Supporting Information

Metal-Free Graphene Oxide-Catalyzed Aza-Semipinacol Rearrangement to Prepare 2-(Indol-2-yl)phenols and Benzofuro[3,2-b]indolines Containing Quaternary Carbon Centers

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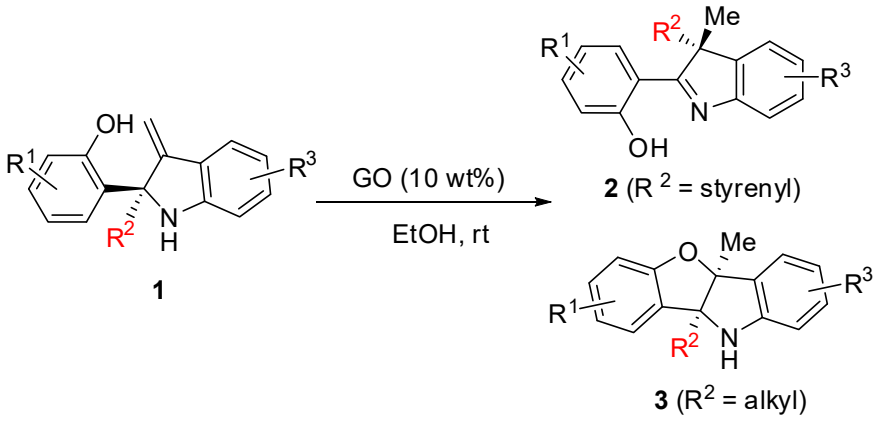
Contents

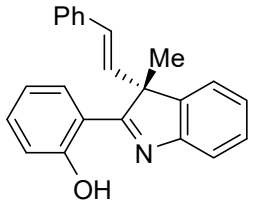
1. General Experimental Information:

^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 or 500 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. Indoline C2-tethered phenols **1a-1r**,[1] **1t**[1] and **1w-x**[1] was prepared according to literature method and their spectral data matched literature values.

2. Synthesis of compounds 2 and 3

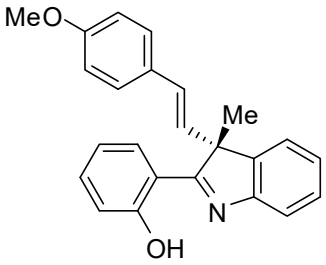


General procedure A: In a Teflon-sealed flask was charged with compound **1** (0.2 mmol), GO (6.5 mg, 10 wt%) and EtOH (2.0 mL). The reaction vessel was stirred vigorously at room temperature (about 25 °C) for 3-7 h until the substrate **1** disappeared (monitored by TLC). At this time, the reaction was filtered and washed with DCM. 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, 1/50 to 1/30, ethyl acetate/petroleum ether) to provide indolines **2** or **3**.



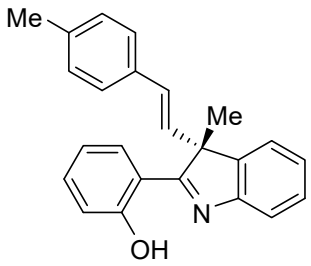
2a

(*E*)-2-(3-Methyl-3-styryl-3H-indol-2-yl)phenol (2a), yellow solid, 0.062 g, 96% yield. Mp: 143−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.00 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.40–7.27 (m, 8H), 7.24–7.21 (m, 1H), 7.11 (d, J = 8.4 Hz, 1H), 6.85–6.82 (m, 1H), 6.78 (d, J = 16.0 Hz, 1H), 6.28 (d, J = 16.0 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 161.9, 151.3, 143.6, 136.5, 132.9, 130.0, 129.4, 129.2, 128.6, 128.4, 127.9, 126.4, 122.4, 119.9, 118.5, 118.0, 115.7, 59.3, 22.5; IR (thin film) 3440, 3059, 2963, 1650, 1492, 1249, 743, 690 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{20}NO$ $[M + H]^+$: 326.1539, found 326.1534.



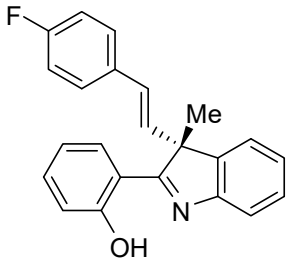
2b

(*E*)-2-(3-(4-Methoxystyryl)-3-methyl-3H-indol-2-yl)phenol (2b), yellow solid, 0.070 g, 99%. Mp: 148−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.03 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.39–7.34 (m, 2H), 7.32–7.27 (m, 4H), 7.11 (d, J = 8.0 Hz, 1H), 6.85–6.82 (m, 3H), 6.71 (d, J = 16.0 Hz, 1H), 6.13 (d, J = 16.0 Hz, 1H), 3.78 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 161.9, 159.4, 151.3, 143.9, 132.8, 129.5, 129.4, 129.3, 128.3, 127.6, 126.9, 126.4, 122.4, 119.9, 118.5, 118.0, 115.7, 114.0, 59.3, 55.3, 22.6; IR (thin film) 3461, 3061, 2856, 1652, 1496, 1261, 748, 652 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO_2$ $[M + H]^+$: 356.1645, found 356.1637.



2c

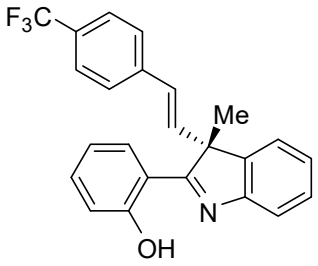
(*E*)-2-(3-Methyl-3-(4-methylstyryl)-3H-indol-2-yl)phenol (2c), yellow solid, 0.065 g, 96% yield. Mp: 158−159 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.92 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.40–7.37 (m, 3H), 7.30–7.24 (m, 3H), 7.06–7.03 (m, 3H), 6.90–6.86 (m, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 2.20 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.0, 161.8, 151.1, 144.6, 137.9, 134.1, 133.9, 130.4, 130.3, 129.9, 129.1, 128.6, 127.4, 127.0, 123.3, 120.3, 119.5, 118.3, 115.7, 59.8, 23.0, 21.4; IR (thin film) 3439, 3130, 2928, 2868, 1645, 1591, 1252, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO$ [M + H]$^{+}$: 340.1696, found 340.1674.



2d

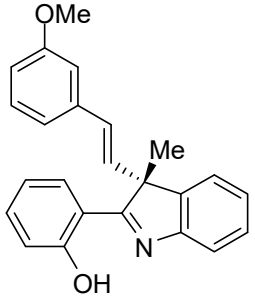
(*E*)-2-(3-(4-Fluorostyryl)-3-methyl-3H-indol-2-yl)phenol (2d), yellow solid, 0.050 g, 73% yield. Mp: 171−172 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, J = 7.6 Hz, 1H), 7.74 (dd, J = 8.4 Hz, 4.8 Hz, 1H), 7.43–7.37 (m, 4H), 7.30–7.22 (m, 4H), 7.06 (d, J = 8.4 Hz, 1H), 6.94–6.90 (m, 1H), 6.70 (d, J = 16.0 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.8, 163.5 (d, J = 243.5 Hz), 161.7, 151.1, 144.4, 133.8, 133.5 (d, J = 2.9 Hz), 130.2, 129.6, 129.2, 129.0, 128.9 127.3, 123.2, 120.2, 119.4, 118.2, 116.1 (d, J = 21.8 Hz), 115.6, 59.7, 22.9; ^{19}F NMR (376 MHz, DMSO-d_6) δ -232.6; IR (thin film) 3439, 3067, 2961, 2872, 1623, 1509,

1232, 762, 692 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}FNO$ $[M + H]^+$: 344.1445, found 344.1437.



2e

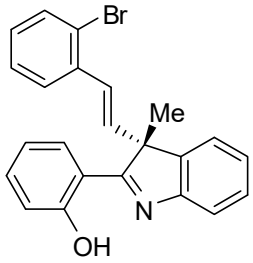
(*E*)-2-(3-Methyl-3-(4-(trifluoromethyl)styryl)-3H-indol-2-yl)phenol (2e), yellow solid, 0.067 g, 85% yield. Mp: 120−121 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.84 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.66–7.61 (m, 4H), 7.47–7.39 (m, 3H), 7.35–7.31 (m, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.93–6.90 (m, 1H), 6.85 (d, J = 16.4 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.7, 161.8, 151.3, 144.2, 141.1, 134.1, 133.1, 130.3, 129.4, 129.3, 129.1 (q, J = 31.4 Hz), 128.9 (q, J = 264.7 Hz), 127.8, 127.6, 126.3 (q, J = 3.6 Hz), 123.5, 120.9, 119.7, 118.4, 115.7, 59.9, 22.9; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.0; IR (thin film) 3446, 3074, 2927, 2856, 1648, 1592, 1259, 801, 753 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{19}F_3NO$ $[M + H]^+$: 394.1413, found 394.1423.



2f

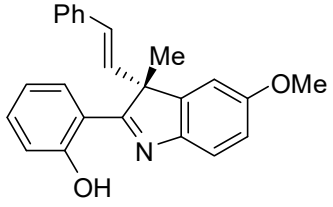
(*E*)-2-(3-(3-Methoxystyryl)-3-methyl-3H-indol-2-yl)phenol (2f), yellow oil, 0.053 g, 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.89 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.47–7.40 (m, 3H), 7.35–7.31 (m, 1H), 7.22–7.18 (m, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.02 (s, 2H), 6.95–6.91 (m, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.72 (d, J = 16.0 Hz, 1H), 6.57 (d, J = 16.4 Hz, 1H), 3.71 (s, 3H), 1.77 (s, 3H); ^{13}C

NMR (100 MHz, DMSO-d_6) δ 183.8, 161.6, 160.0, 151.0, 144.4, 138.3, 133.7, 130.3, 130.2, 130.1, 130.0, 128.9, 127.3, 123.2, 120.2, 119.5, 119.3, 118.1, 115.6, 114.4, 111.8, 59.6, 55.6, 22.9; IR (thin film) 3426, 3068, 2958, 2866, 1681, 1595, 1254, 753, 690 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO_2$ $[M + H]^+$: 356.1645, found 356.1649.



2g

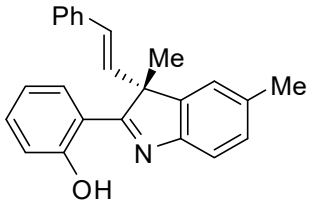
(*E*)-2-(3-(2-Bromostyryl)-3-methyl-3H-indol-2-yl)phenol (2g), yellow oil, 0.063 g, 78% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.85 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.69–7.68 (m, 1H), 7.54–7.53 (m, 2H), 7.48–7.40 (m, 3H), 7.35–7.26 (m, 2H), 7.17–7.14 (m, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.95–6.92 (m, 1H), 6.85 (d, J = 16.0 Hz, 1H), 6.52–6.46 (m, 1H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.5, 161.7, 151.2, 144.1, 136.5, 134.0, 133.7, 133.4, 130.4, 130.3, 129.3, 129.1, 128.7, 128.1, 127.5, 123.5, 123.3, 120.5, 119.6, 118.4, 115.6, 60.0, 23.1; IR (thin film) 3437, 3065, 2928, 2868, 1638, 1590, 1253, 752 , 665 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}BrNO$ $[M + H]^+$: 404.0645, found 404.0633.



2h

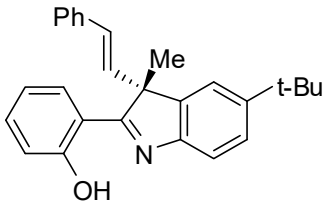
(*E*)-2-(5-Methoxy-3-methyl-3-styryl-3H-indol-2-yl)phenol (2h), yellow solid, 0.061 g, 86% yield. Mp: 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.92 (s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.37–7.35 (m, 2H), 7.32–7.28 (m, 3H), 7.23–7.22 (m, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.92 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.85–6.80 (m, 2H), 6.77 (d, J = 16.0 Hz, 1H), 6.28 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H),

1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 161.4, 159.0, 145.5, 145.0, 136.5, 132.3, 130.0, 129.4, 128.9, 128.6, 127.9, 126.4, 120.5, 118.4, 117.9, 115.9, 113.5, 108.6, 59.5, 55.8, 22.6; IR (thin film) 3448, 3067, 2964, 2858, 1652, 1510, 1261, 747, 691 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO_2$ $[M + H]^+$: 356.1645, found 356.1638.



2i

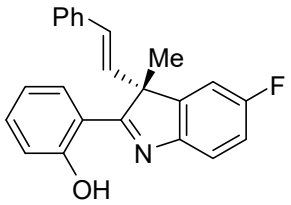
(*E*)-2-(3,5-Dimethyl-3-styryl-3H-indol-2-yl)phenol (2i), yellow oil, 0.051 g, 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.89 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.43–7.41 (m, 2H), 7.38 (d, J = 7.2 Hz, 1H), 7.30–7.25 (m, 3H), 7.22–7.21 (m, 2H), 7.05 (d, J = 8.4 Hz, 1H), 6.92–6.88 (m, 1H), 6.74 (d, J = 16.4 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 2.35 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 182.9, 161.5, 148.9, 144.6, 137.0, 136.8, 133.5, 130.2, 130.0, 129.8, 129.5, 129.1, 128.3, 127.0, 123.7, 119.8, 119.3, 118.1, 115.7, 59.5, 22.9, 21.6; IR (thin film) 3438, 3028, 2928, 2864, 1627, 1584, 1254, 750, 694 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO$ $[M + H]^+$: 340.1696, found 340.1689.



2j

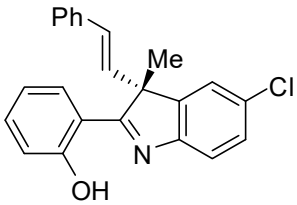
(*E*)-2-(5-tert-Butyl-3-methyl-3-styryl-3H-indol-2-yl)phenol (2j), yellow solid, 0.053 g, 70% yield. Mp: 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.05 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.38−7.36 (m, 2H), 7.32−7.28 (m, 4H), 7.25−7.22 (m, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 16.0 Hz, 1H), 6.28 (d, J = 16.0 Hz, 1H), 1.79 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 161.7, 150.1, 149.1, 143.4, 136.7, 132.6,

129.9, 129.6, 129.2, 128.6, 127.8, 126.5, 125.5, 119.2, 119.1, 118.4, 118.0, 115.9, 59.4, 35.0, 31.6, 22.6; IR (thin film) 3446, 3068, 2963, 2857, 1652, 1579, 1260, 768, 691 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{28}NO$ $[M + H]^+$: 382.2165, found 382.2157.



2k

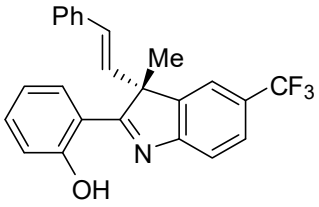
(*E*)-2-(5-Fluoro-3-methyl-3-styryl-3H-indol-2-yl)phenol (2k), yellow oil, 0.053 g, 77% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.50–7.39 (m, 5H), 7.34–7.31 (m, 1H), 7.13–7.09 (m, 2H), 7.07 (d, J = 8.4 Hz, 1H), 6.94–6.91 (m, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.48 (d, J = 16.4 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.0, 163.1 (d, J = 242.8 Hz), 161.4, 147.3, 147.0, 146.9, 136.8, 133.8, 130.9, 130.2, 129.2, 128.5, 127.1, 121.5 (d, J = 8.7 Hz), 119.4, 118.2, 115.9 (d, J = 23.3 Hz), 115.5, 111.1 (d, J = 24.7 Hz), 60.2 (d, J = 2.2 Hz), 22.9; ^{19}F NMR (376 MHz, DMSO-d_6) δ -233.2; IR (thin film) 3441, 3061, 2962, 2872, 1626, 1583, 1257, 750, 694 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}FNO$ $[M + H]^+$: 344.1445, found 344.1436.



2l

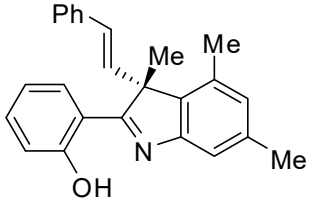
(*E*)-2-(5-Chloro-3-methyl-3-styryl-3H-indol-2-yl)phenol (2l), yellow solid, 0.052 g, 72% yield. Mp: 113−114 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 13.74 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.36–7.28 (m, 7H), 7.11 (d, J = 8.4 Hz, 1H), 6.86–6.82 (m, 1H), 6.78 (d, J = 16.4 Hz, 1H), 6.78 (d, J = 16.4 Hz, 1H), 6.26 (d, J = 16.4 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.3, 161.8, 149.9, 145.4, 136.2, 133.2, 132.2, 130.6, 129.4, 128.7, 128.6, 128.3, 128.1, 126.5, 122.9, 120.8,

118.6, 118.1, 115.4, 59.6, 22.4; IR (thin film) 3450, 3068, 2926, 2867, 1651, 1494, 1260, 749, 688 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}ClNO$ $[M + H]^+$: 360.1150, found 360.1140.



2m

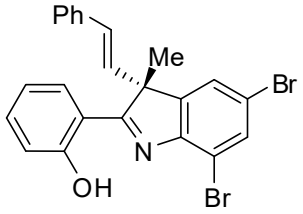
(E)-2-(3-Methyl-3-styryl-5-(trifluoromethyl)-3H-indol-2-yl)phenol (2m), yellow oil, 0.059 g, 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.71 (s, 1H), 7.92–7.87 (m, 3H), 7.80 (d, J = 7.6 Hz, 1H), 7.48–7.43 (m, 3H), 7.31–7.27 (m, 2H), 7.24–7.21 (m, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.97–6.93 (m, 1H), 6.76 (d, J = 16.0 Hz, 1H), 6.60 (d, J = 16.4 Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 186.7, 162.0, 154.2, 145.5, 136.7, 134.6, 131.1, 130.7, 129.1, 129.0 (q, J = 271.2 Hz), 128.7, 128.5, 127.9 (q, J = 30.6 Hz), 127.0, 126.6 (q, J = 3.7 Hz), 120.8, 120.3 (q, J = 3.6 Hz), 119.6, 118.4, 115.2, 60.0, 22.7; ^{19}F NMR (376 MHz, DMSO-d_6) δ -59.9; IR (thin film) 3438, 3030, 2930, 2856, 1640, 1518, 1257, 749, 694 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{19}F_3NO$ $[M + H]^+$: 394.1413, found 394.1409.



2n

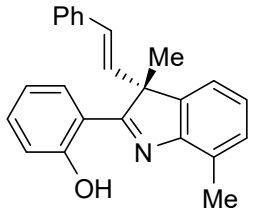
(*E*)-2-(3,4,6-Trimethyl-3-styryl-3H-indol-2-yl)phenol (2n), yellow solid, 0.060 g, 85% yield. Mp: 140−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.10 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.36–7.28 (m, 6H), 7.23–7.21 (m, 1H), 7.09 (d, J = 8.4 Hz, 1H), 6.85–6.80 (m, 2H), 6.74 (d, J = 16.4 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 162.0, 151.9, 138.5, 137.9, 136.6, 133.1, 132.6, 131.1, 129.5, 129.2, 128.6, 127.9, 127.8, 126.4, 118.4, 118.3 118.0, 115.5, 59.7, 21.3, 19.5, 17.6; IR (thin film) 3441, 3029, 2962, 2862,

1652, 1589, 1259, 763, 687 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO$ $[M + H]^+$: 354.1852, found 354.1845.



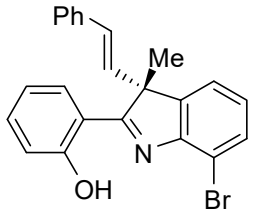
2o

(*E*)-2-(5,7-Dibromo-3-methyl-3-styryl-3H-indol-2-yl)phenol (2o), yellow solid, 0.087 g, 90% yield. Mp: 188−189 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 13.59 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.37–7.34 (m, 3H), 7.32 (s, 1H), 7.30–7.25 (m, 2H), 7.13 (d, J = 8.4 Hz, 1H), 6.86–6.83 (m, 1H), 6.77 (d, J = 16.0 Hz, 1H), 6.25 (d, J = 16.0 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 162.1, 149.2, 146.6, 136.0, 134.1, 133.8, 131.1, 129.5, 128.8, 128.3, 127.5, 126.5, 124.8, 120.2, 118.8, 118.4, 115.1, 114.2, 61.4, 22.6; IR (thin film) 3446, 3029, 2926, 2868, 1652, 1570, 1260, 750, 691 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{18}Br_2NO$ $[M + H]^+$: 481.9750, found 481.9746.



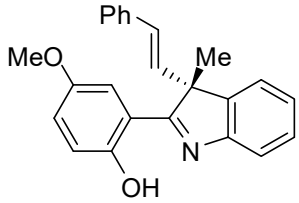
2p

(*E*)-2-(3,7-Dimethyl-3-styryl-3H-indol-2-yl)phenol (2p), yellow solid, 0.067 g, 99% yield. Mp: 127−128 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 14.19 (s, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.35–7.34 (m, 3H), 7.30–7.27 (m, 2H), 7.24–7.10 (m, 5H), 6.86–6.83 (m, 1H), 6.77 (d, J = 16.0 Hz, 1H), 6.27 (d, J = 16.0 Hz, 1H), 2.62 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 162.8, 149.9, 143.3, 136.6, 132.7, 129.9, 129.7, 129.6, 129.4, 129.3, 128.6, 127.8, 126.5, 126.4, 119.8, 118.5 118.0, 115.8, 59.6, 22.5, 16.9; IR (thin film) 3447, 3028, 2926, 2869, 1652, 1511, 1260, 761, 693 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO$ $[M + H]^+$: 340.1696, found 340.1686.



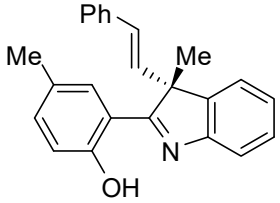
2q

(E)-2-(7-Bromo-3-methyl-3-styryl-3H-indol-2-yl)phenol (2q), yellow solid, 0.069 g, 85% yield. Mp: 118−119 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.46–7.42 (m, 4H), 7.28–7.21 (m, 4H), 7.09 (d, J = 8.4 Hz, 1H), 6.96–6.92 (m, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.56 (d, J = 16.4 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.8, 161.8, 149.5, 146.3, 136.7, 134.4, 131.8, 130.9, 130.4, 129.2, 129.1, 128.9, 128.5, 127.0, 122.6, 119.6, 118.4, 115.4, 113.1, 61.6, 22.8; IR (thin film) 3382, 3043, 2931, 2869, 1616, 1577, 1256, 755, 695 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}BrNO$ $[M + H]^+$: 404.0645, found 404.0636.



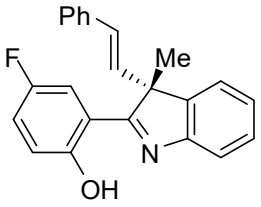
2r

(*E*)-4-Methoxy-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2r), yellow solid, 0.050 g, 71% yield. Mp: 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.5 (s, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.40–7.21 (m, 9H), 7.05 (d, J = 9.2 Hz, 1H), 6.99–6.96 (m, 1H), 6.85 (d, J = 16.0 Hz, 1H), 6.26 (d, J = 15.6 Hz, 1H), 3.66 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5, 156.1, 151.5, 151.4, 143.6, 136.5, 130.1, 129.4, 128.7, 128.4, 127.9, 126.5, 126.3, 122.3, 120.3, 120.0, 118.6, 115.3, 112.6, 59.3, 55.7, 22.2; IR (thin film) 3450, 3054, 2930, 2855, 1637, 1590, 1273, 738, 692 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO_2$ $[M + H]^+$: 356.1645, found 356.1642.



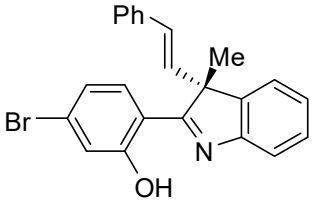
2s

(*E*)-4-Methyl-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2s), yellow solid, 0.058 g, 85% yield. Mp: 127−128 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.69 (s, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.62 (s, 1H), 7.46–7.39 (m, 4H), 7.33–7.26 (m, 3H), 7.23–7.20 (m, 2H), 6.97 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 16.4 Hz, 1H), 6.51 (d, J = 16.4 Hz, 1H), 2.20 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.7, 159.6, 151.1, 144.5, 136.9, 134.7, 130.4, 129.9, 129.8, 129.2, 129.0, 128.3, 127.8, 127.3, 126.9, 123.2, 120.2, 118.1, 115.3, 59.7, 23.0, 20.8; IR (thin film) 3440, 3054, 2962, 2868, 1638, 1591, 1257, 743, 689 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO$ $[M + H]^+$: 340.1696, found 340.1689.



2t

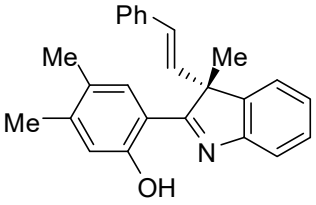
(*E*)-4-Fluoro-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2t), yellow solid, 0.062 g, 90% yield. Mp: 152−153 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.76 (s, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.41–7.38 (m, 1H), 7.36–7.35 (m, 2H), 7.31–7.29 (m, 4H), 7.25–7.23 (m, 1H), 7.10–7.04 (m, 2H), 6.79 (d, J = 16.0 Hz, 1H), 6.23 (d, J = 16.0 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9 (d, J = 3.6 Hz), 158.0, 155.8 (d, J = 235.0 Hz), 151.1, 143.7, 136.3, 130.6, 128.7, 128.6, 128.5, 128.0, 126.8, 126.5, 122.4, 120.2 (d, J = 31.0 Hz), 120.1, 119.0, 118.9, 114.5 (d, J = 24.6 Hz), 59.4, 22.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ -124.7; IR (thin film) 3451, 3048, 2926, 2869, 1652, 1560, 1384, 656 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}FNO$ $[M + H]^+$: 344.1445, found 344.1437.



2u

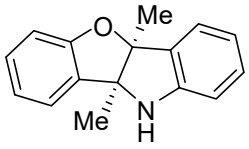
(*E*)-5-Bromo-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2u), yellow oil, 0.062 g, 77% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.23 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H),

7.73 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.44–7.42 (m, 3H), 7.37–7.33 (m, 1H), 7.31–7.27 (m, 3H), 7.24–7.21 (m, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 16.0 Hz, 1H), 6.53 (d, J = 16.4 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.1, 162.4, 150.7, 144.4, 136.7, 131.6, 130.6, 129.3, 129.1, 129.0, 128.4, 127.6, 127.0, 126.8, 123.3, 122.6, 120.9, 120.4, 114.8, 59.6, 22.7; IR (thin film) 3433, 3028, 2929, 2869, 1644, 1480, 1283, 826, 765 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}BrNO$ $[M + H]^+$: 404.0645, found 404.0639.



2v

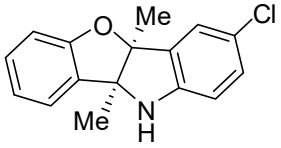
(*E*)-4,5-Dimethyl-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2v), yellow solid, 0.066 g, 93% yield. Mp: 131−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.77 (s, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.55 (s, 1H), 7.35–7.33 (m, 3H), 7.30–7.28 (m, 3H), 7.23–7.22 (m, 2H), 6.92 (s, 1H), 6.78 (d, J = 16.0 Hz, 1H), 6.27 (d, J = 16.0 Hz, 1H), 2.24 (s, 3H), 2.15 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 160.1, 151.6, 143.5, 142.8, 136.7, 129.9, 129.7, 129.6, 128.6, 128.3, 127.7, 126.5, 126.4, 126.0, 122.3, 119.6, 118.8, 113.4, 59.2, 22.6, 20.2, 19.2; IR (thin film) 3443, 3025, 2964, 2858, 1629, 1573, 1262, 741, 689 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO$ $[M + H]^+$: 354.1852, found 354.1849.



3wa

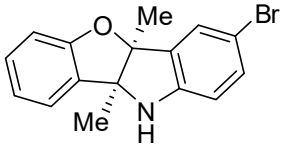
4b,9b-Dimethyl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3wa), white solid, 0.032 g, 67% yield. Mp: 180−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 1H), 7.25–7.22 (m, 1H), 7.15−7.11 (m, 2H), 6.91−6.87 (m, 1H), 6.83−6.76 (m, 2H), 6.62 (d, J = 8.0 Hz, 1H), 4.20 (brs, 1H), 1.73 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 149.0, 133.1, 130.4, 130.1, 129.3, 124.5, 122.9, 120.7,

119.5, 110.6, 110.5, 97.3, 72.5, 22.4, 20.4; IR (thin film) 3406, 2925, 2866, 1612, 1463, 1262, 748 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{16}NO$ $[M + H]^+$: 238.1226, found 238.1223.



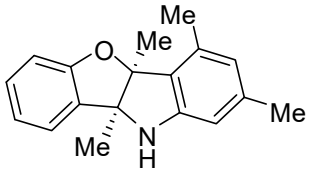
3wb

3-Chloro-4b,9b-dimethyl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3wb), white solid, 0.050 g, 92% yield. Mp: 132−133 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 2.0 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.18−7.15 (m, 1H), 7.08 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 6.93−6.90 (m, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.53 (d, J = 8.5 Hz, 1H), 4.25 (brs, 1H), 1.71 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 147.5, 132.8, 132.3, 130.0, 129.5, 124.6, 123.9, 122.8, 121.0, 111.5, 110.5, 96.7, 73.2, 22.3, 20.3; IR (thin film) 3381, 2973, 2866, 1510, 1483, 1254, 817, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{15}ClNO$ $[M + H]^+$: 272.0837, found 272.0831.



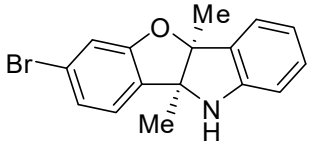
3wc

3-Bromo-4b,9b-dimethyl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3wc), white solid, 0.054 g, 85% yield. Mp: 140−141 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 1.5 Hz, 1H), 7.22−7.18 (m, 2H), 7.16−7.13 (m, 1H), 6.91−6.88 (m, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.48 (d, J = 8.0 Hz, 1H), 4.20 (brs, 1H), 1.69 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 147.9, 132.8, 132.7, 129.5, 127.6, 122.8, 121.0, 112.0, 110.8, 110.5, 96.6, 73.1, 22.3, 20.3; IR (thin film) 3475, 2964, 2869, 1481, 1261, 749, 693 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{15}BrNO$ $[M + H]^+$: 316.0332, found 316.0321.



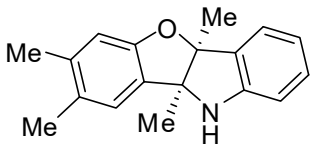
3wd

2,4,4b,9b-Tetramethyl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3wd), white solid, 0.051 g, 97% yield. Mp: 119−120 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.17−7.14 (m, 1H), 7.09−7.06 (m, 1H), 6.85−6.82 (m, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.37 (s, 1H), 6.24 (s, 1H), 4.14 (brs, 1H), 2.46 (s, 3H), 2.16 (s, 3H), 1.75 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 149.2, 139.6, 135.8, 133.9, 129.1, 125.8, 123.0, 122.6, 120.7, 110.3, 108.8, 97.1, 72.7, 22.8, 21.3, 19.8, 17.8; IR (thin film) 3379, 2978, 2868, 1479, 1258, 754, 604 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NO$ [M + H]$^{+}$: 266.1539, found 266.1534.



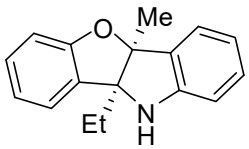
3we

7-Bromo-4b,9b-dimethyl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3we), white solid, 0.045 g, 72% yield. Mp: 153−154 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 6.0 Hz, 1H), 7.16−7.13 (m, 1H), 7.09 (d, J = 6.0 Hz, 1H), 7.02 (d, J = 6.4 Hz, 1H), 6.91 (s, 1H), 6.84−6.81 (m, 1H), 6.62 (d, J = 6.4 Hz, 1H), 4.20 (brs, 1H), 1.71 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 148.8, 132.6, 130.4, 129.9, 124.5, 124.0, 123.8, 122.3, 119.7, 114.0, 110.6, 98.5, 72.1, 22.1, 20.3; IR (thin film) 3351, 2963, 2868, 1609, 1485, 1262, 806, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{15}BrNO$ [M + H]$^{+}$: 316.0332, found 316.0328.



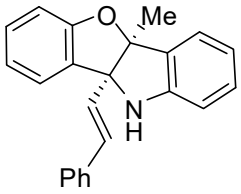
3wf

4b,7,8,9b-Tetramethyl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3wf), white solid, 0.039 g, 73% yield. Mp: 154−155 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 1H), 7.15−7.11 (m, 1H), 7.01 (s, 1H), 6.84−6.81 (m, 1H), 6.63−6.61 (m, 2H), 4.21 (brs, 1H), 2.22 (s, 3H), 2.20 (s, 3H), 1.73 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 149.0, 137.8, 130.7, 130.4, 130.0, 128.6, 124.4, 123.6, 119.5, 111.4, 110.7, 97.1, 72.5, 22.4, 20.4, 20.1, 19.3; IR (thin film) 3474, 3045, 2963, 2868, 1485, 1264, 851, 743 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NO$ $[M + H]^+$: 266.1539, found 266.1533.



3wg

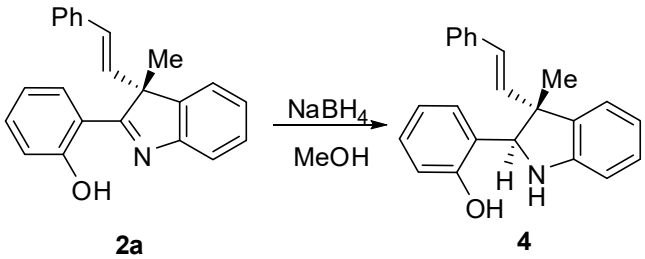
9b-Ethyl-4b-methyl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3wg), colorless oil, 0.037 g, 74% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (d, J = 7.2 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.11–7.07 (m, 1H), 7.03–6.99 (m, 1H), 6.87–6.83 (m, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.61–6.57 (m, 1H), 6.55 (s, 1H), 6.51 (d, J = 7.6 Hz, 1H), 1.87 (d, J = 7.6 Hz, 2H), 1.62 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.6, 150.7, 133.2, 131.3, 130.2, 129.3, 125.3, 124.4, 120.8, 117.9, 110.1, 109.6, 97.2, 75.2, 28.4, 20.7, 9.1; IR (thin film) 3370, 3050, 2965, 2875, 1486, 1279, 844, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{18}NO$ $[M + H]^+$: 252.1383, found 252.1383.



3a

4b-Methyl-9b-styryl-9b,10-dihydro-4bH-benzofuro[3,2-b]indole (3a), white solid, 0.016 g, 25% yield; 89−90 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 3H), 7.33–7.30 (m, 2H), 7.26–7.23 (m, 1H), 7.21–7.14 (m, 3H), 6.93–6.91 (m, 1H), 6.84–6.81 (m, 2H), 6.71–6.70 (m, 1H), 6.69–6.68 (m, 1H), 6.44 (d, J = 16.0 Hz, 1H), 4.35 (s, 1H), 1.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 149.0, 136.5, 131.9, 131.3, 130.3, 130.2, 129.7, 129.4, 128.6, 127.9, 126.7, 126.4, 124.7, 124.5, 121.0, 119.6, 110.7, 110.5, 98.7, 77.2, 22.1; IR (thin film) 3378, 3048, 2962, 2865, 1496, 1259, 848, 736 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{20}NO$ $[M + H]^+$: 326.1539, found 326.1518.

3. Synthesis of indoline 4.



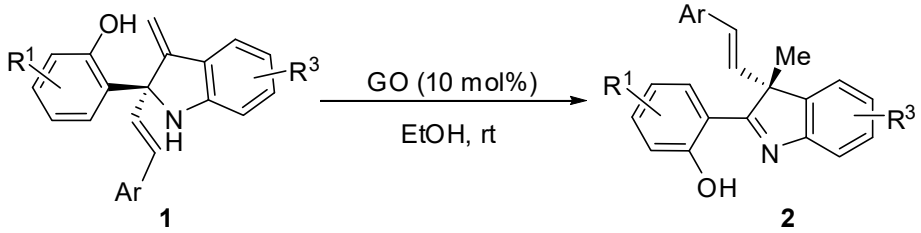
2a **4**

In a 25 mL round-bottom flask was charged with indolenine **2a** (0.800 g, 2.5 mmol) and MeOH (20.0 mL). The mixture was slowly added with $NaBH_4$ (0.285 g, 7.5 mmol, 3.0 equiv.) by portions and stirred vigorously at room temperature for 2 h until the substrate **2a** disappeared (monitored by TLC). At this time, the reaction was quenched by H_2O (10 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried over Na_2SO_4, and filtered. 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, 1/50 to 1/10, ethyl acetate/petroleum ether) to provide product **4**

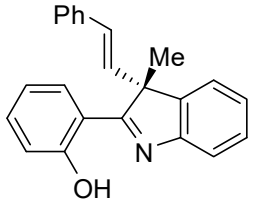
2-(3-Methyl-3-styrylindolin-2-yl)phenol (4), yellow solid, 0.70 g, 87% yield. Mp: 152−153 ℃; *major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.27–7.24 (m, 2H), 7.12–7.08 (m, 3H), 7.03–7.01 (m, 2H), 6.85–6.77 (m, 3H), 6.69 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 16.4 Hz, 1H), 6.38 (d, J = 16.4 Hz, 1H), 4.75 (s, 1H), 4.34 (brs, 1H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 146.7, 138.5, 137.0, 134.6, 130.3, 128.9, 128.7, 128.6, 127.9, 127.6, 126.3, 124.5, 122.0, 120.0, 119.0, 117.0, 112.6, 73.4, 53.1, 19.9; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.27–7.24 (m, 2H), 7.19–7.12 (m, 3H), 6.96–6.93 (m, 2H), 6.89–6.85 (m, 3H), 6.69 (t, J = 7.2 Hz, 1H), 5.88 (d, J = 16.4 Hz, 1H), 5.79 (d, J = 16.4 Hz, 1H), 4.58 (s, 1H), 4.34 (brs, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 147.5, 137.4, 136.1, 132.9, 130.3, 129.3, 129.2, 128.6, 128.2, 127.9, 126.9, 124.7, 121.5, 120.1, 118.9, 117.0, 112.4, 73.4, 52.1, 23.4; IR (thin film) 3442, 3308, 2926, 2854, 1462, 1261, 804, 755 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO$ $[M + H]^+$: 328.1696, found 328.1688.

4. Studies of the stereochemistry of rearrangement from 1 to 2



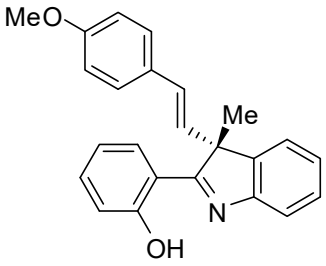
General procedure B: In a Teflon-sealed flask was charged with enantioenriched compound **1** (0.2 mmol) and GO (6.5 mg, 10 wt%), and EtOH (2.0 mL) was added. The reaction vessel was stirred vigorously at room temperature (about 25 °C) for 3-7 h until the substrate **1** disappeared (monitored by TLC). At this time, the reaction was filtered and washed with DCM. 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, 1/50 to 1/30, ethyl acetate/petroleum ether) to provide

indolines **2**. The enantiomeric excess (ee) values of **2** were determined by chiral HPLC analysis.



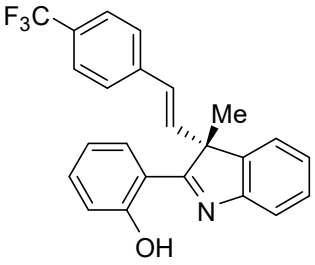
2a

(*R,E*)-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2a), 0.064 g, 99% yield, 92% ee (AD, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_1 = 17.8 min (minor), t_2 = 24.6 min (major)).



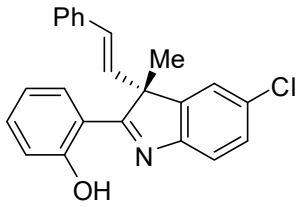
2b

(*R,E*)-2-(3-(4-Methoxystyryl)-3-methyl-3H-indol-2-yl)phenol (2b), 0.053 g, 75% yield, 97% ee (OD, hexane/i-PrOH = 99/1, 254 nm, 0.5 mL/min. t_1 = 42.0 min (minor), t_2 = 47.4 min (major)).



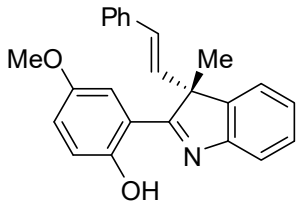
2e

(*R,E*)-2-(3-methyl-3-(4-(trifluoromethyl)styryl)-3H-indol-2-yl)phenol (2e), 0.075 g, 96% yield, 97% ee (AD, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_1 = 6.5 min (minor), t_2 = 8.6 min (major)).



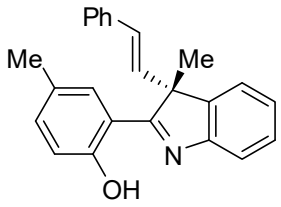
2l

(*R,E*)-2-(5-chloro-3-methyl-3-styryl-3H-indol-2-yl)phenol (2l), 0.071 g, 99% yield, 98% ee (AD, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min. t_1 = 7.1 min (minor), t_2 = 15.6 min (major)).



2r

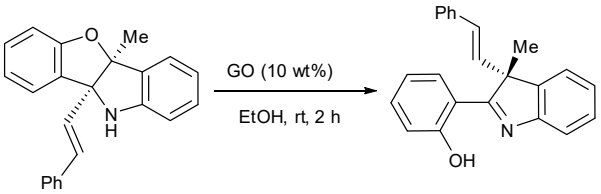
(*R,E*)-4-methoxy-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2r), 0.068 g, 96% yield, 98% ee (AD, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_1 = 8.8 min (minor), t_2 = 12.5 min (major)).



2s

(*R,E*)-4-methyl-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2s), 0.067 g, 99% yield, 94% ee (AD, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min. t_1 = 7.1 min (minor), t_2 = 9.4 min (major)).

5. Studies of the stereochemistry of rearrangement from 3a to 2a

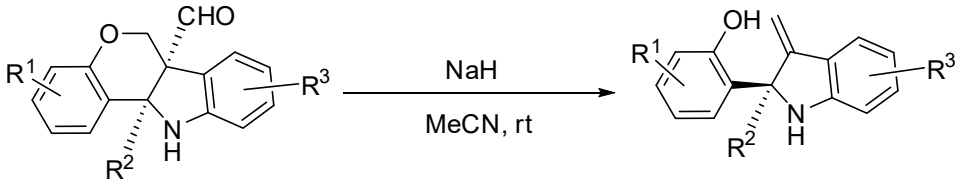


3a, ee = 46% **2a**, 98% yield, 47% ee

In a Teflon-sealed flask was charged with enantioenriched compound **3a** (0.2 mmol, 45% ee) and GO (6.5 mg, 10 wt%), and EtOH (2.0 mL) was added. The reaction vessel was stirred vigorously at room temperature (about 25 °C) for 3-7 h until the substrate **3a** disappeared (monitored by TLC). At this time, the reaction was filtered and washed with DCM. 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, 1/50 to 1/30, ethyl acetate/petroleum ether) to provide indolines **2a**. The enantiomeric excess (ee) values of **2a** were determined by chiral HPLC analysis. The enantioenriched compound **3a** was obtained by a chiral prepared HPLC (AD).

(*R,E*)-2-(3-methyl-3-styryl-3H-indol-2-yl)phenol (2a), 0.064 g, 98% yield, 47% ee (AD, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_1 = 5.9 min (minor), t_2 = 8.4 min (major)).

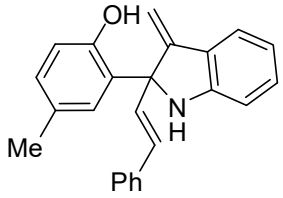
6. Synthesis of compound 1



S1 **1**

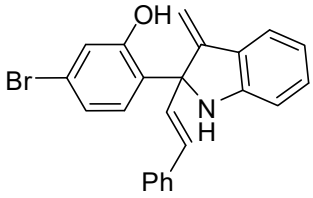
General procedure C: In a Teflon-sealed flask was charged with fused indoline S**1** (0.2 mmol) and NaH (0.6 mmol, 3.0 equiv, 60% NaH (w/w) in mineral oil) under N_2 atmosphere. Then, MeCN (2.0 mL) was added. The reaction vessel was sealed with a Teflon cap and stirred vigorously at room temperature (about 25 °C) for 0.5–24 h until the substrate **1** disappeared (monitored by TLC). At this time, the reaction was quenched by H_2O (5 mL) and extracted with EtOAc (10 mL × 3). The combined

organic layers were dried over Na_2SO_4, and filtered. 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, 1/50 to 1/10, ethyl acetate/petroleum ether) to provide product **1**.



1s

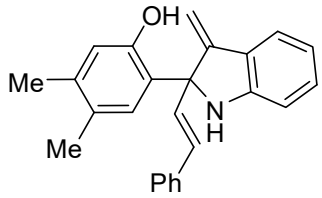
(*E*)-4-Methyl-2-(3-methylene-2-styrylindolin-2-yl)phenol (1s), white solid, 0.054 g, 80% yield. Mp: 160−161 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.39–7.37 (m, 2H), 7.31–7.27 (m, 2H), 7.22–7.18 (m, 1H), 7.11–7.07 (m, 2H), 6.94 (d, J = 8.0 Hz, 1H), 6.75–6.71 (m, 2H), 6.68–6.61 (m, 2H), 6.38 (d, J = 16.0 Hz, 1H), 5.72 (s, 1H), 4.87 (s, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.1, 151.3, 150.8, 137.3, 134.4, 130.7, 129.5, 129.3, 129.0, 128.7, 127.9, 127.6, 127.4, 126.9, 126.3, 121.8, 118.4, 117.0, 110.9, 105.1, 73.1, 21.0; IR (thin film) 3433, 3036, 2960, 2869, 1491, 1249, 750, 693 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{22}NO$ $[M + H]^+$: 340.1696, found 340.1704.



1u

(*E*)-5-Bromo-2-(3-methylene-2-styrylindolin-2-yl)phenol (1u), white solid, 0.060 g, 75% yield. Mp: 154−155 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.43 (s, 1H), 7.42–7.38 (m, 2H), 7.31–7.27 (m, 2H), 7.25–7.19 (m, 2H), 7.09–7.05 (m, 1H), 6.98–6.96 (m, 2H), 6.73 (d, J = 7.6 Hz, 1H), 6.68 (s, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 5.69 (s, 1H), 4.85 (s, 1H); ^{13}C

NMR (100 MHz, DMSO-d_6) δ 157.6, 151.4, 150.9, 137.2, 134.0, 130.8, 130.5, 129.3, 129.1, 128.0, 127.8, 127.0, 125.9, 121.8, 121.4, 119.5, 118.3, 110.7, 104.8, 72.5; IR (thin film) 3436, 3062, 2925, 2869, 1468, 1237, 748, 692 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}BrNO$ $[M + H]^+$: 404.0645, found 404.0660.

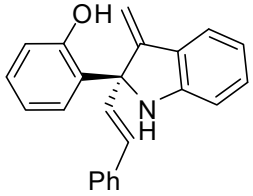


1v

(*E*)-4,5-Dimethyl-2-(3-methylene-2-styrylindolin-2-yl)phenol (1v), white solid, 0.052 g, 74% yield. Mp: 162−163 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.61 (s, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.38–7.36 (m, 2H), 7.31–7.27 (m, 2H), 7.21–7.18 (m, 1H), 7.09–7.05 (m, 1H), 7.02 (s, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.67–6.58 (m, 3H), 6.36 (d, J = 15.6 Hz, 1H), 5.70 (s, 1H), 4.84 (s, 1H), 2.10 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.0, 151.3, 150.9, 137.3, 136.8, 134.4, 130.6, 129.6, 129.3, 127.9, 127.5, 126.9, 126.4, 126.1, 126.0, 121.8, 118.4, 110.9, 105.0, 73.0, 19.6, 19.3; IR (thin film) 3436, 3025, 2925, 2856, 1493, 1269, 751, 692 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO$ $[M + H]^+$: 354.1852, found 354.1862.

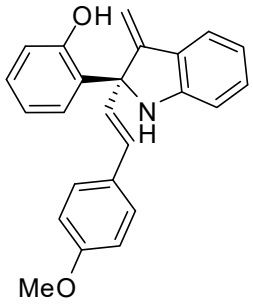
7. Preparation of enantioenriched compound 1a, 1b, 1e, 1l, 1r, and 1s

The enantioenriched compounds **1a, 1b, 1e, 1l, 1r,** and **1s** were obtained by a chiral prepared HPLC (AD).



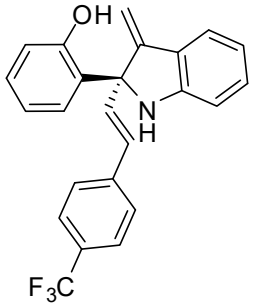
1a

(*R*,*E*)-2-(3-methylene-2-styrylindolin-2-yl)phenol (1a), 95% ee (AD, hexane/*i*-PrOH = 94/6, 254 nm, 1.0 mL/min. t_1 = 23.3 min (minor), t_2 = 31.1 min (major)).



