Supporting Information

Copper(I)-catalyzed [4+2] cycloaddition of aza-ortho-quinone methides with bicyclic alkenes

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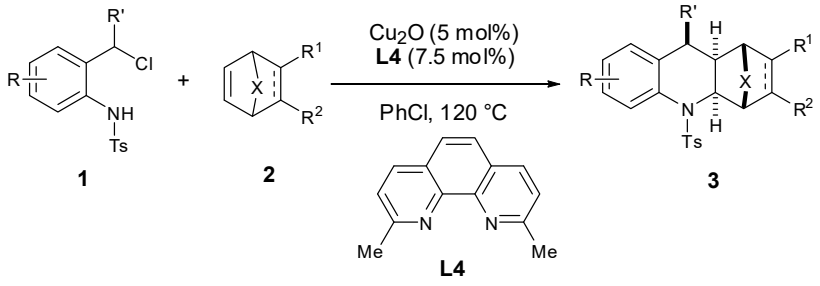
1. General Experimental Information

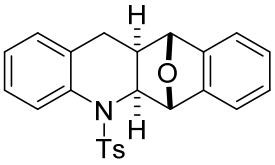
^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400, 500 or 600 MHz spectrometers, Chemical shifts are reported in ppm. TMS (δ 0.00) or $CDCl_3$ (δ 7.26) were used as internal standard in 1H NMR as well as $CDCl_3$ (δ 77.00) were used as internal standard in ^{13}C NMR, multiplicity (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. Diastereomeric ratio was determined by ^{1}H NMR. 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 reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use. The *o*-chloromethyl arylsulfonamides **1a-1j**[1] and bicyclic alkenes **2a-2o**[2] were prepared according the literature methods and their spectral data matched literature values.

2. Synthesis of compounds 3aa-3ko



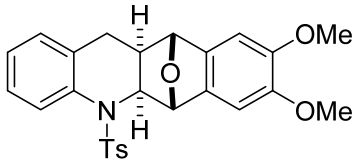
A Schlenk flask was charged with *o*-chloromethyl arylsulfonamides **1** (0.4 mmol), bicyclic alkenes (0.2 mmol), Cu_2O (5 mol%), neocuproine **L4** (7.5 mol%), and chlorobenzene (2 mL). The mixture was stirred vigorously at 120 °C for 6 hours until bicyclic alkenes **2** were completely consumed (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by

flash column chromatography (the crude residue was dry loaded with silica gel, 1/10 to 1/1, ethyl acetate/petroleum ether) to provide tetrahydroquinoline-fused bicycles **3**.



3aa

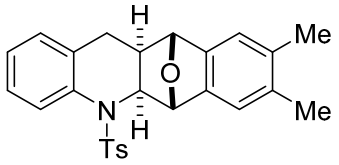
5-Tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3aa). White solid, 0.066 g, 82% yield; Mp: 213−214 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 3H), 7.29 (d, J = 7.6 Hz, 1H), 7.19−7.12 (m, 6H), 6.99 (d, J = 7.2 Hz, 1H), 5.26 (s, 1H), 4.91 (s, 1H), 4.65 (d, J = 8.4 Hz, 1H), 2.49−2.41 (m, 2H), 2.36 (s, 3H), 1.56 (dd, J = 15.6 Hz, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.7, 143.5, 143.4, 136.8, 136.5, 134.0, 129.5, 128.1, 127.6, 127.2, 127.1, 126.9, 126.8, 126.7, 120.4, 118.7, 86.5, 85.2, 60.3, 44.0, 30.1, 21.4; IR (thin film) 3043, 2939, 1915, 1676, 1598, 1488, 1342, 1165, 1077, 962, 818 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{21}NNaO_3S$ $[M + Na]^+$: 426.1135, found 426.1149.



3ab

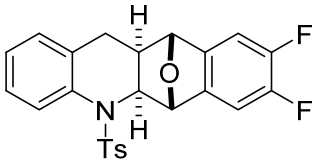
8,9-Dimethoxy-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ab). White solid, 0.068 g, 73% yield; Mp:162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.28−7.25 (m, 1H), 7.17−7.12 (m, 3H), 6.97 (d, J = 7.6 Hz, 2H), 6.74 (s, 1H), 5.21 (s, 1H), 4.84 (s, 1H), 4.59 (d, J = 8.0 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 2.45−2.38 (m, 2H), 2.36 (s, 3H), 1.53−1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 147.9, 143.5, 139.1, 136.8, 136.5, 135.6, 134.0, 129.5, 128.1, 127.5, 127.1, 126.8, 126.7, 104.8, 103.4, 86.7, 85.4, 60.6, 56.1,

44.7, 30.0, 21.4; IR (thin film) 2961, 1597, 1491, 1463, 1347, 1163, 1009, 965, 815 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_5S$ $[M + H]^+$: 464.1526, found 464.1530.



3ac

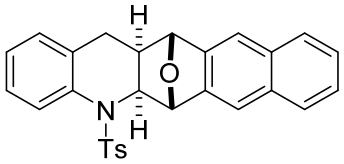
8,9-Dimethyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ac). White solid, 0.068 g, 77% yield; Mp:184−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 5.2 Hz, 1H), 7.15−7.10 (m, 4H), 6.97 (d, J = 7.2 Hz, 1H), 6.91 (s, 1H), 5.20 (s, 1H), 4.84 (s, 1H), 4.61 (d, J = 8.0 Hz, 1H), 2.46−2.37 (m, 2H), 2.35 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H), 1.53−1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 143.4, 141.2, 136.9, 136.5, 135.3, 134.9, 134.1, 129.5, 128.1, 127.5, 127.0, 126.8, 126.7, 121.6, 120.0, 86.4, 85.1, 60.6, 44.5, 30.1, 21.4, 19.9, 19.8; IR (thin film) 2962, 1598, 1489, 1459, 1349, 1166, 1077, 954, 808 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_3S$ $[M + H]^+$: 432.1628, found 432.1621.



3ad

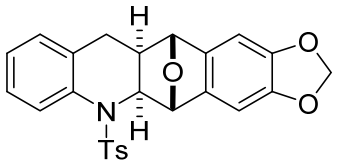
8,9-Difluoro-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ad). White solid, 0.046 g, 53% yield; Mp: 227−228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.22−7.13 (m, 4H), 6.98 (d, J = 6.4 Hz, 2H), 5.24 (s, 1H), 4.89 (s, 1H), 4.62 (d, J = 8.4 Hz, 1H), 2.47 (dd, J = 18.4 Hz, J = 8.0 Hz, 2H), 2.37 (s, 3H), 1.54−1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 136.7, 136.3, 133.6, 129.6, 128.1, 127.6, 127.3,

127.0, 126.7, 110.6, 110.4, 109.0, 108.8, 86.8, 84.8, 60.1, 44.0, 29.9, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −138.2, , −138.8; IR (thin film) 2926, 1734, 1658, 1596, 1449, 1334, 1157, 1040, 934, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{20}F_2NO_3S$ $[M + H]^+$: 440.1126, found 440.1154.



3ae

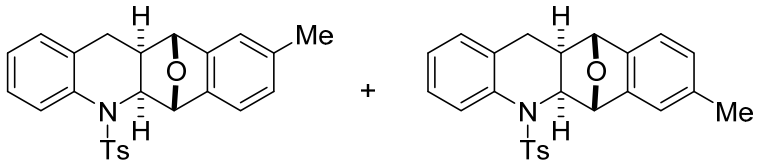
5-Tosyl-5,5a,6,13,13a,14-hexahydro-6,13-epoxynaphtho[2,3-b]acridine (3ae). White solid, 0.055 g, 63% yield; Mp: 153−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85−7.82 (m, 1H), 7.77 (s, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.48 (t, J = 4.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.2 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 7.6 Hz, 1H), 5.41 (s, 1H), 5.04 (s, 1H), 4.75 (d, J = 8.0 Hz, 1H), 2.56−2.50 (m, 2H), 2.35 (s, 3H), 1.55−1.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 143.6, 140.8, 136.8, 136.6, 133.9, 132.9, 132.6, 129.6, 128.4, 128.2, 128.0, 127.6, 127.2, 126.9, 126.7, 126.2, 126.1, 119.0, 116.9, 86.4, 85.1, 60.9, 45.2, 30.1, 21.5; IR (thin film) 2924, 1916, 1597, 1491, 1458, 1345, 1161, 1069, 953, 813 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{24}NO_3S$ $[M + H]^+$: 454.1471, found 454.1441.



3af

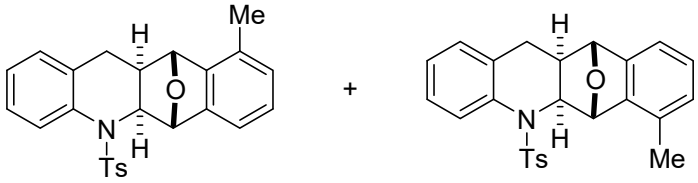
6-Tosyl-5,5a,6,11,11a,12-hexahydro-5,12-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-b]acridine (3af). White solid, 0.064 g, 72% yield; Mp: 268−269 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz,

1H), 7.14−7.12 (m, 3H), 6.96 (d, J = 7.6 Hz, 1H), 6.85 (s, 1H), 6.64 (s, 1 H), 5.93 (s, 2H), 5.15 (s, 1H), 4.81 (s, 1H), 4.59 (d, J = 8.0 Hz, 1H), 2.45−2.39 (m, 2H), 2.36 (s, 3H), 1.55−1.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 146.3, 143.5, 140.6, 137.0, 136.8, 136.4, 134.0, 129.5, 128.0, 127.5, 127.0, 126.8, 126.6, 102.4, 101.2, 101.0, 86.4, 85.1, 60.4, 44.2, 30.0, 21.4; IR (thin film) 2995, 2938, 1598, 1489, 1469, 1308, 1165, 1033, 931, 817 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{22}NO_5S$ [M + H]$^+$: 448.1213, found 448.1217.



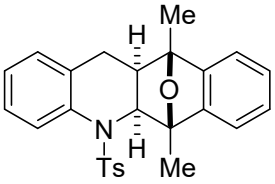
3ag (*isomer ratio* = 1:1)

9-Methyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ag). White solid, 0.071 g, 85% yield; Mp: 110−111 ℃; *isomer one* : ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.25−7.16 (m, 2H), 7.14 (t, J = 6.0 Hz, 3H), 7.01−6.93 (m, 3H), 5.22 (s, 1H), 4.87 (s, 1H), 4.63 (d, J = 3.2 Hz, 1H), 2.47−2.38 (m, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 1.54−1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 143.9, 137.1, 136.8, 136.5, 134.2, 129.5, 128.0, 127.6, 127.1, 126.9, 126.6, 121.2, 119.6, 86.4, 85.1, 60.5, 44.3, 30.0, 21.4, 21.3; *isomer two*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.25−7.16 (m, 2H), 7.14 (t, J = 6.0 Hz, 3H), 7.01−6.93 (m, 3H), 5.21 (s, 1H), 4.85 (s, 1H), 4.61 (d, J = 3.2 Hz, 1H), 2.47−2.38 (m, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.54−1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 143.5, 140.6, 136.8, 136.6, 136.4, 134.1, 129.5, 127.5, 127.0, 126.8, 126.6, 120.0, 118.4, 86.3, 85.1, 60.4, 44.2, 30.0, 21.4, 21.3; IR (thin film) 2928, 2253, 1919, 1599, 1488, 1458, 1348, 1167, 1033, 911, 813 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_3S$ [M + H]$^+$: 418.1471, found 418.1478.



3ah (*isomer ratio* = 1:1)

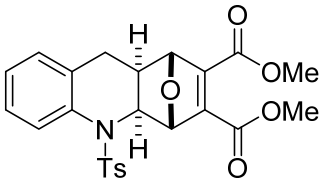
10-Methyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ah). White solid, 0.068 g, 82% yield; Mp: 132−133 ℃; *isomer one* : ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (t, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.28−7.23 (m, 1H), 7.17−7.11 (m, 4H), 7.07 (d, J = 7.6 Hz, 1H), 6.98−6.92 (m, 2H), 5.31 (s, 1H), 4.97 (s, 1H), 4.64 (d, J = 8.0 Hz, 1H), 2.49−2.40 (m, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 1.58−1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 143.5, 142.1, 136.8, 136.5, 134.0, 129.5, 128.6, 128.1, 127.9, 127.5, 127.0, 126.8, 126.6, 117.6, 86.7, 85.1, 60.3, 44.0, 30.2, 21.4, 18.3; *isomer two*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (t, J = 8.8 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.28−7.23 (m, 1H), 7.17−7.11 (m, 4H), 7.04 (d, J = 7.6 Hz, 1H), 6.98−6.92 (m, 2H), 5.24 (s, 1H), 4.90 (s, 1H), 4.61 (d, J = 8.4 Hz, 1H), 2.49−2.40 (m, 2H), 2.34 (s, 3H), 2.23 (s, 3H), 1.58−1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 143.0, 136.9, 136.5, 134.1, 130.4, 129.5, 128.4, 128.0, 127.6, 127.3, 126.8, 126.7, 126.6, 116.0, 85.4, 83.7, 59.7, 43.3, 30.0, 21.4, 18.1; IR (thin film) 2928, 2253, 1920, 1599, 1488, 1458, 1348, 1167, 1091, 911, 813 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_3S$ $[M + H]^+$: 418.1471, found 418.1479.



3ai

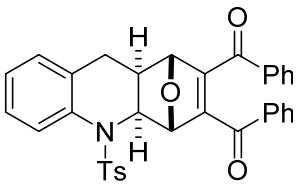
6,11-Dimethyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ai). White solid, 0.046 g, 66% yield; Mp: 228−229 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.31−7.27 (m, 2H), 7.22−7.14 (m,

3H), 7.12 (d, J = 8.0 Hz, 2H), 7.02 (t, J = 7.6 Hz, 2H), 4.60 (d, J = 8.0 Hz, 1H), 2.46−2.42 (m, 2H), 2.35 (s, 3H), 1.80 (s, 3H), 1.53 (s, 3H), 1.41−1.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 147.2, 143.3, 137.4, 137.0, 134.4, 129.5, 128.2, 127.5, 127.3, 127.2, 126.8, 126.7, 126.5, 119.1, 116.9, 88.1, 85.9, 64.0, 48.2, 27.0, 21.4, 14.6, 14.3; IR (thin film) 3026, 2963, 1595, 1489, 1458, 1346, 1261, 1166, 1090, 901, 806 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_3S$ $[M + H]^+$: 432.1628, found 432.1612.



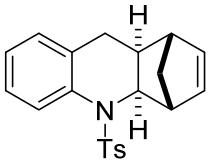
3aj

Dimethyl 10-tosyl-1,4,4a,9,9a,10-hexahydro-1,4-epoxyacridine-2,3-dicarboxylate (3aj). White solid, 0.052 g, 55% yield; Mp: 146−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.24−7.22 (m, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 5.10 (s, 1H), 4.81 (d, J = 8.0 Hz, 1H), 4.76 (s, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 2.57 (t, J = 7.2 Hz, 1H), 2.44−2.39 (m, 4H), 1.67 (dd, J = 12.0 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 162.0, 147.0, 143.8, 143.2, 136.8, 136.3, 133.5, 129.7, 128.0, 127.7, 127.3, 127.0, 126.8, 88.0, 86.6, 58.4, 52.6, 52.4, 40.9, 29.5, 21.5; IR (thin film) 3036, 2955, 1949, 1729, 1714, 1636, 1593, 1488, 1336, 1168, 1002, 926, 820 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{24}NO_7S$ $[M + H]^+$: 470.1268, found 470.1263.



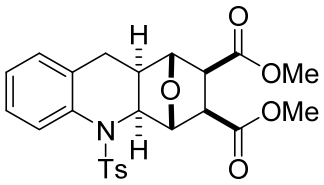
3ak

(10-Tosyl-1,4,4a,9,9a,10-hexahydro-1,4-epoxyacridine-2,3-diyl)bis(phenyl methanone) (3ak). White solid, 0.068 g, 61% yield; Mp: 159−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.6 Hz, 2H), 7.56−7.46 (m, 6H), 7.43 (t, J = 7.2 Hz, 1H), 7.33−7.29 (m, 2H), 7.23−7.19 (m, 5H), 7.17 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 5.31 (s, 1H), 5.02 (d, J = 8.4 Hz, 1H), 4.94 (s, 1H), 2.87 (t, J = 7.2 Hz, 1H), 2.51 (d, J = 15.6 Hz, 1H), 2.39 (s, 3H), 1.78 (dd, J = 15.6 Hz, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 189.9, 153.0, 149.3, 143.8, 136.8, 136.6, 136.4, 136.2, 133.8, 133.7, 133.6, 129.7, 128.6, 128.5, 128.4, 127.8, 127.7, 127.3, 126.9, 126.8, 89.5, 87.9, 58.7, 41.7, 29.6, 21.5; IR (thin film) 2926, 1734, 1658, 1598, 1494, 1334, 1157, 1091, 1040, 934, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{34}H_{28}NO_5S$ $[M + H]^+$: 562.1683, found 562.1668.



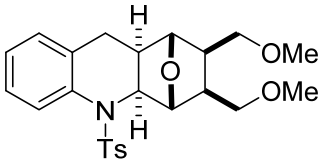
3al

10-Tosyl-1,4,4a,9,9a,10-hexahydro-1,4-methanoacridine (3al). White solid, 0.056 g, 80% yield; Mp: 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.22 (s, 2H), 4.38 (d, J = 8.4 Hz, 1H), 2.85 (s, 1H), 2.42 (s, 1H), 2.38 (s, 3H), 2.20 (m, 2H), 1.65−1.59 (m, 1H), 1.08 (d, J = 9.2 Hz, 1H), 0.88 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 141.6, 137.4, 137.2, 137.1, 134.9, 129.4, 128.8, 128.0, 126.9, 126.8, 126.7, 126.5, 59.0, 50.6, 48.8, 43.7, 40.4, 30.4, 21.4; IR (thin film) 3041, 2984, 1932, 1599, 1489, 1341, 1168, 1046, 961, 812 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{22}NO_2S$ $[M + H]^+$: 352.1366, found 352.1370.



3am

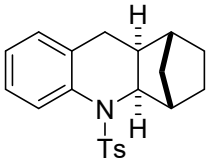
Dimethyl 10-tosyl-1,2,3,4,4a,9,9a,10-octahydro-1,4-epoxyacridine-2,3-dicarboxylate (3am). White solid, 0.056 g, 80% yield; Mp: 196−197 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 4.83 (s, 1H), 4.66 (d, J = 8.4 Hz, 1H), 4.43 (s, 1H), 3.63 (s, 3H), 3.58 (s, 3H), 3.08 (d, J = 9.2 Hz, 1H), 2.94 (d, J = 9.2 Hz, 1H), 2.49 (t, J = 7.2 Hz, 1H), 2.38 (s, 3H), 2.34−2.29 (m, 1H), 1.43 (dd, J = 14.4 Hz, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 143.7, 136.5, 136.0, 133.0, 129.6, 127.9, 127.6, 127.3, 127.0, 126.7, 85.1, 84.0, 61.3, 52.2, 52.1, 51.6, 49.3, 46.8, 29.7, 21.5; IR (thin film) 2960, 2925, 1726, 1598, 1489, 1346, 1263, 1166, 1026, 930, 810 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{26}NO_7S$ $[M + H]^+$: 472.1424, found 472.1405.



3an

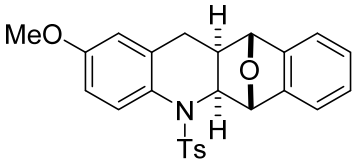
2,3-Bis(methoxymethyl)-10-tosyl-1,2,3,4,4a,9,9a,10-octahydro-1,4-epoxyacridine (3an). White solid, 0.073 g, 83% yield; Mp: 170−171 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 4.63 (d, J = 8.0 Hz, 1H), 4.29 (s, 1H), 4.05 (s, 1H), 3.27 (s, 3H), 3.24 (s, 3H), 3.19 (d, J = 7.2 Hz, 2H), 3.15 (t, J = 8.8 Hz, 1H), 3.05 (d, J = 10.0 Hz, 1H), 2.48 (d, J = 7.2 Hz, 1H), 2.38 (s, 3H), 2.34 (d, J = 10.4 Hz, 1H), 2.22 (dd, J = 14.7 Hz, J = 8.4 Hz, 1H), 2.05-2.00

(m, 1H), 1.45-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 136.9, 136.6, 133.9, 129.5, 127.6, 127.5, 127.1, 126.7, 85.9, 84.6, 70.3, 70.2, 62.2, 58.7, 58.6, 46.9, 45.5, 42.9, 30.0, 21.5; IR (thin film) 3022, 2920, 1930, 1736, 1598, 1487, 1347, 1166, 1033, 920, 820 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{30}NO_5S$ [M + H]$^+$: 444.1839, found 444.1826.



3ao

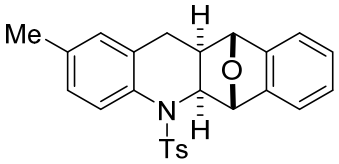
10-Tosyl-1,2,3,4,4a,9,9a,10-octahydro-1,4-methanoacridine (3ao). White solid, 0.055 g, 78% yield; Mp:125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.24−7.22 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 4.30 (d, *J* = 8.8 Hz, 1H), 2.38 (s, 4H), 0.68−0.59 (m, 2H), 1.85 (s 1H), 1.52−1.40 (m, 2H), 1.12−1.09 (m, 1H), 1.12−1.09 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 137.4, 137.1, 134.6, 129.4, 128.2, 127.7, 126.9, 126.7, 126.4, 62.4, 46.6, 45.2, 43.6, 35.0, 30.8, 29.8, 27.3, 21.4; IR (thin film) 3032, 2964, 2875, 1597, 1486, 1348, 1165, 804 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{24}NO_2S$ [M + H]$^+$: 354.1522, found 354.1549.



3ba

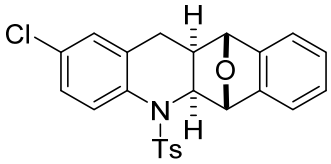
2-Methoxy-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ba). White solid, 0.066 g, 76% yield; Mp: 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.17−7.10 (m, 5H), 6.79 (d, *J* = 10.8 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 5.25 (s, 1H), 4.90 (s, 1H), 4.62 (d, *J* = 8.4 Hz,

1H), 3.77 (s, 3H), 2.40−2.37 (m, 2H), 2.35 (s, 3H), 1.43−1.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 146.6, 143.5, 143.4, 136.6, 135.4, 129.5, 129.2, 129.0, 127.1, 126.8, 126.7, 120.3, 118.7, 113.5, 111.4, 86.4, 85.2, 60.2, 55.1, 43.3, 30.3, 21.4; IR (thin film) 2961, 1929, 1597, 1497, 1450, 1344, 1162, 1035, 1003, 961, 813 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_4S$ $[M + H]^+$: 434.1421, found 434.1396.



3ca

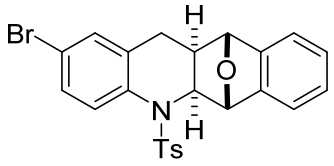
1-Chloro-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ca). White solid, 0.082 g, 99% yield; Mp: 175−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 3H), 7.16−7.05 (m, 5H), 7.07 (d, J = 7.6 Hz, 1H), 6.78 (s, 1H), 5.25 (s, 1H), 4.90 (s, 1H), 4.62 (d, J = 7.6 Hz, 1H), 2.42−2.39 (m, 2H), 2.35 (s, 3H), 2.30 (s, 3H), 1.50-1.42 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.7, 143.5, 143.4, 136.8, 136.5, 133.8, 133.7, 129.5, 128.4, 127.8, 127.7, 127.2, 126.7, 120.3, 118.7, 86.4, 85.2, 60.3, 43.8, 30.0, 21.4, 21.1; IR (thin film) 3049, 2938, 1929, 1598, 1496, 1342, 1162, 961, 758 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_3S$ $[M + H]^+$: 418.1471, found 418.1478.



3da

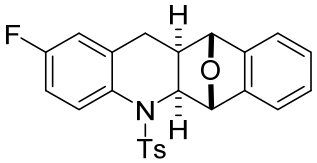
9-Methyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3da). White solid, 0.058 g, 66% yield; Mp: 271−272 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.4 Hz, 3H), 7.24−7.14 (m, 6H), 6.98 (s, 1H), 5.26 (s, 1H), 4.91 (s, 1H), 4.64 (d, J = 8.0 Hz, 1H), 2.45−2.41 (m, 2H), 2.37 (s, 3H),

1.50−1.44 (dd, J = 15.6 Hz, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 143.8, 143.2, 136.6, 135.8, 135.2, 132.1, 129.7, 129.3, 127.6, 127.4, 127.2, 126.9, 126.7, 120.4, 118.8, 86.5, 85.1, 60.3, 43.9, 29.9, 21.5; IR (thin film) 3001, 2940, 1596, 1482, 1431, 1305, 1153, 1089, 961, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{20}ClNO_3SNa$ $[M + Na]^+$: 460.0745, found 460.0760.



3ea

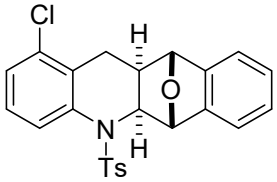
2-Bromo-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ea). White solid, 0.049 g, 51% yield; Mp:176−177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.4 Hz, 1H), 7.39−7.37 (m, 4H), 7.20−7.13 (m, 6H), 5.26 (s, 1H), 4.91 (s, 1H), 4.64 (d, J = 8.0 Hz, 1H), 2.45−2.41 (m, 2H), 2.37 (s, 3H), 1.51−1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 143.8, 143.2, 136.6, 136.2, 135.8, 130.5, 130.2, 129.7, 129.6, 127.4, 127.0, 126.7, 120.5, 120.2, 118.8, 86.5, 85.1, 60.3, 44.0, 29.9, 21.5; IR (thin film) 2962, 1595, 1480, 1349, 1261, 1165, 1003, 961, 811 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{21}BrNO_3S$ $[M + H]^+$: 482.0420, found 482.0438.



3fa

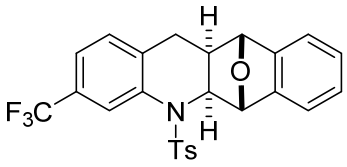
2-Fluoro-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3fa). White solid, 0.056 g, 67% yield; Mp: 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (t, J = 8.8 Hz, 1H), 7.37 (d, J = 8.4 Hz, 3H), 7.20−7.14 (m, 5H), 6.97 (t, J = 8.4 Hz, 1H), 6.71 (d, J = 6.4 Hz, 1H), 5.26 (s, 1H), 4.91 (s, 1H), 4.65 (d, J = 8.0 Hz, 1H), 2.45−2.40 (m, 2H), 2.37 (s, 3H), 1.48−1.42 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ

161.9 (d, J = 244.5 Hz), 146.5, 143.8, 143.3, 136.5, 136.4 (d, J = 9.0 Hz), 132.2, 129.9, 129.8, 129.6, 126.9, 126.7, 120.4, 118.8, 114.7 (d, J = 22.5 Hz), 86.5, 85.2, 60.3, 43.6, 30.2, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −114.7; IR (thin film) 3006, 2963, 1597, 1492, 1342, 1261, 1090, 1020, 961, 802 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{21}FNO_3S$ $[M + H]^+$: 422.1221, found 422.1250.



3ga

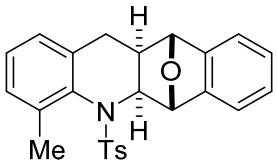
1-Chloro-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ga). White solid, 0.052 g, 59% yield; Mp: 210−211 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 1H), 7.40−7.35 (m, 3H), 7.25 (d, J = 9.6 Hz, 2H), 7.19−7.16 (m, 5H), 5.24 (s, 1H), 4.92 (s, 1H), 4.65 (d, J = 8.4 Hz, 1H), 3.13 (d, J = 16.0 Hz, 1H), 2.50 (t, J = 7.6 Hz, 1H), 2.38 (s, 3H), 1.34-1.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 143.9, 143.1, 138.2, 136.7, 132.3, 132.2, 129.7, 127.4, 127.3, 126.9, 126.7, 120.4, 118.8, 86.4, 85.1, 60.2, 44.1, 29.6, 26.4, 21.5; IR (thin film) 3033, 2962, 1932, 1595, 1454, 1163, 972, 831 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{21}ClNO_3S$ $[M + H]^+$: 438.0925, found 438.0950.



3ha

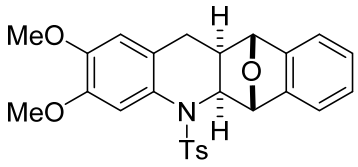
5-Tosyl-3-(trifluoromethyl)-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b] acridine (3ha). White solid, 0.077 g, 72% yield; Mp: 208−209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.40−7.36 (m, 4H), 7.21−7.15 (m, 5H), 7.11 (d, J = 8.0

Hz, 1H), 5.26 (s, 1H), 4.92 (s, 1H), 4.46 (d, J = 7.6 Hz, 1H), 2.58 (d, J = 10.4 Hz, 1H), 2.52 (t, J = 7.6 Hz, 1H), 2.37 (s, 3H), 1.63 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 144.0, 143.1, 138.3, 137.3, 136.6, 129.7, 128.0, 127.4, 127.0, 126.7, 124.9, 123.5, 120.5, 118.8, 86.5, 85.1, 60.3, 44.3, 30.2, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.1; IR (thin film) 2941, 1929, 1593, 1496, 1428, 1329, 1275, 1168, 1069, 961, 818 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{21}F_3NO_3S$ $[M + H]^+$: 472.1189, found 472.1189.



3ia

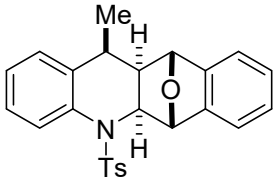
4-Methyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ia). White solid, 0.047 g, 56% yield; Mp: 247−248 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 6.4 Hz, 1H), 7.19−7.08 (m, 7H), 6.82 (t, J = 7.2 Hz, 1H), 5.18 (s, 1H), 4.83 (s, 1H), 4.60 (d, J = 7.6 Hz, 1H), 2.60 (s, 3H), 2.39 (s, 3H), 2.36−2.27 (m, 2H), 1.43−1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 143.7, 143.6, 138.5, 137.0, 135.5, 135.4, 129.7, 129.6, 127.3, 127.2, 127.1, 126.8, 125.5, 120.2, 118.7, 85.7, 85.3, 61.3, 42.9, 30.5, 21.5, 19.1; IR (thin film) 2923, 1593, 1460, 1304, 1161, 1090, 964, 810, 760 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_3S$ $[M + H]^+$: 418.1471, found 418.1470.



3ja

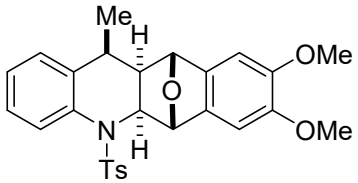
2,3-Dimethoxy-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ja). White solid, 0.050 g, 54% yield; Mp:148−150 ℃; ^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.38−7.33 (m, 3H), 7.19−7.11 (m, 6H), 6.47 (s, 1H), 5.29 (s, 1H), 4.92 (s, 1H), 4.62 (d, J = 8.0 Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 2.36−2.34 (m, 5H), 1.39−1.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 147.4, 146.7, 143.6, 143.5, 136.4, 129.4, 128.7, 127.2, 126.8, 126.1, 120.3, 120.3, 118.7, 112.2, 110.2, 86.6, 85.5, 60.1, 56.0, 55.8, 43.6, 29.6, 21.4; IR (thin film) 2929, 1611, 1597, 1511, 1340, 1162, 1090, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{26}NO_5S$ $[M + H]^+$: 464.1526, found 464.1515.



3ka (*dr* = 14 :1)

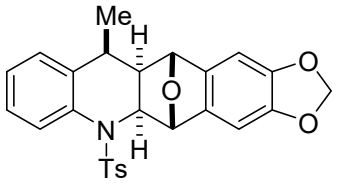
12-Methyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b]acridine (3ka): White solid, 0.043 g, 52% yield; Mp: 227−228 °C; *Major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.35−7.33 (m, 1H), 7.29−7.25 (m, 1H), 7.23 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 7.6 Hz, 4H), 7.10−7.08 (m, 1H), 5.22 (s, 1H), 5.02 (s, 1H), 4.69 (d, J = 8.0 Hz, 1H), 2.40−2.38 (m, 2H), 2.36 (s, 3H), 1.89−1.86 (m, 1H), 1.32 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 143.5, 143.4, 137.5, 137.0, 136.9, 129.5, 127.3, 127.0, 126.9, 126.7, 126.5, 124.1, 120.4, 118.4, 86.3, 78.6, 60.8, 51.7, 30.3, 21.4, 15.0; IR (thin film) 2921, 1486, 1455, 1342, 1161, 1042, 942, 819 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{24}NO_3S$ $[M + H]^+$: 418.1471, found 418.1473.



3kb (*dr* >20 :1)

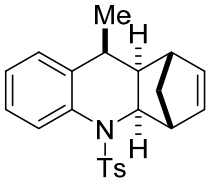
8,9-Dimethoxy-12-methyl-5-tosyl-5,5a,6,11,11a,12-hexahydro-6,11-epoxybenzo[b] acridine (3kb): White solid, 0.047 g, 49% yield; Mp: 156−157 °C; ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.62 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.2 Hz, 1H), 6.96 (s, 1H), 6.71 (s, 1H), 5.19 (s, 1H), 4.96 (s, 1H), 4.64 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.36 (s, 3H), 2.34−2.30 (m, 1H), 1.84 (t, J = 6.8 Hz, 1H), 1.31 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 147.8, 143.4, 139.3, 137.3, 137.0, 136.8, 135.6, 129.5, 127.1, 126.9, 126.6, 126.5, 124.1, 104.9, 103.1, 86.6, 78.8, 61.1, 56.3, 56.2, 52.1, 30.3, 21.4, 15.1; IR (thin film) 2962, 1818, 1593, 1492, 1458, 1347, 1168, 1018, 972, 817 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{28}NO_5S$ $[M + H]^+$: 478.1683, found 478.1675.



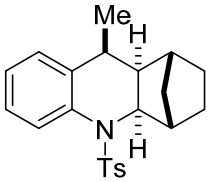
3kf (*dr* > 20 :1)

11-Methyl-6-tosyl-5,5a,6,11,11a,12-hexahydro-5,12-epoxy[1,3]dioxolo[4',5':4,5] benzo[1,2-b]acridine (3kf). White solid, 0.066 g, 72% yield; Mp: 188−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.21−7.14 (m, 4H), 7.08 (d, J = 7.2Hz, 1H), 6.84 (s, 1H), 6.61 (s, 1H), 5.93 (d, J = 2.4 Hz, 2H), 5.11 (s, 1H), 4.92 (s, 1H), 4.63 (d, J = 7.6 Hz, 1H), 2.40−2.31 (m, 4H), 1.88 (t, J = 6.4 Hz, 1H), 1.29 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 146.3, 143.4, 140.8, 137.3, 137.1, 137.0, 136.8, 129.5, 126.9, 126.8, 126.6, 126.5, 124.1, 102.6, 101.2, 100.8, 86.2, 78.6, 60.9, 51.8, 30.3, 21.4, 15.0; IR (thin film) 2964, 2253, 1929, 1598, 1488, 1345, 1166, 1035, 913, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{24}NO_5S$ $[M + H]^+$: 462.1370, found 462.1370.



3kl (*dr* = 2 :1)

9-Methyl-10-tosyl-1,4,4a,9,9a,10-hexahydro-1,4-methanoacridine (3kl). White solid, 0.048 g, 65% yield; Mp: 78−80 °C; *major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 4H), 7.04 (d, *J* = 2.8 Hz, 1H), 6.23−6.10 (m, 2H), 4.43 (d, *J* = 8.4 Hz, 1H), 2.83 (d, *J* = 12.0 Hz, 1H), 2.60 (s, 1H), 2.38 (s, 3H), 2.21 (t, *J* = 7.2 Hz, 1H), 1.95 (t, *J* = 6.8 Hz, 1H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.12−1.04 (m, 2H), 1.00 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 141.9, 138.3, 137.7, 137.5, 136.7, 129.5, 127.8, 127.2, 126.7, 126.3, 124.6, 59.7, 50.5, 48.5, 43.3, 41.3, 30.7, 21.5,15.0; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 4H), 6.98 (d, *J* = 6.8 Hz, 1H), 6.27−6.21 (m, 2H), 4.34 (d, *J* = 8.8 Hz, 1H), 2.74 (d, *J* = 7.2 Hz, 1H), 2.51 (s, 1H), 2.38 (s, 3H), 2.37 (s, 1H), 2.09 (d, *J* = 8.8 Hz, 1H), 1.15−1.12 (m, 1H), 0.75 (d, *J* = 3.2 Hz, 3H), 0.65 (d, *J* = 10.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.8, 138.0, 137.8, 137.6, 136.5, 129.5, 128.4, 126.9, 126.7, 125.2, 125.1, 58.5, 51.1, 48.9, 47.6, 43.5, 37.7, 23.9, 15.0; IR (thin film) 2964, 1488, 1349, 1166, 1091, 945, 821 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{24}NO_2S$ $[M + H]^+$: 366.1522, found 366.1526.

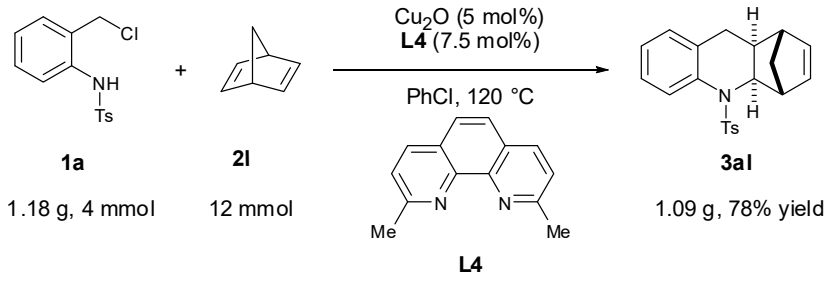


3ko (*dr* = 1.3 :1)

9-Methyl-10-tosyl-1,2,3,4,4a,9,9a,10-octahydro-1,4-methanoacridine (3ko). White solid, 0.043 g, 59% yield; Mp: 89−91 °C; *major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 10.4 Hz, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 4.33 (d, *J* = 4.8 Hz, 1H), 2.37 (s, 3H), 2.35 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H), 1.82 (q, *J* = 6.8 Hz, 1H), 2.01 (s, 1H), 1.45−1.31 (m, 3H), 1.16 (d, *J* = 6.8 Hz,

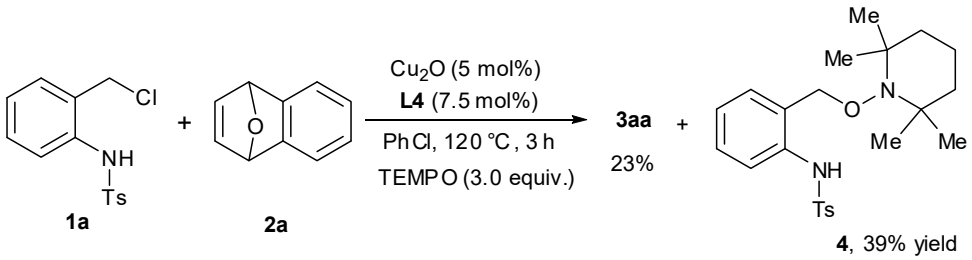
3H), 0.83 (d, J = 10.4 Hz, 1H), 0.60 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 137.6, 137.5, 136.7, 129.4, 127.2, 126.8, 126.7, 126.1, 124.2, 63.2, 53.9, 45.0, 43.7, 35.8, 34.8, 30.9, 30.5, 27.0, 21.4; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 8.0 Hz, 3H), 6.97 (d, J = 6.8 Hz, 1H), 4.28 (d, J = 8.8 Hz, 1H), 2.75 (q, J = 7.6 Hz, 1H), 2.38 (s, 3H), 2.14−2.07 (m, 2H), 1.91 (s, 1H), 1.45−1.31 (m, 3H), 0.77 (d, J = 8.0 Hz, 3H), 0.72 (d, J = 10.4 Hz, 1H), 0.41 (d, J = 13.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 137.8, 137.7, 137.3, 129.5, 128.1, 127.1, 126.6, 125.0, 124.4, 62.0, 53.5, 45.4, 37.8, 34.5, 30.3, 26.4, 23.2, 21.4, 15.1; IR (thin film) 2962, 1600, 1487, 1455, 1349, 1184, 1040, 916, 813 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{26}NO_2S$ $[M + H]^+$: 368.1679, found 368.1667.

