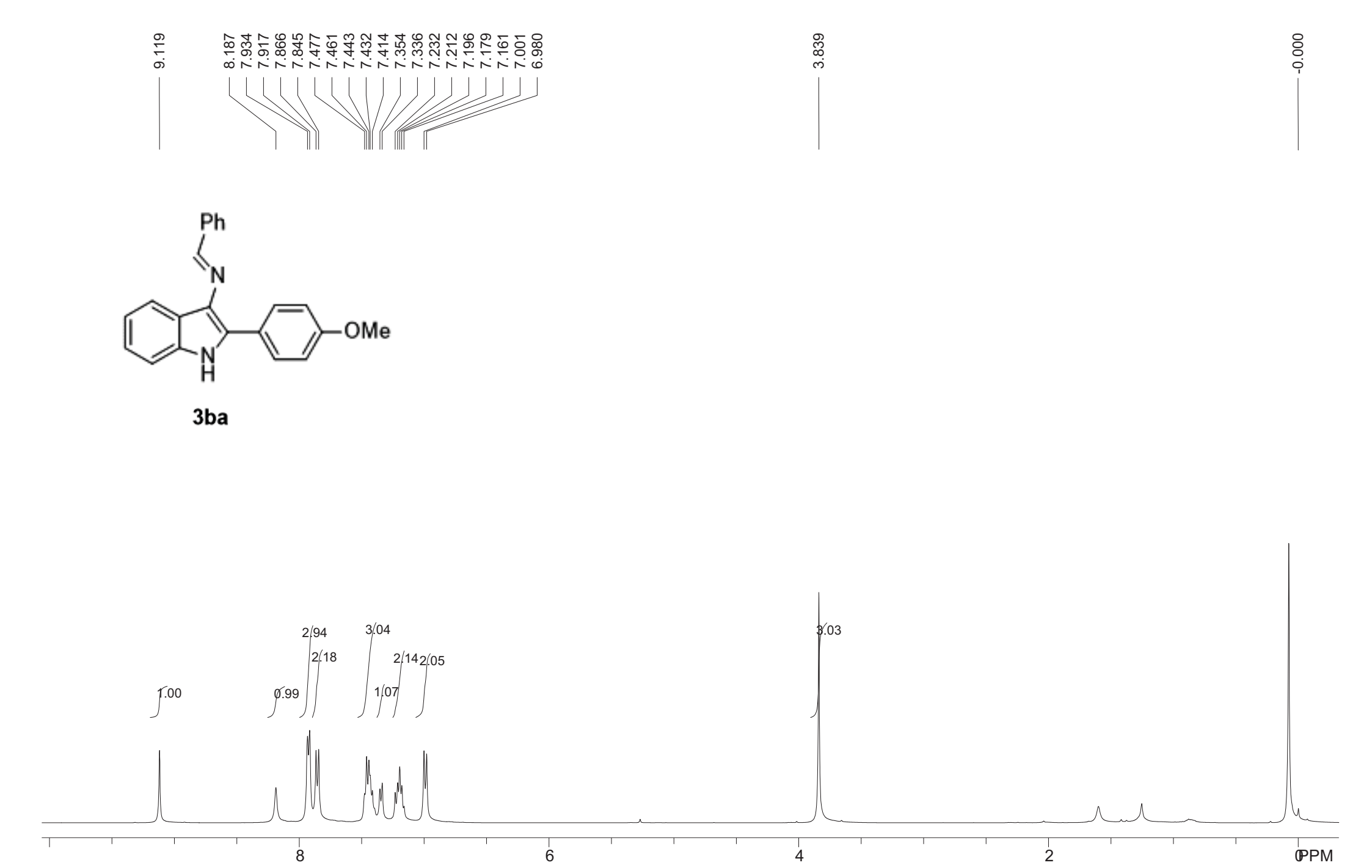
150
100
50
PPM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8.187
7.934
7.917
7.866
7.845
7.477
7.461
7.443
7.432
7.414
7.354
7.336
7.232
7.212
7.196
7.179
7.161
7.001
6.980
3.839
-0.000
Ph
N
OMe
N
H
2.94
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0.99
1.07
8
6
4
2
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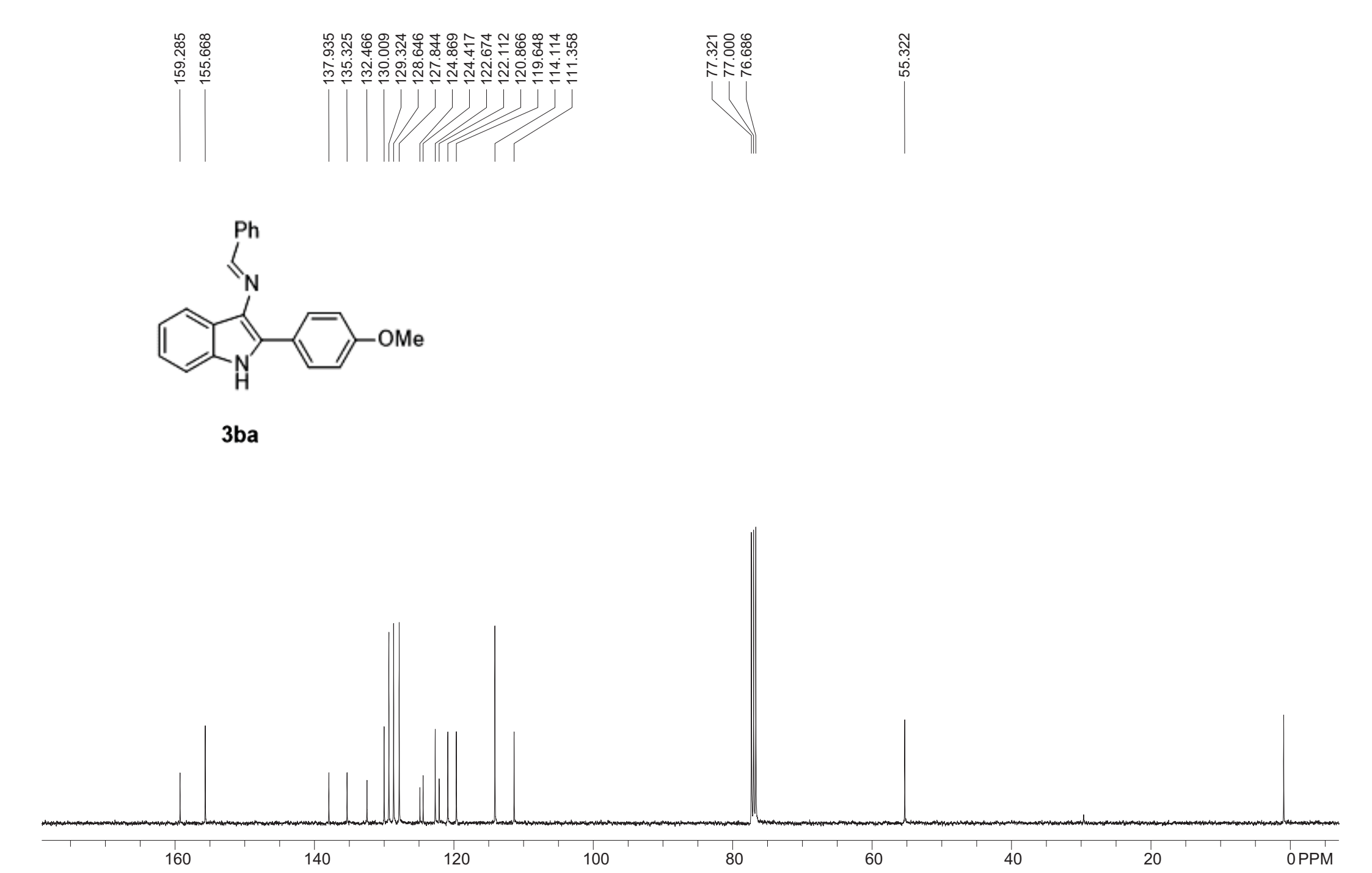
PPM

3ba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137.935
135.325
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130.009
129.324
128.646
127.844
124.869
124.417
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122.112
120.866
119.648
114.114
111.358
77.321
77.000
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Ph
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H
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140
120
100
80
60
40
20
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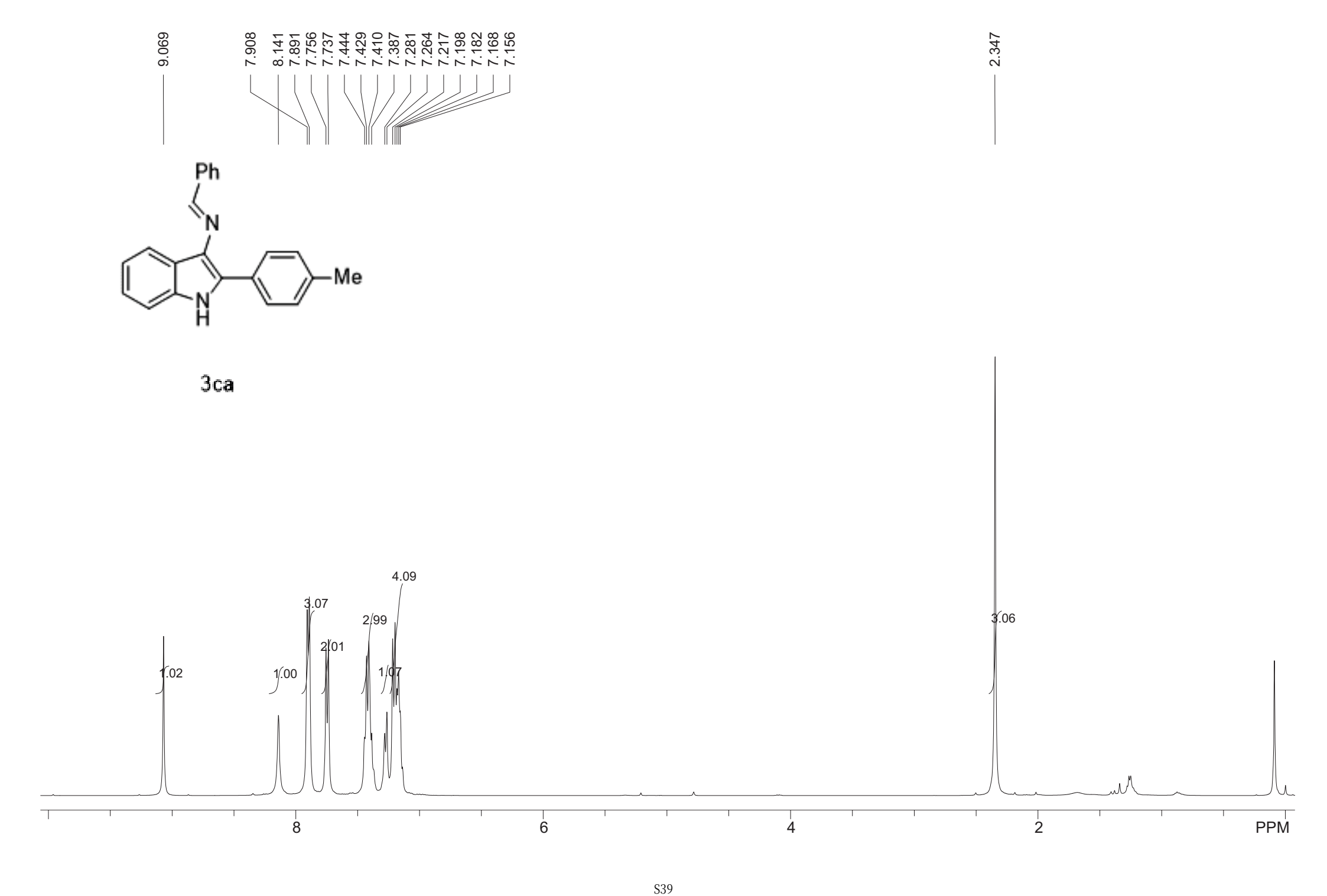
3ba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7.891
7.756
7.737
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7.429
7.410
7.387
7.281
7.264
7.217
7.198
7.182
7.168
7.156
2.347
Ph
N
Me
N
H
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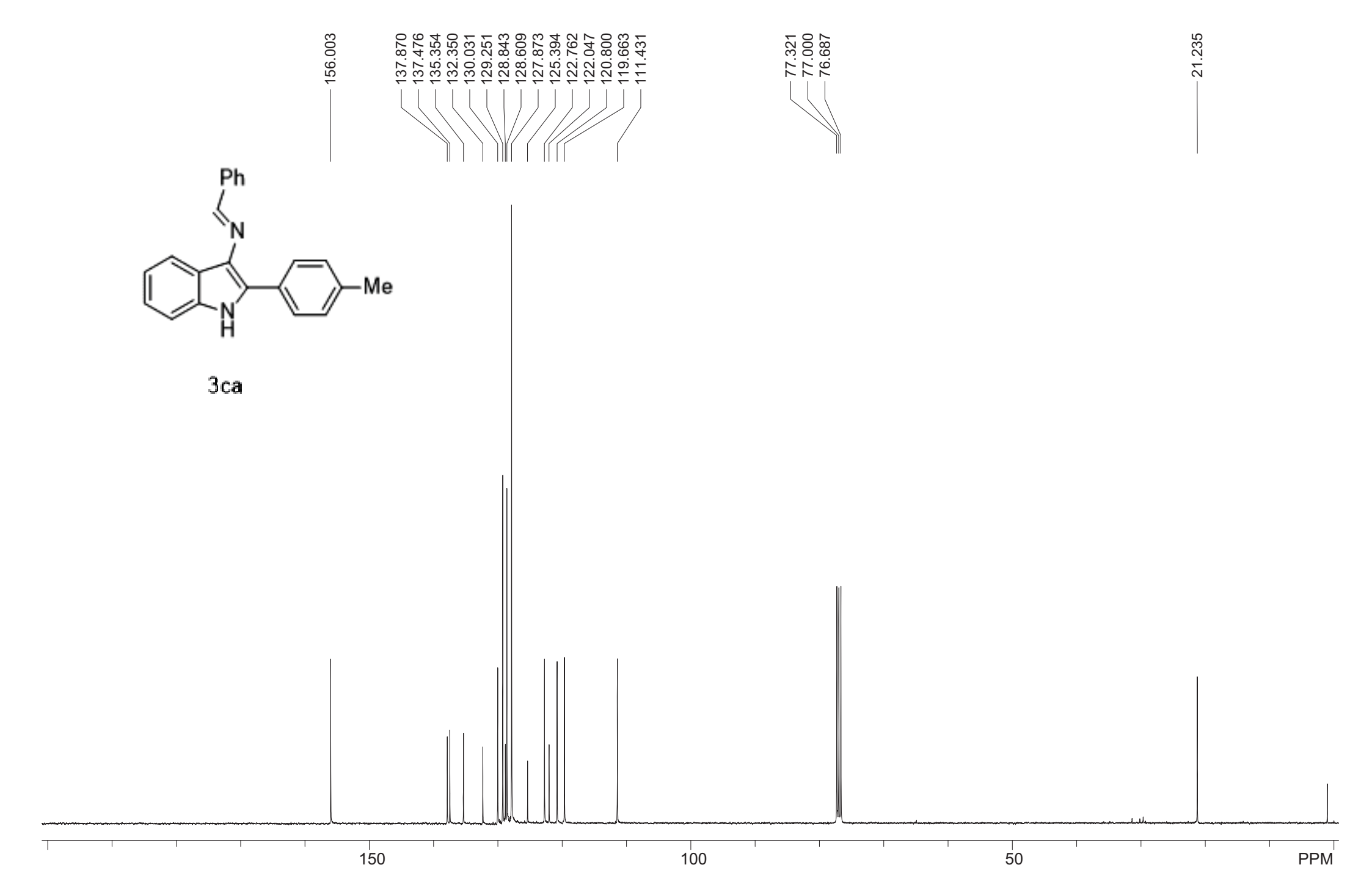
1.02
1.00
1.07
3.06
8
6
4
2
PPM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120.800
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Ph
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H
Me
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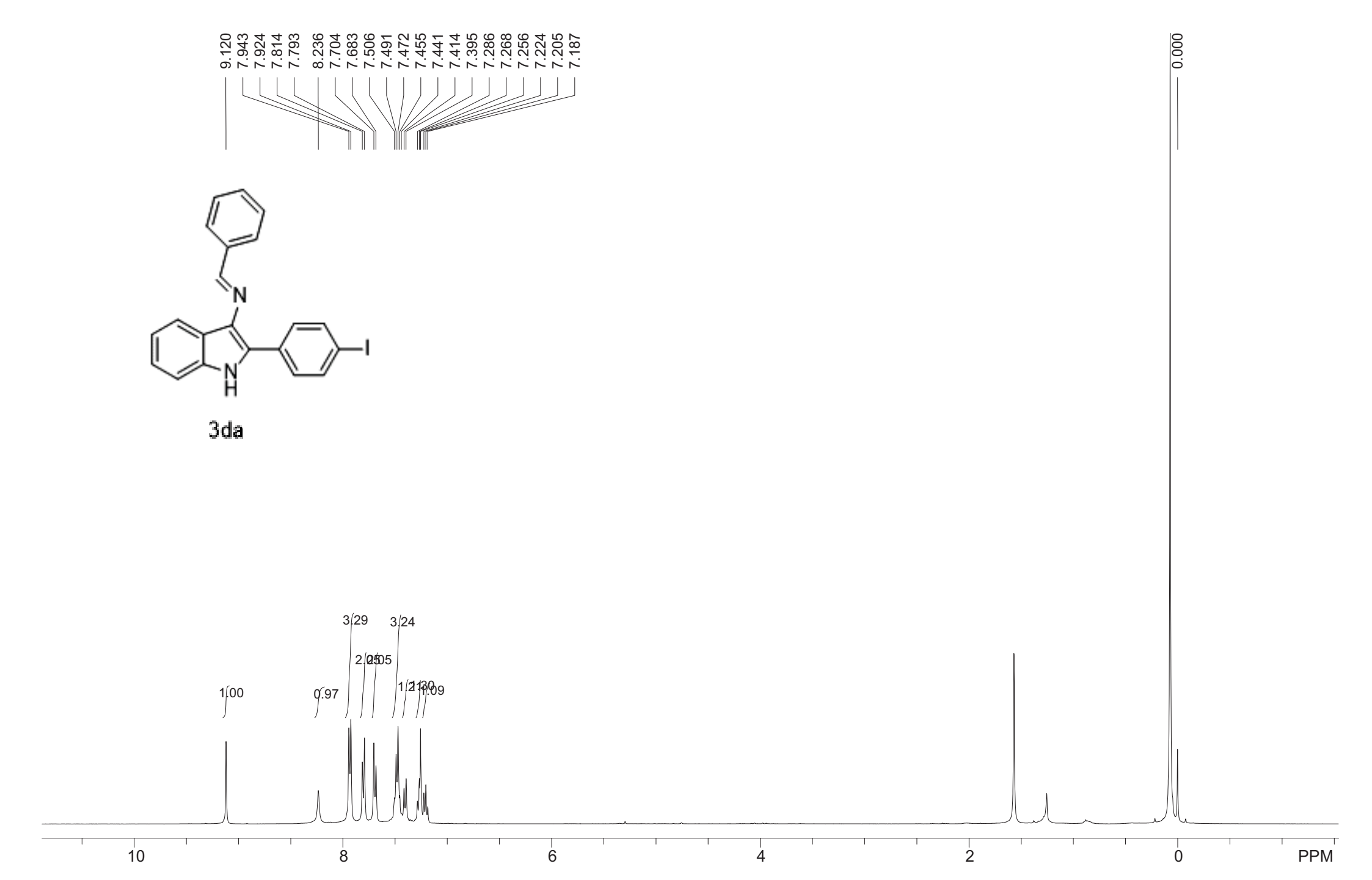
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7.472
7.455
7.441
7.414
7.395
7.286
7.268
7.256
7.224
7.205
7.187
0.000
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N
H
I
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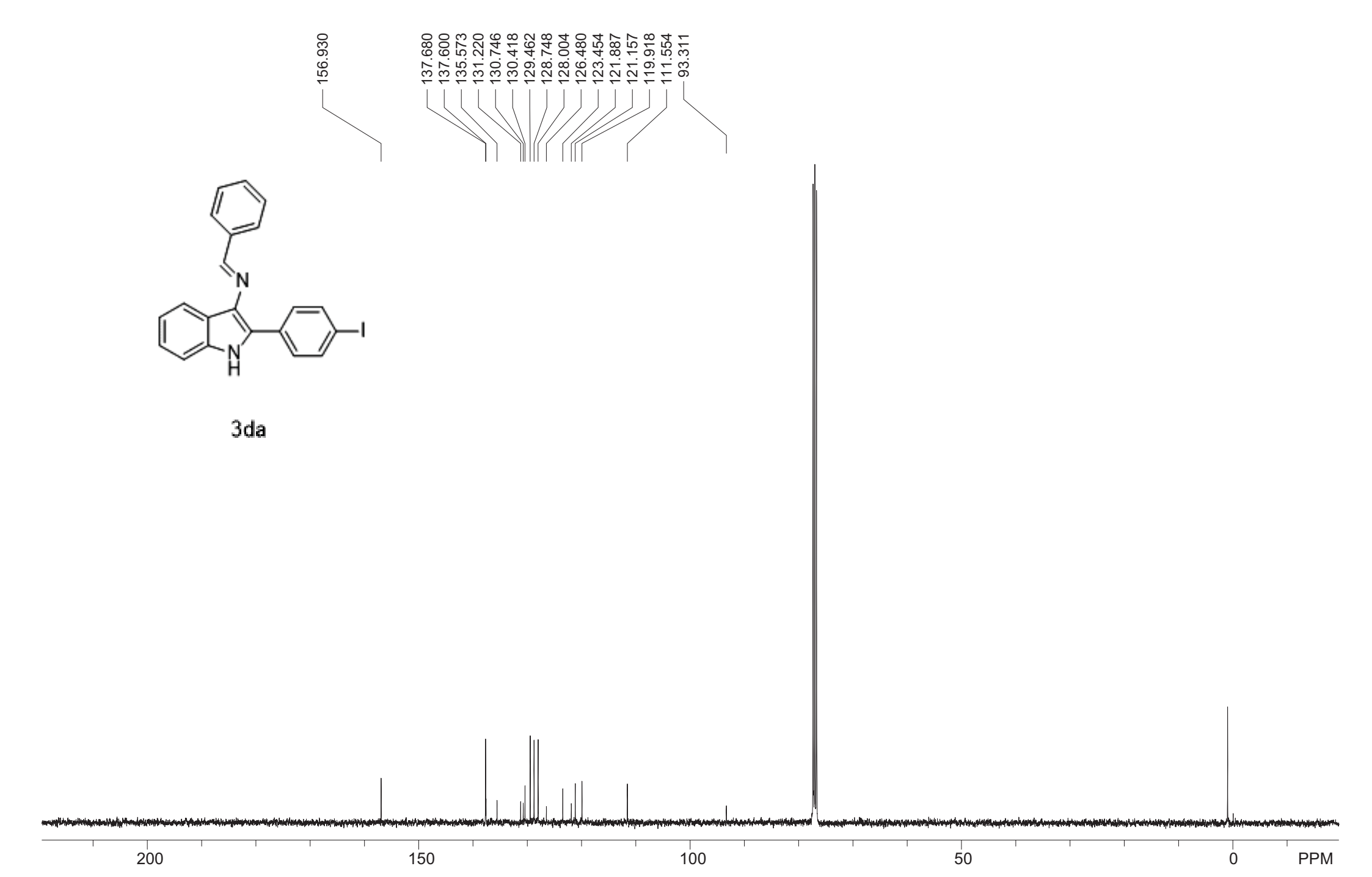
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130.418
129.462
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128.004
126.480
123.454
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111.554
93.311
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H
I
3da
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150
100
50
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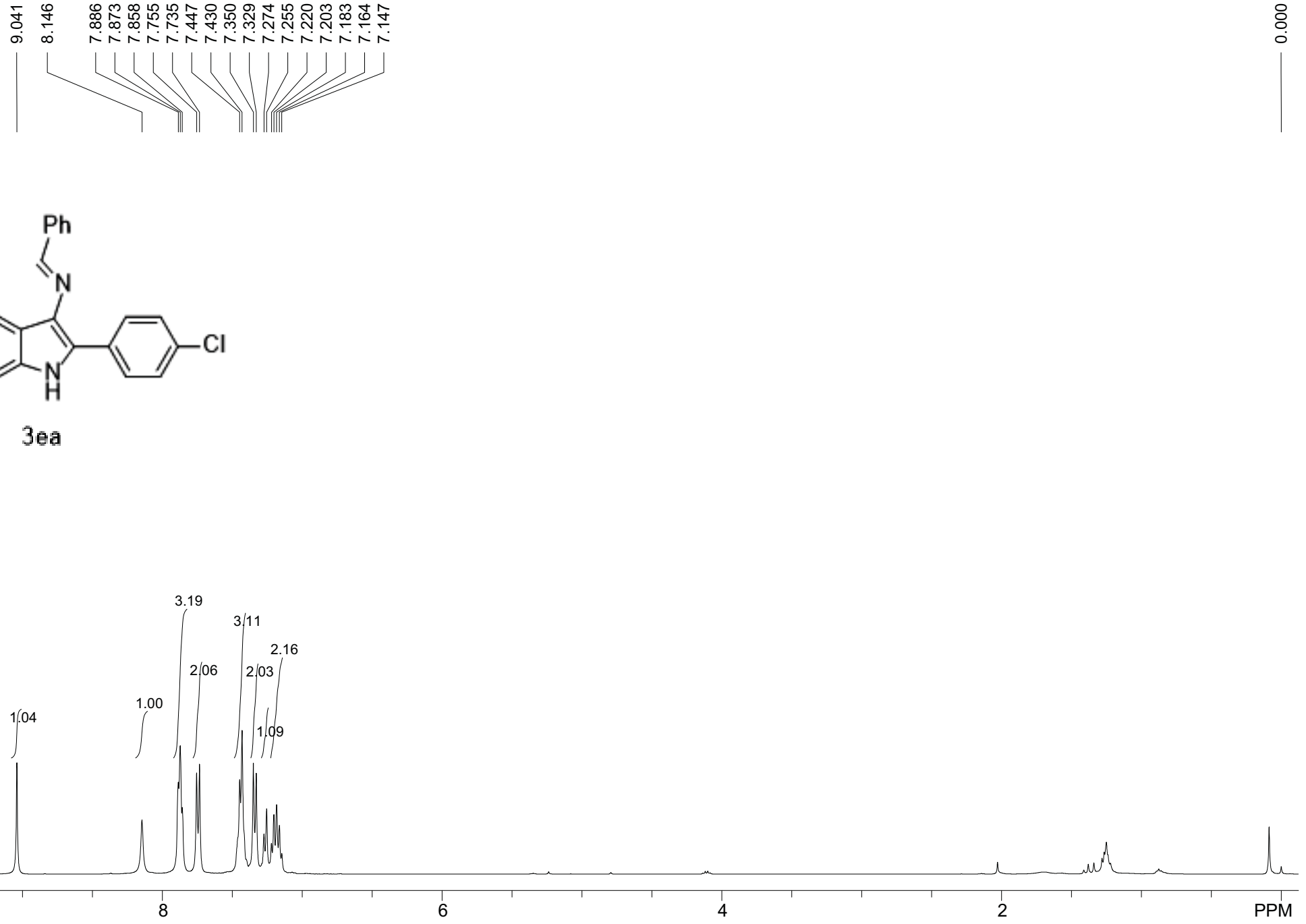
PPM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7.329
7.274
7.255
7.220
7.203
7.183
7.164
7.147
0.000
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Cl
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H
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1.09
10
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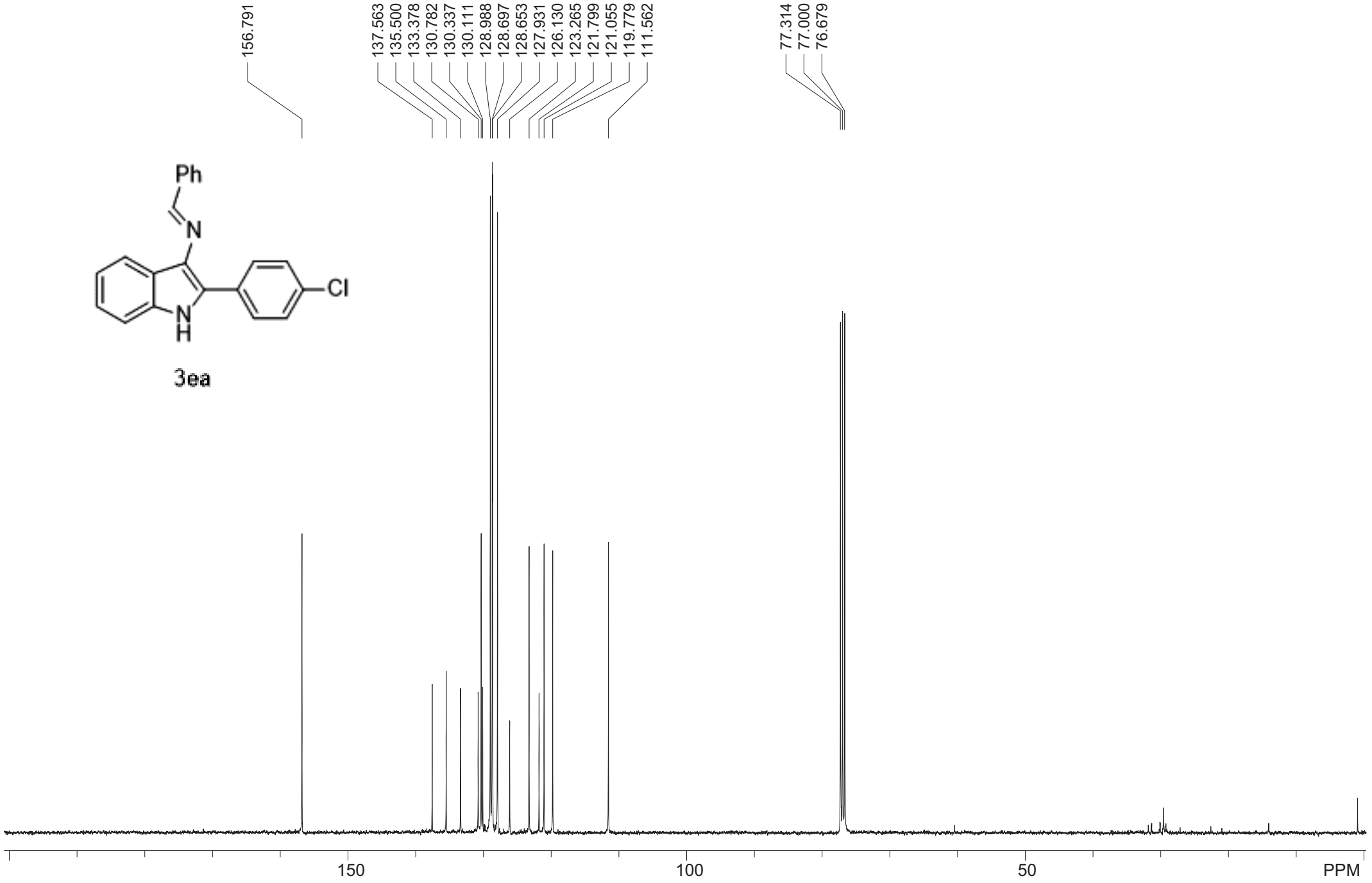
6
4
2
PPM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127.931
126.130
123.265
121.799
121.055
119.779
111.562
77.314
77.000
76.679
Ph
N
Cl
N
H
3ea
150
100
50
PPM


9.063
8.180
7.900
7.892
7.887
7.876
7.733
7.712
7.532
7.510
7.475
7.462
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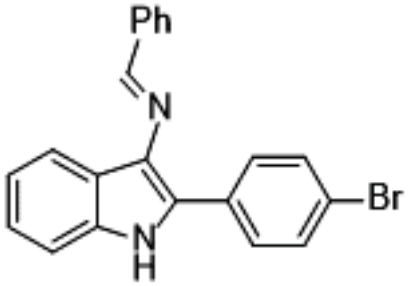
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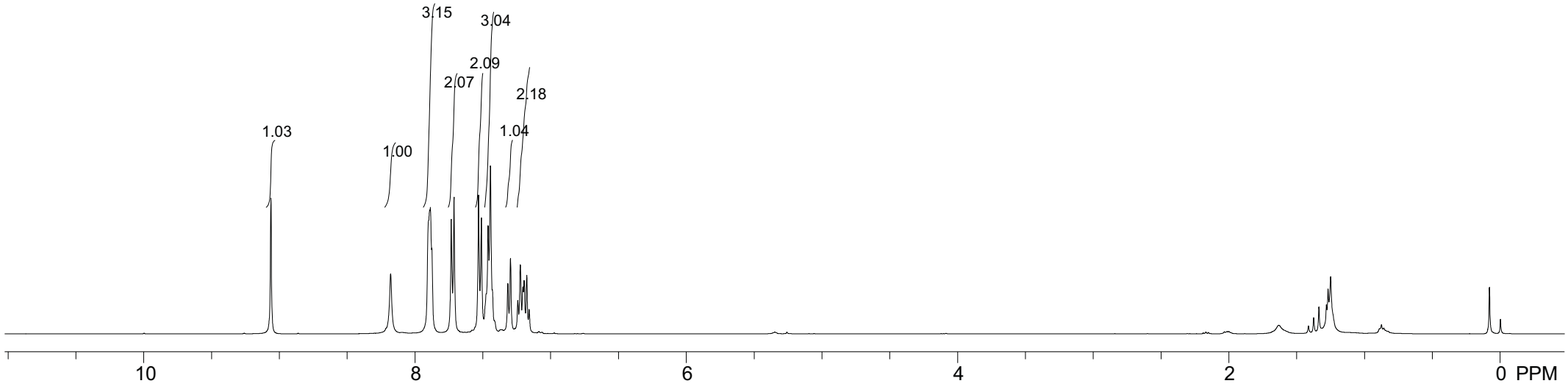
Br
N
H