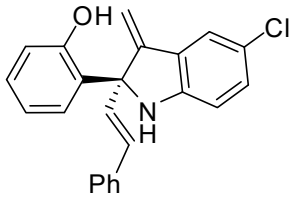
1b

(*R*,*E*)-2-(2-(4-methoxystyryl)-3-methyleneindolin-2-yl)phenol (1b), 95% ee (AD, hexane/*i*-PrOH = 94/6, 254 nm, 1.0 mL/min. t_1 = 39.5 min (minor), t_2 = 57.9 min (major)).



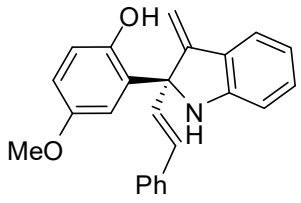
1e

(*R*,*E*)-2-(3-methylene-2-(4-(trifluoromethyl)styryl)indolin-2-yl)phenol (1e), 98% ee (AD, hexane/*i*-PrOH = 92/8, 254 nm, 0.8 mL/min. t_1 = 6.4 min (minor), t_2 = 9.0 min (major)).



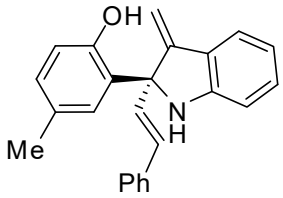
1l

(*R*,*E*)-2-(5-chloro-3-methylene-2-styrylindolin-2-yl)phenol (1l), 93% ee (AD, hexane/*i*-PrOH = 94/6, 254 nm, 1.0 mL/min. t_1 = 27.6 min (minor), t_2 = 36.2 min (major)).



1r

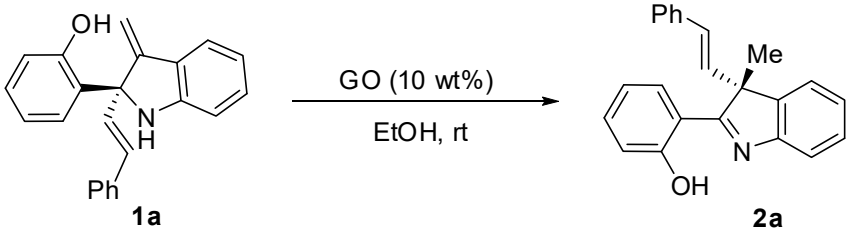
(*R,E*)-4-methoxy-2-(3-methylene-2-styrylindolin-2-yl)phenol (1r), 95% ee (AD, hexane/*i*-PrOH = 94/6, 254 nm, 1.0 mL/min. t_1 = 55.7 min (minor), t_2 = 74.4 min (major)).



1s

(*R,E*)-4-methyl-2-(3-methylene-2-styrylindolin-2-yl)phenol (1s), 93% ee (AD, hexane/*i*-PrOH = 94/6, 254 nm, 1.0 mL/min. t_1 = 27.2 min (minor), t_2 = 53.6 min (major)).

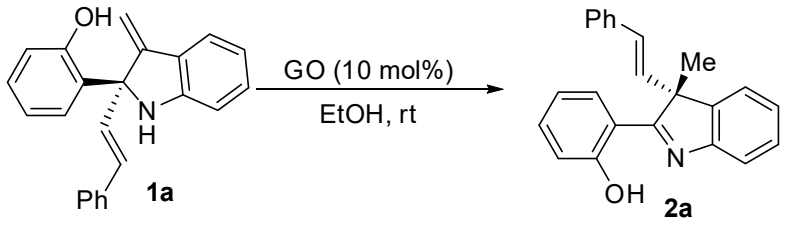
8. Graphene oxide-recyled experiment



General procedure C: In a Teflon-sealed flask was charged with compound **1a** (1.0 mmol), GO (32 mg, 10 wt%), and EtOH (5.0 mL). The reaction vessel was stirred vigorously at room temperature (about 25 °C) for 4 h until the substrate **1a** disappeared (monitored by TLC). At this time, the reaction was filtered and washed with DCM. The filtrate was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/50, ethyl acetate/petroleum ether) to provide indolines **2a**. The filtered

graphene oxide was washed three times, and then used directly for the next cycle experiment.

Recycling catalyst-in-ethanol system.



time	yield
1	99%
2	98%
3	98%
4	92%
5	97%
6	98%
7	96%

9. Preparation of graphene oxide by Hummers method

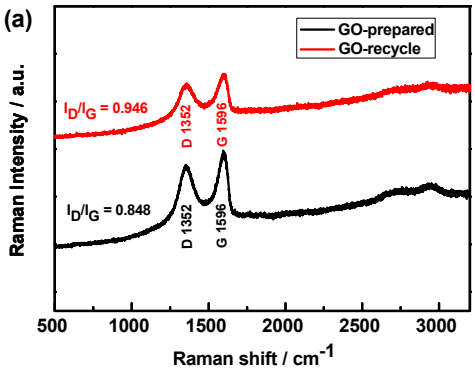
Low temperature reaction: In a beaker was charged with concentrated sulfuric acid (23 mL), put the beaker into an ice bath and cool it to below 4 °C, graphite powder (1 g) and sodium nitrate (0.5 g) was added in the beaker. The reaction mixture was stirred vigorously for 1 h, potassium permanganate (3 g) was added slowly and control temperature does not exceed 10 ° C, the reaction time is about 2 h;

Medium temperature reaction: The beaker is moved to a constant temperature water bath, and the temperature of the water bath is controlled at 38 ° C for 30 min, and stirring is maintained;

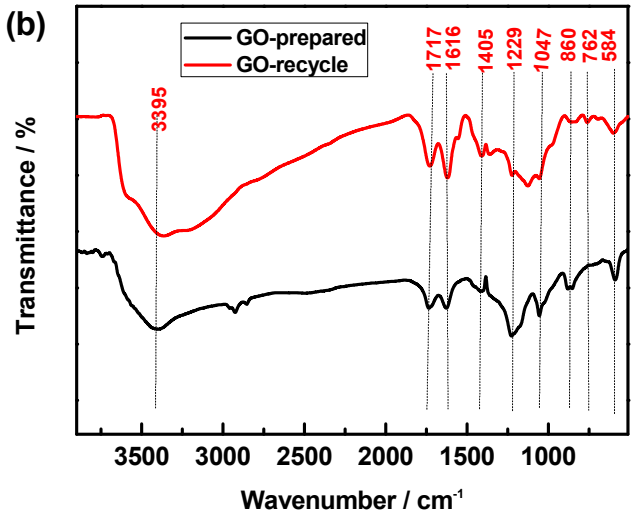
High temperature reaction: Slowly add deionized water (80 mL) to the resulting mixture, and keep the temperature of the mixture about 95 ℃ for 30 min, while maintaining moderate agitation. After high temperature reaction, add deionized water (60 mL) to terminate the reaction, and add hydrogen peroxide (30Vol% 15 mL), and wait for 15 min before adding hydrochloric acid solution (10Vol% 40 mL). Low-speed centrifugation washing removes excess acid and by-products, disperses

the neutral graphene oxide in water after washing, and exfoliates for 40 min after ultrasonic vibration. After ultrasonication, it is centrifuged at 2500 r.min^{-1} for 30 min. The upper layer liquid is a graphene oxide suspension. The graphene oxide suspension is dried in an oven at 40 ℃ to obtain a solid graphene oxide.

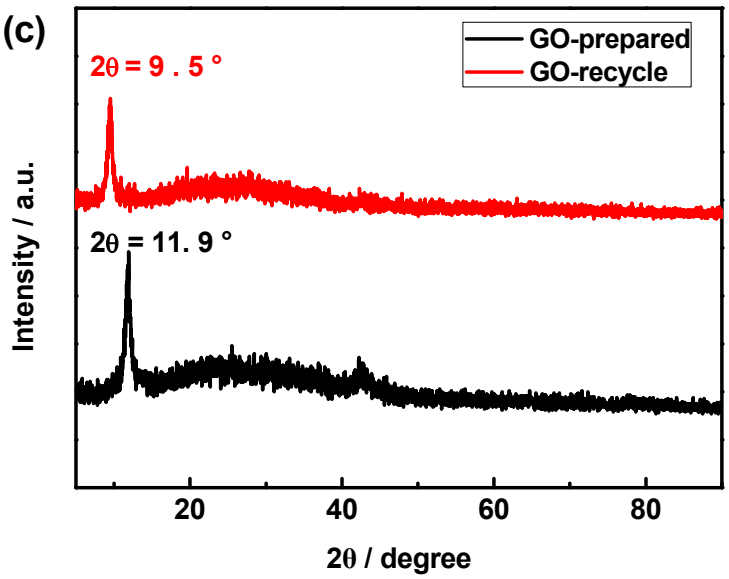
Raman spectroscopy of graphene oxide:



FTIR of graphene oxide:

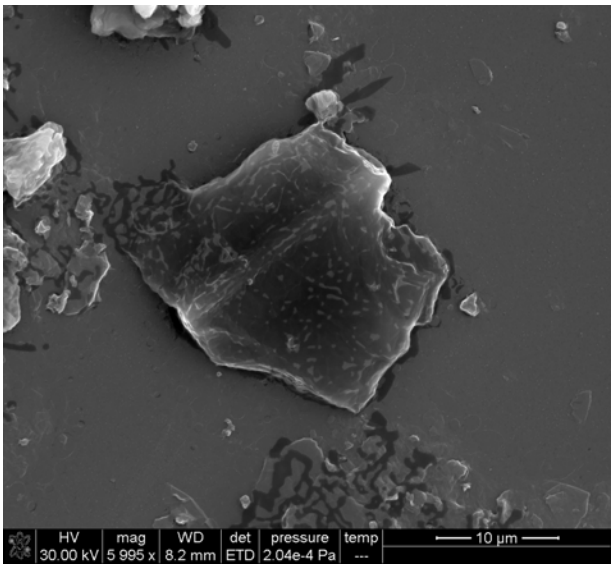


XRD of graphene oxide:

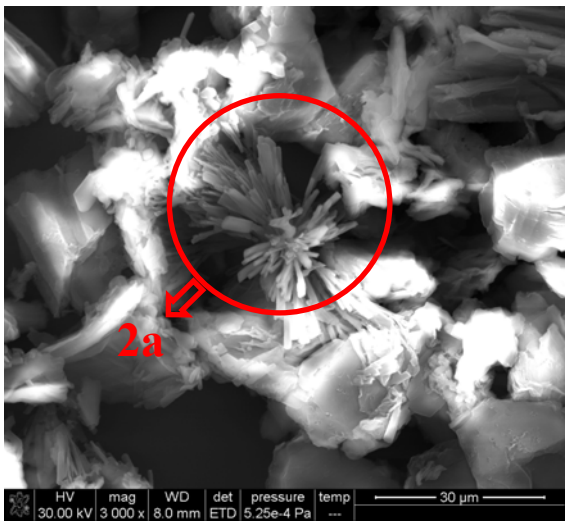


SEM of graphene oxide:

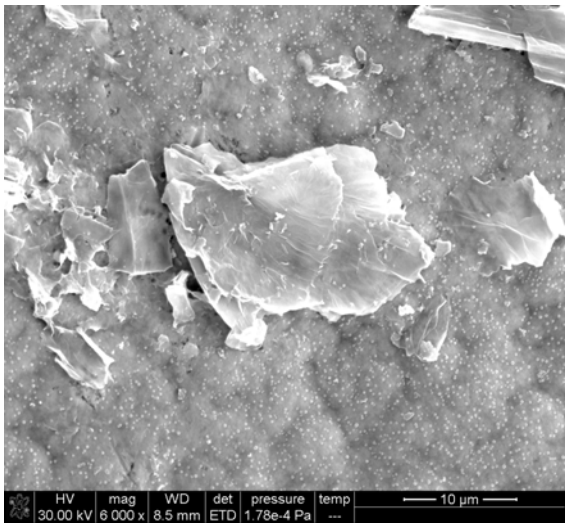
a) Prepared graphene oxide:



b) Graphene oxide in reaction:



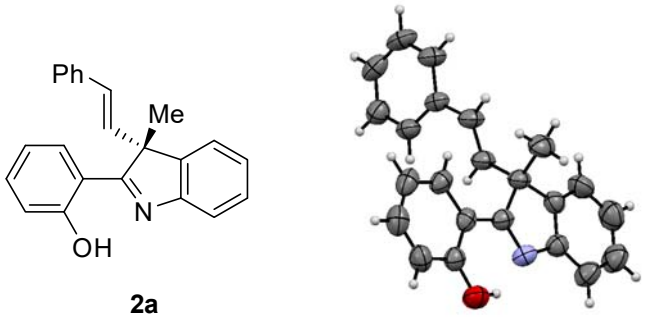
c) Recovered graphene oxide:



10. Reference

[1] Liu, F.-P.; Zhao, H.-P.; Tan, S.; Lu, X.; Mo, D.-L. *Synthesis* **2019**, *51*, 3477.

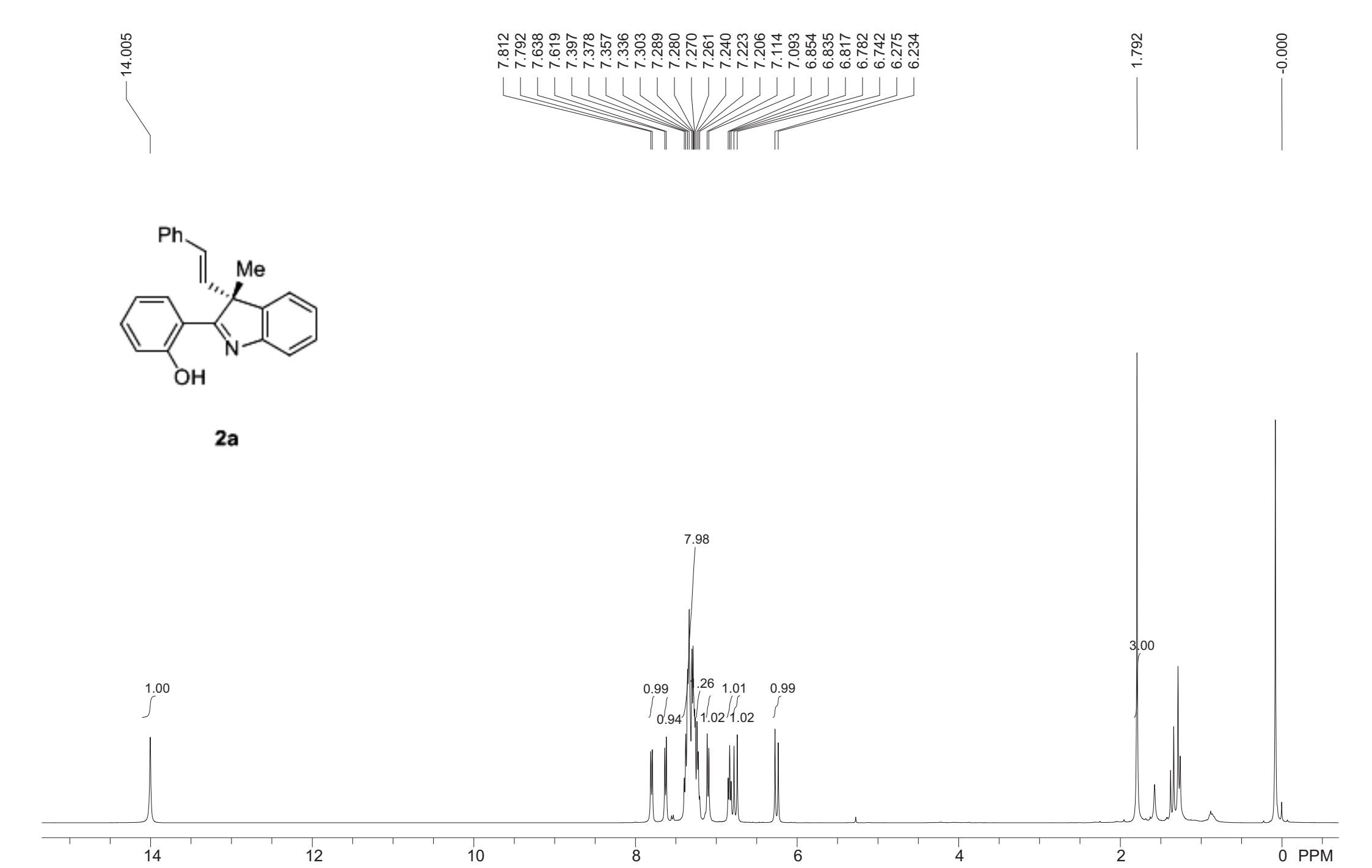
11. X-ray structure for compound 2a



2a

Figure S1: ORTEP diagram of **2a** at 50% ellipsoid probability

12. NMR spectra for 2, 3, 4 and HPLC spectra of compound 1, 2, and 3a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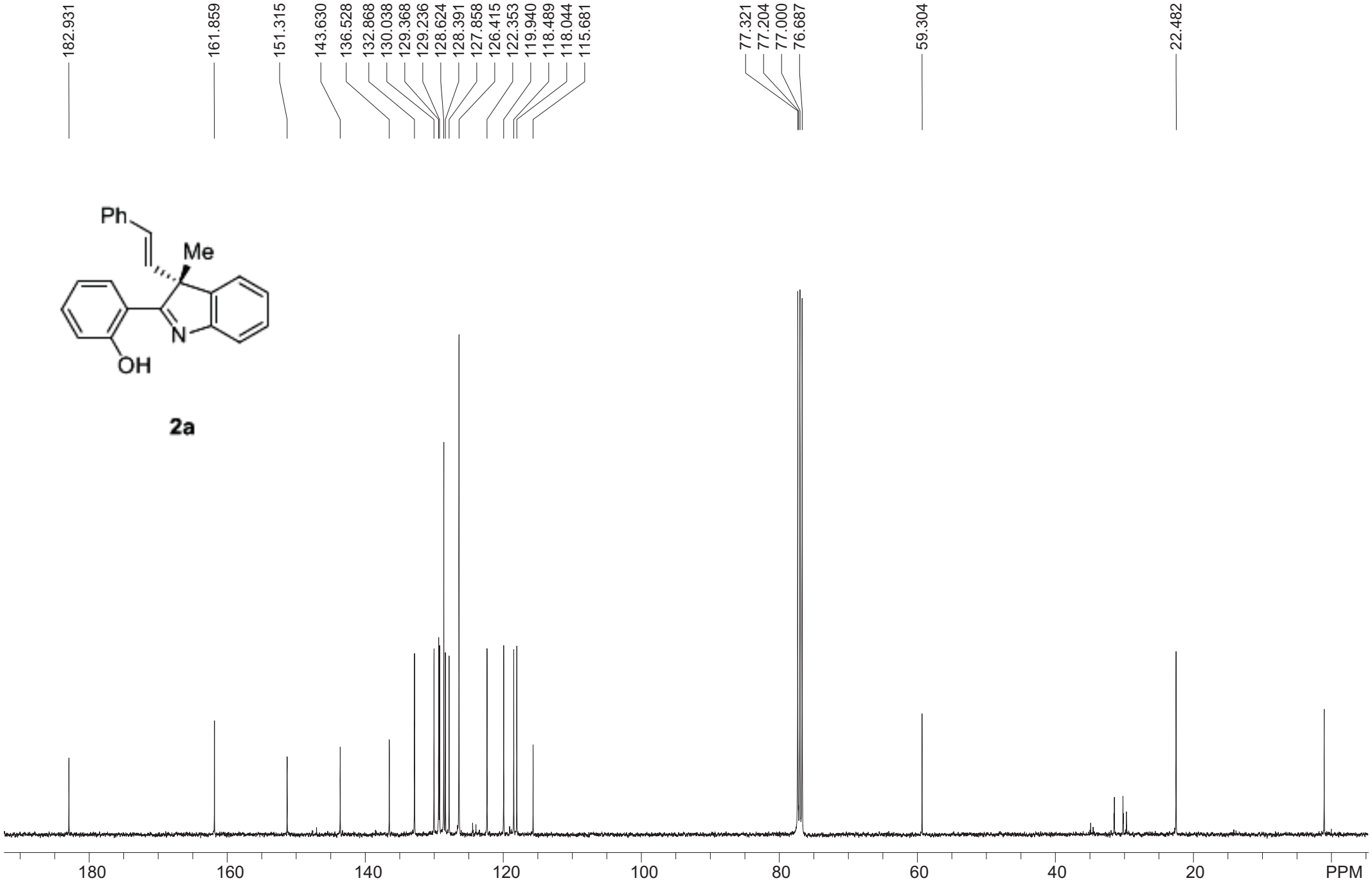
7.378
7.357
7.336
7.303
7.289
7.280
7.270
7.261
7.240
7.223
7.206
7.114
7.093
6.854
6.835
6.817
6.782
6.742
6.275
6.234
1.792
-0.000
Ph
Me
N
OH
2a
1.00
0.99
0.94
7.98
1.26
1.02
1.01
1.02
0.99
3.00
14
12
10
8
6
4
2
0
PPM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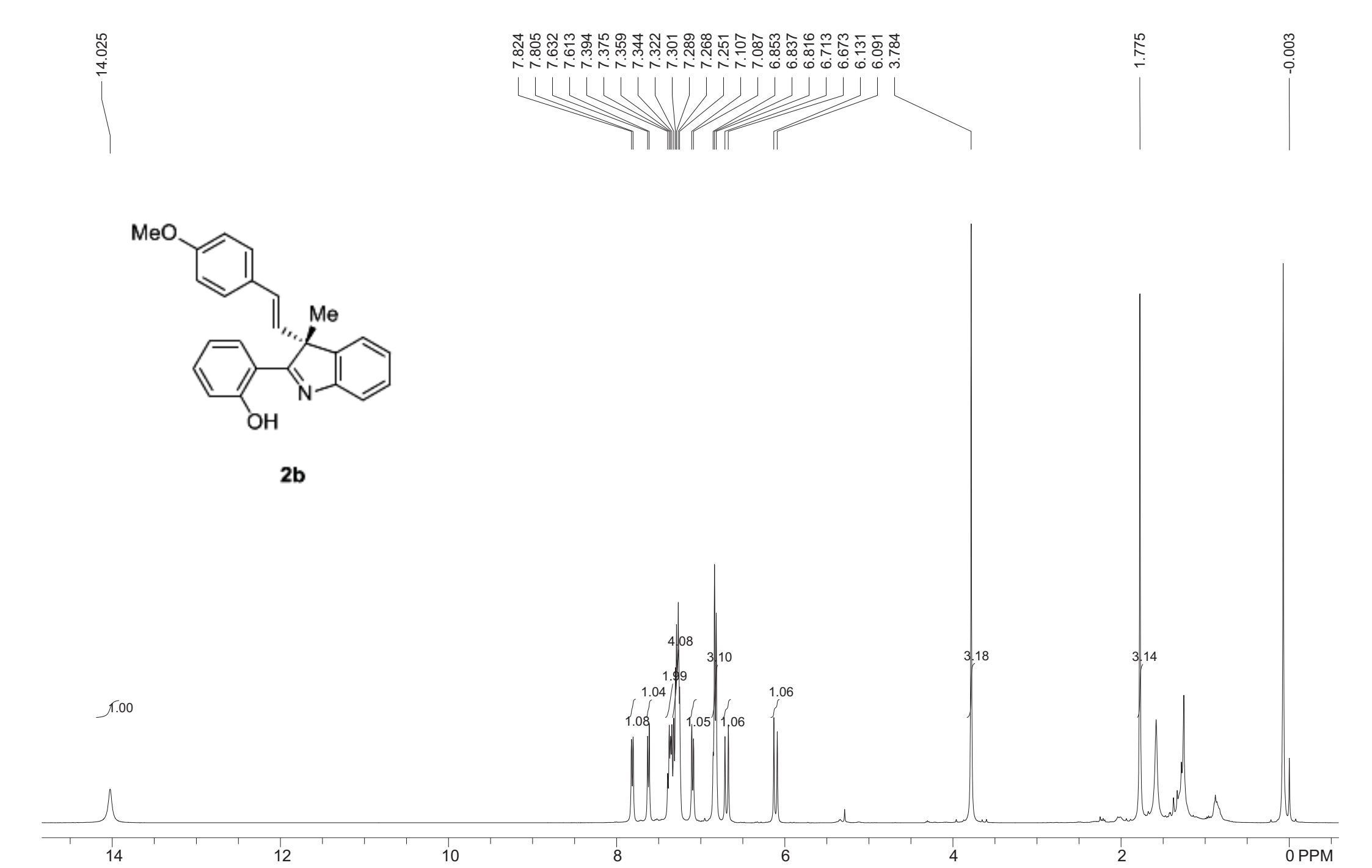
151.315
143.630
136.528
132.868
130.038
129.368
129.236
128.624
128.391
127.858
126.415
122.353
119.940
118.489
118.044
115.681
77.321
77.204
77.000
76.687
59.304
22.482
Ph
Me
N
OH
2a
180
160
140
120
100
80
60
40
20
PPM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7.632
7.613
7.394
7.375
7.359
7.344
7.322
7.301
7.289
7.268
7.251
7.107
7.087
6.853
6.837
6.816
6.713
6.673
6.131
6.091
3.784
1.775
-0.003
MeO
Me
N
OH
2b
1.00
1.08
1.04
1.99
4.08
3.10
1.05
1.06
1.06
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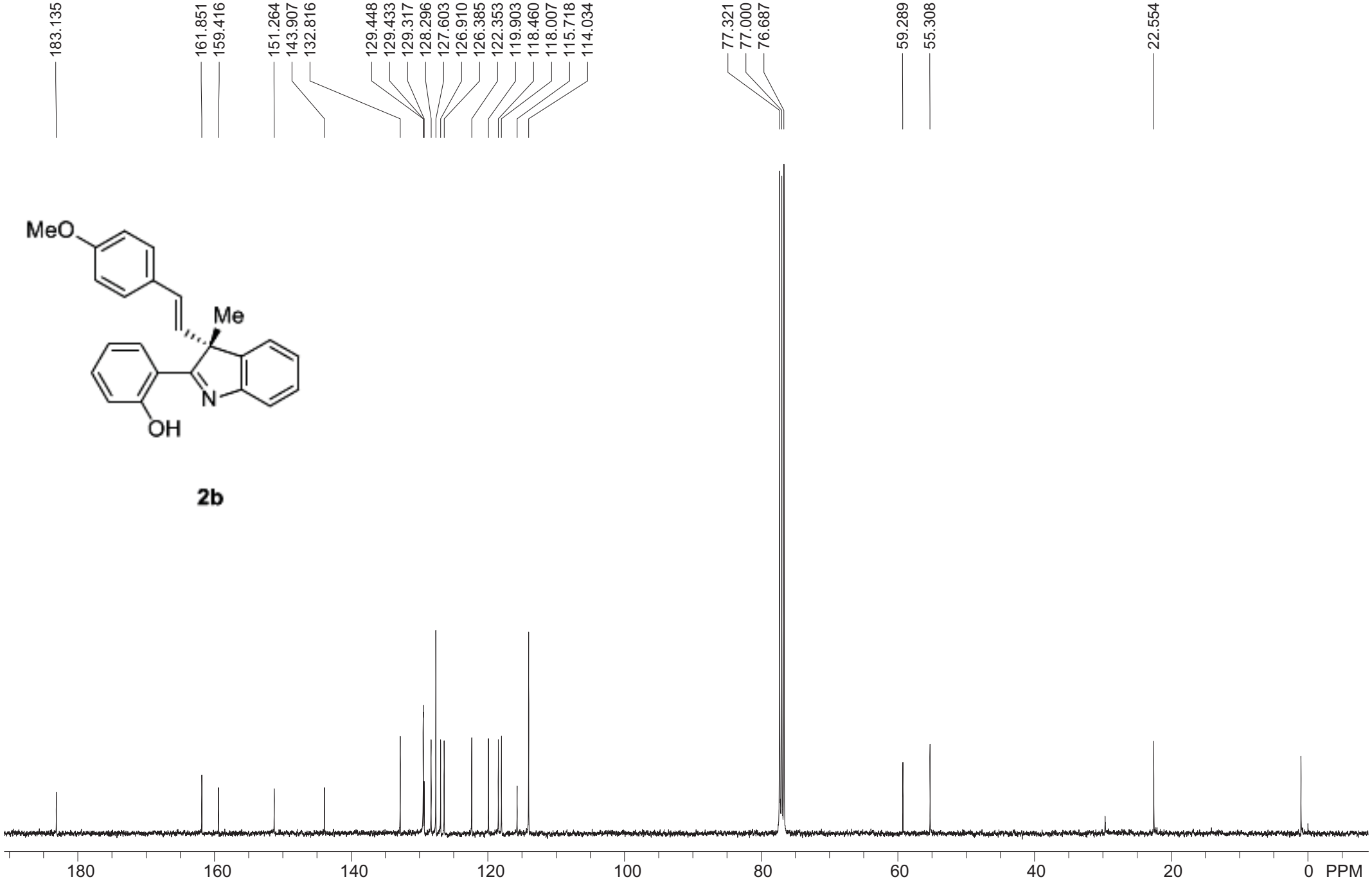
3.14
14
12
10
8
6
4
2
0 PPM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159.416
151.264
143.907
132.816
129.448
129.433
129.317
128.296
127.603
126.910
126.385
122.353
119.903
118.460
118.007
115.718
114.034
77.321
77.000
76.687
59.289
55.308
22.554
MeO
Me
N
OH
2b
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160
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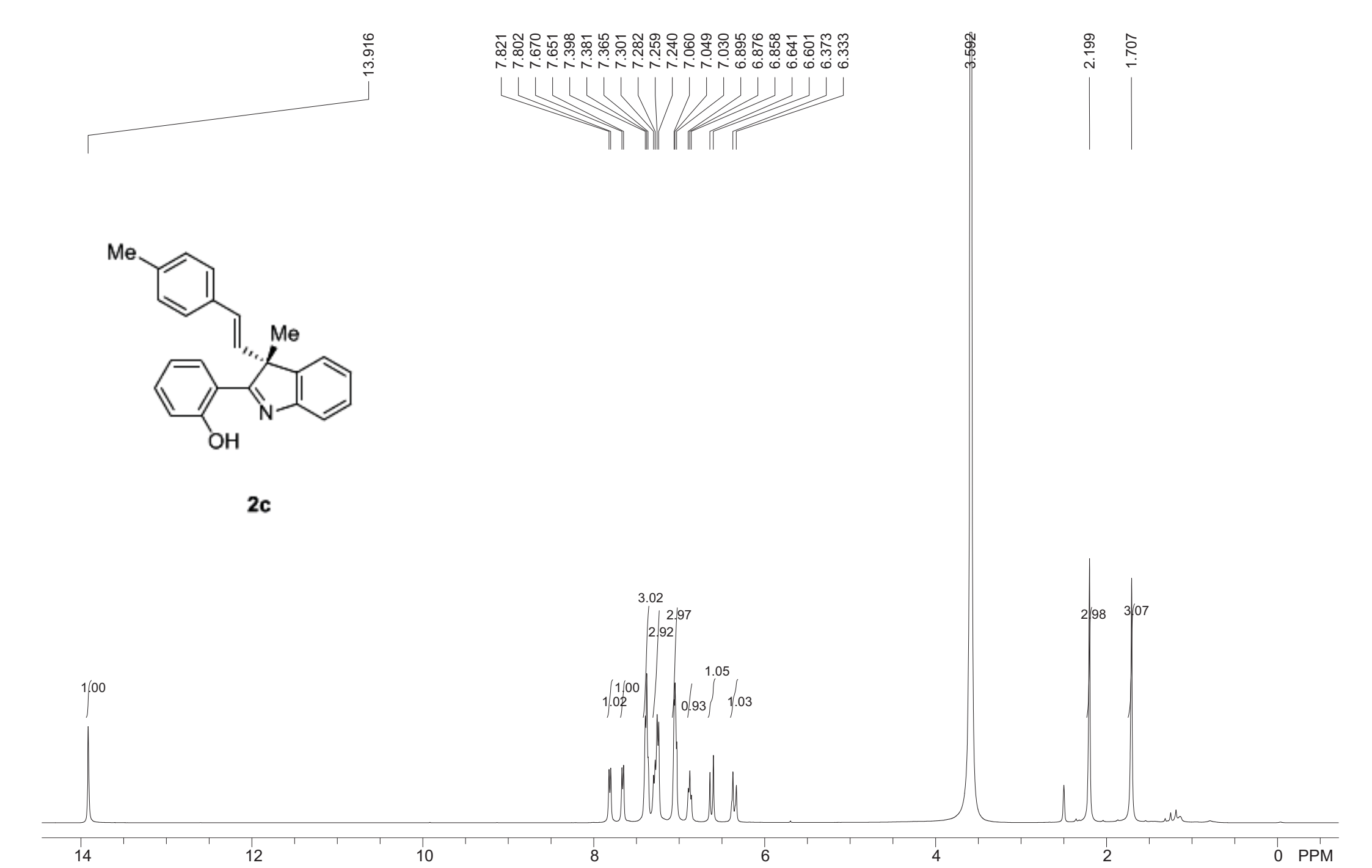
120
100
80
60
40
20
0
PPM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7.802
7.670
7.651
7.398
7.381
7.365
7.301
7.282
7.259
7.240
7.060
7.049
7.030
6.895
6.876
6.858
6.641
6.601
6.373
6.333
3.592
2.199
1.707
Me
Me
N
OH
2c
1.00
1.02
1.00
3.02
2.92
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2.98
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12
10
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6
4
2
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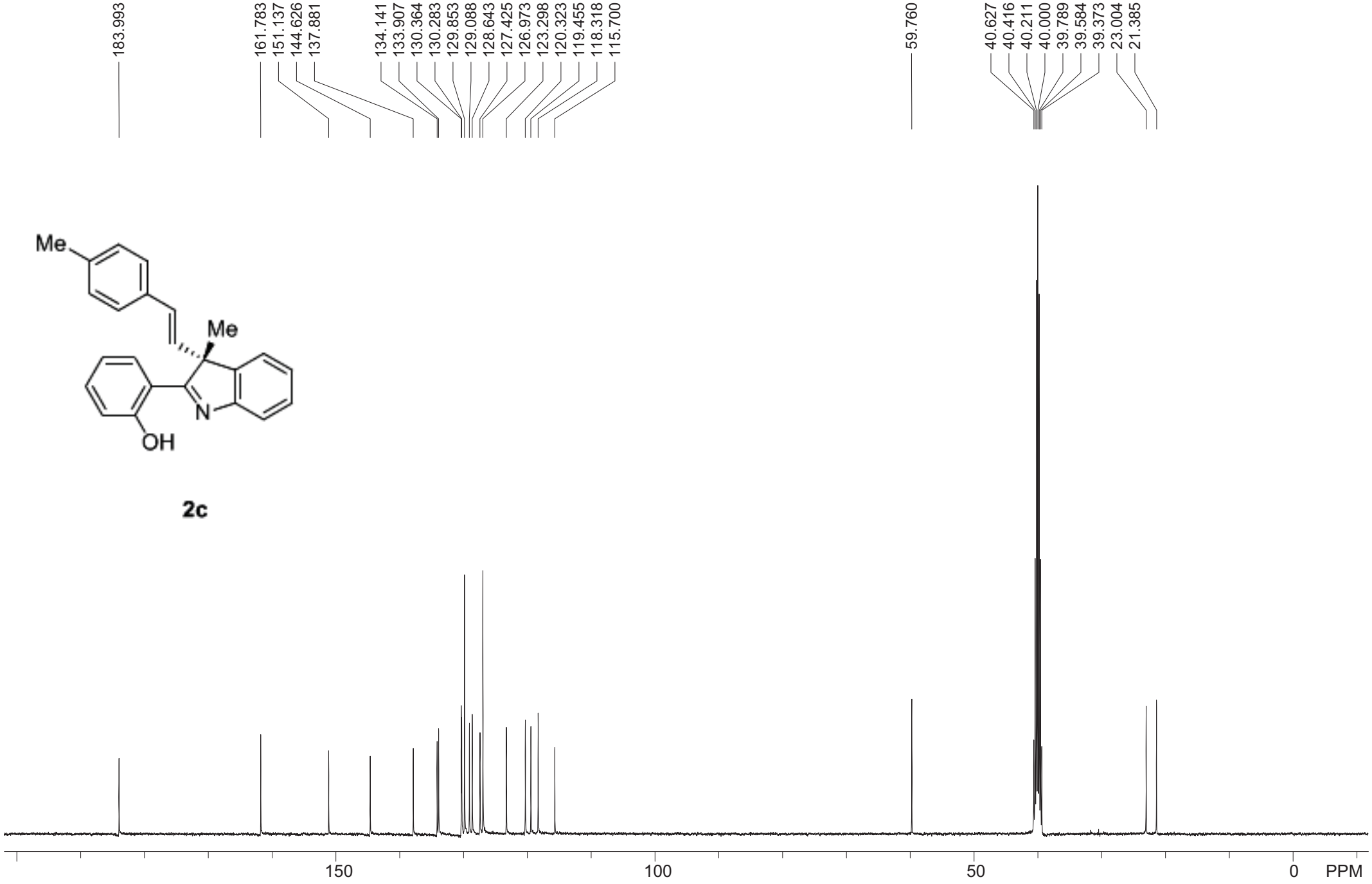
PPM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137.881
134.141
133.907
130.364
130.283
129.853
129.088
128.643
127.425
126.973
123.298
120.323
119.455
118.318
115.700
59.760
40.627
40.416
40.211
40.000
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OH
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50
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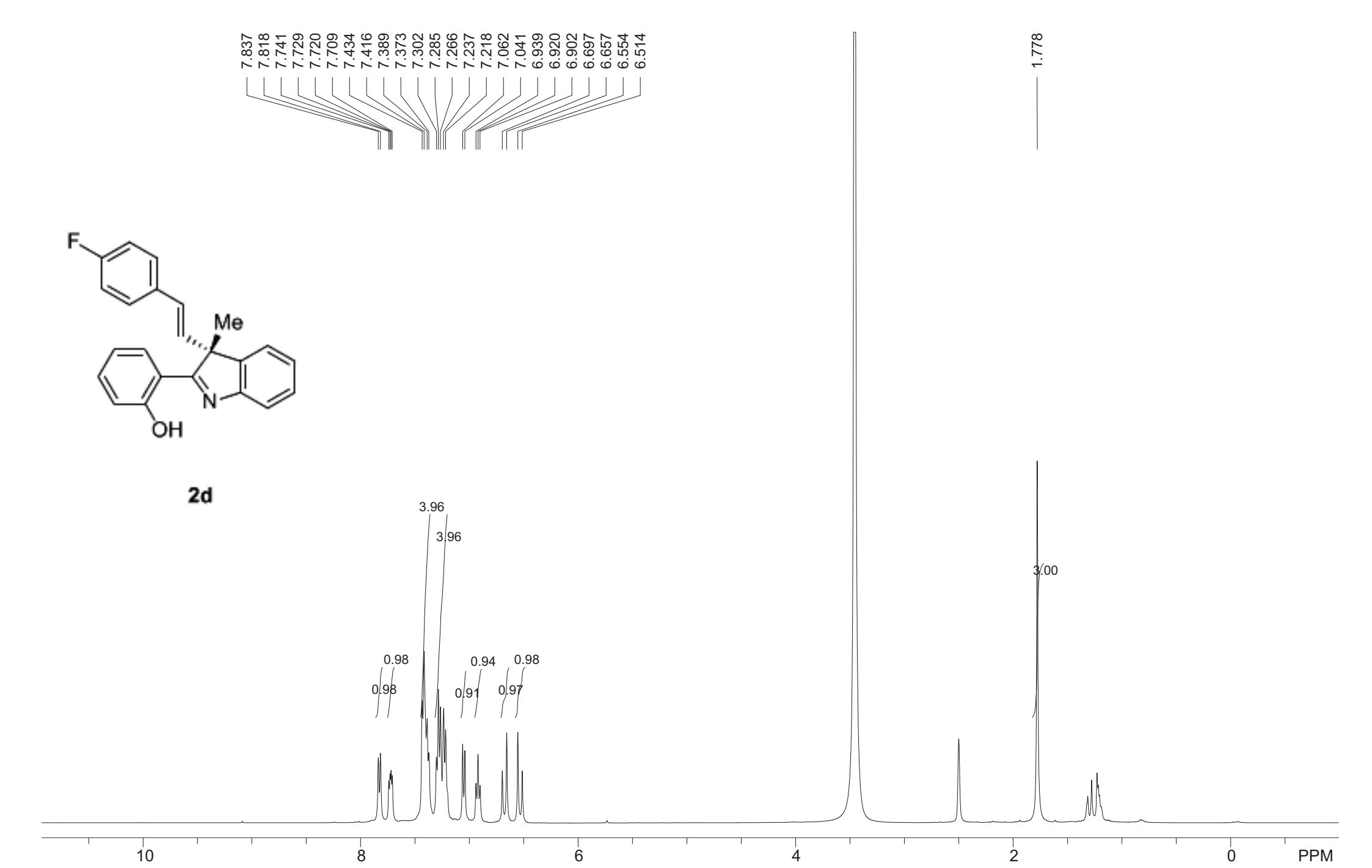
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7.237
7.218
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7.041
6.939
6.920
6.902
6.697
6.657
6.554
6.514
1.778
F
Me
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OH
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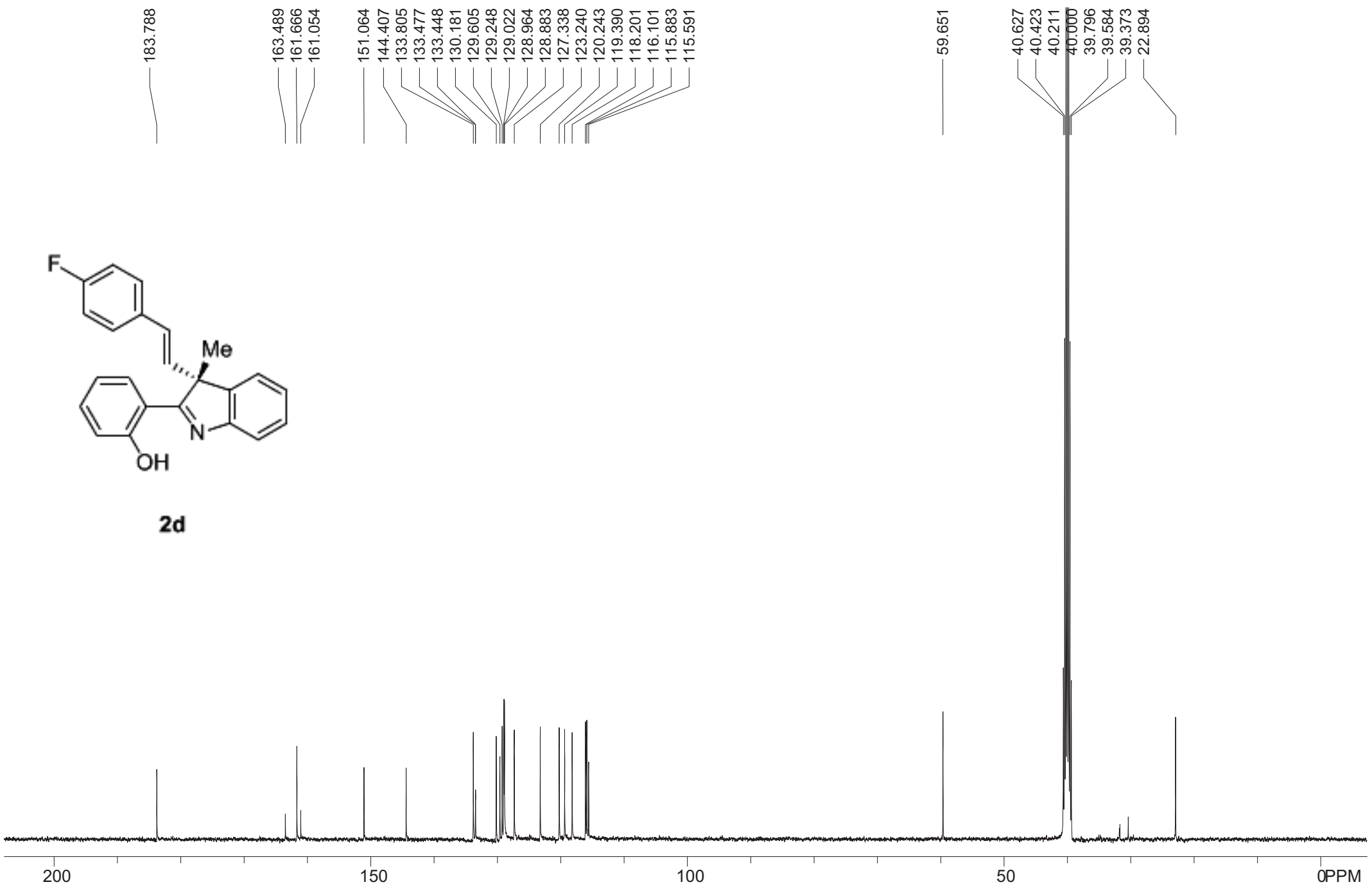
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129.022
128.964
128.883
127.338
123.240
120.243
119.390
118.201
116.101
115.883
115.591
59.651
40.627
40.423
40.211
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150
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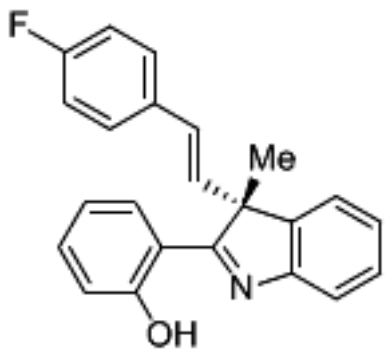
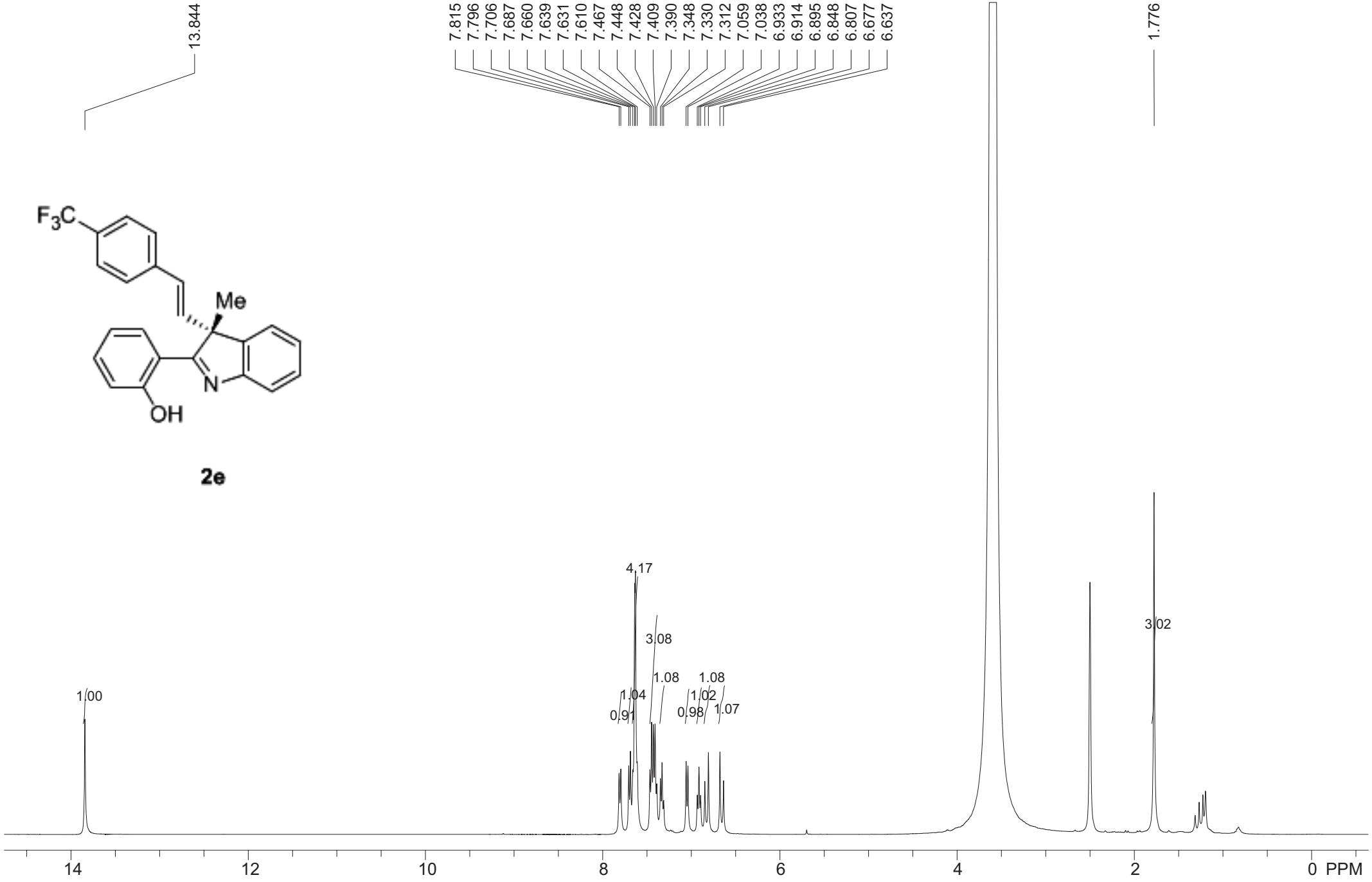
PPM