3. Gram scale preparation of compound 3al

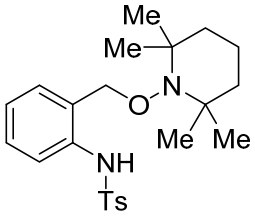


A Schlenk flask was charged with *o*-chloromethyl arylsulfonamides **1a** (4 mmol, 1.18 g), bicyclic alkene **2l** (3.0 equiv.), Cu_2O (5 mol%), neocuproine **L4** (7.5 mol%), and chlorobenzene (20 mL). The mixture was stirred vigorously at 120 °C for 12 hours until bicyclic alkene **2l** were completely consumed (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to provide desired tetrahydroquinoline **3al**.

4. Synthesis of compound 4



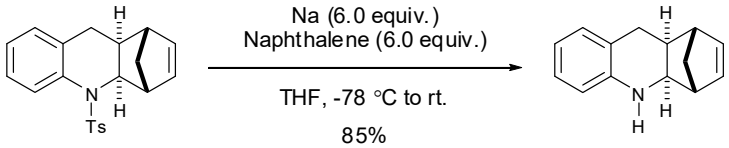
A Schlenk flask was charged with *o*-chloromethyl arylsulfonamides **1a** (0.4 mmol), bicyclic alkene **2a** (0.2 mmol), Cu_2O (5 mol %), neocuproine (7.5 mol%), 2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) (3.0 equiv), and chlorobenzene (2 mL). The mixture was stirred vigorously at 120 °C for 3 hours until bicyclic alkene **2a** were completely consumed (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/50 to 1/20, ethyl acetate/petroleum ether) to provide **3aa** and **4**.



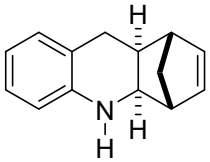
4

4-Methyl-N-(2-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)phenyl)benzene sulfonamide (4). White solid, 0.032 g, 39% yield; Mp: 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.28−7.23 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 4.0 Hz, 2H), 4.52 (s, 2H), 2.35 (s, 3H), 1.53−1.33 (m, 6H), 1.13 (d, J = 4.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.0, 136.7, 129.5, 129.4, 129.0, 128.9, 126.8, 124.5, 121.6, 77.8, 60.1, 39.5, 32.8, 21.4, 20.3, 16.8; IR (thin film) 2970, 2188, 1592, 1494, 1340, 1165, 1020, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{33}N_2O_3S$ $[M + H]^+$: 417.2206, found 417.2221.

5. Synthesis of compound 5



To a solution of naphthalene (150 mg, 1.2 mmol, 6.0 equiv) in anhydrous THF (3 mL) at room temperature under inert atmosphere was added sodium metal (25 mg, 1.2 mmol, 6.0 equiv). The resulting mixture was stirred until complete consumption of sodium, which was then cooled to -78 °C. A solution of compound **3al** (70 mg, 0.2 mmol) in THF (1 mL) was added to the Nanaphthalene solution, and it was stirred overnight at ambient temperature. It was quenched with saturated NH_4Cl (5 mL) and extracted with EtOAc (10 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to provide **5**.

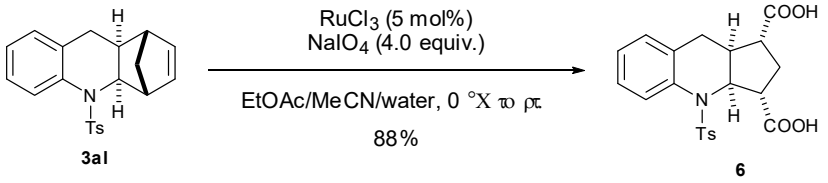


5

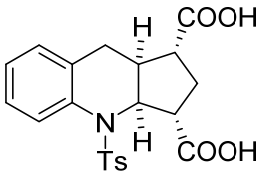
1,4,4a,9,9a,10-Hexahydro-1,4-methanoacridine (5): Light gray solid, 0.033 g, 85% yield; Mp: 68−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02−7.00 (m, 2H), 6.73 (t, J = 7.6 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.24 (dd, J = 5.6 Hz, J = 3.2 Hz, 1H), 6.01 (dd, J = 5.2 Hz, J = 2.8 Hz, 1H), 3.16 (d, J = 7.6 Hz, 1H), 2.84 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 2.70 (d, J = 9.6 Hz, 2H), 2.32 (t, J = 11.6 Hz, 1H), 2.22 (d, J = 8.8 Hz, 1H), 1.99 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 1.51 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 139.1, 134.5, 128.0, 127.4, 126.7, 118.8, 114.4, 58.2, 49.2, 47.5,

42.9, 41.6, 32.3; IR (thin film) 3058, 2963, 1590, 1497, 1472, 1342, 1263, 1164, 900, 795 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N$ $[M + H]^+$: 198.1277, found 198.1271.

6. Synthesis of compounds 6



To a solution of $RuCl_3$ (2 mg, 2.2 mol %) in EtOAc/MeCN/water (3.5 mL, v/v/v = 1:1:1.5), $NaIO_4$ (171 m, 0.8 mmol) was added and the mixture was cooled to 0 °C. **3al** (70 mg, 0.2 mmol) was then added slowly, and the mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched and extracted with EtOAc and water. The aqueous layer was extracted by EtOAc and the organic layers were dried and concentrated under vacuum to obtain the desired product compound **6**.

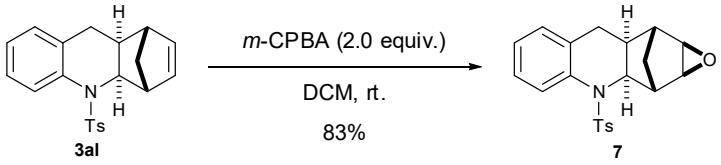


6

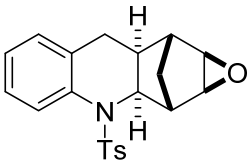
4-Tosyl-2,3,3a,4,9,9a-hexahydro-1H-cyclopenta[b]quinoline-1,3-dicarboxylic acid (6), Light gray solid, 0.063 g, 88% yield; Mp: 165−166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 6.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 3H), 7.07 (d, J = 7.6 Hz, 1H), 5.16 (t, J = 8.0 Hz, 1H), 3.05 (dd, J = 16.0 Hz, J = 10.4 Hz, 1H), 2.62−2.55 (m, 1H), 2.38 (s, 3H), 2.35−2.26 (m, 2H), 2.24−2.19 (m, 1H), 2.00 (q, J = 12. Hz, 1H), 1.57 (dd, J = 15.2 Hz, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.0, 178.4, 143.8, 136.9, 135.3, 133.9, 129.7, 129.3, 129.2, 127.7, 127.4, 126.8, 62.1, 51.0, 47.0, 44.6, 31.8, 28.6, 21.5;

IR (thin film) 3467, 3350, 2925, 1748, 1594, 1492, 1261, 1165, 1092, 971, 802 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_6SNa$ $[M + Na]^+$: 438.0982, found 438.0972.

7. Synthesis of compound 7



To a magnetically stirred solution of compound **3al** (70 mg, 0.2 mmol) in DCM (2 mL) was added m-CPBA (2.0 equiv) portionwise at 0 °C and allowed to stir at rt for 8 h. After completion of the starting material (by TLC monitoring), the reaction mixture was poured into ice water and extracted with DCM (3 × 10 mL) and the combined organics were washed with aqueous saturated $NaHCO_3$ solution (3 × 10 mL), water, and then brine. the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to provide **7**.

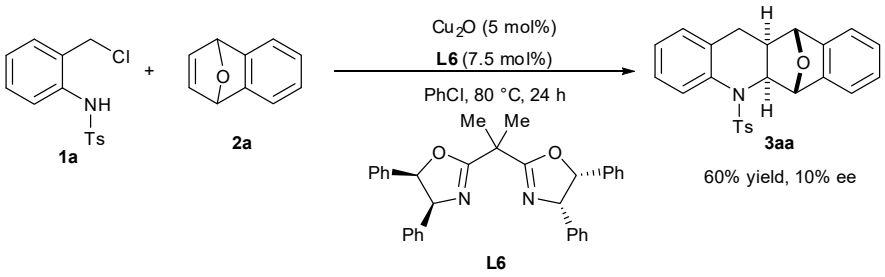


7

3-Tosyl-1a,2,2a,3,8,8a,9,9a-octahydro-2,9-methanooxireno[2,3-b]acridine (7): White solid, 0.074 g, 83% yield; Mp: 196−197 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 6.8 Hz, 1H), 4.78 (dd, J = 10.8 Hz, J = 4.4 Hz, 1H), 2.91 (s, 1H), 2.63 (d, J = 2.0 Hz, 1H), 2.58−2.52 (m, 1H), 2.43−2.39 (m, 5H), 2.31 (d, J = 16.4 Hz, 1H), 1.56−1.50 (m, 1H), 1.36−1.25 (m, 1H), 0.82 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.7, 136.7, 134.6, 129.6, 128.2, 127.6, 127.4, 127.0, 126.7, 58.7, 50.6, 50.0, 45.3, 43.6, 41.2, 27.4, 26.3, 21.5;

IR (thin film) 3042, 2924, 1937, 1597, 1458, 1341, 1167, 1054, 963, 822 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{22}NO_3S$ $[M + H]^+$: 368.1315, found 368.1303.

8. Testing asymmetric synthesis of 3aa



A Schlenk flask was charged with *o*-chloromethyl arylsulfonamides **1a** (0.2 mmol), bicyclic alkene **2a** (0.1 mmol), Cu_2O (5 mol%), ligand **L6** (7.5 mol%), and chlorobenzene (2 mL). The mixture was stirred vigorously at 80 °C for 24 hours until bicyclic alkene **2a** was completely consumed (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to provide chiral tetrahydroquinoline **3aa** (60% yield. 10% ee). 10% ee (OD, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min. t_1 = 9.7 min (minor), t_2 = 16.9 min (major)).

9. References:

[1] L. Lei, Y.-Y. Yao, L.-J. Jiang, X. Lu, C. Liang, and D.-L. Mo, *J. Org. Chem.* **2020***, 85,* 3059−3070.

[2] D.-L. Mo, T.-K. Zhang, G.-C. Ge, X.-J. Huang, C.-H. Ding, L.-X. Dai, and X.-L Hou, *Synlett* **2014***, 25,* 2686–2702.

10. X-ray structures of compounds 3aa and 3ka

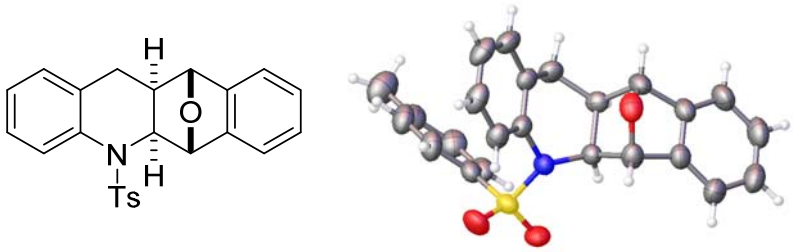
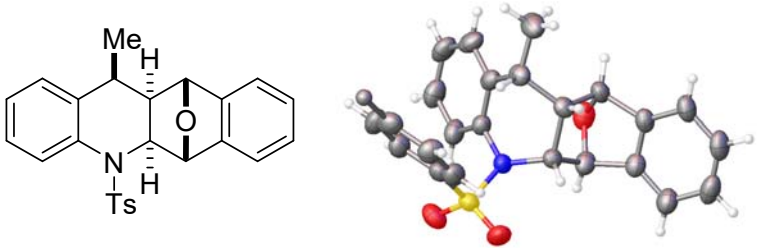


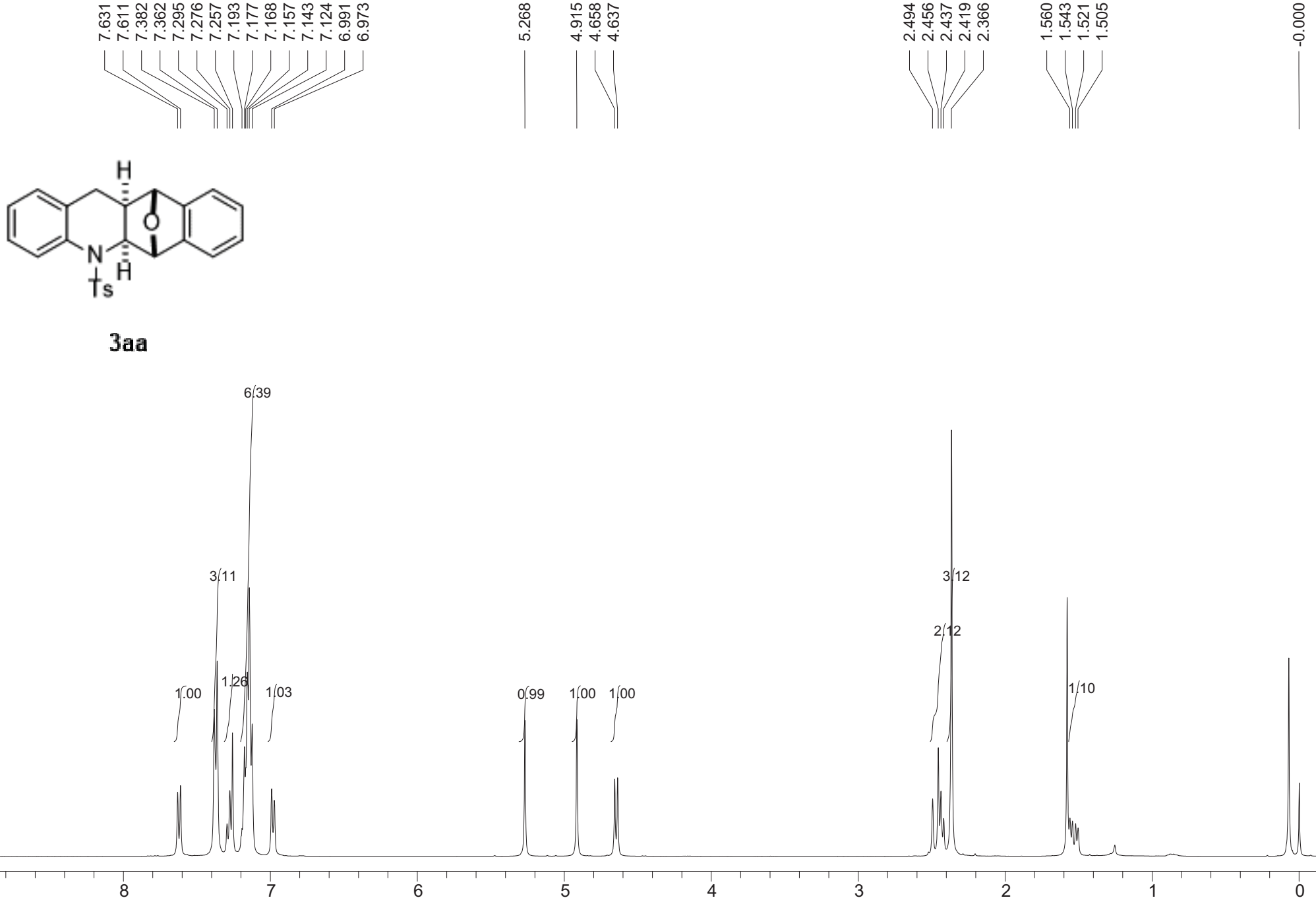
Figure S1: ORTEP diagram of **3aa** at 50% ellipsoid probability



3ka

Figure S2: ORTEP diagram of **3ka** at 50% ellipsoid probability

11. NMR spectra of 3aa-3ko, 4, 5, 6, 7 and HPLC for 3aa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7.193
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7.143
7.124
6.991
6.973
5.268
4.915
4.658
4.637
2.494
2.456
2.437
2.419
2.366
1.560
1.543
1.521
1.505
-0.000
H
O
N
H
Ts
3aa
6.39
3.11
1.26
1.00
1.03
0.99
1.00
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2.12
1.10
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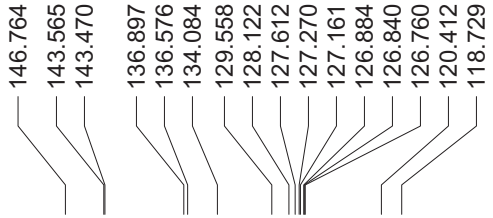
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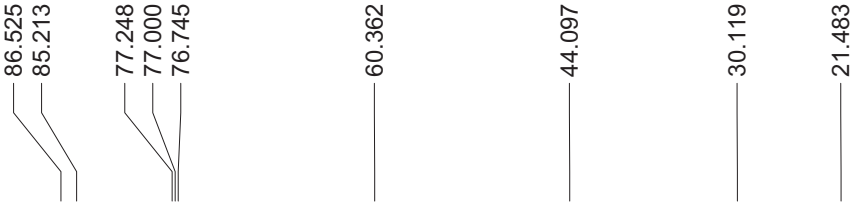
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44.097
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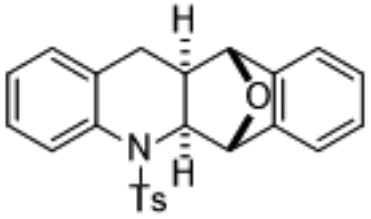
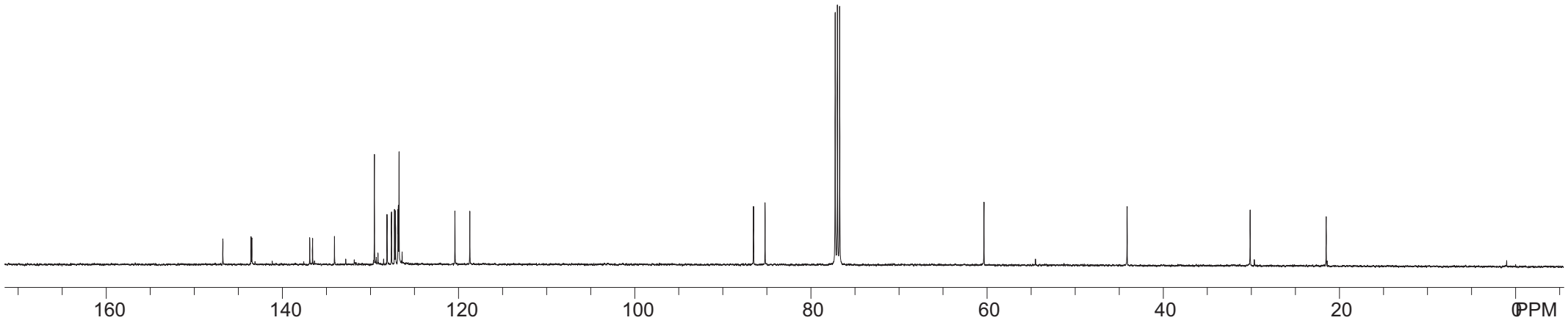
21.483


H
O
N
H
Ts

3aa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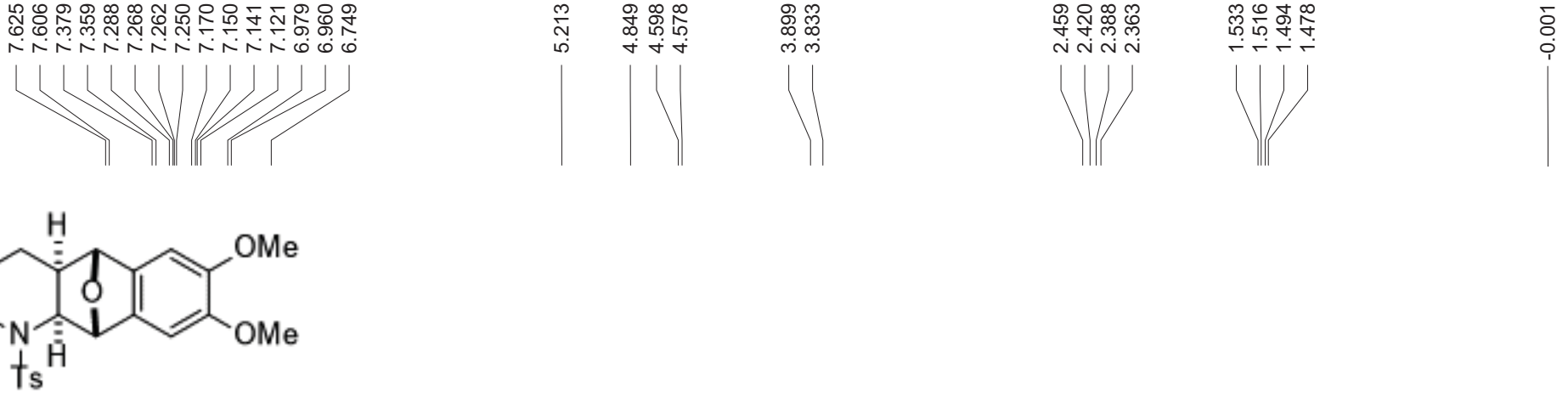
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6.960
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4.578
3.899
3.833
2.459
2.420
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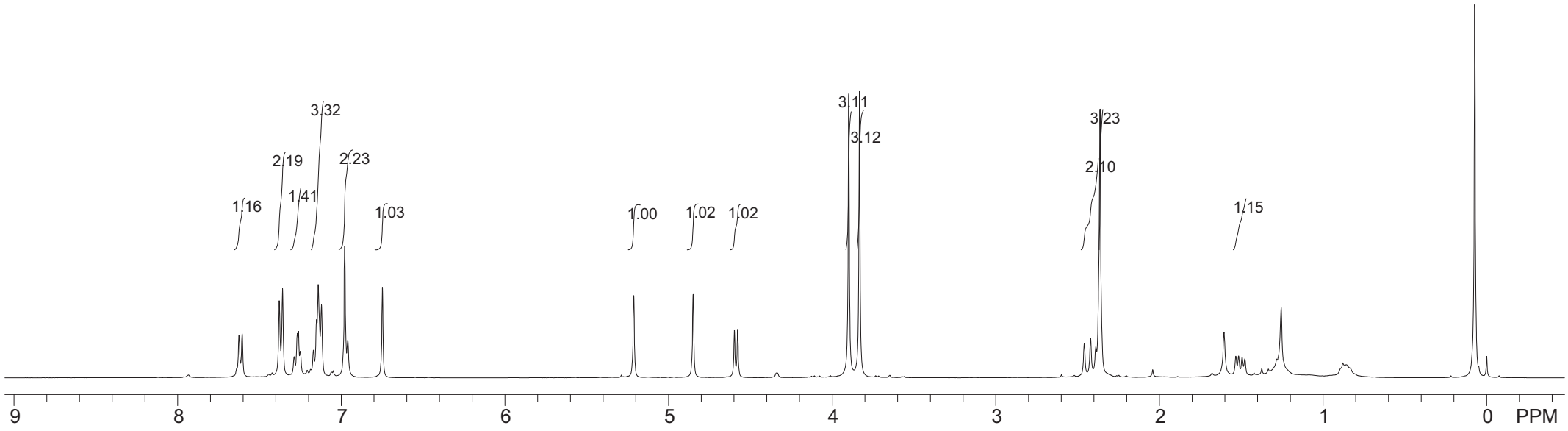
H
OMe
O
OMe
N
H
Ts

3ab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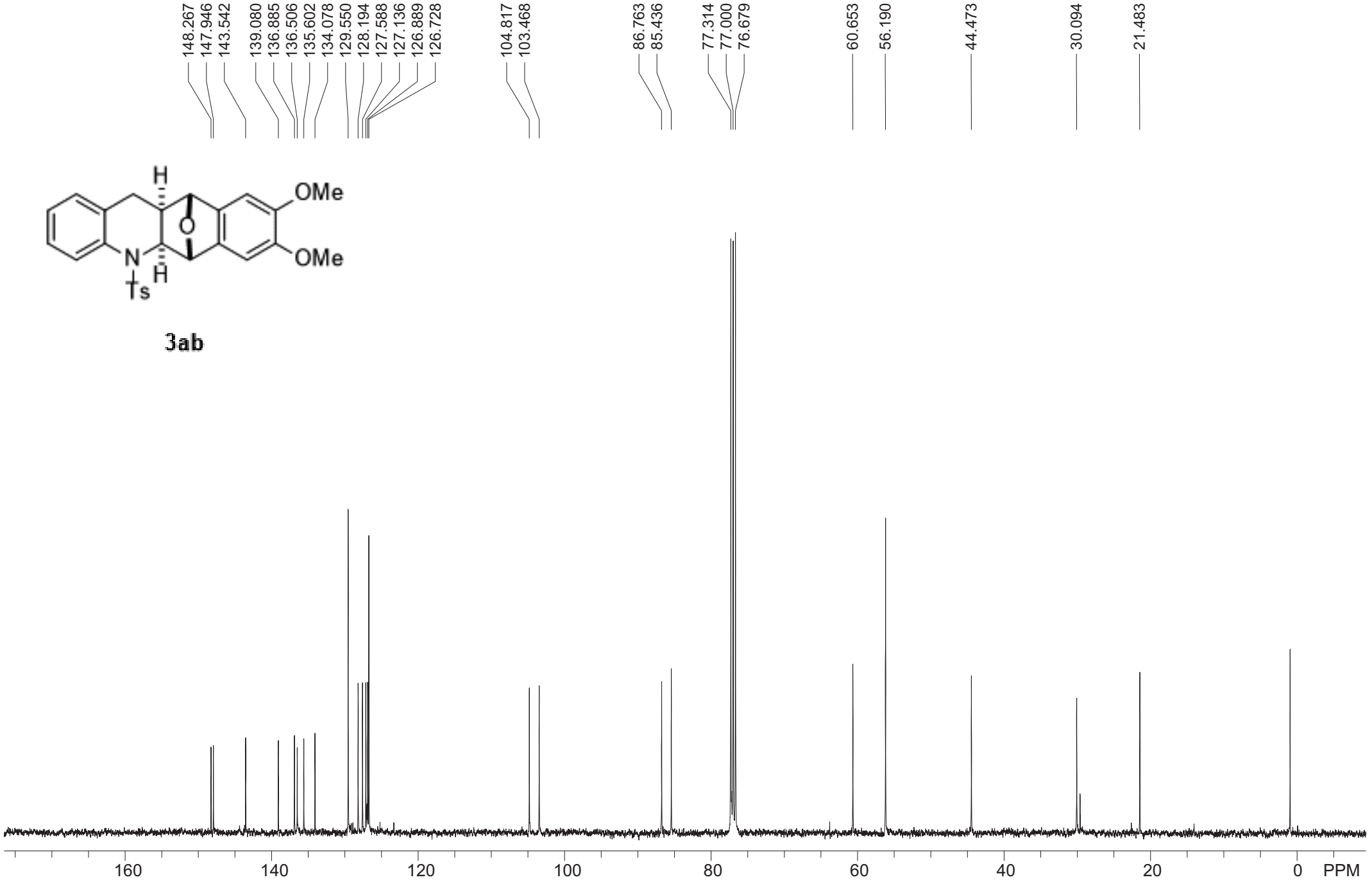
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126.728
104.817
103.468
86.763
85.436
77.314
77.000
76.679
60.653
56.190
44.473
30.094
21.483
H
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O
OMe
N
H
Ts
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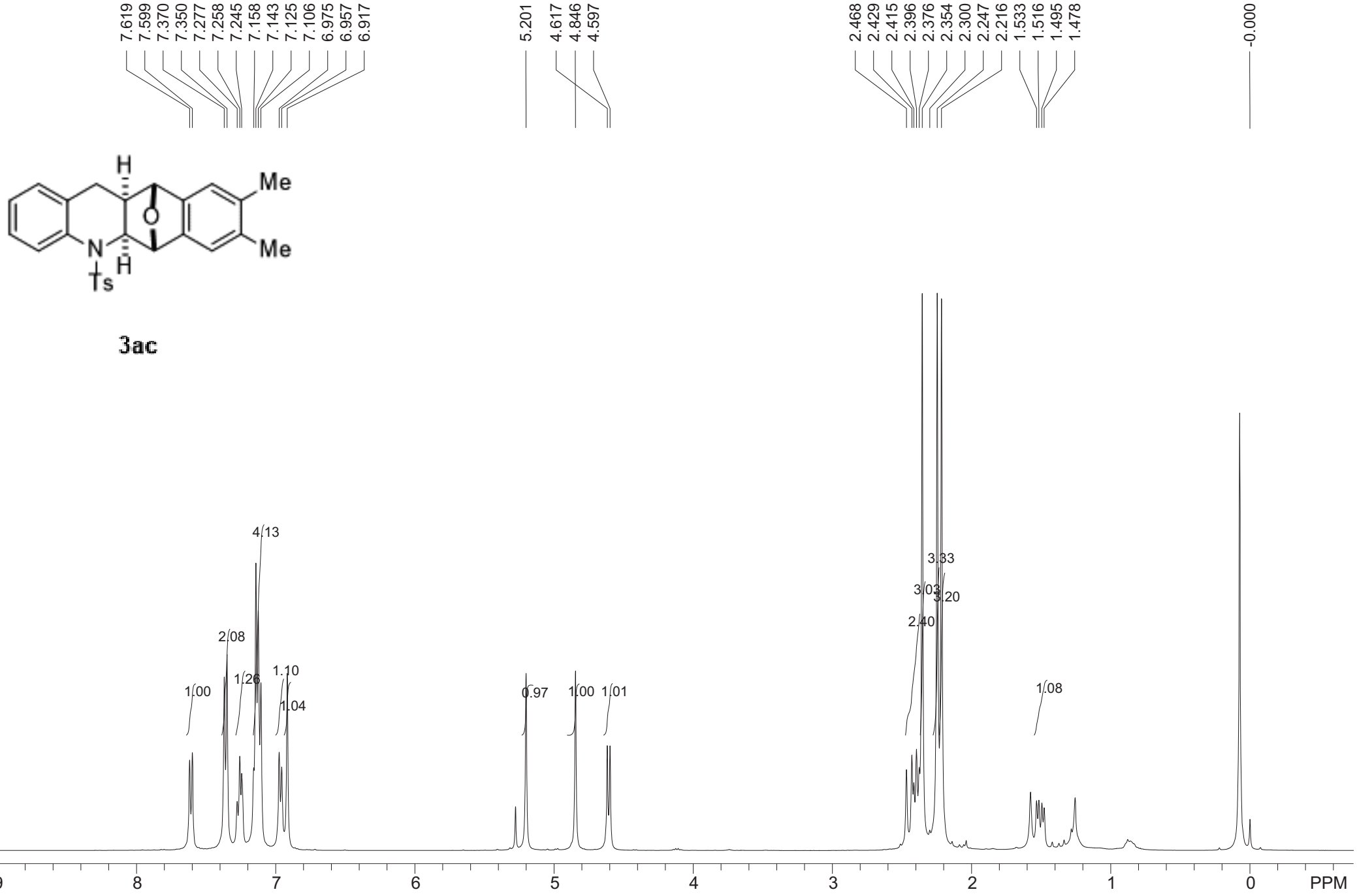
PPM

3ab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6.917
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4.846
4.597
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2.396
2.376
2.354
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1.516
1.495
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Me
O
N
H
Ts
Me
3ac
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1.26
1.10
1.04
1.00
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1.00
1.01
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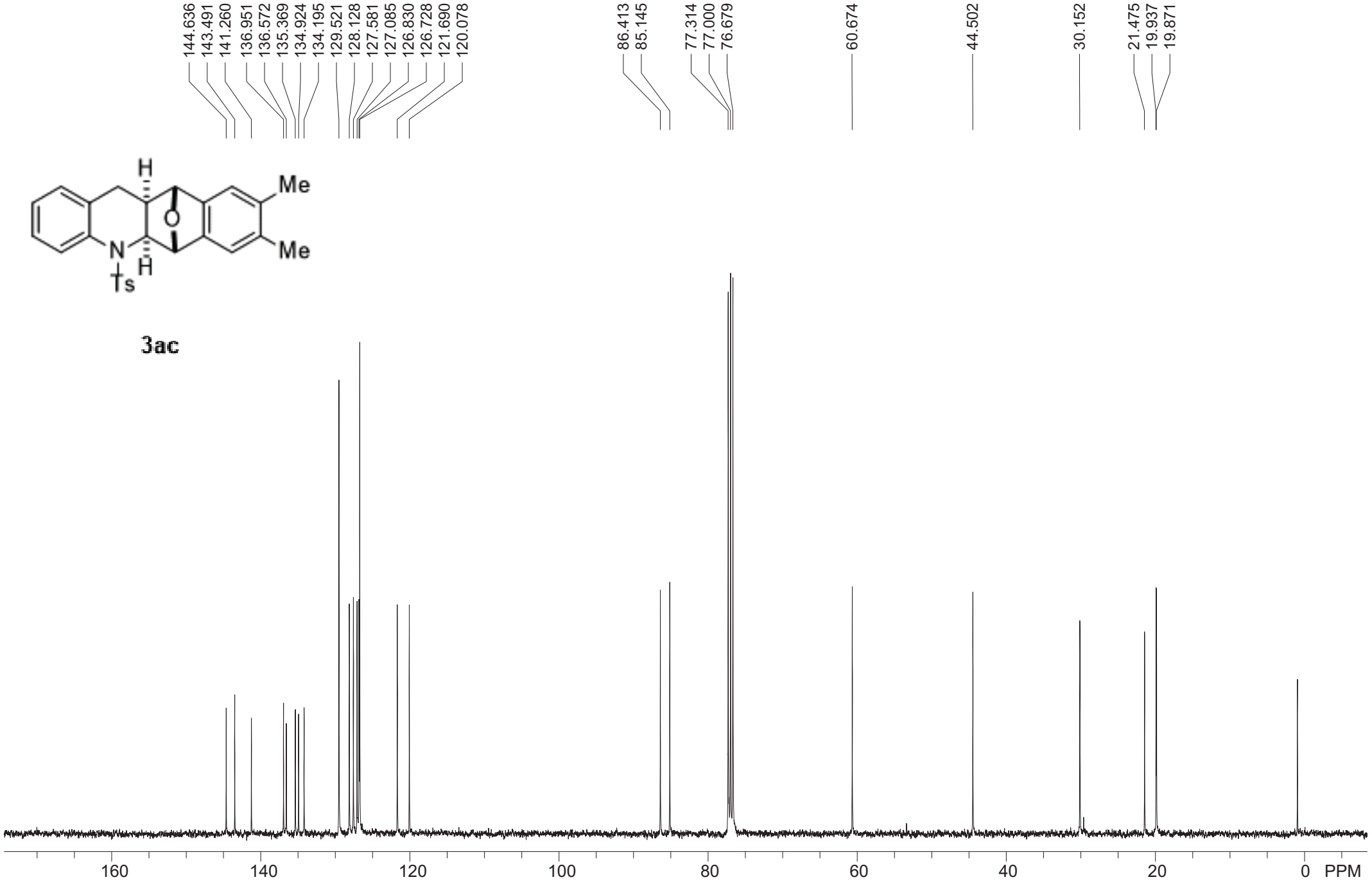
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126.728
121.690
120.078
86.413
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77.000
76.679
60.674
44.502
30.152
21.475
19.937
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N
H
Me
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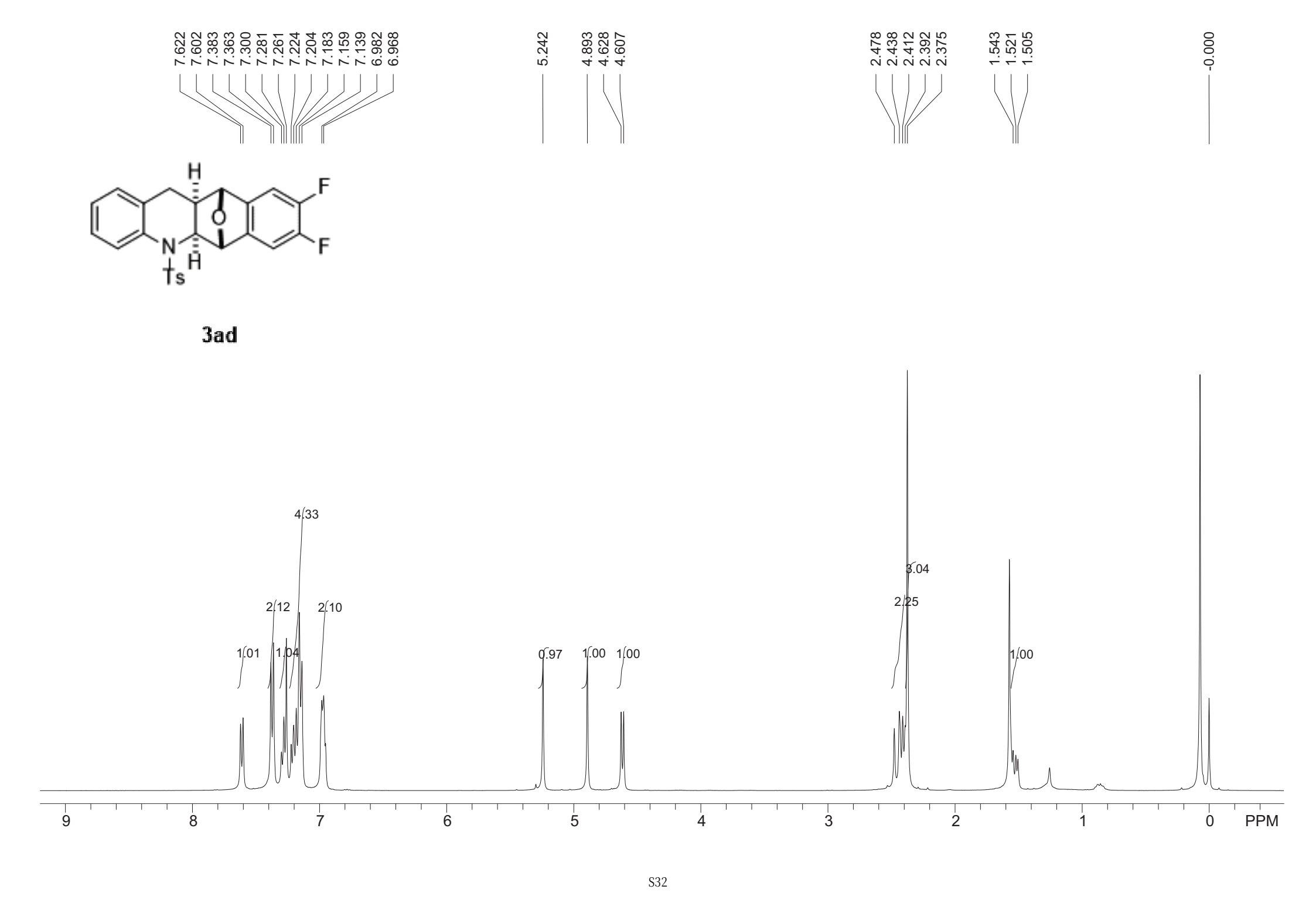
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5.242
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2.375
1.543
1.521
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F
O
F
N
H
Ts
3ad
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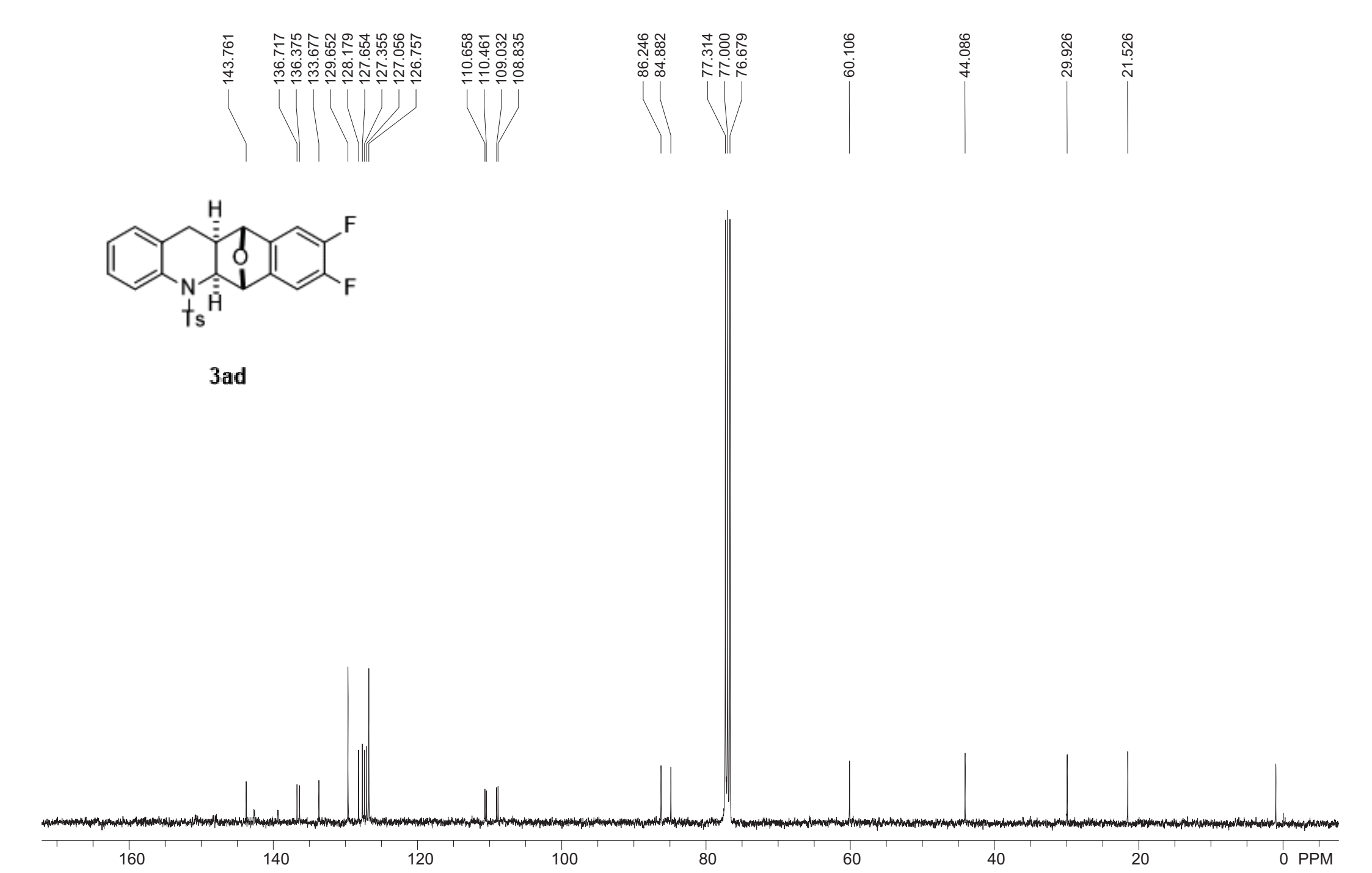
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77.000
76.679
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44.086
29.926
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F
F
N
H
Ts
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100
80
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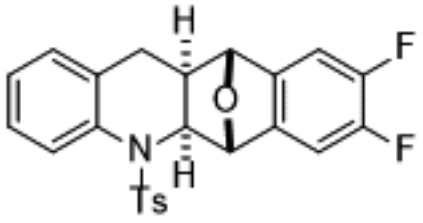
20
0 PPM