3fa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2.09
2.18
1.04
10
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4
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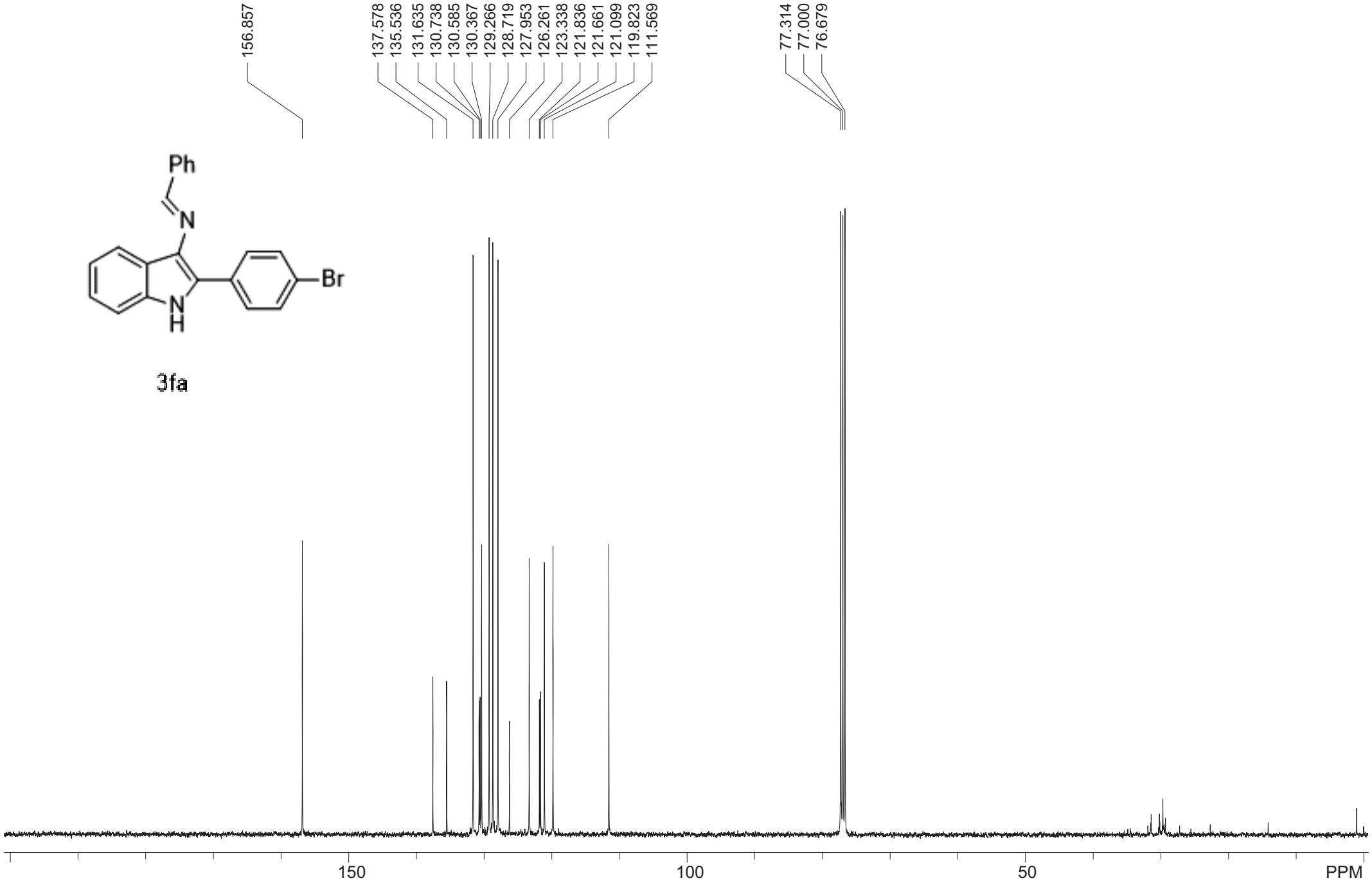
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121.661
121.099
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76.679
Ph
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Br
N
H
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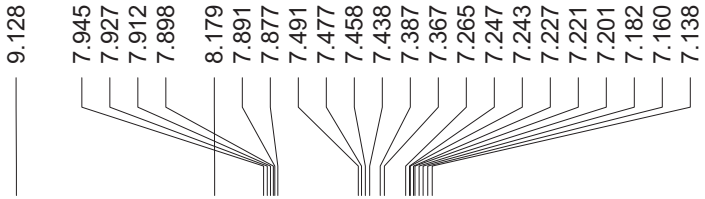
100
50
PPM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7.877
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7.477
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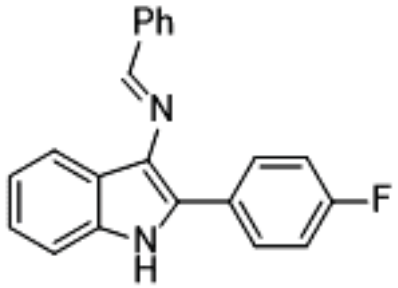
7.160
7.138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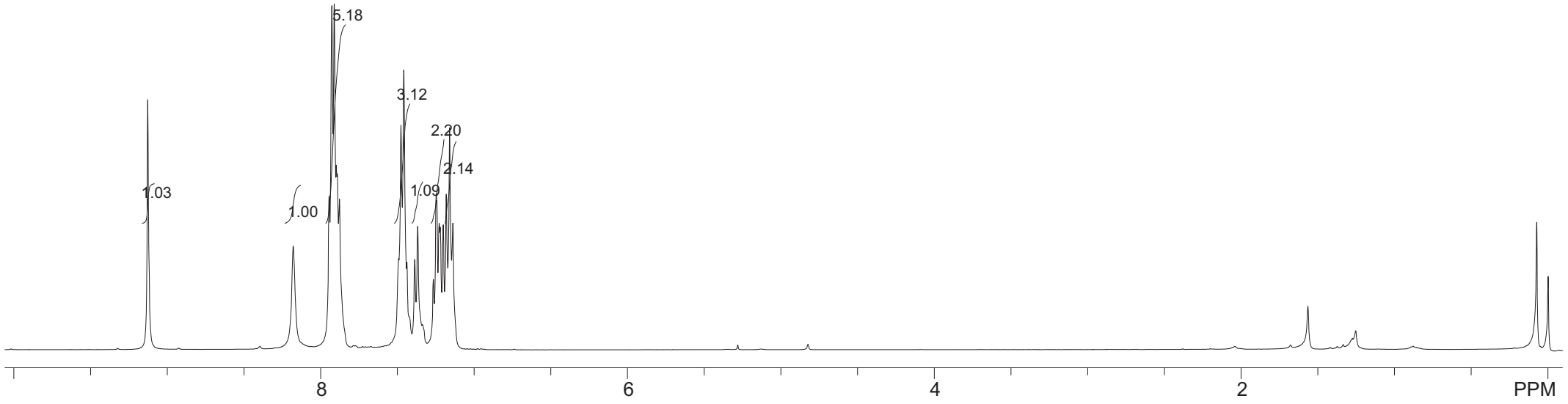
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1.00
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6
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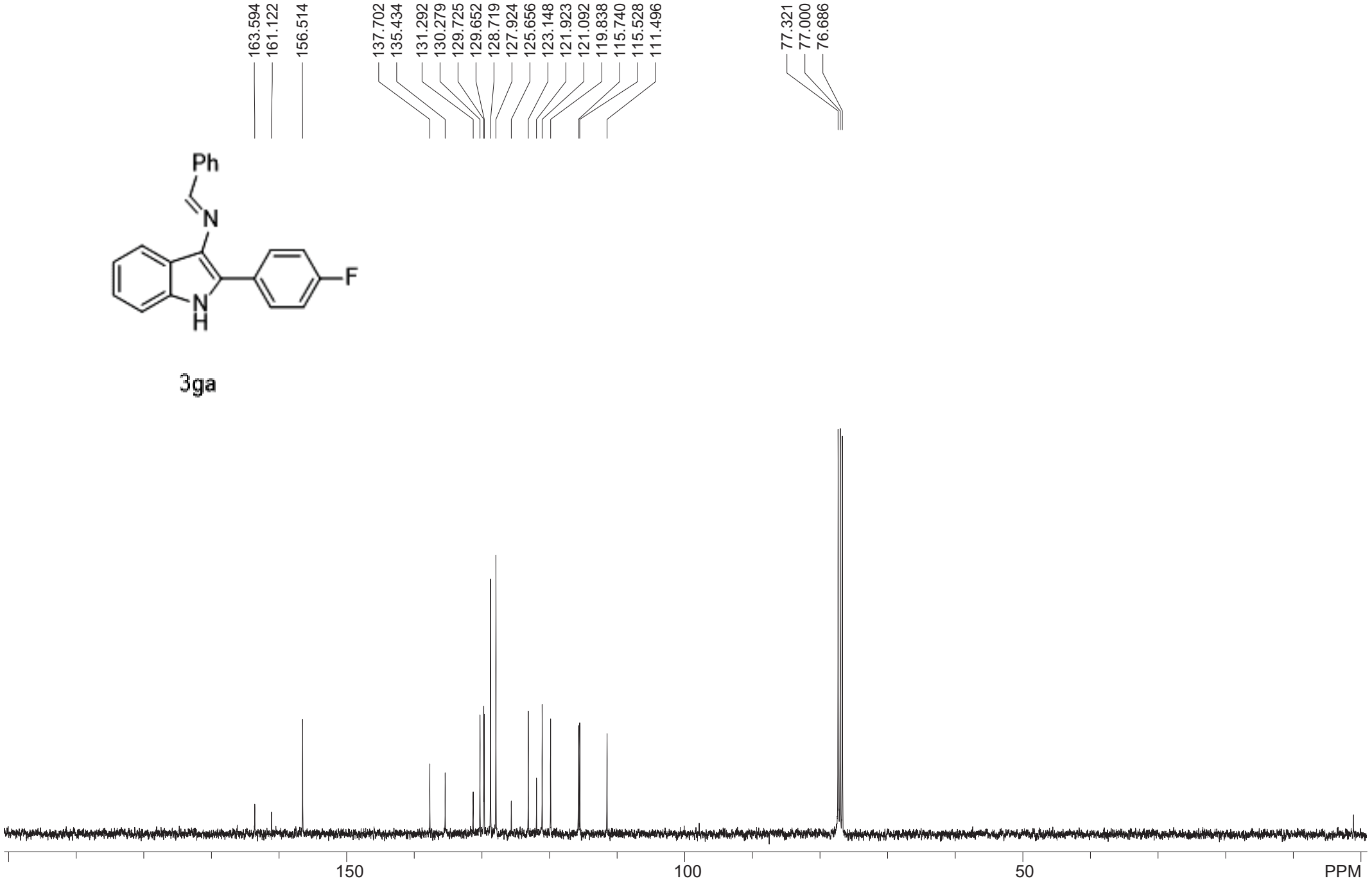
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121.092
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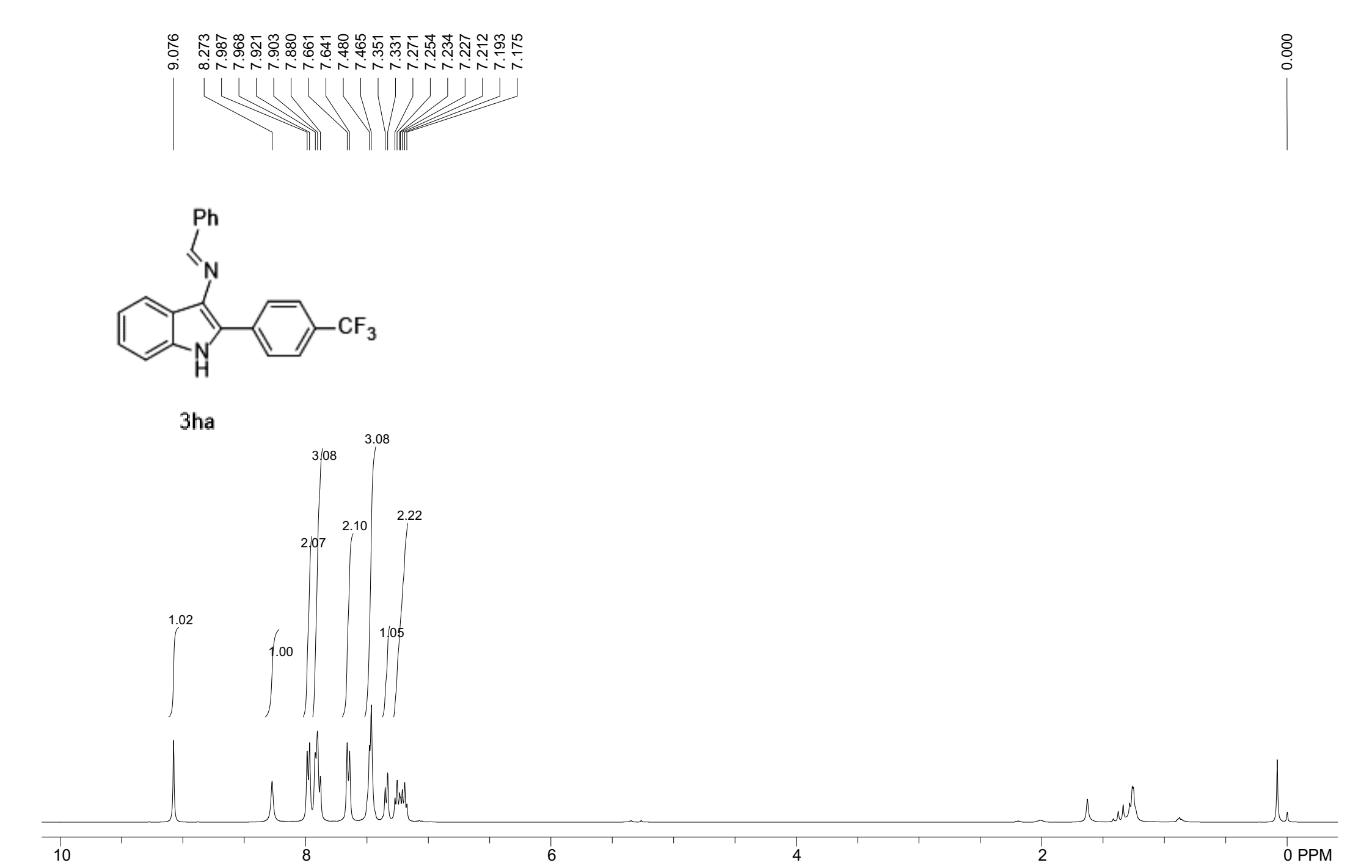
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7.661
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7.480
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7.331
7.271
7.254
7.234
7.227
7.212
7.193
7.175
0.000
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N
H
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3ha
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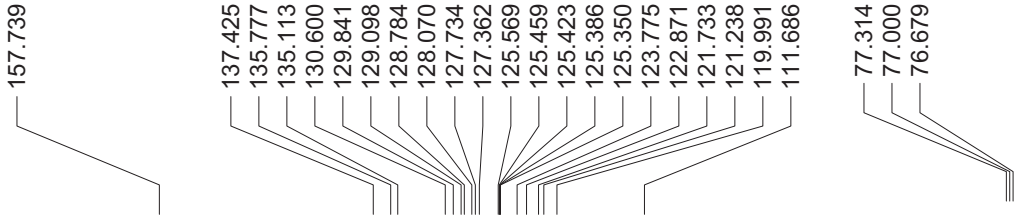
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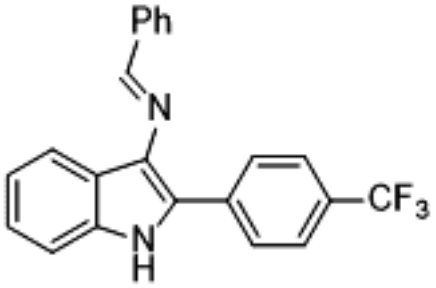
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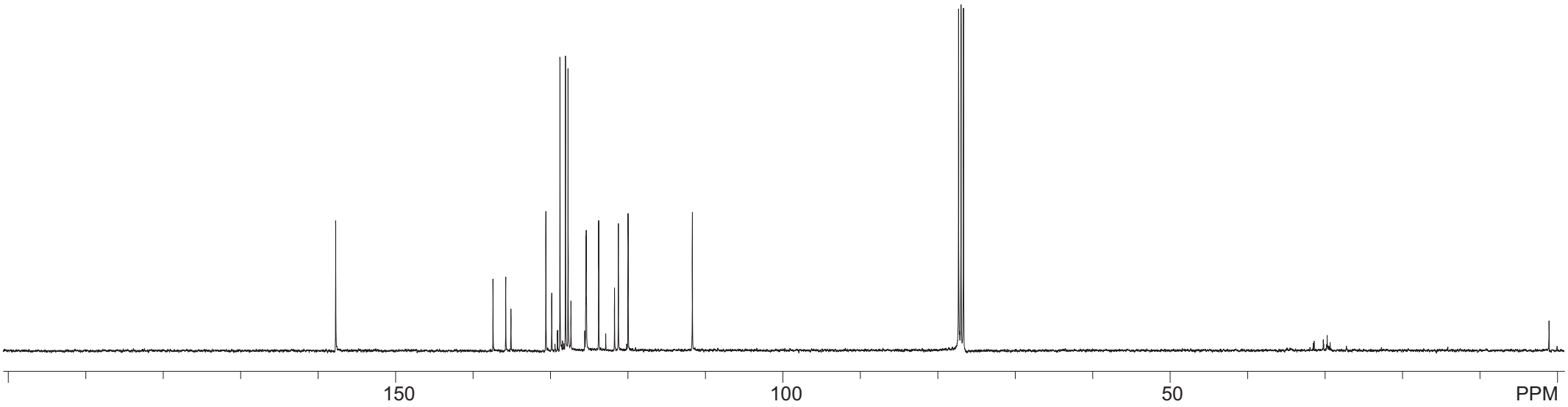
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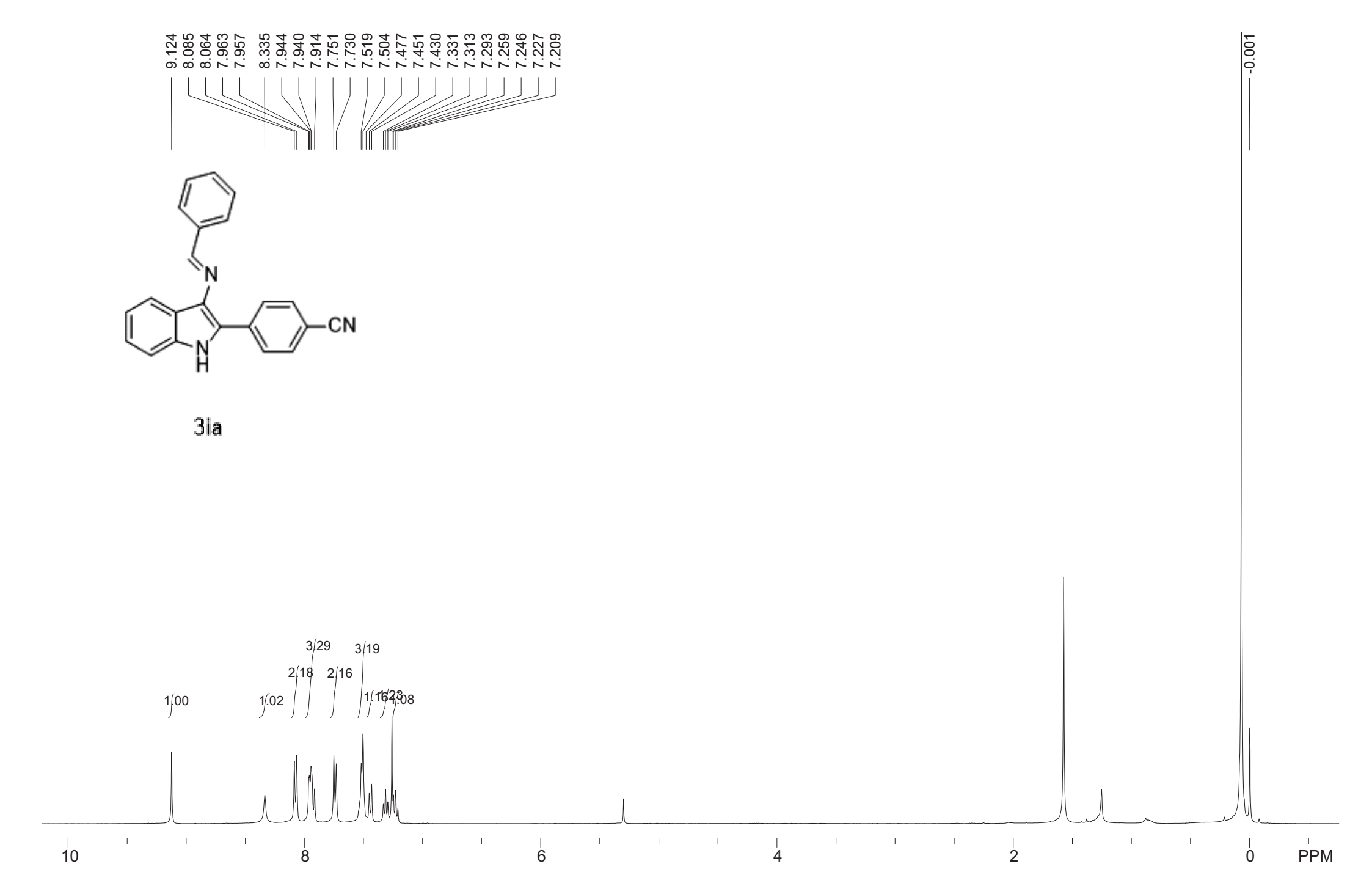
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7.504
7.477
7.451
7.430
7.331
7.313
7.293
7.259
7.246
7.227
7.209
-0.001
N
N
H
CN
3ia
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10
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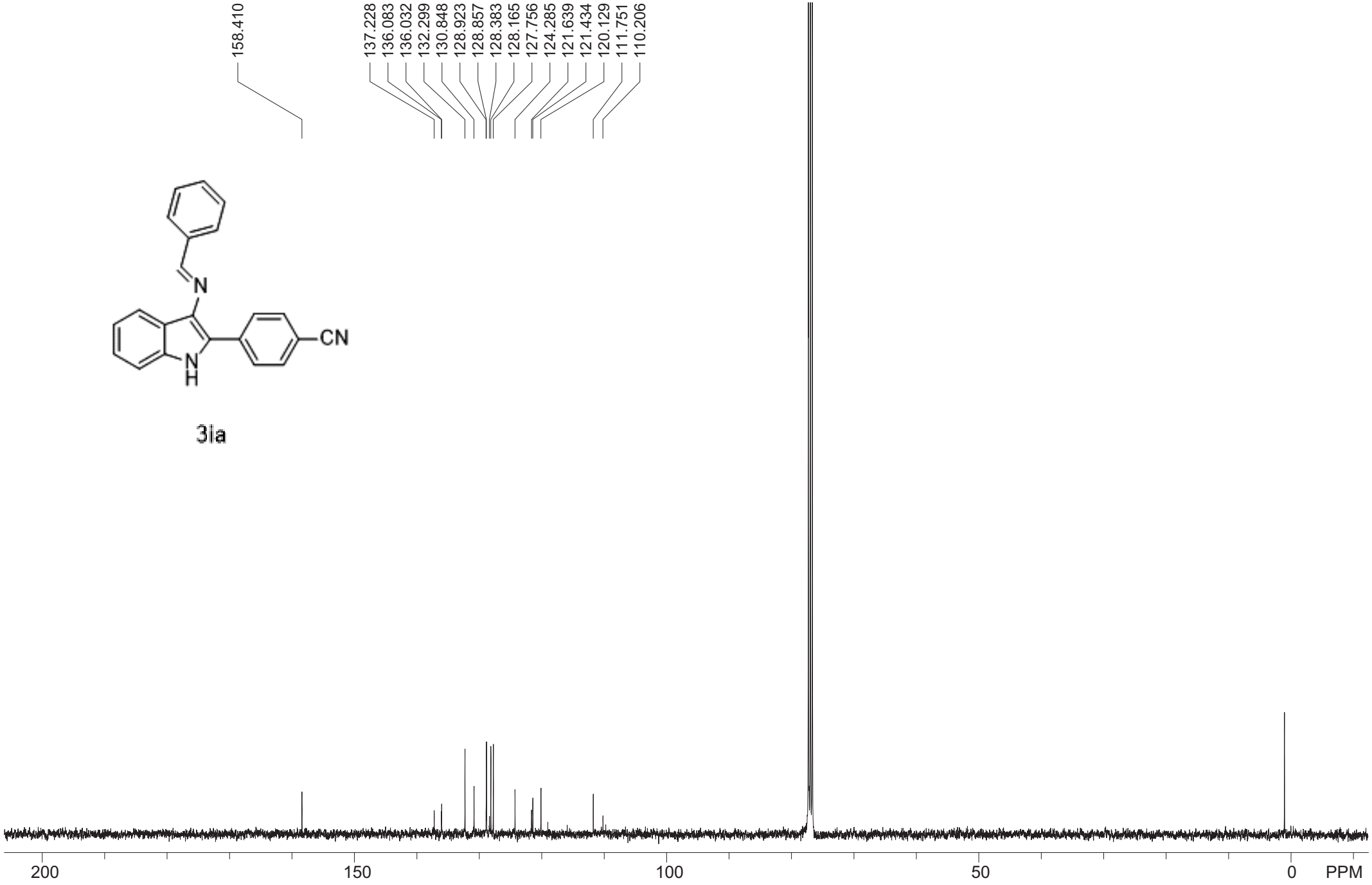
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128.857
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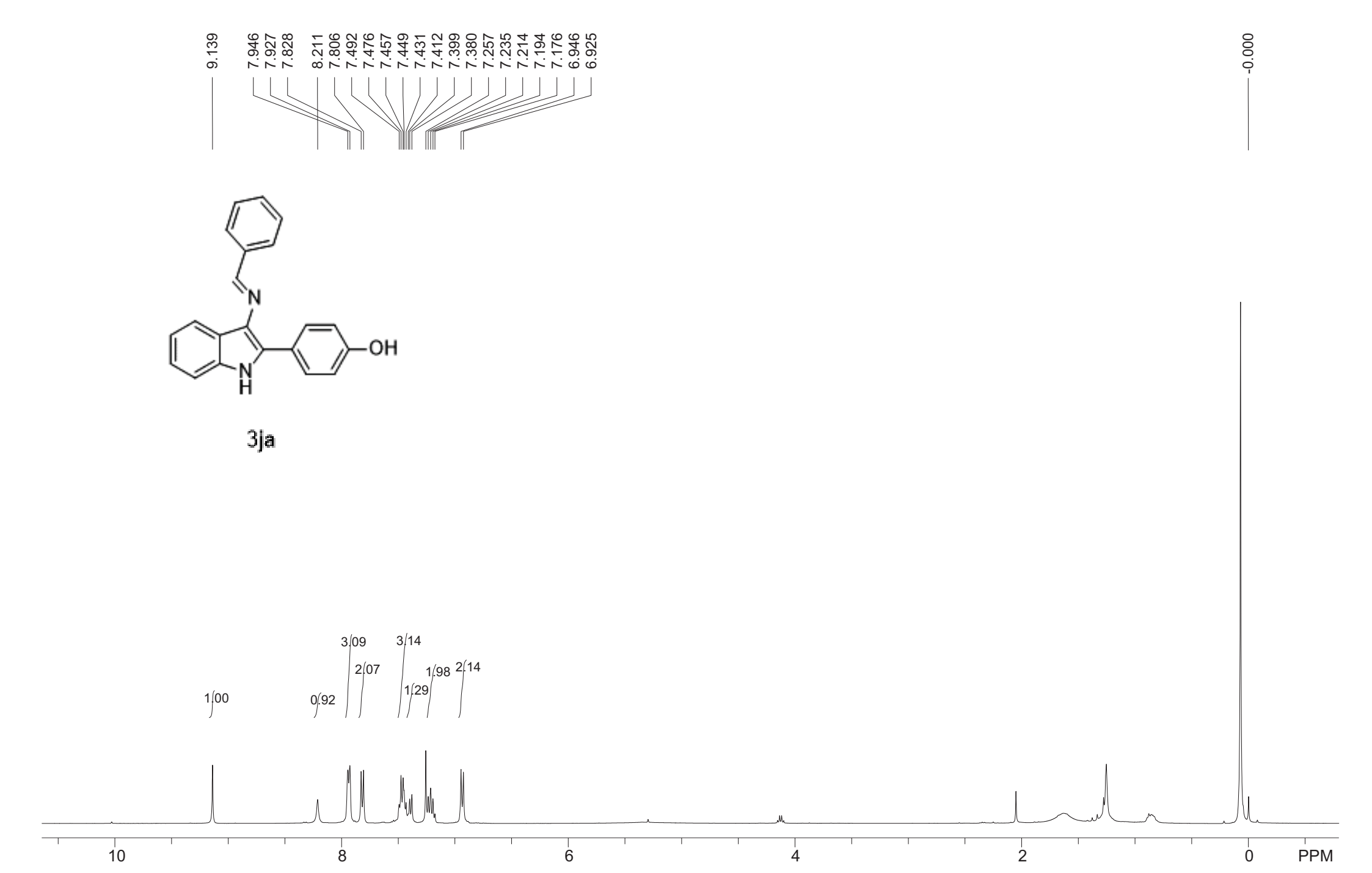
PPM

3ia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7.412
7.399
7.380
7.257
7.235
7.214
7.194
7.176
6.946
6.925
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N
H
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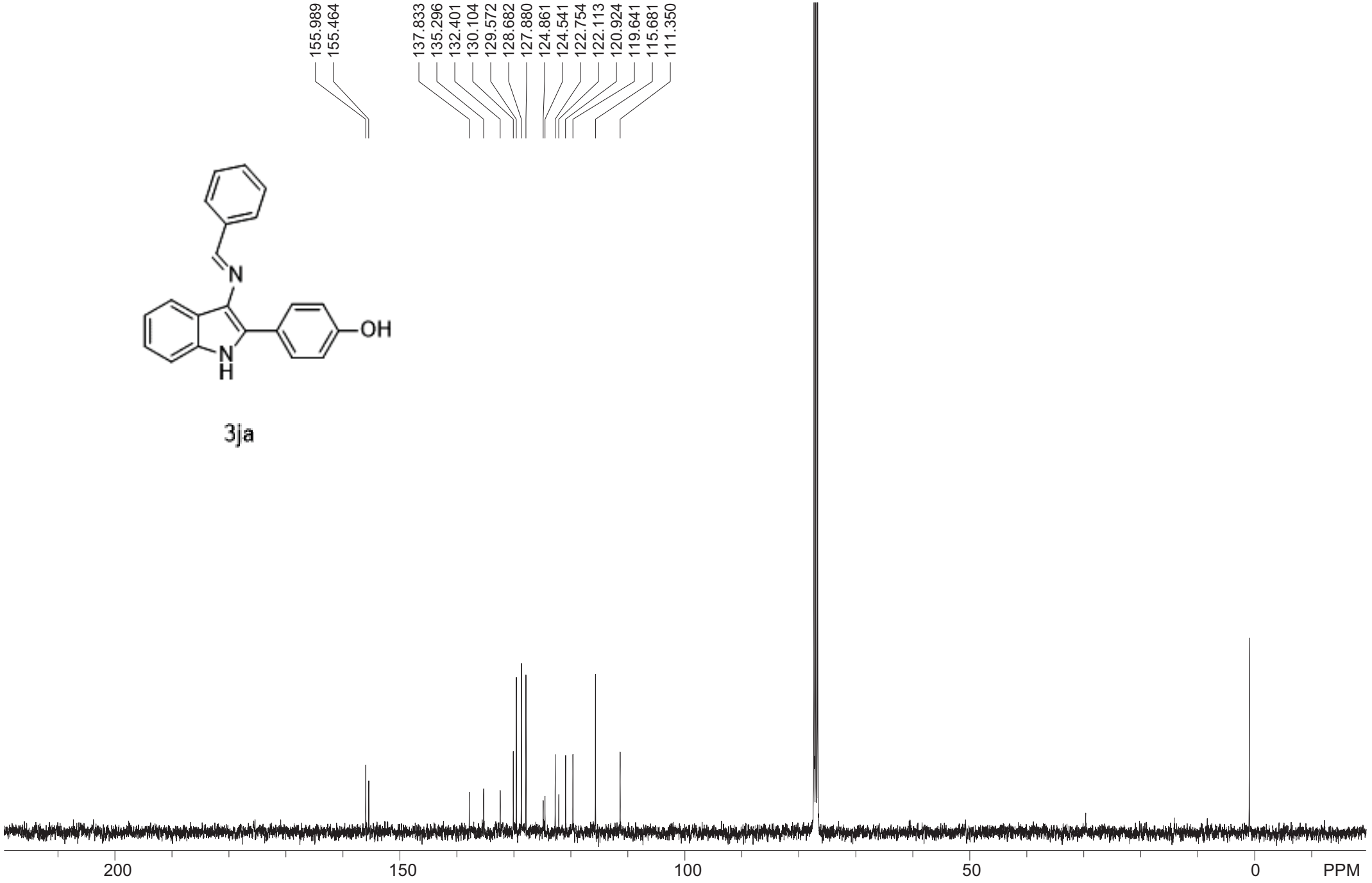
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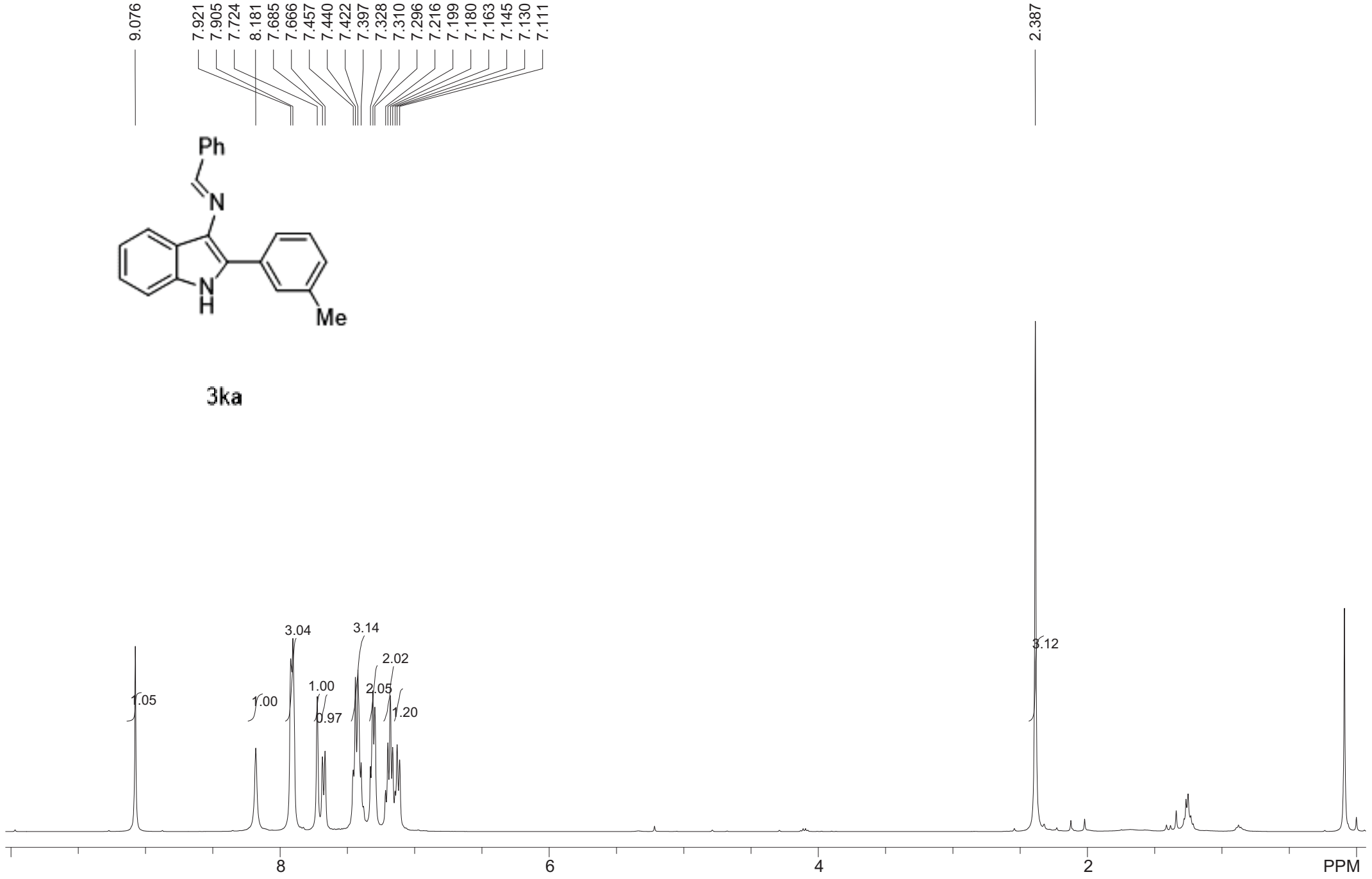
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7.296
7.216
7.199
7.180
7.163
7.145
7.130
7.111
2.387
Ph
N
N
H
Me
3ka
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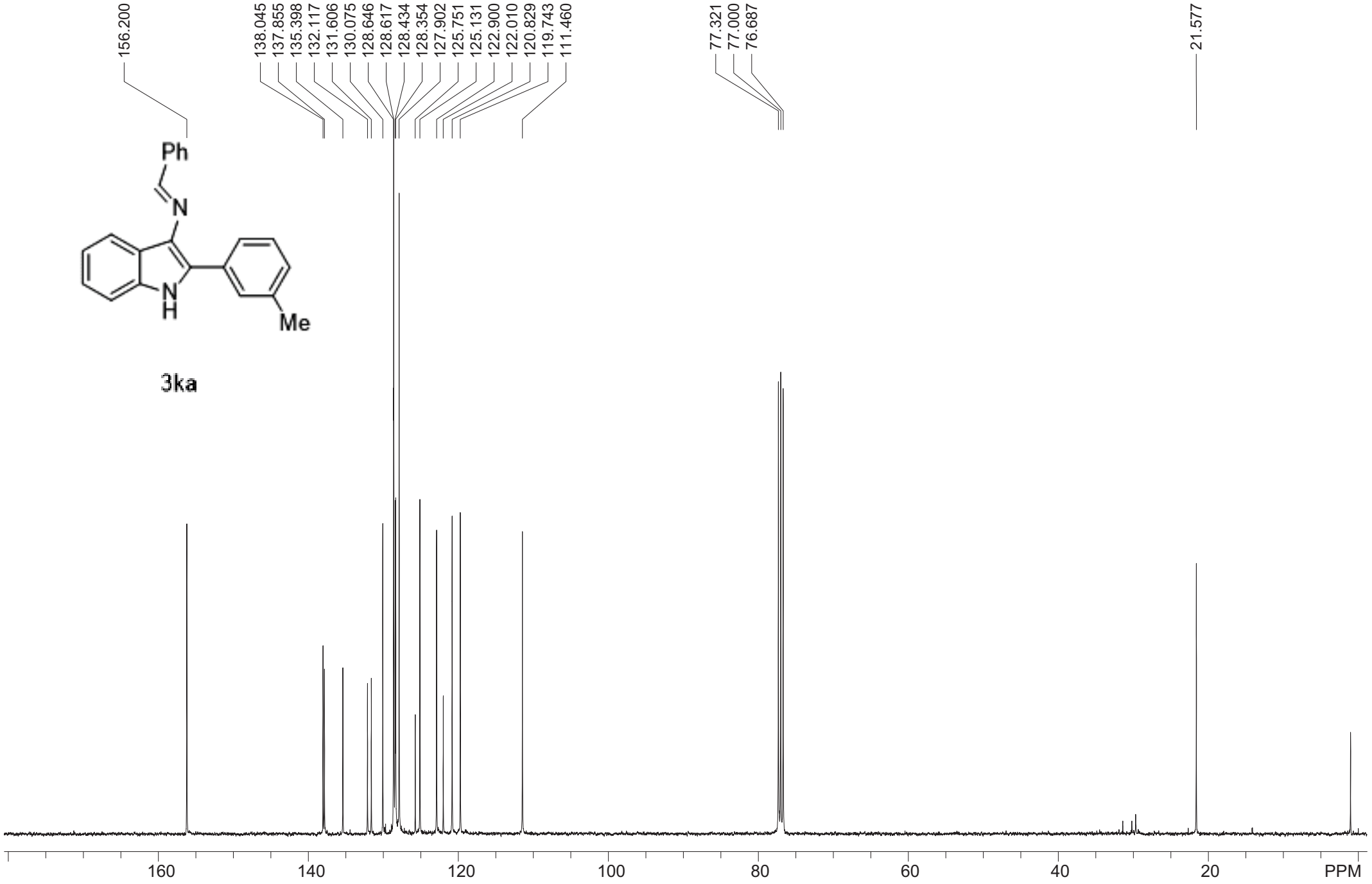
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122.010
120.829
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111.460
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77.000
76.687
21.577
Ph
N
N
H
Me
160
140
120
100
80
60
40
20
PPM

3ka


9.063
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8.128
7.930
7.912
7.901
7.880
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7.484
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7.429
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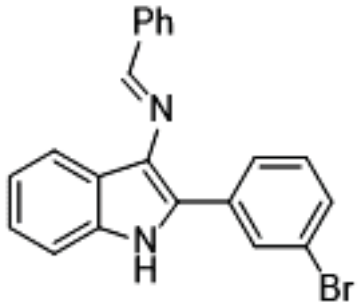
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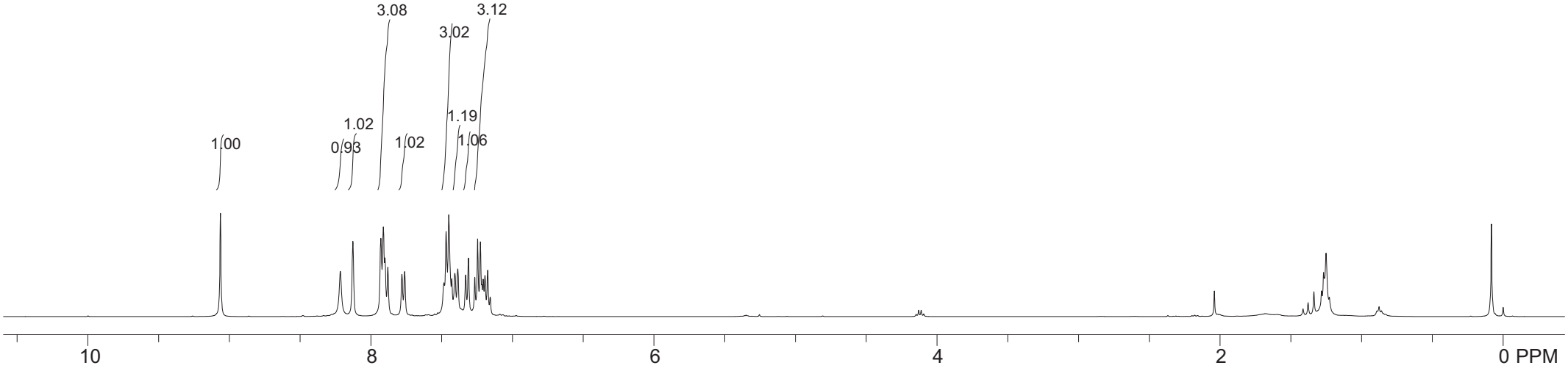
Br

3la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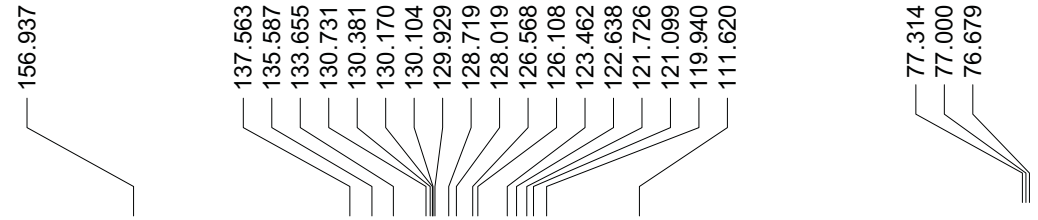
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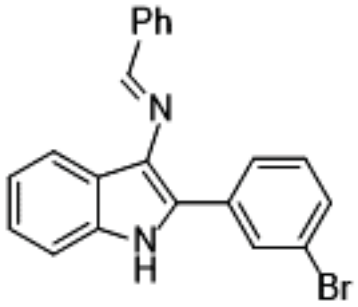
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N
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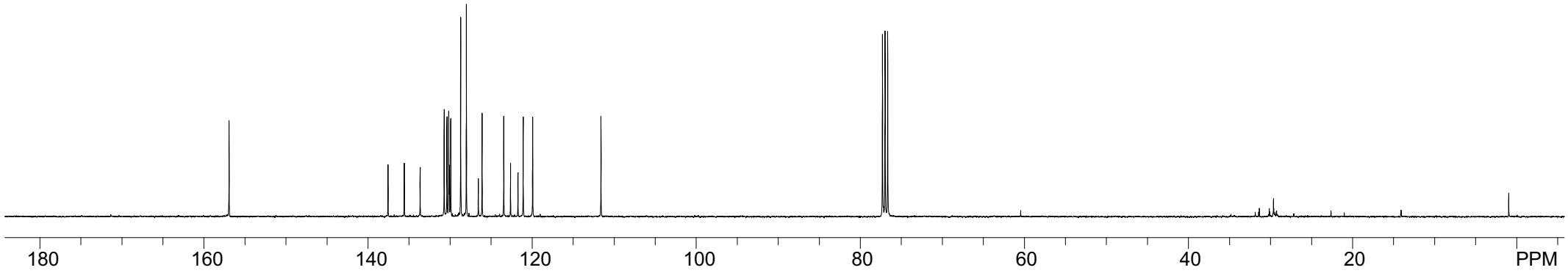
Br