2d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7.467
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7.409
7.390
7.348
7.330
7.312
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7.038
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6.914
6.895
6.848
6.807
6.677
6.637
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Me
N
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1.08
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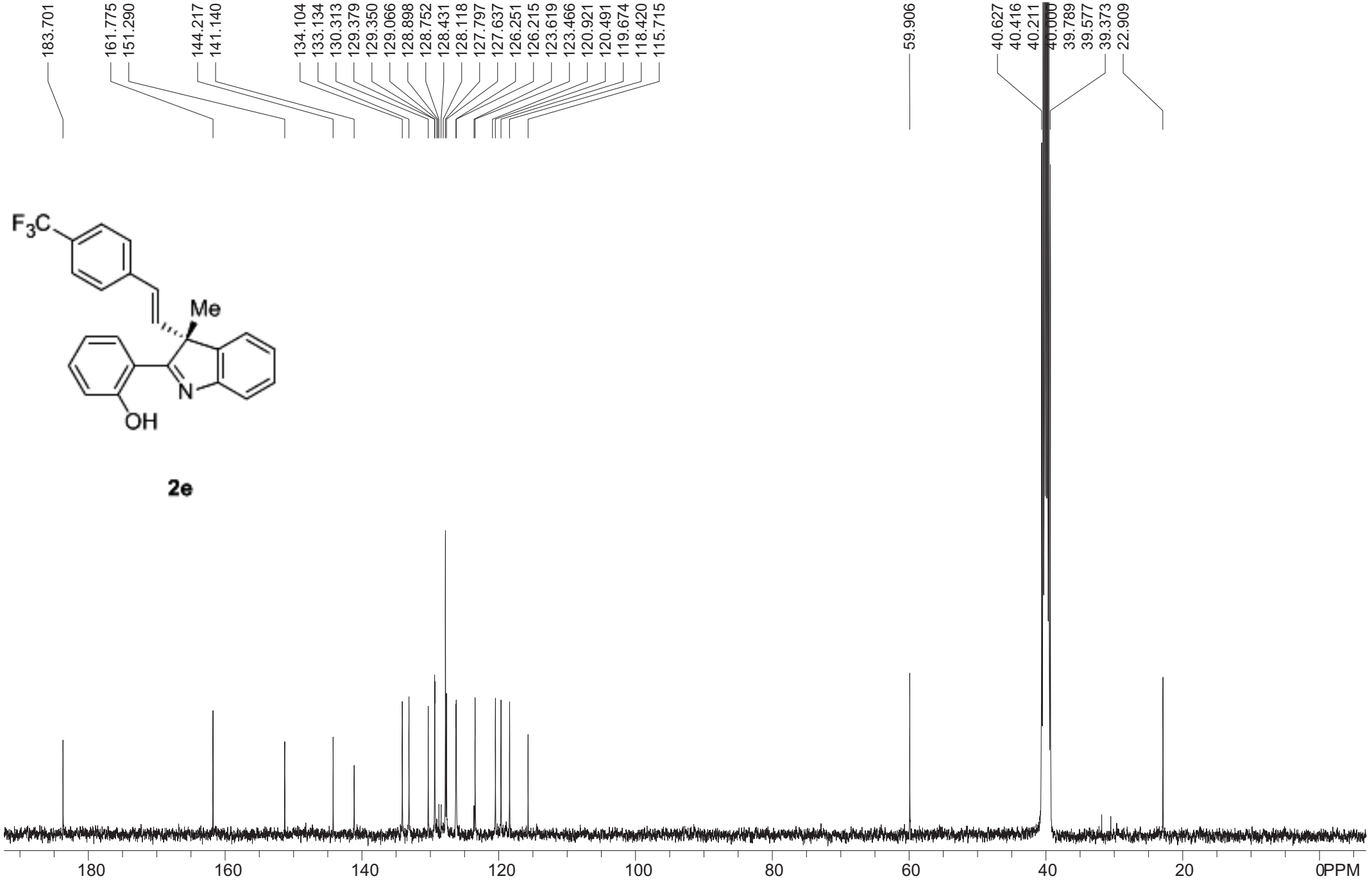
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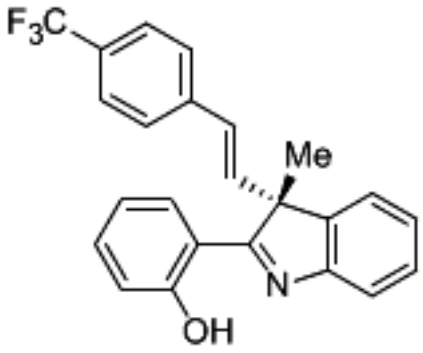

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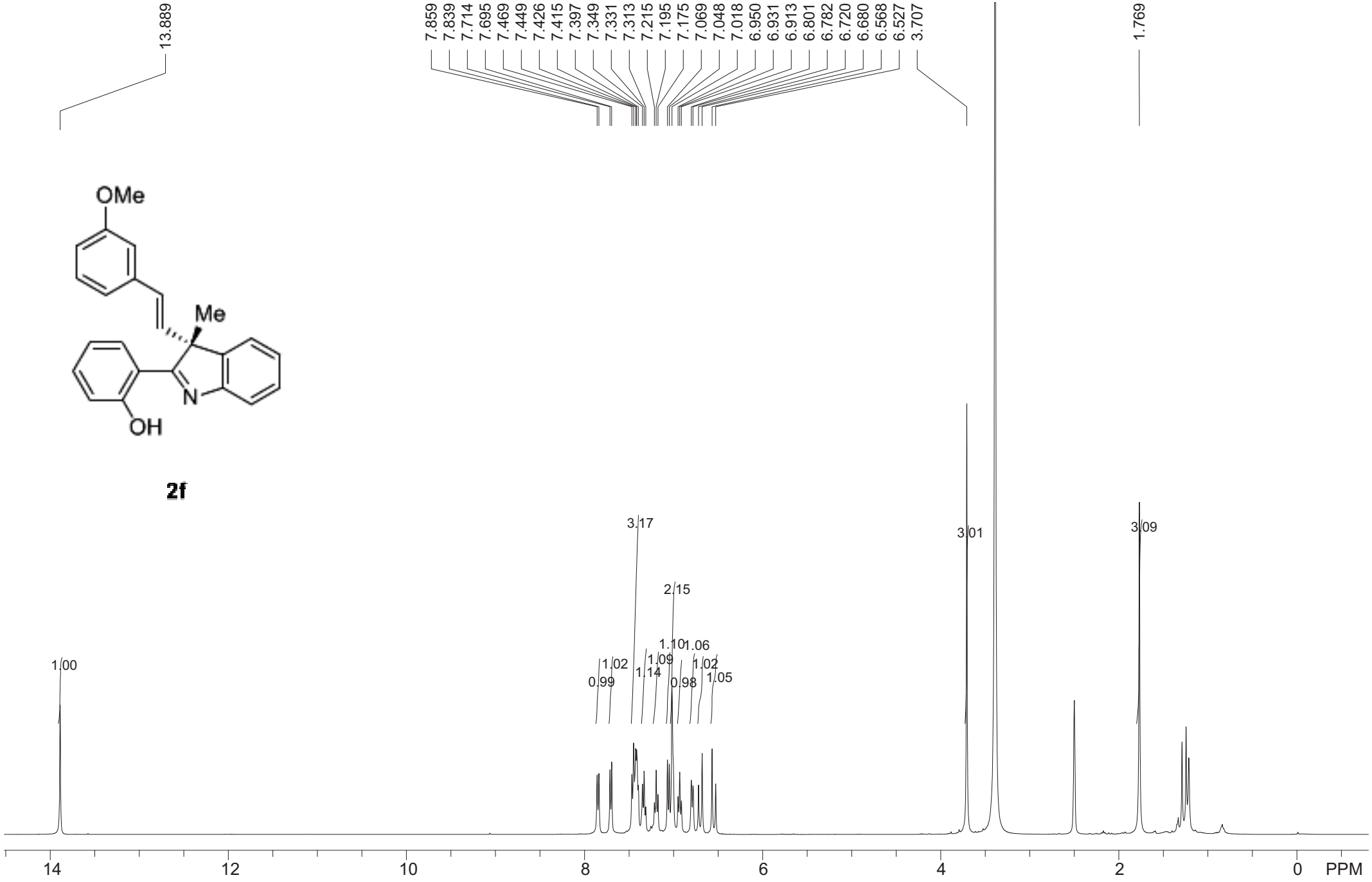
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1.769
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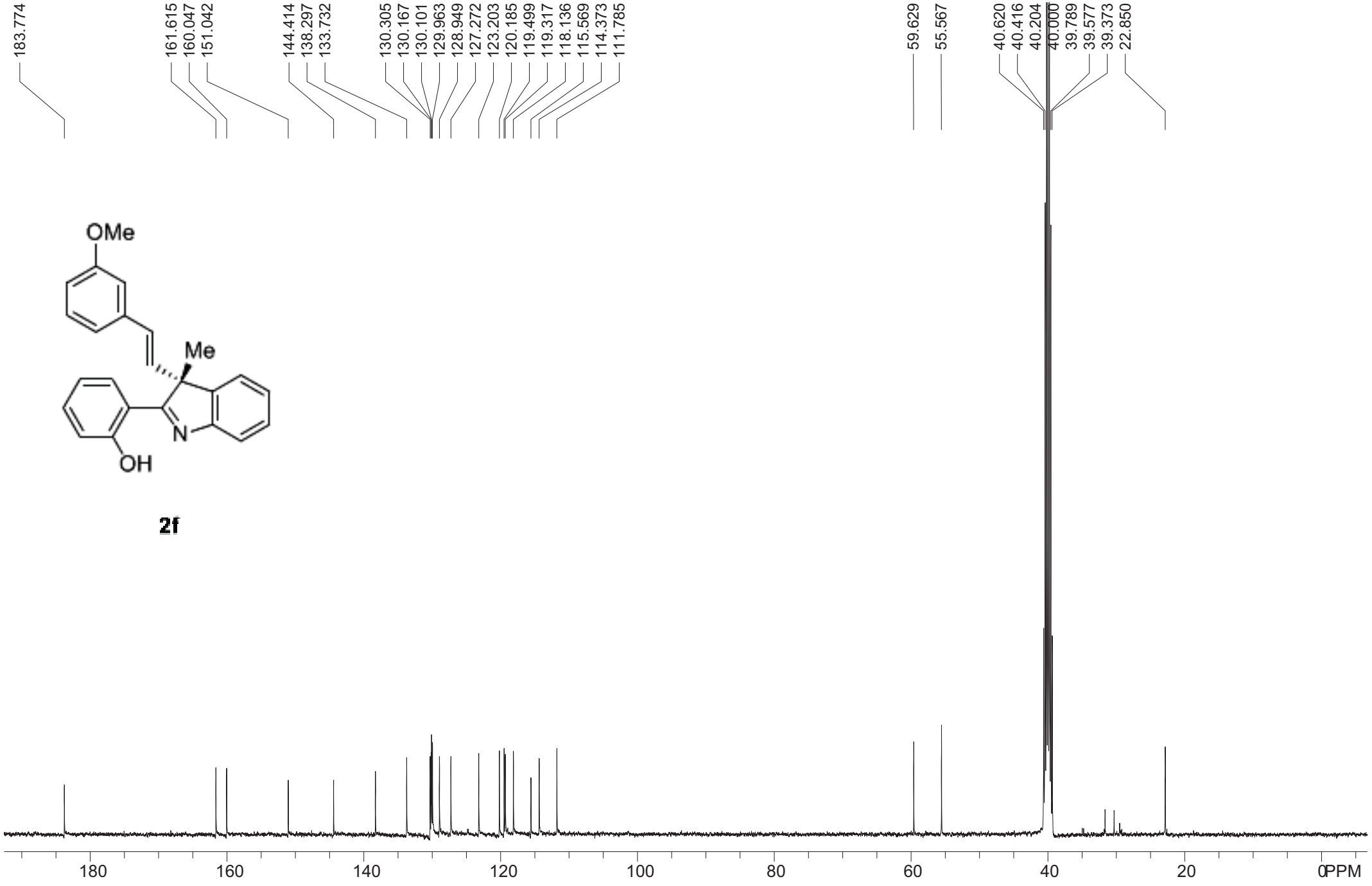
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118.136
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111.785
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40.620
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40.204
40.000
39.789
39.577
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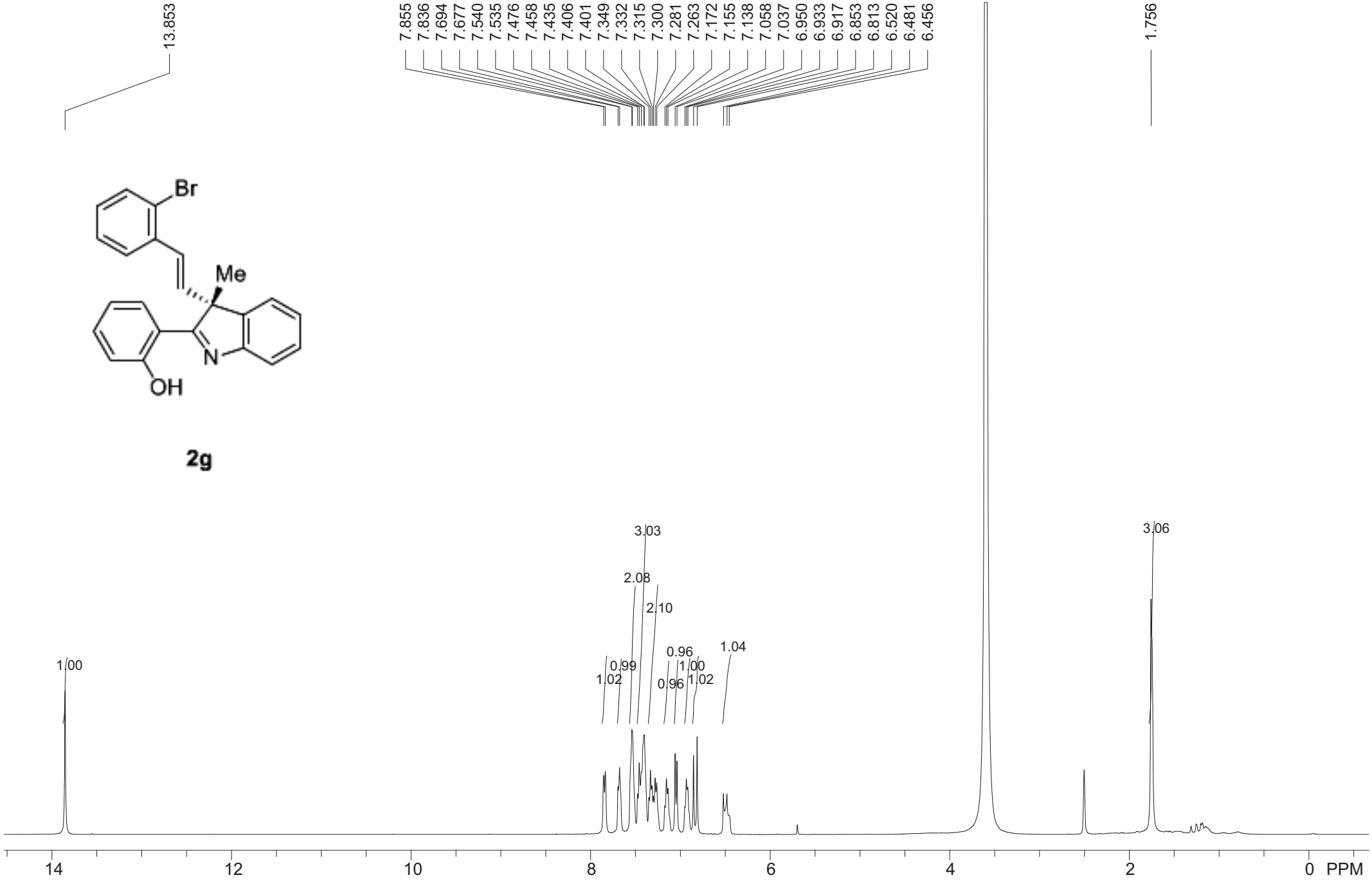
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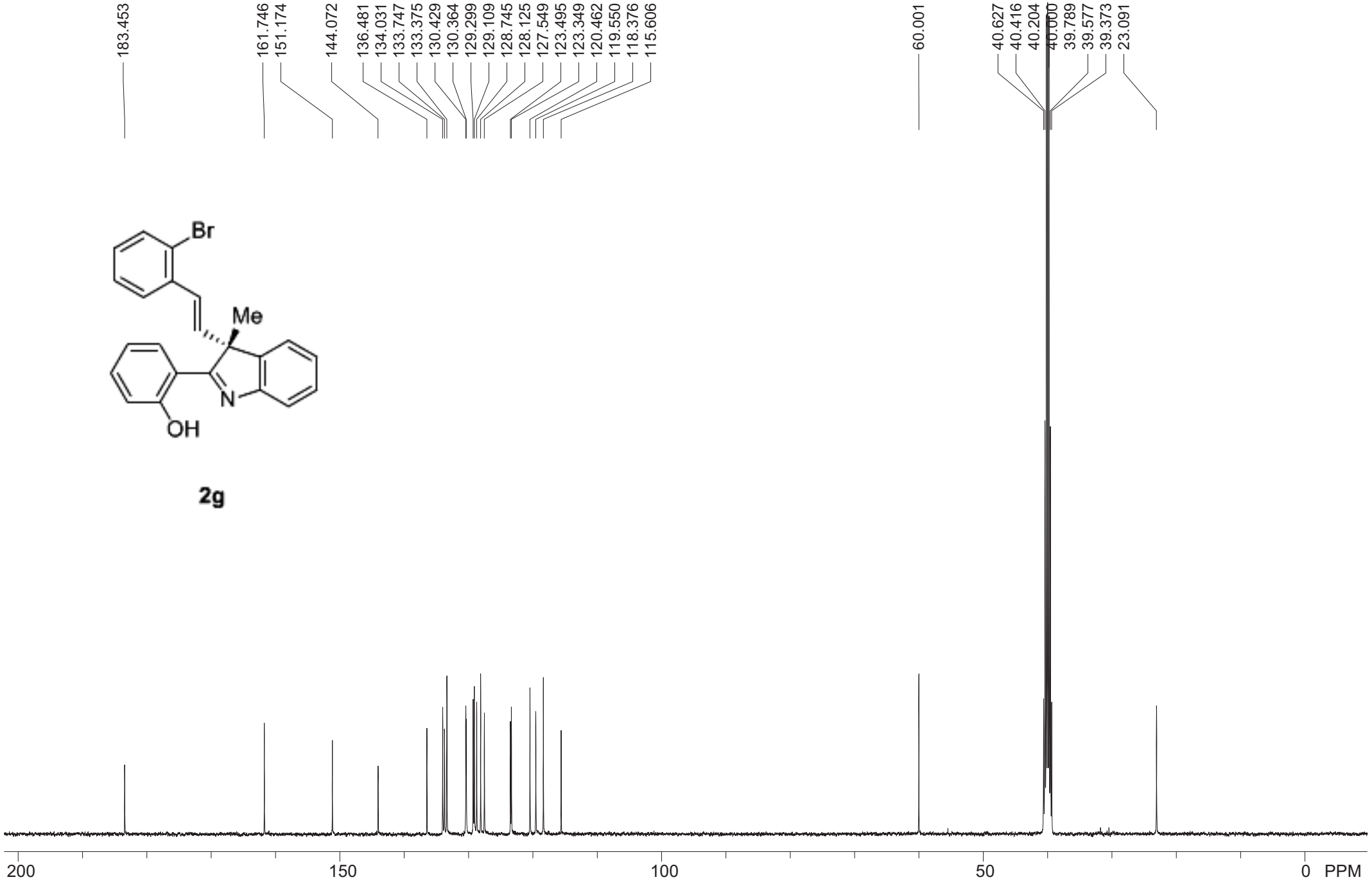
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120.462
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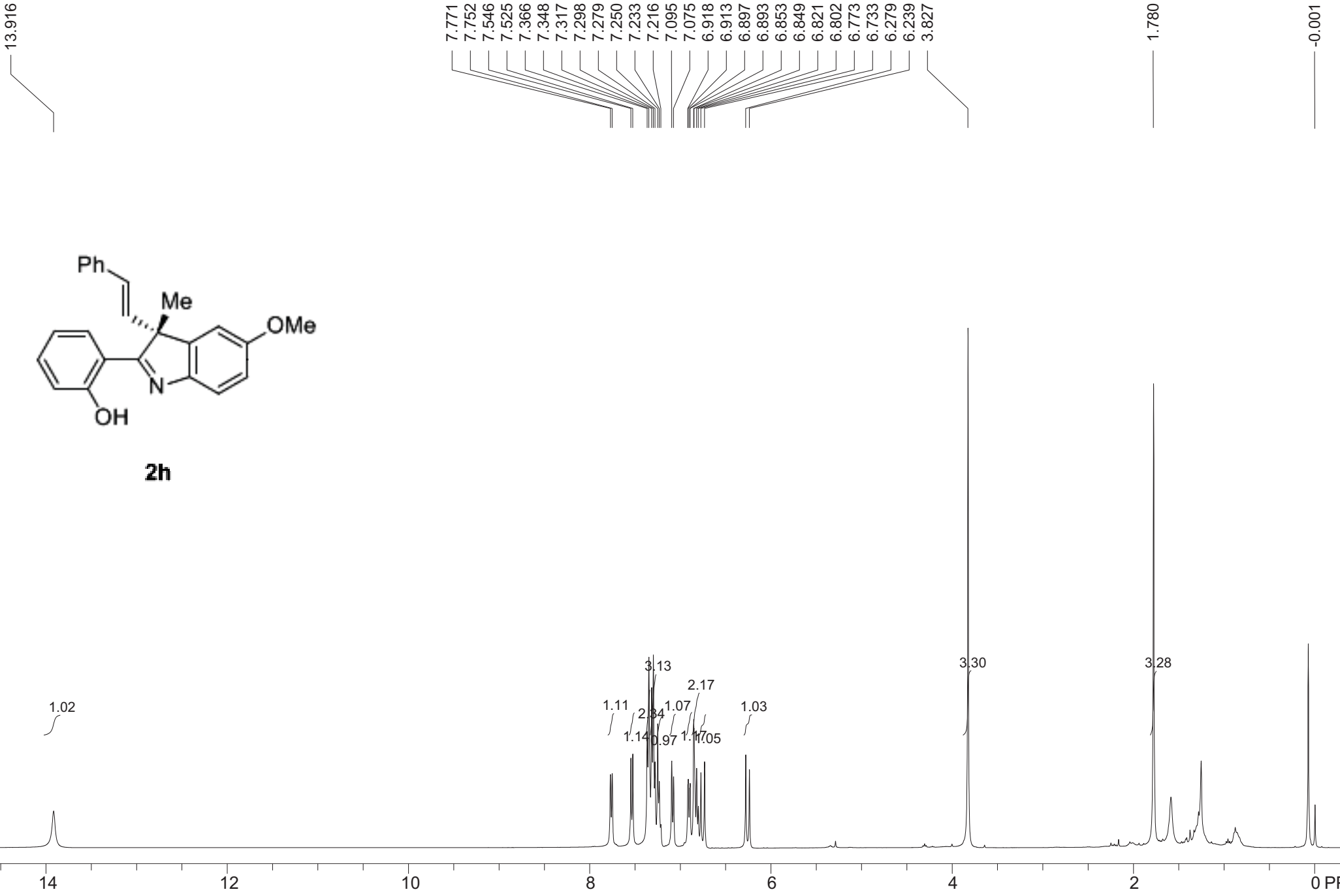
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Ph
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OMe
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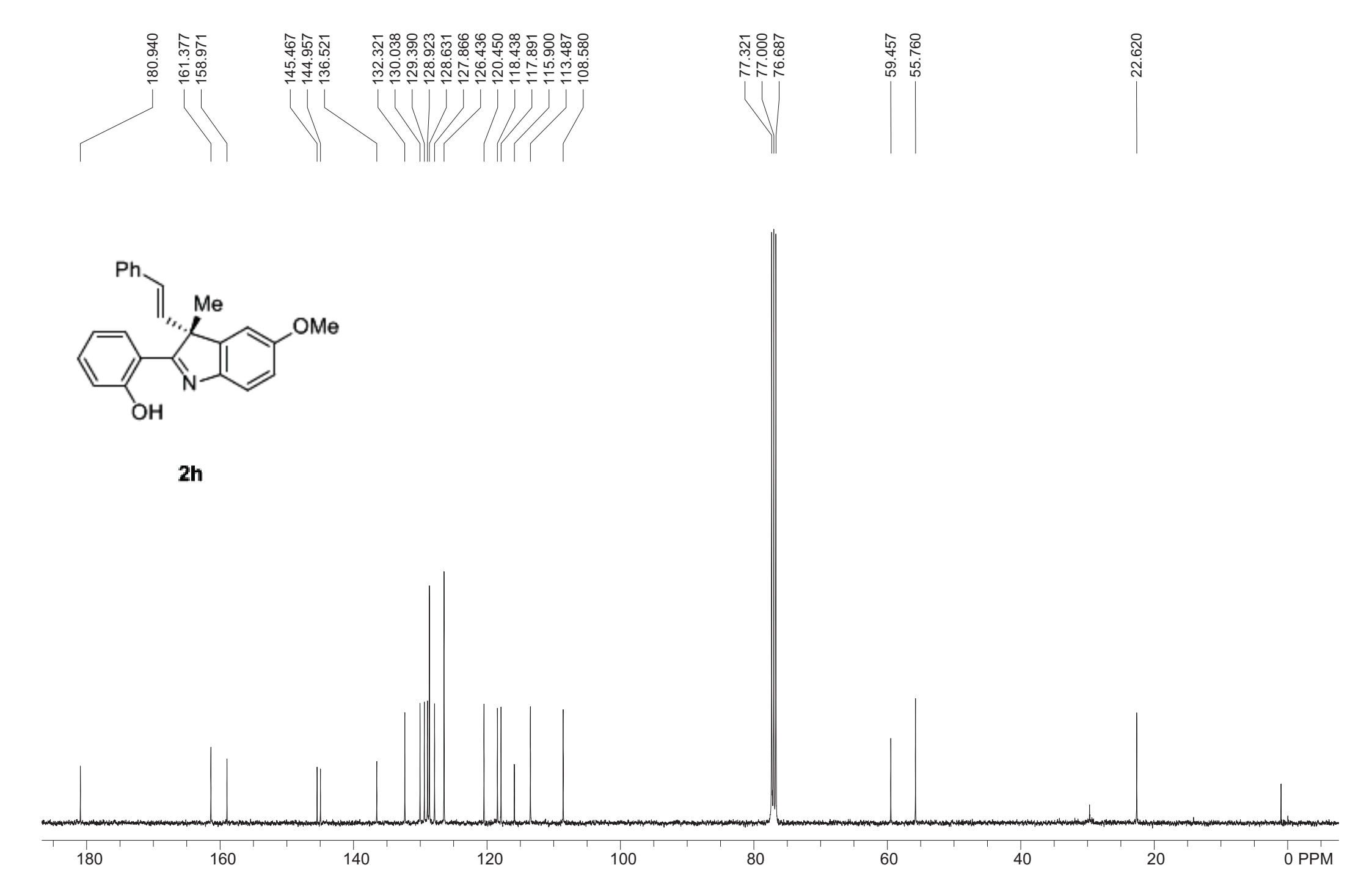
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120.450
118.438
117.891
115.900
113.487
108.580
77.321
77.000
76.687
59.457
55.760
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Me
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120
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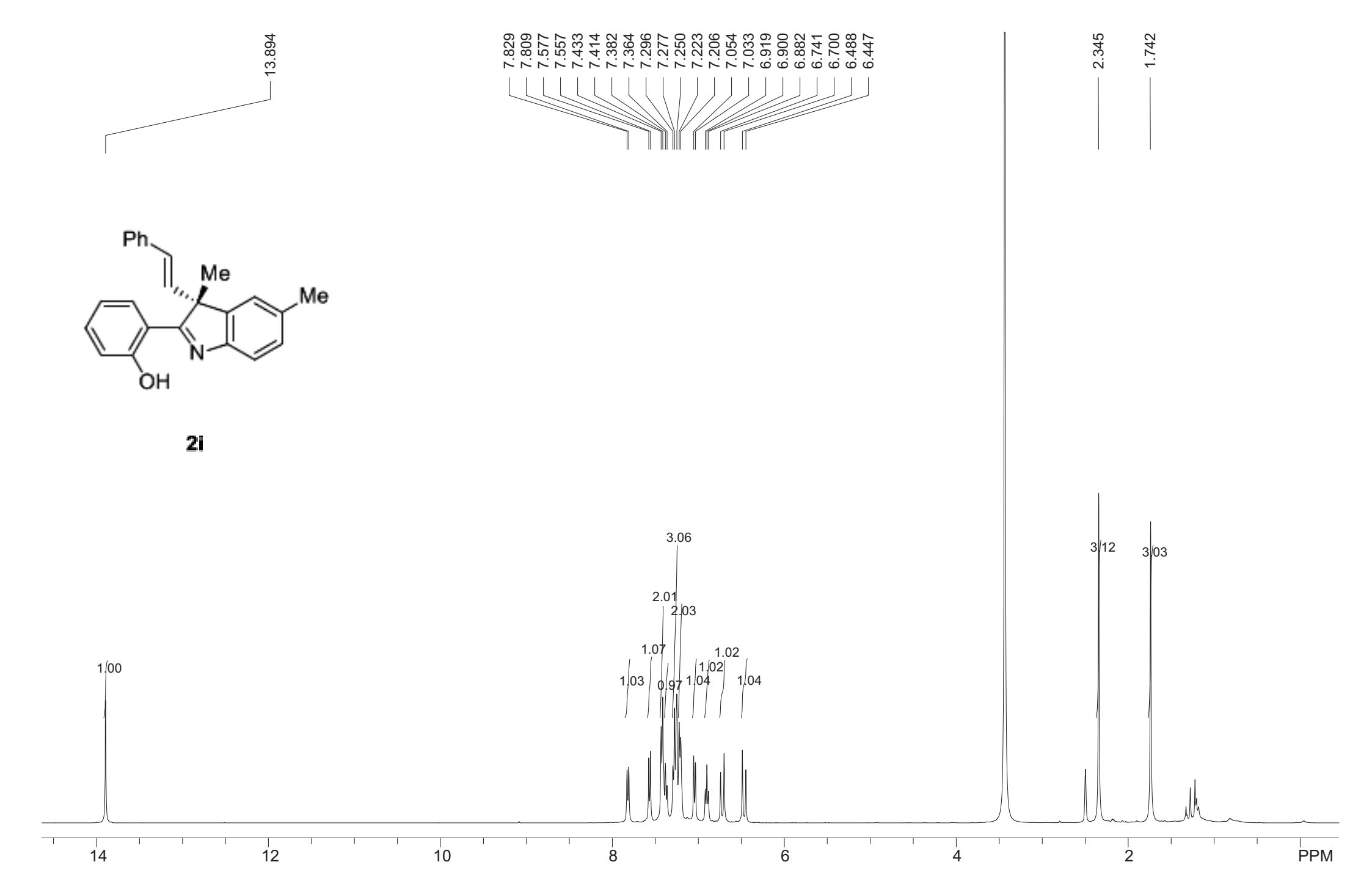
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2.345
1.742
Ph
Me
Me
N
OH
2i
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1.03
1.07
2.01
2.03
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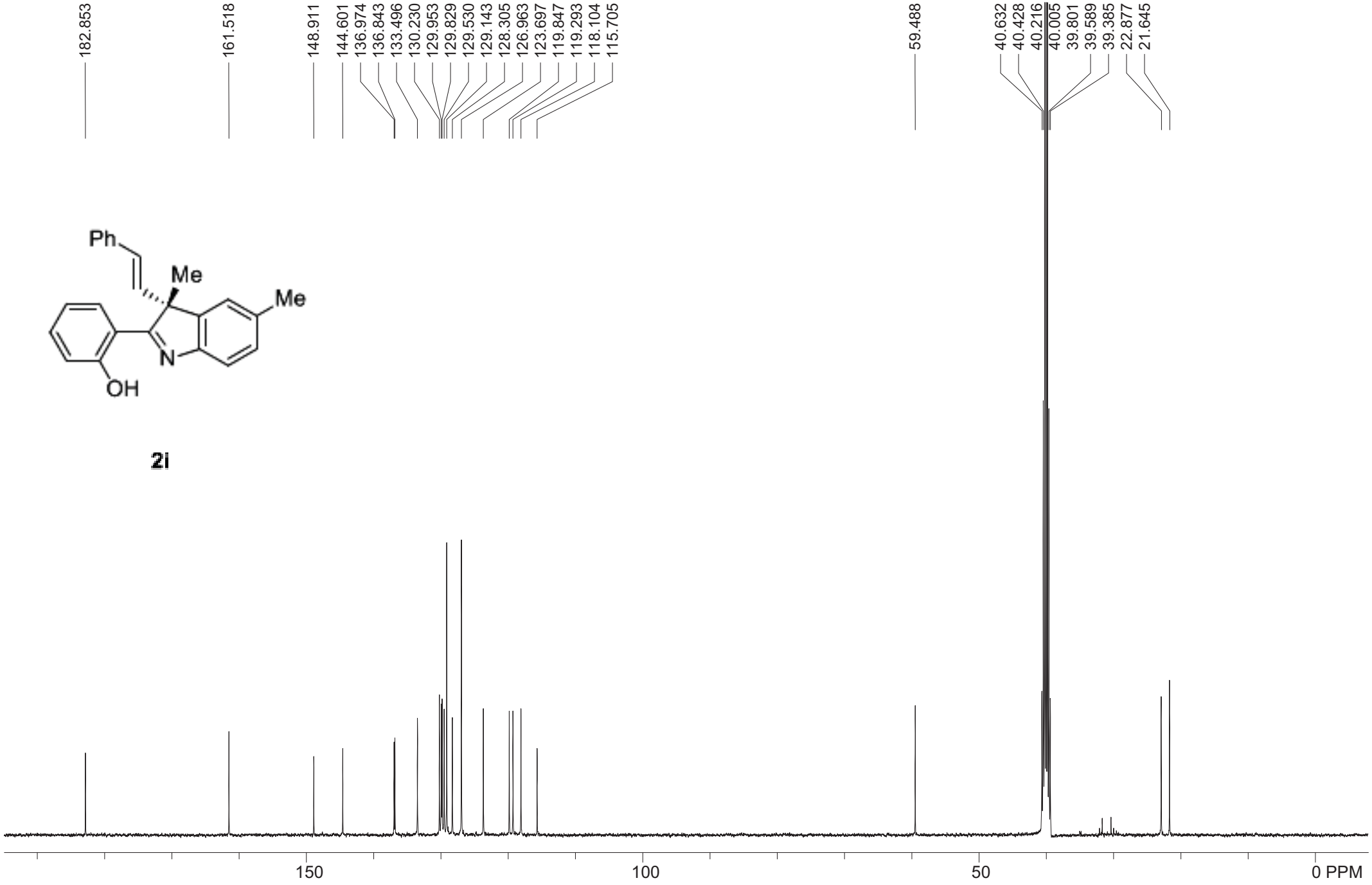
2
PPM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161.518
148.911
144.601
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136.843
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129.530
129.143
128.305
126.963
123.697
119.847
119.293
118.104
115.705
59.488
40.632
40.428
40.216
40.005
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39.385
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21.645
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Me
N
OH
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50
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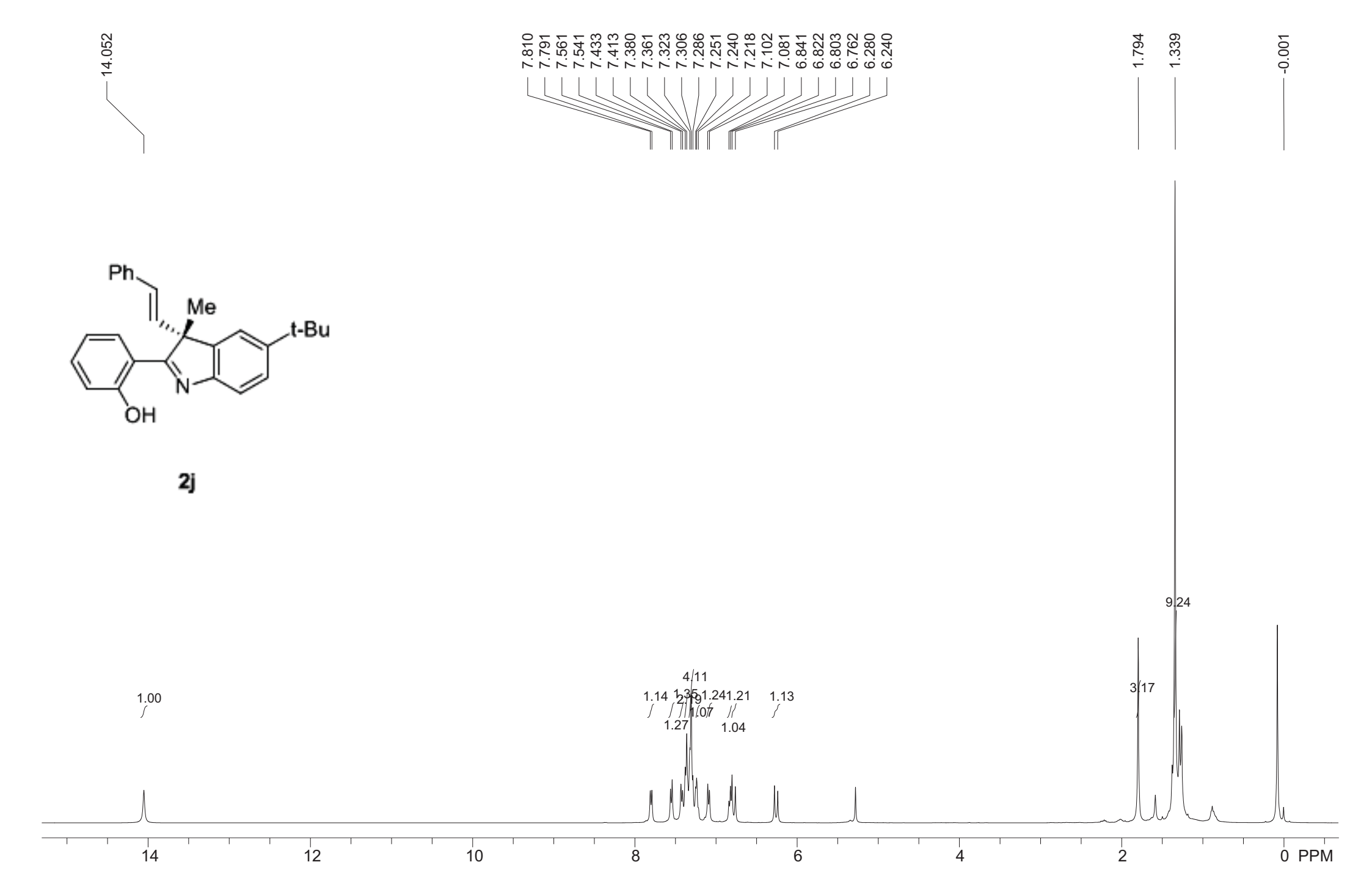
2l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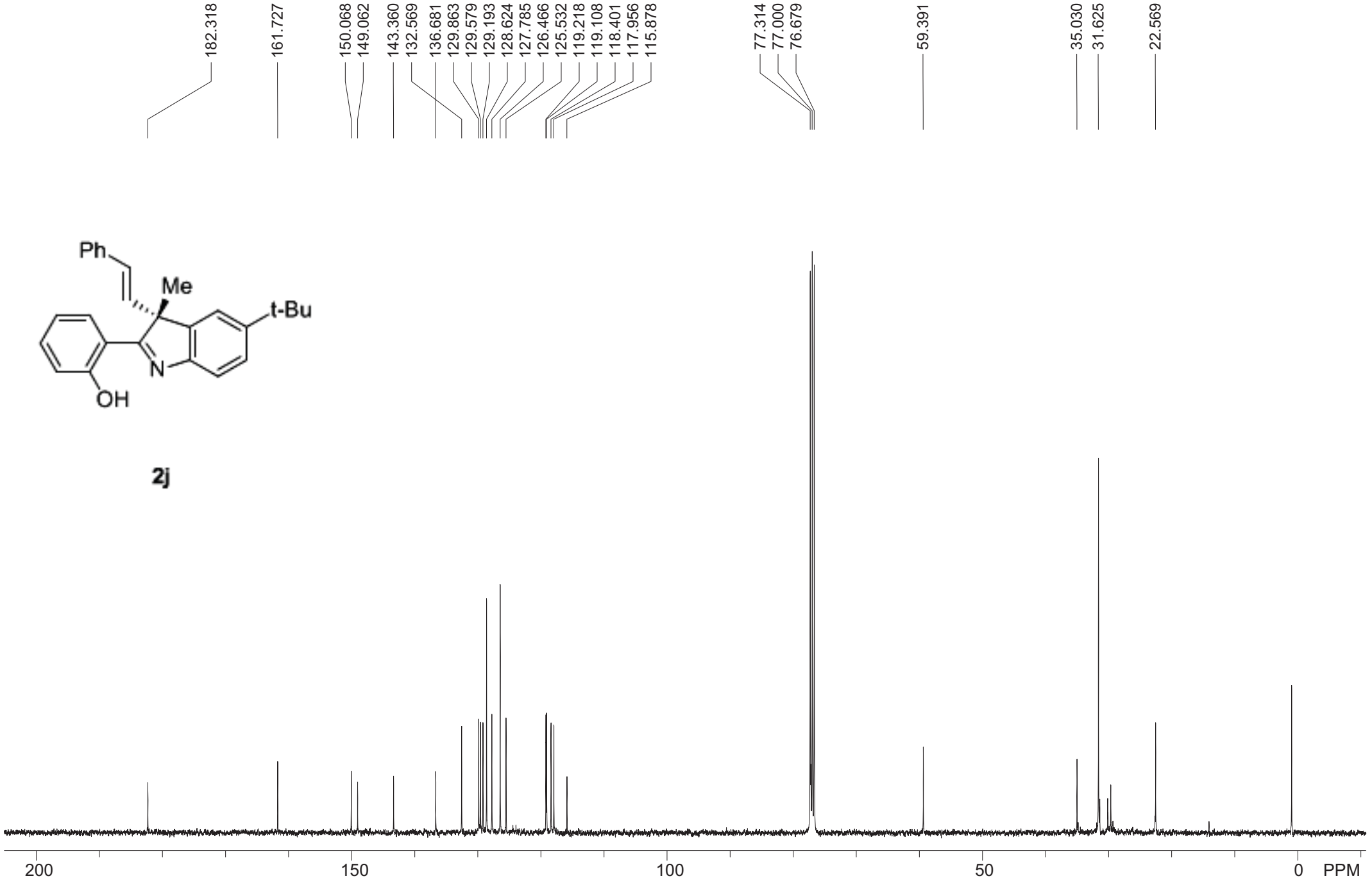
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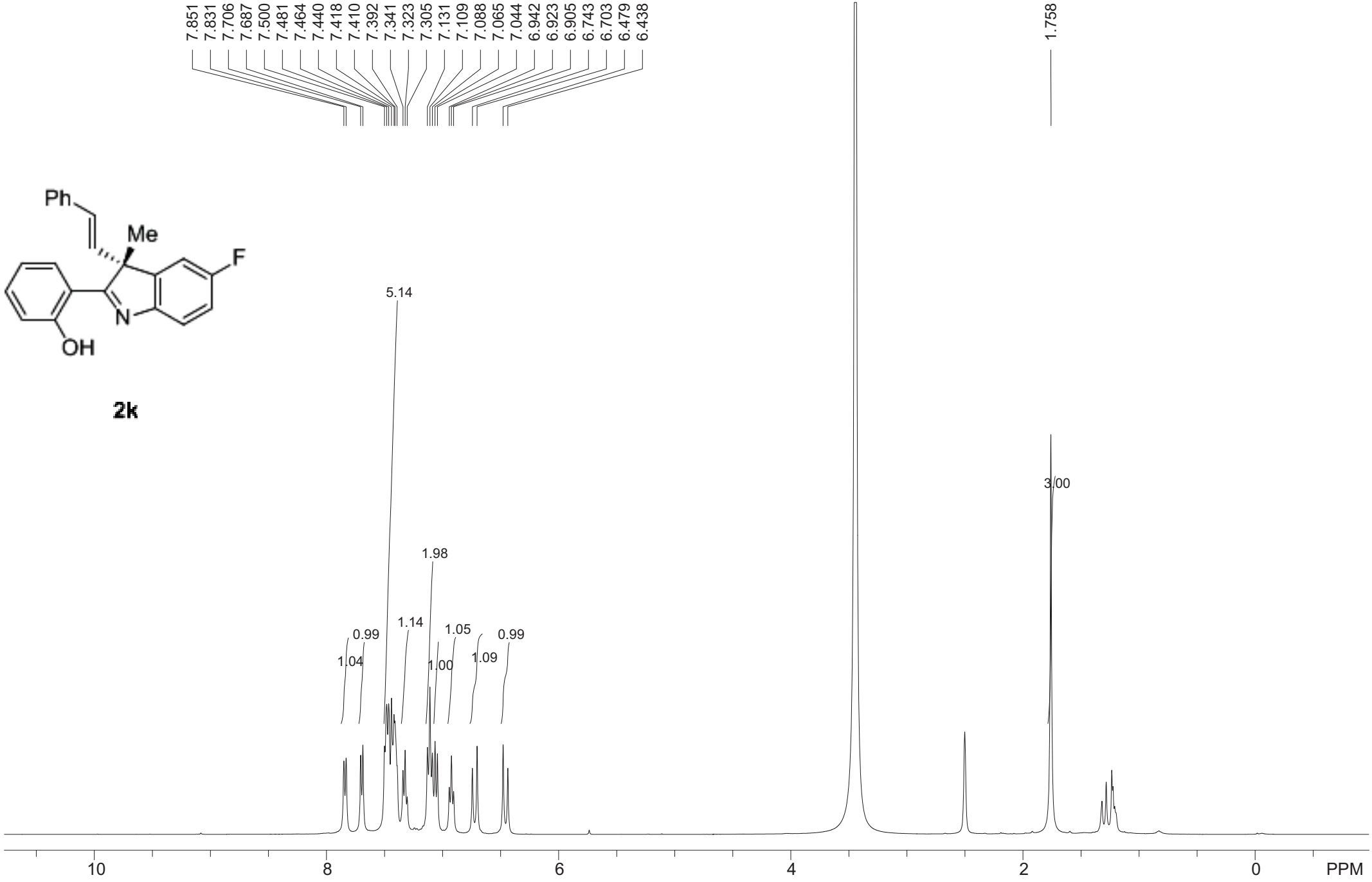
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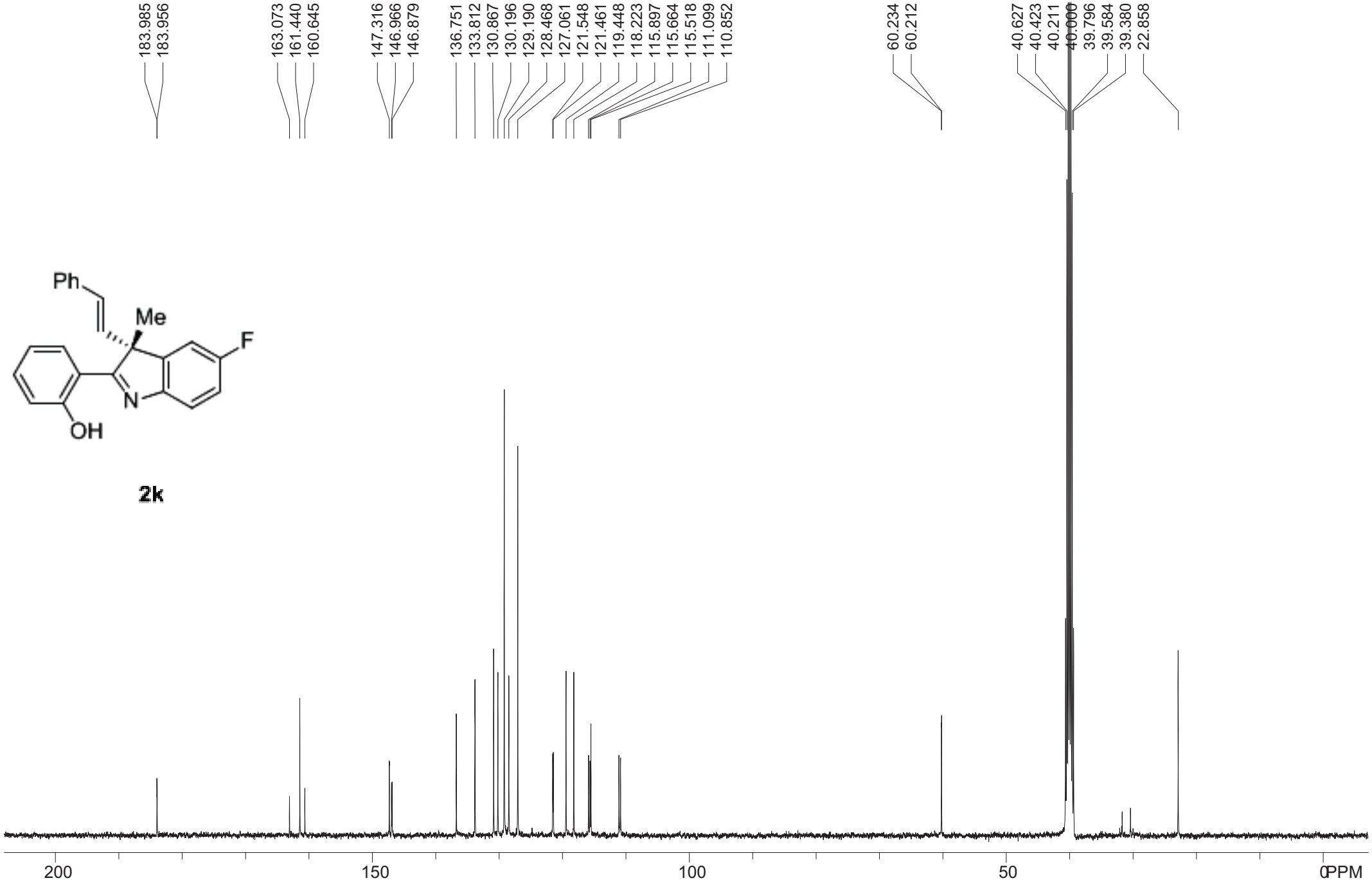
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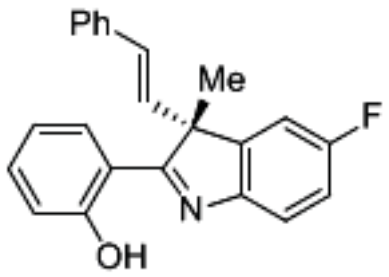