3ad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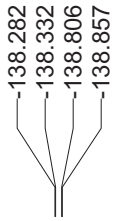
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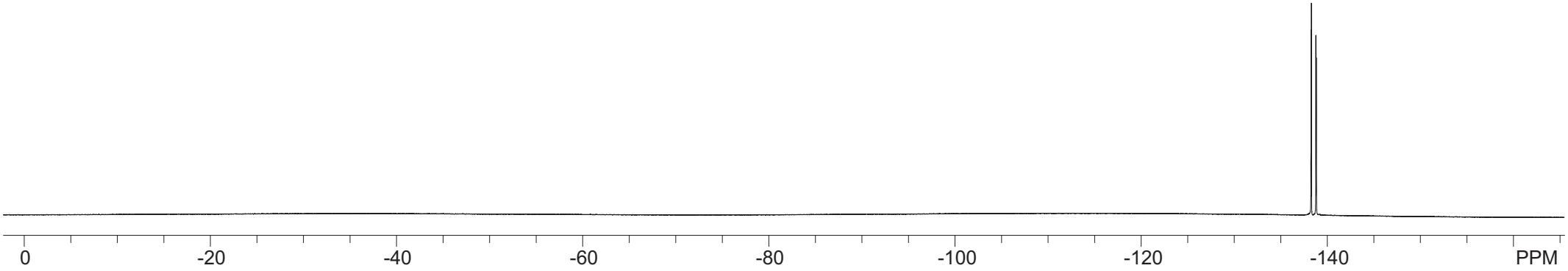
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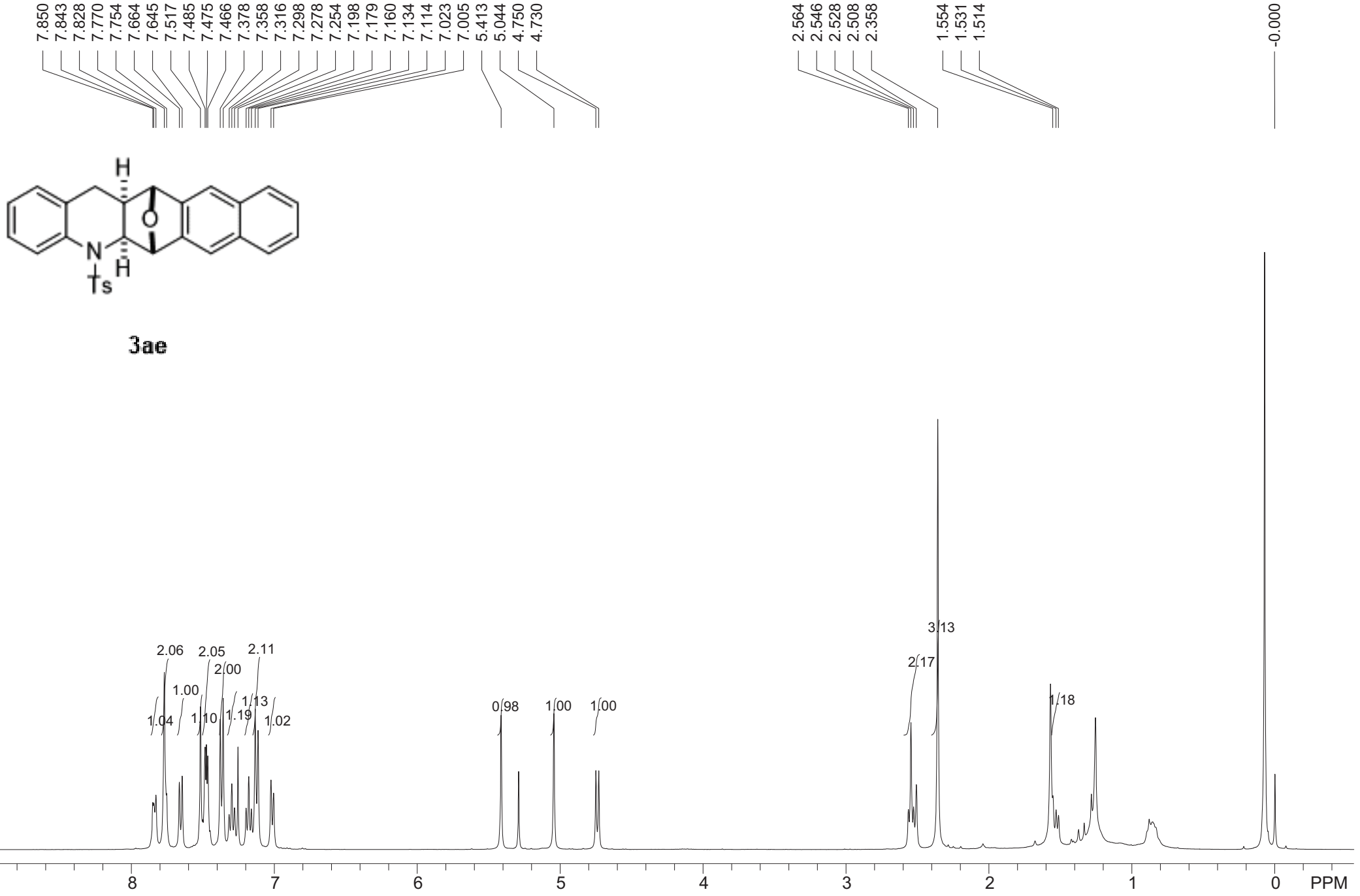
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H
Ts
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2.05
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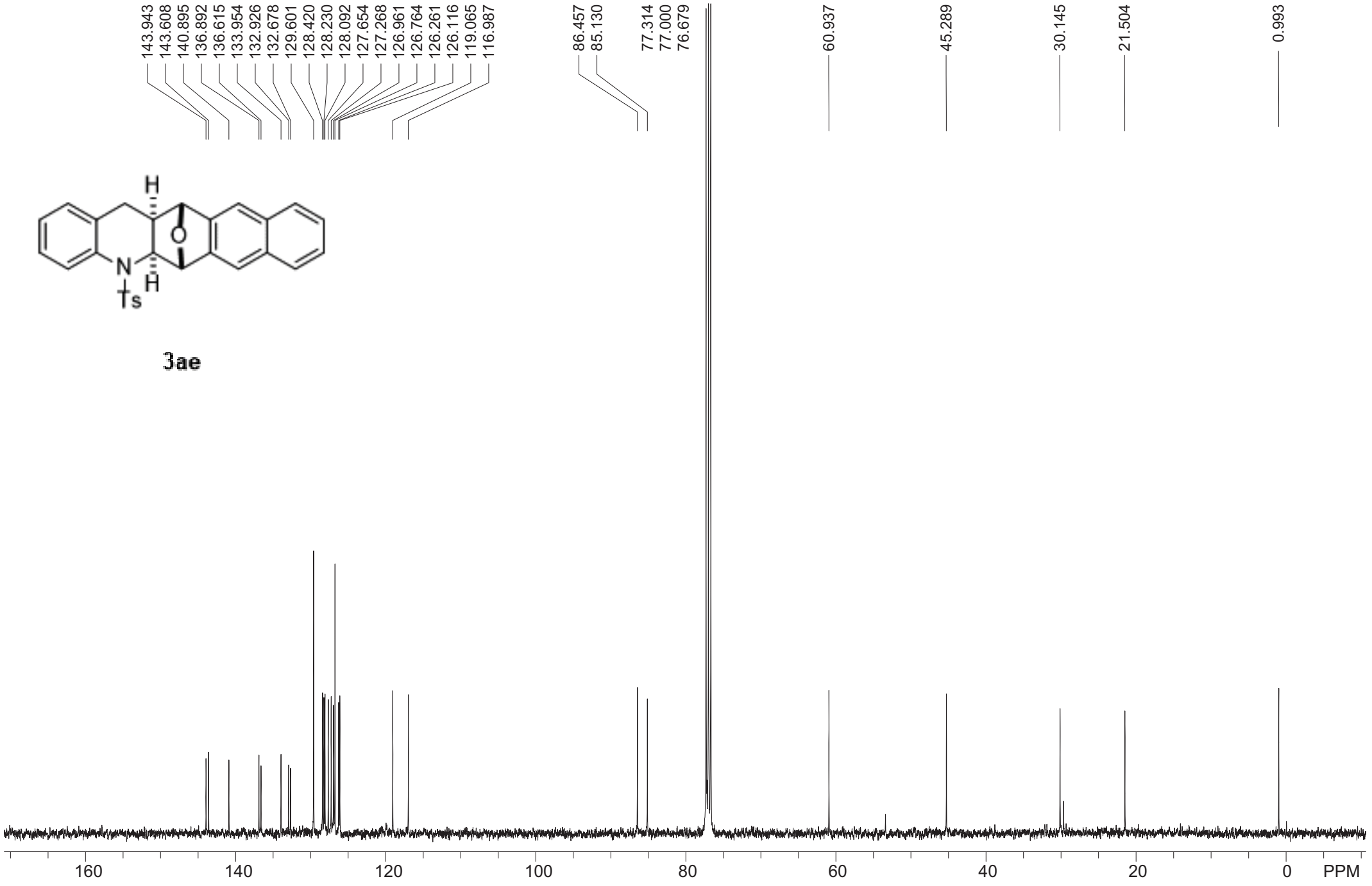
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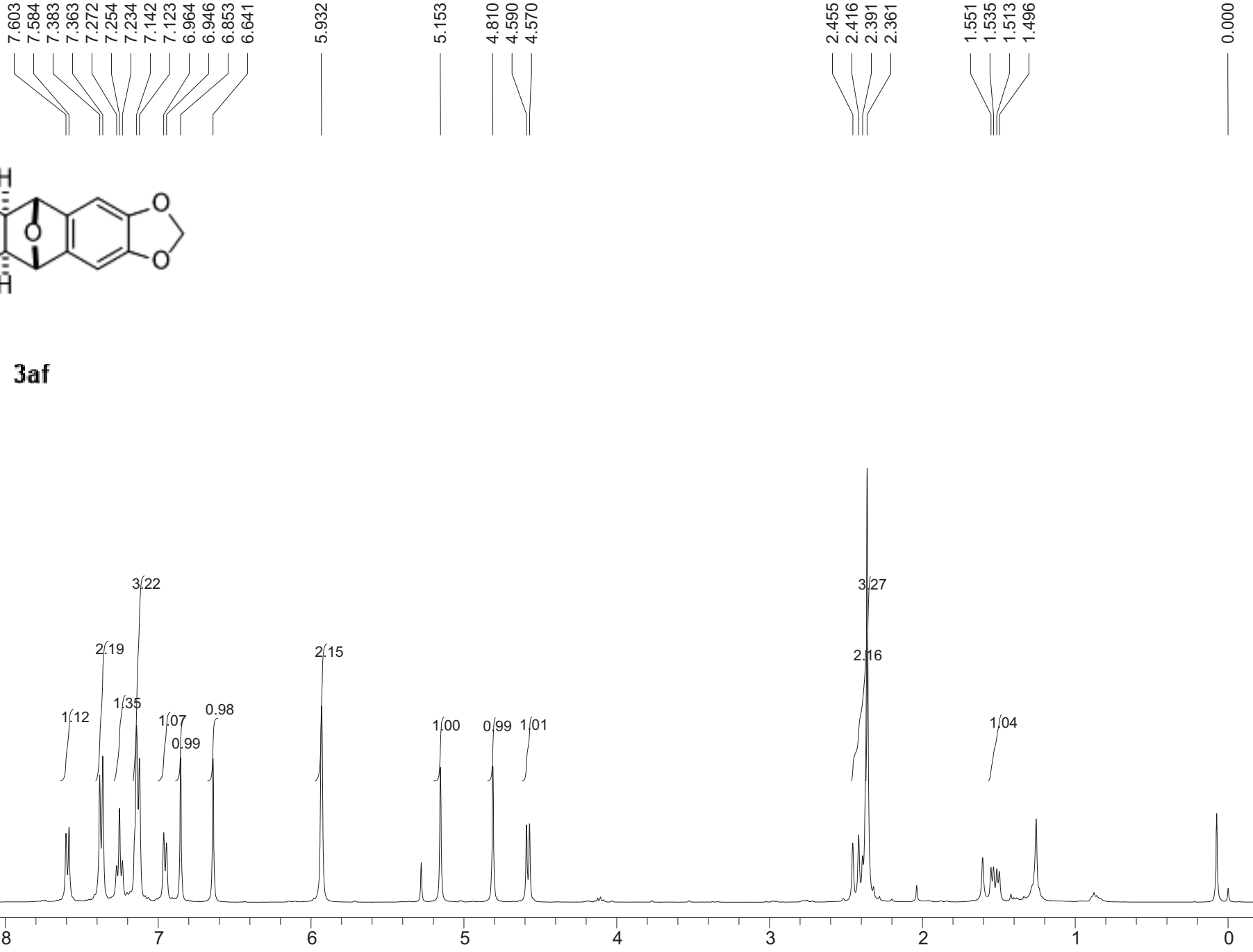
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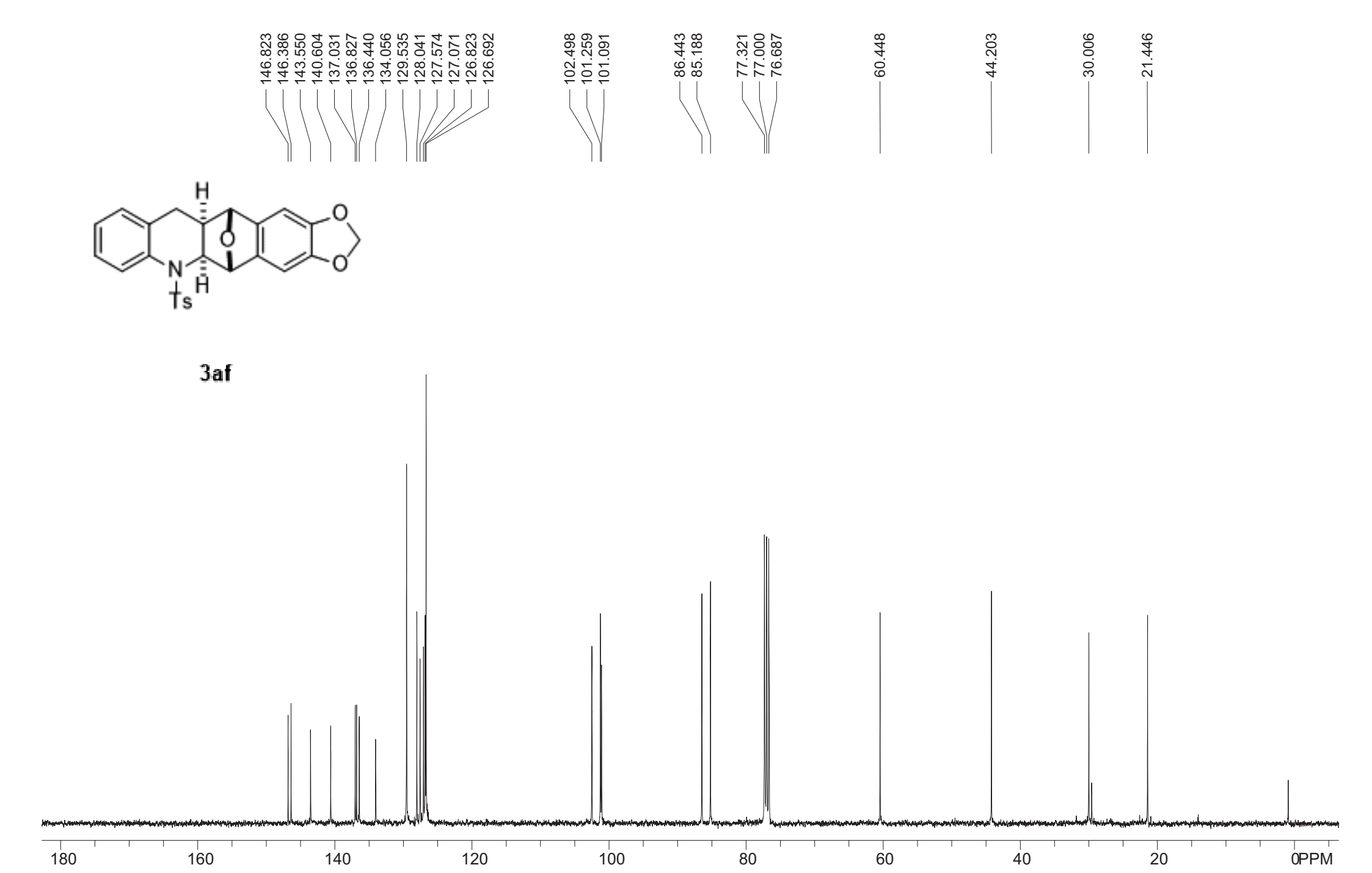
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102.498
101.259
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85.188
77.321
77.000
76.687
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44.203
30.006
21.446
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N
H
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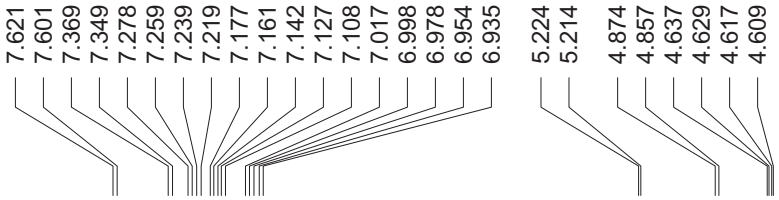

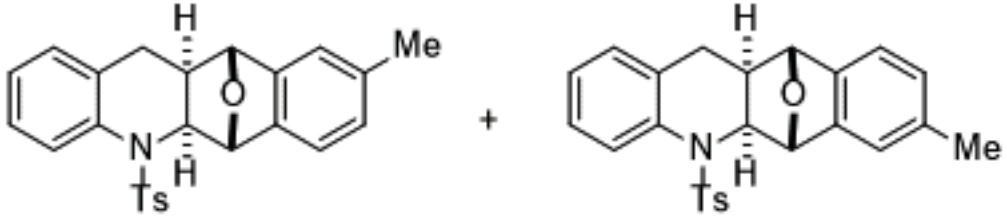

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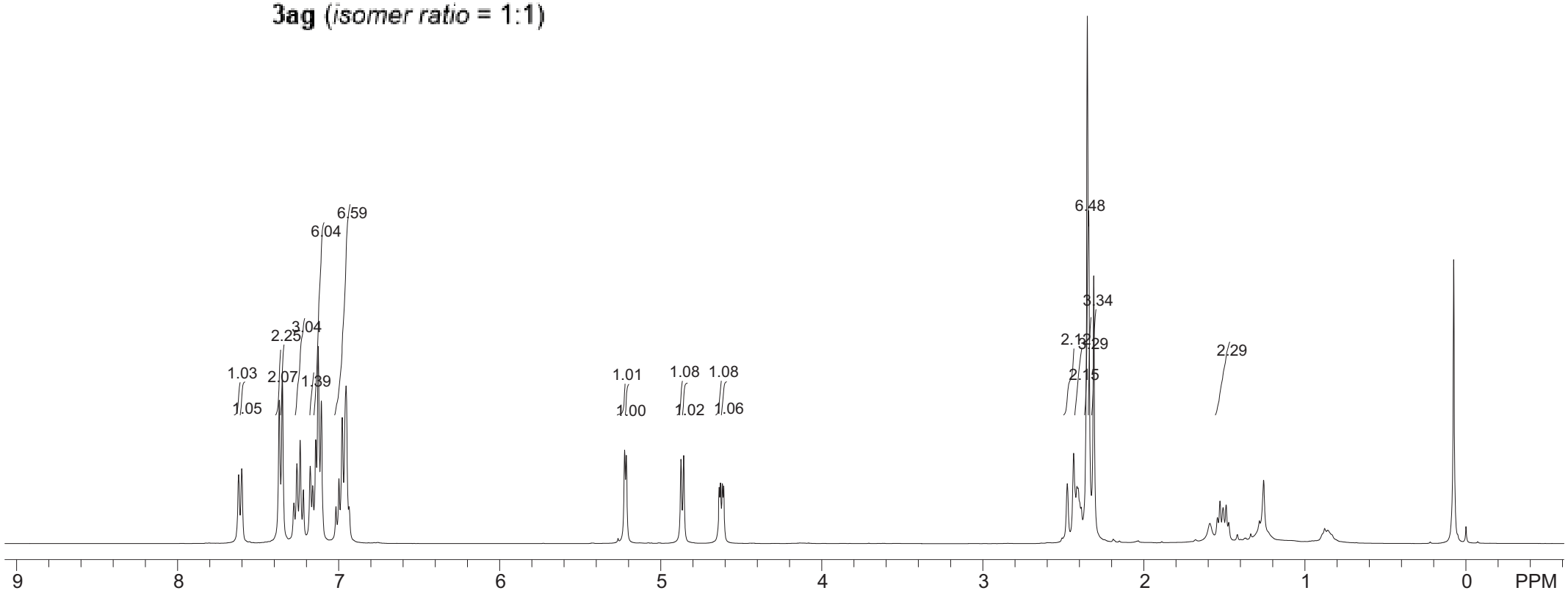

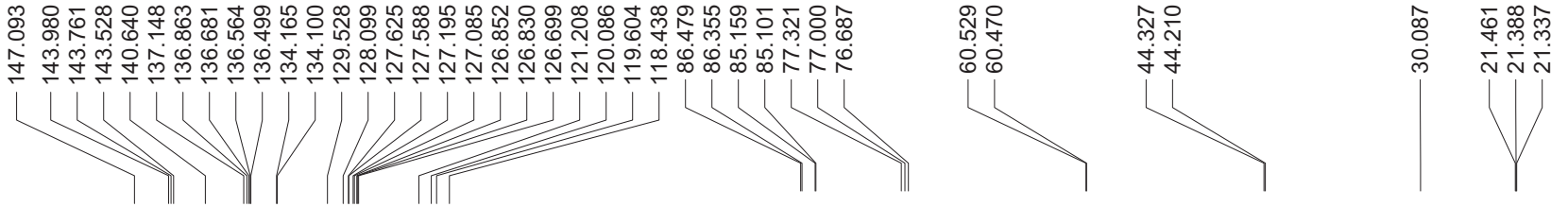

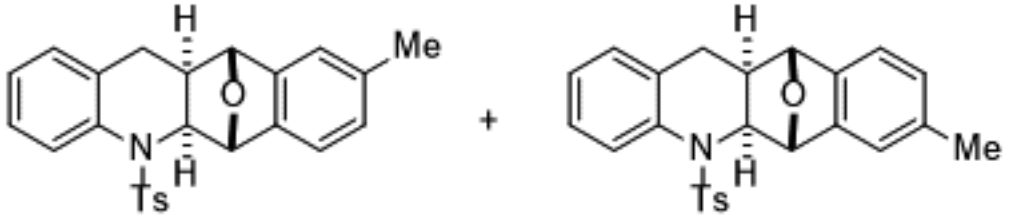

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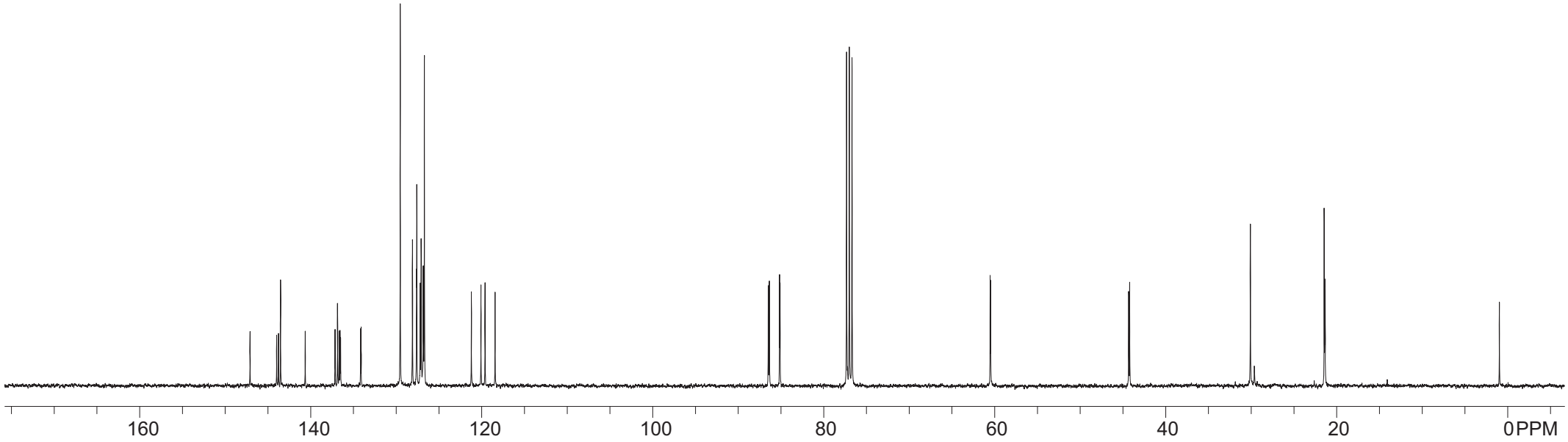

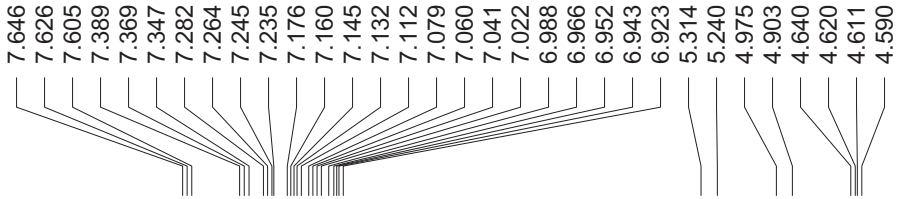

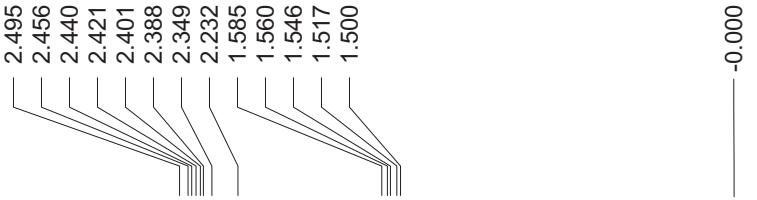

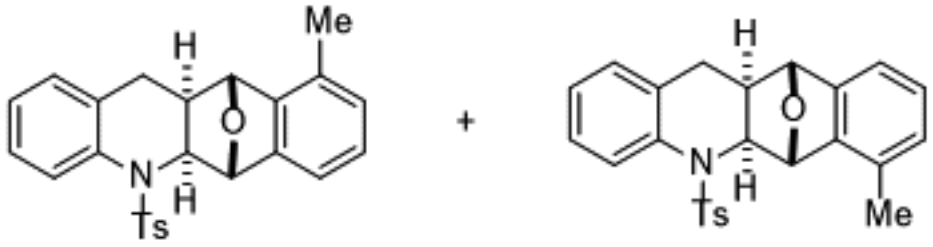

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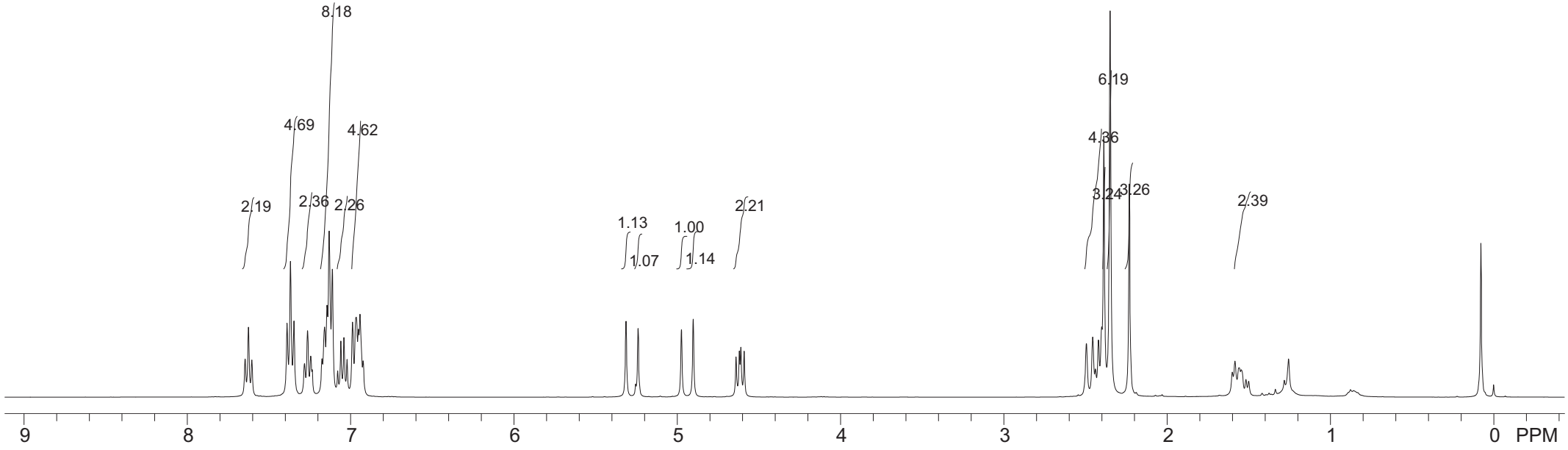

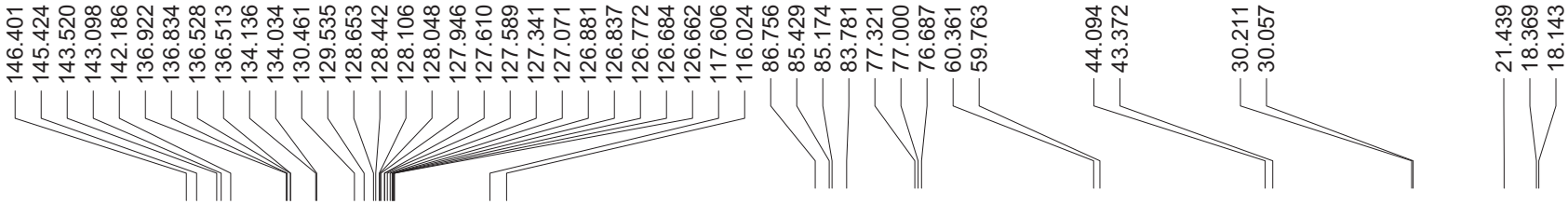

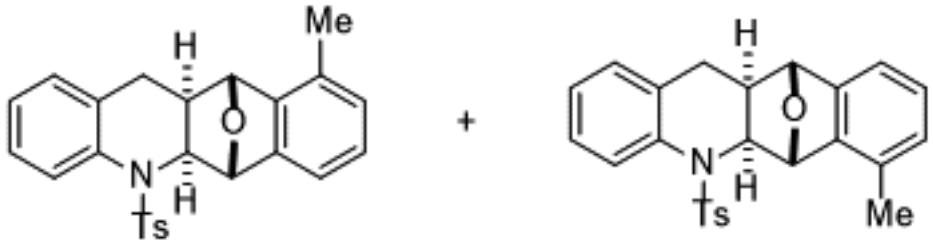

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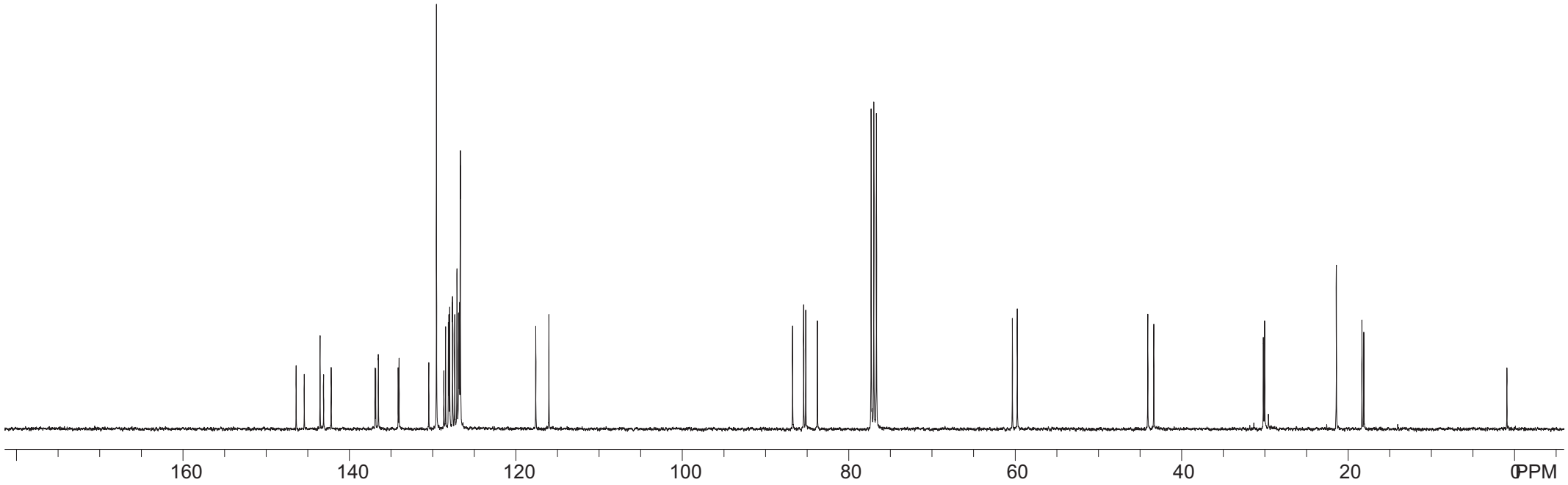