3la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140
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100
80
60
40
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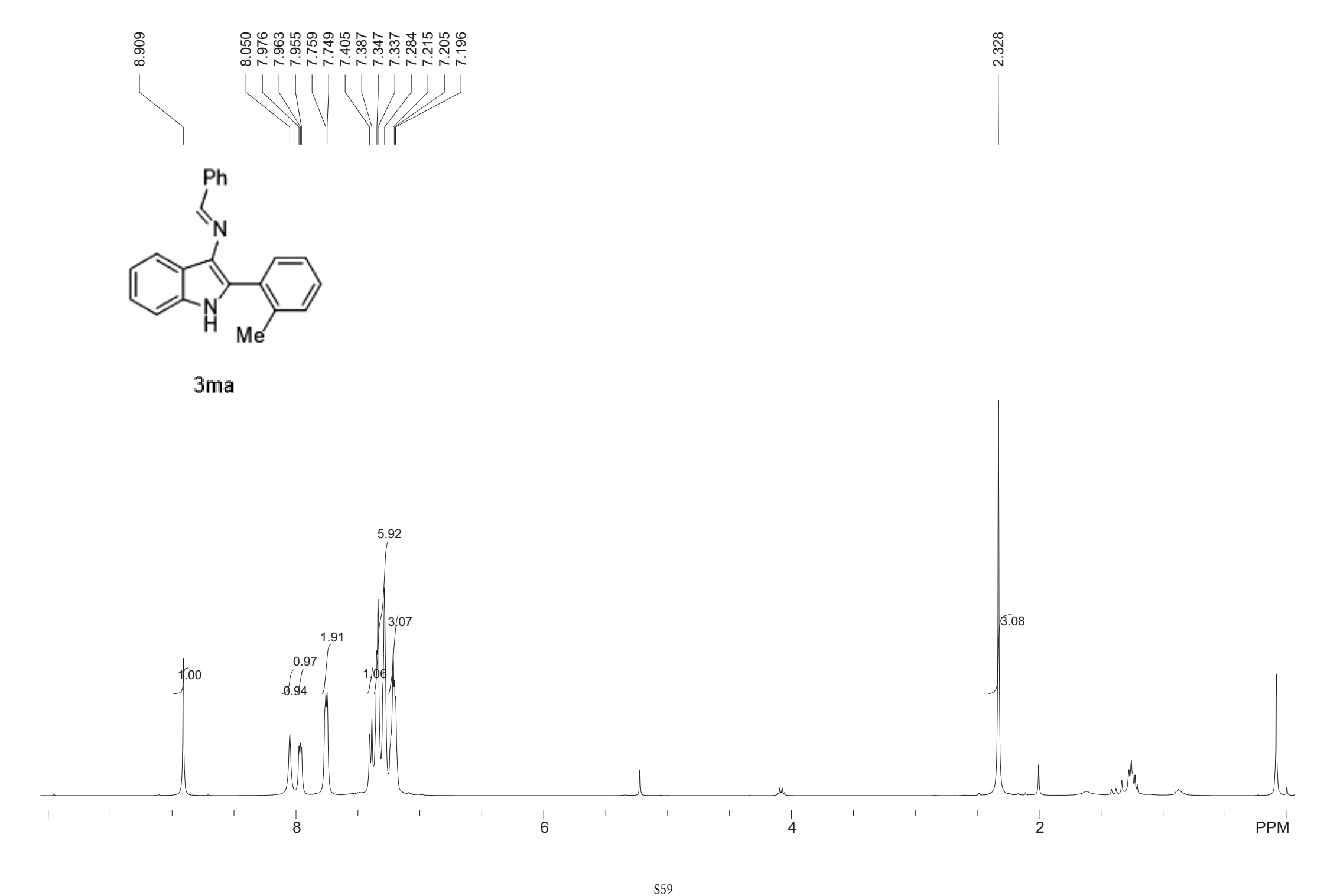
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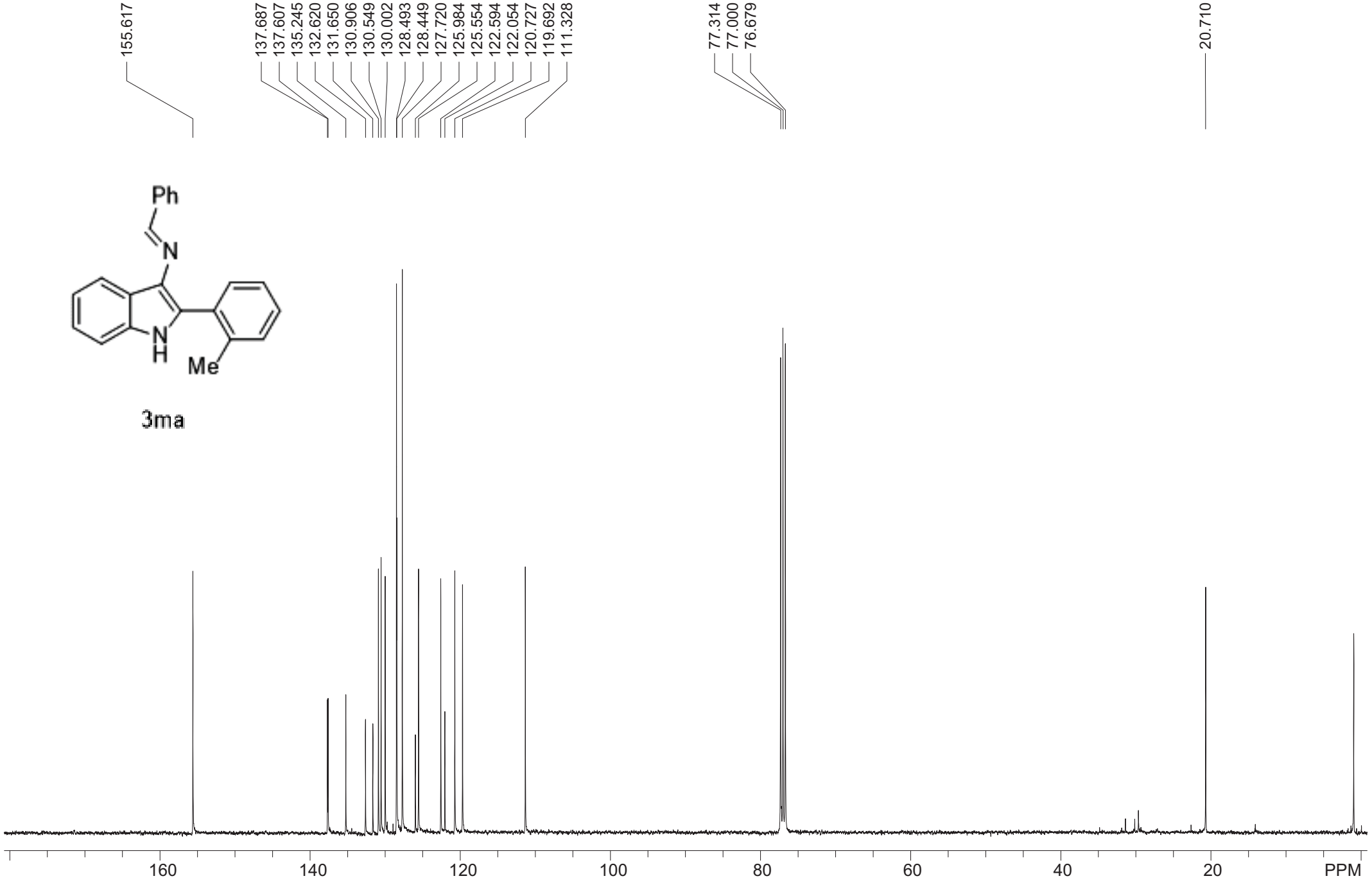
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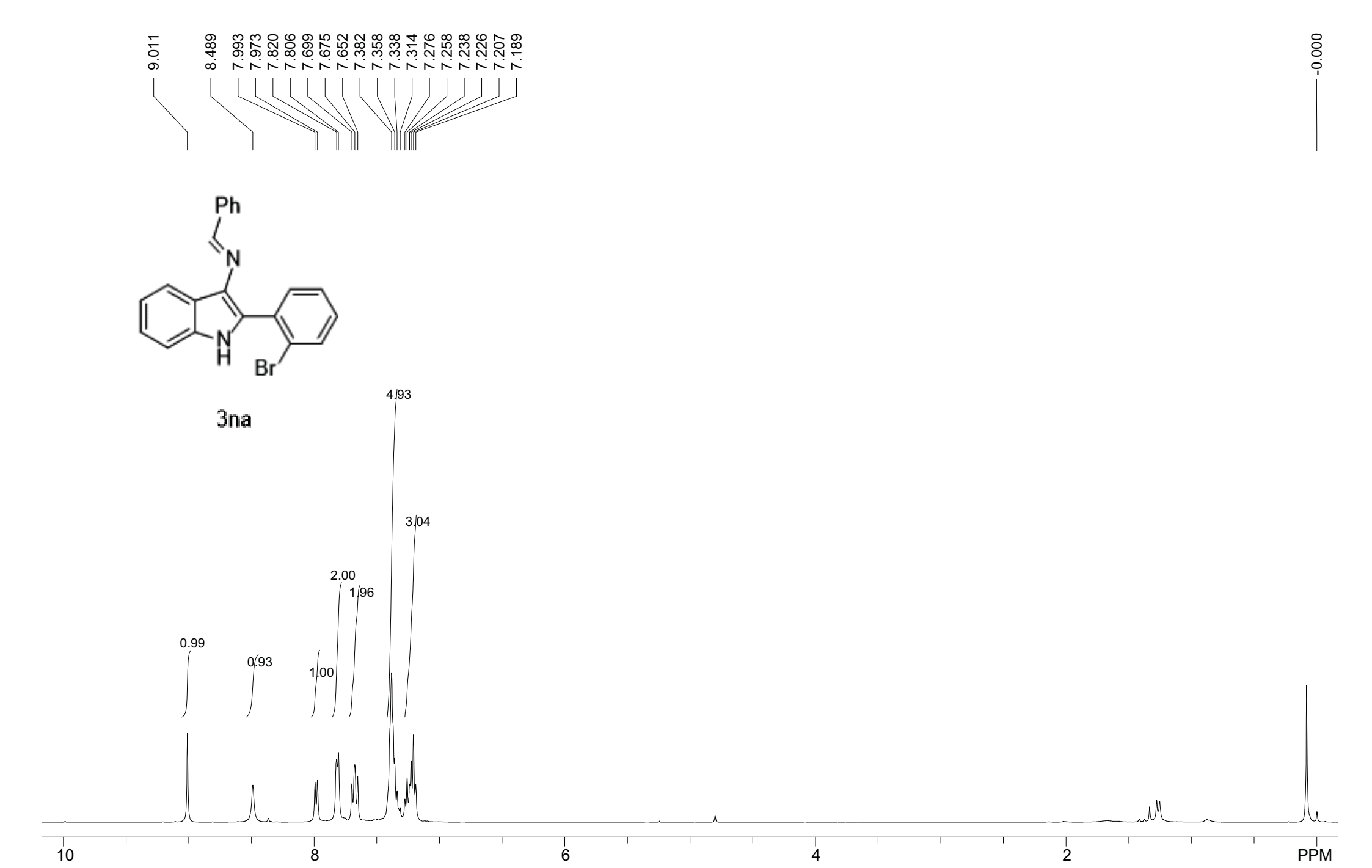
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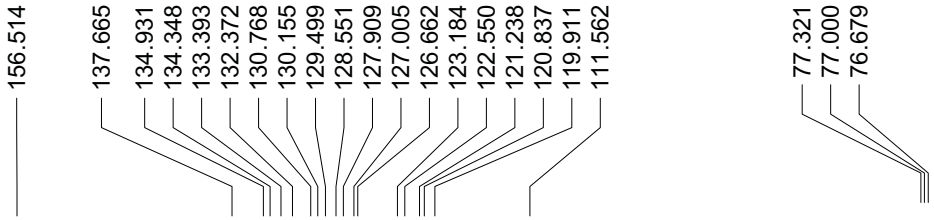
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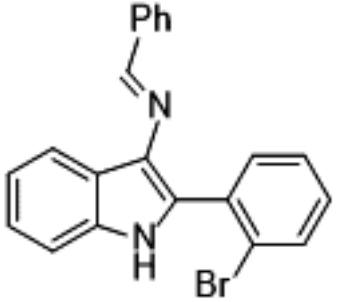
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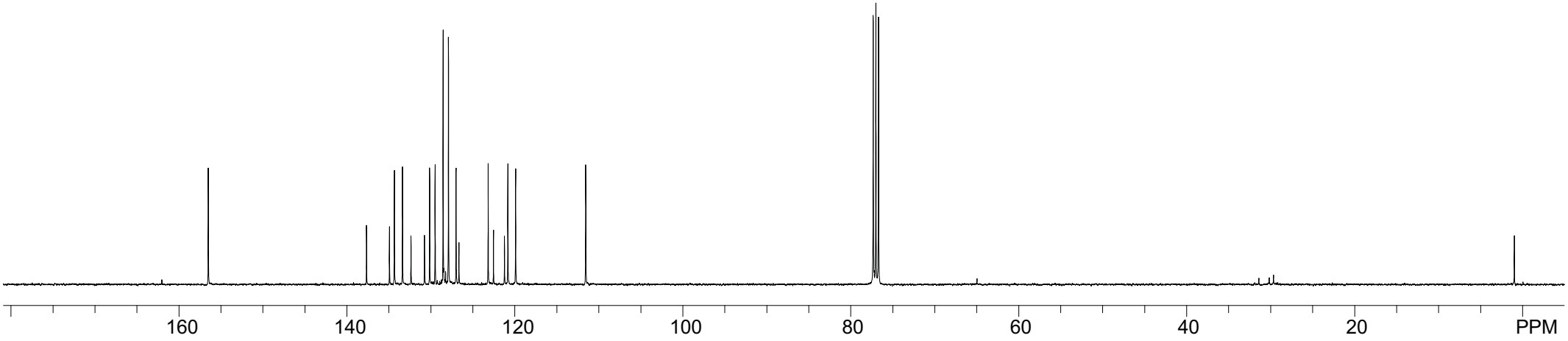
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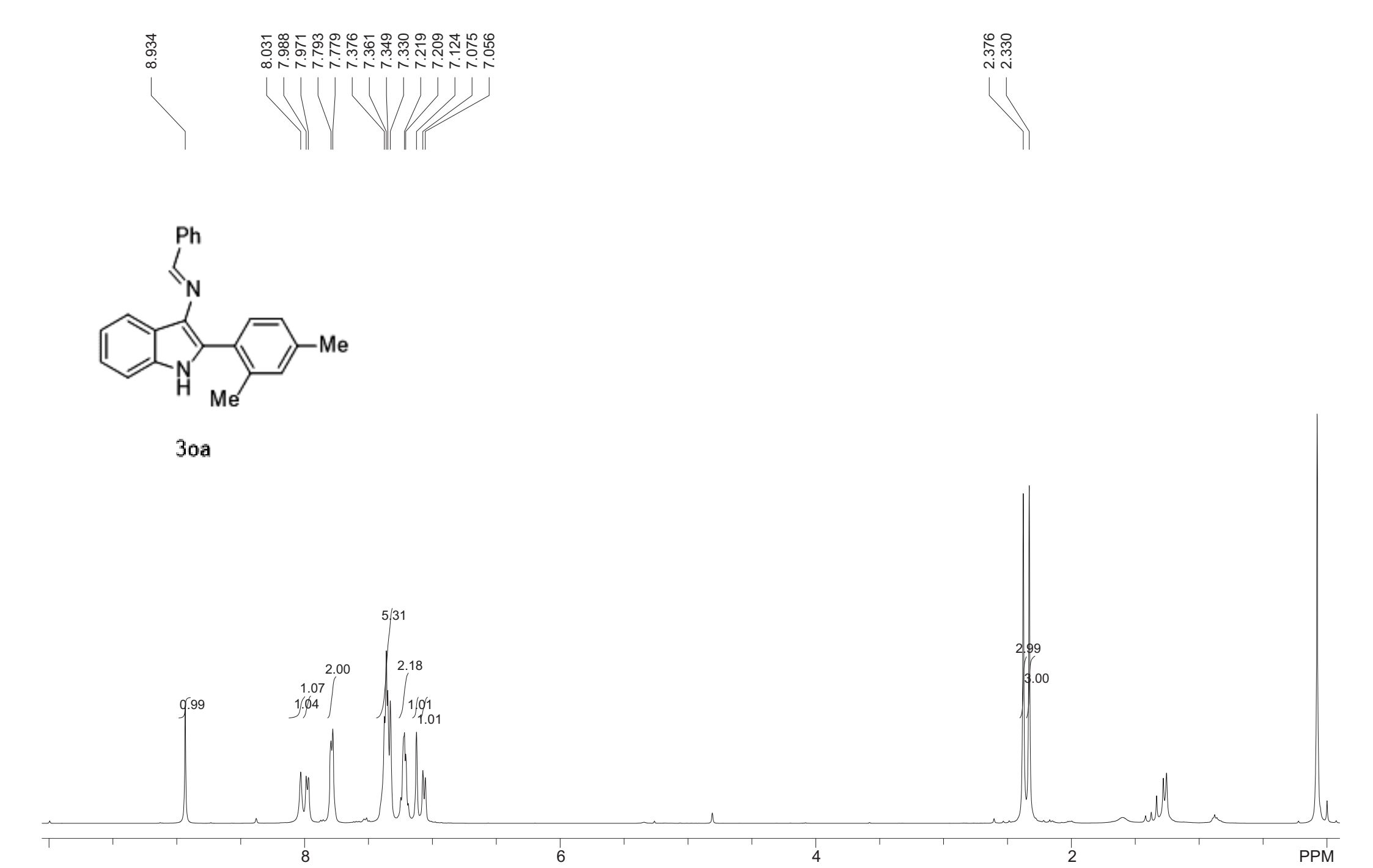
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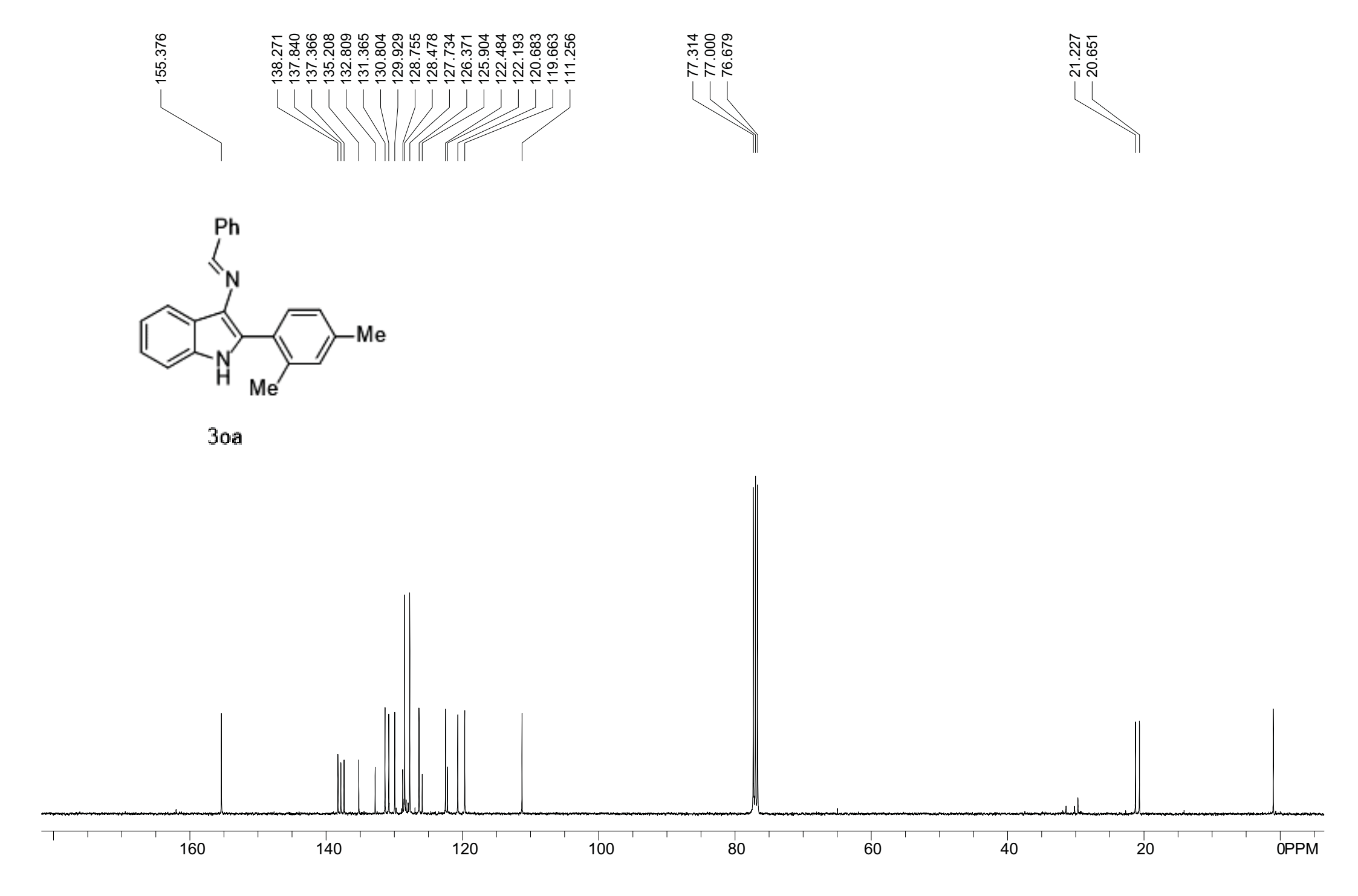
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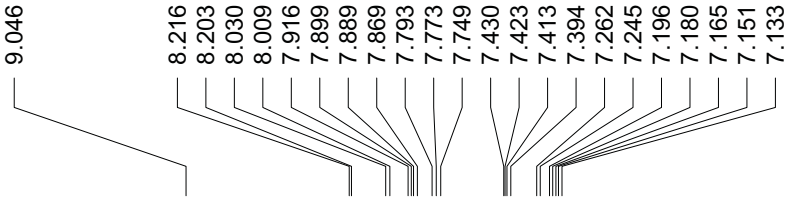
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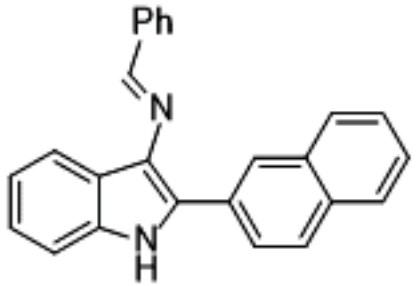
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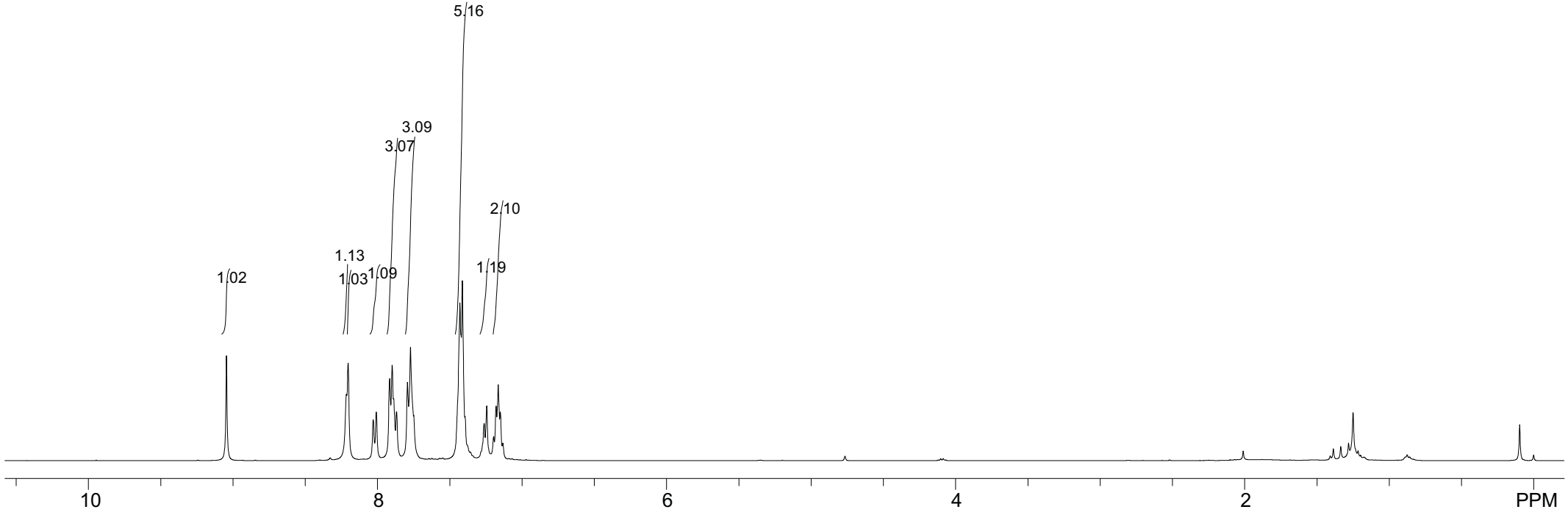
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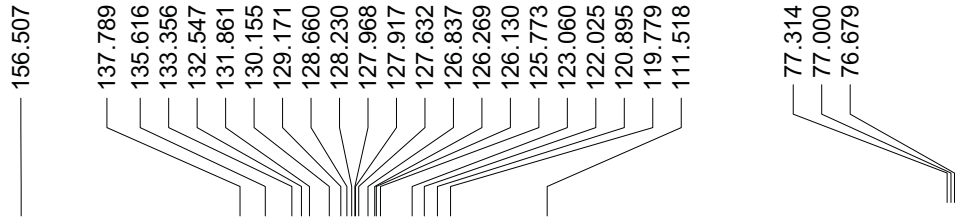
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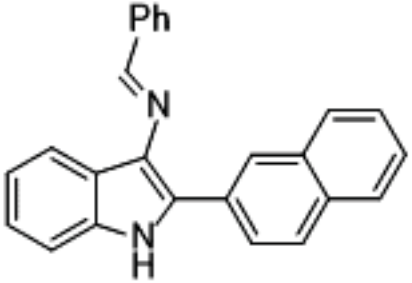
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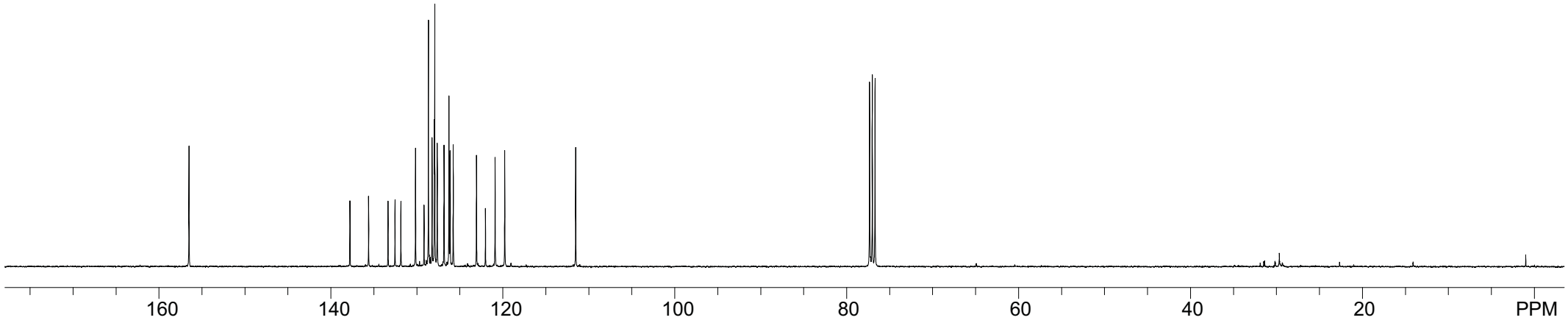
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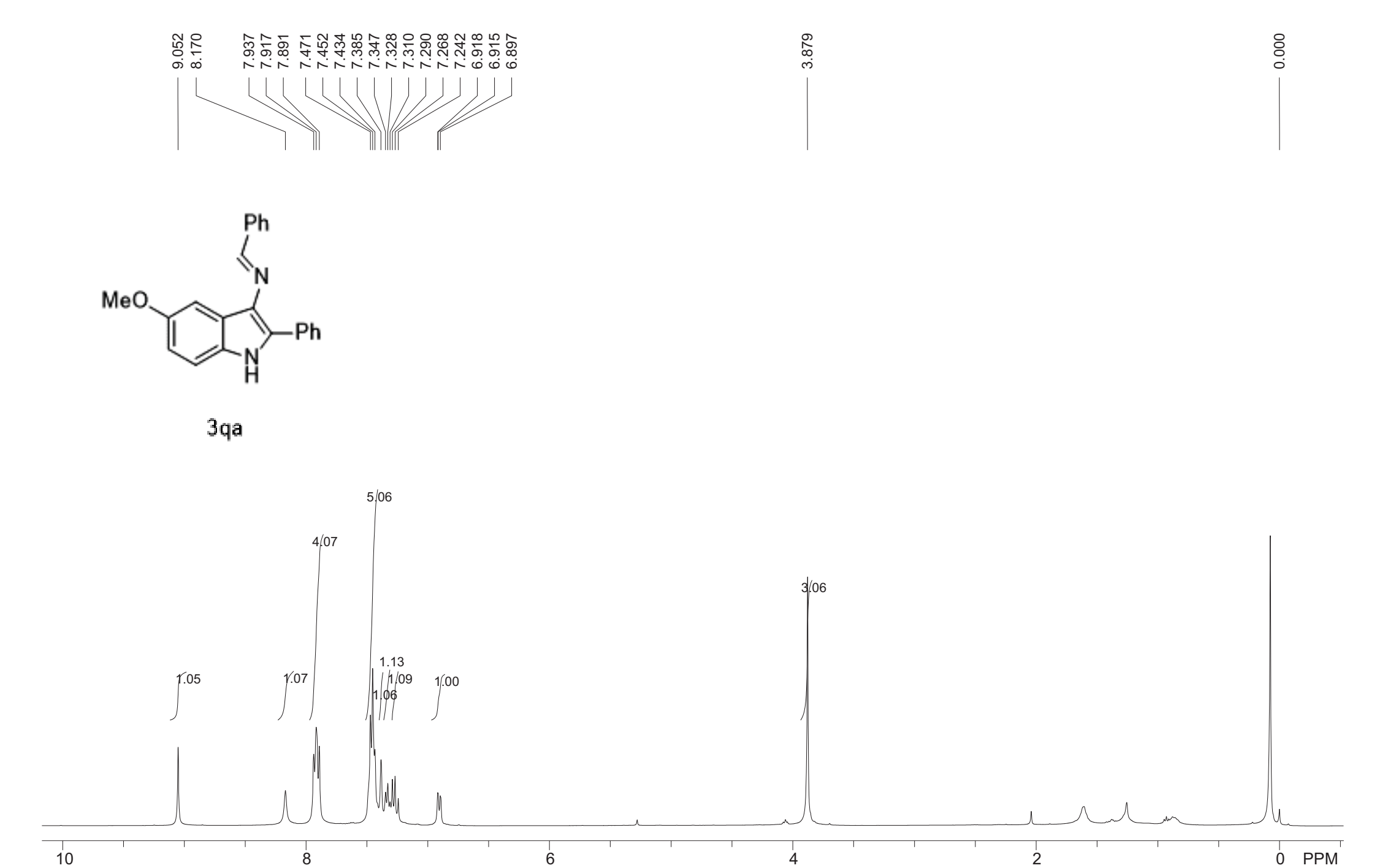
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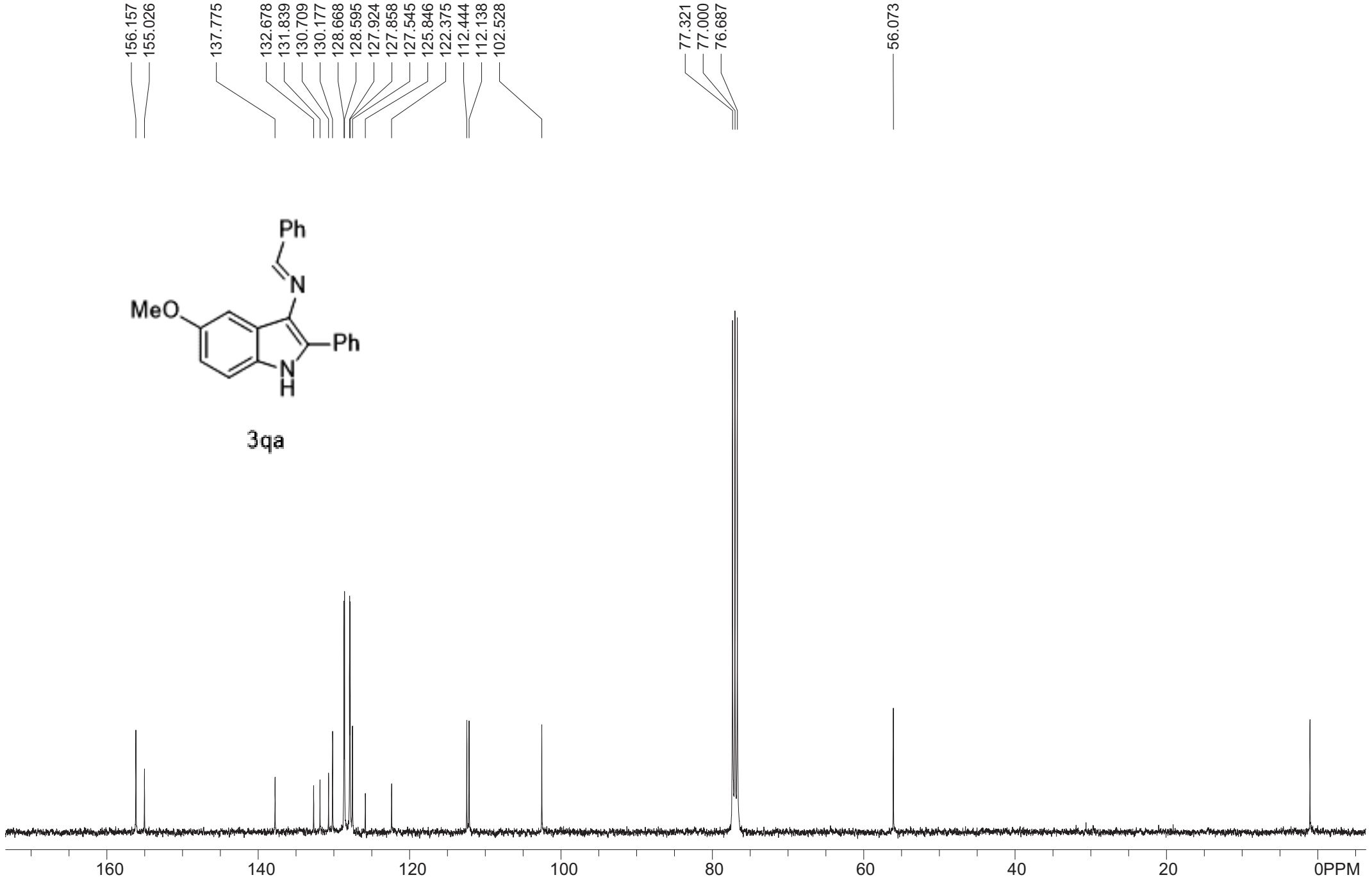
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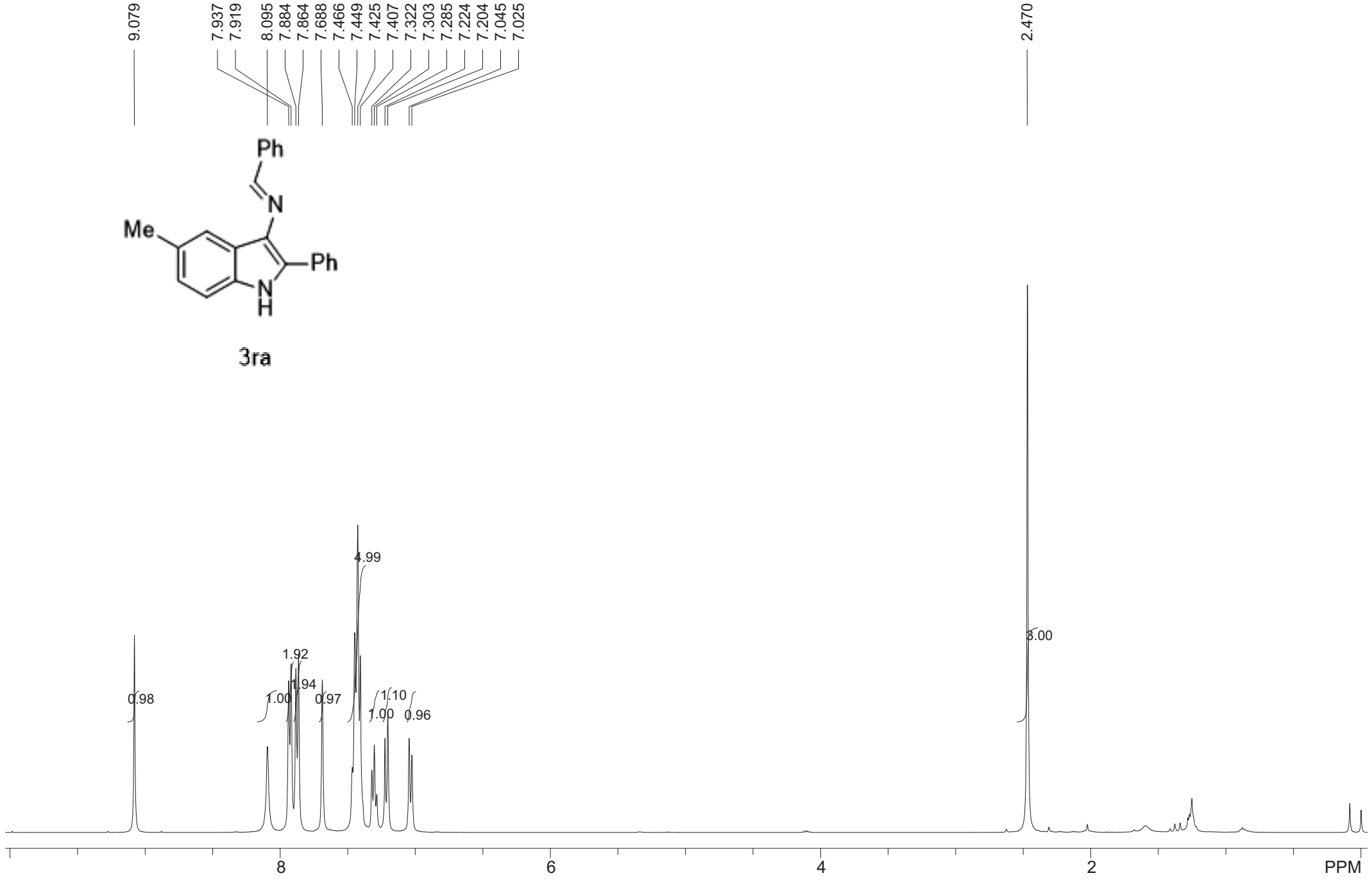
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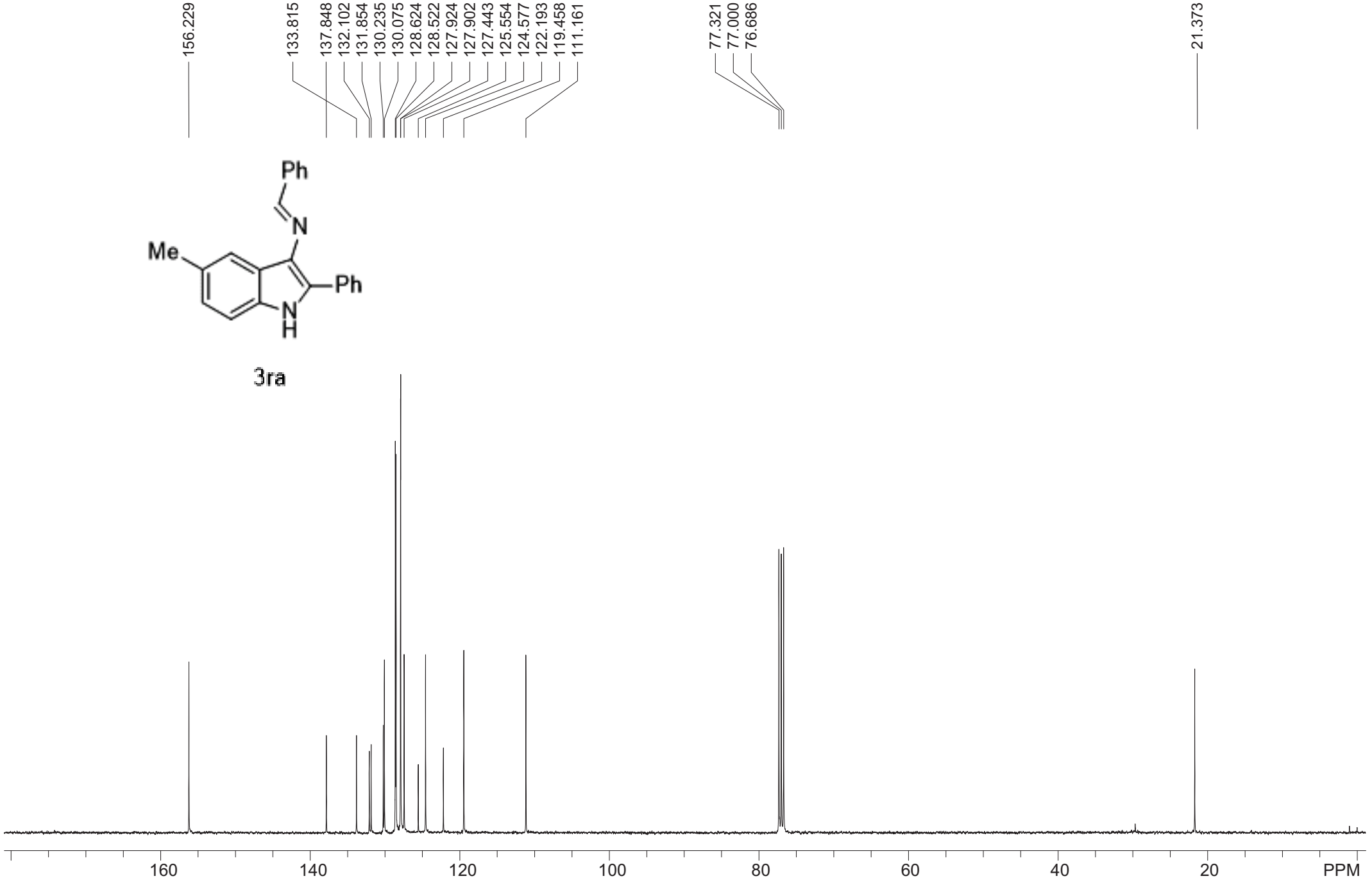
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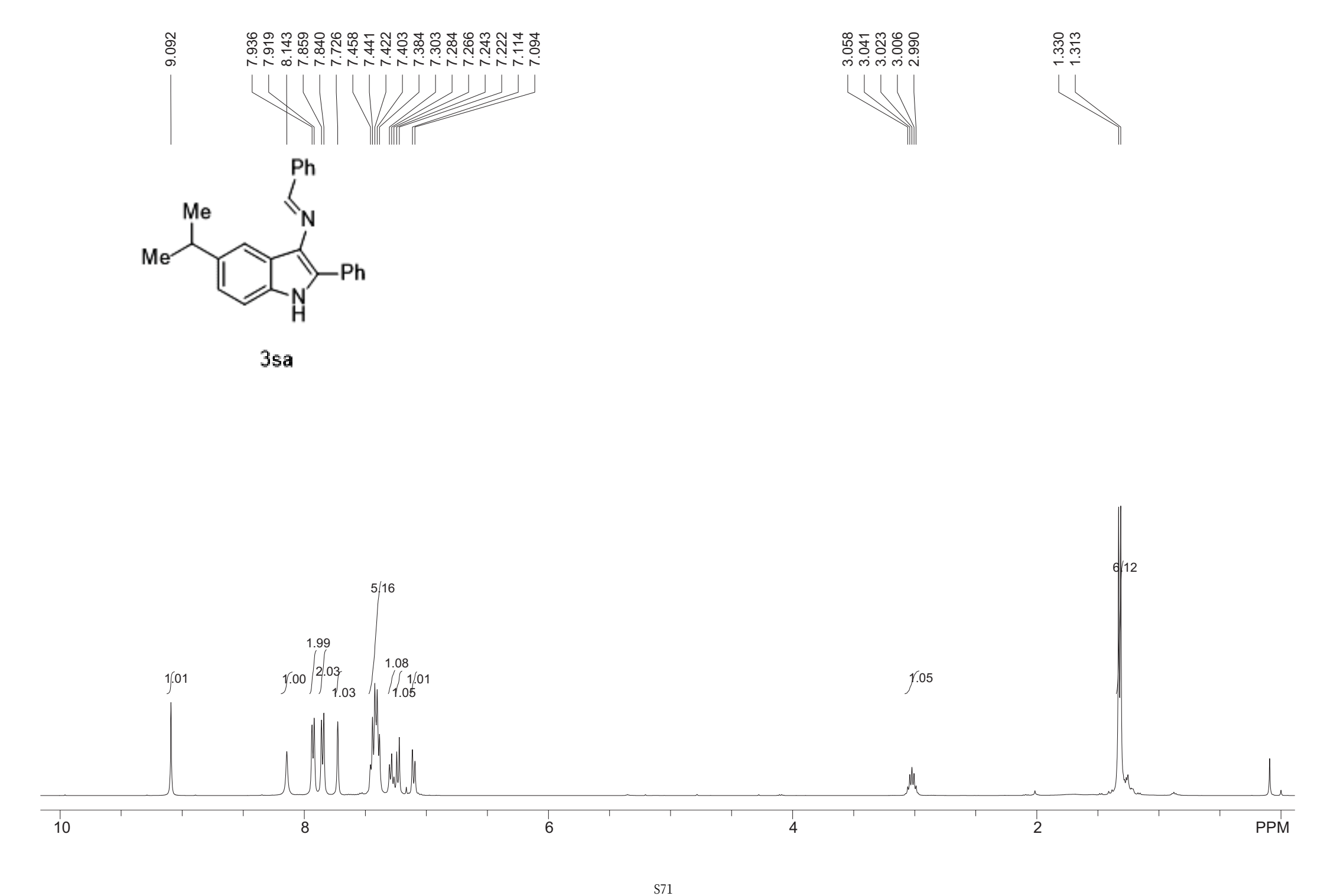
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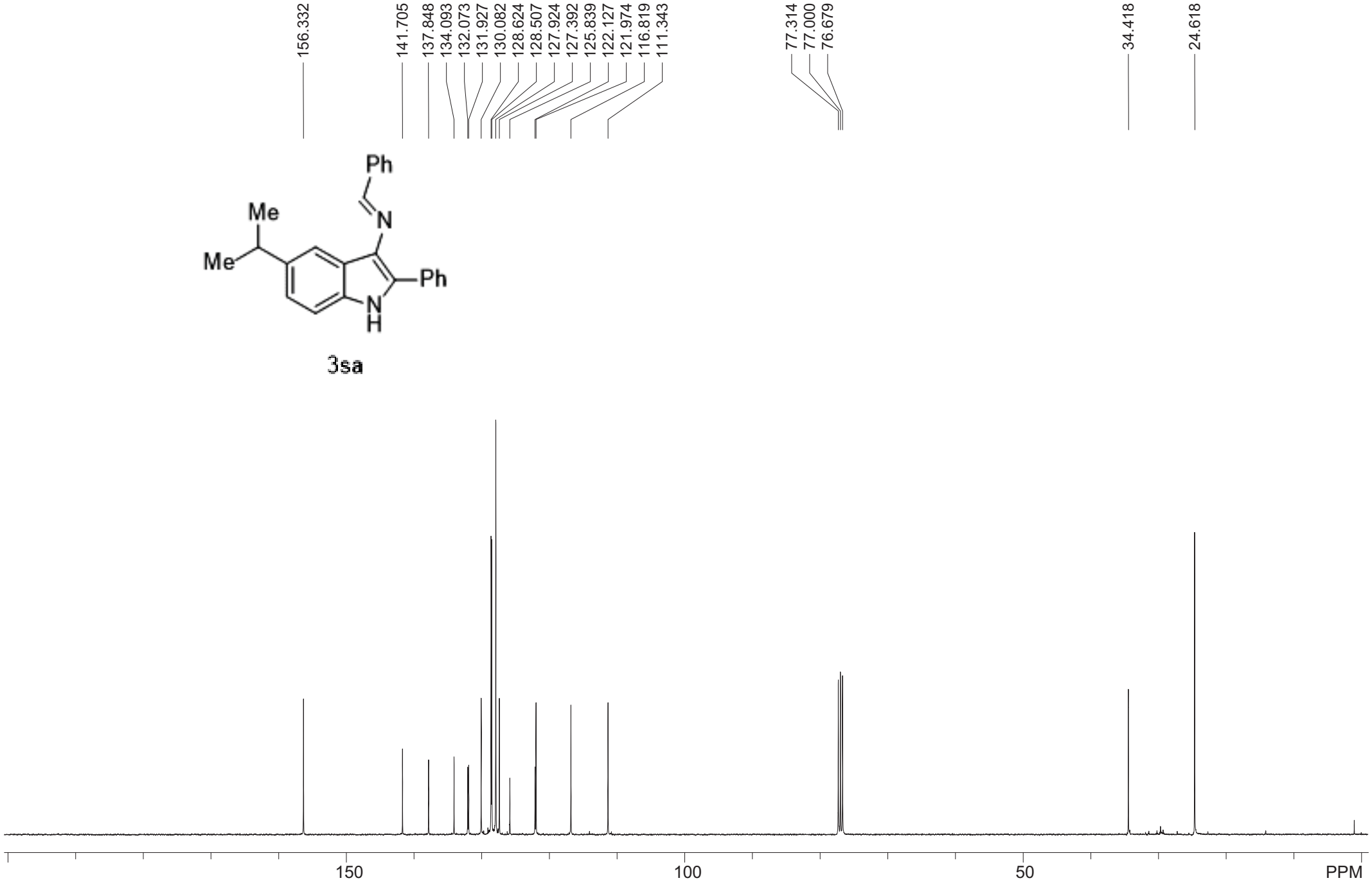
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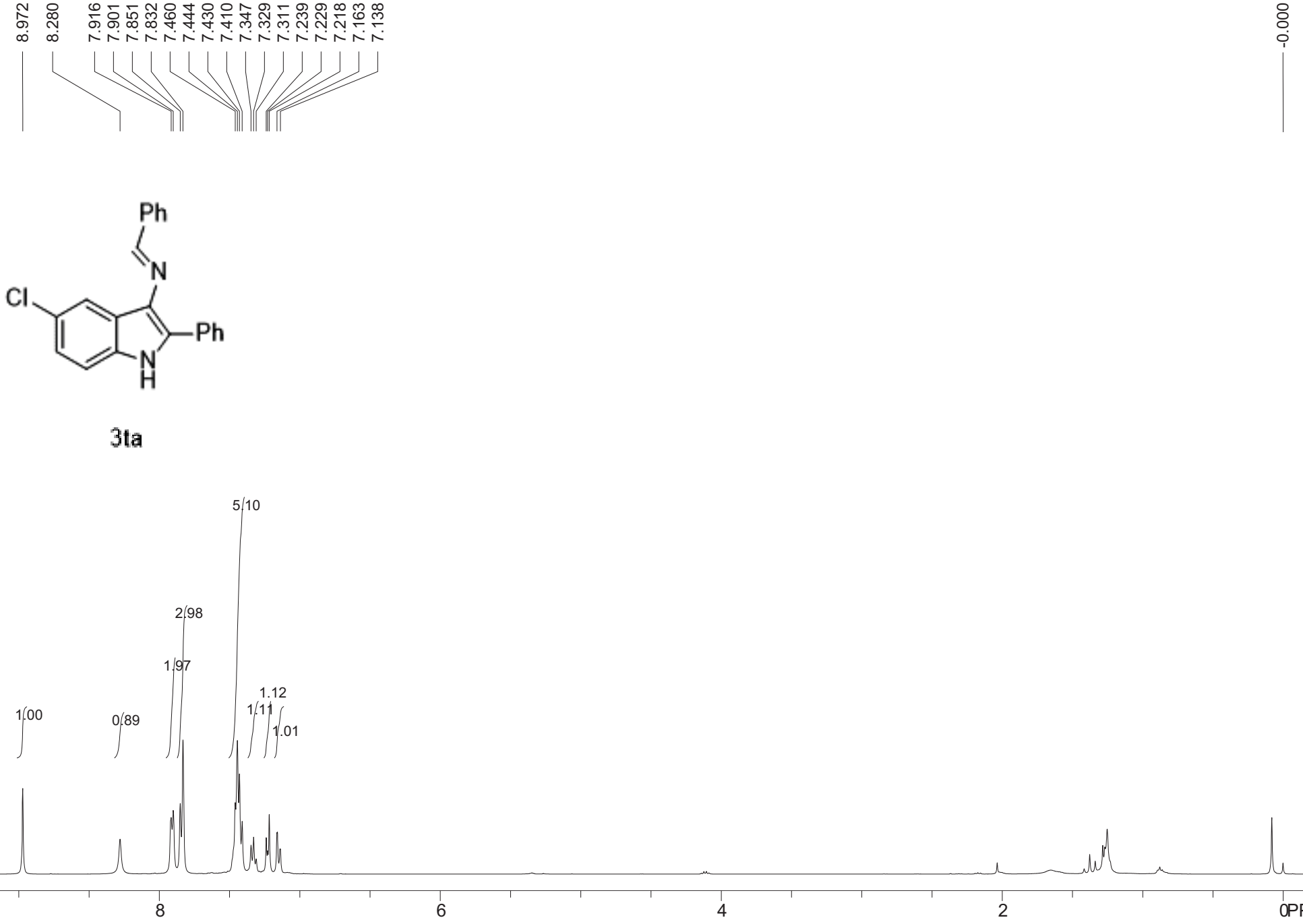
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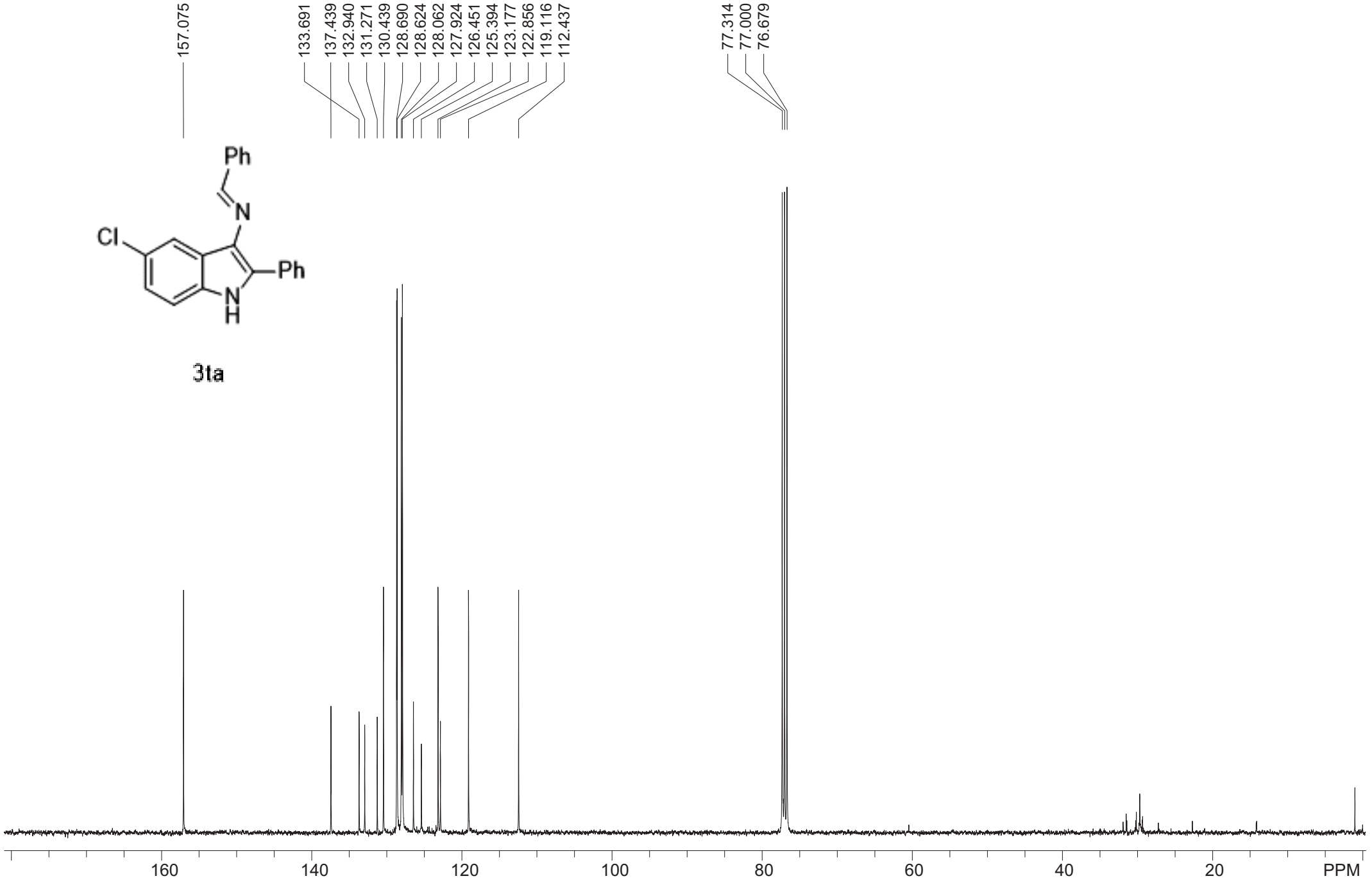
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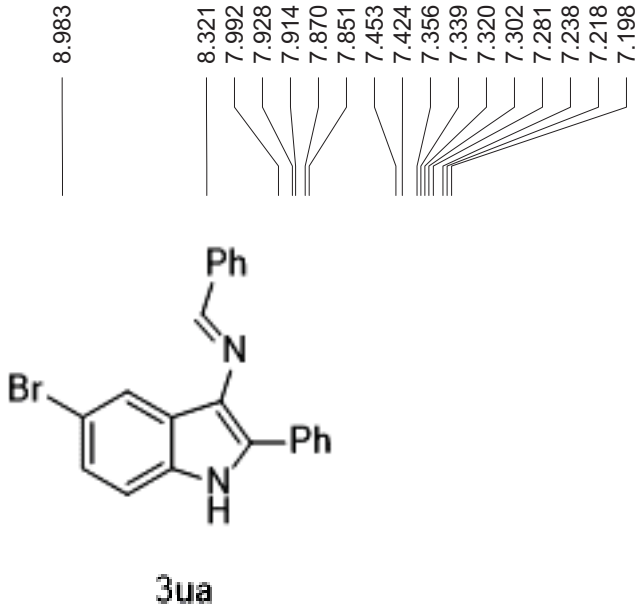
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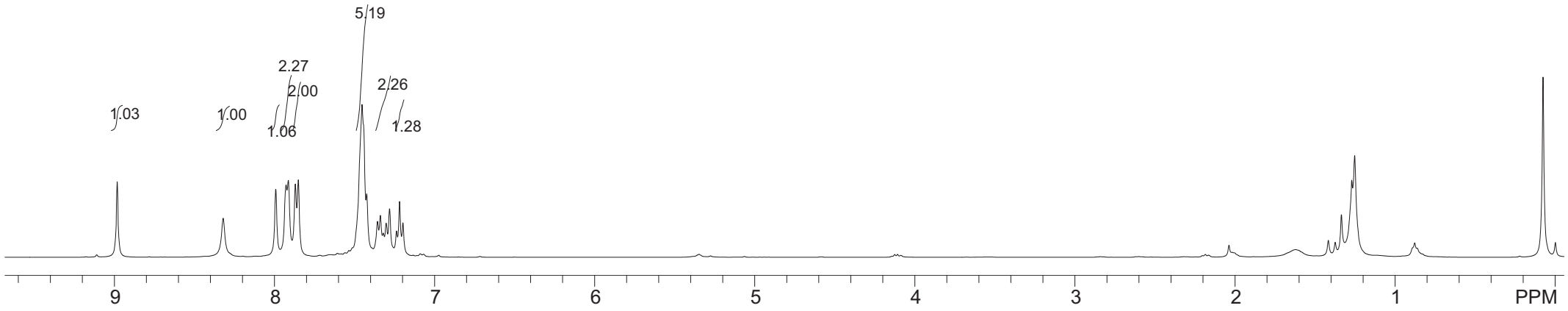
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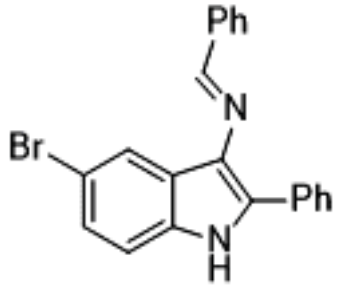

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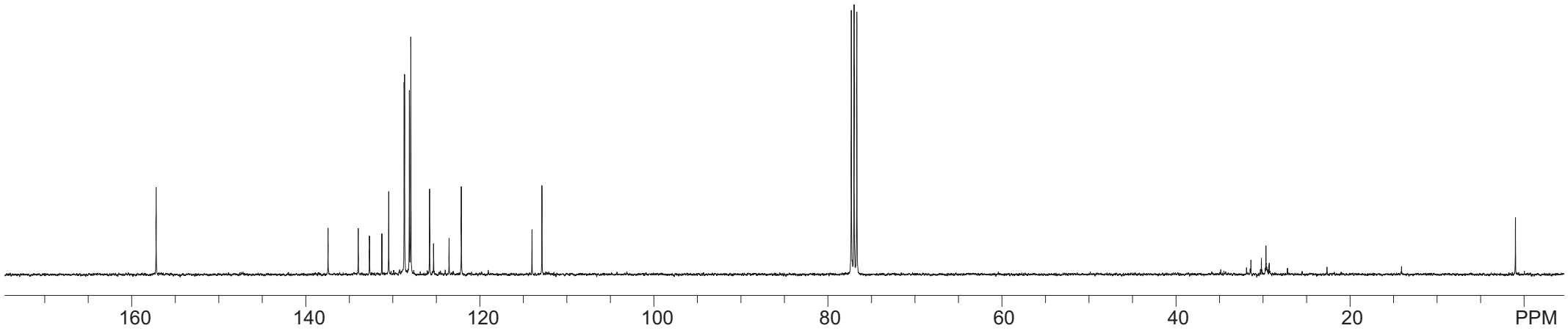