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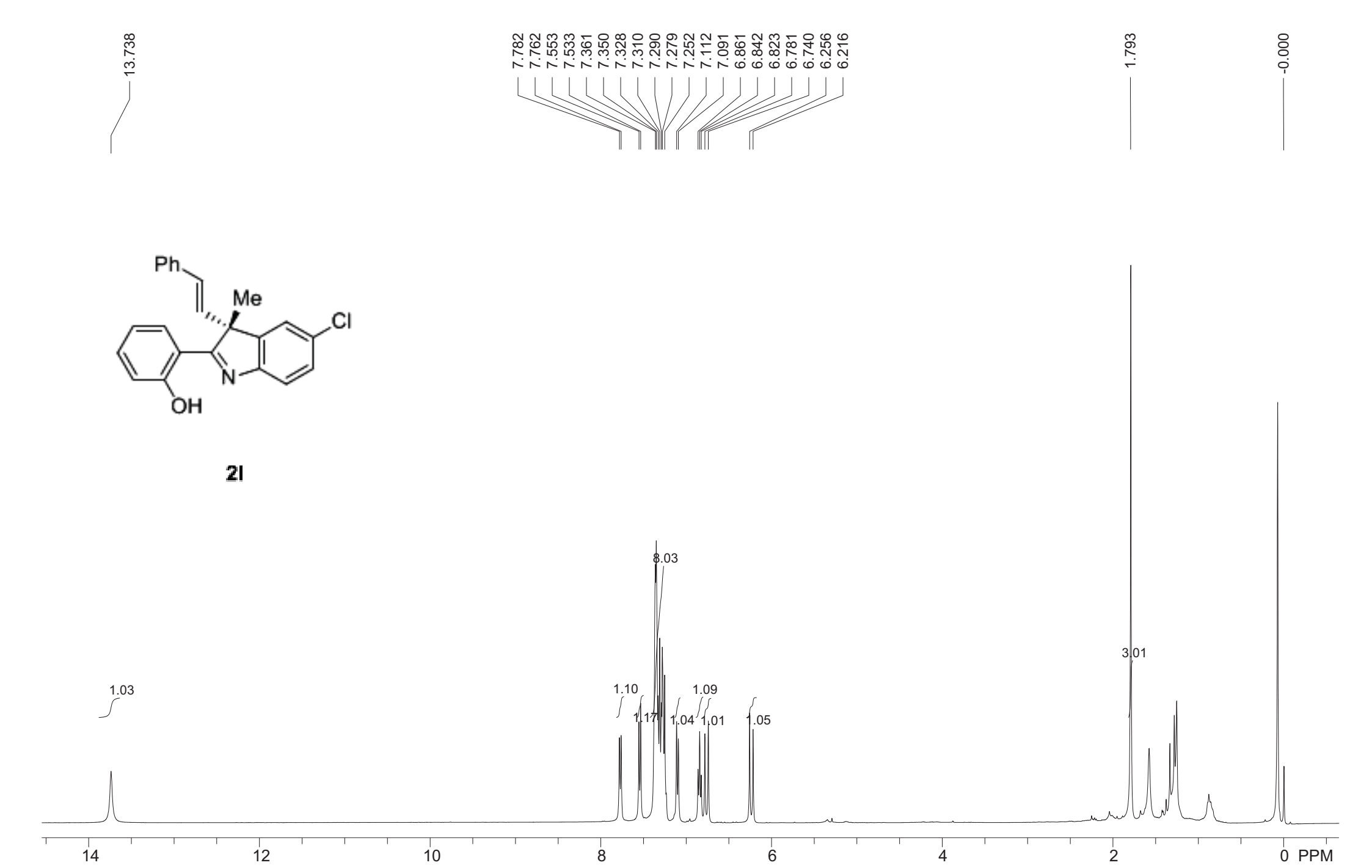
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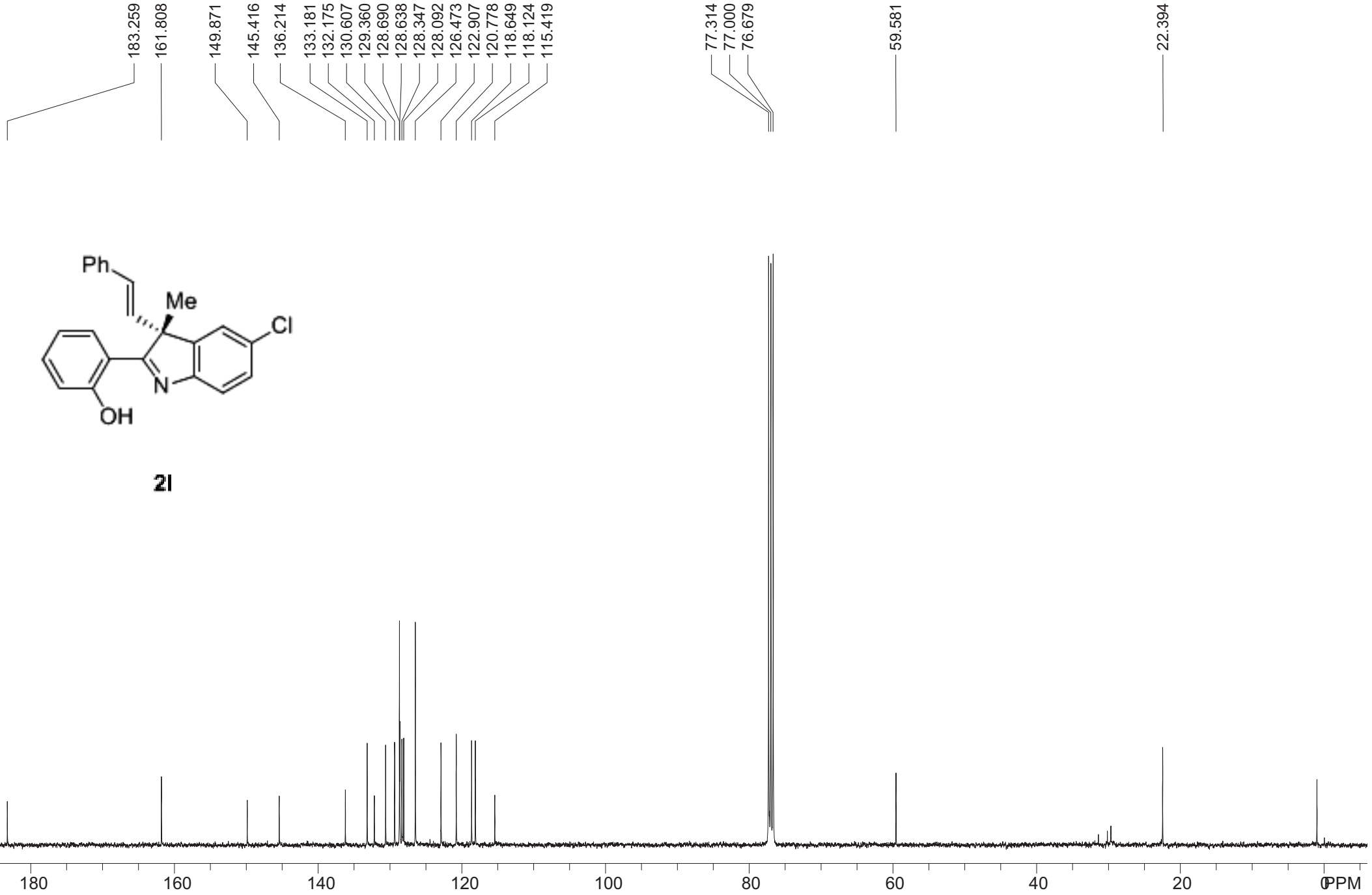
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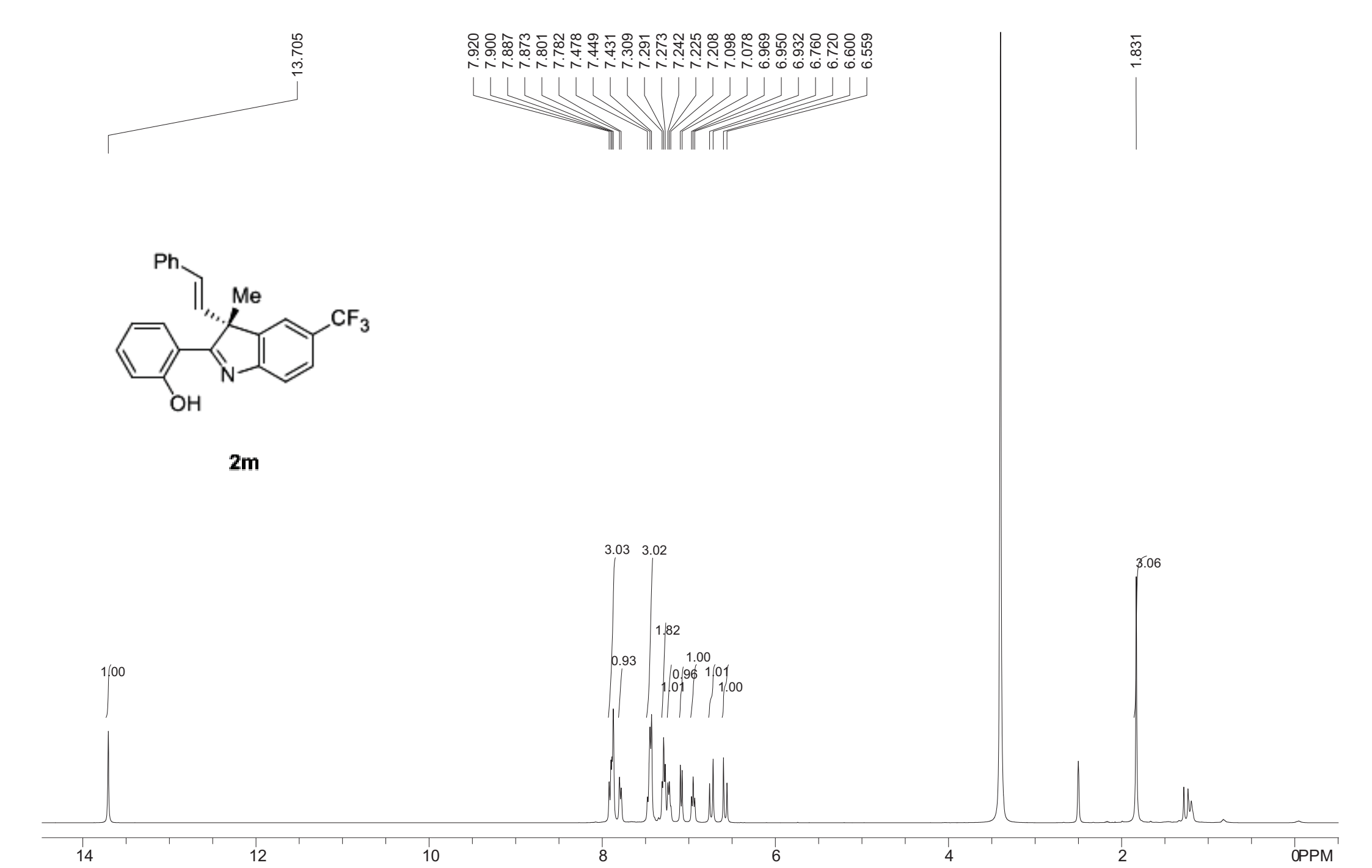
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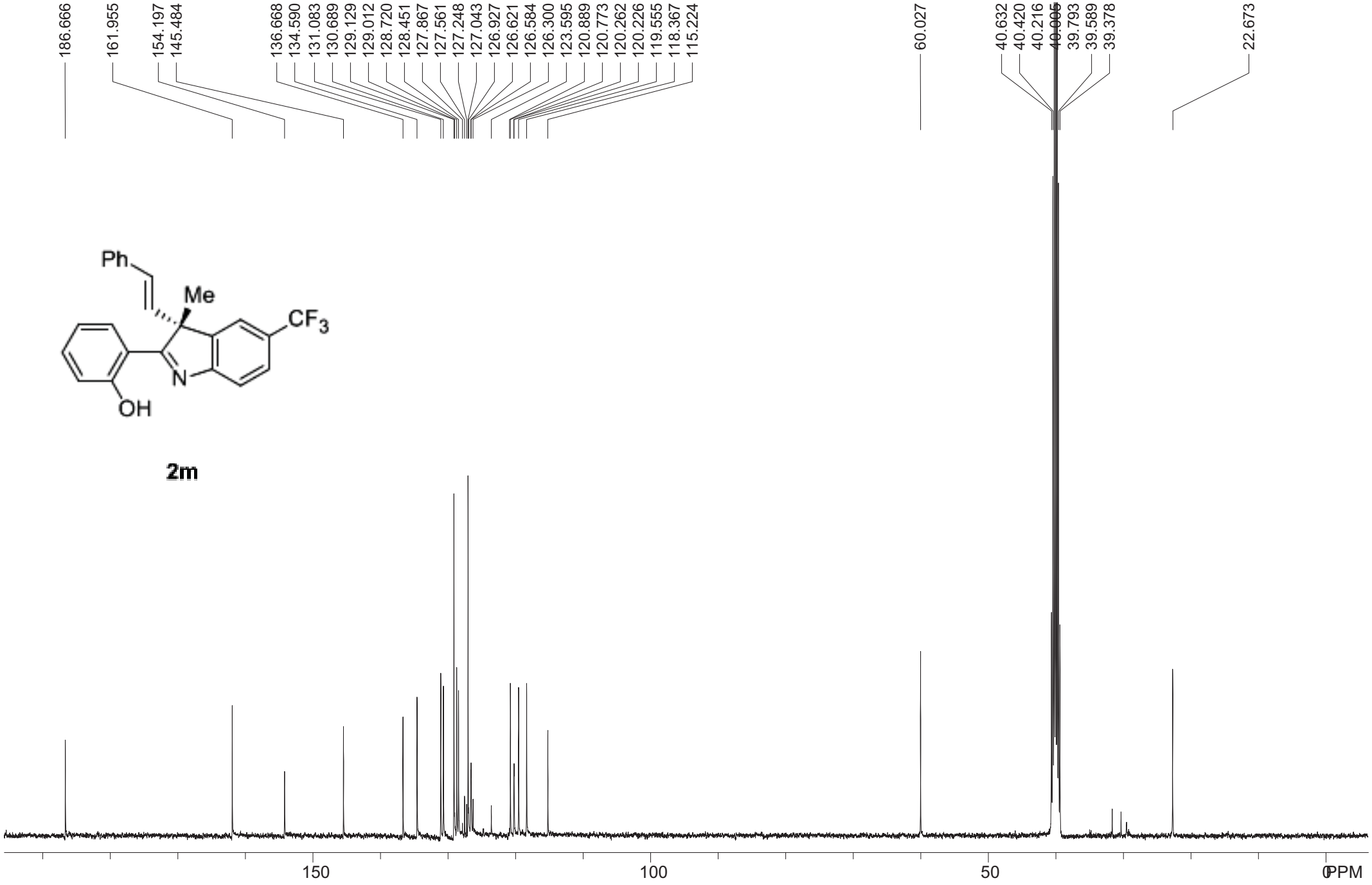
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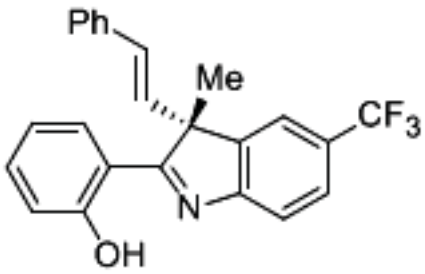

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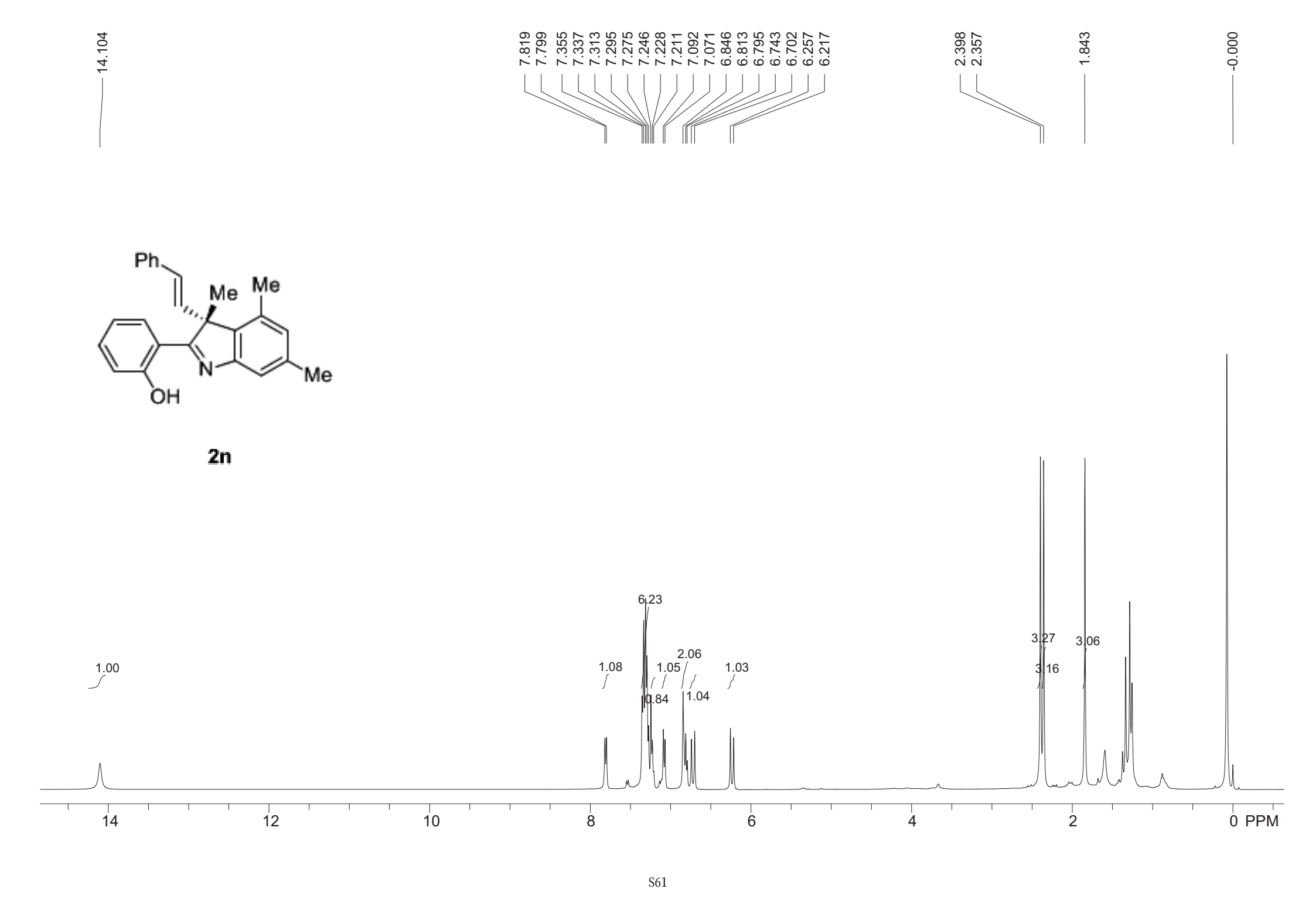
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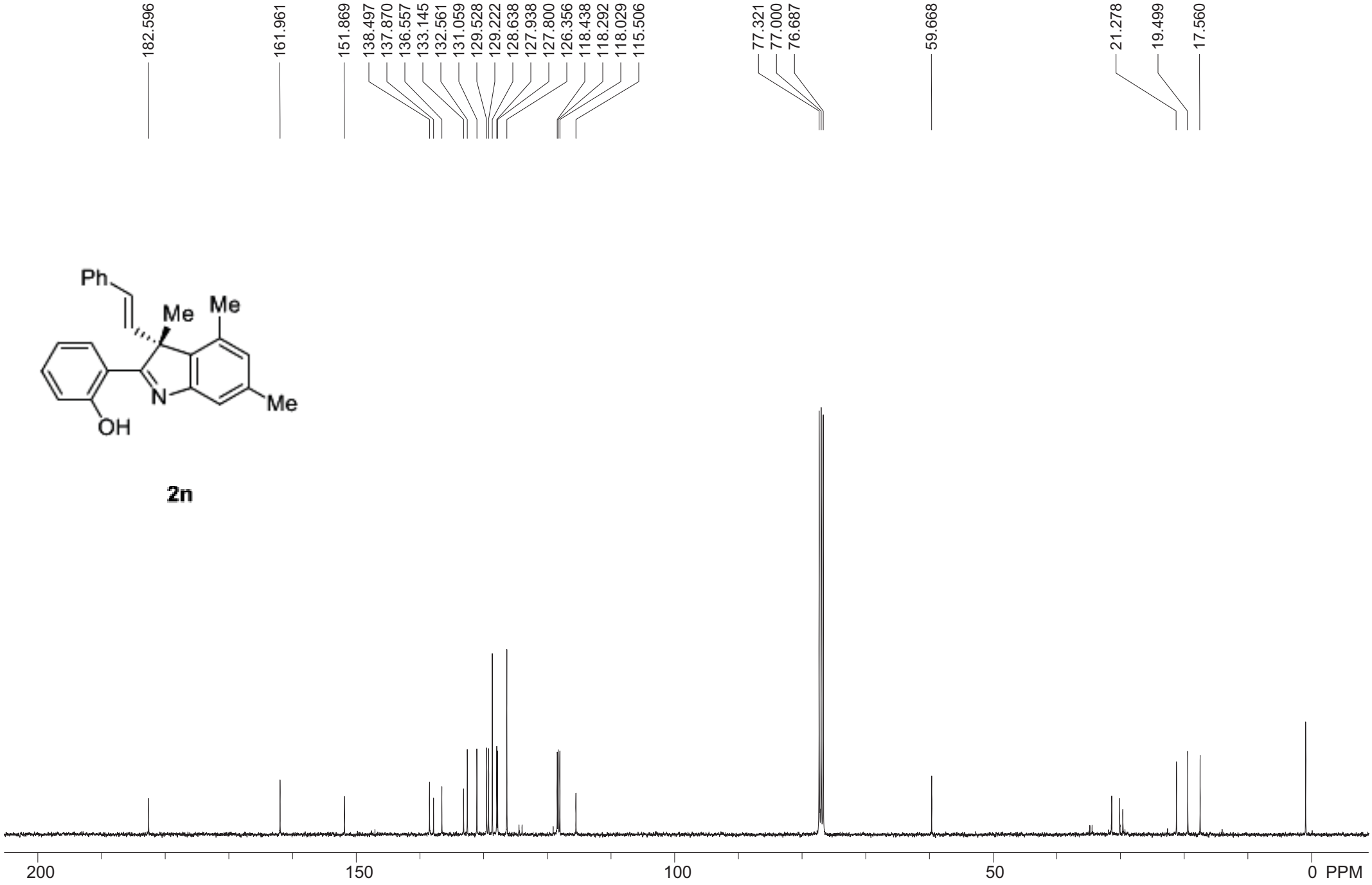
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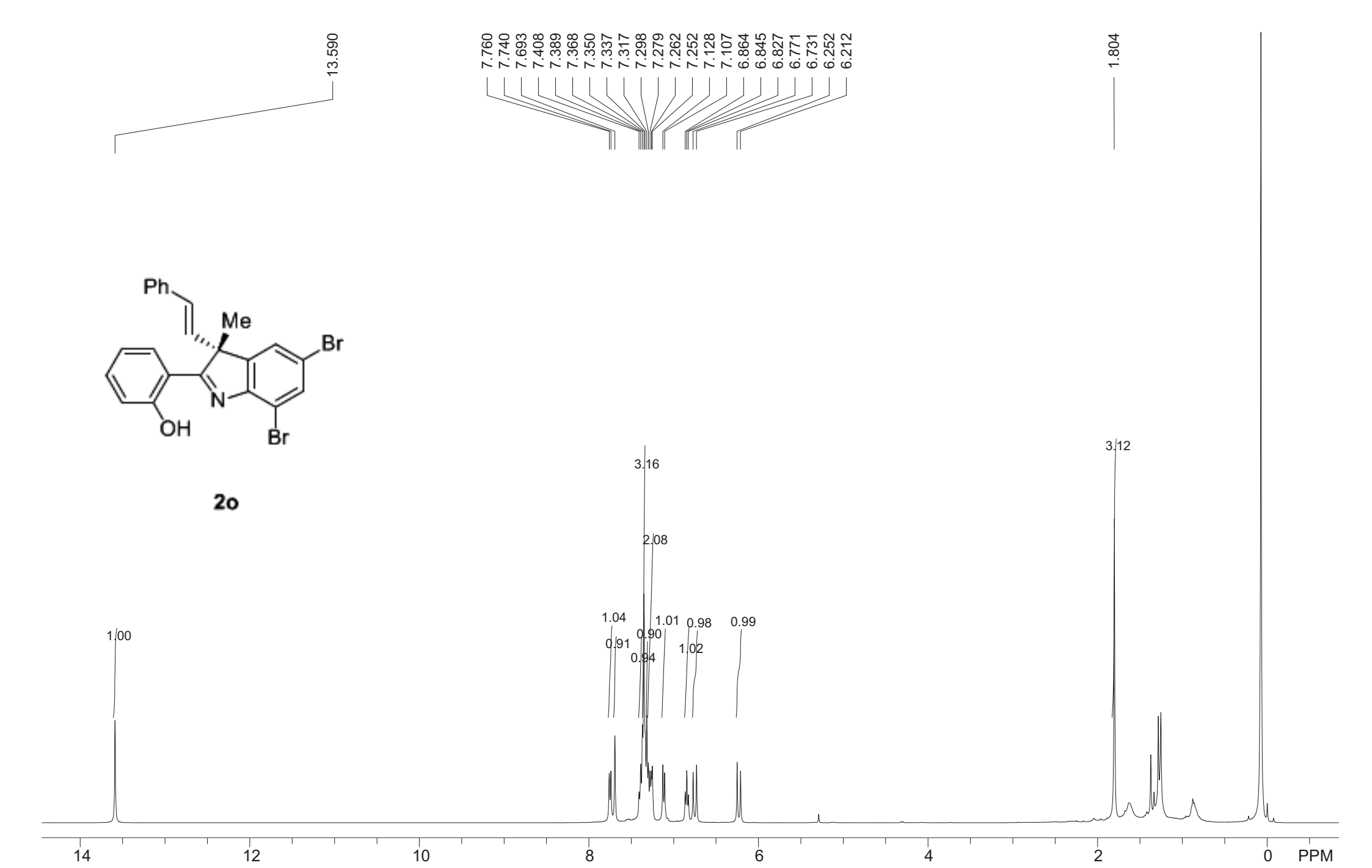
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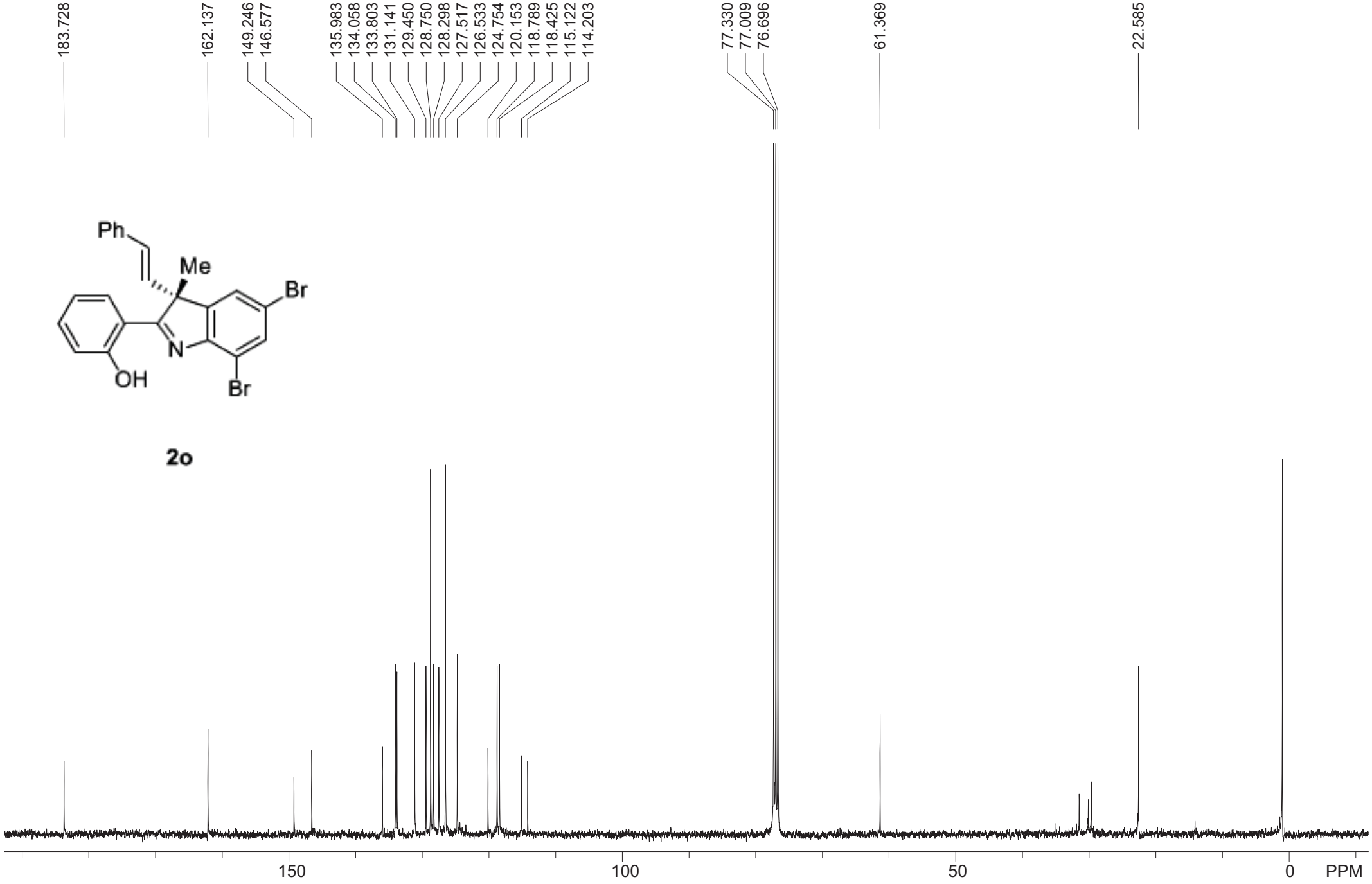
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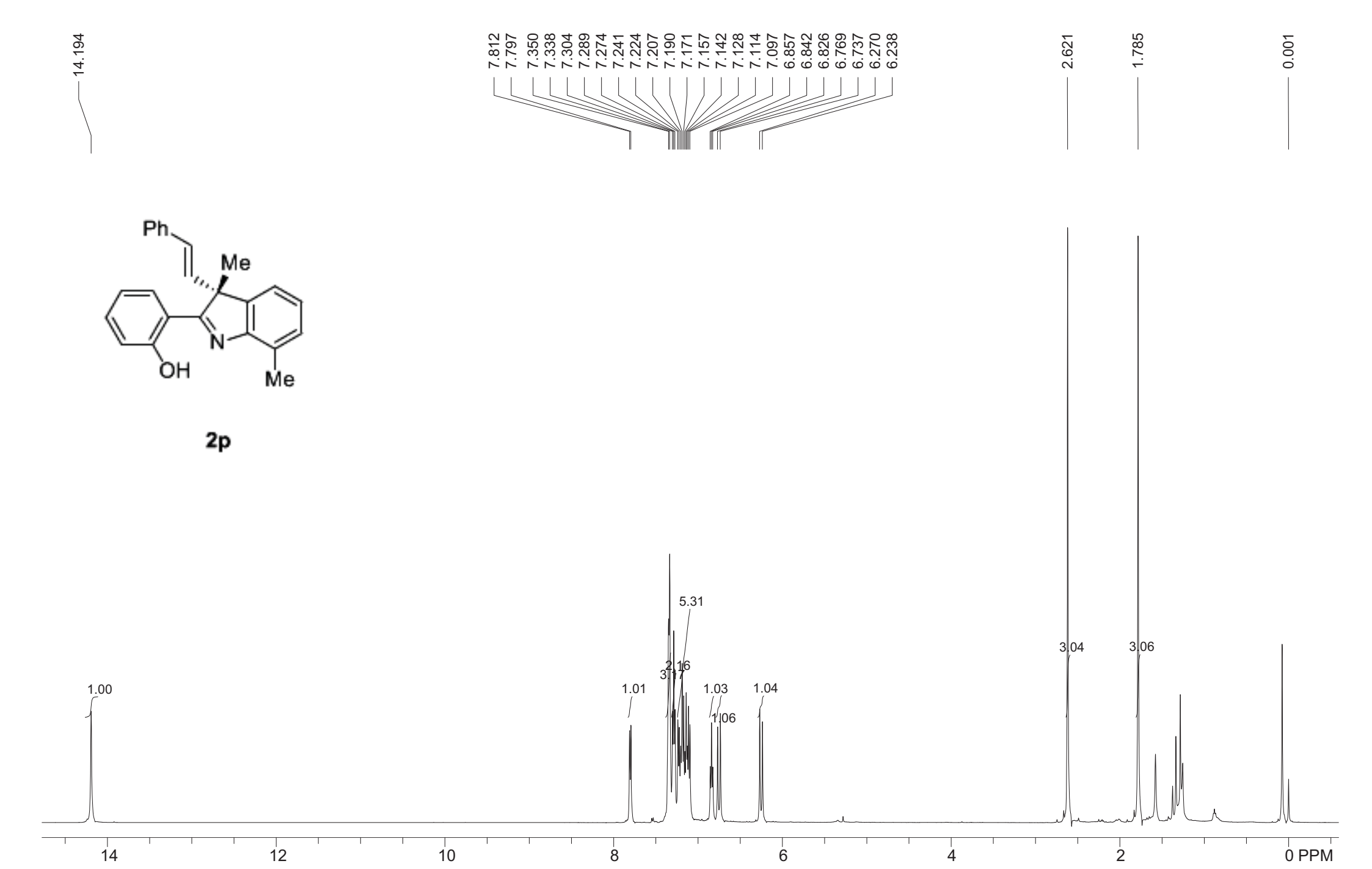
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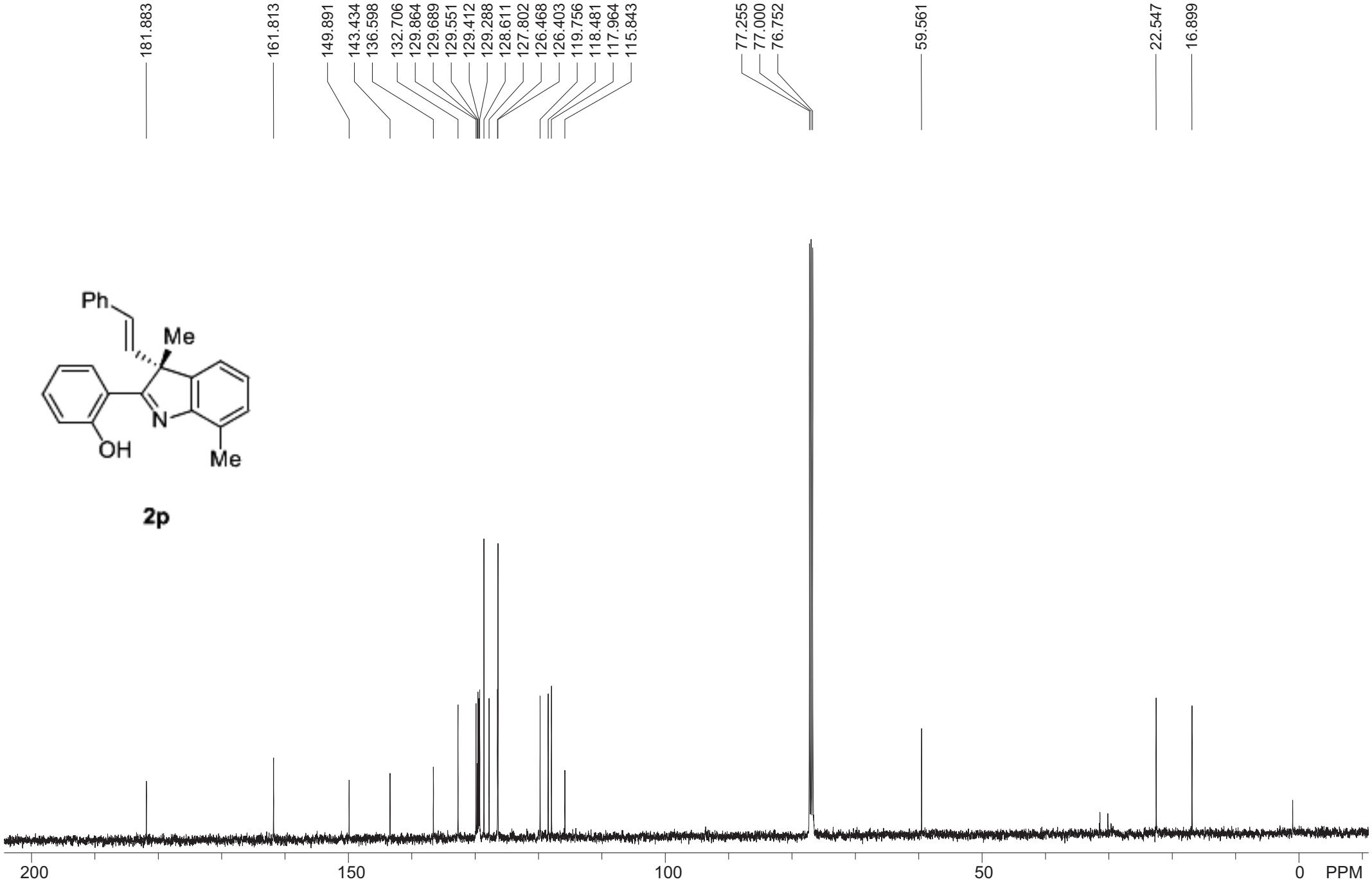
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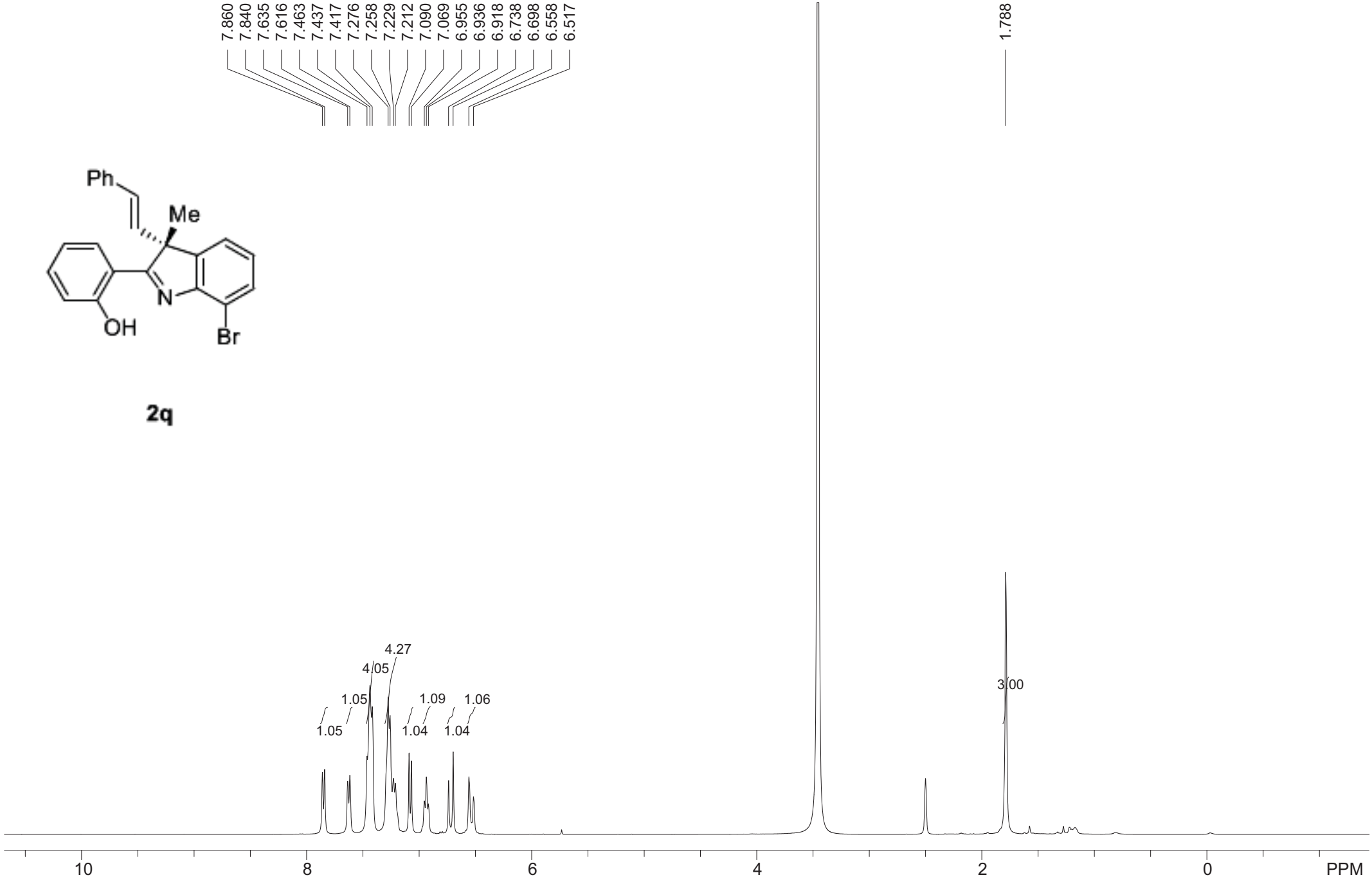
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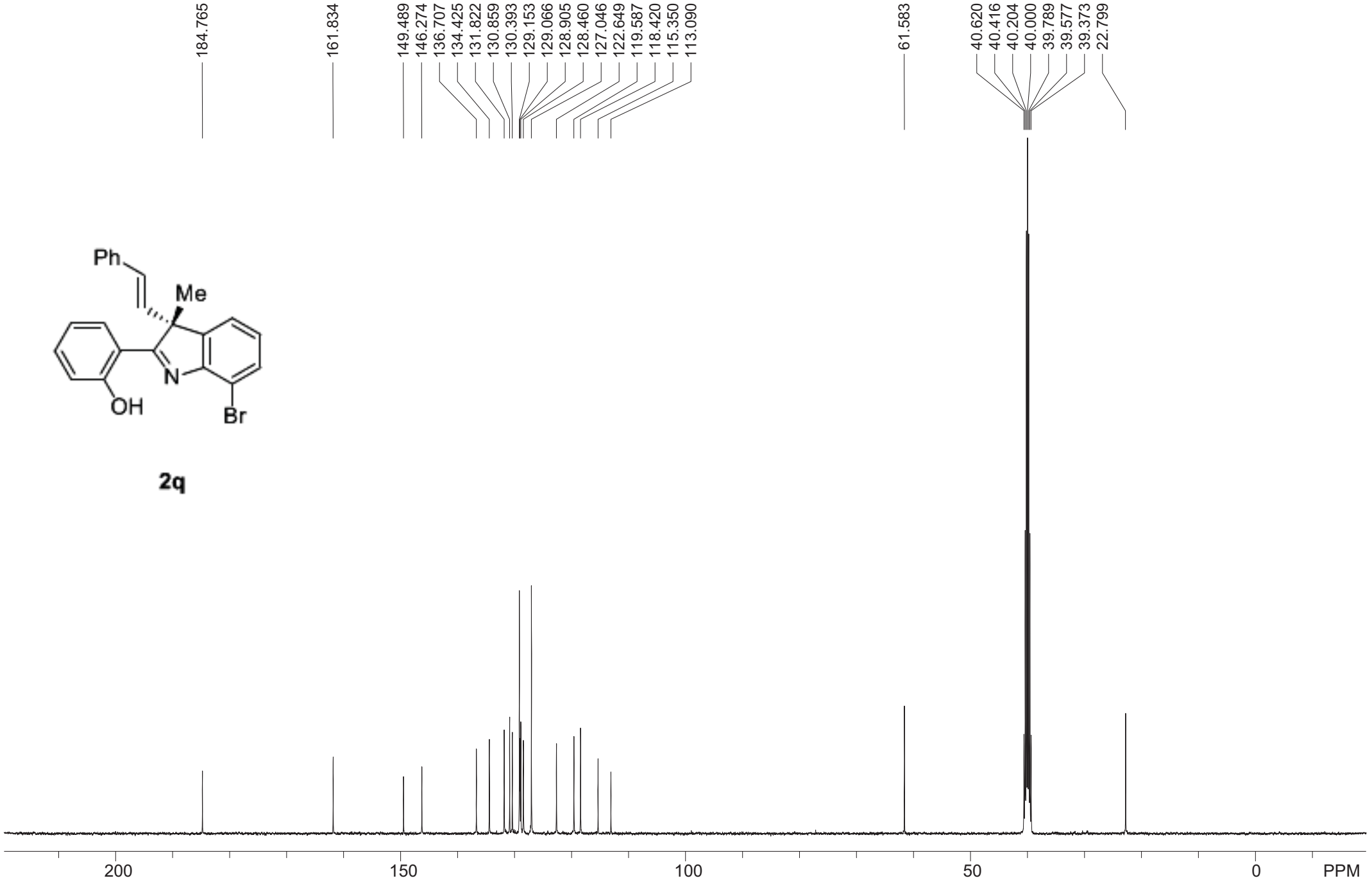
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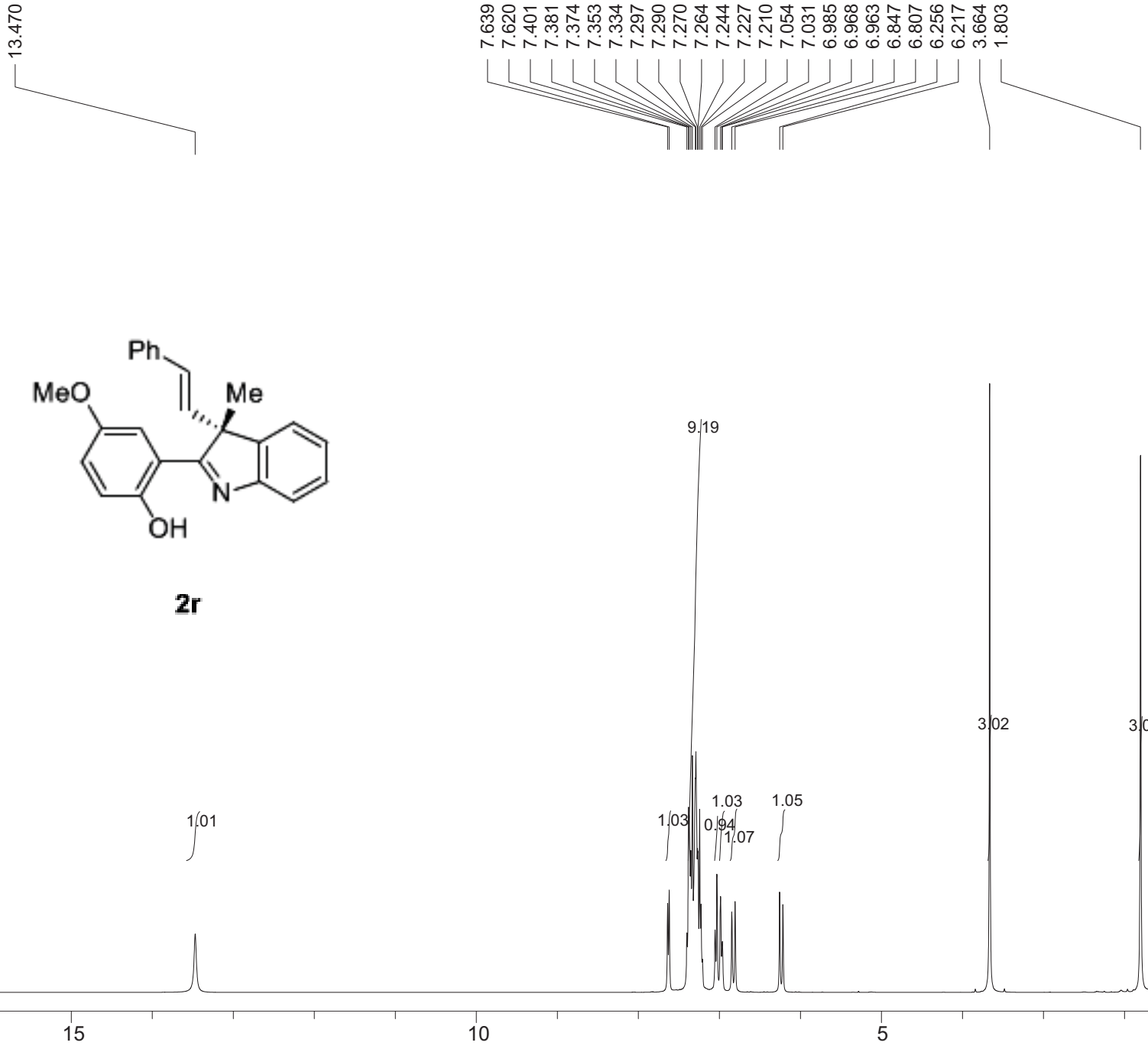
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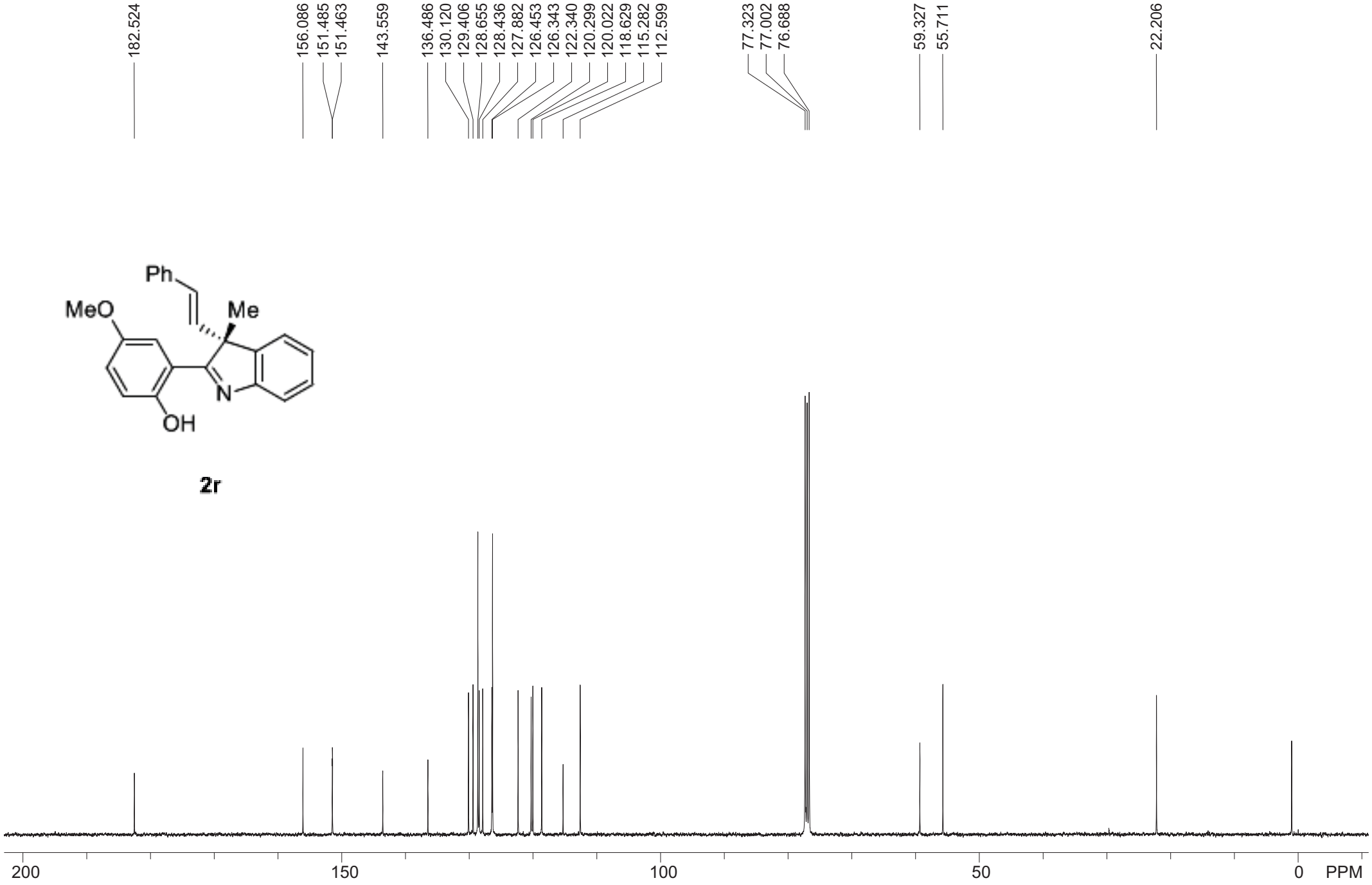
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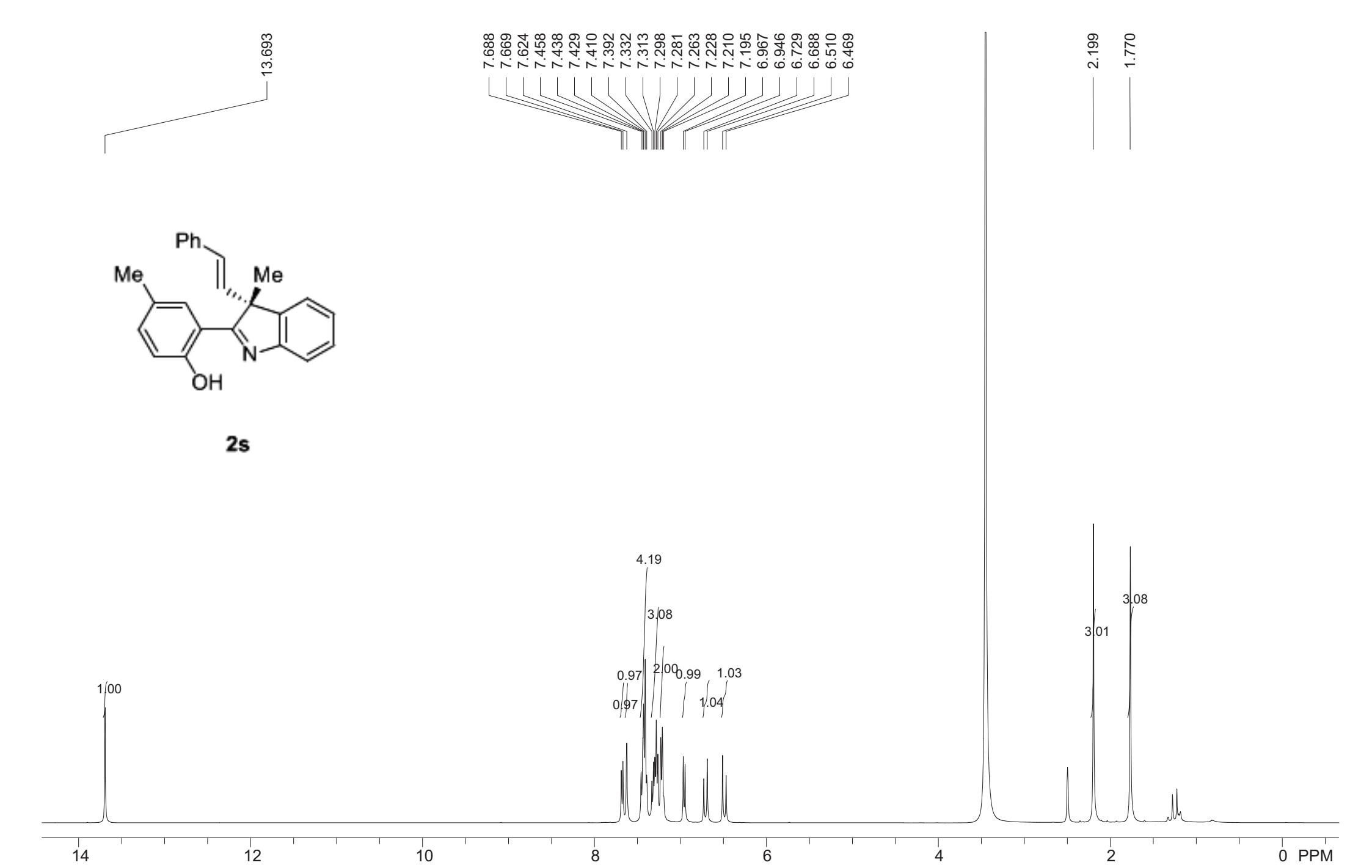
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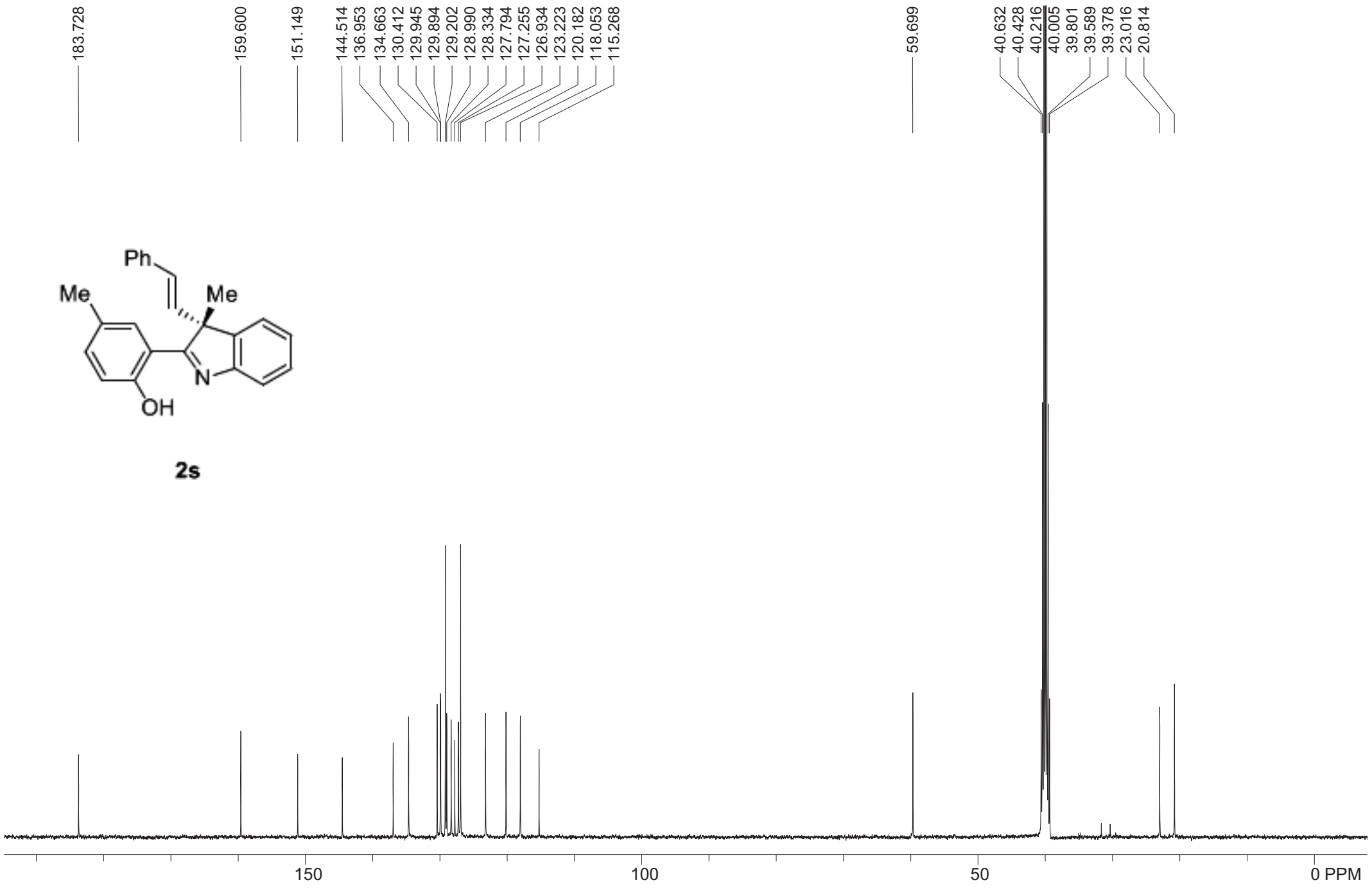
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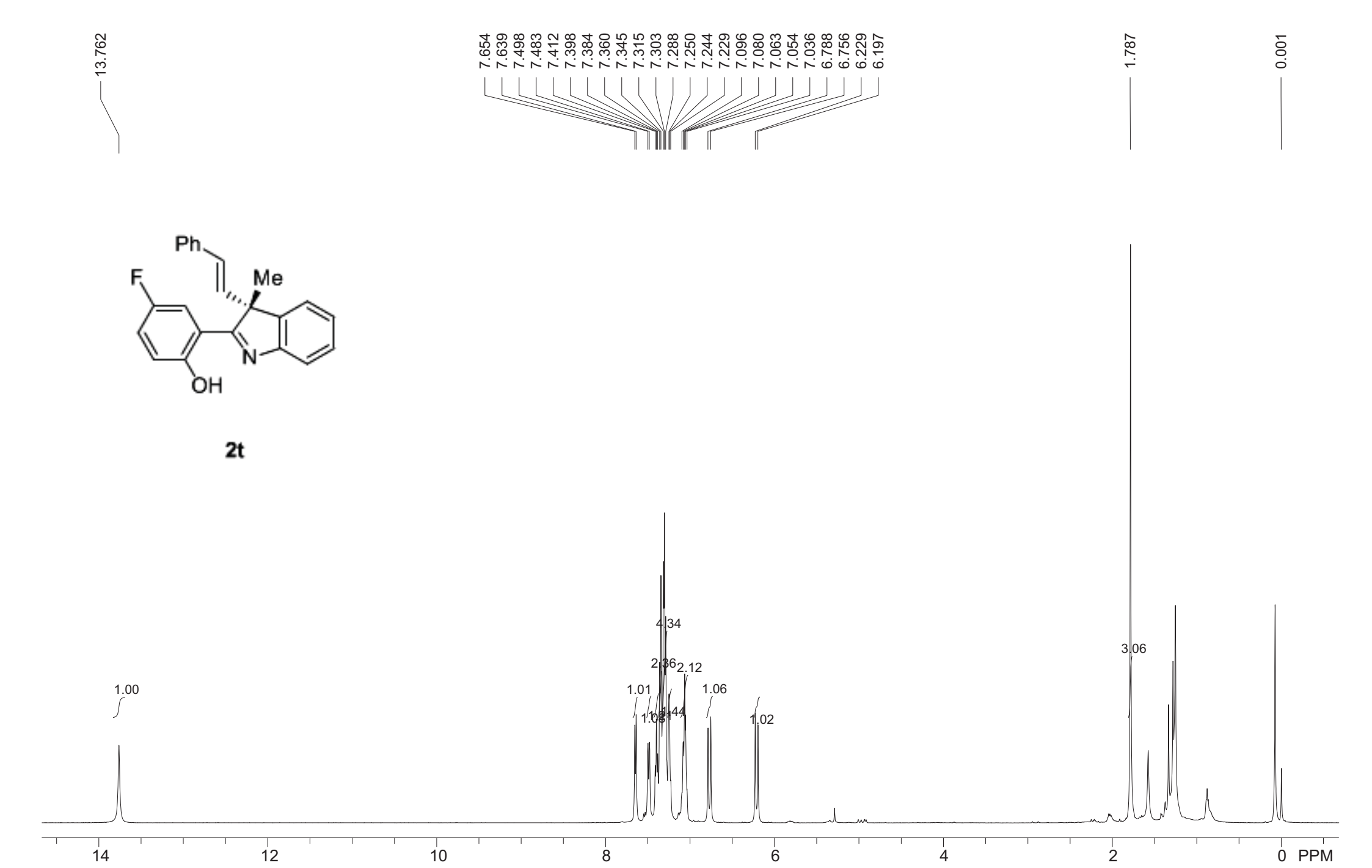
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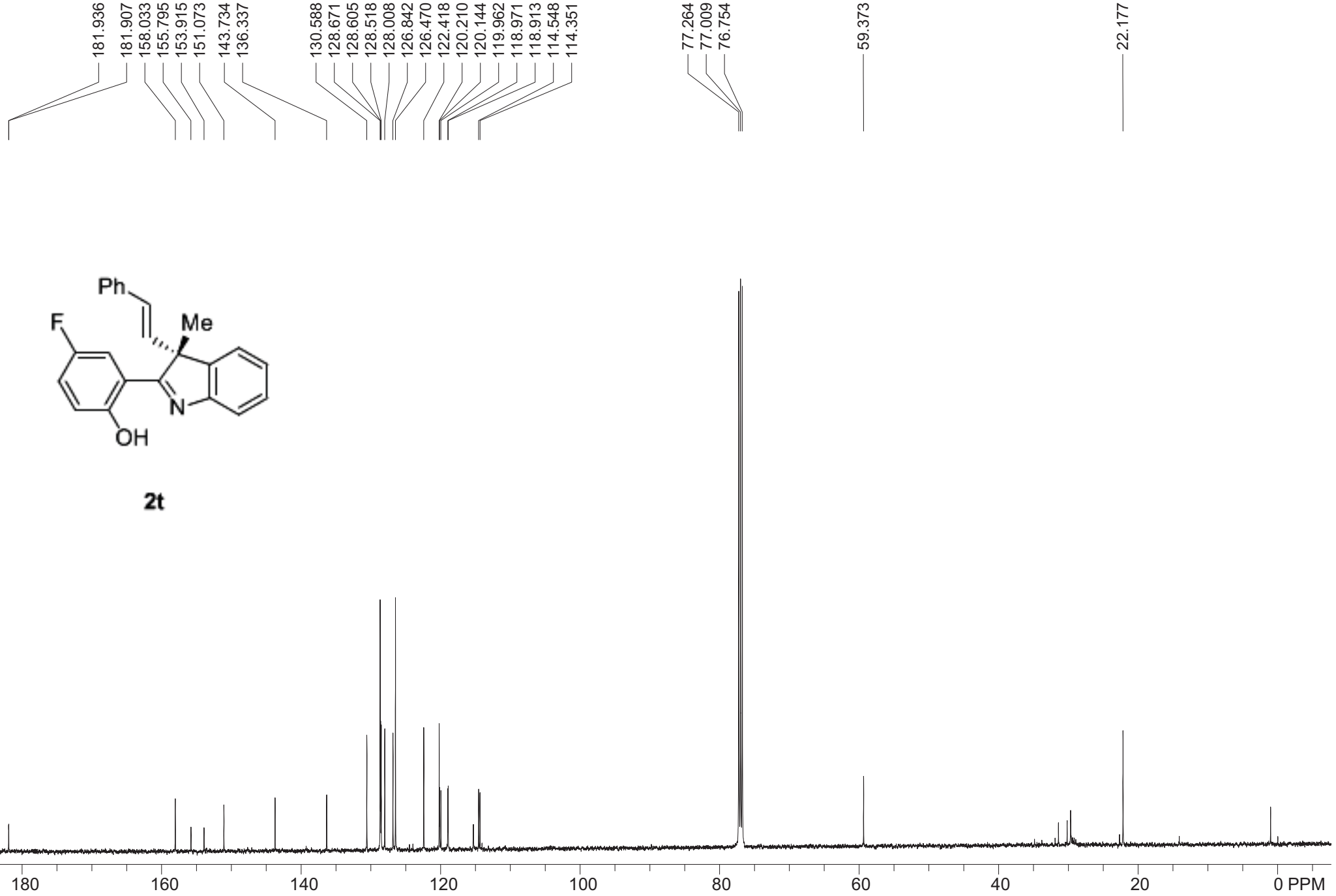
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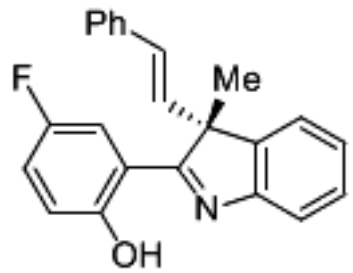