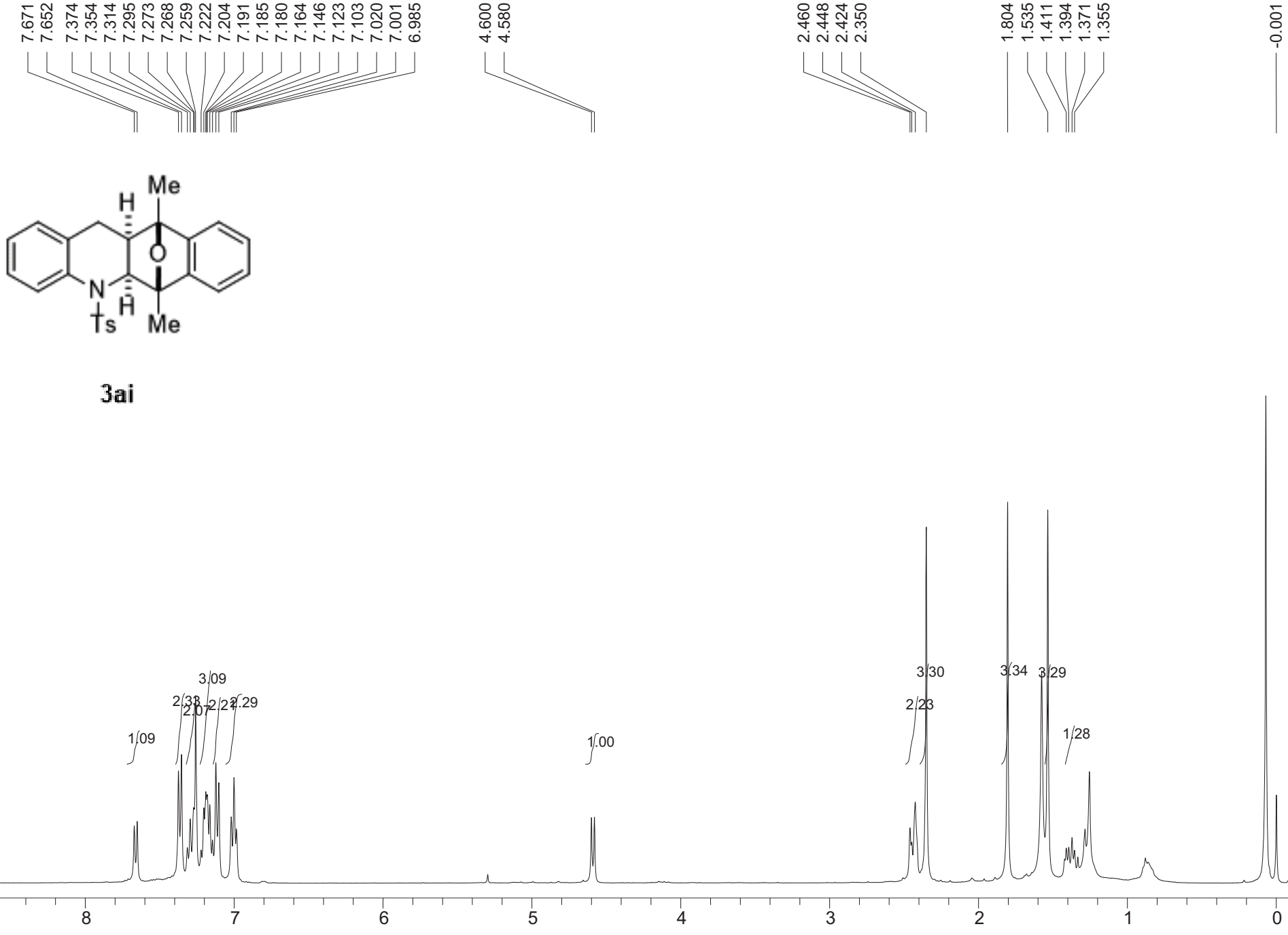
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O
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H
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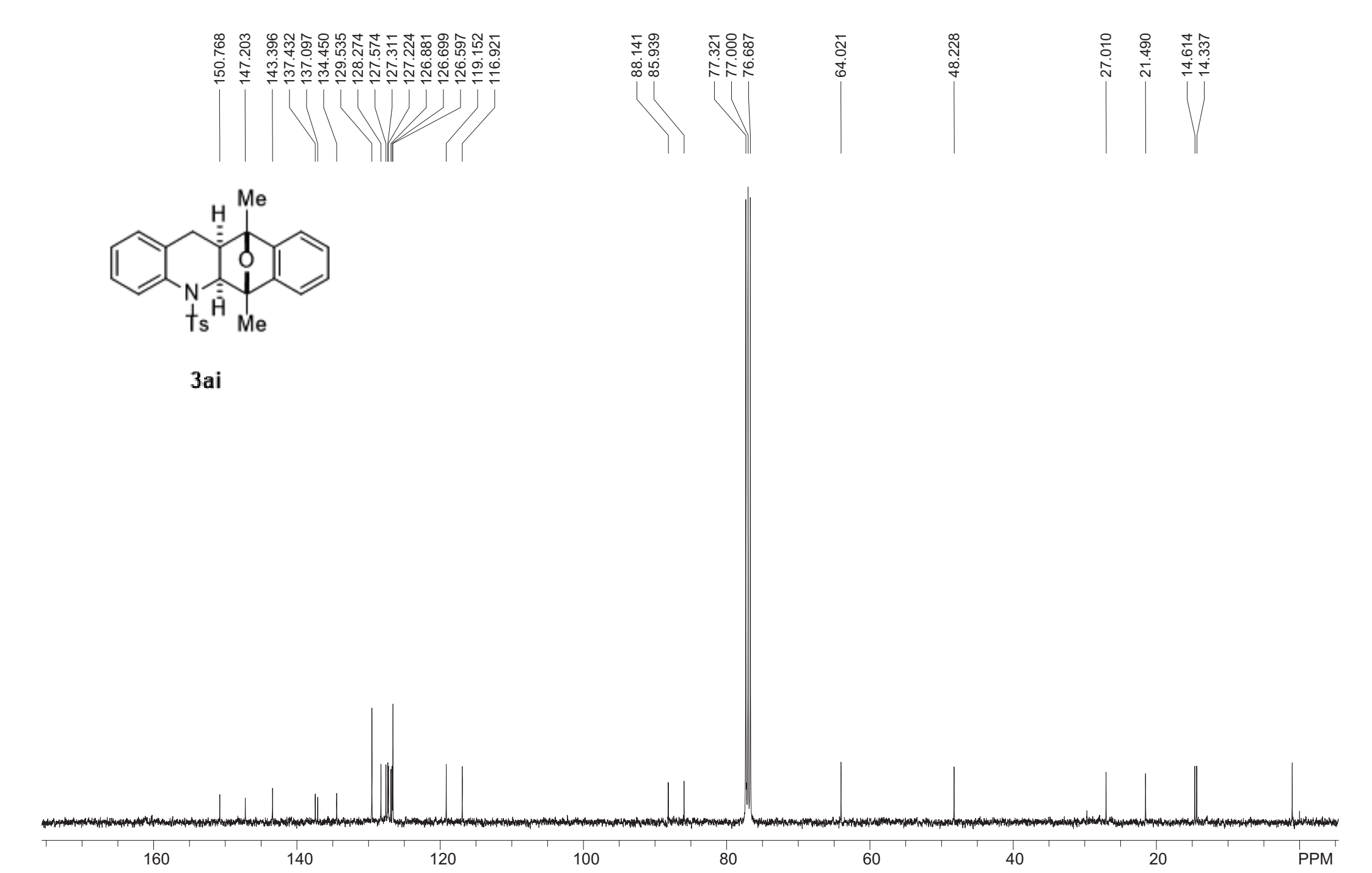
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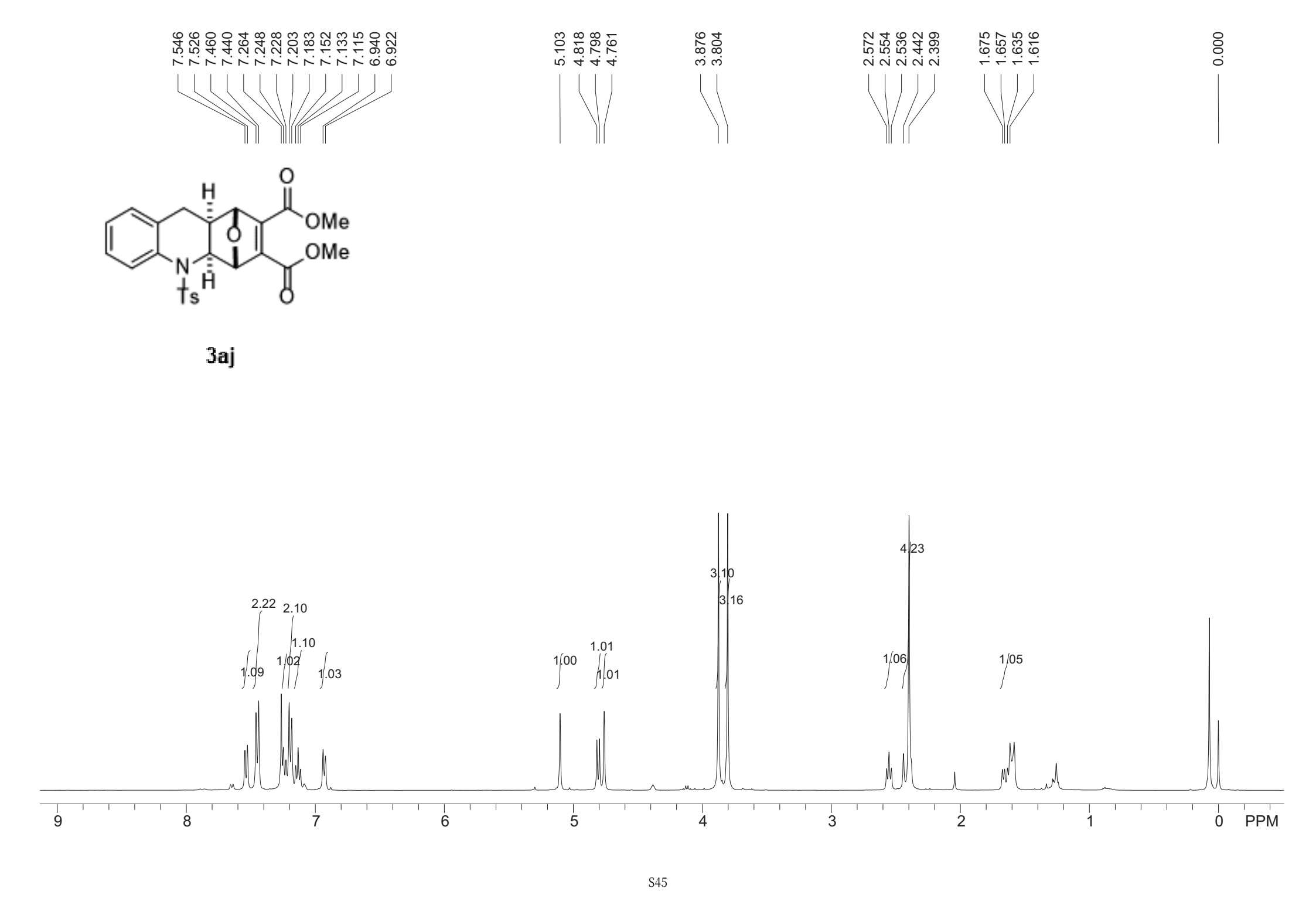
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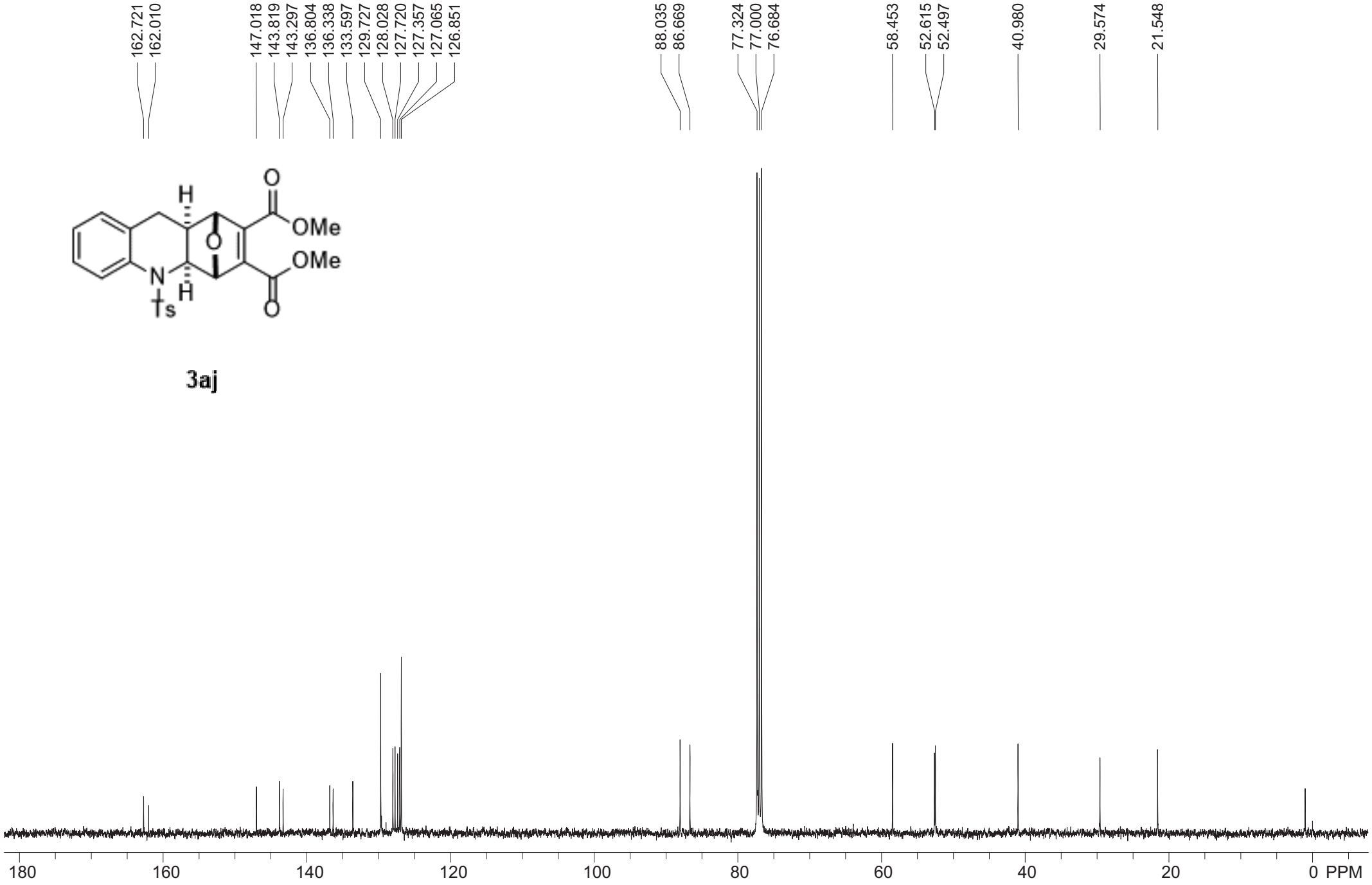
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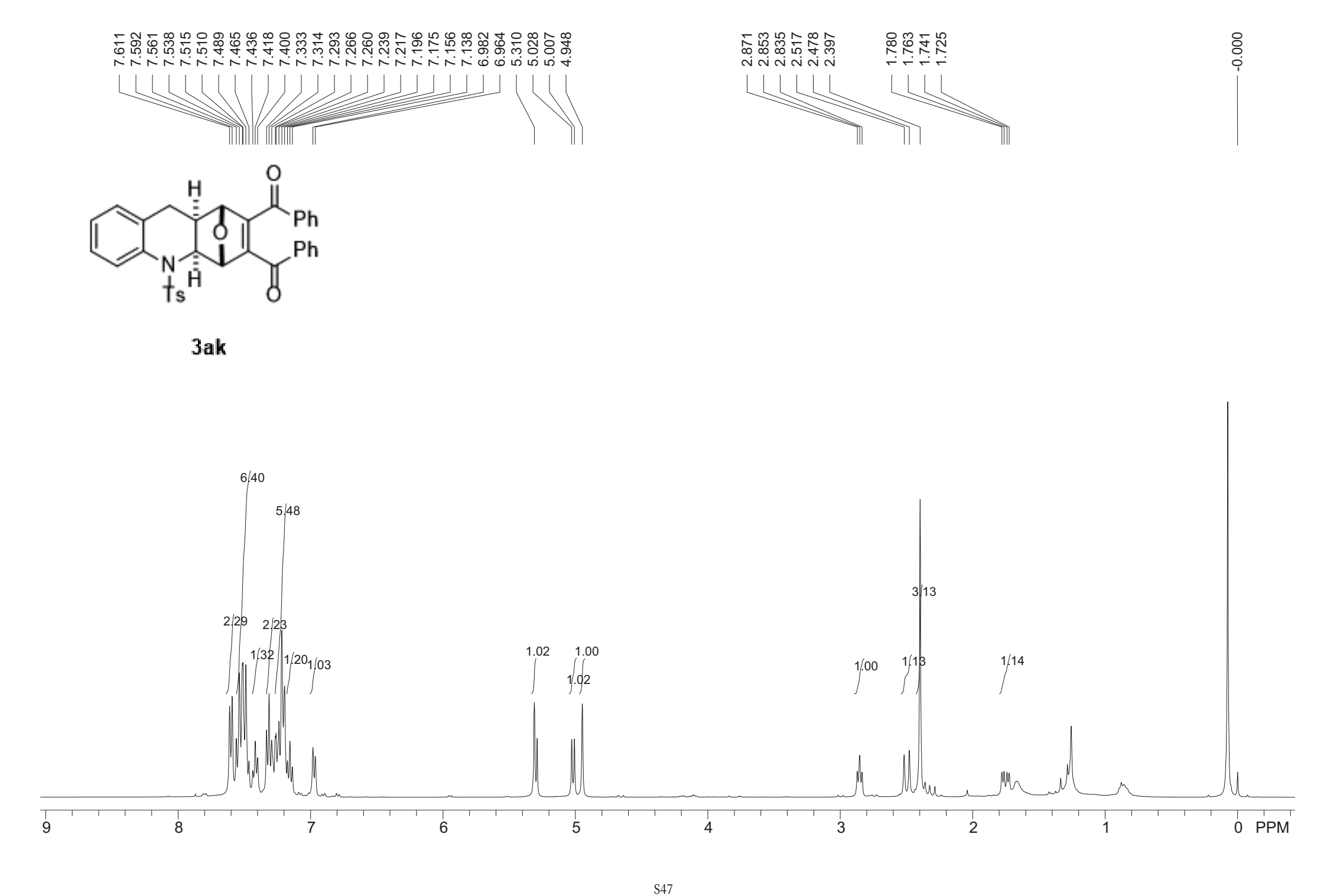
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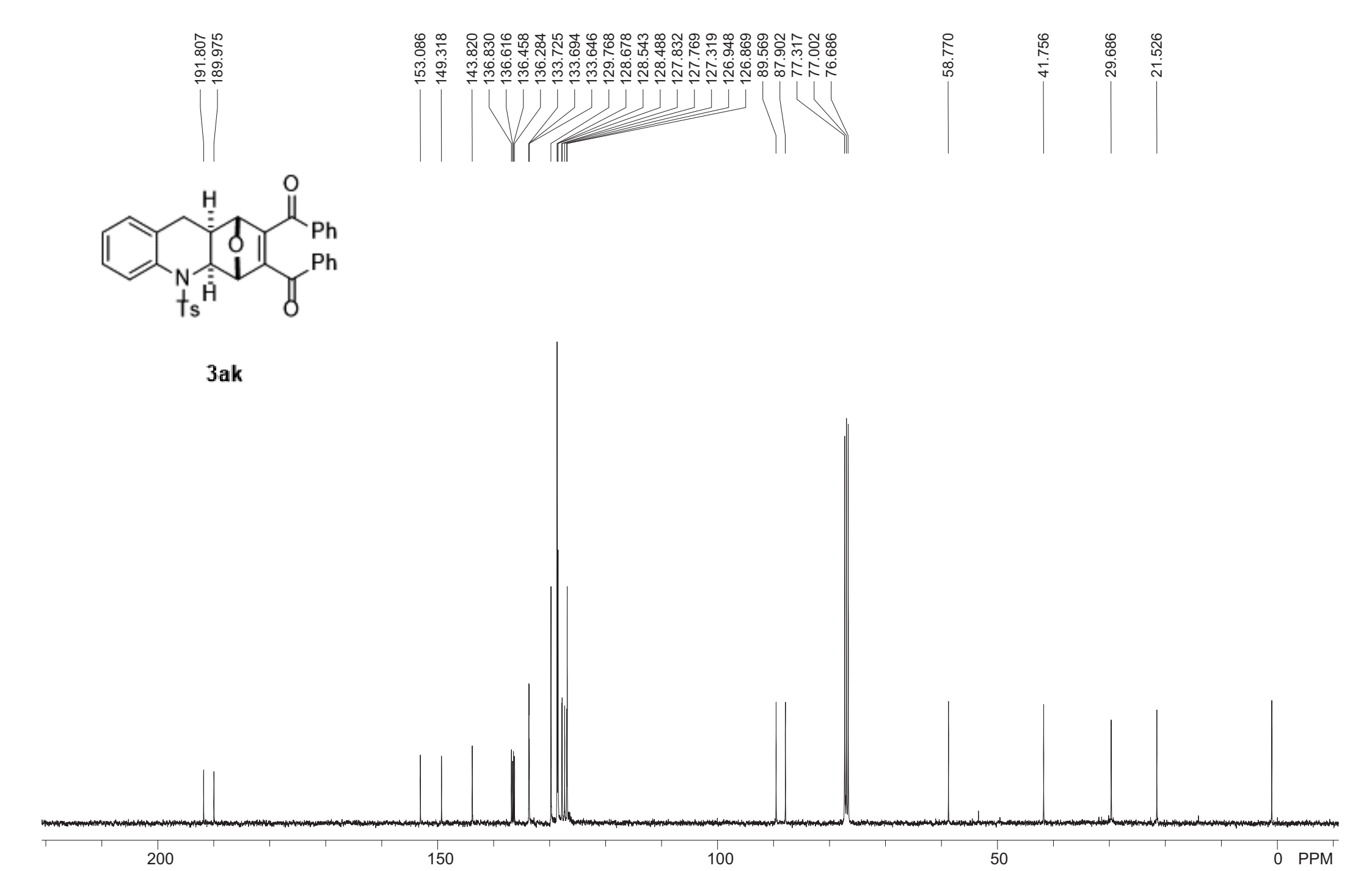
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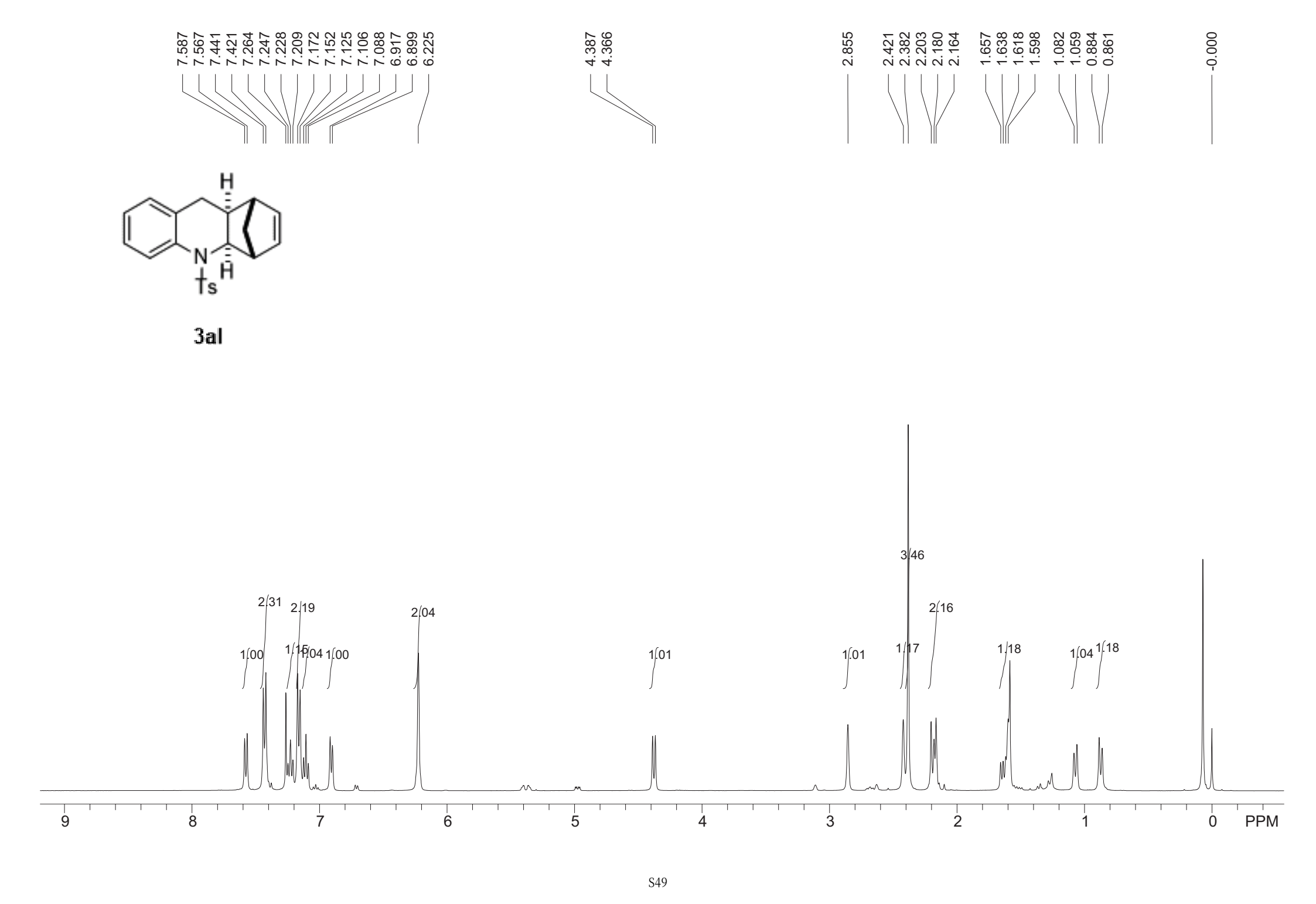
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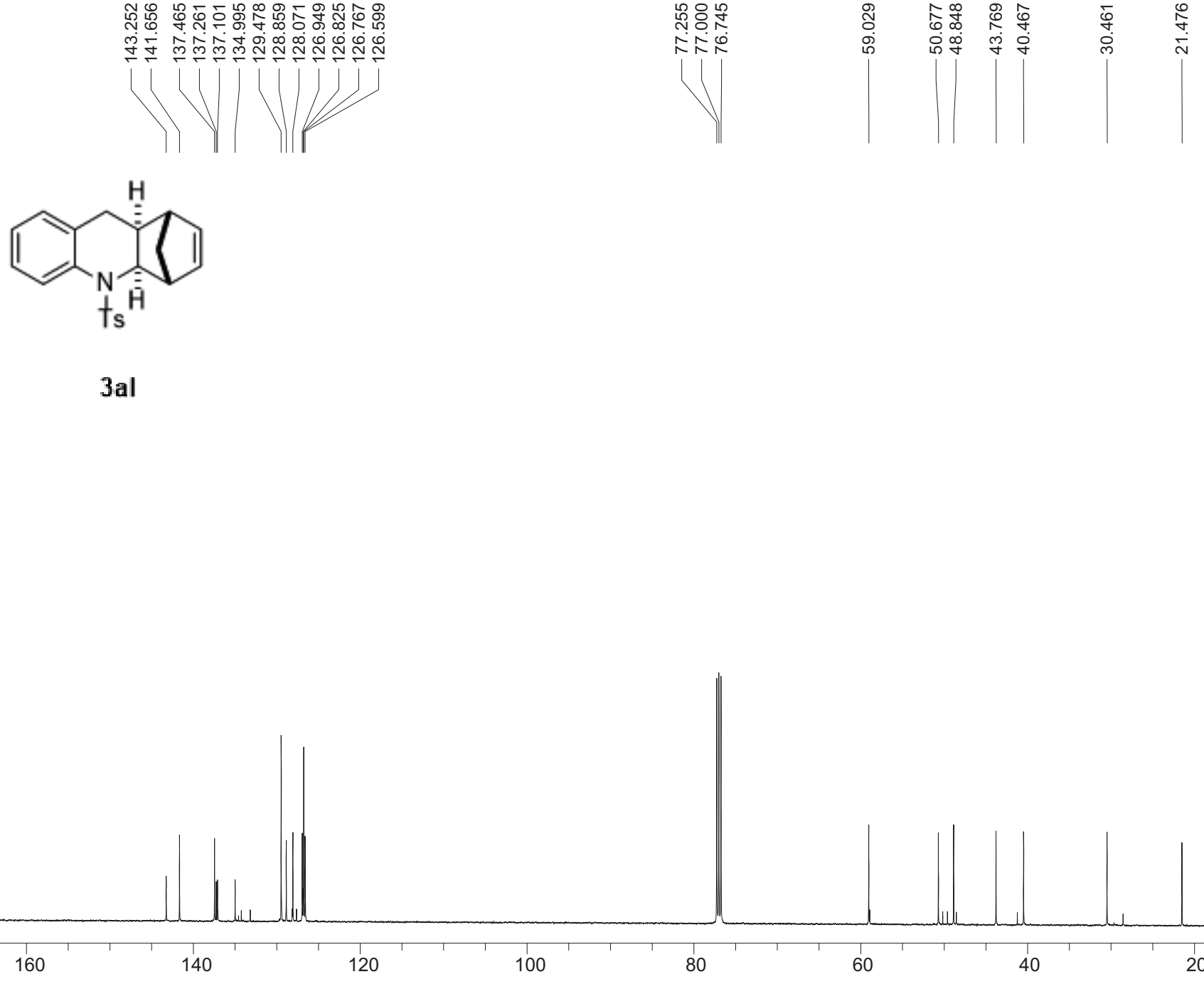
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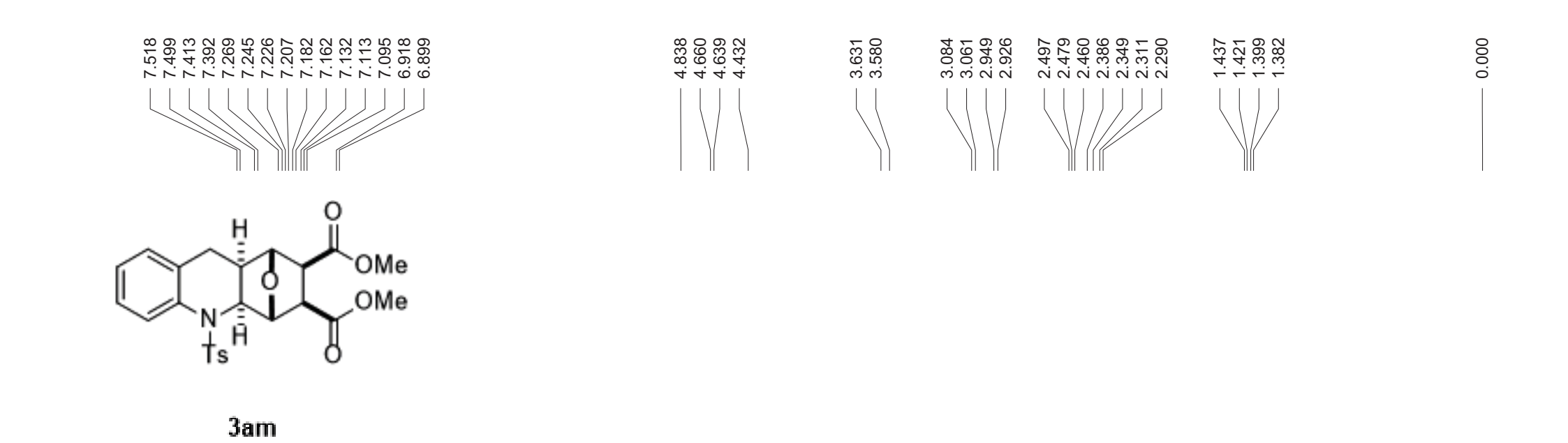
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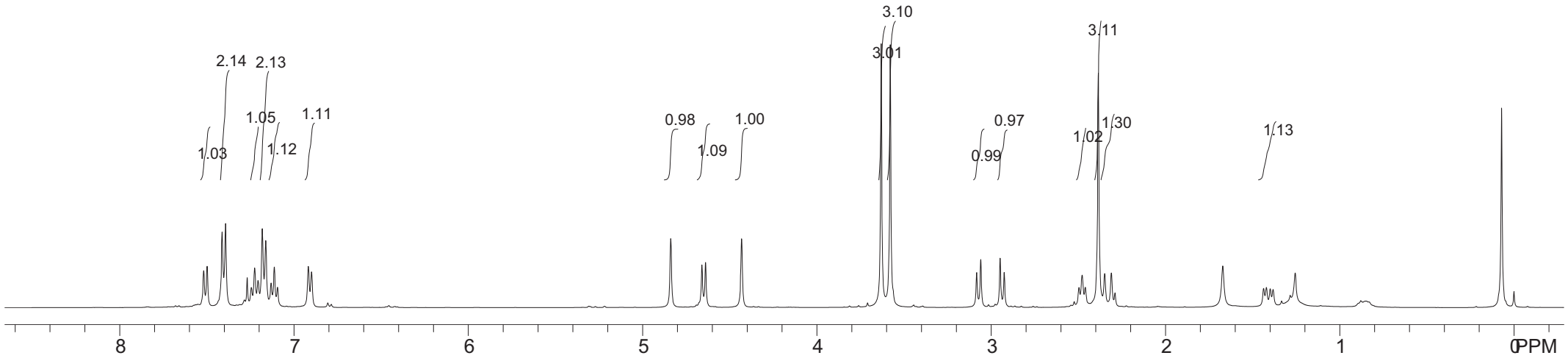
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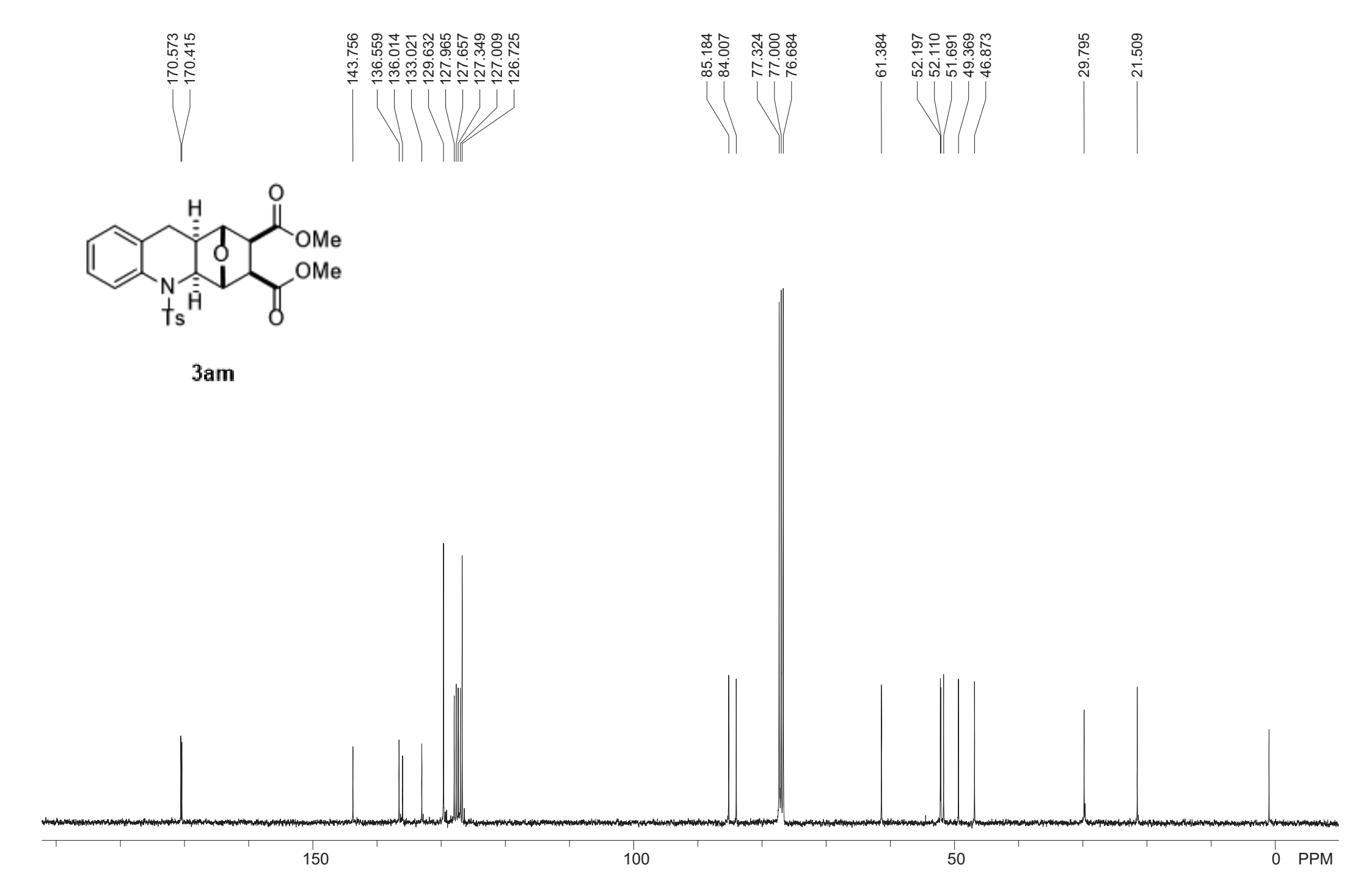
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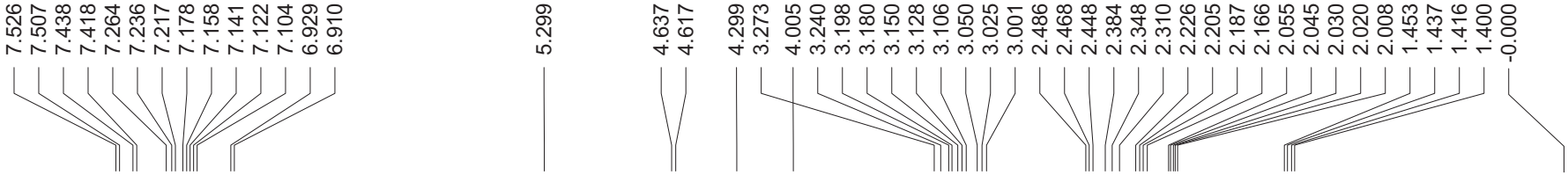
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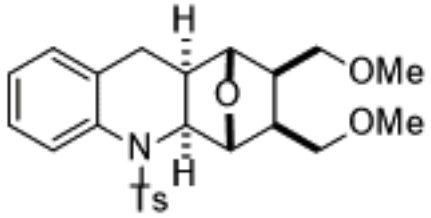
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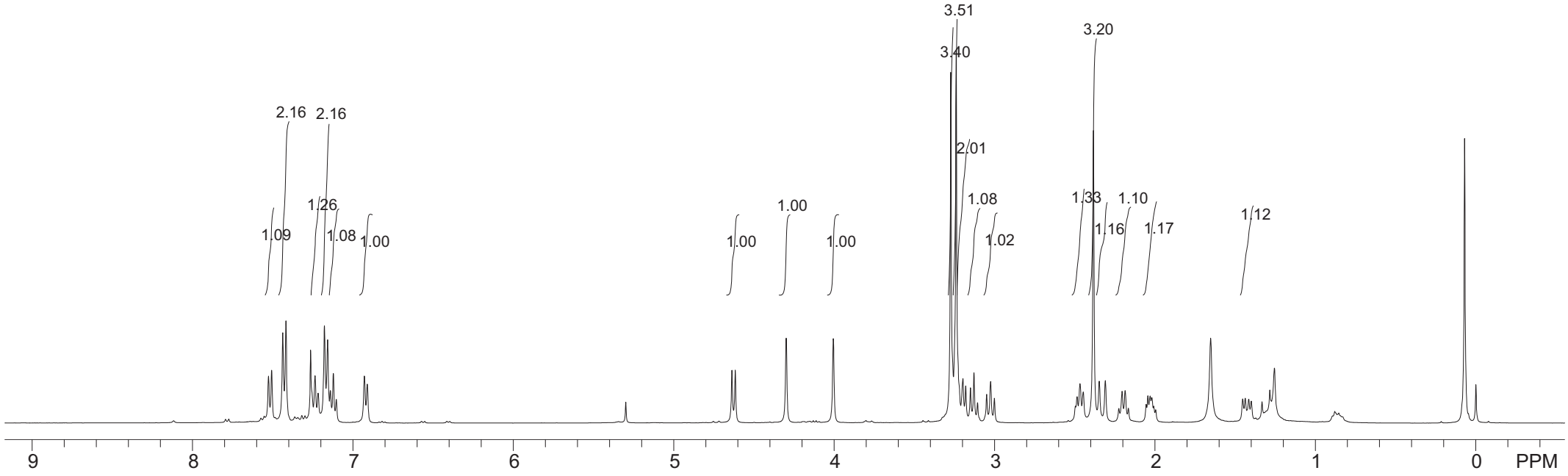
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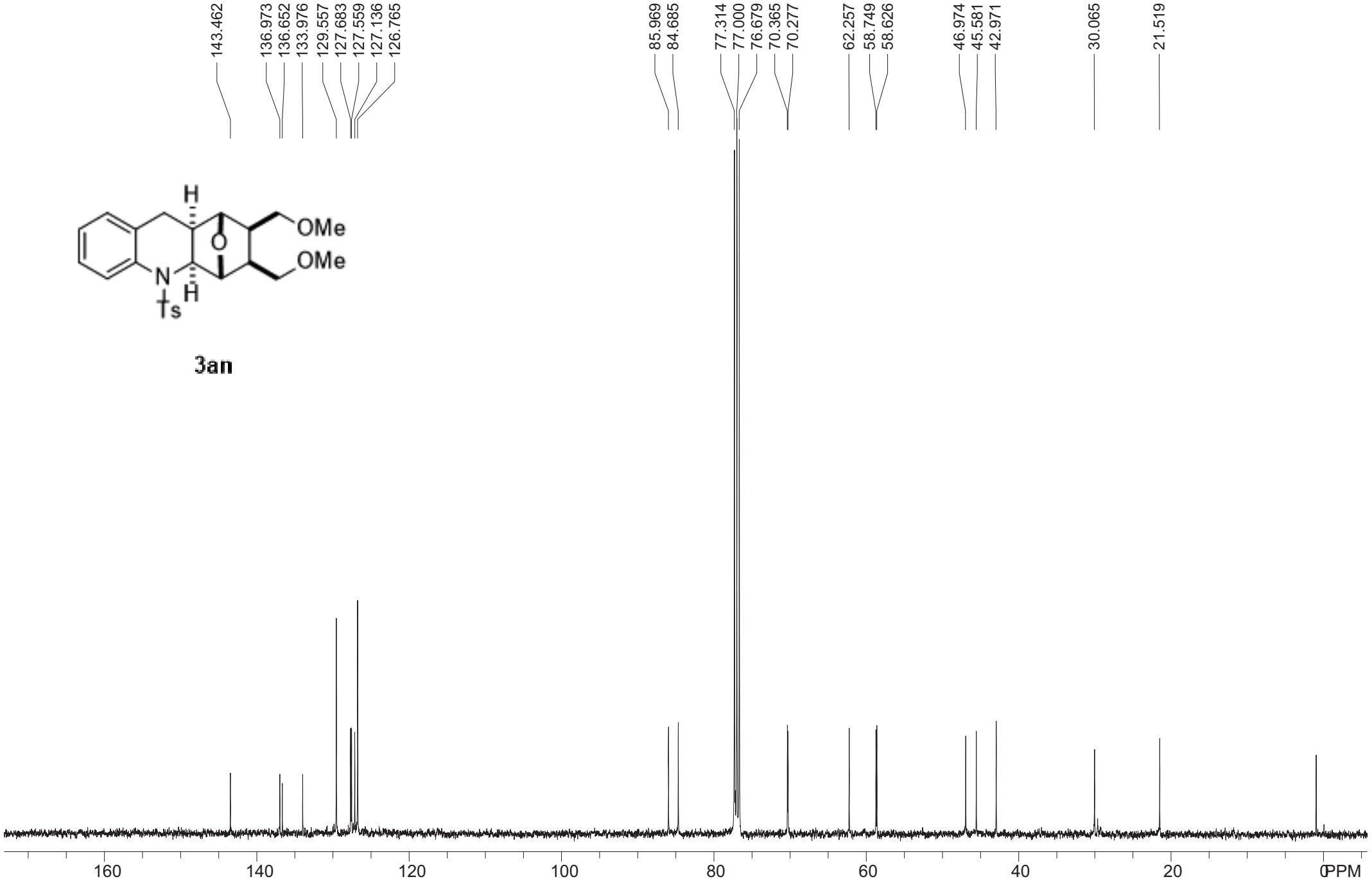
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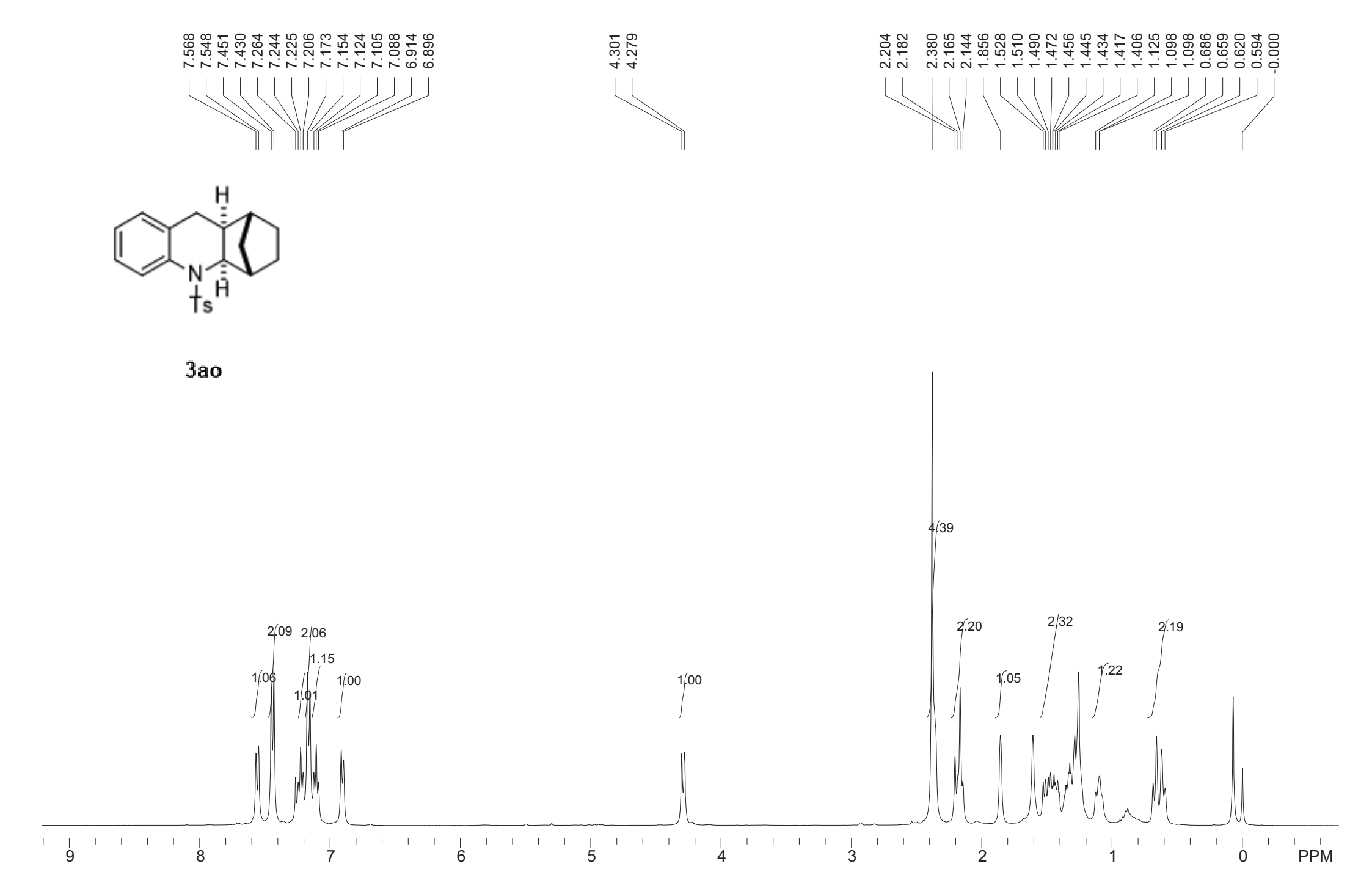
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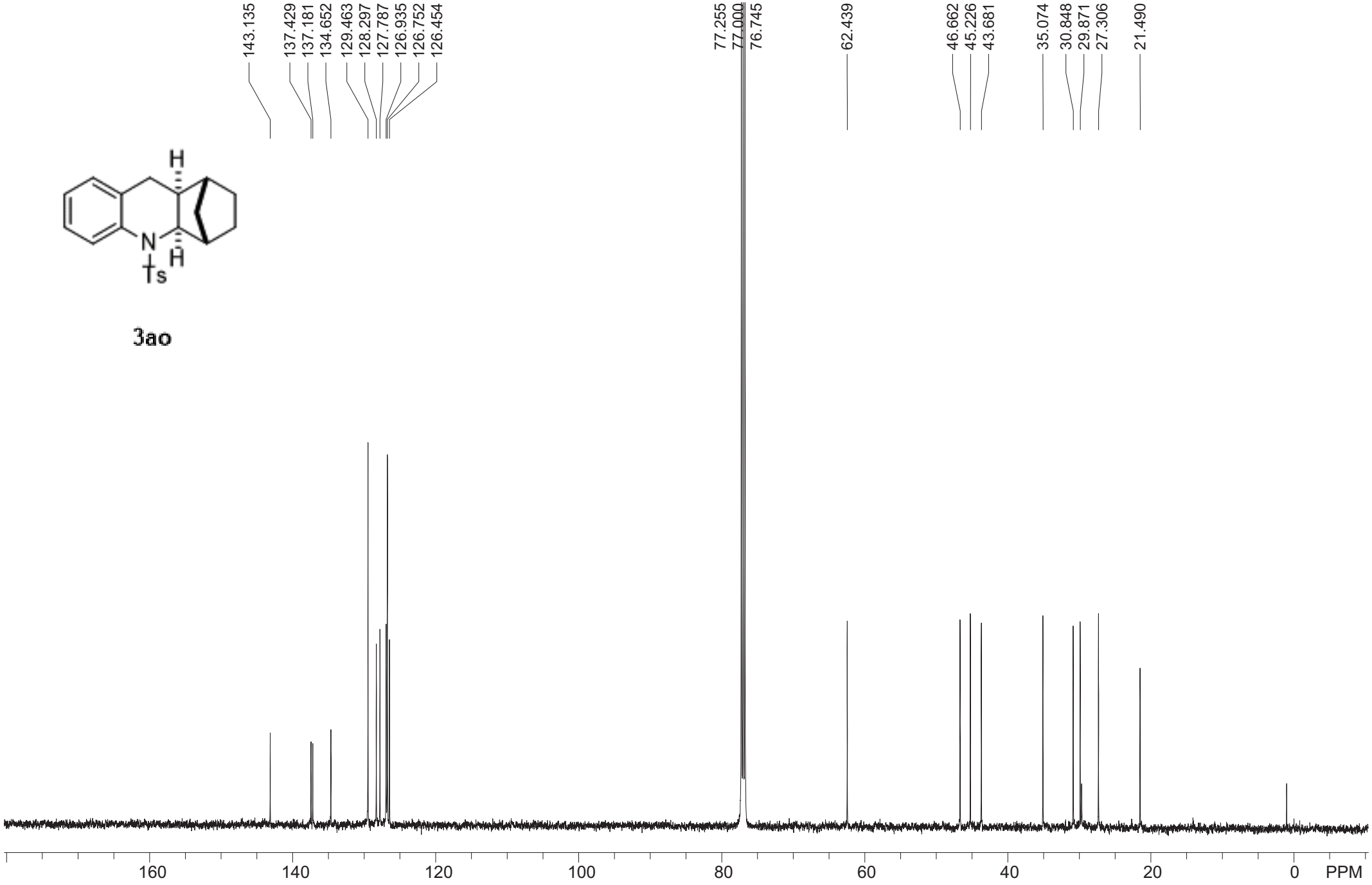