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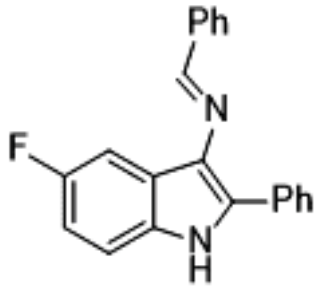
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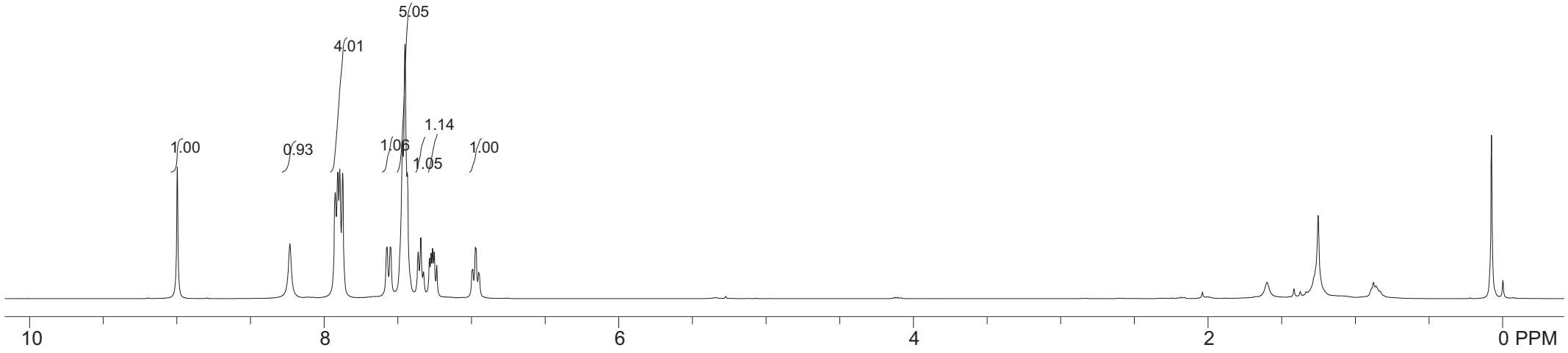
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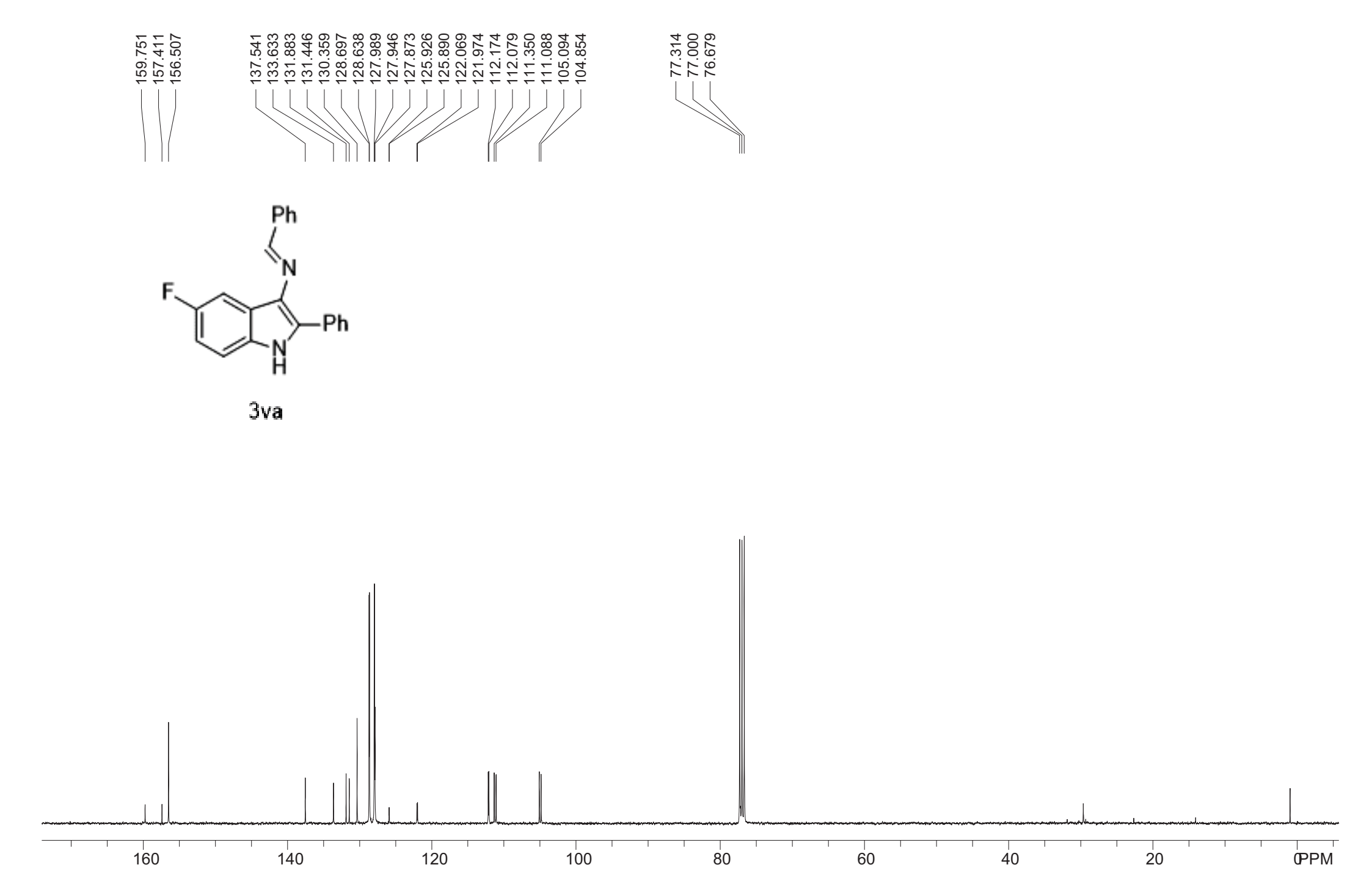
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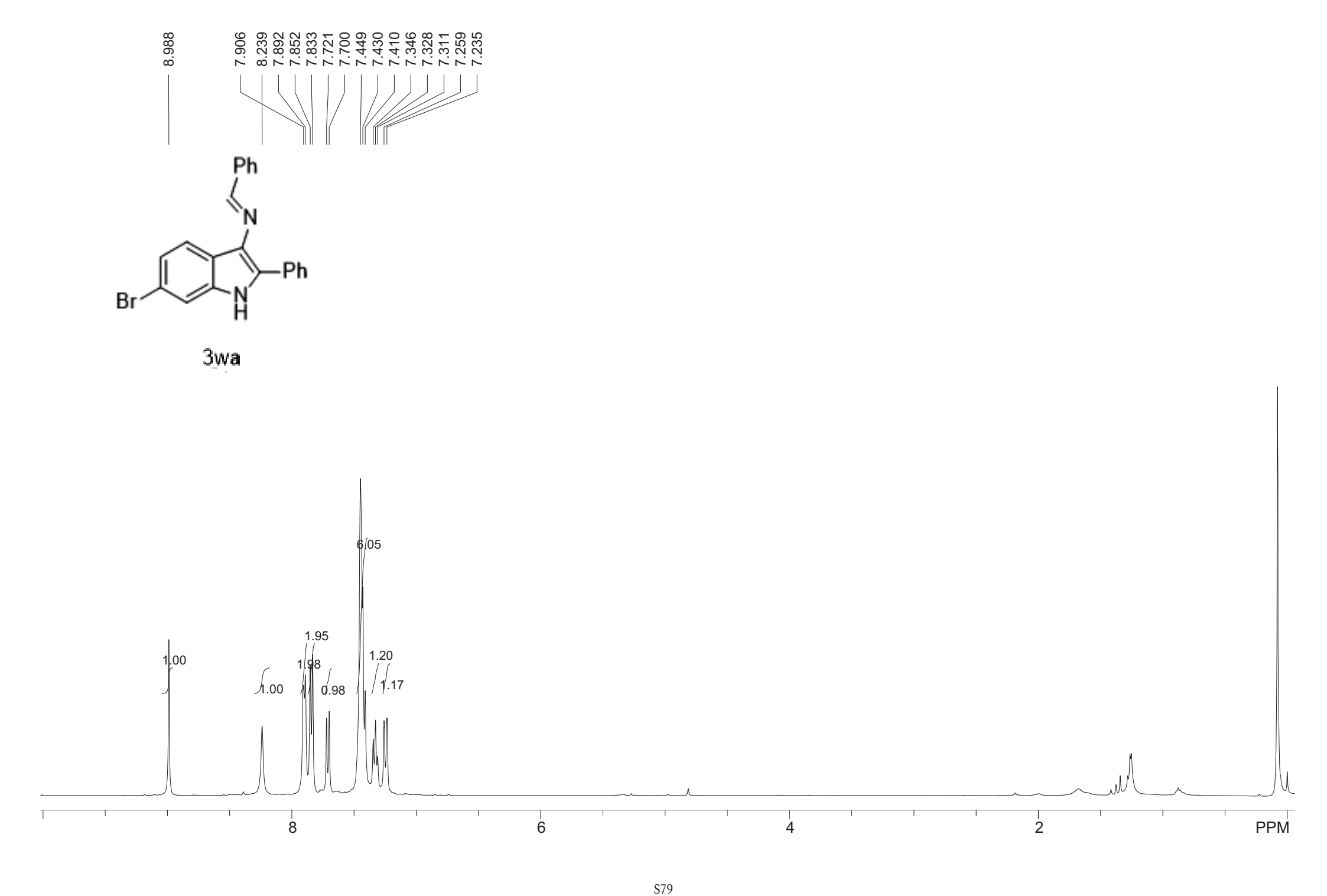
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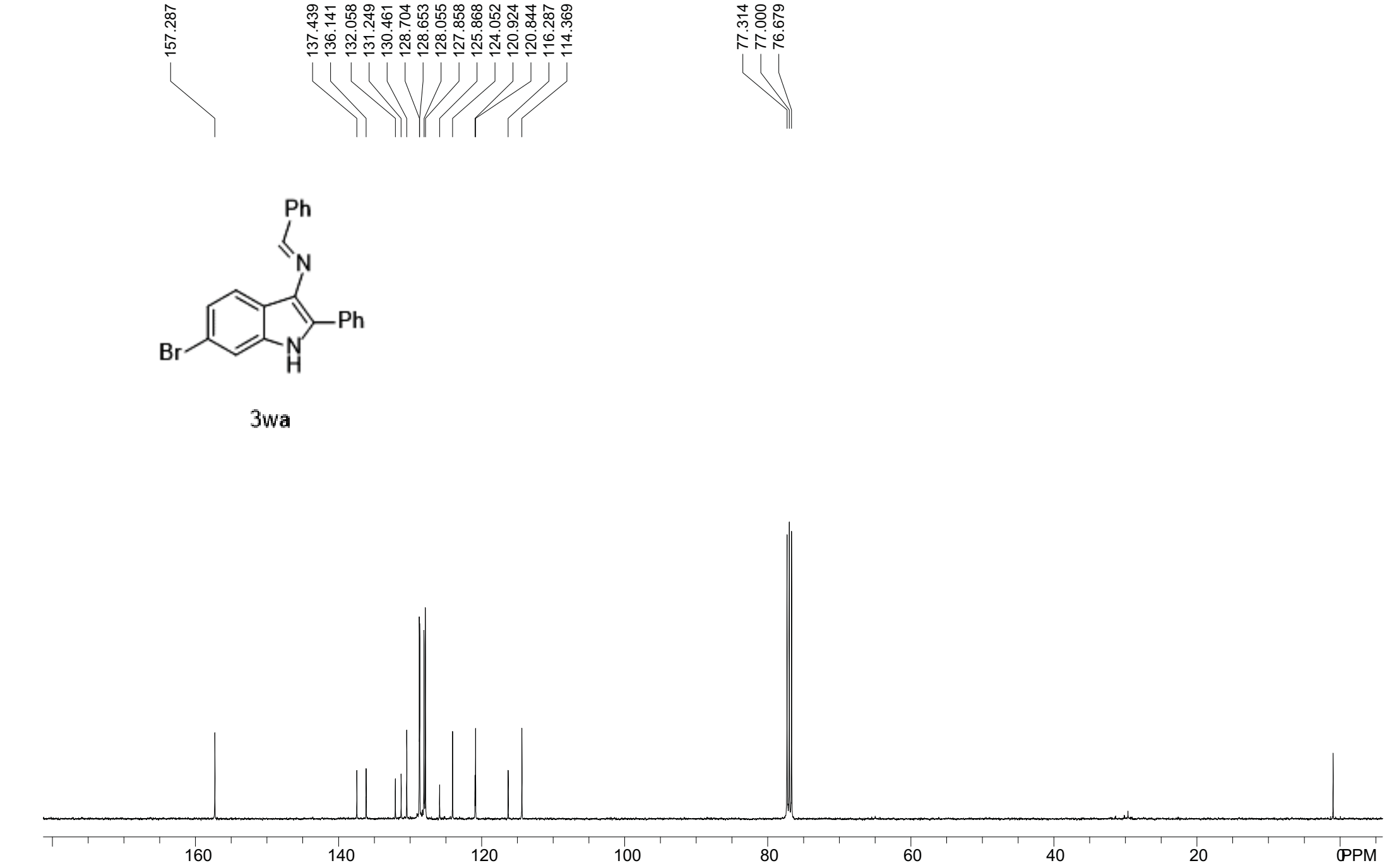
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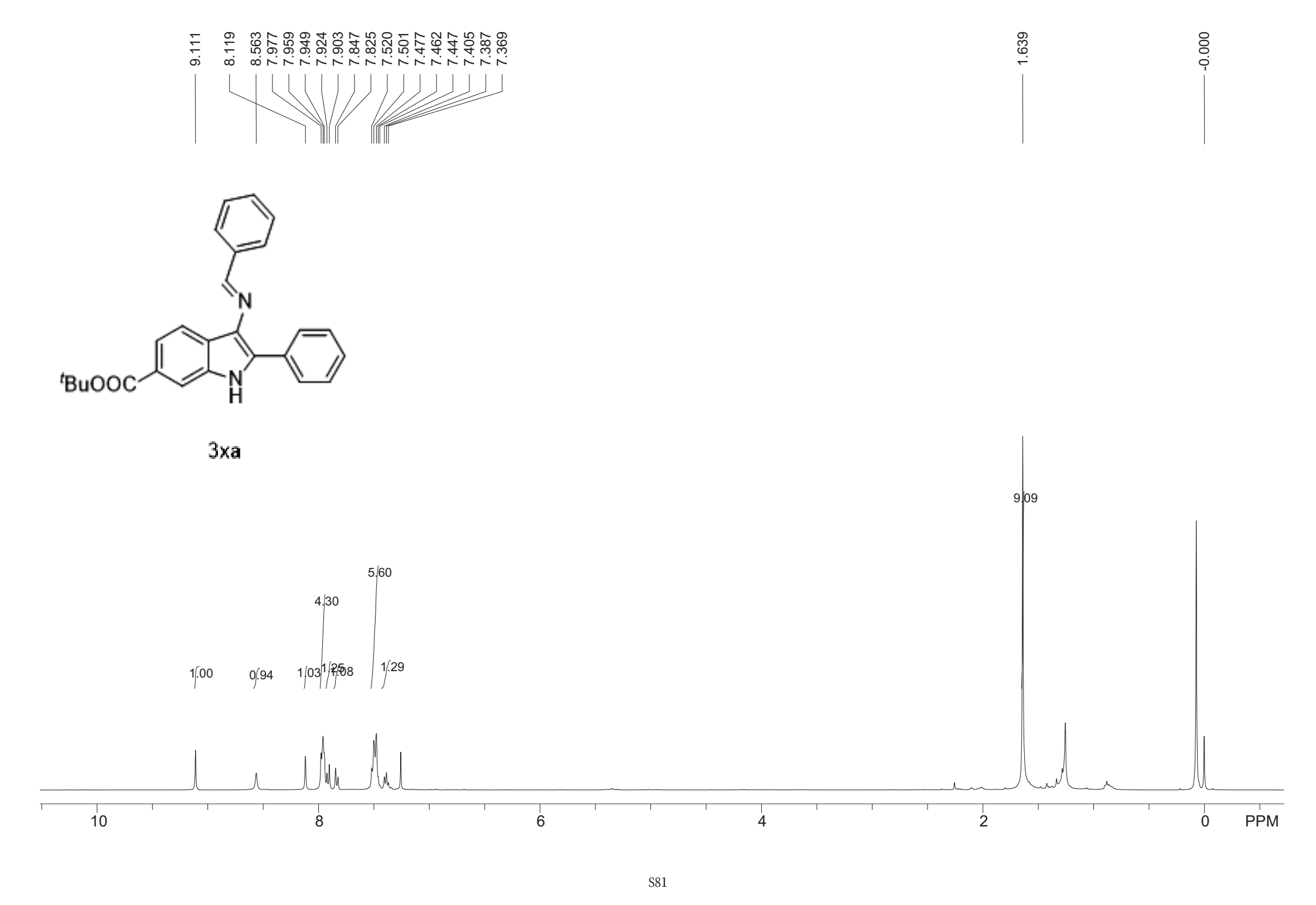
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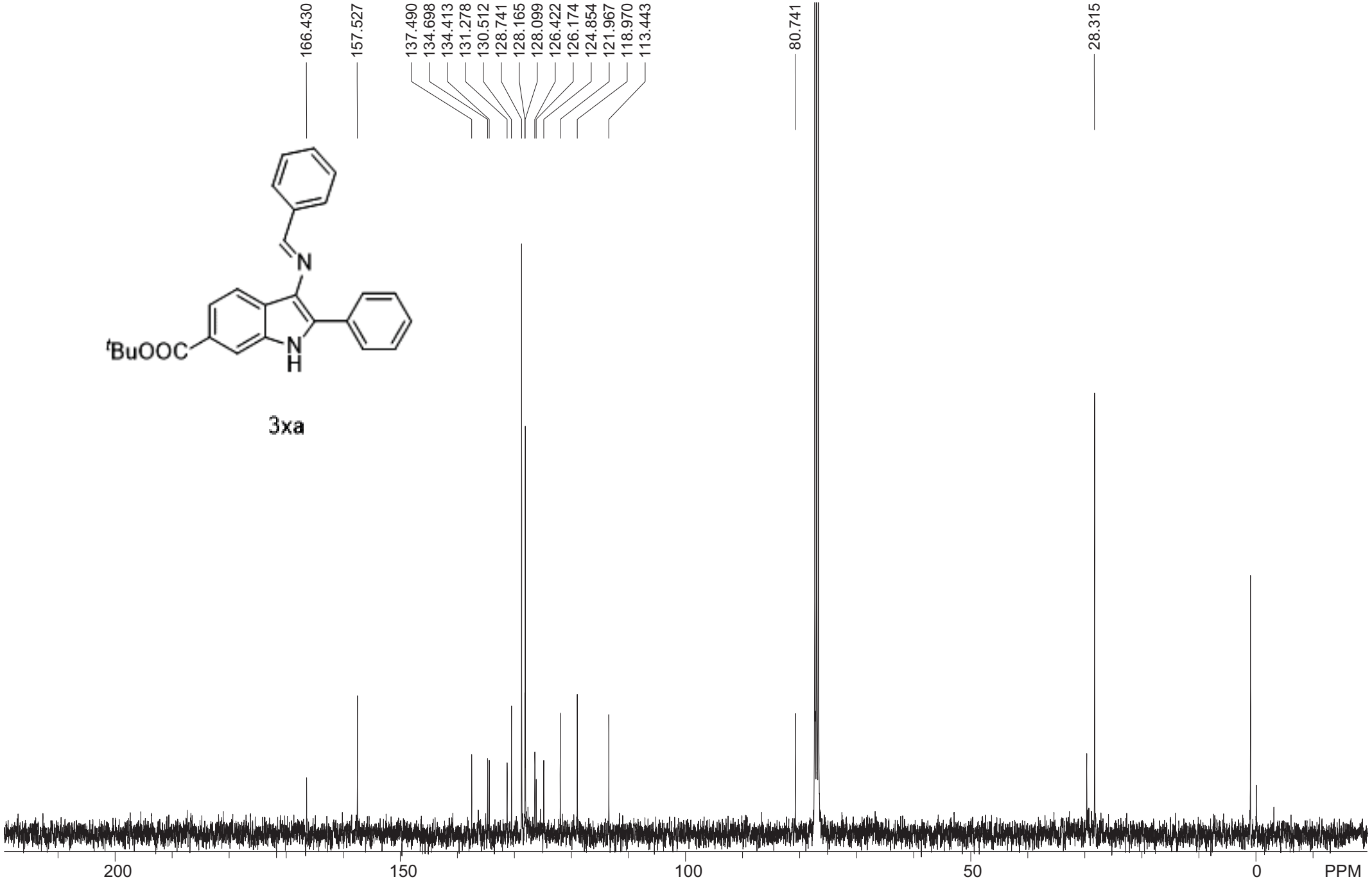
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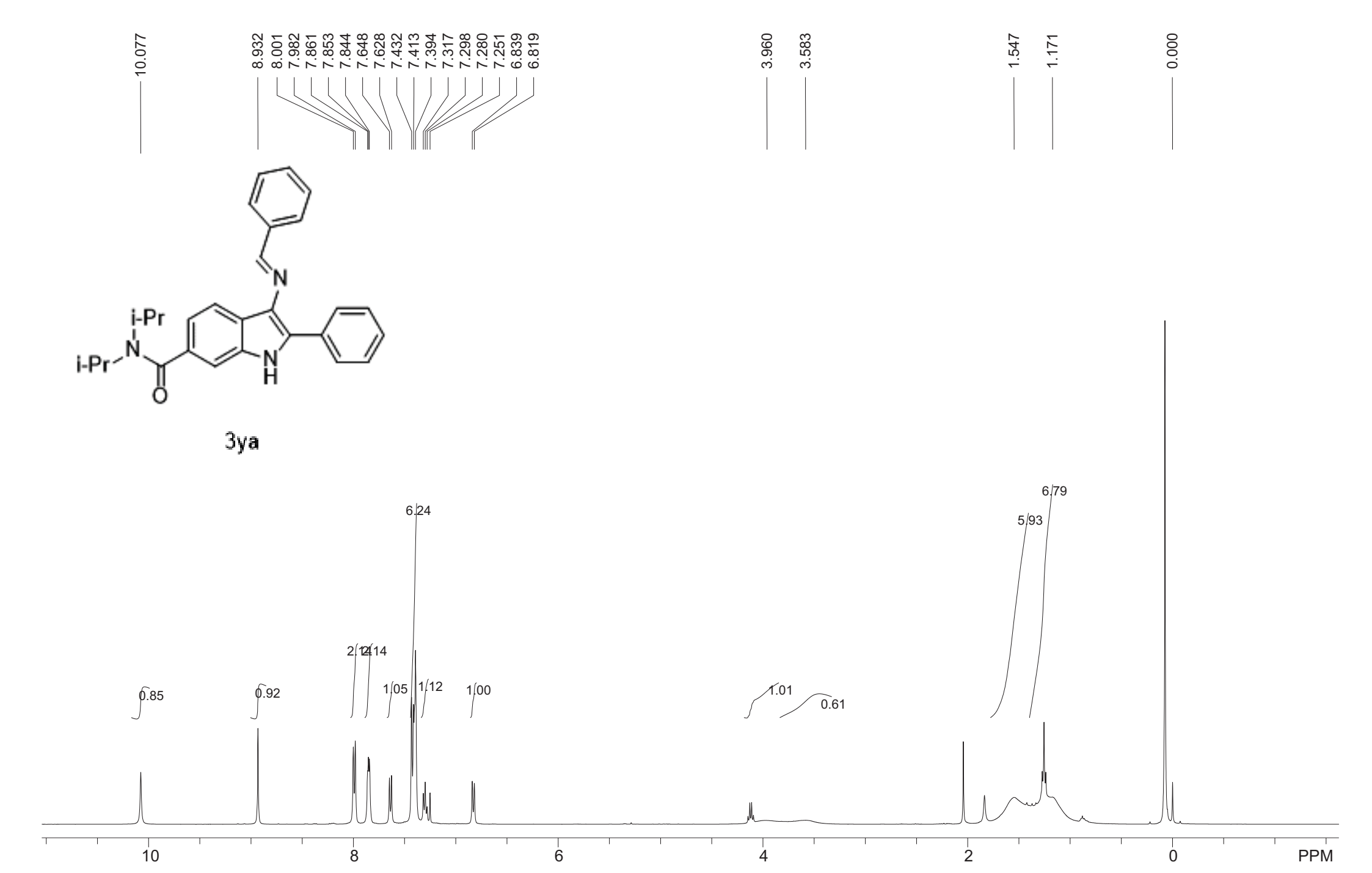
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i-Pr
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O
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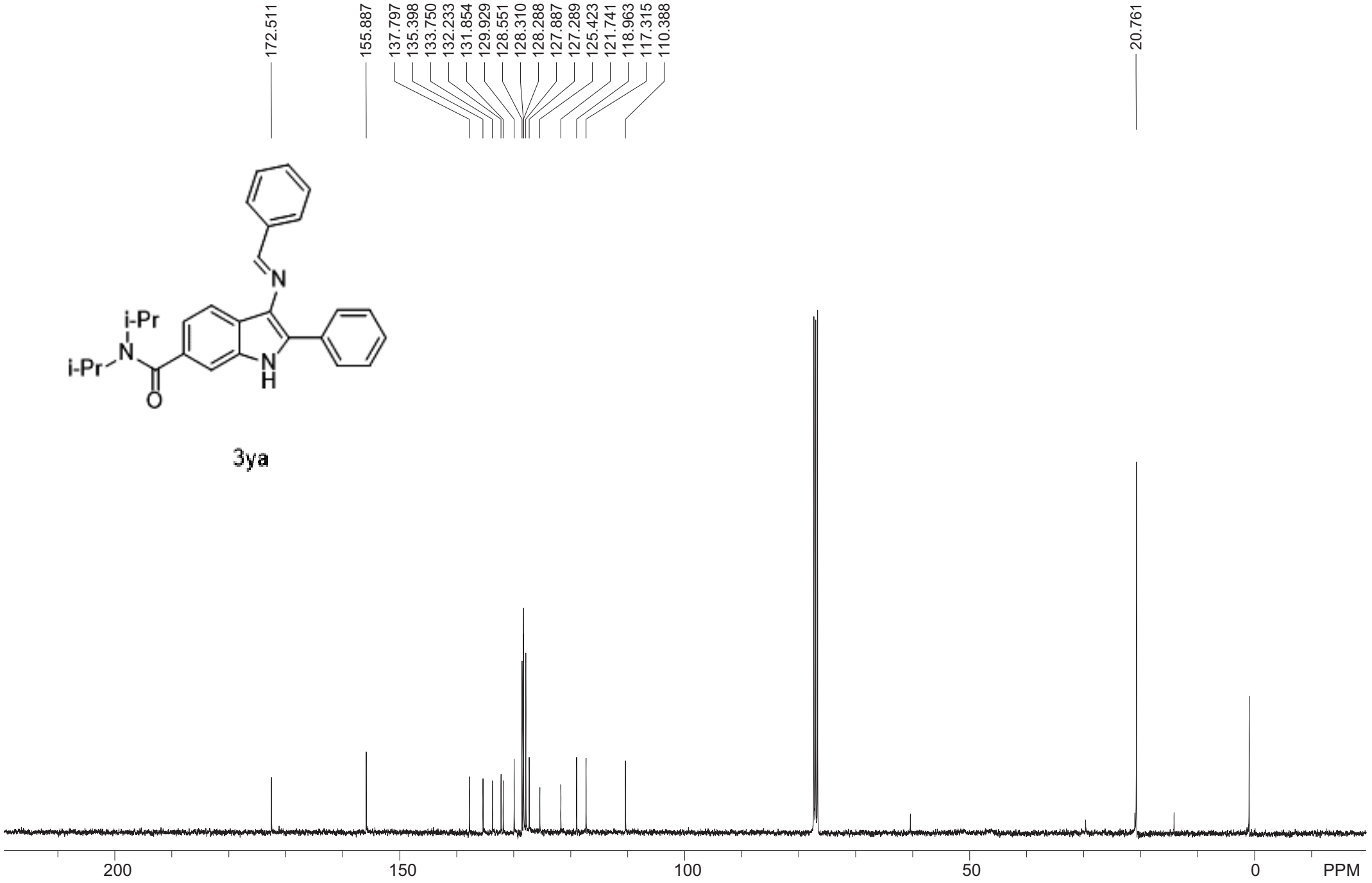
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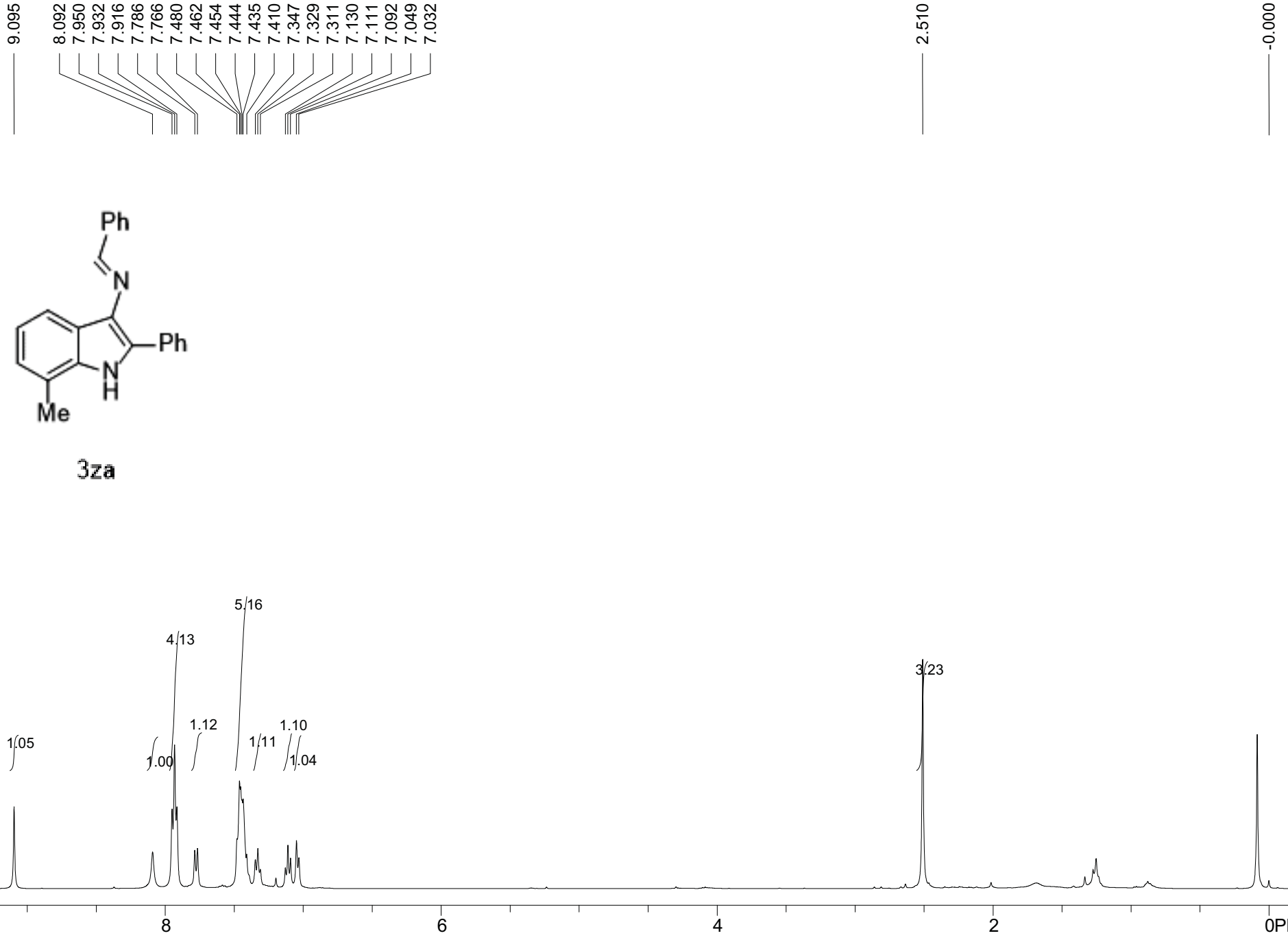
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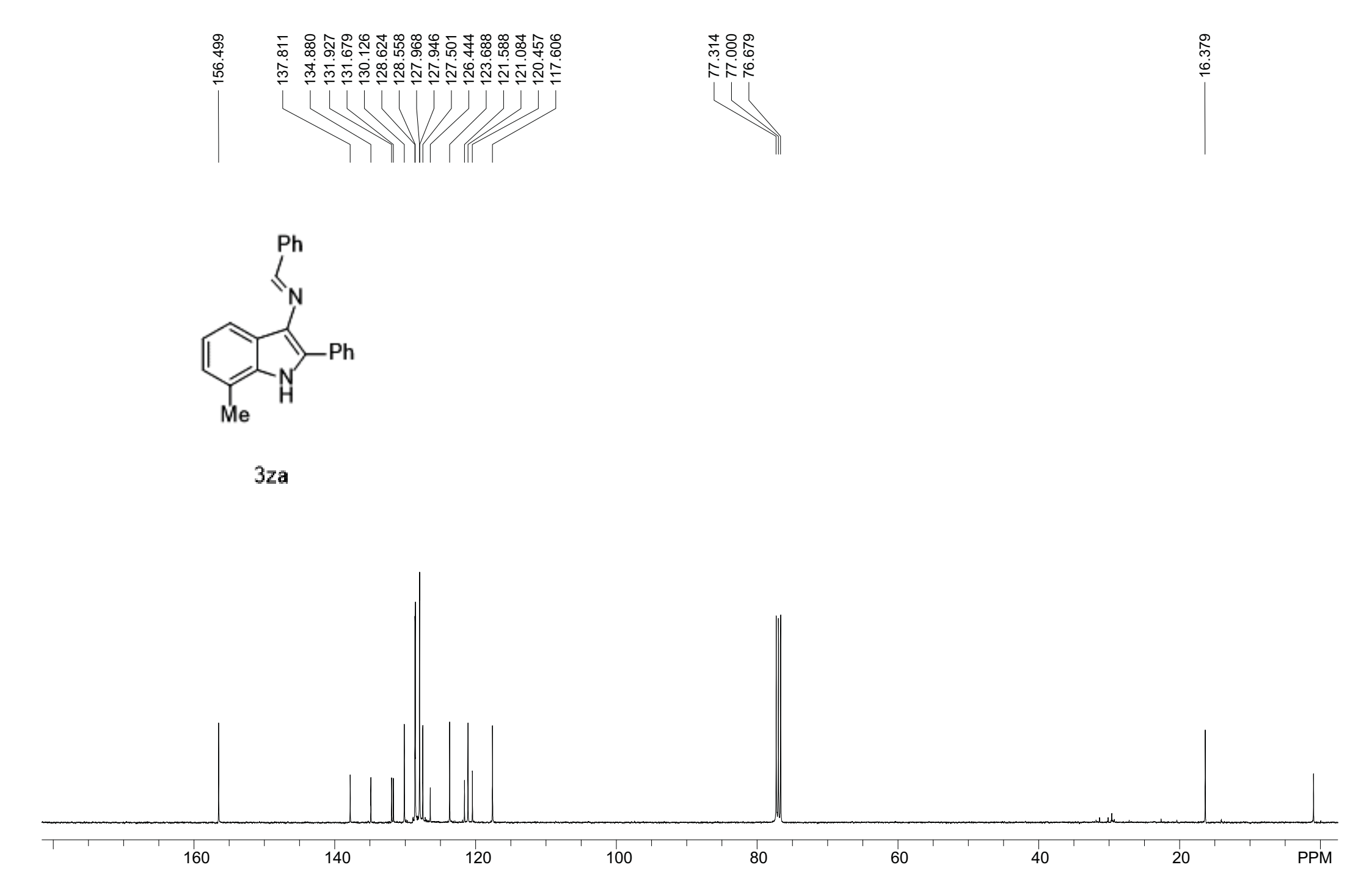
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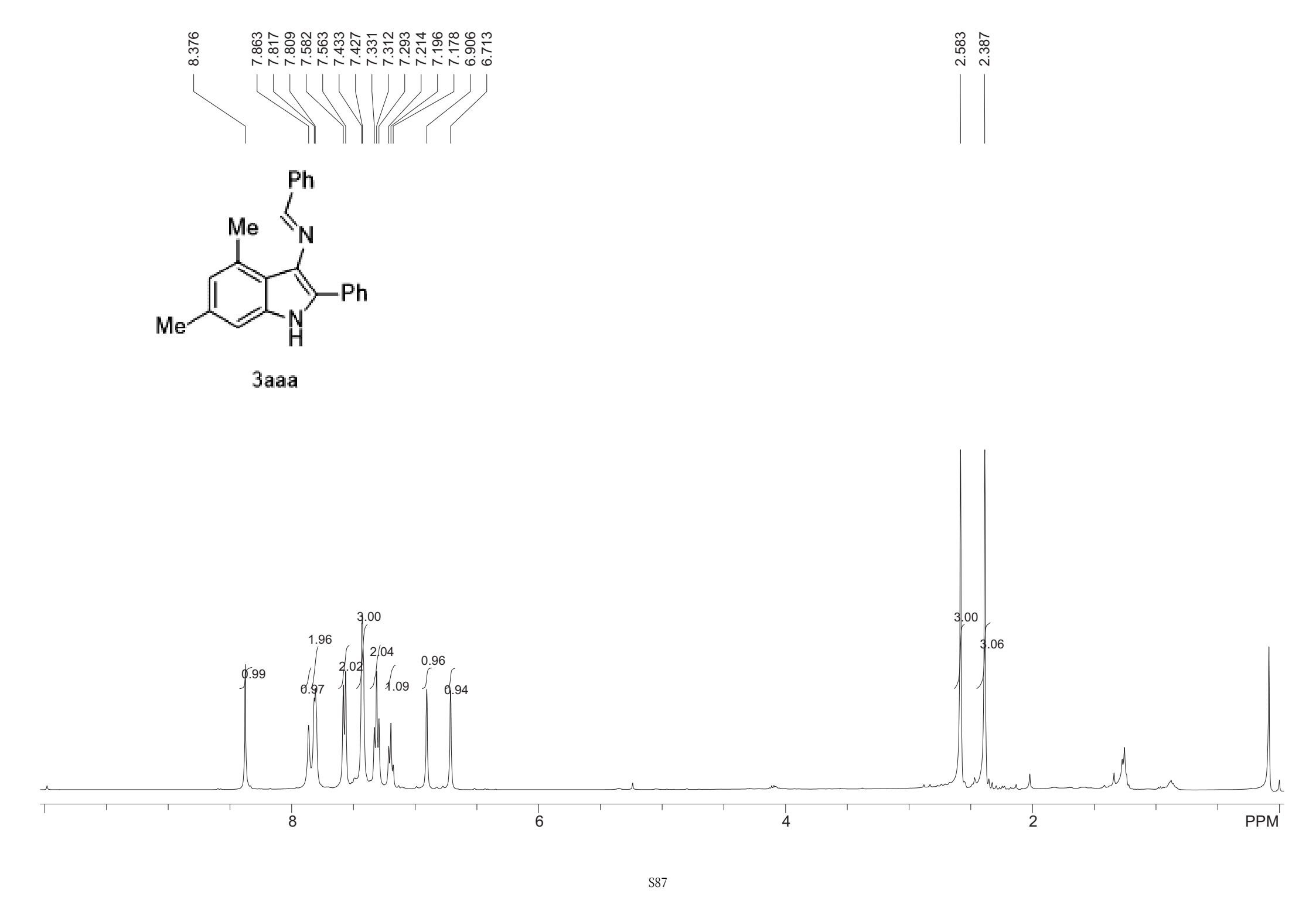