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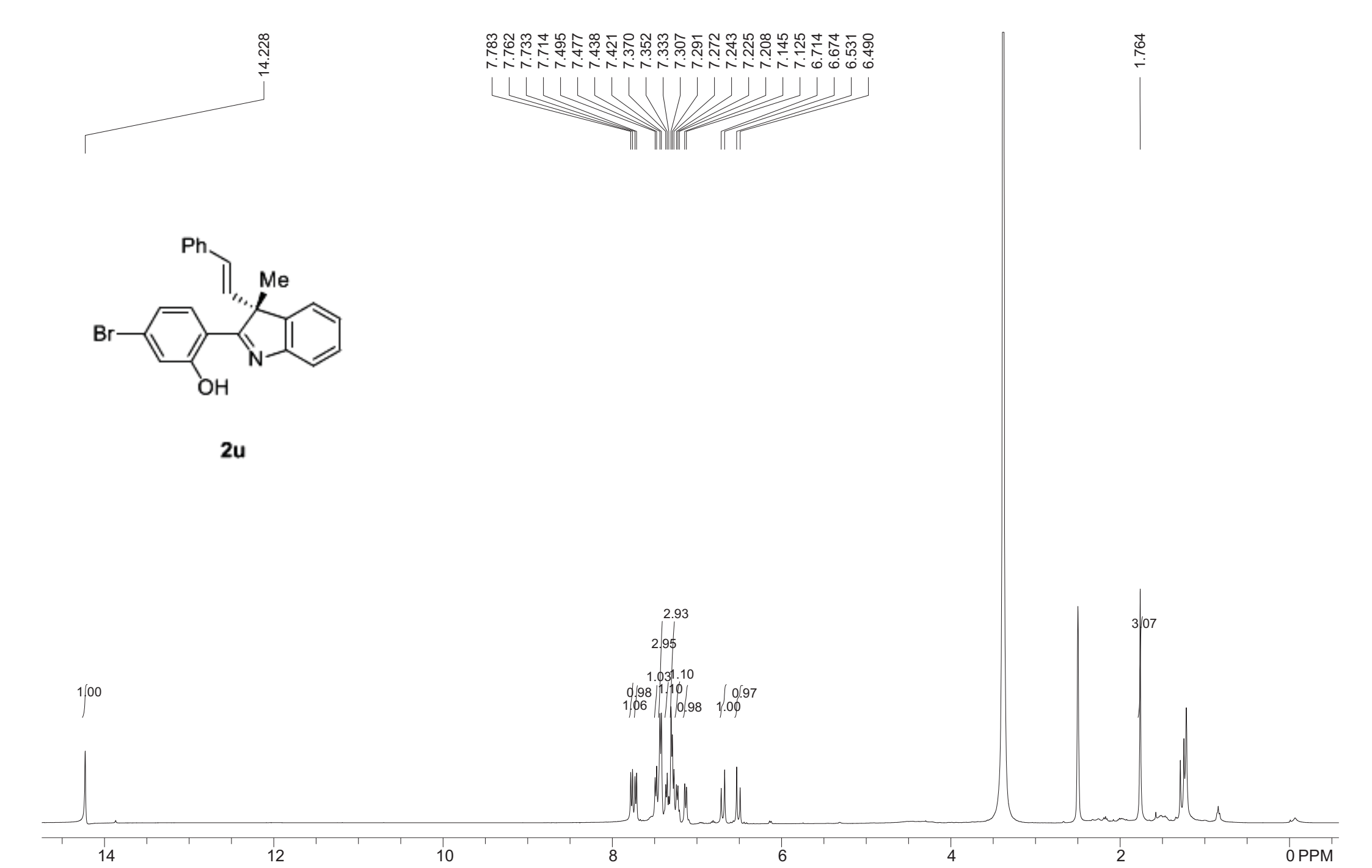
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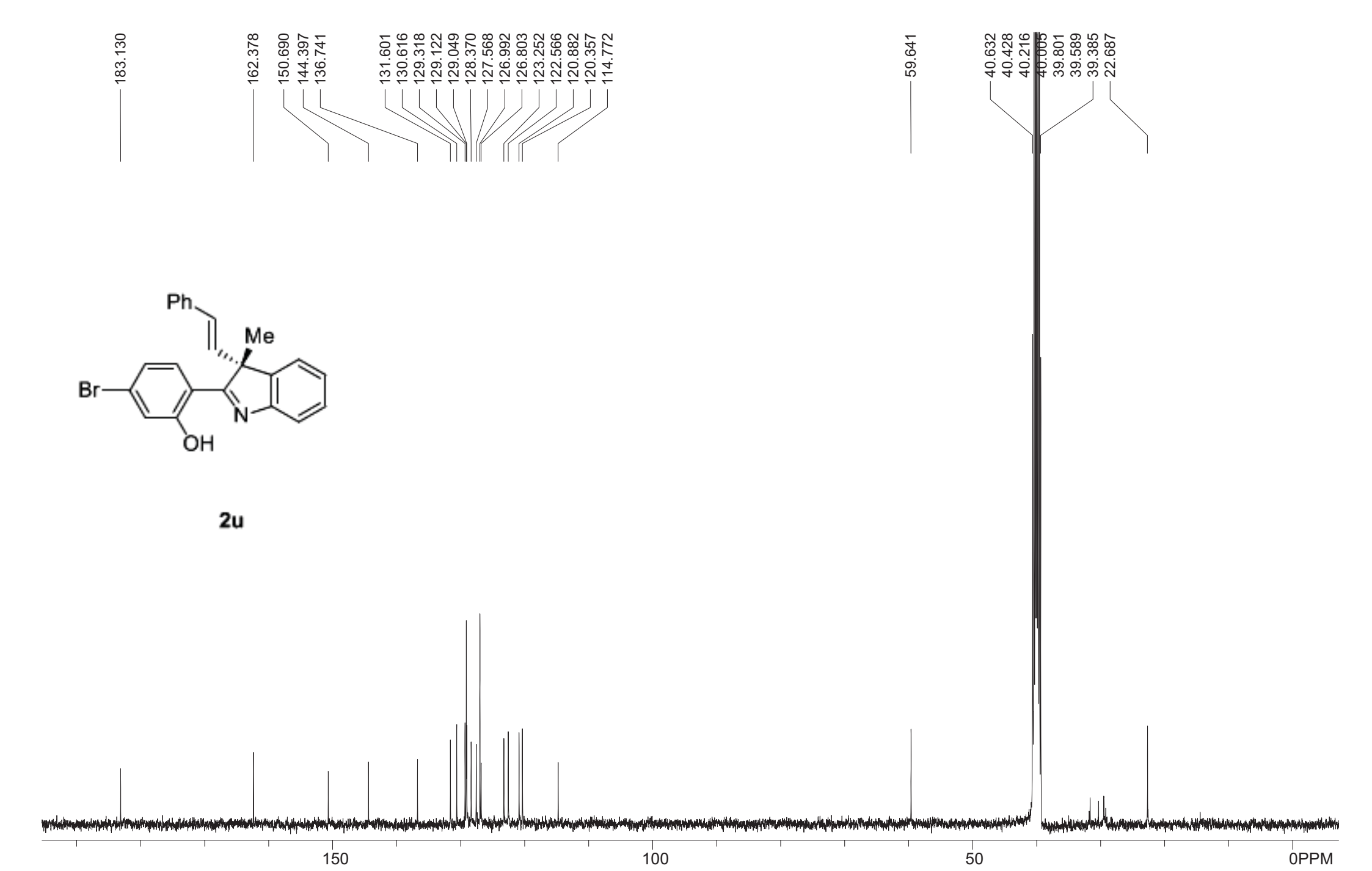
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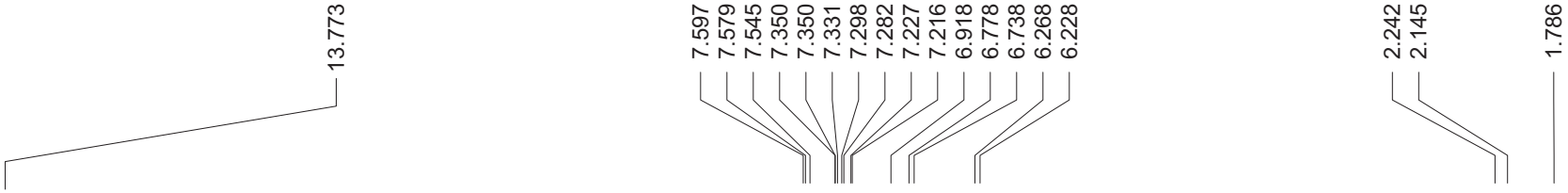
2u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7.350
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7.216
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6.778
6.738
6.268
6.228
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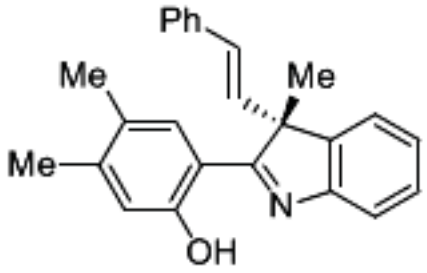
2.145
1.786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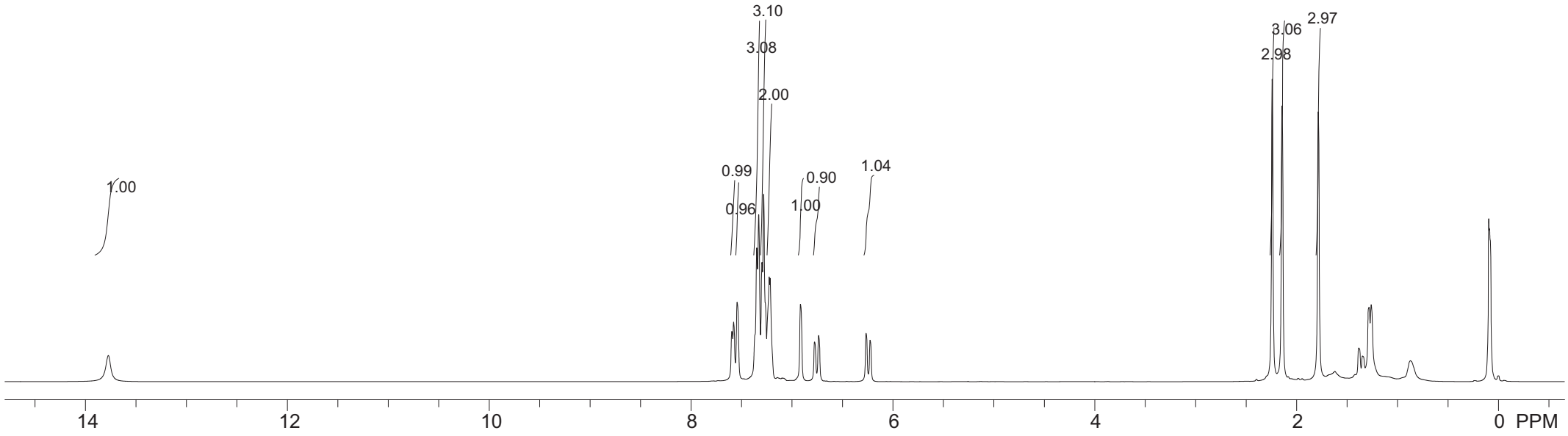
Me
Me
Me
N
OH

2v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2.97
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12
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4
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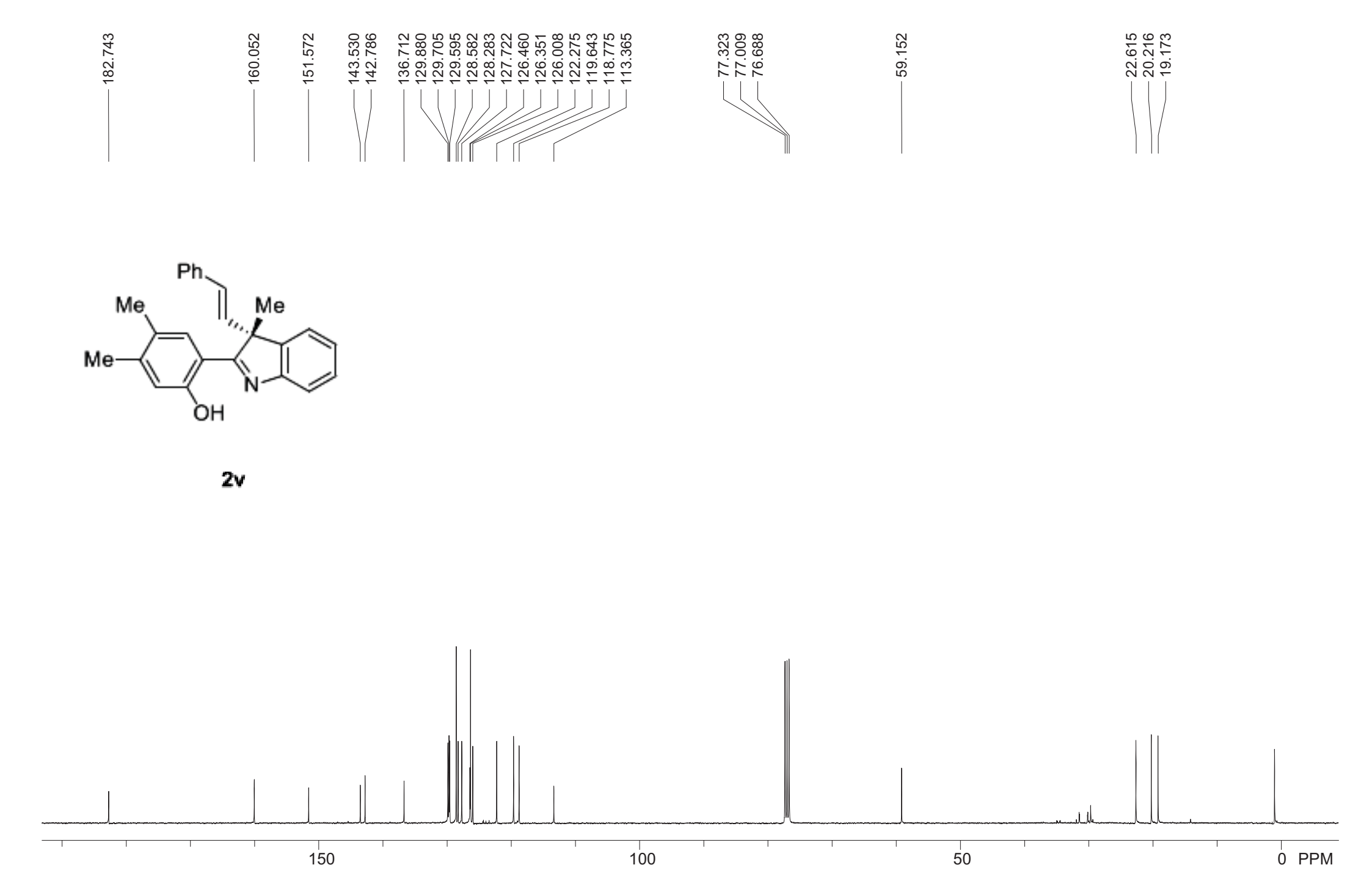
0 PPM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128.582
128.283
127.722
126.460
126.351
126.008
122.275
119.643
118.775
113.365
77.323
77.009
76.688
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20.216
19.173
Ph
Me
Me
Me
N
OH
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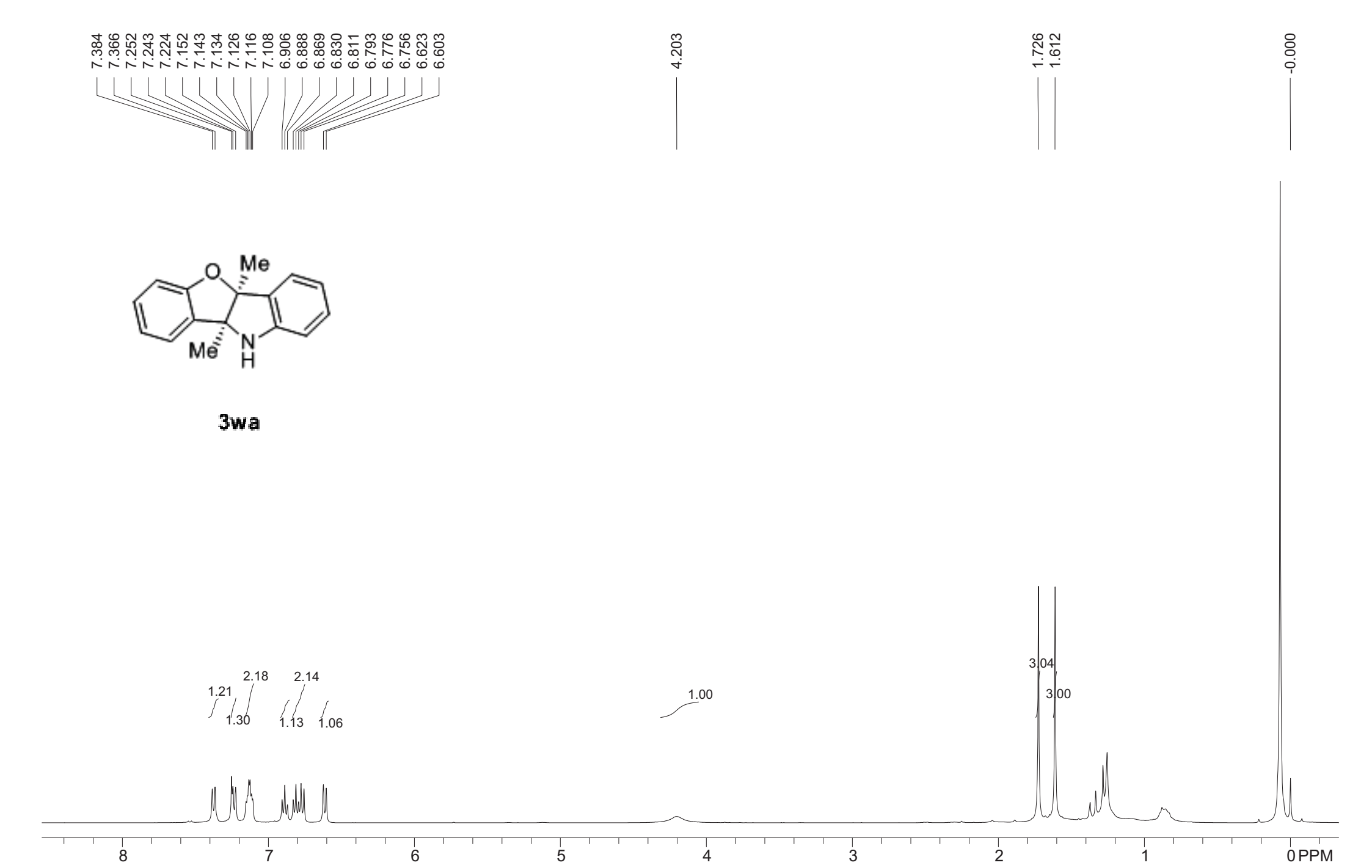
100
50
0
PPM

2v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7.134
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7.116
7.108
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6.869
6.830
6.811
6.793
6.776
6.756
6.623
6.603
4.203
1.726
1.612
-0.000
Me
O
Me
N
H
3wa
1.21
2.18
2.14
1.30
1.13
1.06
1.00
3.04
3.00
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7
6
5
4
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2
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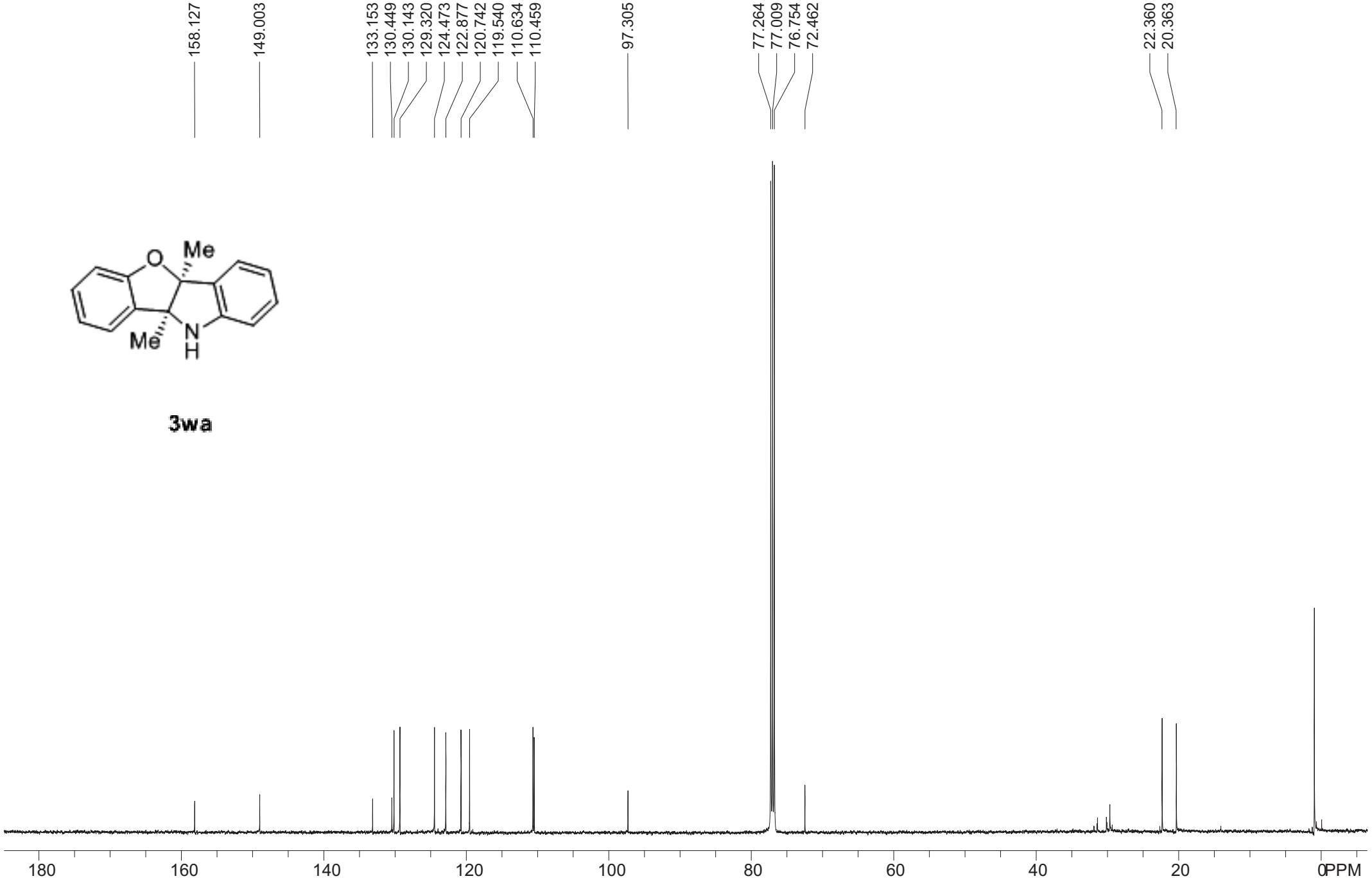
0 PPM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122.877
120.742
119.540
110.634
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97.305
77.264
77.009
76.754
72.462
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Me
Me
N
H
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100
80
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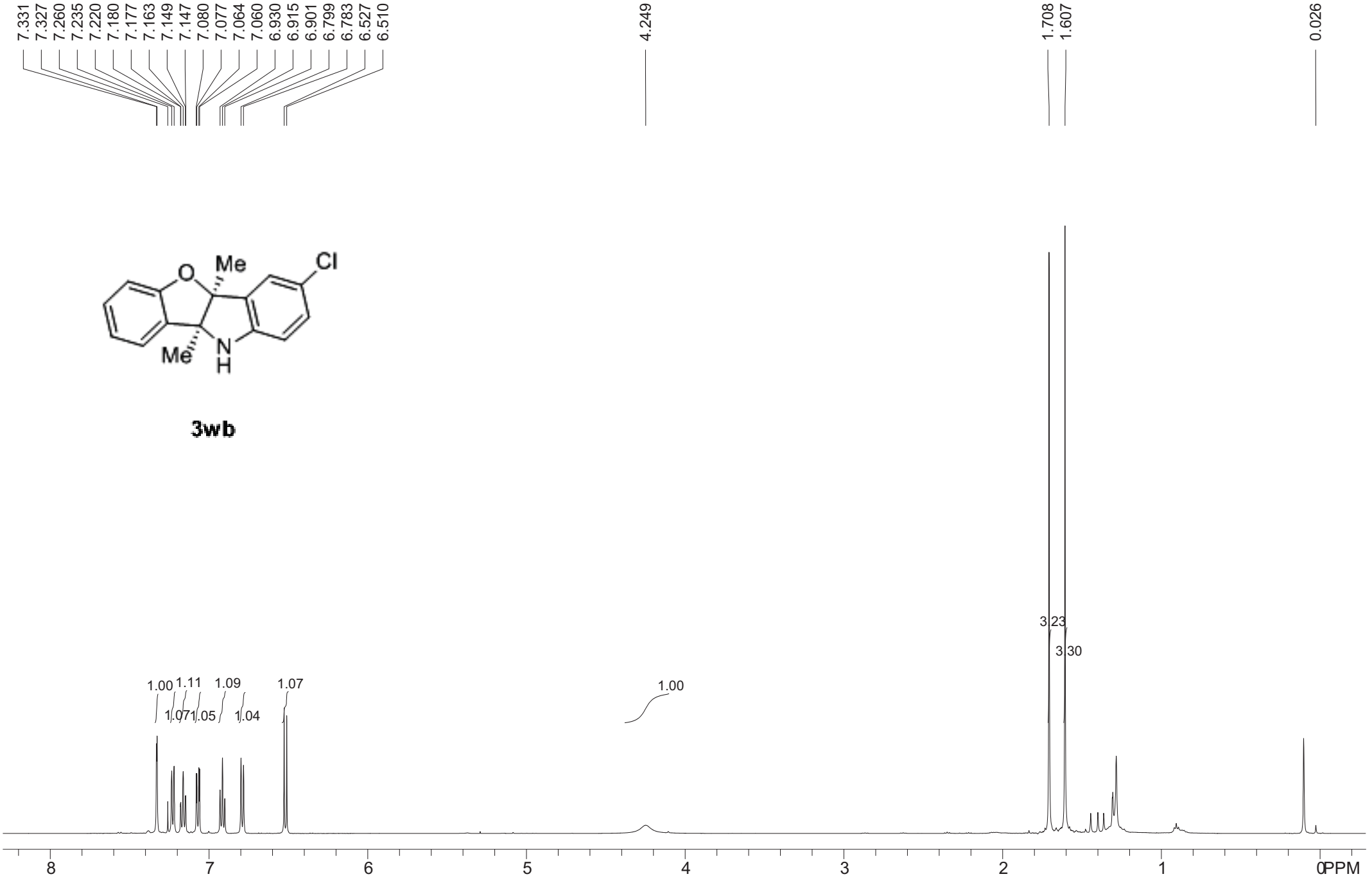
20
0
PPM