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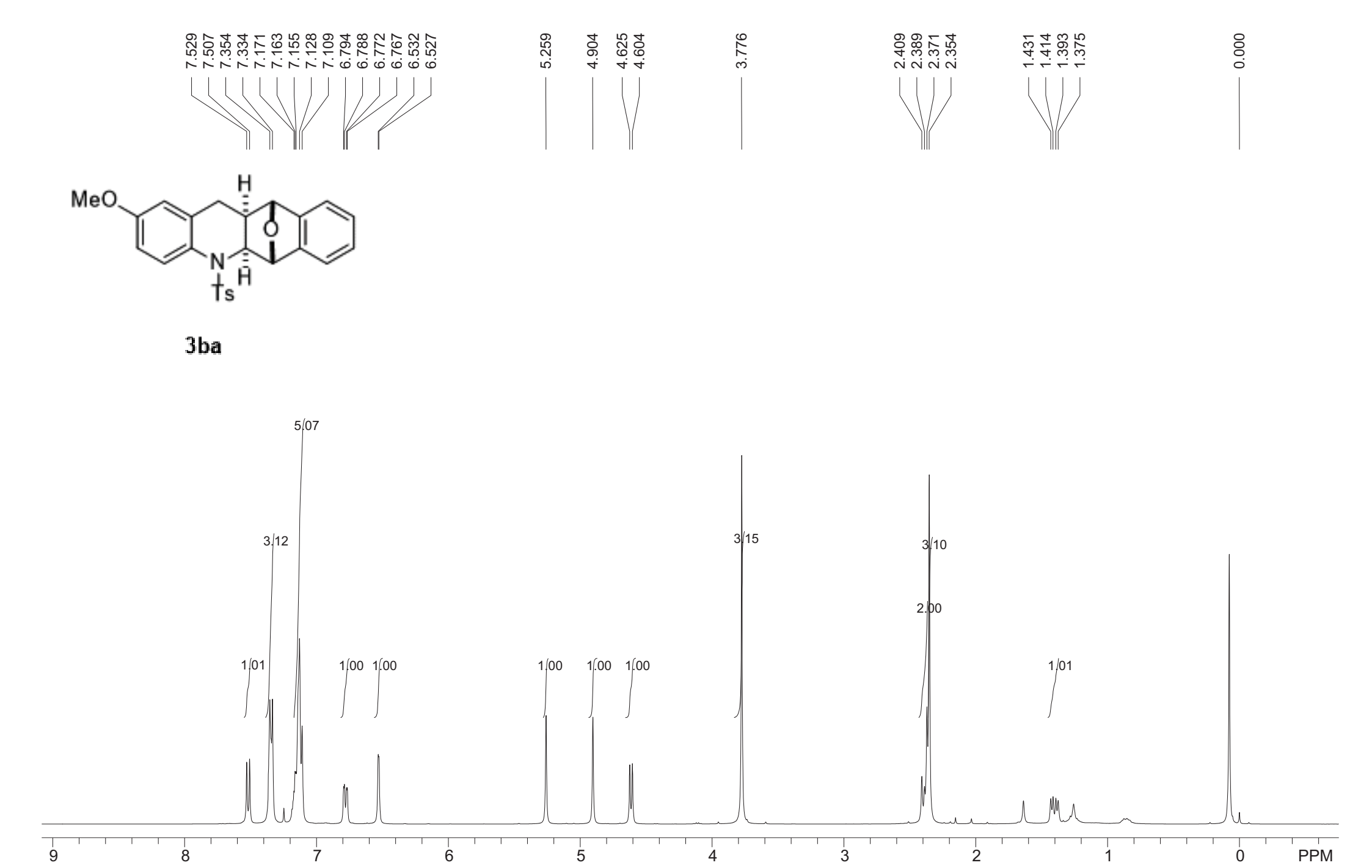
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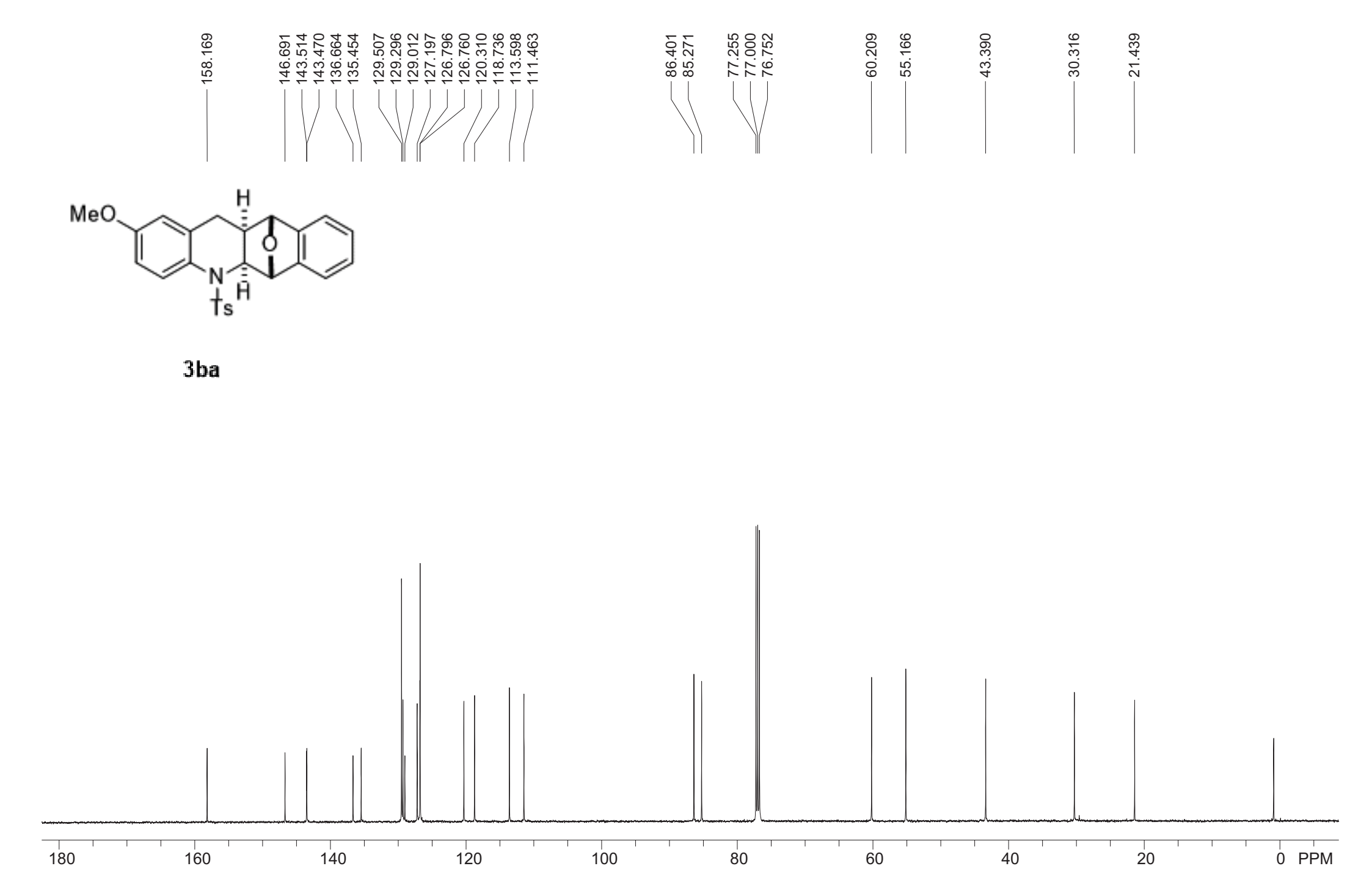
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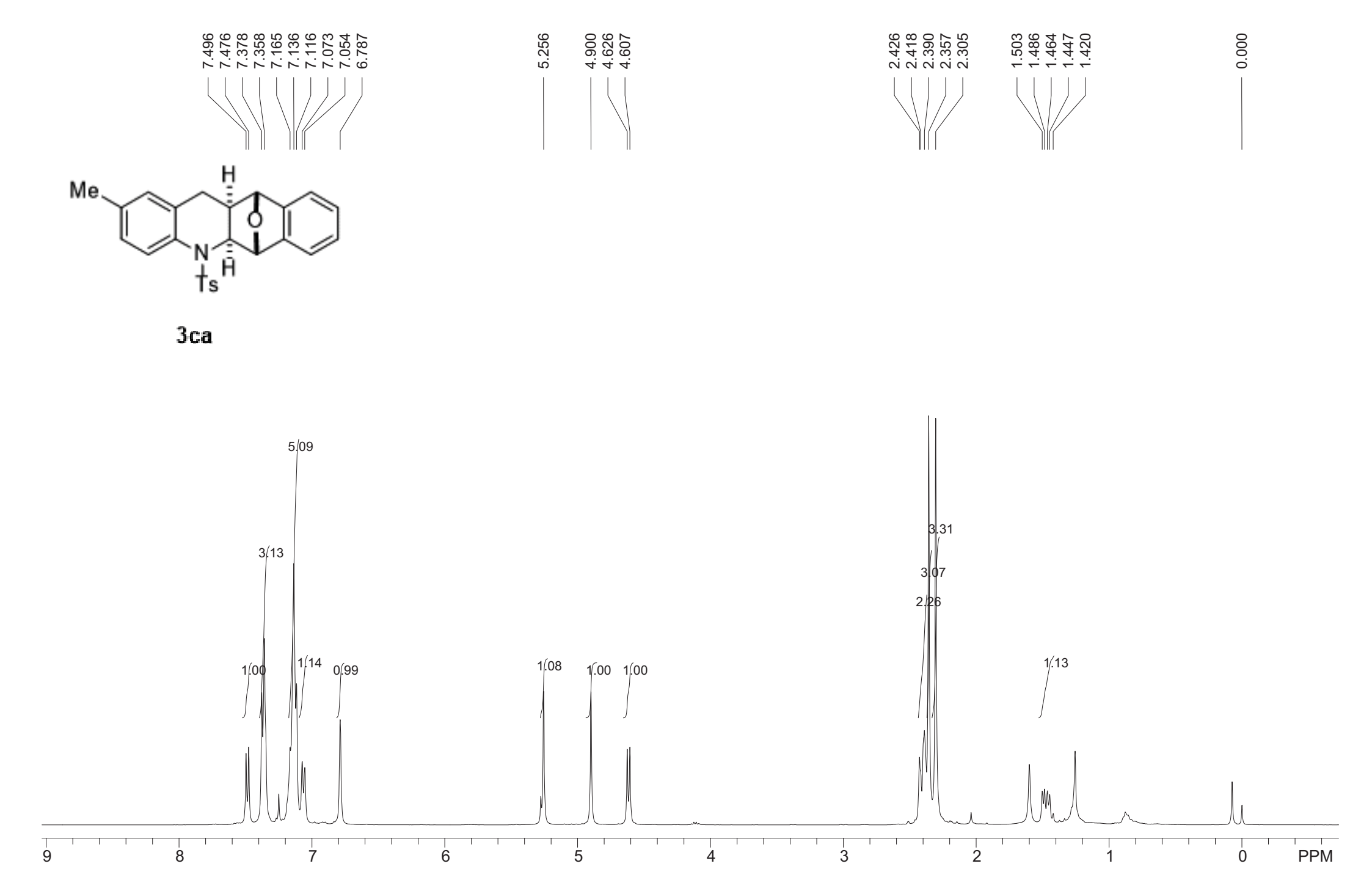
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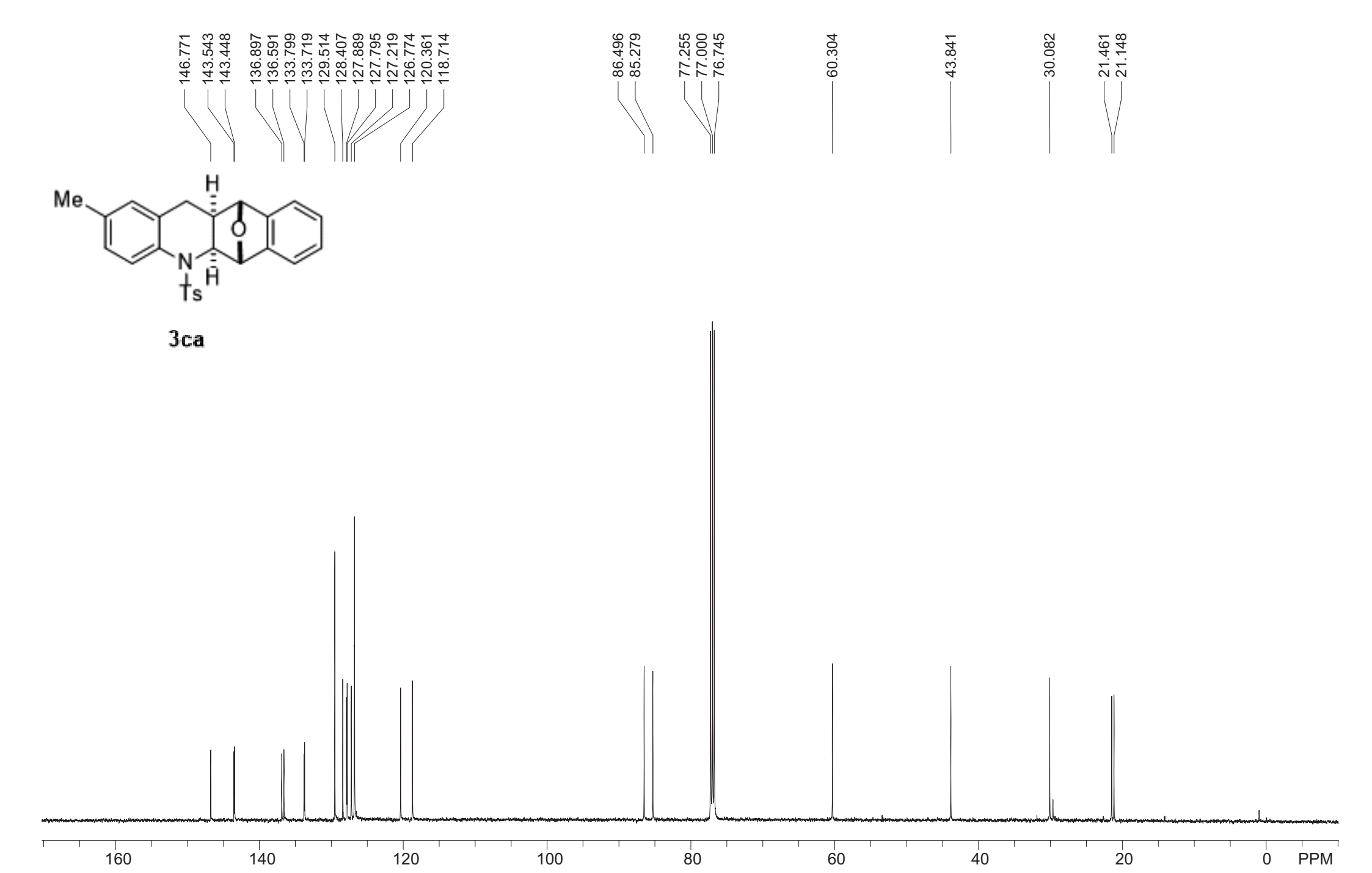
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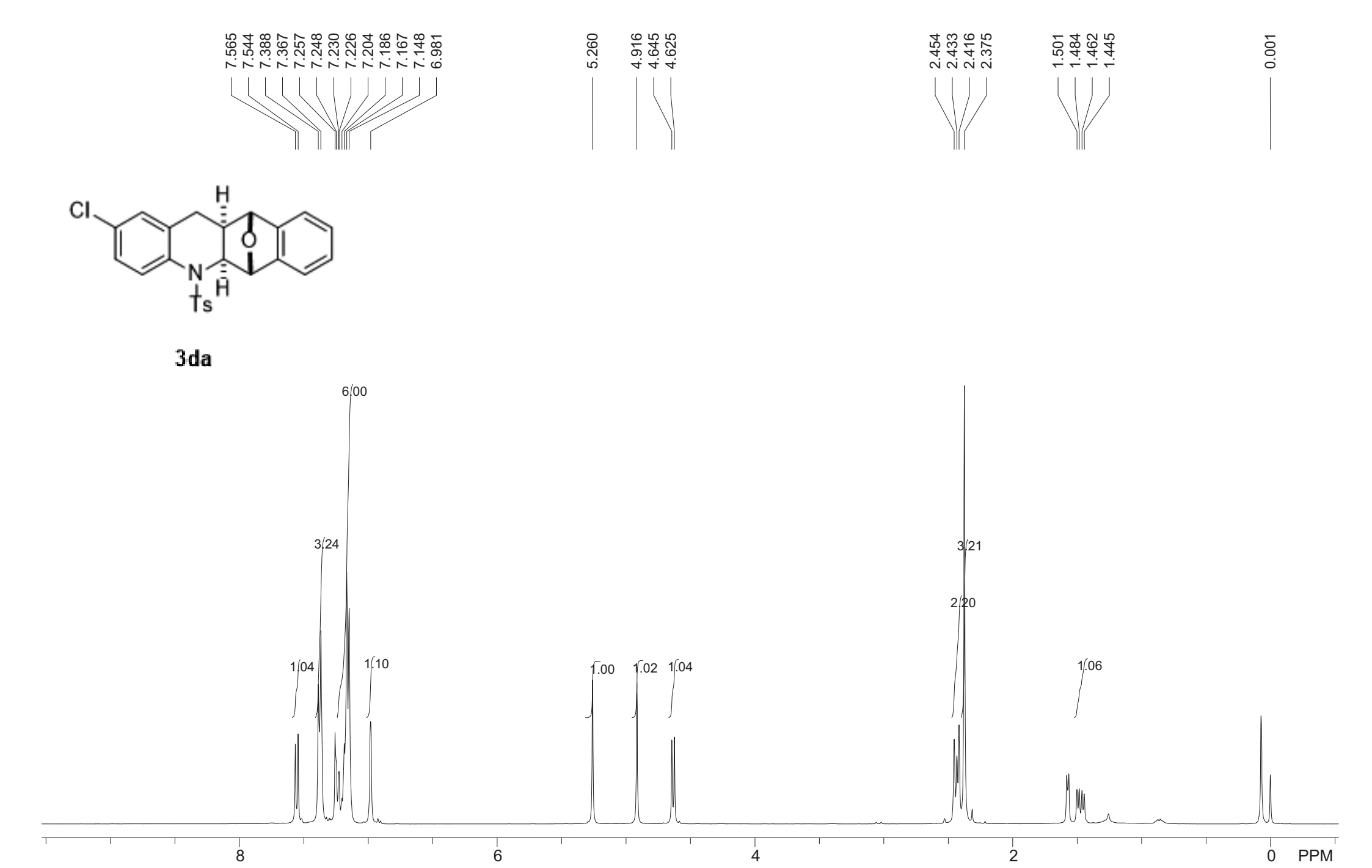
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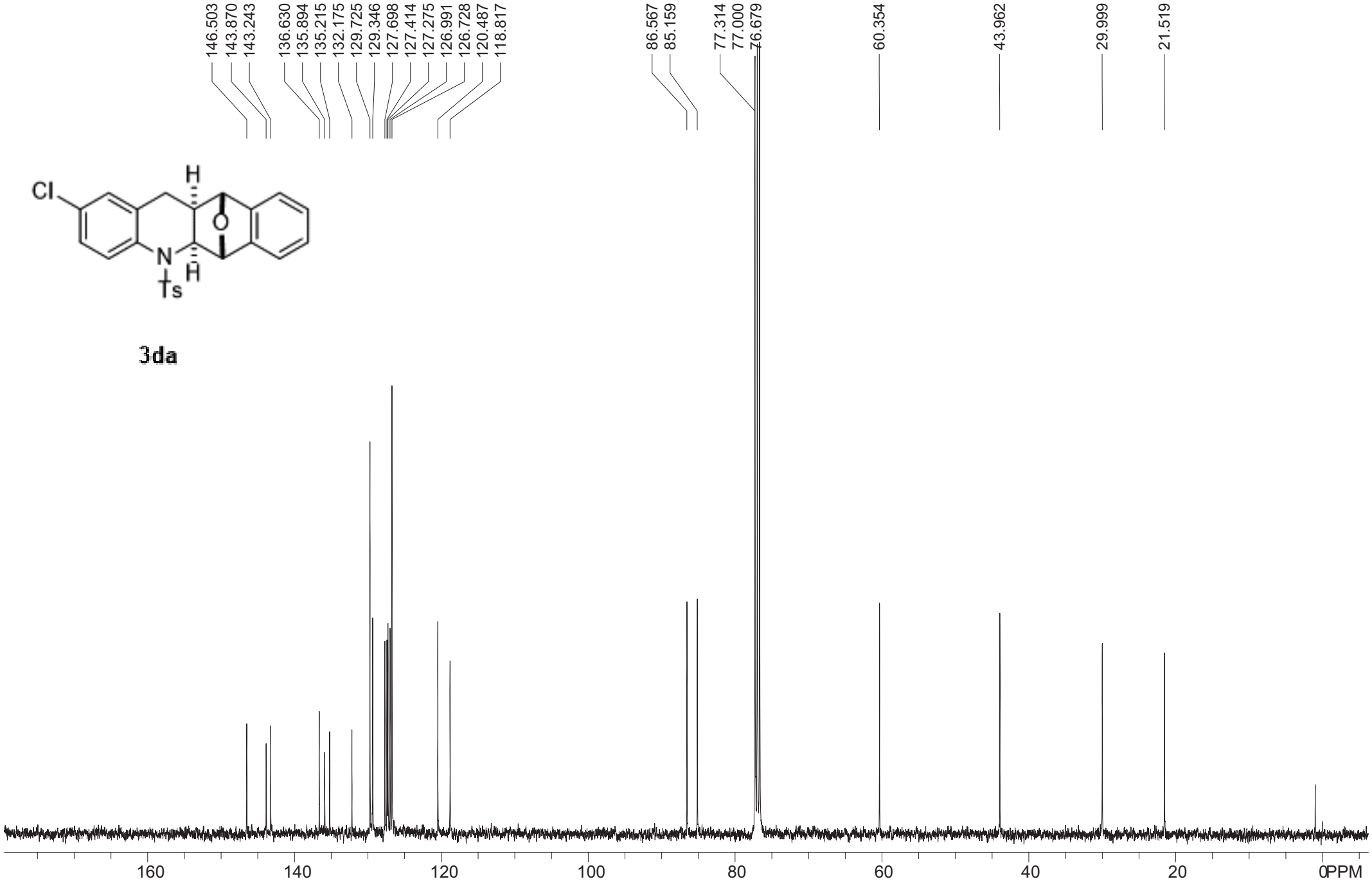
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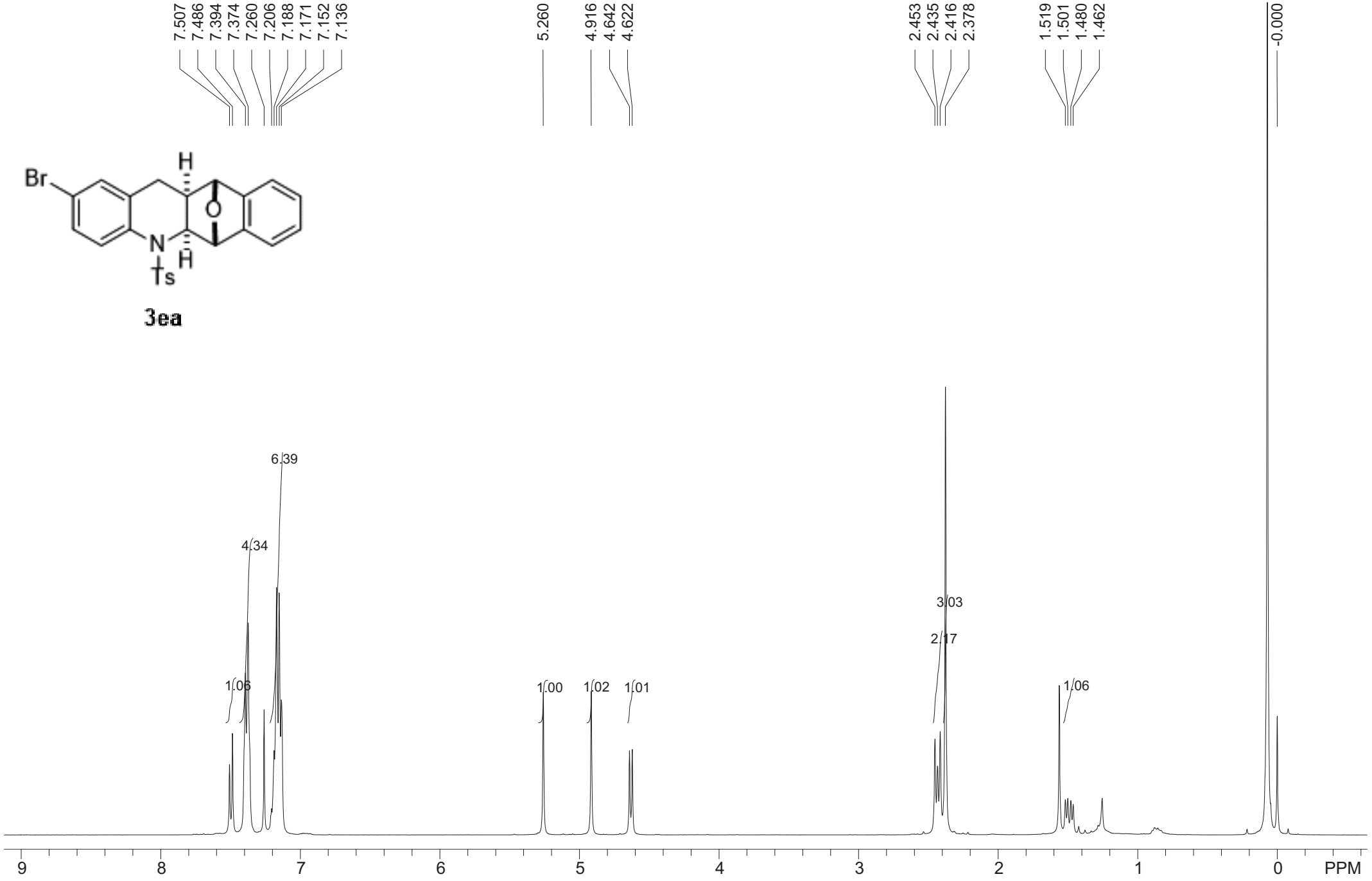
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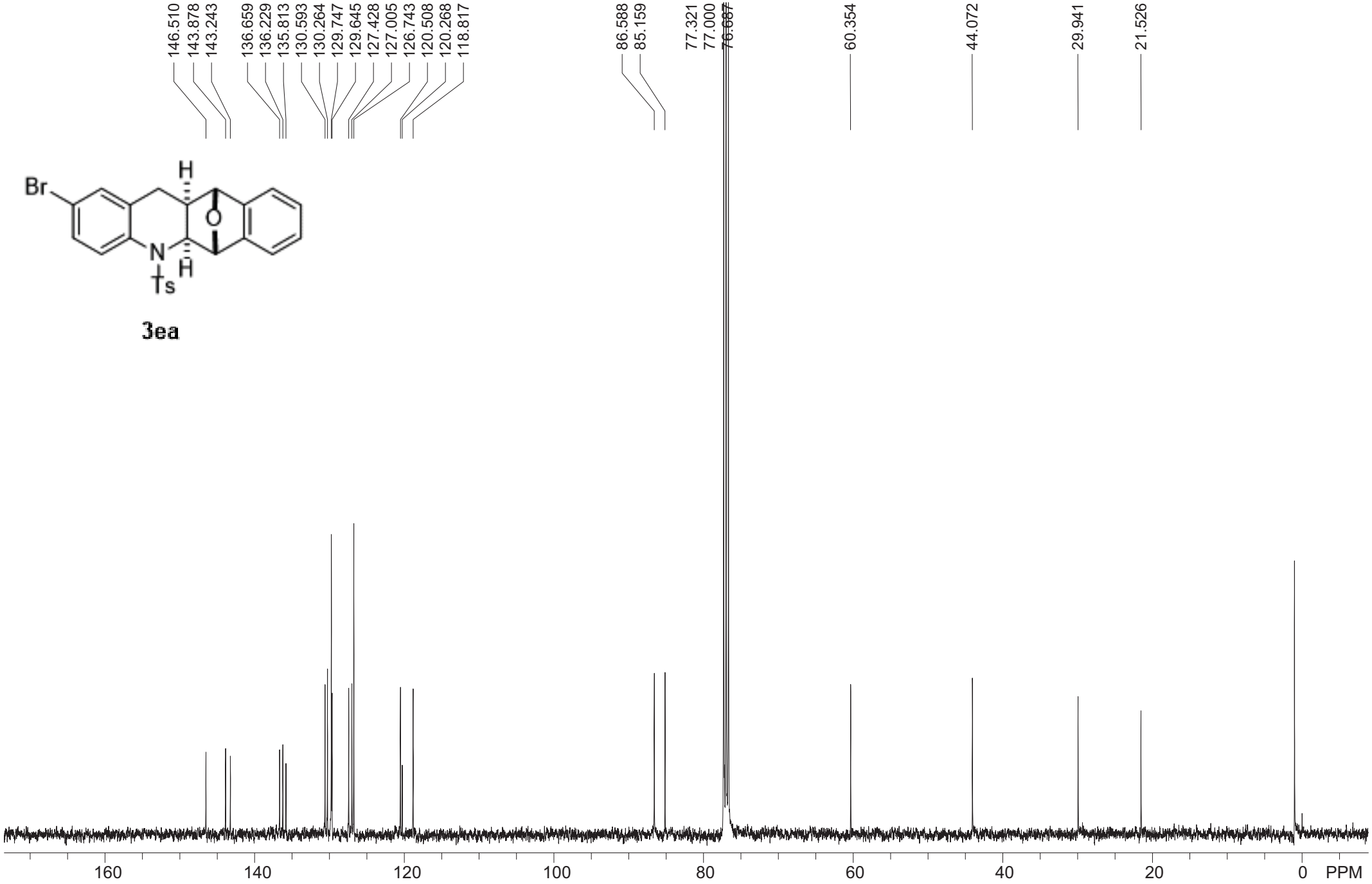
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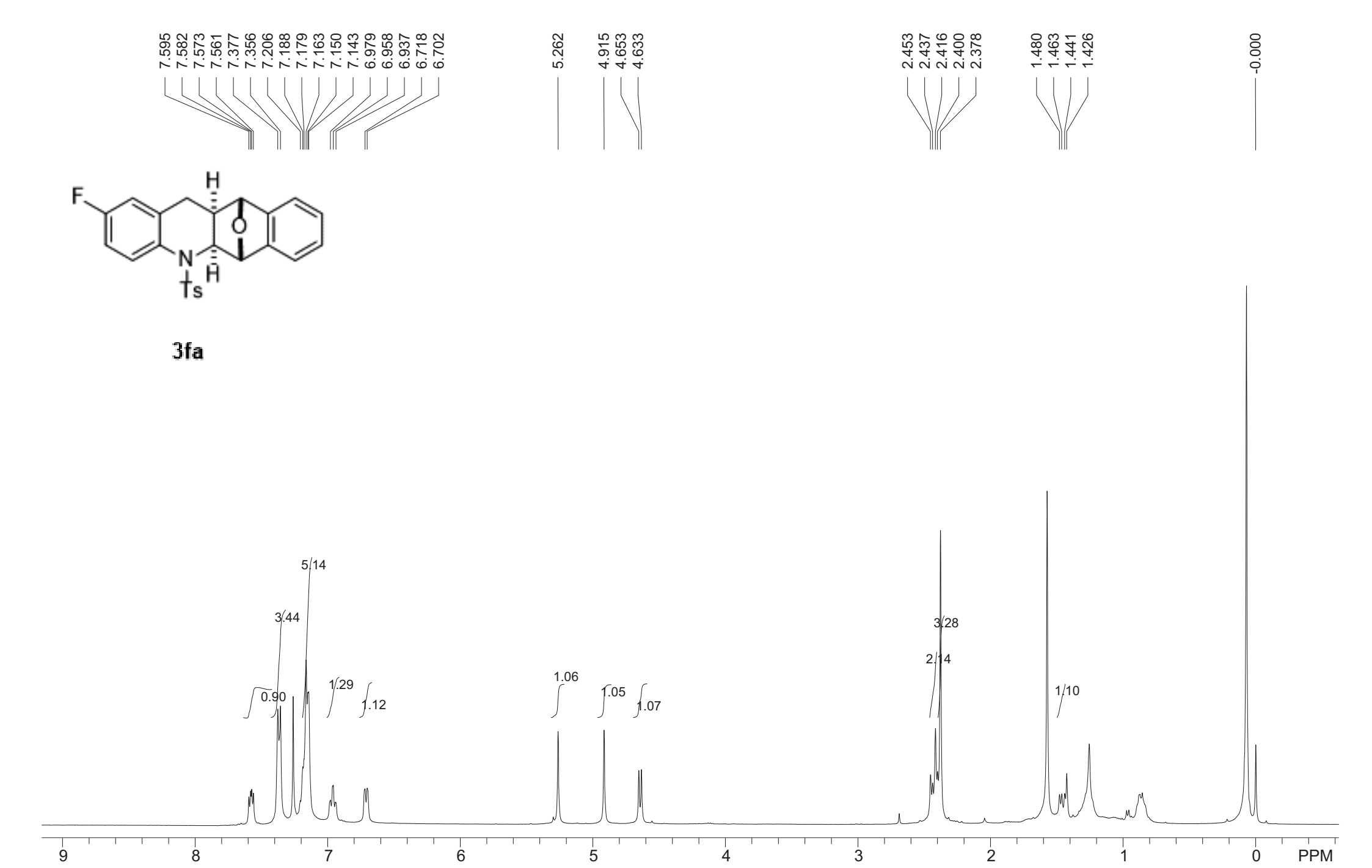
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2.437
2.416
2.400
2.378
1.480
1.463
1.441
1.426
-0.000
F
H
O
N
H
Ts
3fa
5.14
3.44
0.90
1.29
1.12
1.06
1.05
1.07
3.28
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1.10
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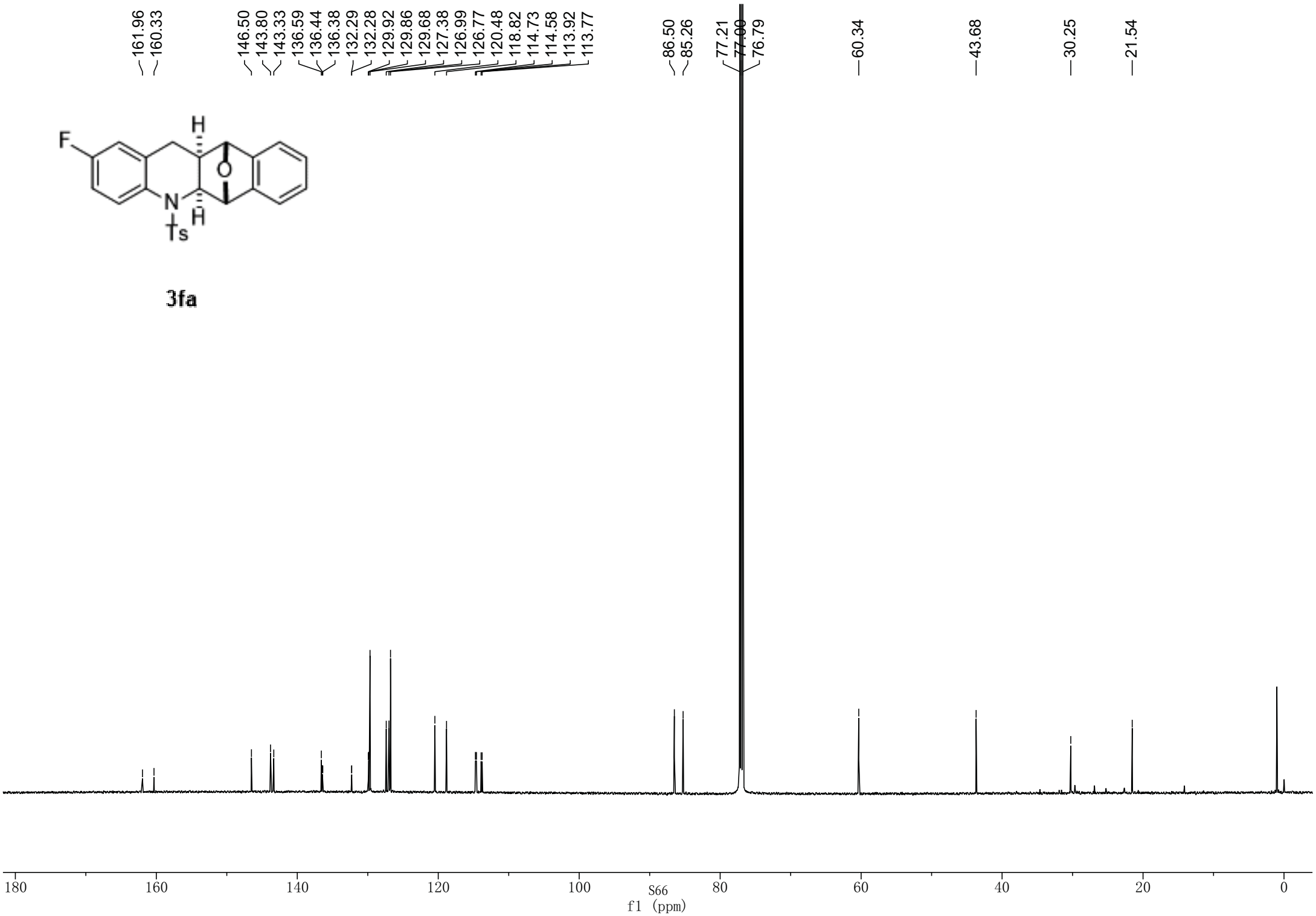
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136.38
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132.28
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129.68
127.38
126.99
126.77
120.48
118.82
114.73
114.58
113.92
113.77
86.50
85.26
77.21
77.00
76.79
60.34
43.68
30.25
21.54
F
H
O
N
H
Ts
3fa
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140
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60
40
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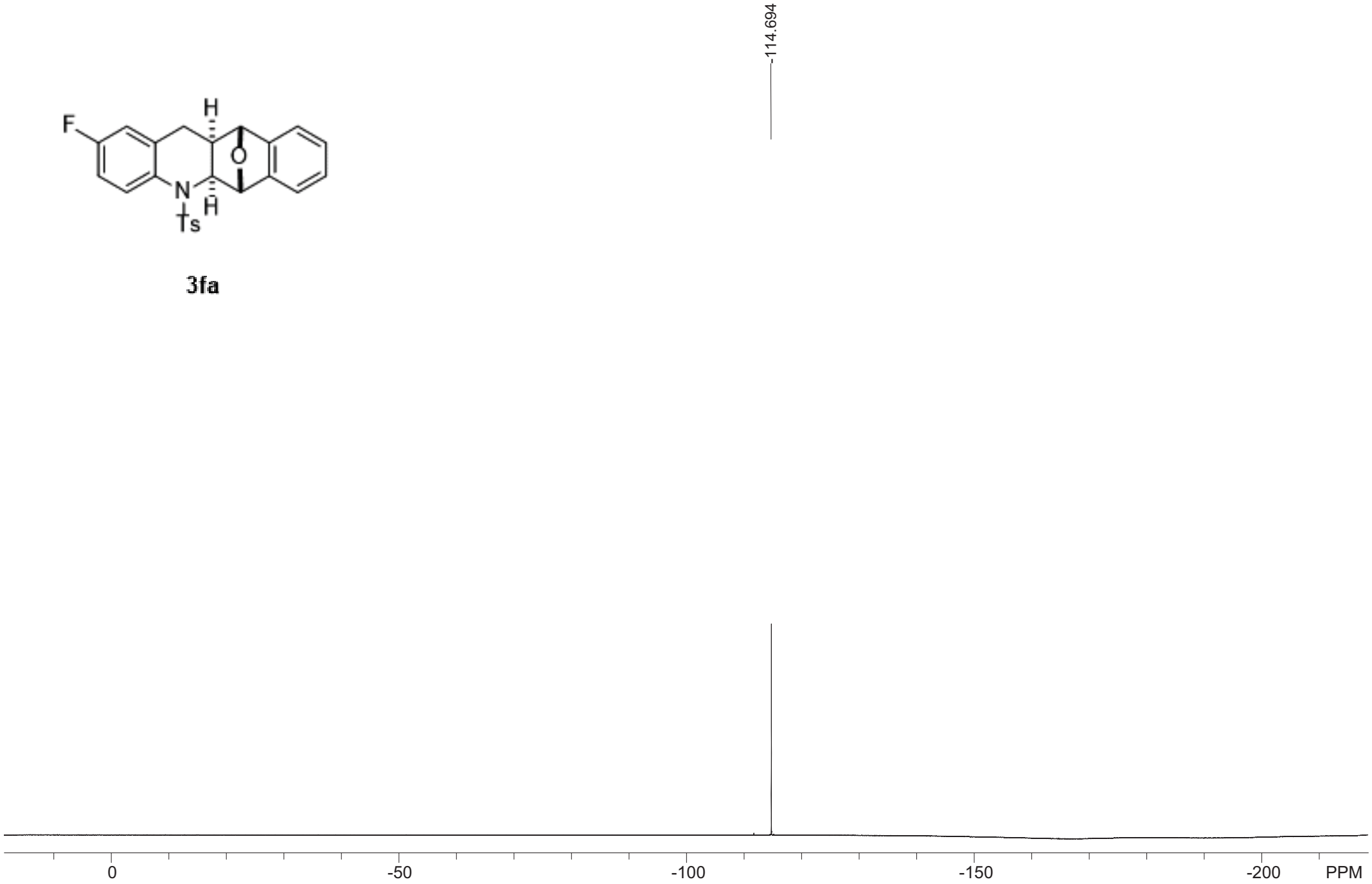
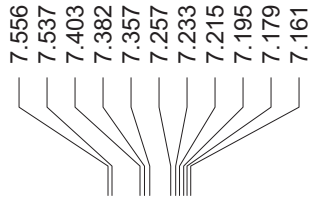
0
f1 (ppm)