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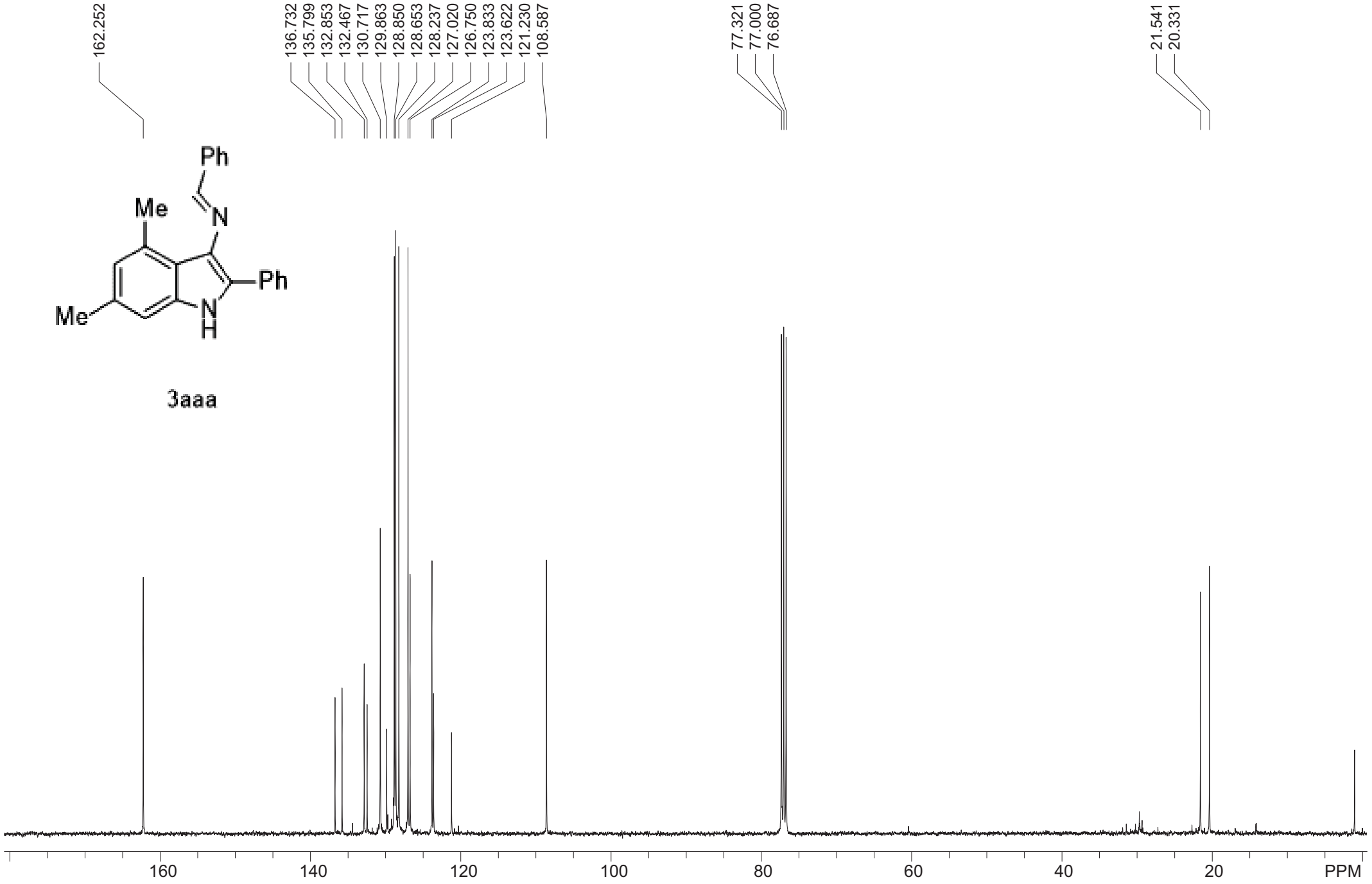
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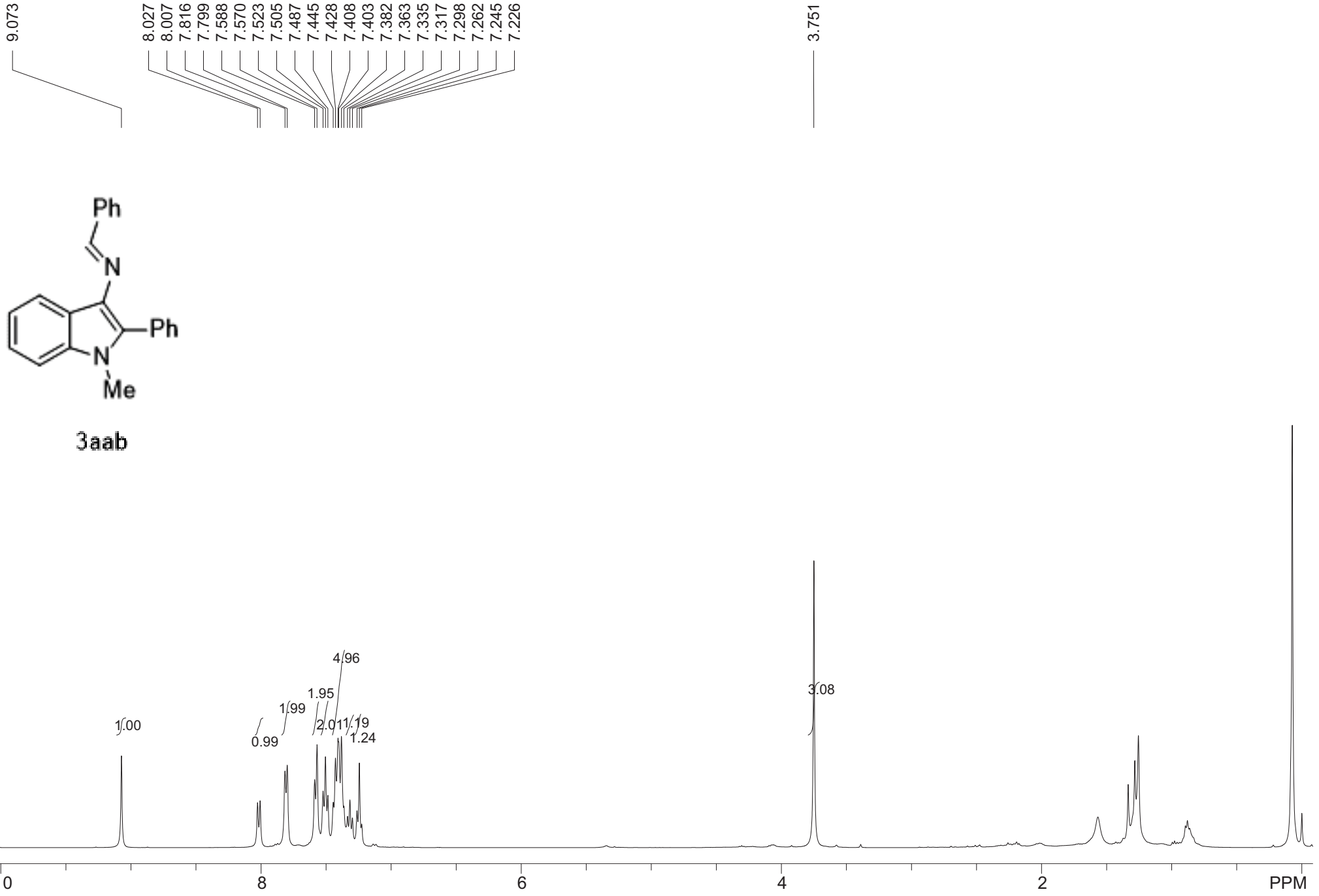
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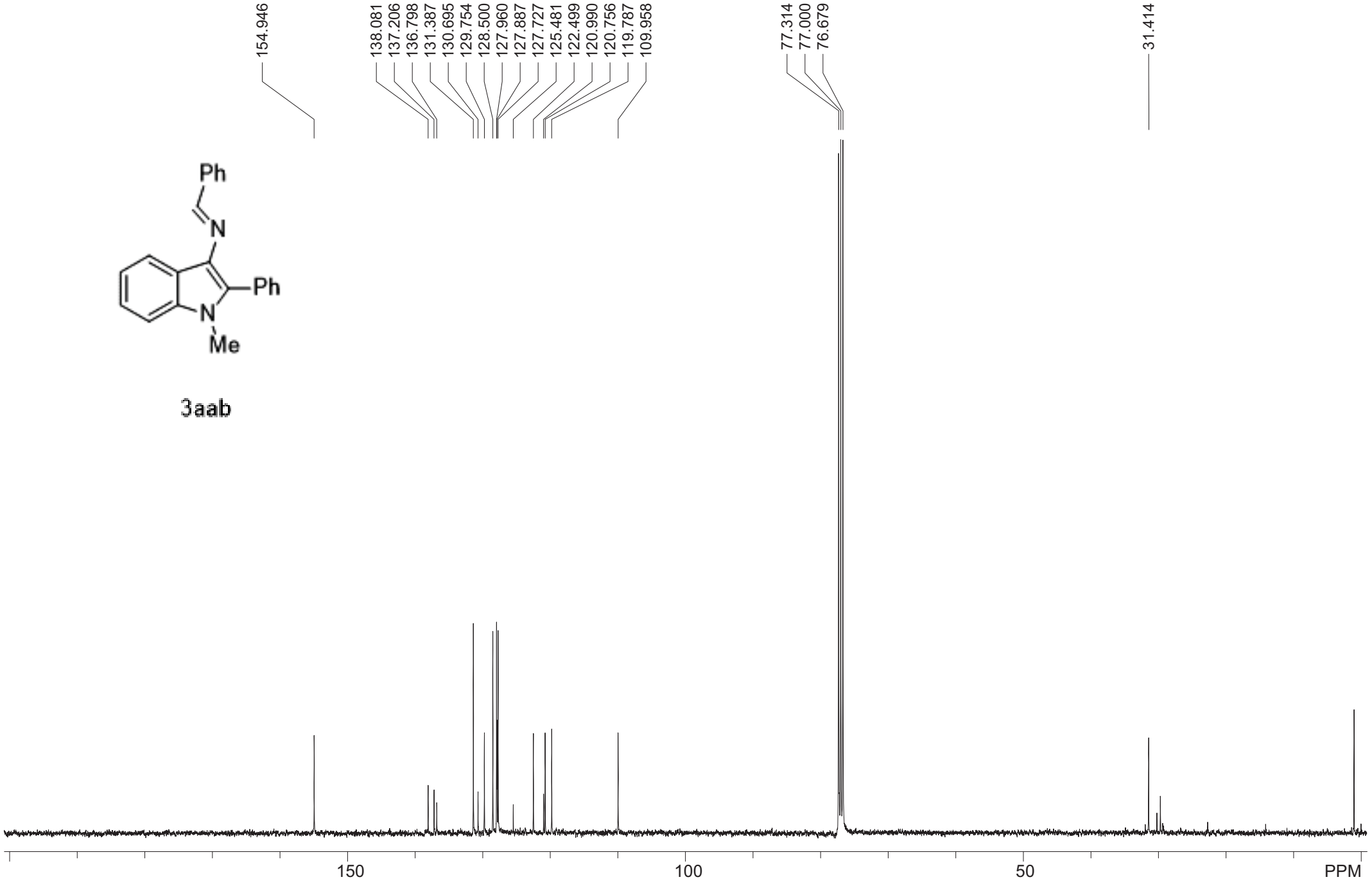
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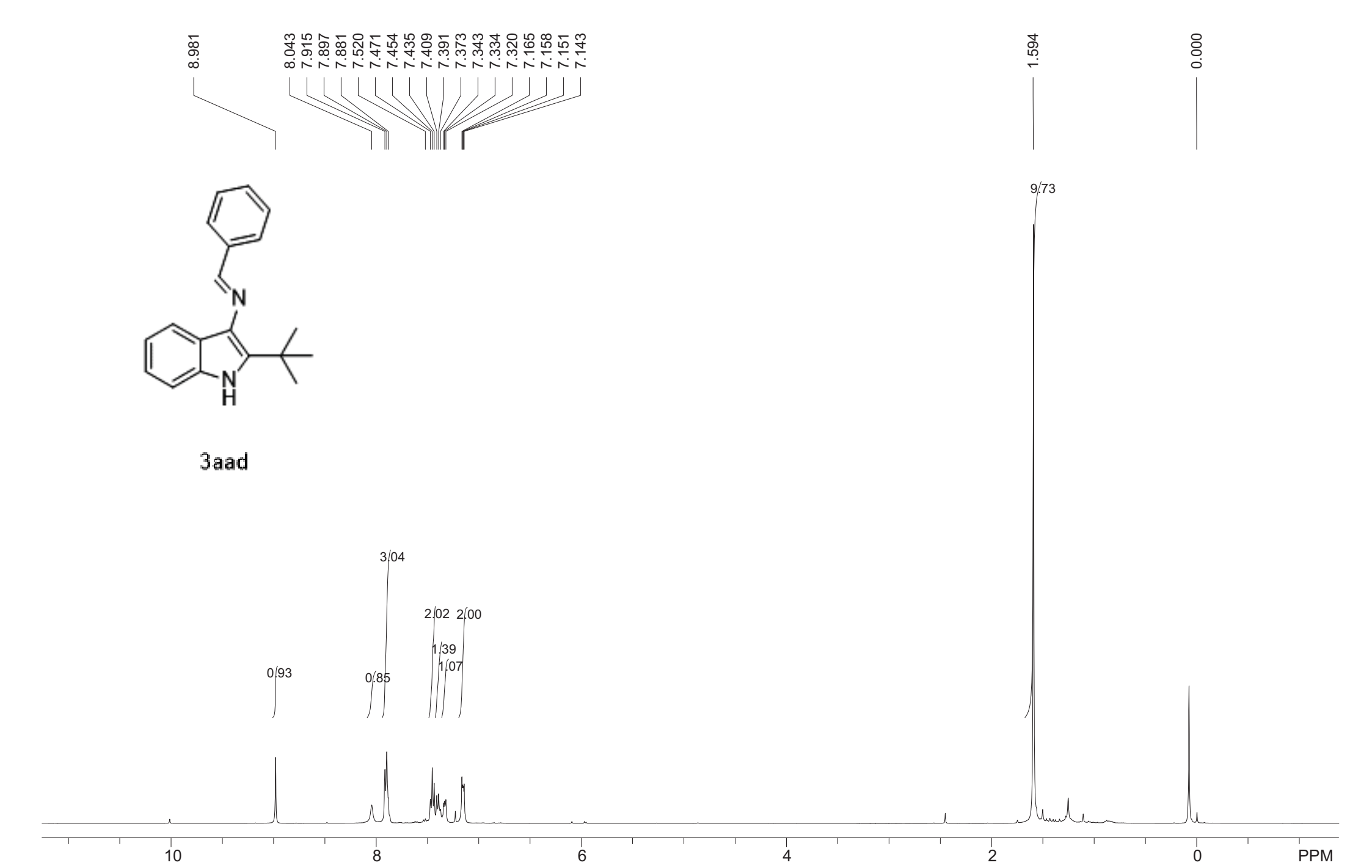
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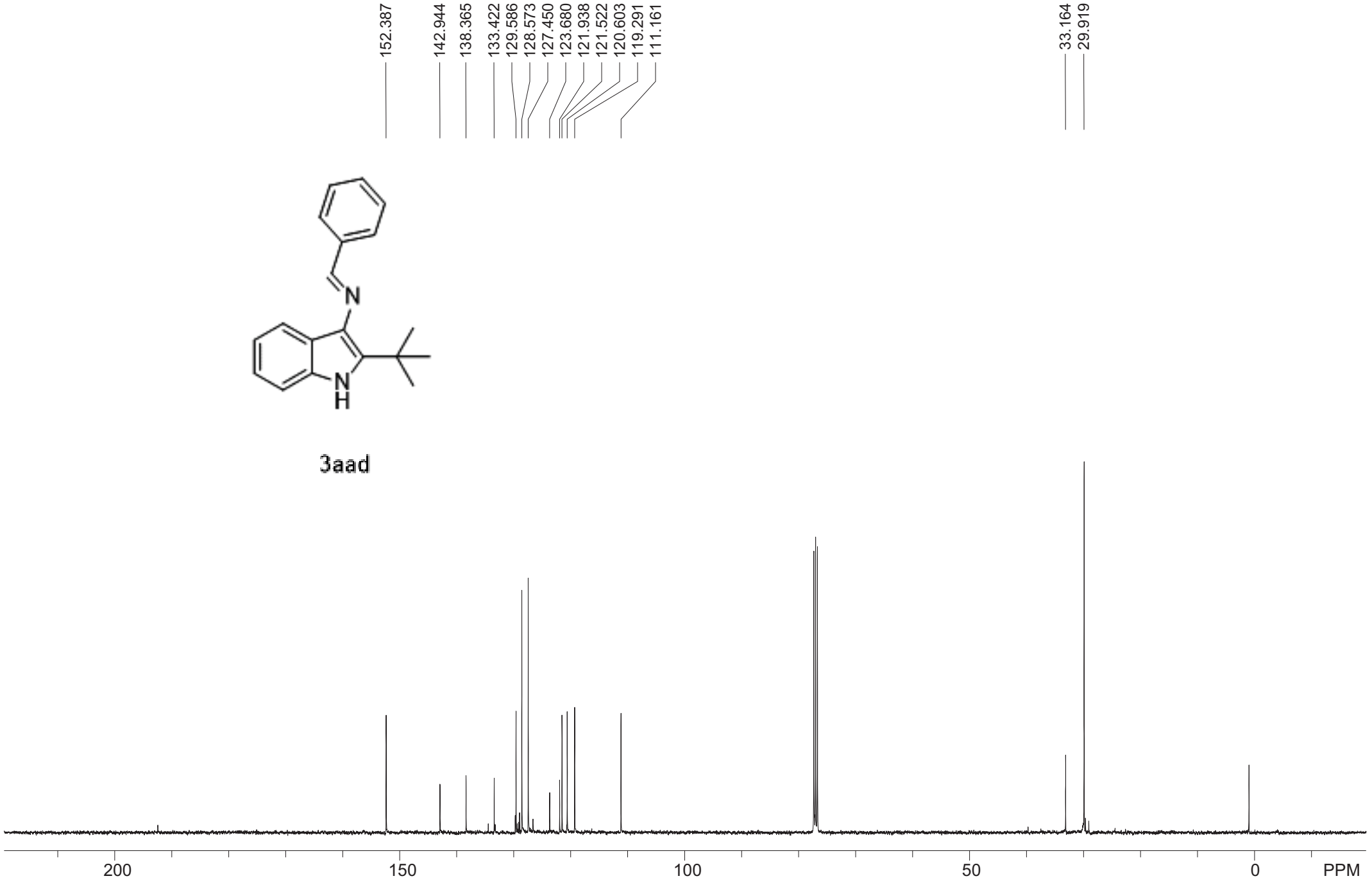
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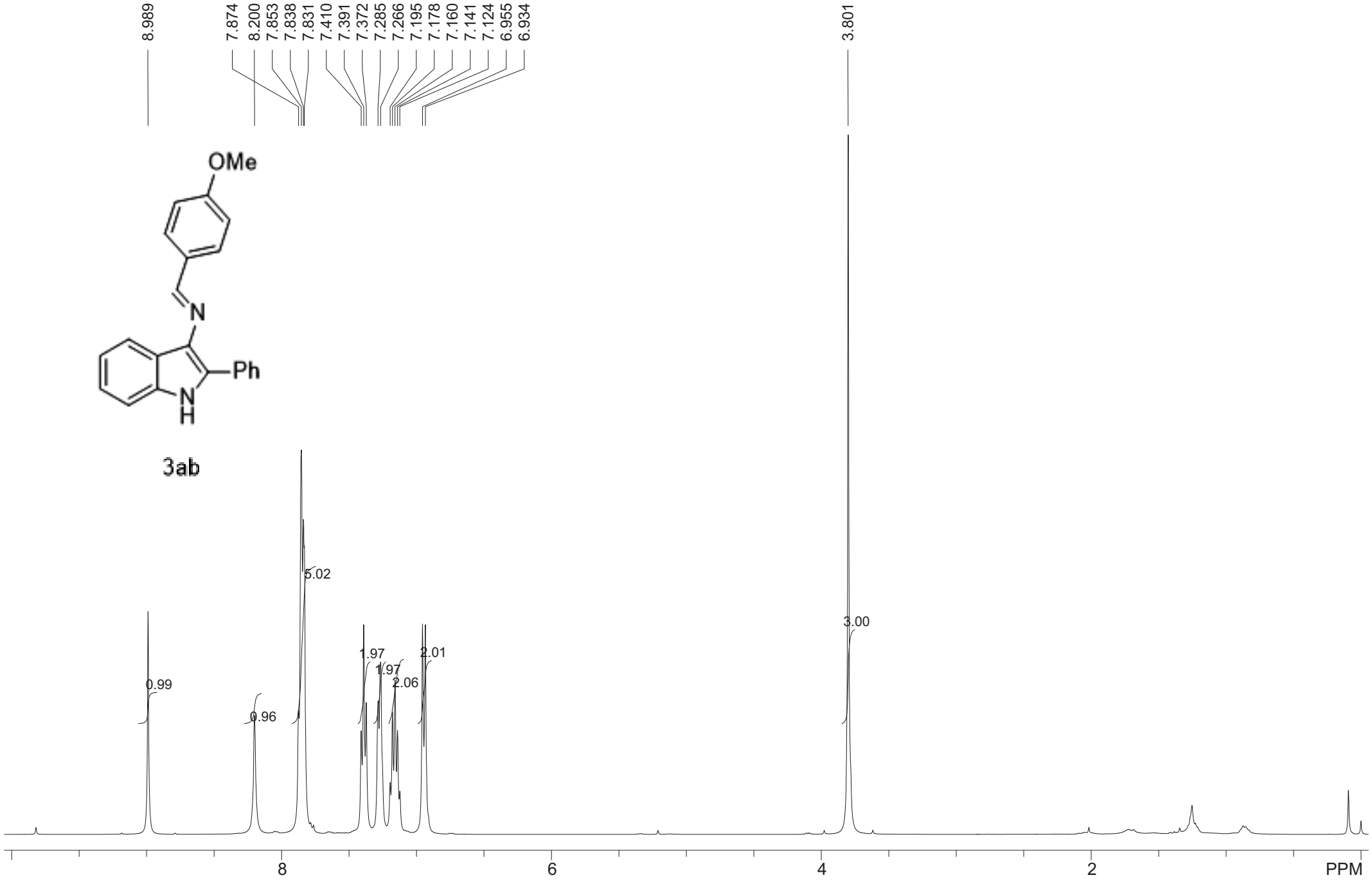
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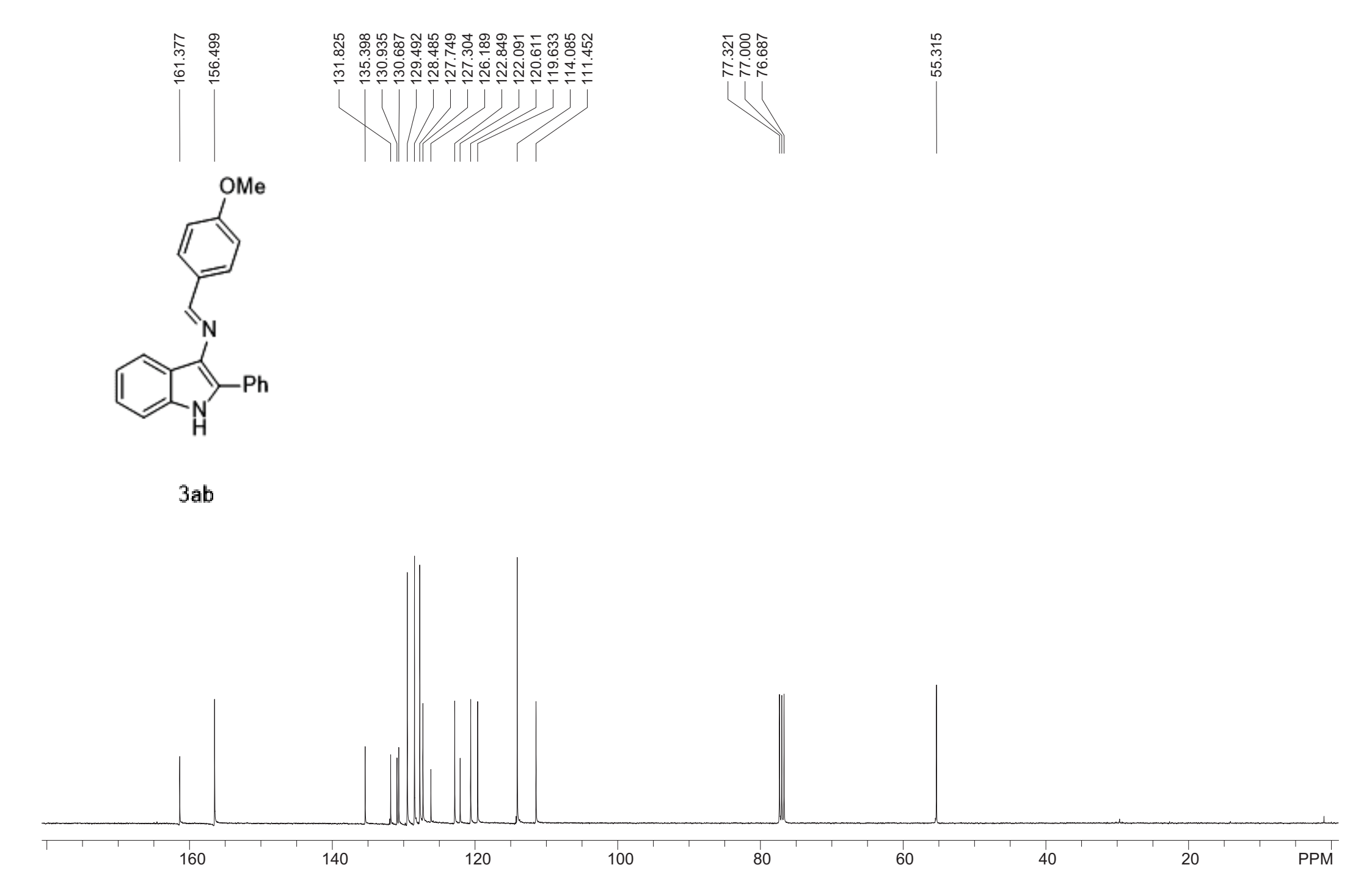
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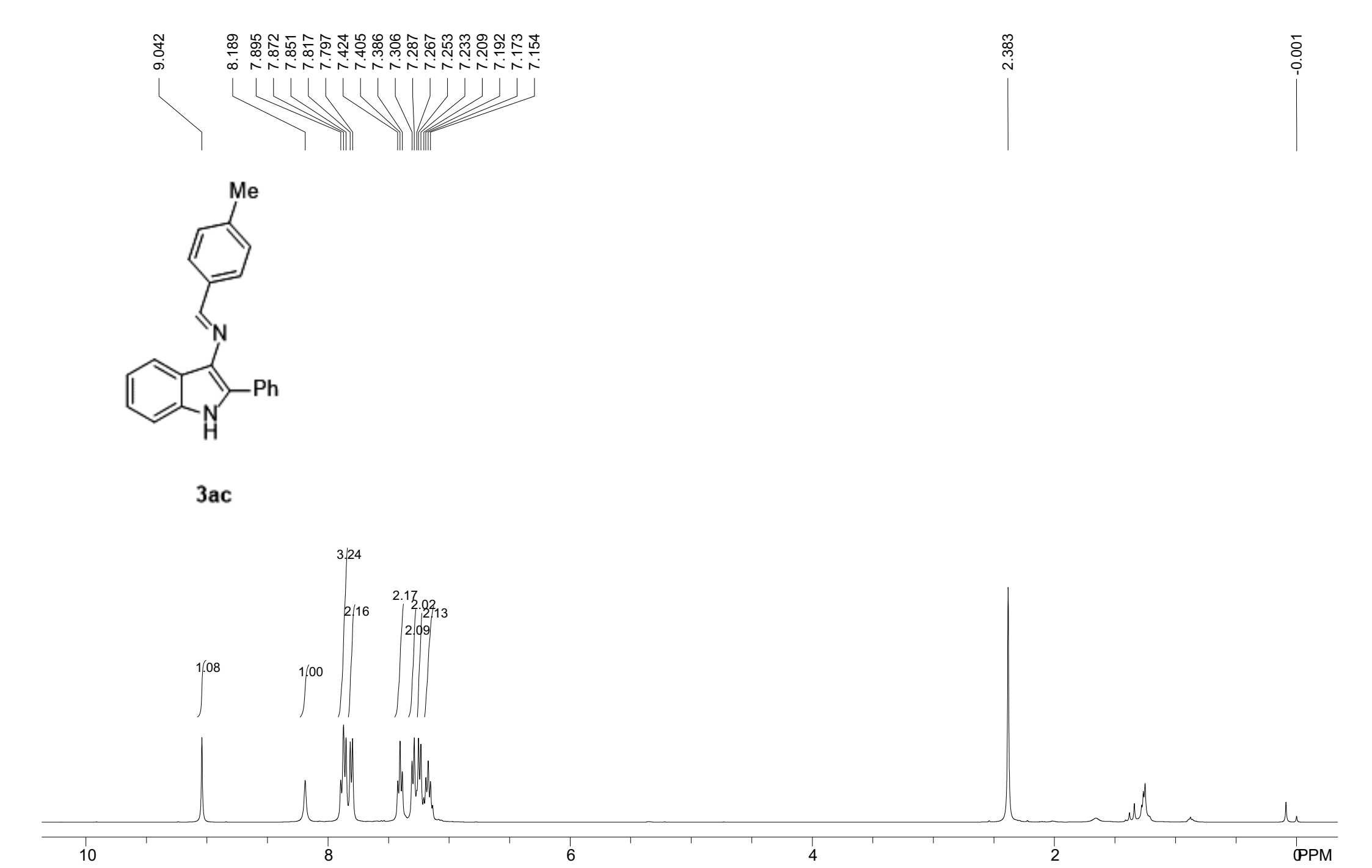
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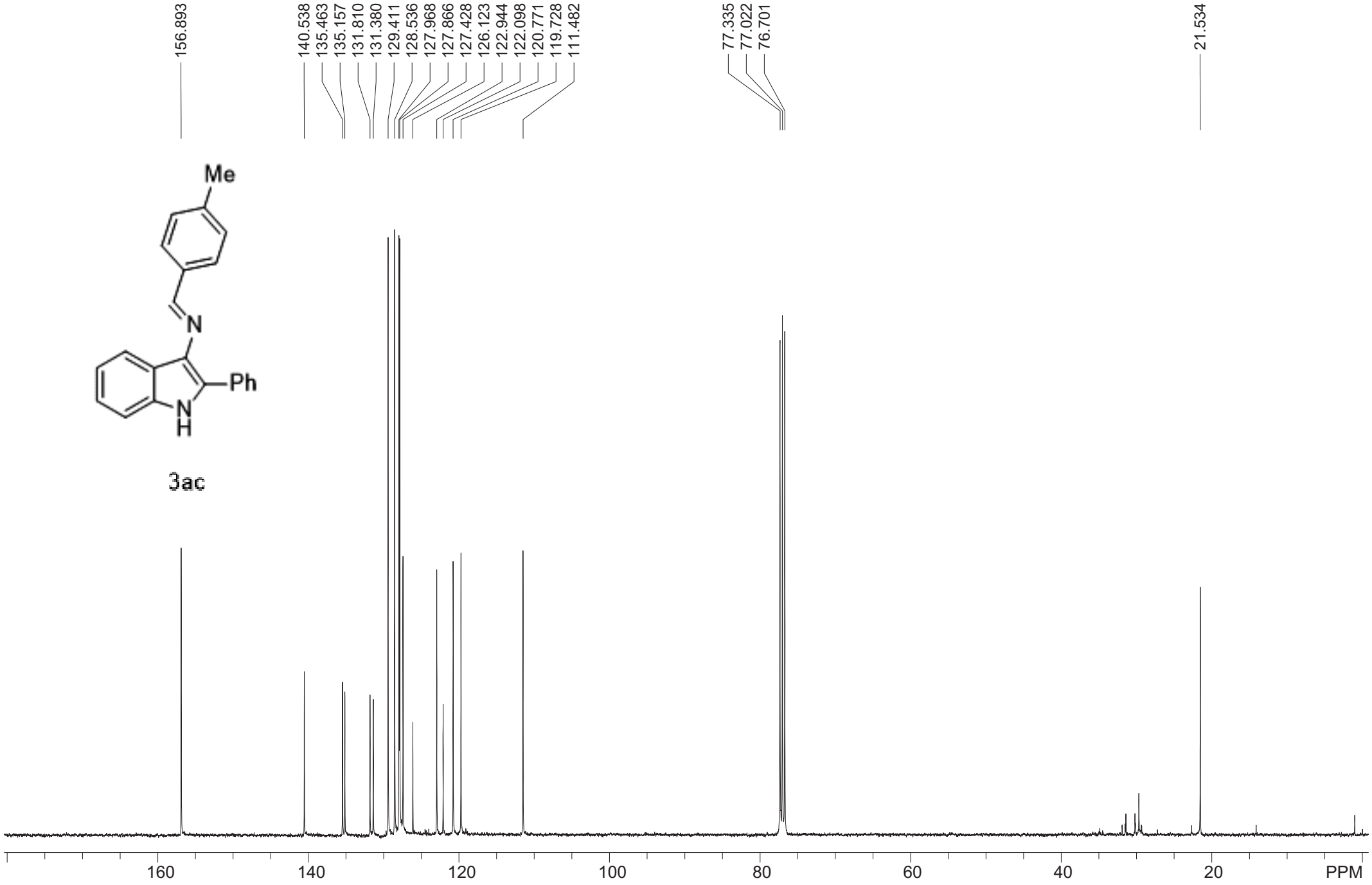
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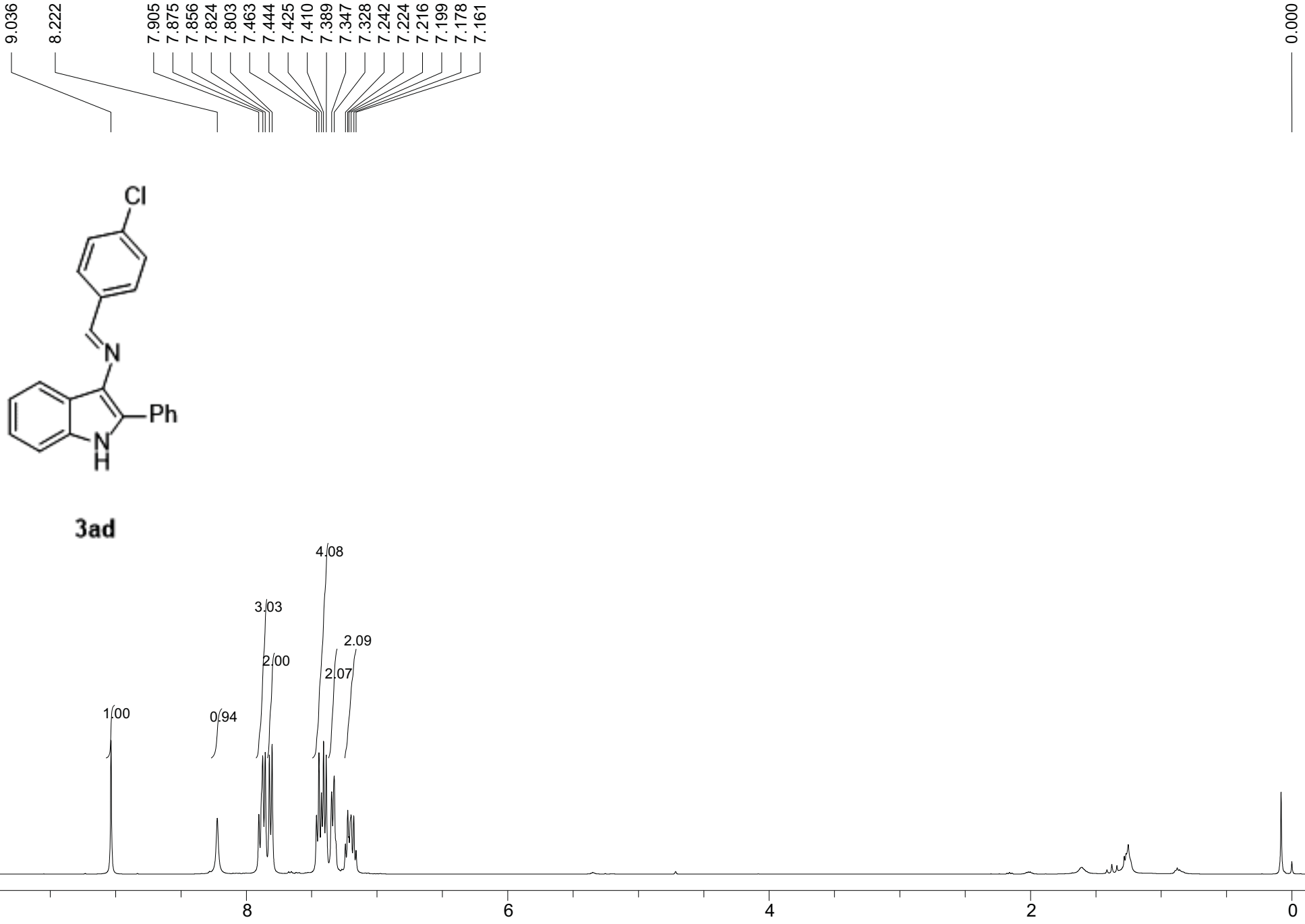
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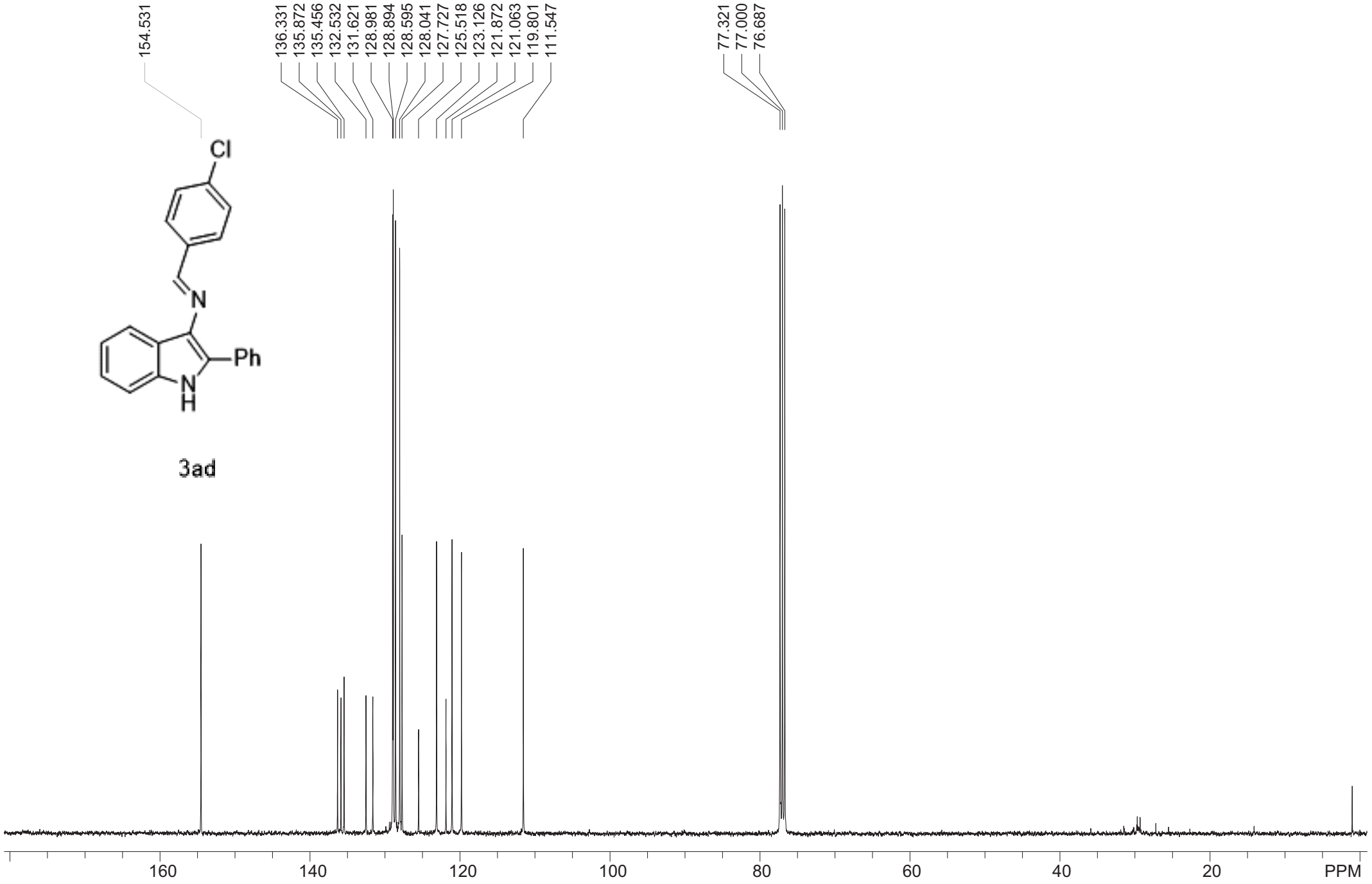
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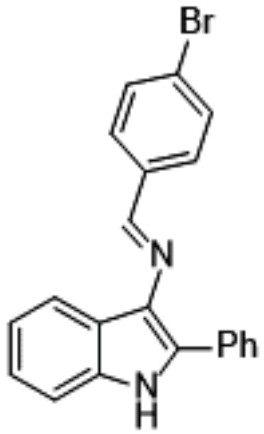
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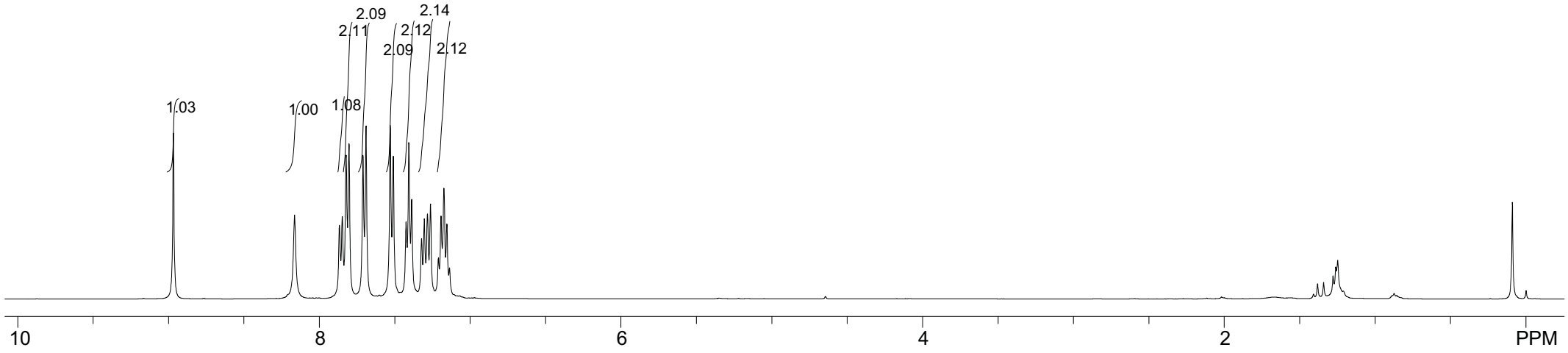
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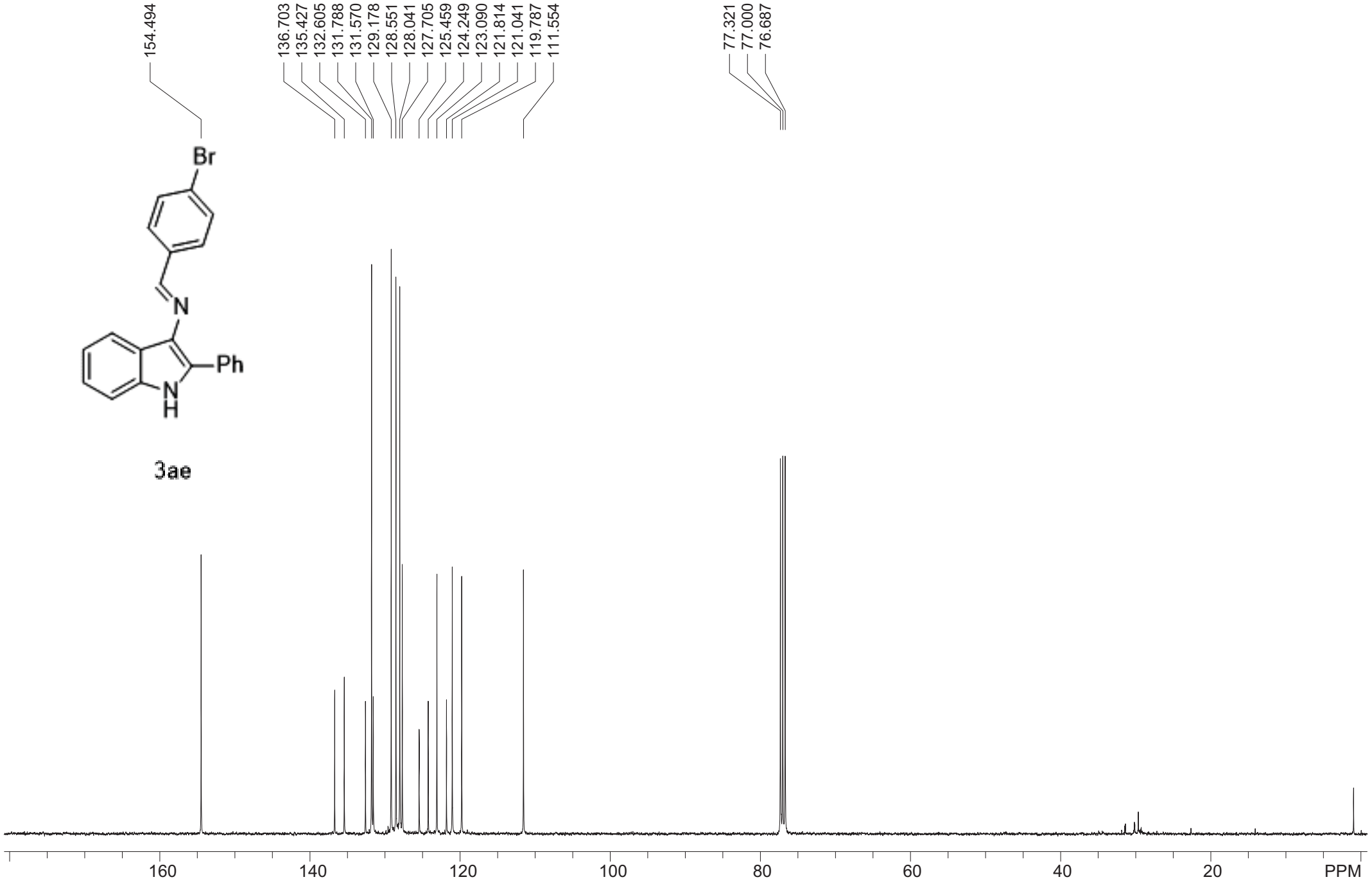