3wa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7.177
7.163
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7.147
7.080
7.077
7.064
7.060
6.930
6.915
6.901
6.799
6.783
6.527
6.510
4.249
1.708
1.607
0.026
O
Me
Cl
Me
N
H
3wb
1.00
1.11
1.09
1.07
1.00
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1.04
3.23
3.30
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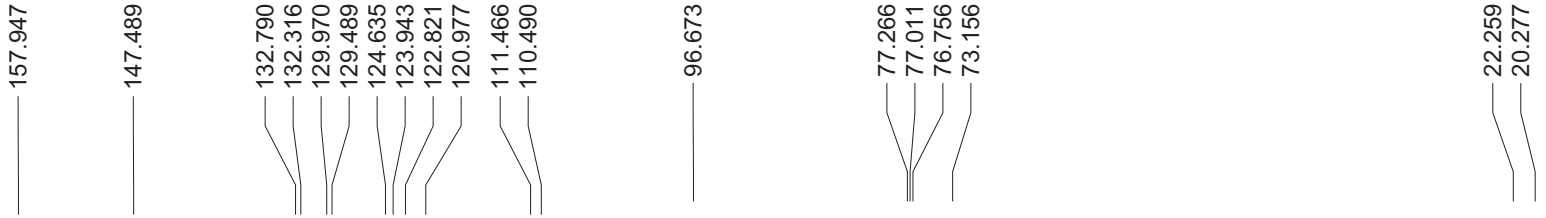
PPM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110.490
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77.011
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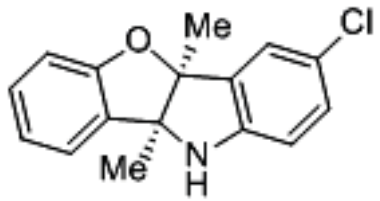
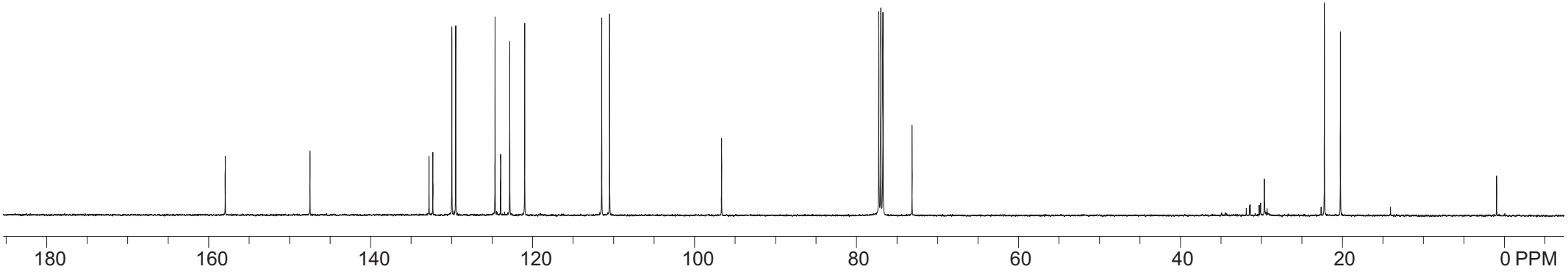
73.156
22.259
20.277


O
Me
Cl
Me
N
H

3wb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140
120
100
80
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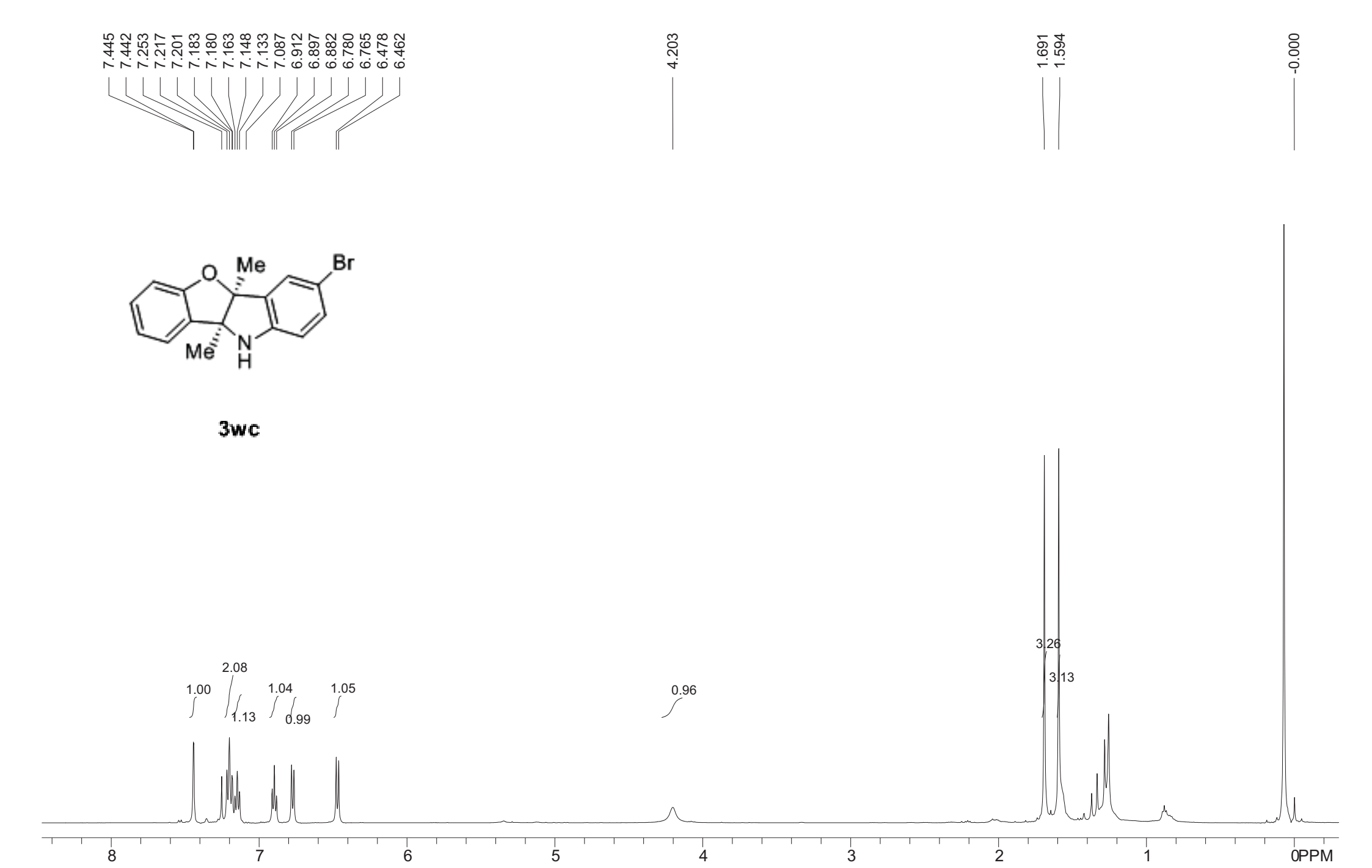
20
0 PPM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7.217
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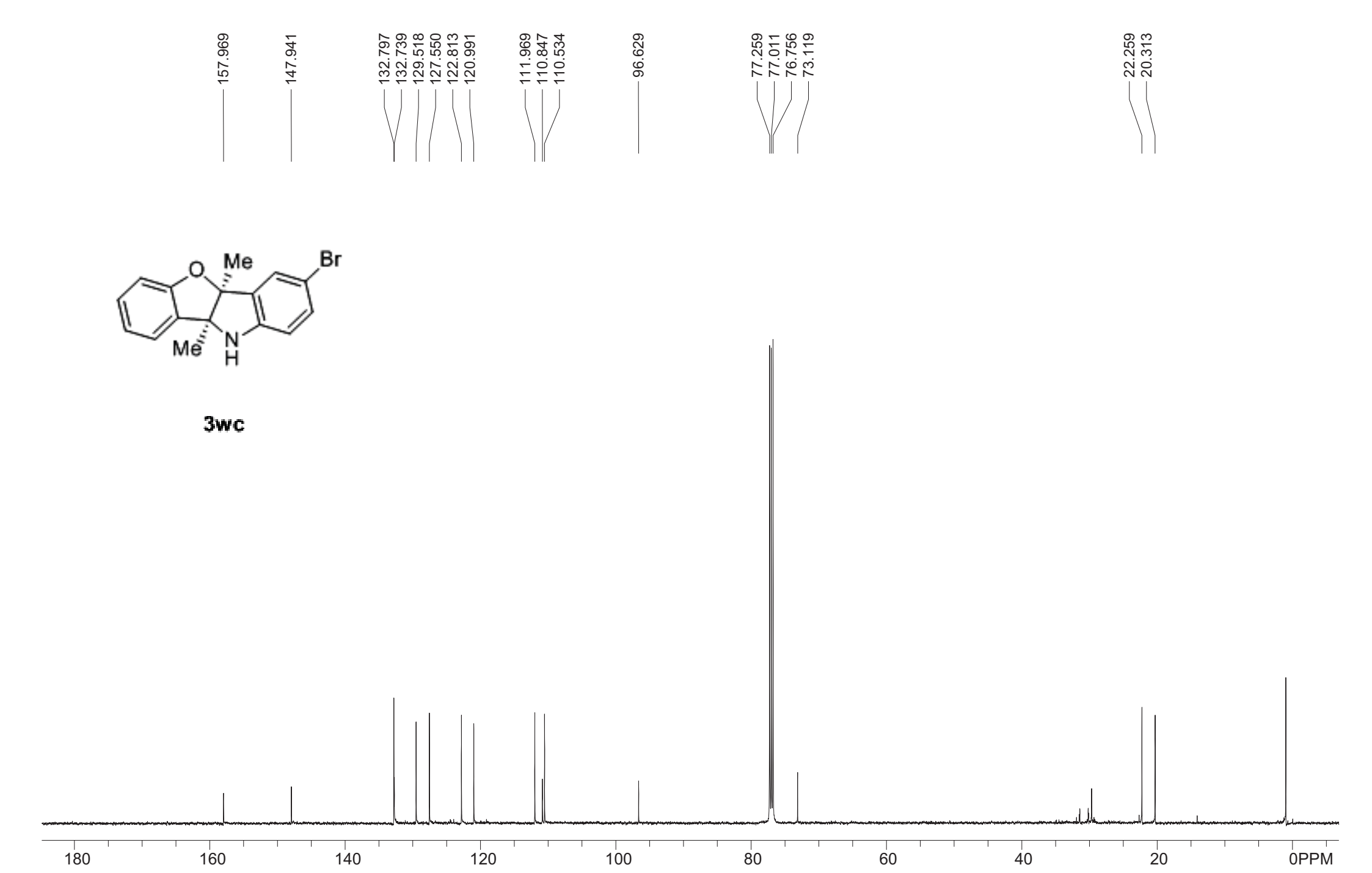
7.183
7.180
7.163
7.148
7.133
7.087
6.912
6.897
6.882
6.780
6.765
6.478
6.462
4.203
1.691
1.594
-0.000
O
Me
Br
Me
N
H
3wc
1.00
2.08
1.13
1.04
0.99
1.05
0.96
3.26
3.13
8
7
6
5
4
3
2
1
0PPM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127.550
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120.991
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110.847
110.534
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77.259
77.011
76.756
73.119
22.259
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Br
Me
N
H
3wc
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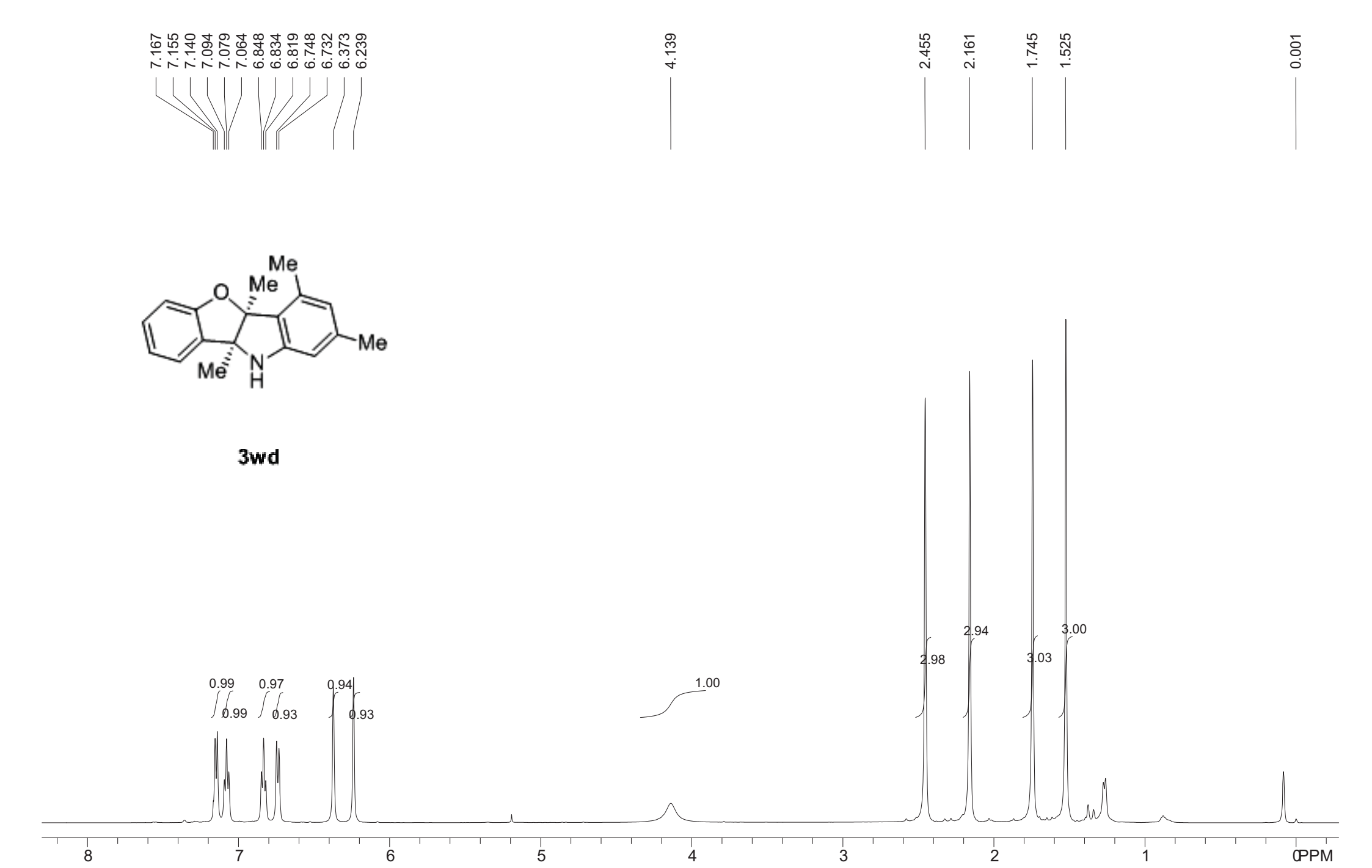
140
120
100
80
60
40
20
0PPM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6.834
6.819
6.748
6.732
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6.239
4.139
2.455
2.161
1.745
1.525
0.001
Me
Me
O
Me
N
H
Me
Me
3wd
0.99
0.99
0.97
0.93
0.94
0.93
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2.94
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3.00
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6
5
4
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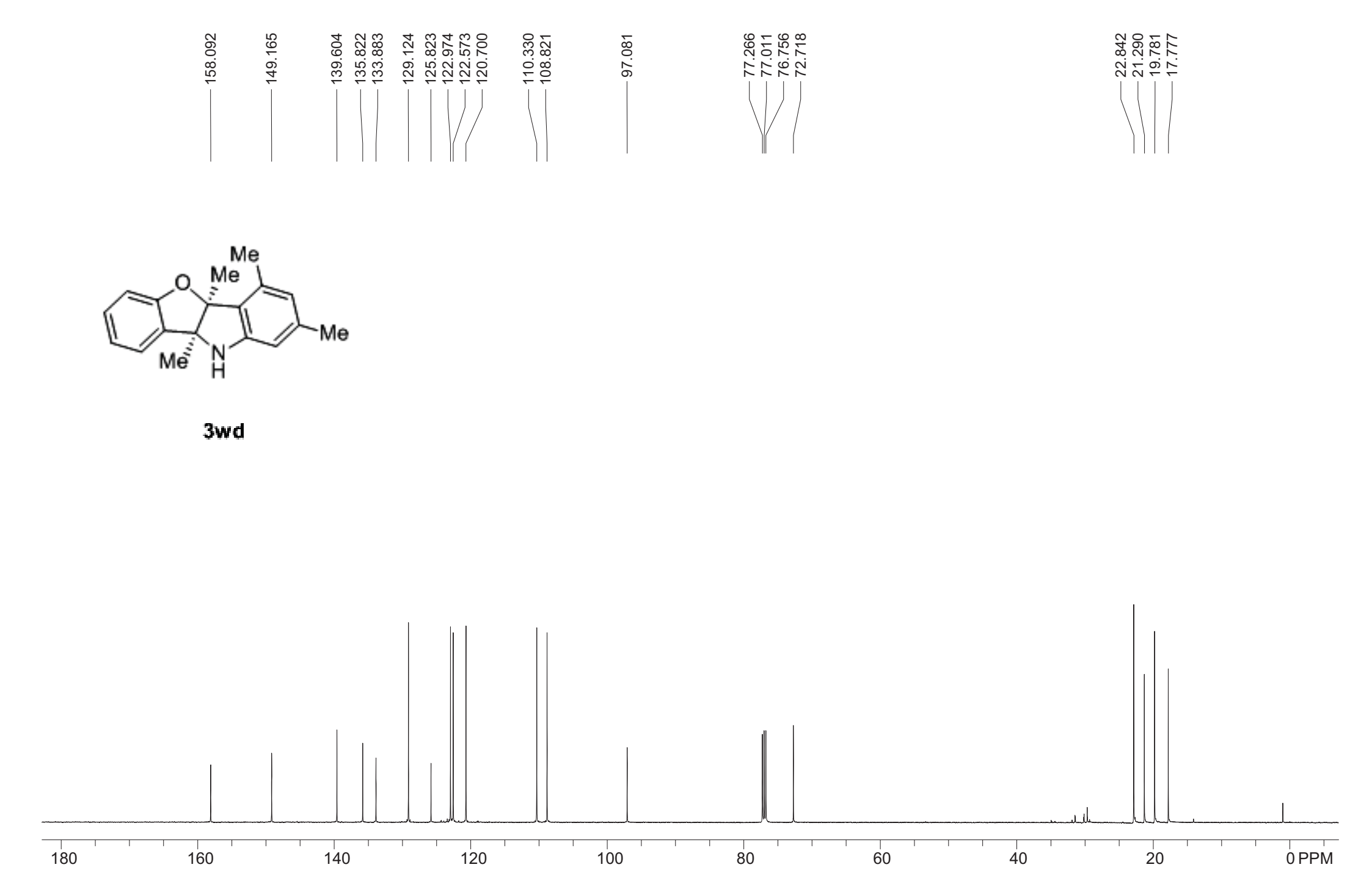
2
1
0
PPM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122.573
120.700
110.330
108.821
97.081
77.266
77.011
76.756
72.718
22.842
21.290
19.781
17.777
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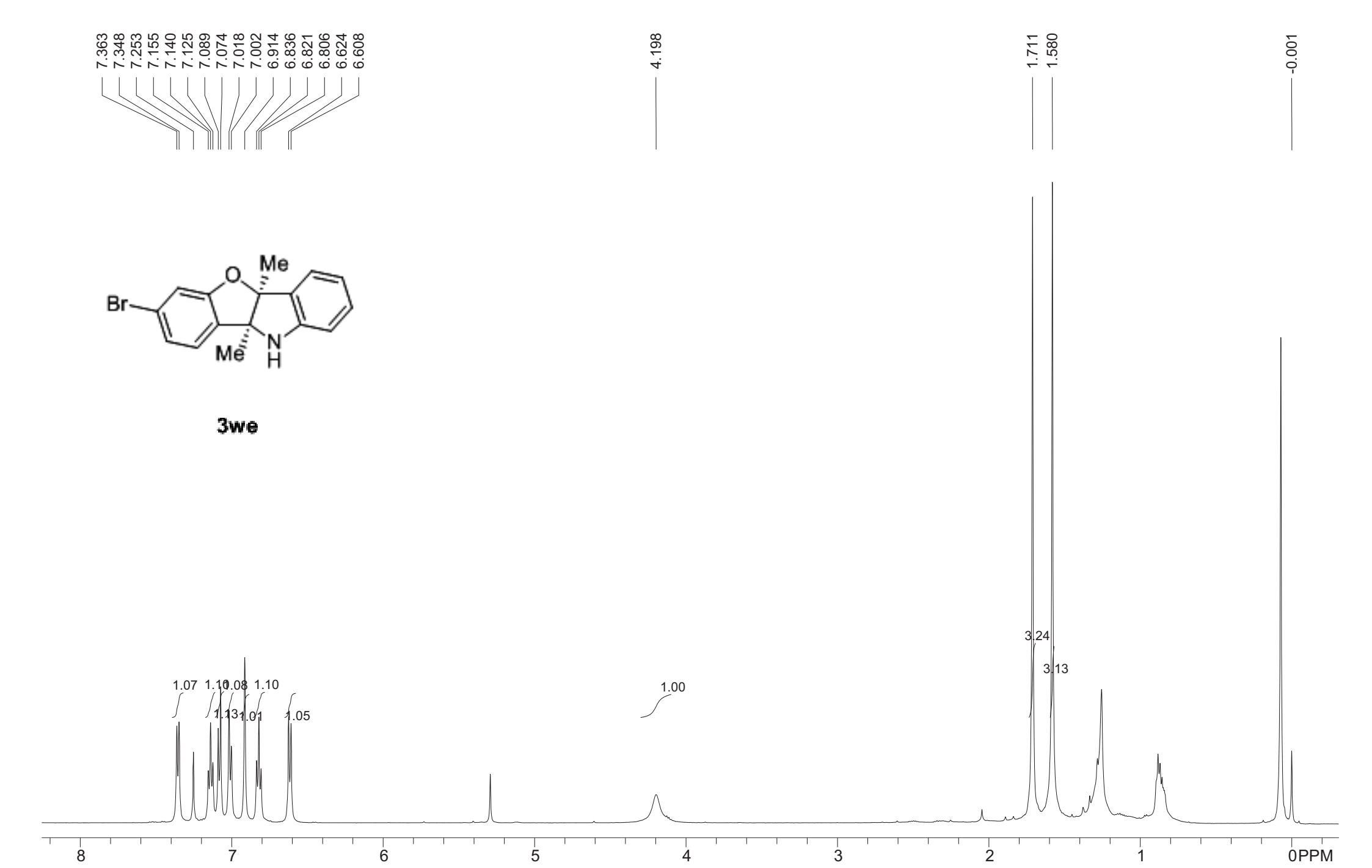
O
Me
N
H
Me
Me
180
160
140
120
100
80
60
40
20
0 PPM

3wd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7.125
7.089
7.074
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6.836
6.821
6.806
6.624
6.608
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1.711
1.580
-0.001
Br
O
Me
Me
N
H
3we
1.07
1.10
1.08
1.10
1.13
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1.05
1.00
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3.13
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7
6
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4
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2
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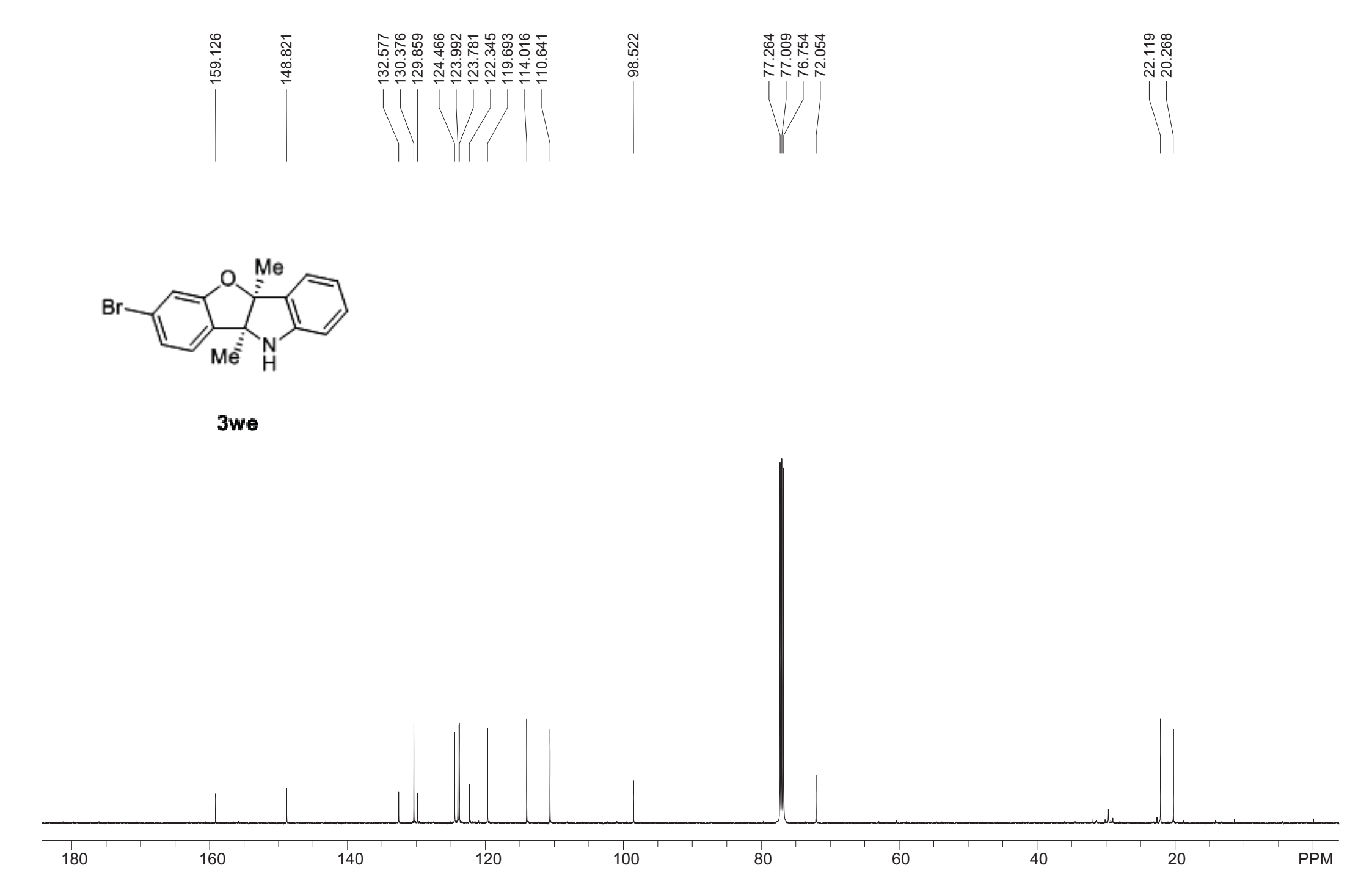
0PPM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129.859
124.466
123.992
123.781
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119.693
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77.009
76.754
72.054
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Me
Me
N
H
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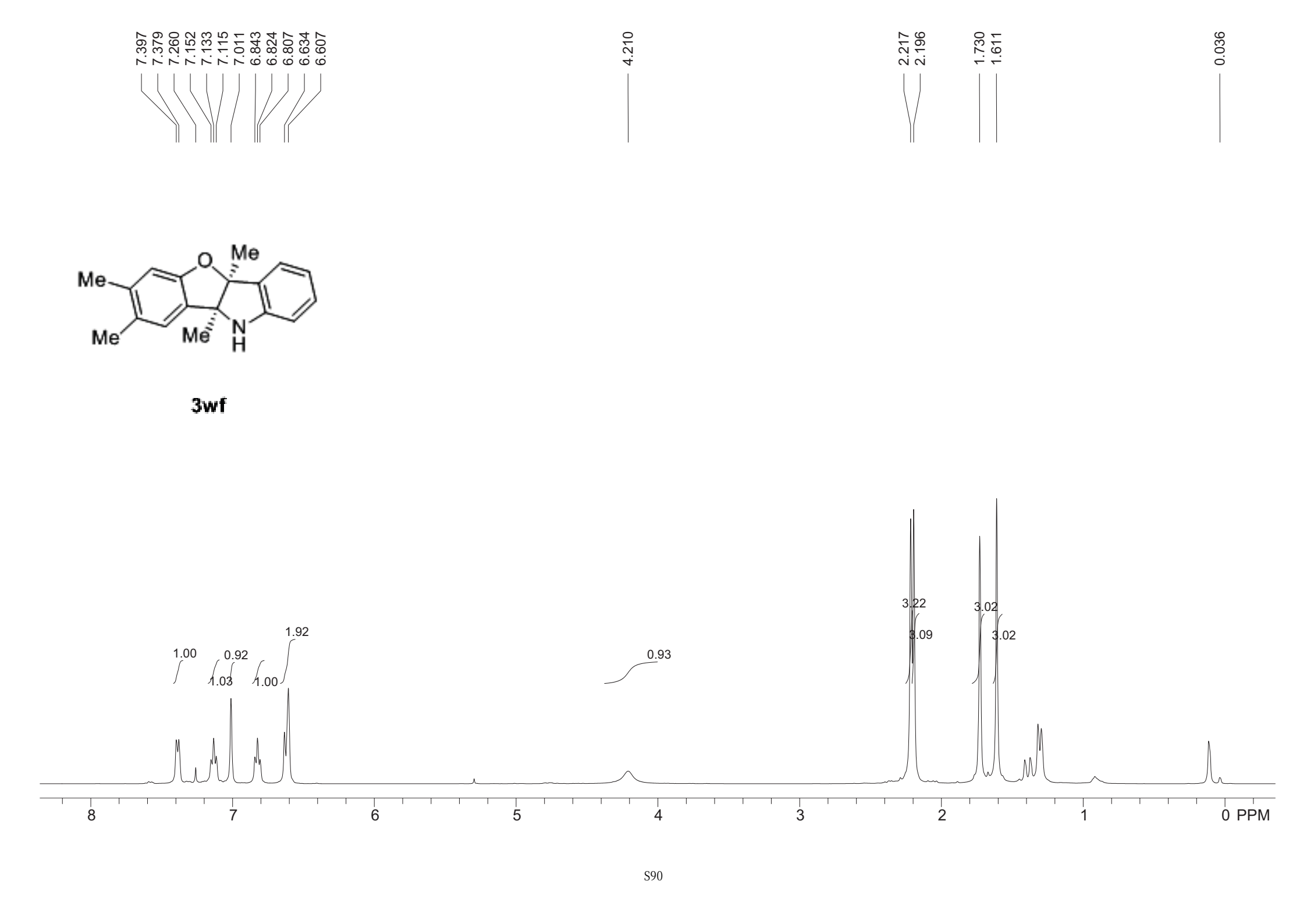
120
100
80
60
40
20
PPM

3we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7.152
7.133
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6.824
6.807
6.634
6.607
4.210
2.217
2.196
1.730
1.611
0.036
Me
O
Me
Me
Me
N
H
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0.92
1.03
1.00
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3.22
3.09
3.02
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6
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2
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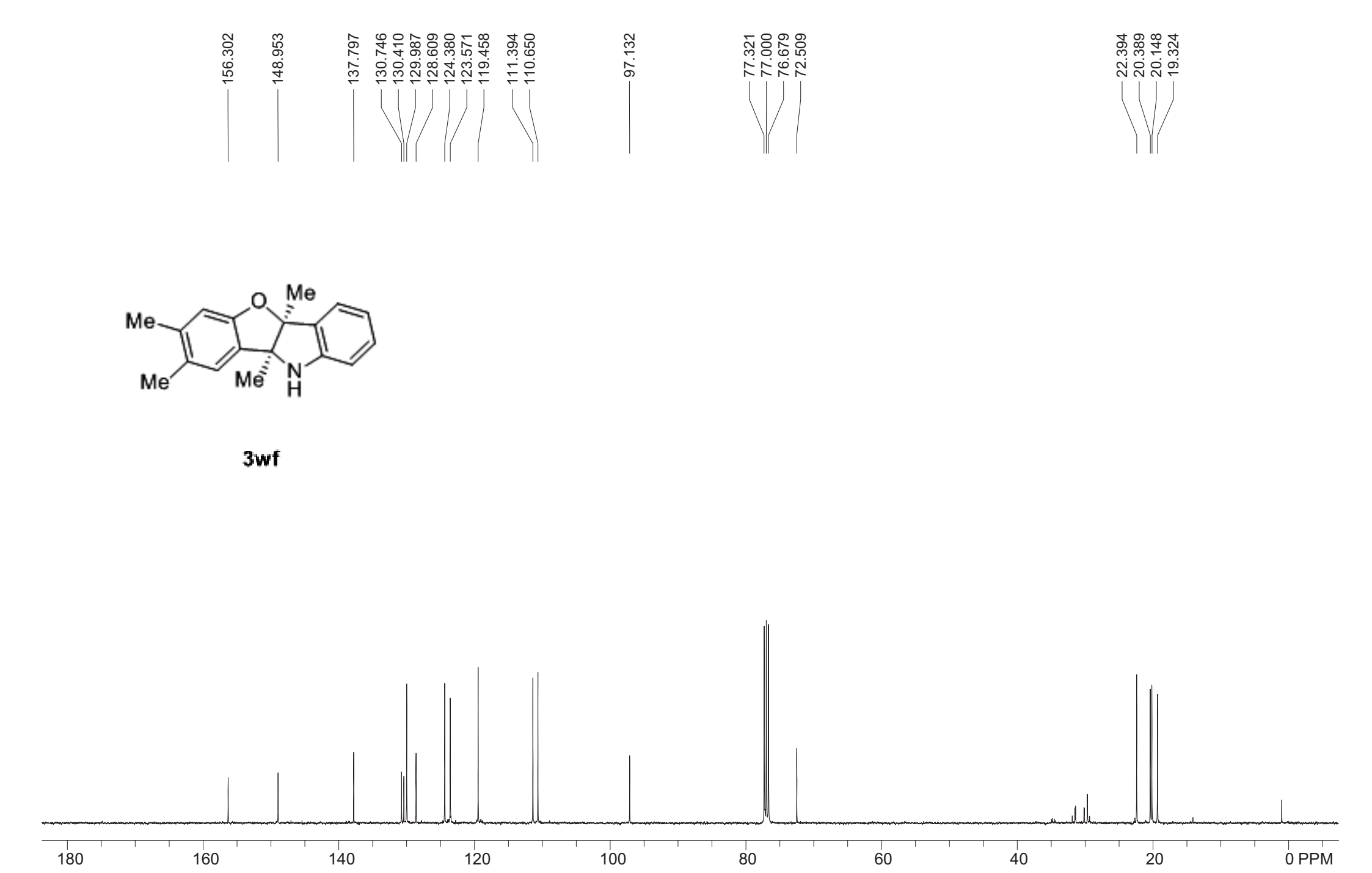
0 PPM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119.458
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110.650
97.132
77.321
77.000
76.679
72.509
22.394
20.389
20.148
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Me
Me
N
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120
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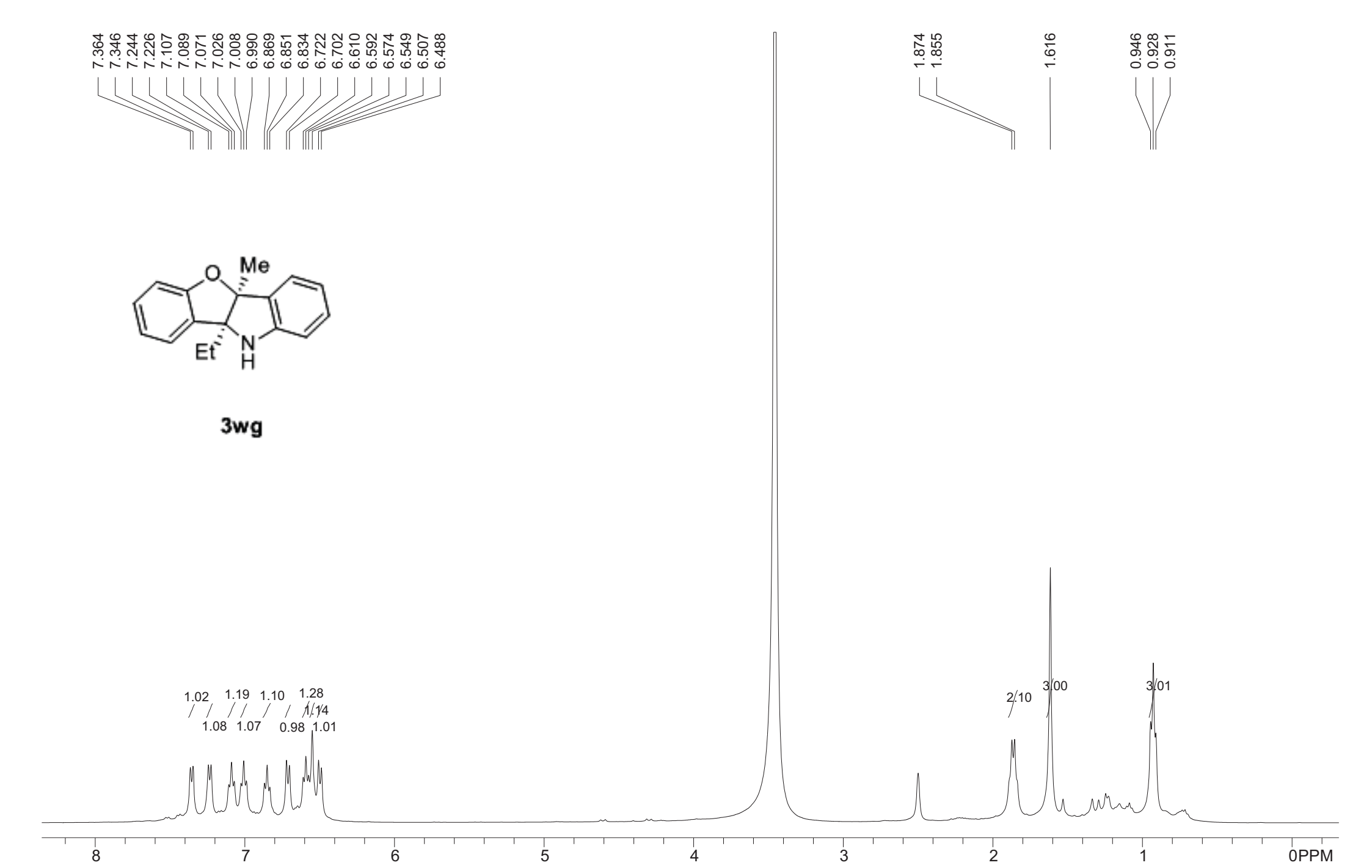
0 PPM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7.026
7.008
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6.851
6.834
6.722
6.702
6.610
6.592
6.574
6.549
6.507
6.488
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1.855
1.616
0.946
0.928
0.911
Me
O
Et
N
H
3wg
1.02
1.08
1.19
1.07
1.10
0.98
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2.10
3.00
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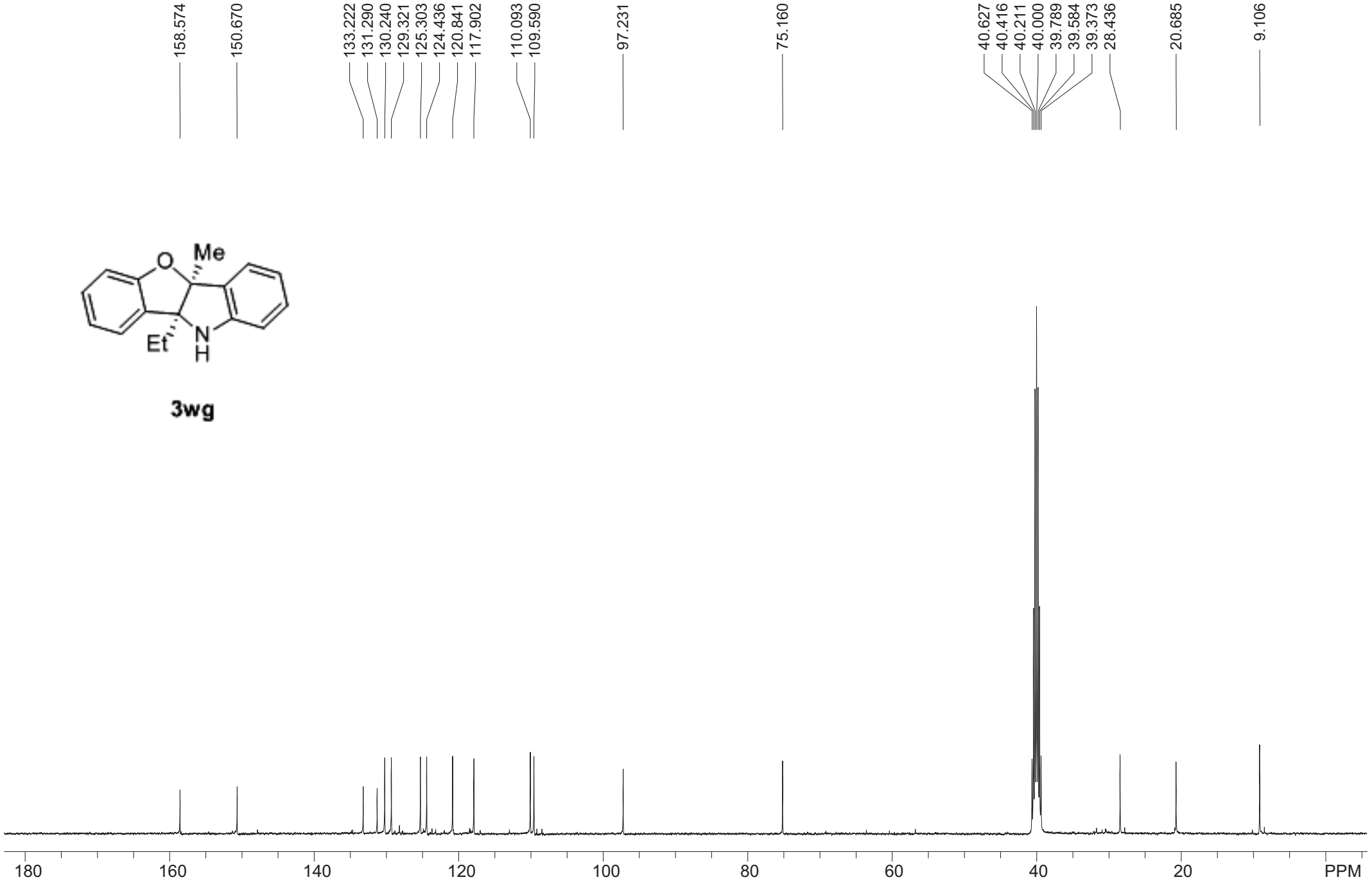
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109.590
97.231
75.160
40.627
40.416
40.211
40.000
39.789
39.584
39.373
28.436
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Et
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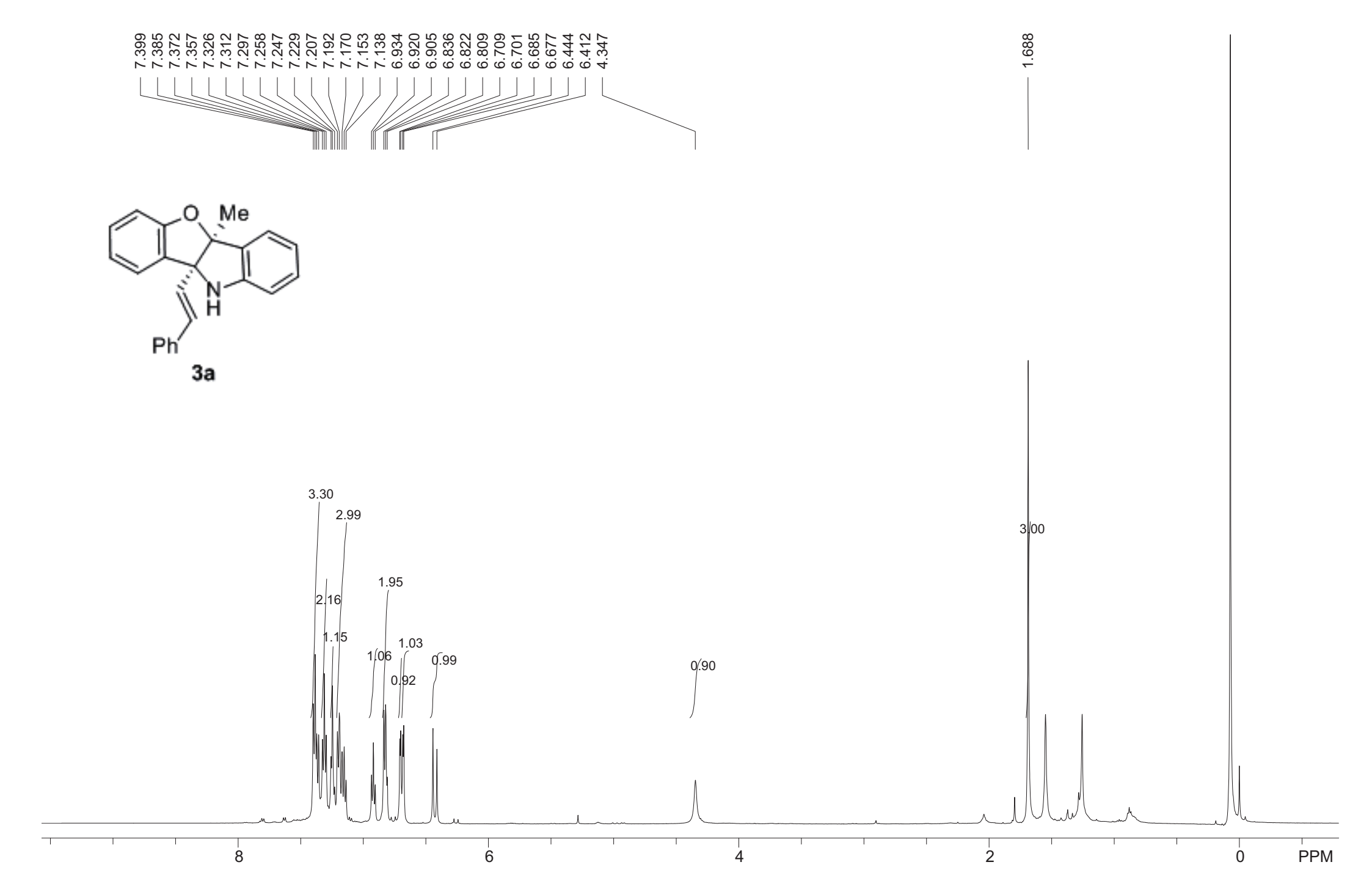
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7.170
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6.905
6.836
6.822
6.809
6.709
6.701
6.685
6.677
6.444
6.412
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O
Me
N
H
Ph
3a
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2.16
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1.06
1.03
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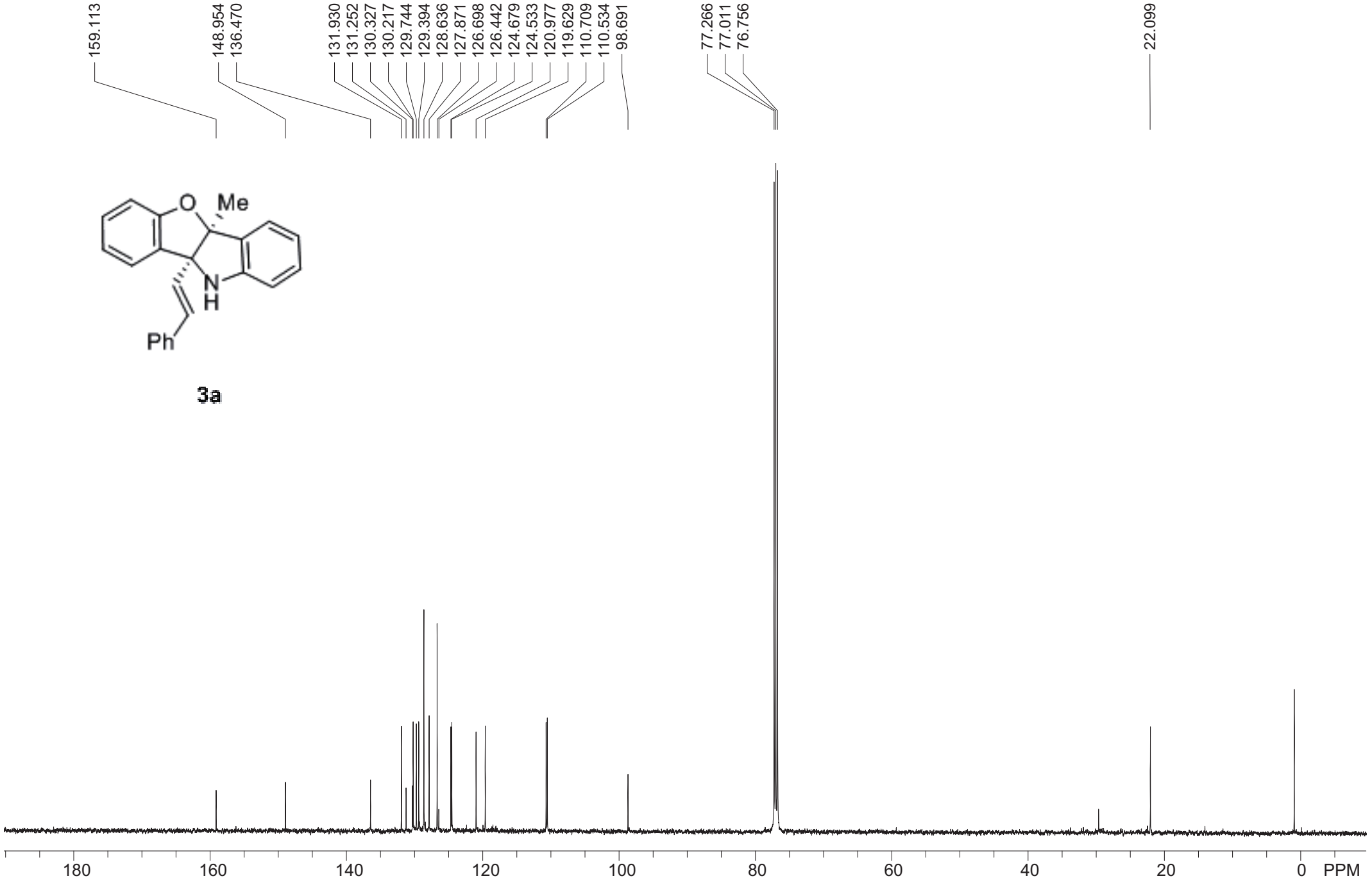
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124.533
120.977
119.629
110.709
110.534
98.691
77.266
77.011
76.756
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Me
N
H
Ph
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80
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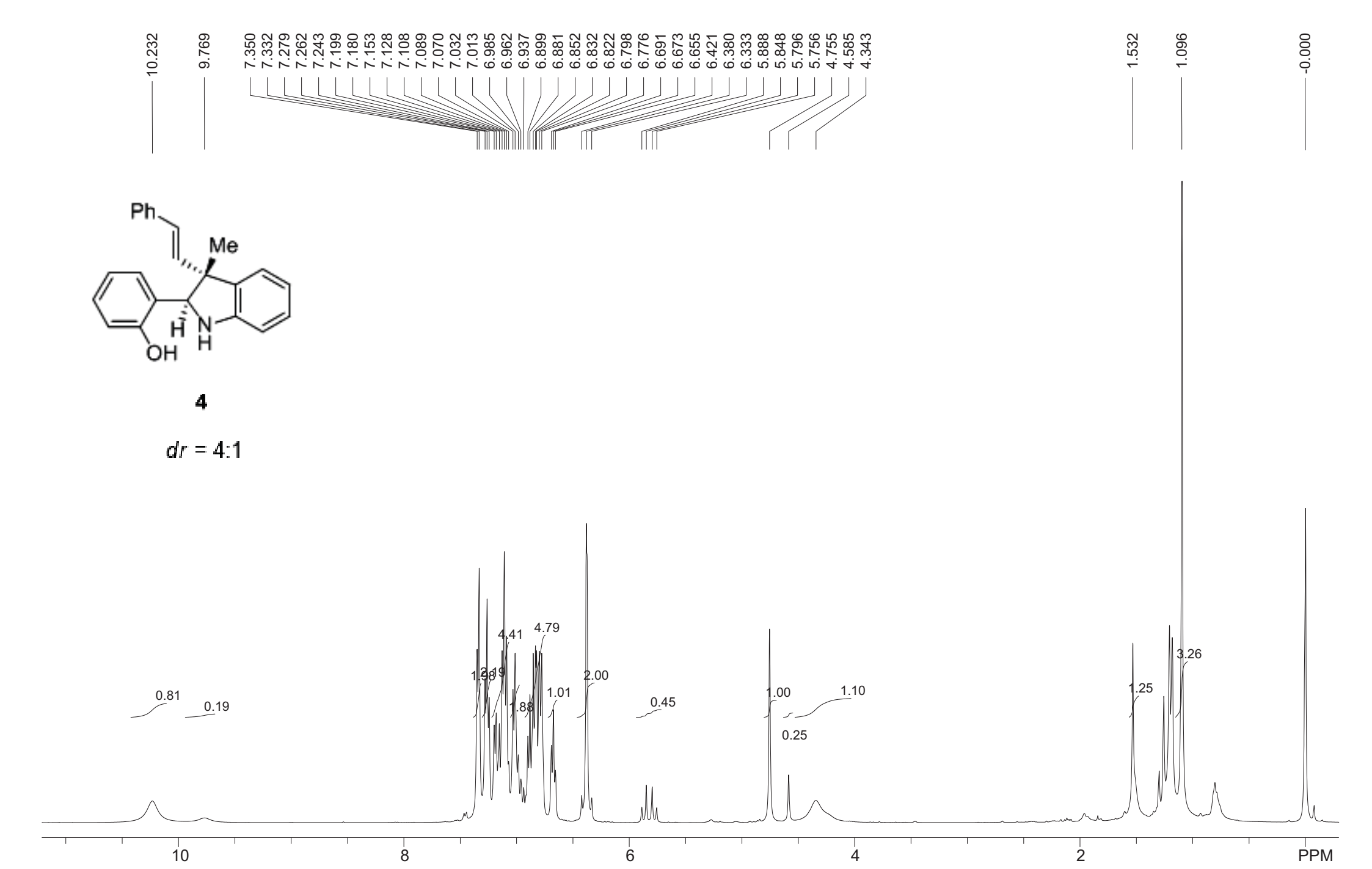
20
0
PPM