3fa

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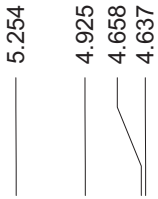
7.257
7.233
7.215
7.195
7.179
7.161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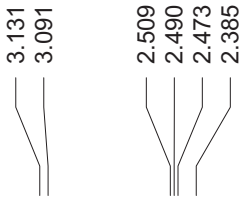
4.925
4.658
4.637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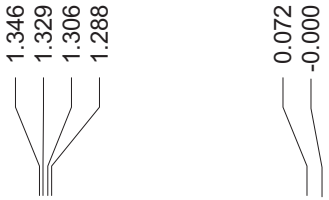
3.091
2.509
2.490
2.473
2.385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1.288
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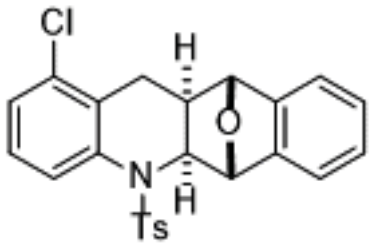
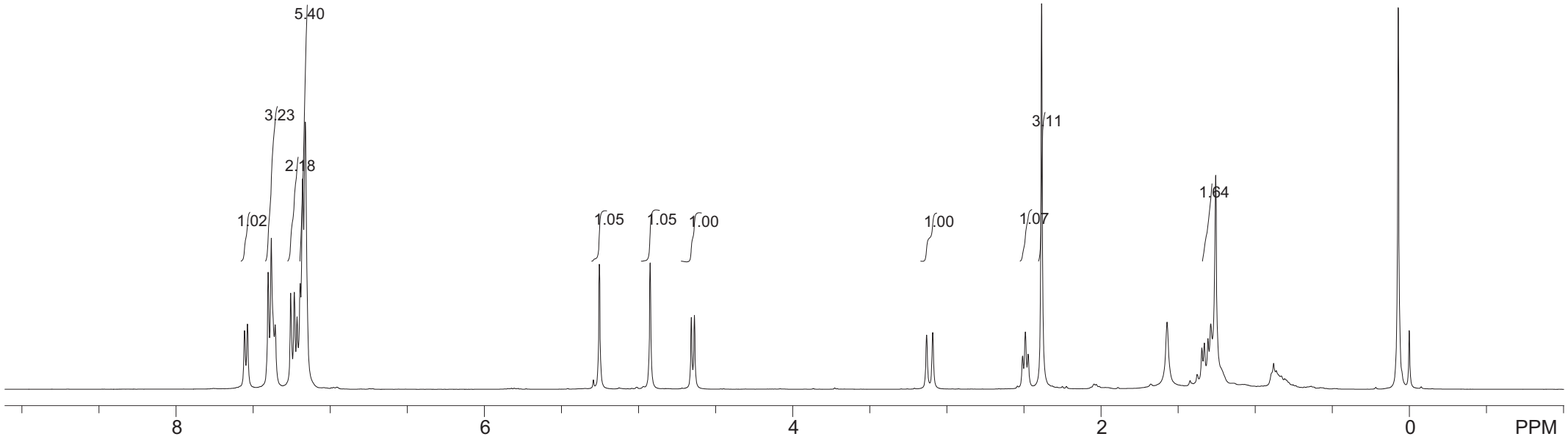
-0.000


Cl
H
O
N
H
Ts

3ga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3.23
2.18
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1.05
1.00
1.00
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1.64
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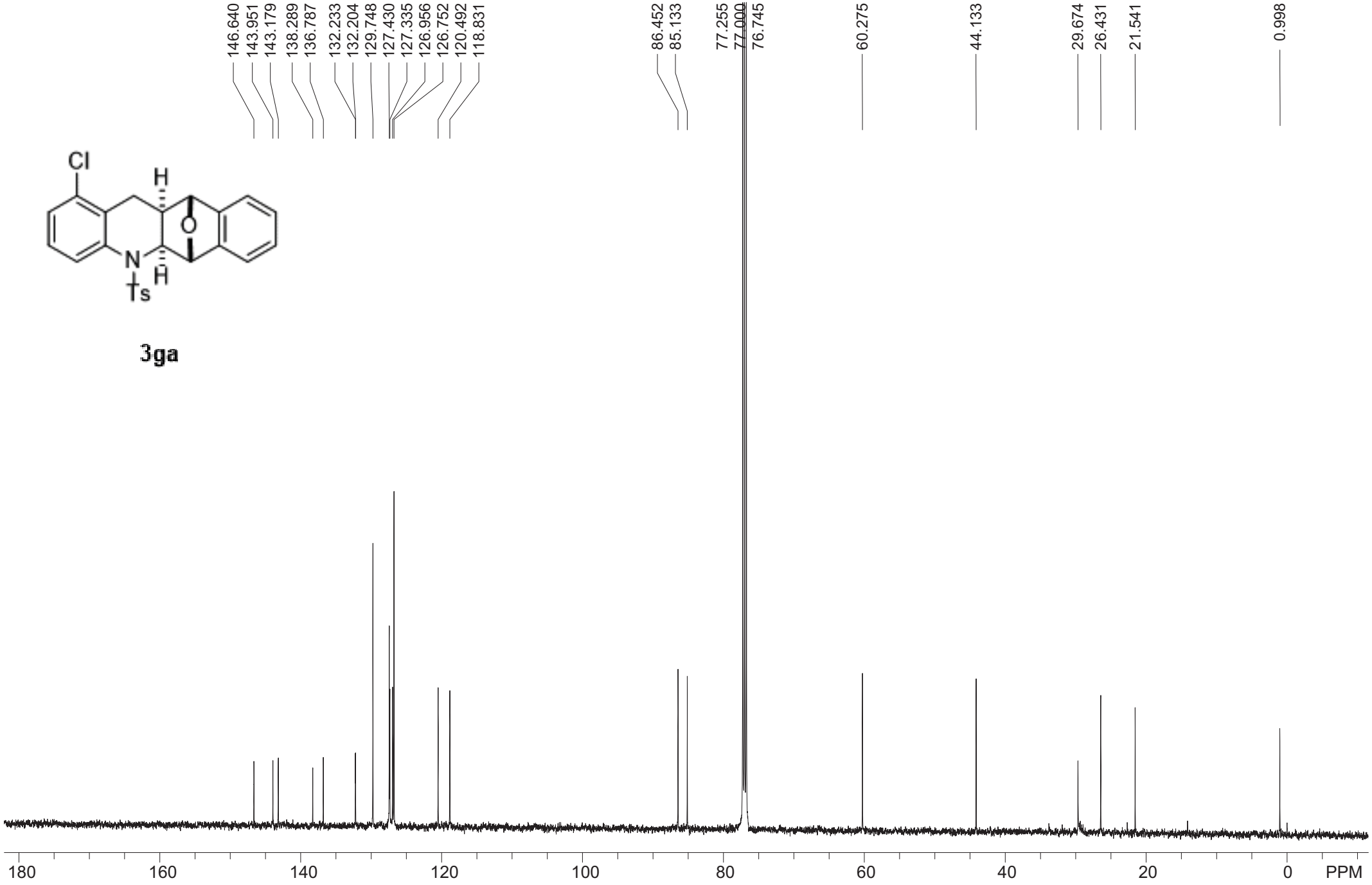
PPM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143.179
138.289
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132.233
132.204
129.748
127.430
127.335
126.956
126.752
120.492
118.831
86.452
85.133
77.255
77.000
76.745
60.275
44.133
29.674
26.431
21.541
0.998
Cl
H
O
N
H
Ts
3ga
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140
120
100
80
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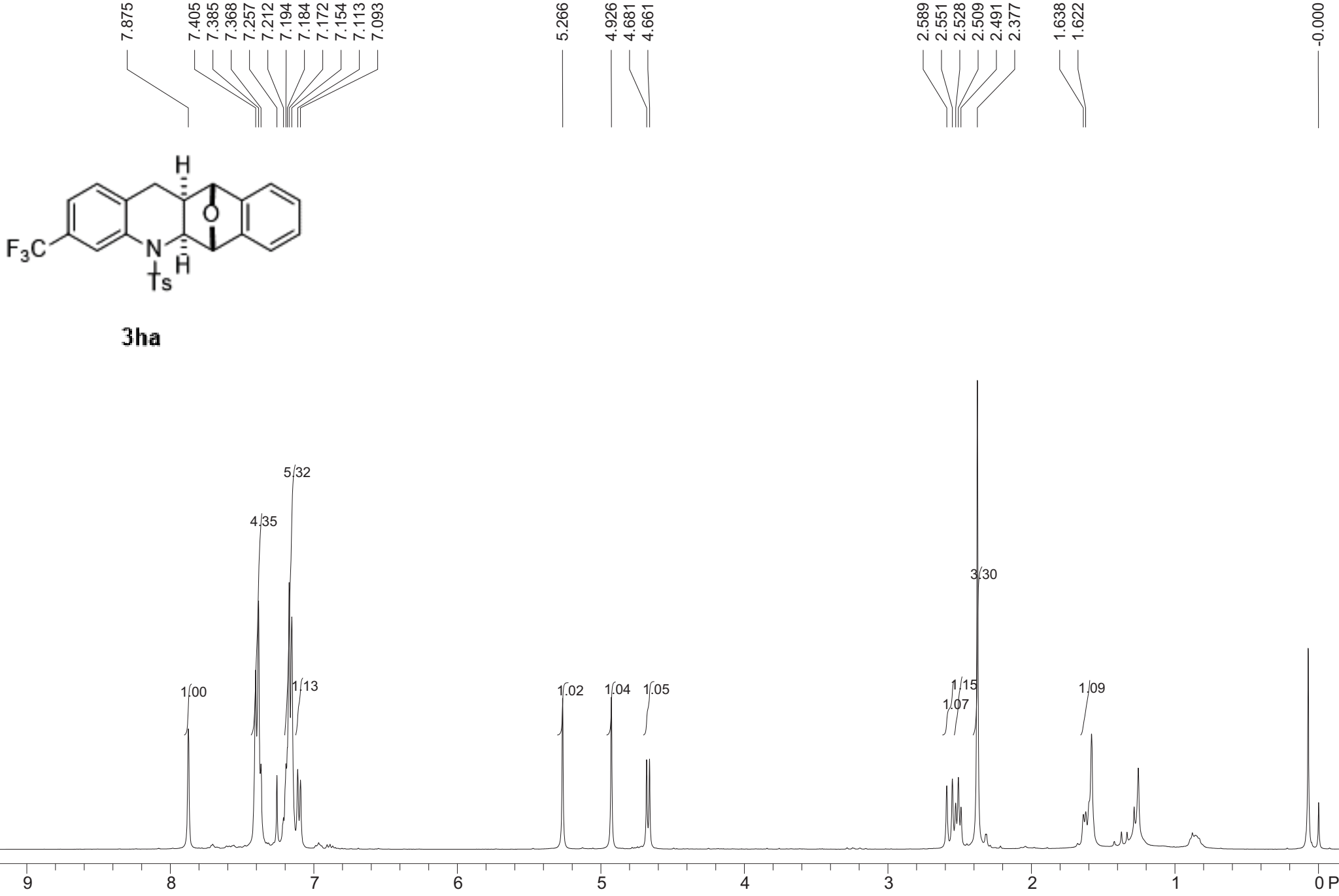
40
20
0
PPM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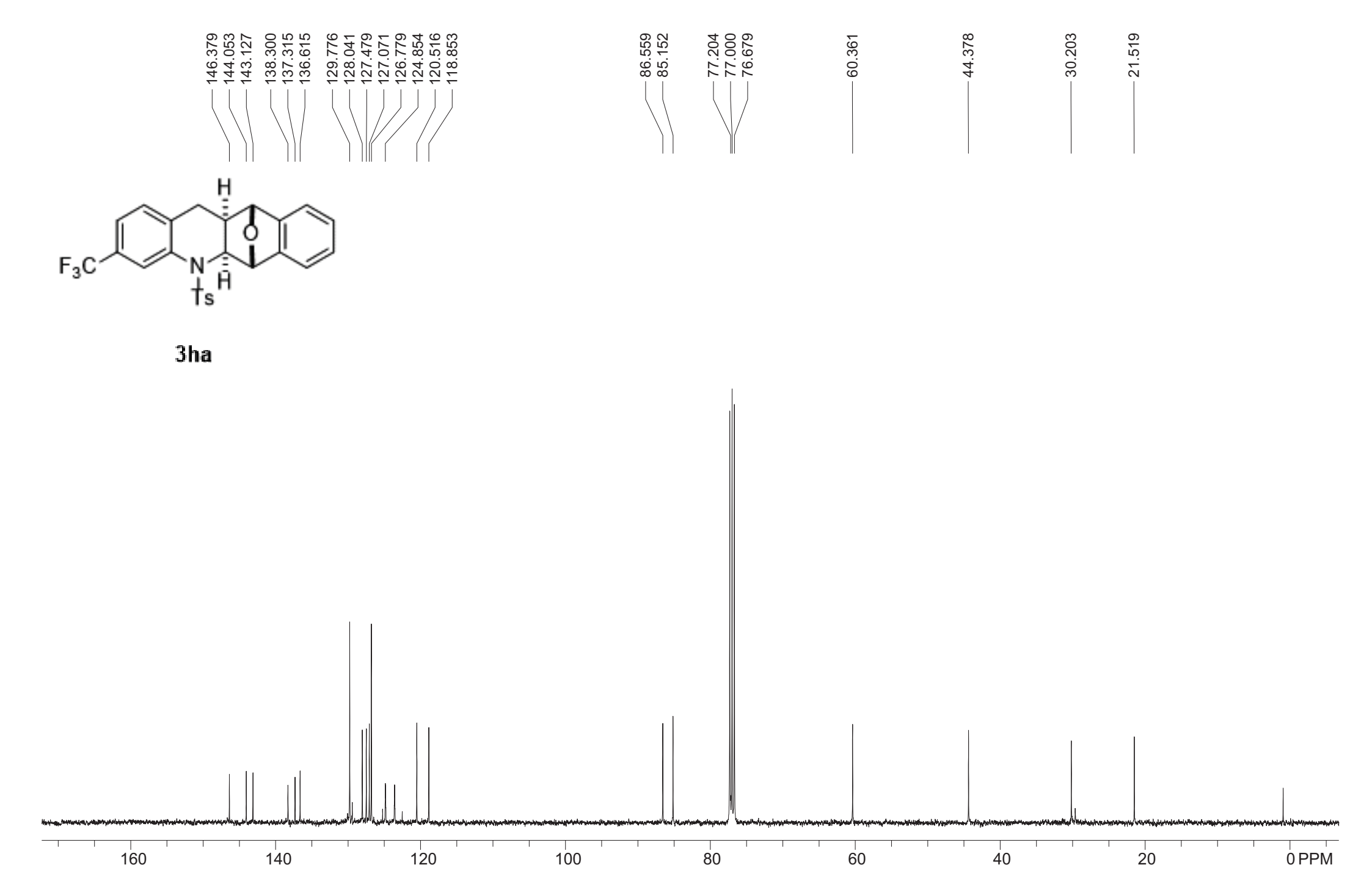
7.385
7.368
7.257
7.212
7.194
7.184
7.172
7.154
7.113
7.093
5.266
4.926
4.681
4.661
2.589
2.551
2.528
2.509
2.491
2.377
1.638
1.622
-0.000
H
O
F3C
N
H
Ts
3ha
5.32
4.35
3.30
1.00
1.13
1.02
1.04
1.05
1.15
1.07
1.09
9
8
7
6
5
4
3
2
1
0 PPM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137.315
136.615
129.776
128.041
127.479
127.071
126.779
124.854
120.516
118.853
86.559
85.152
77.204
77.000
76.679
60.361
44.378
30.203
21.519
H
O
F3C
N
H
Ts
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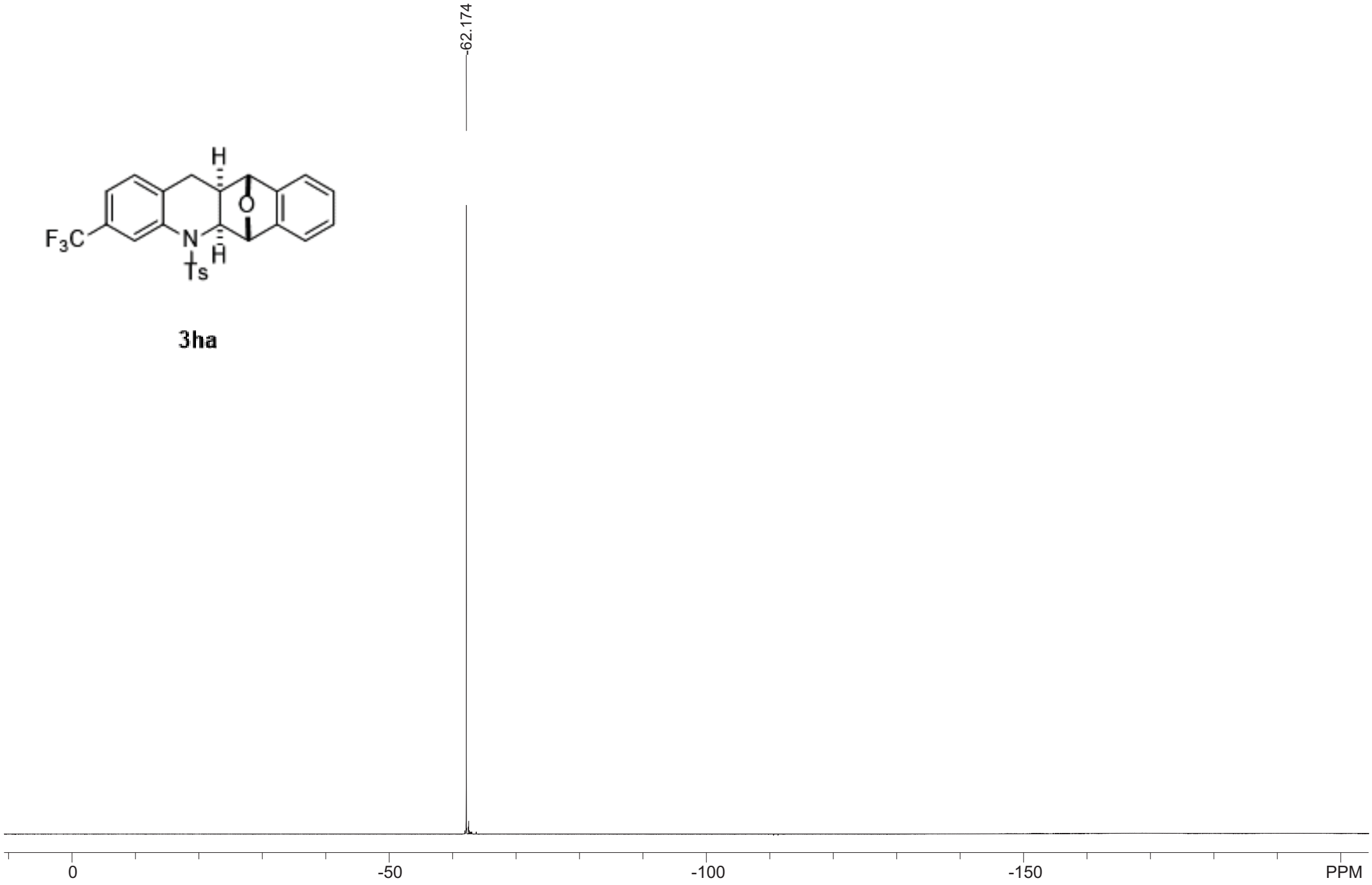
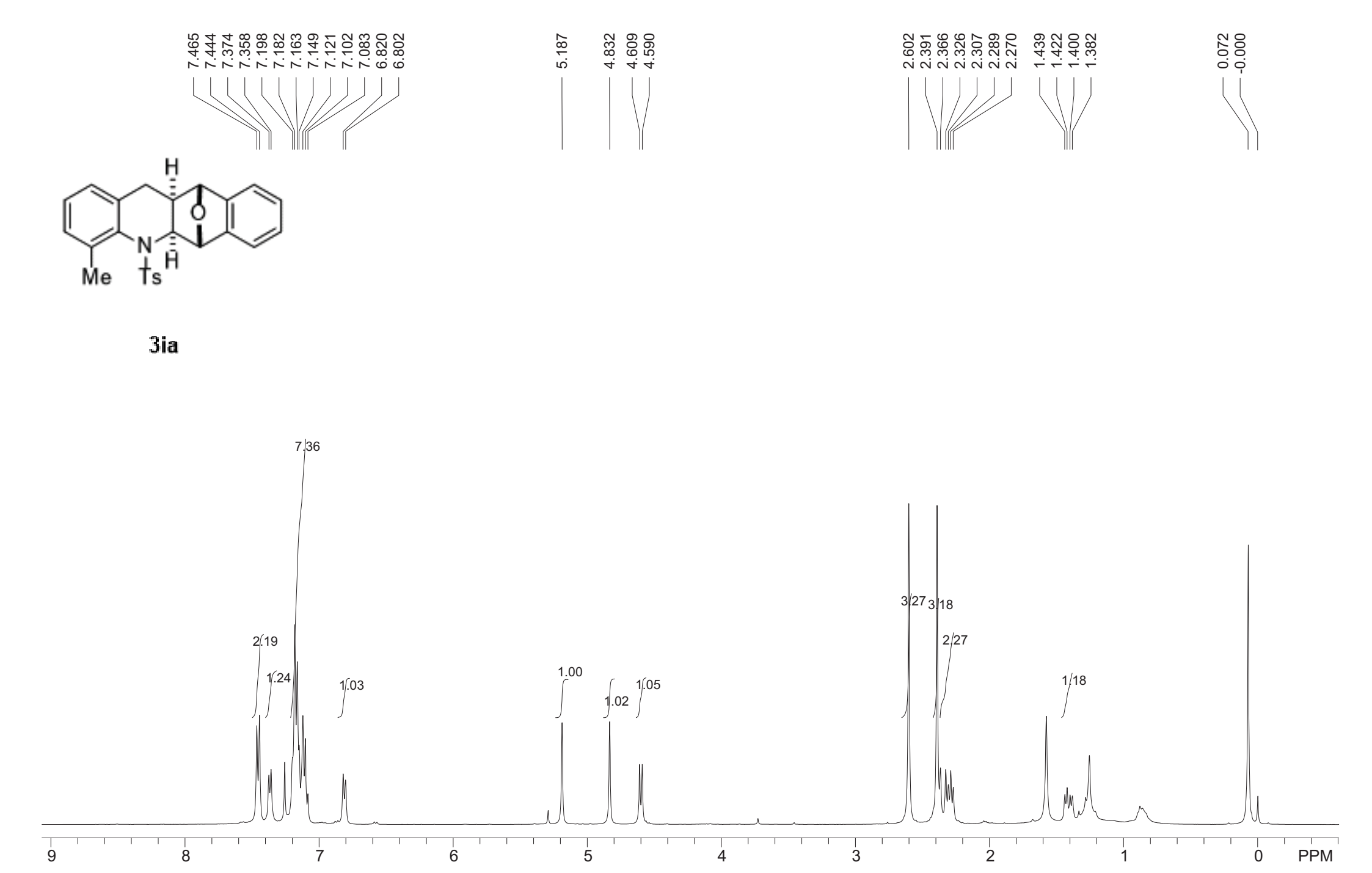
140
120
100
80
60
40
20
0 PPM

3ha

3ha

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7.374
7.358
7.198
7.182
7.163
7.149
7.121
7.102
7.083
6.820
6.802
5.187
4.832
4.609
4.590
2.602
2.391
2.366
2.326
2.307
2.289
2.270
1.439
1.422
1.400
1.382
0.072
-0.000
H
O
N
H
Me
Ts
3ia
7.36
2.19
1.24
1.03
1.00
1.02
1.05
3.27
3.18
2.27
1.18
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8
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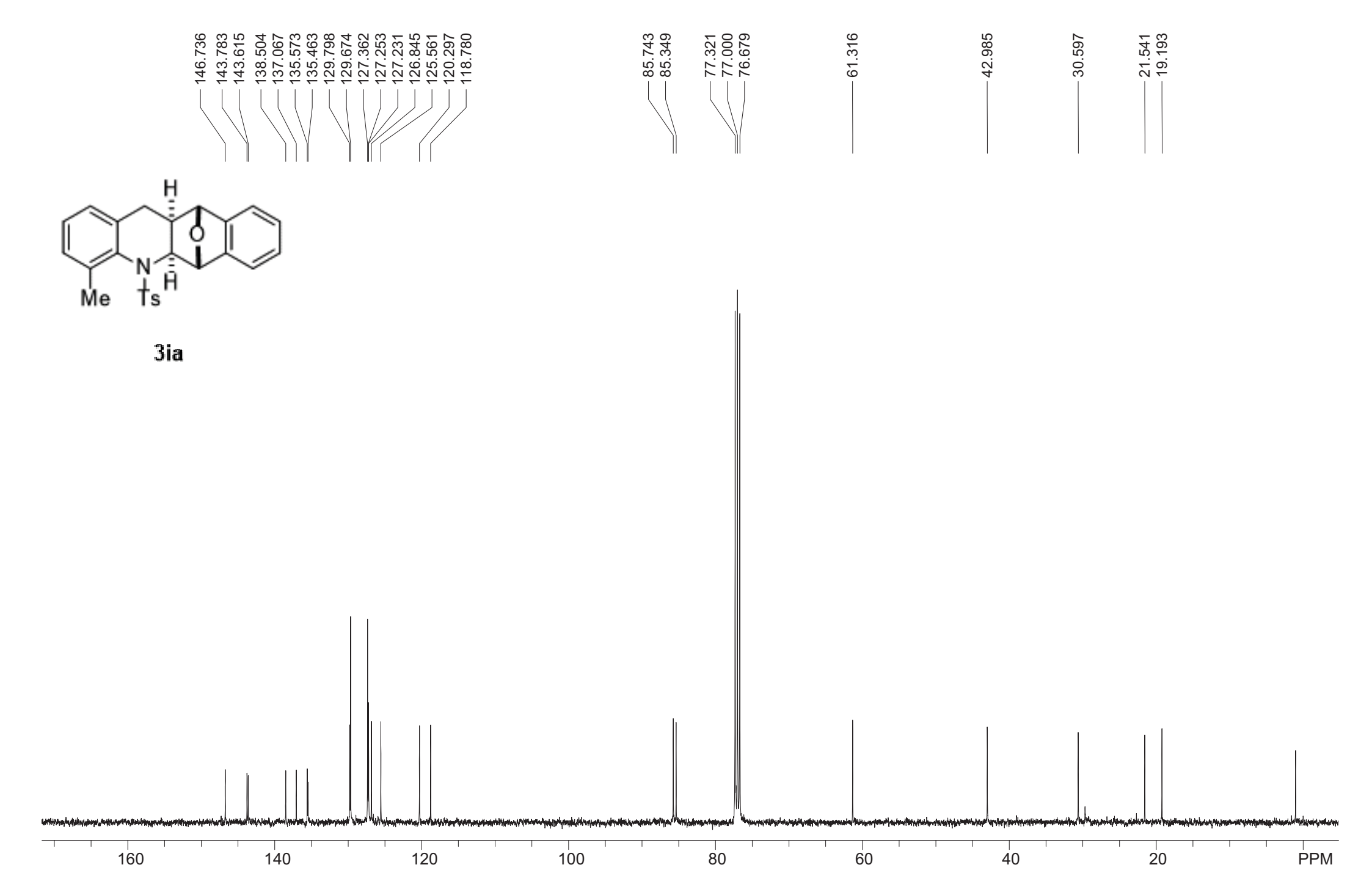
6
5
4
3
2
1
0
PPM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143.615
138.504
137.067
135.573
135.463
129.798
129.674
127.362
127.253
127.231
126.845
125.561
120.297
118.780
85.743
85.349
77.321
77.000
76.679
61.316
42.985
30.597
21.541
19.193
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O
N
H
Me
Ts
3ia
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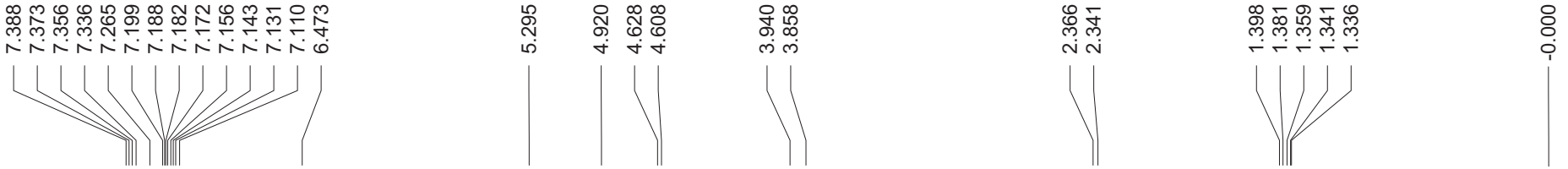
140
120
100
80
60
40
20
PPM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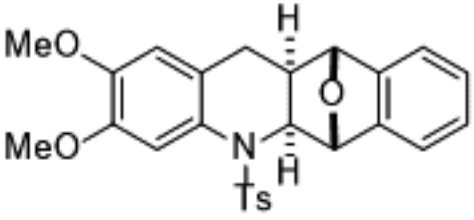
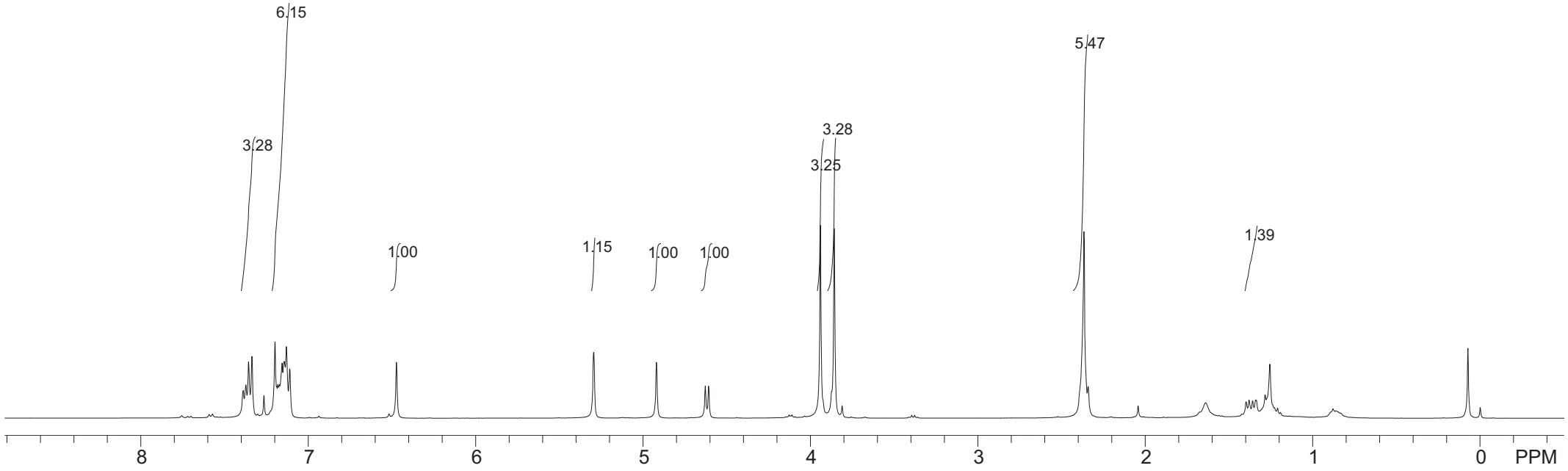
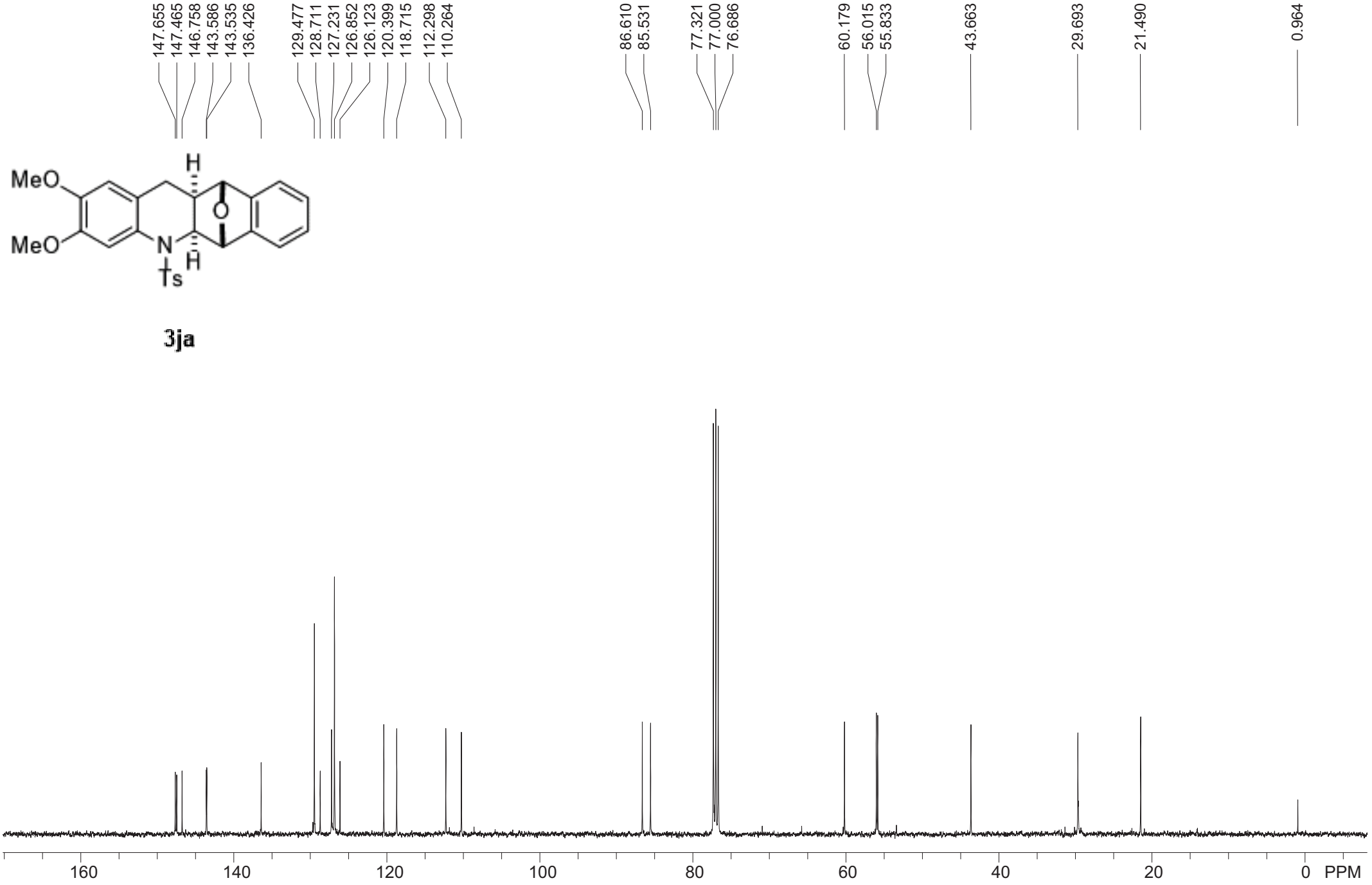
7.336
7.265
7.199
7.188
7.182
7.172
7.156
7.143
7.131
7.110
6.473
5.295
4.920
4.628
4.608
3.940
3.858
2.366
2.341
1.398
1.381
1.359
1.341
1.336
-0.000