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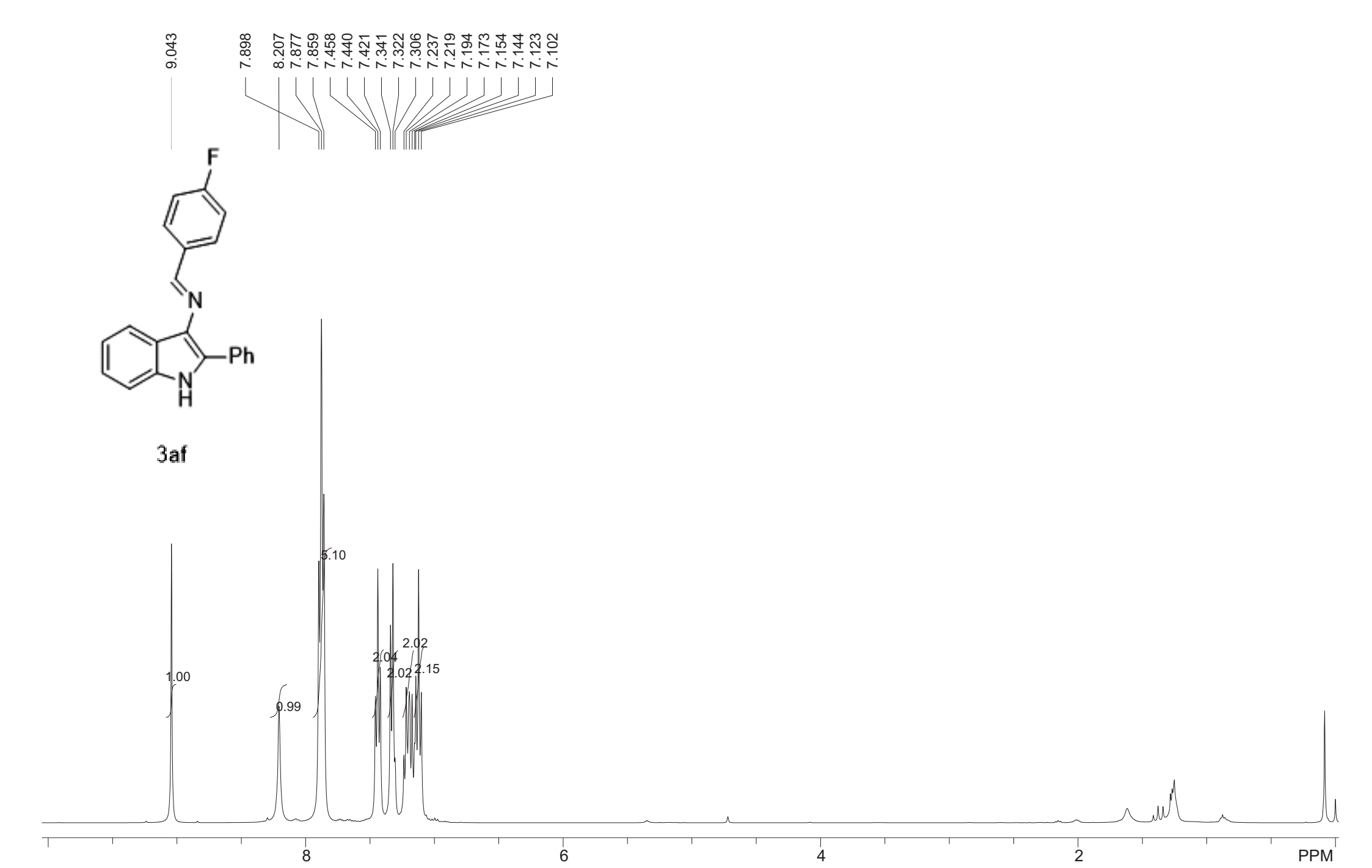
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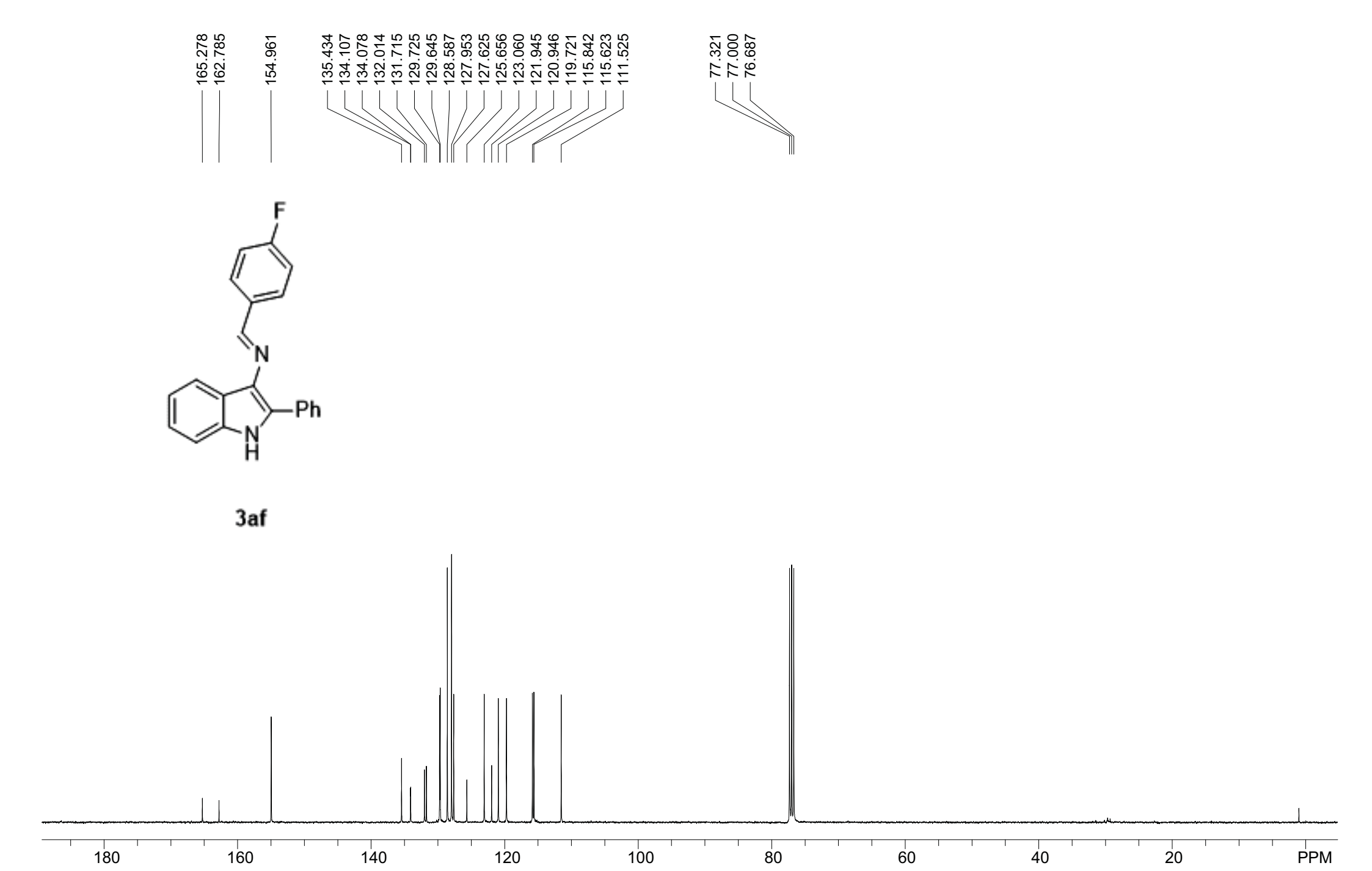
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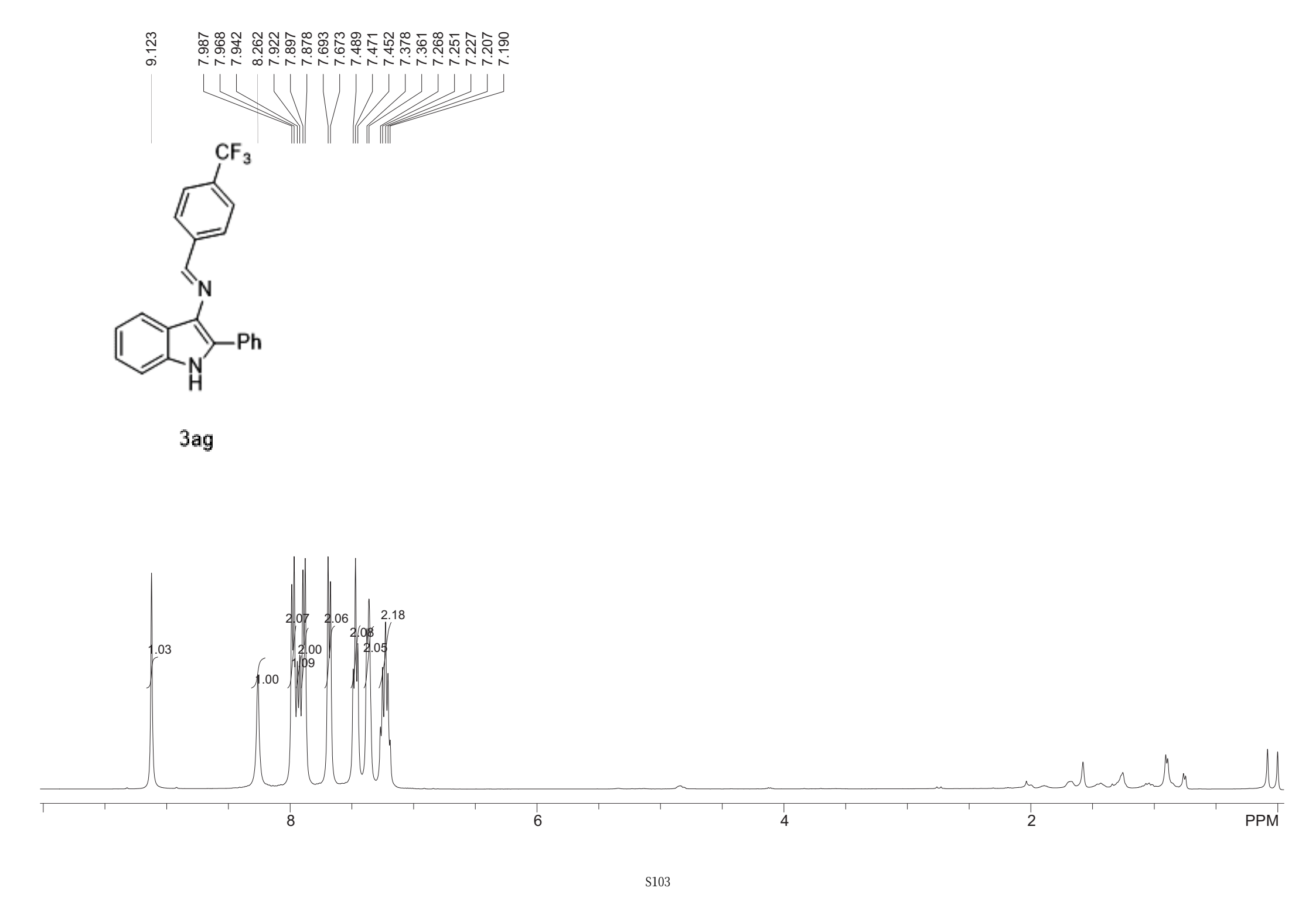
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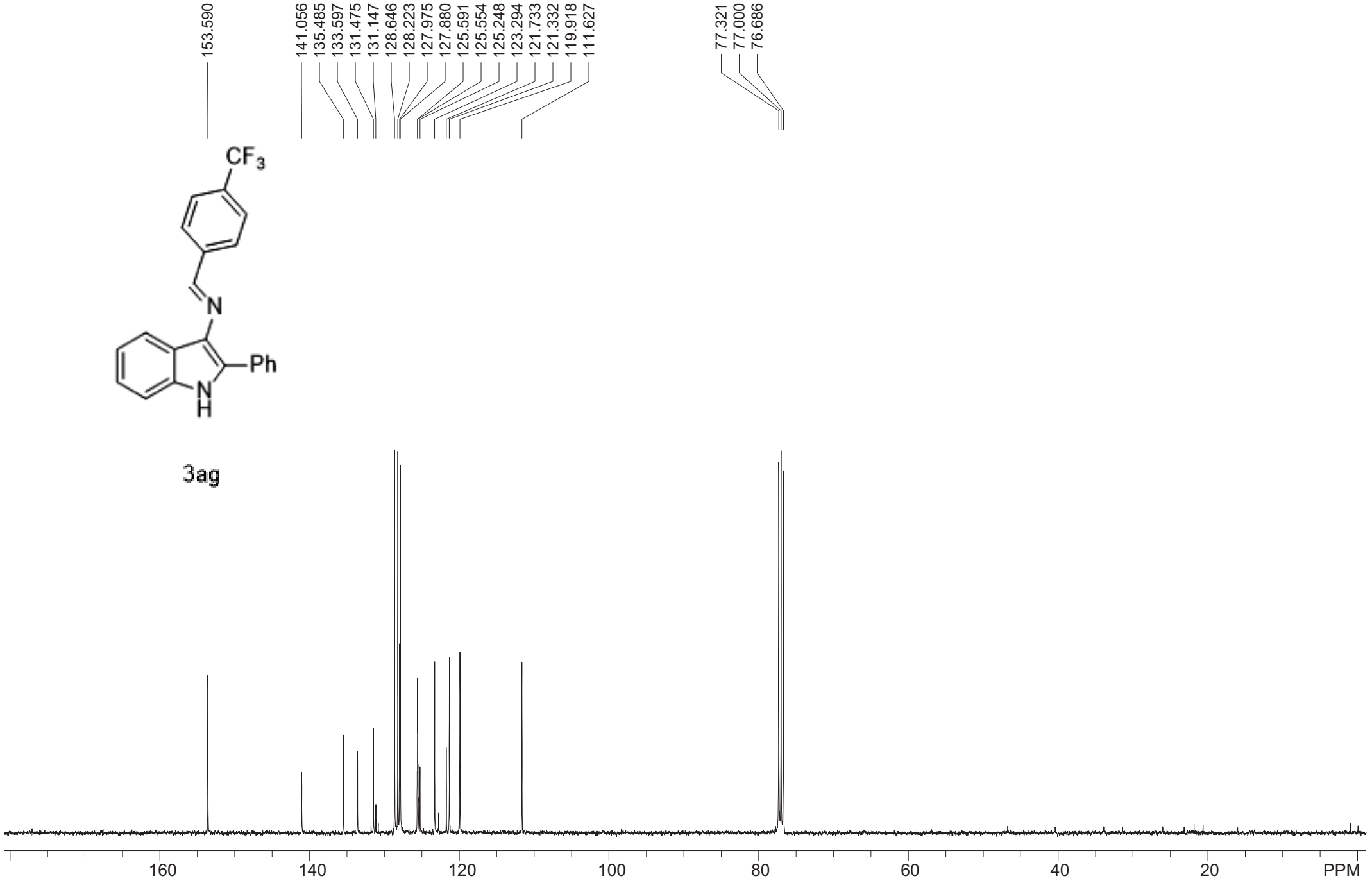
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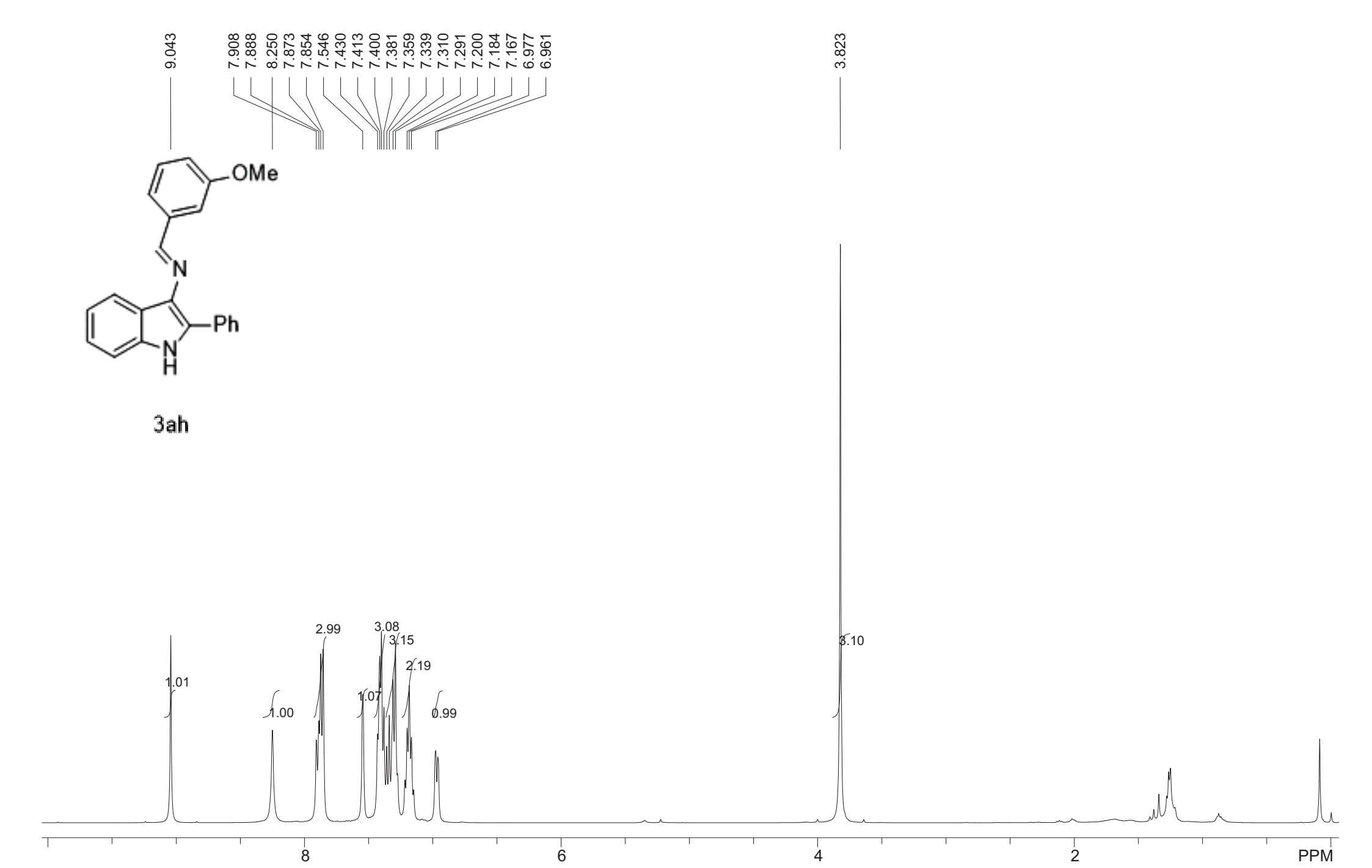
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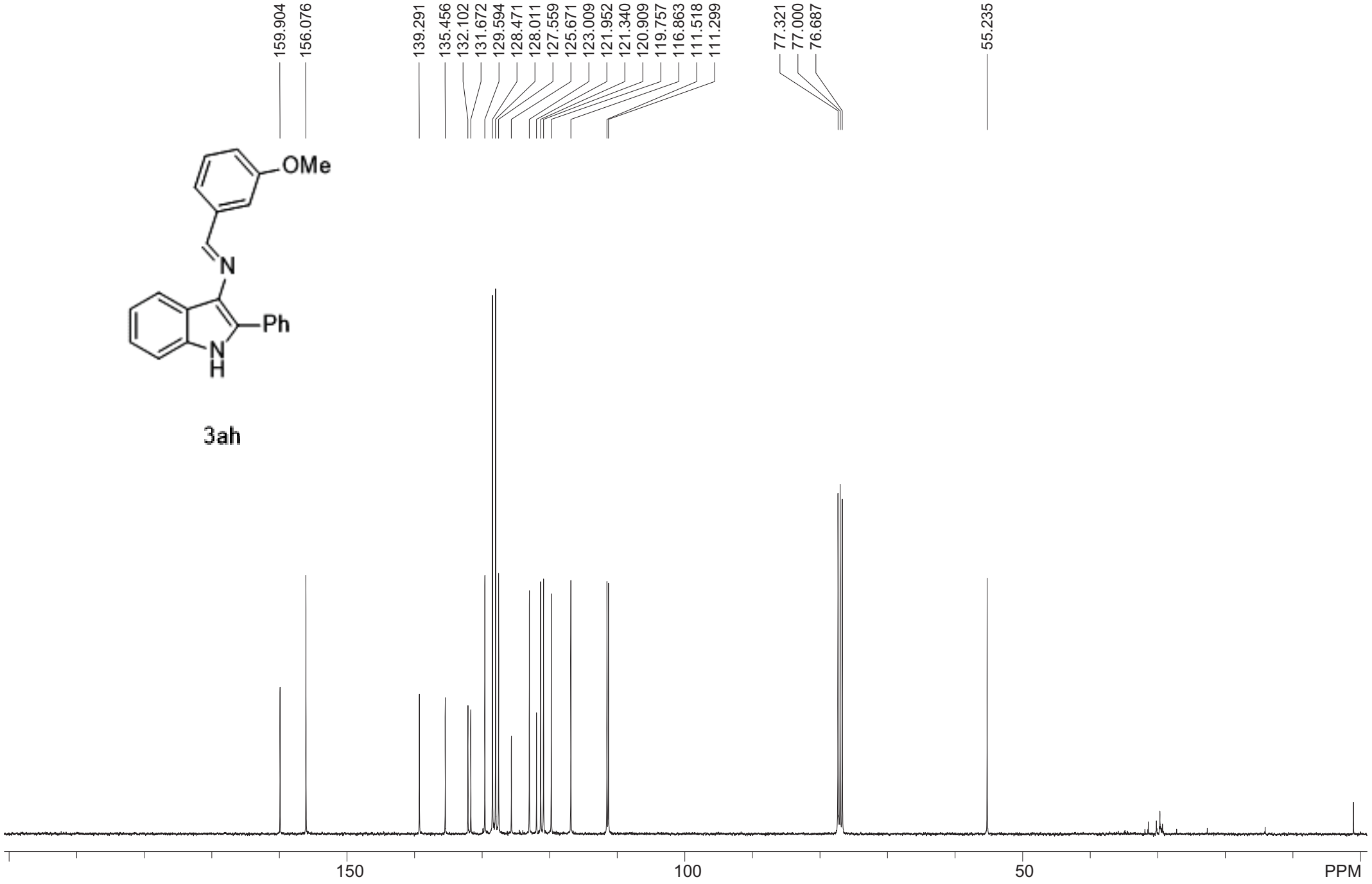
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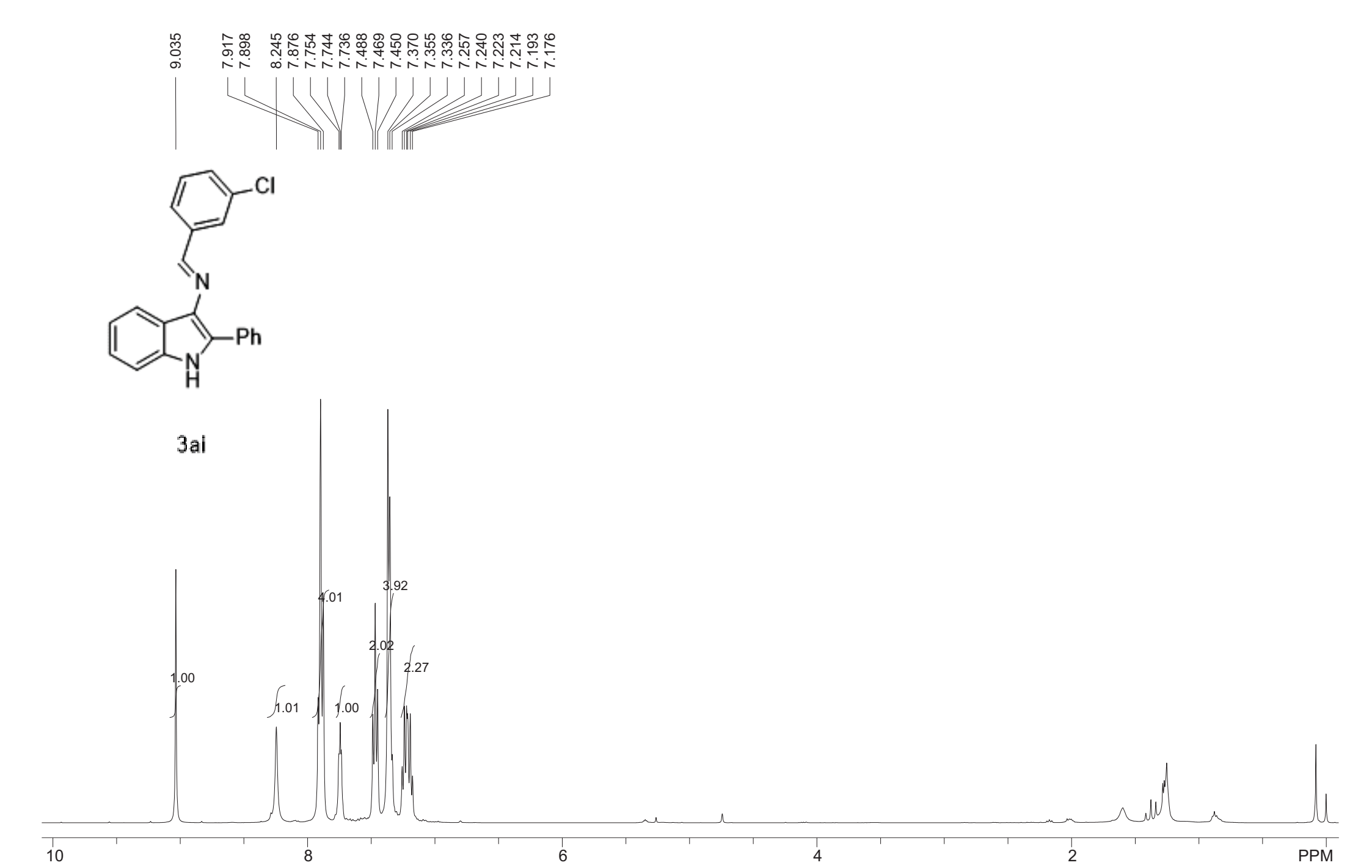
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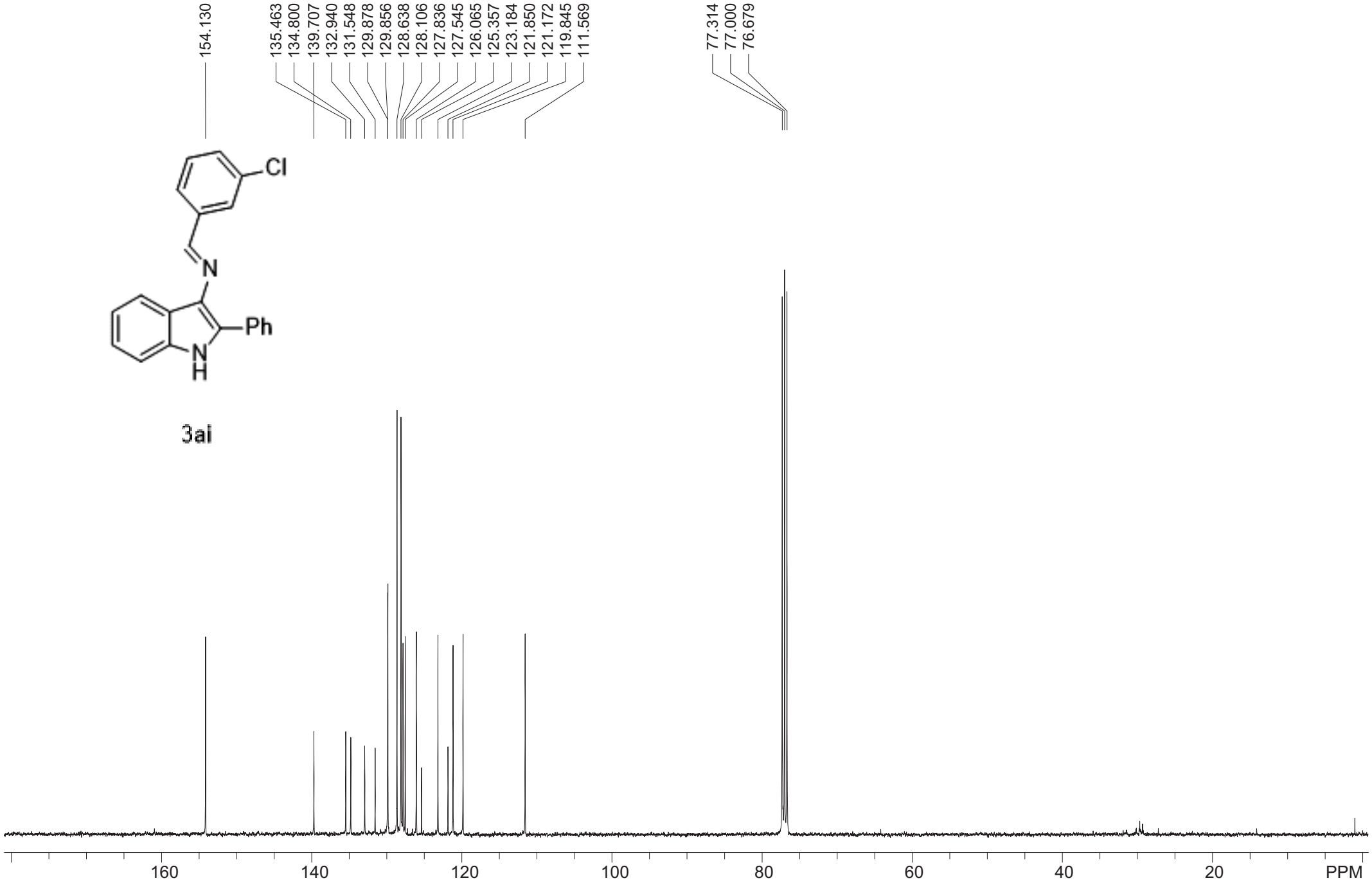
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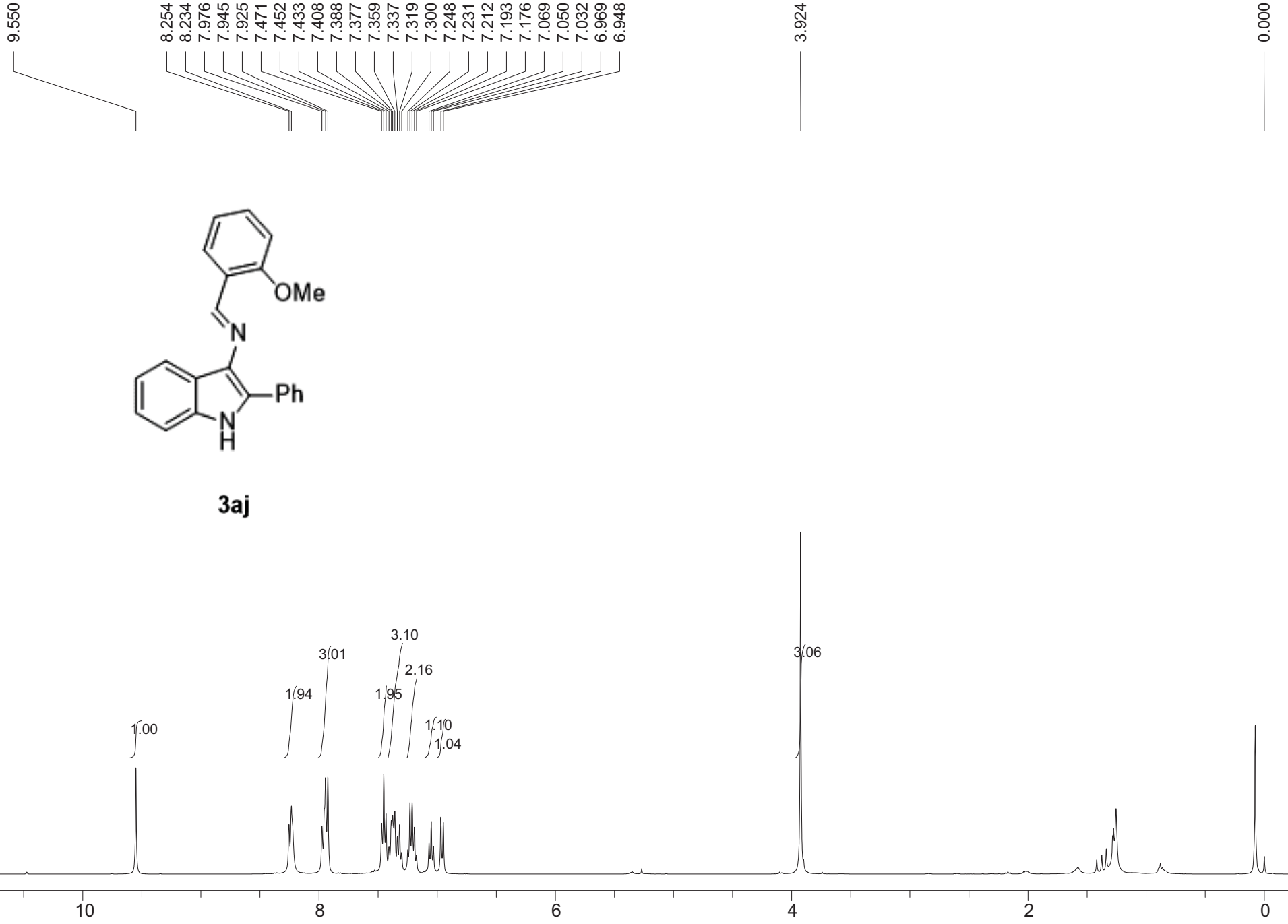
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OMe
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Ph
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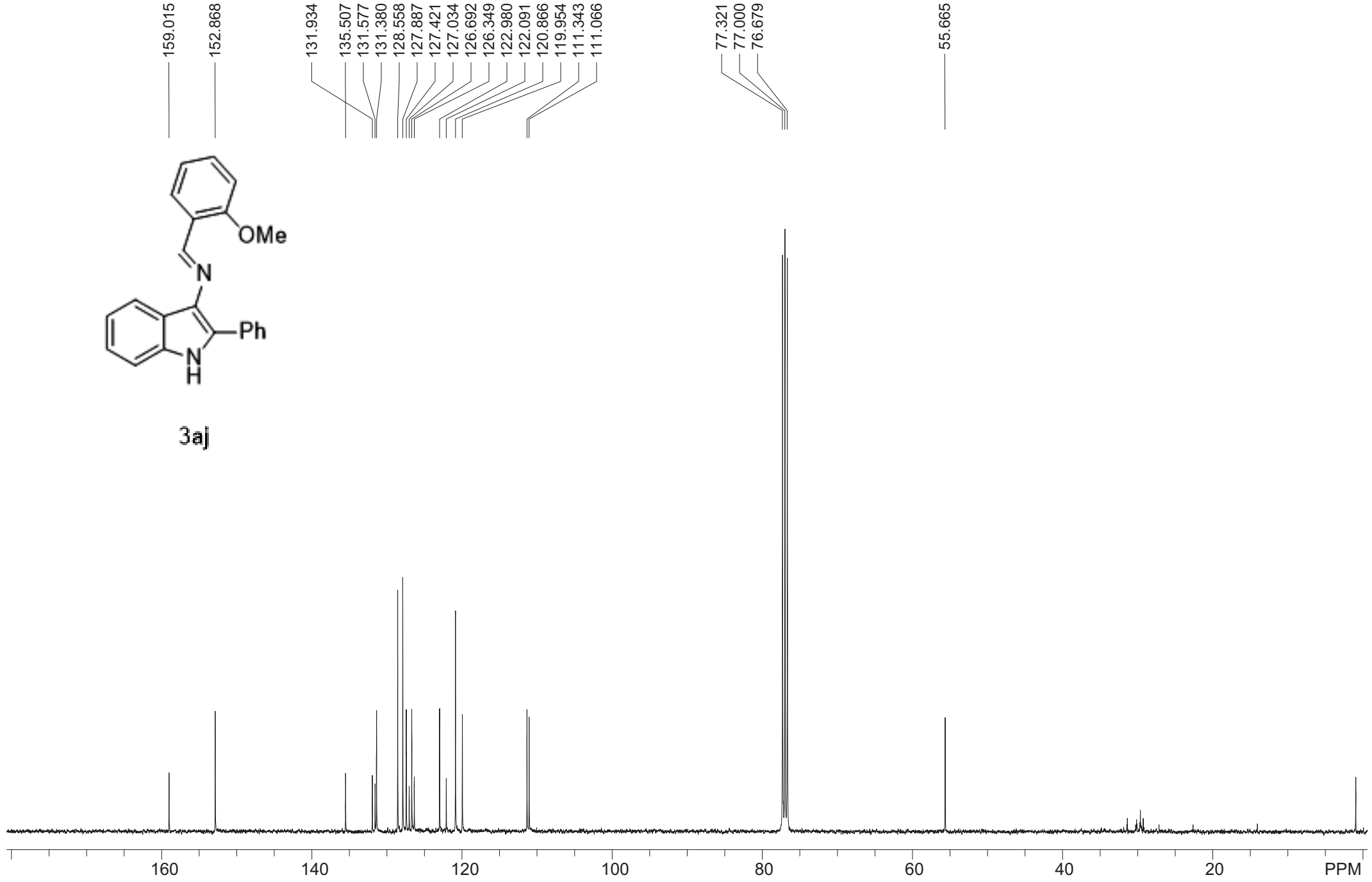
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OMe
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Ph
N
H
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PPM