3a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7.153
7.128
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7.089
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4.585
4.343
1.532
1.096
-0.000
Ph
Me
H
N
H
OH
4
dr = 4:1
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0.19
1.98
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4.41
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1.88
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0.45
1.00
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3.26
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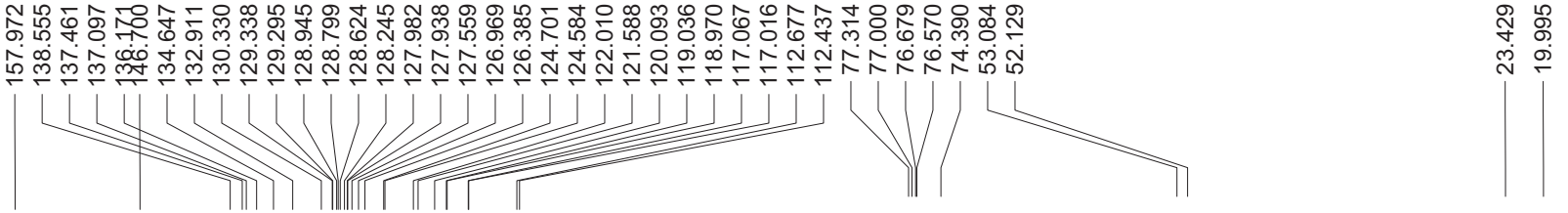
6
4
2
PPM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128.945
128.799
128.624
128.245
127.982
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127.559
126.969
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124.701
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122.010
121.588
120.093
119.036
118.970
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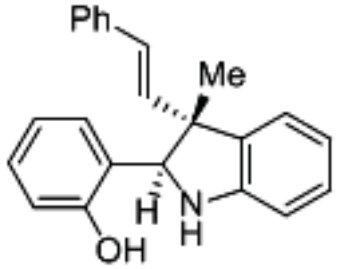
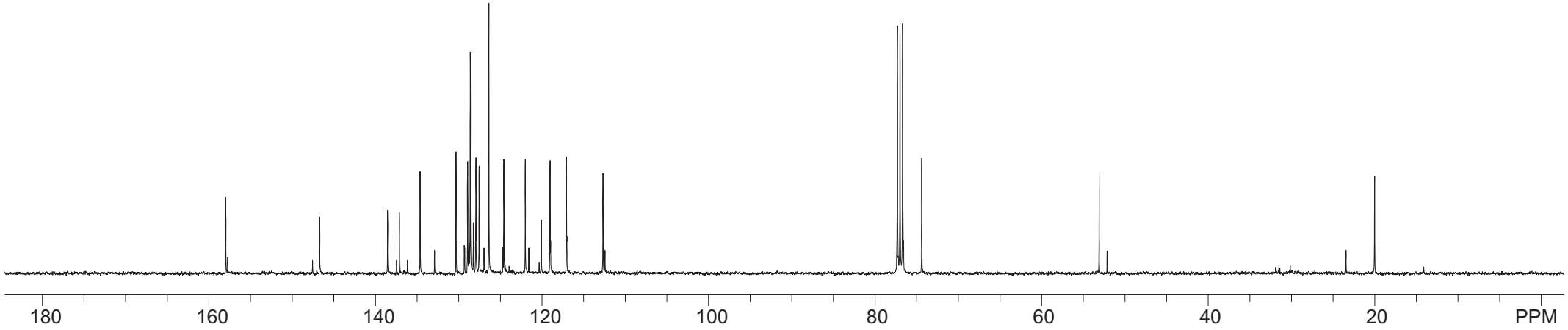
53.084
52.129
23.429
19.995


Ph
Me
H
N
H
OH

4

dr = 4:1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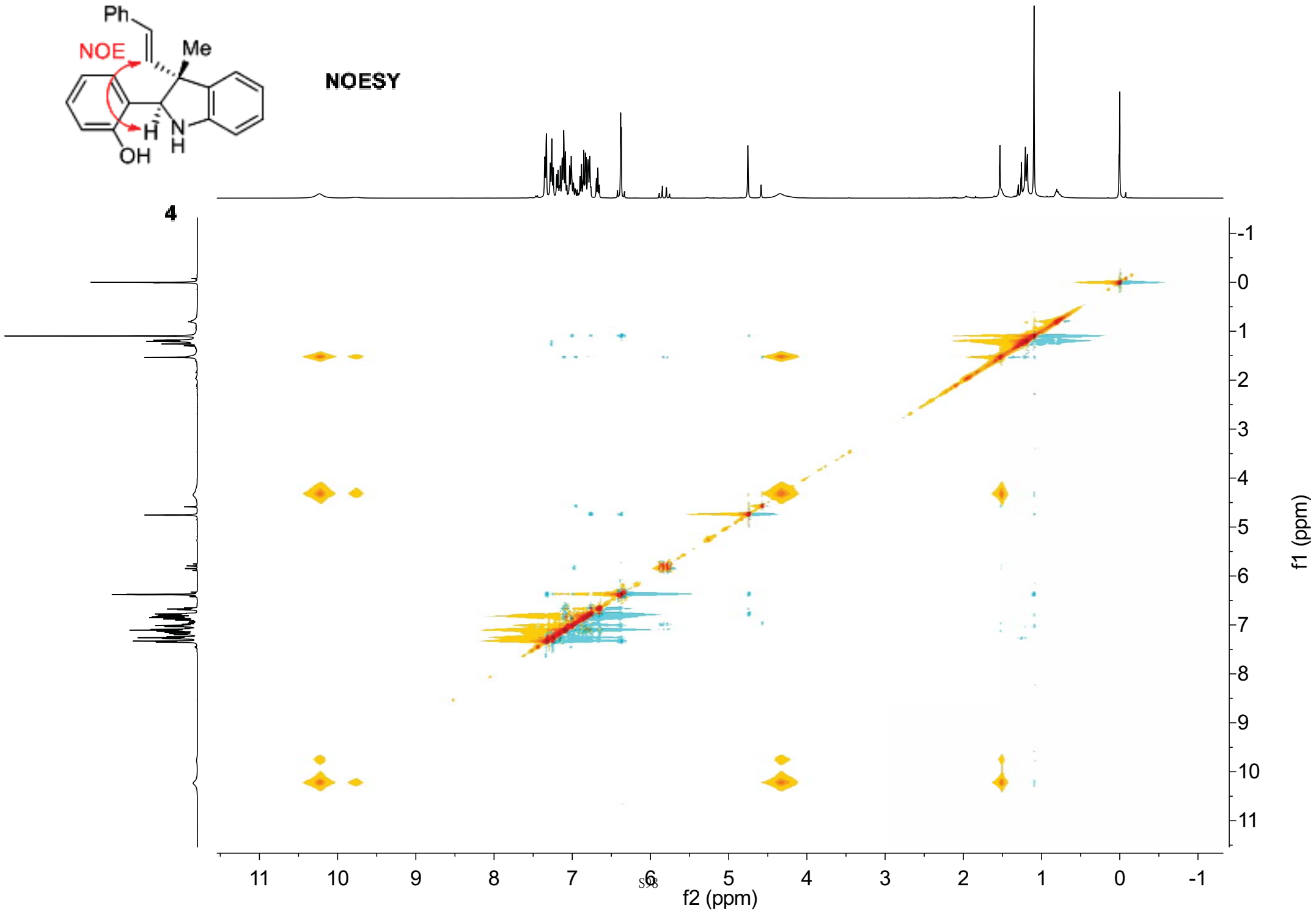
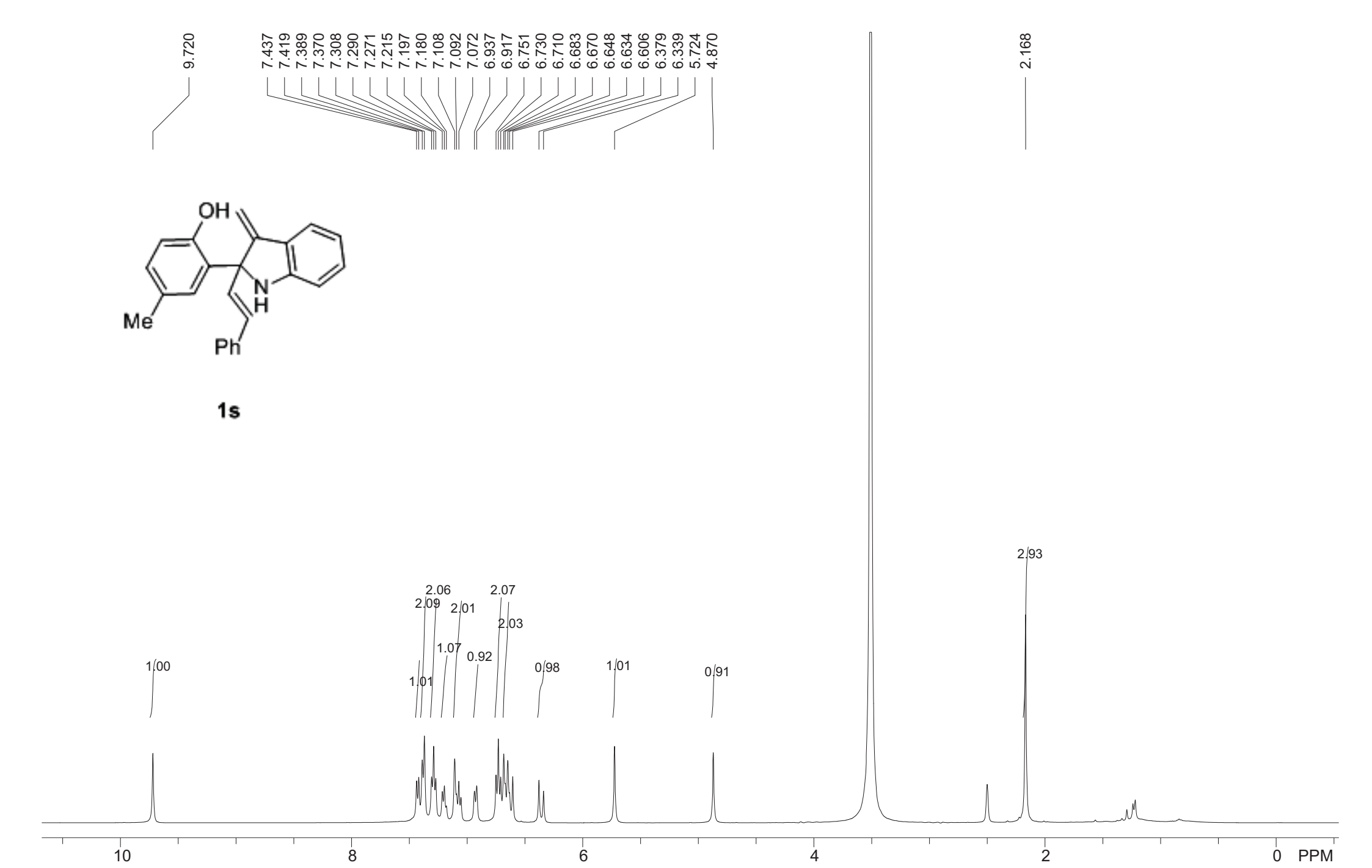
40
20
PPM


Ph
NOE
Me
H
N
H
OH
NOESY
4
f2 (ppm)
f1 (ppm)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6.648
6.634
6.606
6.379
6.339
5.724
4.870
2.168
OH
N
H
Me
Ph
1s
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2.06
2.09
2.01
2.07
2.03
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1.01
0.98
1.01
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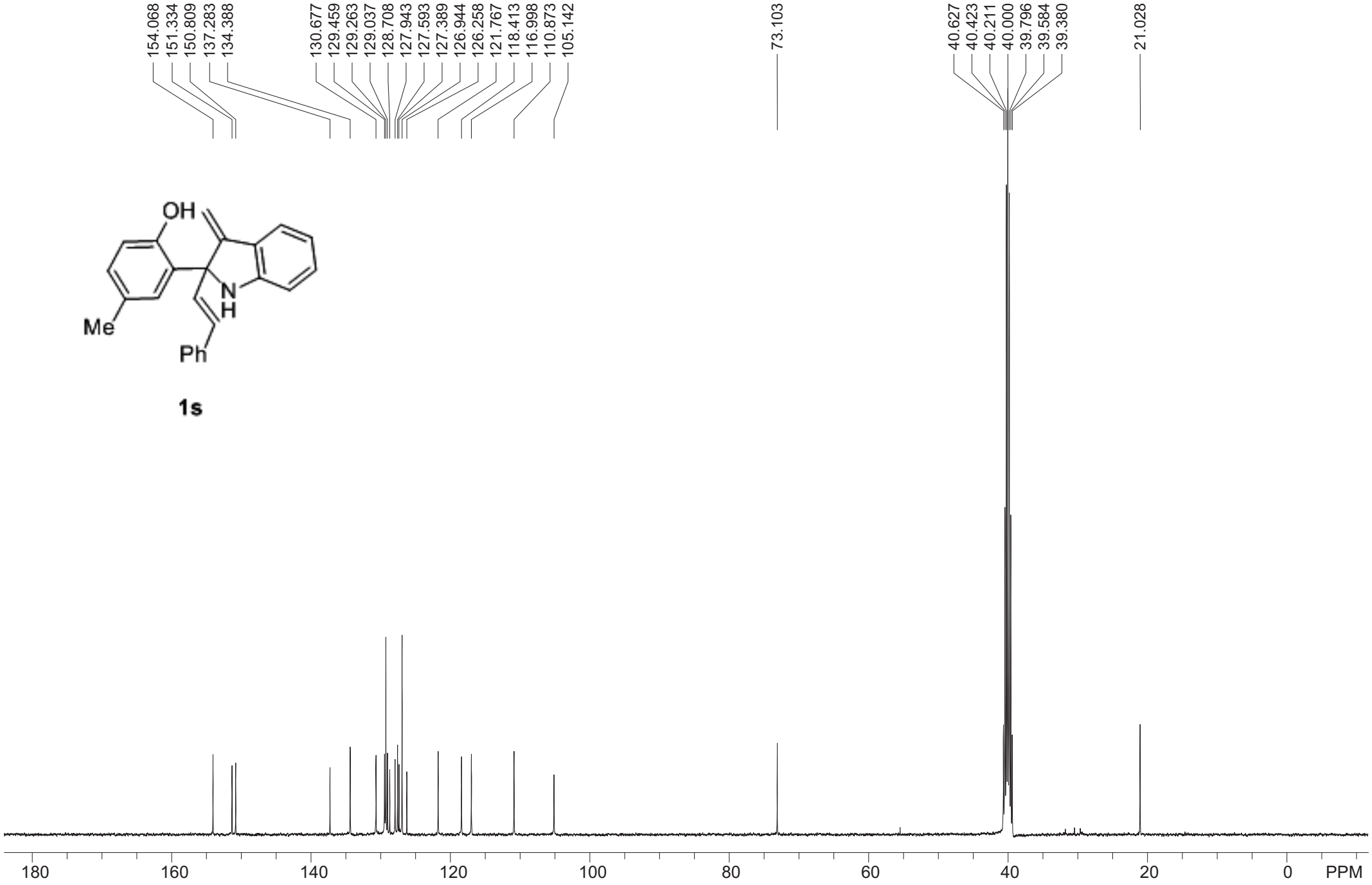
PPM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137.283
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126.258
121.767
118.413
116.998
110.873
105.142
73.103
40.627
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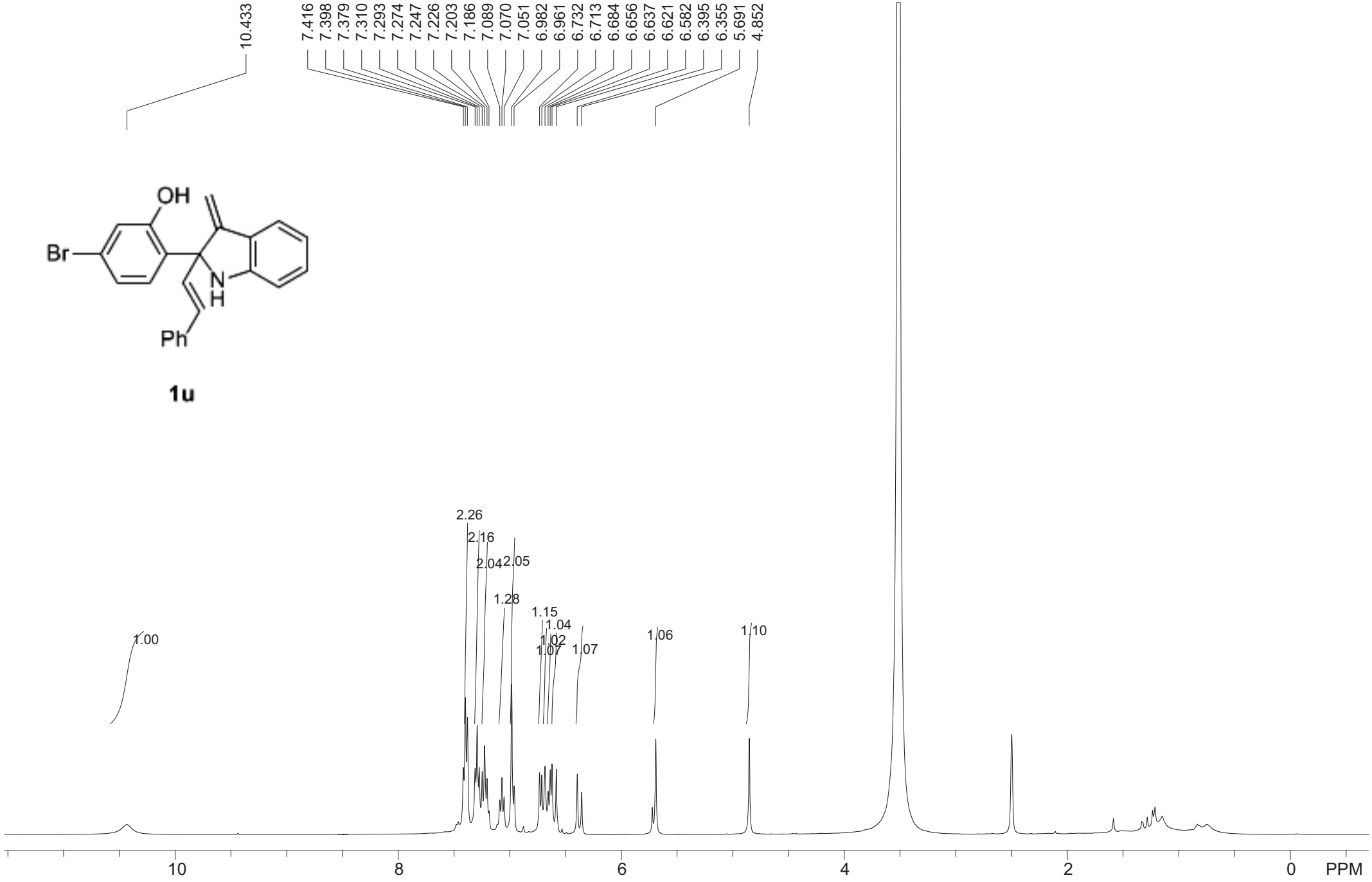
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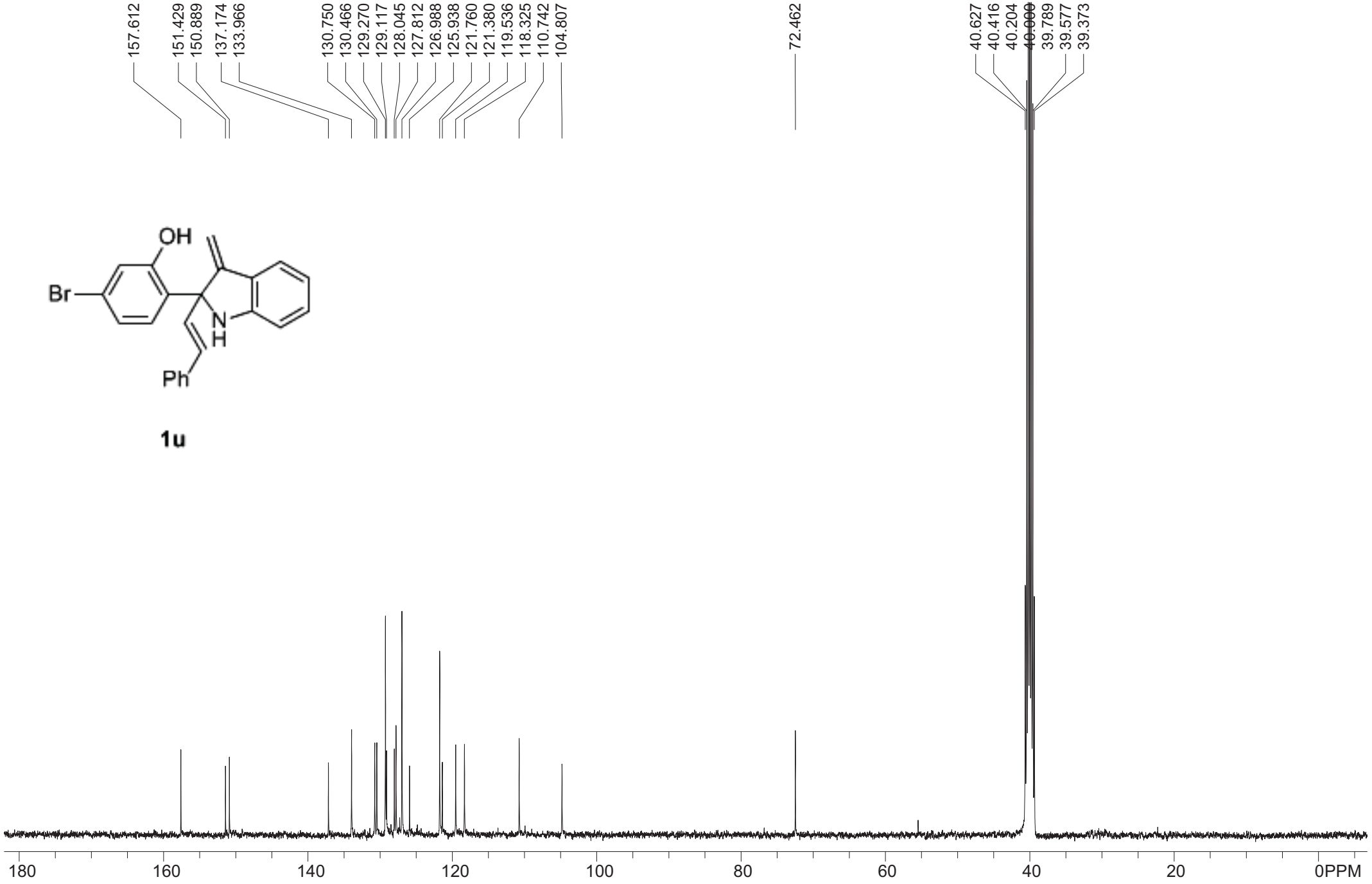
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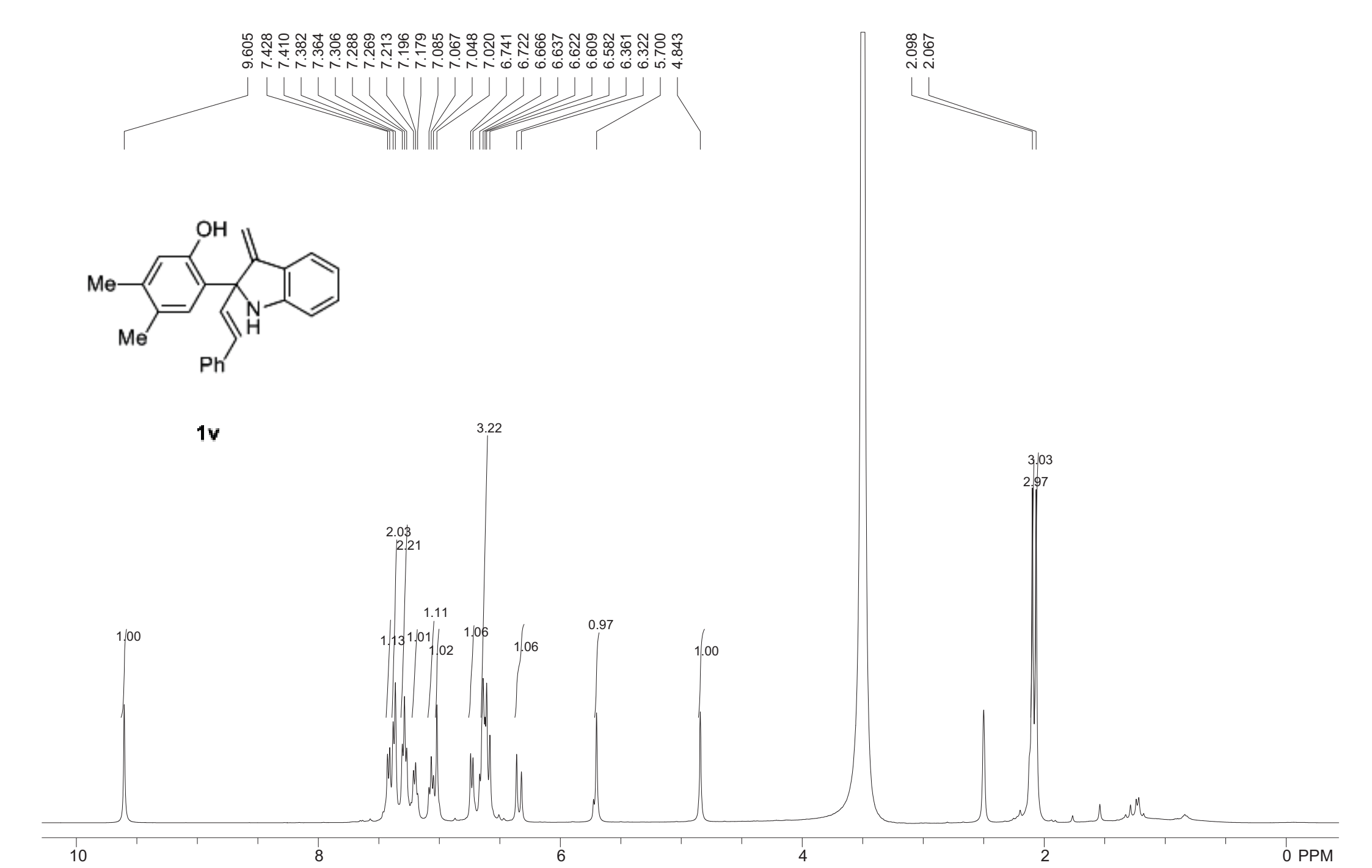
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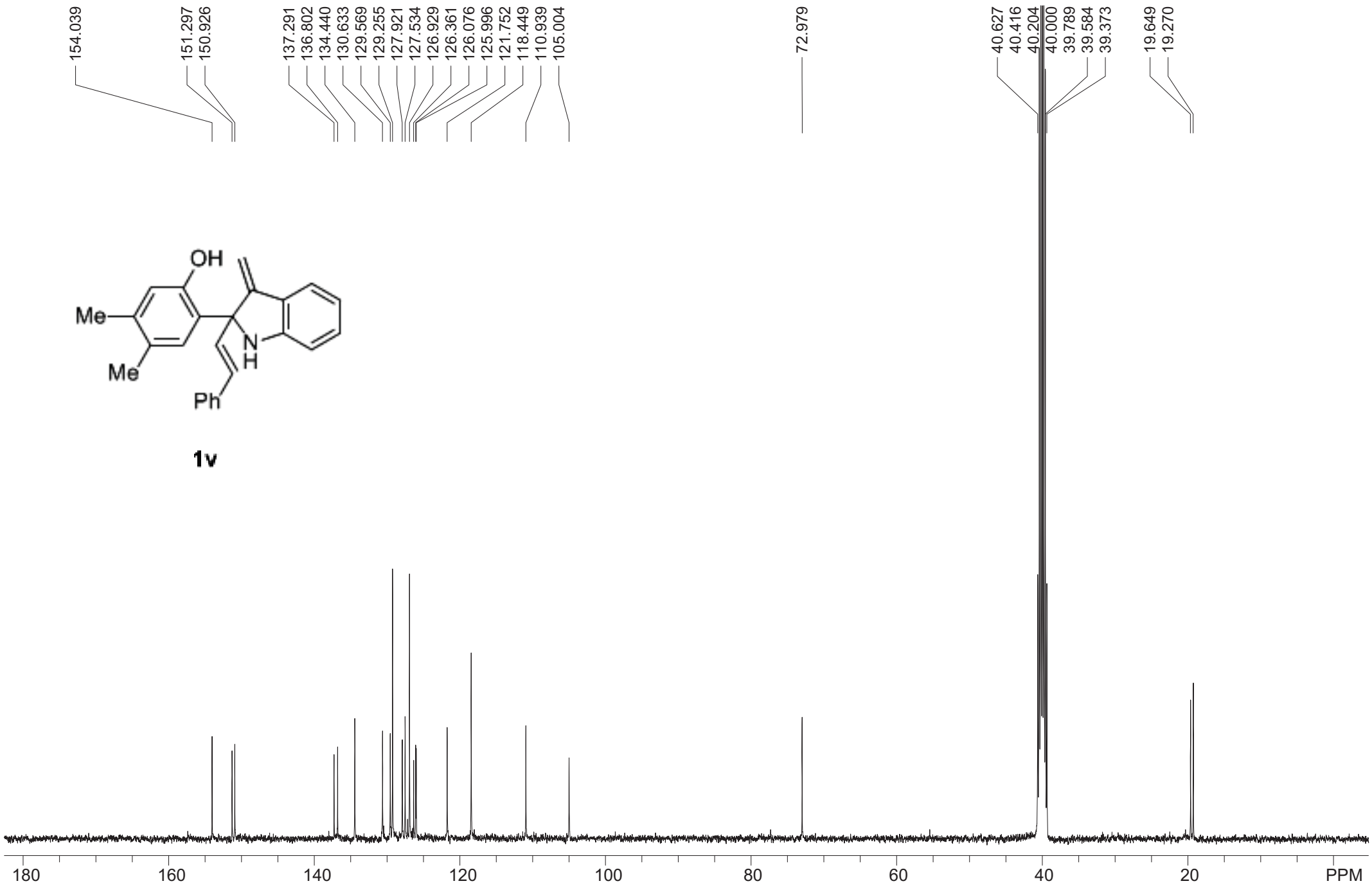
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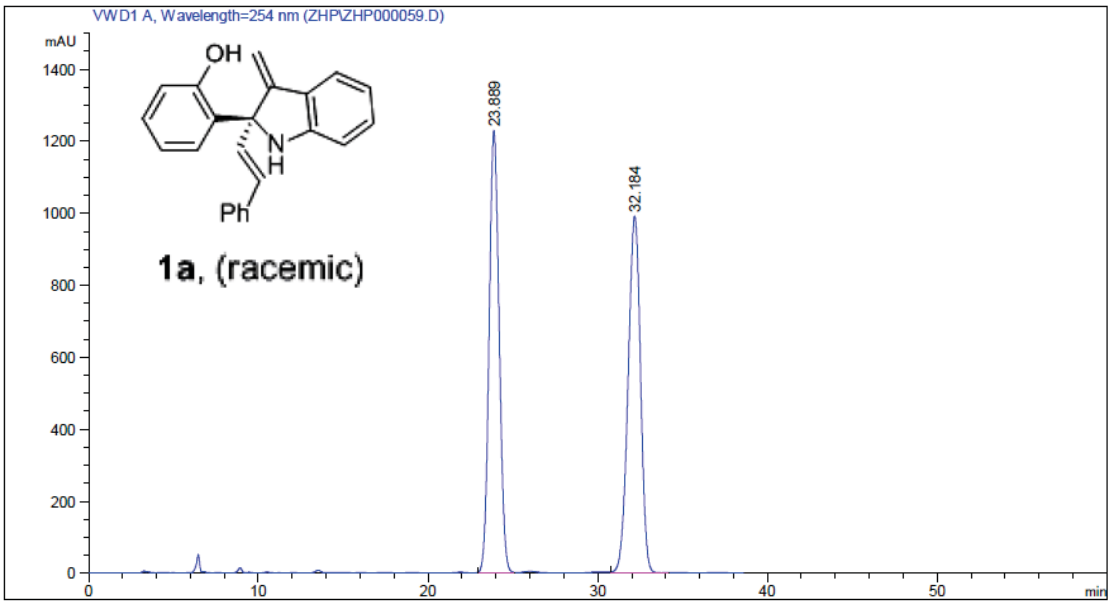
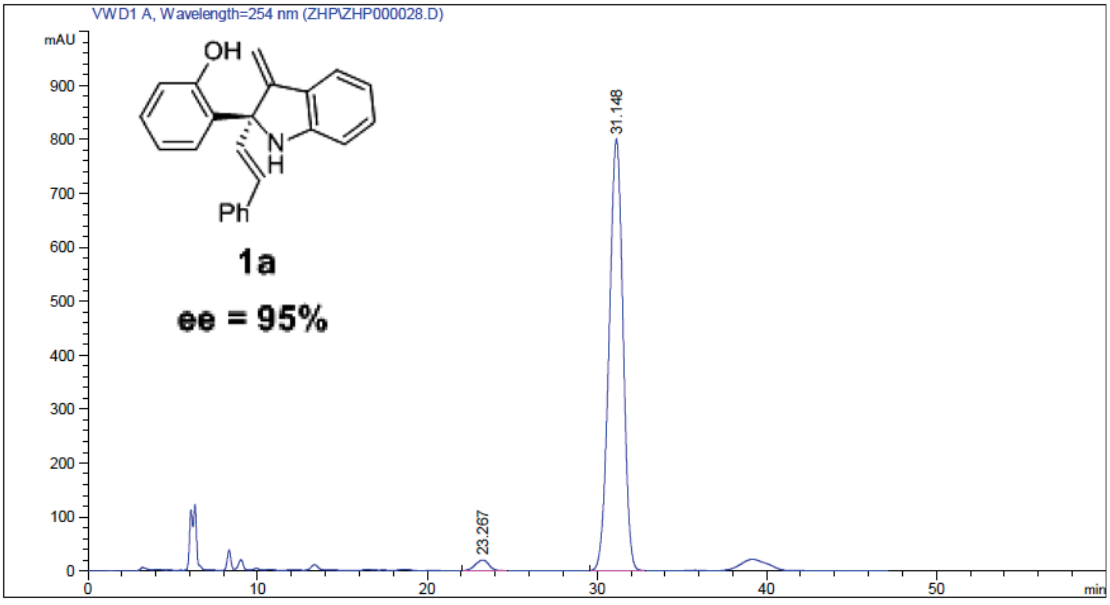
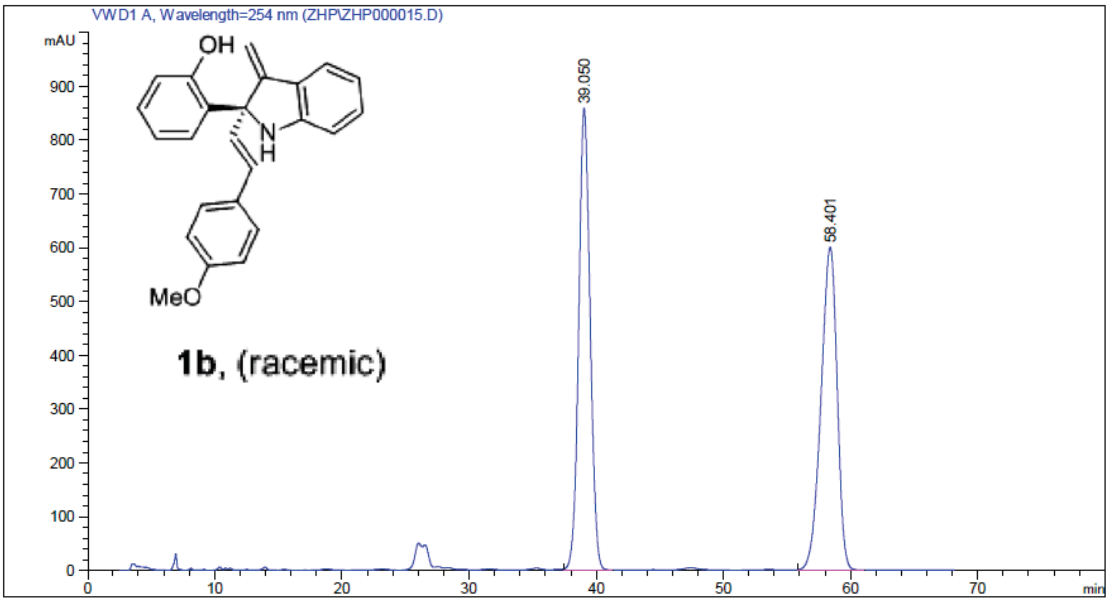


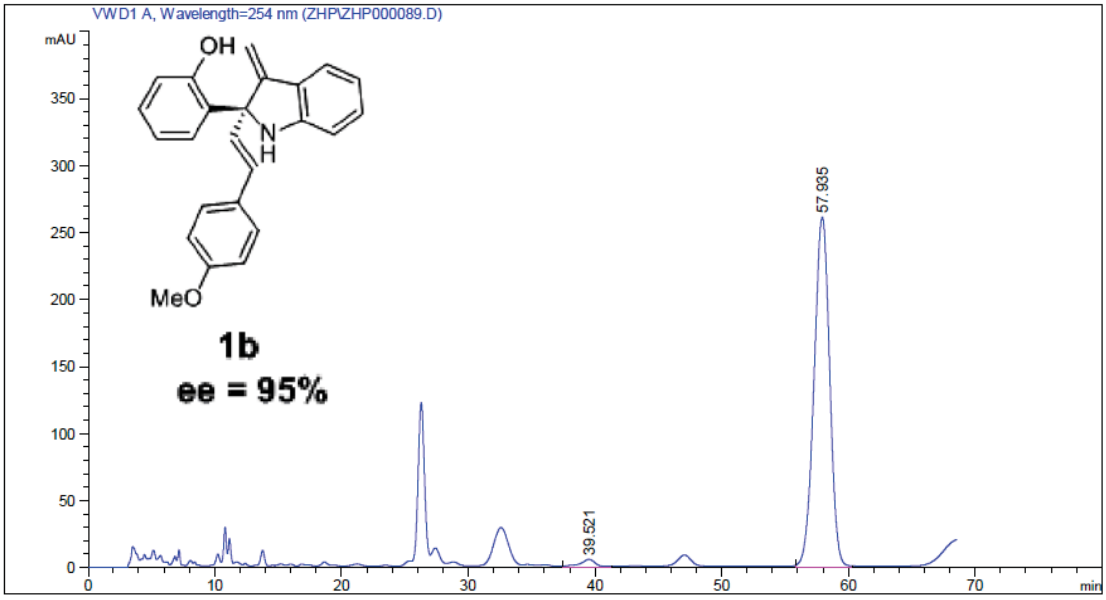
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	23.889	MM	0.6831	5.04226e4	1230.16675	49.9265
2	32.184	MM	0.8499	5.05710e4	991.67493	50.0735



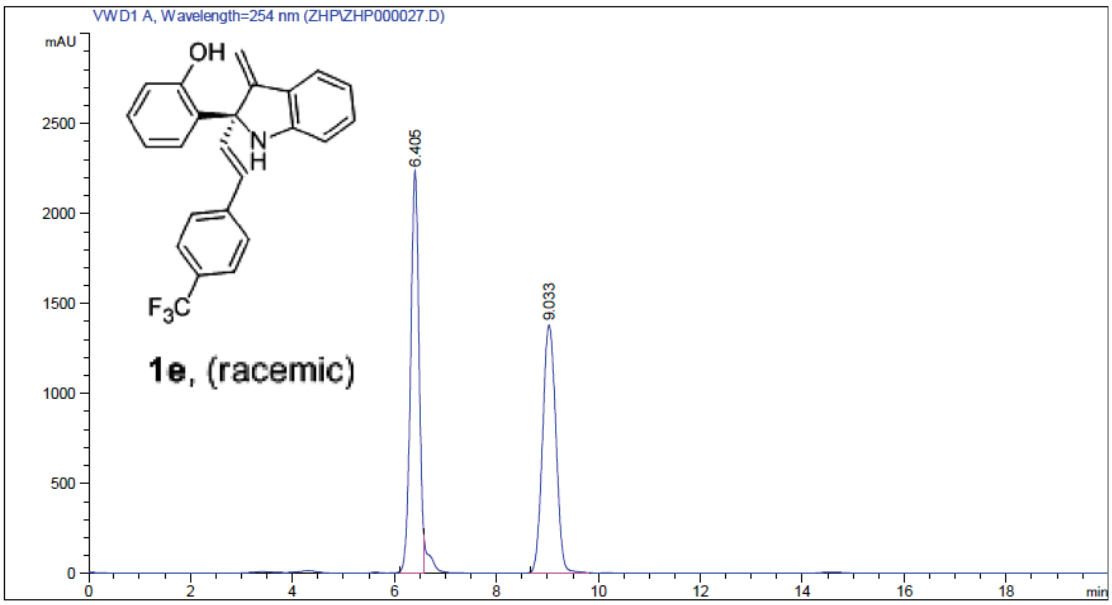
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	23.267	MM	0.9780	1212.54773	20.66305	2.5858
2	31.148	MM	0.9512	4.56802e4	800.37146	97.4142



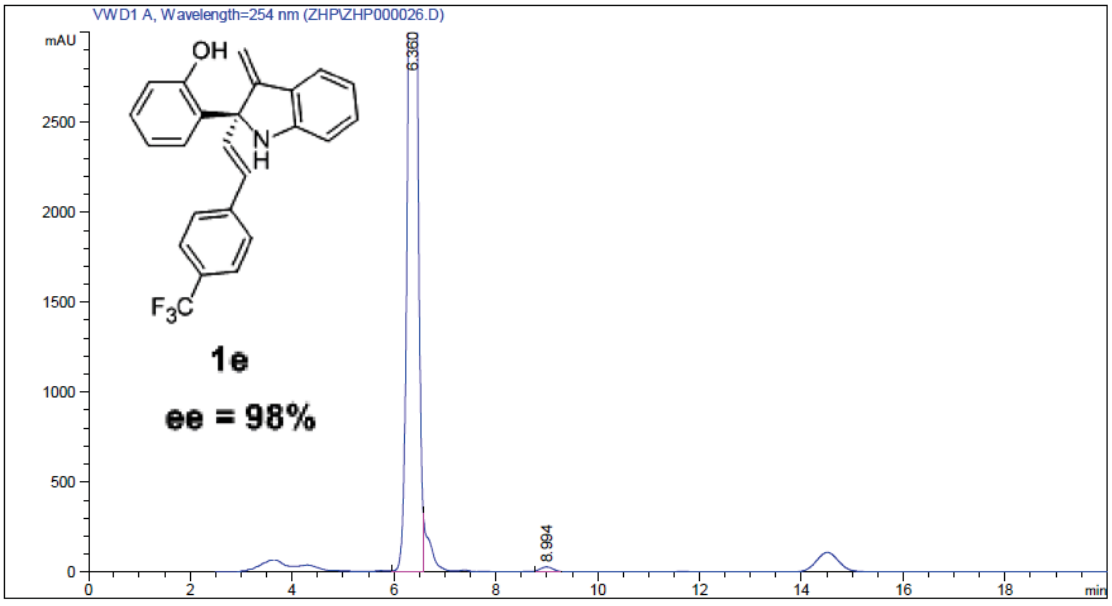
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	39.050	MM	1.0391	5.35976e4	859.68671	50.1753
2	58.401	MM	1.4758	5.32230e4	601.04700	49.8247



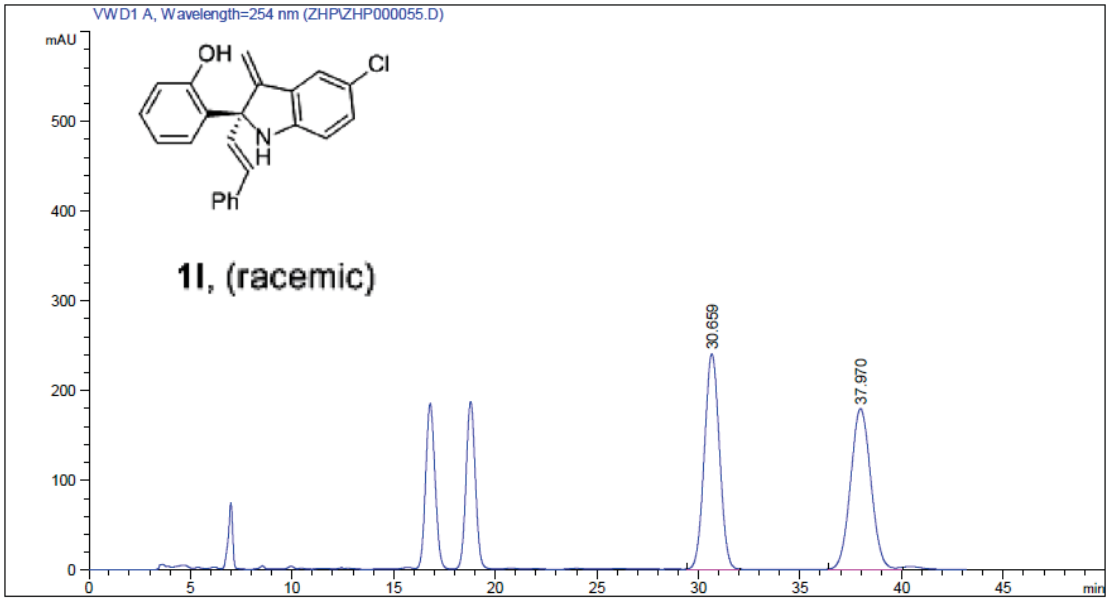
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	39.521	MM	1.6870	630.88171	6.23288	2.7295
2	57.935	MM	1.4340	2.24823e4	261.29758	97.2705