MeO
MeO
H
O
N
H
Ts

3ja


6.15
3.28
1.00
1.15
1.00
1.00
3.28
3.25
5.47
1.39
8
7
6
5
4
3
2
1
0
PPM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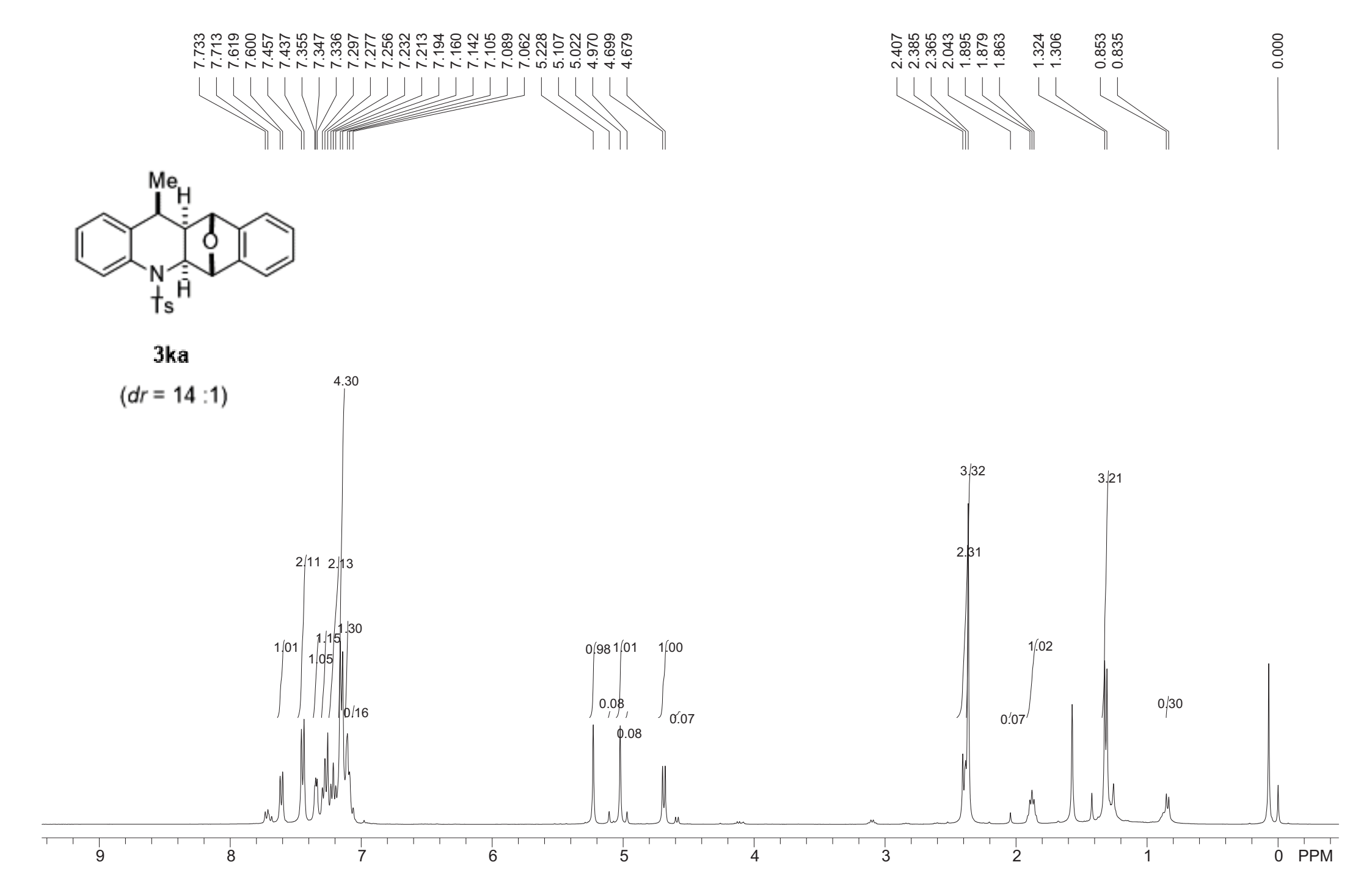
147.465
146.758
143.586
143.535
136.426
129.477
128.711
127.231
126.852
126.123
120.399
118.715
112.298
110.264
86.610
85.531
77.321
77.000
76.686
60.179
56.015
55.833
43.663
29.693
21.490
0.964
MeO
MeO
H
O
N
H
Ts
160
140
120
100
80
60
40
20
0
PPM

3ja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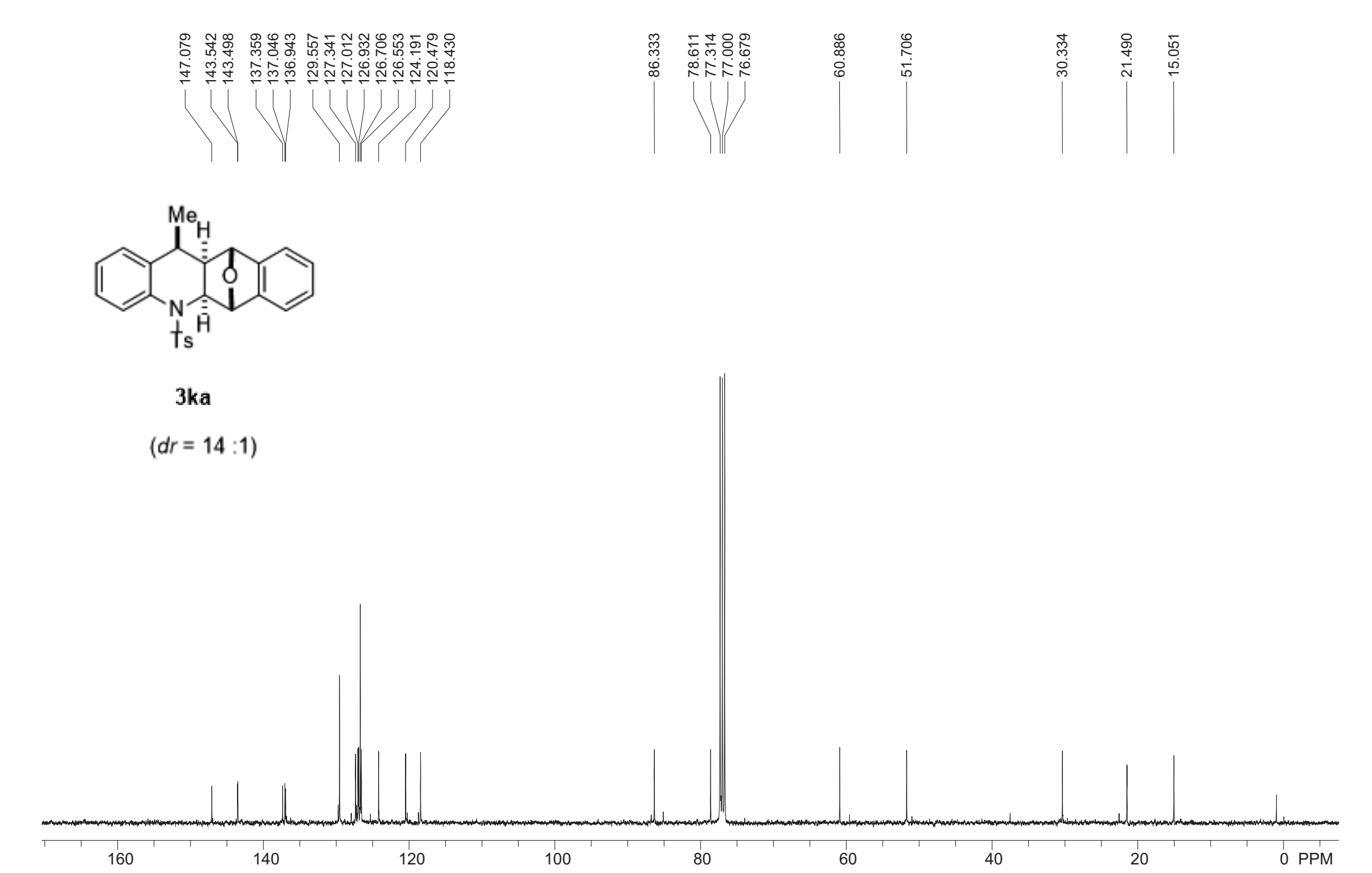
7.457
7.437
7.355
7.347
7.336
7.297
7.277
7.256
7.232
7.213
7.194
7.160
7.142
7.105
7.089
7.062
5.228
5.107
5.022
4.970
4.699
4.679
2.407
2.385
2.365
2.043
1.895
1.879
1.863
1.324
1.306
0.853
0.835
0.000
Me
H
O
N
H
Ts
3ka
(dr = 14 :1)
4.30
2.11
2.13
1.30
1.15
1.01
1.05
0.16
0.98
1.01
1.00
0.08
0.08
0.07
3.32
2.31
3.21
1.02
0.07
0.30
9
8
7
6
5
4
3
2
1
0
PPM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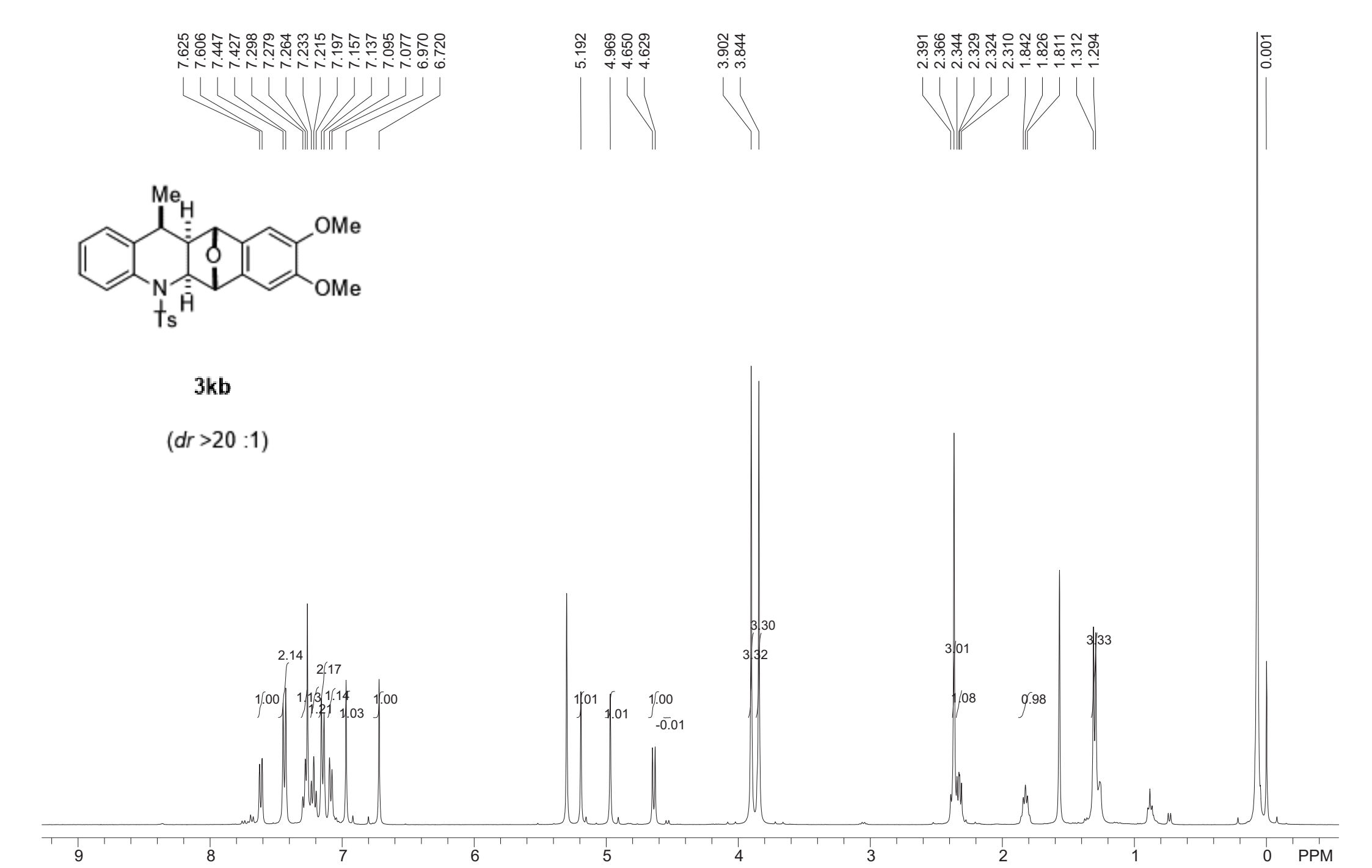
126.553
124.191
120.479
118.430
86.333
78.611
77.314
77.000
76.679
60.886
51.706
30.334
21.490
15.051
Me
H
O
N
H
Ts
3ka
(dr = 14 :1)
160
140
120
100
80
60
40
20
0 PPM


7.625
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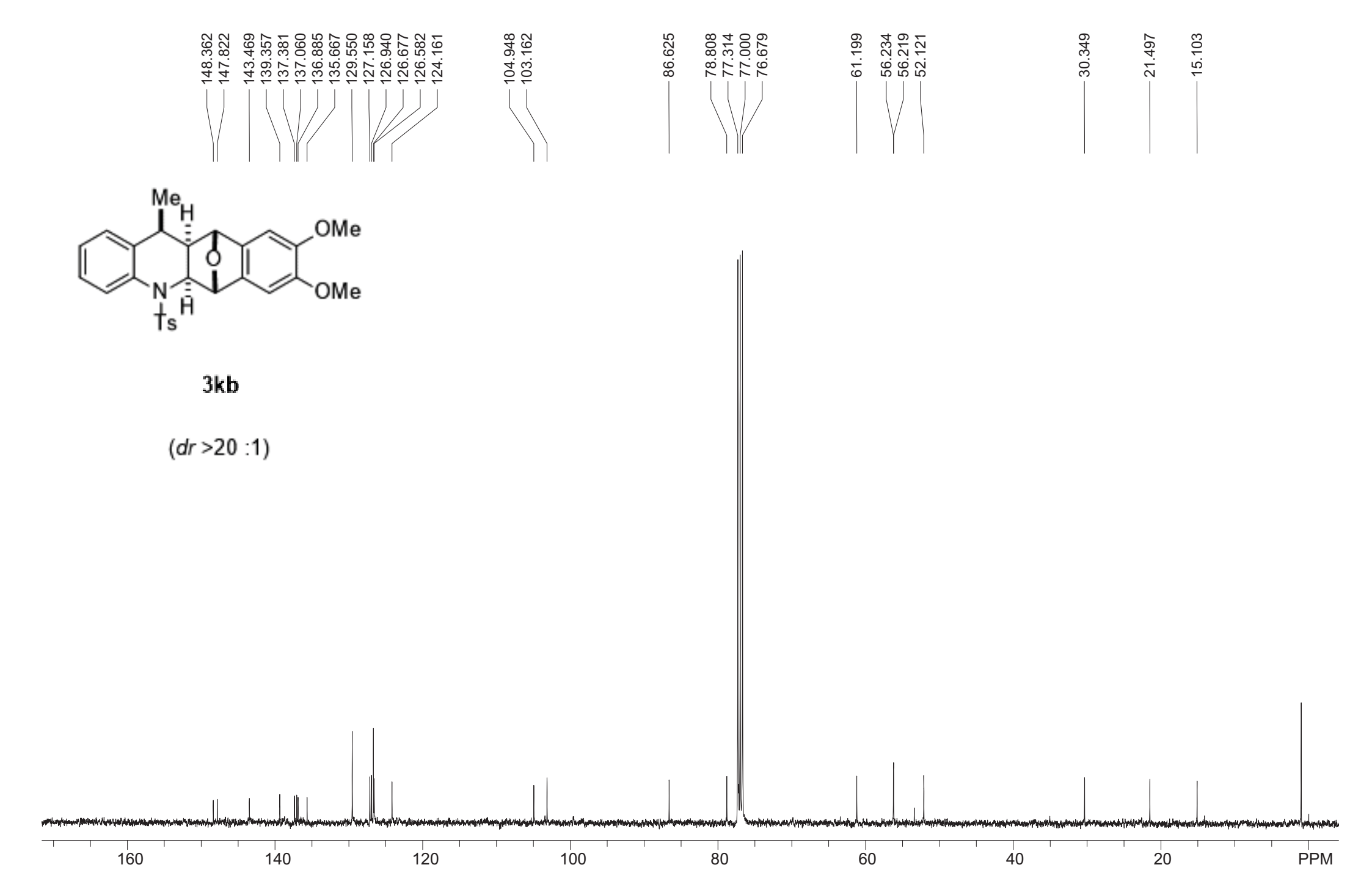
7.447
7.427
7.298
7.279
7.264
7.233
7.215
7.197
7.157
7.137
7.095
7.077
6.970
6.720
5.192
4.969
4.650
4.629
3.902
3.844
2.391
2.366
2.344
2.329
2.324
2.310
1.842
1.826
1.811
1.312
1.294
0.001
Me
H
OMe
O
N
H
Ts
OMe
3kb
(dr >20 :1)
2.14
2.17
1.00
1.13
1.14
1.21
1.03
1.00
1.01
1.01
1.00
-0.01
3.30
3.32
3.01
1.08
0.98
3.33
9
8
7
6
5
4
3
2
1
0
PPM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135.667
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127.158
126.940
126.677
126.582
124.161
104.948
103.162
86.625
78.808
77.314
77.000
76.679
61.199
56.234
56.219
52.121
30.349
21.497
15.103
Me
H
OMe
O
N
H
Ts
OMe
160
140
120
100
80
60
40
20
PPM

3kb

(*dr* >20 :1)


7.594
7.575
7.459
7.439
7.279
7.258
7.243
7.217
7.199
7.179
7.165
7.145
7.083
7.065
6.844
6.619
5.937
5.931
5.118
4.925
4.634
4.615
2.407
2.367
2.347
2.332
2.327
2.313
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1.871
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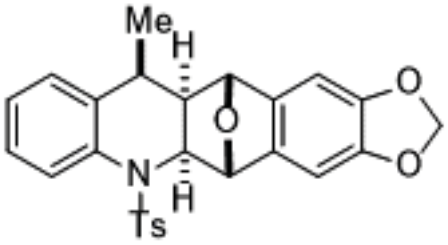
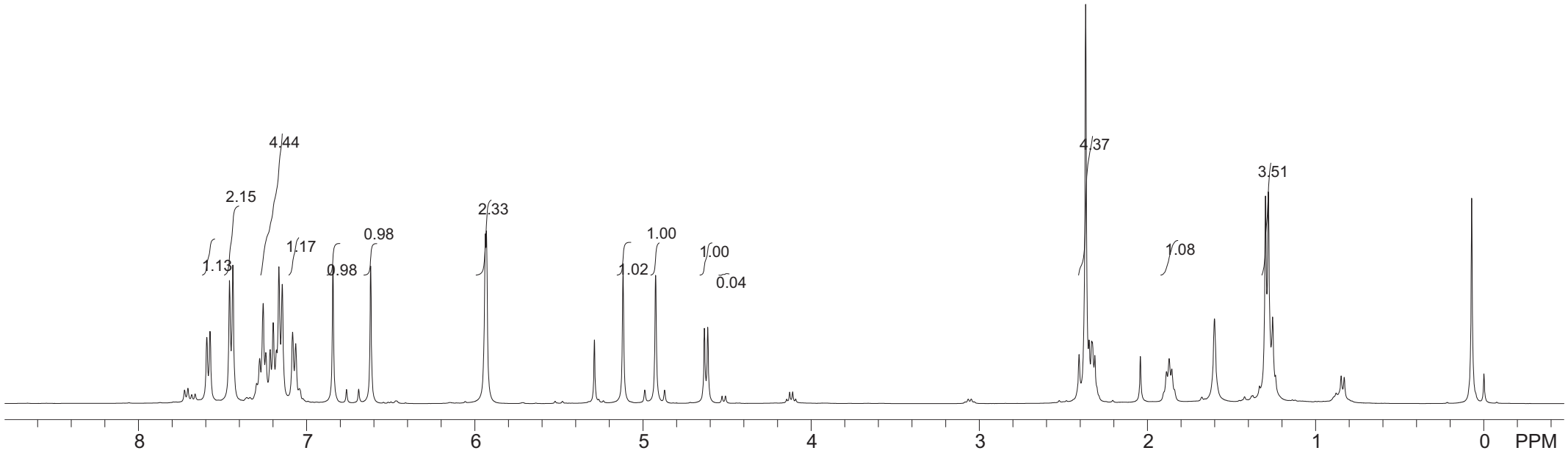
1.256
1.239
-0.000


Me
H
O
O
O
N
H
Ts

3kf

(*dr* >20 :1)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1.13
1.17
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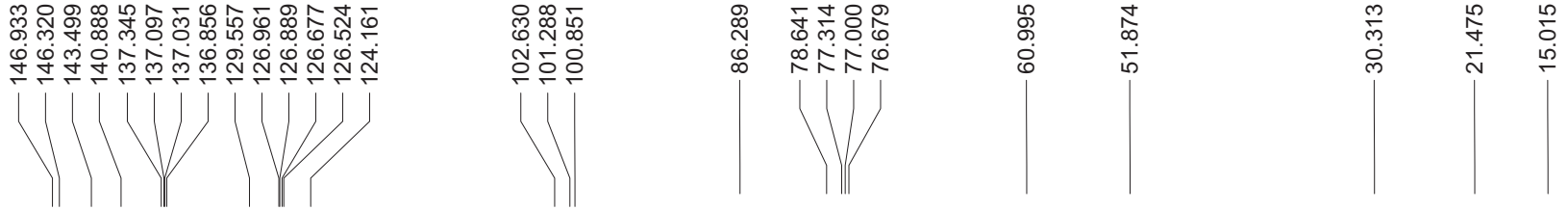
0.98
2.33
1.02
1.00
1.00
0.04
4.37
1.08
3.51
8
7
6
5
4
3
2
1
0
PPM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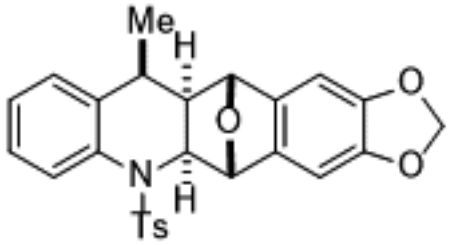
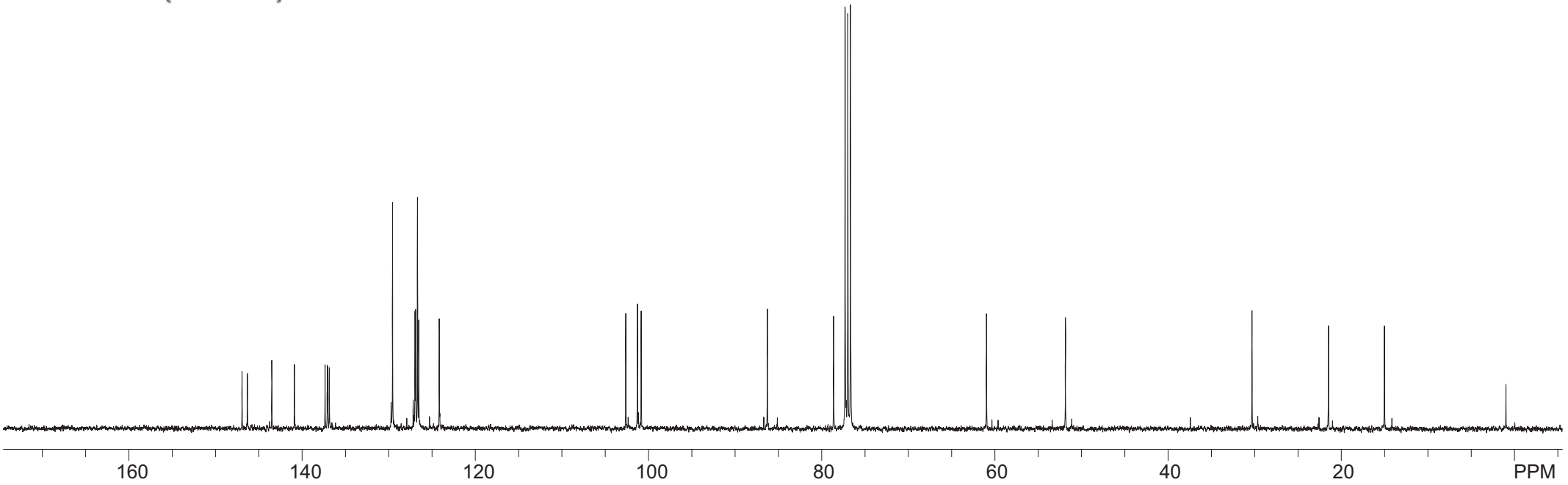
137.345
137.097
137.031
136.856
129.557
126.961
126.889
126.677
126.524
124.161
102.630
101.288
100.851
86.289
78.641
77.314
77.000
76.679
60.995
51.874
30.313
21.475
15.015


Me
H
O
O
O
N
H
Ts

3kf

(*dr* >20 :1)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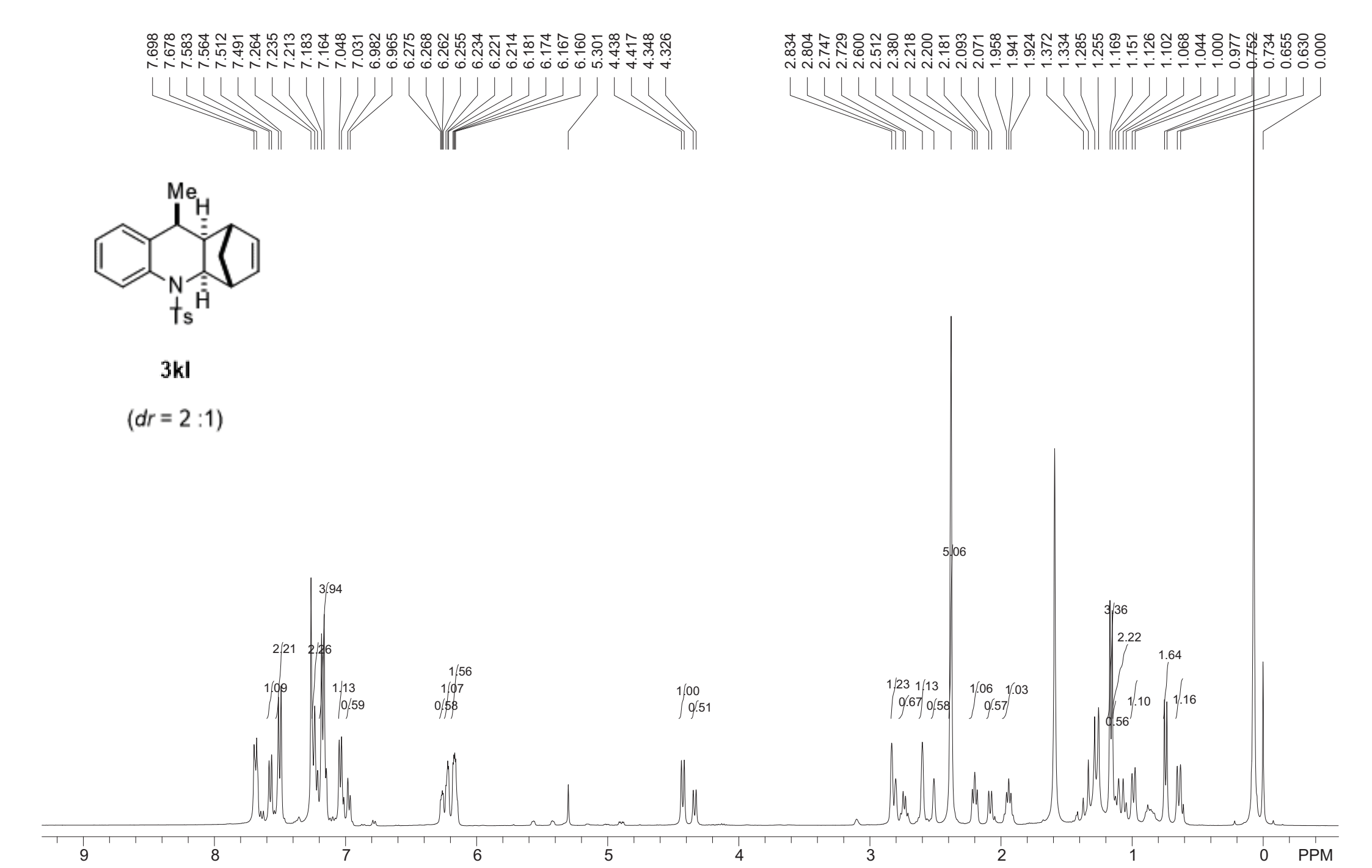
140
120
100
80
60
40
20
PPM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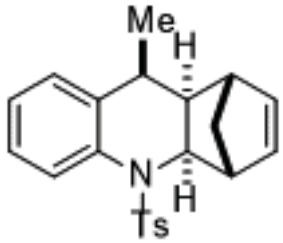
7.512
7.491
7.264
7.235
7.213
7.183
7.164
7.048
7.031
6.982
6.965
6.275
6.268
6.262
6.255
6.234
6.221
6.214
6.181
6.174
6.167
6.160
5.301
4.438
4.417
4.348
4.326
2.834
2.804
2.747
2.729
2.600
2.512
2.380
2.218
2.200
2.181
2.093
2.071
1.958
1.941
1.924
1.372
1.334
1.285
1.255
1.169
1.151
1.126
1.102
1.068
1.044
1.000
0.977
0.752
0.734
0.655
0.630
0.000
Me
H
N
H
Ts
3kl
(dr = 2 :1)
1.09
2.21
2.26
3.94
1.13
0.59
0.58
1.07
1.56
1.00
0.51
1.23
0.67
1.13
0.58
5.06
1.06
0.57
1.03
3.36
2.22
0.56
1.10
1.64
1.16
9
8
7
6
5
4
3
2
1
0
PPM



3kl

(*dr* = 2 :1)

143.353
143.192
141.953
141.873
138.300
138.052
137.833
137.760
137.600
137.534
136.732
136.506
129.557
129.513
128.478
127.866
127.217
126.918
126.735
126.349
125.255
125.182
124.606
77.321
77.000
76.687
59.770
58.545
51.166
50.590
48.993
48.519
47.696
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43.364
41.352
37.757
30.706
23.947
21.512
15.059

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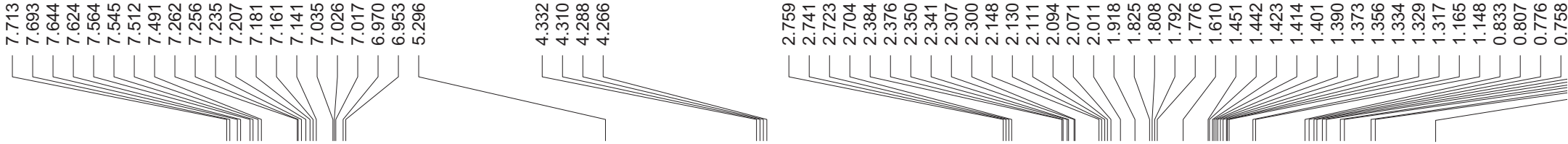
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7.256
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7.207
7.181
7.161
7.141
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7.026
7.017
6.970
6.953
5.296
4.332
4.310
4.288
4.266
2.759
2.741
2.723
2.704
2.384
2.376
2.350
2.341
2.307
2.300
2.148
2.130
2.111
2.094
2.071
2.011
1.918
1.825
1.808
1.792
1.776
1.610
1.451
1.442
1.423
1.414
1.401
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1.165
1.148
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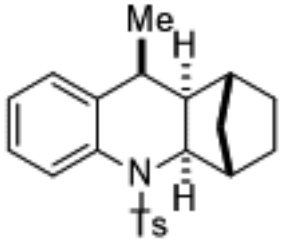
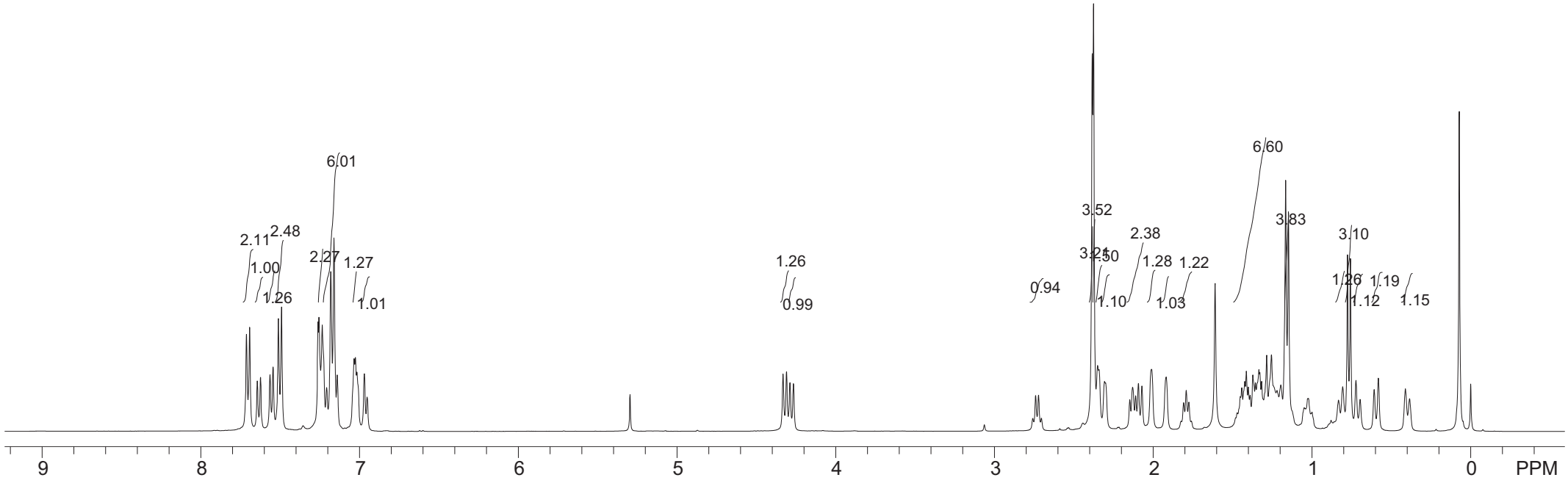
0.807
0.776
0.758