3aj


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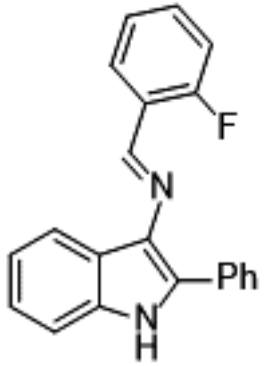
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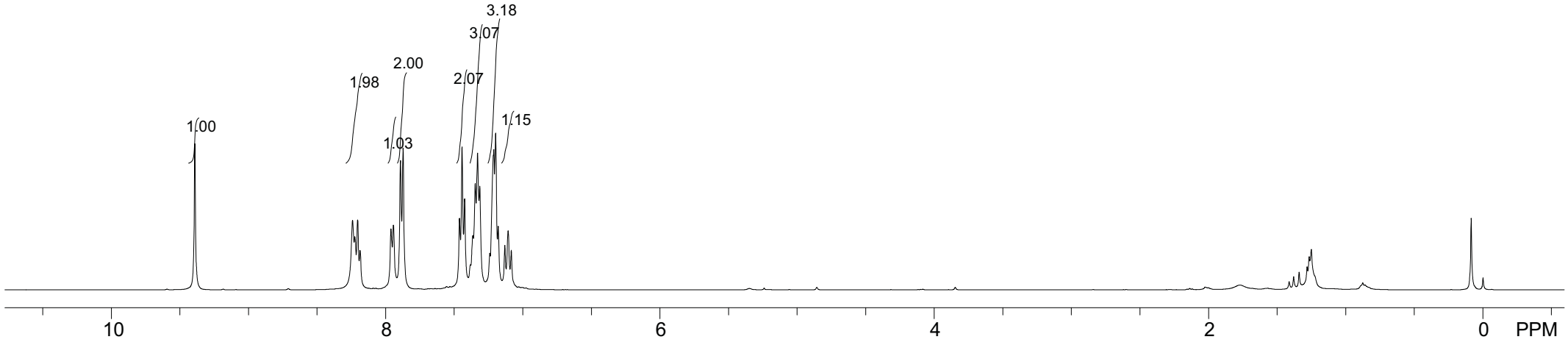
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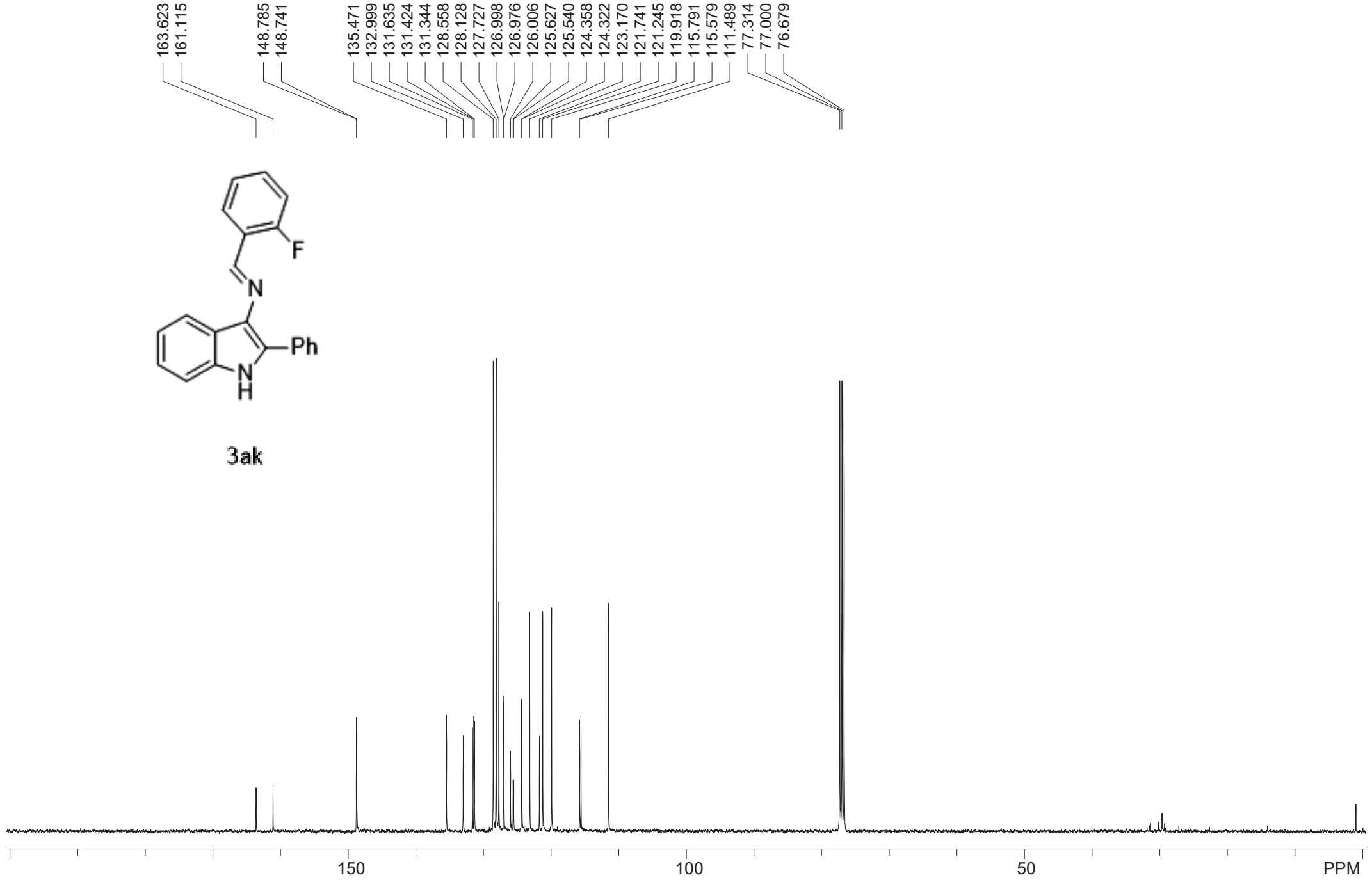
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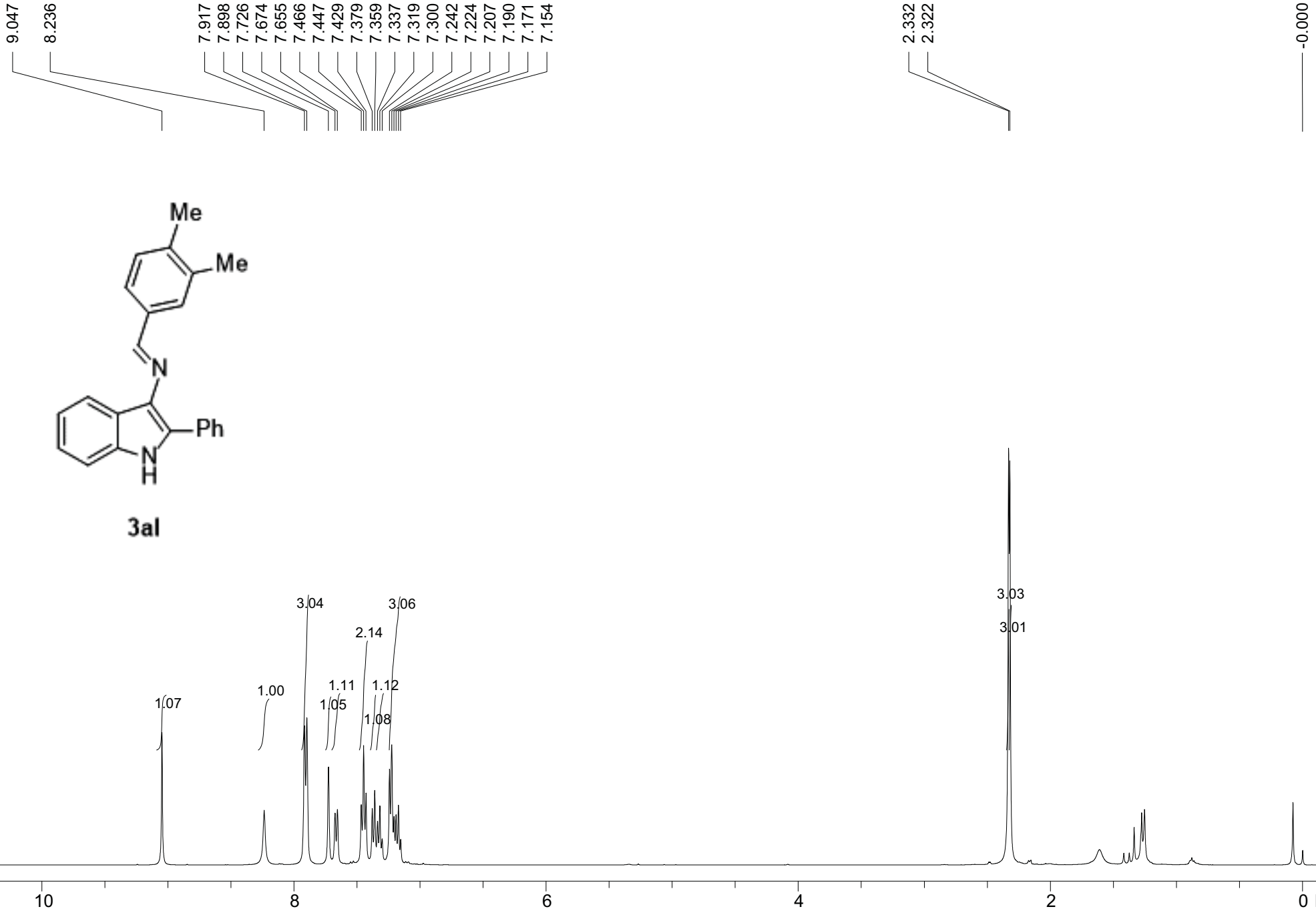
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Me
N
Ph
N
H
3al
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1.00
3.04
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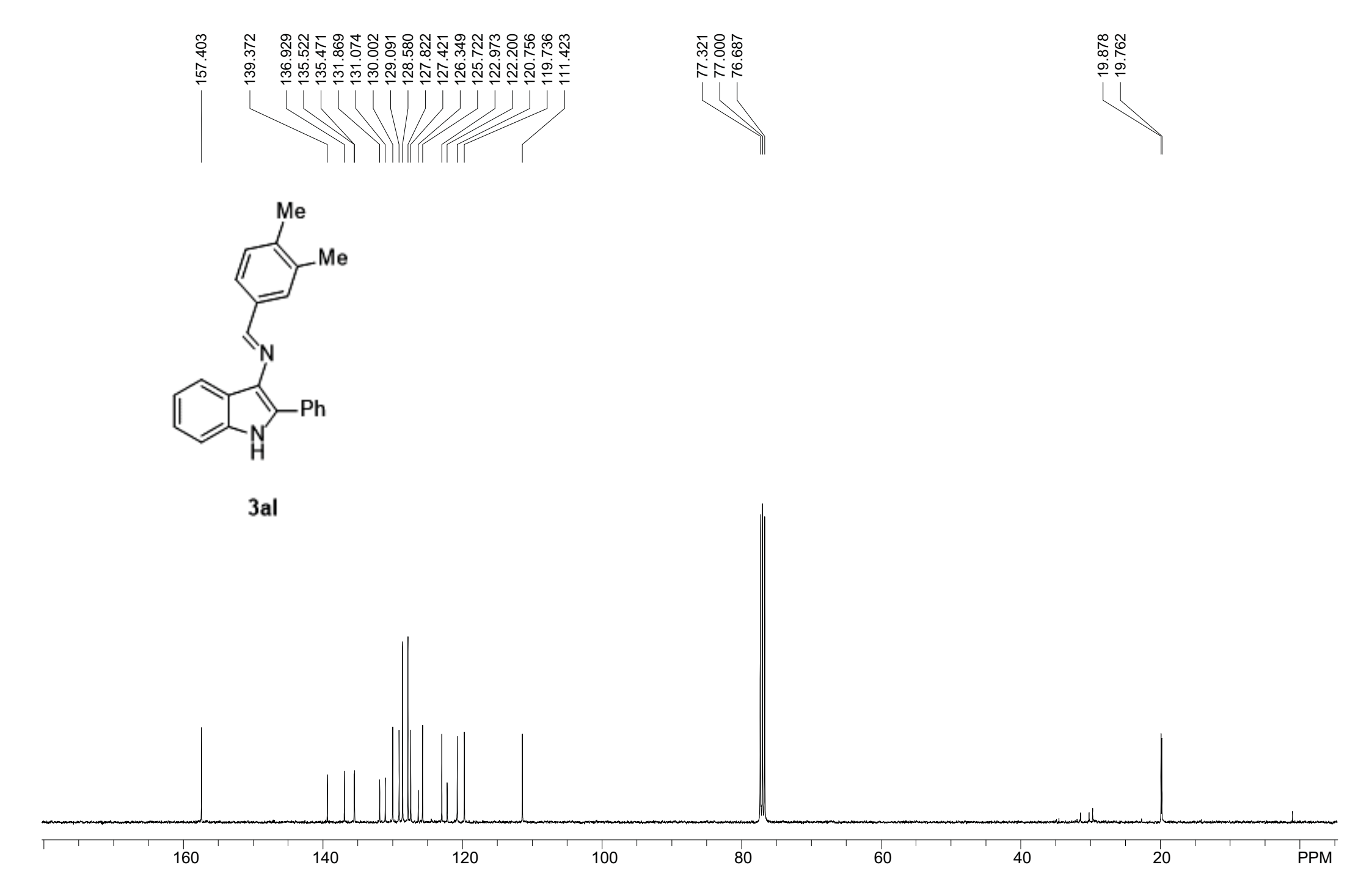
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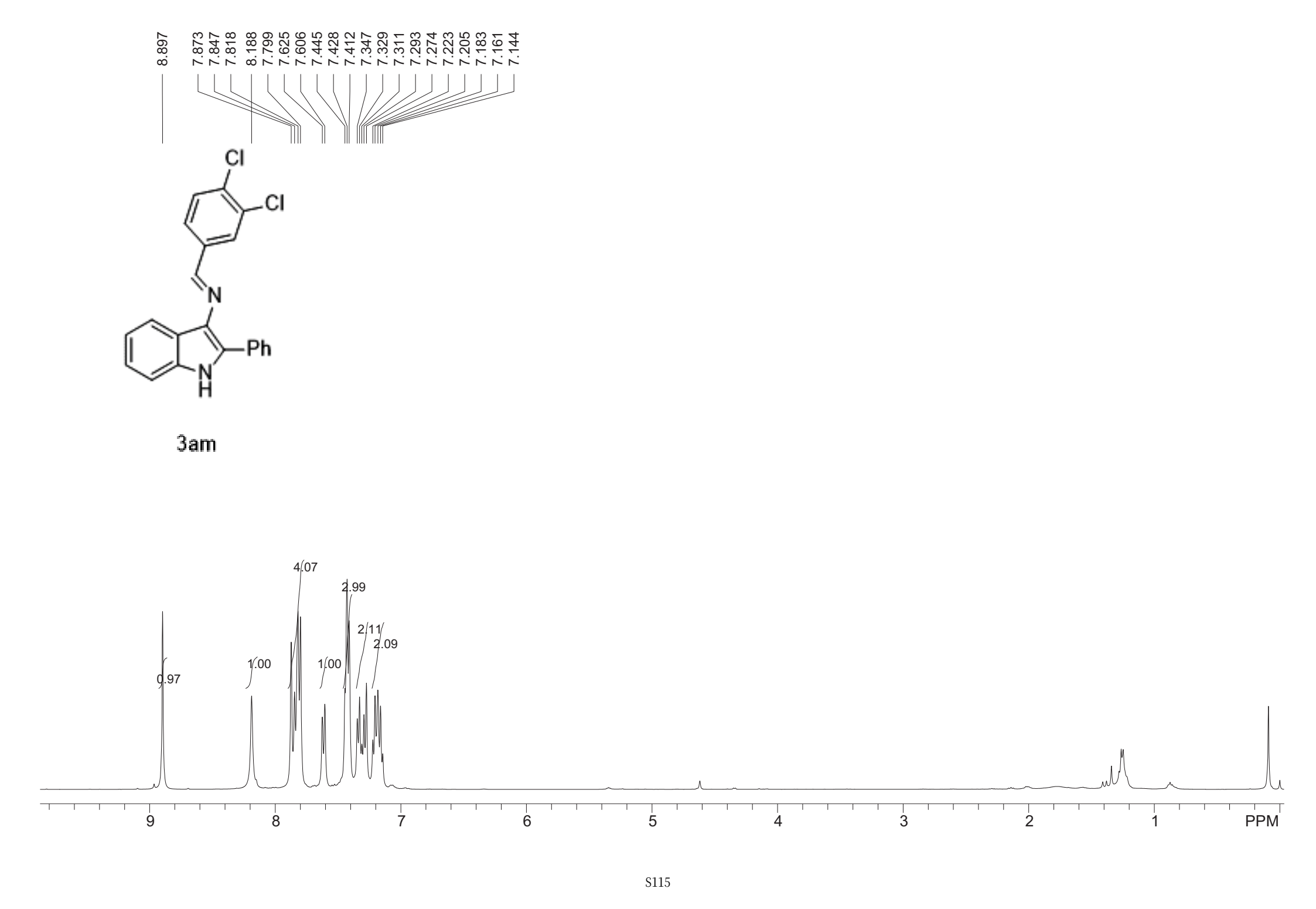
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7.223
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Cl
Cl
N
Ph
N
H
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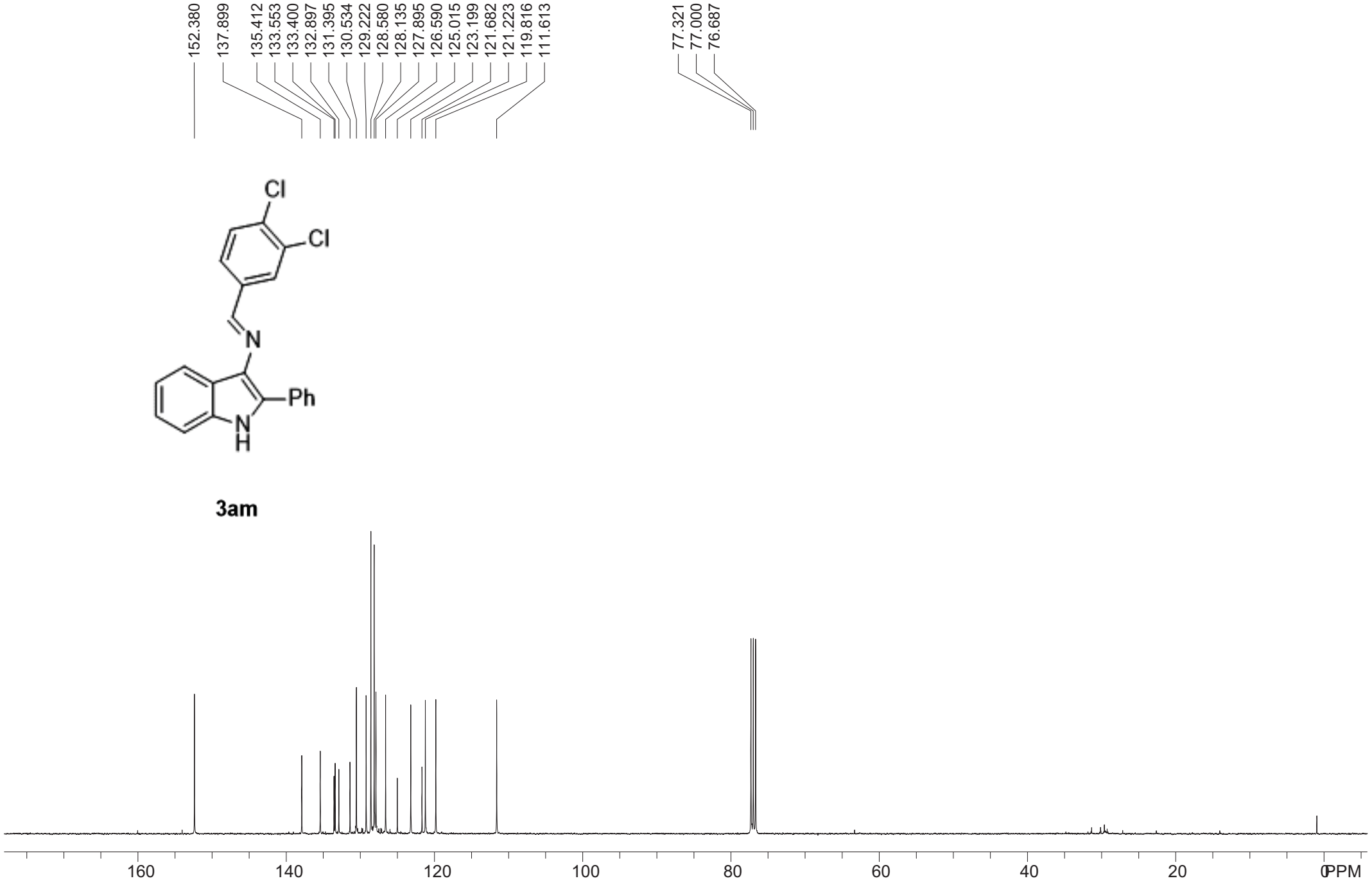
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77.321
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Ph
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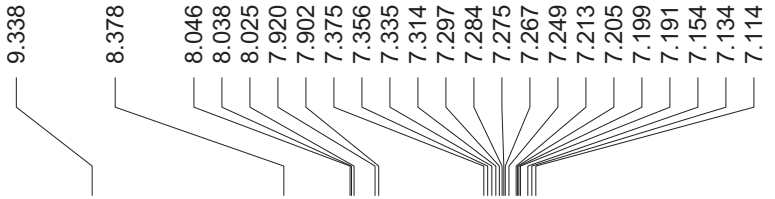
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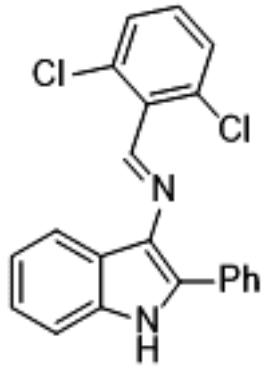
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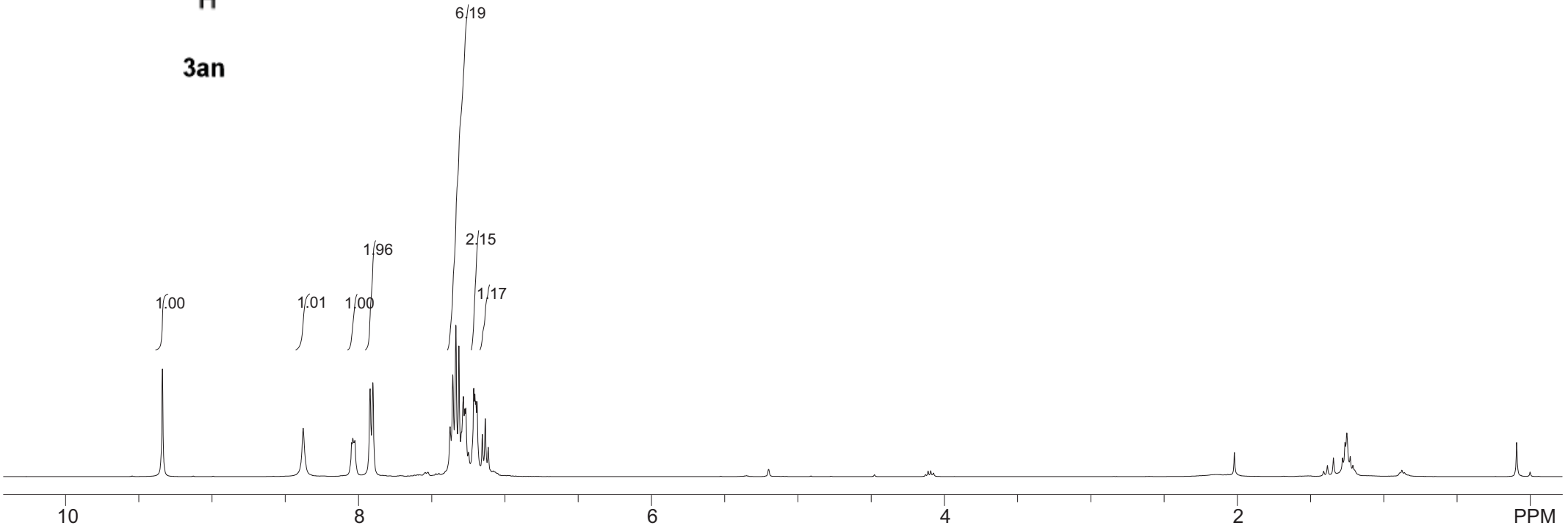
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1.00
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8
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2
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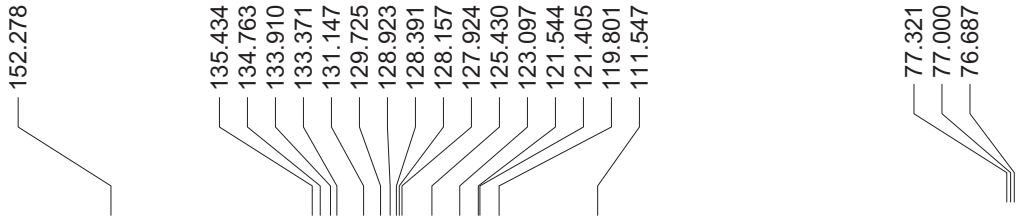
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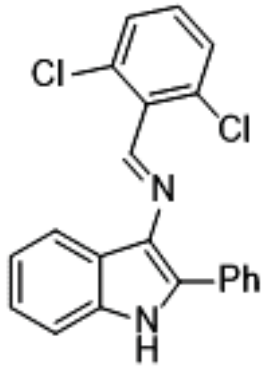
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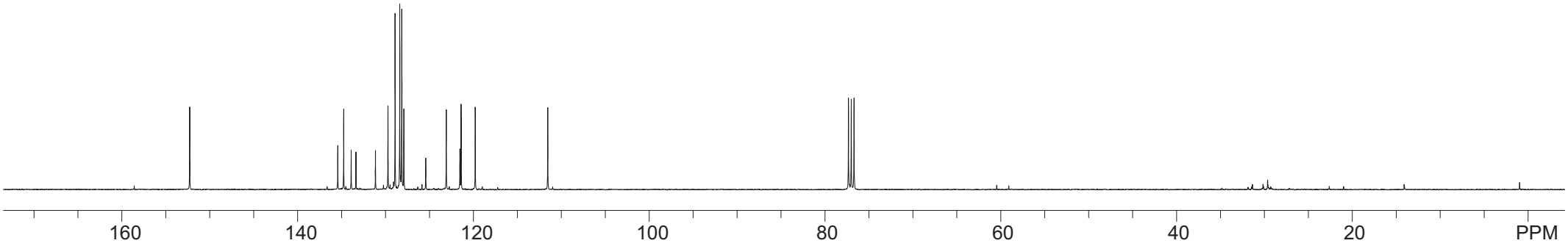
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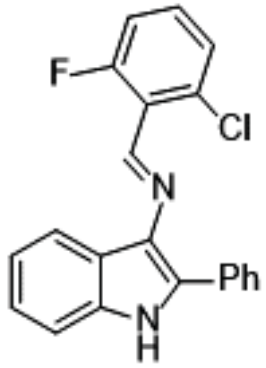
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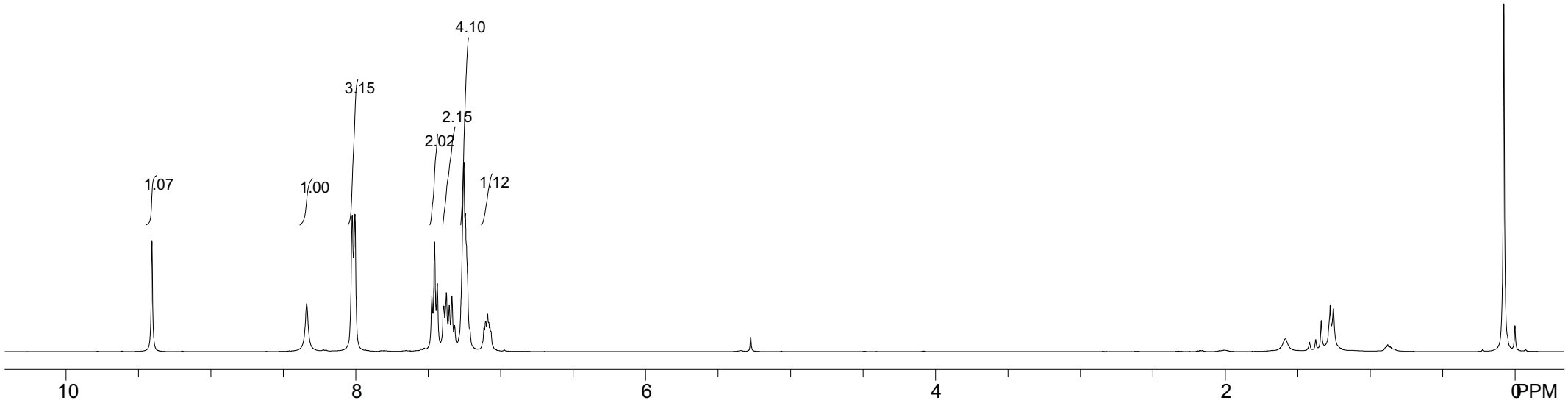
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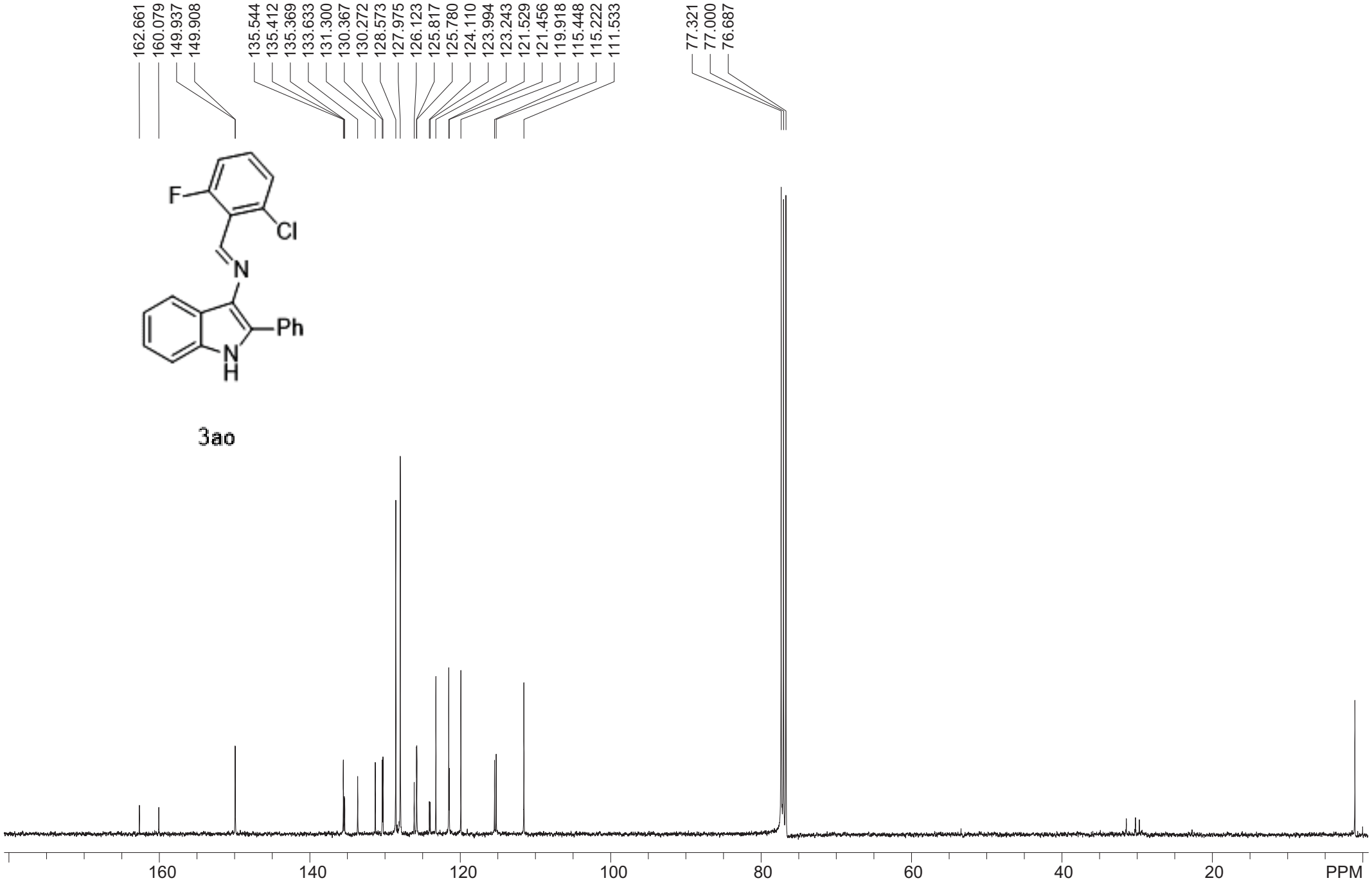
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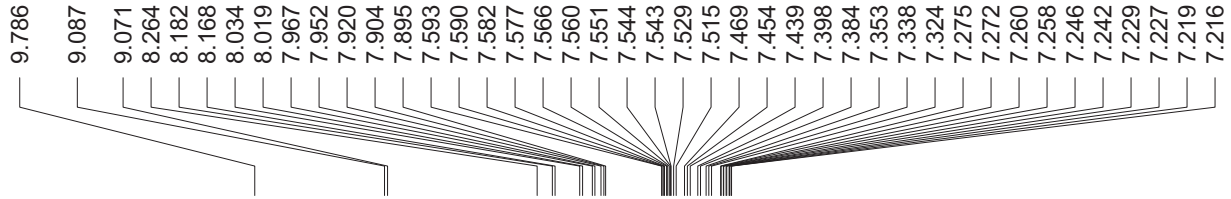
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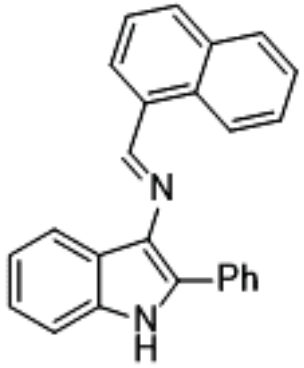
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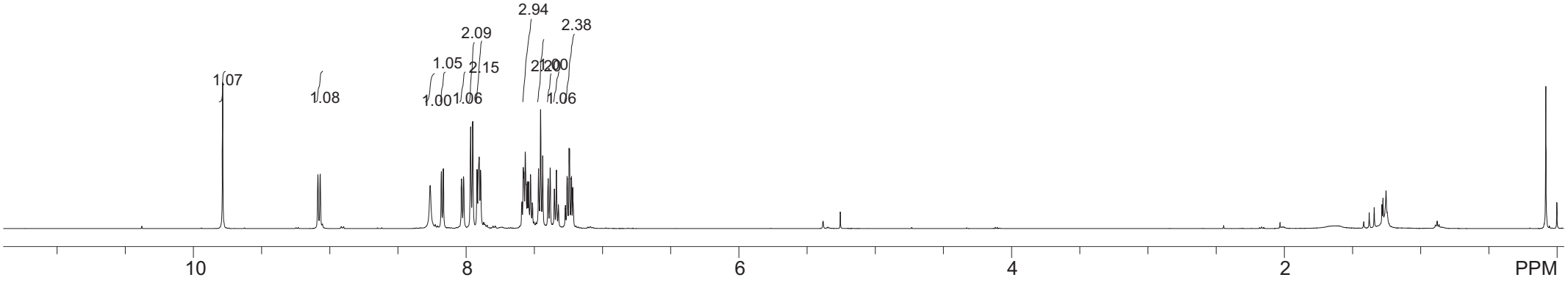
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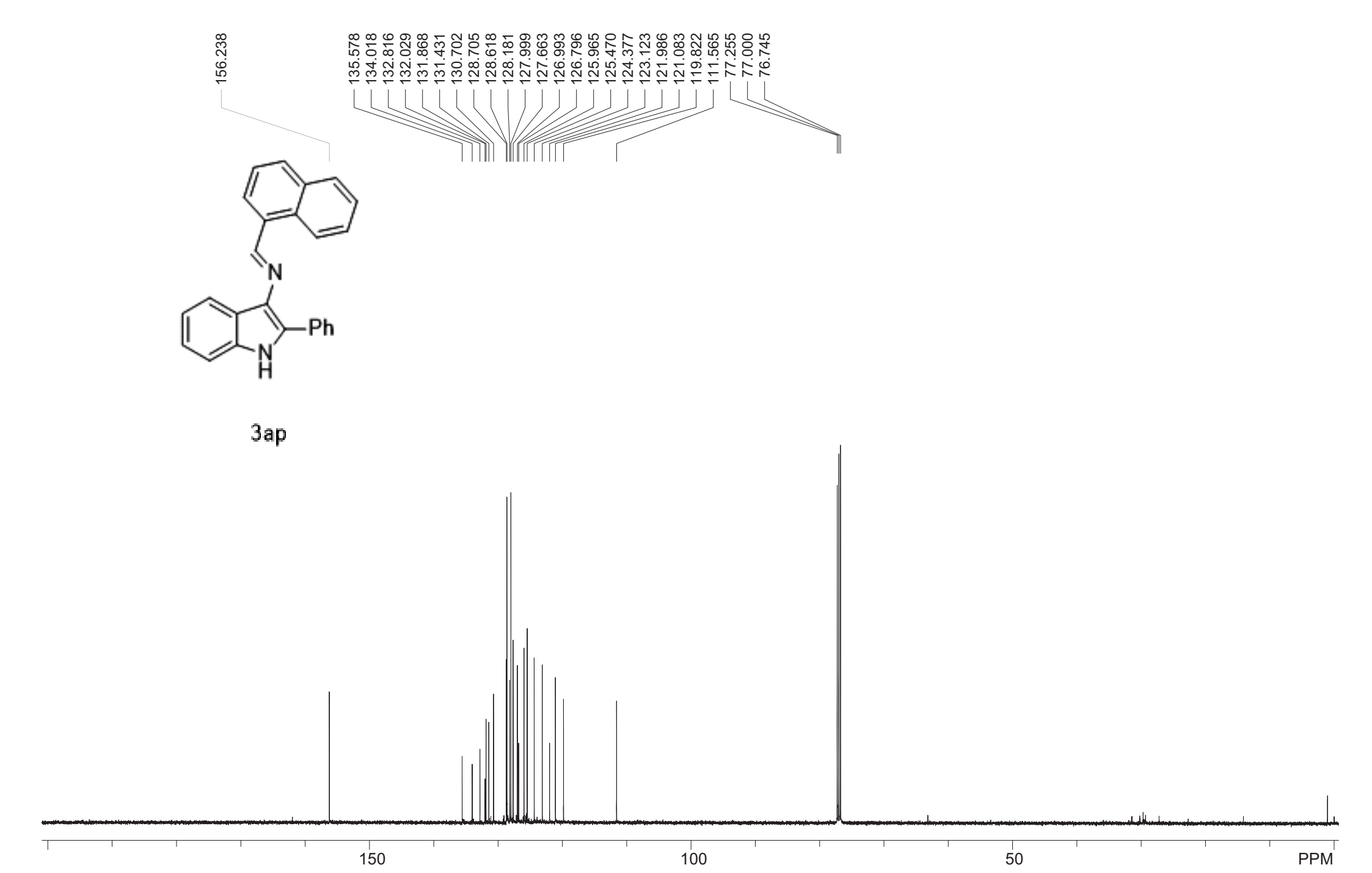
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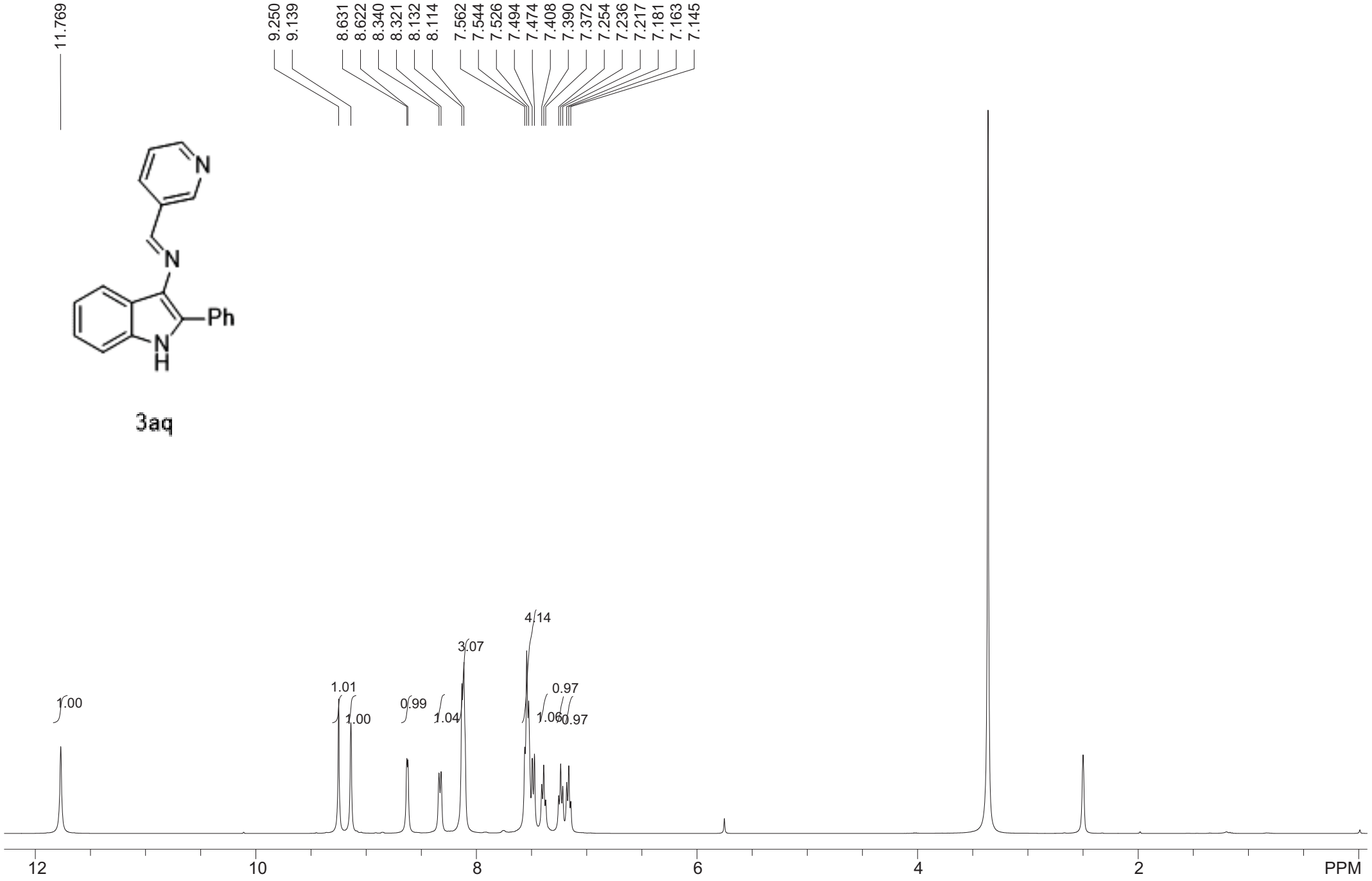
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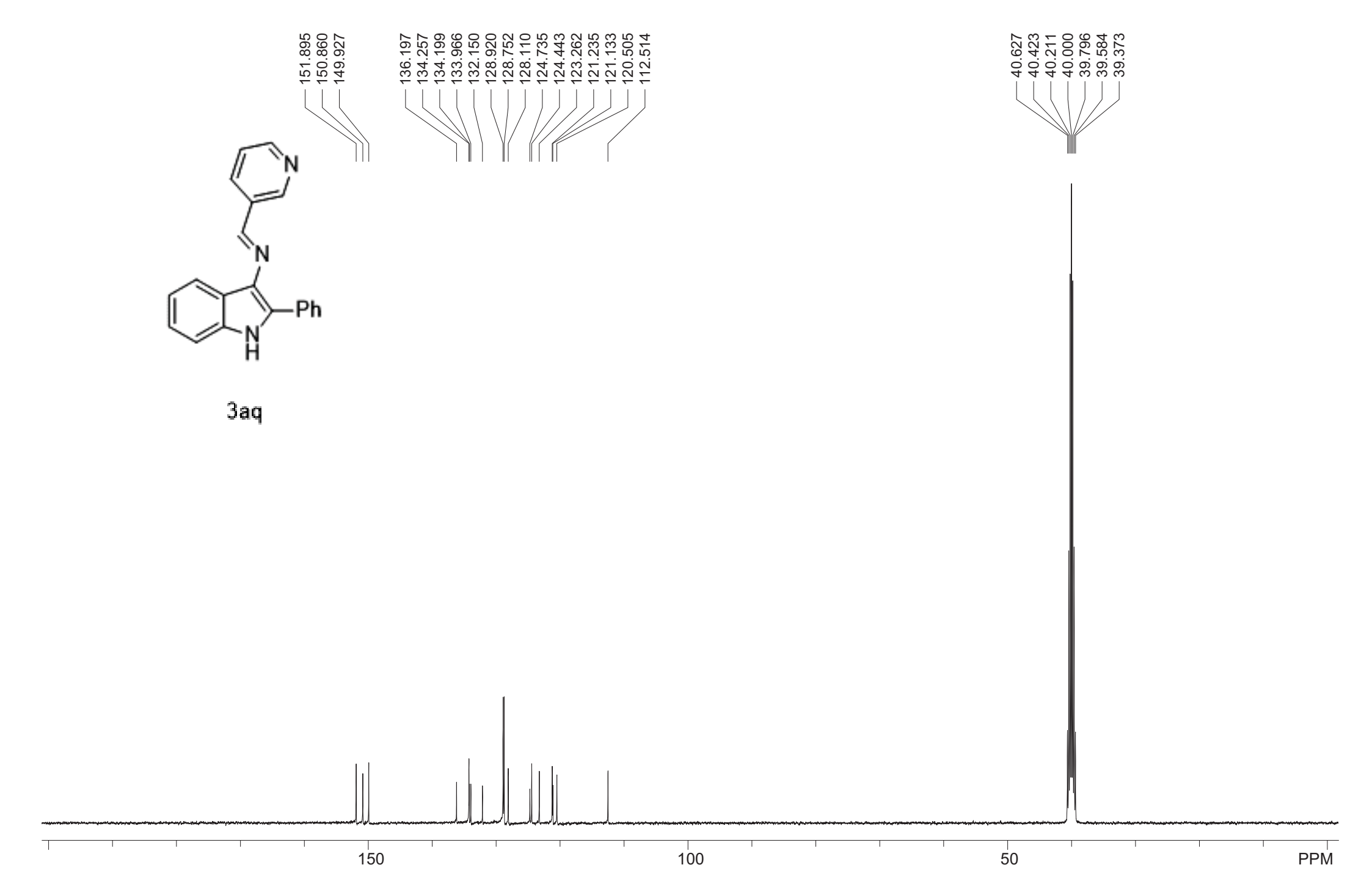
PPM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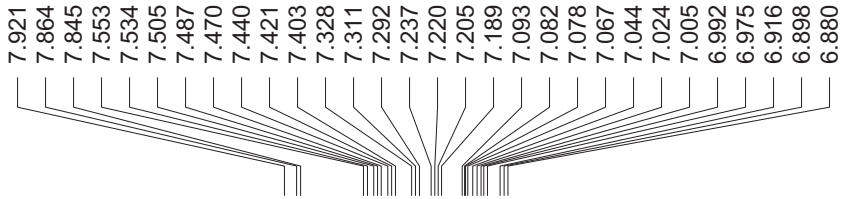
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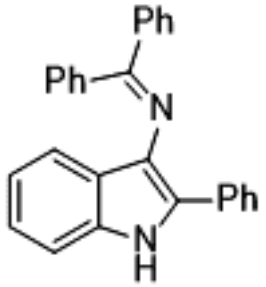
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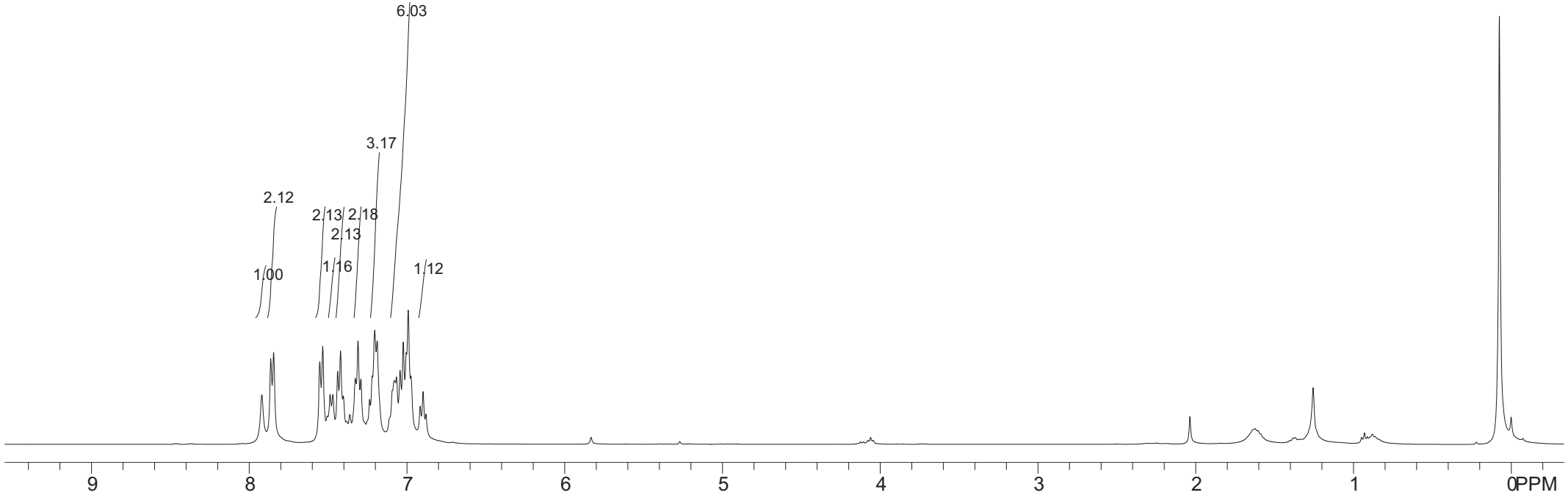
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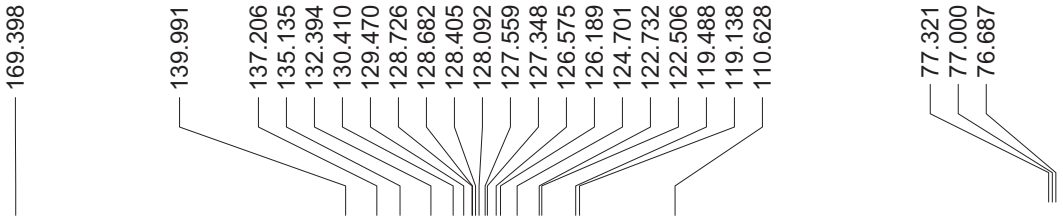
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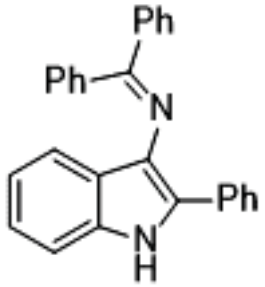
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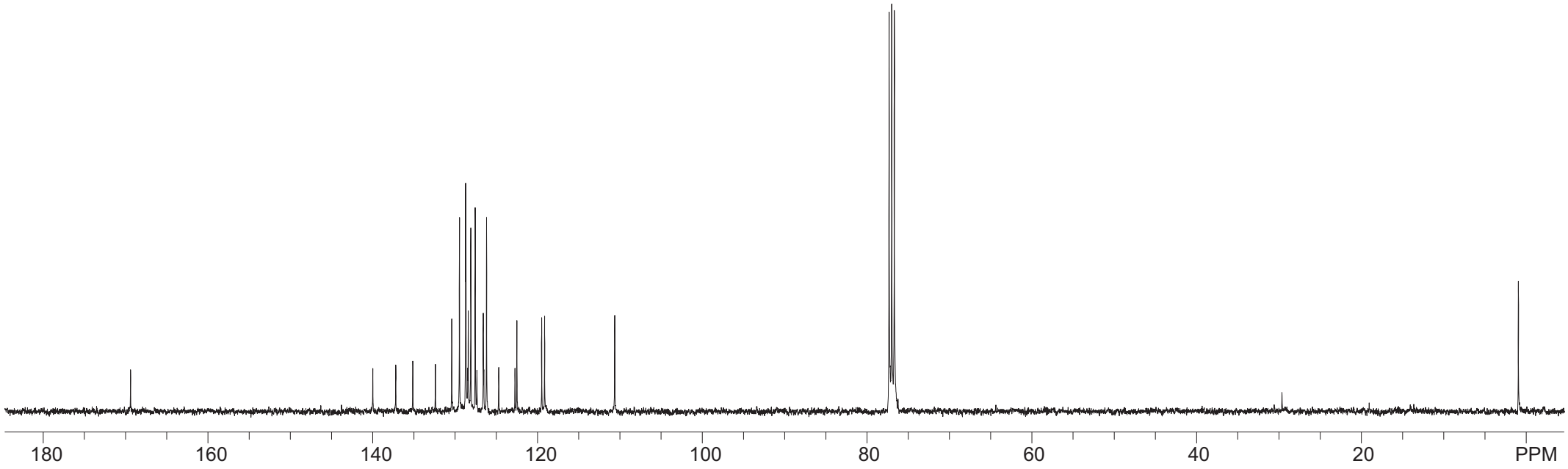
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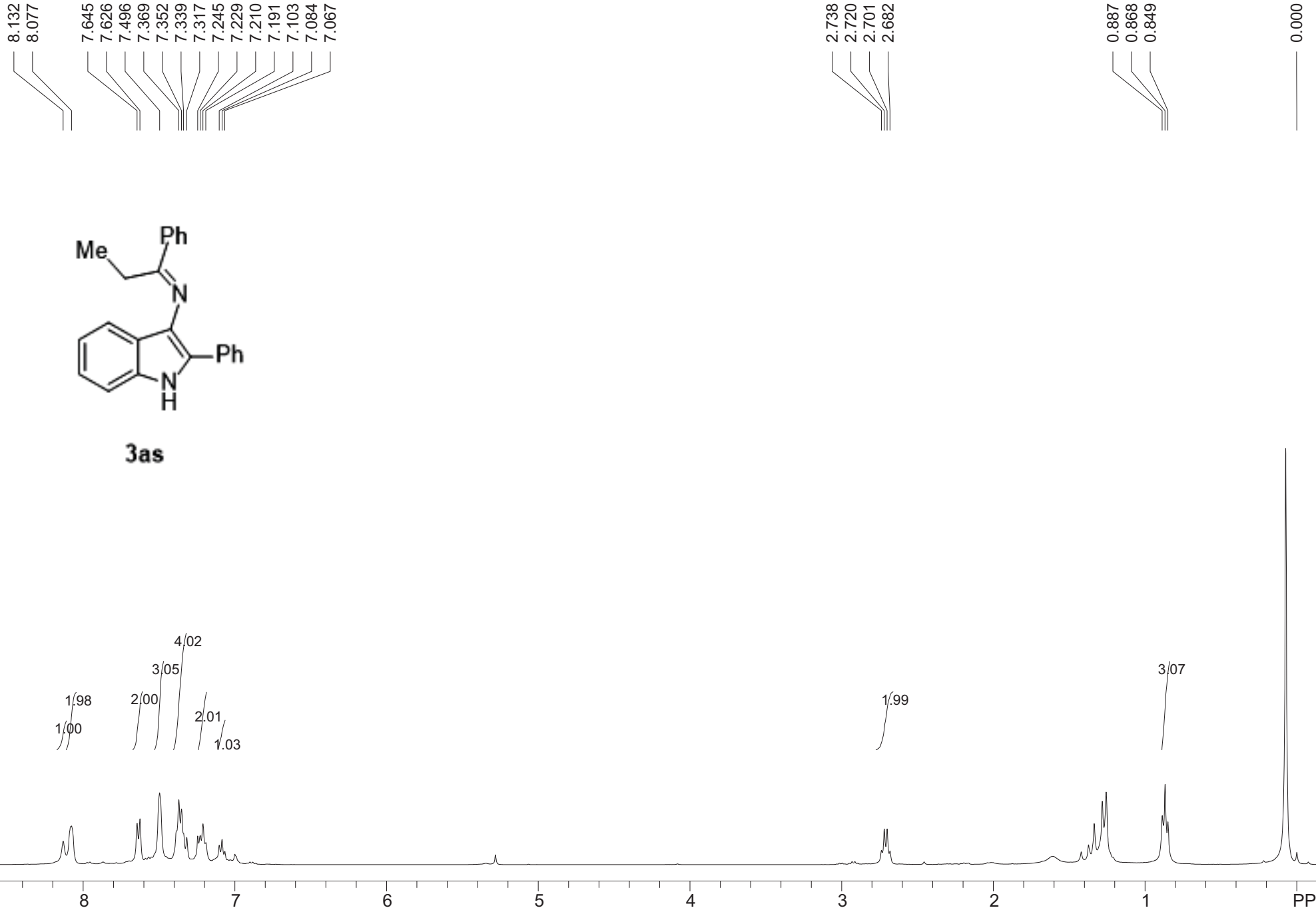
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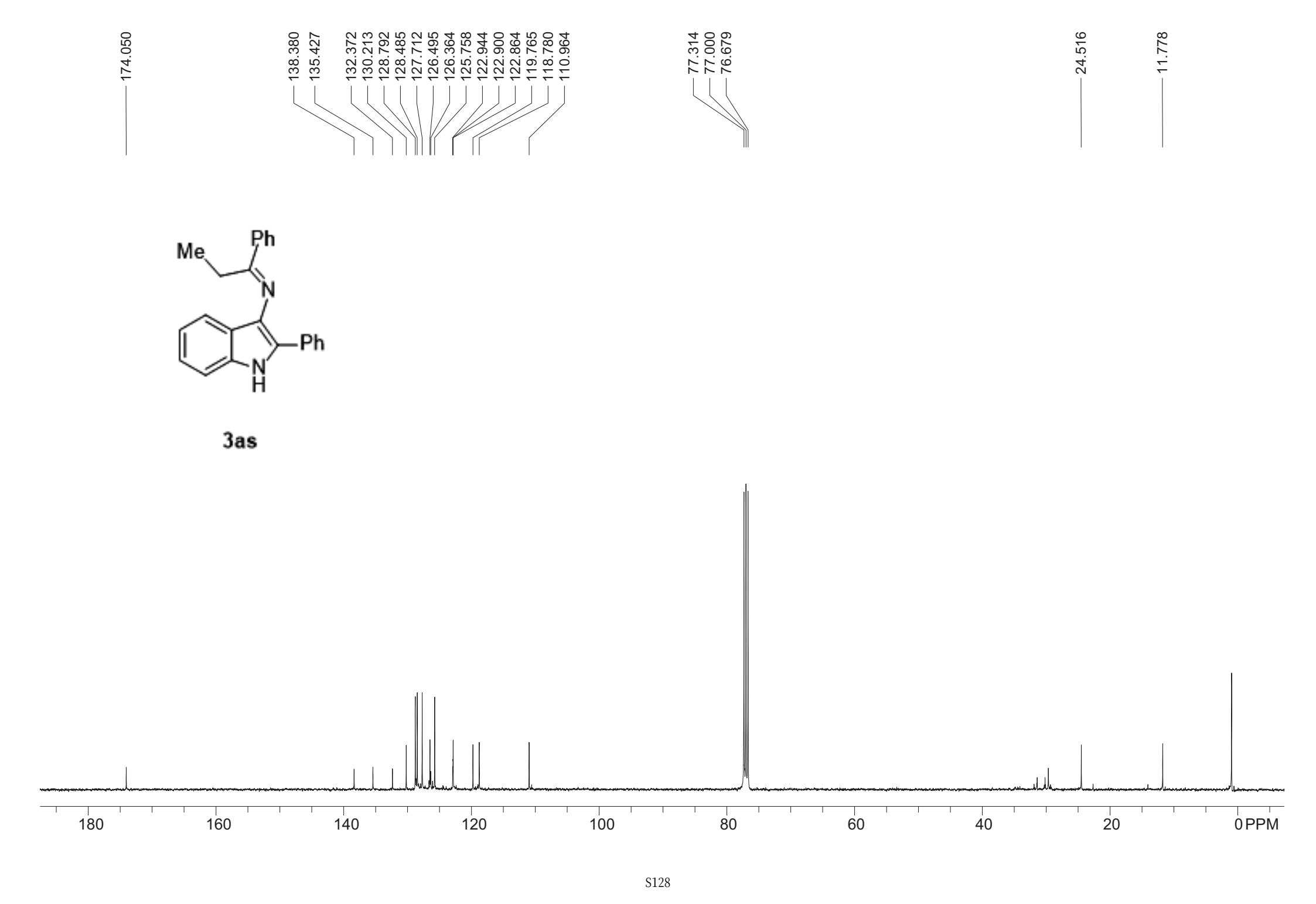
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H
3as
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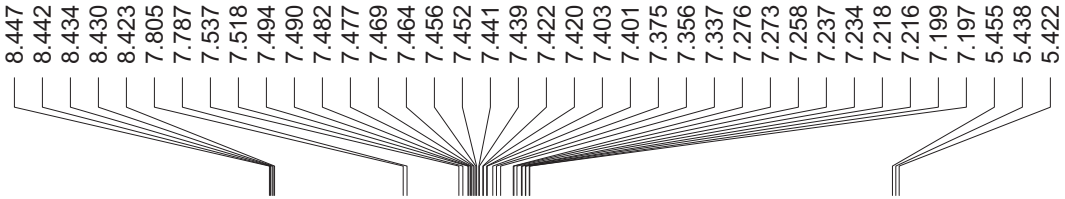
20
0 PPM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7.537
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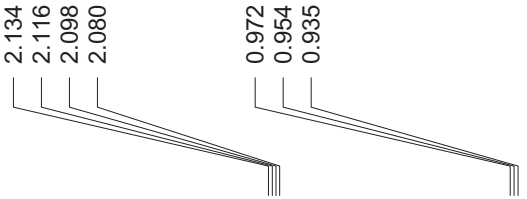
7.490
7.482
7.477
7.469
7.464
7.456
7.452
7.441
7.439
7.422
7.420
7.403
7.401
7.375
7.356
7.337
7.276
7.273
7.258
7.237
7.234
7.218
7.216
7.199
7.197
5.455
5.438
5.422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2.116
2.098
2.080
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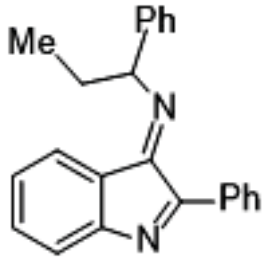
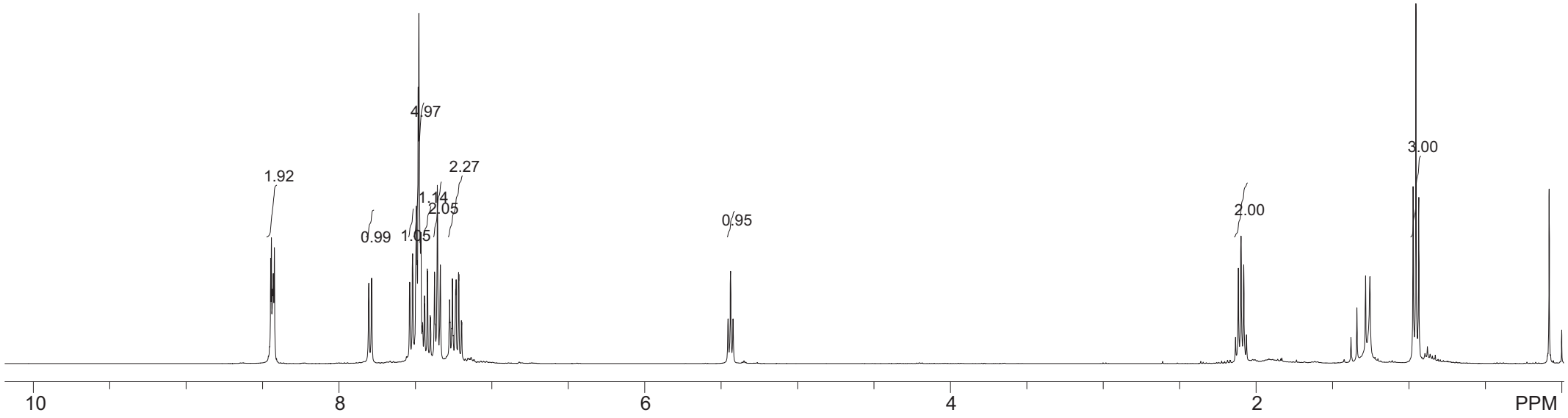
0.954
0.935