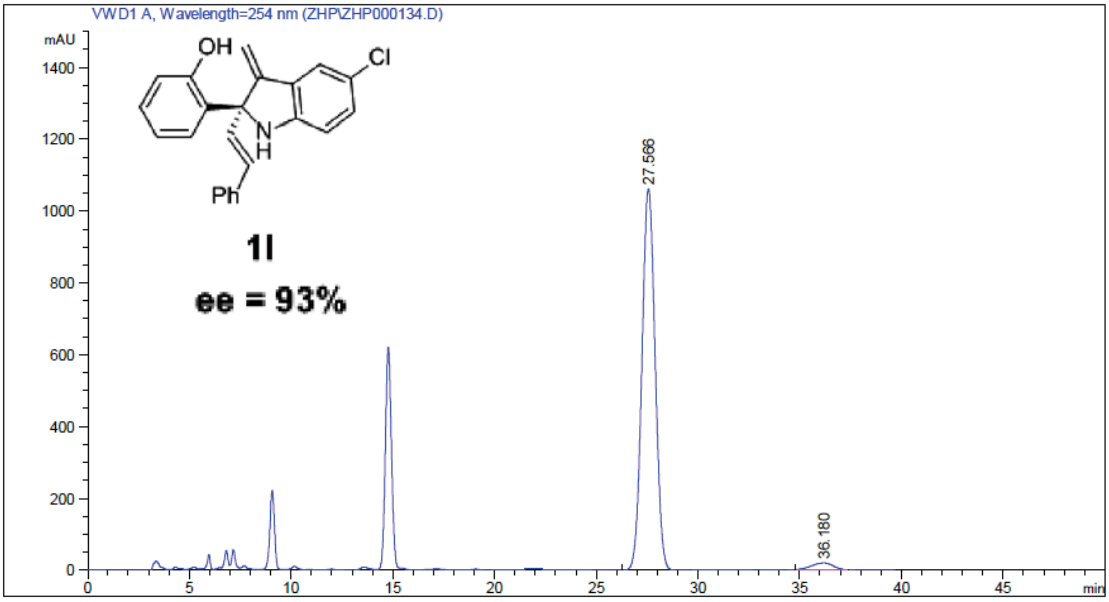
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	6.405	MM	0.1909	2.56397e4	2238.31274	50.5135
2	9.033	MM	0.3034	2.51184e4	1379.86108	49.4865



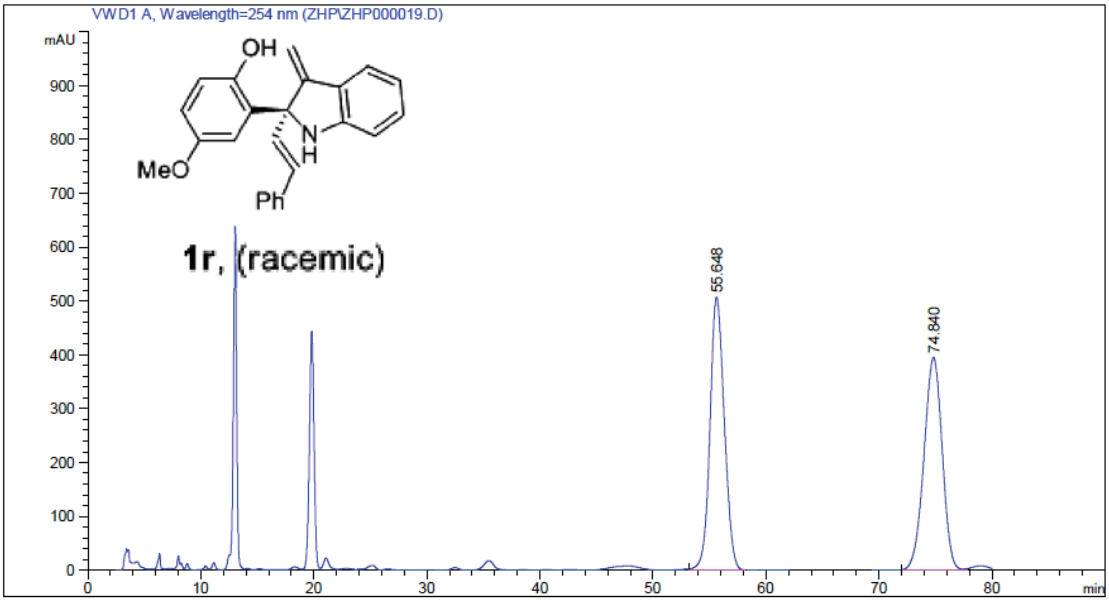
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	6.360	MM	0.2107	7.13806e4	5646.61035	99.2775
2	8.994	MM	0.3026	519.50677	28.61106	0.7225



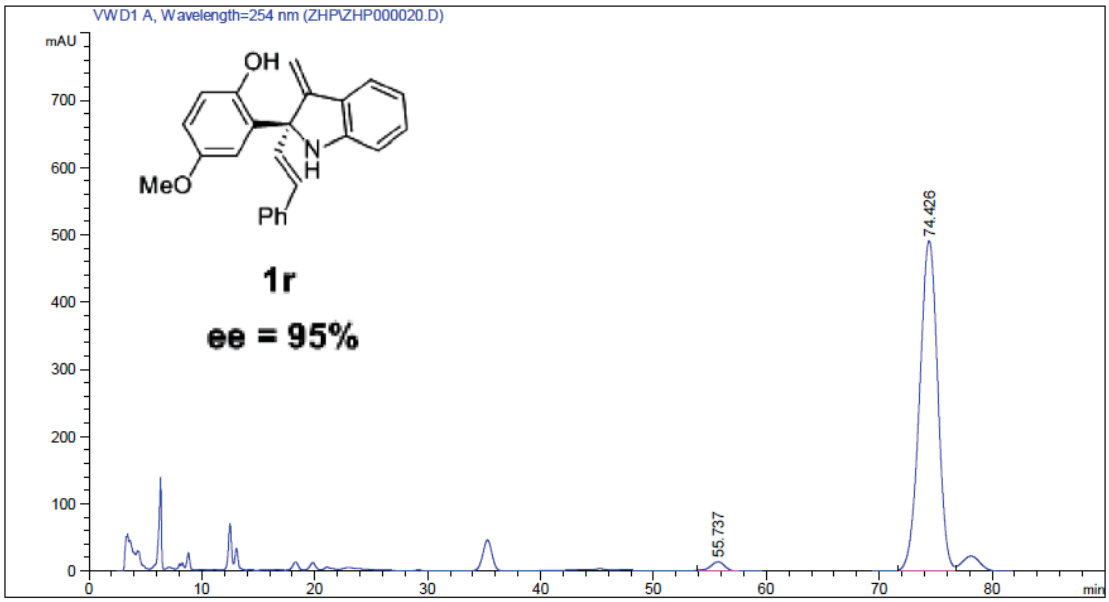
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	30.659	MM	0.8659	1.25208e4	240.99625	49.7515
2	37.970	MM	1.1713	1.26458e4	179.94440	50.2485



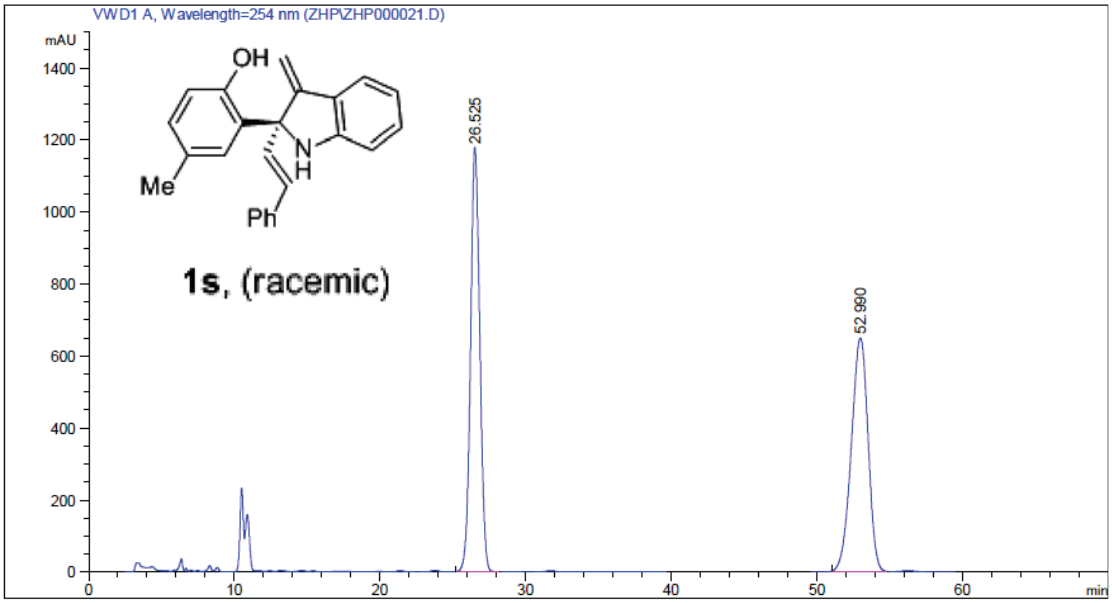
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	27.566	MM	0.7482	4.77050e4	1062.67090	96.8655
2	36.180	MM	1.3072	1543.70862	19.68251	3.1345



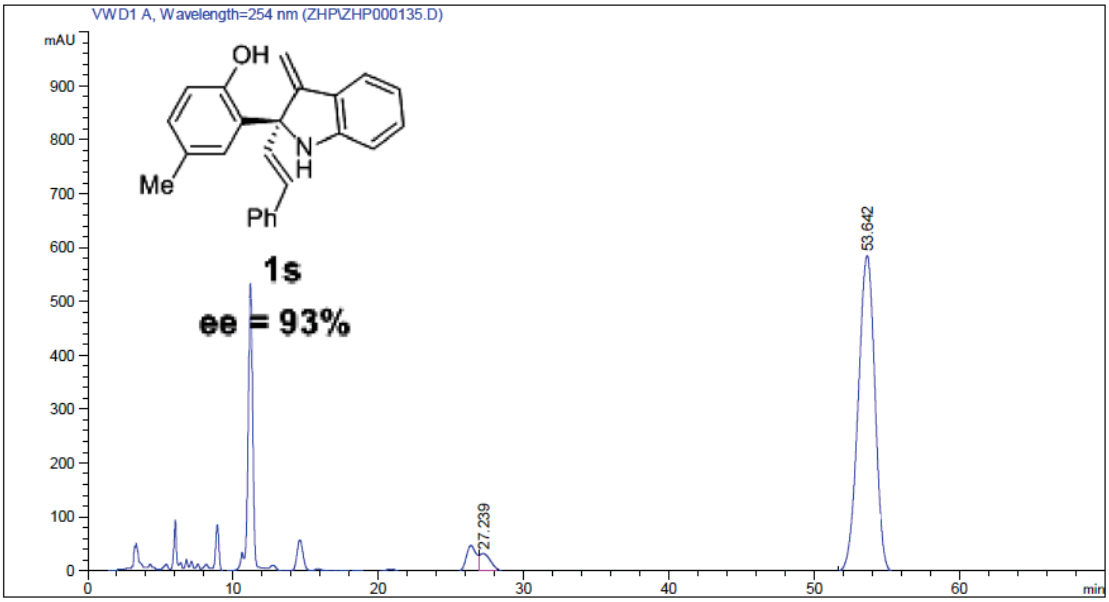
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	55.648	MM	1.4703	4.47667e4	507.46753	50.2001
2	74.840	MM	1.8691	4.44099e4	396.00937	49.7999



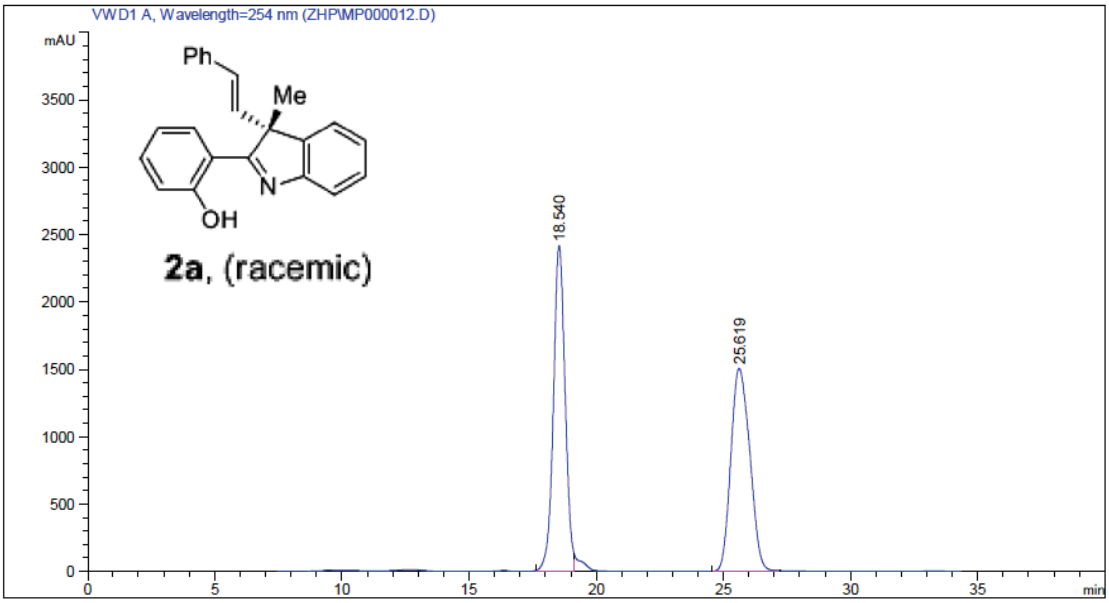
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	55.737	MM	1.4716	1229.03308	13.91958	2.1916
2	74.426	MM	1.8614	5.48507e4	491.12411	97.8084



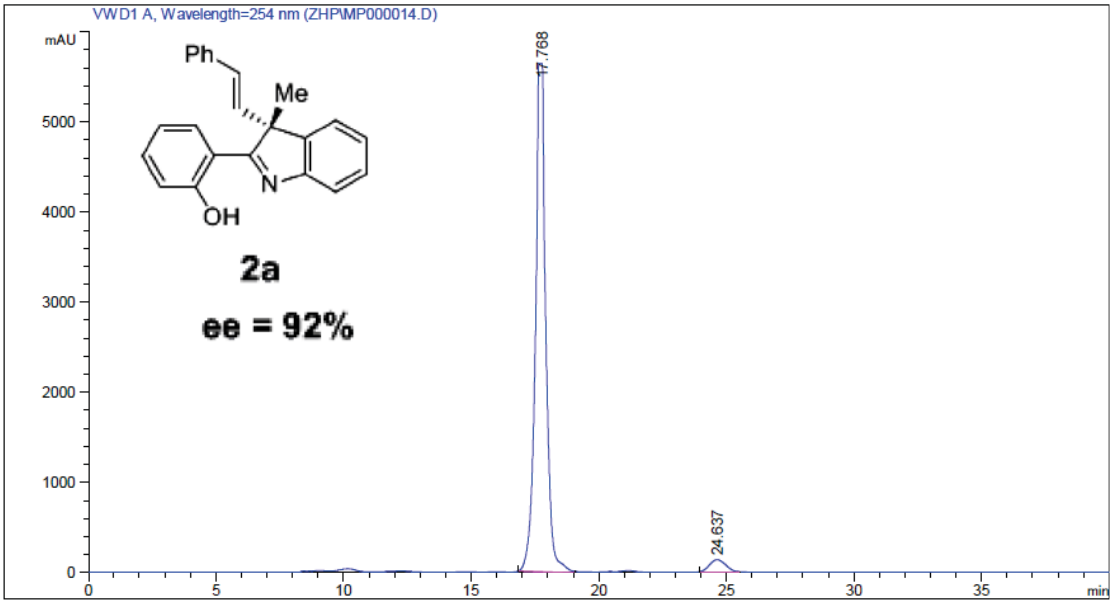
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	26.525	MM	0.7369	5.21659e4	1179.85779	50.0421
2	52.990	MM	1.3352	5.20781e4	650.09009	49.9579



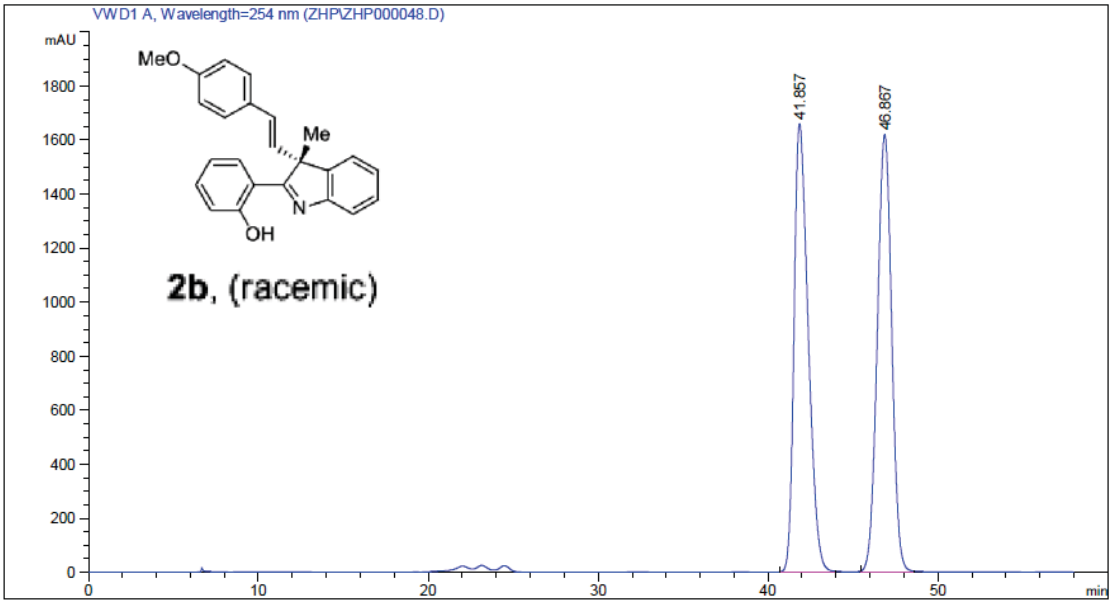
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	27.239	MM	0.8158	1570.63477	32.08923	3.2661
2	53.642	MM	1.3251	4.65190e4	585.09613	96.7339



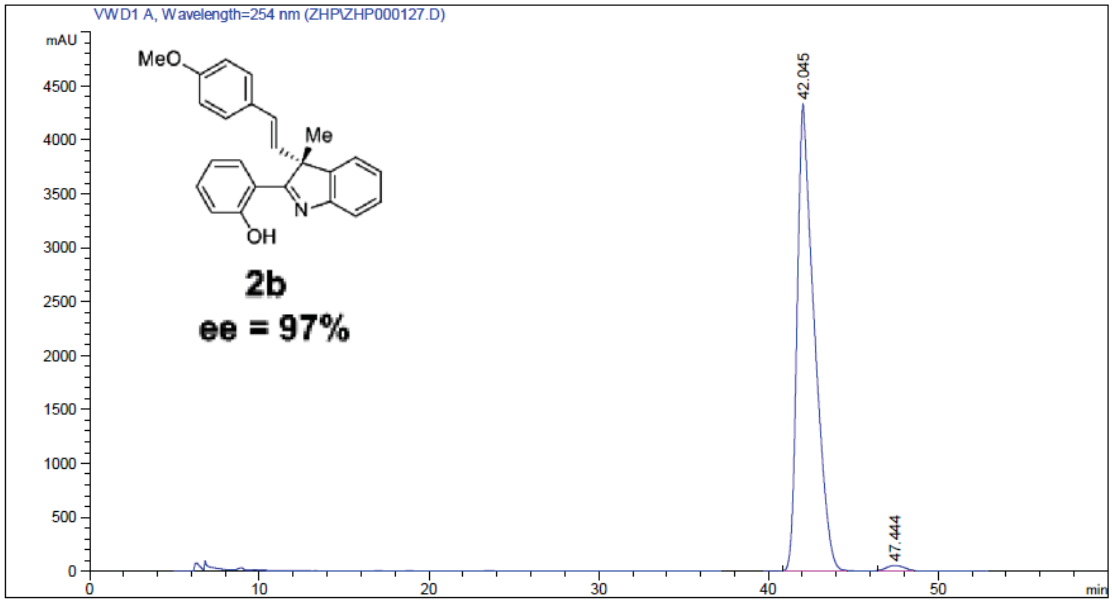
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	18.540	MM	0.5344	7.75691e4	2419.22656	49.7661
2	25.619	MM	0.8659	7.82984e4	1507.03088	50.2339



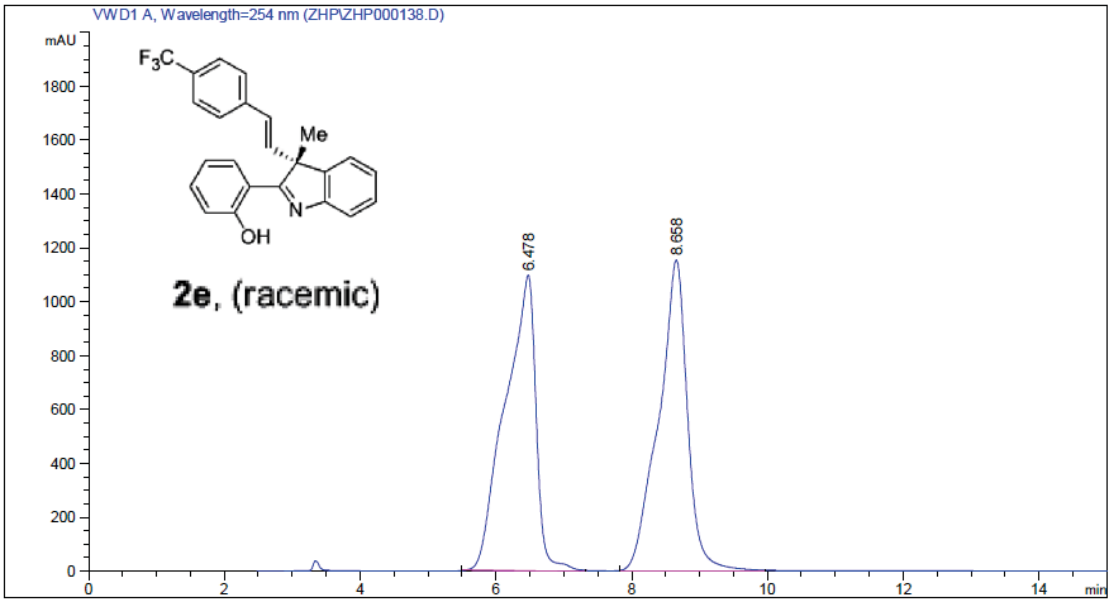
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	17.768	MM	0.4732	1.60102e5	5639.30713	96.0454
2	24.637	MM	0.7729	6592.06689	142.15352	3.9546



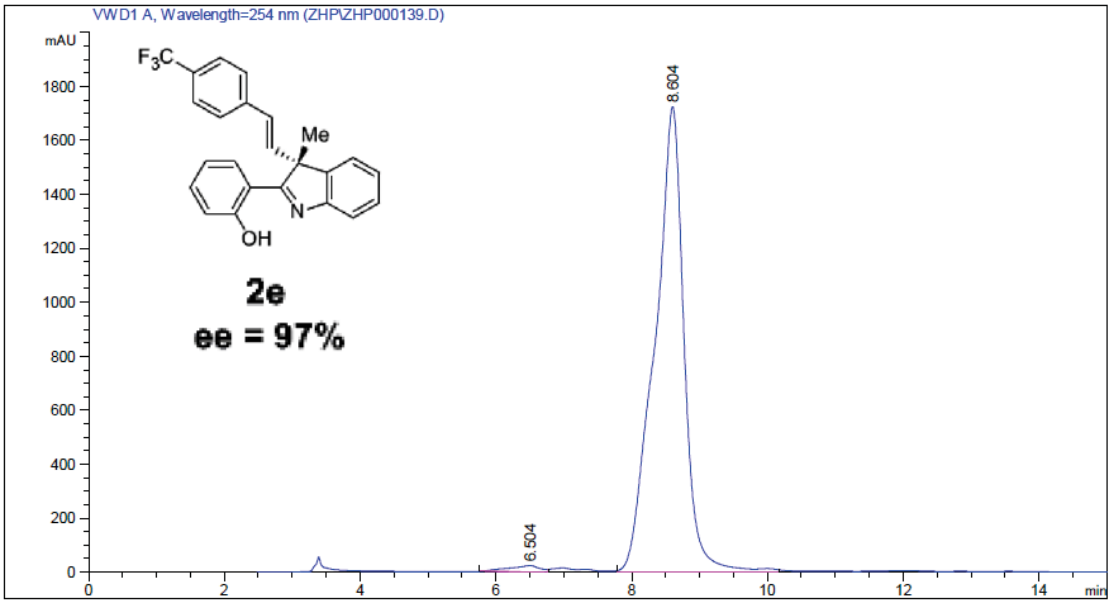
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	41.857	MM	0.9615	9.57987e4	1660.54272	50.0156
2	46.867	MM	0.9844	9.57391e4	1620.88562	49.9844



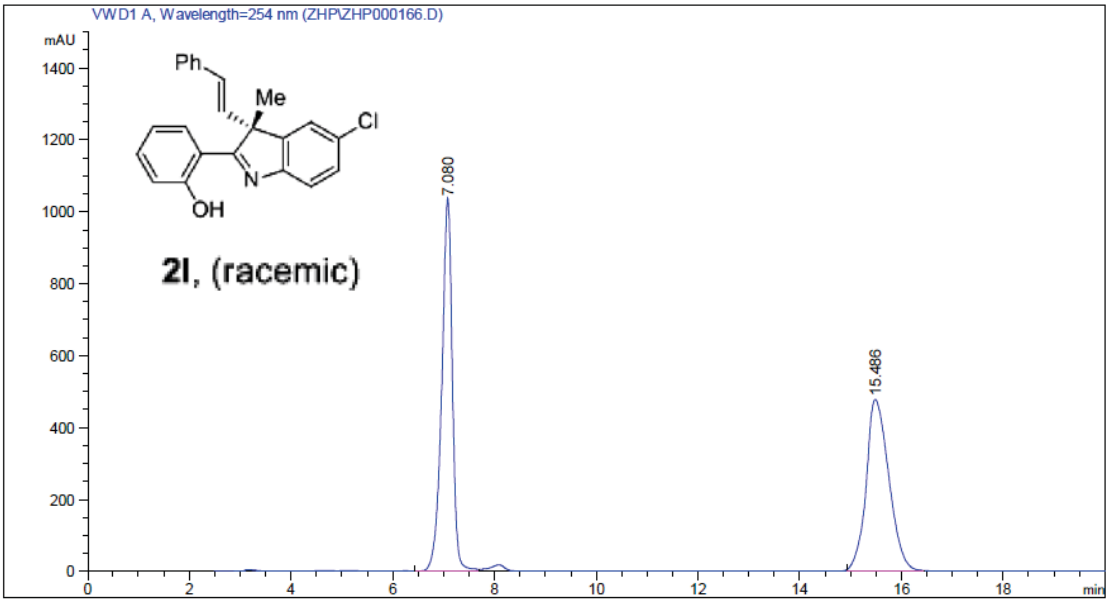
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	42.045	MM	1.1644	3.03069e5	4337.81055	98.6284
2	47.444	MM	1.3056	4214.54883	53.80146	1.3716



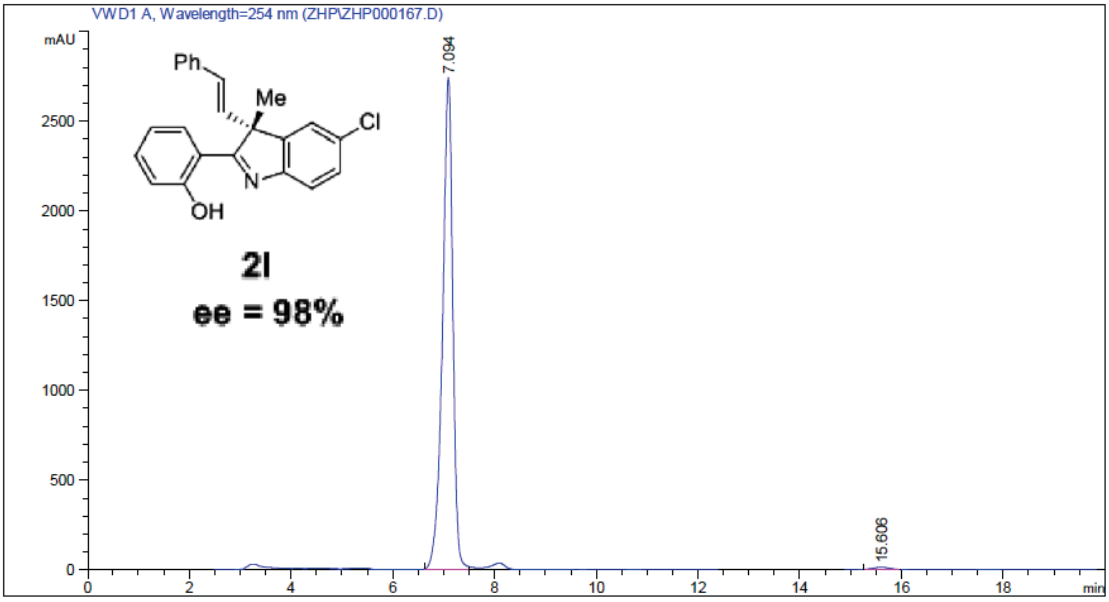
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	6.478	MM	0.5260	3.46136e4	1096.77844	50.3038
2	8.658	MM	0.4933	3.41955e4	1155.37244	49.6962



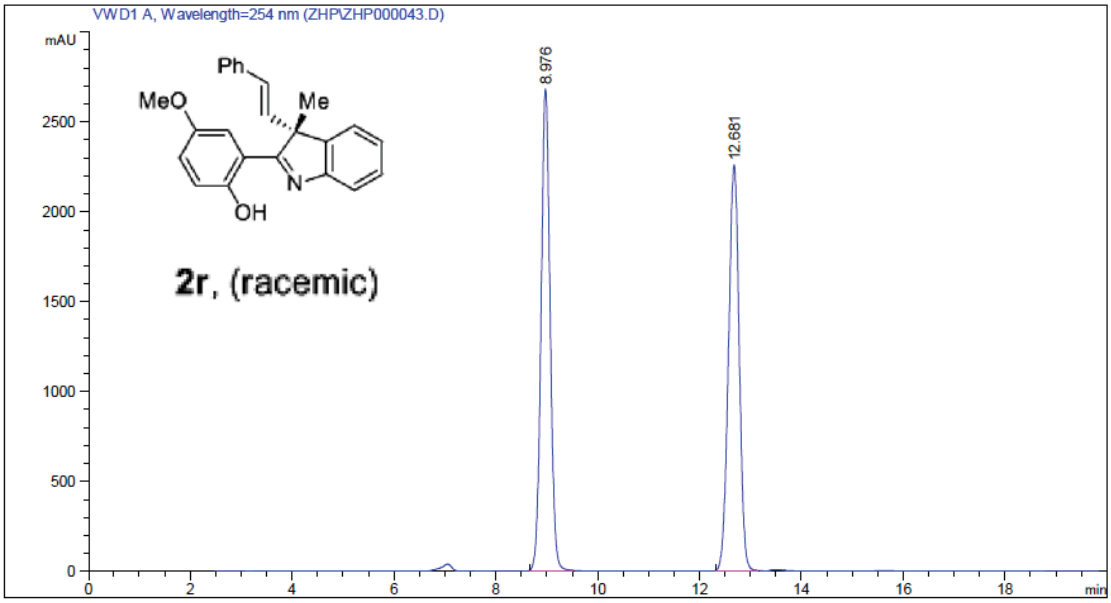
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	6.504	MM	0.5241	732.60345	23.29523	1.4009
2	8.604	MM	0.4983	5.15629e4	1724.47021	98.5991



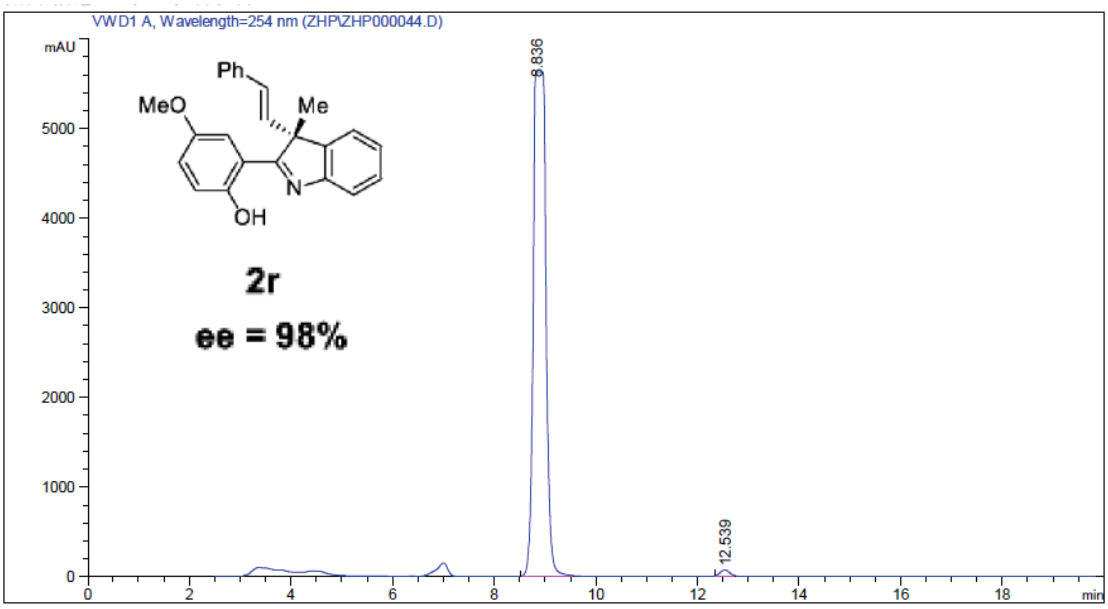
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	7.080	BV	0.2161	1.50152e4	1033.72107	50.2288
2	15.486	MM	0.5186	1.48784e4	478.17123	49.7712



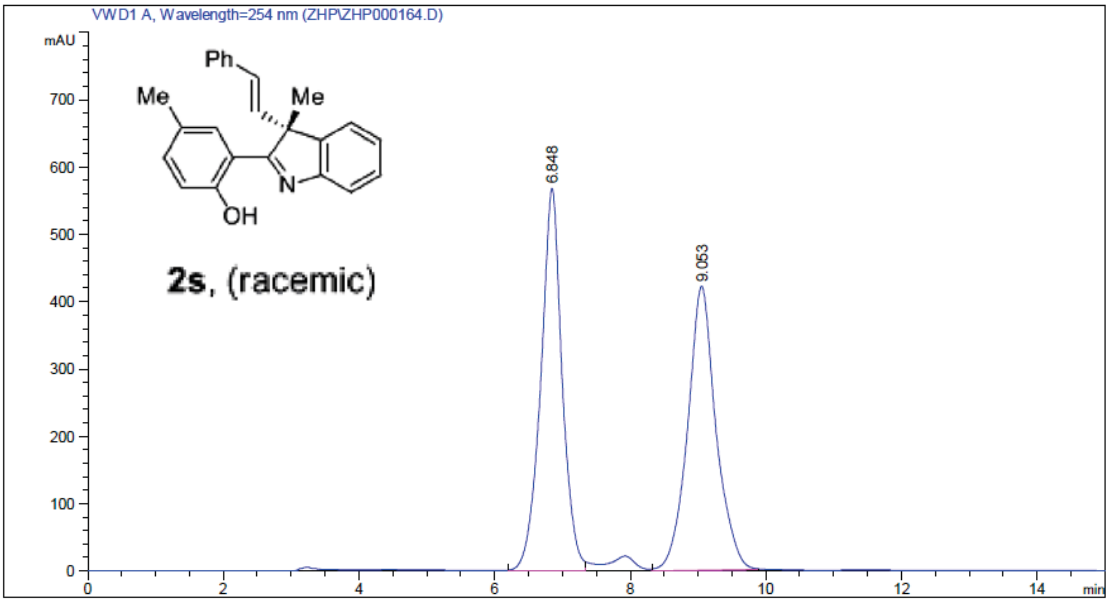
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	7.094	MM	0.2351	3.87010e4	2744.07300	99.0711
2	15.606	MM	0.4100	362.85883	14.74977	0.9289



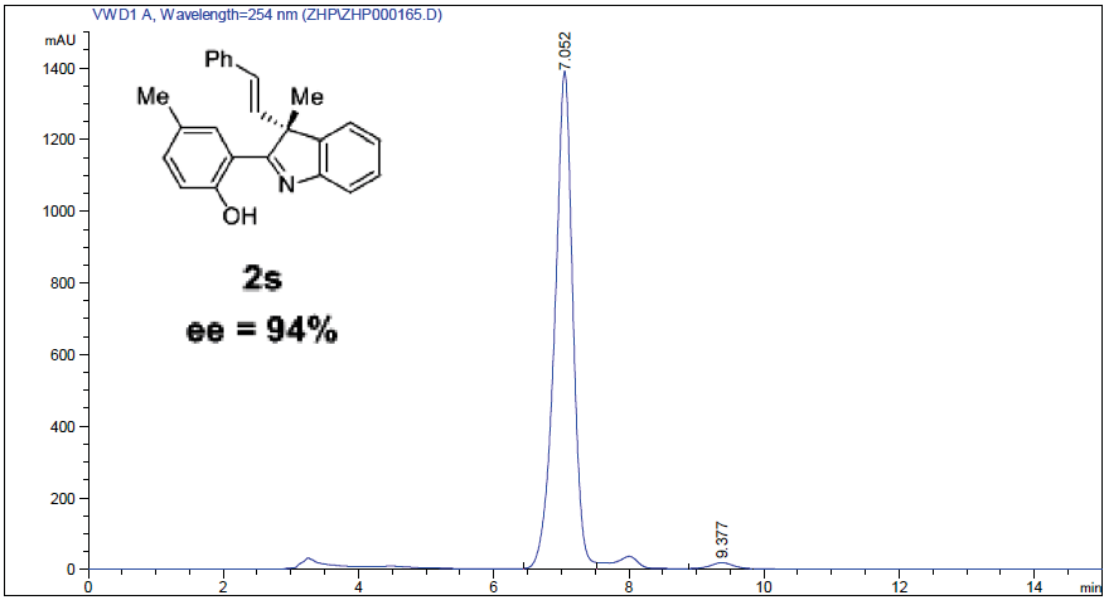
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	8.976	MM	0.2062	3.31937e4	2682.78149	50.1206
2	12.681	MM	0.2435	3.30339e4	2261.48511	49.8794



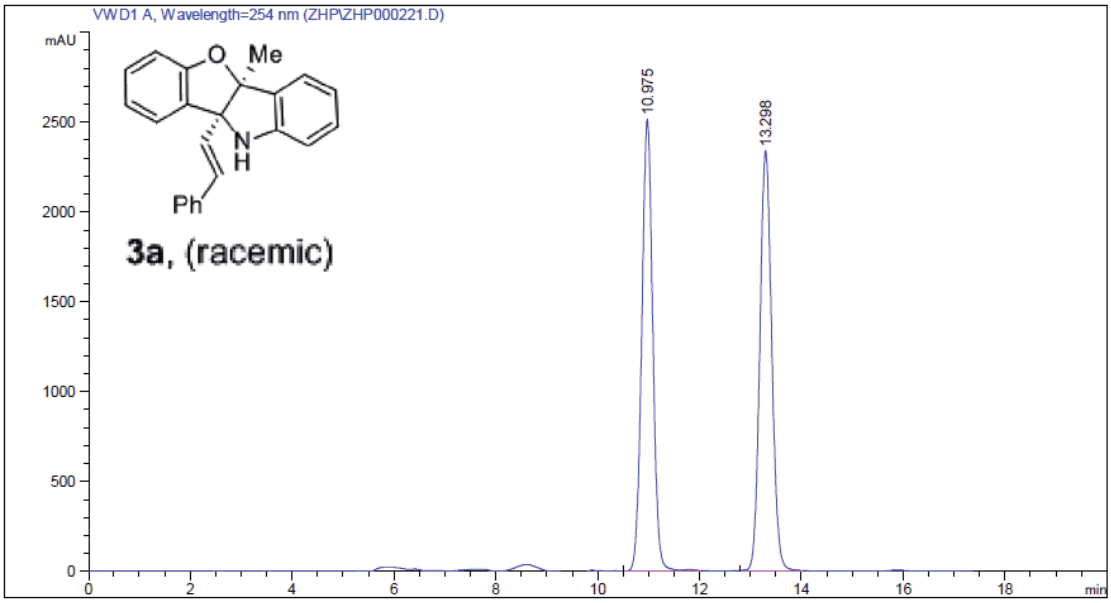
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	8.836	MM	0.2869	9.68953e4	5628.89160	98.9485
2	12.539	MM	0.2293	1029.72449	74.85501	1.0515



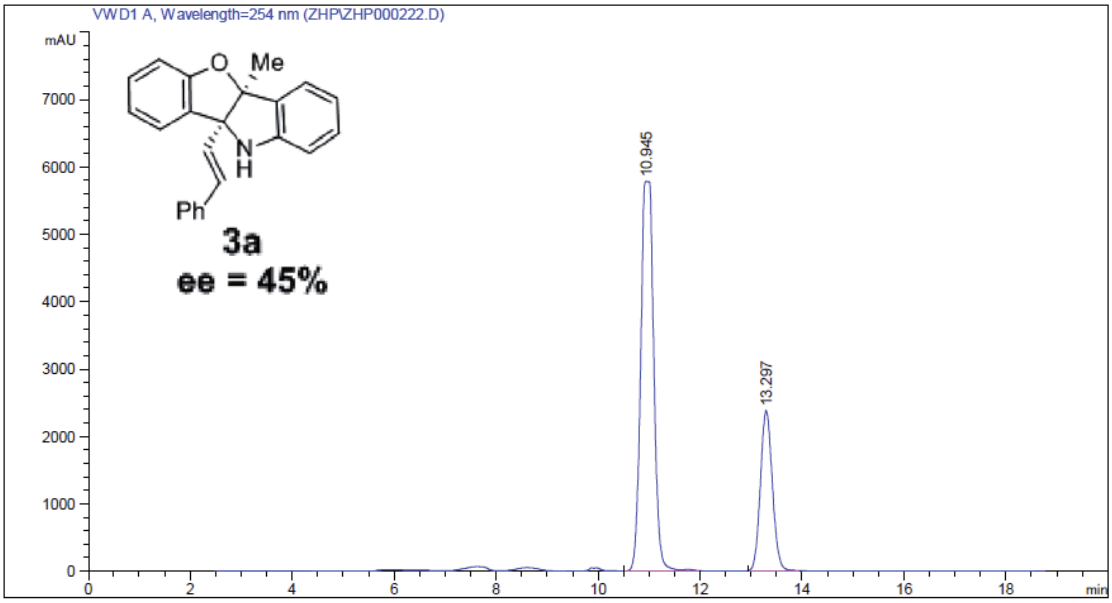
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	6.848	MM	0.3639	1.24137e4	568.48212	50.3364
2	9.053	MM	0.4837	1.22478e4	421.98074	49.6636



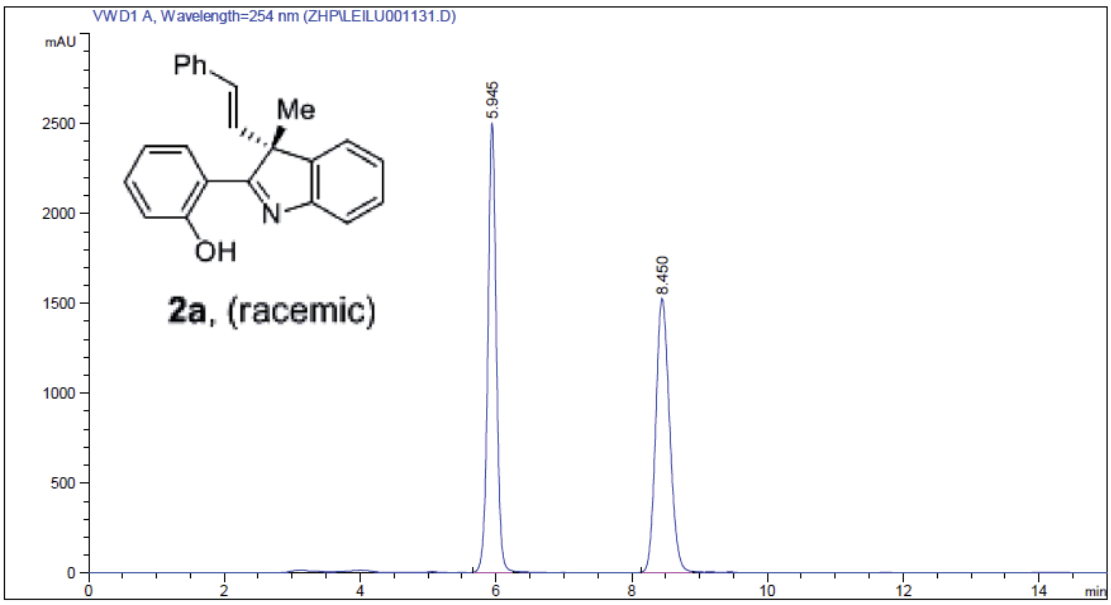
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	7.052	MM	0.3139	2.63408e4	1398.70508	96.9761
2	9.377	MM	0.5554	821.34686	24.64776	3.0239



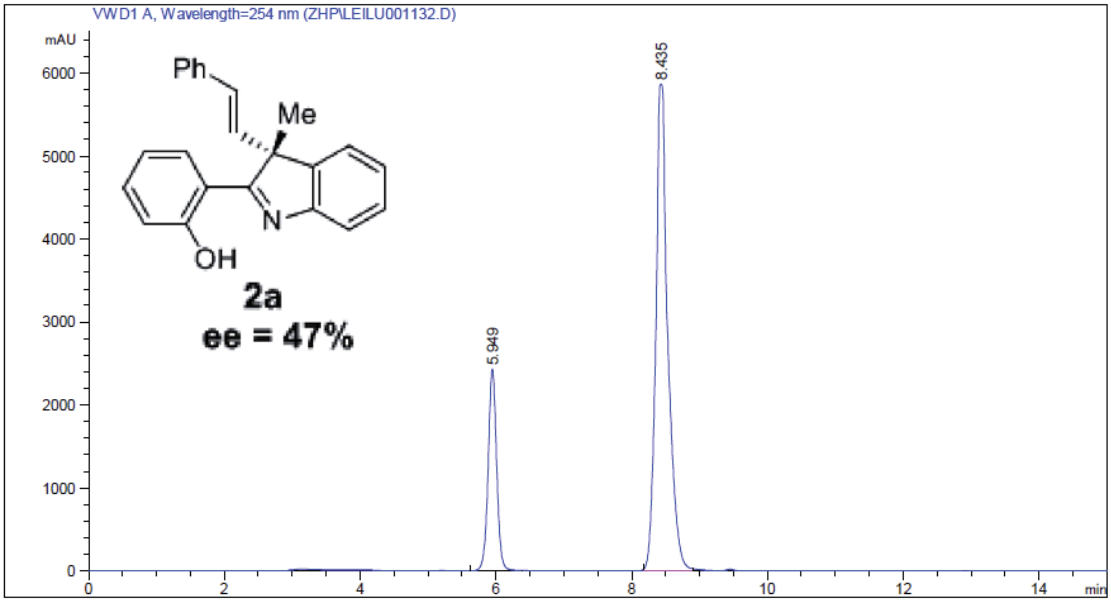
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	10.975	MM	0.2507	3.78690e4	2517.75708	49.8085
2	13.298	MM	0.2716	3.81601e4	2341.47388	50.1915



Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	10.945	MM	0.2962	1.02801e5	5783.92041	72.4163
2	13.297	MM	0.2738	3.91574e4	2383.94873	27.5837



Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	5.945	MM	0.1442	2.16556e4	2502.36719	49.9173
2	8.450	MM	0.2373	2.17273e4	1526.26038	50.0827



Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	5.949	MM	0.1707	2.59234e4	2531.04004	26.3534
2	8.435	MM	0.2060	7.24447e4	5862.62305	73.6466