Me
H
N
H
Ts

3ko

(*dr* = 1.3 :1)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2.27
1.27
1.01
1.26
0.99
0.94
3.52
3.21
3.50
1.10
2.38
1.28
1.03
1.22
6.60
3.83
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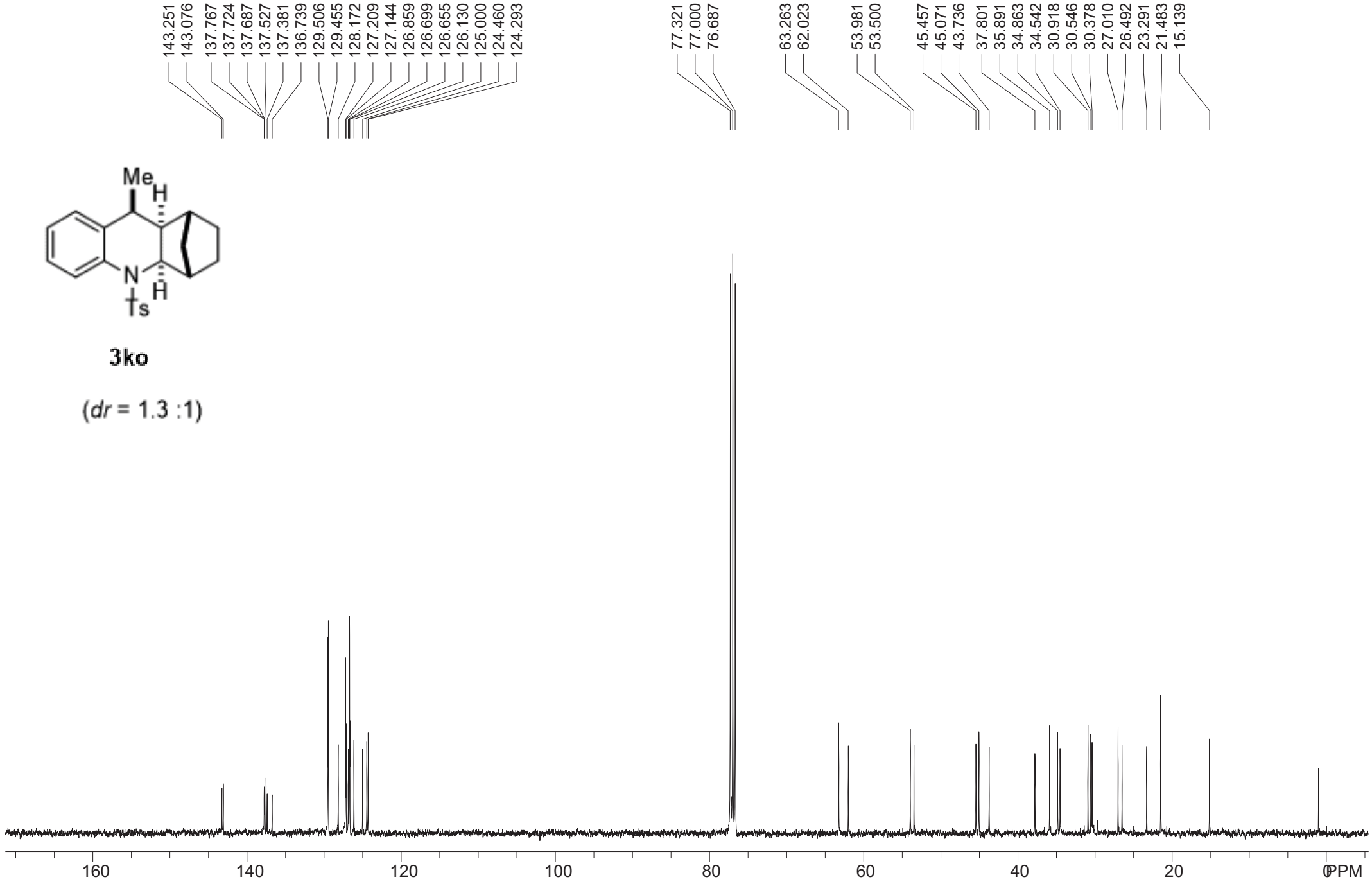
1.26
1.19
1.12
1.15
9
8
7
6
5
4
3
2
1
0
PPM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136.739
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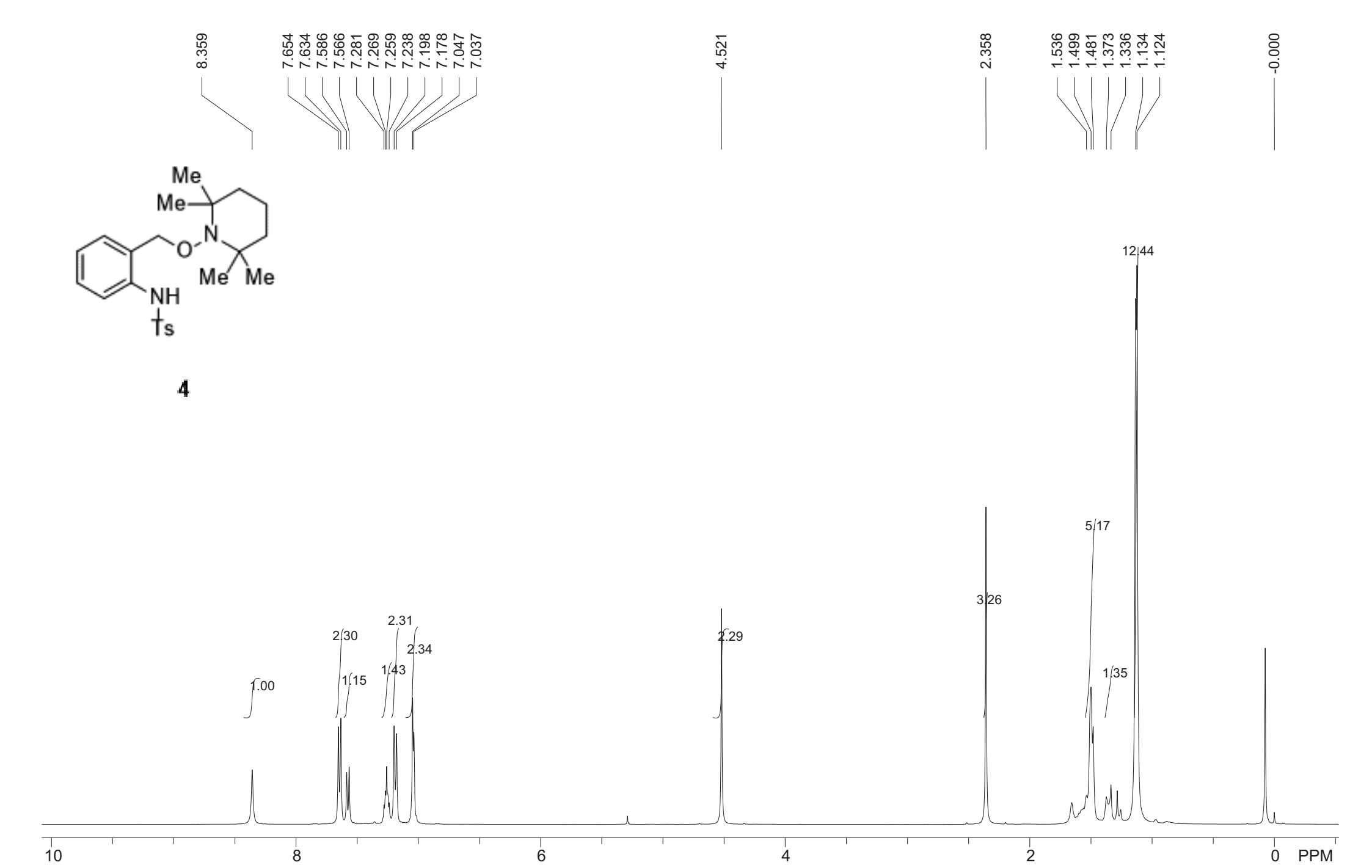
128.172
127.209
127.144
126.859
126.699
126.655
126.130
125.000
124.460
124.293
77.321
77.000
76.687
63.263
62.023
53.981
53.500
45.457
45.071
43.736
37.801
35.891
34.863
34.542
30.918
30.546
30.378
27.010
26.492
23.291
21.483
15.139
Me
H
N
H
Ts
160
140
120
100
80
60
40
20
0
PPM

3ko

(*dr* = 1.3 :1)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7.566
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7.269
7.259
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7.198
7.178
7.047
7.037
4.521
2.358
1.536
1.499
1.481
1.373
1.336
1.134
1.124
-0.000
Me
Me
N
O
Me
Me
NH
Ts
4
12.44
5.17
3.26
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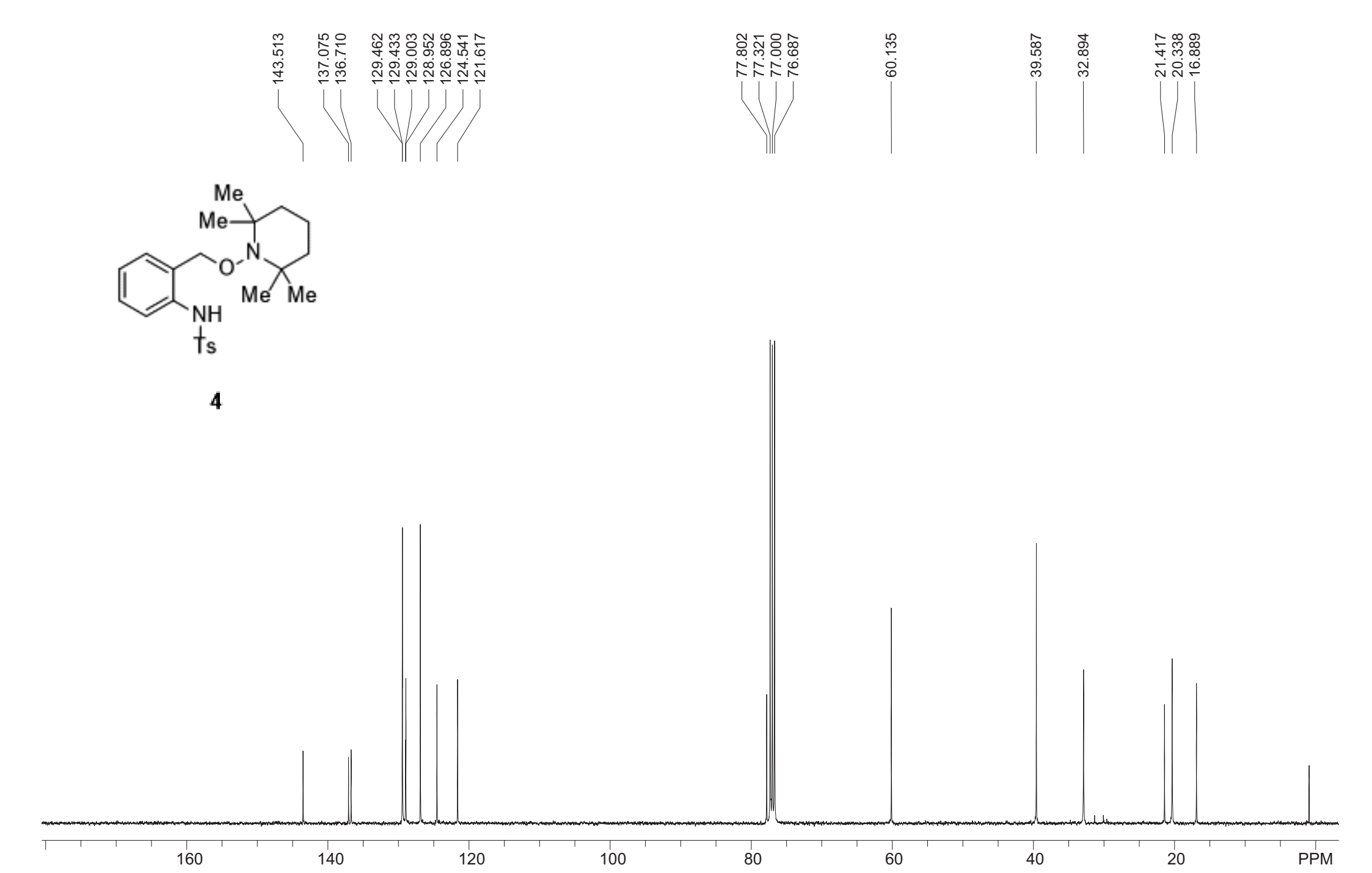
2.30
2.34
2.29
1.43
1.15
1.35
1.00
10
8
6
4
2
0
PPM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77.000
76.687
60.135
39.587
32.894
21.417
20.338
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Me
N
O
Me
Me
NH
Ts
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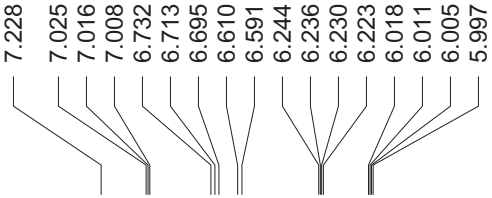
140
120
100
80
60
40
20
PPM

4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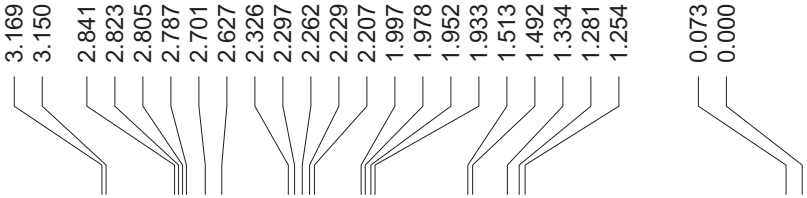
6.610
6.591
6.244
6.236
6.230
6.223
6.018
6.011
6.005
5.997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3.150
2.841
2.823
2.805
2.787
2.701
2.627
2.326
2.297
2.262
2.229
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1.997
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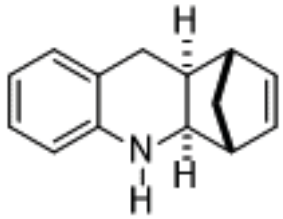
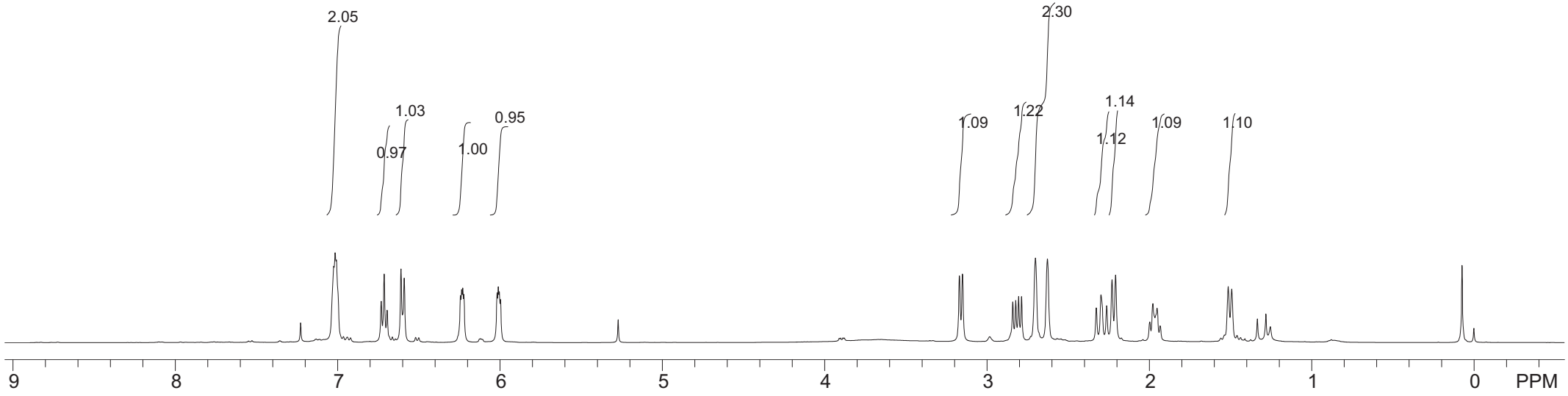
1.952
1.933
1.513
1.492
1.334
1.281
1.254
0.073
0.000


H
N
H
H

5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1.03
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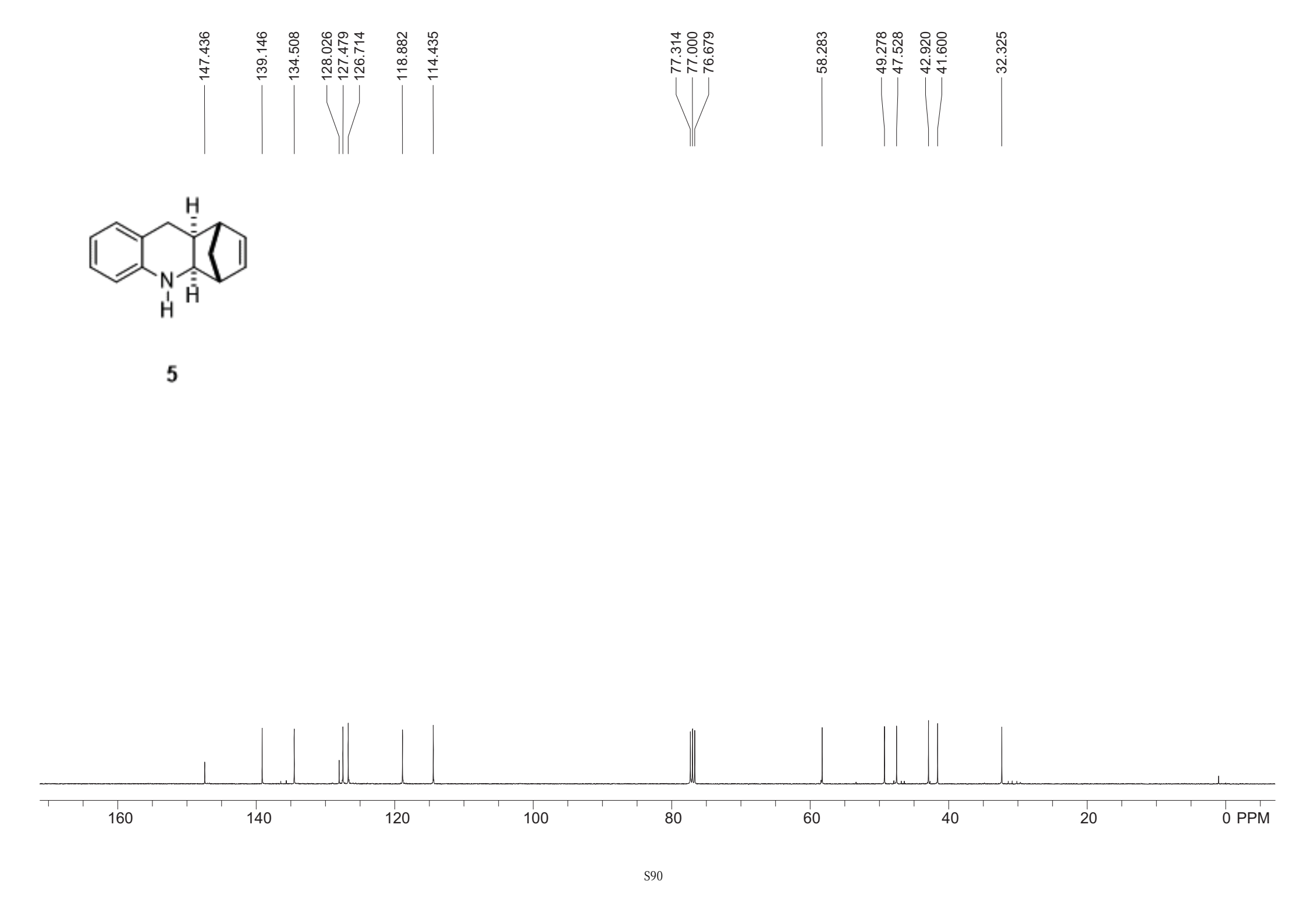
0.95
1.09
1.22
2.30
1.12
1.14
1.09
1.10
9
8
7
6
5
4
3
2
1
0
PPM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114.435
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77.000
76.679
58.283
49.278
47.528
42.920
41.600
32.325
H
N
H
H
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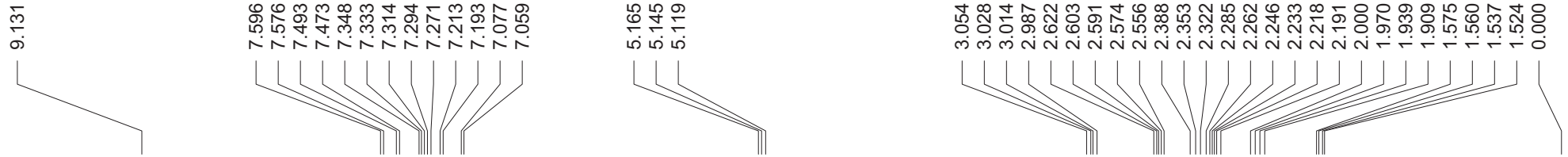
120
100
80
60
40
20
0 PPM

5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7.314
7.294
7.271
7.213
7.193
7.077
7.059
5.165
5.145
5.119
3.054
3.028
3.014
2.987
2.622
2.603
2.591
2.574
2.556
2.388
2.353
2.322
2.285
2.262
2.246
2.233
2.218
2.191
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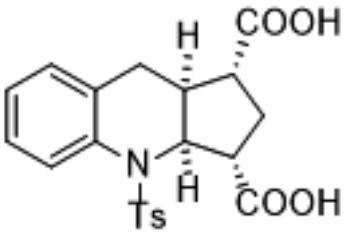
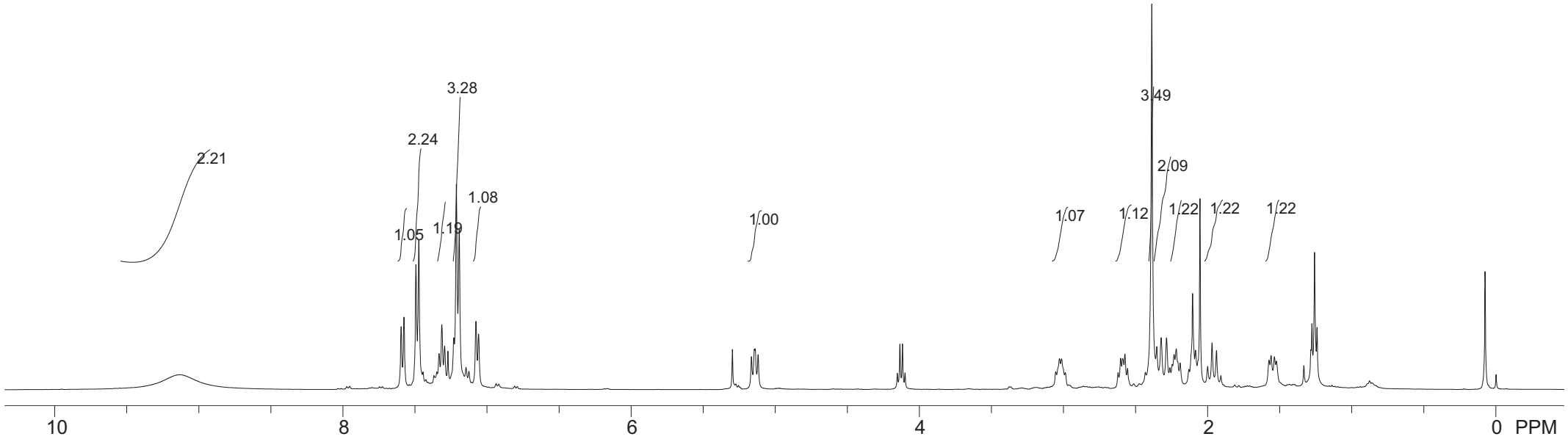
1.909
1.575
1.560
1.537
1.524
0.000


H
COOH
N
Ts
H
COOH

6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1.22
1.22
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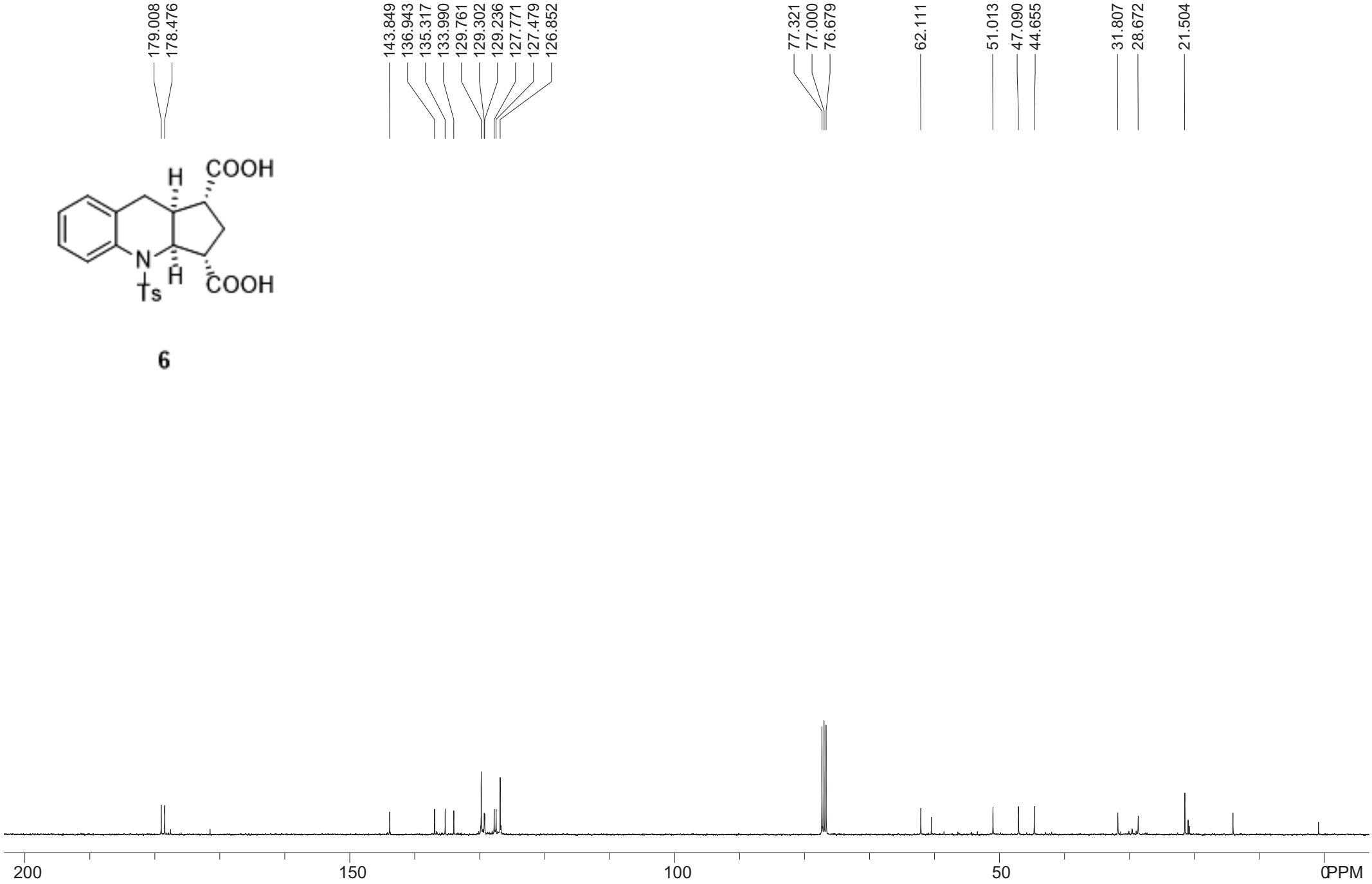
PPM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77.321
77.000
76.679
62.111
51.013
47.090
44.655
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21.504
H
COOH
N
H
COOH
Ts
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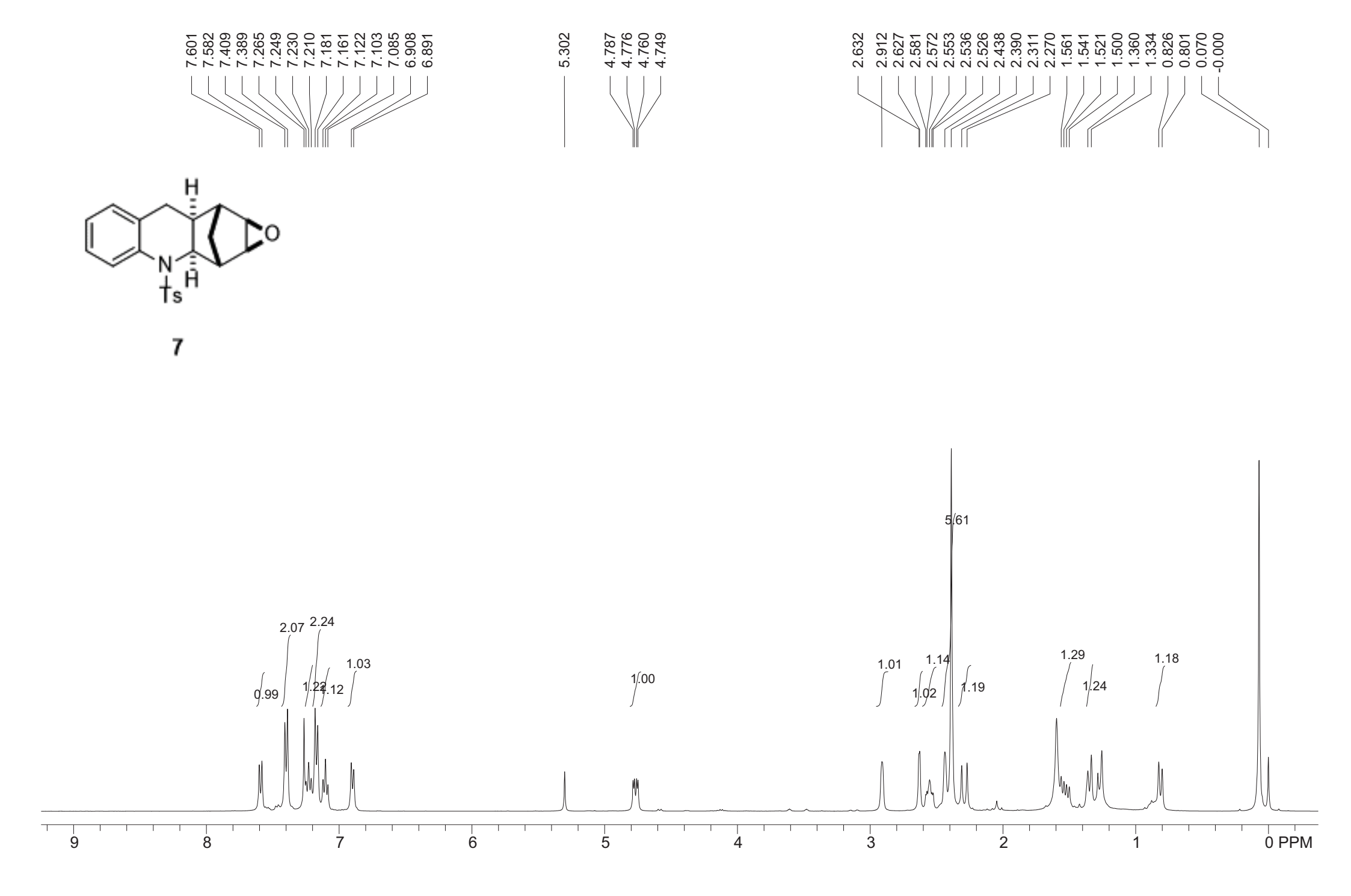
50
0
PPM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7.210
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7.161
7.122
7.103
7.085
6.908
6.891
5.302
4.787
4.776
4.760
4.749
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2.912
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2.572
2.553
2.536
2.526
2.438
2.390
2.311
2.270
1.561
1.541
1.521
1.500
1.360
1.334
0.826
0.801
0.070
-0.000
H
O
N
H
Ts
7
0.99
2.07
2.24
1.23
1.12
1.03
1.00
1.01
1.02
1.14
5.61
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1.29
1.24
1.18
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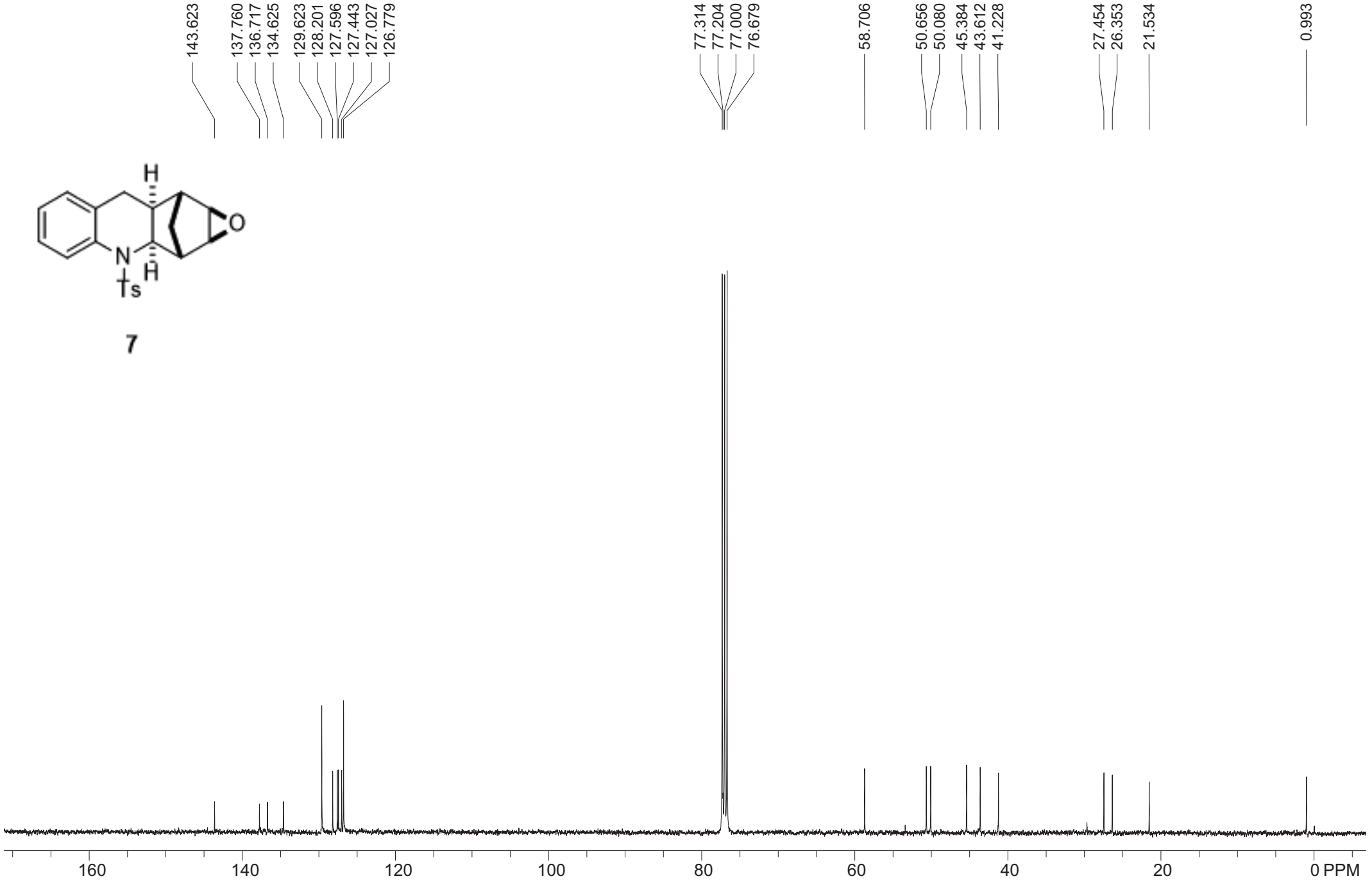
7
6
5
4
3
2
1
0 PPM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127.027
126.779
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77.000
76.679
58.706
50.656
50.080
45.384
43.612
41.228
27.454
26.353
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H
O
N
H
Ts
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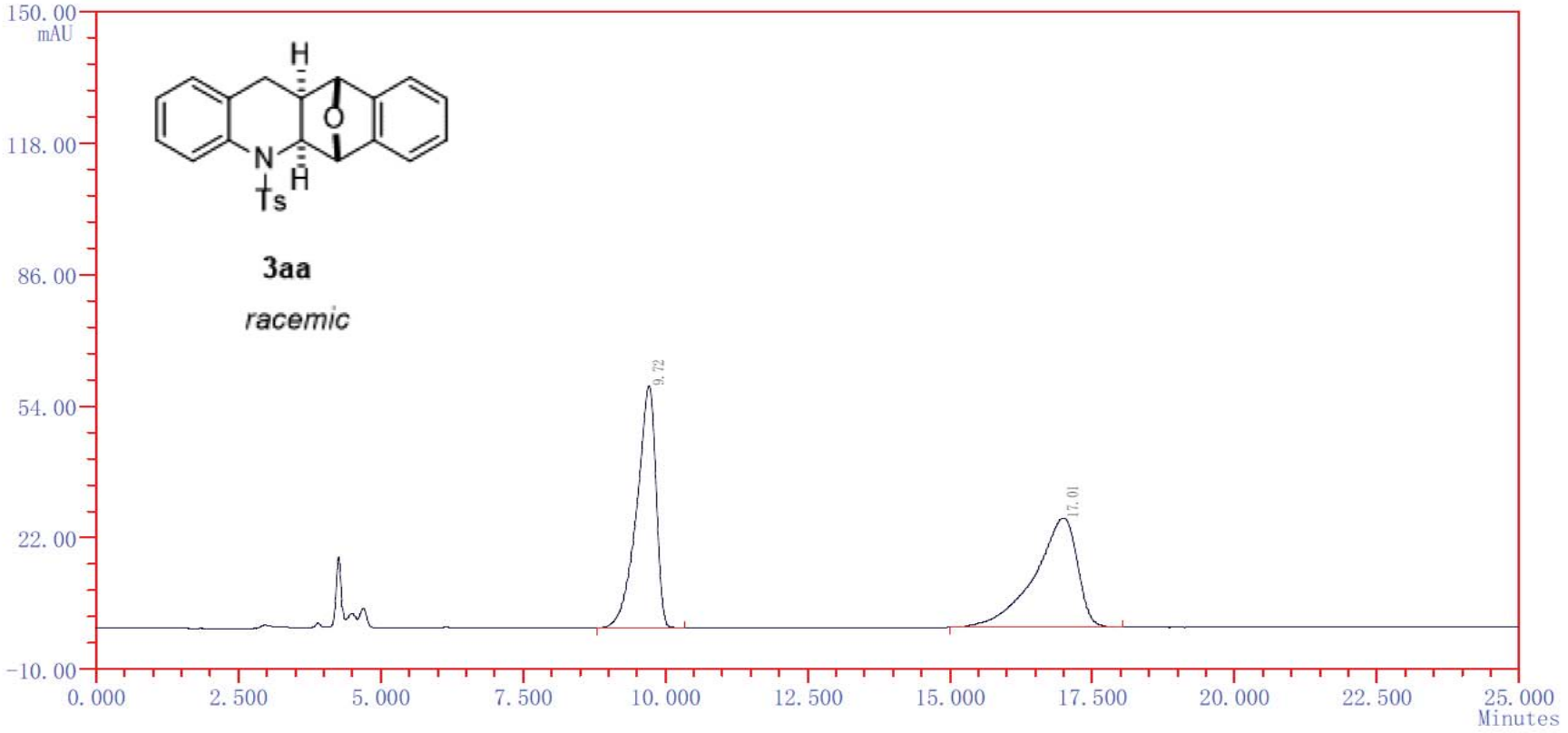
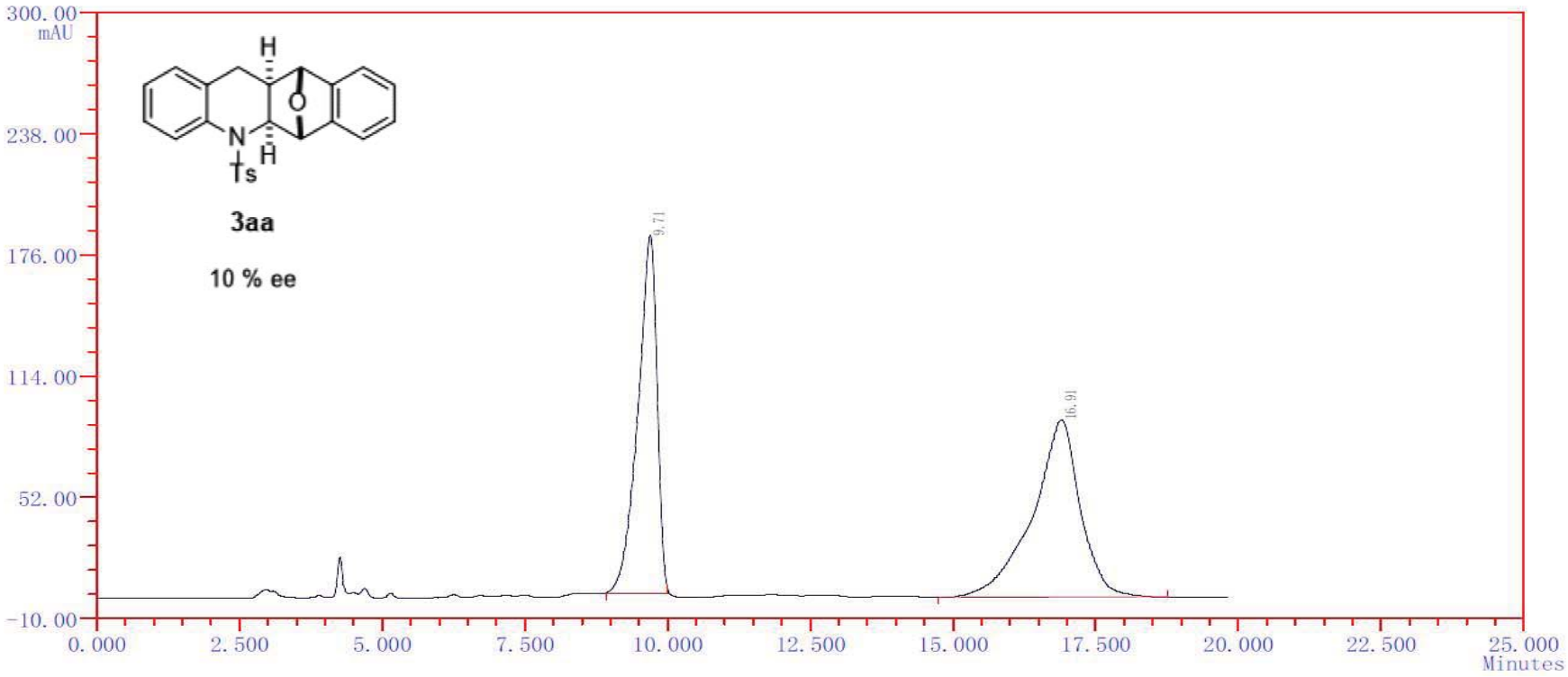
120
100
80
60
40
20
0 PPM

7



Peak	ReTime [min]	Half width [second]	Area [MAU*S]	Height [mAU]	Area %
1	9.723	21.97	1377.671	58.94	49.697
2	17.007	49.26	1394.497	26.61	50.303



Peak	ReTime [min]	Half width [second]	Area [MAU*S]	Height [mAU]	Area %
1	9.707	21.97	4282.155	183.19	44.889
2	16.907	54.54	5257.364	90.61	55.111