Me
Ph
N
Ph
N

4as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0.99
1.05
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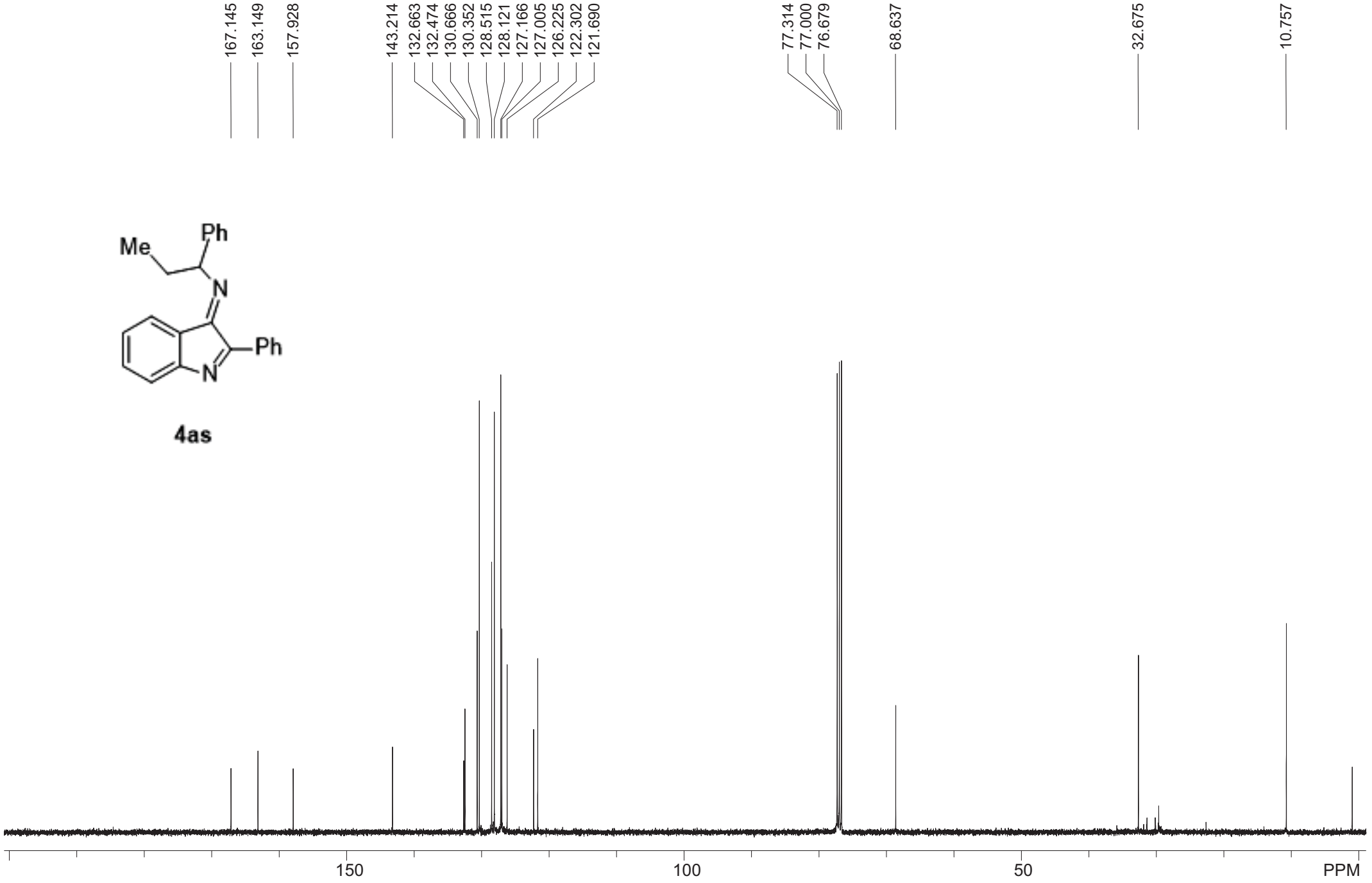
1.14
2.05
2.27
0.95
2.00
3.00
10
8
6
4
2
PPM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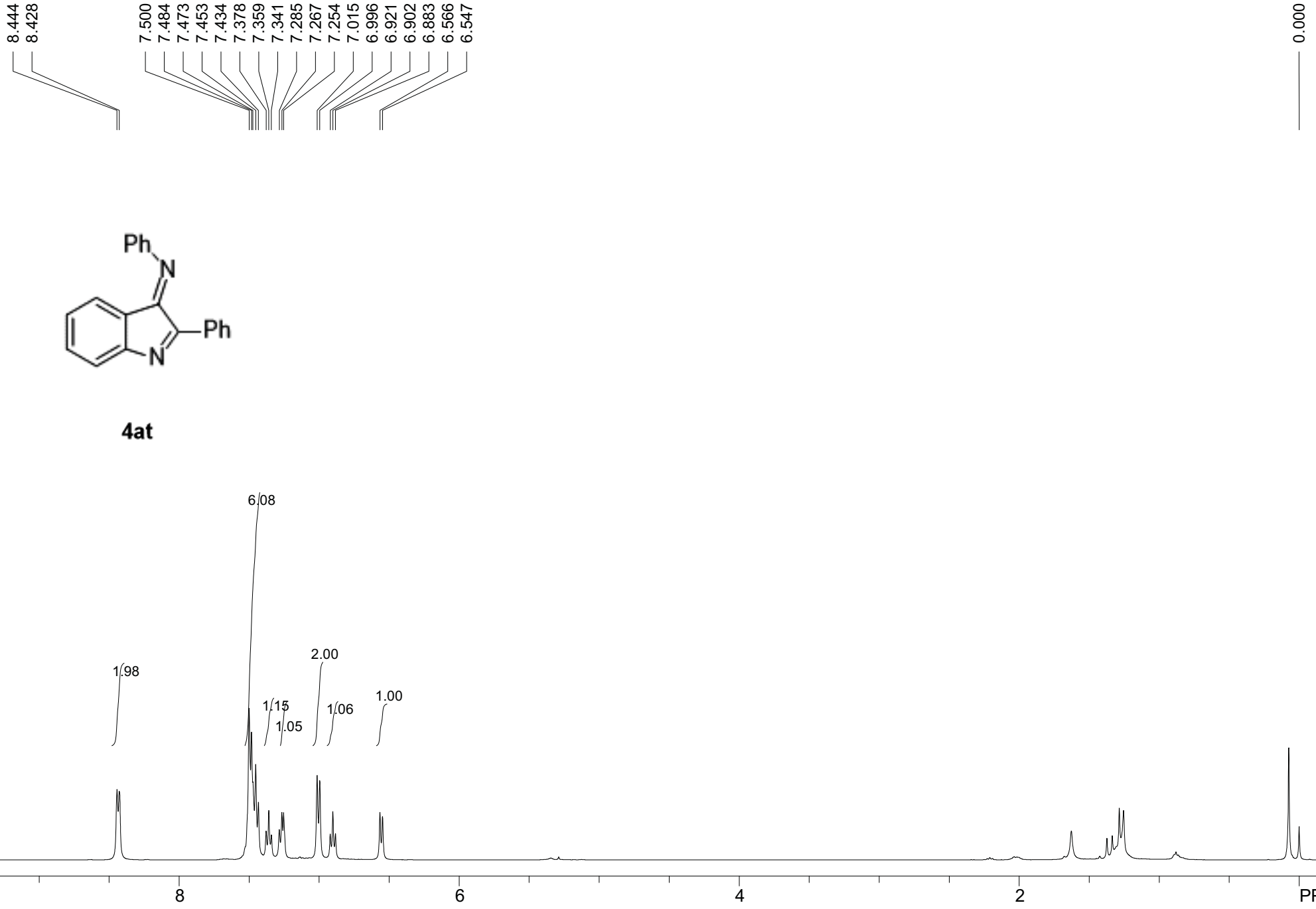
163.149
157.928
143.214
132.663
132.474
130.666
130.352
128.515
128.121
127.166
127.005
126.225
122.302
121.690
77.314
77.000
76.679
68.637
32.675
10.757
Me
Ph
N
Ph
N
4as
150
100
50
PPM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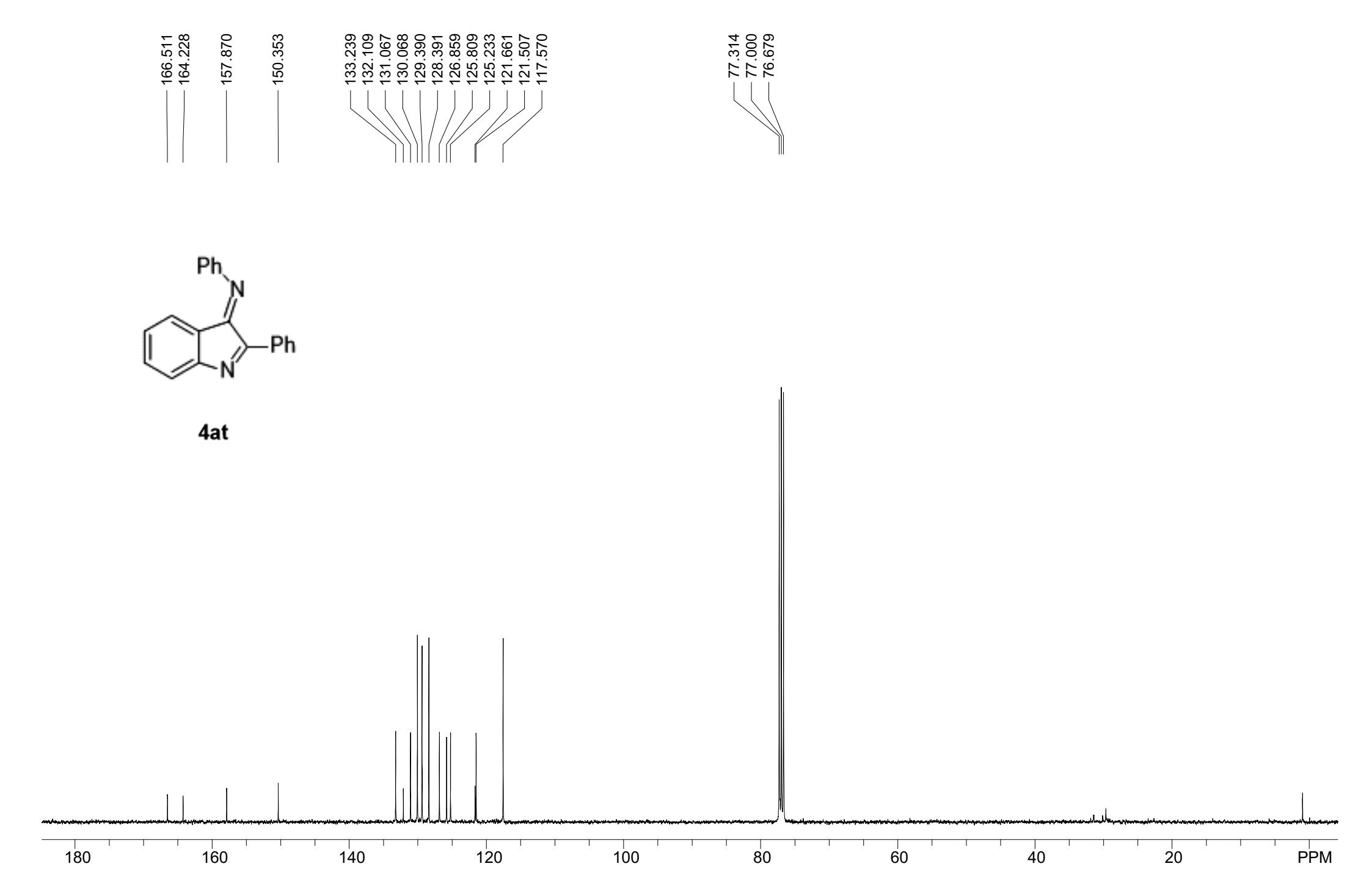
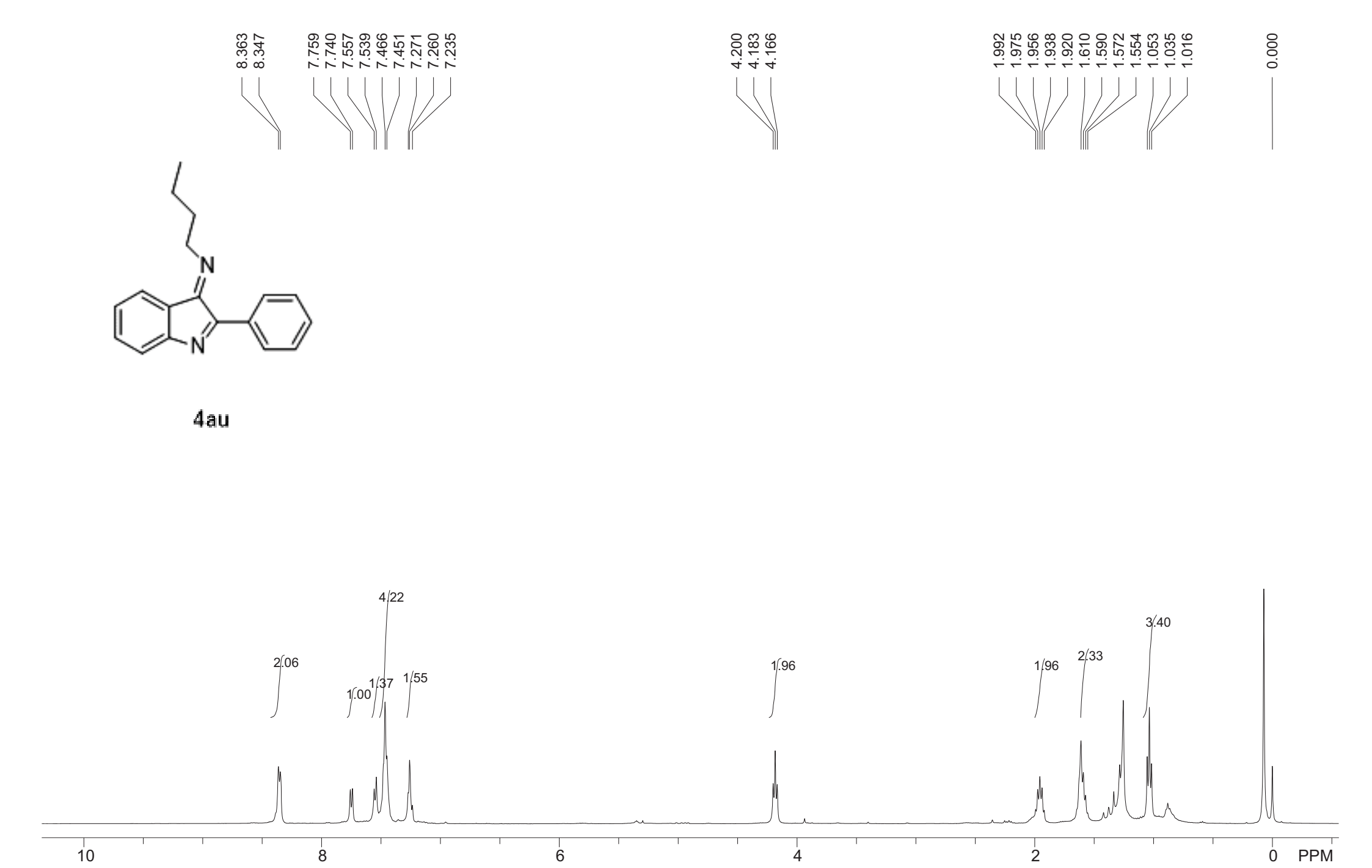
8.428
7.500
7.484
7.473
7.453
7.434
7.378
7.359
7.341
7.285
7.267
7.254
7.015
6.996
6.921
6.902
6.883
6.566
6.547
0.000
Ph
N
Ph
N
4at
6.08
1.98
2.00
1.15
1.05
1.06
1.00
8
6
4
2
PPM


166.511
164.228
157.870
150.353
133.239
132.109
131.067
130.068
129.390
128.391
126.859
125.809
125.233
121.661
121.507
117.570
77.314
77.000
76.679
Ph
N
Ph
N
4at
180
160
140
120
100
80
60
40
20
PPM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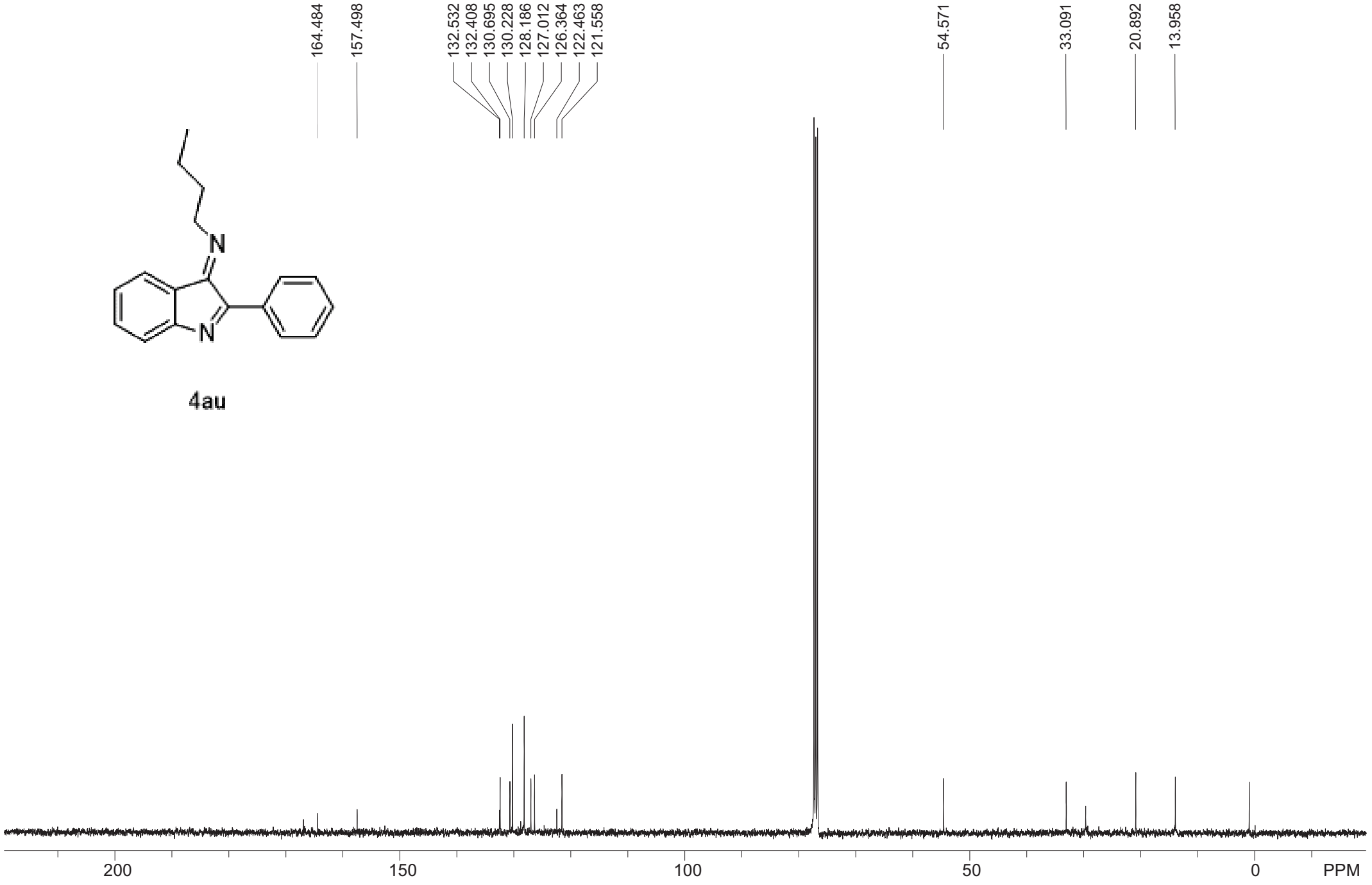
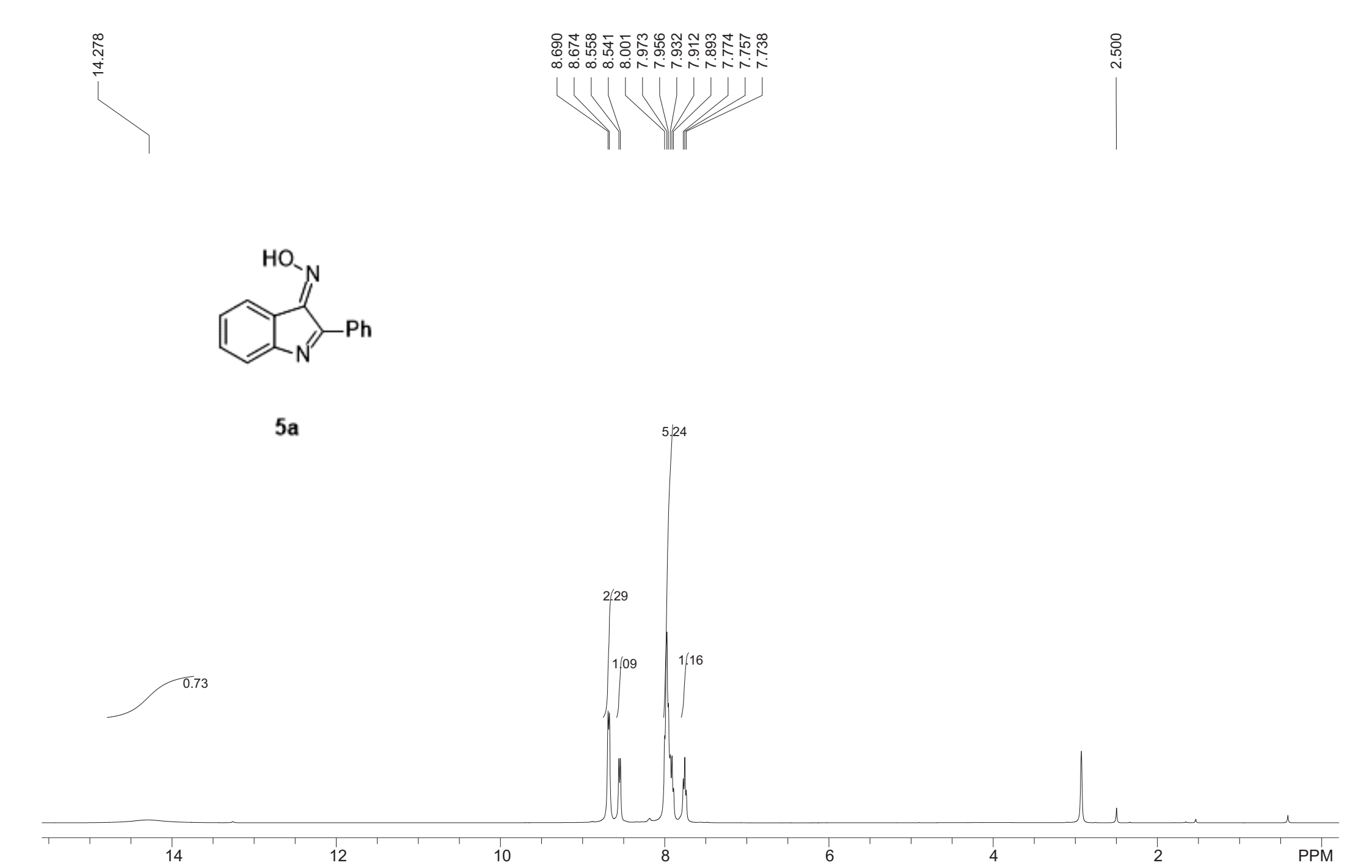
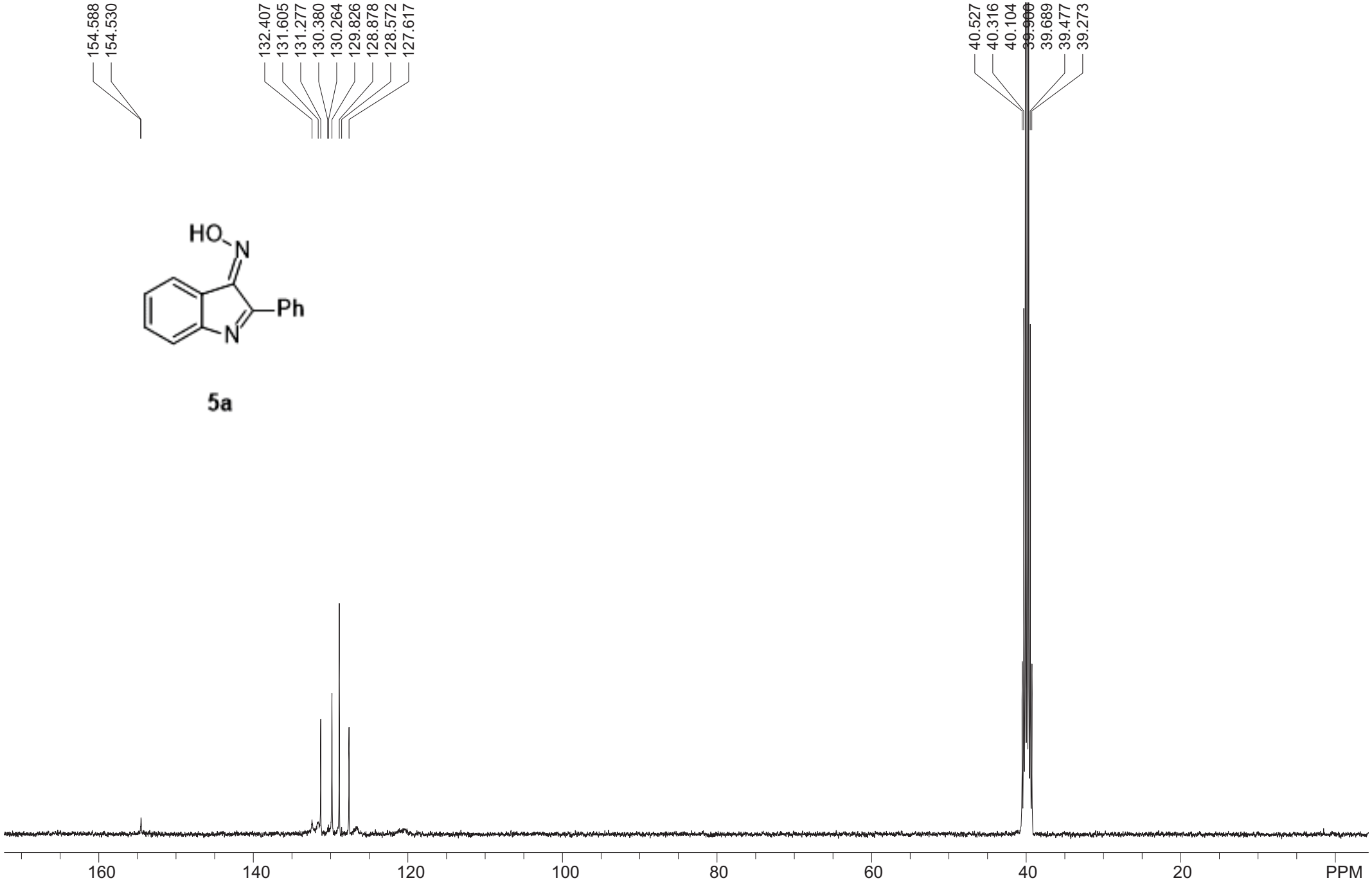
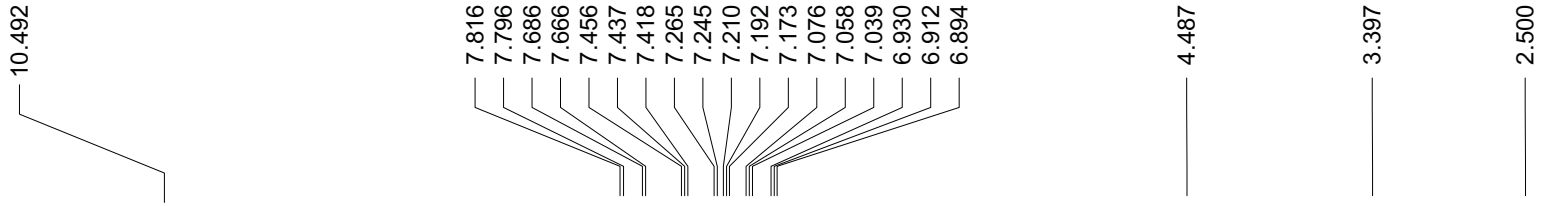
8.347
7.759
7.740
7.557
7.539
7.466
7.451
7.271
7.260
7.235
4.200
4.183
4.166
1.992
1.975
1.956
1.938
1.920
1.610
1.590
1.572
1.554
1.053
1.035
1.016
0.000
N
N
4au
4.22
2.06
1.00
1.37
1.55
1.96
1.96
2.33
3.40
10
8
6
4
2
0
PPM


164.484
157.498
132.532
132.408
130.695
130.228
128.186
127.012
126.364
122.463
121.558
54.571
33.091
20.892
13.958
N
N
4au
200
150
100
50
0
PPM


14.278
8.690
8.674
8.558
8.541
8.001
7.973
7.956
7.932
7.912
7.893
7.774
7.757
7.738
2.500
HO
N
Ph
N
5a
5.24
2.29
1.09
1.16
0.73
14
12
10
8
6
4
2
PPM


154.588
154.530
132.407
131.605
131.277
130.380
130.264
129.826
128.878
128.572
127.617
40.527
40.316
40.104
39.689
39.477
39.273
HO
N
Ph
N
160
140
120
100
80
60
40
20
PPM

5a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7.816
7.796
7.686
7.666
7.456
7.437
7.418
7.265
7.245
7.210
7.192
7.173
7.076
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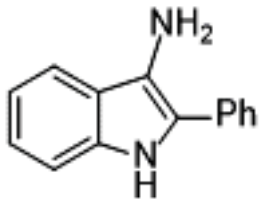
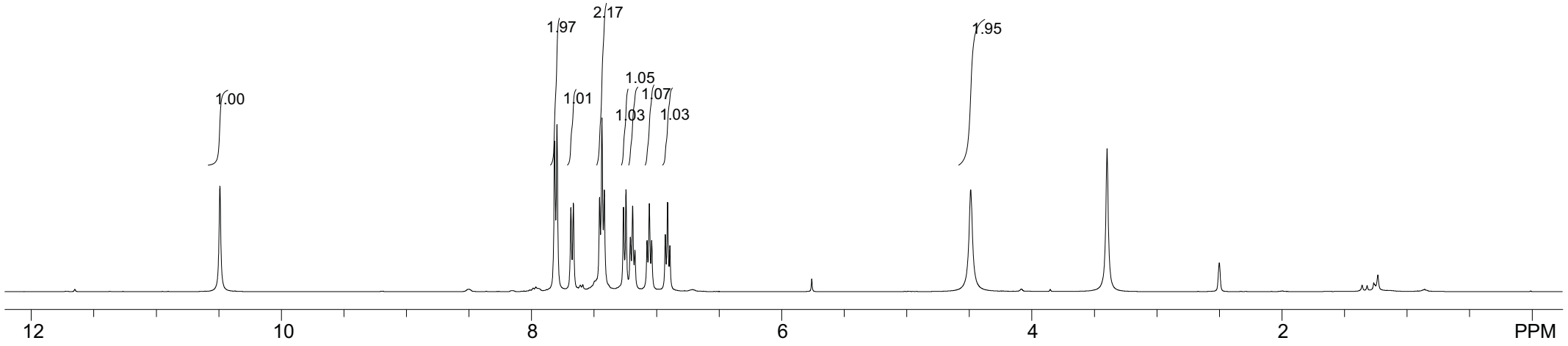
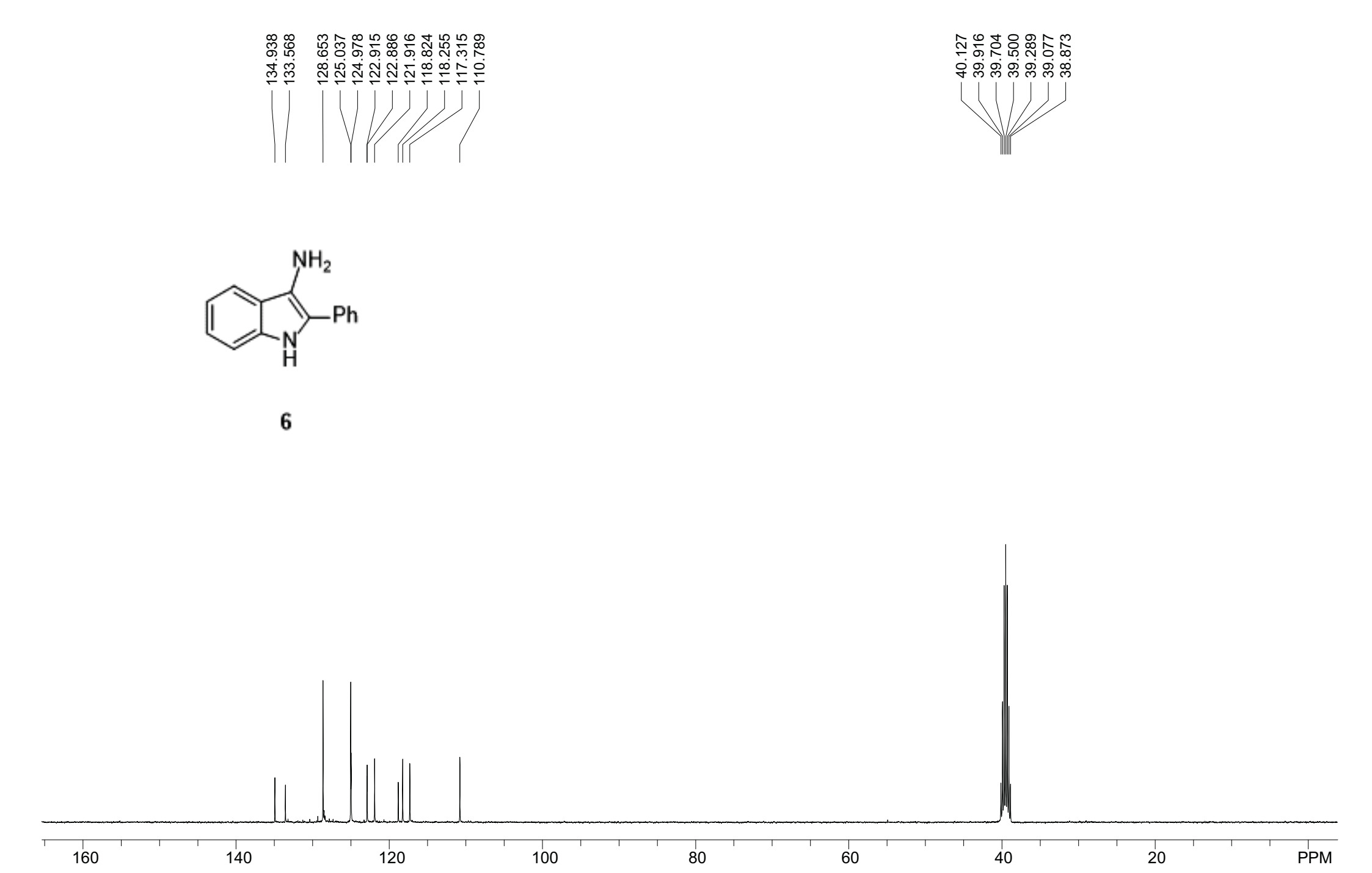
6.930
6.912
6.894
4.487
3.397
2.500


NH2
Ph
N
H

6


1.00
1.97
2.17
1.01
1.05
1.07
1.03
1.03
1.95
12
10
8
6
4
2
PPM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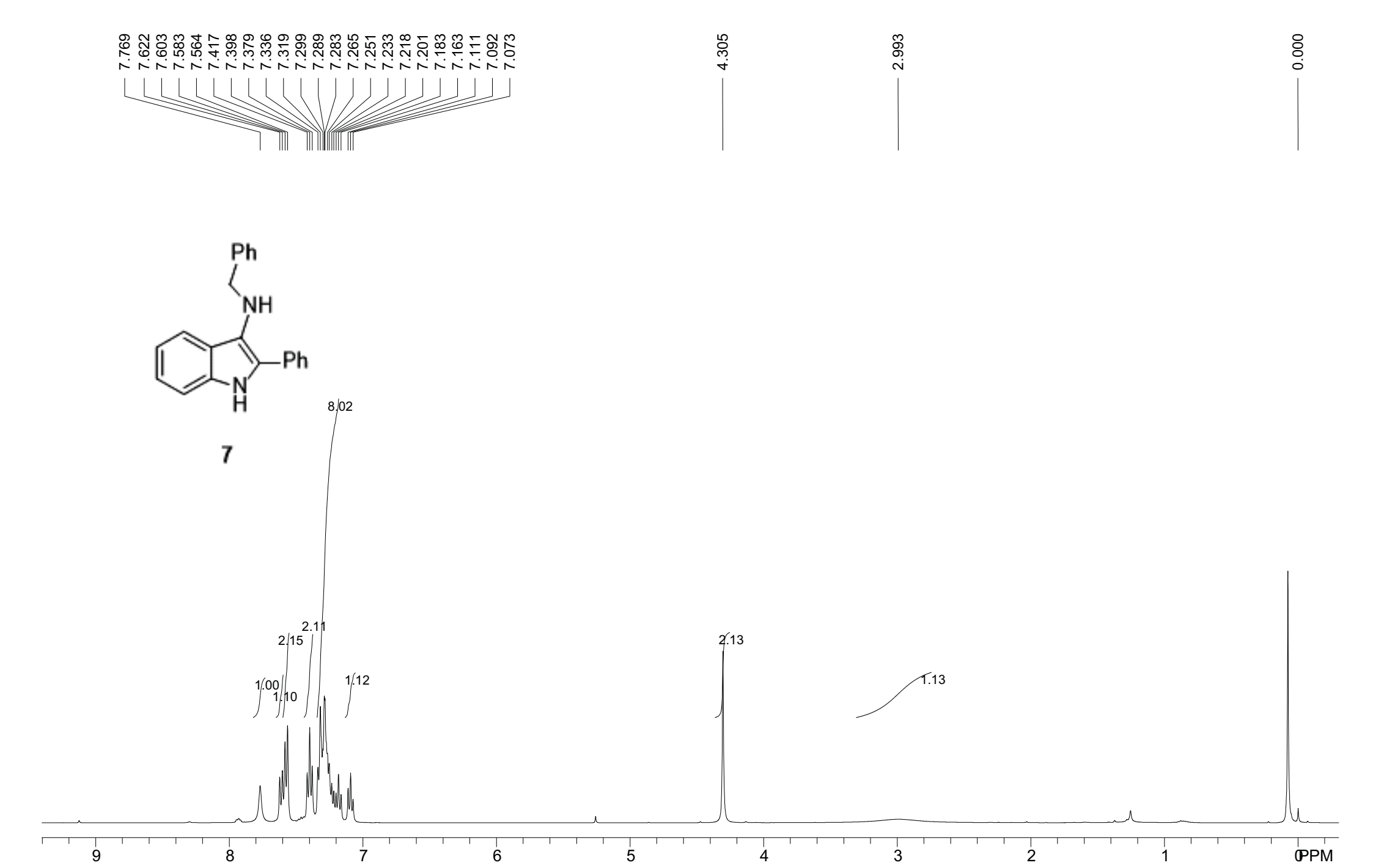
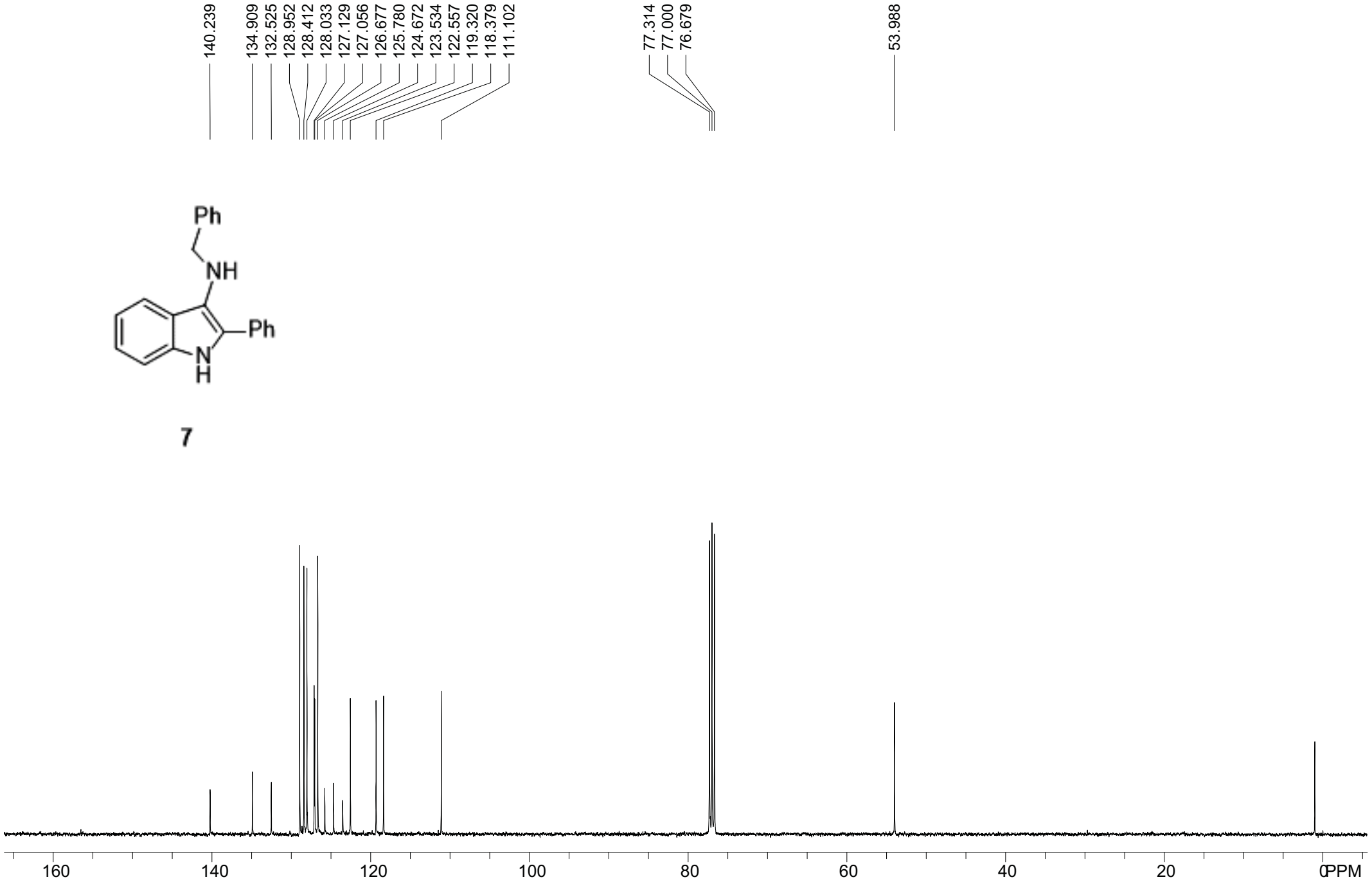
133.568
128.653
125.037
124.978
122.915
122.886
121.916
118.824
118.255
117.315
110.789
40.127
39.916
39.704
39.500
39.289
39.077
38.873
NH2
Ph
N
H
160
140
120
100
80
60
40
20
PPM

6


7.769
7.622
7.603
7.583
7.564
7.417
7.398
7.379
7.336
7.319
7.299
7.289
7.283
7.265
7.251
7.233
7.218
7.201
7.183
7.163
7.111
7.092
7.073
4.305
2.993
0.000
Ph
NH
Ph
N
H
7
8.02
2.11
2.15
1.00
1.10
1.12
2.13
1.13
9
8
7
6
5
4
3
2
1
0
PPM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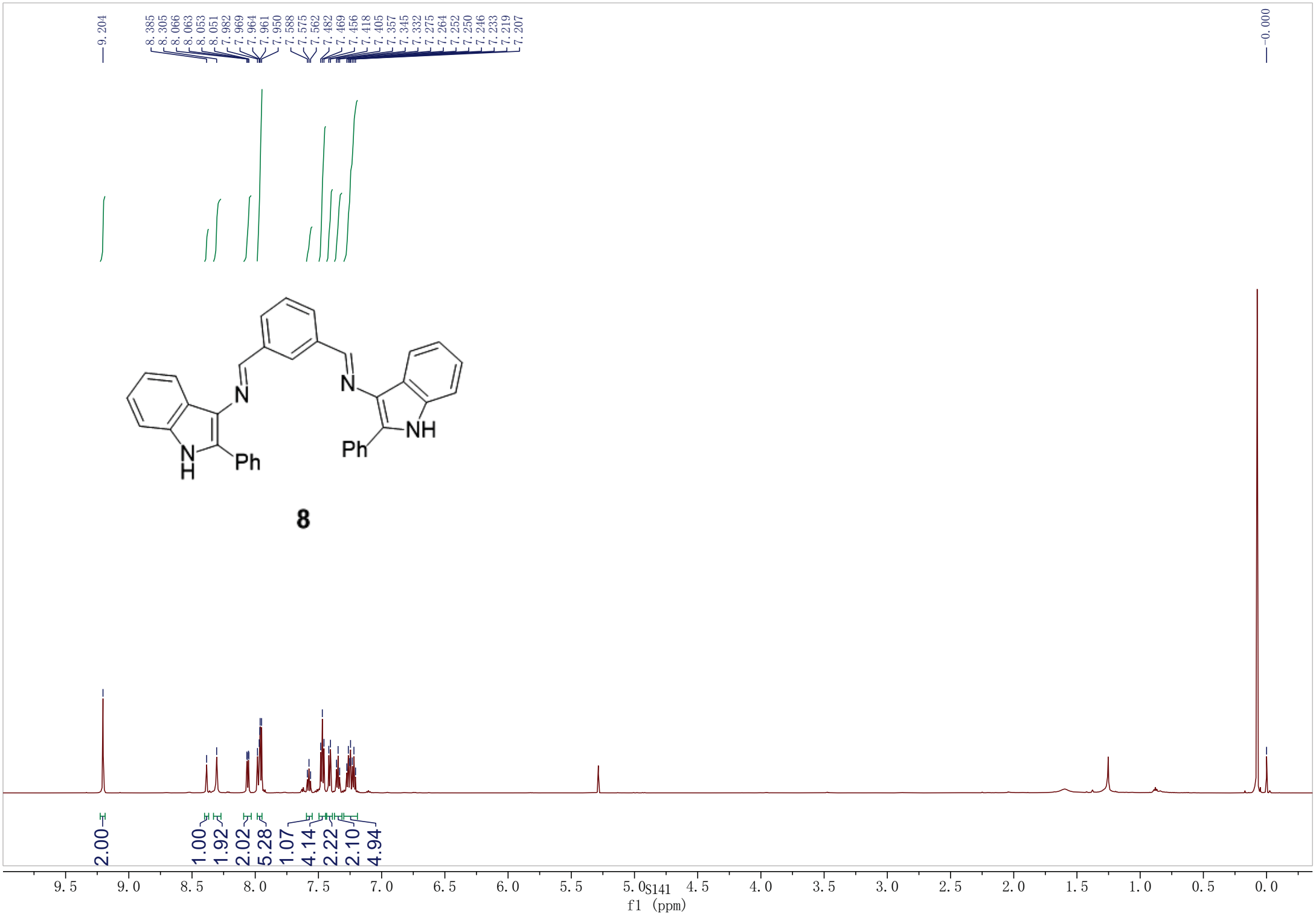
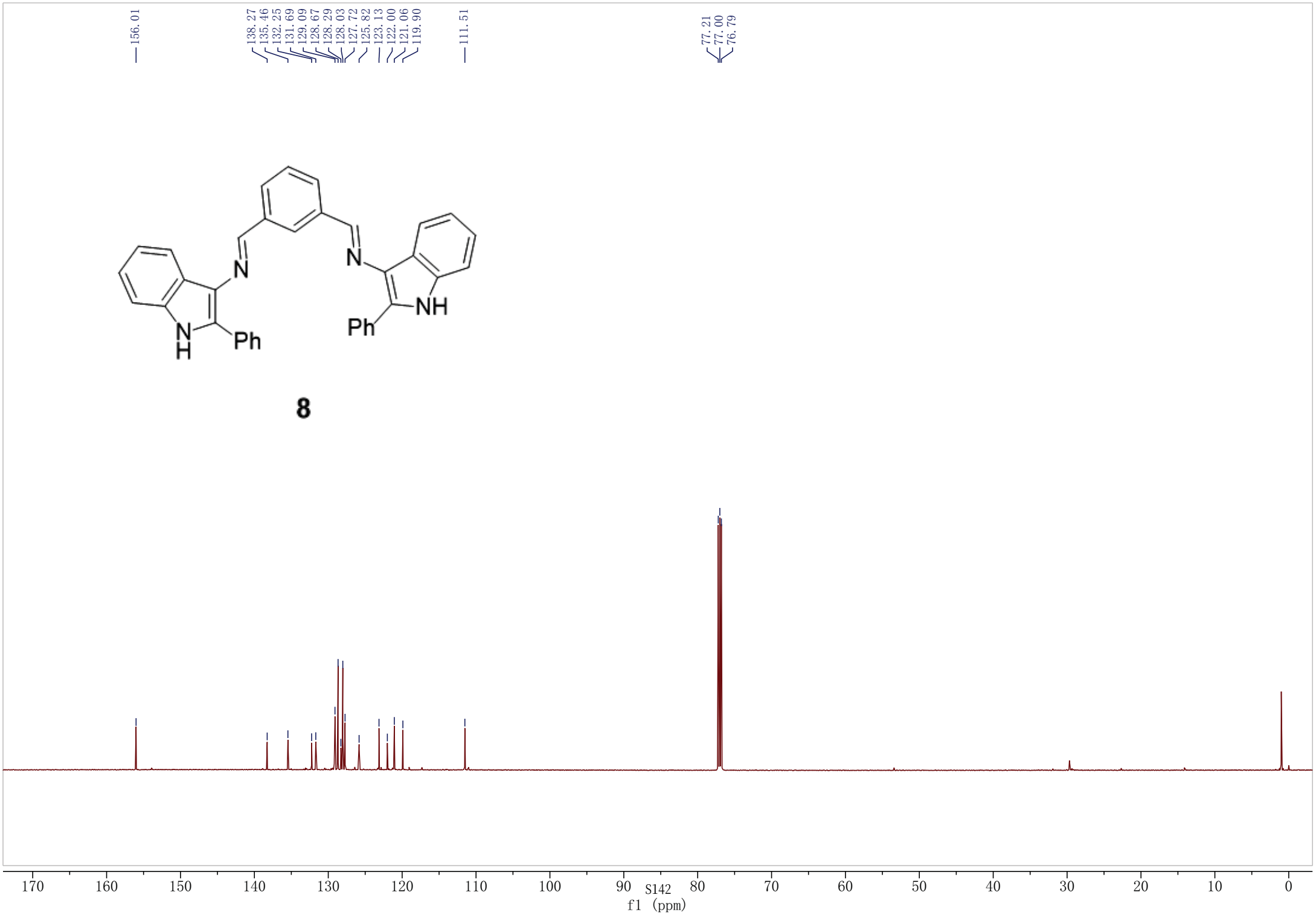
134.909
132.525
128.952
128.412
128.033
127.129
127.056
126.677
125.780
124.672
123.534
122.557
119.320
118.379
111.102
77.314
77.000
76.679
53.988
Ph
NH
Ph
N
H
160
140
120
100
80
60
40
20
0
PPM

7


9.204
8.385
8.305
8.066
8.063
8.053
8.051
7.982
7.969
7.964
7.961
7.950
7.588
7.575
7.562
7.482
7.469
7.456
7.418
7.405
7.357
7.345
7.332
7.275
7.264
7.252
7.250
7.246
7.233
7.219
7.207
0.000
N
N
H
Ph
N
NH
Ph
8
2.00
1.00
1.92
2.02
5.28
1.07
4.14
2.22
2.10
4.94
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
f1 (ppm)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135.46
132.25
131.69
129.09
128.67
128.29
128.03
127.72
125.82
123.13
122.00
121.06
119.90
111.51
77.21
77.00
76.79
N
N
H
Ph
N
NH
Ph
8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)